

Supplementary Information

Remarkably Efficient Iridium Catalysts for Directed C(sp²)-H and C(sp³)-H Borylation of Diverse Classes of Substrates

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General information

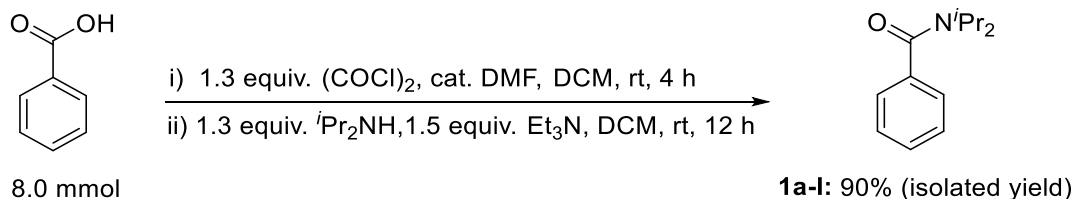
All commercially available chemicals were used as received unless otherwise indicated. Pinacolborane (HBPin) and bis(pinacolato)diboron (B_2Pin_2) were procured from Sigma-Aldrich. Bis(η^4 -1,5-cyclooctadiene)-di- μ -methoxy-diiridium(I) $[Ir(OMe)COD]_2$ was procured from Sigma-Aldrich. Tetrahydrofuran (THF) was refluxed over sodium/benzophenone ketyl, distilled and degassed twice before borylation. Column chromatography was performed on flash silica gel (ACME). Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates purchased from Merck and visualized with ultraviolet light ($\lambda = 254$ nm).

1H , ^{13}C , and ^{11}B spectra were recorded on Bruker 400 MHz NMR spectrometer. The boron bearing carbon atom was not observed due to quadrupolar relaxation. All coupling constants are apparent J values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, br s = broad singlet, br m = broad multiplet, dt = doublet of triplet, td = triplet of doublet, ddd = doublet of doublets of doublets, p = pentate, sept = septet). High-resolution mass spectra (HRMS) were obtained using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electrospray ionization (ESI+). GC/MS (Agilent Technology) was obtained and for the analysis RAM temperature was used 50 °C for each sample.

The two X-ray crystal structures in the manuscript have been deposited in the CCDC with numbers 2002759 and 2002760.

Preparation of amides:

Preparation of *N,N*-diisopropylbenzamide (**1a-I**):



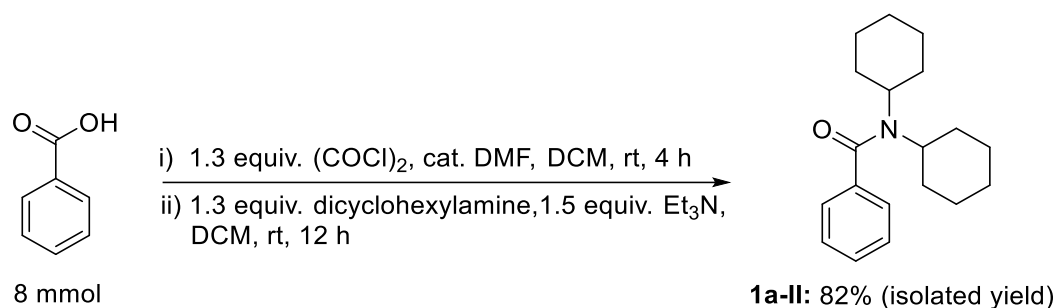
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then, (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (1.46 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.48 g (90%) of the *N,N*-diisopropylbenzamide (**1a-I**) as off white solid. Spectral data are in accordance with the reported data.¹

Preparation of *N,N*-dicyclohexylbenzamide (**1a-II**):



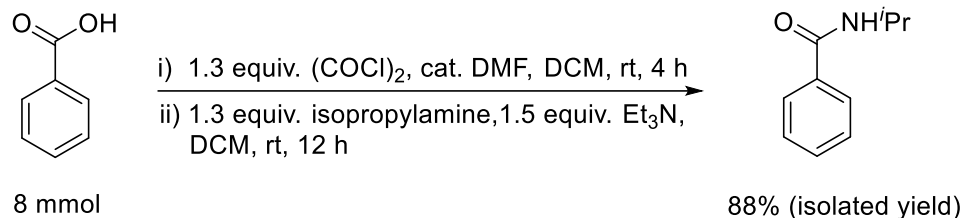
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of dicyclohexylamine (2.0 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and then reaction mixture was stirred at room temperature for 12 h. After that, water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.87 g (82%) of the *N,N*-dicyclohexylbenzamide (**1a-II**) as white solid. Spectral data are in accordance with the reported data.²

Preparation of N-isopropylbenzamide:



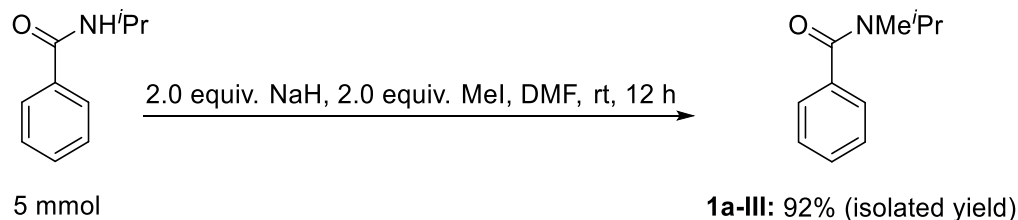
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of isopropylamine (0.851 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.15 g (88%) *N*-isopropylbenzamide (**1a-III**) as white solid.³

Preparation of *N*-isopropyl-*N*-methylbenzamide (**1a-III**):



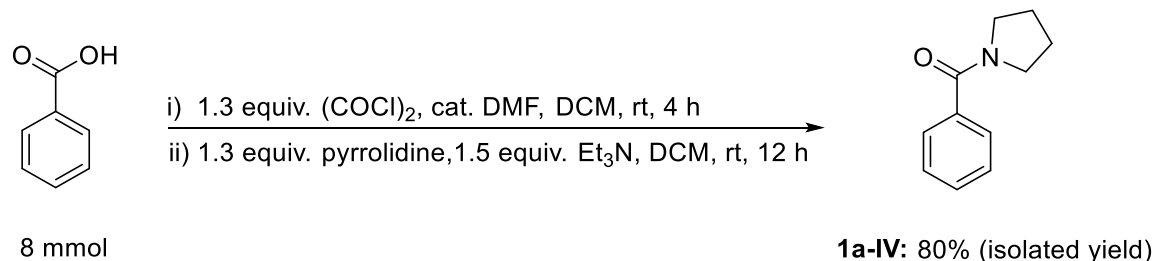
A 100 mL round bottom flask was charged with *N*-isopropylbenzamide (816.1 mg, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55 % dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h, the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 815.3 mg (92%) of the *N*-isopropyl-*N*-methylbenzamide (**1a-III**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.34-7.37 (m, 5H), 4.92-4.95 (m, 0.34H), 3.90-3.97 (m, 0.65H), 2.92 (s, 1.9H), 2.75 (s, 1.1H), 1.19 (d, J = 6.0 Hz, 2.1H), 1.11 (d, J = 6.4 Hz, 3.9H).

¹³C NMR (100 MHz, CDCl₃): δ 171.4, 171.1, 137.1, 129.0, 128.3, 126.6, 126.0, 49.6, 44.2, 30.5, 25.8, 20.2, 19.2.(due to rotamer)

HRMS (ESI) *m/z* calcd for C₁₁H₁₆NO [M+H]⁺ 178.1226, found 178.1223.

Preparation of phenyl(pyrrolidin-1-yl)methanone (**1a-IV**):



Step-I:

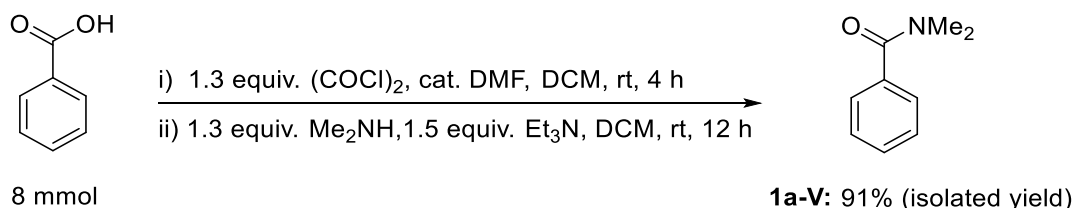
A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure

to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of pyrrolidine (0.85 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to afford 1.12 g (80%) of the phenyl(pyrrolidin-1-yl)methanone (**1a-IV**) as oil. Spectral data are in accordance with the reported data.⁴

Preparation of *N,N*-dimethylbenzamide (**1a-V**):



Step-I:

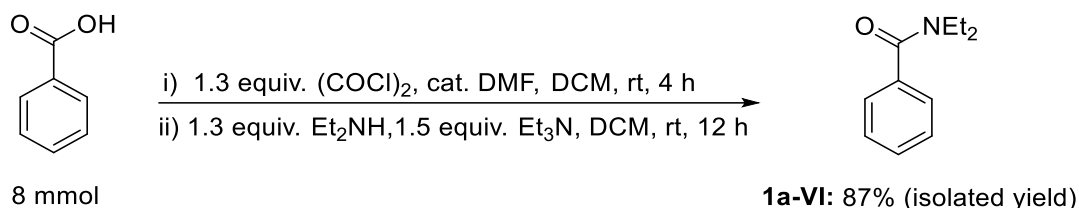
A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of dimethylamine (2.0 M in THF) (5.2 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic

layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.09 g (91%) of the *N,N*-dimethylbenzamide (**1a-V**) as oil. Spectral data are in accordance with the reported data.⁴

Preparation of N,N-diethylbenzamide (1a-VI):



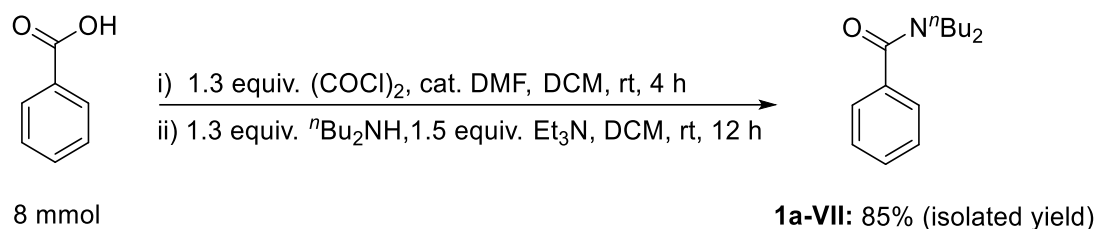
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diethylamine (1.07 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.23 g (87%) of the *N,N*-diethylbenzamide (**1a-VI**) as oil. Spectral data are in accordance with the reported data.⁴

Preparation of *N,N*-dibutylbenzamide (**1a-VII**):



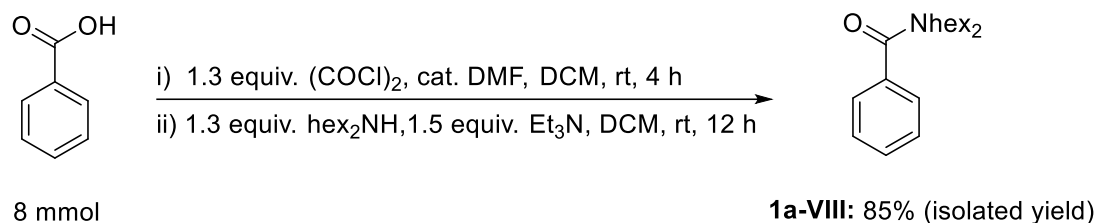
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of dibutylamine (1.75 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.59 g (85%) of the *N,N*-dibutylbenzamide (**1a-VII**) as oil. Spectral data are in accordance with the reported data.⁴

Preparation of N,N-dihexylbenzamide (1a-VIII):



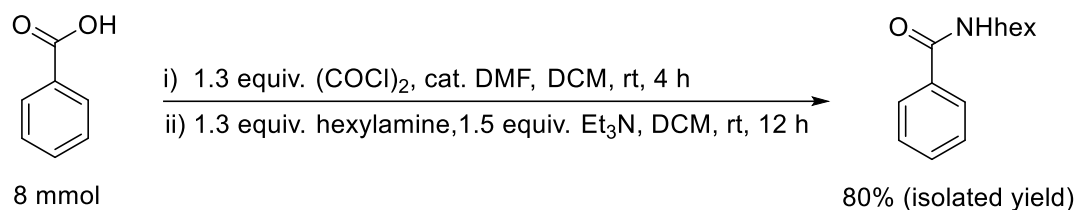
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of dihexylamine (2.42 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.97 g (85%) of the *N,N*-dihexylbenzamide (**1a-VIII**) as oil. Spectral data are in accordance with the reported data.⁴

Preparation of N-hexylbenzamide:



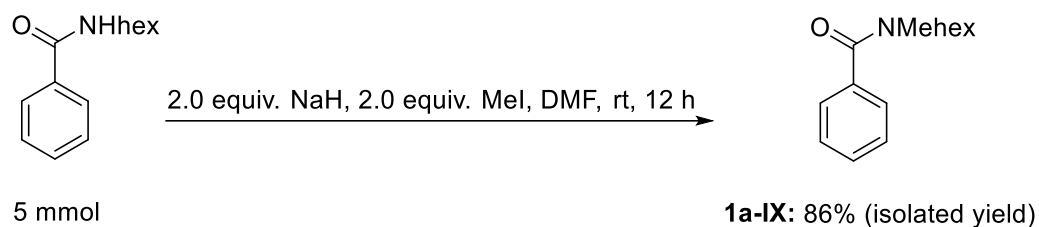
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of hexylamine (1.37 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.31 g (80%) of the *N*-hexylbenzamide as white solid. Spectral data are in accordance with the reported data.⁵

Preparation of N-hexyl-N-methylbenzamide (1a-IX):



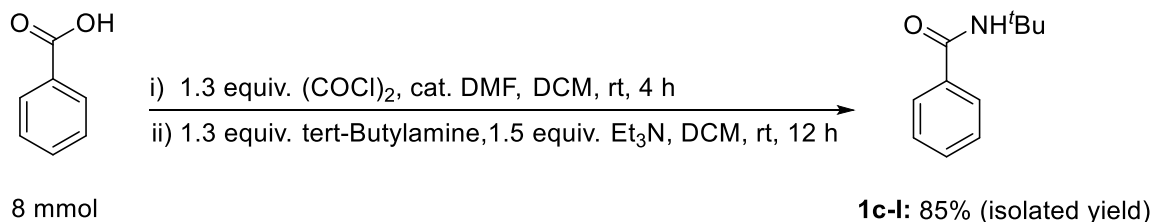
A 100 mL round bottom flask was charged with *N*-hexylbenzamide (1.03 g, 5 mmol) in dry DMF (20 mL) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55% dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (15% ethyl acetate in hexane as eluent) afforded 943.1 mg (86%) of the *N*-hexyl-*N*-methylbenzamide (**1a-IX**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.37 (br s, 5H), 3.51 (t, J = 7.6 Hz, 0.9H), 3.20 (t, J = 7.2 Hz, 1.1H), 3.05 (s, 1.65H), 2.91 (s, 1.35H), 1.62-1.70 (m, 0.9H), 1.48-1.52 (m, 1.1H), 1.33 (br s, 2.6H), 1.18-1.23 (m, 1.4H), 1.10-1.18 (m, 2.0H), 0.89 (m, 1.4H), 0.79-0.83 (m, 1.6H).

¹³C NMR (100 MHz, CDCl₃): δ 171.8, 171.1, 136.8, 136.7, 129.1, 128.2, 126.7, 126.5, 51.1, 47.3, 37.3, 32.5, 31.5, 31.1, 28.0, 26.8, 26.4, 25.9, 22.5, 22.3, 13.9, 13.8. (due to rotamer)

HRMS (ESI) *m/z* calcd for C₁₄H₂₂NO [M+H]⁺ 220.1696, found 220.1693.

Preparation of N-(tert-butyl)benzamide (1c-I):



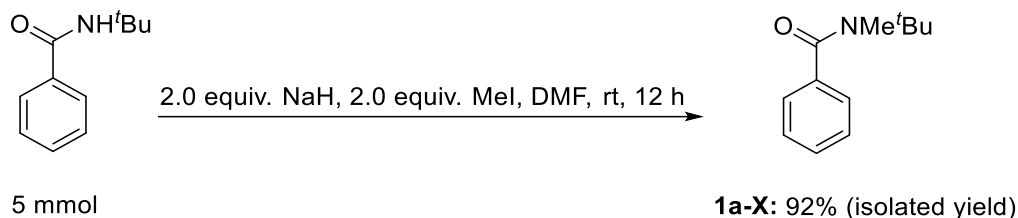
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

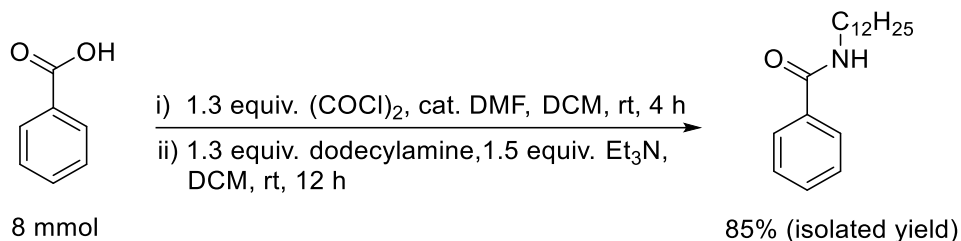
To a solution of *tert*-butylamine (1.09 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.21 g (85%) of the *N*-(*tert*-butyl)benzamide (**1c-I**) as white solid. Spectral data are in accordance with the reported data.⁶

Preparation of *N*-(*tert*-butyl)-*N*-methylbenzamide (**1a-X**):



A 100 mL round bottom flask was charged with *N*-*tert*butylbenzamide (886.0 mg, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55% dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) afforded 880.0 mg (92%) of the *N*-(*tert*-butyl)-*N*-methylbenzamide (**1a-X**) as white solid. Spectral data are in accordance with the reported data.⁷

Preparation of *N*-dodecylbenzamide:



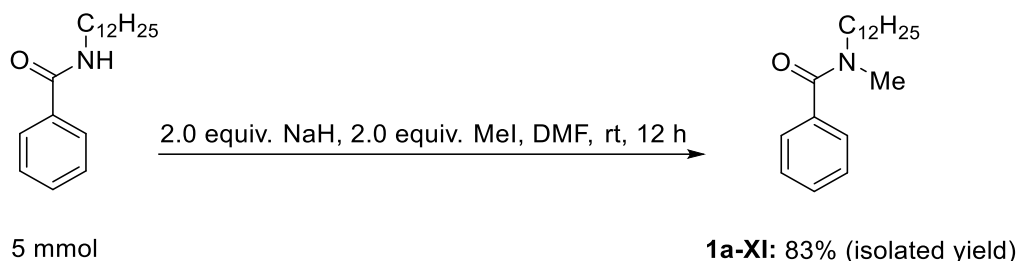
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

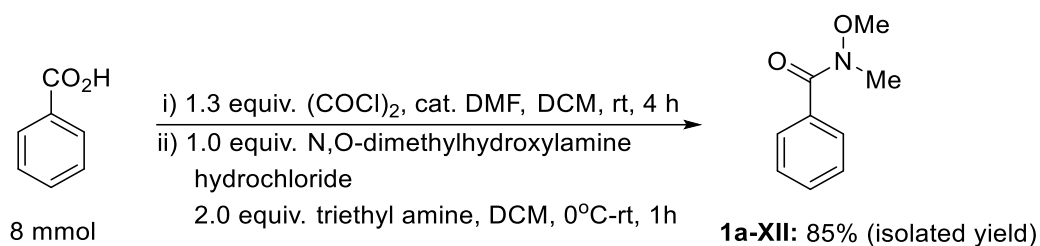
To a solution of dodecyl amine (2.39 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.97 g (85%) of the *N*-dodecylbenzamide as white solid. Spectral data are in accordance with the reported data.³

Preparation of *N*-dodecyl-*N*-methylbenzamide (**1a-XI**):



A 100 mL round bottom flask was charged with *N*-dodecylbenzamide (723.7 mg, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55% dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 1.26 g (83%) of the *N*-dodecyl-*N*-methylbenzamide (**1a-XI**) as oil. Spectral data are in accordance with the reported data.⁸

Preparation of *N*-methoxy-*N*-methylbenzamide (**1a-XII**):



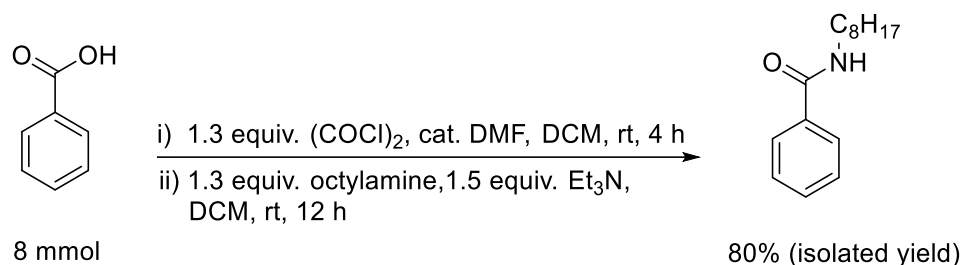
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of *N,O*-dimethylhydroxylamine hydrochloride (780.3 mg, 8 mmol), Et₃N (2.23 mL, 2.0 equiv.), in anhydrous DCM (10 mL) was added crude benzoyl chloride (1.0 equiv.) at 0 °C. Then the reaction mixture was stirred at rt for 1 h. After that water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 1.12 g (85%) of the *N*-methoxy-*N*-methylbenzamide (**1a-XII**) as oil. Spectral data are in accordance with the reported data.⁹

Preparation of N-octylbenzamide:



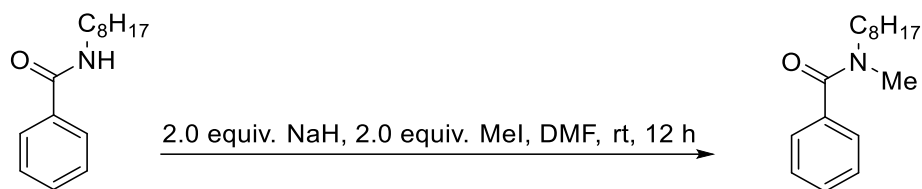
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of octyl amine (1.72 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.49 g (80%) of the *N*-octylbenzamide as white solid. Spectral data are in accordance with the reported data.¹⁰

Preparation of *N*-octyl-*N*-methylbenzamide (**1a-XIII**):



5 mmol

1a-XIII: 85% (isolated yield)

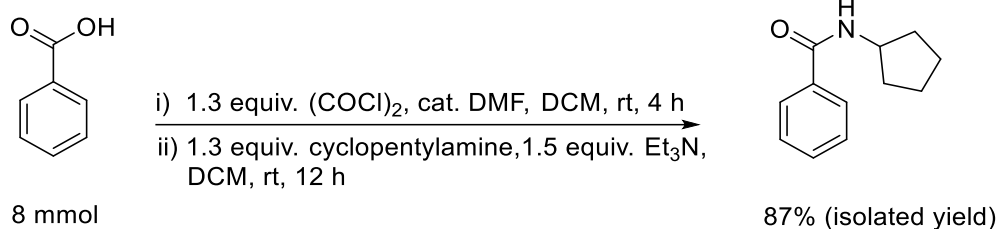
A 100 mL round bottom flask was charged with *N*-octylbenzamide (1.16 g, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55% dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) afforded 1.05 g (85%) of the *N*-methyl-*N*-octylbenzamide (**1a-XIII**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.36 (br s, 5H), 3.51 (br s, 0.9H), 3.19-3.21 (m, 1.1H), 3.05 (br s, 1.6 H), 2.90 (br s, 1.4H), 1.63 (br s, 1H), 1.50 (br s, 1H), 1.12-1.34 (m, 10H), 0.85-0.86 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.8, 171.1, 136.8, 129.1, 128.2, 126.8, 126.5, 51.2, 47.4, 37.3, 32.6, 31.6, 29.3, 29.2, 29.0, 28.1, 26.9, 26.8, 26.3, 22.5, 14.0.

HRMS (ESI) *m/z* calcd for C₁₆H₂₆NO [M+H]⁺ 248.2009, found 248.1992.

Preparation of N-cyclopentylbenzamide:



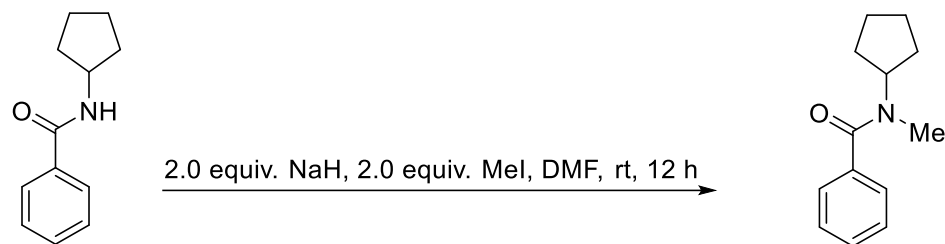
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of cyclopentylamine (1.03 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.32 g (87%) of the *N*-cyclopentylbenzamide as white solid. Spectral data are in accordance with the reported data.¹¹

Preparation of *N*-cyclopentyl-*N*-methylbenzamide (**1a-XIV**):



5 mmol

1a-XIV: 90% (isolated yield)

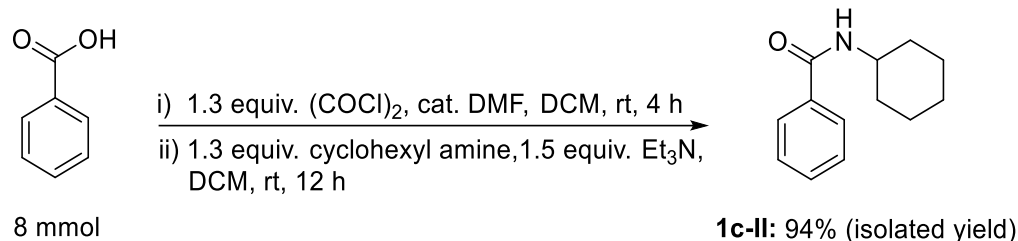
A 100 mL round bottom flask was charged with *N*-cyclopentylbenzamide (946.3 mg, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55% dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (15% ethyl acetate in hexane as eluent) afforded 914.8 mg (90%) of the *N*-cyclopentyl-*N*-methylbenzamide (**1a-XIV**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.35 (br s, 5H), 5.0 (br s, 0.3H), 4.07 (br s, 0.7H), 2.92 (br s, 3H), 1.42-1.64 (m, 8H).

¹³C NMR (100 MHz, CDCl₃): δ 171.6, 137.1, 129.0, 128.2, 126.4, 59.8, 54.7, 37.5, 31.9, 29.0, 27.4, 24.4. (due to rotamer)

HRMS (ESI) *m/z* calcd for C₁₃H₁₇NNaO [M+Na]⁺ 226.1202, found 226.1200.

Preparation of N-cyclohexylbenzamide (1c-II):



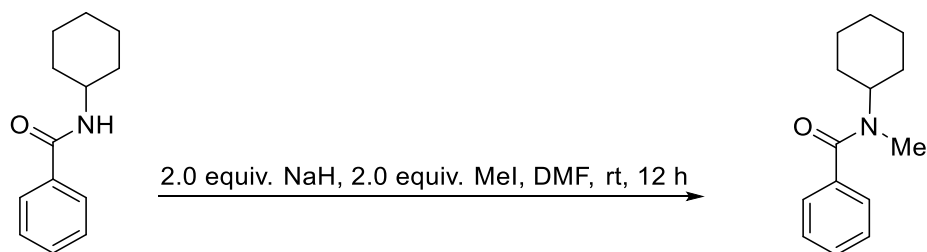
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of cyclohexyl amine (1.2 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 1.53 g (94%) of the *N*-cyclohexylbenzamide (**1c-II**) as white solid. Spectral data are in accordance with the reported data.¹²

Preparation of *N*-(cyclohexyl)-*N*-methylbenzamide (**1a-XV**):

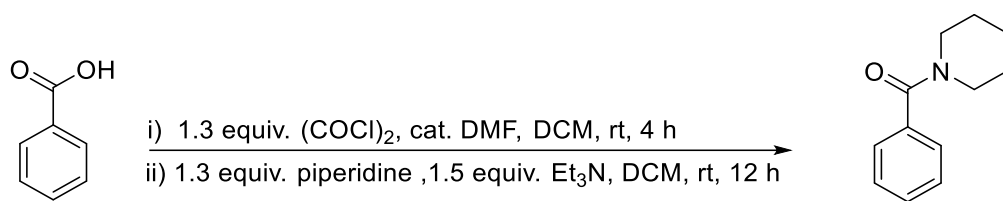


5 mmol

1a-XV: 90% (isolated yield)

A 100 mL round bottom flask was charged with *N*-cyclohexylbenzamide (1.01 g, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55% dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h the reaction mixture was diluted with ice water and extracted with DCM (3 x 30 mL) and dried over Na₂SO₄. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (15% ethyl acetate in hexane as eluent) to afford 978.0 mg (90%) of the *N*-cyclohexyl-*N*-methylbenzamide (**1a-XV**) as oil. Spectral data are in accordance with the reported data.¹³

Preparation of phenyl(piperidin-1-yl)methanone (**1a-XVI**):



8 mmol

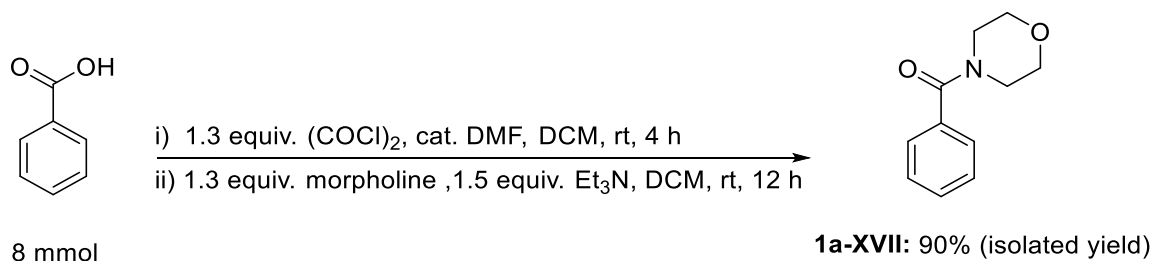
1a-XVI: 90% (isolated yield)

Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of piperidine (1.02 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.36 g (90%) phenyl(piperidin-1-yl)methanone (**1a-XVI**) as oil. Spectral data are in accordance with the reported data.⁴

Preparation of morpholino(phenyl)methanone (1a-XVII):**Step-I:**

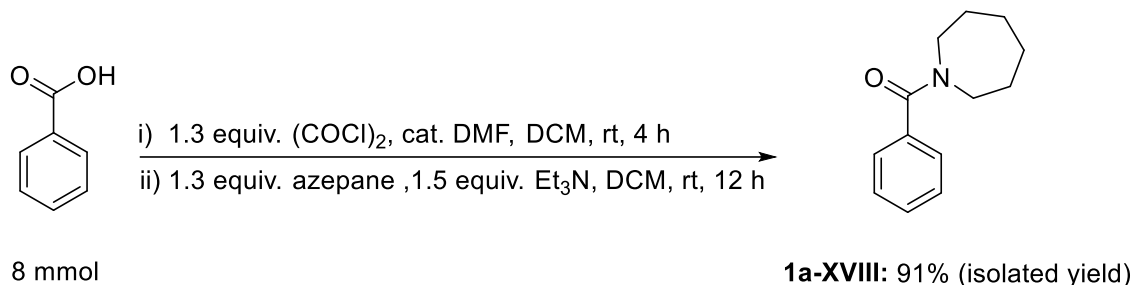
A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of morpholine (0.9 mL, 1.3 equiv.) and Et₃N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic

layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.38 g (90%) of the morpholino(phenyl)methanone (**1a-XVII**) as off white solid. Spectral data are in accordance with the reported data.⁴

Preparation of azepan-1-yl(phenyl)methanone (1a-XVIII):



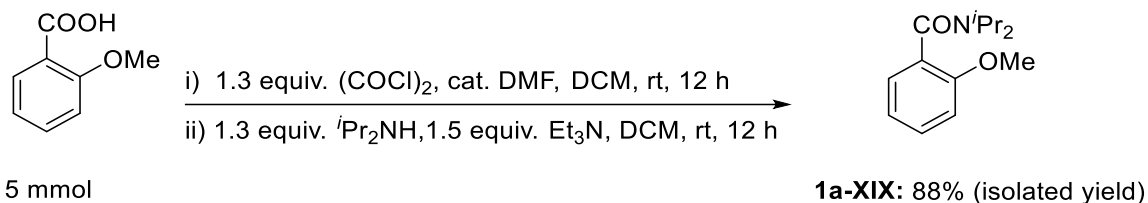
Step-I:

A 100 mL round-bottom flask was charged with benzoic acid (977.0 mg, 8 mmol), dry DCM (20 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then $(\text{COCl})_2$ (0.89 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of azepane (1.17 mL, 1.3 equiv.) and Et_3N (1.67 mL, 1.5 equiv.) in dry DCM (20 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added, the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO_3 (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.48 g (91%) of the azepan-1-yl(phenyl)methanone (**1a-XVIII**) as oil. Spectral data are in accordance with the reported data.¹⁴

Preparation of *N,N*-diisopropyl-2-methoxybenzamide (**1a-XIX**):



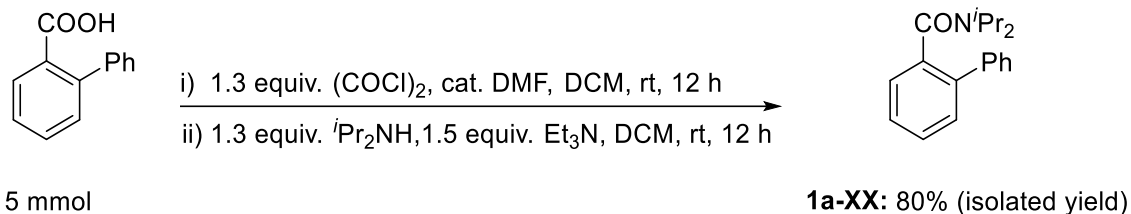
Step-I:

A 100 mL round-bottom flask was charged with 2-methoxybenzoic acid (761.0 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minute. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and the organic layer was separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 1.04 g (88%) of the *N,N*-diisopropyl-2-methoxybenzamide (**1a-XIX**) as white solid. Spectral data are in accordance with the reported data.¹

Preparation of *N,N*-diisopropyl-[1,1'-biphenyl]-2-carboxamide (**1a-XX**):



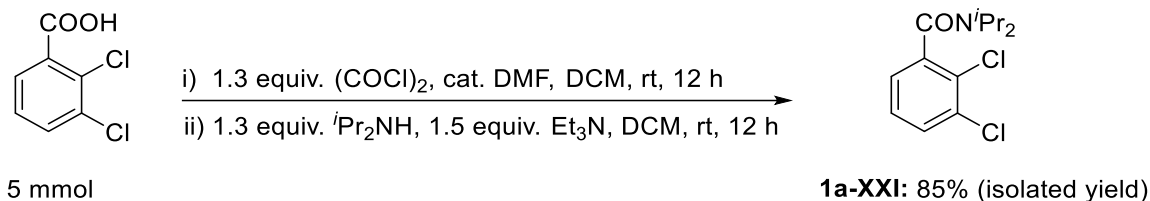
Step-I:

A 100 mL round-bottom flask was charged with [1,1'-biphenyl]-2-carboxylic acid (991.0 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.13 g (80%) of the *N,N*-diisopropyl-[1,1'-biphenyl]-2-carboxamide (**1a-XX**) as white solid. Spectral data are in accordance with the reported data.¹⁵

Preparation of 2,3-dichloro-*N,N*-diisopropylbenzamide (**1a-XXI**):



Step-I:

A 100 mL round-bottom flask was charged with 2,3-dichlorobenzoic acid (955.0 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

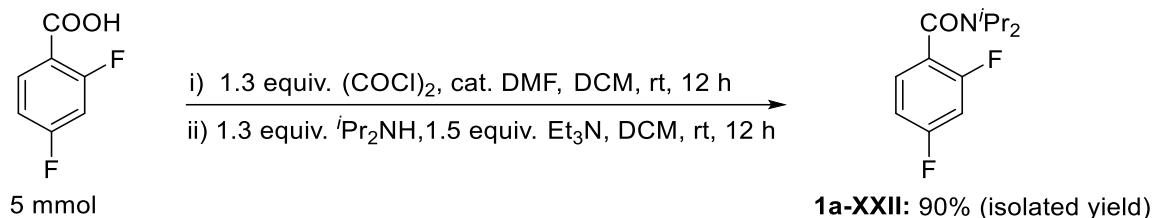
To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.16 g (85%) of the 2,3-dichloro-*N,N*-diisopropylbenzamide (**1a-XXI**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.41 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.09 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 3.46-3.60 (m, 2H), 1.55 (t, J = 6.4 Hz, 6H), 1.20 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 166.4, 139.9, 133.4, 129.9, 128.5, 127.9, 124.6, 51.2, 46.0, 20.7, 20.6, 20.5, 20.0.

HRMS (ESI) *m/z* calcd for C₁₃H₁₈Cl₂NO [M+H]⁺ 274.0760, found 274.0758.

Preparation of 2,4-difluoro-*N,N*-diisopropylbenzamide (**1a-XXII**):



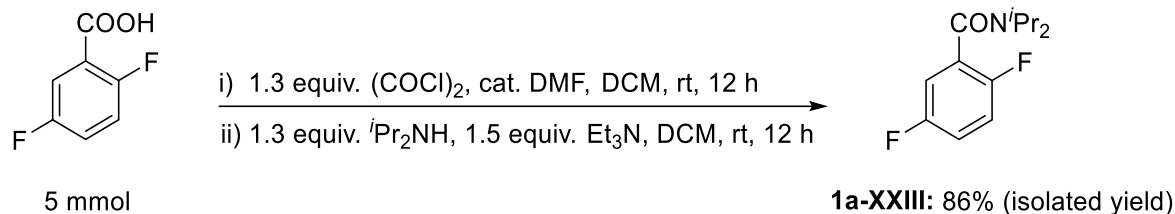
Step-I:

A 100 mL round-bottom flask was charged with 2,4-difluorobenzoic acid (790.5 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.09 g (90%) of the 2,4-difluoro-*N,N*-diisopropylbenzamide (**1a-XXII**) as white solid. Spectral data are in accordance with the reported data.⁷

Preparation of 2,5-difluoro-*N,N*-diisopropylbenzamide (**1a-XXIII**):



Step-I:

A 100 mL round-bottom flask was charged with 2,5-difluorobenzoic acid (790.5 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

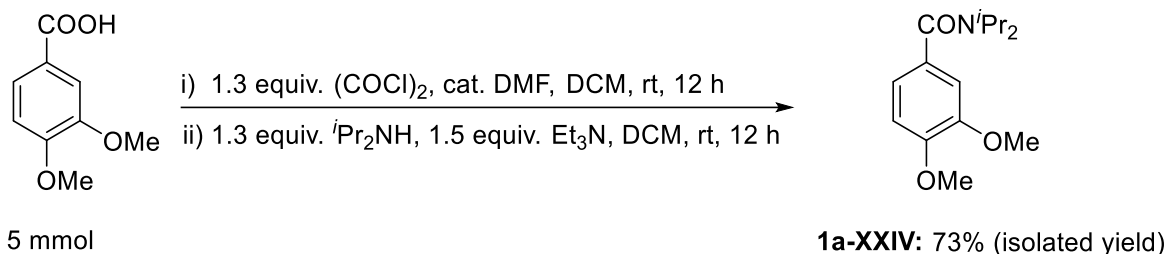
To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.04 g (86%) of the 2,5-difluoro-*N,N*-diisopropylbenzamide (**1a-XXIII**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 6.99-7.06 (m, 2H), 6.94-6.98 (m, 1H), 3.70 (sept, J = 6.8 Hz, 1H), 3.52 (sept, J = 6.8 Hz, 1H), 1.53 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 5.2 Hz, 3H), 1.10 (d, J = 5.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 164.2 (d, J = 1.1 Hz), 158.6 (dd, J = 242.8 Hz, 2.3 Hz), 153.8 (dd, J = 240.8 Hz, 2.5 Hz), 127.8 (dd, J = 22.3 Hz, 7.2 Hz), 117.0 (dd, J = 24.5 Hz, 8.5 Hz), 116.6 (dd, J = 23.9 Hz, 8.1 Hz), 114.4 (dd, J = 25.1 Hz, 4.8 Hz), 51.2, 46.1, 20.9, 20.5, 20.4, 20.2

HRMS (ESI) *m/z* calcd for C₁₃H₁₈F₂NO [M+H]⁺ 242.1351, found 242.1383.

Preparation of *N,N*-diisopropyl-3,4-dimethoxybenzamide (**1a-XXIV**):



Step-I:

A 100 mL round-bottom flask was charged with 3,4-dimethoxybenzoic acid (910.9 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

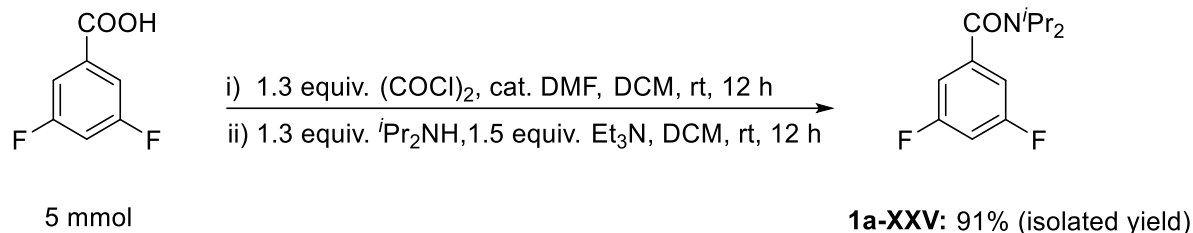
To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (25% ethyl acetate in hexane as eluent) to afford 968.6 mg (73%) of the *N,N*-diisopropyl-3,4-dimethoxybenzamide (**1a-XXIV**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 6.82-6.89 (m, 3H), 3.78 (br s, 8H), 1.32 (br s, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 170.8, 149.3, 148.8, 131.3, 118.2, 110.5, 109.6, 55.9, 55.8, 43.4, 40.0, 20.8.

HRMS (ESI) *m/z* calcd for C₁₅H₂₄NO₃ [M+H]⁺ 266.1751, found 266.1770.

Preparation of 3,5-difluoro-*N,N*-diisopropylbenzamide (**1a-XXV**):



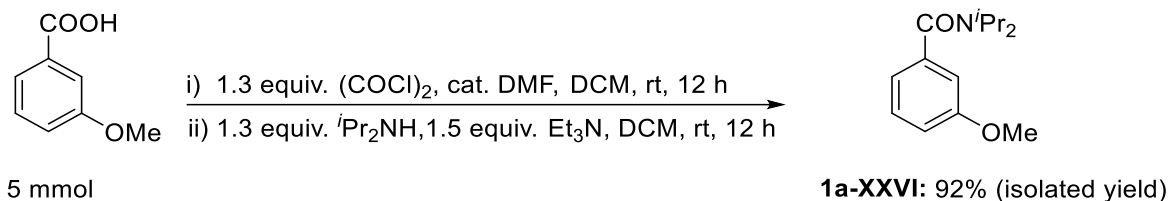
Step-I:

A 100 mL round-bottom flask was charged with 3,5-difluorobenzoic acid (790.5 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in DCM (15 mL), acid chloride (1.0 equiv.) was added at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.10 g (91%) of the 3,5-difluoro-*N,N*-diisopropylbenzamide (**1a-XXV**) as white solid. Spectral data are in accordance with the reported data.¹⁶

Preparation of *N,N*-diisopropyl-3-methoxybenzamide (**1a-XXVI**):



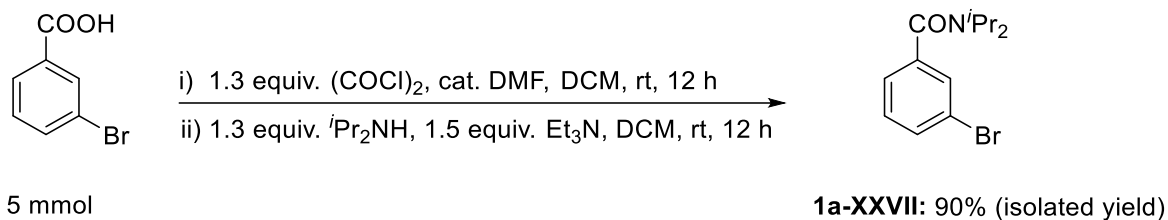
Step-I:

A 100 mL round-bottom flask was charged with 3-methoxybenzoic acid (760.8 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.08 g (92%) of the *N,N*-diisopropyl-3-methoxybenzamide (**1a-XXVI**) as white solid. Spectral data are in accordance with the reported data.¹⁷

Preparation of 3-bromo-*N,N*-diisopropylbenzamide (**1a-XXVII**):



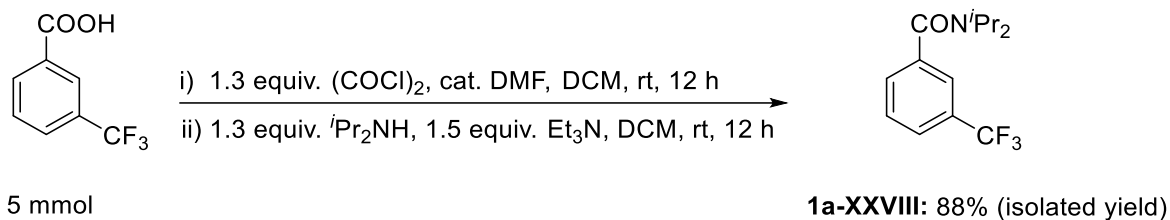
Step-I:

A 100 mL round-bottom flask was charged with 3-bromobenzoic acid (1.0 g, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.28 g (90%) of the 3-bromo-*N,N*-diisopropylbenzamide (**1a-XXVII**) as white solid. Spectral data are in accordance with the reported data.¹⁷

Preparation of *N,N*-diisopropyl-3-(trifluoromethyl)benzamide (**1a-XXVIII**):



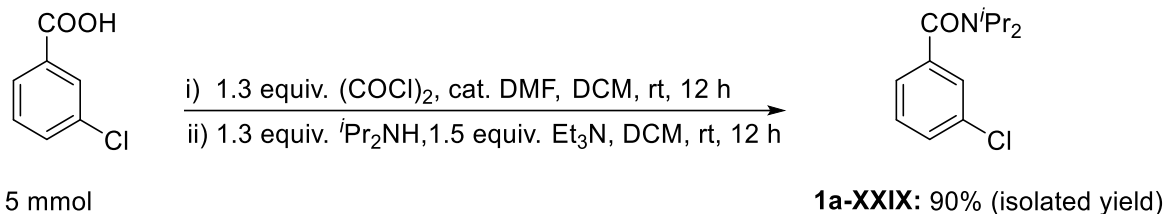
Step-I:

A 100 mL round-bottom flask was charged with 3-(trifluoromethyl) benzoic acid (950.6 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.20 g (88%) of the *N,N*-diisopropyl-3-(trifluoromethyl)benzamide (**1a-XXVIII**) as white solid. Spectral data are in accordance with the reported data.¹⁷

Preparation of 3-chloro-*N,N*-diisopropylbenzamide (**1a-XXIX**):



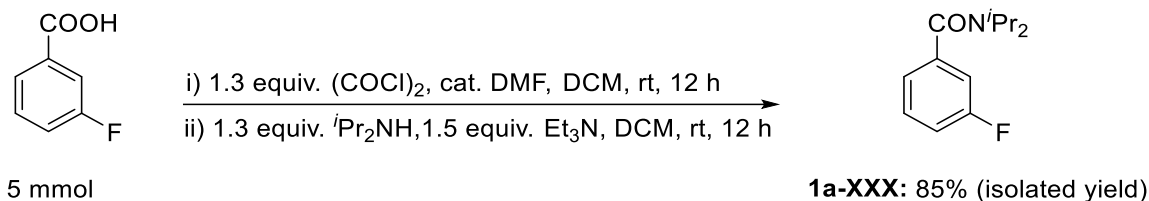
Step-I:

A 100 mL round-bottom flask was charged with 3-chlorobenzoic acid (782.9 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.08 g (90%) of the 3-chloro-*N,N*-diisopropylbenzamide (**1a-XXIX**) as white solid. Spectral data are in accordance with the reported data.¹⁸

Preparation of 3-fluoro-*N,N*-diisopropylbenzamide (**1a-XXX**):



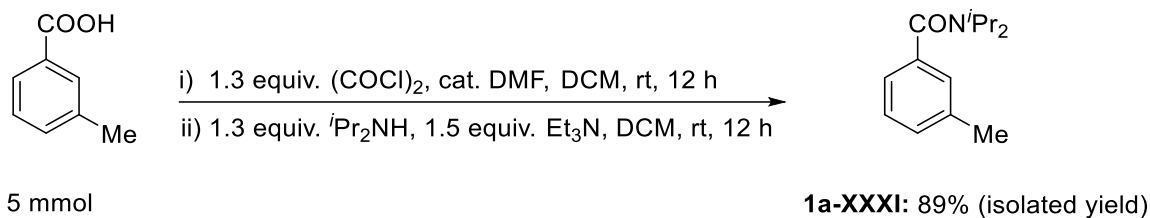
Step-I:

A 100 mL round-bottom flask was charged with 3-fluorobenzoic acid (700.6 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 949.0 mg (85%) of the 3-fluoro-*N,N*-diisopropylbenzamide (**1a-XXX**) as off white solid. Spectral data are in accordance with the reported data.¹⁹

Preparation of *N,N*-diisopropyl-3-methylbenzamide (**1a-XXXI**):



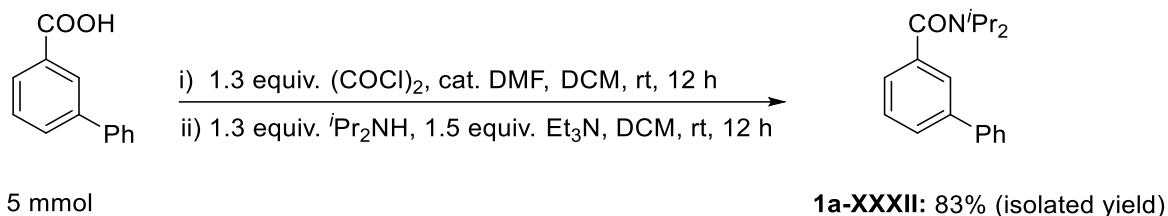
Step-I:

A 100 mL round-bottom flask was charged with 3-methylbenzoic acid (680.8 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 976.0 mg (89%) of the *N,N*-diisopropyl-3-methylbenzamide (**1a-XXXI**) as off white solid. Spectral data are in accordance with the reported data.¹⁷

Preparation of *N,N*-diisopropyl-[1,1'-biphenyl]-3-carboxamide (**1a-XXXII**):



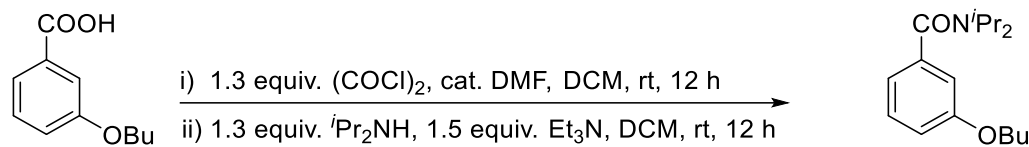
Step-I:

A 100 mL round-bottom flask was charged with [1,1'-biphenyl]-3-carboxylic acid (991.1 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.17 g (83%) of the *N,N*-diisopropyl-[1,1'-biphenyl]-3-carboxamide (**1a-XXXII**) as off white solid. Spectral data are in accordance with the reported data.¹⁹

Preparation of 3-butoxy-*N,N*-diisopropylbenzamide (**1a-XXXIII**):



Step-I:

A 100 mL round-bottom flask was charged with 3-butoxybenzoic acid (971.2 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

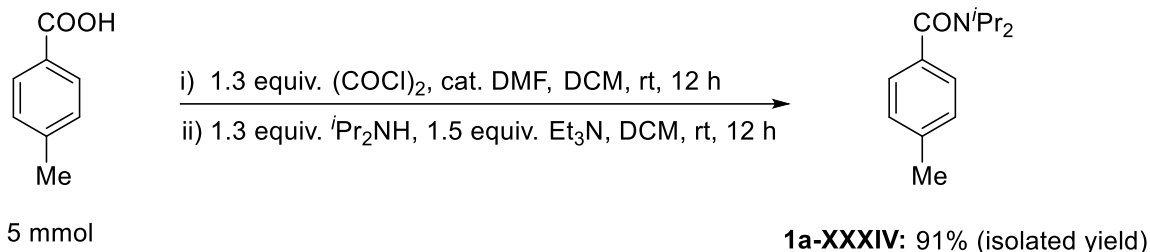
To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 1.18 g (85%) of the 3-butoxy-*N,N*-diisopropylbenzamide (**1a-XXXIII**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.25 (t, J = 8.0 Hz, 1H), 6.83-6.89 (m, 3H), 3.96 (t, J = 6.4 Hz, 2H), 3.85 (br s, 1H), 3.49 (b s, 1H), 1.72-1.79 (m, 2H), 1.45-1.50 (m, 8H), 1.13 (br s, 6H), 0.96 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 170.7, 159.1, 140.1, 129.5, 117.4, 115.5, 111.5, 67.7, 50.8, 45.8, 31.2, 20.7, 19.2, 13.8.

HRMS (ESI) *m/z* calcd for C₁₇H₂₈NO₂ [M+H]⁺ 278.2115, found 278.2112.

Preparation of *N,N*-diisopropyl-4-methylbenzamide (**1a-XXXIV**):



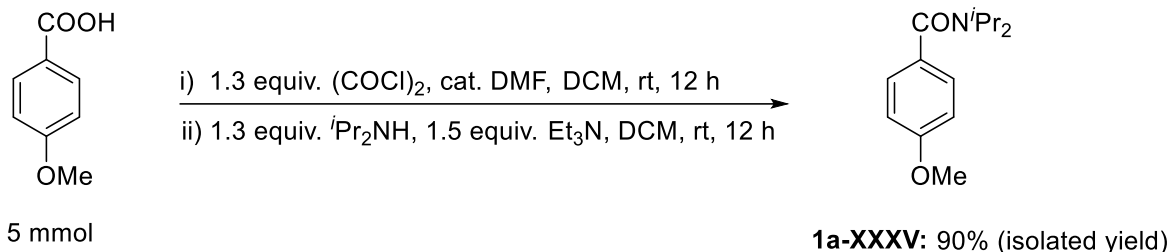
Step-I:

A 100 mL round-bottom flask was charged with 4-methylbenzoic acid (680.8 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 998 mg (91%) of the *N,N*-diisopropyl-4-methylbenzamide (**1a-XXXIV**) as off white solid. Spectral data are in accordance with the reported data.²⁰

Preparation of *N,N*-diisopropyl-4-methoxybenzamide (**1a-XXXV**):



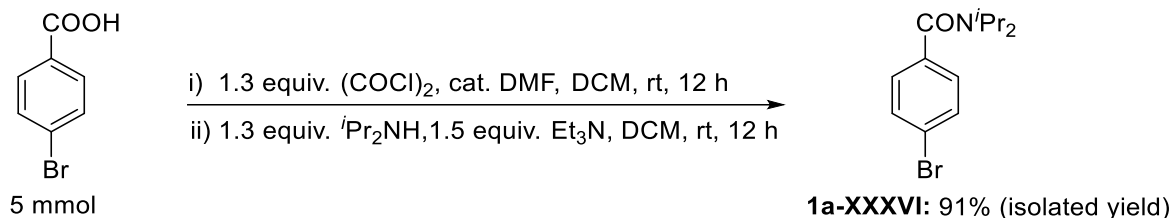
Step-I:

A 100 mL round-bottom flask was charged with 4-methoxybenzoic acid (760.8 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.06 g (90%) *N,N*-diisopropyl-4-methoxybenzamide (**1a-XXXV**) as off white solid. Spectral data are in accordance with the reported data.¹⁷

Preparation of 4-bromo-*N,N*-diisopropylbenzamide (**1a-XXXVI**):



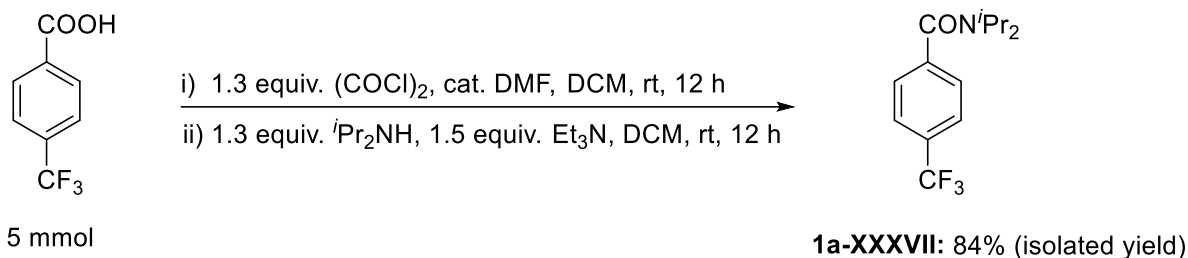
Step-I:

A 100 mL round-bottom flask was charged with 4-bromobenzoic acid (1.0 g, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.29 g (91%) of the 4-bromo-*N,N*-diisopropylbenzamide (**1a-XXXVI**) as white solid. Spectral data are in accordance with the reported data.²¹

Preparation of *N,N*-diisopropyl-4-(trifluoromethyl)benzamide (**1a-XXXVII**):



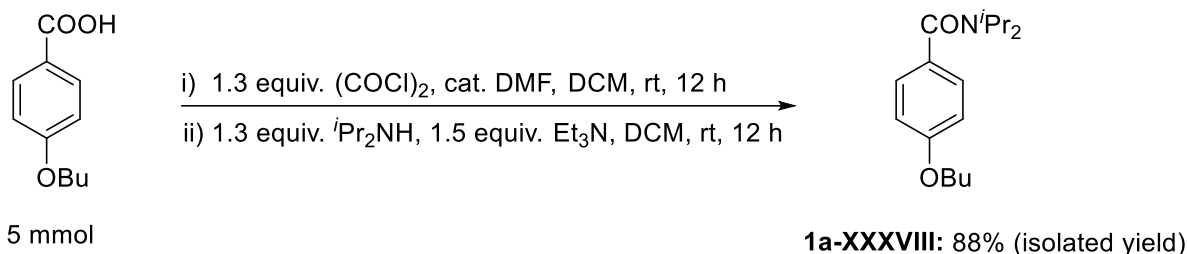
Step-I:

A 100 mL round-bottom flask was charged with 4-(trifluoromethyl)benzoic acid (950.6 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.15 g (84%) of the *N,N*-diisopropyl-4-(trifluoromethyl)benzamide (**1a-XXXVII**) as off white solid. Spectral data are in accordance with the reported data.¹⁷

Preparation of 4-butoxy-*N,N*-diisopropylbenzamide (**1a-XXXVIII**):



Step-I:

A 100 mL round-bottom flask was charged with 4-butoxybenzoic acid (971.2 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

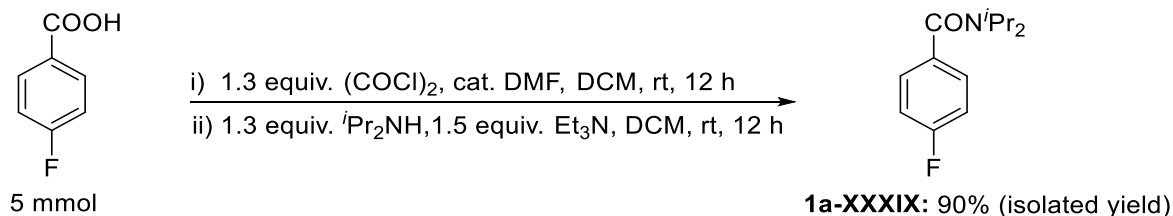
To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.22 g (88%) of the 4-butoxy-*N,N*-diisopropylbenzamide (**1a-XXXVIII**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.70 (br s, 2H), 1.72-1.79 (m, 2H), 1.43-1.53 (m, 2H), 1.32 (br s, 12 H), 0.96 (t, J = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.0, 159.4, 131.1, 127.4, 114.1, 67.6, 48.7, 46.4, 31.2, 20.8, 19.2, 13.8.

HRMS (ESI) *m/z*. calcd for C₁₇H₂₈NO₂ [M+H]⁺ 278.2115, found 278.2112.

Preparation of 4-fluoro-*N,N*-diisopropylbenzamide (**1a-XXXIX**):



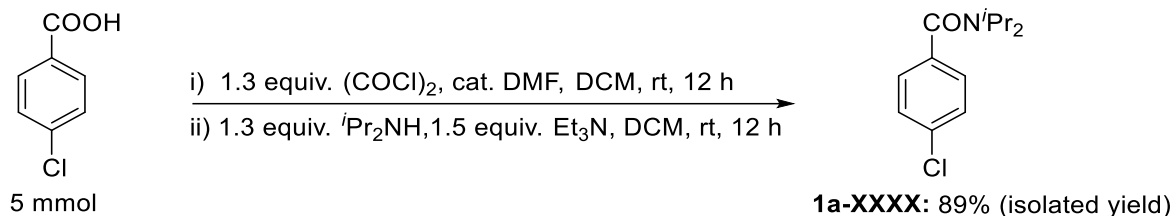
Step-I:

A 100 mL round-bottom flask was charged with 4-fluorobenzoic acid (700.6 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in DCM (15 mL), acid chloride (1.0 equiv.) was added at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethylacetate in hexane as eluent) to afford 1.0 g (90%) of the 4-fluoro-*N,N*-diisopropylbenzamide (**1a-XXXIX**) as white solid. Spectral data are in accordance with the reported data.²²

Preparation of 4-chloro-*N,N*-diisopropylbenzamide (**1a-XXXX**):



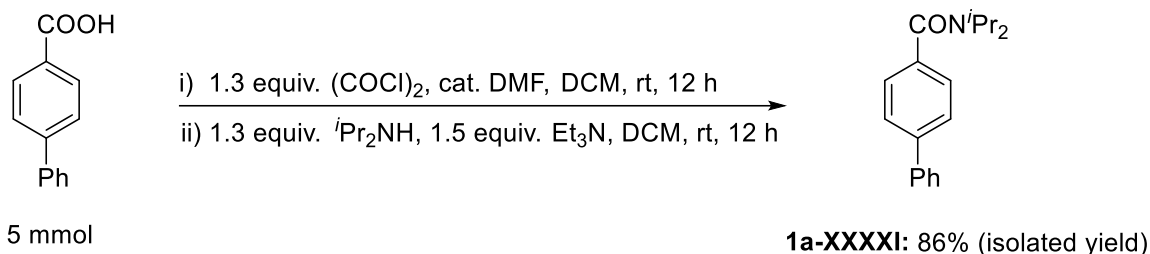
Step-I:

A 100 mL round-bottom flask was charged with 4-chlorobenzoic acid (782.9 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.07 g (89%) of the 4-chloro-*N,N*-diisopropylbenzamide (**1a-XXXX**) as white solid. Spectral data are in accordance with the reported data.²³

Preparation of *N,N*-diisopropyl-[1,1'-biphenyl]-4-carboxamide (**1a-XXXXI**):



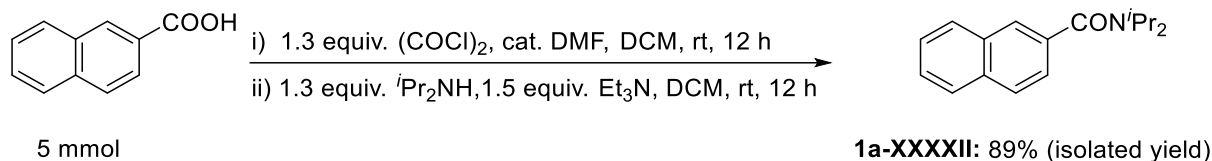
Step-I:

A 100 mL round-bottom flask was charged with [1,1'-biphenyl]-4-carboxylic acid (991.1 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.21 g (86%) of the *N,N*-diisopropyl-[1,1'-biphenyl]-4-carboxamide (**1a-XXXXI**) as off white solid. Spectral data are in accordance with the reported data.¹⁹

Preparation of *N,N*-diisopropyl-2-naphthamide (**1a-XXXXII**):



Step-I:

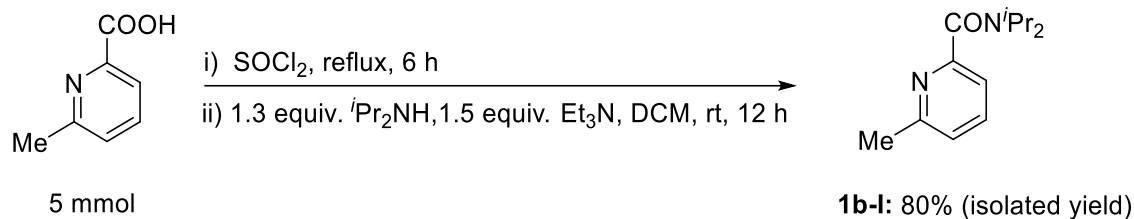
A 100 mL round-bottom flask was charged with 2-naphthoic acid (861.0 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and aqueous layer was extracted with DCM (3 x 30 mL). The combined organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to afford 1.14 g (89%) of the *N,N*-diisopropyl-2-naphthamide (**1a-XXXXII**) as white solid. Spectral data are in accordance with the reported data.²³

Pyridine containing heterocyclic amide preparation:

Preparation of *N,N*-diisopropyl-6-methylpicolinamide (**1b-I**):



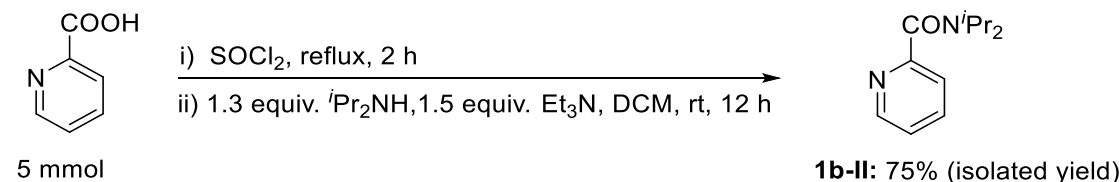
Step-I:

A 100 mL round-bottom flask was charged with 6-methylpicolinic acid (685.7 mg, 5 mmol) and SOCl_2 (10 mL) and refluxed for 6 h. The mixture was cooled to room temperature and the excess SOCl_2 was removed under vacuum to give corresponding acid chloride, which was directly used without further purification to the next step.

Step-II:

The acid chloride was dissolved in dry DCM (10 mL) and was added dropwise to a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et_3N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL) at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO_3 (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (35% ethyl acetate in hexane as eluent) to afford 881.0 mg (80%) of the *N,N*-diisopropyl-6-methylpicolinamide (**1b-I**) as white solid. Spectral data are in accordance with the reported data.⁷

Preparation of N,N-diisopropylpicolinamide (1b-II):



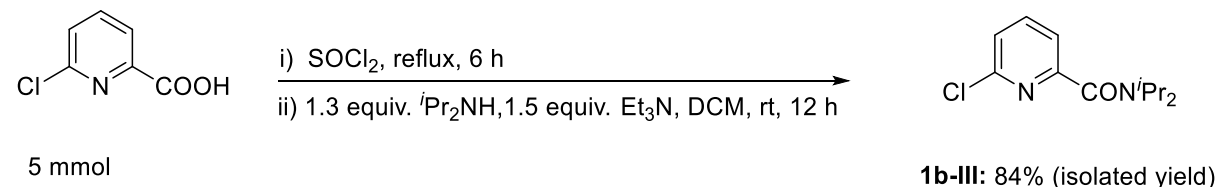
Step-I:

A 100 mL round-bottom flask was charged with picolinic acid (615.6 mg, 5 mmol) and SOCl₂ (10 mL) and refluxed for 2 h. The mixture was cooled to room temperature and the excess SOCl₂ was removed under vacuum to give corresponding acid chloride, which was directly used without further purification to the next step.

Step-II:

The acid chloride was dissolved in dry DCM (10 mL) and was added dropwise to a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in DCM (15 mL) at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to afford 773.0 mg (75%) of the *N,N*-diisopropylpicolinamide (**1b-II**) as off white solid. Spectral data are in accordance with the reported data.²⁴

Preparation of 6-chloro-N,N-diisopropylpicolinamide (1b-III):



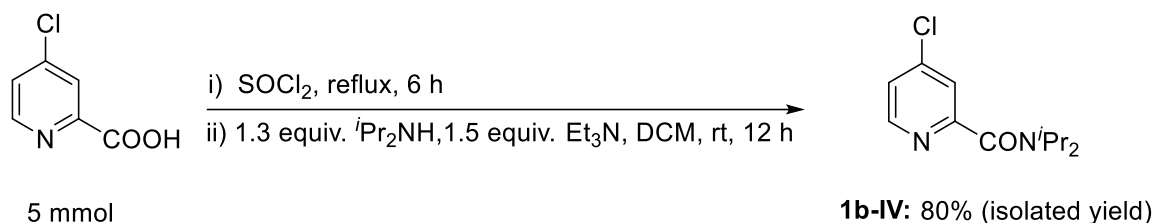
Step-I:

A 100 mL round-bottom flask was charged with 6-chloropicolinic acid (787.8 mg, 5 mmol) and SOCl₂ (10 mL) and refluxed for 6 h. The mixture was cooled to rt and the excess SOCl₂ was removed under vacuum to give corresponding acid chloride, which was directly used without further purification to the next step.

Step-II:

The acid chloride was dissolved in dry DCM (10 mL) and was added dropwise to a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL) at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (35% ethyl acetate in hexane as eluent) to afford 1.01 g (84%) of the 6-chloro-*N,N*-diisopropylpicolinamide (**1b-III**) as white solid. Spectral data are in accordance with the reported data.⁷

*Preparation of 4-chloro-*N,N*-diisopropylpicolinamide (1b-IV):*



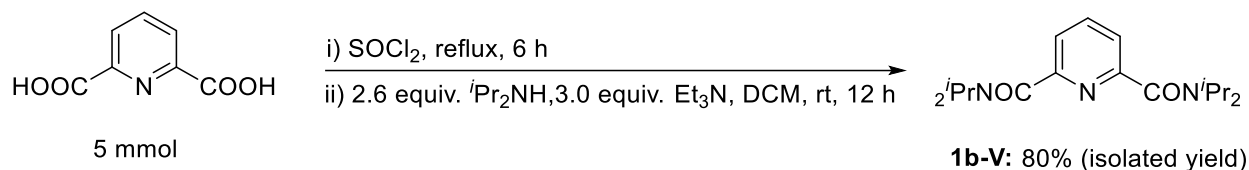
Step-I:

A 100 mL round-bottom flask was charged with 4-chloropicolinic acid (787.8mg, 5 mmol) and SOCl₂ (10 mL) and refluxed for 6 h. The mixture was cooled to room temperature and the excess SOCl₂ was removed under vacuum to give corresponding acid chloride, which was directly used without further purification to the next step.

Step-II:

The acid chloride was dissolved in dry DCM (10 mL) and was added dropwise to a solution of diisopropylamine (0.92 mL, 1.3 equiv) and Et₃N (1.05 mL, 1.5 equiv) in dry DCM (15 mL) at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to afford 963.0 mg (80%) of the 4-chloro-*N,N*-diisopropylpicolinamide (**1b-IV**) as white solid.²⁵

Preparation of *N*²,*N*²,*N*⁶,*N*⁶-tetraisopropylpyridine-2,6-dicarboxamide (**1b-V**):



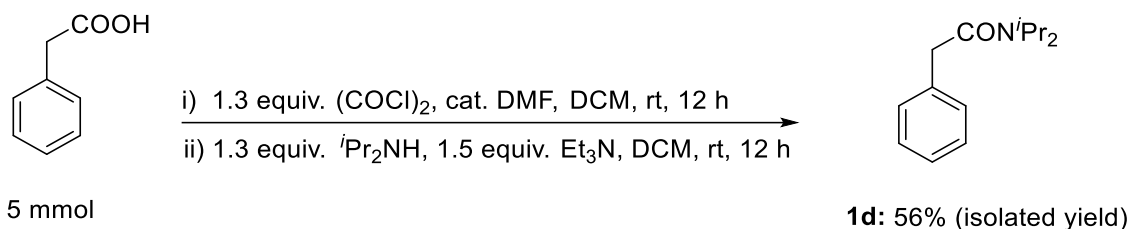
Step-I:

A 100 mL round-bottom flask was charged with pyridine-2,6-dicarboxylic acid (835.6 mg, 5 mmol) and SOCl₂ (10 mL) and refluxed for 6 h. The mixture was cooled to rt and the excess SOCl₂ was removed under vacuum to give corresponding acid chloride, which was directly used without further purification to the next step.

Step-II:

The acid chloride was dissolved in dry DCM (10 mL) and was added dropwise to a solution of diisopropylamine (1.83 mL, 2.6 equiv) and Et₃N (2.1 mL, 3.0 equiv) in dry DCM (15 mL) at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to afford 1.33 g (80%) of the *N*²,*N*²,*N*⁶,*N*⁶-tetraisopropylpyridine-2,6-dicarboxamide (**1b-V**) as white solid. Spectral data are in accordance with the reported data.²⁶

Preparation of *N,N*-diisopropyl-2-phenylacetamide (**1d**):



Step-I:

A 100 mL round-bottom flask was charged with 2-phenylacetic acid (680.8 mg, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added dropwise to the reaction mixture and

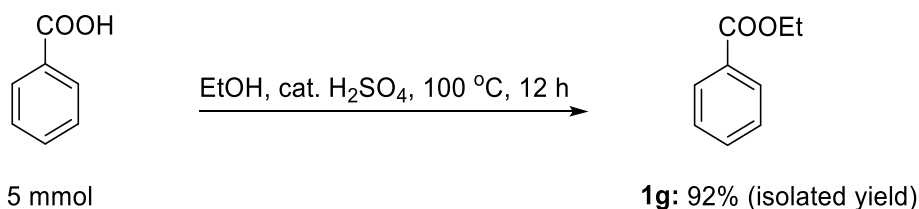
stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 614.0 mg (56%) of the *N,N*-diisopropyl-2-phenylacetamide (**1d**) as off white solid. Spectral data are in accordance with the reported data.²⁷

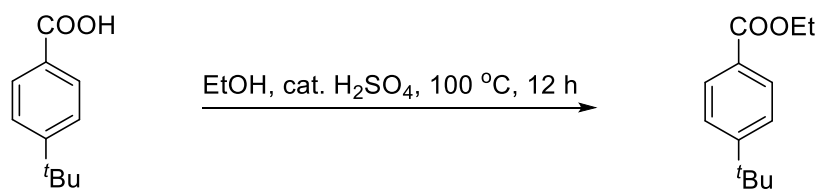
Preparation of other starting materials:

Preparation of ethyl benzoate (**1g**):



In a 15 mL pressure tube, a mixture of benzoic acid (610.6 mg, 5 mmol), EtOH (10 mL) and catalytic amount of H₂SO₄ was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralized with aqueous Na₂CO₃. The whole mixture was then extracted three times with DCM (25 mL) and washed with water. DCM layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mass was then purified by a short pad of silica (5% ethyl acetate in hexane as eluent) to afford 691 mg (92%) of the ethyl benzoate (**1g**) as oil. Spectral data are in accordance with the reported data.²⁸

Preparation of ethyl 4-(tert-butyl)benzoate (1g-II):



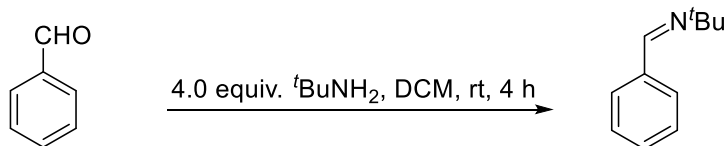
5 mmol

1g-II: 90% (isolated yield)

In a 15 mL pressure tube, a mixture of 4-(*tert*-butyl) benzoic acid (891.2 mg, 5 mmol), EtOH (10 mL) and catalytic amount of H₂SO₄ was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralize with aqueous Na₂CO₃. The whole mixture was then extracted three times with DCM (25 mL) and washed with water. DCM layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mass was then purified by a short pad of silica (5% ethyl acetate in hexane as eluent) to afford 928.0 mg (90%) of the ethyl 4-(*tert*-butyl) benzoate (**1g-II**) as oil. Spectral data are in accordance with the reported data.²⁹

Preparation of Aldimine:

Preparation of N-tert-butyl-1-phenylmethanimine (1h-I):

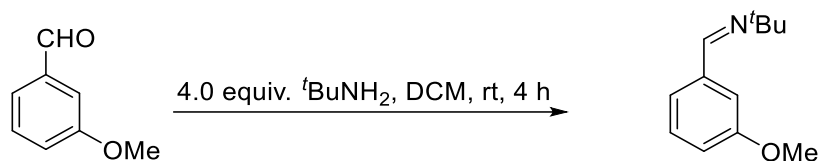


2.0 mmol

1h-I: Quantitative conversion

To a solution of benzaldehydes (212.3 mg, 2.0 mmol) in dry DCM (5.0 mL) and *tert*-butylamine (840.7 μ l, 4 equiv.) was added slowly by a syringe and the mixture was stirred for 4 h at room temperature. The reaction mixture was evaporated under reduced pressure to afford imines quantitatively. Spectral data are in accordance with the reported data.³⁰

Preparation of N-tert-butyl-1-(3-methoxyphenyl)methanimine (1h-II):

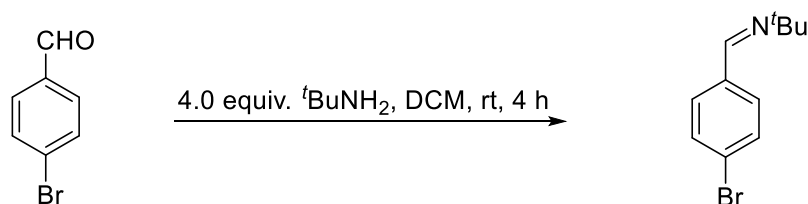


2.0 mmol

1h-II: Quantitative conversion

To a solution of 3-methoxybenzaldehyde (272.3 mg, 2.0 mmol), in dry DCM (5.0 mL) and *tert*-butylamine (840.7 μ L, 4.0 equiv.) was added slowly by a syringe and the mixture was stirred for 4 h at room temperature. The reaction mixture was evaporated under reduced pressure to afford imines quantitatively. Spectral data are in accordance with the reported data.³⁰

Preparation of N-tert-butyl-1-(4-bromophenyl)methanimine (1h-III):

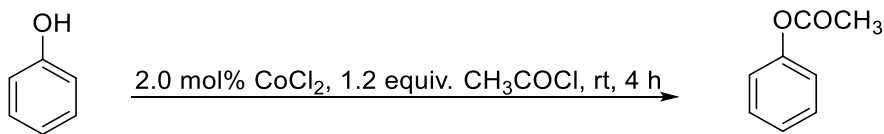


2.0 mmol

1h-III: Quantitative conversion

To a solution of 4-bromobenzaldehyde (370.0 mg, 2.0 mmol), in dry DCM (5.0 mL) and *tert*-butylamine (840.7 μ L, 4.0 equiv.) was added slowly by a syringe and the mixture was stirred for 4 h at room temperature. The reaction mixture was evaporated under reduced pressure to afford imines quantitatively. Spectral data are in accordance with the reported data.³¹

Preparation of phenyl acetate (1i):



5.0 mmol

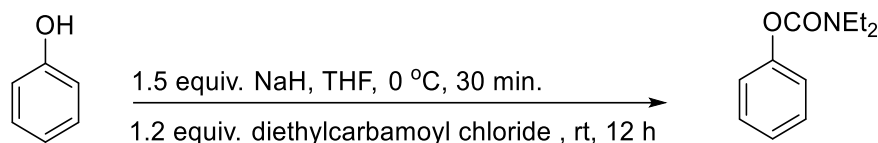
1i: 90% (isolated yield)

A 25 mL round-bottom flask was charged with phenol (5 mmol, 470.6 mg) and CoCl₂ (13.0 mg, 2 mol%). Then acetyl chloride (428 μ L, 1.2 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was

added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to afford 613.0 mg (90%) the phenyl acetate (**1i**) as oil. Spectral data are in accordance with the reported data.³²

Preparation of diethylcarbamate protected phenols:

Preparation of phenyl diethylcarbamate (1j-I):

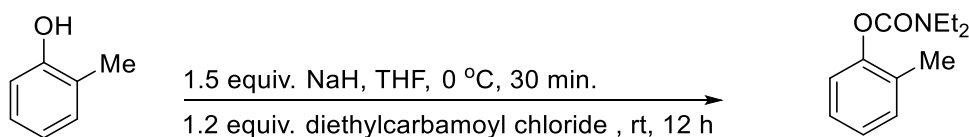


5.0 mmol

1j-I: 86% (isolated yield)

A 100 mL round-bottom flask was charged with phenol (470.6 mg, 5 mmol), dry THF (15 mL) and stir at 0 °C for 5 min. Then NaH (327.3 mg of 55% suspension in mineral oil, 1.5 equiv.) was added portion wise to the mixture over 5 min at 0 °C and stirred for 30 min. Next diethylcarbamoyl chloride (760 μL, 1.2 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to afford 831.0 mg (86%) of the phenyl diethylcarbamate (**1j-I**) as oil. Spectral data are in accordance with the reported data.³³

Preparation of o-tolyldiethylcarbamate (1j-II):



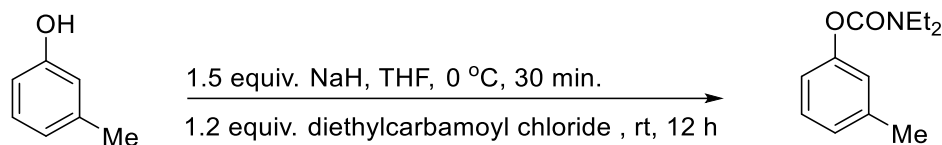
5.0 mmol

1j-II: 88% (isolated yield)

A 100 mL round-bottom flask was charged with 2-methylphenol (540.7 mg, 5 mmol), dry THF (15 mL) and stir at 0 °C for 5 min. Then NaH (327.3 mg of 55% suspension in mineral oil, 1.5 equiv.) was added portion wise to the mixture over 5 min at 0 °C and stirred for 30 min. Next

diethylcarbamoyl chloride (760 μ L, 1.2 equiv.) was added dropwise to the mixture over 5 min at 0 $^{\circ}$ C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to afford 912.0 mg (88%) of the *o*-tolyl diethylcarbamate (**1j-II**) as oil. Spectral data are in accordance with the reported data.³³

Preparation of m-tolyl diethylcarbamate (1j-III):

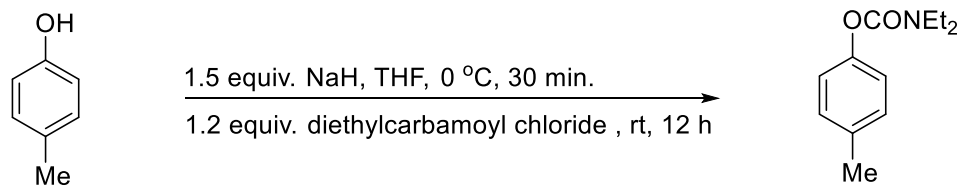


5.0 mmol

1j-III: 85% (isolated yield)

A 100 mL round-bottom flask was charged with 3-methylphenol (540.7 mg, 5 mmol), dry THF (15 mL) and stir at 0 $^{\circ}$ C for 5 min. Then NaH (327.3 mg of 55% suspension in mineral oil, 1.5 equiv.) was added portion wise to the mixture over 5 min at 0 $^{\circ}$ C and stirred for 30 min. Next diethylcarbamoyl chloride (760 μ L, 1.2 equiv.) was added dropwise to the mixture over 5 min at 0 $^{\circ}$ C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to afford 881.0 mg (85%) of the *m*-tolyl diethylcarbamate (**1j-III**) as oil. Spectral data are in accordance with the reported data.³³

Preparation of p-tolyl diethylcarbamate (1j-IV):



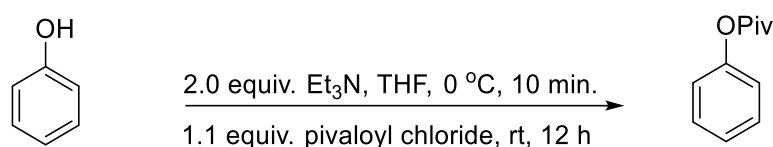
5.0 mmol

1j-IV: 84% (isolated yield)

A 100 mL round-bottom flask was charged with 4-methylphenol (540.7 mg, 5 mmol), dry THF (15 mL) and stir at 0 $^{\circ}$ C for 5 min. Then NaH (327.3 mg of 55% suspension in mineral oil, 1.5

equiv.) was added portion wise to the mixture over 5 min at 0 °C and stirred for 30 min. Next diethylcarbamoyl chloride (760 μ L, 1.2 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to afford 870.6 mg (84%) the *p*-tolyl-diethylcarbamate (**1j-IV**) as oil. Spectral data are in accordance with the reported data.³³

Preparation of phenyl pivalate (1k):

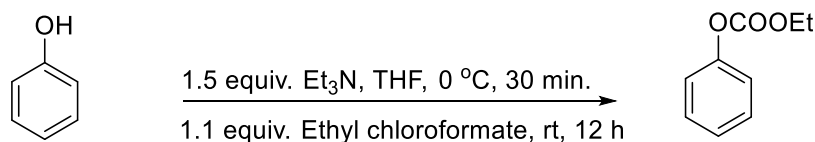


5.0 mmol

1k: 80% (isolated yield)

A 100 mL round-bottom flask was charged with phenol (470.6 mg, 5 mmol), triethylamine (1.4 mL, 2.0 equiv.) and dry THF (15 mL) and stir at 0 °C for 10 min. Pivaloyl chloride (673 μ L, 1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (1% ethyl acetate in hexane as eluent) to afford 713.0 mg (80%) of the phenyl pivalate (**1k**) as oil. Spectral data are in accordance with the reported data.³⁴

Preparation of ethyl phenyl carbonate (1l):



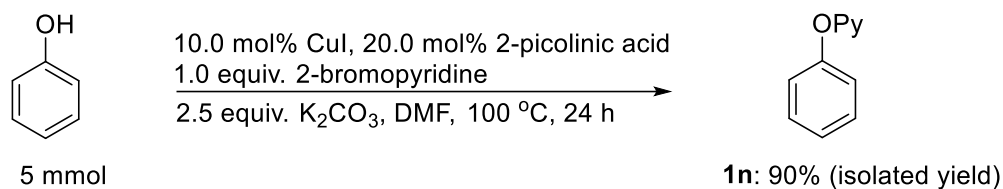
5.0 mmol

1l: 92% (isolated yield)

A 100 mL round-bottom flask was charged with phenol (470.6 mg, 5 mmol), triethylamine (0.91 mL, 1.3 equiv.) and dry THF (15 mL) and stir at 0 °C for 30 min. Ethyl chloroformate (524 μ L,

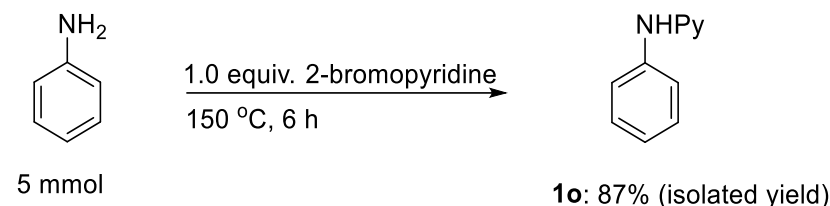
1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to get 764.0 mg (92%) of the ethyl phenyl carbonate (**11**) as oil. Spectral data are in accordance with the reported data.³⁵

Preparation of 2-phenoxy pyridine (1n):



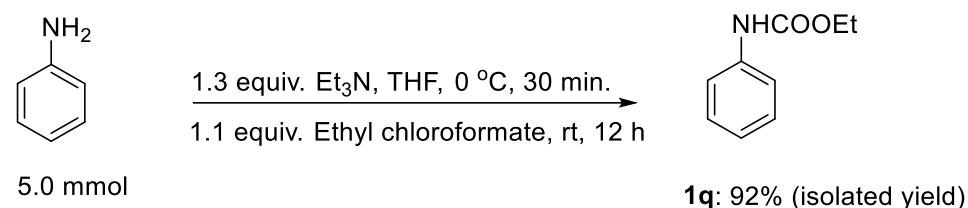
An oven dried 15 mL pressure tube was charged with phenol (470.6 mg, 5 mmol), CuI (95.3 mg, 10.0 mol%), 2-picolinic acid (123.1 mg, 20.0 mol%), anhydrous K₂CO₃ (1.73 g, 2.5 equiv.), 2-bromopyridine (790 mg, 1.0 equiv.) and dry DMF (8.0 mL) sequentially. Then, the reaction mixture was degassed well with nitrogen gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 100 °C and stirred for 24 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 770.0 mg (90%) of 2-phenoxy pyridine (**1n**) as white solid. Spectral data are in accordance with the reported data.³⁶

Preparation of N-phenylpyridin-2-amine (1o):



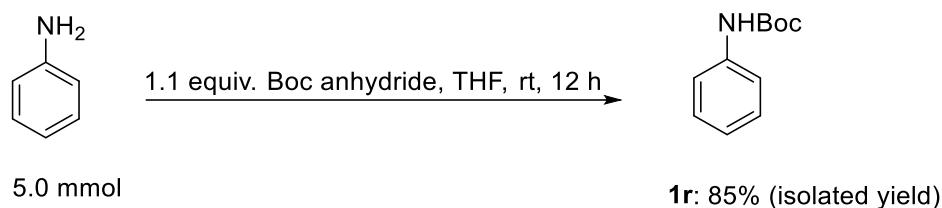
An oven dried 5.0 mL Wheaton microreactor was charged with aniline (465.7 mg, 5 mmol) and 2-bromopyridine (790 mg, 1.0 equiv.). The microreactor was capped with a teflon pressure cap and placed into a preheated aluminium block at 150 °C. The reaction mixture was stirred for 6 h. After completion (turned to solid), the reaction mixture was cooled to room temperature, neutralized by saturated aqueous sodium bicarbonate and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 740.0 mg (87%) of *N*-phenylpyridin-2-amine (**1o**) as off white solid. Spectral data are in accordance with the reported data.³⁷

Preparation of ethyl phenylcarbamate (1q):



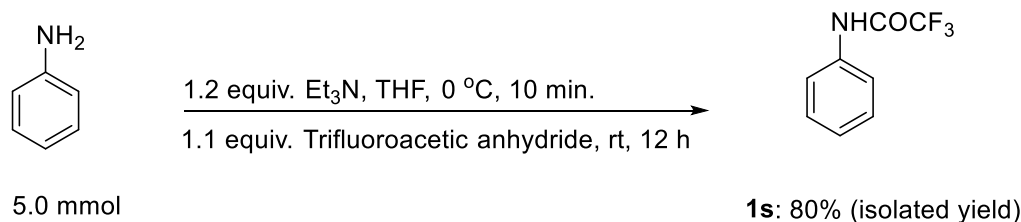
A 100 mL round-bottom flask was charged with aniline (465.7 mg, 5 mmol), triethylamine (0.91 mL, 1.3 equiv.) and dry THF (15 mL) and stir at 0 °C for 30 min. Ethyl chloroformate (524 μL, 1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to get 760.0 mg (92%) of the ethyl phenylcarbamate (**1q**) as white solid. Spectral data are in accordance with the reported data.³⁸

Preparation of ethyl phenylcarbamate (1r):



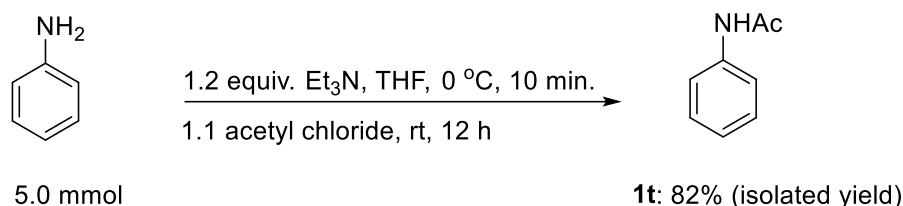
A 100 mL round-bottom flask was charged with aniline (5 mmol, 465.7 mg) and dry THF (15 mL) and stir at 0 °C for 5 min. Boc anhydride (1.26 mL, 1.1 equiv.) in 5 mL dry THF was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. After 12 h the reaction mixture was concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (3% ethyl acetate in hexane as eluent) to afford 821.0 mg (85%) of the *tert*-butyl phenylcarbamate (**1r**) as white solid. Spectral data are in accordance with the reported data.³⁹

Preparation of 2,2,2-trifluoro-N-phenylacetamide (1s):



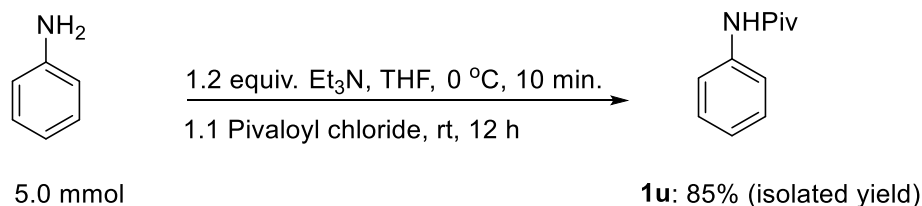
A 100 mL round-bottom flask was charged with aniline (465.7 mg, 5 mmol), triethylamine (836 μ L, 1.2 equiv.) dry THF (15 mL) and stir at 0 °C for 10 min. Trifluoroacetic anhydride (836 μ L, 1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to afford 757.0 mg (80%) the 2,2,2-trifluoro-*N*-phenylacetamide (**1s**) as white solid. Spectral data are in accordance with the reported data.⁴⁰

Preparation of N-phenylacetamide (1t):



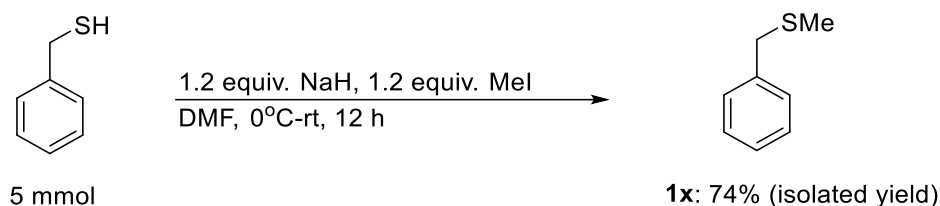
A 100 mL round-bottom flask was charged with aniline (465.7 mg, 5 mmol), triethylamine (836 μ L, 1.2 equiv.) and dry THF (15 mL) and stir at 0 °C for 30 min. Acetyl chloride (393 μ L, 1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (50% ethyl acetate in hexane as eluent) to afford 554.0 mg (82%) of the *N*-phenylacetamide (**1t**) as white solid. Spectral data are in accordance with the reported data.⁴¹

Preparation of N-phenylpivalamide (1u):



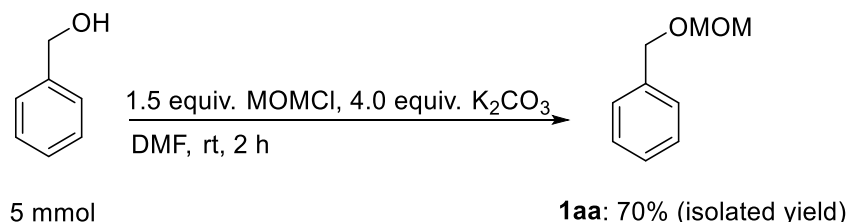
A 100 mL round-bottom flask was charged with aniline (465.7 mg, 5 mmol), triethylamine (836 μ L, 1.2 equiv.) and dry THF (15 mL) and stir at 0 °C for 30 min. Pivaloyl chloride (673 μ L, 1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (50% ethyl acetate in hexane as eluent) to afford 753 mg (85%) of the *N*-phenylpivalamide (**1u**) as white solid. Spectral data are in accordance with the reported data.⁴²

Preparation of benzyl(methyl)sulfane (1x):



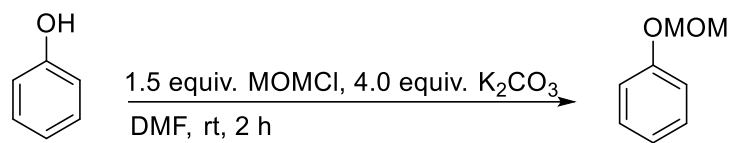
An oven dried 100 mL round bottom was charged with phenylmethanethiol (621.0 mg, 5 mmol) in DMF (10.0 mL) and stirred at 0 °C for 15 min. NaH (262 mg, 55% suspension in mineral oil, 1.2 equiv.) was added and the mixture was stirred at 0°C for 15 min. MeI (374 μ L, 1.2 equiv.) was added at 0 °C, warmed to room temperature and stirred at room temperature for 11 h 30 minutes. Upon completion (checked by TLC), the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (hexane as eluent) gave 511.0 mg (74%) of benzyl(methyl)sulfane (**1x**) as liquid. Spectral data are in accordance with the reported data.⁴³

Preparation of ((methoxymethoxy)methyl) benzene (1aa):



To a 100 ml round bottom flask benzyl alcohol (540.7 mg, 5 mmol) was dissolved in DMF (20.0 mL) and K₂CO₃ (2.76 g, 4.0 equiv.) was added and the mixture was stirred at rt for 30 min. MOMCl (570 μ L, 1.5 equiv.) was added slowly at rt and stirred at room temperature for 2 h. Upon completion (checked by TLC), the reaction mixture was diluted with water (10 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 533.0 mg (70%) of ((methoxymethoxy)methyl) benzene (**1aa**) as colourless liquid. Spectral data are in accordance with the reported data.⁴⁴

Preparation of ((methoxymethoxy)methyl) benzene (1bb):

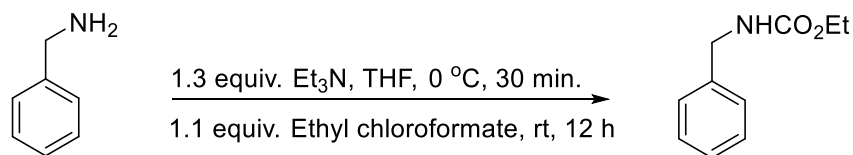


5 mmol

1bb: 75% (isolated yield)

To a 100 ml round bottom flask phenol (470.1 mg, 5 mmol) was dissolved in DMF (20.0 mL) and K_2CO_3 (2.76 g, 4.0 equiv.) was added and the mixture was stirred at rt for 30 min. MOMCl (570 μL , 1.5 equiv.) was added slowly at rt and stirred at room temperature for 2 h. Upon completion (checked by TLC), the reaction mixture was diluted with water (10 mL) and extracted with diethyl ether (3 x 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 518.1 mg (75%) of ((methoxymethoxy)methyl)benzene (**1bb**) as colourless liquid. Spectral data are in accordance with the reported data.⁴⁵

Preparation of ethyl benzylcarbamate (1cc):

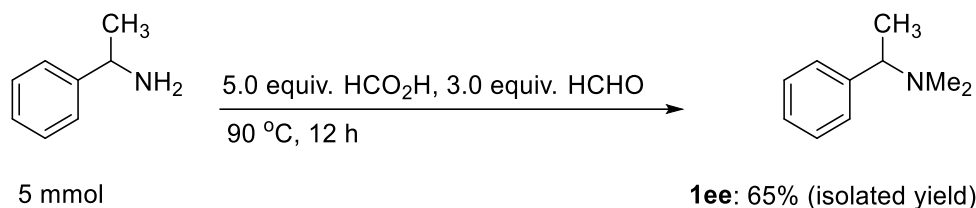


5.0 mmol

1cc: 86% (isolated yield)

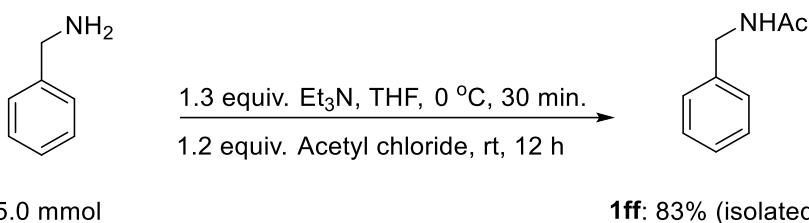
A 100 mL round-bottom flask was charged with benzyl amine (5 mmol, 535.8 mg), triethylamine (0.91 mL, 1.3 equiv.) and dry THF (15 mL) and stir at 0 °C for 30 min. Ethyl chloroformate (524 μL , 1.1 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (6% ethyl acetate in hexane as eluent) to afford 771.0 mg (86%) of the ethyl benzylcarbamate (**1cc**) as white solid. Spectral data are in accordance with the reported data.⁴⁶

Preparation of *N,N*-dimethyl-1-phenylethan-1-amine (**1ee**):



A 100 mL round-bottom flask was charged with Formic acid (0.95 mL, 5 equiv.), cooled in running tap water, and add slowly 1-phenylethan-1-amine (605.9 mg, 5 mmol). To this resulting clear solution formaldehyde (37% solution) (1.23 mL, 3.0 equiv.) are added and a small boiling stone. The flask is connected to a reflux condenser and is placed in an oil bath which has been heated to 90 °C. A vigorous evolution of carbon dioxide begins after 2-3 minutes, at which time the flask is removed from the bath until the gas evolution subsides (15-20 minutes), then it was returned to the bath and heated at 90 °C for 12 h. After the solution has been cooled, 10 mL of 4(N) hydrochloric acid is added and the solution is evaporated to dryness under reduced pressure. The syrupy residue is dissolved in 10 mL of water. Extracts with Hexane (30 mL x 2) collect the aqueous part add 5 mL of 18(N) sodium hydroxide solution. Extracts with DCM (50 mL x 2) washed with brine (50 mL) and dried over Na₂SO₄. Solvent was evaporated under reduced pressure to afford 485.0 mg (65%) of (R)-*N,N*-dimethyl-1-phenylethan-1-amine (**1ee**) as light yellow oil. Spectral data in accordance with the reported data.⁴⁷

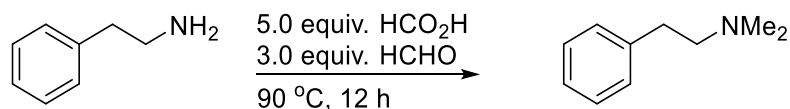
Preparation of *N*-benzylacetamide (**1ff**):



A 100 mL round-bottom flask was charged with benzyl amine (535.8 mg, 5 mmol), triethylamine (0.91 mL, 1.3 equiv.) and dry THF (15 mL) and stir at 0 °C for 30 min. Acetyl chloride (430 μL, 1.2 equiv.) was added dropwise to the mixture over 5 min at 0 °C. Then warmed to room temperature and stirred for about 12 h. Then water (10 mL) was added and extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (30% ethyl acetate in

hexane as eluent) to afford 620.0 mg (83%) the *N*-benzylacetamide (**1ff**) as white solid. Spectral data are in accordance with the reported data.⁴⁸

Preparation of N,N-dimethyl-2-phenylethan-1-amine (1gg):

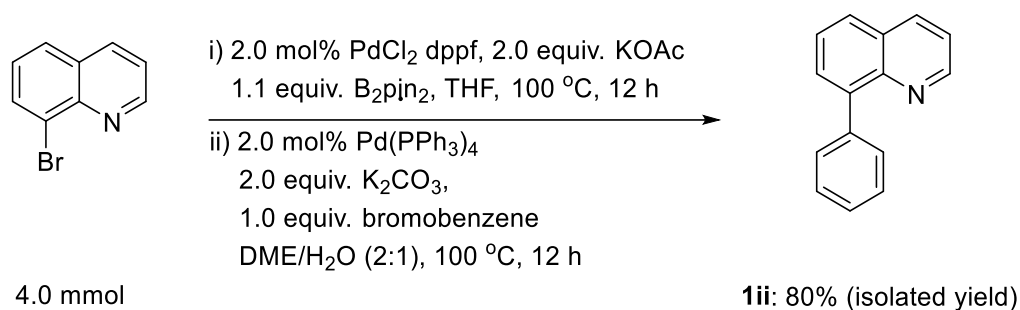


5 mmol

1gg: 80% (isolated yield)

An oven dried 100 mL round-bottom flask was charged with formic acid (0.95 mL, 5.0 equiv.) and 2-phenylethan-1-amine (605.9 mg, 5 mmol) slowly. To this resulting clear solution, formaldehyde (37% solution) (1.23 mL, 3.0 equiv.) was added and placed in a preheated oil bath at 90 °C. A vigorous evolution of carbon dioxide was observed after 2-3 minutes, then the flask is removed from the bath until the gas evolution subsides (15-20 minutes), then it was again placed into the oil bath and heated at 90 °C for 12 hours. The reaction mixture was cooled to room temperature, 4(N) HCl (6.0 mL) is added and the solution is evaporated to dryness under reduced pressure. The syrupy residue was dissolved in water (10 mL), extracted with hexane (30 mL x 2). The aqueous part was basified with 18(N) aq. NaOH (20 mL) and extracted with DCM (50 mL x 2), washed with brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (DCM as eluent) gave 597.0 mg (80%) of *N,N*-dimethyl-2-phenylethan-1-amine (**1gg**) as light yellow oil. Spectral data are in accordance with reported data.⁴⁹

Preparation of 8-phenylquinoline (1ii):



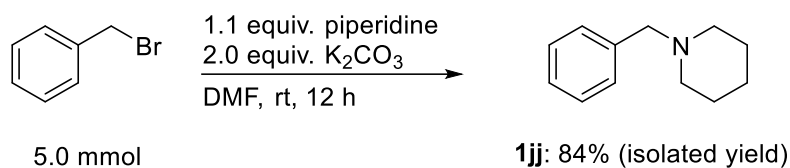
Step I:

In an argon-filled glovebox, a 15 mL pressure tube was charged with PdCl₂•dppf (58.5 mg, 2.0 mol%), KOAc (784.8 mg, 2.0 equiv.), B₂pin₂ (1.12 g, 1.1 equiv.), 8-bromoquinoline (832.2 mg, 4.0 mmol) and dry THF (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature and filtered through a short pad of celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step II:

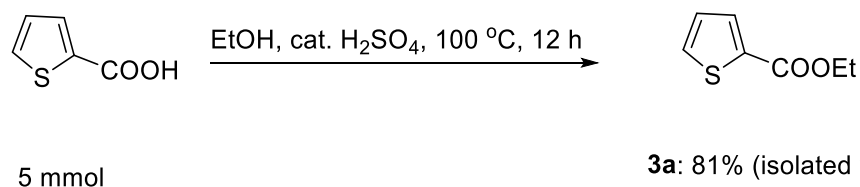
An oven dried 15 mL pressure tube was charged with crude borylated product in DME (6.0 mL), Pd(PPh₃)₄ (92.4 mg, 2.0 mol%), K₂CO₃ (1.1 g, 2.0 equiv.), bromobenzene (628.0 mg, 1.0 equiv.), water (3.0 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (20 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (30 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as a eluent) gave 657.0 mg (80%) of 8-phenylquinoline (**1ii**) as white solid. Spectral data are in accordance with the reported data.⁵⁰

Preparation of 1-benzylpiperidine (1jj):



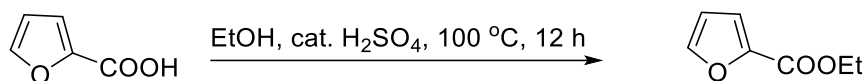
An oven dried 100 mL round bottom flask was charged with K_2CO_3 (1.38 g, 2.0 equiv), and piperidine (543.3 μ L, 1.1 equiv) and dry DMF (15.0 mL) was added sequentially. Then in the stirred reaction mixture benzylbromide (594.0 μ L, 5.0 mmol) was added slowly. Then the reaction mixture was stirred for 12 h. Upon completion (checked by TLC), it was diluted with water (20 mL) and extracted with diethyl ether (20 mL x 3). The combined organic layer was washed with 10% aq. HCl (10 mL x 3). After that, the combined aqueous layer were neutralized with saturated aq. $NaHCO_3$ solution and extracted with CH_2Cl_2 (20 mL x 3). The combined organic part was washed with brine (20 mL) and dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and chromatographic separation with basic alumina (80% ethyl acetate in hexane as eluent) gave 735.6 mg (84%) of 1-benzylpiperidine (**1jj**) as colourless liquid. Spectral data are in accordance with the reported data.⁵¹

Preparation of Ethyl thiophene-2-carboxylate (3a):



In a 15 mL pressure tube, a mixture of thiophene-2-carboxylic acid (640.7 mg, 5 mmol), EtOH (10 mL) and catalytic amount of H_2SO_4 was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralized with aqueous Na_2CO_3 . The whole mixture was then extracted three times with dichloromethane (3 x 25 mL) and washed with water. Dichloromethane layer was dried over Na_2SO_4 and evaporated under reduced pressure. The crude mass was then purified by a short pad of silica using ethylacetate as eluent to afford 633.0 mg (81%) of the ethyl thiophene-2-carboxylate (**3a**) as oil. Spectral data are in accordance with the reported data.⁵²

Preparation of Ethyl furan-2-carboxylate (3j):

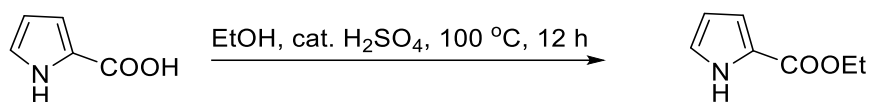


5 mmol

3j: 83% (isolated yield)

In a 15 mL pressure tube, a mixture of furan-2-carboxylic acid (560.4 g, 5 mmol), EtOH (10 mL) and catalytic amount of H₂SO₄ was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralized with aqueous Na₂CO₃. The whole mixture was then extracted three times with dichloromethane (3 x 25 mL) and washed with water. Dichloromethane layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mass was then purified by a short pad of silica using ethylacetate as eluent to afford 582.0 mg (83%) of the ethyl furan-2-carboxylate (**3j**) as oil. Spectral data are in accordance with the reported data.⁵³

Preparation of Ethyl pyrrole-2-carboxylate (3l):

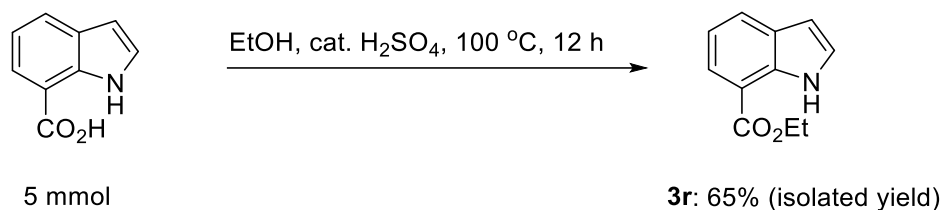


5 mmol

3l: 90% (isolated yield)

In a 15 mL pressure tube, a mixture of pyrrole-2-carboxylic acid (555.5mg, 5 mmol), EtOH (10 mL) and catalytic amount of H₂SO₄ was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralized with aqueous Na₂CO₃. The whole mixture was then extracted three times with dichloromethane (3 x 25 mL) and washed with water. Dichloromethane layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mass was then purified by a short pad of silica using ethylacetate as eluent to afford 626.0 mg (90%) of the ethyl pyrrole-2-carboxylate (**3l**) as oil. Spectral data are in accordance with the reported data.⁵⁴

Preparation of ethyl 1*H*-indole-7-carboxylate (**3r**):



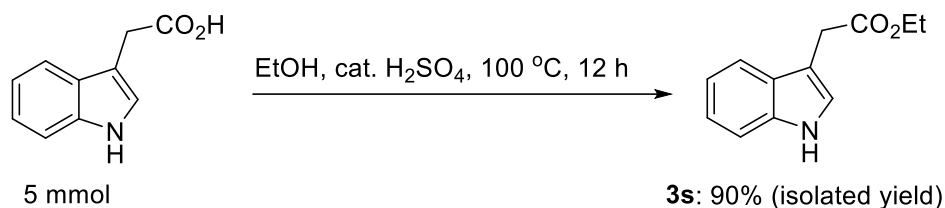
In a 15 mL pressure tube, a mixture of 1*H*-indole-7-carboxylic acid (805.8 mg, 5 mmol), EtOH (10 mL) and catalytic amount of H₂SO₄ was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralized with aqueous NaHCO₃. The whole mixture was then extracted three times with dichloromethane (3 x 25 mL) and washed with water. Dichloromethane layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mass was then purified by a short pad of silica using ethylacetate as eluent to afford 615.0 mg (65%) of the ethyl 1*H*-indole-7-carboxylate (**3r**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 9.89 (s, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 2.0 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 6.61 (t, J = 2.4 Hz, 1H), 4.47 (q, J = 7.2 Hz, 2H), 1.46 (t, J = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 167.5, 135.7, 129.0, 126.3, 125.1, 124.2, 118.9, 112.8, 102.5, 60.7, 14.4.

HRMS (ESI) *m/z* calcd for C₁₁H₁₂NO₂ [M+H]⁺ 190.0868, found 190.0878.

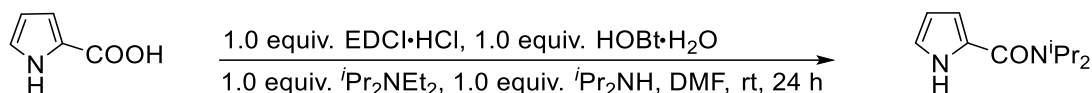
Preparation of ethyl 2-(1*H*-indol-3-yl)acetate (**3s**):



In a 15 mL pressure tube, a mixture of 2-(1*H*-indol-3-yl)acetic acid (876.0 mg, 5 mmol), EtOH (10 mL) and catalytic amount of H₂SO₄ was refluxed. After 12 h, the reaction mixture was cooled to room temperature and neutralized with aqueous Na₂CO₃. The whole mixture was then extracted three times with dichloromethane (3 x 25 mL) and washed with water. Dichloromethane layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude mass was then purified by a

short pad of silica using ethylacetate as eluent to afford 915.0 mg (90%) of the ethyl 2-(1*H*-indol-3-yl)acetate (**3s**) as oil. Spectral data are in accordance with the reported data.⁵⁵

Preparation of N,N-diisopropyl-1H-pyrrole-2-carboxamide(3u):

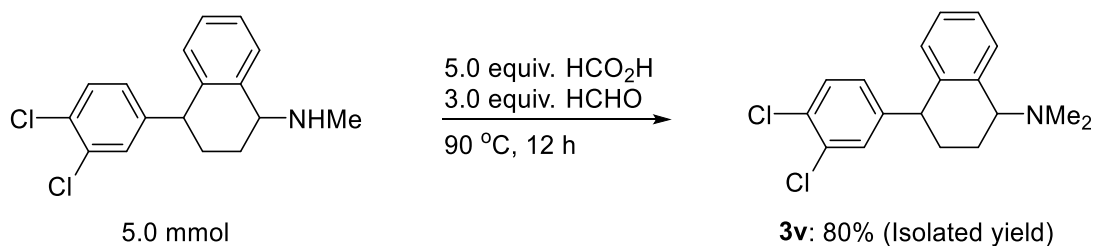


9 mmol

Yield: 30 %

A 100 mL round-bottom flask was charged with pyrrole-2-carboxylic acid (1.0 g, 9.0 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl) (1.73 g, 1.0 equiv.), 1-hydroxybenzotriazole monohydrate (HOBT·H₂O) (1.38 g, 1.0 equiv.), ethyldiisopropylamine (*i*Pr₂NEt, 1.56 mL, 1.0 equiv.) and DMF (70 mL). To the reaction mixture, diisopropylamine (1.27 mL, 1.0 equiv.) was added dropwise. Next, the reaction mixture stirred at room temperature for 24 h. After completion (monitored by TLC), all the solvent evaporated under reduced pressure. Then the residue was diluted with ethyl acetate (100 mL) and washed with H₂O (2×20 mL). The organic extract was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to give 524 mg (30%) of *N,N*-diisopropyl-1*H*-pyrrole-2-carboxamide as white solid. Spectral data are in accordance with the reported data.⁷

Preparation of 4-(3,4-dichlorophenyl)-N,N-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (3v):



5.0 mmol

3v: 80% (Isolated yield)

An oven dried 100 mL round-bottom flask was charged with formic acid (0.95 mL, 5.0 equiv.) and 4-(3,4-dichlorophenyl)-*N*-methyl-1,2,3,4-tetrahydronaphthalen-1-amine (1.53 g, 5 mmol) slowly. To this resulting clear solution, formaldehyde (37%) (1.22 mL, 3.0 equiv.) was added and was placed in an preheated oil bath at 90 °C. A vigorous evolution of carbon dioxide was observed after 2-3 minutes, then the flask is removed from the bath until the gas evolution subsides (15-20

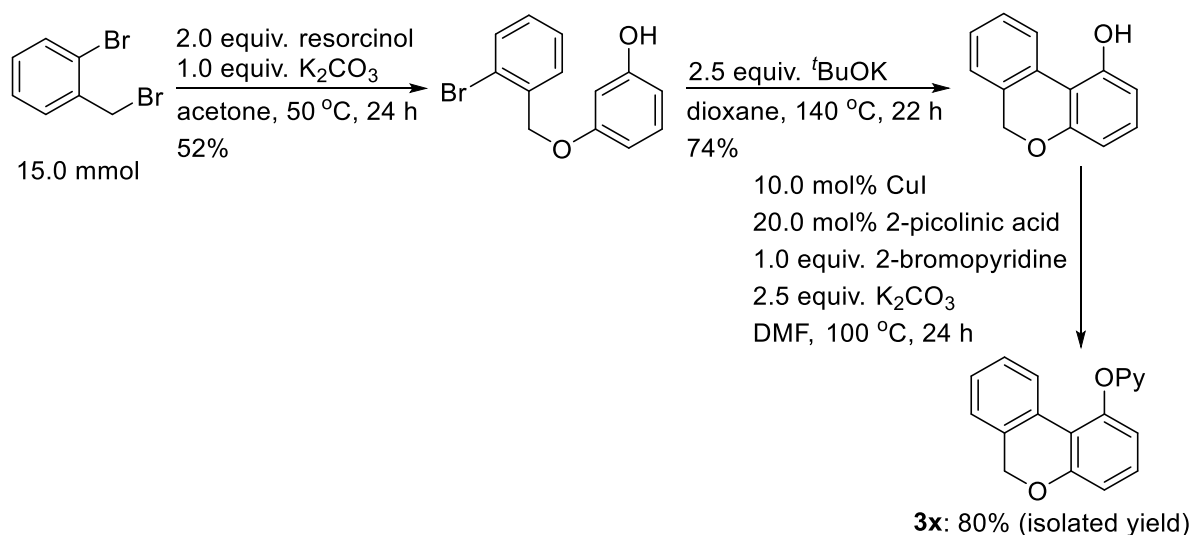
minutes). Then it was again placed into the oil bath and heated at 90 °C for 12 hours. The reaction mixture was cooled to room temperature, 4(N) HCl (20 mL) is added and the solution is evaporated to dryness under reduced pressure. The syrupy residue is dissolved in of water (20 mL), extracted with hexane (30 mL x 3). The aqueous part was basified with 18(N) aq. NaOH (50 mL) and extracted with DCM (50 mL x 2), washed with brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (DCM as eluent) gave 1.28 g (80%) of 4-(3,4-dichlorophenyl)-*N,N*-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (**3v**) as gummy liquid.

¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.13-7.16 (m, 2H), 6.84-6.90 (m, 2H), 4.12 (t, J = 5.6 Hz, 1H), 3.77 (t, J = 7.6 Hz, 1H), 2.31 (s, 6H), 2.01-2.16 (m, 2H), 1.68-1.74 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 147.7, 139.2, 138.1, 132.1, 130.7, 130.1, 129.9, 129.8, 128.9, 128.2, 126.8, 126.7, 62.5, 43.9, 40.9, 29.7, 15.8.

HRMS (ESI) *m/z*calcd for C₁₈H₂₀Cl₂N [M+H]⁺ 320.0973, found 320.0967.

Preparation of 2-((6H-benzo[c]chromen-1-yl)oxy)pyridine (3x):



Step-I:

An oven dried 100 mL round bottom flask was charged with resorcinol (4.95 g, 30.0 mmol), K₂CO₃ (2.07 g, 1.0 equiv.) and acetone (75.0 mL). This mixture was stirred at room temperature for 30 minutes. 2-Bromobenzyl bromide (3.75 g, 15.0 mmol) was added to the mixture and placed into

preheated oil bath at 50 °C for 23 h 30 minutes. Upon total consumption of 2-bromobenzyl bromide (checked by TLC), the reaction mixture was cooled to room temperature, poured into aqueous 2(N) NaOH (75 mL) and extracted with ethyl acetate (50 mL x 3). The combined organic layer was washed with brine (40 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 2.18 g (52%) of 3-((2-bromobenzyl)oxy)phenol as white solid. Spectral data are in accordance with the reported data.⁵⁶

Step-II:

In an argon-filled glove box, an oven dried 15 mL pressure tube was charged with 3-((2-bromobenzyl)oxy)phenol (1.67 g, 6.0 mmol), ^tBuOK (1.68 g, 2.5 equiv.), sealed with a rubber septum and taken out from the glove box. Dioxane (10.0 mL) was added to the mixture, capped with a teflon pressure cap and stirred at room temperature for 5 minutes. The pressure tube was placed in a preheated silicon oil bath at 140 °C and stirred for 22 h. After cooling to room temperature, the reaction mixture was quenched with 2(N) HCl (50 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (40 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (40% dichloromethane in hexane as eluent) gave 880.0 mg (74%) of 6*H*-benzo[*c*]chromen-1-ol as white solid. Spectral data are in accordance with the reported data.⁵⁶

Step-III:

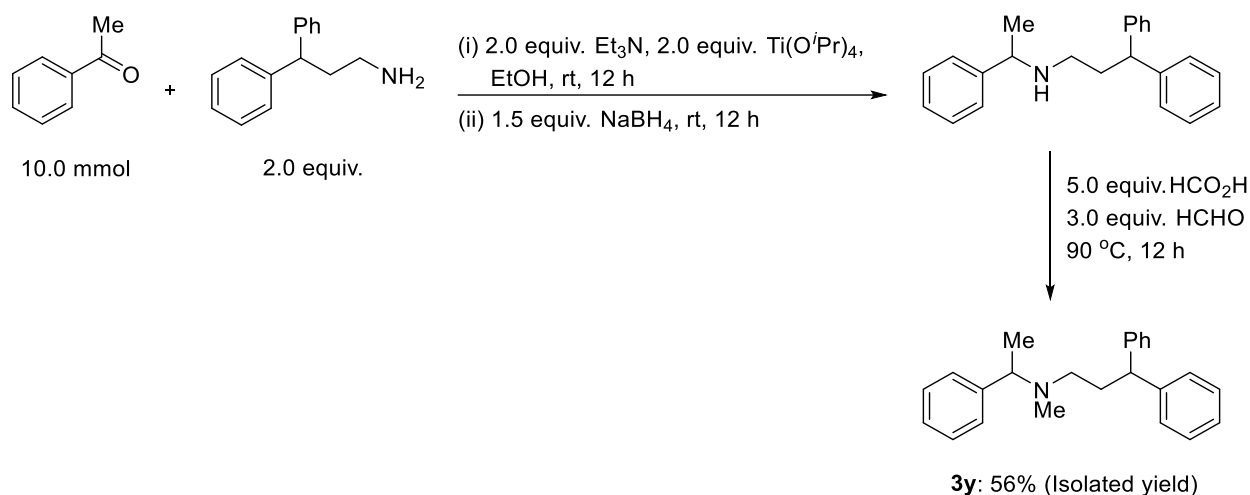
An oven dried 15 mL pressure tube was charged with 6*H*-benzo[*c*]chromen-1-ol (594.6 mg, 3.0 mmol), CuI (57.1 mg, 10 mol%), 2-picolinic acid (73.8 mg, 20 mol%), anhydrous K₂CO₃ (1.04 g, 2.5 equiv.), 2-bromopyridine (474 mg, 1.0 equiv.) and dry DMF (6.0 mL) sequentially. Then, the reaction mixture was degassed well with nitrogen gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 100 °C and stirred for 24 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 660.7 mg (80%) of 2-((6*H*-benzo[*c*]chromen-1-yl)oxy)pyridine (**3x**) as white solid.

^1H NMR (400 MHz, CDCl_3): δ 8.19-8.21 (m, 2H), 7.67 (ddd, $J = 8.4$ Hz, 7.6 Hz, 2.4 Hz, 1H), 7.21-7.29 (m, 3H), 7.14-7.16 (m, 1H), 6.91-6.99 (m, 3H), 6.79 (d, $J = 8.0$ Hz, 1H), 5.06 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 163.2, 157.0, 151.6, 148.0, 139.4, 132.1, 128.9, 128.3, 128.1, 127.5, 126.1, 124.5, 118.6, 116.9, 116.2, 114.0, 111.3, 68.9.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 276.1025, found 276.1018.

Preparation of N-methyl-3,3-diphenyl-N-(1-phenylethyl)propan-1-amine (3y):



An oven dried 250 mL two neck round-bottom flask was charged with triethylamine (2.8 mL, 2.0 equiv.), absolute EtOH (20.0 mL), 3,3-Diphenylpropylamine (4.22 g, 2.0 equiv.), titanium(IV)isopropoxide (6.1 mL, 2.0 equiv.), and acetophenone (1.20 g, 10 mmol) sequentially under nitrogen atmosphere. Then the reaction mixture was stirred at room temperature for 12 h.

After 12 h, sodium borohydride (567.4 mg, 1.5 equiv.) was added to this reaction mixture and the resulting mixture was further stirred for 12 h at room temperature. Upon completion (checked by TLC), the reaction mixture was diluted with water (20 mL) and white precipitate was appeared. The solid precipitate was filtered off, washed with DCM (20 mL) and the filtrate part was extracted with DCM (20 mL x 3). The combined organic part was washed with brine (20 mL) and dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and the crude reaction mixture was used for next step without further purification.

Step-II:

An oven dried 100 mL round-bottom flask was charged with formic acid (1.9 mL, 5.0 equiv.) and crude material obtained from previous step. To this resulting clear solution, formaldehyde (37%)

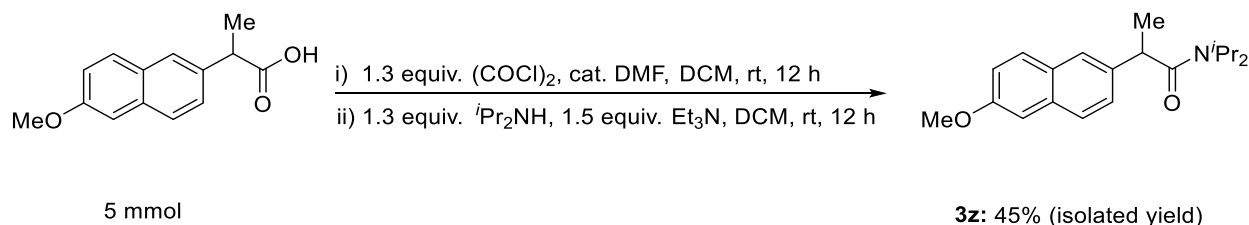
(2.23 mL, 3.0 equiv.) was added and placed in an preheated oil bath at 90 °C. A vigorous evolution of carbon dioxide was observed after 2-3 minutes, then the flask is removed from the bath until the gas evolution notably subsides (15-20 minutes); then it was again placed into the oil bath and heated at 90 °C for 12 hours. The reaction mixture was cooled to room temperature, 4(N) HCl (20 mL) is added and the solution is evaporated to dryness under reduced pressure. The syrupy residue is dissolved in of water (20 mL), extracted with hexane (30 mL x 2). The aqueous part was basified with 18N aq. NaOH (30 mL) and extracted with DCM (50 mL x 3), washed with brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (40 % ethyl acetate in hexane as eluent) gave 1.84 g (56%) of the *N*-methyl-3,3-diphenyl-*N*-(1-phenylethyl)propan-1-amine (**3y**) as gummy liquid.

¹H NMR (400 MHz, CDCl₃): δ 7.05-7.17 (m, 15H), 3.88 (t, J = 7.2 Hz, 1H), 3.43 (q, J = 6.8 Hz, 1H), 2.07-2.32 (m, 7H), 1.17 (d, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 145.1, 145.0, 143.9, 128.3, 128.0, 127.8, 127.8, 127.6, 126.6, 126.0, 63.1, 52.5, 48.7, 38.4, 33.2, 18.1.

HRMS (ESI) *m/z* calcd for C₂₄H₂₈N [M+H]⁺ 330.2222, found 330.2218.

Preparation of N,N-diisopropyl-2-(6-methoxynaphthalen-2-yl)propenamide (3z):



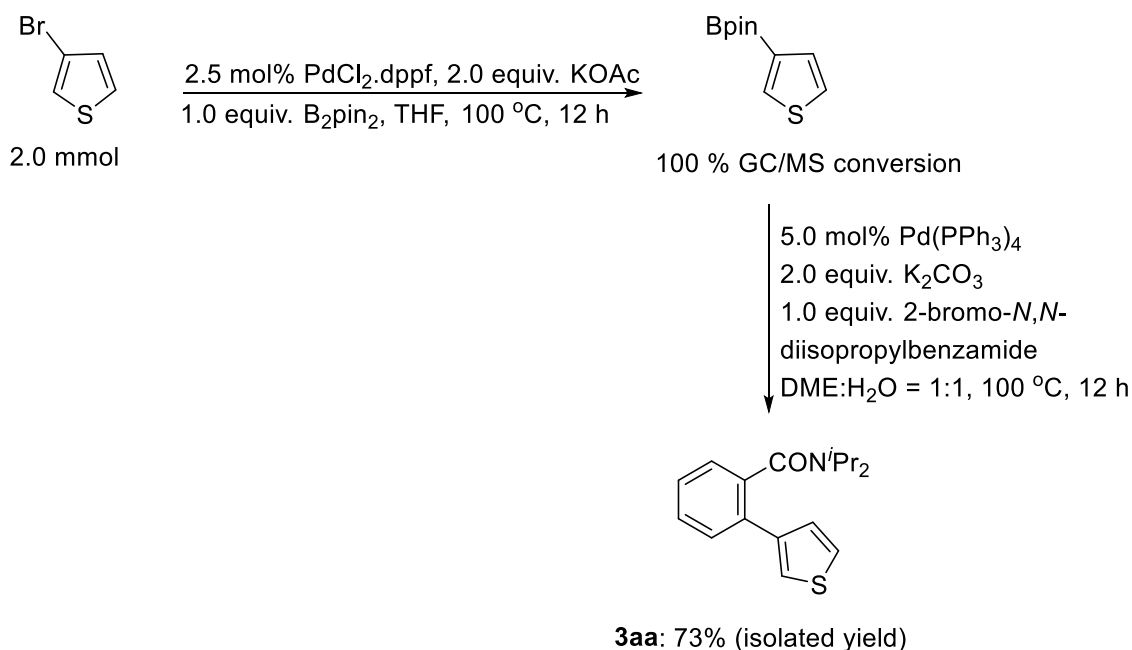
Step-I:

A 100 mL round-bottom flask was charged with Naproxen (1.15 g, 5 mmol), dry DCM (15 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then (COCl)₂ (0.56 mL, 1.3 equiv.) was added drop wise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diisopropylamine (0.92 mL, 1.3 equiv.) and Et₃N (1.05 mL, 1.5 equiv.) in dry DCM (15 mL), acid chloride (1.0 equiv.) was added drop wise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (40 mL) was added and extracted with DCM (3 x 30 mL). The organic layer was washed with saturated aqueous NaHCO₃ (30 mL) solution followed by water (30 mL). After that, the organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (10% ethyl acetate in hexane as eluent) to give 705.2 mg (45%) of the *N,N*-diisopropyl-2-(6-methoxynaphthalen-2-yl)propenamide (**3z**) as white solid. Spectral data are in accordance with the reported data.⁵⁷

Preparation of N,N-diisopropyl-2-(thiophen-3-yl)benzamide (3aa):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled

to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

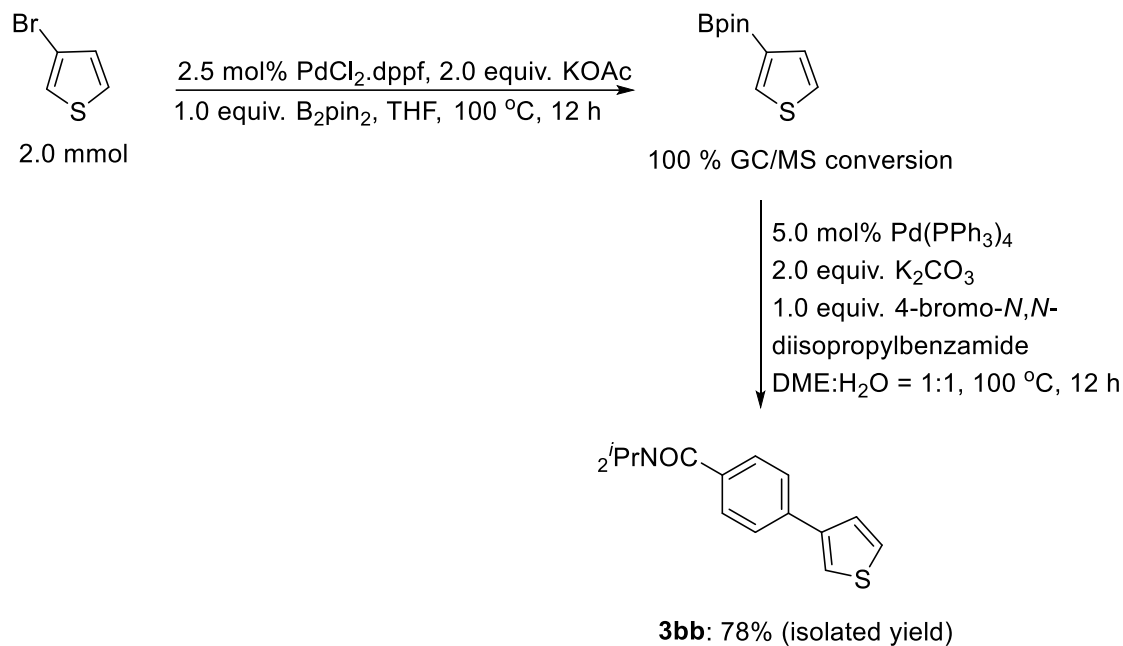
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-*N,N*-diisopropylbenzamide (568.4 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as a eluent) gave 419 mg (73%) of *N,N*-diisopropyl-2-(thiophen-3-yl)benzamide (**3aa**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.50 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.31-7.39 (m, 4H), 7.25 (m, 1H), 3.45 (sept, J = 6.8 Hz, 1H), 3.29 (sept, J = 6.8 Hz, 1H), 1.53 (d, J = 6.8 Hz, 3H), 1.40 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.46 (d, J = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 170.5, 140.3, 137.7, 132.4, 128.7, 128.6, 128.3, 127.5, 126.3, 125.3, 123.6, 50.6, 45.6, 20.7, 20.5, 19.7, 19.5.

HRMS (ESI) m/z calcd for C₁₇H₂₁NOS [M+H]⁺ 288.1417, found 288.1415.

Preparation of *N,N*-diisopropyl-4-(thiophen-3-yl)benzamide (**3bb**):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 4-bromo-*N,N*-diisopropylbenzamide (568.4 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced

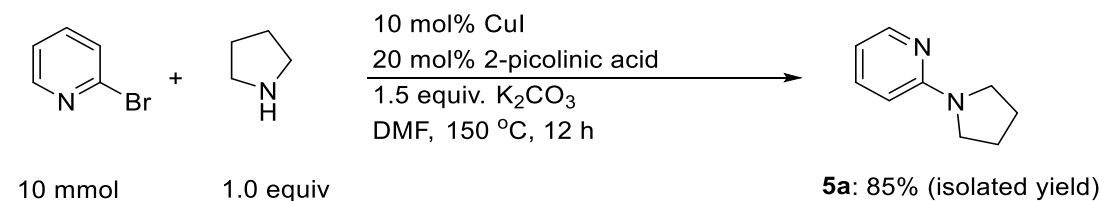
pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as a eluent) gave 448 mg (78%) of *N,N*-diisopropyl-4-(thiophen-3-yl)benzamide (**3bb**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.48 (s, 1H), 7.39 (d, *J* = 1.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.87 (br s, 1H), 3.57 (br s, 1H), 1.50 (br s, 6H), 1.23 (br s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 170.7, 141.5, 137.5, 136.1, 126.4, 126.3, 126.2, 126.1, 120.7, 50.7, 45.7, 20.7.

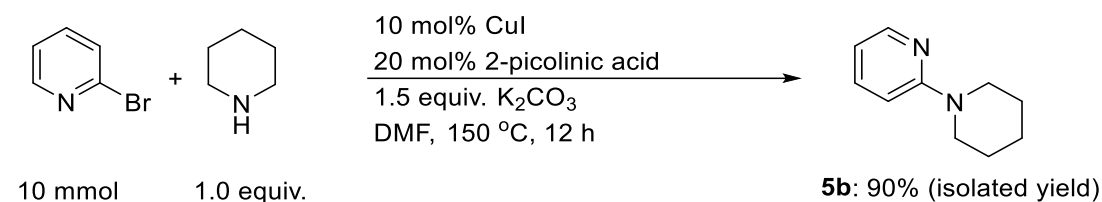
HRMS (ESI) *m/z* calcd for C₁₇H₂₁NOS [M+H]⁺ 288.1417, found 288.1418.

Preparation of 2-(pyrrolidin-1-yl)pyridine (5a):



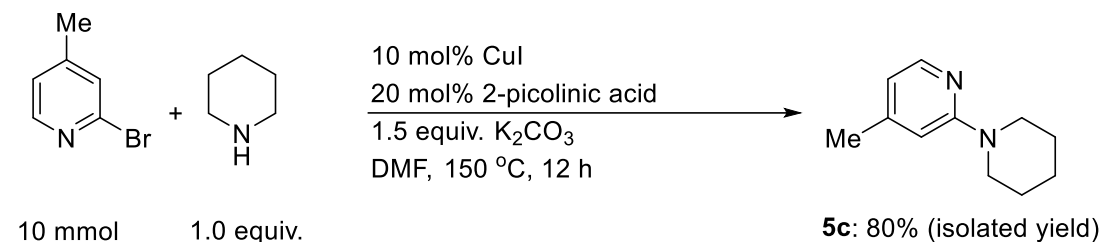
An oven dried 15 mL pressure tube was charged with 2-bromopyridine (1.57 g, 10 mmol), CuI (190.4 mg, 10 mol%), 2-picolinic acid (246.2 mg, 20 mol%), anhydrous K₂CO₃ (2.07 g, 1.5 equiv.), Pyrrolidine (711.2 mg, 1.0 equiv.), and dry DMF (8 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 1.26 g (85%) of 2-(pyrrolidin-1-yl)pyridine (**5a**) as brown oil. Spectral data are in accordance with the reported data.⁵⁸

Preparation of 2-(piperidin-1-yl)pyridine (5b):



An oven dried 15 mL pressure tube was charged with 2-bromopyridine (1.57 g, 10 mmol), CuI (190.4 mg, 10 mol%), 2-picolinic acid (246.2 mg, 20 mol%), anhydrous K₂CO₃ (2.07 g, 1.5 equiv.), piperidine (851.5 mg, 1.0 equiv.) and dry DMF (8 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 1.46 g (90%) of 2-(piperidin-1-yl)pyridine (**5b**) as oil. Spectral data are in accordance with the reported data.⁵⁹

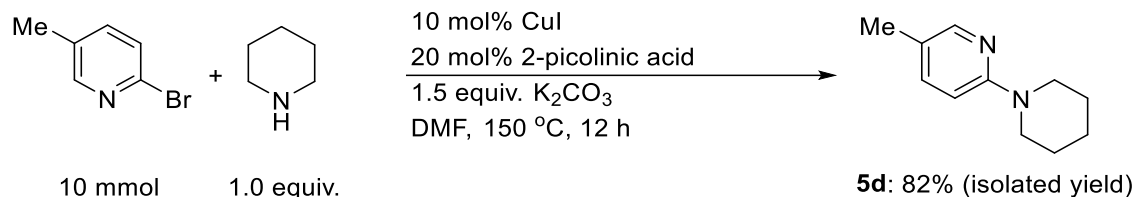
Preparation of 4-methyl-2-(piperidin-1-yl)pyridine (5c):



An oven dried 15 mL pressure tube was charged with 4-methyl-2-bromopyridine (1.72 g, 10 mmol), CuI (190.4 mg, 10 mol%), 2-picolinic acid (246.2 mg, 20 mol%), anhydrous K₂CO₃ (2.07 g, 1.5 equiv.), piperidine (851.5 mg, 1.0 equiv.) and dry DMF (8 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic

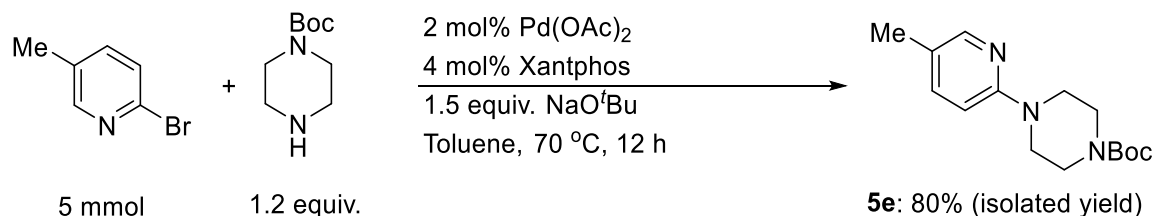
extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 1.41 g (80%) of 4-methyl-2-(piperidin-1-yl)pyridine (**5c**) as oil. Spectral data are in accordance with the reported data.⁵⁹

Preparation of 5-methyl-2-(piperidin-1-yl)pyridine (5d):



An oven dried 15 mL pressure tube was charged with 5-methyl-2-bromopyridine (1.72 g, 10 mmol), CuI (190.4 mg, 10 mol%), 2-picolinic acid (246.2 mg, 20 mol%), anhydrous K₂CO₃ (2.07 g, 1.5 equiv.), piperidine (851.5 mg, 1.0 equiv.) and dry DMF (8 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 1.44 g (82%) of 5-methyl-2-(piperidin-1-yl)pyridine (**5d**) as oil. Spectral data are in accordance with the reported data.⁵⁹

Preparation of tert-butyl 4-(5-methylpyridin-2-yl)piperazine-1-carboxylate (5e):



In an argon-filled glovebox, a 15 mL pressure tube was charged with Pd(OAc)₂ (22.4 mg, 2.0 mol%), Xantphos (115.7 mg, 4.0 mol%), NaO^tBu (720.8 mg, 1.5 equiv.), 2-bromo-5-methylpyridine (860.1 mg, 5.0 mmol), *N*-(tert-butyloxycarbonyl)-piperazine (1.12 g, 1.2 equiv.) and dry Toluene (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and

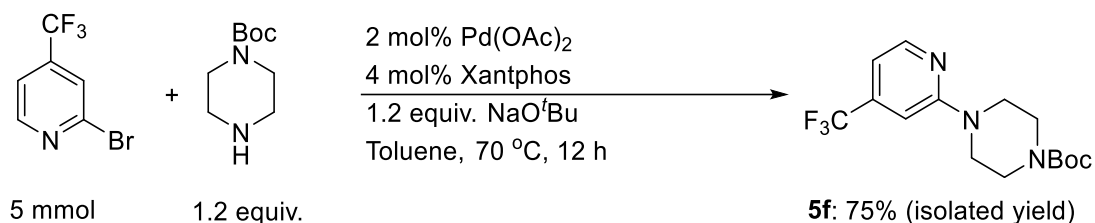
heated at 70 °C for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 1.1 g (80%) of *tert*-butyl 4-(5-methylpyridin-2-yl)piperazine-1-carboxylate (**5e**) as white solid.

¹H NMR (400 MHz, CDCl₃): δ 8.01 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 3.44-3.53 (m, 8H), 2.19 (s, 3H), 1.47 (s, 9H).

¹³C NMR (100 MHz, CDCl₃): δ 157.9, 154.8, 147.7, 138.4, 122.7, 107.1, 79.8, 45.6, 43.6, 28.4, 17.3.

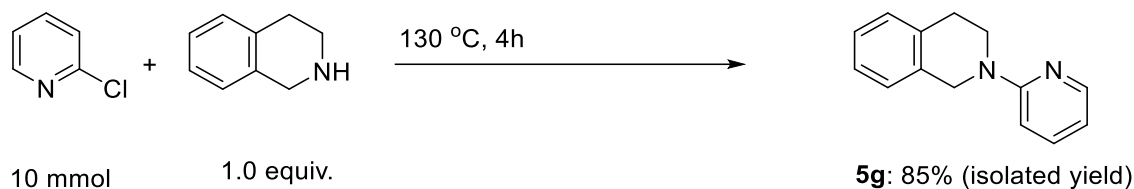
HRMS (ESI) m/z calcd for C₁₅H₂₄N₃O₂ [M+H]⁺ 278.1863, found 278.1862.

Preparation of tert-butyl 4-(4-(trifluoromethyl)pyridin-2-yl)piperazine-1-carboxylate (5f):



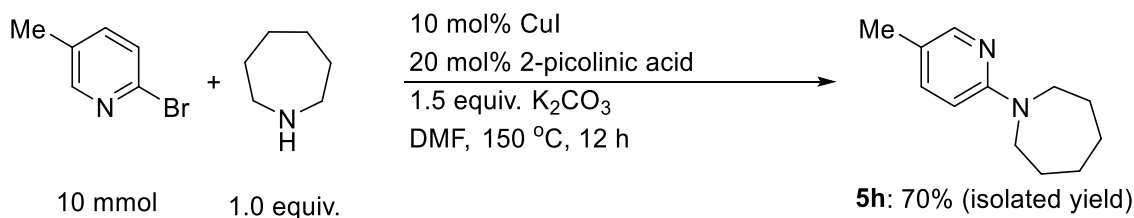
In an argon-filled glovebox, a 15 mL pressure tube was charged with Pd(OAc)₂ (22.4 mg, 2.0 mol%), Xantphos (115.7 mg, 4.0 mol%), NaO^tBu (720.8 mg, 1.5 equiv.), 2-Bromo-4-(trifluoromethyl)pyridine (1.13 g, 5.0 mmol), *N*-(*tert*-butyloxycarbonyl)-piperazine (1.12 g, 1.2 equiv.) and dry Toluene (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and heated at 70 °C for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 1.24 g (75%) of *tert*-butyl 4-(4-(trifluoromethyl)pyridin-2-yl)piperazine-1-carboxylate (**5f**) as white solid. Spectral data are in accordance with the reported data.⁶⁰

Preparation of 2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (5g):



An oven dried 15 mL pressure tube was charged with 2-chloropyridine (1.13 g, 10 mmol) and 1,2,3,4-tetrahydroisoquinoline (1.33 g, 1.0 equiv.). Then, the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, quenched with saturated K₂CO₃ solution and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 1.79 g (85%) of 2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (**5g**) as oil. Spectral data are in accordance with the reported data.⁶¹

Preparation of 1-(5-methylpyridin-2-yl)azepane (5h):



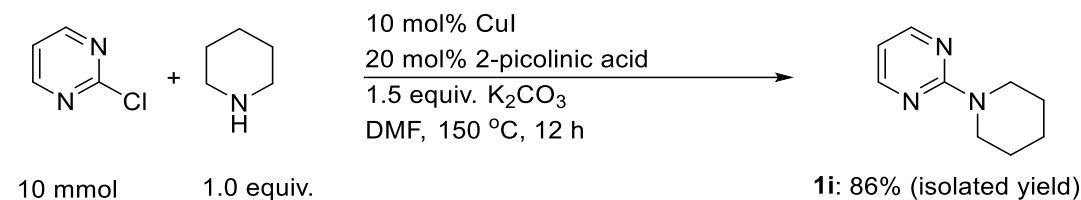
An oven dried 15 mL pressure tube was charged with 5-methyl-2-bromopyridine (1.72 g, 10 mmol), CuI (190.4 mg, 10 mol%), 2-picolinic acid (246.2 mg, 20 mol%), anhydrous K₂CO₃ (2.07 g, 1.5 equiv.), azepane (1.13 mL, 1.0 equiv.) and dry DMF (8 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (15% ethyl acetate in hexane as eluent) gave 1.33 g (70%) of 1-(5-methylpyridin-2-yl)azepane (**5h**) as oil.

^1H NMR (400 MHz, CDCl_3): δ 7.96 (s, 1H), 7.24 (dd, $J = 8.8$ Hz, 1.6 Hz, 1H), 6.41 (d, $J = 8.4$ Hz, 1H), 3.59 (t, $J = 6.0$ Hz, 4H), 2.16 (s, 3H), 1.77 (m, 4H), 1.51-1.56 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3): δ 156.7, 147.6, 138.1, 119.3, 105.0, 47.5, 27.9, 27.3, 17.2.

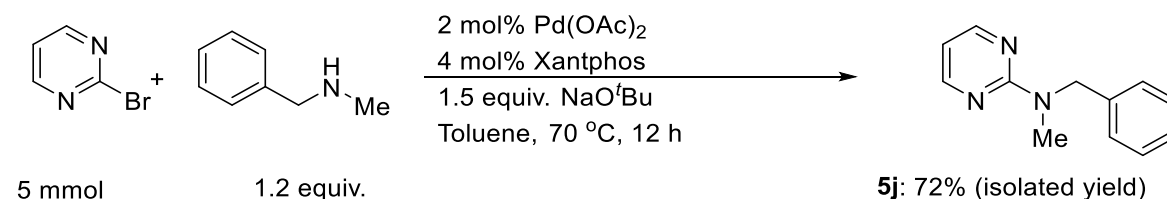
HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}]^+$ 191.1543, found 191.1542.

Preparation of 2-(piperidin-1-yl)pyrimidine (**5i**):



An oven dried 15 mL pressure tube was charged with 2-chloropyrimidine (1.14 g, 10 mmol), CuI (190.4 mg, 10 mol%), 2-picolinic acid (246.2 mg, 20 mol%), anhydrous K_2CO_3 (2.07 g, 1.5 equiv.), piperidine (851.5 mg, 1.0 equiv.) and dry DMF (8 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 1.40 g (86%) of 2-(piperidin-1-yl)pyrimidine (**5i**) as oil. Spectral data are in accordance with the reported data.⁶²

Preparation of *N*-benzyl-*N*-methylpyrimidin-2-amine (**5j**):



In an argon-filled glovebox, a 15 mL pressure tube was charged with $\text{Pd}(\text{OAc})_2$ (22.4 mg, 2.0 mol%), Xantphos (115.7 mg, 4.0 mol%), NaO^tBu (720.8 mg, 1.5 equiv.), 2-Bromopyrimidine (795 mg, 5.0 mmol), *N*-methyl-1-phenylmethanamine (727 mg, 1.2 equiv.) and dry Toluene (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and heated at 70 °C for

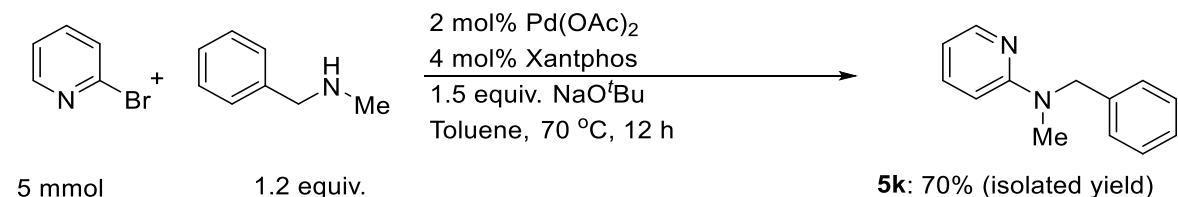
12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 717.3 mg (72%) of *N*-benzyl-*N*-methylpyrimidin-2-amine (**5j**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, J = 4.8 Hz, 2H), 7.24-7.33 (m, 5H), 6.49 (t, J = 4.8 Hz, 1H), 4.93 (s, 2H), 3.14 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 162.2, 157.7, 138.3, 128.5, 127.3, 127.0, 109.4, 52.2, 34.8.

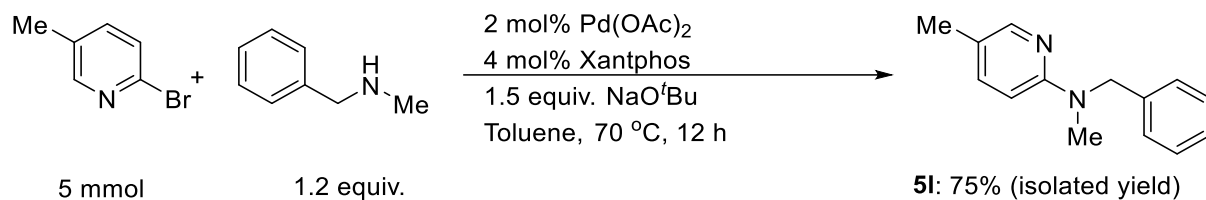
HRMS (ESI) m/z calcd for C₁₂H₁₄N₃ [M+H]⁺ 200.1182, found 200.1188.

Preparation of N-benzyl-N-methylpyridin-2-amine (5k):



In an argon-filled glovebox, a 15 mL pressure tube was charged with Pd(OAc)₂ (22.4 mg, 2.0 mol%), Xantphos (115.7 mg, 4.0 mol%), NaO^tBu (720.8 mg, 1.5 equiv.), 2-Bromopyridine (790 mg, 5.0 mmol), *N*-methyl-1-phenylmethanamine (727 mg, 1.2 equiv.) and dry Toluene (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and heated at 70 °C for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 694 mg (70%) of *N*-benzyl-*N*-methylpyridin-2-amine (**5k**) as oil. Spectral data are in accordance with the reported data.⁶³

Preparation of N-benzyl-N,5-dimethylpyridin-2-amine (5l):



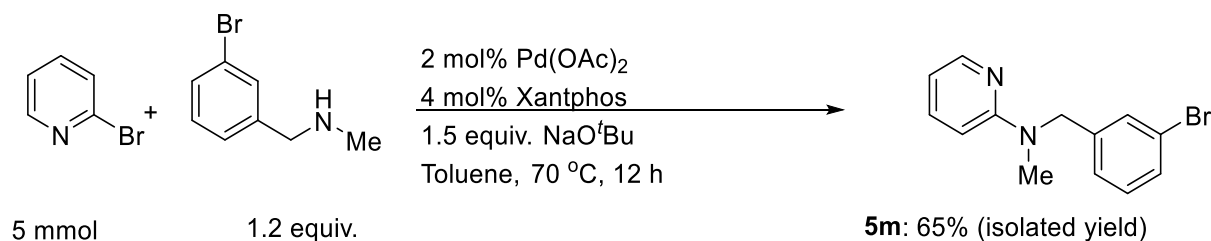
In an argon-filled glovebox, a 15 mL pressure tube was charged with Pd(OAc)₂ (22.4 mg, 2.0 mol%), Xantphos (115.7 mg, 4.0 mol%), NaO^tBu (720.8 mg, 1.5 equiv.), 2-bromo-5-methylpyridine (860.1 mg, 5.0 mmol), *N*-methyl-1-phenylmethanamine (727 mg, 1.2 equiv.) and dry Toluene (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and heated at 70 °C for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 796 mg (75%) of *N*-benzyl-*N*,5-dimethylpyridin-2-amine (**5l**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H), 7.22-7.33 (m, 6H), 6.46 (d, J = 8.4 Hz, 1H), 4.78 (s, 2H), 3.06 (s, 3H), 2.20 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 157.3, 147.6, 138.9, 138.3, 128.4, 126.9, 126.7, 120.4, 105.4, 53.4, 36.2, 17.2.

HRMS (ESI) m/z calcd for C₁₄H₁₇N₂ [M+H]⁺ 213.1386, found 213.1386.

Preparation of N-(3-bromobenzyl)-N-methylpyridin-2-aminecarboxylate (5m):



In an argon-filled glovebox, a 15 mL pressure tube was charged with Pd(OAc)₂ (22.4 mg, 2.0 mol%), Xantphos (115.7 mg, 4.0 mol%), NaO^tBu (720.8 mg, 1.5 equiv.), 2-bromopyridine (790 mg, 5.0 mmol), 1-(3-bromophenyl)-*N*-methylmethanamine (1.2 g, 1.2 equiv.) and dry Toluene (8.0 mL) sequentially. The pressure tube was placed into a preheated silicon oil bath and heated at 70 °C for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room

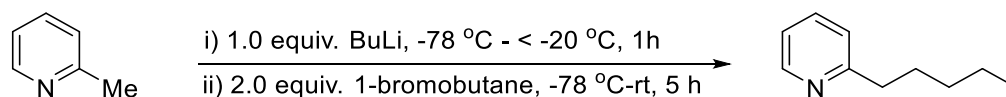
temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 900.8 mg (65%) of *N*-(3-bromobenzyl)-*N*-methylpyridin-2-amine (**5m**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, J = 4.4 Hz, 1H), 7.44-7.48 (m, 1H), 7.36-7.38 (m, 2H), 7.15-7.19 (m, 2H), 6.57-6.60 (m, 1H), 6.50 (d, J = 8.4 Hz, 1H), 4.79 (s, 2H), 3.04 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 158.7, 148.0, 141.4, 137.4, 130.1, 130.04, 130.0, 125.7, 122.7, 112.2, 105.6, 52.6, 36.1.

HRMS (ESI) m/z calcd for C₁₃H₁₄BrN₂ [M+H]⁺ 277.0335, found 277.0334.

Preparation of 2-pentylpyridine (**1n**):

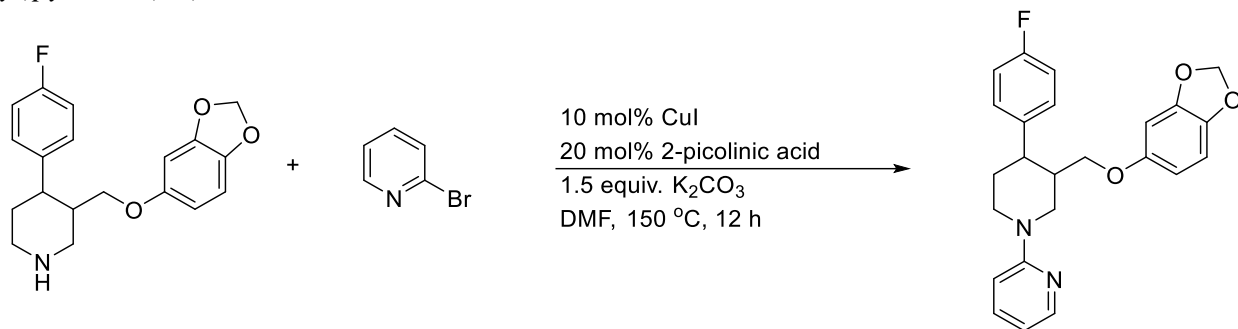


20 mmol

1n: 85% (isolated yield)

An oven dried 250 mL two necked round bottom flask was charged with 2-picoline (1.86 g, 20 mmol) and anhydrous THF (20 mL) under nitrogen atmosphere. The reaction mixture was cooled to -78 °C and *n*-BuLi (8.0 mL, 2.5 M in Hexane, 20 mmol) was slowly added over 10 minutes. After stirring for 1 h, while keeping the temperature below -20 °C, the obtained deep red solution was cooled again to -78 °C and a solution of the 1-bromobutane (5.48 g, 4.31 mL, 2.0 equiv.) in anhydrous THF was slowly added. The reaction mixture was allowed to gradually warm up to room temperature and stirred for 5 h. After the completion of reaction, the reaction mixture was quenched with saturated ammonium chloride solution and extracted with DCM (20 mL x 3). The combined organic layer was washed with brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 2.54 g (85%) of 2-pentylpyridine (**1n**) as oil. Spectral data are in accordance with the reported data.⁶⁴

Preparation of 2-(3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)pyridine (**5o**):



3.04 mmol

5o: 55% (isolated yield)

An oven dried 15 mL pressure tube was charged with Paroxetine (1.0 g, 3.04 mmol), CuI (57.8 mg, 10 mol%), 2-picolinic acid (74.8 mg, 20 mol%), anhydrous K₂CO₃ (630.2 mg, 1.5 equiv.), 2-bromopyridine (477.2 mg, 1.0 equiv.) and dry DMF (5 mL). Then, the reaction mixture was degassed well with argon gas and the pressure tube was capped with a teflon pressure cap. The pressure tube was placed in a preheated silicon oil bath at 150 °C and stirred for 12 h. After completion (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL x 3), brine (50 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 679.6 mg (55%) of 2-(3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)pyridine (**5o**) as oil.

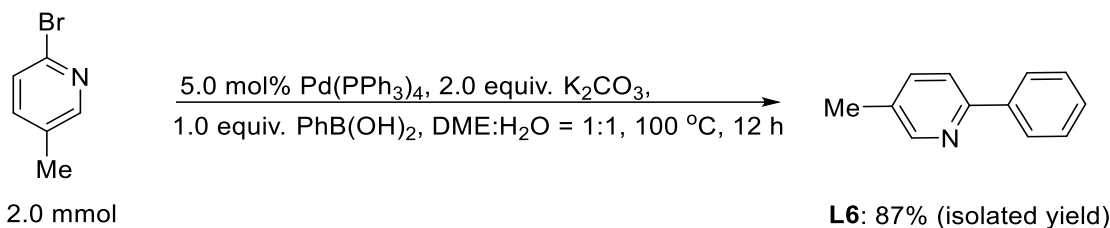
¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, J = 4.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.16 (dd, J = 8.0 Hz, 5.6 Hz, 2H), 6.98 (t, J = 8.4 Hz, 2H), 6.75 (d, J = 8.8 Hz, 1H), 6.61-6.65 (m, 2H), 6.40 (d, J = 2.0 Hz, 1H), 6.18 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 5.88 (s, 2H), 4.62 (dd, J = 13.2 Hz, 2.8 Hz, 1H), 4.49 (d, J = 13.2 Hz, 1H), 3.68 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 3.54 (dd, J = 9.2 Hz, 6.8 Hz, 1H), 2.90-3.00 (m, 2H), 2.76 (dt, J = 11.6 Hz, 4.0 Hz, 1H), 2.13-2.21 (m, 1H), 1.79-1.93 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 161.5 (d, J = 243.0 Hz), 159.3, 154.3, 148.1, 148.0, 141.6, 139.4 (d, J = 3.2 Hz), 137.5, 128.7 (d, J = 7.7 Hz), 115.4 (d, J = 21.0 Hz), 113.0, 107.8, 107.3, 105.7, 101.0, 98.0, 69.2, 49.2, 46.0, 44.4, 41.5, 33.7.

HRMS (ESI) *m/z* calcd for C₂₄H₂₄FN₂O₃ [M+H]⁺ 407.1765, found 407.1761.

Synthesis of ligands:

Synthesis of ligand 5-methyl-2-phenylpyridine (**L6**):



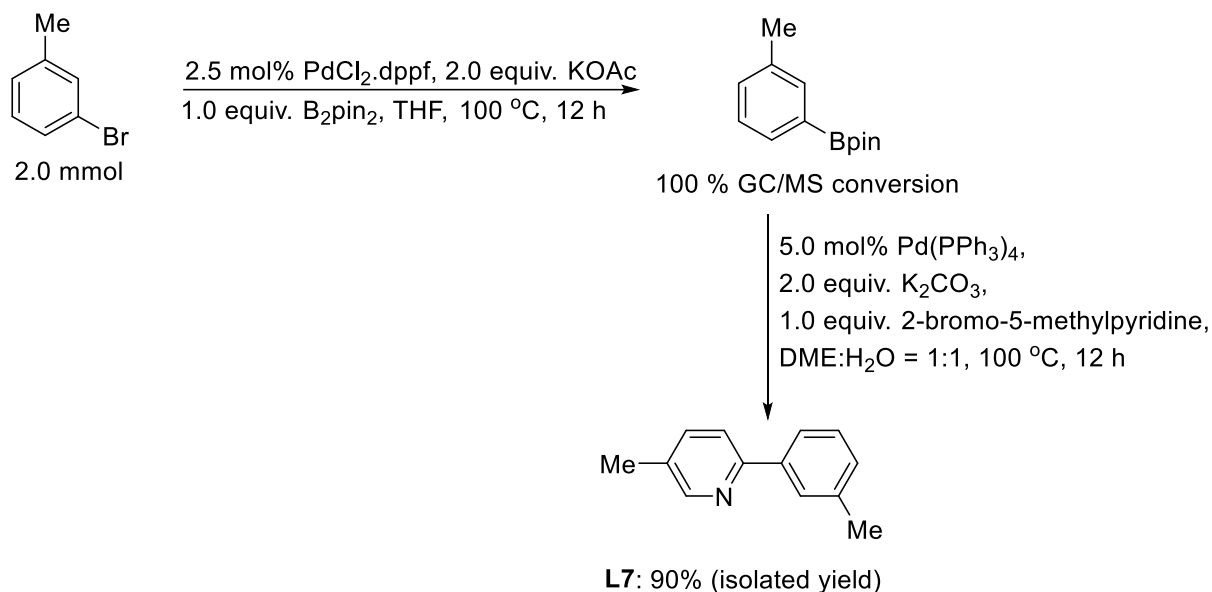
An oven dried 100 mL pressure tube was charged with 2-bromo-5-methylpyridine (344.1 mg, 2.0 mmol), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), phenyl boronic acid (243.9 mg, 1.0 equiv.), water (8 mL) and DME (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as eluent) gave 294.0 mg (87%) of 5-methyl-2-phenylpyridine (**L6**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 8.53 (s, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.56 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 2.37 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 154.7, 149.9, 139.3, 137.4, 131.6, 128.7, 128.6, 126.7, 120.1, 18.1.

HRMS (ESI) *m/z* calcd for C₁₂H₁₂N [M+H]⁺ 170.0964, found 170.0965.

Synthesis of ligand 5-methyl-2-(m-tolyl)pyridine (L7):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromotoluene (342.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over

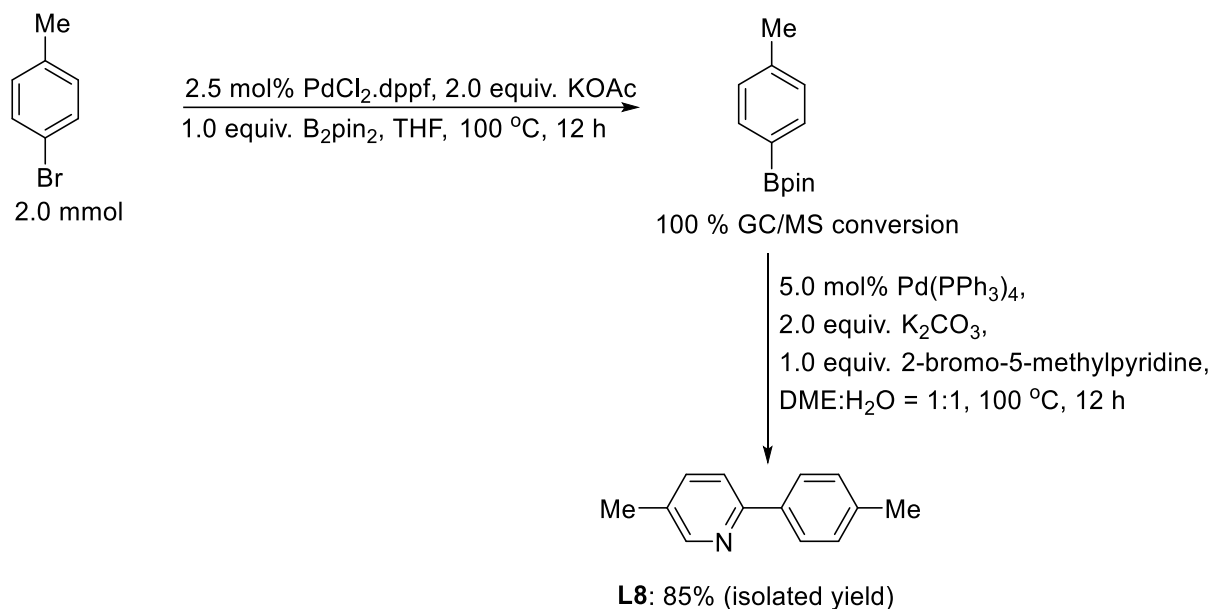
anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 330.0 mg (90%) of 5-methyl-2-(*m*-tolyl)pyridine (**L7**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 8.52 (s, 1H), 7.82 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.54 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 154.9, 150.0, 139.3, 138.3, 137.2, 131.4, 129.3, 128.5, 127.4, 123.7, 120.1, 21.5, 18.1.

HRMS (ESI) *m/z* calcd for C₁₃H₁₄N [M+H]⁺ 184.1121, found 184.1129.

Synthesis of ligand 5-methyl-2-(p-tolyl)pyridine (L8):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 4-bromotoluene (342.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and

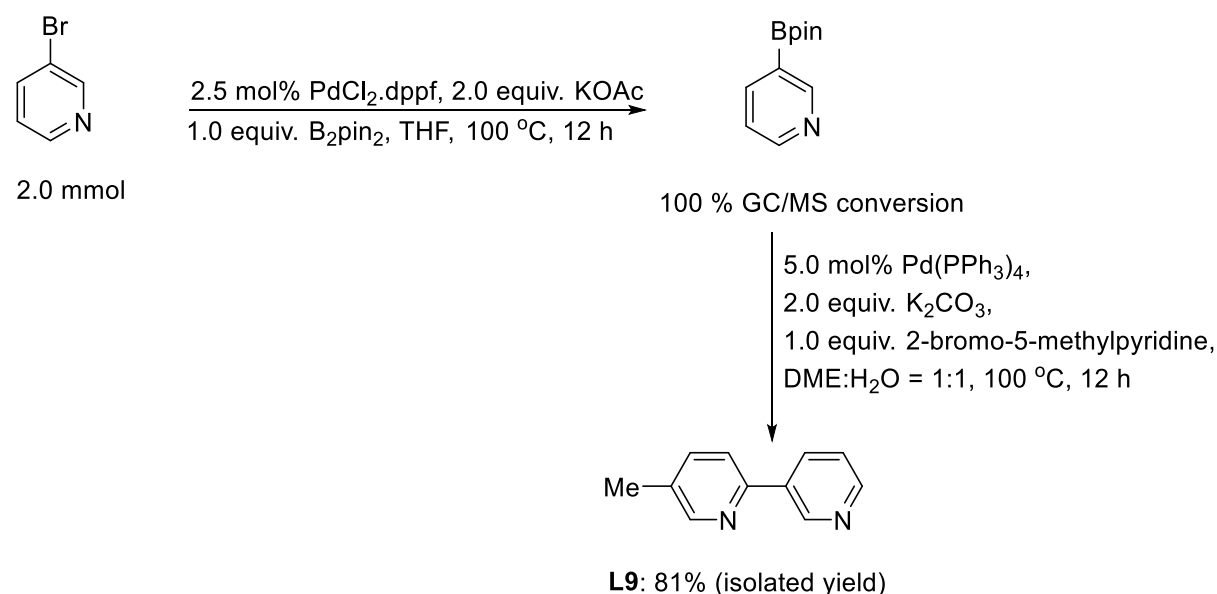
chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 311.0 mg (85%) of 5-methyl-2-(p-tolyl)pyridine (**L8**) as oil.

^1H NMR (400 MHz, CDCl_3): δ 8.51 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.51 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 154.7, 149.9, 138.4, 137.1, 136.5, 131.1, 129.3, 126.5, 119.6, 21.1, 18.0.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{N}$ $[\text{M}+\text{H}]^+$ 184.1121, found 184.1138.

Synthesis of ligand 5-methyl-2,3'-bipyridine (L9):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with $\text{PdCl}_2\cdot\text{dppf}$ (36.6 mg, 2.5 mol%), B_2pin_2 (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromopyridine (316.0 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

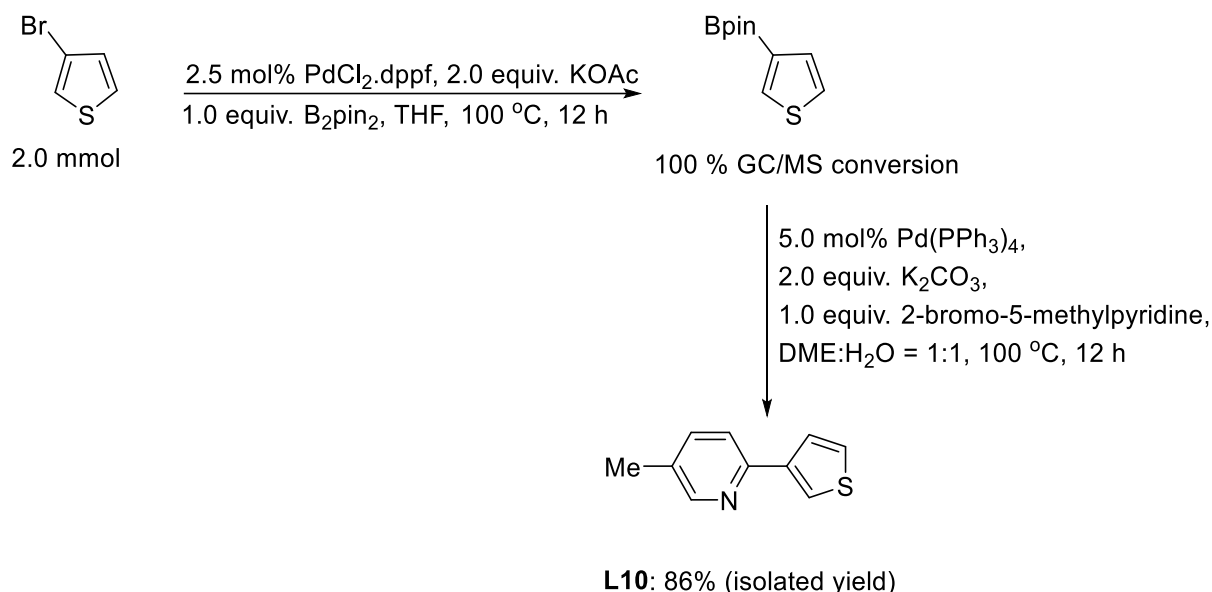
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane as a eluent) gave 276.0 mg (81%) of 5-methyl-2,3'-bipyridine (**L9**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 9.14 (d, J = 2.0 Hz, 1H), 8.60 (dd, J = 4.8 Hz, 1.6 Hz, 1H), 8.52 (s, 1H), 8.27 (td, J = 8.0 Hz, 2.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.57 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.37 (dd, J = 8.0 Hz, 4.8 Hz, 1H) 2.36 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 151.9, 150.4, 149.5, 147.9, 137.4, 134.8, 134.0, 132.5, 123.5, 120.0, 18.2.

HRMS (ESI) *m/z* calcd for C₁₁H₁₁N₂ [M+H]⁺ 171.0917, found 171.0905.

Synthesis of ligand 5-methyl-2-(thiophen-3-yl)pyridine (L10):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

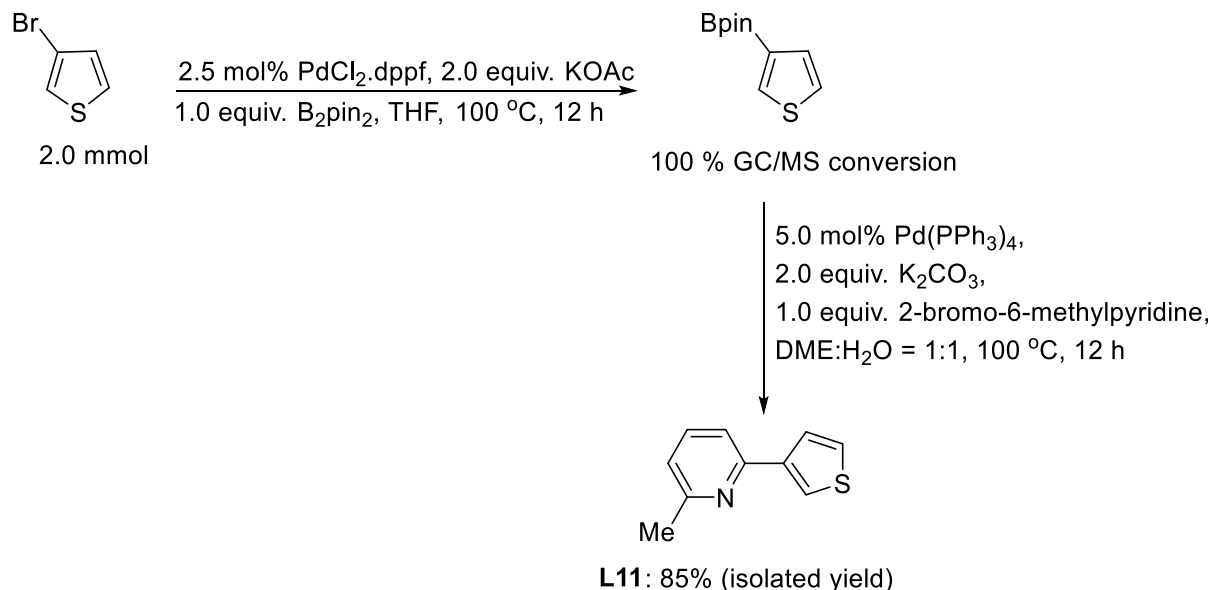
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 301.0 mg (86%) of 5-methyl-2-(thiophen-3-yl)pyridine (**L10**) as offwhite solid.

^1H NMR (400 MHz, CDCl_3): δ 8.44 (s, 1H), 7.83 (d, $J = 2.8$ Hz, 1H), 7.63 (d, $J = 5.2$ Hz, 1H), 7.50 (s, 2H), 7.37 (dd, $J = 4.8$ Hz, 3.2 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 150.9, 149.9, 142.1, 137.2, 131.2, 126.1, 122.7, 119.8, 18.1.

HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{NS}$ $[\text{M}+\text{H}]^+$ 176.0528, found 176.0553.

Synthesis of ligand 2-methyl-6-(thiophen-3-yl)pyridine (L11):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with $\text{PdCl}_2\cdot\text{dppf}$ (36.6 mg, 2.5 mol%), B_2pin_2 (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), $\text{Pd}(\text{PPh}_3)_4$ (115.6 mg, 5.0 mol%), K_2CO_3 (552.8 mg, 2.0 equiv.), 2-bromo-6-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and

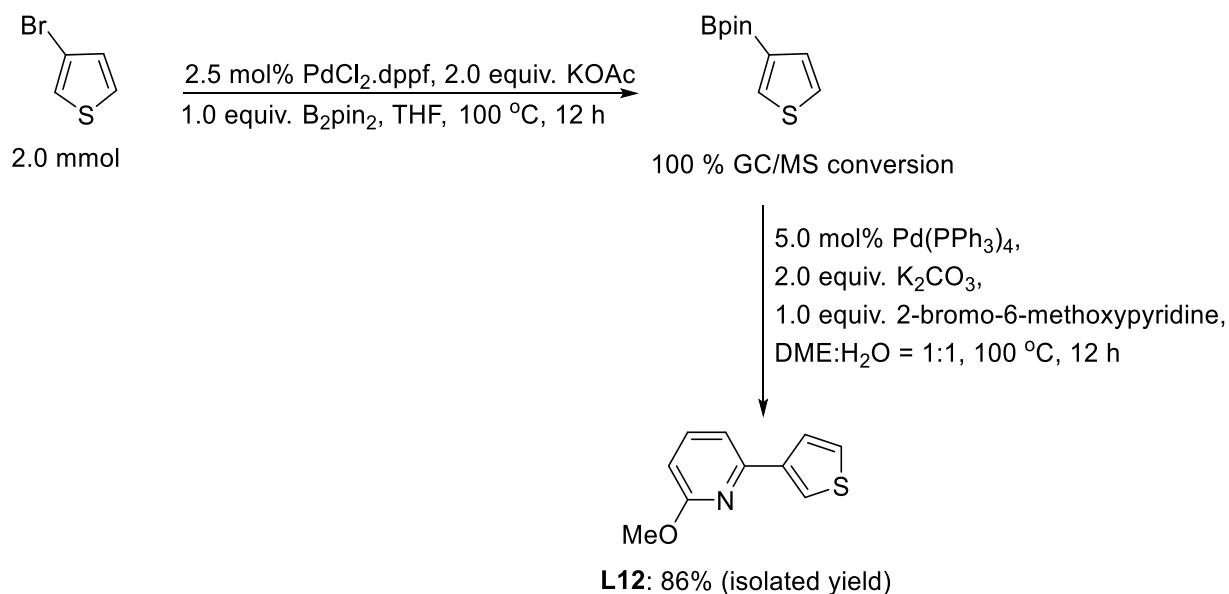
heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 298.0 mg (85%) of 2-methyl-6-(thiophen-3-yl)pyridine (**L11**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.89 (dd, J = 3.2 Hz, 1.2 Hz, 1H), 7.65 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.36-7.41 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 2.60 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 158.3, 152.9, 142.5, 136.8, 126.2, 126.0, 123.2, 121.2, 117.2, 24.6.

HRMS (ESI) *m/z* calcd for C₁₀H₁₀NS [M+H]⁺ 176.0528, found 176.0525.

Synthesis of ligand 2-methoxy-6-(thiophen-3-yl)pyridine (L12):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled

to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

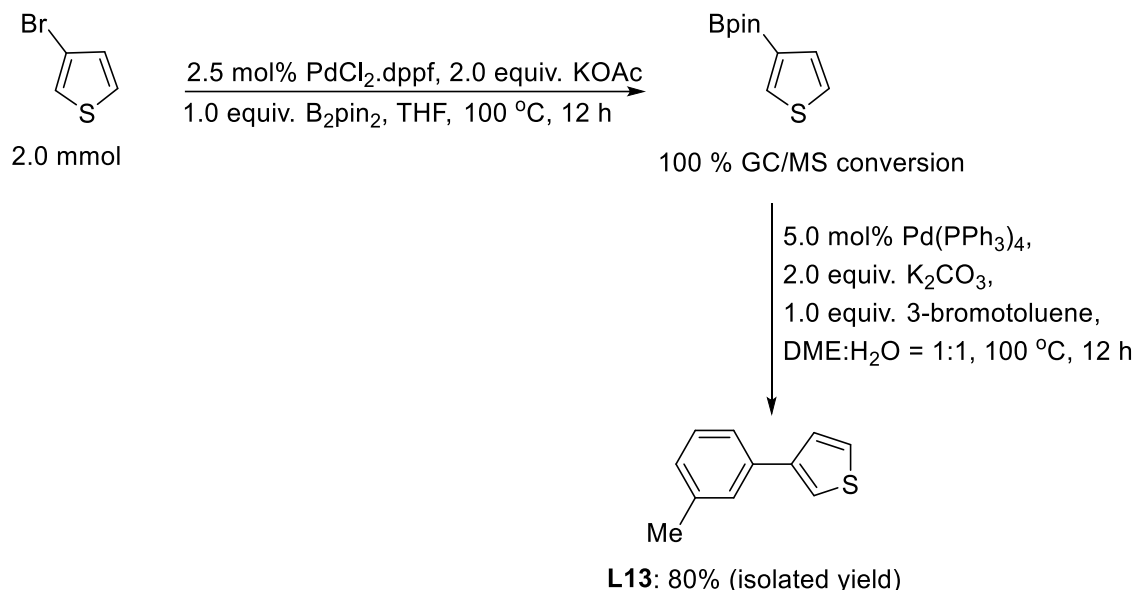
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-6-methoxypyridine (376.0 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 329.0 mg (86%) of 2-methoxy-6-(thiophen-3-yl)pyridine (**L12**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 7.93 (d, J = 2.4 Hz, 1H), 7.66 (d, J = 4.8 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.36-7.38 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 4.02 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 163.6, 150.9, 142.1, 139.1, 126.1, 126.0, 123.2, 112.6, 108.8, 53.1.

HRMS (ESI) *m/z* calcd for C₁₀H₁₀NOS [M+H]⁺ 192.0478, found 192.0470.

Synthesis of ligand 3-(m-tolyl)thiophene (L13):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

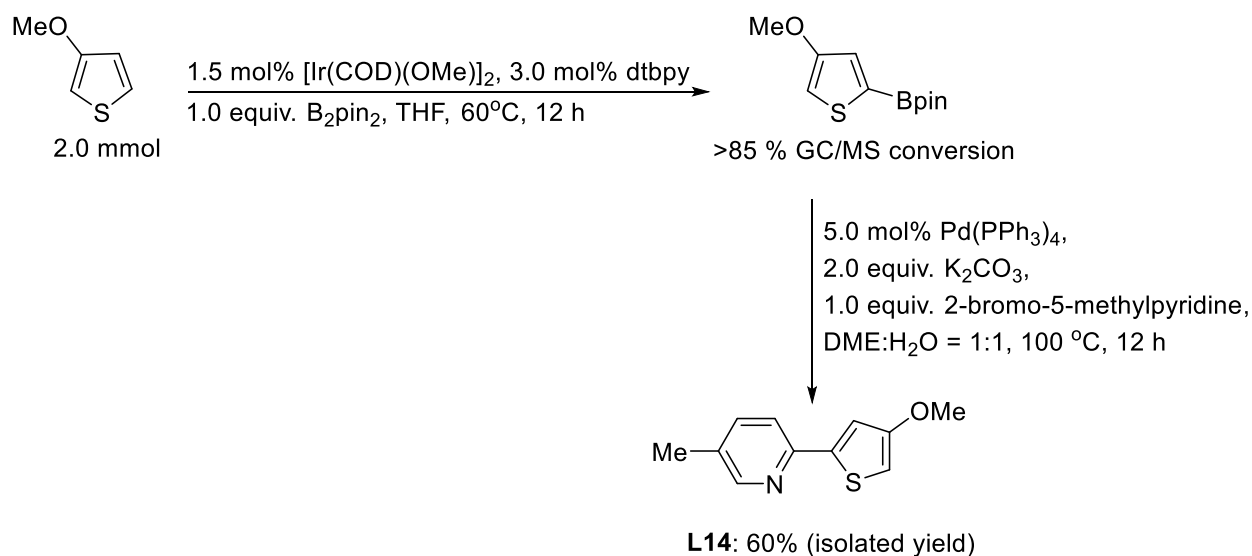
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 3-bromotoluene (342.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 279.0 mg (80%) of 5-methyl-2-(m-tolyl)pyridine (**L13**) as oil.

^1H NMR (400 MHz, CDCl_3): δ 7.45-7.47 (m, 2H), 7.39-7.43 (m, 3H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 142.4, 138.3, 135.7, 128.7, 127.9, 127.2, 126.4, 126.0, 123.5, 120.1, 21.5.

HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{S}$ $[\text{M}+\text{H}]^+$ 175.0576, found 175.0589.

Synthesis of ligand 2-(4-methoxythiophen-2-yl)-5-methylpyridine (L14):



Step-I:

In an argon filled glove box, a 5.0 mL wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (19.9 mg, 1.5 mol%), dtbpy ligand (16.1 mg, 3.0 mol%), B_2pin_2 (508 mg, 1.0 equiv.) dry THF (4.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-methoxythiophene (228.4 mg, 2.0 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60°C . The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and the crude product used for the next step without purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), $\text{Pd}(\text{PPh}_3)_4$ (115.6 mg, 5.0 mol%), K_2CO_3 (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen

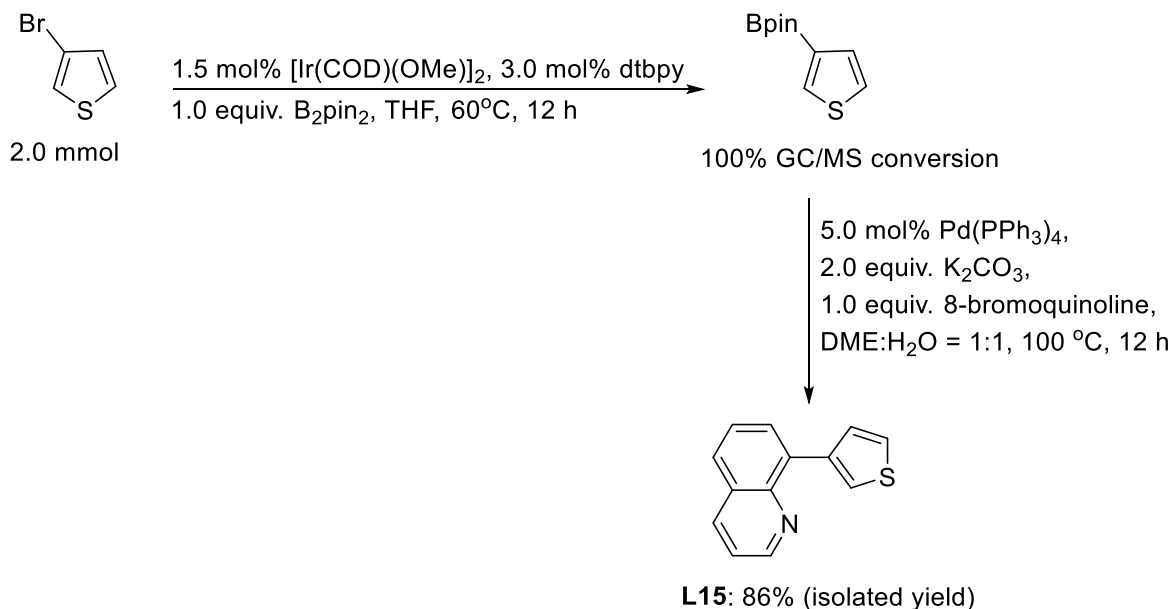
and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 246.0 mg (60%) of 2-(4-methoxythiophen-2-yl)-5-methylpyridine (**L14**) as off white solid.

¹H NMR (400 MHz, CDCl₃): δ 8.37 (s, 1H), 7.44-7.49 (m, 2H), 7.17 (d, J = 1.6 Hz, 1H), 6.29 (d, J = 1.6 Hz, 1H), 3.82 (s, 3H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 158.5, 149.7, 149.5, 143.1, 137.1, 131.8, 117.9, 115.8, 98.5, 57.2, 18.2.

HRMS (ESI) *m/z* calcd for C₁₁H₁₂NOS [M+H]⁺ 206.0634, found 206.0649.

Synthesis of ligand 8-(thiophen-3-yl)quinoline (L15):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and

heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

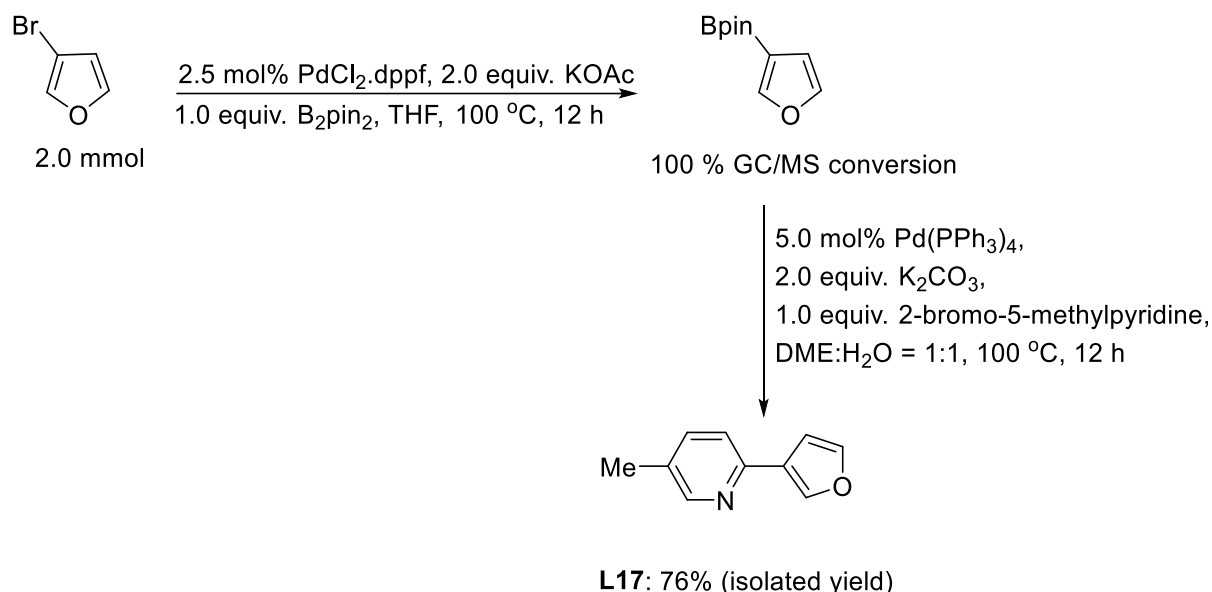
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 8-bromoquinoline (416.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 363.0 mg (86%) of 8-(thiophen-3-yl)quinolone (**L15**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 9.00 (dd, J = 4.0 Hz, 2.0 Hz, 1H), 8.18 (dd, J = 8.4 Hz, 2.0 Hz 1H), 7.93 (dd, J = 2.8 Hz, 1.2 Hz, 1H), 7.88 (dd, J = 7.2 Hz, 1.6Hz, 1H), 7.78 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.70 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 7.58 (dd, J = 8.0 Hz, 7.2 Hz, 1H), 7.41-7.47 (m, 2H).

¹³C NMR (100 MHz, CDCl₃): δ 150.0, 145.9, 139.5, 136.2, 135.1, 129.7, 129.4, 128.7, 127.3, 126.3, 124.7, 124.5, 120.9.

HRMS (ESI) *m/z* calcd for C₁₃H₁₀NS [M+H]⁺ 212.0528, found 212.0510.

Synthesis of ligand 2-(furan-3-yl)-5-methylpyridine (**L17**):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromofuran (294 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

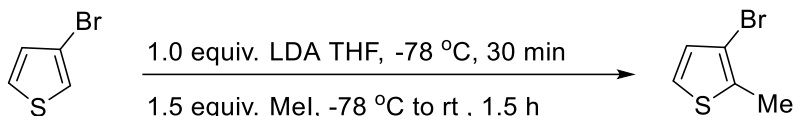
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 242.0 mg (76%) of 2-(furan-3-yl)-5-methylpyridine (**L17**) as oil.

^1H NMR (400 MHz, CDCl_3): δ 8.41 (s, 1H), 7.98 (br s, 1H), 7.48-7.47 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 1H), 6.87 (br s, 1H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 149.9, 149.0, 143.7, 140.7, 137.1, 131.1, 126.9, 119.6, 108.6, 18.2.

HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{10}\text{NO}$ $[\text{M}+\text{H}]^+$ 160.0757, found 160.0753.

Synthesis of 3-bromo-2-methylthiophene:

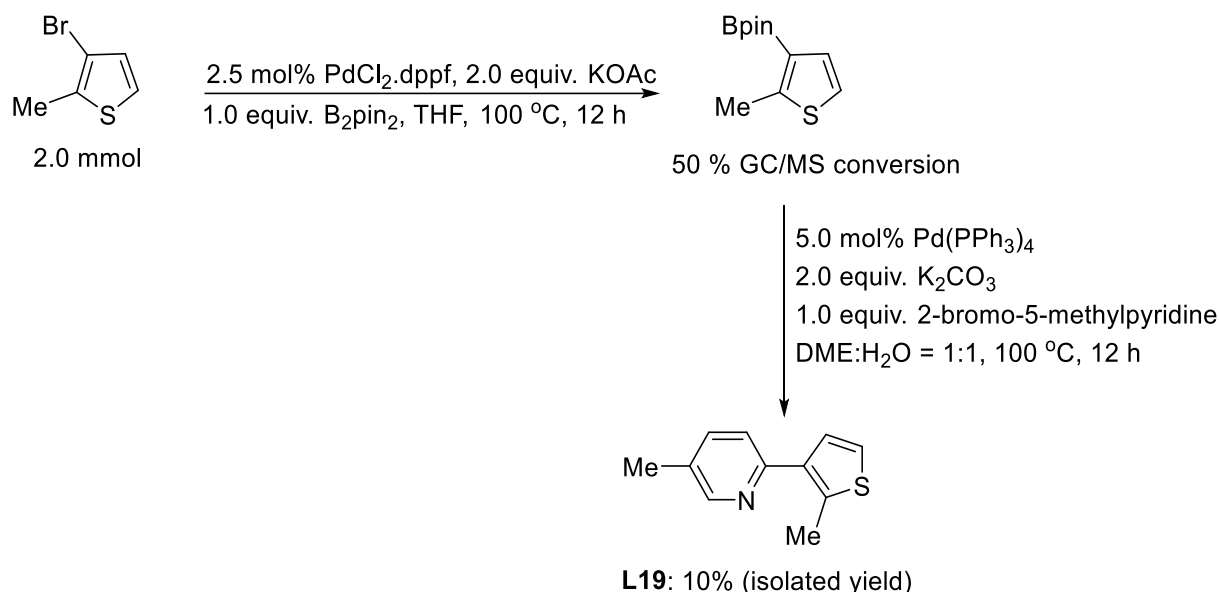


6.13 mmol

50% (isolated yield)

An oven dried 100 mL two necked round bottom flasked charged with lithium diisopropylamide (2.0 M in THF, 6.13 mmol, 3.1 mL) under nitrogen atmosphere and cooled to $-78\text{ }^\circ\text{C}$, and then a solution containing 3-bromothiophene (1 g, 6.13 mmol) dissolved in THF (10 mL) was added dropwise. After addition was complete, the solution was warmed to $0\text{ }^\circ\text{C}$ (ice bath) and stirred an additional 30 min. The temperature of the reaction slurry was lowered to $-78\text{ }^\circ\text{C}$, and a solution containing iodomethane (1.5 equiv., 9.19 mmol, 573 μL) dissolved in 2 mL of THF was added in one portion. The reaction mixture was stirred an additional 30 min at $-78\text{ }^\circ\text{C}$ and then warmed to room temperature and stirred for 1h. The organic layer was collected with ether, washed with water, dried over Na_2SO_4 , and filtered, and then solvents were removed in vacuum to gave 542.6 mg (50%) of 3-bromo-2-methylthiophene as oil. Spectral data are in accordance with the reported data.⁶⁵

Synthesis of ligand 5-methyl-2-(2-methylthiophen-3-yl)pyridine (L19):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromo-2-methylthiophene (354.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 120 °C for 36 h. After 36 h (50 % conversion by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromo-5-methylpyridine (344.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and

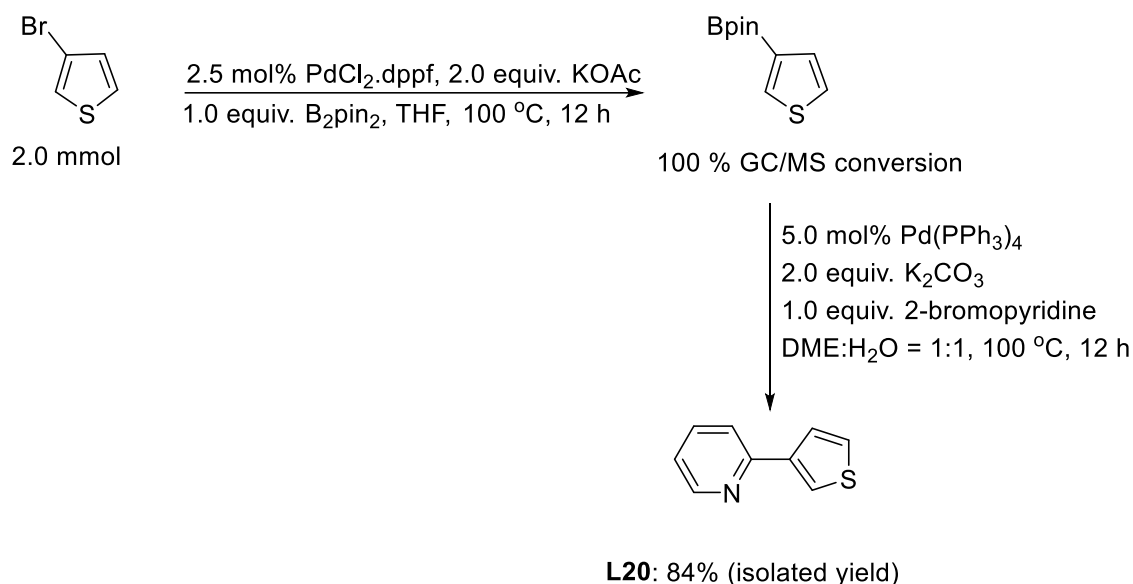
chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 37.8 mg (10%) of 5-methyl-2-(2-methylthiophen-3-yl)pyridine (**L19**) as oil.

^1H NMR (400 MHz, CDCl_3): δ 8.49 (s, 1H), 7.52 (d, $J = 6.8$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 5.2$ Hz, 1H), 7.09 (d, $J = 5.2$ Hz, 1H), 2.65 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 152.5, 149.8, 137.3, 137.0, 136.8, 130.6, 128.8, 122.2, 121.4, 18.2, 14.7.

HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_{11}\text{NS}$ $[\text{M}+\text{H}]^+$ 190.0685, found 190.0755.

Synthesis of ligand 2-(thiophen-3-yl)pyridine (L20):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with $\text{PdCl}_2\cdot\text{dppf}$ (36.6 mg, 2.5 mol%), B_2pin_2 (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

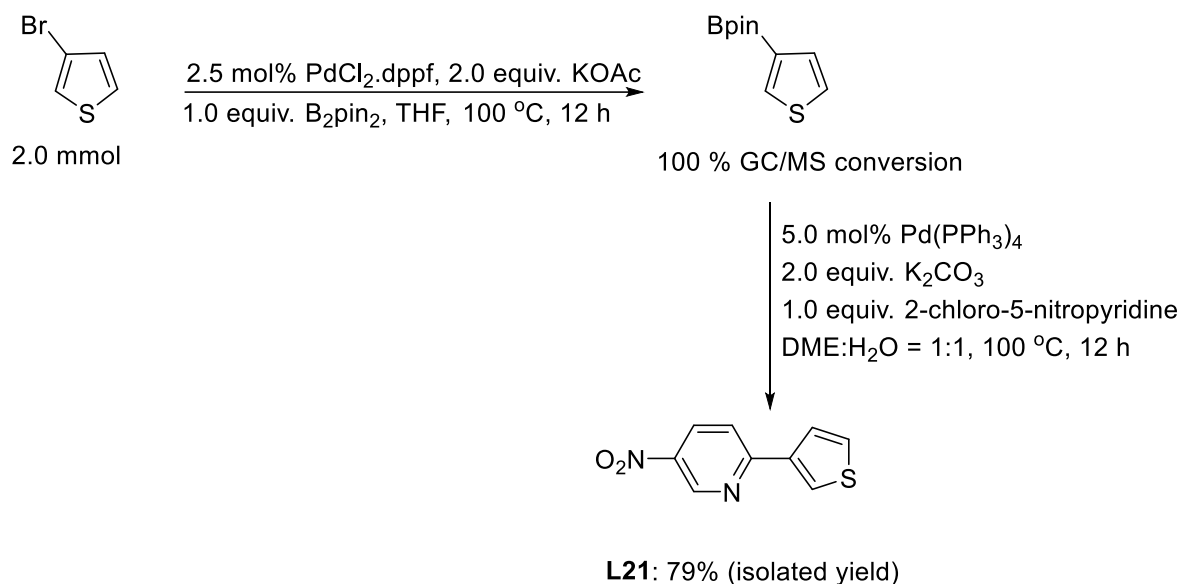
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-bromopyridine (316.0 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as a eluent) gave 271 mg (84%) of 2-(thiophen-3-yl)pyridine (**L20**) as oil.

¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 4.4Hz, 1H), 7.88 (dd, J = 2.8Hz, 1.2Hz, 1H), 7.63-7.67 (m, 2H), 7.58 (d, J = 8.0Hz, 1H), 7.37(dd, J = 5.2Hz, 3.2Hz, 1H), 7.11-7.14(m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 153.4, 149.5, 142.0, 136.6, 126.2, 126.1, 123.4, 121.7, 120.2.

HRMS (ESI) *m/z* calcd for C₉H₈NS [M+H]⁺ 162.0372, found 162.0359.

Synthesis of ligand 5-nitro-2-(thiophen-3-yl)pyridine (L21):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with PdCl₂•dppf (36.6 mg, 2.5 mol%), B₂pin₂ (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

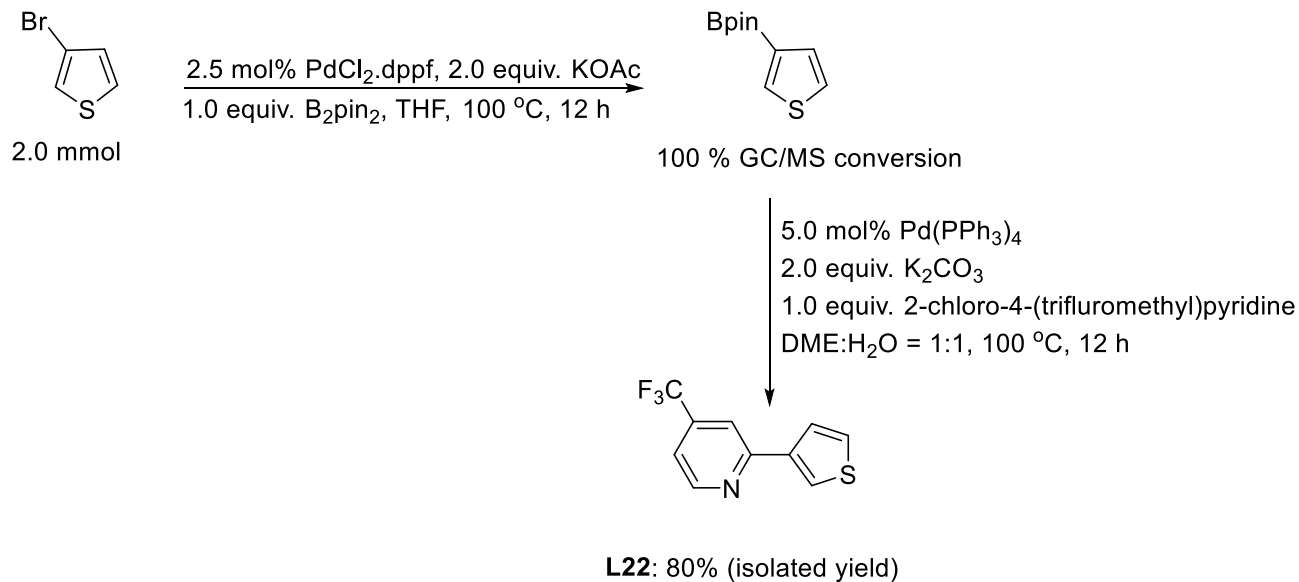
An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), Pd(PPh₃)₄ (115.6 mg, 5.0 mol%), K₂CO₃ (552.8 mg, 2.0 equiv.), 2-chloro-5-nitropyridine (317.1 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (6% ethyl acetate in hexane as a eluent) gave 325.8 mg (79%) of 5-nitro-2-(thiophen-3-yl)pyridine (**L21**) as oil.

^1H NMR (400 MHz, CDCl_3): δ 9.43 (d, $J = 2.0$ Hz, 1H), 7.48 (dd, $J = 8.8$ Hz, 2.4 Hz, 1H), 8.13 (d, $J = 2.4$ Hz, 1H), 7.71-7.77 (m, 2H), 7.46 (dd, $J = 4.4$ Hz, 3.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.1, 145.5, 140.2, 132.0, 127.3, 127.2, 126.3, 119.6.

HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_7\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 207.0223, found 207.0221.

Synthesis of ligand 2-(thiophen-3-yl)-4-(trifluoromethyl)pyridine(L22):



Step-I:

In an argon-filled glove box, a 15 mL pressure tube was charged with $\text{PdCl}_2\cdot\text{dppf}$ (36.6 mg, 2.5 mol%), B_2pin_2 (508 mg, 1.0 equiv.), KOAc (392 mg, 2.0 equiv.), 3-bromothiophene (326.1 mg, 2 mmol) and THF (4 mL) sequentially. Then, the pressure tube was sealed with teflon screw cap and taken out from glove box. The reaction mixture was placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature, diluted with ethyl acetate and passed through celite. The filtrate was concentrated under reduced pressure and used for the next step without further purification.

Step-II:

An oven dried 100 mL pressure tube was charged with crude borylated product in DME (8 mL), $\text{Pd}(\text{PPh}_3)_4$ (115.6 mg, 5.0 mol%), K_2CO_3 (552.8 mg, 2.0 equiv.), 2-chloro-4-(trifluoromethyl)pyridine (363.0 mg, 1.0 equiv.) and water (8 mL) sequentially. The reaction

mixture was degassed with nitrogen and sealed with teflon screw cap. Then, pressure tube placed in a preheated silicon oil bath and heated at 100 °C for 12 h. After completion (checked by GC/MS), the reaction mixture was cooled to room temperature and diluted with water (10 mL) and extracted with ethyl acetate (20 mL x 3). The combined organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as a eluent) gave 367 mg (80%) of 2-(thiophen-3-yl)-4-(trifluoromethyl)pyridine (**L22**) as oil.

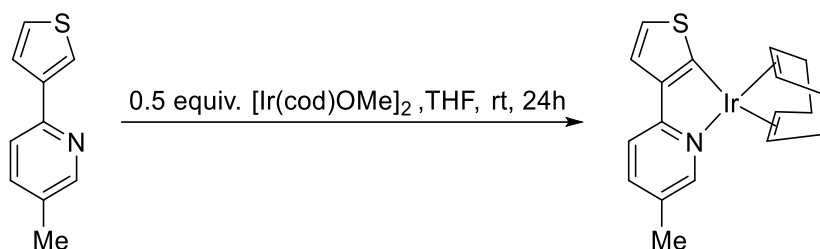
¹H NMR (400 MHz, CDCl₃): δ 8.78 (d, J = 4.8 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 7.79 (s, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.42 (dd, J = 4.4 Hz, 3.2 Hz, 1H), 7.37 (d, J = 4.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 154.7, 150.6, 140.9, 138.5 (q, J = 33.6 Hz), 126.8, 126.0, 124.9, 122.9 (q, J = 271.5 Hz), 117.1 (q, J = 3.4 Hz), 115.6 (q, J = 3.6 Hz),

HRMS (ESI) *m/z* calcd for C₁₀H₇F₃NS [M+H]⁺ 230.0246, found 230.0247.

Synthesis of catalyst **CB1** & **CB2**:

Preparation of catalyst **CB1**:

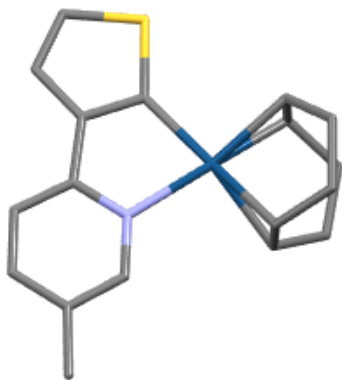


In an argon filled glove box, a 5.0 mL wheaton microreactor was charged with **L10** ligand (35.0mg, 0.2 mmol), [Ir(cod)OMe]₂ (66.3 mg, 0.5 equiv.), and dry THF (1.0 mL). Then the reaction mixture was stirred for 24 h at room temperature. After 24 h solvent was evaporated under reduced pressure under argon atmosphere and dried for 20 minutes under vacuum. A black powder was obtained. Isolated yield 85.4 mg (90%). Crystallization was carried out in THF/Hexane solvent. This compound stable under inert atmosphere.

¹H NMR (400 MHz, CDCl₃): δ 7.65 (s, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 5.2 Hz, 1H), 7.19 (d, J = 4.8 Hz, 1H), 4.35 (br s, 2H), 4.20 (br s, 2H), 2.34-2.37 (m, 4H), 2.25 (s, 3H), 1.87-1.91 (m, 4H).

HRMS (ESI) *m/z* calcd for C₁₈H₂₂IrNS [M+H]⁺ 476.1018, found 476.1009.

Catalyst **CB1** structure was confirmed from crystal structure. Here are the details.



CCDC No: 2002760

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

Bond precision: C-C = 0.0084 A Wavelength=0.71073

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 alpha=63.838(3) beta=73.559(3) gamma=72.269(3)

Temperature: 100 K

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Hall group	-P 1	-P 1
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Sum formula	C18 H20 Ir N S	C18 H20 Ir N S
Mr	474.63	474.65
Dx,g cm-3	2.102	2.102
Z	2	2
Mu (mm-1)	9.036	9.035
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F000'	453.65	
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Nref	3744	3728
Tmin,Tmax	0.214,0.338	0.214,0.338
Tmin'	0.151	

Correction method= # Reported T Limits: Tmin=0.214 Tmax=0.338
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 28.340

R(reflections)= 0.0282(3442) wR2(reflections)= 0.0856(3728)

S = 0.905 Npar= 190

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as multi-scan

PLAT213_ALERT_2_C	Atom C18	has ADP max/min Ratio	3.1	prolat
PLAT220_ALERT_2_C	NonSolvent Resd 1	C	Ueq(max) / Ueq(min) Range	3.9	Ratio
PLAT241_ALERT_2_C	High 'MainMol'	Ueq as Compared to Neighbors of		C15	Check
PLAT241_ALERT_2_C	High 'MainMol'	Ueq as Compared to Neighbors of		C16	Check
PLAT342_ALERT_3_C	Low Bond Precision on	C-C Bonds	0.00835	Ang.
PLAT911_ALERT_3_C	Missing FCF Refl Between	Thmin & STh/L=	0.600	2	Report
PLAT971_ALERT_2_C	Check Calcd Resid. Dens.	0.87A	From Ir1	1.68	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens.	0.76A	From Ir1	-2.49	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens.	0.90A	From Ir1	-2.41	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens.	0.75A	From Ir1	-1.94	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens.	0.71A	From Ir1	-1.82	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens.	0.70A	From Ir1	-1.78	eA-3
PLAT972_ALERT_2_C	Check Calcd Resid. Dens.	0.82A	From Ir1	-1.71	eA-3
PLAT973_ALERT_2_C	Check Calcd Positive Resid. Density on		Ir1	1.08	eA-3

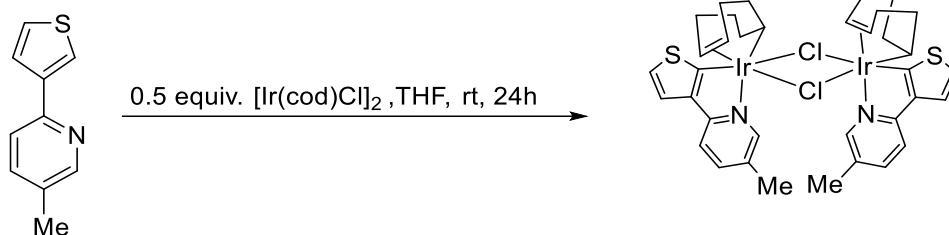
Alert level G

PLAT066_ALERT_1_G	Predicted and Reported Tmin&Tmax Range Identical			?	Check
PLAT068_ALERT_1_G	Reported F000 Differs from Calcd (or Missing)...			Please	Check
PLAT073_ALERT_1_G	H-atoms ref, but _hydrogen_treatment Reported as			constr	Check
PLAT154_ALERT_1_G	The s.u.'s on the Cell Angles are Equal ..(Note)			0.003	Degree
PLAT380_ALERT_4_G	Incorrectly? Oriented X(sp2)-Methyl Moiety		C10	Check
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).			1	Note
PLAT912_ALERT_4_G	Missing # of FCF Reflections Above STh/L=	0.600		14	Note
PLAT933_ALERT_2_G	Number of OMIT Records in Embedded .res File	...		2	Note
PLAT960_ALERT_3_G	Number of Intensities with I < - 2*sig(I)	...		2	Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.			0	Info
PLAT982_ALERT_1_G	The Ir-f'="	-1.3039	Deviates from IT-value =	-1.4442	Check
PLAT983_ALERT_1_G	The Ir-f'="	7.9811	Deviates from IT-Value =	7.9887	Check
PLAT983_ALERT_1_G	The S-f'="	0.1244	Deviates from IT-Value =	0.1234	Check

- 0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
15 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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- 8 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
14 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check
-

Preparation of catalyst **CB2**:



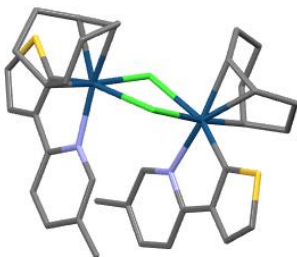
In an argon filled glove box, a 5.0 mL wheaton microreactor was charged with **L10** ligand (35 mg, 0.2 mmol), $[\text{Ir}(\text{cod})\text{Cl}]_2$ (67.17 mg, 0.5 equiv.), and dry THF (1.0 mL). Then the reaction mixture was stirred for 24 h at room temperature. After 24 h solvent was evaporated under reduced pressure under argon atmosphere and dried for 20 minutes under vacuum. A yellowish solid was obtained. Isolated yield 90.0 mg (88%). Crystallization was carried out in THF solvent. This compound is air stable.

^1H NMR (400 MHz, CDCl_3): δ 8.61 (s, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.26-7.29 (m, 4H), 7.09 (d, $J = 8.0$ Hz, 2H), 5.54-5.68 (m, 4H), 2.87-2.98 (m, 2H), 2.67-2.73 (m, 2H), 2.45-2.53 (m, 2H), 2.36 (d, $J = 10.4$ Hz, 1H), 1.97-1.99 (m, 1H), 1.93 (s, 6H), 1.58-1.62 (m, 2H), 1.47-1.55 (m, 2H), 1.37 (br s, 2H), 1.10-1.16 (m, 4H), 0.54 (dd, $J = 13.2$ Hz, $J = 8.0$ Hz, 2H), (-) 0.13 (d, $J = 12.0$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.0, 148.3, 146.6, 140.5, 137.4, 128.4, 123.3, 122.2, 116.2, 81.5, 79.1, 44.3, 33.4, 28.2, 26.9, 23.1, 19.1, 18.4.

HRMS (ESI) m/z calcd for $\text{C}_{36}\text{H}_{43}\text{Cl}_2\text{Ir}_2\text{N}_2\text{S}_2$ $[\text{M}+\text{H}]^+$ 1023.1503, found 1023.1303..

Catalyst **CB2** structure was confirmed from crystal structure. Here are the details.



CCDC No: 2002759

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: shelx

Bond precision:	C-C = 0.0073 Å	Wavelength=0.71073	
Cell:	a=40.671(3)	b=15.6269(9)	c=19.7447(12)
	alpha=90	beta=90	gamma=90
Temperature:	100 K		
	Calculated	Reported	
Volume	12549.0(14)	12549.1(14)	
Space group	P b c n	P b c n	
Hall group	-P 2n 2ab	-P 2n 2ab	
Moiety formula	C36 H42 Cl2 Ir2 N2 S2, 2(C4 H8 O)	C36 H42 Cl2 Ir2 N2 S2,2(C4 H8 O)	
Sum formula	C44 H58 Cl2 Ir2 N2 O2 S2	C44 H58 Cl2 Ir2 N2 O2 S2	
Mr	1166.38	1166.38	
Dx, g cm-3	1.852	1.852	
Z	12	12	
Mu (mm-1)	6.624	6.624	
F000	6864.0	6864.0	
F000'	6839.20		
h,k,lmax	54,20,26	54,20,26	
Nref	15603	15560	
Tmin,Tmax	0.316,0.452	0.316,0.452	
Tmin'	0.256		
Correction method= # Reported T Limits: Tmin=0.316 Tmax=0.452			
AbsCorr = MULTI-SCAN			
Data completeness=	0.997	Theta(max)=	28.290
R(reflections)=	0.0319(13632)	wR2(reflections)=	0.0738(15560)
S =	1.199	Npar=	730

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without
a literature citation. This should be contained in the
_exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C58 Check
PLAT411_ALERT_2_C Short Inter H...H Contact H51 ..H51 . 2.06 Ang.
1-x,2-y,2-z = 5_677 Check

Alert level G

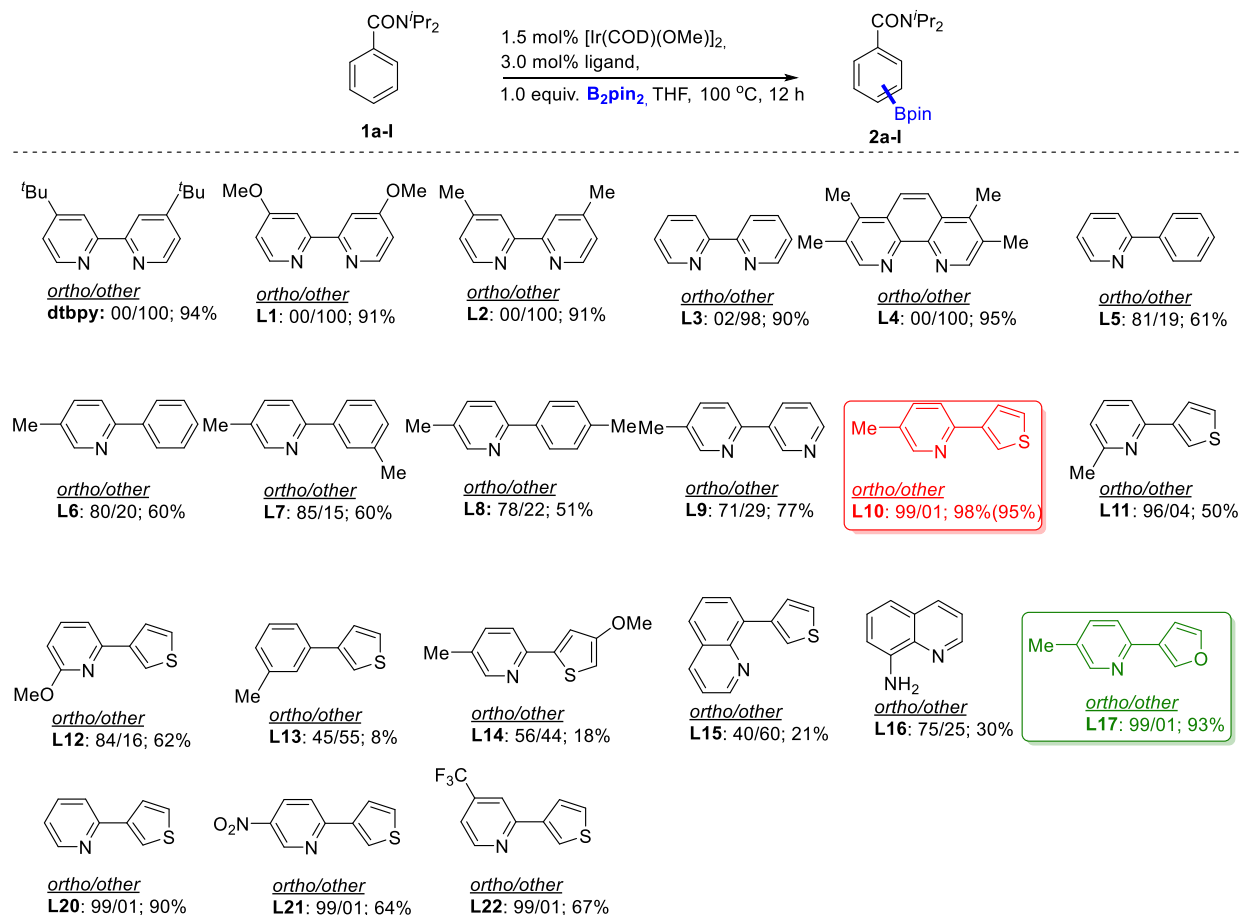
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 91.06 Why ?
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ir1 --Cl2 . 5.2 s.u.
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Ir2 --Cl2 . 5.6 s.u.
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety C1 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety C19 Check
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety C37 Check
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O1 108.5 Degree
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O2 107.7 Degree
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O3 107.7 Degree
PLAT793_ALERT_4_G Model has Chirality at C11 (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C29 (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C51 (Centro SPGR) R Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 6 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
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8 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
7 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Ligand screening for borylation:

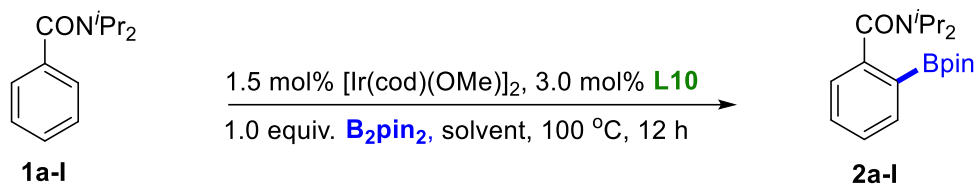
General Procedure^a: In an argon filled glove box, a 5.0 mL wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), ligand (**dtbpy**: 1.6 mg; **L1**: 1.3 mg; **L2**: 1.1 mg; **L3**: 0.94 mg; **L4**: 1.4 mg; **L5**: 0.93 mg; **L6**: 1.0 mg; **L7**: 1.1 mg; **L8**: 1.1 mg; **L9**: 1.0 mg; **L10**: 1.1 mg; **L11**: 1.1 mg; **L12**: 1.2 mg; **L13**: 1.1 mg; **L14**: 1.2 mg; **L15**: 1.3 mg; **L16**: 0.9 mg; **L17**: 1.0 mg, **L20**: 1.0 mg, **L21**: 1.2 mg, **L22**: 1.3 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, substrate **1a-I** (41.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into preheated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After 12 h, 50.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC/MS) and results are summarised in the figure.



^[a] Reaction scale 0.2 mmol. GC/MS ratios; conversions are based on dodecane as internal standard. ratios of mono:di, with **L5**: 95:05, with **L6**: 96:04, with **L9**: 92:08, with **L12**: 96:04 where di is *ortho-ortho* di. In parenthesis isolated yield. The ratio of *ortho/other* = *ortho*/(*meta*+*para* and diborylation). The digit 00 indicates no *ortho* isomer formed.

Solvent screening for borylation:

General Procedure^a: In an argon filled glove box, a 5.0 mL wheaton microreactor was charged with [Ir(cod)(OMe)₂] (1.98 mg, 1.5 mol%), **L10** (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry solvent (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, substrate **1a-I** (41.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After 12 h, 50.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC/MS) and results are summarised in the figure.

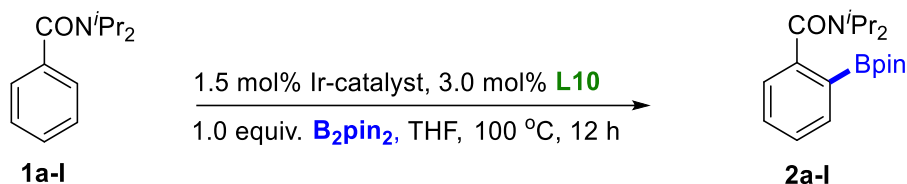


Solvent	conversion	isomer ortho/others
THF	98%	99/01
Cyclohexane	97%	99/01
Hexane	95%	99/01
MTBE	70%	99/01

^[a] Reaction scale 0.2 mmol. GC/MS ratios; conversions are based on dodecane as internal standard.

Catalyst Screening for borylation:

General Procedure^a: In an argon filled glove box, a 5.0 mL wheaton microreactor was charged with Ir-catalyst ([Ir(cod)(OMe)]₂: 1.98 mg; [Ir(cod)(Cl)]₂: 2.0 mg; [Ir(coe)₂(Cl)]₂: 2.69 mg, 1.5 mol%), **L10** (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, substrate **1a-I** (41.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After 12 h, 50.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC/MS) and results are summarised in the figure.

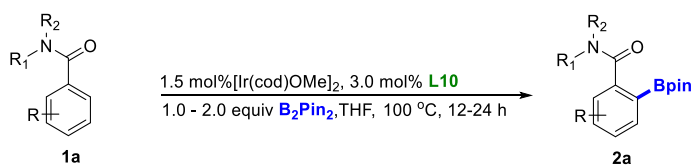


Catalyst	conversion	isomer <i>ortho/others</i>
[Ir(cod)(Cl)] ₂	98%	99/01 ^b
[Ir(cod)(OMe)] ₂	98%	99/01
[Ir(coe) ₂ (Cl)] ₂	97%	99/01

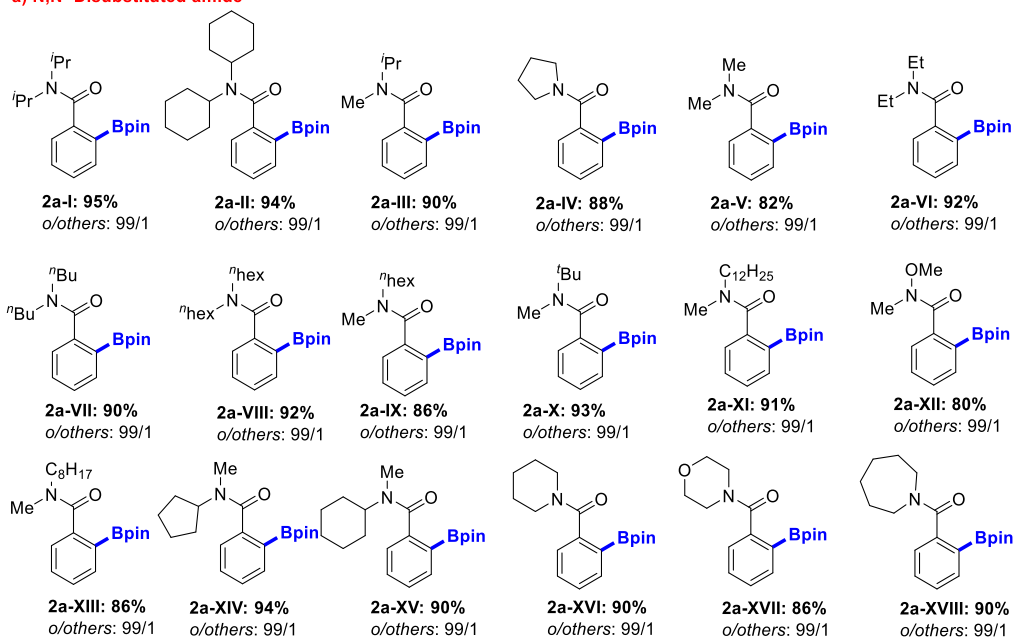
^[a] Reaction scale 0.2 mmol. GC/MS ratios; conversions are based on dodecane as internal standard. ^b 1.2 equiv. B₂pin₂ used.

Directed borylation:

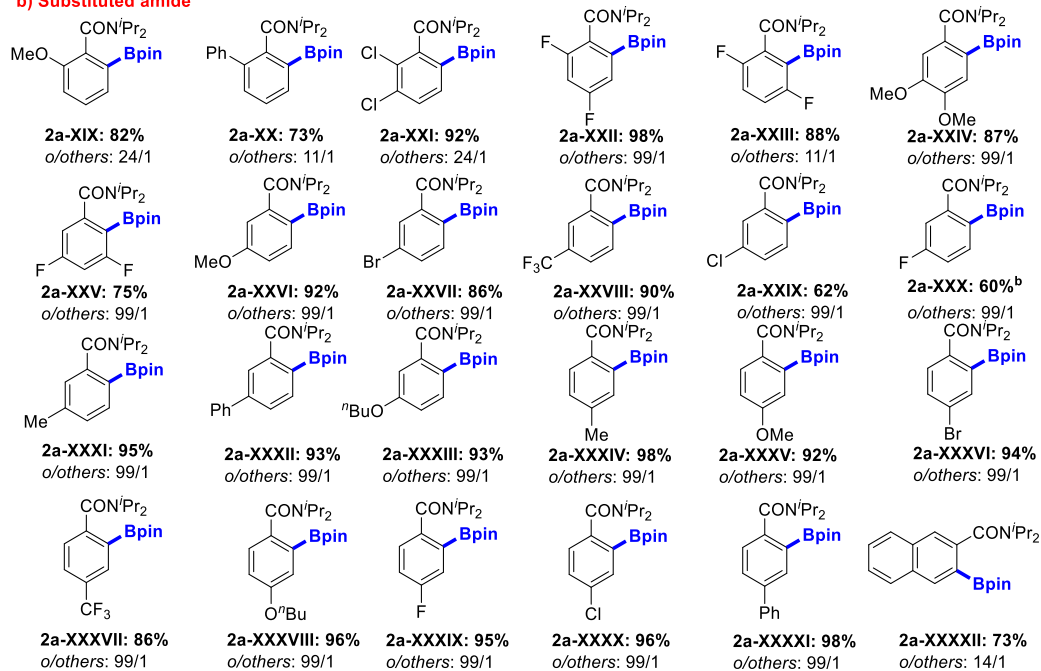
Borylation of *N,N* disubstituted amide^a:



a) *N,N*-Disubstituted amide

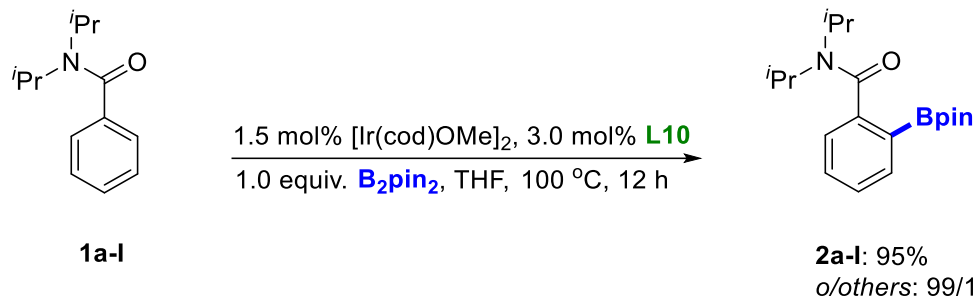


b) Substituted amide



^a Reaction scale 0.2 mmol. GC/MS ratios are given using dodecane as internal standard. ^b here two ortho isomers formed with ratio; 68:32, major is C6 isomer.

Borylation of N,N-diisopropylbenzamide (1a-I):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropylbenzamide (41.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 62.9 mg of borylated product **2a-I** (95%) as white solid. Spectral data are in accordance with the reported data.⁷

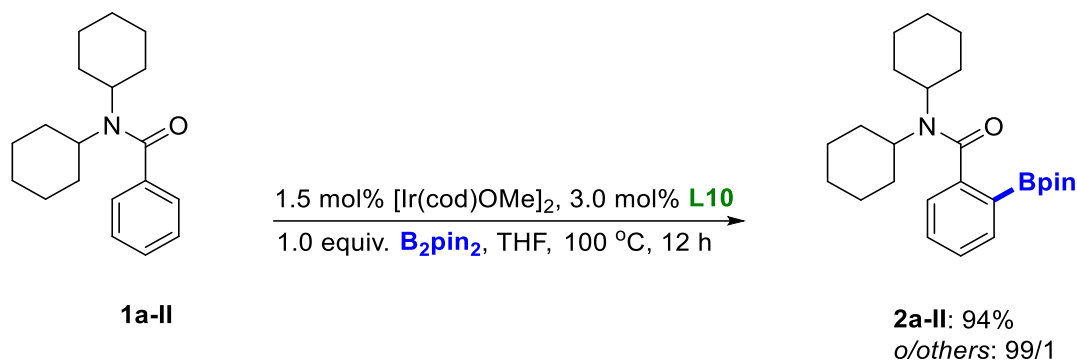
¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 3.81-3.84 (m, 1H), 3.58-3.61 (m, 1H), 1.68 (d, J = 6.0 Hz, 6H), 1.41 (s, 12H), 1.21 (d, J = 5.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 171.1, 145.0, 135.4, 130.4, 127.2, 124.5, 83.6, 50.7, 45.6, 24.7, 20.3, 20.1.

¹¹B NMR (128 MHz, CDCl₃): δ 29.9.

HRMS (ESI) *m/z* calcd for C₁₉H₃₁BNO₃ [M+H]⁺ 332.2392, found 332.2381.

Borylation of N,N-dicyclohexylbenzamide (1a-II):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dicyclohexylbenzamide (57.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 77.3 mg of borylated product **2a-II** (94%) as off white solid.

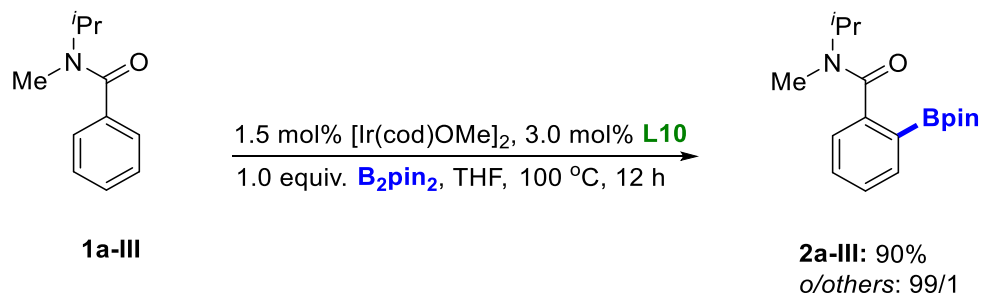
^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.2$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 1H), 3.26-3.29 (m, 1H), 3.03 (br s, 1H), 2.66-2.68 (m, 2H), 1.81 (br s, 4H), 1.67 (br s, 5H), 1.43-1.49 (m, 3H), 1.30 (s, 12H), 1.25 (br s, 3H), 0.97 (br s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.5, 144.6, 135.1, 130.2, 127.4, 124.4, 83.4, 59.6, 56.1, 30.7, 29.8, 26.7, 25.6, 25.3, 25.2, 24.8.

^{11}B NMR (128 MHz, CDCl_3): δ 28.8.

HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{39}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 412.3018, found 412.3015.

Borylation of *N*-isopropyl-*N*-methylbenzamide (**1a-III**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-isopropyl-*N*-methylbenzamide (35.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 54.6 mg of borylated product **2a-III** (90%) as white solid.

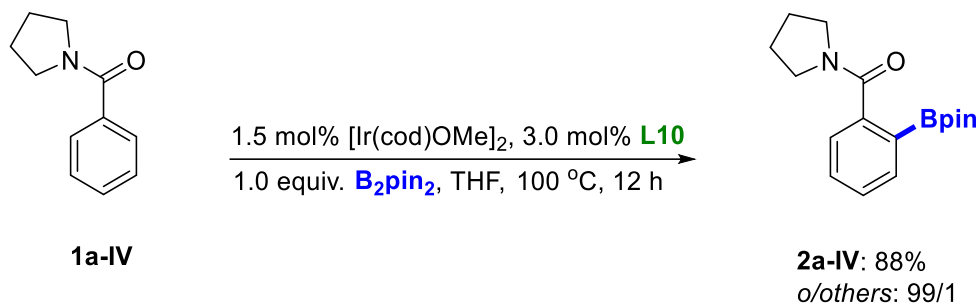
^1H NMR (400 MHz, CDCl_3): δ 7.79 (t, $J = 6.4$ Hz, 1H), 7.39-7.42 (m, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.20-7.23 (m, 1H), 5.02 (sept, $J = 6.8$ Hz, 0.5H), 3.77 (sept, $J = 6.8$ Hz, 0.5H), 2.92 (s, 1.5H), 2.65 (s, 1.5H), 1.28 (s, 12H), 1.21 (d, $J = 6.8$ Hz, 3H), 1.10 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 171.7, 143.4, 143.3, 135.3, 135.2, 130.8, 130.5, 127.8, 127.7, 125.4, 124.8, 83.6, 83.5, 49.5, 44.0, 30.0, 25.8, 24.8, 24.7, 19.8, 19.0.

^{11}B NMR (128 MHz, CDCl_3): δ 29.2.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 304.2079, found 304.2102.

Borylation of phenyl(pyrrolidin-1-yl)methanone (**1a-IV**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, phenyl(pyrrolidin-1-yl)methanone (35.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (35% ethyl acetate in hexane as eluent) gave 53.0 mg of borylated product **2a-IV** (88%) as oil.

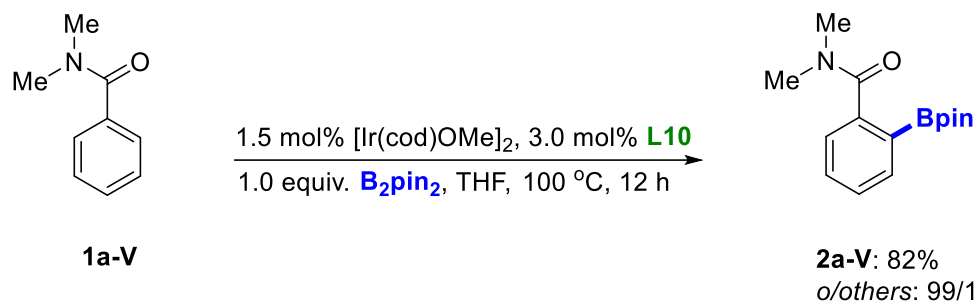
^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, $J = 7.2$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 3.82 (t, $J = 6.4$ Hz, 2H), 3.69 (t, $J = 6.4$ Hz, 2H), 1.92-2.05 (m, 4H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.4, 136.6, 132.3, 131.3, 128.5, 124.9, 81.3, 48.7, 48.5, 26.3, 25.2, 23.8.

^{11}B NMR (128 MHz, CDCl_3): δ 19.1.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{BNNaO}_3$ $[\text{M}+\text{Na}]^+$ 324.1741, found 324.1475.

Borylation of N,N-dimethylbenzamide (1a-V):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dimethylbenzamide (29.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (40% ethyl acetate in hexane as eluent) gave 45.1 mg of borylated product **2a-V** (82%) as liquid. Spectral data are in accordance with the reported data.⁶⁶

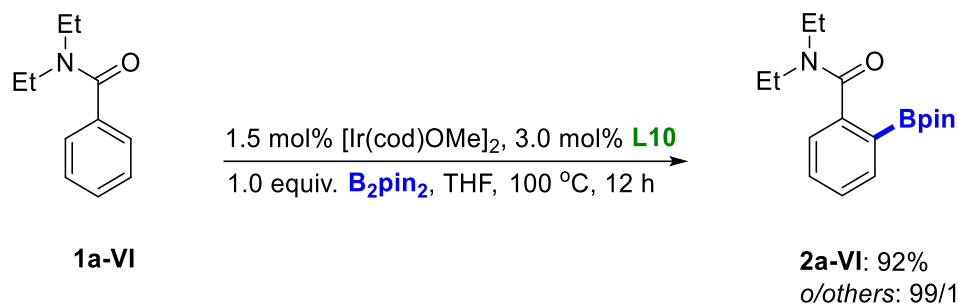
^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 7.2$ Hz, 1H), 2.93 (br s, 6H), 1.28 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.3, 142.6, 134.9, 130.8, 128.0, 125.4, 83.4, 38.9, 35.4, 24.8.

^{11}B NMR (128 MHz, CDCl_3): δ 29.3.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{BNNaO}_3$ $[\text{M}+\text{Na}]^+$ 298.1585, found 298.1599.

Borylation of N,N-diethylbenzamide (1a-VI):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diethylbenzamide (35.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 55.8 mg of borylated product **2a-VI** (92%) as white solid. Spectral data are in accordance with the reported data.⁶⁷

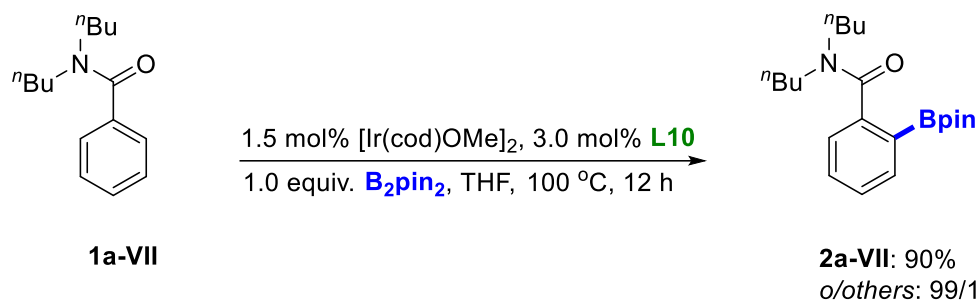
^1H NMR (400 MHz, CDCl_3): δ 7.79 (d, $J = 7.2$ Hz, 1H), 7.40 (t, $J = 7.2$ Hz, 1H), 7.34 (t, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 7.2$ Hz, 1H), 3.56 (q, $J = 7.2$ Hz, 2H), 3.20 (q, $J = 7.2$ Hz, 2H), 1.30-1.34 (m, 3H), 1.28 (s, 12H), 1.04 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 142.3, 135.0, 130.4, 128.1, 125.3, 83.3, 42.9, 39.7, 24.8, 13.6, 12.4.

^{11}B NMR (128 MHz, CDCl_3): δ 28.4.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 304.2079, found 304.2098.

Borylation of *N,N*-dibutylbenzamide (**1a-VII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dibutylbenzamide (46.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 64.7 mg of borylated product **2a-VII** (90%) as liquid.

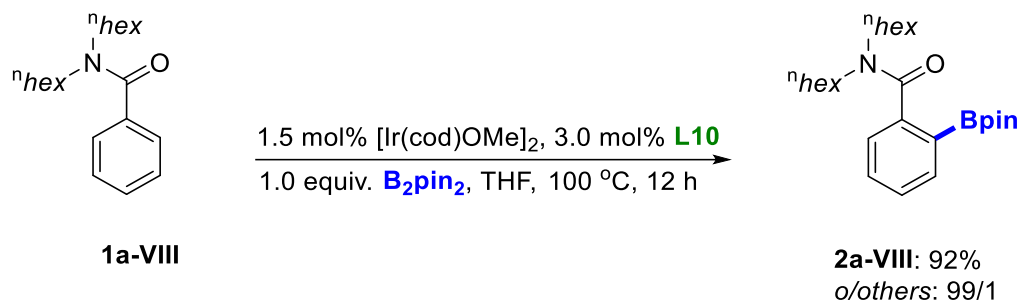
^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 6.8$ Hz, 1H), 7.29-7.38 (m, 2H), 7.22 (d, $J = 7.2$ Hz, 1H), 3.45 (t, $J = 7.6$ Hz, 2H), 3.12 (t, $J = 7.6$ Hz, 2H), 1.64-1.72 (m, 2H), 1.40-1.47 (m, 2H), 1.34-1.38 (m, 2H), 1.27 (s, 12H), 1.11 (sextet, $J = 7.2$ Hz, 2H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.74 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 141.8, 134.6, 130.1, 128.2, 125.5, 83.0, 48.6, 45.8, 30.3, 29.2, 24.8, 20.3, 19.7, 13.9, 13.5.

^{11}B NMR (128 MHz, CDCl_3): δ 27.4.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{35}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 360.2705, found 360.2711.

Borylation of *N,N*-dihexylbenzamide (**1a-VIII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dihexylbenzamide (57.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 76.4 mg of borylated product **2a-VIII** (92%) as off white solid.

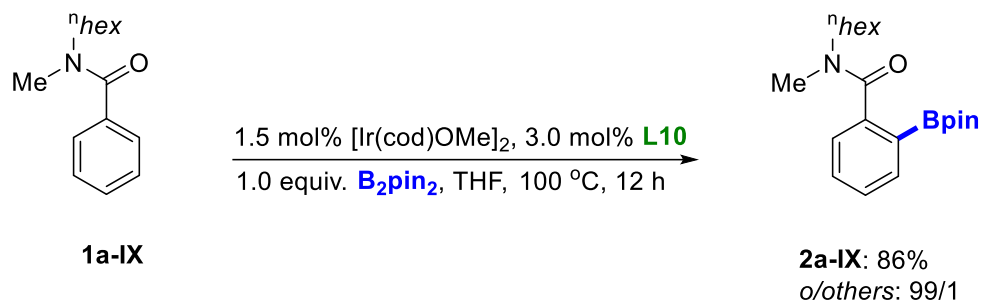
^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, $J = 6.8$ Hz, 1H), 7.32-7.41 (m, 2H), 7.25 (d, $J = 7.2$ Hz, 1H), 3.44-3.48 (m, 2H), 3.12-3.16 (m, 2H), 1.70-1.72 (m, 2H), 1.45-1.51 (m, 2H), 1.34 (br s, 6H), 1.29 (s, 12H), 1.23-1.25 (m, 2H), 1.10-1.12 (m, 4H), 0.89 (t, $J = 6.4$ Hz, 3H), 0.81 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.8, 141.7, 134.6, 130.1, 128.4, 125.6, 83.1, 48.9, 46.3, 31.7, 31.2, 28.2, 27.1, 26.9, 26.2, 24.9, 22.6, 22.4, 14.0, 13.9.

^{11}B NMR (128 MHz, CDCl_3): δ 27.2.

HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{43}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 416.3331, found 416.3330.

Borylation of *N*-hexyl-*N*-methylbenzamide (**1a-IX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-hexyl-*N*-methylbenzamide (43.9mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 59.4 mg of borylated product **2a-IX** (86%) as liquid.

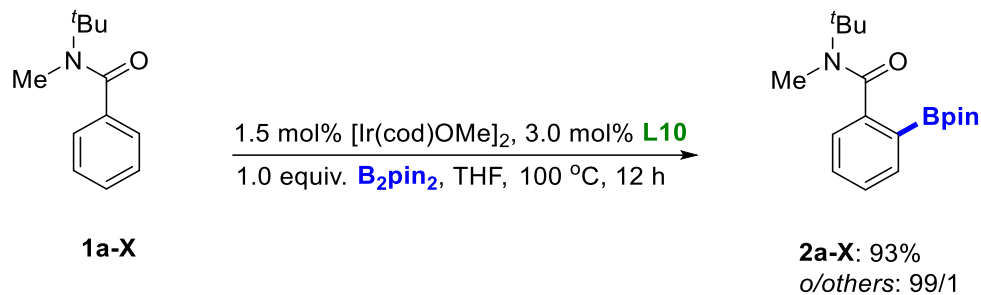
^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, $J = 7.2$ Hz, 1H), 7.40 (dt, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 7.6$ Hz, 1H), 3.47-3.51 (m, 1H), 3.06-3.11 (m, 2.5H), 2.81 (s, 1.5H), 1.67 (br s, 1H), 1.44-1.46 (m, 1H), 1.33 (br s, 3H), 1.28 (s, 12H), 1.10-1.18 (m, 3H), 0.87-0.89 (m, 1.5H), 0.80 (t, $J = 7.2$ Hz, 1.5H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 171.8, 142.3, 141.9, 134.8, 134.7, 130.5, 130.4, 128.1, 125.5, 83.2, 74.7, 51.0, 48.0, 36.9, 32.9, 31.6, 31.2, 27.7, 26.6, 25.9, 24.8, 24.6, 22.5, 22.3, 13.9, 13.8.

^{11}B NMR (128 MHz, CDCl_3): δ 28.3.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 346.2548, found 346.2567.

Borylation of *N*-(*tert*-butyl)-*N*-methylbenzamide (**1a-X**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-(*tert*-butyl)-*N*-methylbenzamide (38.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (15% ethyl acetate in hexane as eluent) gave 59.0 mg of borylated product **2a-X** (93%) as white solid.

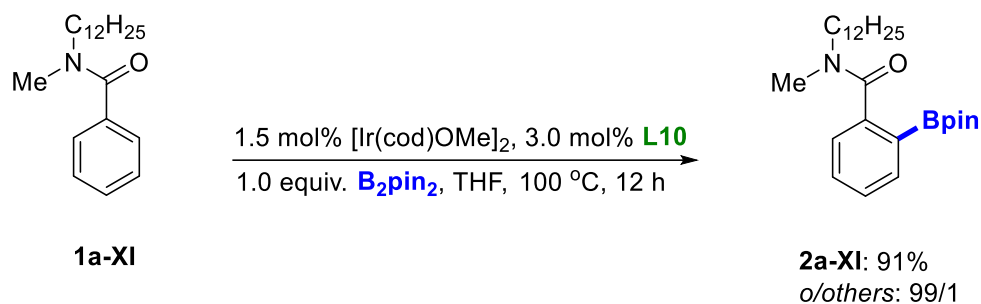
^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 7.2$ Hz, 1H), 7.39 (dt, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.30 (dt, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 2.78 (s, 3H), 1.53 (s, 9H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 145.4, 135.0, 130.5, 127.5, 125.3, 83.5, 56.6, 34.6, 27.9, 24.8.

^{11}B NMR (128 MHz, CDCl_3): δ 29.6.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{29}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 318.2235, found 318.2247.

Borylation of *N*-dodecyl-*N*-methylbenzamide (**1a-XI**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-dodecyl-*N*-methylbenzamide (60.7mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 78.1 mg of borylated product **2a-XI** (91%) as liquid.

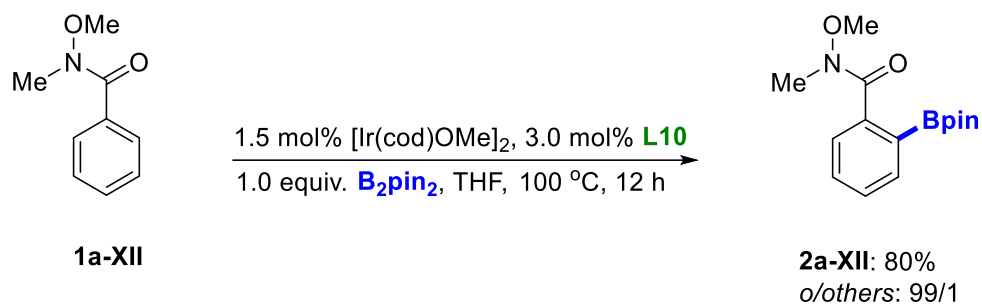
^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 7.2$ Hz, 1H), 7.36-7.40 (m, 1H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 1H), 3.45-3.49 (m, 1H), 3.05-3.10 (m, 2.5H), 2.80 (s, 1.5H), 1.66 (s, 1H), 1.42-1.45 (m, 1H), 1.30-1.33 (m, 2H), 1.27 (s, 12H), 1.11-1.13 (m, 16H), 0.84 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 171.8, 142.3, 141.9, 138.0, 137.7, 134.8, 134.7, 130.5, 130.4, 128.1, 125.4, 83.3, 50.9, 47.9, 36.9, 32.9, 31.7, 29.5, 29.4, 29.3, 29.2, 29.0, 27.7, 26.9, 26.6, 26.2, 24.8, 22.5, 14.0.

^{11}B NMR (128 MHz, CDCl_3): δ 28.2.

HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{45}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 430.3487, found 430.3489.

Borylation of *N*-methoxy-*N*-methylbenzamide (**1a-XII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-methoxy-*N*-methylbenzamide (33.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane as eluent) gave 46.6 mg of borylated product **2a-XII** (80%) as liquid. Spectral data are in accordance with the reported data.⁶⁸

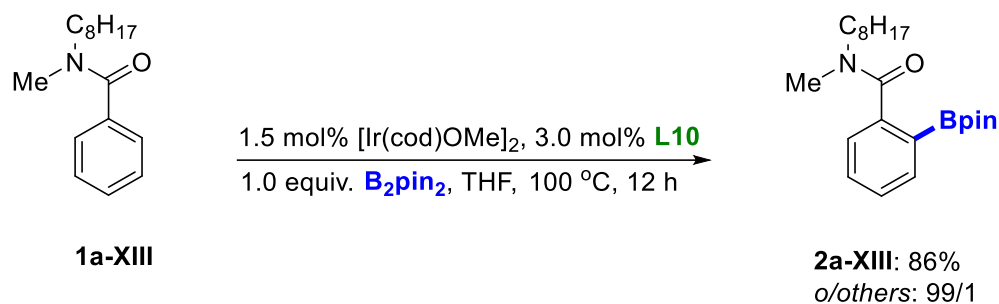
^1H NMR (400 MHz, CDCl_3): δ 7.73-7.75 (m, 1H), 7.51 (d, $J = 5.6$ Hz, 1H), 7.39-7.45 (m, 2H), 3.50 (br s, 3H), 3.34 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.2, 138.9, 133.6, 130.0, 129.4, 126.4, 83.3, 60.9, 34.0, 24.9.

^{11}B NMR (128 MHz, CDCl_3): δ 27.7.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{23}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 292.1715, found 292.1705.

Borylation of N-methyl-N-octylbenzamide (1a-XIII):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-methyl-*N*-octylbenzamide (49.5mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethylacetate in hexane as eluent) gave 64.2mg of borylated product **2a-XIII** (86%) as liquid.

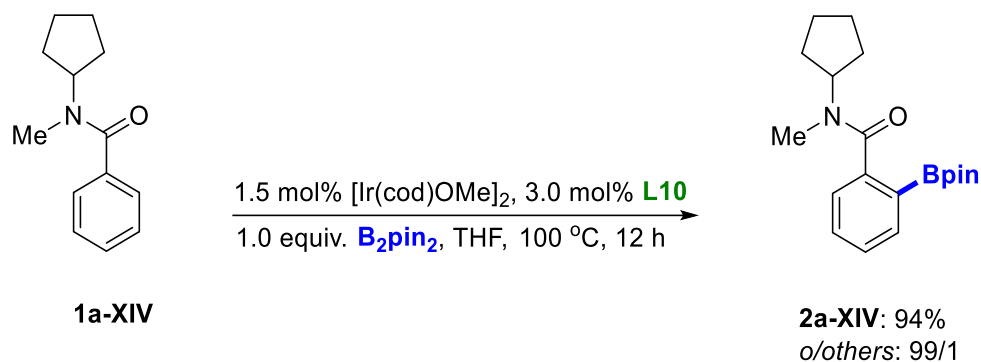
¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 7.2 Hz, 1H) 3.47-3.51 (m, 1H), 3.03-3.10 (m, 2.6H), 2.81 (s, 1.4H), 1.68 (br s, 1H), 1.44-1.47 (m, 1H), 1.15-1.34 (m & s, 22H), 0.82-0.87 (m, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 172.3, 171.8, 142.6, 142.2, 134.9, 134.8, 130.6, 130.5, 128.1, 125.6, 83.3, 51.0, 47.9, 36.9, 32.9, 31.8, 31.6, 29.6, 29.4, 29.2, 29.0, 28.9, 27.8, 27.0, 26.7, 26.4, 24.8, 22.6, 22.5, 14.0.

¹¹B NMR (128 MHz, CDCl₃): δ 28.7.

HRMS (ESI) *m/z* calcd for C₂₂H₃₇BNO₃ [M+H]⁺ 374.2861, found 374.2845.

Borylation of *N*-cyclopentyl-*N*-methylbenzamide (**1a-XIV**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-cyclopentyl-*N*-methylbenzamide (40.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 61.9 mg of borylated product **2a-XIV** (94%) as liquid.

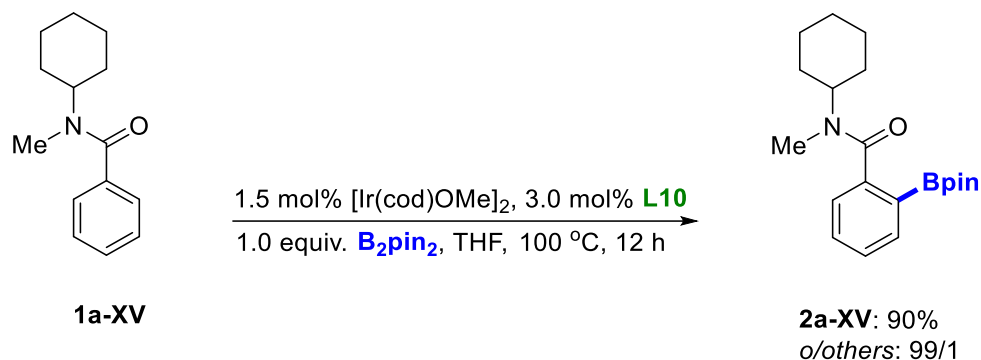
^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 7.2$ Hz, 1H), 7.39 (dt, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.30 (dt, $J = 7.6$ Hz, 0.8 Hz, 1H), 7.18-7.22 (m, 1H), 5.09-5.13 (m, 0.4H), 3.85-3.89 (m, 0.6H), 2.92 (s, 1.8H), 2.66 (s, 1.2H), 1.91-1.92 (m, 0.7H), 1.58-1.67 (, 5.3H), 1.37-1.42 (m, 2H), 1.26 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.3, 172.1, 143.4, 143.3, 135.1, 135.0, 130.7, 130.6, 127.8, 127.6, 125.3, 124.9, 83.5, 83.4, 59.6, 54.2, 31.3, 29.5, 28.7, 27.7, 27.1, 24.7, 24.4, 24.2.

^{11}B NMR (128 MHz, CDCl_3): δ 29.2.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 330.2235, found 330.2245.

Borylation of N-cyclohexyl-N-methylbenzamide (1a-XV):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-cyclohexyl-*N*-methylbenzamide (43.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 61.8 mg of borylated product **2a-XV** (90%) as off white solid.

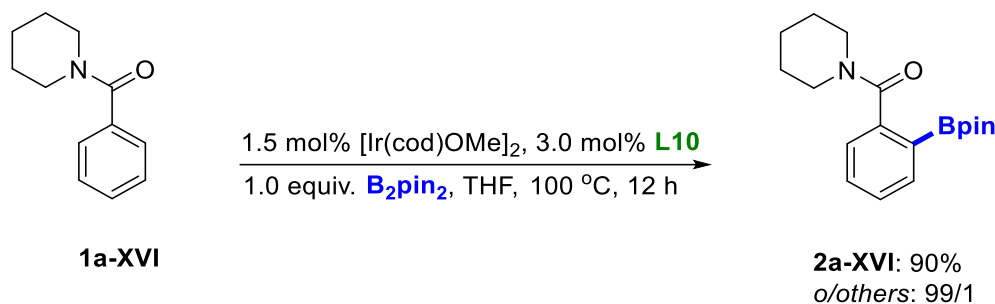
¹H NMR (400 MHz, CDCl₃): δ 7.73-7.76 (m, 1H), 7.33-7.38 (m, 1H), 7.26-7.31 (m, 1H), 7.15-7.19 (m, 1H), 4.54-4.56 (m, 0.4H), 3.25-3.31 (m, 0.6H), 2.92 (s, 1.4H), 2.64 (s, 1.6H), 1.65-1.84 (m, 5H), 1.24-1.47(m & s, 17H).

¹³C NMR (100 MHz, CDCl₃): δ 171.9, 171.6, 143.2, 142.6, 134.9, 134.8, 130.6, 130.2, 127.8, 127.7, 125.3, 124.6, 83.3, 57.9, 52.4, 31.2, 30.1, 29.2, 27.3, 25.5, 25.4, 25.2, 25.0, 24.7, 24.6.

¹¹B NMR (128 MHz, CDCl₃): δ28.7.

HRMS (ESI) *m/z* calcd for C₂₀H₃₁BNO₃ [M+H]⁺ 344.2392, found 344.2406.

Borylation of phenyl(piperidin-1-yl)methanone (1a-XVI):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, phenyl(piperidin-1-yl)methanone (37.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethylacetate in hexane as eluent) gave 56.7mg of borylated product **2a-XVI** (90%) as liquid.

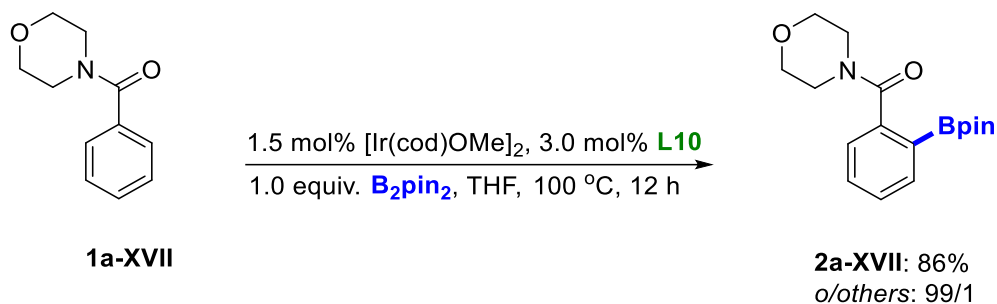
^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.2$ Hz, 1H), 7.20 (d, $J = 7.6$ Hz, 1H), 3.67-3.69 (m, 2H), 3.11-3.14 (m, 2H), 1.63 (br s, 4H), 1.45 (br s, 2H), 1.29 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 143.2, 135.3, 130.8, 127.6, 125.3, 83.7, 48.2, 42.5, 25.6, 25.0, 24.8, 24.5.

^{11}B NMR (128 MHz, CDCl_3): δ 30.0.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{27}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 316.2079, found 316.2084.

Borylation of morpholino(phenyl)methanone (**1a-XVII**):



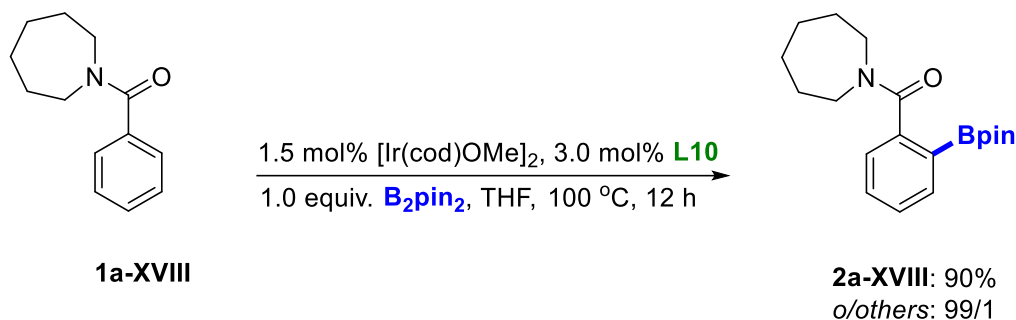
In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, morpholino(phenyl)methanone (38.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (15% ethyl acetate in hexane as eluent) gave 54.5 mg of borylated product **2a-XVII** (86%) as off white solid.

^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, $J = 7.6$ Hz, 1H), 7.43-7.46 (m, 1H), 7.35 (t, $J = 7.2$ Hz, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 3.78 (br s, 4H), 3.58-3.59 (m, 2H), 3.18-3.19 (m, 2H), 1.31 (s, 12H).
 ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 142.4, 135.5, 131.1, 128.0, 125.4, 84.0, 66.4, 66.3, 47.5, 41.9, 24.9.

^{11}B NMR (128 MHz, CDCl_3): δ 30.6.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{BNNaO}_4$ $[\text{M}+\text{Na}]^+$ 340.1691, found 340.1696.

Borylation of azepan-1-yl(phenyl)methanone (1a-XVIII):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, azepan-1-yl(phenyl)methanone (40.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 59.3mg of borylated product **2a-XVIII** (90%) as liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 7.2$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 1H), 7.25 (d, $J = 7.2$ Hz, 1H), 3.65–3.68 (m, 2H), 3.29 (br s, 2H), 1.84 (br s, 2H), 1.58 (br s, 6H), 1.28 (s, 12H).

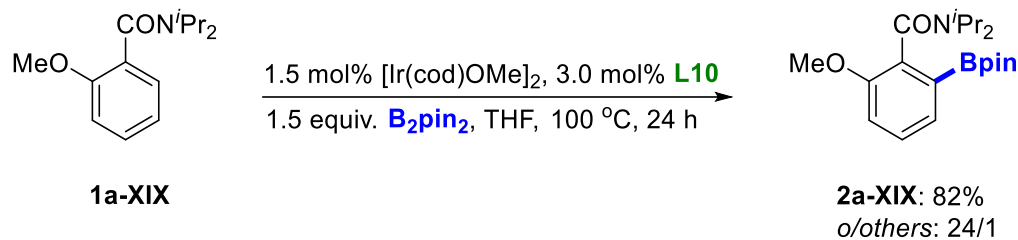
^{13}C NMR (100 MHz, CDCl_3): δ 172.0, 142.0, 134.7, 130.2, 128.2, 125.4, 83.2, 74.7, 49.3, 45.8, 28.7, 27.8, 27.0, 26.4, 24.8, 24.6.

^{11}B NMR (128 MHz, CDCl_3): δ 28.0.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 330.2235, found 330.2240.

Borylation of ring substituted amide:

Borylation of *N,N*-diisopropyl-2-methoxybenzamide (**1a-XIX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-2-methoxybenzamide (47.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 59.2 mg of borylated product **2a-XIX** (82%) as white solid. Spectral data are in accordance with the reported data.⁶⁹

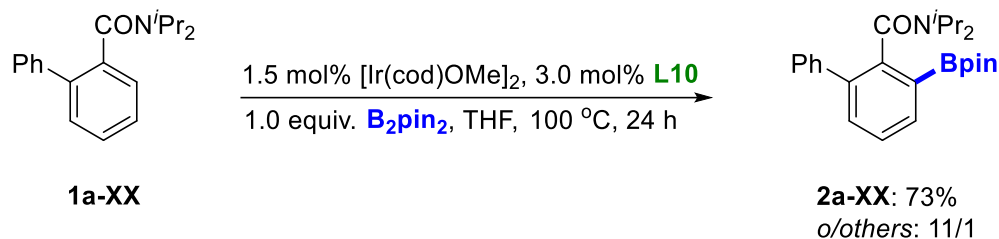
^1H NMR (400 MHz, CDCl_3): δ 7.39 (d, $J = 7.2$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 3.77 (s, 3H), 3.61 (sept, $J = 6.8$ Hz, 1H), 3.47 (sept, $J = 6.8$ Hz, 1H), 1.57 (d, $J = 6.8$ Hz, 6H), 1.29 (s, 12H), 1.09 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.1, 154.8, 134.4, 128.1, 127.8, 113.5, 83.8, 55.5, 50.9, 45.6, 24.8, 20.3, 20.2.

^{11}B NMR (128 MHz, CDCl_3): δ 30.5.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 362.2497, found 362.2500.

Borylation of *N,N*-diisopropyl-[1,1'-biphenyl]-2-carboxamide (**1a-XX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), $\mathbf{B}_2\text{pin}_2$ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-[1,1'-biphenyl]-2-carboxamide (56.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 59.5 mg of borylated product **2a-XX** (73%) as off white solid.

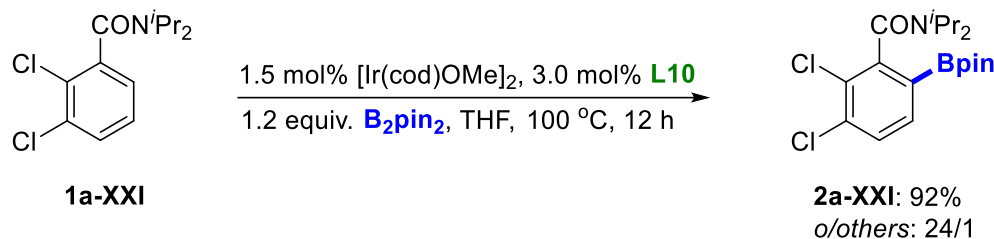
^1H NMR (400 MHz, CDCl_3): δ 7.82 (dd, $J = 7.2 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.55-7.57 (m, 2H), 7.28-7.43 (m, 5H), 3.36-3.43 (m, 1H), 3.15-3.23 (m, 1H), 1.36-1.38 (m, 6H), 1.32 (s, 13H), 0.61 (br s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 143.0, 140.2, 137.5, 135.0, 132.4, 129.8, 128.0, 127.3, 127.2, 83.9, 50.6, 45.6, 24.7, 20.0, 19.8.

^{11}B NMR (128 MHz, CDCl_3): δ 30.3.

HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 408.2705, found 408.2707.

Borylation of 2,3-dichloro-*N,N*-diisopropylbenzamide (**1a-XXI**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2,3-dichloro-*N,N*-diisopropylbenzamide (54.8mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 73.6mg of borylated product **2a-XXI** (92%) as off white solid.

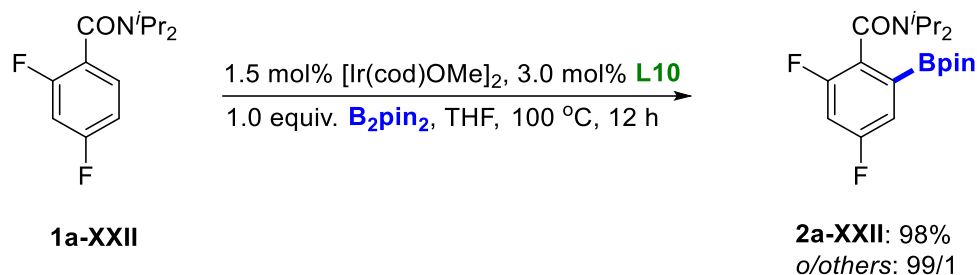
^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 3.45-3.55 (m, 2H), 1.57-1.61 (m, 6H), 1.29 (s, 12H), 1.11-1.19 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 166.2, 145.2, 136.1, 135.2, 129.0, 128.8, 84.4, 51.2, 46.1, 25.1, 24.3, 20.7, 20.0.

^{11}B NMR (128 MHz, CDCl_3): δ 30.0.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BCl}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$ 400.1612, found 400.1612.

Borylation of 2,4-difluoro-*N,N*-diisopropylbenzamide (**1a-XXII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2,4-difluoro-*N,N*-diisopropylbenzamide (48.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 72.0 mg of borylated product **2a-XXII** (98%) as white solid.

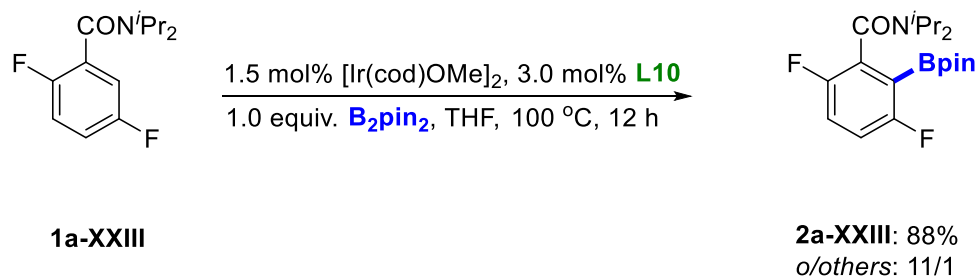
^1H NMR (400 MHz, CDCl_3): δ 7.27 (dd, $J = 8.4 \text{ Hz, } 2.4 \text{ Hz, } 1\text{H}$), 6.81 (dt, $J = 8.8 \text{ Hz, } 2.4 \text{ Hz, } 1\text{H}$), 3.57-3.64 (m, 1H), 3.44-3.50 (m, 1H), 1.53 (d, $J = 6.8 \text{ Hz, } 6\text{H}$), 1.27 (s, 12H), 1.10 (d, $J = 6.8 \text{ Hz, } 6\text{H}$).

^{13}C NMR (100 MHz, CDCl_3): δ 164.7, 161.8 (dd, $J = 249.1 \text{ Hz, } 10.7\text{Hz}$), 158.7 (dd, $J = 246.6 \text{ Hz, } 10.6 \text{ Hz}$), 128.5 (dd, $J = 18.1\text{Hz, } 3.8 \text{ Hz}$), 117.9 (dd, $J = 19.4 \text{ Hz, } 3.3 \text{ Hz}$), 106.0 (t, $J = 25.4 \text{ Hz}$), 84.4, 51.2, 45.8, 24.6, 20.1, 20.0.

^{11}B NMR (128 MHz, CDCl_3): δ 29.7.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BF}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$ 368.2203, found 368.2208.

Borylation of 2,5-difluoro-*N,N*-diisopropylbenzamide (**1a-XXIII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2,5-difluoro-*N,N*-diisopropylbenzamide (48.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 64.6 mg of borylated product **2a-XXIII** (88%) as white solid.

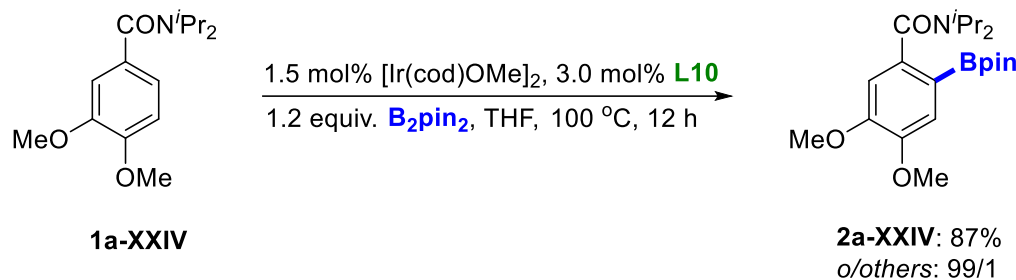
^1H NMR (400 MHz, CDCl_3): δ 6.99-7.04 (m, 1H), 6.89-6.94 (m, 1H), 3.65 (sept, $J = 6.8$ Hz, 1H), 3.49 (sept, $J = 6.8$ Hz, 1H), 1.52 (d, $J = 6.8$ Hz, 6H), 1.30 (s, 12H), 1.14 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 164.5 (d, $J = 0.7$ Hz), 162.5 (dd, $J = 244.0$ Hz, 1.9 Hz), 153.7 (dd, $J = 240.1$ Hz, 2.2 Hz), 132.6 (dd, $J = 20.5$ Hz, 7.8 Hz), 118.8 (dd, $J = 25.1$ Hz, 9.4 Hz), 116.2 (dd, $J = 27.5$ Hz, 7.9 Hz), 84.4, 51.4, 45.9, 24.6, 20.2, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.7.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BF}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$ 368.2203, found 368.2208.

Borylation of N,N-diisopropyl-3,4-dimethoxybenzamide (1a-XXIV):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-3,4-dimethoxybenzamide (53.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (35% ethyl acetate in hexane as eluent) gave 68.1 mg of borylated product **2a-XXIV** (87%) as off white solid.

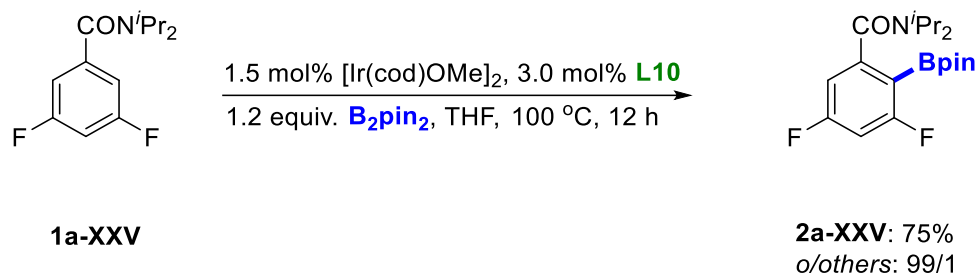
^1H NMR (400 MHz, CDCl_3): δ 7.23 (s, 1H), 6.63 (s, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.67-3.70 (m, 1H), 3.45 (br s, 1H), 1.54 (d, $J = 4.4$ Hz, 6H), 1.26 (s, 12H), 1.08 (d, $J = 4.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 150.7, 147.8, 138.9, 117.3, 108.1, 83.5, 55.8, 55.7, 50.7, 45.6, 24.7, 20.3, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.1.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{35}\text{BNO}_5$ $[\text{M}+\text{H}]^+$ 392.2603, found 392.2607.

Borylation of 3,5-difluoro-*N,N*-diisopropylbenzamide (**1a-XXV**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3,5-difluoro-*N,N*-diisopropylbenzamide (48.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethylacetate in hexane as eluent) gave 55.1 mg of borylated product **2a-XXV** (75%) as white solid.

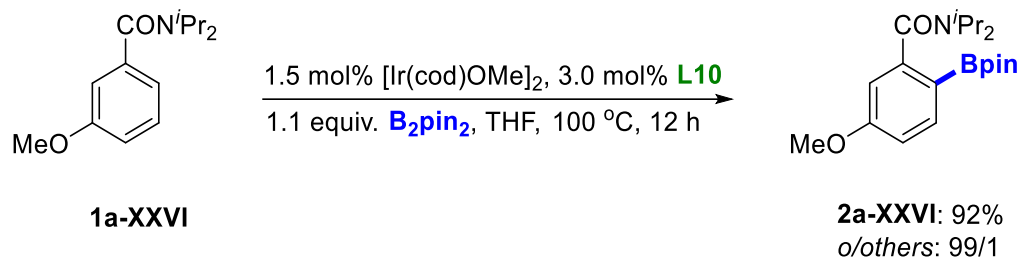
^1H NMR (400 MHz, CDCl_3): δ 6.68-6.76 (m, 2H), 3.76 (br s, 1H), 3.50 (br s, 1H), 1.52 (br s, 2H), 1.31 (s, 12H), 1.16 (br s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.6 (t, $J = 2.6$ Hz), 167.1 (dd, $J = 250.3$ Hz, 11.9 Hz), 163.8 (dd, $J = 251.2$ Hz, 12.6 Hz), 147.1 (t, $J = 8.1$ Hz), 108.1 (dd, $J = 21.6$ Hz, 3.5 Hz), 103.5 (dd, $J = 28.4$ Hz, 24.0 Hz), 83.7, 50.9, 45.9, 24.5, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 28.3.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BF}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$ 368.2203, found 368.2191.

Borylation of *N,N*-diisopropyl-3-methoxybenzamide (**1a-XXVI**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-3-methoxybenzamide (47.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 66.5mg of borylated product **2a-XXVI** (92%) as off white solid.

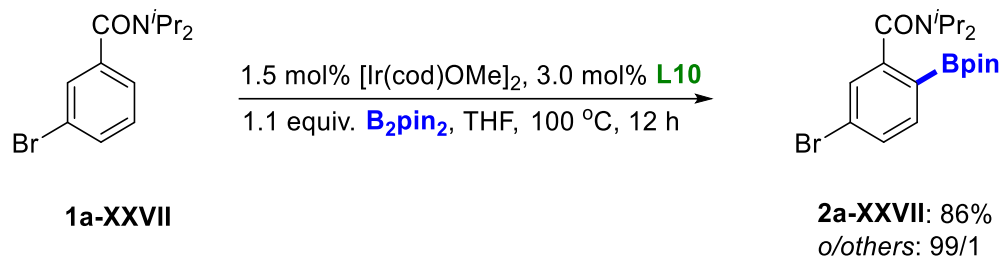
^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 8.4$ Hz, 1H), 6.83 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 6.66 (d, $J = 2.0$ Hz, 1H), 3.81 (s, 3H), 3.62-3.69 (m, 1H), 3.44-3.51 (m, 1H), 1.57 (d, $J = 6.8$ Hz, 6H), 1.29 (s, 12H), 1.10 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 161.6, 147.3, 137.8, 112.7, 110.4, 83.6, 55.2, 50.7, 45.5, 24.8, 20.4, 20.2.

^{11}B NMR (128 MHz, CDCl_3): δ 30.2.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 362.2497, found 362.2499.

Borylation of 3-bromo-*N,N*-diisopropylbenzamide (**1a-XXVII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-bromo-*N,N*-diisopropylbenzamide (56.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 70.4 mg of borylated product **2a-XXVII** (86%) as off white solid.

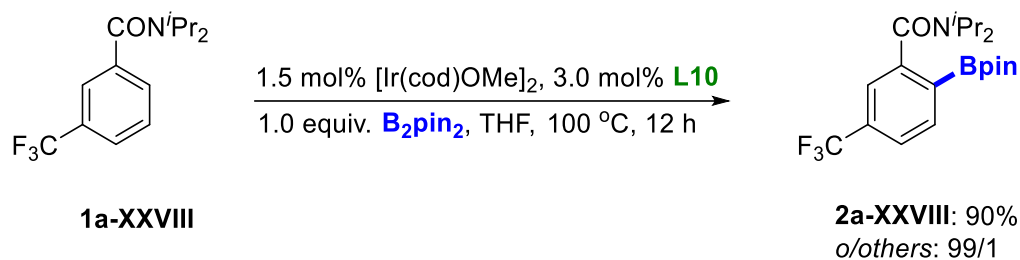
^1H NMR (400 MHz, CDCl_3): δ 7.64 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.26 (s, 1H), 3.61-3.64 (m, 1H), 3.45-3.49 (m, 1H), 1.54 (d, $J = 6.0$ Hz, 6H), 1.27 (s, 12H), 1.10 (d, $J = 6.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.4, 146.9, 137.3, 130.3, 127.6, 125.4, 84.1, 50.9, 45.7, 24.8, 20.3, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.9.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{BBrNO}_3$ $[\text{M}+\text{H}]^+$ 410.1497, found 410.1497.

Borylation of *N,N*-diisopropyl-3-(trifluoromethyl)benzamide (**1a-XXVIII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-3-(trifluoromethyl)benzamide (54.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethylacetate in hexane as eluent) gave 71.9 mg of borylated product **2a-XXVIII** (90%) as off white solid.

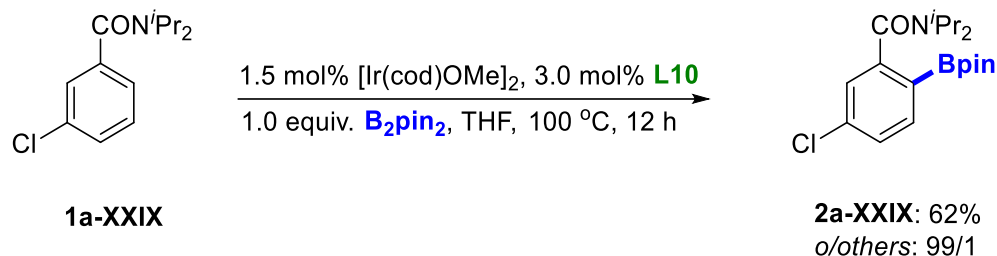
^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.38 (s, 1H), 3.59-3.66 (m, 1H), 3.48-3.55 (m, 1H), 1.57 (d, $J = 6.8$ Hz, 6H), 1.31 (s, 12H), 1.12 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 145.4, 136.1, 132.3 (q, $J = 32.3$ Hz), 123.9 (q, $J = 3.6$ Hz), 123.7 (q, $J = 270.9$ Hz), 121.2 (q, $J = 3.7$ Hz), 84.3, 51.0, 45.9, 24.8, 20.3, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.7.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{30}\text{BF}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$ 400.2265, found 400.2263.

Borylation of 3-chloro-*N,N*-diisopropylbenzamide (**1a-XXIX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-chloro-*N,N*-diisopropylbenzamide (47.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (15% ethylacetate in hexane as eluent) gave 45.0 mg of borylated product **2a-XXIX** (62%) as off white solid.

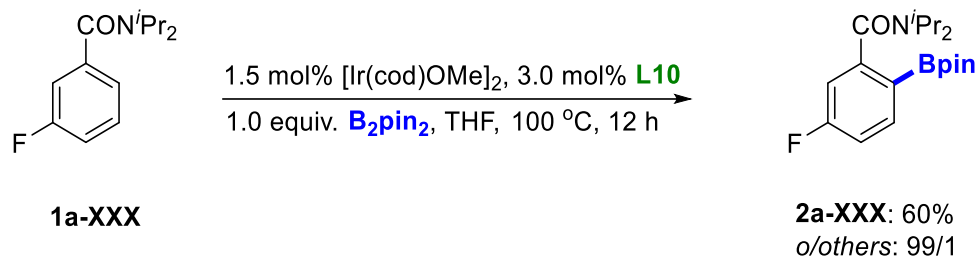
^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, $J = 8.0$ Hz, 1H), 7.27 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 7.11 (d, $J = 1.6$ Hz, 1H), 3.63 (sept, $J = 6.0$ Hz, 1H), 3.48 (sept, $J = 6.8$ Hz, 1H), 1.55 (d, $J = 6.8$ Hz, 6H), 1.29 (s, 12H), 1.11 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 146.7, 137.2, 136.9, 127.4, 124.7, 84.0, 50.9, 45.7, 24.7, 20.2, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.7.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{BCINO}_3$ $[\text{M}+\text{H}]^+$ 366.2002, found 366.2002.

Borylation of 3-fluoro-*N,N*-diisopropylbenzamide (**1a-XXX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-fluoro-*N,N*-diisopropylbenzamide (44.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 41.9 mg of borylated product **2a-XXX** (60%) as liquid. (Here some amount other *ortho* isomer also formed ratio; 68:32).

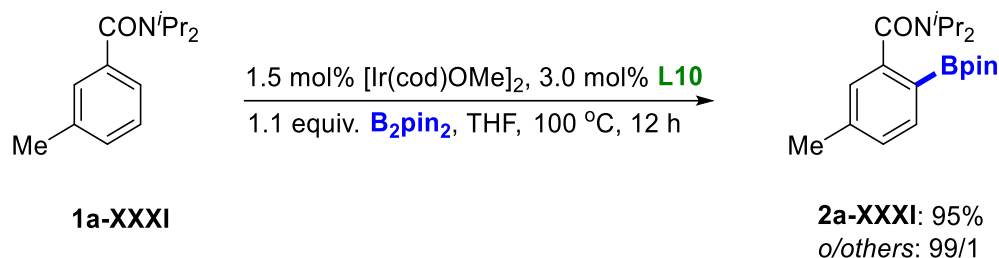
^1H NMR (400 MHz, CDCl_3): δ 7.77-7.81 (m, 1H), 6.98 (dt, $J = 8.8 \text{ Hz, } 2.0 \text{ Hz}$, 1H), 6.83 (dd, $J = 8.8 \text{ Hz, } 2.0 \text{ Hz}$, 1H), 3.63 (sept, $J = 6.8 \text{ Hz}$, 1H), 3.48 (sept, $J = 6.8 \text{ Hz}$, 1H), 1.55 (d, $J = 6.8 \text{ Hz}$, 6H), 1.29 (s, 12H), 1.10 (d, $J = 6.4 \text{ Hz}$, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.6 (d, $J = 2.0 \text{ Hz}$), 164.3 (d, $J = 250.5 \text{ Hz}$), 147.7 (d, $J = 6.6 \text{ Hz}$), 138.2 (d, $J = 8.3 \text{ Hz}$), 114.2 (d, $J = 19.8 \text{ Hz}$), 111.9 (d, $J = 21.4 \text{ Hz}$), 83.9, 50.8, 45.6, 24.7, 20.2, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 30.0.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{BFNO}_3$ $[\text{M}+\text{H}]^+$ 350.2297, found 350.2297.

Borylation of *N,N*-diisopropyl-3-methylbenzamide (**1a-XXXI**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-3-methylbenzamide (43.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 65.6 mg of borylated product **2a-XXXI** (95%) as white solid.

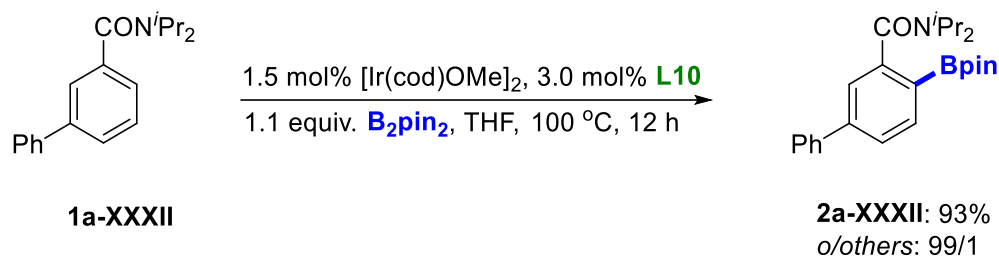
^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.95 (s, 1H), 3.69 (sept, $J = 6.8$ Hz, 1H), 3.49 (sept, $J = 6.8$ Hz, 1H), 2.34 (s, 3H), 1.58 (d, $J = 6.8$ Hz, 6H), 1.30 (s, 12H), 1.10 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.3, 145.4, 140.9, 135.8, 127.9, 125.2, 83.6, 50.7, 45.5, 24.8, 21.5, 20.4, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 30.4.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_3[\text{M}+\text{H}]^+$ 346.2548, found 346.2550.

Borylation of *N,N*-diisopropyl-[1,1'-biphenyl]-3-carboxamide (**1a-XXXII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-[1,1'-biphenyl]-3-carboxamide (56.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 75.8 mg of borylated product **2a-XXXII** (93%) as off white solid.

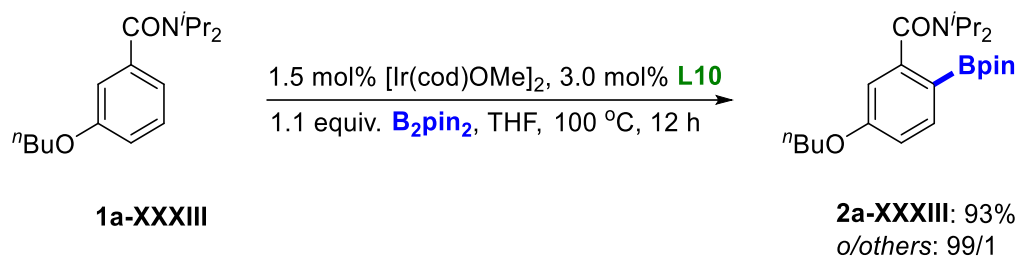
^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 1.6$ Hz, 1H), 7.60-7.63 (m, 3H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 3.82-3.85 (m, 1H), 3.49-3.53 (m, 1H), 1.60 (d, $J = 6.4$ Hz, 6H), 1.32 (s, 12H), 1.14 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 143.5, 140.3, 140.0, 133.9, 128.9, 128.5, 127.1, 126.9, 124.9, 83.5, 50.7, 45.6, 24.7, 20.2, 20.0.

^{11}B NMR (128 MHz, CDCl_3): δ 29.0.

HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 408.2705, found 408.2706.

Borylation of 3-butoxy-*N,N*-diisopropylbenzamide (**1a-XXXIII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-butoxy-*N,N*-diisopropylbenzamide (55.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 75.0 mg of borylated product **2a-XXXIII** (93%) as liquid.

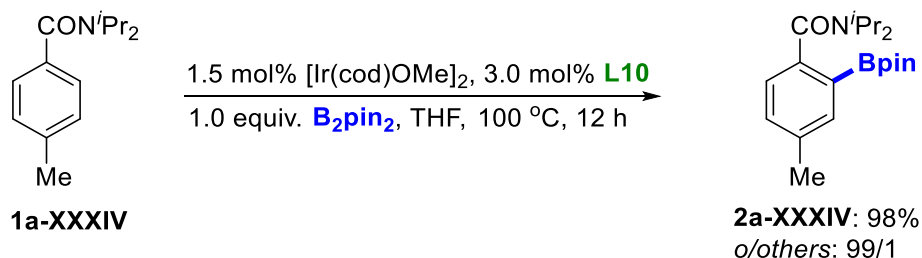
^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 2.4$ Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 6.91 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 4.20 (br s, 1H), 4.07 (t, $J = 6.4$ Hz, 2H), 3.63 (br s, 1H), 1.79-1.86 (m, 2H), 1.62 (br s, 6H), 1.53-1.58 (m, 2H), 1.38 (s, 12H), 1.26 (br s, 6H), 1.03 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.2, 159.5, 133.5, 126.0, 118.5, 115.9, 82.2, 67.3, 50.6, 46.5, 31.1, 24.8, 20.3, 20.1, 19.0, 13.6.

^{11}B NMR (128 MHz, CDCl_3): δ 24.1.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{39}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 404.2967, found 404.2970.

Borylation of *N,N*-diisopropyl-4-methylbenzamide (**1a-XXXIV**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-4-methylbenzamide (43.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 67.7 mg of borylated product **2a-XXXIV** (98%) as white solid.

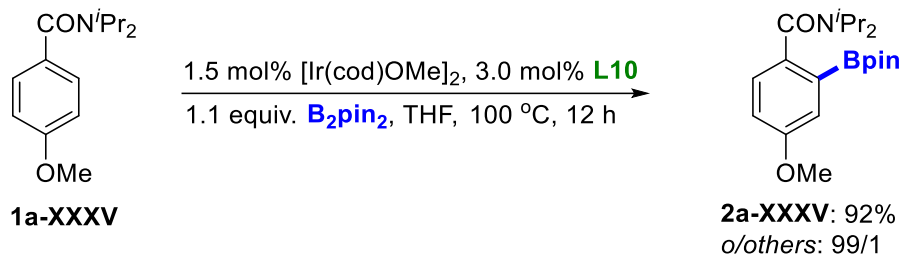
^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.18 (dd, $J = 7.6 \text{ Hz, } 1.2 \text{ Hz}$, 1H), 7.05 (d, $J = 7.6 \text{ Hz}$, 1H), 3.75-3.78 (m, 1H), 3.46-3.49 (m, 1H), 2.32 (s, 3H), 1.55 (d, $J = 6.4 \text{ Hz}$, 6H), 1.29 (s, 12H), 1.10 (d, $J = 6.4 \text{ Hz}$, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.3, 141.9, 137.0, 135.8, 131.0, 124.5, 83.5, 50.7, 45.6, 24.8, 21.0, 20.4, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.3.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 346.2548, found 346.2552.

Borylation of *N,N*-diisopropyl-4-methoxybenzamide (**1a-XXXV**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-4-methoxybenzamide (47.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 66.5 mg of borylated product **2a-XXXV** (92%) as liquid.

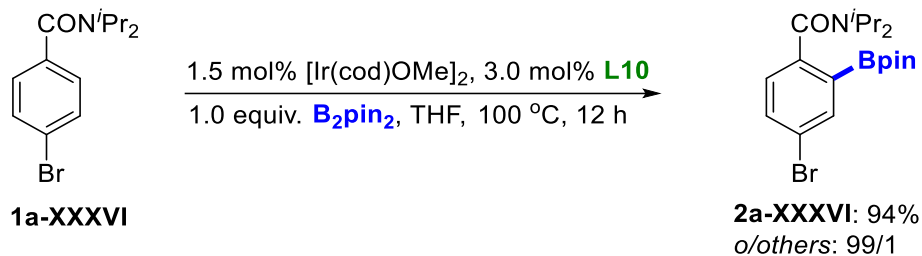
^1H NMR (400 MHz, CDCl_3): δ 7.19-7.24 (m, 2H), 6.85 (dd, $J = 8.4 \text{ Hz, } 2.4 \text{ Hz}$, 1H), 4.12 (br s, 1H), 3.83 (s, 3H), 3.55 (br s, 1H), 1.54 (br s, 6H), 1.30 (s, 12H), 1.19 (br s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 160.0, 134.0, 126.2, 117.8, 115.9, 82.5, 55.3, 50.8, 46.8, 29.6, 25.0, 20.3.

^{11}B NMR (128 MHz, CDCl_3): δ 24.1.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 362.2497, found 362.2495.

Borylation of 4-bromo-*N,N*-diisopropylbenzamide (**1a-XXXVI**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-bromo-*N,N*-diisopropylbenzamide (56.8mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (25% ethyl acetate in hexane as eluent) gave 77.1mg of borylated product **2a-XXXVI** (94%) as off white solid.

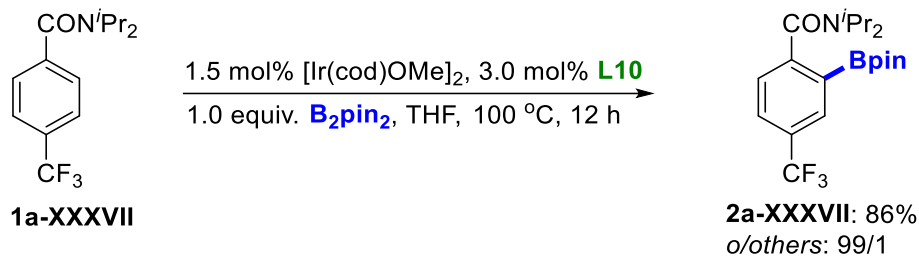
^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, $J = 1.2$ Hz, 1H), 7.50 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 3.68-3.71 (m, 1H), 3.49 (sept, $J = 6.4$ Hz, 1H), 1.54 (d, $J = 6.4$ Hz, 6H), 1.29 (s, 12H), 1.11 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 143.3, 138.1, 133.3, 126.3, 122.1, 84.0, 50.9, 45.9, 24.8, 20.3, 20.2.

^{11}B NMR (128 MHz, CDCl_3): δ 28.7.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{BBrNO}_3$ $[\text{M}+\text{H}]^+$ 410.1497, found 410.1495.

Borylation of *N,N*-diisopropyl-4-(trifluoromethyl)benzamide (**1a-XXXVII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-4-(trifluoromethyl)benzamide (54.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 68.7 mg of borylated product **2a-XXXVII** (86%) as solid.

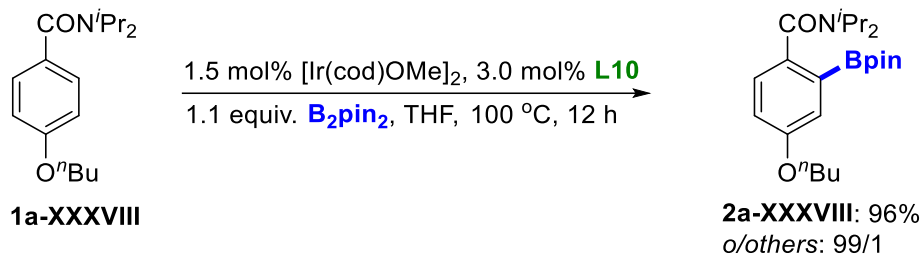
^1H NMR (400 MHz, CDCl_3): δ 8.05 (s, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 3.59 (sept, $J = 6.8$ Hz, 1H), 3.51 (sept, $J = 6.8$ Hz, 1H), 1.56 (d, $J = 6.8$ Hz, 6H), 1.31 (s, 12H), 1.11 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.8, 148.4, 132.5 (q, $J = 3.6$ Hz), 129.4 (q, $J = 32.3$ Hz), 127.4 (q, $J = 3.7$ Hz), 124.9, 124.0 (q, $J = 270.6$ Hz), 84.3, 50.9, 45.8, 24.8, 20.3, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.8.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{30}\text{BF}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$ 400.2265, found 400.2268.

Borylation of 4-butoxy-*N,N*-diisopropylbenzamide (**1a-XXXVIII**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-butoxy-*N,N*-diisopropylbenzamide (55.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 77.4 mg of borylated product **2a-XXXVIII** (96%) as liquid.

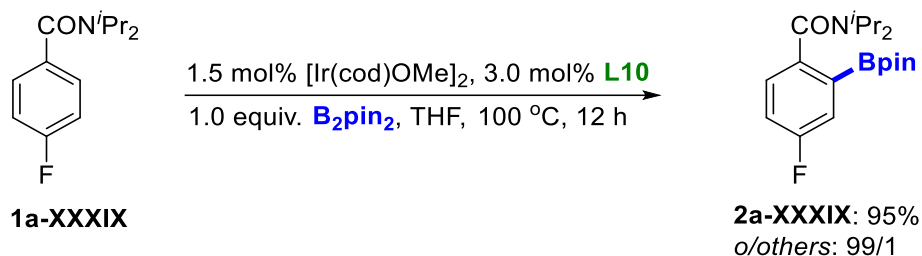
^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, $J = 8.4$ Hz, 1H), 6.80 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 6.64 (d, $J = 2.0$ Hz, 1H), 3.95 (t, $J = 6.8$ Hz, 2H), 3.65 (sept, $J = 6.4$ Hz, 1H), 3.46 (sept, $J = 6.4$ Hz, 1H), 1.73 (p, $J = 6.4$ Hz, 2H), 1.56 (d, $J = 6.8$ Hz, 6H), 1.41-1.50 (m, 2H), 1.27 (s, 12H), 1.08 (d, $J = 6.4$ Hz, 6H), 0.94 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 161.2, 147.2, 137.6, 113.2, 110.8, 83.5, 67.5, 50.7, 45.4, 31.1, 24.7, 20.3, 20.1, 19.1, 13.7.

^{11}B NMR (128 MHz, CDCl_3): δ 29.5.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{39}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 404.2967, found 404.2973.

Borylation of 4-fluoro-*N,N*-diisopropylbenzamide (**1a-XXXIX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-fluoro-*N,N*-diisopropylbenzamide (44.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 66.3mg of borylated product **2a-XXXIX** (95%) as white solid.

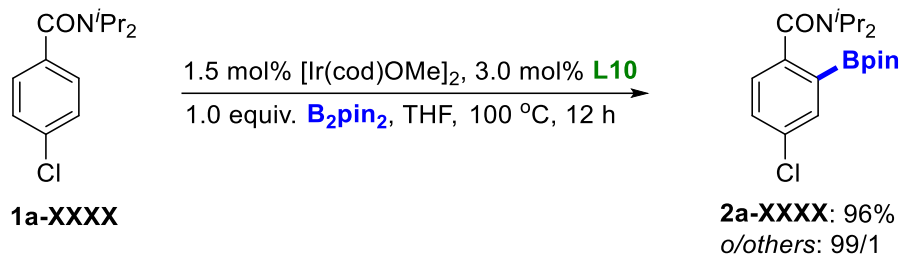
^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 8.8 \text{ Hz, } 2.4 \text{ Hz, } 1\text{H}$), 7.18 (dd, $J = 8.0 \text{ Hz, } 4.8 \text{ Hz, } 1\text{H}$), 7.04 (dt, $J = 8.4 \text{ Hz, } 2.4 \text{ Hz, } 1\text{H}$), 3.83-3.86 (m, 1H), 3.51-3.54 (m, 1H), 1.55 (d, $J = 6.0 \text{ Hz, } 6\text{H}$), 1.30 (s, 12H), 1.14 (d, $J = 5.6 \text{ Hz, } 6\text{H}$).

^{13}C NMR (100 MHz, CDCl_3): δ 170.4, 162.3 (d, $J = 247.6 \text{ Hz}$), 139.5, 126.6 (d, $J = 7.5 \text{ Hz}$), 121.2 (d, $J = 19.5 \text{ Hz}$), 117.0 (d, $J = 21.7 \text{ Hz}$), 83.5, 50.9, 46.2, 24.8, 20.3, 20.2.

^{11}B NMR (128 MHz, CDCl_3): δ 27.2.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{BFNO}_3$ $[\text{M}+\text{H}]^+$ 350.2297, found 350.2301.

Borylation of 4-chloro-*N,N*-diisopropylbenzamide (**1a-XXXX**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-chloro-*N,N*-diisopropylbenzamide (47.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 70.2 mg of borylated product **2a-XXXX** (96%) as white solid.

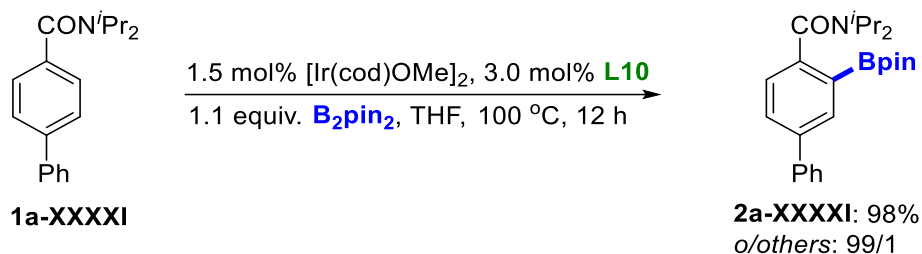
^1H NMR (400 MHz, CDCl_3): δ 7.75 (d, $J = 2.0$ Hz, 1H), 7.35 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 7.10 (d, $J = 8.4$ Hz, 1H), 3.72 (sept, $J = 6.4$ Hz, 1H), 3.50 (sept, $J = 6.4$ Hz, 1H), 1.55 (d, $J = 6.4$ Hz, 6H), 1.30 (s, 12H), 1.12 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 142.6, 135.1, 133.8, 130.4, 126.1, 83.9, 50.9, 46.0, 24.8, 20.3, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 28.7.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{BCINO}_3$ $[\text{M}+\text{H}]^+$ 366.2002, found 366.2001.

Borylation of *N,N*-diisopropyl-[1,1'-biphenyl]-4-carboxamide (**1a-XXXXI**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.0 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-[1,1'-biphenyl]-4-carboxamide (56.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 79.8 mg of borylated product **2a-XXXXI** (98%) as off white solid.

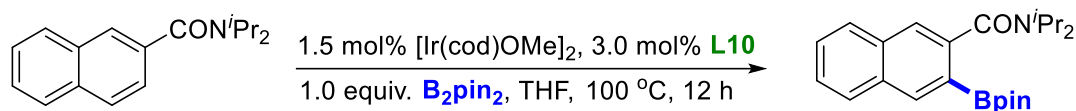
^1H NMR (400 MHz, CDCl_3): δ 7.90 (d, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.55 (dd, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.34-7.37 (m, 2H), 3.77 (sept, $J = 6.4$ Hz, 1H), 3.53 (sept, $J = 6.8$ Hz, 1H), 1.61 (d, $J = 6.4$ Hz, 6H), 1.33 (s, 12H), 1.13 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.0, 145.8, 143.4, 140.4, 136.2, 128.7, 127.7, 127.1, 125.8, 123.2, 83.8, 50.8, 45.6, 24.8, 20.3, 20.2.

^{11}B NMR (128 MHz, CDCl_3): δ 29.9.

HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 408.2705, found 408.2709.

Borylation of *N,N*-diisopropyl-2-naphthamide (**1a-XXXXII**):



1a-XXXXII

2a-XXXXII: 73%
o/others: 14/1

In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-2-naphthamide (51.1mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 55.7mg of borylated product **2a-XXXXII** (73%) as liquid.

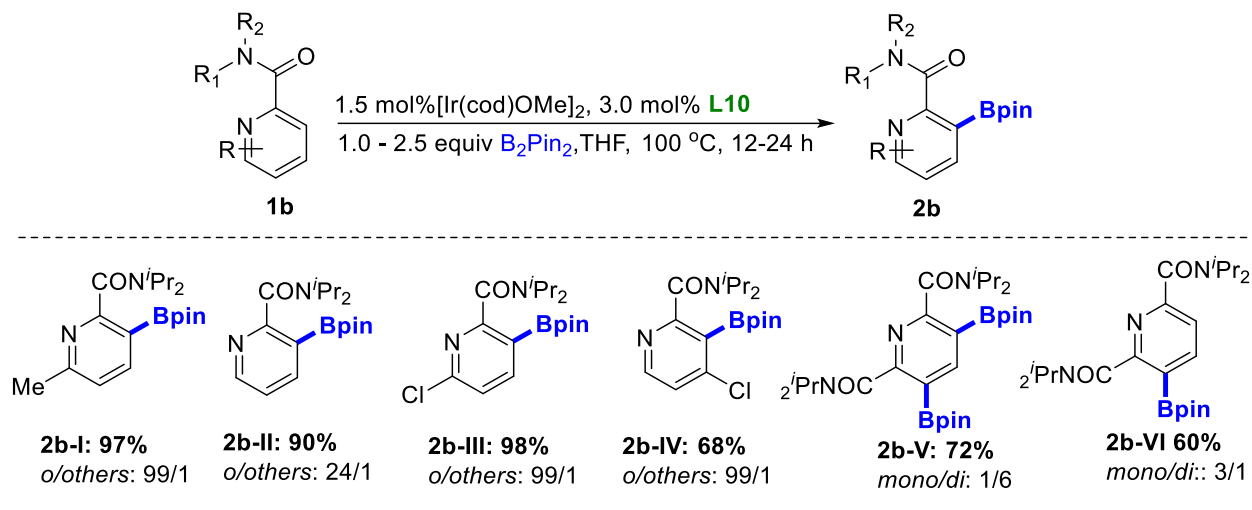
¹H NMR (400 MHz, CDCl₃): δ 8.38 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.60 (s, 1H), 7.44-7.53 (m, 2H), 3.79 (sept, J = 6.4 Hz, 1H), 3.54 (sept, J = 6.4 Hz, 1H), 1.63 (d, J = 6.8 Hz, 6H), 1.35 (s, 12 H), 1.13 (d, J = 6.8 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 171.2, 141.1, 137.3, 134.0, 132.1, 128.3, 127.7, 127.4, 126.1, 123.1, 83.9, 50.9, 45.6, 24.8, 20.4, 20.2.

¹¹B NMR (128 MHz, CDCl₃): δ 30.2.

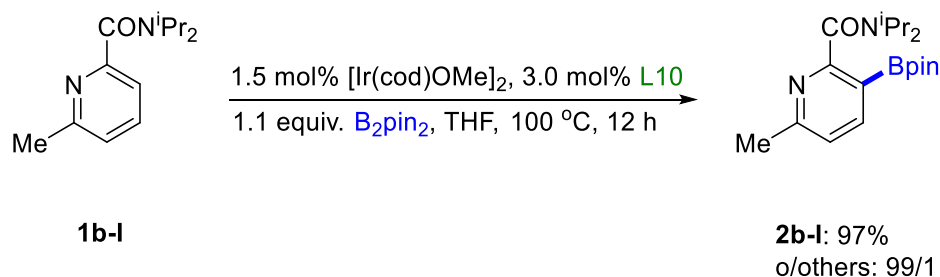
HRMS (ESI) *m/z* calcd for C₂₃H₃₃BNO₃ [M+H]⁺ 382.2548, found 382.2549.

Borylation of Heterocyclic amide^a:



^[a] Reaction scale 0.2 mmol. GC/MS ratios are given using dodecane as internal standard

Borylation of *N,N*-diisopropyl-6-methylpicolinamide (**1b-I**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-6-methylpicolinamide (44.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at $100 \text{ }^\circ\text{C}$. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane as eluent) gave 67.2 mg of borylated product **2b-I** (97%) as white solid.

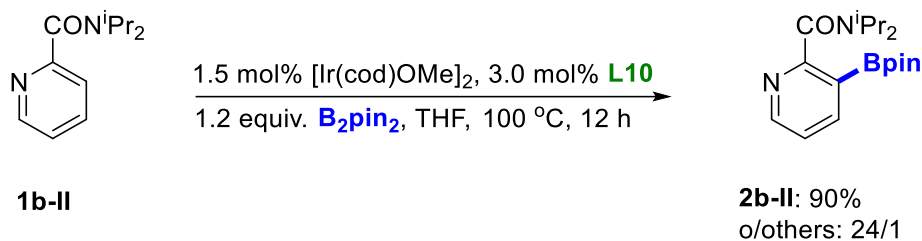
¹H NMR (400 MHz, CDCl_3): δ 7.82 (d, $J = 7.6 \text{ Hz}$, 1H), 7.08 (d, $J = 7.2 \text{ Hz}$, 1H), 6.22 (sept, $J = 6.8 \text{ Hz}$, 1H), 3.69 (sept $J = 6.8 \text{ Hz}$, 1H), 2.46 (s, 3H), 1.52 (d, $J = 6.8 \text{ Hz}$, 6H), 1.26 (s, 12H), 1.21 (d, $J = 6.8 \text{ Hz}$, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.9, 157.5, 155.6, 139.9, 124.8, 80.7, 48.9, 48.5, 25.1, 24.3, 20.2, 19.9.

^{11}B NMR (128 MHz, CDCl_3): δ 16.8.

HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{32}\text{BN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 347.2500, found 347.2504.

Borylation of N,N-diisopropylpicolinamide (1b-II):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropylpicolinamide (41.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane as eluent) gave 59.8 mg of borylated product **2b-II** (90%) as grey solid.

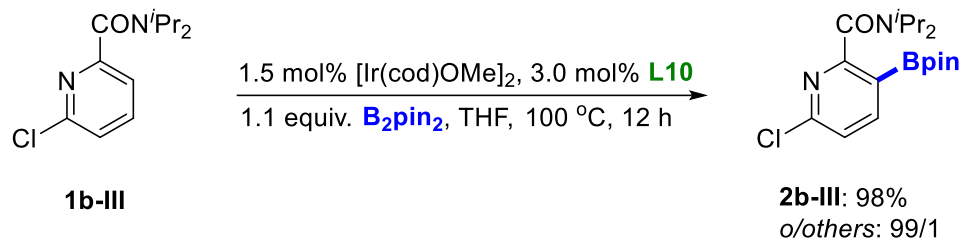
^1H NMR (400 MHz, CDCl_3): δ 8.43 (dd, $J = 4.8 \text{ Hz, } 1.6 \text{ Hz}$, 1H), 7.94 (dd, $J = 7.2 \text{ Hz, } 1.6 \text{ Hz}$, 1H), 7.24 (dd, $J = 7.2 \text{ Hz, } 4.8 \text{ Hz}$, 1H), 6.54 (sept, $J = 6.8 \text{ Hz}$, 1H), 3.74 (sept, $J = 6.8 \text{ Hz}$, 1H), 1.53 (d, $J = 6.8 \text{ Hz}$, 6H), 1.28 (s, 12H), 1.24 (d, $J = 6.4 \text{ Hz}$, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.7, 155.2, 148.3, 139.5, 125.5, 80.5, 48.9, 48.8, 25.2, 20.2, 20.0.

^{11}B NMR (128 MHz, CDCl_3): δ 15.1.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{29}\text{BN}_2\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 355.2163, found 355.2163.

Borylation of 6-chloro-N,N-diisopropylpicolinamide (1b-III):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (55.9 mg, 1.1 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 6-chloro-*N,N*-diisopropylpicolinamide (48.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (40% ethyl acetate in hexane as eluent) gave 71.9 mg of borylated product **2b-III** (98%) as white solid.

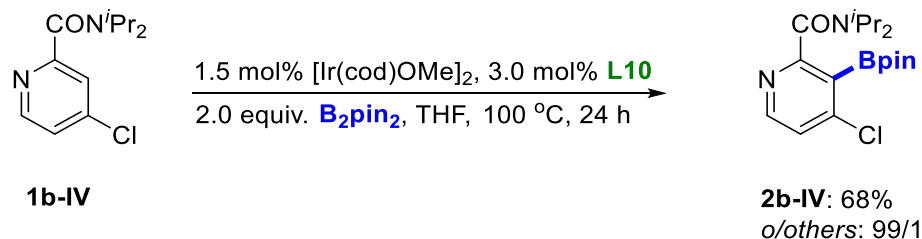
^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, $J = 7.6$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 5.92 (sept, $J = 6.4$ Hz, 1H), 3.73 (sept, $J = 6.8$ Hz, 1H), 1.52 (d, $J = 6.8$ Hz, 6H), 1.28 (s, 12H), 1.25 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 167.4, 155.7, 150.3, 142.5, 126.0, 81.1, 49.5, 48.8, 25.1, 20.2, 20.0.

^{11}B NMR (128 MHz, CDCl_3): δ 16.5.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{28}\text{BClN}_2\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 389.1774, found 389.1774.

Borylation of 4-chloro-N,N-diisopropylpicolinamide (1b-IV):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The

reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-chloro-*N,N*-diisopropylpicolinamide (48.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane as eluent) gave 49.8 mg of borylated product **2b-IV** (68%) as white solid.

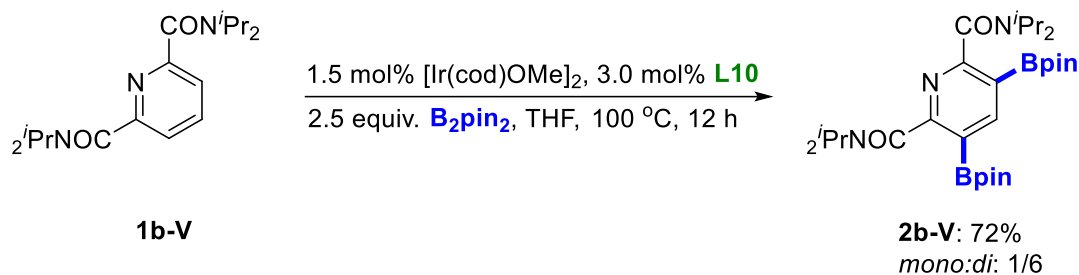
¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, J = 5.2 Hz, 1H), 7.26 (d, J = 5.2 Hz, 1H), 6.82 (sept, J = 6.8 Hz, 1H), 3.79 (sept, J = 6.8 Hz, 1H), 1.53 (d, J = 6.8 Hz, 6H), 1.34 (s, 12H), 1.26 (d, J = 6.4 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 167.1, 156.1, 148.8, 148.7, 126.7, 80.7, 49.4, 49.0, 26.1, 20.1, 20.0.

¹¹B NMR (128 MHz, CDCl₃): δ 13.3.

HRMS (ESI) *m/z* calcd for C₁₈H₂₈BClN₂NaO₃ [M+Na]⁺ 389.1774, found 389.1771.

Di Borylation of N²,N²,N⁶,N⁶-tetraisopropylpyridine-2,6-dicarboxamide (1b-V):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (127.0 mg, 2.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N²,N²,N⁶,N⁶*-tetraisopropylpyridine-2,6-dicarboxamide (66.7mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (90% ethyl acetate in hexane as eluent) gave 84.3 mg of borylated product **2b-V** (72%) as white solid.

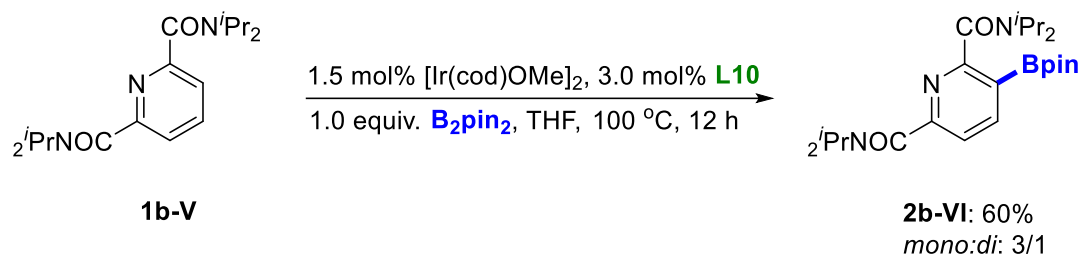
¹H NMR (400 MHz, CDCl₃): δ 8.29 (s, 1H), 5.56 (sept, J = 6.8 Hz, 2H), 3.66 (sept J = 6.8 Hz, 2H), 1.54 (d, J = 6.8 Hz, 12H), 1.29 (s, 24H), 1.18 (d, J = 6.4 Hz, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.5, 156.1, 145.5, 81.6, 49.2, 48.2, 25.1, 20.3, 20.0.

^{11}B NMR (128 MHz, CDCl_3): δ 18.7.

HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{54}\text{B}_2\text{N}_3\text{O}_6$ $[\text{M}+\text{H}]^+$ 586.4193, found 586.4202.

*Mono Borylation of N^2, N^2, N^6, N^6 -tetraisopropylpyridine-2,6-dicarboxamide (**1b-V**):*



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, N^2, N^2, N^6, N^6 -tetraisopropylpyridine-2,6-dicarboxamide (66.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (70% ethyl acetate in hexane as eluent) gave 55.1 mg of borylated product **2b-VI** (60%) as white solid.

^1H NMR (400 MHz, CDCl_3): δ 8.03 (d, $J = 7.2$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 6.46 (sept, $J = 6.8$ Hz, 1H), 3.75 (sept, $J = 6.8$ Hz, 1H), 3.63 (sept, $J = 6.8$ Hz, 1H), 3.47 (sept, $J = 6.8$ Hz, 1H), 1.50-1.54 (m, 12H), 1.28 (s, 12H), 1.23 (d, $J = 6.8$ Hz, 6H), 1.04 (d, $J = 6.4$ Hz, 6H).

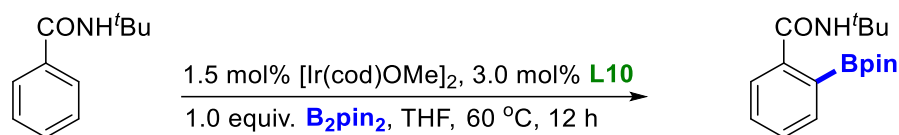
^{13}C NMR (100 MHz, CDCl_3): δ 168.3, 168.29, 155.1, 153.5, 140.6, 123.9, 80.5, 50.3, 49.1, 49.0, 45.9, 25.2, 20.4, 20.2, 20.1.

^{11}B NMR (128 MHz, CDCl_3): δ 14.5.

HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{43}\text{BN}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 460.3341, found 460.3351.

Borylation of mono N-Substituted amide:

Borylation of N-(tert-butyl)benzamide (1c-I):



1c-I

2c-I: 90%
o/others: 99/1

In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-(*tert*-butyl)benzamide (35.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 54.6 mg of borylated product **2c-I** (90%) as white solid.

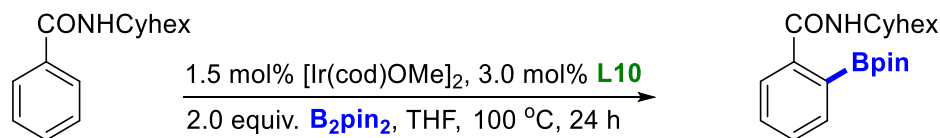
¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, J = 7.2 Hz, 1H), 7.40-7.46 (m, 2H), 7.30 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 6.23 (s, 1H), 1.48 (s, 9H), 1.36 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 169.6, 137.2, 132.1, 131.4, 128.2, 122.5, 82.1, 52.8, 28.8, 25.0.

¹¹B NMR (128 MHz, CDCl₃): δ 23.9.

HRMS (ESI) *m/z* calcd for C₁₇H₂₆BNNaO₃ [M+Na]⁺ 326.1898, found 326.1897.

Borylation of N-cyclohexylbenzamide (1c-II):



1c-II

2c-II: 60%
o/others: 99/1

In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-

cyclohexylbenzamide (40.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane as eluent) gave 39.5 mg of borylated product **2c-II** (60%) as white solid.

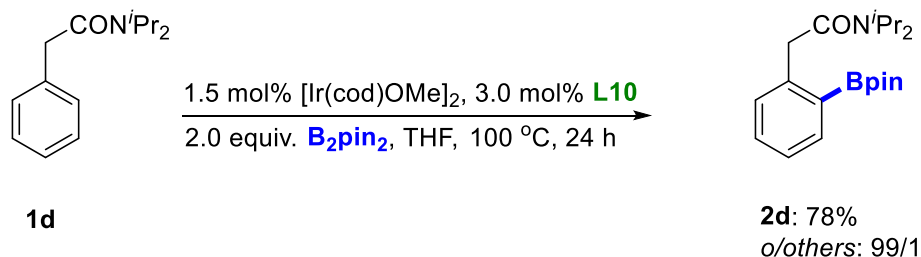
¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, J = 5.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 3.76-3.78 (d, J = 7.6 Hz, 1H), 1.59-1.61 (m, 5H), 1.36 (s, 12H), 1.09 -1.25 (m, 5H).

¹³C NMR (100 MHz, CDCl₃): δ 170.2, 134.6, 131.9, 131.2, 127.5, 123.4, 81.4, 50.7, 32.1, 25.2, 25.1, 24.9.

¹¹B NMR (128 MHz, CDCl₃): δ 19.4.

HRMS (ESI) *m/z* calcd for C₁₉H₂₈BNNaO₃ [M+Na]⁺ 352.2054, found 352.2053.

Borylation of Homologous amide (N,N-diisopropyl-2-phenylacetamide) (1d):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-2-phenylacetamide (43.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethylacetate in hexane as eluent) gave 26.2 mg of borylated product **2d** (78% yield based on recovered starting material) as off white solid and 22.5 mg of *N,N*-diisopropyl-2-phenylacetamide(**1d**) .

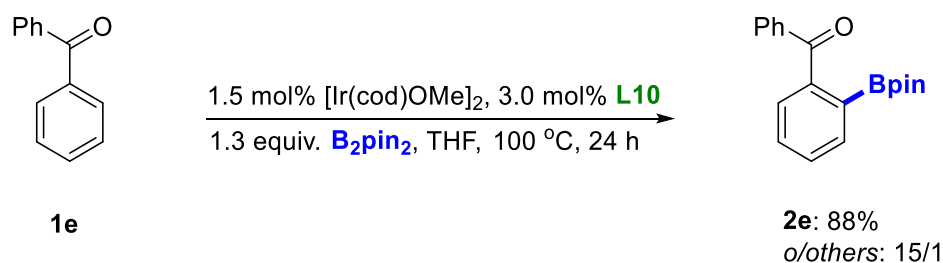
^1H NMR (400 MHz, CDCl_3): δ 7.83 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.36 (dt, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.21 (t, $J = 7.2$ Hz, 1H), 4.06 (sept, $J = 6.8$ Hz, 1H), 4.03 (s, 2H), 3.34-3.37 (m, 1H), 1.41 (d, $J = 6.8$ Hz, 6H), 1.32 (s, 12H), 1.04 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 142.4, 136.2, 131.0, 128.9, 125.7, 83.4, 48.8, 45.6, 42.3, 24.9, 20.6, 20.5.

^{11}B NMR (128 MHz, CDCl_3): δ 30.6.

HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{33}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 346.2548, found 346.2549.

Borylation of benzophenone (1e):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (66.0 mg, 1.3 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, benzophenone (36.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100°C . The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 54.2 mg of borylated product **2e** (88%) as white solid. Spectral data are in accordance with the reported data.⁷⁰

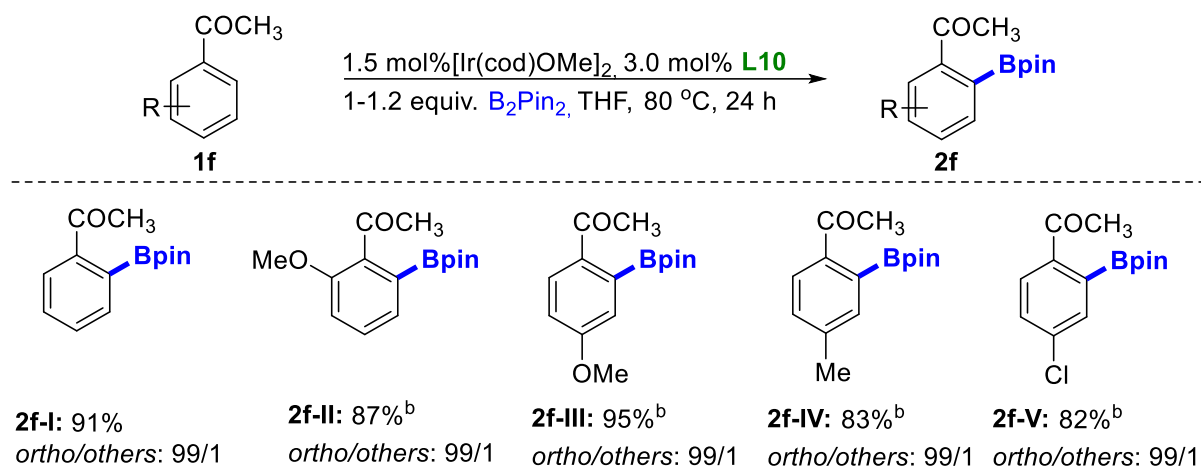
^1H NMR (400 MHz, CDCl_3): δ 7.74-7.79 (m, 3H), 7.40-7.55 (m, 6H), 1.18 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 198.1, 143.6, 138.0, 133.7, 132.3, 130.2, 129.9, 129.6, 128.8, 128.1, 83.5, 24.5.

^{11}B NMR (128 MHz, CDCl_3): δ 30.9.

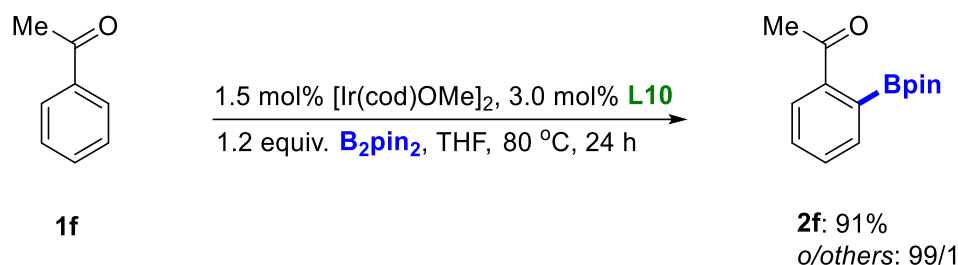
HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{BNaO}_3$ $[\text{M}+\text{Na}]^+$ 331.1476, found 331.1477.

Borylation of acetophenone (1f)^a:



[^a] Reaction scale 0.2 mmol. ^b GC ratios; conversions are based on dodecane as internal standard.

Borylation of acetophenone (1f-I):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, acetophenone (24.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 44.8 mg of borylated product **2f-I** (91%) as liquid. Spectral data are in accordance with the reported data.⁷¹

¹H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 7.6$ Hz, 1H), 7.50-7.56 (m, 2H), 7.41-7.45 (m, 1H), 2.61 (s, 3H), 1.44 (s, 12H).

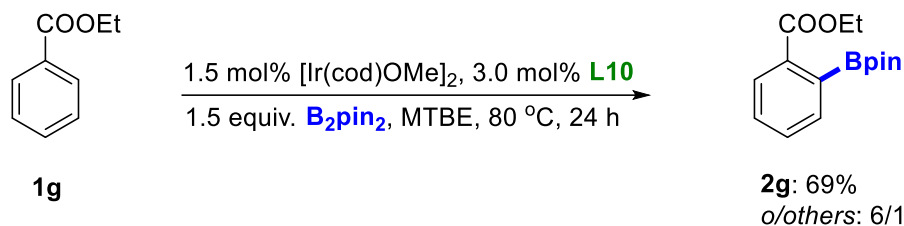
¹³C NMR (100 MHz, CDCl_3): δ 199.7, 140.4, 132.3, 132.1, 128.8, 128.3, 83.6, 25.3, 24.8.

¹¹B NMR (128 MHz, CDCl_3): δ 30.9.

HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{BNaO}_3$ $[\text{M}+\text{Na}]^+$ 269.1319, found 269.1318.

Next we have tested some substituted acetophenone to check the applicability of the developed method. The outcomes are shown in the above general figure.

*Borylation of ethyl benzoate (**1g**):*



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry MTBE (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl benzoate (30.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), MTBE was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 38.0 mg of borylated product **2g** (69%) as white solid. Spectral data are in accordance with the reported data.⁸³

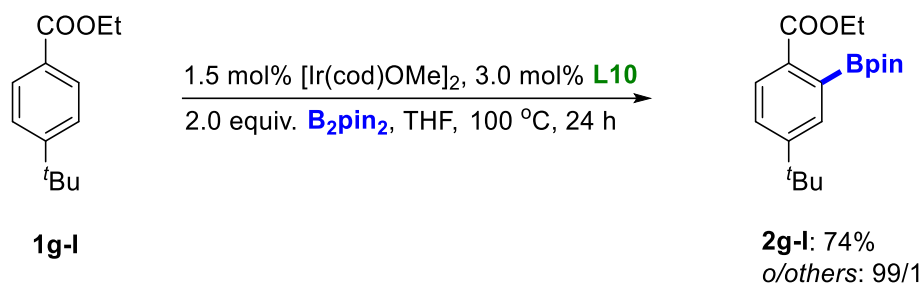
^1H NMR (400 MHz, CDCl_3): δ 7.93 (tt, $J = 7.6$ Hz, 1.0 Hz, 1H), 7.48-7.52 (m, 2H), 7.38-7.42 (m, 1H), 4.38 (q, $J = 7.2$ Hz, 2H), 1.42 (s, 12H), 1.38 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.0, 133.8, 132.0, 131.7, 128.8, 128.5, 83.9, 61.2, 24.8, 14.3.

^{11}B NMR (128 MHz, CDCl_3): δ 31.7.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{BO}_4$ $[\text{M}+\text{H}]^+$ 277.1611, found 277.1622.

Borylation of ethyl 4-(*tert*-butyl)benzoate (**1g-I**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl 4-(*tert*-butyl)benzoate (41.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 22.6 mg of borylated product **2g-I** (74% yield based on recovered starting material) as liquid and 22.5 mg of ethyl 4-(*tert*-butyl)benzoate (**1g-I**).

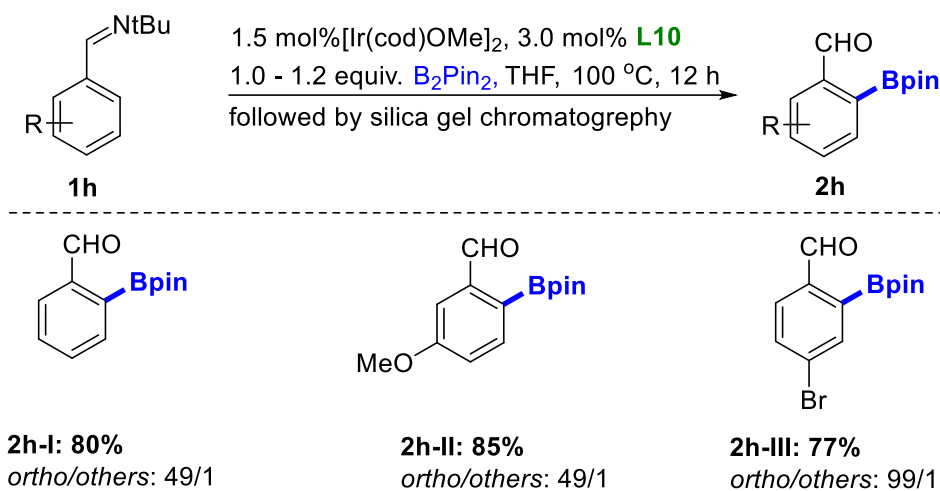
^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 1.6$ Hz, 1H), 7.41 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.42 (s, 12H), 1.36 (t, $J = 7.2$ Hz, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ 168.0, 154.8, 131.1, 128.6, 128.4, 126.0, 83.9, 60.9, 34.9, 31.1, 24.8, 14.3.

^{11}B NMR (128 MHz, CDCl_3): δ 31.3.

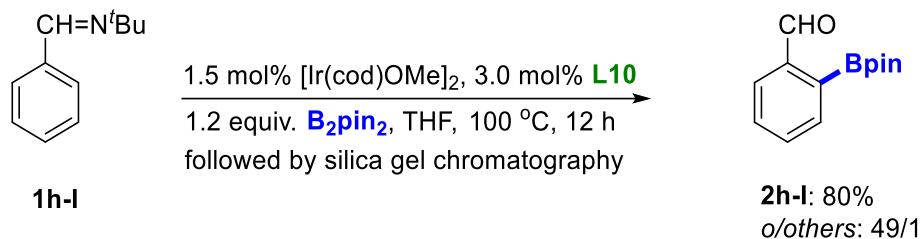
HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{29}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$ 355.2051, found 355.2064.

Borylation of Aldimine (1h):^a



[^a] Reaction scale 0.2 mmol. GC/MS ratios are given using dodecane as internal standard.

Borylation of N-tert-butyl-1-phenylmethanimine (1h-I):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N-tert-butyl-1-phenylmethanimine* (32.2mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 37.1mg of borylated product **2h-I** (80%) as white solid. Spectral data are in accordance with the reported data.³⁰ (Here during silica gel column chromatography product deprotect to aldehyde)

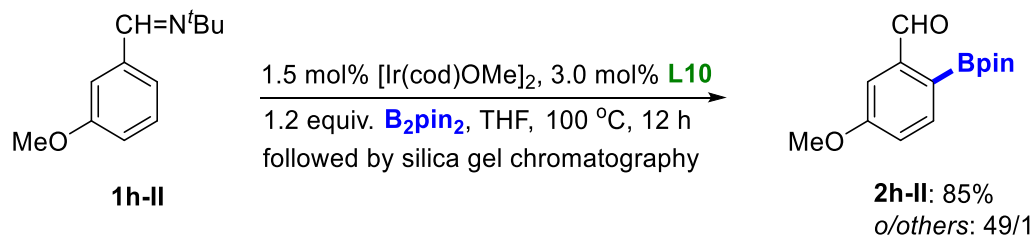
¹H NMR (400 MHz, CDCl₃): δ 10.54 (br s, 1H), 7.94-7.96 (m, 1H), 7.84-7.86 (m, 1H), 7.53-7.60 (m, 2H), 1.39 (s, 12H)

¹³C NMR (100 MHz, CDCl₃): δ 194.8, 141.2, 135.4, 133.0, 130.7, 127.9, 84.4, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 31.1.

HRMS (ESI) m/z calcd for $C_{13}H_{18}BO_3$ $[M+H]^+$ 233.1344, found 233.1363.

Borylation of N-tert-butyl-1-(3-methoxyphenyl)methanimine (1h-II):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[Ir(cod)(OMe)]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N-tert-butyl-1-(3-methoxyphenyl)methanimine* (38.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (7% ethyl acetate in hexane) gave 44.5 mg of borylated product **2h-II** (85%) as liquid. Spectral data are in accordance with the reported data.³⁰ (Here during silica gel column chromatography product deprotect to aldehyde)

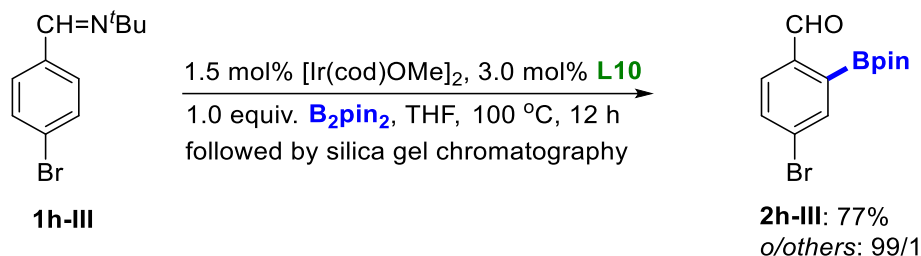
1H NMR (400 MHz, $CDCl_3$): δ 10.66 (br s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.10 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 3.85 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.8, 161.9, 143.5, 137.9, 119.9, 110.2, 84.1, 55.4, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) m/z calcd for $C_{14}H_{19}BNaO_4$ $[M+Na]^+$ 285.1274, found 285.1264.

Borylation of 1-(4-bromophenyl)-N-(tert-butyl)methanimine (1h-III):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1-(4-bromophenyl)-N-(tert-butyl)methanimine (48.0mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 47.9mg of borylated product **2h-III** (77%) as liquid. (Here during silica gel column chromatography product deprotect to aldehyde)

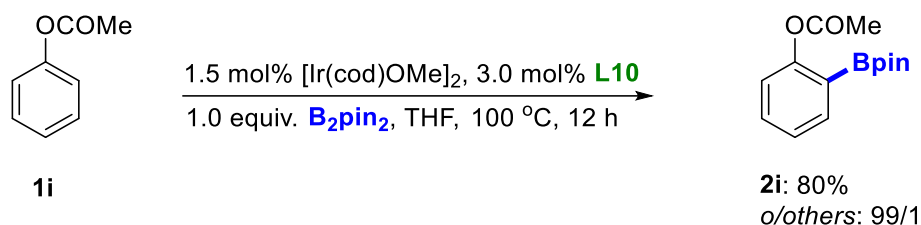
¹H NMR (400 MHz, CDCl₃): δ 10.50 (br s, 1H), 7.99 (d, J = 1.6 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.68 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 1.38 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 193.5, 139.9, 138.4, 134.0, 129.2, 128.8, 84.8, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 30.5.

HRMS (ESI) *m/z* calcd for C₁₃H₂₀BBrNO₃[M+NH₄]⁺ 328.0659, found 328.0672.

Borylation of phenyl acetate (1i):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, phenyl acetate (27.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 41.9 mg of borylated product **2i** (80%) as liquid. (Compound **2i** decomposes to *ortho* borylated phenol slowly).

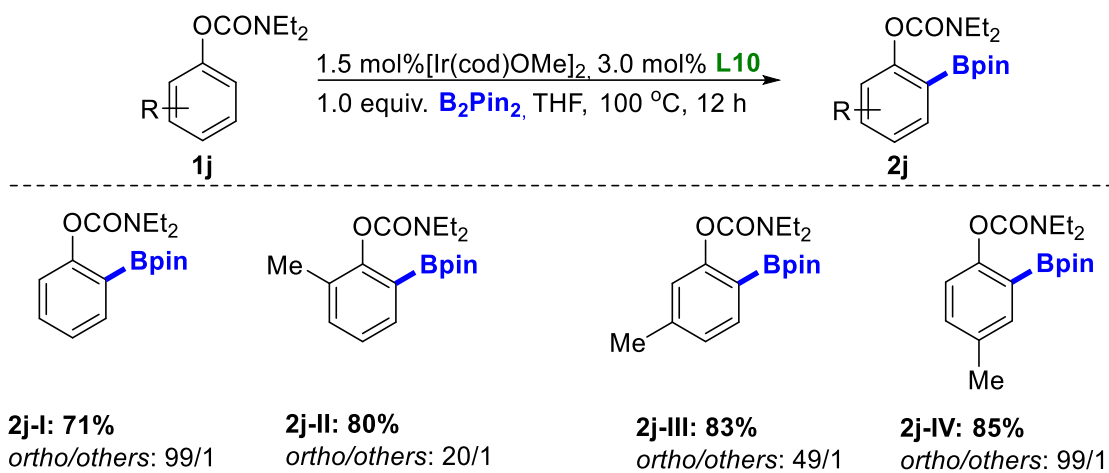
^1H NMR (400 MHz, CDCl_3): δ 7.83 (dd, $J = 7.6 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.47 (dt, $J = 8.0 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.24 (dt, $J = 7.6 \text{ Hz, } 0.8 \text{ Hz, } 1\text{H}$), 7.01 (dd, $J = 8.0 \text{ Hz, } 0.4 \text{ Hz, } 1\text{H}$), 2.31 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.4, 155.6, 136.5, 132.6, 125.4, 121.6, 83.7, 24.8, 21.1.

^{11}B NMR (128 MHz, CDCl_3): δ 30.0.

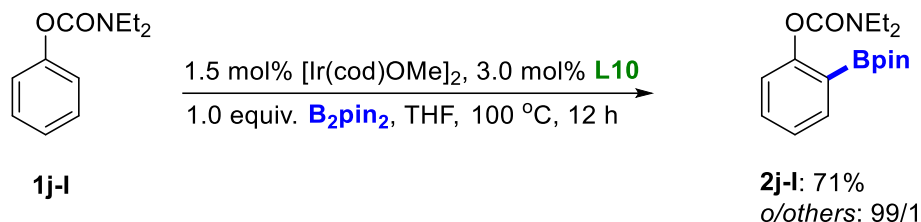
HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{BNaO}_4$ $[\text{M}+\text{Na}]^+$ 285.1269, found 285.1274.

Borylation of carbamoyl protected phenol (1j):^a



^[a] Reaction scale 0.2 mmol. GC/MS ratios are given using dodecane as internal standard.

Borylation of phenyl diethylcarbamate (1j-I):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, phenyl diethylcarbamate (38.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 45.3 mg of borylated product **2j-I** (71%) as liquid. Spectral data are in accordance with the reported data.⁷²

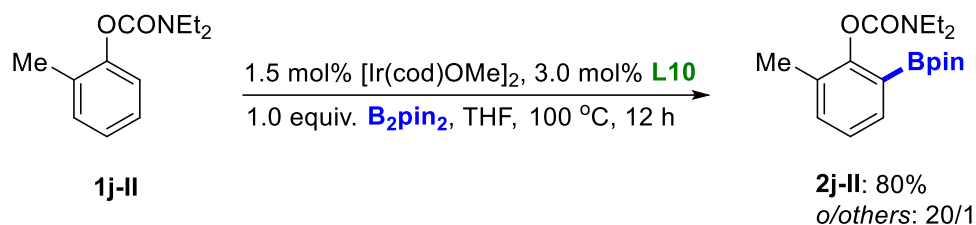
¹H NMR (400 MHz, CDCl_3): δ 7.78 (dd, $J = 7.2$ Hz, 1.2 Hz, 1H), 7.43 (dt, $J = 8.0$ Hz, 1.6 Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 1H), 3.51 (q, $J = 7.2$ Hz, 2H), 3.38 (q, $J = 6.8$ Hz, 2H), 1.30 (m & s, 15H), 1.19 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 156.2, 154.8, 136.1, 132.1, 124.7, 122.2, 83.4, 41.9, 41.6, 24.8, 14.0, 13.4.

^{11}B NMR (128 MHz, CDCl_3): δ 30.1.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 320.2028, found 320.2030.

*Borylation of *o*-tolyl diethylcarbamate (1j-II):*



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *o*-tolyl diethylcarbamate (41.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 53.3 mg of borylated product **2j-II** (80%) as liquid. Spectral data are in accordance with the reported data.⁷²

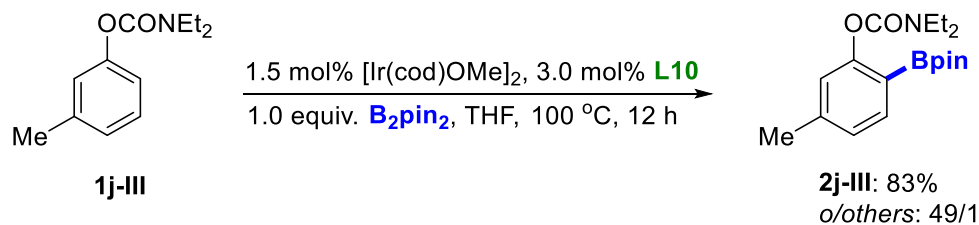
^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 7.2$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 1H), 3.52 (q, $J = 7.2$ Hz, 2H), 3.39 (q, $J = 7.2$ Hz), 2.21(s, 3H), 1.29-1.33 (m & s, 15H), 1.21(t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 154.5, 154.1, 133.7, 133.6, 130.3, 124.7, 83.2, 41.9, 41.5, 24.7, 16.2, 14.1, 13.4.

^{11}B NMR (128 MHz, CDCl_3): δ 30.1.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{29}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 334.2184, found 334.2189.

Borylation of m-tolyl diethylcarbamate (1j-III):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *m*-tolyl diethylcarbamate (41.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 55.3 mg of borylated product **2j-III** (83%) as liquid. Spectral data are in accordance with the reported data.⁷²

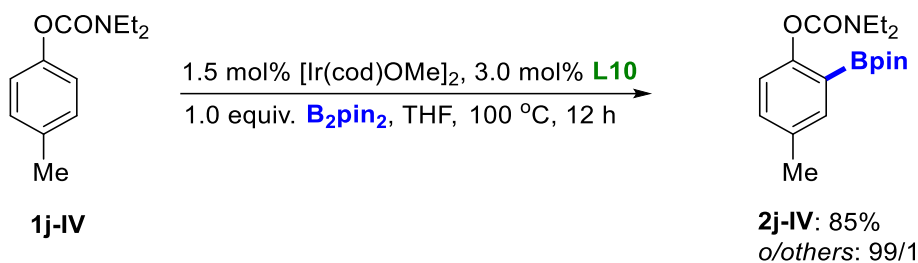
¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, J = 2.0 Hz, 1H), 7.21 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 3.46-3.50 (m, 2H), 3.33-3.37 (m, 2H), 2.31 (s, 3H), 1.27-1.29 (m & s, 15H), 1.18 (t, J = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 154.8, 153.9, 136.4, 133.9, 132.6, 121.8, 83.2, 41.8, 41.4, 24.7, 20.5, 13.9, 13.3.

¹¹B NMR (128 MHz, CDCl₃): δ 30.1.

HRMS (ESI) m/z calcd for C₁₈H₂₉BNO₄ [M+H]⁺ 334.2184, found 334.2192.

Borylation of p-tolyl diethylcarbamate (1j-IV):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.), and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *p*-tolyl diethylcarbamate (41.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 56.6 mg of borylated product **2j-IV** (85%) as liquid. Spectral data are in accordance with the reported data.⁷²

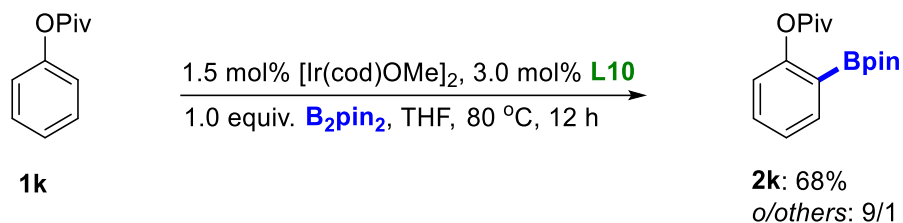
¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 3.49 (q, *J* = 6.8 Hz, 2H), 3.37 (q, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.26-1.28 (m & s, 15H), 1.19 (t, *J* = 6.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 156.2, 154.7, 142.6, 136.0, 125.5, 122.8, 83.1, 41.8, 41.5, 24.7, 21.2, 13.9, 13.3.

¹¹B NMR (128 MHz, CDCl₃): δ 30.2.

HRMS (ESI) *m/z* calcd for C₁₈H₂₉BNO₄ [M+H]⁺ 334.2184, found 334.2189.

Borylation of phenyl pivalate (1k):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, phenyl pivalate (35.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as eluent) gave 29.2 mg of borylated product **2k** (68% yield based on recovered starting material) as oil and 10.5 mg of phenyl pivalate (**1k**).

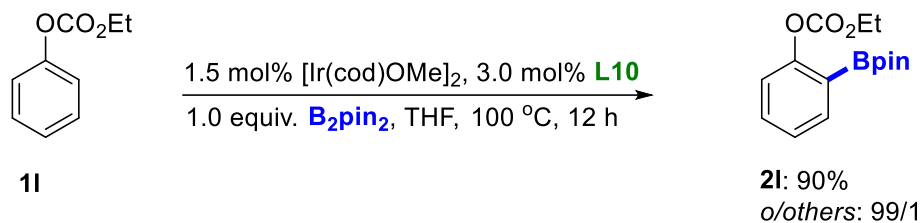
^1H NMR (400 MHz, CDCl_3): δ 7.83 (dd, $J = 7.2 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.45 (dt, $J = 8.0 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.22 (dt, $J = 7.2 \text{ Hz, } 0.8 \text{ Hz, } 1\text{H}$), 6.96 (dd, $J = 8.0 \text{ Hz, } 0.8 \text{ Hz, } 1\text{H}$), 1.39 (s, 9H), 1.31 (s, 12 H).

^{13}C NMR (100 MHz, CDCl_3): δ 177.3, 155.9, 136.6, 132.4, 125.2, 121.7, 83.6, 38.9, 27.3, 24.9.

^{11}B NMR (128 MHz, CDCl_3): δ 29.9.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{26}\text{BO}_4$ $[\text{M}+\text{H}]^+$ 305.1919, found 305.1919.

Borylation of ethyl phenyl carbonate (11):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl phenyl carbonate (33.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as eluent) gave 52.6 mg of borylated product **21** (90%) as liquid.

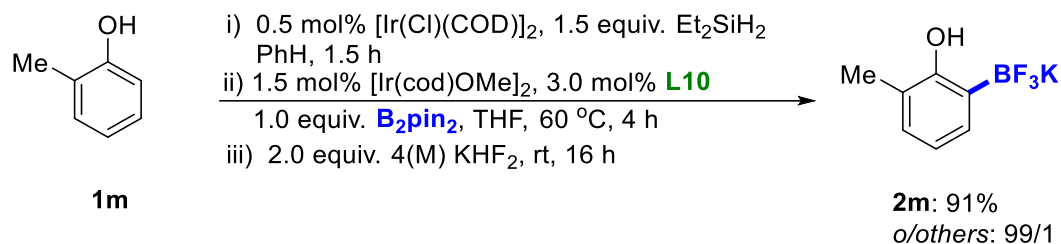
^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, $J = 7.2$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 1H), 4.31 (q, $J = 7.2$ Hz, 2H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 155.8, 154.1, 136.4, 132.5, 125.7, 121.3, 83.8, 64.3, 24.8, 14.3.

^{11}B NMR (128 MHz, CDCl_3): δ 30.2.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{BNaO}_5$ $[\text{M}+\text{Na}]^+$ 315.1374, found 315.1392.

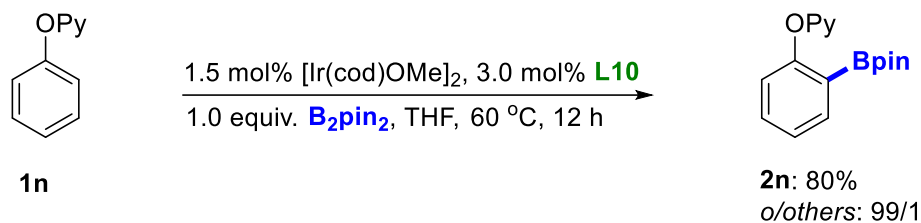
*Borylation of diethyl(phenoxy)silane (**1m**):*



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)Cl]₂ (0.67 mg, 0.5 mmol%), benzene (0.25 mL) and diethylsilane (39 μ L, 0.3 mmol). 2-Methyl-phenol (21.6 mg, 0.2 mmol) was added to the solution, and rapid gas evolution occurred. After 1.5 h, gas evolution had ceased and GC/MS analysis indicated complete consumption of the phenol to give the corresponding 2-methyl phenoxy-hydrosilane. The crude mixture was concentrated under high vacuum.

In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-methyl phenoxy-hydrosilane (38.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 4 h. After 4 h, GC/MS showed complete consumption of the phenoxy-hydrosilane. The reaction was cooled to room temperature and diluted with 0.5 mL THF. 4.0 M KHF₂ in water (100 μ L, 0.4 mmol) was added slowly, and vigorous gas evolution was observed. Then it was stirred for another 16 h at rt. Volatile materials were removed by rotary evaporation, and the resulting aqueous mixture was dried under high vacuum. Then the residue was dissolved in minimum volume of acetone and then toluene was added and acetone was removed by slow evaporation. Then it was cooled to -20 °C and the solid product precipitated out. The solid product was collected through filtration and it gave **2m** (36.4 mg, 91%) as a grey powder. Spectral data are in accordance with the reported data.⁷³

Borylation of 2-phenoxy pyridine (1n):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-phenoxy pyridine (34.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 47.5 mg of borylated product **2n** (80%) as pale yellow solid. Spectral data are in accordance with the reported data.⁹²

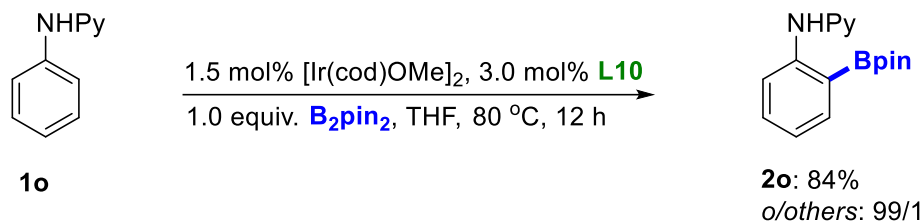
^1H NMR (400 MHz, CDCl_3): δ 8.46-8.48 (m, 1H), 7.81 (ddd, $J = 8.4 \text{ Hz, } 7.2 \text{ Hz, } 2.0 \text{ Hz, } 1\text{H}$), 7.76 (dd, $J = 7.2 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.37 (ddd, $J = 8.4 \text{ Hz, } 7.6 \text{ Hz, } 2.0 \text{ Hz, } 1\text{H}$), 7.23 (td, $J = 7.6 \text{ Hz, } 1.2 \text{ Hz, } 1\text{H}$), 7.08-7.15 (m, 3H), 1.20 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.6, 157.4, 143.2, 140.7, 133.8, 130.0, 125.0, 118.7, 117.8, 113.7, 81.9, 25.6.

^{11}B NMR (128 MHz, CDCl_3): δ 16.9.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{21}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 298.1614, found 299.1622.

Borylation of N-phenylpyridin-2-amine (1o):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-phenylpyridin-2-amine (34.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (monitored by GC/MS), the reaction mixture was cooled to room temperature. THF was decanted and washing with ethyl acetate/hexane (1:1) gave white solid. The solid was dried under vacuum and obtained 49.8 mg of borylated product **2o** (84%) as white solid.

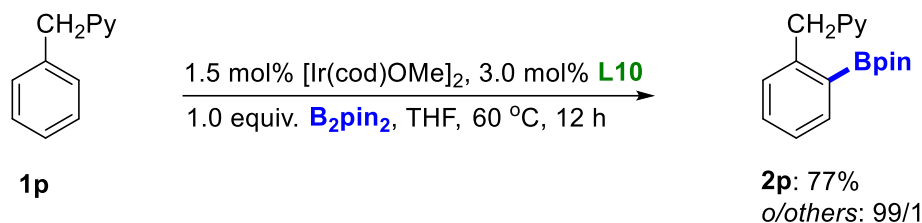
^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.50 (br s, 1H), 8.51 (d, $J = 4.8$ Hz, 1H), 7.84 (ddd, $J = 8.4$ Hz, 6.8 Hz, 1.6 Hz, 1H), 7.51 (dd, $J = 7.2$ Hz, 1.2 Hz, 1H), 7.14-7.18 (m, 2H), 6.95-7.05 (m, 3H), 1.11 (s, 12H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 151.1, 140.8, 139.8, 138.6, 130.8, 126.5, 122.2, 114.0, 113.8, 113.4, 79.2, 26.8.

^{11}B NMR (128 MHz, $\text{DMSO}-d_6$): δ 5.4.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{22}\text{BN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 297.1774, found 297.1786.

Borylation of 2-benzylpyridine (1p):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-benzylpyridine (33.8mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane as eluent) gave 45.5 mg of borylated product **2p** (77%) as liquid. Spectral data are in accordance with the reported data.⁷⁴

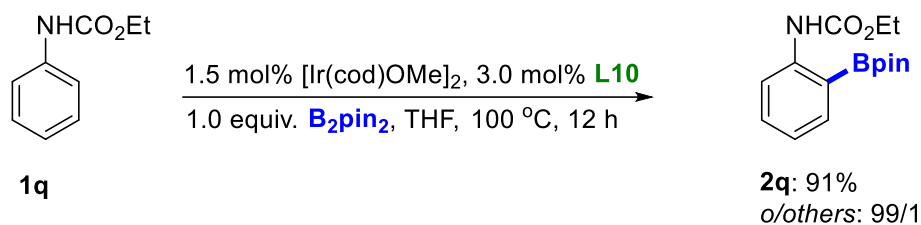
^1H NMR (400 MHz, CDCl_3): δ 9.10 (dd, $J = 5.6 \text{ Hz, } 0.8 \text{ Hz, } 1\text{H}$), 7.79 (dt, $J = 7.6 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.71 (d, $J = 7.2 \text{ Hz, } 1\text{H}$), 7.45 (d, $J = 7.6 \text{ Hz, } 1\text{H}$), 7.36 (t, $J = 6.4 \text{ Hz, } 1\text{H}$), 7.12-7.22 (m, 3H), 4.34 (s, 2H), 1.25 (s, 12 H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.6, 143.5, 139.6, 138.9, 130.8, 126.7, 126.4, 125.9, 125.1, 121.9, 80.8, 39.7, 25.9.

^{11}B NMR (128 MHz, CDCl_3): δ 10.3.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{BNO}_2$ $[\text{M}+\text{H}]^+$ 296.1816, found 296.1832.

Borylation of ethyl phenylcarbamate(1q):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl phenylcarbamate (33.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (6% ethyl acetate in hexane as eluent) gave 53.0 mg of borylated product **2q** (91%) as liquid.

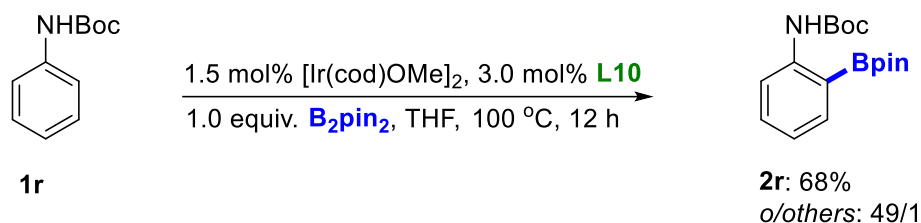
^1H NMR (400 MHz, CDCl_3): δ 8.79 (br s, 1H), 8.23 (d, $J = 8.4$ Hz, 1H), 7.74 (d, $J = 7.2$ Hz, 1H), 7.42-7.46 (m, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 1.37 (s, 12H), 1.32 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 153.8, 144.9, 136.2, 132.8, 121.7, 117.6, 84.2, 60.7, 24.8, 14.6.

^{11}B NMR (128 MHz, CDCl_3): δ 30.3.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{BNNaO}_4$ $[\text{M}+\text{Na}]^+$ 314.1534, found 314.1539.

Borylation of tert-butyl phenylcarbamate (1r):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *tert*-butyl phenylcarbamate (38.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane as eluent) gave 43.4 mg of borylated product **2r** (68%) as white solid.

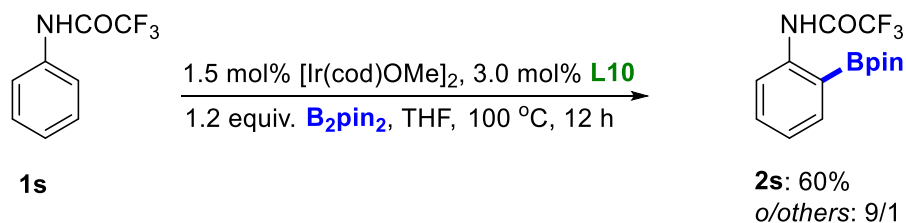
¹H NMR (400 MHz, CDCl₃): δ 8.68 (br s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.72 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.39-7.44 (m, 1H), 6.98 (dt, J = 7.2 Hz, 0.4 Hz, 1H), 1.53 (s, 9H), 1.36 (s, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 153.1, 145.2, 136.1, 132.7, 121.5, 117.6, 84.2, 79.7, 28.3, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 30.5.

HRMS (ESI) *m/z* calcd for C₁₇H₂₆BNNaO₄ [M+Na]⁺ 342.1847, found 342.1849.

Borylation of 2,2,2-trifluoro-N-phenylacetamide (1s):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (61.0 mg, 1.5 equiv.), and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2,2,2-trifluoro-*N*-phenylacetamide (37.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was

stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane as eluent) gave 37.8 mg of borylated product **2s** (60%) as liquid.

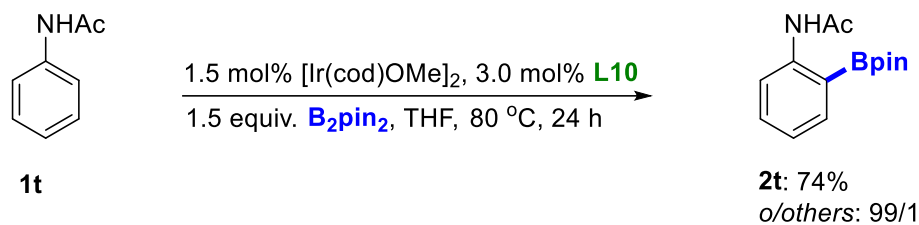
^1H NMR (400 MHz, CDCl_3): δ 10.57 (br s, 1H), 8.46 (d, $J = 8.4$ Hz, 1H), 7.82 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H), 7.51-7.55 (m, 1H), 7.20 (dt, $J = 7.2$ Hz, 0.8 Hz, 1H), 1.39 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 154.6 (q, $J = 36.7$ Hz), 142.2, 136.3, 133.0, 124.7, 119.5, 115.9 (q, $J = 287.2$ Hz), 84.9, 24.6.

^{11}B NMR (128 MHz, CDCl_3): δ 30.3.

HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{BF}_3\text{NNaO}_3$ [$\text{M}+\text{Na}$] $^+$ 338.1146, found 338.1178.

Borylation of *N*-phenylacetamide (**1t**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-phenylacetamide (27.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (ethyl acetate as eluent) gave 38.6 mg of borylated product **2t** (74%) as off white powder. Spectral data are in accordance with the reported data.⁷⁵

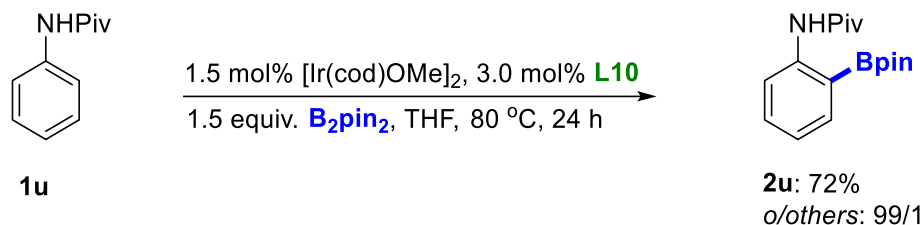
^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 11.86 (br s, 1H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.23 (t, $J = 7.2$ Hz, 1H), 7.13 (t, $J = 7.2$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 2.27 (s, 3H), 1.16 (s, 12H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 169.9, 138.1, 132.7, 127.5, 125.4, 115.5, 79.5, 26.1, 21.8.

^{11}B NMR (128 MHz, $\text{DMSO}-d_6$): δ 20.1.

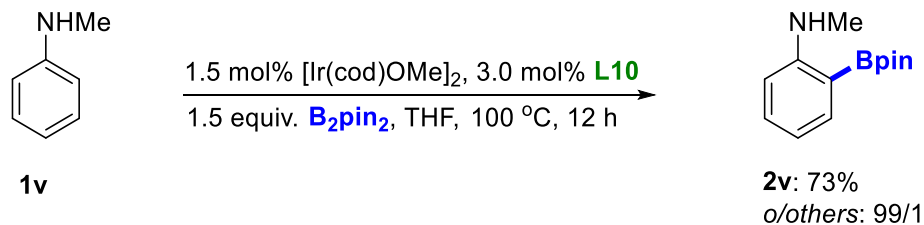
HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{20}\text{BNNaO}_3$ [$\text{M}+\text{Na}$] $^+$ 284.1428, found 284.1429.

Borylation of N-phenylpivalamide (1u):



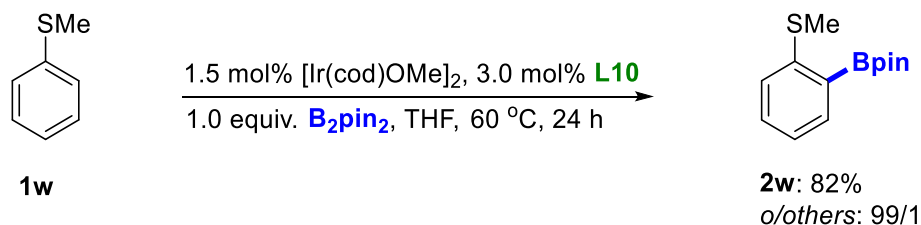
In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-phenylpivalamide (35.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate as eluent) gave 43.7 mg of borylated product **2u** (72%) as off white power. Spectral data are in accordance with the reported data.⁷⁶

Borylation of N-methylaniline (1v):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-methylaniline (21.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 13.0 mg of borylated product **2v** (73% yield based on recovered starting material) as liquid and 13.3 mg of *N*-methylaniline. Spectral data are in accordance with the reported data.⁷⁷

Borylation of methyl(phenyl)sulfane (1w):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.0 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, methyl(phenyl)sulfane (24.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 41.0 mg of borylated product **2w** (82%) as liquid. Spectral data are in accordance with the reported data.⁷⁸

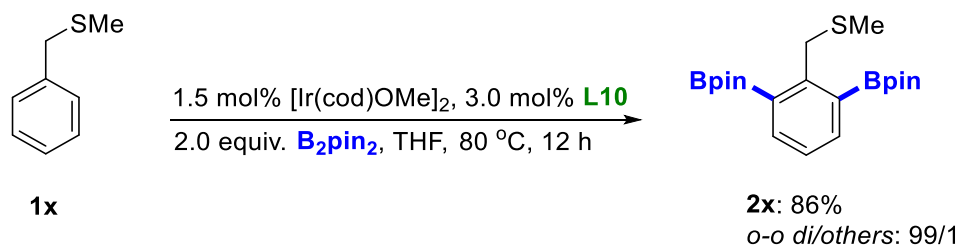
^1H NMR (400 MHz, CDCl_3): δ 7.68 (dd, $J = 7.2 \text{ Hz}, 1.2 \text{ Hz}, 1\text{H}$), 7.37 (dt, $J = 7.6 \text{ Hz}, 1.2 \text{ Hz}, 1\text{H}$), 7.16 (d, $J = 8.0 \text{ Hz}, 1\text{H}$), 7.10 (t, $J = 7.6 \text{ Hz}, 1\text{H}$), 2.45 (s, 3H), 1.38 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 135.9, 131.2, 123.9, 123.6, 83.9, 24.8, 15.7.

^{11}B NMR (128 MHz, CDCl_3): δ 30.9.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{19}\text{BO}_2\text{NaS}$ $[\text{M}+\text{Na}]^+$ 273.1091, found 273.1110.

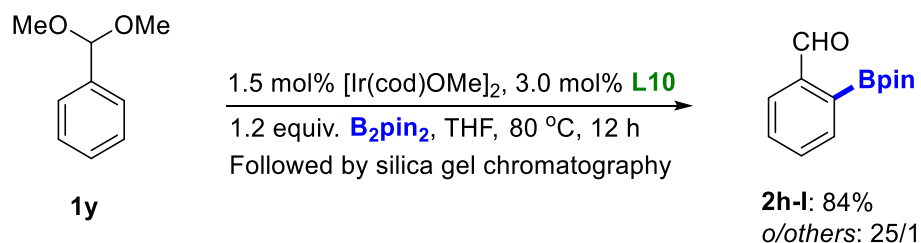
Borylation of phenylmethanethiol (1x):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, phenylmethanethiol (27.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80°C. The reaction mixture was stirred

for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 67.1 mg of borylated product **2x** (86%) as liquid. Spectral data are in accordance with the reported data.⁷⁹

Borylation of (dimethoxymethyl)benzene (1y):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), **B₂pin₂** (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, (dimethoxymethyl)benzene (30.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 39.0 mg of borylated product **2h-I** (84%) as white solid. (Here during silica gel column chromatography product deprotect to aldehyde and final product is ortho borylated aldehyde)

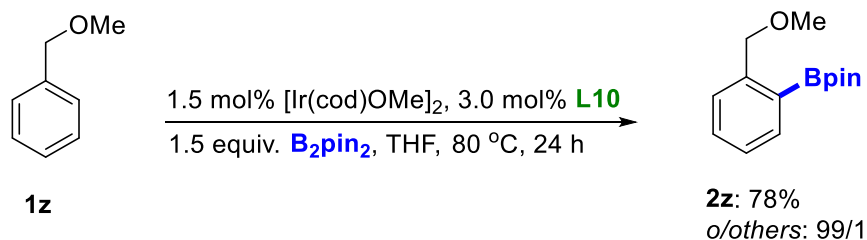
¹H NMR (400 MHz, CDCl₃): δ 10.54 (br s, 1H), 7.94-7.96 (m, 1H), 7.84-7.86 (m, 1H), 7.53-7.60 (m, 2H), 1.39 (s, 12H)

¹³C NMR (100 MHz, CDCl₃): δ 194.6, 141.2, 135.4, 133.0, 130.7, 127.9, 84.4, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 31.1.

HRMS (ESI) *m/z* calcd for C₁₃H₁₈BO₃ [M+H]⁺ 233.1344, found 233.1363.

Borylation of (methoxymethyl)benzene (1z):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, (methoxymethyl)benzene (24.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 38.7 mg of borylated product **2z** (78%) as liquid.

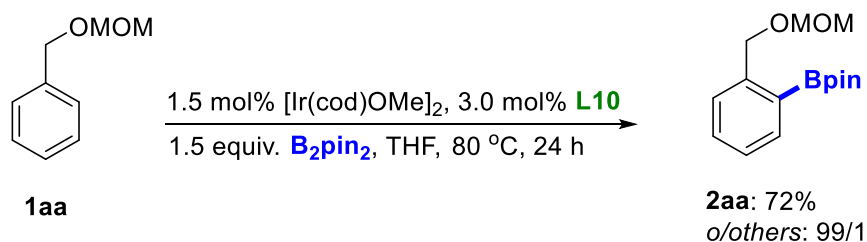
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.79 (d, $J = 7.2$ Hz, 1H), 7.40-7.44 (m, 2H), 7.27-7.30 (m, 1H), 4.72 (s, 2H), 3.42 (s, 3H), 1.36 (s, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.3, 135.5, 130.7, 127.5, 126.6, 83.5, 73.9, 58.1, 24.8.

$^{11}\text{B NMR}$ (128 MHz, CDCl_3): δ 31.1.

HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{21}\text{BNaO}_3$ $[\text{M}+\text{Na}]^+$ 271.1476, found 271.1471.

Borylation of (methoxymethoxy)methylbenzene (1aa):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, (methoxymethoxy)methylbenzene (30.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction

mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (6% ethyl acetate in hexane as eluent) gave 40.0 mg of borylated product **2aa** (72%) as liquid. Spectral data are in accordance with the reported data.⁶⁶

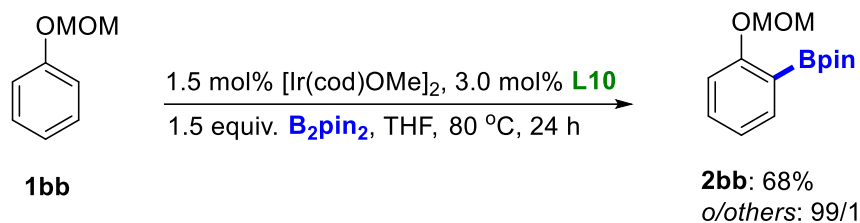
¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 7.2 Hz, 1H), 7.41-7.48 (m, 2H), 7.26-7.30 (m, 1H), 4.85 (s, 2H), 4.76 (s, 2H), 3.42 (s, 3H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 144.1, 135.8, 130.9, 128.0, 126.8, 96.3, 83.6, 69.1, 55.3, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 31.0.

HRMS (ESI) *m/z* calcd for C₁₅H₂₄BO₄ [M+H]⁺ 301.1582, found 301.1549.

Borylation of (methoxymethoxy)benzene (1bb):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, (methoxymethoxy)benzene (27.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (6% ethyl acetate in hexane as eluent) gave 35.9 mg of borylated product **2bb** (68%) as liquid.

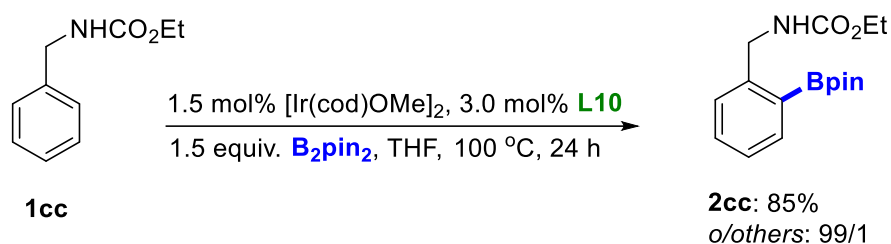
¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.00-7.04 (m, 2H), 5.20 (s, 2H), 3.51 (s, 3H), 1.35 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 161.6, 136.6, 132.2, 121.7, 115.5, 95.1, 83.4, 55.9, 24.7.

¹¹B NMR (128 MHz, CDCl₃): δ 30.8.

HRMS (ESI) *m/z* calcd for C₁₄H₂₁NaBO₄ [M+Na]⁺ 287.1425, found 287.1431.

Borylation of ethyl benzylcarbamate (1cc):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl benzylcarbamate (35.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane as eluent) gave 51.9 mg of borylated product **2cc** (85%) as liquid.

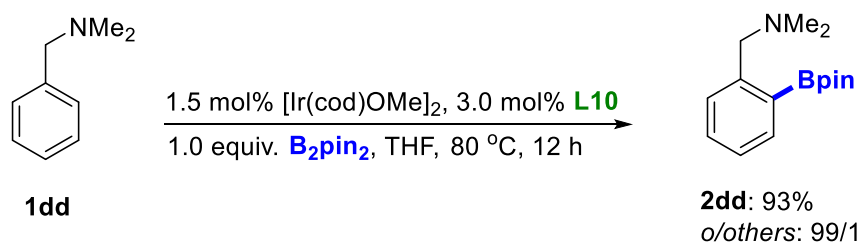
^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.38-7.41 (m, 2H), 7.25-7.29 (m, 1H), 5.64 (br s, 1H), 4.46 (d, $J = 6.4$ Hz, 2H), 4.08 (q, $J = 7.2$ Hz, 2H), 1.36 (s, 12H), 1.21 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 156.5, 145.1, 136.4, 131.4, 129.4, 126.7, 83.9, 60.5, 45.2, 24.8, 14.6.

^{11}B NMR (128 MHz, CDCl_3): δ 30.7.

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{BNNaO}_4$ $[\text{M}+\text{Na}]^+$ 328.1691, found 328.1694.

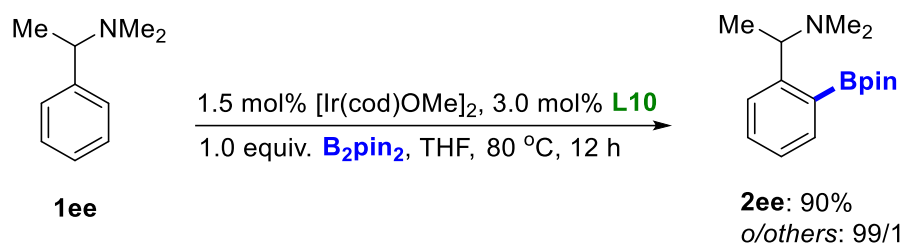
*Borylation of *N,N*-dimethyl-1-phenylmethanamine (1dd):*



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dimethyl-1-

phenylmethanamine (27.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (1% methanol in DCM as eluent) gave 48.6 mg of borylated product **2dd** (93%) as liquid. Spectral data are in accordance with the reported data.⁸⁰

Borylation of N,N-dimethyl-1-phenylethan-1-amine (1ee):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dimethyl-1-phenylethan-1-amine (29.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (1% methanol in DCM as eluent) gave 49.5 mg of borylated product **2ee** (90%) as liquid. Spectral data are in accordance with the reported data.⁸⁰

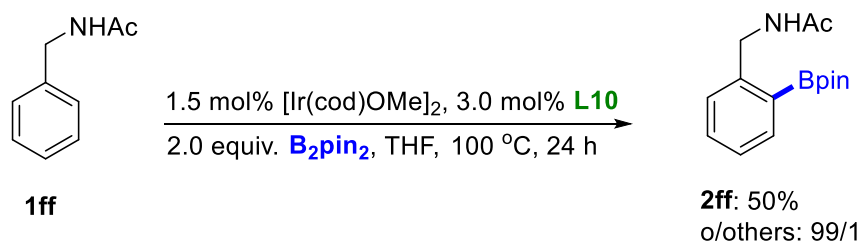
¹H NMR (400 MHz, CDCl₃): δ 7.51-7.53 (m, 1H), 7.16-7.23 (m, 2H), 7.00 (d, J = 6.8 Hz, 1H), 4.13 (q, J = 6.8 Hz, 1H), 2.42 (s, 6H), 1.43 (d, J = 6.8 Hz, 3H), 1.31 (s, 6H), 1.29 (s, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 144.0, 130.5, 127.3, 121.6, 99.9, 80.0, 65.6, 40.5, 27.2, 26.4, 12.0.

¹¹B NMR (128 MHz, CDCl₃): δ 13.2.

HRMS (ESI) *m/z* calcd for C₁₆H₂₇BNO₂ [M+H]⁺ 276.2135, found 276.2130.

Borylation of N-benzylacetamide (1ff):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-benzylacetamide (29.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (70% ethyl acetate in hexane as eluent) gave 27.5 mg of borylated product **2ff** (50%) as off white solid.

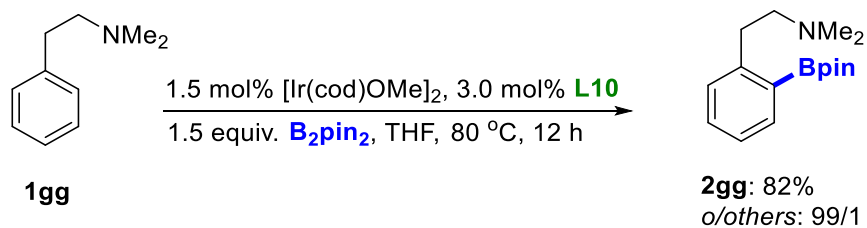
^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 4.0$ Hz, 1H), 7.23-7.27 (m, 1H), 6.61 (br s, 1H), 4.52 (d, $J = 6.0$ Hz, 2H), 1.90 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 144.6, 136.5, 131.5, 129.6, 126.8, 83.9, 43.7, 24.9, 23.4.

^{11}B NMR (128 MHz, CDCl_3): δ 31.0.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{BNNaO}_3$ $[\text{M}+\text{Na}]^+$ 298.1585, found 298.1591.

Borylation of N,N-dimethyl-2-phenylethan-1-amine (1gg):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-dimethyl-2-phenylethan-1-amine (29.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred

for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (1% methanol in DCM as eluent) gave 45.2 mg of borylated product **2gg** (82%) as liquid. Spectral data are in accordance with the reported data.⁸⁰

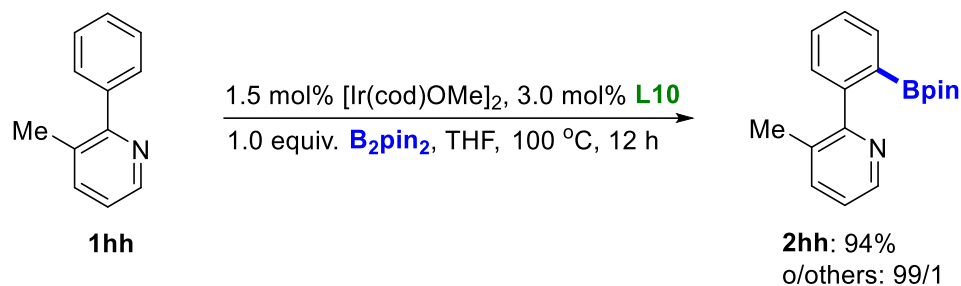
¹H NMR (400 MHz, CDCl₃): δ 7.76 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.27-7.31 (m, 1H), 7.13-7.19 (m, 2H), 3.04-3.08 (m, 2H), 2.64-2.69 (m, 2H), 2.38 (s, 6H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 144.9, 135.5, 129.9, 128.9, 125.3, 82.7, 61.2, 45.2, 32.3, 25.6.

¹¹B NMR (128 MHz, CDCl₃): δ 25.5.

HRMS (ESI) *m/z* calcd for C₁₆H₂₈BNO₂ [M+H]⁺ 276.2135, found 276.2124.

Borylation of 3-methyl-2-phenylpyridine (1hh):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-methyl-2-phenylpyridine (33.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and washed with hexane to give 55.5 mg of borylated product **2hh** (94%) as brown solid.

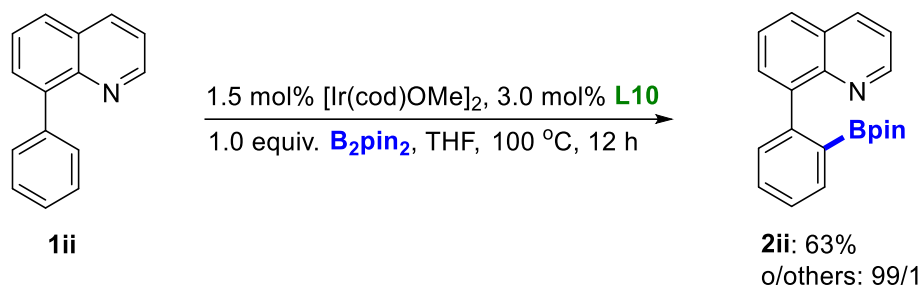
¹H NMR (400 MHz, CDCl₃): δ 8.60 (d, J = 5.2 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.74-7.79 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.27-7.31 (m, 2H), 2.71 (s, 3H), 1.42 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 154.4, 144.6, 140.8, 138.6, 131.2, 131.1, 130.6, 127.6, 125.0, 122.0, 80.1, 24.5, 21.3.

¹¹B NMR (128 MHz, CDCl₃): δ 12.2.

HRMS (ESI) *m/z* calcd for C₁₈H₂₃BNO₂ [M+H]⁺ 296.1816, found 296.1818.

*Borylation of 8-phenyl quinoline (**1ii**):*



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 8-phenylquinoline (41.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 41.7 mg of borylated product **2ii** (63%) as off white solid.

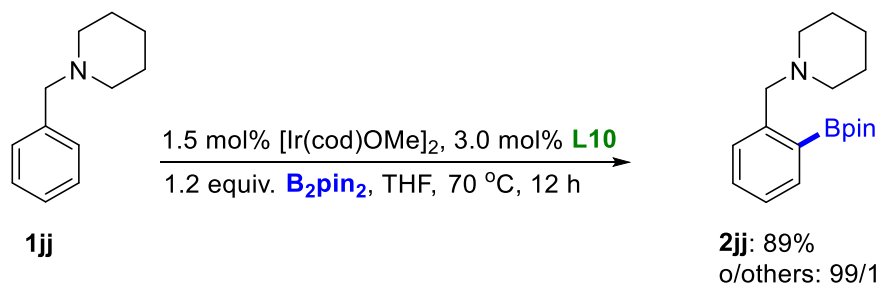
^1H NMR (400 MHz, CDCl_3): δ 9.60 (d, $J = 4.8$ Hz, 1H), 8.49 (d, $J = 8.0$ Hz, 1H), 8.43 (d, $J = 7.2$ Hz, 1H), 7.94-7.96 (m, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.73-7.78 (m, 2H), 7.66 (dd, $J = 7.6$ Hz, 5.2 Hz, 1H), 7.34-7.39 (m, 2H), 1.22 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 145.4, 141.8, 139.8, 135.9, 133.1, 131.4, 129.4, 128.7, 127.9, 127.6, 127.2, 126.8, 124.9, 120.0, 80.6, 26.7.

^{11}B NMR (128 MHz, CDCl_3): δ 8.7.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{23}\text{BNO}_2$ $[\text{M}+\text{H}]^+$ 332.1816, found 332.1818.

Borylation of 1-benzylpiperidine (**1jj**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1-benzylpiperidine (35.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (1% MeOH in DCM as eluent) gave 53.6 mg of borylated product **2jj** (89%) as gummy liquid. Spectral data are in accordance with the reported data.⁸¹

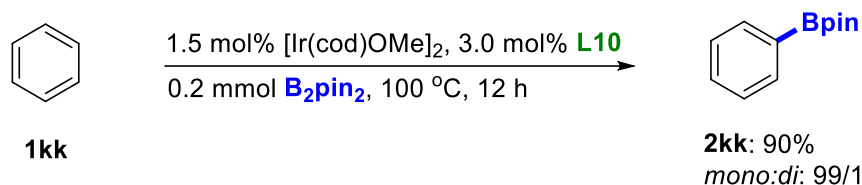
¹H NMR (400 MHz, CDCl₃): δ 7.60-7.62 (m, 1H), 7.14-7.26 (m, 3H), 3.77 (s, 2H), 2.56-2.58 (m, 4H), 1.49-1.60 (m, 6H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 142.6, 133.3, 128.7, 126.7, 126.5, 82.0, 60.3, 53.0, 25.8, 24.1, 23.8.

¹¹B NMR (128 MHz, CDCl₃): δ 24.2.

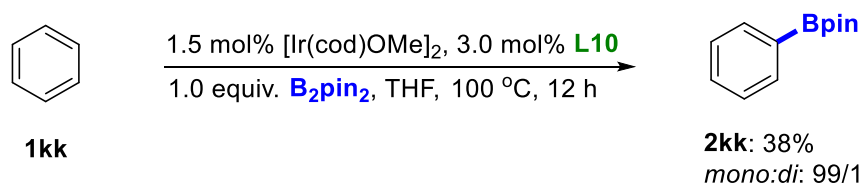
HRMS (ESI) *m/z* calcd. for C₁₈H₂₉BNO₂ [M+H]⁺ 302.2291, found 302.2286.

Borylation of benzene (1kk):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 0.2 mmol) and dry Benzene (1.0 mL), the reaction mixture was stirred for 2 minutes at room temperature. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminum block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), excess benzene was removed under reduced pressure and chromatographic separation with silica gel (2% ethyl acetate in hexane as eluent) gave 36.7 mg of borylated product **2kk** (90%) as solid. (Here yield is calculated based on B_2pin_2 as limiting reagent). Spectral data are in accordance with the reported data.⁸²

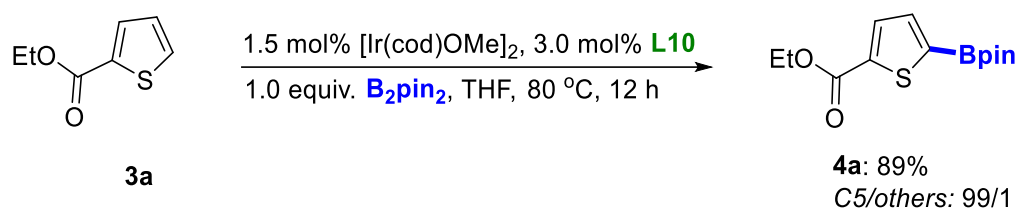
Borylation of benzene (1kk):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 0.2 mmol) and dry THF (1.0 mL), the reaction mixture was stirred for 2 minutes at room temperature. To this mixture, Benzene (15.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminum block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), excess benzene was removed under reduced pressure and chromatographic separation with silica gel (2% ethyl acetate in hexane as eluent) gave 15.5 mg of borylated product **2kk** (38%) as solid.

Heterocyclic molecule Borylation :

Borylation of ethyl thiophene-2-carboxylate (**3a**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl thiophene-2-carboxylate (31.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 50.2 mg of borylated product **4a** (89%) as white solid. Spectral data are in accordance with the reported data.⁸³

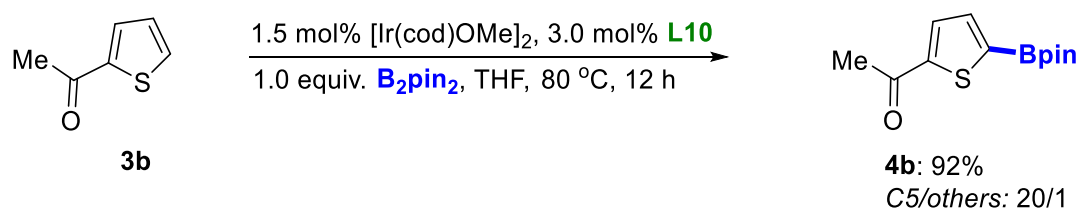
^1H (400 MHz, CDCl_3): δ 7.80 (d, $J = 3.6$ Hz, 1H), 7.54 (d, $J = 3.6$ Hz, 1H), 4.33 (q, $J = 7.2$ Hz, 2H), 1.36 (t, $J = 7.2$ Hz, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 139.9, 136.8, 133.7, 84.5, 61.2, 24.7, 14.2.

^{11}B (128 MHz, CDCl_3): δ 28.6.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{20}\text{BO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 283.1170, found 283.1183.

Borylation of 1-(thiophen-2-yl)ethan-1-one (**3b**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1-(thiophen-2-yl)ethan-1-one (25.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred

for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane) gave 46.4 mg of borylated product **4b**(92%) as liquid. Spectral data are in accordance with the reported data.⁸⁴

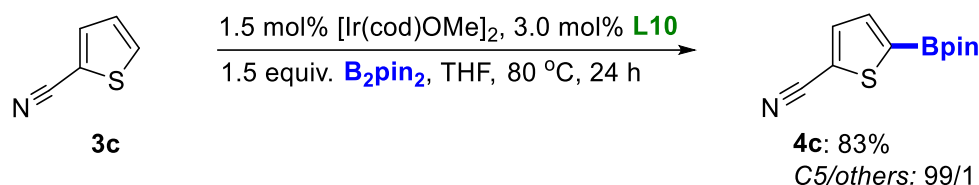
¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, J = 3.6 Hz, 1H) 7.54 (d, J = 3.6 Hz, 1H), 2.53 (s, 3H), 1.31 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 190.5, 149.4, 137.2, 132.6, 84.5, 27.3, 24.6.

¹¹B NMR (128 MHz, CDCl₃): δ 28.7.

HRMS (ESI) *m/z* calcd for C₁₂H₁₈BO₃S [M+H]⁺ 253.1064, found 253.1063.

Borylation of thiophene-2-carbonitrile (3c):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, thiophene-2-carbonitrile (21.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane) gave 39.0 mg of borylated product **4c**(83%) as off white solid. Spectral data are in accordance with the reported data.⁸⁵

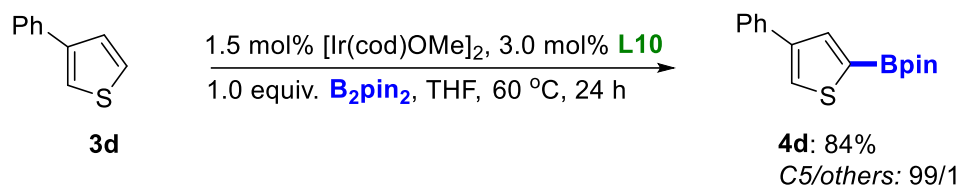
¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, J = 3.6 Hz, 1H), 7.56 (d, J = 4.0 Hz, 1H), 1.35 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 137.8, 136.5, 115.3, 114.2, 85.0, 24.7.

¹¹B NMR (128 MHz, CDCl₃): δ 28.3.

HRMS (ESI) *m/z* calcd for C₁₁H₁₅BNO₂S [M+H]⁺ 236.0911, found 236.0910.

Borylation of 3-phenylthiophene (3d):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-phenylthiophene (32.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 48.1 mg of borylated product **4d**(84%) as liquid. Spectral data are in accordance with the reported data.⁸⁶

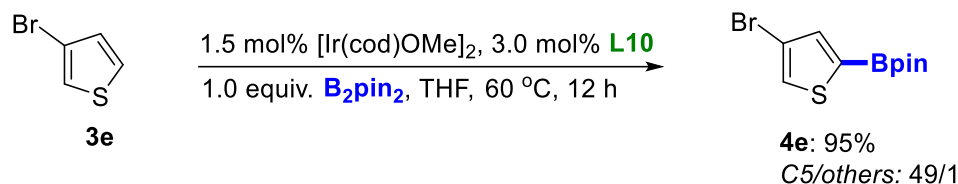
^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, $J = 1.2$ Hz, 1H), 7.75 (d, $J = 0.8$ Hz, 1H), 7.63-7.66 (m, 2H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 1H), 1.40 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.7, 136.2, 135.5, 128.7, 127.5, 127.1, 126.4, 84.2, 24.7.

^{11}B NMR (128 MHz, CDCl_3): δ 29.2.

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{BO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 287.1272, found 287.1251.

Borylation of 3-bromothiophene (3e):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-bromothiophene (32.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic

separation with silica gel (5% ethyl acetate in hexane) gave 54.9 mg of borylated product **4e**(95%) as white solid. Spectral data are in accordance with the reported data.⁸⁴

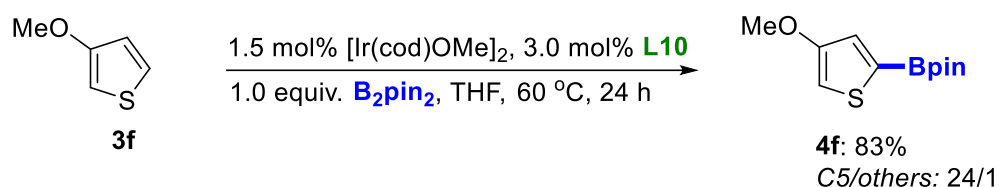
¹H (400 MHz, CDCl₃): δ 7.52 (s, 1H), 7.48 (s, 1H), 1.34 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 139.3, 129.6, 111.2, 84.4, 24.7.

¹¹B (128 MHz, CDCl₃): δ 28.4.

HRMS (ESI) *m/z* calcd for C₁₀H₁₈BBrNO₂S [M+NH₄]⁺ 306.0329, found 306.0335.

Borylation of 3-methoxythiophene (**3f**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), **B₂pin₂** (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-methoxythiophene (22.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane) gave 39.8 mg of borylated product **4f** (83%) as oil. (here 6% di isomer formed)

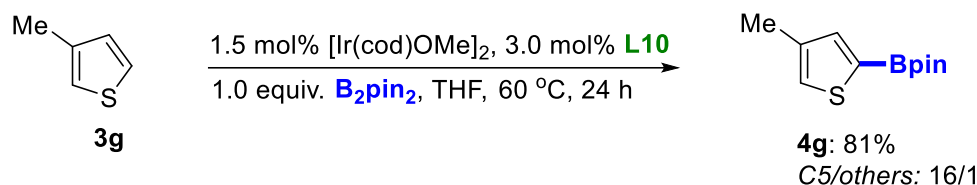
¹H NMR (400 MHz, CDCl₃): δ 7.24 (s, 1H), 6.58 (s, 1H), 3.81 (s, 3H), 1.33 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 159.9, 127.8, 104.9, 84.2, 57.7, 24.7.

¹¹B NMR (128 MHz, CDCl₃): δ 28.7.

HRMS (ESI) *m/z* calcd for C₁₁H₁₈BO₃S [M+H]⁺ 241.1064, found 241.1062.

Borylation of 3-methylthiophene (3g):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 3-methylthiophene (19.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 36.3 mg of borylated product **4g** (81%) as oil. Spectral data are in accordance with the reported data.⁸⁴ (here 8% di isomer formed)

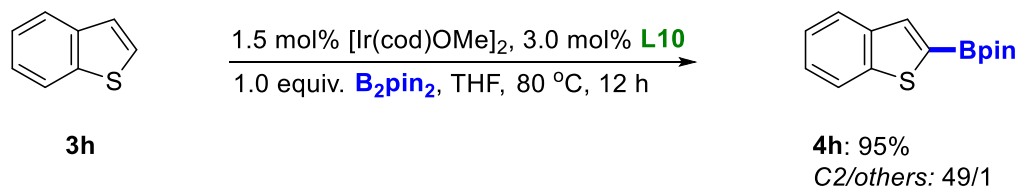
^1H NMR (400 MHz, CDCl_3): δ 7.45 (s, 1H), 7.20 (s, 1H), 2.29 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.5, 139.0, 128.1, 84.0, 24.7, 15.1.

^{11}B NMR (128 MHz, CDCl_3): δ 29.1.

HRMS (ESI) m/z , calcd for $\text{C}_{11}\text{H}_{17}\text{BO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 225.1115, found 225.1098.

Borylation of benzo[b]thiophene (3h):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, benzo[b]thiophene (26.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 49.5 mg of borylated product **4h**(95%) as solid. Spectral data are in accordance with the reported data.⁸⁷

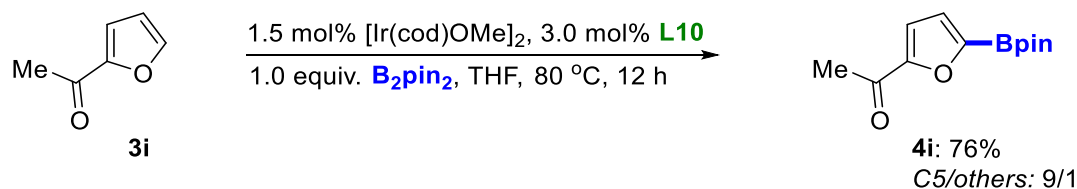
^1H NMR (400 MHz, CDCl_3): δ 7.90-7.92 (m, 2H), 7.86-7.88 (m, 1H), 7.34-7.40 (m, 2H), 1.39 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.7, 140.4, 134.5, 125.3, 124.3, 124.1, 122.5, 84.4, 24.8.

^{11}B NMR (128 MHz, CDCl_3): δ 29.3.

HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{18}\text{BO}_2\text{S}$ $[\text{M}+\text{H}]^+$ 261.1115, found 261.1105.

Borylation of 1-(furan-2-yl)ethan-1-one (3i):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1-(furan-2-yl)ethan-1-one (22.0mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane) gave 35.9 mg of borylated product **4i** (76%) as liquid.

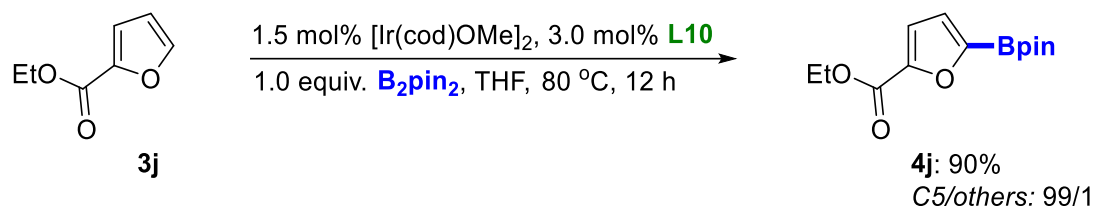
^1H NMR (400 MHz, CDCl_3): δ 7.13 (d, $J = 3.6$ Hz, 1H) 7.05 (d, $J = 3.6$ Hz, 1H), 2.45 (s, 3H), 1.31 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 187.6, 156.3, 124.4, 116.2, 84.6, 26.4, 24.6.

^{11}B NMR (128 MHz, CDCl_3): δ 27.1.

HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{17}\text{BKO}_4$ $[\text{M}+\text{K}]^+$ 275.0851, found 275.0885.

Borylation of ethyl furan-2-carboxylate (3j):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl furan-2-carboxylate (28.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 47.9 mg of borylated product **4j**(90%) as liquid. Spectral data are in accordance with the reported data.⁸³

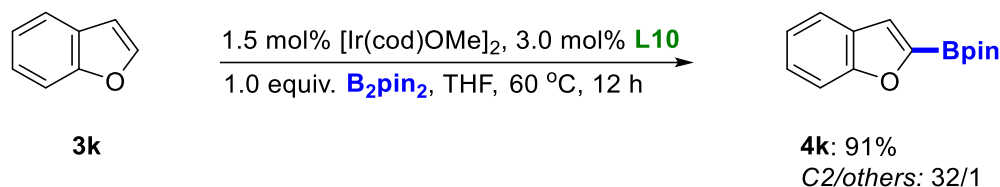
^1H (400 MHz, CDCl_3): δ 7.16 (d, $J = 3.6$ Hz, 1H), 7.07 (d, $J = 3.6$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.7, 148.7, 124.1, 117.7, 84.7, 61.0, 24.7, 14.3.

^{11}B (128 MHz, CDCl_3): δ 27.1.

HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{20}\text{BO}_5$ $[\text{M}+\text{H}]^+$ 267.1404, found 267.1384.

Borylation of benzofuran (3k):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, benzofuran (23.6 mg, 0.2 mmol) was added. The microreactor was capped with a Teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic

separation with silica gel (5% ethyl acetate in hexane) gave 44.4 mg of borylated product **4k**(91%) as solid. Spectral data are in accordance with the reported data.⁸⁷

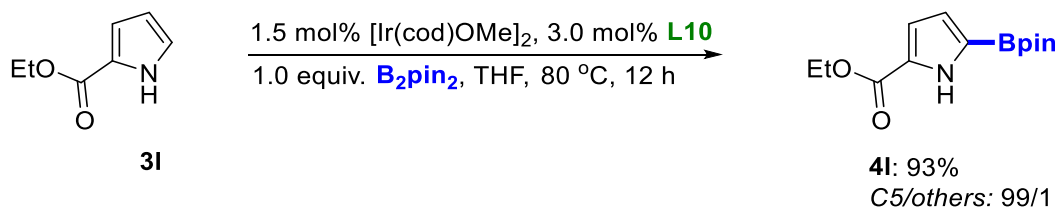
¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, J = 7.6 Hz, 1H), 7.57(d, J = 8.4 Hz, 1H),7.40(s, 1H), 7.32-7.36 (m, 1H), 7.23 (t, J = 7.2 Hz, 1H), 1.39 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 157.5, 127.5, 125.9, 122.7, 121.9, 119.5, 111.9, 84.7, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 27.6.

HRMS (ESI) *m/z* calcd for C₁₄H₁₇BNaO₃ [M+Na]⁺ 267.1163, found 267.1195.

Borylation of ethyl 1H-pyrrole-2-carboxylate (3l):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl 1H-pyrrole-2-carboxylate (27.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 49.3 mg of borylated product **4l**(93%) as solid. Spectral data are in accordance with the reported data.⁸³

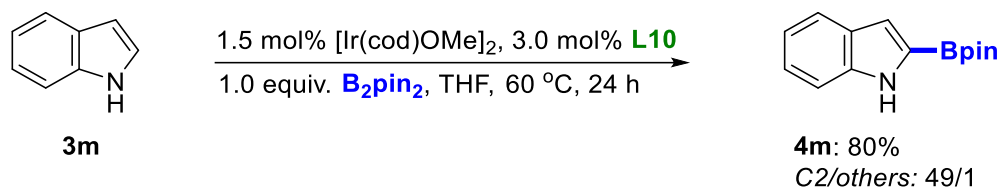
¹H (400 MHz, CDCl₃): δ 9.46 (br s, 1H), 6.90 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.76 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.32 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 160.8, 126.9, 120.6, 115.4, 84.2, 60.5, 24.7, 14.4.

¹¹B (128 MHz, CDCl₃): δ 28.0.

HRMS (ESI) *m/z* calcd for C₁₃H₂₀BNNaO₄ [M+Na]⁺ 288.1383, found 288.1392.

Borylation of 1H-indole (3m):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1*H*-indole (23.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane) gave 38.9 mg of borylated product **4m** (80%) as off white solid. Spectral data are in accordance with the reported data.⁸⁸

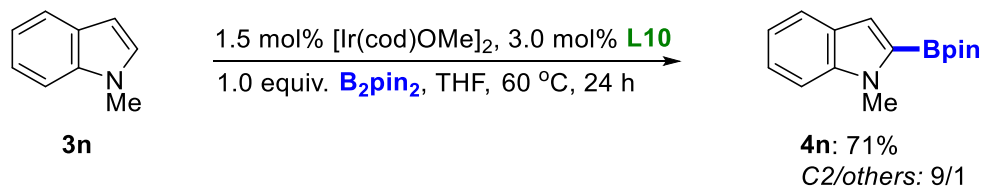
^1H (400 MHz, CDCl_3): δ 8.72 (br s, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.41(d, $J = 8.0$ Hz, 1H), 7.27 (t, $J = 7.2$ Hz, 1H), 7.18 (s, 1H), 7.14 (t, $J = 7.6$ Hz, 1H), 1.40 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 138.2, 128.3, 123.6, 121.6, 119.7, 113.9, 111.3, 84.1, 24.8.

^{11}B (128 MHz, CDCl_3): δ 28.6.

HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{BNO}_2$ $[\text{M}+\text{H}]^+$ 244.1503, found 244.1501.

Borylation of 1-methyl-1H-indole (3n):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1-methyl-1*H*-indole (26.2mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and

chromatographic separation with silica gel (3% ethyl acetate in hexane) gave 36.5 mg of borylated product **4n** (71%) as liquid. Spectral data are in accordance with the reported data.⁸⁸

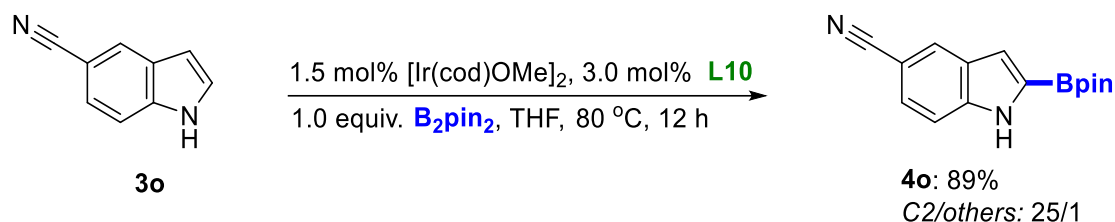
¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 8.0 Hz, 1H) 7.36 (d, J = 8.4 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.17 (s, 1H), 7.11(t, J = 7.6 Hz, 1H), 4.00 (s, 3H), 1.39 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 140.1, 127.8, 123.1, 121.6, 119.3, 114.2, 109.6, 83.7, 32.2, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 28.7.

HRMS (ESI) *m/z* calcd for C₁₅H₂₁BNO₂ [M+H]⁺ 258.1660, found 258.1659.

Borylation of 1H-indole-5-carbonitrile (3o):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1H-indole-5-carbonitrile (28.4mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane) gave 47.7 mg of borylated product **4o** (89%) as white solid.

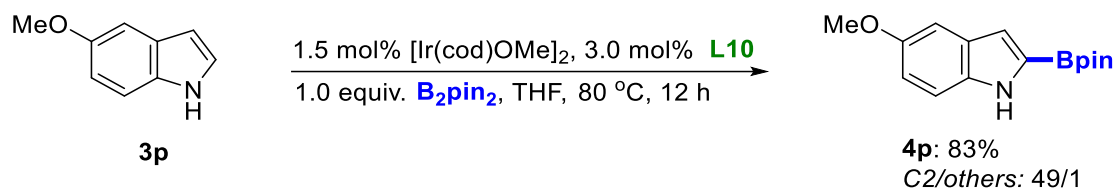
¹H NMR (400 MHz, CDCl₃): δ 8.94 (br s, 1H), 8.02 (s, 1H), 7.43 (s, 1H), 7.15 (d, J = 2.0 Hz, 1H), 1.36 (s, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 139.5, 127.9, 127.4, 126.0, 120.6, 114.2, 112.2, 103.0, 84.6, 24.8.

¹¹B NMR (128 MHz, CDCl₃): δ 28.1.

HRMS (ESI) *m/z* calcd for C₁₅H₁₇BN₂NaO₂ [M+Na]⁺ 291.1275, found 291.1263.

Borylation of 5-methoxy-1H-indole (3p):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 5-methoxy-1H-indole (29.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane) gave 45.3 mg of borylated product **4p** (83%) as white solid. Spectral data are in accordance with the reported data.⁸⁸

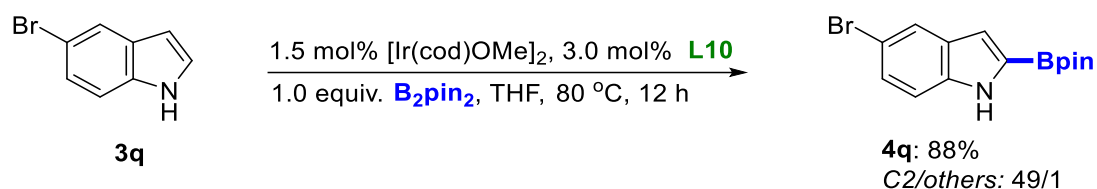
^1H NMR (400 MHz, CDCl_3): δ 8.57 (br s, 1H), 7.27 (d, $J = 8.8$ Hz, 1H), 7.09 (d, $J = 1.6$ Hz, 1H), 7.04 (s, 1H), 6.91 (dd, $J = 8.8$ Hz, 2.0 Hz, 1H), 3.85 (s, 3H), 1.36 (s, 12 H).

^{13}C NMR (100 MHz, CDCl_3): δ 154.1, 133.6, 128.6, 114.9, 113.3, 112.0, 102.0, 84.1, 55.7, 24.8.

^{11}B NMR (128 MHz, CDCl_3): δ 28.4.

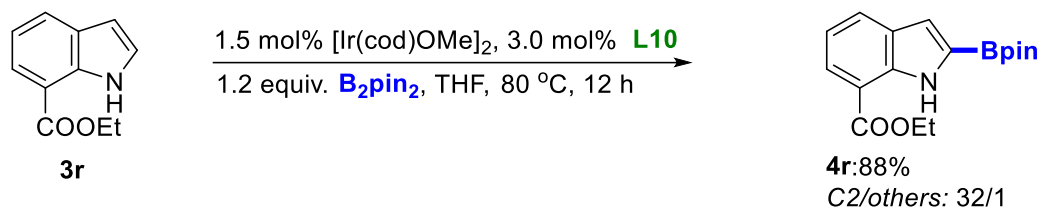
HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{BNO}_3$ $[\text{M}+\text{H}]^+$ 274.1609, found 274.1580.

Borylation of 5-bromo-1H-indole (3q):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 5-bromo-1H-indole (39.2 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane) gave 56.7 mg of borylated product **4q** (88%) as solid. Spectral data are in accordance with the reported data.⁸⁸

Borylation of ethyl 1*H*-indole-7-carboxylate (**3r**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl 1*H*-indole-7-carboxylate (37.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane) gave 55.4 mg of borylated product **4r** (88%) as white solid. Spectral data are in accordance with the reported data.⁸³

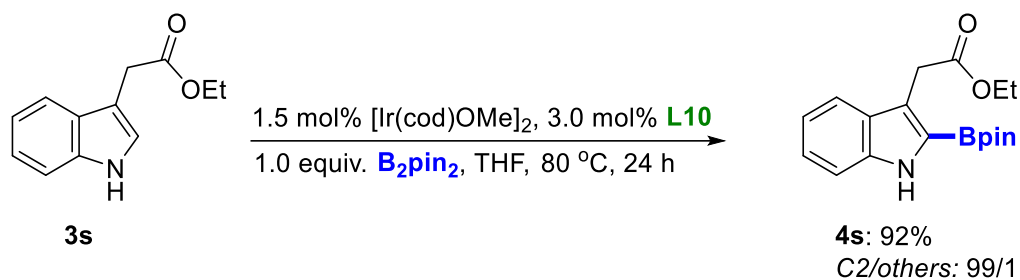
^1H NMR (400 MHz, CDCl_3): δ 10.11 (br s, 1H), 7.94 (dd, $J = 7.6$ Hz, 1.2 Hz, 1H), 7.87 (d, $J = 7.6$ Hz, 1H), 7.11-7.15 (m, 2H), 4.46 (q, $J = 7.2$ Hz, 2H), 1.46 (t, $J = 7.2$ Hz, 3H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 167.4, 137.9, 129.6, 127.2, 125.8, 119.0, 113.6, 113.1, 84.2, 60.7, 24.8, 14.4.

^{11}B NMR (128 MHz, CDCl_3): δ 28.8.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{23}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 316.1715, found 316.1717.

Borylation of ethyl 2-(1H-indol-3-yl)acetate (3s):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, ethyl 2-(1*H*-indol-3-yl)acetate (40.6mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (8% ethyl acetate in hexane) gave 60.6mg of borylated product **4s**(92%) as liquid.

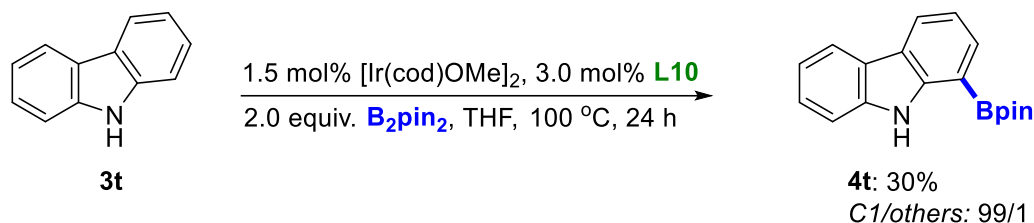
^1H NMR (400 MHz, CDCl_3): δ 8.54 (br s, 1H), 7.66 (d, $J = 8.0\text{Hz}$, 1H), 7.35 (d, $J = 8.4 \text{ Hz}$, 1H), 7.22-7.26 (m, 1H), 7.11 (dt, $J = 8.0 \text{ Hz}$, 0.8Hz, 1H), 4.16 (q, $J = 7.2 \text{ Hz}$, 2H), 4.11 (s, 2H), 1.36 (s, 12 H), 1.26 (t, $J = 7.2\text{Hz}$, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 138.0, 128.0, 123.7, 120.6, 119.9, 119.5, 111.3, 83.9, 60.5, 31.4, 24.8, 14.2.

^{11}B NMR (128 MHz, CDCl_3): δ 28.4.

HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{25}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 330.1871, found 330.1851.

Borylation of 9H-carbazole (3t):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 9H-carbazole (33.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane) gave 17.6mg of borylated product **4t** (30%) as white solid. Spectral data are in accordance with the reported data.⁸⁹

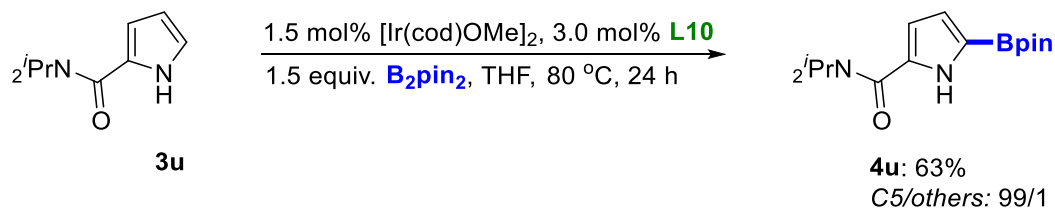
¹H (400 MHz, CDCl₃): δ 9.18 (br s, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 6.8 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.23-7.28 (m, 2H), 1.46(s, 12H).

¹³C (100 MHz, CDCl₃): δ 145.0, 139.3, 132.8, 125.7, 123.6, 122.9, 122.3, 120.3, 119.1, 118.7, 110.6, 84.0, 25.0.

¹¹B (128 MHz, CDCl₃): δ 30.8.

HRMS (ESI) *m/z* calcd for C₁₈H₂₁BNO₂ [M+H]⁺ 294.1660, found 294.1656.

Borylation of N,N-diisopropyl-1H-pyrrole-2-carboxamide (3u):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, N,N-diisopropyl-1H-pyrrole-2-carboxamide (38.9 mg, 0.2 mmol) was added. The microreactor was capped with a

teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane) gave 40.4 mg of borylated product **4u**(63%) as solid. Spectral data are in accordance with the reported data.⁸³

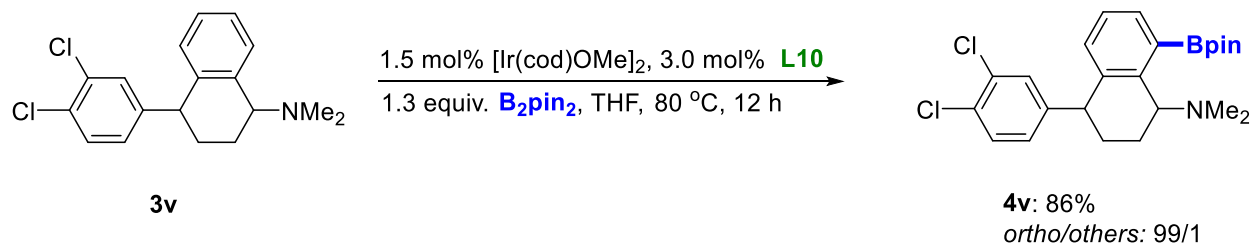
¹H NMR (400 MHz, CDCl₃): δ 9.73 (br s, 1H), 6.74 (t, J = 3.0 Hz, 1H), 6.44 (dd, J = 3.6 Hz, J = 2.4 Hz, 1H), 4.1 (br s, 2H), 1.38 (br s, 12 H), 1.29 (s, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 161.8, 130.5, 119.6, 110.9, 83.8, 48.2, 24.7, 20.9.

¹¹B NMR (128 MHz, CDCl₃): δ 27.5.

HRMS (ESI) m/z calcd for C₁₇H₃₀BN₂O₃ [M+H]⁺ 321.2349, found 321.2360.

Borylation of 4-(3,4-dichlorophenyl)-N,N-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (3v):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (66 mg, 1.3 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-(3,4-dichlorophenyl)-N,N-dimethyl-1,2,3,4-tetrahydronaphthalen-1-amine (64.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (1% methanol in DCM) gave 76.7 mg of borylated product **4v** (86%) as gummy liquid.

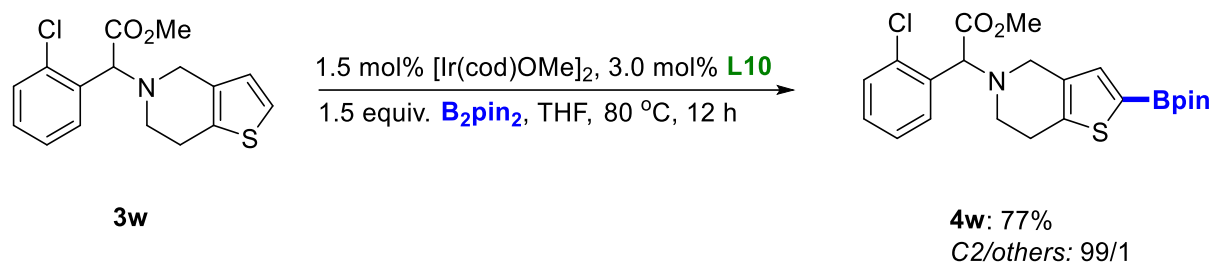
¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, J = 7.2 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.83 (s, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 4.17 (d, J = 5.2 Hz, 1H), 4.08 (dd, J = 12.0 Hz, 5.2 Hz, 1H), 2.66 (s, 3H), 2.21 (br s, 4H), 2.00-2.01 (m, 1H), 1.72-1.74 (m, 1H), 1.47 (q, J = 12.0 Hz, 1H), 1.32 (s, 6H), 1.30 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 147.6, 139.7, 133.0, 132.0, 130.4, 129.8, 129.7, 129.5, 128.2, 128.1, 127.8, 80.2, 66.6, 41.4, 30.4, 27.2, 26.0, 15.3.

^{11}B NMR (128 MHz, CDCl_3): δ 14.8.

HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{31}\text{BCl}_2\text{NO}_2$ $[\text{M}+\text{H}]^+$ 446.1825, found 446.1820.

Borylation of Clopidogrel drug (3w):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), **B₂pin₂** (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, clopidogrel (64.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (1% methanol in DCM as eluent) gave 68.9 mg of borylated product **4w** (77%) as gummy liquid. Spectral data are in accordance with the reported data.⁹⁰

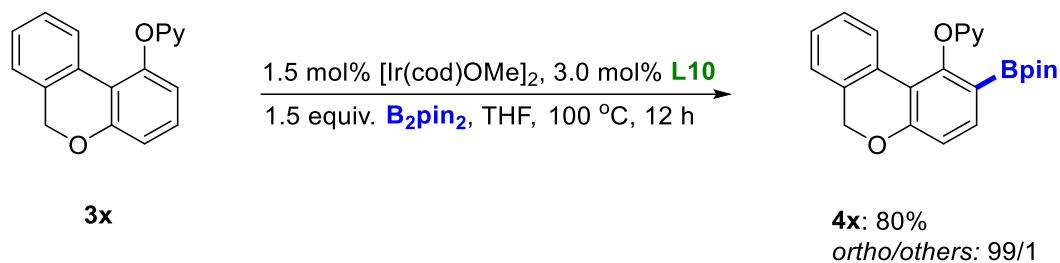
^1H NMR (400 MHz, CDCl_3): δ 7.65 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H), 7.36-7.38 (m, 1H), 7.23-7.28 (m, 2H), 7.21 (s, 1H), 4.90 (s, 1H), 3.61-3.77 (m, 5H), 2.87-2.88 (m, 4H), 1.29 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 141.1, 135.5, 134.9, 134.5, 133.7, 129.8, 129.7, 129.3, 127.0, 83.8, 67.6, 52.0, 50.4, 47.9, 25.8, 24.6.

^{11}B NMR (128 MHz, CDCl_3): δ 29.7.

HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{28}\text{BCINO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 448.1521, found 448.1533.

Borylation of 2-((6*H*-benzo[*c*]chromen-1-yl)oxy)pyridine (**3x**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-((6*H*-benzo[*c*]chromen-1-yl)oxy)pyridine (55.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane) gave 64.2 mg of borylated product **4x** (80%) as white solid.

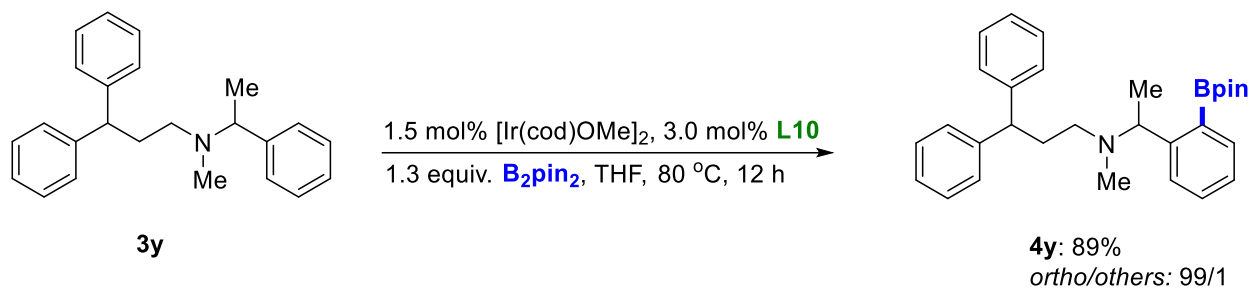
^1H NMR (400 MHz, CDCl_3): δ 8.34-8.38 (m, 2H), 7.75 (ddd, $J = 8.4 \text{ Hz, } 7.2 \text{ Hz, } 2.0 \text{ Hz, } 1\text{H}$), 7.67 (d, $J = 8.0 \text{ Hz, } 1\text{H}$), 7.31 (td, $J = 8.0 \text{ Hz, } 1.6 \text{ Hz, } 1\text{H}$), 7.23 (td, $J = 7.2 \text{ Hz, } 0.8 \text{ Hz, } 1\text{H}$), 7.13-7.15 (m, 2H), 7.02-7.06 (m, 1H), 6.96 (d, $J = 8.0 \text{ Hz, } 1\text{H}$), 5.02 (s, 2H), 1.17 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.5, 158.0, 154.8, 144.0, 140.3, 134.5, 132.3, 128.24, 128.2, 127.2, 126.6, 124.5, 117.9, 115.2, 114.5, 113.1, 82.0, 68.9, 25.3.

^{11}B NMR (128 MHz, CDCl_3): δ 19.4.

HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{25}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 402.1877, found 402.1878.

Borylation of *N*-methyl-3,3-diphenyl-*N*-(1-phenylethyl)propan-1-amine (**3y**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})_2]$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (66.0 mg, 1.3 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-methyl-3,3-diphenyl-*N*-(1-phenylethyl)propan-1-amine (65.9 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80°C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane) gave 81.1 mg of borylated product **4y** (89%) as gummy liquid.

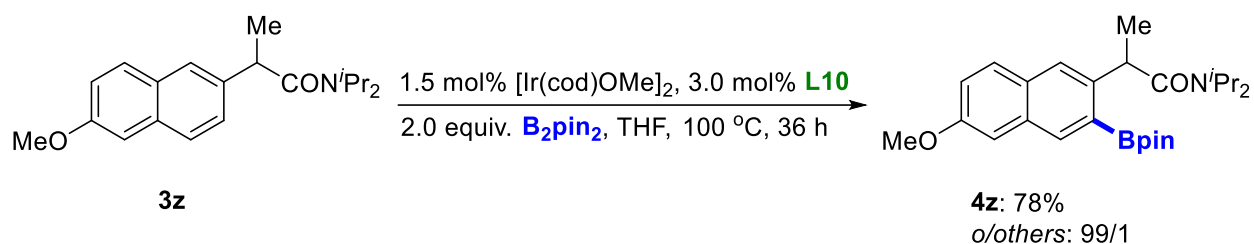
^1H NMR (400 MHz, CDCl_3): δ 7.50-7.52 (m, 1H), 7.12-7.28 (m, 12H), 7.01-7.02 (m, 1H), 4.03 (q, $J = 6.4$ Hz, 1H), 3.80 (t, $J = 7.6$ Hz, 1H), 2.70-2.77 (m, 1H), 2.59-2.67 (m, 1H), 2.25- 2.42 (m, 5H), 1.35 (d, $J = 6.8$ Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 146.8, 144.1, 144.0, 131.5, 128.5, 128.5, 127.7, 127.6, 127.6, 126.8, 126.3, 126.3, 122.8, 80.6, 63.1, 52.2, 49.6, 39.6, 29.9, 26.5, 26.4, 17.3.

^{11}B NMR (128 MHz, CDCl_3): δ 17.9.

HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{39}\text{BNO}_2$ $[\text{M}+\text{H}]^+$ 456.3074, found 456.3073.

Borylation of N,N-diisopropyl-2-(6-methoxynaphthalen-2-yl)propanamide (3z):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-2-(6-methoxynaphthalen-2-yl)propanamide (62.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 36 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (50% ethyl acetate in hexane as eluent) gave 26.4 mg of borylated product **4z** (78% yield based on recovered starting material) as gummy liquid and 38.6 mg of *N,N*-diisopropyl-2-(6-methoxynaphthalen-2-yl)propanamide (**3y**).

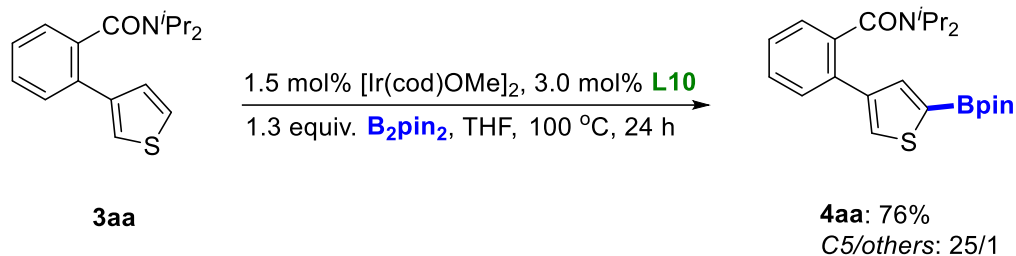
^1H NMR (400 MHz, CDCl_3): δ 8.13 (s, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.60 (s, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.04 (s, 1H), 4.04-4.11 (m, 1H), 3.19 (s, 3H), 3.25-3.31 (m, 1H), 1.42-1.46 (m, 6H), 1.39-1.42 (s & m, 15H), 1.12 (d, $J = 6.8\text{Hz}$), 0.48 (d, $J = 6.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 160.8, 138.0, 137.8, 135.0, 128.6, 127.1, 126.9, 126.1, 104.5, 83.7, 55.7, 48.3, 45.8, 44.7, 24.8, 21.0, 20.93, 20.90, 20.1, 19.7.

^{11}B NMR (128 MHz, CDCl_3): δ 31.7.

HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{39}\text{BNO}_4$ $[\text{M}+\text{H}]^+$ 440.2967, found 440.2968.

Borylation of N,N-diisopropyl-2-(thiophen-3-yl)benzamide (3aa):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (66.1 mg, 1.3 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-2-(thiophen-3-yl)benzamide (57.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 62.8 mg of borylated product **4aa** (76%) as gummy liquid.

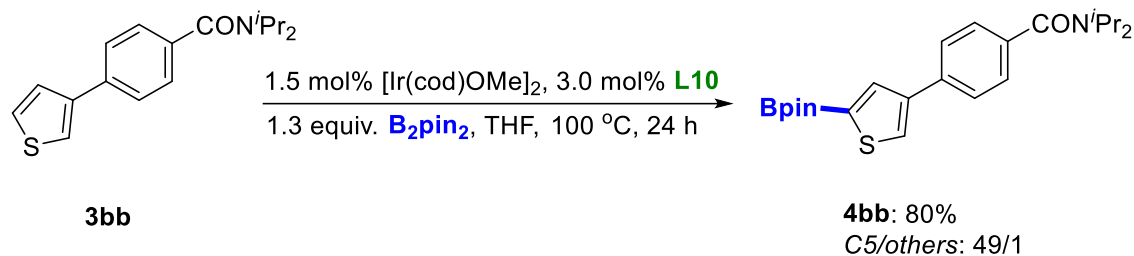
^1H NMR (400 MHz, CDCl_3): δ 7.80 (s, 1H), 7.77 (d, $J = 0.8$ Hz, 1H), 7.44-7.46 (m, 1H), 7.22-7.35 (m, 3H), 3.40 (sept, $J = 6.8$ Hz, 1H), 3.27 (sept, $J = 6.8$ Hz, 1H), 1.52 (d, $J = 6.8$ Hz, 3H), 1.39 (d, $J = 6.8$ Hz, 3H), 1.32 (s, 12H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.42 (d, $J = 6.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.4, 141.5, 138.5, 137.6, 131.9, 130.8, 128.6, 128.3, 127.4, 126.2, 84.0, 50.5, 45.6, 24.7, 24.6, 20.7, 20.5, 19.6, 19.4.

^{11}B NMR (128 MHz, CDCl_3): δ 28.7.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{BNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 414.2269, found 414.2276.

Borylation of *N,N*-diisopropyl-4-(thiophen-3-yl)benzamide (**3bb**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (66.1 mg, 1.3 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropyl-4-(thiophen-3-yl)benzamide (57.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 66 mg of borylated product **4bb** (80%) as gummy liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.91 (s, 1H), 7.74 (s, 1H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 3.67 (br s, 2H), 1.12-1.157 (br s, 24H).

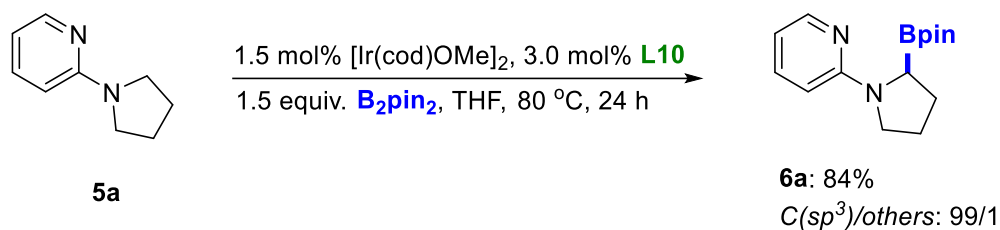
^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 142.9, 137.5, 136.0, 135.8, 127.8, 126.4, 126.2, 84.2, 50.8, 45.7, 24.7, 20.7.

^{11}B NMR (128 MHz, CDCl_3): δ 29.2.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{BNO}_3\text{S}$ $[\text{M}+\text{H}]^+$ 414.2269, found 414.2274.

Borylation of strong aliphatic C(sp³)-H bonds:

Borylation of 2-(pyrrolidin-1-yl)pyridine (5a):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-(pyrrolidin-1-yl)pyridine (29.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 46.1 mg of borylated product **5a** (84%) as white solid. Spectral data are in accordance with the reported data.⁹¹

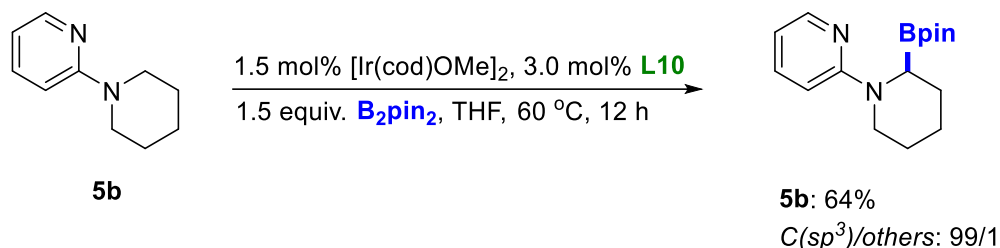
¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 5.6 Hz, 1H), 7.45-7.50 (m, 1H), 6.51 (dt, J = 6.8 Hz, 0.8 Hz, 1H), 6.40 (d, J = 8.8 Hz, 1H), 3.44 (dt, J = 9.2 Hz, 2.0 Hz, 1H), 3.06 (dd, J = 17.2 Hz, 9.6 Hz, 1H), 2.74 (dd, J = 12 Hz, 6.4 Hz, 1H), 2.06-2.15 (m, 1H), 1.94-2.00 (m, 1H), 1.81-1.87 (m, 1H), 1.43-1.54 (m, 1H), 1.22 (s, 12H)

¹³C NMR (100 MHz, CDCl₃): δ 159.0, 141.2, 139.5, 111.2, 108.2, 79.2, 47.3, 28.9, 27.2, 26.0, 25.8.

¹¹B NMR (128 MHz, CDCl₃): δ 10.4.

HRMS (ESI) *m/z* calcd for C₁₅H₂₃BN₂NaO₂ [M+Na]⁺ 275.1925, found 275.1924.

Borylation of 2-(piperidin-1-yl)pyridine (5b):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-(piperidin-1-yl)pyridine (32.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 36.9 mg of borylated product **5b** (64%) as white solid. (Notably, minor amount di borylation observed). Spectral data are in accordance with the reported data.⁹²

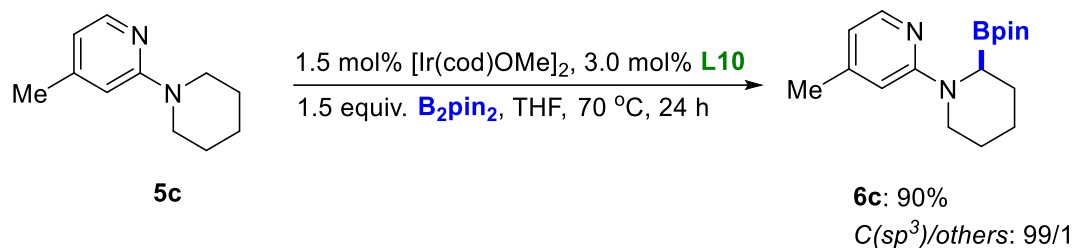
¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, J = 5.6 Hz, 1H), 7.41-7.45 (m, 1H), 6.43 (d, J = 8.8 Hz, 1H), 6.73 (dt, J = 6.8 Hz, 0.4 Hz, 1H), 3.66-3.70 (m, 1H), 2.98 (dt, J = 12.4 Hz, 3.2 Hz, 1H), 2.36 (dd, J = 12.0 Hz, 2.8 Hz, 1H), 1.88-1.89 (m, 1H), 1.76-1.79 (m, 1H), 1.68-1.71 (m, 1H), 1.35-1.48 (m, 3H), 1.17-1.28 (m, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 156.0, 141.0, 139.4, 109.2, 105.4, 79.0, 43.7, 27.1, 26.7, 26.3, 26.1, 25.9, 25.7, 25.2.

¹¹B NMR (128 MHz, CDCl₃): δ 9.6.

HRMS (ESI) *m/z* calcd for C₁₆H₂₆BN₂O₂ [M+H]⁺ 289.2082, found 289.2085.

Borylation of 4-methyl-2-(piperidin-1-yl)pyridine (**5c**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 4-methyl-2-(piperidin-1-yl)pyridine (35.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 54.4 mg of borylated product **5c** (90%) as white solid. Spectral data are in accordance with the reported data.⁹¹

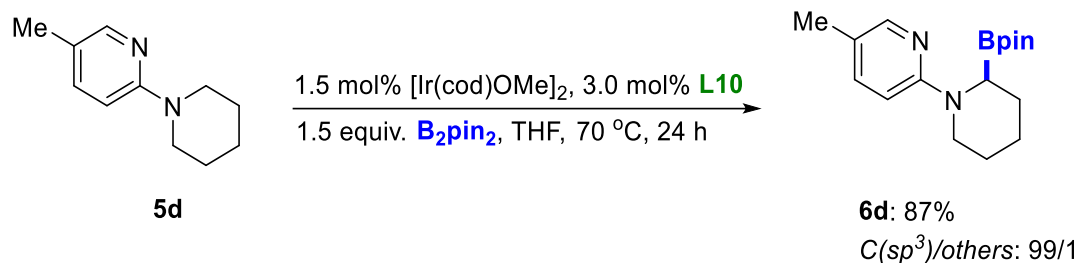
¹H NMR (400 MHz, CDCl_3): δ 7.74 (d, $J = 7.2$ Hz, 1H), 6.19-6.20 (m, 2H), 3.65-3.67 (m, 1H), 2.94 (dt, $J = 12.8$ Hz, 3.6 Hz, 1H), 2.33 (dd, $J = 12.4$ Hz, 3.2 Hz, 1H), 2.22 (s, 12 H), 1.84-1.87 (m, 1H), 1.72-1.76 (m, 1H), 1.65-1.68 (m, 1H), 1.32-1.45 (m, 3H), 1.14-1.26 (m, 12 H).

¹³C NMR (100 MHz, CDCl_3): δ 156.2, 152.9, 138.6, 111.3, 104.8, 78.9, 43.7, 27.2, 26.7, 26.3, 26.2, 25.9, 25.8, 25.3, 21.8.

¹¹B NMR (128 MHz, CDCl_3): δ 9.4.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{BN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 303.2238, found 303.2237.

Borylation of 5-methyl-2-(piperidin-1-yl)pyridine (**5d**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 5-methyl-2-(piperidin-1-yl)pyridine (32.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 52.6 mg of borylated product **6d** (87%) as white solid.

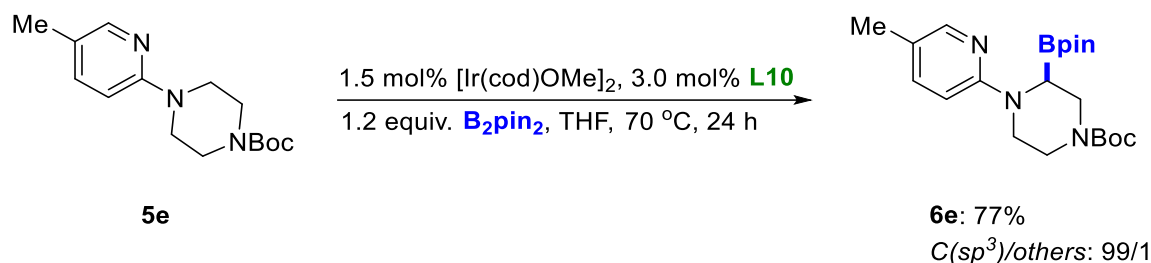
^1H NMR (400 MHz, CDCl_3): δ 7.67 (s, 1H), 7.27 (dd, $J = 8.8 \text{ Hz, } 1.6 \text{ Hz}$, 1H), 6.36 (d, $J = 8.8 \text{ Hz}$, 1H), 3.62-3.65 (m, 1H), 2.95 (dt, $J = 12.8 \text{ Hz, } 3.2 \text{ Hz}$, 1H), 2.33 (dd, $J = 12.0 \text{ Hz, } 2.8 \text{ Hz}$, 1H), 2.11 (s, 3H), 1.83-1.86 (m, 1H), 1.72-1.75 (m, 1H), 1.64-1.67 (m, 1H), 1.32-1.45 (m, 3H), 1.16-1.28 (m, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 155.0, 143.0, 137.8, 118.3, 105.1, 79.0, 43.8, 27.2, 26.9, 26.4, 26.3, 26.0, 25.8, 25.3, 17.2.

^{11}B NMR (128 MHz, CDCl_3): δ 9.7.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{27}\text{BN}_2\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 303.2238, found 303.2240.

Borylation of *tert*-butyl 4-(5-methylpyridin-2-yl)piperazine-1-carboxylate (**5e**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *tert*-butyl 4-(5-methylpyridin-2-yl)piperazine-1-carboxylate (55.5 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 62.1 mg of borylated product **6e** (77%) as white solid.

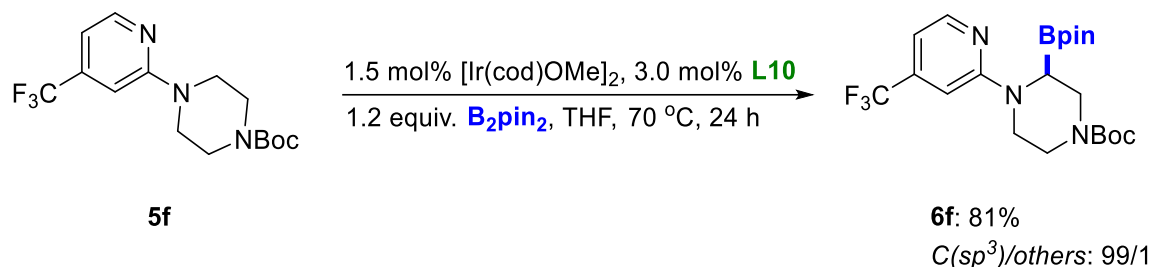
¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 1H), 7.37 (J = 8.8 Hz, 1H), 6.42 (d, J = 8.8 Hz, 1H), 4.10 (br s, 2H), 3.53 (d, J = 12.4), 3.13 (m, 1H), 2.79-2.86 (m, 2H), 2.49-2.53 (m, 2H), 2.16 (s, 3H), 1.47 (s, 9H), 1.19-1.28 (m, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 163.1, 155.2, 143.5, 138.0, 119.8, 105.3, 79.6, 79.3, 47.1, 43.0, 42.7, 28.4, 26.8, 26.2, 25.8, 17.6.

¹¹B NMR (128 MHz, CDCl₃): δ 9.4.

HRMS (ESI) *m/z* calcd for C₂₁H₃₅BN₃O₄ [M+H]⁺ 404.2715, found 404.2717.

Borylation of *tert*-butyl 4-(4-(trifluoromethyl)pyridin-2-yl)piperazine-1-carboxylate (**5f**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B_2pin_2 (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *tert*-butyl 4-(4-(trifluoromethyl)pyridin-2-yl)piperazine-1-carboxylate (66.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 74.1 mg of borylated product **6f** (81%) as white solid.

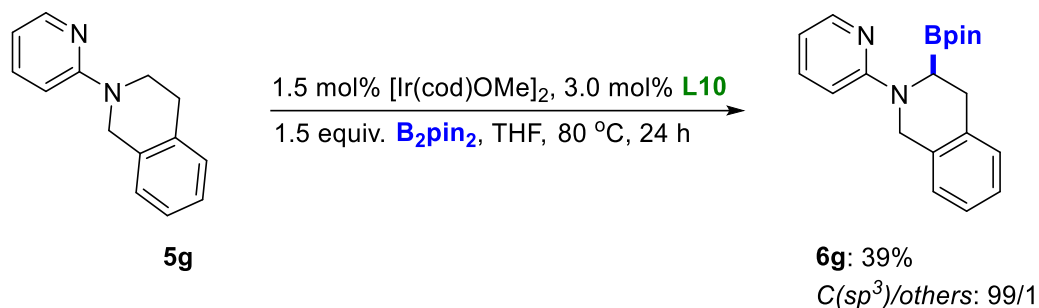
^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J = 6.4$ Hz, 1H), 6.70 (s, 1H), 6.30 (d, $J = 6.4$ Hz, 1H), 4.16 (br s, 2H), 3.61 (d, $J = 12.4$ Hz, 1H), 3.21 (br s, 1H), 2.85-2.88 (m, 2H), 2.57-2.59 (m, 1H), 1.46 (s, 9H), 1.22 (s, 12H).

^{13}C NMR (100 MHz, CDCl_3): δ 156.1, 154.7, 143.5 (q, $J = 34.0$ Hz), 141.5, 121.0 (q, $J = 272.5$ Hz), 106.0 (q, $J = 2.8$ Hz), 102.6 (q, $J = 3.4$ Hz), 79.9, 79.7, 51.5, 46.7, 43.2, 28.3, 26.4, 25.9.

^{11}B NMR (128 MHz, CDCl_3): δ 9.7.

HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{32}\text{BF}_3\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$ 458.2432, found 458.2436.

Borylation of 2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (**5g**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinoline (42.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 26.2 mg of borylated product **6g** (39%) as white solid.

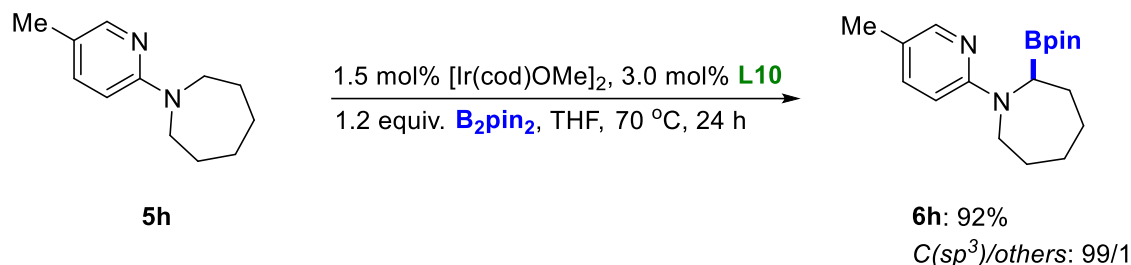
¹H NMR (400 MHz, CDCl₃): δ 7.99-8.01 (m, 1H), 7.53-7.58 (m, 1H), 7.11-7.23 (m, 4H), 6.51-6.54 (m, 2H), 4.57 (d, J = 16 Hz, 1H), 4.44 (d, J = 16 Hz, 1H), 2.83-2.85 (m, 2H), 2.69 (t, J = 7.2 Hz, 1H), 1.21-1.35 (br m, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 156.5, 141.6, 139.6, 137.7, 131.6, 129.4, 126.5, 126.1, 125.7, 110.4, 105.9, 79.4, 44.8, 31.0, 26.8, 26.4, 26.2, 26.1.

¹¹B NMR (128 MHz, CDCl₃): δ 9.8.

HRMS (ESI) *m/z* calcd for C₂₀H₂₆BN₂O₂ [M+H]⁺ 337.2082, found 337.2085.

Borylation of 1-(5-methylpyridin-2-yl)azepane (**5h**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (61.0 mg, 1.2 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 1-(5-methylpyridin-2-yl)azepane (38.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 58.2 mg of borylated product **6h** (92%) as white solid.

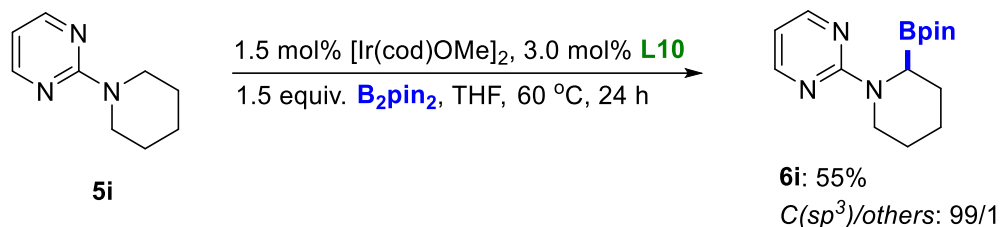
¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 1H), 7.30 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 6.30 (d, J = 8.8 Hz, 1H), 3.30-3.35 (m, 1H), 3.18-3.324 (m, 1H), 2.56 (d, J = 9.6 Hz, 1H), 2.11 (s, 3H), 2.01-2.06 (m, 1H), 1.73-1.91 (m, 3H), 1.13-1.34 (m, 16H).

¹³C NMR (100 MHz, CDCl₃): δ 155.7, 143.1, 137.5, 118.6, 105.4, 79.2, 78.9, 47.8, 32.1, 30.1, 30.3, 29.6, 26.8, 26.2, 26.1, 25.9, 17.2.

¹¹B NMR (128 MHz, CDCl₃): δ 9.6.

HRMS (ESI) m/z calcd for C₁₈H₃₀BN₂O₂ [M+H]⁺ 317.2395, found 317.2396.

Borylation of 2-(piperidin-1-yl)pyrimidine (**5i**):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-(piperidin-1-yl)pyrimidine (32.6 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 31.8 mg of borylated product **6i** (55%) as gummy liquid. (Notably, minor amount di borylation observed).

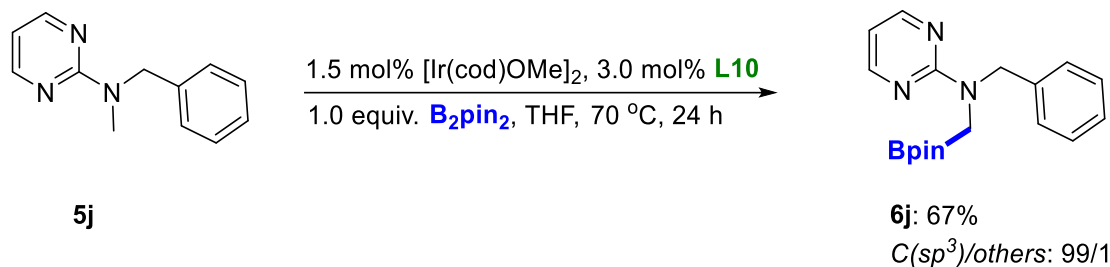
¹H NMR (400 MHz, CDCl₃): δ 8.34 (dd, J = 4.4 Hz, 2.4 Hz, 1H), 8.12 (dd, J = 6.0 Hz, 2.4 Hz, 1H), 6.36 (dd, J = 5.6 Hz, 4.8 Hz, 1H), 4.32-4.36 (m, 1H), 2.87 (dt, J = 12.8 Hz, 3.2 Hz, 1H), 2.45 (dd, 12.4 Hz, 3.2 Hz, 1H), 1.86-1.89 (m, 1H), 1.76-1.80 (m, 1H), 1.69-1.73 (m, 1H), 1.31-1.48 (m, 3H), 1.19-1.21 (m, 12 H).

¹³C NMR (100 MHz, CDCl₃): δ 163.7, 157.9, 149.5, 106.6, 79.3, 42.4, 27.3, 26.3, 25.9, 25.7, 25.0.

¹¹B NMR (128 MHz, CDCl₃): δ 9.1.

HRMS (ESI) *m/z* calcd for C₁₅H₂₅BN₃O₂ [M+H]⁺ 290.2034, found 290.2040.

Borylation of N-benzyl-N-methylpyrimidin-2-amine (5j):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-benzyl-*N*-methylpyrimidin-2-amine (40.0 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 43.6 mg of borylated product **6j** (67%) as white solid. (Notably, trace amount of benzylic borylation observed).

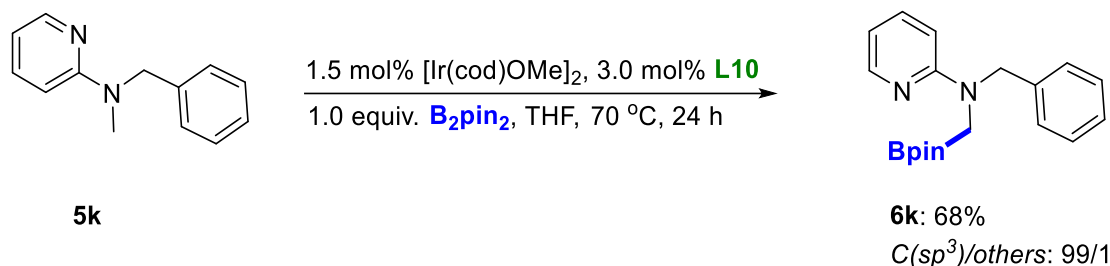
¹H NMR (400 MHz, CDCl₃): δ 8.43 (d, J = 4.4 Hz, 2.4 Hz, 1H), 8.18 (d, J = 5.6 Hz, 2.0 Hz, 1H), 7.22-7.31 (m, 5H), 6.49 (dd, J = 5.6 Hz, 4.4 Hz, 1H), 4.73 (s, 2H), 2.45 (s, 2H), 1.19 (s, 12H).

¹³C NMR (100 MHz, CDCl₃): δ 163.9, 149.5, 136.1, 128.5, 128.0, 127.5, 107.5, 79.5, 50.3, 25.7.

¹¹B NMR (128 MHz, CDCl₃): δ 9.2.

HRMS (ESI) m/z calcd for C₁₈H₂₅BN₃O₂ [M+H]⁺ 326.2034, found 326.2036.

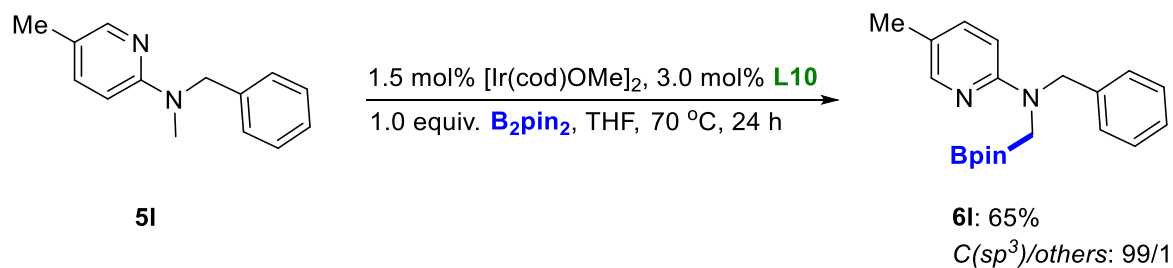
Borylation of N-benzyl-N-methylpyridin-2-amine (5k):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-benzyl-*N*-

methylpyridin-2-amine (39.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 44.1 mg of borylated product **6k** (68%) as white solid. Spectral data are in accordance with the reported data.⁹³

Borylation of N-benzyl-N,5-dimethylpyridin-2-amine (5l):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-benzyl-*N*,5-dimethylpyridin-2-amine (39.7 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 44.0 mg of borylated product **6l** (65%) as white solid.

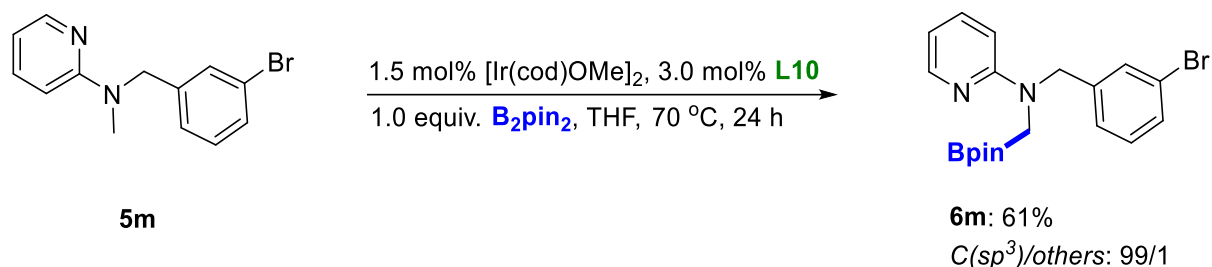
¹H NMR (400 MHz, CDCl₃): δ 7.75 (s, 1H), 7.27-7.31 (m, 4H), 7.17 (d, J = 7.2 Hz, 2H), 6.42 (d, J = 9.2 Hz, 1H), 4.49 (s, 2H), 2.53 (s, 2H), 2.15 (s, 3H), 1.22 (s, 12H)

¹³C NMR (100 MHz, CDCl₃): δ 156.9, 143.3, 137.9, 136.3, 128.7, 127.4, 126.9, 119.4, 105.8, 79.2, 52.0, 25.9, 17.2.

¹¹B NMR (128 MHz, CDCl₃): δ 9.6.

HRMS (ESI) *m/z* calcd for C₂₀H₂₈BN₂O₂ [M+H]⁺ 339.2238, found 339.2242.

Borylation of N-(3-bromobenzyl)-N-methylpyridin-2-amine (5m):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-(3-bromobenzyl)-*N*-methylpyridin-2-amine (55.4 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 70 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 49.2 mg of borylated product **6k** (61%) as white solid.

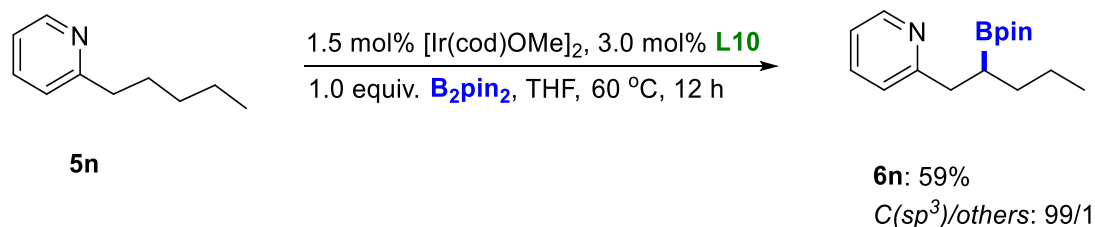
¹H NMR (400 MHz, CDCl₃): δ 8.99 (d, J = 4.8 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.52 (t, J = 6.8 Hz, 1H), 6.47 (d, J = 8.8 Hz, 1H), 4.48 (s, 2H), 2.53 (s, 2H), 1.22 (s, 12H)

¹³C NMR (100 MHz, CDCl₃): δ 158.1, 141.7, 139.7, 138.5, 130.8, 130.4, 130.0, 125.6, 122.9, 110.7, 106.0, 79.4, 51.7, 25.9.

¹¹B NMR (128 MHz, CDCl₃): δ 9.4.

HRMS (ESI) m/z calcd for C₁₉H₂₅BBrN₂O₂ [M+H]⁺ 403.1187, found 403.1186.

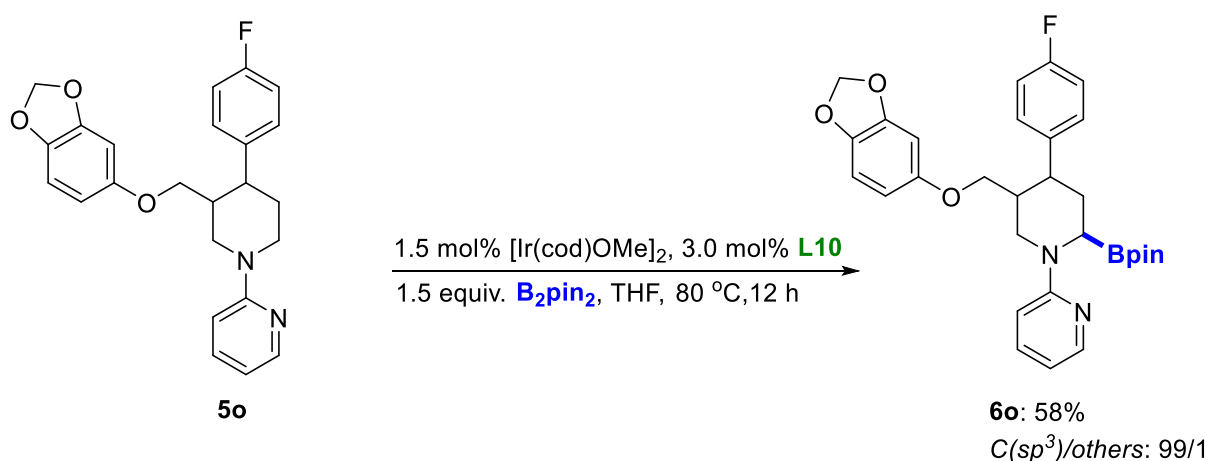
Borylation of 2-pentylpyridine (5n):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (50.8 mg, 1.0 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-pentylpyridine

(29.8 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 60 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 32.5 mg of borylated product **6n** (59%) as liquid. Spectral data are in accordance with the reported data.⁹⁴ (Notably, minor amount di borylation observed).

Borylation of 2-(3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)pyridine (5o):



In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L10** ligand (1.1 mg, 3.0 mol%), B₂pin₂ (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, 2-(3-((benzo[d][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidin-1-yl)pyridine (81.3 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 61.8 mg of borylated product **6o** (58%) as gummy liquid.

¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, J = 6.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.14 (dd, J = 7.6 Hz, 5.6 Hz, 2H), 6.96 (t, J = 8.4 Hz, 2H), 6.63 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 8.8 Hz, 1H), 6.36 (d, J = 1.6 Hz, 1H), 6.14 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 5.89 (s, 2H), 4.12 (dd, J = 13.2 Hz, 4.4 Hz, 1H), 3.58 (dd, J = 9.6 Hz, 3.2 Hz, 1H), 3.49 (t, J = 8.4 Hz, 1H), 3.07 (t, J = 12.4 Hz, 1H), 2.69 (dt,

$J = 12.4$ Hz, 2.4 Hz, 1H), 2.56 (dd, $J = 12.0$ Hz, 2.0 Hz, 1H), 2.00 - 2.08 (m, 1H), 1.91 - 1.96 (m, 1H), 1.63 - 1.73 (m, 1H), 1.12 - 1.29 (m, 12H).

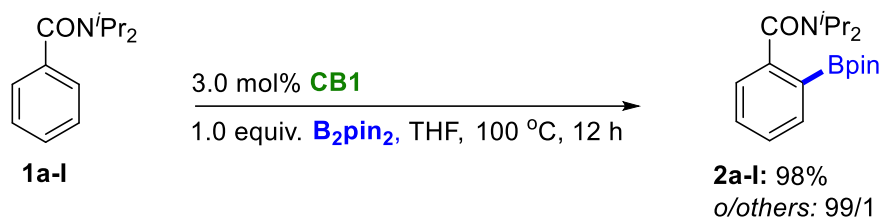
^{13}C NMR (100 MHz , CDCl_3): δ 161.5 (d, $J = 243.0$ Hz), 156.3 , 154.1 , 148.2 , 141.8 , 141.6 , 139.7 (d, $J = 3.5$ Hz), 139.6 , 128.8 (d, $J = 7.4$ Hz), 115.4 (d, $J = 21.0$ Hz), 110.1 , 107.9 , 105.7 , 105.6 , 101.1 , 97.9 , 79.31 , 79.29 , 69.4 , 46.7 , 45.6 , 42.0 , 35.0 , 35.7 , 26.9 , 26.4 , 26.2 , 26.0 .

^{11}B NMR (128 MHz , CDCl_3): δ 9.4 .

HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{35}\text{BFN}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 533.2618 , found 533.2622 .

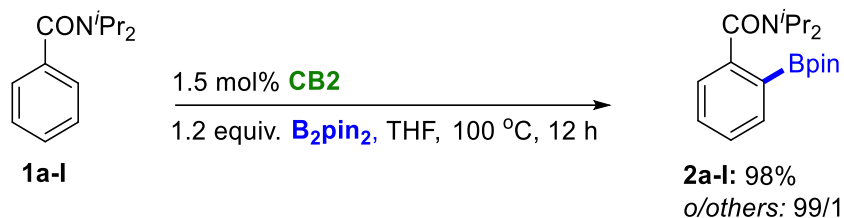
Comparative Studies of $\text{C}(\text{Sp}^2)\text{-H}$ & $\text{C}(\text{sp}^3)$ Borylation by Developed Catalyst **CB1** & **CB2**:

Borylation of *N,N*-diisopropylbenzamide (**1a-I**) with catalyst **CB1**:



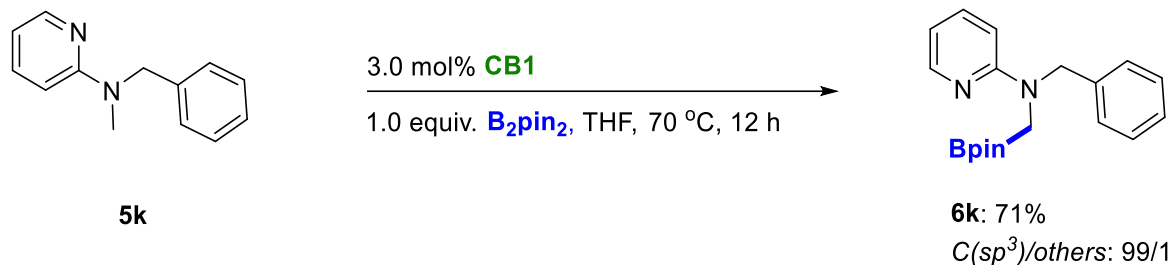
In a glove box, a 5.0 mL Wheaton microreactor was charged with catalyst **CB1** (7.1 mg , 3.0 mol\%), B_2pin_2 (127 mg , 1.0 equiv.) and dry THF (150 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropylbenzamide (102.7 mg , 0.5 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at $100\text{ }^\circ\text{C}$. The reaction mixture was stirred for 12 h . The reaction mixture was stirred for 12 h . After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 162.3 mg of borylated product **2a-I** (98%) as white solid.

*Borylation of *N,N*-diisopropylbenzamide (**1a-I**) with catalyst **CB2**:*



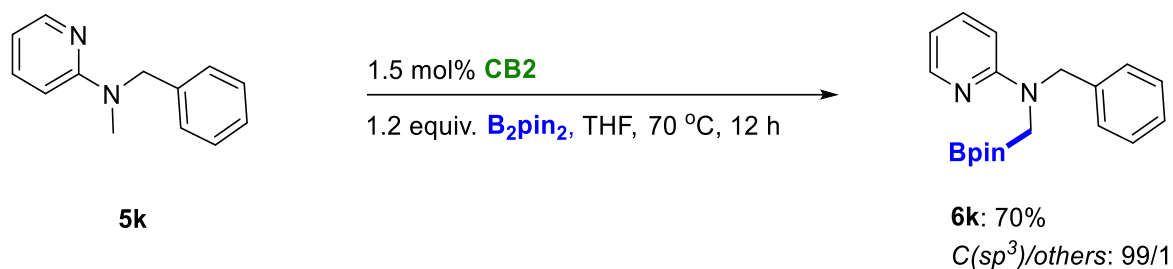
In a glove box, a 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (7.8 mg, 1.5 mol%), B_2pin_2 (152.4 mg, 1.2 equiv.) and dry THF (1.5 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropylbenzamide (102.7 mg, 0.5 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 162.3 mg of borylated product **2a-I** (98%) as white solid.

*Borylation of *N*-benzyl-*N*-methylpyridin-2-amine (**5k**) with catalyst **CB1**:*



In a glove box, a 5.0 mL Wheaton microreactor was charged with catalyst **CB1** (7.1 mg, 3.0 mol%), B_2pin_2 (127 mg, 1.0 equiv.) and dry THF (1.5 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-benzyl-*N*-methylpyridin-2-amine (99.1 mg, 0.5 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 115.0 mg of borylated product **6k** (71%) as white solid.

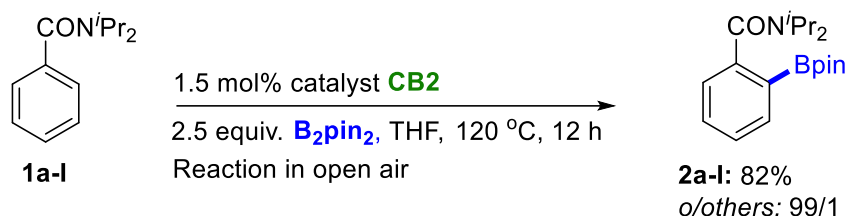
Borylation of N-benzyl-N-methylpyridin-2-amine (5k) with catalyst CB2:



In a glove box, a 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (7.8 mg, 1.5 mol%), B₂pin₂ (152.4 mg, 1.2 equiv.) and dry THF (1.5 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N*-benzyl-*N*-methylpyridin-2-amine (99.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 113.5 mg of borylated product **6k** (70%) as white solid.

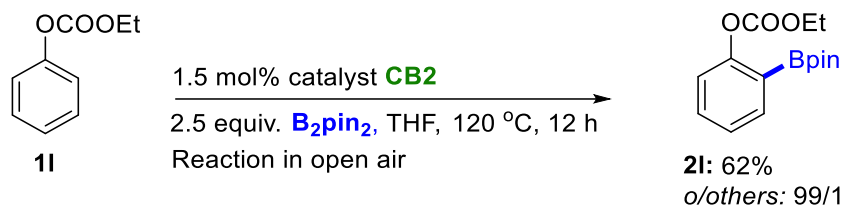
Borylation reaction in open air with catalyst CB2:

Borylation of N,N-diisopropylbenzamide (1a-I) with catalyst CB2 in open air:



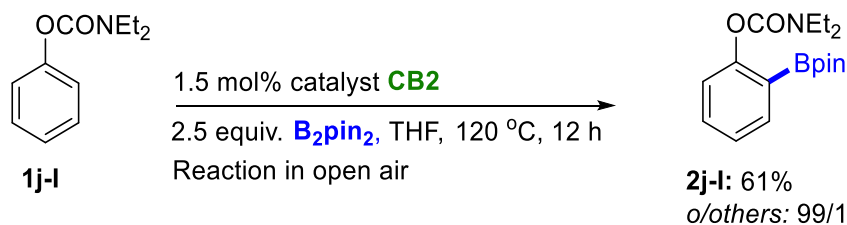
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), B₂pin₂ (127 mg, 2.5 equiv.), *N,N*-diisopropylbenzamide (41.1 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 54.3 mg of borylated product **2a-I** (82%) as white solid.

*Borylation of ethyl phenyl carbonate (**1i**) with catalyst **CB2** in open air:*



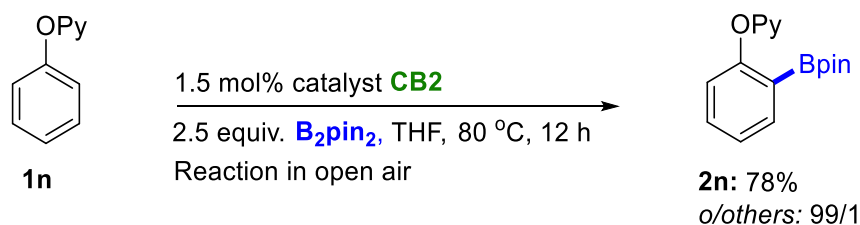
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), ethyl phenyl carbonate (33.2 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as eluent) gave 36.2 mg of borylated product **2i** (62%) as liquid.

*Borylation of phenyl diethylcarbamate (**1j**) with catalyst **CB2** in open air:*



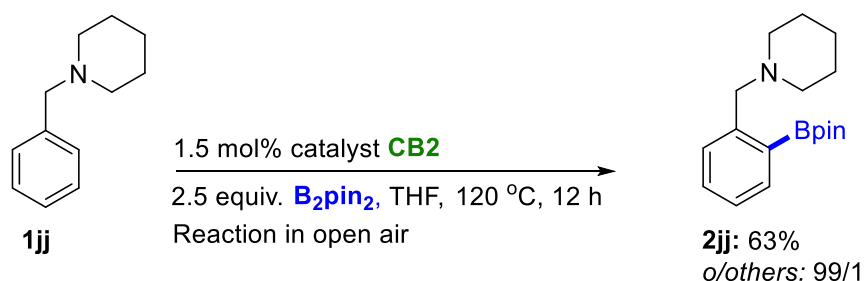
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), phenyl diethylcarbamate (38.6 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (4% ethyl acetate in hexane as eluent) gave 38.9 mg of borylated product **2j-I** (61%) as liquid.

Borylation of 2-phenoxyppyridine (1n) with catalyst CB2 in open air:



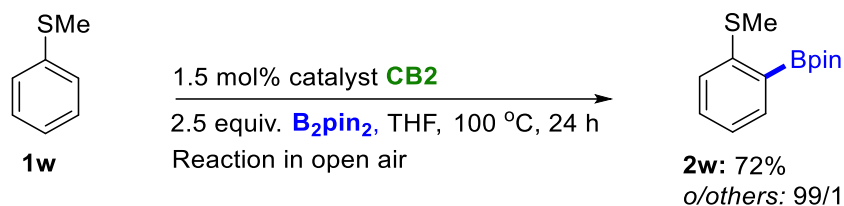
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), 2-phenoxyppyridine (34.2 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 80 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 46.4 mg of borylated product **2n** (78%) as pale yellow solid. (Notably, minor amount di borylation observed).

Borylation of 1-benzylpiperidine (1jj) with catalyst CB2 in open air:



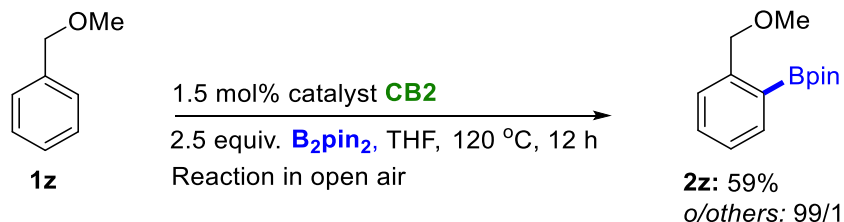
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), 1-benzylpiperidine (35.1 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (1% MeOH in DCM as eluent) gave 37.9 mg of borylated product **2jj** (63%) as gummy liquid.

Borylation of methyl(phenyl)sulfane (1w) with catalyst CB2 in open air:



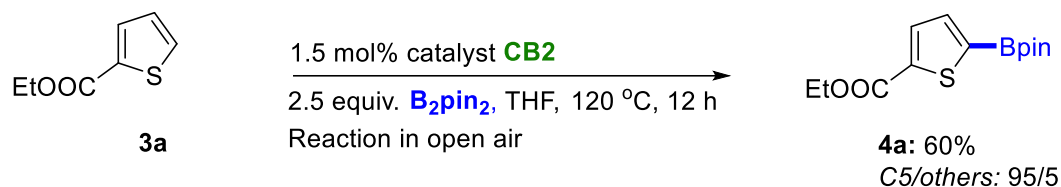
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), methyl(phenyl)sulfane (24.9 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 24 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (3% ethyl acetate in hexane as eluent) gave 36.0 mg of borylated product **2w** (72%) as liquid. (Notably, minor amount di borylation observed).

Borylation of (methoxymethyl)benzene (1z) with catalyst CB2 in open air:



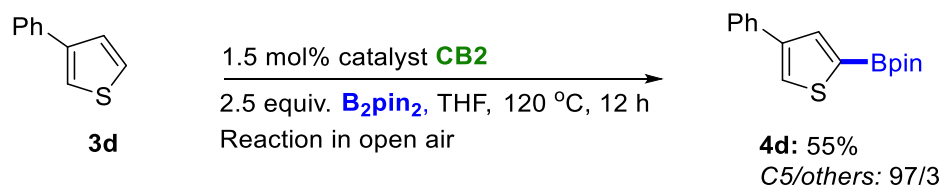
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), (methoxymethyl)benzene (24.4 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 29.3 mg of borylated product **2z** (59%) as liquid.

Borylation of ethyl thiophene-2-carboxylate (3a) with catalyst CB2 in open air:



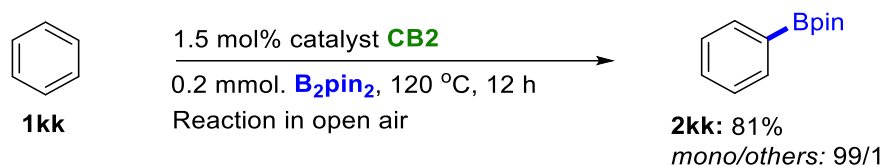
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), ethyl thiophene-2-carboxylate (31.2 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 33.8 mg of borylated product **4a** (60%) as white solid.

Borylation of 3-phenylthiophene (3d) with catalyst CB2 in open air:



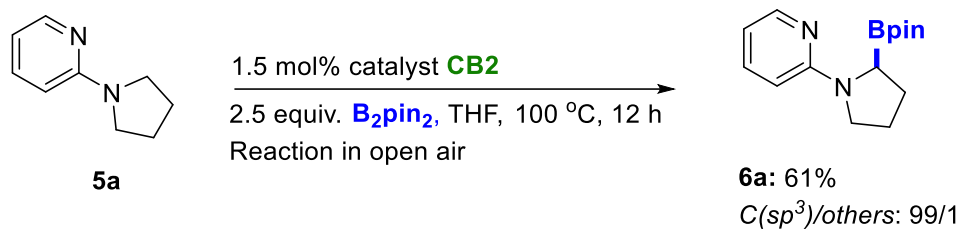
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), 3-phenylthiophene (32.0 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% ethyl acetate in hexane as eluent) gave 31.4 mg of borylated product **4d** (55%) as liquid.

Borylation of benzene (**1kk**) with catalyst **CB2** in open air:



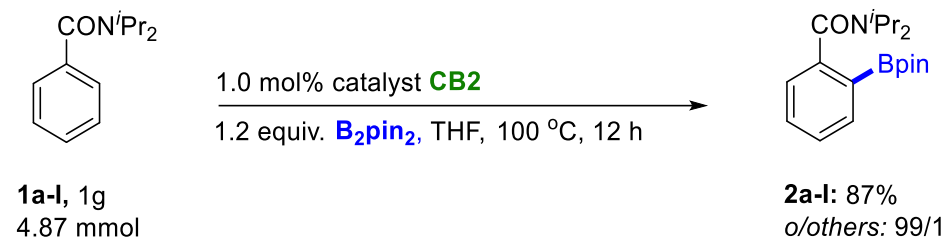
A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (50.8 mg, 0.2 mmol) and dry benzene (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 120 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), excess benzene was removed under reduced pressure and chromatographic separation with silica gel (2% ethyl acetate in hexane as eluent) gave 33.0 mg of borylated product **2kk** (81%) as solid. (Notably, yield is reported based on **B₂pin₂** as limiting reagent).

Borylation of 2-(pyrrolidin-1-yl)pyridine (**5a**) with catalyst **CB2** in open air:



A 5.0 mL Wheaton microreactor was charged with catalyst **CB2** (3.1 mg, 1.5 mol%), **B₂pin₂** (127 mg, 2.5 equiv.), 2-(pyrrolidin-1-yl)pyridine (29.6 mg, 0.2 mmol) and dry THF (1.0 mL) under open air atmosphere. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with basic alumina (50% ethyl acetate in hexane as eluent) gave 33.4 mg of borylated product **6a** (61%) as white solid.

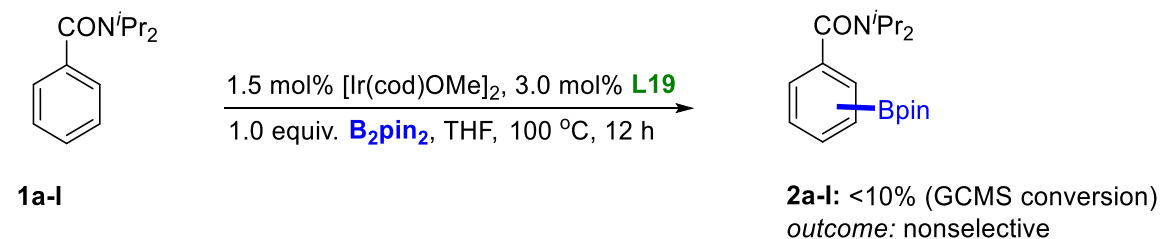
Gram scale Borylation of *N,N*-diisopropylbenzamide (**1a-I**):



In a glove box, a 15.0 mL Pressure tube was charged with catalyst **CB2** (49.8 mg, 1.0 mol%), **B₂pin₂** (1.48 g, 1.2 equiv.) and dry THF (10.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropylbenzamide (1 g, 4.87 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After completion (judged by GC/MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 1.41 g of borylated product **2a-I** (87%) as white solid.

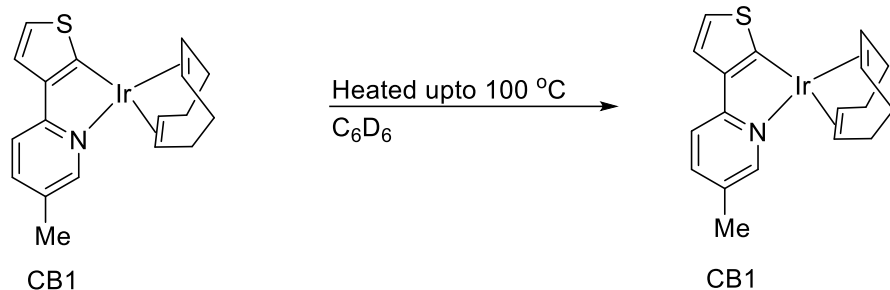
Control experiments for mechanistic investigation:

Control experiment with **L19** ligand with **1a-I**:

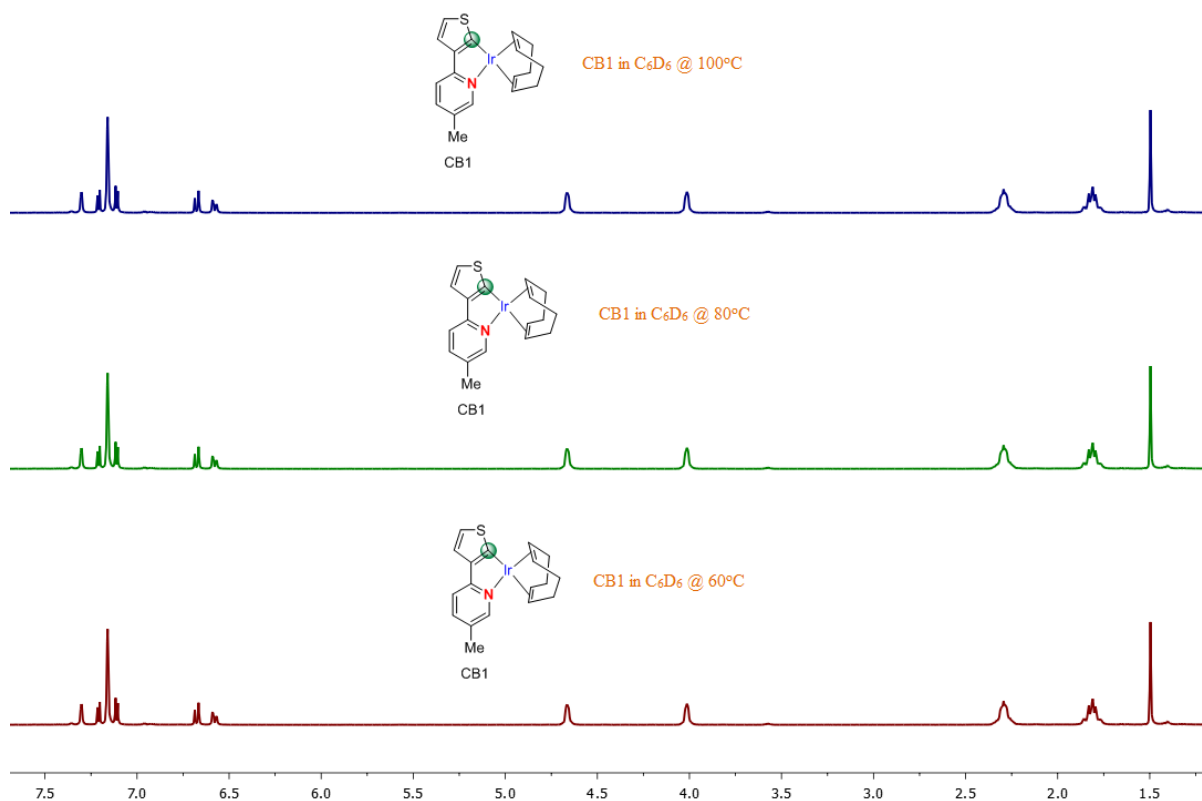


In a glove box, a 5.0 mL Wheaton microreactor was charged with [Ir(cod)(OMe)]₂ (1.98 mg, 1.5 mol%), **L19** ligand (1.1 mg, 3.0 mol%), **B₂pin₂** (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL). The reaction mixture was stirred for 2 minutes at room temperature. To this mixture, *N,N*-diisopropylbenzamide (**1a-I**) (41.1 mg, 0.2 mmol) was added. The microreactor was capped with a teflon pressure cap and placed into pre-heated aluminium block at 100 °C. The reaction mixture was stirred for 12 h. After 12 h, 50.0 μL of aliquot was withdrawn and conversion was checked by gas chromatography (GC/MS) and results are summarised in the Scheme.

Heating experiment of **CB1** catalyst:

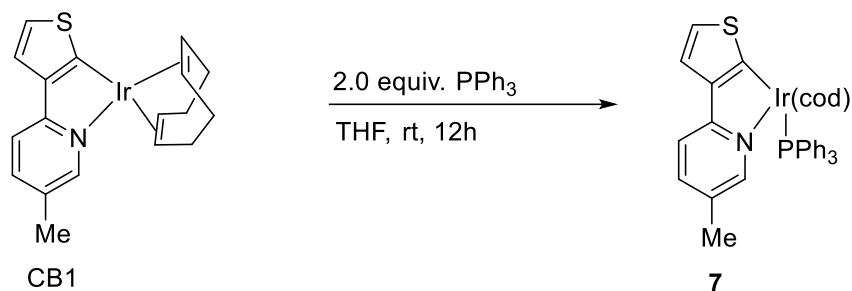


In a J-Young NMR tube **CB1** catalyst (20 mg, 0.042 mmol) was dissolved in 0.6 mL C₆D₆ and heated to 60°C for 4 h. ¹H-NMR was recorded. After that J-Young NMR tube again heated to 80°C and 100°C for 4 h and 12 h respectively, each time ¹H-NMR was recorded. **CB1** catalyst was showed high stability at high temperature without decomposition. A representative ¹H NMR was given below at various temperature.



Stability of **CB1** catalyst in C₆D₆ at Various Temperature (25 °C, 400 MHz, C₆D₆)

Reaction of **CB1** with Triphenyl phosphine (PPh_3):



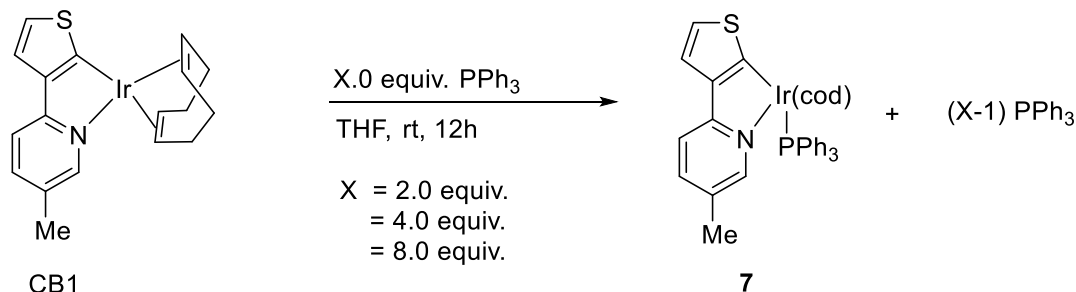
In an argon filled glove box, a 5 ml reaction vial was charged with **CB1** (10 mg, 0.02 mmol), PPh_3 (11.0 mg, 2.0 equiv.) and THF (1.0 mL). The vial was screw capped and stirred at room temperature for 12 h. After 12 h, THF was evaporated by vacuum and the crude reaction mixture was washed with cooled dry pentane, a yellow solid was obtained. The complex was determined by 1H , ^{31}P NMR and HRMS.

1H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 6.96-7.25 (m, 19H), 3.90 (br s, 2H), 3.02 (br s, 2H), 2.48 (br s, 4H), 2.39 (s, 3H), 1.85 (m, 2H), 1.42 (br s, 2H).

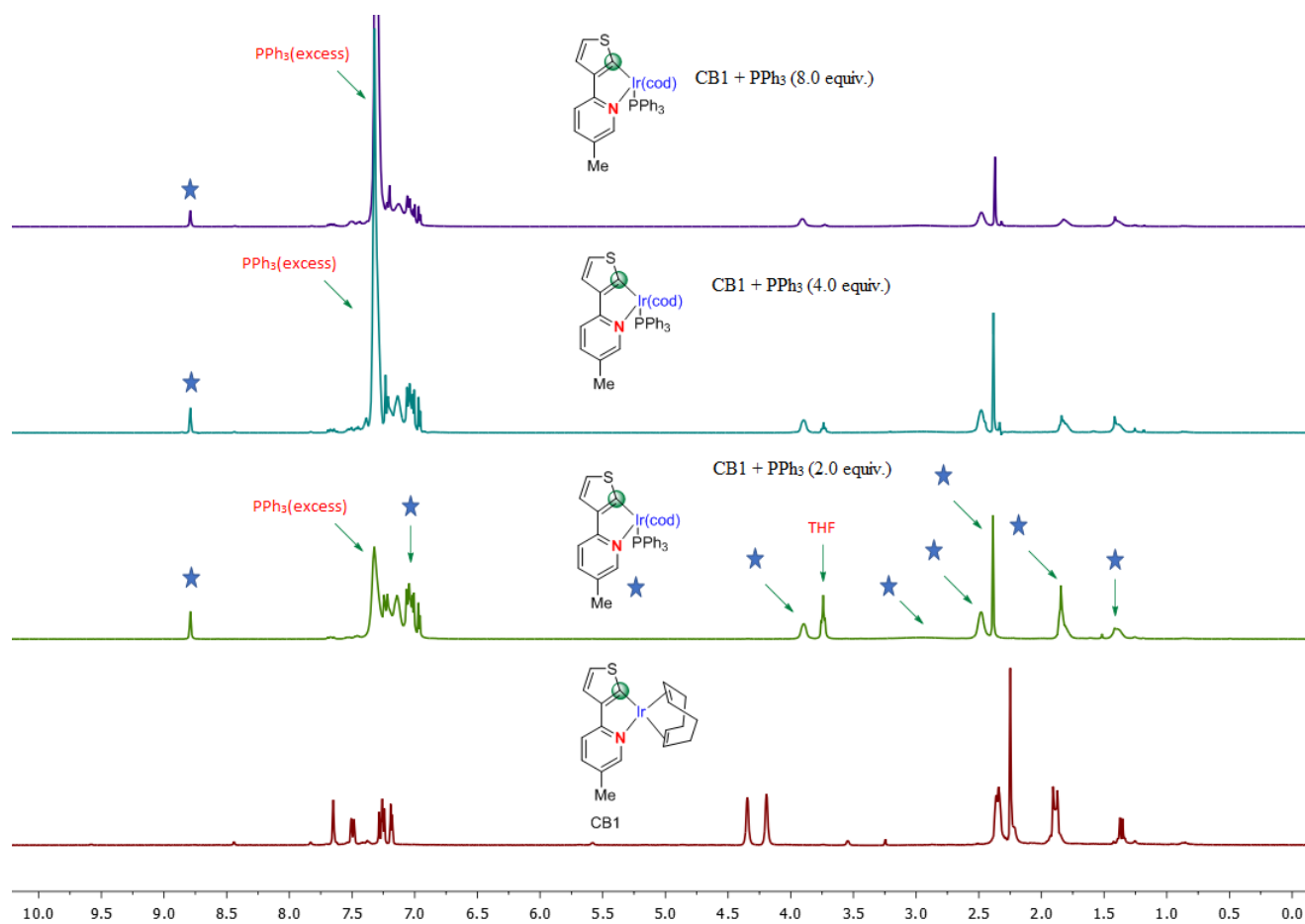
^{31}P NMR (162 MHz, $CDCl_3$): δ 8.25.

HRMS (ESI) m/z calcd for $C_{36}H_{35}IrNPS$ $[M]^+$ 737.1857, found 737.1856.

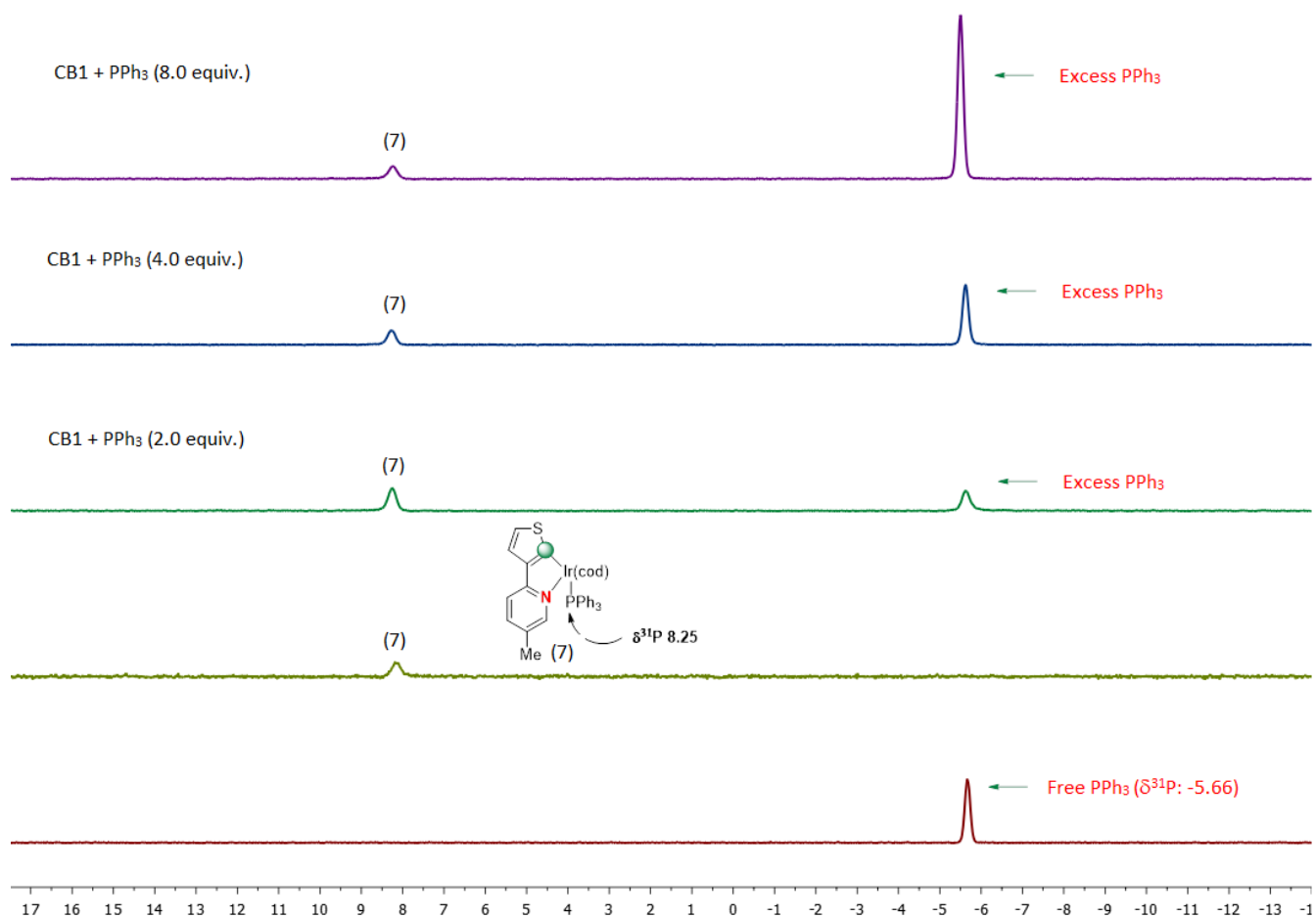
Control experiment with Triphenylphosphine with **CB1**:



In an argon filled glove box, a 5 ml reaction vial was charged with **CB1** (10 mg, 0.02 mmol), PPh_3 (11.0 mg, 2.0 equiv.) and THF (1.0 mL). The vial was screw capped and stirred at room temperature for 12 h. After 12 h, THF was evaporated by vacuum and crude NMR was taken. Then Subsequent addition of increasing amounts of PPh_3 (up to 8.0 equiv.) were monitored by 1H NMR and ^{31}P NMR.

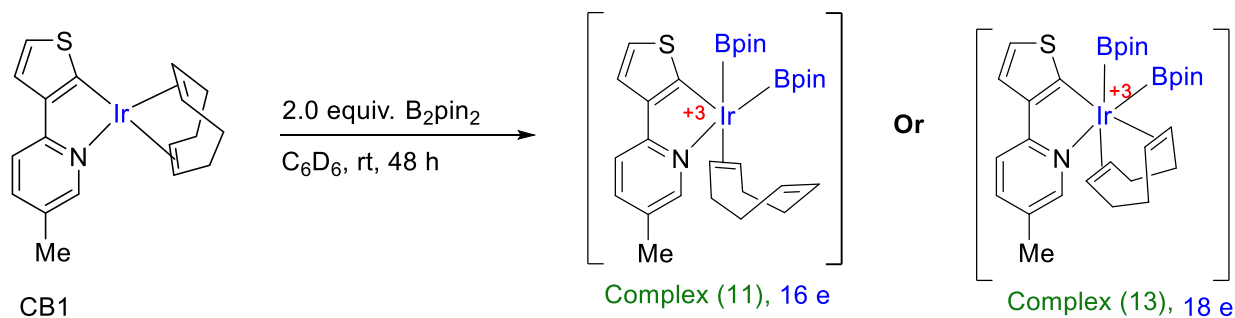


Ligand titration of **CB1** catalyst with increasing amount of PPh₃ ligand by ¹H NMR study
(25 °C, 400 MHz, CDCl₃)



Ligand titration of **CB1** catalyst with increasing amount of PPh₃ ligand by ³¹P NMR study (25 °C, 162 MHz, CDCl₃)

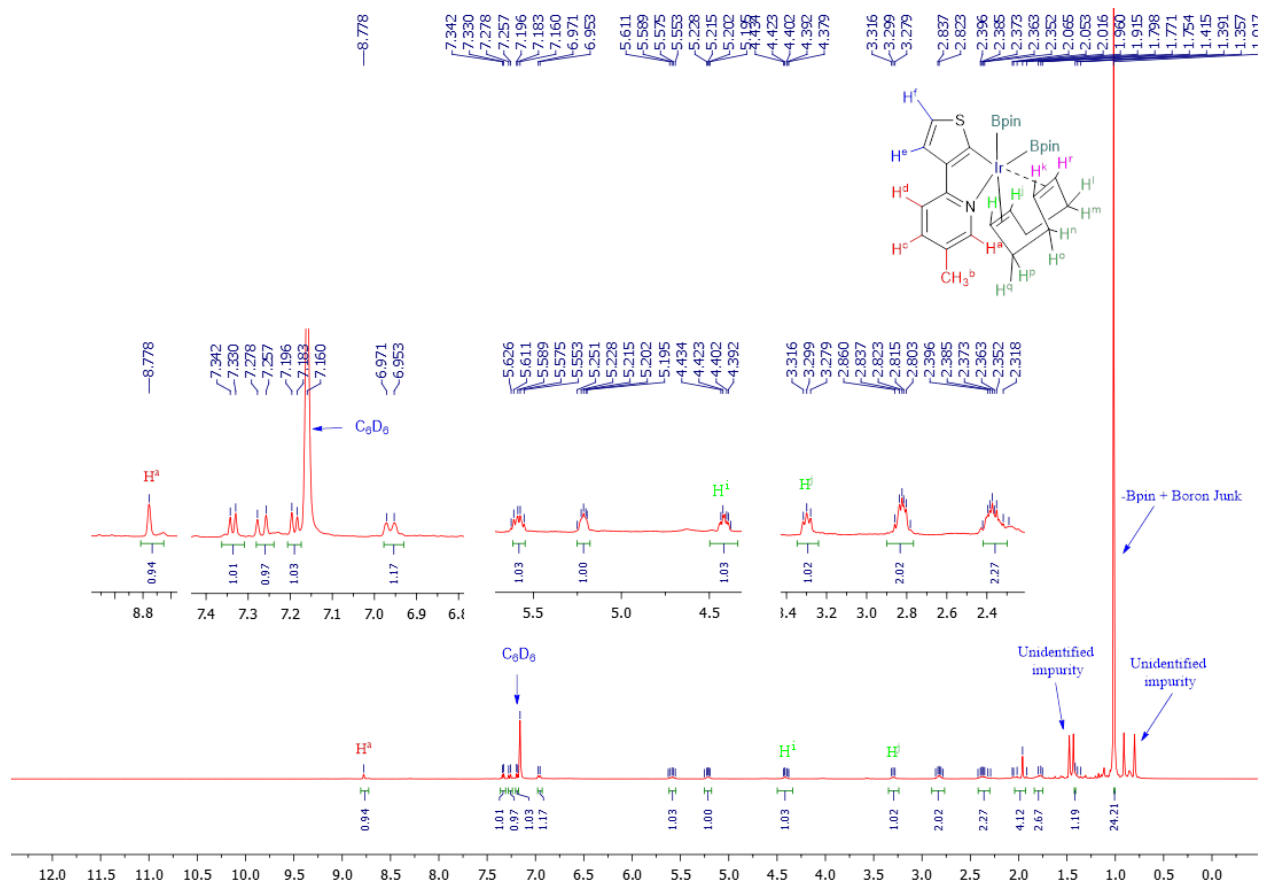
Identification of the active catalytic Intermediate:



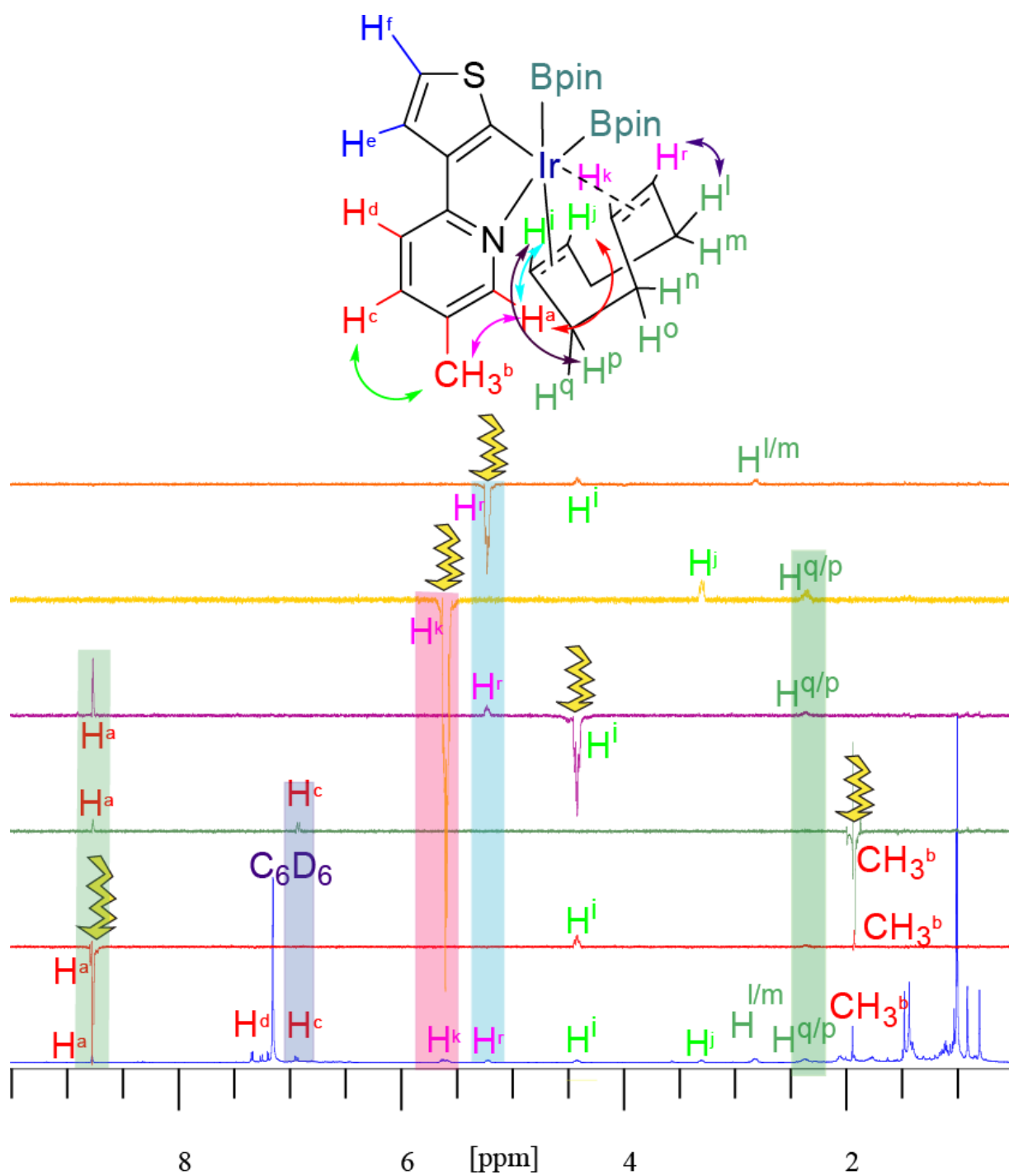
In an argon filled glove box, a J-Young NMR tube was charged with **CB1** catalyst (20 mg, .042 mmol), B₂pin₂ (10.7 mg, 1.0 equiv.) and C₆D₆ (0.6 mL). The NMR tube was screw capped and taken out from glove box and the reaction was monitored by ¹H NMR. After 48 h, complex (**11**)

or complex **13** was formed. The complex **11** or **13** was proposed by ^1H (1-D gradient selective TOCSY and 1-D gradient selective NOESY, 2-D) NMR and ^{11}B NMR and HRMS (ESI).

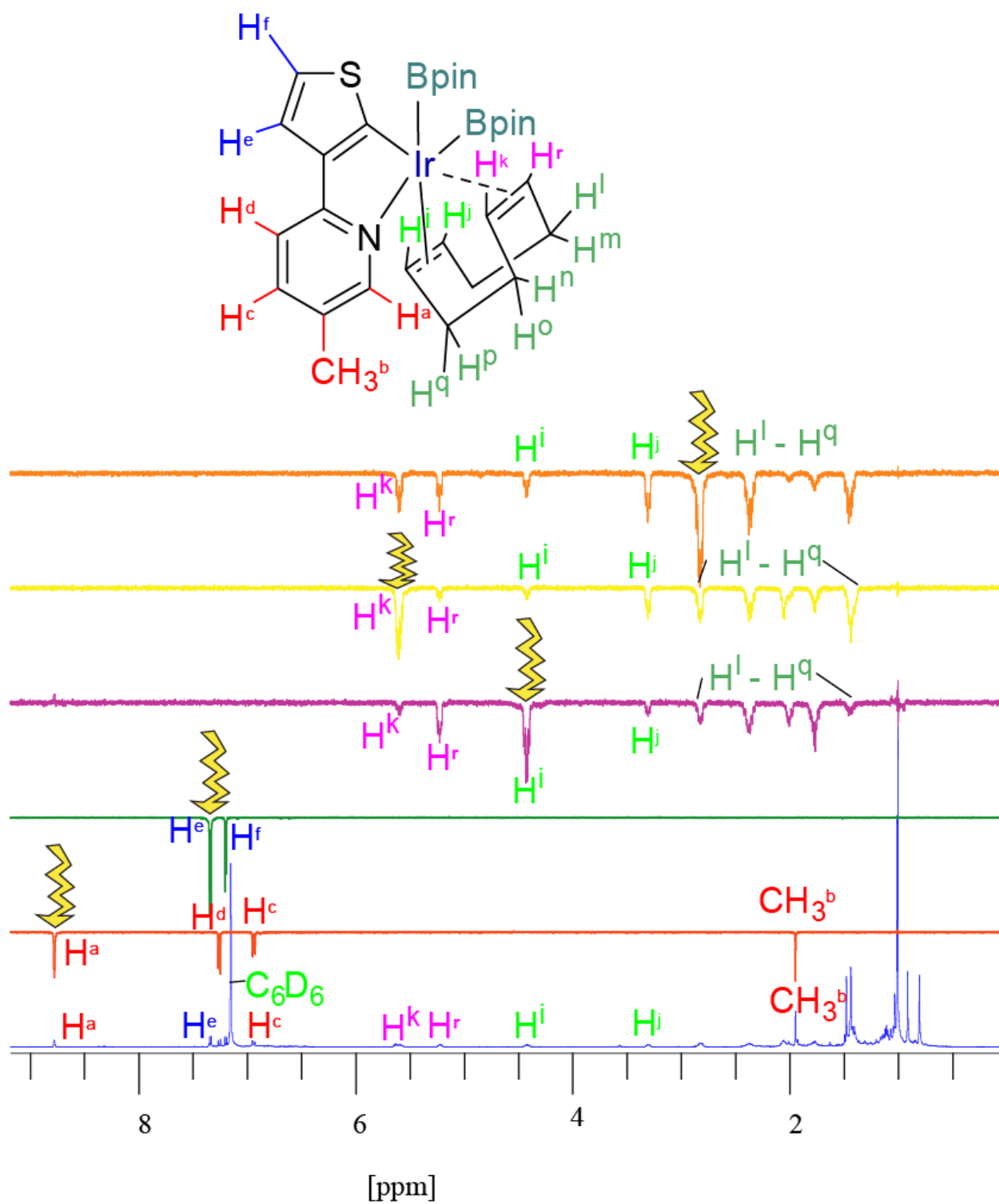
HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{45}\text{B}_2\text{IrNO}_4\text{S} [\text{M}+\text{H}]^+$ 730.2876, found 730.2879.



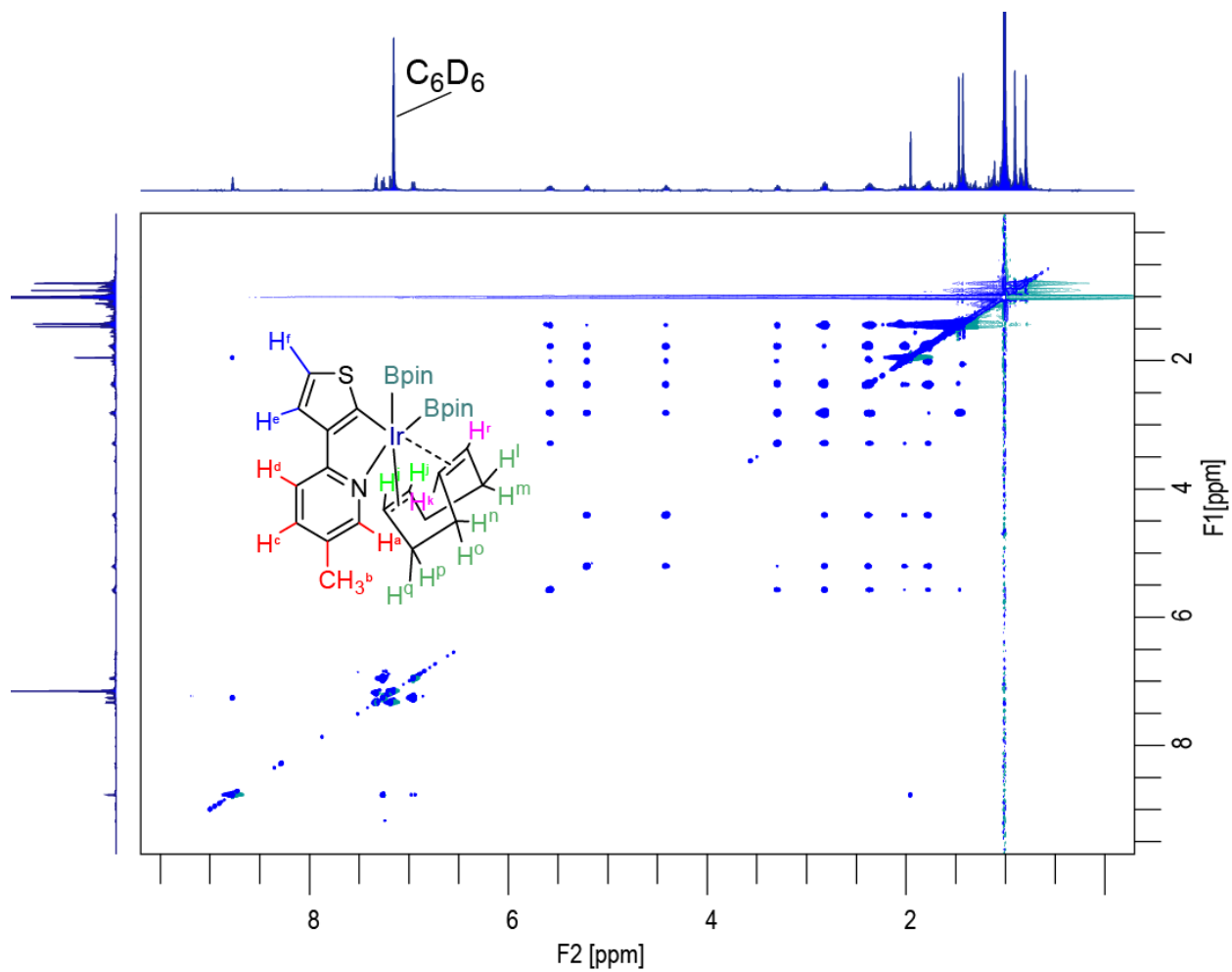
^1H -NMR of Complex **11** or **13** (25 °C, 400 MHz, C_6D_6)



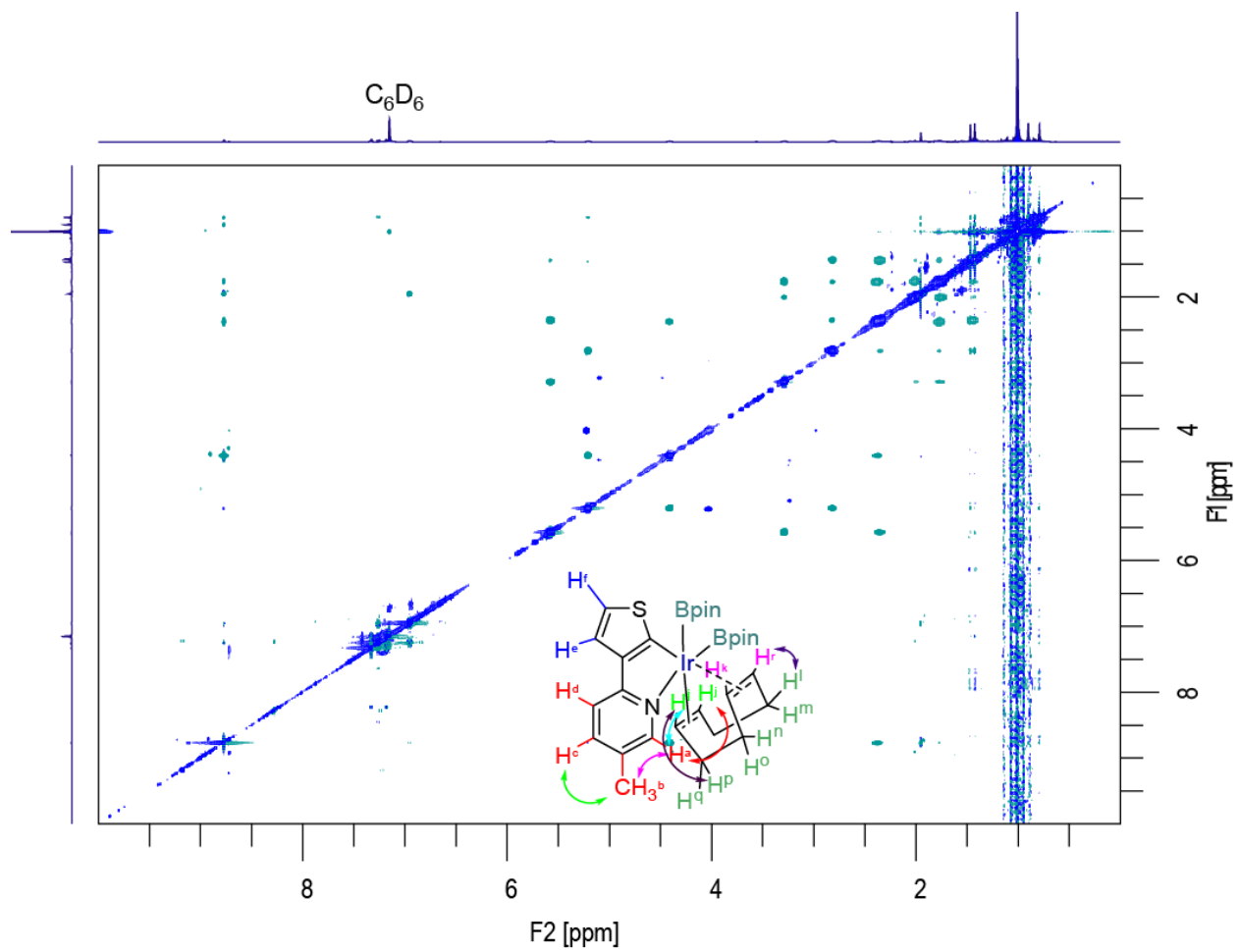
1-D Selective Gradient NOESY of Complex **11** or **13** (25 °C, 400 MHz, C₆D₆)



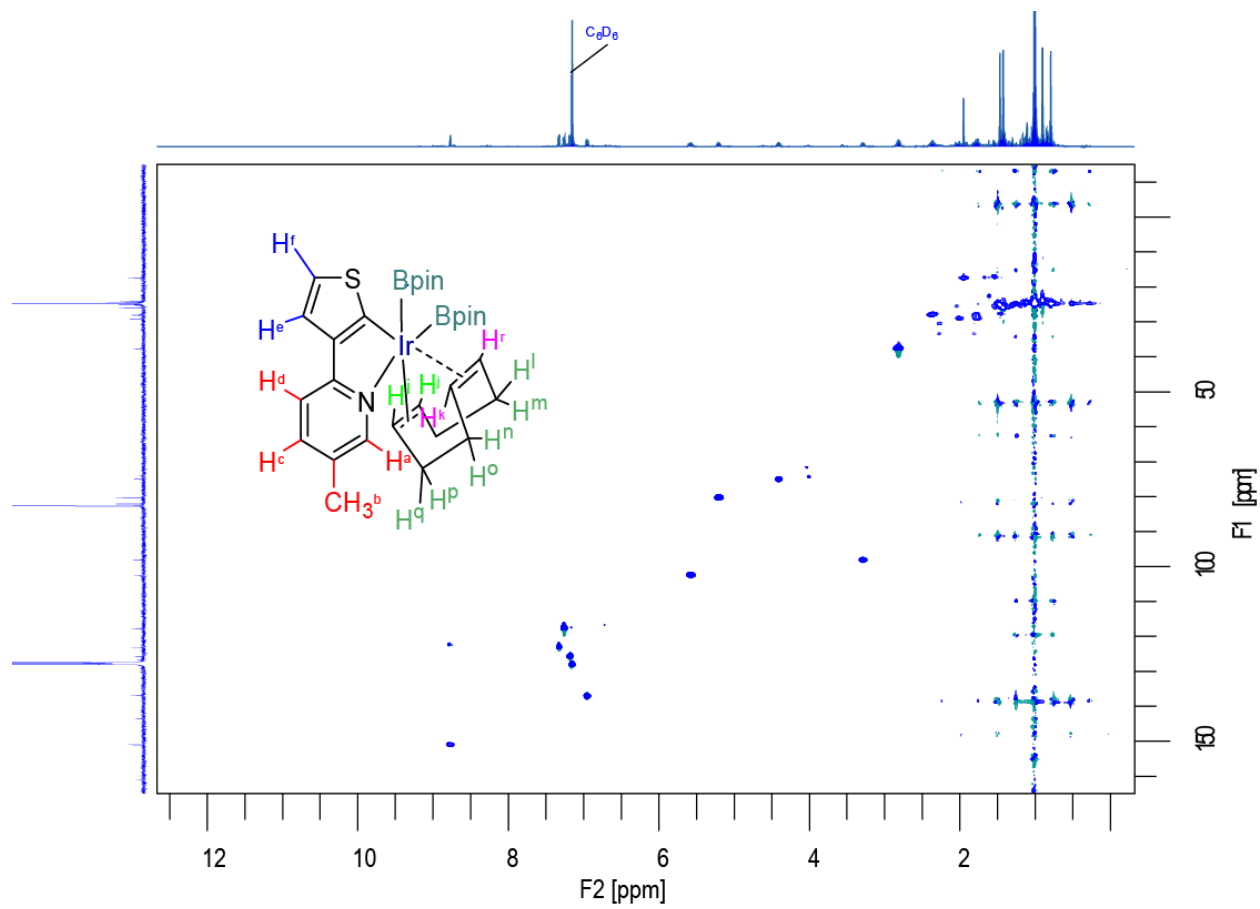
1-D Selective Gradient TOCSY of Complex **11** or **13** (25 °C, 400 MHz, C_6D_6)



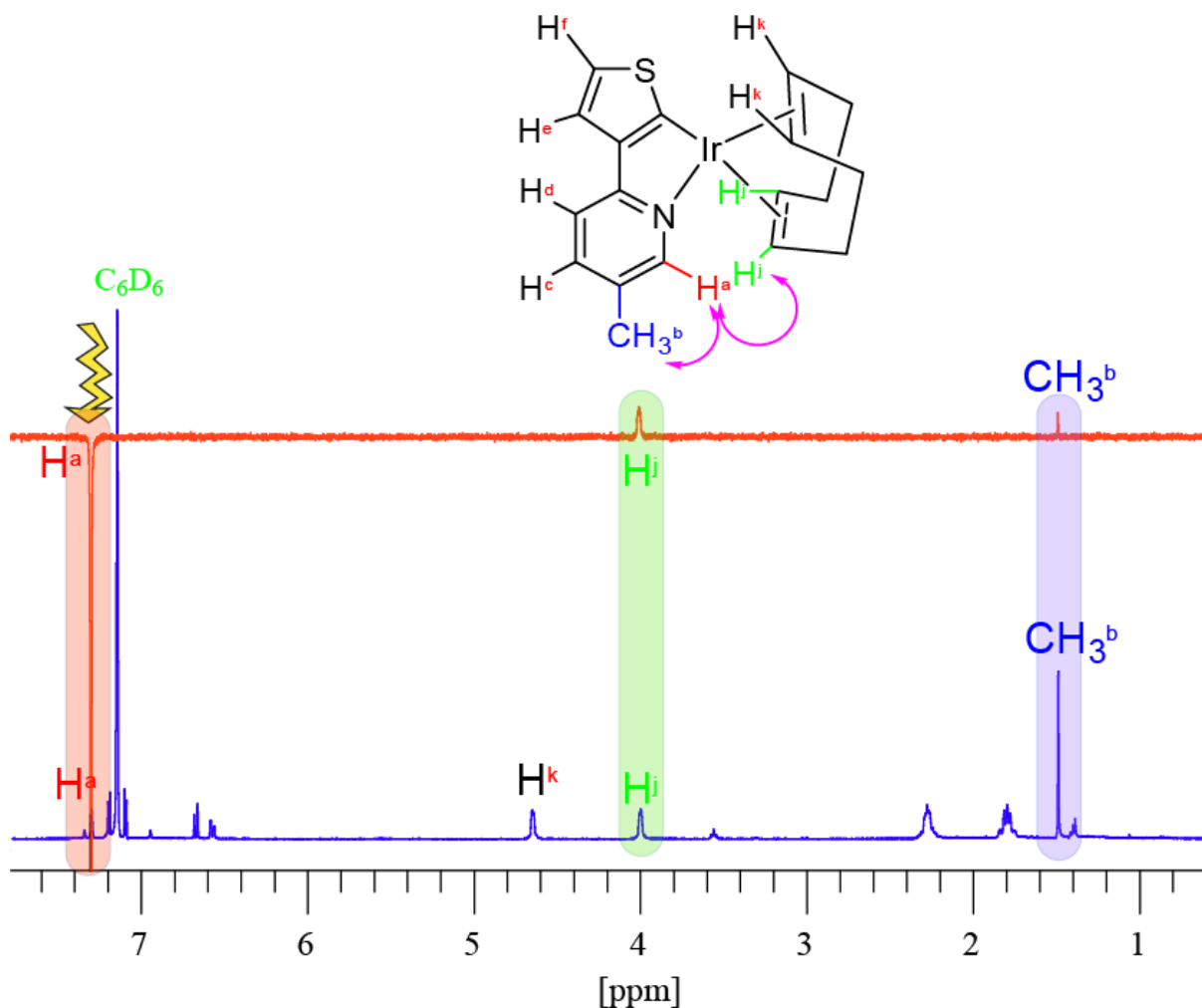
2-D TOCSY of Complex **11** or **13** (25 °C, 400 MHz, C₆D₆)



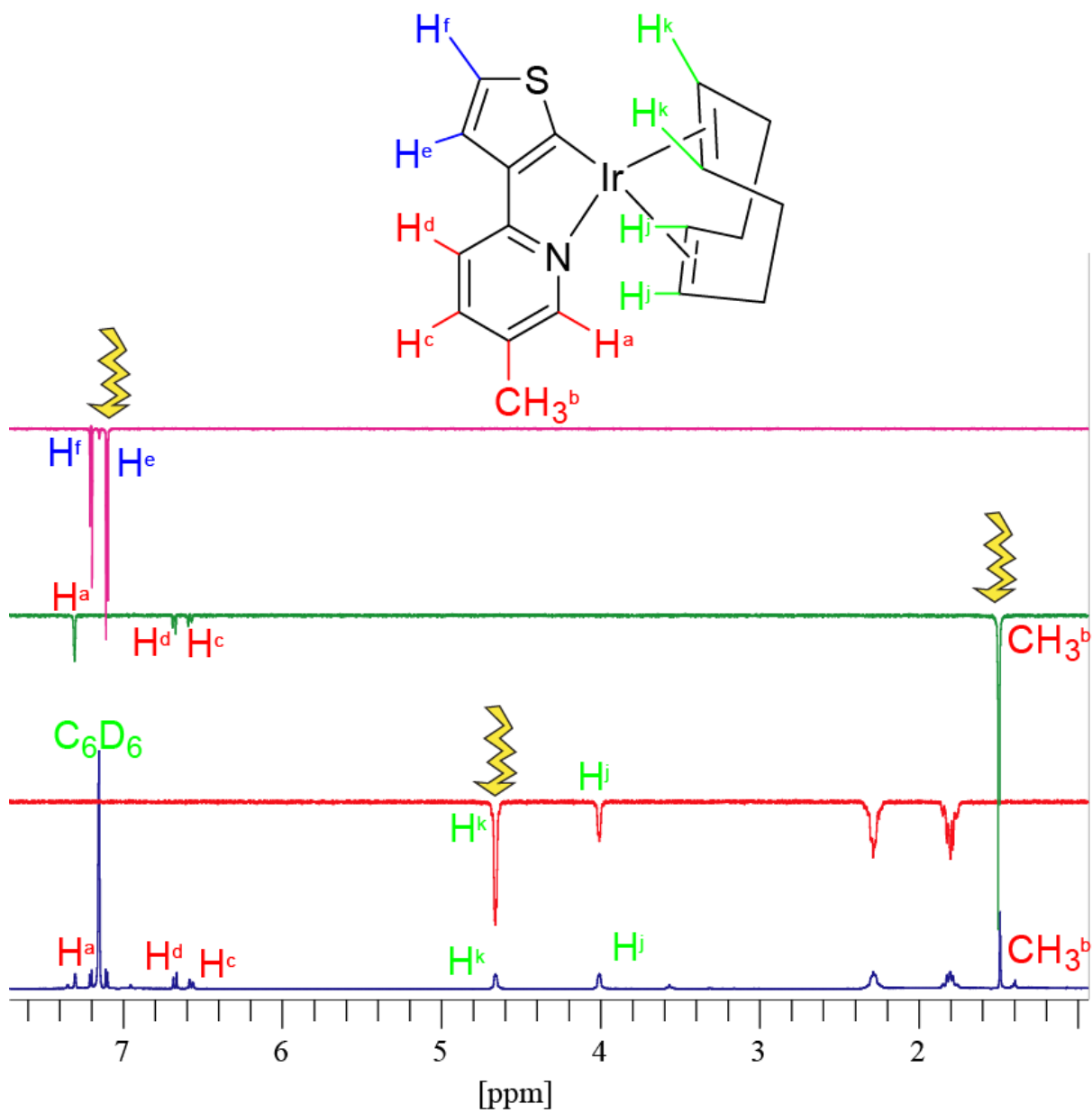
2-D NOESY of Complex **11** or **13** (25 °C, 400 MHz, C₆D₆)



2-D HSQC of Complex **11** or **13** (25 °C, 400 MHz, C_6D_6)



1-D Selective Gradient NOESY of **CB1** catalyst (25 °C, 400 MHz, C_6D_6)



1-D Selective Gradient TOCSY of **CB1** catalyst (25 °C, 400 MHz, C_6D_6)

Qualitative Compound Report

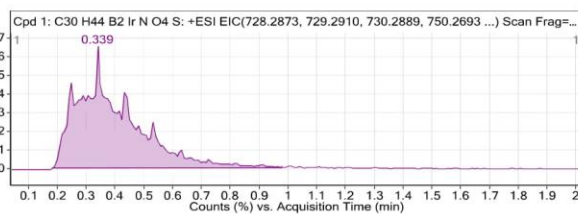
Data File	MH-AB-5.d	Sample Name	MH-AB-5
Sample Type	Sample	Position	Vial 45
Instrument Name	Instrument 1	User Name	
Acq Method	Direct Mass-2017.m	Acquired Time	4/18/2020 9:37:53 PM
IRM Calibration Status	Some Ions Missed	DA Method	Default.m
Comment			

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.00 (B5042.0)	

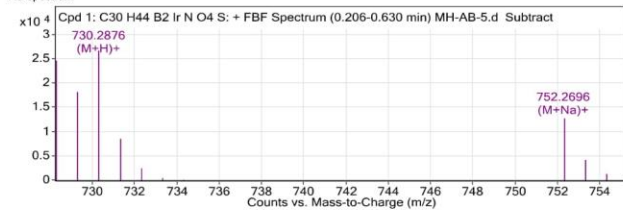
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C30 H44 B2 Ir N O4 S	0.339	725.2828	12822	C30 H44 B2 Ir N O4 S	725.2856	-3.77	C30 H44 B2 Ir N O4 S	C30 H44 B2 Ir N O4 S

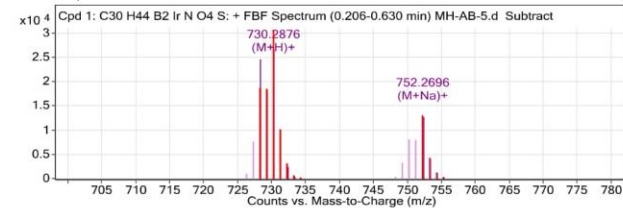
Compound Label	m/z	RT	Algorithm	Mass
Cpd 1: C30 H44 B2 Ir N O4 S	752.2696	0.339	Find By Formula	725.2828



MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
728.2814	1	24624.08	C30H45B2IrNO4S	(M+H)+
729.288	1	18253.29	C30H45B2IrNO4S	(M+H)+
730.2876	1	26827.67	C30H45B2IrNO4S	(M+H)+

Qualitative Compound Report

731.2902	1	8693.55	C30H45B2IrNO4S	(M+H)+
732.2891	1	2576.2	C30H45B2IrNO4S	(M+H)+
733.2902	1	577.27	C30H45B2IrNO4S	(M+H)+
752.2696	1	12821.94	C30H44B2IrNNaO4S	(M+Na)+
753.2721	1	4309.6	C30H44B2IrNNaO4S	(M+Na)+
754.2704	1	1414.81	C30H44B2IrNNaO4S	(M+Na)+
755.2698	1	405.18	C30H44B2IrNNaO4S	(M+Na)+

--- End Of Report ---

In the same experiment, in HRMS (ESI) we also got mass of another catalytic intermediate (**Int-I**), which is generated via COD dissociation (**Int-I**).

HRMS (ESI) m/z calcd for $C_{22}H_{32}B_2IrNO_4S$ $[M+Na]^+$ 644.1760, found 644.1767.

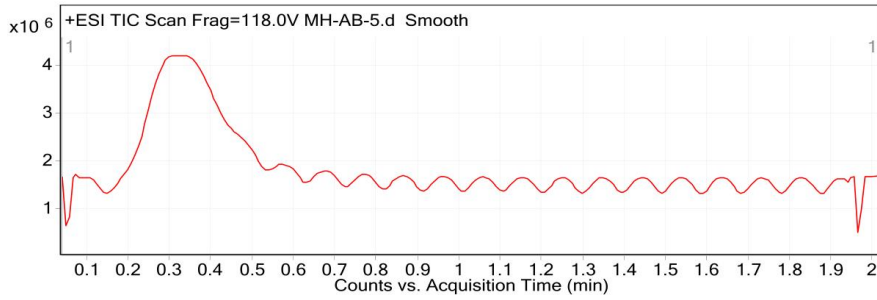
Qualitative Analysis Report

Data Filename	MH-AB-5.d	Sample Name	MH-AB-5
Sample Type	Sample	Position	Vial 45
Instrument Name	Instrument 1	User Name	
Acq Method	Direct Mass-2017.m	Acquired Time	4/18/2020 9:37:53 PM
IRM Calibration Status	Some Ions Missed	DA Method	Default.m
Comment			

Sample Group	Info.
Acquisition SW	6200 series TOF/6500 series
Version	Q-TOF B.05.00 (B5042.0)

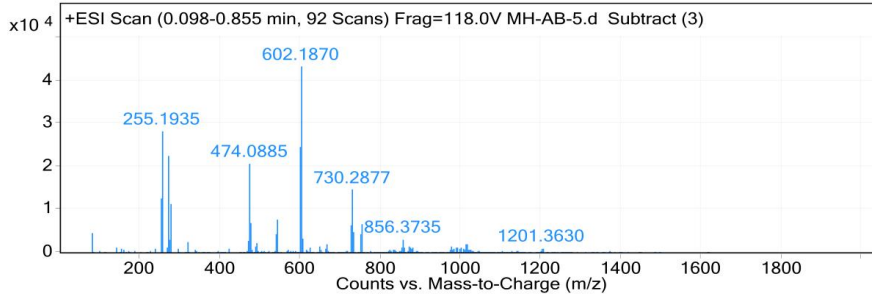
User Chromatograms

Fragmentor Voltage 118 Collision Energy 0 Ionization Mode ESI



User Spectra

Fragmentor Voltage 118 Collision Energy 0 Ionization Mode ESI



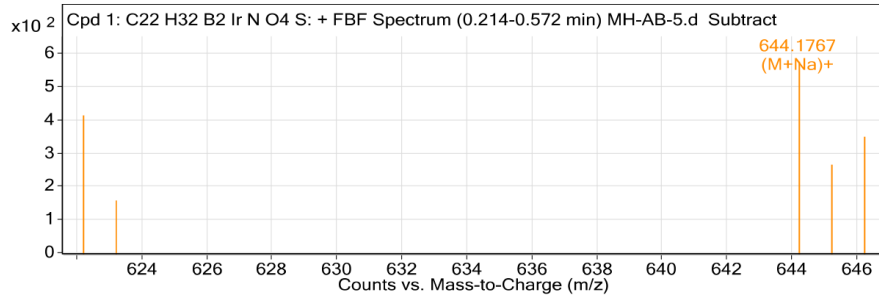
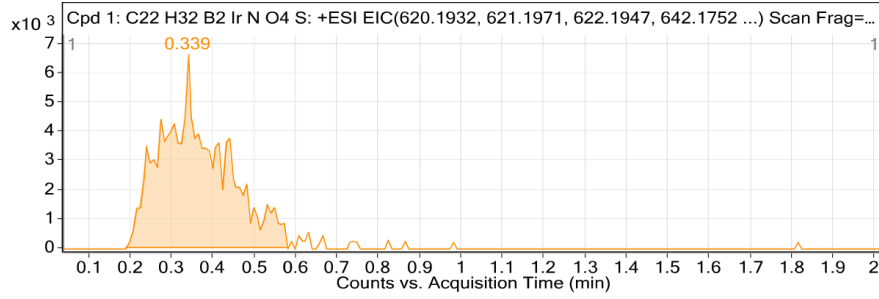
Peak List

m/z	z	Abund
254.1968		12668.81
255.1935	1	28357.63
272.2201	1	22588.73
472.0803	1	13349.31
474.0885	1	20823.35
600.1841	1	24561.89

Qualitative Analysis Report

601.1888	1	15875.95
602.187		43419.66
728.2813	1	13517.7
730.2877	1	14677.99

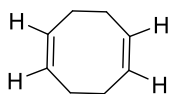
Compounds



Peak List

m/z	z	Abund	Formula	Ion
622.194	1	414.98	C ₂₂ H ₃₃ B ₂ IrNO ₄ S	(M+H)+
623.1968	1	162.84	C ₂₂ H ₃₃ B ₂ IrNO ₄ S	(M+H)+
644.1767	1	579	C ₂₂ H ₃₂ B ₂ IrNNaO ₄ S	(M+Na)+
645.1828	1	267.48	C ₂₂ H ₃₂ B ₂ IrNNaO ₄ S	(M+Na)+
646.1838	1	351.69	C ₂₂ H ₃₂ B ₂ IrNNaO ₄ S	(M+Na)+

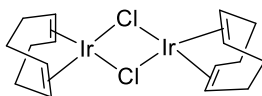
Identification of the active catalytic Intermediate:



1,5 cyclooctadiene

δ (CH=CH) 5.58 ppm (4H)

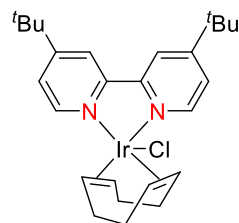
Observation: Four olefinic protons appear together at 5.58 ppm due to Symmetrical nature



[Ir(cod)Cl]₂

δ (CH=CH) 4.24 ppm (4H)

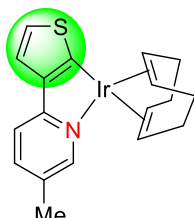
Observation: Four olefinic protons appear together at 4.24 ppm due to symmetrical nature



δ (CH=CH) 3.69 ppm (4H)

Hartwig, JACS, **2002**, 124, 390–391

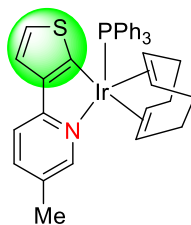
Observation: Four olefinic protons appear together at 3.69 ppm due to symmetrical nature of attached ligand



CB1

δ (CH=CH) 4.35 ppm (2H) & 4.20 ppm (2H)

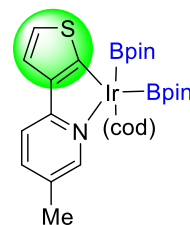
Observation: Due to unsymmetrical nature of ligand environment two olefinic protons appear at 4.35 ppm and other two protons appear at 4.20 ppm



Complex 7

δ (CH=CH) 3.90 ppm (2H) & 3.02 ppm (2H)

Observation: Due to unsymmetrical nature of ligand environment two olefinic protons appear at 3.90 ppm and other two protons appear at 3.02 ppm



Complex (11) or (13)

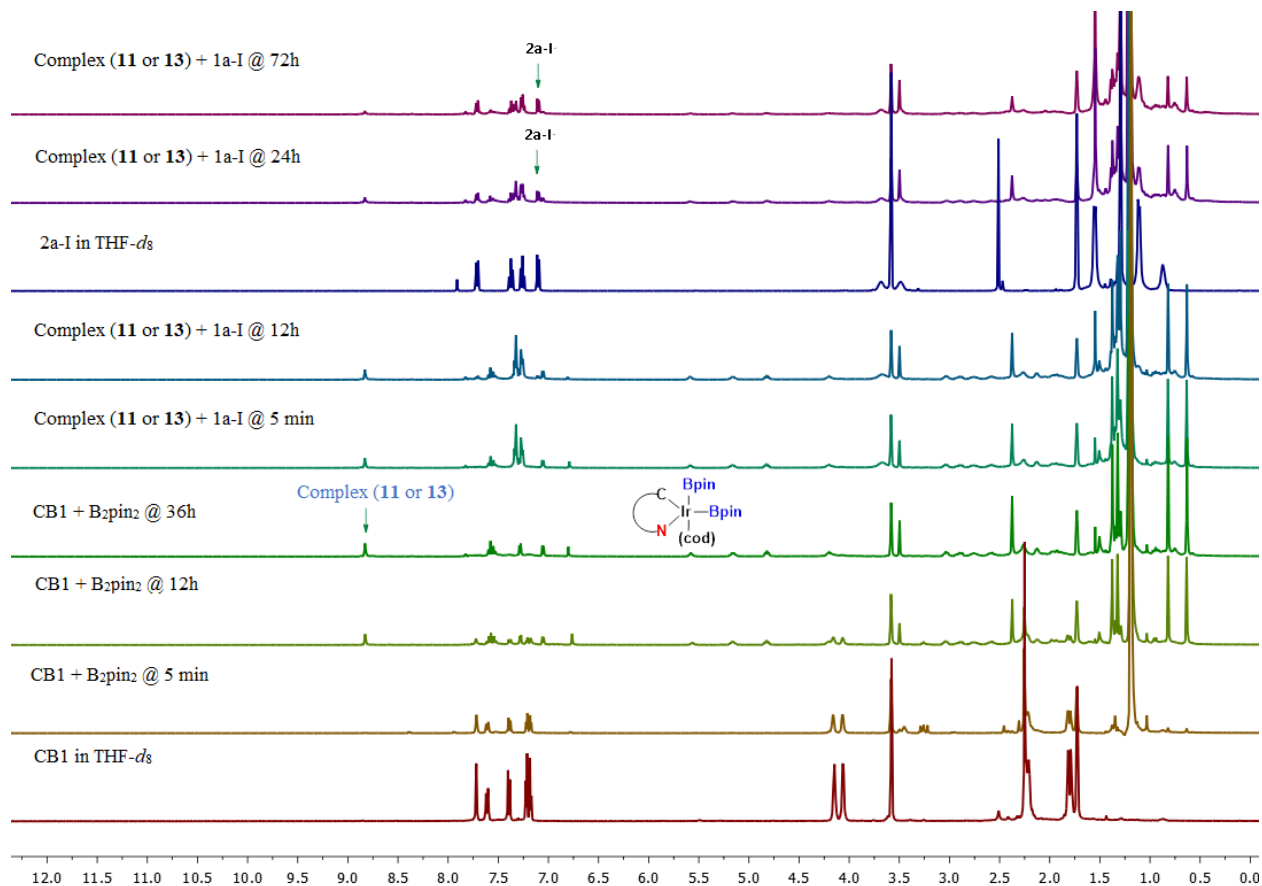
δ (CH=CH) 5.59 ppm (1H), 5.2 ppm (1H), 4.42 ppm (1H), 3.29 ppm (1H)

Observation: Here four olefinic protons appear separately at 5.59 ppm, 5.52 ppm, 4.42 ppm, and 3.29 ppm.

To identify the complex **(11)** or **(13)** we have done several spectroscopic experiments like ¹H (1D selective gradient NOESY and TOCSY), 2D NMR, ¹¹B NMR and HRMS. All the data collectively says that two complexes may possible. From literature value of olefinic protons of 1, 5 cyclooctadiene in several coordination mode and comparison with our complex **CB1**, **complex 7**, it give a most probable structure of complex **(11)**, as in the proton NMR value of olefinic double bond of boron complex **(11)** or **(13)** is identical value of one olefinic double bond of 1, 5 cyclooctadiene. However, we can't rule out the complex **(13)** completely as it may be in equilibrium with the complex **(11)**. To proceeds in catalytic cycle **Int-I** will be formed from complex **(11)** or **(13)** by dissociation of COD.

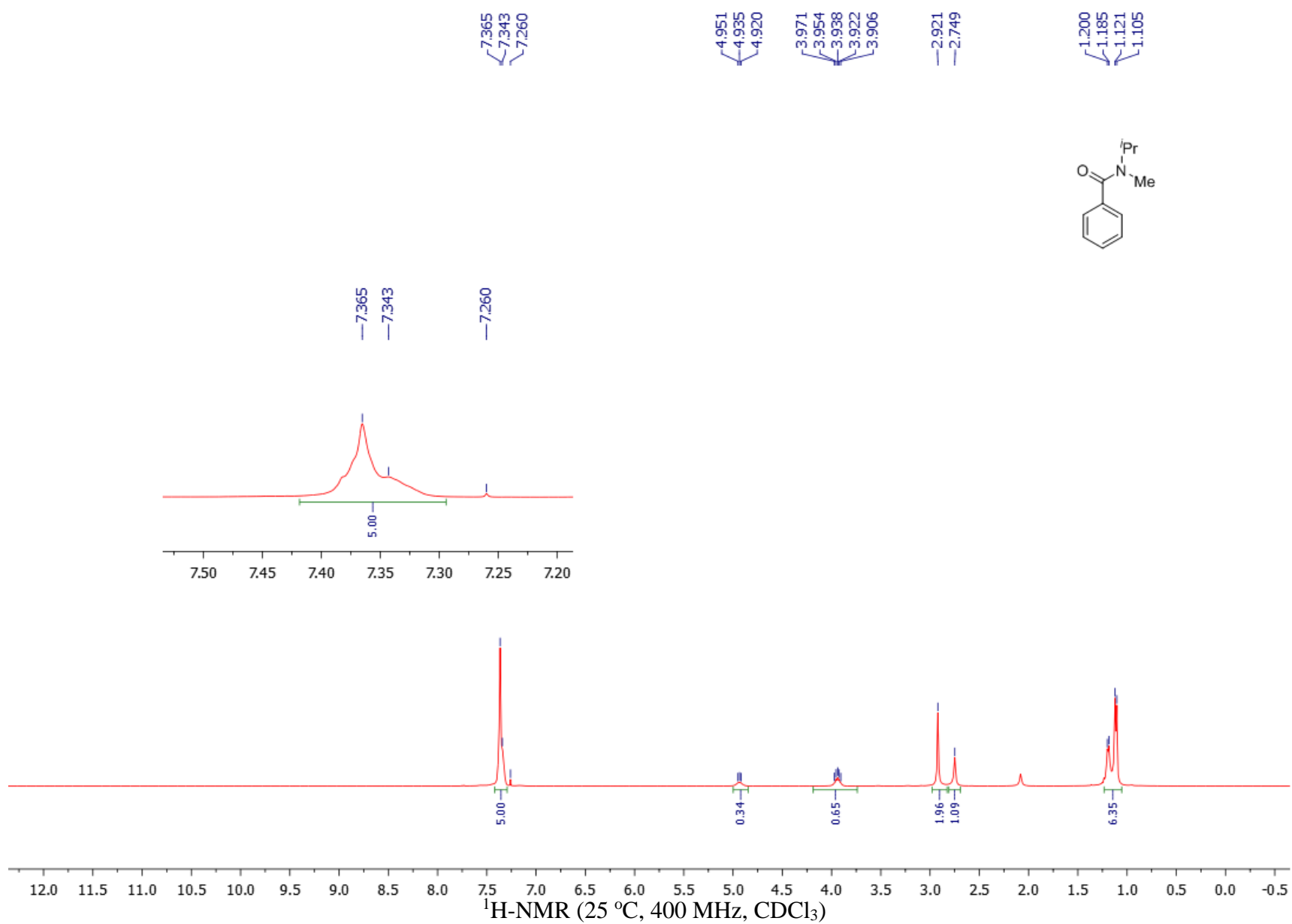
Detailed Investigation of Borylation with CB1 catalyst:

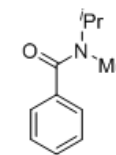
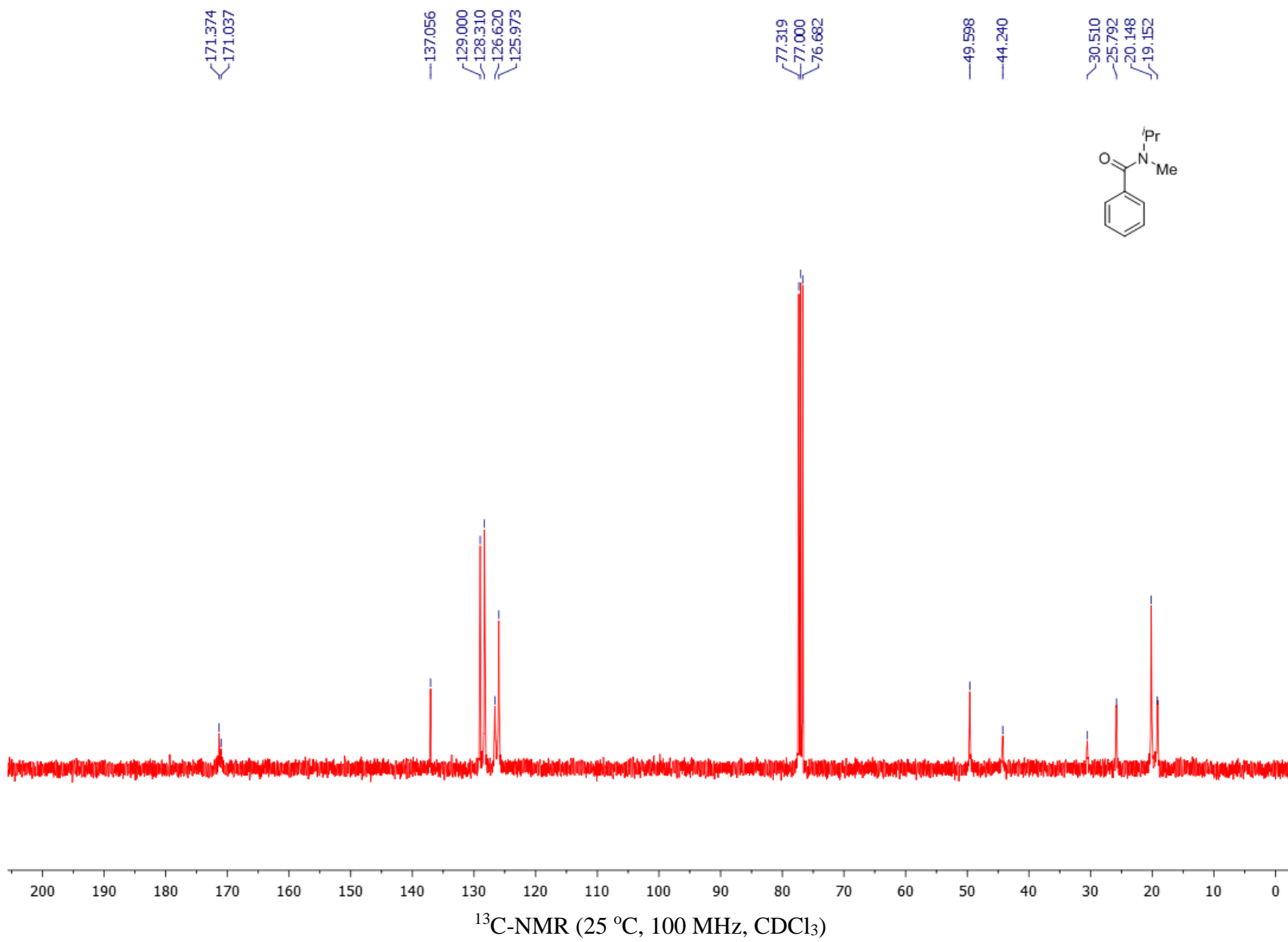
In an argon filled glove box, a J. Young NMR tube was charged with **CB1** catalyst (20 mg, .042 mmol), B₂pin₂ (21.4 mg, 2.0 equiv.) and THF-*d*₈ (0.6 mL). The NMR tube was screw capped and taken out from glove box and the reaction was monitored by ¹H NMR. After 36 h, a new complex was formed and in the NMR tube **1a-I** (8.65 mg, 1.0 equiv.) was added. The reaction mixture was monitored by ¹H NMR and ¹¹B NMR at various time duration.

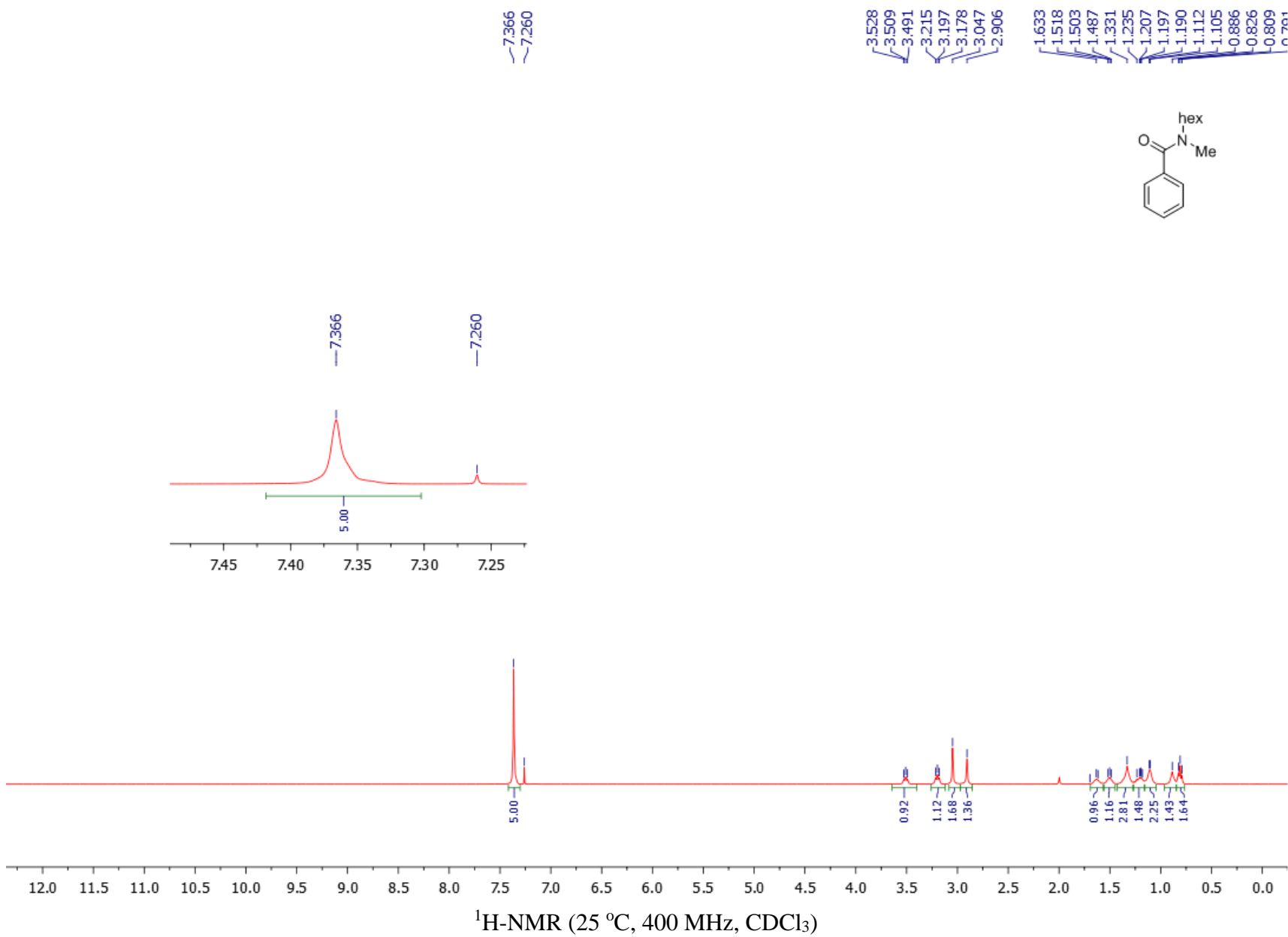


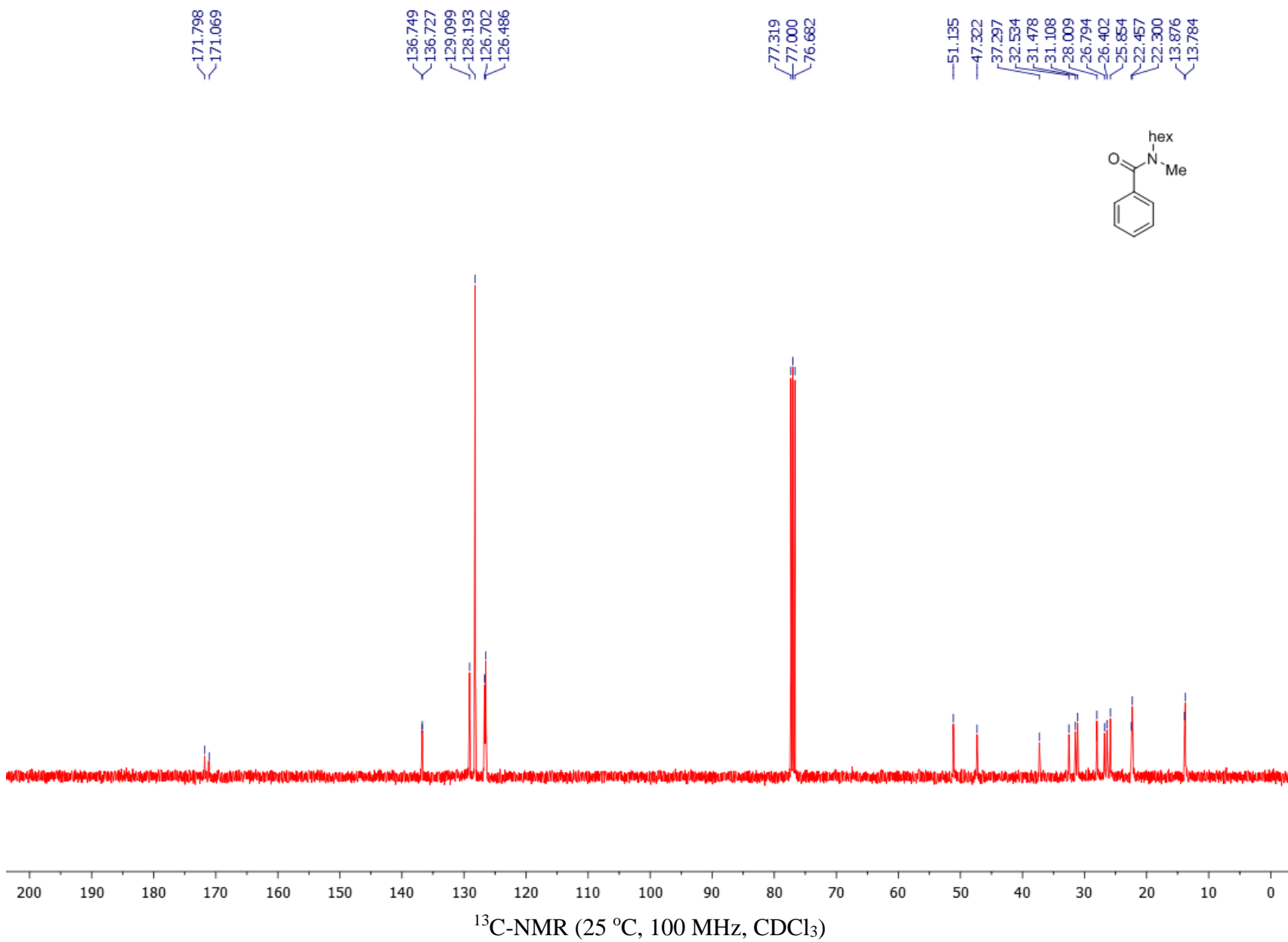
¹H-NMR for detailed Investigation of Borylation with **CB1** (25 °C, 400 MHz, THF-*d*₈)

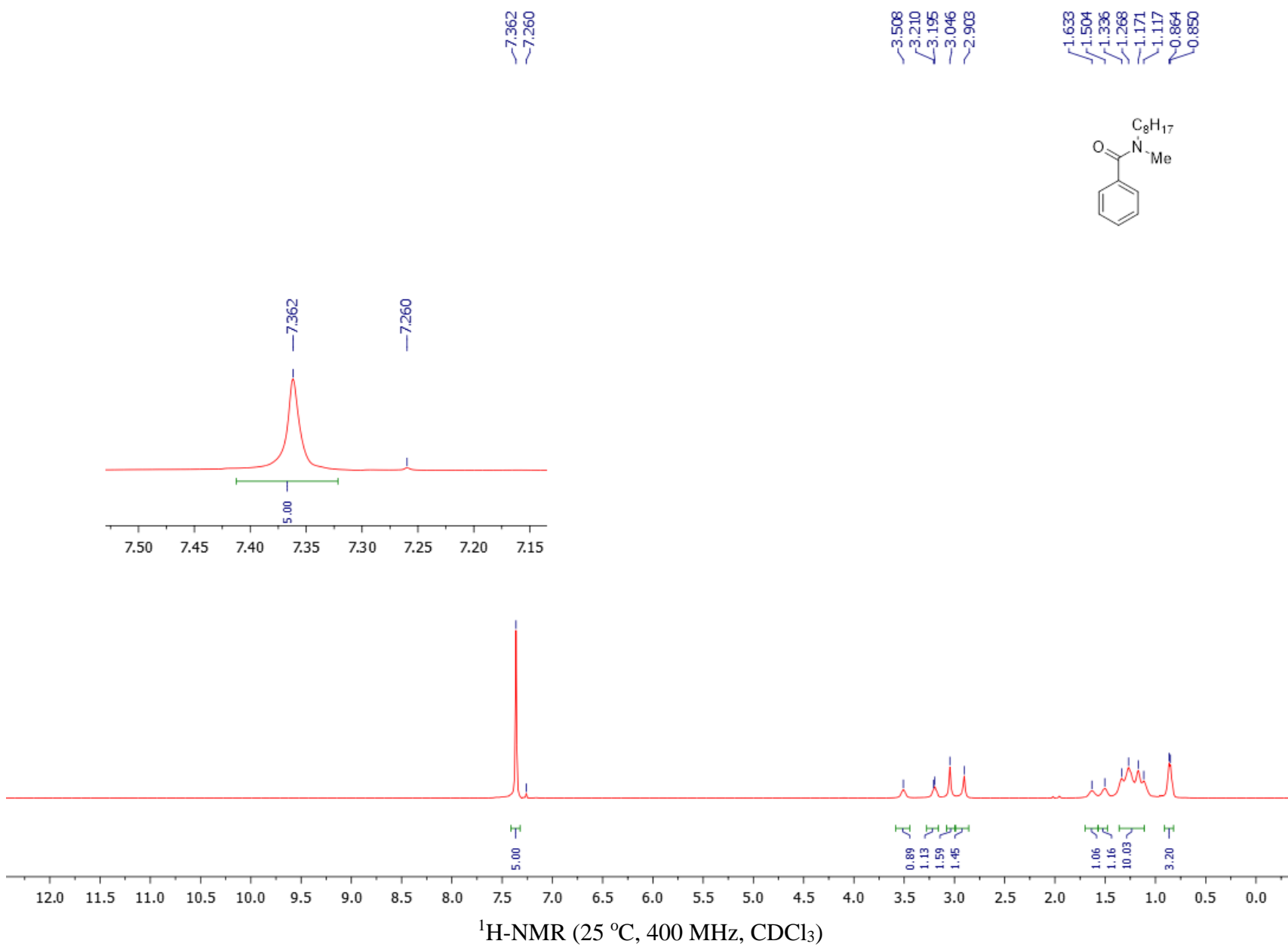
Spectral Copies:

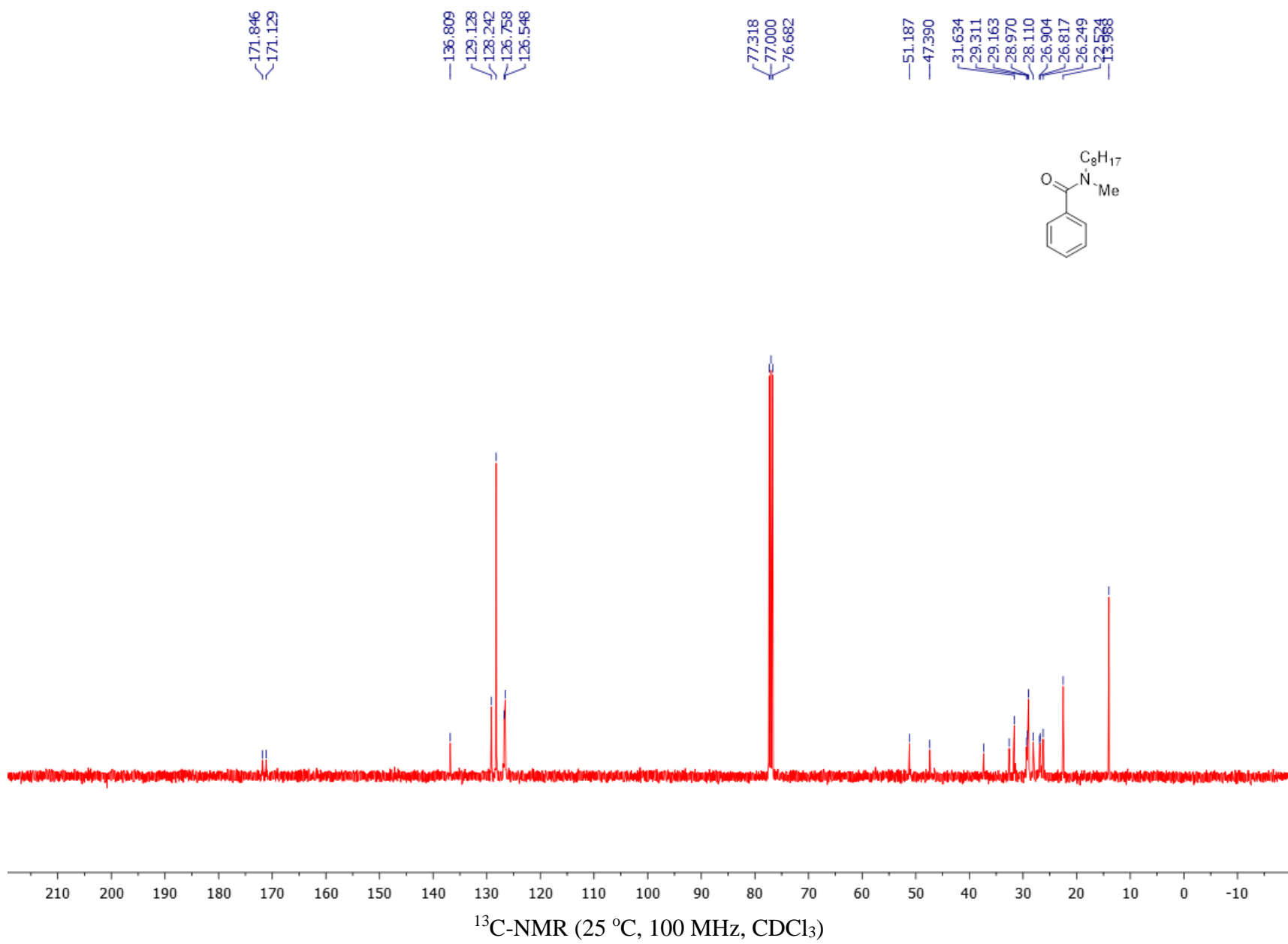


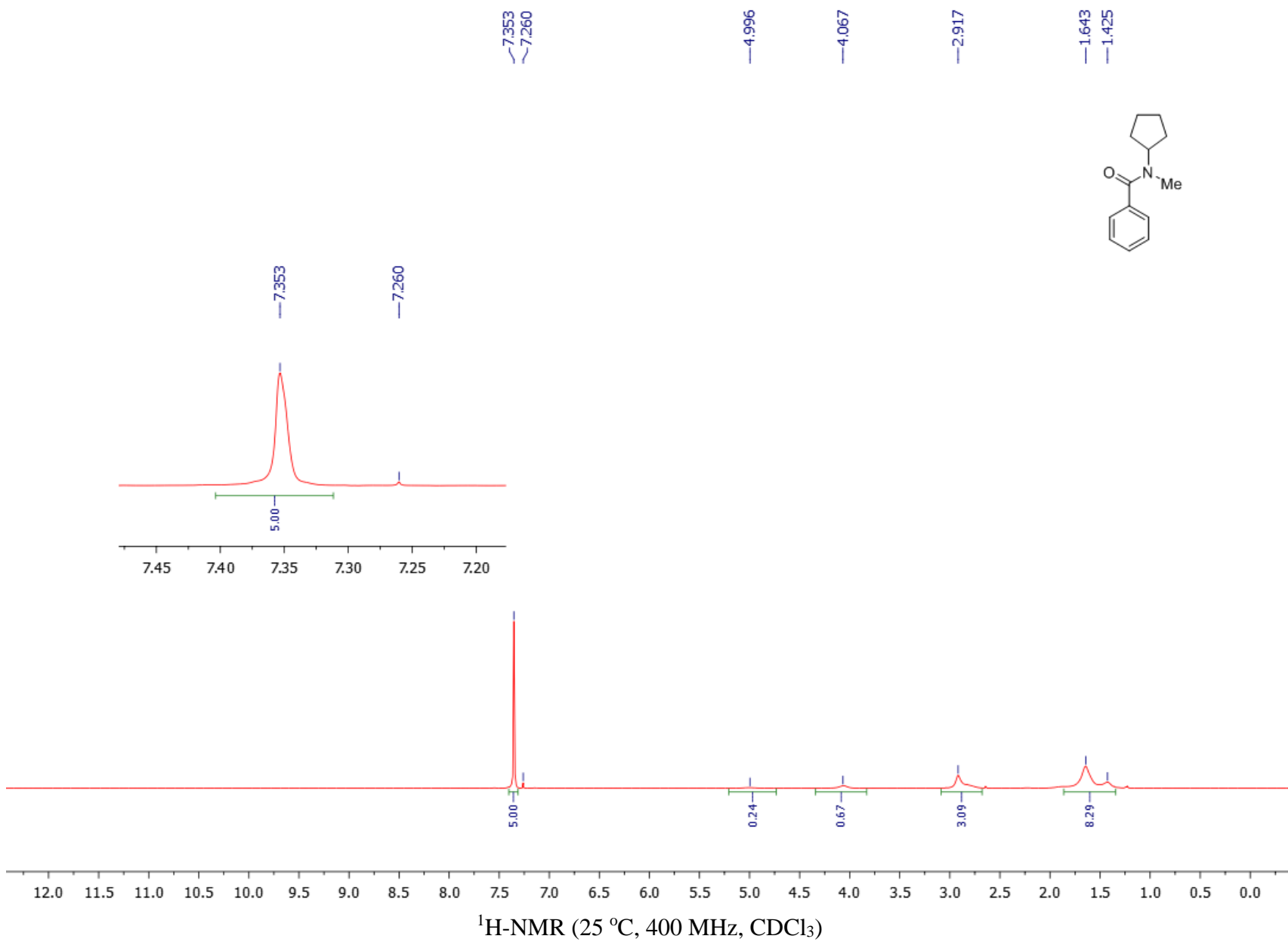


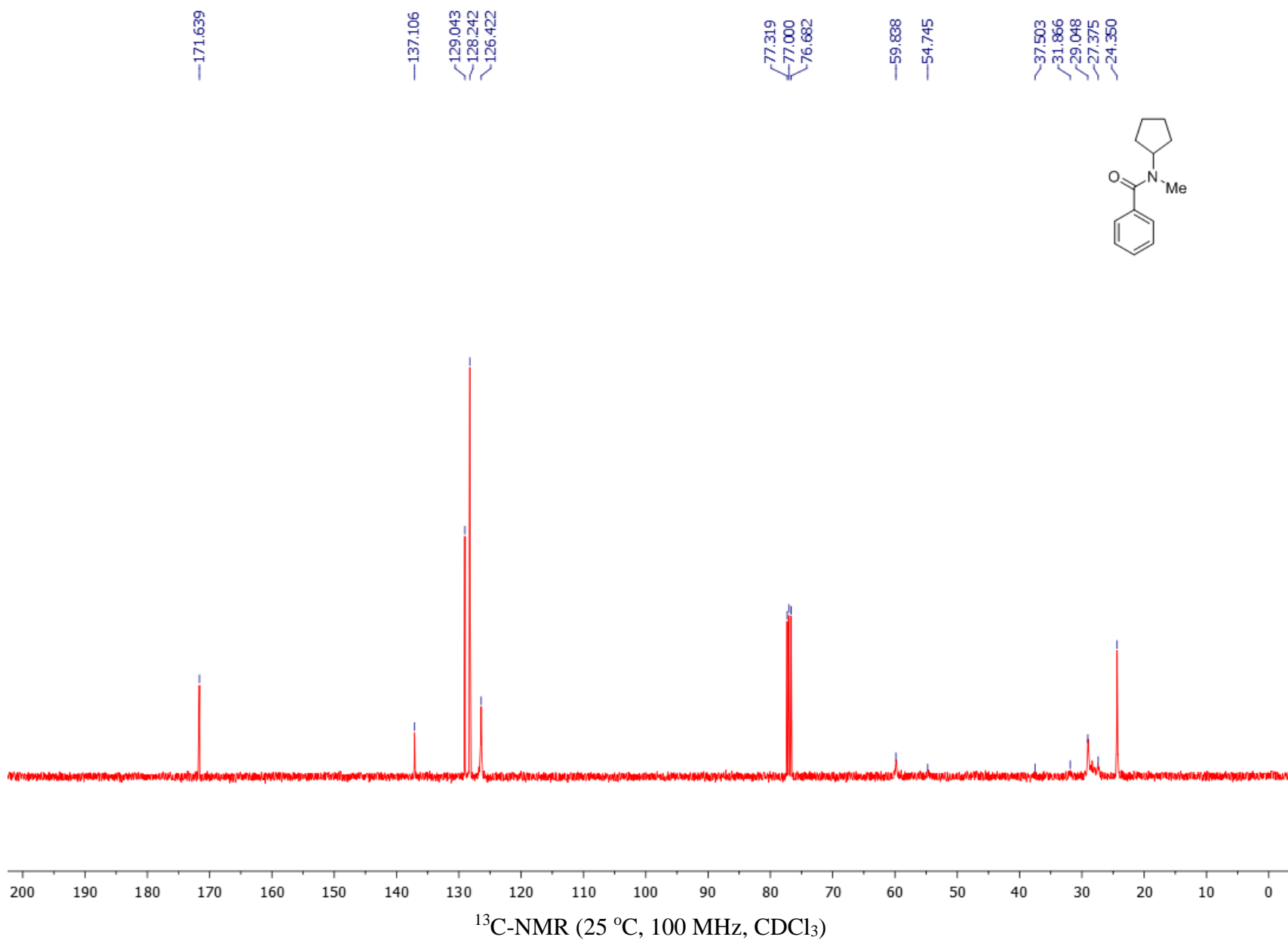


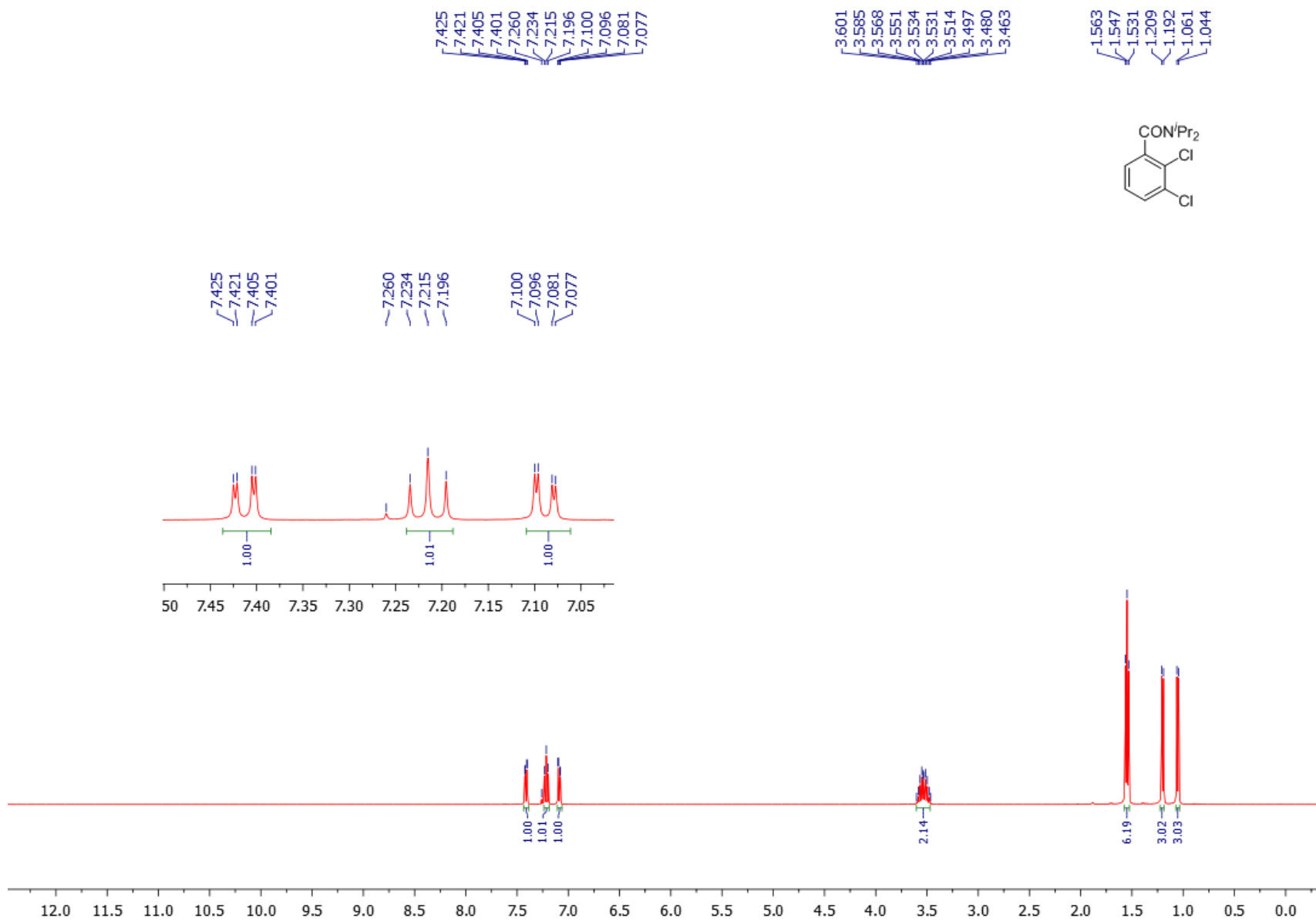


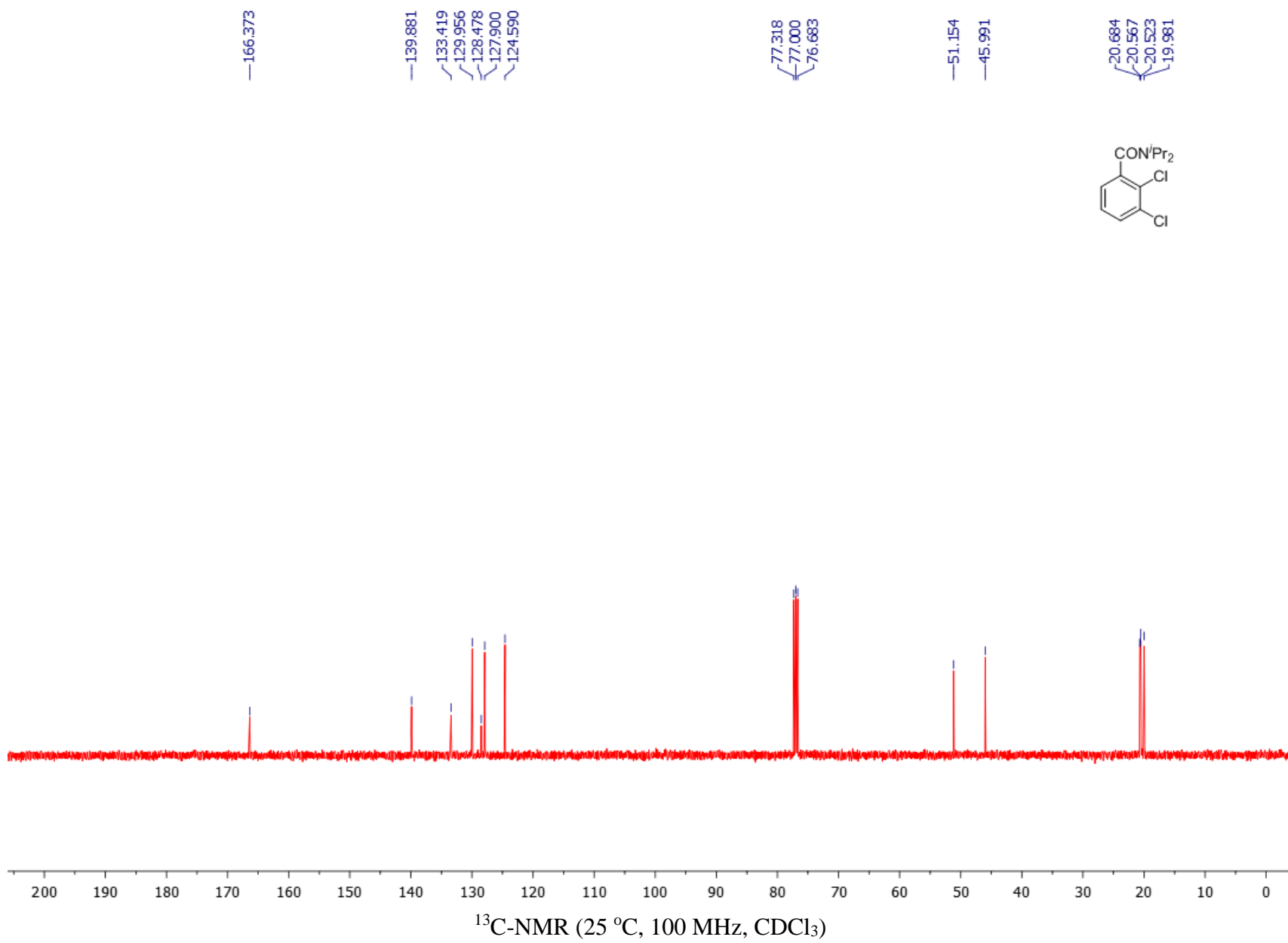


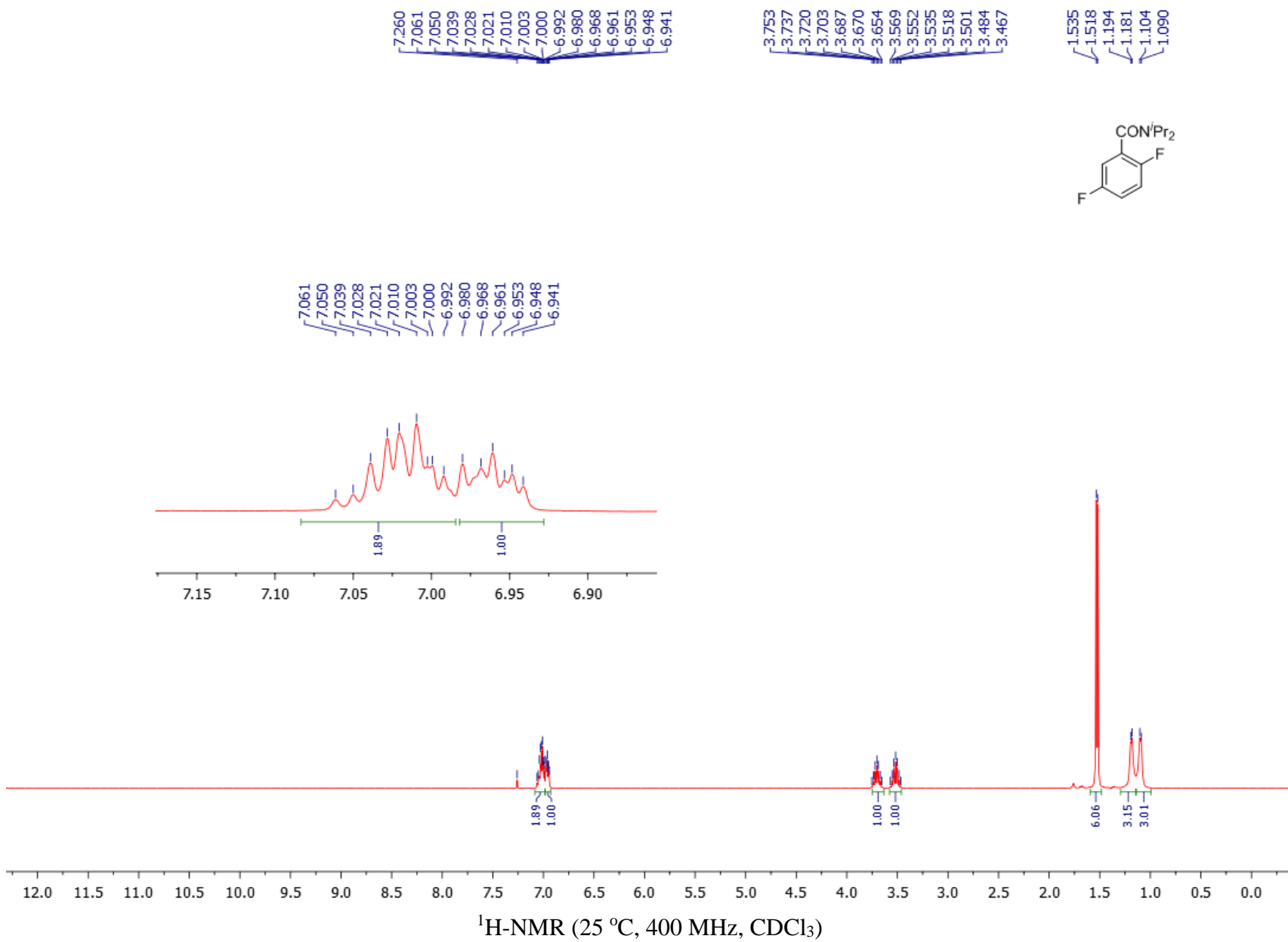


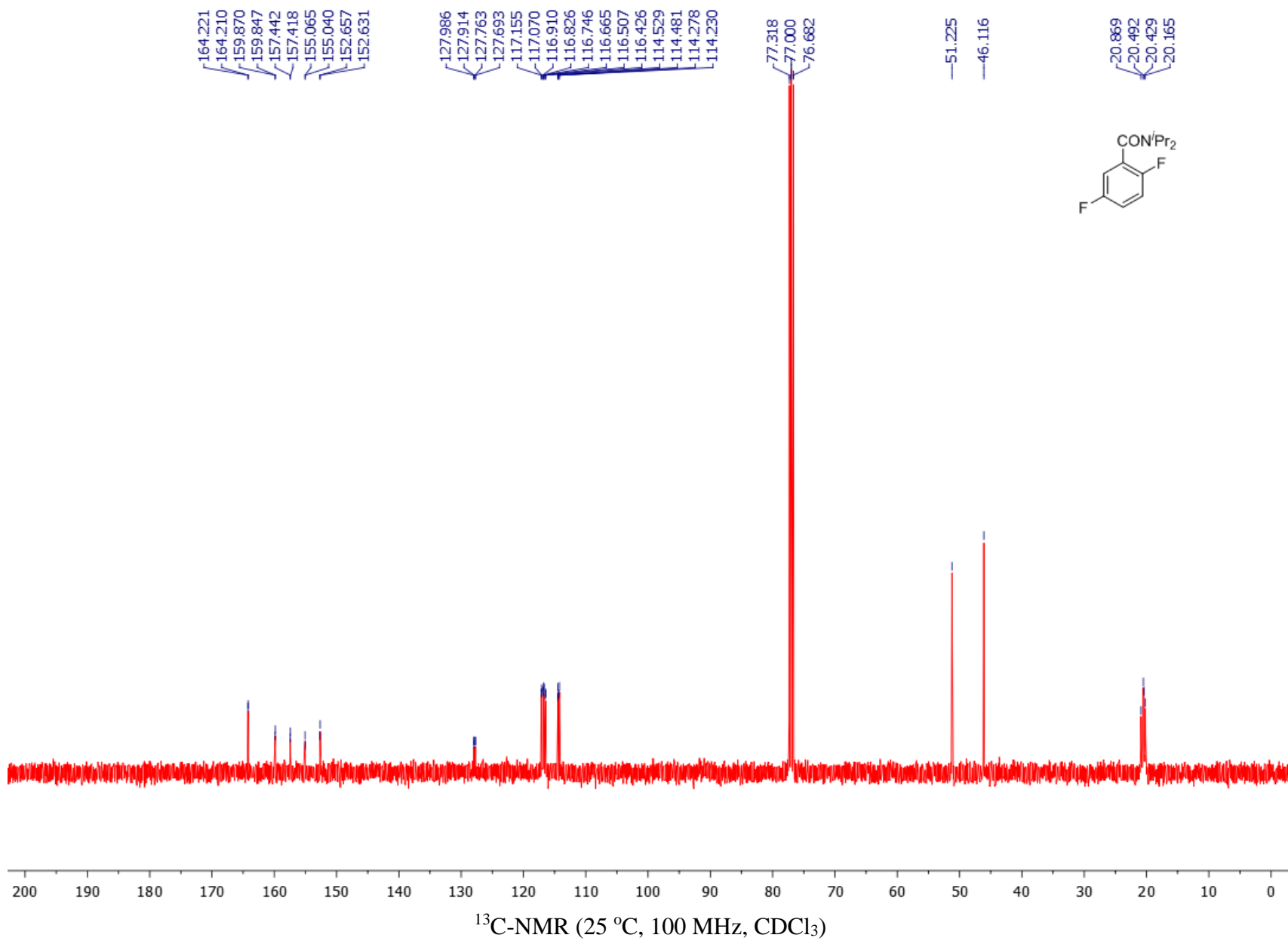


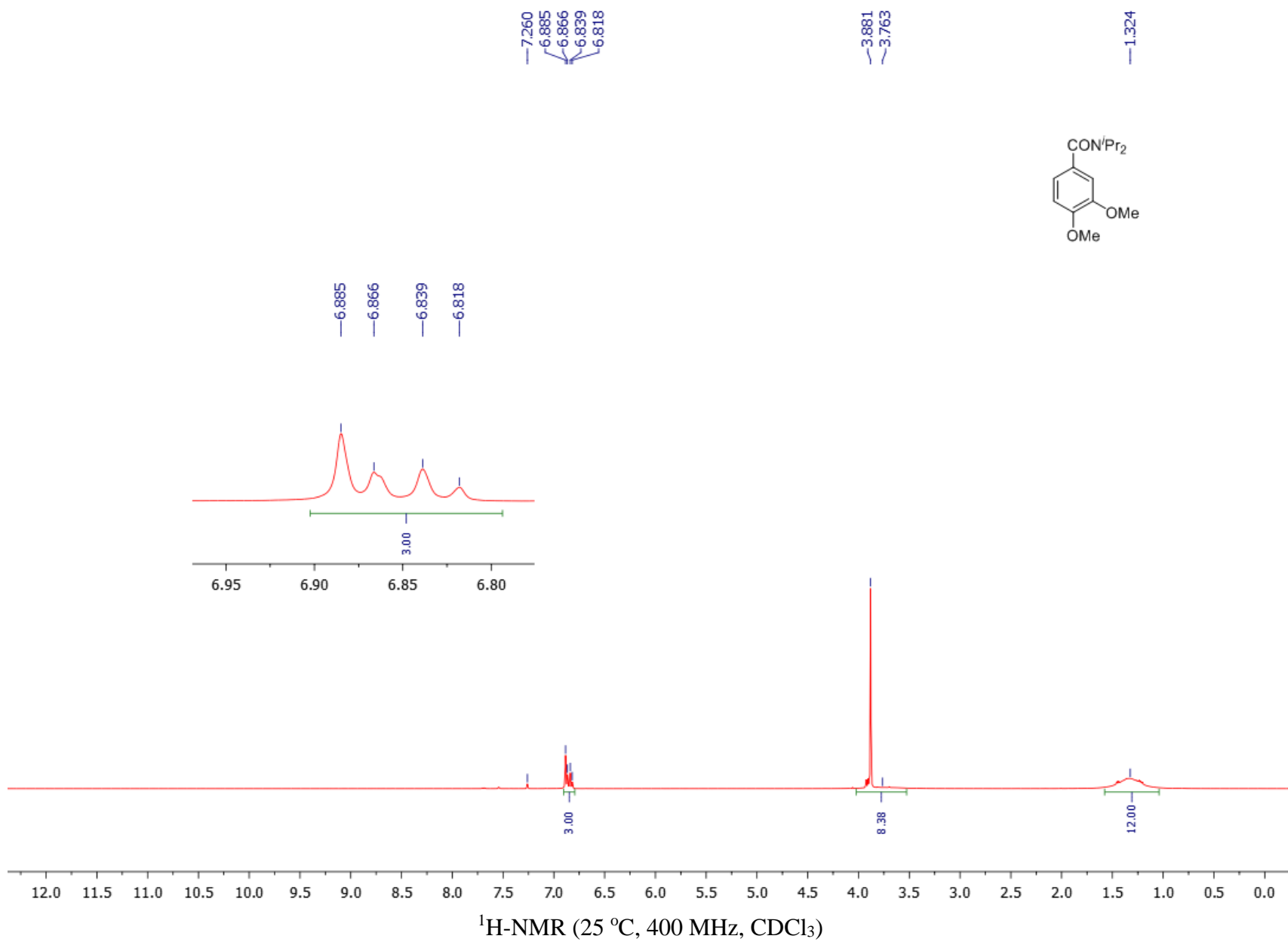


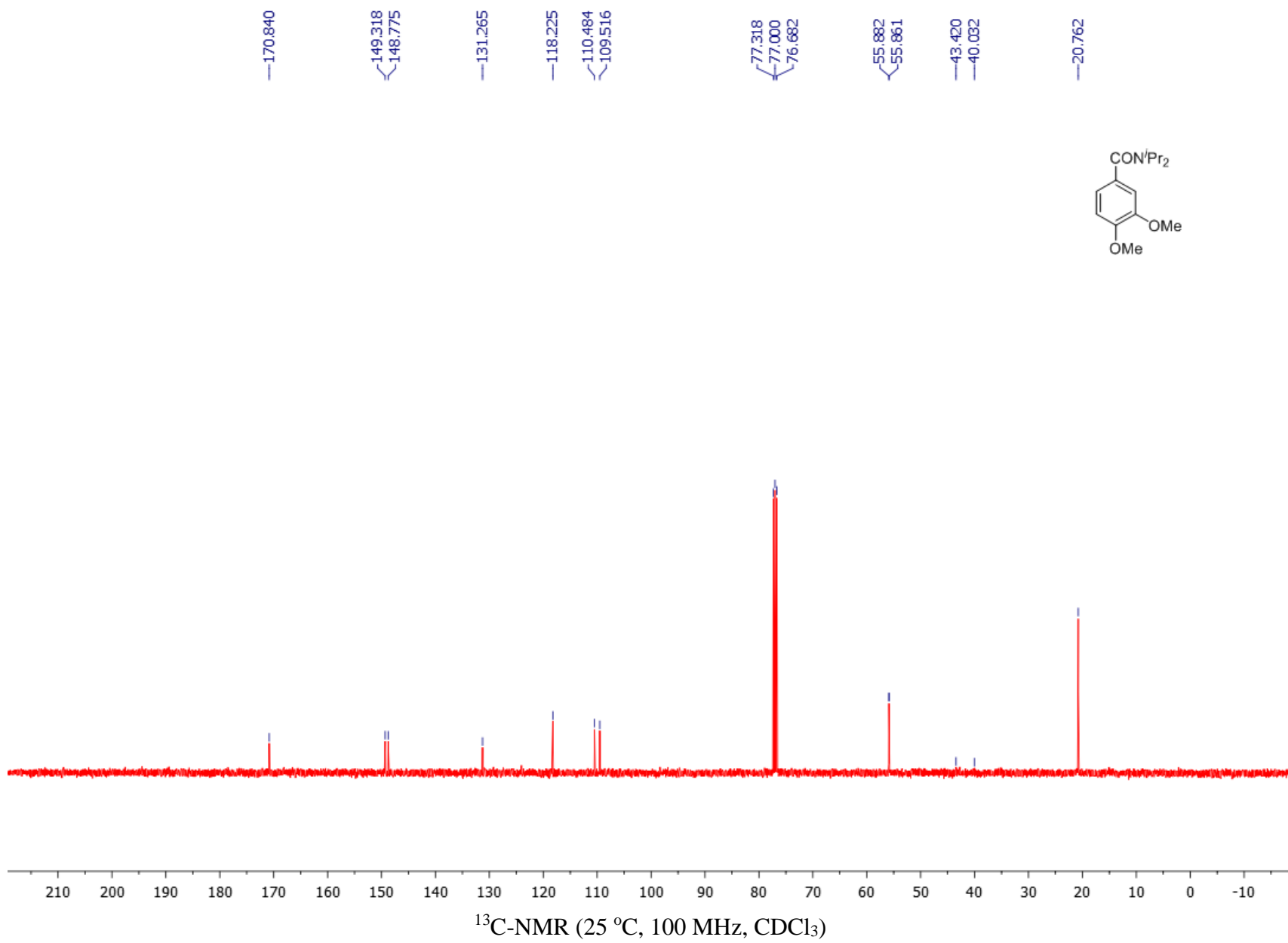


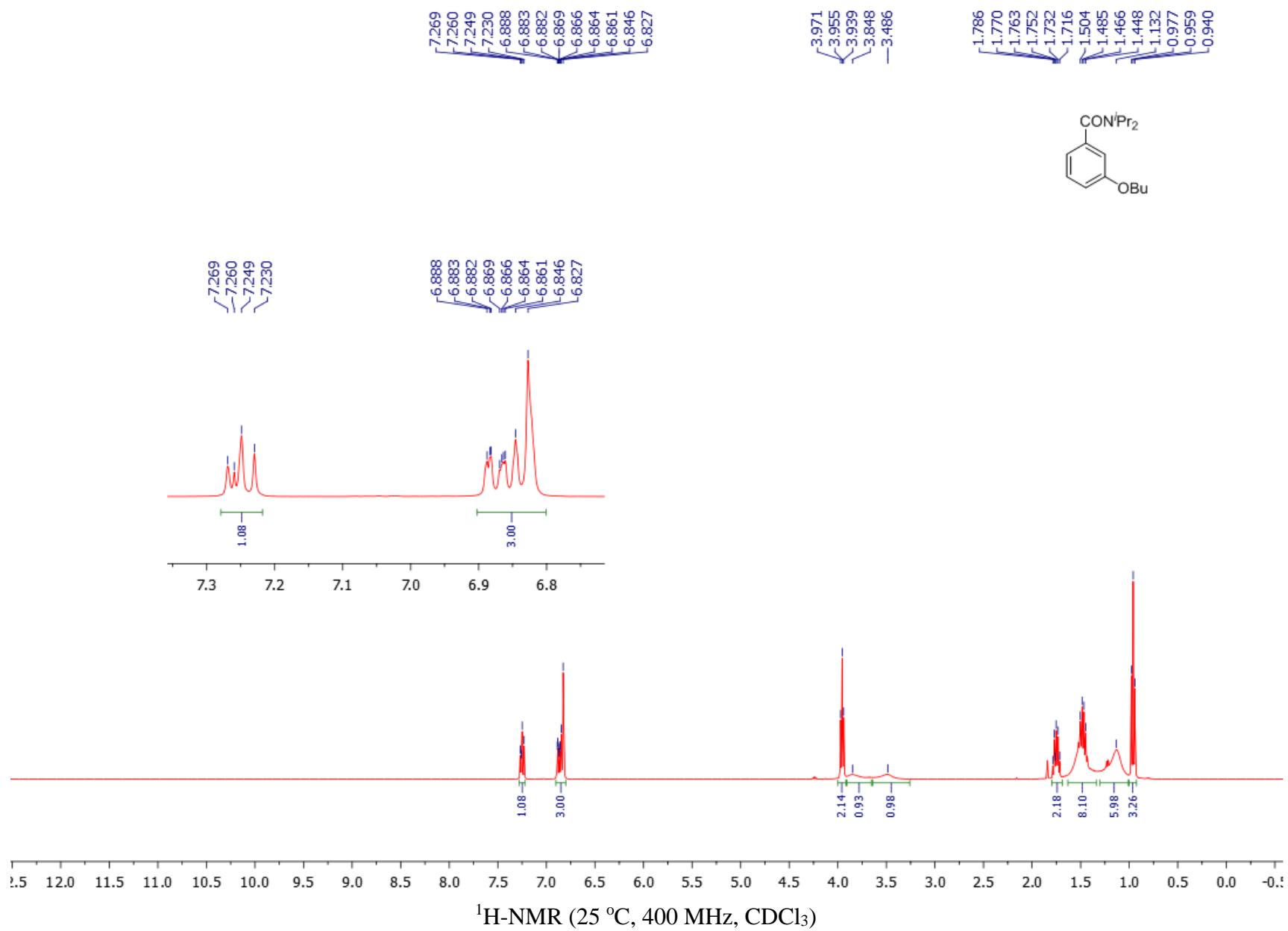


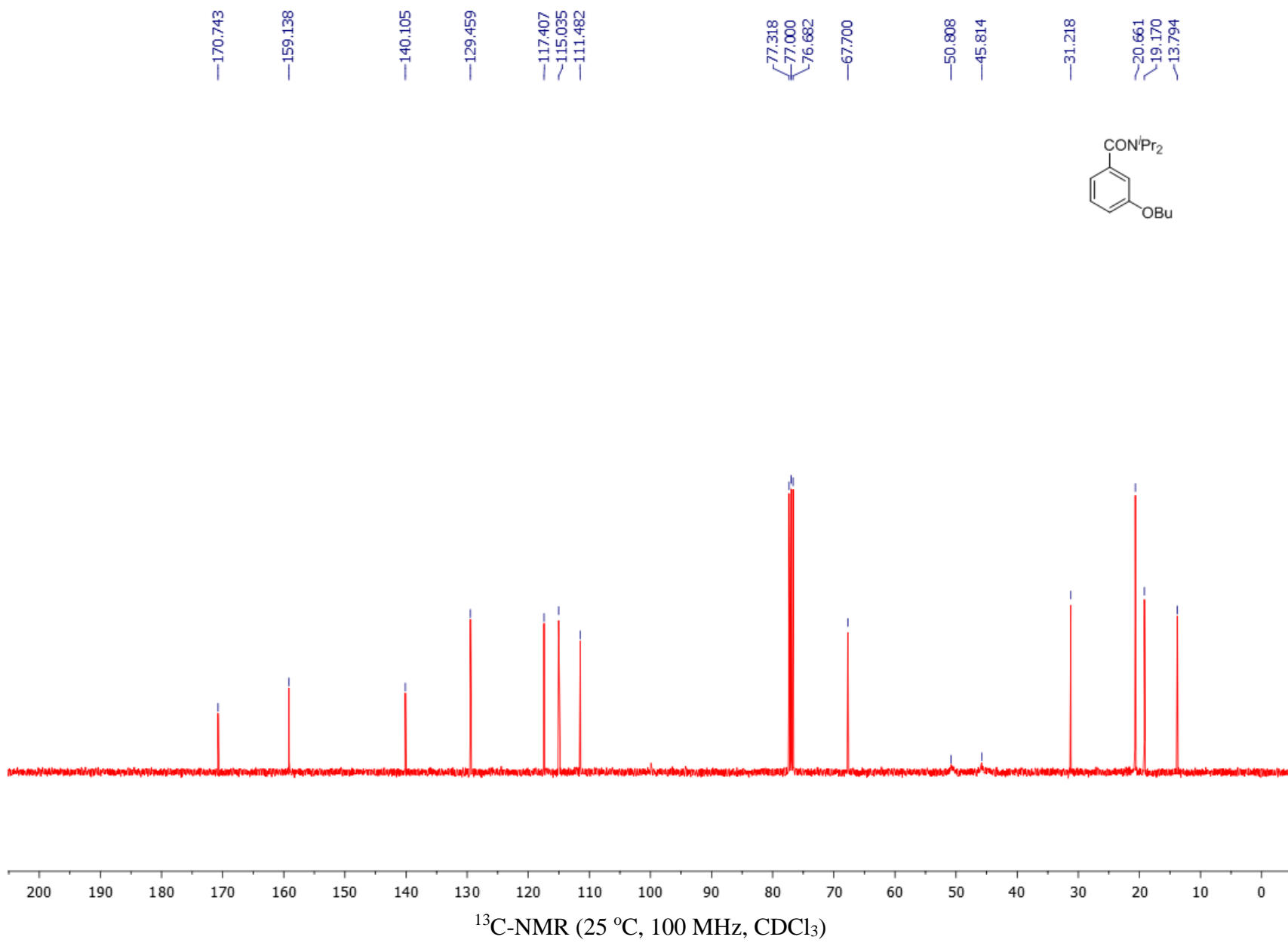


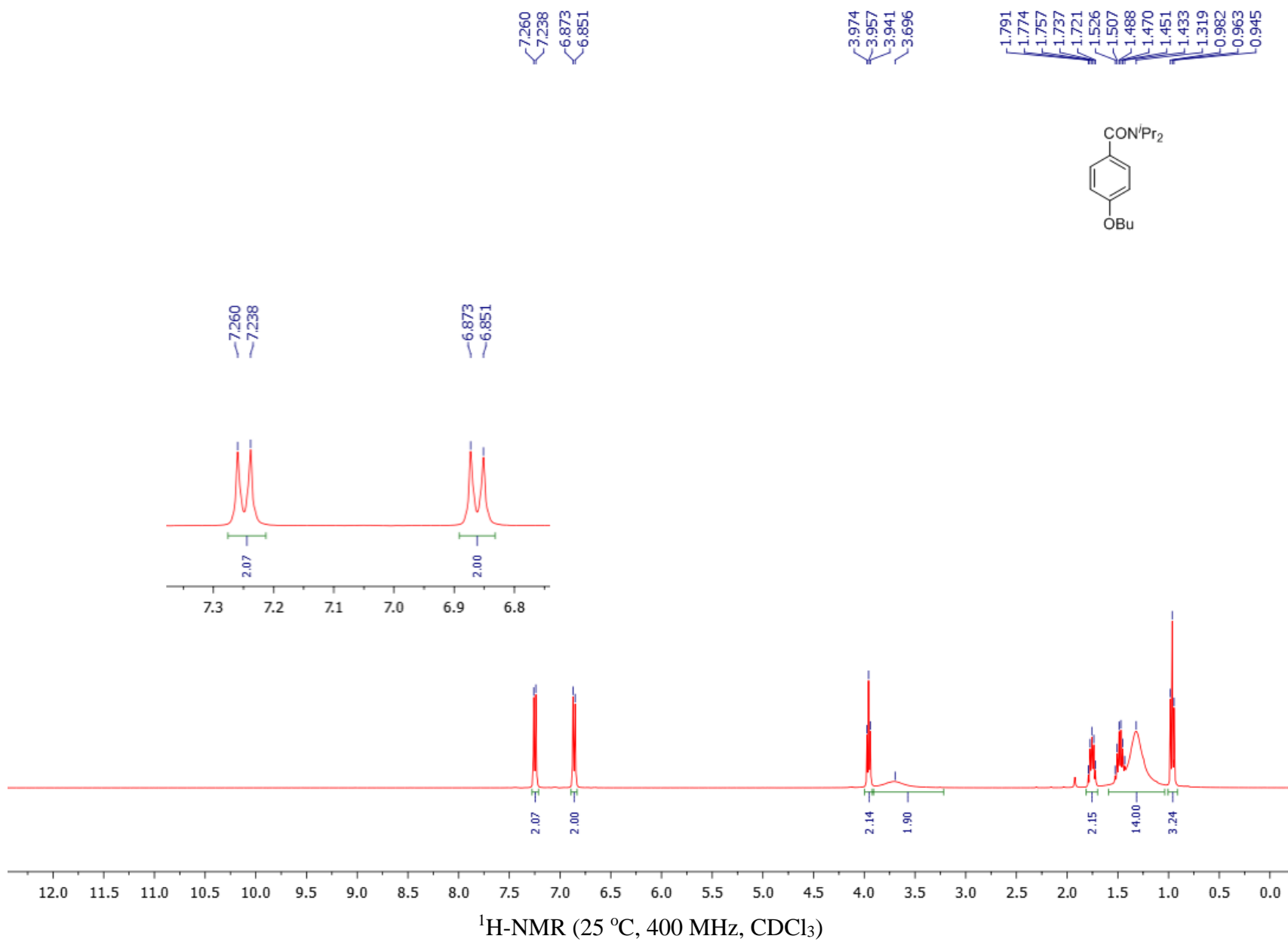


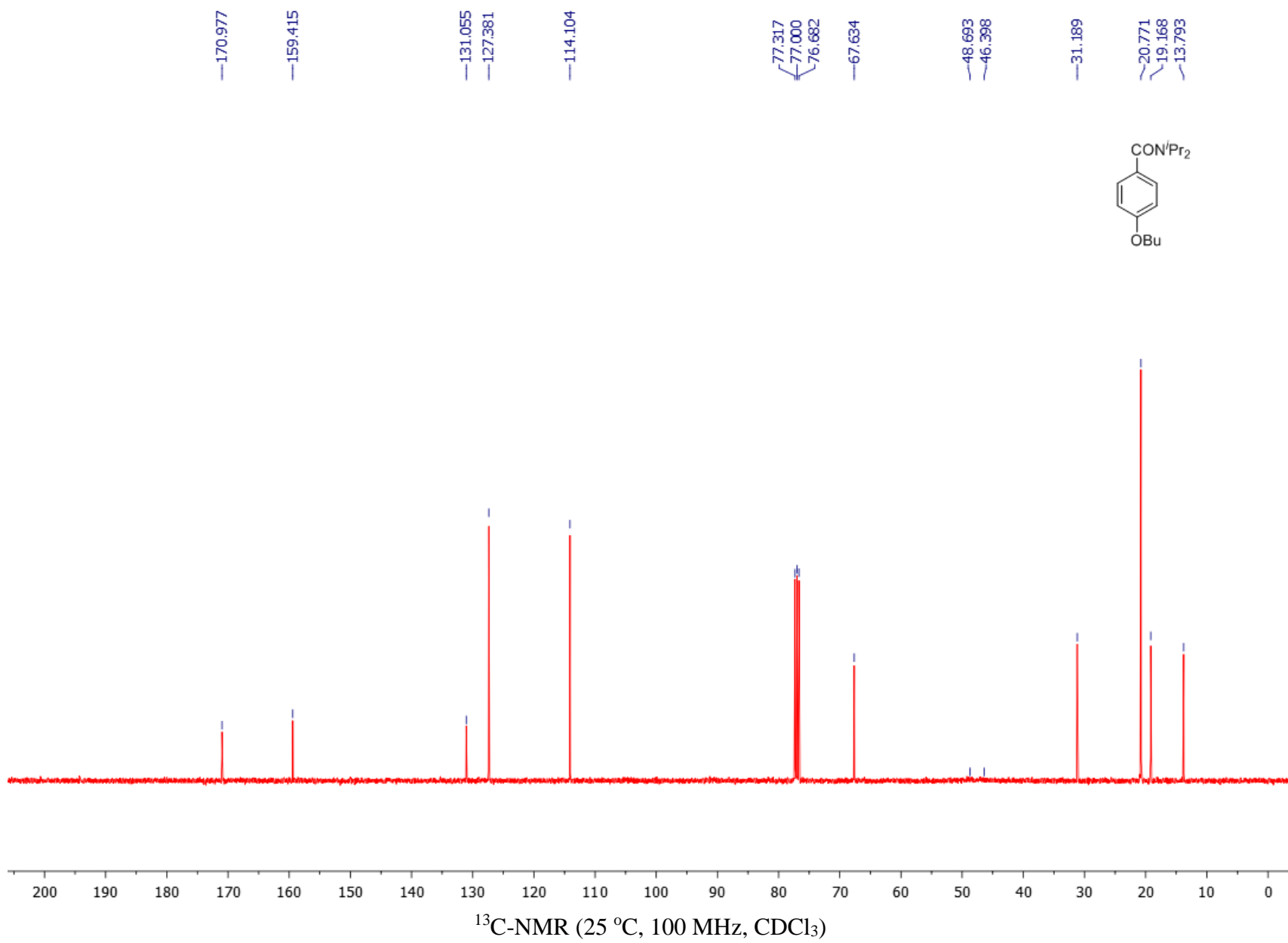


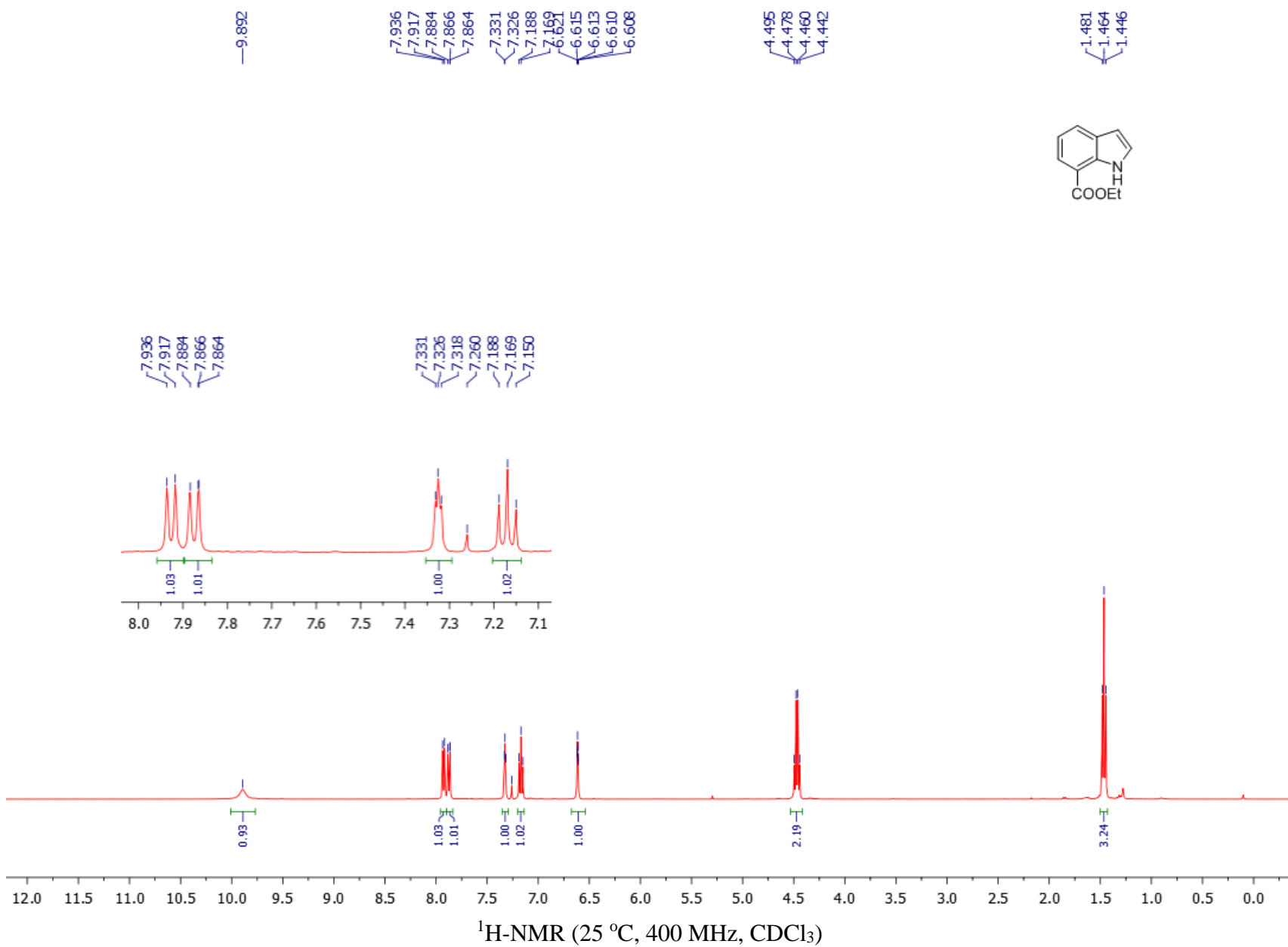


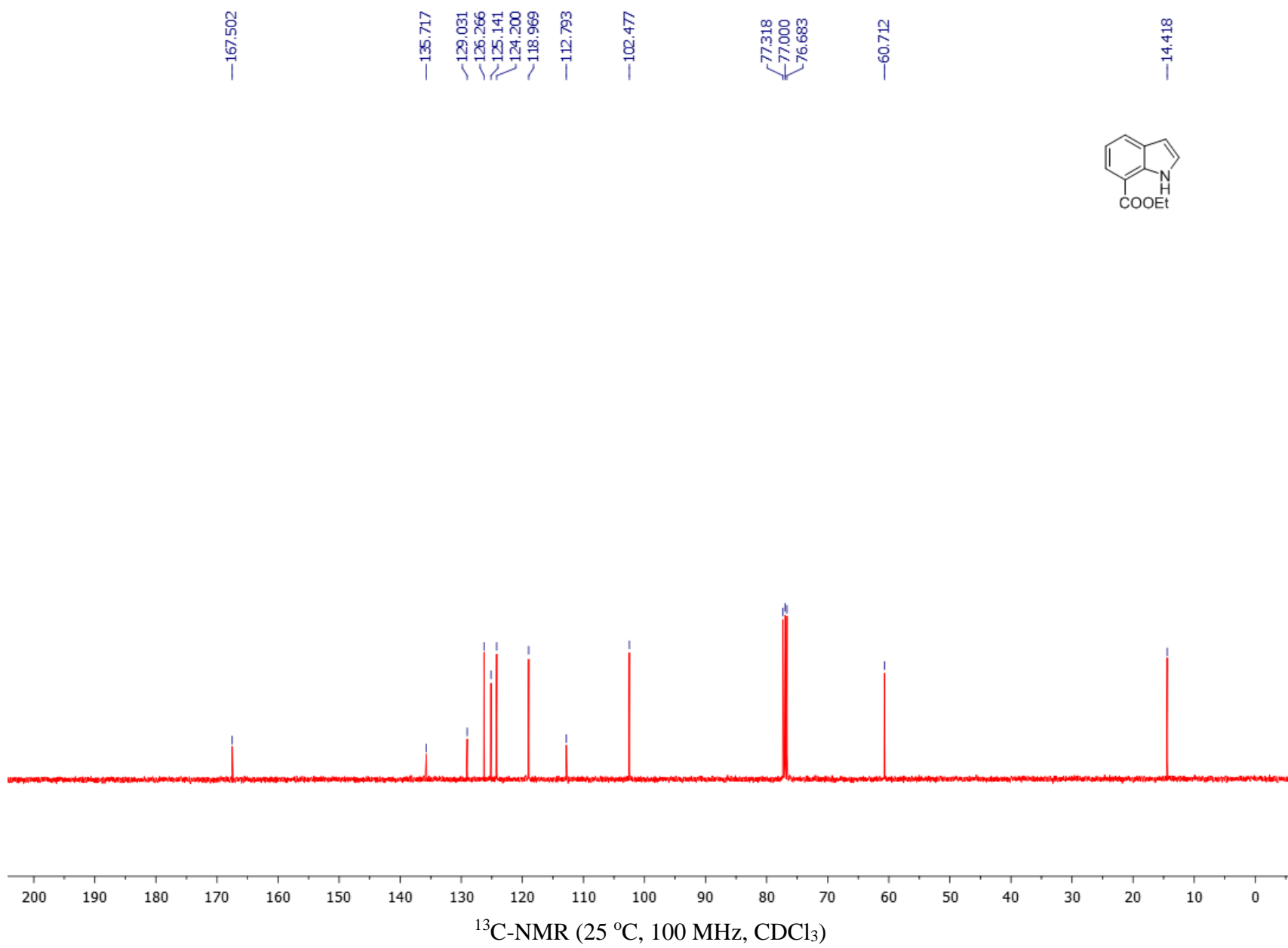


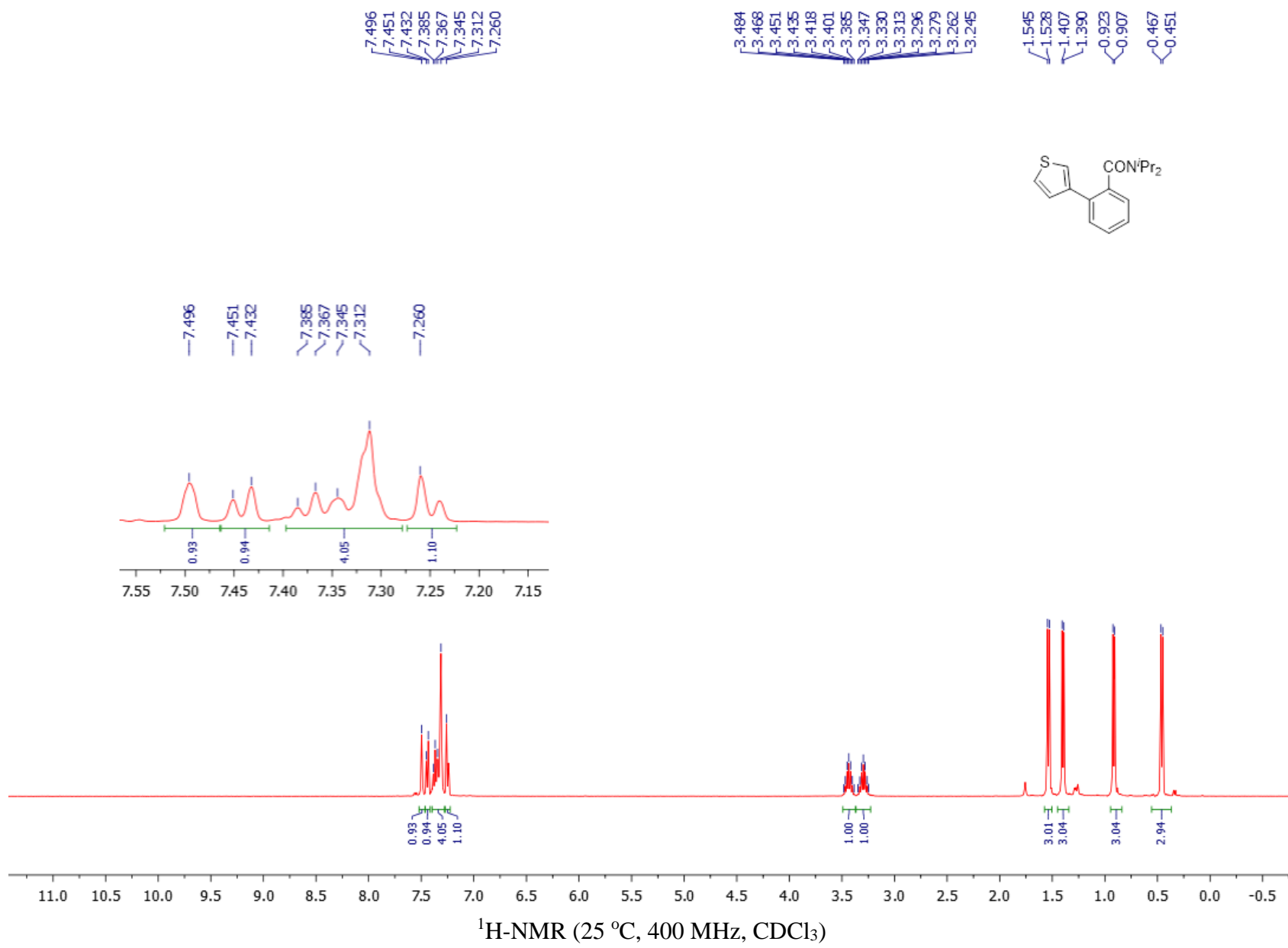


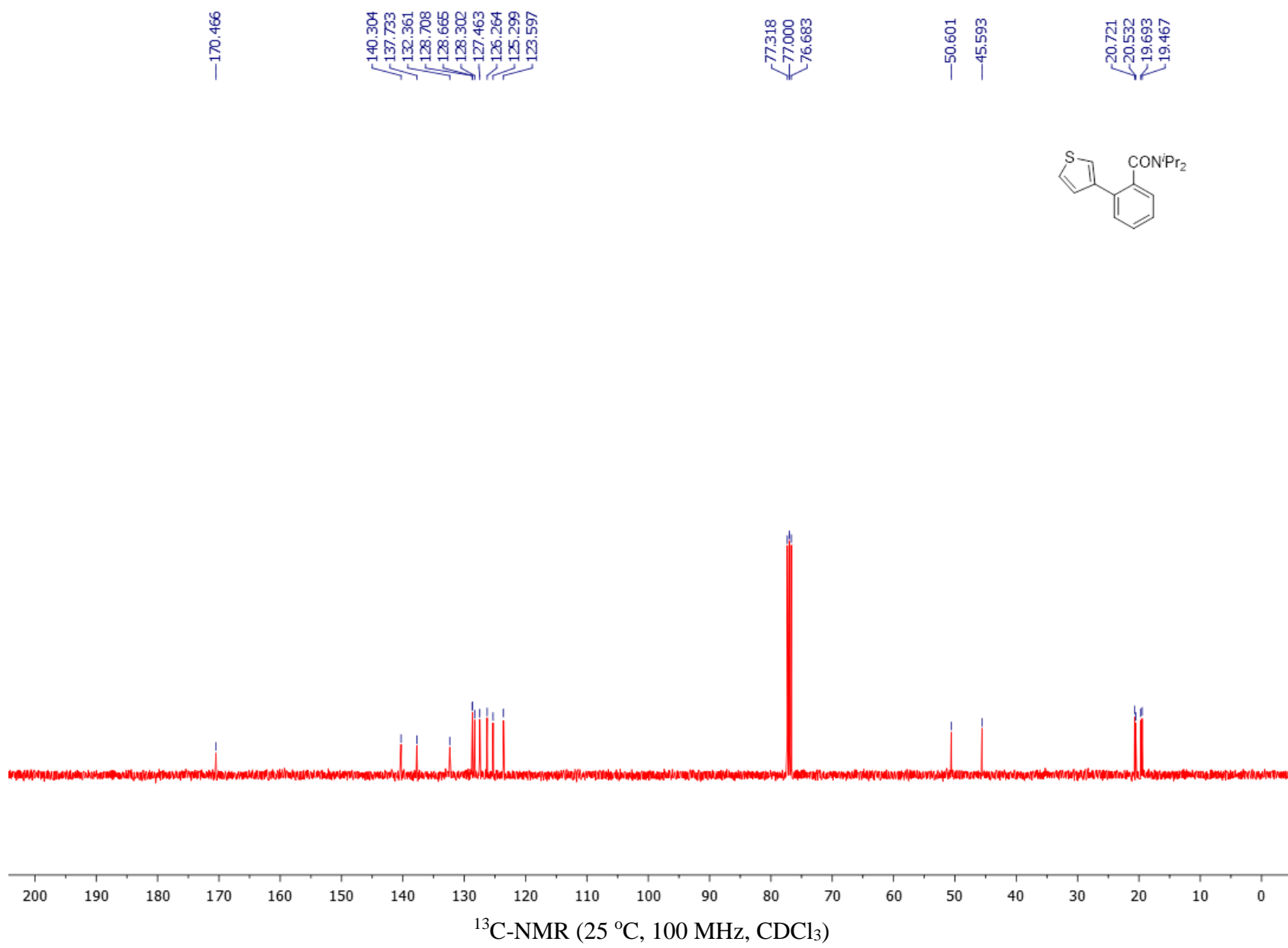


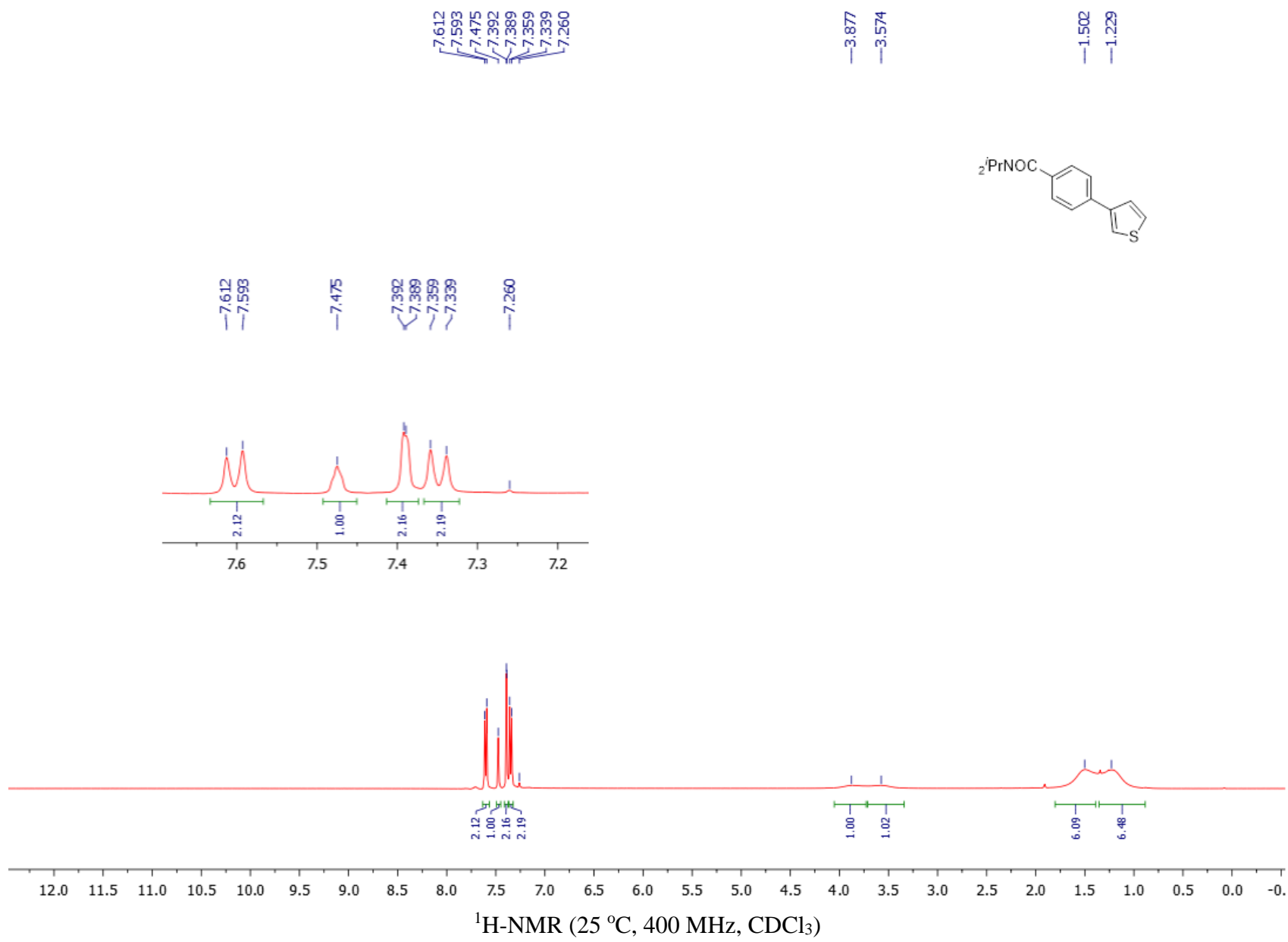


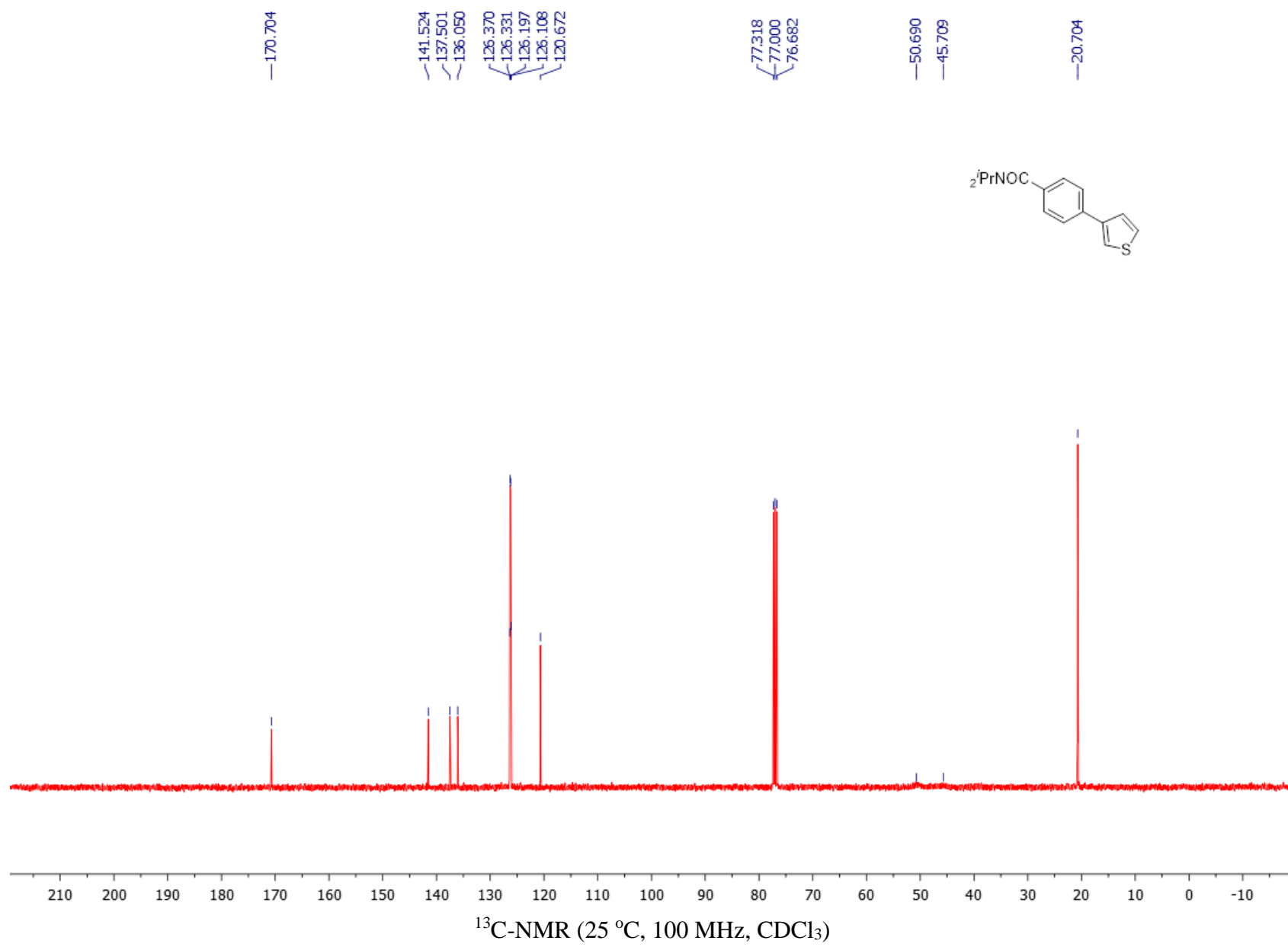


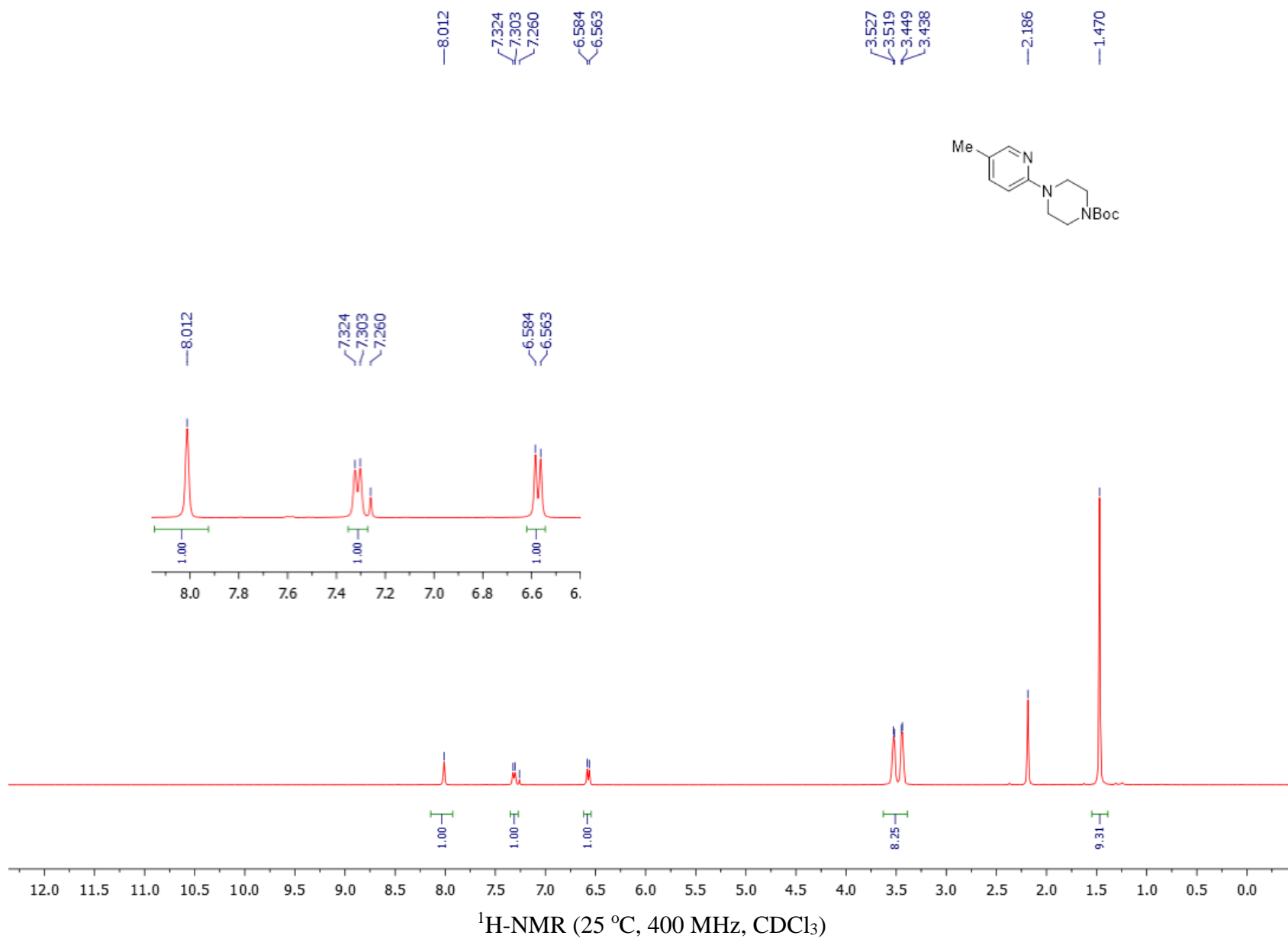


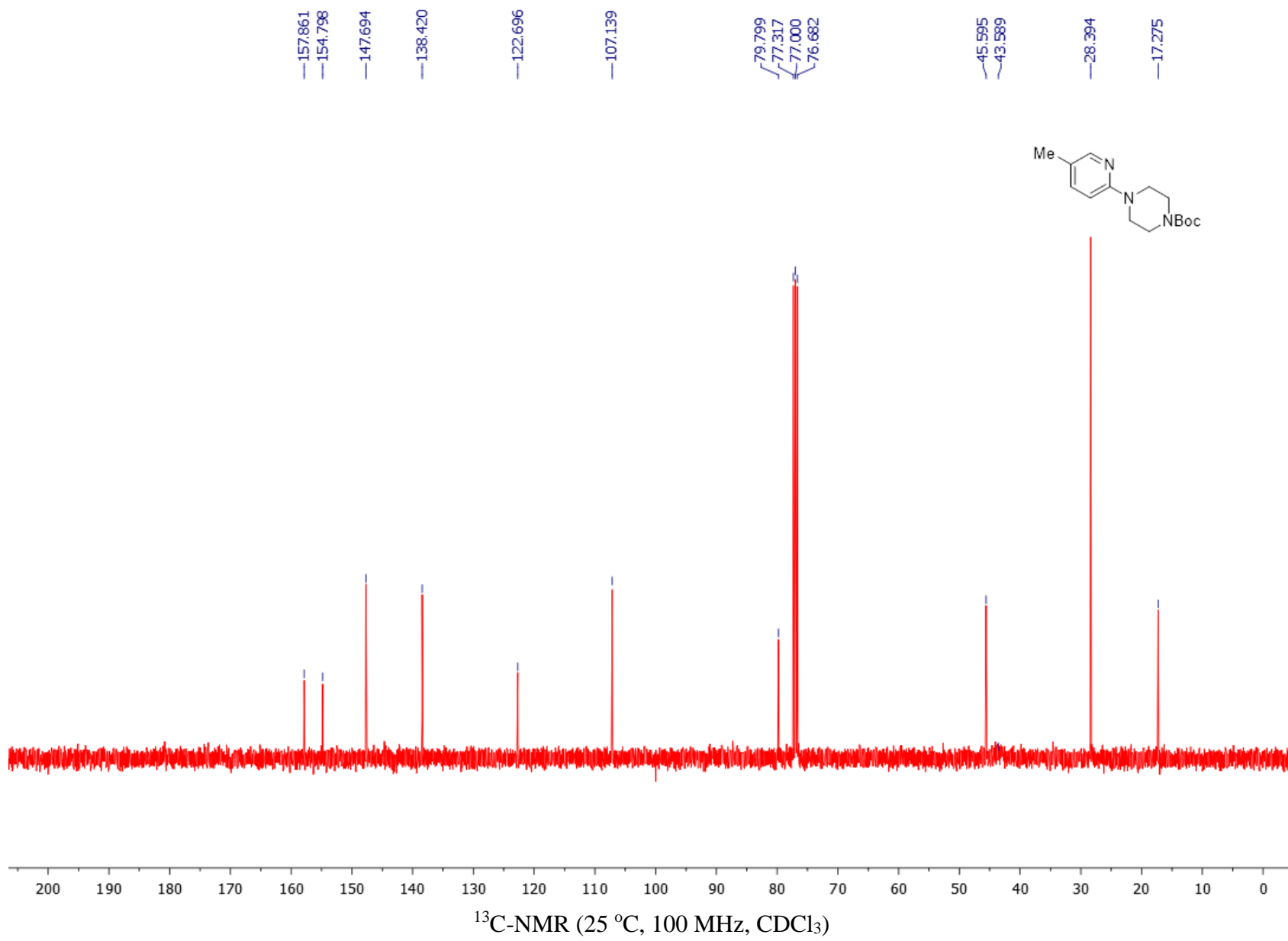


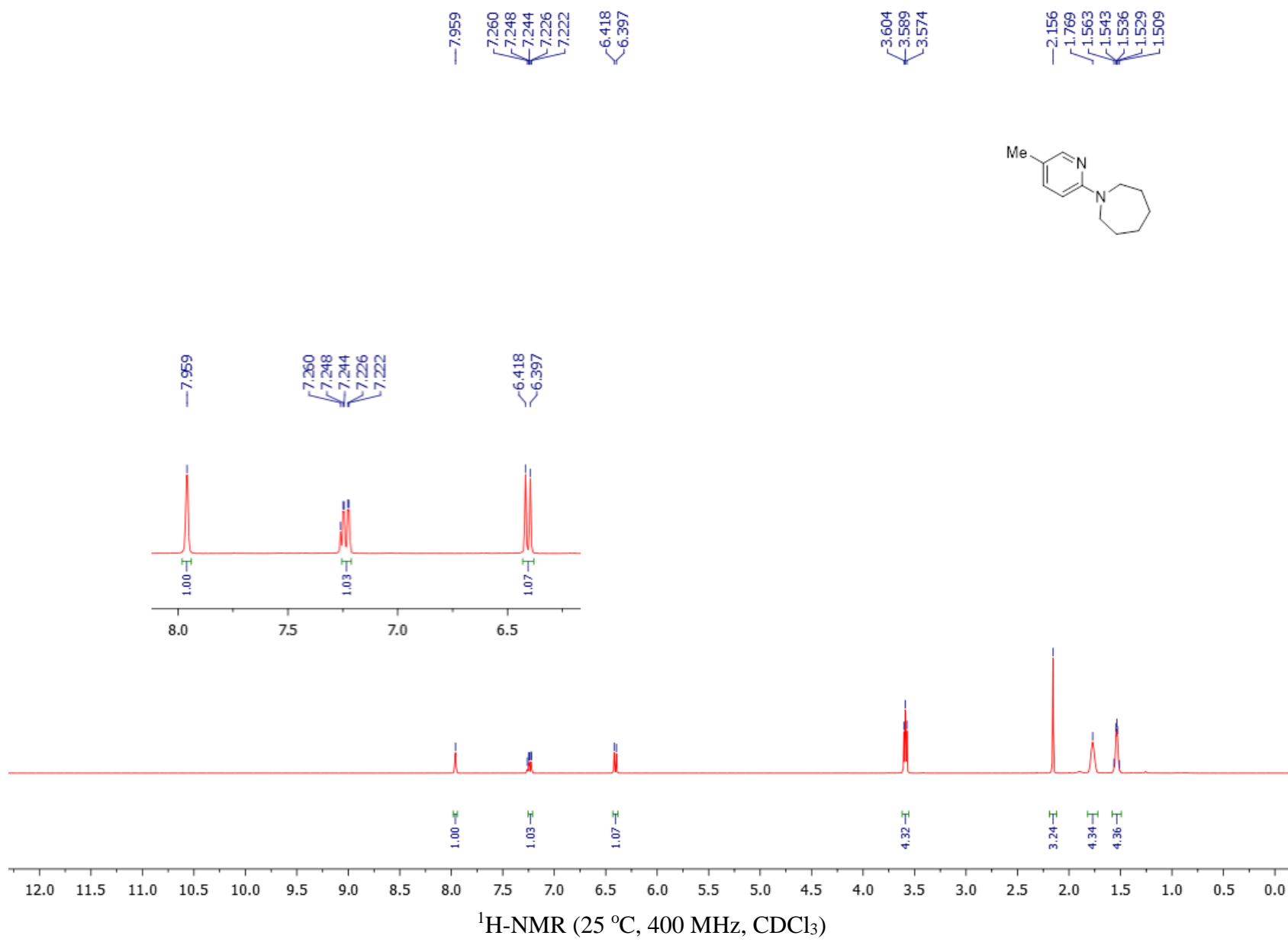


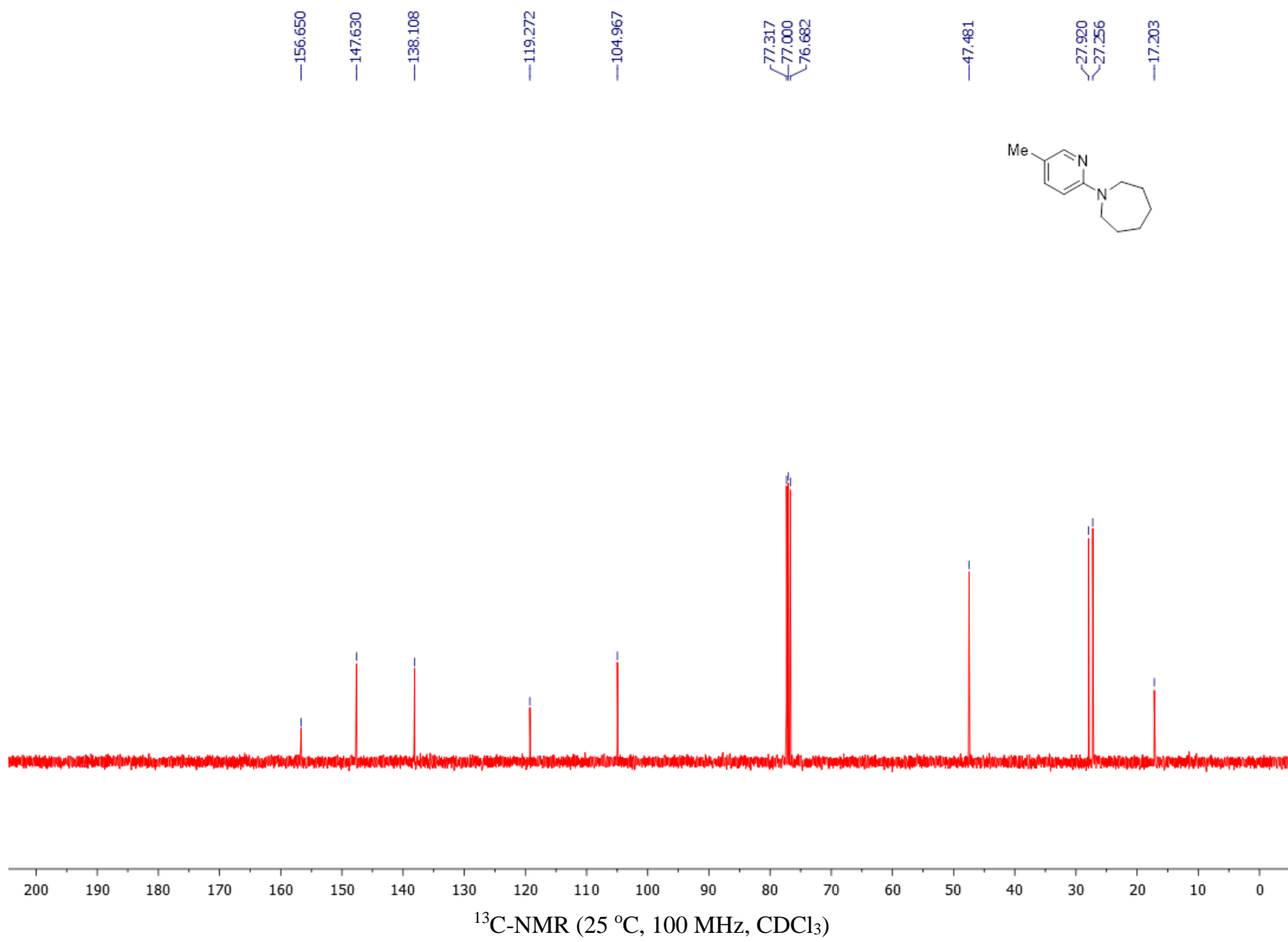


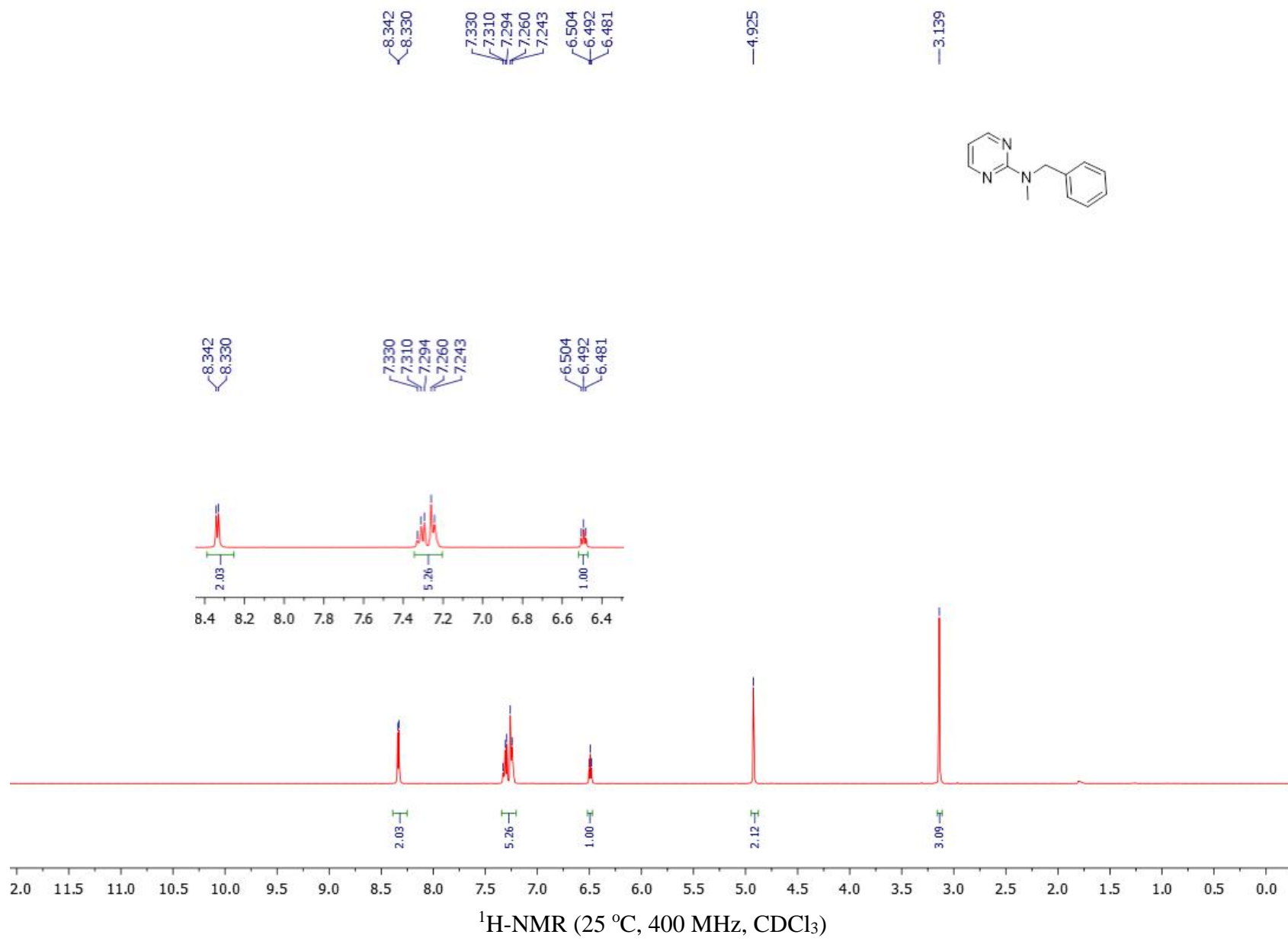


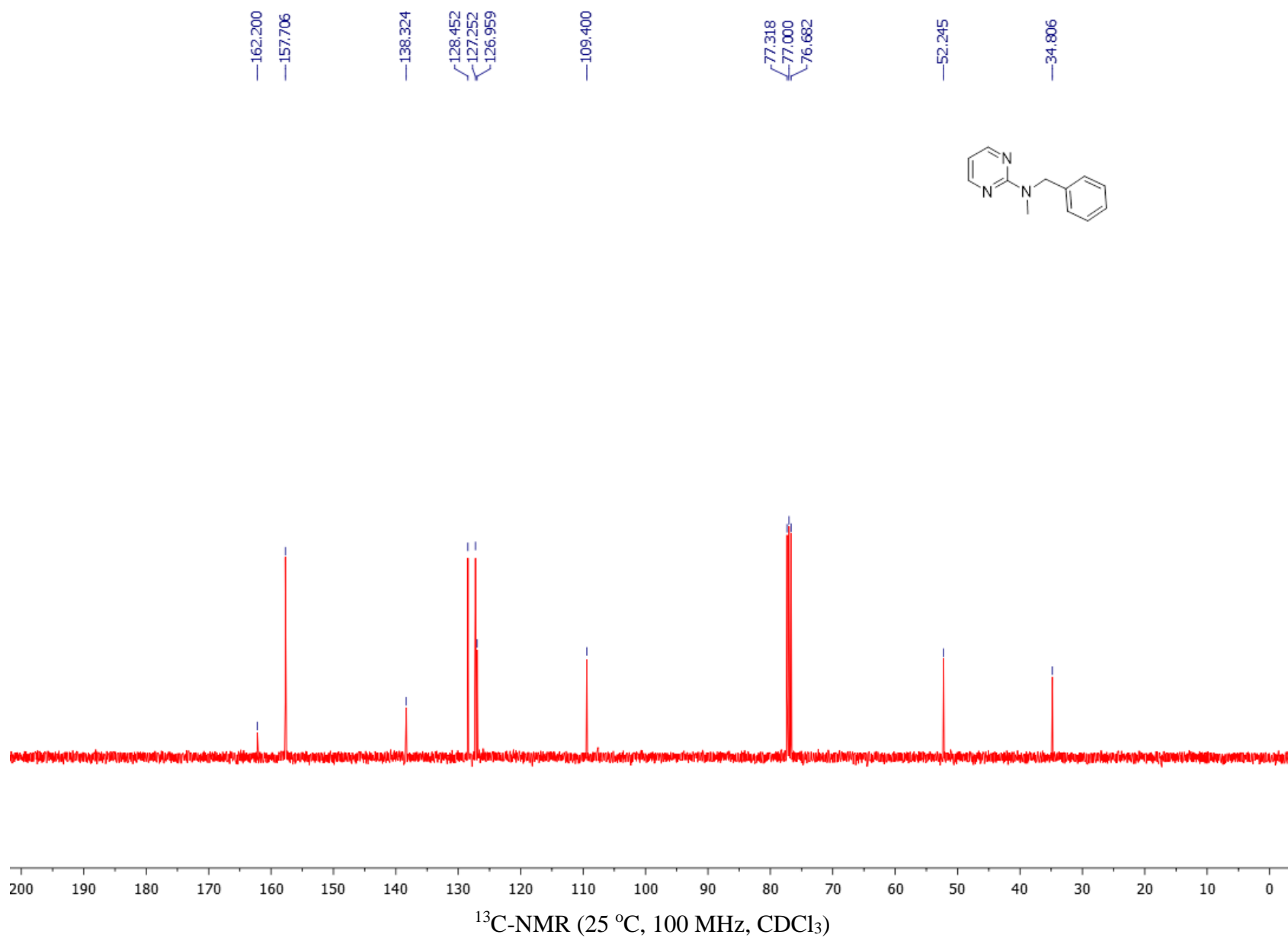


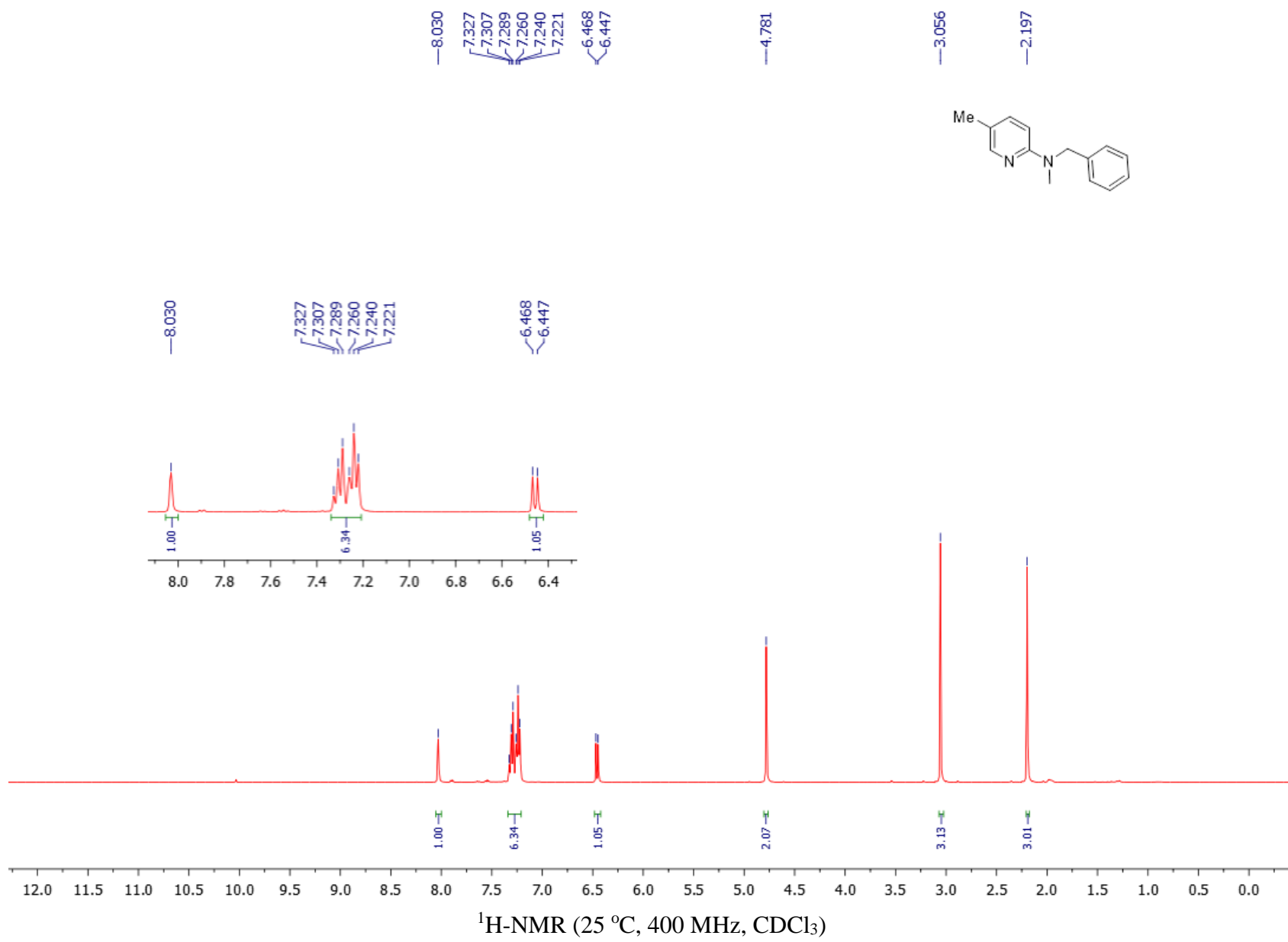


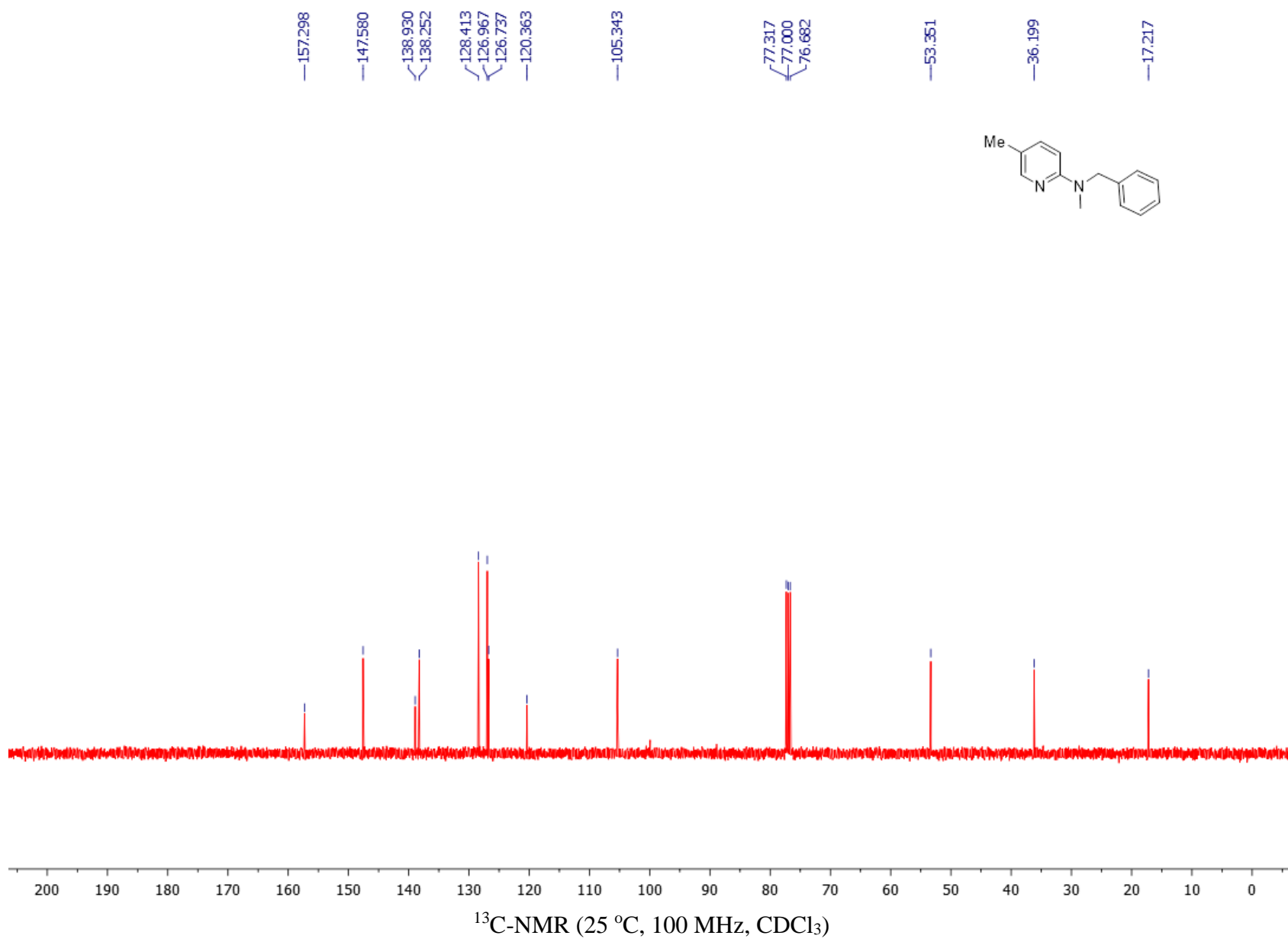


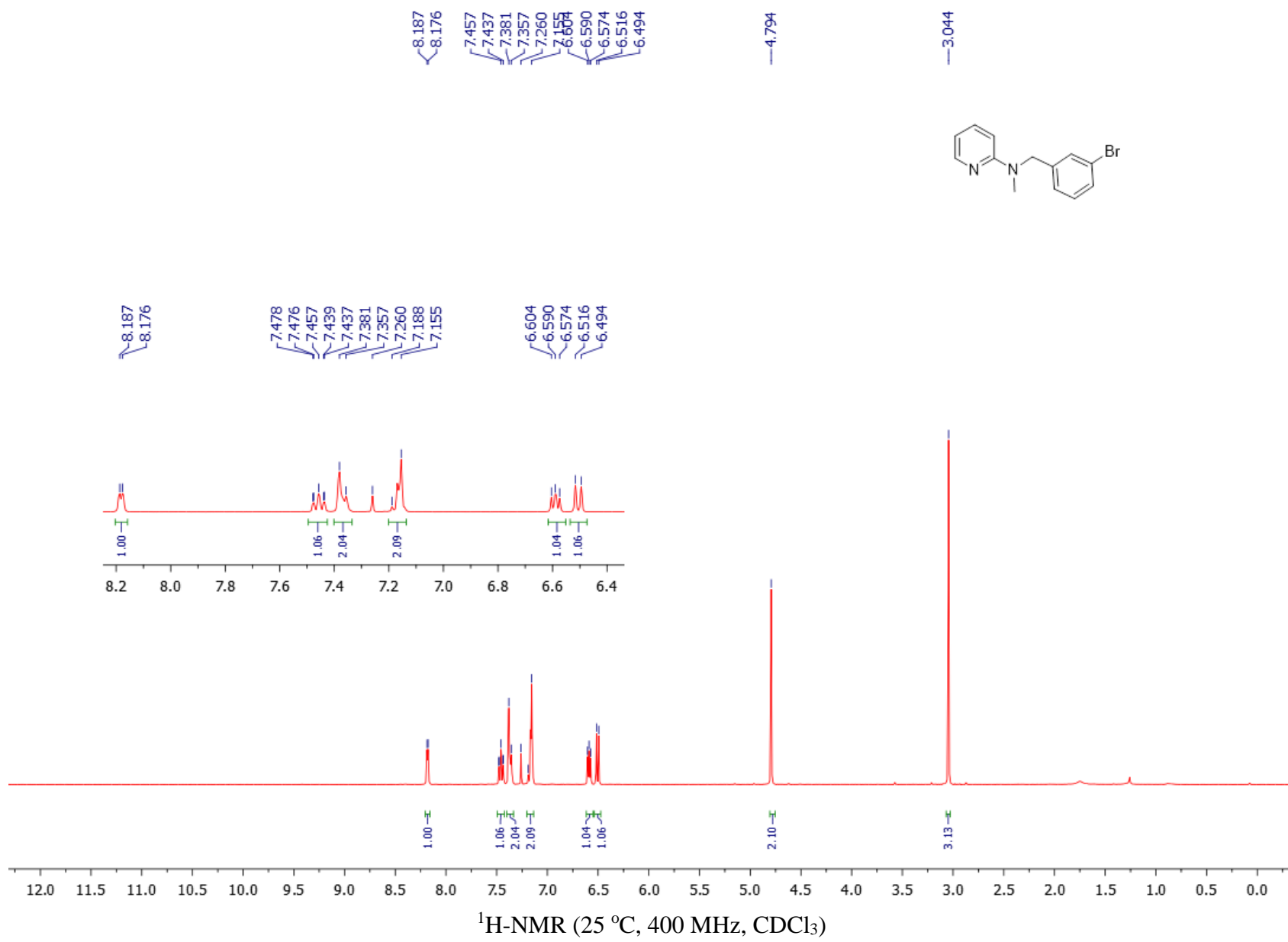


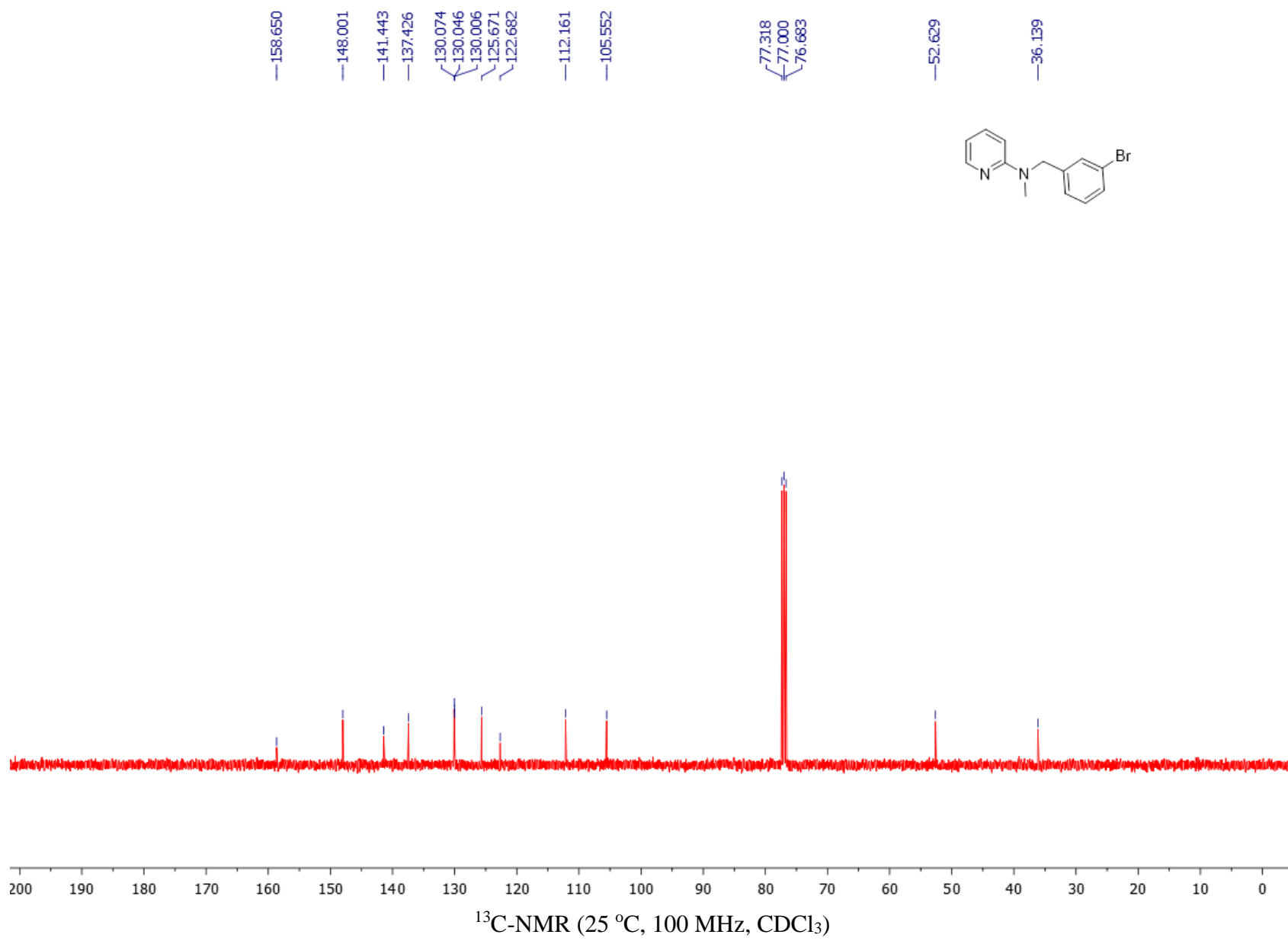


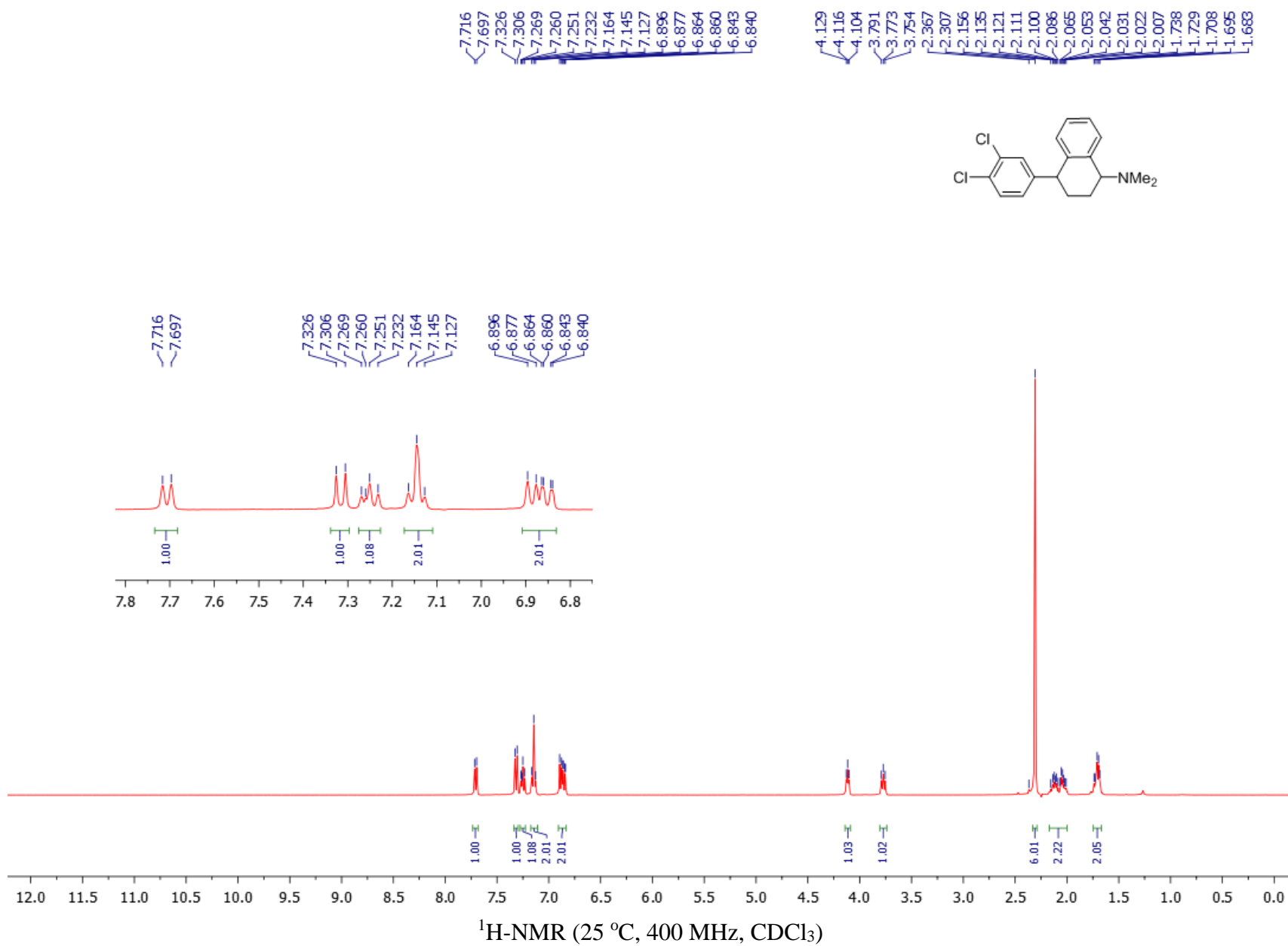


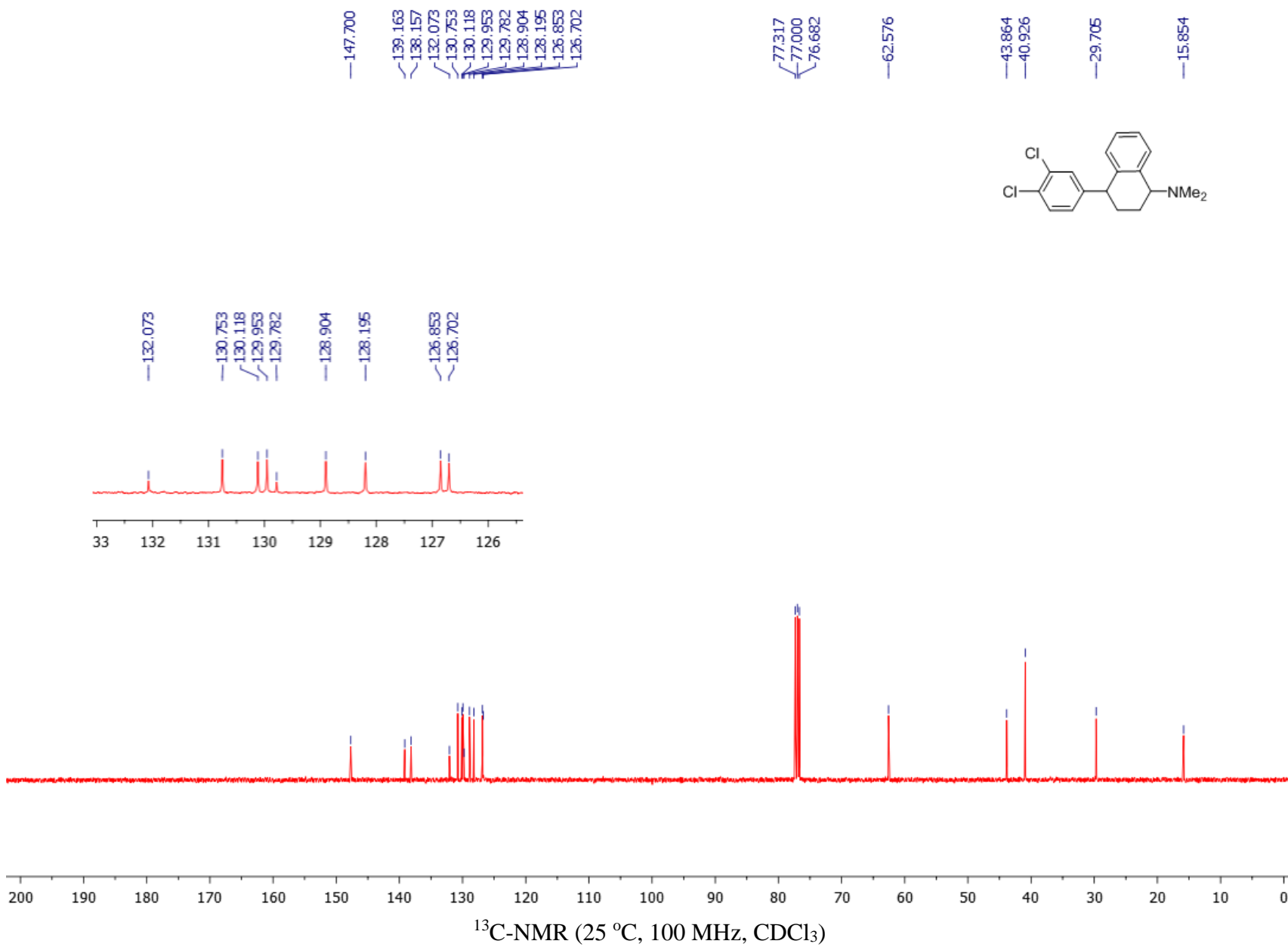


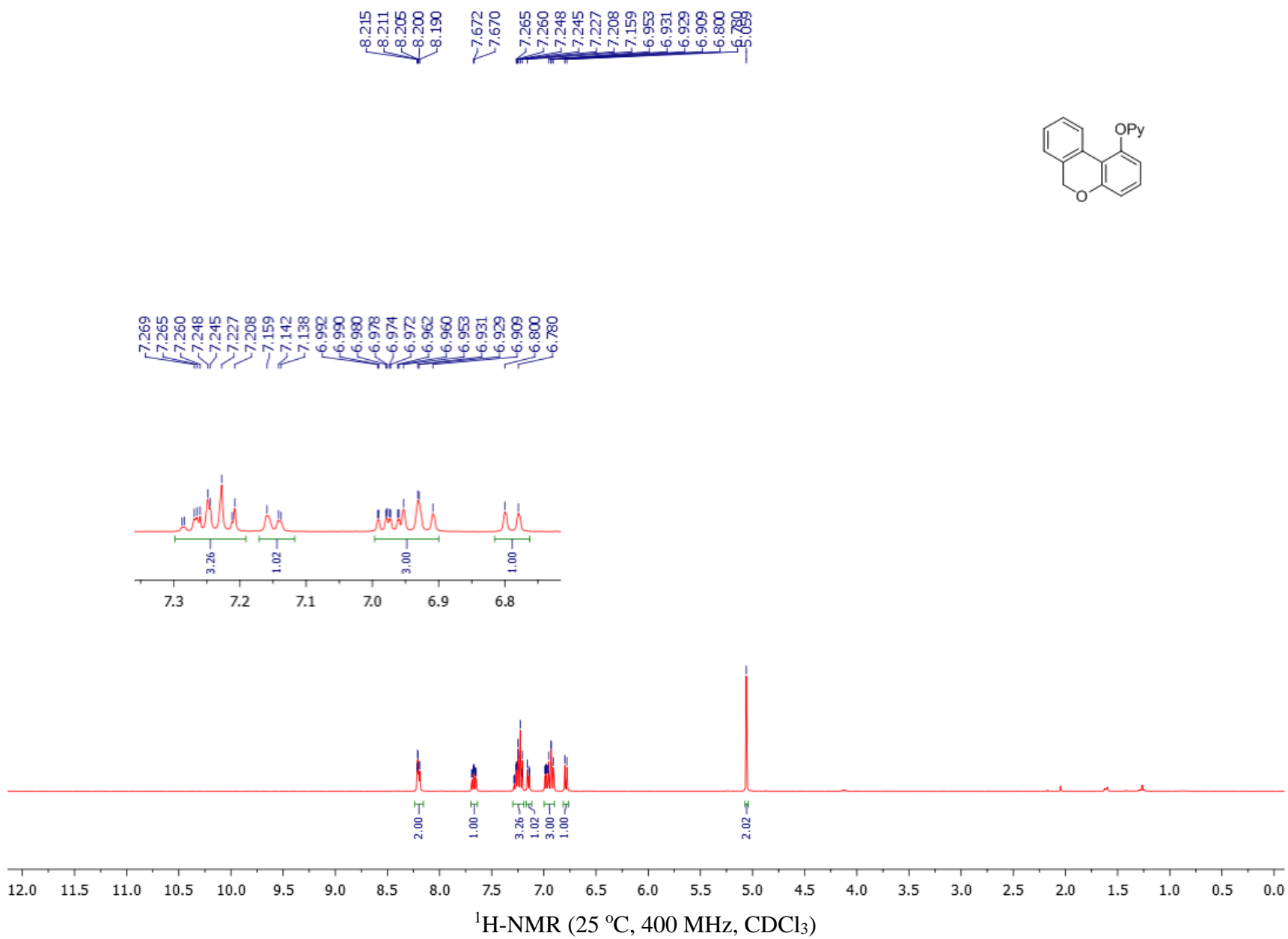
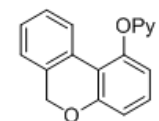


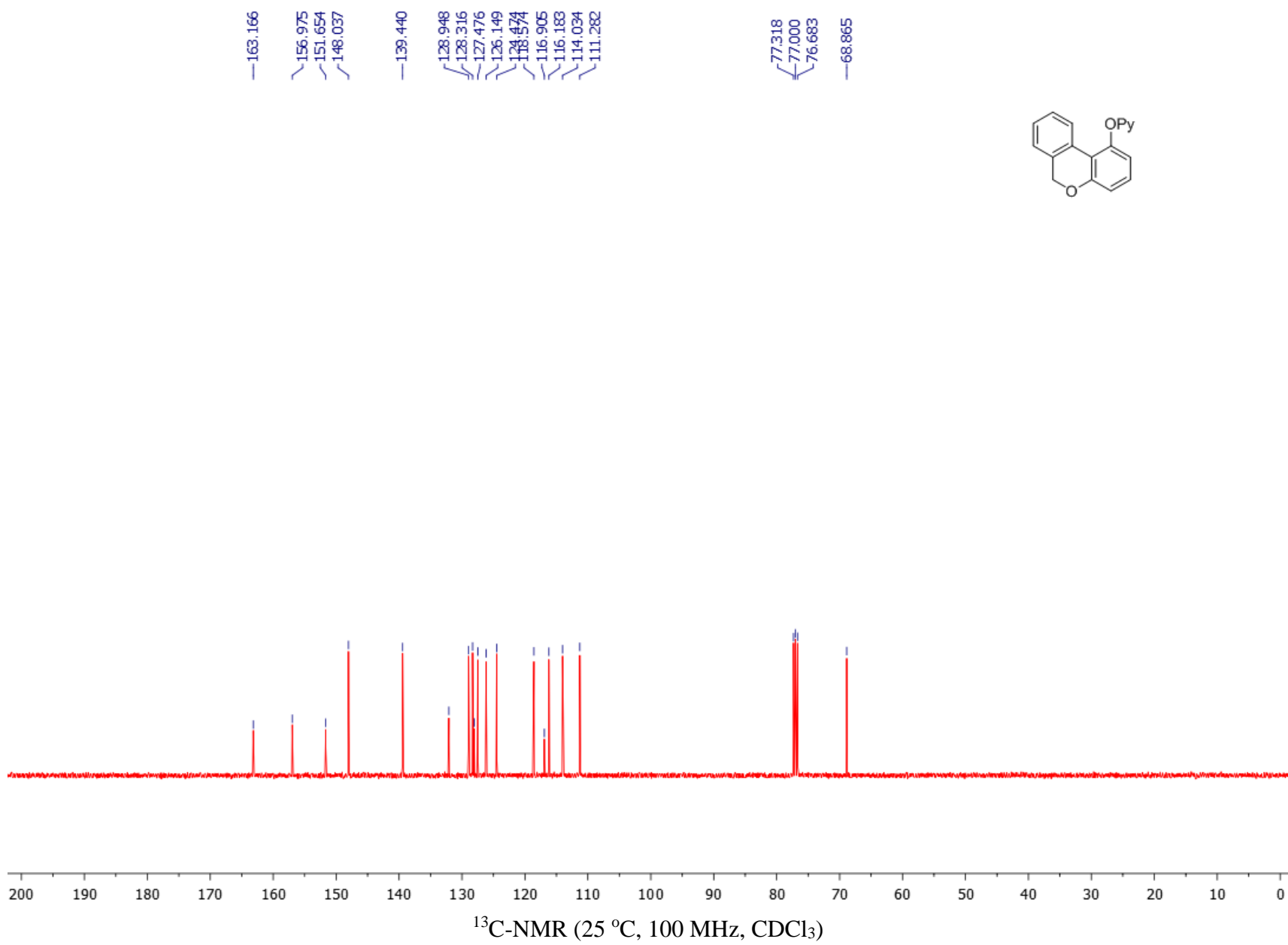


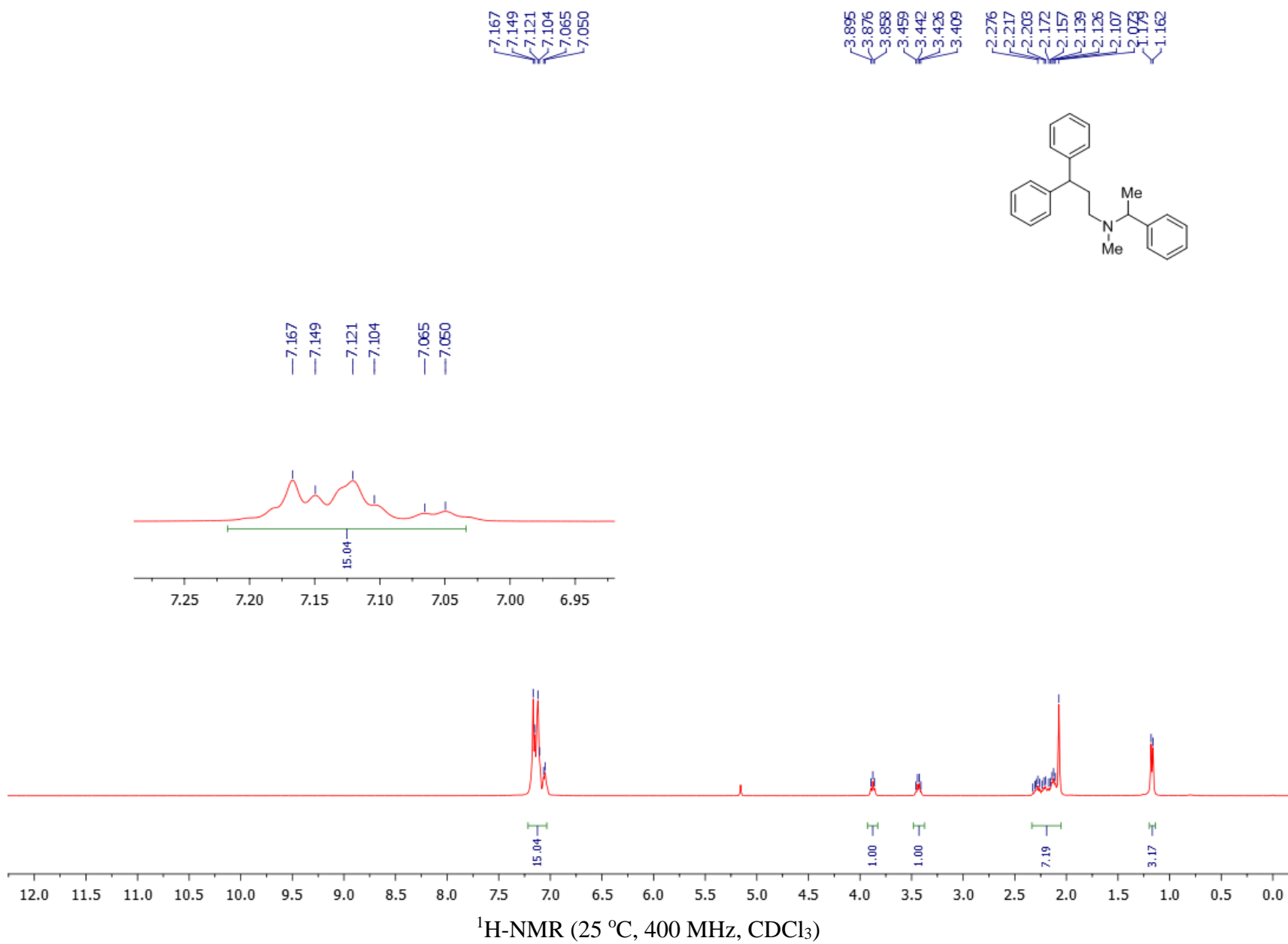


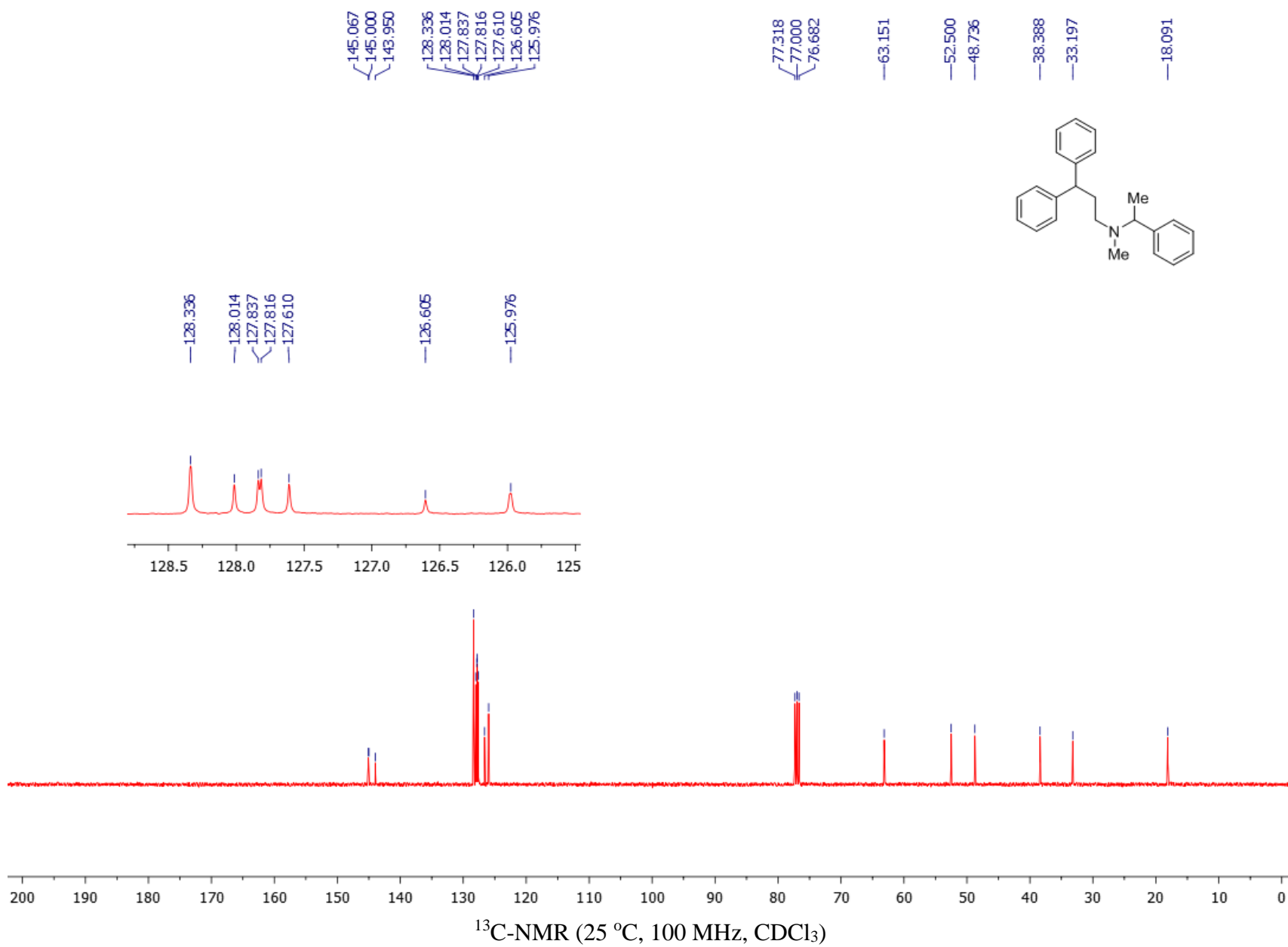


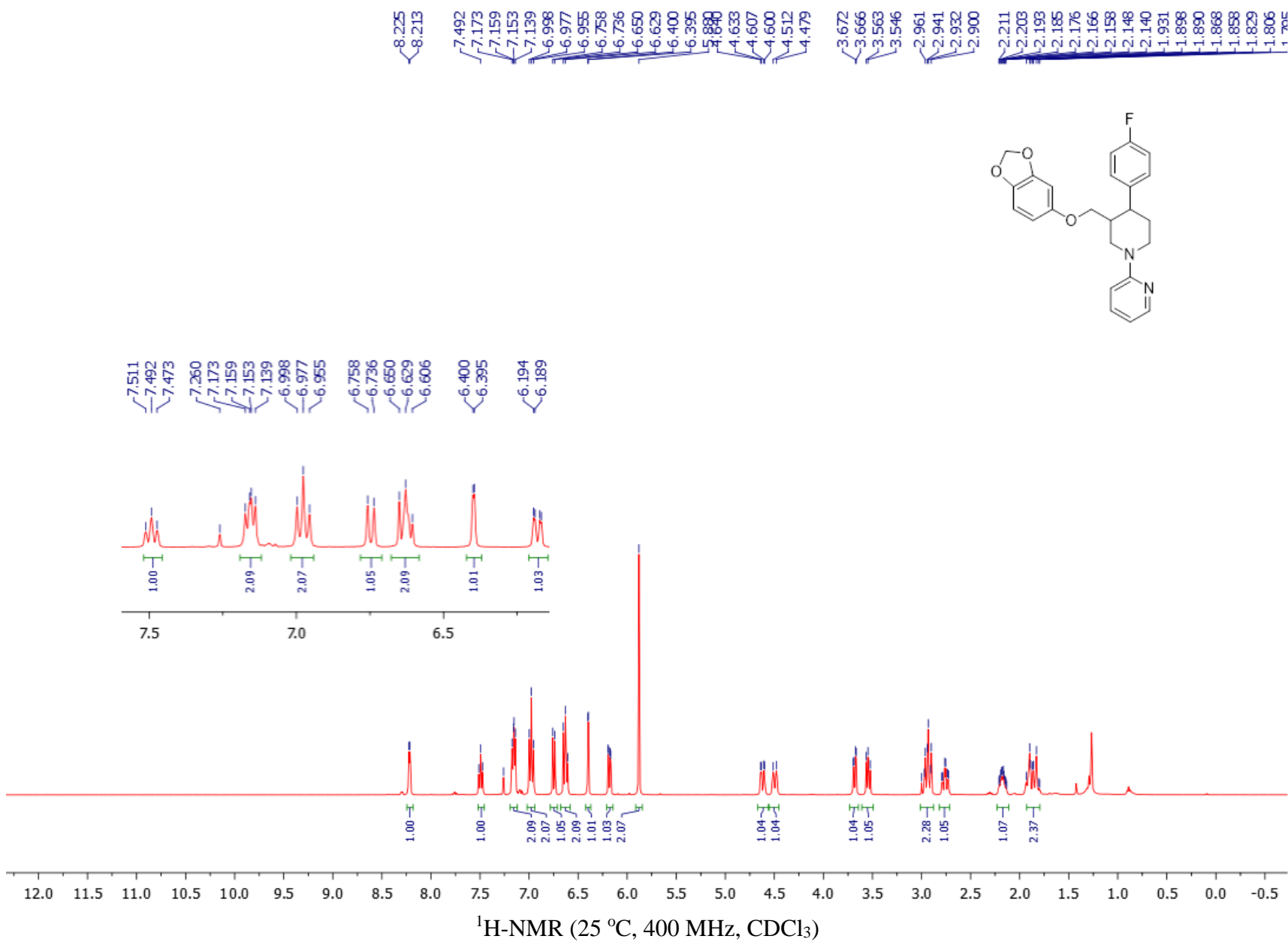


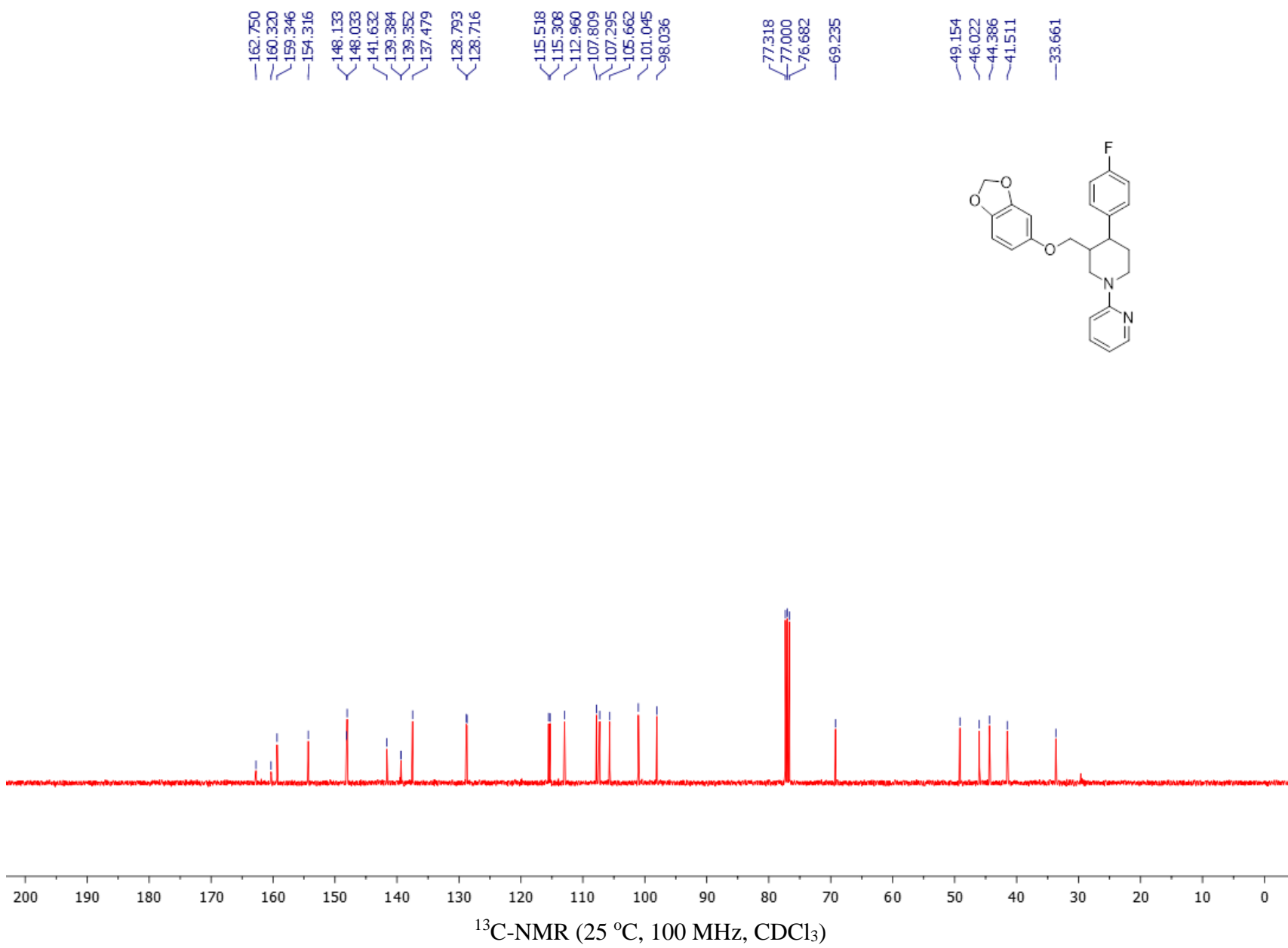










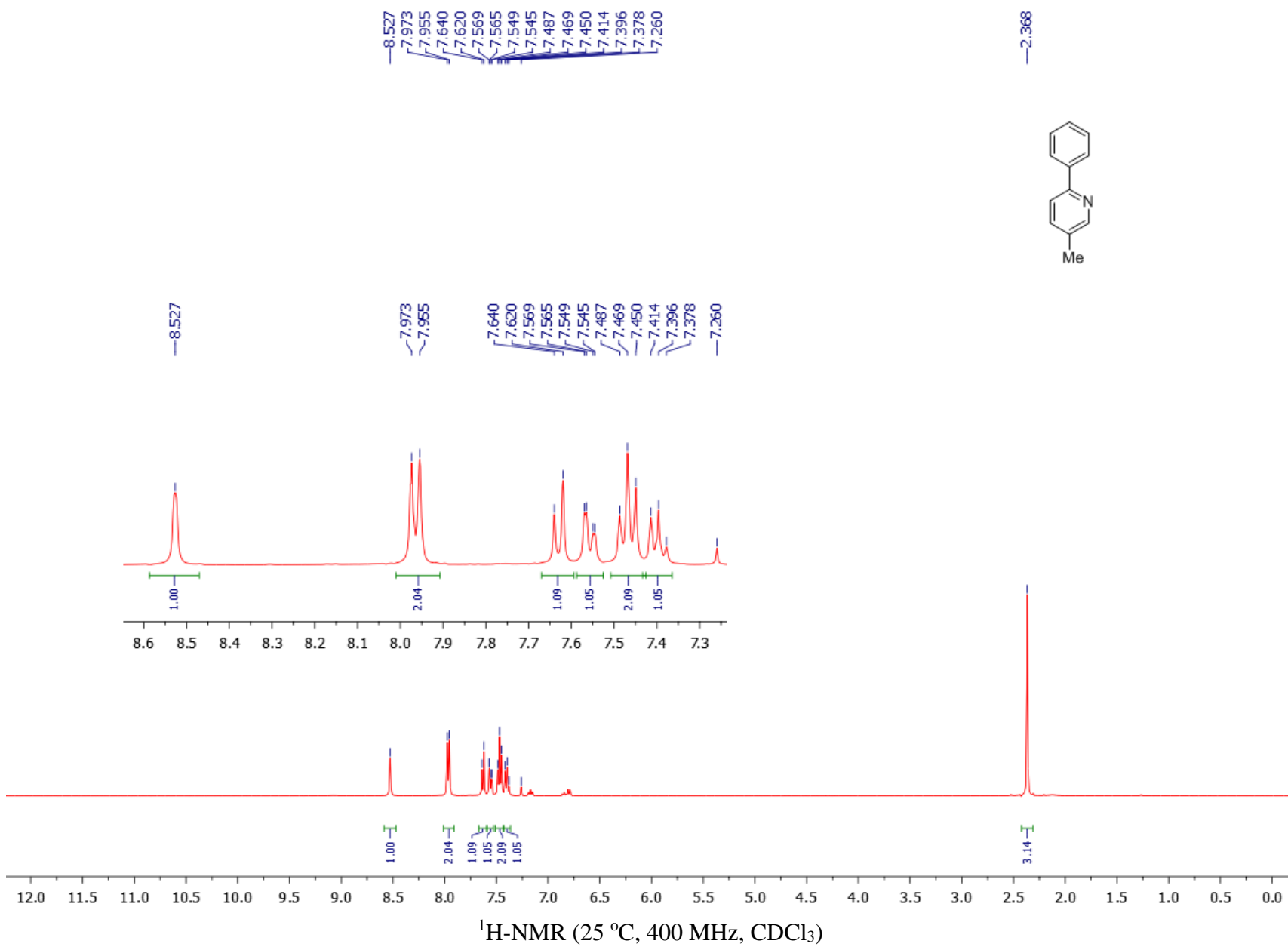


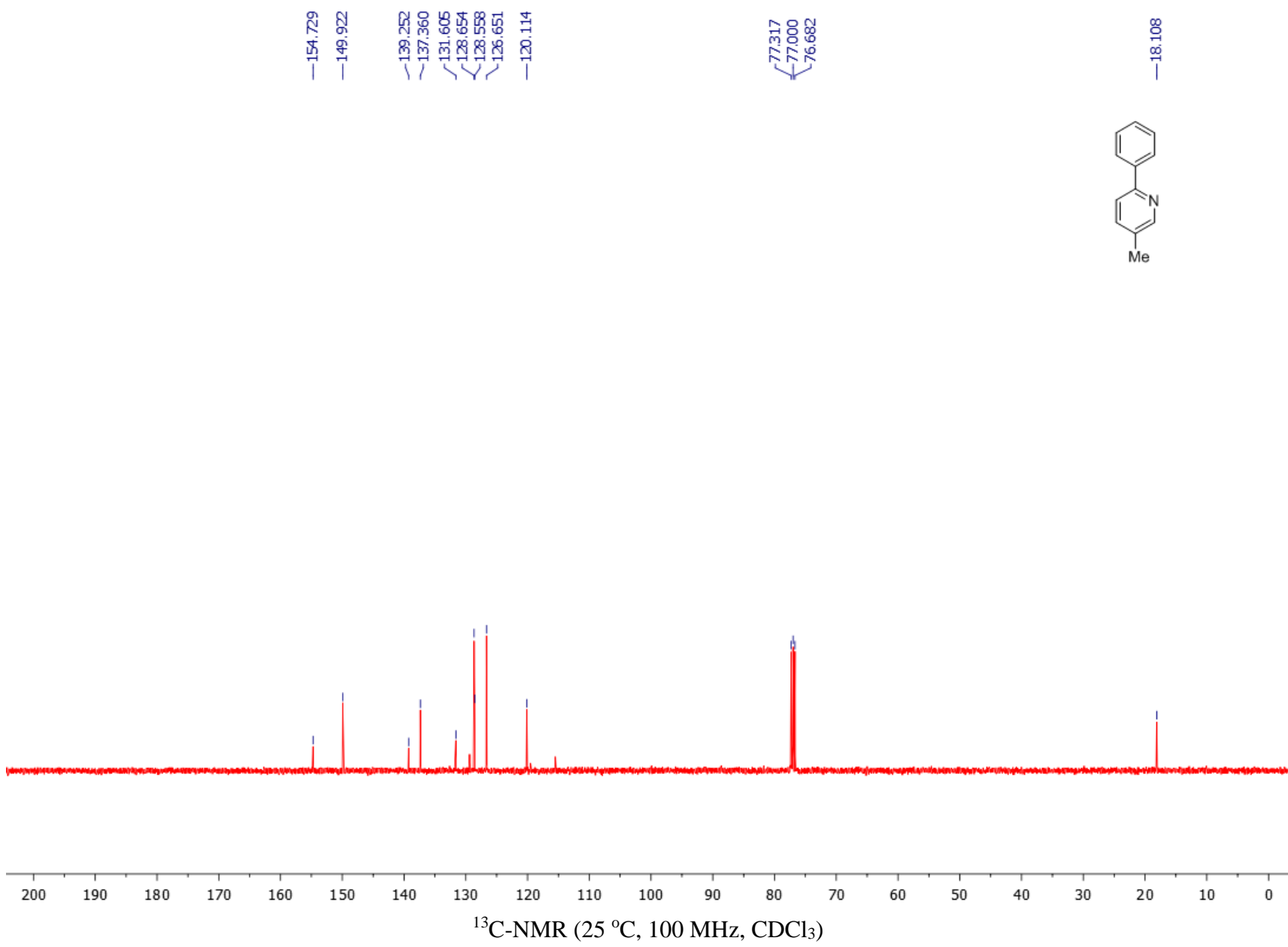
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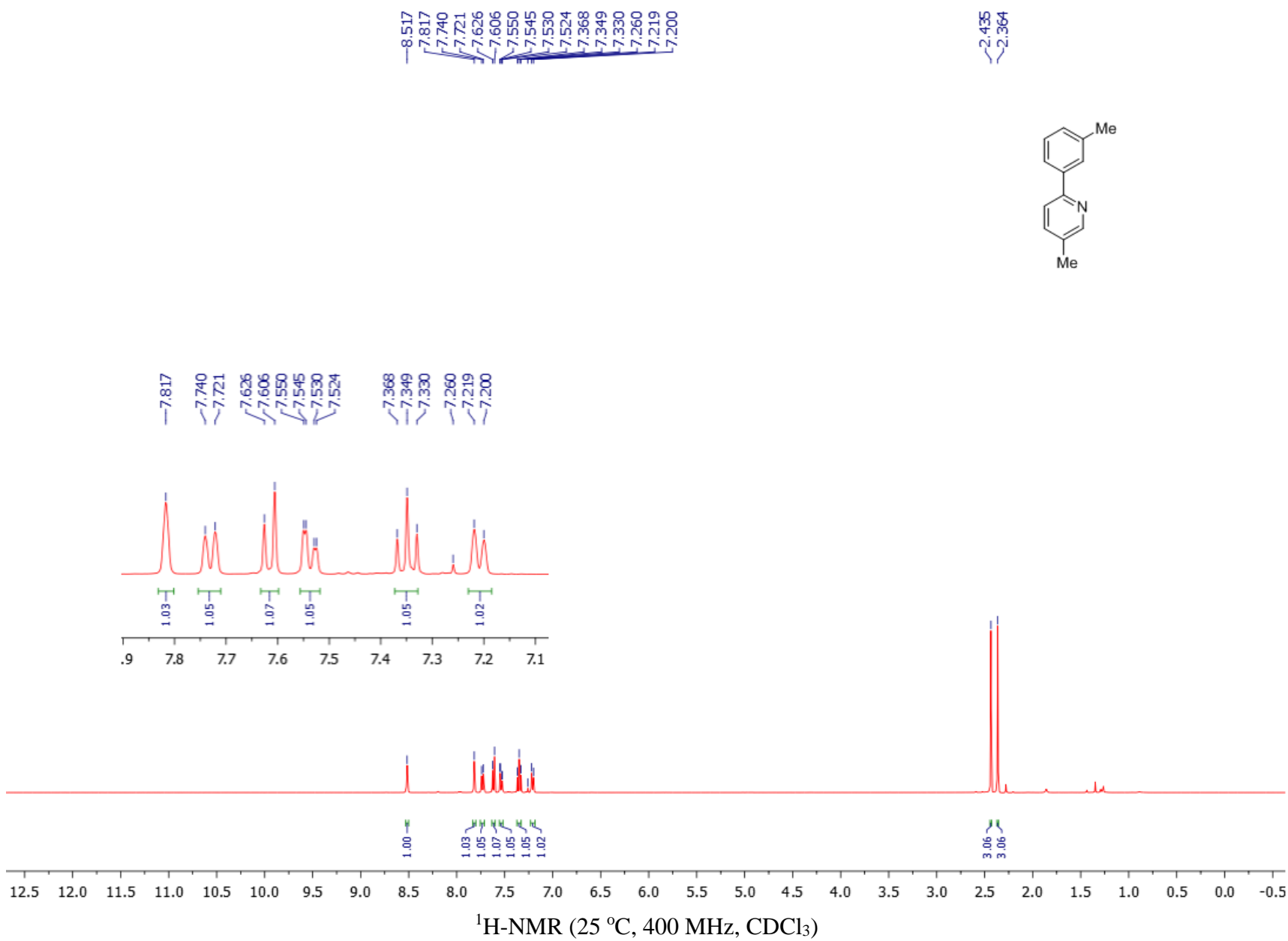
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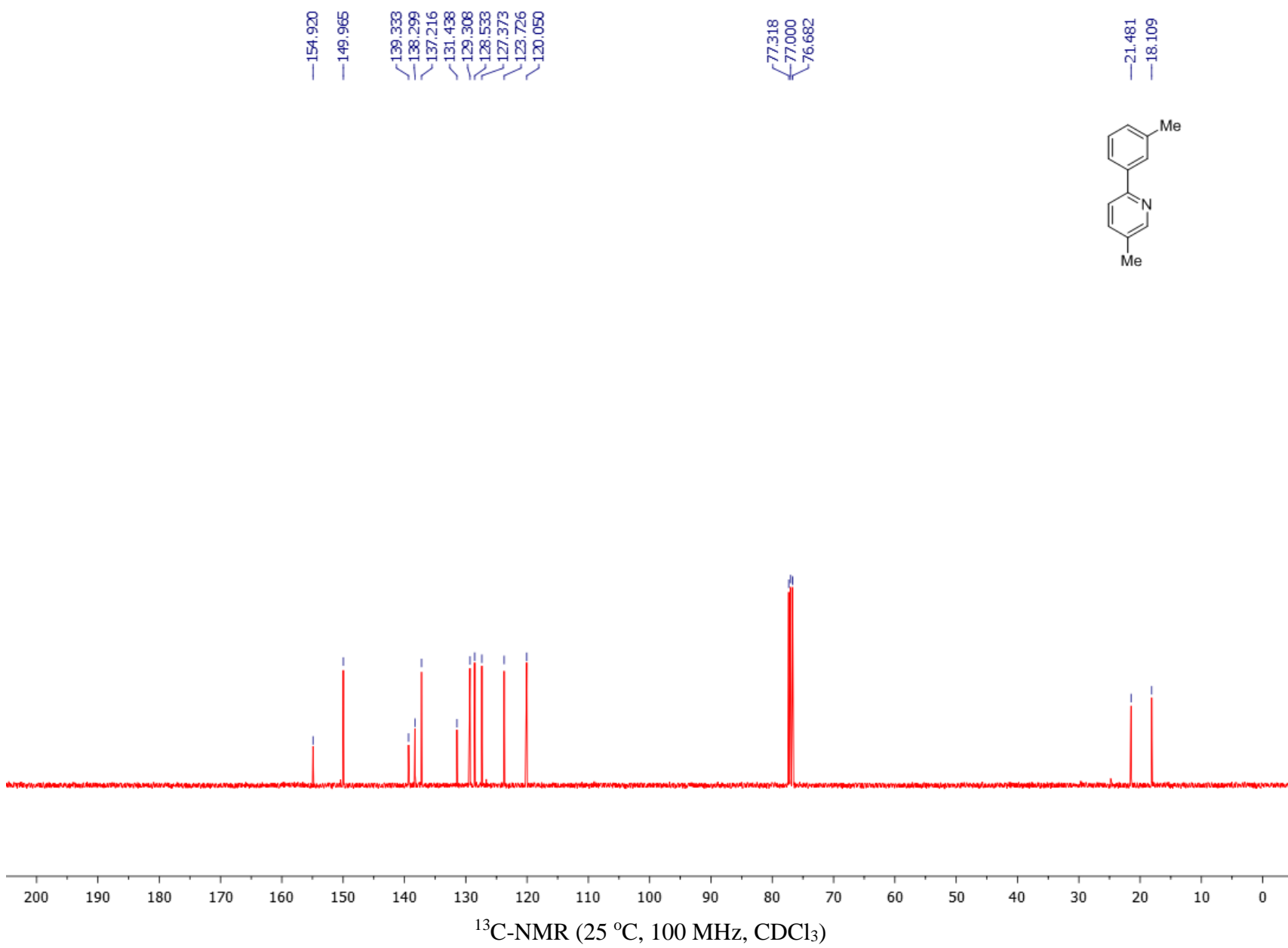
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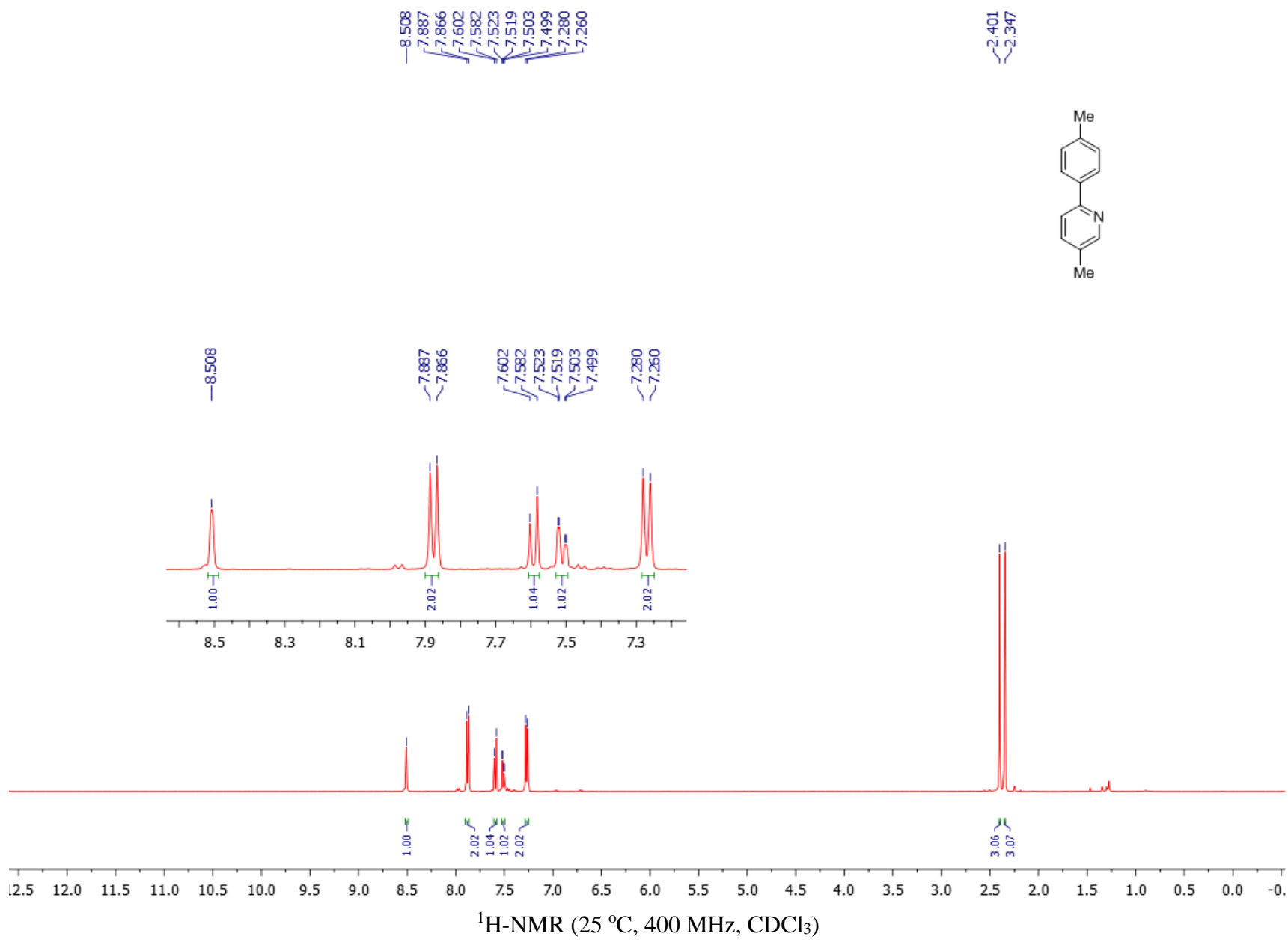
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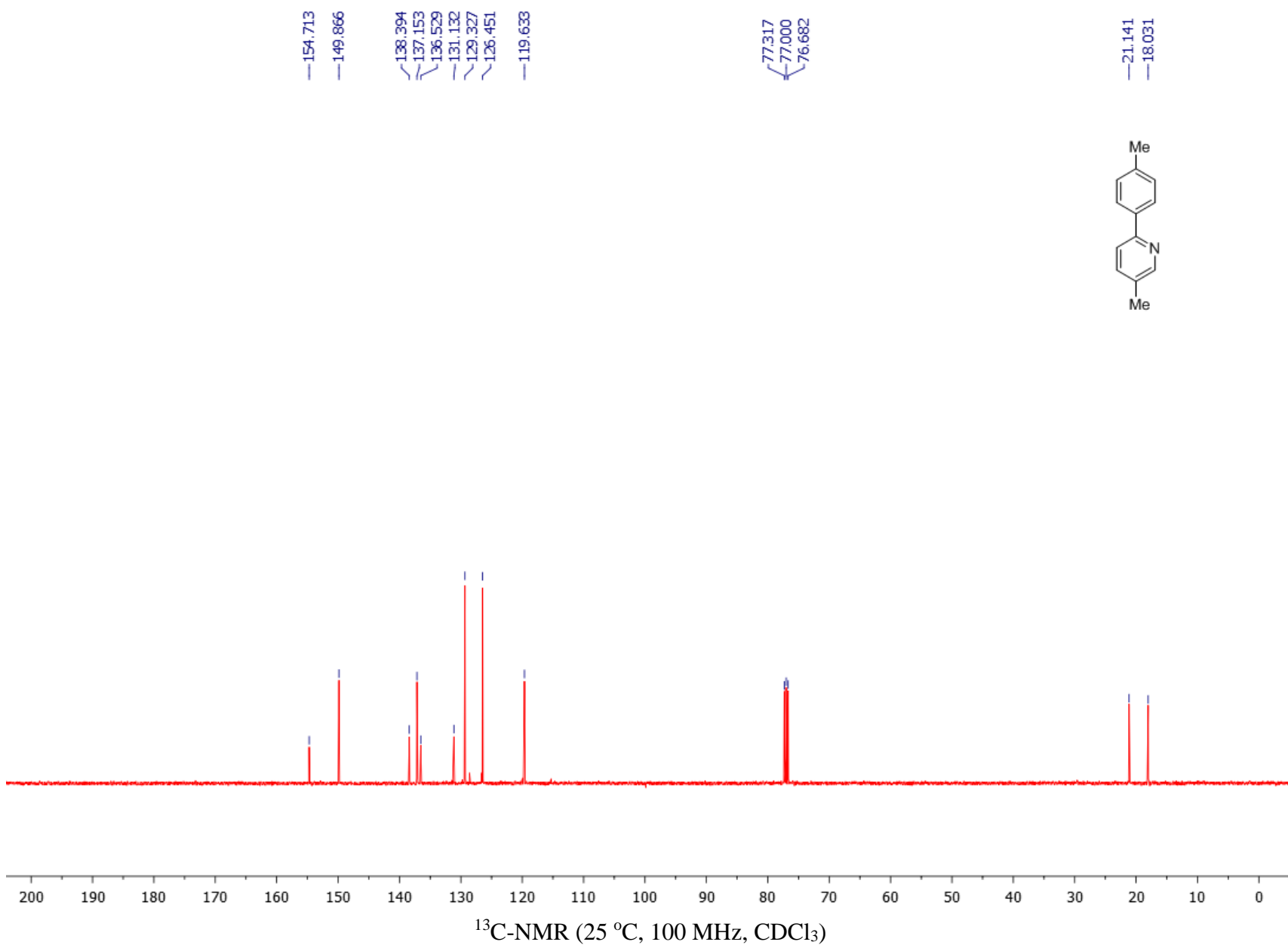


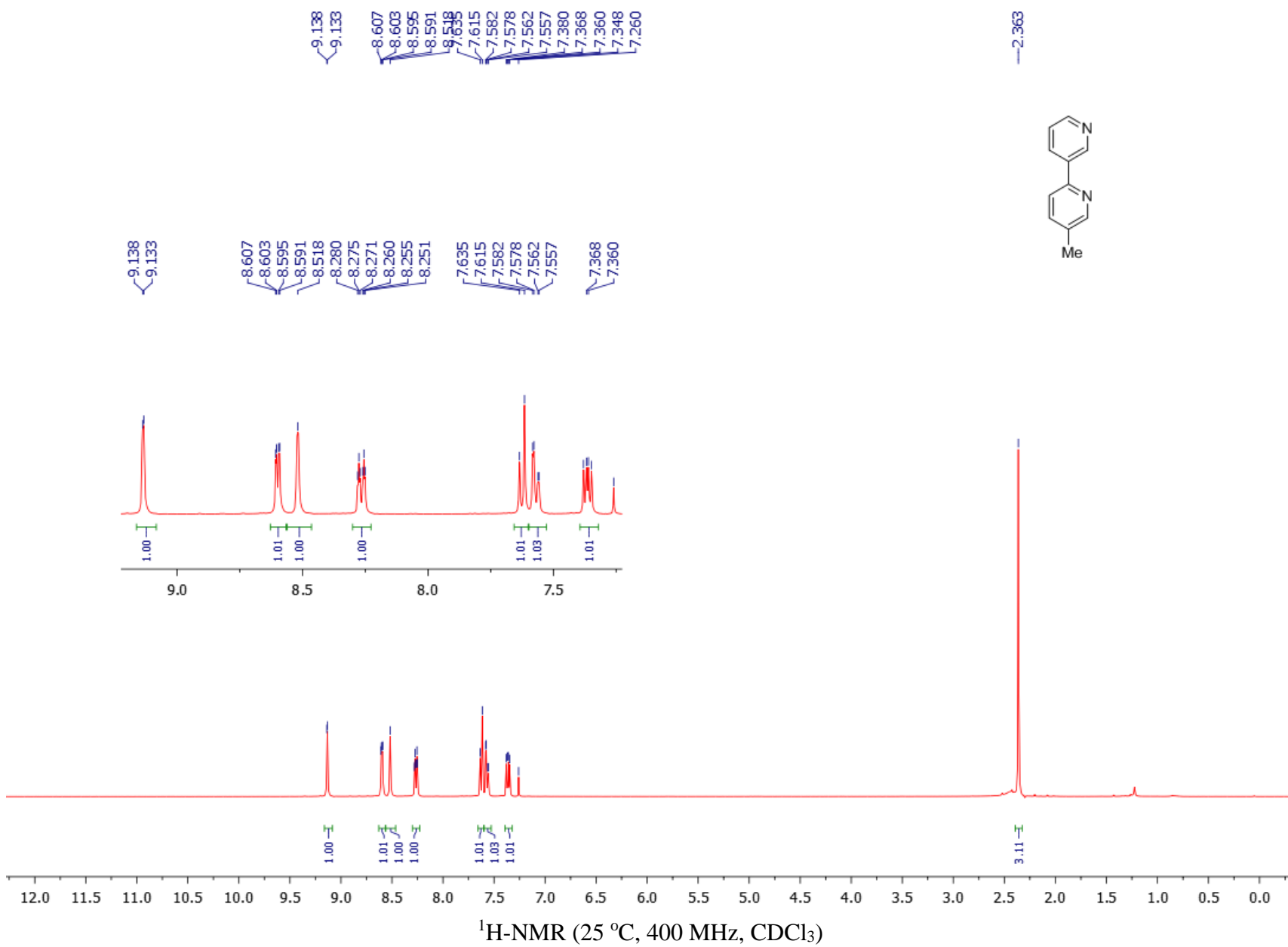


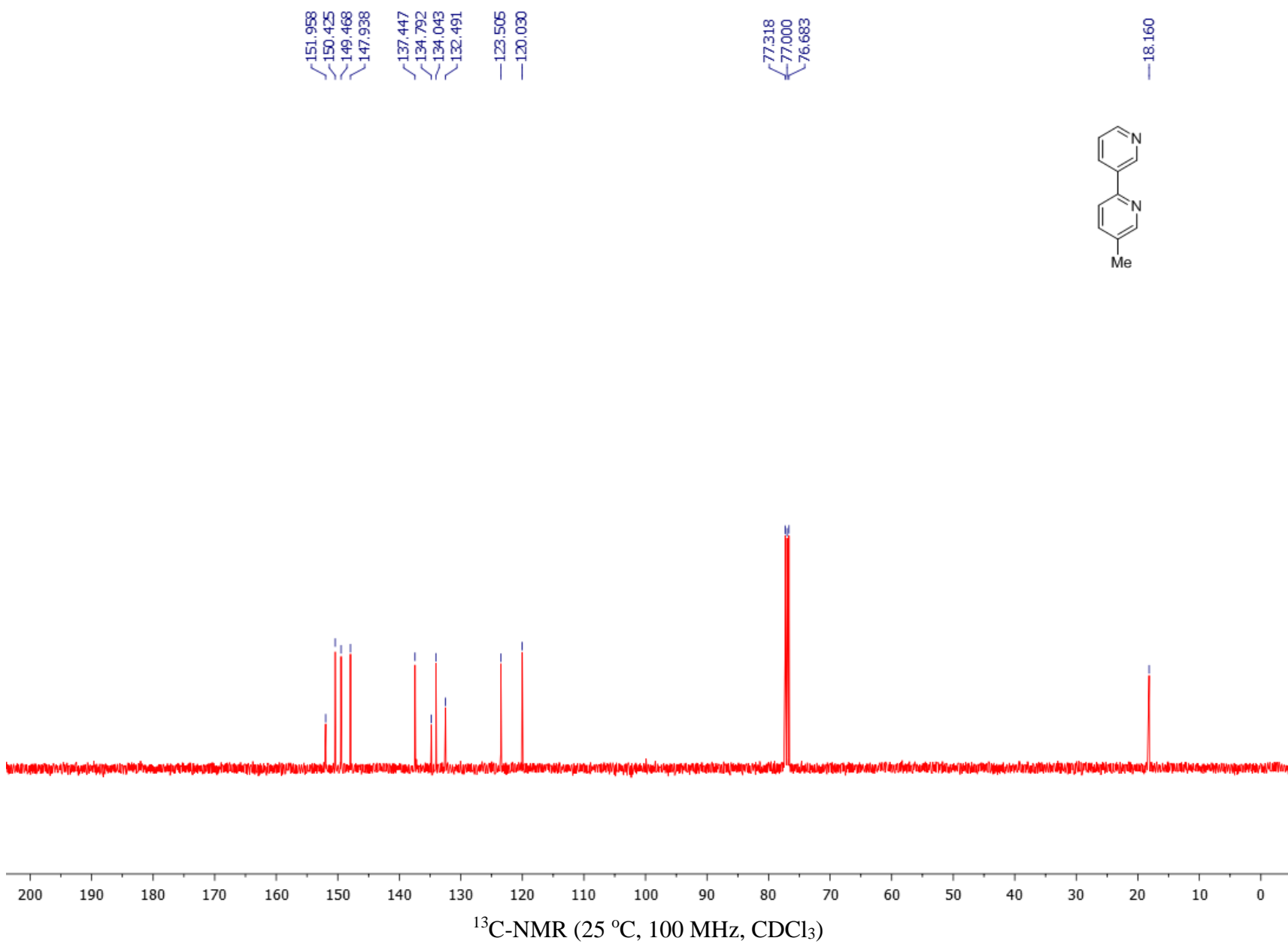


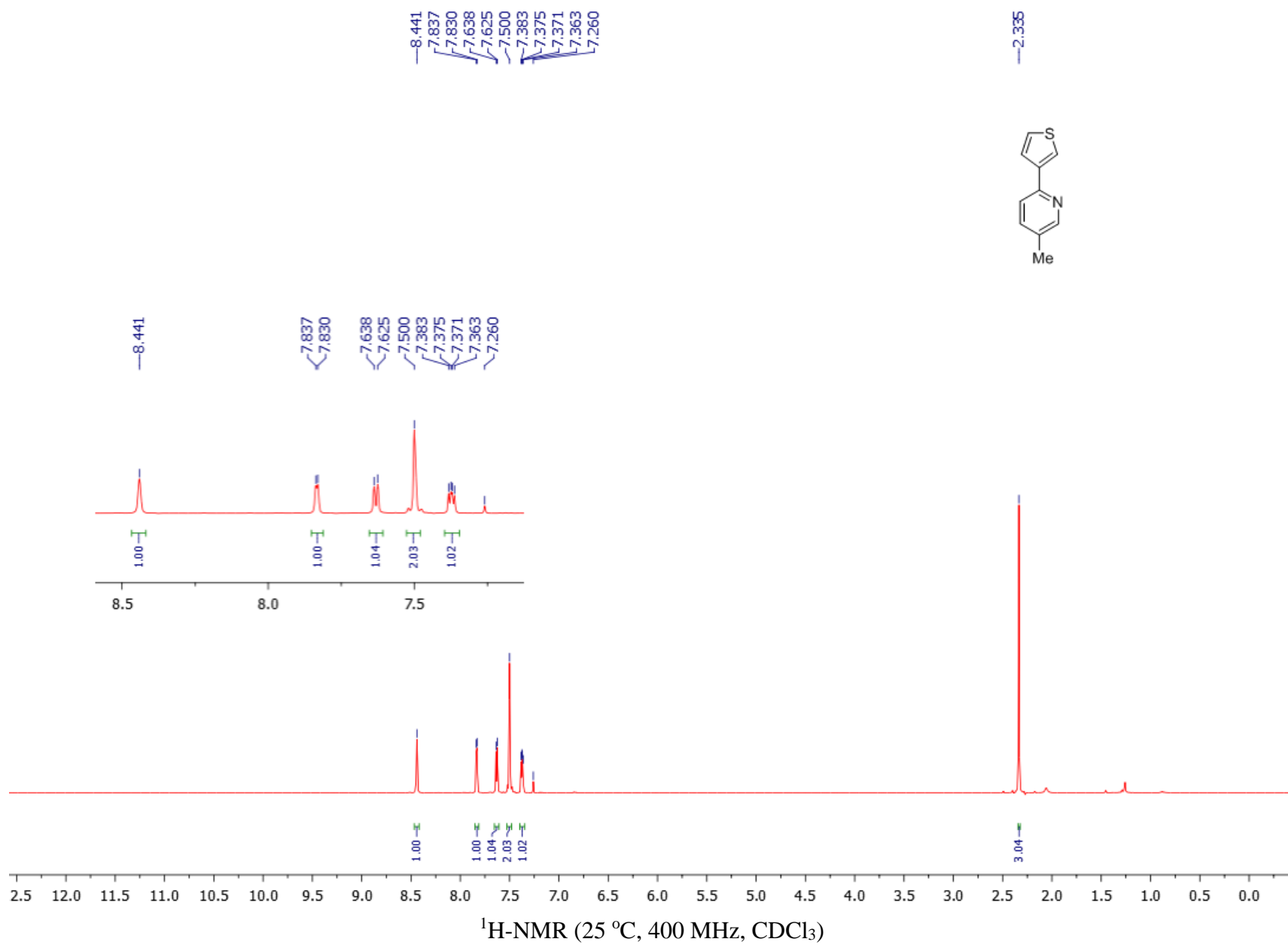


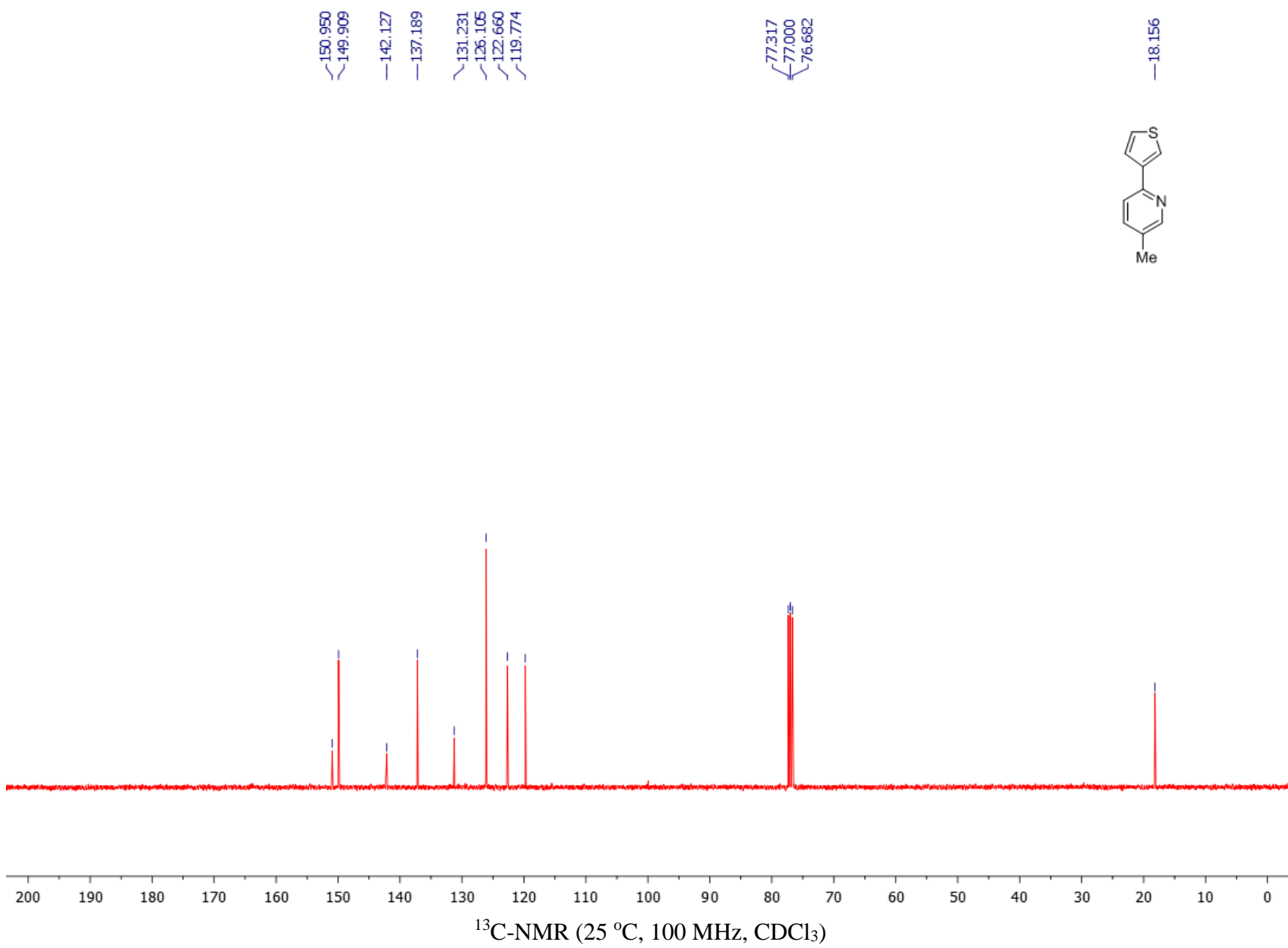


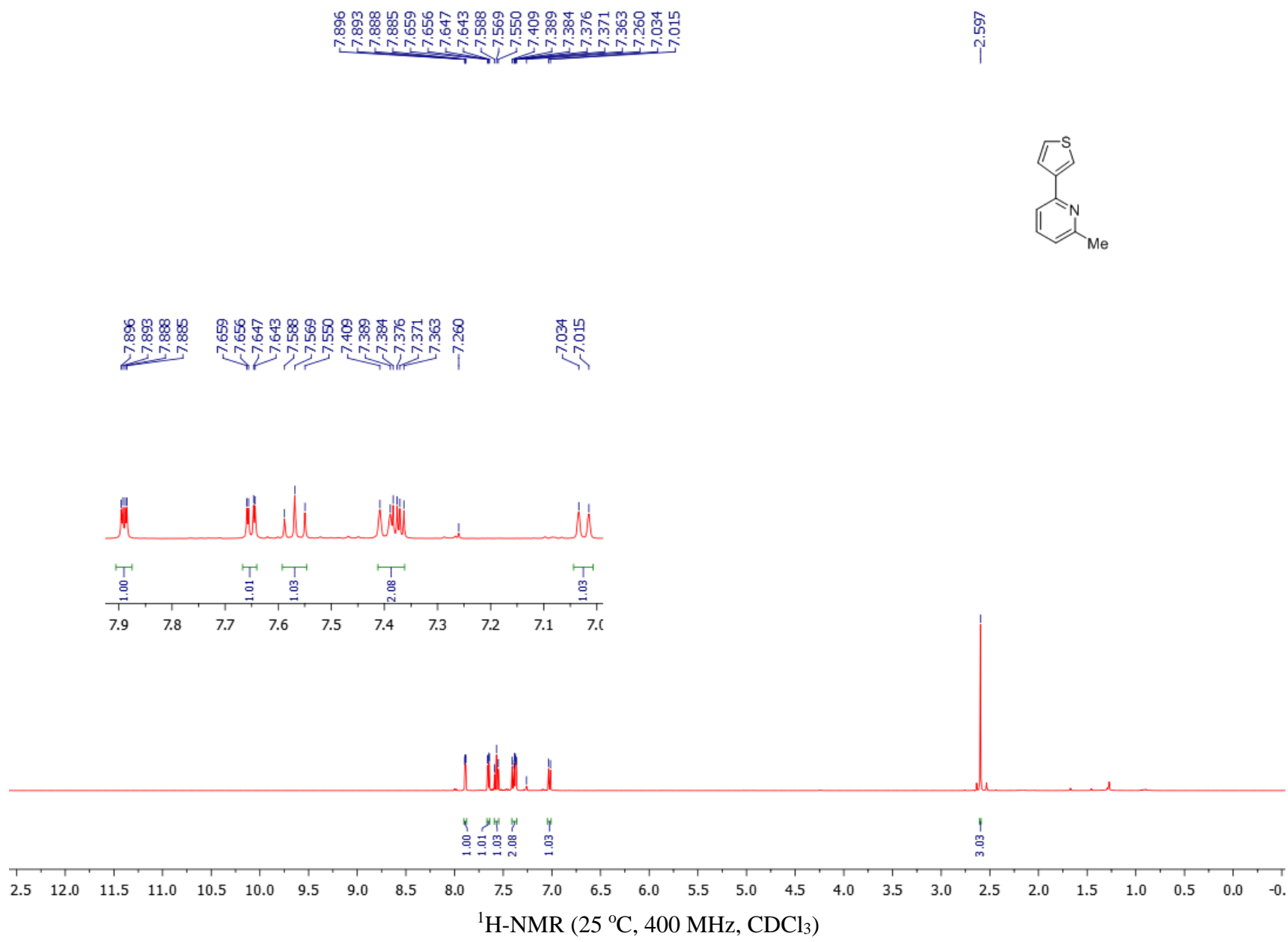


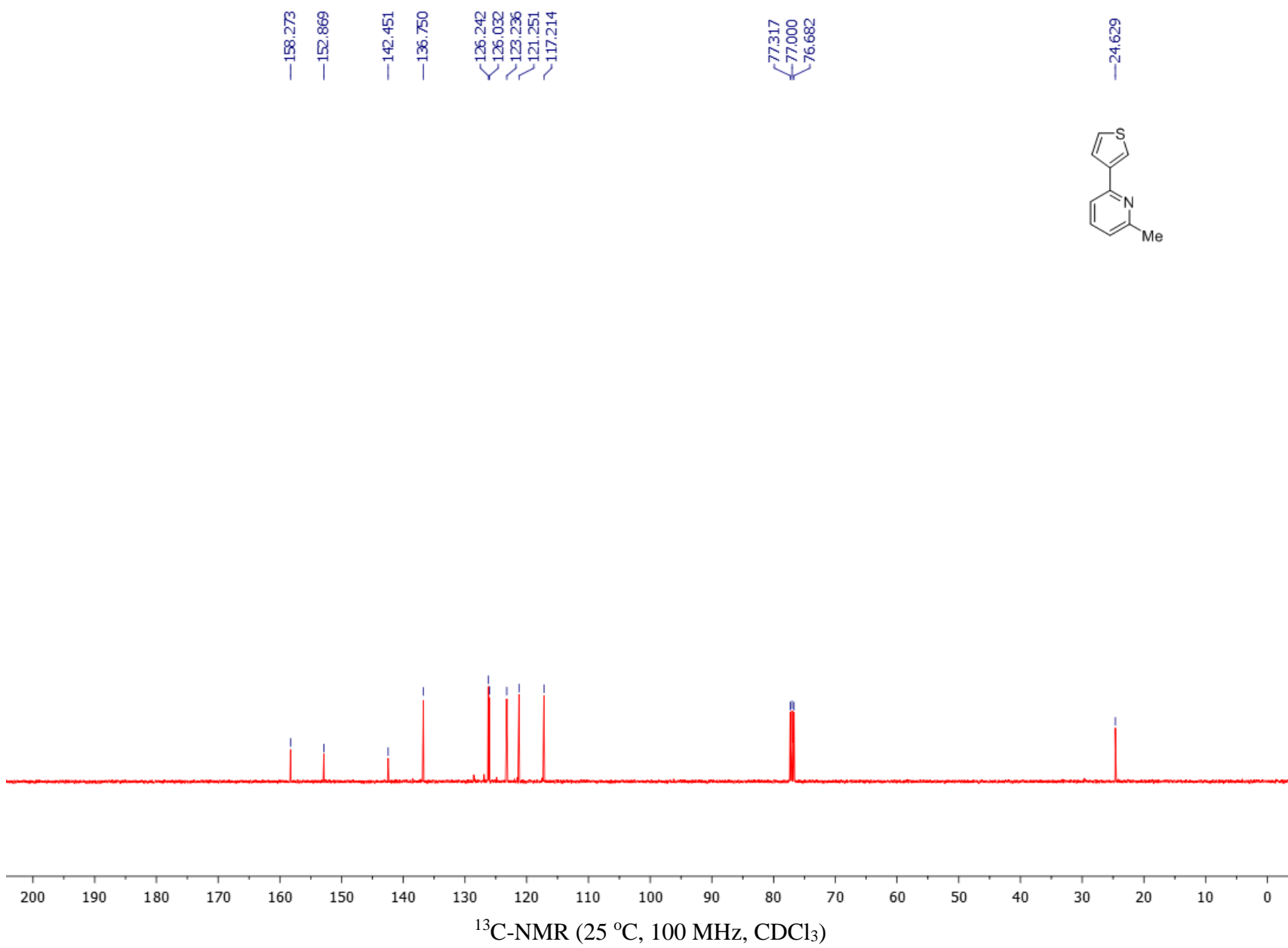


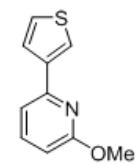


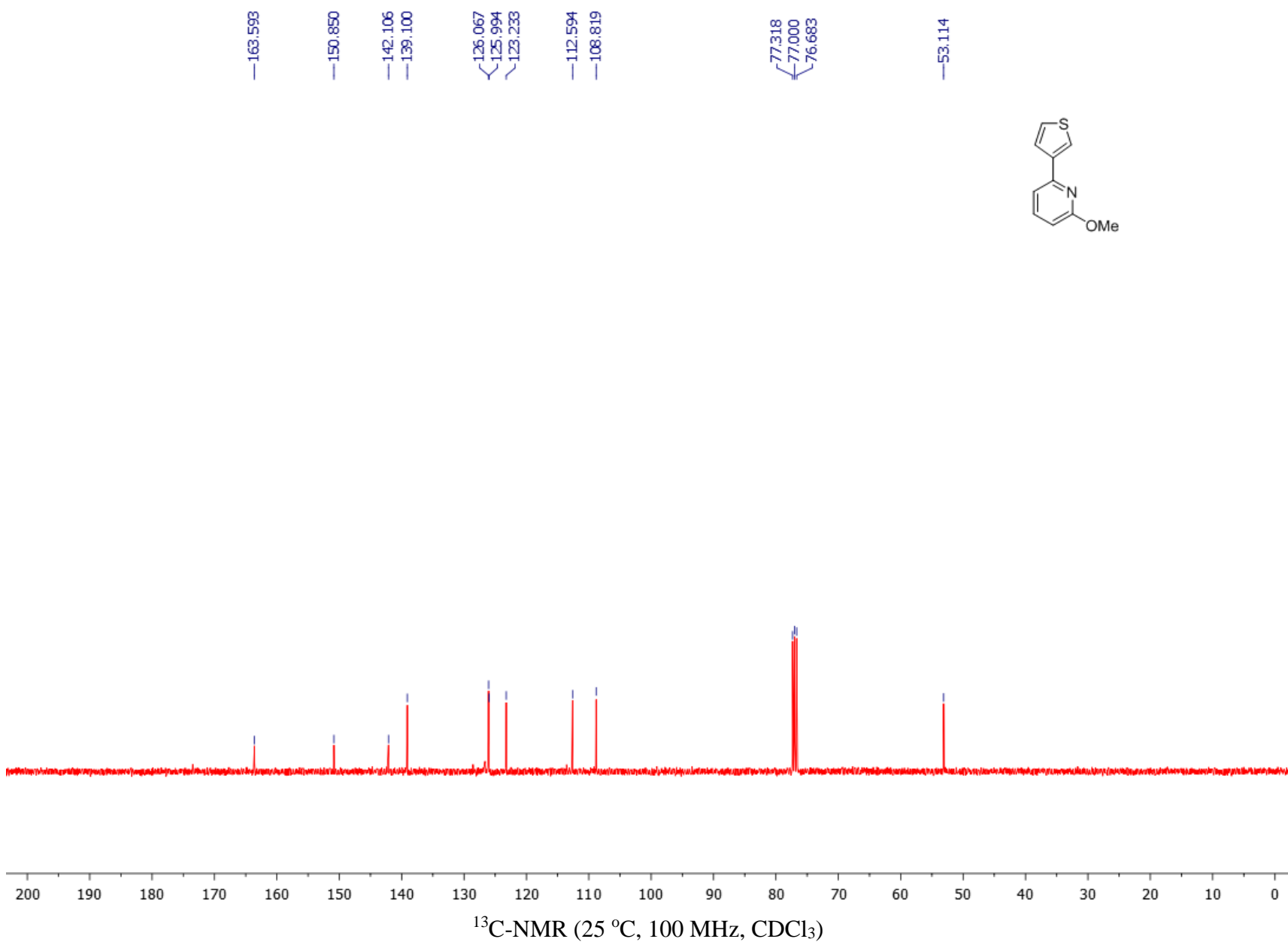


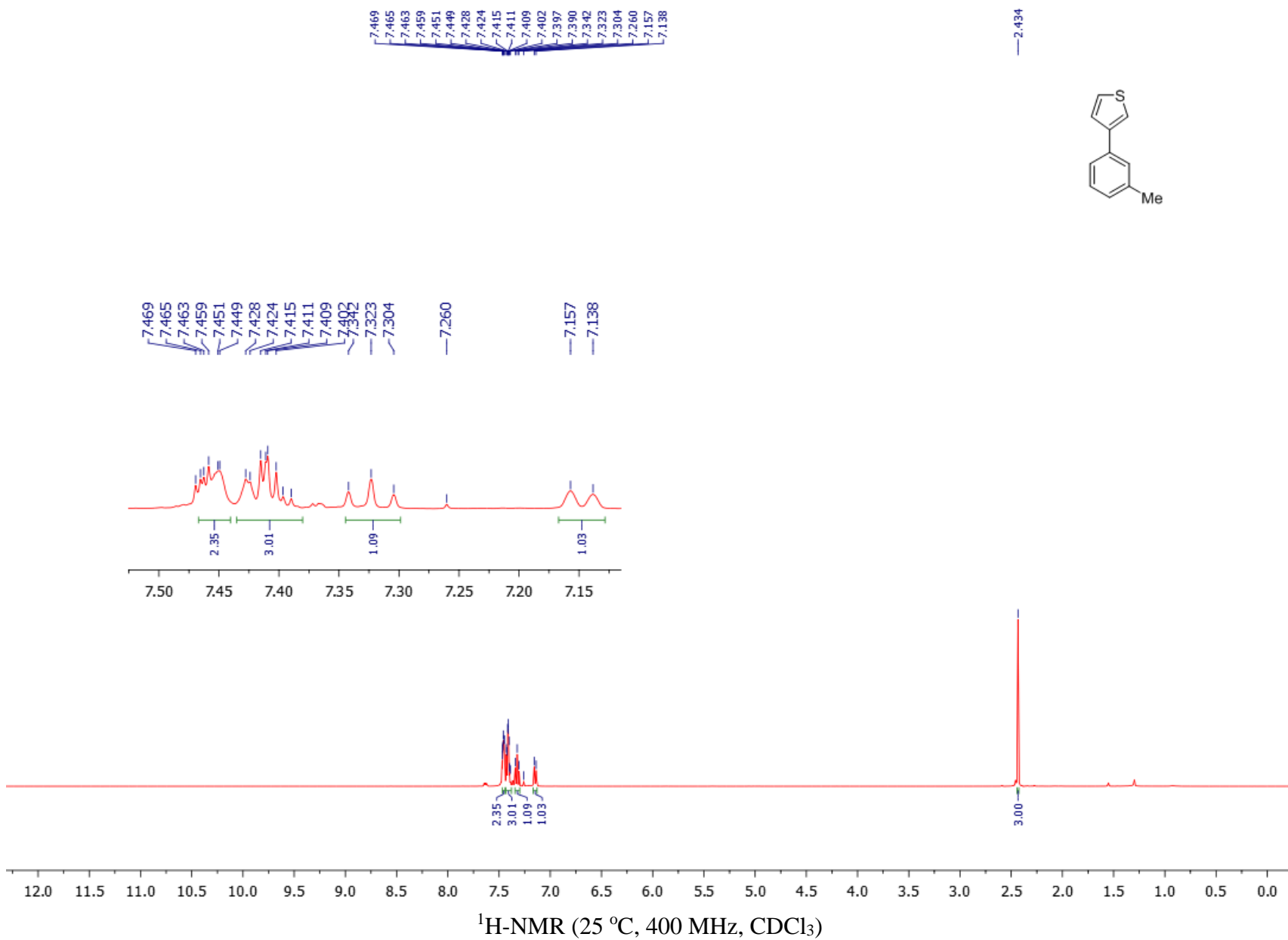


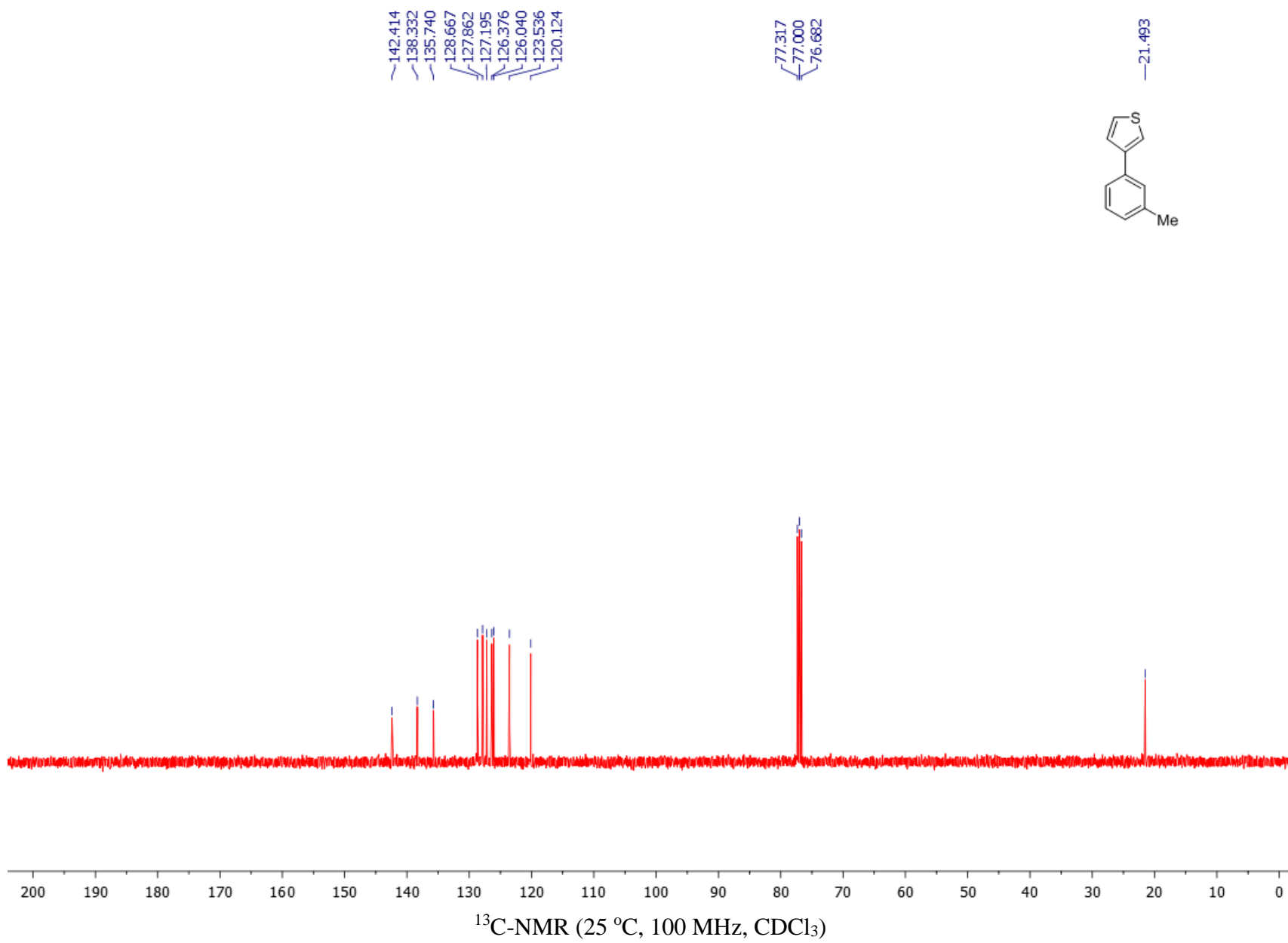


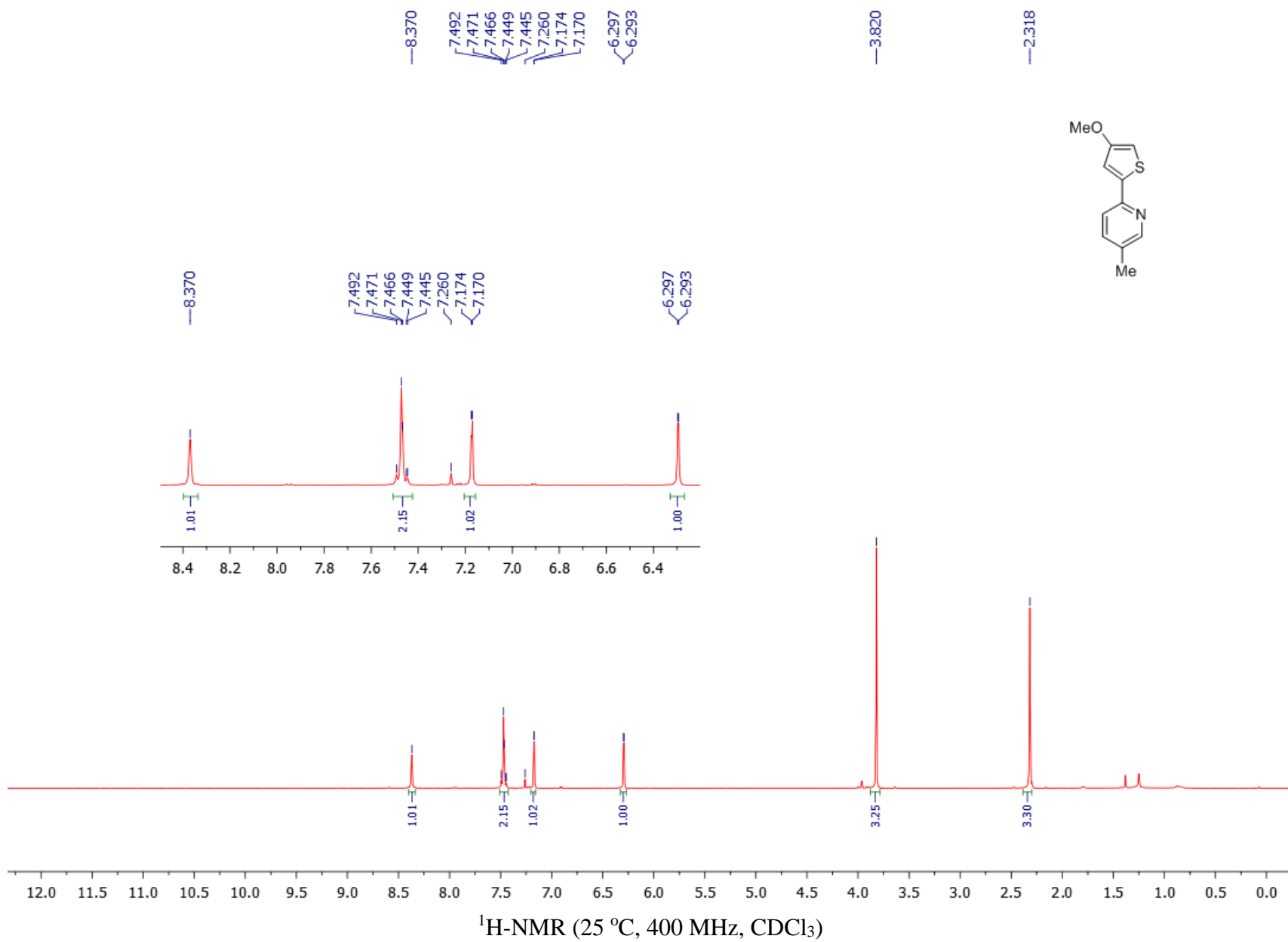


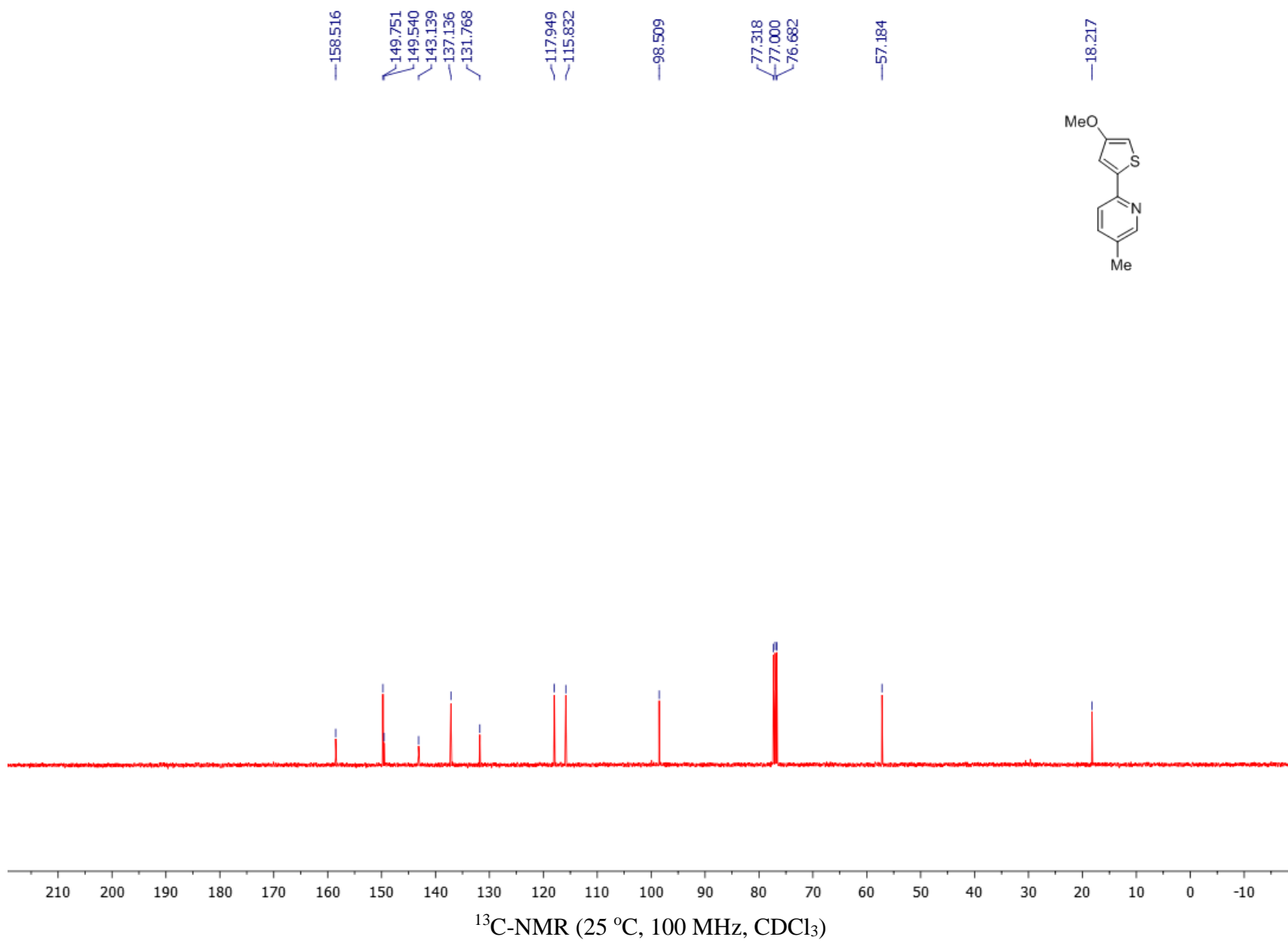


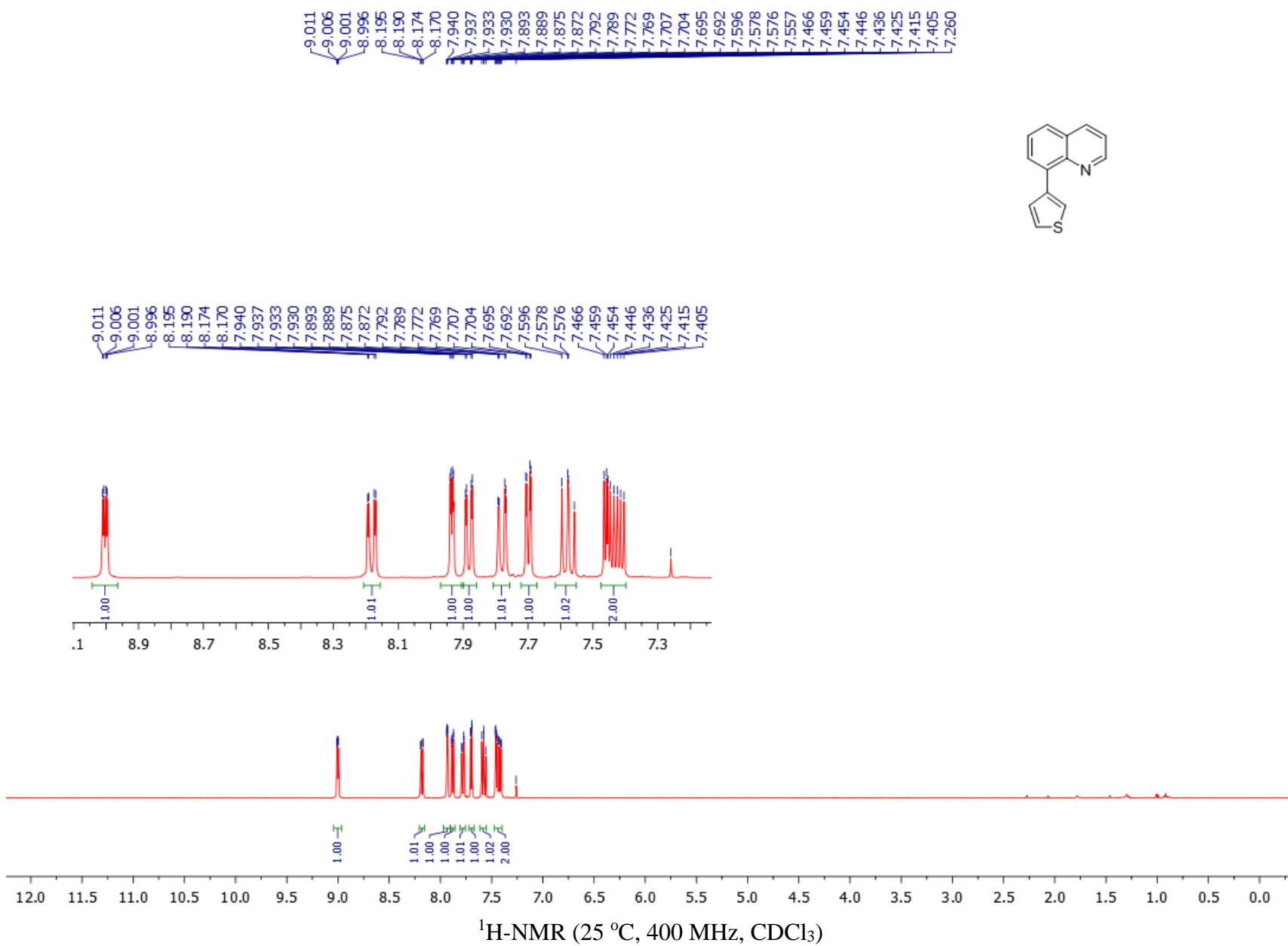


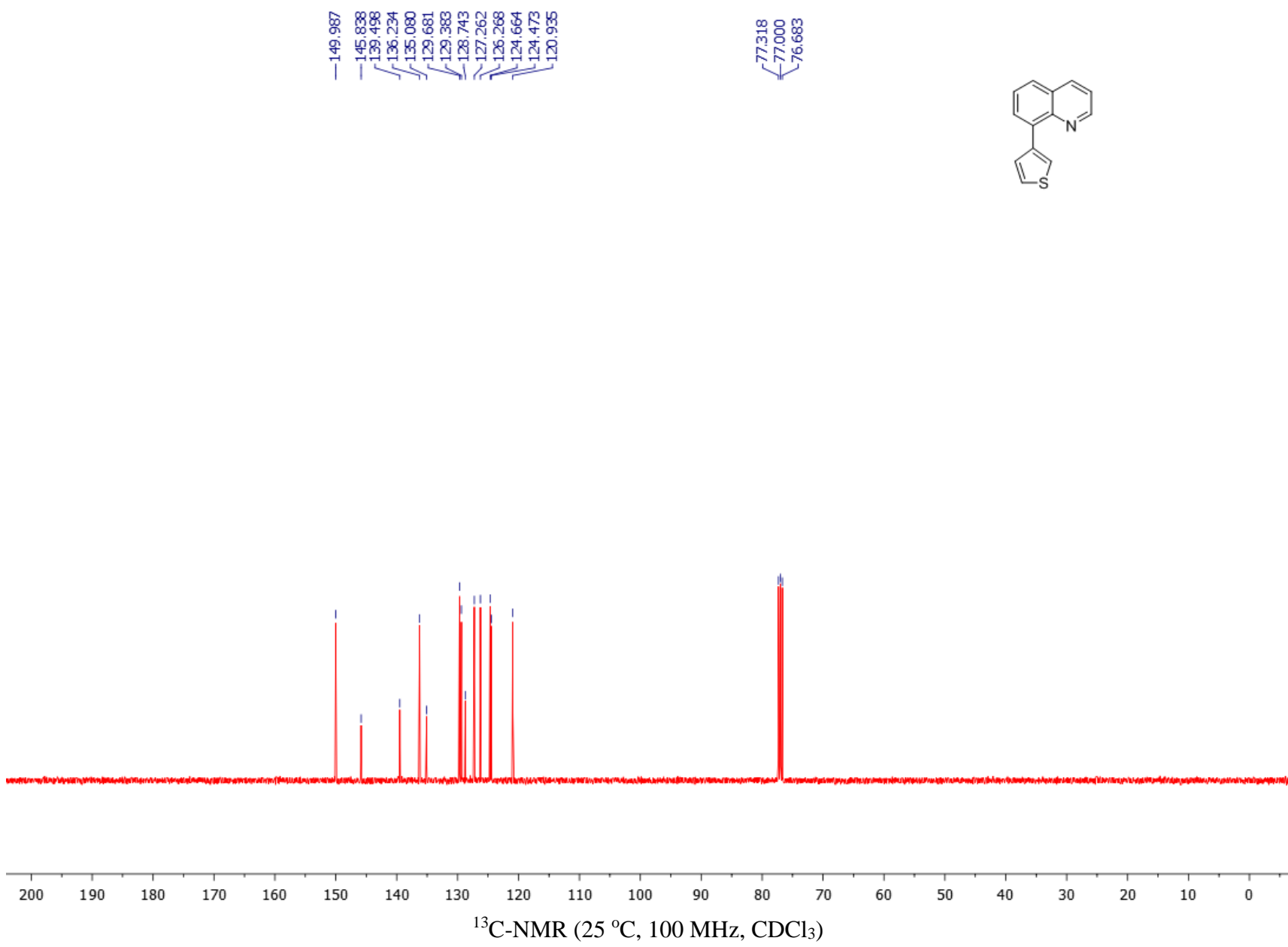


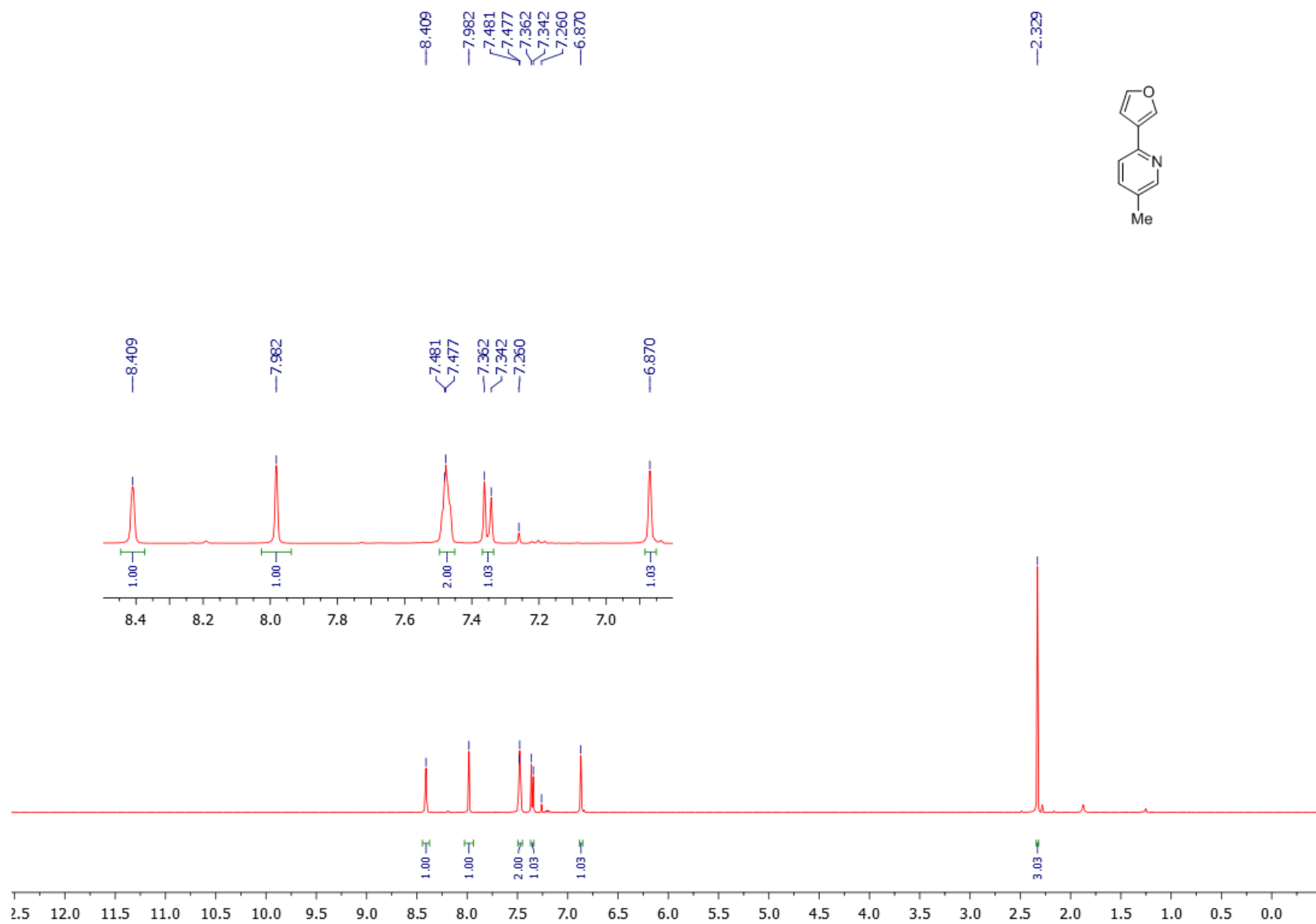




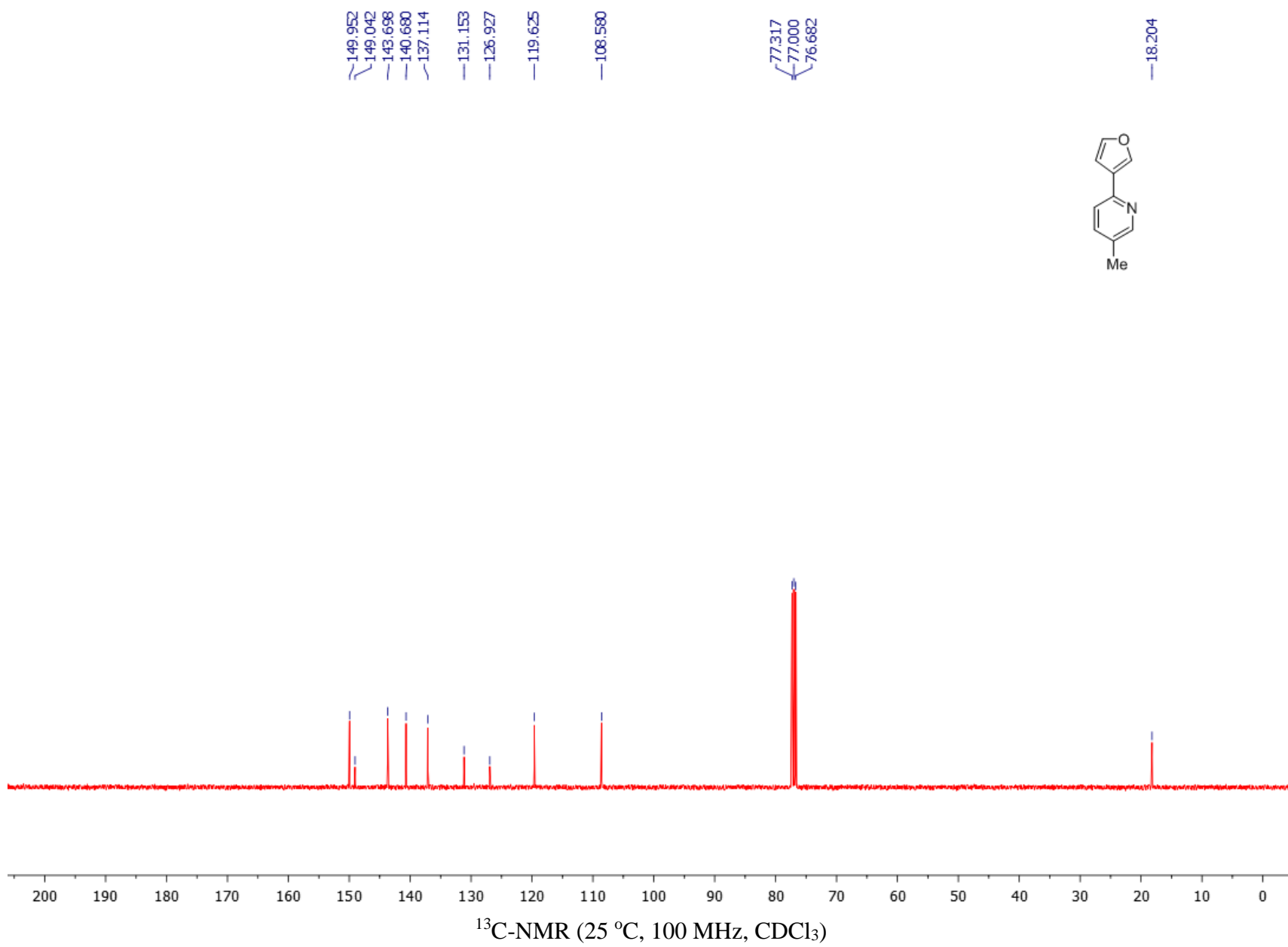


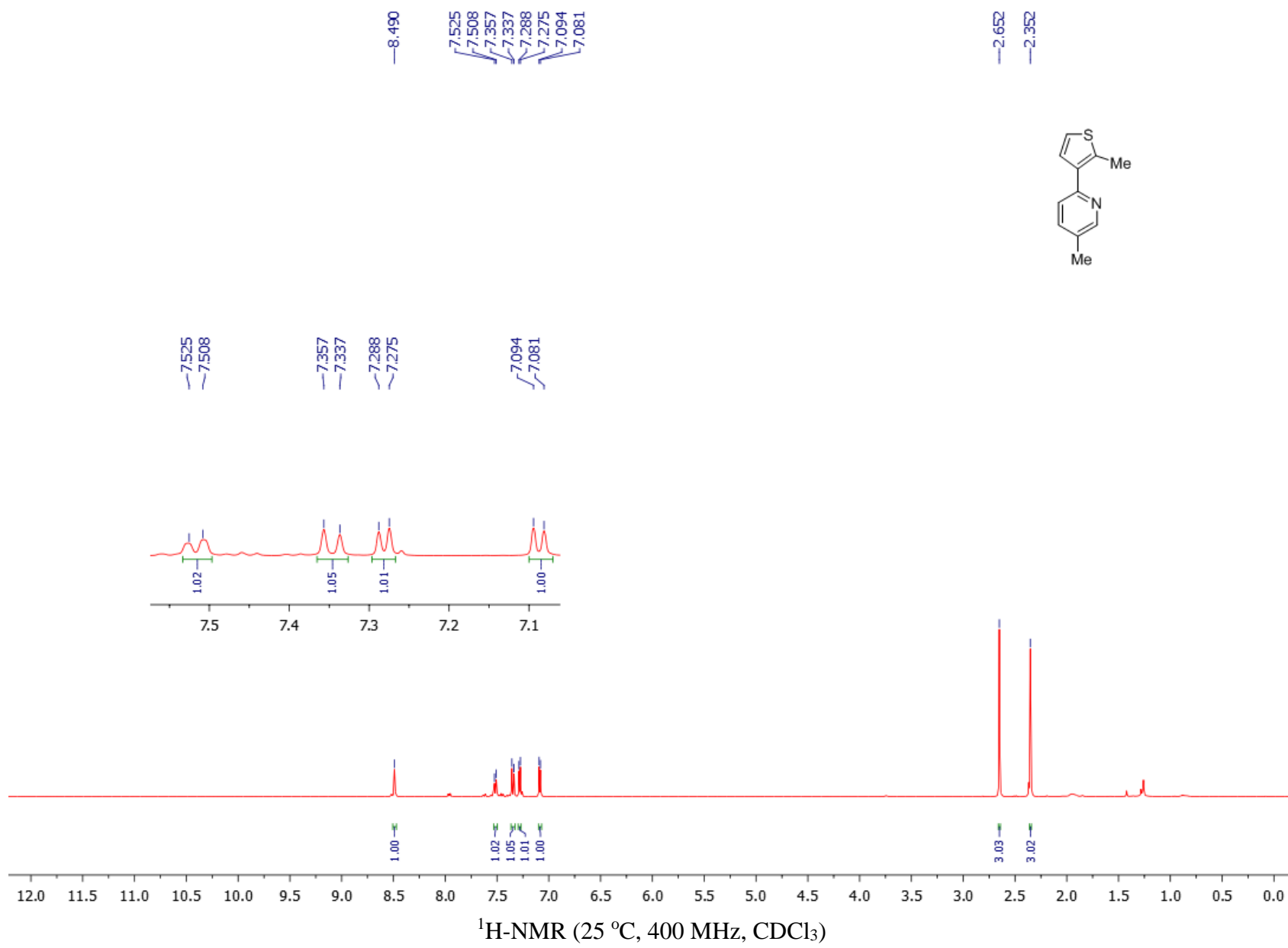


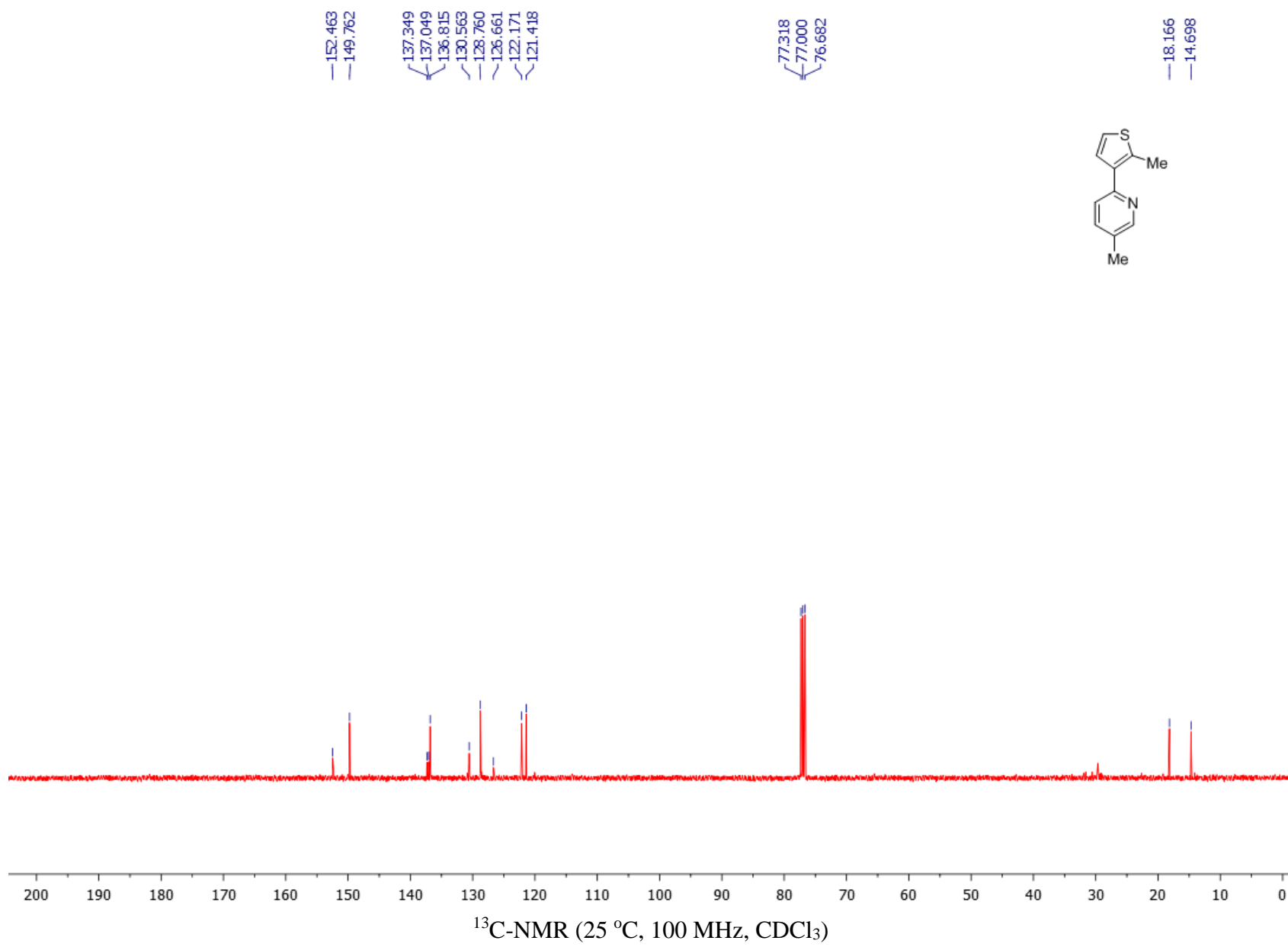


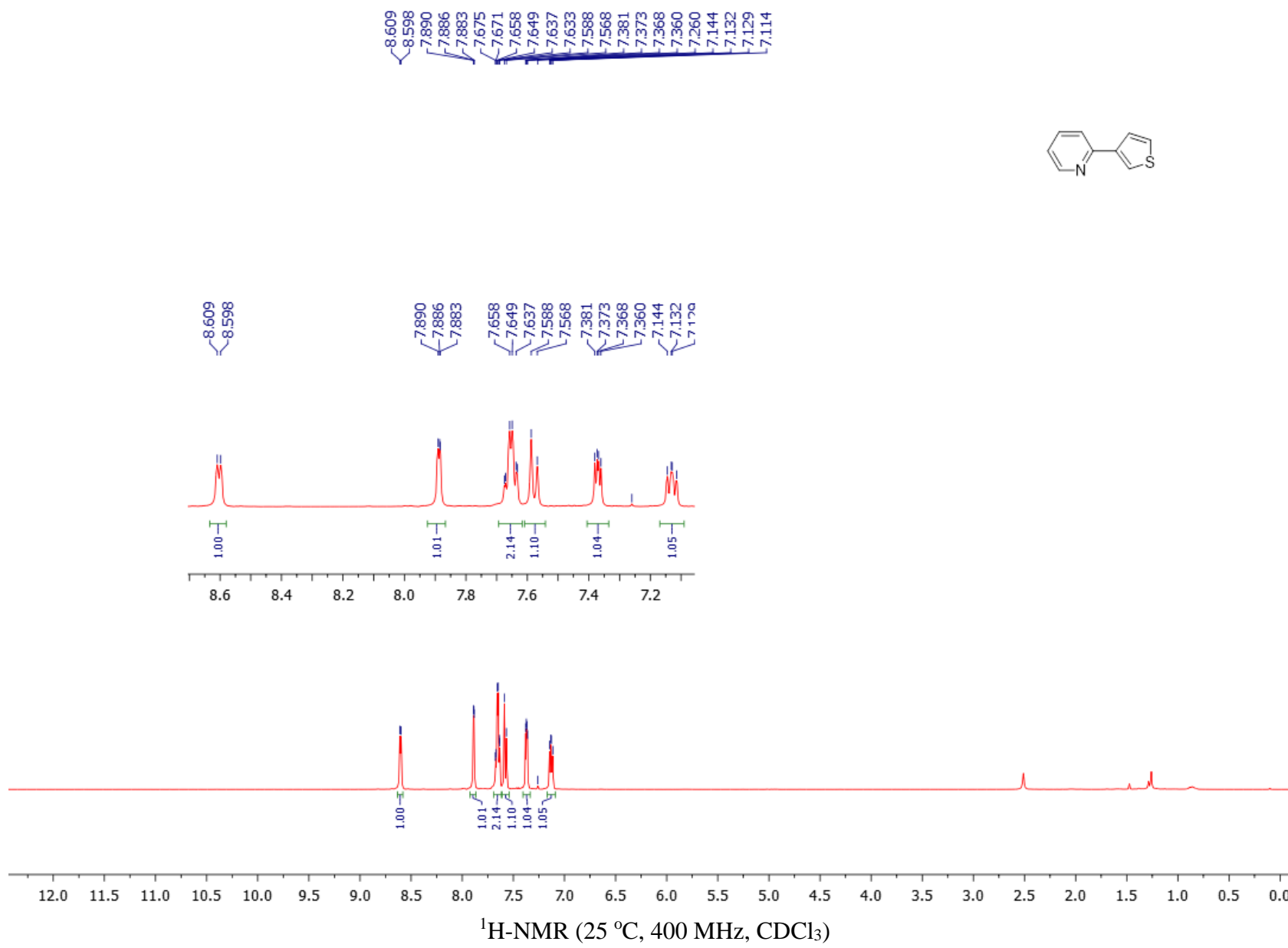
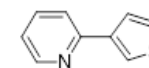


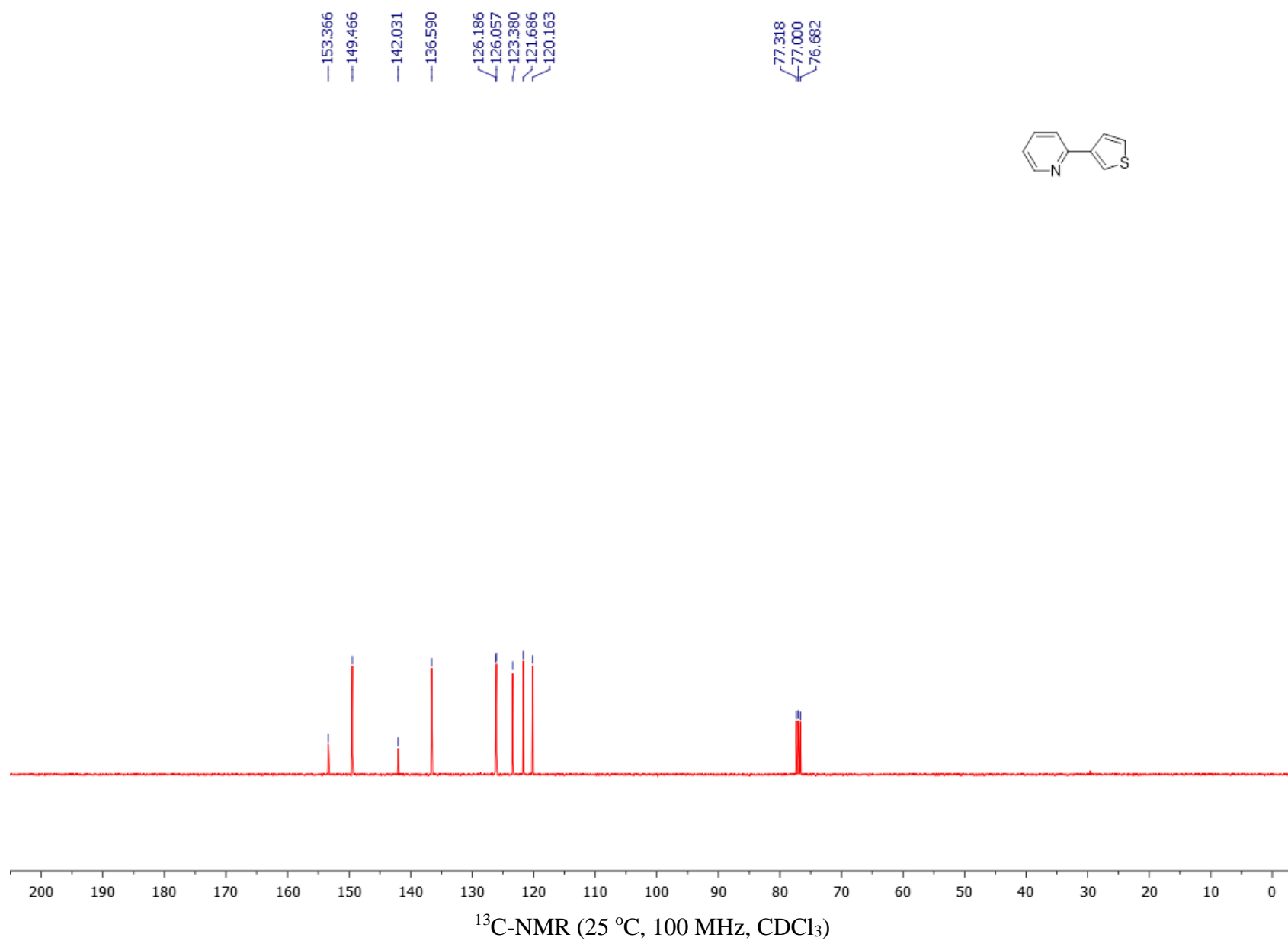
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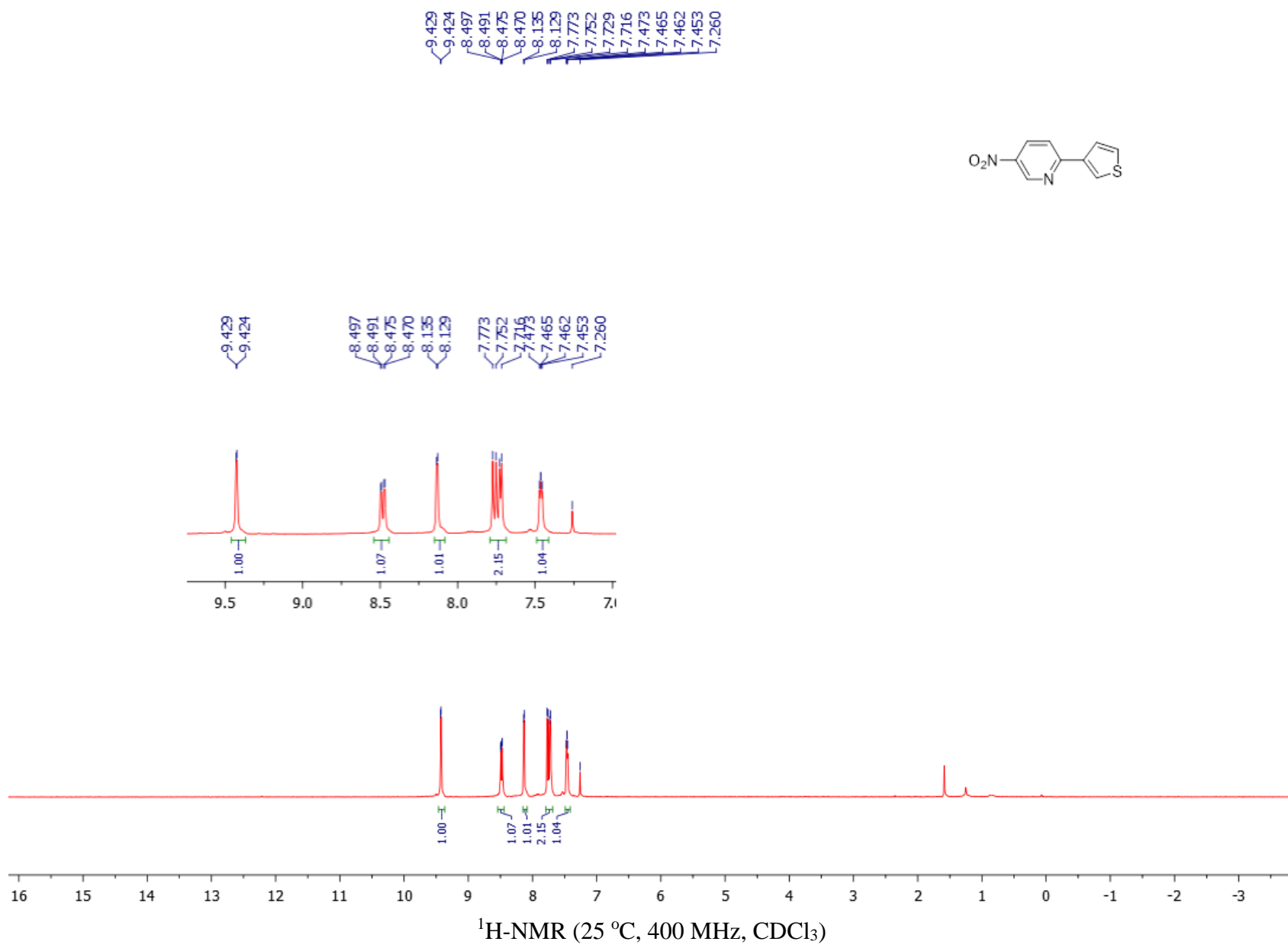
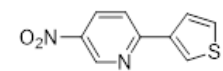


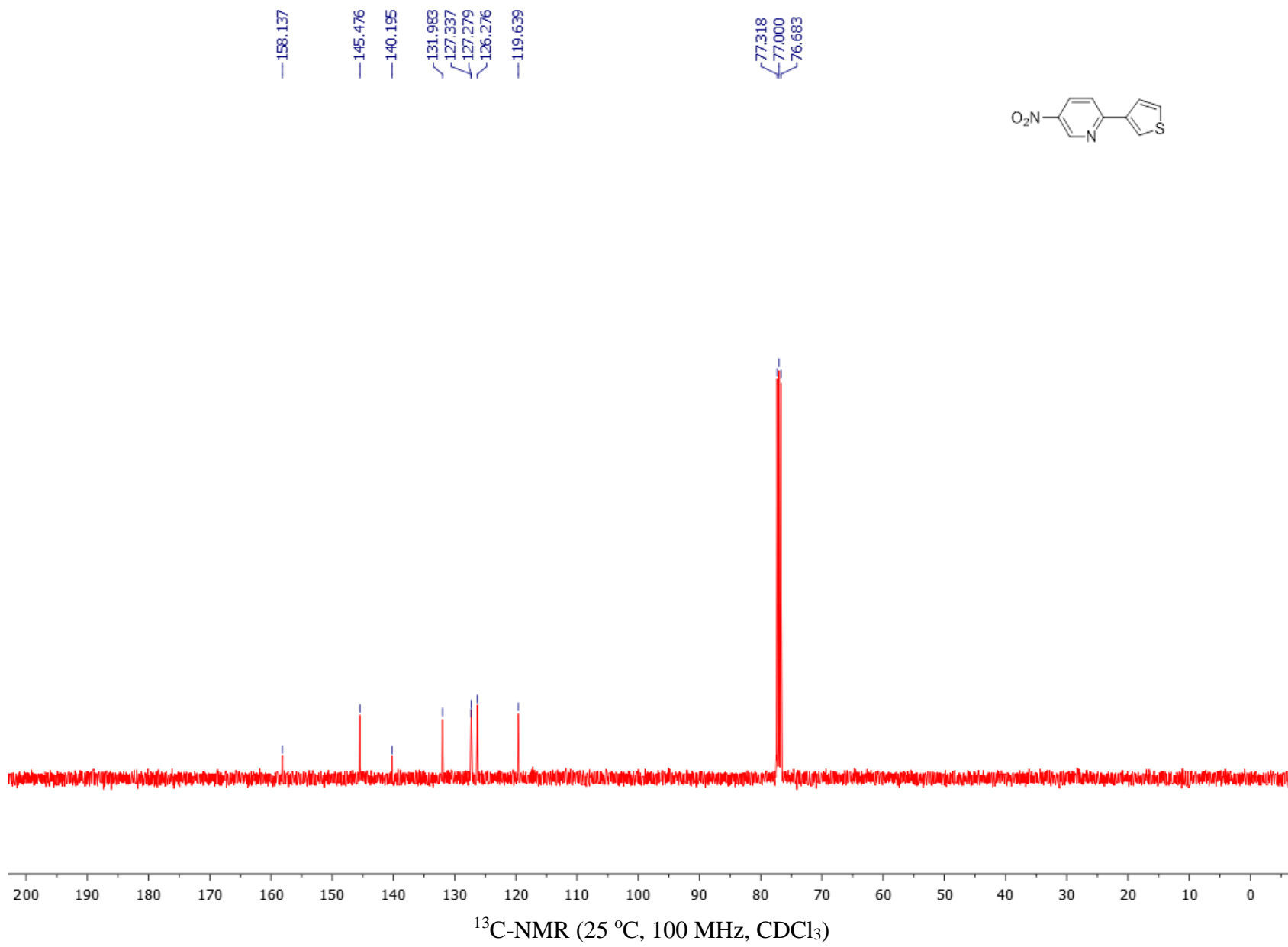


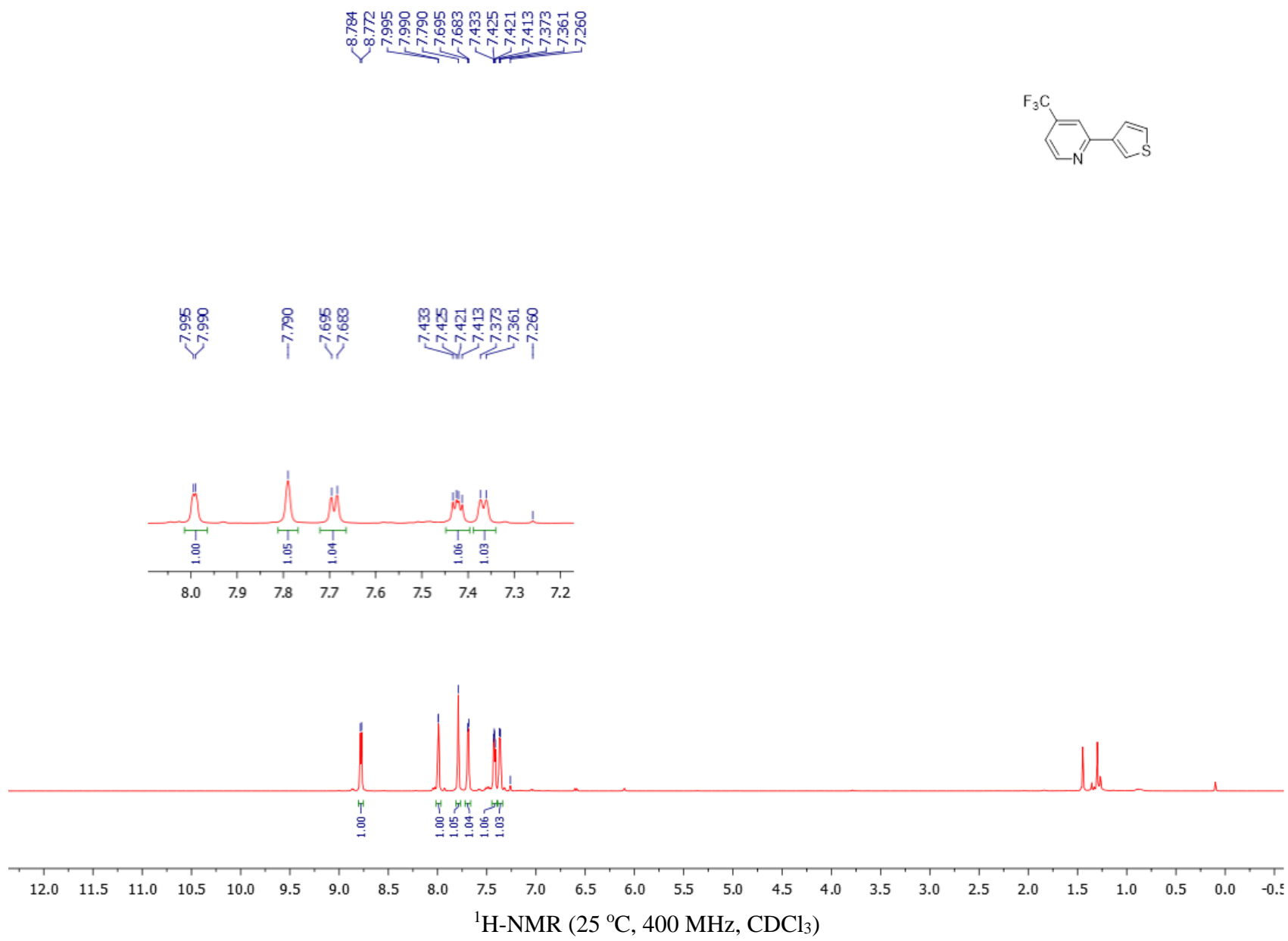
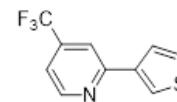


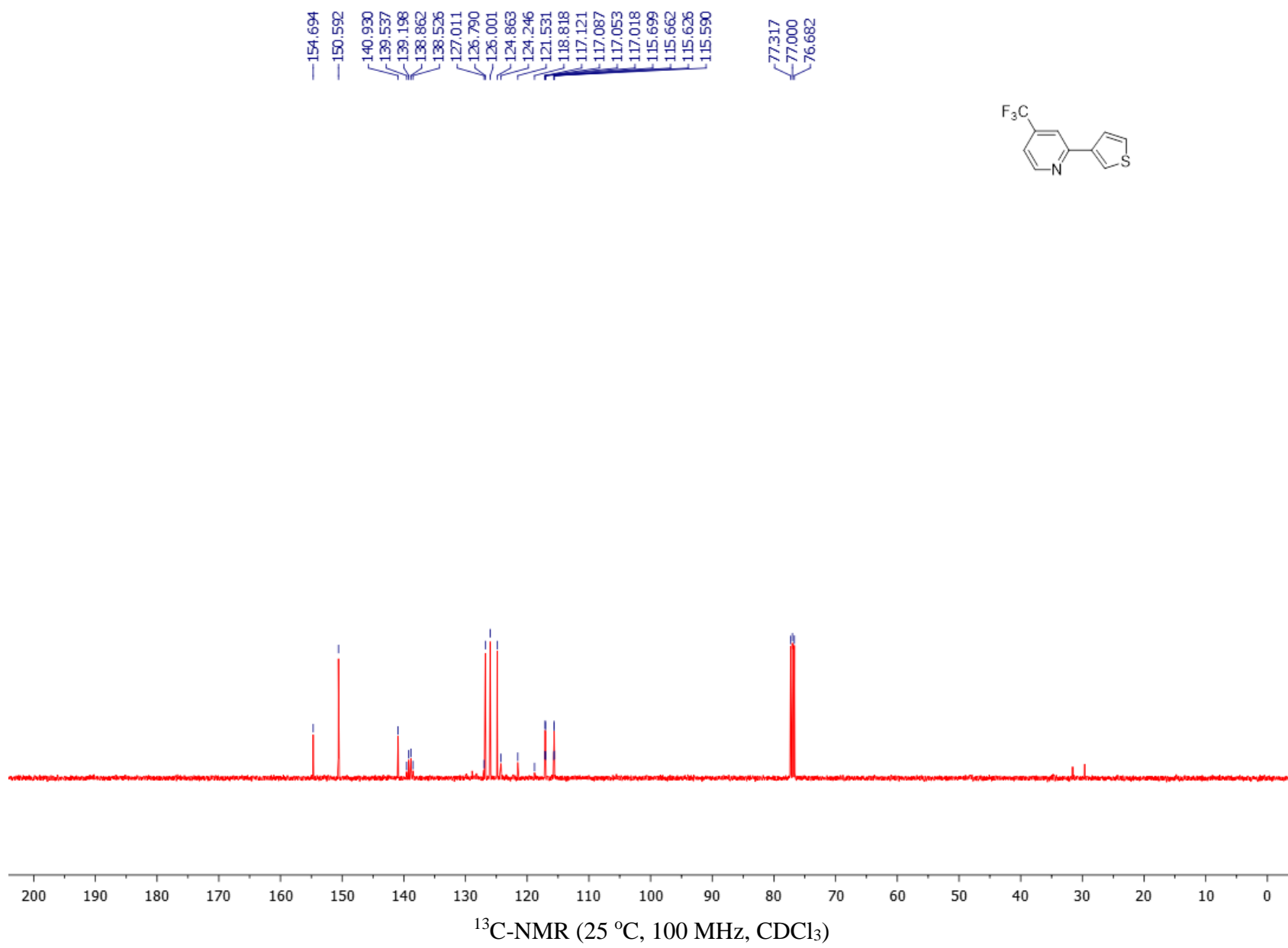


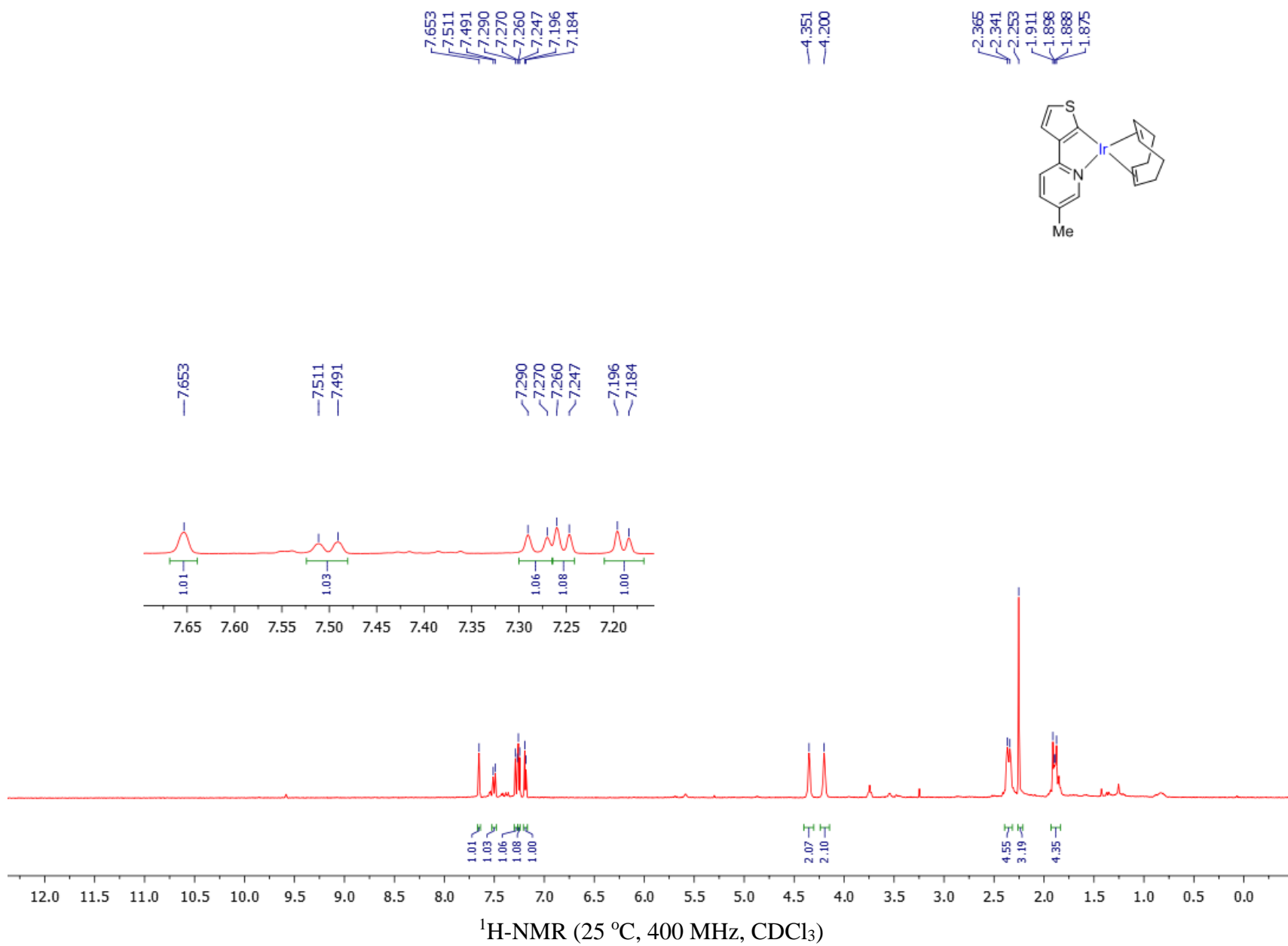


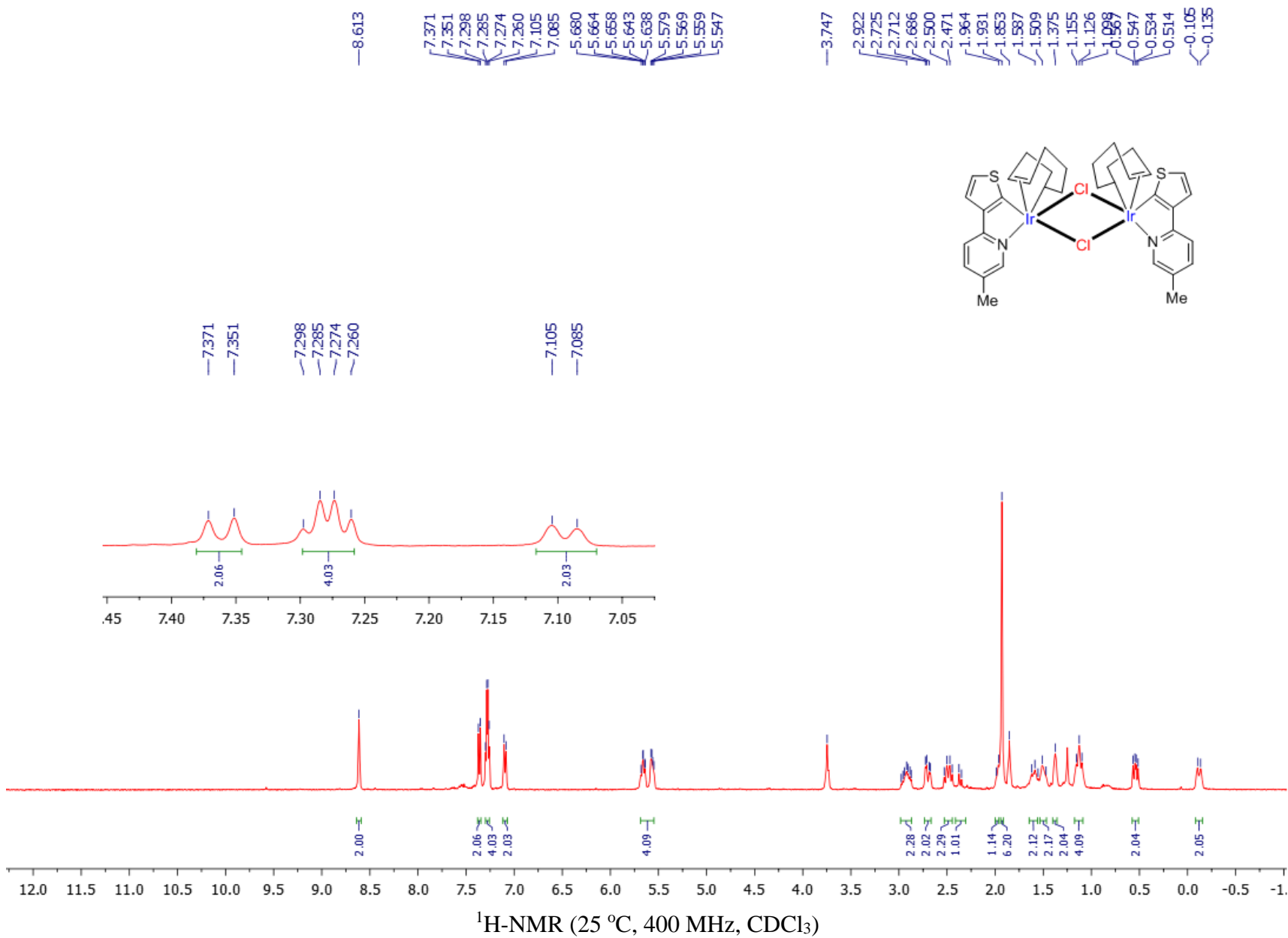


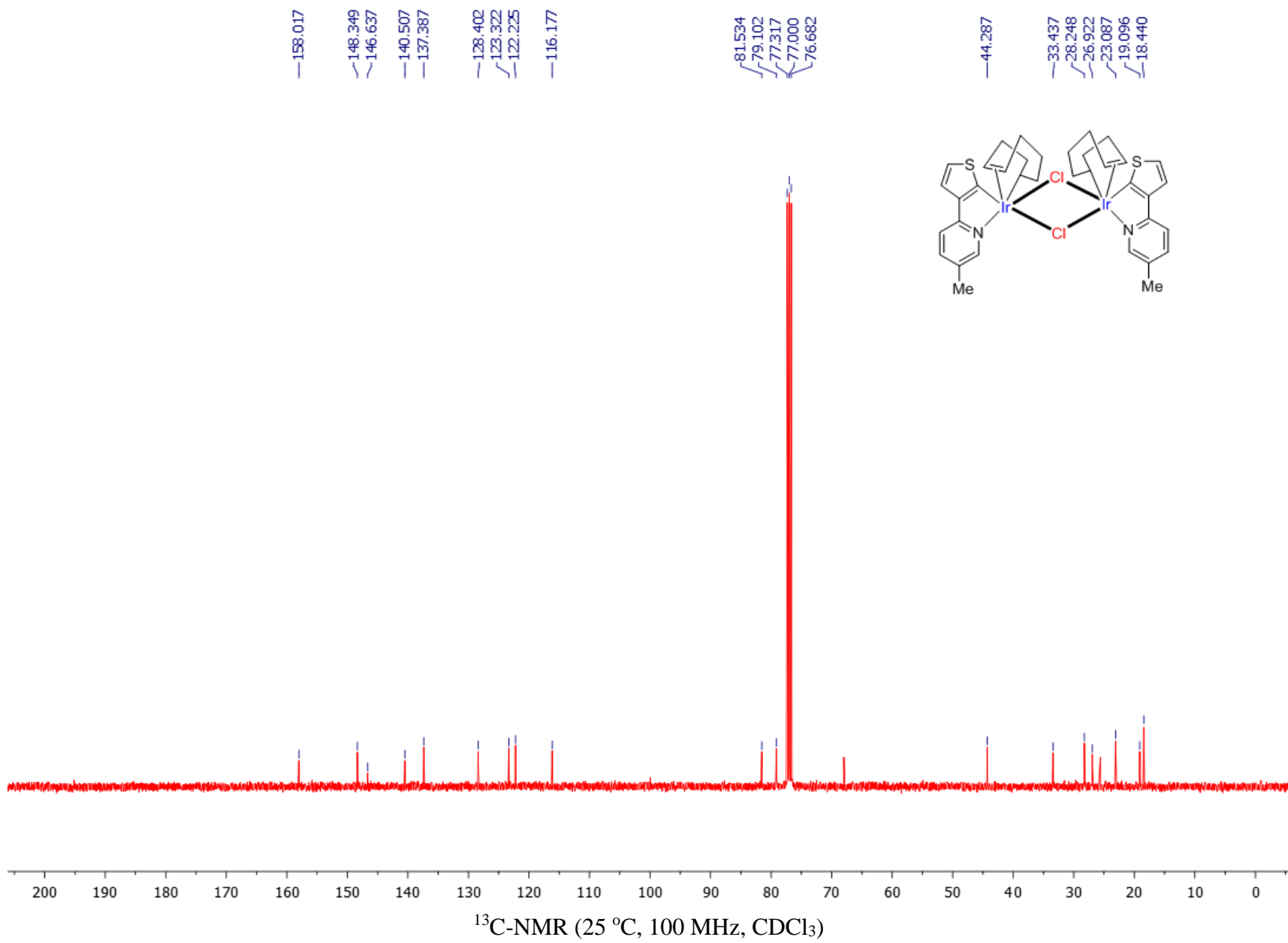




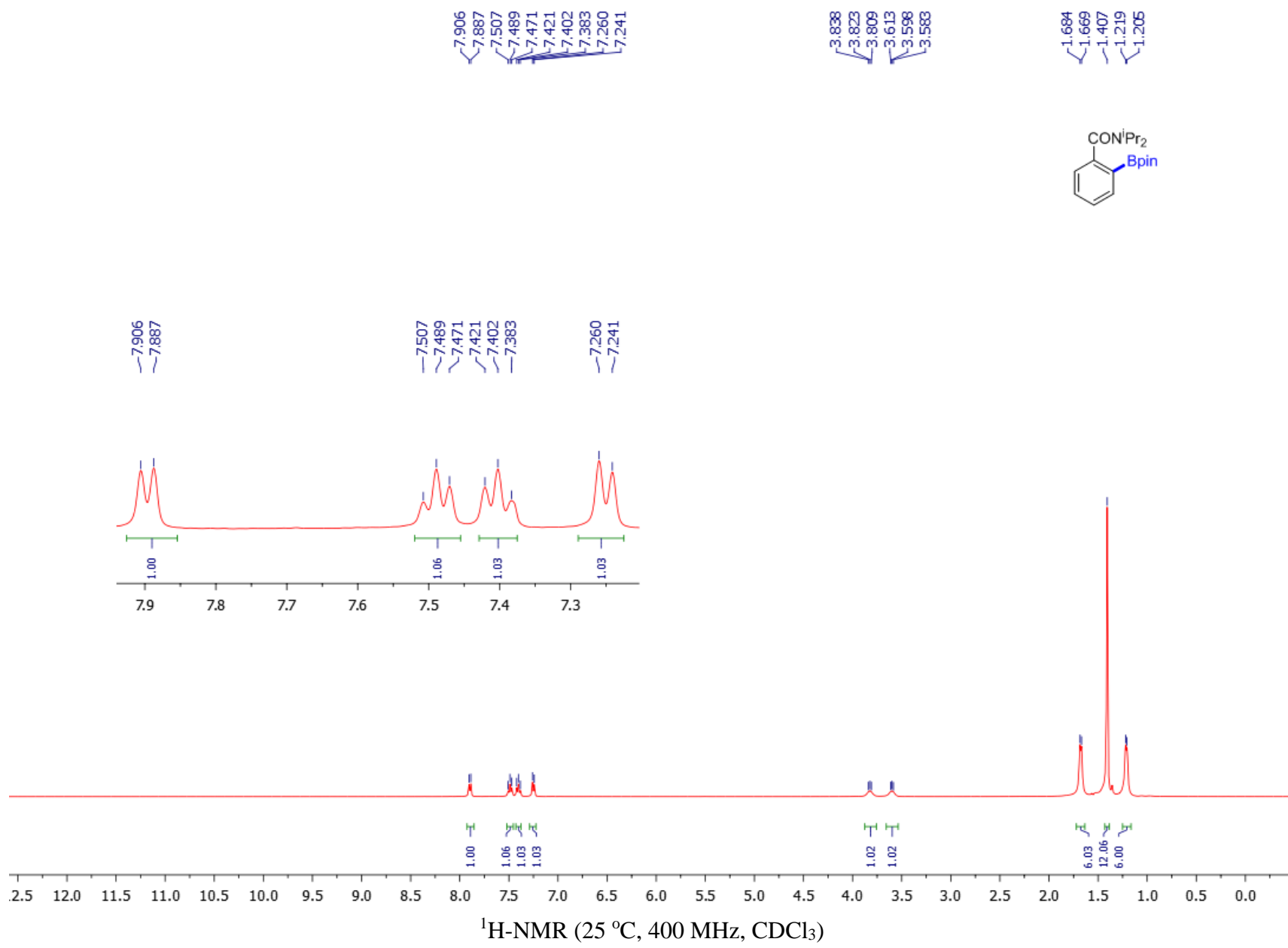


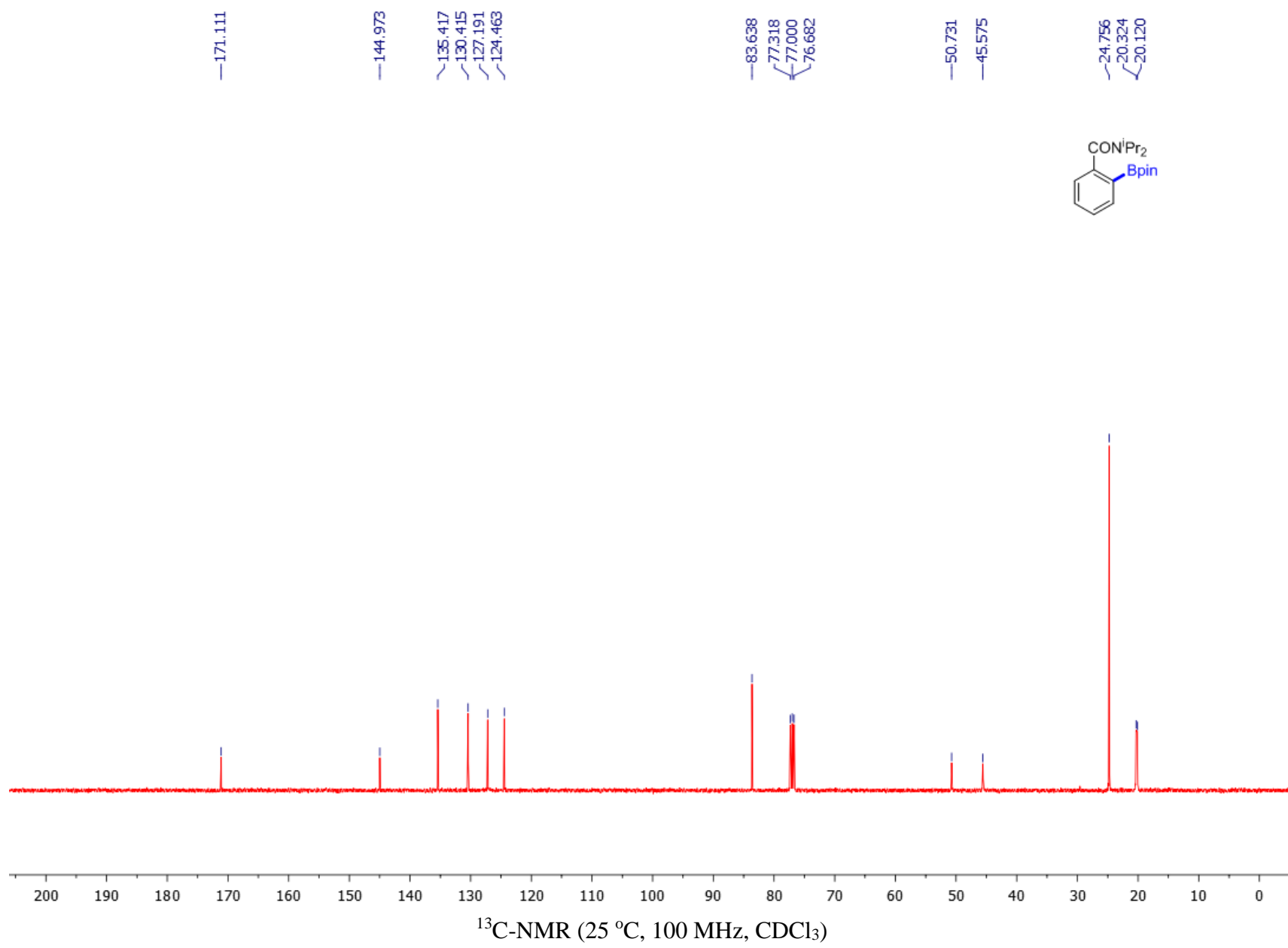


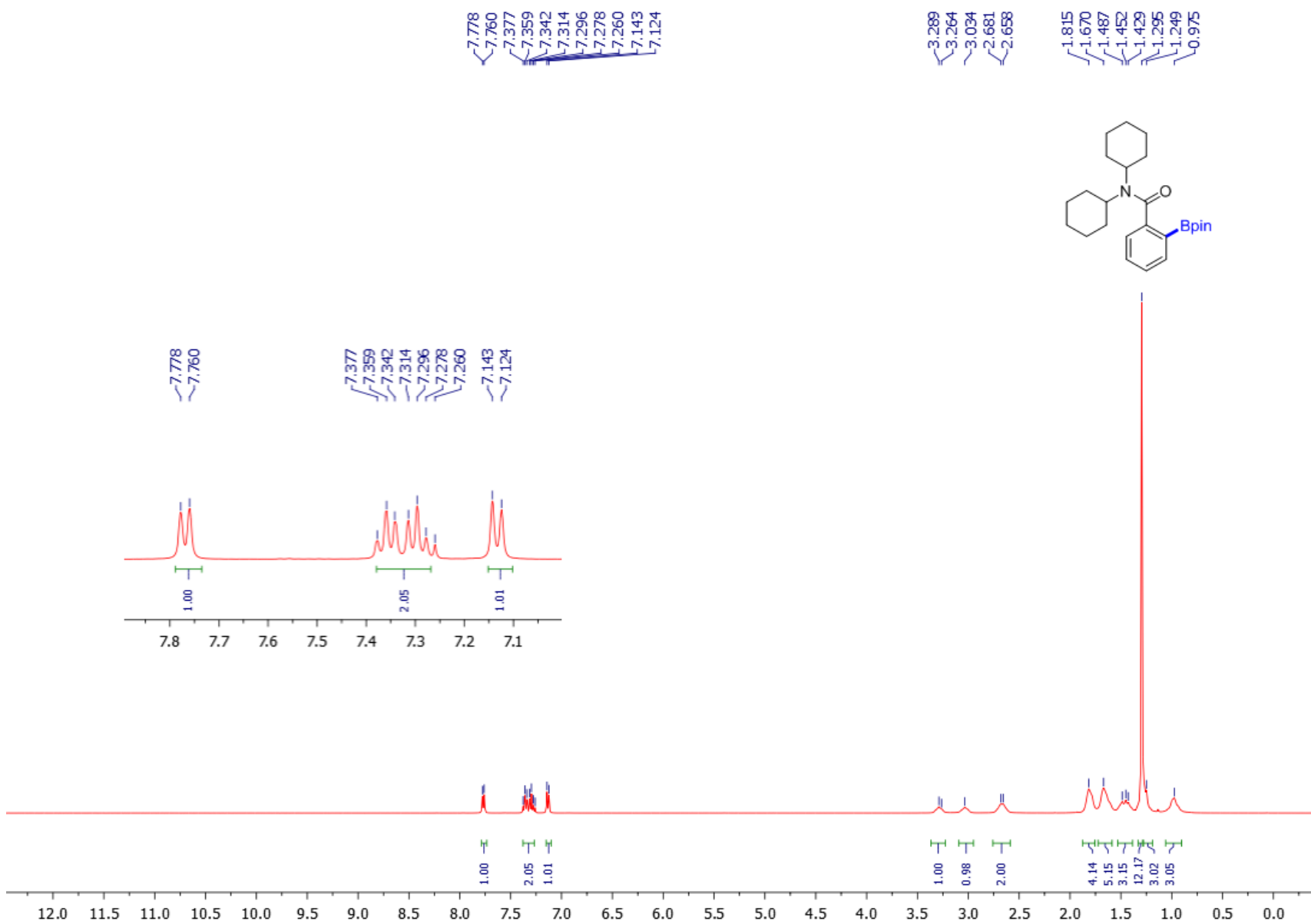




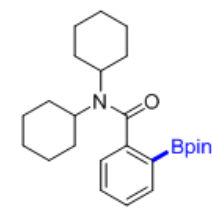
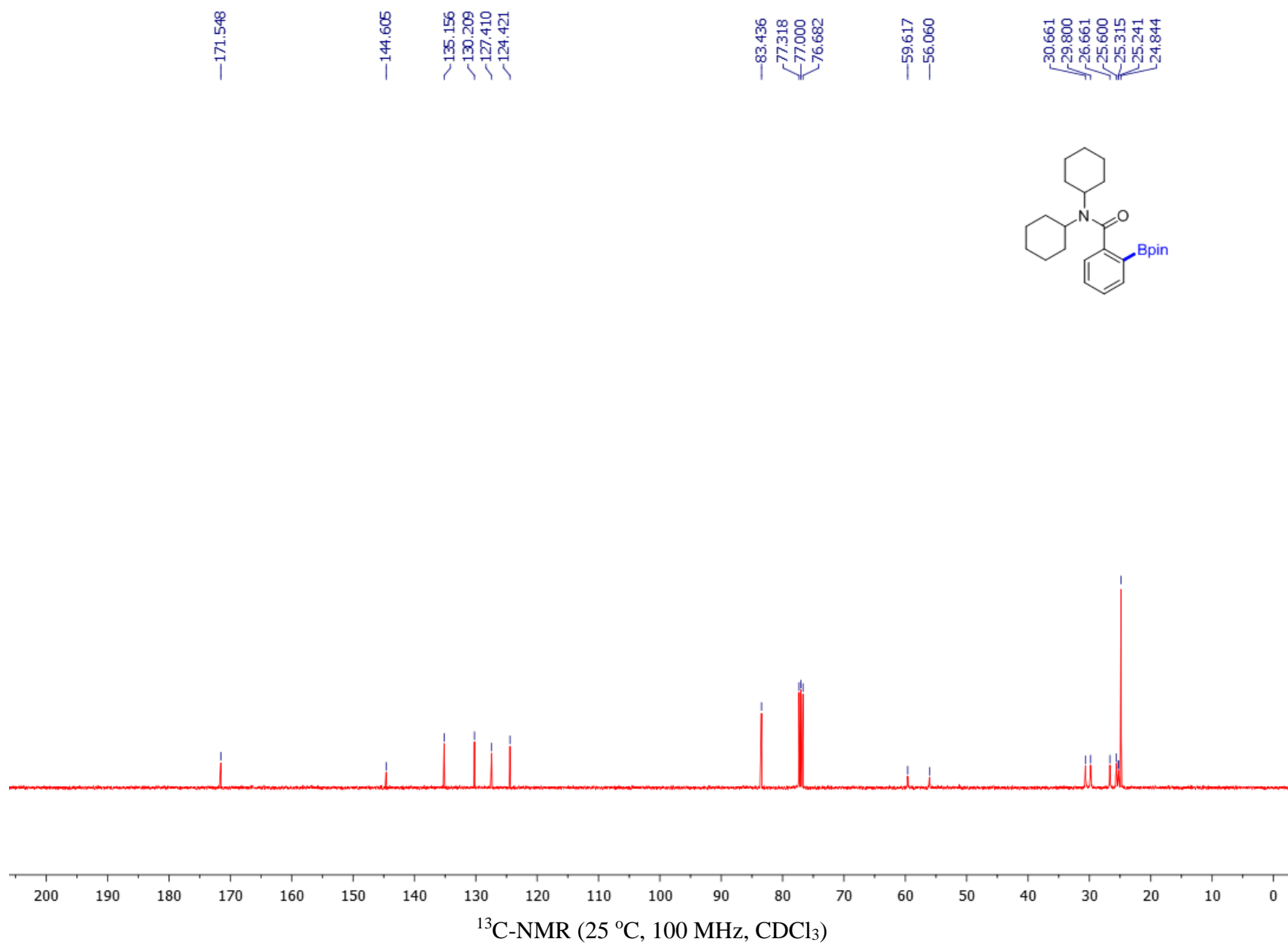
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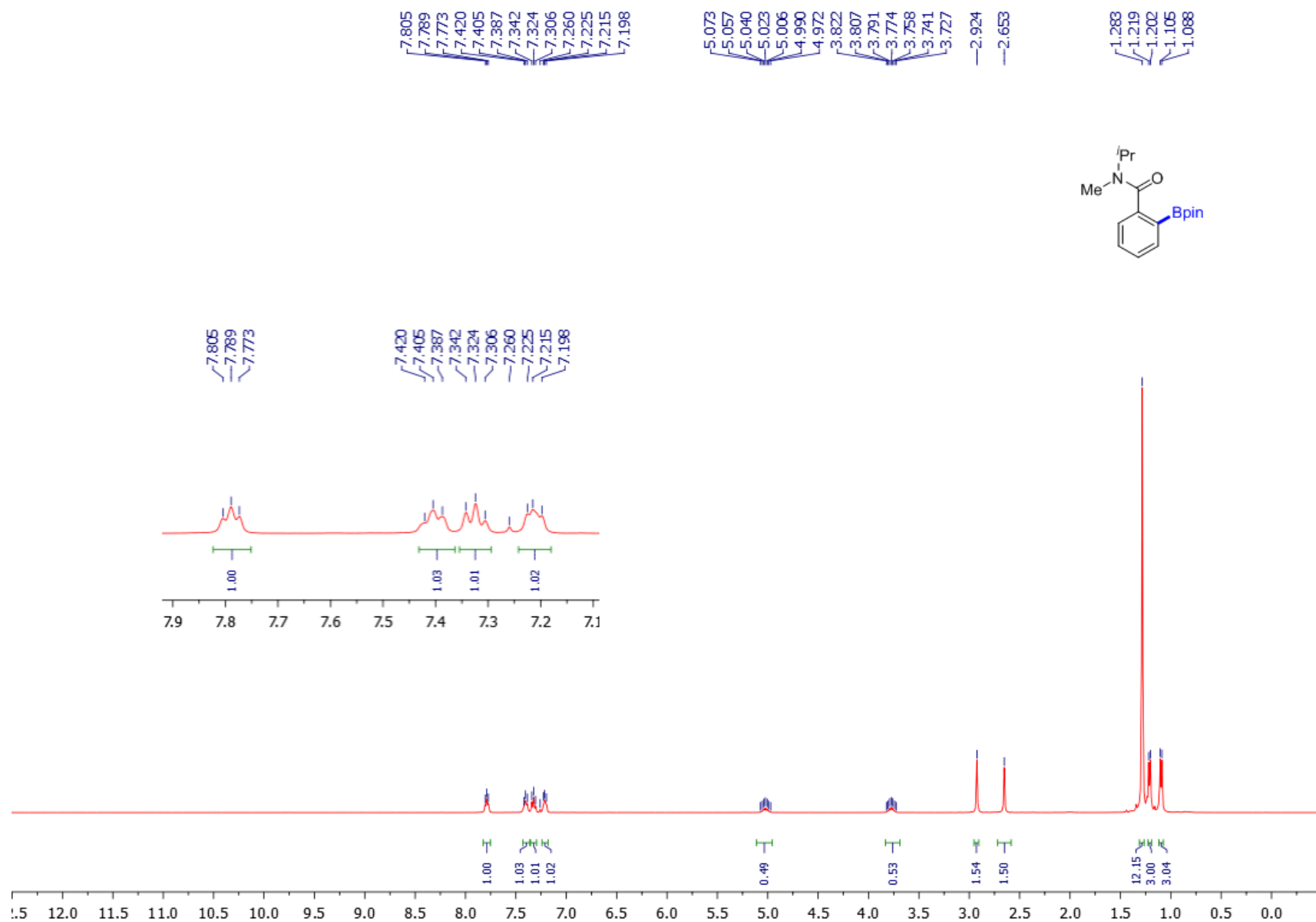




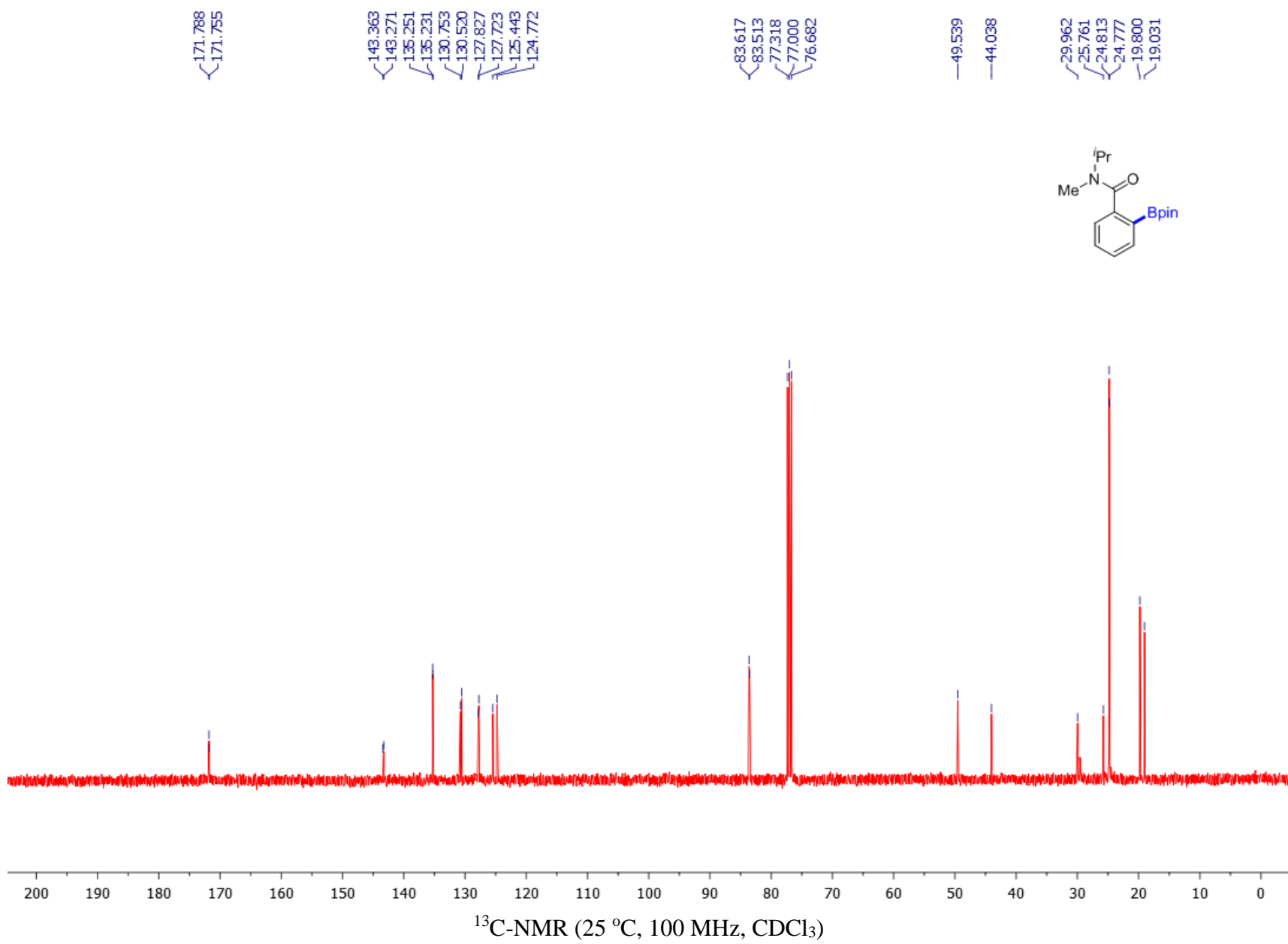


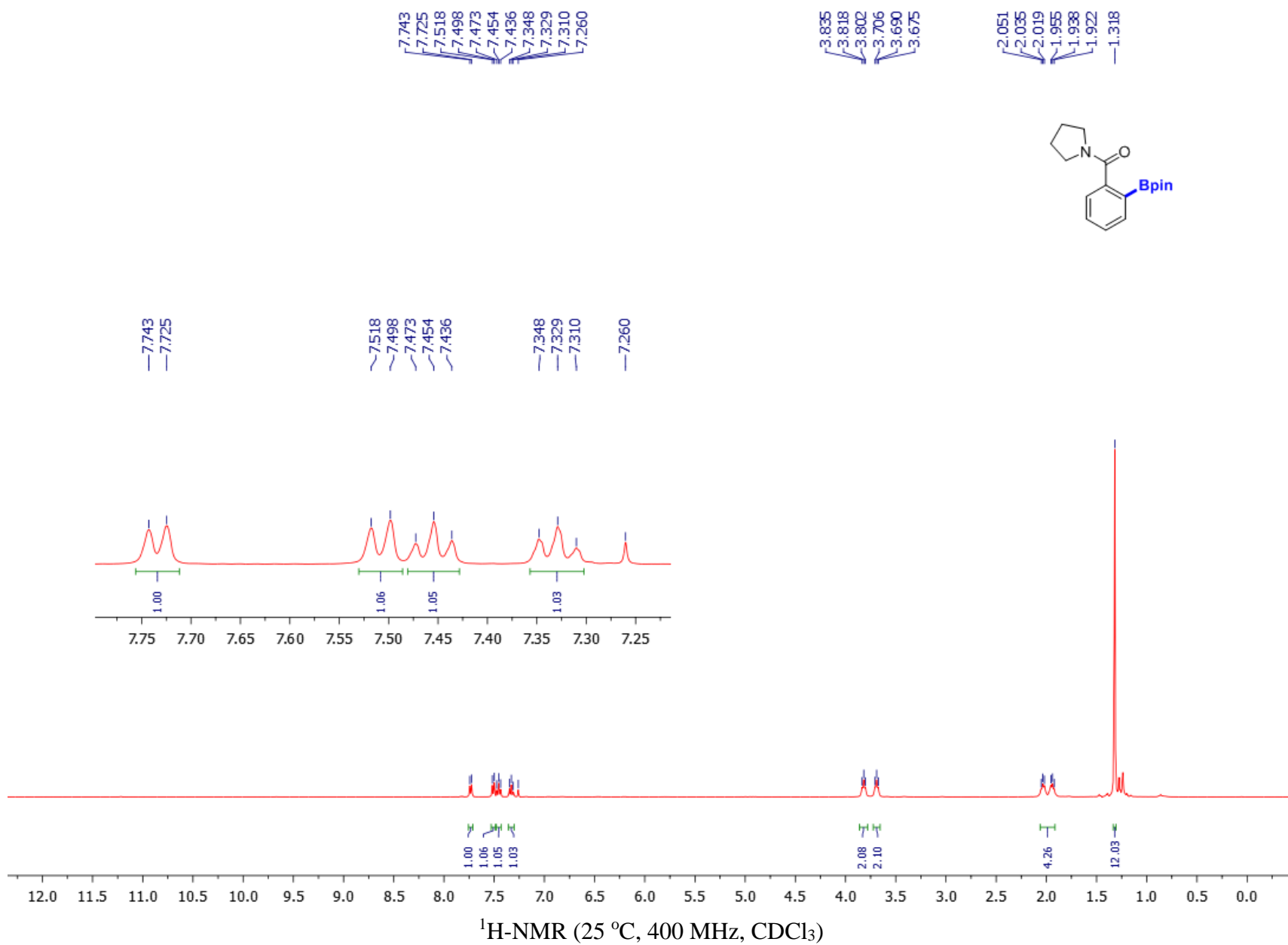
$^1\text{H-NMR}$ (25 °C, 400 MHz, CDCl_3)

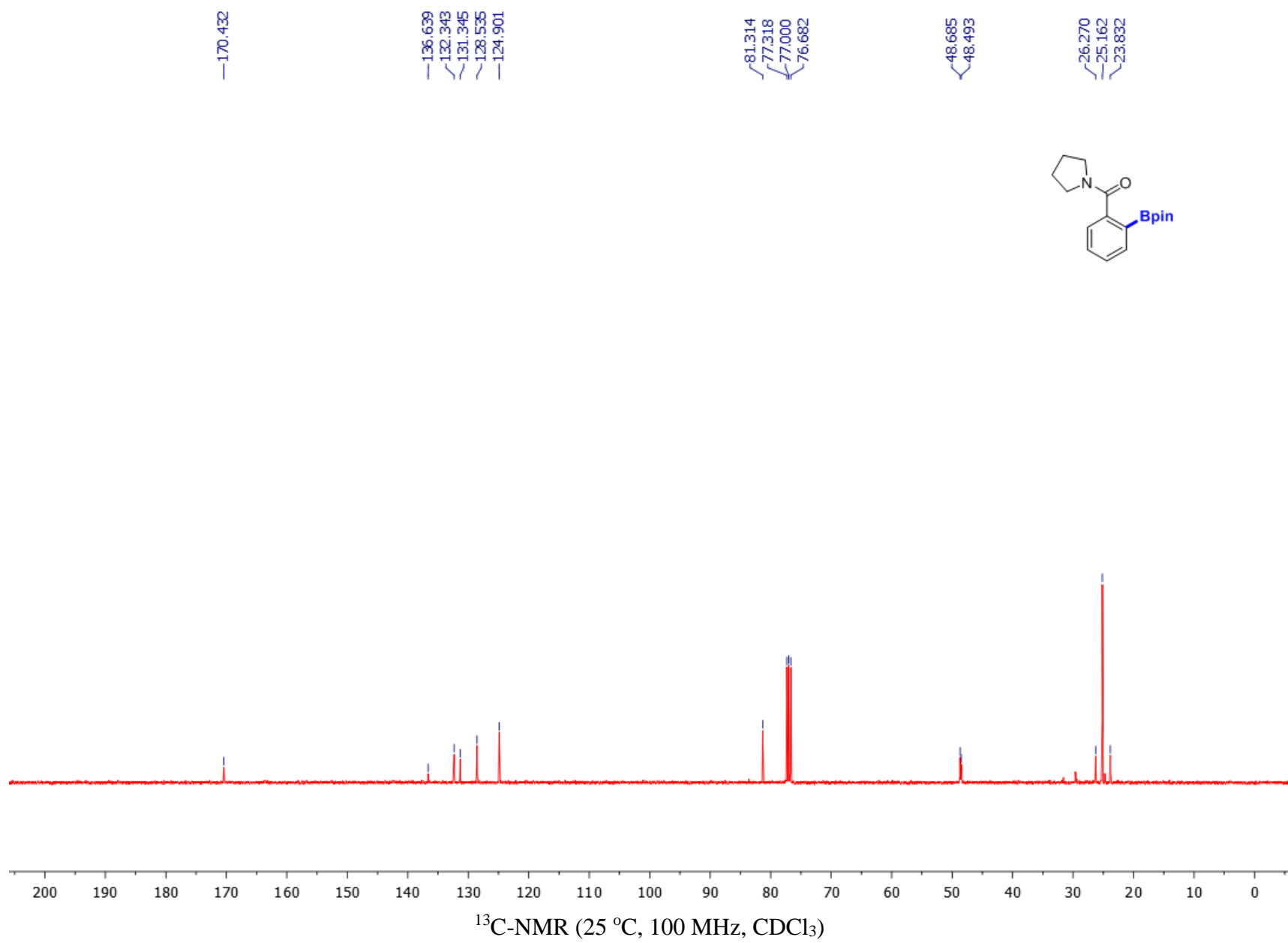


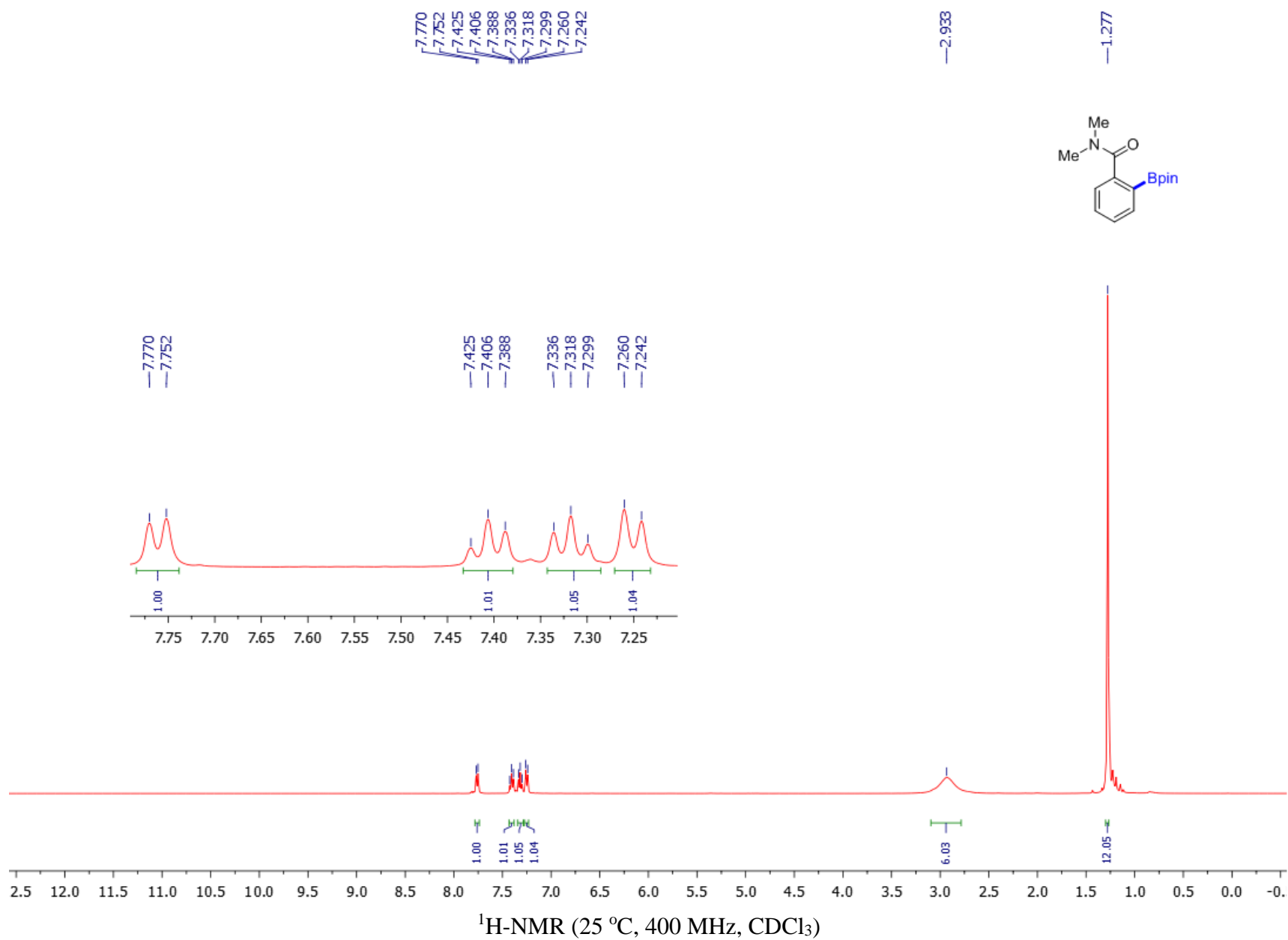


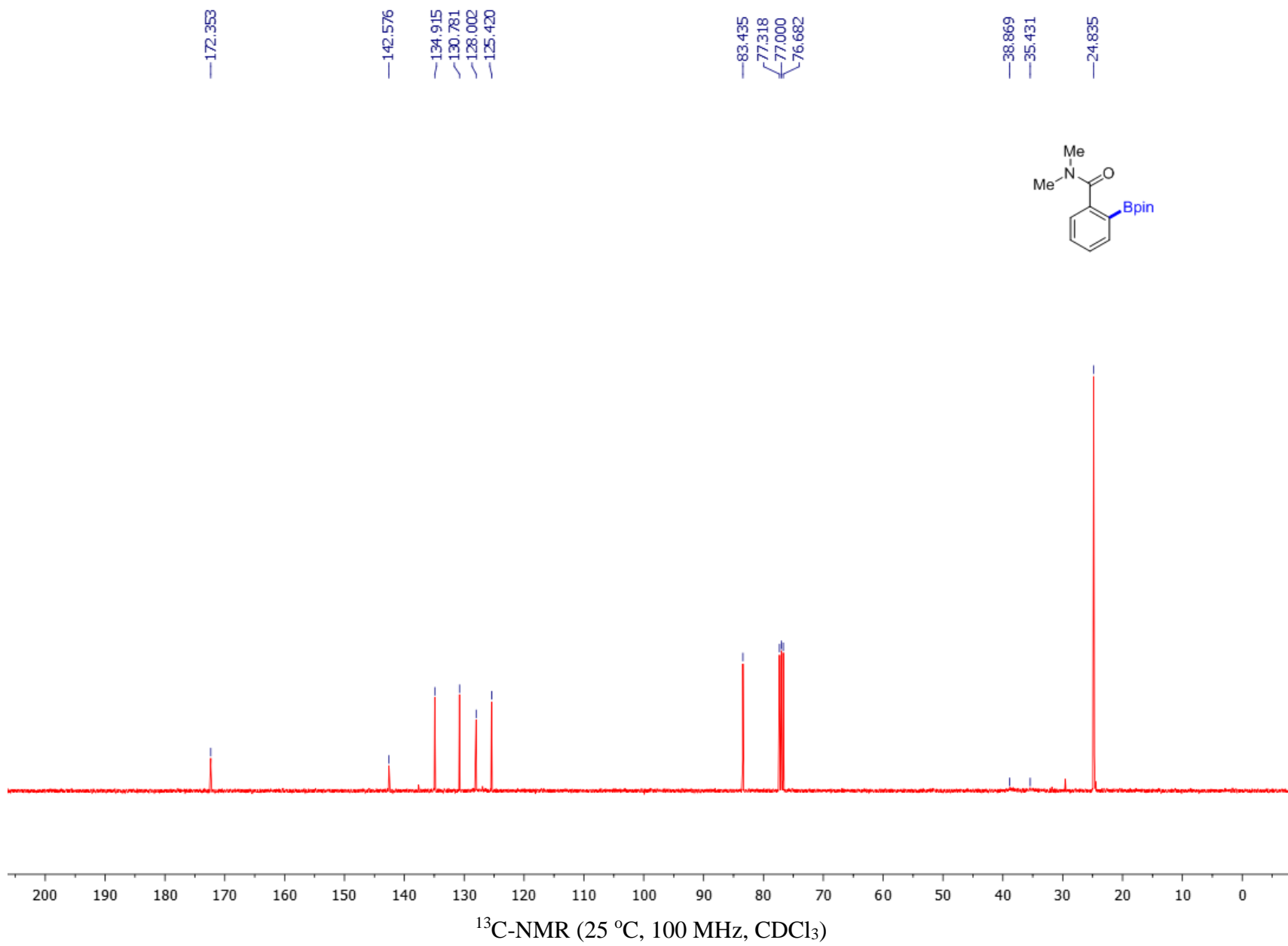
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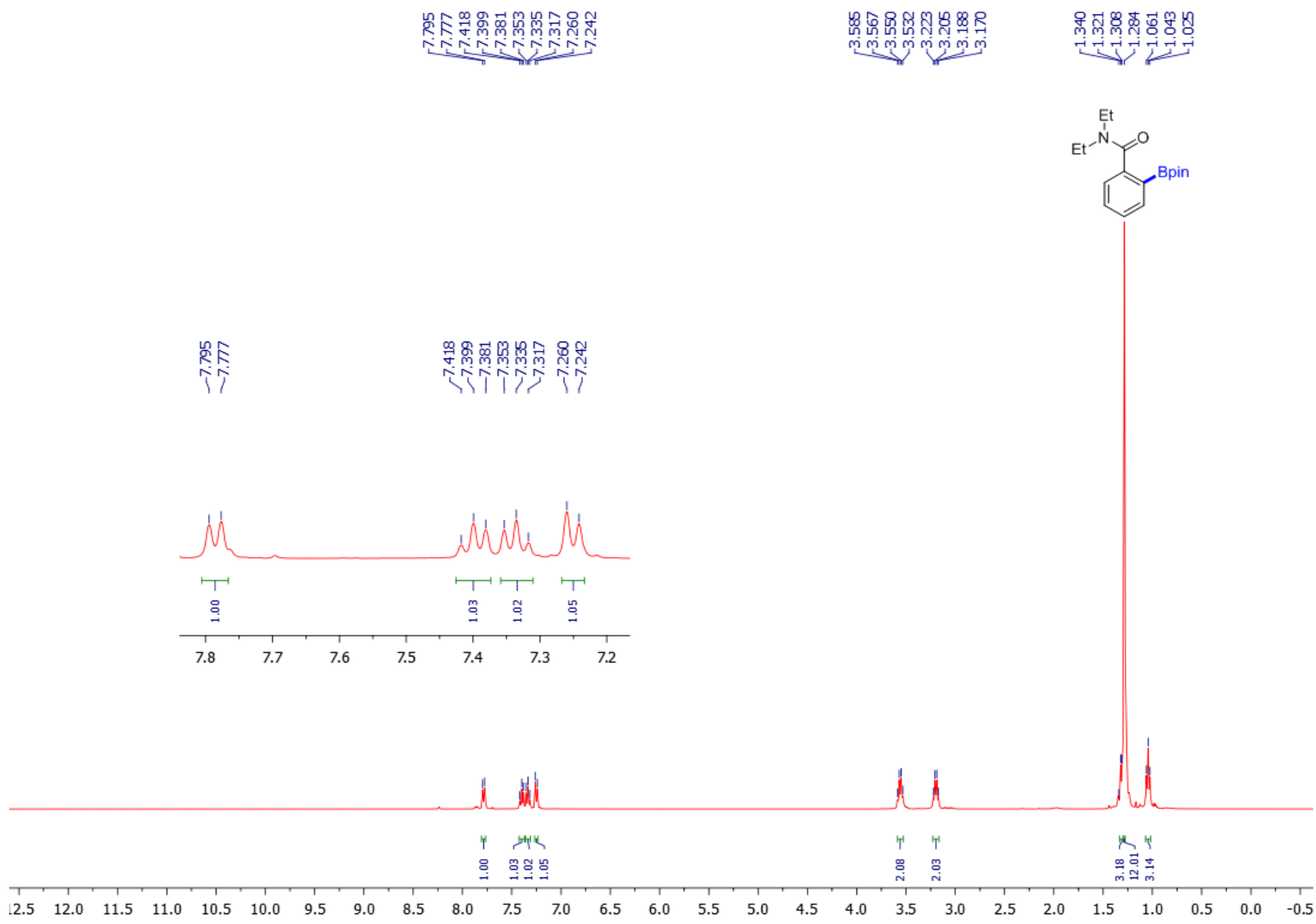




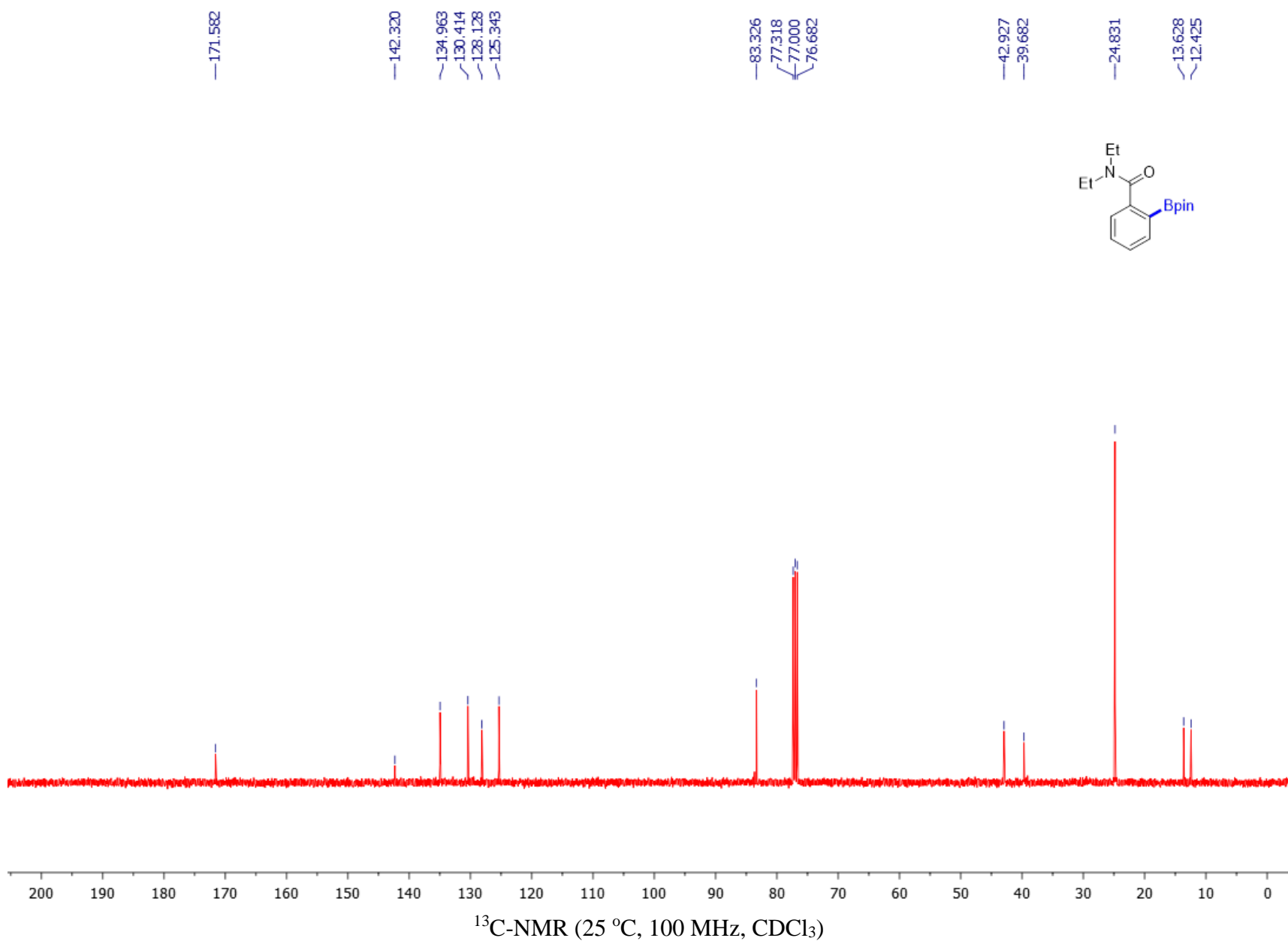


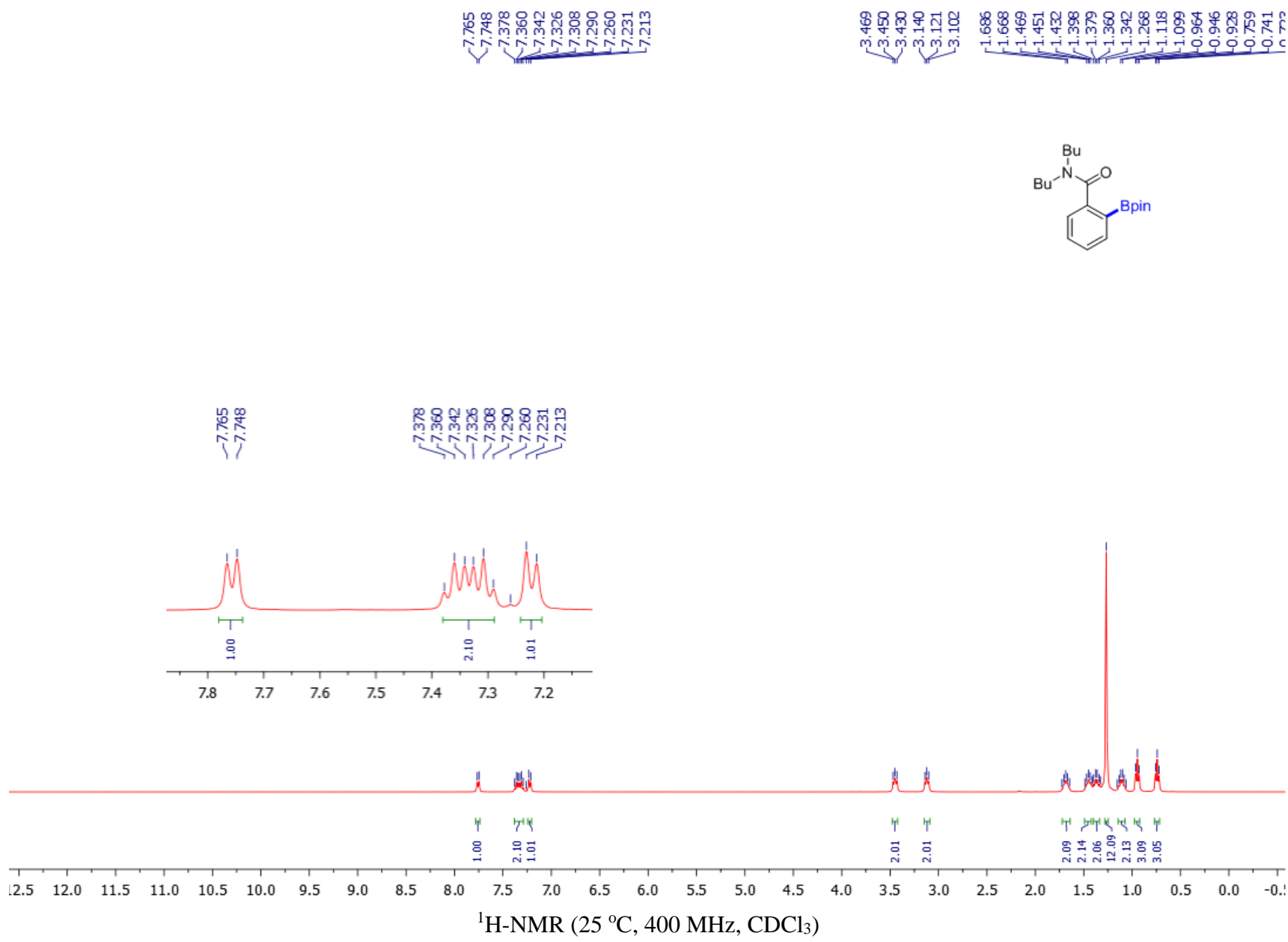


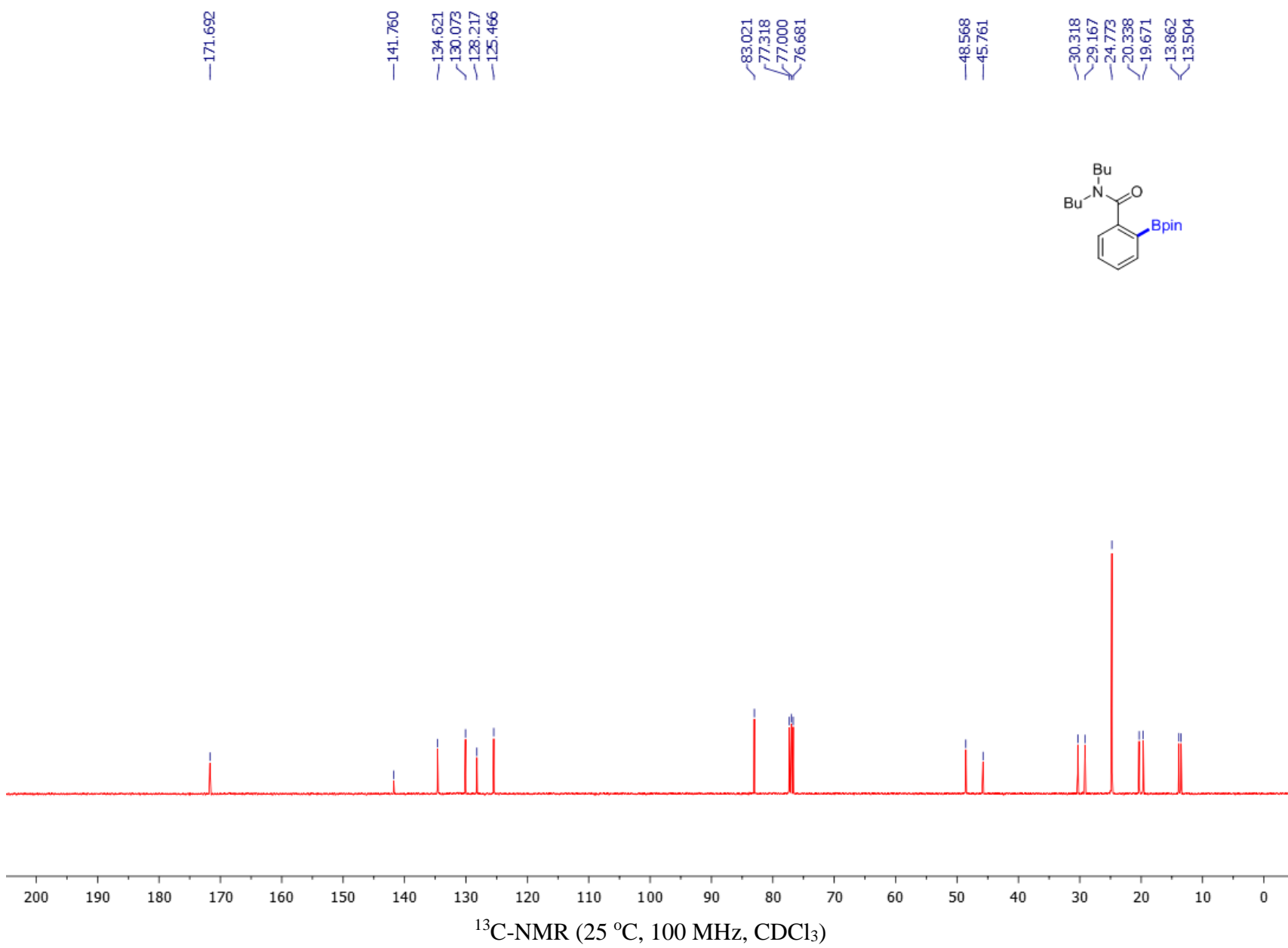


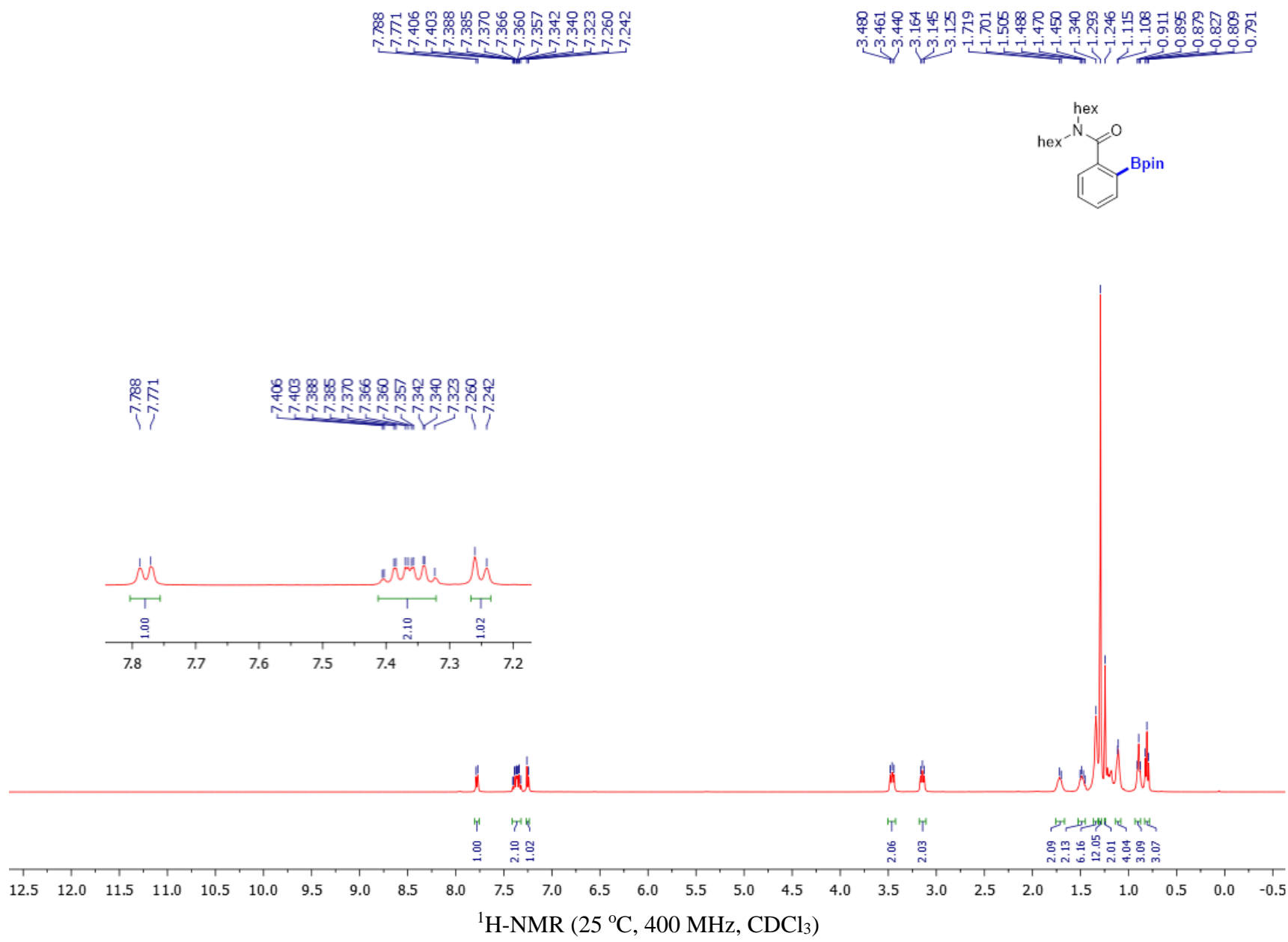


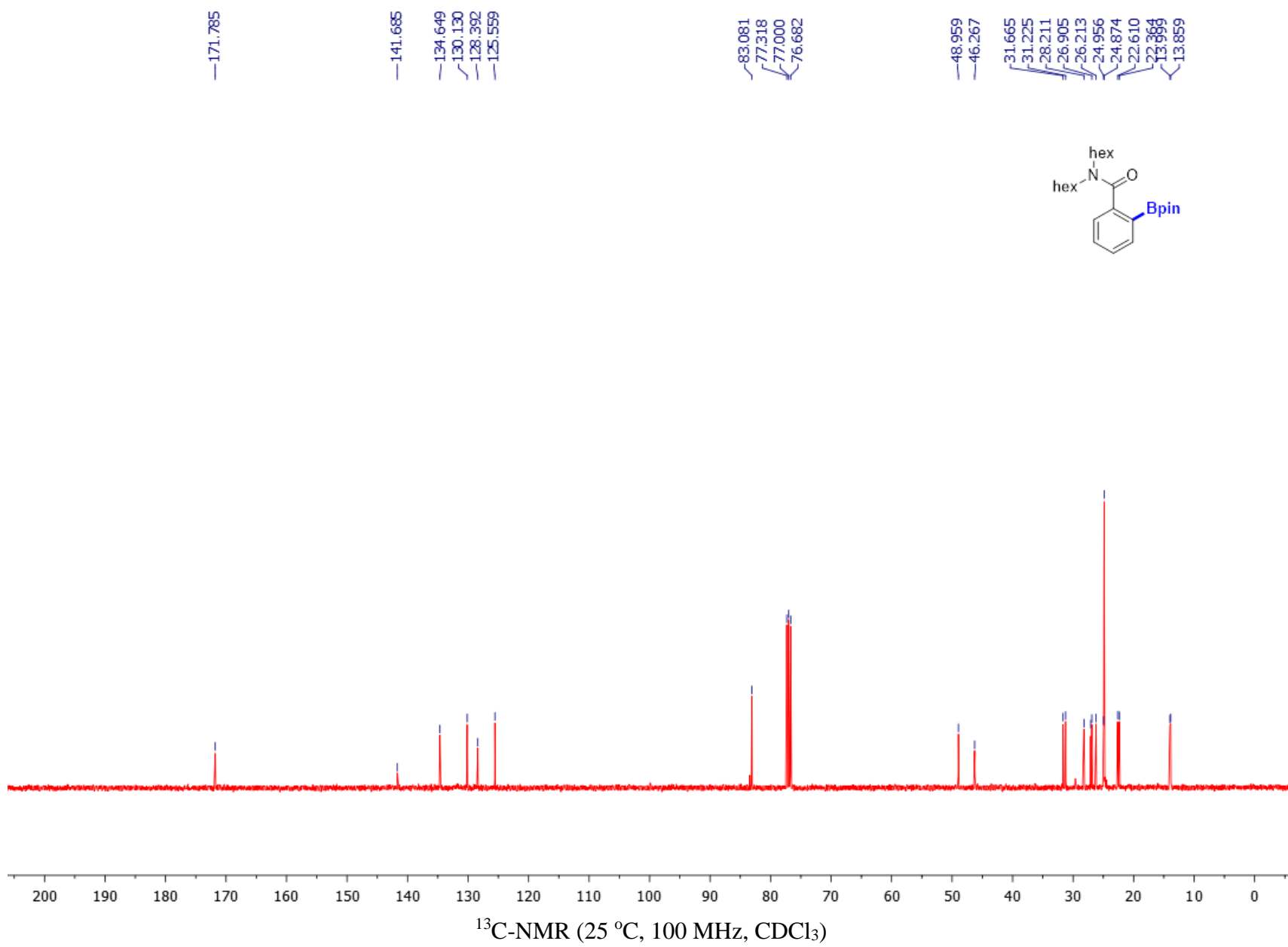
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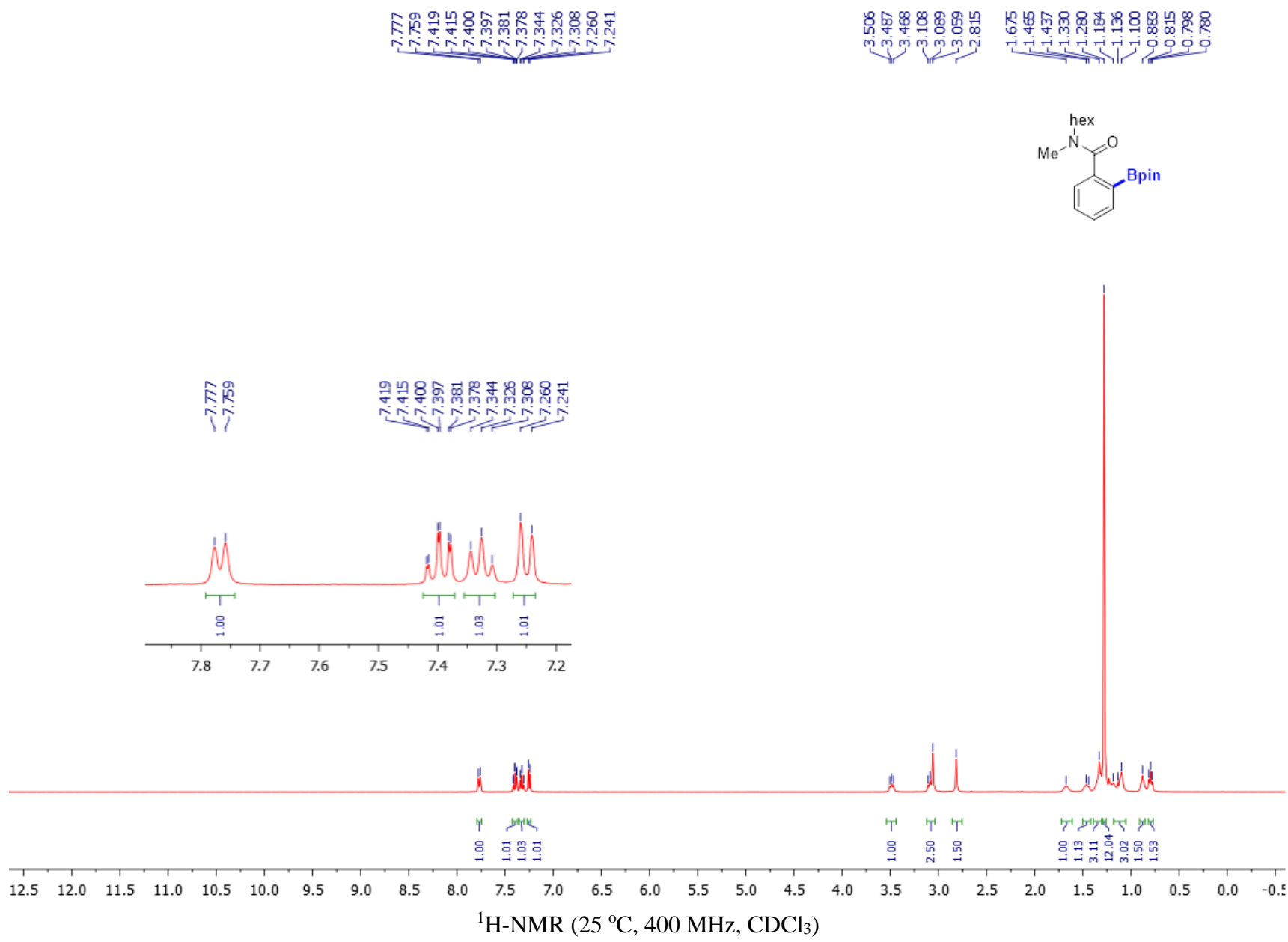


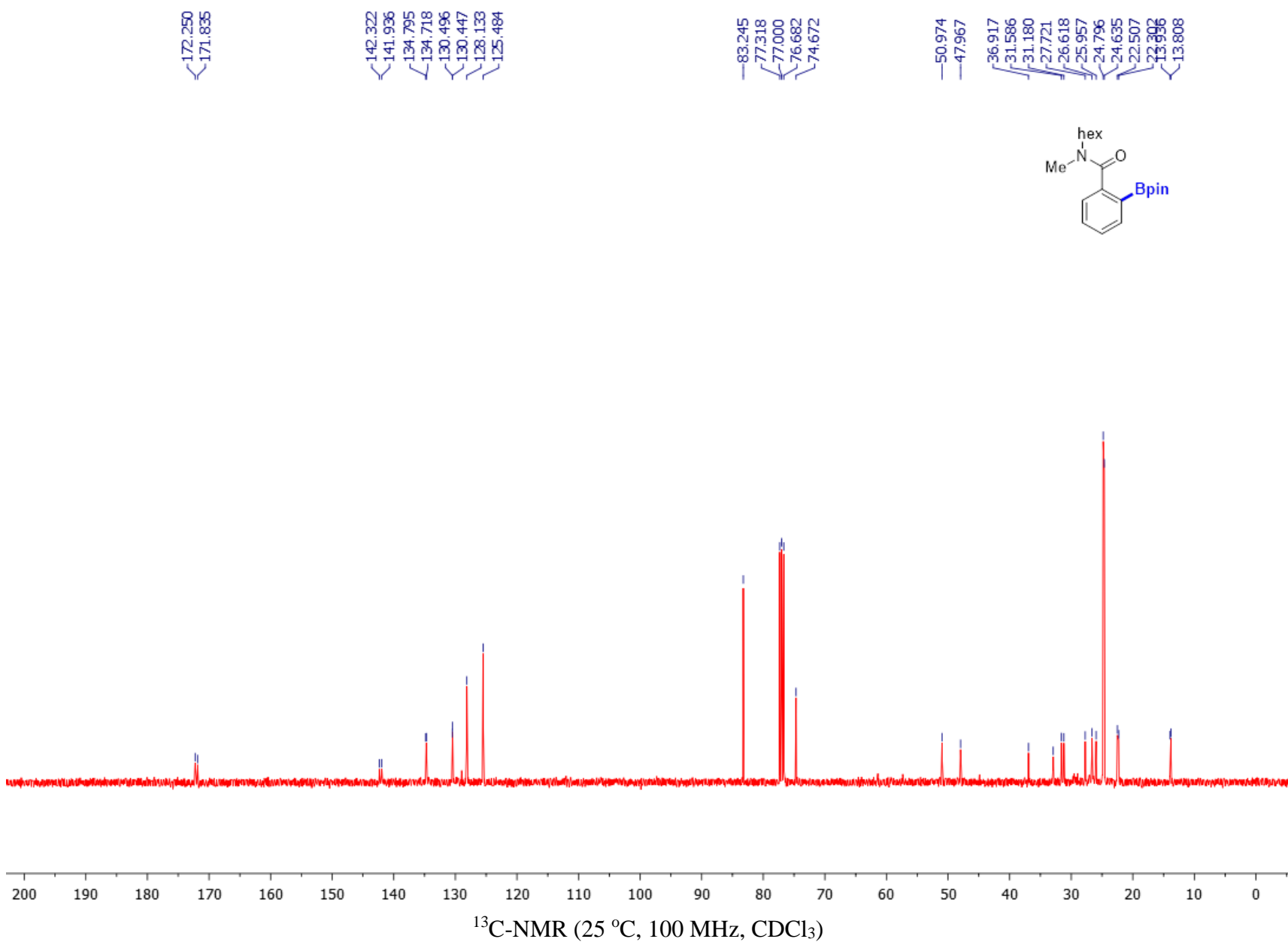


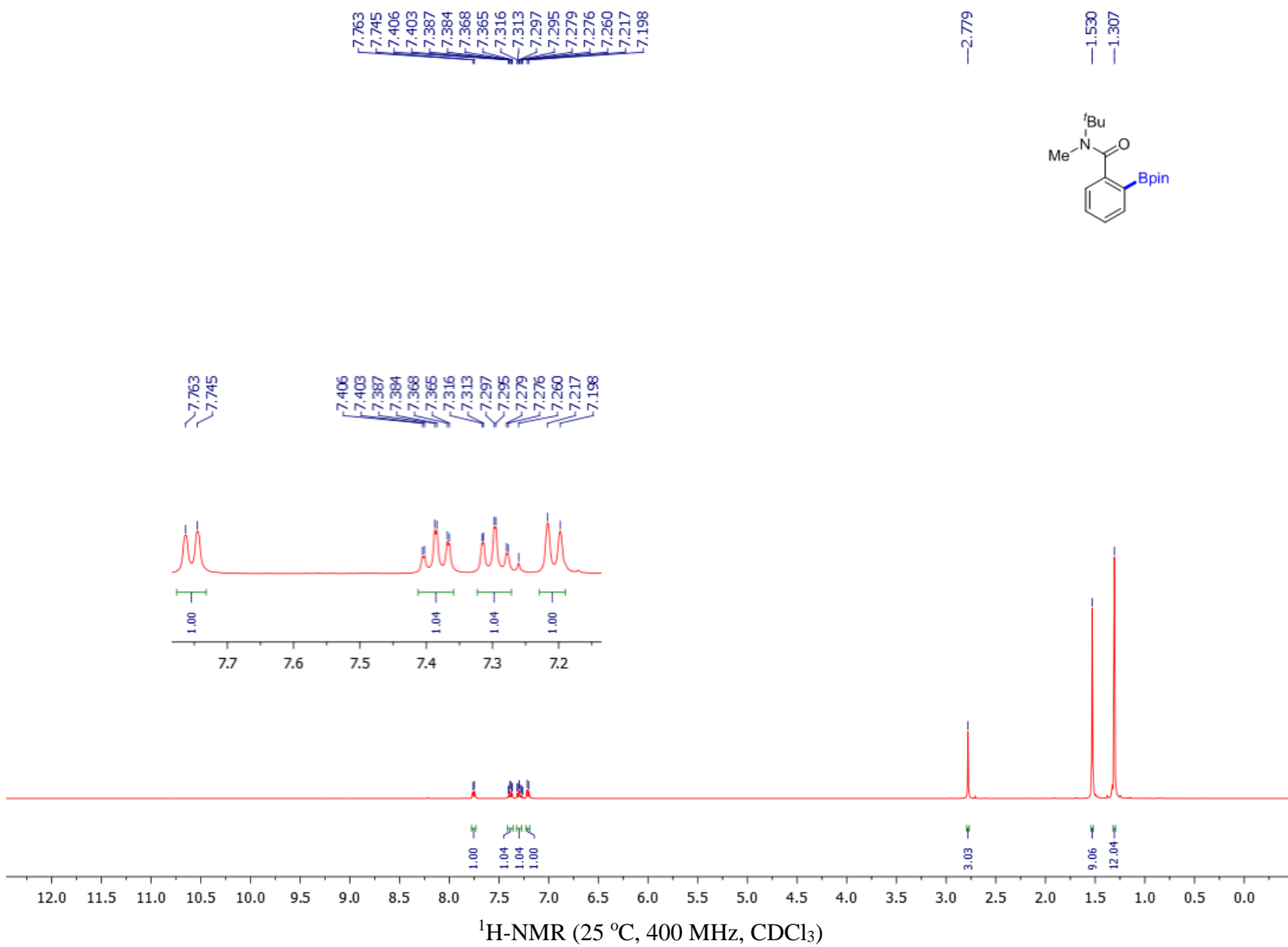


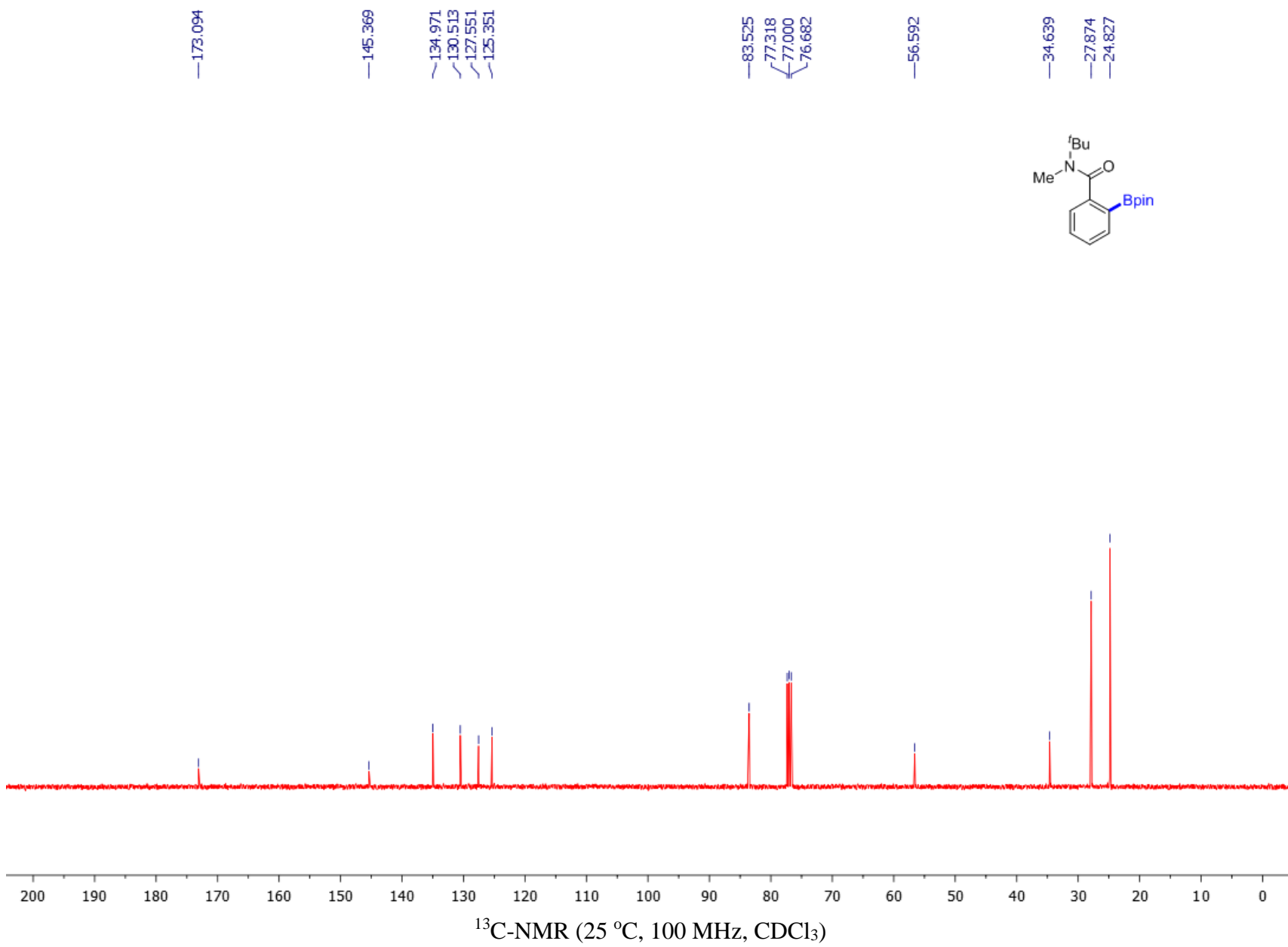


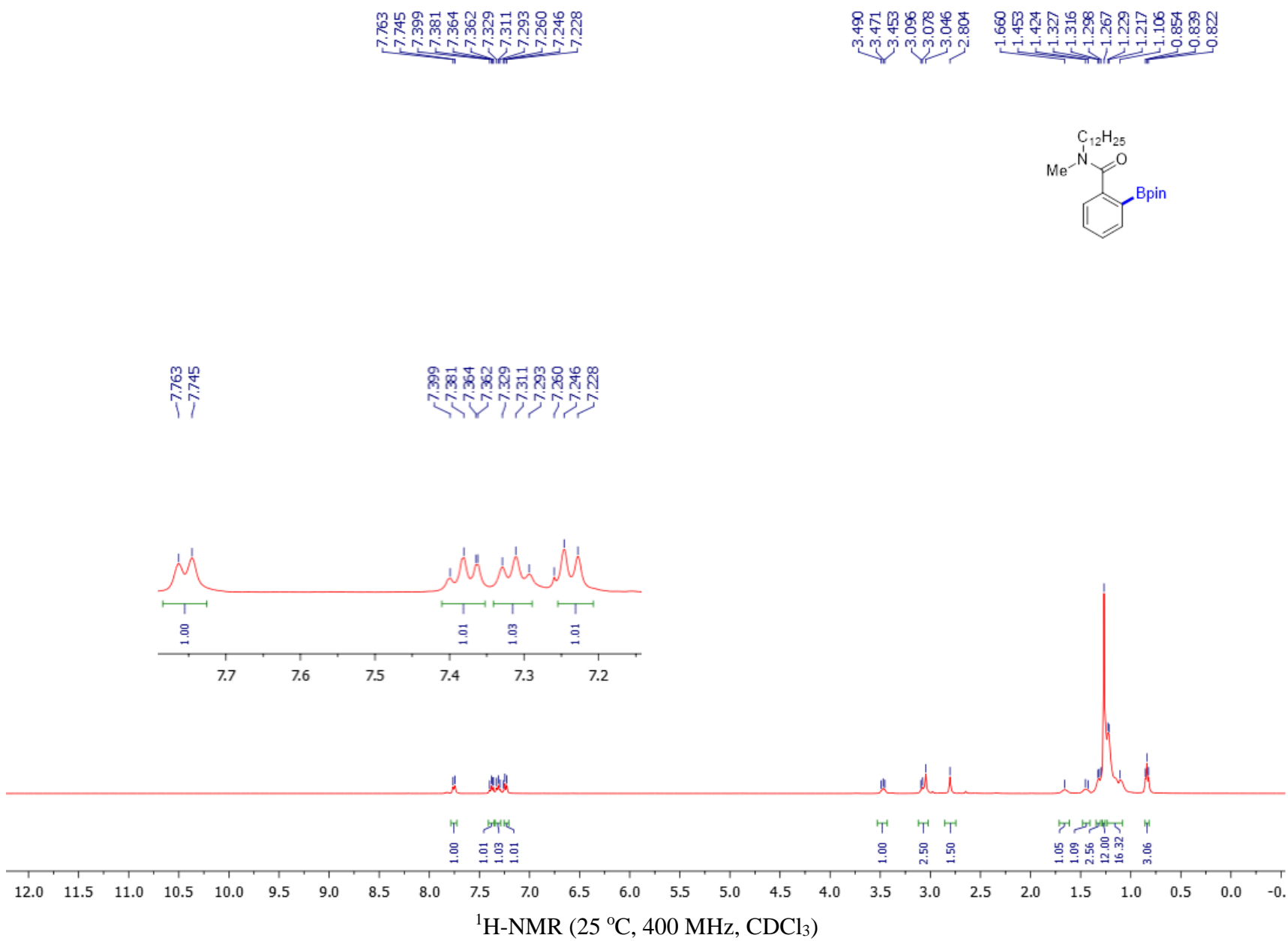


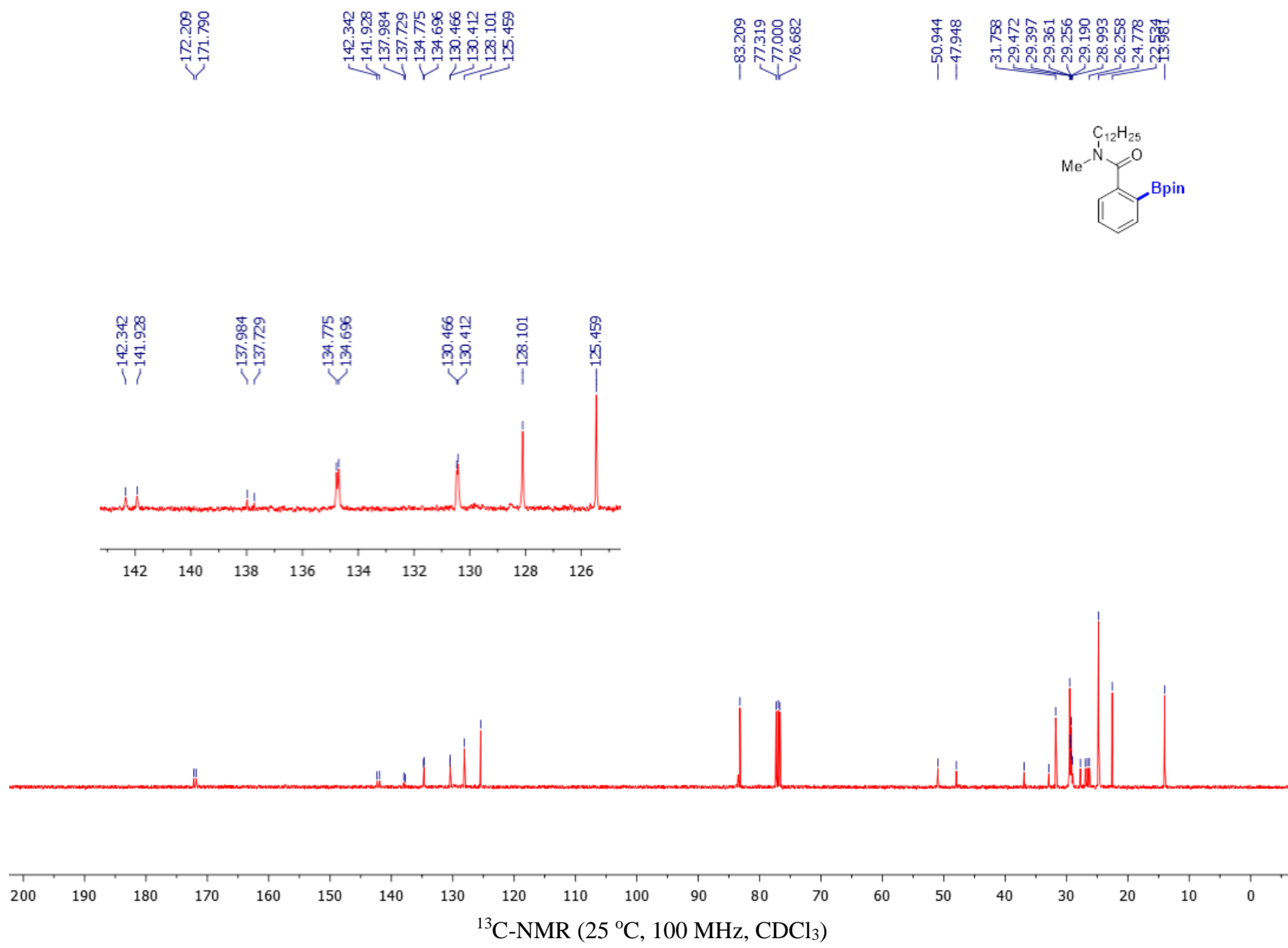


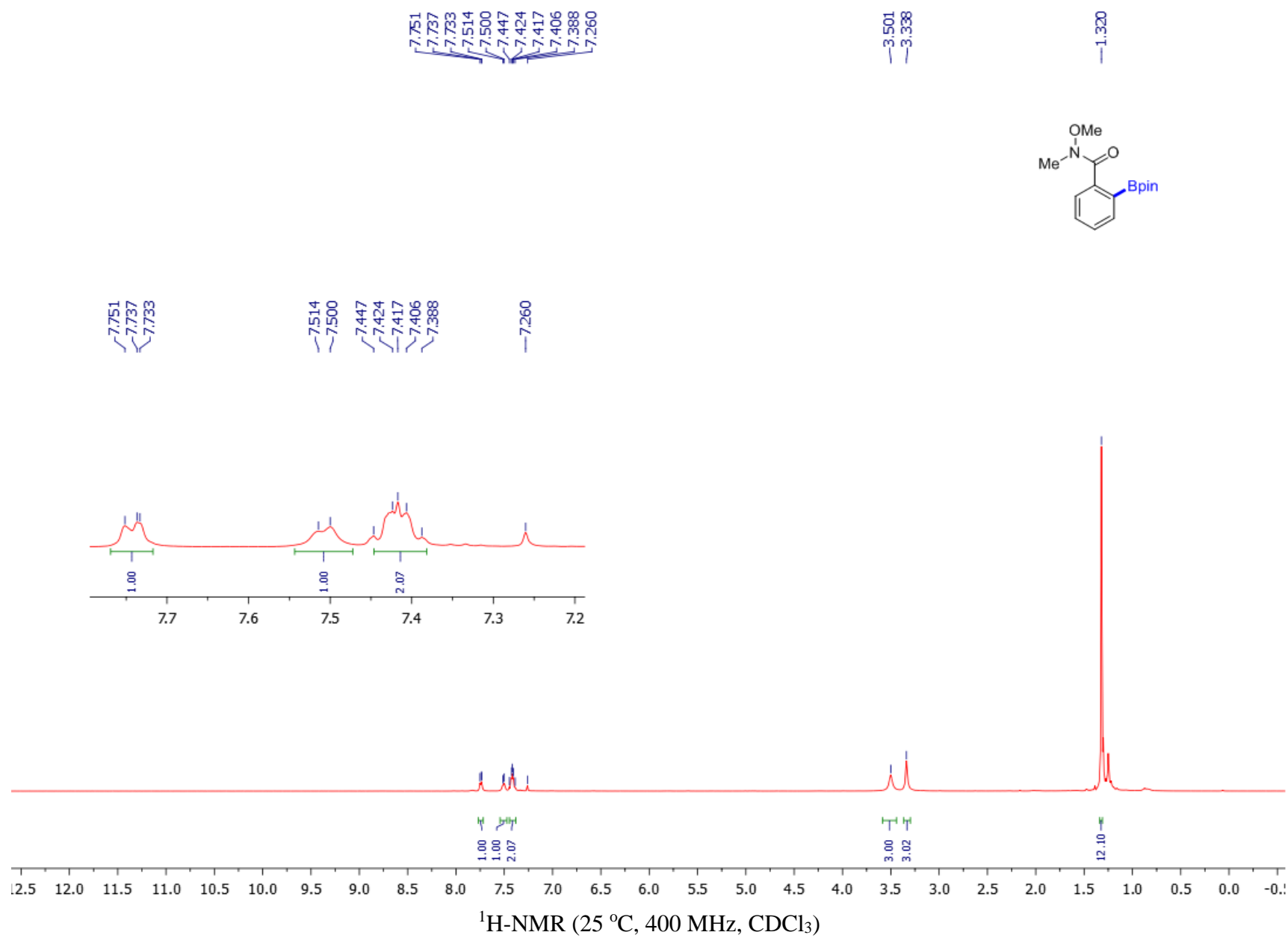


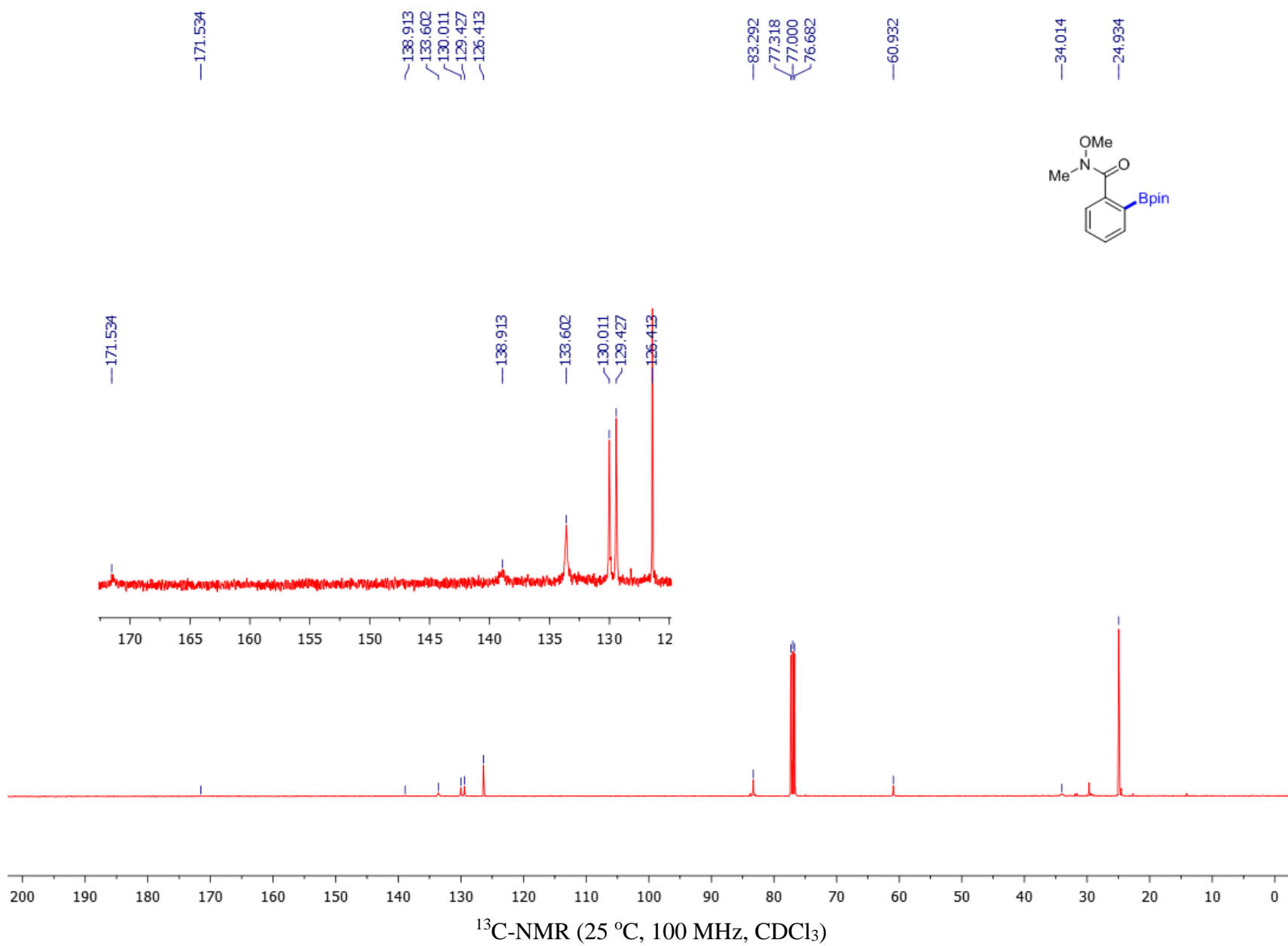


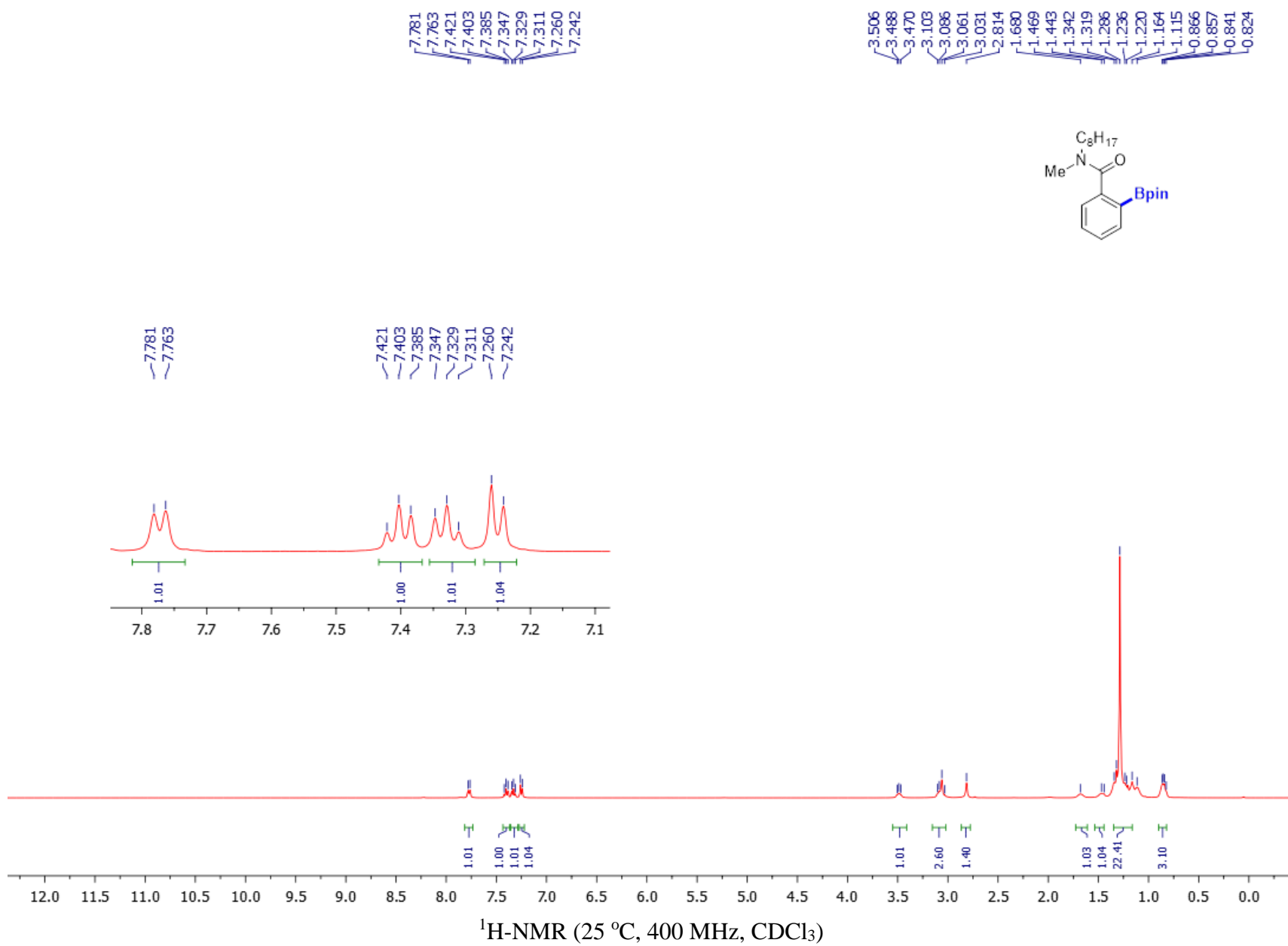


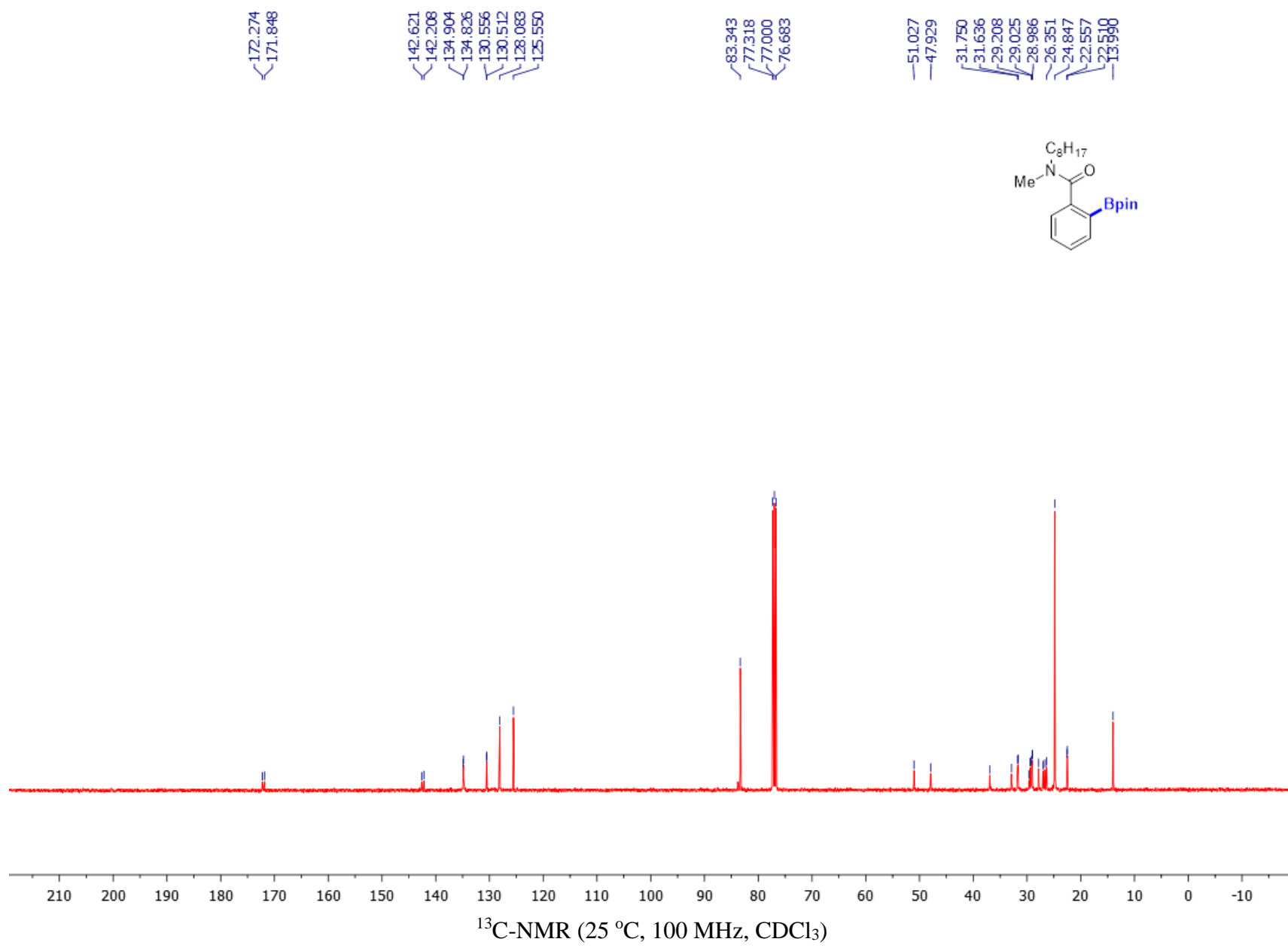


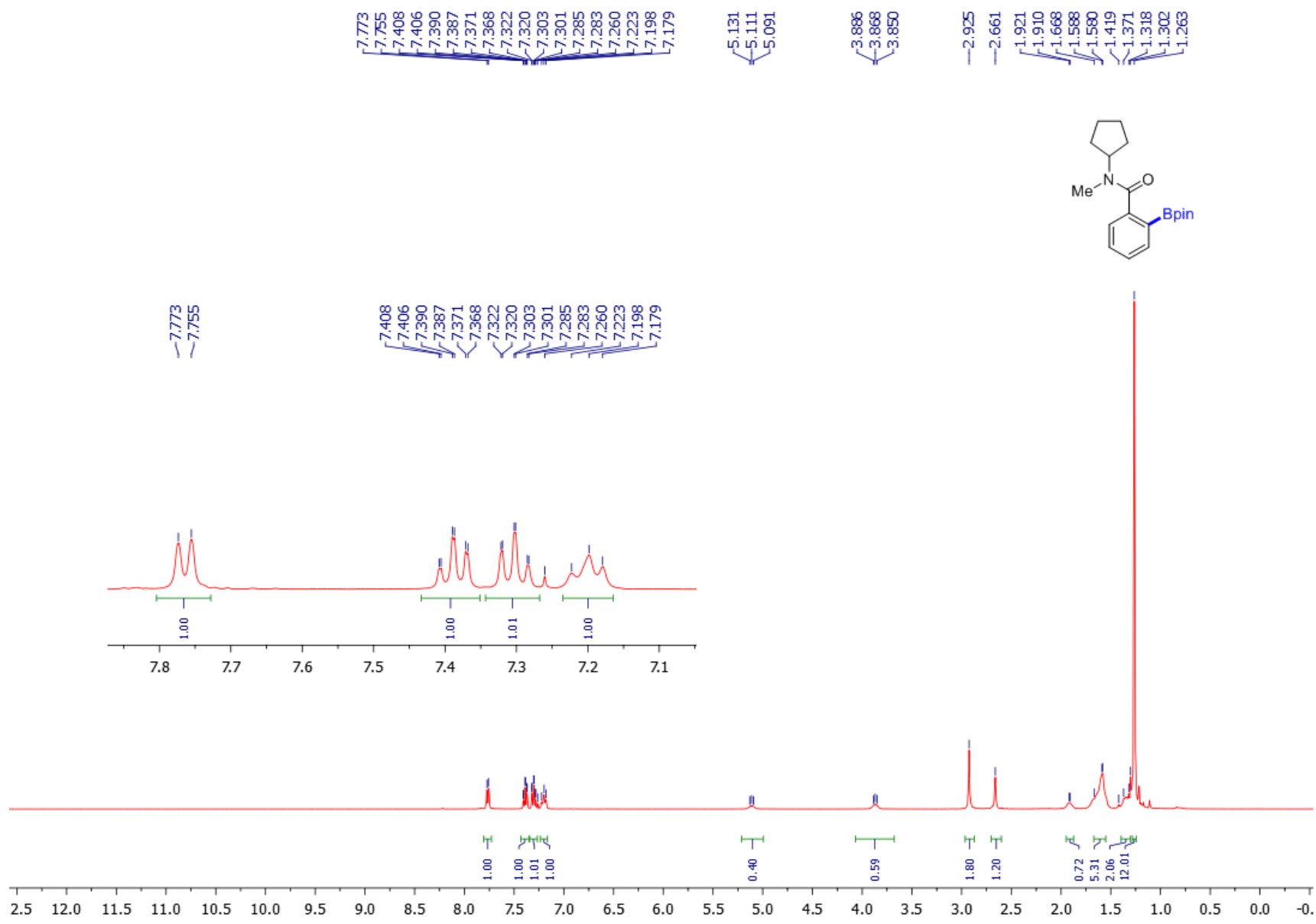




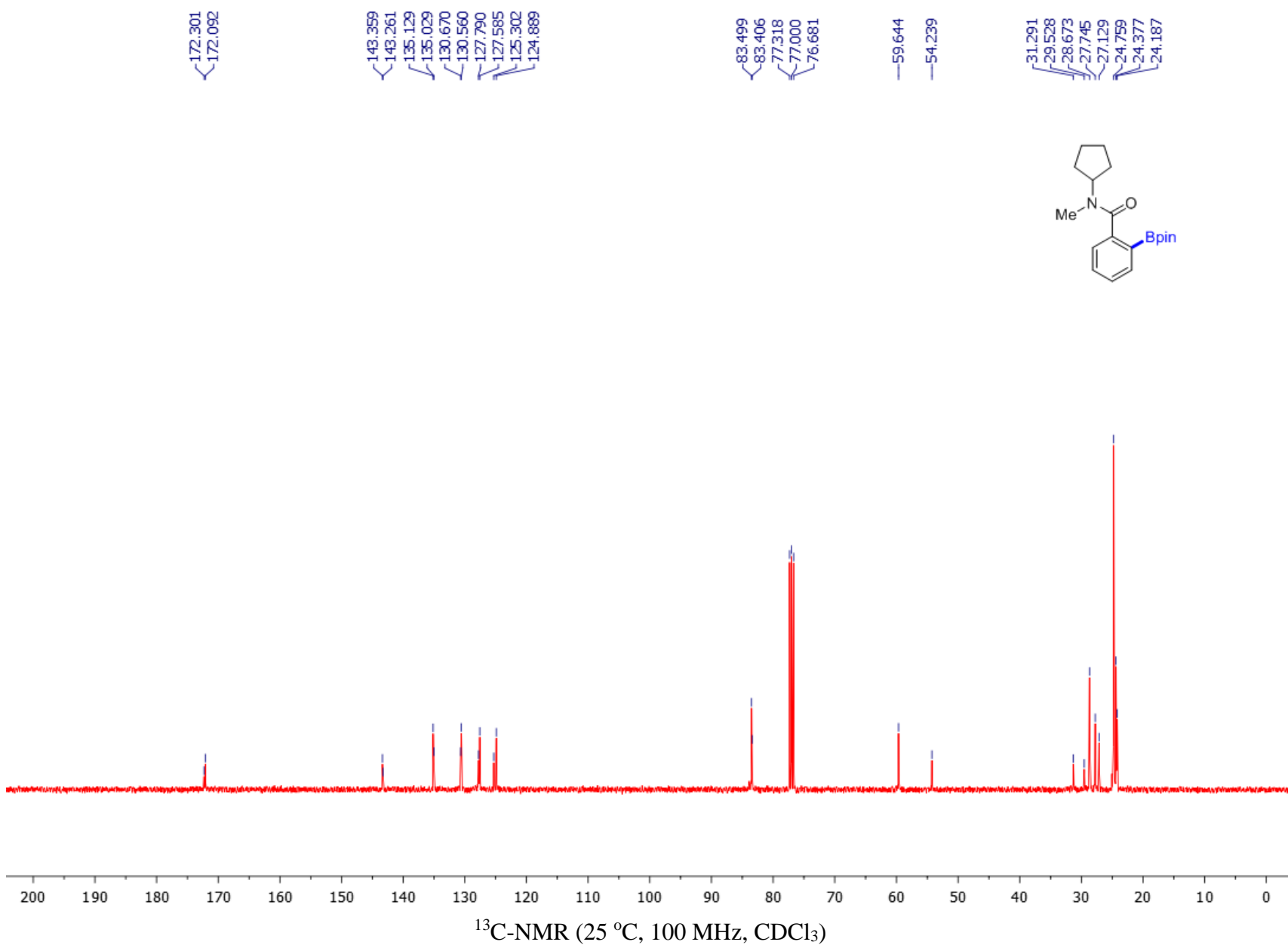


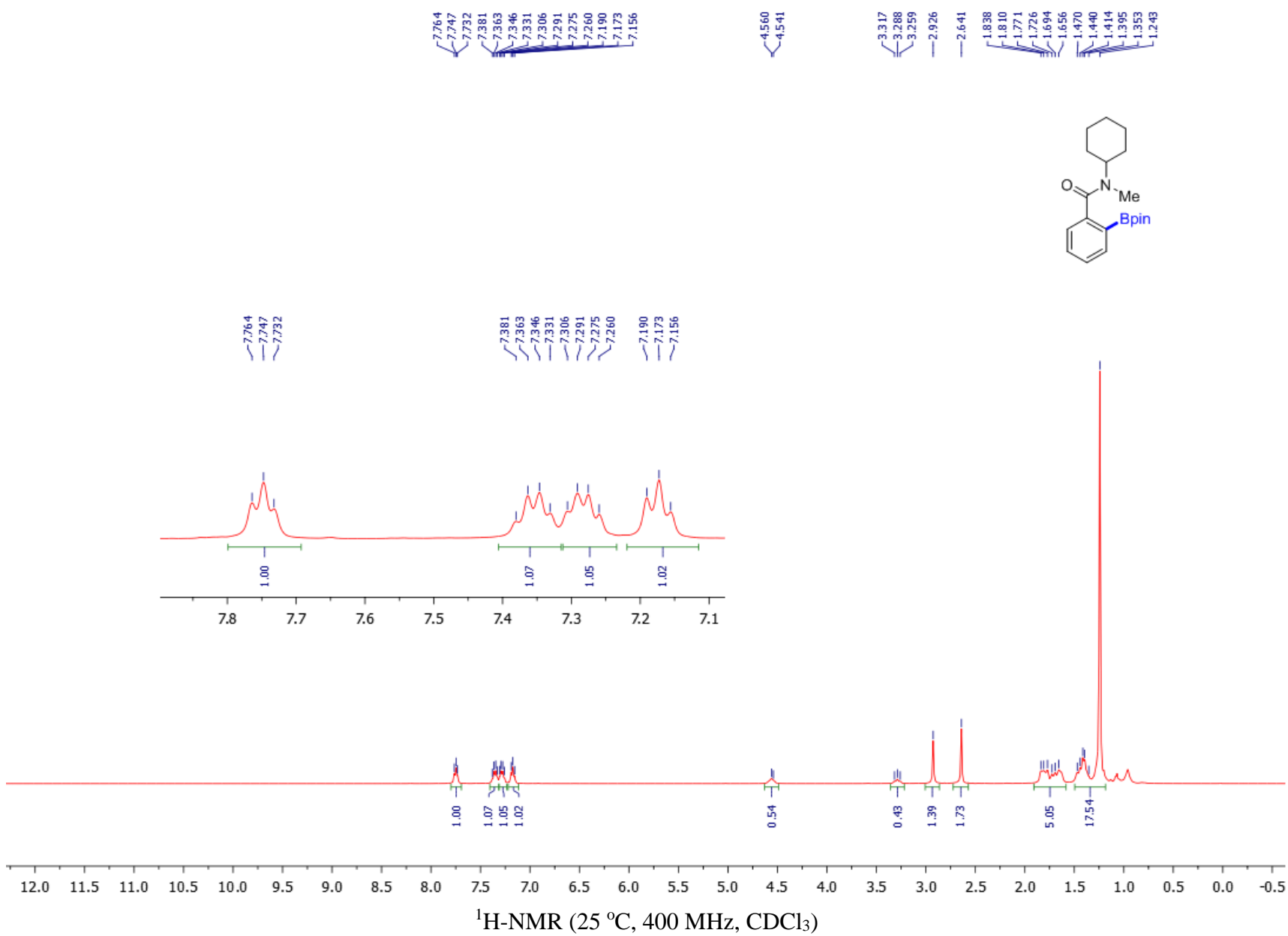


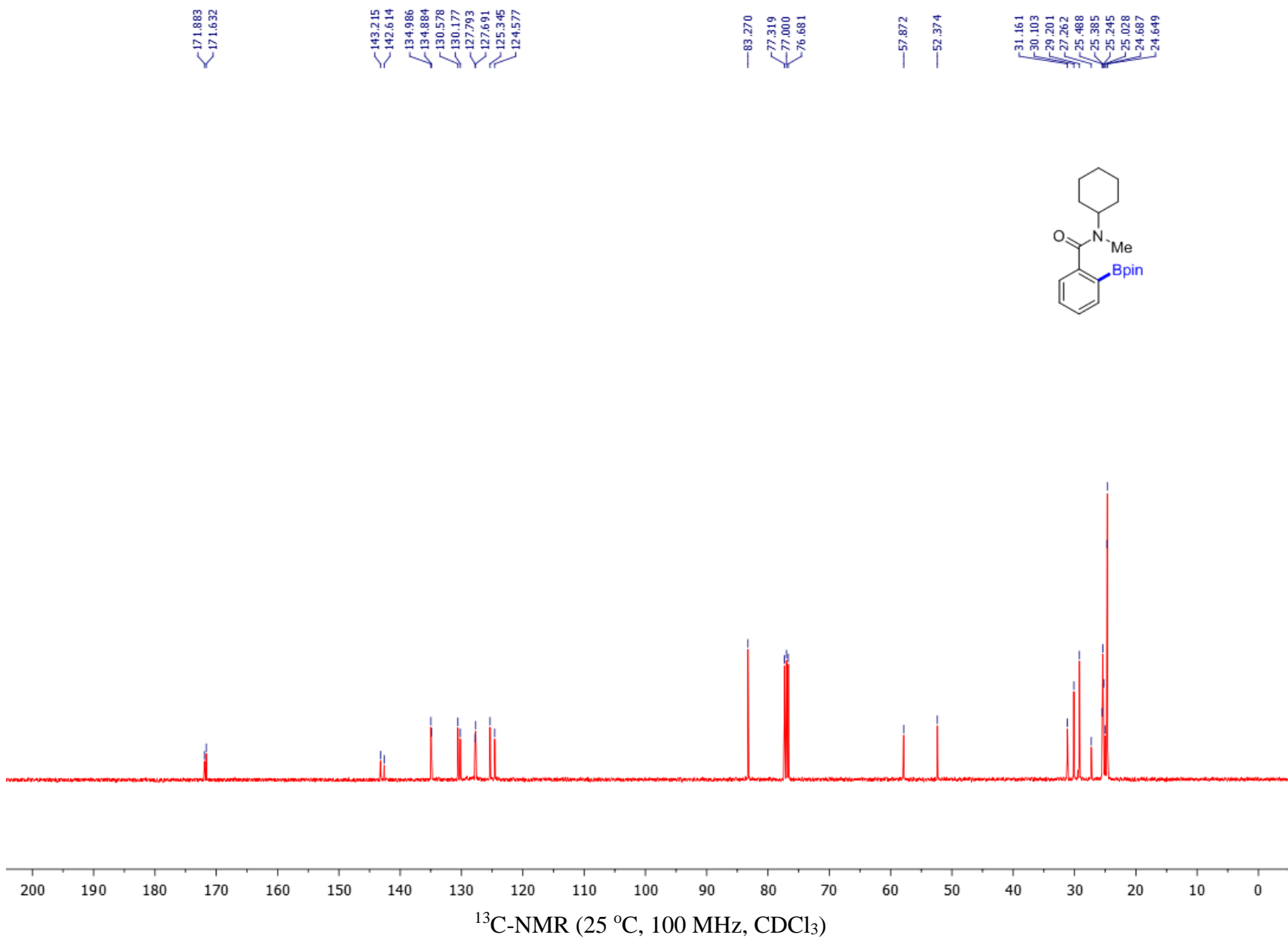


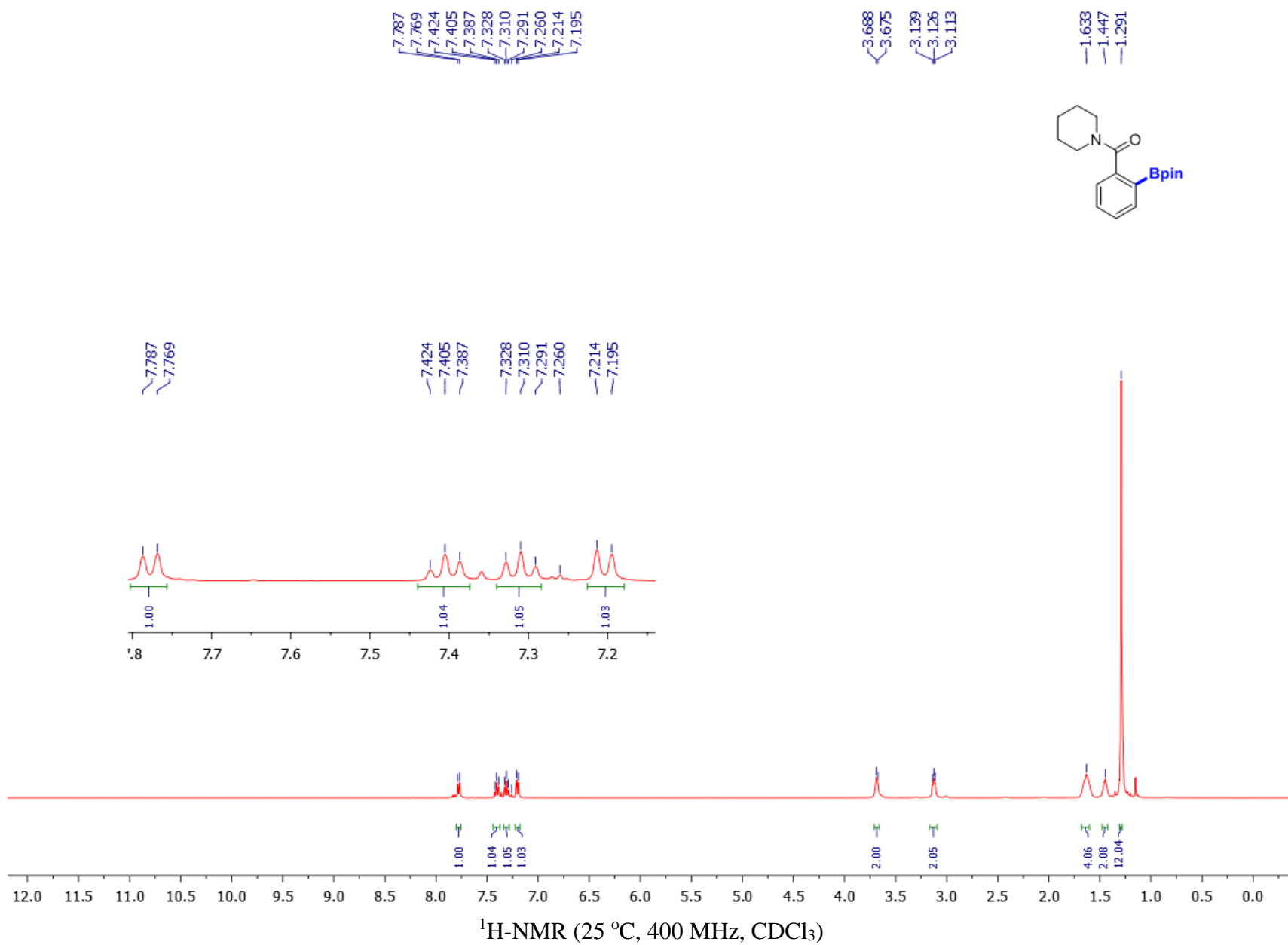


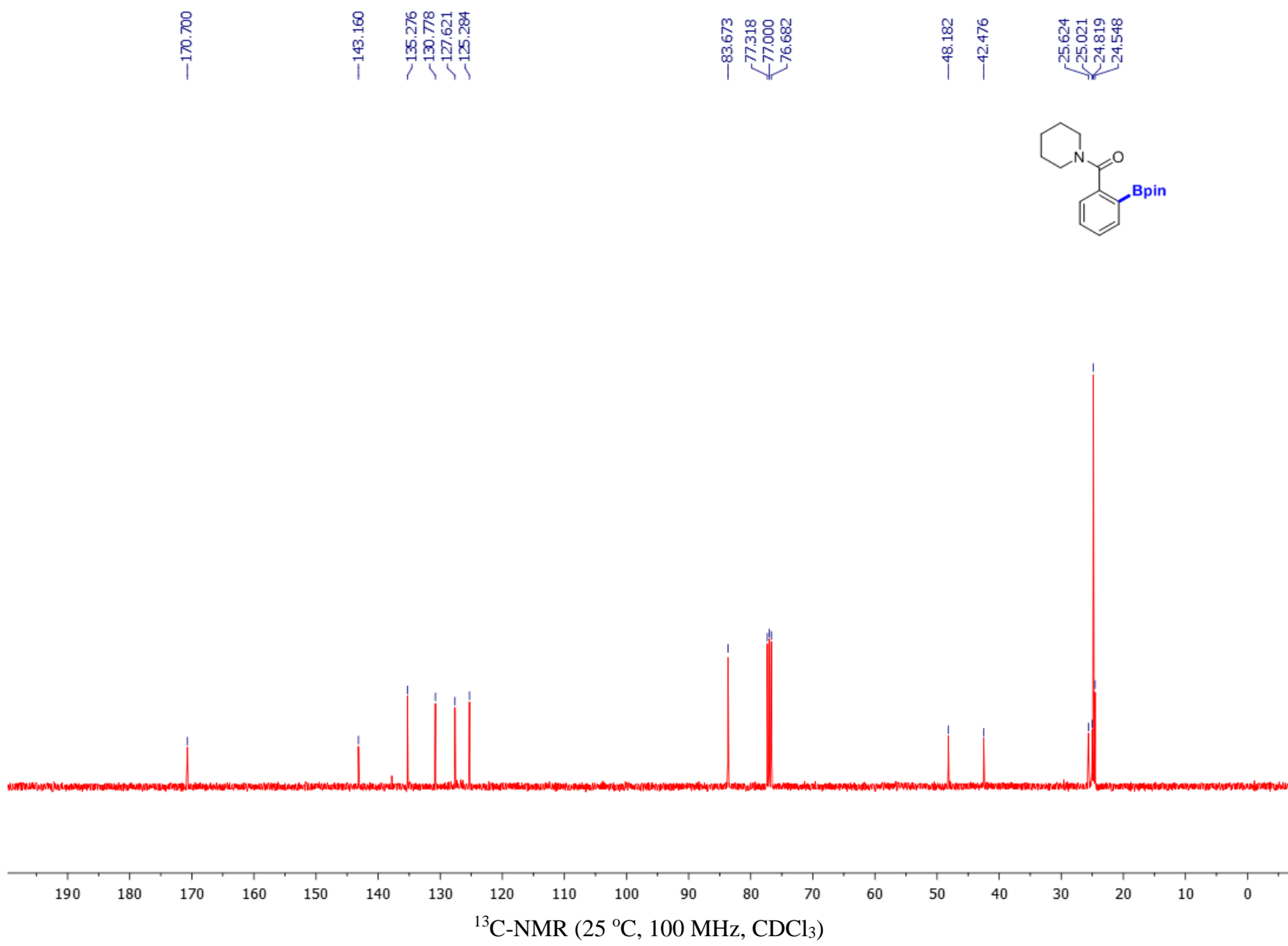
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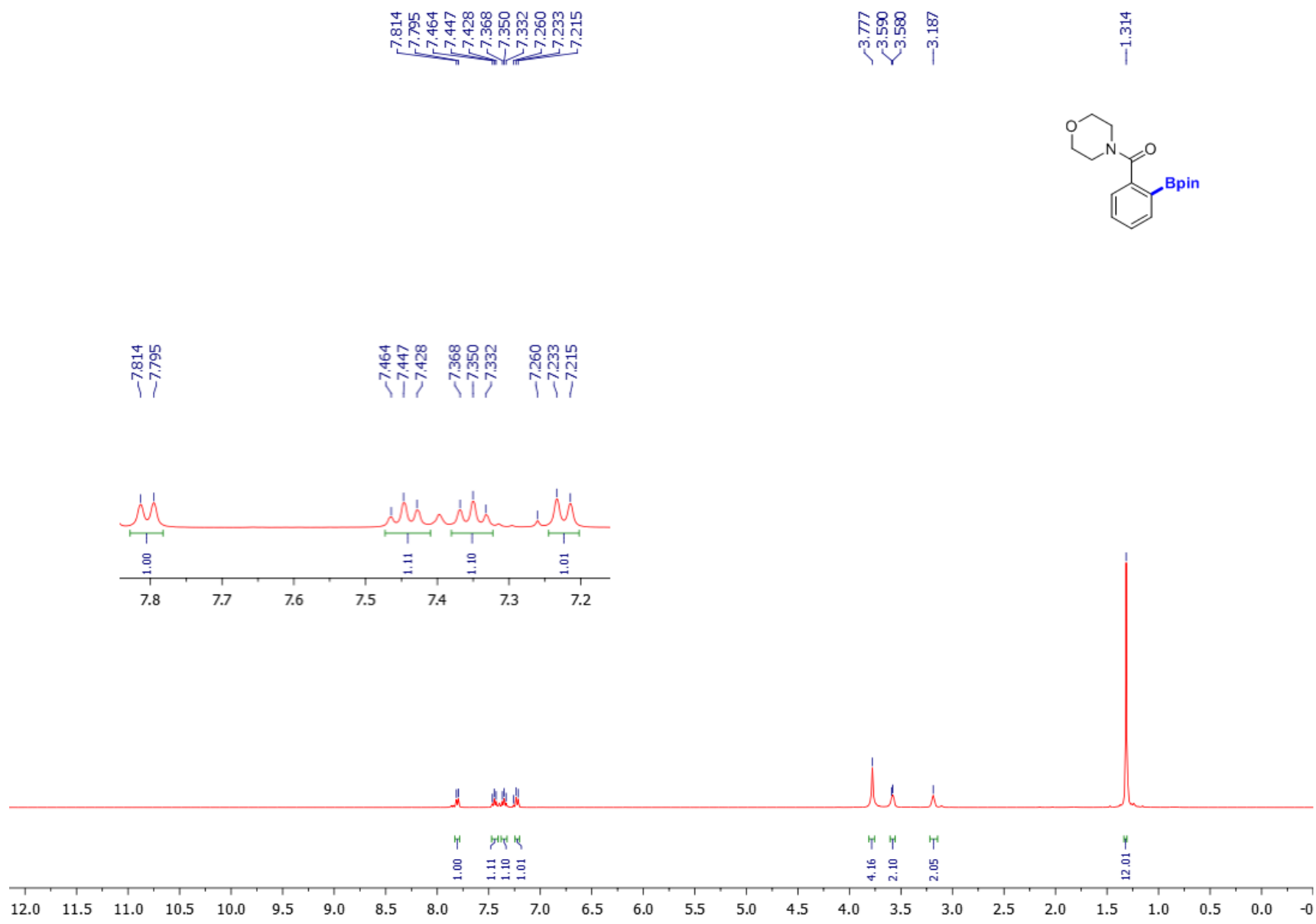


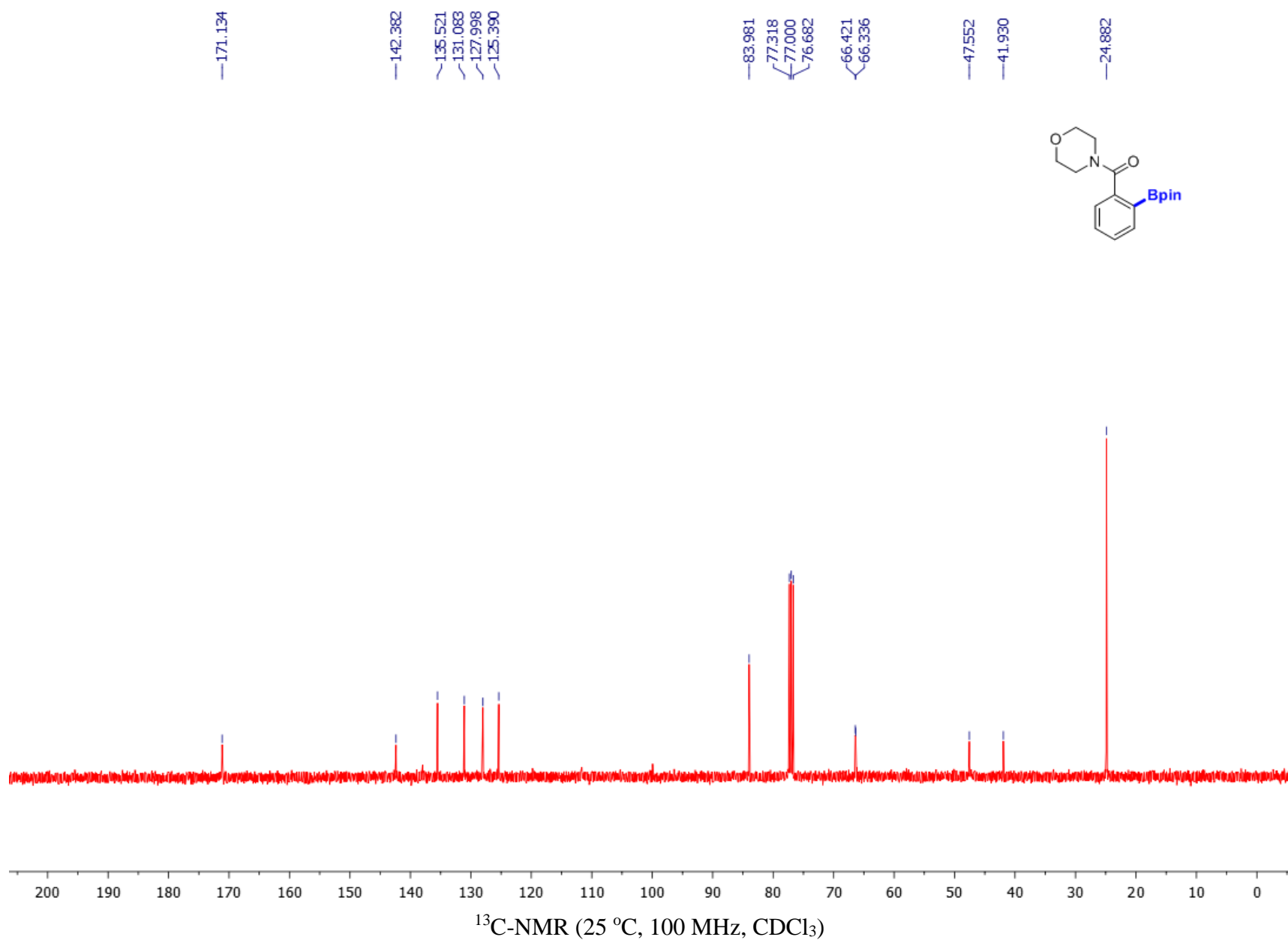


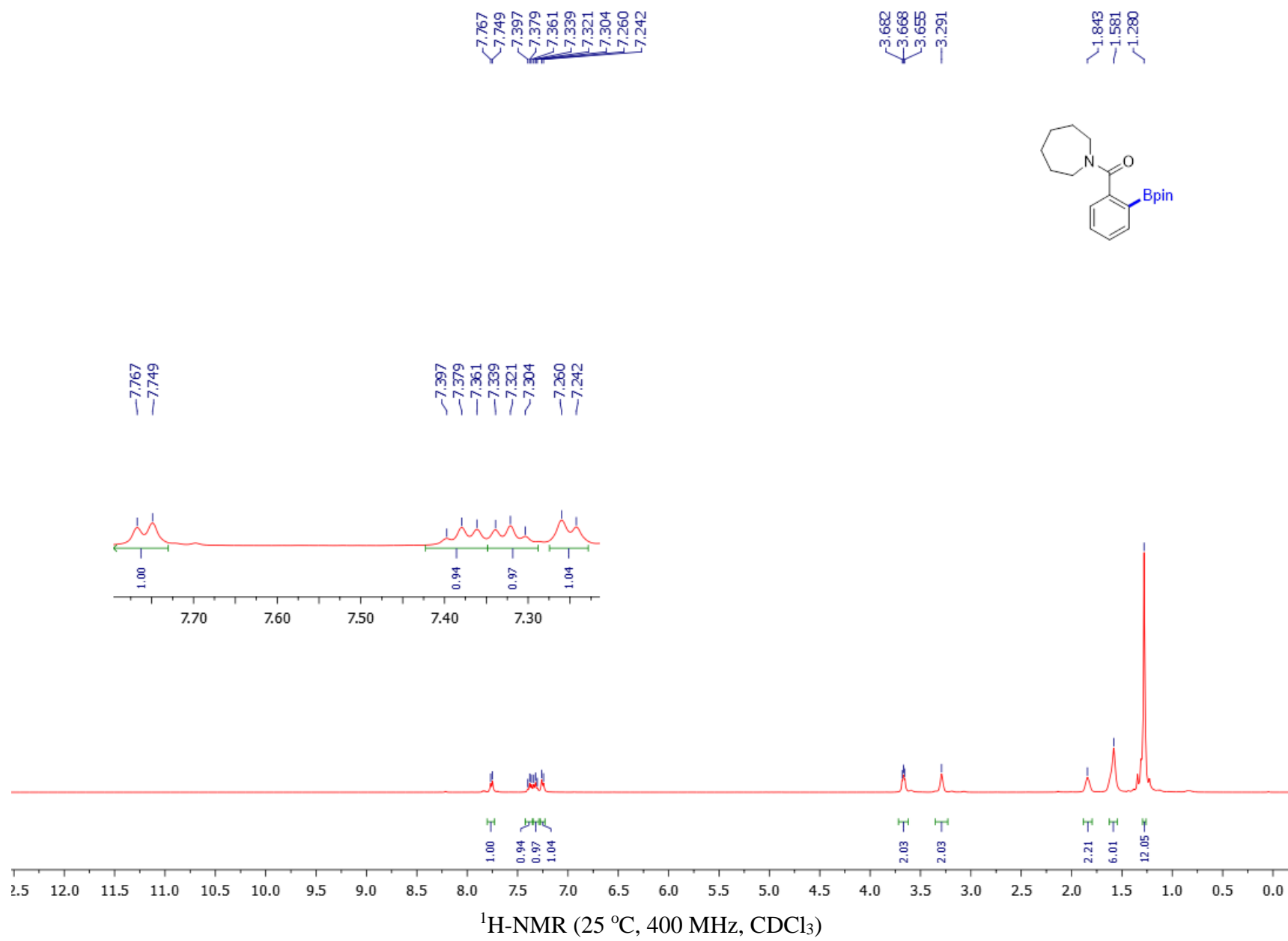


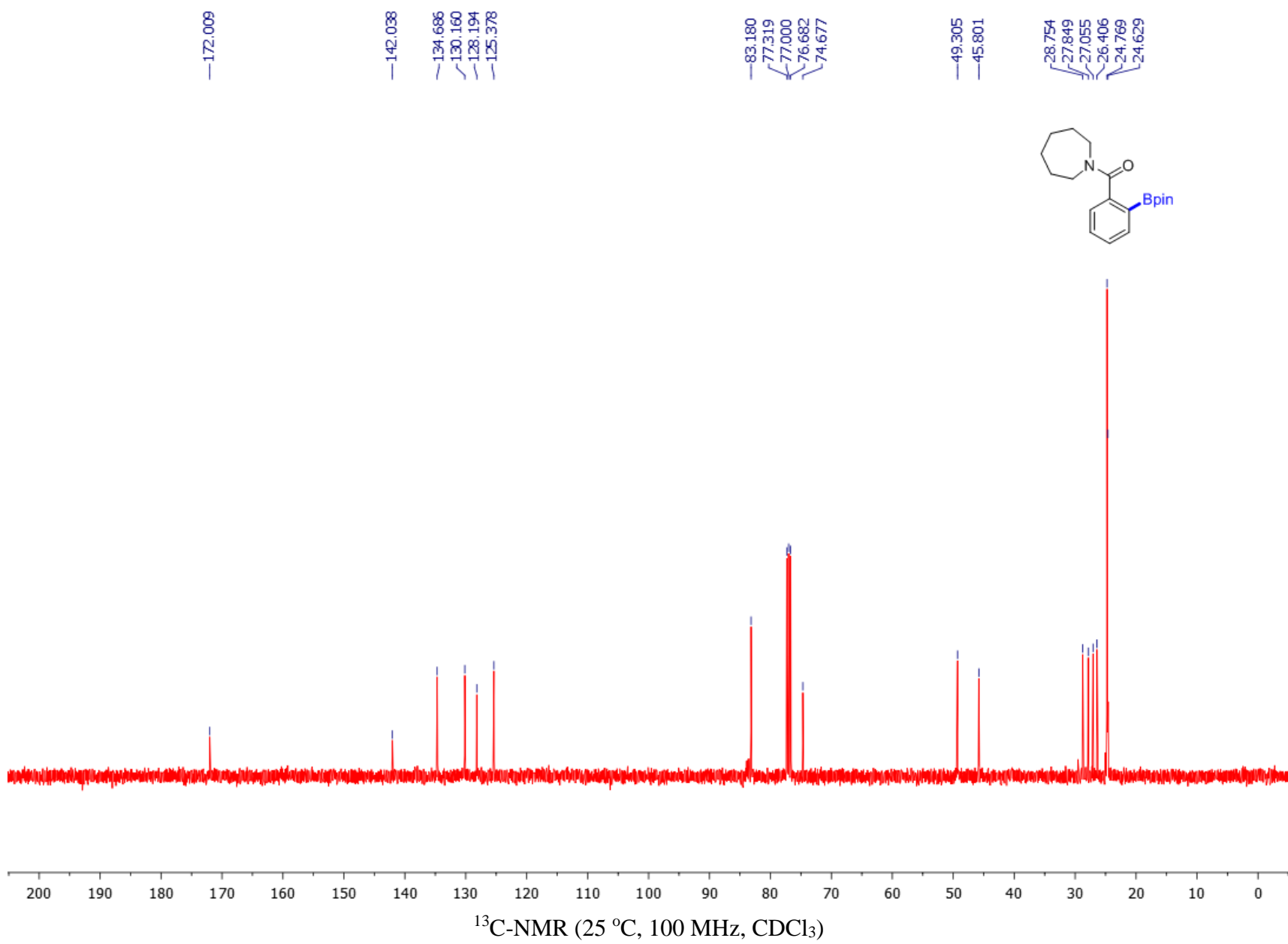


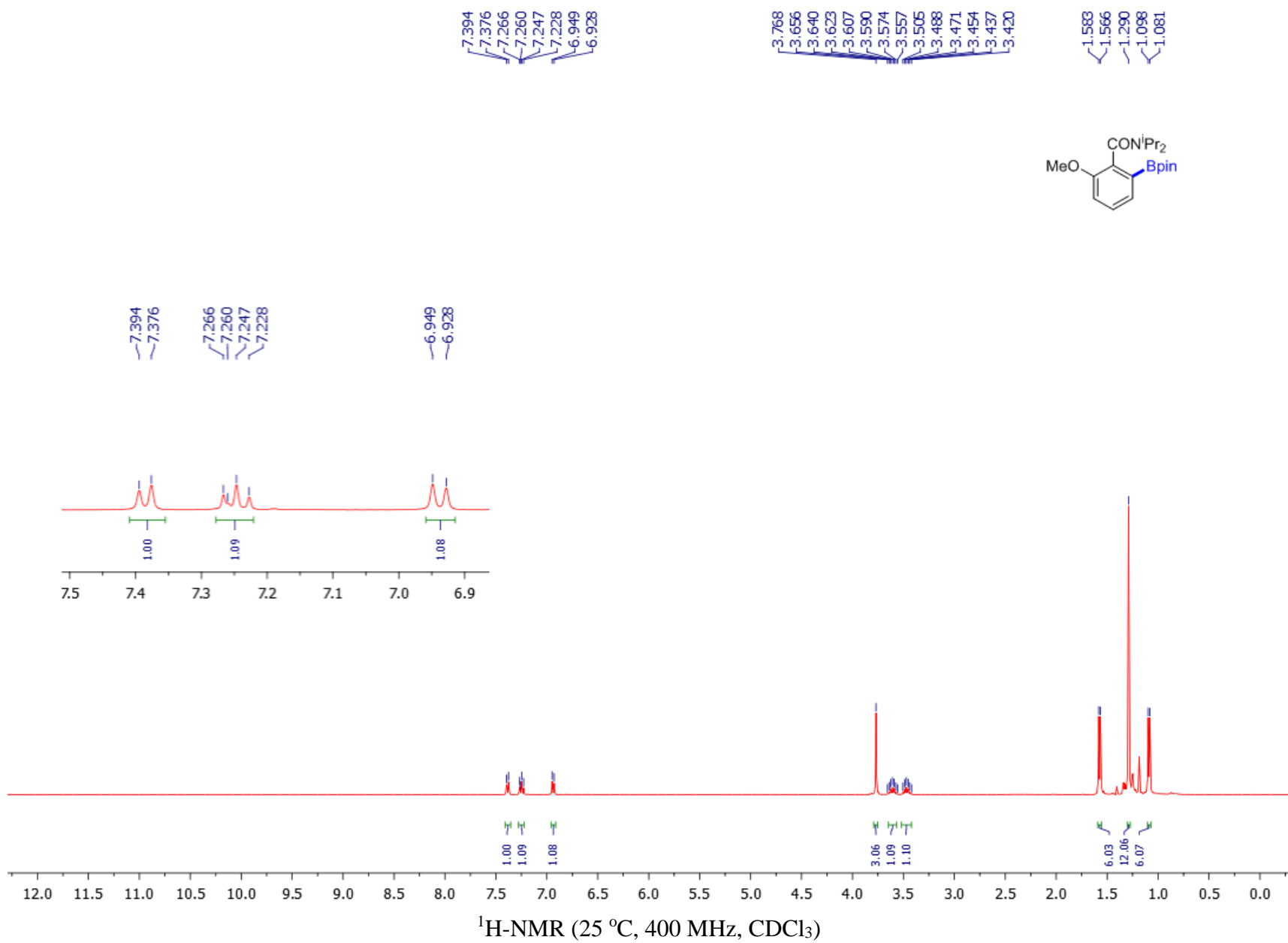


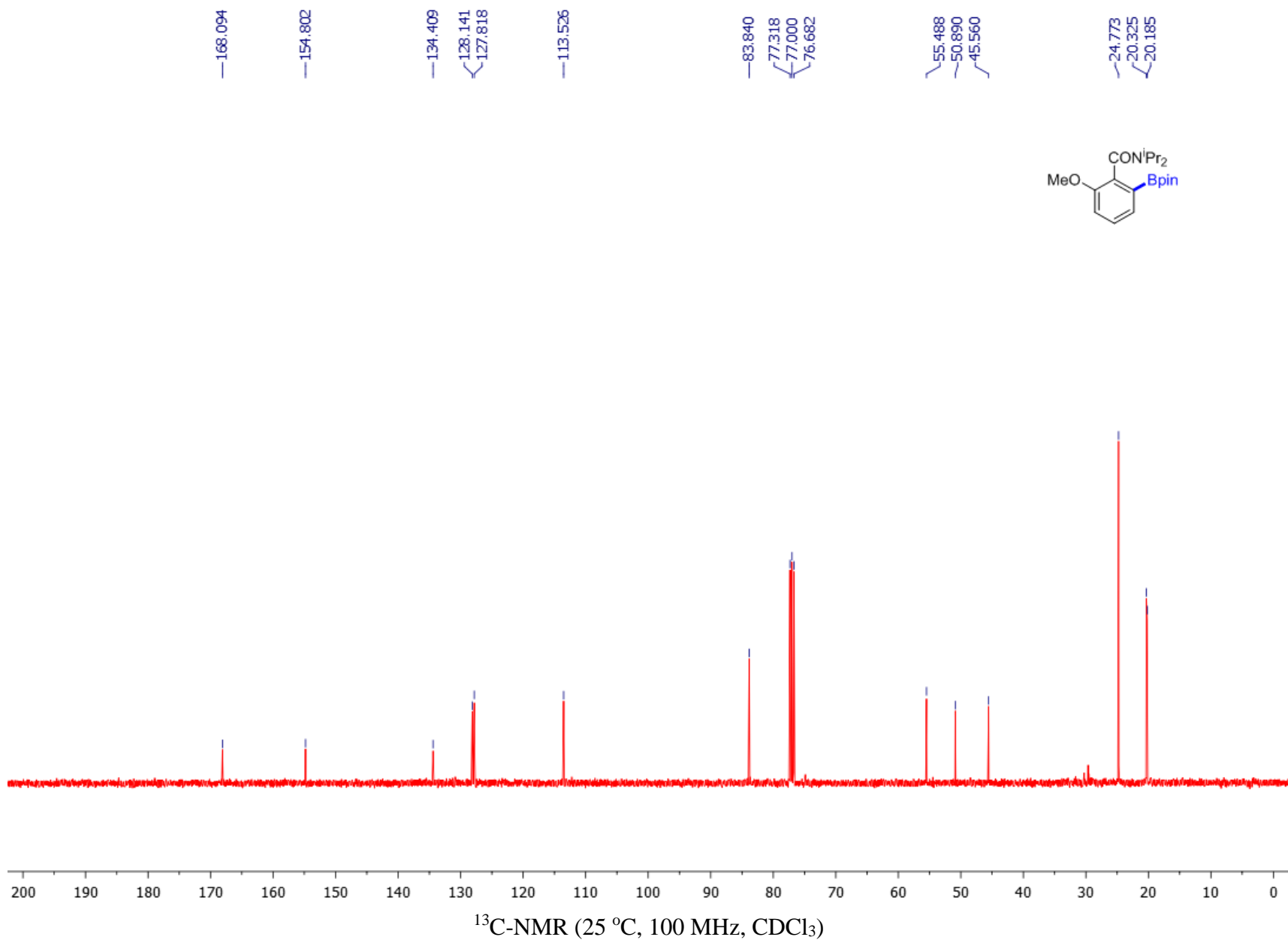


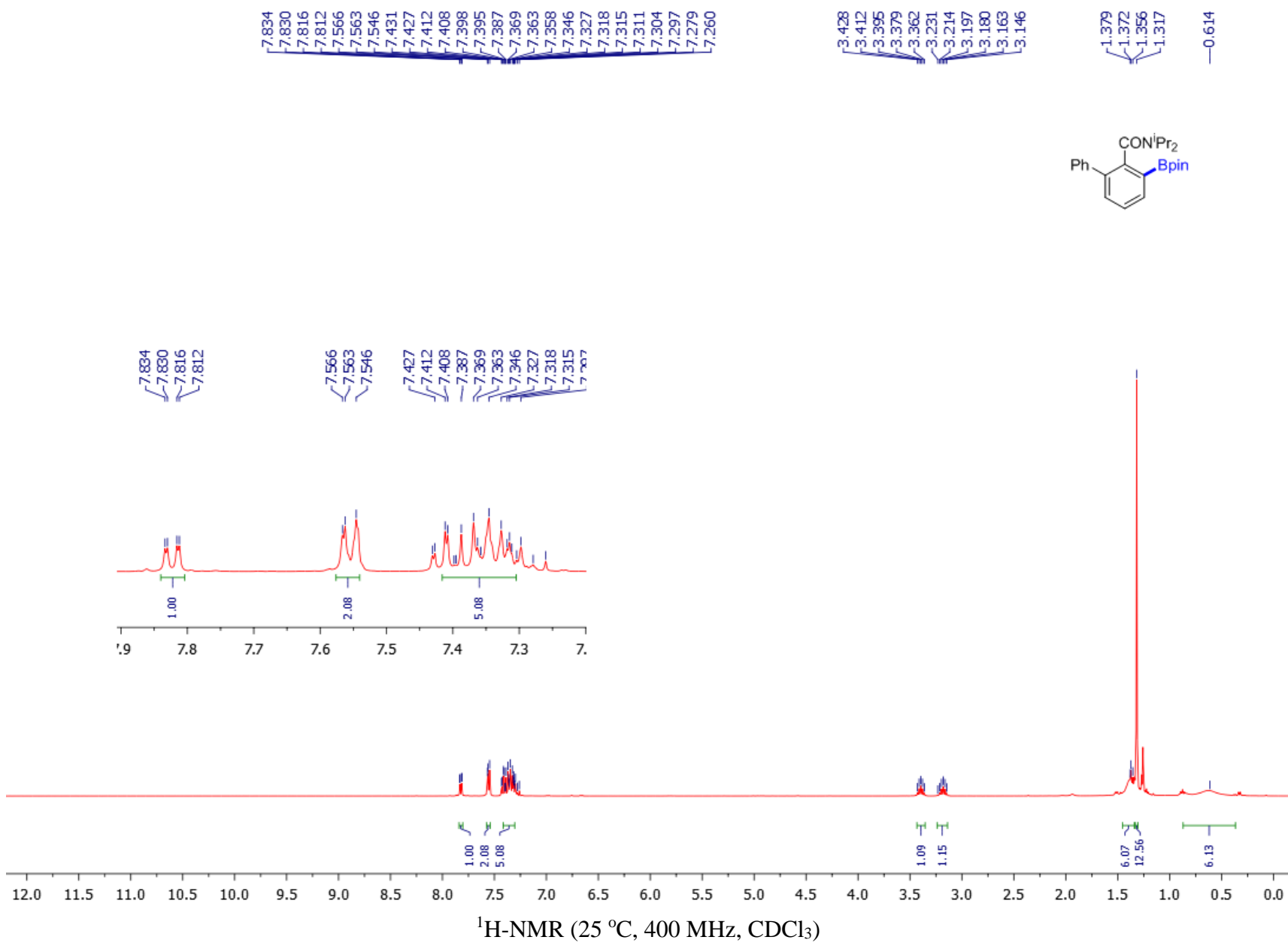


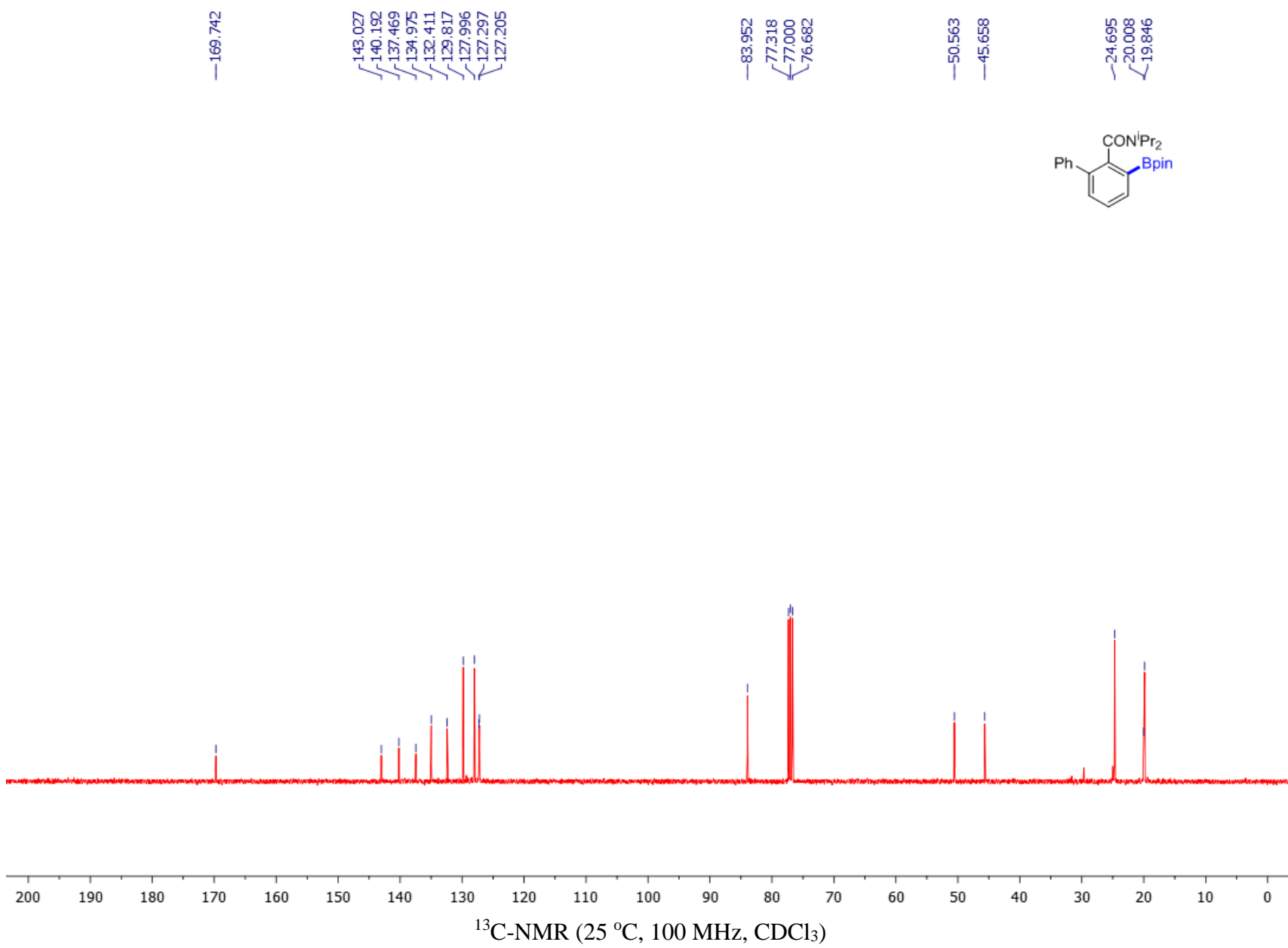


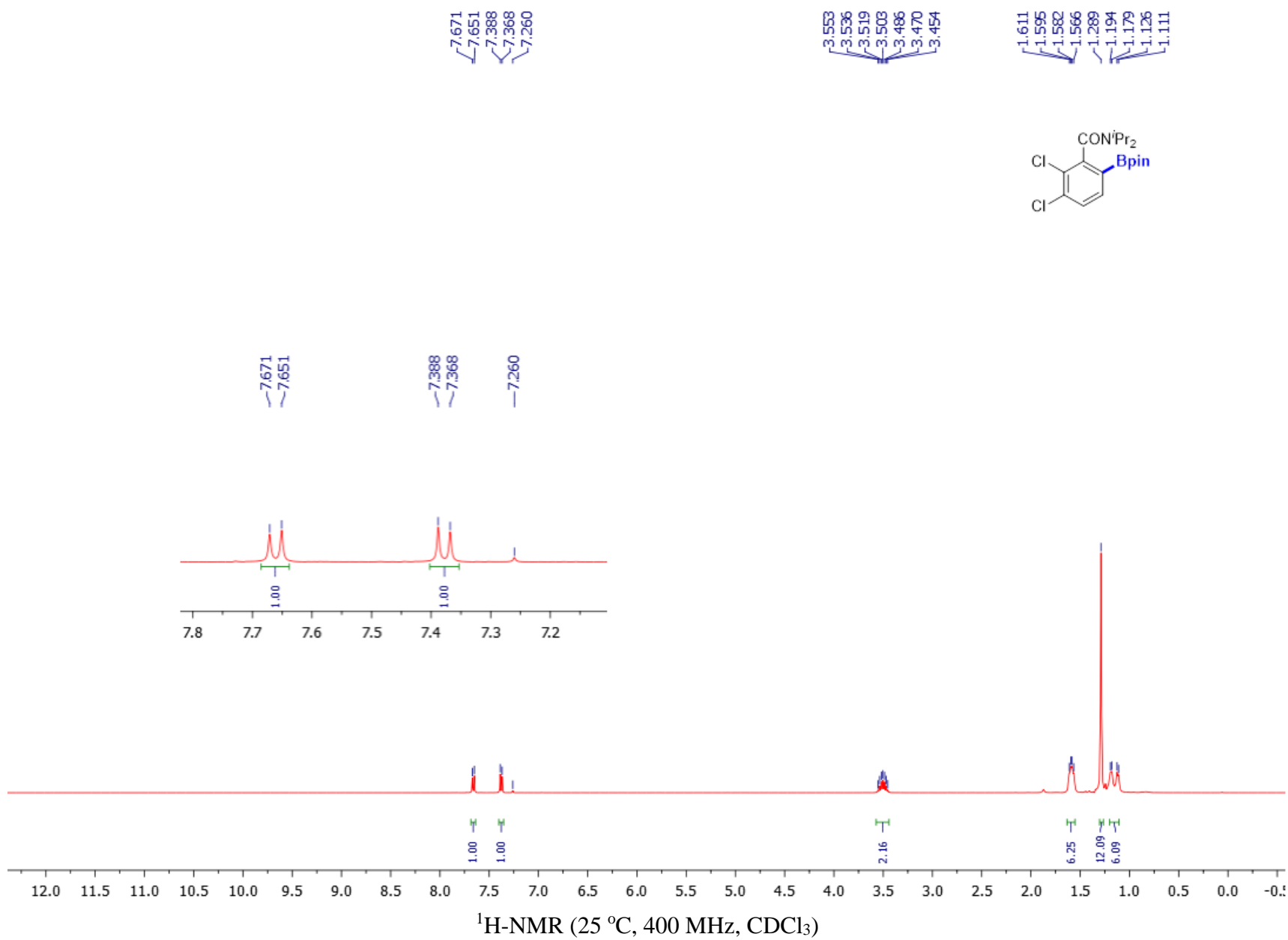


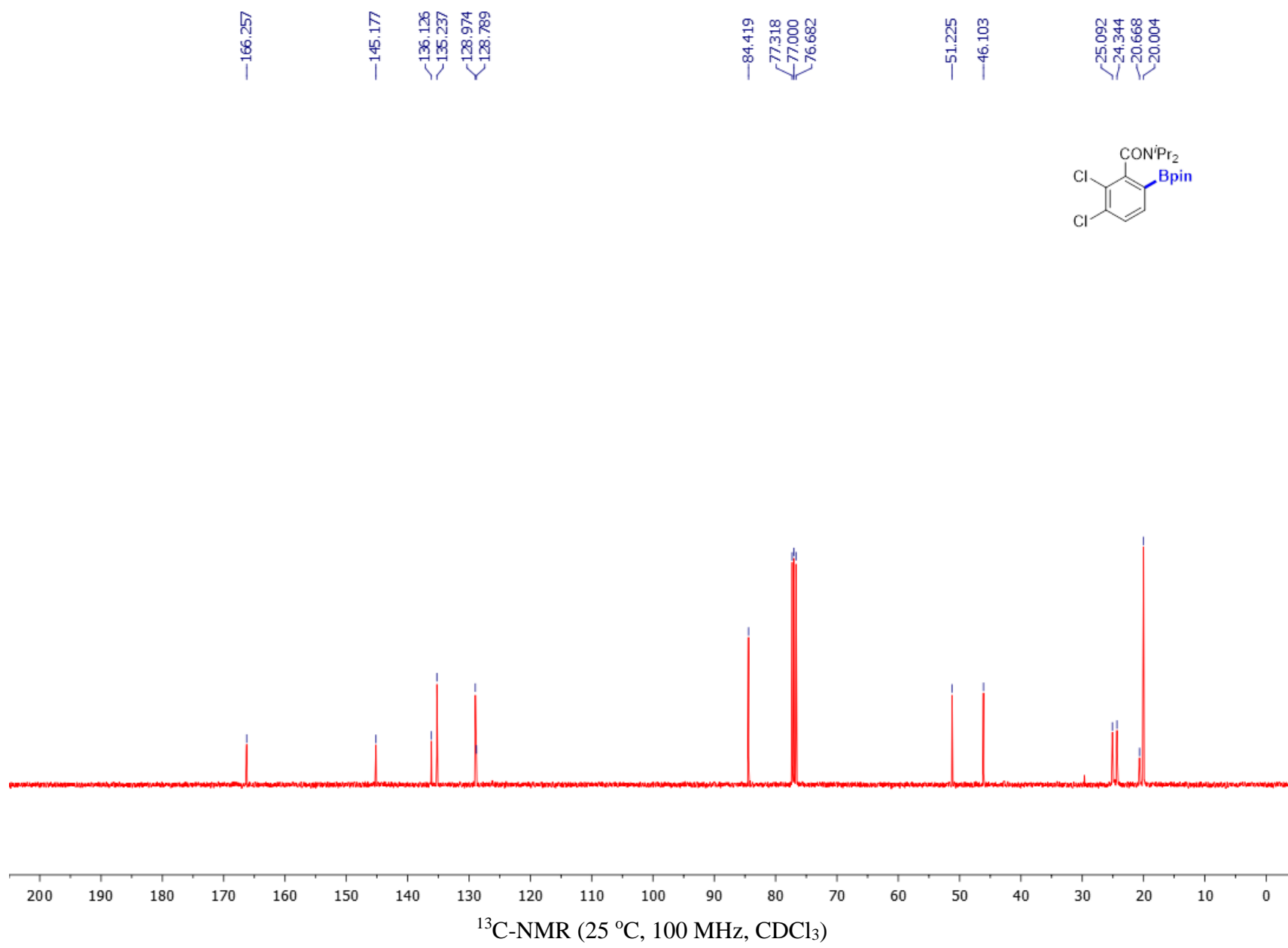


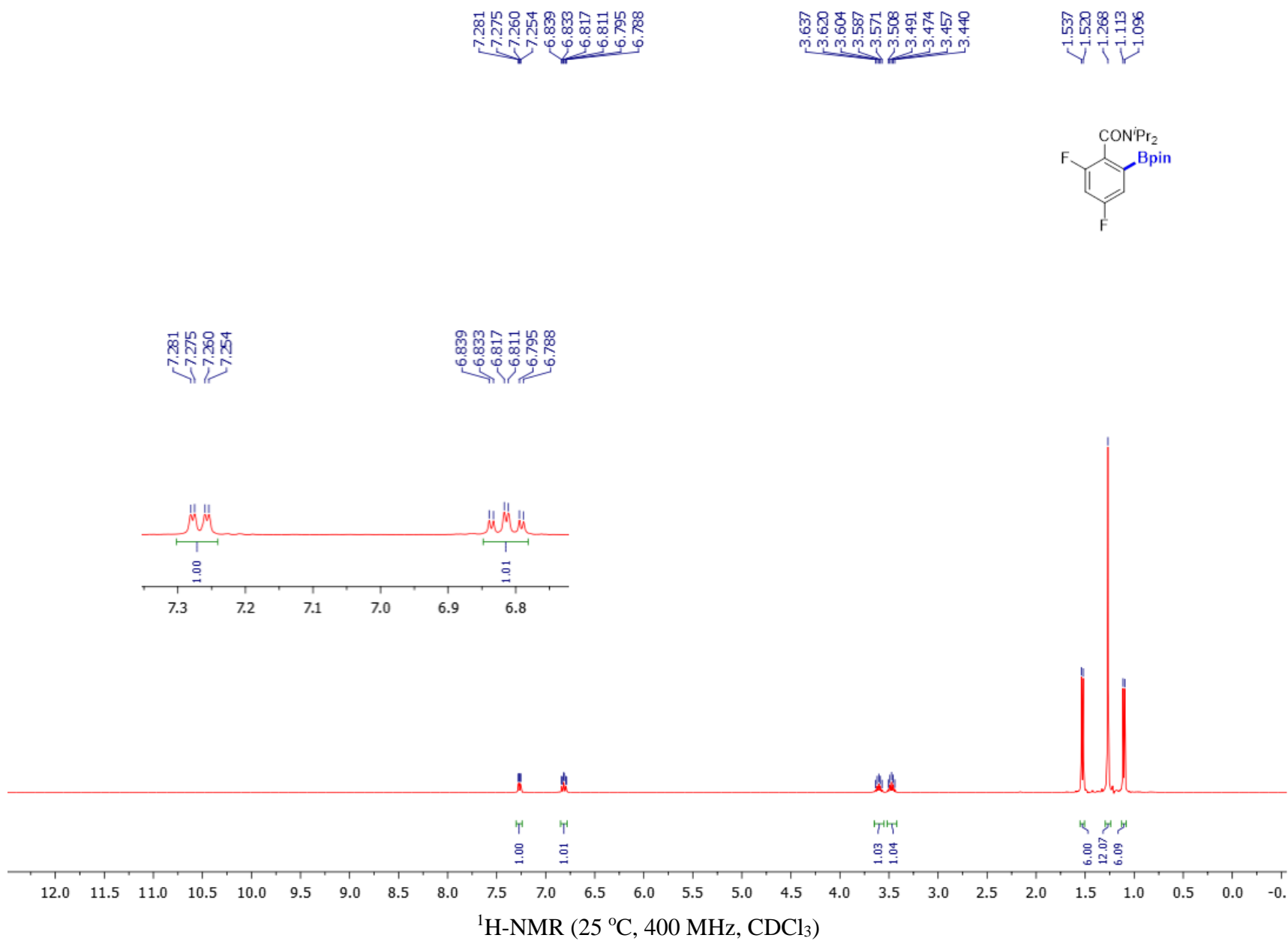


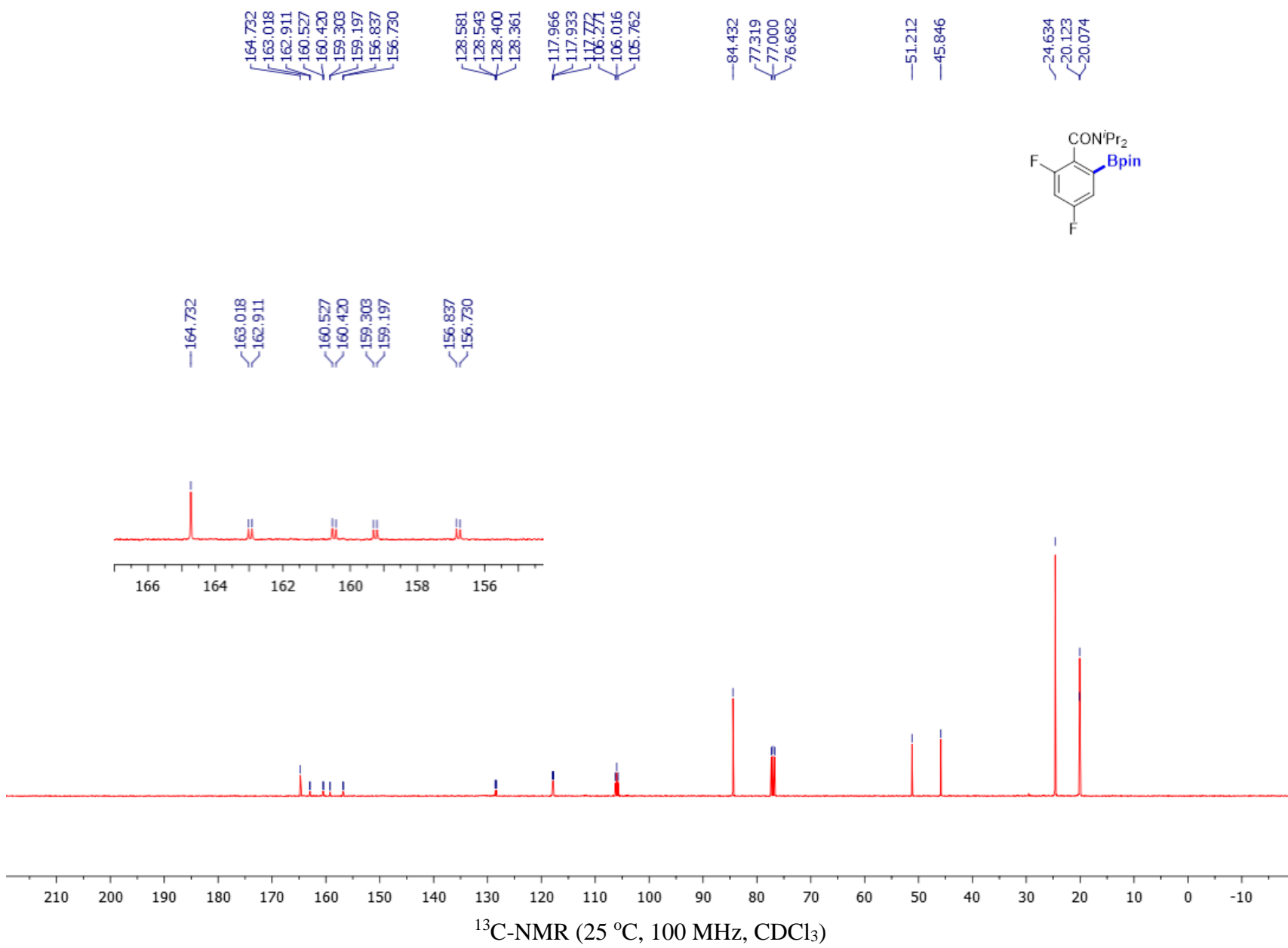


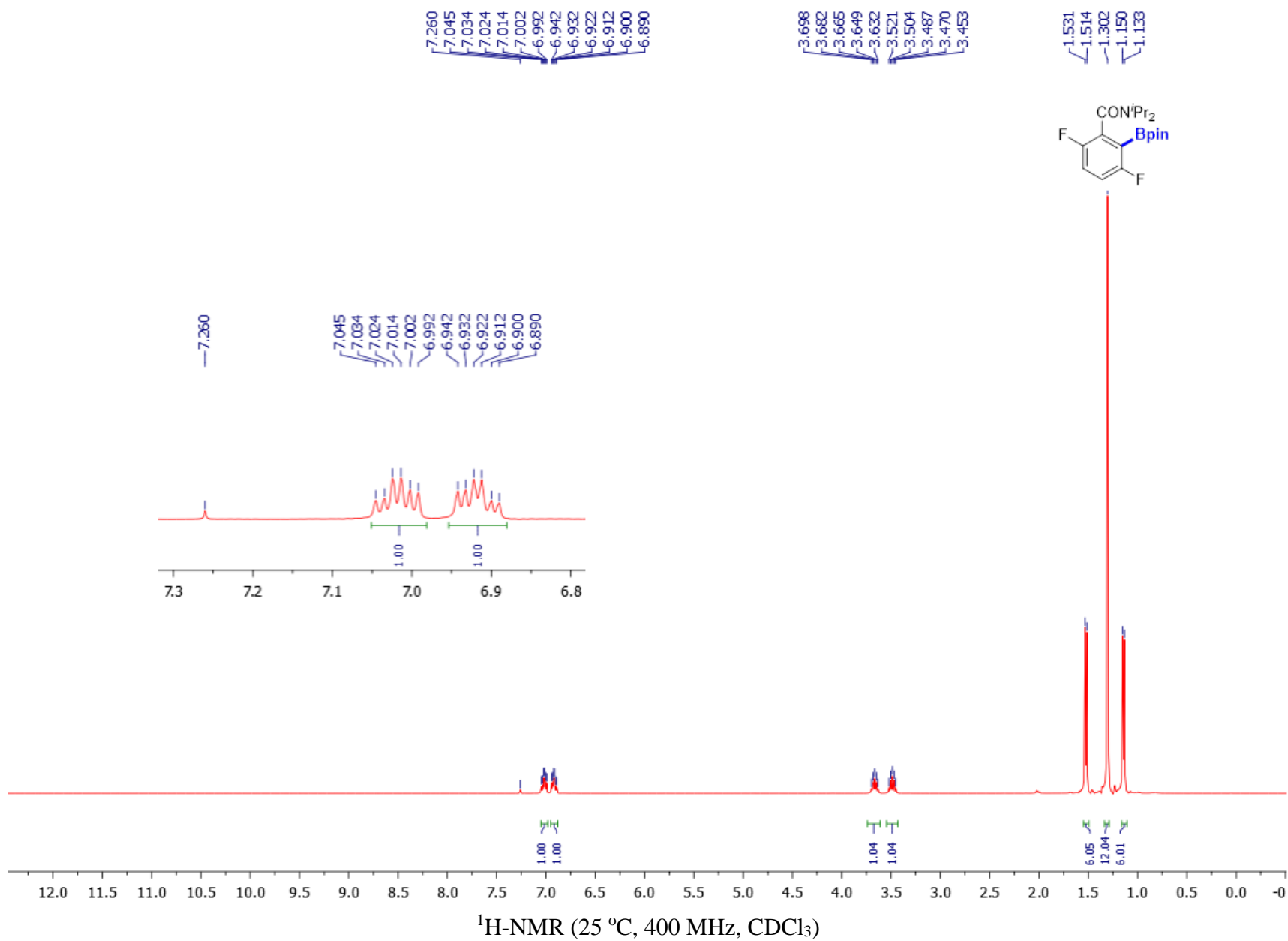


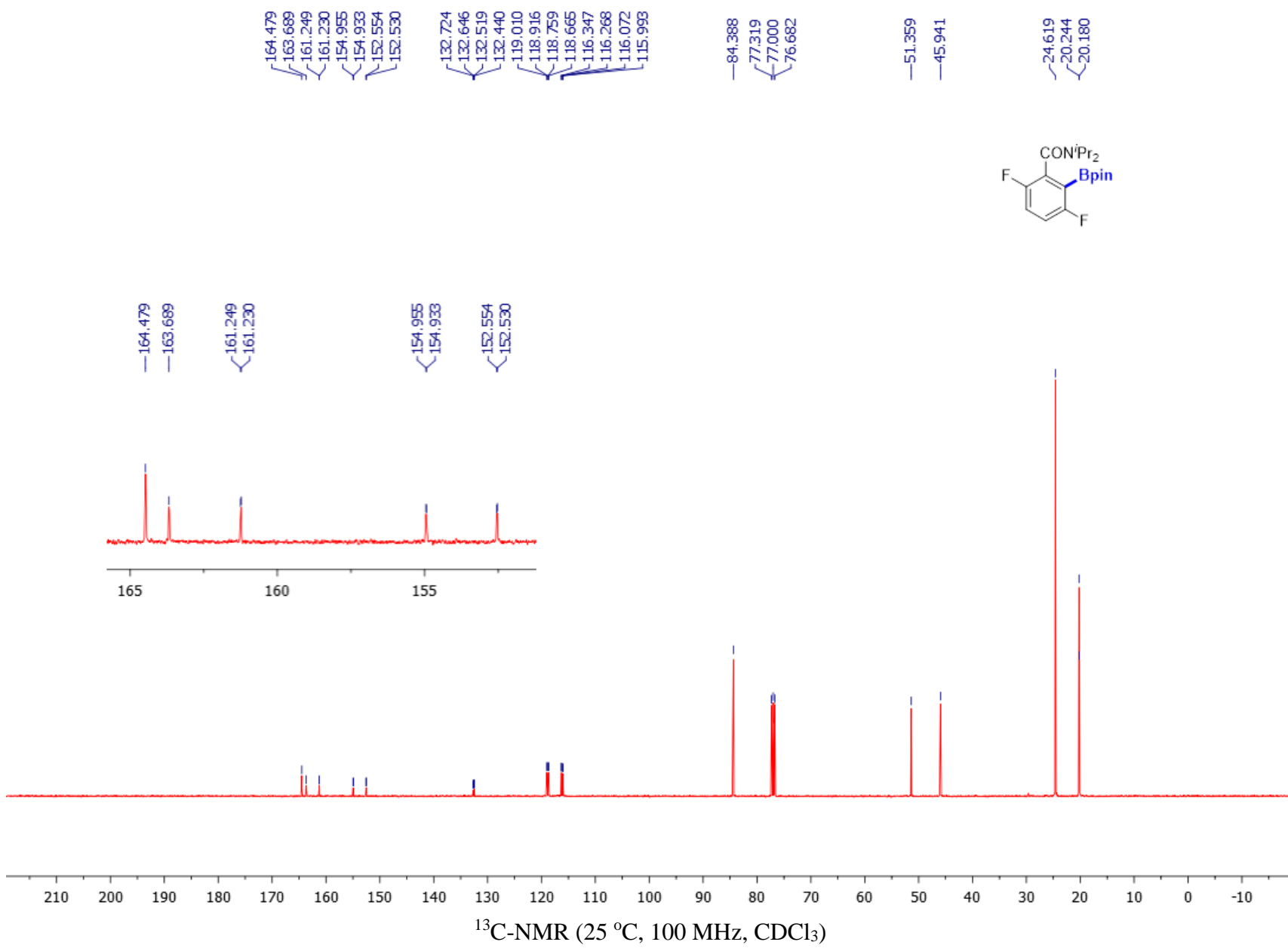


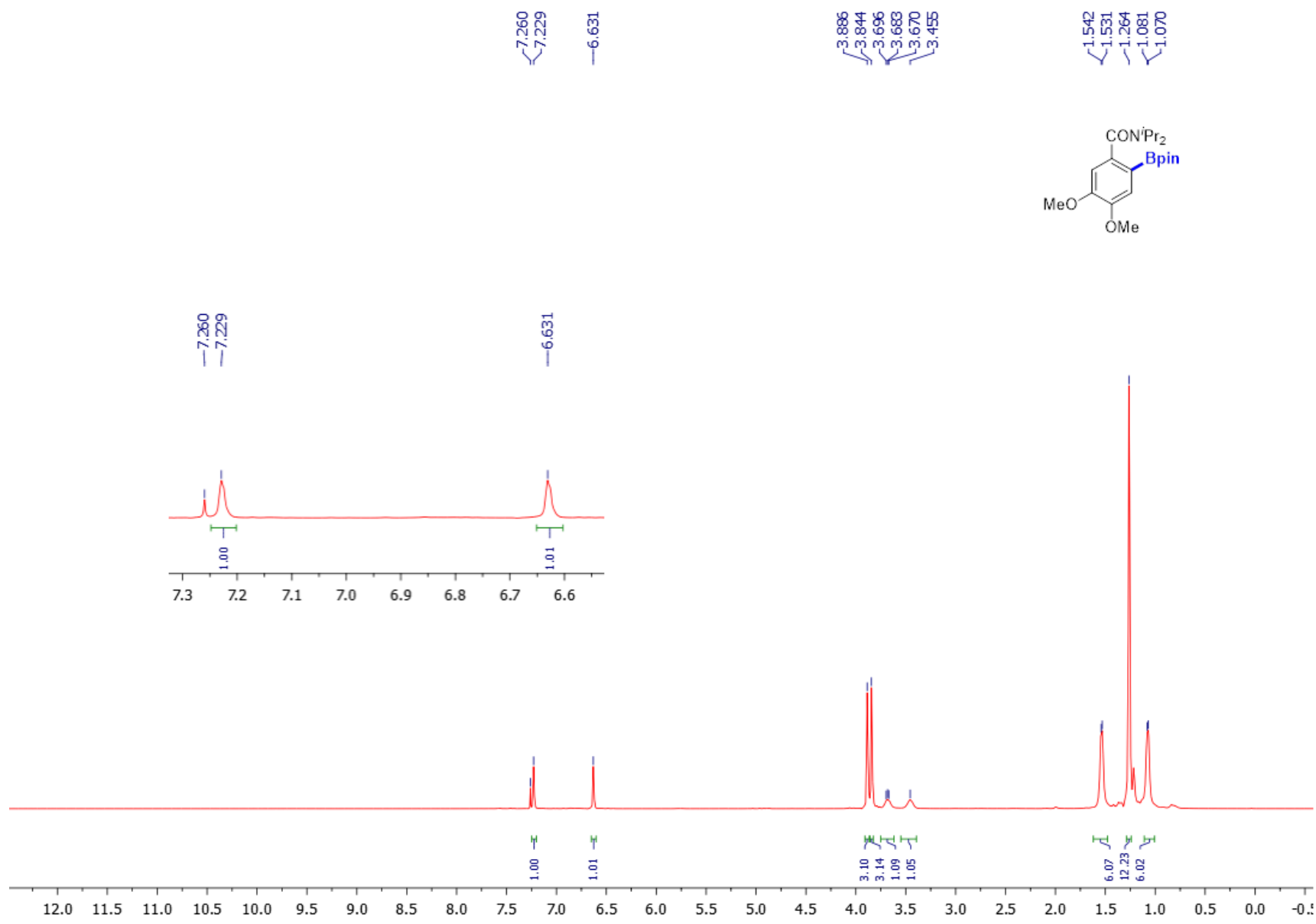




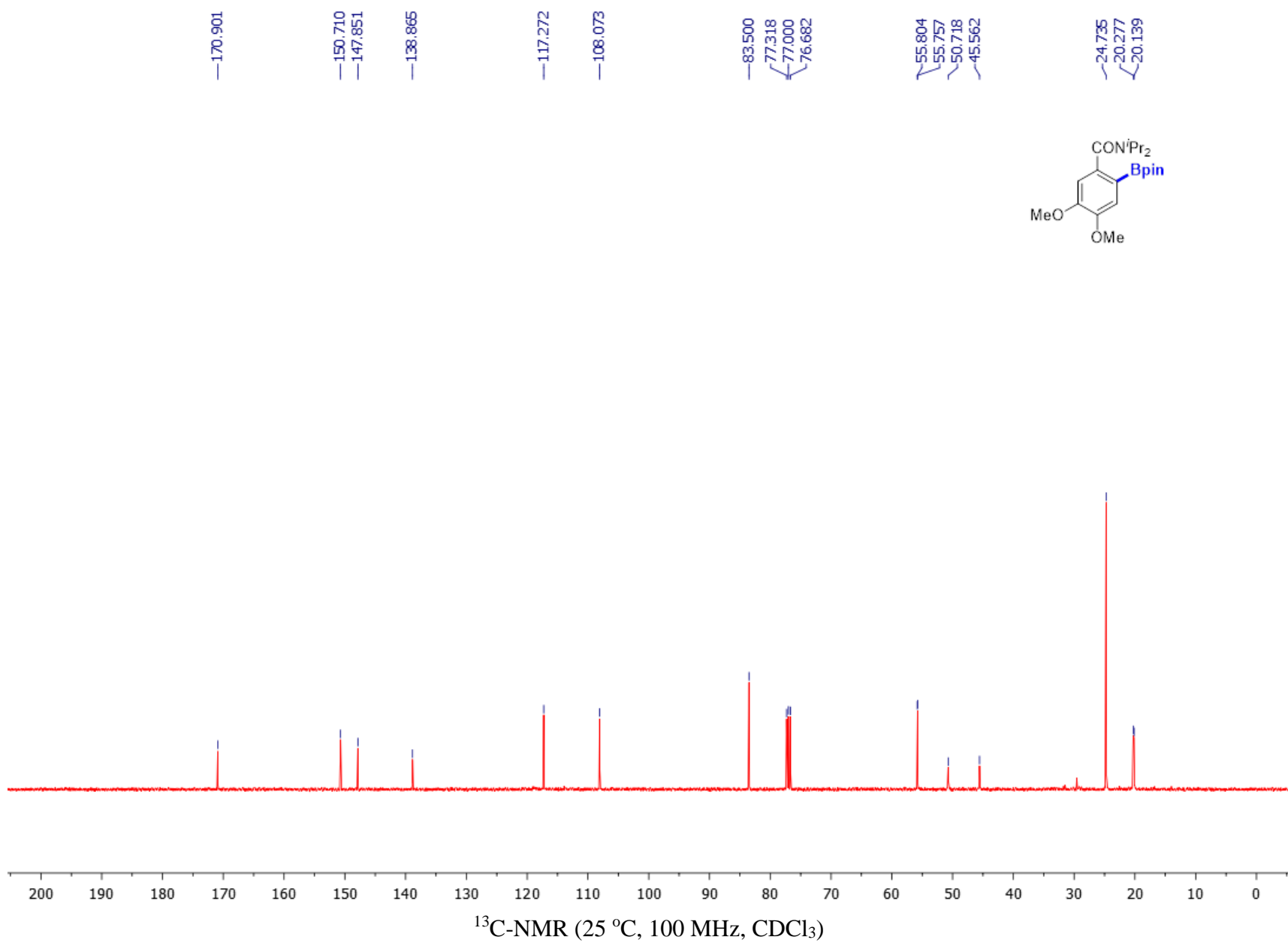


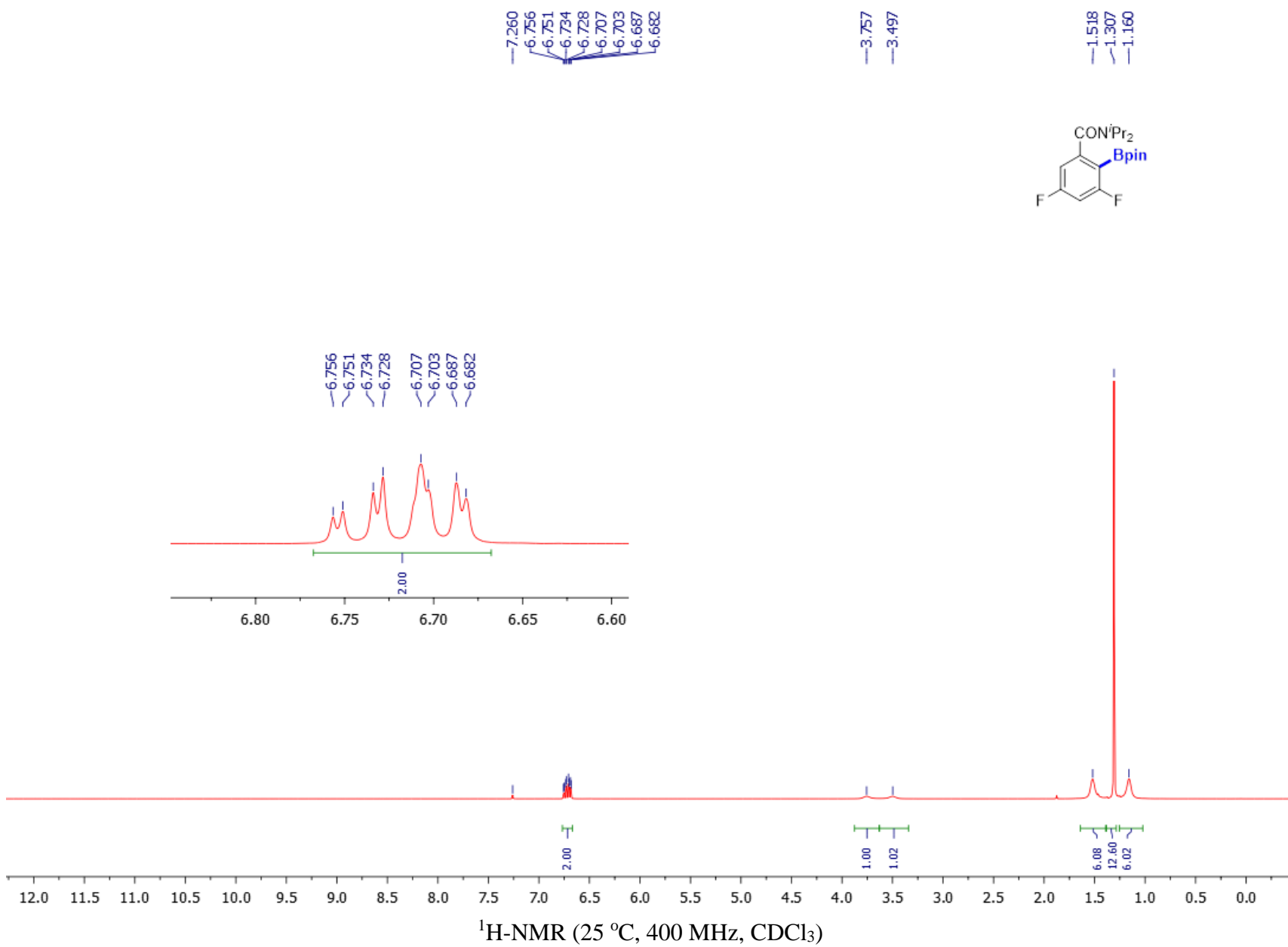


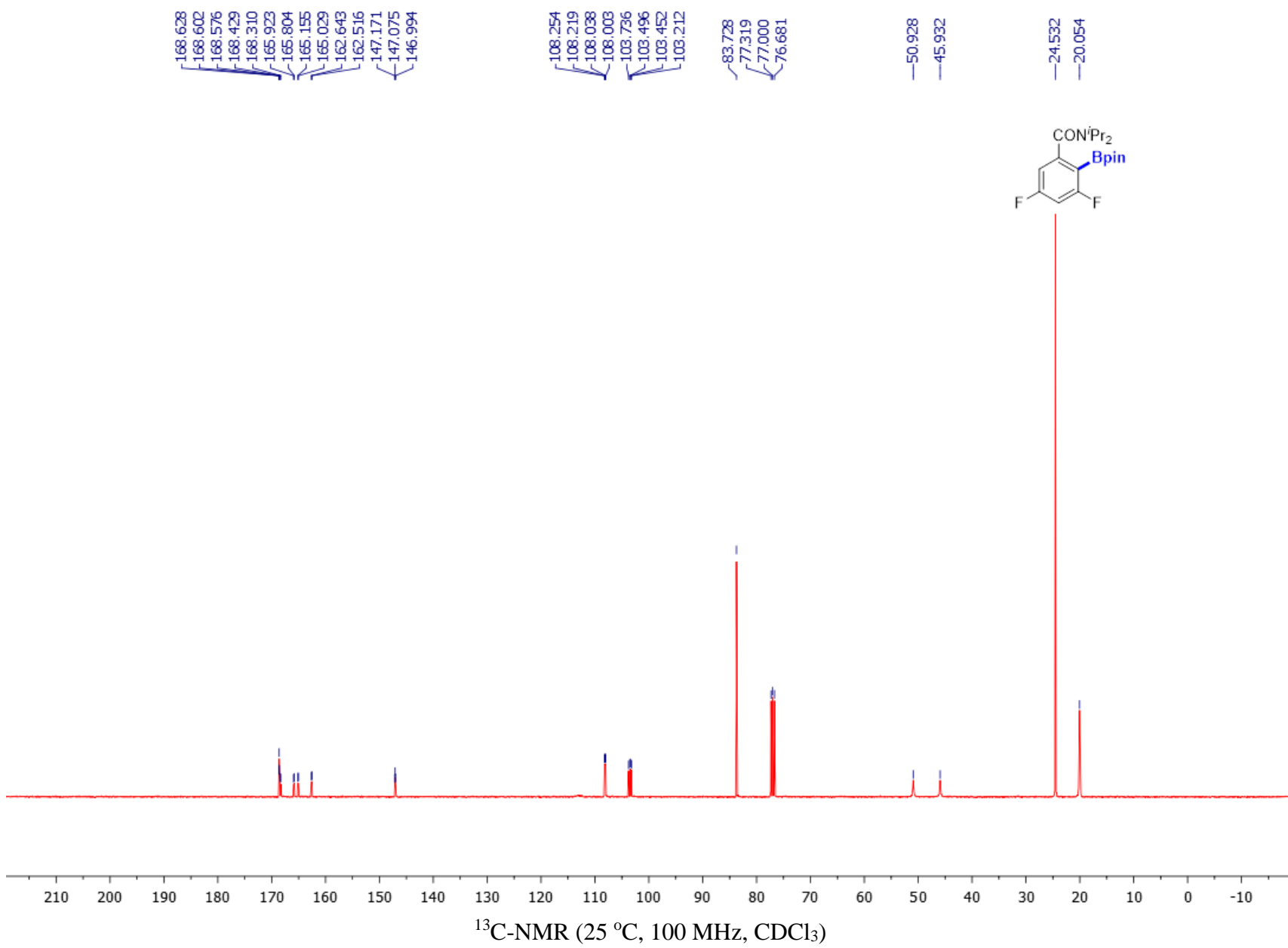


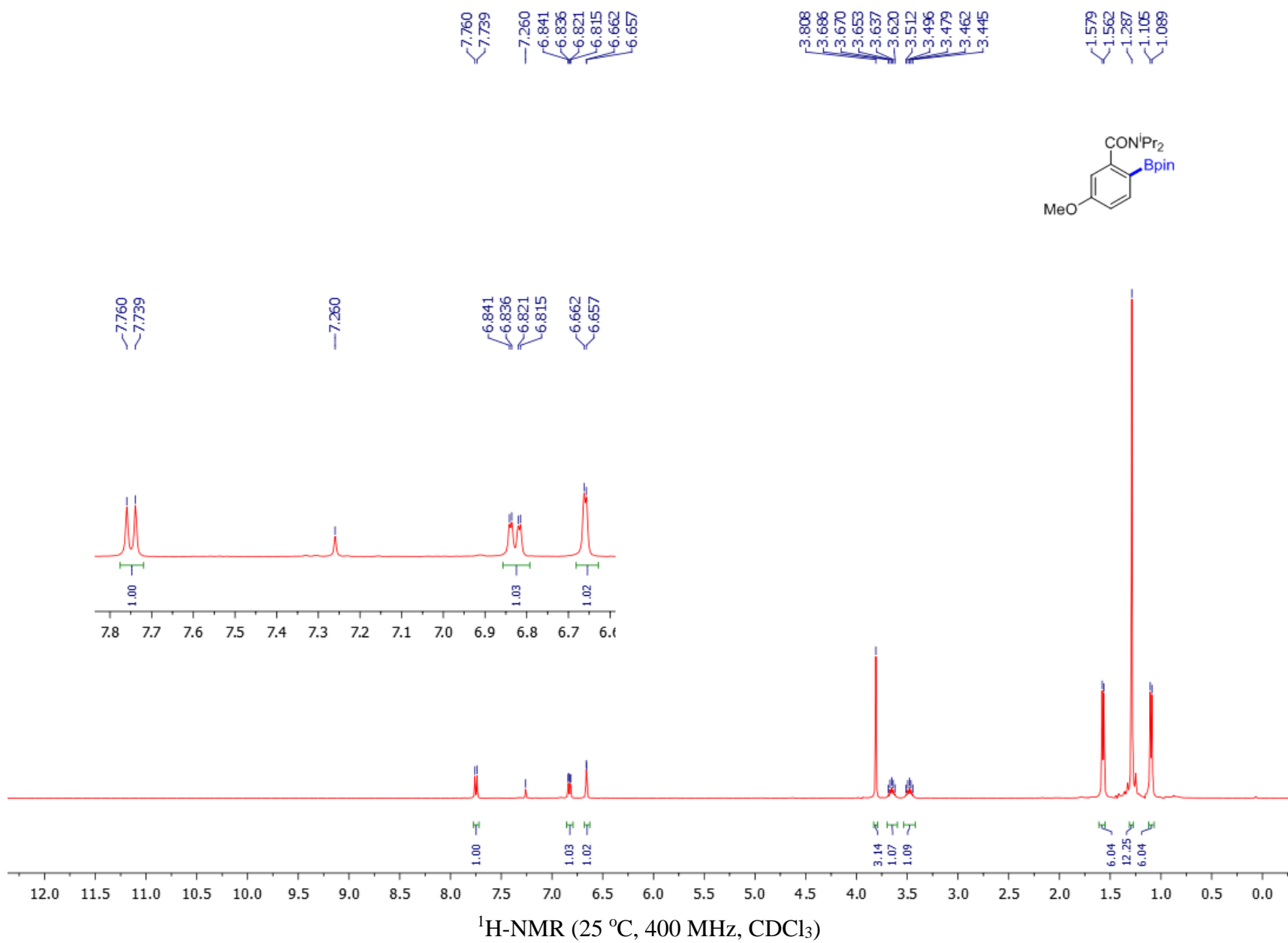


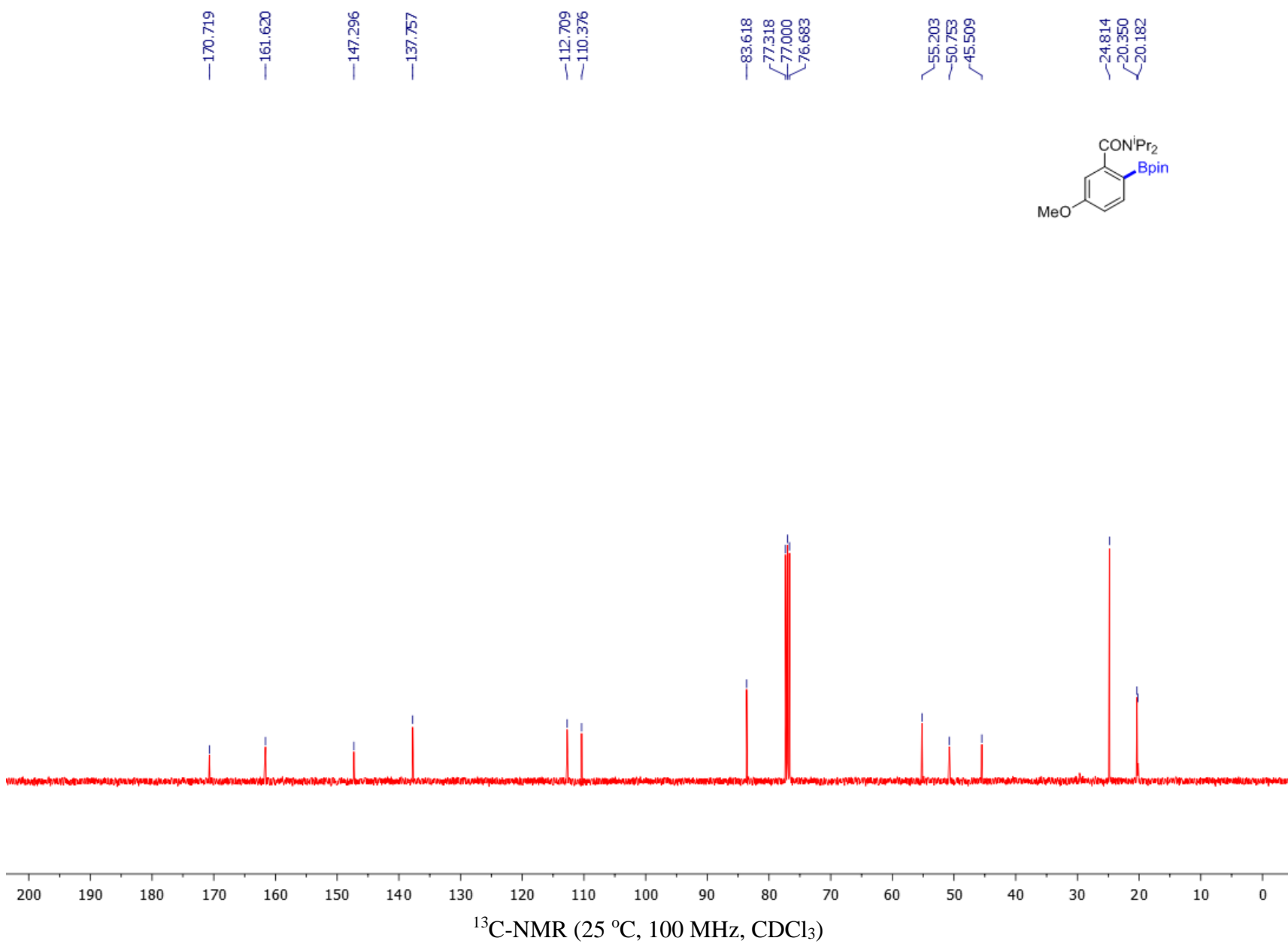
$^1\text{H-NMR}$ (25 °C, 400 MHz, CDCl_3)

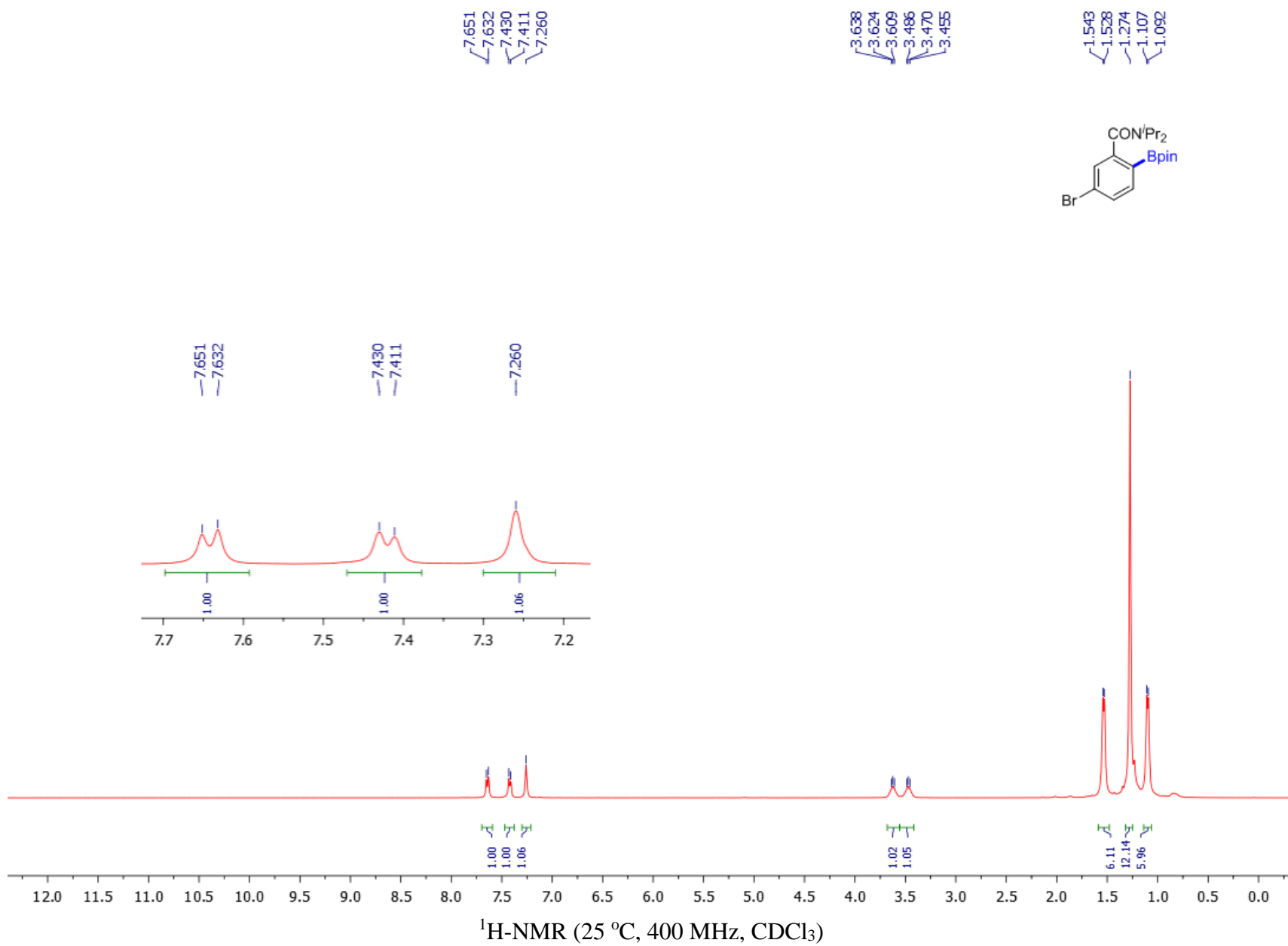


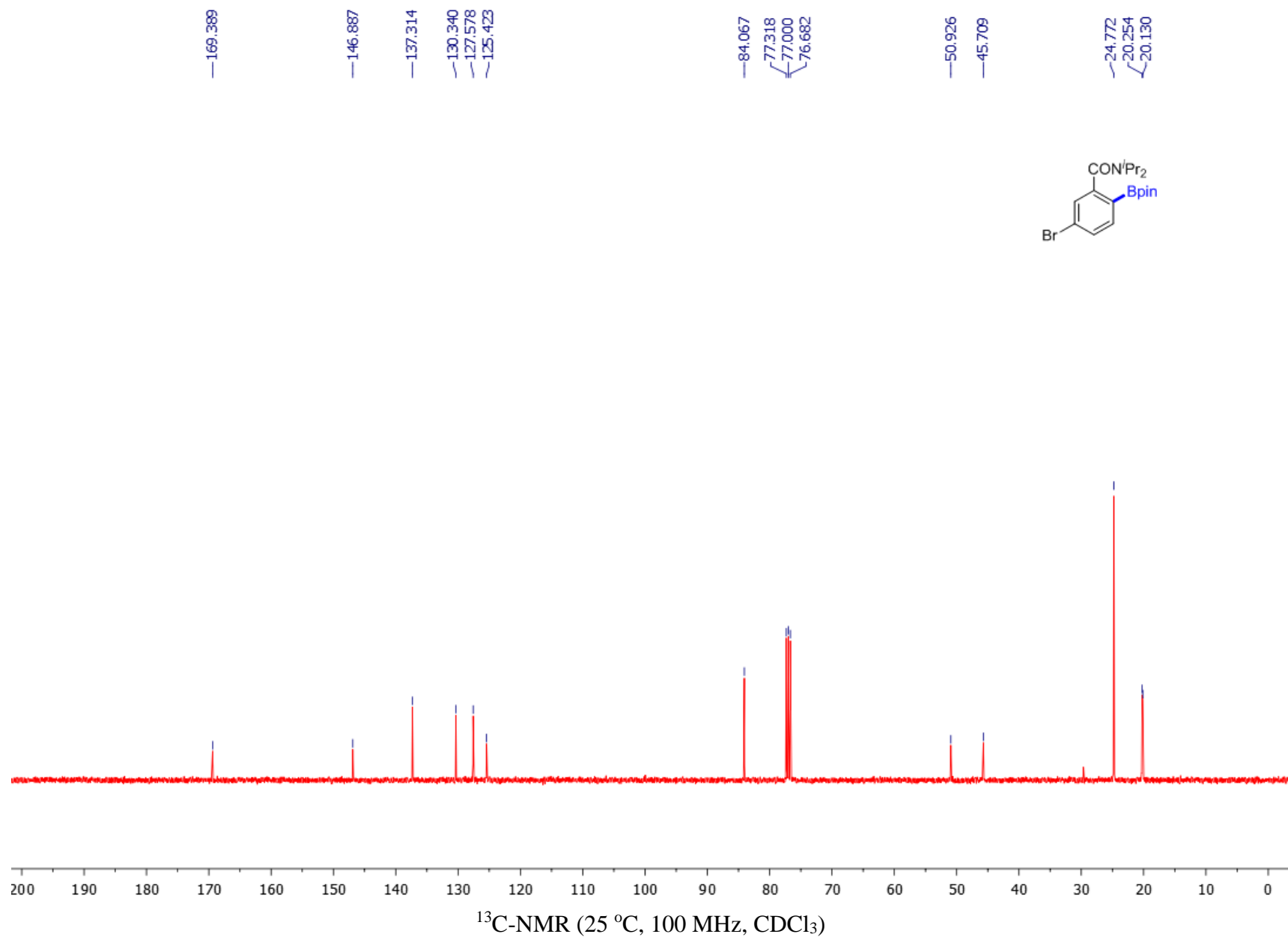


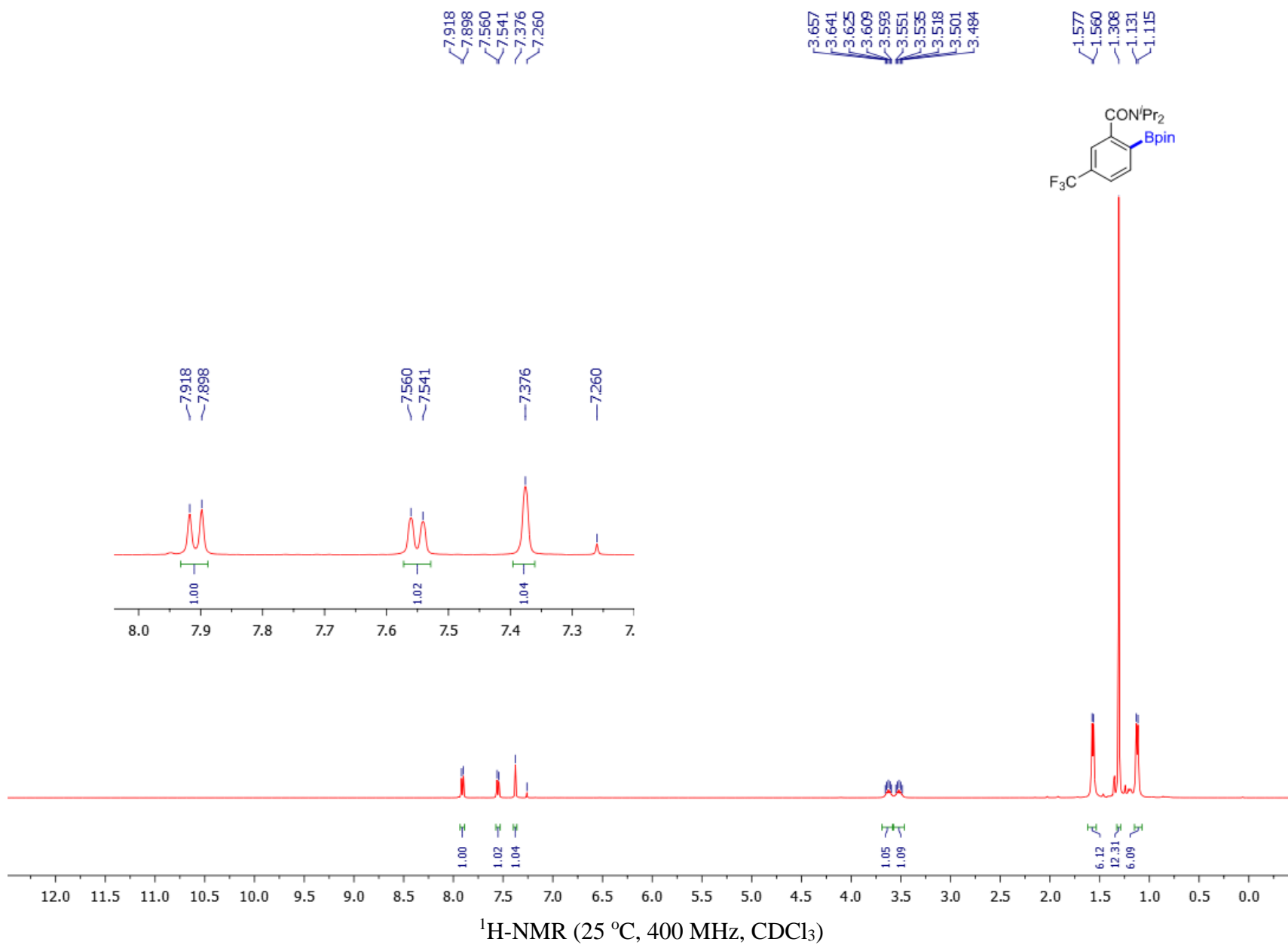


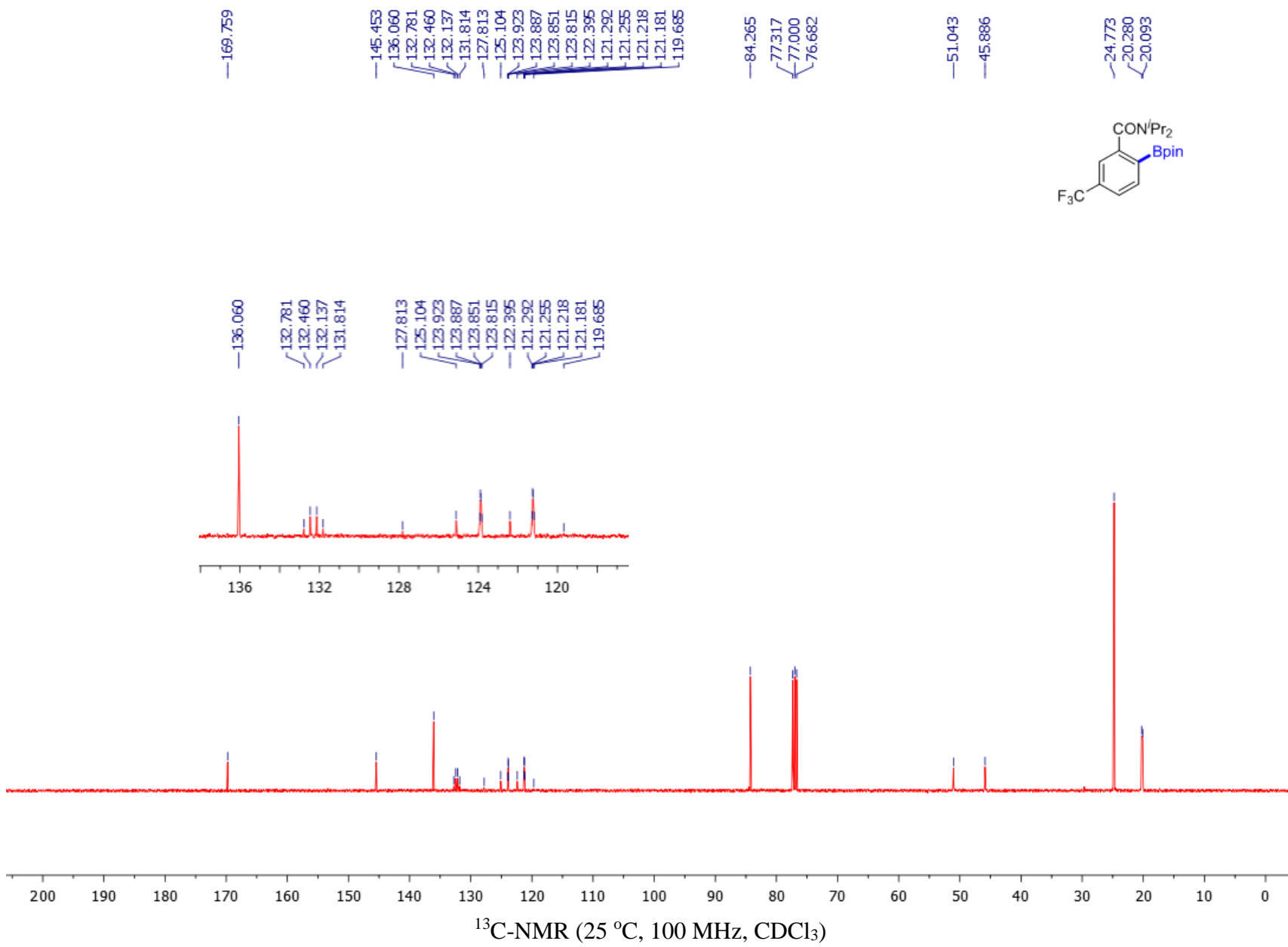


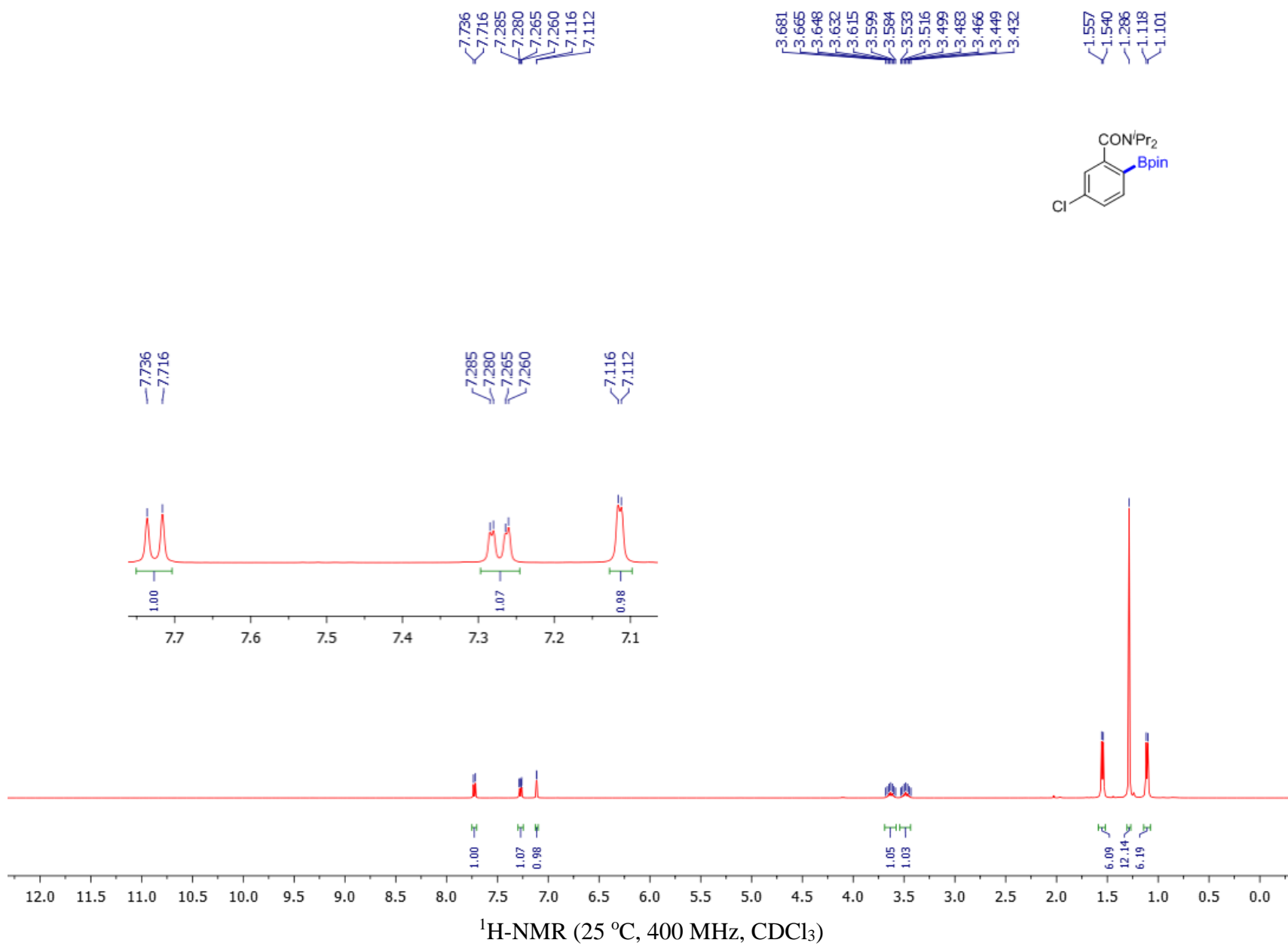


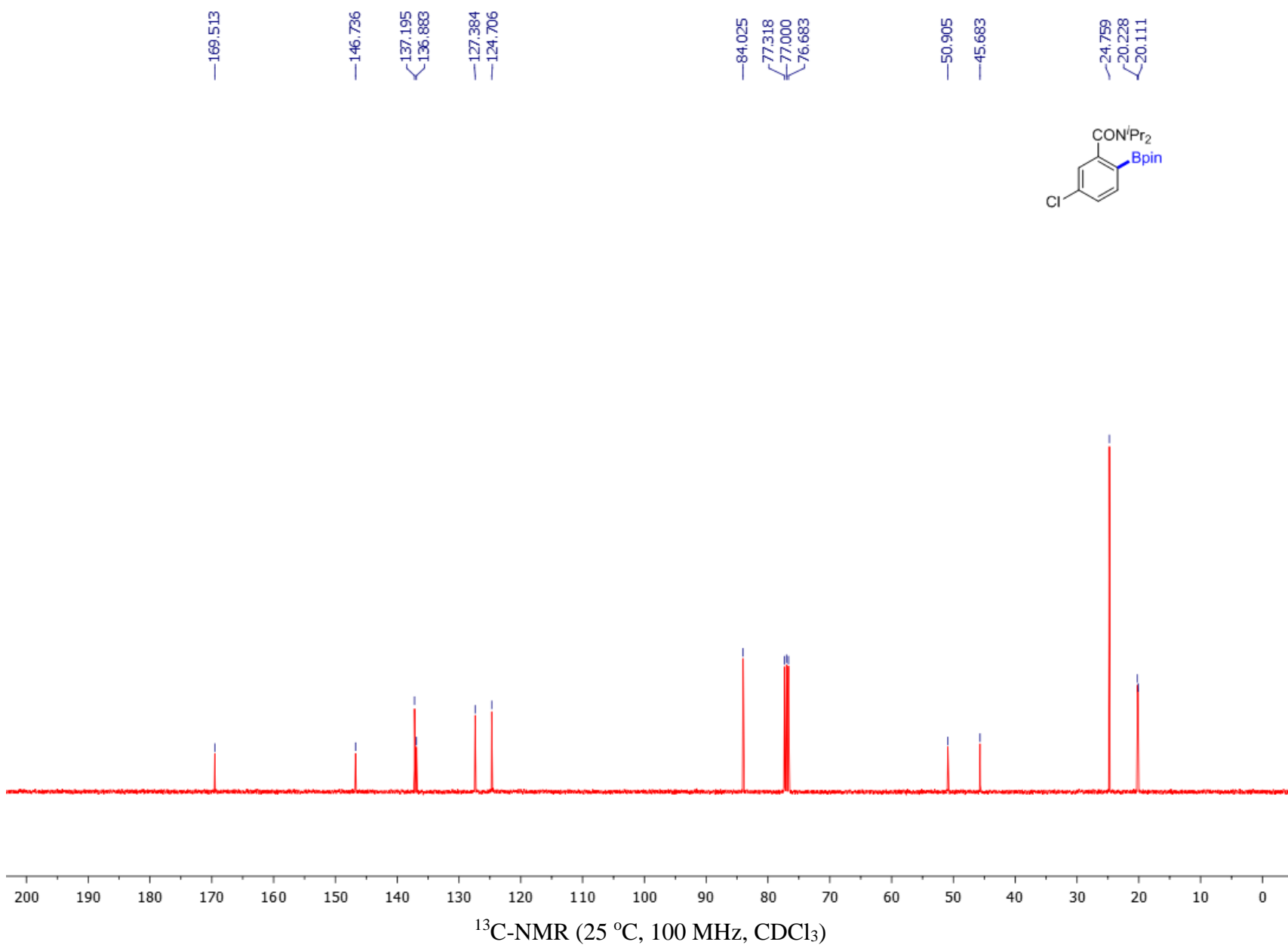


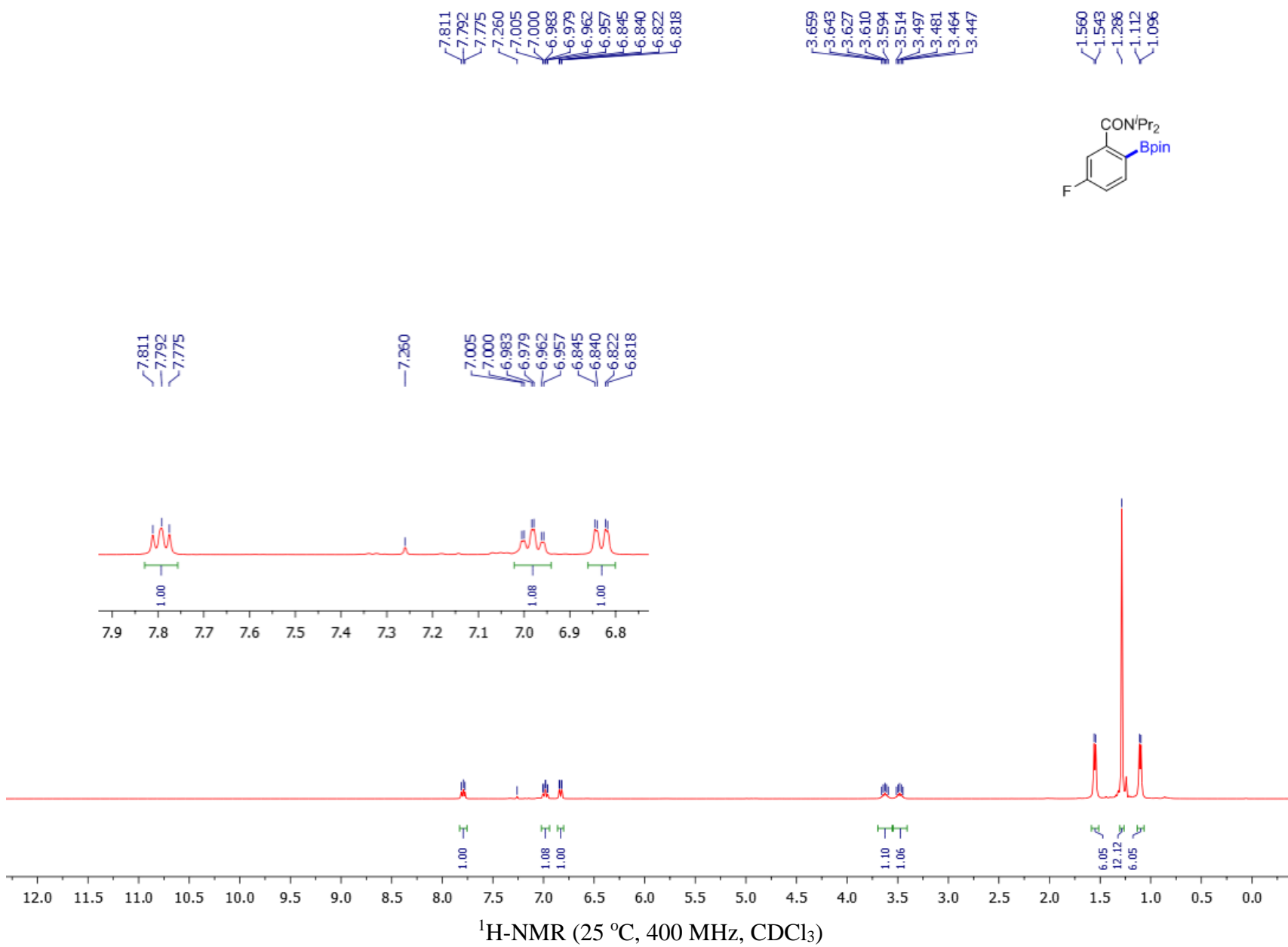


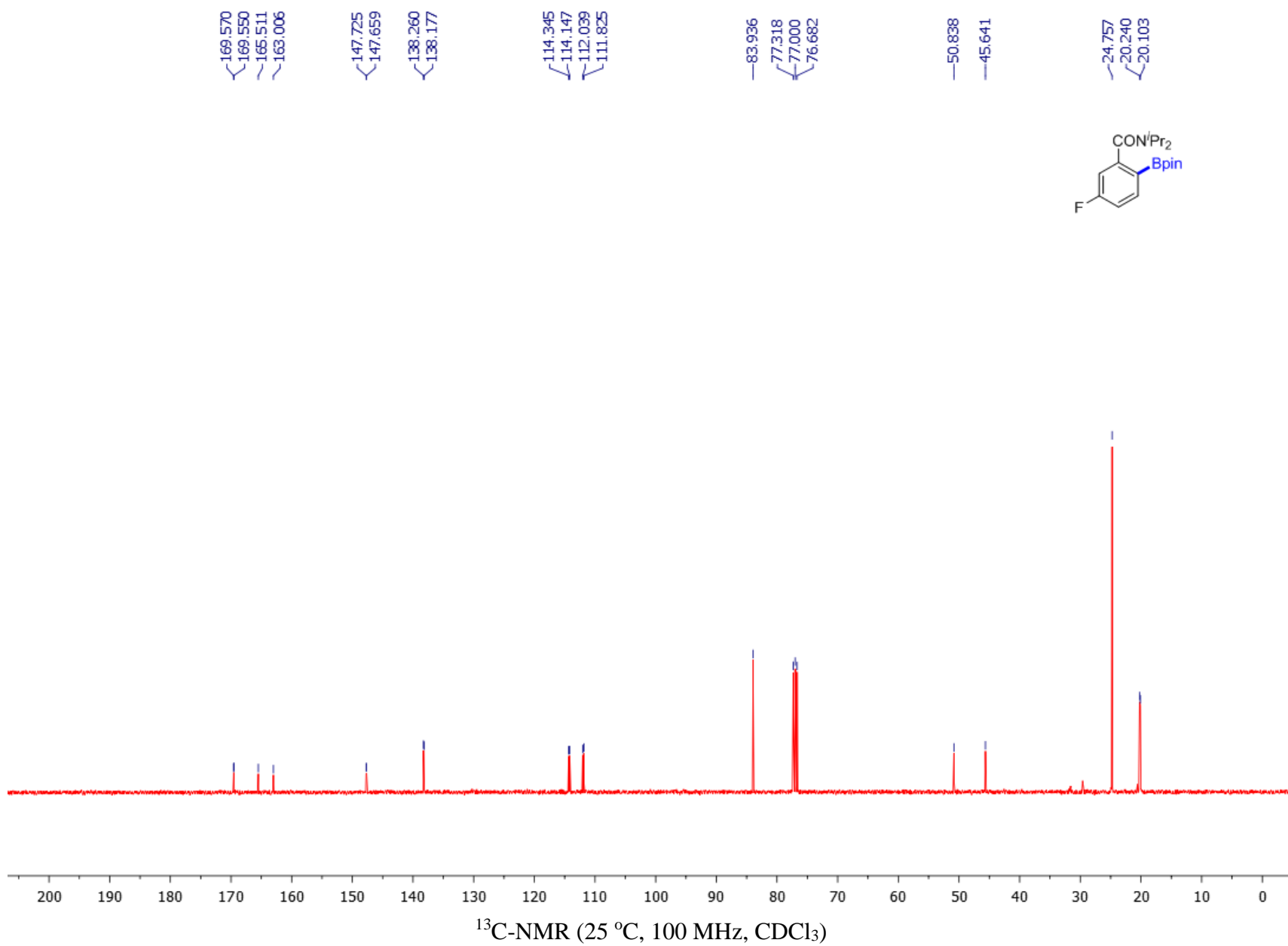


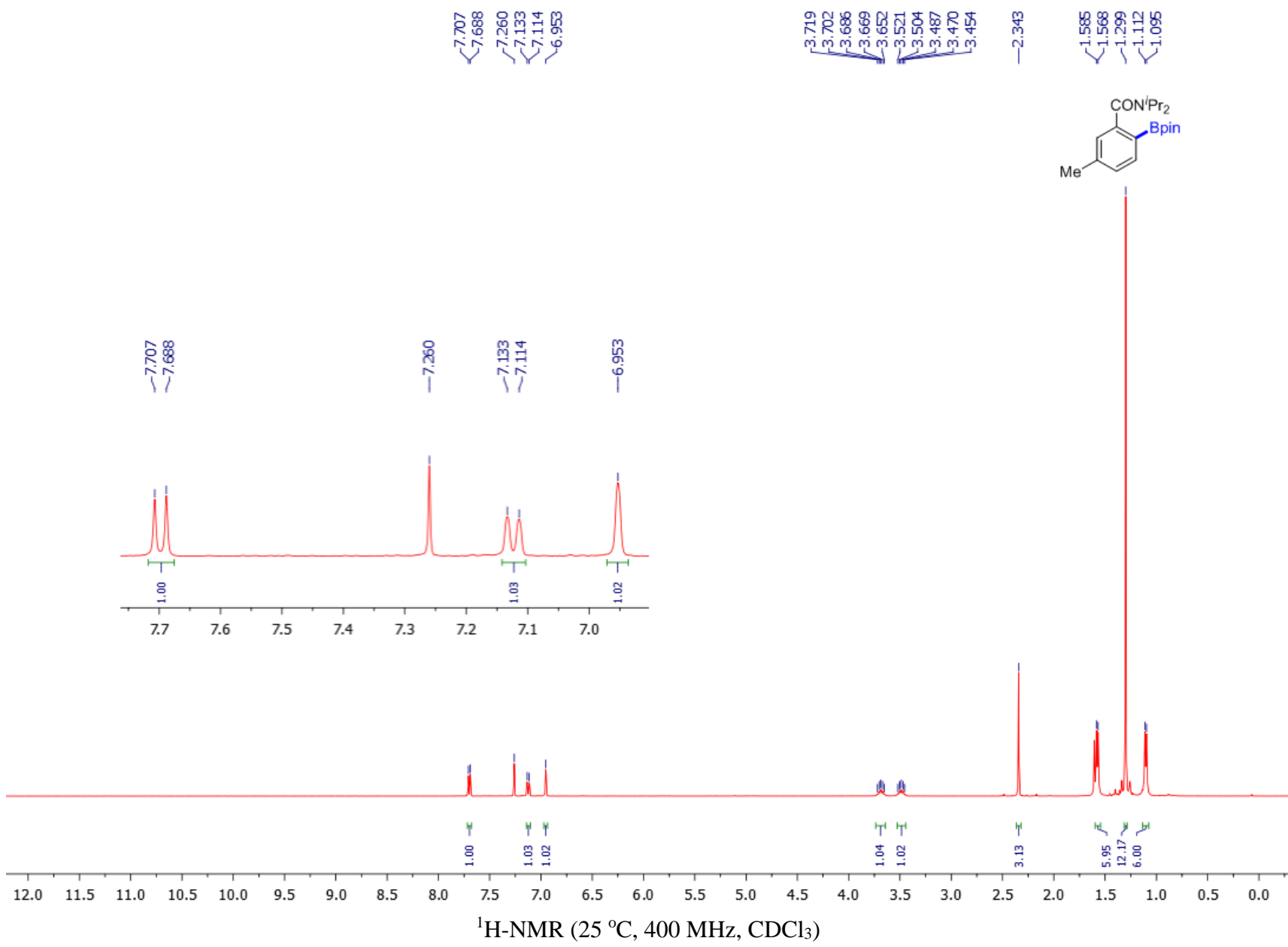


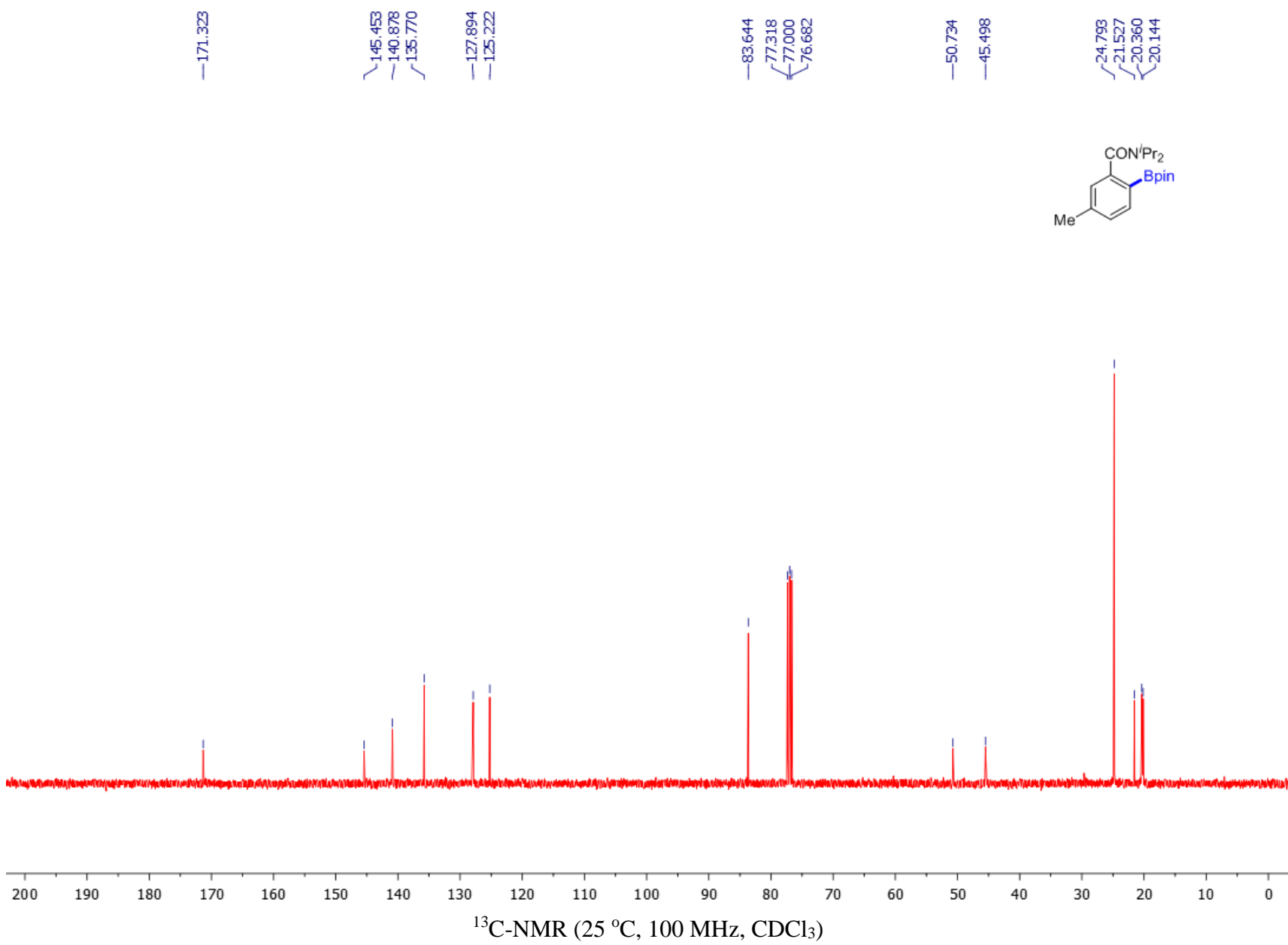


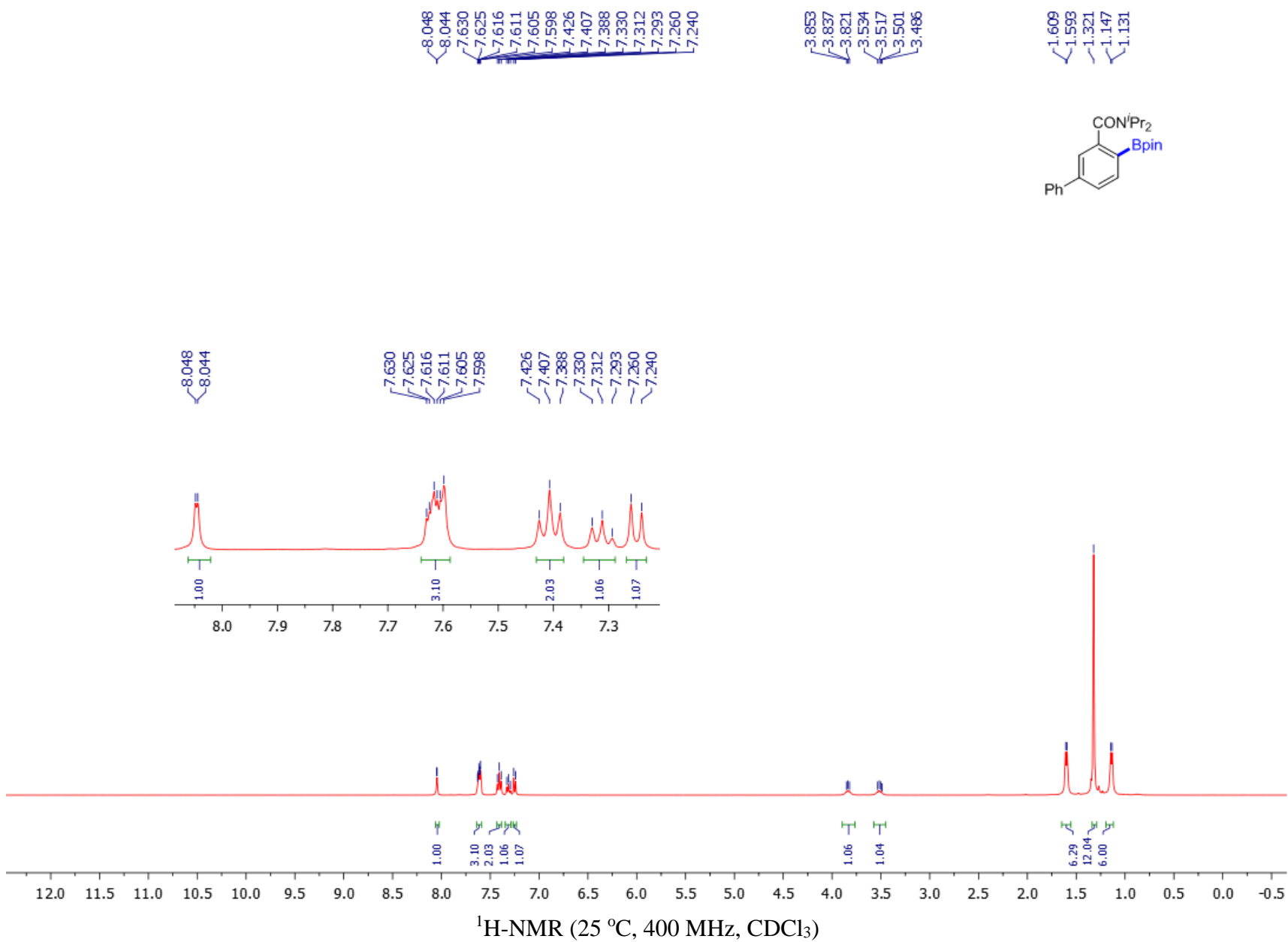


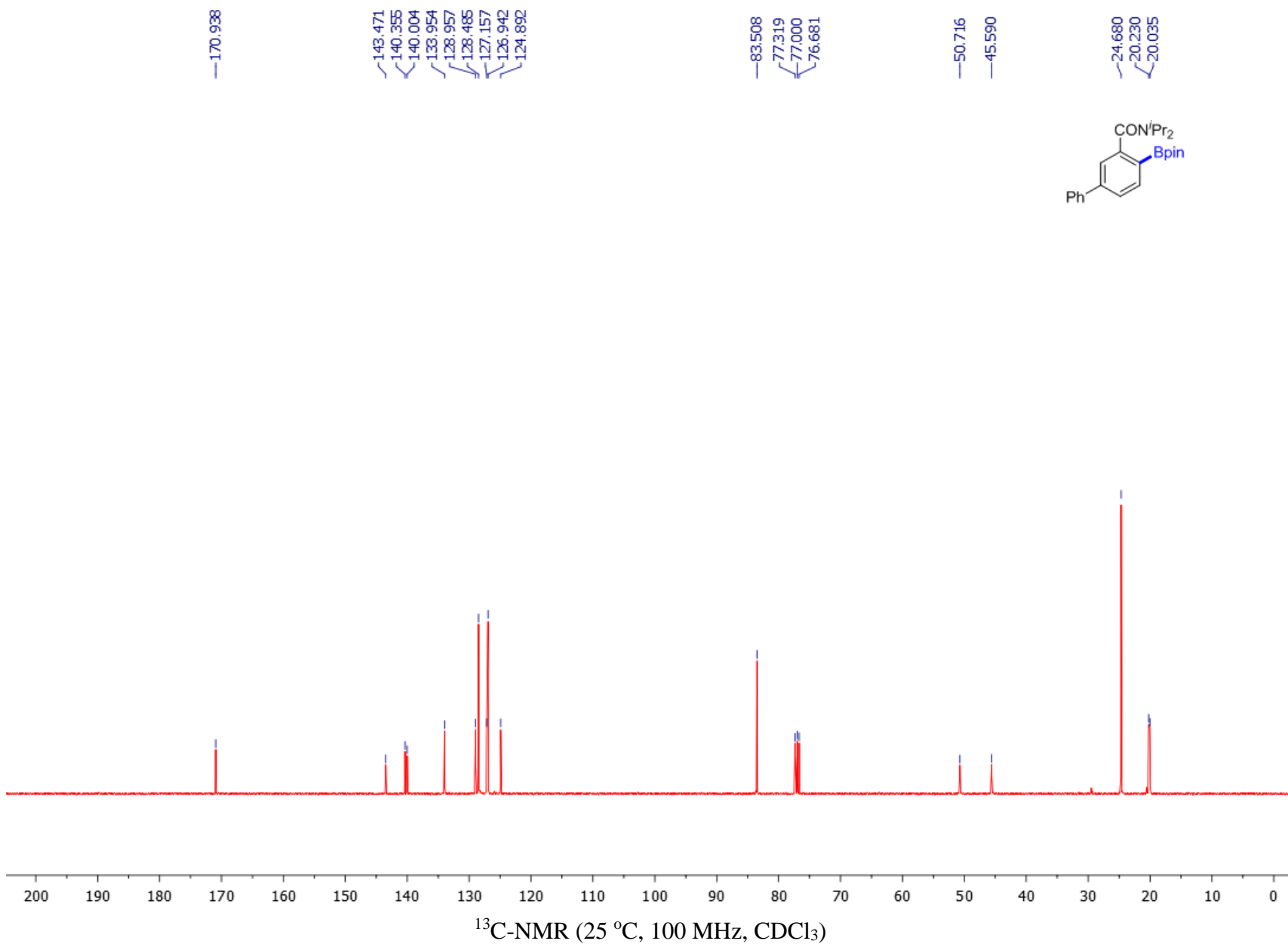


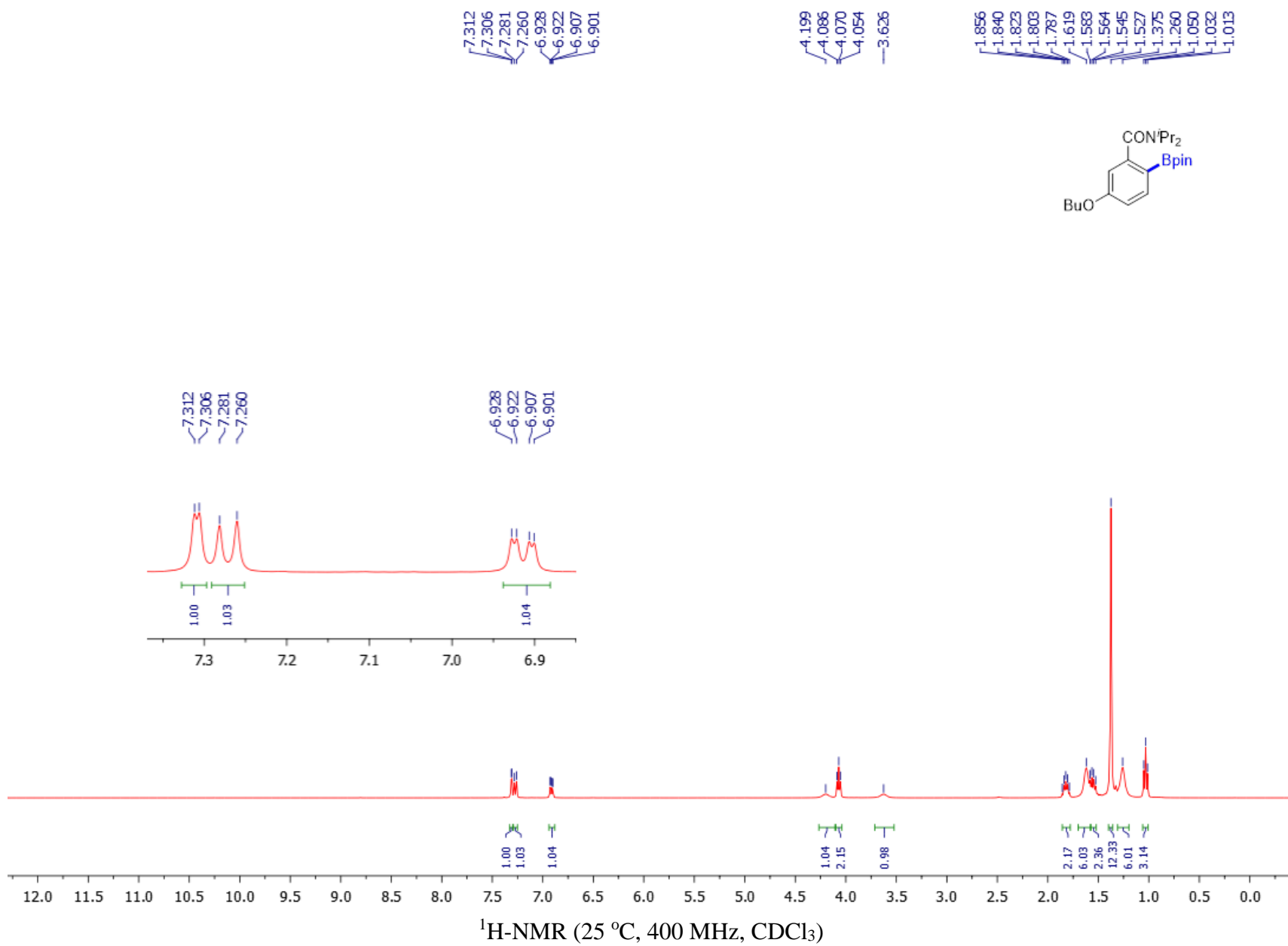


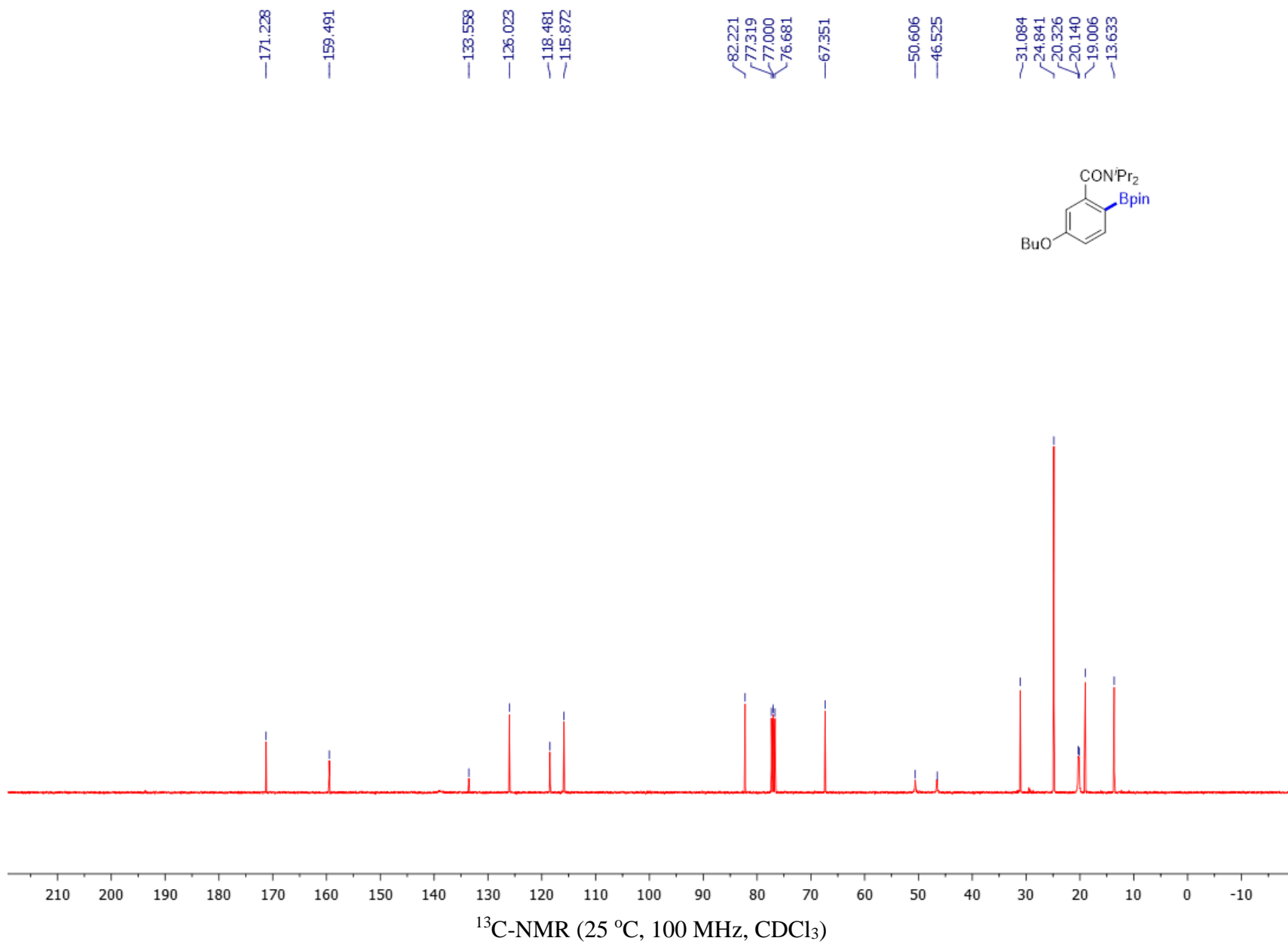


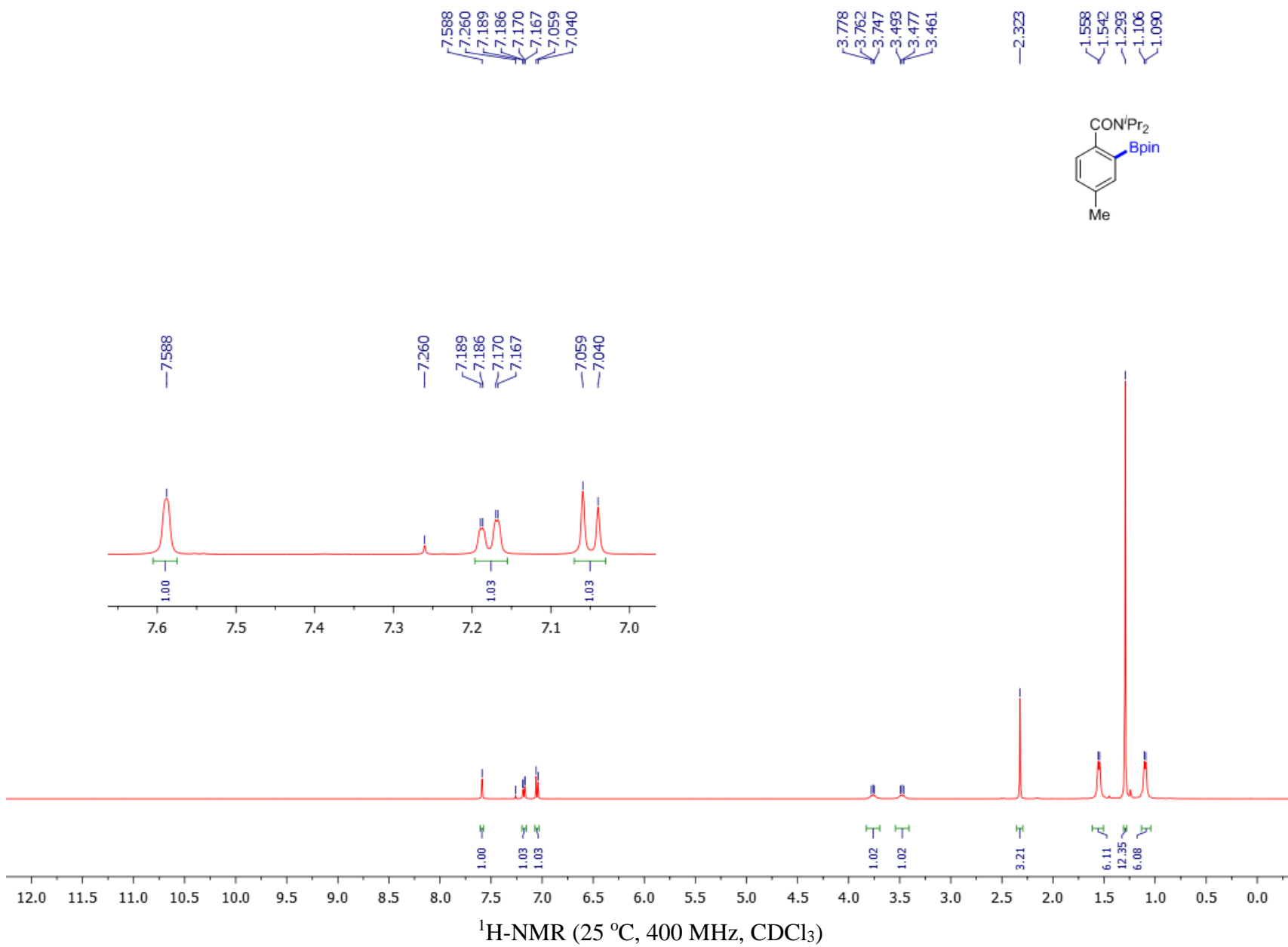


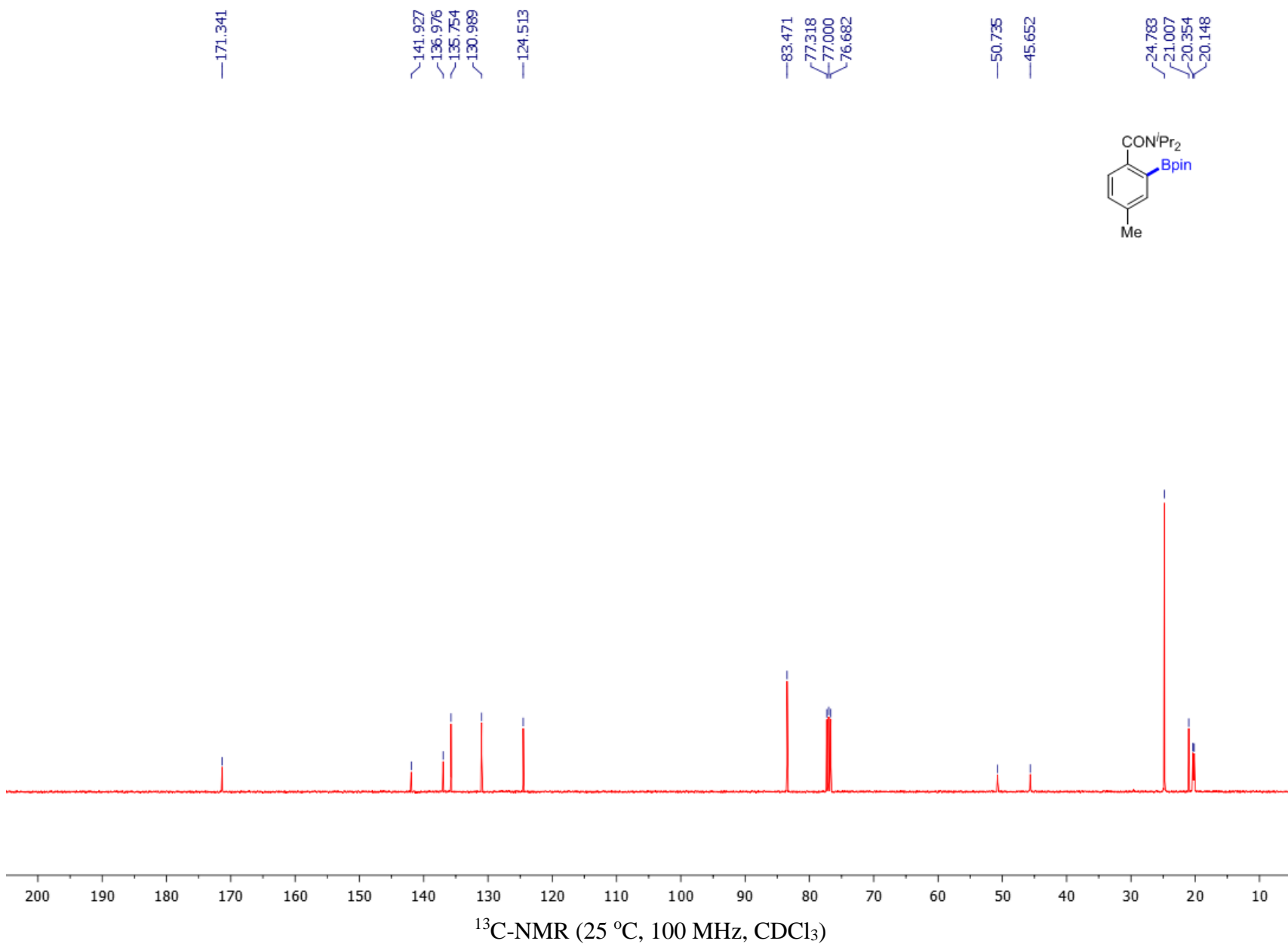


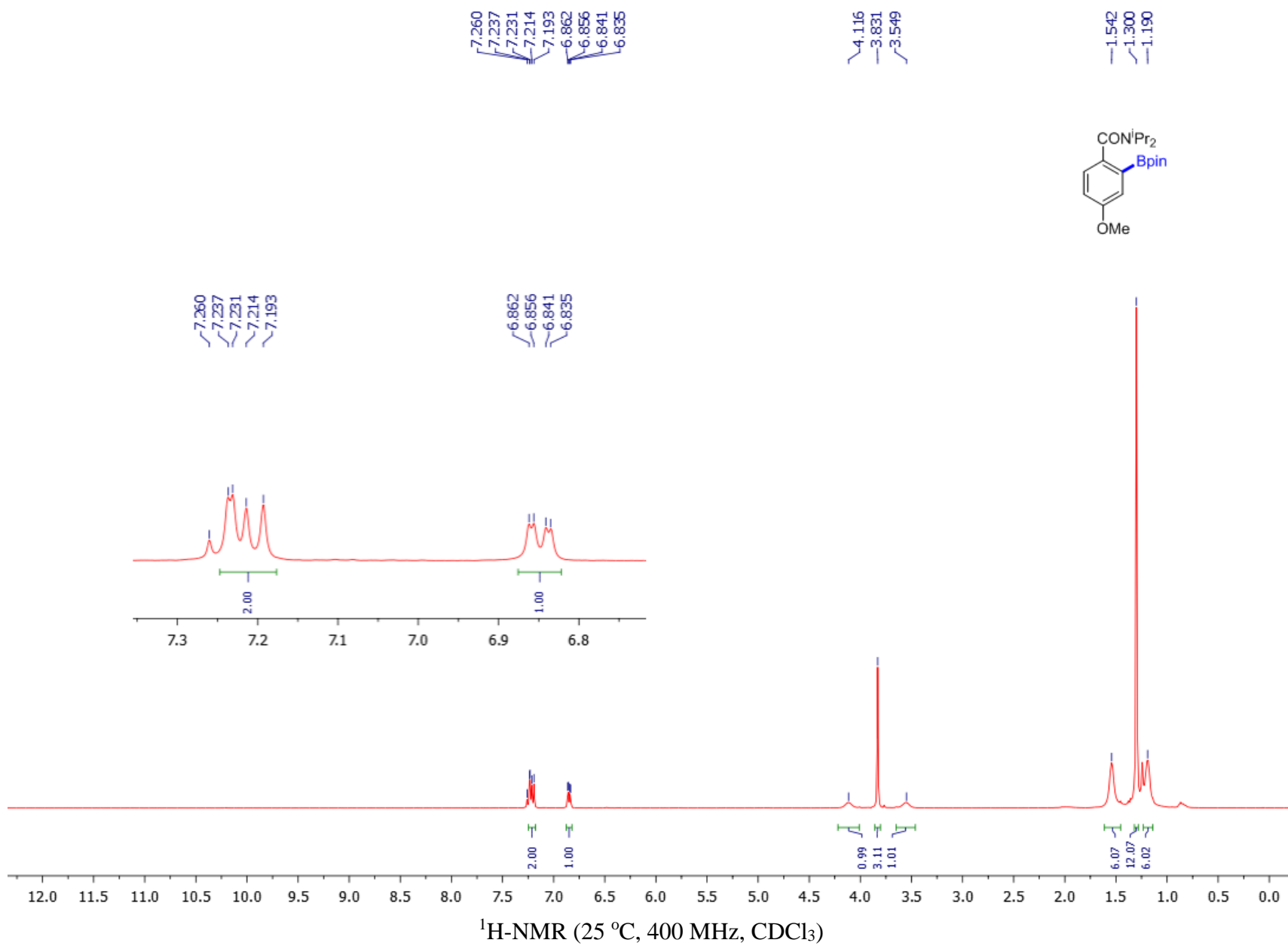


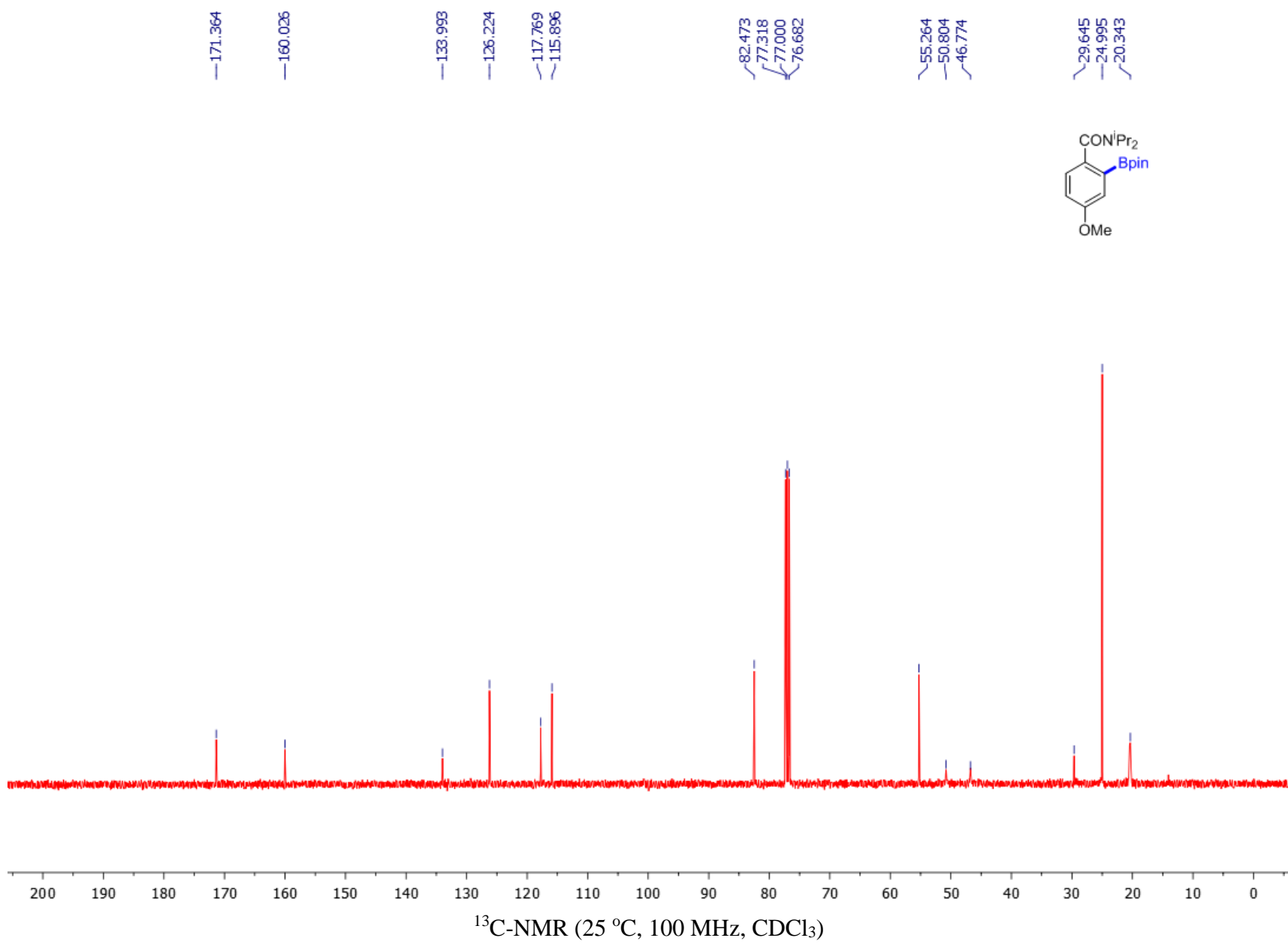


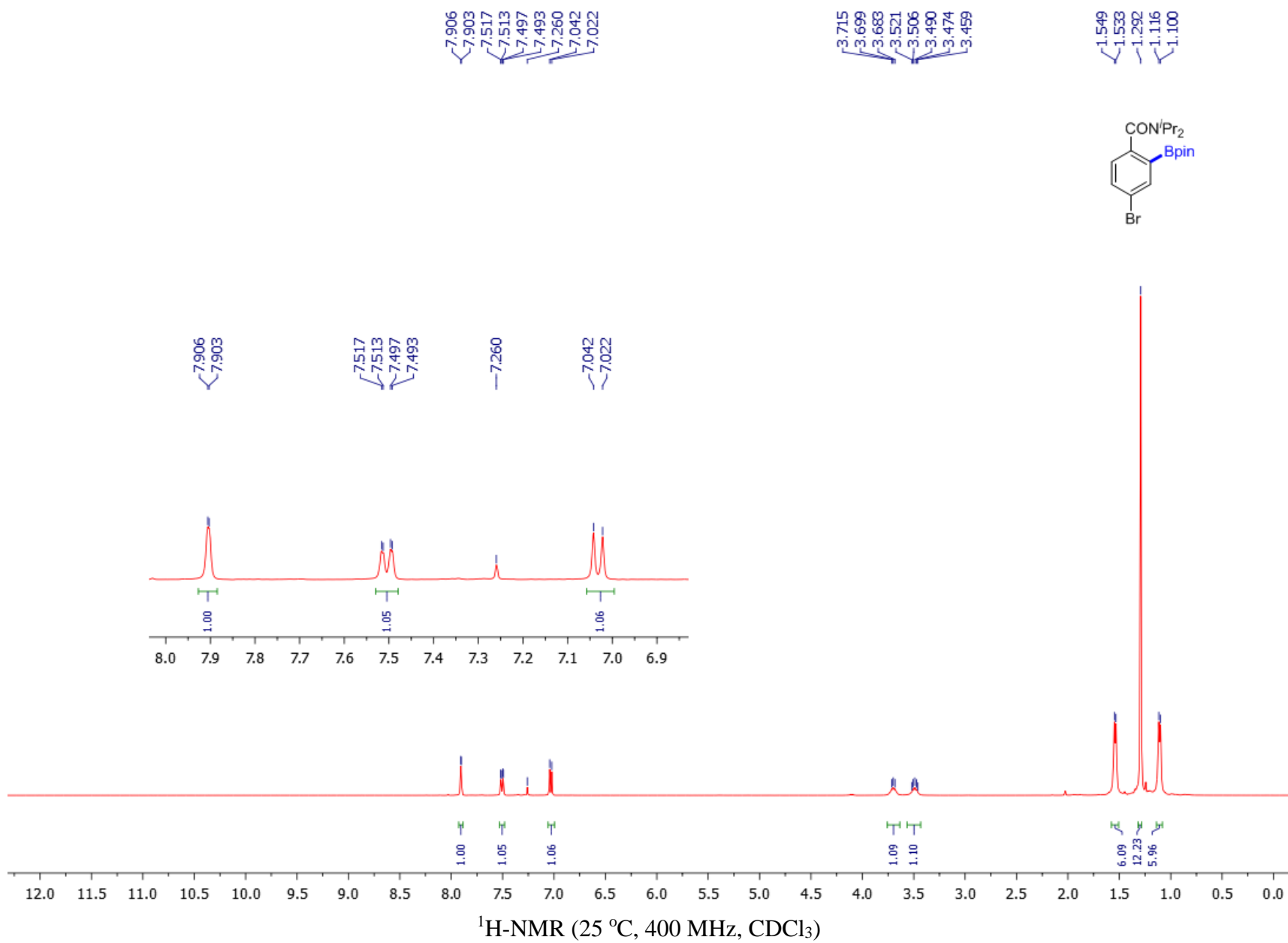


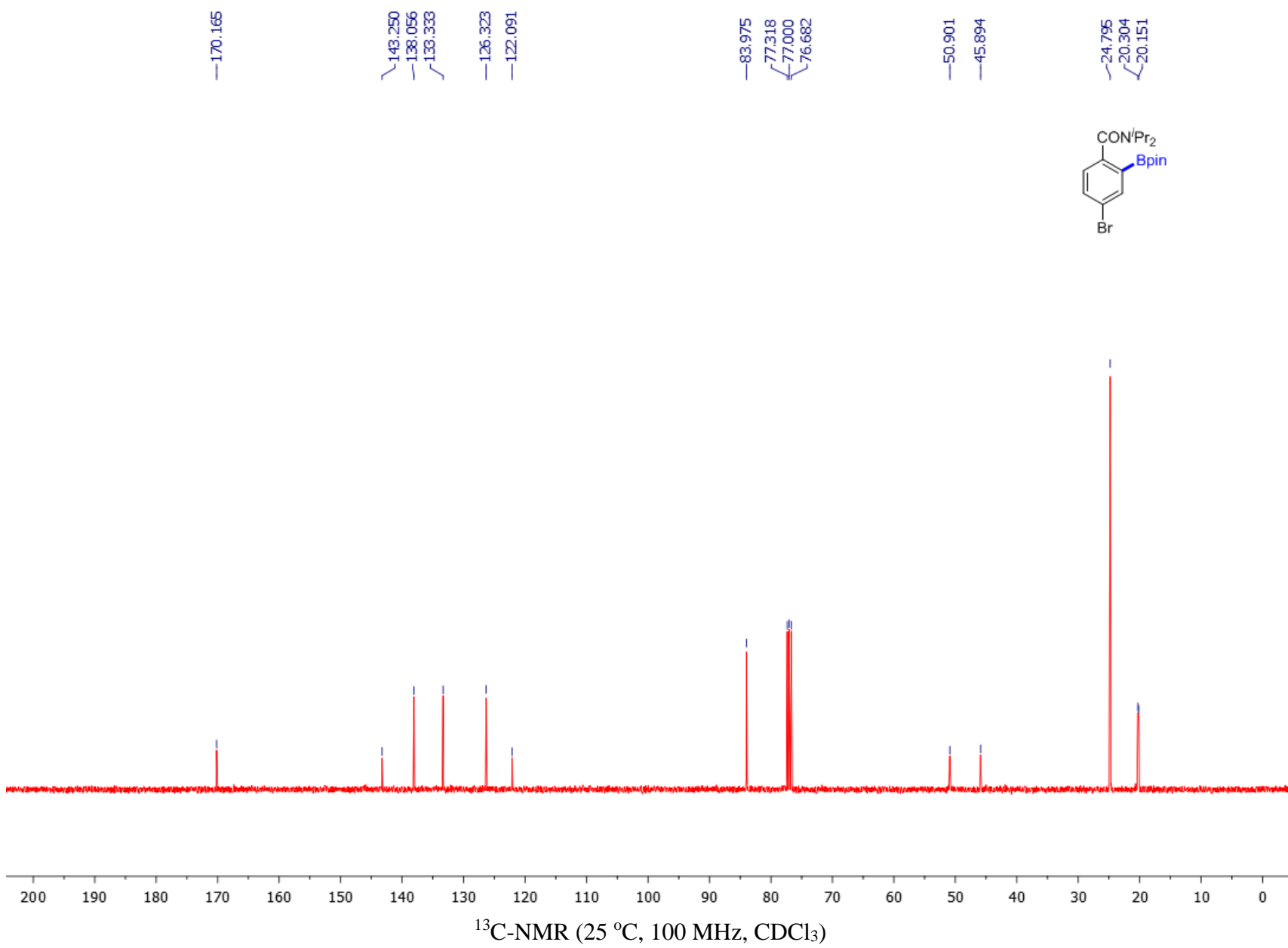


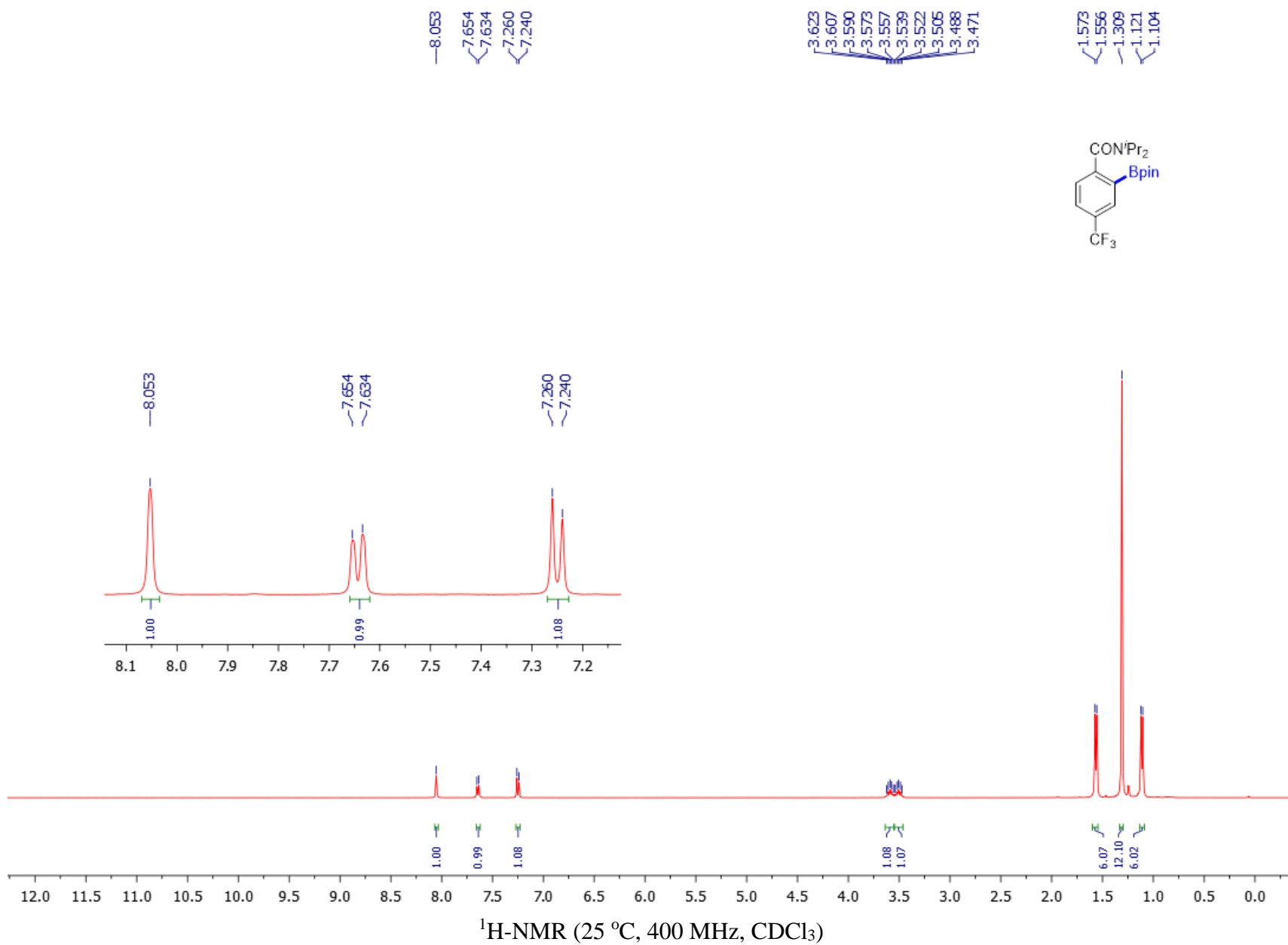


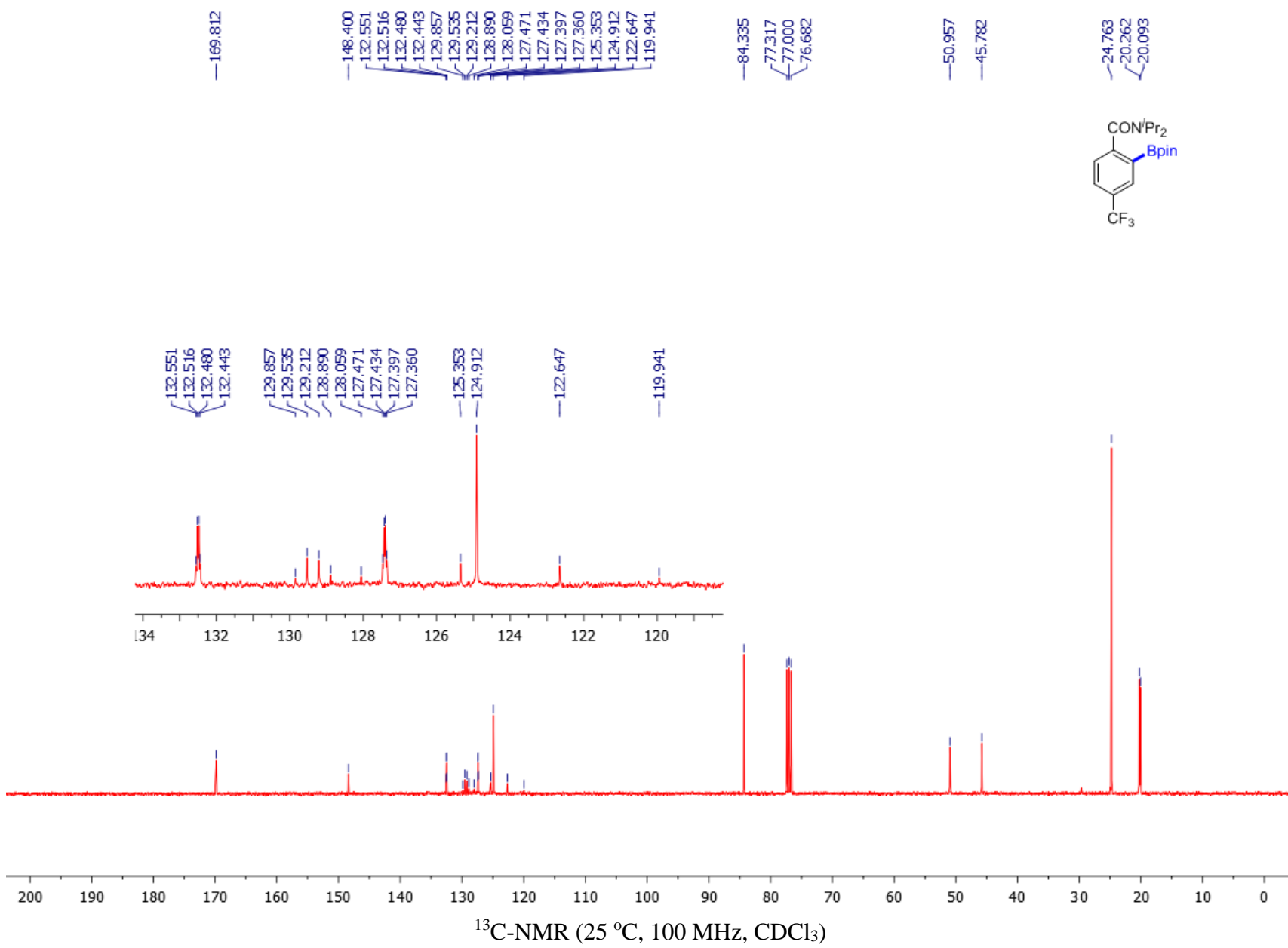


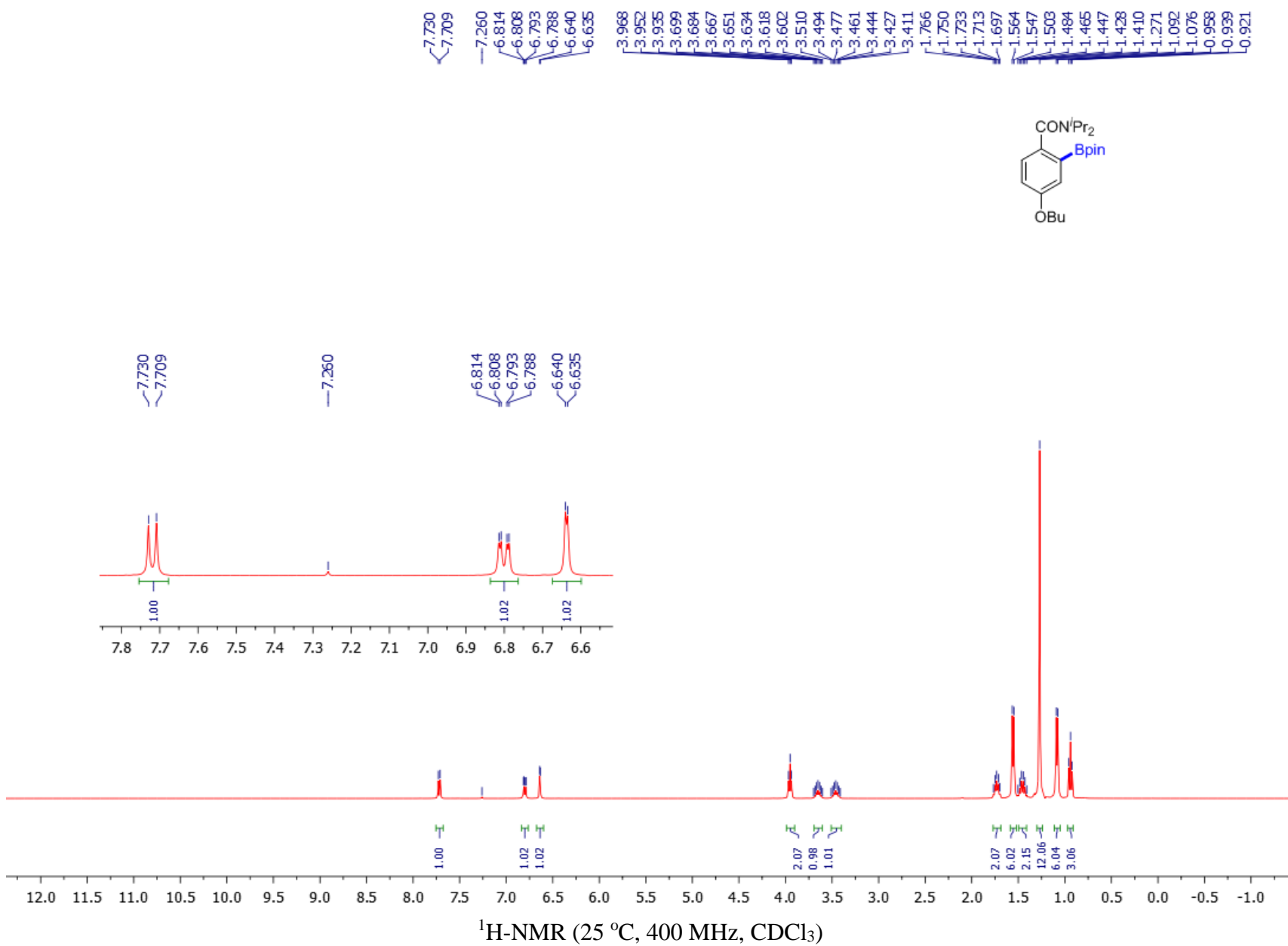


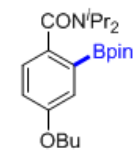
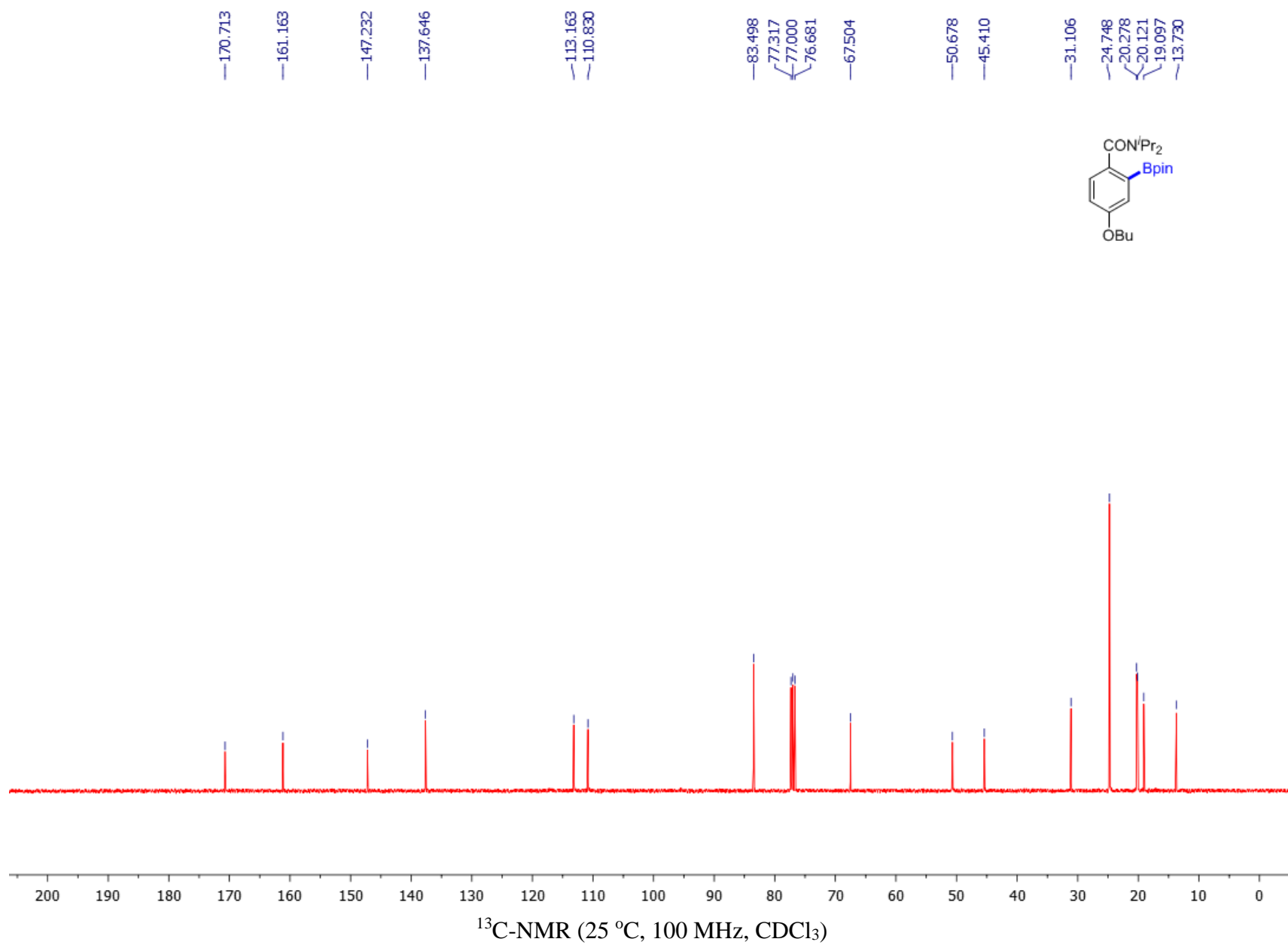


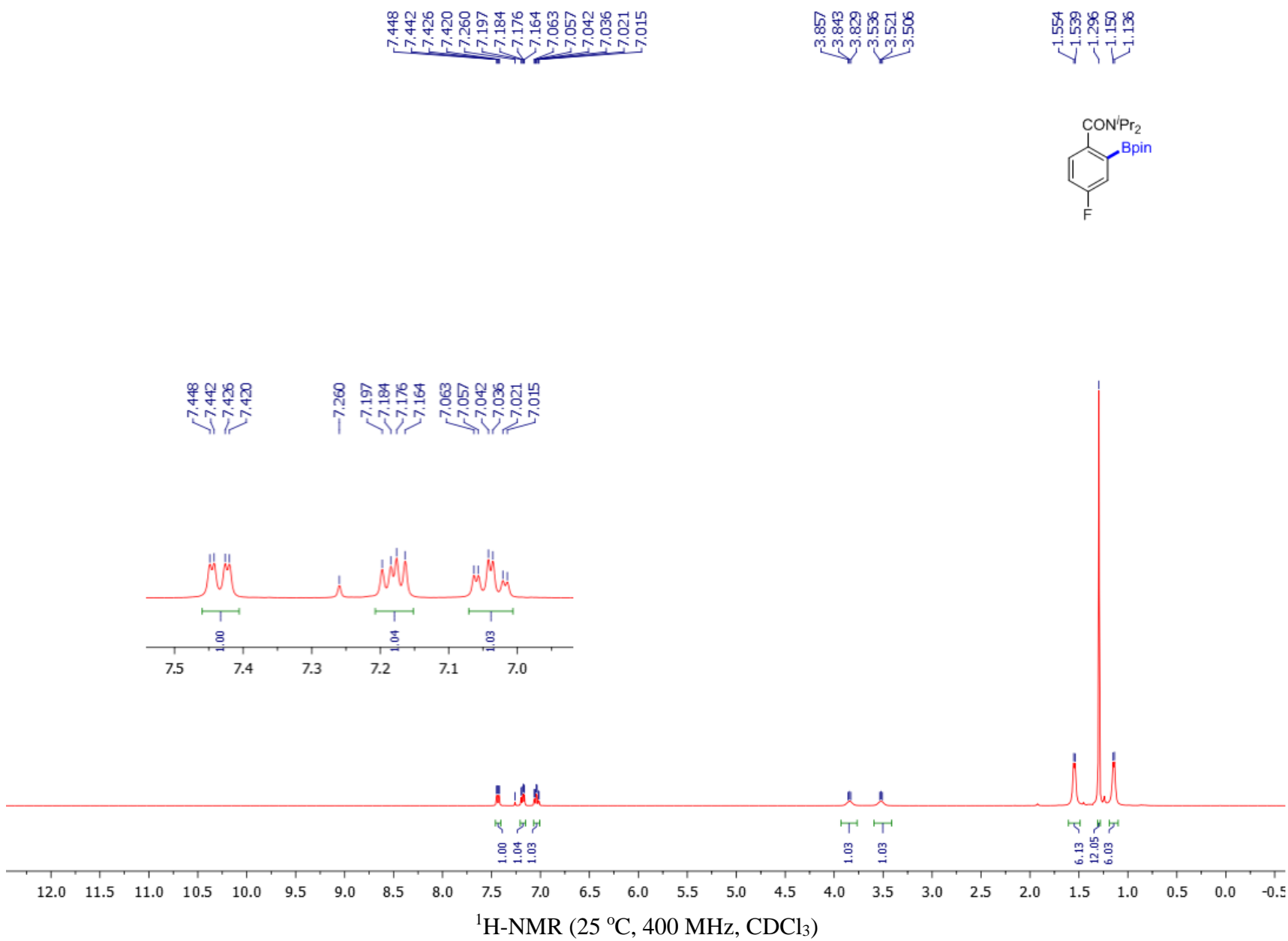


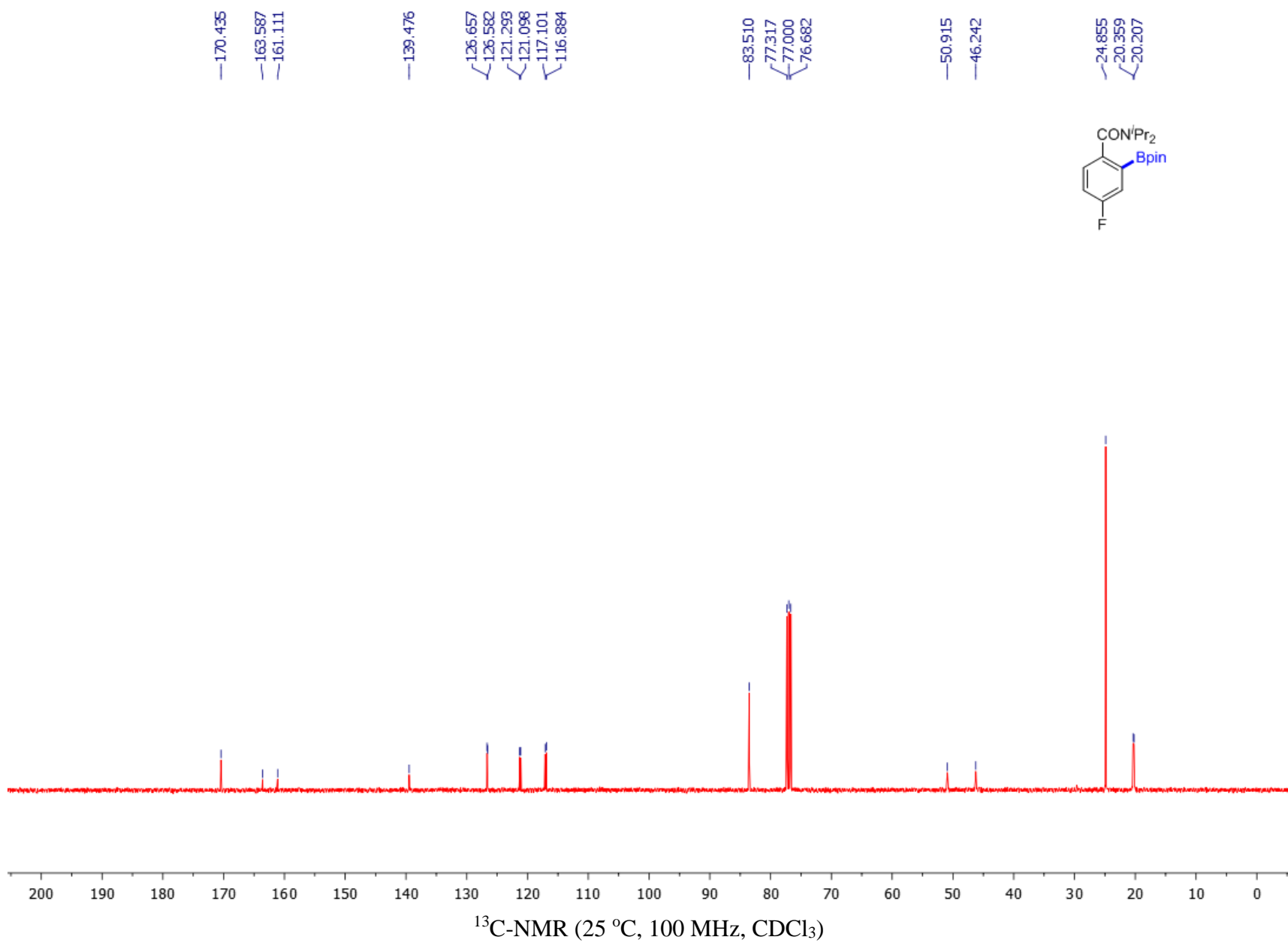


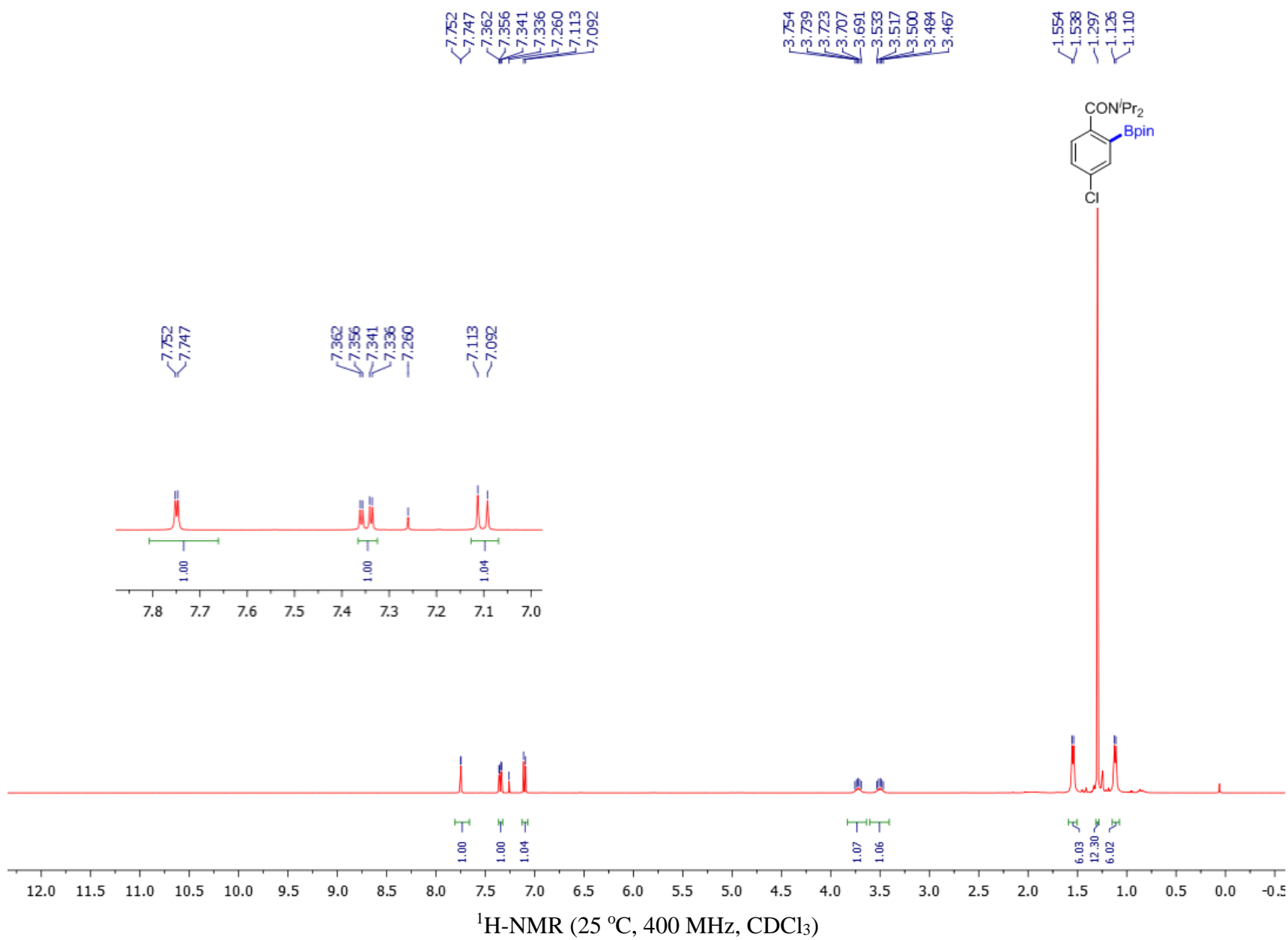


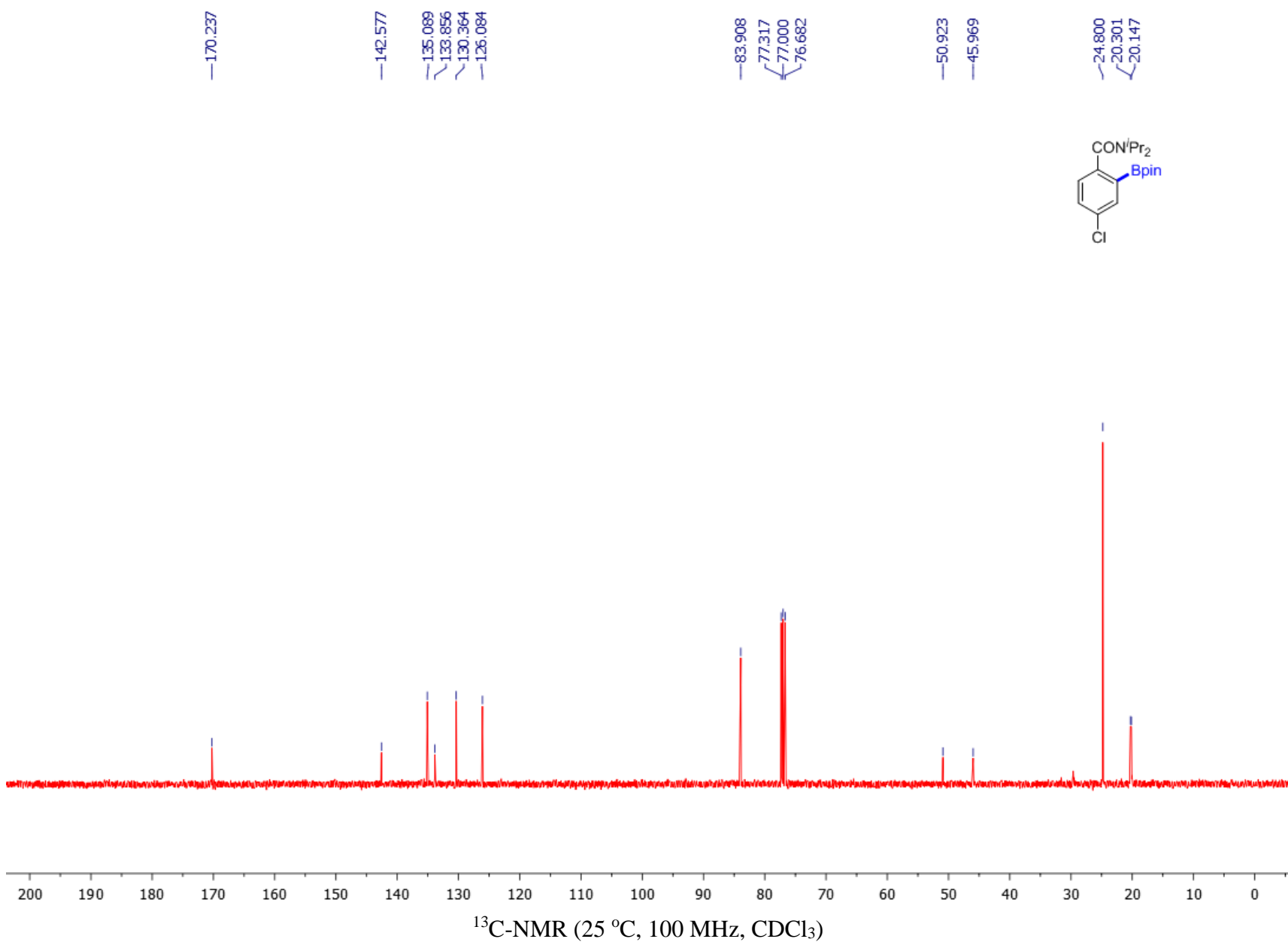


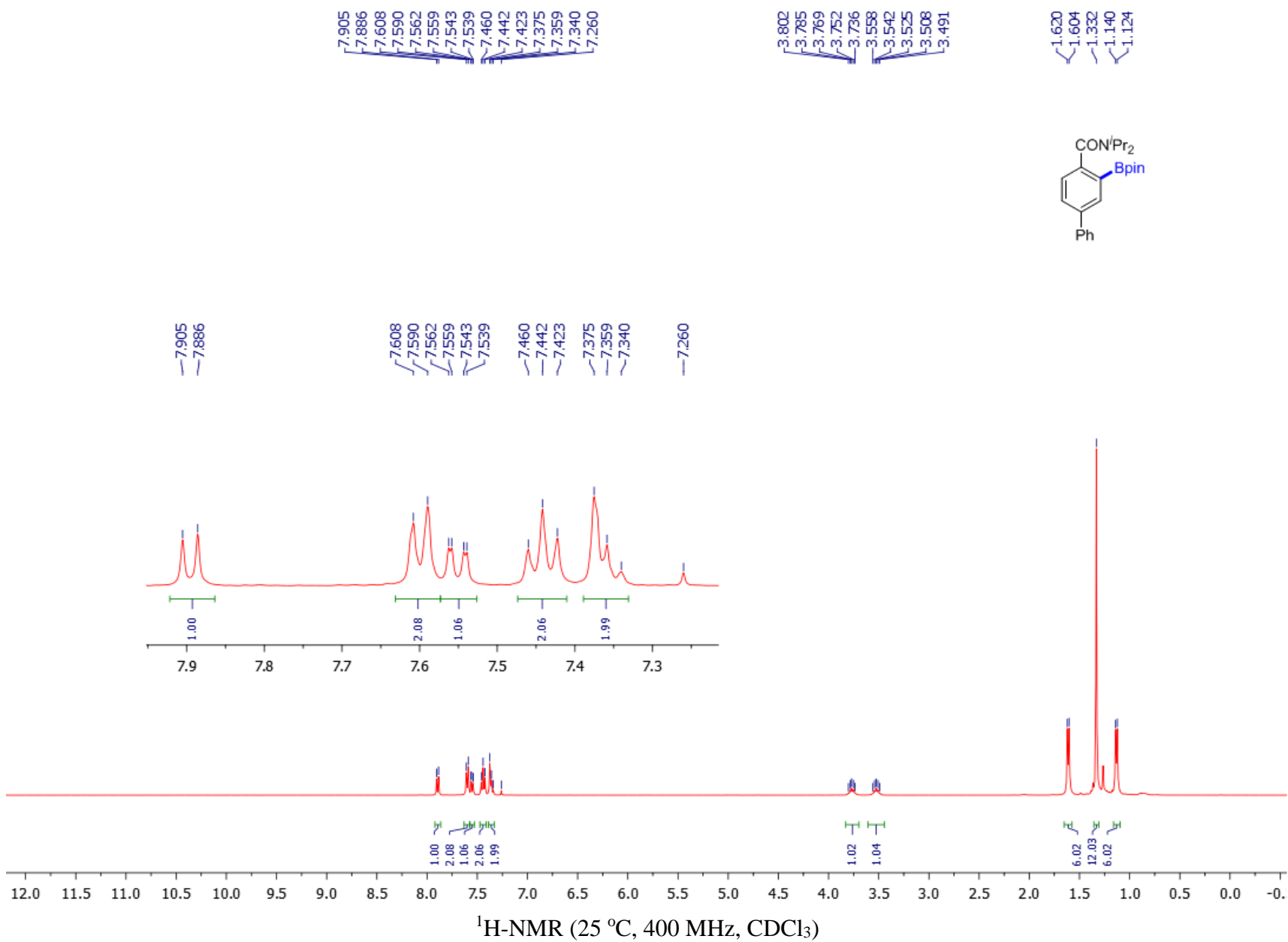


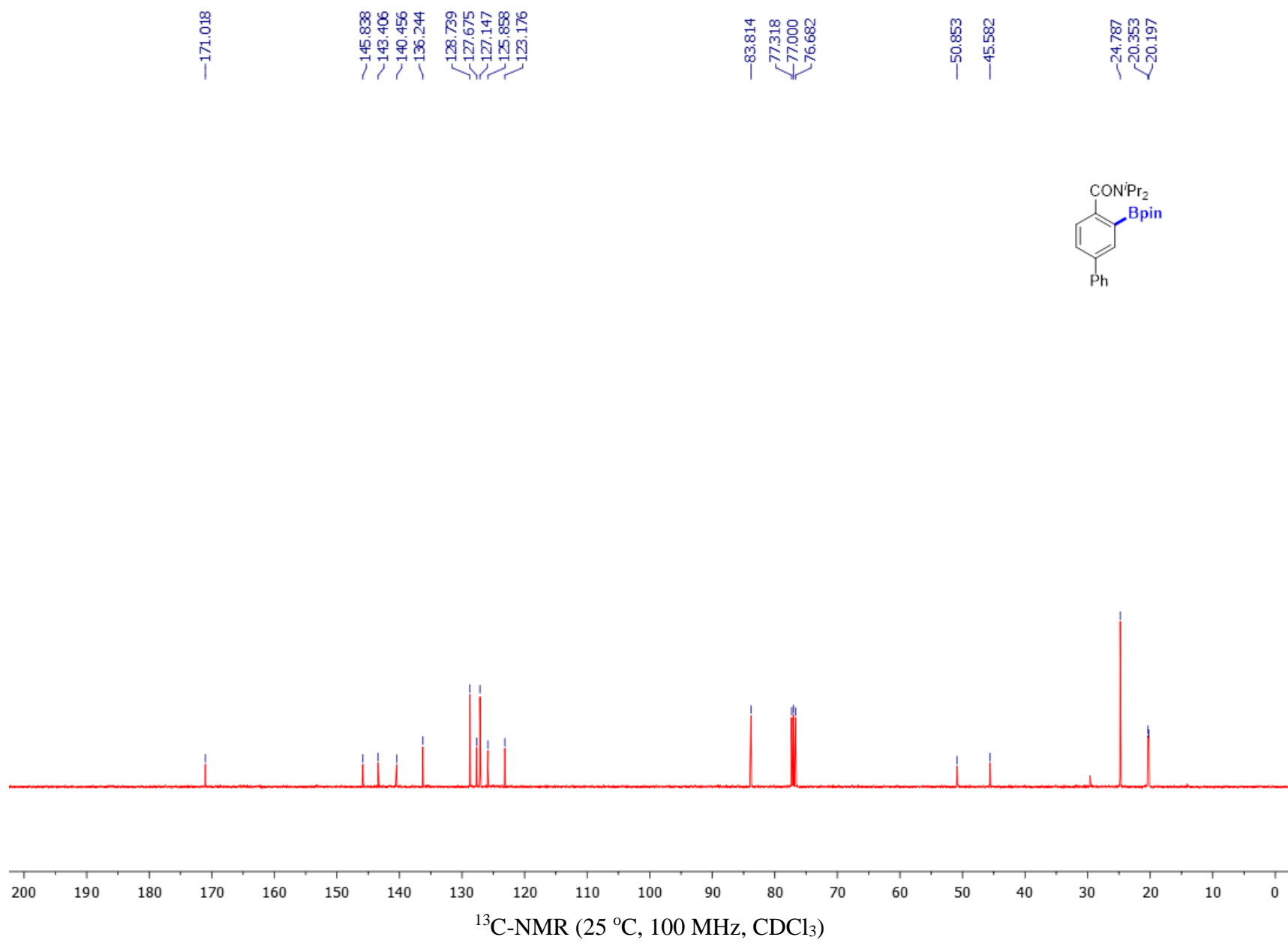


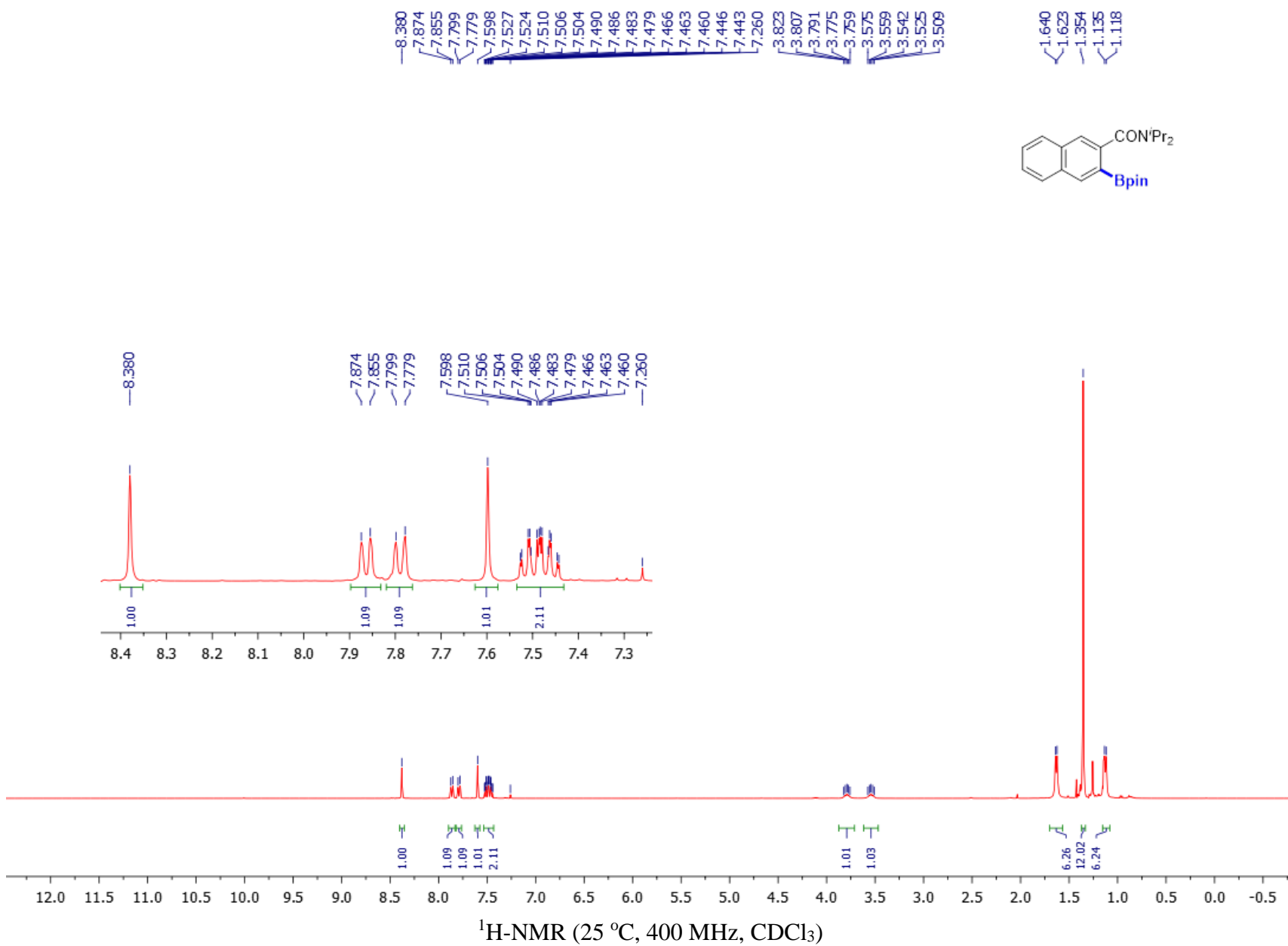


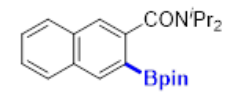
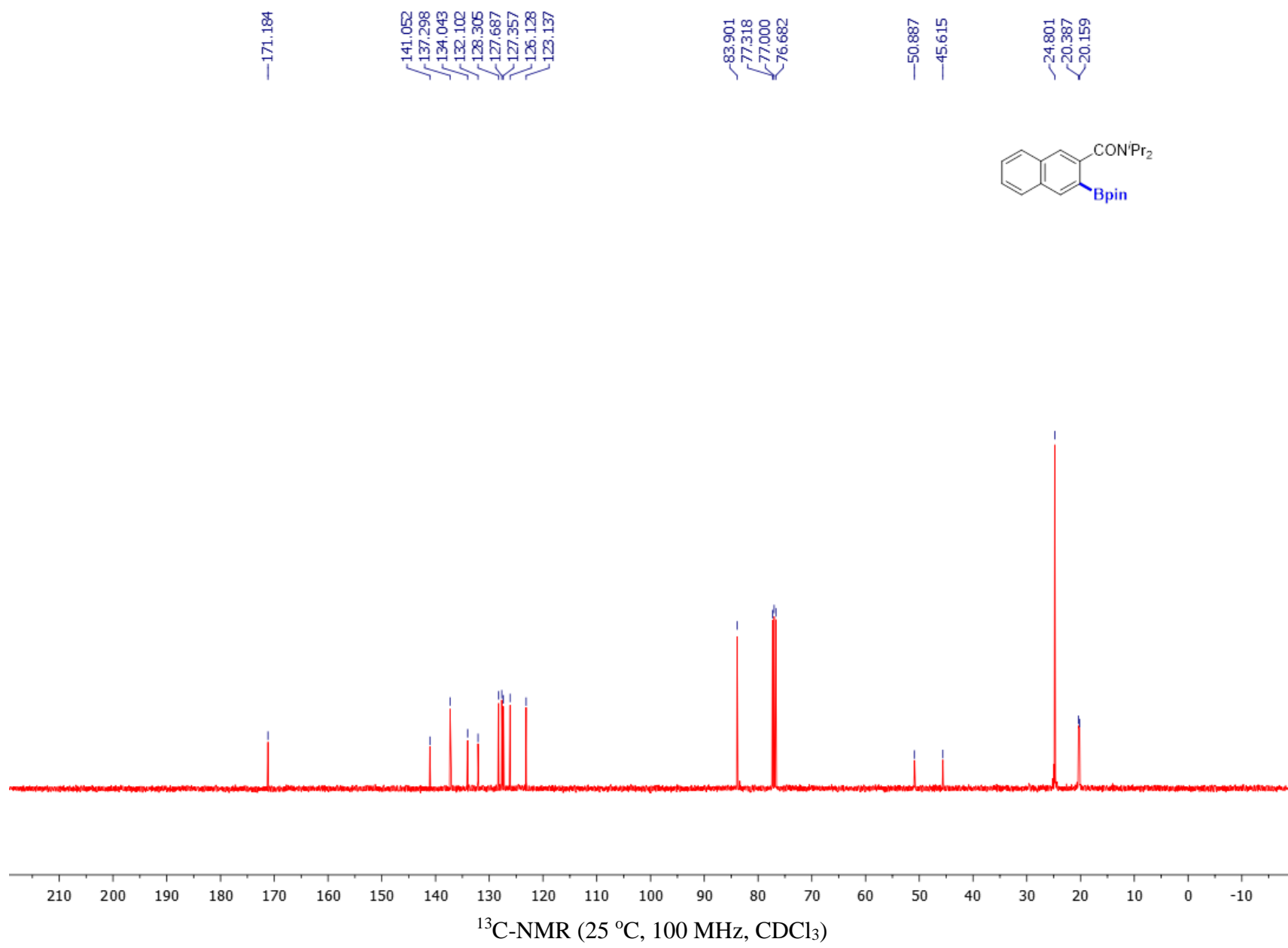


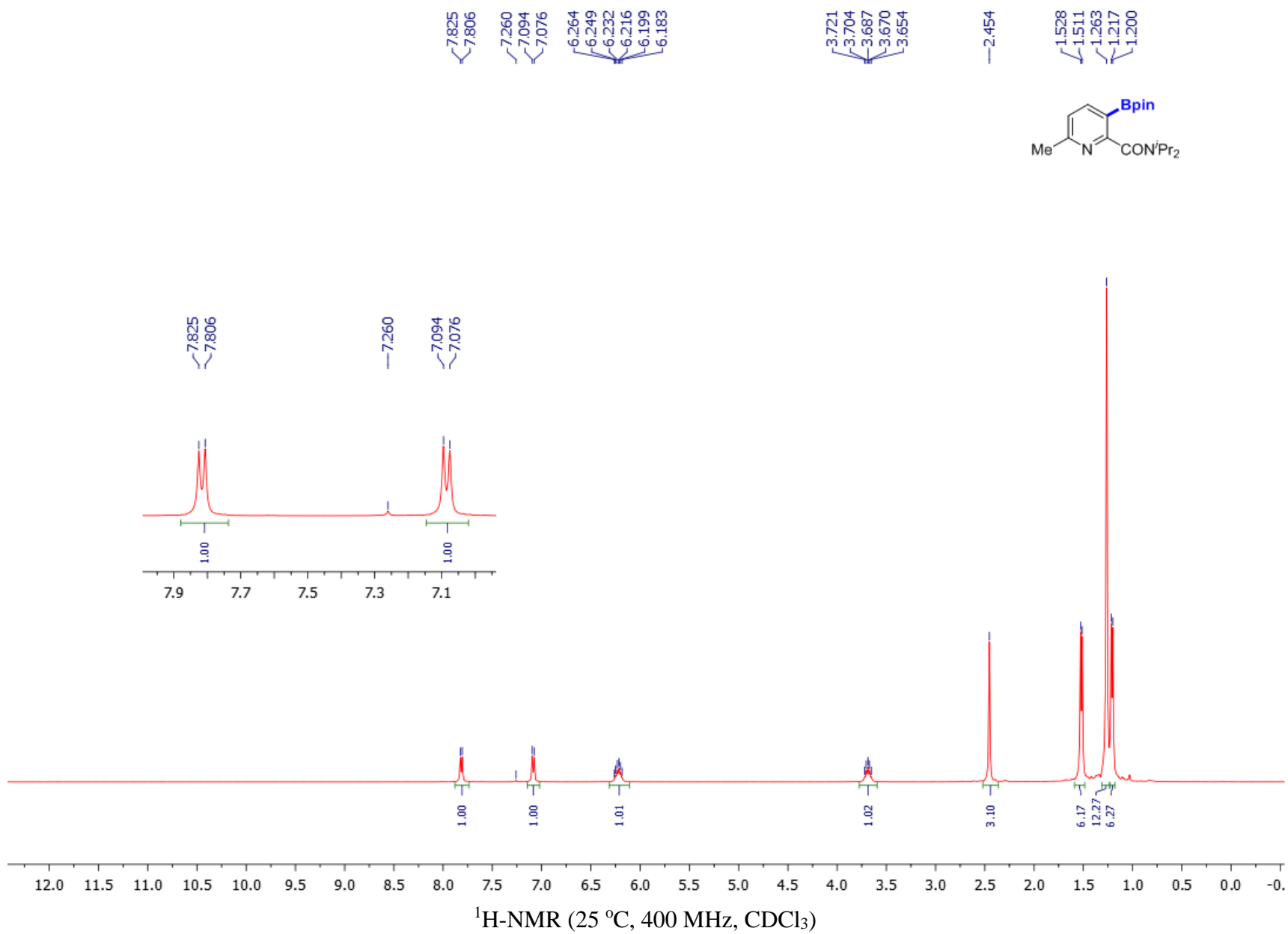


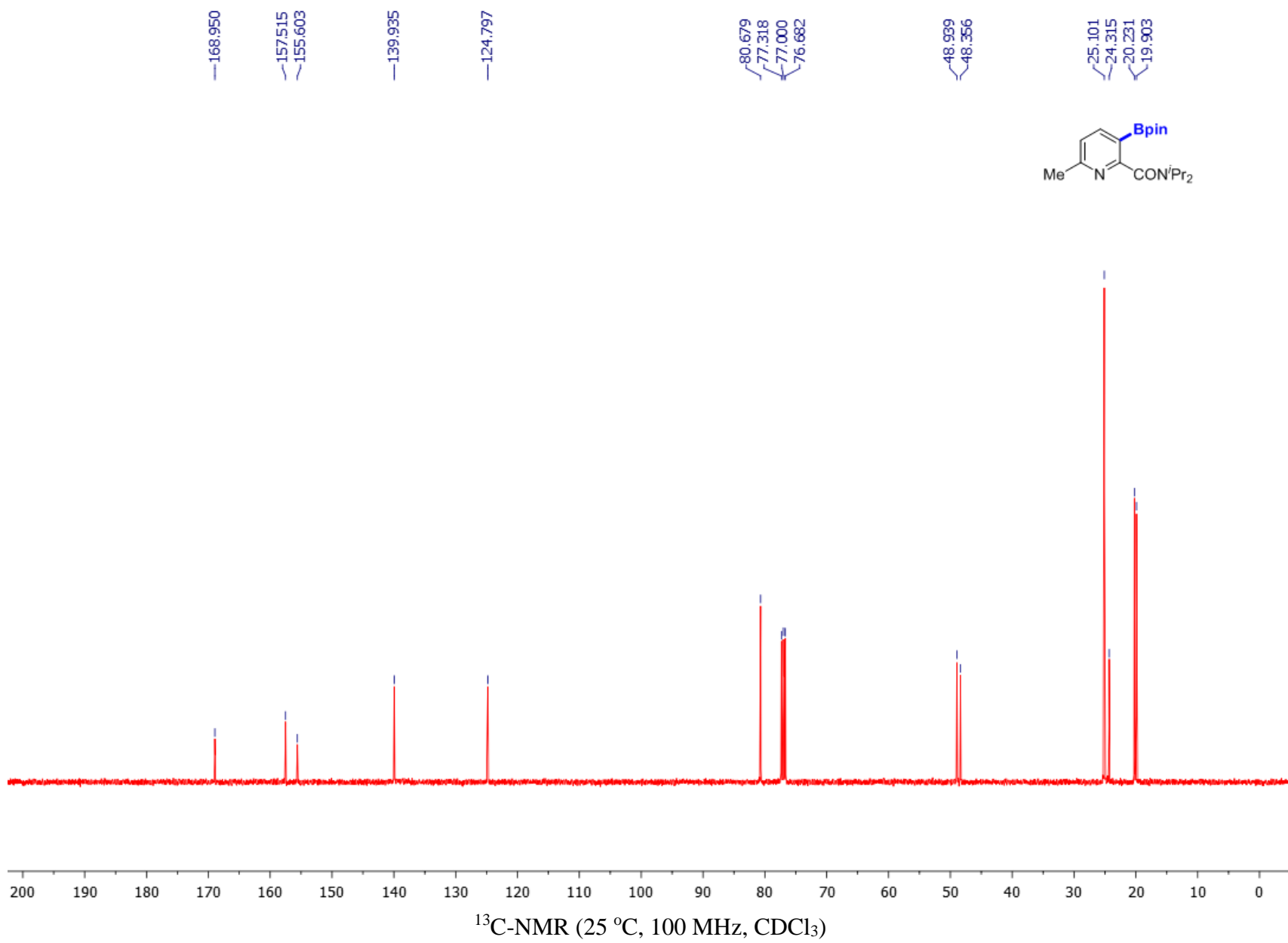


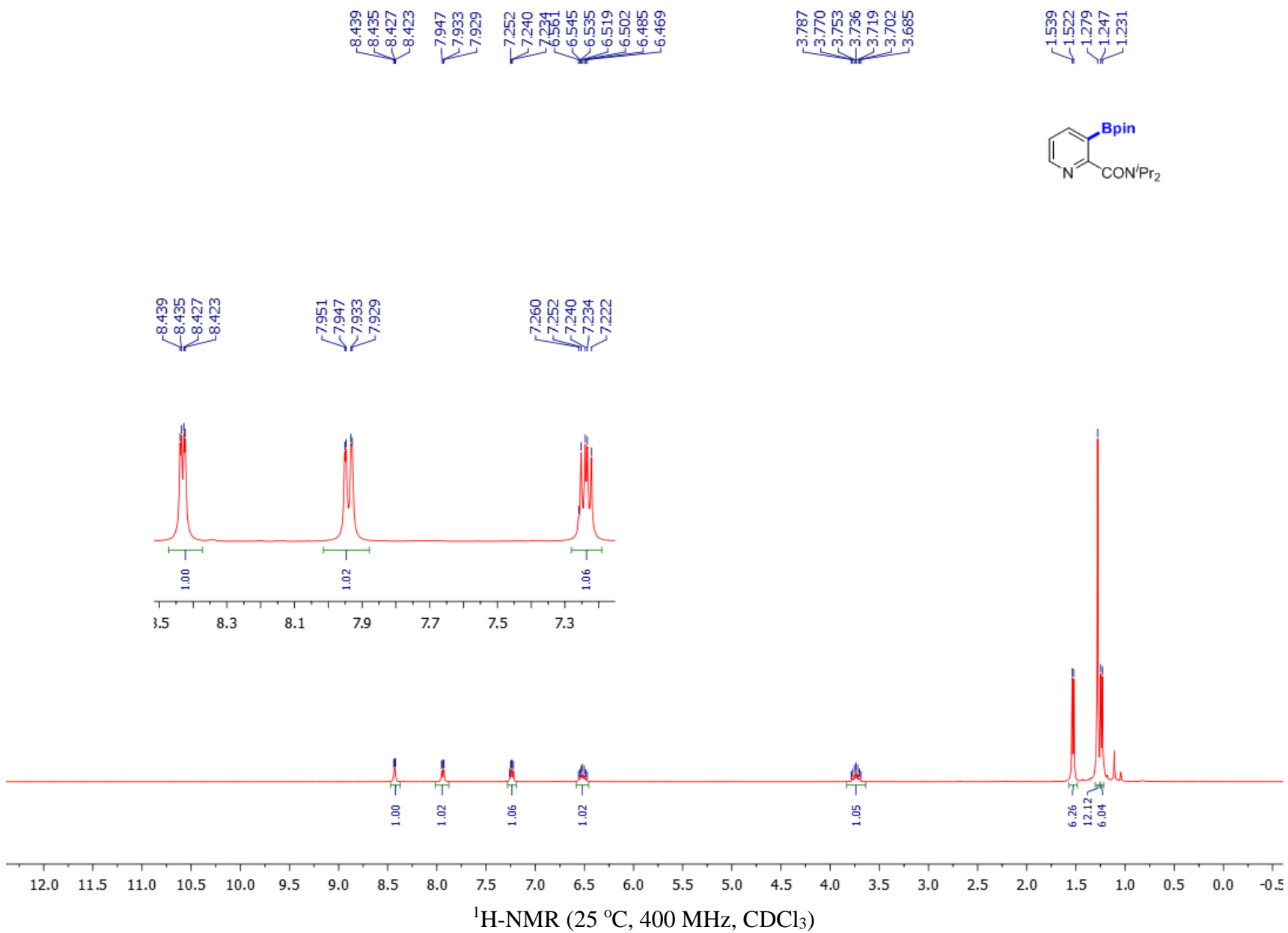


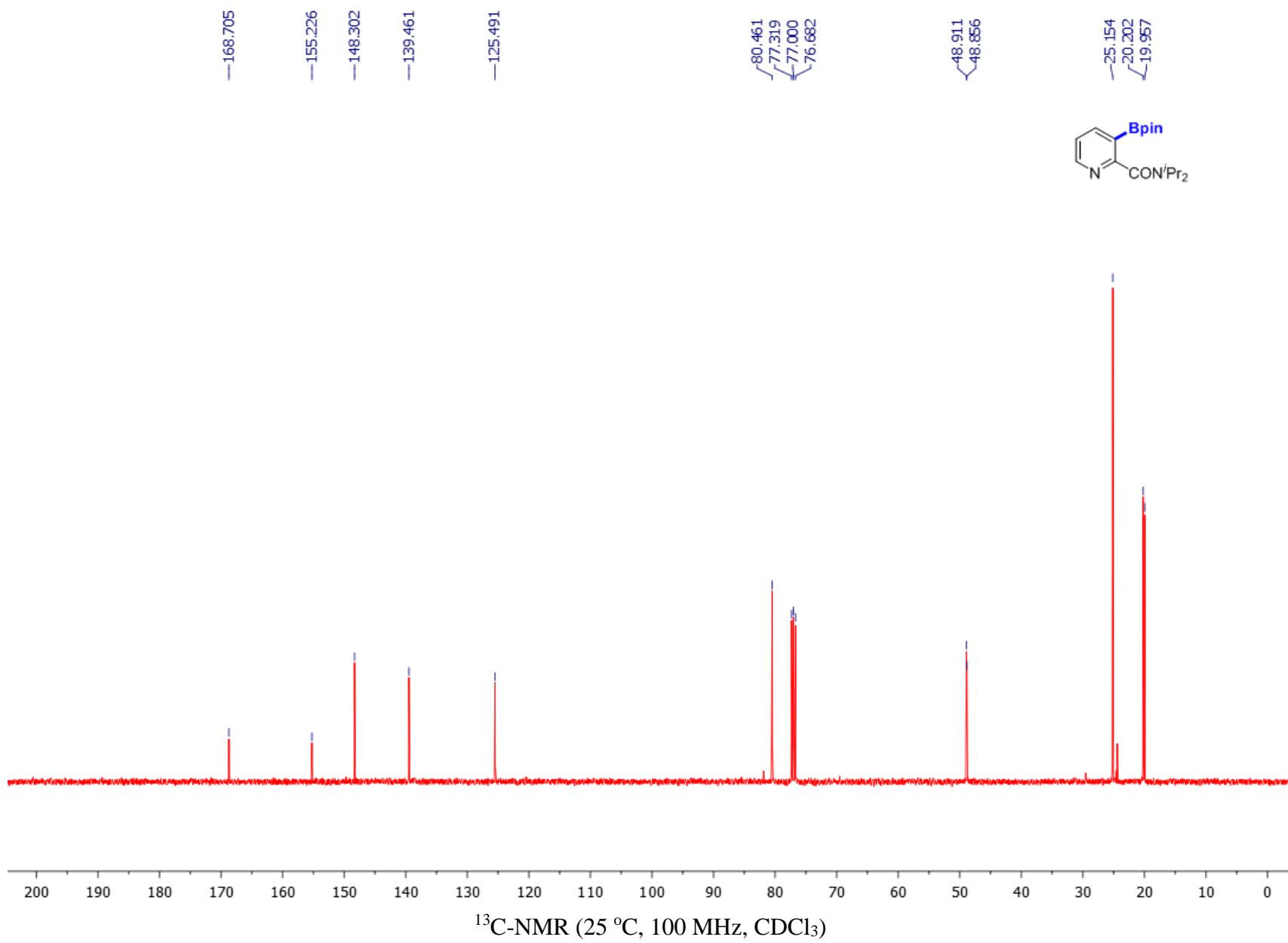


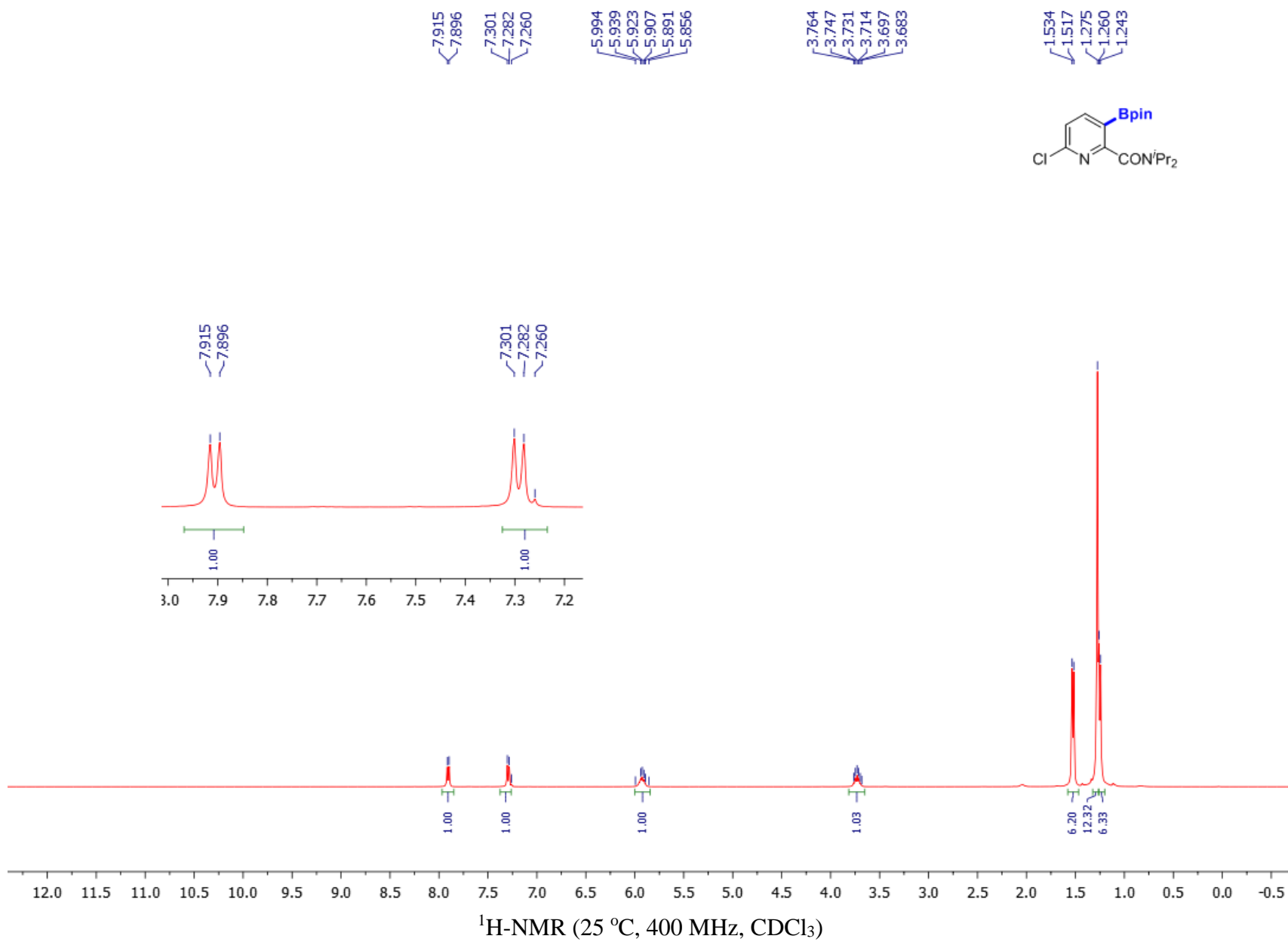


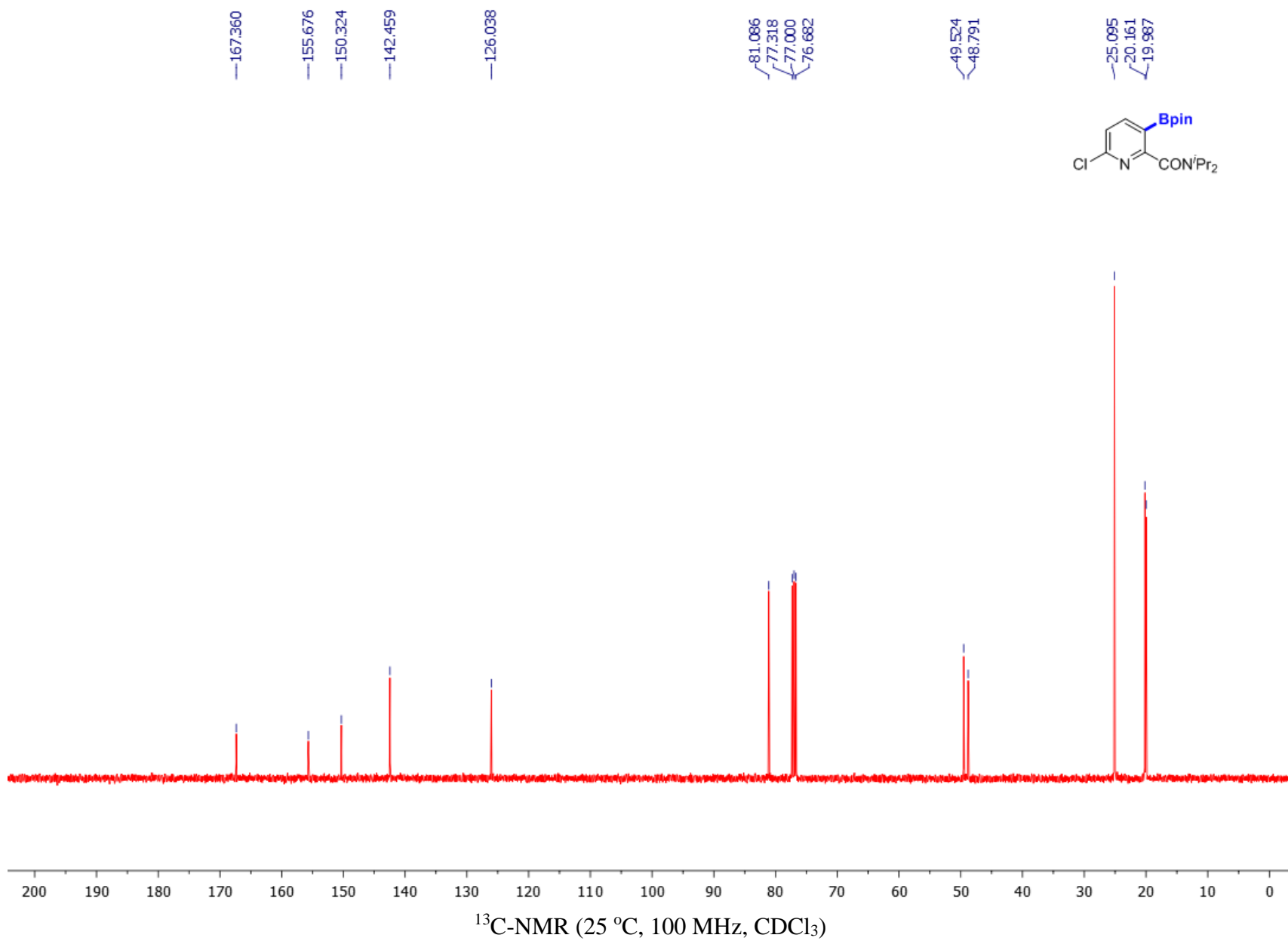


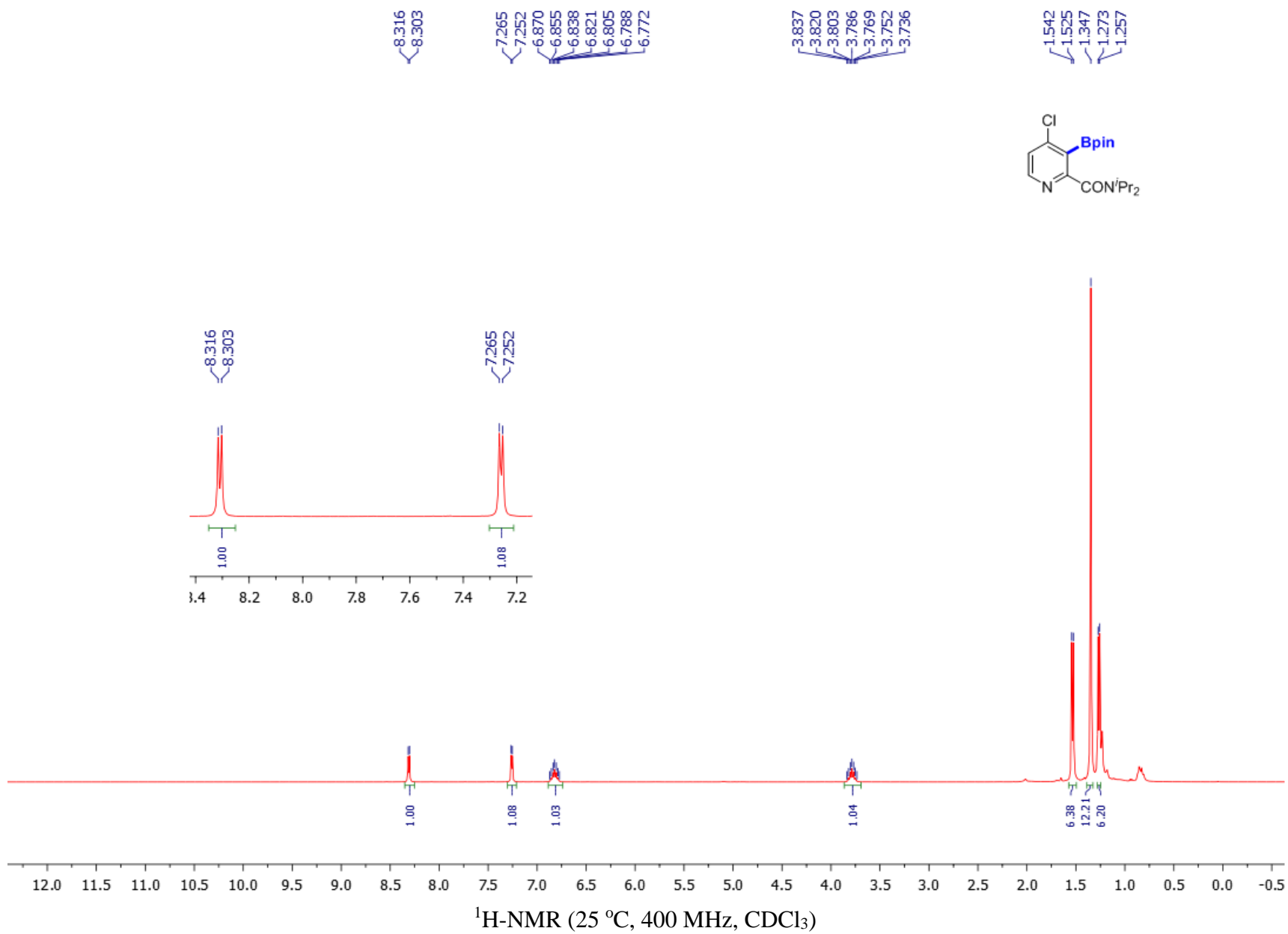


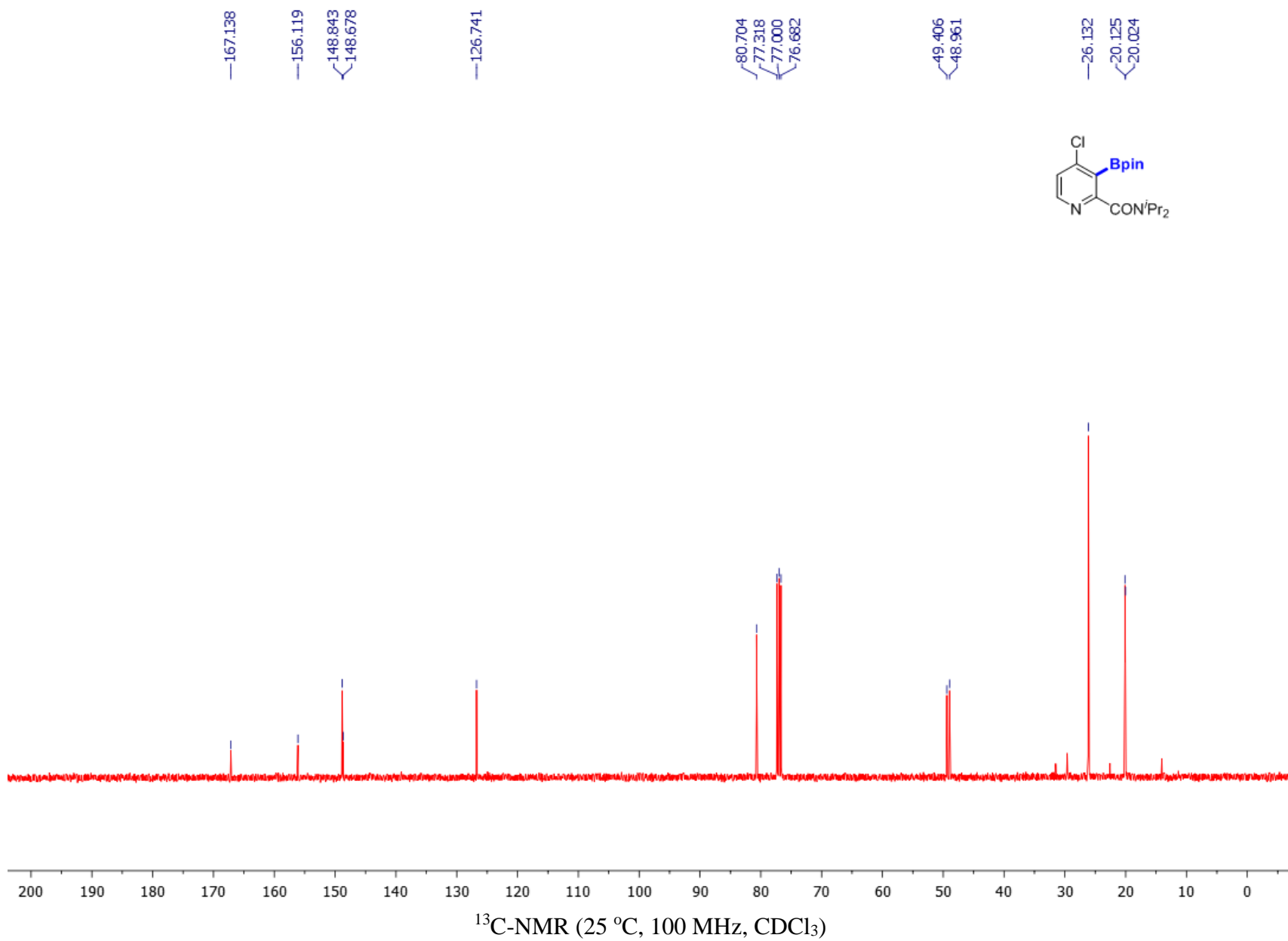


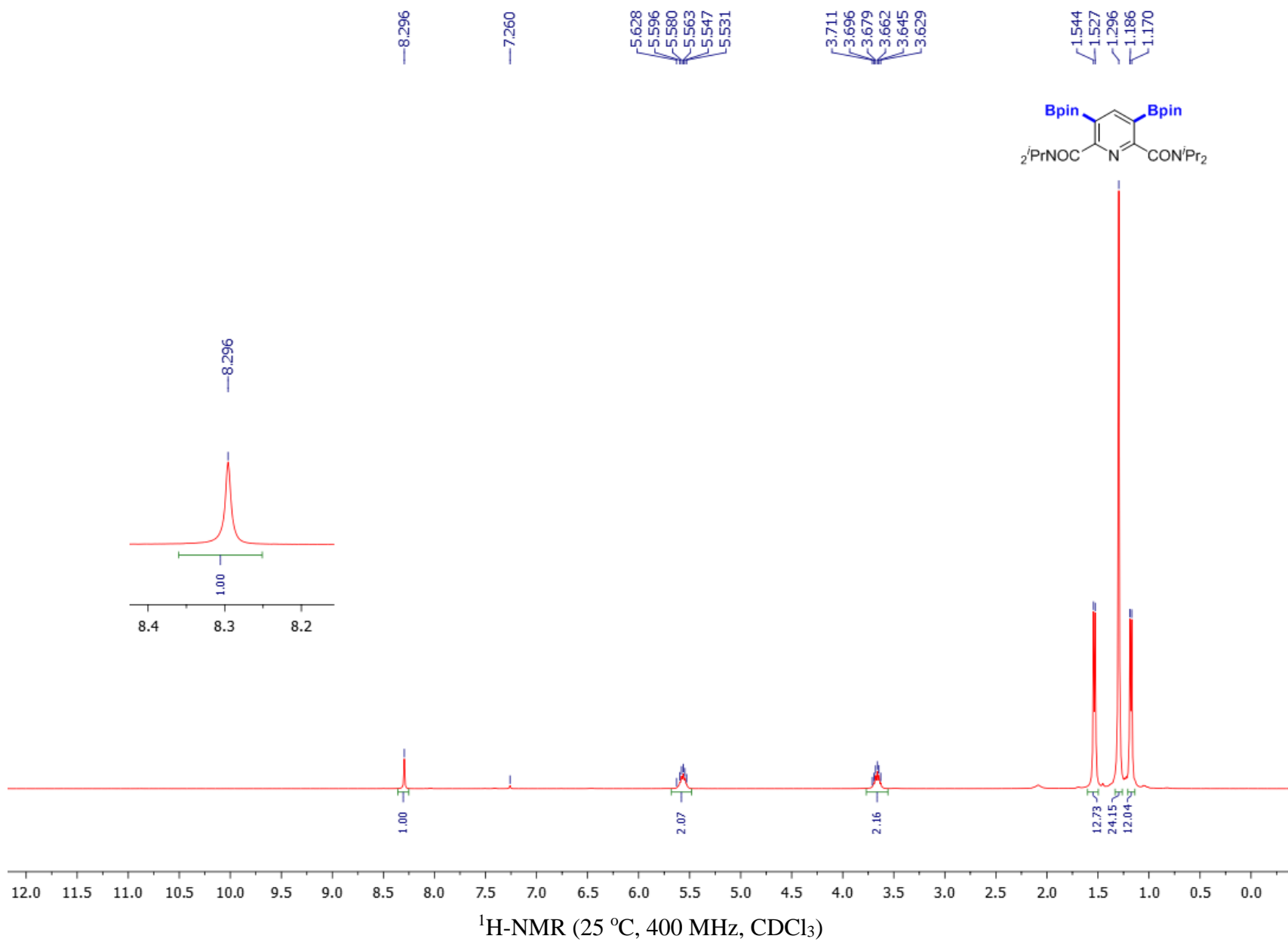


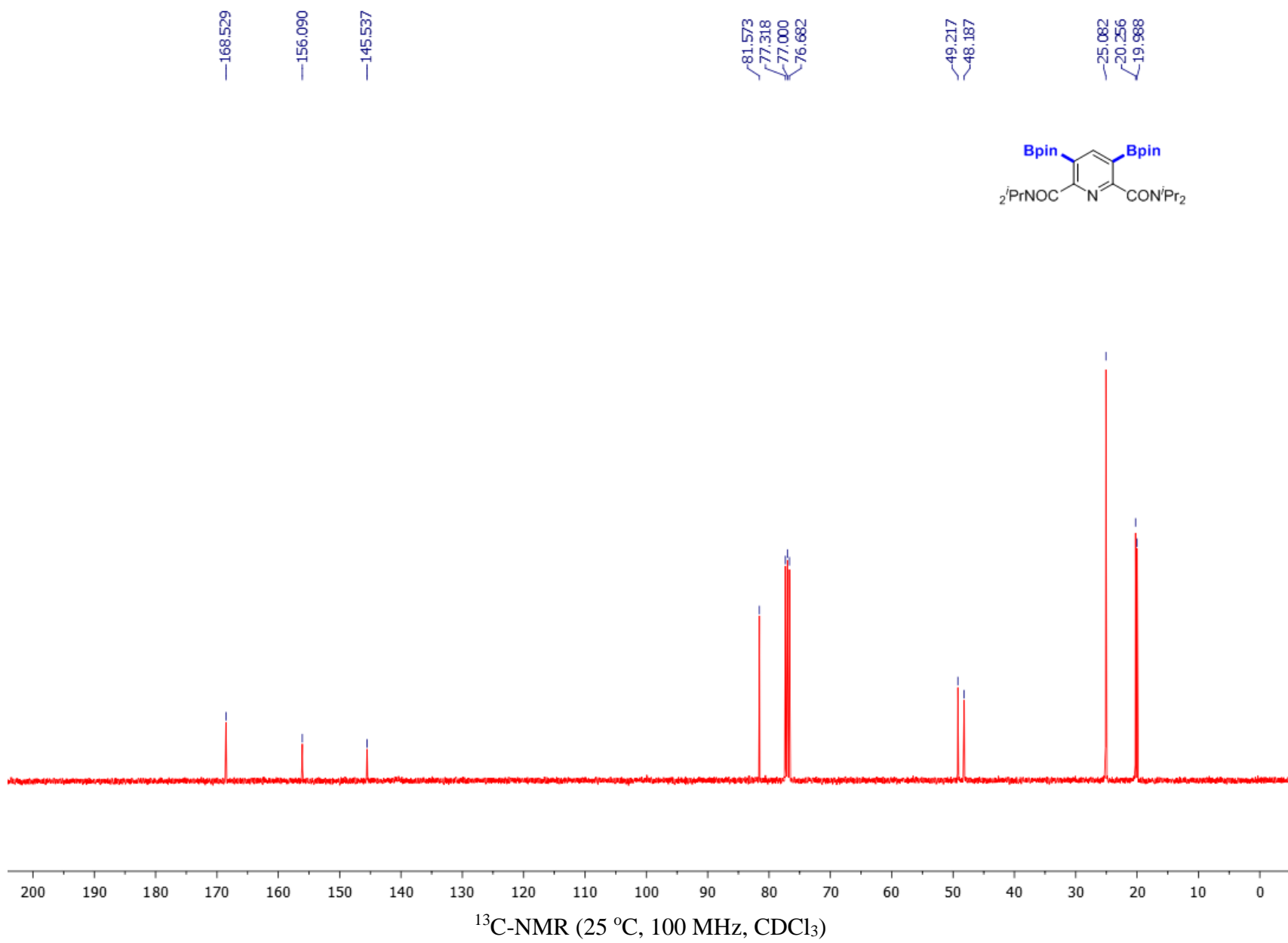


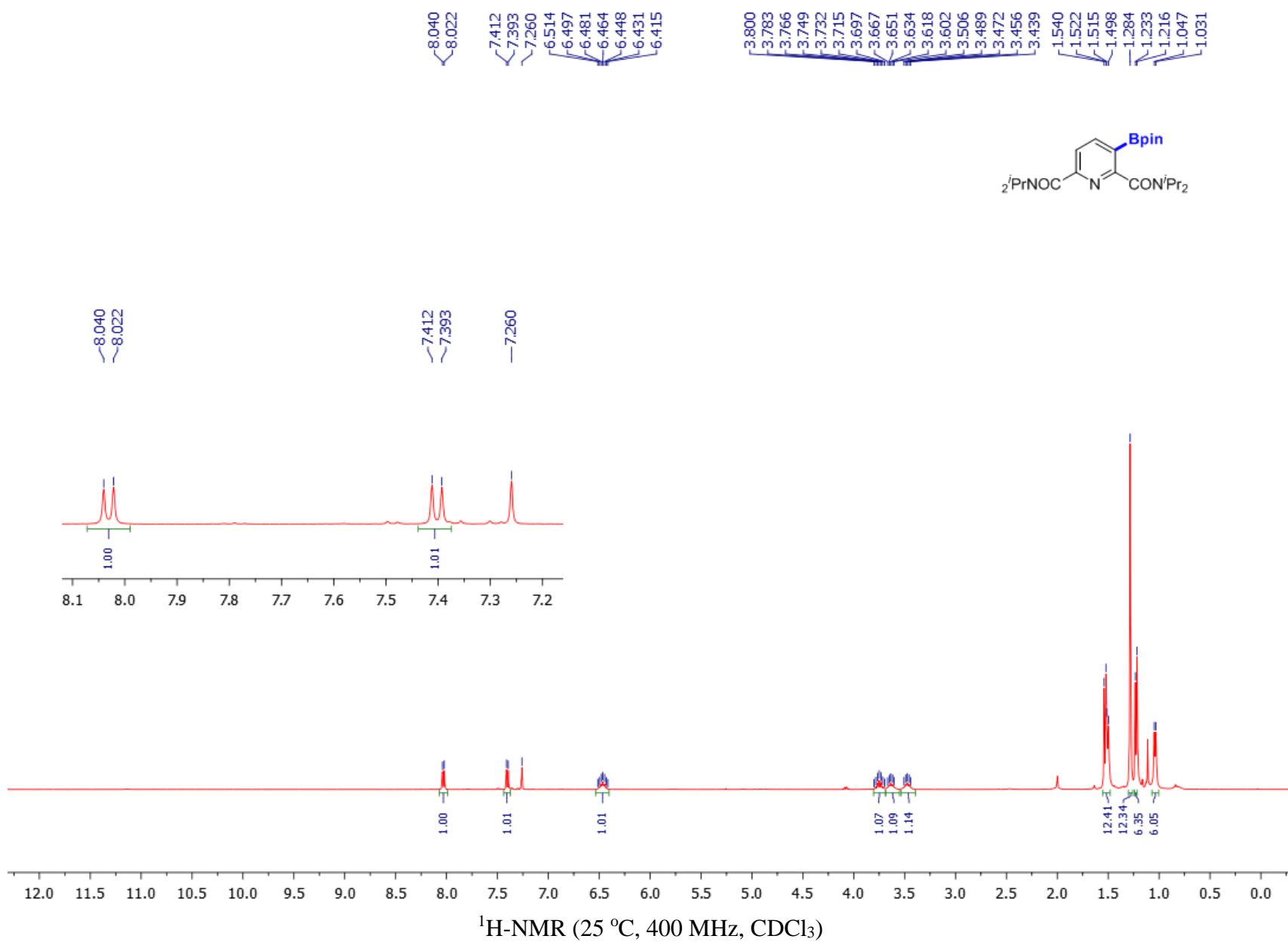


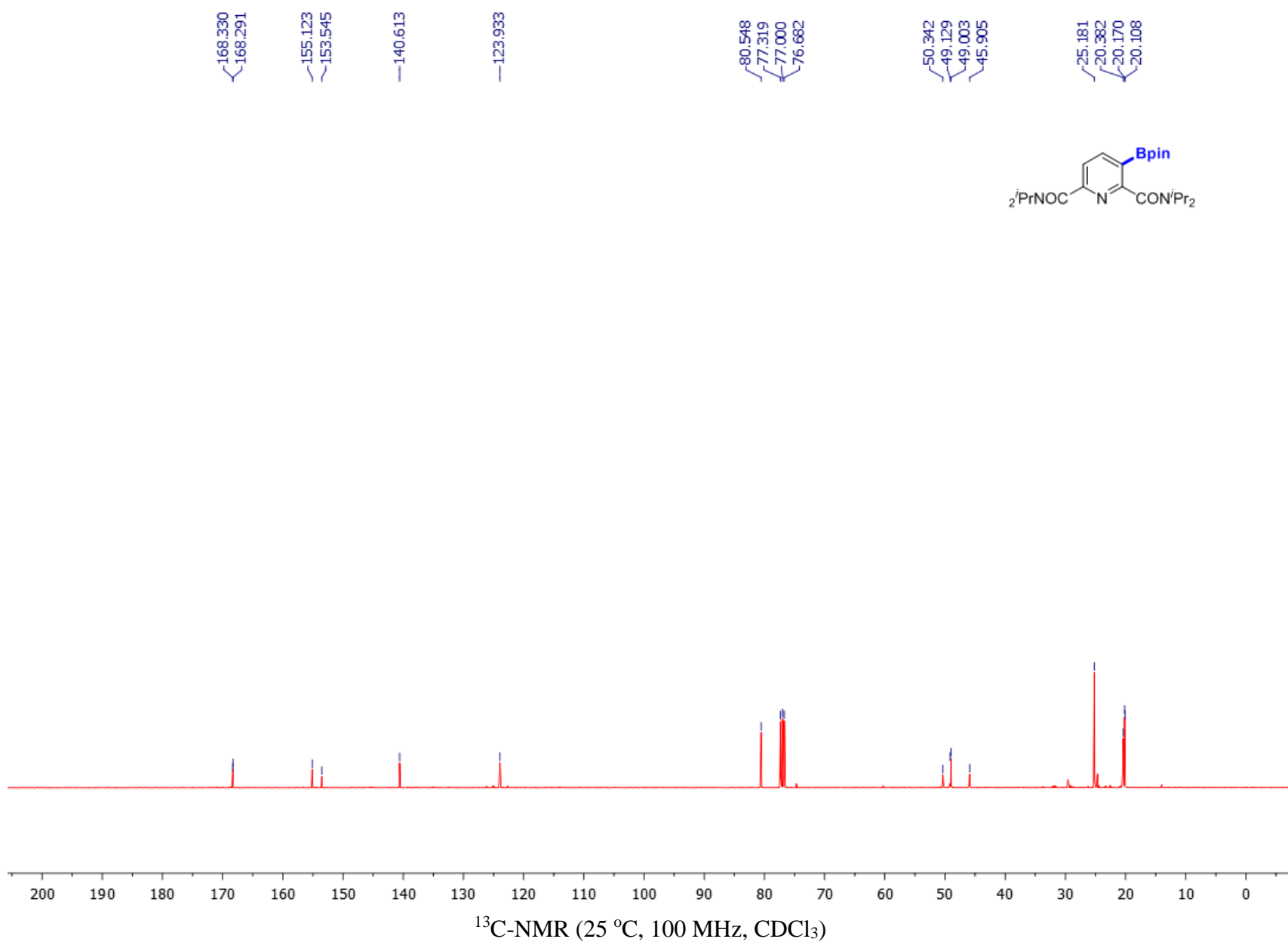


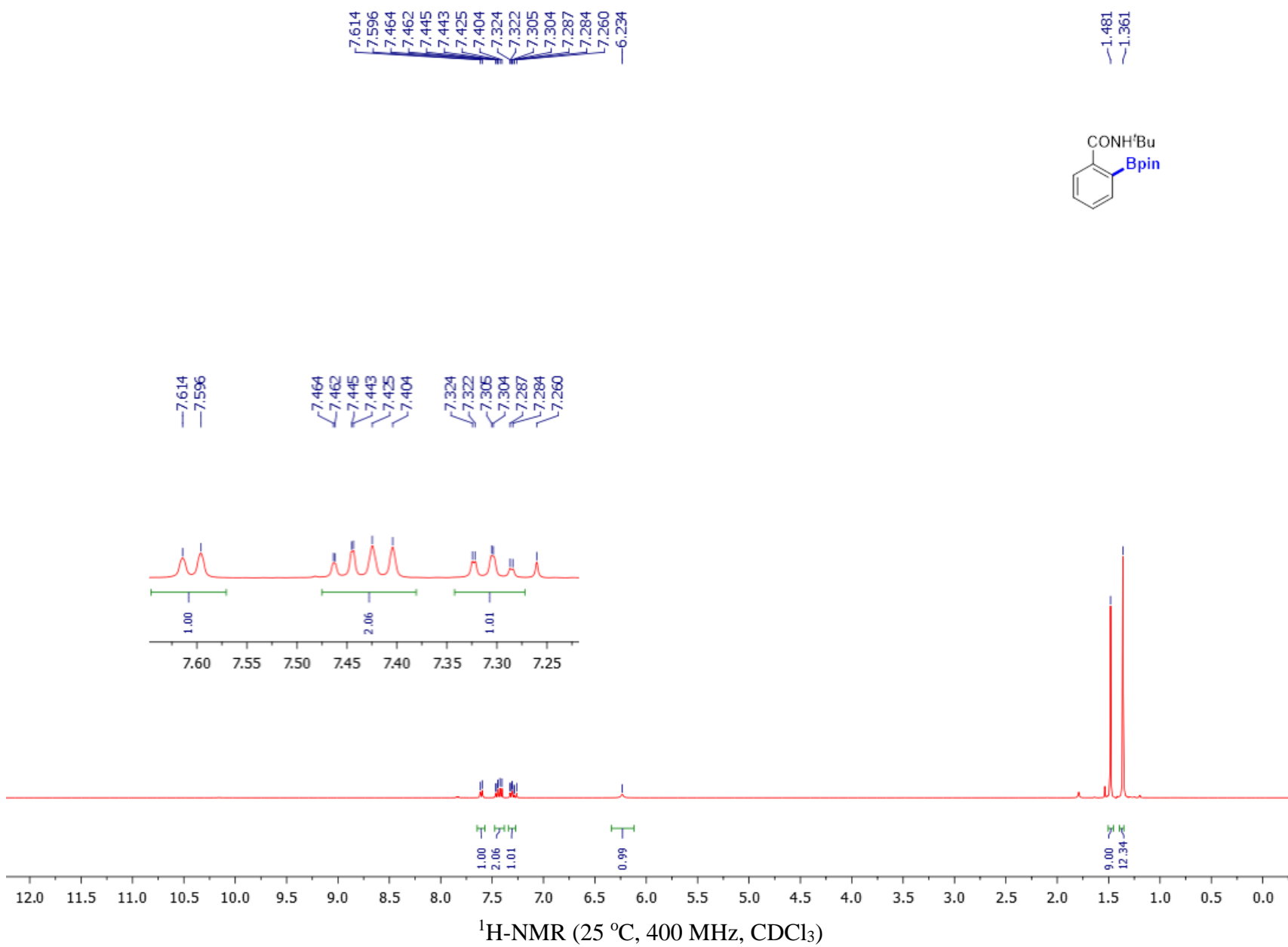


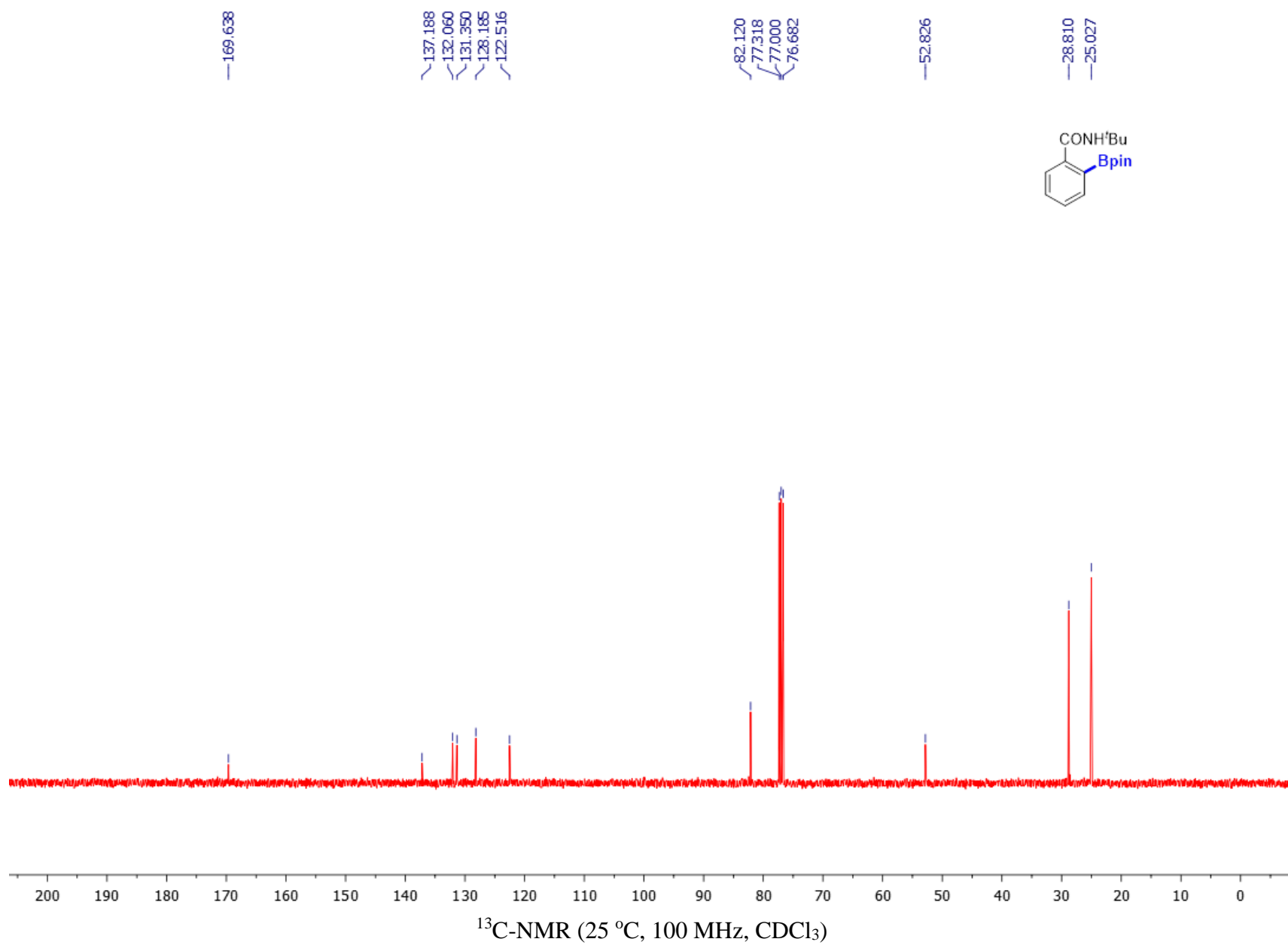


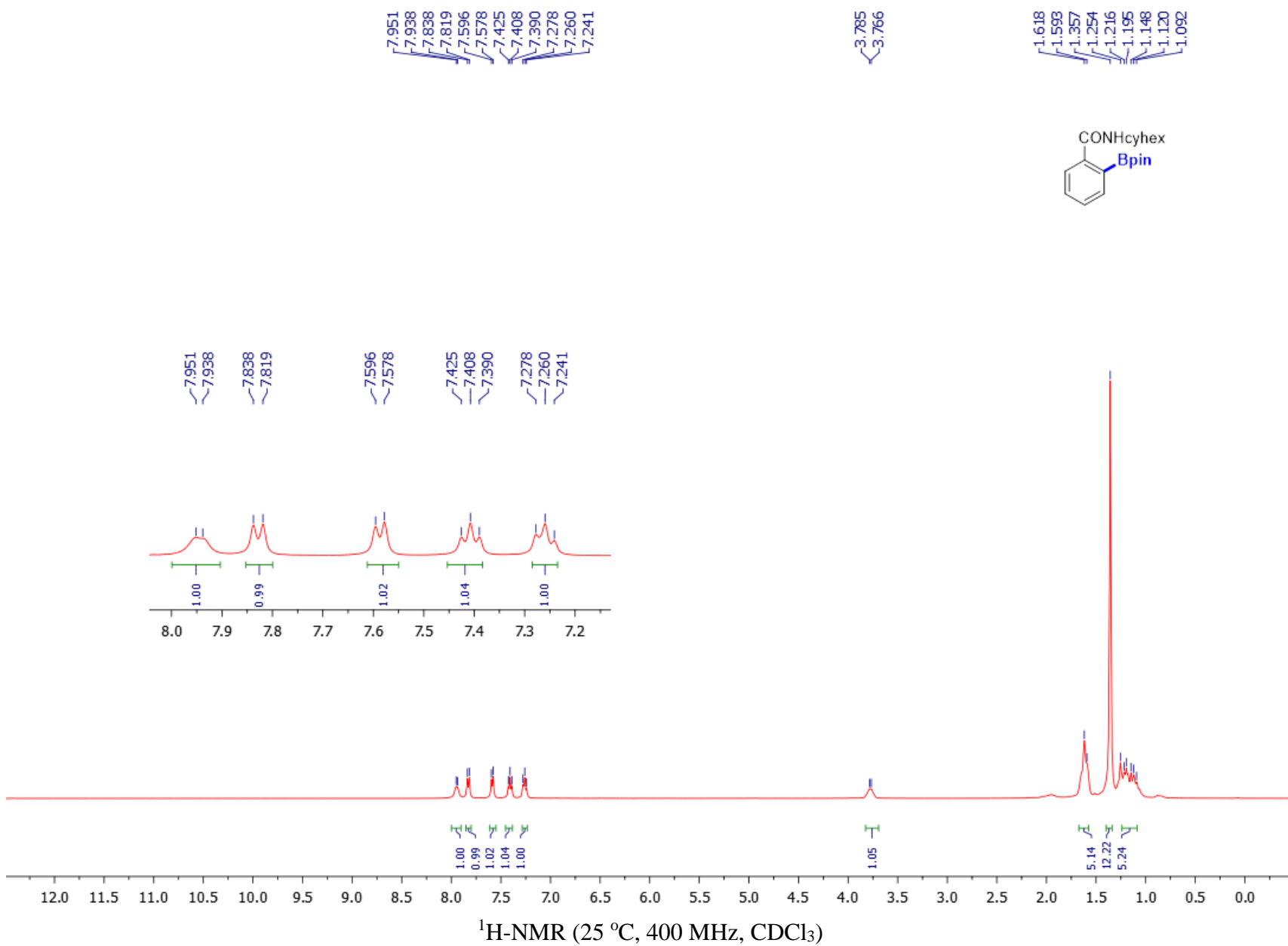


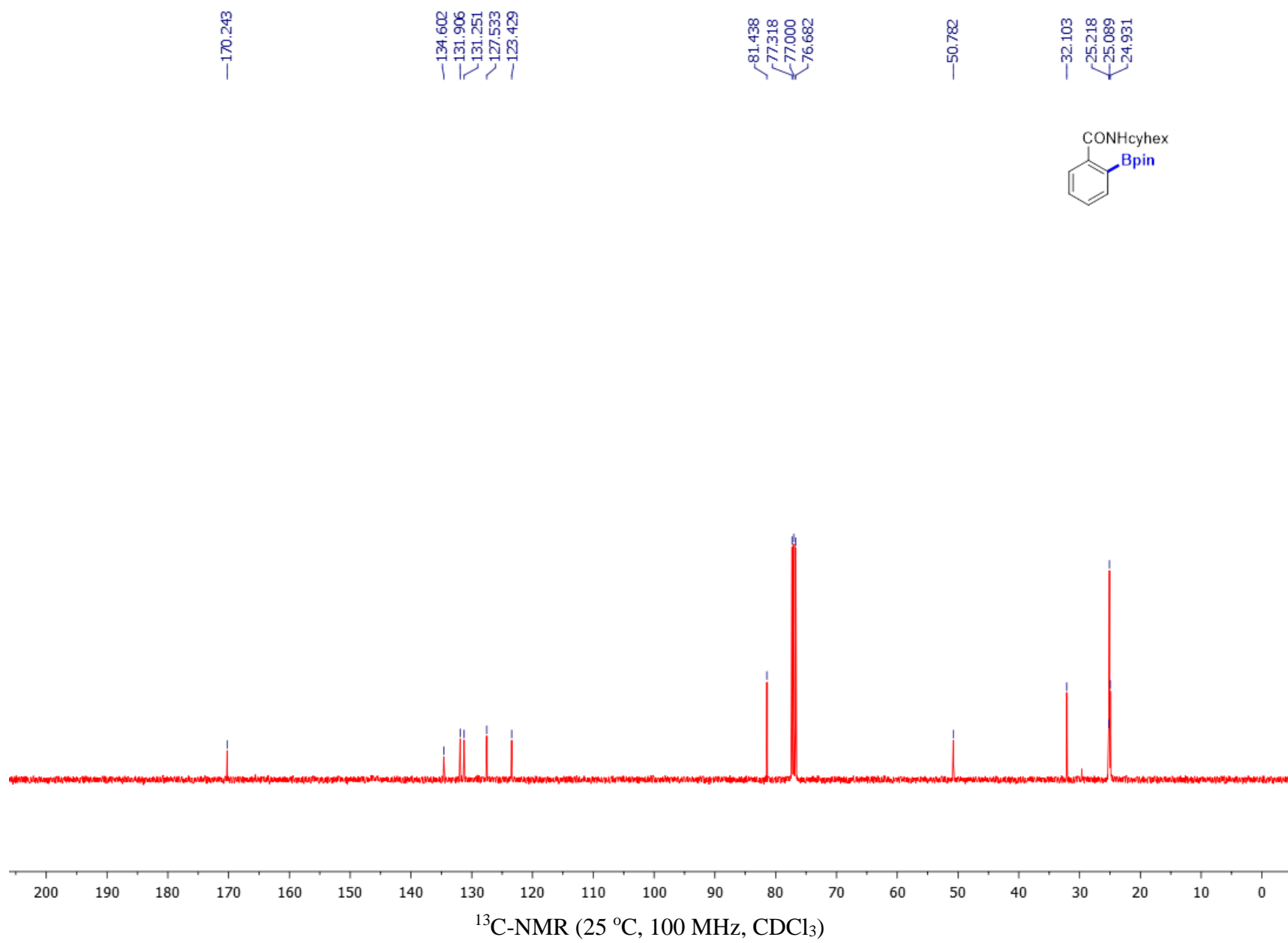


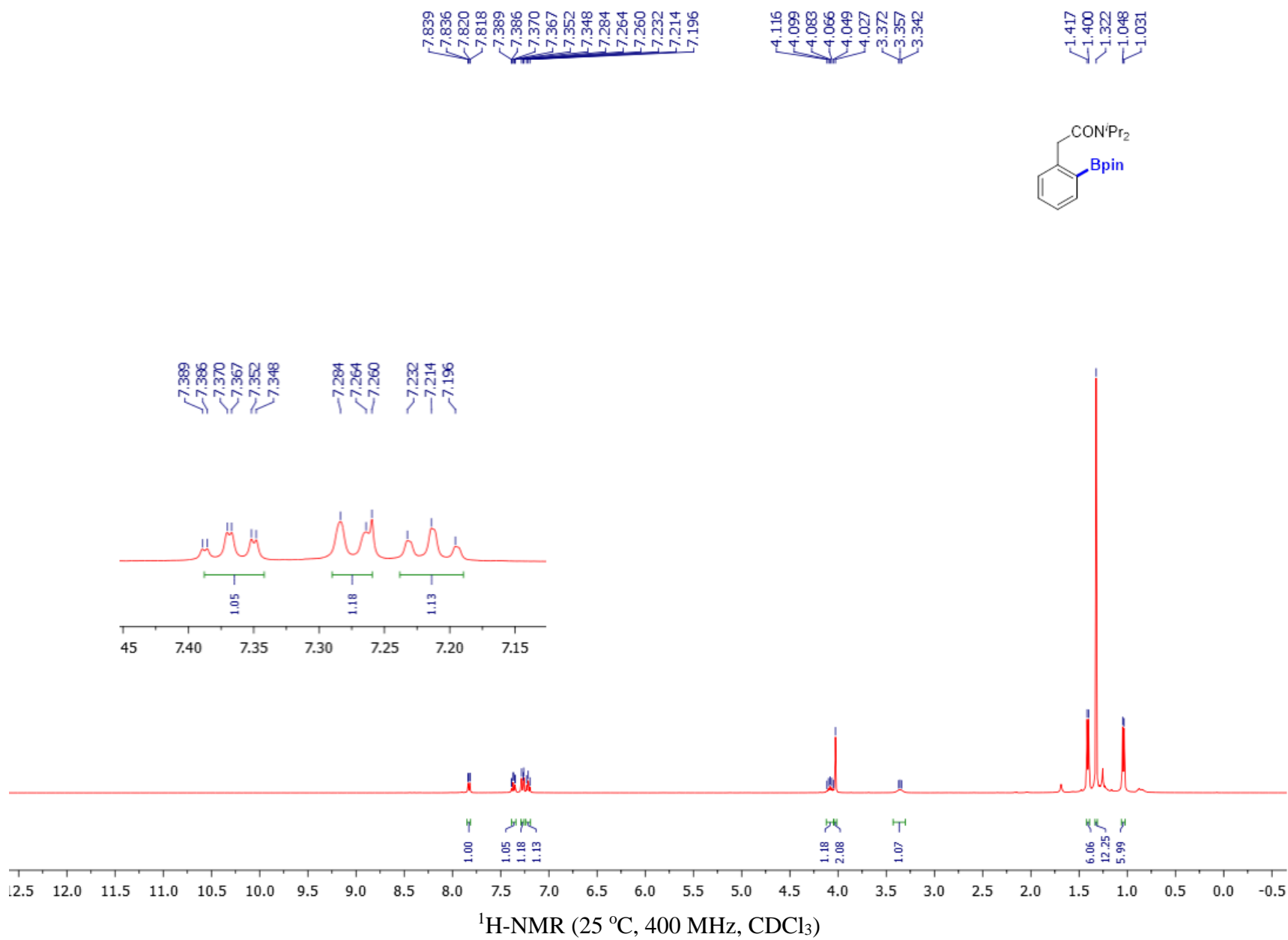


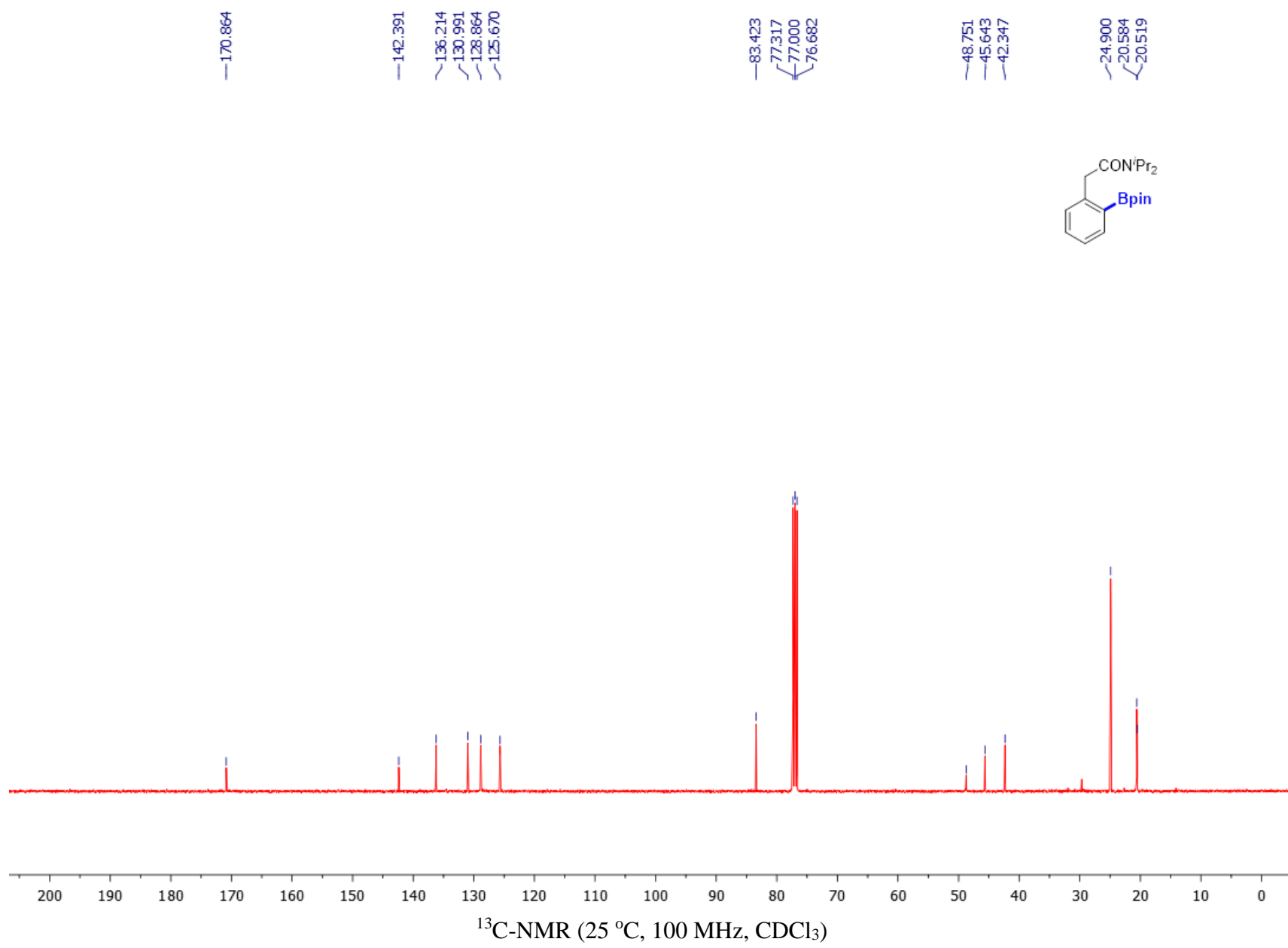


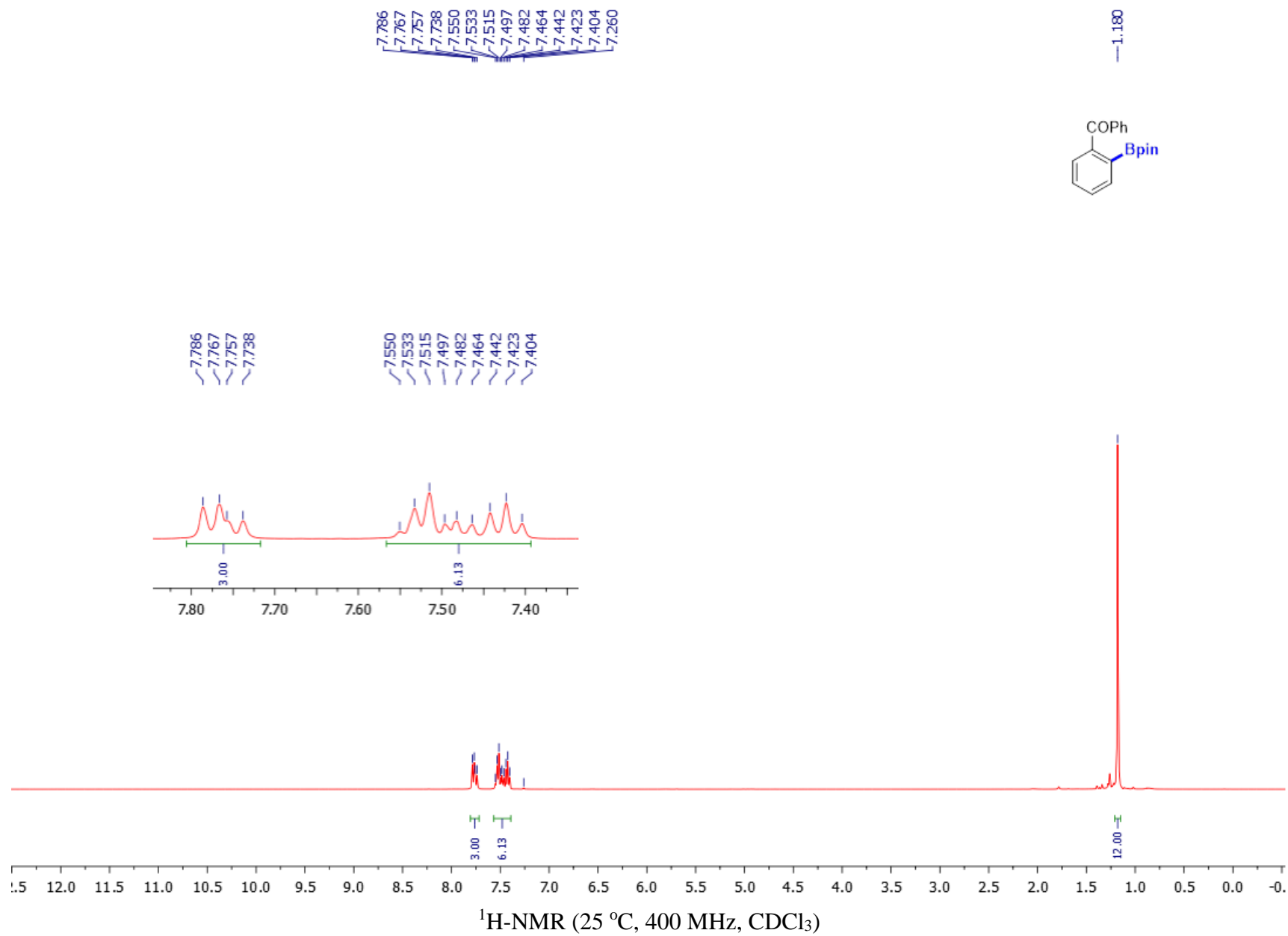


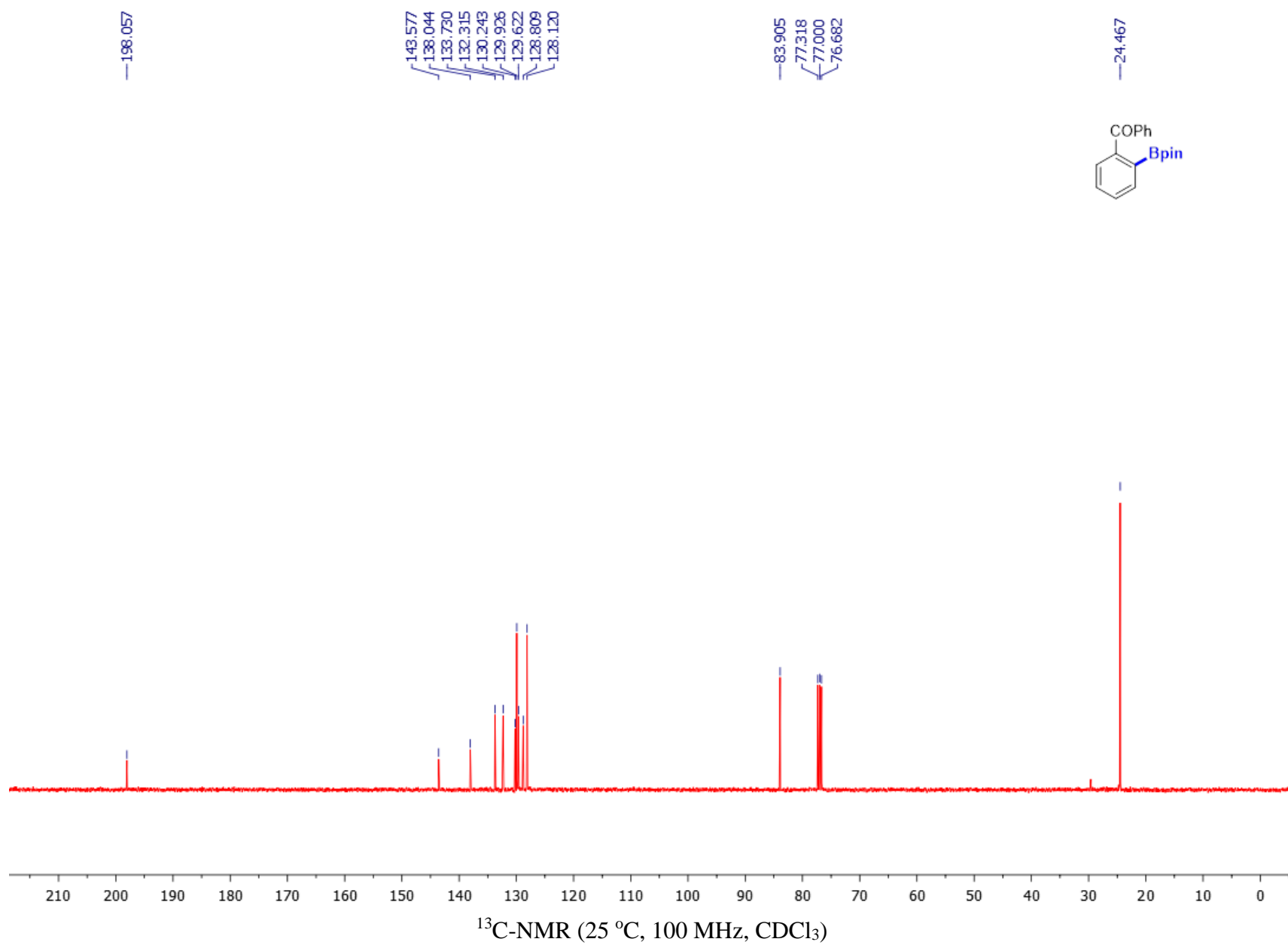


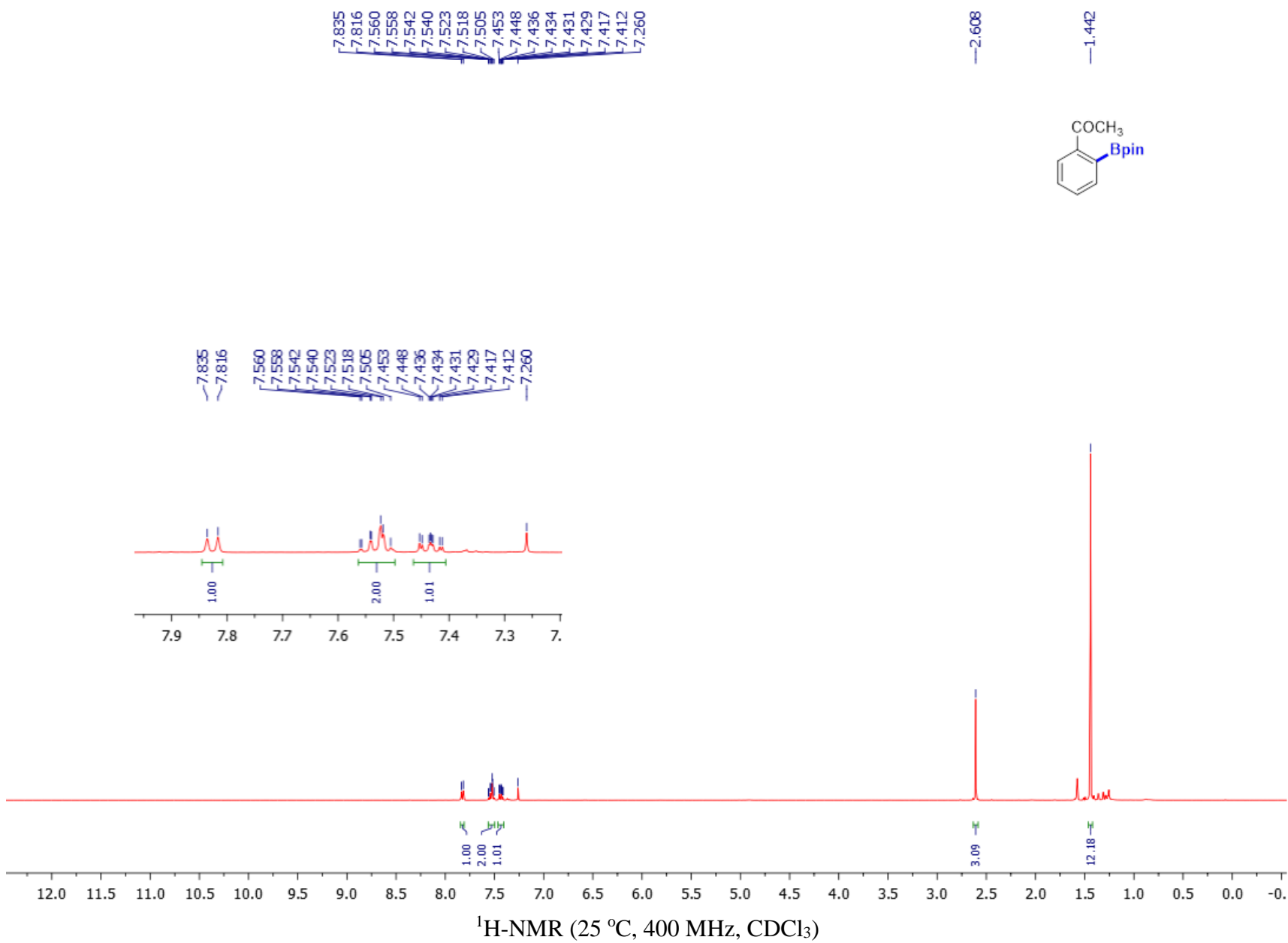


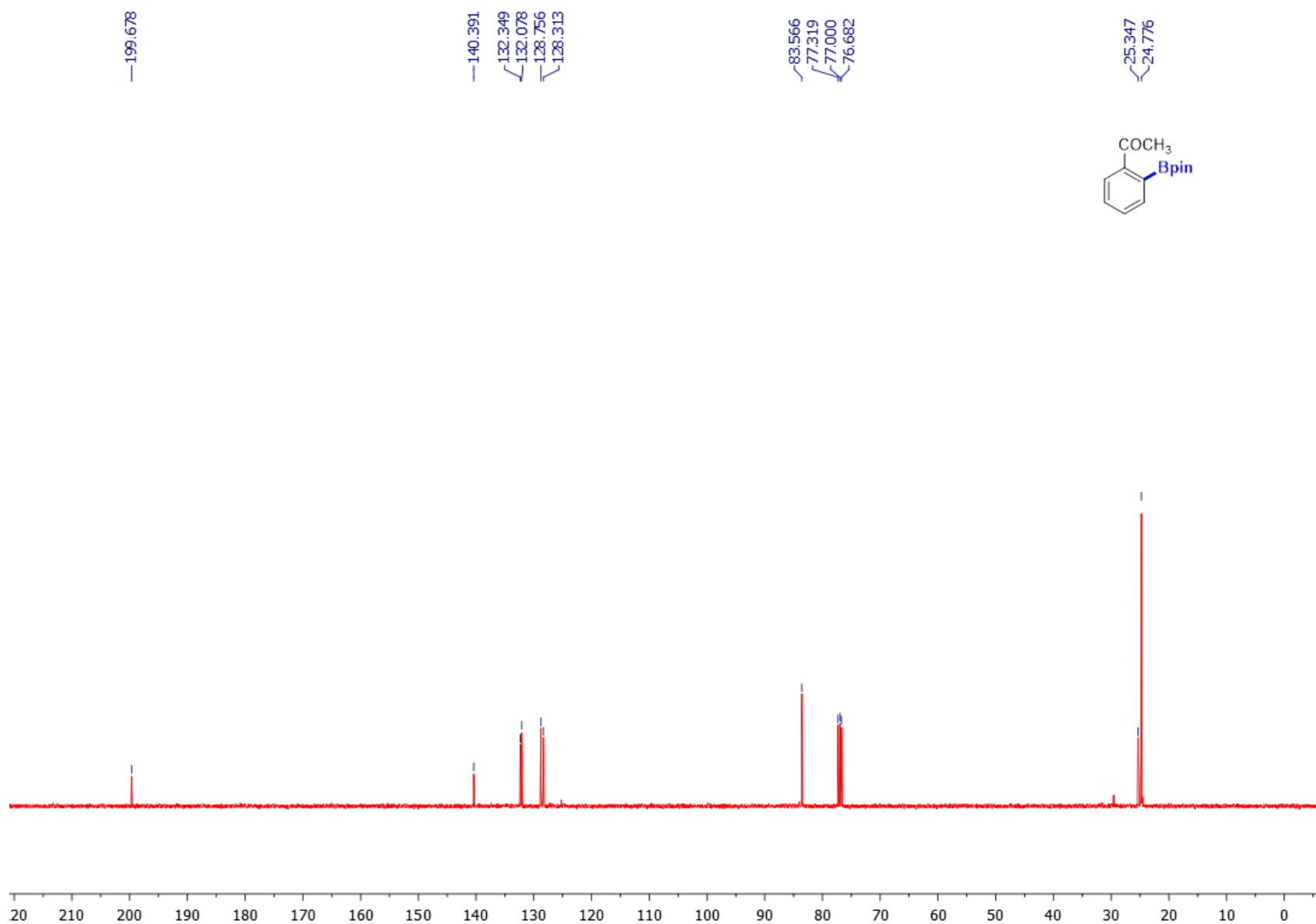




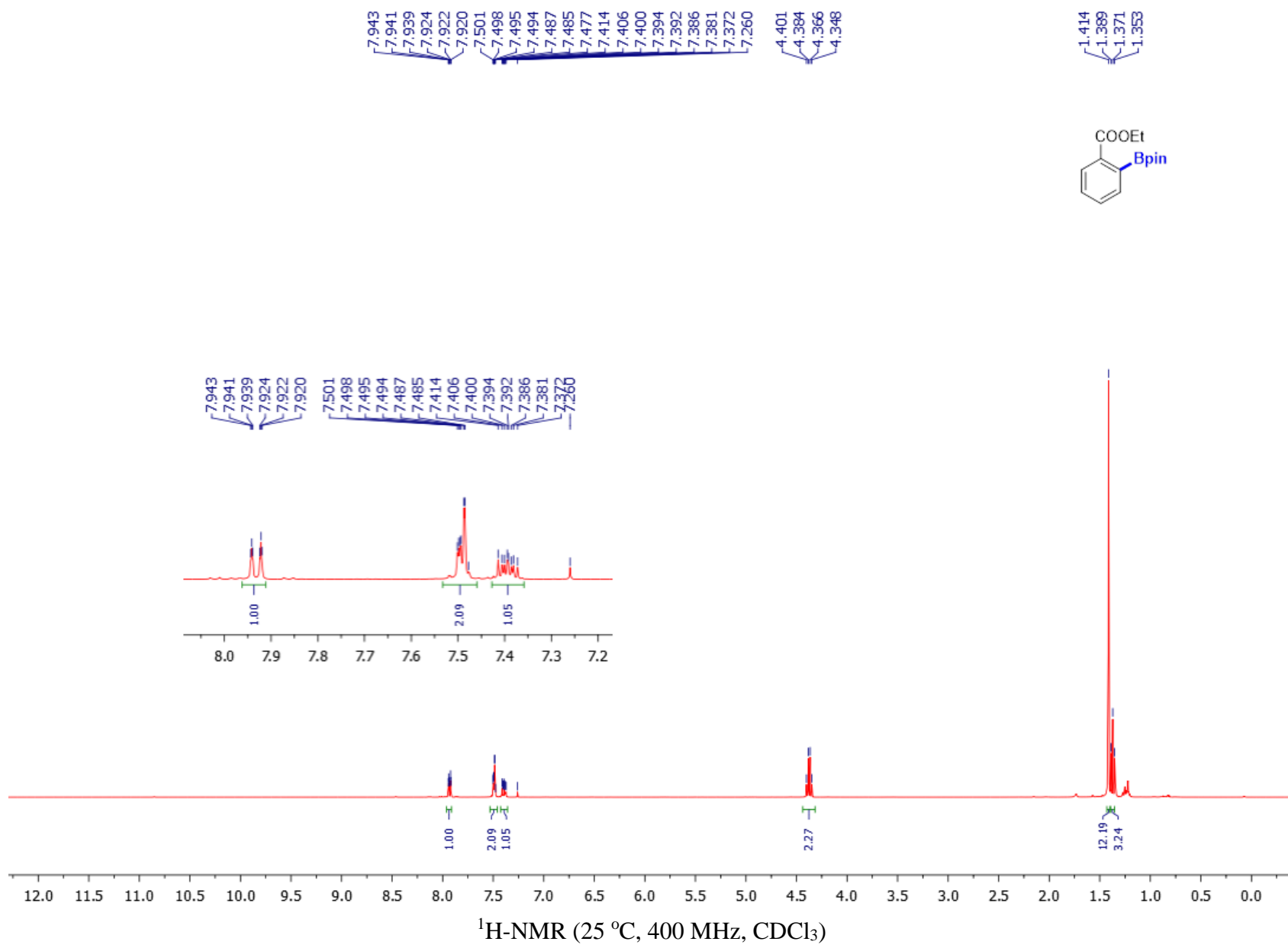


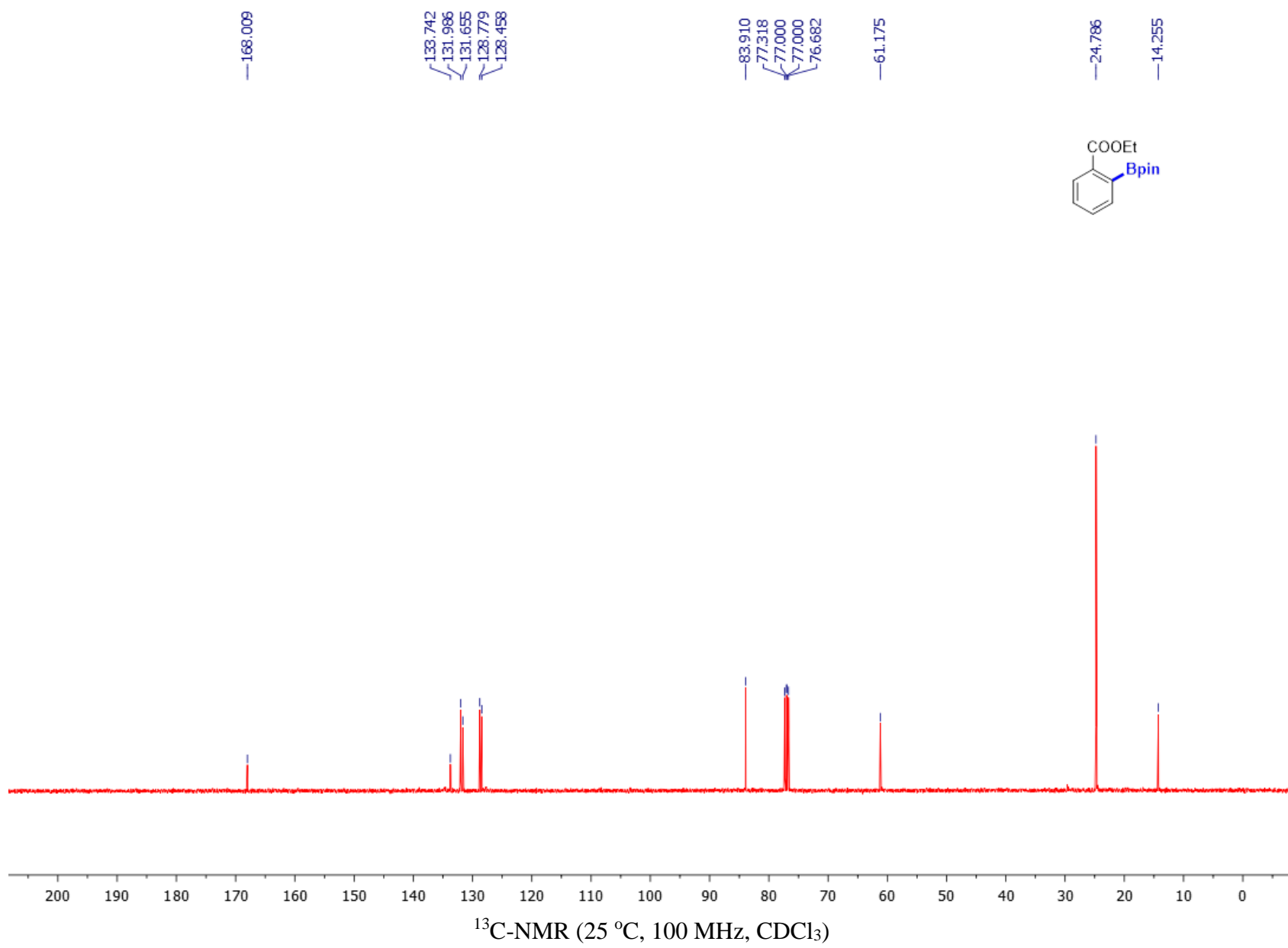


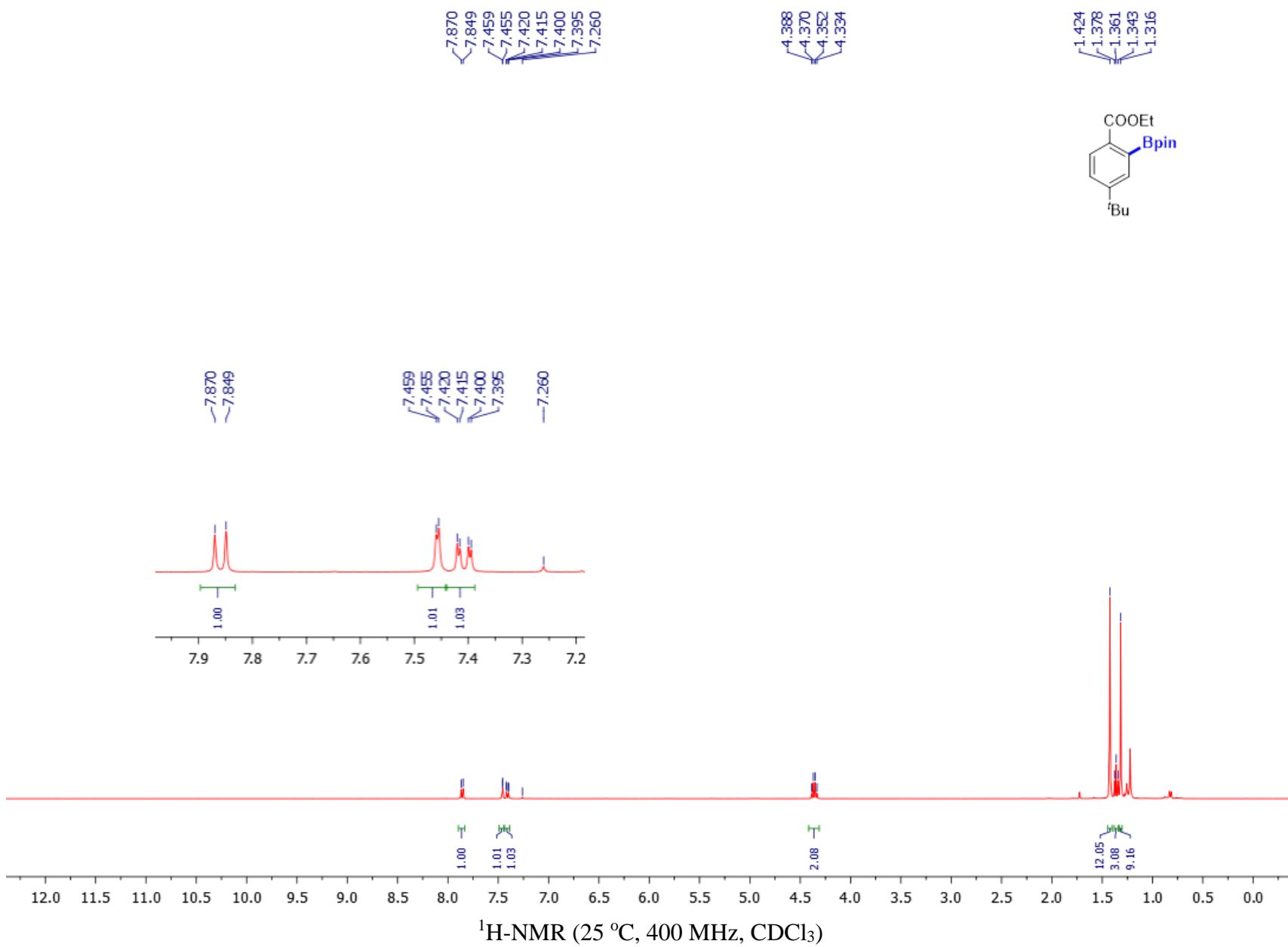


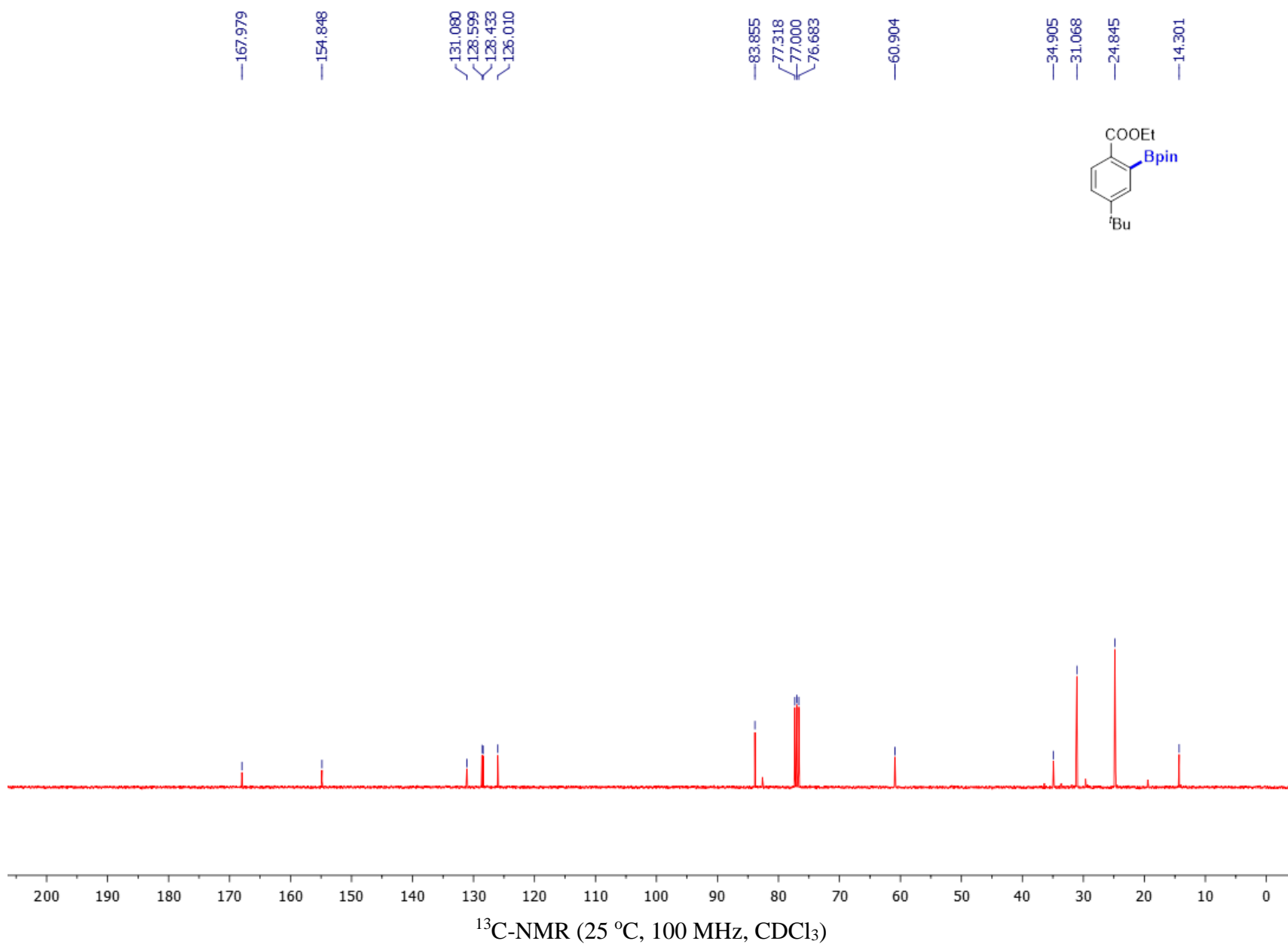


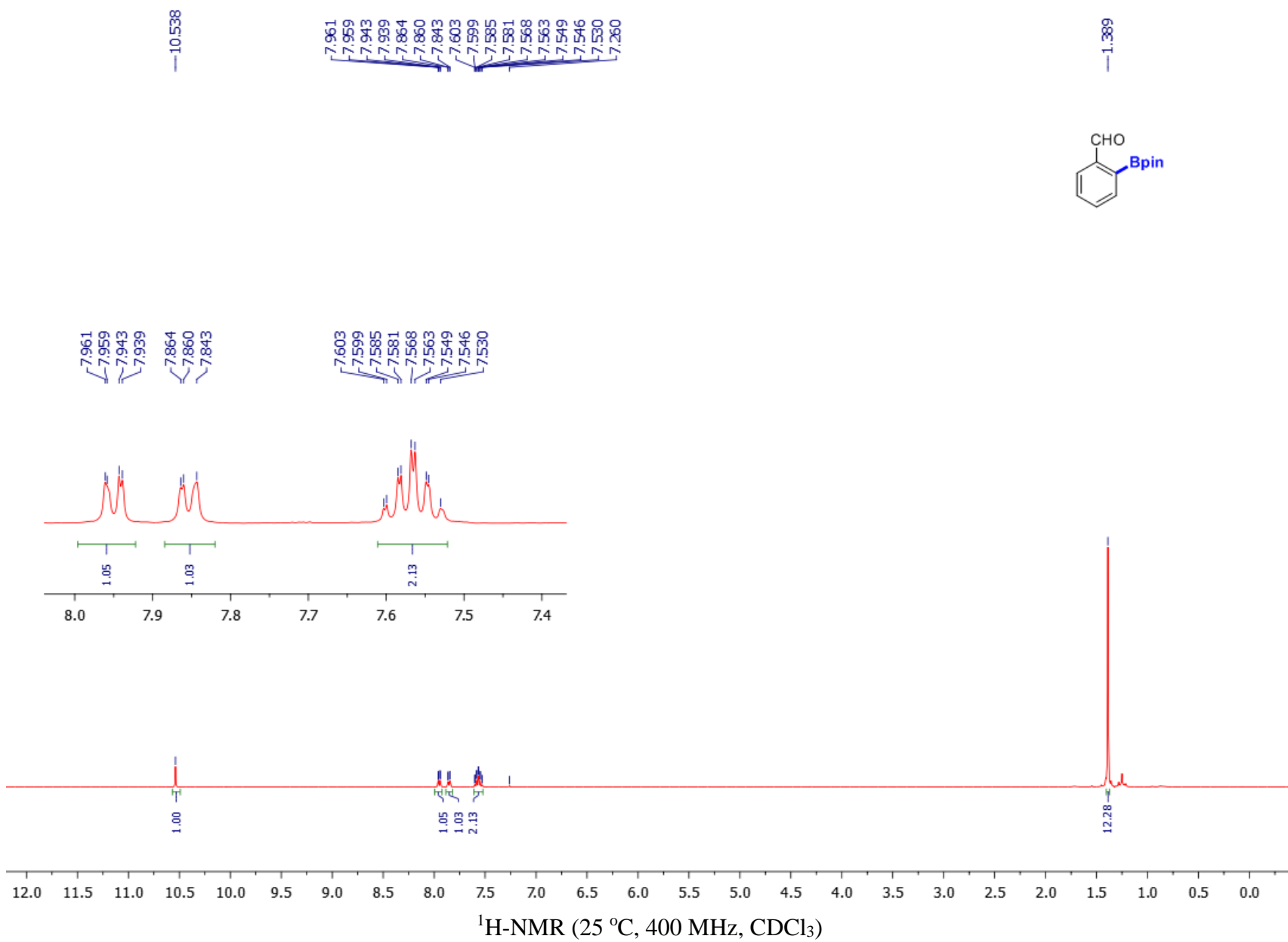
¹³C-NMR (25 °C, 100 MHz, CDCl₃)

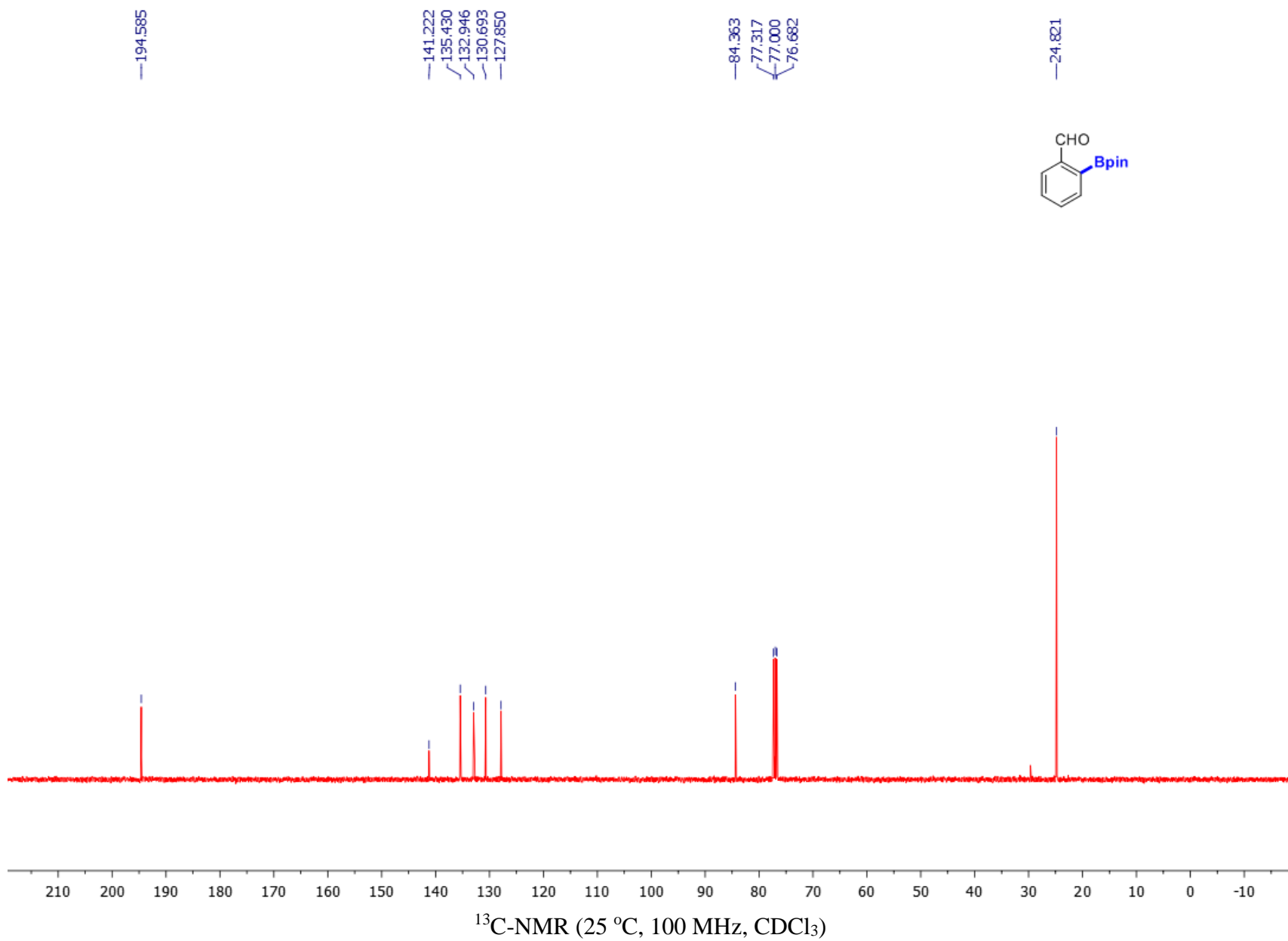


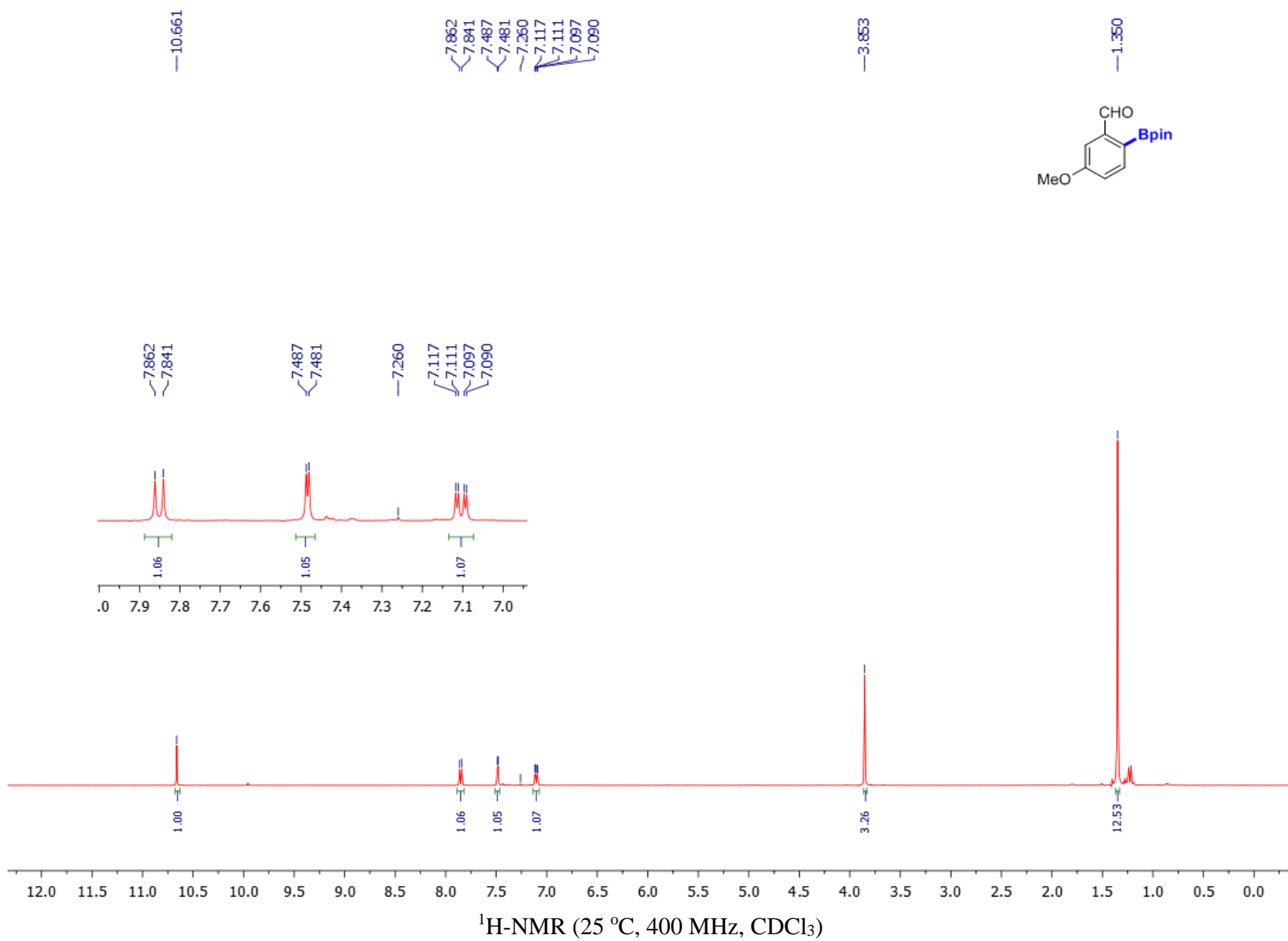


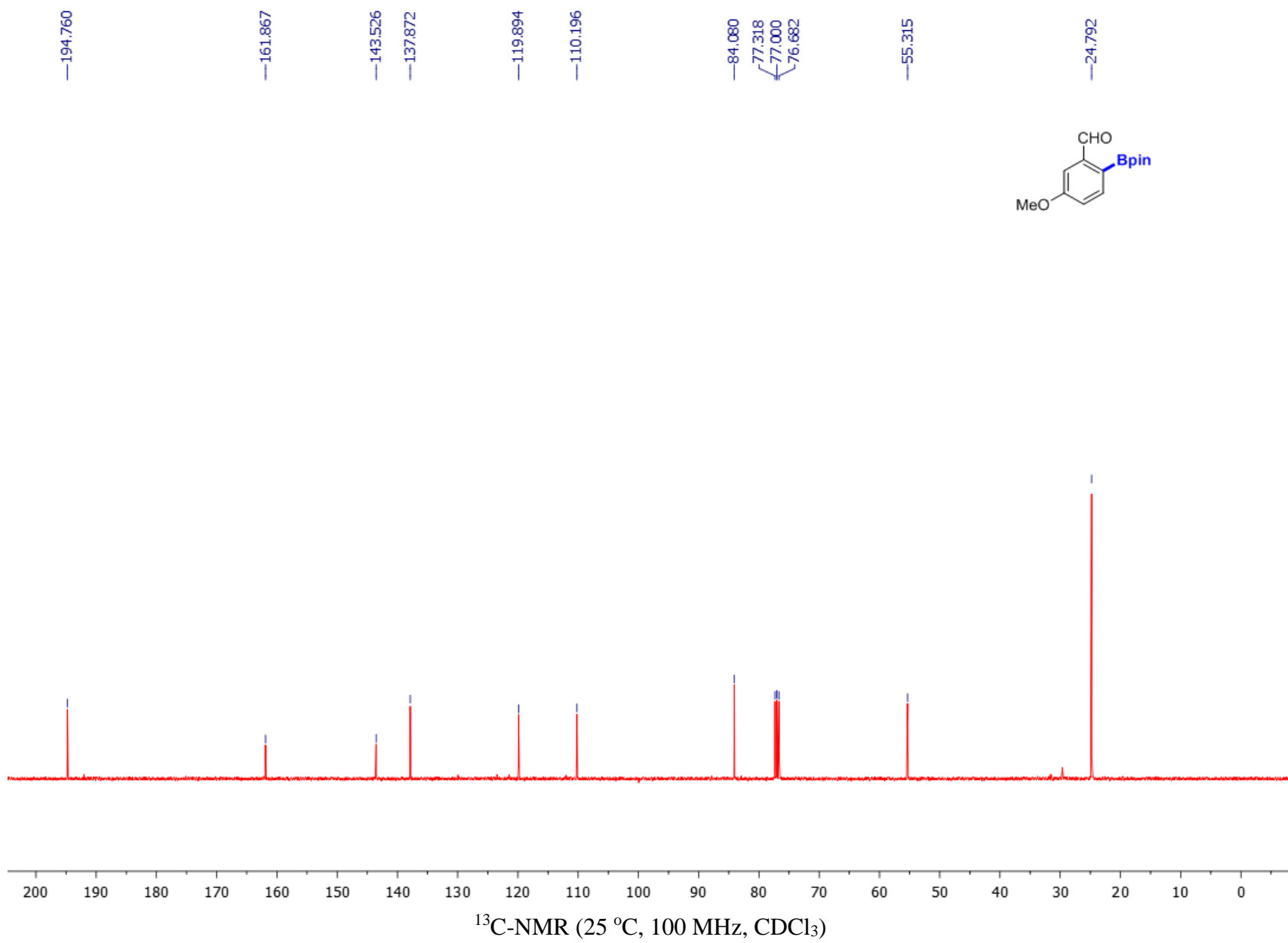


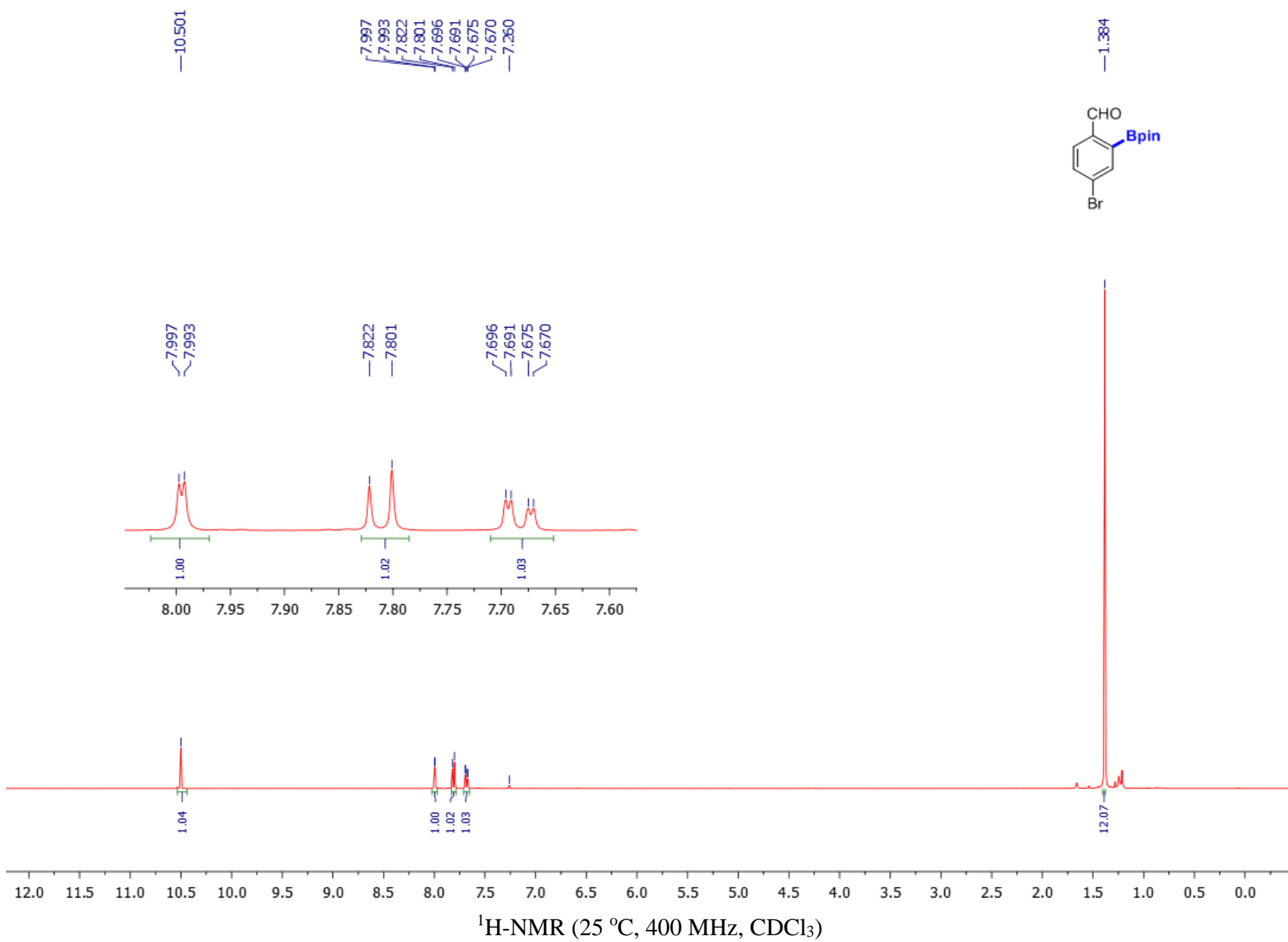


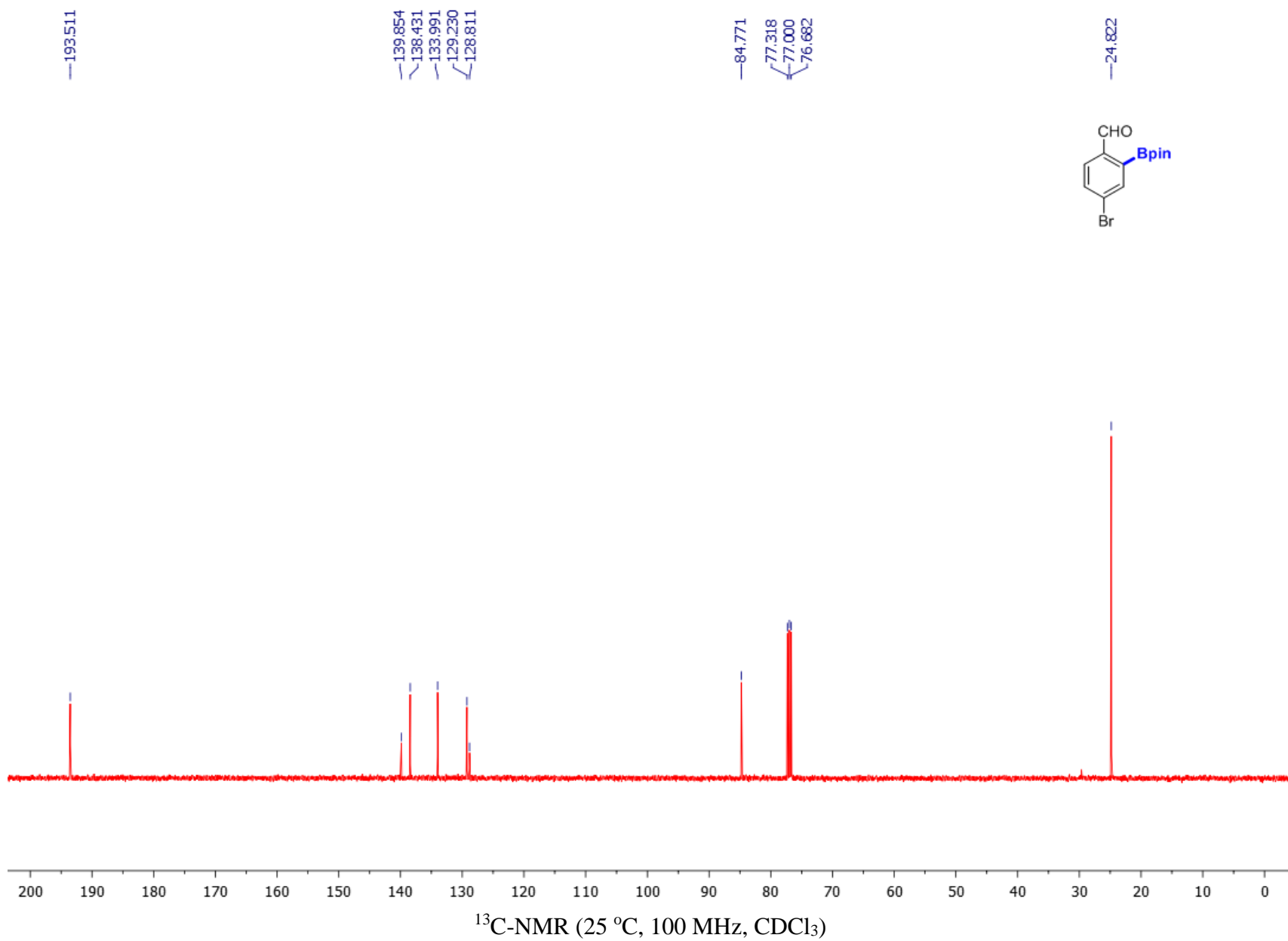


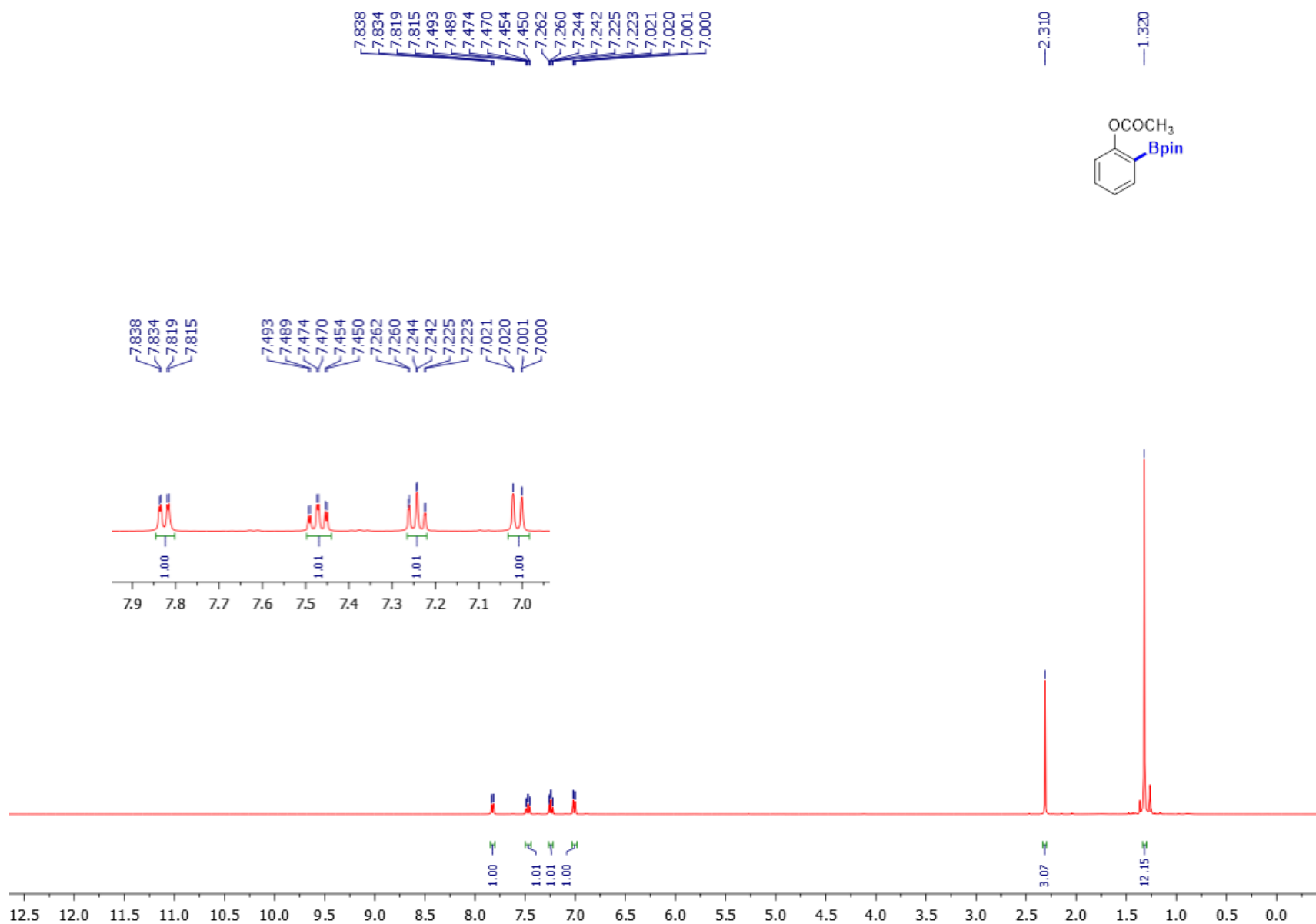




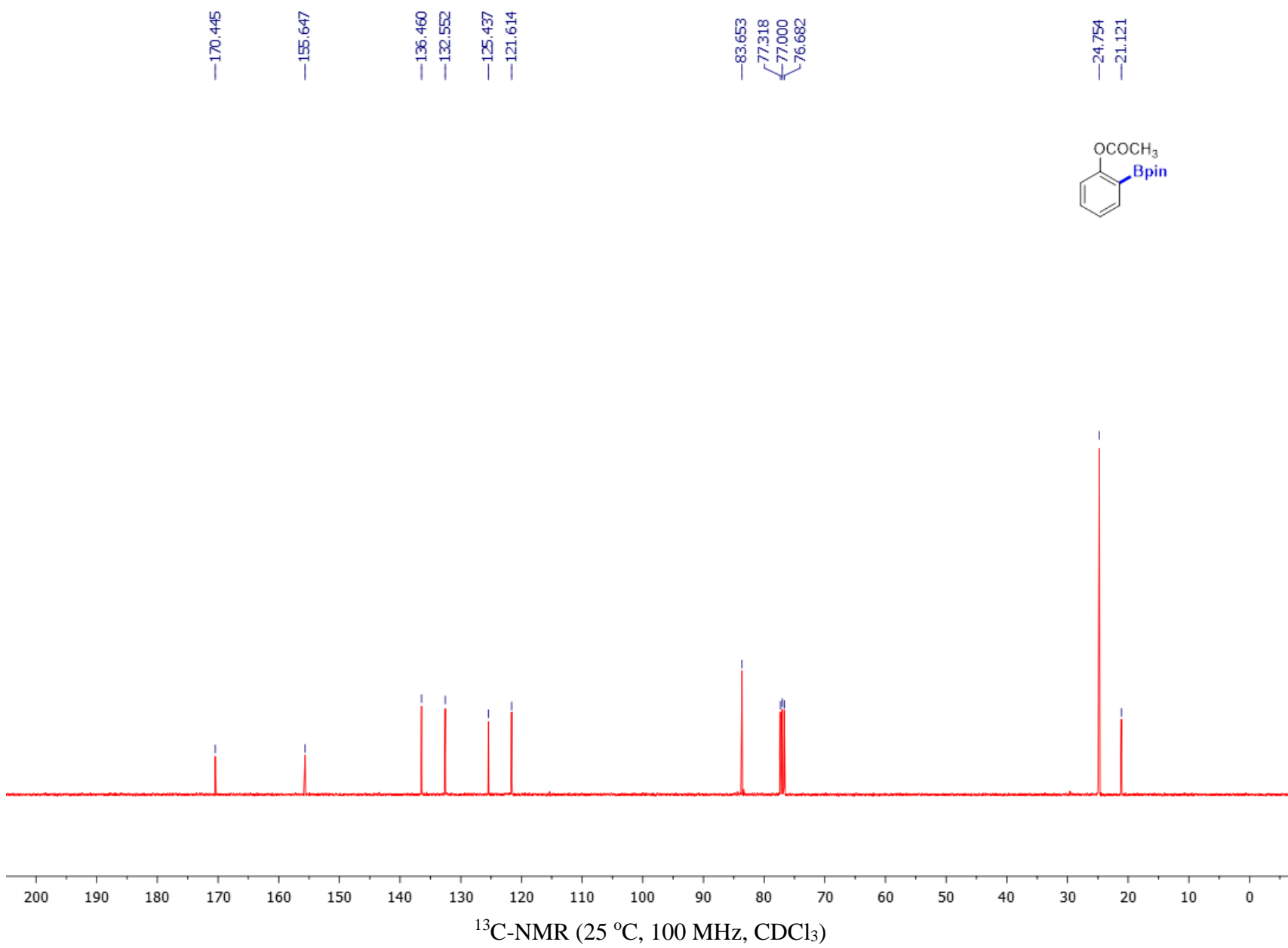


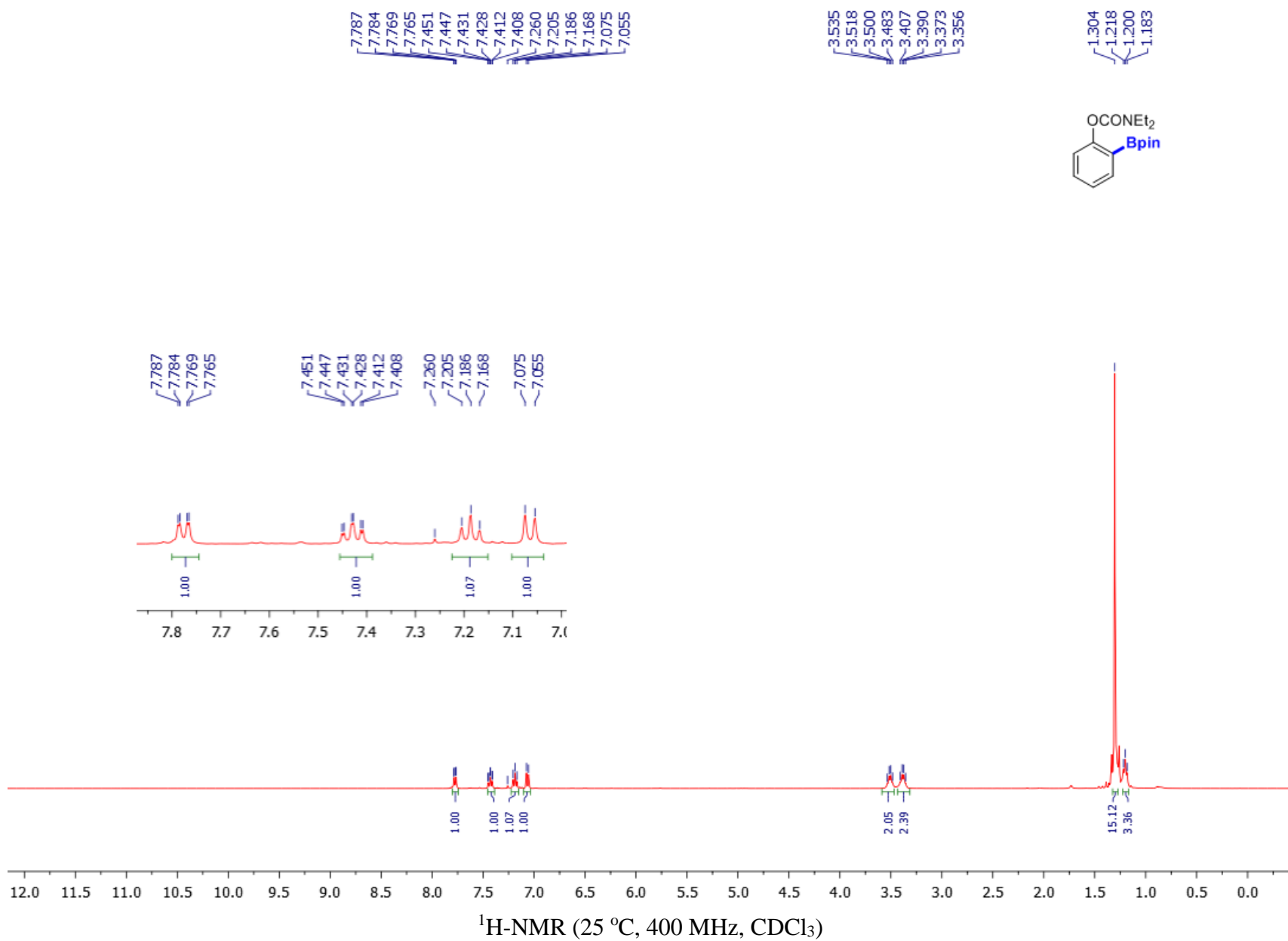


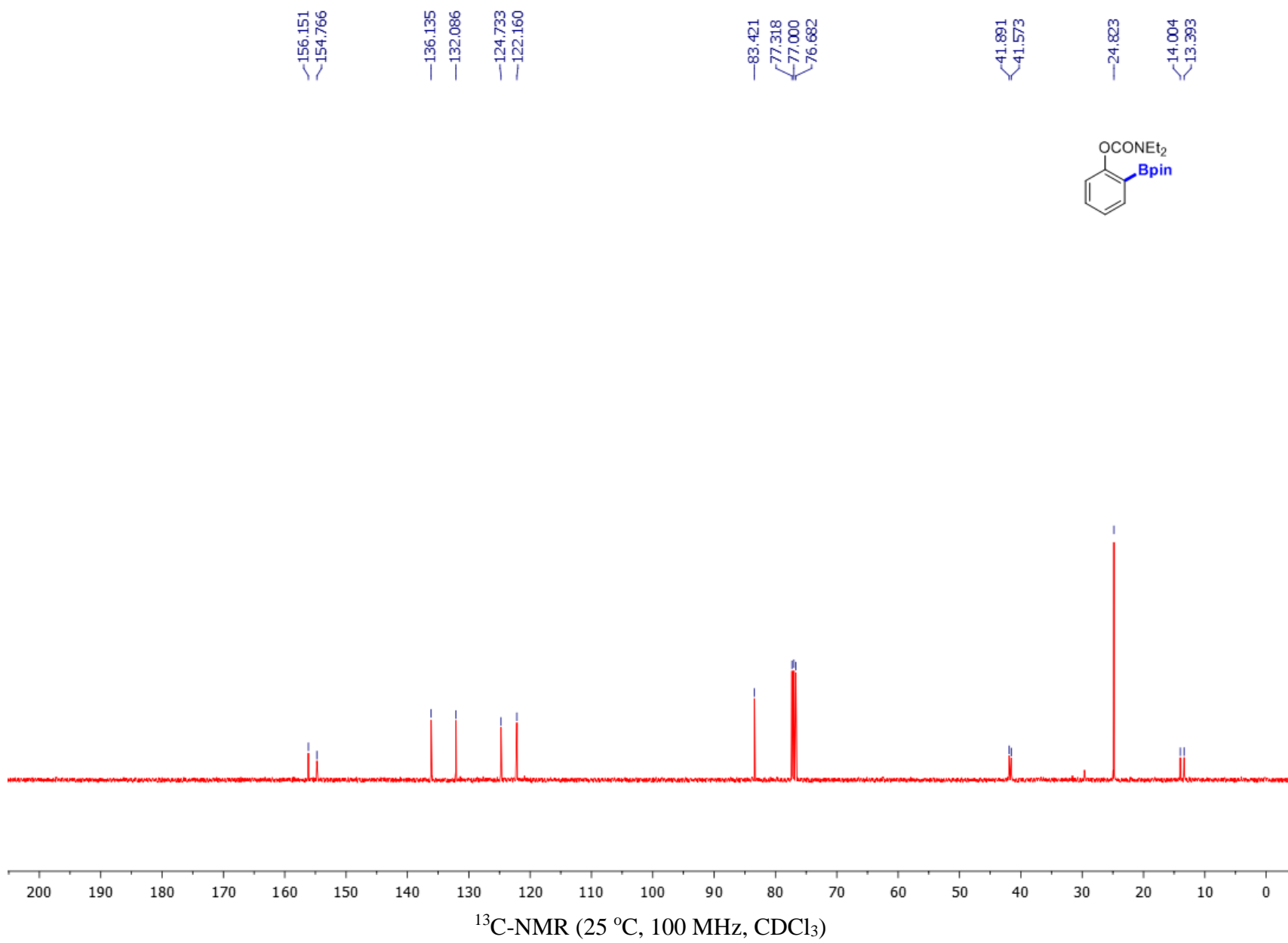


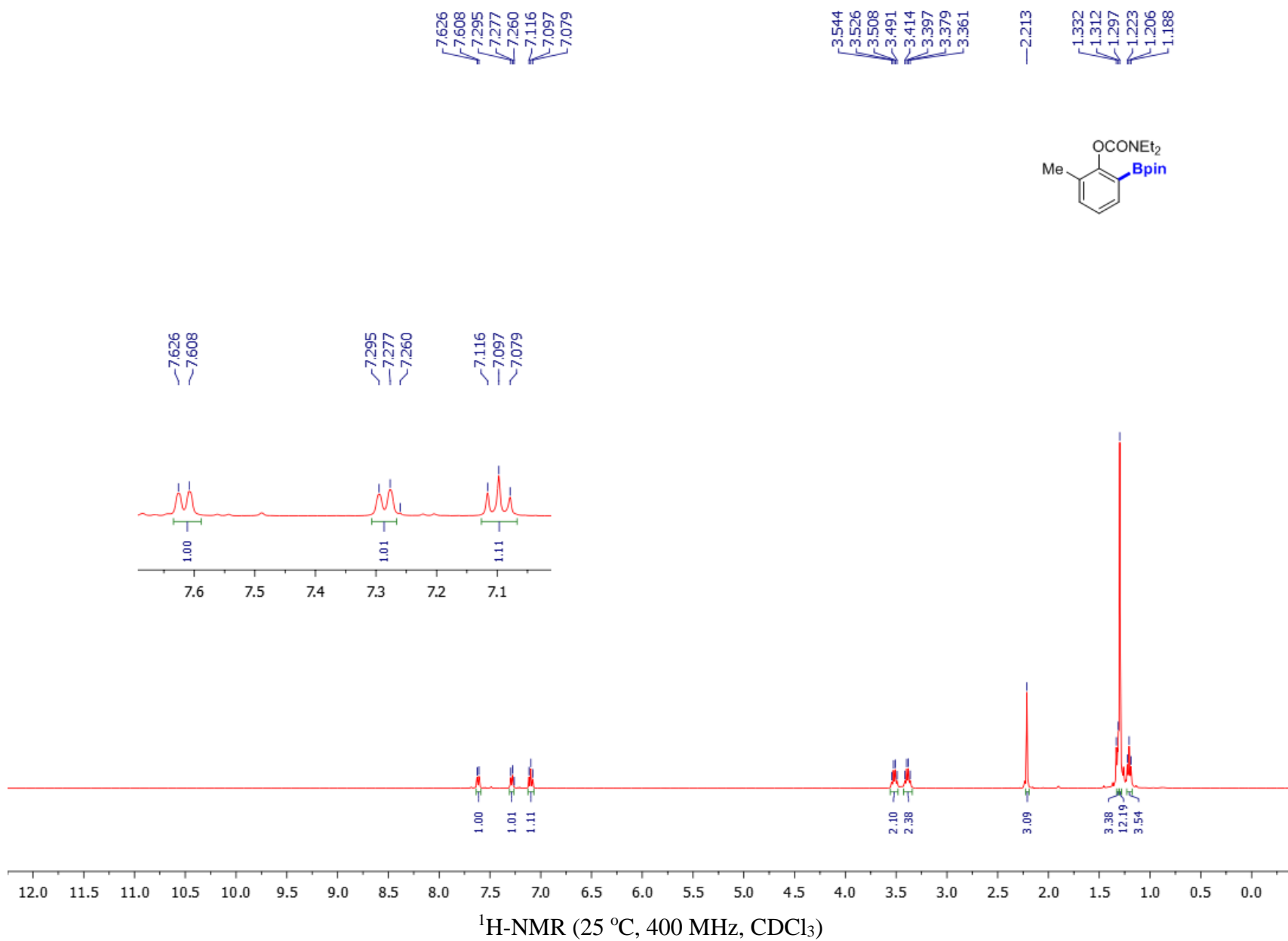


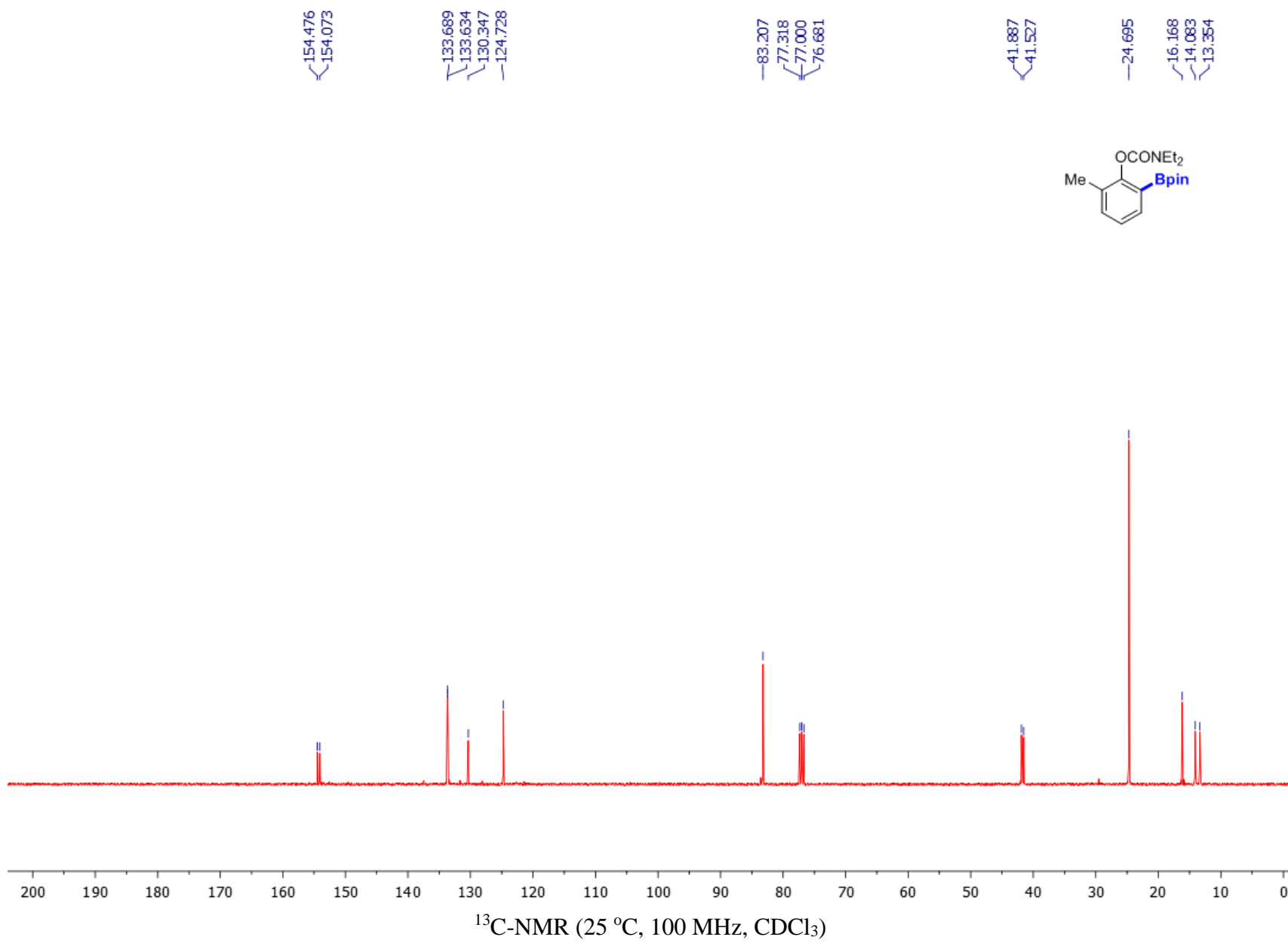
$^1\text{H-NMR}$ (25 °C, 400 MHz, CDCl_3)

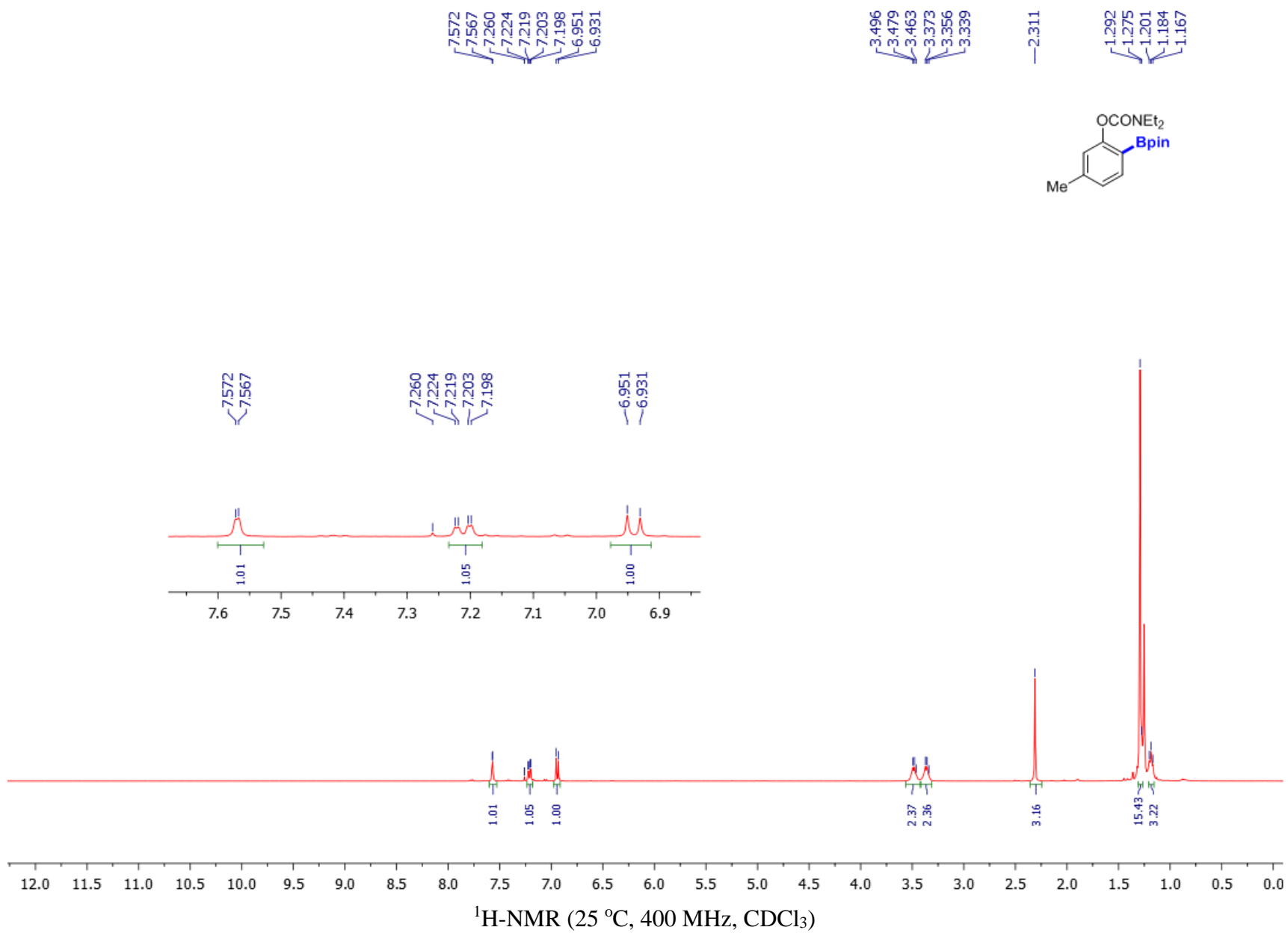


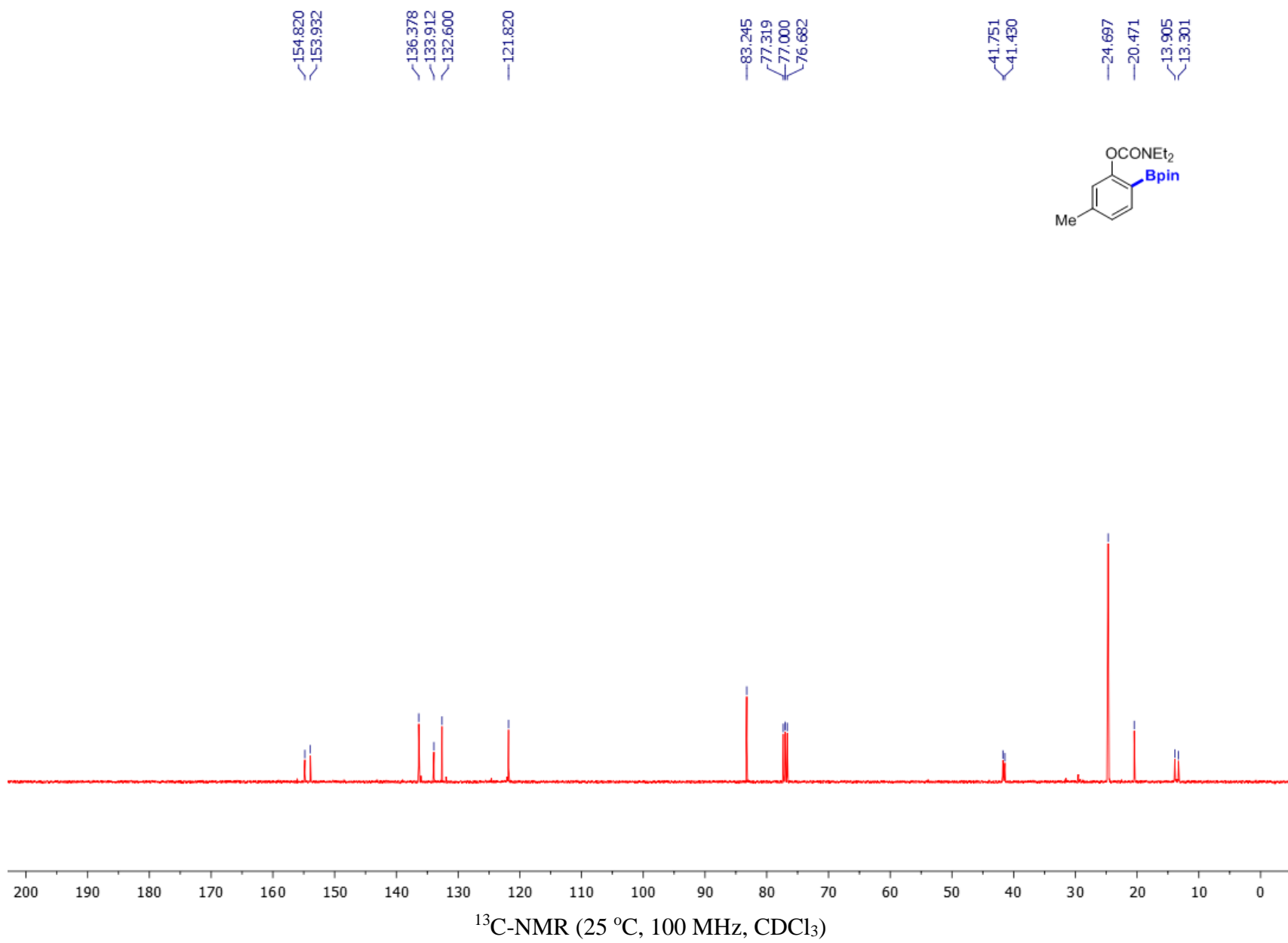


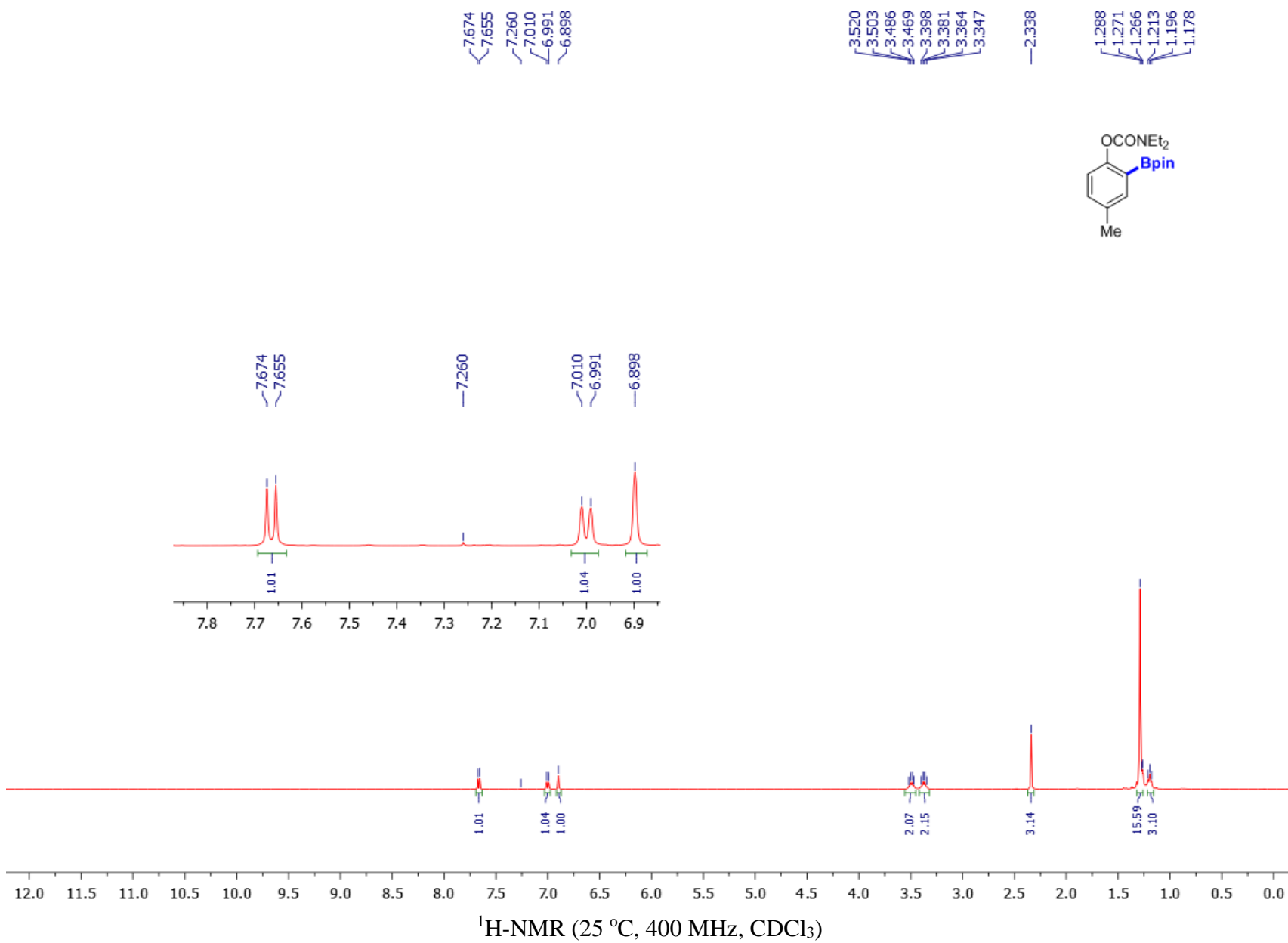


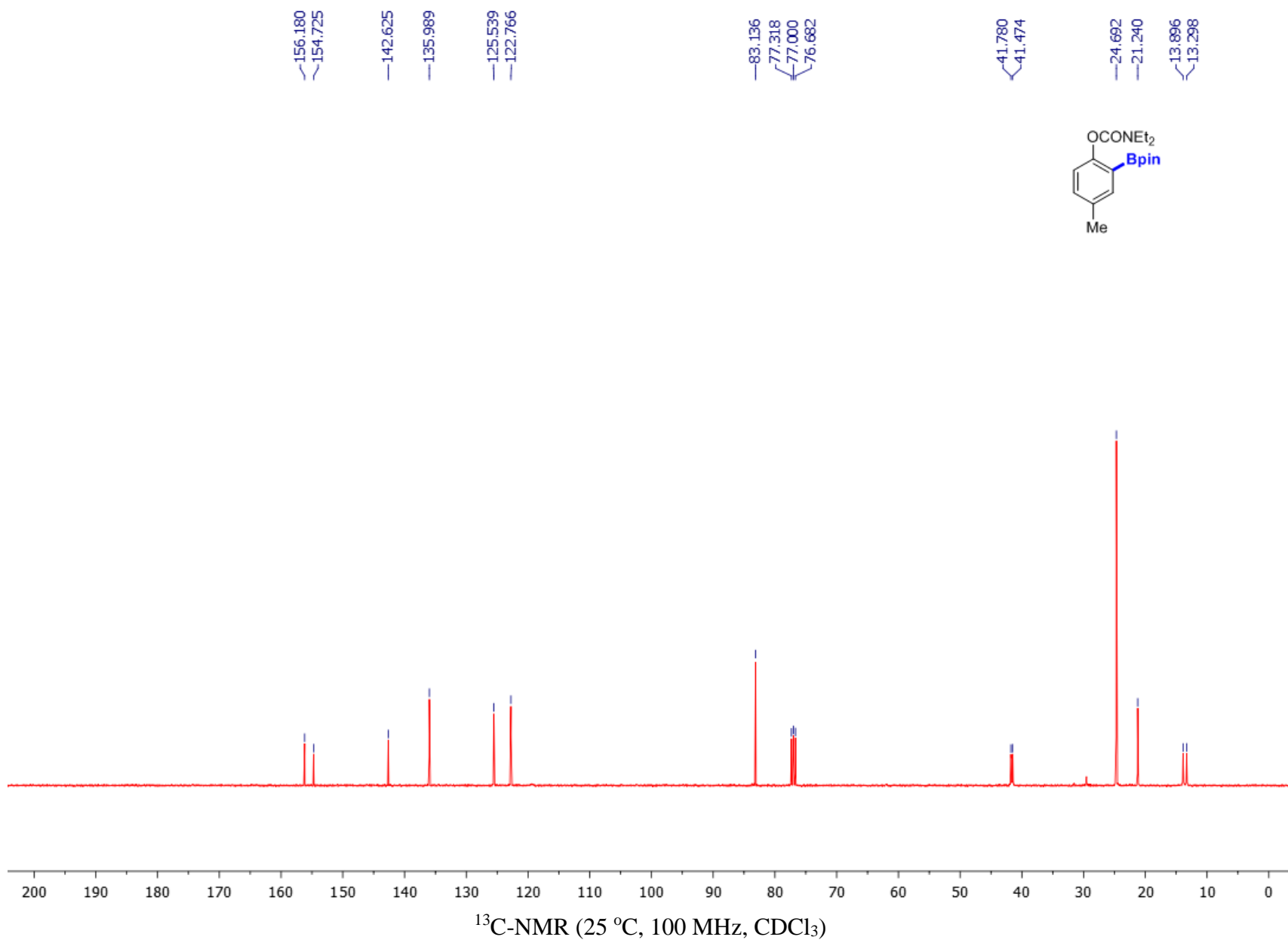


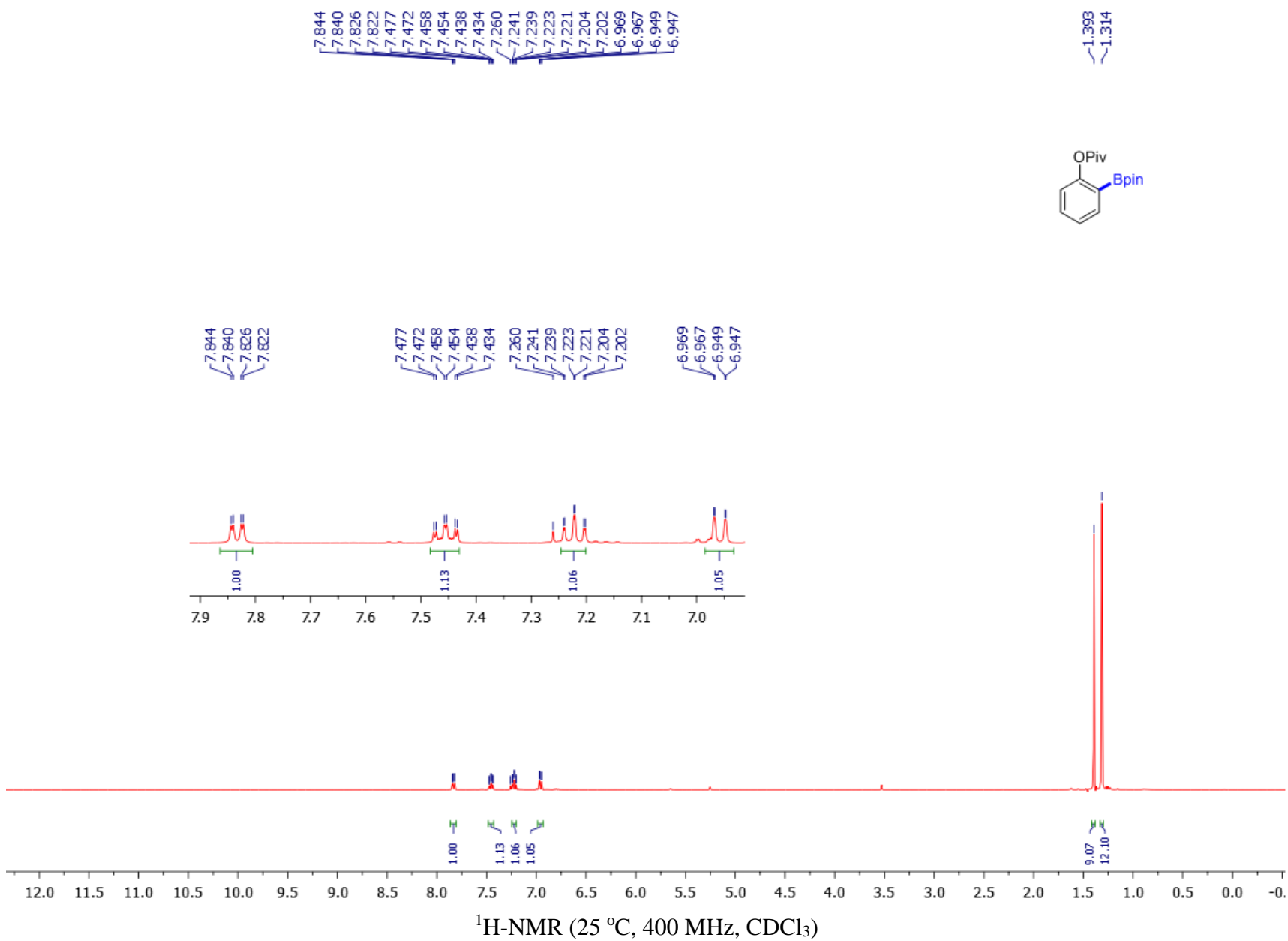


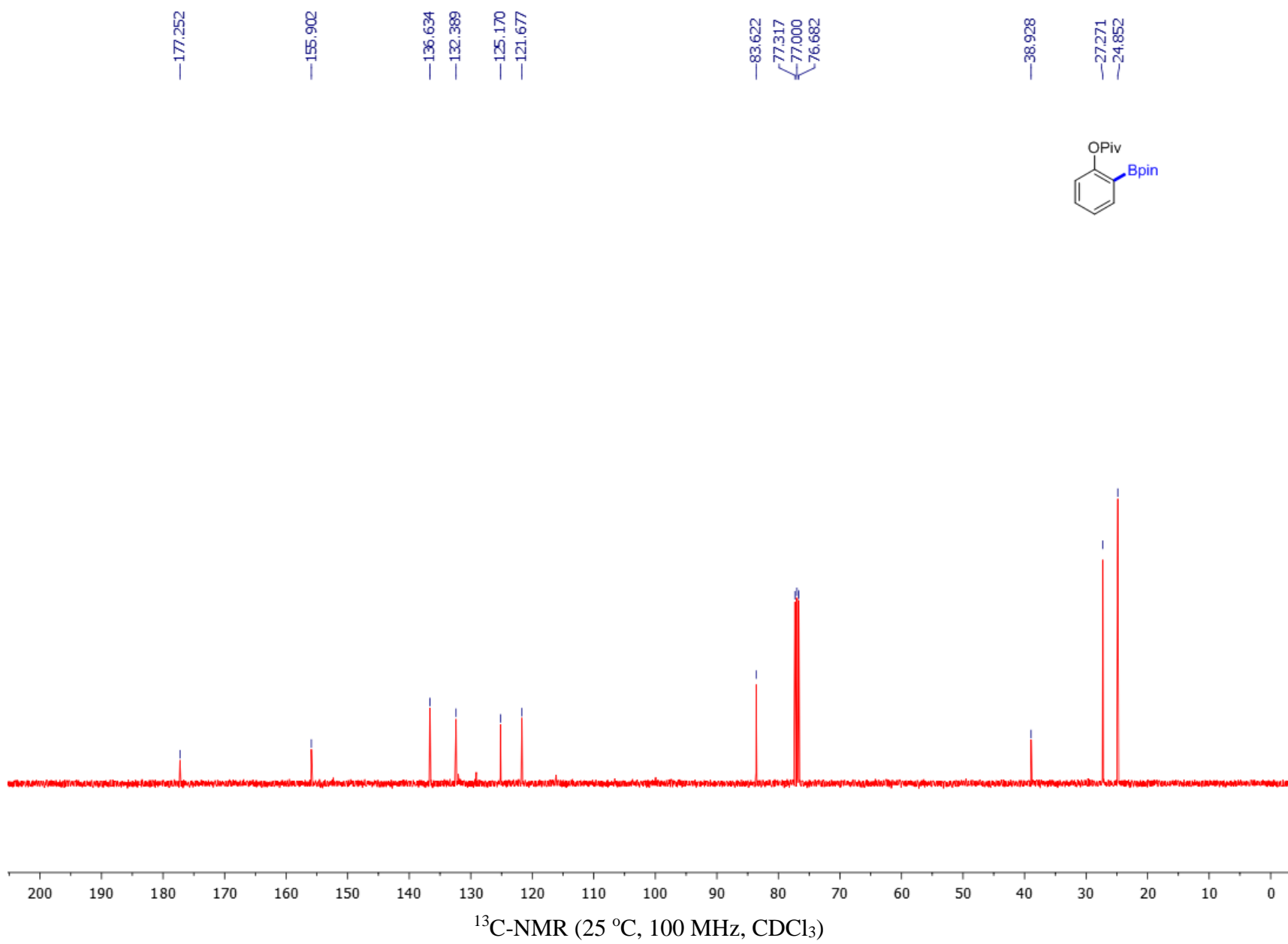


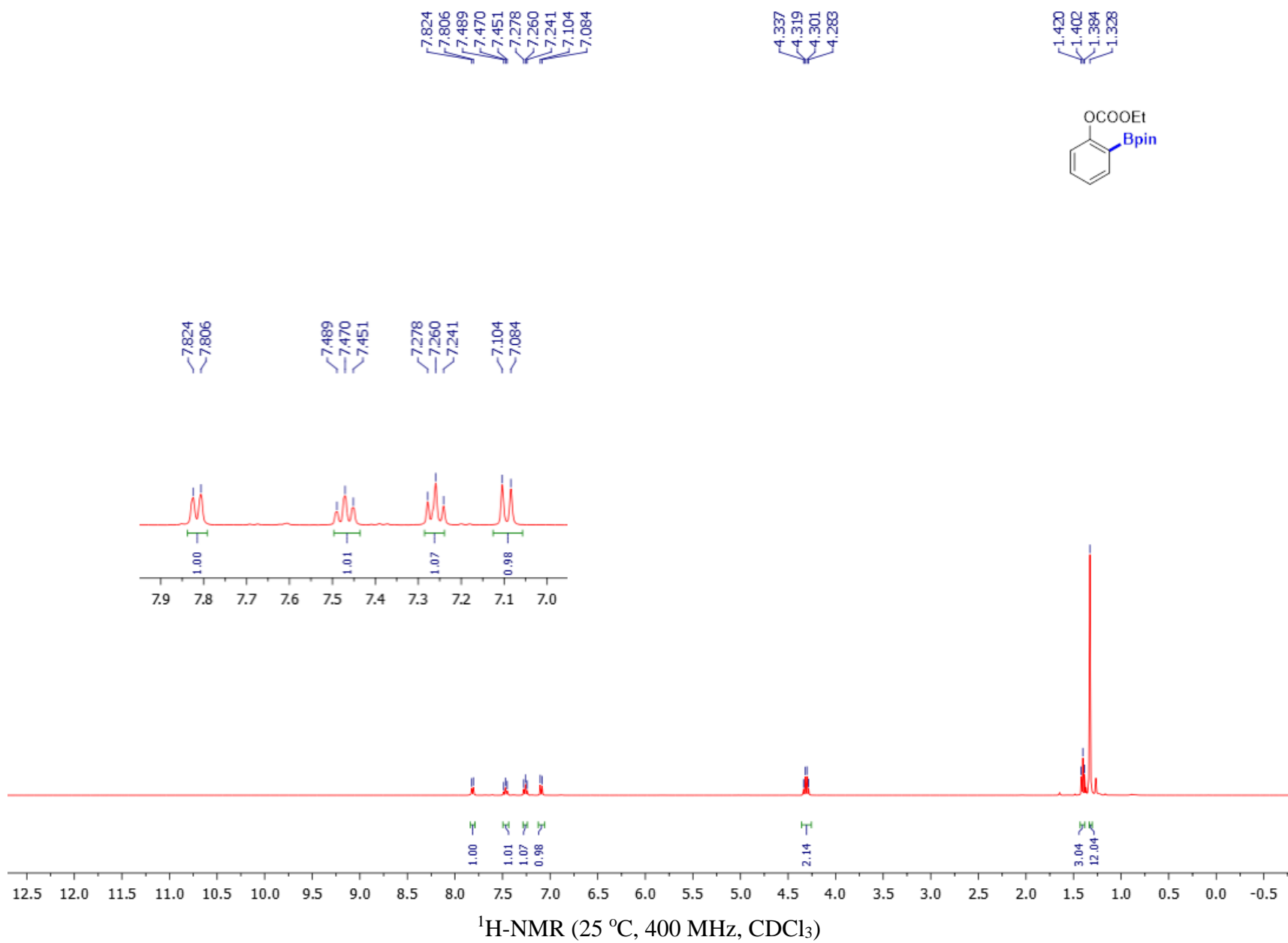


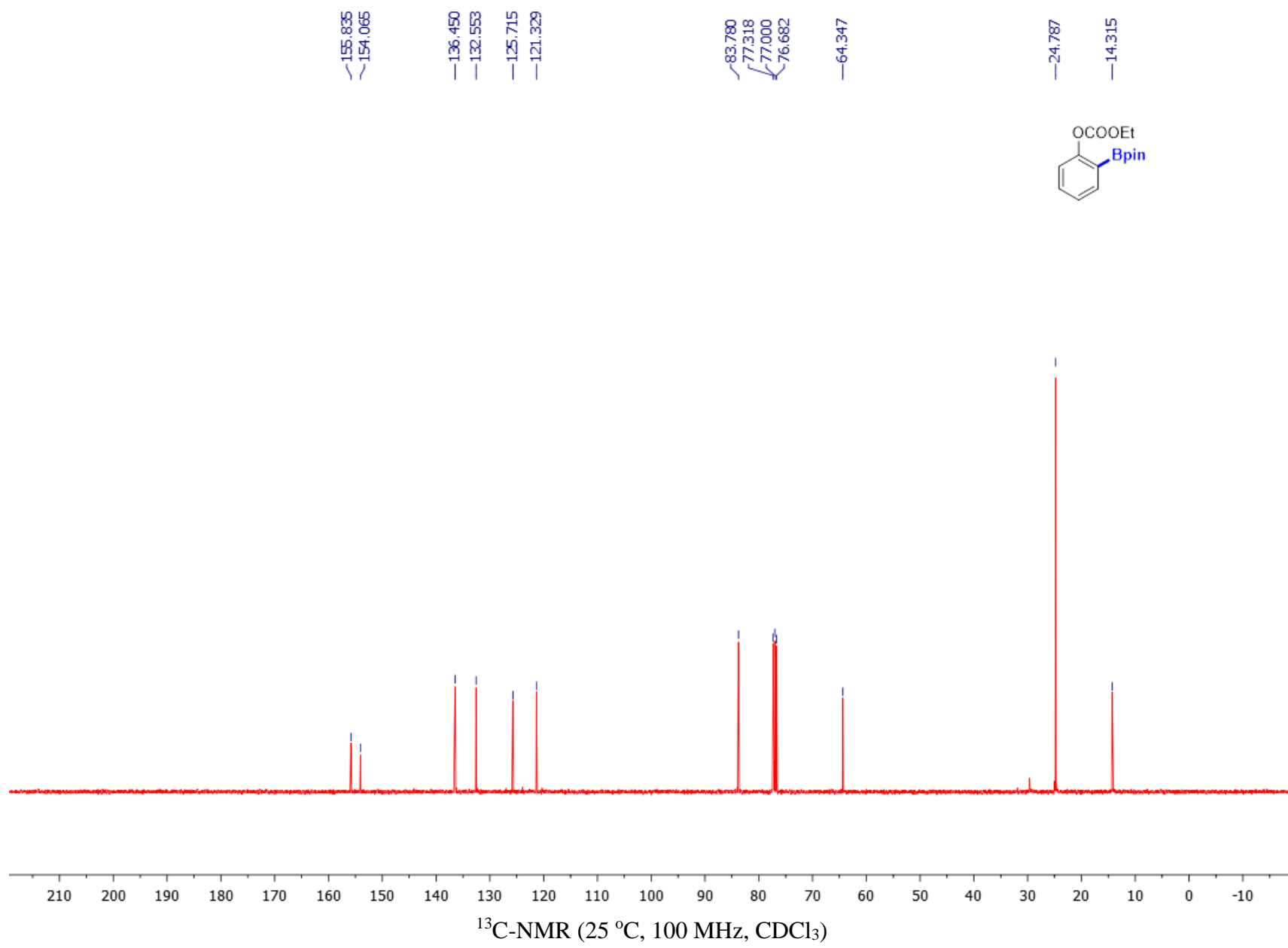


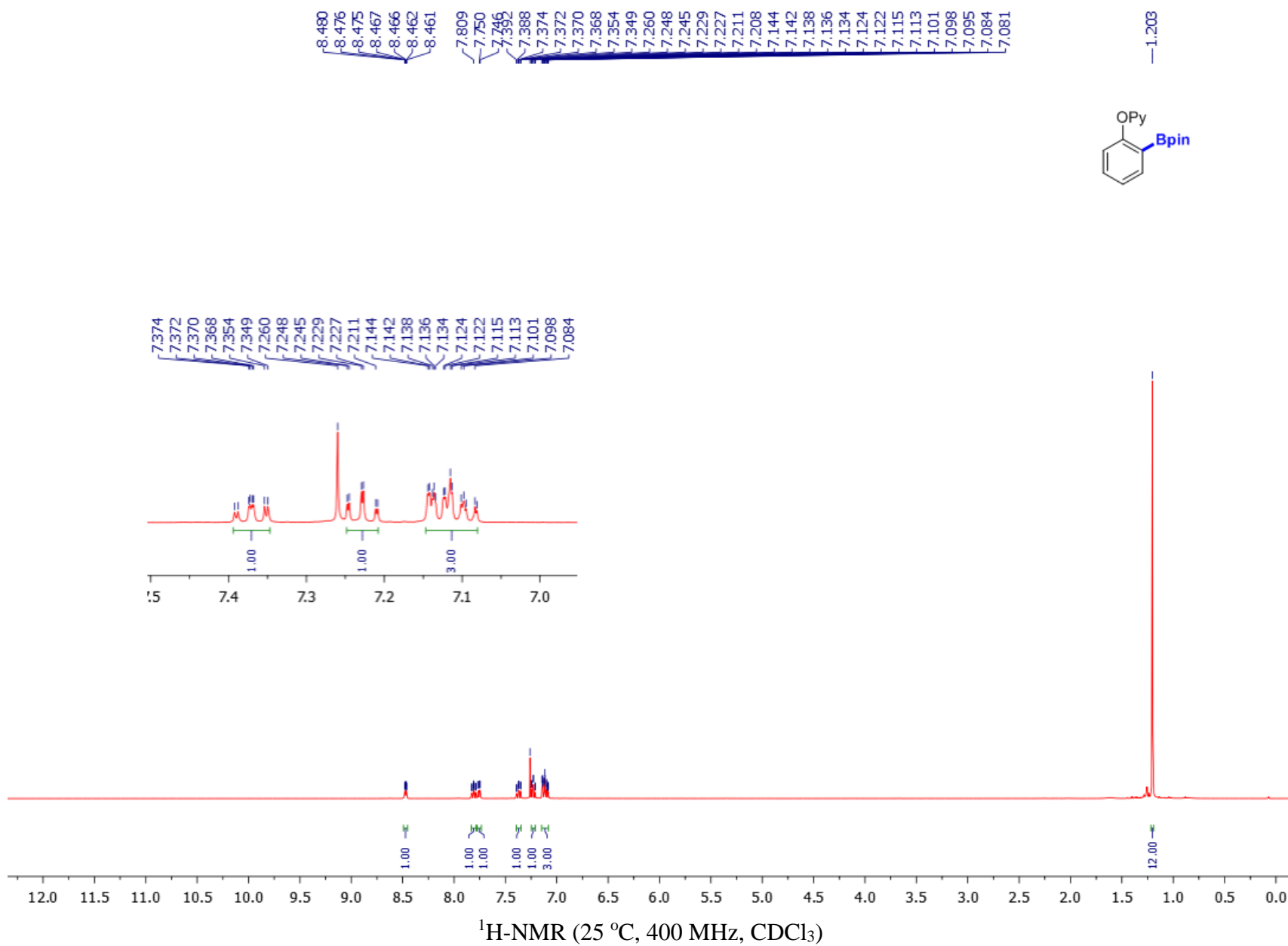


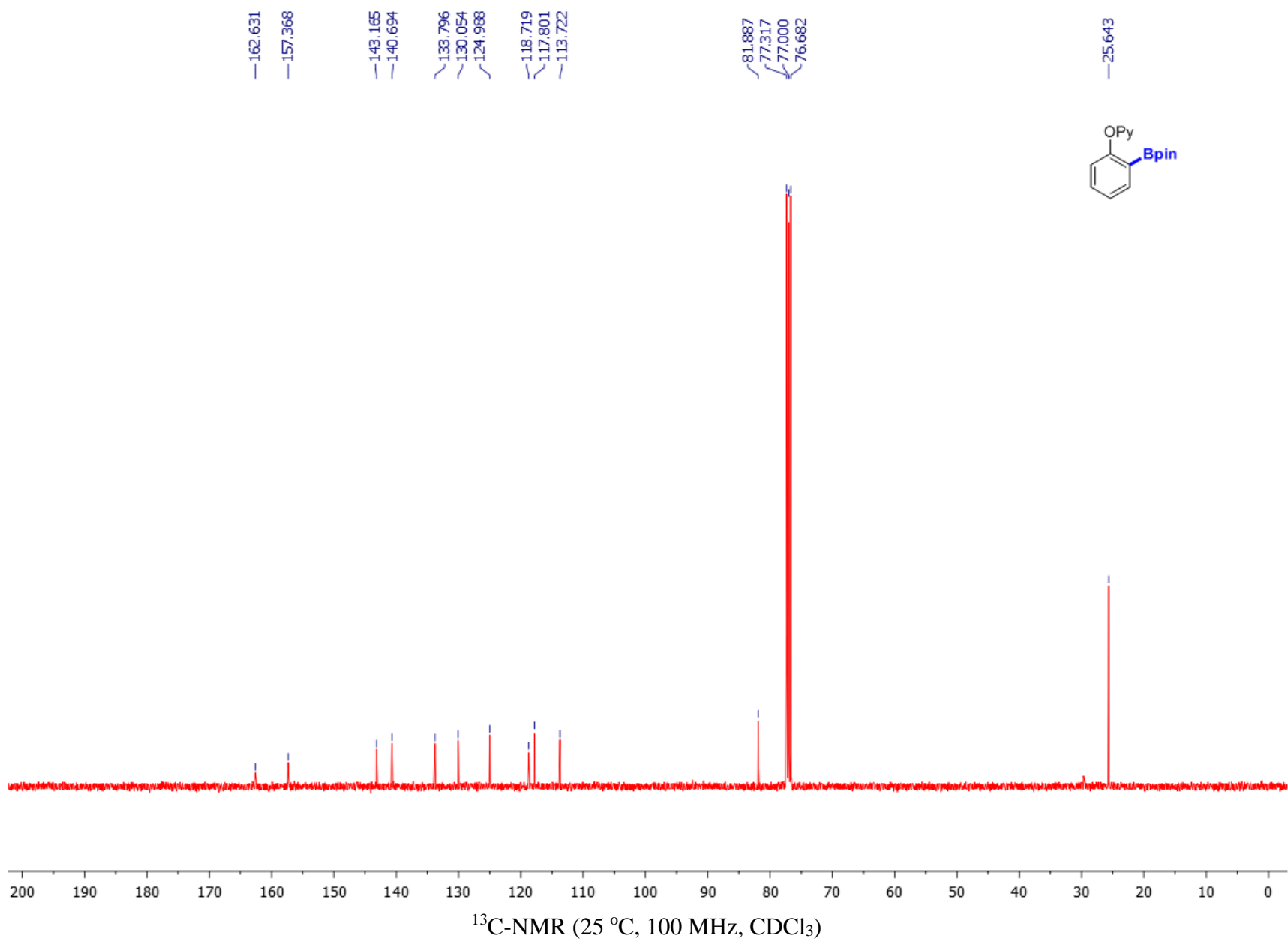


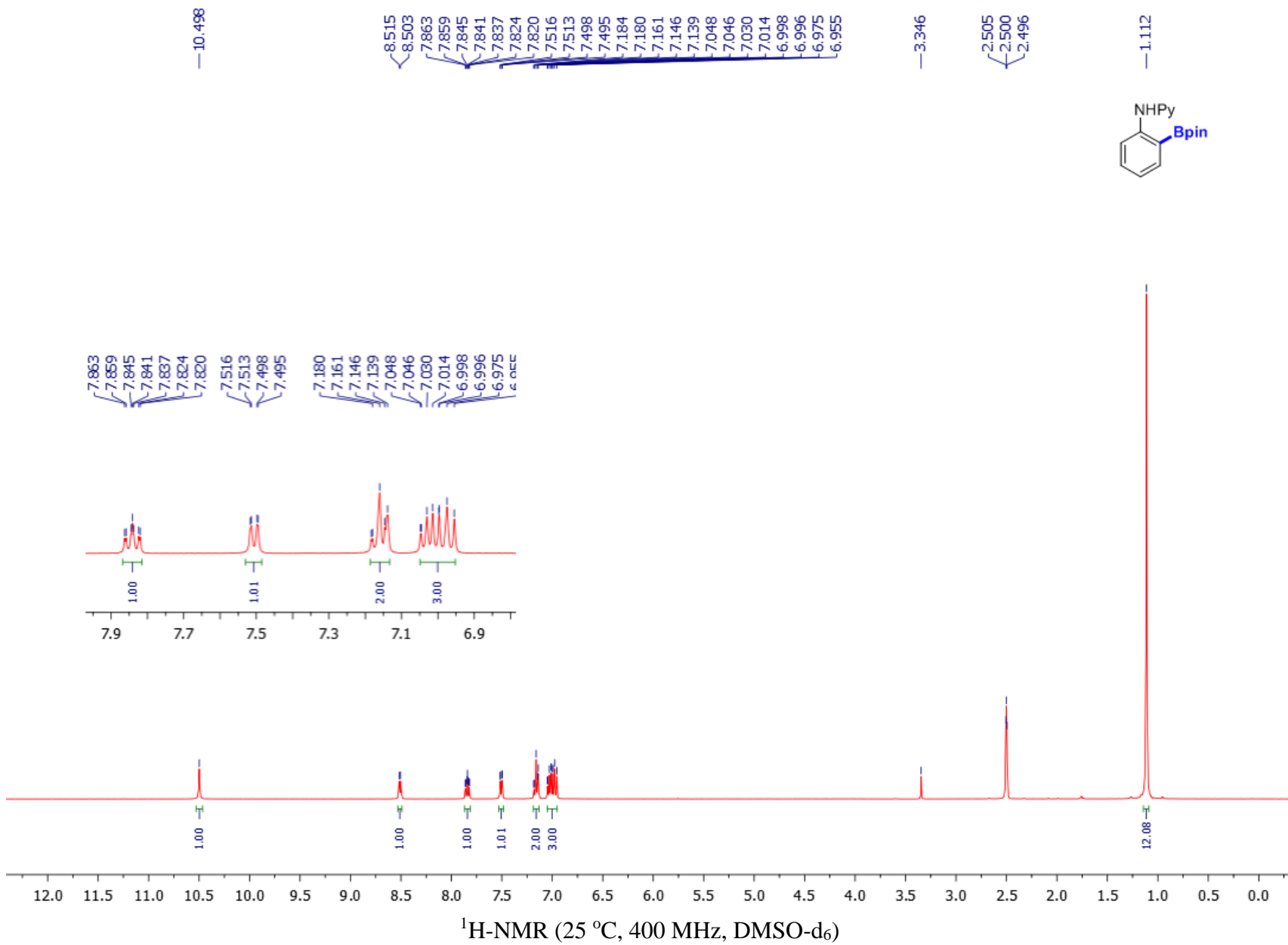


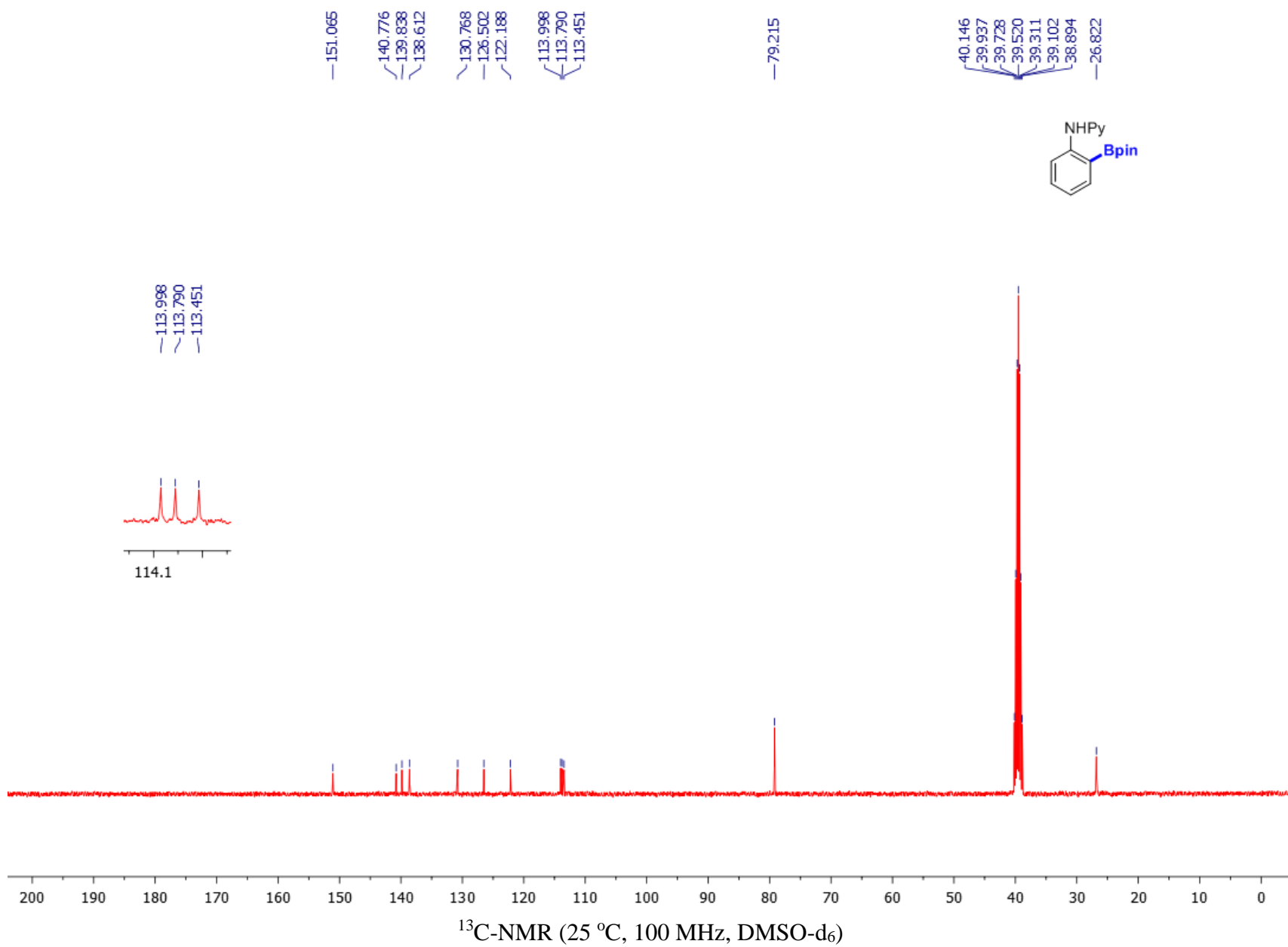


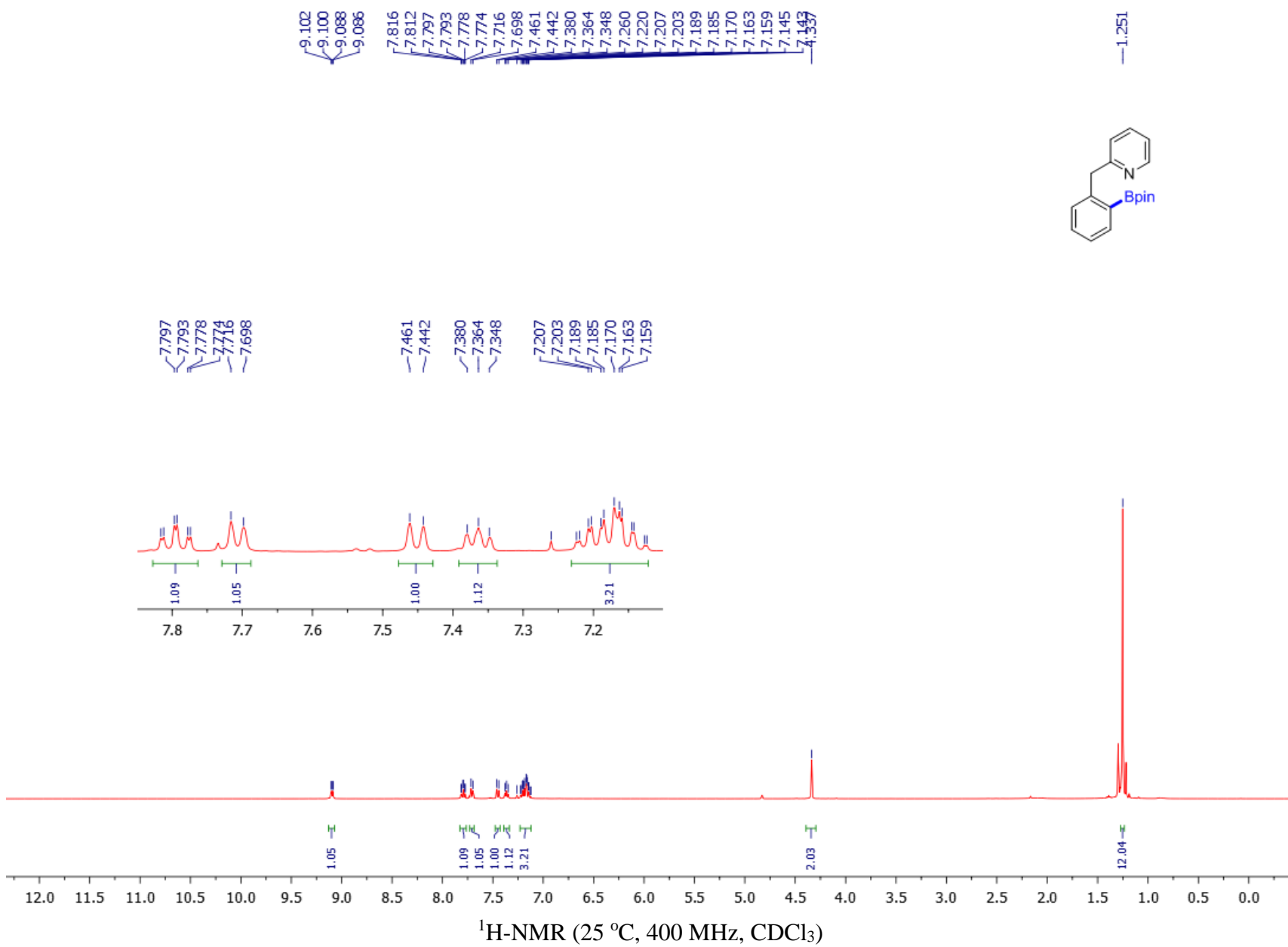


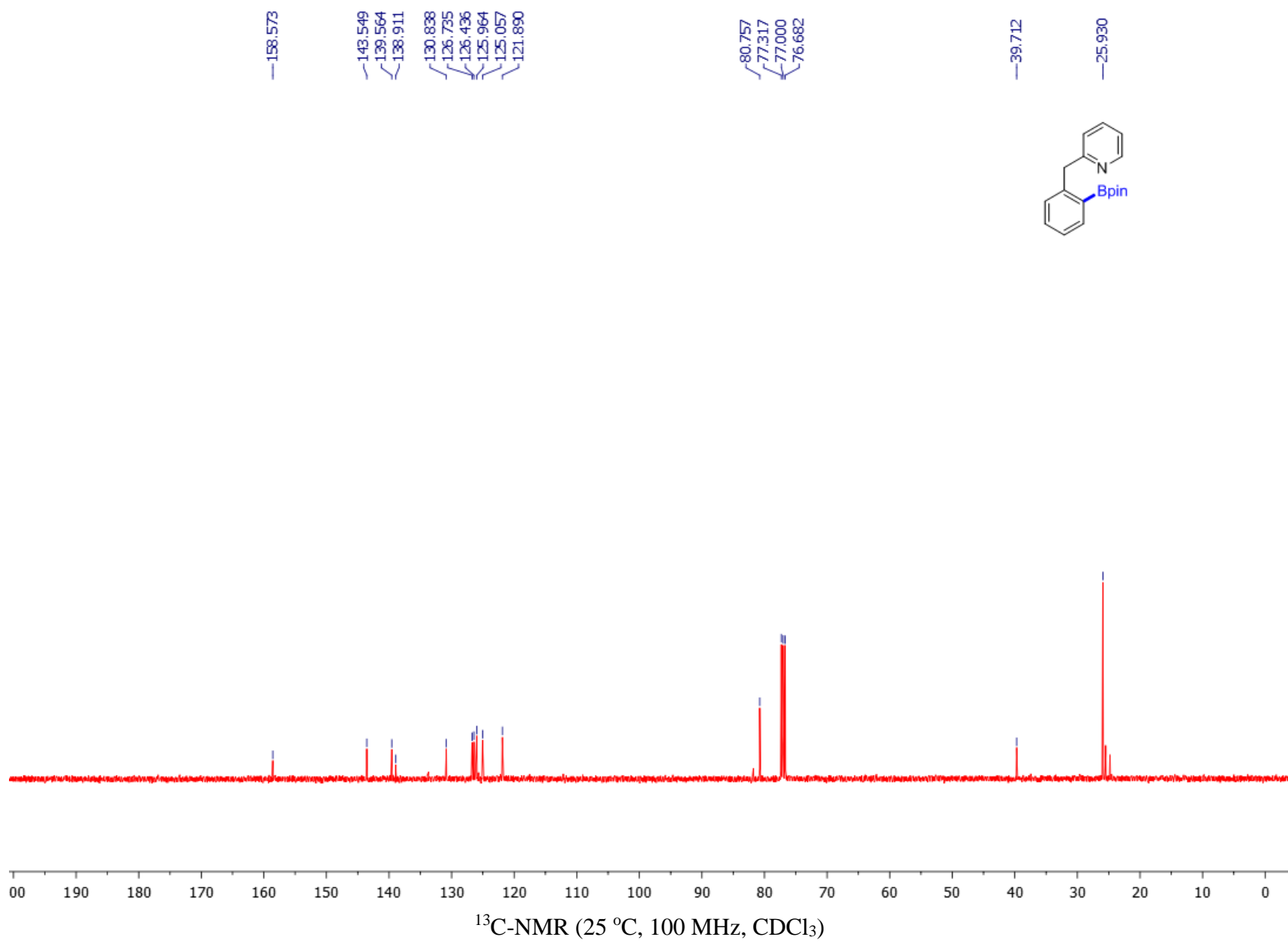


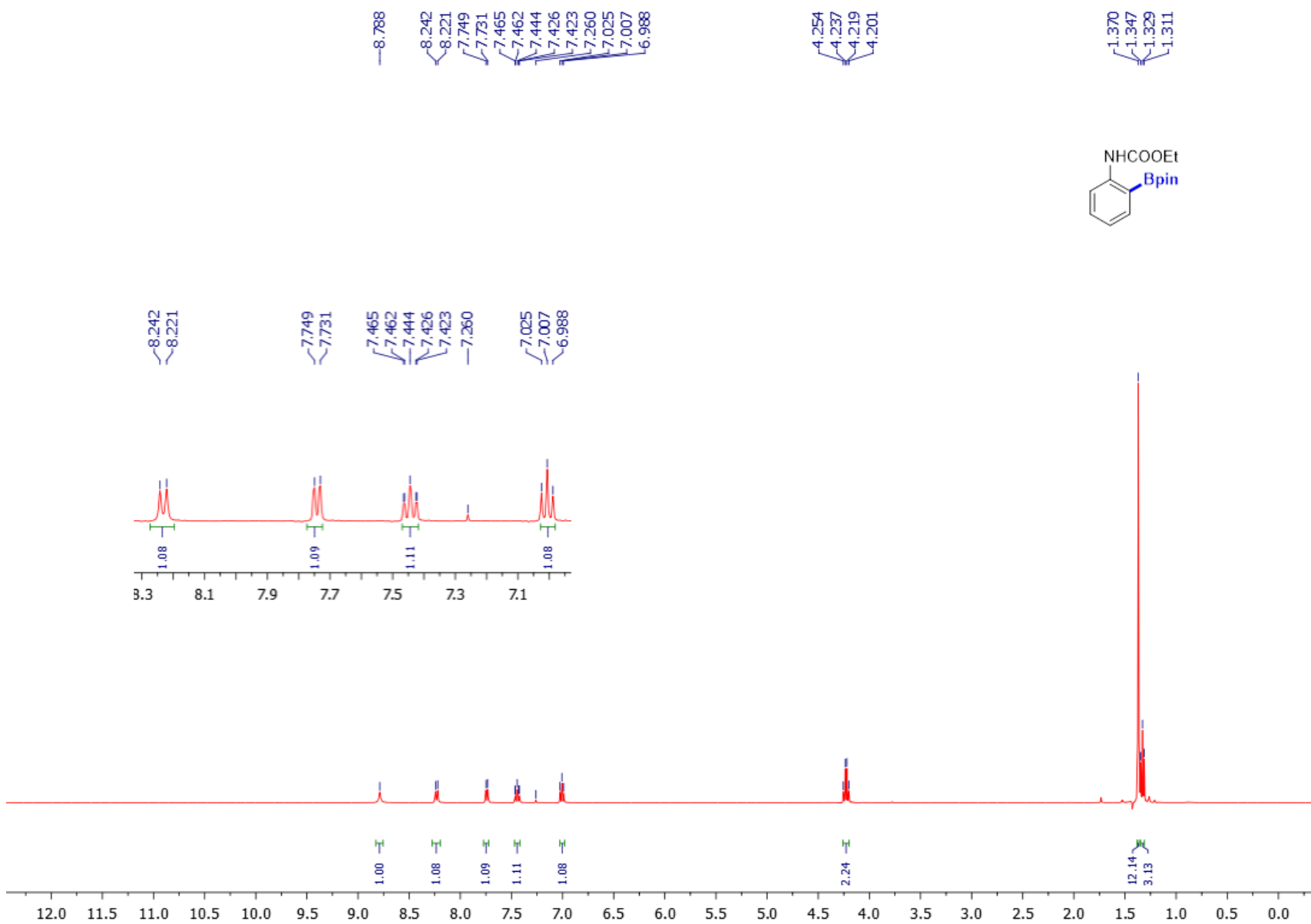




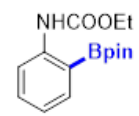
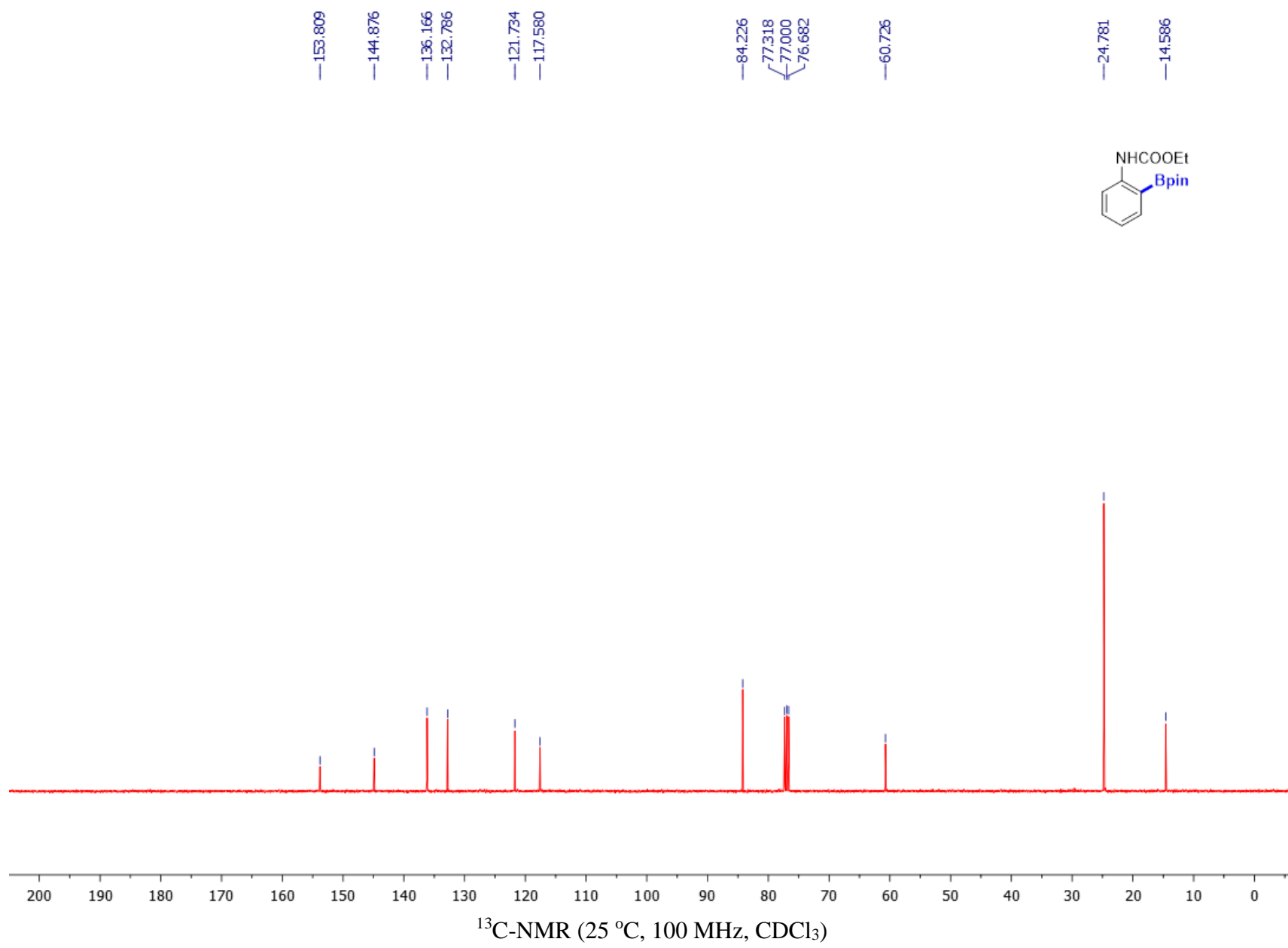


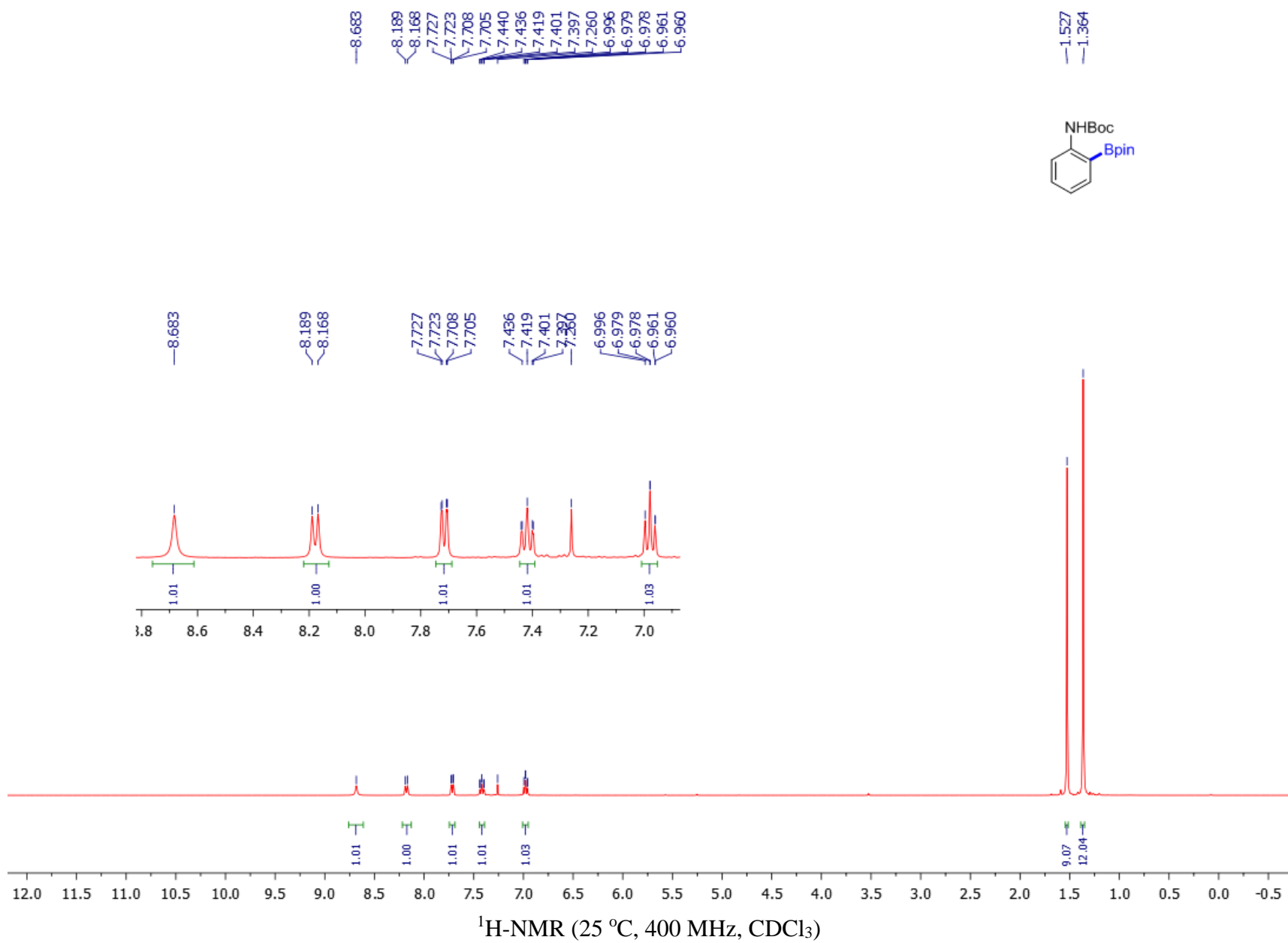


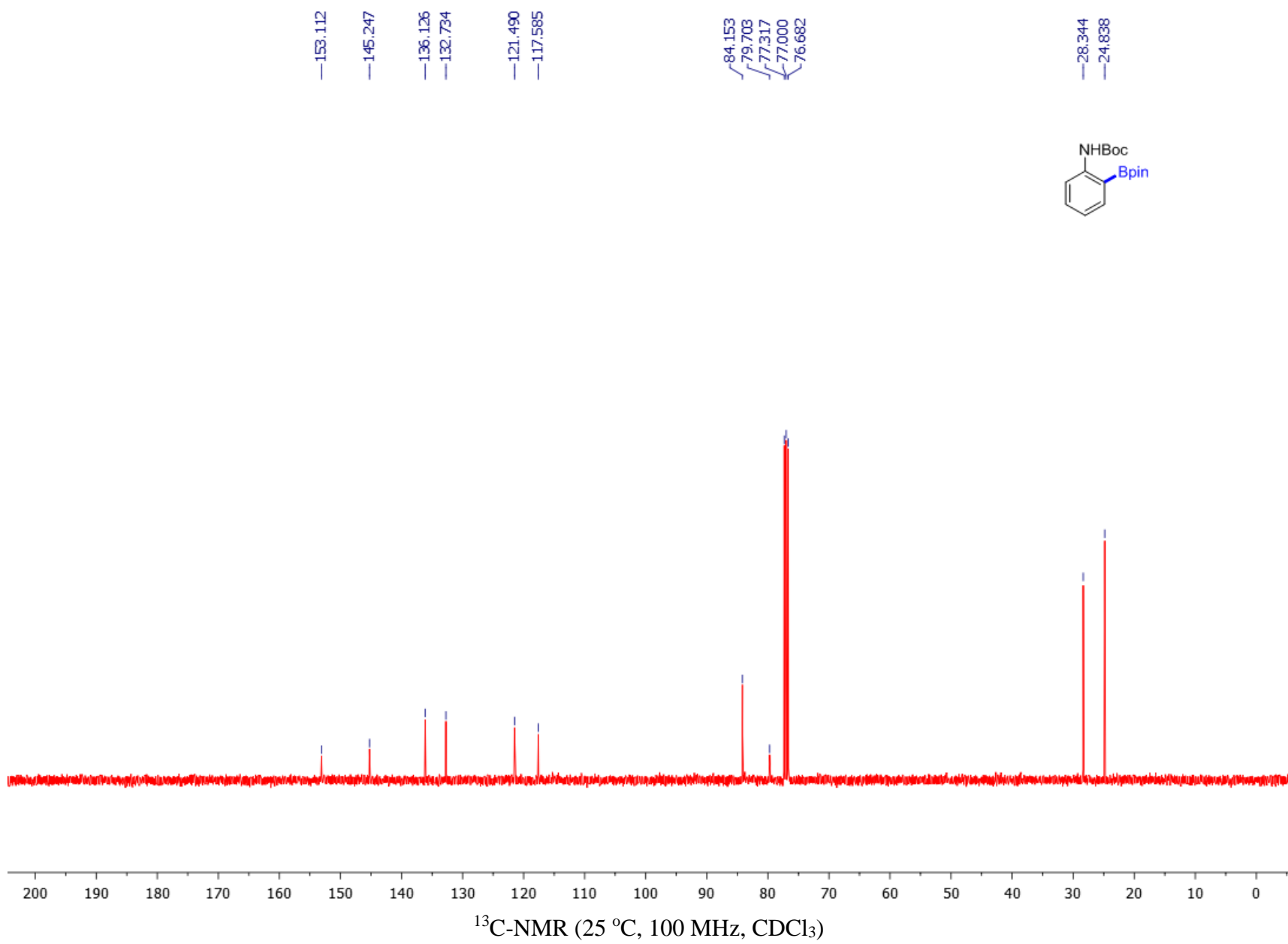


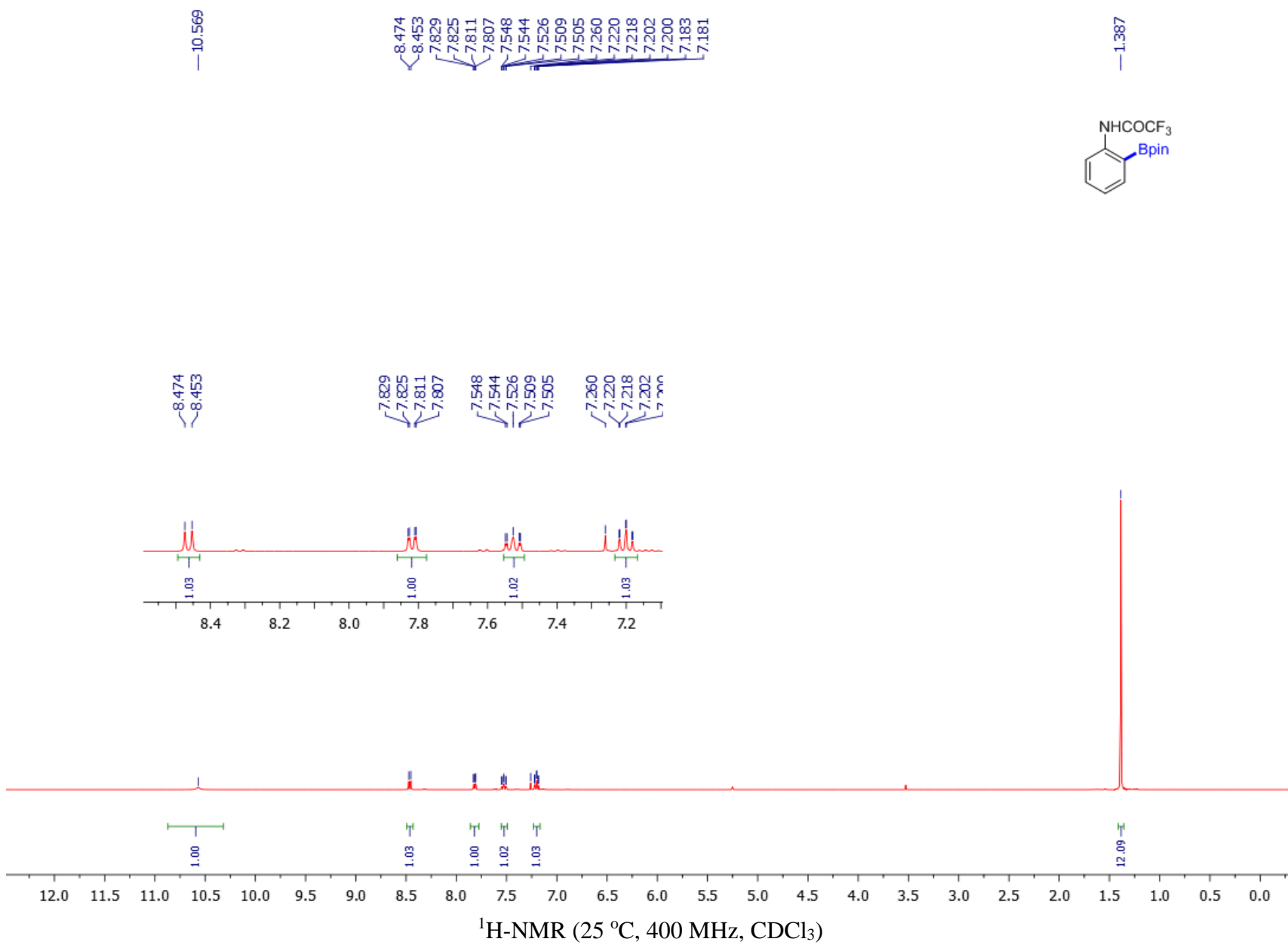


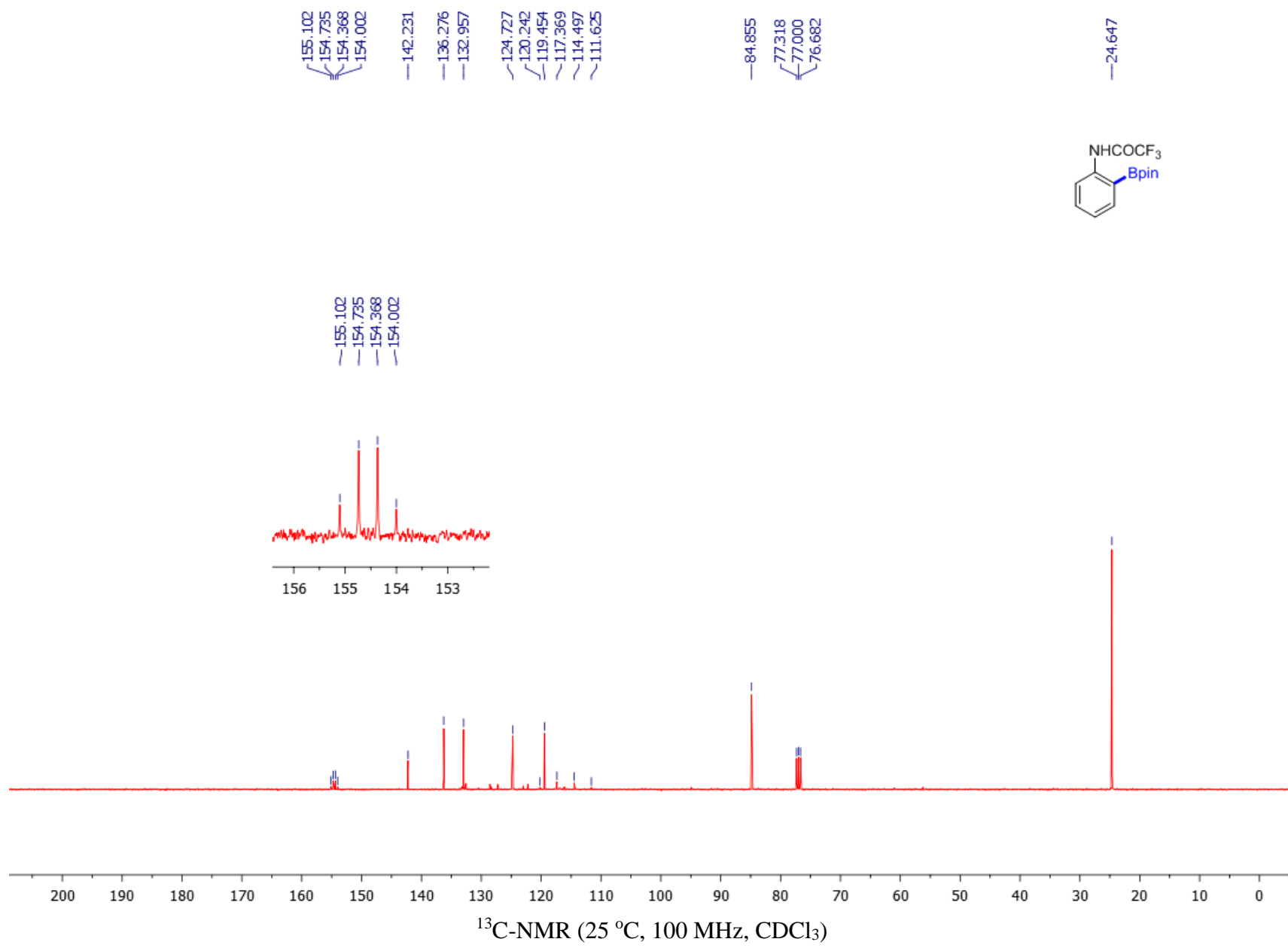
¹H-NMR (25 °C, 400 MHz, CDCl₃)

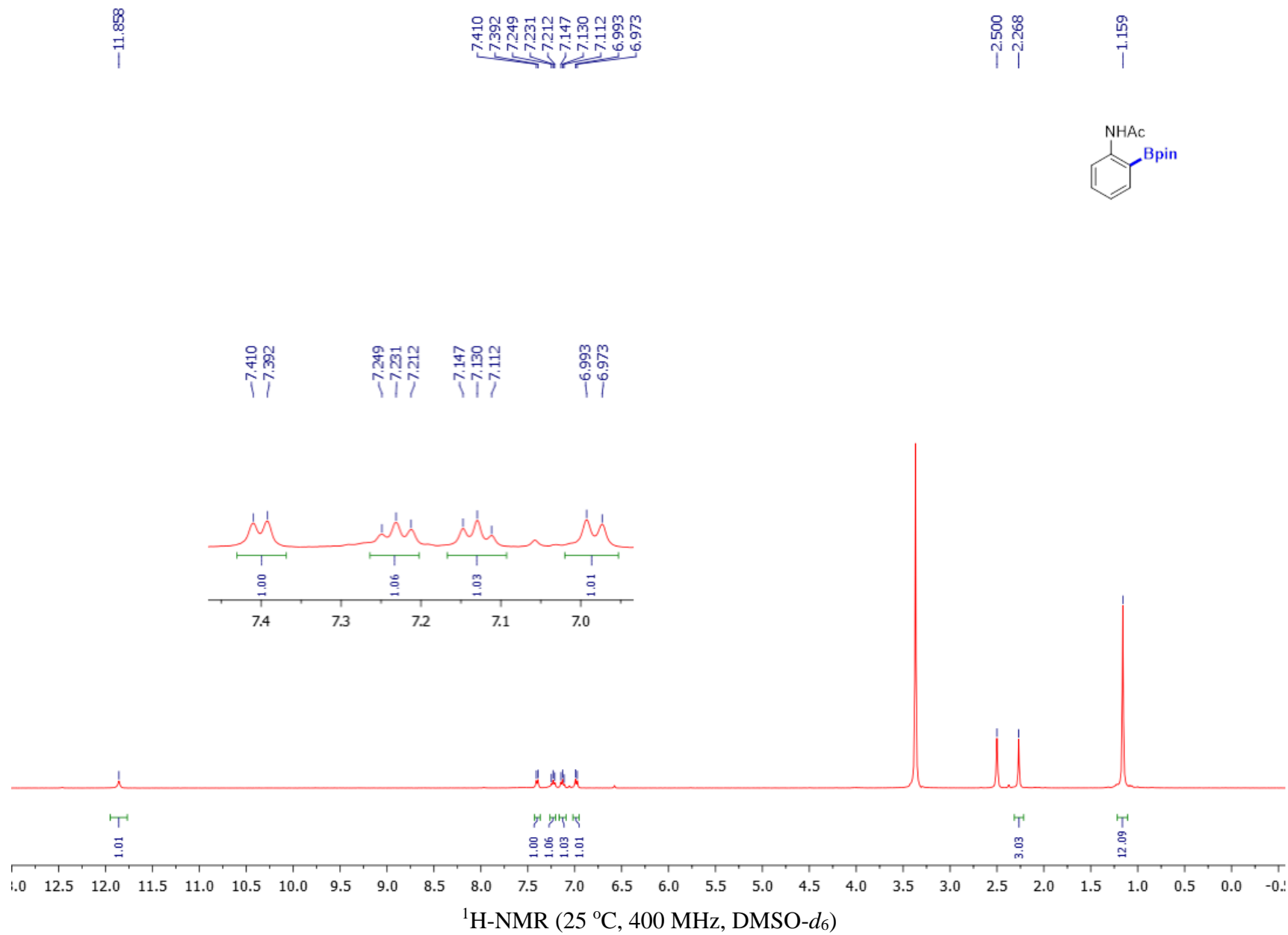


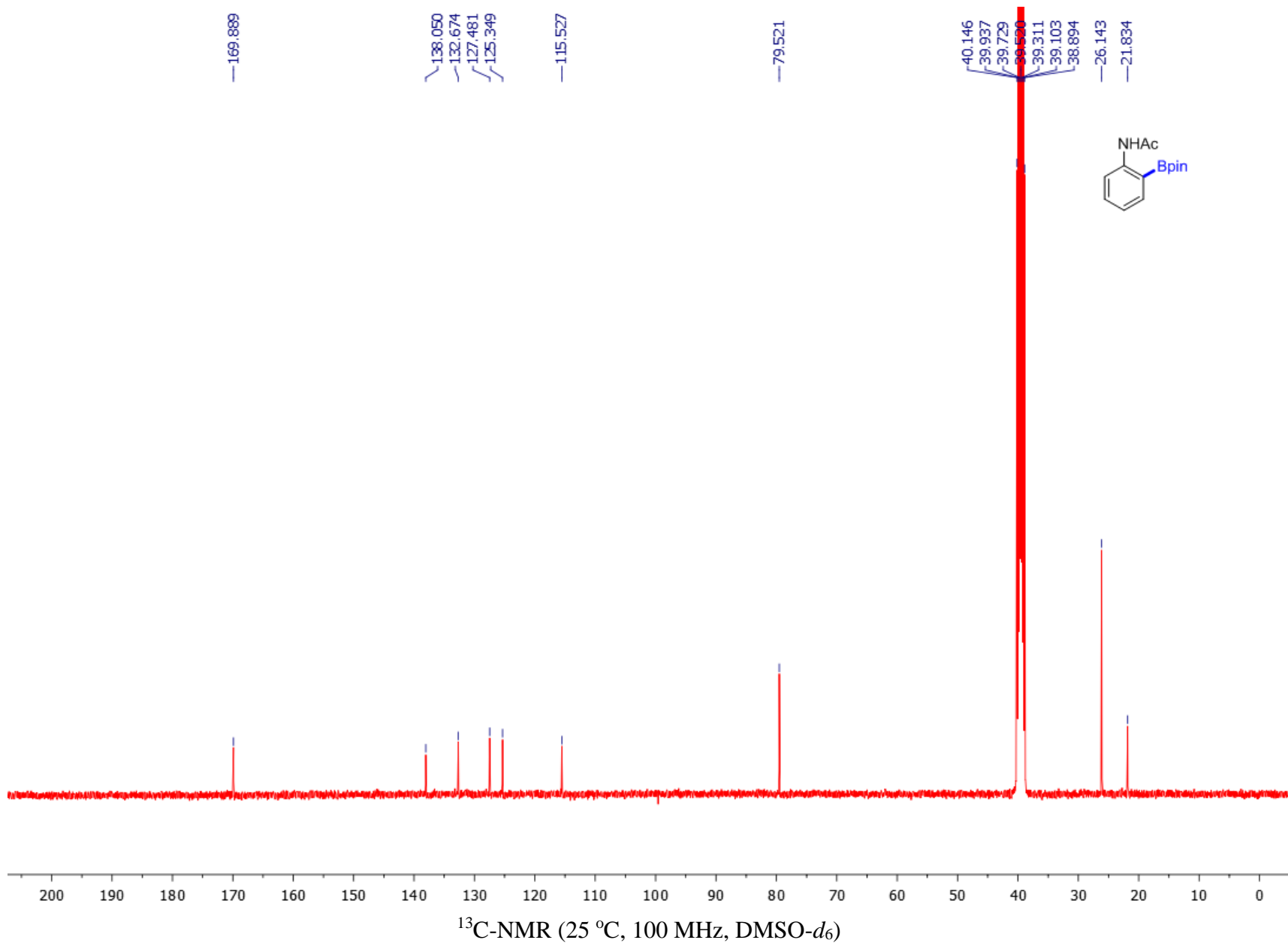


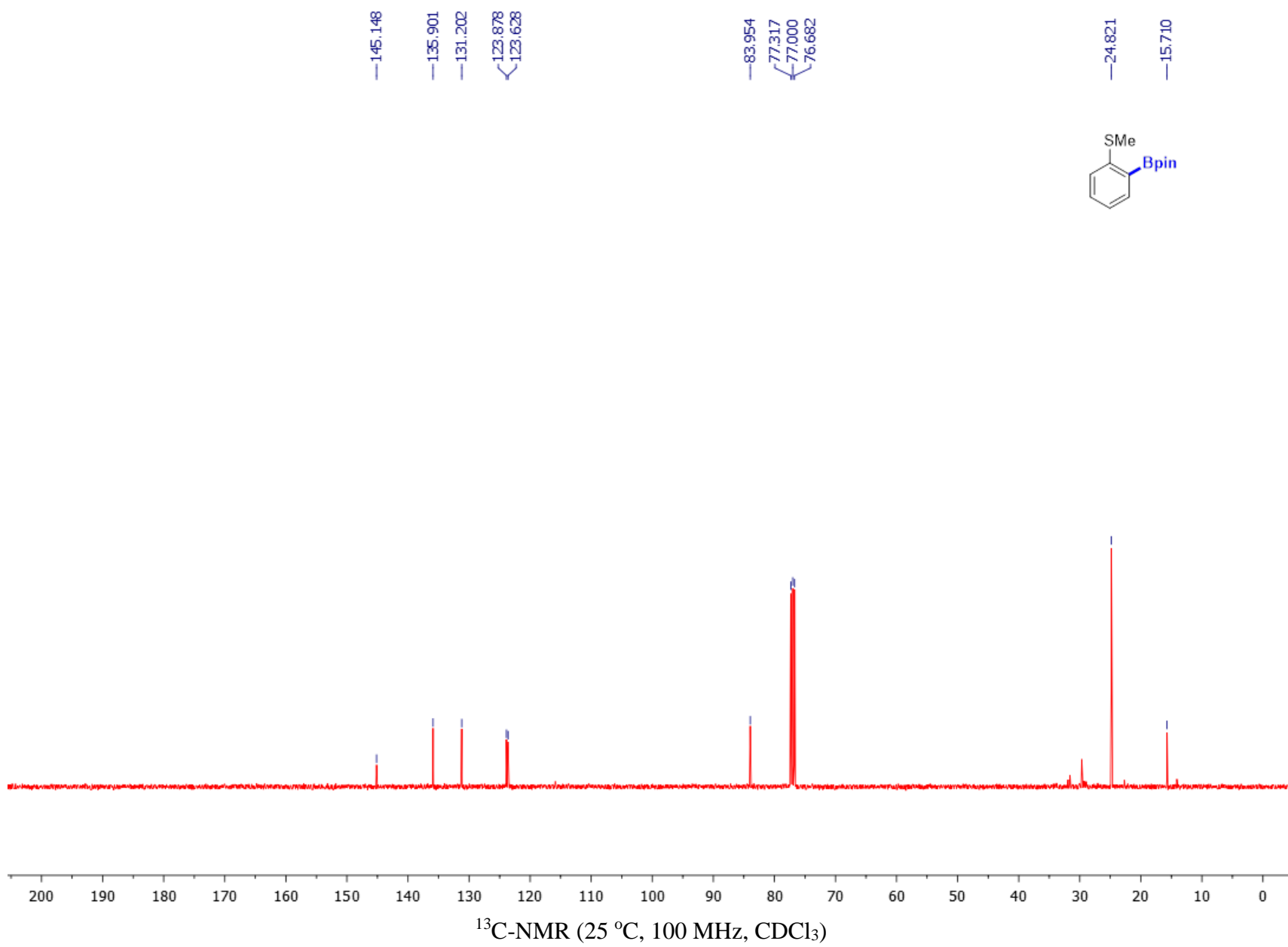


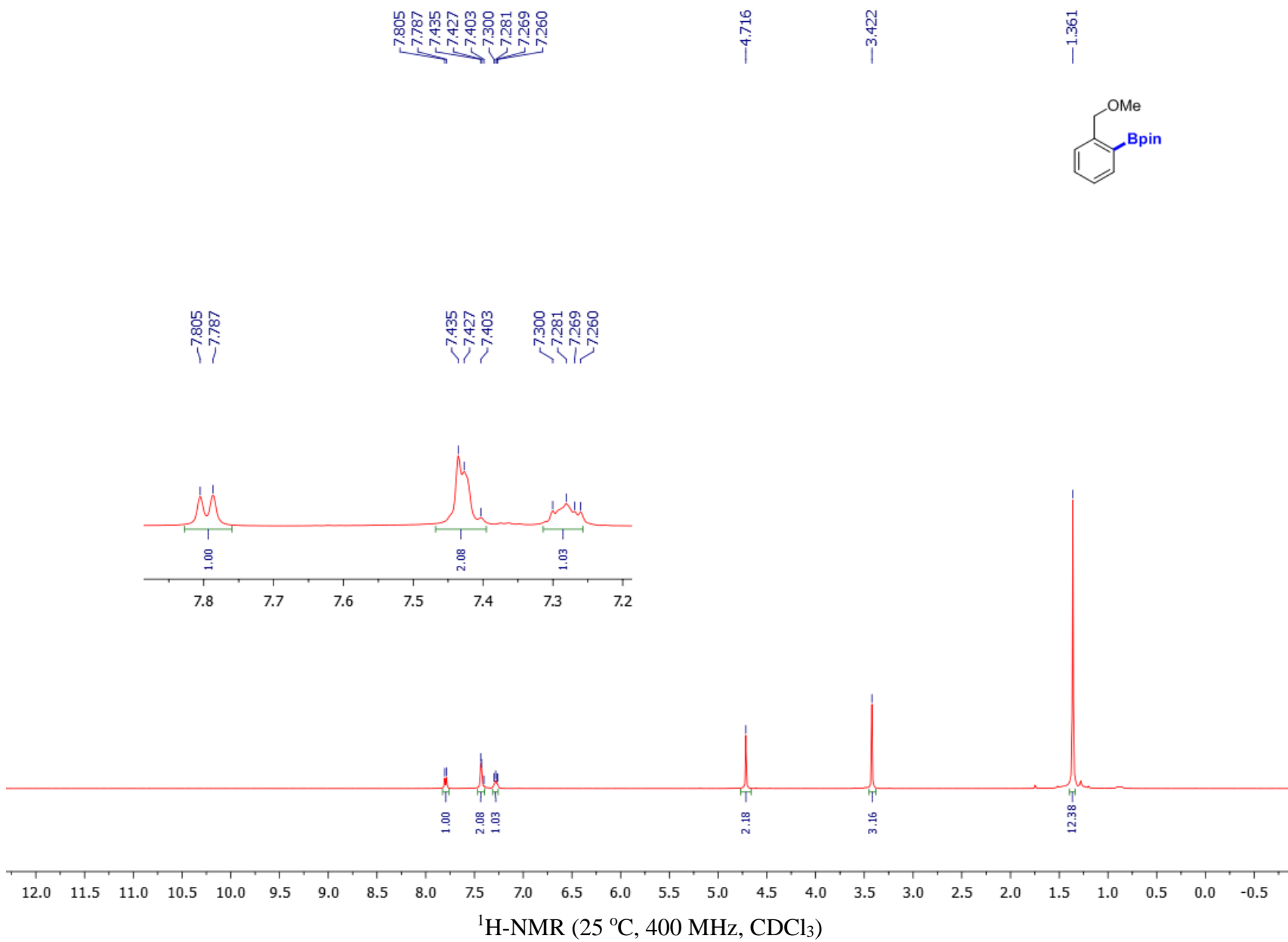


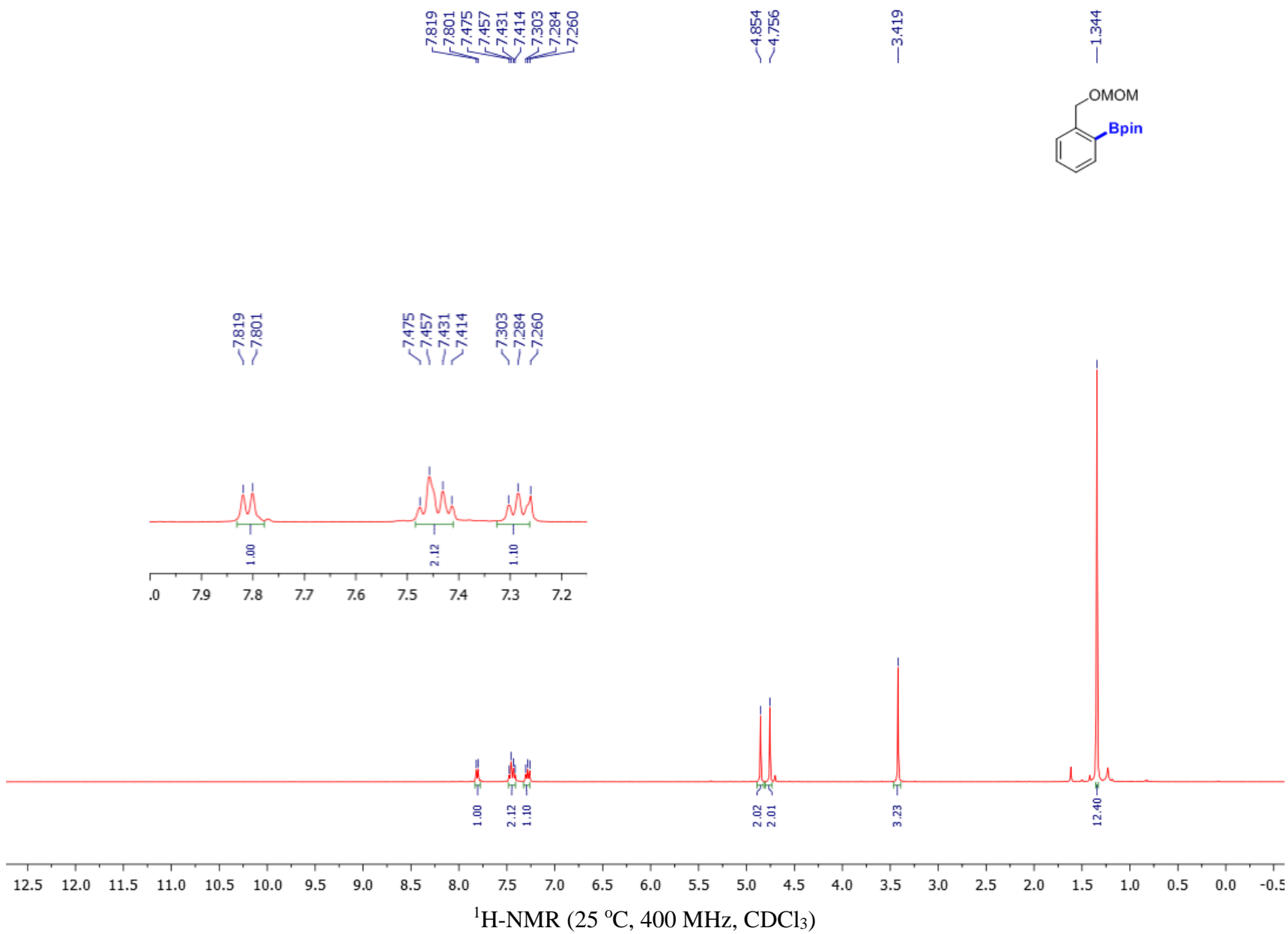


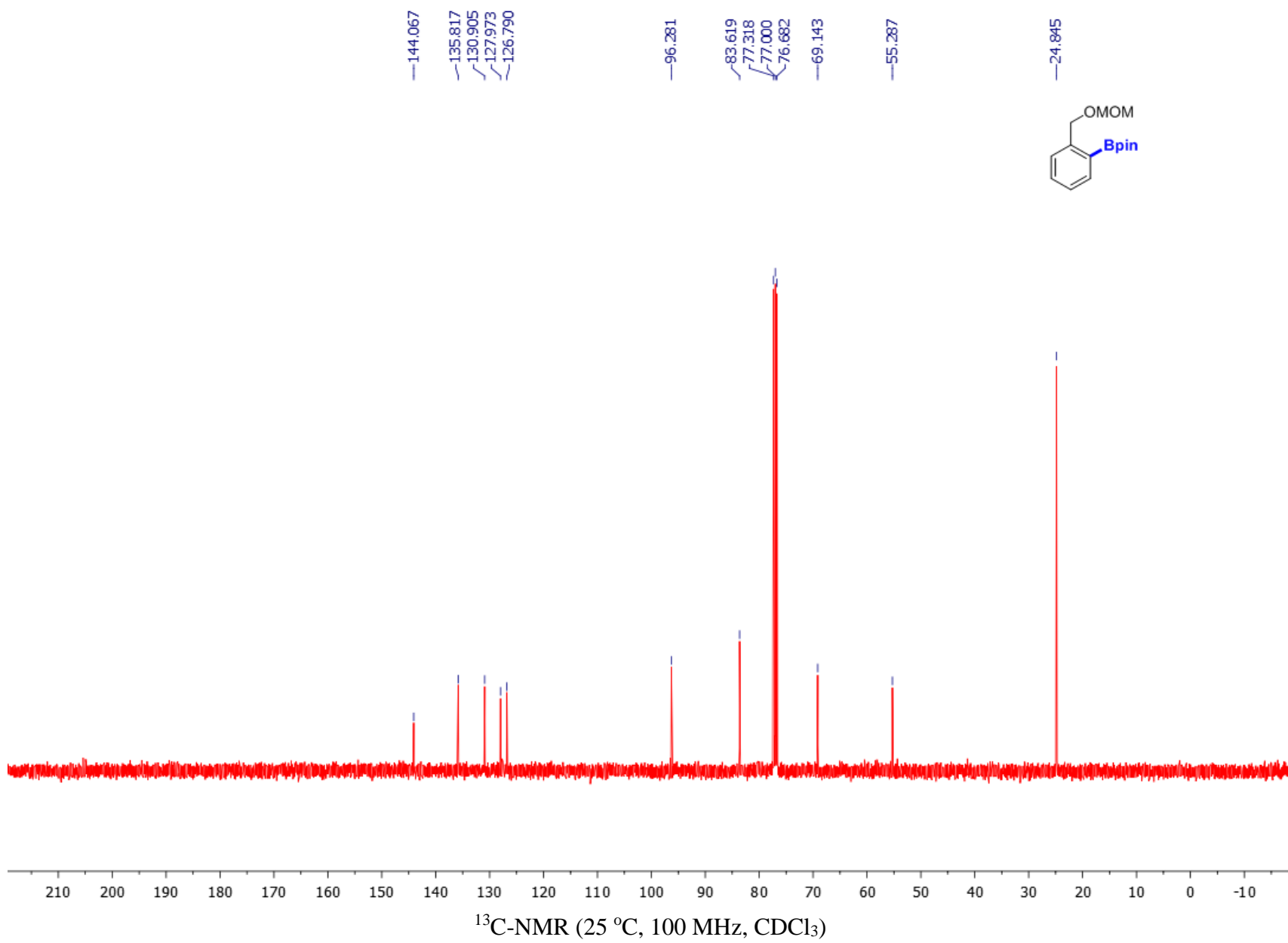


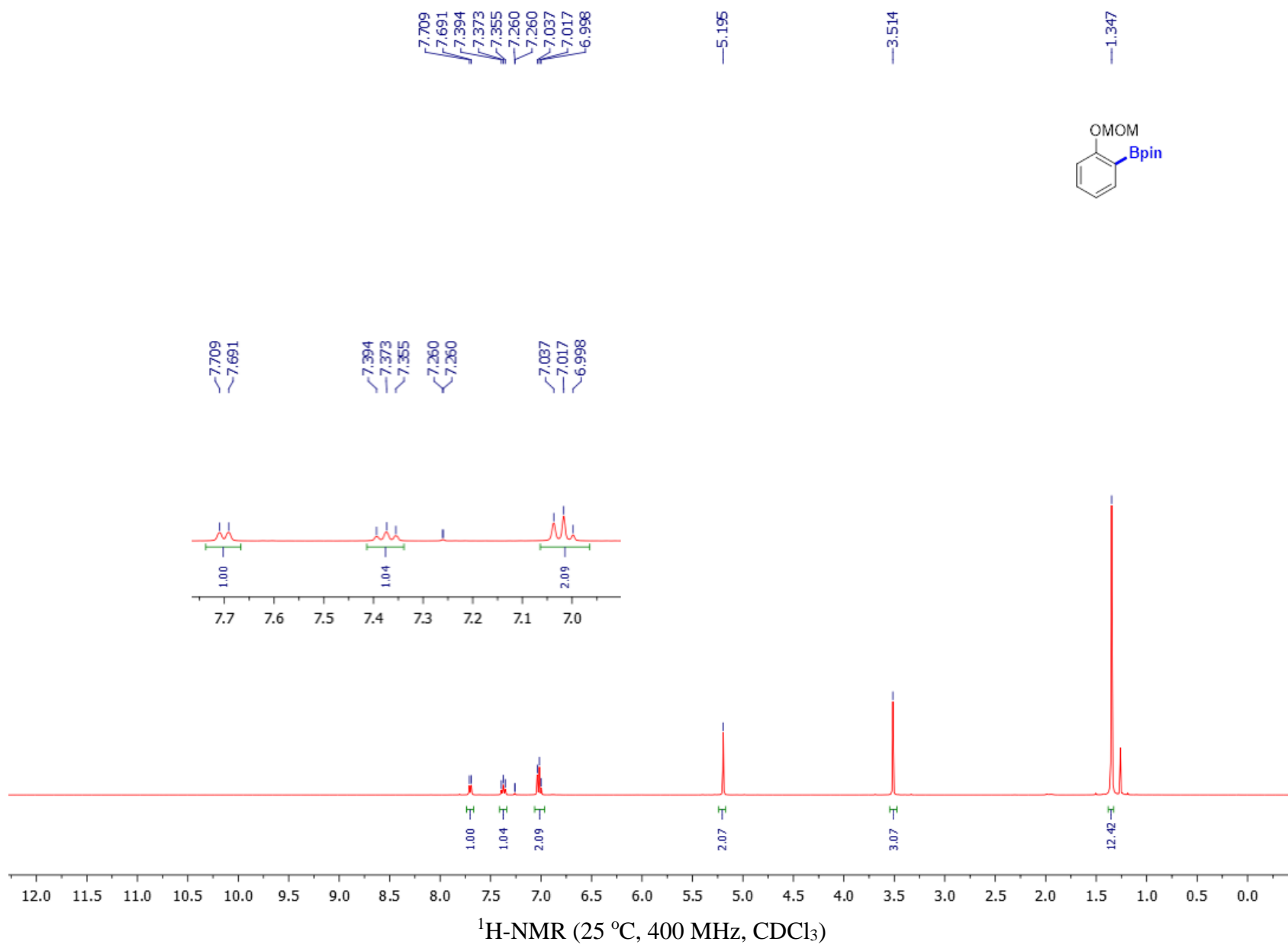


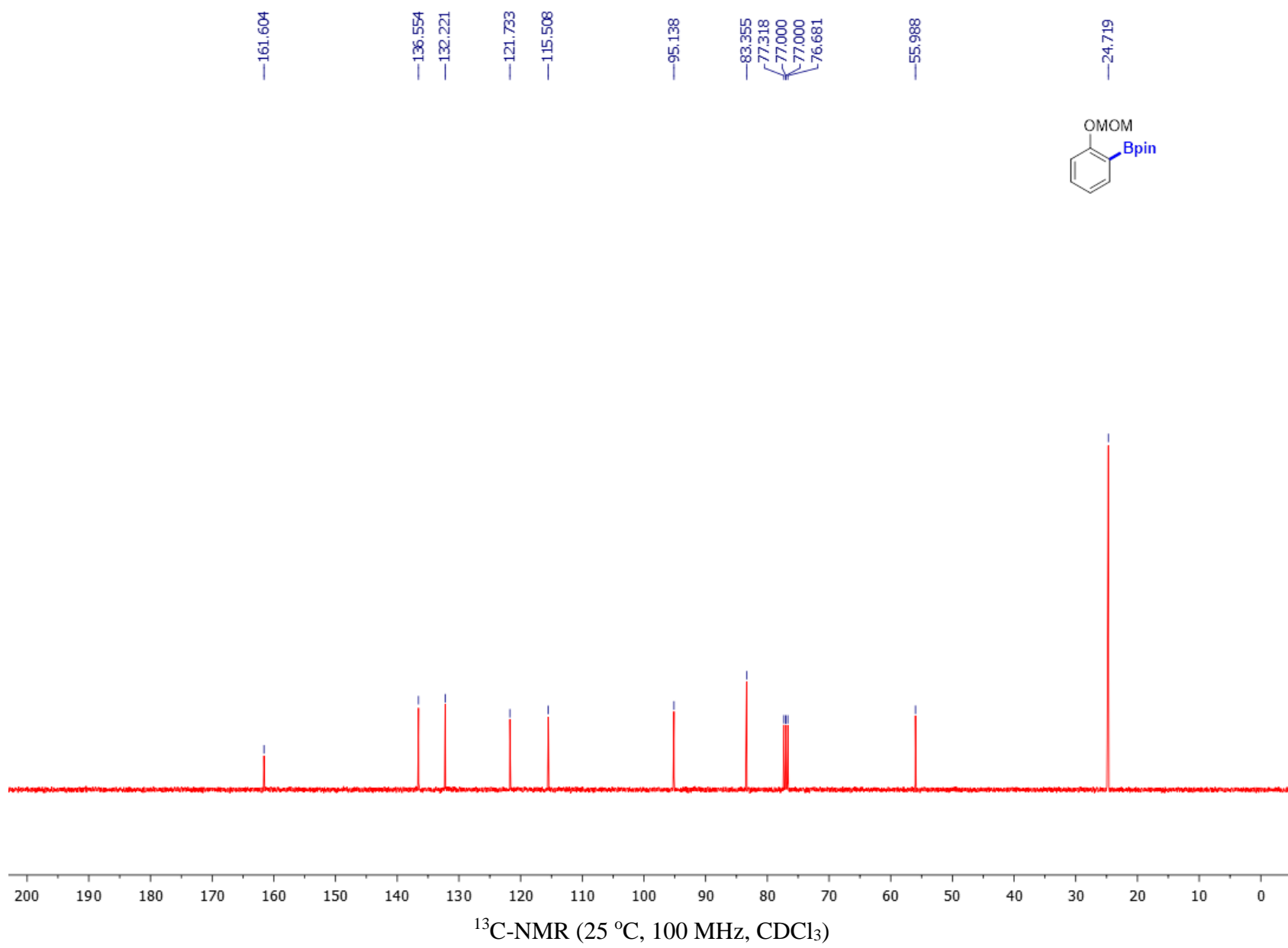


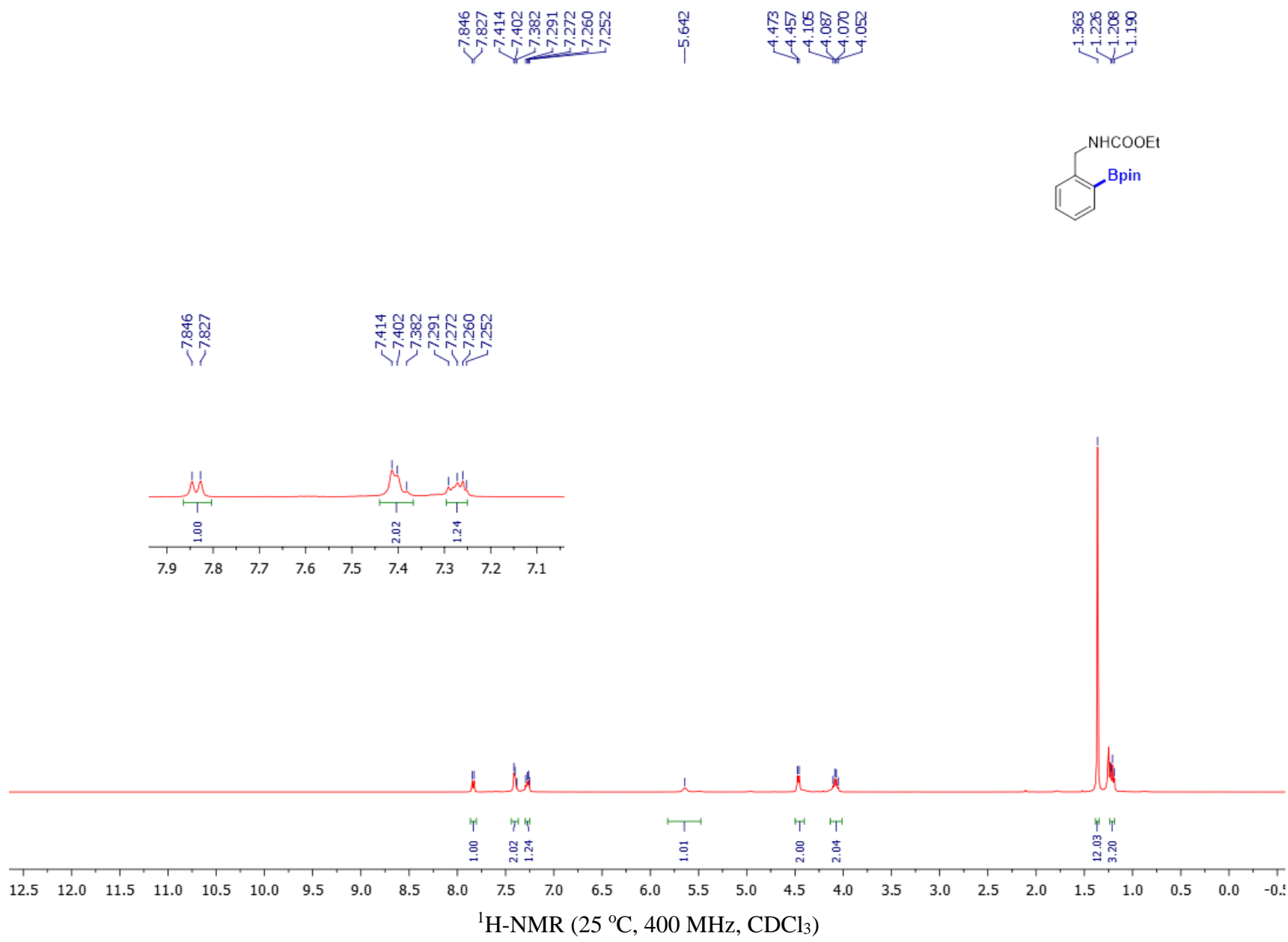


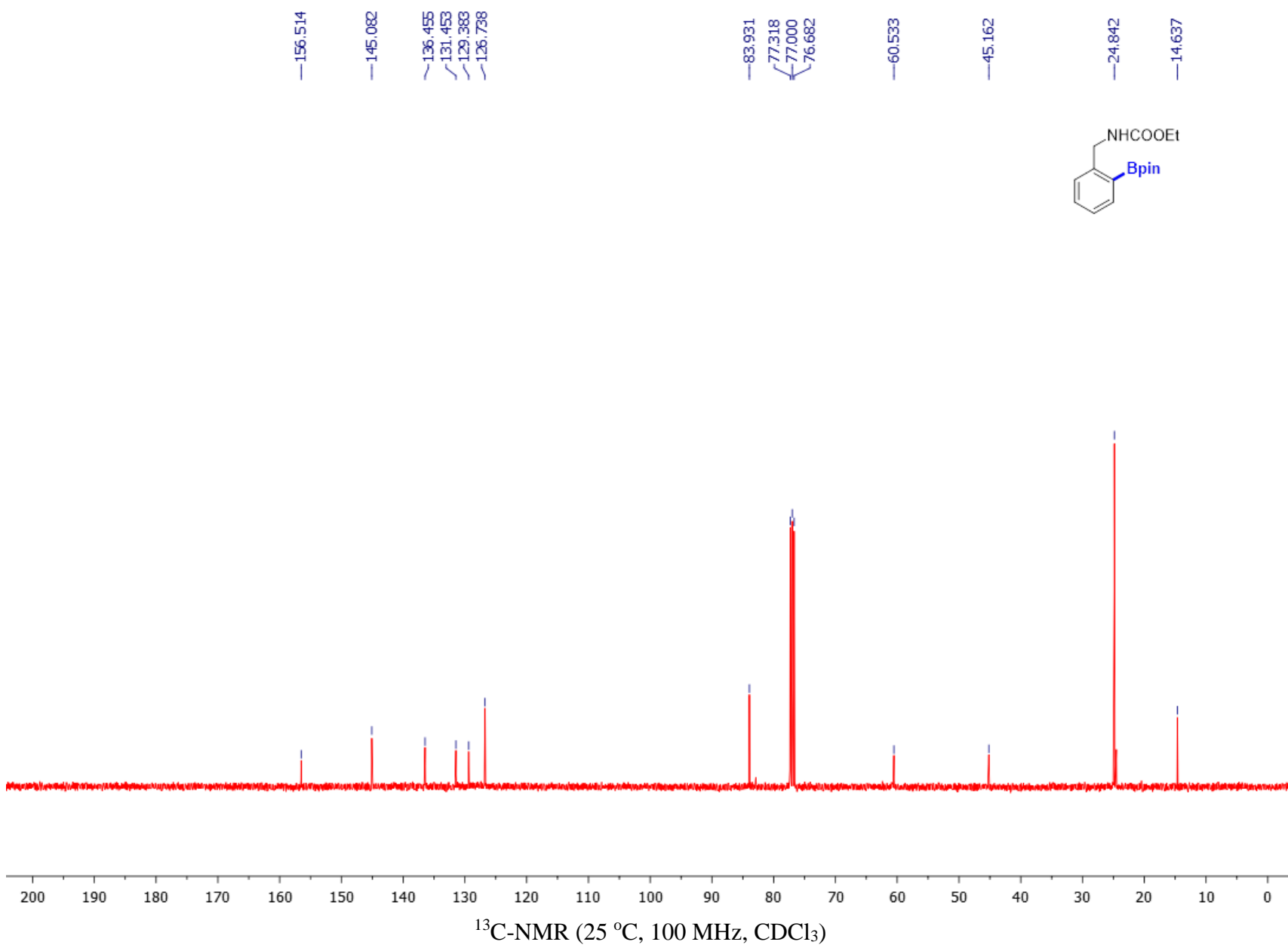


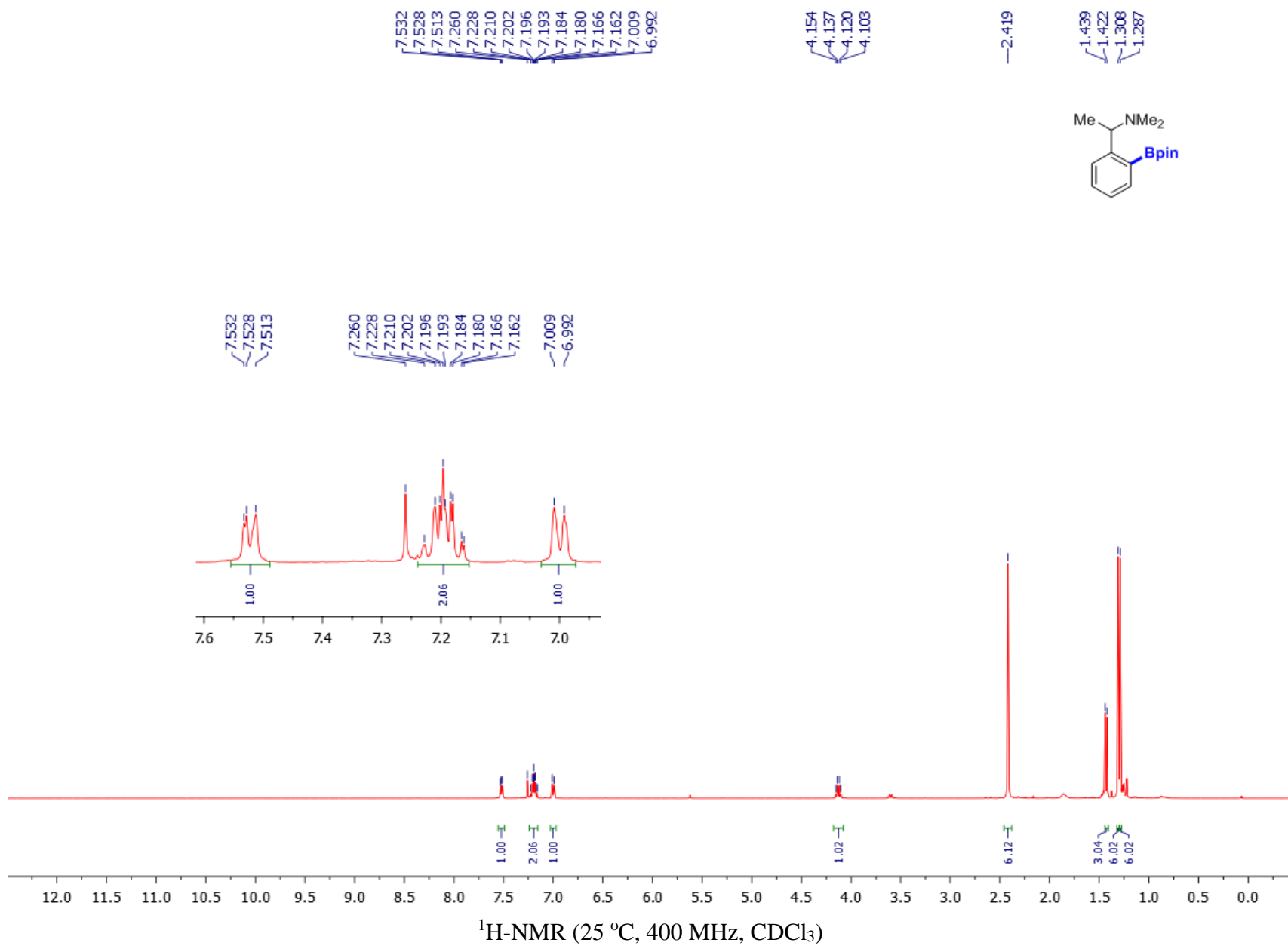


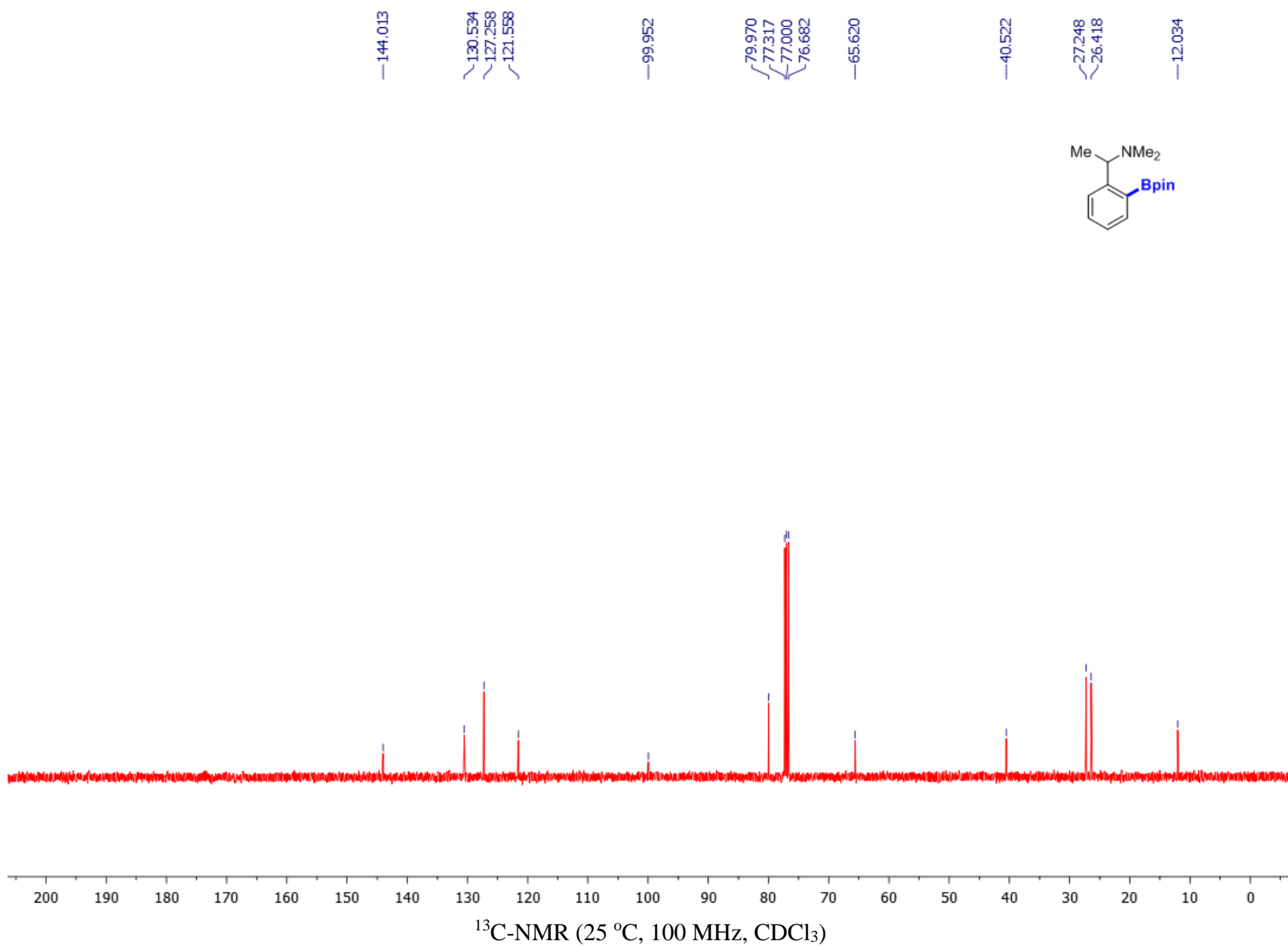






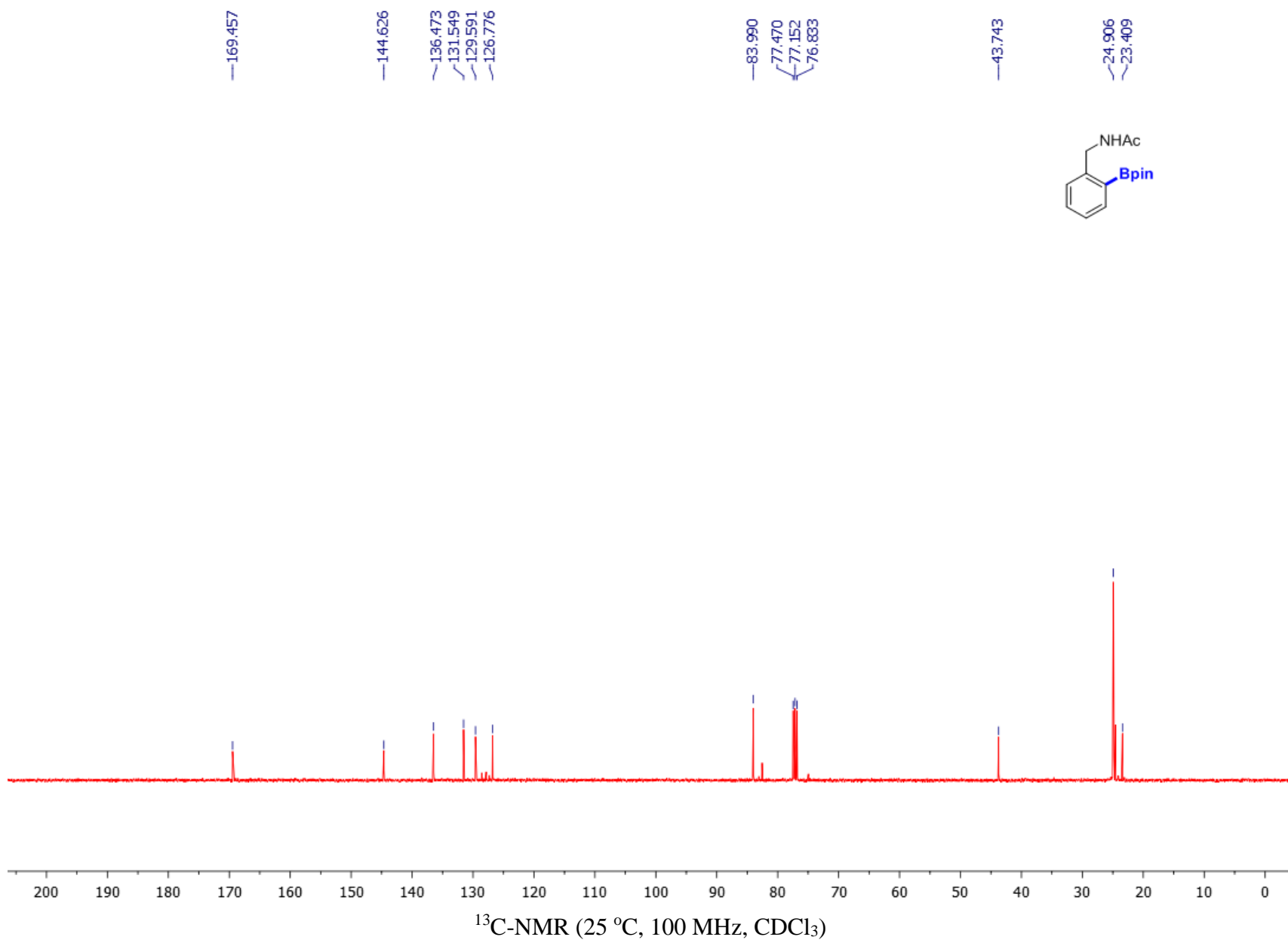


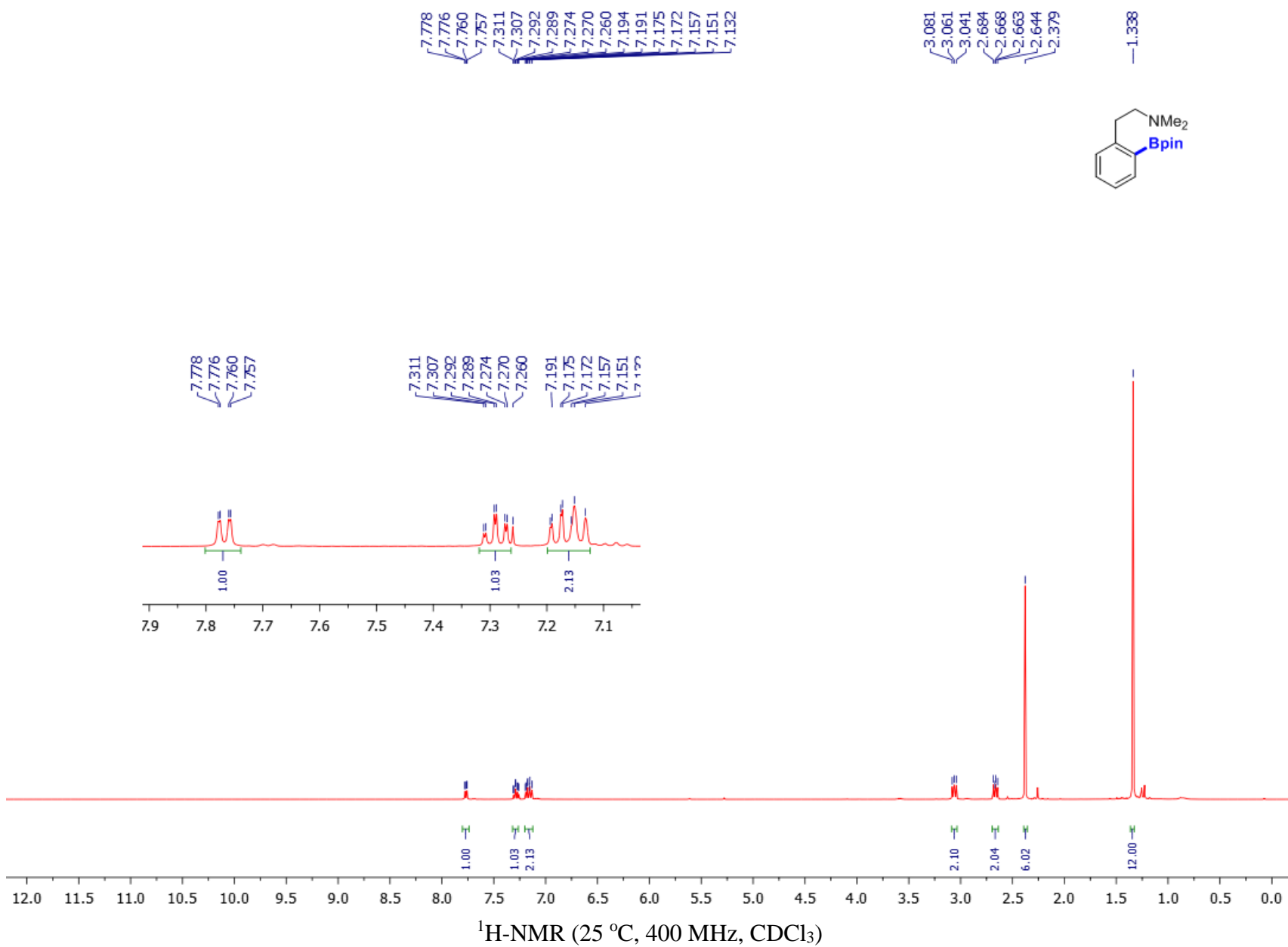


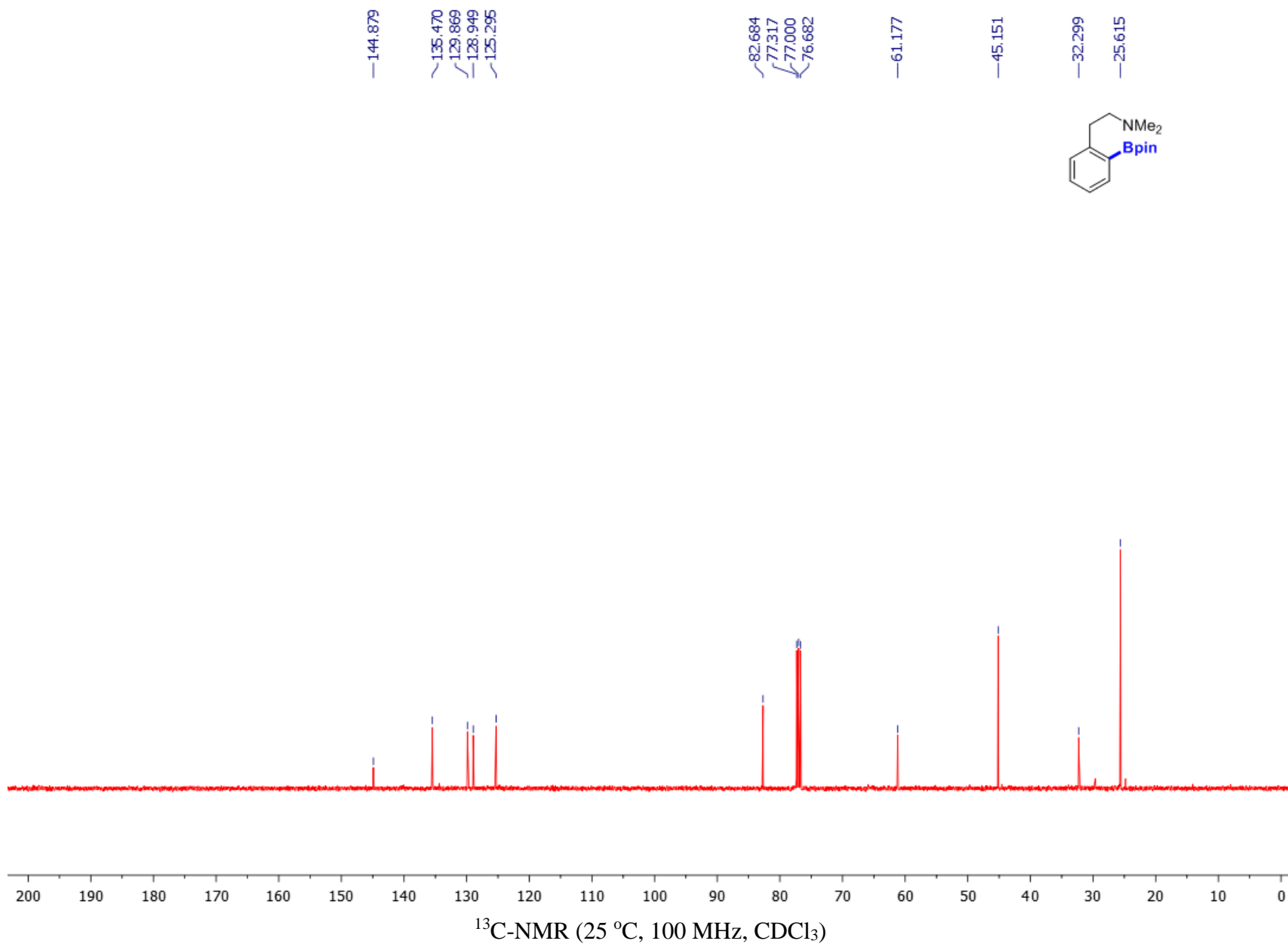


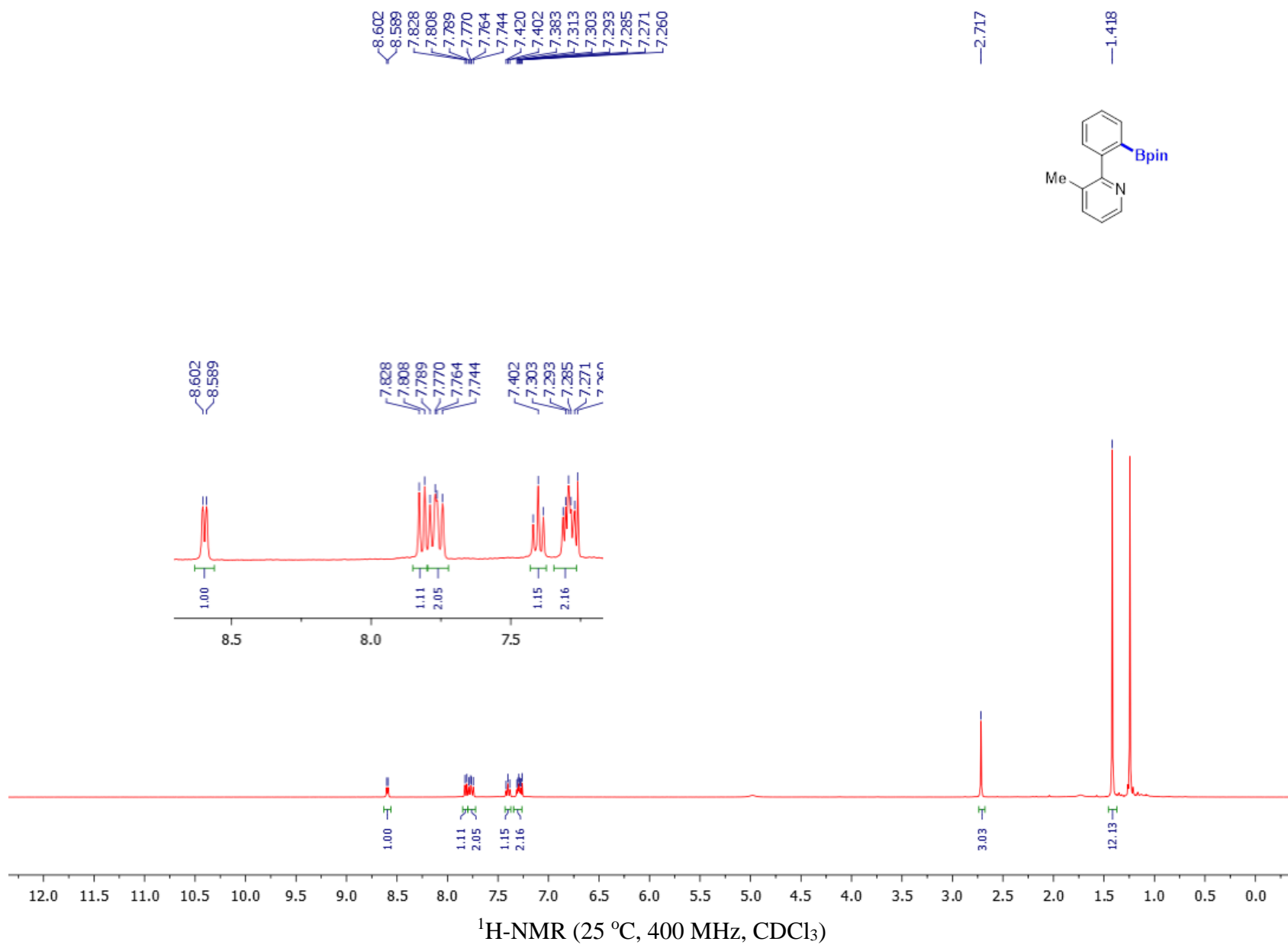


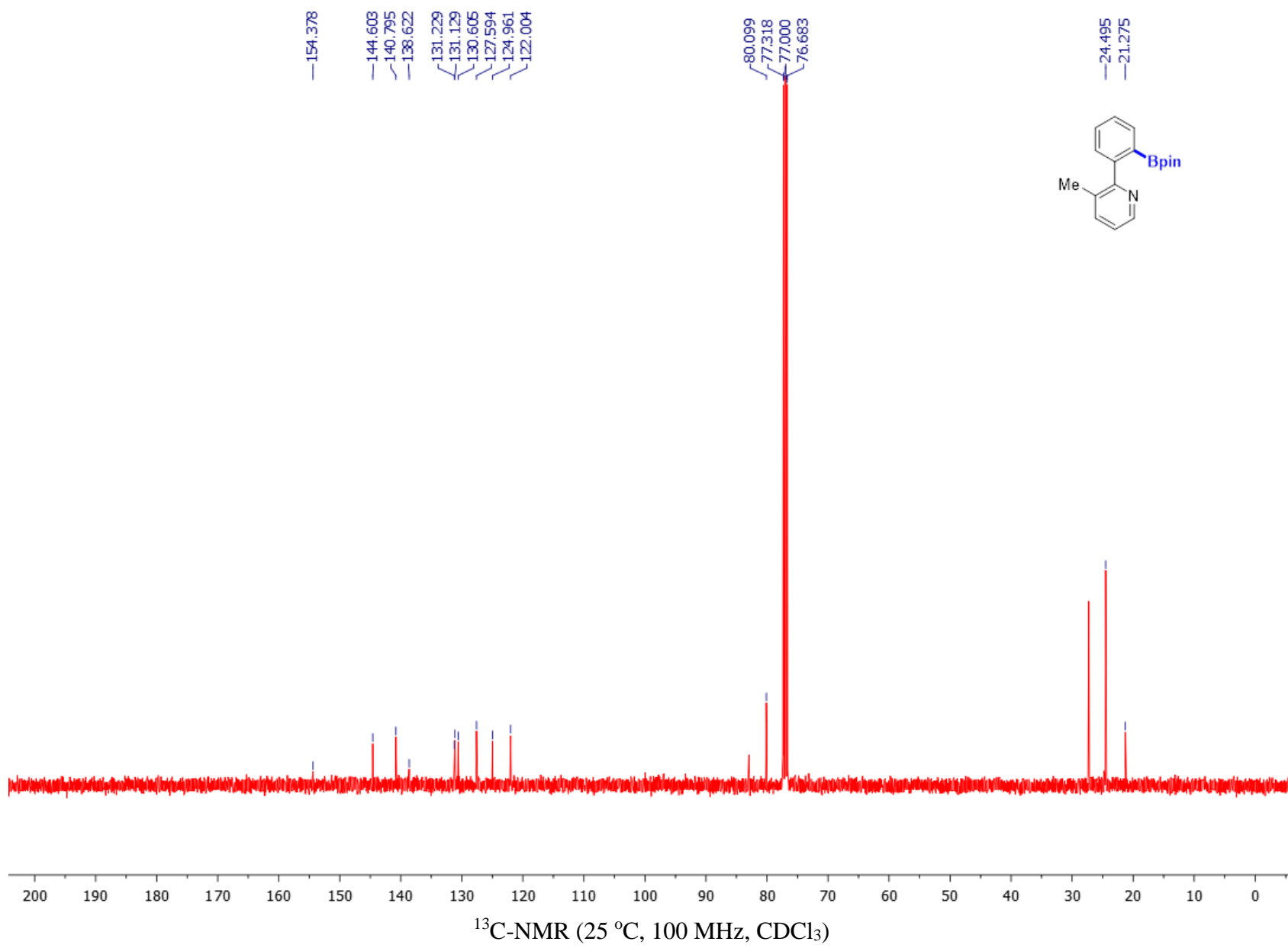
¹H-NMR (25 °C, 400 MHz, CDCl₃)

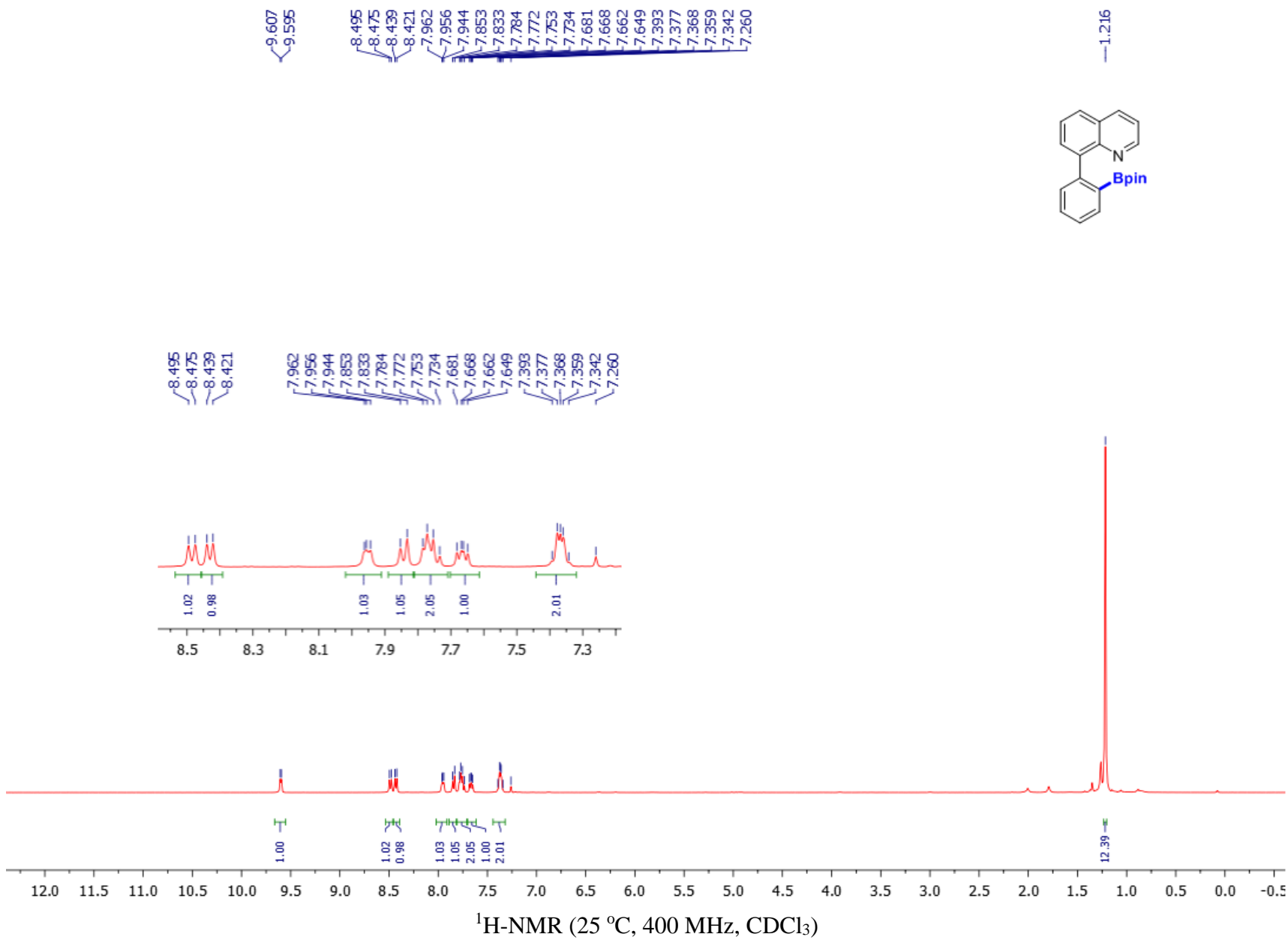


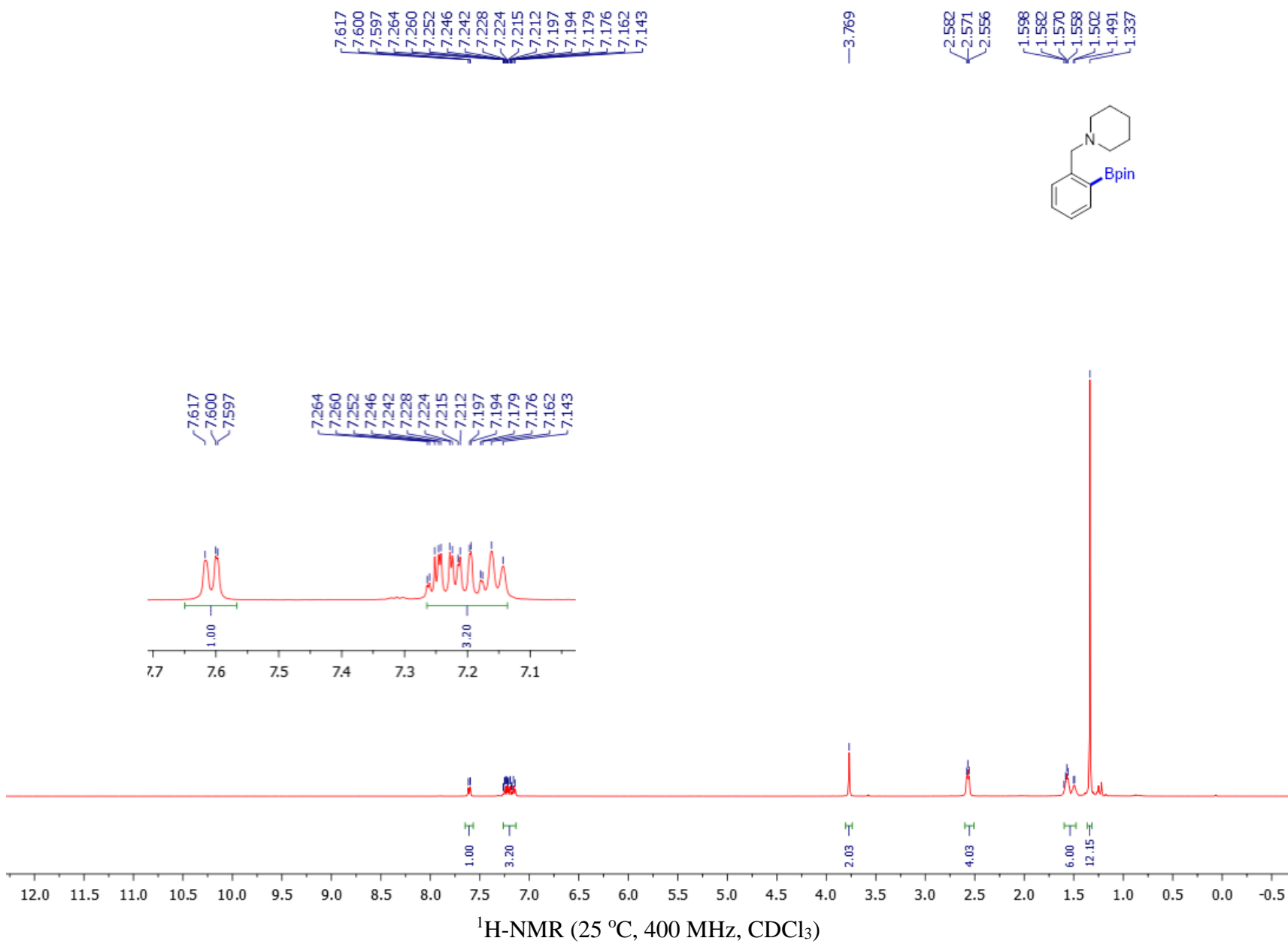


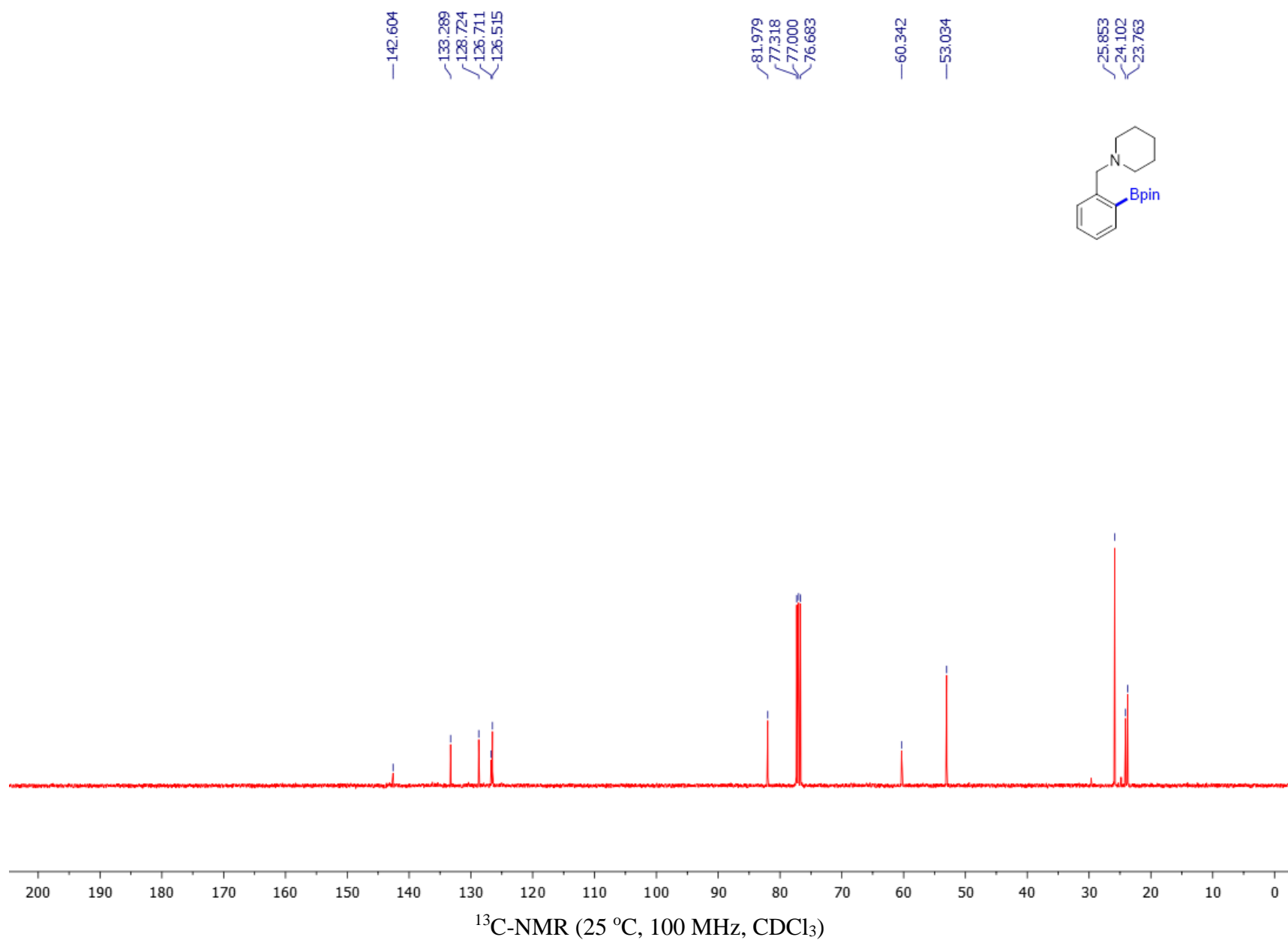


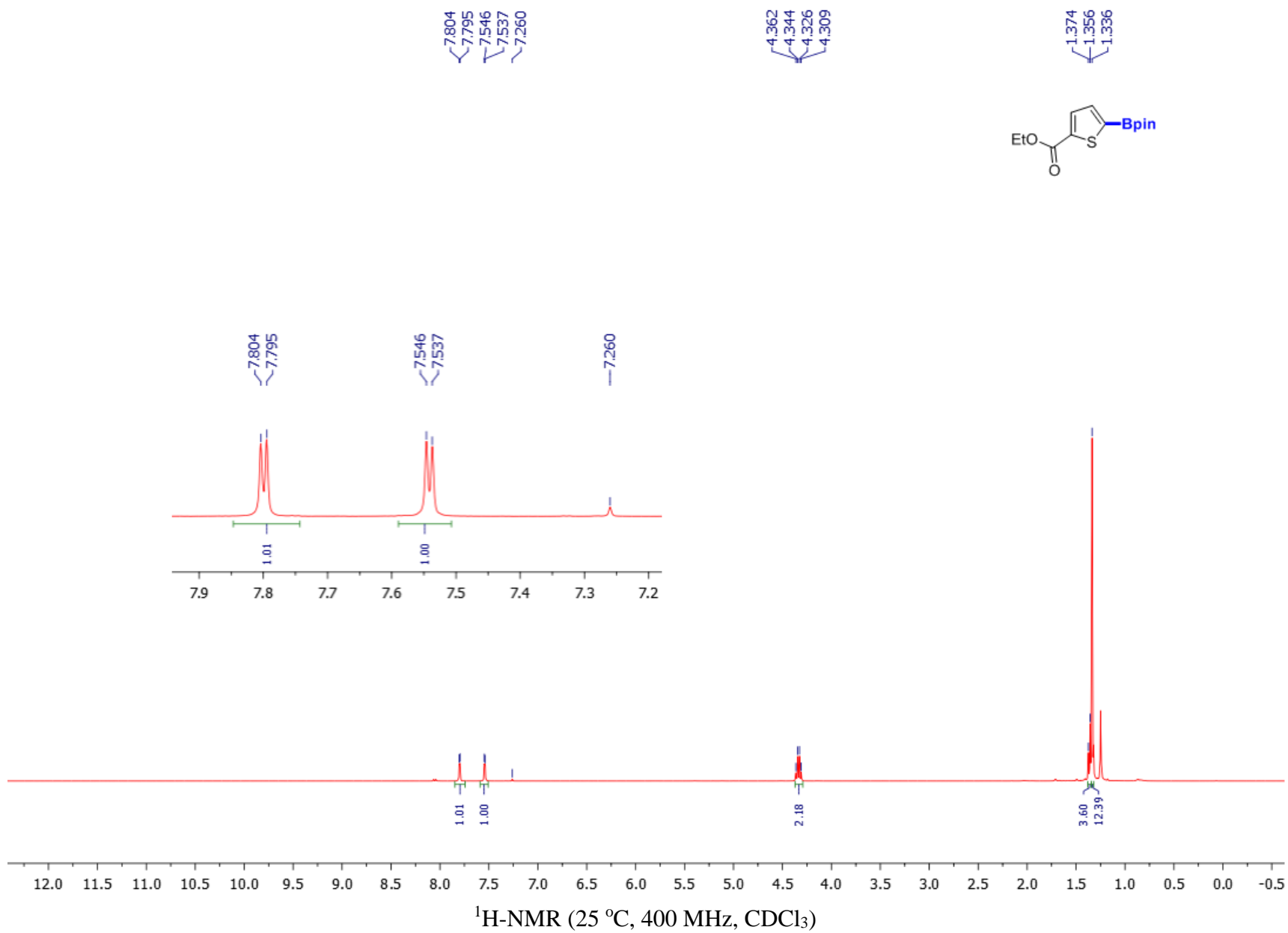


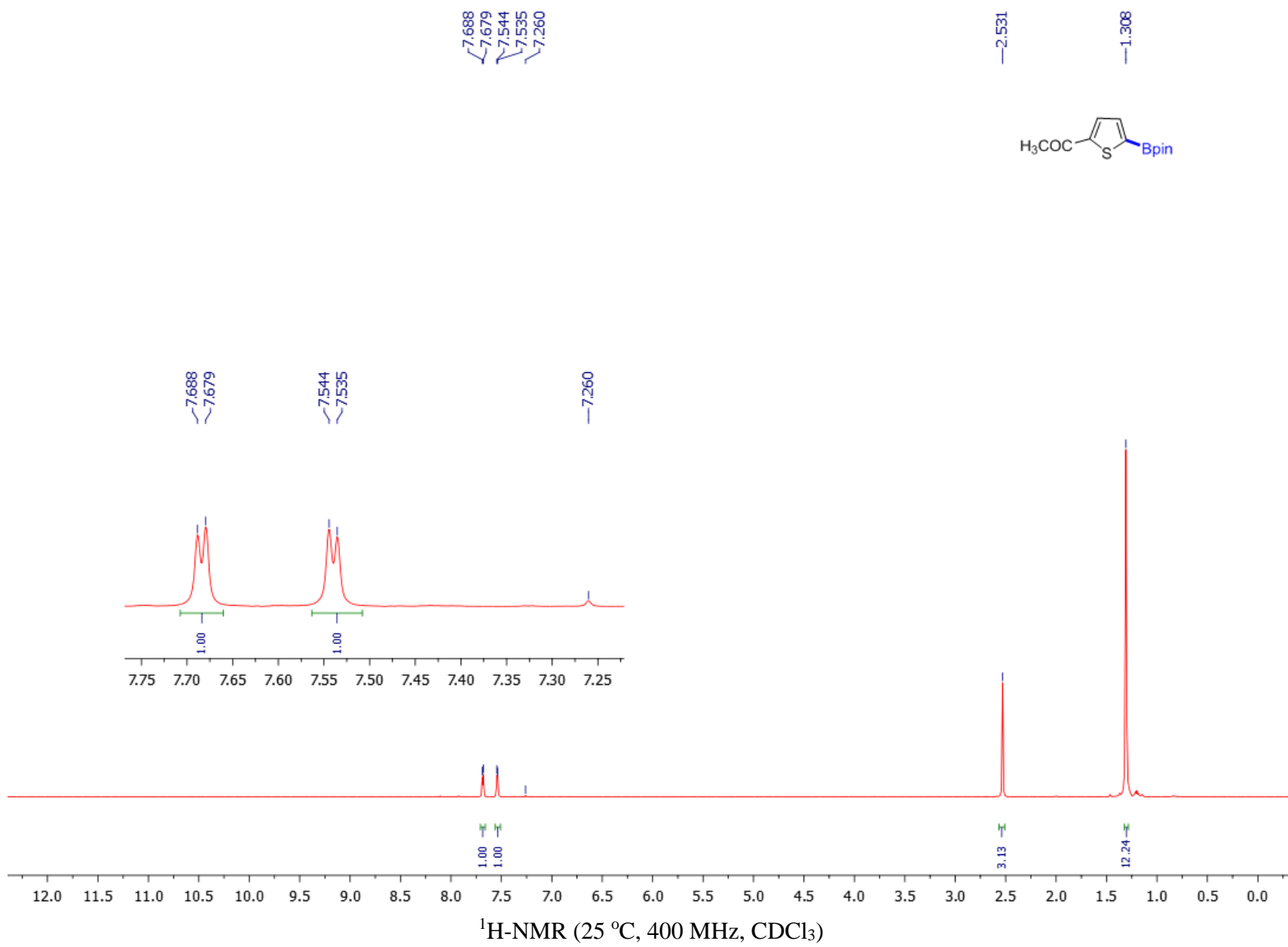


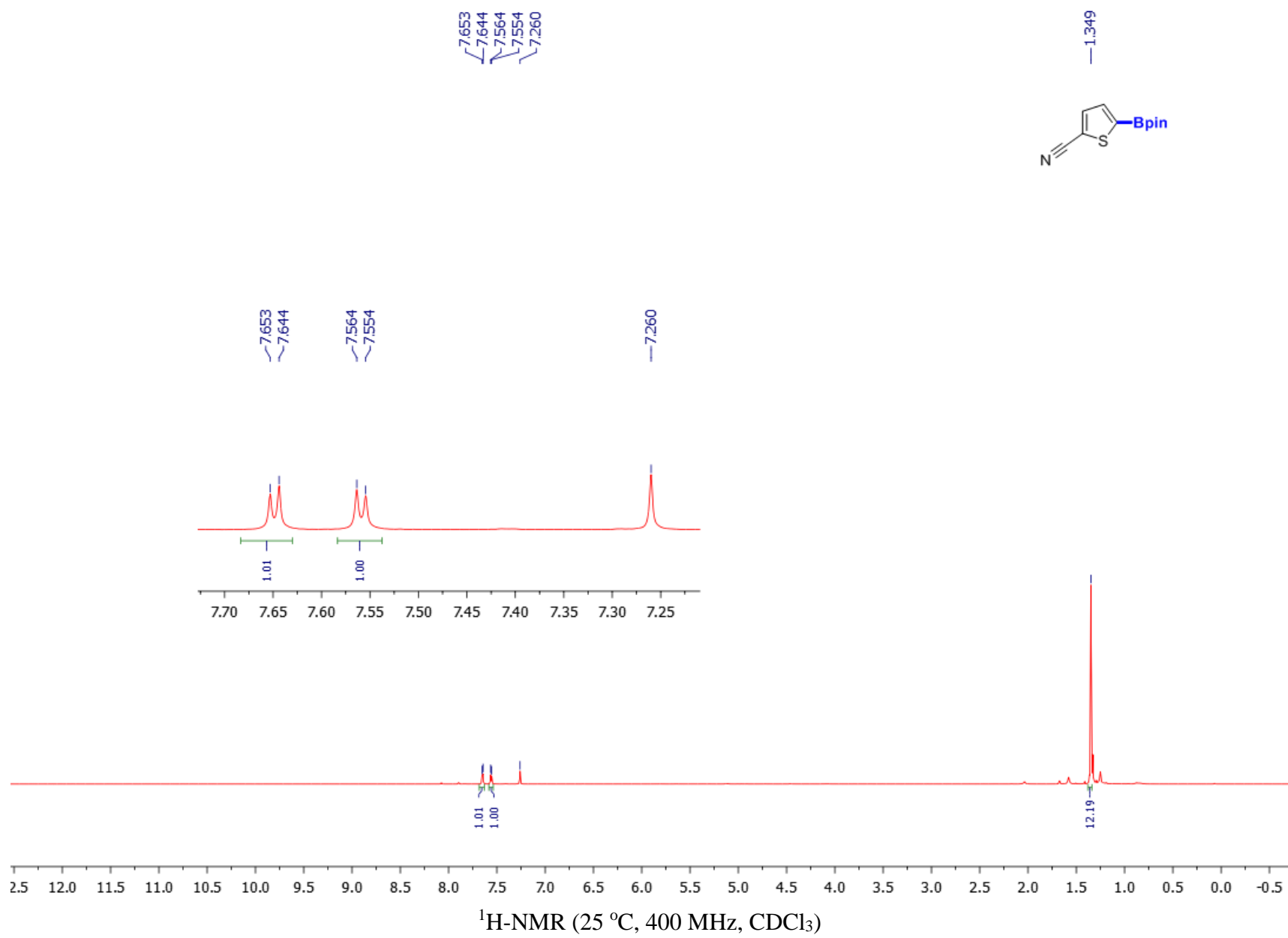


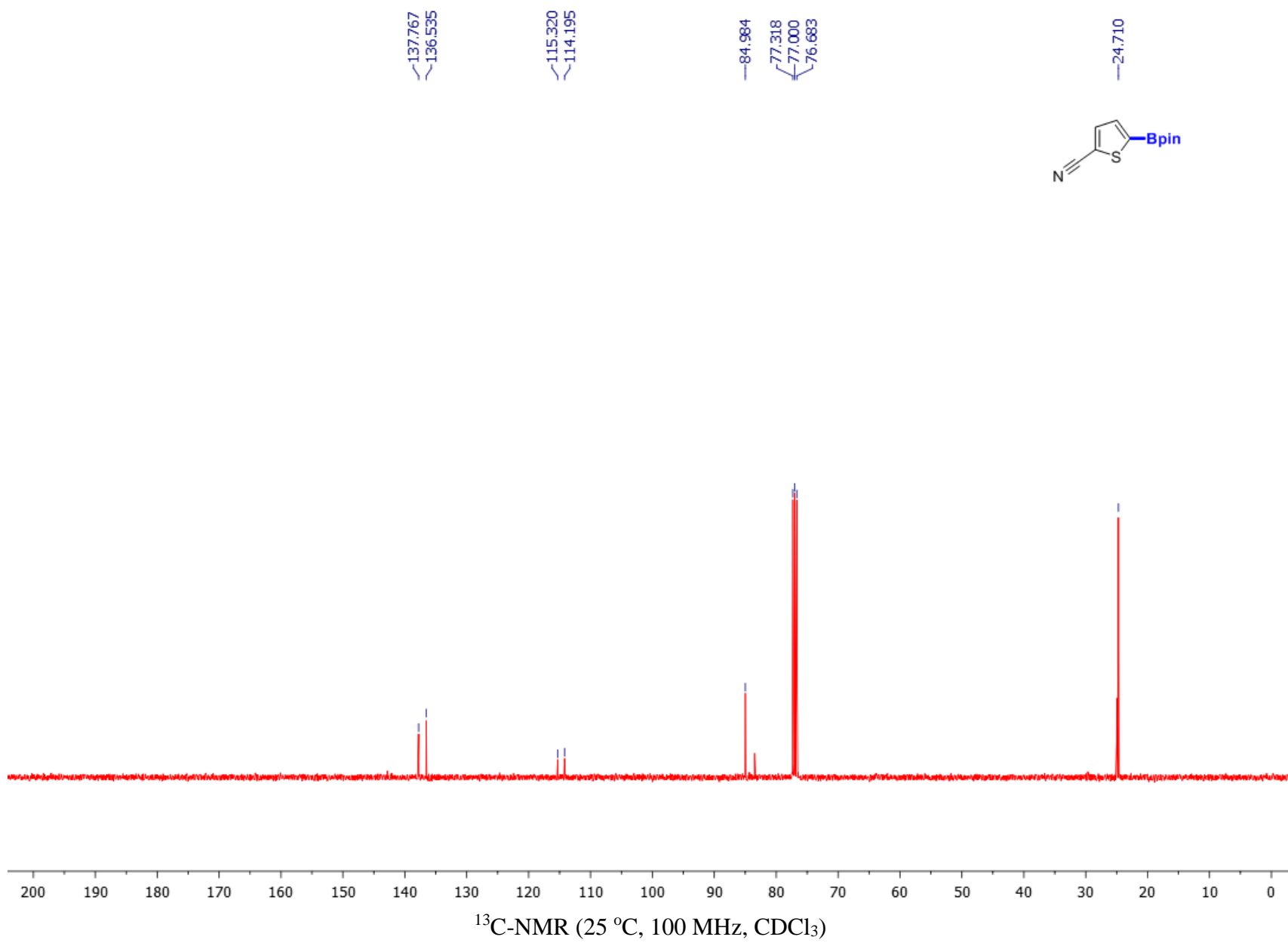


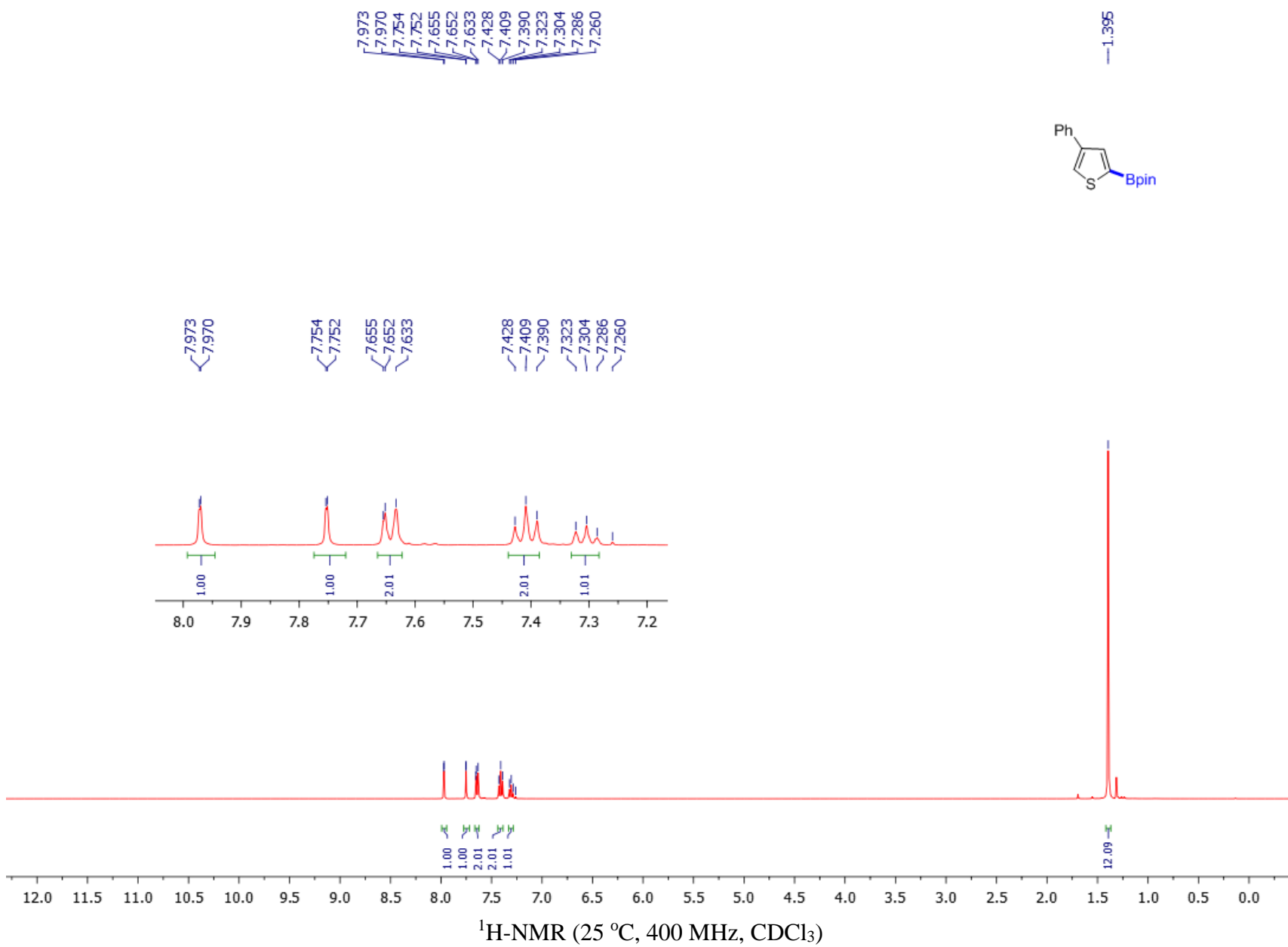


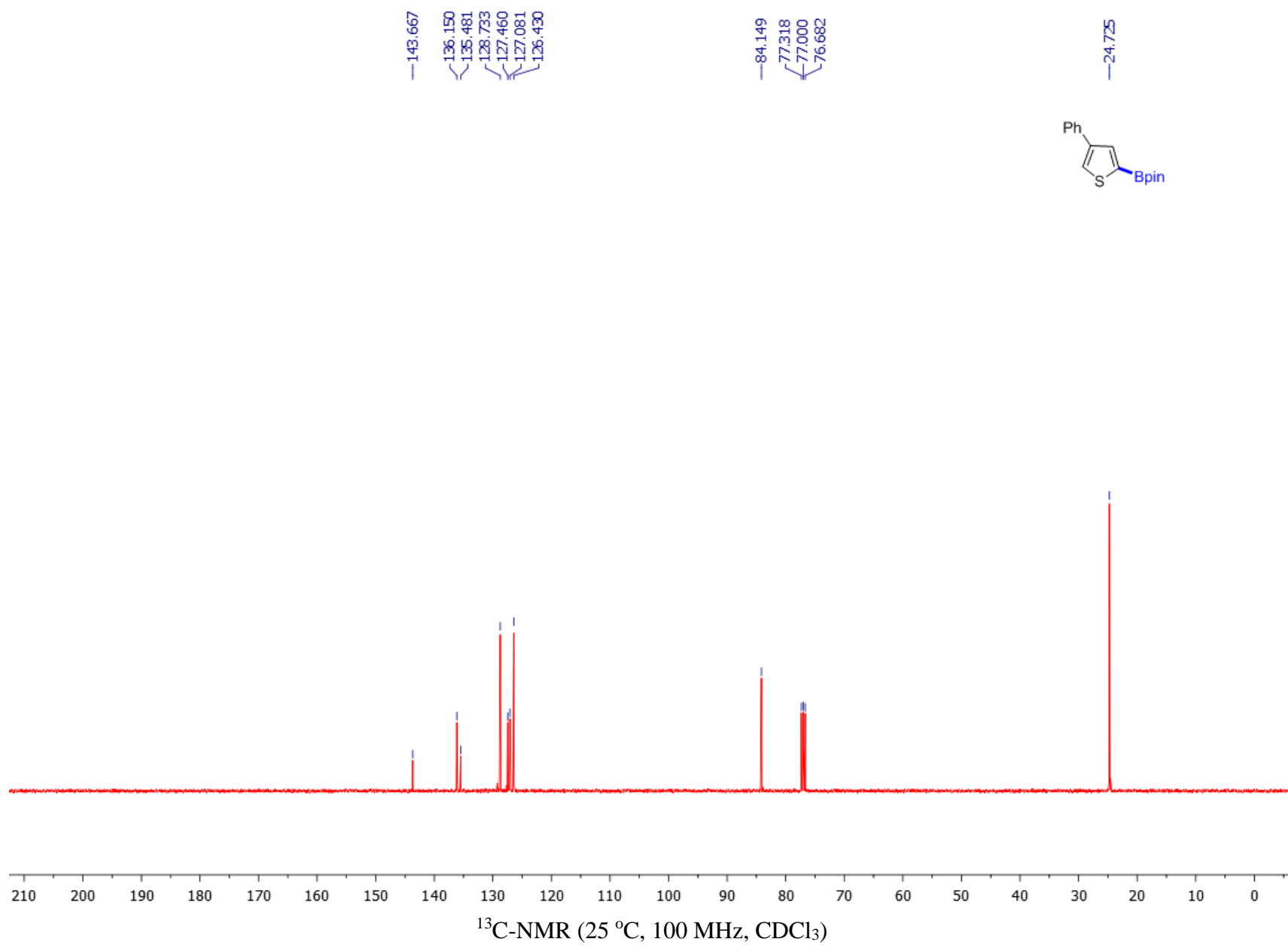


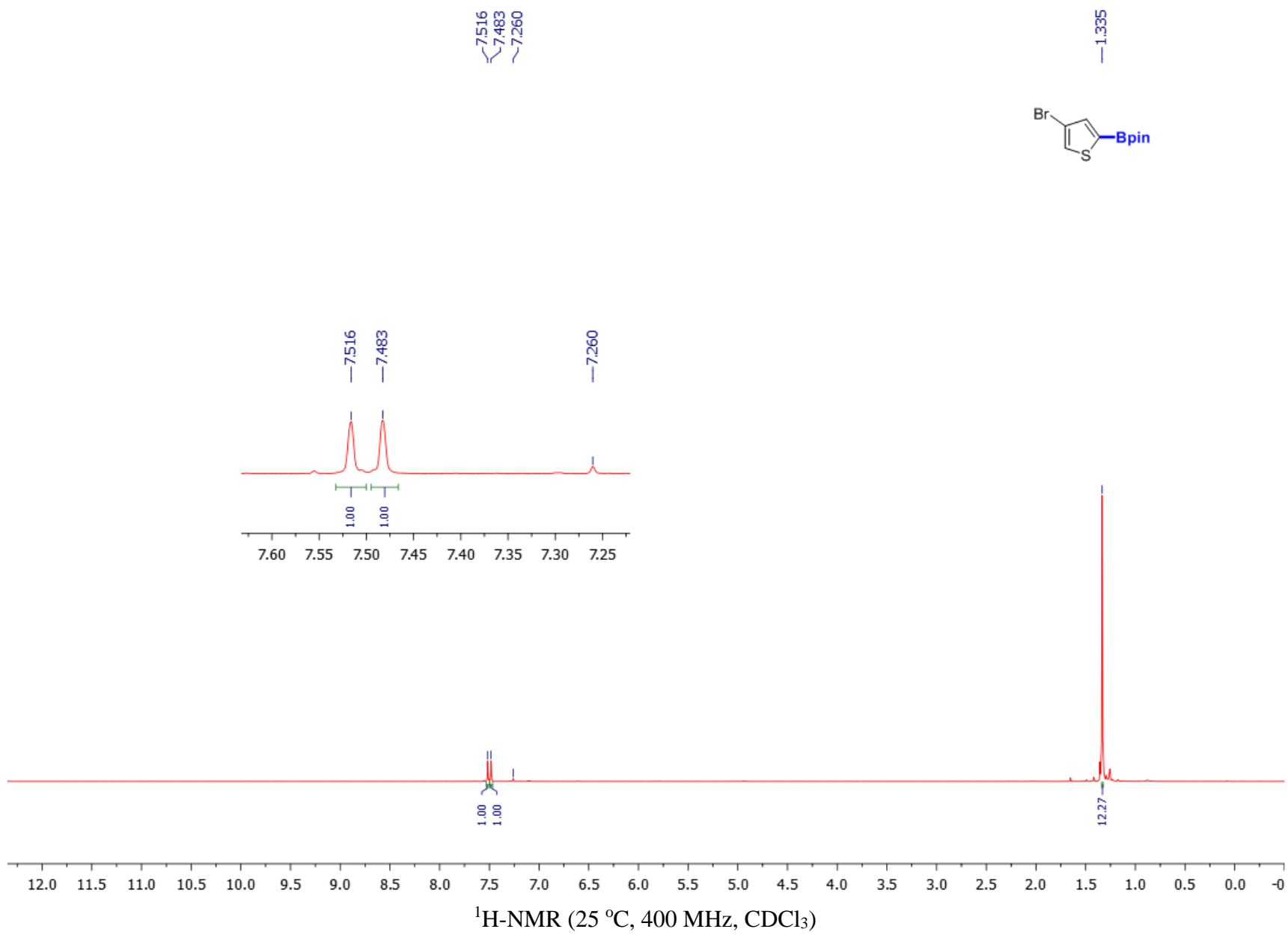


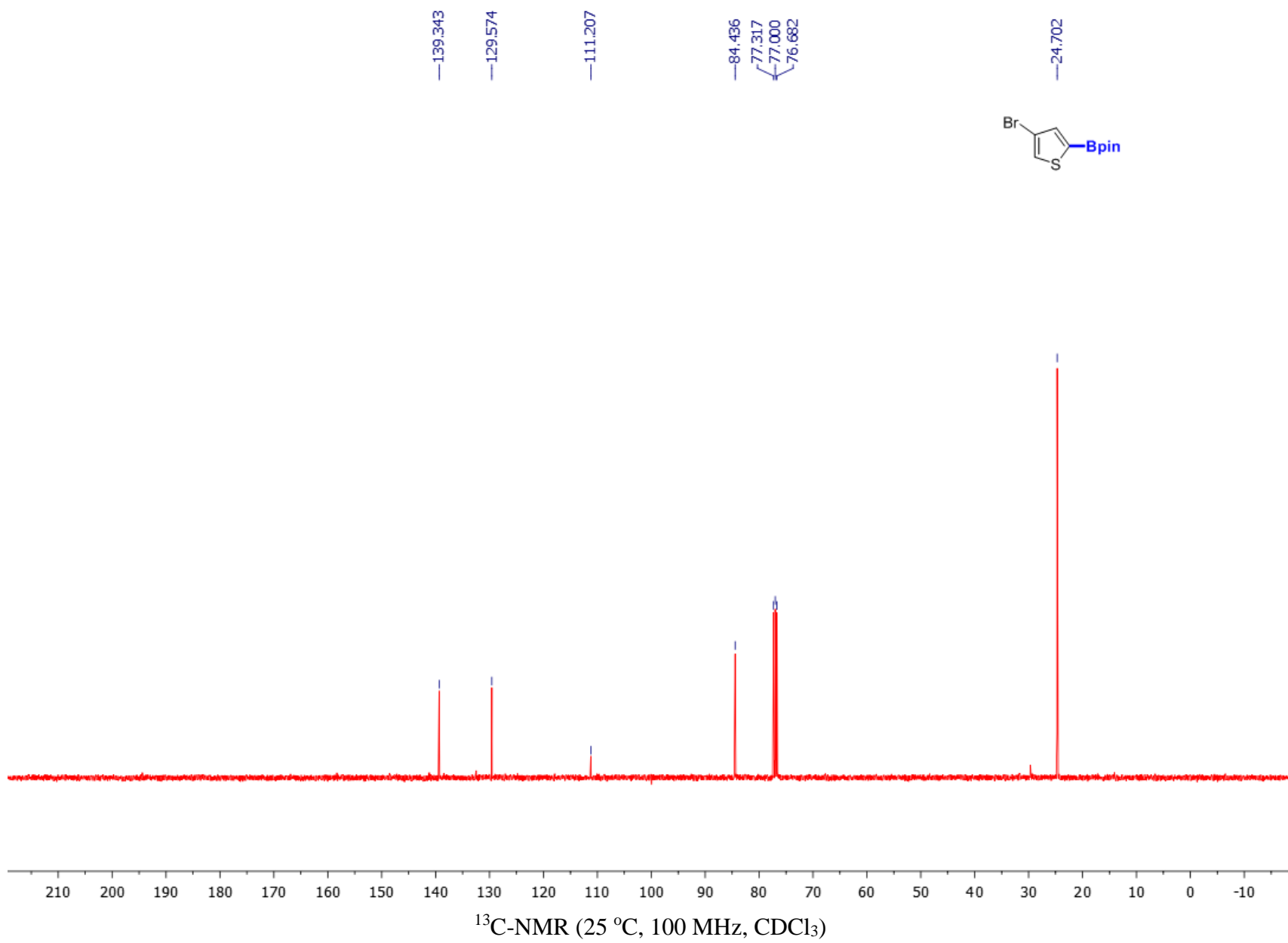


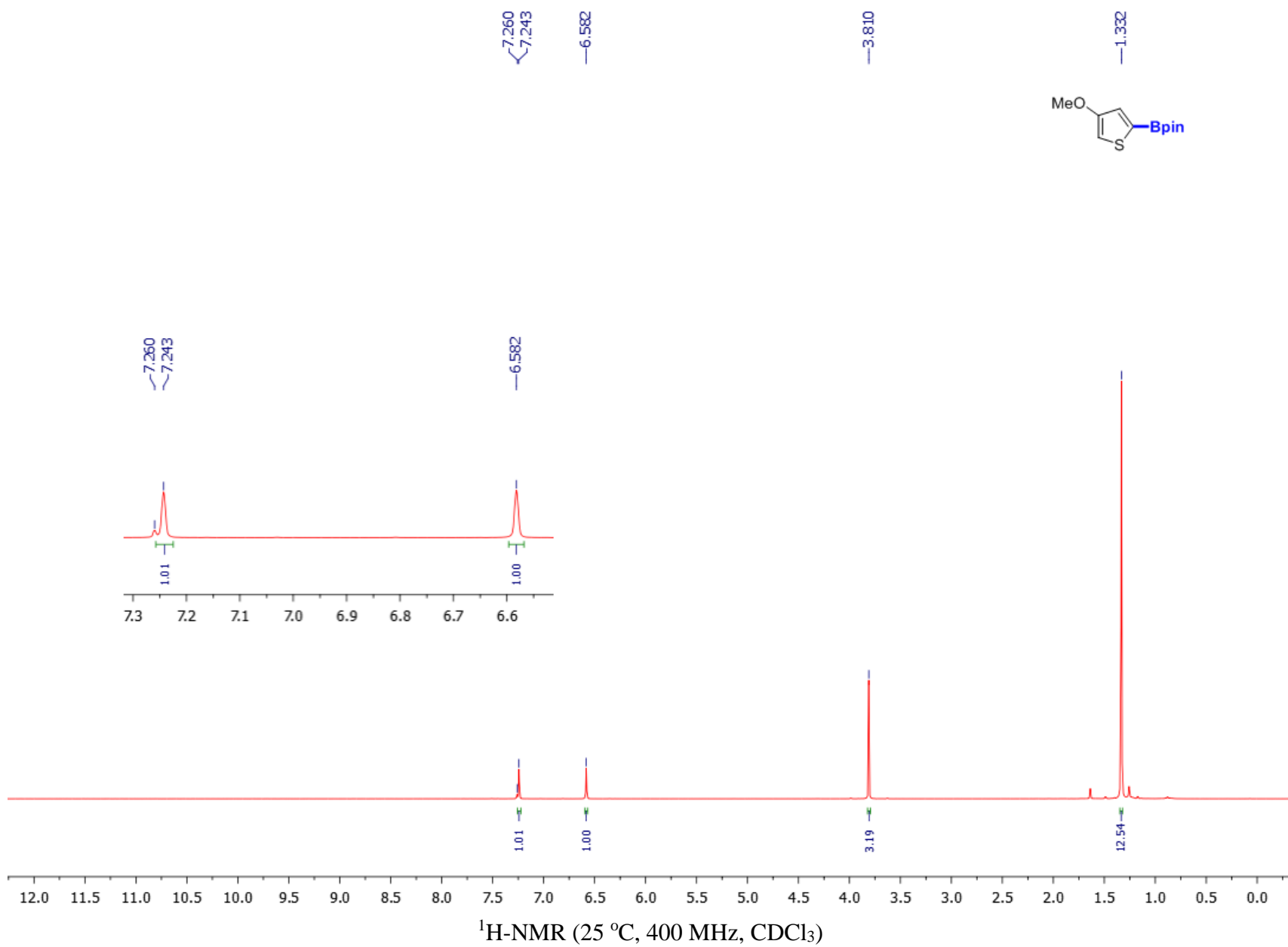


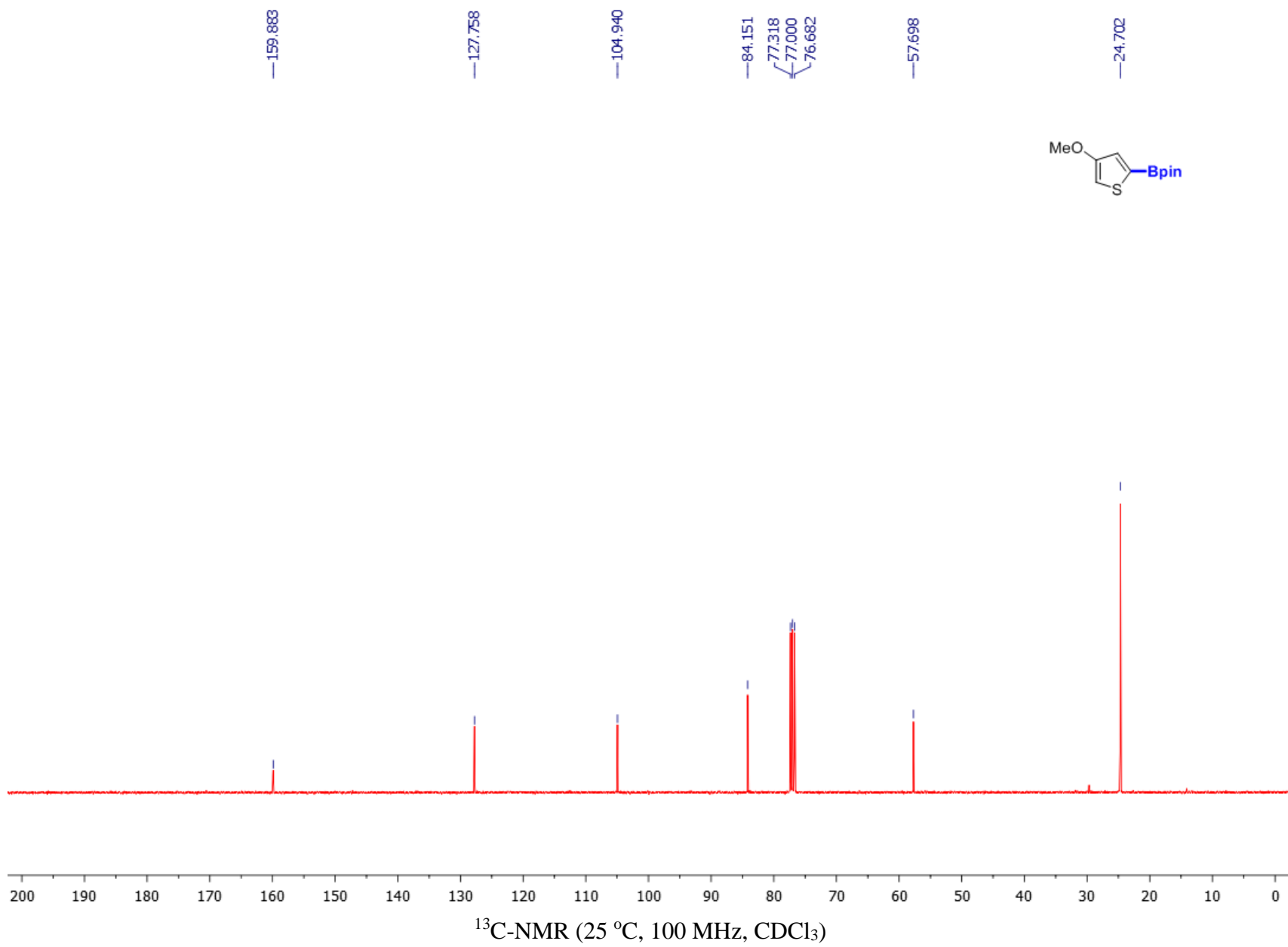


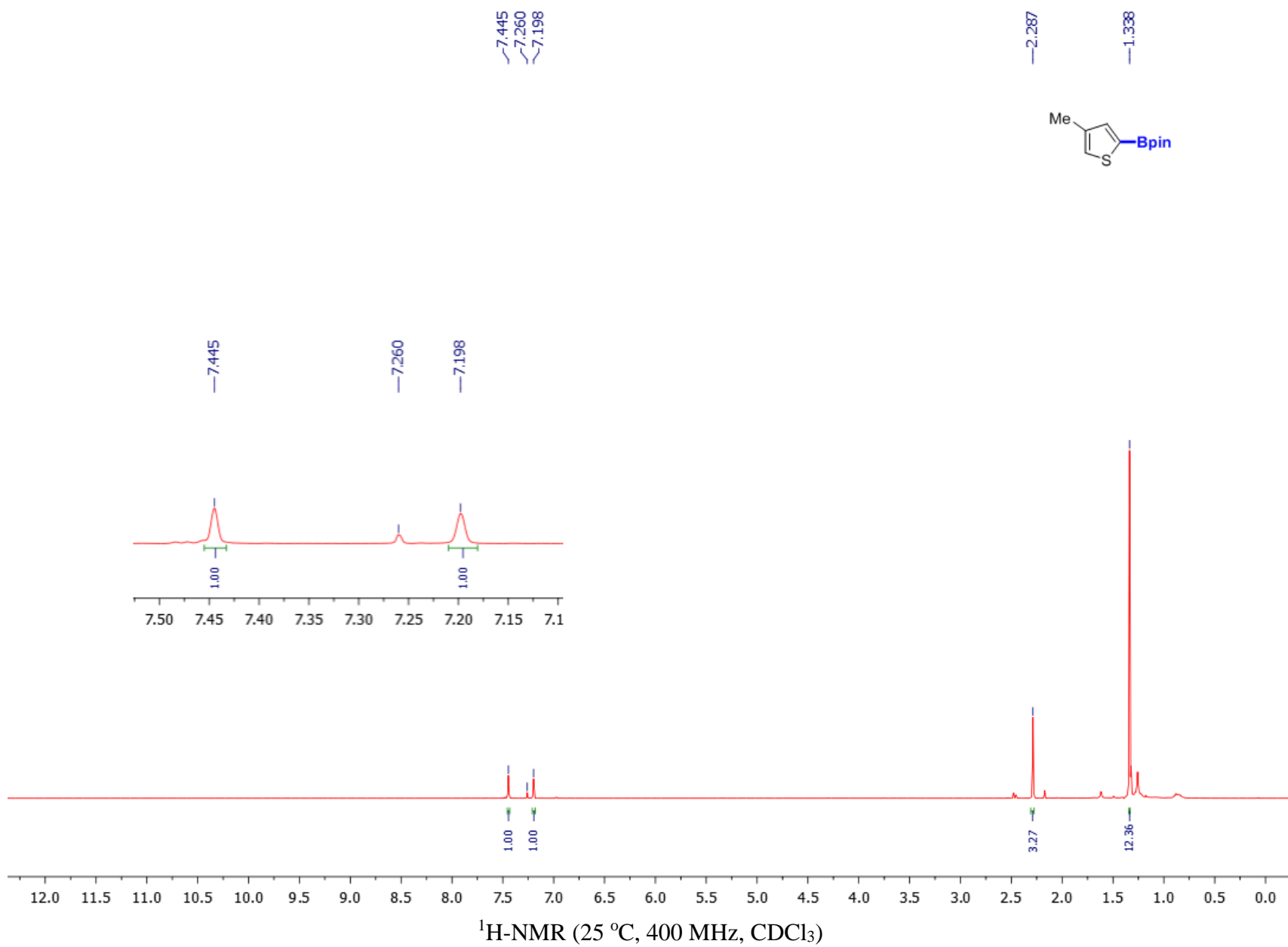


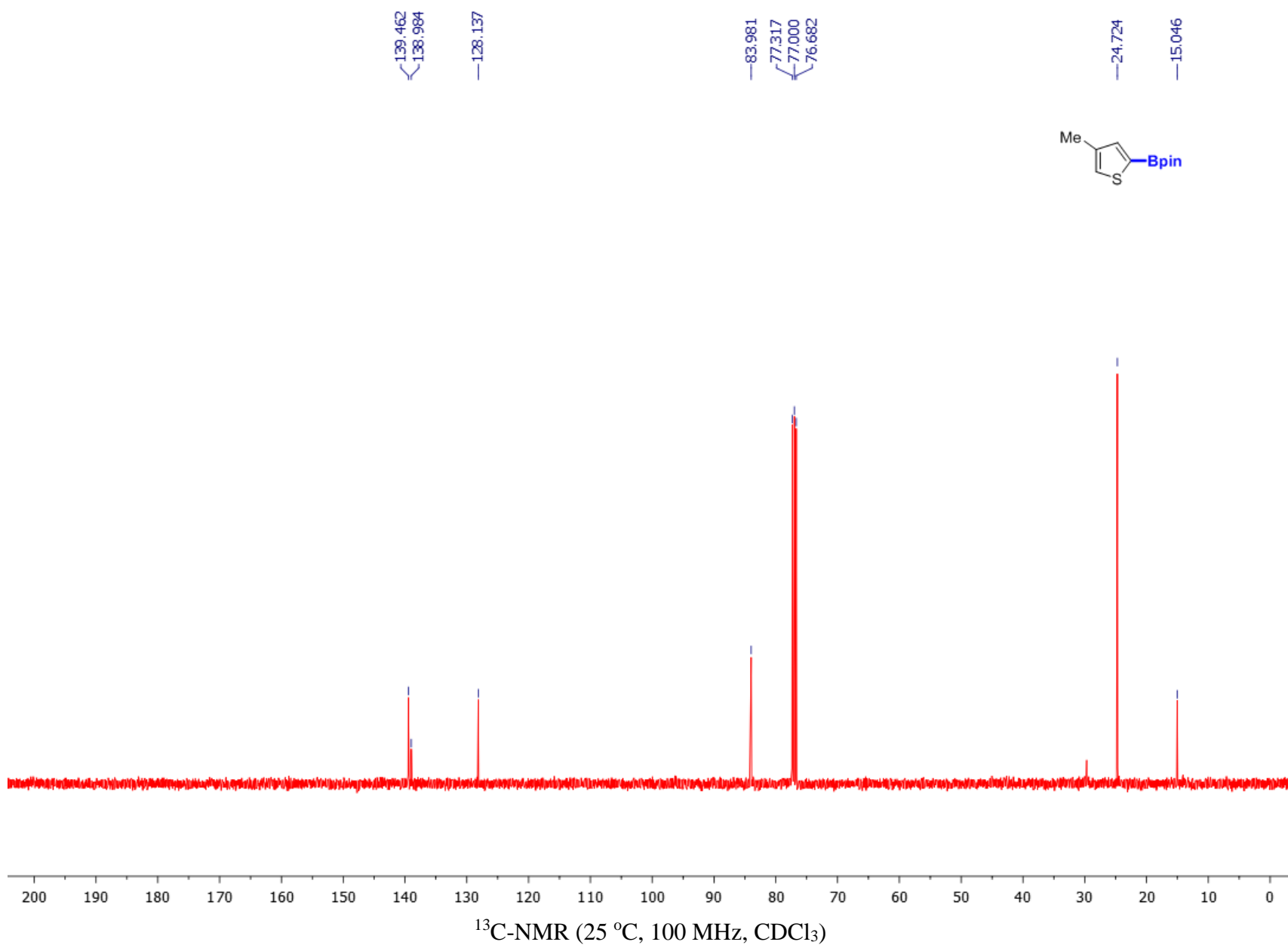


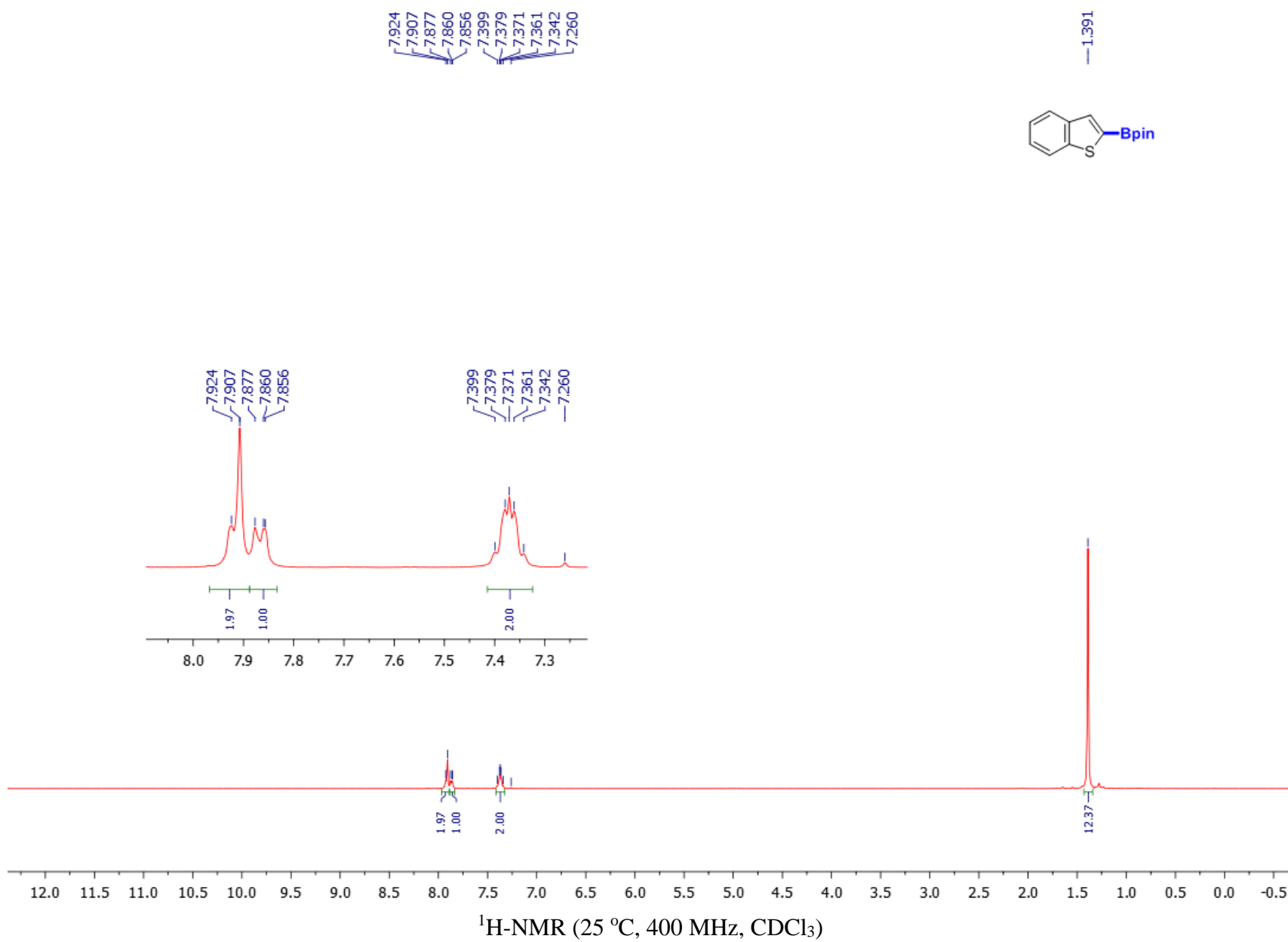


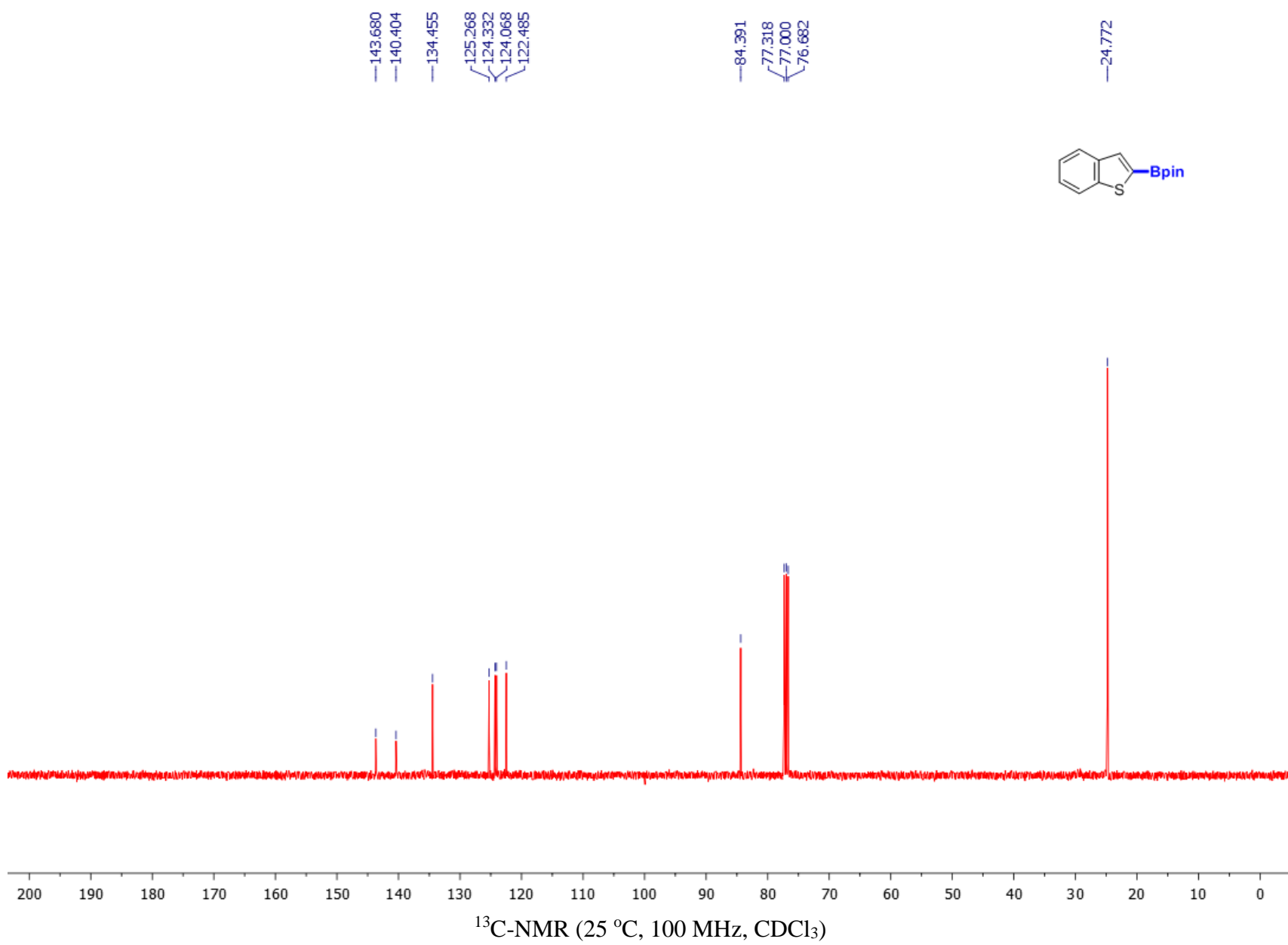


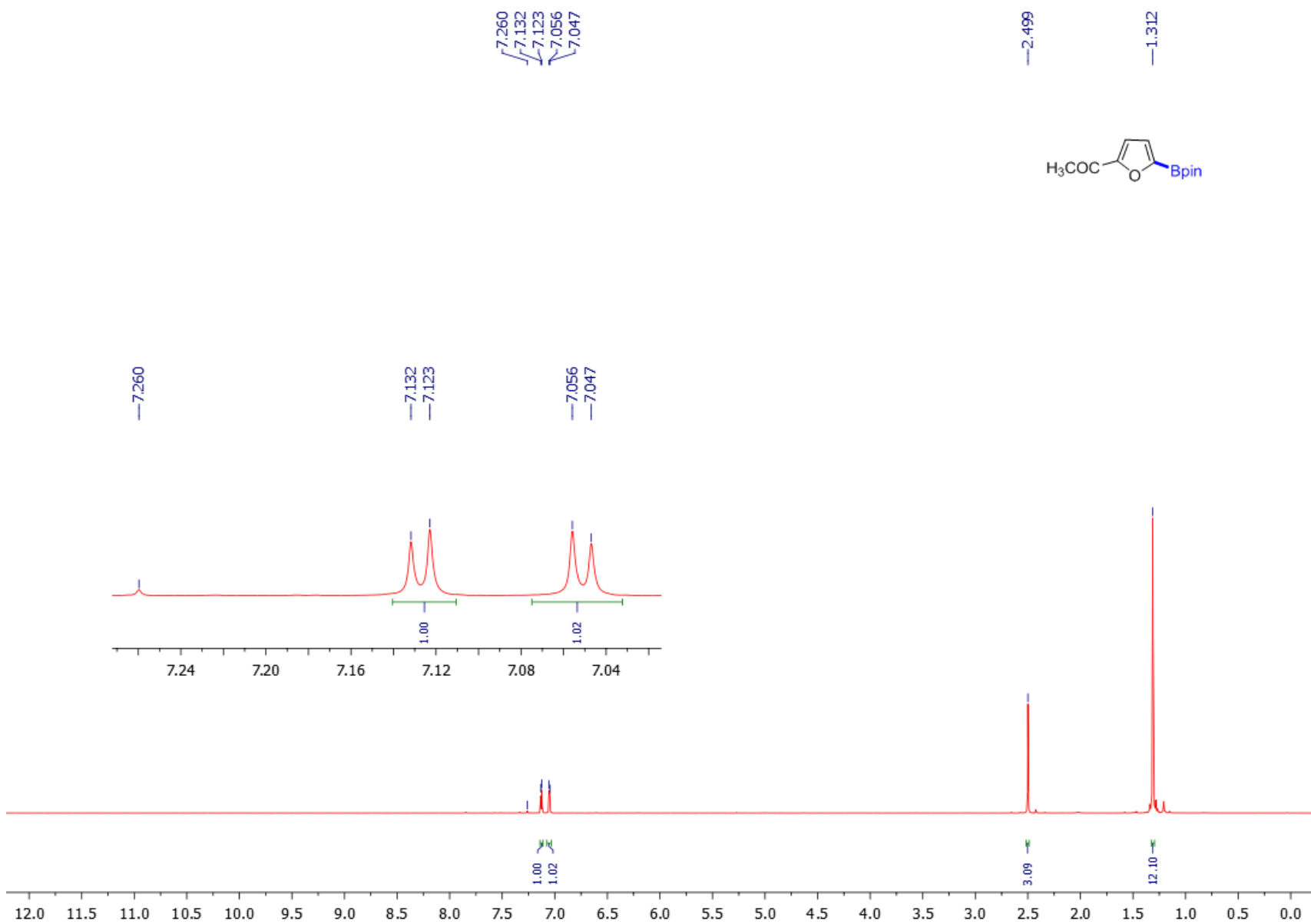




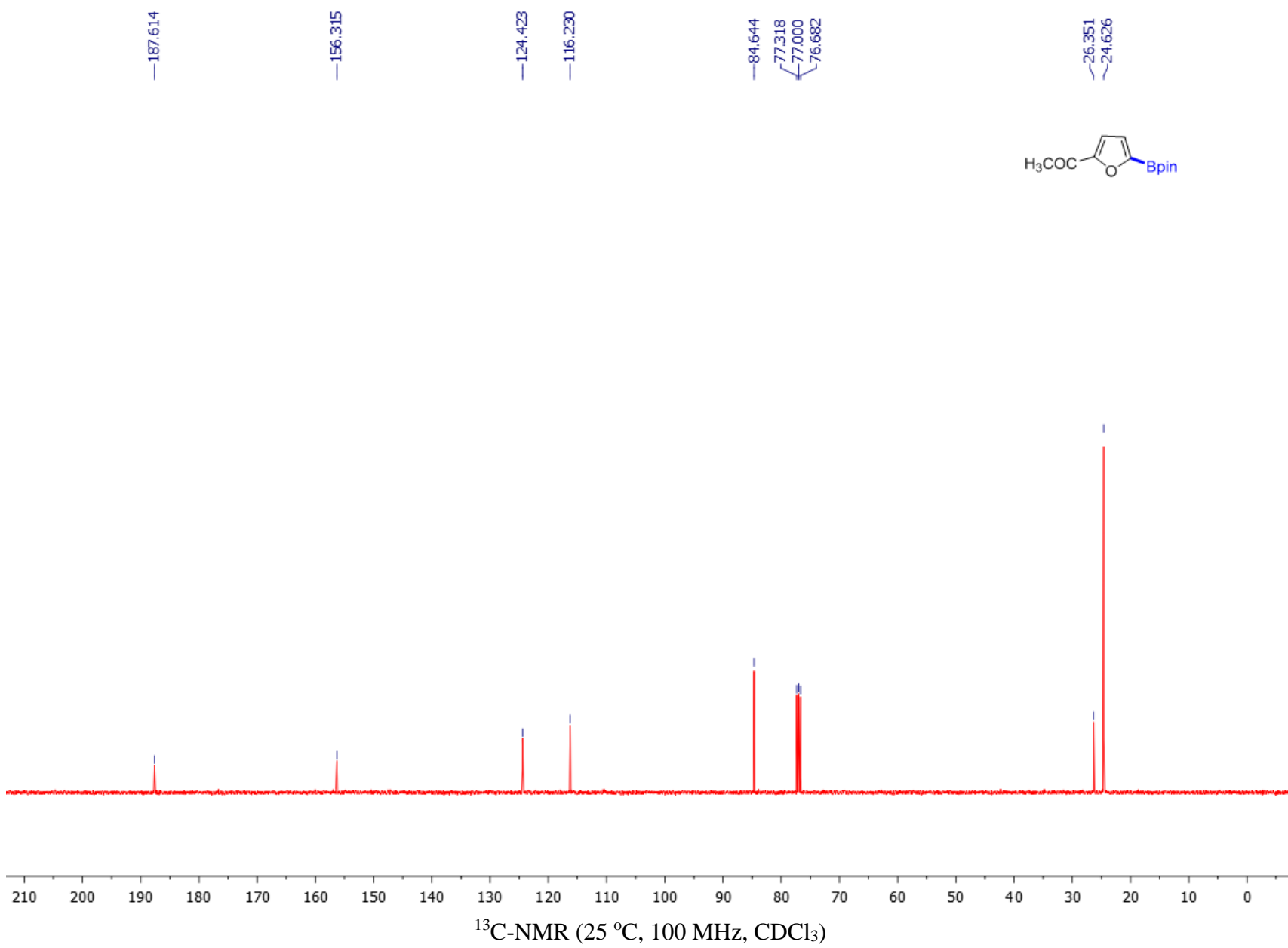


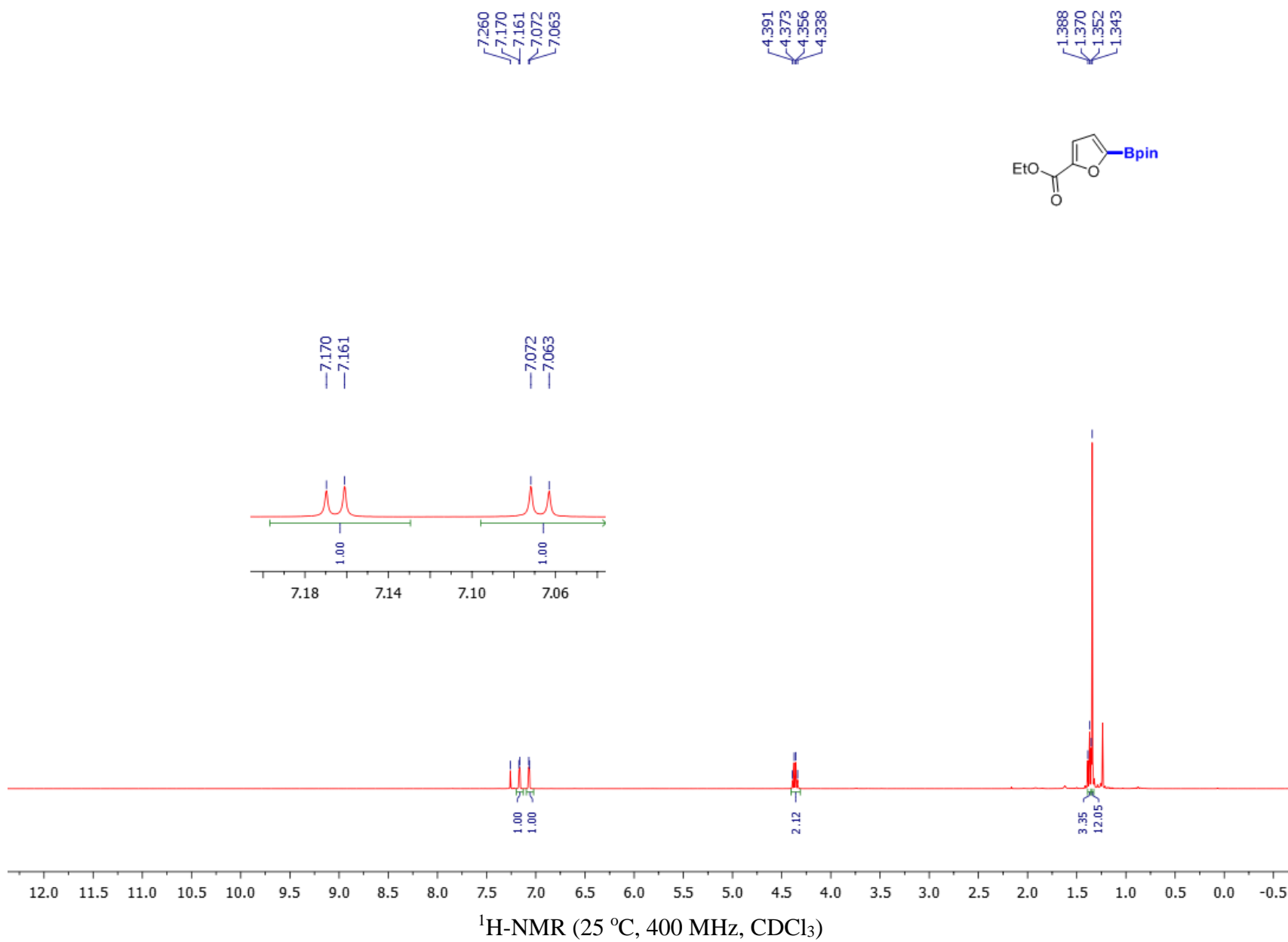


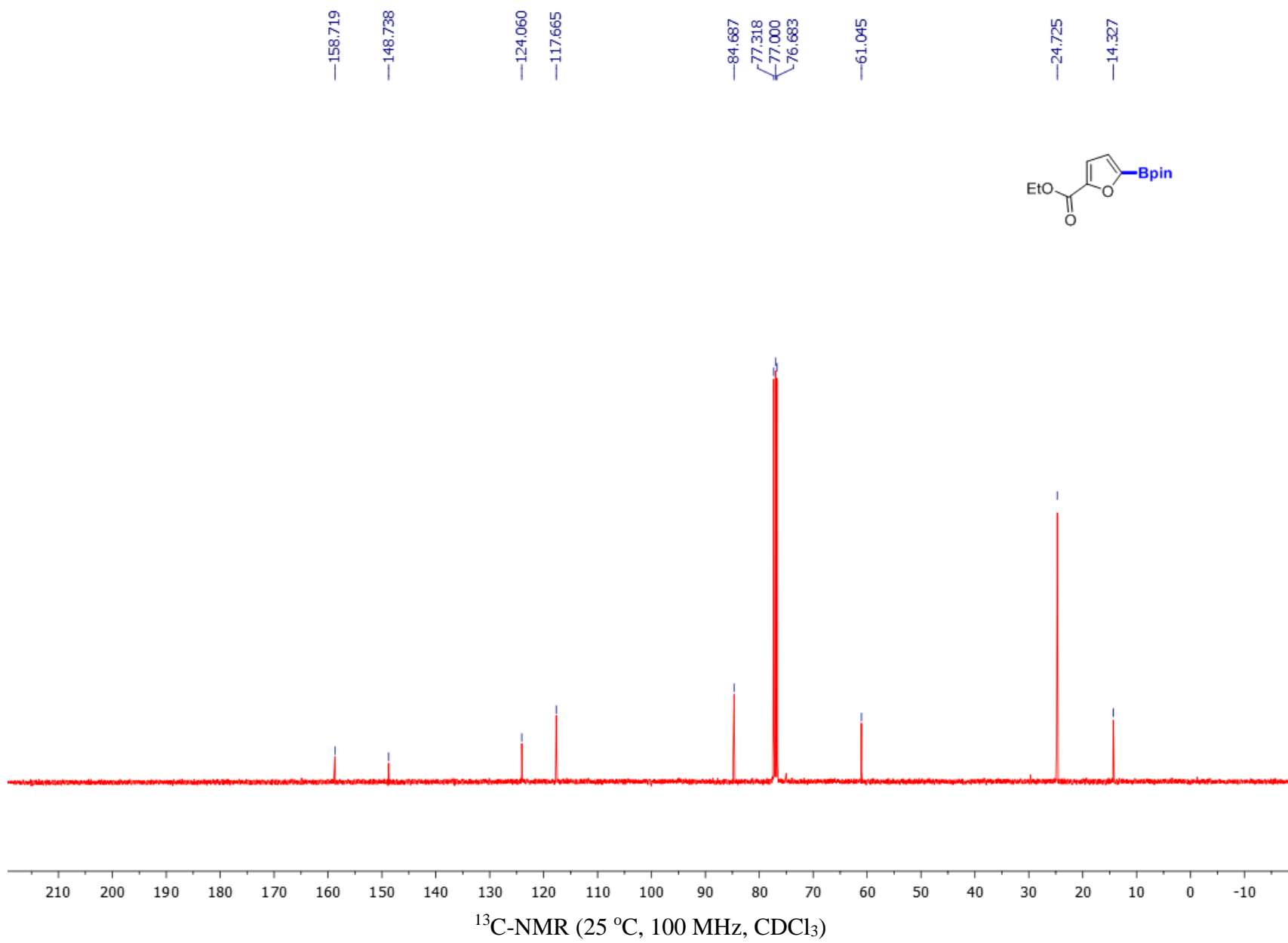


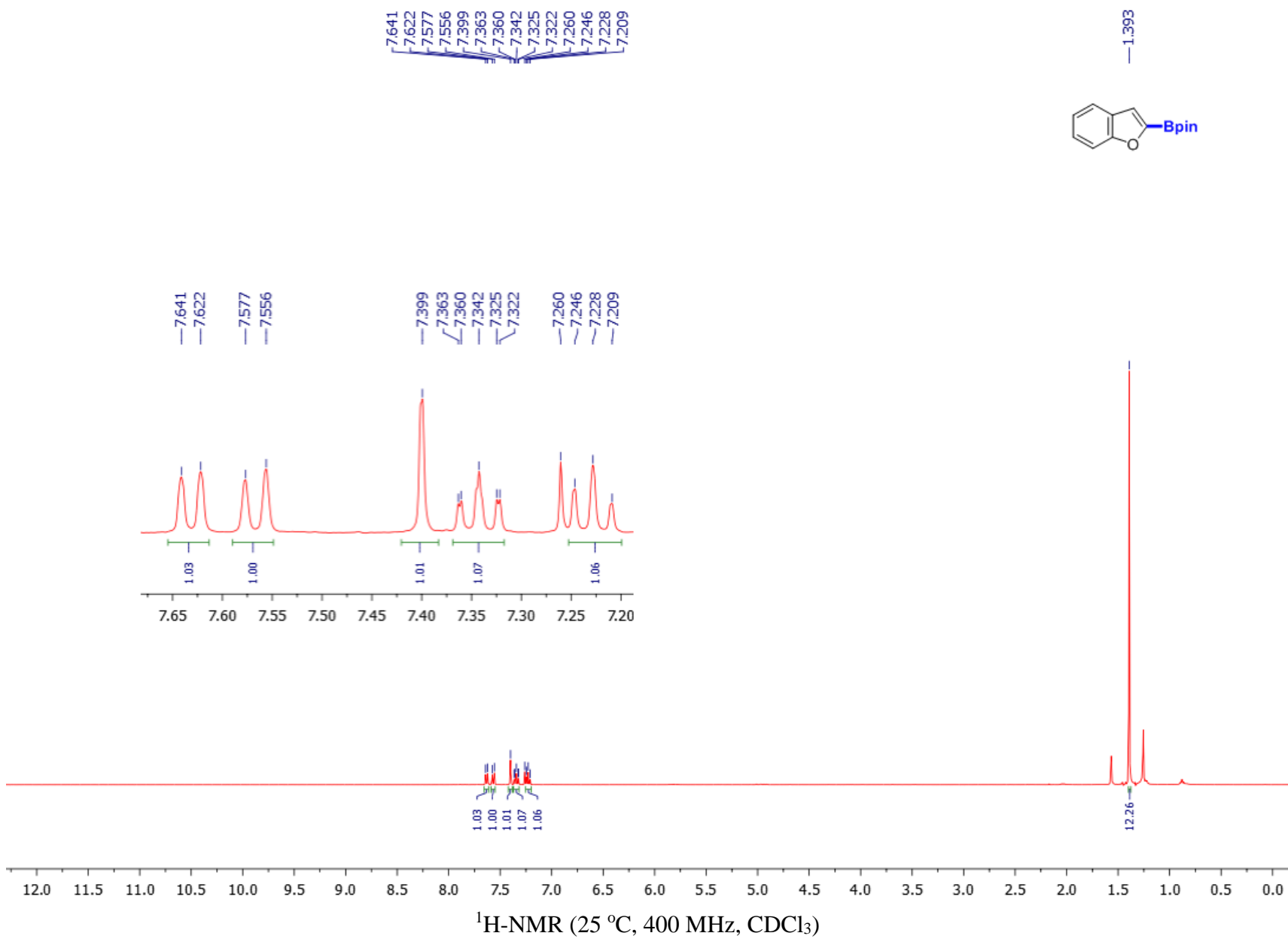


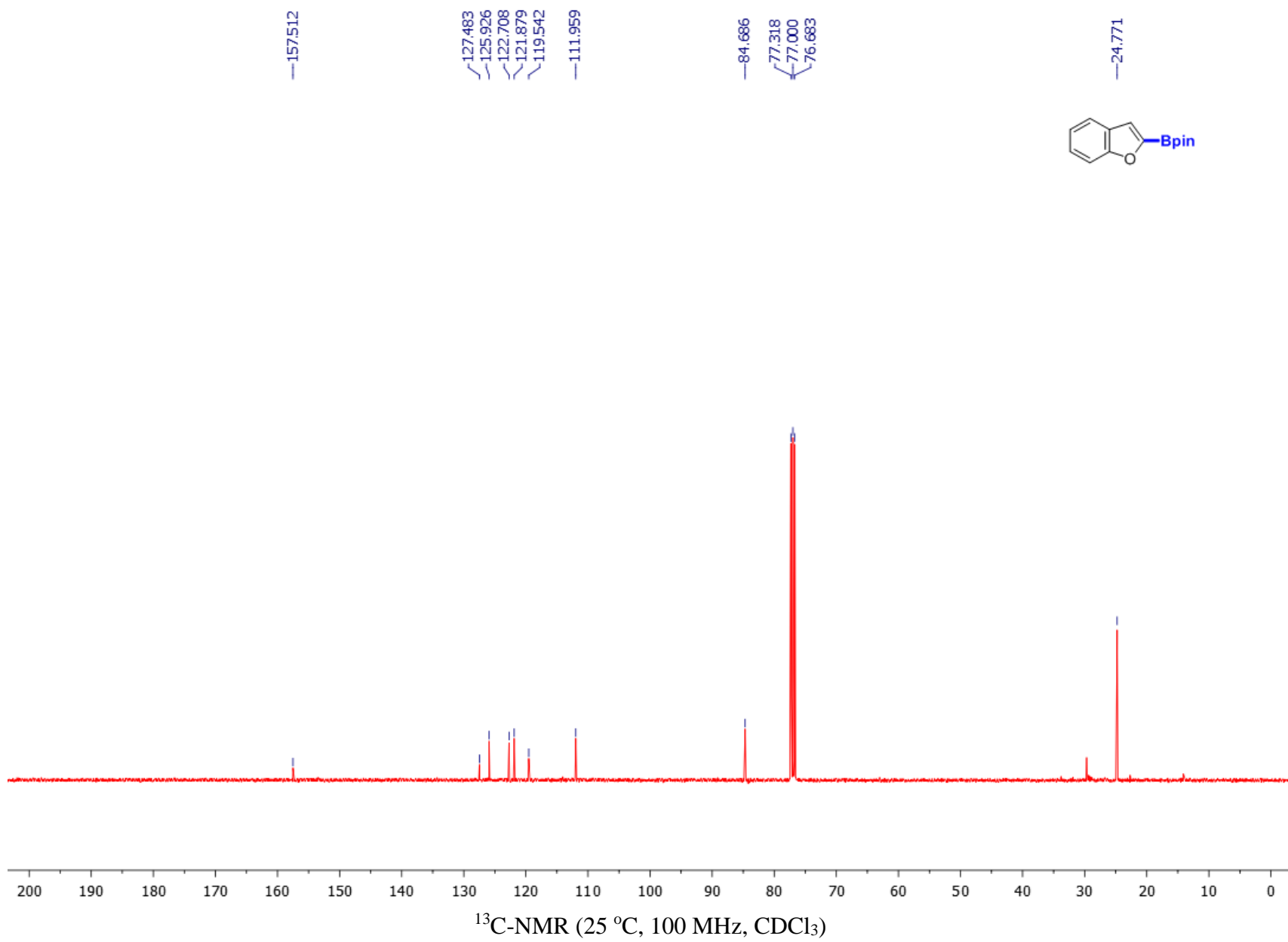
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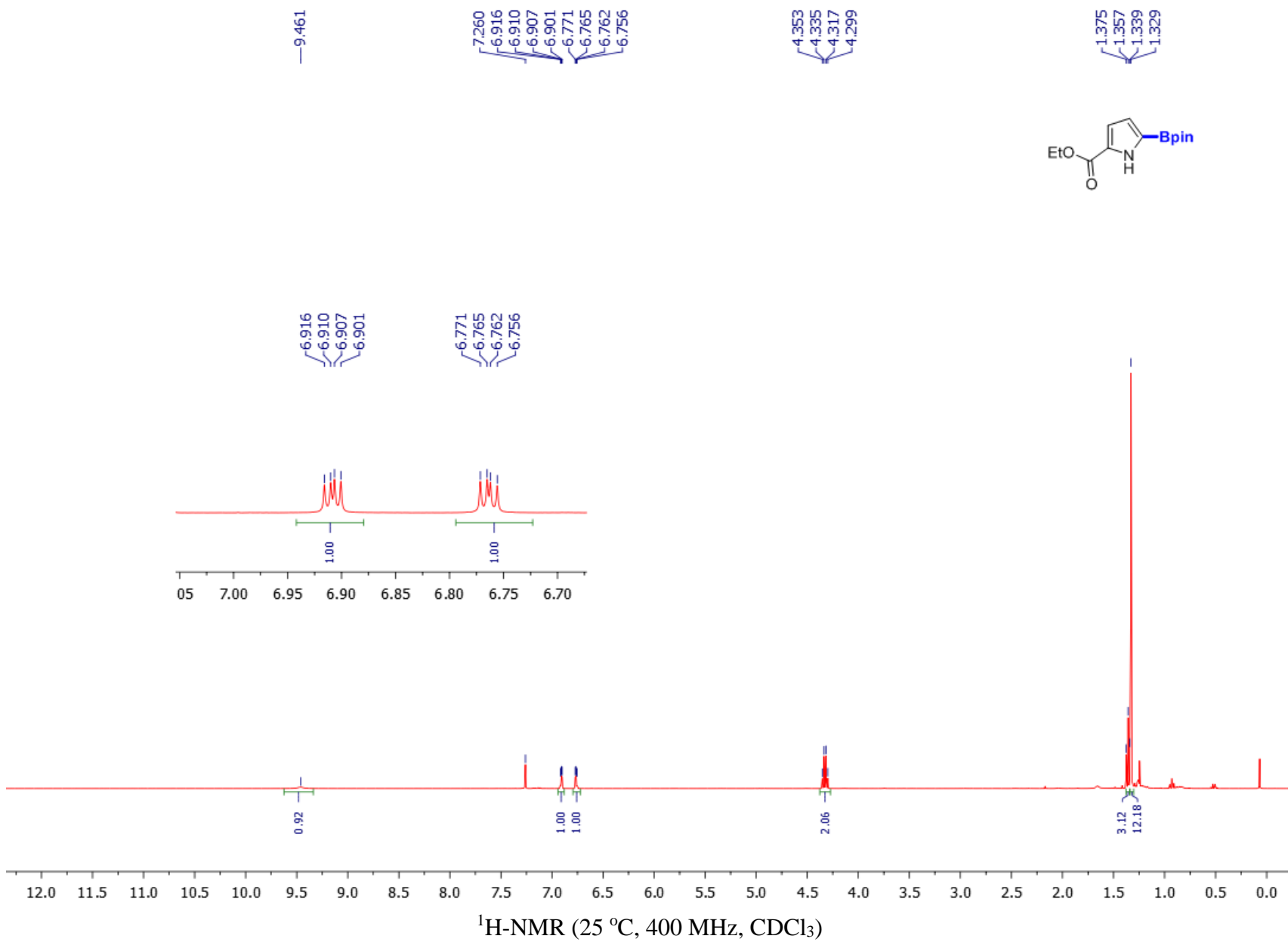


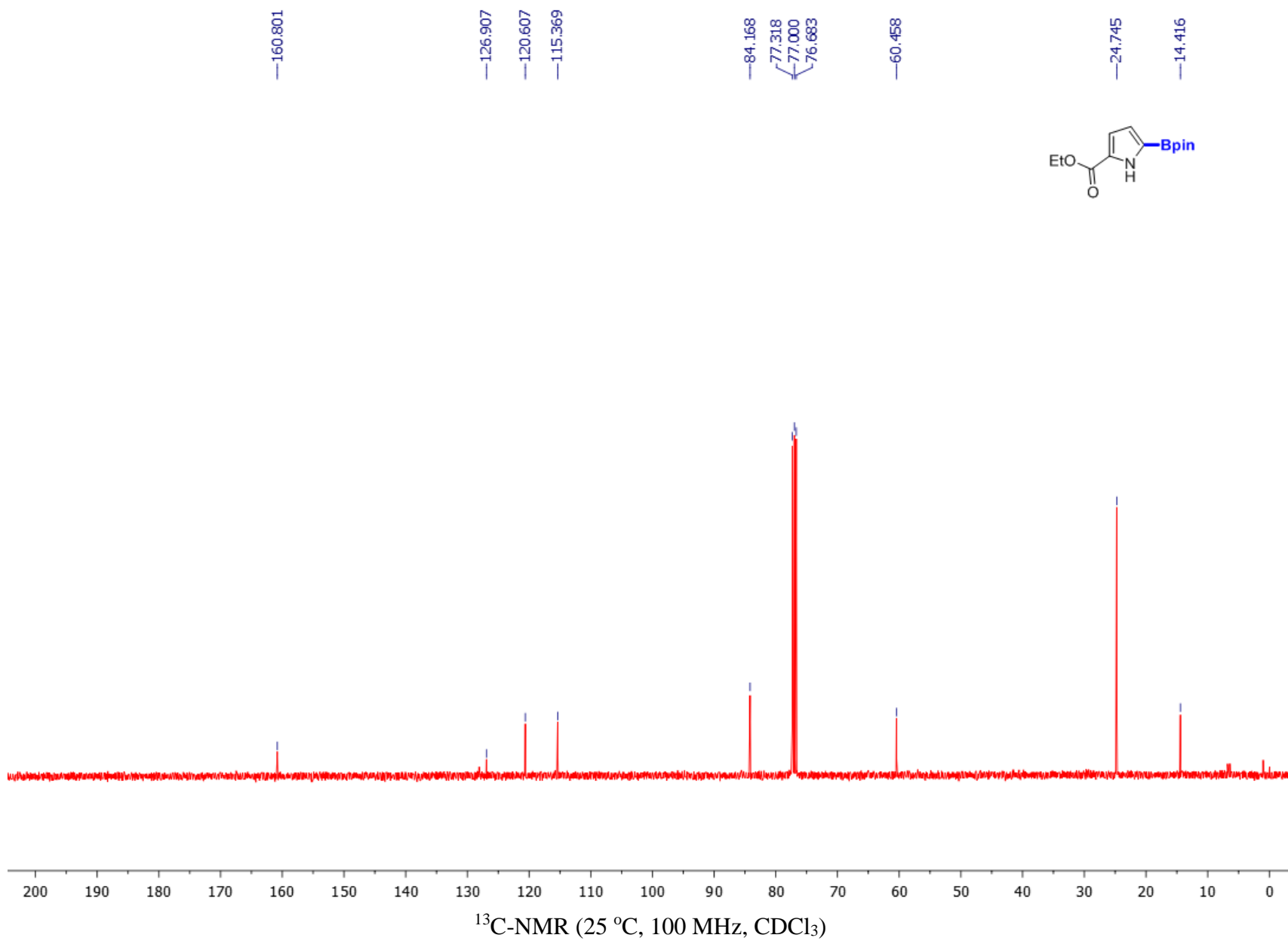


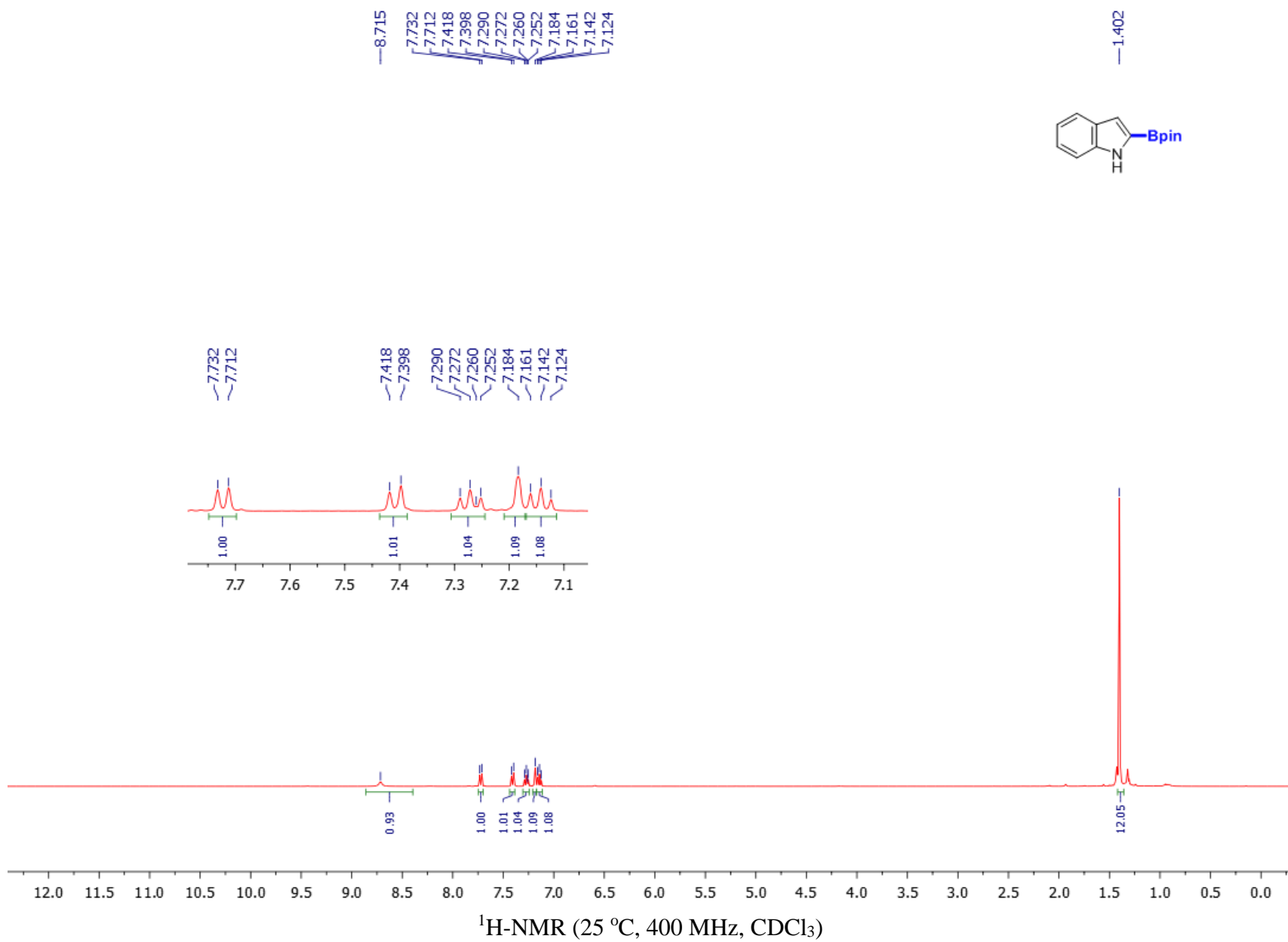


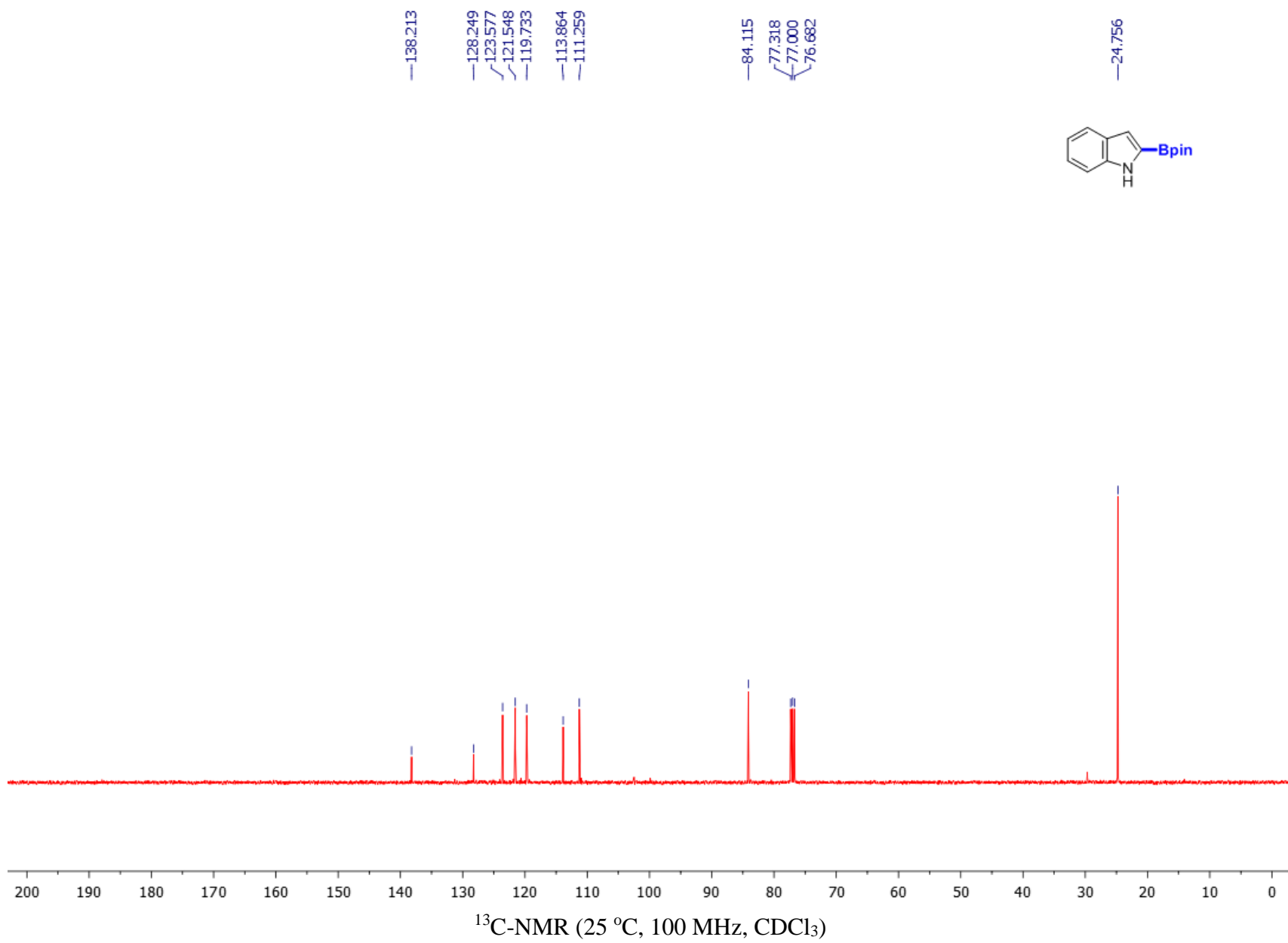


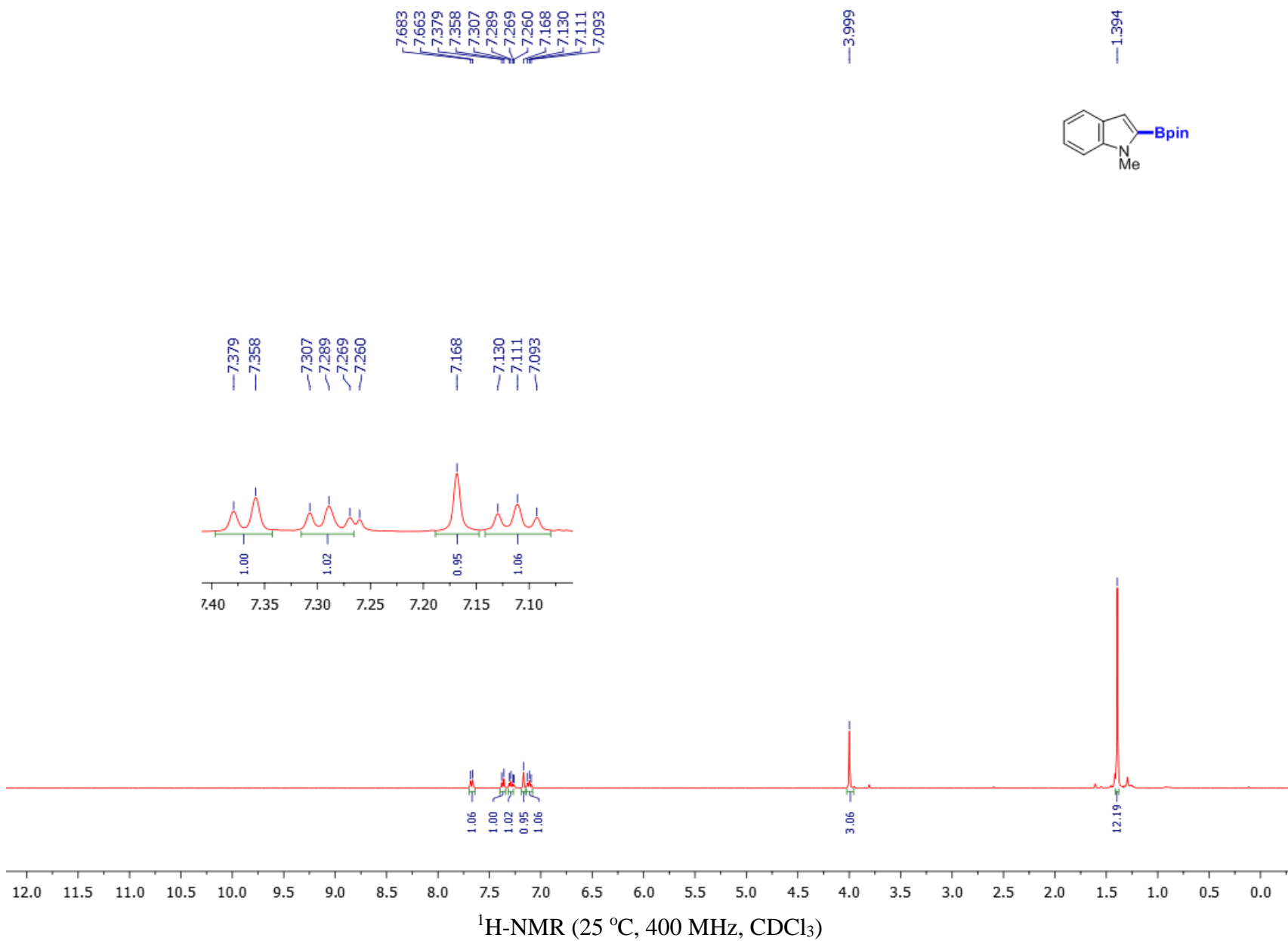


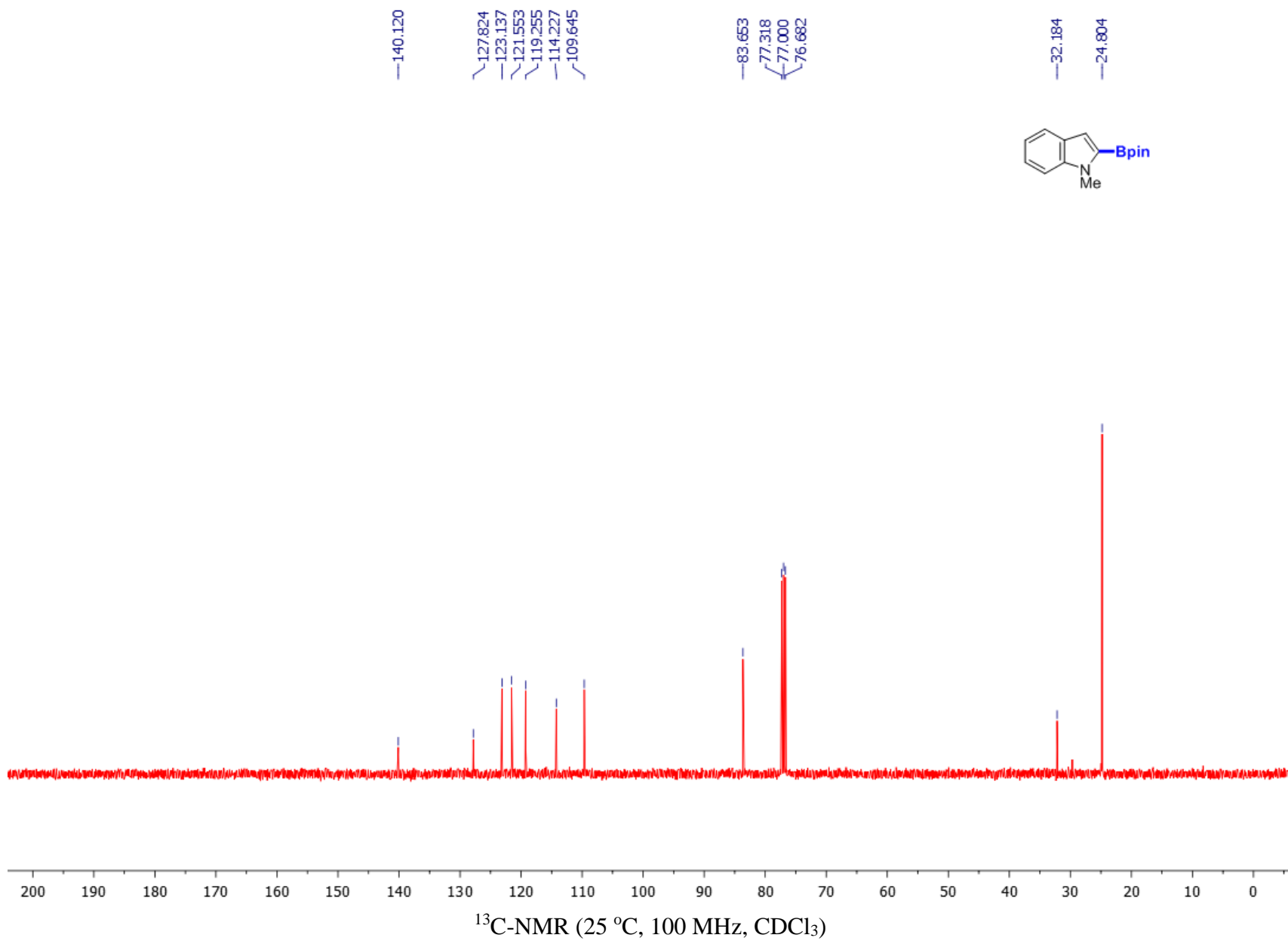


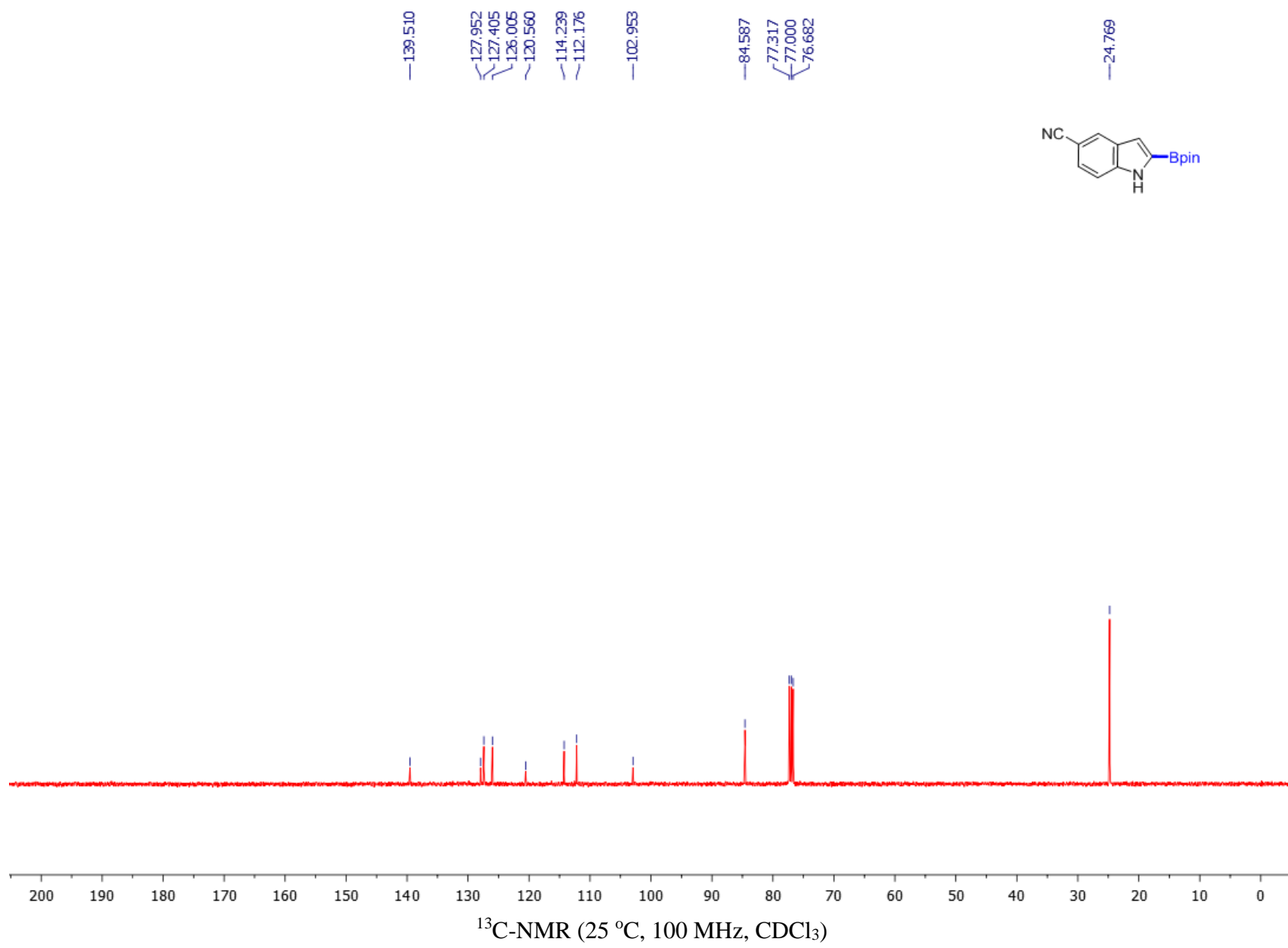


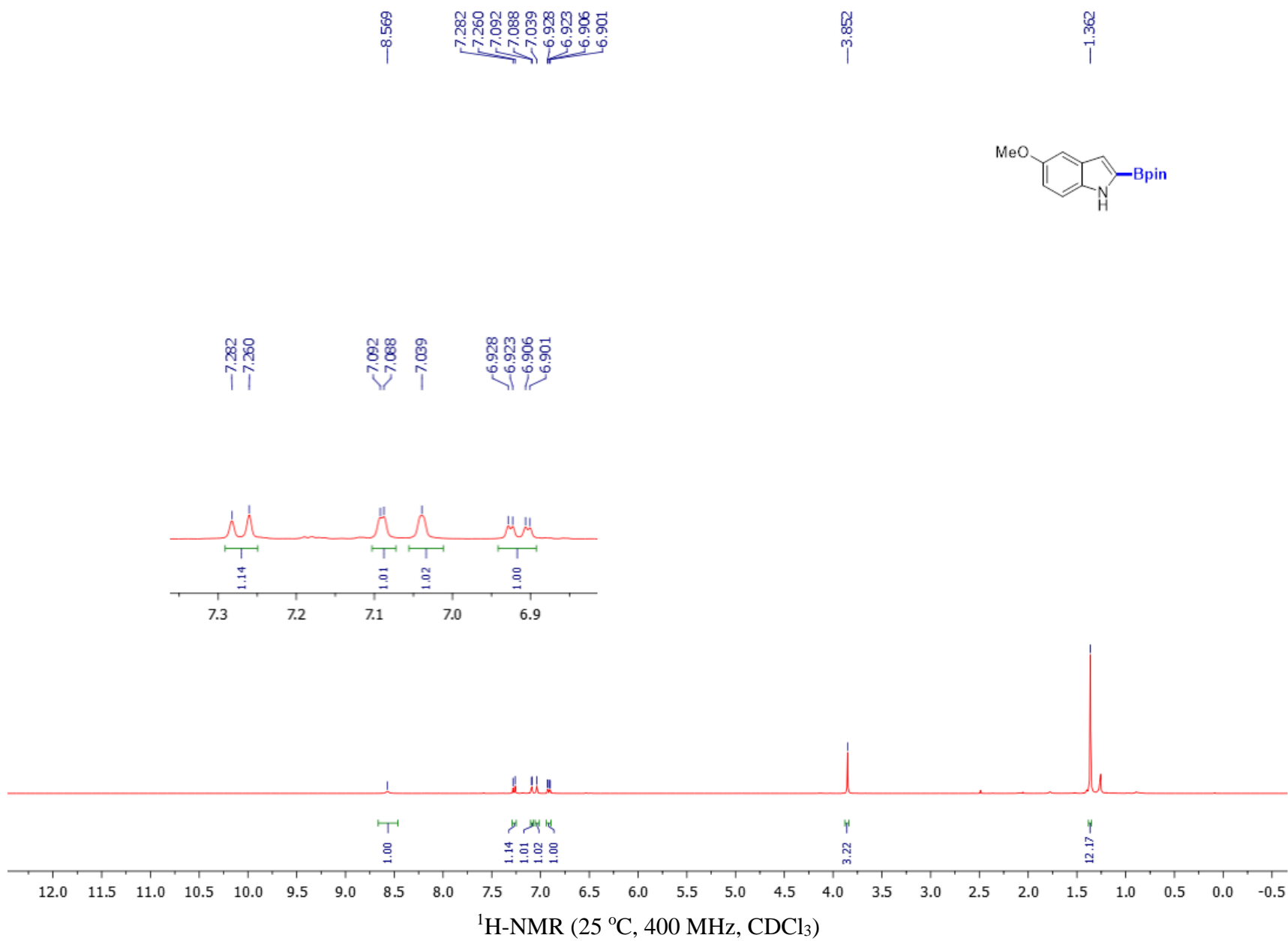


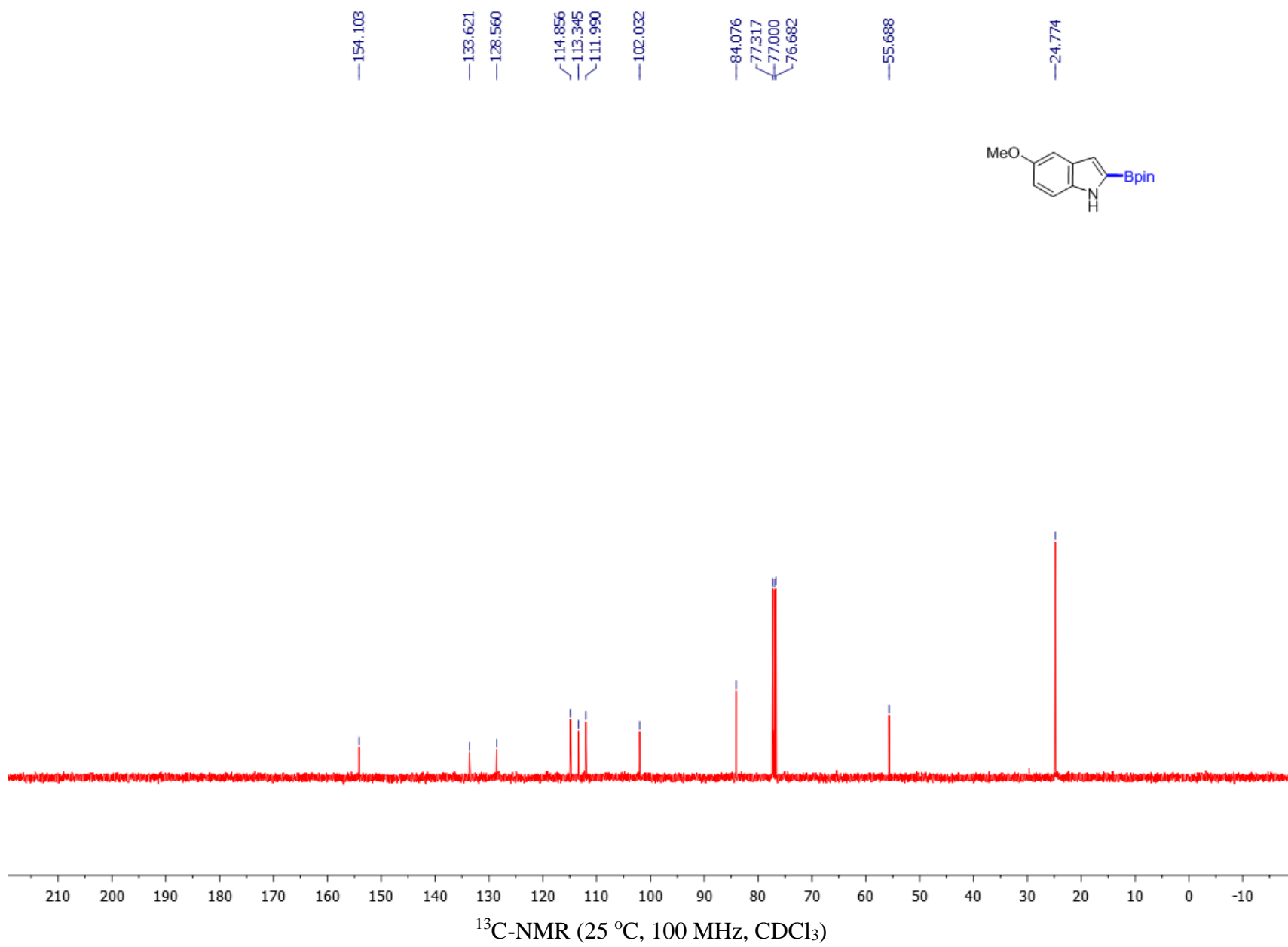


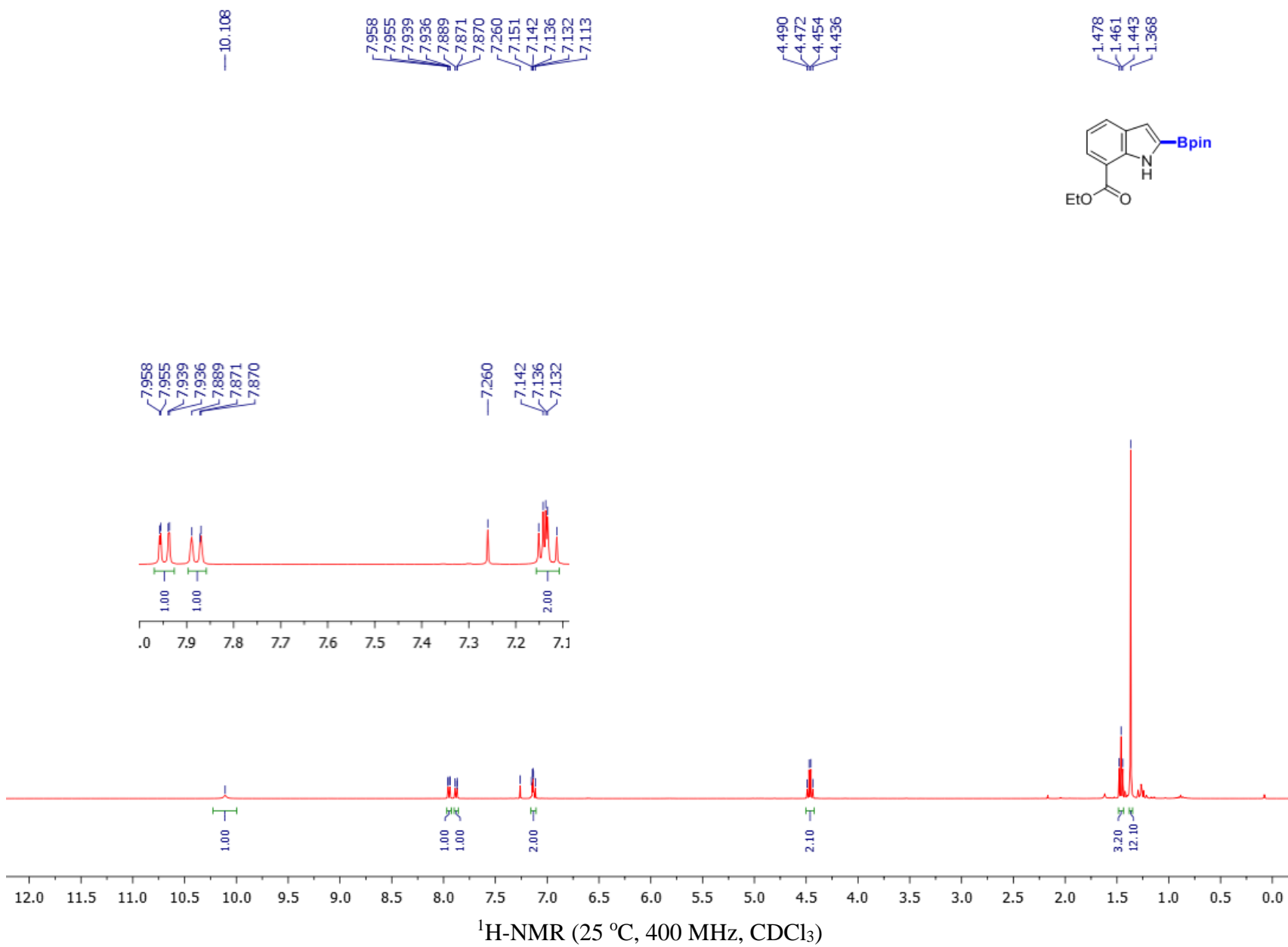


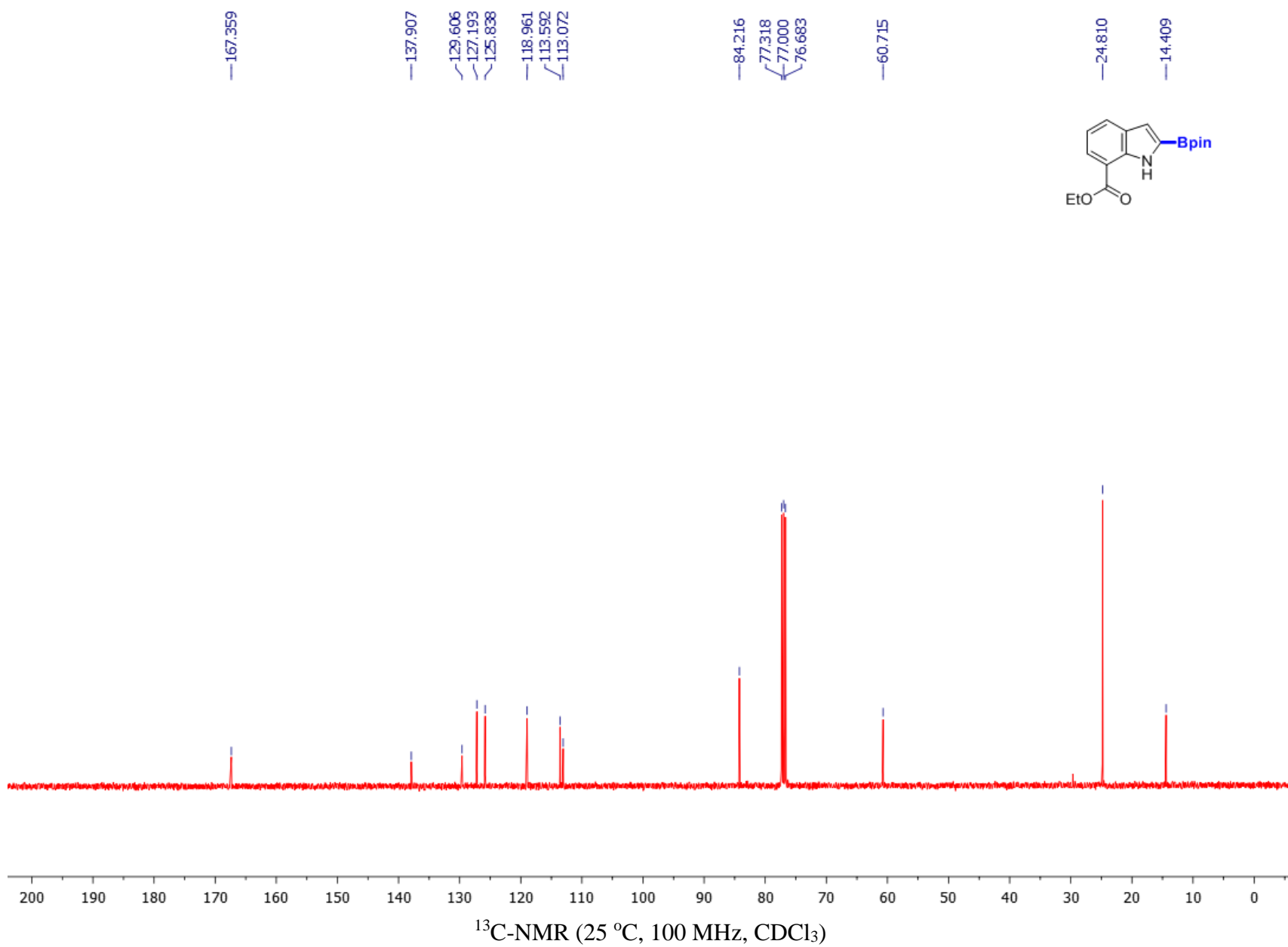


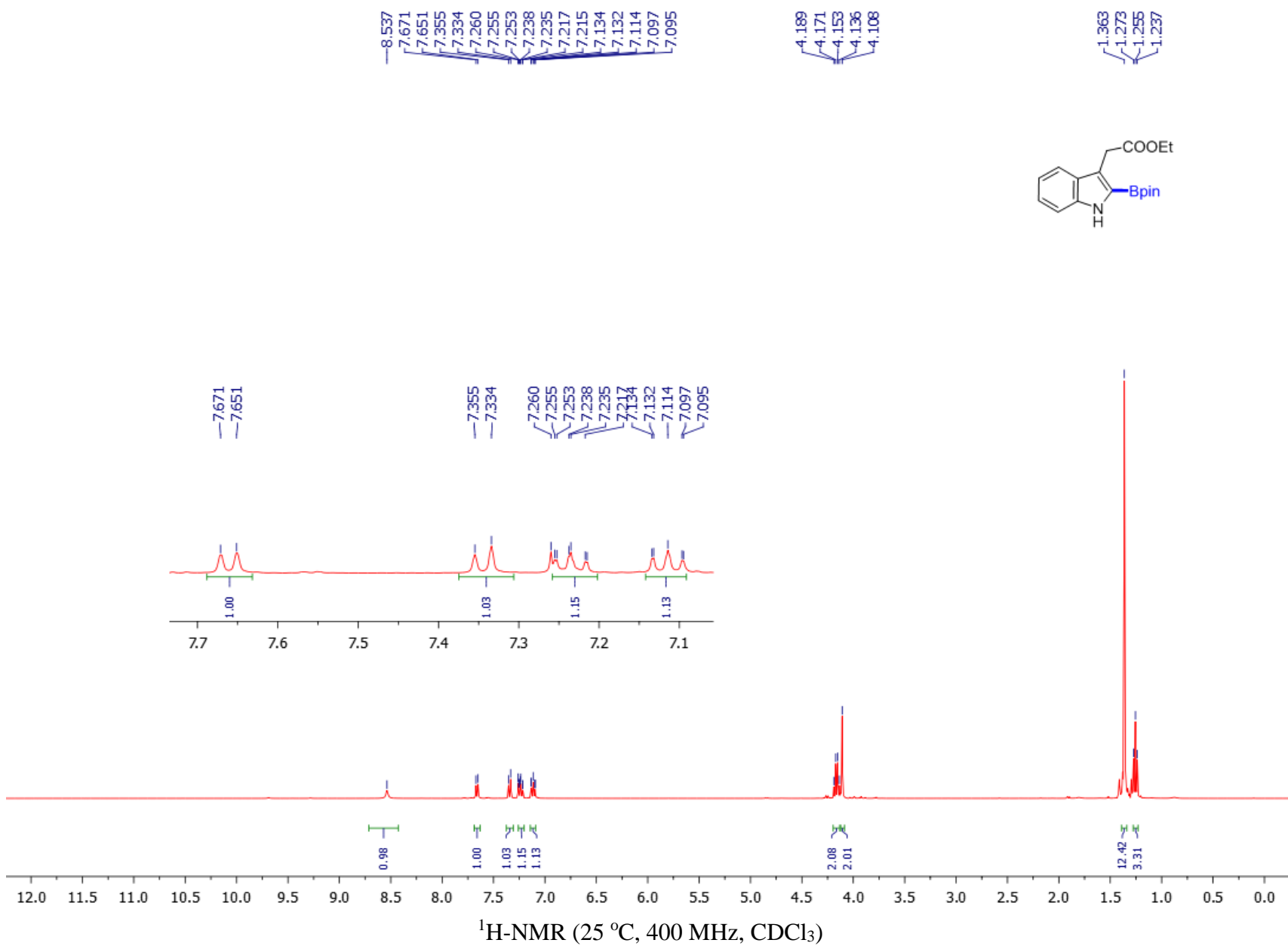


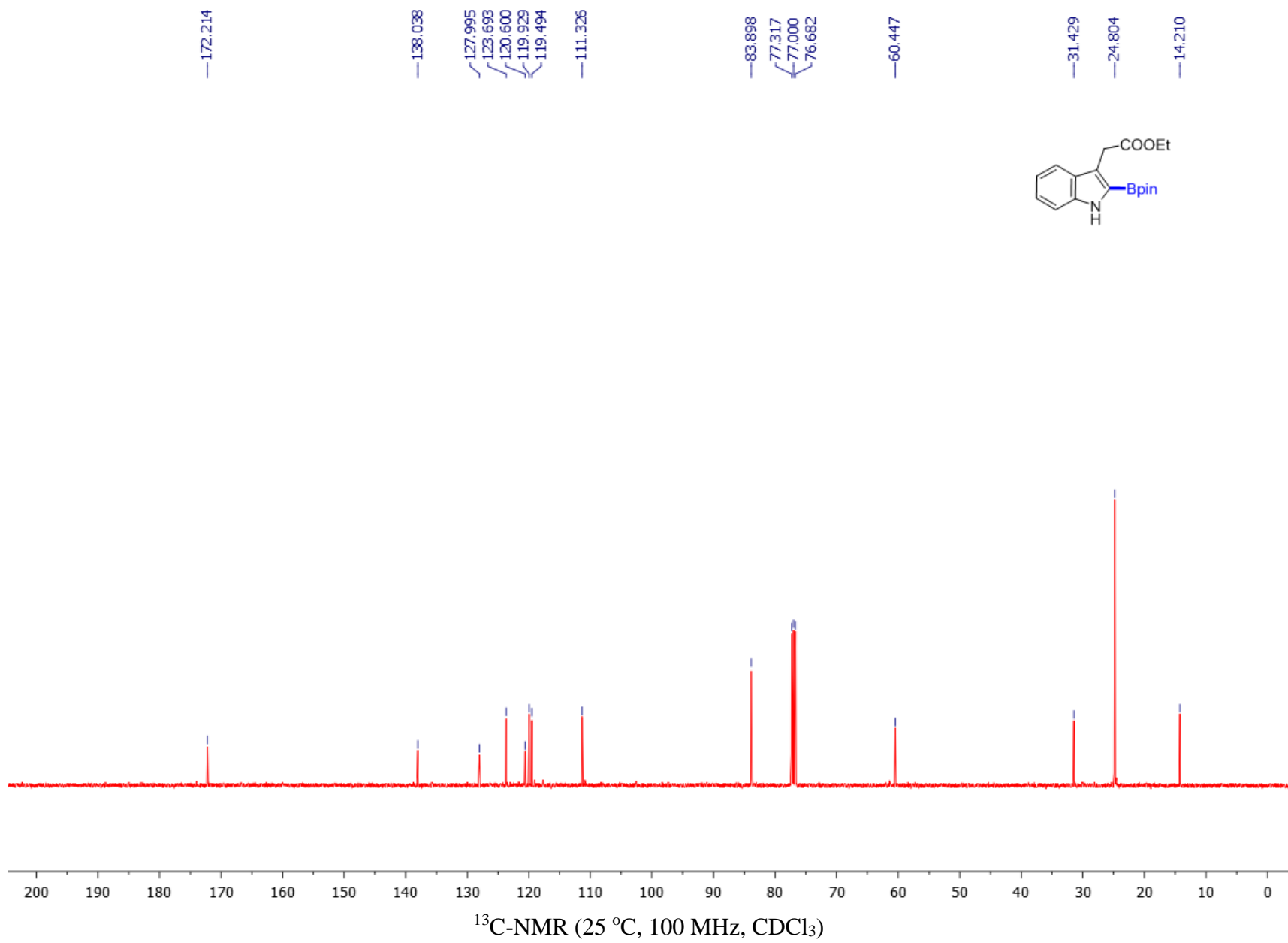


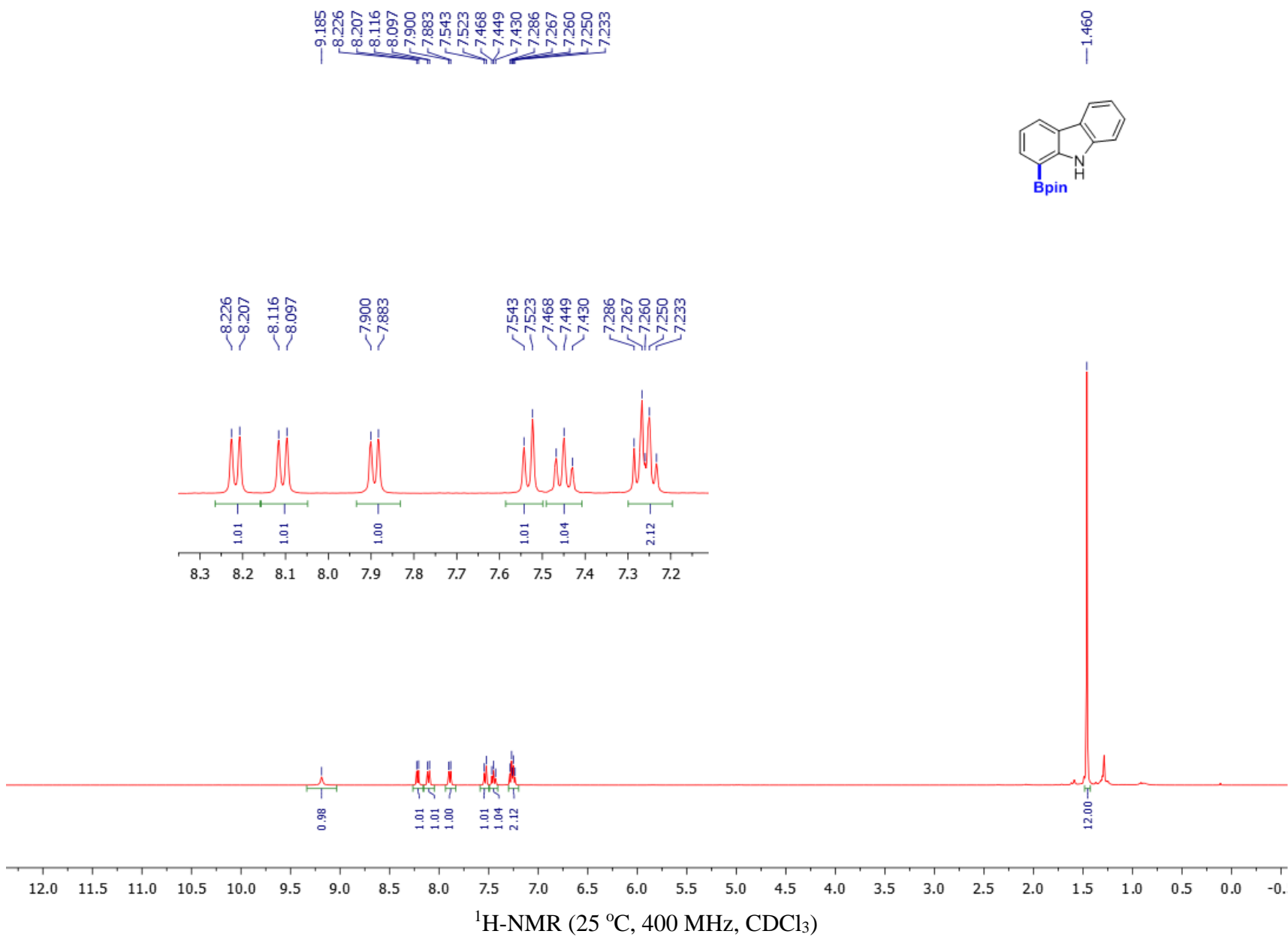


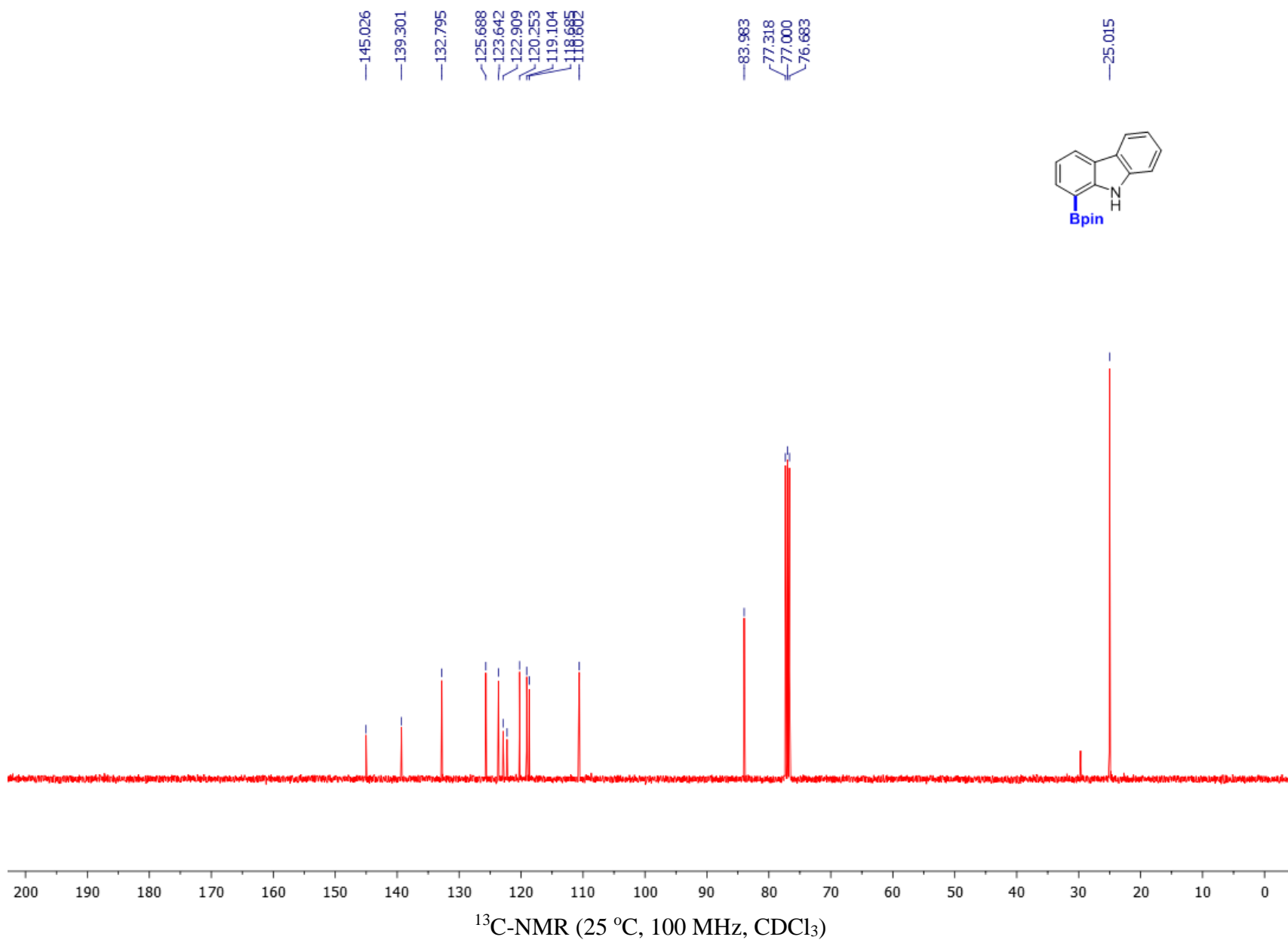


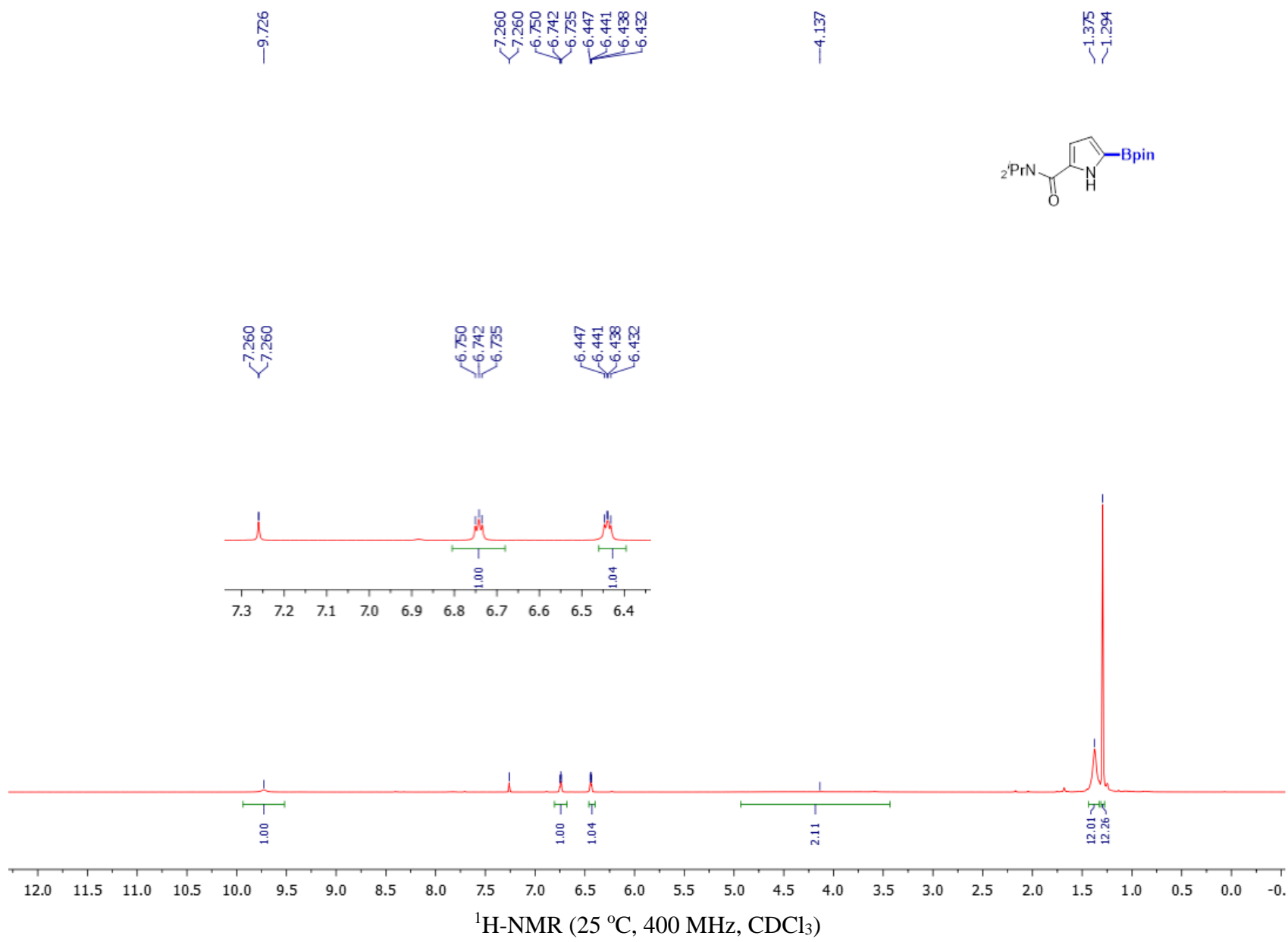


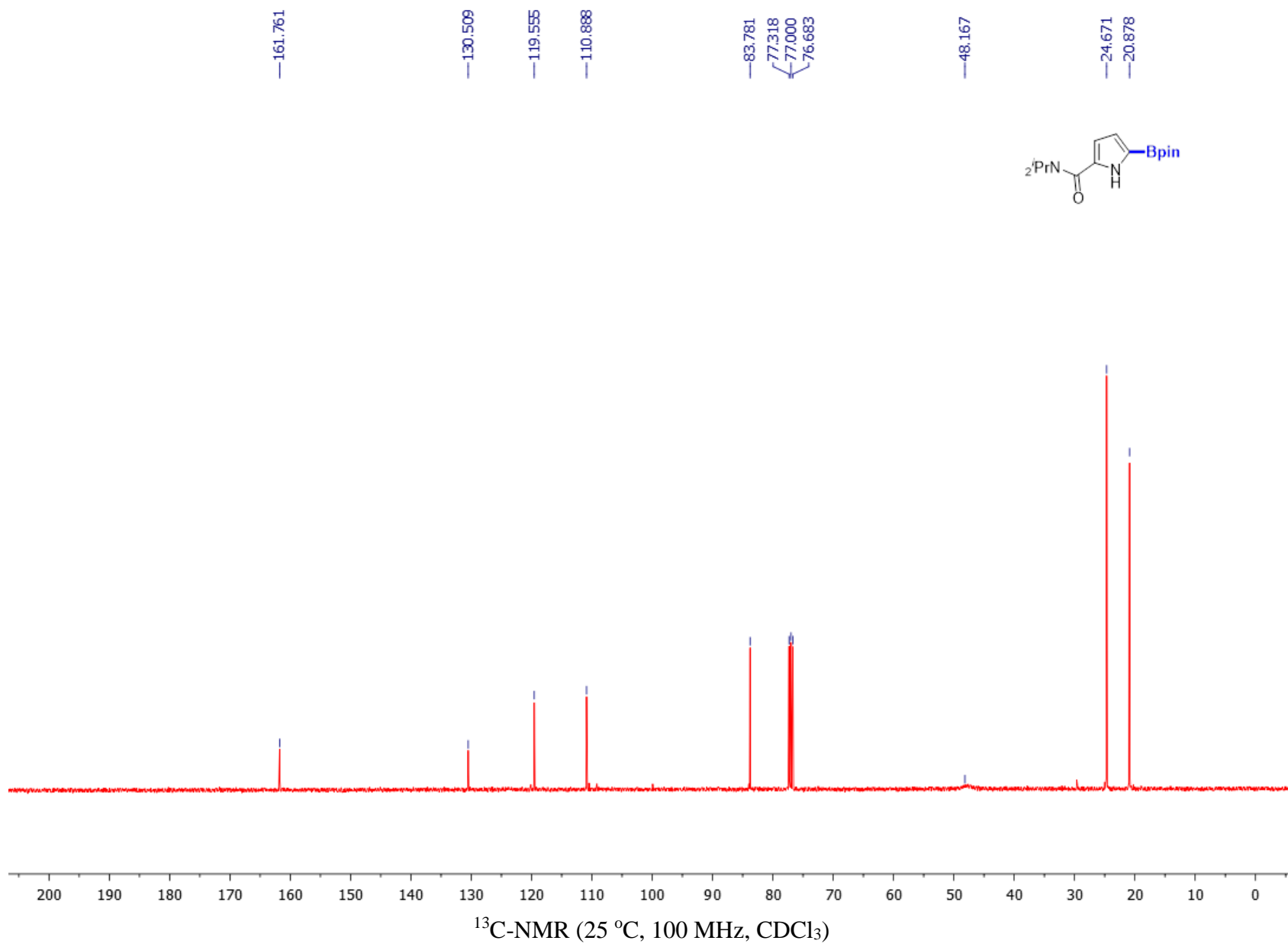


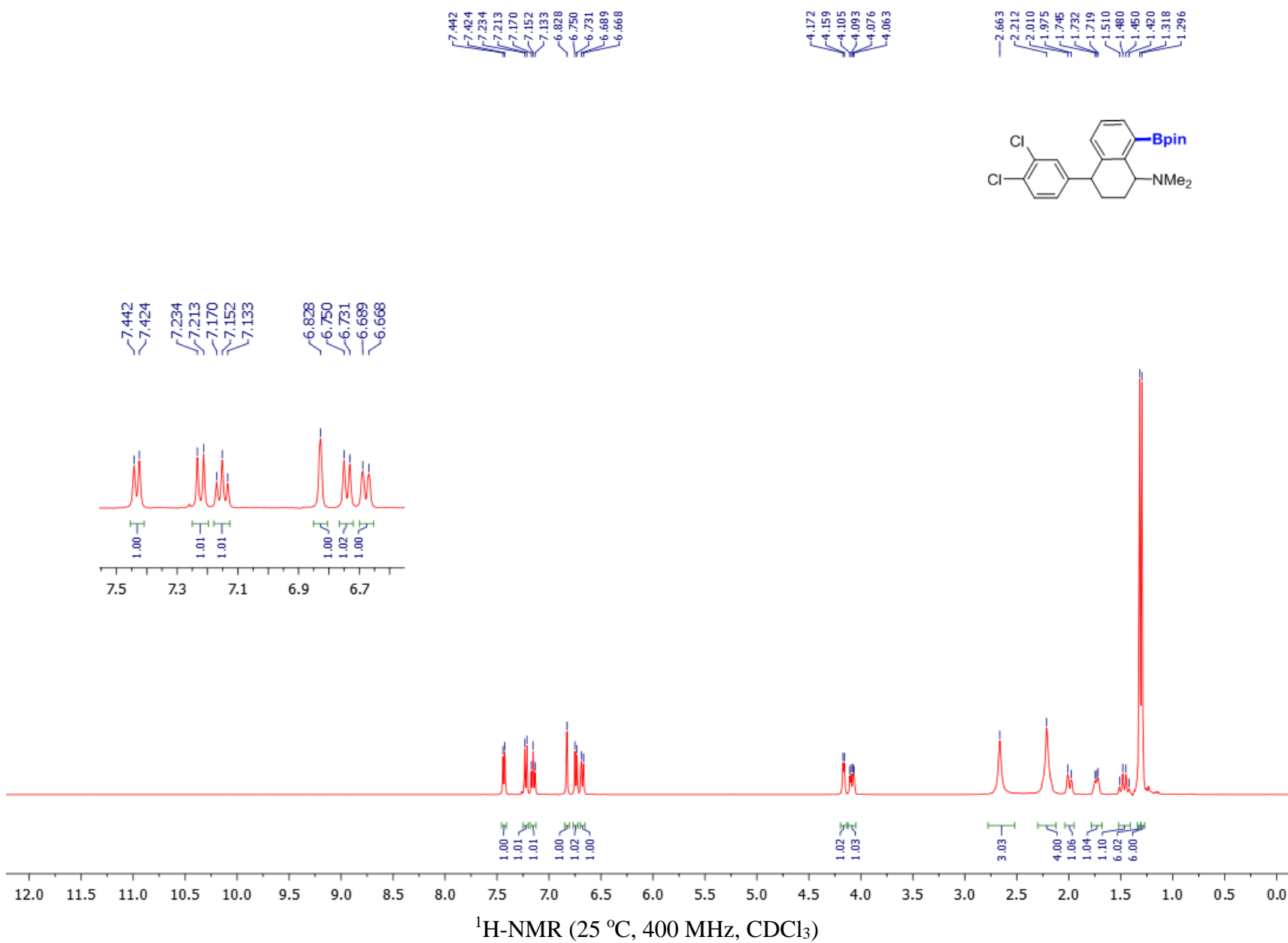


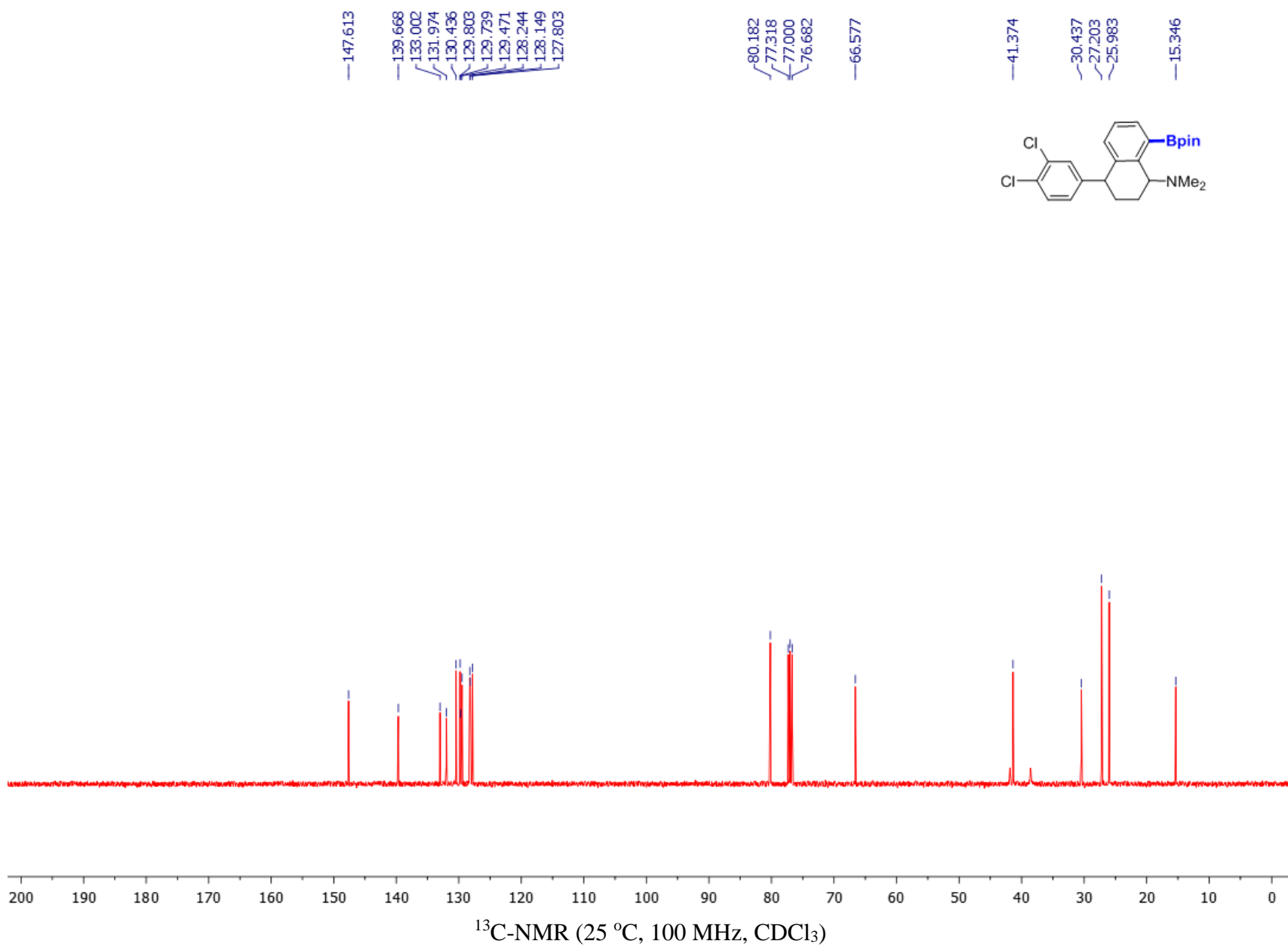


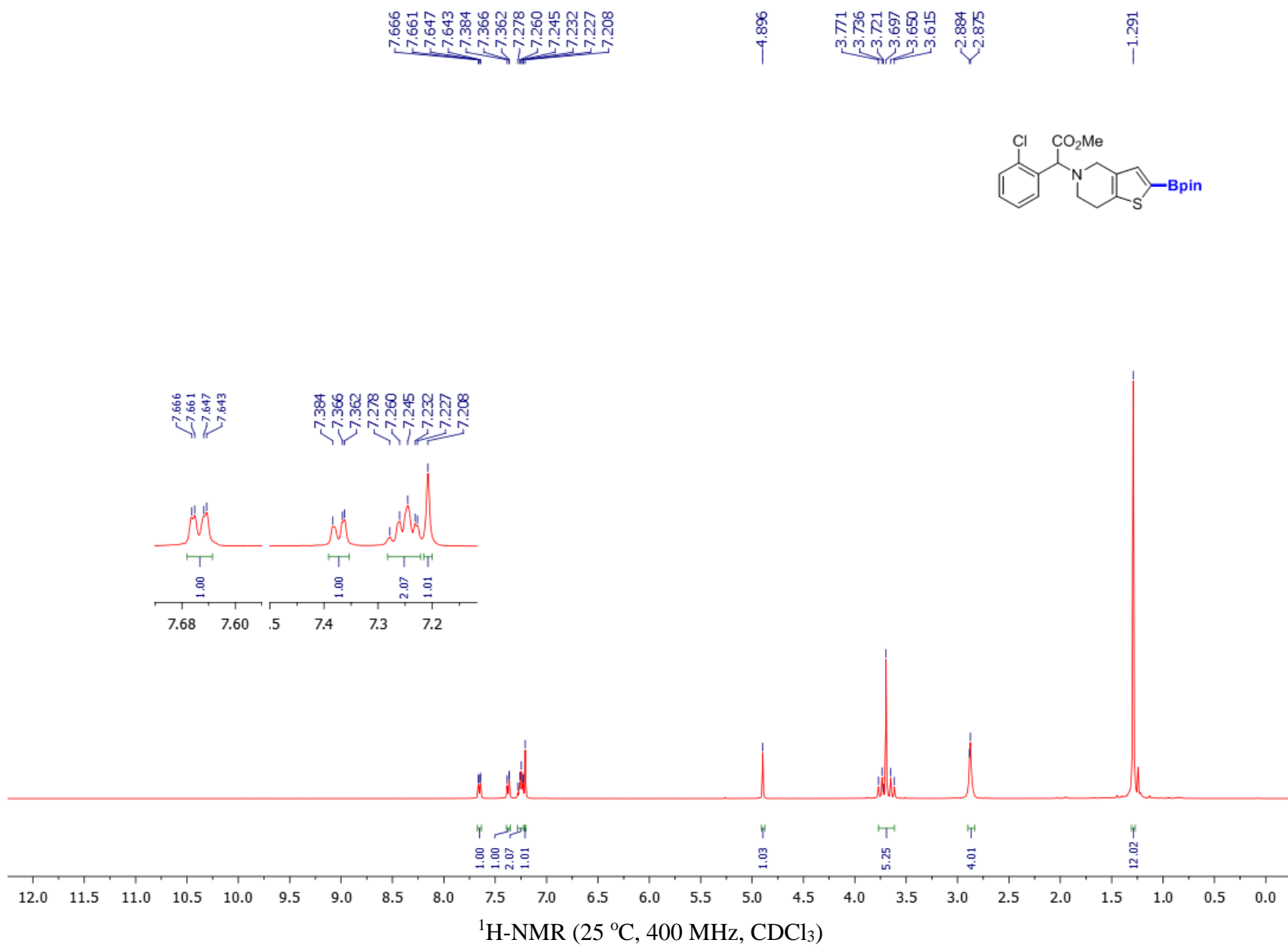


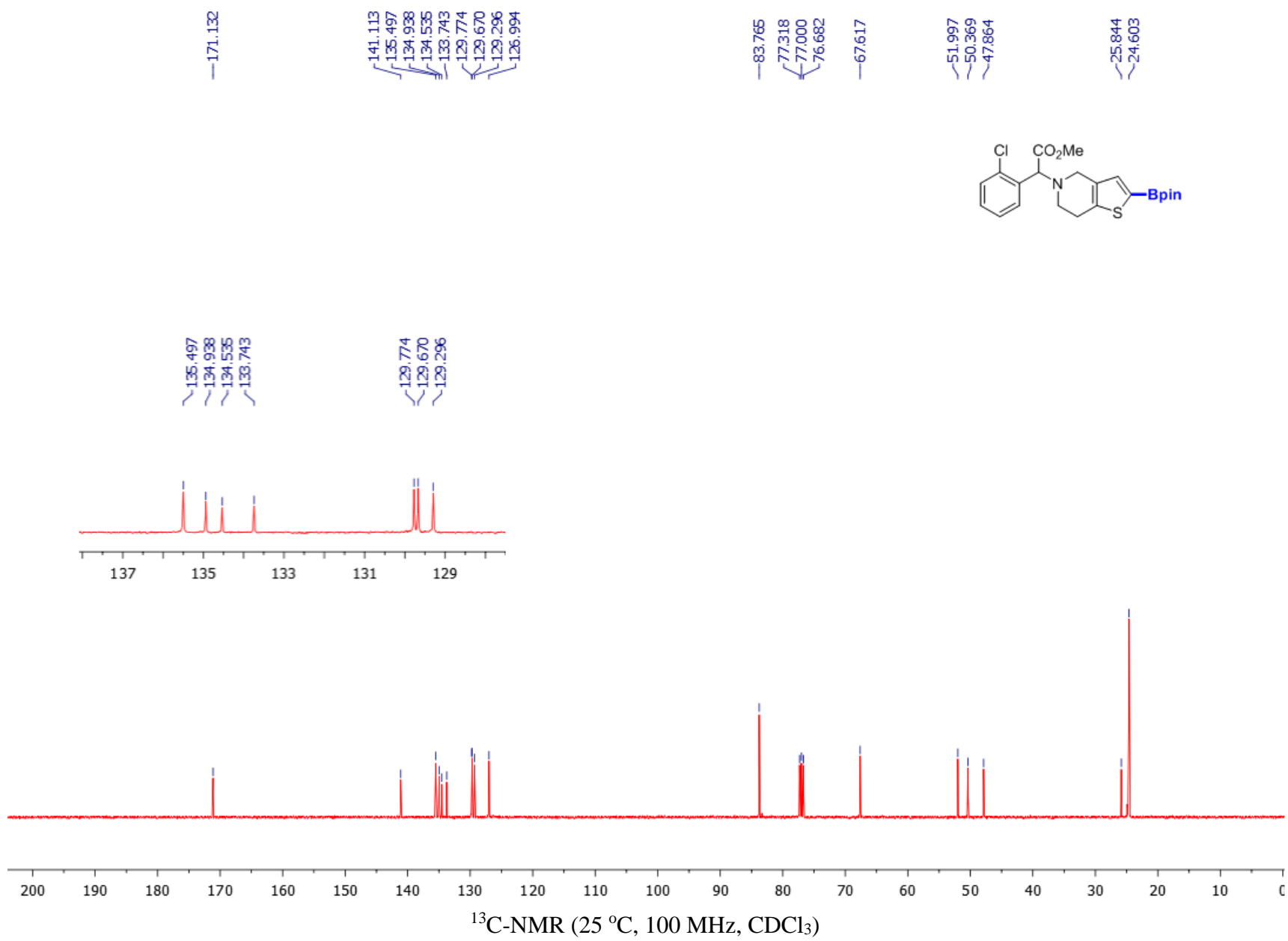


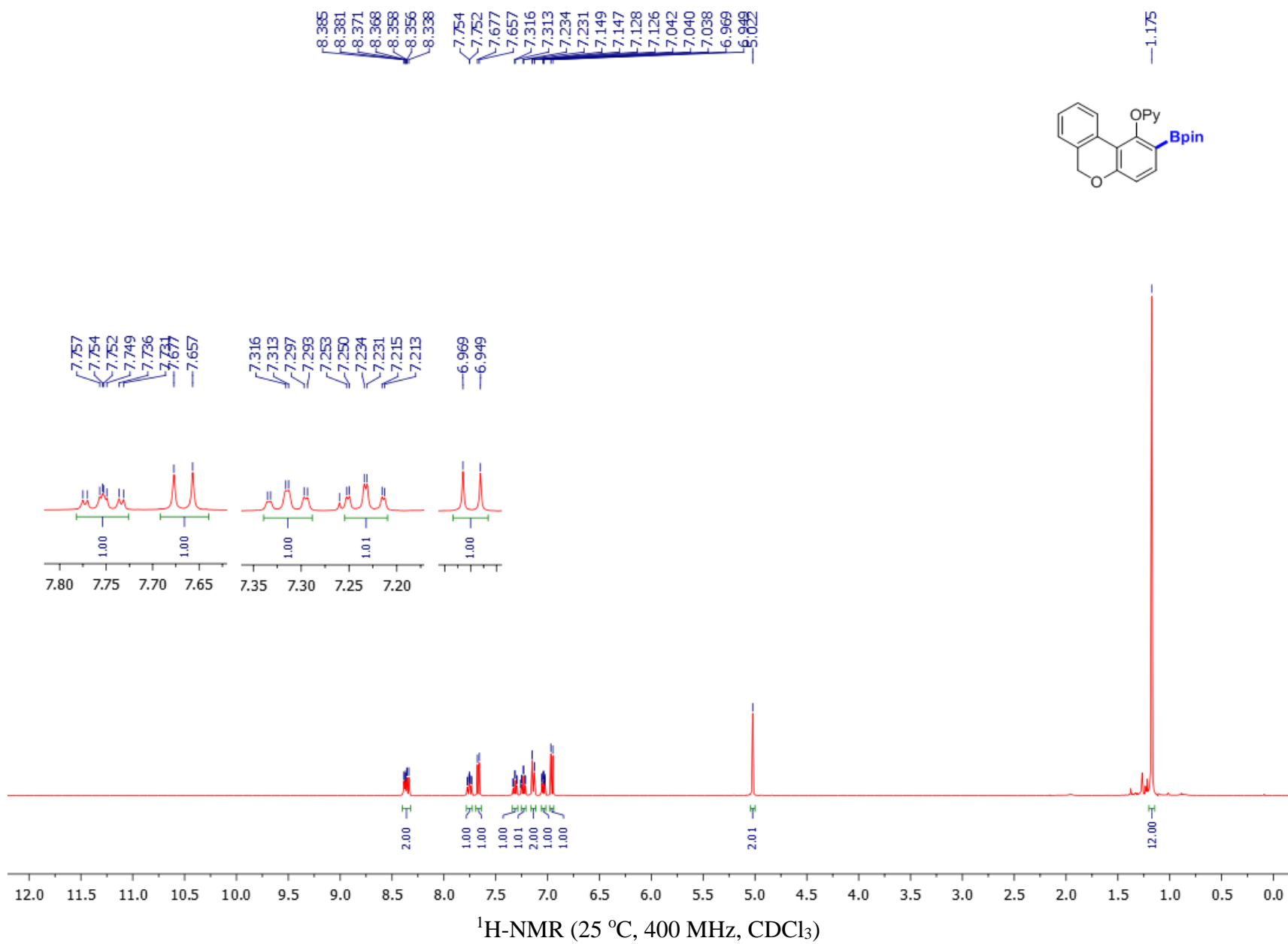


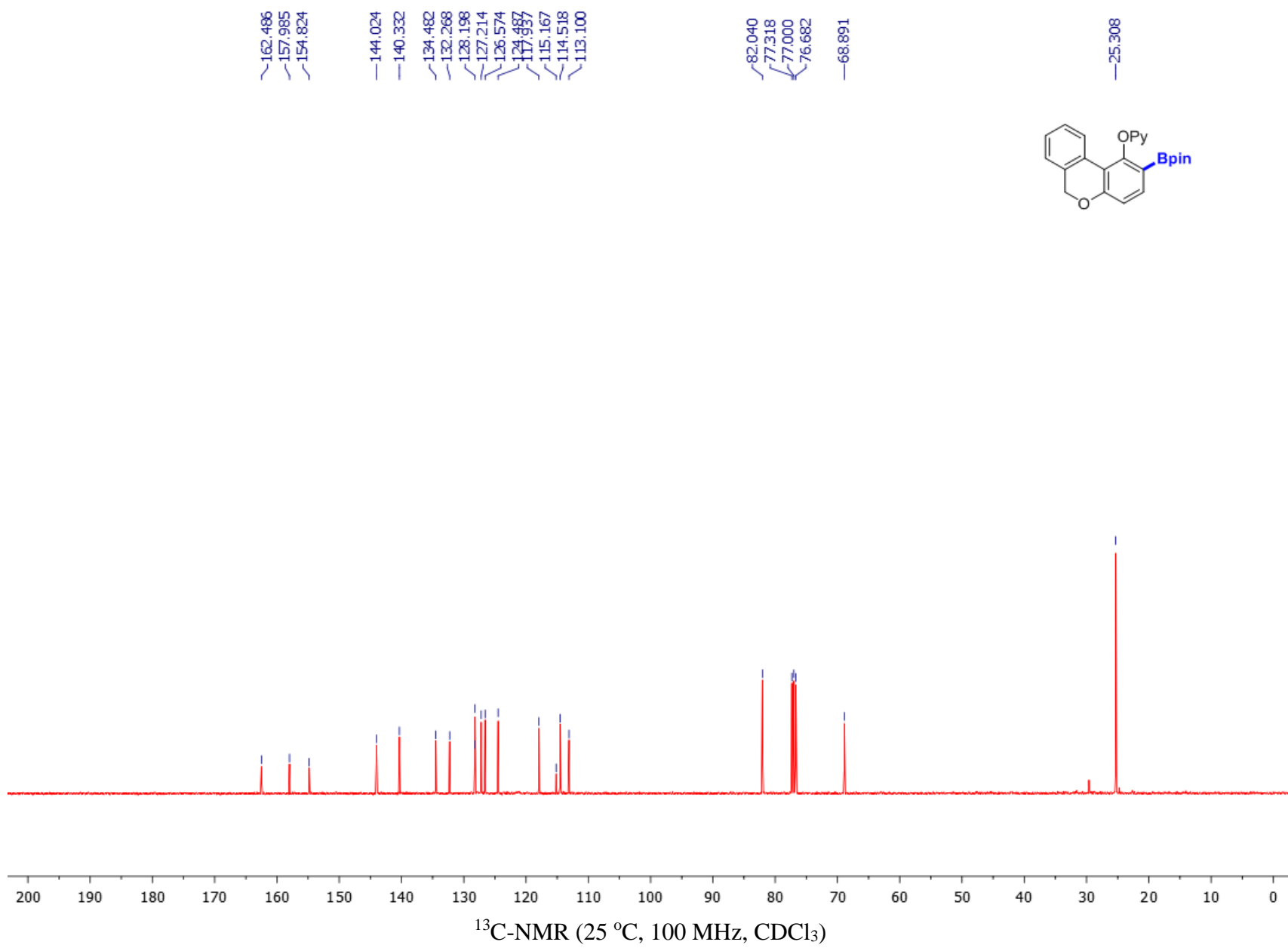


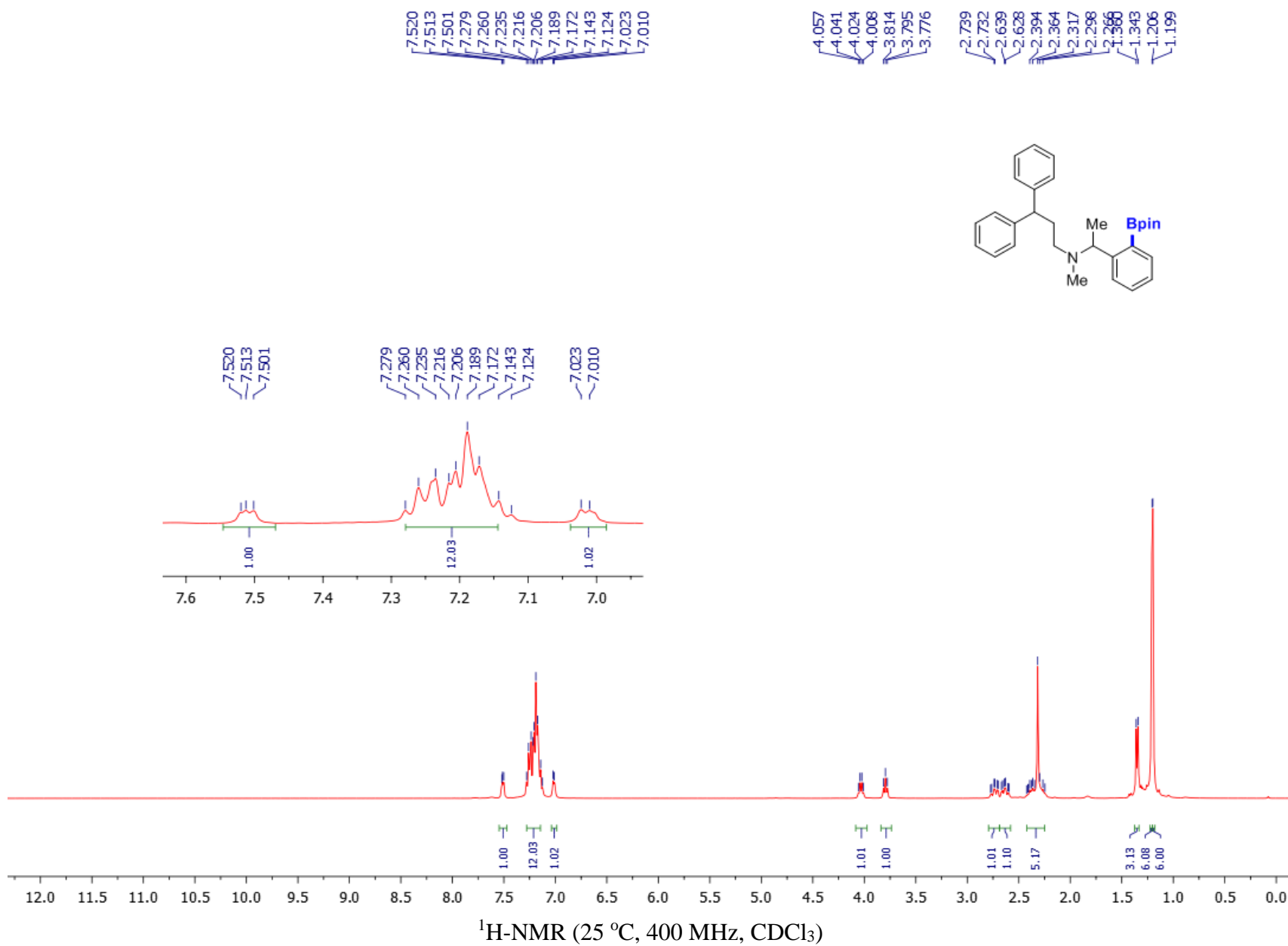


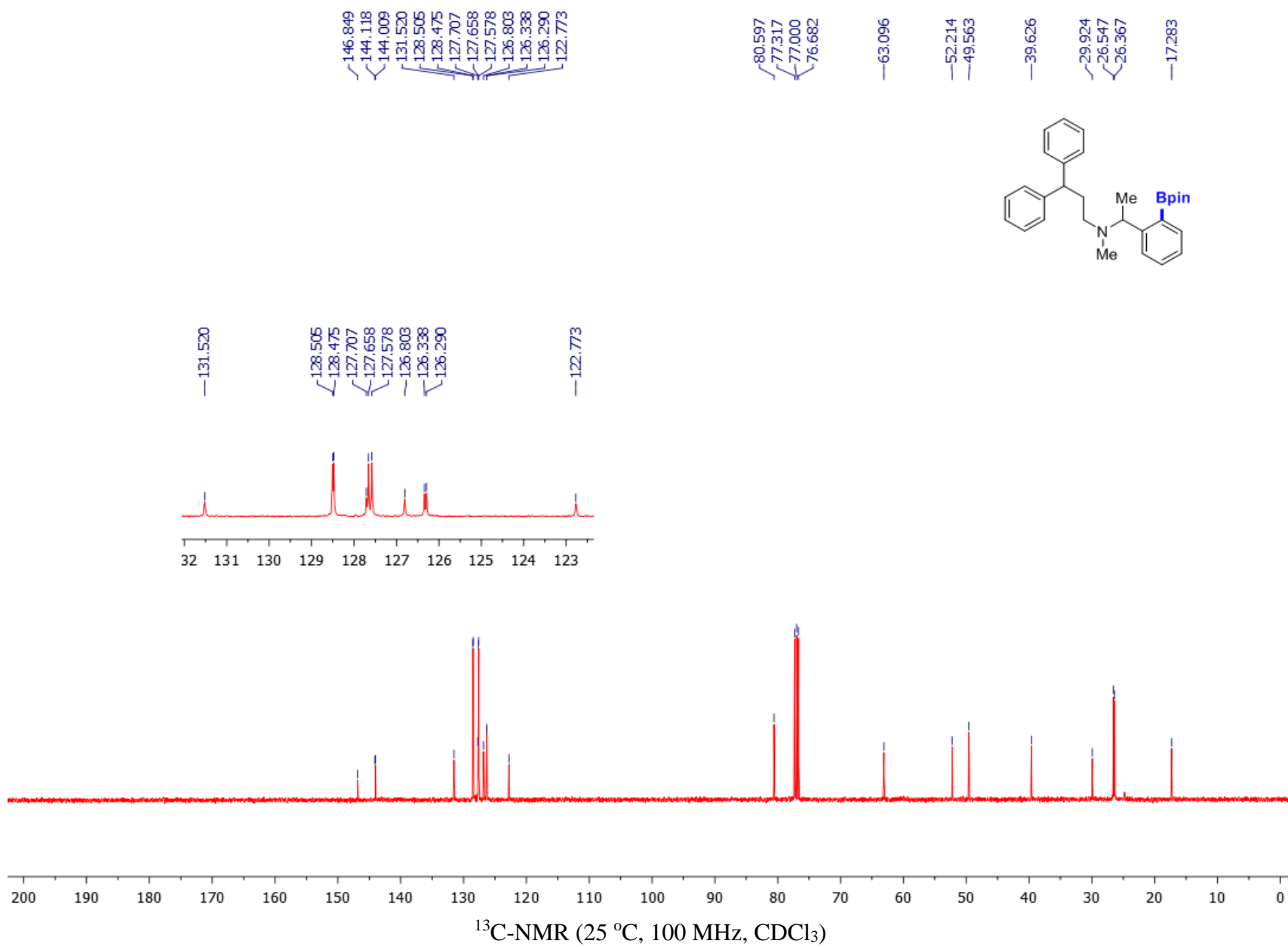


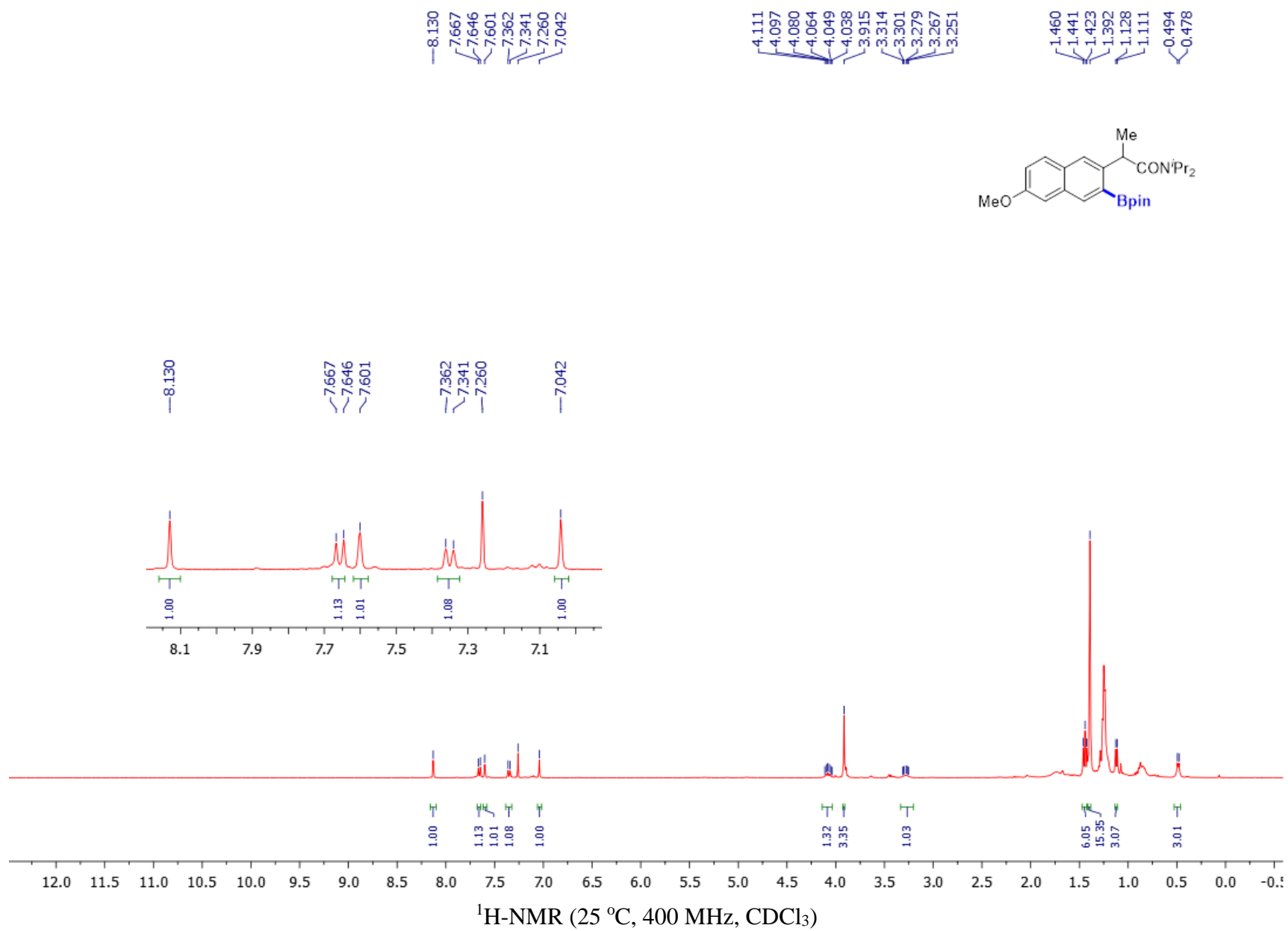


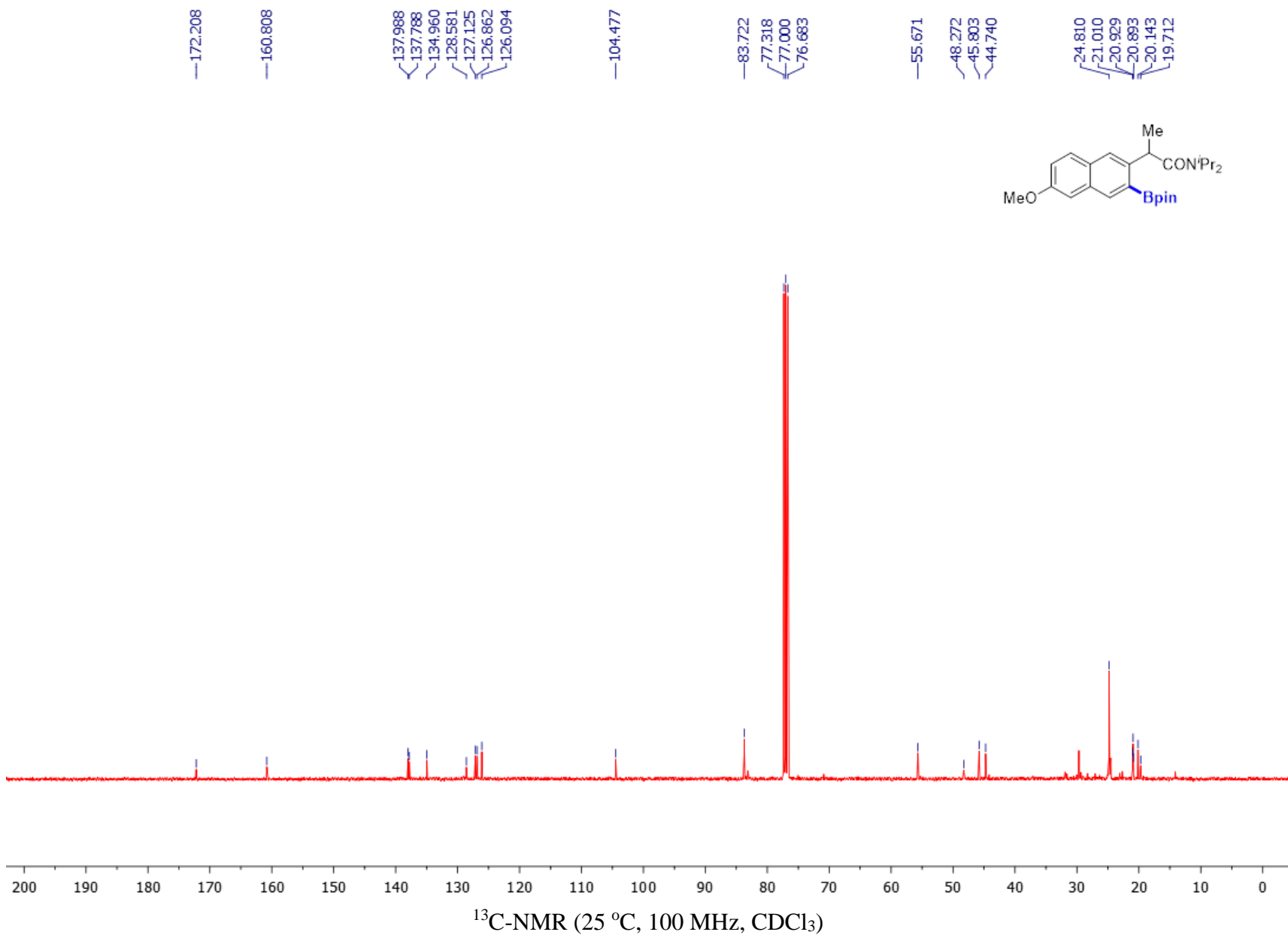


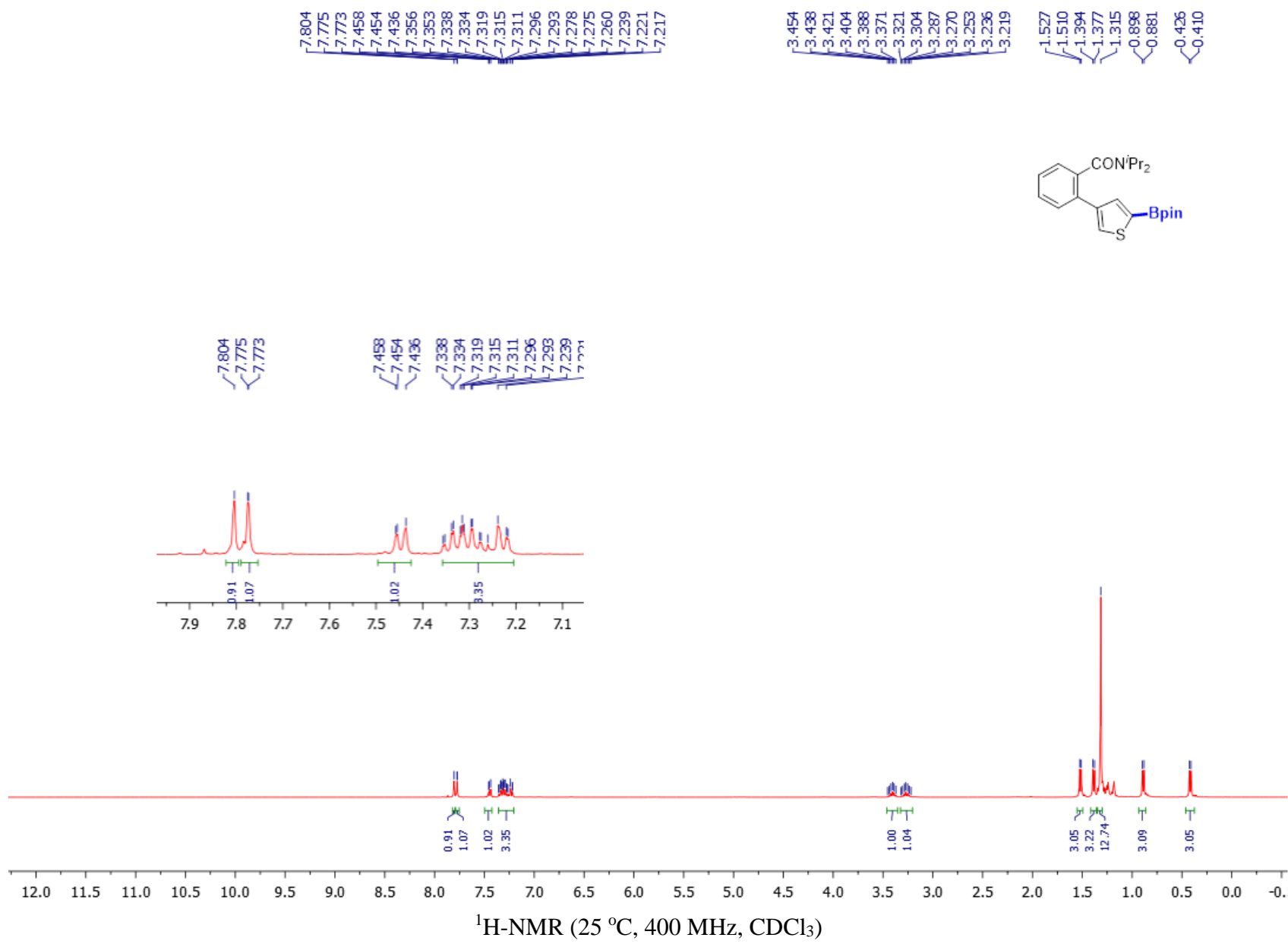


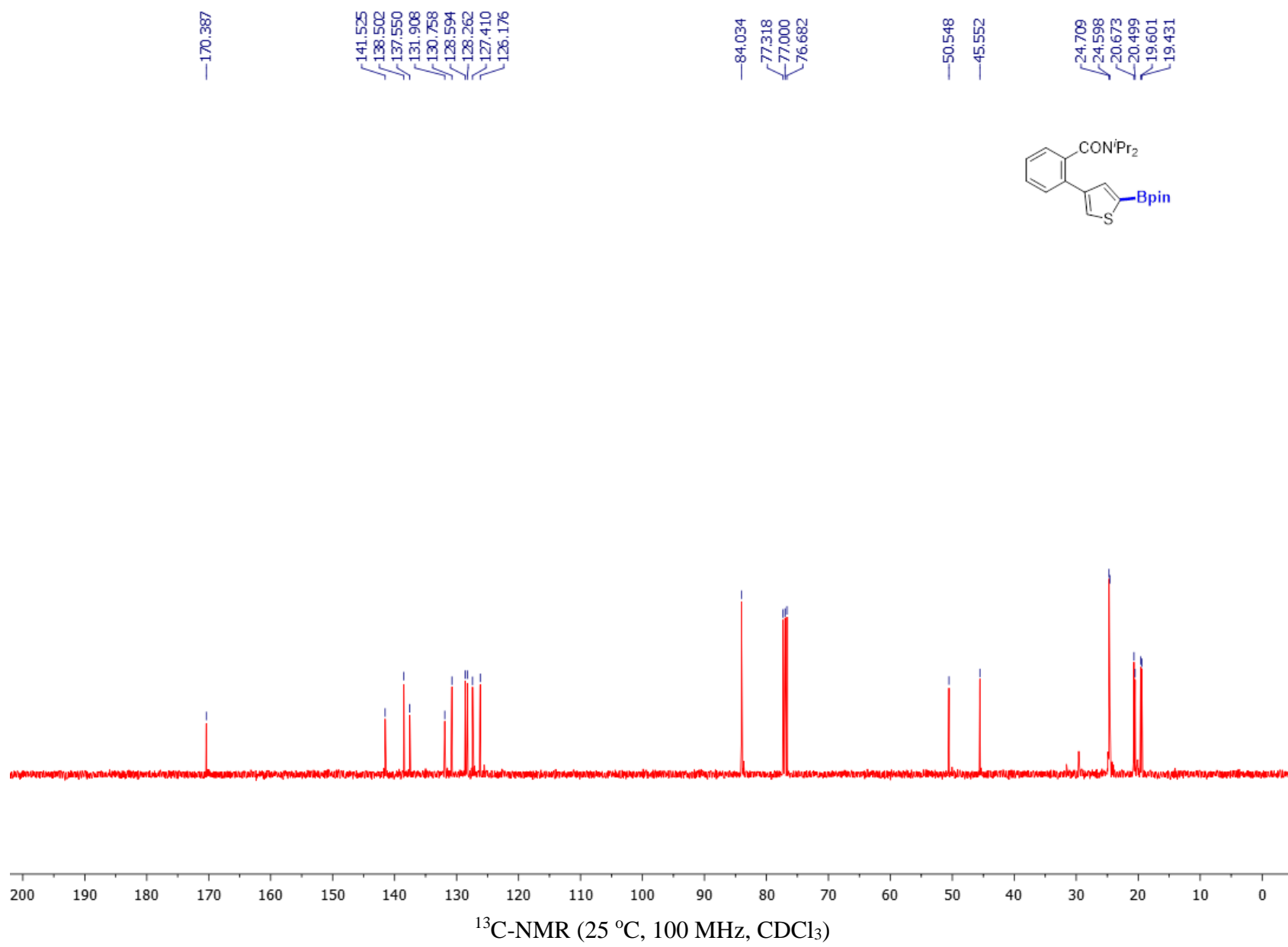


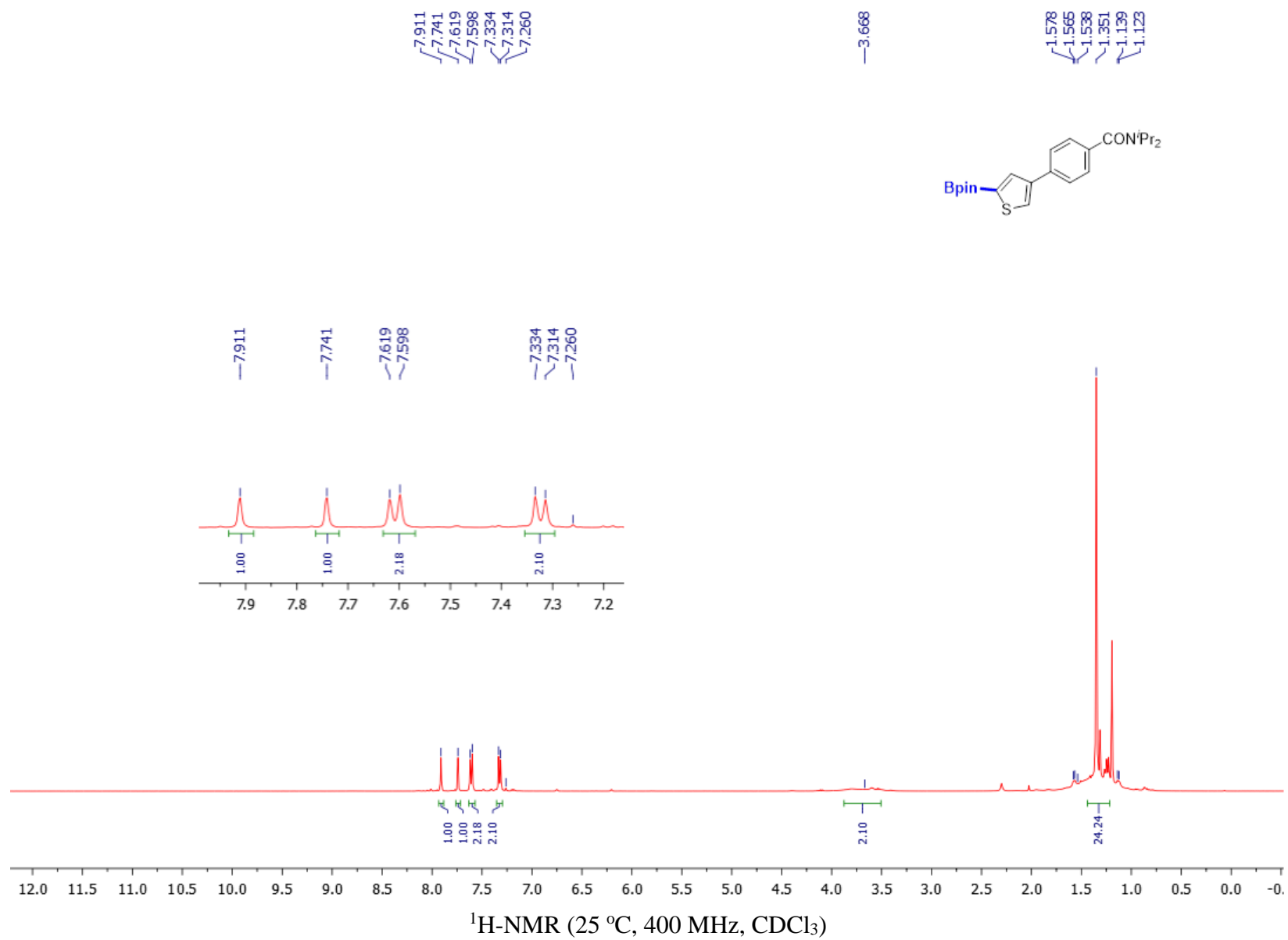


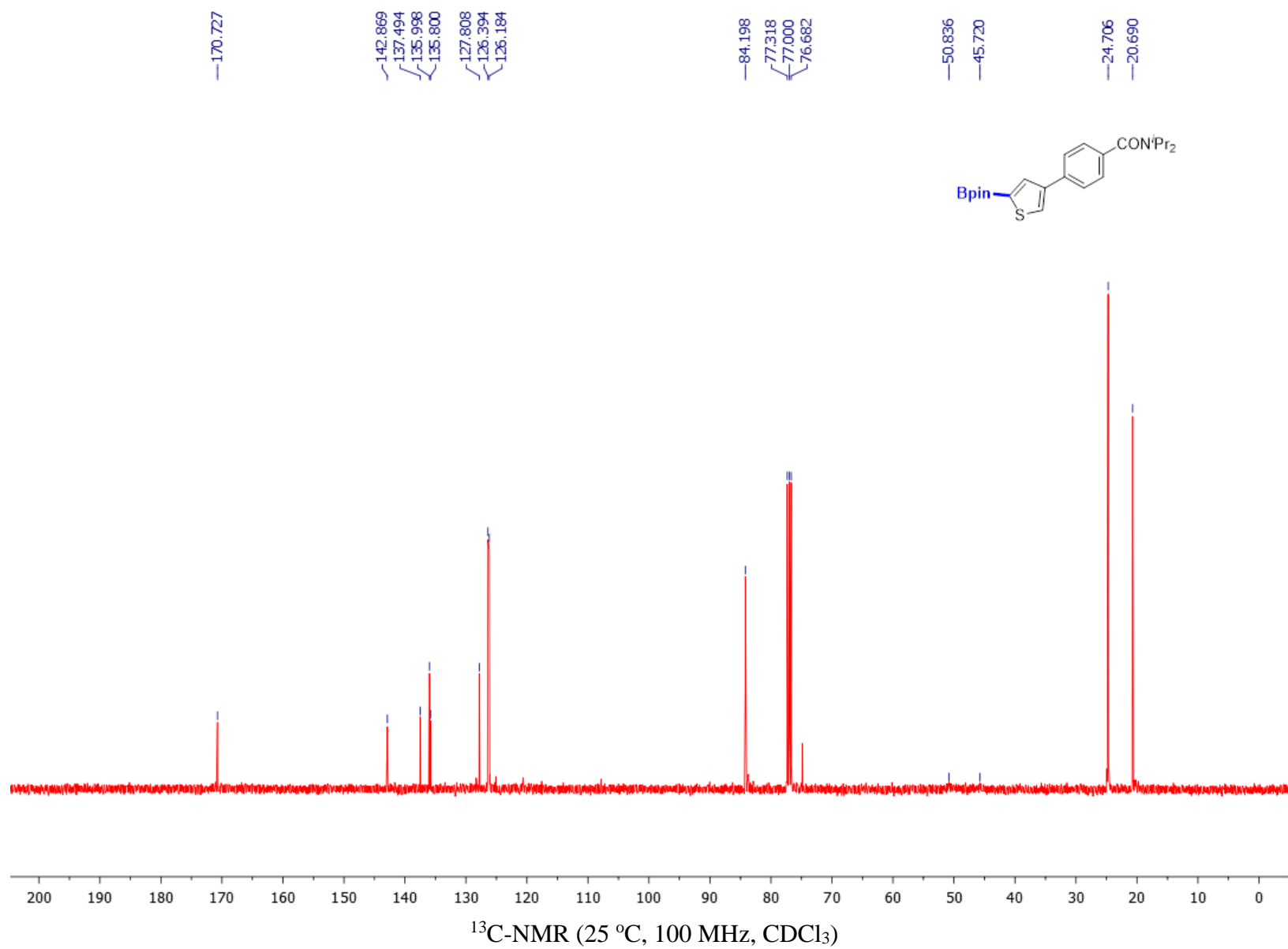


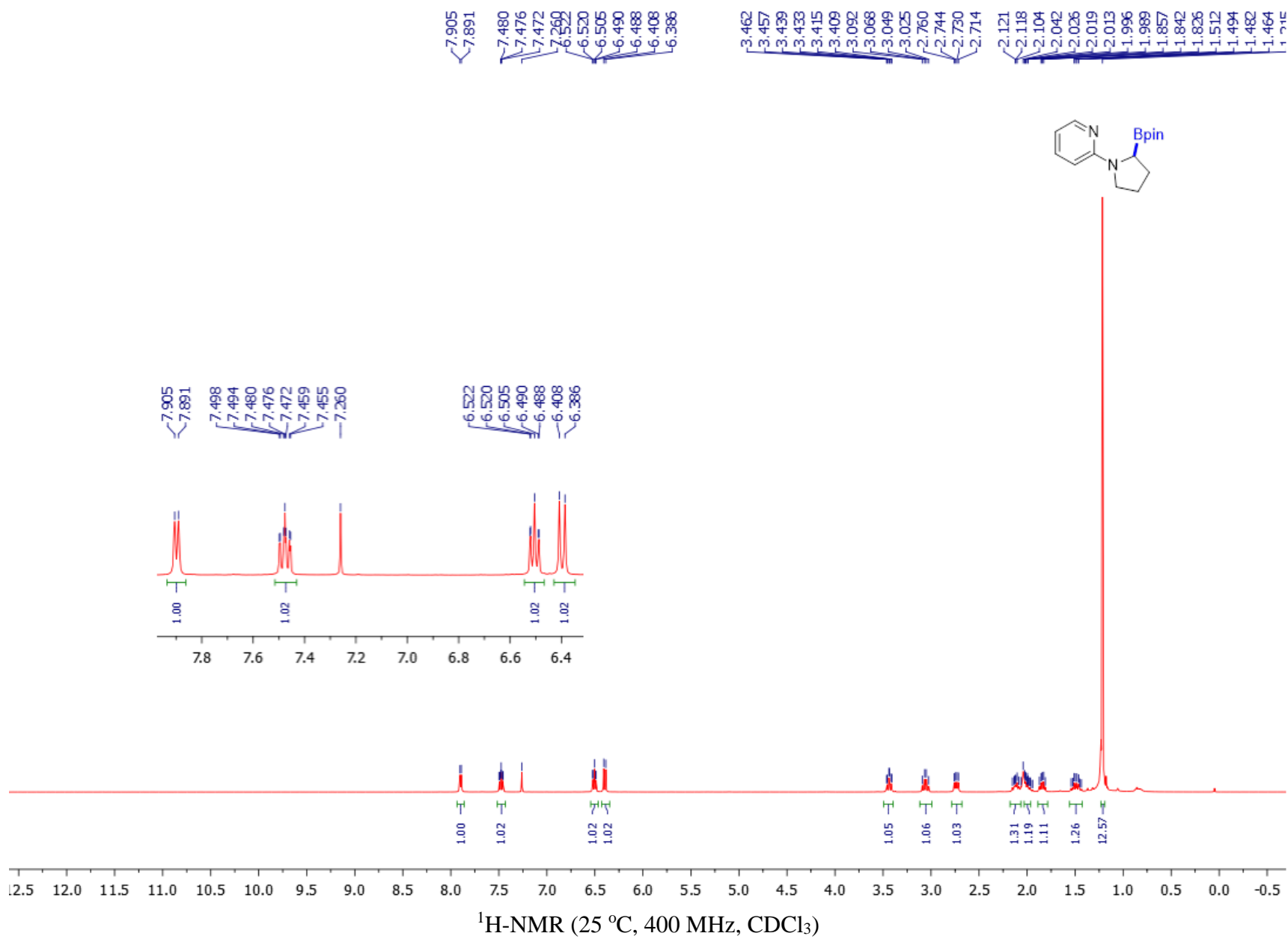


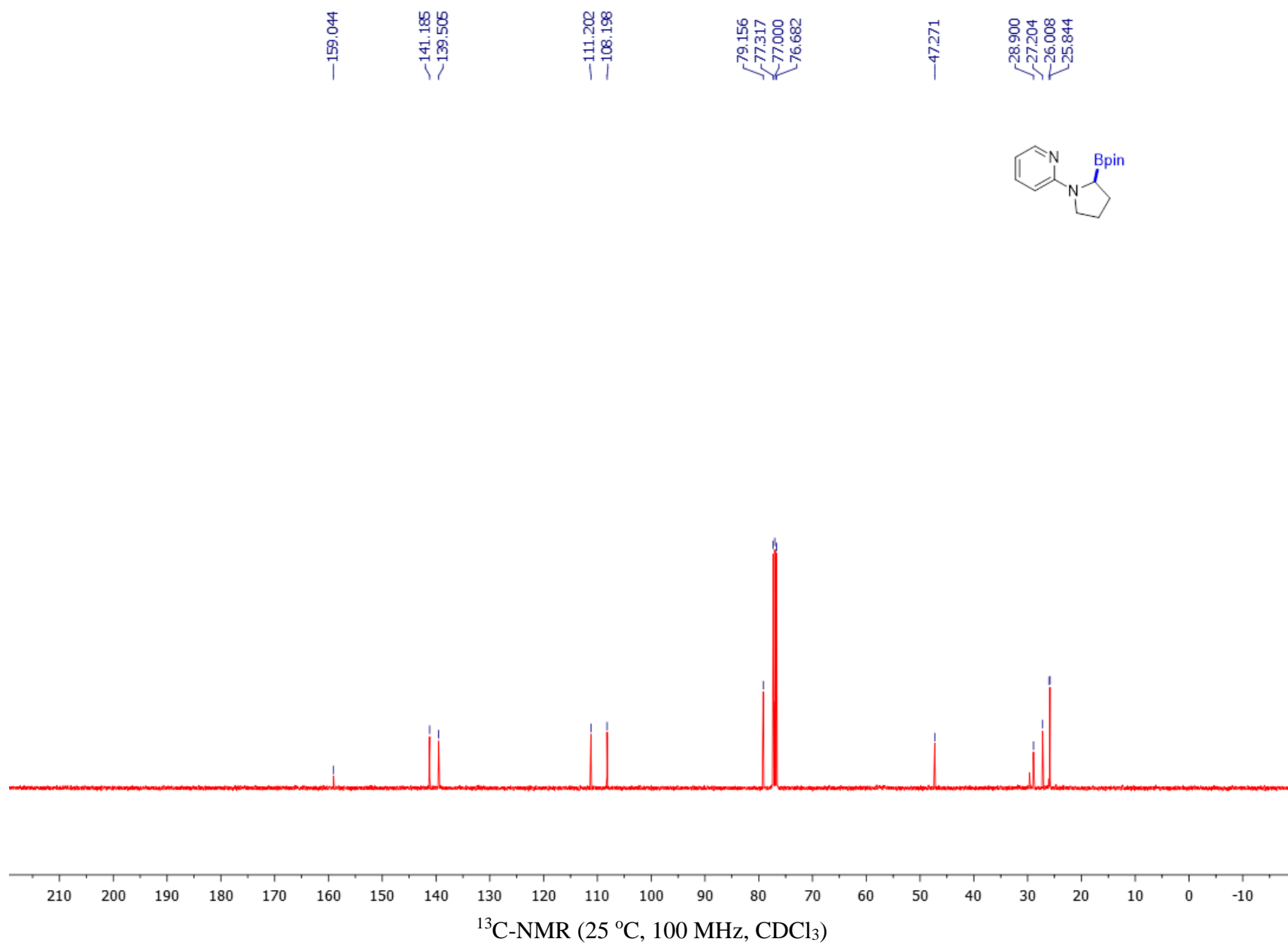


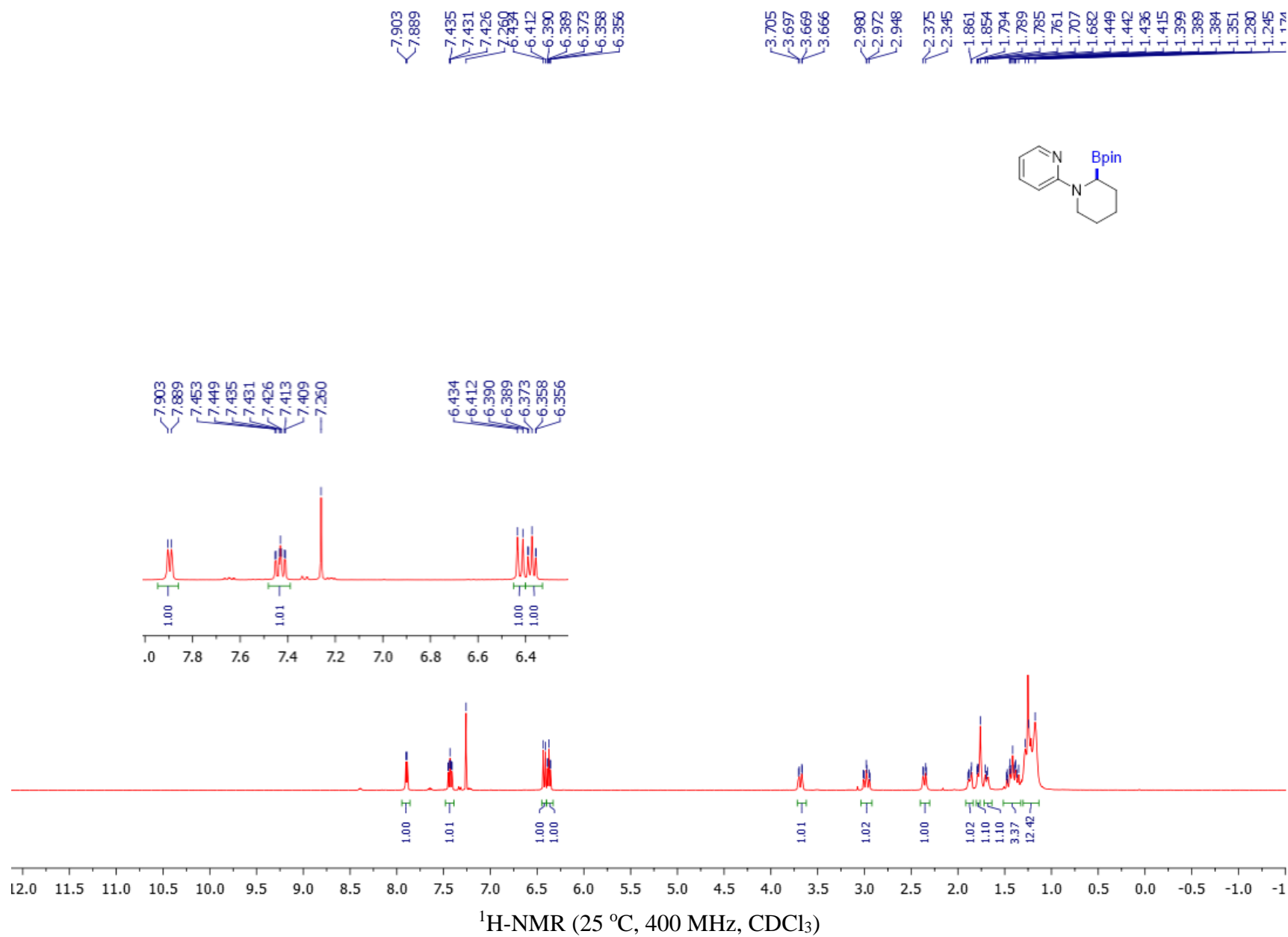


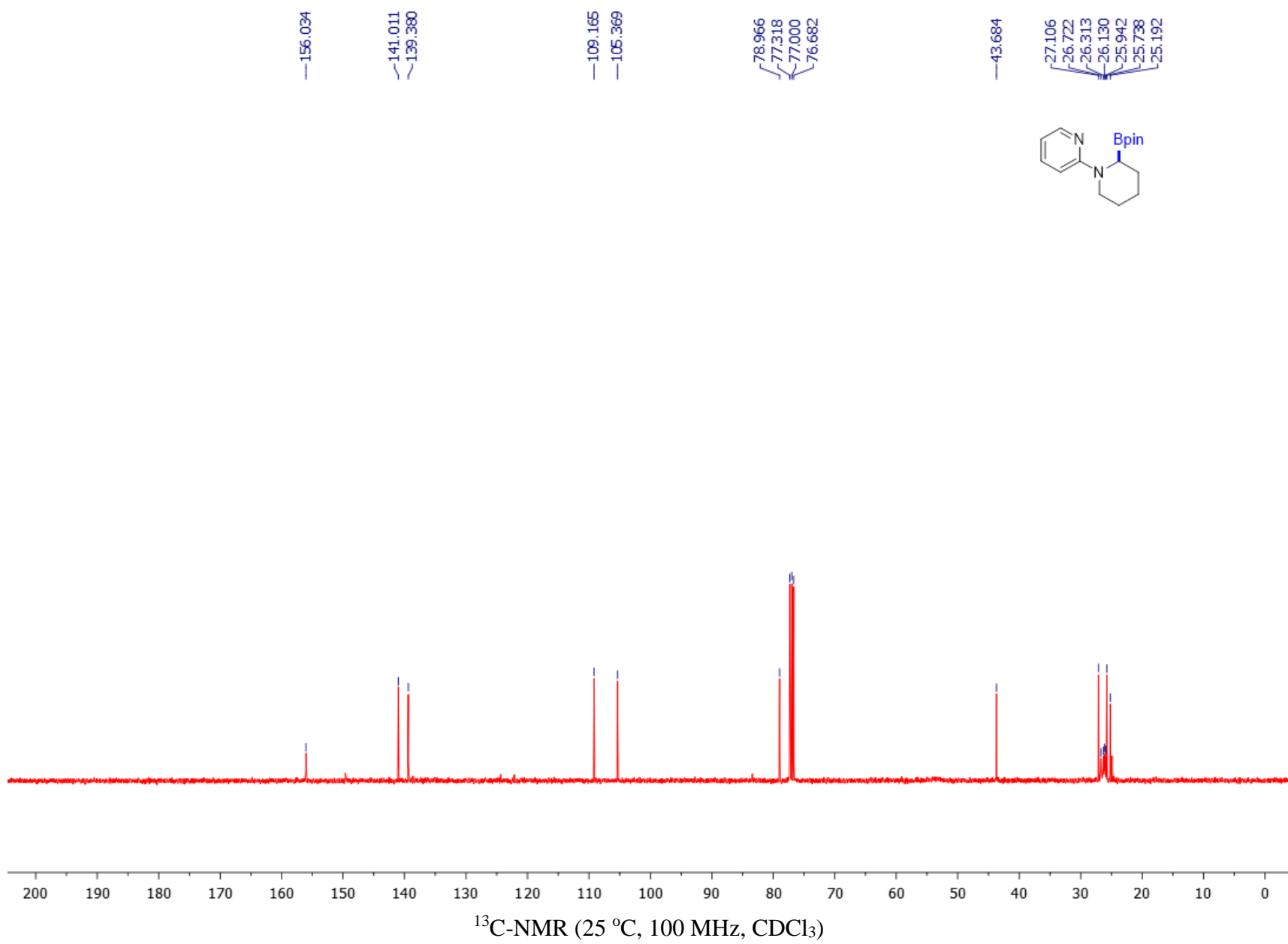


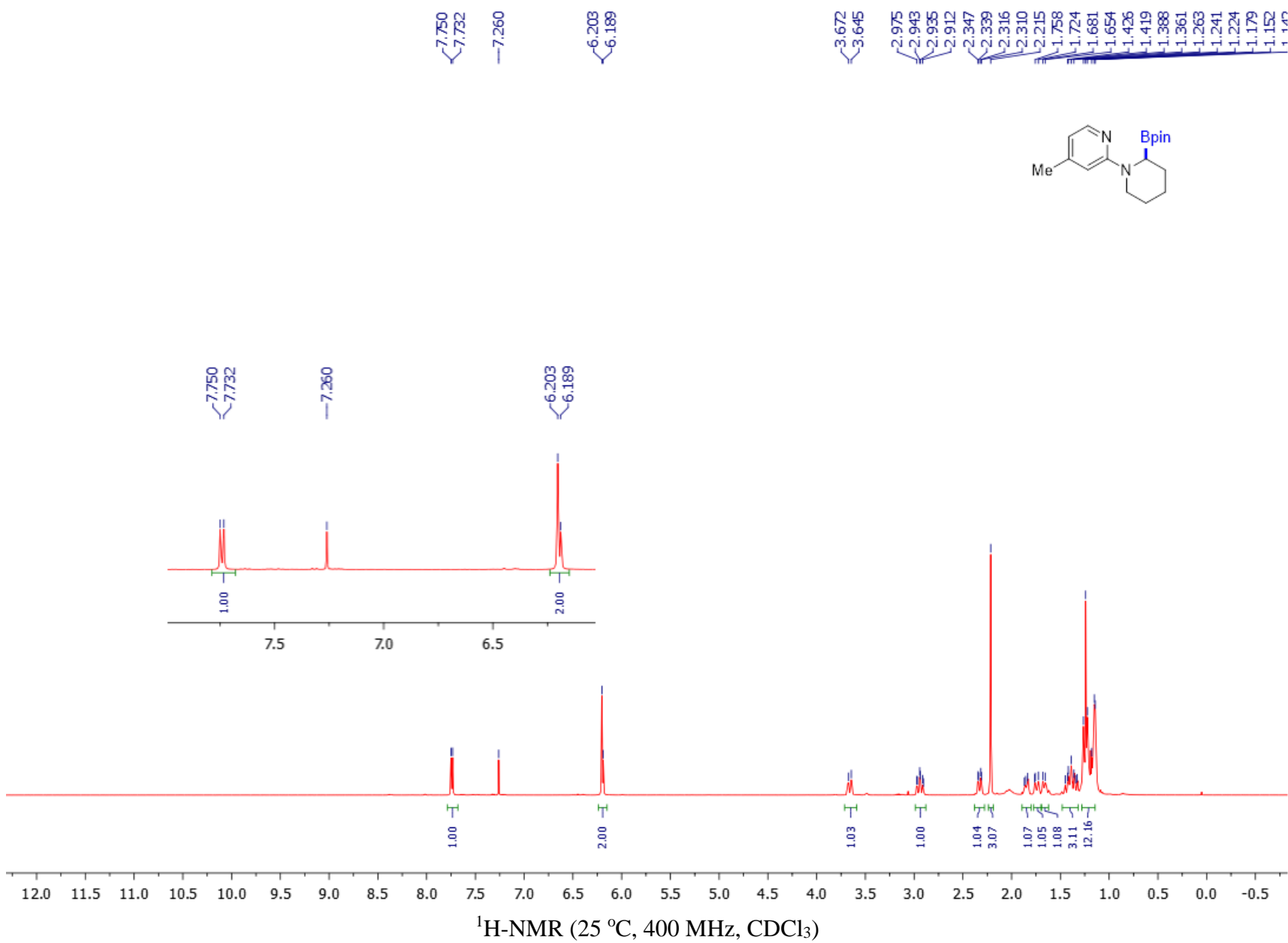


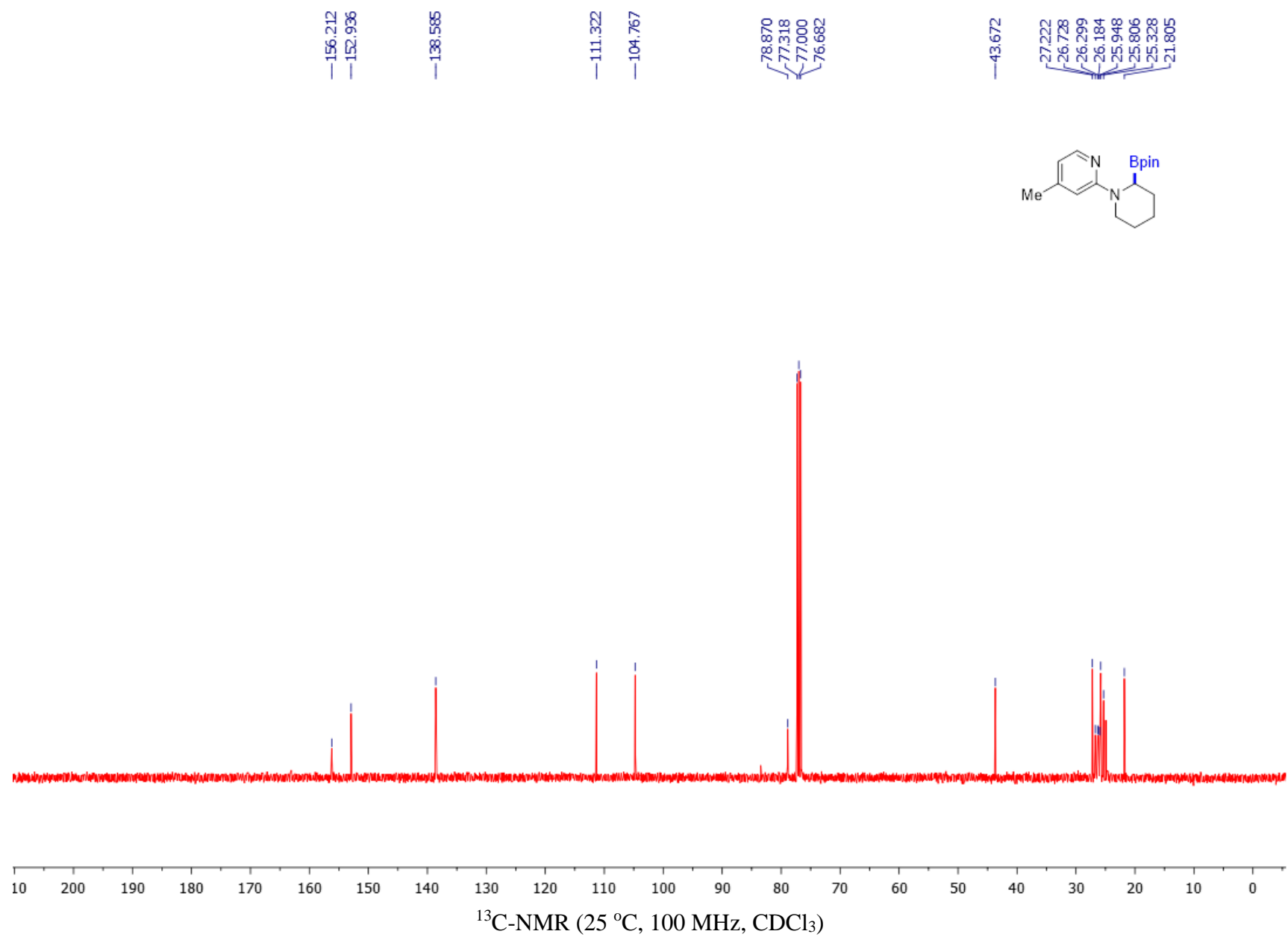


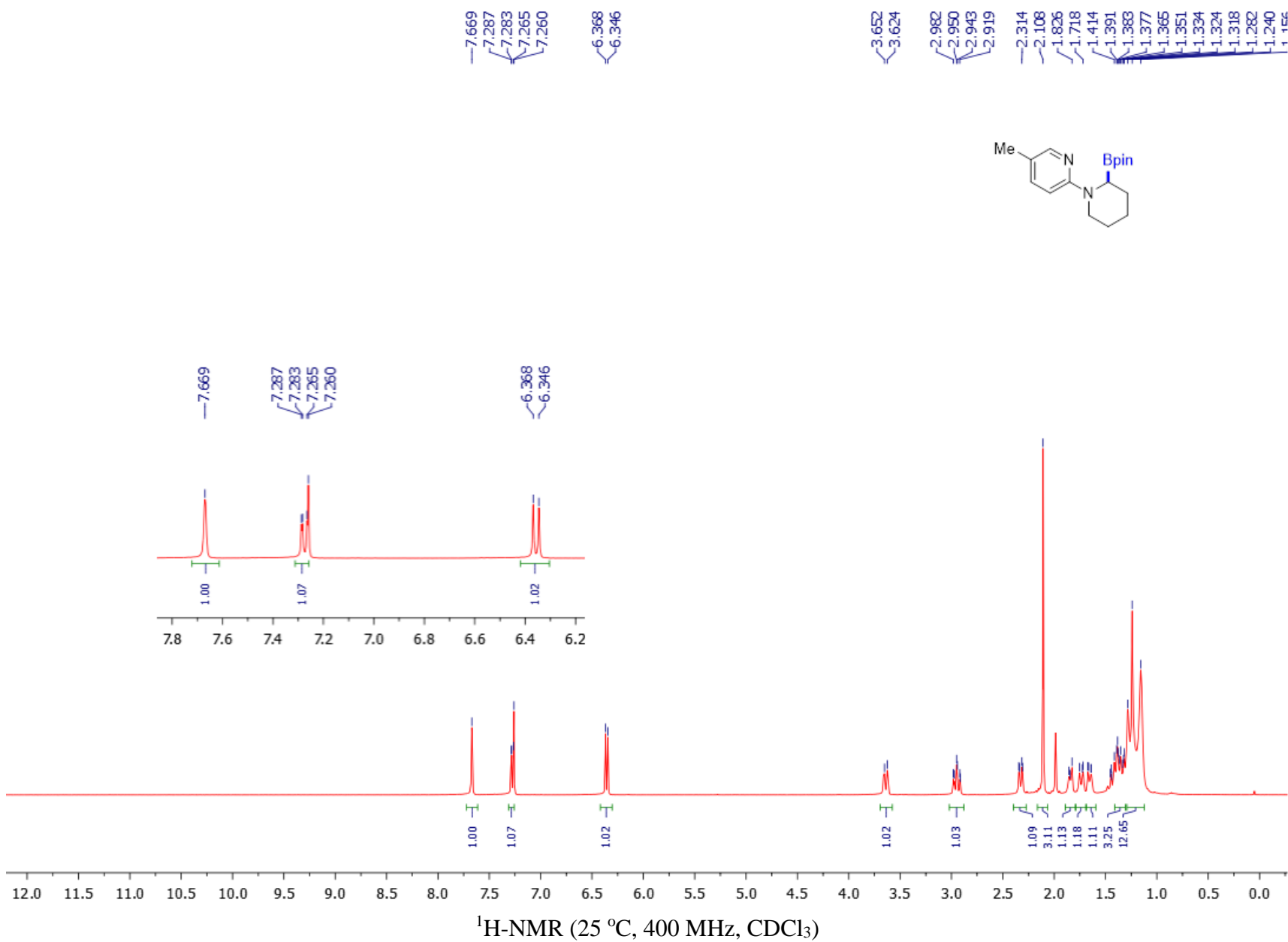


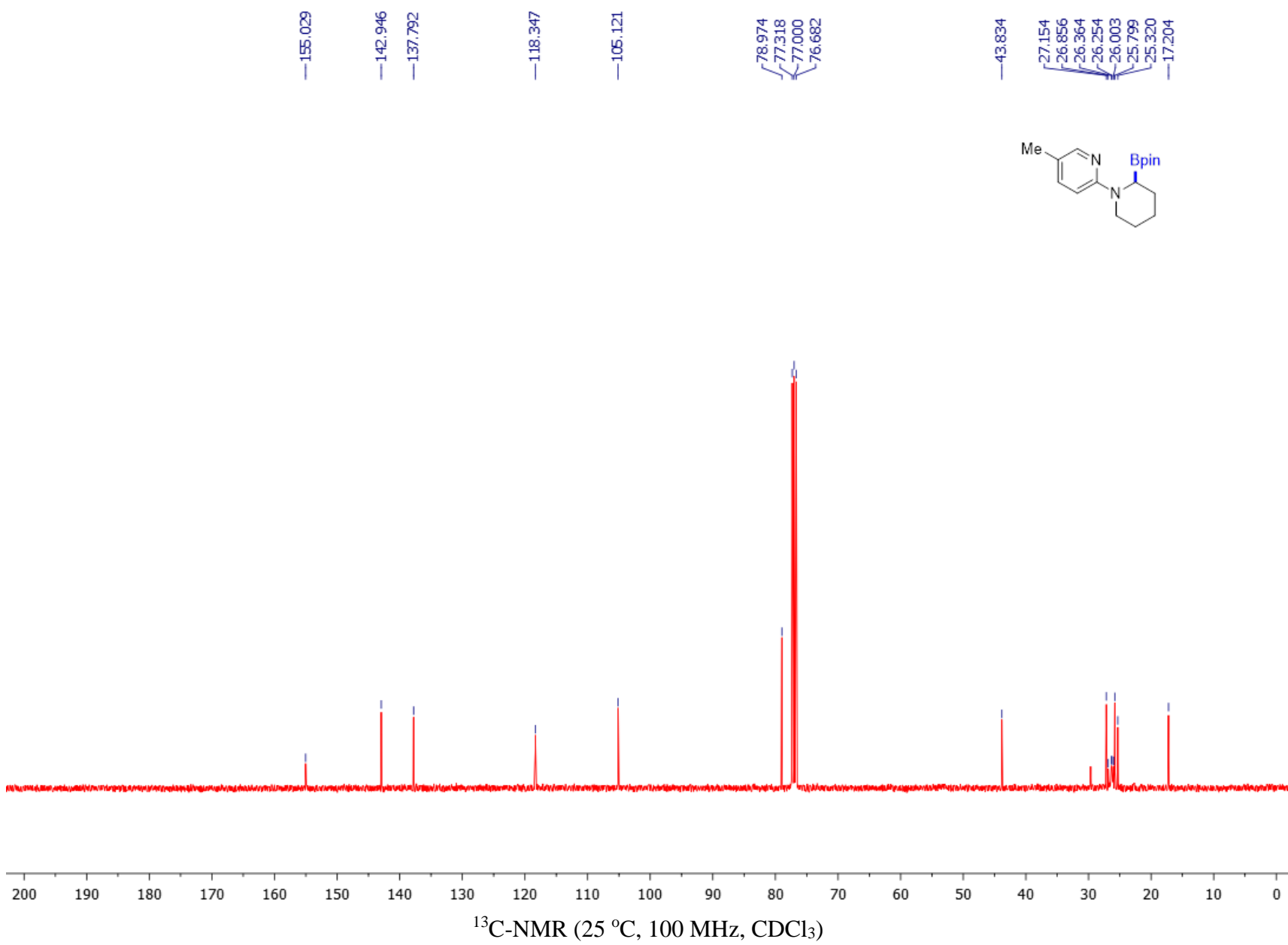


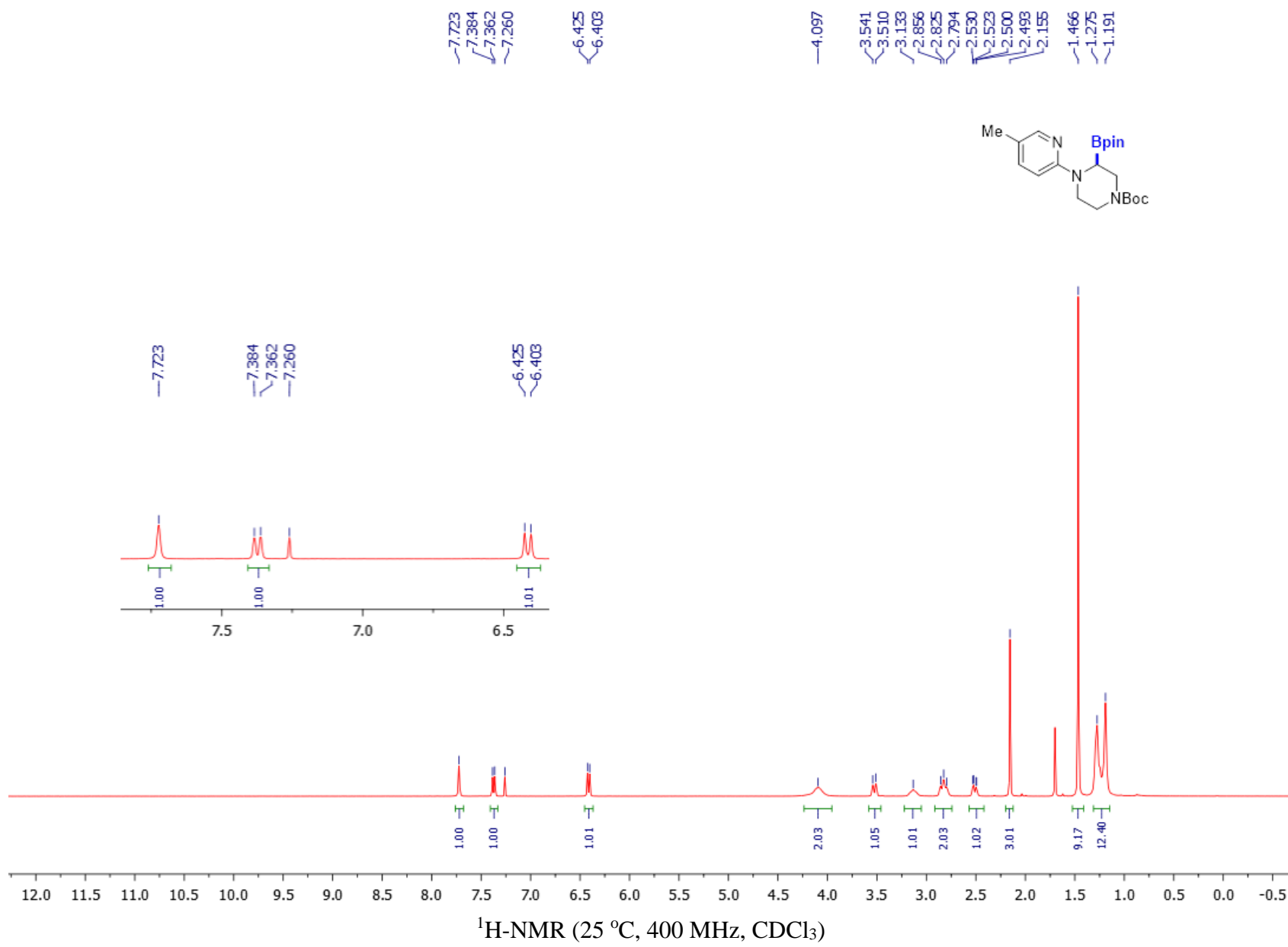


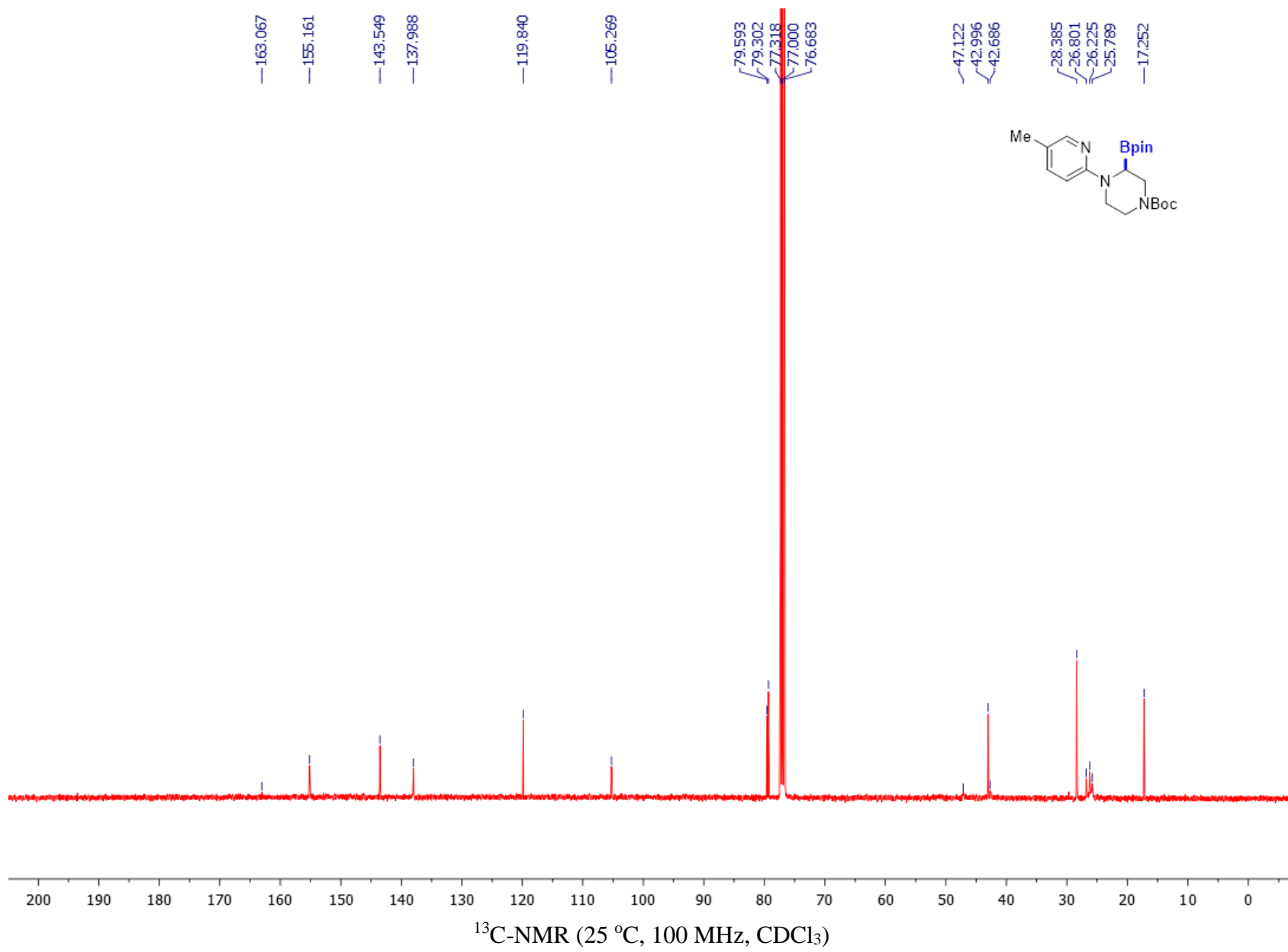


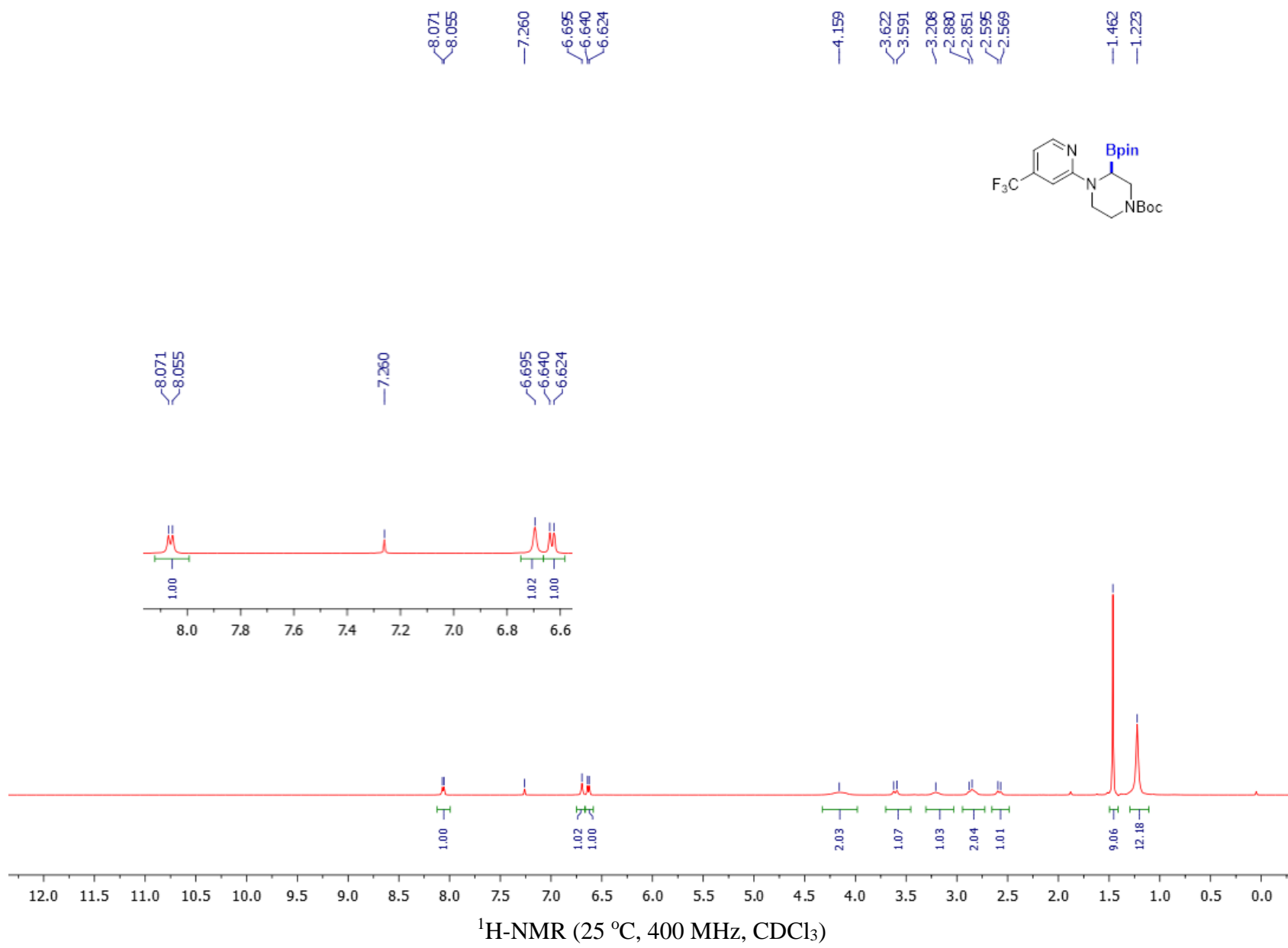


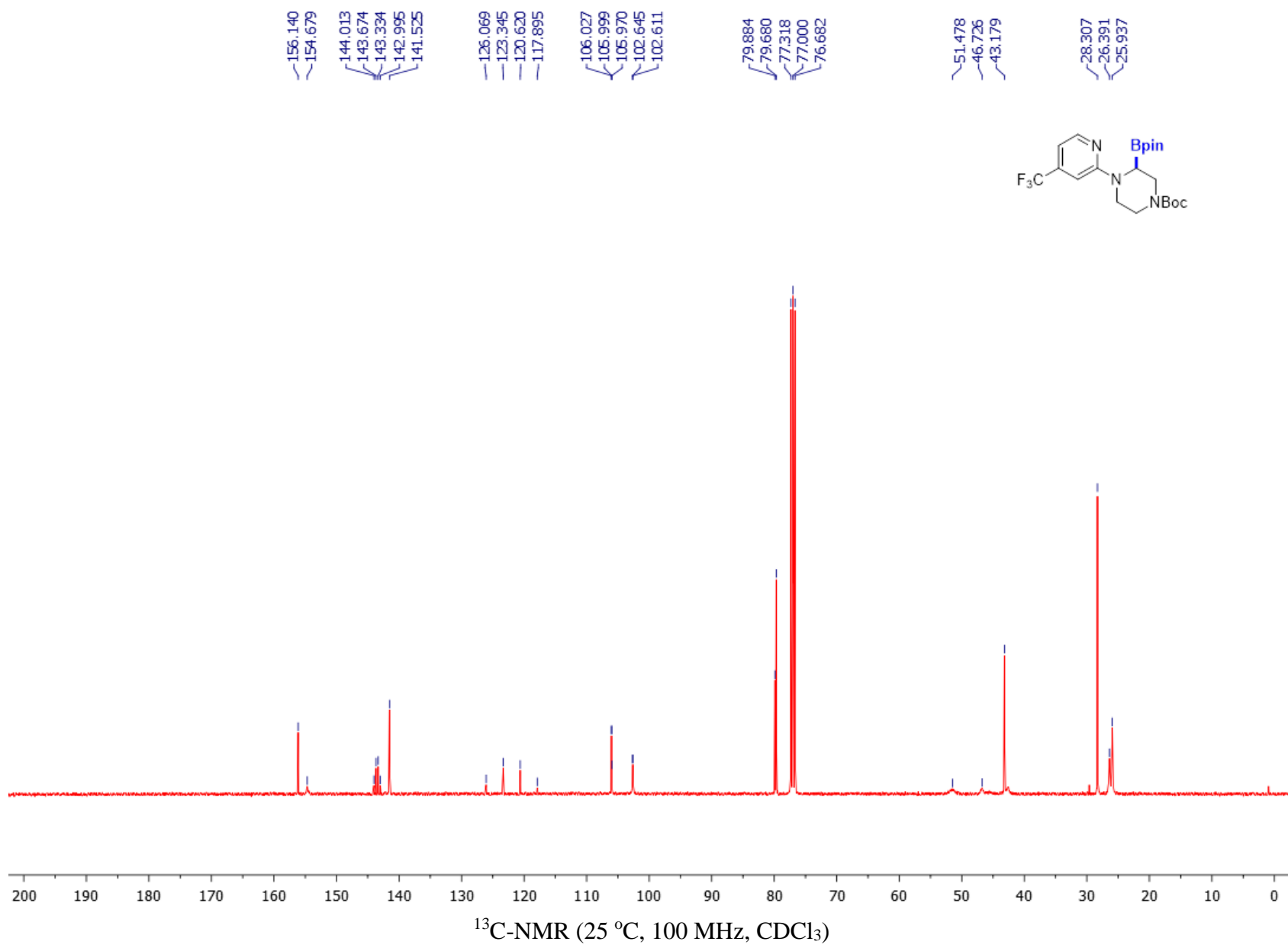


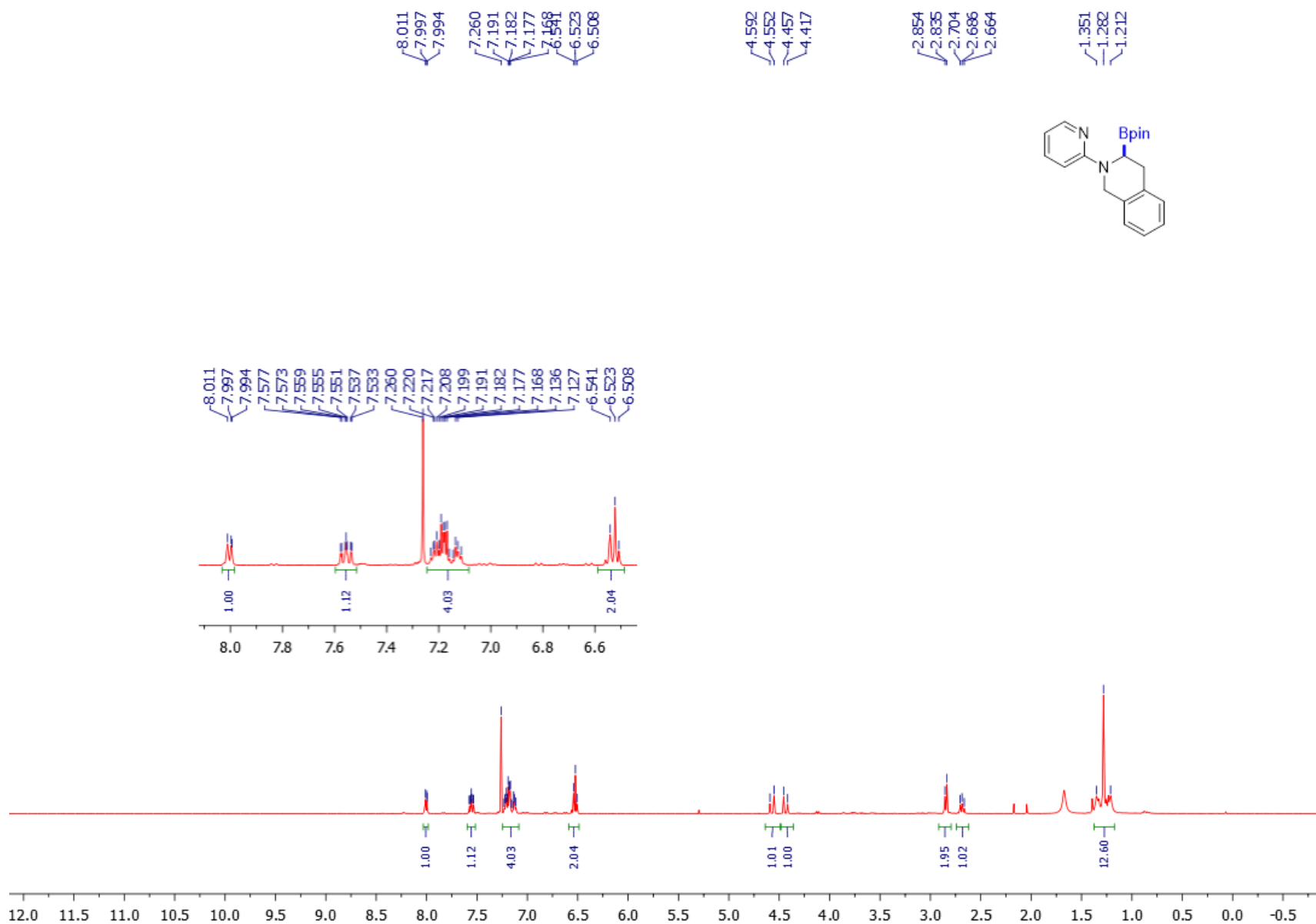




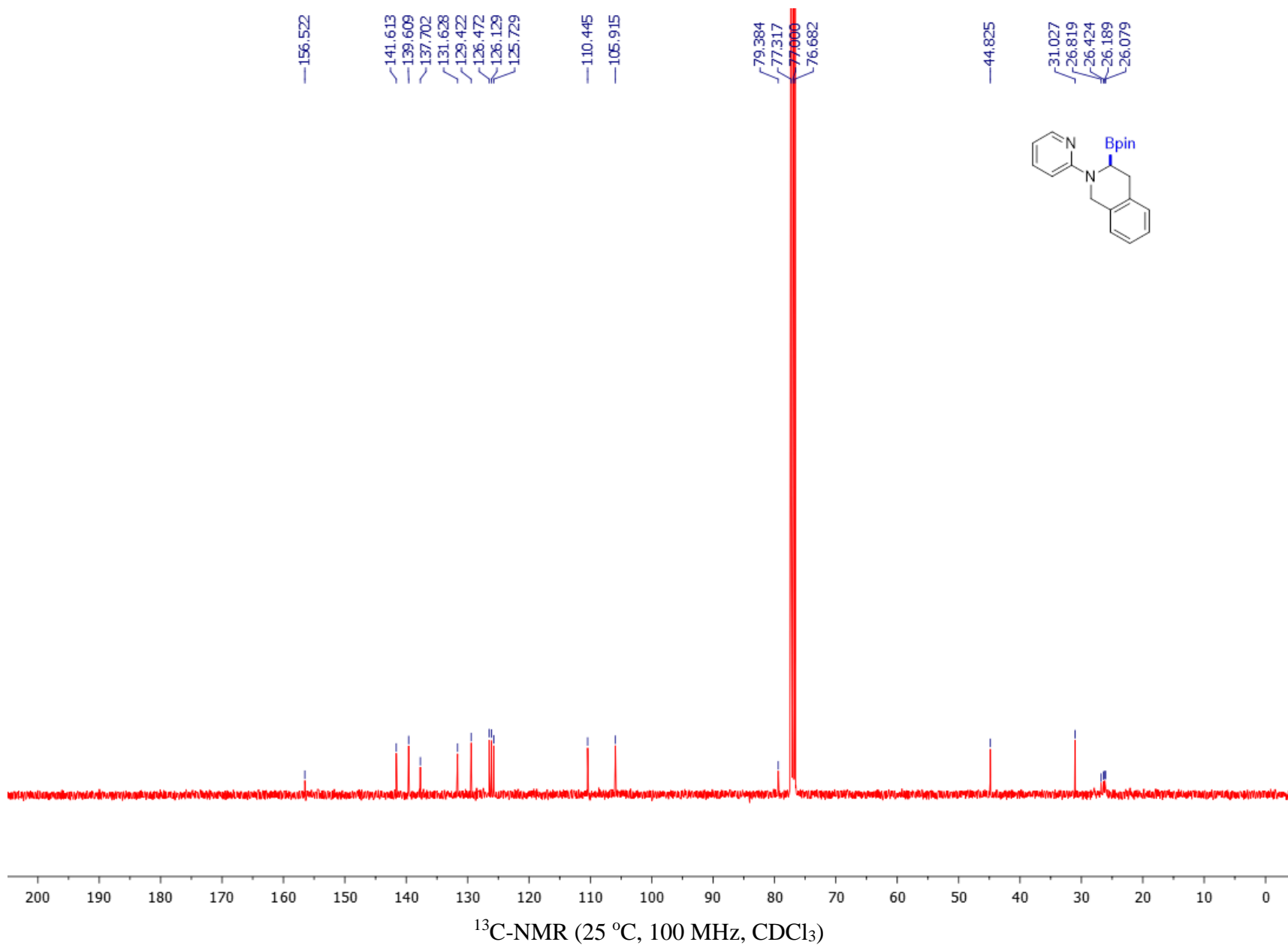


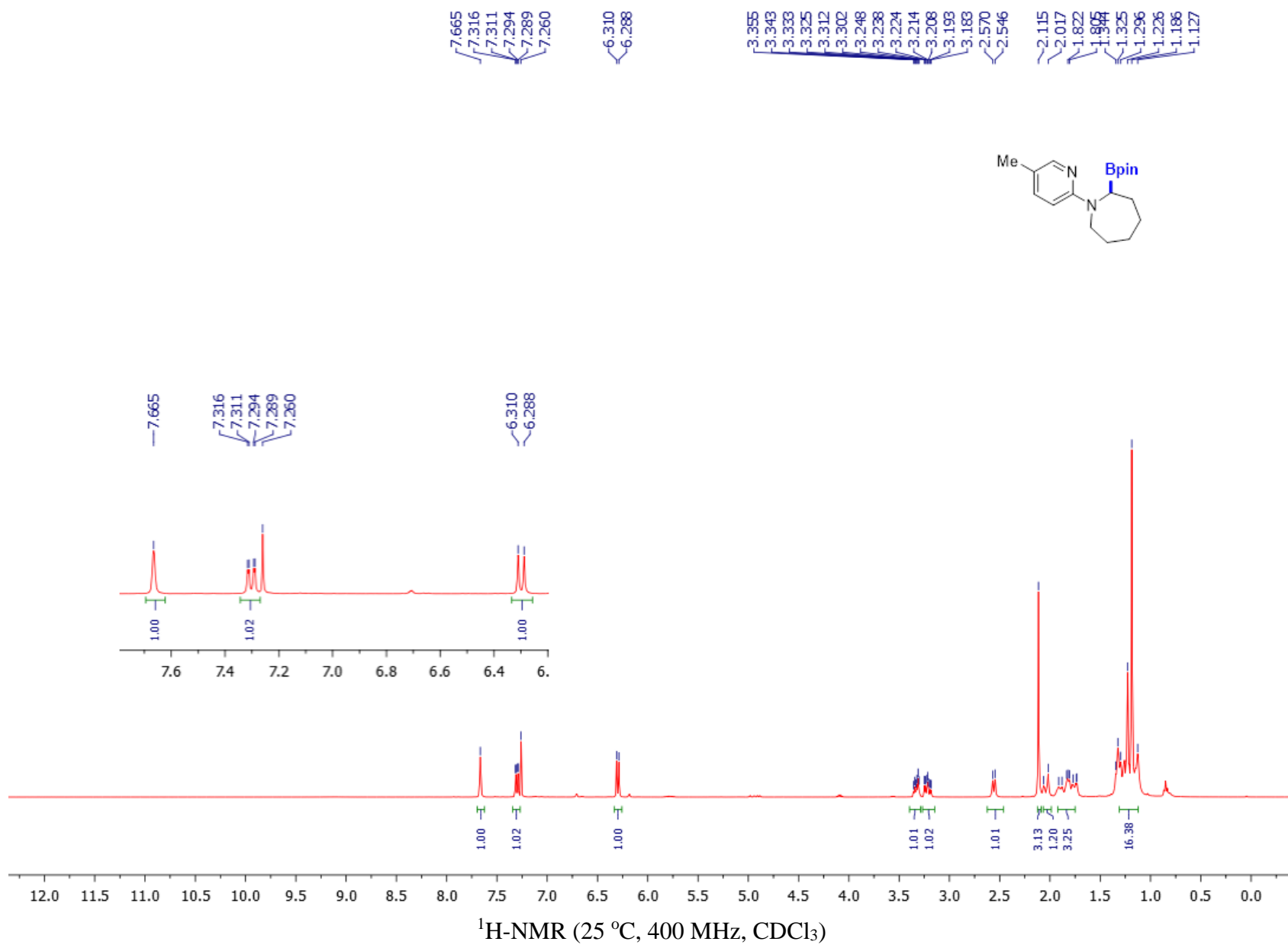


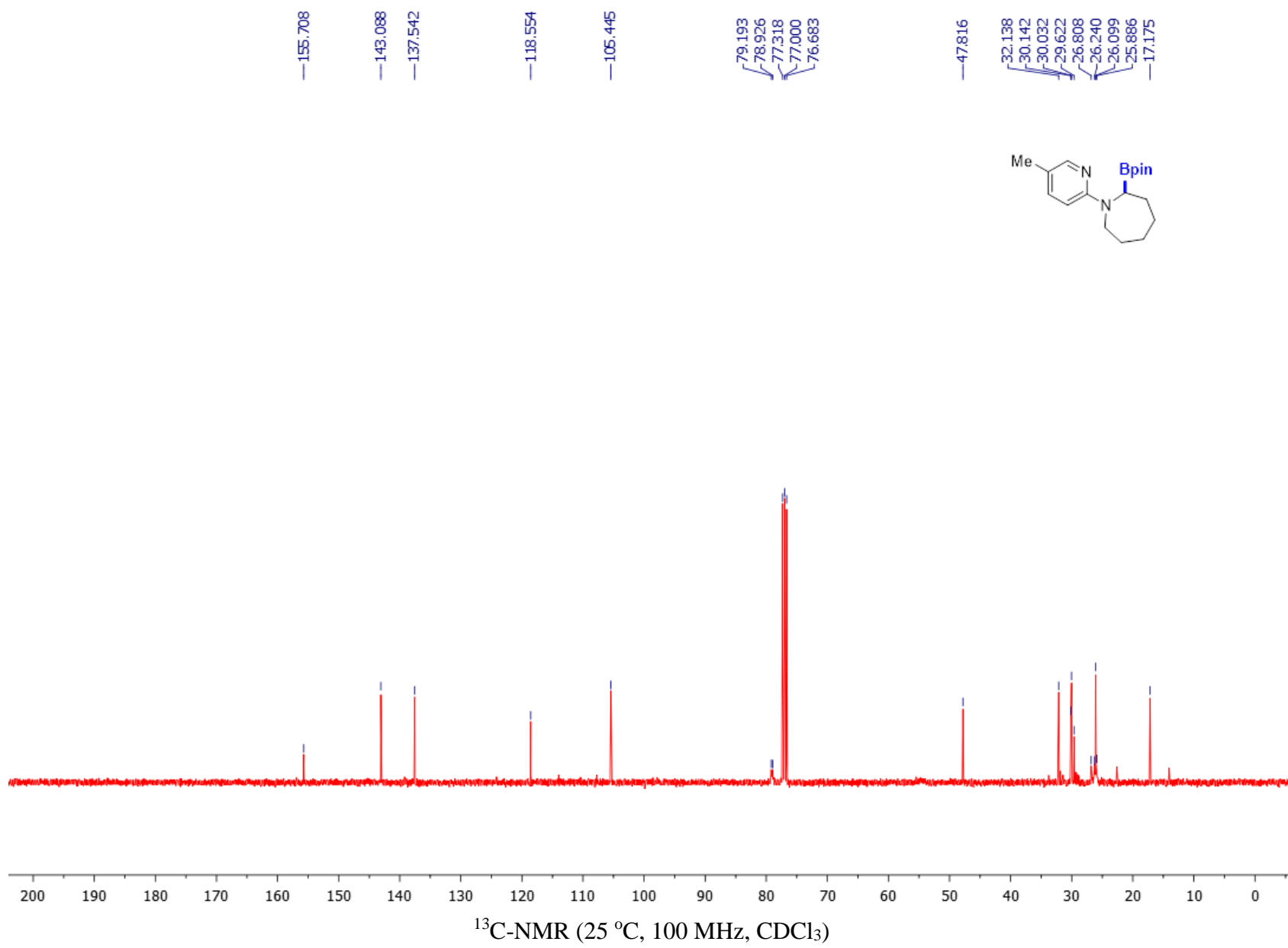


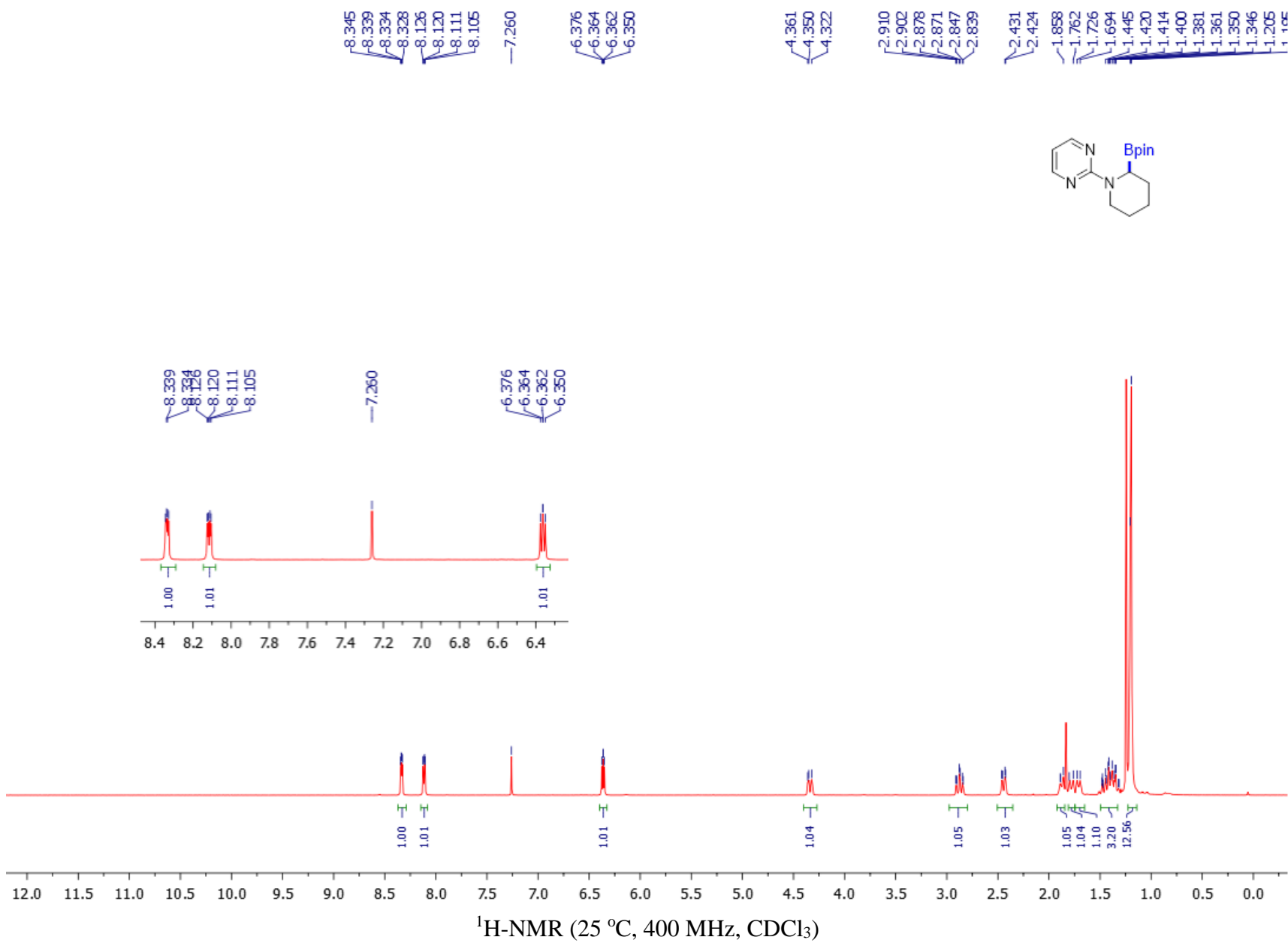


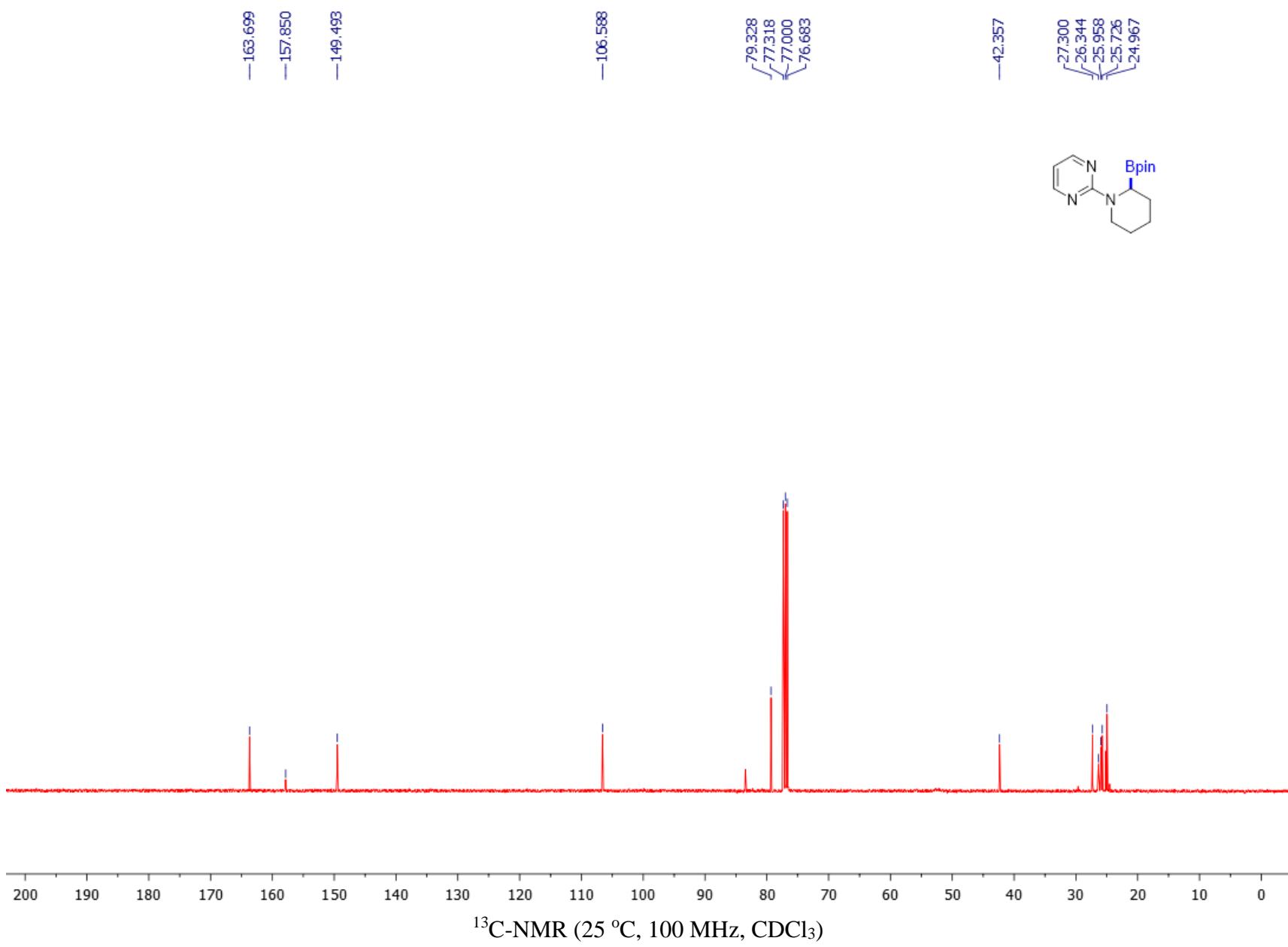
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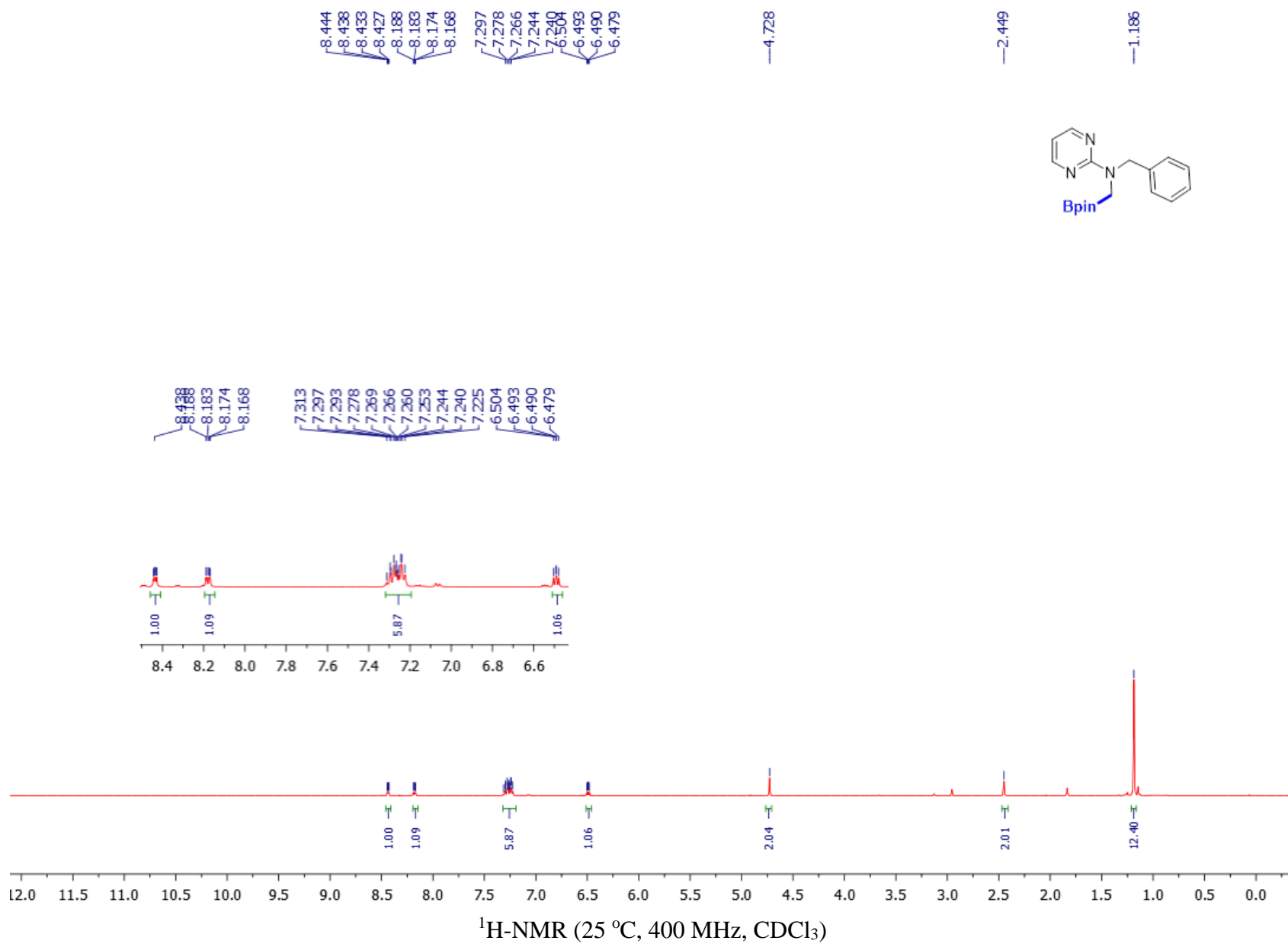


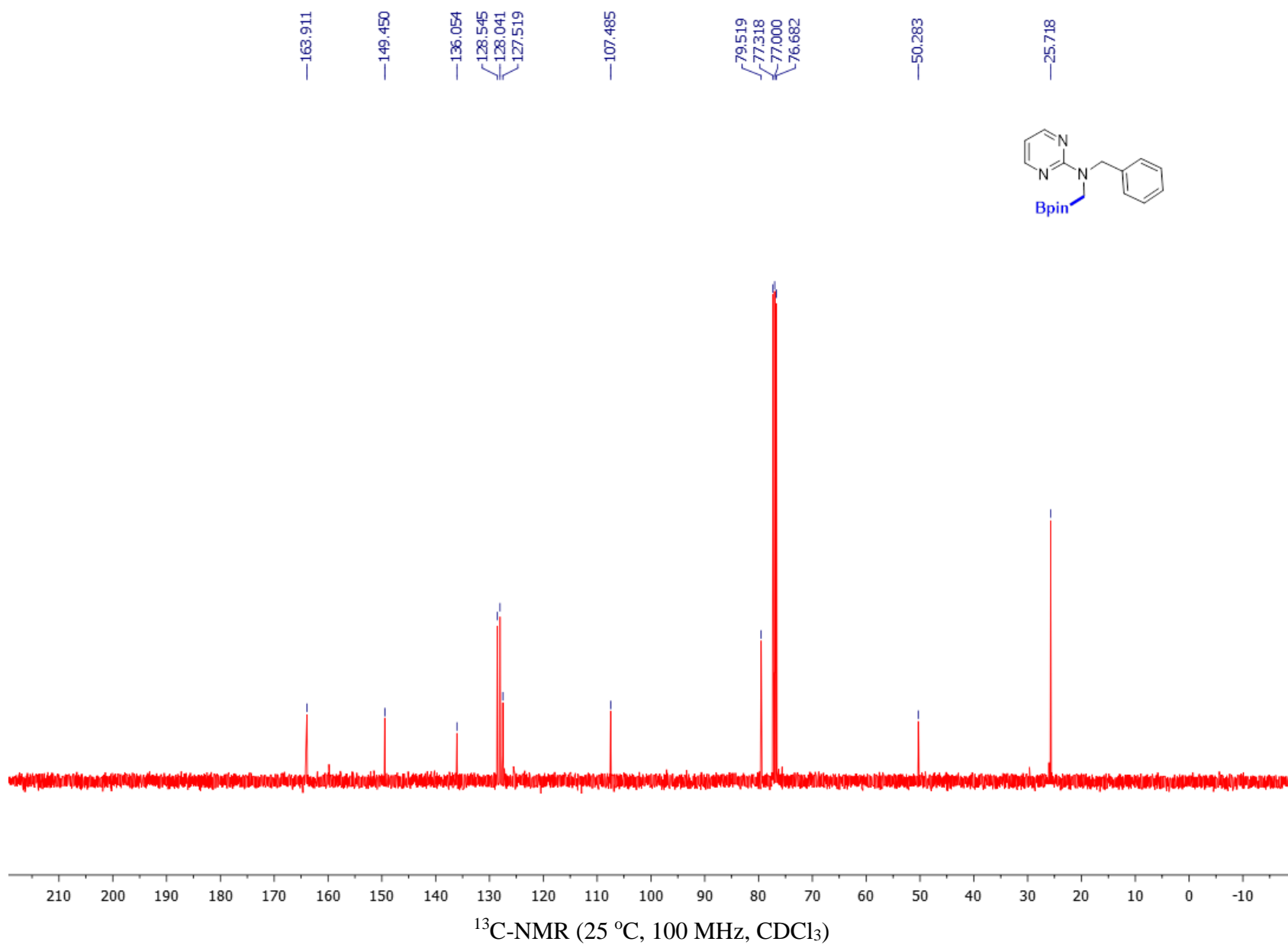


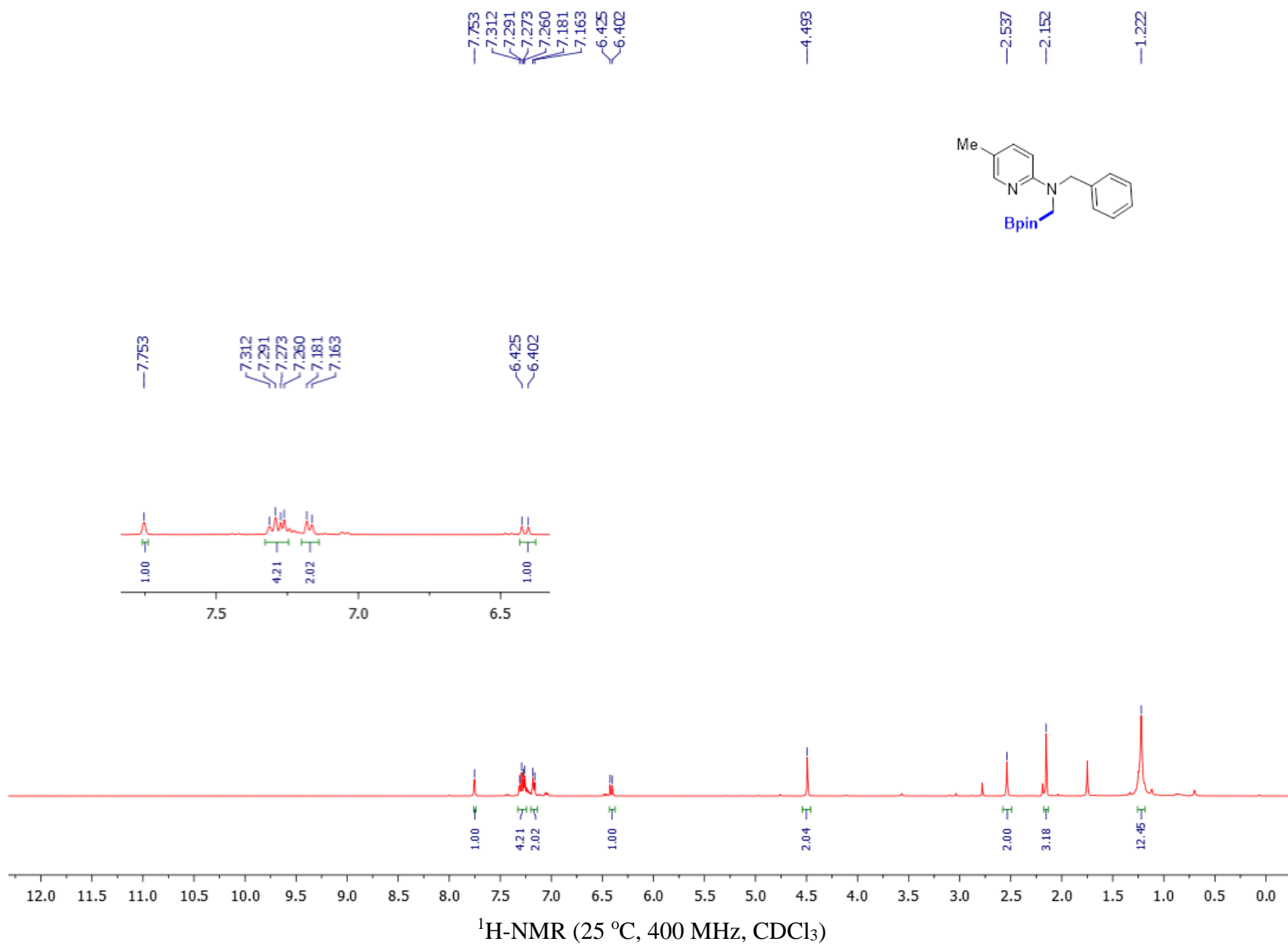


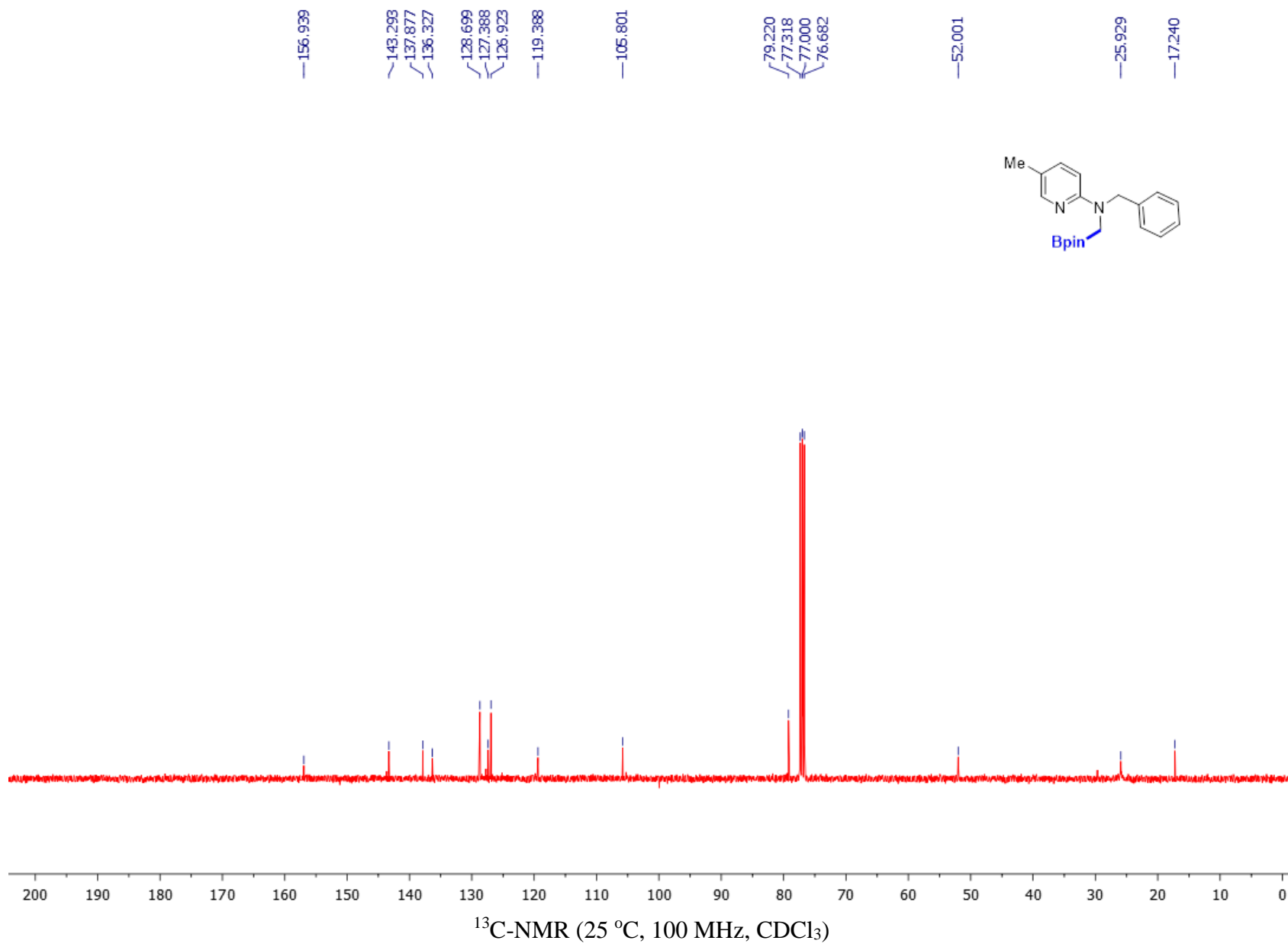


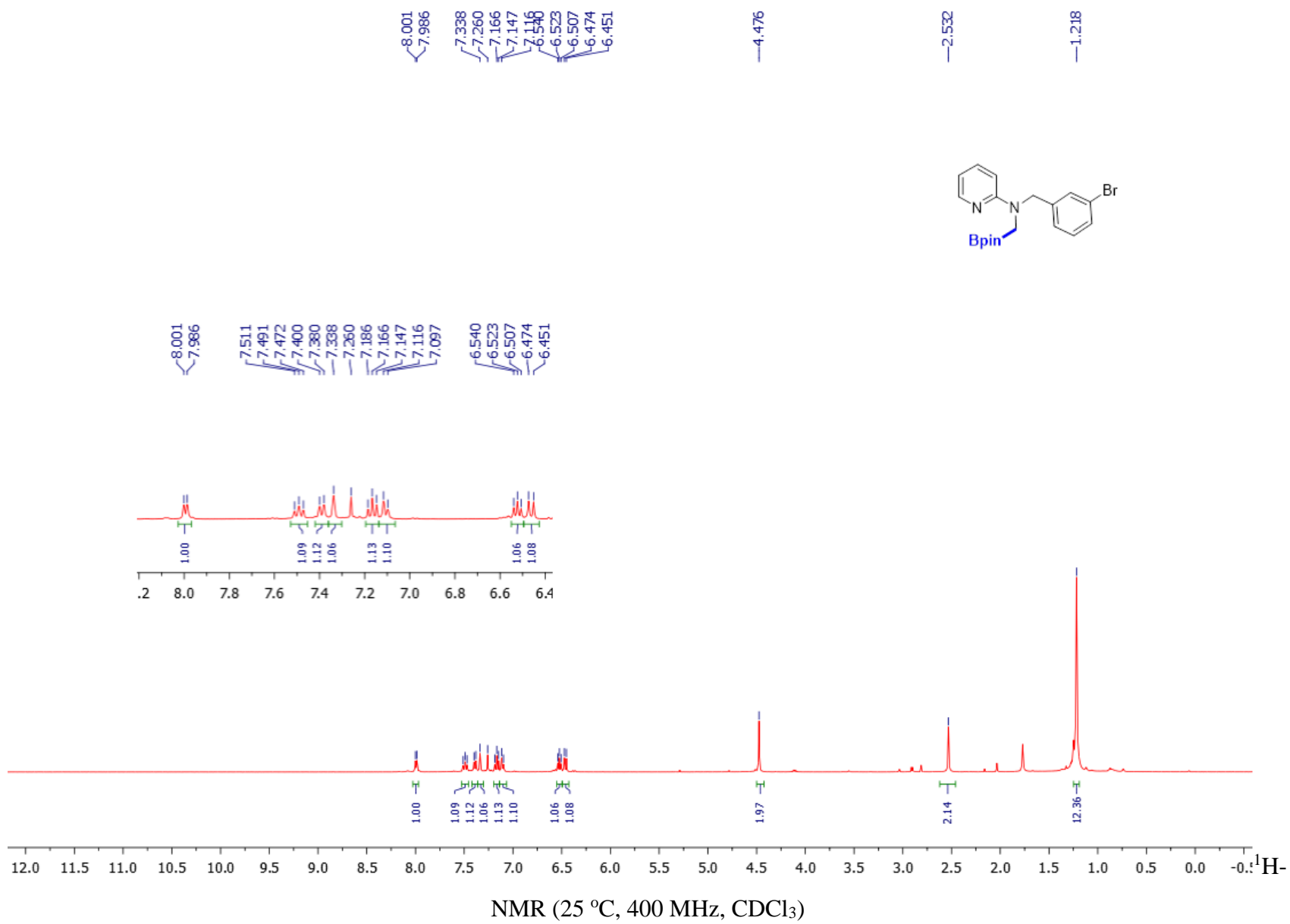


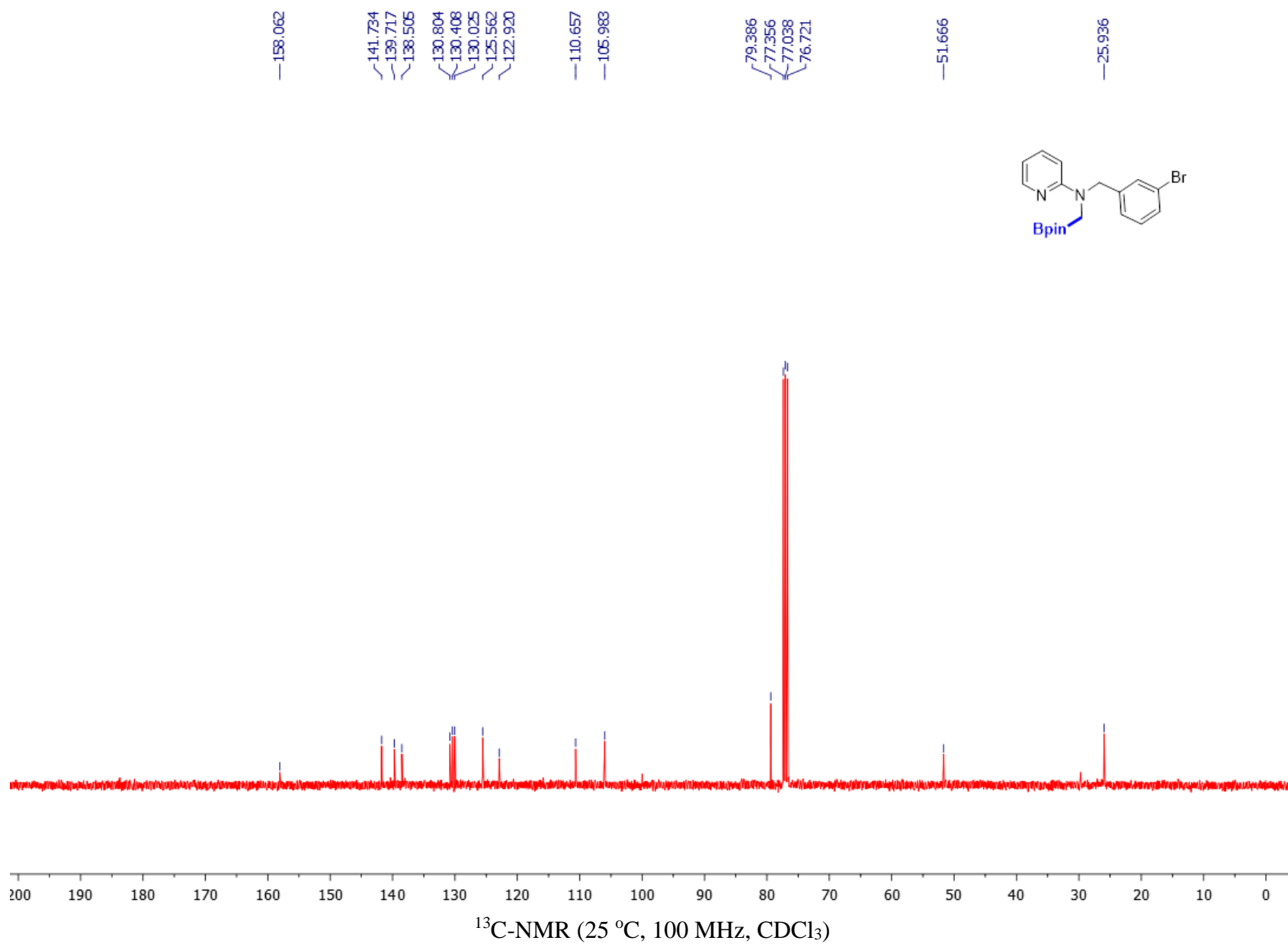


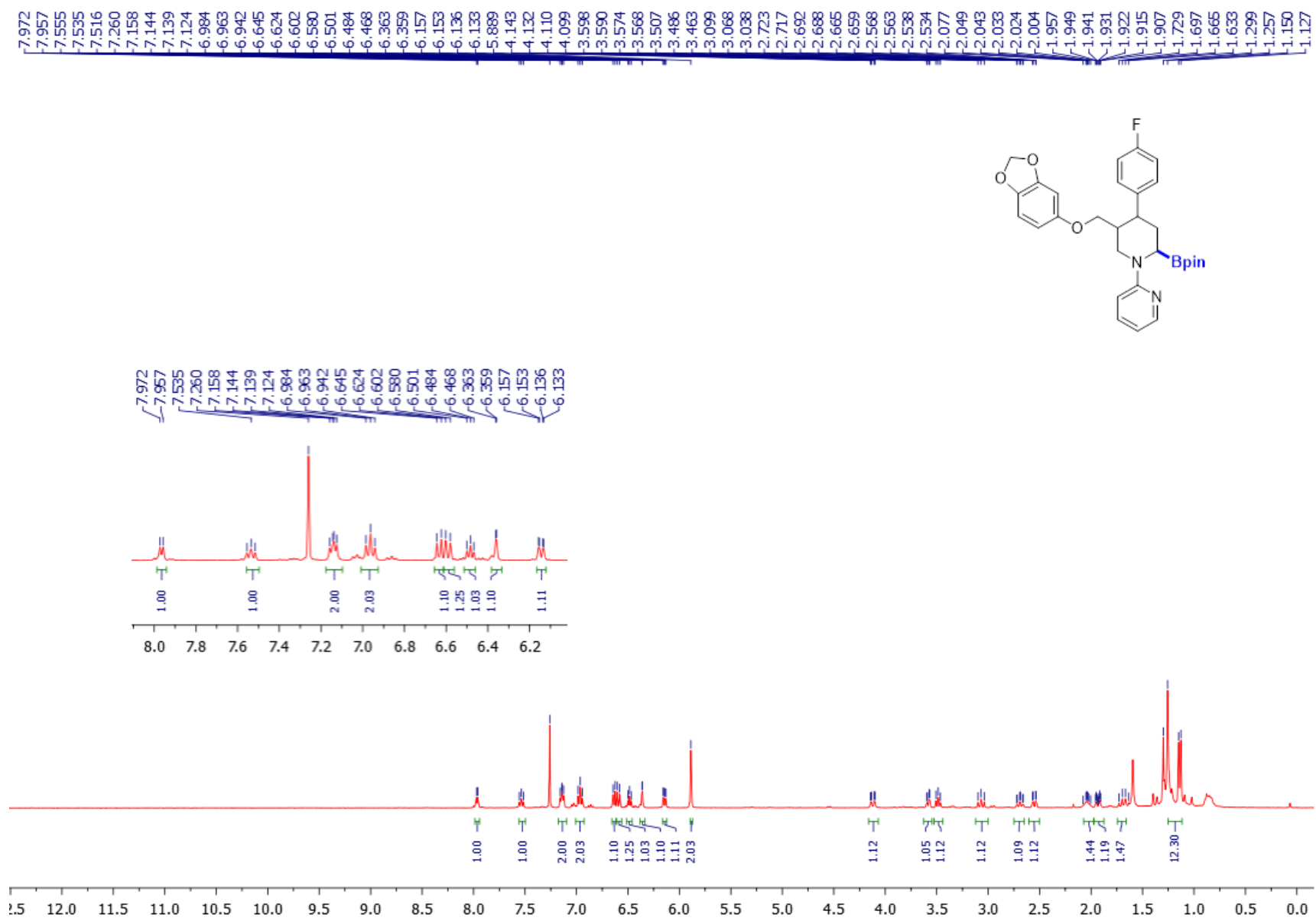


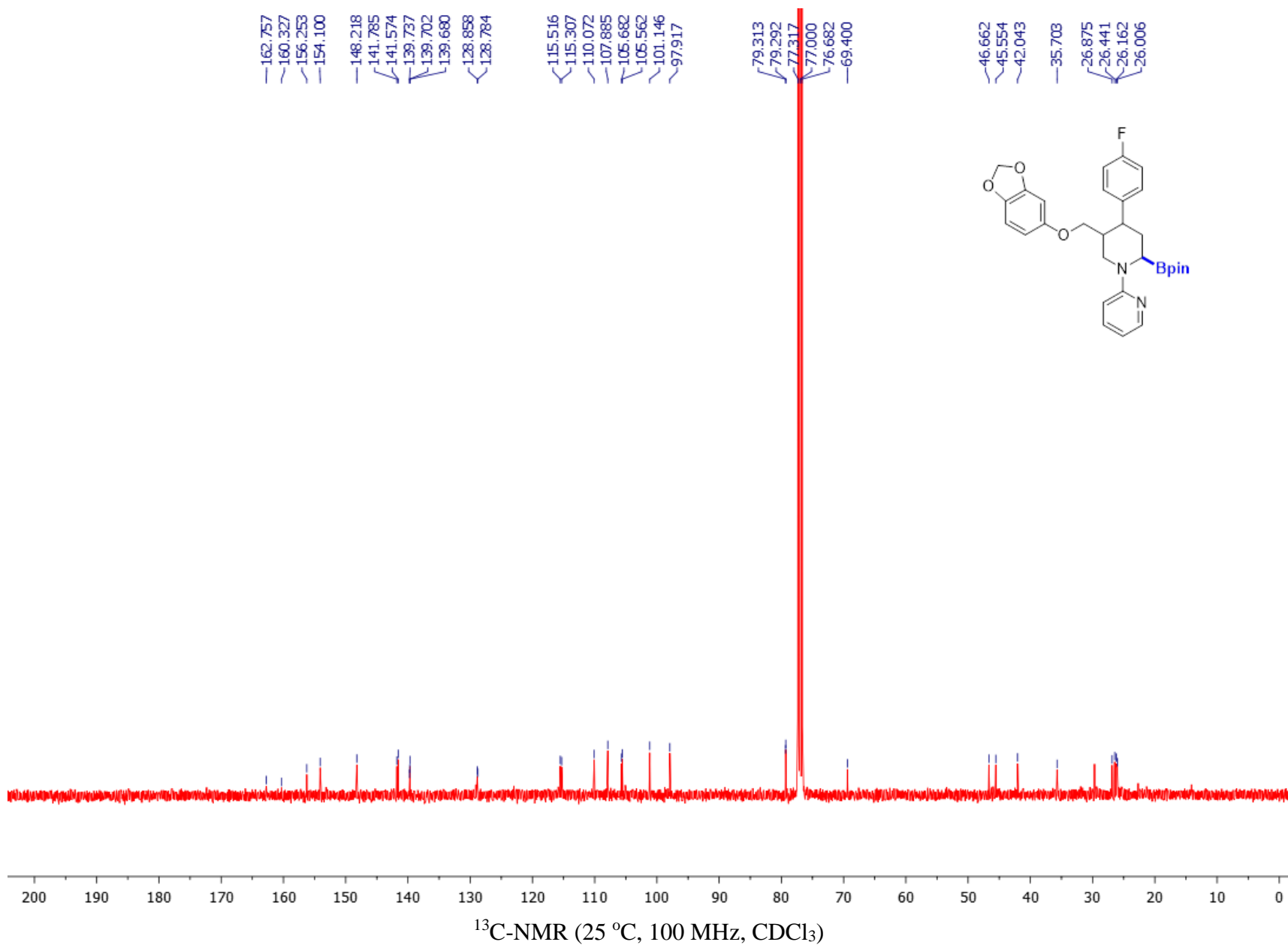


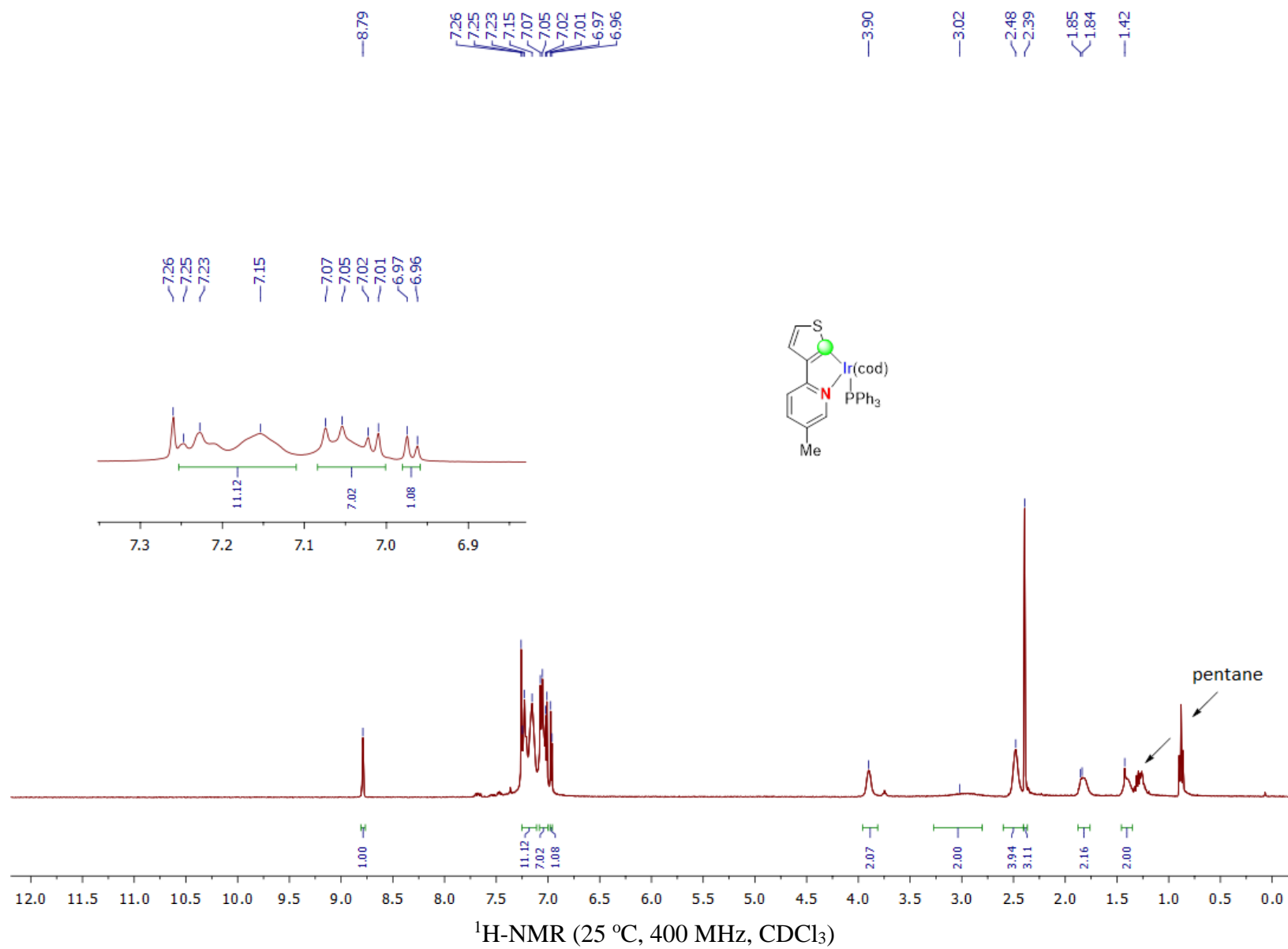




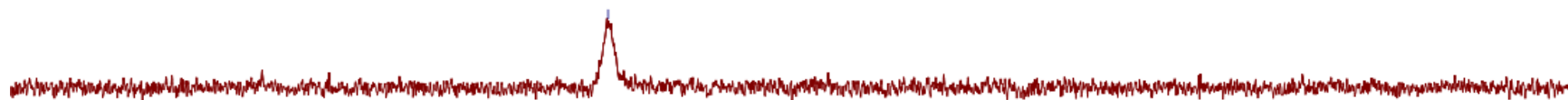








—8.25



19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9

$^{31}\text{P-NMR}$ (25 °C, 162 MHz, CDCl_3)

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