

Supplementary Information

Direct Alkoxy carbonylation of Heteroarenes *via* Cu-Mediated Trichloromethylation and *in situ* Alcoholysis

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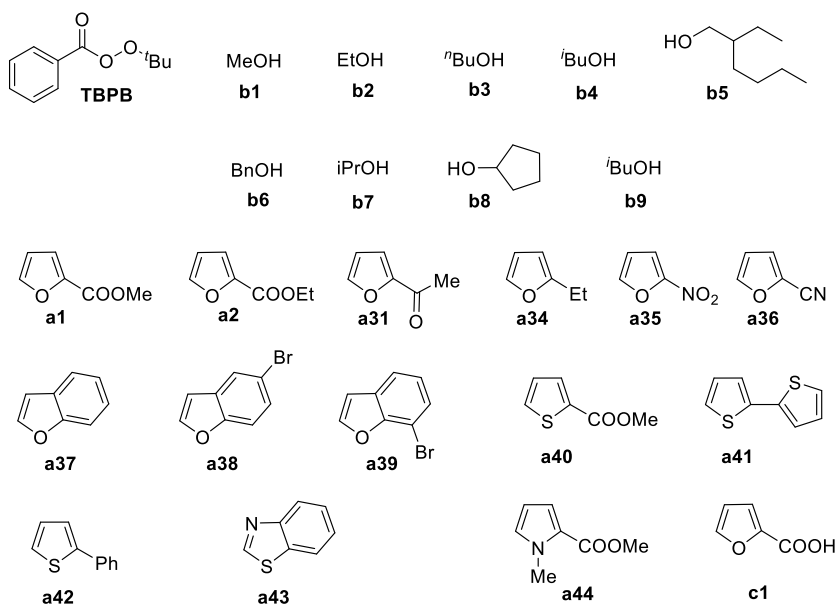
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1. General Experimental

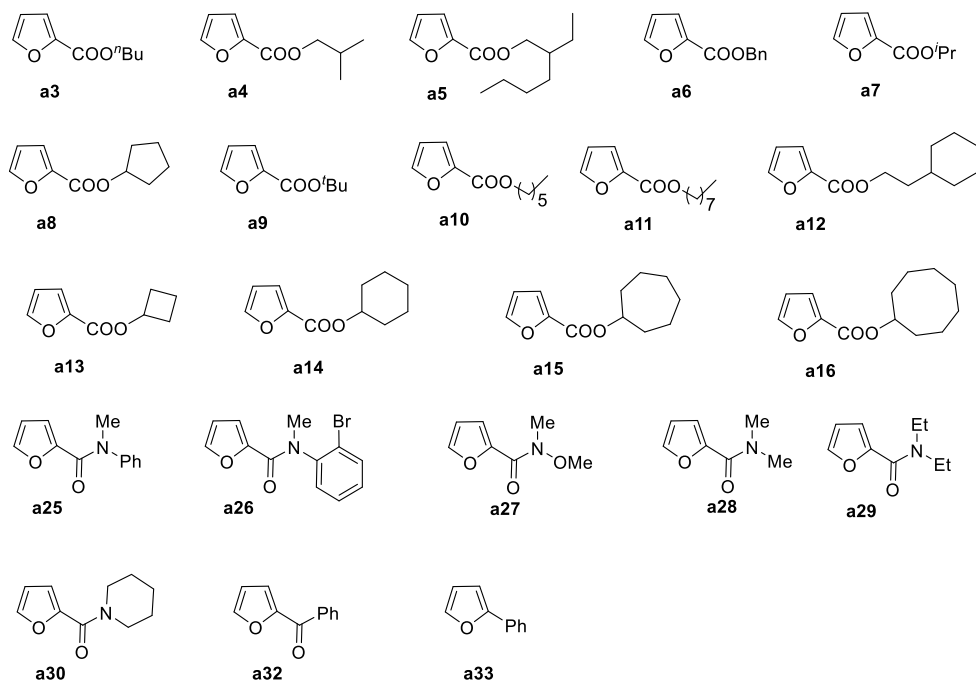
NMR spectra were recorded using CDCl_3 as a solvent, including ^1H (400 MHz), ^1H (500 MHz), ^{13}C (100 MHz) and ^{13}C (126 MHz). Chemical shifts for ^1H NMR spectra are reported in ppm downfield to tetramethylsilane (CDCl_3 : δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl_3 : δ 77.16 ppm). Coupling constants are reported and expressed in Hz; the following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad signal. IR spectra were recorded with FT-IR as a thin film or using KBr pellets and are expressed in cm^{-1} ; the following abbreviations are used to describe peak intensity: s = strong, m = medium, w = weak. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All reactions were carried out using freshly distilled and dry solvents. Column chromatography was performed over silica gel (200-300 Mesh) using petroleum ether and ethyl acetate as the eluent. Unless otherwise noted, all commercially available compounds were purchased from Adamas, TCI, Bide-pharm and Energy.

2. The reagents used in the reaction

Commercially available compounds are as follows:



Synthesized compounds are as follows:

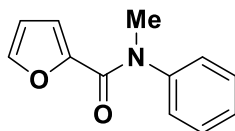


3. Procedures for the preparation of starting materials

3.1 General method A for the synthesis of the starting materials

The amine (30 mmol, 1 equiv) and Et₃N (60 mmol, 2 equiv, 8.40 mL) were dissolved in 120 mL of dry CH₂Cl₂ and cooled to 0 °C using an ice bath. Furan-2-carbonyl chloride (33 mmol, 1.1 equiv, 3.25 mL) was added to the amine solution drop-wise over 10 min. The reaction mixture was stirred overnight at room temperature. The mixture was then poured into a separatory funnel and washed with saturated NaCl (aq). The organic layer was then dried over anhydrous Na₂SO₄, and concentrated under reduced pressure for silica gel column. The crude material was purified by silica gel column chromatography using hexane and EtOAc as eluent.

N-methyl-*N*-phenylfuran-2-carboxamide (a25)



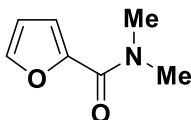
Yield: 84%, white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.45-7.33 (m, 3H), 7.33-7.29 (m, 1H), 7.23-7.19 (m, 1H), 6.20 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.84 (d, *J* = 3.6 Hz, 1H), 3.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 147.2, 144.3, 129.7, 127.9, 127.5, 116.4, 111.0, 38.6.

Product identity was confirmed by comparison to literature spectra.^[1]

N,N-dimethylfuran-2-carboxamide (a28)



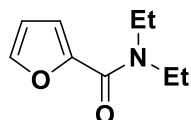
Yield: 83%, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.49 (br, 1H), 6.98 (br, 1H), 6.47 (br, 1H), 3.36-2.95 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 160.2, 148.1, 143.7, 115.9, 111.1. Note: The methyl peaks from the amide group are not visible in ¹³C NMR.

Product identity was confirmed by comparison to literature spectra.^[2]

N,N-diethylfuran-2-carboxamide (a29)



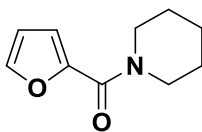
Yield: 85%, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.47 (br, 1H), 7.00 (br, 1H), 6.47 (br, 1H), 3.56 (br, 4H), 1.25 (br, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 148.7, 143.4, 115.6, 111.1. Note: The ethyl peaks from the amide group are not visible in ¹³C NMR.

Product identity was confirmed by comparison to literature spectra.^[3]

Furan-2-yl(piperidin-1-yl)methanone (a30)



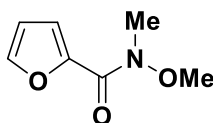
Yield: 92%, white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.47 (br, 1H), 6.92 (d, $J = 3.2$ Hz, 1H), 6.49-6.43 (m, 1H), 3.69 (br, 4H), 1.75-1.58 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 148.1, 143.4, 115.4, 111.0, 24.6. Note: The four methylene peaks from the amide group are not visible in ^{13}C NMR.

Product identity was confirmed by comparison to literature spectra.^[4]

N-methoxy-*N*-methylfuran-2-carboxamide (a27)



Yield: 85%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.60 (br, 1H), 7.15 (d, $J = 3.2$ Hz, 1H), 6.52 (dd, $J = 3.2, 1.2$ Hz, 1H), 3.77 (s, 3H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 145.7, 145.3, 117.5, 111.7, 61.4, 33.2.

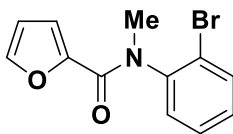
Product identity was confirmed by comparison to literature spectra.^[5]

3.2 Synthesis of a26

Step 1: The aniline (30 mmol, 1 equiv) and Et_3N (60 mmol, 2 equiv, 8.40 mL) were dissolved in 120 mL of dry CH_2Cl_2 and cooled to 0 °C using an ice bath. Furan-2-carbonyl chloride (33 mmol, 1.1 equiv, 3.25 mL) was added to the amine solution drop-wise over 10 min. Afterwards the reaction mixture was stirred overnight at room temperature. The mixture was then poured into a separatory funnel and washed with saturated NaCl (aq). The organic layer was then dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo. The crude amide was obtained in 99% yield without further purification.

Step 2: The crude amide was directly dissolved in 100 mL dry DMF and cooled to 0 °C using an ice bath. NaH (45 mmol, 1.5 equiv, 1.80 g) was added to the mixture solution carefully. Afterwards the reaction mixture was stirred 1 h at 0 °C. Then methyl iodide (60 mmol, 2 equiv, 3.74 mL) was added to the mixture solution drop-wise over 20 min. Subsequently, the reaction mixture was stirred overnight at room temperature. The solution, diluted with CH_2Cl_2 , was washed with saturated NaCl (aq), dried over Na_2SO_4 and concentrated under reduced pressure for silica gel column. The crude material was purified by silica gel column chromatography using hexane and EtOAc as eluent.

N-(2-bromophenyl)-*N*-methylfuran-2-carboxamide (a26)



Yield: 78%, white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.33-7.27 (m, 3H), 6.21 (s, 1H), 5.90 (s, 1H), 3.36 (s, 3H).

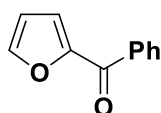
^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 147.0, 144.6, 142.9, 133.9, 130.1, 129.9, 128.9, 123.5, 115.9, 111.1, 37.1.

Product identity was confirmed by comparison to literature spectra.^[6]

3.3 Synthesis of a32

Benzoyl chloride (5 mmol, 1 equiv, 576 μL) and ZnO (0.5 mmol, 0.5 equiv, 203 mg) were dissolved in 5 mL of dry CH_2Cl_2 and cooled to 0 °C using an ice bath. Furan (12.5 mmol, 2.5 equiv, 903 μL) was added to the mixture solution drop-wise over 10 min. Afterwards the reaction mixture was stirred 0.25 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2 , the solution was filtered to separate the catalyst, and CH_2Cl_2 extract was then washed with an aqueous solution of sodium bicarbonate and dried over anhydrous sodium sulfate. Evaporation of solvent furnished practically pure corresponding product.

Furan-2-yl(phenyl)methanone (a32)



Yield: 81%, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.2$ Hz, 1H), 7.70 (s, 1H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 3.6$ Hz, 1H), 6.59 (dd, $J = 3.2, 1.6$ Hz, 1H).

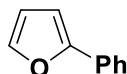
^{13}C NMR (100 MHz, CDCl_3) δ 182.6, 152.4, 147.2, 137.4, 132.7, 129.4, 128.5, 120.6, 112.3.

Product identity was confirmed by comparison to literature spectra.^[7]

3.4 Synthesis of a33

Furan boronic acid (5 mmol, 1 equiv, 560 mg), bromobenzene (6 mmol, 1.2 equiv, 628 μL), K_3PO_4 (6 mmol, 1.2 equiv, 1.27 g) and $\text{Pd}(\text{PPh}_3)_4$ (0.25 mmol, 0.05 equiv, 289 mg) were added in MeOH (40 mL). The reaction was heated for 12 h at 80 °C until the consumption of the starting material detected by TLC. The reaction mixture was filtered through a lay of silica gel and the filtrate was evaporated under reduced pressure to provide the residue. The resulting mixture was then re-dissolved in EtOAc and washed with water. The combined organic layers were dried by Na_2SO_4 and the solvents removed in vacuo. The residue was transferred to silica gel column directly and purified by column chromatography on silica gel with petroleum ether as eluent to afford the colorless oil product in 95% yield.

2-Phenylfuran (a33)



Yield: 95%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.68-7.63 (m, 2H), 7.43 (s, 1H), 7.38-7.30 (m, 2H), 7.23 (t, $J = 7.2$ Hz, 1H), 6.62 (d, $J = 3.2$ Hz, 1H), 6.43 (s, 1H).

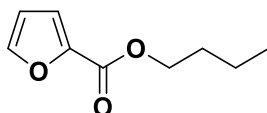
^{13}C NMR (100 MHz, CDCl_3) δ 154.1, 142.1, 131.0, 128.8, 127.4, 123.9, 111.7, 105.1.

Product identity was confirmed by comparison to literature spectra.^[8]

3.5 General method B for the synthesis of the starting materials

The alcohol (30 mmol, 1 equiv) and Et_3N (60 mmol, 2 equiv, 8.40 mL) were dissolved in 120 mL of dry CH_2Cl_2 and cooled to 0 °C using an ice bath. Furan-2-carbonyl chloride (33 mmol, 1.1 equiv, 3.25 mL) was added to the amine solution drop-wise over 10 min. The reaction mixture was stirred overnight at room temperature. The mixture was then poured into a separatory funnel and washed with saturated NaCl (aq). The organic layer was then dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure for silica gel column. The crude material was purified by silica gel column chromatography using hexane and EtOAc as eluent.

Butyl furan-2-carboxylate (a3)



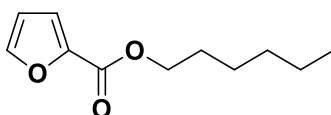
Yield: 95%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.57 (br, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 6.60-6.39 (m, 1H), 4.31 (t, $J = 6.6$ Hz, 2H), 1.79-1.67 (m, 2H), 1.51-1.39 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 146.3, 145.1, 117.8, 111.9, 64.9, 30.9, 19.2, 13.8.

Product identity was confirmed by comparison to literature spectra.^[9]

Hexyl furan-2-carboxylate (a10)



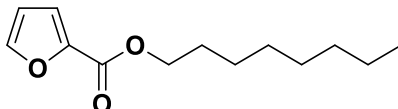
Yield: 93%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.57 (br, 1H), 7.17 (d, $J = 3.4$ Hz, 1H), 6.55-6.44 (m, 1H), 4.30 (t, $J = 6.8$ Hz, 2H), 1.78-1.70 (m, 2H), 1.45-1.30 (m, 6H), 0.90 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 146.3, 145.1, 117.8, 111.9, 65.2, 31.6, 28.8, 25.7, 22.6, 14.1.

Product identity was confirmed by comparison to literature spectra.^[10]

Octyl furan-2-carboxylate (a11)



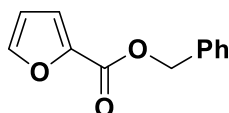
Yield: 89%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.57 (br, 1H), 7.16 (d, $J = 3.2$ Hz, 1H), 6.55-6.43 (m, 1H), 4.29 (t, $J = 6.8$ Hz, 2H), 1.78-1.68 (m, 2H), 1.44-1.27 (m, 10H), 0.88 (t, $J = 6.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 146.3, 145.1, 117.8, 111.9, 65.2, 31.9, 29.3, 29.3, 28.8, 26.0, 22.7, 14.2.

Product identity was confirmed by comparison to literature spectra.^[11]

Benzyl furan-2-carboxylate (a6)



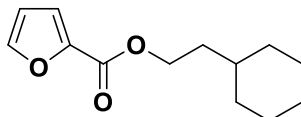
Yield: 92%, yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.57 (br, 1H), 7.46-7.31 (m, 5H), 7.20 (d, $J = 3.6$ Hz, 1H), 6.49 (dd, $J = 3.2, 1.6$ Hz, 1H), 5.34 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 146.5, 144.7, 135.7, 128.7, 128.5, 128.5, 118.3, 112.0, 66.6.

Product identity was confirmed by comparison to literature spectra.^[12]

2-cyclohexylethyl furan-2-carboxylate (a12)



Yield: 94%, colorless oil.

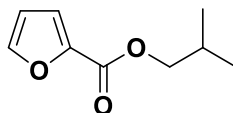
^1H NMR (500 MHz, CDCl_3) δ 7.57 (br, 1H), 7.16 (br, 1H), 6.51 (br, 1H), 4.34 (t, $J = 6.8$ Hz, 1H), 1.80-1.60 (m, 7H), 1.48-1.38 (m, 1H), 1.30-1.11 (m, 3H), 1.01-0.91 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 159.0, 146.3, 145.1, 117.8, 111.9, 63.5, 36.2, 34.7, 33.3, 26.6, 26.3.

IR ν (cm^{-1}) 2924 (m), 2850 (w), 1717 (s), 1476 (m), 1296 (s), 1119 (m), 762 (m).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{18}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 245.1154; found: 245.1149.

Isobutyl furan-2-carboxylate (a4)



Yield: 92%, colorless oil.

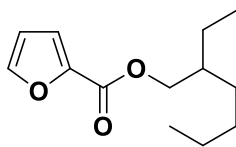
^1H NMR (400 MHz, CDCl_3) δ 7.58 (br, 1H), 7.17 (d, $J = 3.2$ Hz, 1H), 6.58-6.44 (m, 1H), 4.09 (d, $J = 6.8$ Hz, 2H), 2.12-2.00 (m, 1H), 1.00 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 146.3, 145.0, 117.8, 111.9, 71.0, 28.0, 19.2.

IR ν (cm^{-1}) 2930 (w), 1734 (s), 1473 (m), 1122 (m), 762 (m).

HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_{12}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 191.0684; found: 191.0682.

2-ethylhexyl furan-2-carboxylate (a5)



Yield: 90%, colorless oil.

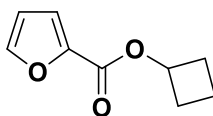
^1H NMR (400 MHz, CDCl_3) δ 7.57 (br, 1H), 7.22-7.06 (m, 1H), 6.52-6.48 (m, 1H), 4.25-4.16 (m, 2H), 1.79-1.60 (m, 1H), 1.52-1.29 (m, 8H), 0.96-0.86 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 146.3, 145.1, 117.7, 111.8, 67.5, 39.0, 30.6, 29.1, 24.0, 23.1, 14.1, 11.1.

IR ν (cm^{-1}) 2927 (m), 1733 (s), 1292 (m), 1118 (m), 983 (m), 763 (m).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{20}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 247.1310; found: 247.1310.

Cyclobutyl furan-2-carboxylate (a13)



Yield: 60%, colorless oil.

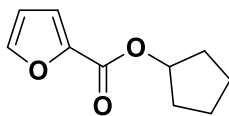
^1H NMR (400 MHz, CDCl_3) δ 7.57 (br, 1H), 7.19-7.16 (m, 1H), 6.52-6.49 (m, 1H), 5.26-5.16 (m, 1H), 2.54-2.36 (m, 2H), 2.30-2.12 (m, 2H), 1.91-1.64 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.29, 146.3, 145.0, 117.9, 111.9, 69.4, 30.5, 13.6.

IR ν (cm^{-1}) 2956 (m), 1734 (s), 1473 (m), 1299 (s), 1181 (m), 1122 (m), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_{11}\text{O}_3$ ($[\text{M} + \text{H}]^+$): 167.0708; found: 167.0706.

Cyclopentyl furan-2-carboxylate (a8)



Yield: 67%, colorless oil.

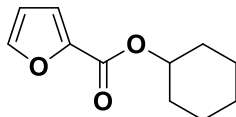
^1H NMR (400 MHz, CDCl_3) δ 7.55 (br, 1H), 7.13 (t, $J = 3.0$ Hz, 1H), 6.50-6.47 (m, 1H), 5.49-5.26 (m, 1H), 2.06-1.54 (m, 8H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 146.1, 145.4, 117.5, 111.8, 77.9, 32.8, 23.9.

IR ν (cm^{-1}) 2963 (m), 1713 (s), 1474 (m), 1295 (s), 1176 (m), 1121 (m), 764 (m).

HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{12}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 203.0684; found: 203.0677.

Cyclohexyl furan-2-carboxylate (a14)



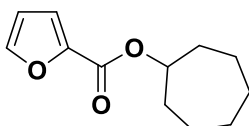
Yield: 68%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.56 (br, 1H), 7.15 (d, $J = 3.0$ Hz, 1H), 6.50-6.47 (m, 1H), 4.99 (td, $J = 9.2, 4.0$ Hz, 1H), 1.94 (d, $J = 9.2$ Hz, 2H), 1.86-1.74 (m, 2H), 1.64-1.49 (m, 3H), 1.46-1.23 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 146.1, 145.4, 117.6, 111.8, 73.5, 31.8, 25.5, 23.9.

Product identity was confirmed by comparison to literature spectra.^[13]

Cycloheptyl furan-2-carboxylate (a15)



Yield: 65%, colorless oil.

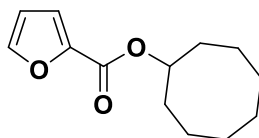
^1H NMR (400 MHz, CDCl_3) δ 7.56 (br, 1H), 7.14 (d, $J = 2.8$ Hz, 1H), 6.50-6.47 (m, 1H), 5.23-5.07 (m, 1H), 2.03-1.95 (m, 2H), 1.84-1.47 (m, 10H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 146.1, 145.5, 117.5, 111.8, 76.1, 34.0, 28.4, 23.0.

IR ν (cm^{-1}) 2929 (s), 2859 (m), 1713 (s), 1475 (m), 1295 (s), 1177 (m), 1120 (s), 763 (m).

HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{16}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 231.0997; found: 231.0989.

Cyclooctyl furan-2-carboxylate (a16)



Yield: 61%, colorless oil.

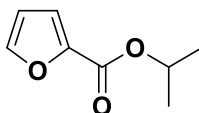
^1H NMR (400 MHz, CDCl_3) δ 7.56 (br, 1H), 7.14 (d, $J = 2.8$ Hz, 1H), 6.54-6.41 (m, 1H), 5.21-5.10 (m, 1H), 1.97-1.55 (m, 14H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 146.1, 145.6, 117.5, 111.8, 76.1, 31.7, 27.2, 25.5, 23.0.

IR ν (cm^{-1}) 2924 (m), 1717 (s), 1474 (m), 1295 (s), 1181 (m), 1122 (s), 764 (m).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3$ ($[\text{M} + \text{H}]^+$): 223.1334; found: 223.1333.

Isopropyl furan-2-carboxylate (a7)



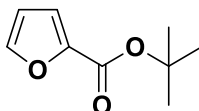
Yield: 58%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.56 (br, 1H), 7.15 (d, $J = 3.4$ Hz, 1H), 6.49 (dd, $J = 3.4, 1.7$ Hz, 1H), 5.24 (hept, $J = 6.4$ Hz, 1H), 1.36 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 146.1, 145.3, 117.6, 111.8, 68.7, 22.0.

Product identity was confirmed by comparison to literature spectra.^[14]

tert-Butyl furan-2-carboxylate (a9)



Yield: 10%, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.53 (br, 1H), 7.07 (br, 1H), 6.47 (br, 1H), 1.58 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.2, 146.1, 145.8, 117.1, 111.7, 82.0, 28.4.

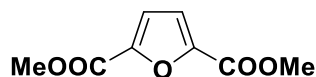
Product identity was confirmed by comparison to literature spectra.^[15]

4. General experimental procedures and characterization data

4.1 General procedure C for the synthesis of symmetrical di-furoate 1-8

An oven-dried 10 mL reaction vessel was charged with furoates (1 equiv, 0.3 mmol, 0.3 M), alcohols (7.5 equiv, 2.25 mmol), $\text{Cu}(\text{OAc})_2$ (0.2 equiv, 0.06 mmol, 10.8 mg), TBPB (2.5 equiv, 0.75 mmol, 145 μL), CHCl_3 (solvent) under air. The vessel was sealed and heated at 120 $^\circ\text{C}$ (oil bath temperature) for 12 h. The reaction mixture was cooled to room temperature. Afterwards the reaction was quenched with saturated NaHCO_3 solution (25 mL) and extracted with CH_2Cl_2 (3*25 mL), dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and purified by column chromatography on silica gel with a mixture of EtOAc in petroleum ether as eluent to afford the pure product.

Dimethyl furan-2,5-dicarboxylate (1)



Yield: 80%, white solid.

Melting point: 101-102 °C

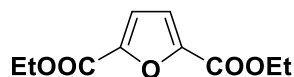
^1H NMR (400 MHz, CDCl_3) δ 7.22 (s, 2H), 3.94 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 146.8, 118.6, 52.5.

IR ν (cm^{-1}) 1718 (s), 1300 (s), 1195 (m), 1153 (m), 979 (w), 758 (w).

HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_8\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 207.0269; found: 207.0257.

Diethyl furan-2,5-dicarboxylate (2)



Yield: 81%, white solid.

Melting point: 41-42 °C

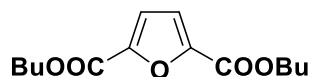
^1H NMR (400 MHz, CDCl_3) δ 7.20 (s, 2H), 4.40 (q, $J = 7.0$ Hz, 4H), 1.39 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.2, 147.0, 118.3, 61.7, 14.3.

IR ν (cm^{-1}) 1721 (s), 1277 (s), 1224 (m), 1133 (m), 1019 (w), 766 (w).

HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{12}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 235.0582; found: 235.0570.

Dibutyl furan-2,5-dicarboxylate (3)



Yield: 66%, white solid.

Melting point: 40-41 °C

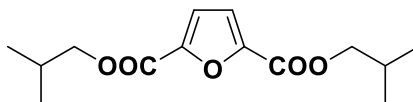
^1H NMR (400 MHz, CDCl_3) δ 7.19 (s, 2H), 4.34 (t, $J = 6.8$ Hz, 4H), 1.80-1.68 (m, 4H), 1.53-1.39 (m, 4H), 0.97 (t, $J = 7.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 147.1, 118.3, 65.5, 30.7, 19.2, 13.8.

IR ν (cm^{-1}) 3119 (m), 2959 (s), 2870 (m), 1711 (s), 1470 (m), 1302 (s), 1163 (s), 1031 (m), 972 (m), 857 (w), 772 (w).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{20}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 291.1208; found: 291.1203.

Diisobutyl furan-2,5-dicarboxylate (4)



Yield: 58%, white solid.

Melting point: 85-86 °C

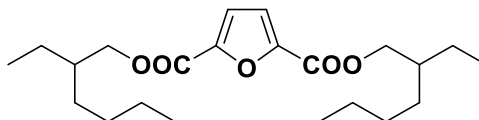
^1H NMR (400 MHz, CDCl_3) δ 7.20 (s, 2H), 4.12 (d, $J = 6.8$ Hz, 4H), 2.13-2.02 (m, 2H), 1.00 (d, $J = 6.8$ Hz, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 147.1, 118.3, 71.6, 28.0, 19.2.

IR ν (cm^{-1}) 3118 (w), 2955 (w), 1725 (s), 1298 (m), 1155 (m), 1033 (m), 857 (w), 774 (w).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{20}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 291.1208; found: 291.1203.

Bis(2-ethylhexyl) furan-2,5-dicarboxylate (5)



Yield: 53%, colorless oil.

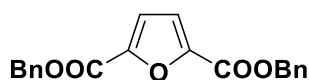
^1H NMR (400 MHz, CDCl_3) δ 7.18 (s, 2H), 4.31-4.19 (m, 4H), 1.71 (dt, $J = 12.2, 6.0$ Hz, 2H), 1.46-1.30 (m, 16H), 0.98-0.87 (m, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 147.1, 118.2, 68.1, 39.0, 30.5, 29.1, 24.0, 23.1, 14.1, 11.1.

IR ν (cm^{-1}) 2960 (s), 2930 (s), 2866 (m), 1722 (s), 1275 (s), 1222 (m), 1131 (m), 765 (m).

HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{36}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 403.2460; found: 403.2441.

Dibenzyl furan-2,5-dicarboxylate (6)



Yield: 45%, white solid.

Melting point: 83-84 °C

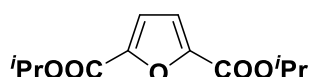
¹H NMR (400 MHz, CDCl₃) δ 7.45-7.31 (m, 10H), 7.21 (s, 2H), 5.36 (s, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 158.0, 147.0, 135.3, 128.8, 128.7, 128.6, 118.8, 67.2.

IR ν (cm⁻¹) 1715 (s), 1270 (s), 1218 (s), 1122 (m), 756 (m), 692 (m).

HRMS (ESI): m/z calcd for C₂₀H₁₆NaO₅ ([M + Na]⁺): 359.0895; found: 359.0877.

Diisopropyl furan-2,5-dicarboxylate (7)



Yield: 41%, white solid.

Melting point: 43-44 °C

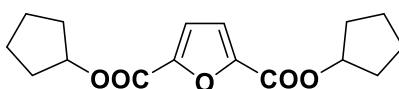
¹H NMR (400 MHz, CDCl₃) δ 7.16 (s, 2H), 5.31-5.20 (m, 2H), 1.37 (d, *J* = 6.4 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 157.8, 147.3, 118.1, 69.5, 21.9.

IR ν (cm⁻¹) 2983 (m), 1717 (s), 1580 (m), 1278 (s), 1225 (s), 1143 (s), 1103 (s), 966 (m), 832 (m), 768 (m).

HRMS (ESI): m/z calcd for C₁₂H₁₆NaO₅ ([M + Na]⁺): 263.0895; found: 263.0888.

Dicyclopentyl furan-2,5-dicarboxylate (8)



Yield: 42%, white solid.

Melting point: 118-119 °C

¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 2H), 5.39 (br, 2H), 2.08-1.58 (m, 16H).

¹³C NMR (100 MHz, CDCl₃) δ 158.2, 147.3, 118.1, 78.8, 32.8, 23.9.

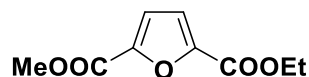
IR ν (cm⁻¹) 3115 (w), 2959 (m), 1716 (s), 1281 (s), 1151 (s), 1033 (m), 966 (m), 860 (m), 772 (m), 736 (m).

HRMS (ESI): m/z calcd for C₁₆H₂₀NaO₅ ([M + Na]⁺): 315.1208; found: 315.1200.

4.2 General procedure D for the synthesis of unsymmetric di-furoate 10-23

An oven-dried 10 mL reaction vessel was charged with furoates (1 equiv, 0.3 mmol, 0.3 M), alcohols (2.5 equiv, 0.75 mmol), Cu(OAc)₂ (0.2 equiv, 0.06 mmol, 10.8 mg), TBPB (2.5 equiv, 0.75 mmol, 145 uL), CHCl₃ (solvent) under air. The vessel was sealed and heated at 120 °C (oil bath temperature) for 12 h. The reaction mixture was cooled to room temperature. Afterwards the reaction was quenched with saturated NaHCO₃ solution (25 mL) and extracted with dichloromethane (3*25 mL), dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and purified by column chromatography on silica gel with a mixture of EtOAc in petroleum ether as eluent to afford the pure product.

2-ethyl 5-methyl furan-2,5-dicarboxylate (10)



Yield: 75%, yellow solid.

Melting point: 46-47 °C

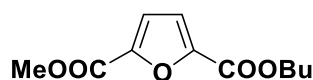
¹H NMR (400 MHz, CDCl₃) δ 7.23-7.19 (m, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 158.6, 158.1, 147.1, 146.7, 118.6, 118.3, 61.7, 52.4, 14.3.

IR ν (cm⁻¹) 1724 (s), 1280 (s), 1226 (s), 1133 (s), 1019 (m), 766 (m).

HRMS (ESI): m/z calcd for C₉H₁₀NaO₅ ([M + Na]⁺): 221.0426; found: 221.0412.

2-butyl 5-methyl furan-2,5-dicarboxylate (11)



Yield: 65%, yellow solid.

Melting point: 49-50 °C

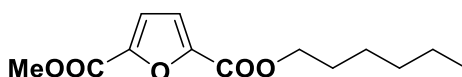
^1H NMR (400 MHz, CDCl_3) δ 7.23-7.18 (m, 2H), 4.34 (t, $J = 6.8$ Hz, 2H), 3.93 (s, 3H), 1.78-1.71 (m, 2H), 1.51-1.40 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.2, 147.1, 146.7, 118.5, 118.3, 65.5, 52.4, 30.7, 19.2, 13.8.

IR ν (cm^{-1}) 2959 (m), 1721 (s), 1280 (s), 1226 (m), 1130 (s), 1022 (w), 982 (w), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{14}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 249.0739; found: 249.0729.

2-hexyl 5-methyl furan-2,5-dicarboxylate (12)



Yield: 52%, yellow solid.

Melting point: 34-35 °C

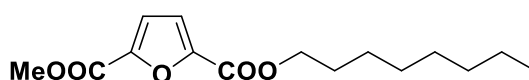
^1H NMR (400 MHz, CDCl_3) δ 7.23-7.18 (m, 2H), 4.33 (t, $J = 6.8$ Hz, 2H), 3.93 (s, 3H), 1.85-1.66 (m, 2H), 1.48-1.27 (m, 6H), 0.90 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.2, 147.1, 146.7, 118.5, 118.3, 65.8, 52.4, 31.5, 28.6, 25.6, 22.6, 14.0.

IR ν (cm^{-1}) 2957 (m), 2931 (m), 2860 (w), 1724 (s), 1279 (s), 1225 (m), 1132 (m), 989 (w), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{18}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 277.1052; found: 277.1048.

2-methyl 5-octyl furan-2,5-dicarboxylate (13)



Yield: 52%, yellow solid.

Melting point: 35-36 °C

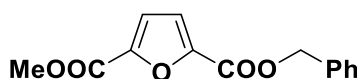
^1H NMR (400 MHz, CDCl_3) δ 7.23-7.18 (m, 2H), 4.33 (t, $J = 6.8$ Hz, 2H), 3.93 (s, 3H), 1.80-1.72 (m, 2H), 1.43-1.26 (m, 10H), 0.88 (t, $J = 6.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.2, 147.2, 146.8, 118.6, 118.3, 65.9, 52.5, 31.9, 29.3, 29.3, 28.7, 26.0, 22.7, 14.2.

IR ν (cm^{-1}) 2955 (m), 2927 (m), 2856 (w), 1724 (s), 1279 (s), 1225 (m), 1132 (m), 1019 (m), 989 (w), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{22}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 305.1365; found: 305.1358.

2-benzyl 5-methyl furan-2,5-dicarboxylate (14)



Yield: 61%, yellow solid.

Melting point: 90-91 °C

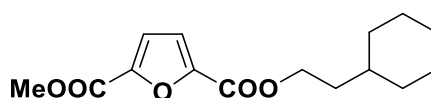
^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, $J = 7.2$ Hz, 2H), 7.40-7.33 (m, 3H), 7.23-7.19 (m, 2H), 5.37 (s, 2H), 3.91 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 157.9, 146.9, 146.8, 135.3, 128.7, 128.7, 128.6, 118.7, 118.6, 67.2, 52.5.

IR ν (cm^{-1}) 1723 (s), 1279 (s), 1225 (m), 1132 (m), 988 (w), 763 (m).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{12}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 283.0582; found: 283.0575.

2-(2-cyclohexylethyl) 5-methyl furan-2,5-dicarboxylate (15)



Yield: 56%, yellow solid.

Melting point: 64-65 °C

^1H NMR (400 MHz, CDCl_3) δ 7.23-7.18 (m, 2H), 4.37 (t, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 1.80-1.62 (m, 7H), 1.47-1.37 (m, 1H), 1.30-1.14 (m, 3H),

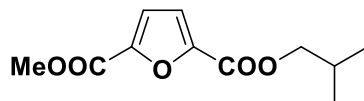
1.03-0.91 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.2, 147.2, 146.7, 118.6, 118.3, 64.1, 52.4, 36.0, 34.7, 33.3, 26.6, 26.3.

IR ν (cm^{-1}) 2924 (s), 2851 (m), 1723 (s), 1280 (s), 1225 (m), 1133 (m), 978 (w), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 303.1208; found: 303.1202.

2-isobutyl 5-methyl furan-2,5-dicarboxylate (16)



Yield: 58%, yellow solid.

Melting point: 75-76 °C

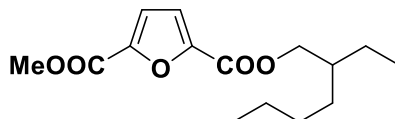
^1H NMR (400 MHz, CDCl_3) δ 7.23-7.18 (m, 2H), 4.12 (d, J = 6.8 Hz, 2H), 3.93 (s, 3H), 2.13-2.03 (m, 1H), 1.00 (d, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.0, 147.5, 146.6, 118.5, 118.1, 78.8, 52.4, 32.8, 23.9.

IR ν (cm^{-1}) 2927 (w), 2856 (w), 1724 (s), 1279 (s), 1225 (m), 1132 (m), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{14}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 249.0739; found: 249.0729.

2-(2-ethylhexyl) 5-methyl furan-2,5-dicarboxylate (17)



Yield: 51%, colorless oil.

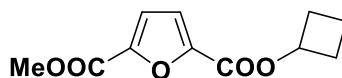
^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 3.6 Hz, 1H), 7.18 (d, J = 3.6 Hz, 1H), 4.26 (d, J = 6.0 Hz, 2H), 3.93 (s, 3H), 1.76-1.67 (m, 1H), 1.47-1.27 (m, 8H), 0.96-0.88 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.2, 147.1, 146.8, 118.5, 118.1, 68.1, 52.4, 38.9, 30.5, 29.0, 23.9, 23.0, 14.1, 11.0.

IR ν (cm^{-1}) 2959 (m), 2930 (m), 2866 (w), 1725 (s), 1279 (s), 1225 (m), 1132 (m), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{15}\text{H}_{22}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 305.1365; found: 305.1359.

2-cyclobutyl 5-methyl furan-2,5-dicarboxylate (18)



Yield: 53%, yellow solid.

Melting point: 74-75 °C

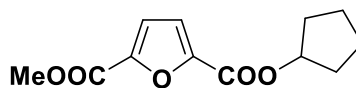
^1H NMR (400 MHz, CDCl_3) δ 7.22-7.18 (m, 2H), 5.28-5.15 (m, 1H), 3.93 (s, 3H), 2.49-2.40 (m, 2H), 2.31-2.19 (m, 2H), 1.92-1.81 (m, 1H), 1.73-1.63 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 157.5, 147.1, 146.7, 118.6, 118.4, 70.1, 52.5, 30.4, 13.6.

IR ν (cm^{-1}) 2992 (w), 2952 (w), 1722 (s), 1280 (s), 1225 (m), 1133 (m), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{12}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 247.0582; found: 247.0573.

2-cyclopentyl 5-methyl furan-2,5-dicarboxylate (19)



Yield: 62%, yellow solid.

Melting point: 64-65 °C

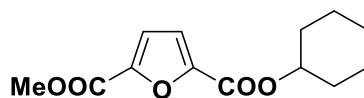
^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, J = 3.6 Hz, 1H), 7.16 (d, J = 3.6 Hz, 1H), 5.43-5.37 (m, 1H), 3.93 (s, 3H), 2.02-1.92 (m, 2H), 1.89-1.75 (m, 4H), 1.70-1.59 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 158.0, 147.5, 146.6, 118.5, 118.1, 78.8, 52.4, 32.8, 23.9.

IR ν (cm^{-1}) 2960 (m), 2874 (w), 1721 (s), 1280 (s), 1226 (m), 1134 (m), 767 (m).

HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{14}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 261.0739; found: 261.0731.

2-cyclohexyl 5-methyl furan-2,5-dicarboxylate (20)



Yield: 63%, yellow solid.

Melting point: 69-70 °C

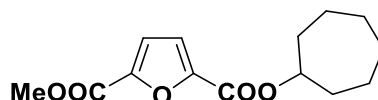
^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 3.6$ Hz, 1H), 7.18 (d, $J = 3.6$ Hz, 1H), 5.06-4.97 (m, 1H), 3.93 (s, 3H), 1.99-1.92 (m, 2H), 1.82-1.76 (m, 2H), 1.63-1.52 (m, 3H), 1.47-1.26 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 157.6, 147.5, 146.6, 118.5, 118.1, 74.4, 52.4, 31.6, 25.4, 23.8.

IR ν (cm^{-1}) 2938 (m), 2859 (w), 1721 (s), 1281 (s), 1225 (s), 1134 (s), 1014 (m), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{16}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 275.0895; found: 275.0889.

2-cycloheptyl 5-methyl furan-2,5-dicarboxylate (21)



Yield: 63%, yellow solid.

Melting point: 65-66 °C

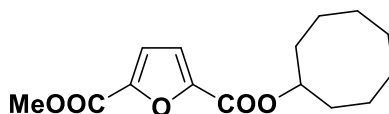
^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, $J = 3.6$ Hz, 1H), 7.17 (d, $J = 3.6$ Hz, 1H), 5.24-5.12 (m, 1H), 3.93 (s, 3H), 2.05-1.97 (m, 2H), 1.86-1.76 (m, 2H), 1.73-1.48 (m, 8H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 157.6, 147.7, 146.6, 118.6, 118.0, 77.1, 52.4, 33.9, 28.4, 23.0.

IR ν (cm^{-1}) 2930 (m), 2859 (w), 1721 (s), 1279 (s), 1225 (m), 1134 (m), 989 (w), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 289.1052; found: 289.1048.

2-cyclooctyl 5-methyl furan-2,5-dicarboxylate (22)



Yield: 59%, yellow solid.

Melting point: 45-46 °C

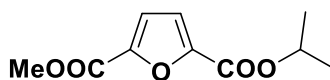
^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, $J = 3.6$ Hz, 1H), 7.16 (d, $J = 3.6$ Hz, 1H), 5.25-5.15 (m, 1H), 3.93 (s, 3H), 1.97-1.73 (m, 6H), 1.67-1.49 (m, 8H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 157.6, 147.7, 146.6, 118.5, 118.0, 77.1, 52.4, 31.6, 27.2, 25.5, 23.0.

IR ν (cm^{-1}) 2925 (m), 2857 (w), 1721 (s), 1279 (s), 1224 (m), 1134 (m), 766 (m).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 303.1208; found: 303.1203.

2-isopropyl 5-methyl furan-2,5-dicarboxylate (23)



Yield: 70%, yellow solid.

Melting point: 39-40 °C

^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 3.6$ Hz, 1H), 7.18 (d, $J = 3.6$ Hz, 1H), 5.31-5.21 (m, 1H), 3.93 (s, 3H), 1.37 (d, $J = 6.4$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.6, 157.8, 147.5, 146.6, 118.5, 118.1, 69.7, 52.4, 21.9.

IR ν (cm^{-1}) 2984 (w), 1721 (s), 1280 (s), 1226 (m), 1103 (m), 766 (m).

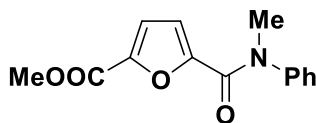
HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{12}\text{NaO}_5$ ($[\text{M} + \text{Na}]^+$): 235.0582; found: 235.0570.

4.3 General procedure E for the synthesis of heteroarenes 25-33, 37-44

An oven-dried 10 mL reaction vessel was charged with heteroarenes (1 equiv, 0.3 mmol, 0.3 M), alcohols (2.5 equiv, 0.75 mmol), $\text{Cu}(\text{OAc})_2$ (0.2 equiv, 0.06 mmol, 10.8 mg), TBPB (2.5 equiv, 0.75 mmol, 145 μL), CHCl_3 (solvent) under air. The vessel was sealed and heated at 120 °C (oil bath temperature) for 12 h. The reaction mixture was cooled to room temperature. Afterwards the reaction was quenched with saturated NaHCO_3 solution (25 mL) and extracted with dichloromethane (3*25 mL), dried over anhydrous Na_2SO_4 . The organic extract was concentrated under

reduced pressure and purified by column chromatography on silica gel with a mixture of EtOAc in petroleum ether as eluent to afford the pure product.

Methyl 5-(methyl(phenyl)carbamoyl)furan-2-carboxylate (25)



Yield: 80%, yellow solid.

Melting point: 91-92 °C

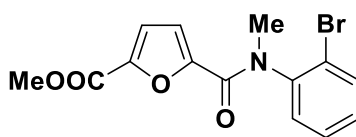
^1H NMR (400 MHz, CDCl_3) δ 7.45-7.35 (m, 3H), 7.21 (d, J = 7.0 Hz, 2H), 6.94 (d, J = 3.6 Hz, 1H), 6.16 (br, 1H), 3.81 (s, 3H), 3.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 158.5, 149.7, 144.9, 143.6, 129.7, 128.1, 127.2, 117.9, 116.9, 52.1, 38.6.

IR ν (cm^{-1}) 2953 (w), 1732 (s), 1651 (s), 1297 (s), 1143 (m), 762 (m), 699 (m).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_4$ ($[\text{M} + \text{H}]^+$): 260.0923; found: 260.0915.

Methyl 5-((2-bromophenyl)(methyl)carbamoyl)furan-2-carboxylate (26)



Yield: 72%, yellow solid.

Melting point: 81-82 °C

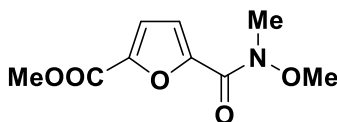
^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.34-7.27 (m, 2H), 6.96 (d, J = 3.2 Hz, 1H), 6.36 (d, J = 3.2 Hz, 1H), 3.79 (s, 3H), 3.38 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.4, 158.4, 149.6, 145.1, 142.4, 133.8, 130.0, 129.9, 128.9, 123.3, 118.0, 116.8, 52.0, 37.3.

IR ν (cm^{-1}) 1732 (s), 1656 (s), 1296 (s), 1143 (m), 764 (m).

HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_4\text{Br}$ ($[\text{M} + \text{H}]^+$): 338.0028; found: 338.0008.

Methyl 5-(methoxy(methyl)carbamoyl)furan-2-carboxylate (27)



Yield: 52%, yellow solid.

Melting point: 75-76 °C

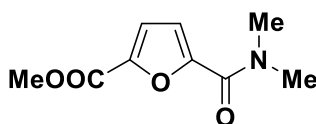
^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 3.6 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 158.5, 148.4, 145.6, 118.5, 118.0, 62.0, 52.3, 33.5.

IR ν (cm^{-1}) 2950 (w), 1732 (s), 1648 (m), 1298 (s), 1217 (m), 1143 (m), 982 (m), 765 (m).

HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_{12}\text{NO}_5$ ($[\text{M} + \text{H}]^+$): 214.0715; found: 214.0702.

Methyl 5-(dimethylcarbamoyl)furan-2-carboxylate (28)



Yield: 65%, yellow solid.

Melting point: 98-99 °C

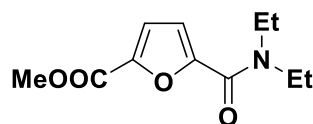
^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, J = 3.6 Hz, 1H), 7.08 (d, J = 3.6 Hz, 1H), 3.91 (s, 3H), 3.33 (s, 3H), 3.11 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.5, 158.8, 151.1, 144.7, 118.4, 117.0, 52.2, 38.3, 36.6.

IR ν (cm^{-1}) 2954 (w), 1727 (s), 1628 (s), 1302 (s), 1219 (m), 1146 (m), 764 (m).

HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_{12}\text{NO}_4$ ($[\text{M} + \text{H}]^+$): 198.0766; found: 198.0754.

Methyl 5-(diethylcarbamoyl)furan-2-carboxylate (29)



Yield: 58%, yellow oil.

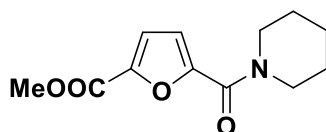
^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 3.6$ Hz, 1H), 7.07 (d, $J = 3.6$ Hz, 1H), 3.91 (s, 3H), 3.66-3.46 (m, 4H), 1.39-1.19 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 158.8, 151.4, 144.4, 118.4, 116.7, 52.2, 43.2, 41.6, 14.7, 12.8.

IR ν (cm^{-1}) 2976 (m), 1732 (s), 1630 (s), 1431 (m), 1301 (s), 1280 (s), 1213 (m), 1143 (m), 762 (m).

HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_4\text{Na}$ ($[\text{M} + \text{Na}]^+$): 248.0899; found: 248.0886.

Methyl 5-(piperidine-1-carbonyl)furan-2-carboxylate (30)



Yield: 59%, yellow solid.

Melting point: 84-85 °C

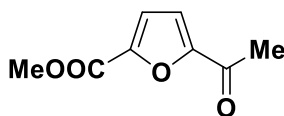
^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 3.6$ Hz, 1H), 6.99 (d, $J = 3.6$ Hz, 1H), 3.91 (s, 3H), 3.70 (s, 4H), 1.74-1.62 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 158.3, 151.2, 144.4, 118.4, 116.4, 52.2, 24.6. Note: The four methylene peaks from the amide group are not visible in ^{13}C NMR.

IR ν (cm^{-1}) 2940 (m), 2858 (w), 1731 (s), 1630 (s), 1437 (s), 1300 (s), 1270 (s), 1213 (m), 1141 (m), 763 (m).

HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{Na}$ ($[\text{M} + \text{Na}]^+$): 260.0899; found: 260.0891.

Methyl 5-acetylfuran-2-carboxylate (31)



Yield: 45%, yellow solid.

Melting point: 95-96 °C

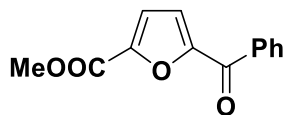
^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 3.6$ Hz, 1H), 7.20 (d, $J = 3.6$ Hz, 1H), 3.94 (s, 3H), 2.57 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 187.5, 158.6, 154.3, 146.3, 118.8, 116.7, 52.4, 26.4.

IR ν (cm^{-1}) 1720 (s), 1675 (m), 1304 (s), 1284 (m).

HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_8\text{O}_4\text{Na}$ ($[\text{M} + \text{Na}]^+$): 191.0320; found: 191.0309.

Methyl 5-benzoylfuran-2-carboxylate (32)



Yield: 60%, yellow solid.

Melting point: 95-96 °C

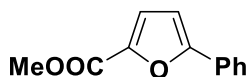
^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 7.6$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.33-7.25 (m, 2H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 182.3, 158.8, 154.1, 146.9, 136.4, 133.4, 129.8, 128.8, 120.0, 118.7, 52.5.

IR ν (cm^{-1}) 1733 (s), 1651 (m), 1571 (m), 1276 (m), 880 (m), 764 (w), 723 (w).

HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{10}\text{O}_4\text{Na}$ ($[\text{M} + \text{Na}]^+$): 253.0477; found: 253.0466.

Methyl 5-phenylfuran-2-carboxylate (33)



Yield: 46%, yellow solid.

Melting point: 48-49 °C

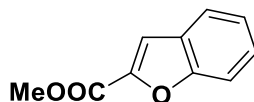
^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 6.71 (d, J = 3.6 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 157.6, 143.6, 129.6, 129.0, 128.9, 124.9, 120.1, 106.9, 51.9.

IR ν (cm^{-1}) 1727 (s), 1478 (m), 1306 (s), 1140 (s), 1025 (m), 990 (w), 920 (w), 801 (w), 762 (s), 691 (m).

HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{10}\text{O}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 225.0528; found: 225.0514.

Methyl benzofuran-2-carboxylate (37)



Yield: 74%, yellow solid.

Melting point: 45-46 °C

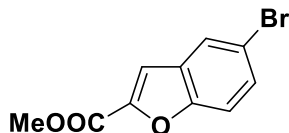
^1H NMR (500 MHz, CDCl_3) δ 7.69 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.54 (s, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 3.98 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 160.1, 155.9, 145.5, 127.8, 127.1, 124.0, 123.0, 114.1, 112.5, 52.5.

IR ν (cm^{-1}) 1730 (s), 1567 (m), 1437 (m), 1298 (s), 1178 (s), 1094 (m), 750 (s).

HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_8\text{O}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 199.0371; found: 199.0359.

Methyl 5-bromobenzofuran-2-carboxylate (38)



Yield: 59%, yellow solid.

Melting point: 110-110 °C

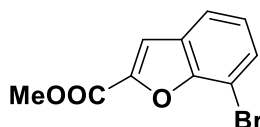
^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, J = 2.0 Hz, 1H), 7.53 (dd, J = 8.5, 2.0 Hz, 1H), 7.47-7.44 (m, 2H), 3.98 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 154.5, 146.6, 130.8, 128.9, 125.5, 117.0, 114.0, 113.1, 52.7.

IR ν (cm^{-1}) 1731 (s), 1568 (m), 1437 (m), 1298 (s), 1178 (s), 1095 (m), 752 (s).

HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_7\text{BrO}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 276.9476; found: 276.9467.

Methyl 7-bromobenzofuran-2-carboxylate (39)



Yield: 56%, yellow solid.

Melting point: 53-54 °C

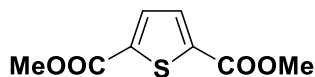
^1H NMR (500 MHz, CDCl_3) δ 7.64-7.59 (m, 2H), 7.58 (s, 1H), 7.19 (t, J = 7.5 Hz, 1H), 3.99 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 159.6, 153.0, 146.3, 130.7, 128.3, 125.2, 122.1, 114.6, 105.1, 52.7.

IR ν (cm^{-1}) 1729 (s), 1300 (s), 1179 (s), 750 (s).

HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_7\text{BrO}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 276.9476; found: 276.9468.

Dimethyl thiophene-2,5-dicarboxylate (40)



Yield: 70%, yellow solid.

Melting point: 120-121 °C

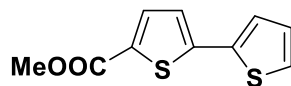
^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 2H), 3.92 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 138.9, 133.2, 52.7.

IR ν (cm^{-1}) 1725 (s), 1349 (m), 1246 (s), 1102 (m), 746 (s).

HRMS (ESI): m/z calcd for $\text{C}_8\text{H}_8\text{SO}_4\text{Na}$ ($[\text{M} + \text{Na}]^+$): 223.0041; found: 223.0032.

Methyl [2,2'-bithiophene]-5-carboxylate (**41**)



Yield: 57%, dark green solid.

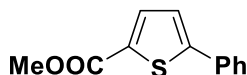
Melting point: 120-121 °C

¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, J = 4.0 Hz, 1H), 7.31-7.25 (m, 2H), 7.13 (d, J = 4.0 Hz, 1H), 7.05-7.02 (m, 1H), 3.88 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 162.6, 144.3, 136.4, 134.4, 131.4, 128.2, 126.2, 125.4, 124.0, 52.3.

Product identity was confirmed by comparison to literature spectra.^[16]

Methyl 5-phenylthiophene-2-carboxylate (**42**)



Yield: 60%, dark green solid.

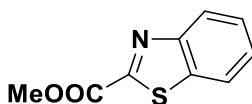
Melting point: 89-90 °C

¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, J = 4.0 Hz, 1H), 7.62 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.28-7.24 (m, 1H), 3.89 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 162.8, 151.4, 134.5, 133.5, 132.1, 129.2, 128.9, 126.3, 123.7, 52.3.

Product identity was confirmed by comparison to literature spectra.^[17]

Methyl benzo[d]thiazole-2-carboxylate (**43**)



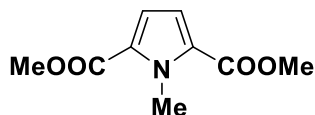
Yield: 37%, yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 3.45 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 170.2, 137.9, 126.5, 123.3, 122.7, 122.6, 110.5, 29.1.

Product identity was confirmed by comparison to literature spectra.^[18]

Dimethyl 1-methyl-1H-pyrrole-2,5-dicarboxylate (**44**)



Yield: 68%, yellow solid.

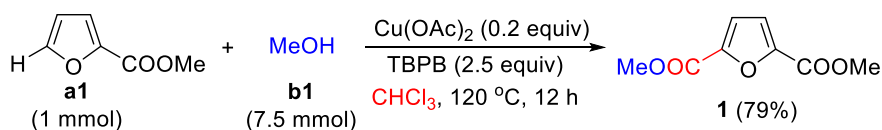
Melting point: 78-79 °C

¹H NMR (400 MHz, CDCl₃) δ 6.87 (s, 2H), 4.27 (s, 3H), 3.85 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 161.5, 128.0, 116.4, 51.7, 34.6.

Product identity was confirmed by comparison to literature spectra.^[19]

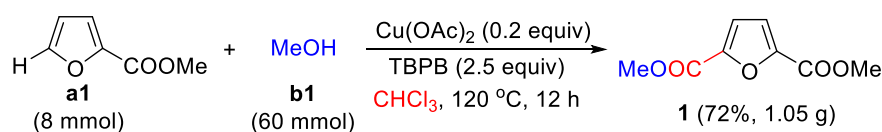
4.4 Procedure for larger scale catalytic reactions to synthesize symmetrical di-furoate **1**



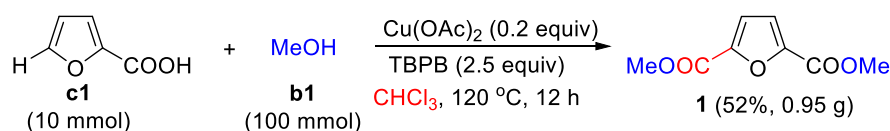
An oven-dried 25 mL reaction vessel was charged with methyl-2-furoate (**a1**, 1 equiv, 1 mmol, 122 μ L, 0.3 M), methanol (**b1**, 7.5 equiv, 7.5 mmol, 297 μ L), Cu(OAc)₂ (0.2 equiv, 0.2 mmol, 35.6 mg), TBPB (2.5 equiv, 2.5 mmol, 478 μ L), CHCl₃ (2.4 mL) under air. The vessel was sealed and heated at 120 °C (oil bath temperature) for 12 h. The reaction mixture was cooled to room temperature. Afterwards the reaction was quenched with saturated NaHCO₃ solution (25 mL) and extracted with dichloromethane (3*25 mL), dried over anhydrous Na₂SO₄. The organic extract was concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:8 as eluent) to afford the

pure product **1** in 79% yield.

4.5 Procedure for preparative gram-scale reaction to synthesize symmetrical di-furoate **1**



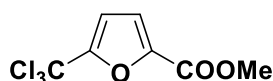
An oven-dried 250 mL reaction vessel was charged with methyl-2-furoate (**a1**, 1 equiv, 8 mmol, 976 μL , 0.3 M), methanol (**b1**, 7.5 equiv, 60 mmol, 2.4 mL), $\text{Cu}(\text{OAc})_2$ (0.2 equiv, 1.6 mmol, 285 mg), TBPB (2.5 equiv, 20 mmol, 3.8 mL), CHCl_3 (20 mL) under air. The vessel was sealed and heated at 120 °C (oil bath temperature) for 12 h. The reaction mixture was cooled to room temperature. Afterwards the reaction was quenched with saturated NaHCO_3 solution (75 mL) and extracted with dichloromethane (3*75 mL), dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:8 as eluent) to afford the pure product **1** in 72% yield.



An oven-dried 250 mL reaction vessel was charged with furoic acid (**c1**, 1 equiv, 10 mmol, 1.12 g, 0.3 M), methanol (**b1**, 10 equiv, 100 mmol, 4 mL), $\text{Cu}(\text{OAc})_2$ (0.2 equiv, 2 mmol, 356 mg), TBPB (2.5 equiv, 25 mmol, 4.75 mL), CHCl_3 (24.5 mL) under air. The vessel was sealed and heated at 120 °C (oil bath temperature) for 12 h. The reaction mixture was cooled to room temperature. Afterwards the reaction was quenched with saturated NaHCO_3 solution (75 mL) and extracted with dichloromethane (3*75 mL), dried over anhydrous Na_2SO_4 . The organic extract was concentrated under reduced pressure and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:8 as eluent) to afford the pure product **1** in 52% yield.

4.6 Characterization data of copper additive effect experiments (45-48)

Methyl 5-(trichloromethyl)furan-2-carboxylate (**45**)



White solid. Melting point: 84-85 °C

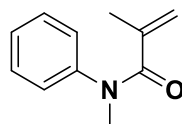
^1H NMR (500 MHz, CDCl_3) δ 7.15 (d, J = 3.5 Hz, 1H), 6.84 (d, J = 3.5 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 158.5, 154.5, 146.0, 118.1, 111.1, 86.3, 52.5.

IR ν (cm^{-1}) 1746 (s), 1297 (s), 1218 (s), 1137 (s), 826 (m), 791 (m), 760 (s), 653 (m).

HRMS (ESI): m/z calcd for $\text{C}_7\text{H}_5\text{Cl}_3\text{O}_3\text{Na}$ ($[\text{M} + \text{Na}]^+$): 264.9202; found: 264.9198.

N-methyl-N-phenylmethacrylamide (**46**)

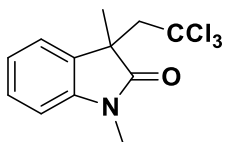


^1H NMR (500 MHz, CDCl_3) δ 7.38-7.32 (m, 2H), 7.30-7.22 (m, 1H), 7.18-7.10 (m, 2H), 5.05-4.97 (m, 2H), 3.43-3.27 (m, 3H), 1.76 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.1, 144.7, 140.8, 129.3, 127.0, 126.6, 119.4, 37.7, 20.4.

Product identity was confirmed by comparison to literature spectra.^[20]

1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one (**47**)

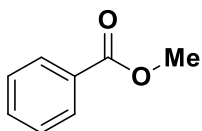


^1H NMR (500 MHz, CDCl_3) δ 7.35 (d, $J = 7.0$ Hz, 1H), 7.31 (td, $J = 7.5, 1.0$ Hz, 1H), 7.06 (td, $J = 7.5, 1.0$ Hz, 1H), 6.88 (d, $J = 7.5$ Hz, 1H), 3.70 (d, $J = 15.0$ Hz, 1H), 3.34 (d, $J = 15.0$ Hz, 1H), 3.24 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 178.8, 143.4, 129.7, 128.6, 125.8, 122.2, 108.5, 96.3, 60.0, 48.1, 26.9, 26.7.

Product identity was confirmed by comparison to literature spectra.^[20]

Methyl benzoate (48)



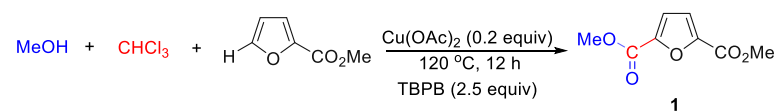
^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 3.92 (s, 3H).

Product identity was confirmed by comparison to literature spectra.^[21]

5. Optimization and additional control experiments

5.1 Optimization of alkoxycarbonylation of methyl-2-furoate

Table S1. Screening of optimal reaction conditions.



Entry	Variations from the initial conditions ^[a]	Yield [%] ^[b]
1	none	80
2	MeOH (2.5 equiv)	74
3	MeOH (12.5 equiv)	33
4	MeOH (40 equiv)	15
5	methyl-2-furoate (0.25 M)	75
6	methyl-2-furoate (0.2 M)	68
7	without TBPB	0
8	without Cu(OAc) ₂	54
9	CuOAc instead of Cu(OAc) ₂	72
10	CuBr instead of Cu(OAc) ₂	71
11	Cu(acac) ₂ instead of Cu(OAc) ₂	80
12	Fe(acac) ₂ instead of Cu(OAc) ₂	25
13	Ni(acac) ₂ instead of Cu(OAc) ₂	27
14	Pd(OAc) ₂ instead of Cu(OAc) ₂	0
15	Mn(OAc) ₂ instead of Cu(OAc) ₂	14
16	TBPB (1.5 equiv)	44
17	TBPB (3.5 equiv)	78
18	K ₂ S ₂ O ₈ instead of TBPB	0
19	DCP instead of TBPB	0
20	BPO instead of TBPB	74
21	DTBP instead of TBPB	16
22	TBHP instead of TBPB	0
23	at 110 °C	68
24	at 130 °C	79
25	Cu(OAc) ₂ (0.1 equiv)	66
26	Cu(OAc) ₂ (0.4 equiv)	57
27	CHCl ₃ (6 equiv, 150 uL), PhCl as solvent (0.3 M)	39

Abbreviation: TBPB, *tert*-butyl perbenzoate. DCP, dicumyl peroxide. BPO, dibenzoyl peroxide. DTBP, di-*tert*-butyl peroxide. TBHP, *tert*-butyl hydroperoxide.

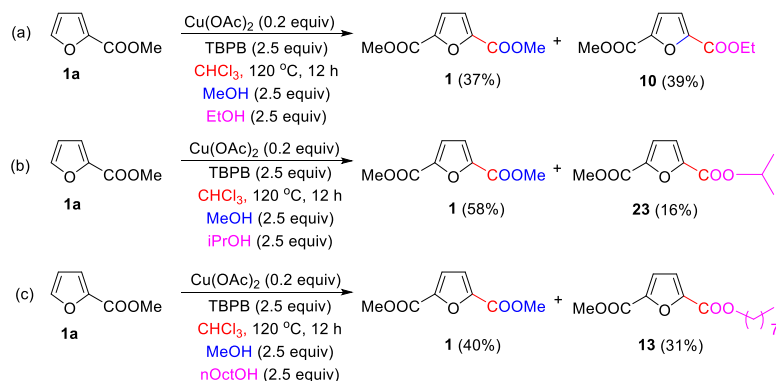
[a] Initial condition: methyl-2-furoate (0.3 mmol, 1 equiv, 0.3 M), MeOH (7.5 equiv), Cu(OAc)₂ (0.2 equiv), TBPB (2.5 equiv), CHCl₃, 120 °C, 12 h, under air. [b] Isolated yield.

5.2 Competition and kinetic isotope effect experiments

The reactivity of different type alcohols was evaluated by several competition experiments. Reactions were performed on a 0.3 mmol scale in CHCl₃ (0.3 M). First, Submission of equal equivalent of methanol and ethanol led to the corresponding α -alkoxycarbonylation products (**1** and **10**) in 37% and 39% yields, respectively (Scheme S1a). Second, methanol and isopropanol were tested in the same way, which gave product **1** in 58% yield and product **23** in 16% yield (Scheme S1b). Last, when different lengths of carbon chain of primary alcohols were added in reaction,

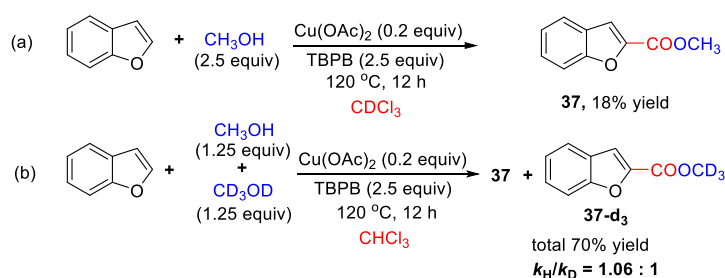
methanol and octanol reacted to give the desired product **1** and product **13** in 40% and 31% yield, respectively (Scheme S1c). The above results indicate that the alcohols with different carbon chain lengths are less influence of reaction, but its steric hindrance has a greater influence on the reaction.

Scheme S1. Competition experiments.



As shown in Scheme S2, the kinetic isotope effect of this reaction was evaluated by several experiments. Reactions were performed on a 0.3 mmol scale in CHCl_3 or CDCl_3 (0.3 M). Reaction in deuterated chloroform instead of chloroform gave **37** in a low yield (18%), with most of the reactant **a37** remaining unconsumed (Scheme S2a). And reaction in the presence of an equimolar mixture of CD_3OD and CH_3OH showed an intermolecular kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.06$), suggesting that cleavage of the $\text{C}(\text{sp}^3)\text{--H}$ bond of chloroform was involved in the rate-determining step (Scheme S2b).

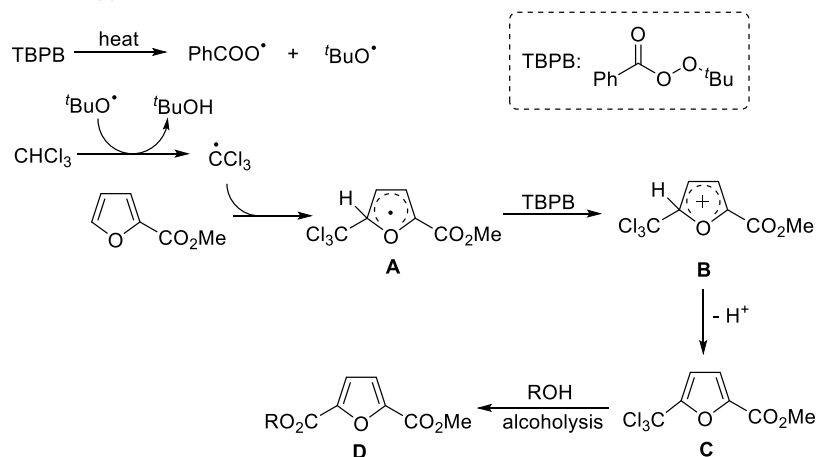
Scheme S2. Kinetic isotope effect experiment.



6. Other possible mechanism

In the absence of copper, possible mechanism is shown in Scheme S2. Firstly, homolytic cleavage of TBPB forms *tert*-butoxyl radical and benzoyloxy radical under heat. Secondly, *tert*-butoxyl radical abstracts the hydrogen atom of CHCl_3 to generate CCl_3 radical. Subsequent CCl_3 radical addition of methyl-2-furoate generates delocalized radical intermediate **A**, followed by the oxidation of TBPB to carbocation **B** at high temperature. Then, the aromatization-driven deprotonation carries out to afford intermediate **C**. Eventually, intermediate **C** forms target product **D** by alcoholysis.

Without copper:



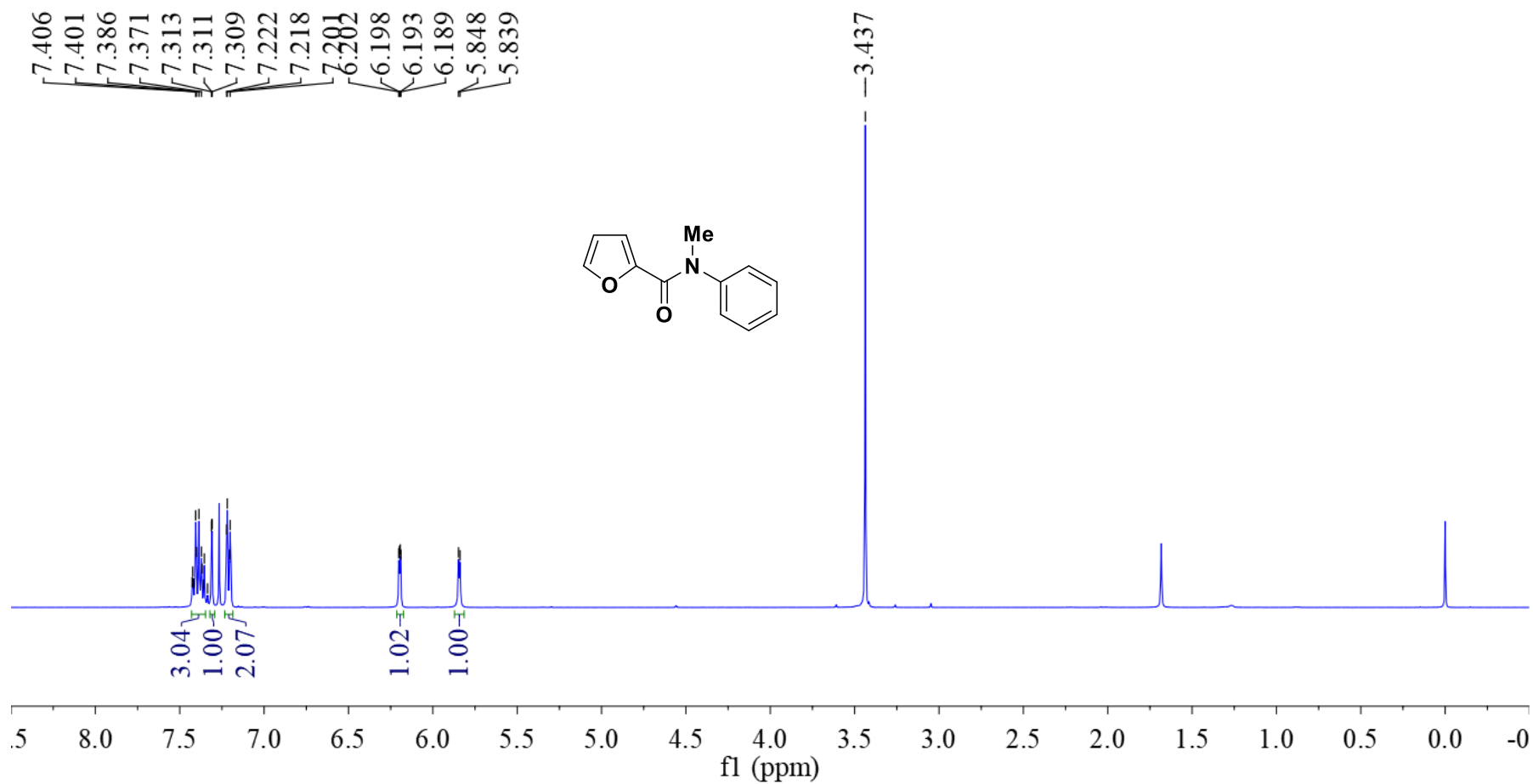
Scheme S2. possible mechanism in the absence of copper.

7. References

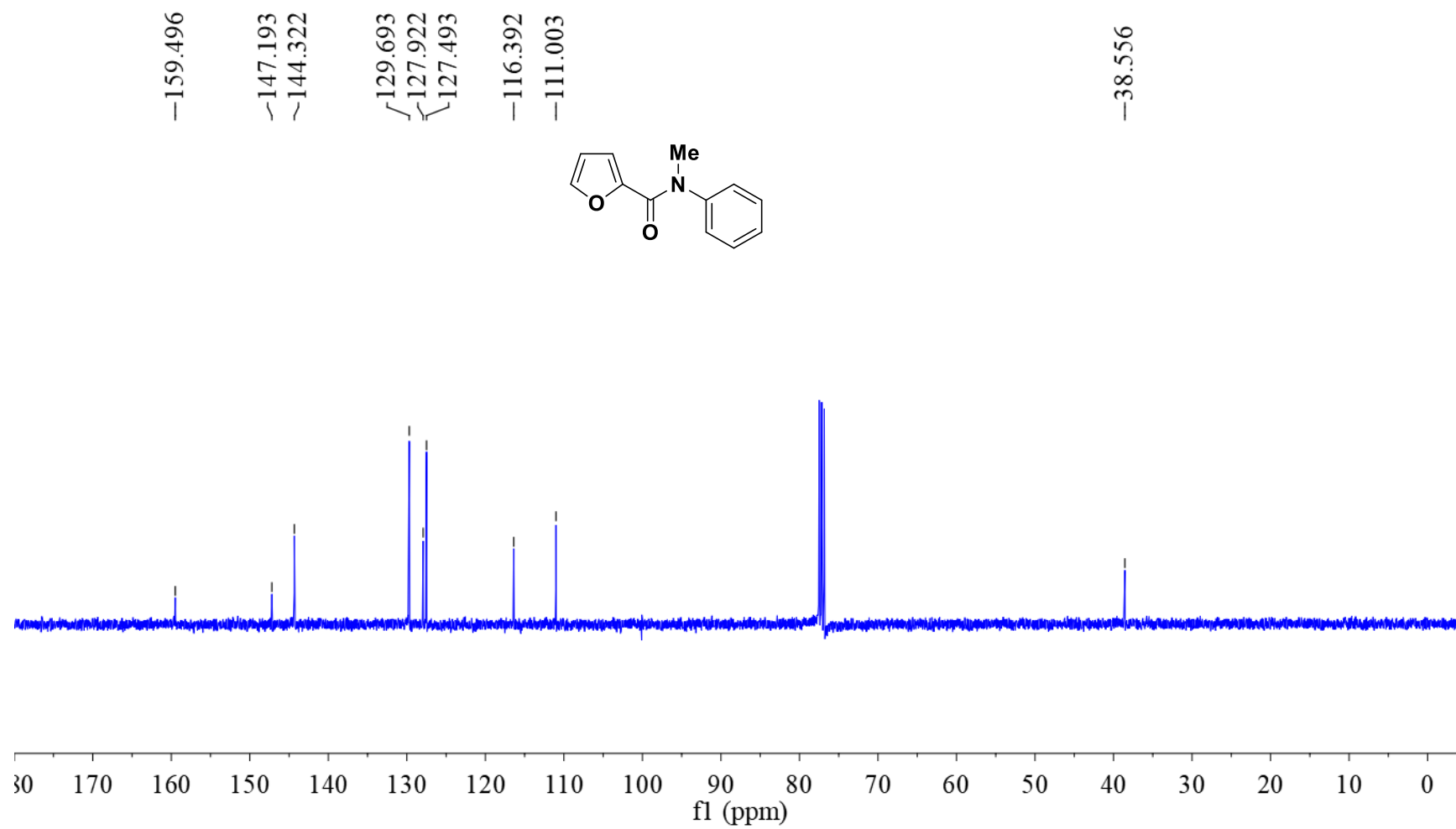
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8. Copies of ^1H and ^{13}C NMR spectra of starting materials

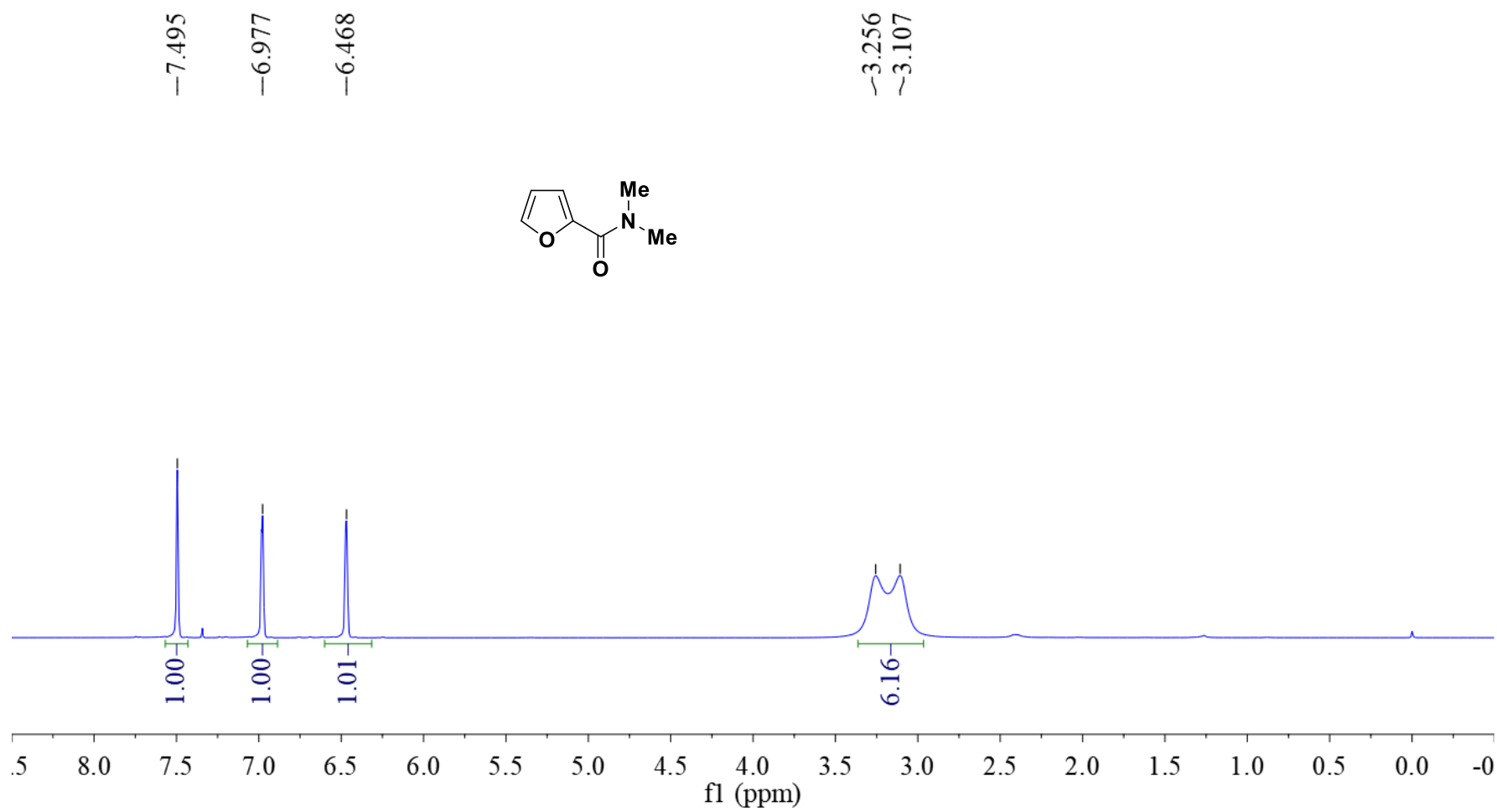
N-methyl-*N*-phenylfuran-2-carboxamide (a25)



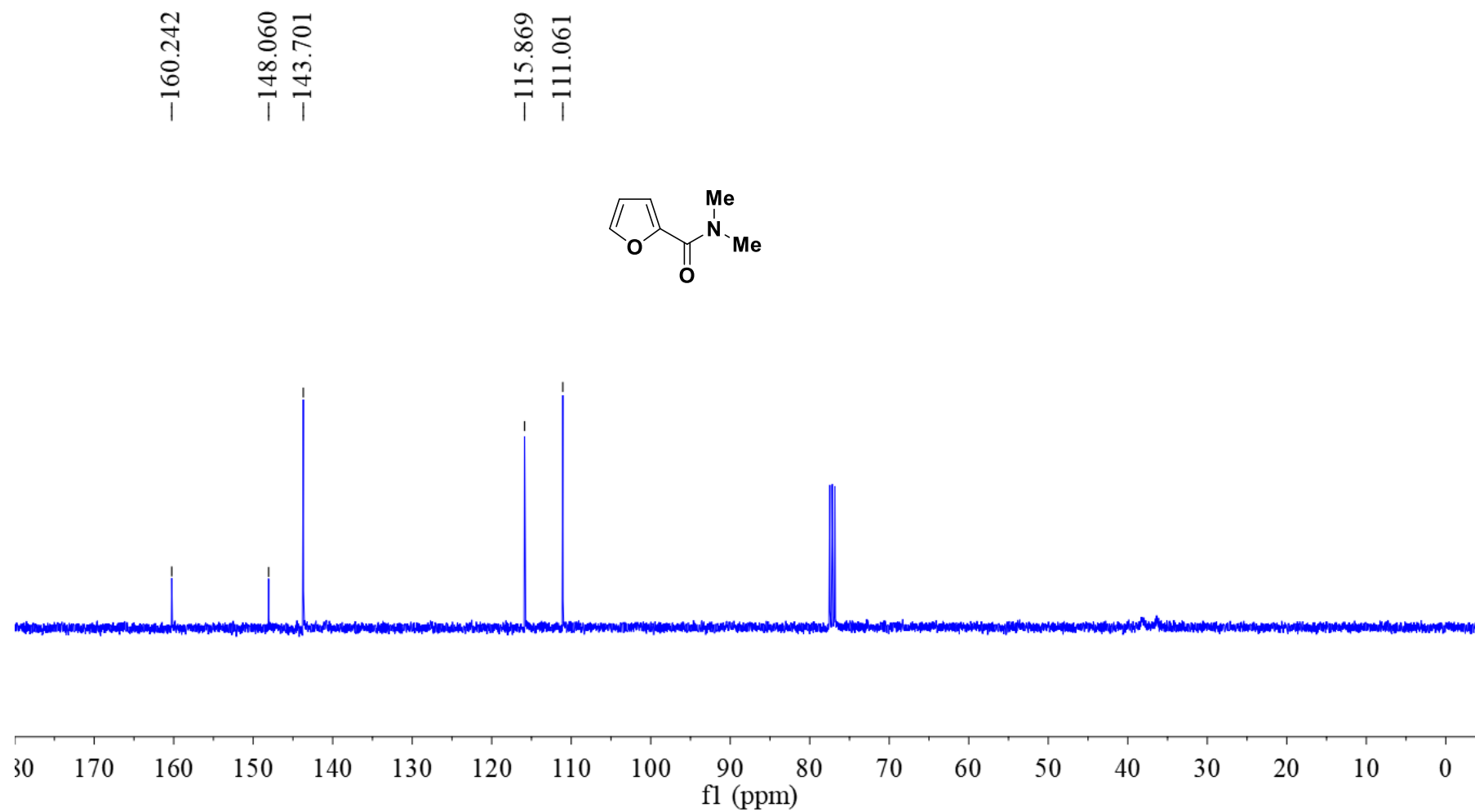
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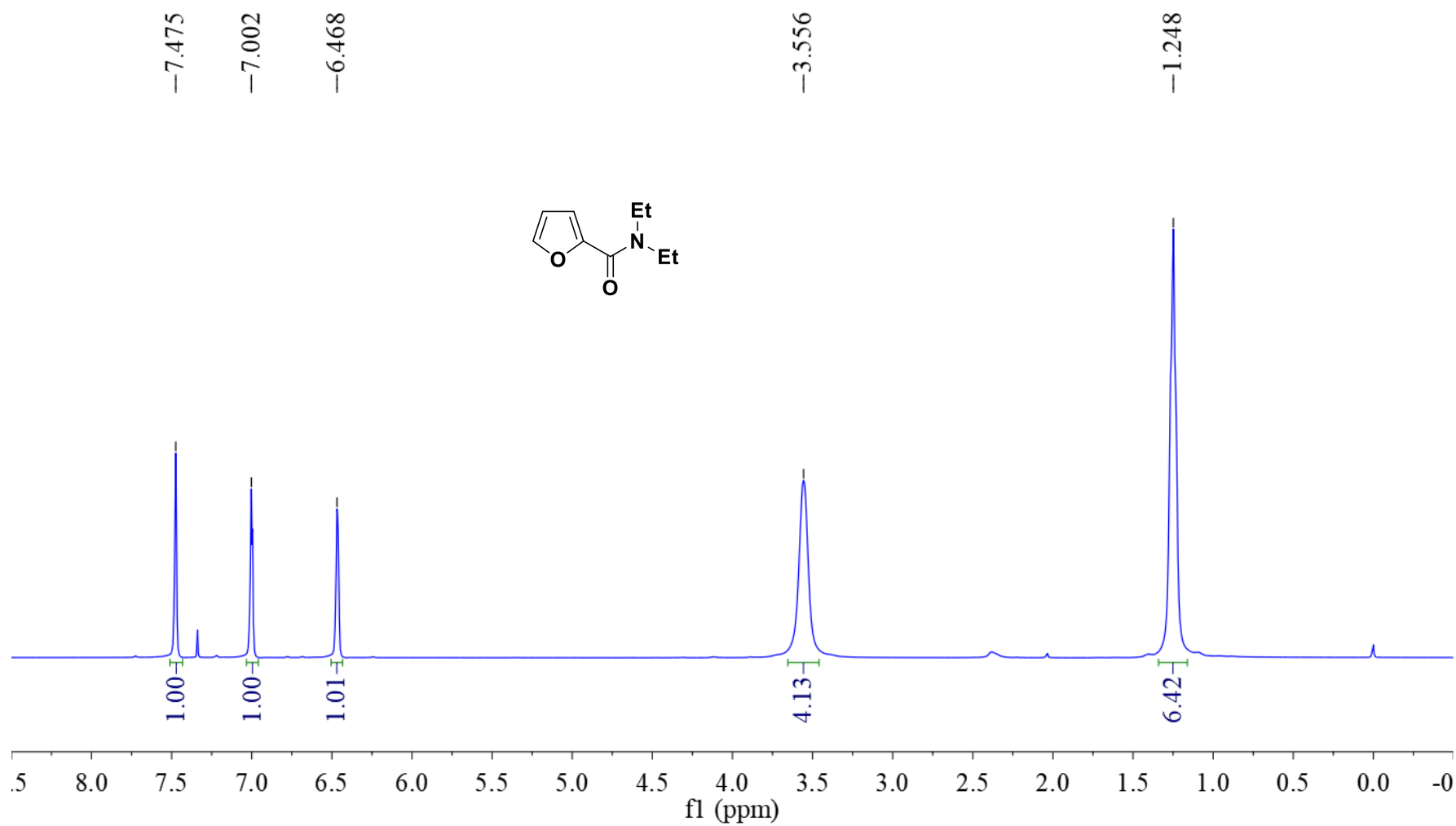
N,N-dimethylfuran-2-carboxamide (a28)



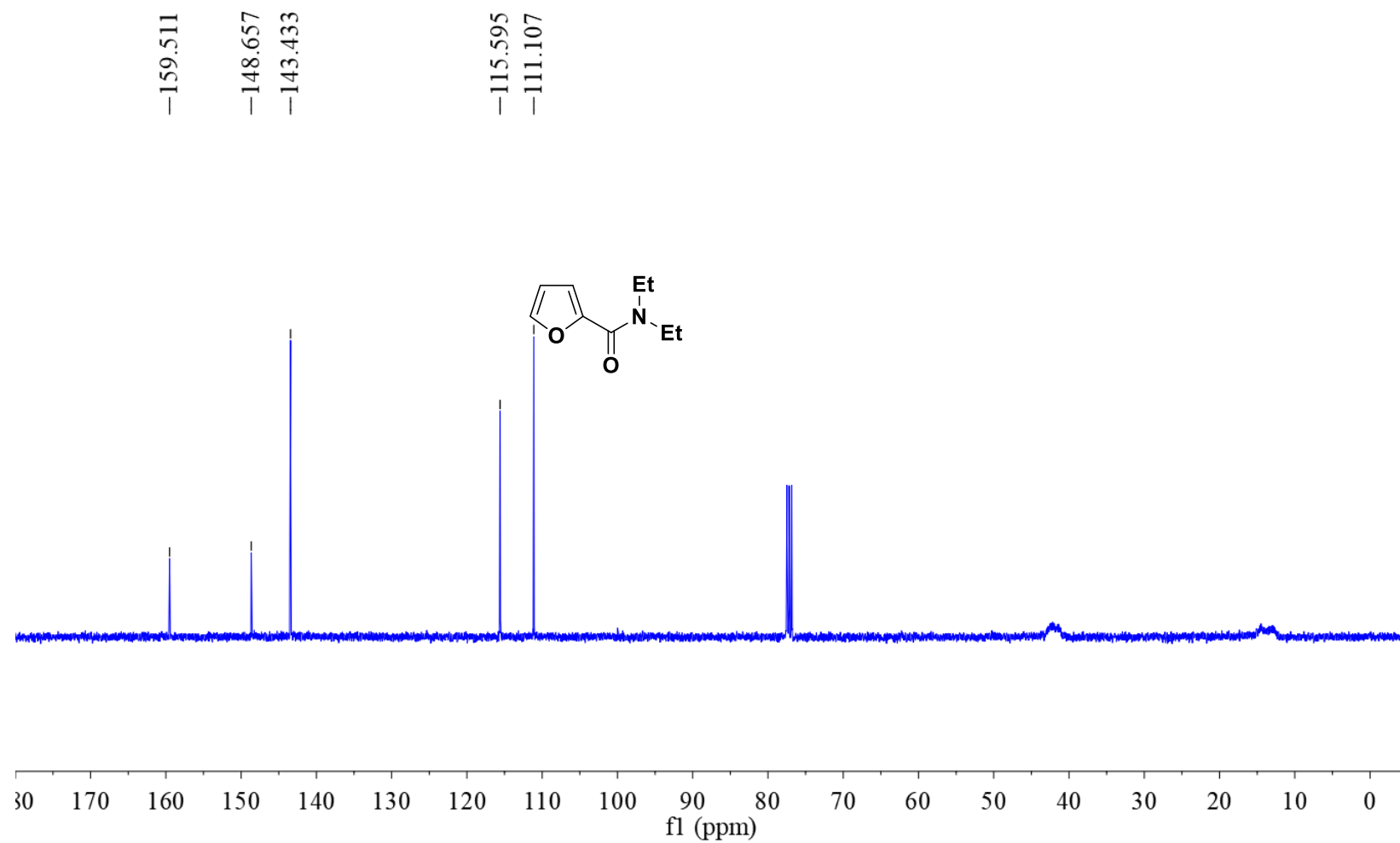
N,N-dimethylfuran-2-carboxamide (a28)



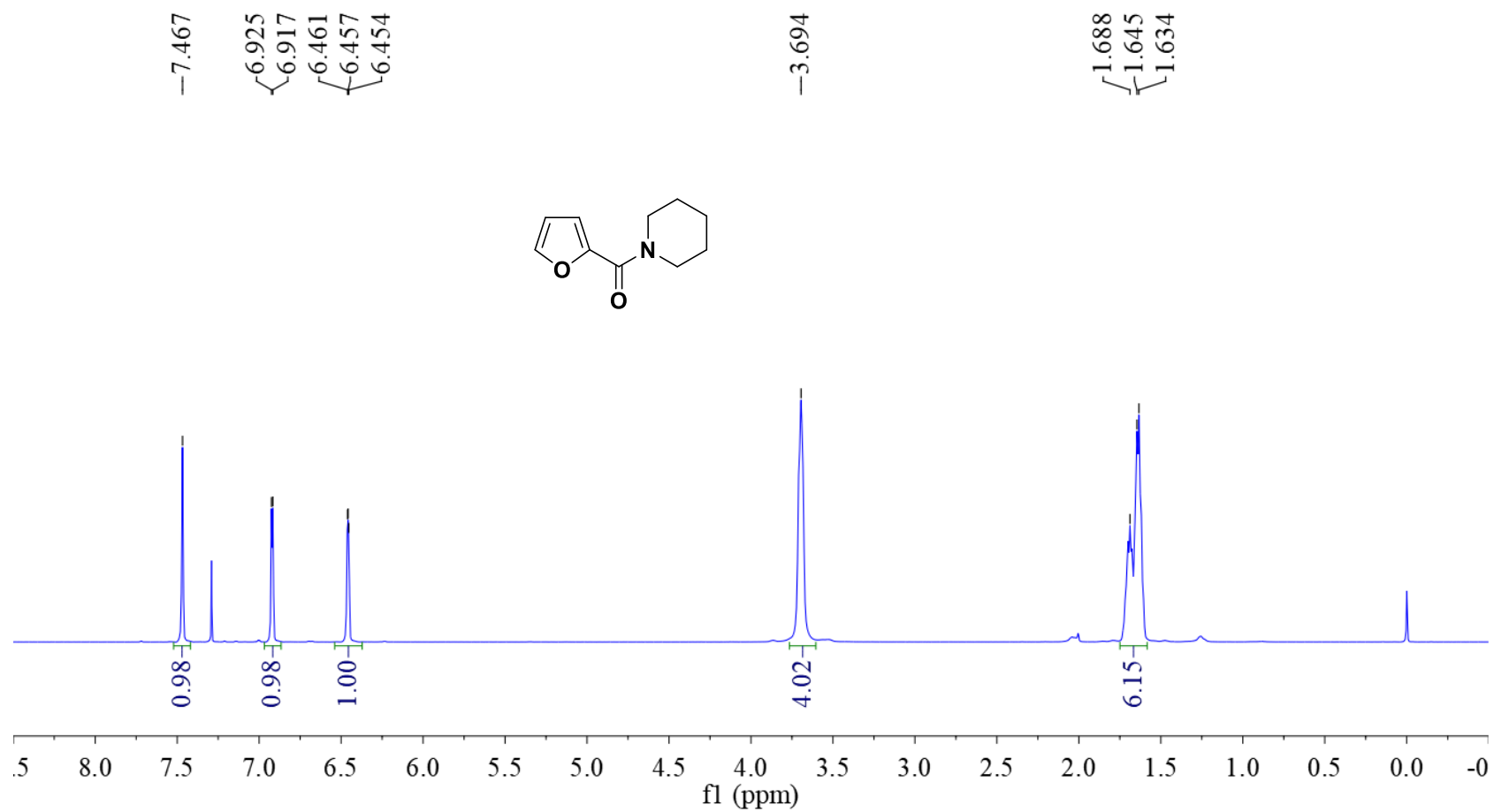
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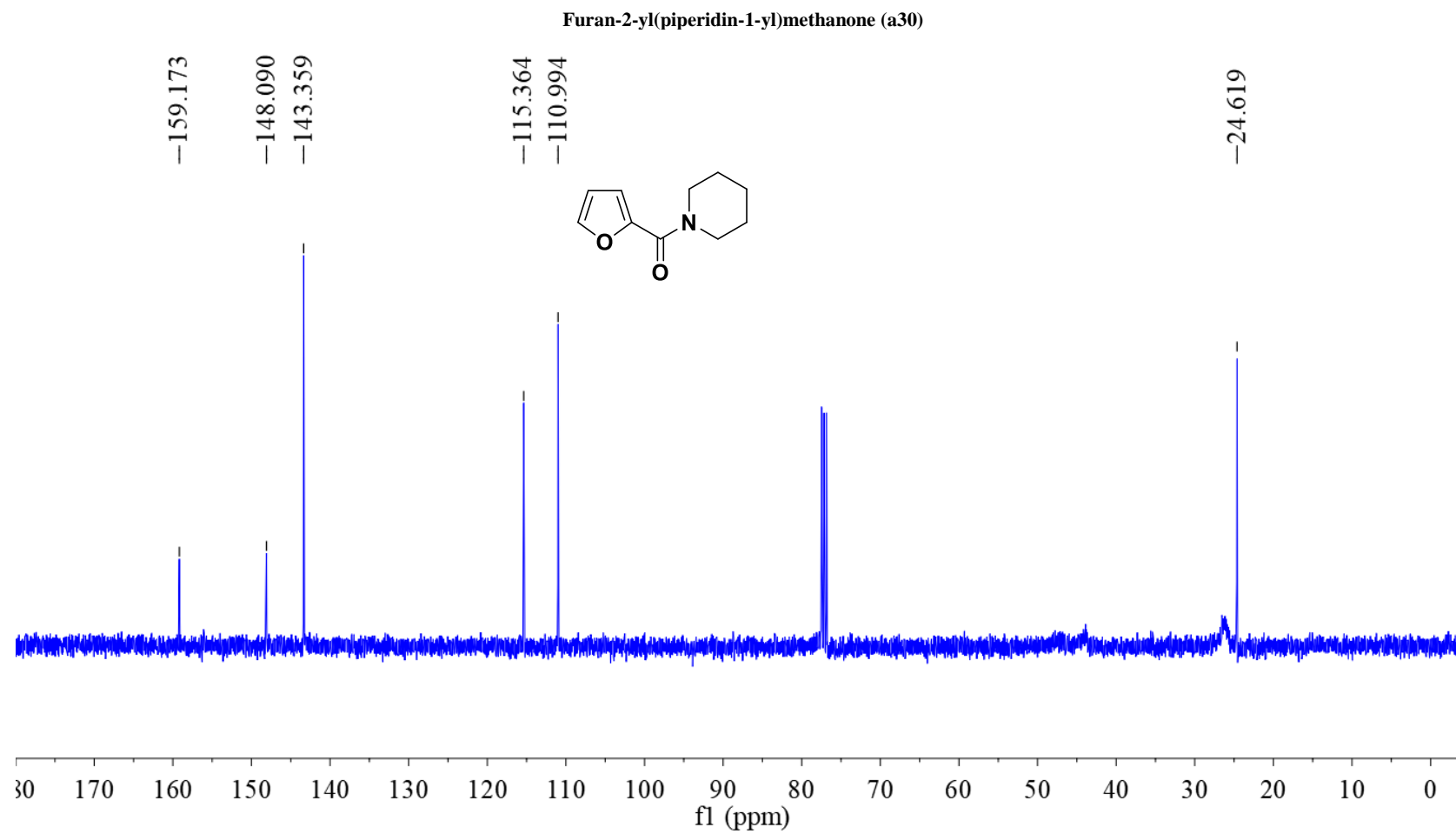


N,N-diethylfuran-2-carboxamide (a29)

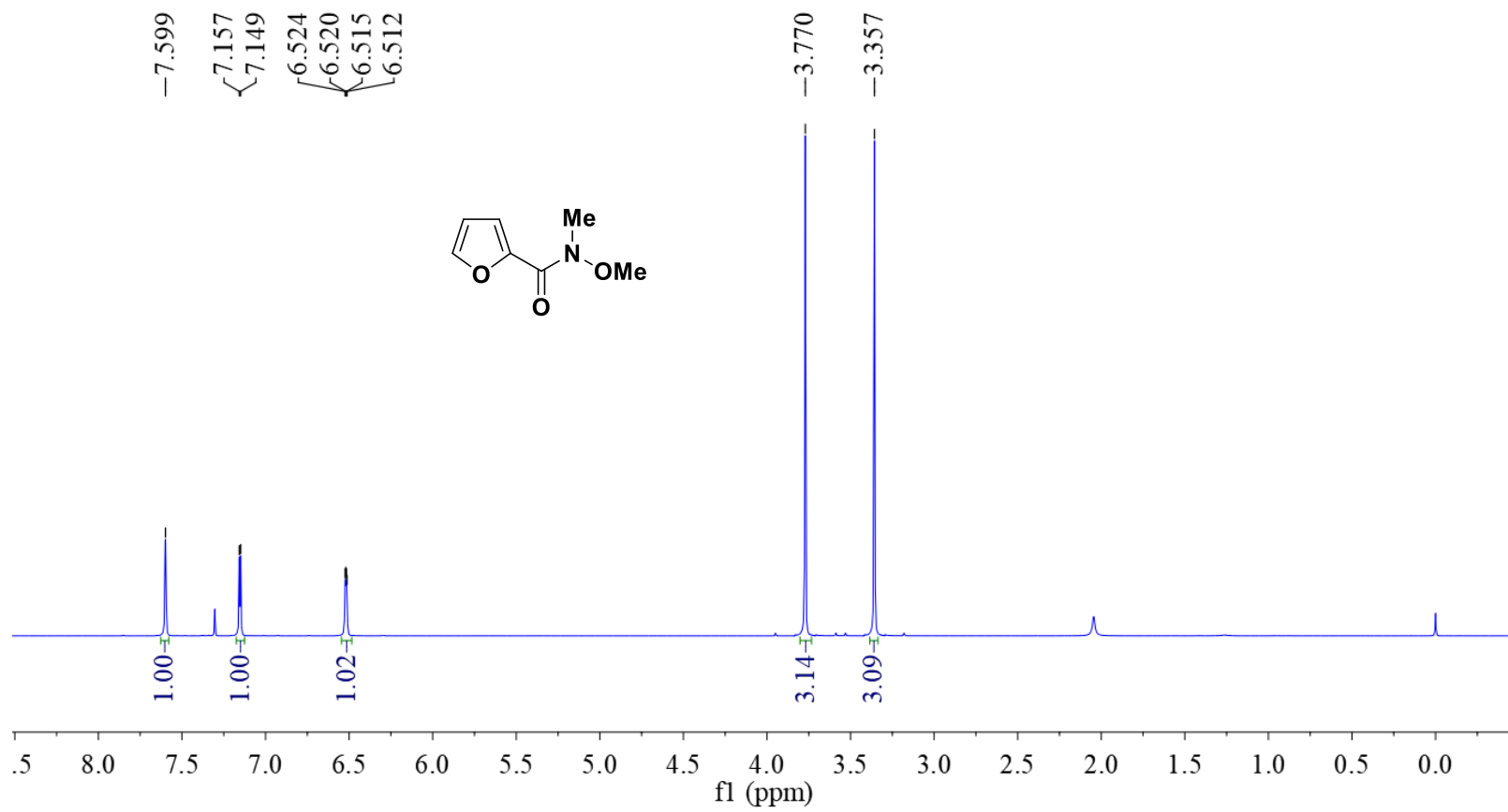


Furan-2-yl(piperidin-1-yl)methanone (a30)

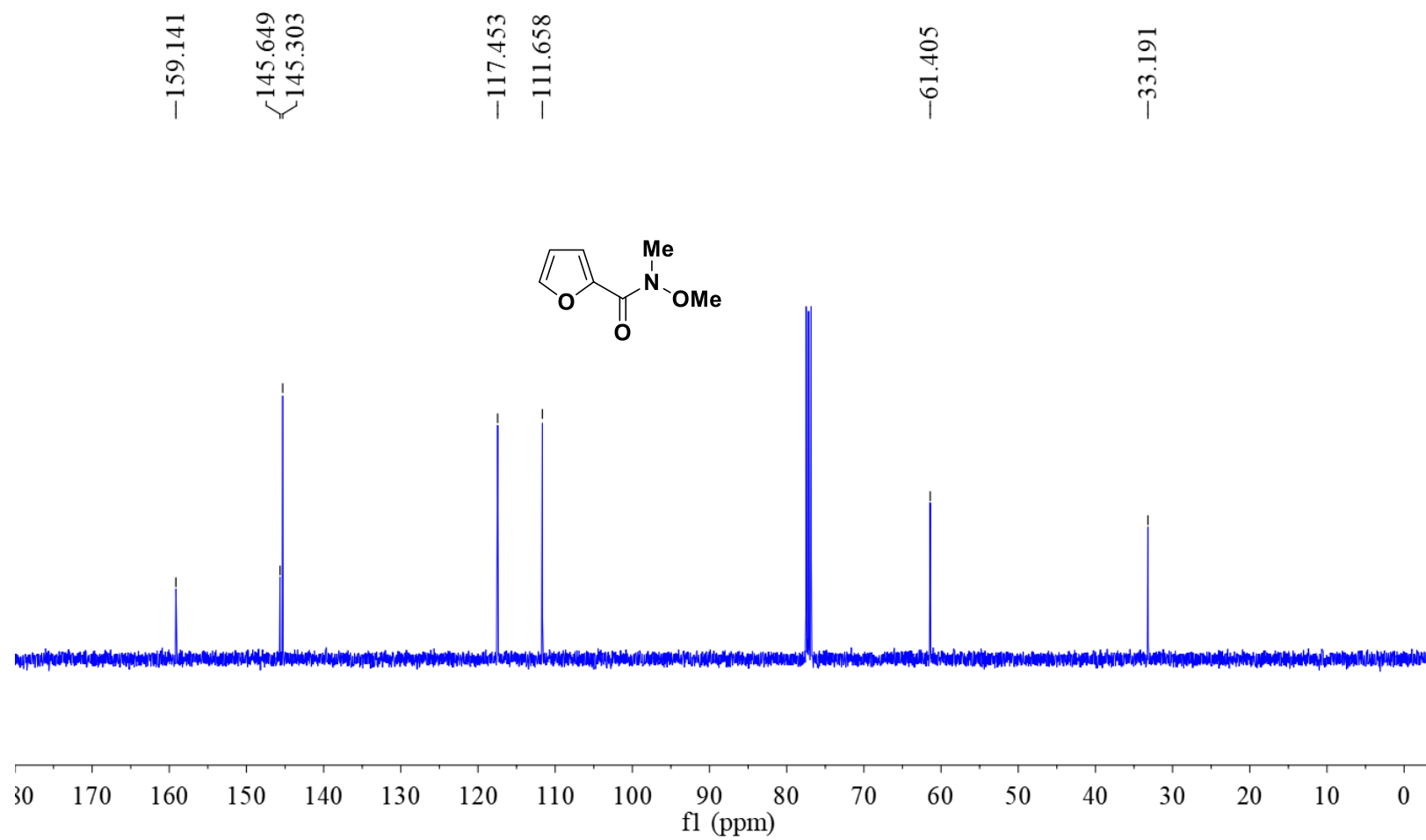




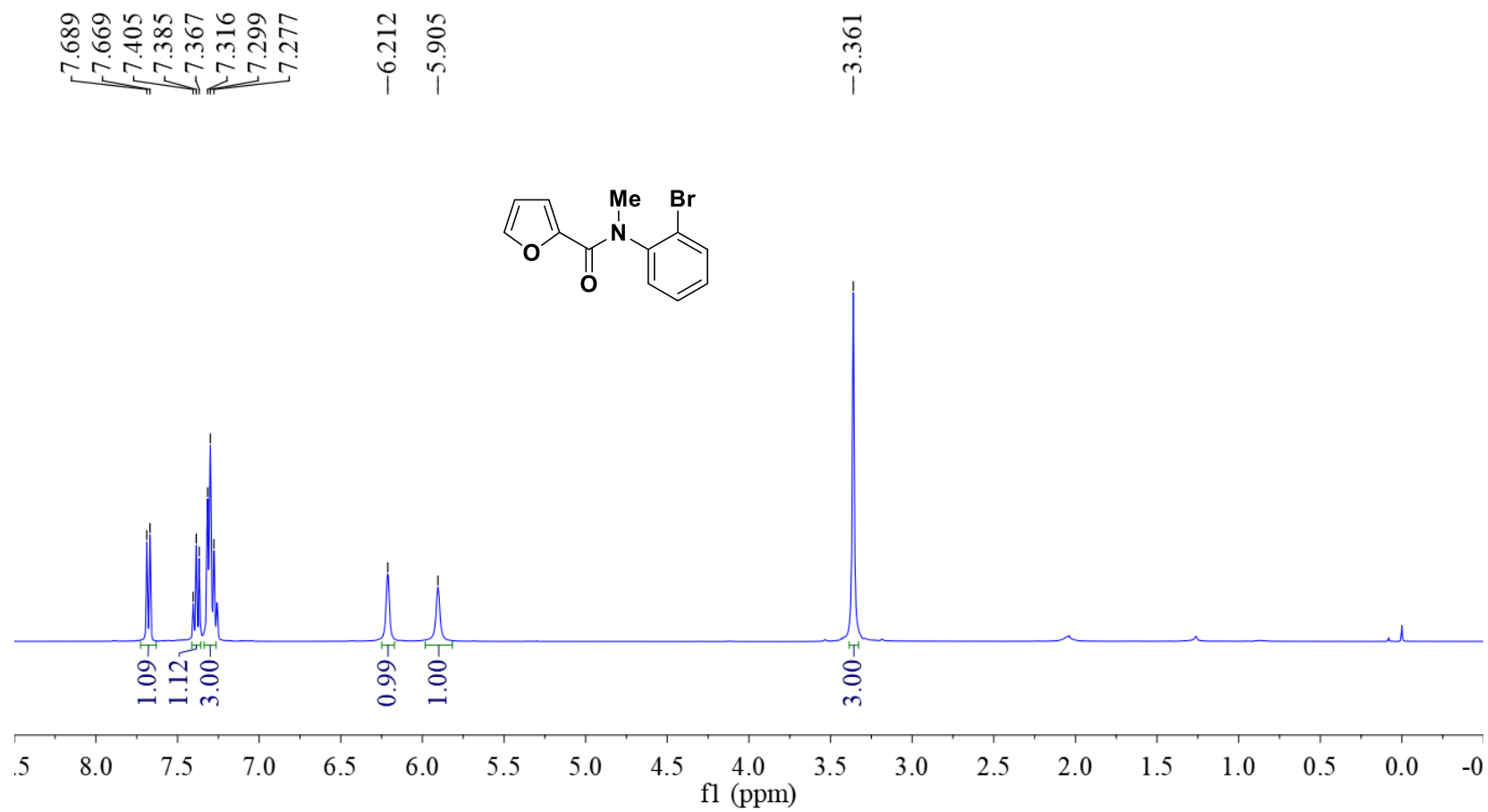
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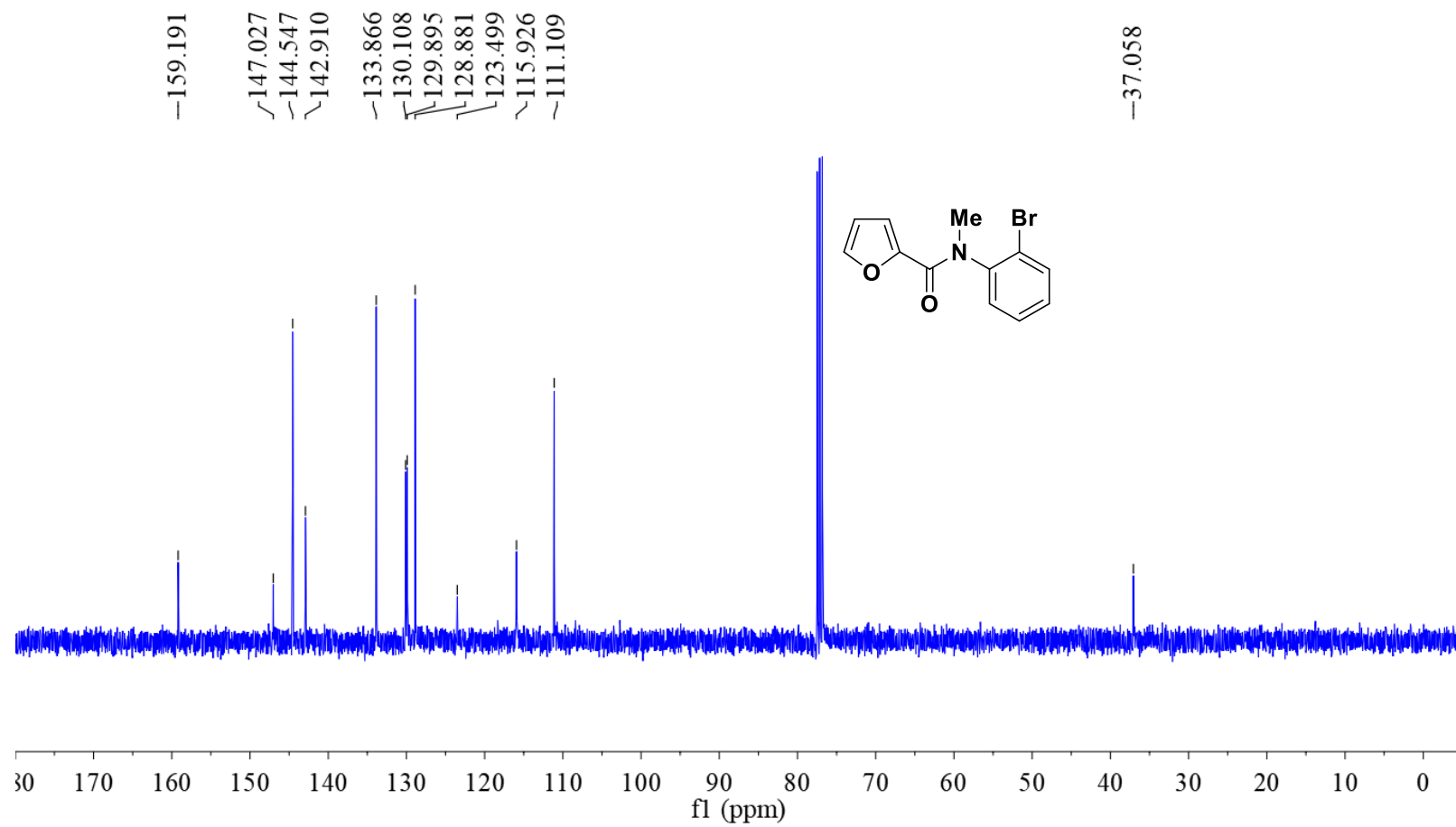
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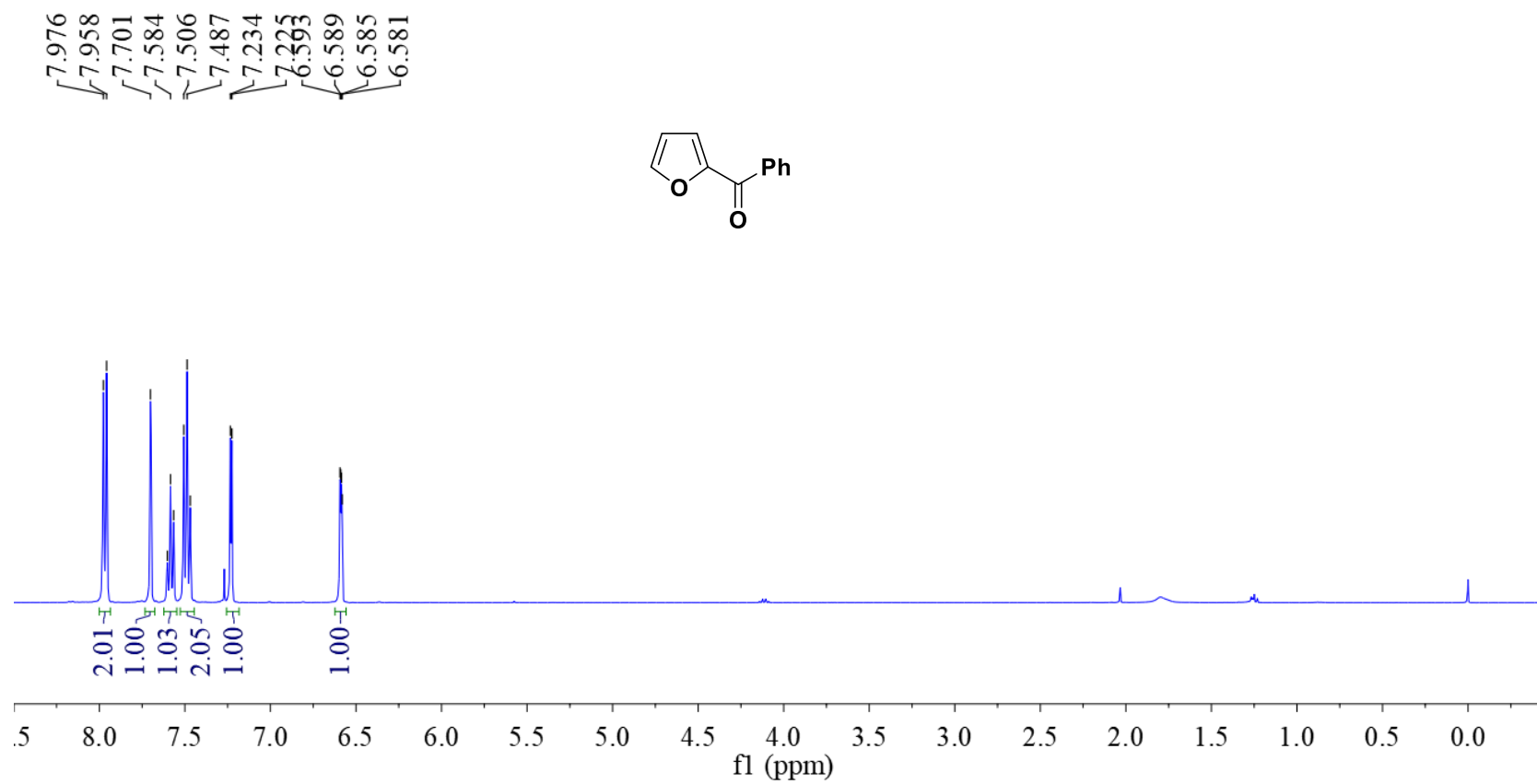
N-(2-bromophenyl)-*N*-methylfuran-2-carboxamide (a26)



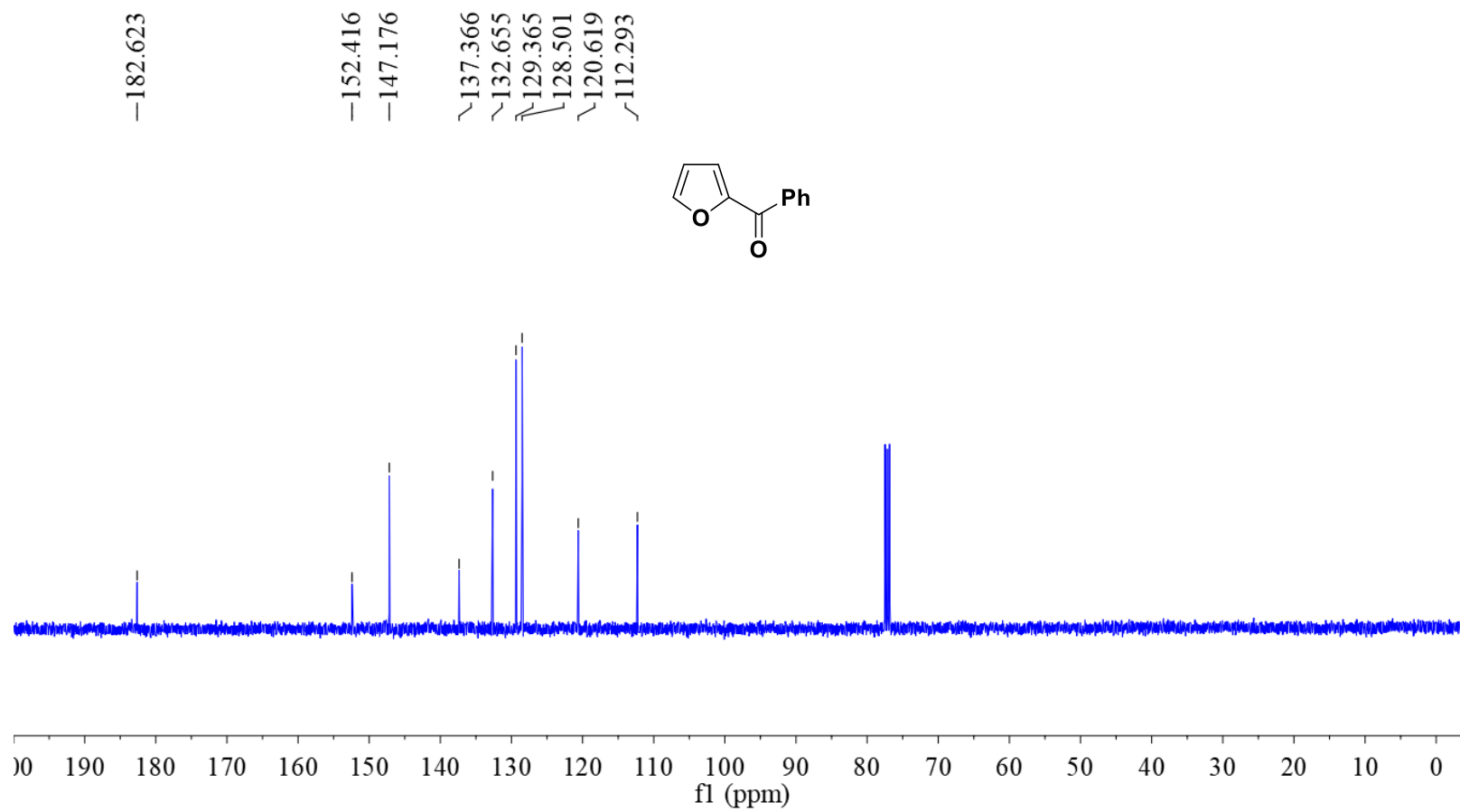
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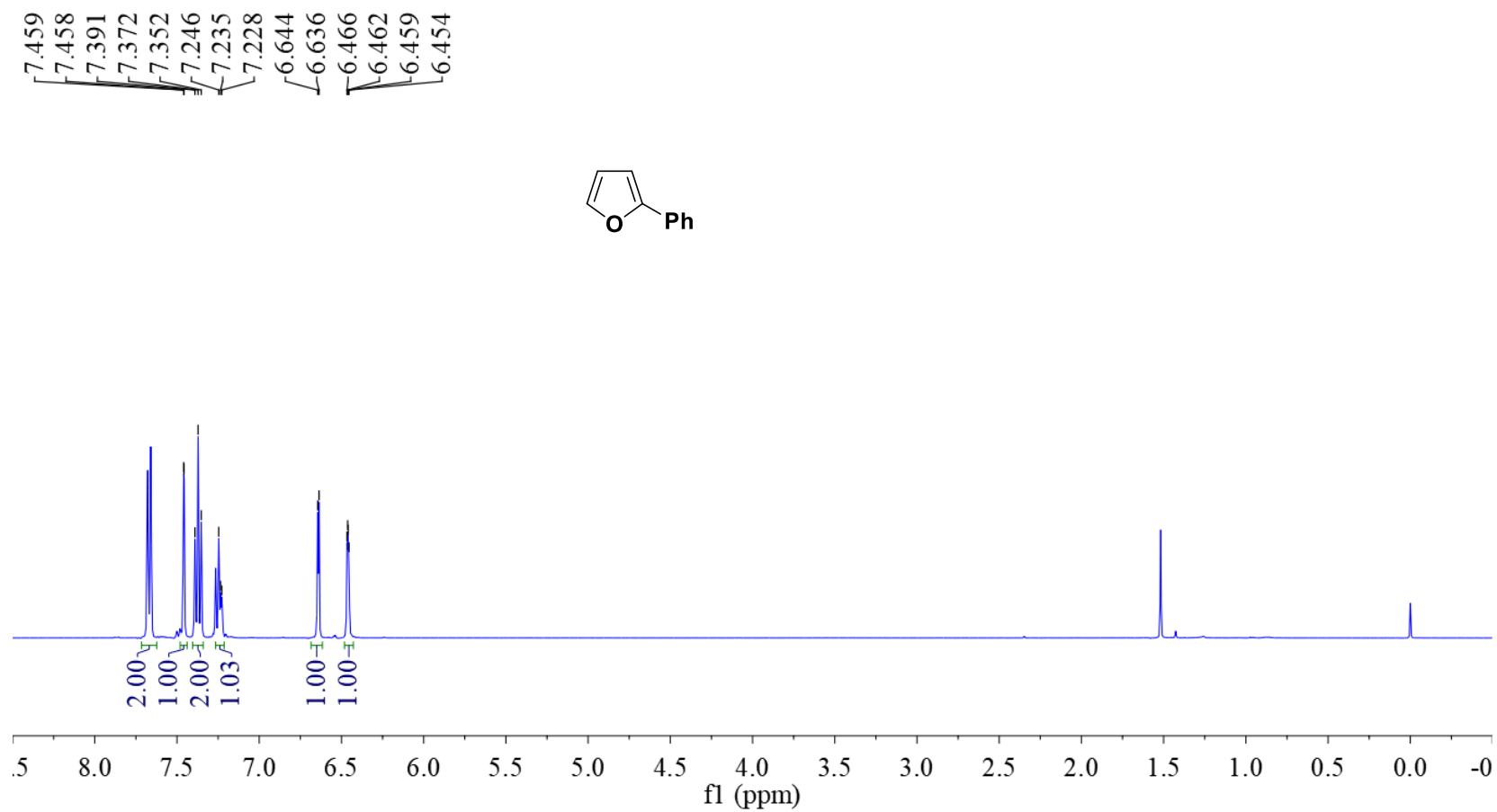
Furan-2-yl(phenyl)methanone (a32)



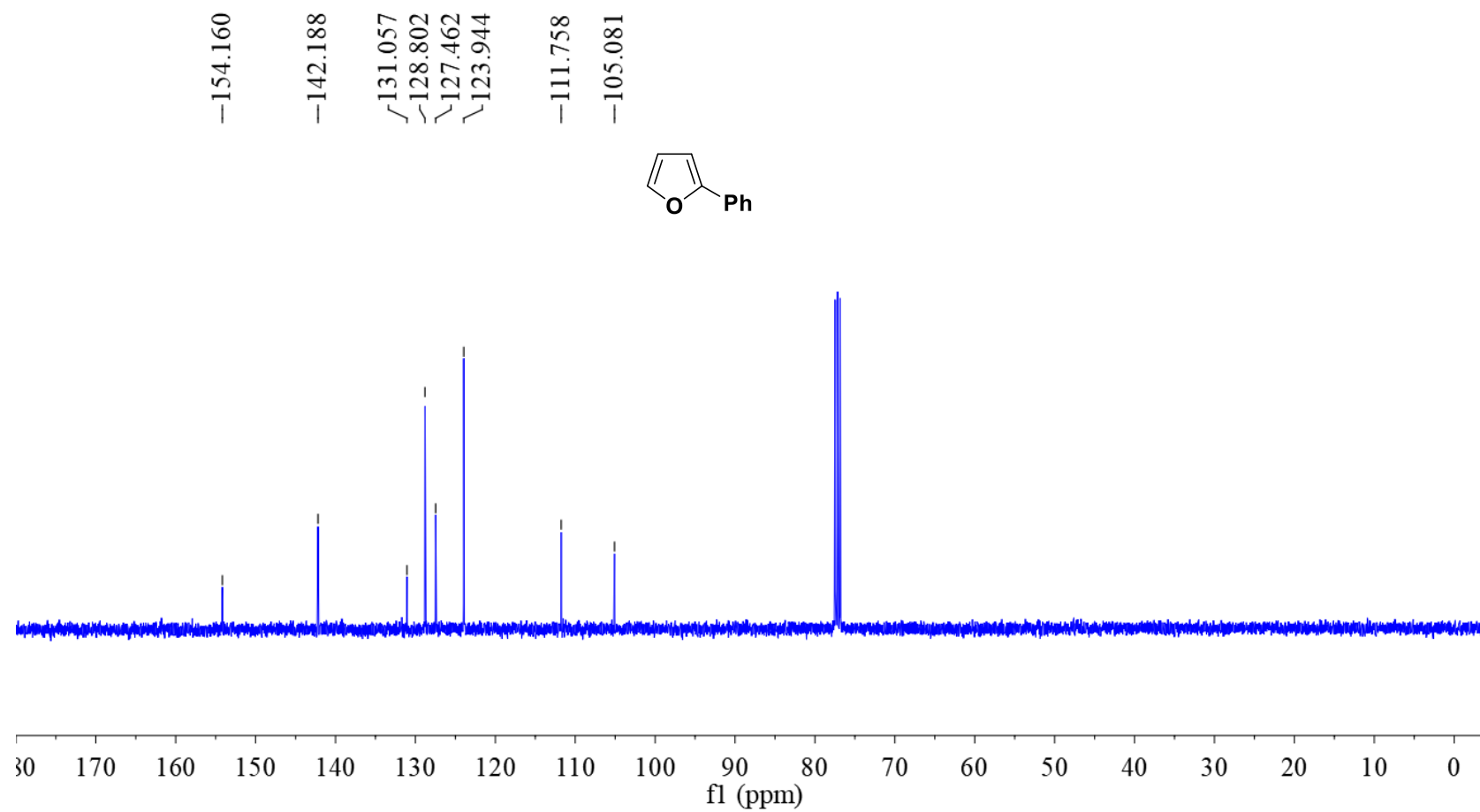
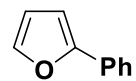
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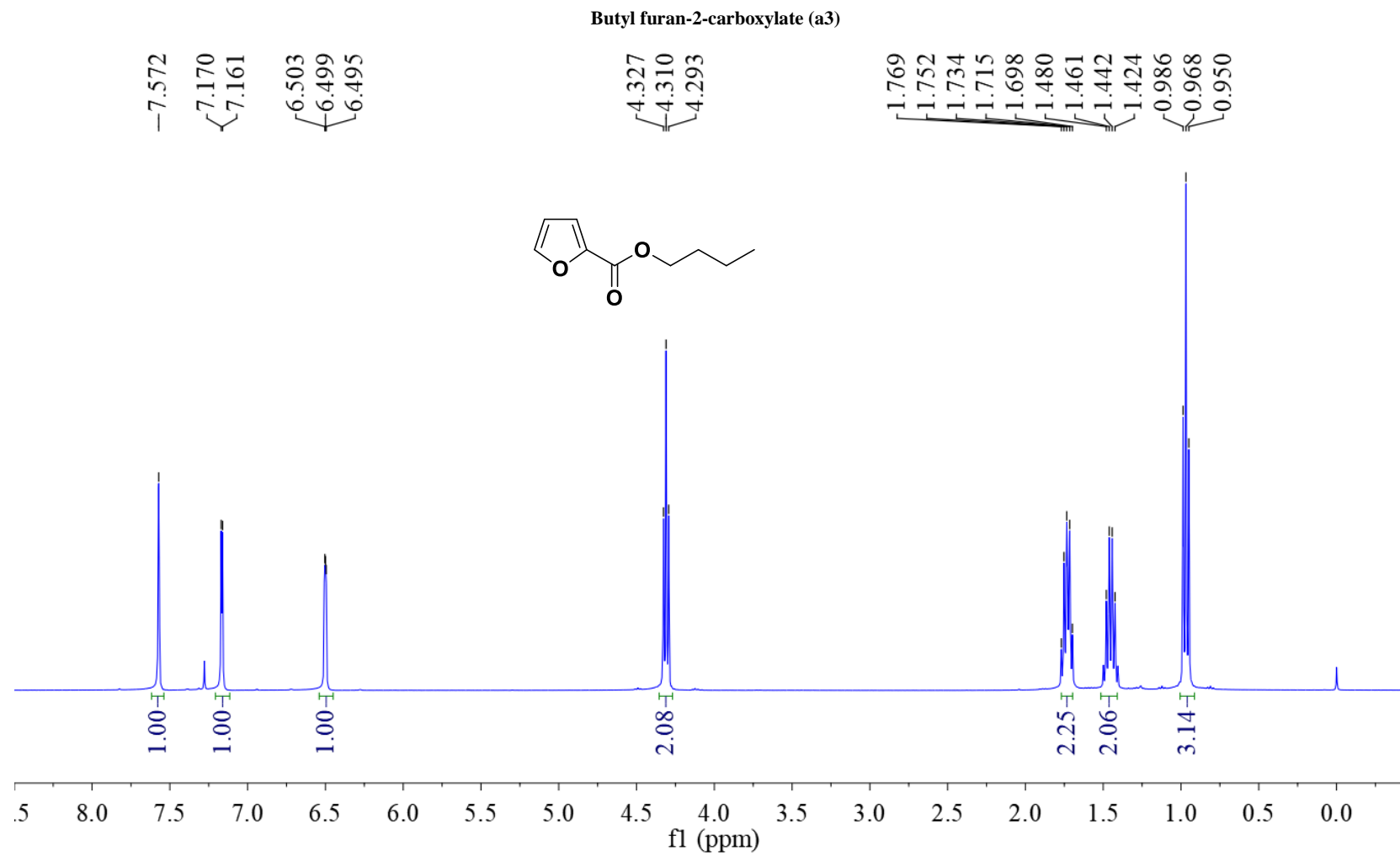


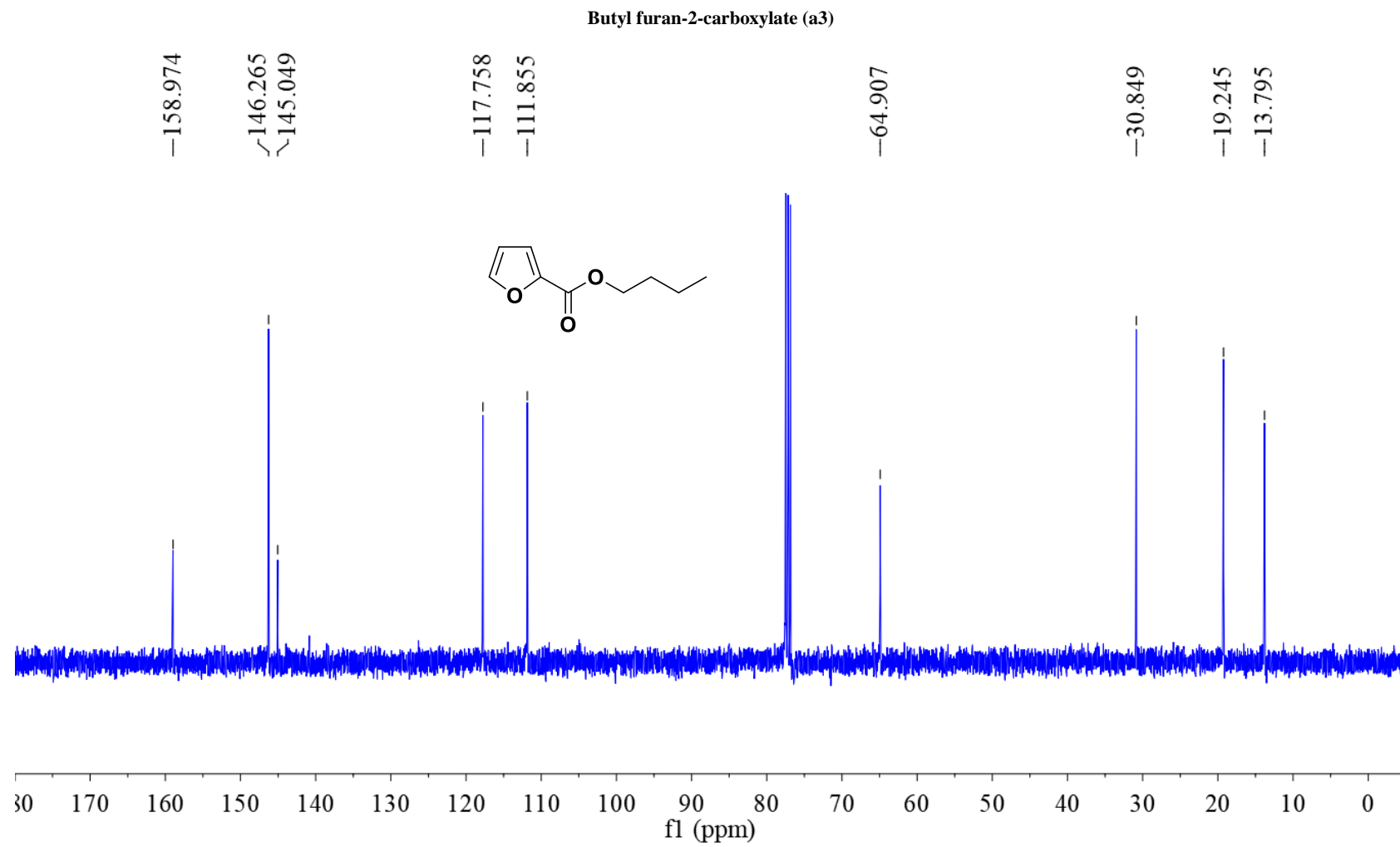
2-phenylfuran (a33)



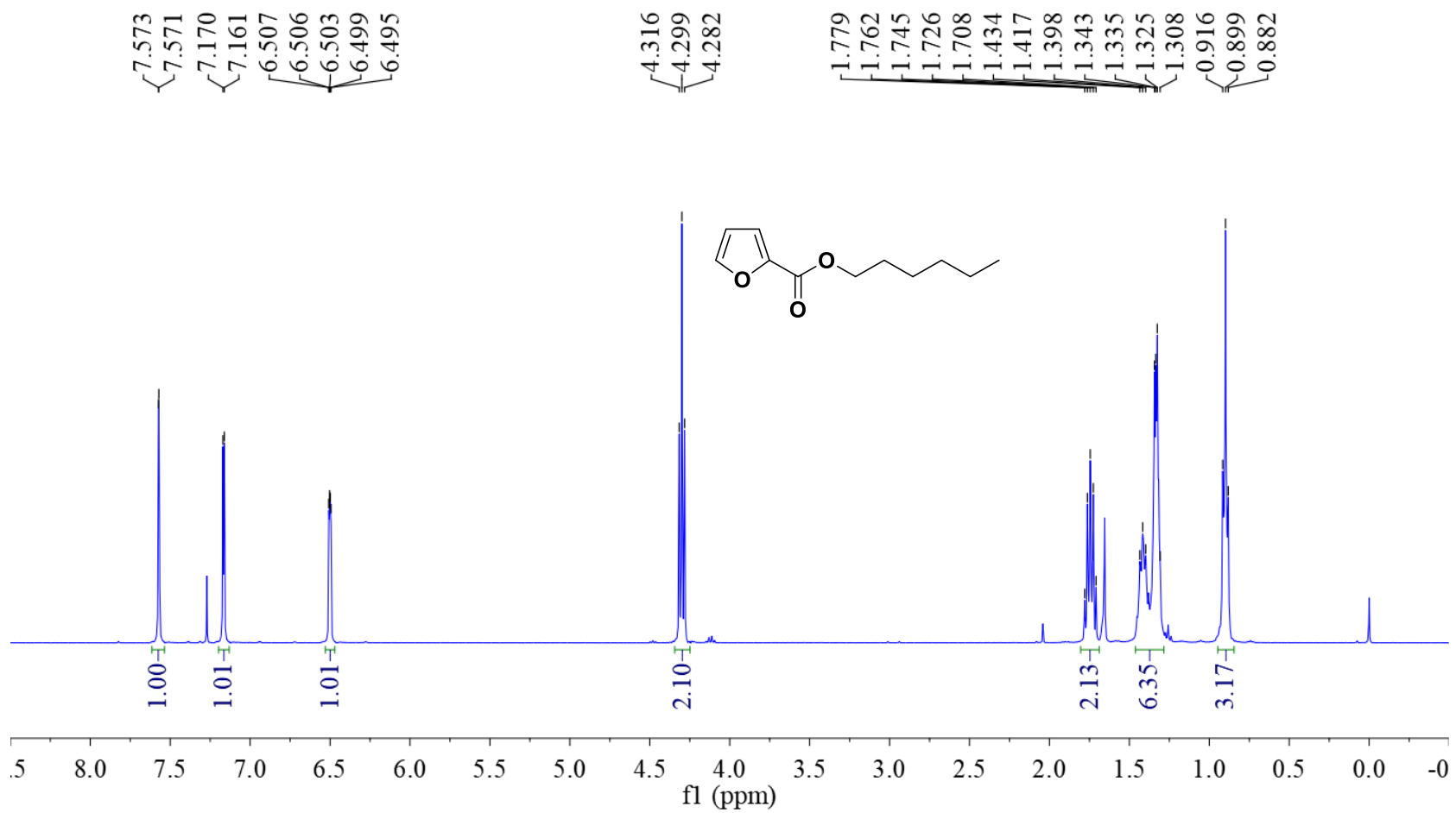
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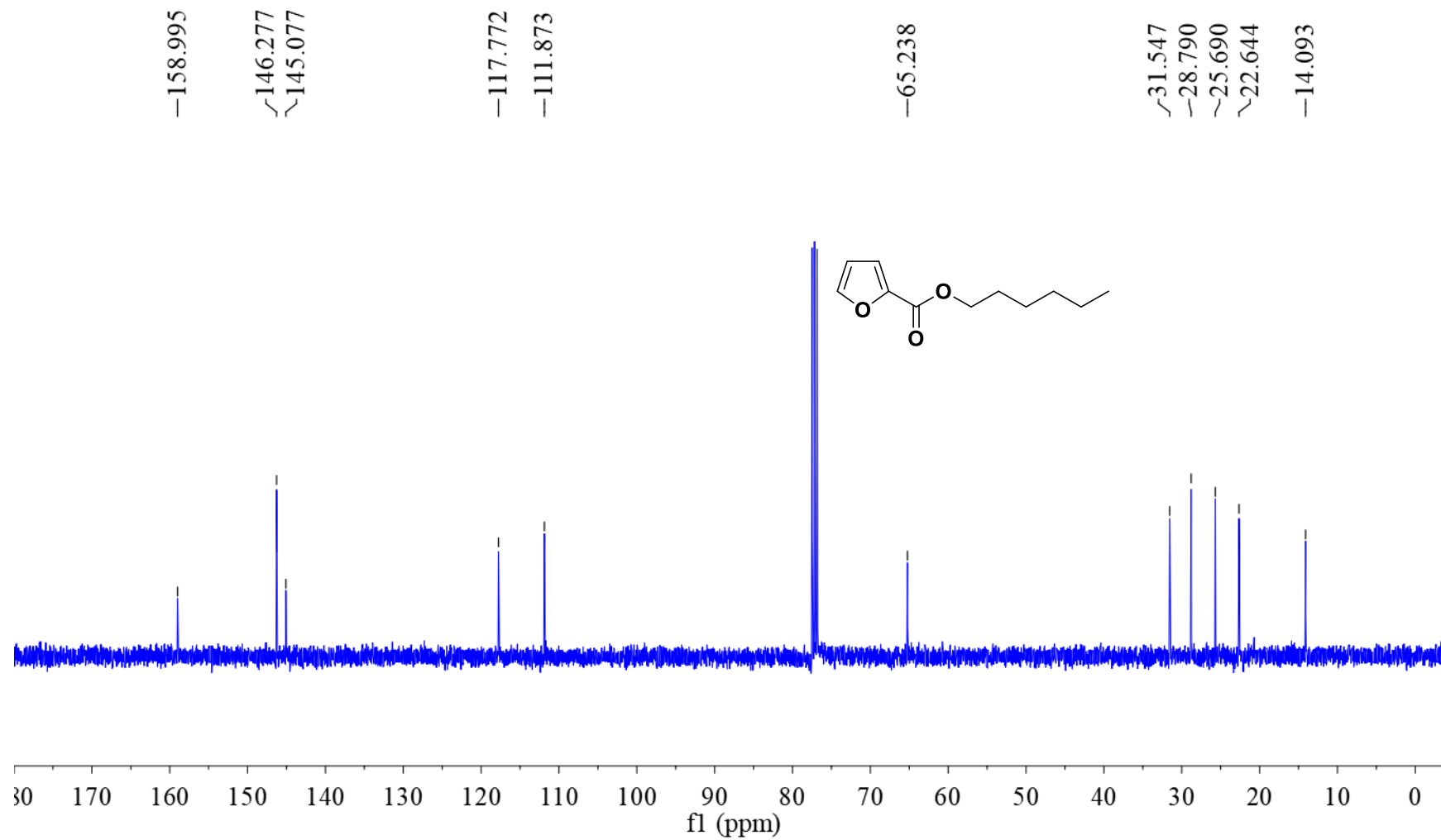




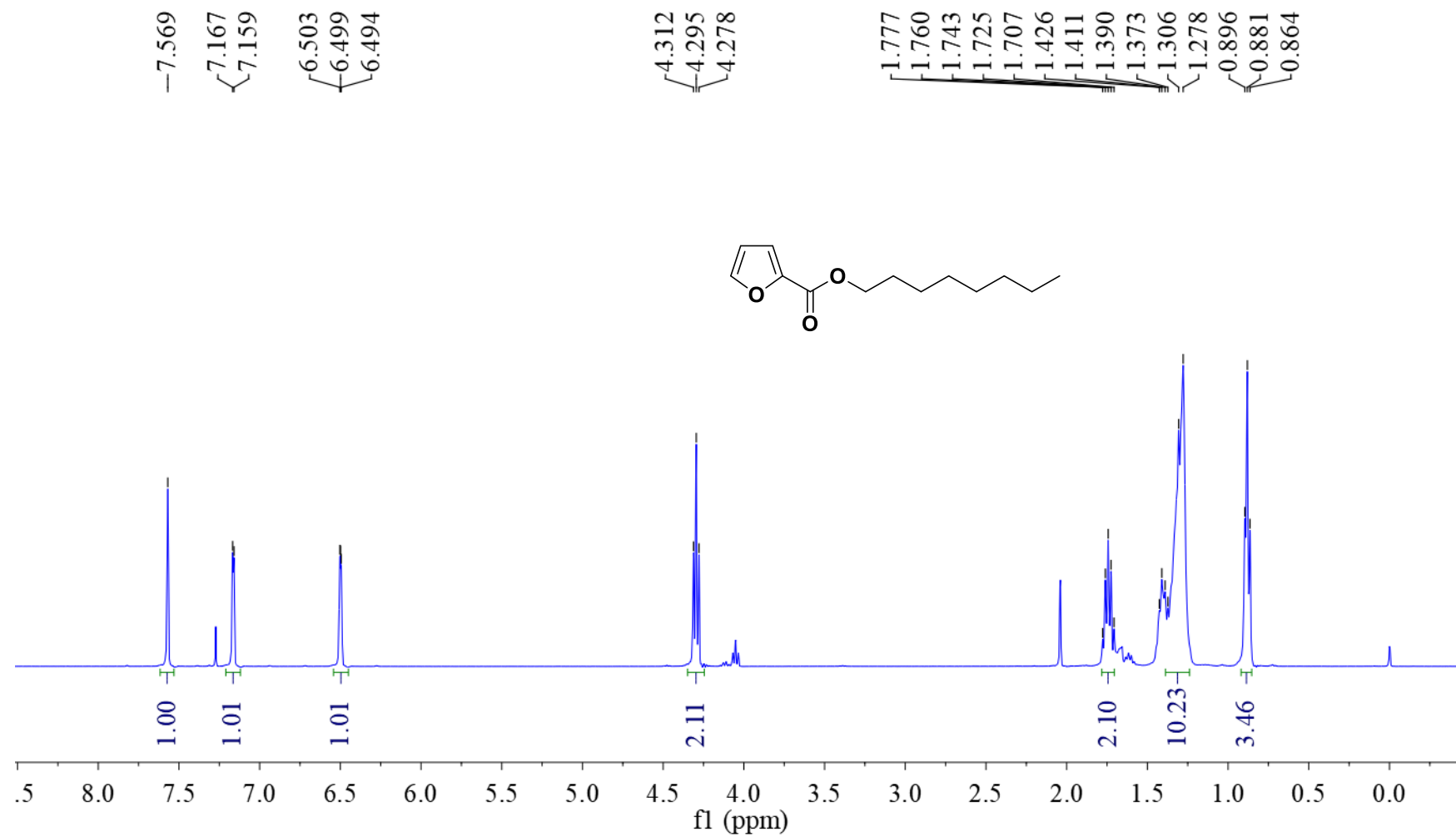
Hexyl furan-2-carboxylate (a10)



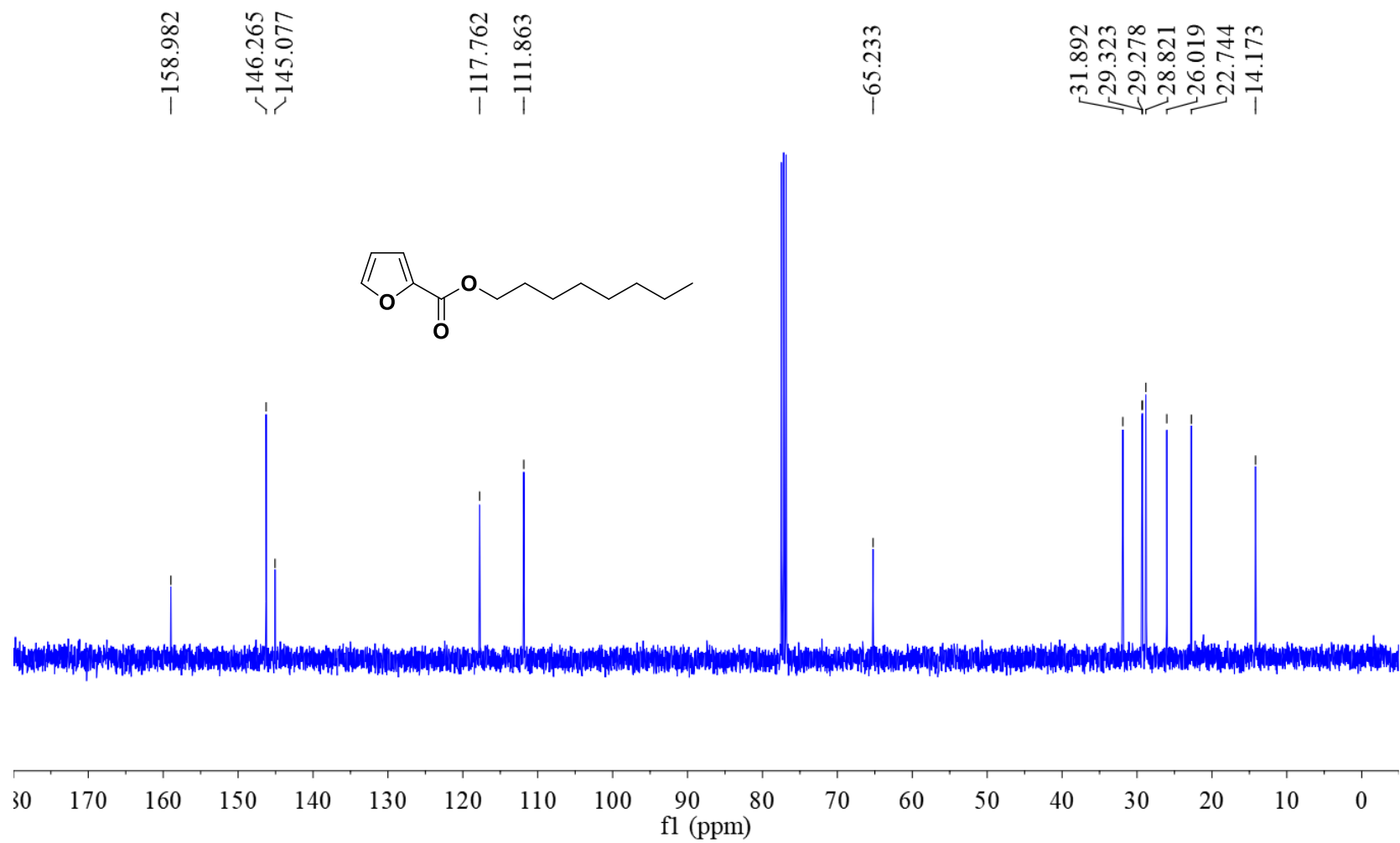
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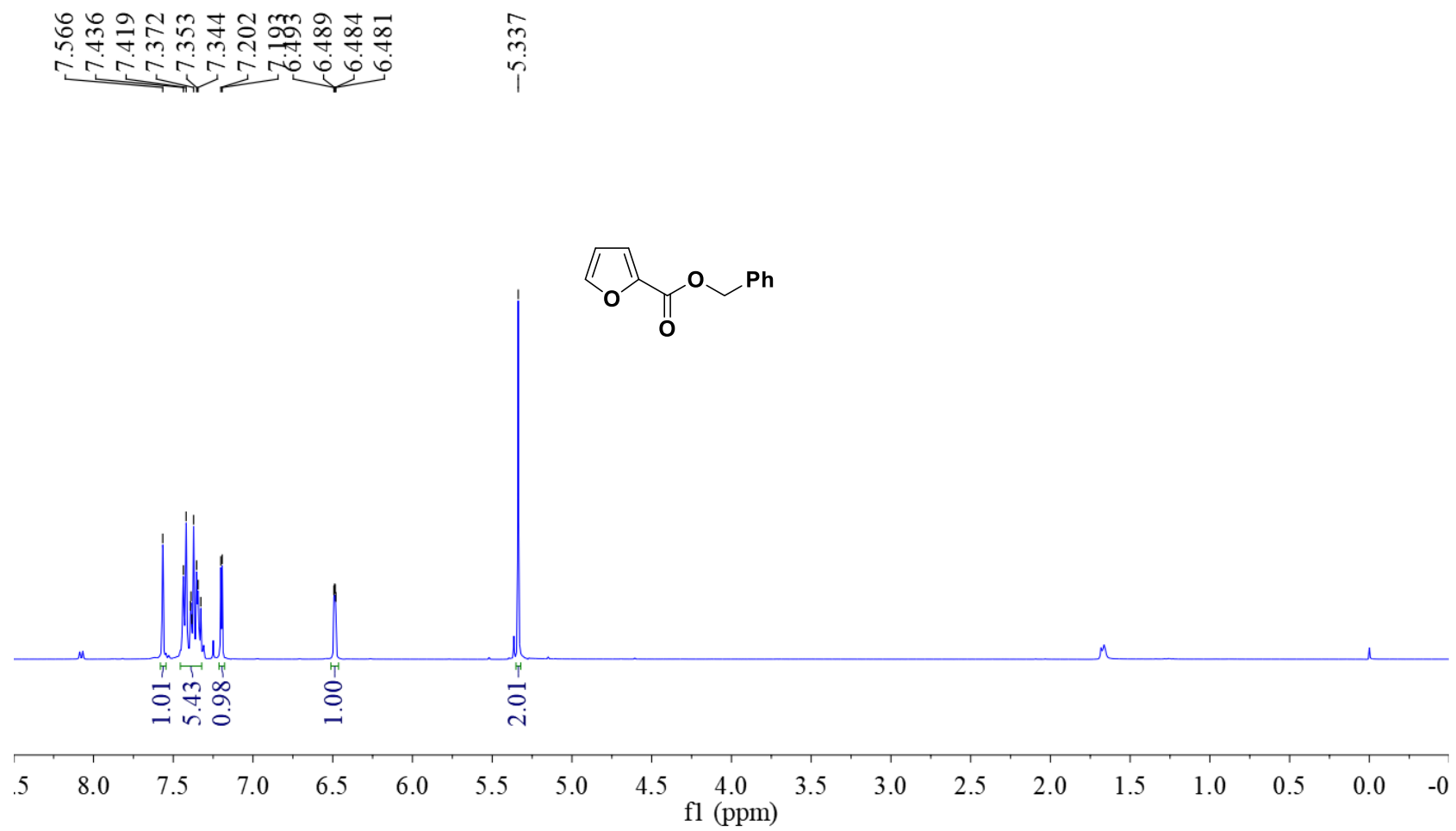
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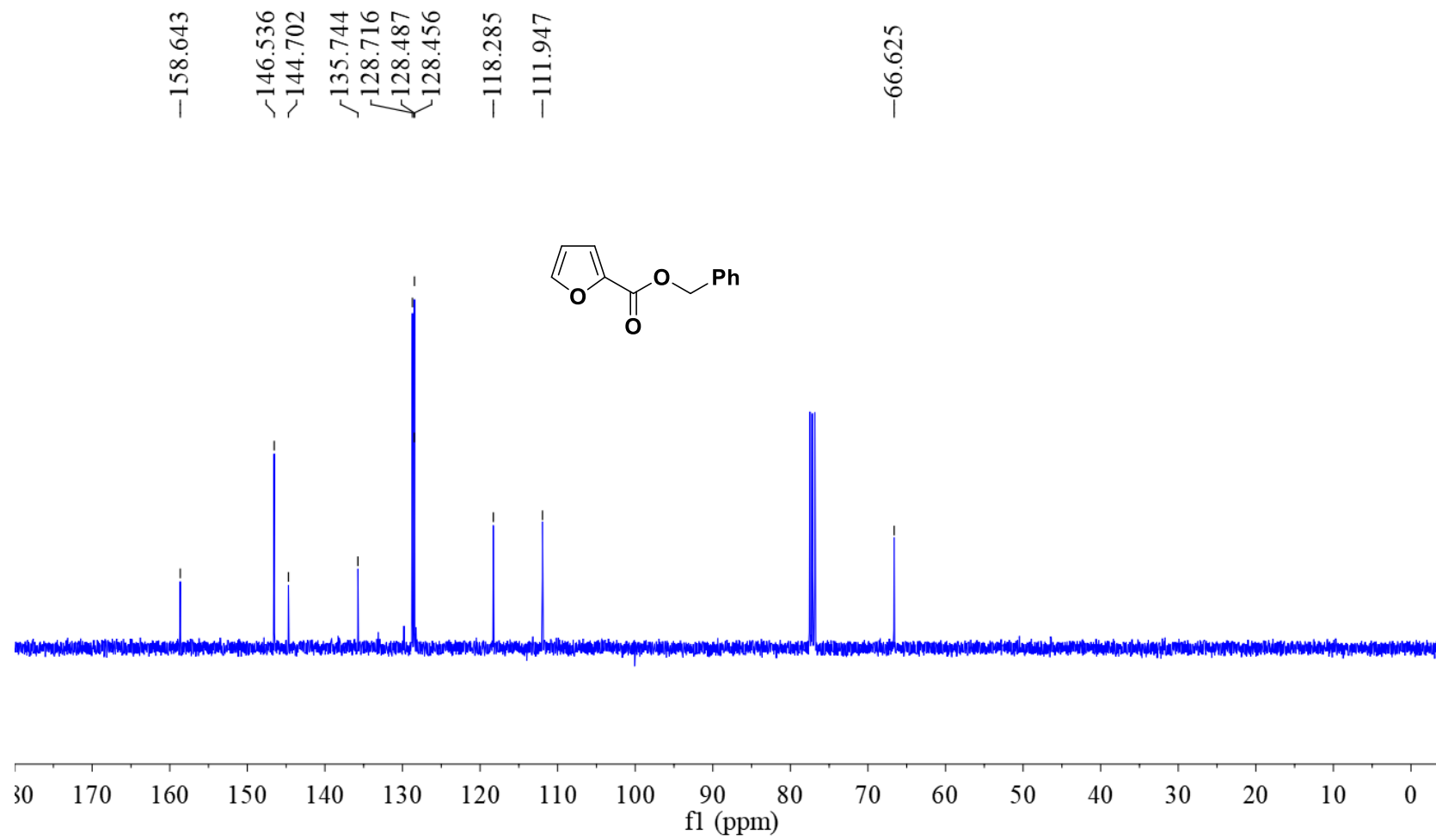
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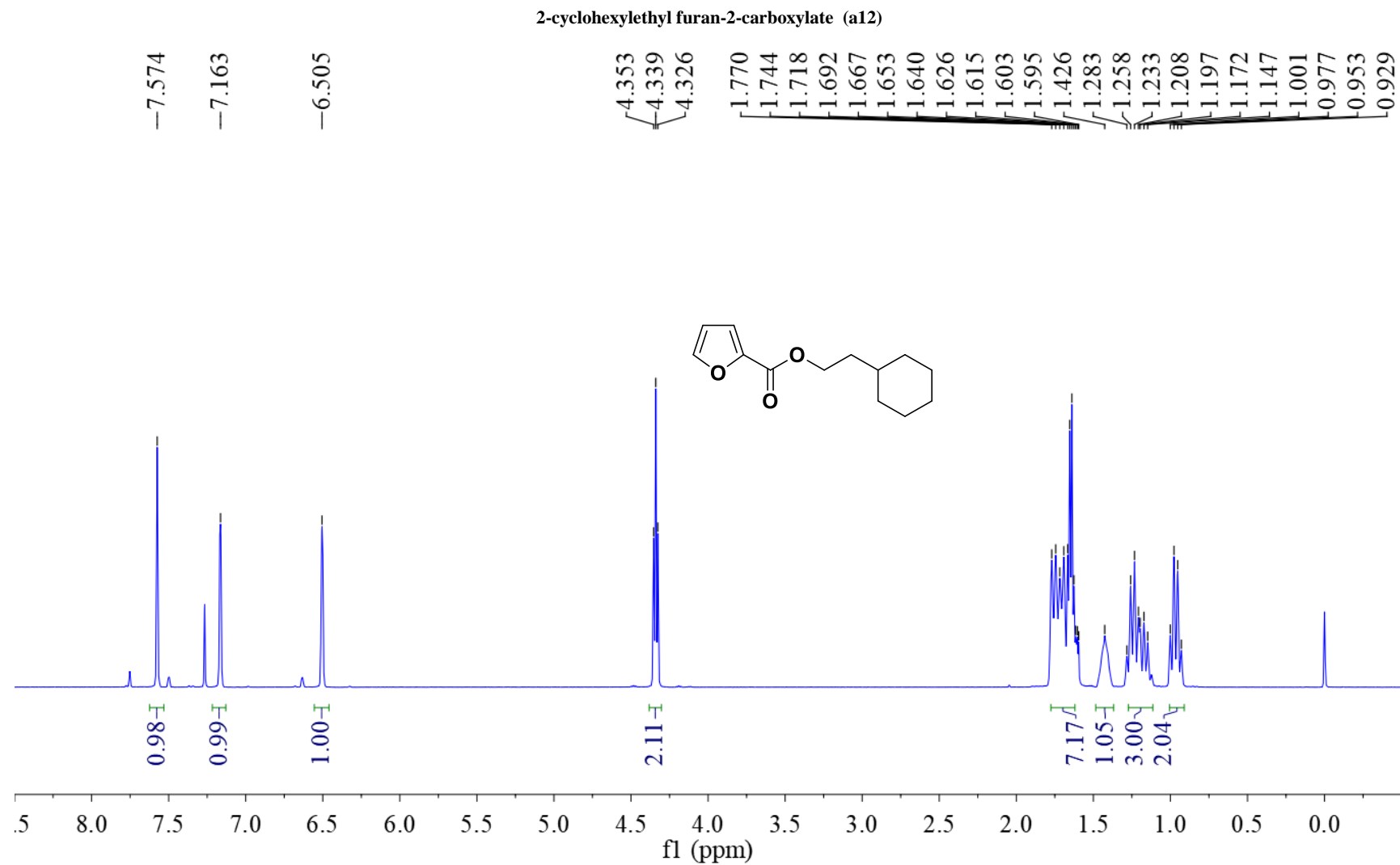


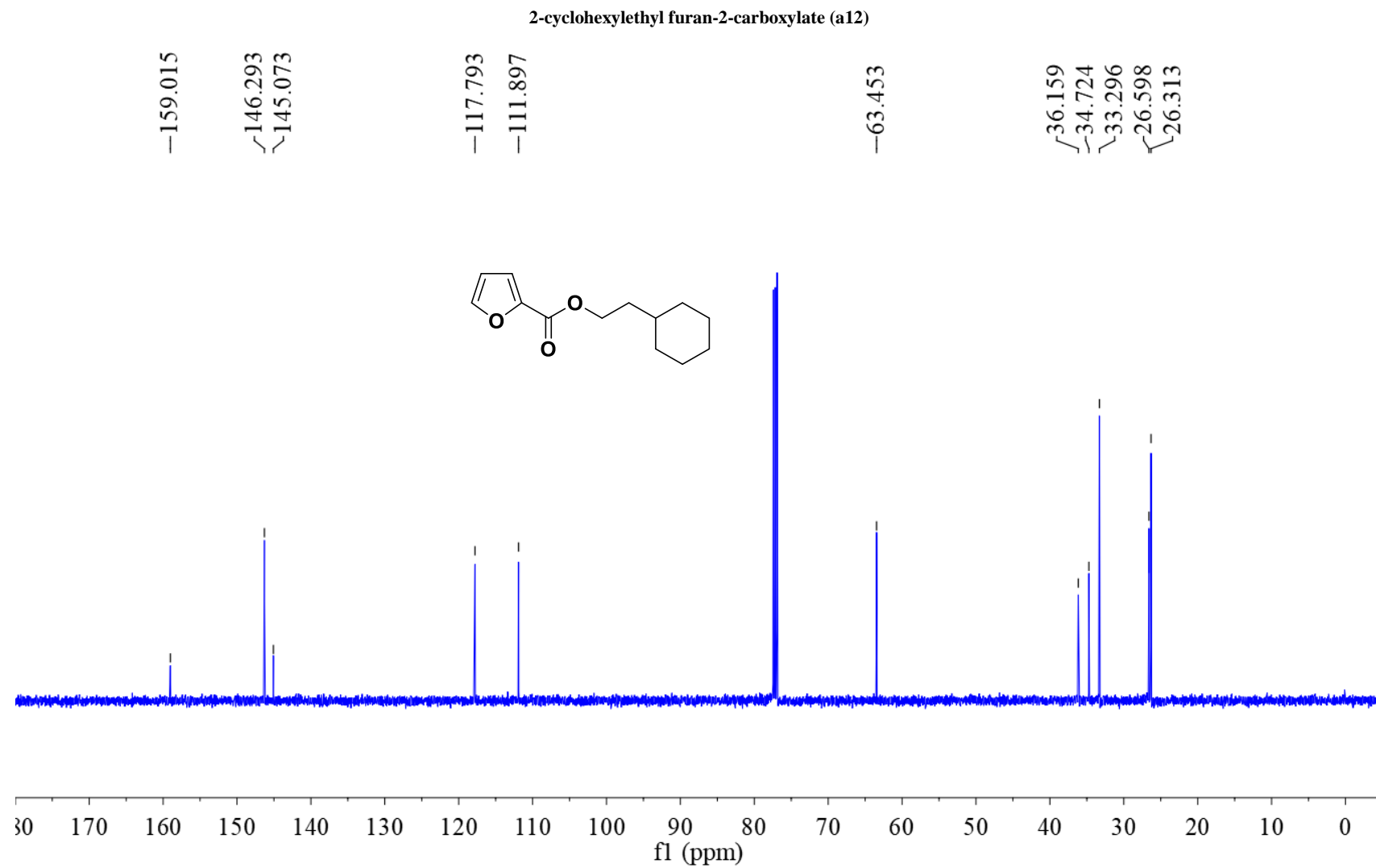
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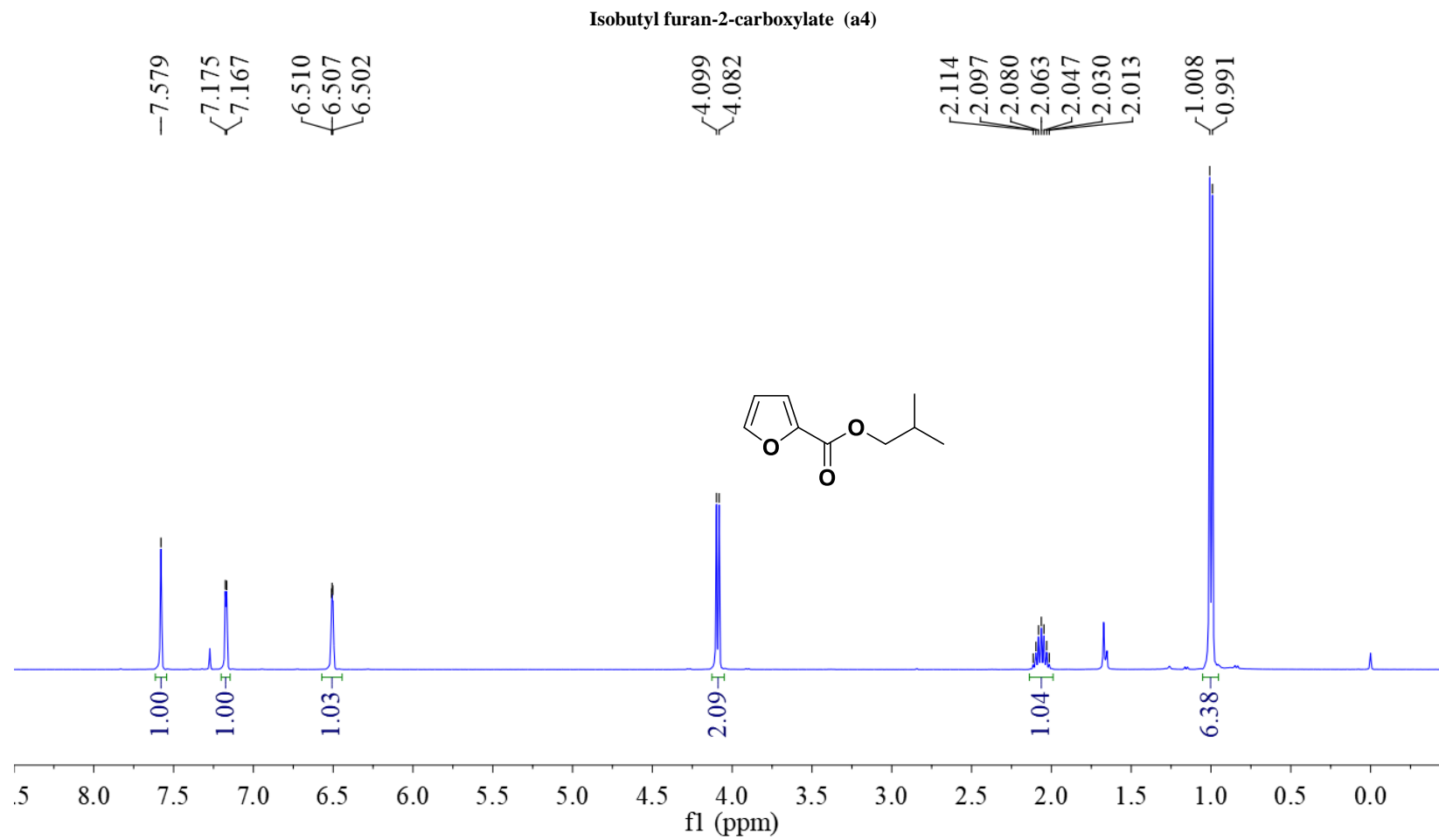


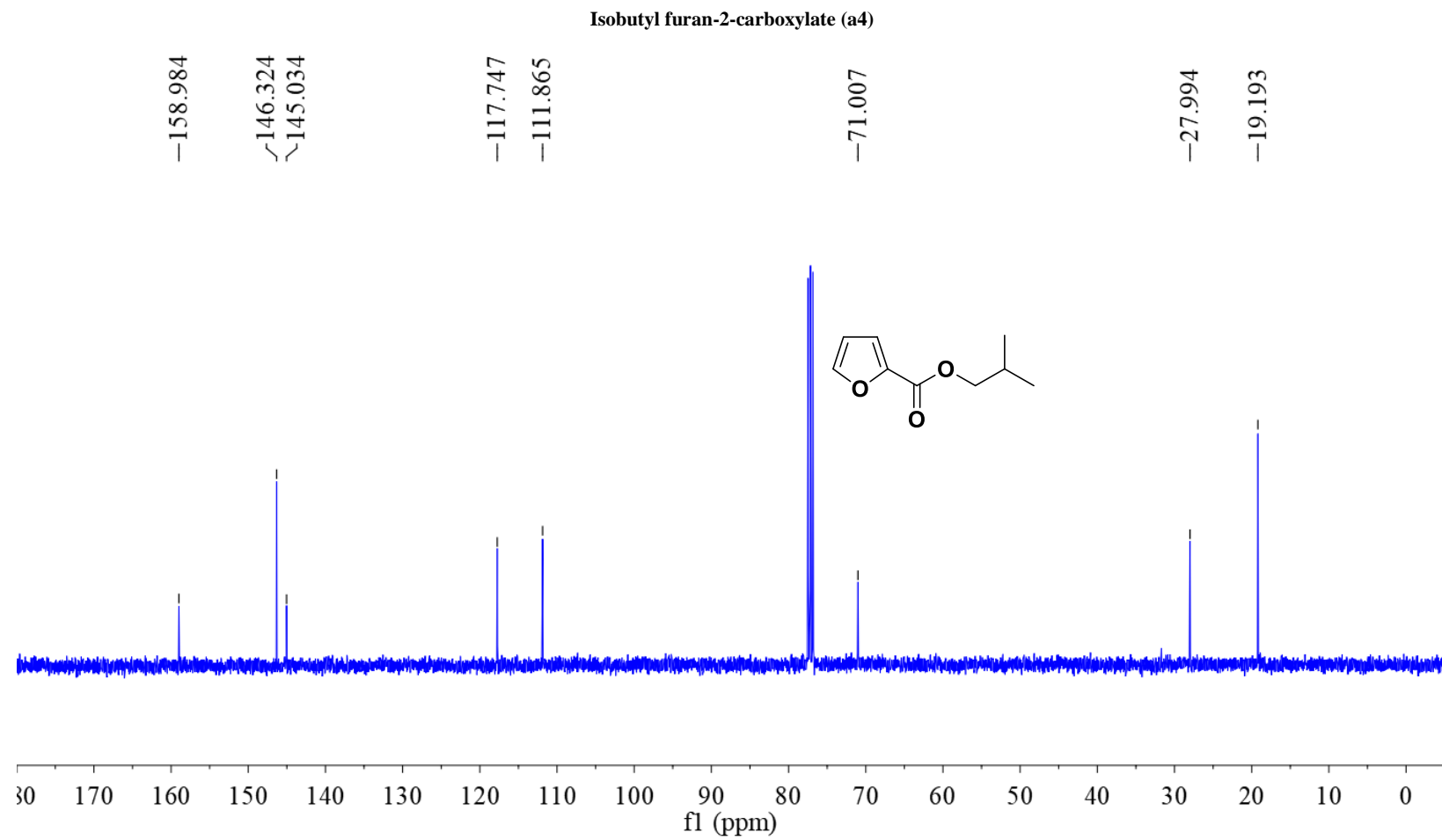
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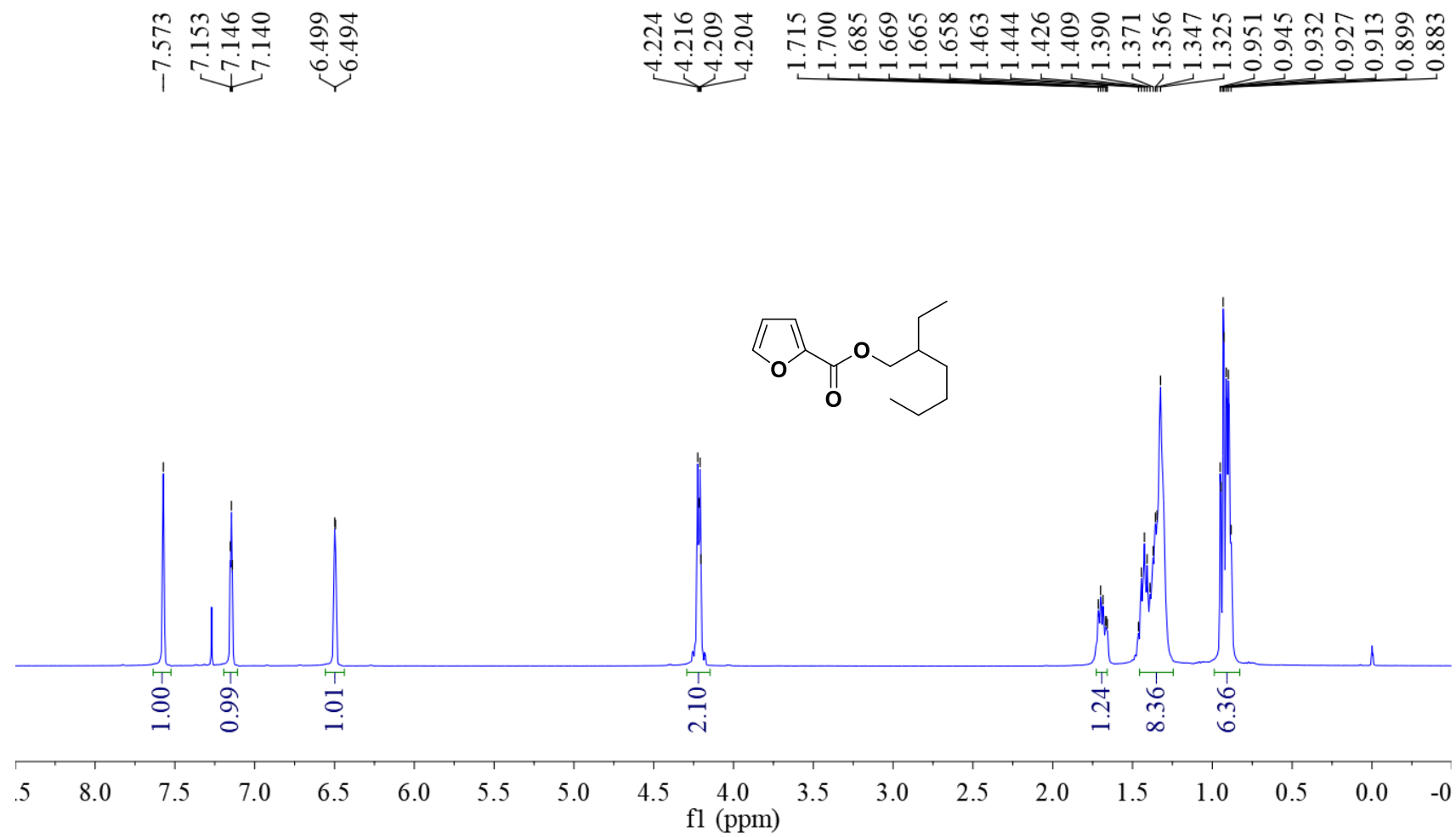


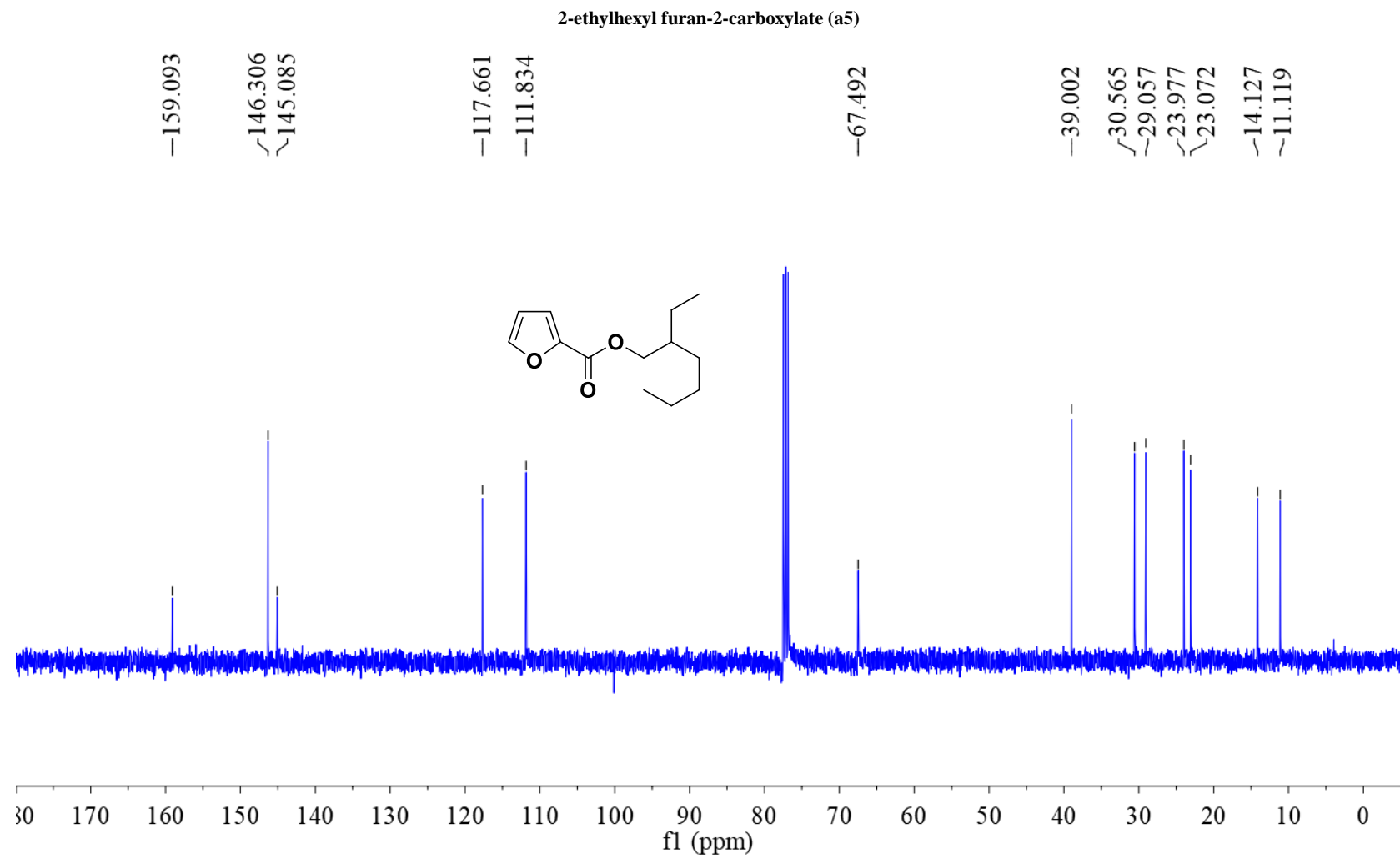


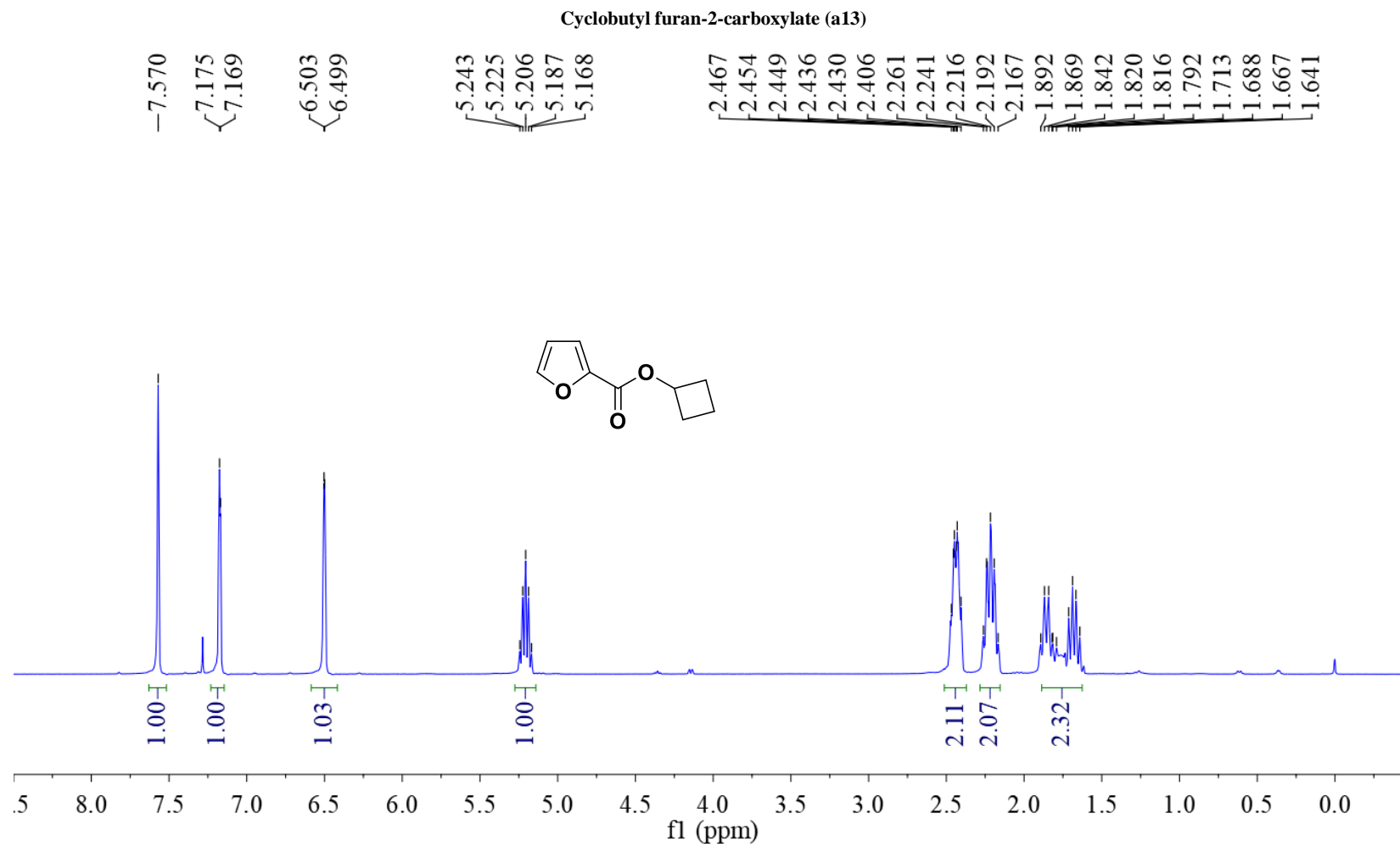




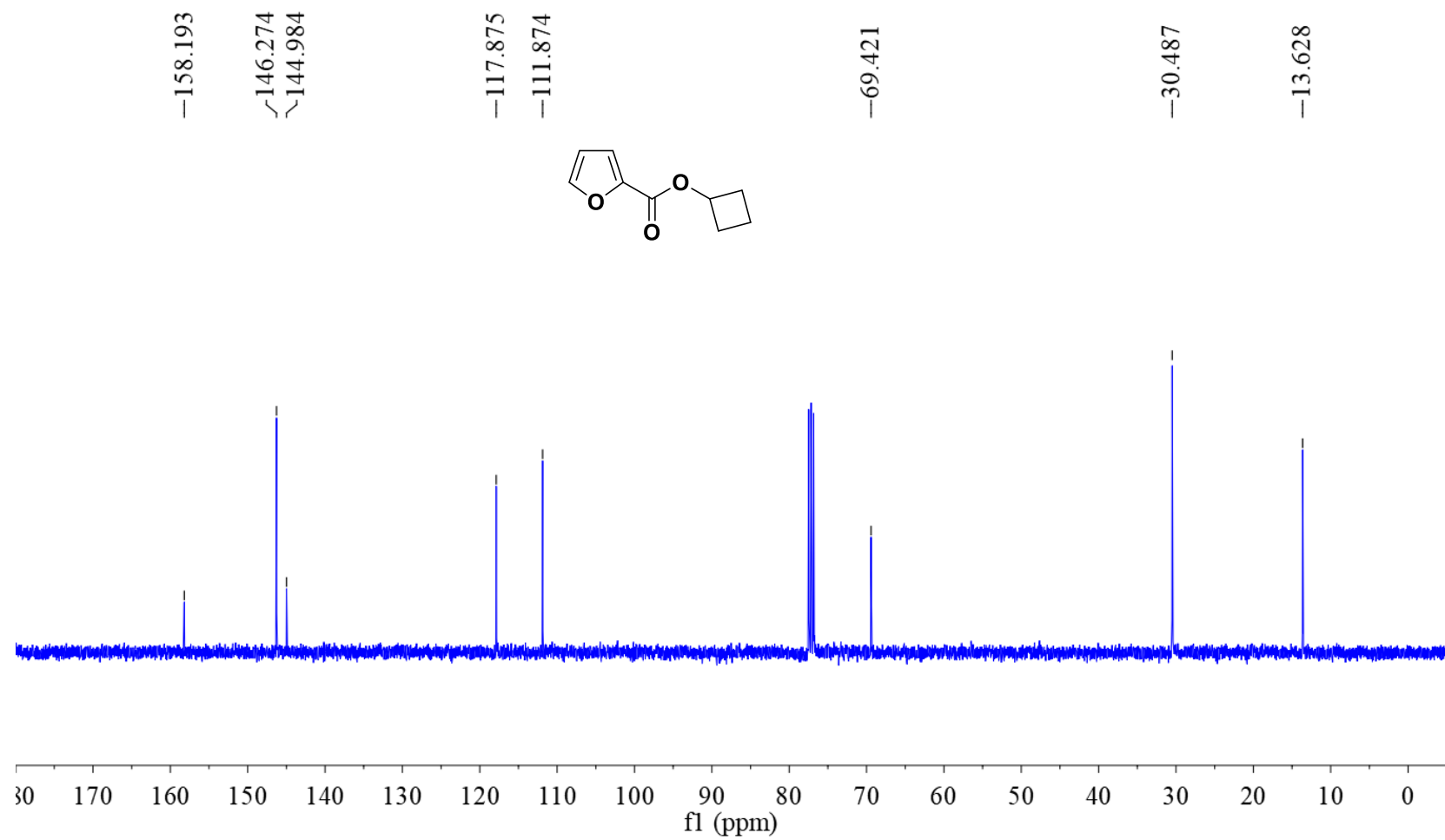
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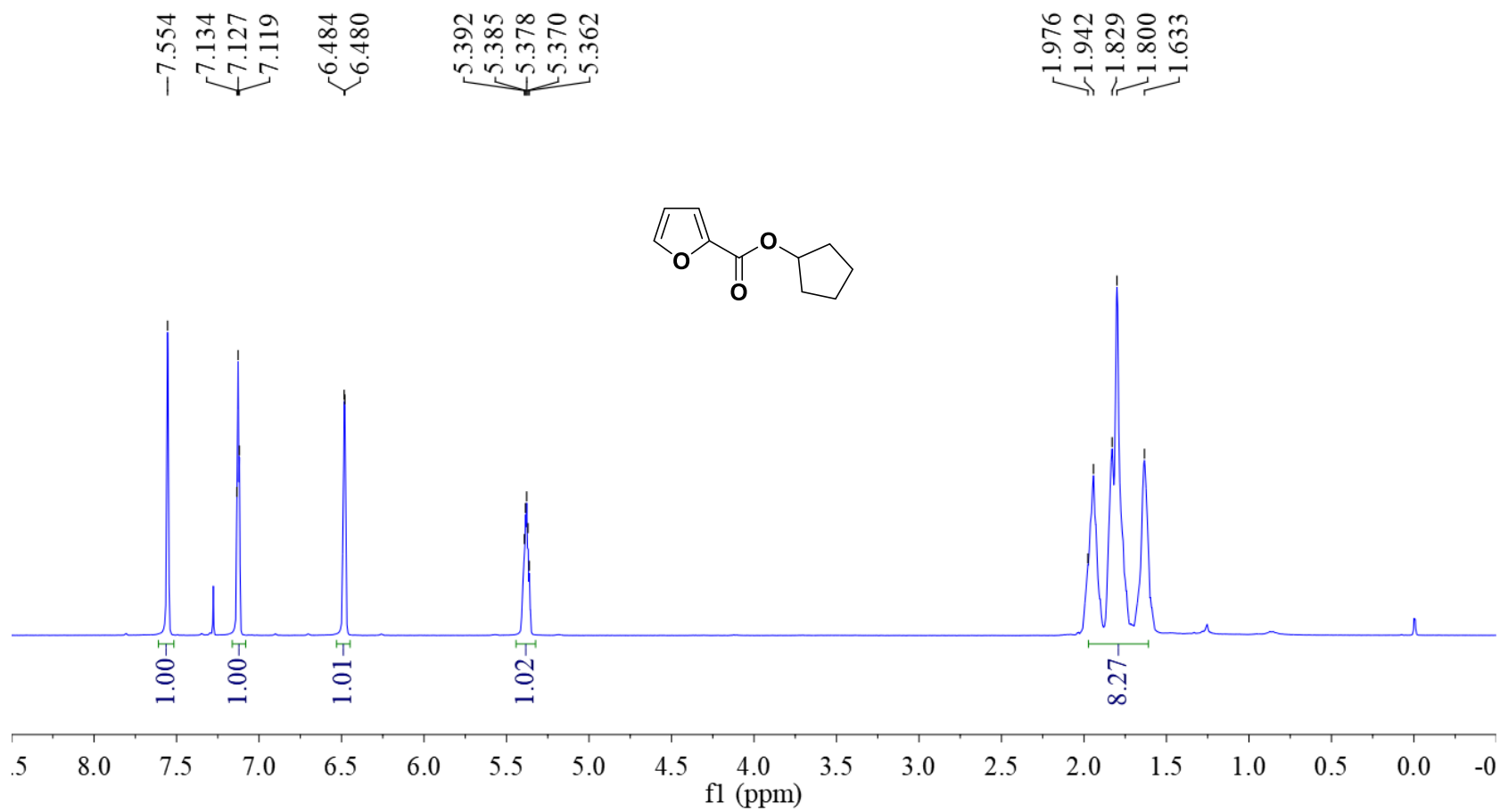




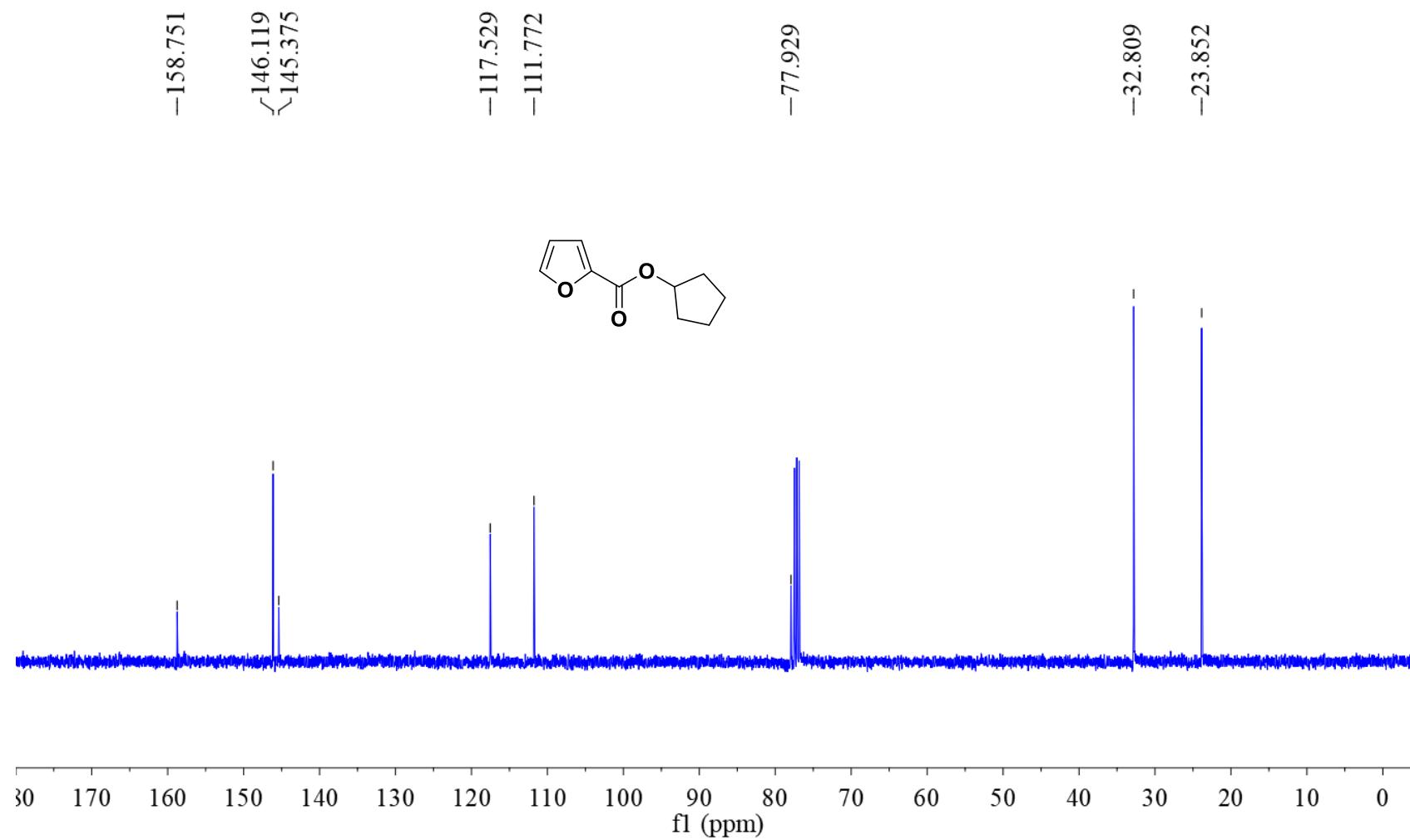
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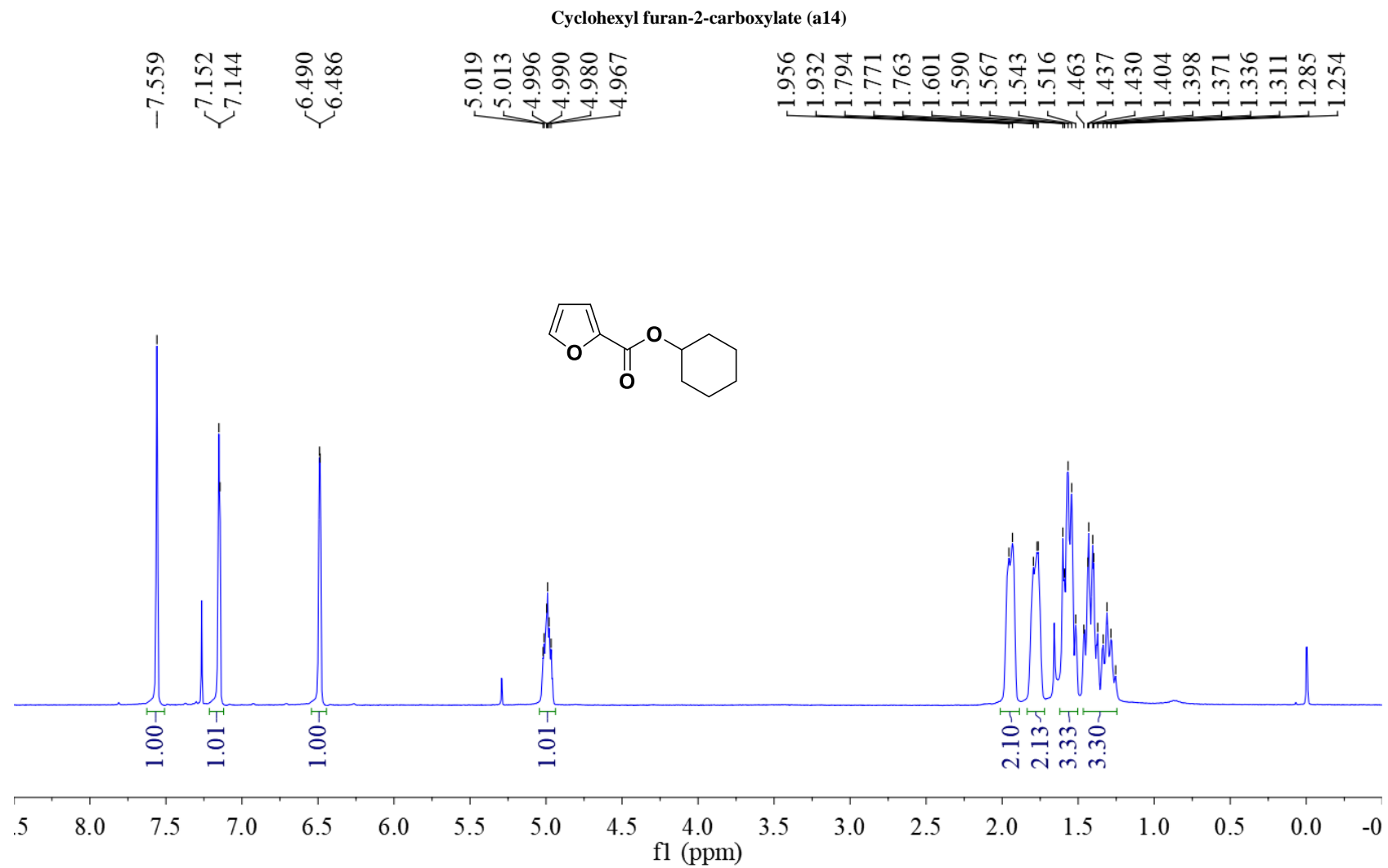


Cyclopentyl furan-2-carboxylate (a8)

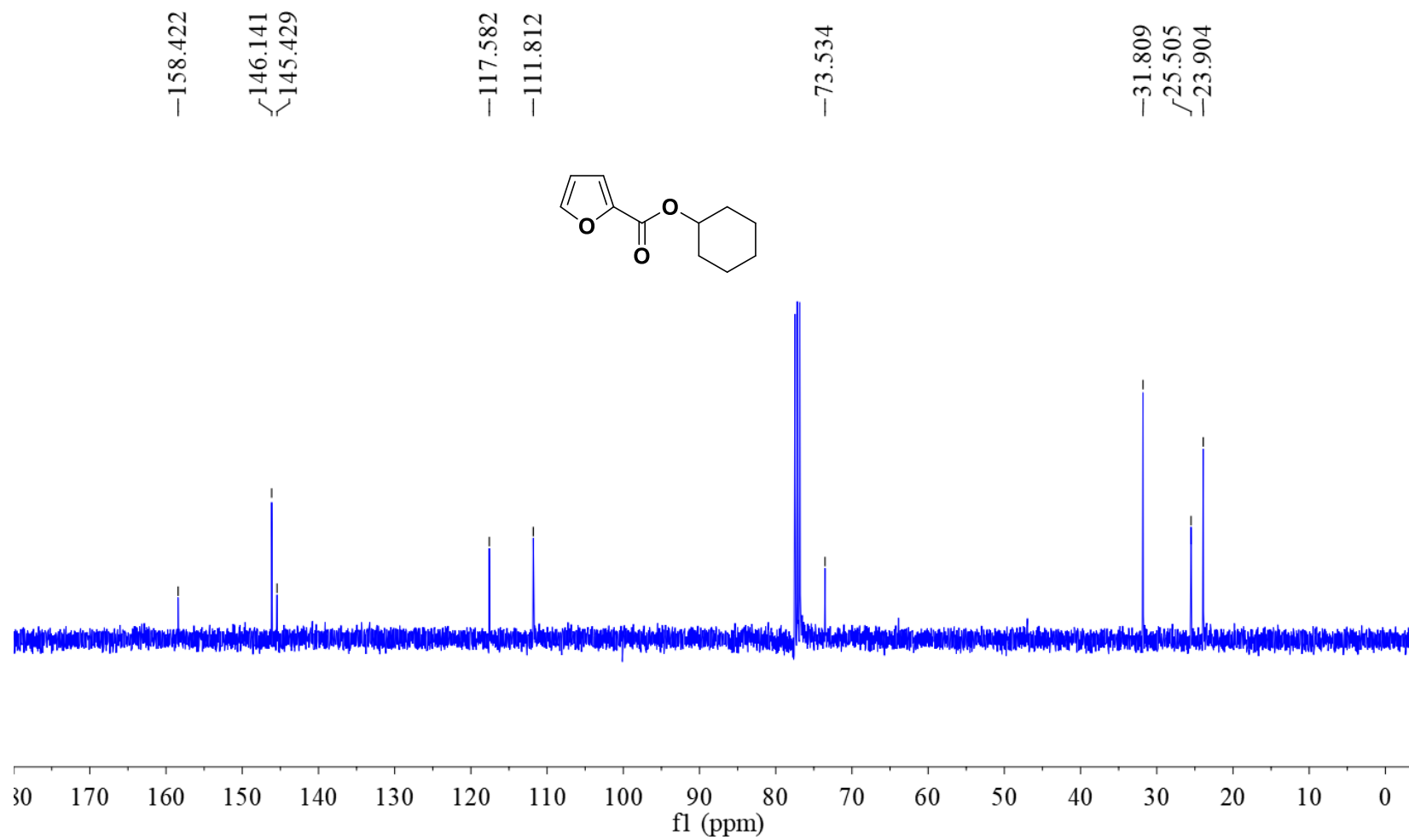


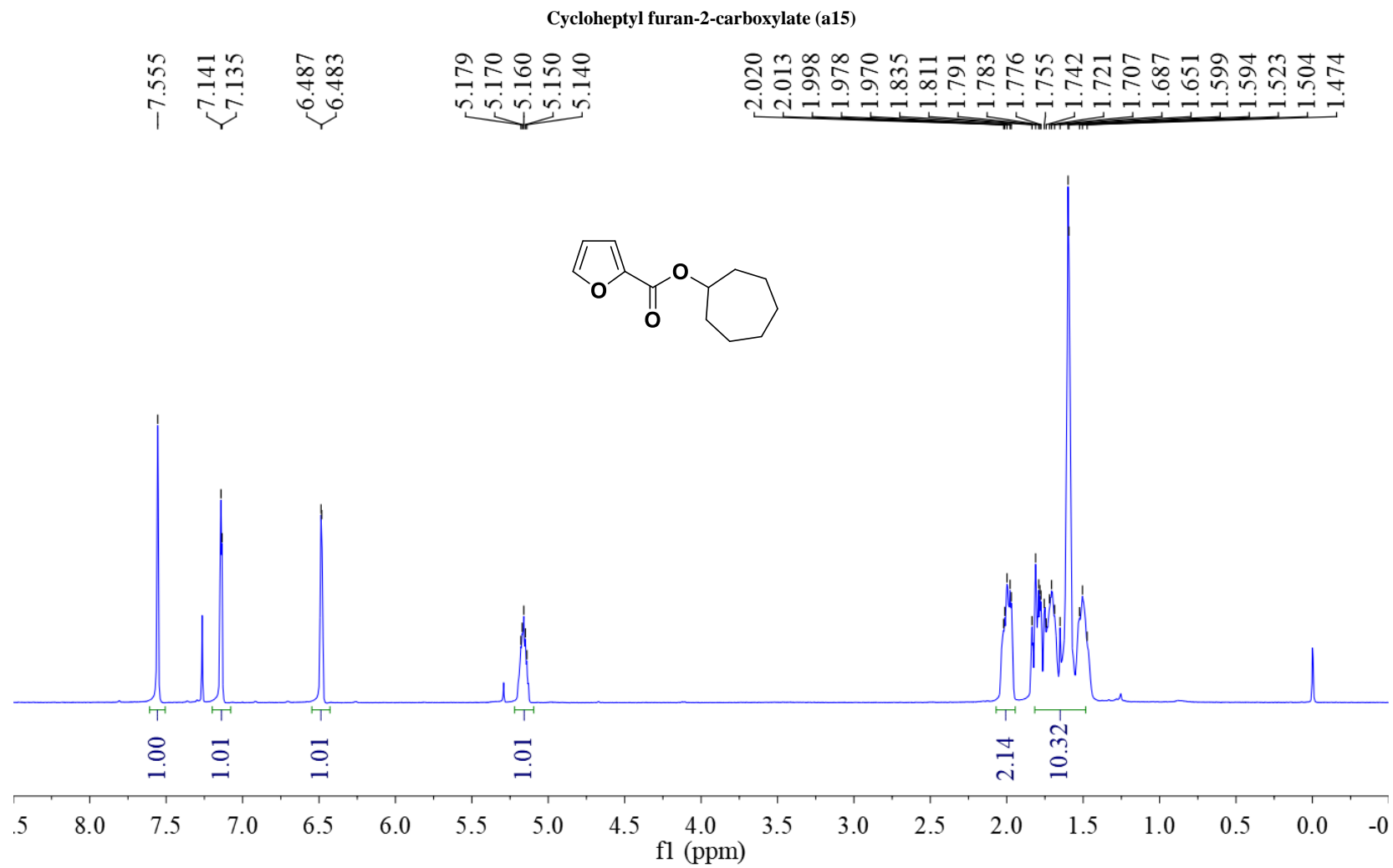
Cyclopentyl furan-2-carboxylate (a8)



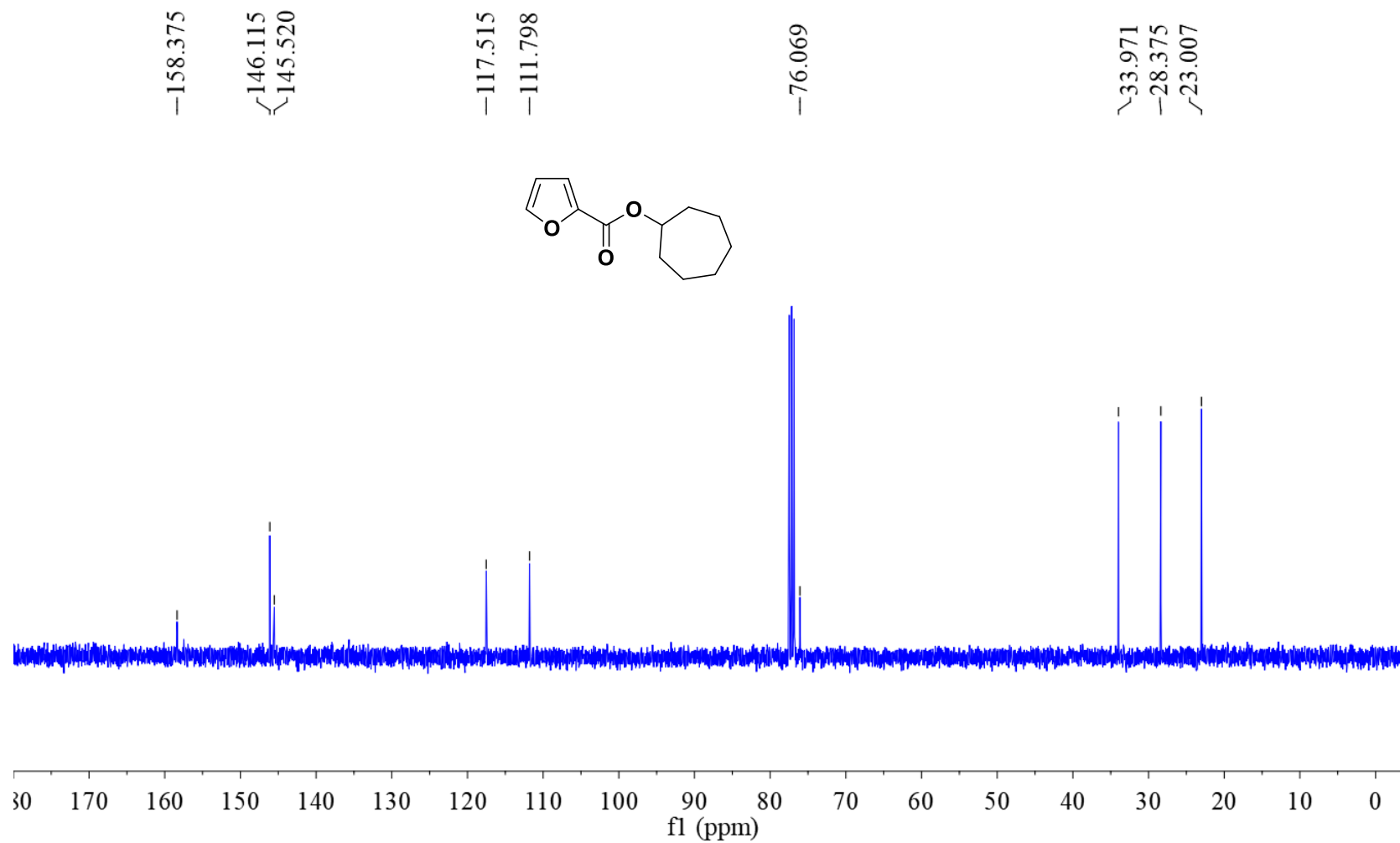


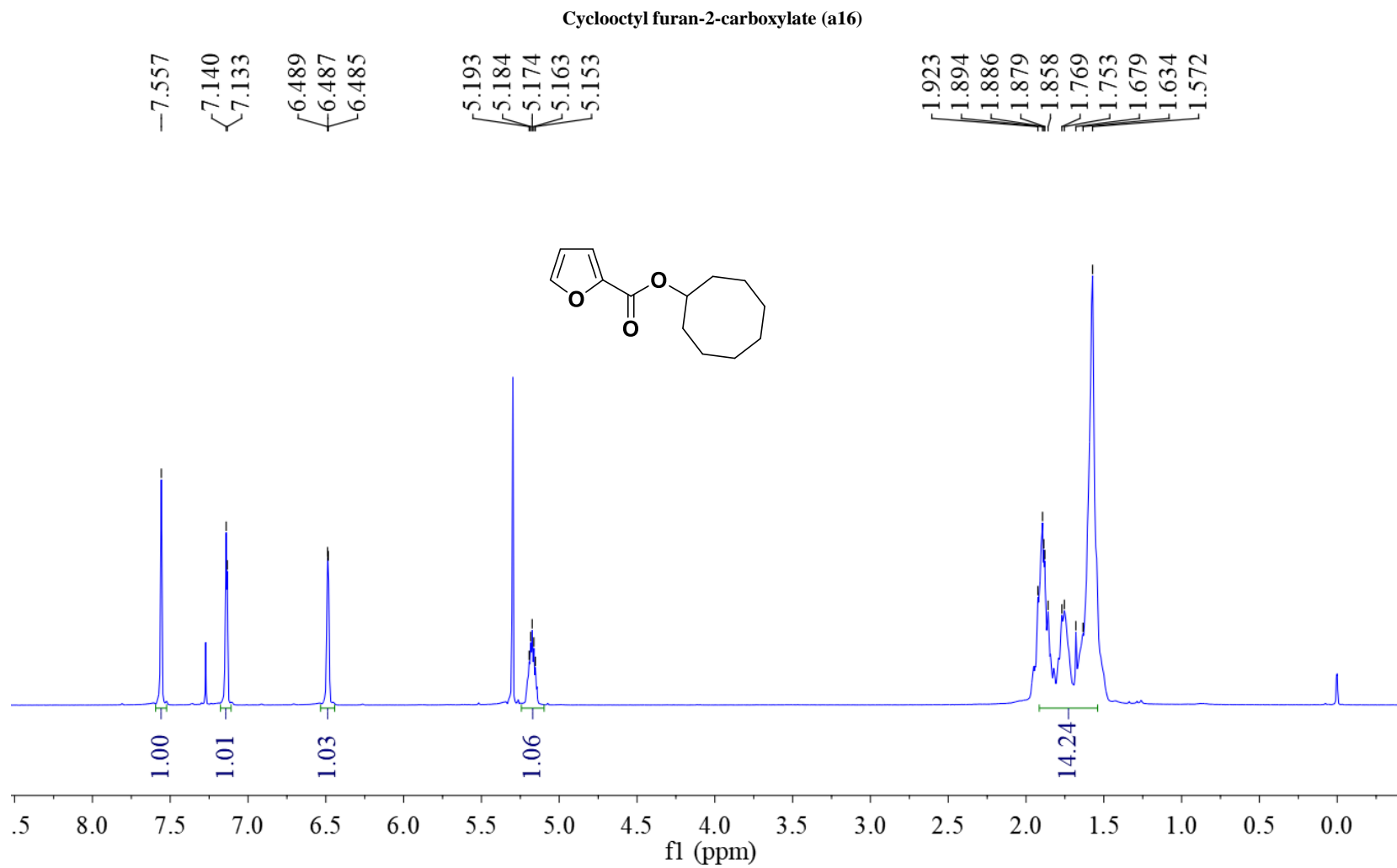
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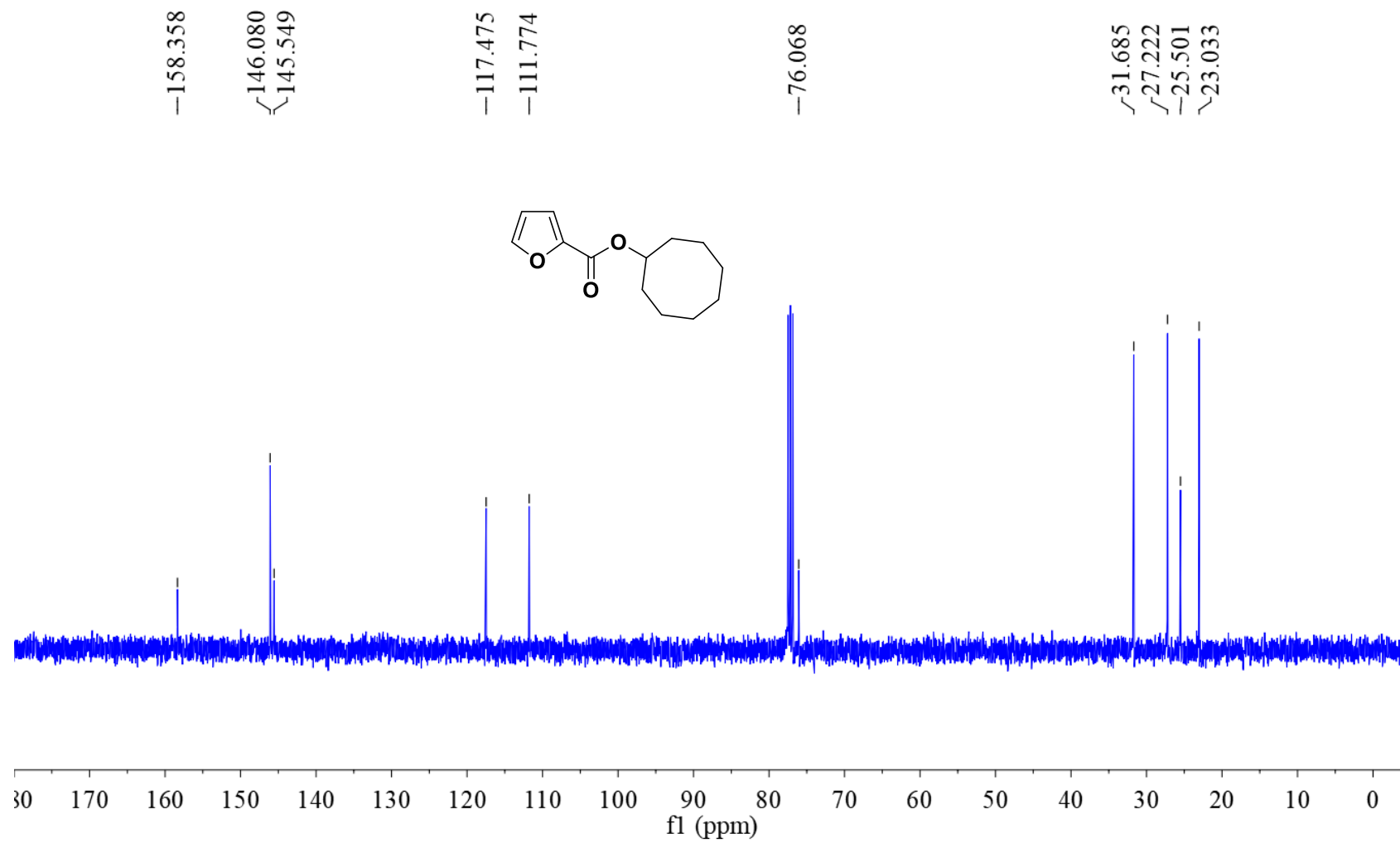


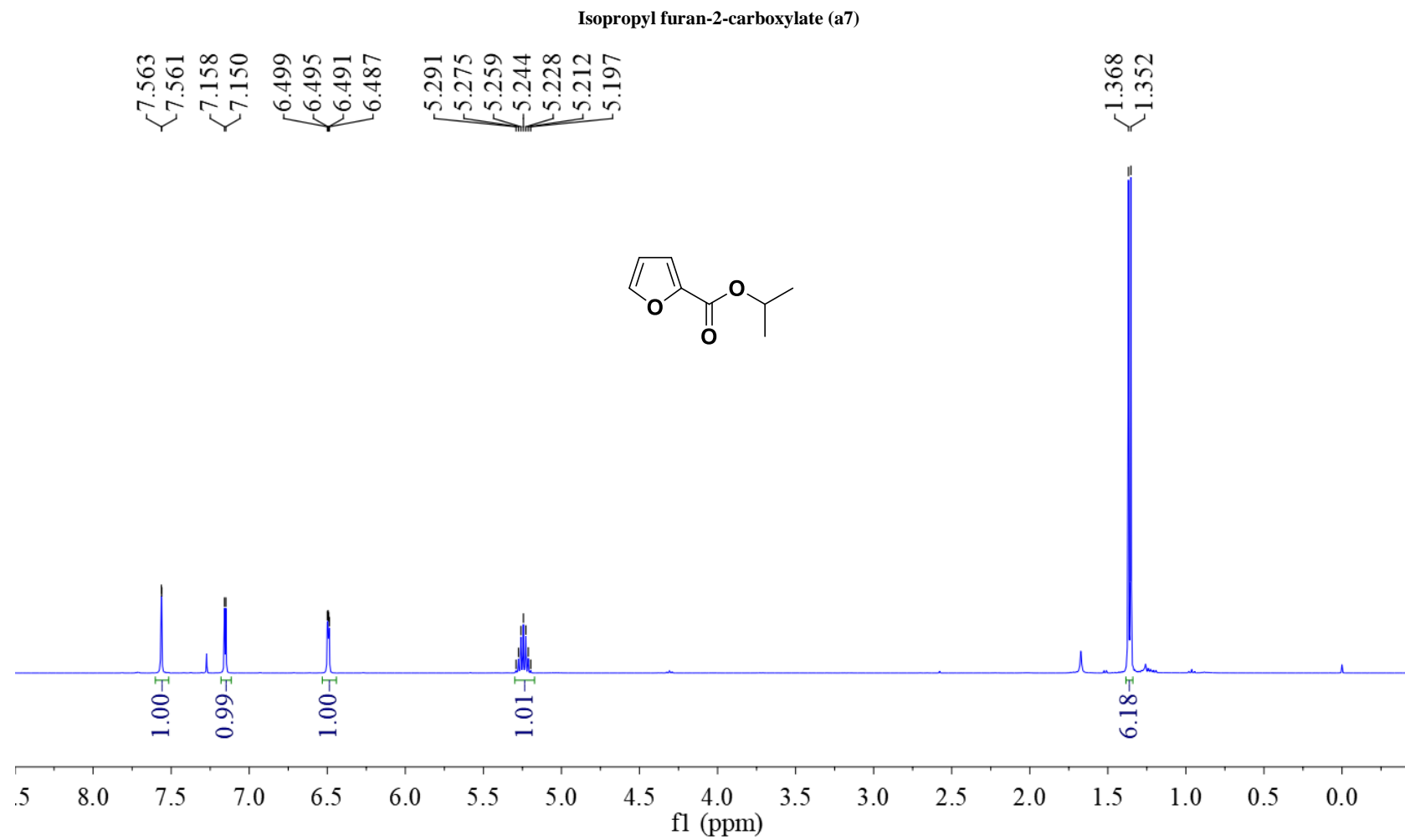
Cycloheptyl furan-2-carboxylate (a15)

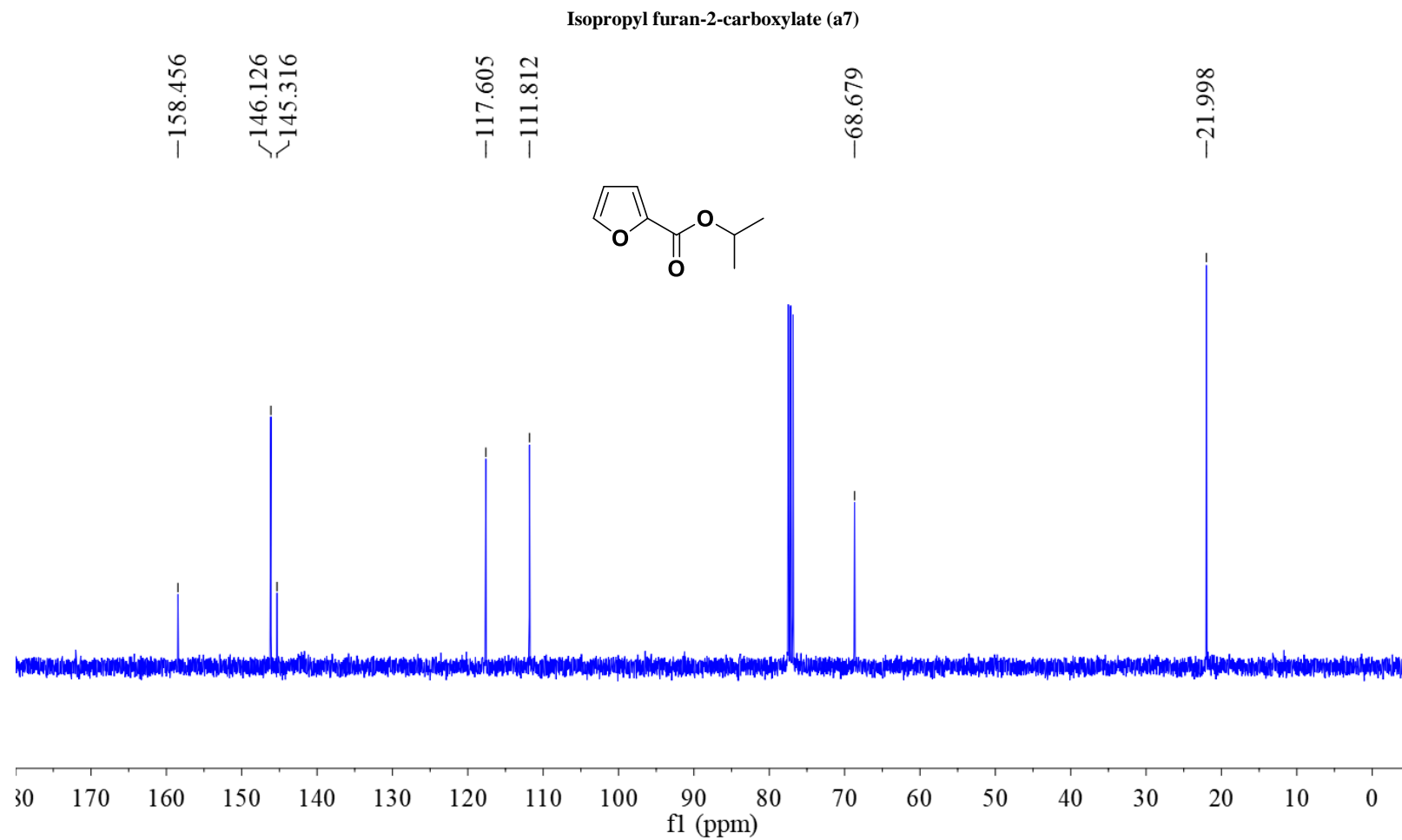




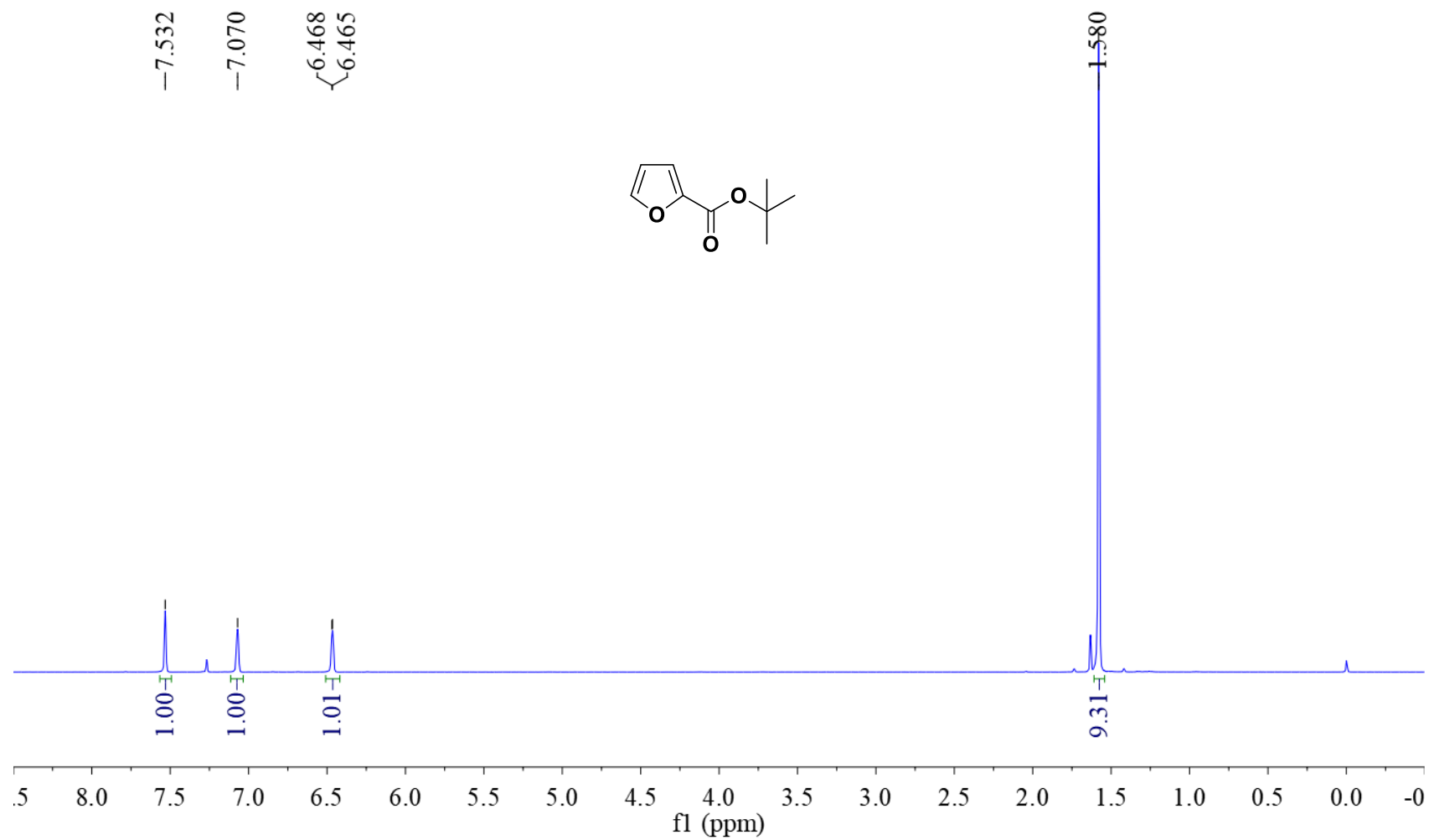
Cyclooctyl furan-2-carboxylate (a16)



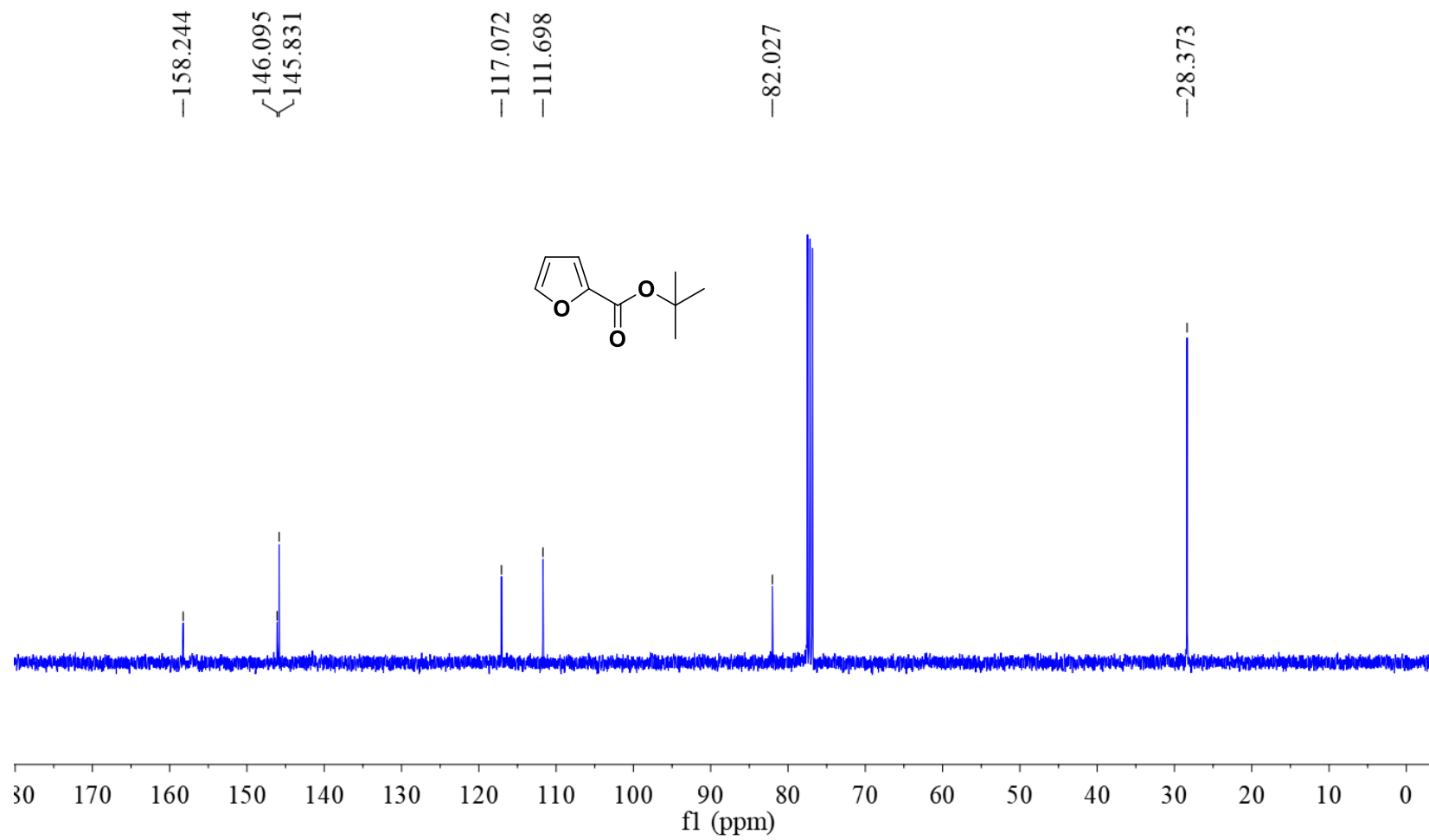




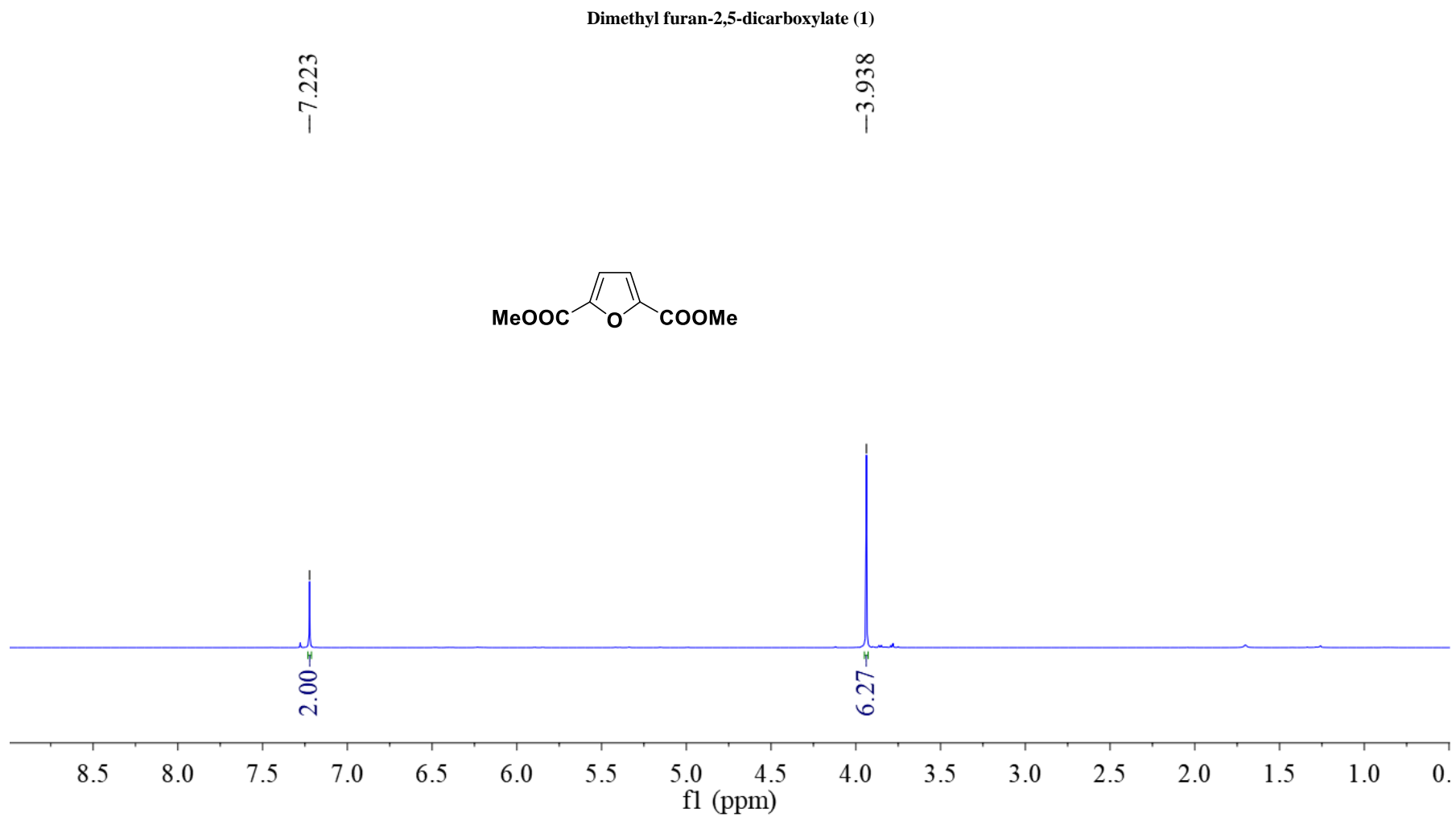
tert-Butyl furan-2-carboxylate (a9)



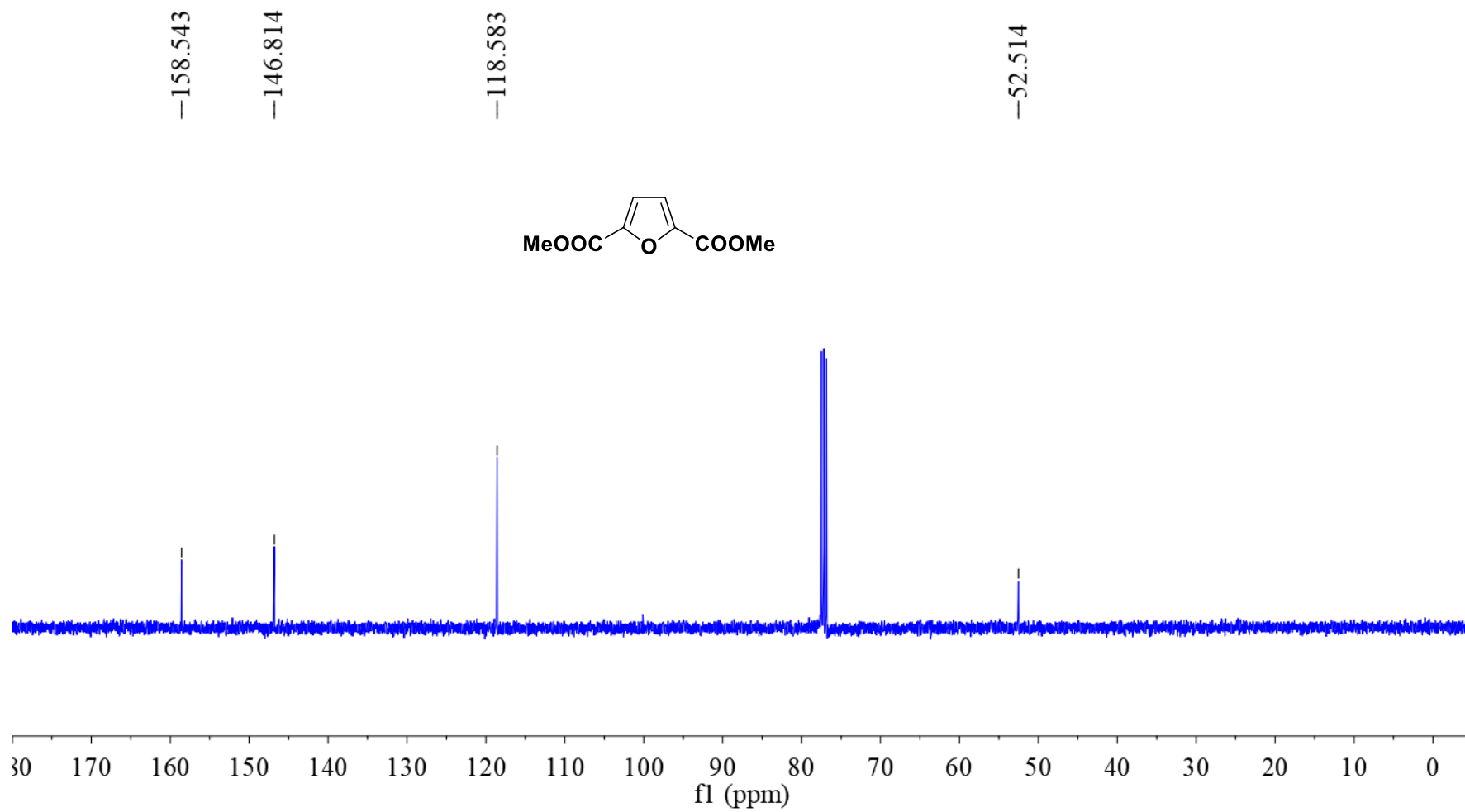
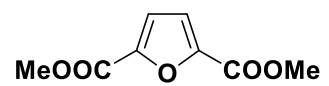
tert-Butyl furan-2-carboxylate (a9)



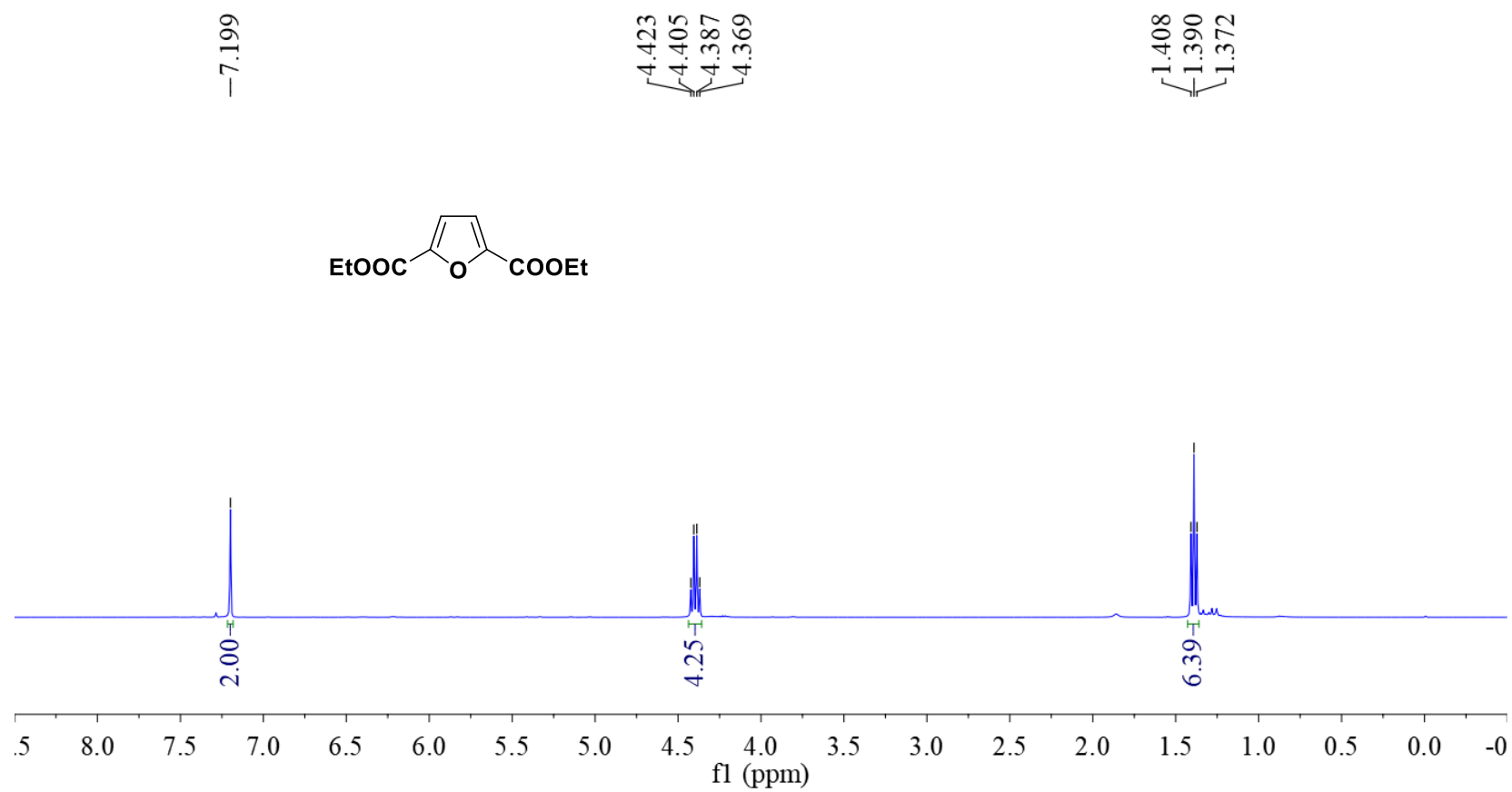
9. Copies of ^1H and ^{13}C NMR spectra of products



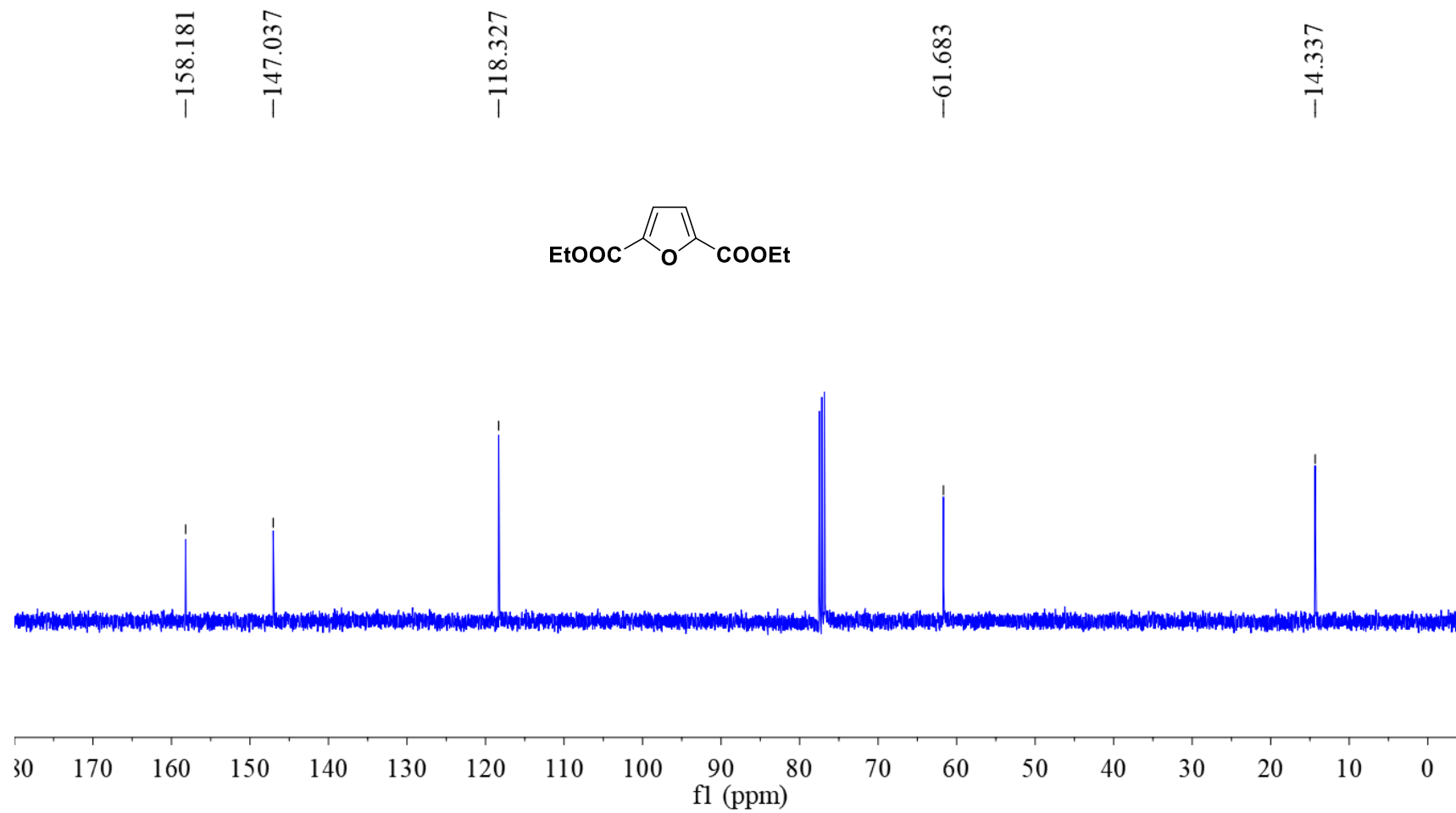
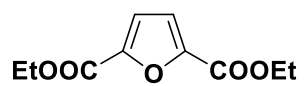
Dimethyl furan-2,5-dicarboxylate (1)



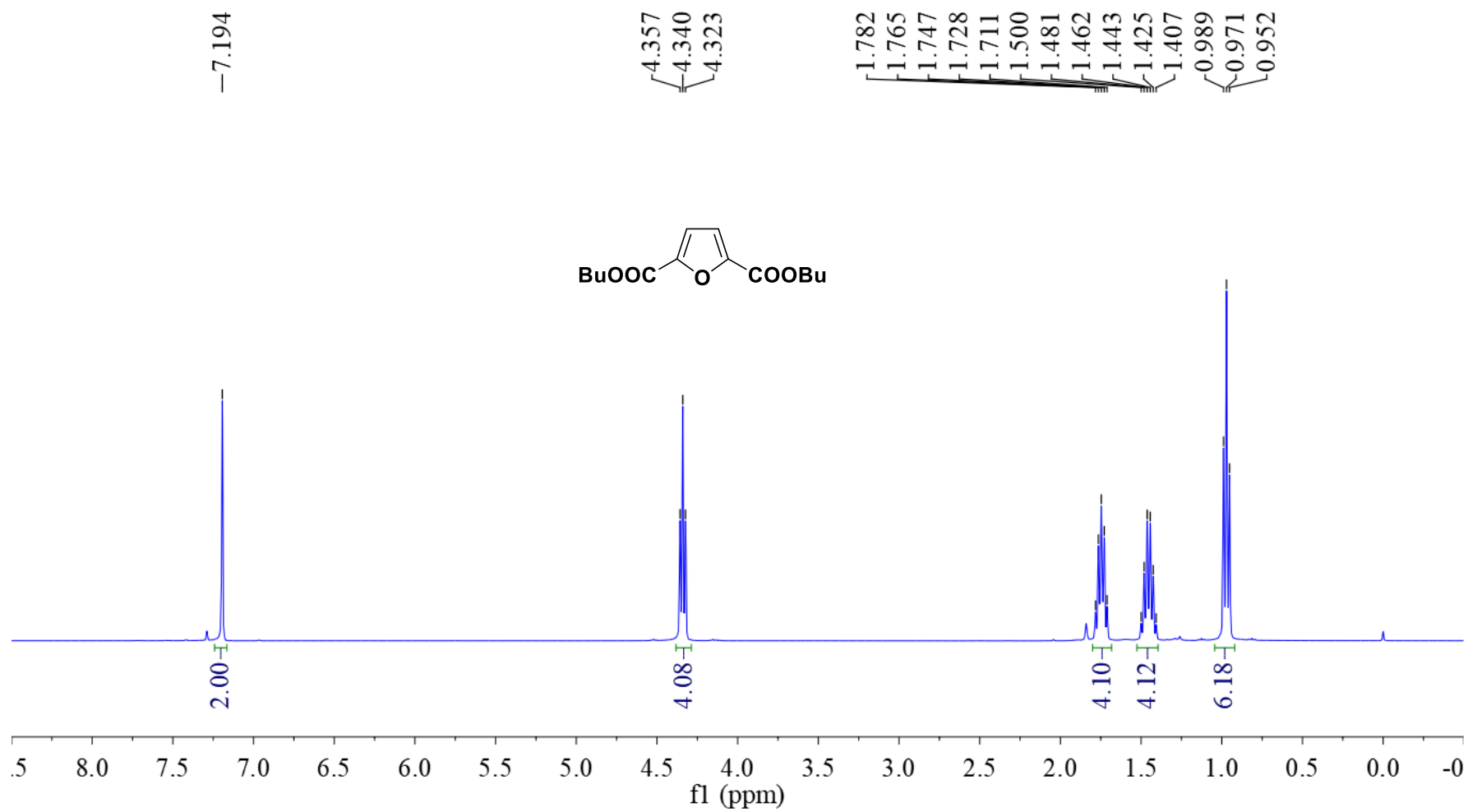
Diethyl furan-2,5-dicarboxylate (2)



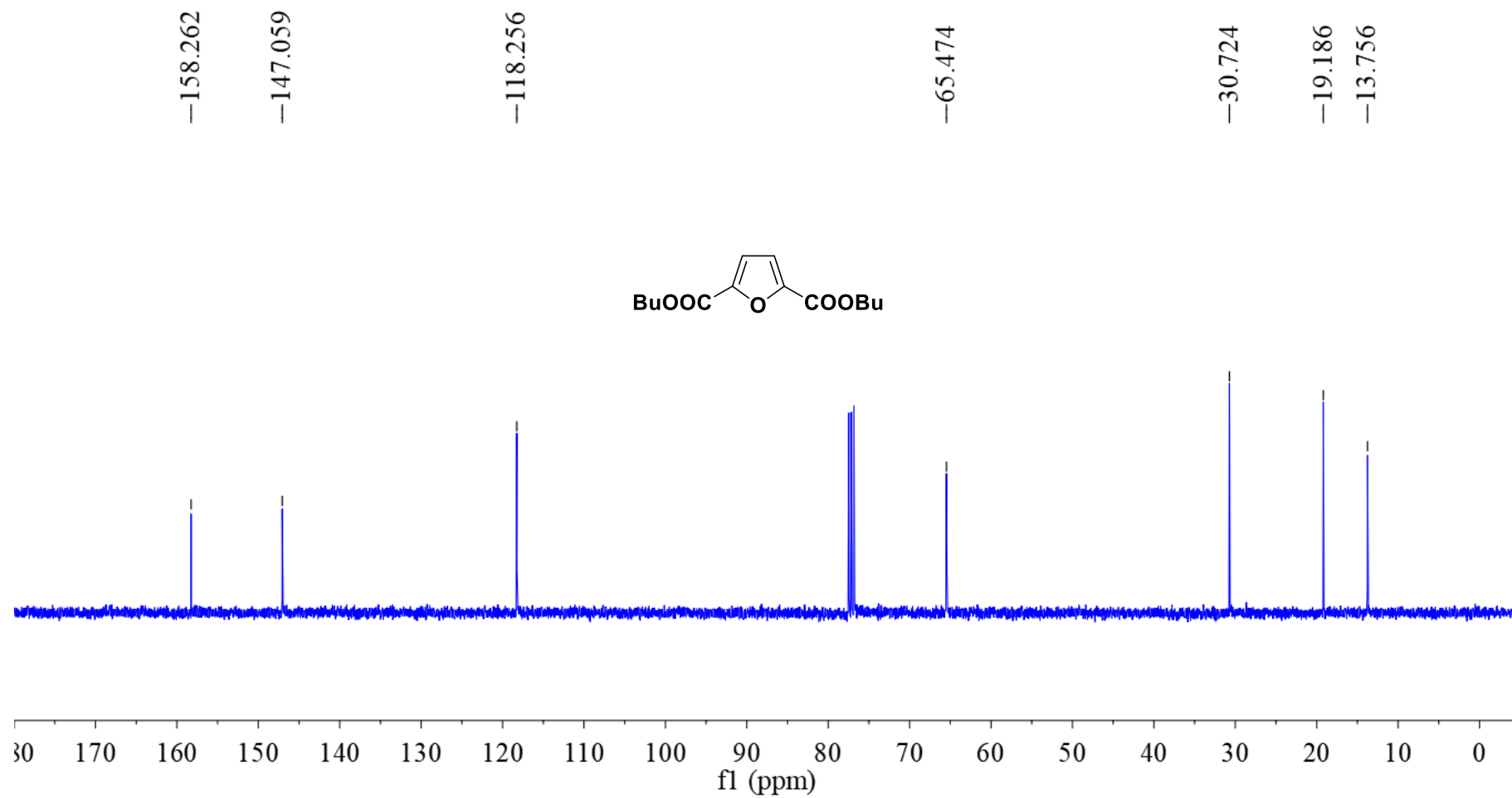
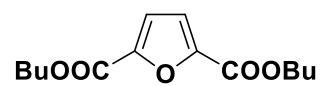
Diethyl furan-2,5-dicarboxylate (2)



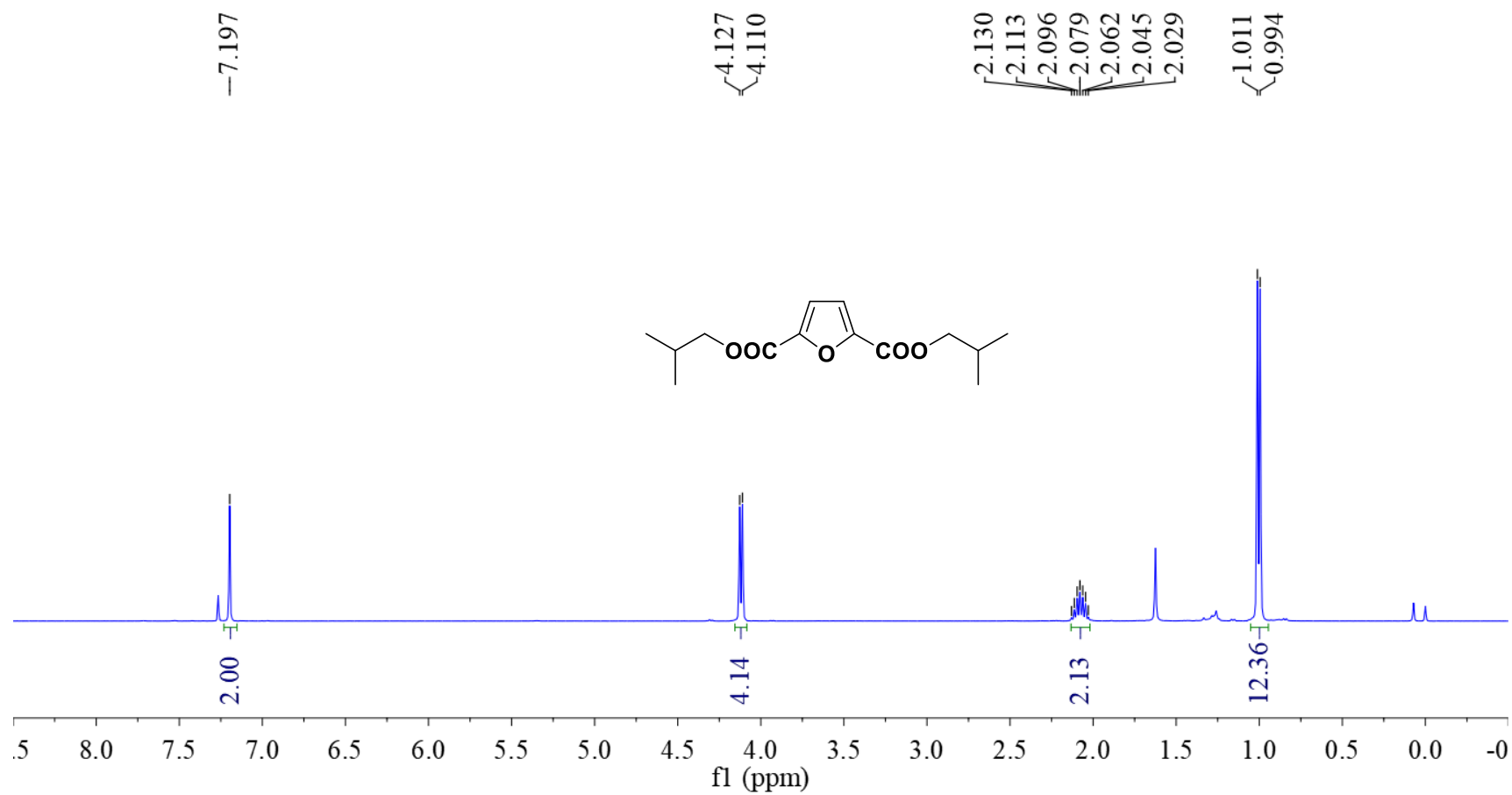
Dibutyl furan-2,5-dicarboxylate (3)



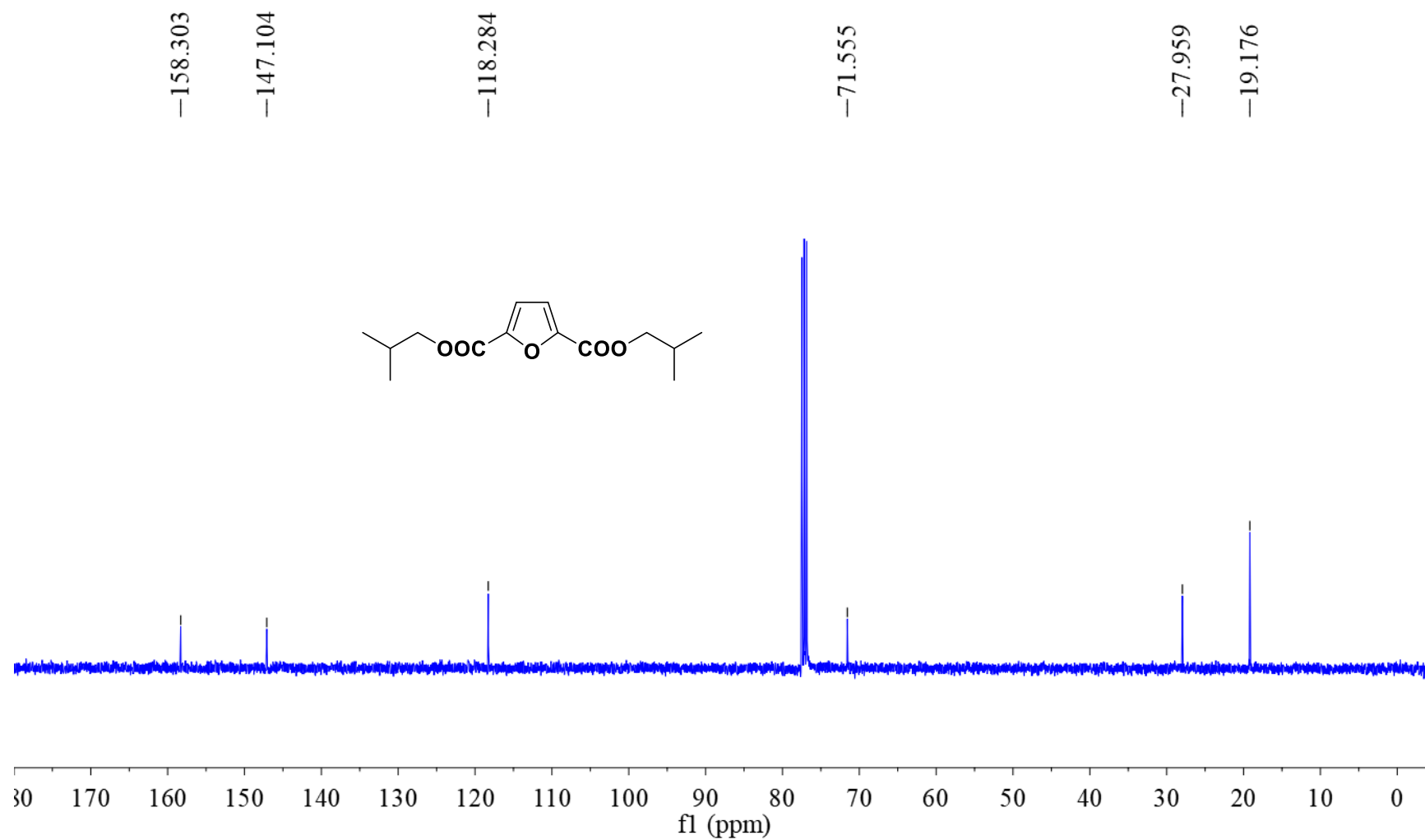
Dibutyl furan-2,5-dicarboxylate (3)

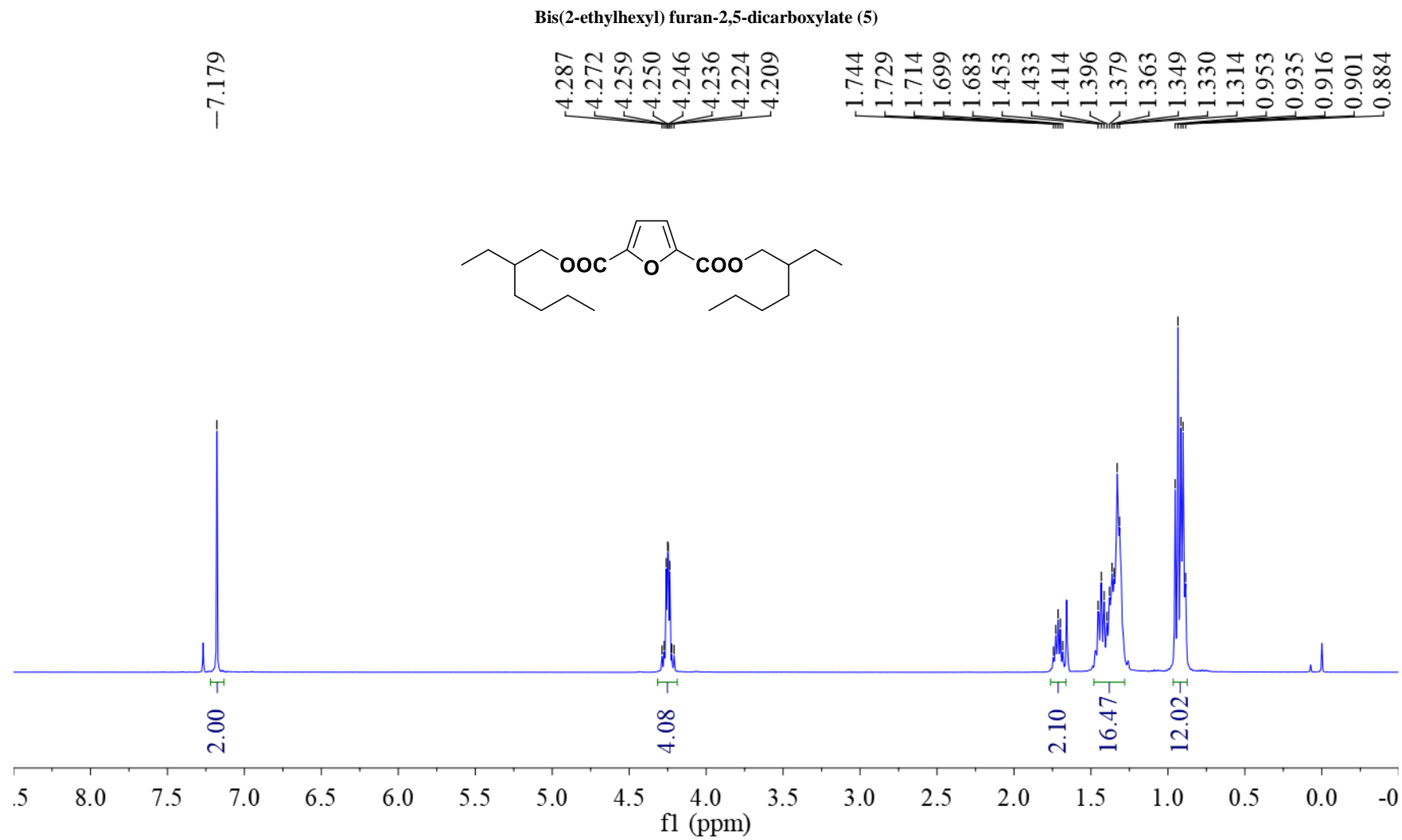


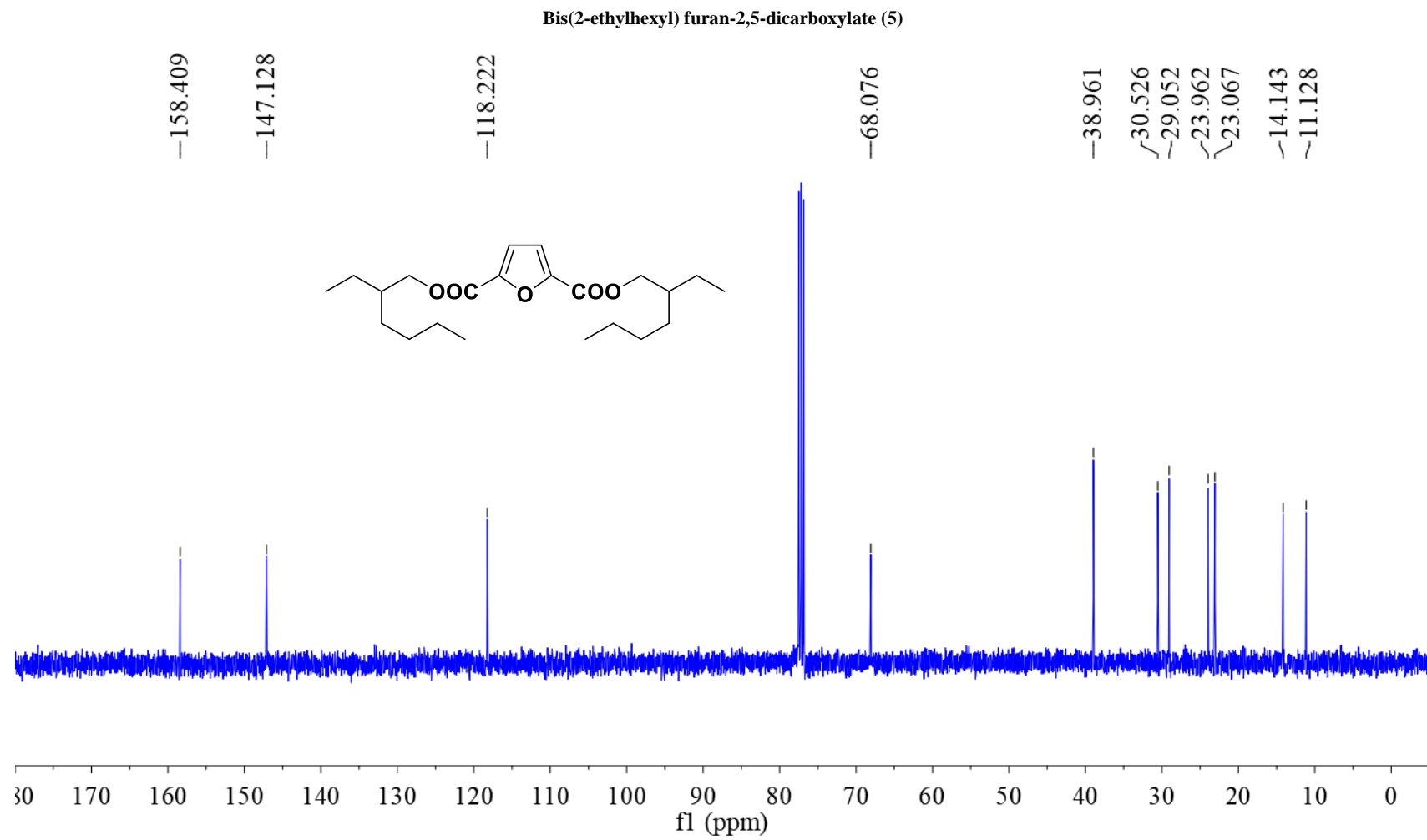
Diisobutyl furan-2,5-dicarboxylate (4)



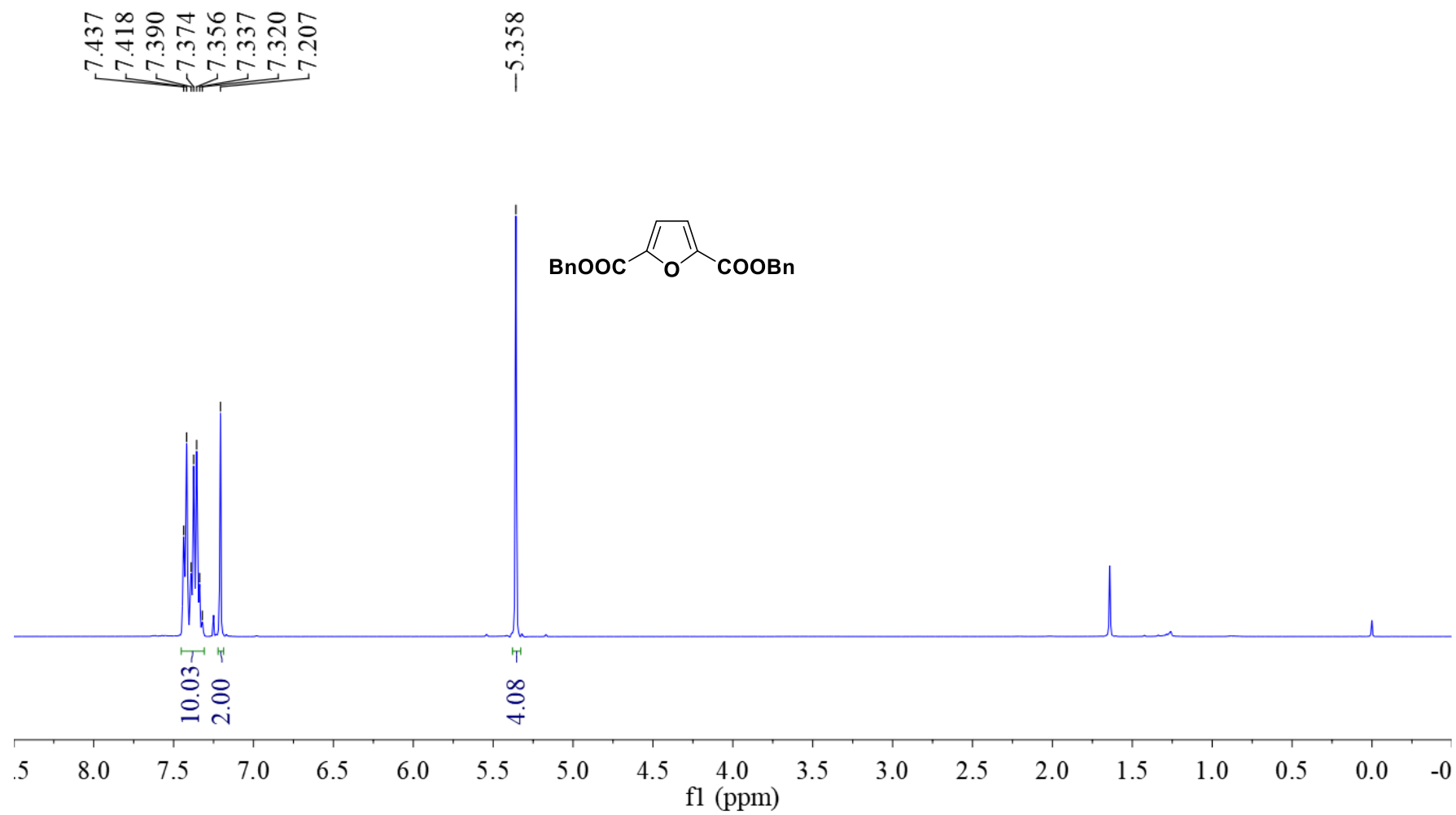
Diisobutyl furan-2,5-dicarboxylate (4)



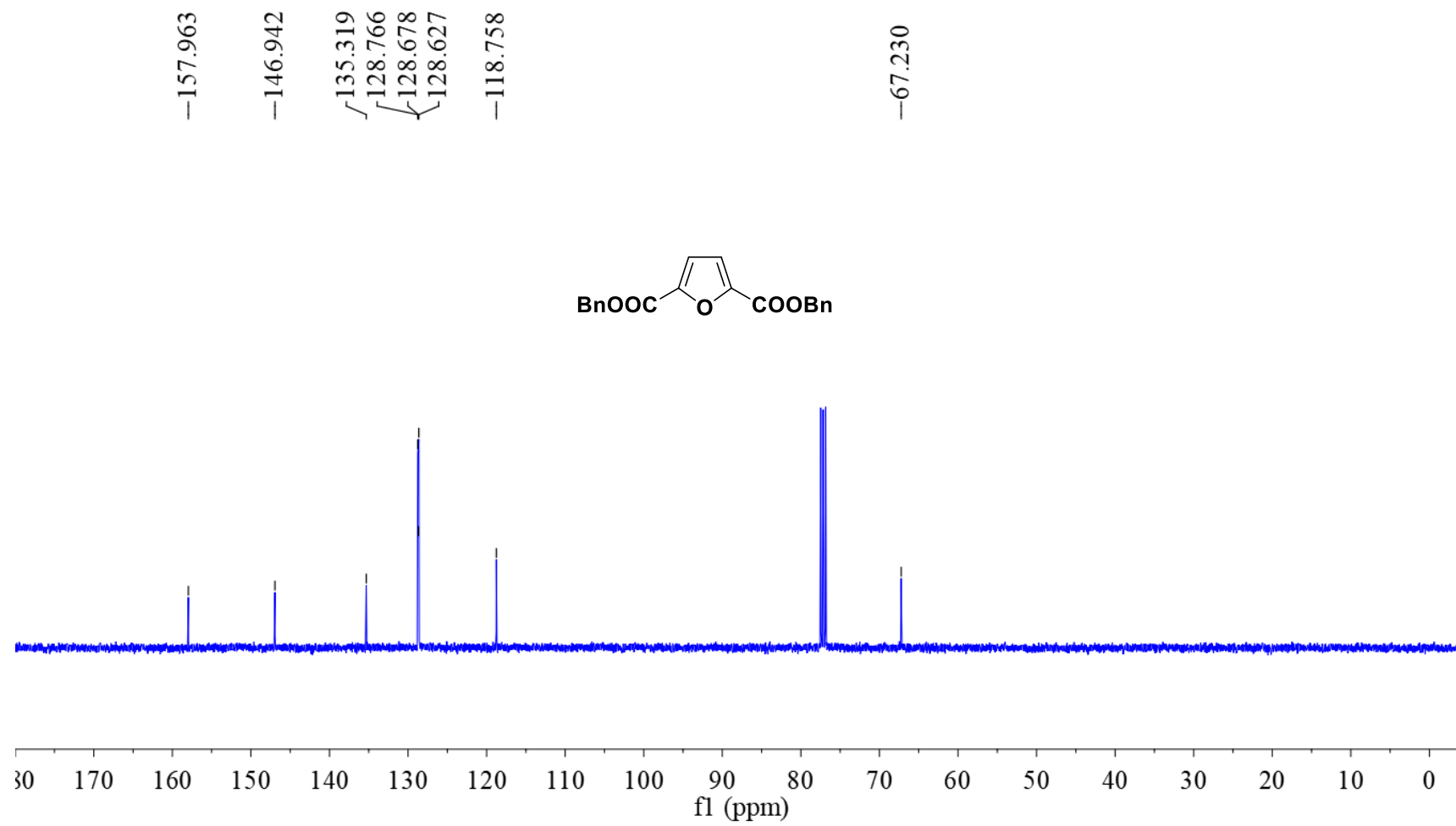




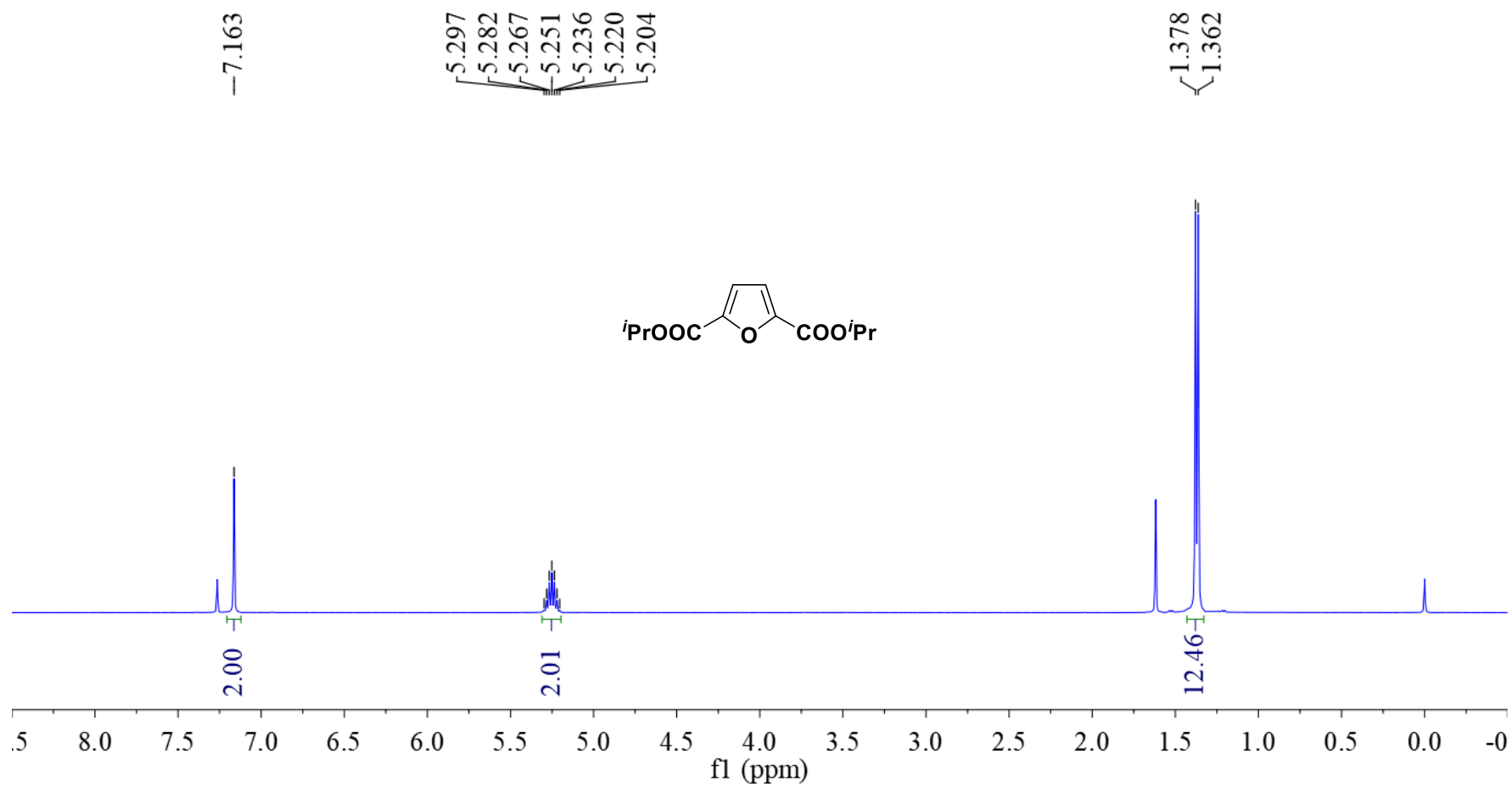
Dibenzyl furan-2,5-dicarboxylate (6)



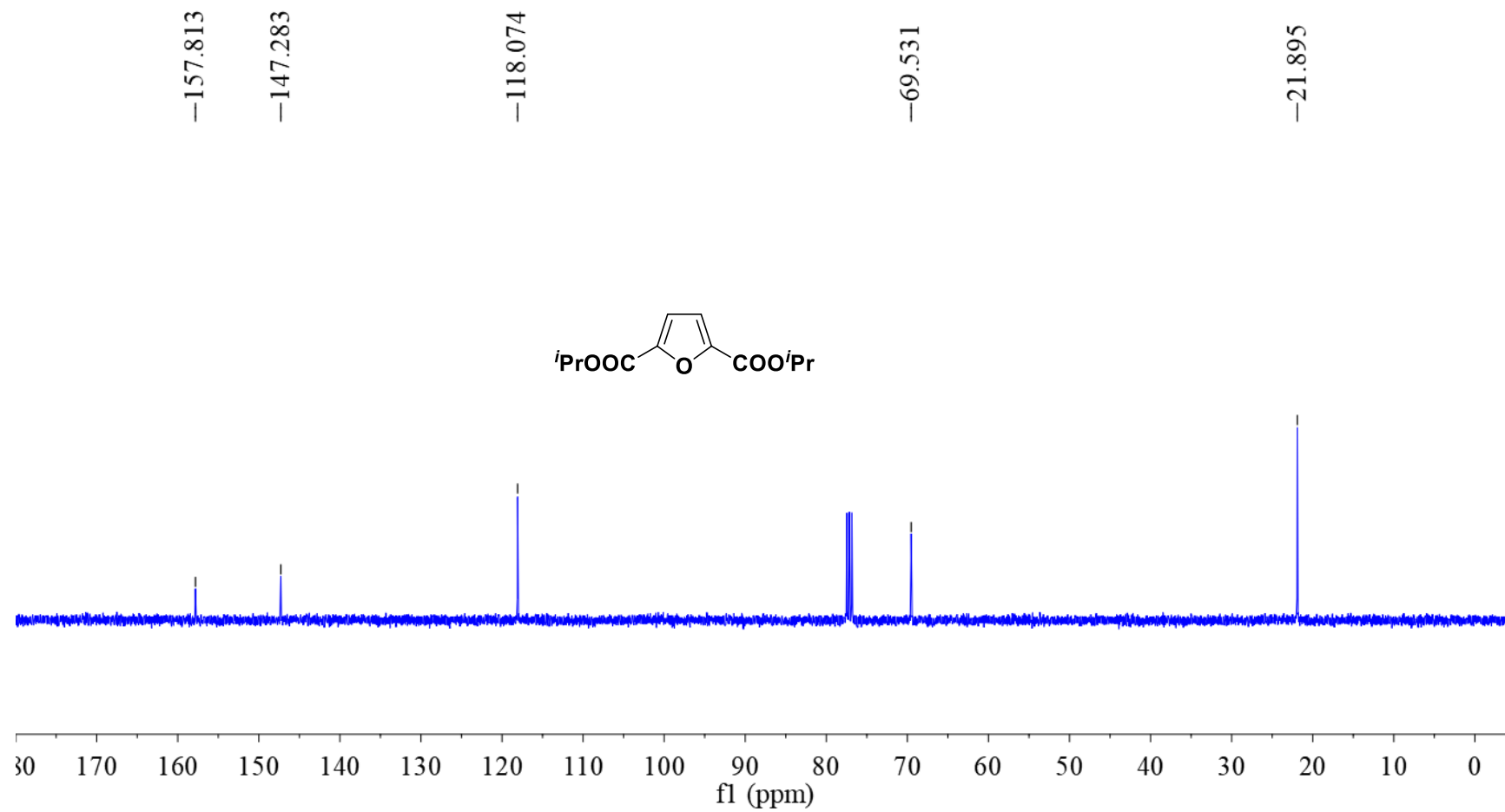
Dibenzyl furan-2,5-dicarboxylate (6)



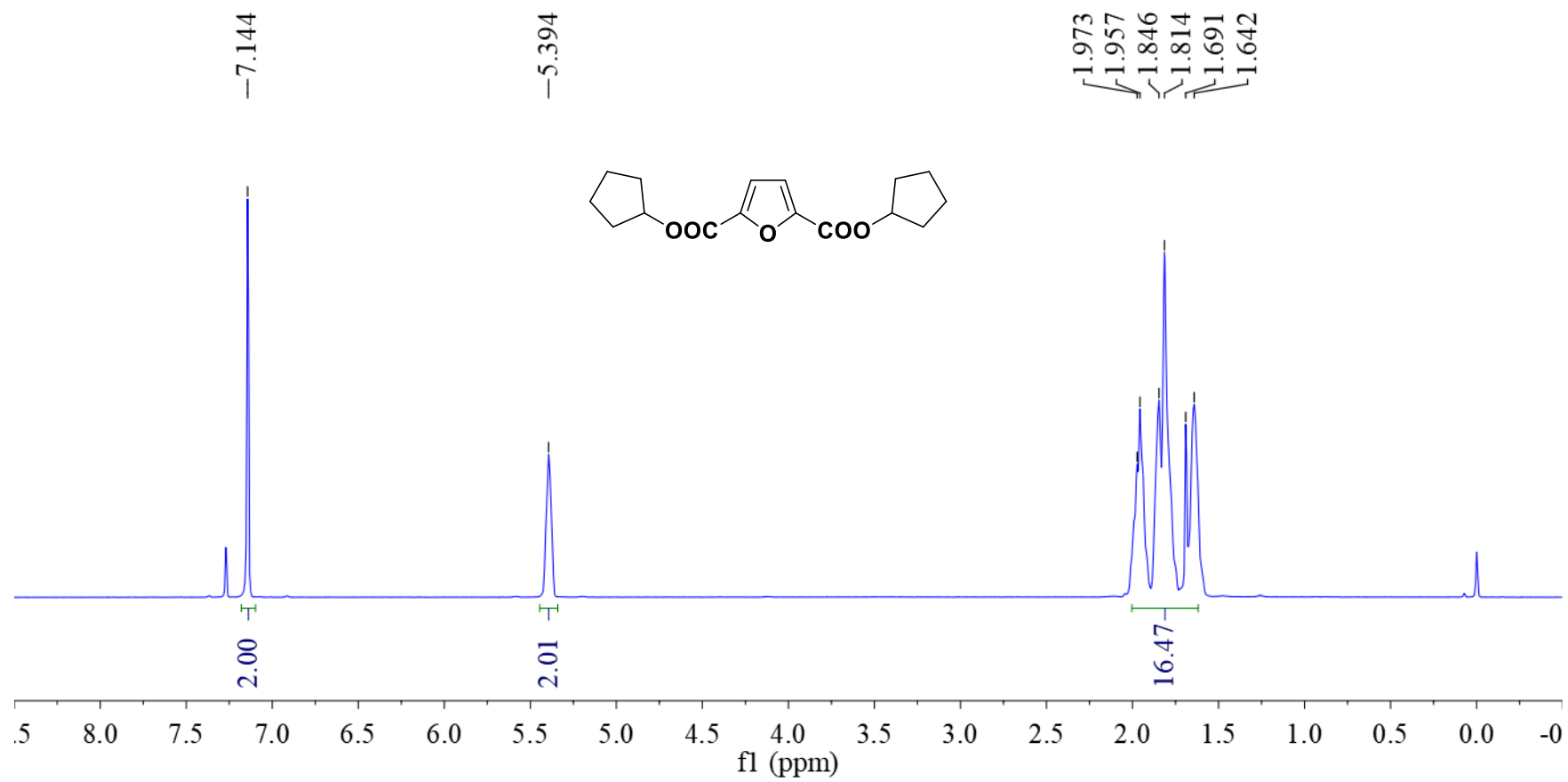
Diisopropyl furan-2,5-dicarboxylate (7)



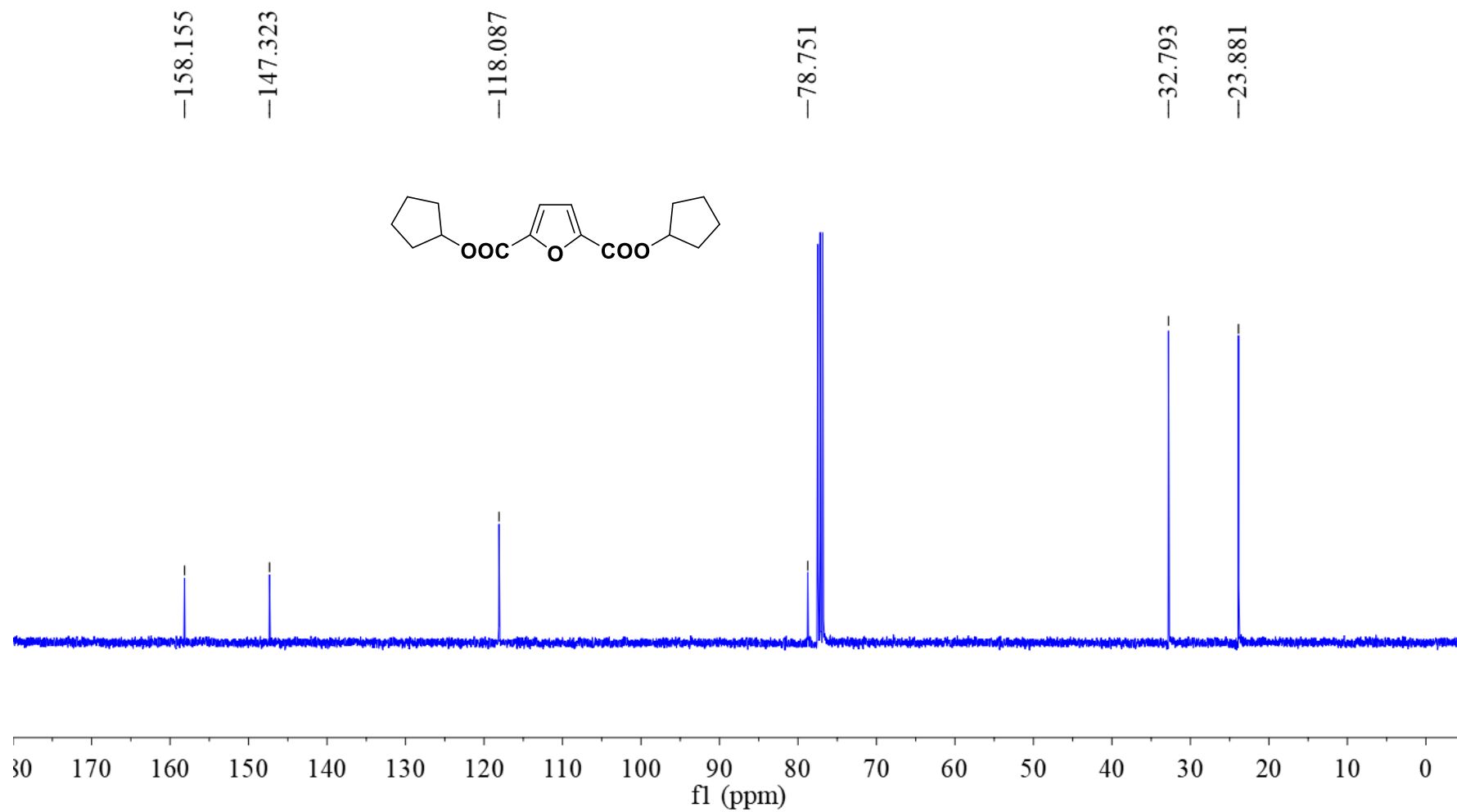
Diisopropyl furan-2,5-dicarboxylate (7)



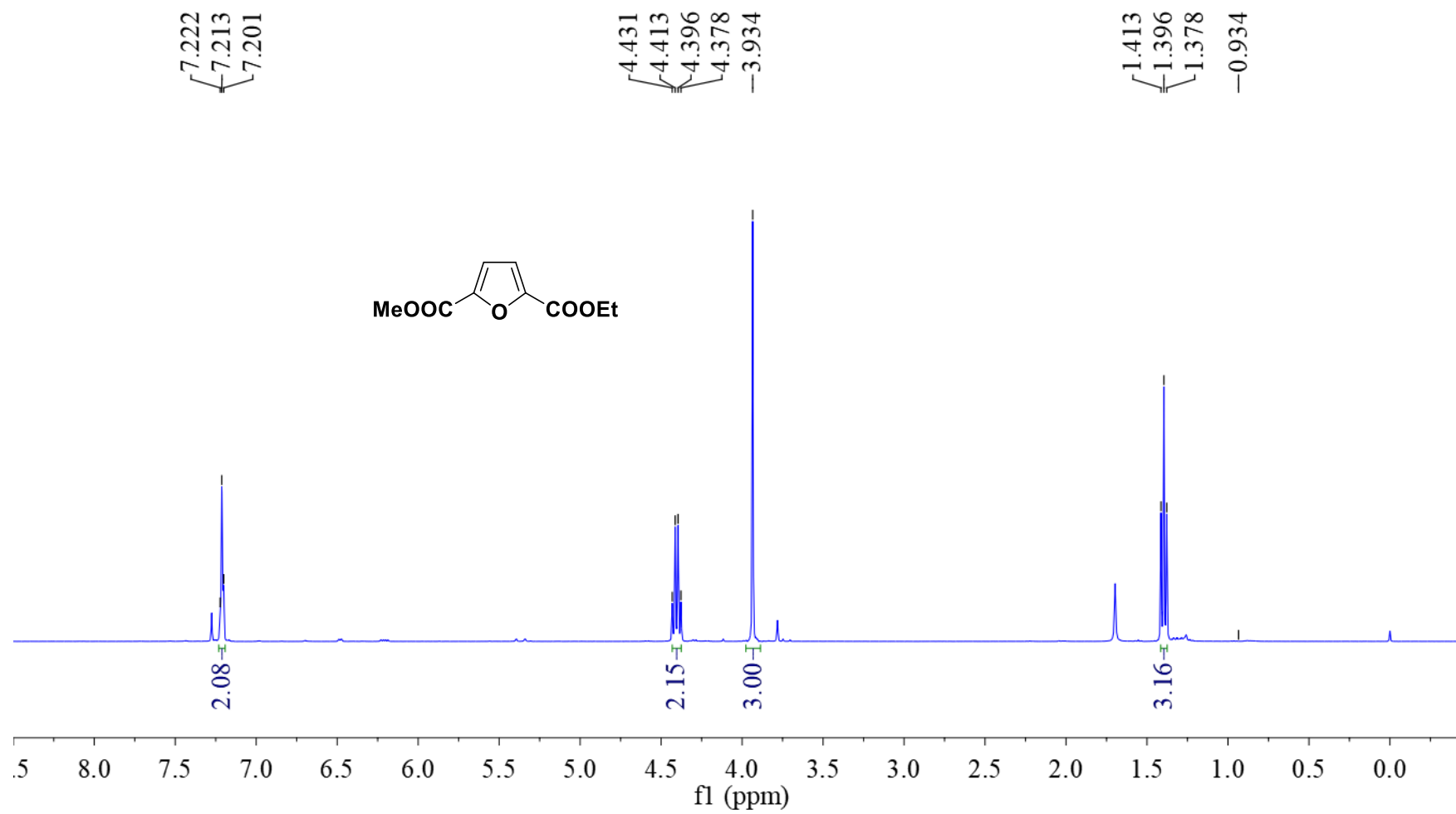
Dicyclopentyl furan-2,5-dicarboxylate (8)



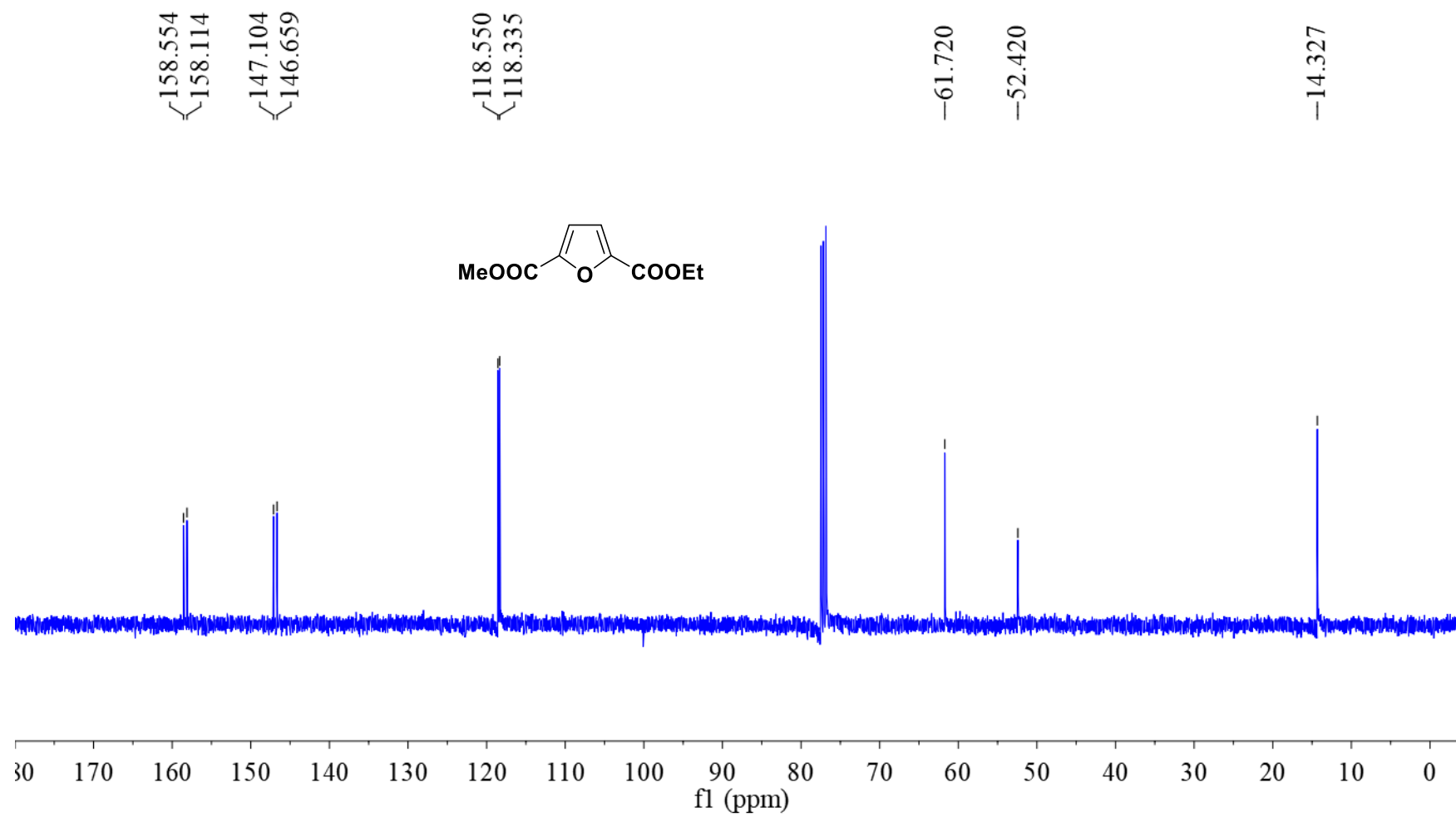
Dicyclopentyl furan-2,5-dicarboxylate (8)



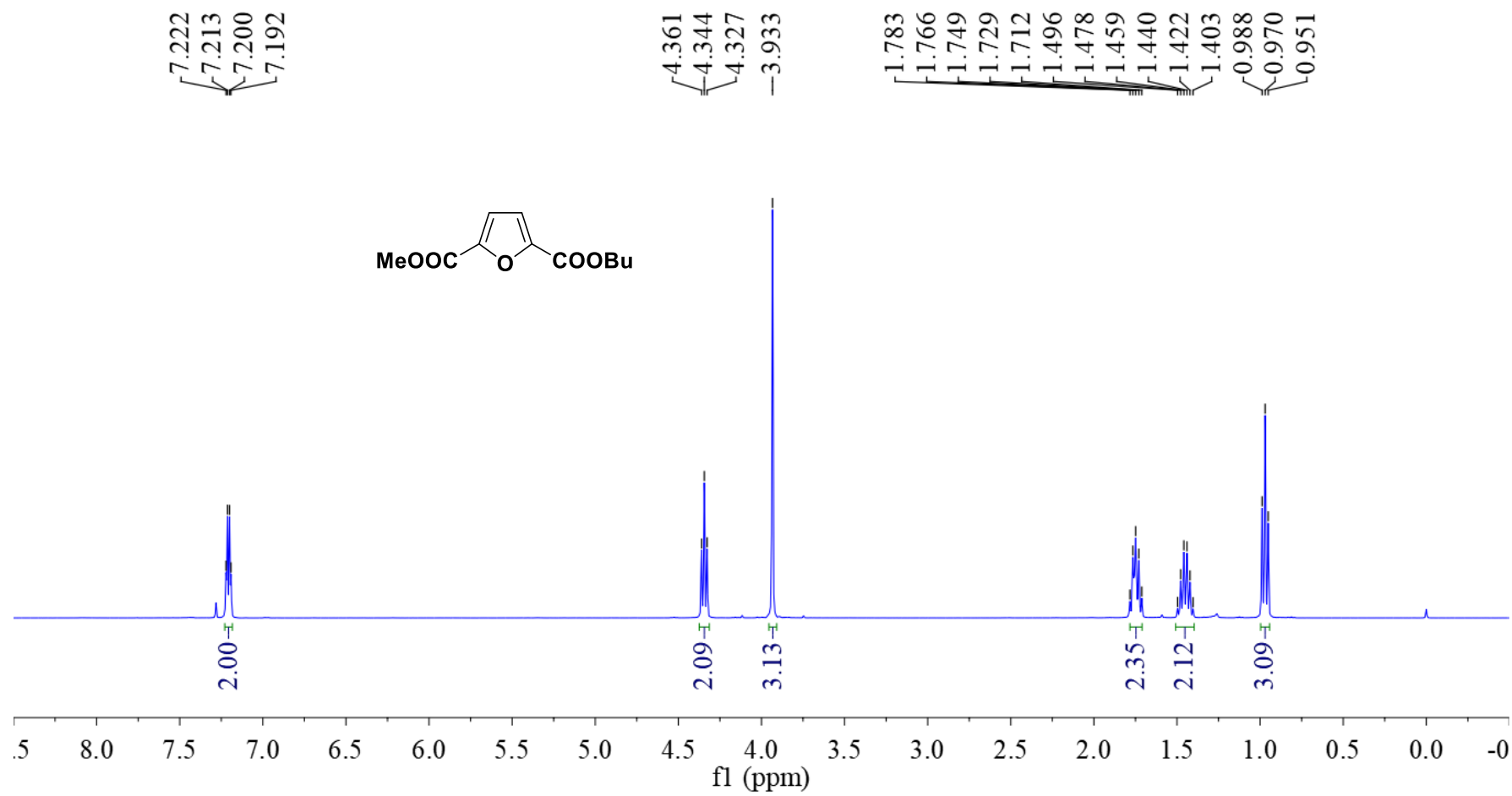
2-ethyl 5-methyl furan-2,5-dicarboxylate (10)



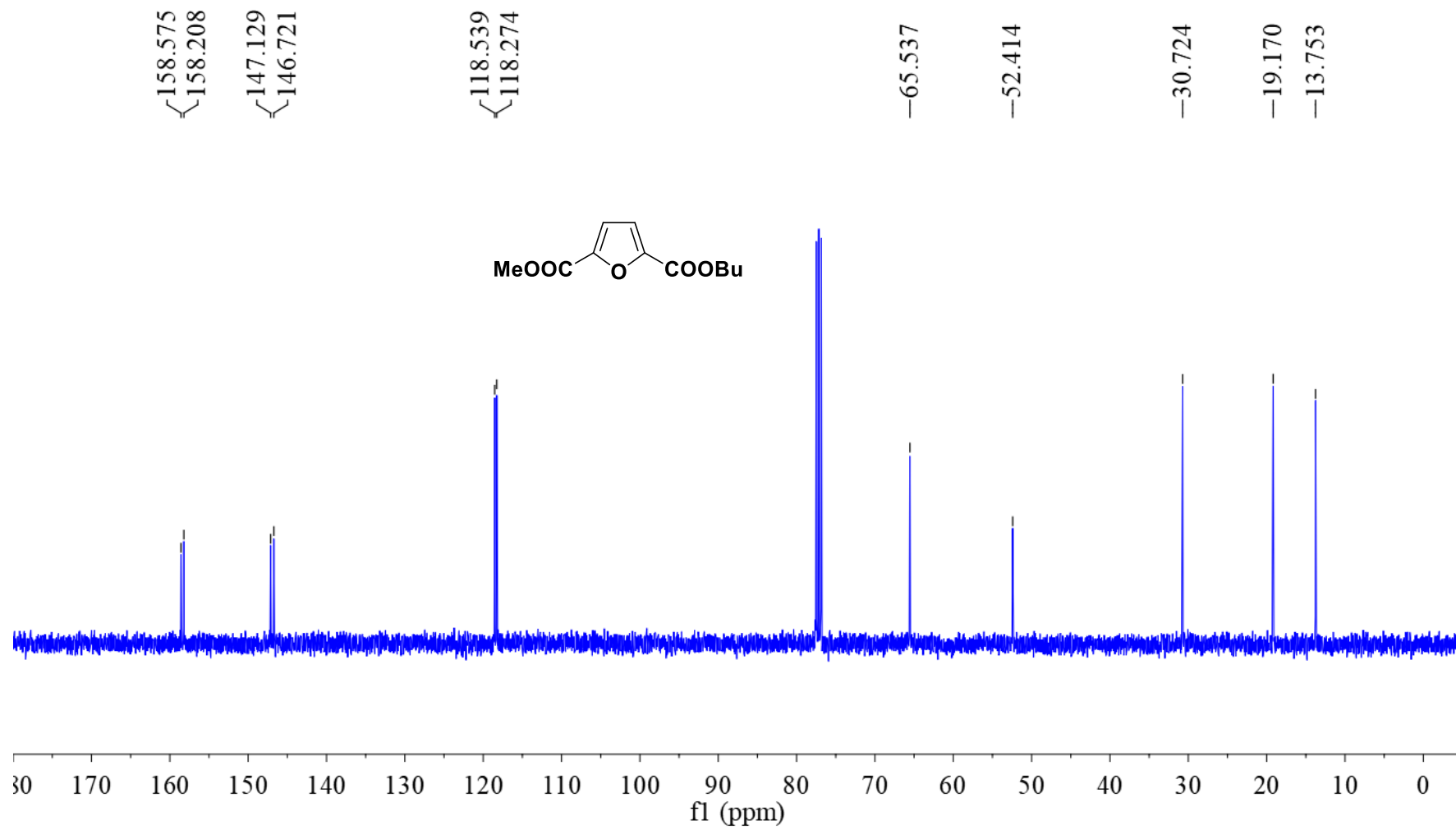
2-ethyl 5-methyl furan-2,5-dicarboxylate (10)



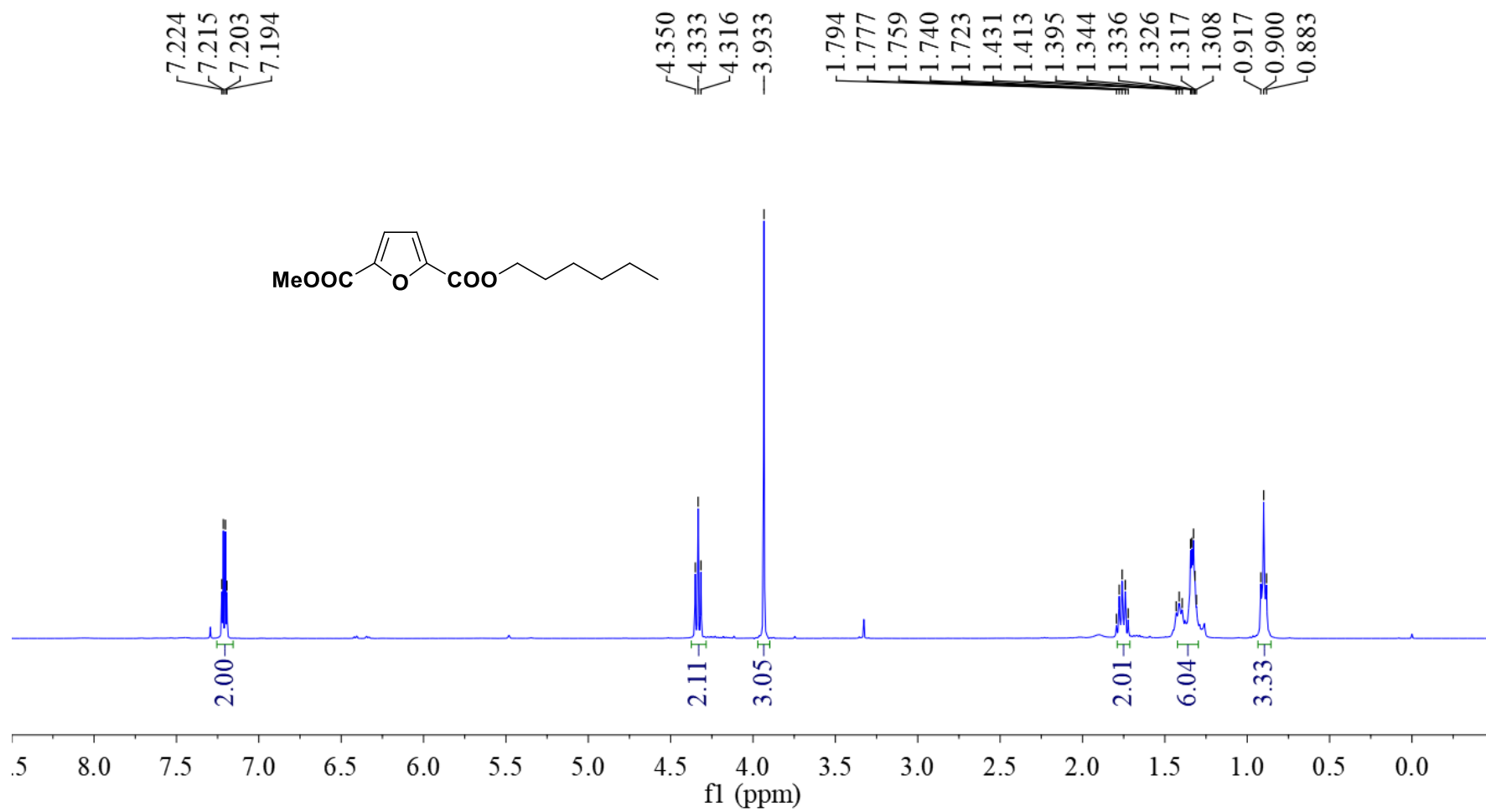
2-butyl 5-methyl furan-2,5-dicarboxylate (11)



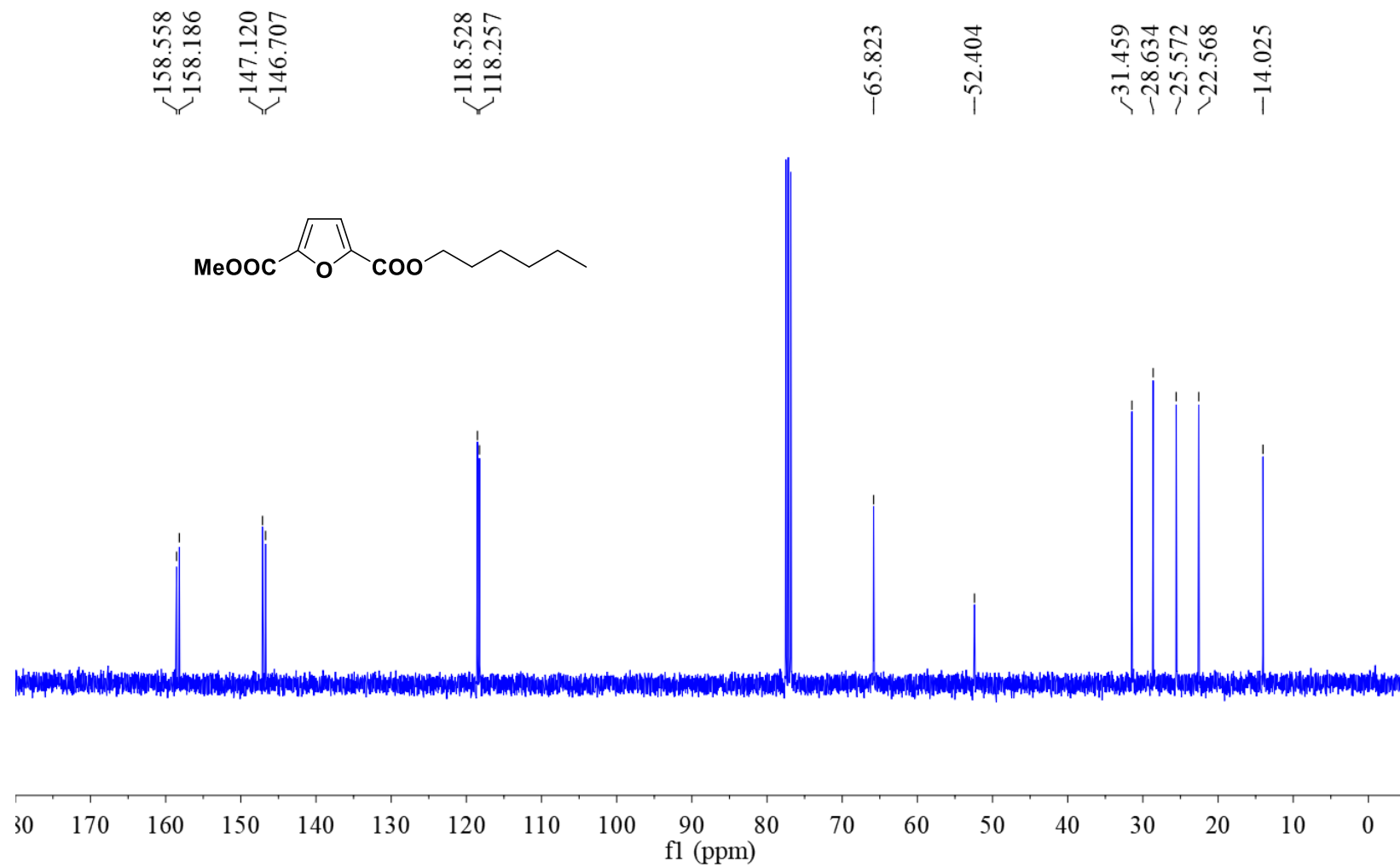
2-butyl 5-methyl furan-2,5-dicarboxylate (11)



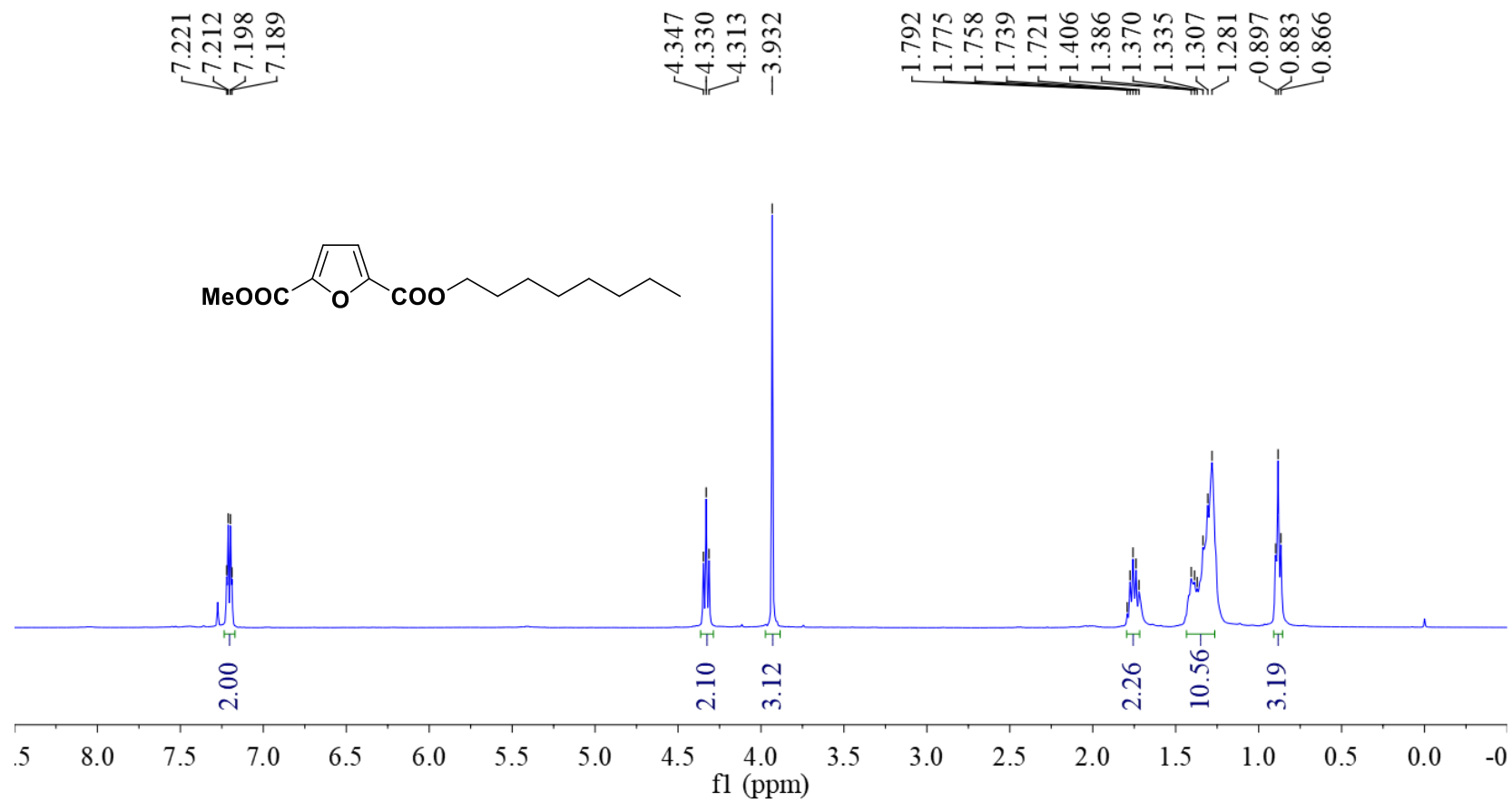
2-hexyl 5-methyl furan-2,5-dicarboxylate (12)



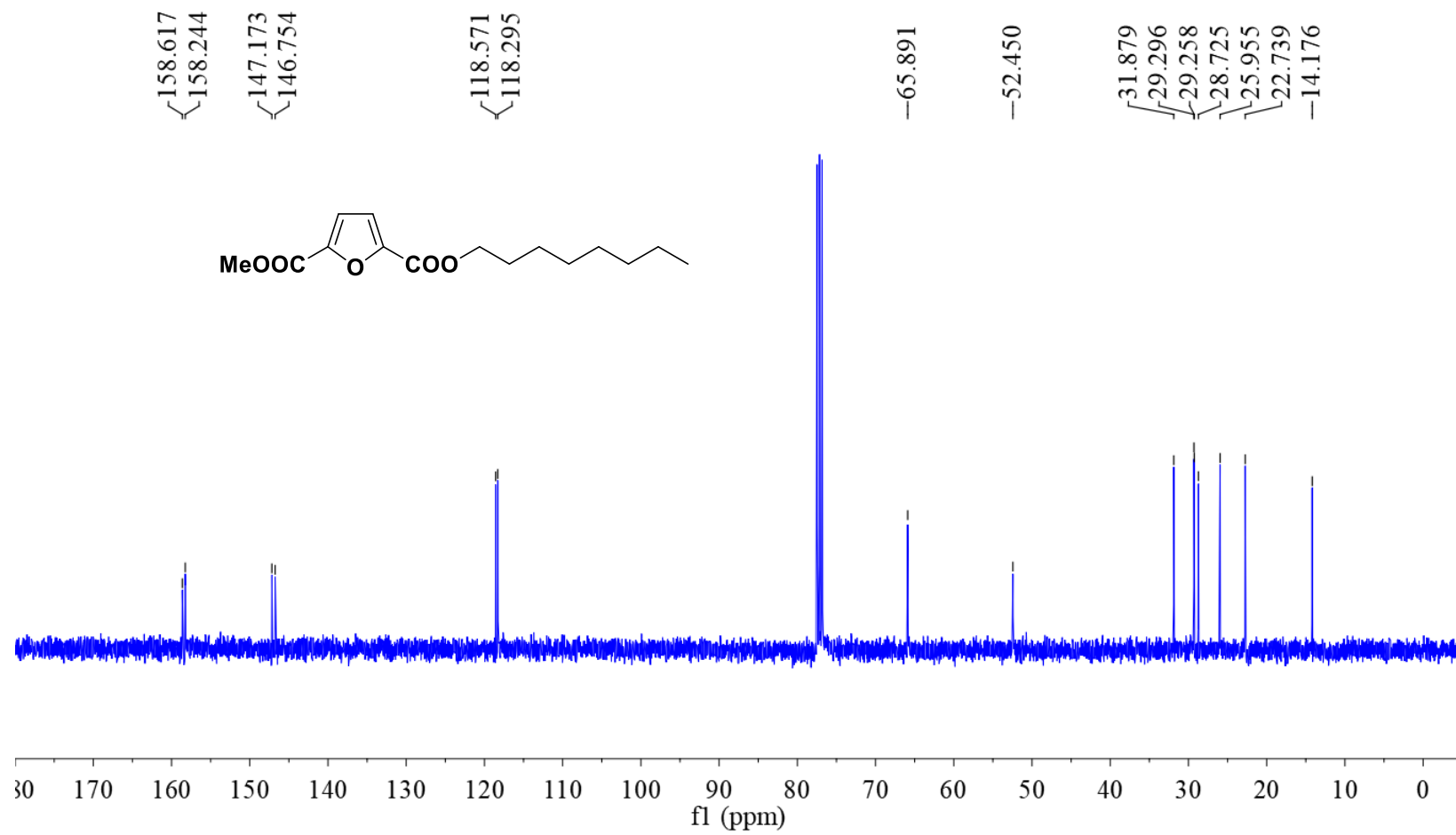
2-hexyl 5-methyl furan-2,5-dicarboxylate (12)



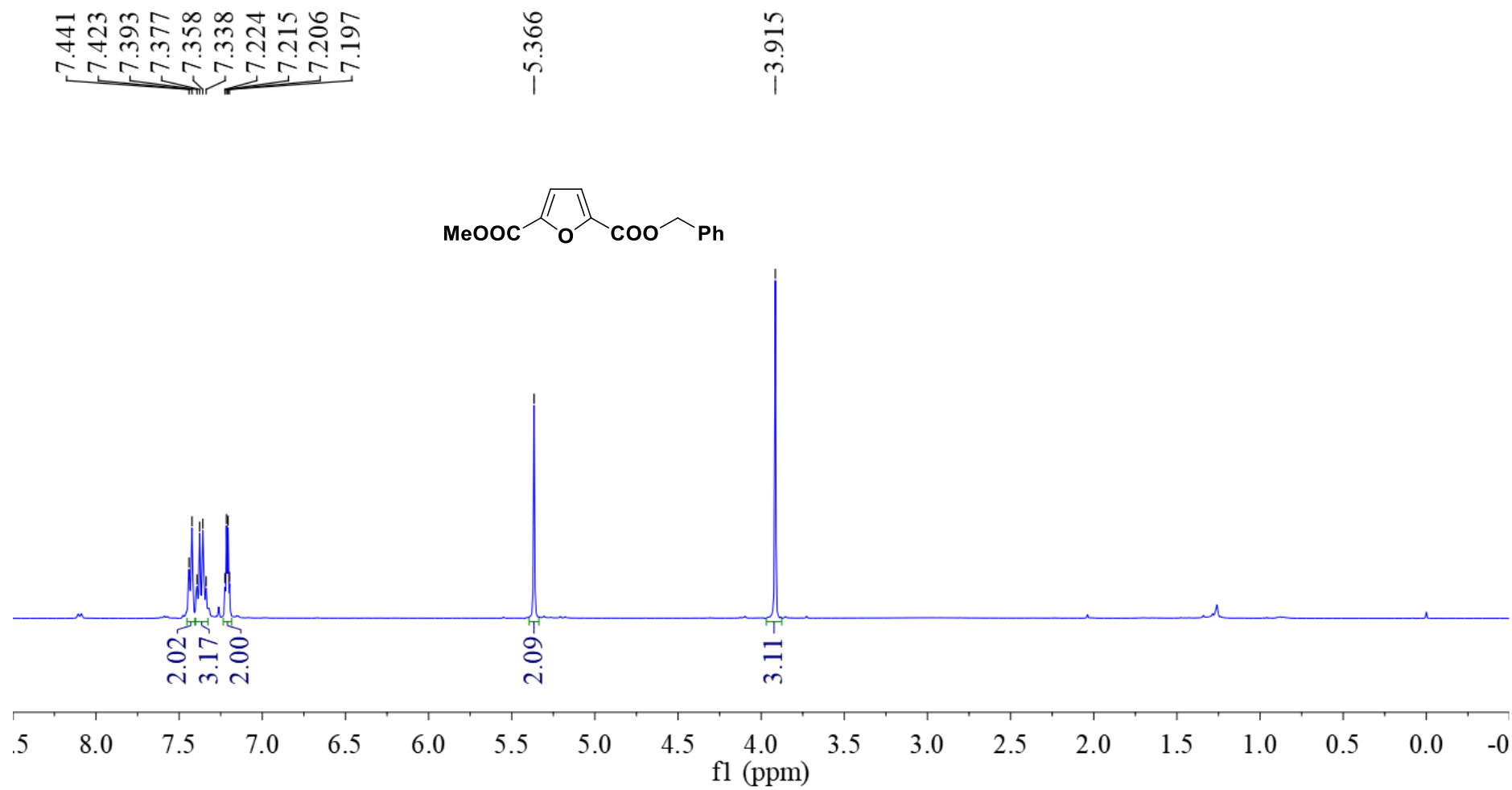
2-methyl 5-octyl furan-2,5-dicarboxylate (13)



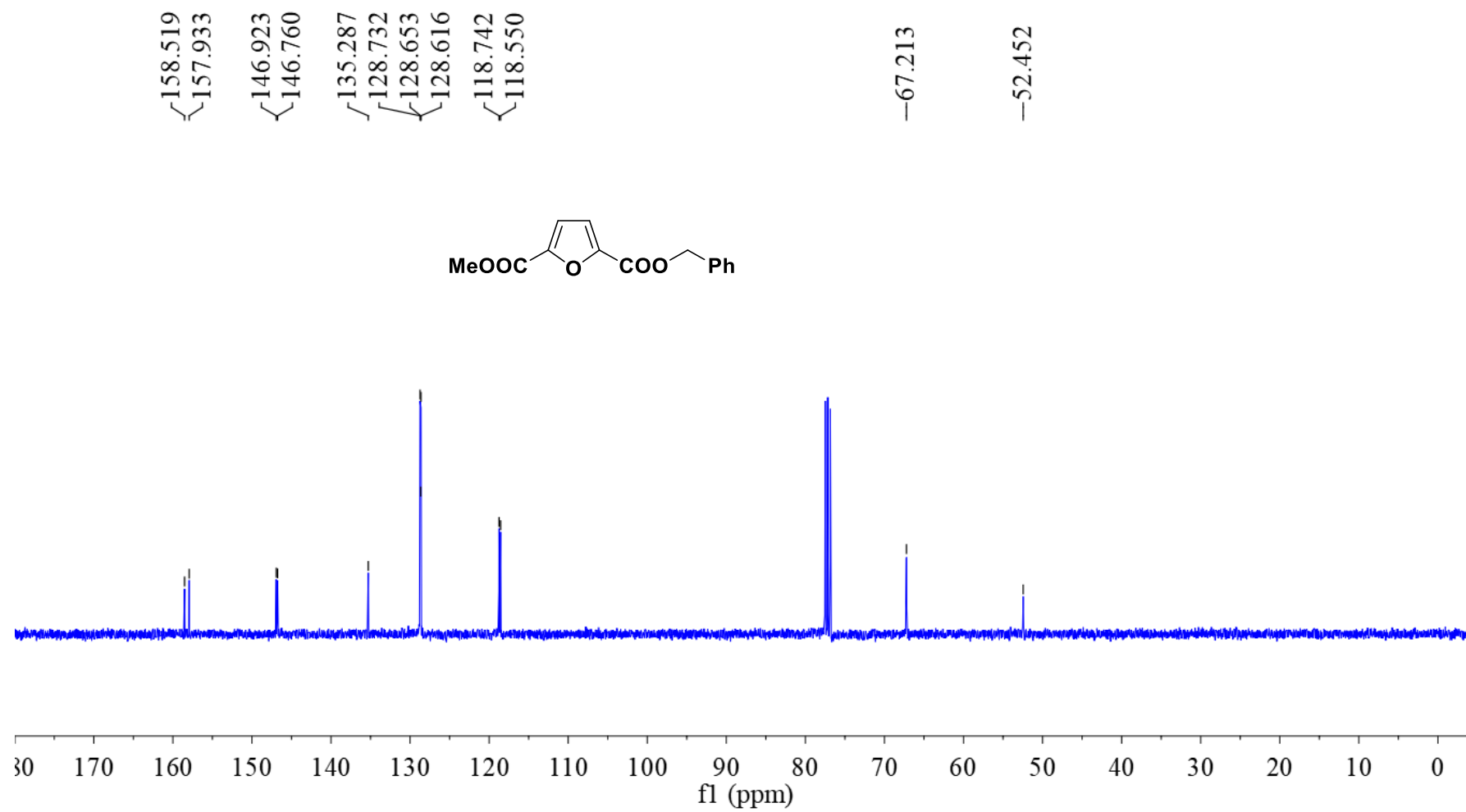
2-methyl 5-octyl furan-2,5-dicarboxylate (13)



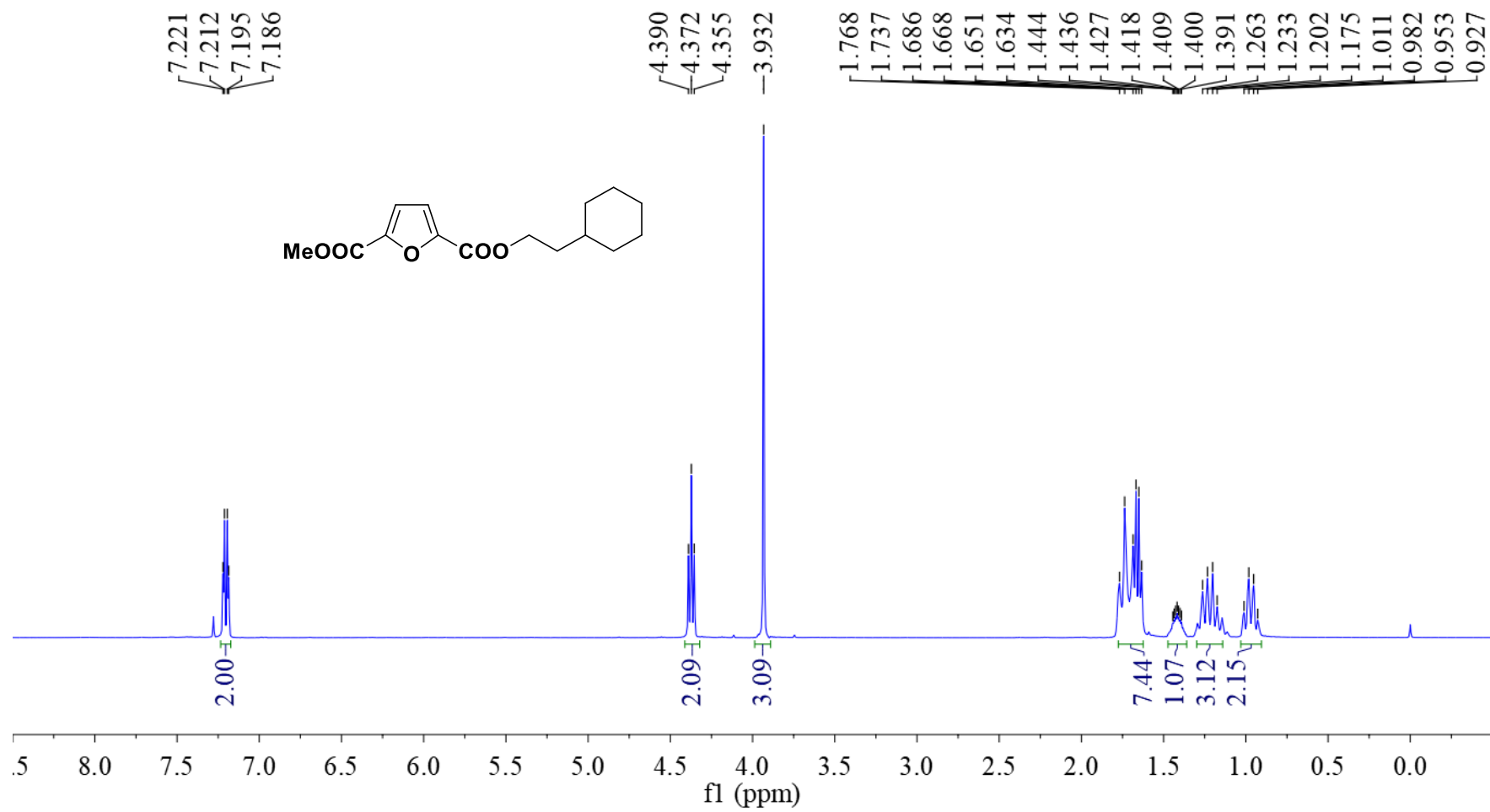
2-benzyl 5-methyl furan-2,5-dicarboxylate (14)



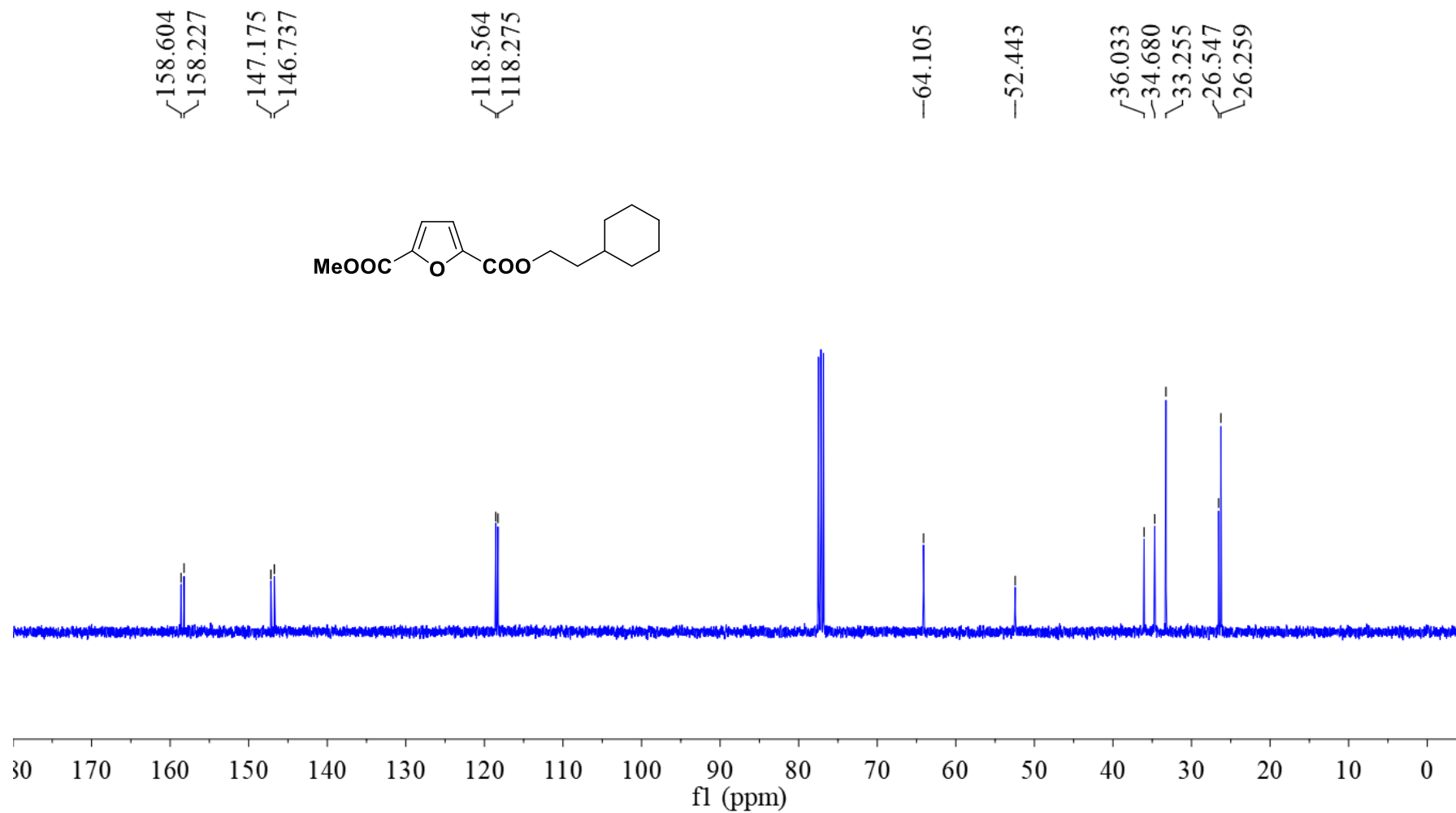
2-benzyl 5-methyl furan-2,5-dicarboxylate (14)



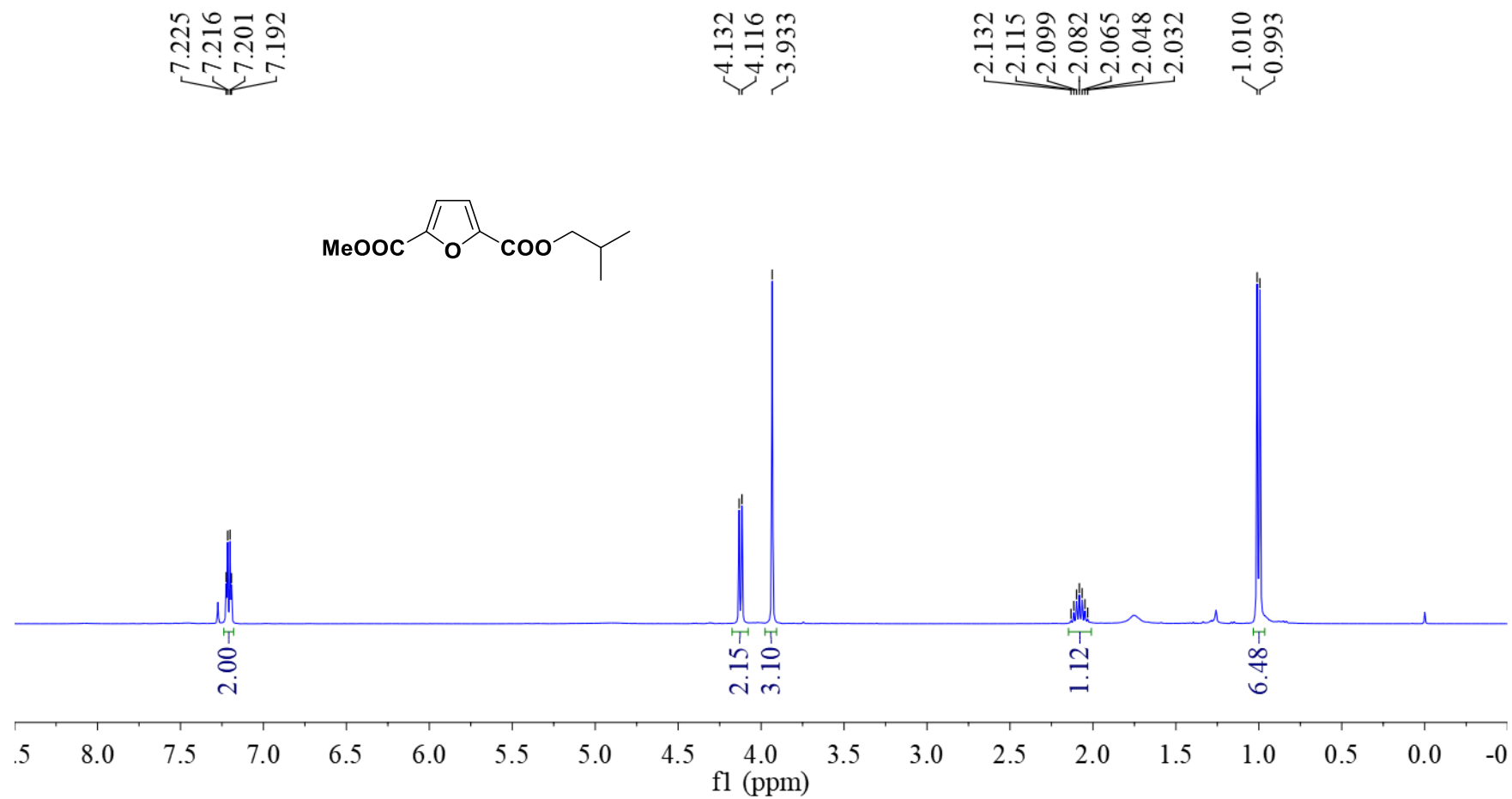
2-(2-cyclohexylethyl) 5-methyl furan-2,5-dicarboxylate (15)



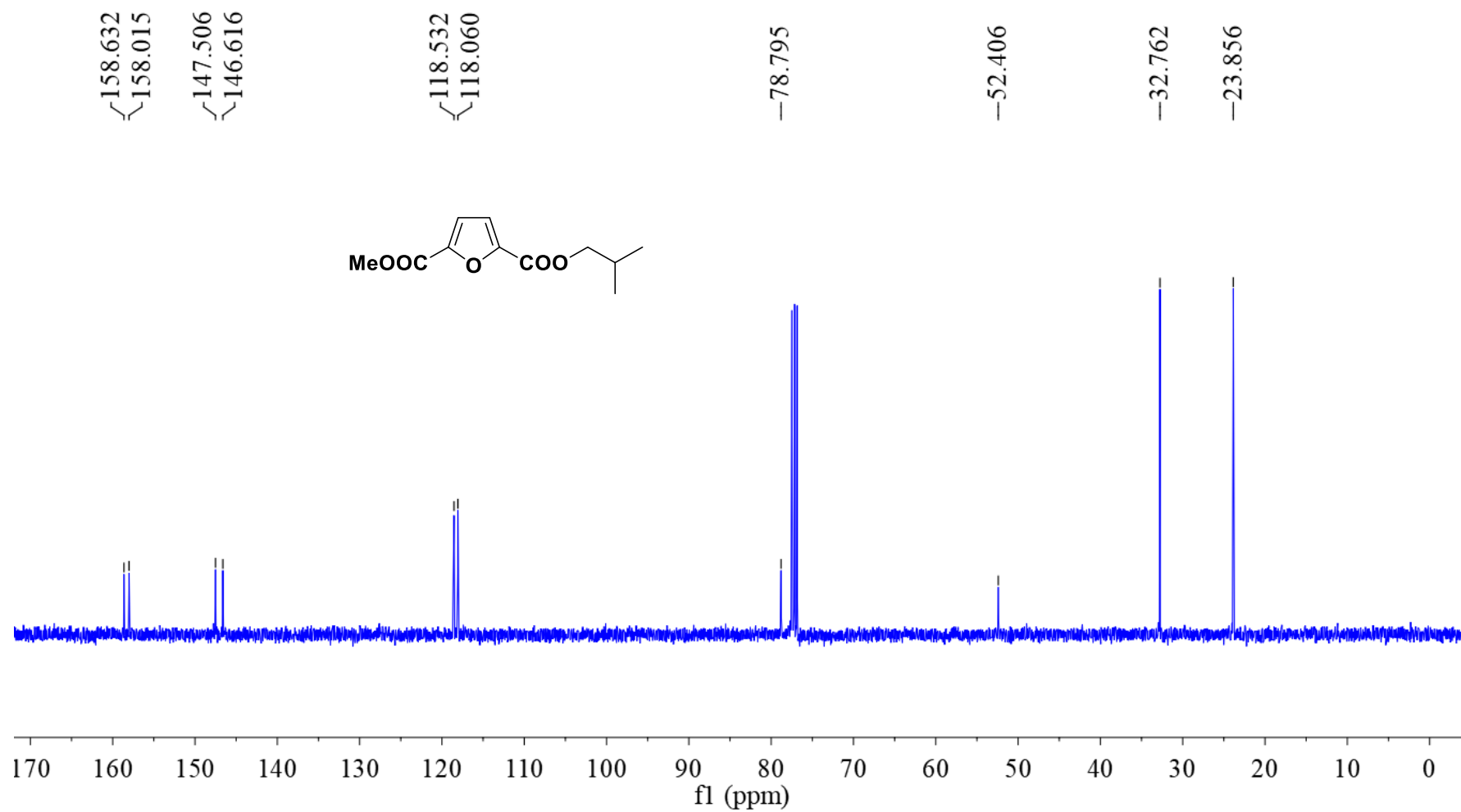
2-(2-cyclohexylethyl) 5-methyl furan-2,5-dicarboxylate (15)



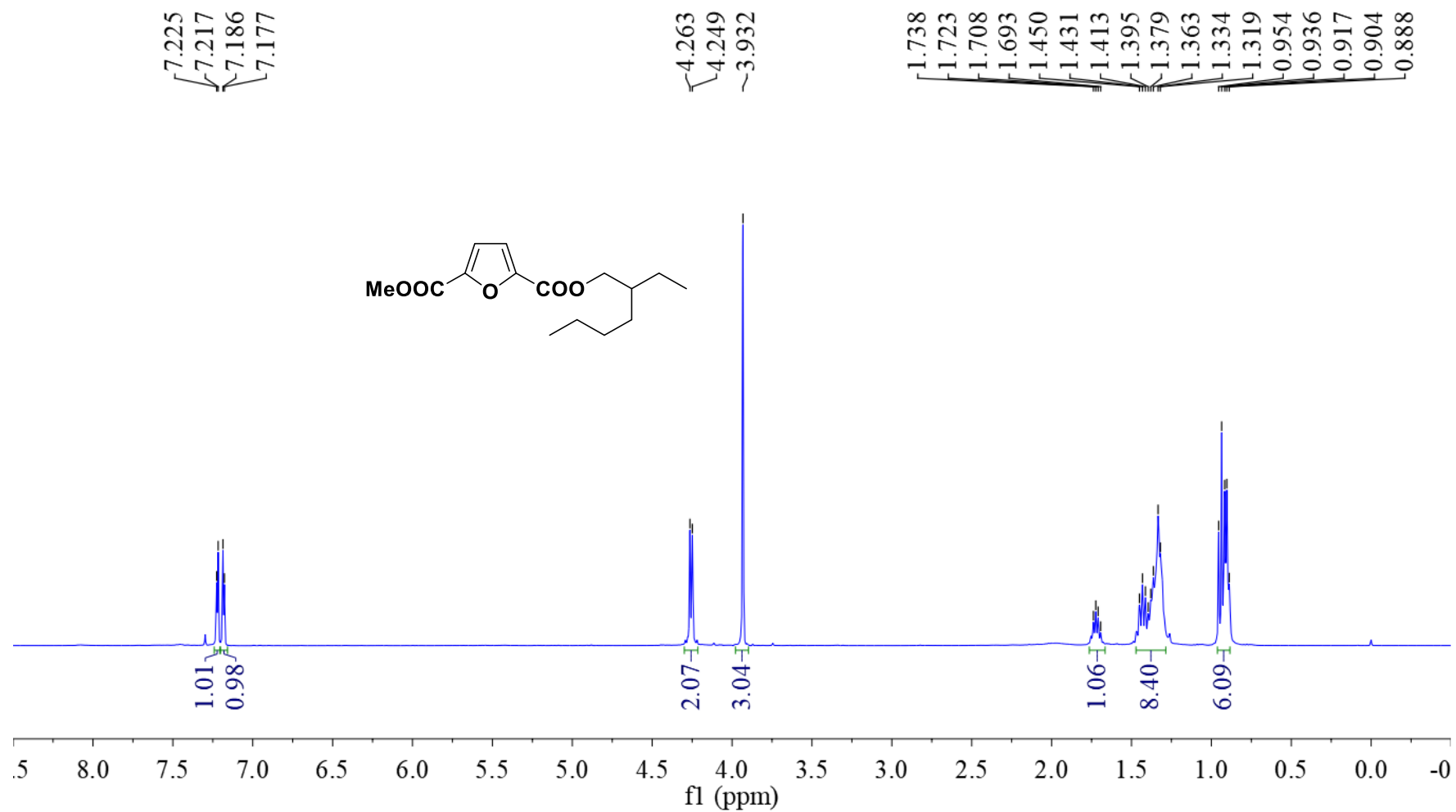
2-isobutyl 5-methyl furan-2,5-dicarboxylate (16)



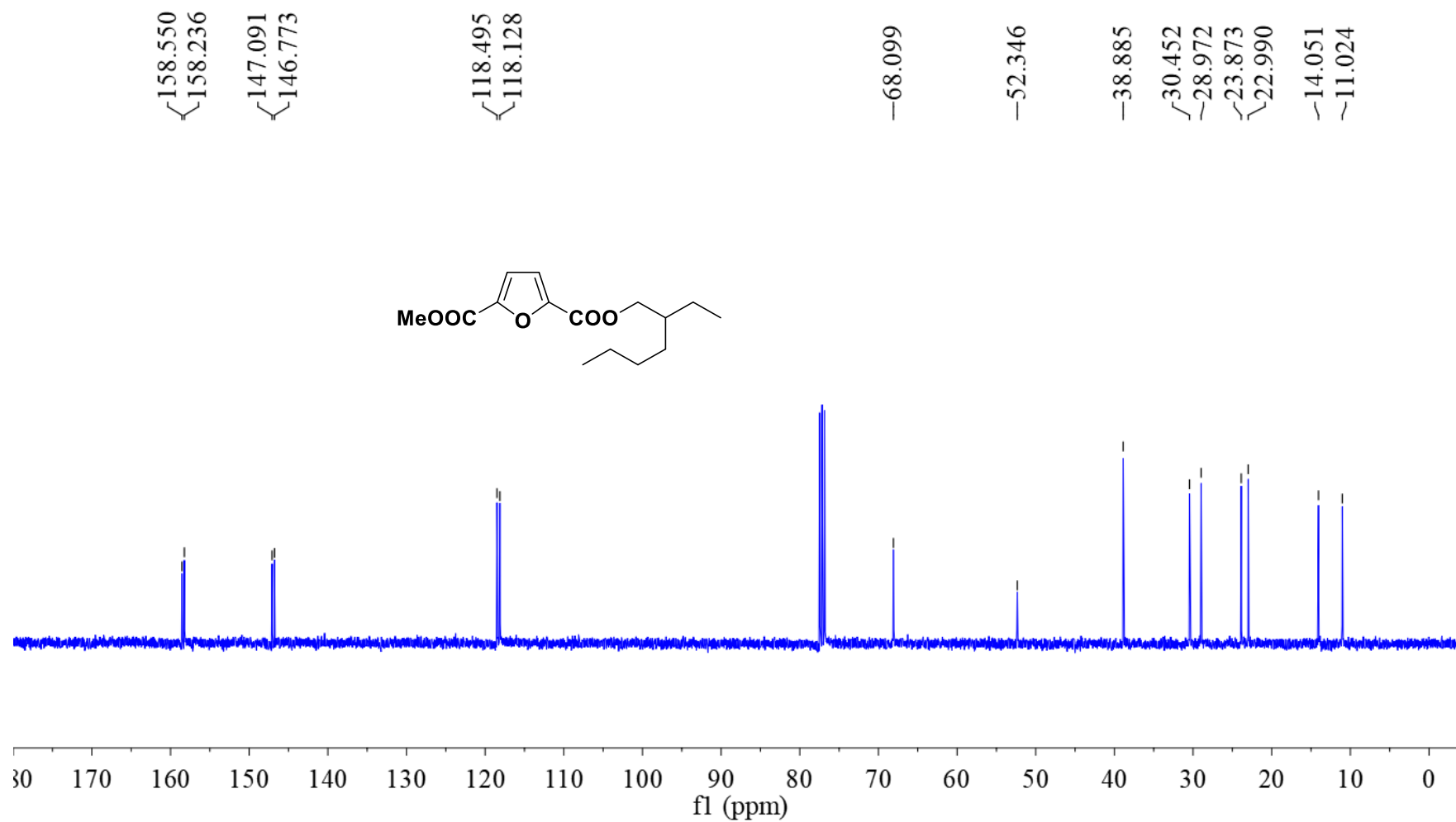
2-isobutyl 5-methyl furan-2,5-dicarboxylate (16)



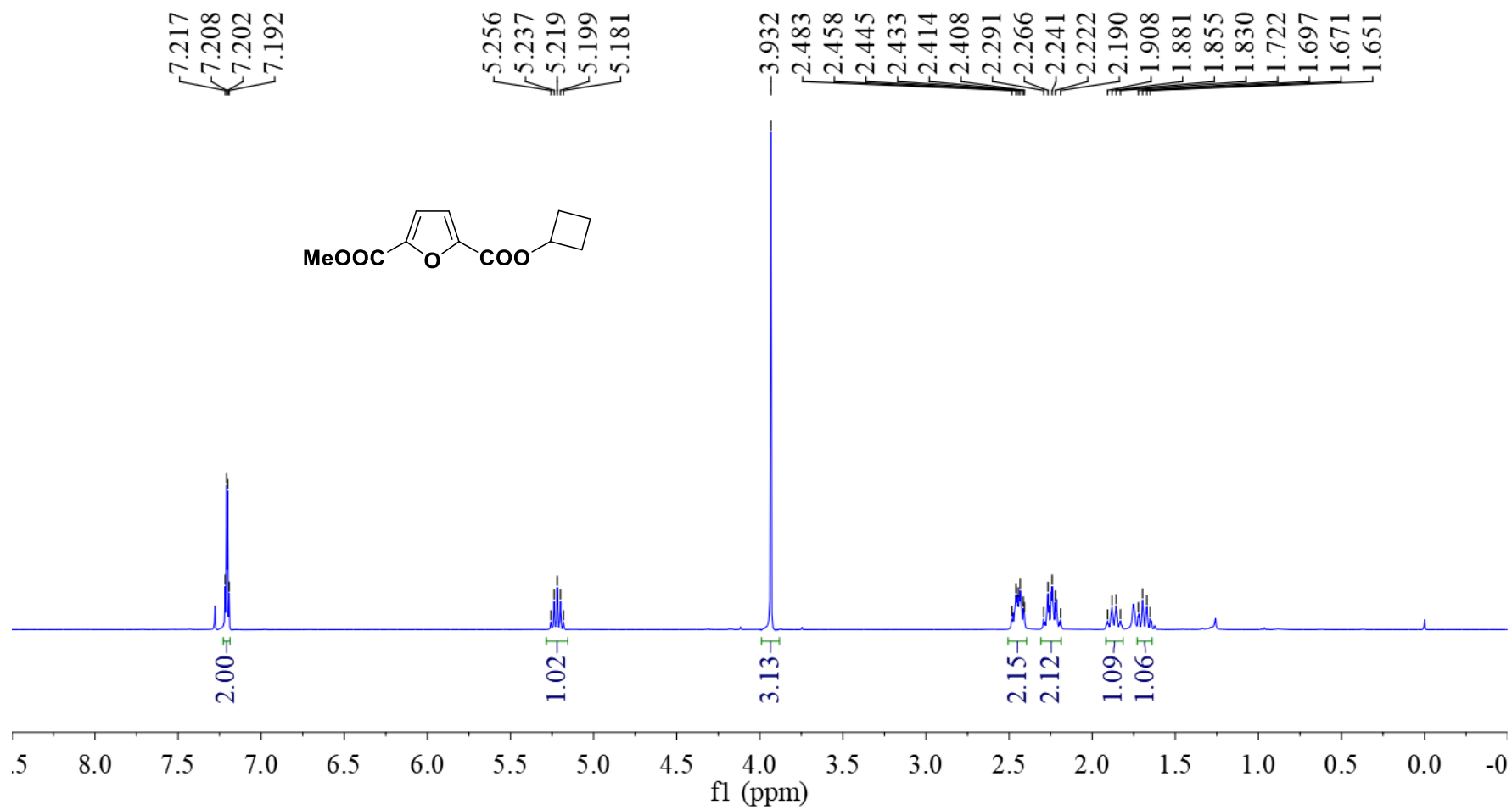
2-(2-ethylhexyl) 5-methyl furan-2,5-dicarboxylate (17)



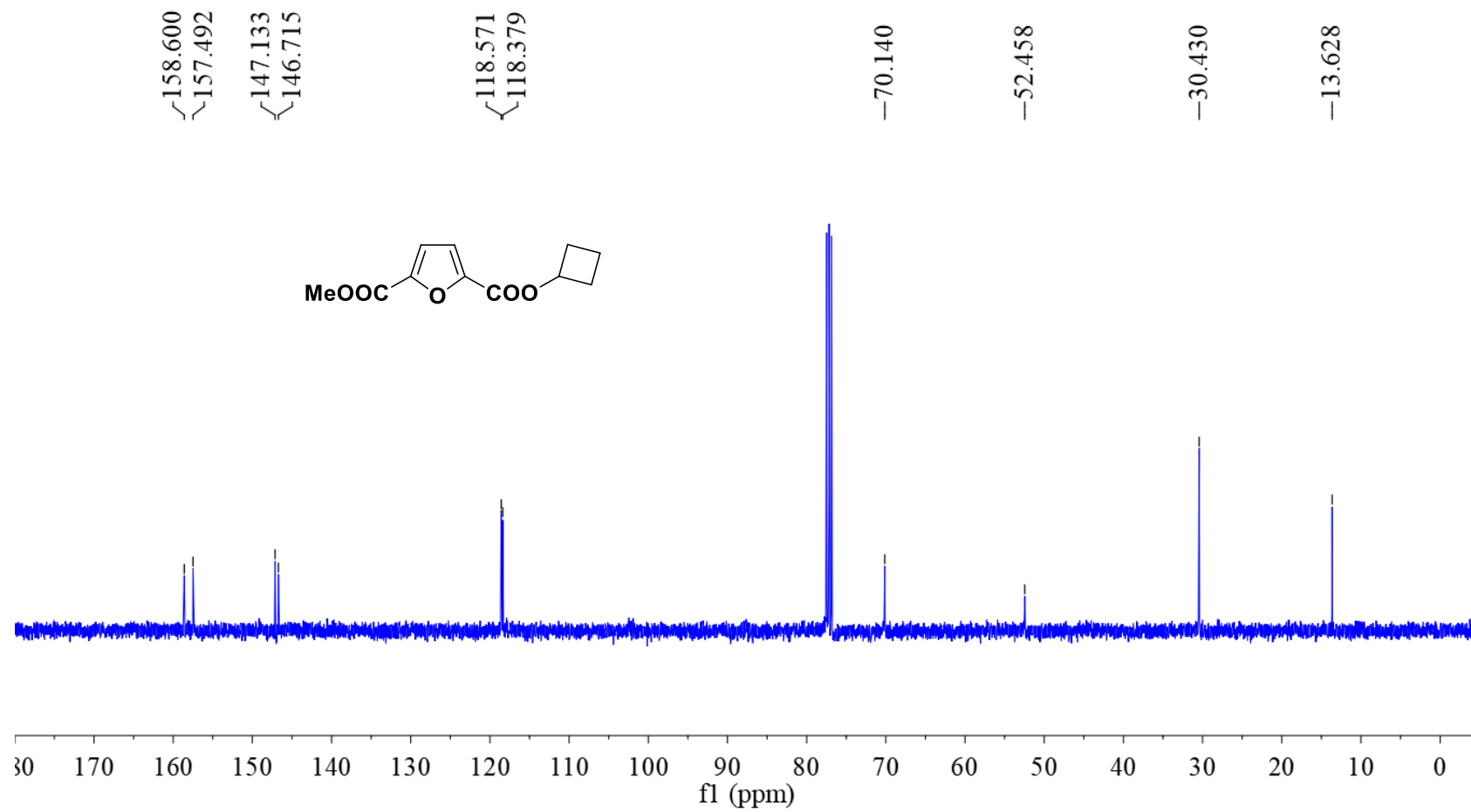
2-(2-ethylhexyl) 5-methyl furan-2,5-dicarboxylate (17)



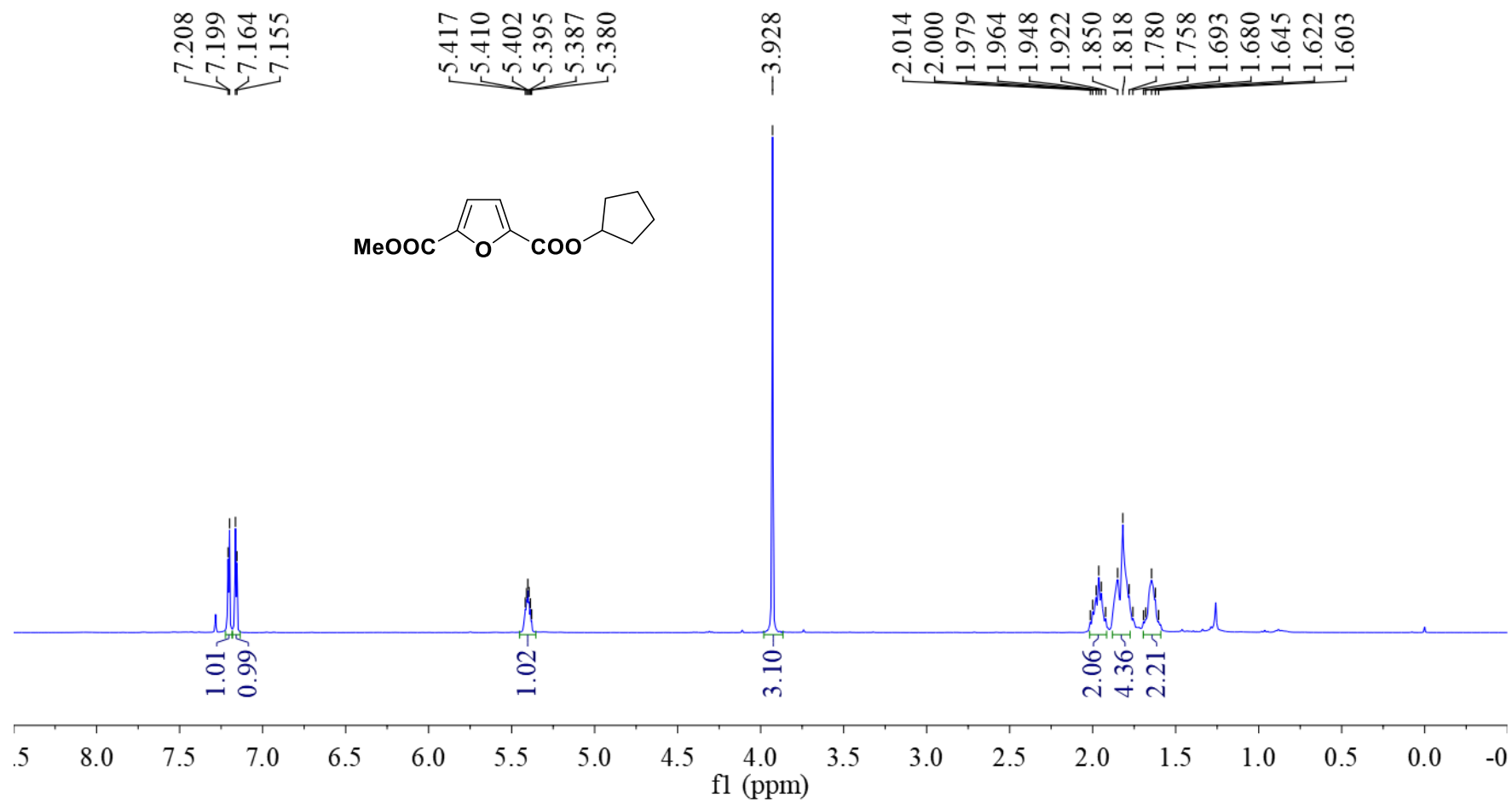
2-cyclobutyl 5-methyl furan-2,5-dicarboxylate (18)



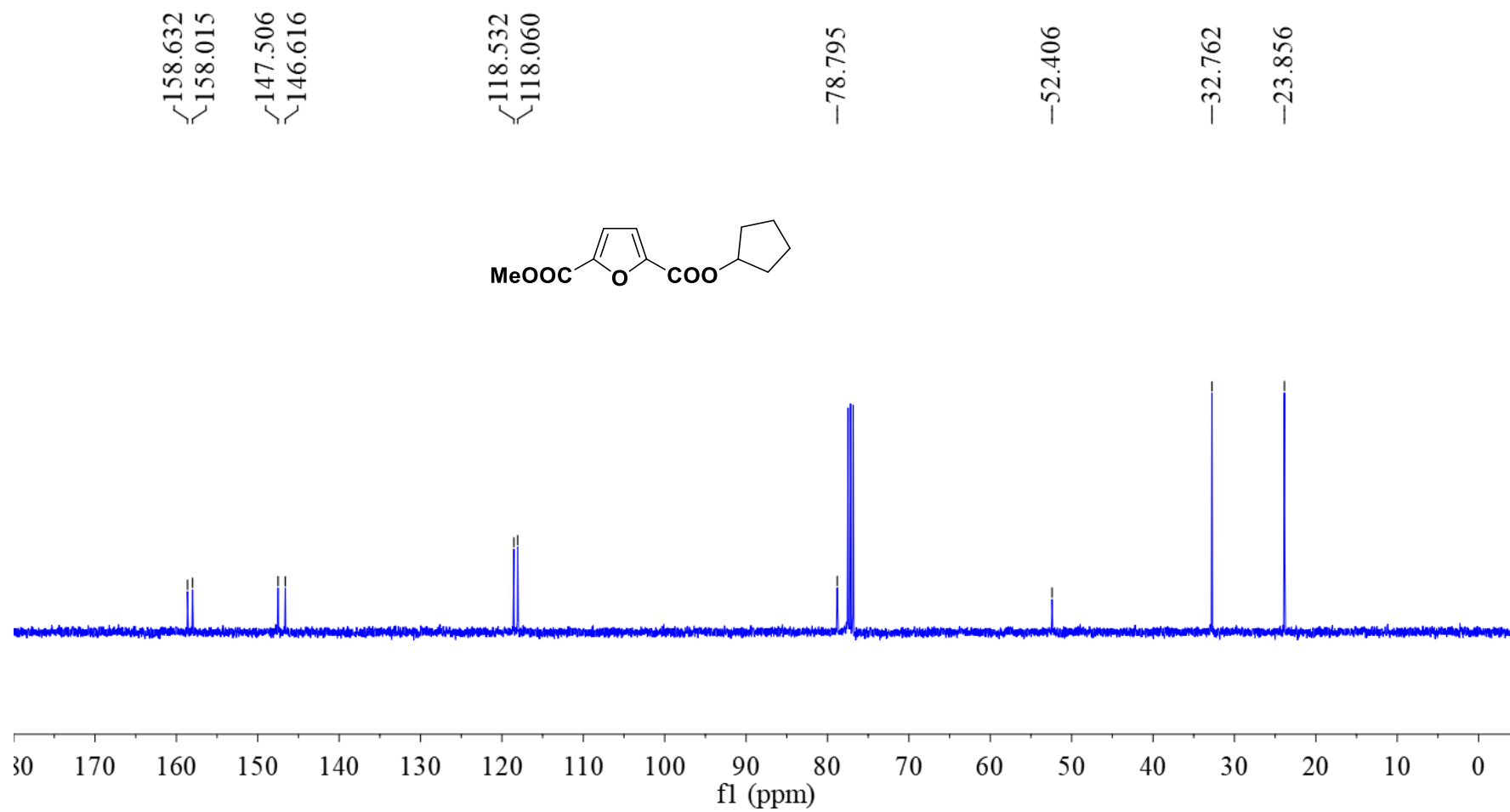
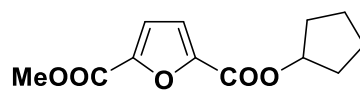
2-cyclobutyl 5-methyl furan-2,5-dicarboxylate (18)



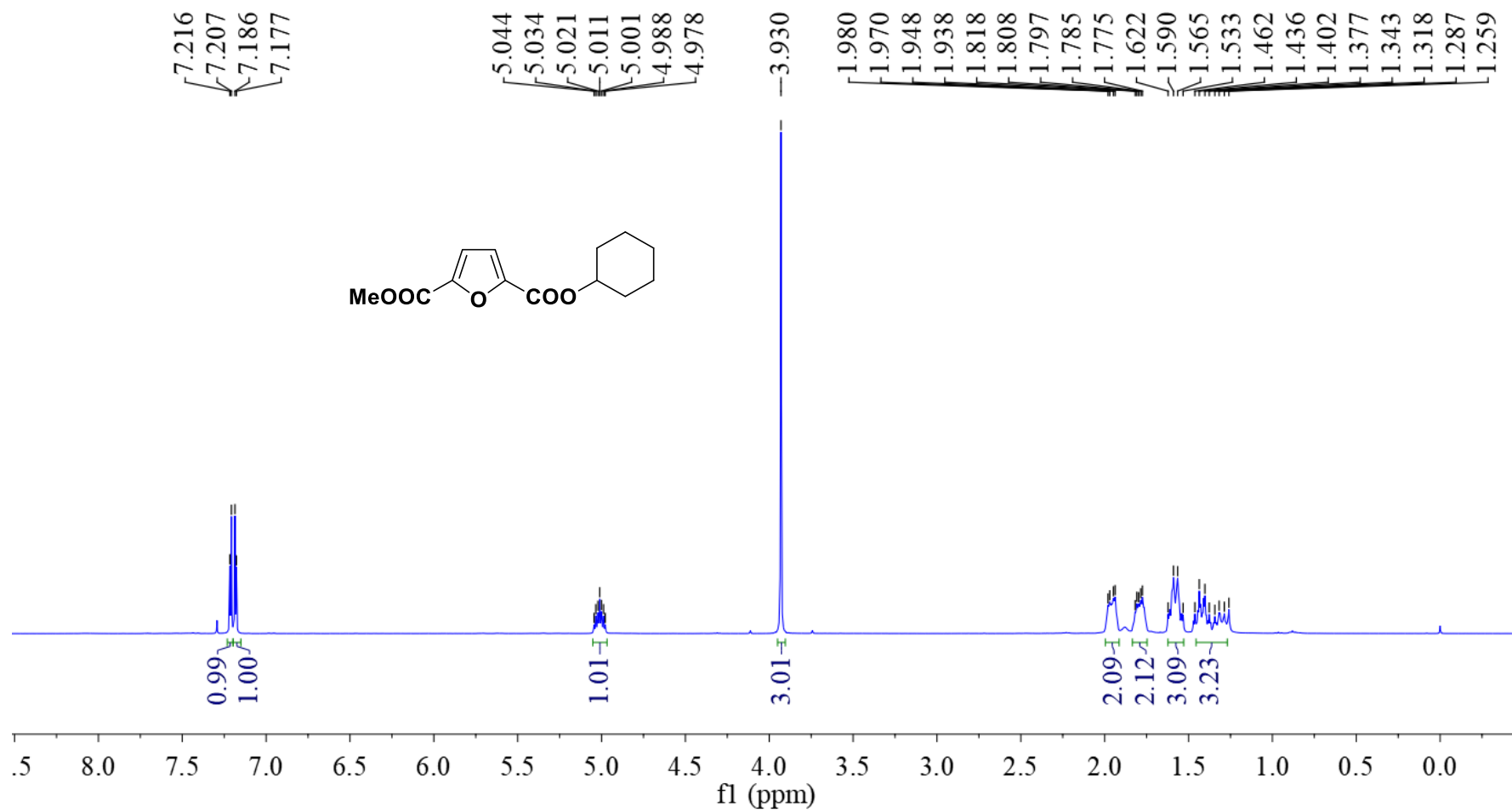
2-cyclopentyl 5-methyl furan-2,5-dicarboxylate (19)



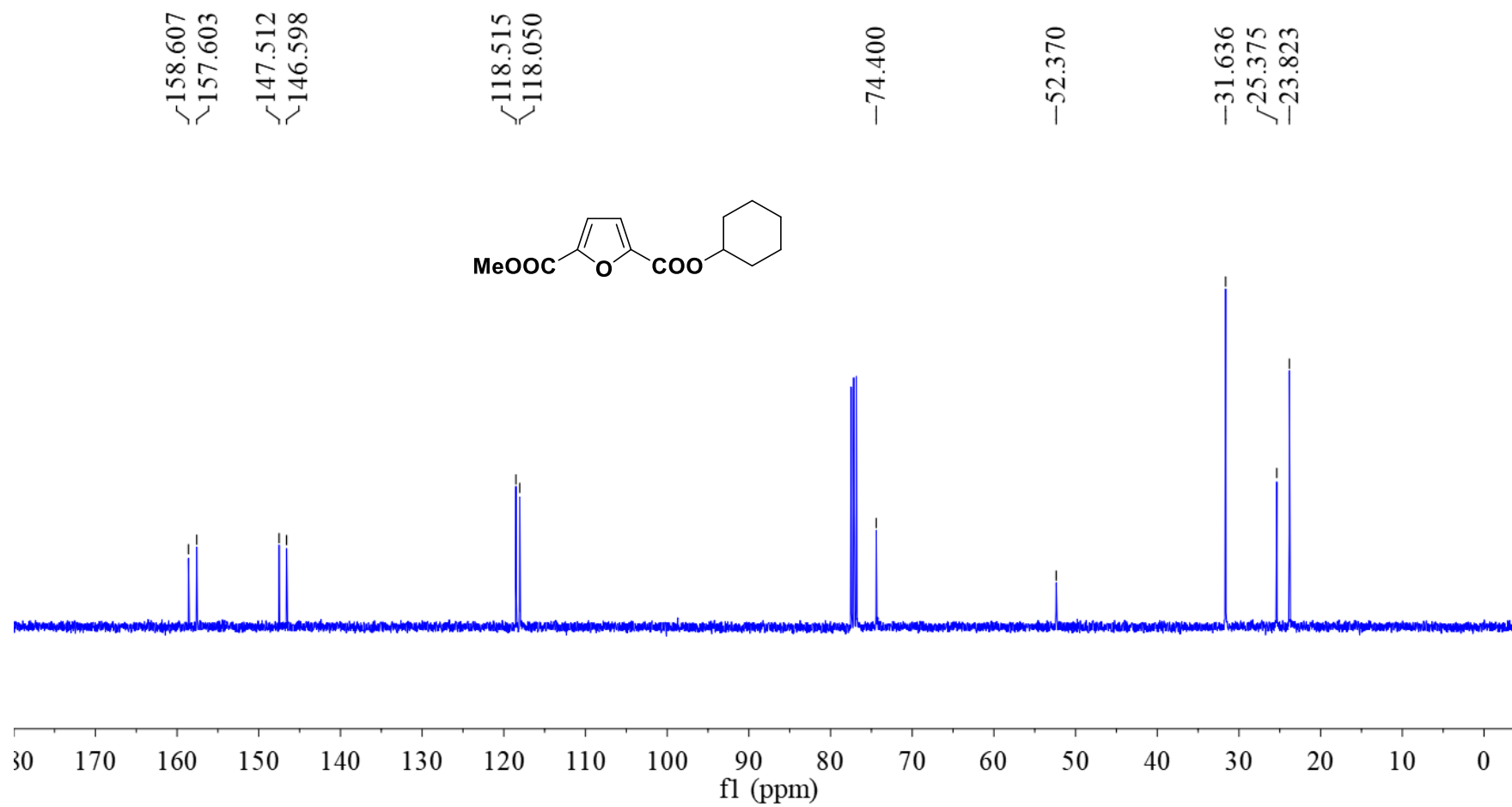
2-cyclopentyl 5-methyl furan-2,5-dicarboxylate (19)



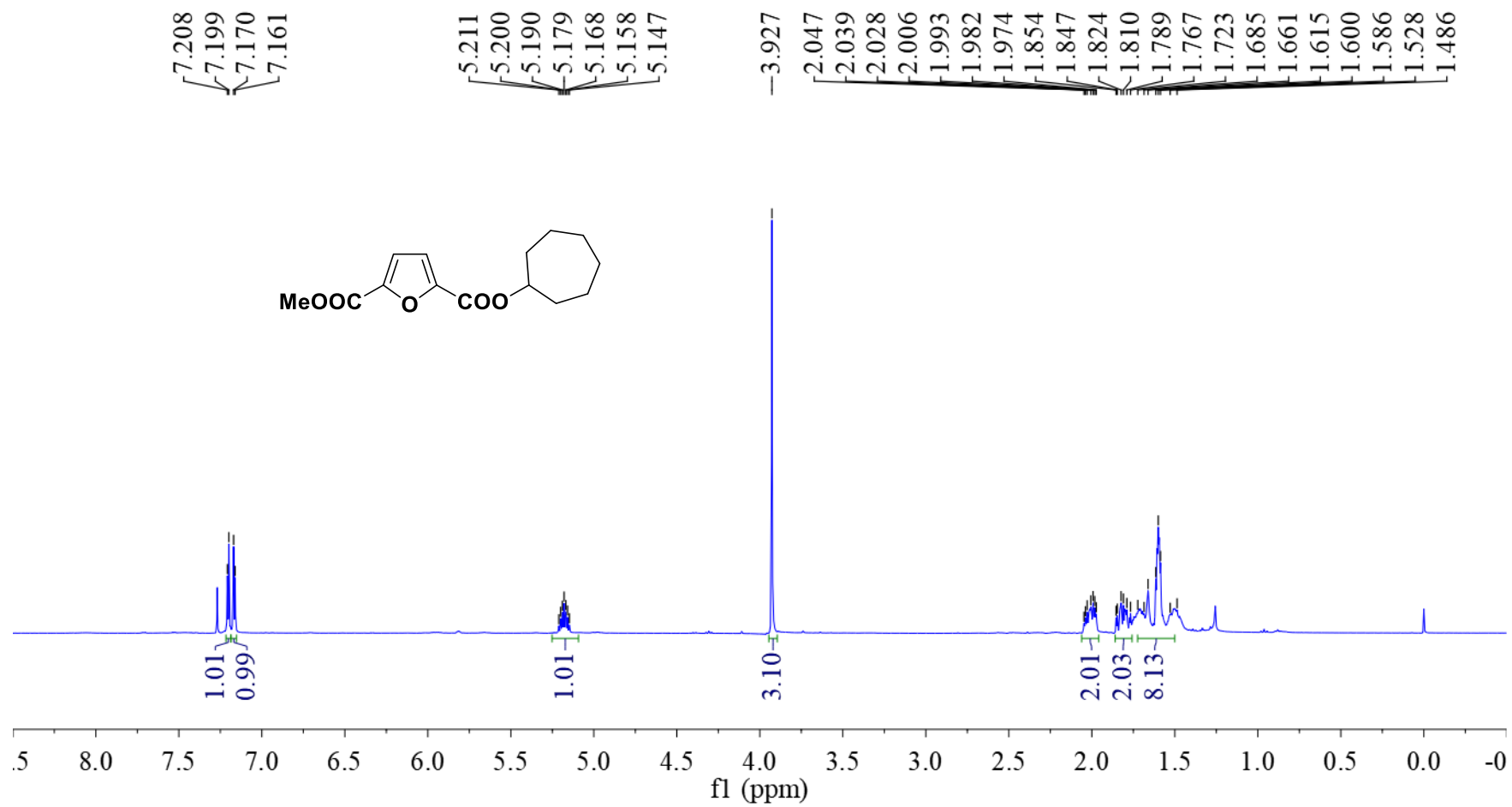
2-cyclohexyl 5-methyl furan-2,5-dicarboxylate (20)



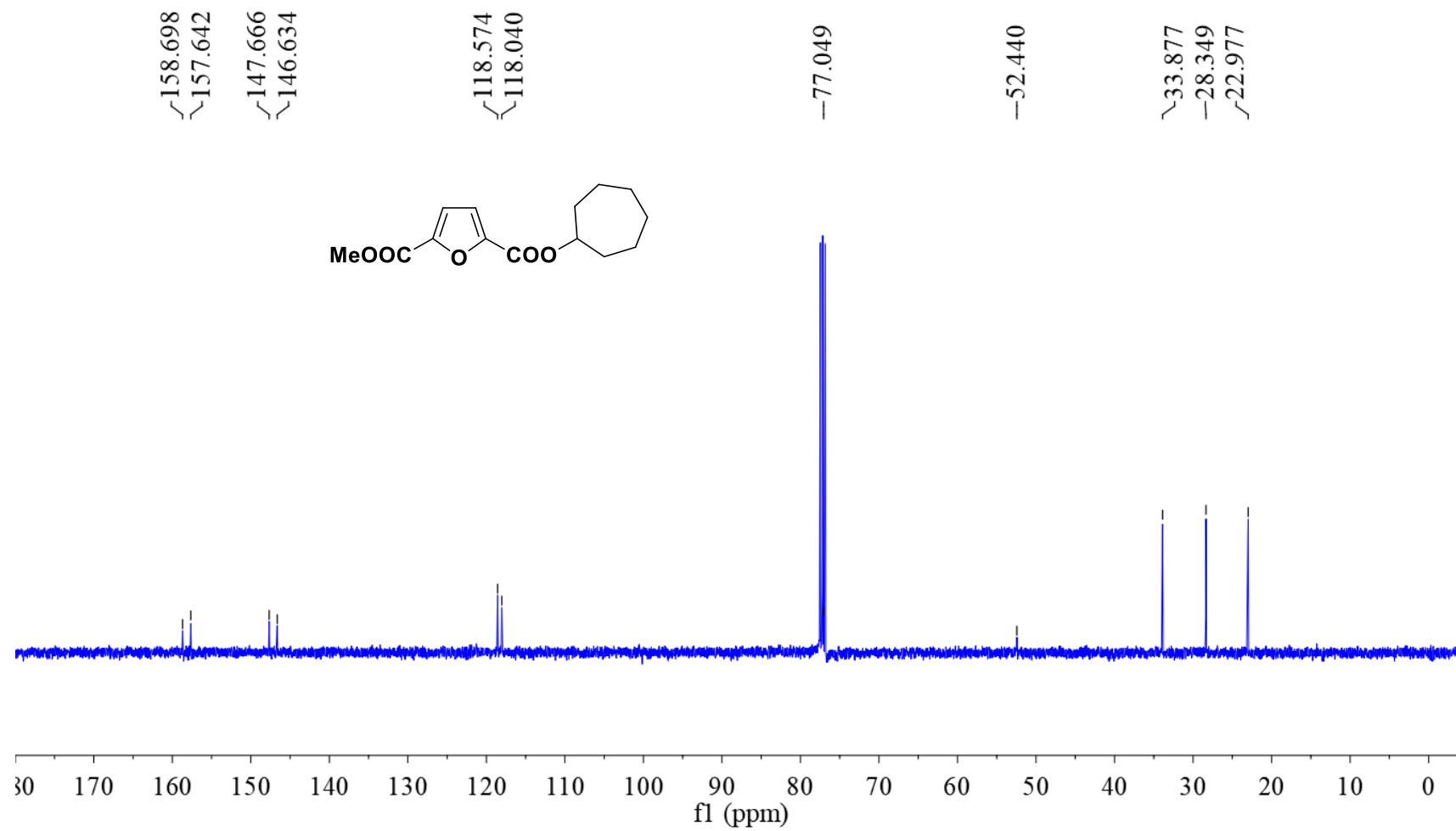
2-cyclohexyl 5-methyl furan-2,5-dicarboxylate (20)



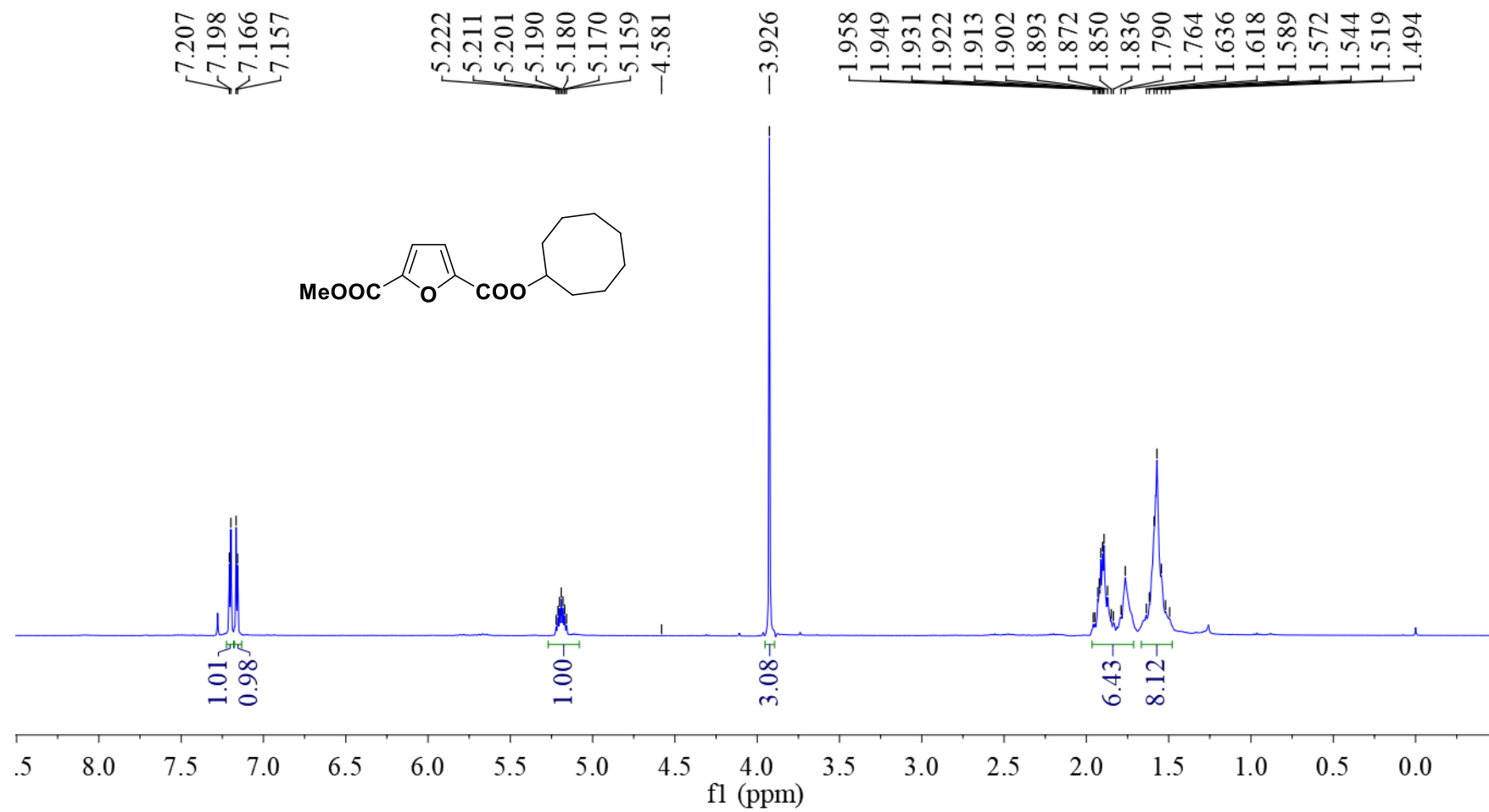
2-cycloheptyl 5-methyl furan-2,5-dicarboxylate (21)



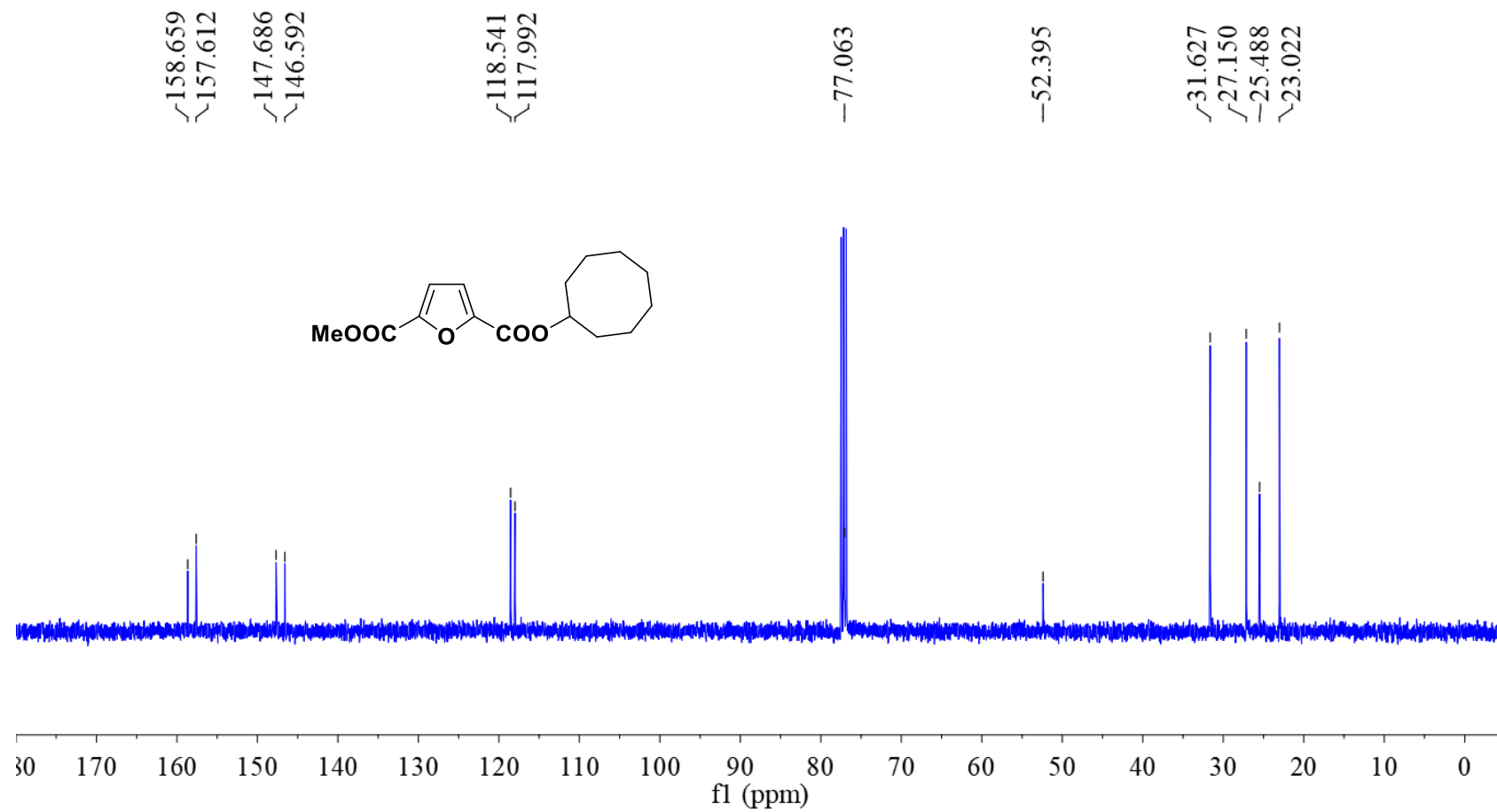
2-cycloheptyl 5-methyl furan-2,5-dicarboxylate (21)



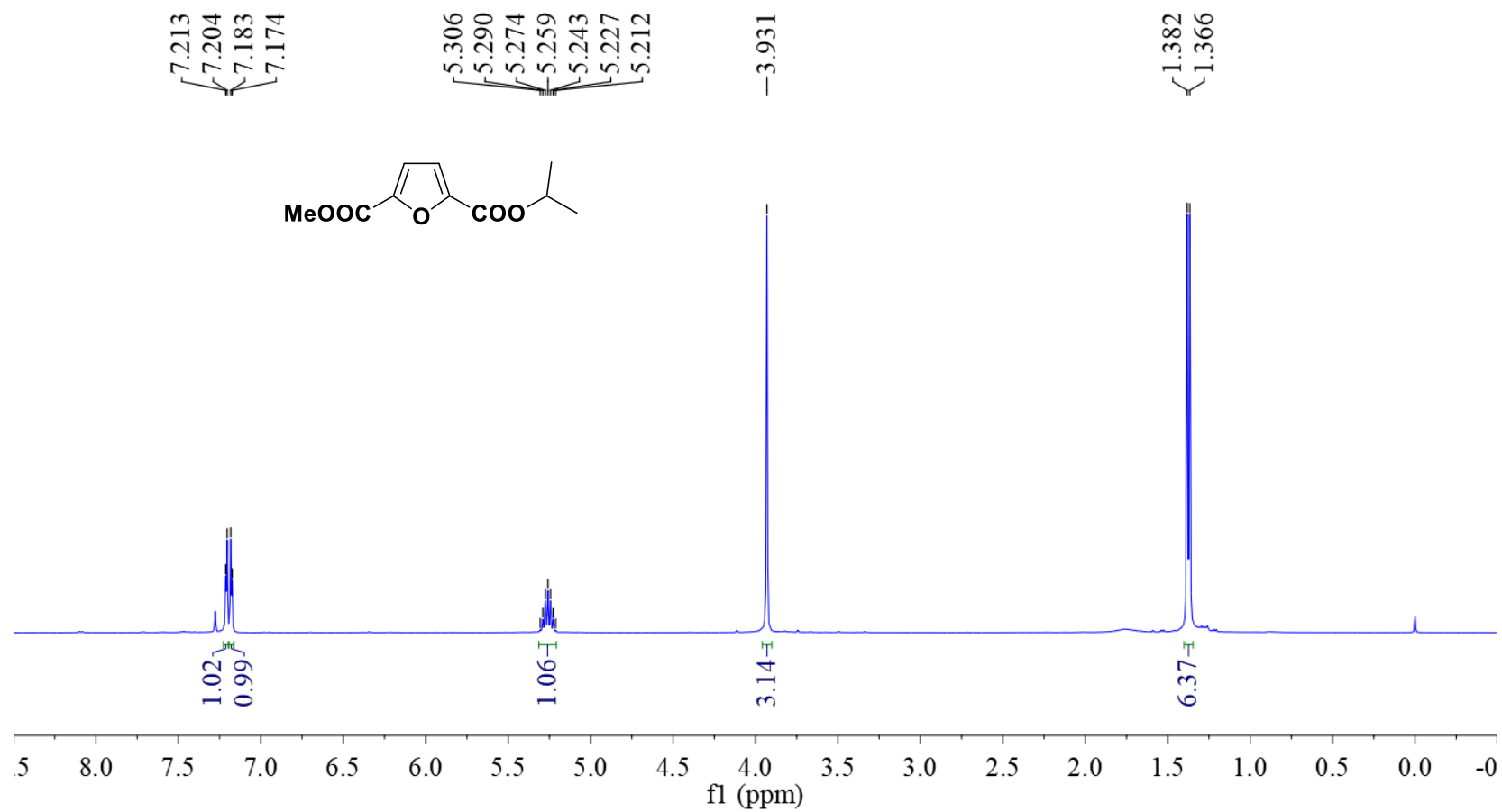
2-cyclooctyl 5-methyl furan-2,5-dicarboxylate (22)



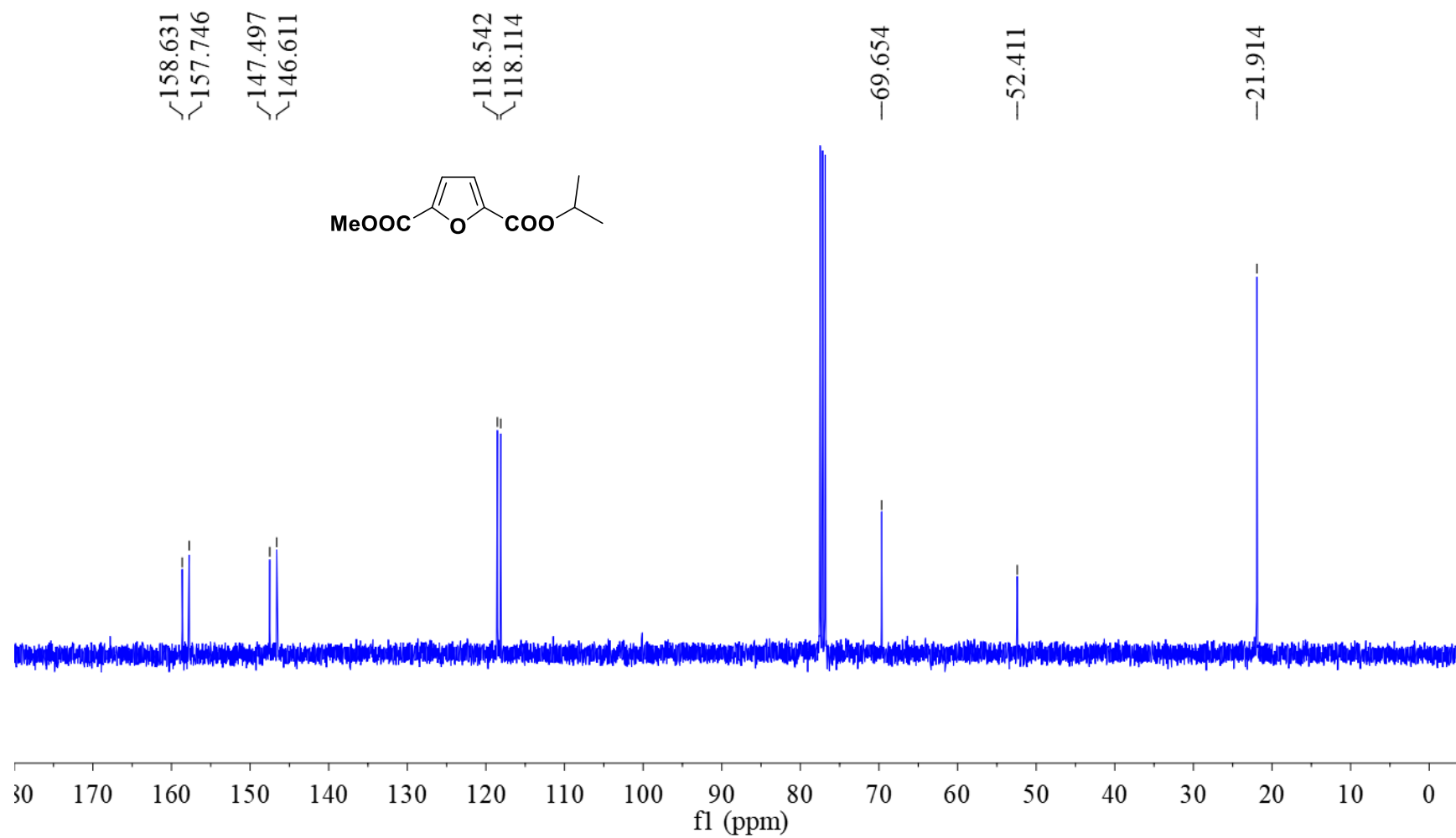
2-cyclooctyl 5-methyl furan-2,5-dicarboxylate (22)



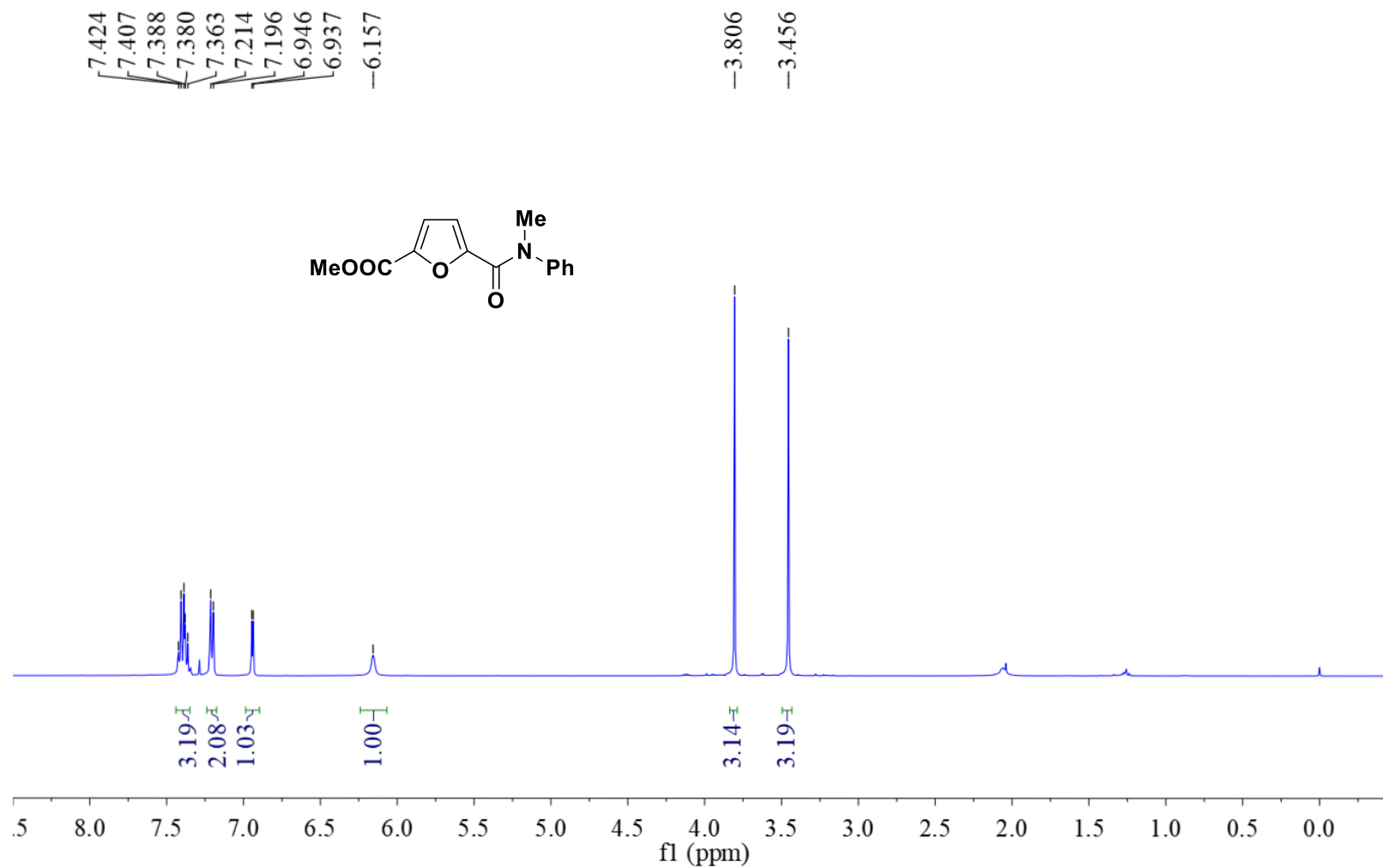
2-isopropyl 5-methyl furan-2,5-dicarboxylate (23)



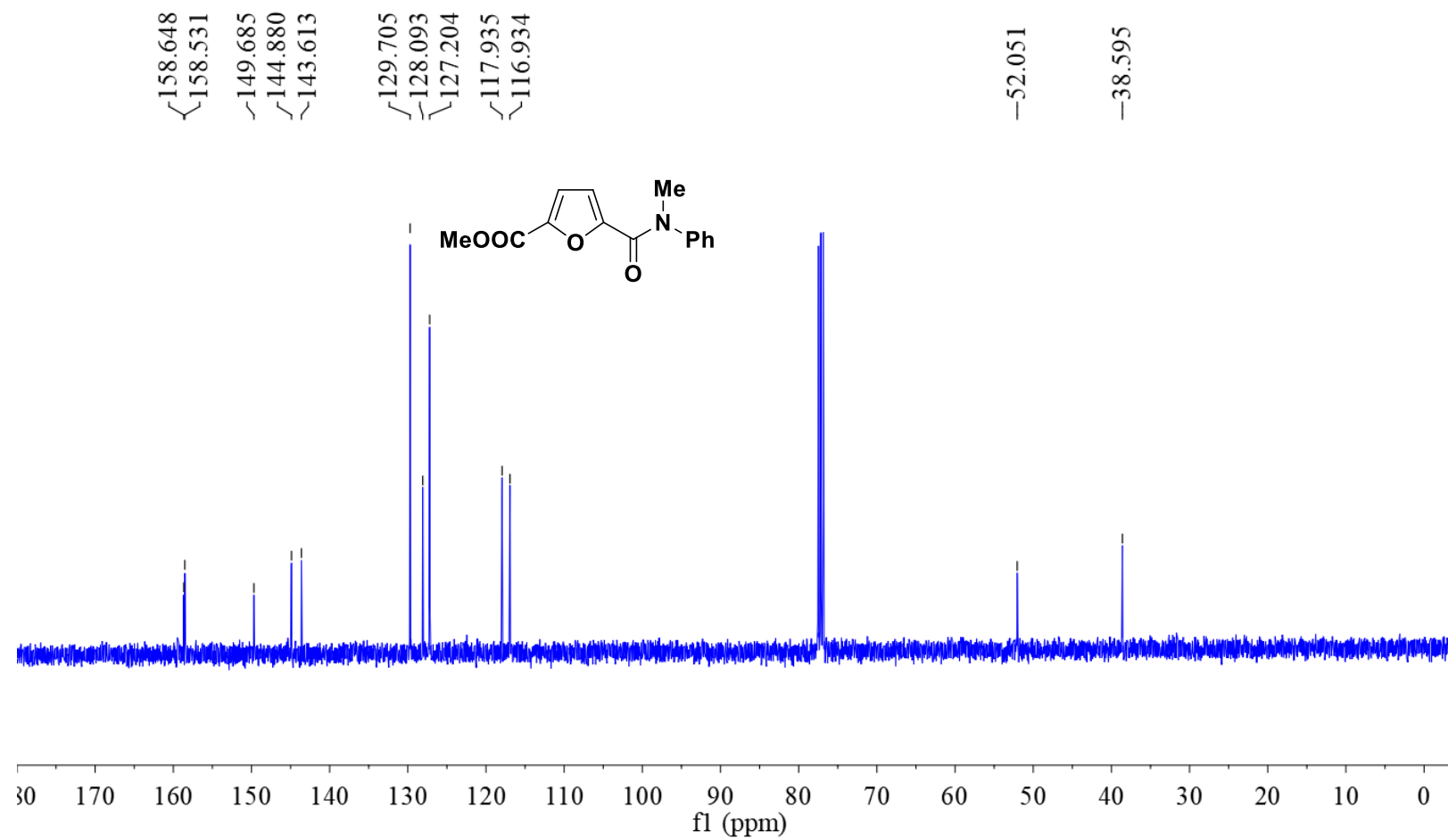
2-isopropyl 5-methyl furan-2,5-dicarboxylate (23)



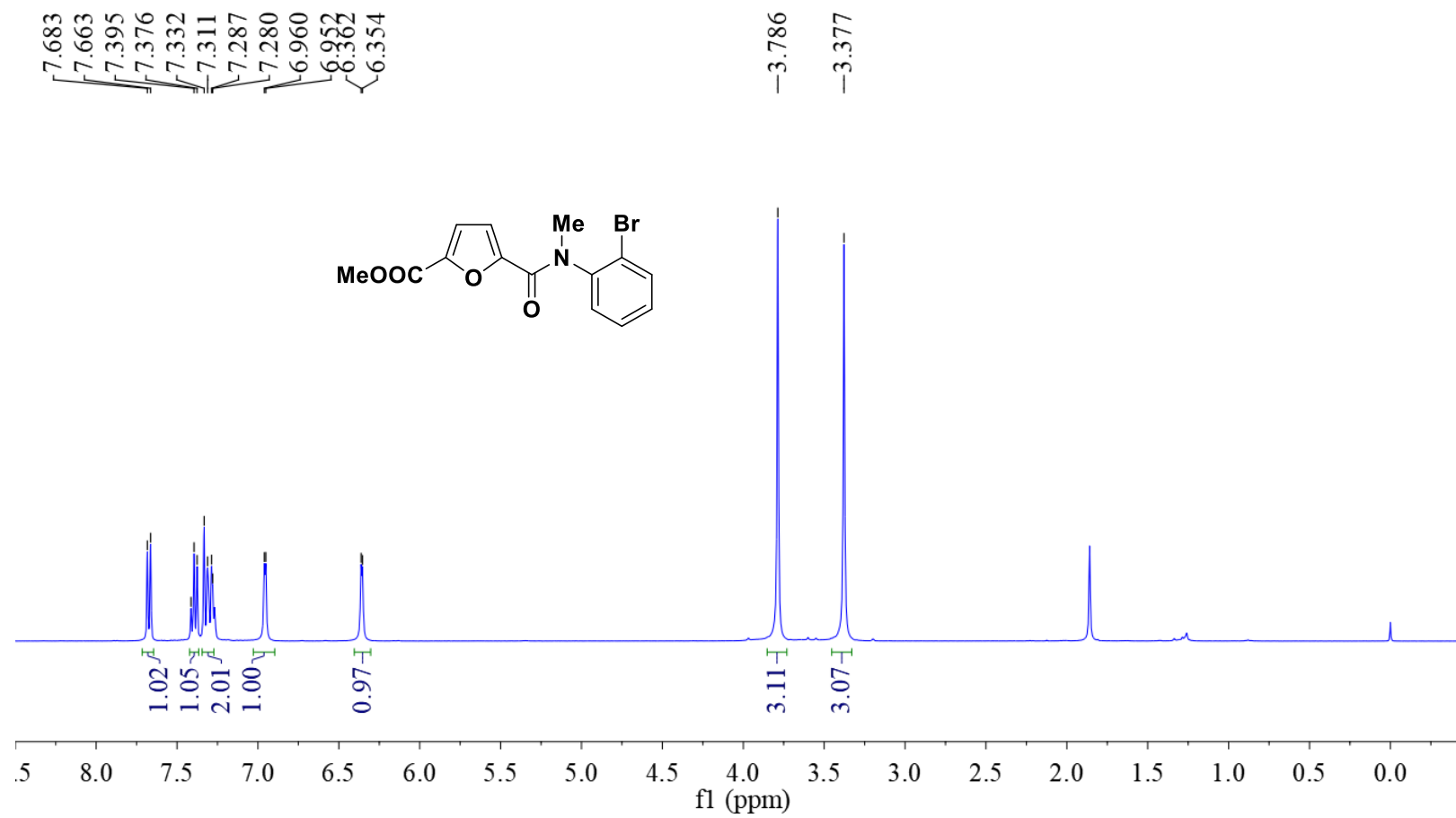
Methyl 5-(methyl(phenyl)carbamoyl)furan-2-carboxylate (25)



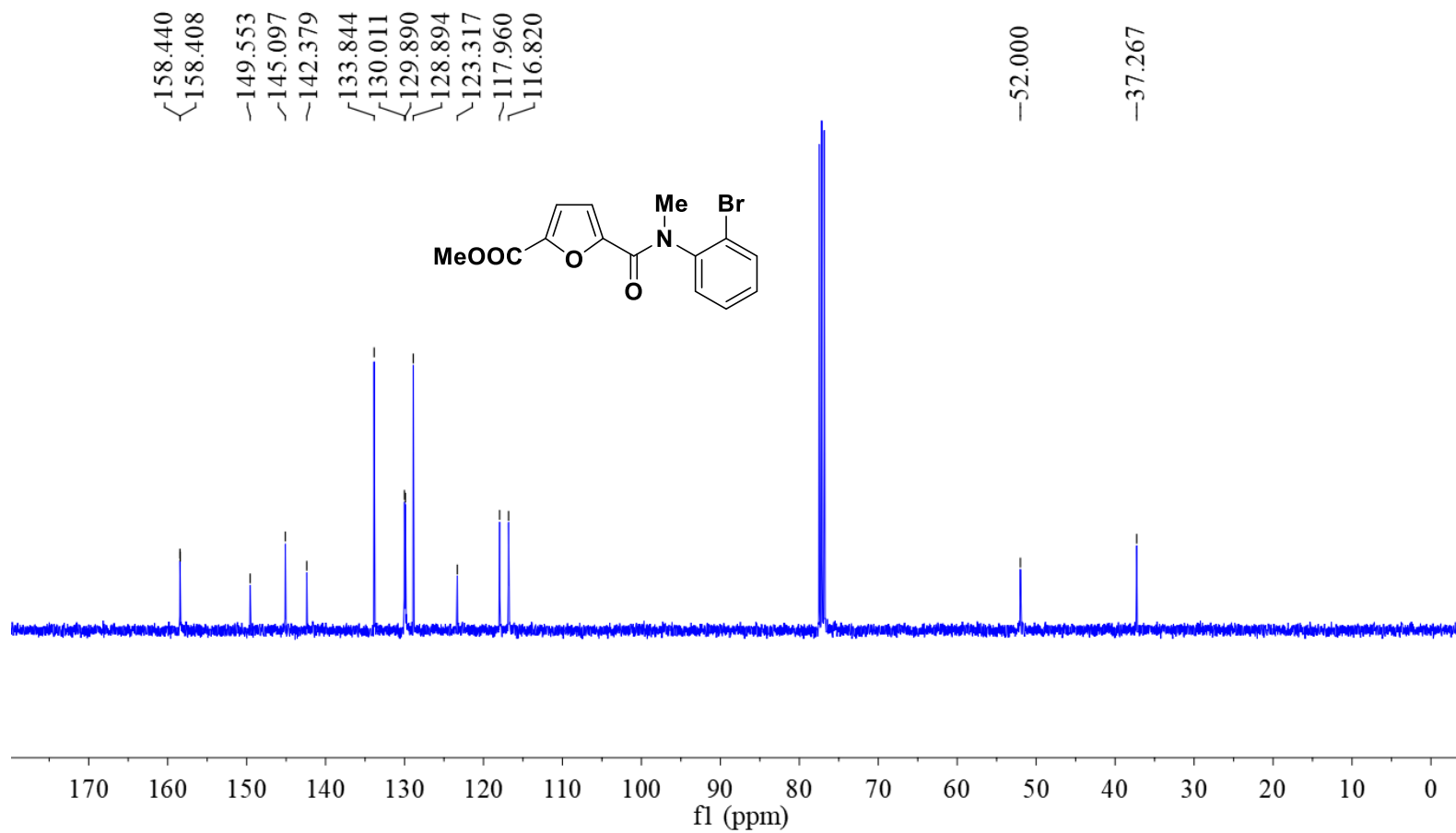
Methyl 5-(methyl(phenyl)carbamoyl)furan-2-carboxylate (25)



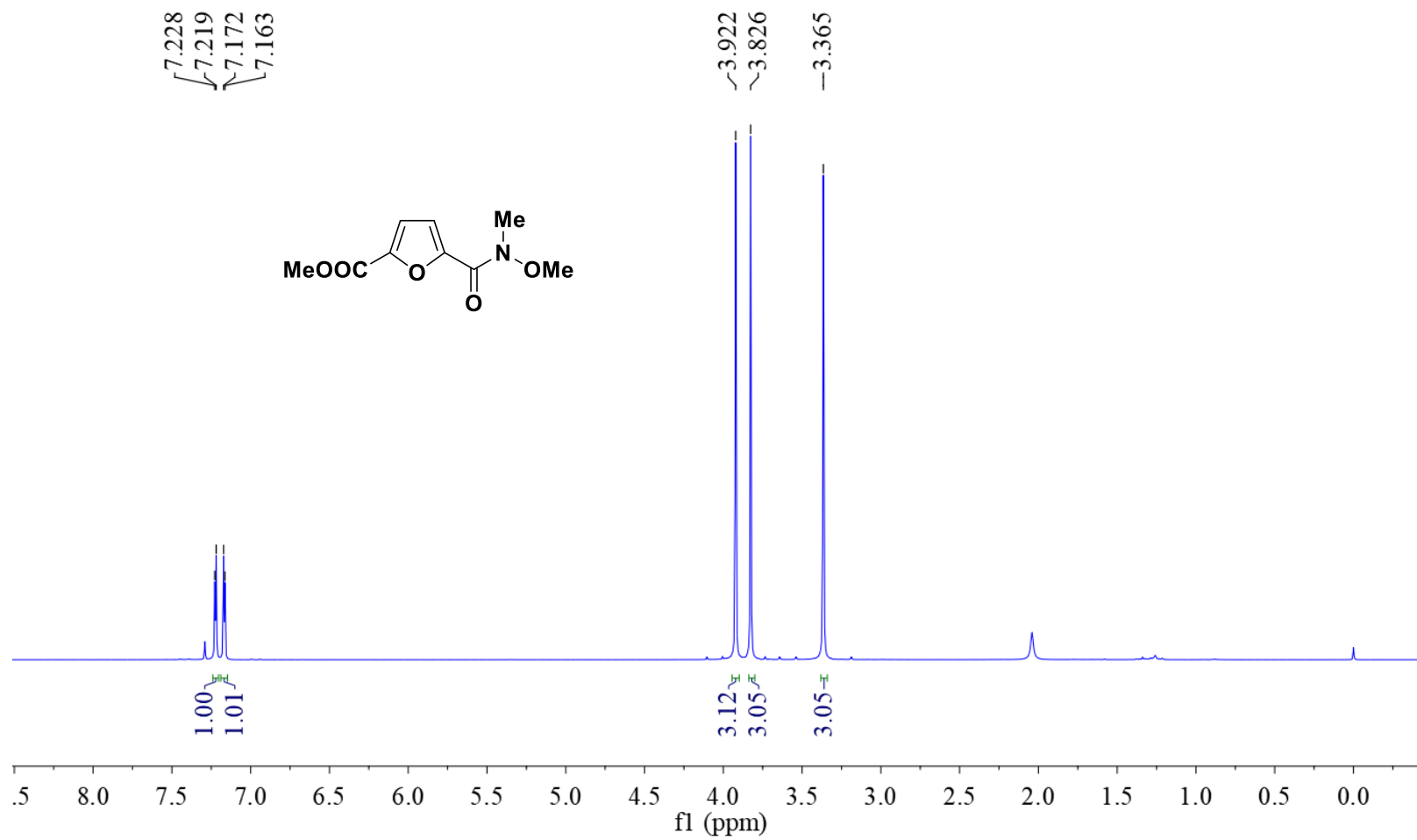
Methyl 5-((2-bromophenyl)(methyl)carbamoyl)furan-2-carboxylate (26)



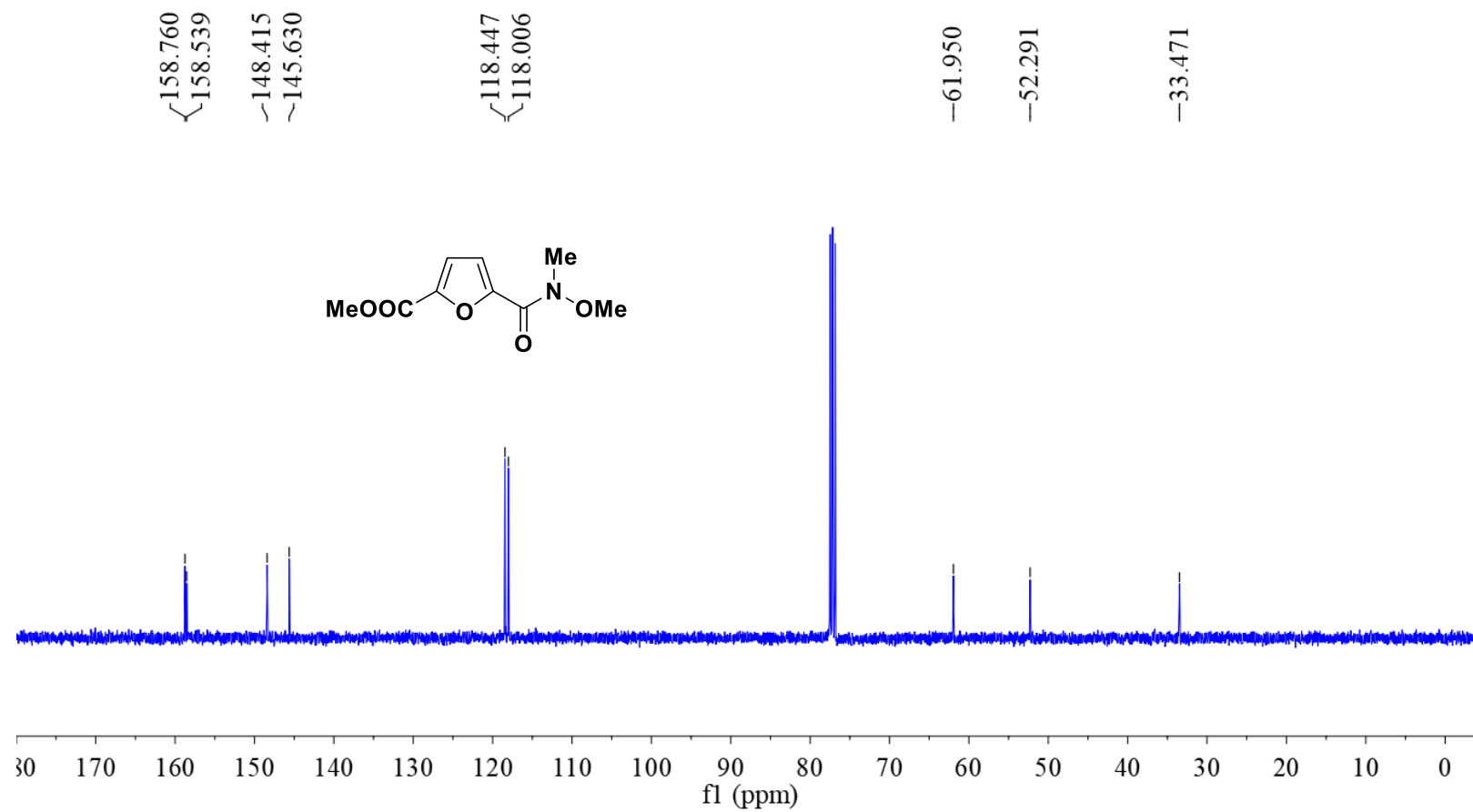
Methyl 5-((2-bromophenyl)(methyl)carbamoyl)furan-2-carboxylate (26)



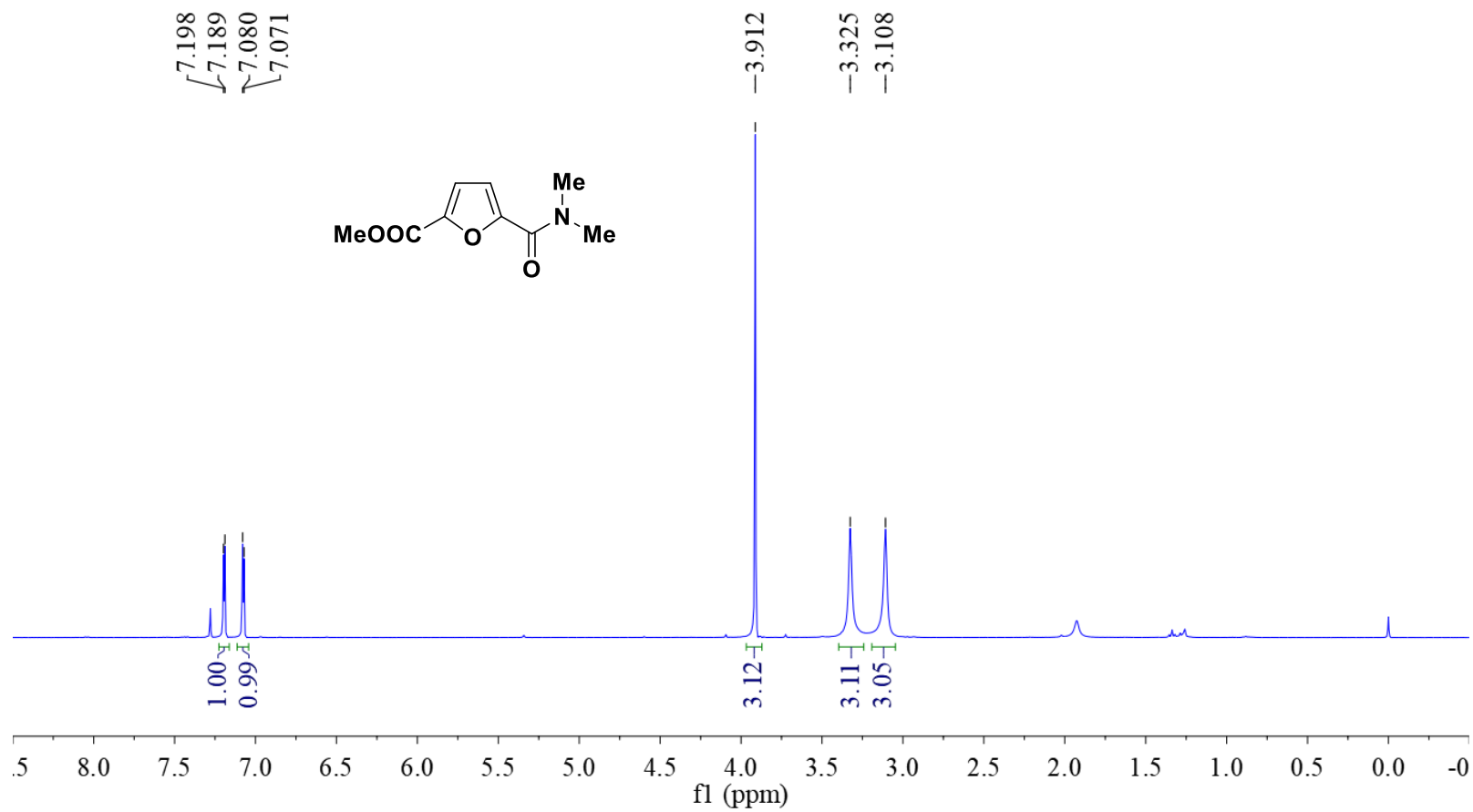
Methyl 5-(methoxy(methyl)carbamoyl)furan-2-carboxylate (27)



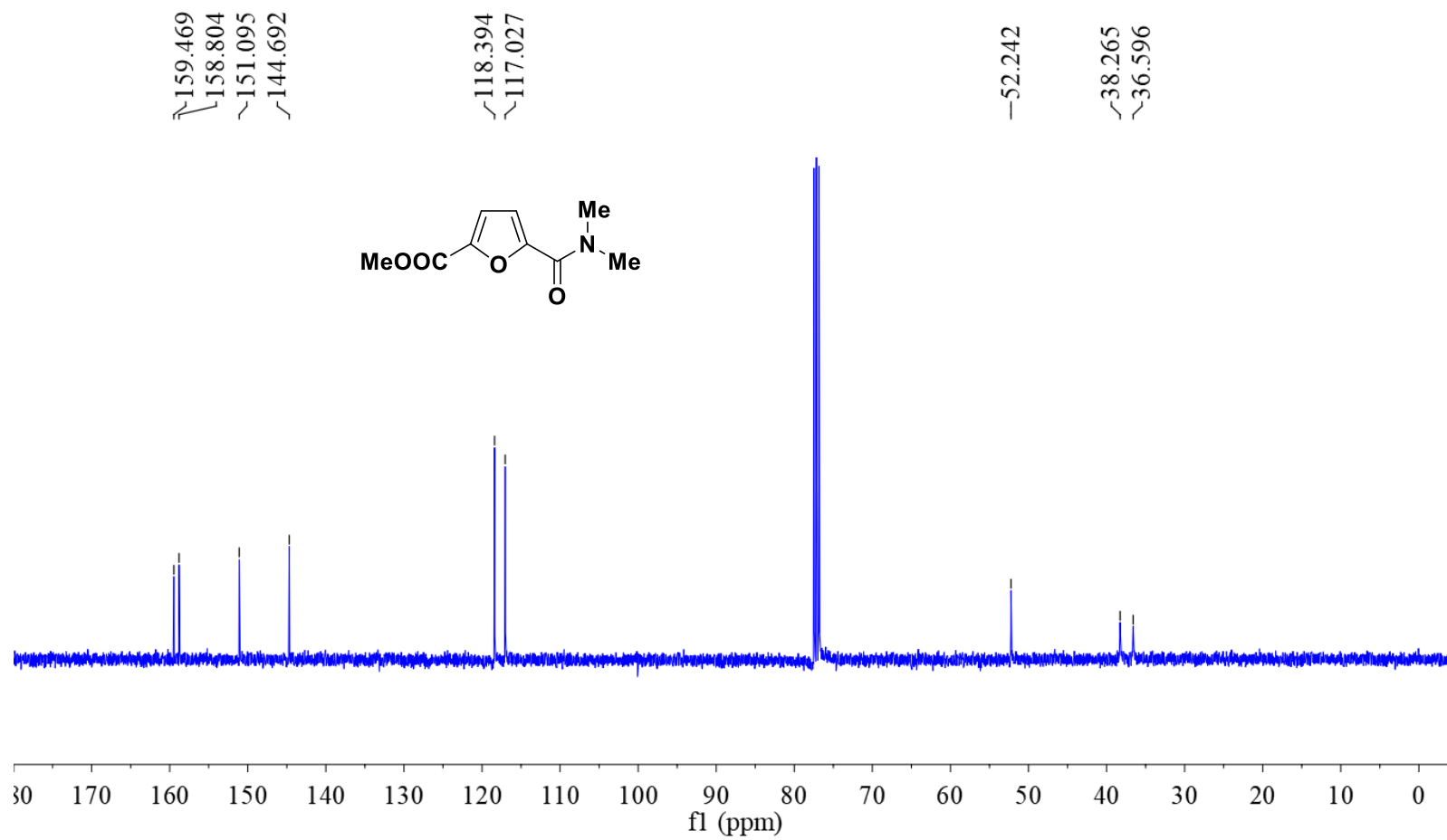
Methyl 5-(methoxy(methyl)carbamoyl)furan-2-carboxylate (27)



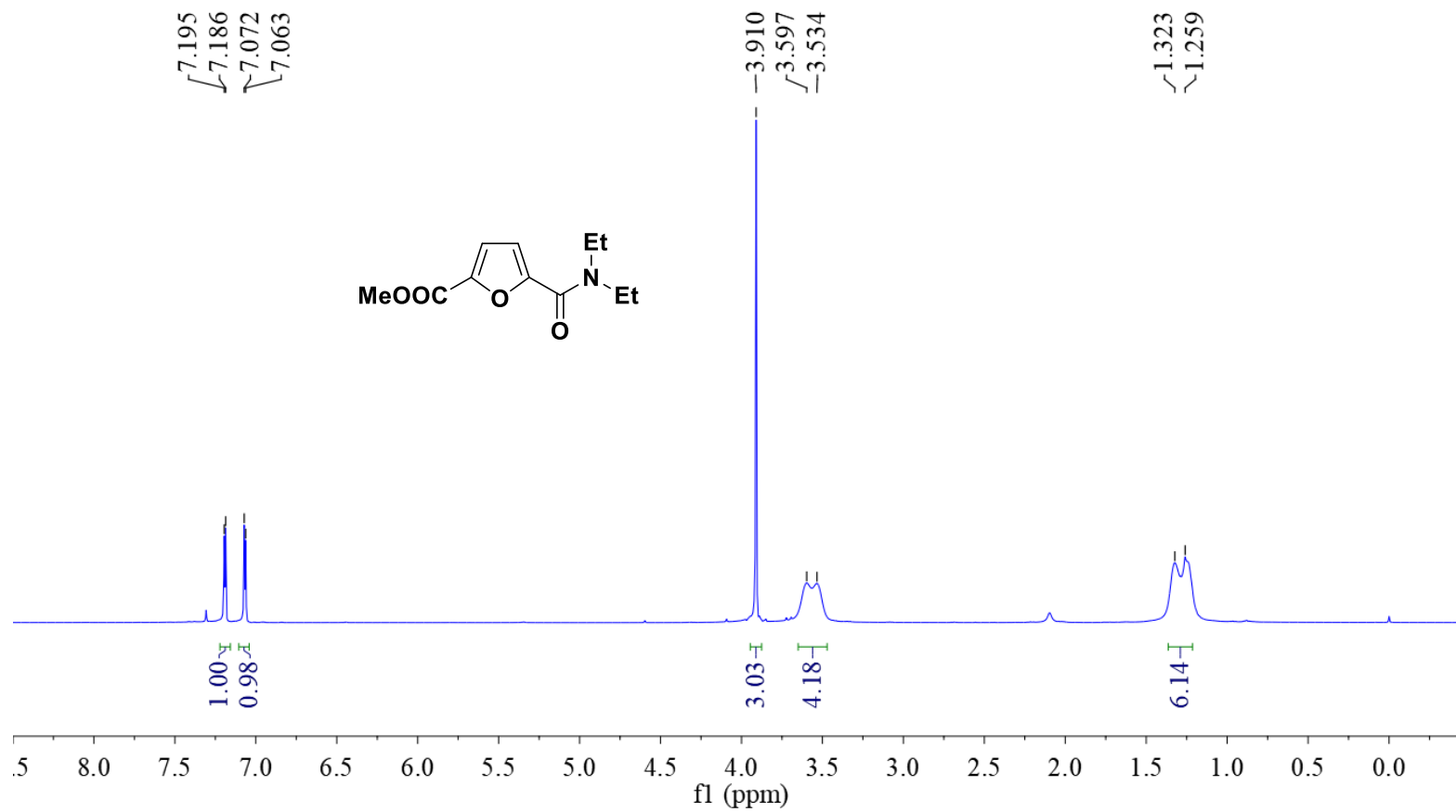
Methyl 5-(dimethylcarbamoyl)furan-2-carboxylate (28)



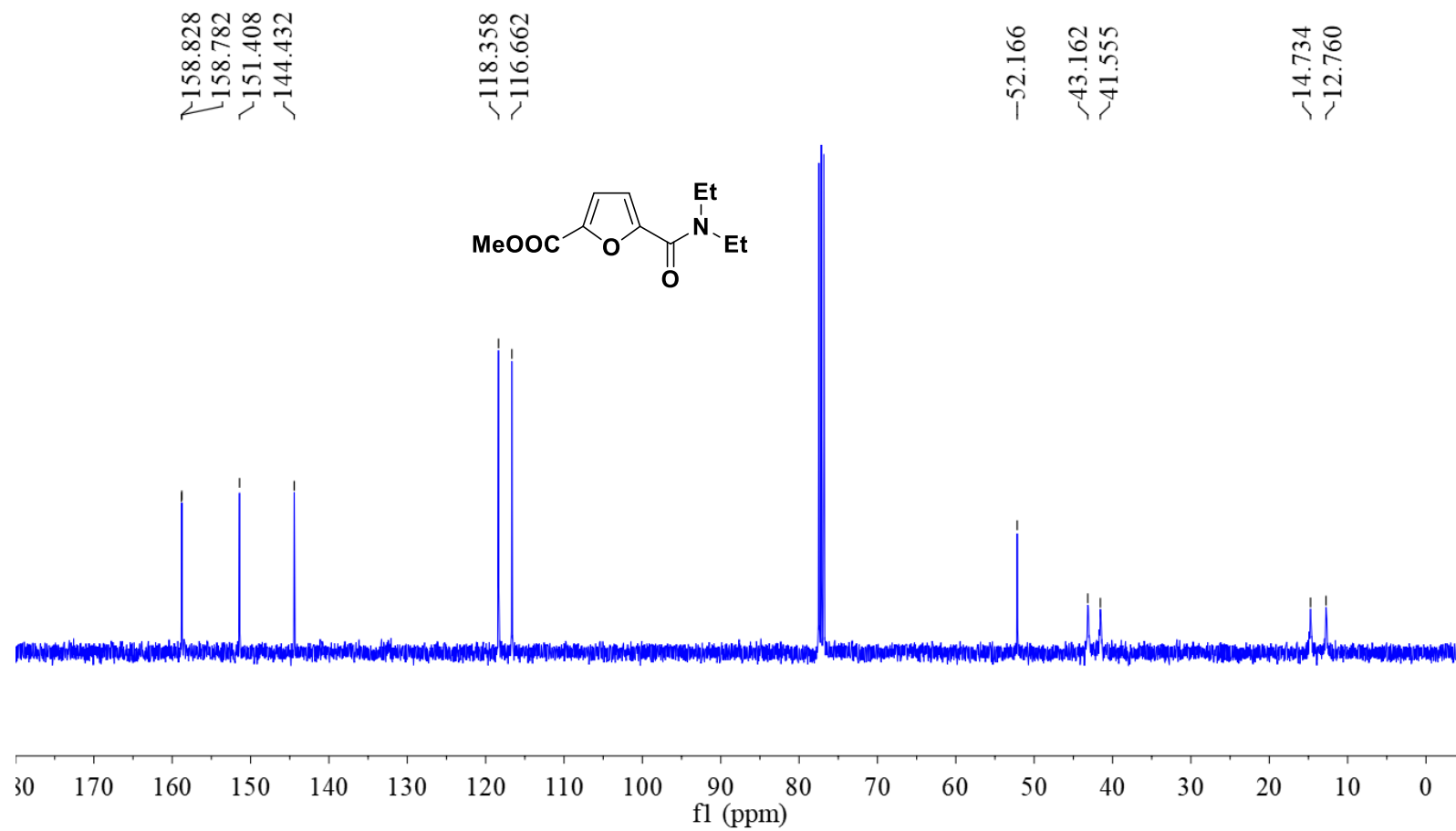
Methyl 5-(dimethylcarbamoyl)furan-2-carboxylate (28)



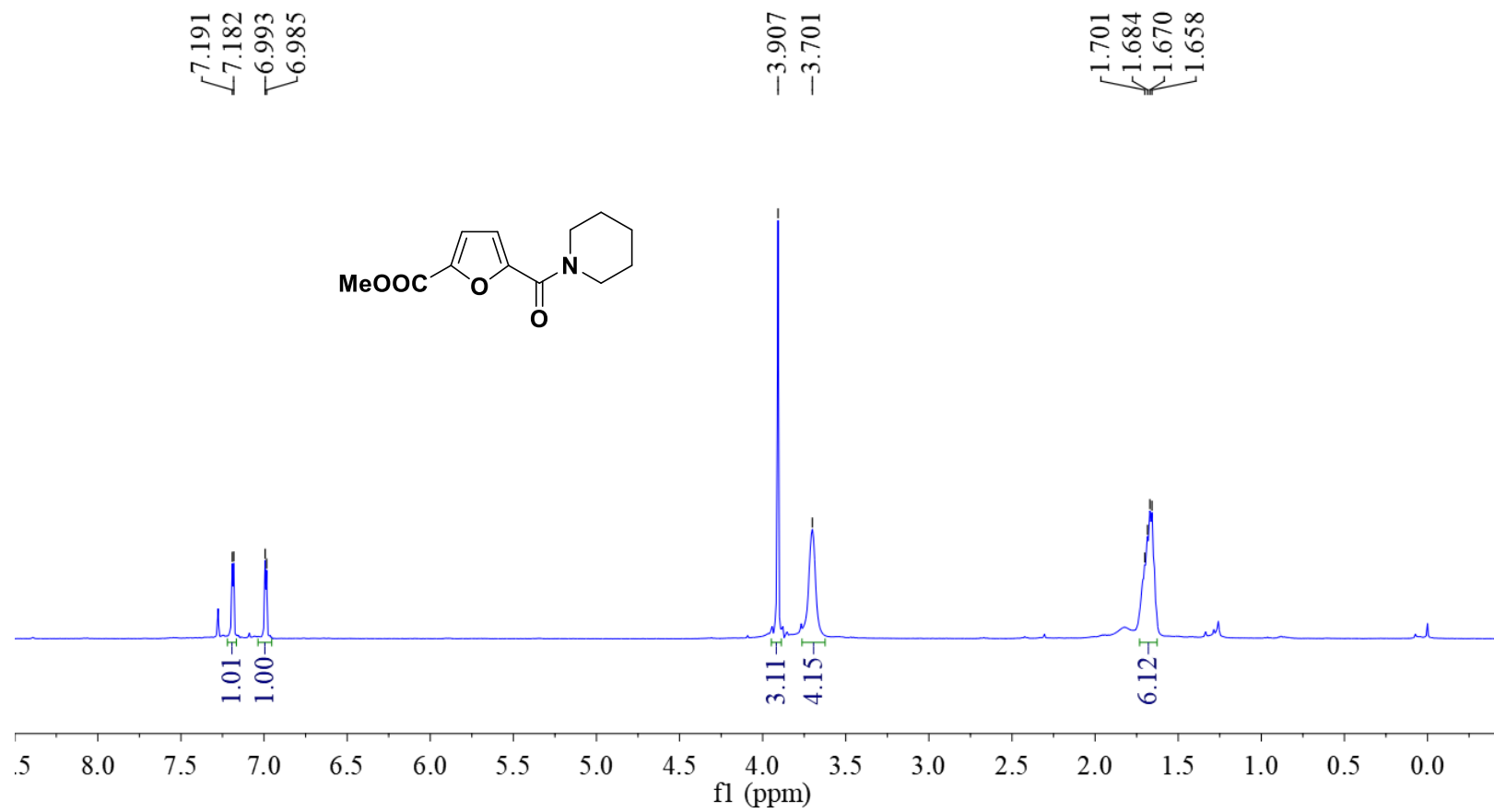
Methyl 5-(diethylcarbamoyl)furan-2-carboxylate (29)



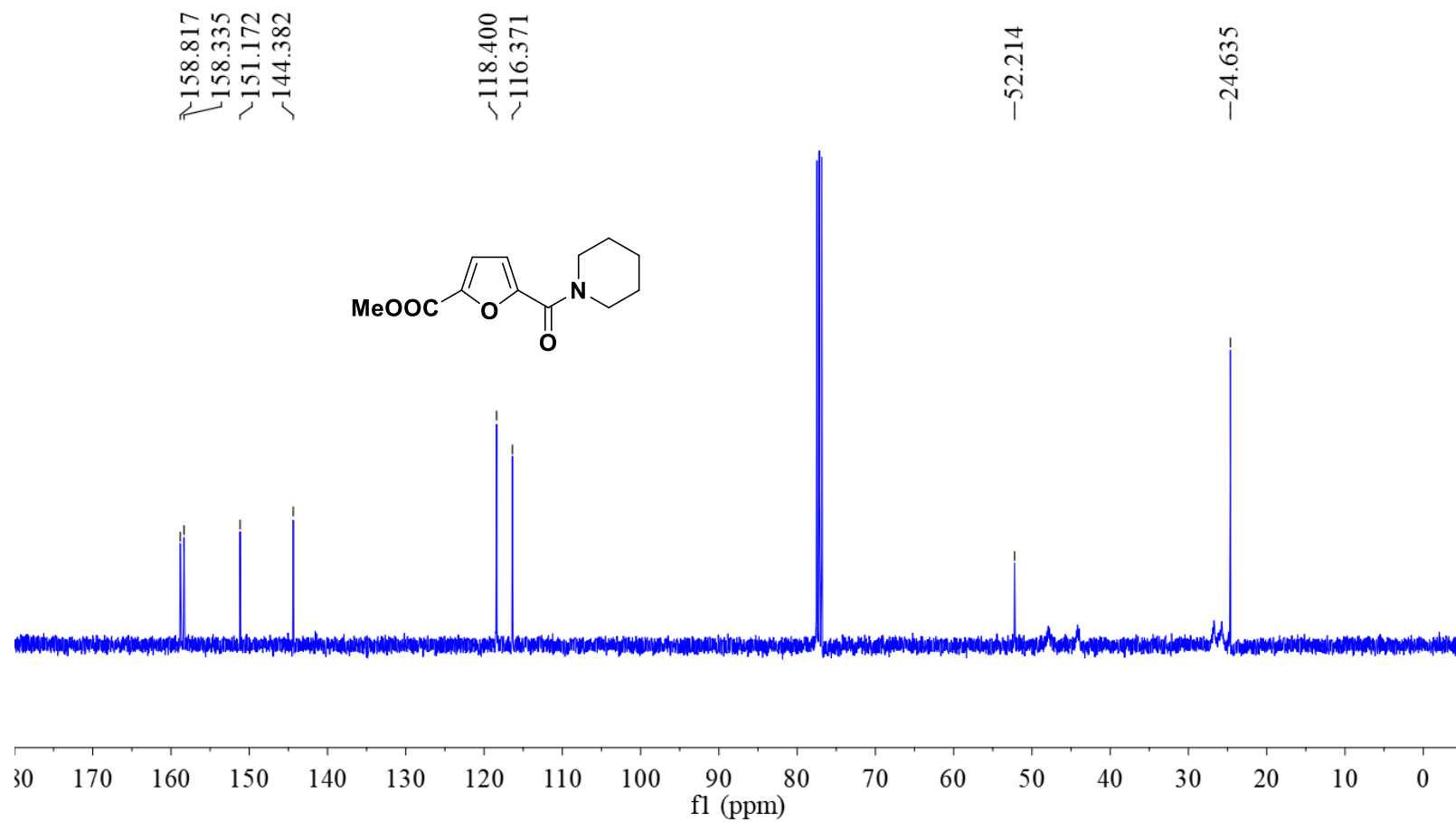
Methyl 5-(diethylcarbamoyl)furan-2-carboxylate (29)

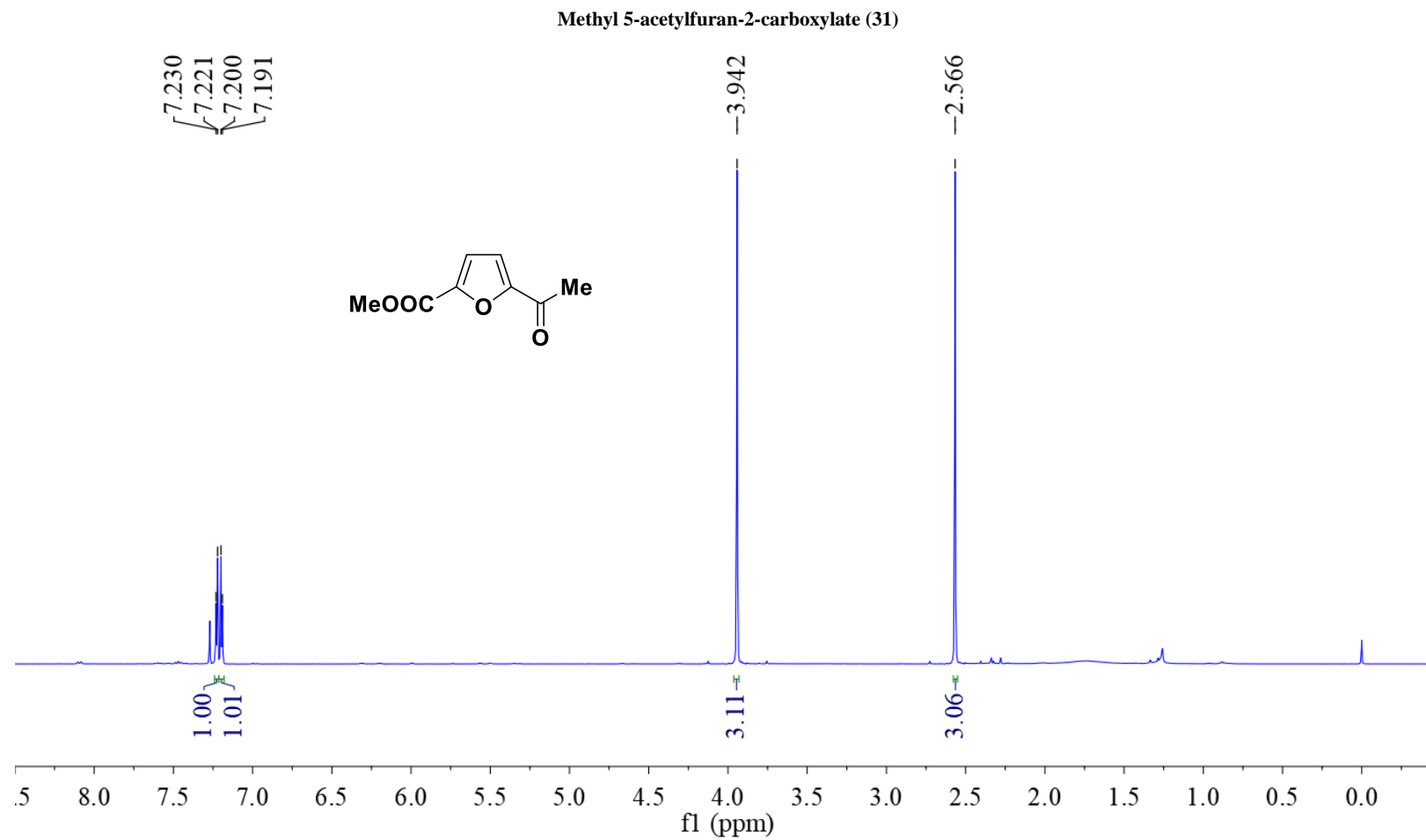


Methyl 5-(piperidine-1-carbonyl)furan-2-carboxylate (30)

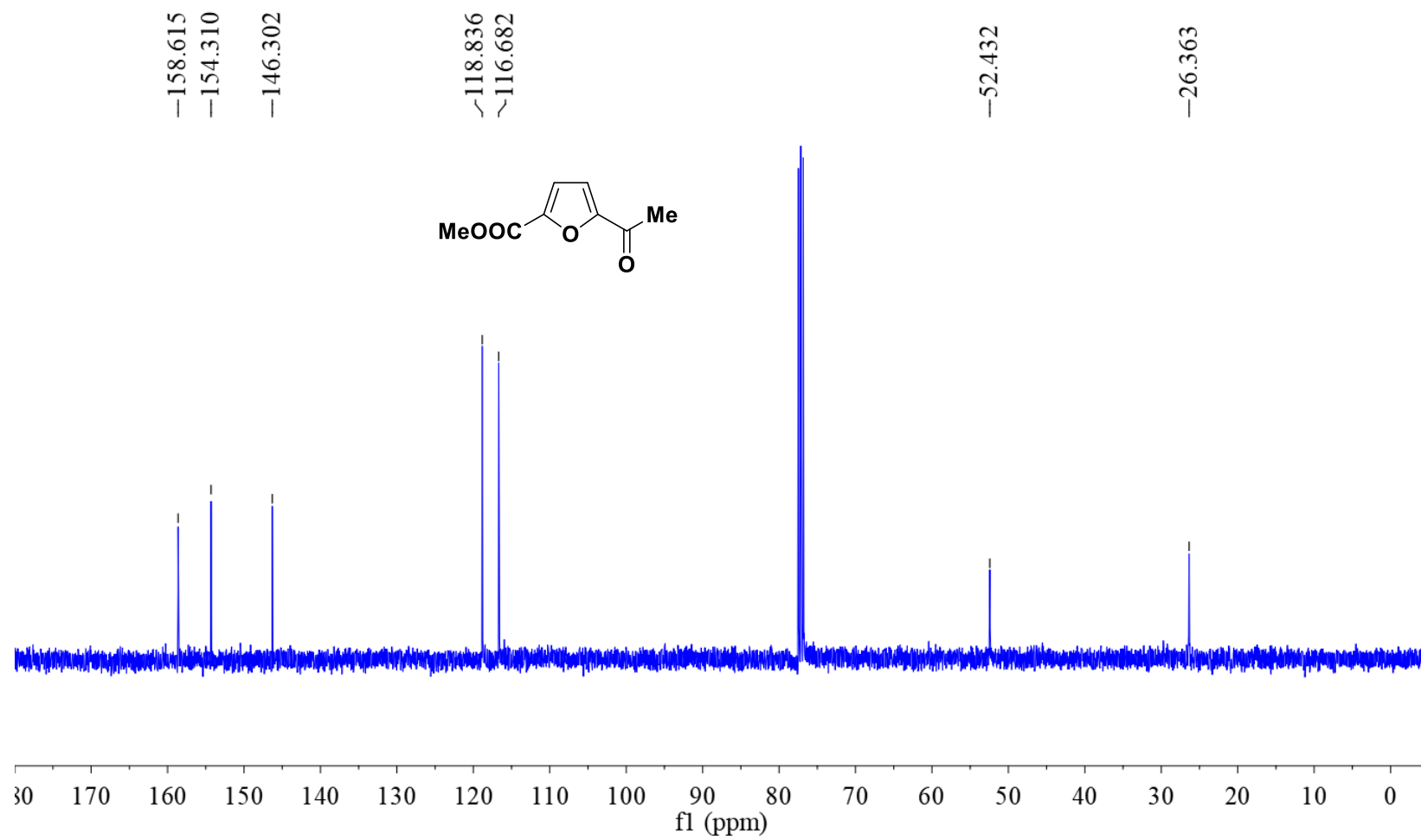


Methyl 5-(piperidine-1-carbonyl)furan-2-carboxylate (30)

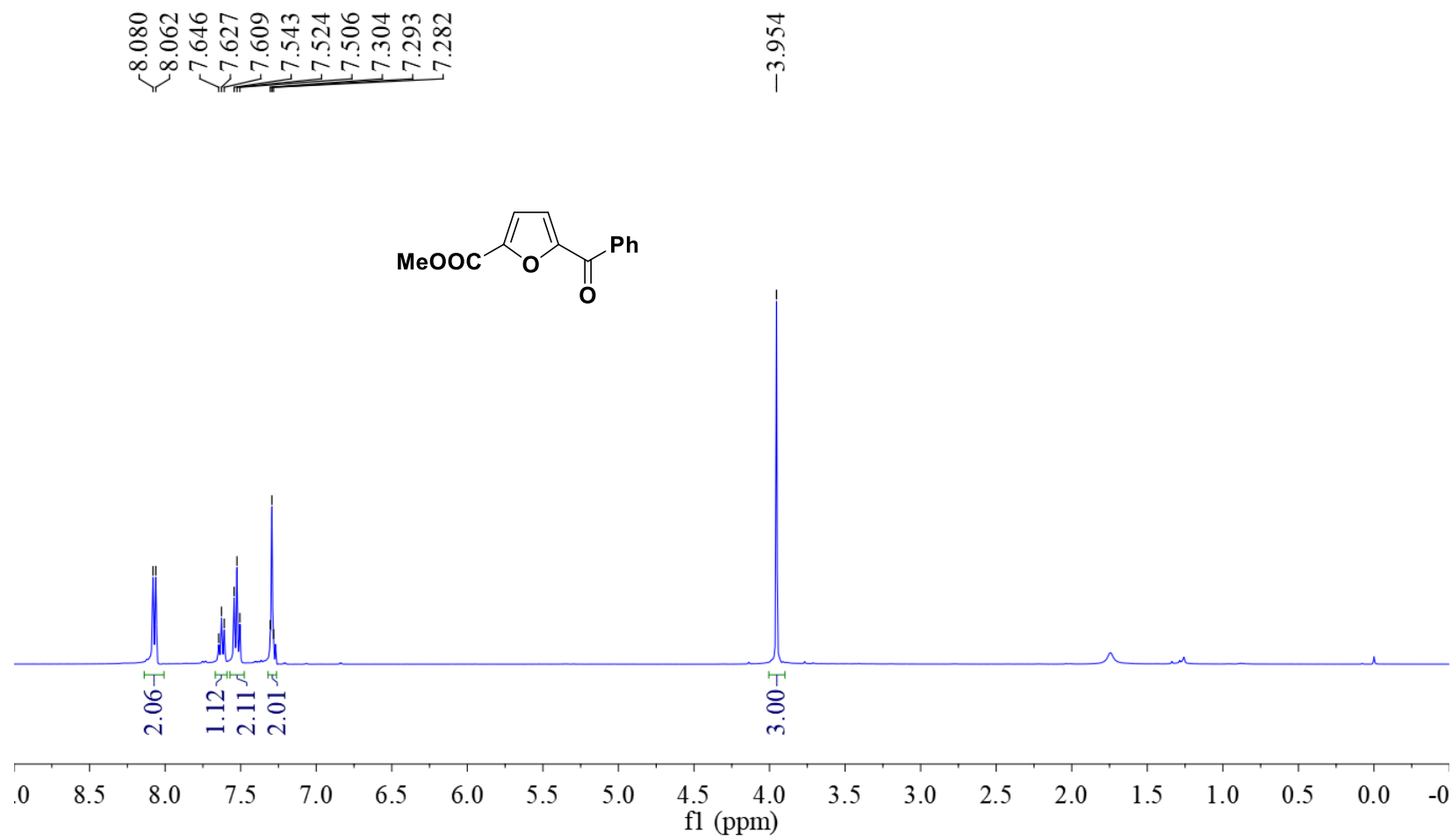




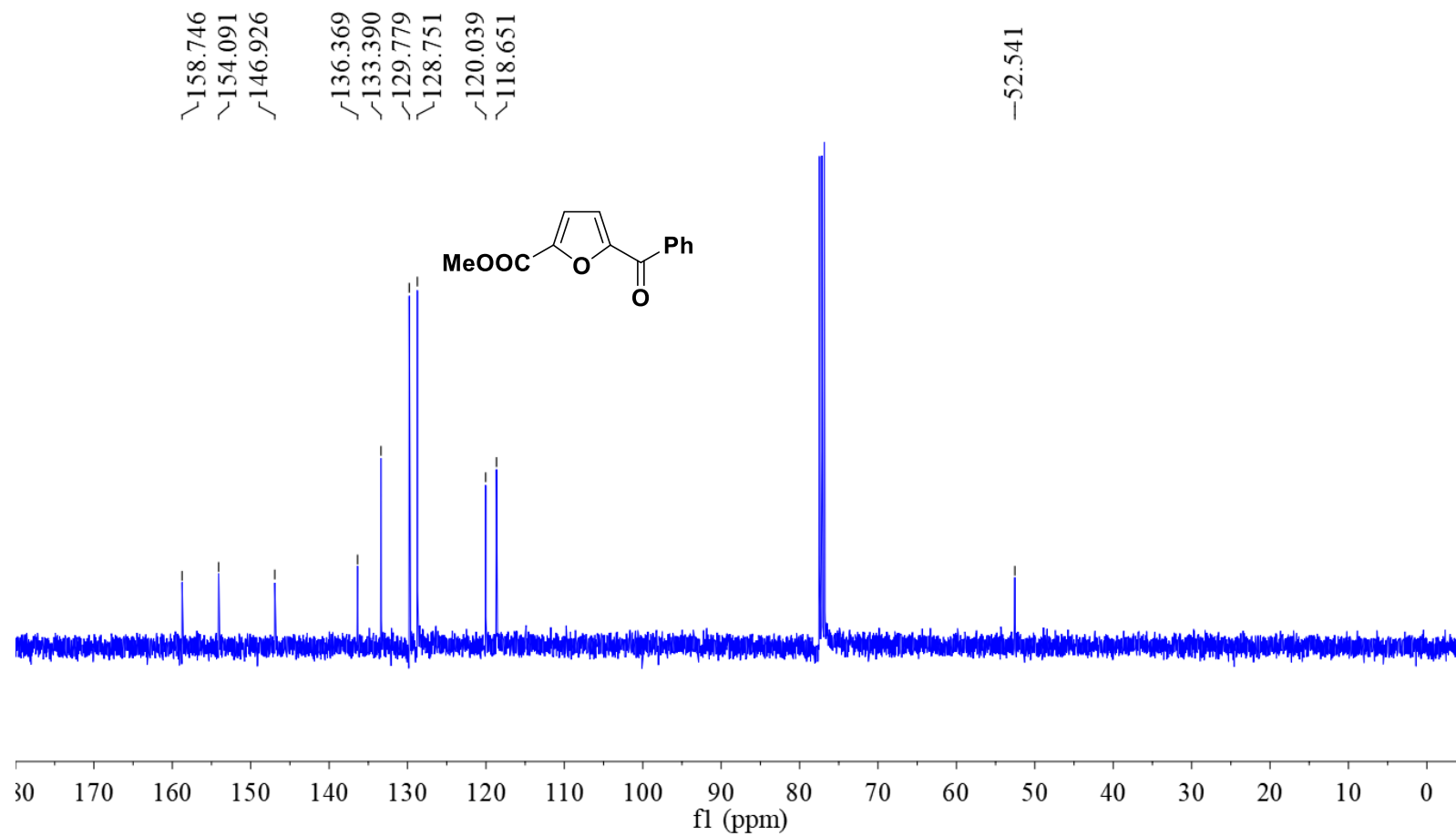
Methyl 5-acetylfuran-2-carboxylate (31)



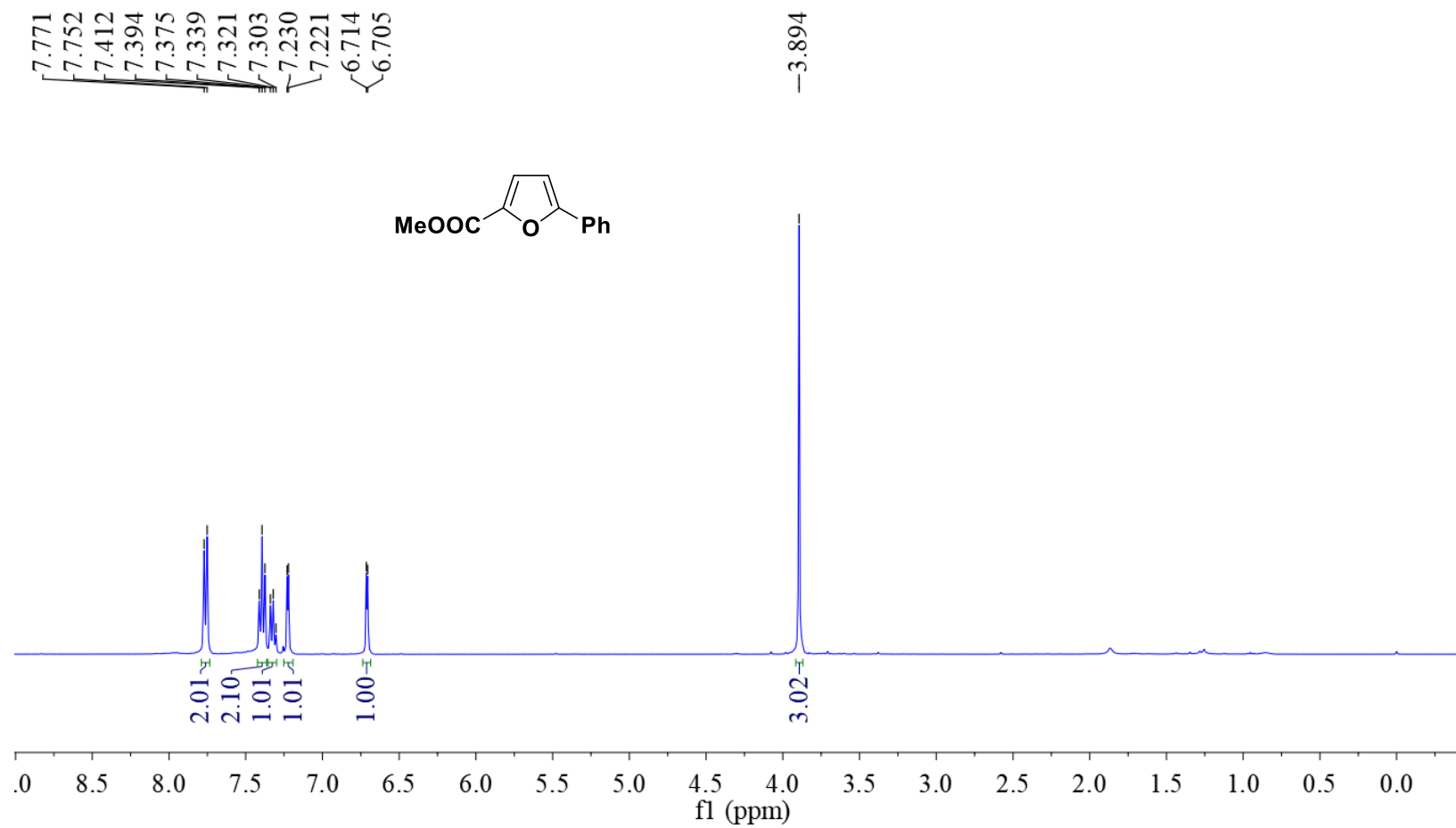
Methyl 5-benzoylfuran-2-carboxylate (32)

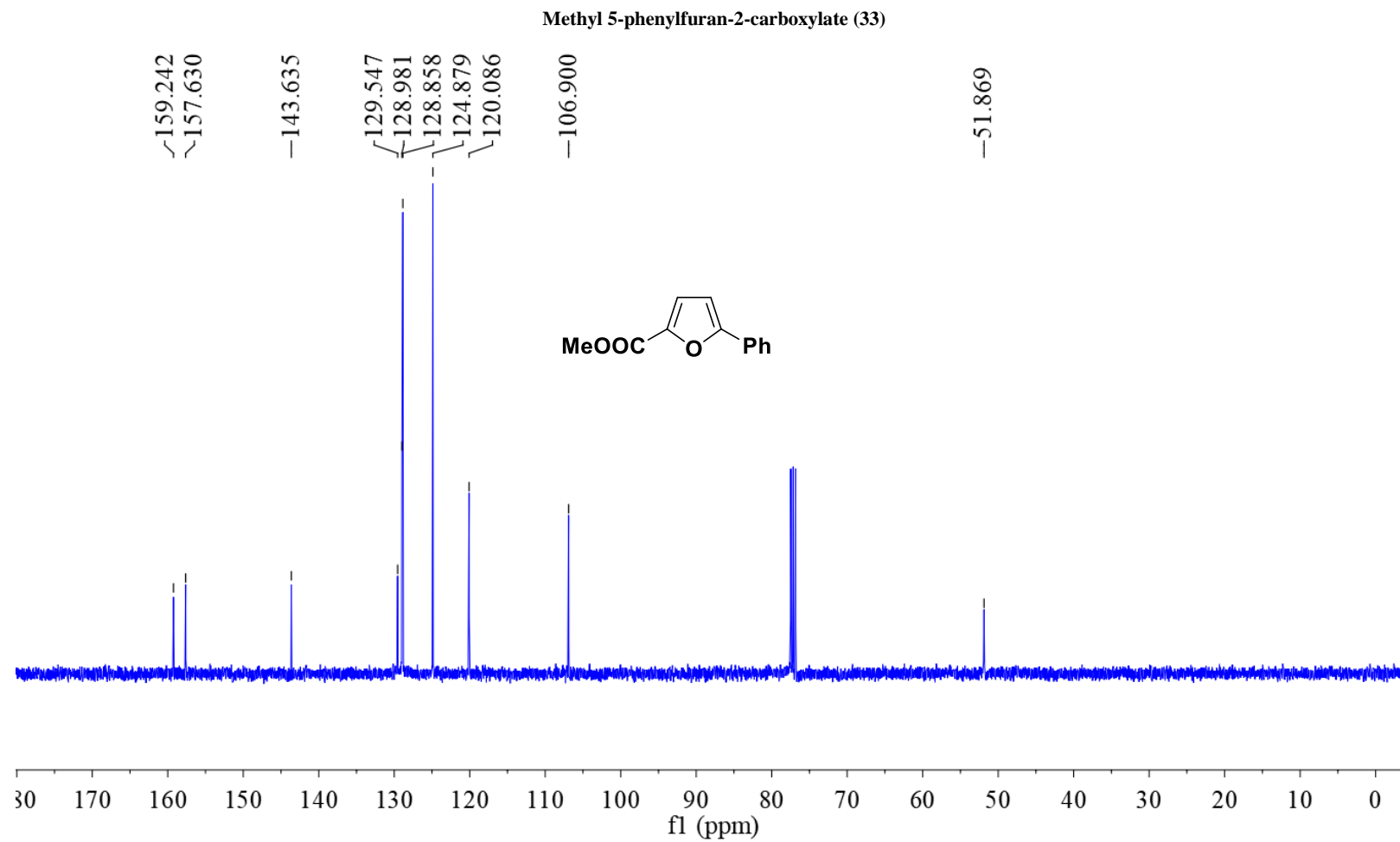


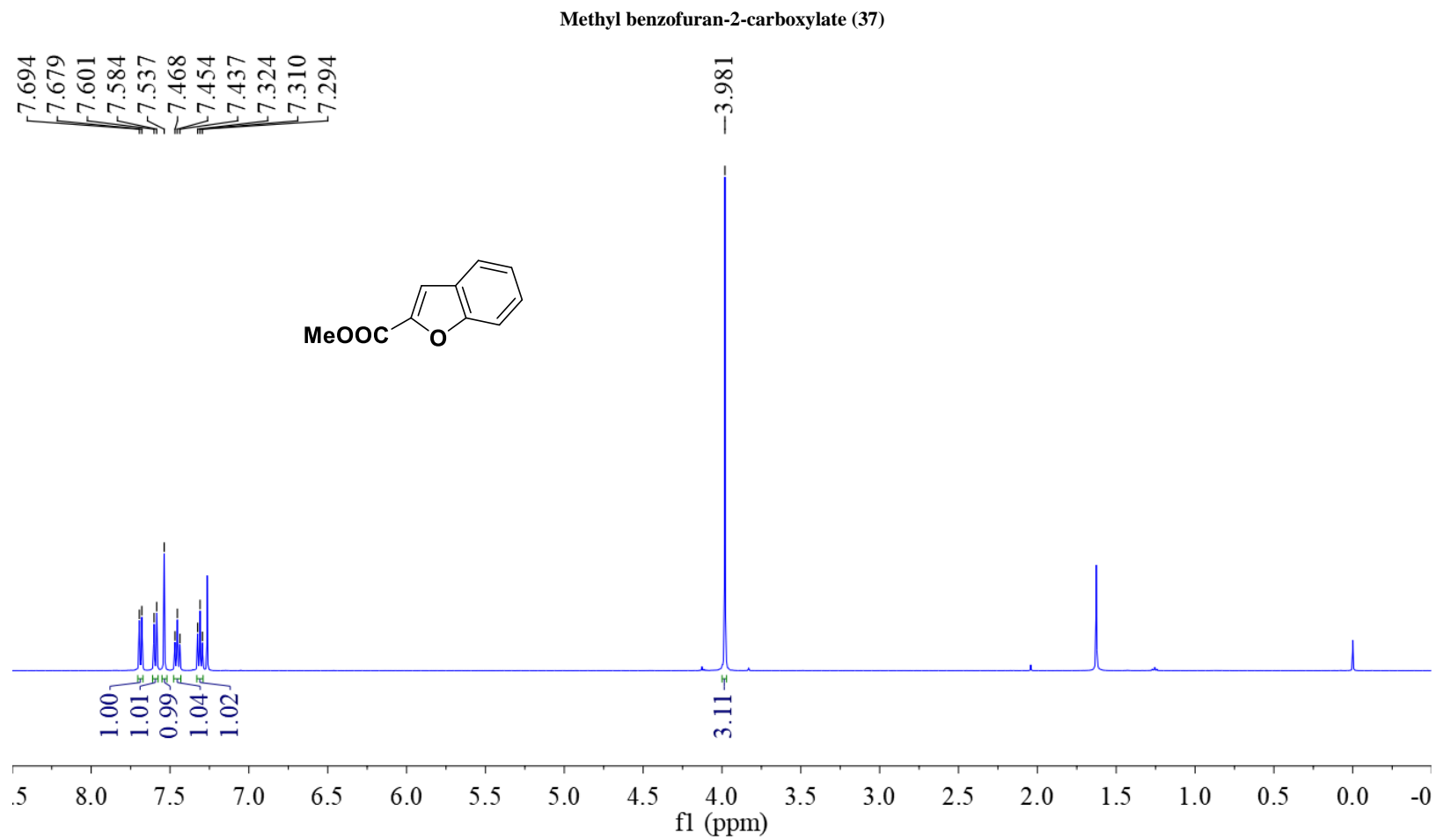
Methyl 5-benzoylfuran-2-carboxylate (32)



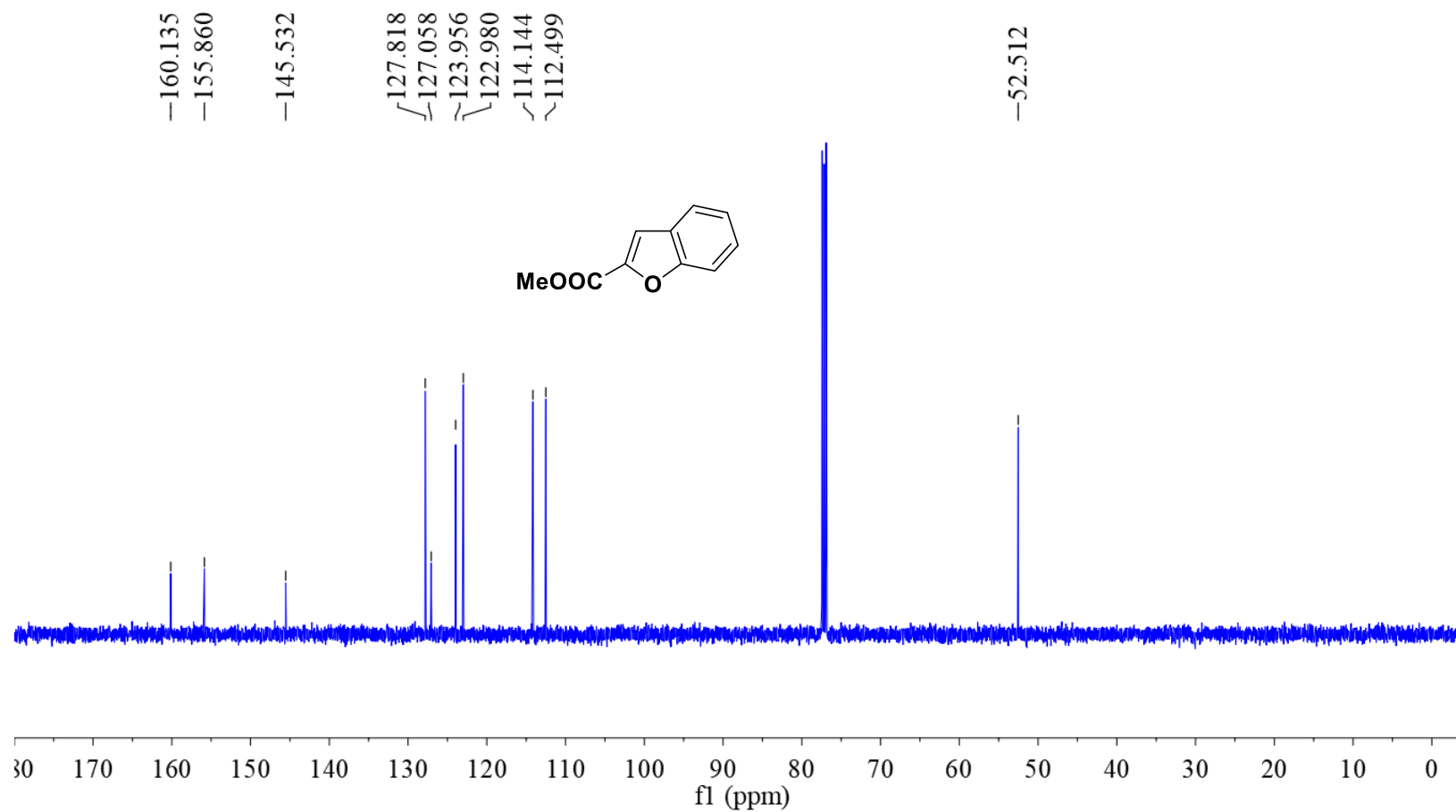
Methyl 5-phenylfuran-2-carboxylate (33)



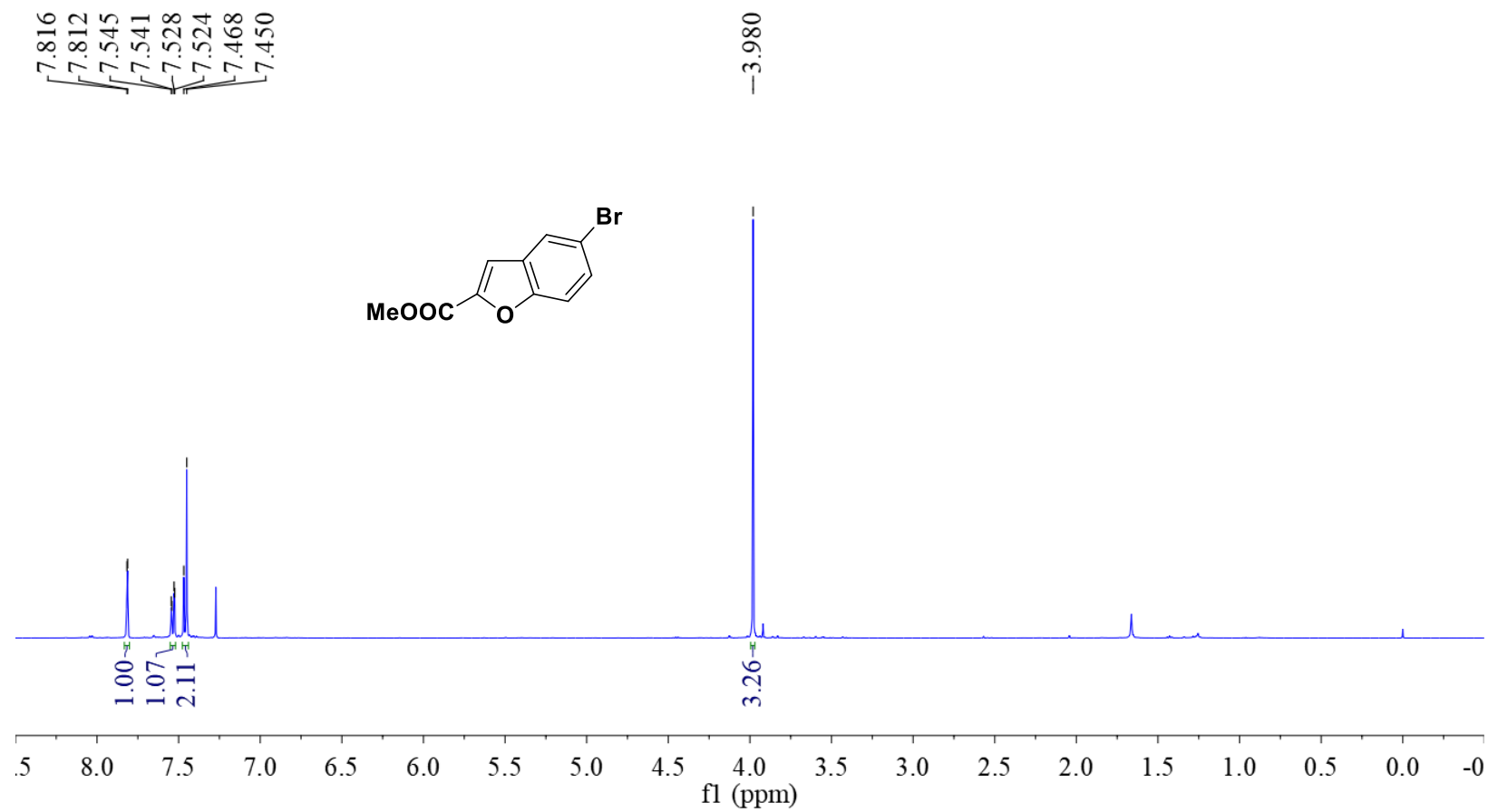




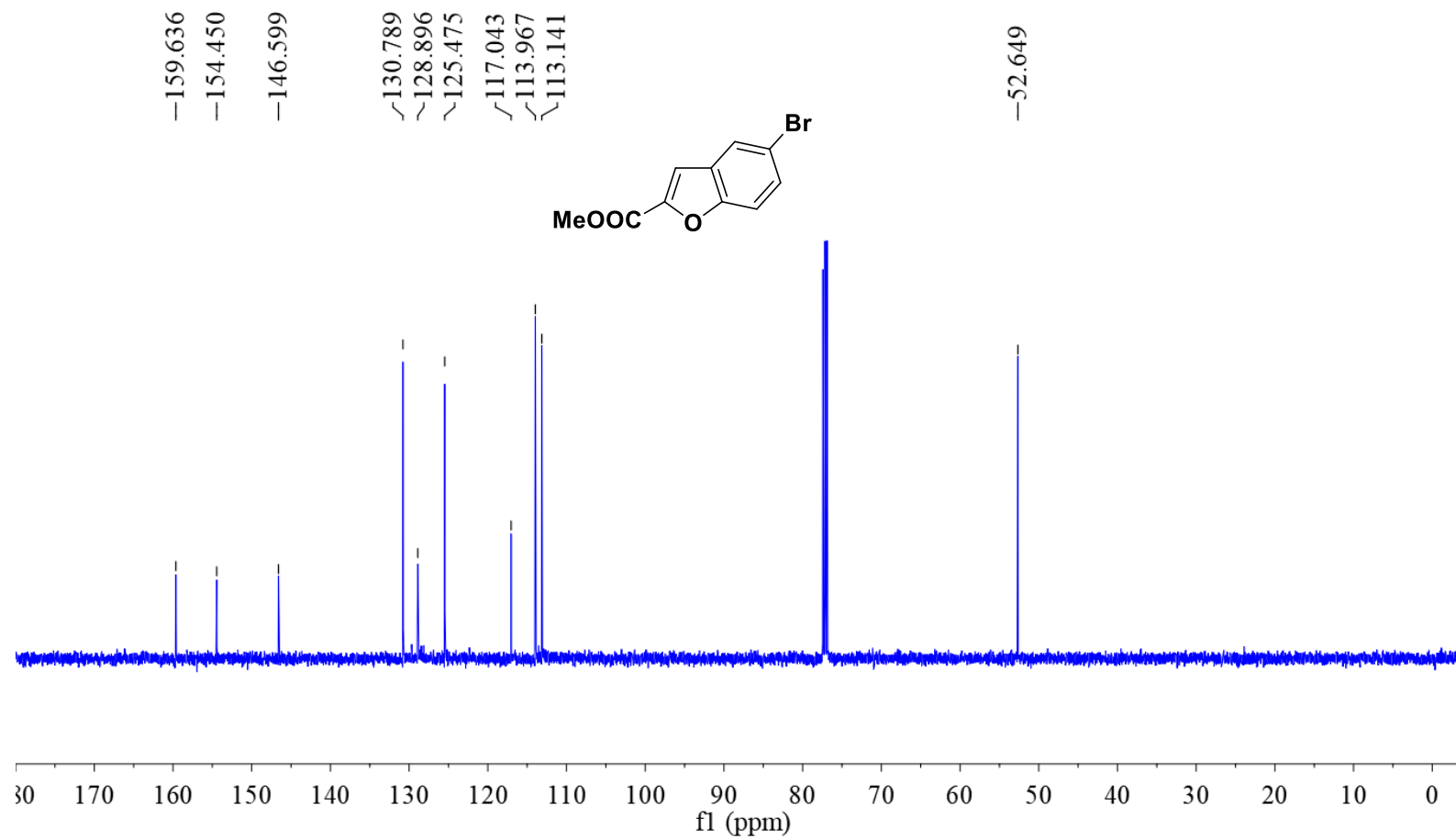
Methyl benzofuran-2-carboxylate (37)



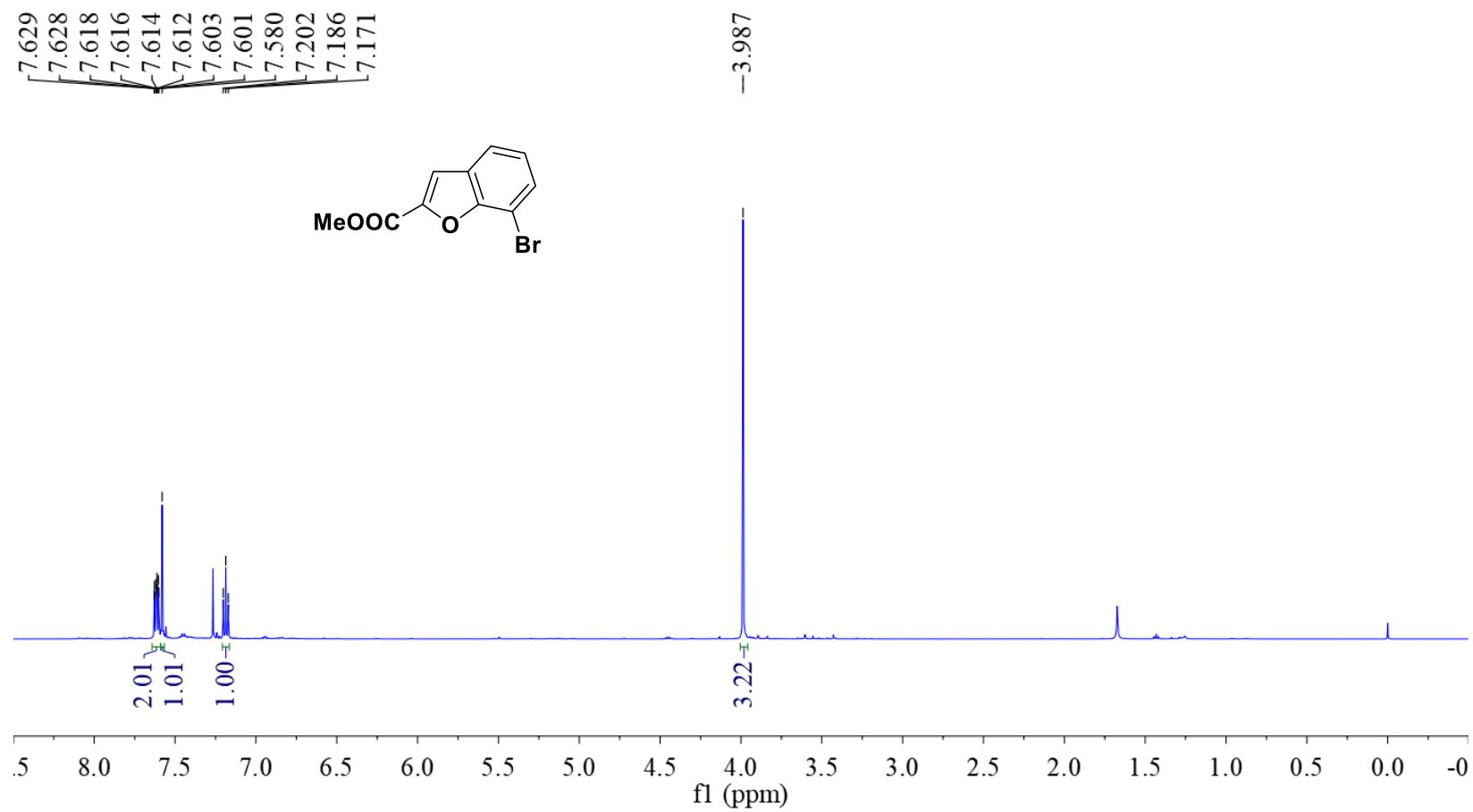
Methyl 5-bromobenzofuran-2-carboxylate (38)



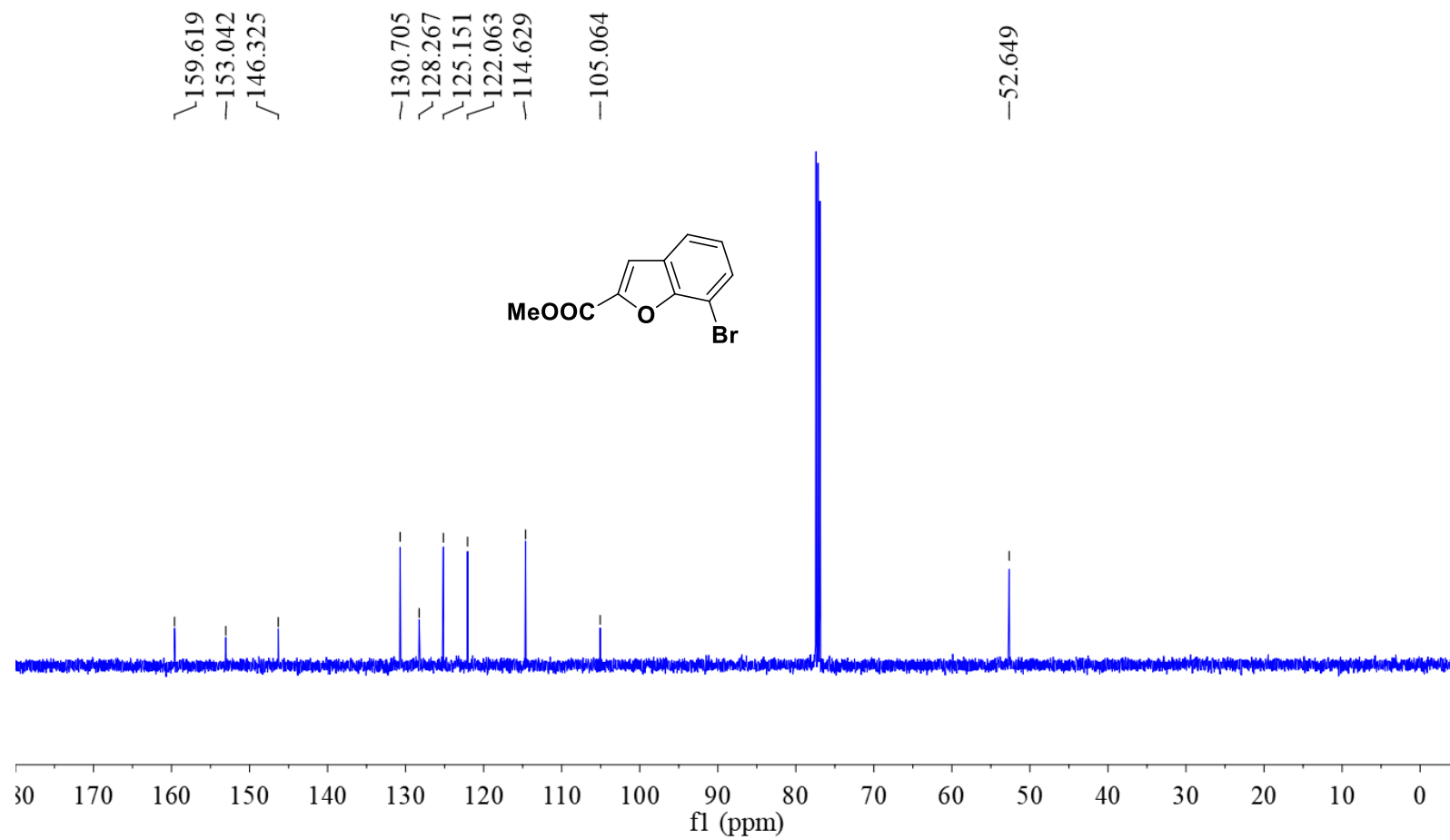
Methyl 5-bromobenzofuran-2-carboxylate (38)



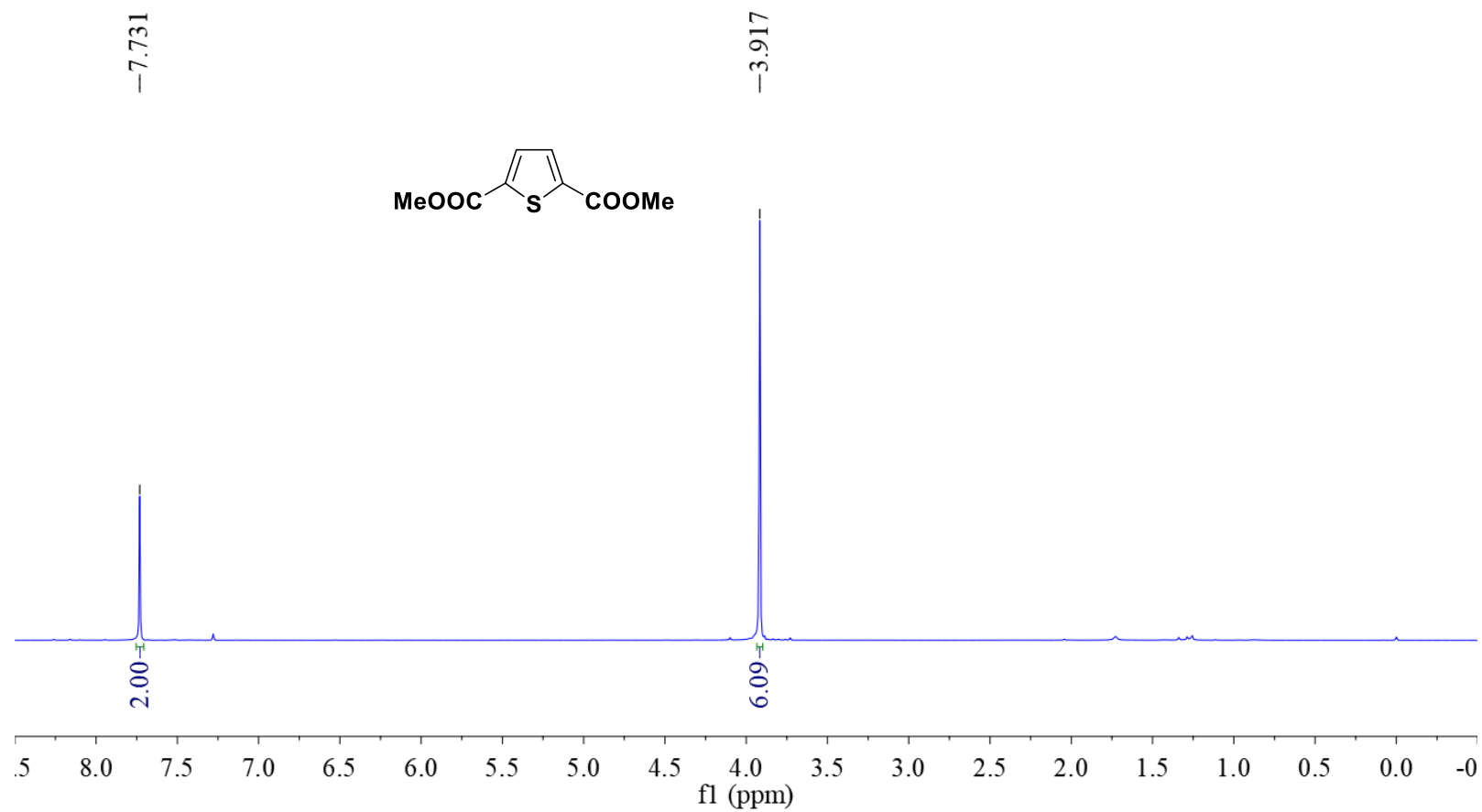
Methyl 7-bromobenzofuran-2-carboxylate (39)



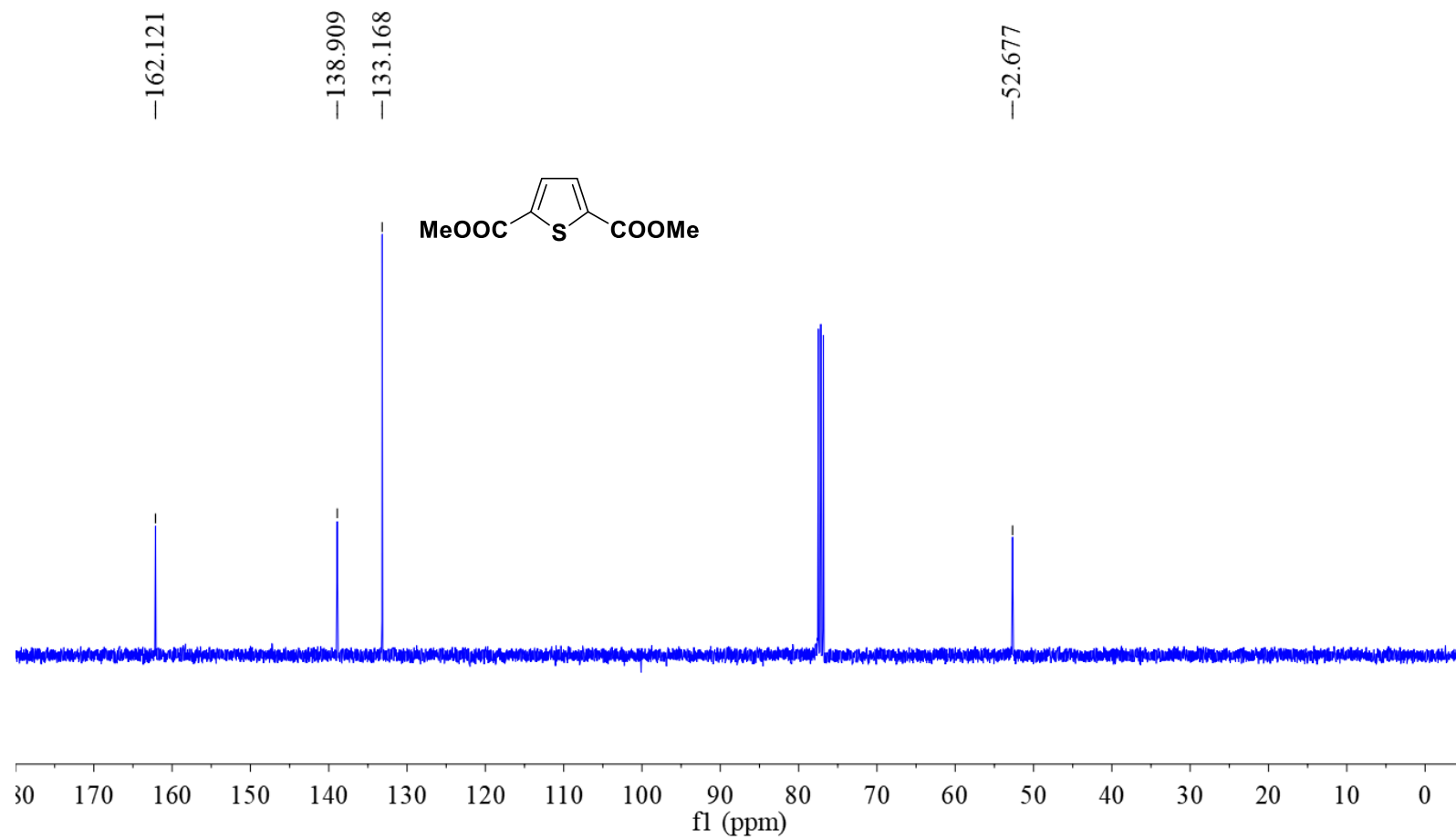
Methyl 7-bromobenzofuran-2-carboxylate (39)



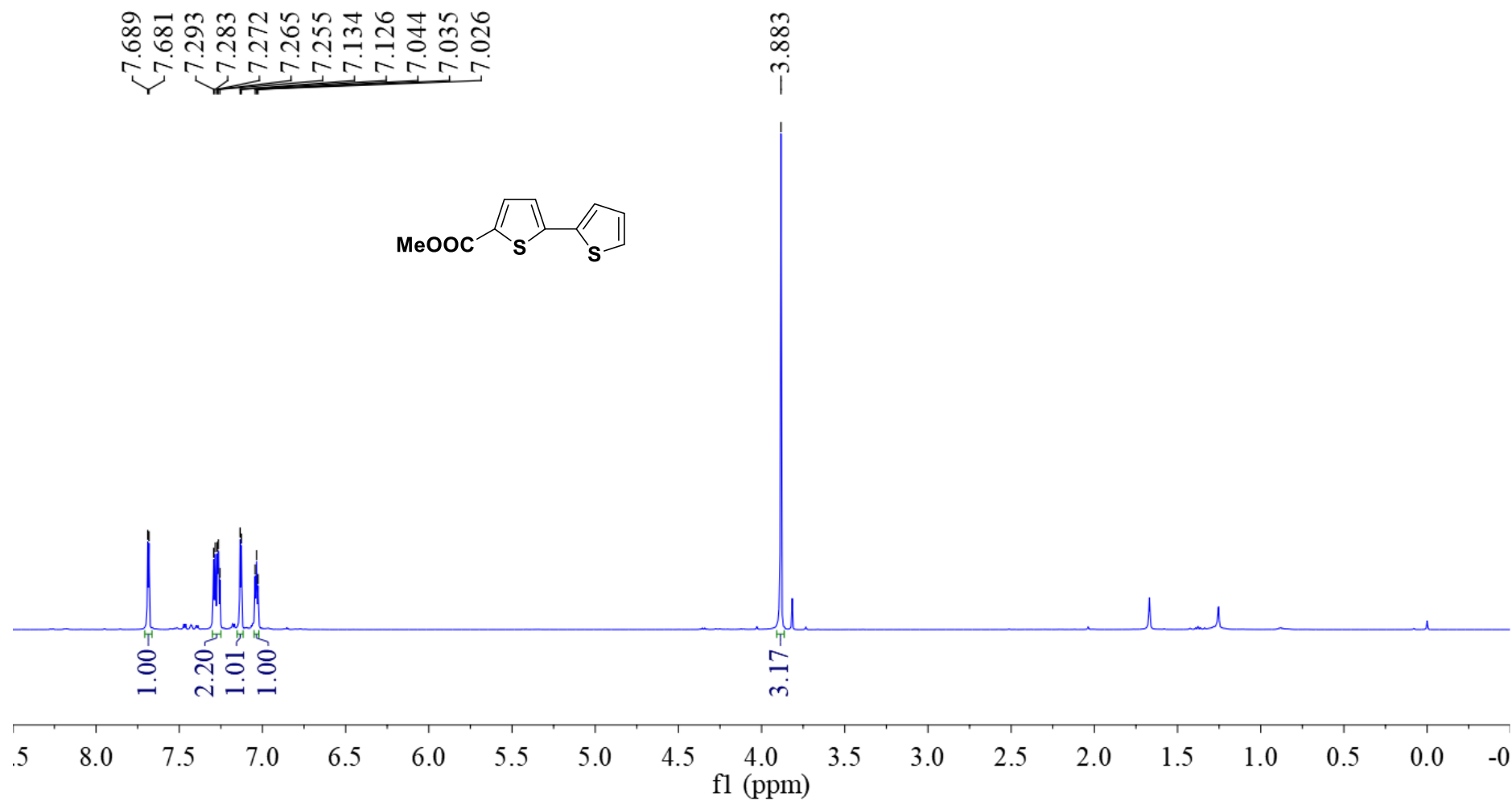
Dimethyl thiophene-2,5-dicarboxylate (40)



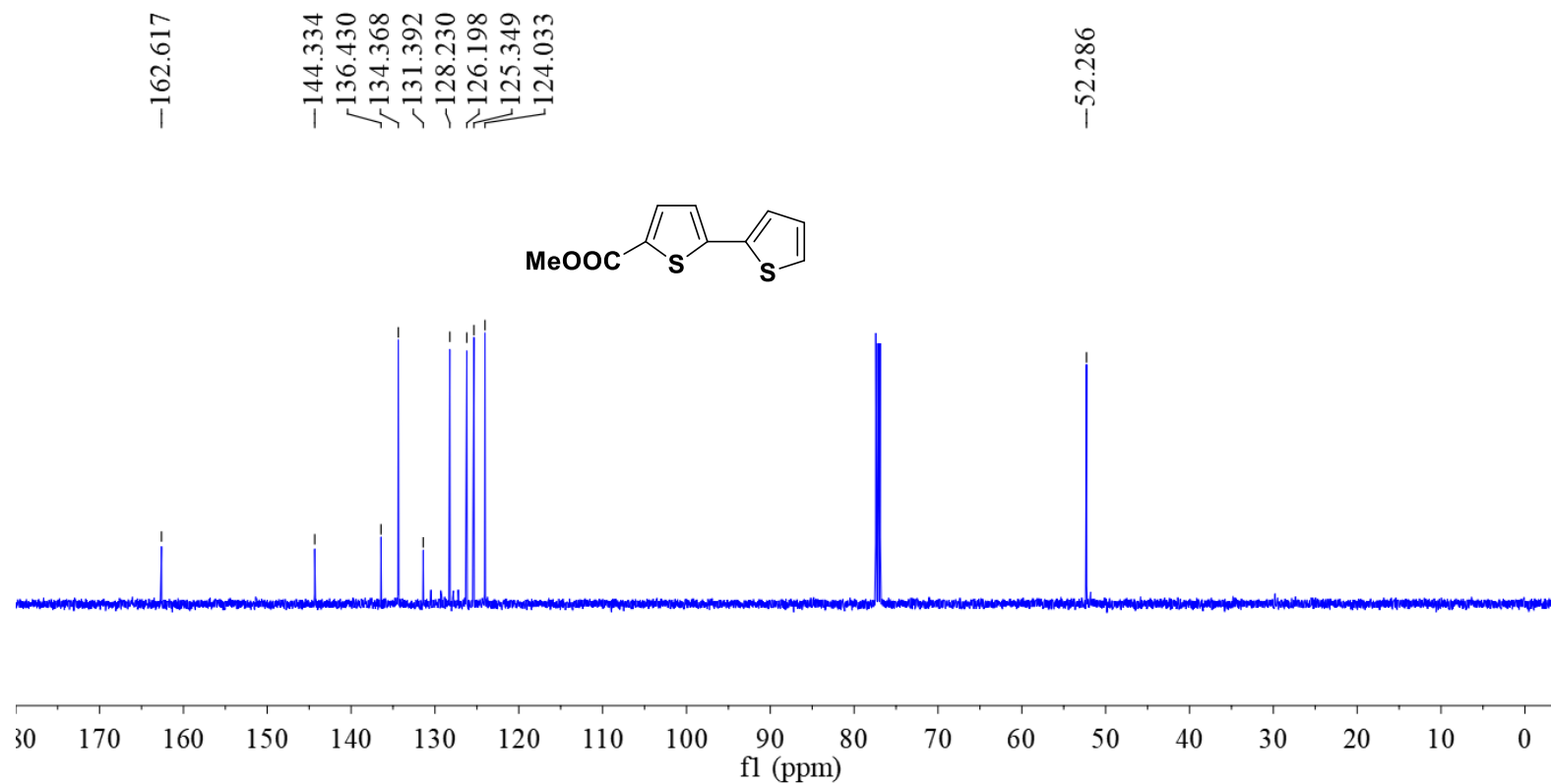
Dimethyl thiophene-2,5-dicarboxylate (40)



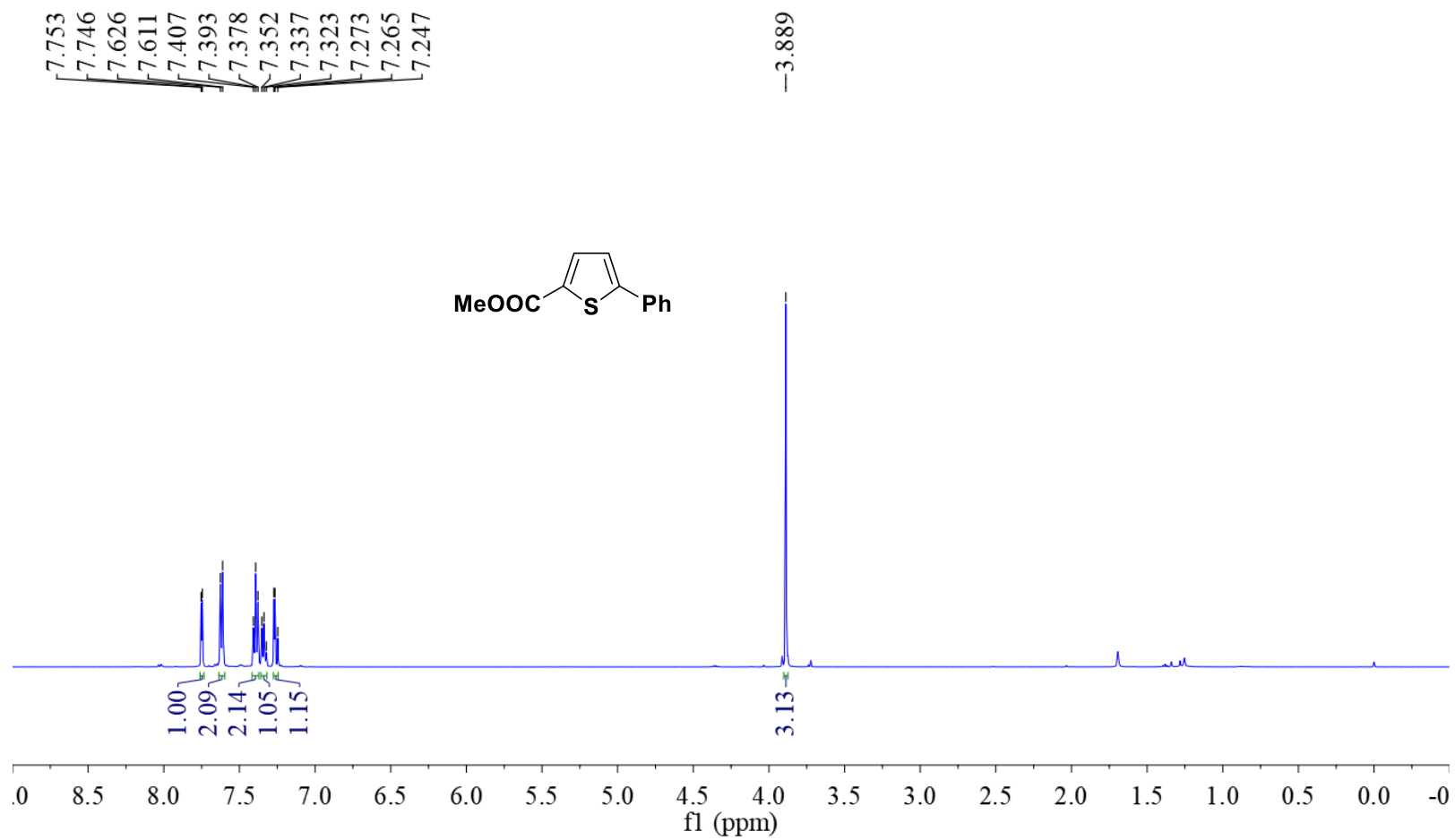
Methyl [2,2'-bithiophene]-5-carboxylate (41)



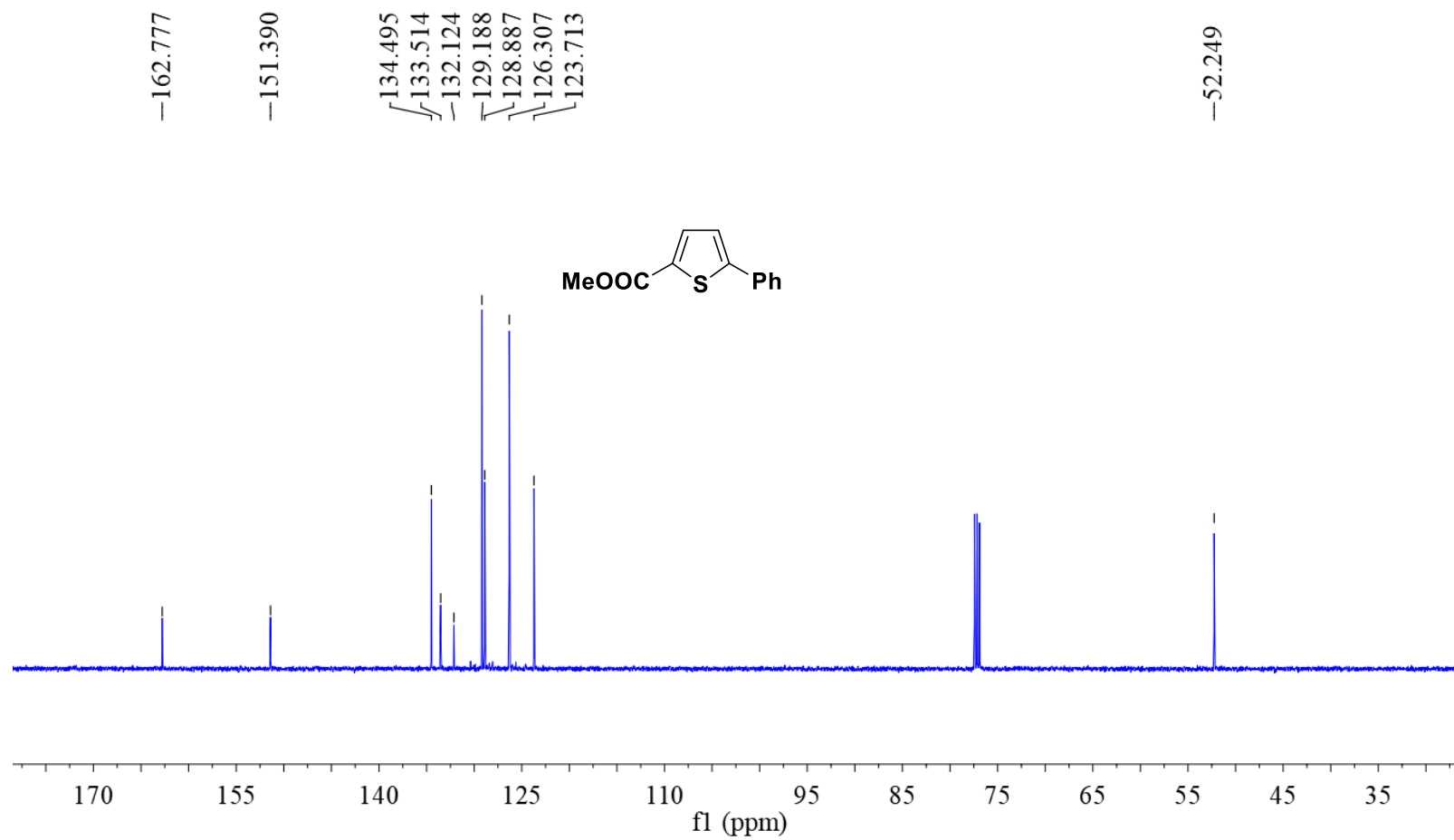
Methyl [2,2'-bithiophene]-5-carboxylate (41)

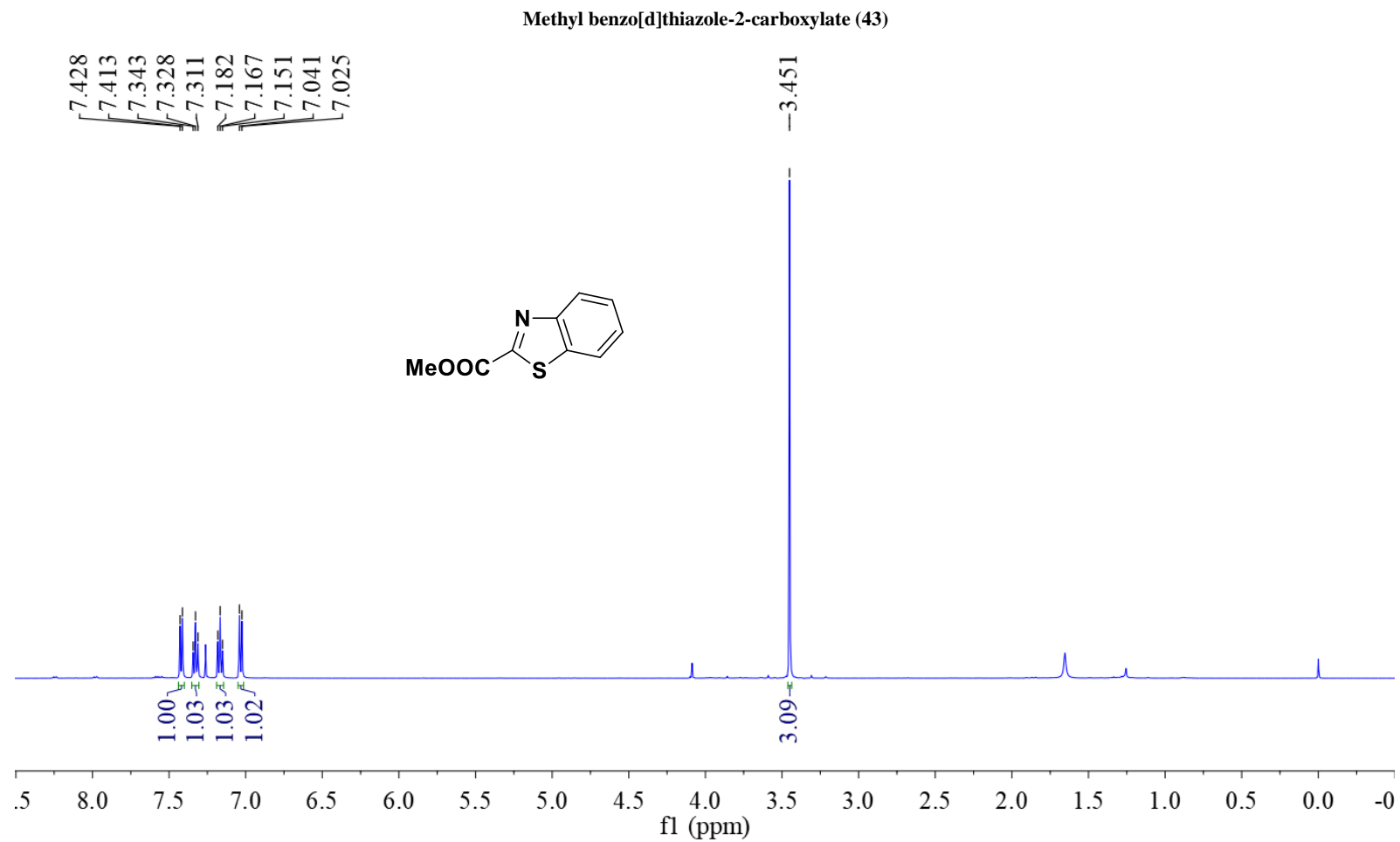


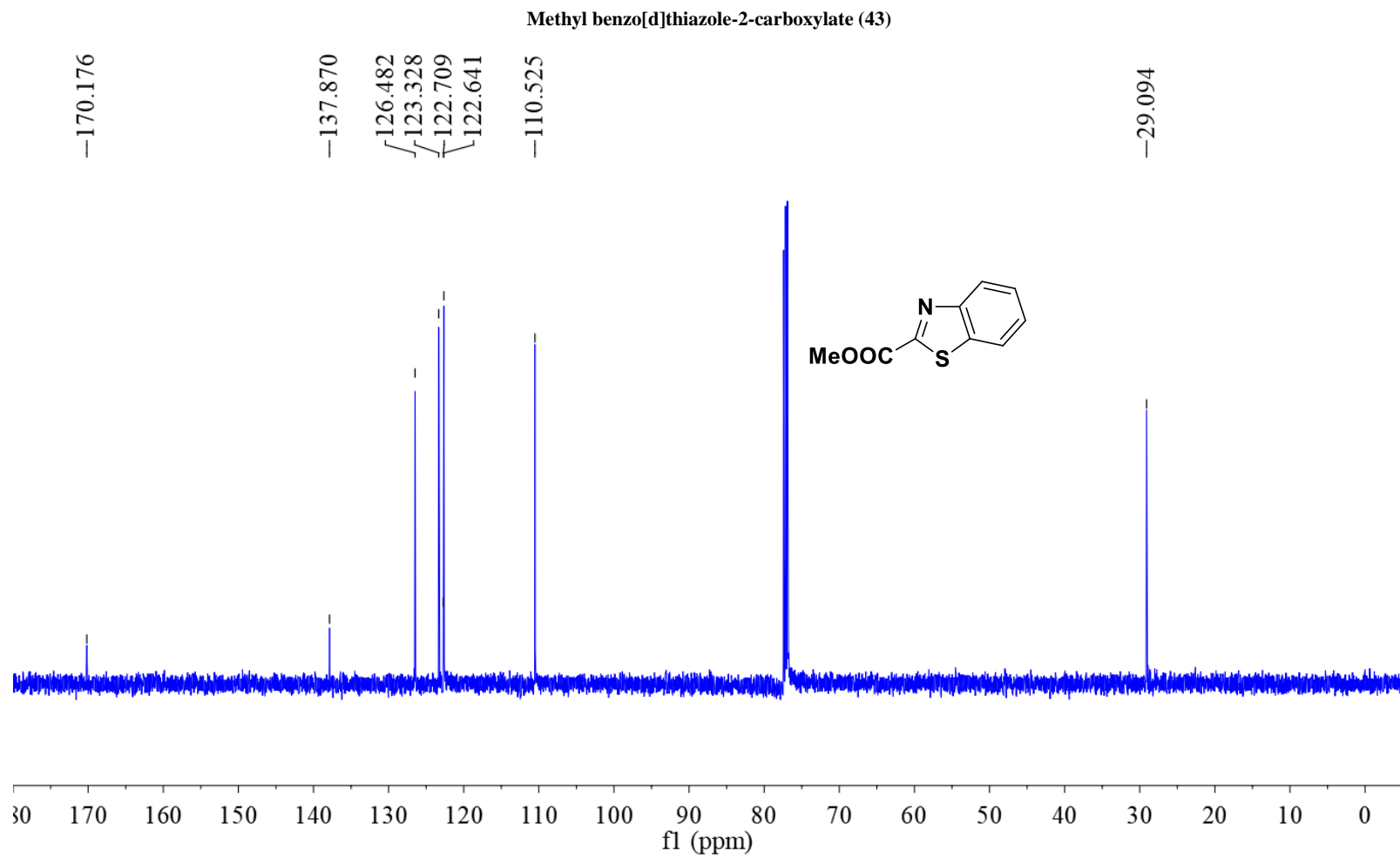
Methyl 5-phenylthiophene-2-carboxylate (42)



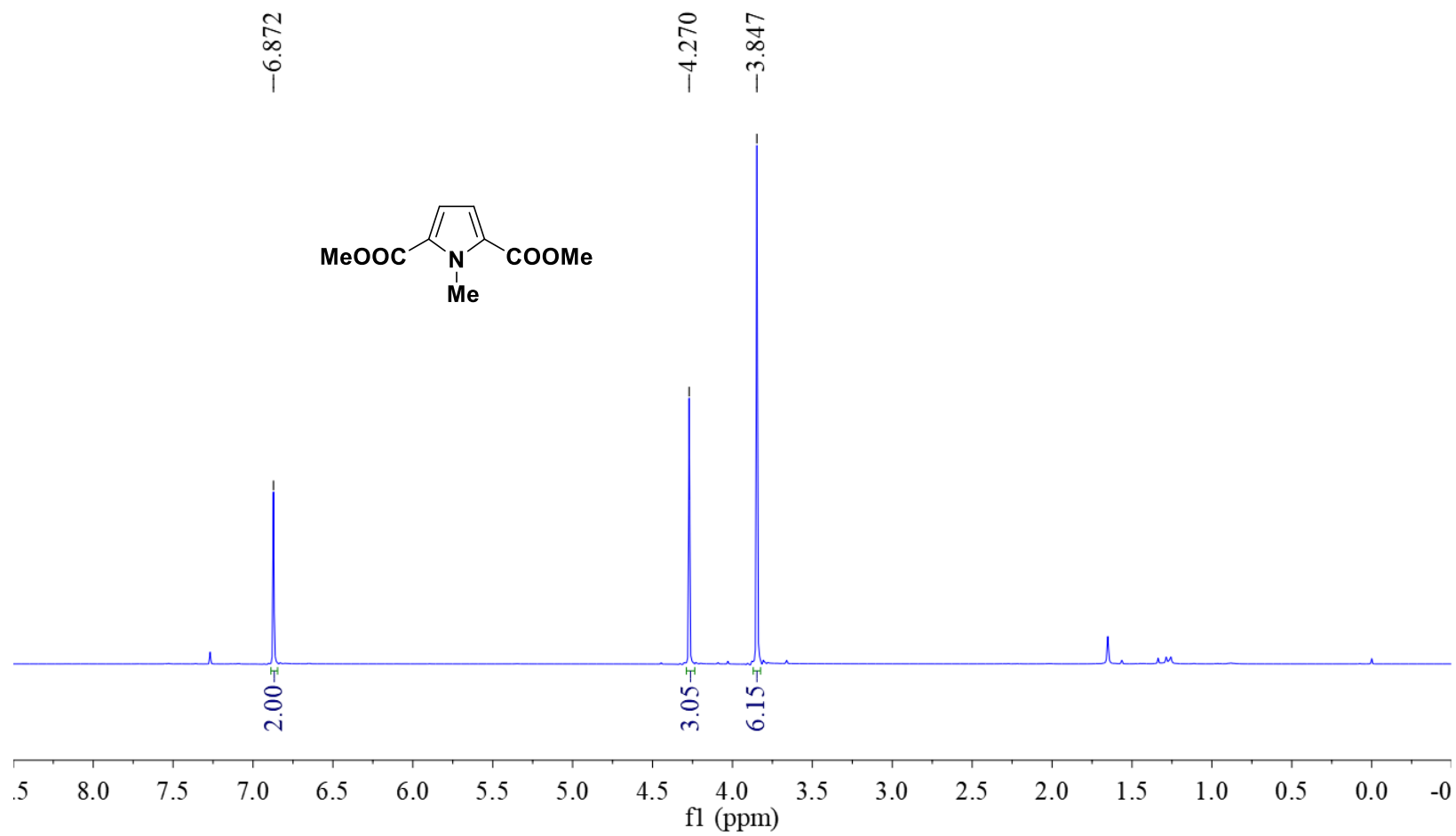
Methyl 5-phenylthiophene-2-carboxylate (42)



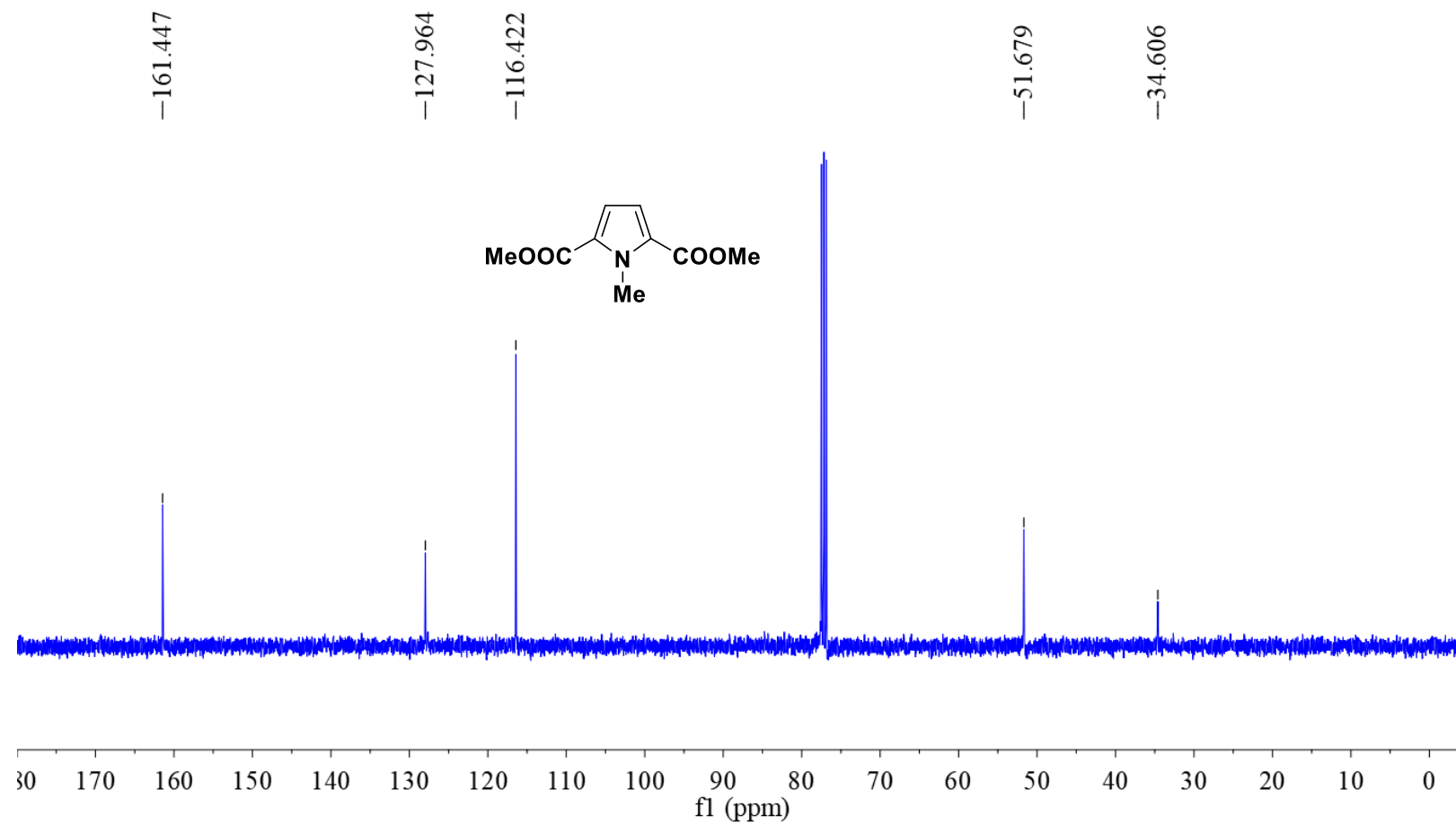




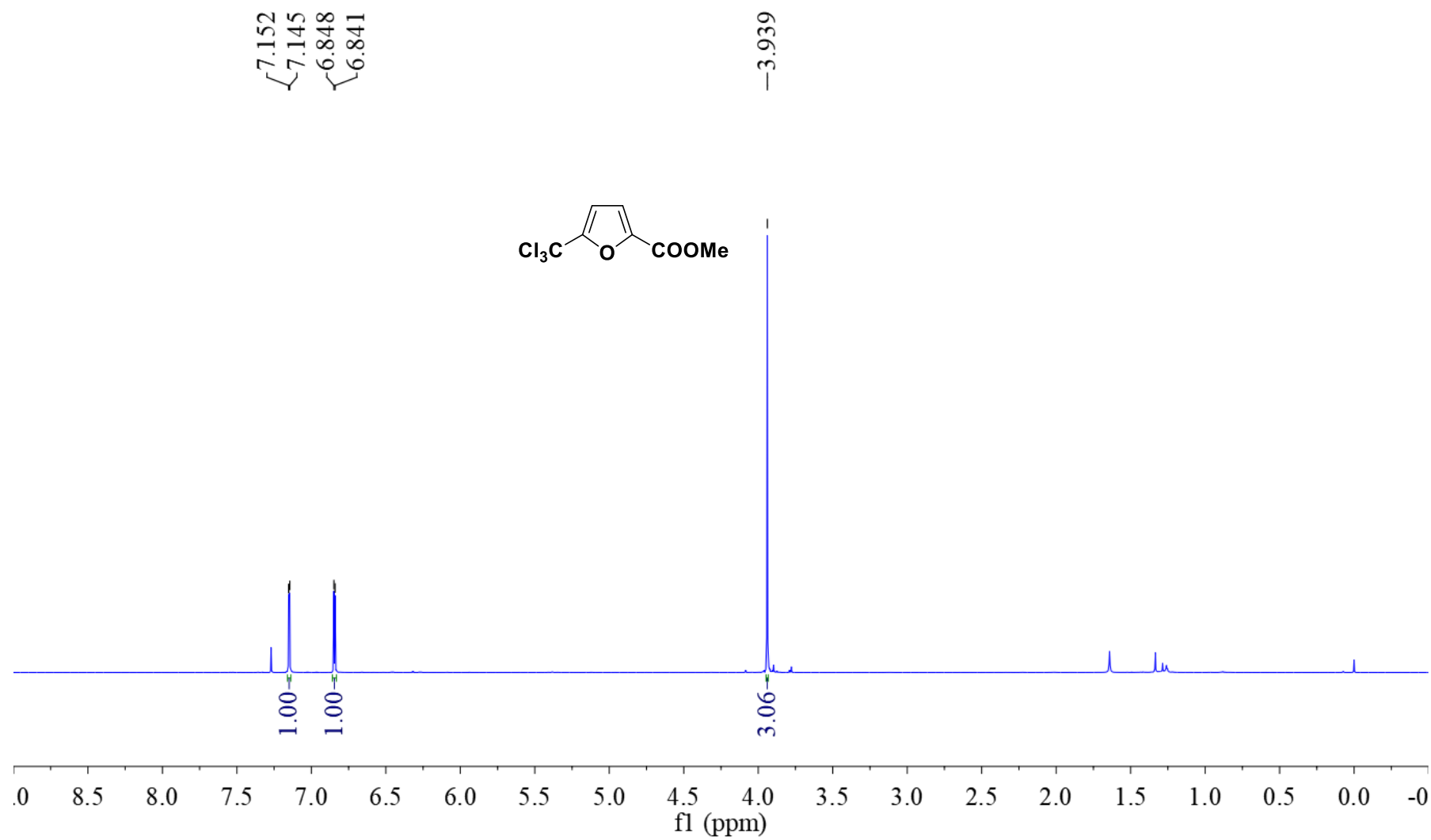
Dimethyl 1-methyl-1H-pyrrole-2,5-dicarboxylate (44)



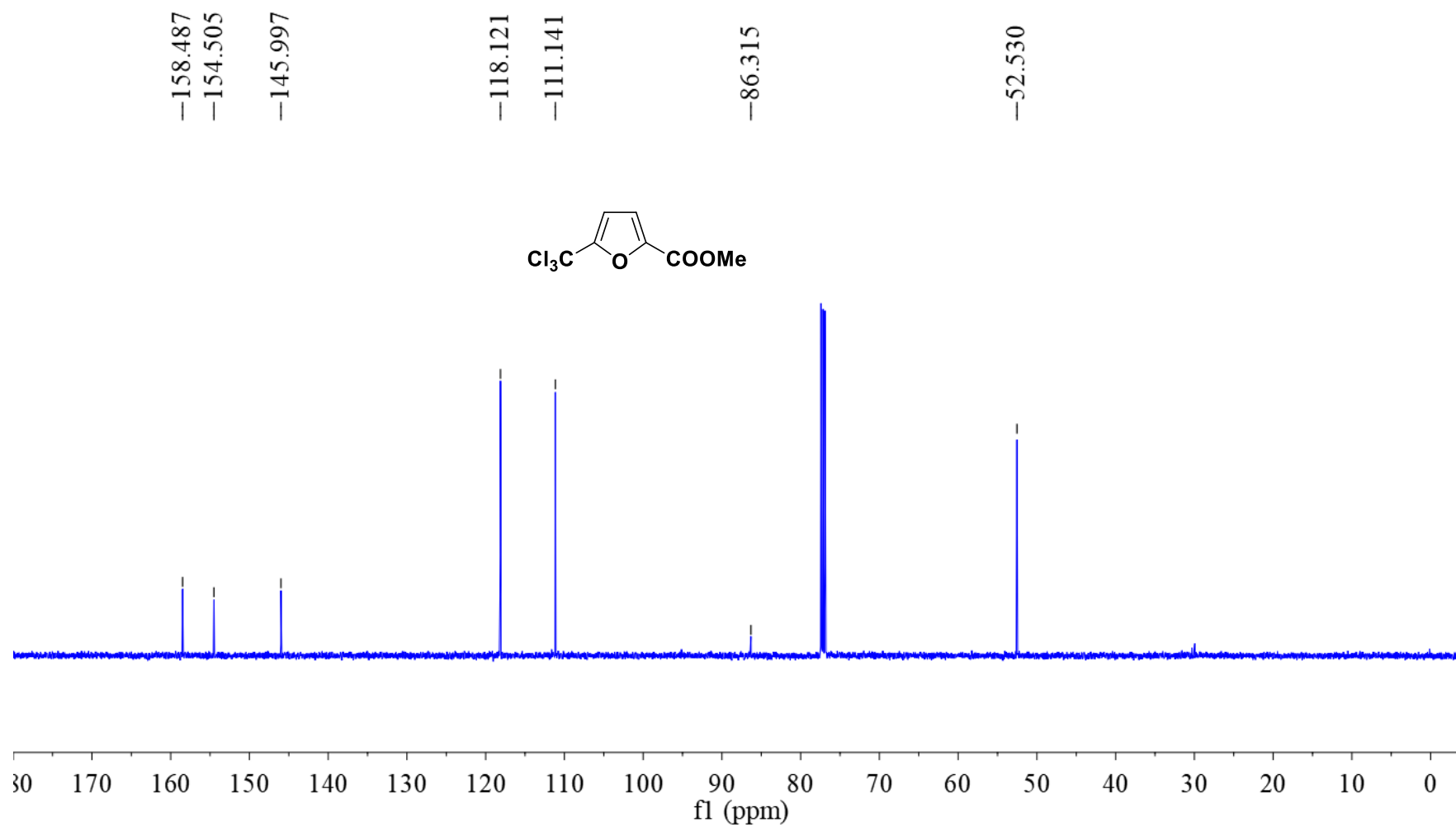
Dimethyl 1-methyl-1H-pyrrole-2,5-dicarboxylate (44)

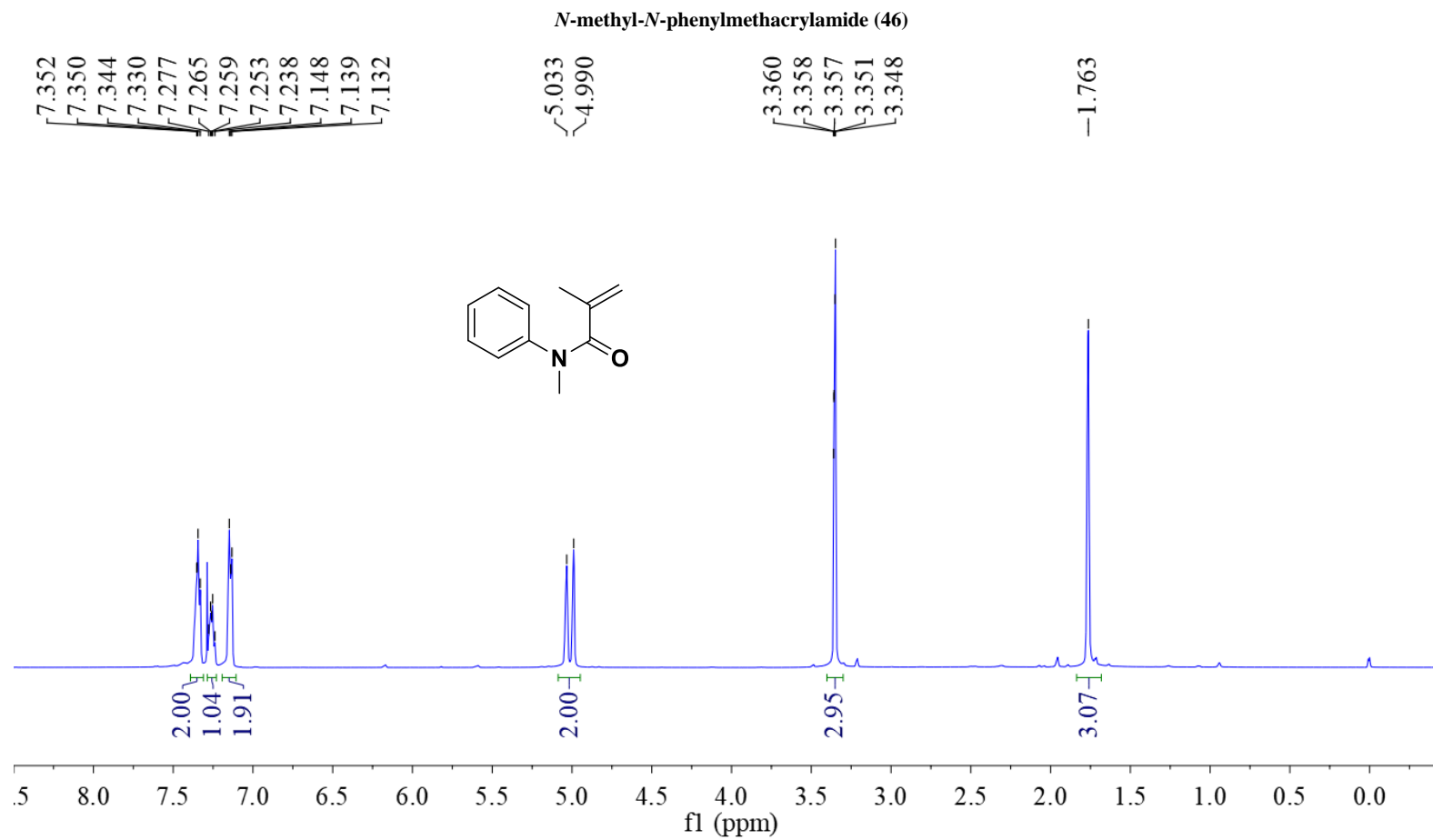


Methyl 5-(trichloromethyl)furan-2-carboxylate (45)

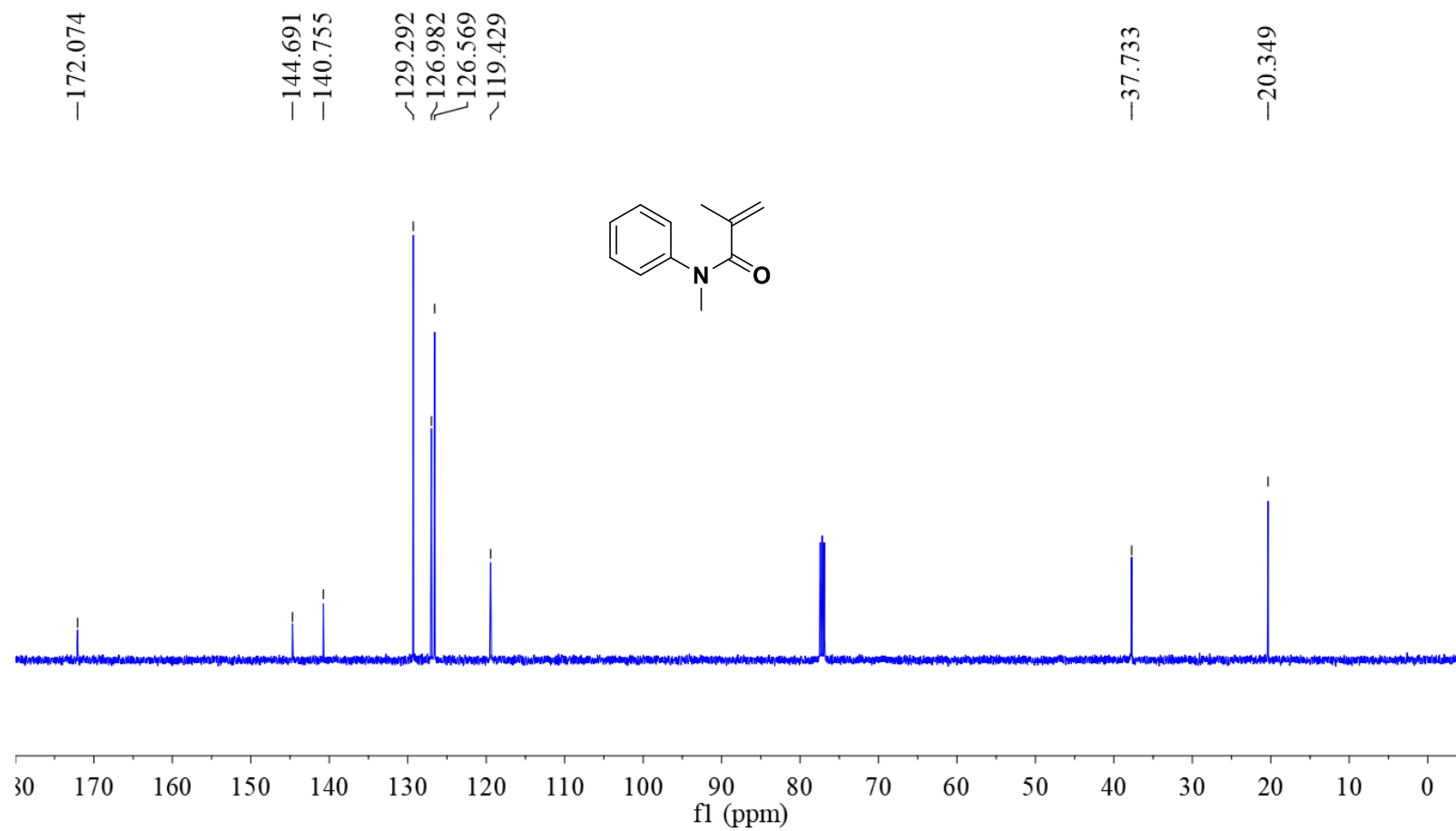


Methyl 5-(trichloromethyl)furan-2-carboxylate (45)

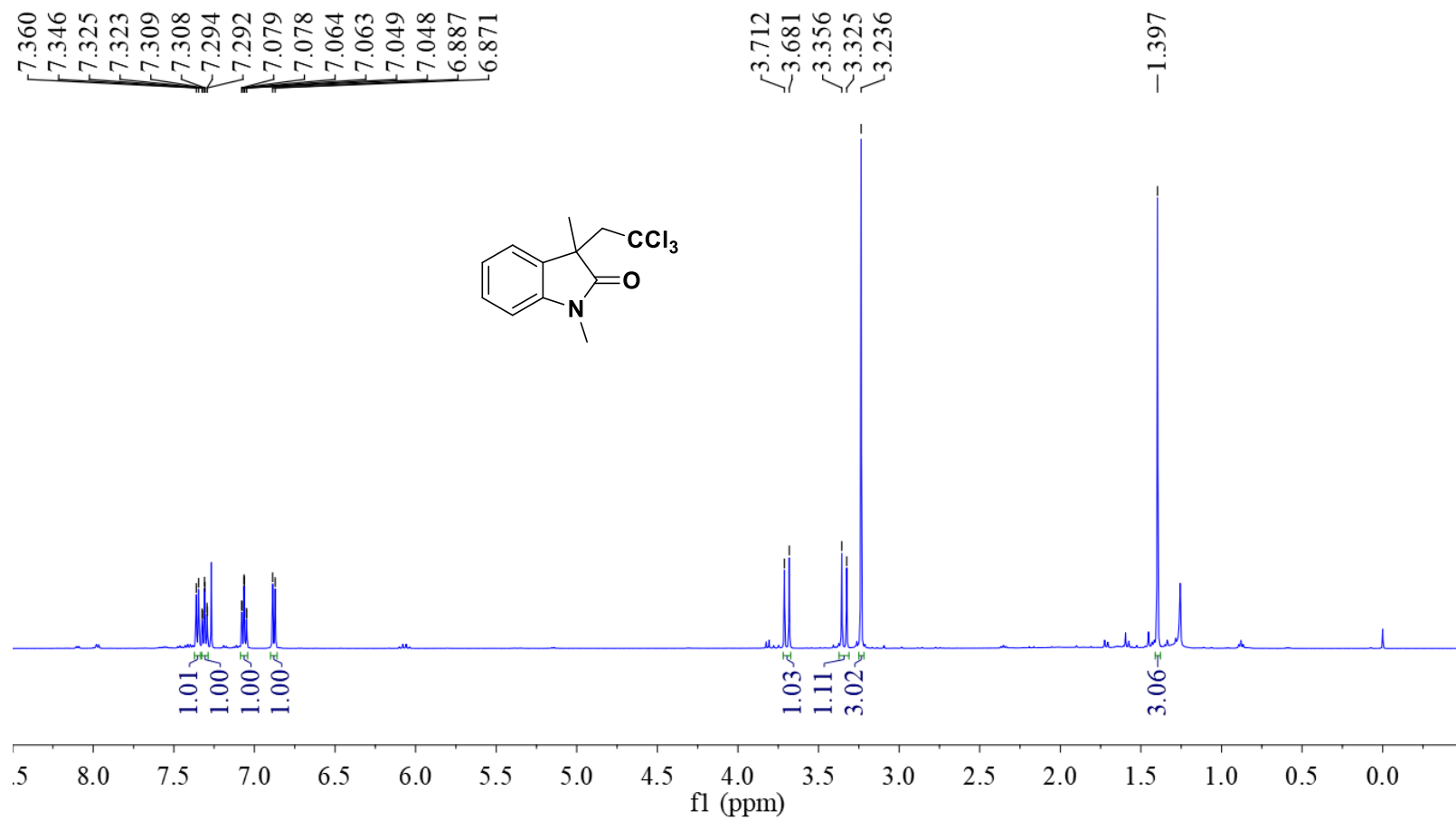




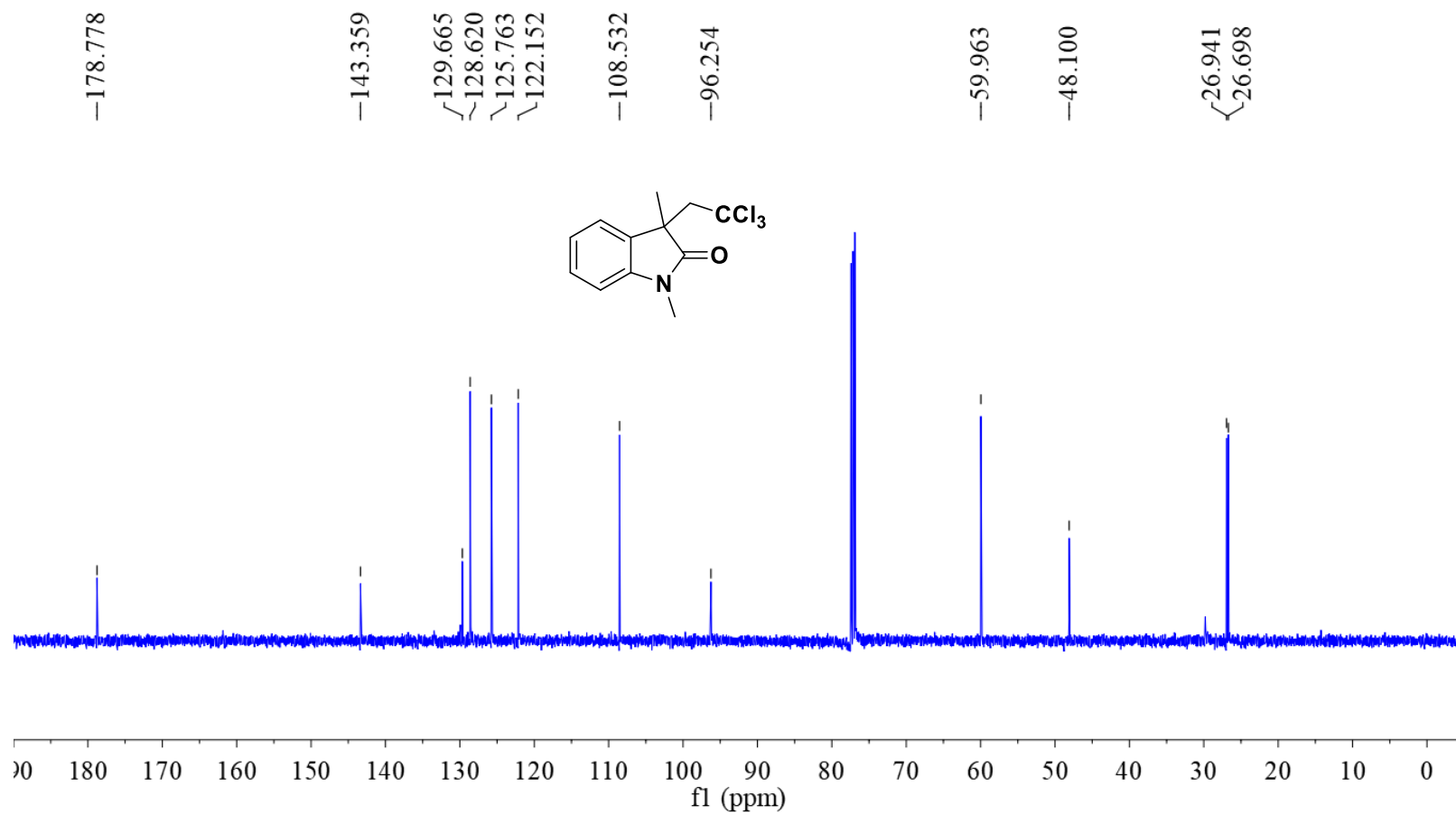
N-methyl-*N*-phenylmethacrylamide (46)



1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one (47)



1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one (47)



Methyl benzoate (48)

