

Synthesis of Pyridylsulfonium Salts and their Application in the Formation of Functionalized Bipyridines

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Supporting information

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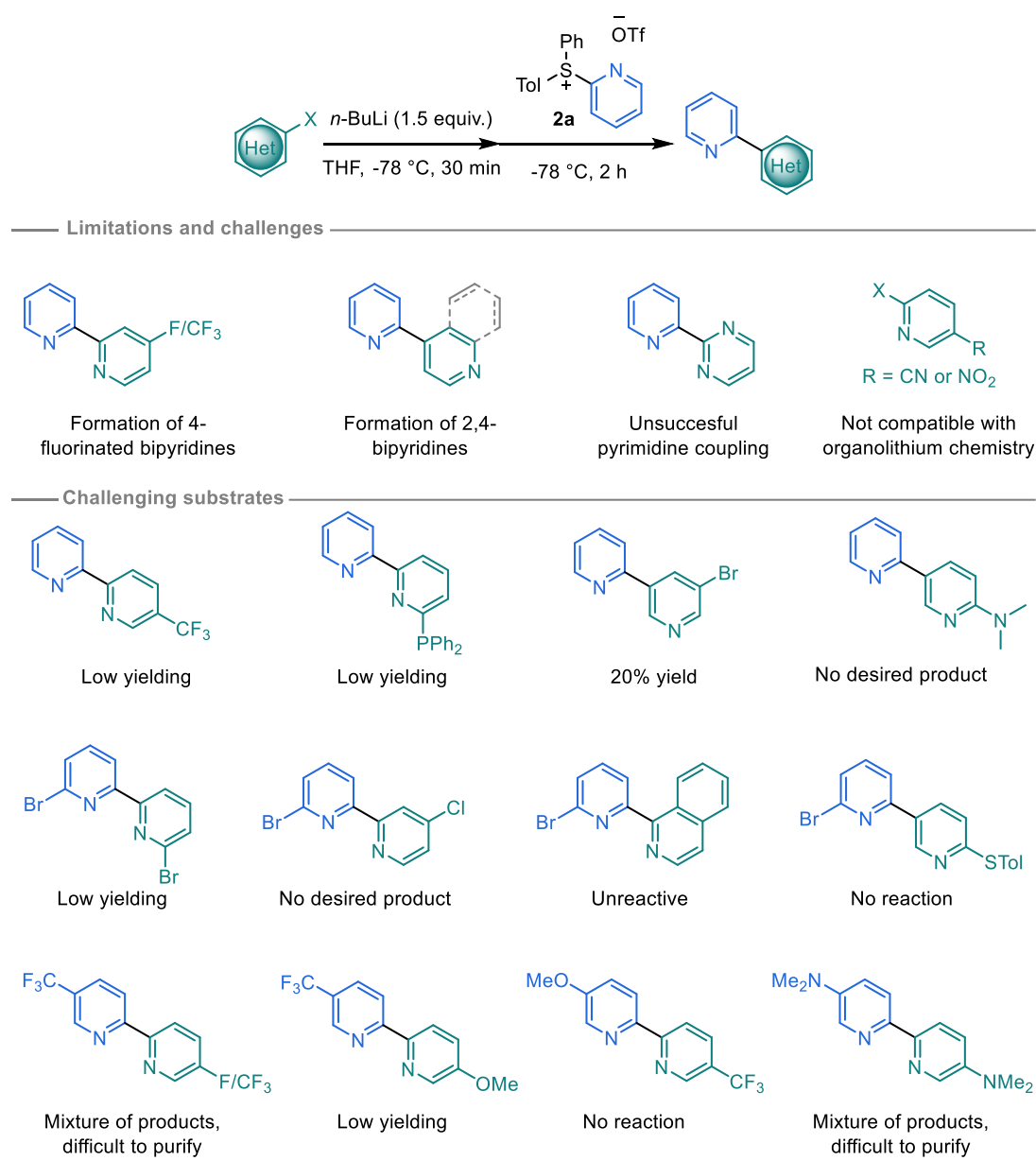
1. General experimental

Chemicals were purchased and used without further purification unless otherwise stated. 2-Methyltetrahydrofuran was transferred to a Schlenk tube, dried over freshly activated 4Å molecular sieves and stored under N₂. Solvents were dried using a Grubbs-type still, a Pure Solv-400-3-MD solvent purification system supplied by Innovative Technology Inc. design and stored in Strauss flasks over activated 4Å molecular sieves. Diphenyliodonium trifluoromethanesulfonate,¹ 2-bromo-5-(1,3-dioxolan-2-yl)pyridine² and 2-bromo-5-((trimethylsilyl)ethynyl)pyridine³ were prepared according to literature procedures.

Reactions requiring anhydrous conditions were performed under N₂; glassware was flame-dried immediately prior to use and allowed to cool under reduced pressure. Reaction monitoring by TLC was performed on Merck pre-coated Kieselgel 60 F₂₅₄ aluminium plates. Visualization was accomplished under UV light (254 nm). Flash column chromatography (FCC) was performed using either silica gel [Davisil, 230-400 mesh (40-63 µm)] or using a Biotage Isolera™ UV-VIS Flash Purification System Version 2.3.1 with SNAP Ultra (25 µm), SNAP KP-Sil (50 µm) or SNAP KP-NH (50 µm) prepacked silica cartridges. High-resolution mass spectra were run on a Waters Micromass GCT system or on an Agilent 6546 QTOF system in electrospray ionization mode (ESI). Extracts were concentrated *in vacuo* using both a rotary evaporator (bath temperatures up to 55 °C), and a high vacuum line at room temperature. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were measured in the solvent stated at 300 MHz, 400 MHz or 500 MHz. Chemical shifts (δ) are quoted in parts per million (ppm) referenced to residual solvent peak (e.g., CDCl₃: ¹H – 7.26 ppm and ¹³C – 77.16 ppm) or TMS (¹H – 0.00 ppm) and coupling constants (*J*) are given in Hertz. Multiplicities are abbreviated as: b (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or combinations thereof. Assignments were made, where necessary, with the aid of COSY, HSQC, HMBC and NOESY NMR experiments.

2. Limitations and challenges

Table 1: Limitations and challenging substrates with the methodology



3. Notes and guidelines for coupling reactions

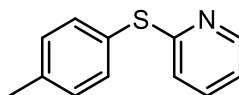
1. The ligand coupling sequence produces at least three products: sulfide, dehalogenated material and bipyridine, making the purification potentially tricky. However, the desired bipyridine product is generally the most polar material by TLC relative to sulfide and dehalogenated pyridine starting material.
2. Some sulfonium salts can require some stirring before they fully dissolve in THF. We recommend preparing a solution of the pyridylsulfonium salt by stirring in THF in a separate flask while the organolithium is generated in the reaction flask.
3. Amine-containing bipyridines can be rather basic and require the addition of Et₃N (1%) in the eluent for flash column chromatography.
4. 2,2-Bipyridines are generally less polar than 2,3-bipyridines on silica.
5. For S_NAr-active substrates (i.e. Cl-, Br- or F-containing pyridines), addition of sulfonium to the reaction flask can be carried out after 15 min rather than 30 min. This minimizes the amount of homocoupling (reaction between lithiated pyridine with halogenated pyridine starting material).
6. Iodopyridines can be lithiated in the presence of sulfonium salt, removing the need for a sulfonium addition step.

4. Synthesis of sulfides 1a-i and halopyridine starting material S1

General procedure A: 4-methylbenzenethiol (1 equiv.) was added to a round bottomed flask, followed by halopyridine (1 equiv.) and H₂O (0.5 M). The reaction was heated under reflux for 24 h (the flask sitting in an aluminium block placed on a stirrer hotplate). Then, the reaction was allowed to cool, followed by extraction with EtOAc. The combined organic layers were washed with water and brine and dried over Na₂SO₄. The solvent was evaporated and the product was isolated by FCC.

General procedure B: 4-methylbenzenethiol (1 equiv.) was added to a crimp top vial followed by halopyridine (1 equiv.) and K₂CO₃ (1.1 equiv.) and closed. The vial was evacuated and purged with N₂ three times. Anhydrous DMF (0.8–1 M wrt thiol/halopyridine) was added. The reaction was heated to 100 °C for 24 h (the flask sitting in an aluminium block placed on a stirrer hotplate). Then the reaction was allowed to cool, followed by the addition of water and extraction with EtOAc. The combined organic layers were washed with water and brine and dried over Na₂SO₄. Details of purification are given below for each compound.

2-(*p*-Tolylthio)pyridine 1a



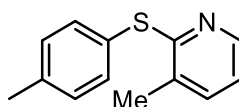
Prepared from General procedure A with 4-methylbenzenethiol (14.0 g, 113 mmol), 2-bromopyridine (10.8 mL, 113 mmol) and H₂O (226 mL). The reaction was extracted with EtOAc (3 x 200 mL). The combined organic layers were washed with water (200 mL) and brine (200 mL) and dried over Na₂SO₄. The solvent was evaporated and purification by FCC (10% Et₂O in pentane) gave pyridylsulfide **1a** as a yellow oil (21.05 g, 93%).

¹H NMR (400 MHz, Chloroform-*d*): δ 8.41 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 (ddd, *J* = 8.2, 7.4, 1.9 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.97 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 6.84 (dt, *J* = 8.1, 1.0 Hz, 1H), 2.40 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 162.4, 149.6, 139.6, 136.7, 135.4, 130.6, 127.4, 121.0, 119.7, 21.5.

Spectra were consistent with literature data.⁴

3-Methyl-2-(*p*-tolylthio)pyridine 1b



Prepared from General procedure A with 4-methylbenzenethiol (1.00 g, 8.05 mmol), 3-bromo-2-methylpyridine (0.89 mL, 8.0 mmol) and H₂O (15 mL). The reaction was extracted with EtOAc (3 x 20

mL). The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over Na₂SO₄. The solvent was evaporated and purification by FCC (5% Et₂O in pentane) gave pyridylsulfide **1b** as a clear oil (0.93 g, 54%).

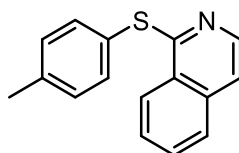
TLC: *R*_f = 0.33 (10% Et₂O in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.22 (ddd, *J* = 4.9, 1.9, 0.8 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.37 (ddd, *J* = 7.4, 1.7, 0.8 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.95 (dd, *J* = 7.5, 4.8 Hz, 1H), 2.38 (s, 3H, CH₃), 2.36 (s, 3H, CH₃).

¹³C NMR (126 MHz, Chloroform-*d*) δ 158.3 (C), 147.4 (CH), 138.5 (C), 137.1 (CH), 134.5 (CH), 131.6 (C), 130.0 (CH), 127.7 (C), 120.3 (CH), 21.5 (CH₃), 19.2 (CH₃).

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₃H₁₄NS 216.0841; Found 216.0852.

1-(*p*-Tolylthio)isoquinoline **1c**



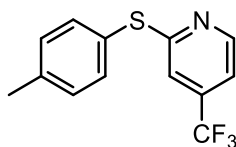
Prepared from General procedure B with 4-methylbenzenethiol (1.52 g, 12.2 mmol), 1-chloroisoquinoline (2.0 g, 12 mmol), K₂CO₃ (1.86 g, 13.4 mmol) and DMF (12 mL). The reaction was extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL) and dried over Na₂SO₄. The solvent was evaporated and purification by FCC (10% Et₂O in pentane) gave pyridylsulfide **1c** as a yellow oil (3.02 g, 98%).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.23 (d, *J* = 5.7 Hz, 1H), 7.77 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.68 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.60 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.36 (dd, *J* = 5.7, 0.9 Hz, 1H), 7.27 – 7.21 (m, 2H), 2.39 (s, 3H, CH₃).

¹³C NMR (126 MHz, Chloroform-*d*) δ 160.0, 142.6, 138.9, 136.0, 135.2, 130.5, 130.18, 127.4, 127.3, 127.1, 126.9, 125.1, 118.3, 21.5 (CH₃).

Spectra are consistent with literature data.⁵

2-(*p*-Tolylthio)-4-(trifluoromethyl)pyridine **1d**



Prepared from General procedure B with 4-methylbenzenethiol (1.10 g, 8.85 mmol), 2-bromo-4-(trifluoromethyl)pyridine (1.10 mL, 8.85 mmol), K₂CO₃ (1.34 g, 9.73 mmol) and DMF (3 mL). The reaction was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over Na₂SO₄. The solvent was evaporated and purification by FCC (10% Et₂O in pentane) gave pyridylsulfide **1d** as a yellow oil (2.30 g, 97%).

TLC: *R*_f = 0.45 (10% Et₂O in pentane).

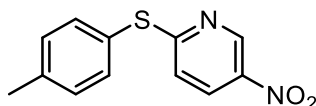
¹H NMR (500 MHz, Chloroform-*d*) δ 8.56 (dt, *J* = 5.1, 0.7 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.16 (ddd, *J* = 5.1, 1.5, 0.7 Hz, 1H), 7.03 (dt, *J* = 1.6, 0.8 Hz, 1H), 2.42 (s, 3H, CH₃).

¹³C NMR (126 MHz, Chloroform-*d*) δ 164.5 (C), 150.6 (CH), 140.4 (C), 139.1 (q, *J* = 34.0 Hz, CCF₃), 135.5 (CH), 130.9 (CH), 125.8 (C), 122.7 (q, *J* = 273.3 Hz, CF₃), 116.2 (q, *J* = 3.8 Hz, CH), 115.1 (q, *J* = 3.5 Hz, CH), 21.5 (CH₃).

¹⁹F NMR (470 MHz, Chloroform-*d*) δ -65.11.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₃H₁₁F₃NS 270.0559; Found 270.0560.

5-Nitro-2-(*p*-tolylthio)pyridine **1e**



Prepared from General procedure A with 4-methylbenzenethiol (1.0 g, 8.05 mmol), 2-bromo-5-nitropyridine (1.63 g, 8.05 mmol) and H₂O (15 mL). The reaction was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over Na₂SO₄. The solvent was evaporated to give pyridylsulfide **1e** as a colourless oil without further purification (1.98 g, quantitative yield).

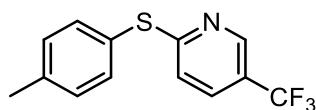
¹H NMR (500 MHz, Chloroform-*d*) δ 9.21 (dd, *J* = 2.7, 0.7 Hz, 1H), 8.17 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.36 – 7.29 (m, 2H), 6.91 (dd, *J* = 9.0, 0.7 Hz, 1H), 2.44 (s, 3H, CH₃).

¹³C NMR (126 MHz, Chloroform-*d*) δ 171.1, 145.2, 141.14, 141.08, 135.7, 131.3, 131.2, 125.0, 119.8, 21.6 (CH₃).

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₂H₁₁N₂O₂S 247.0536; Found 247.0538.

Spectra are consistent with literature data.⁶

2-(*p*-Tolylthio)-5-(trifluoromethyl)pyridine **1f**



Prepared from General procedure B with 4-methylbenzenethiol (1.0 g, 8.0 mmol), 2-bromo-5-(trifluoromethyl)pyridine (1.32 g, 8.0 mmol), K₂CO₃ (1.22 g, 8.8 mmol) and DMF (10 mL). The reaction was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL) and dried over Na₂SO₄. The solvent was evaporated to give pyridylsulfide **1f** as a white solid which was used without further purification (2.12 g, 98%).

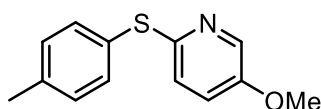
¹H NMR (500 MHz, Chloroform-*d*) δ 8.64 (dt, *J* = 2.6, 0.9 Hz, 1H), 7.66 – 7.55 (m, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.27 (m, 2H), 6.89 (dt, *J* = 8.5, 0.8 Hz, 1H), 2.42 (s, 3H, CH₃).

¹³C NMR (126 MHz, Chloroform-*d*) δ 167.6 (C), 146.5 (q, *J* = 4.3 Hz, CH), 140.50 (C), 135.7 (CH), 133.5 (q, *J* = 3.5 Hz, CH), 130.9 (CH), 125.8 (C), 123.8 (q, *J* = 271.8 Hz, CF₃), 122.5 (q, *J* = 33.4 Hz, CCF₃), 120.0 (CH), 21.5 (CH₃).

¹⁹F NMR (470 MHz, Chloroform-*d*) δ -62.21.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₃H₁₁F₃NS 270.0559; Found 270.0558.

5-Methoxy-2-(*p*-tolylthio)pyridine **1g**



Prepared from General procedure A with slight modifications, with 4-methylbenzenethiol (1.19 g, 9.60 mmol), 2-bromo-5-methoxypyridine (1.50 g, 7.98 mmol) and H₂O (8 mL). The reaction was heated under reflux for 48 h (the flask sitting in an aluminium block placed on a stirrer hotplate). The reaction was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL) and dried over Na₂SO₄. The solvent was evaporated and purification by FCC (10% Et₂O in pentane) gave pyridylsulfide **1g** a white solid (0.95 g, 51%).

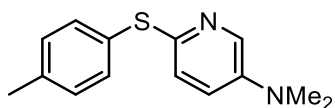
TLC: *R*_f = 0.10 (10% Et₂O in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 3.0 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.04 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 3.80 (s, 3H, OMe), 2.36 (s, 3H, Me).

¹³C NMR (126 MHz, Chloroform-*d*) δ 153.8 (COMe), 151.6 (C), 138.7 (C), 136.9 (CH), 134.0 (CH), 130.3 (CH), 129.4 (C), 123.4 (CH), 122.6 (CH), 55.8 (OMe), 21.3 (CH₃).

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{14}NOS$ 232.0791; Found 232.0807.

***N,N*-Dimethyl-6-(*p*-tolylthio)pyridin-3-amine 1h**



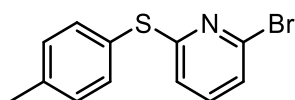
Prepared from General procedure B with 4-methylbenzenethiol (500 mg, 4.0 mmol), 6-bromo-*N,N*-dimethylpyridin-3-amine (804 mg, 4.0 mmol), K_2CO_3 (611 mg, 4.4 mmol) and DMF (5 mL). The reaction was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over Na_2SO_4 . The solvent was evaporated to give pyridylsulfide **1h** as a white solid which was used without further purification (814 mg, 83%).

1H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dd, J = 3.2, 0.6 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.15 – 7.09 (m, 2H), 7.04 (dd, J = 8.8, 0.7 Hz, 1H), 6.87 (dd, J = 8.7, 3.2 Hz, 1H), 2.94 (s, 6H, NMe_2), 2.32 (s, 3H, CH_3).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.8 (C), 144.7 (C), 137.5 (C), 135.2 (CH), 132.3 (CH), 131.6 (C), 130.0 (CH), 125.4 (CH), 120.3 (CH), 40.3 (NMe_2), 21.2 (CH_3).

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{14}H_{17}N_2S$ 245.1107; Found 245.1095.

2-Bromo-6-(*p*-tolylthio)pyridine 1i



Prepared from General procedure B with slight modifications, with 4-methylbenzenethiol (1.49 g, 12.0 mmol), 2,6-dibromopyridine (1.90 g, 8.02 mmol), K_2CO_3 (2.5 g, 18 mmol) and DMF (10 mL). The reaction was heated to 140 °C for 3 d (the flask sitting in an aluminium block placed on a stirrer hotplate). The reaction was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with water (3 x 30 mL) and brine (3 x 30 mL) and dried over Na_2SO_4 . The solvent was evaporated and purification by FCC (5% Et_2O in pentane) gave pyridylsulfide **1i** as a white solid (0.86 g, 38%).

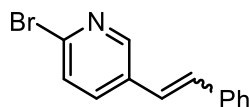
TLC: R_f = 0.42 (5% Et_2O in pentane).

1H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.2 Hz, 2H), 7.27 – 7.21 (m, 3H), 7.13 (d, J = 7.8 Hz, 1H), 6.67 (d, J = 8.2 Hz, 1H), 2.40 (s, 3H, CH_3).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.2 (C), 141.4 (C), 140.2 (C), 138.6 (CH), 135.6 (CH), 130.8 (CH), 126.4 (C), 123.5 (CH), 119.2 (CH), 21.5 (CH_3).

HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd for $C_{12}H_{10}BrNNaS$ 301.9610, 303.9589; Found 301.9609, 303.9614.

(E)- and (Z)-2-Bromo-5-styrylpyridine S1



6-Bromonicotinaldehyde (200 mg, 1.08 mmol) and benzyltriphenylphosphonium bromide (466 mg, 1.08 mmol) were added to a crimp-top vial and sealed. The vial was evacuated and purged with N_2 three times. The reagents were dissolved in dry THF (4 mL) and cooled to 0 °C. t BuOK (1.08 mL, 1.0 M in THF) was added dropwise to the vial over 2 min. The reaction was stirred at 0 °C for 1 h. Sat. aq. $NaHCO_3$ (5 mL) was added to quench the reaction. The product was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with H_2O (30 mL) and brine (30 mL). The solvent was evaporated and purification by FCC (5% Et_2O in pentane) gave the *Z* isomer of the bromopyridine as an opaque oil (129 mg, 46%) and the *E* isomer of the bromopyridine as a white solid (102 mg, 36%).

Z isomer:

TLC: R_f = 0.55 (25% Et_2O in pentane).

1H NMR (400 MHz, Chloroform- d) δ 8.23 – 8.18 (m, 1H), 7.35 (ddd, J = 8.3, 2.5, 0.6 Hz, 1H), 7.32 – 7.22 (m, 4H), 7.20 – 7.17 (m, 2H), 6.79 (d, J = 12.2 Hz, 1H, CH=CH), 6.45 (d, J = 12.1 Hz, 1H, CH=CH).

^{13}C NMR (101 MHz, Chloroform- d) δ 150.5 (CH), 140.3 (C), 138.4 (CH), 136.2 (C), 133.6 (CH), 132.3 (C), 128.8 (CH), 128.7 (CH), 128.0 (CH), 127.6 (CH), 125.1 (CH).

E isomer:

TLC: R_f = 0.35 (25% Et_2O in pentane).

1H NMR (400 MHz, Chloroform- d) δ 8.44 (d, J = 2.5 Hz, 1H), 7.68 (dd, J = 8.3, 2.5 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.45 (d, J = 8.3 Hz, 1H), 7.42 – 7.34 (m, 2H), 7.35 – 7.28 (m, 1H), 7.14 (d, J = 16.4 Hz, 1H, CH=CH), 6.99 (d, J = 16.4 Hz, 1H, CH=CH).

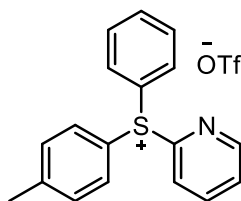
^{13}C NMR (101 MHz, Chloroform- d) δ 148.7 (CH), 140.6 (C), 136.4 (C), 135.1 (CH), 132.5 (C), 131.8 (CH), 129.0 (CH), 128.6 (CH), 128.1 (CH), 126.9 (CH), 123.5 (CH).

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{11}BrN$ 260.0069, 262.0049; Found 260.0068, 262.0039.

5. Synthesis of sulfonium salts

General procedure C: Sulfide (1.1 equiv.), Ph₂IOTf (1.0 equiv.) and Cu(OTf)₂ (5 mol%) were added to a crimp-top vial and sealed. The vial was evacuated and purged with N₂ three times. Dry DCE (0.6 M) was added to the vial and the reaction was heated to 95 °C for 16 h (the flask sitting in an aluminium block placed on a stirrer hotplate). Then the reaction was allowed to cool and sat. aq. NH₄Cl (20 mL) was added. The product was extracted using CH₂Cl₂ (3 x 20 mL) and washed with H₂O (2 x 20 mL) and brine (20 mL). The solvent was evaporated and product was isolated by FCC.

Phenyl(pyridin-2-yl)(*p*-tolyl)sulfonium trifluoromethanesulfonate **2a**



Product **2a** was synthesized via General procedure C with sulfide **1a** (2.21 g, 11.0 mmol), Ph₂IOTf (4.30 g, 10.0 mmol) and Cu(OTf)₂ (0.18 g, 0.50 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2a** as a light brown solid (2.94 g, 69%).

TLC: *R*_f = 0.47 (5% MeOH in CH₂Cl₂).

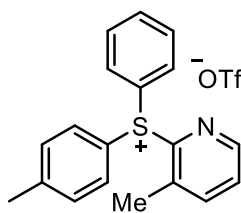
¹H NMR (400 MHz, Chloroform-*d*) δ 8.74 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 8.07 (td, *J* = 7.7, 1.8 Hz, 1H), 7.85 – 7.80 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.66 – 7.60 (m, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 2.42 (s, 3H, CH₃).

¹³C NMR (101 MHz, Chloroform-*d*) δ 152.5 (CH), 147.0 (C), 146.6 (C), 140.7 (CH), 134.6 (CH), 132.1 (CH), 131.9 (CH), 131.5 (CH), 131.3 (CH), 129.2 (CH), 128.7 (CH), 124.9 (C), 120.9 (q, *J* = 320.9 Hz, OTf), 120.6 (C), 21.7 (CH₃).

¹⁹F NMR (282 MHz, Chloroform-*d*) δ -78.2.

HRMS (ESI-TOF) *m/z*: [M-OTf]⁺ Calcd for C₁₈H₁₆NS 278.0998; Found 278.1003.

(3-Methylpyridin-2-yl)(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate **2b**



Product **2b** was synthesized via General procedure C with sulfide **1b** (1.00 g, 4.65 mmol), Ph₂IOTf (1.82 g, 4.22 mmol) and Cu(OTf)₂ (76.3 mg, 0.21 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2b** as a brown solid (632 mg, 34%).

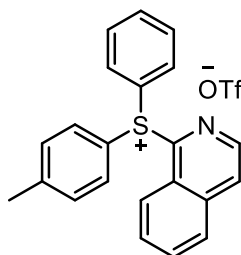
TLC: *R*_f = 0.42 (5% MeOH in CH₂Cl₂).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.55 (ddd, *J* = 4.6, 1.8, 0.7 Hz, 1H), 7.94 – 7.87 (m, 1H), 7.83 – 7.77 (m, 2H), 7.75 – 7.69 (m, 3H), 7.68 – 7.63 (m, 2H), 7.61 – 7.57 (m, 1H), 7.51 – 7.41 (m, 2H), 2.67 (s, 3H), 2.45 (s, 3H, CH₃).

¹³C NMR (101 MHz, Chloroform-*d*) δ 149.7 (CH), 146.4 (C), 145.3 (C), 142.1 (CH), 138.8 (C), 134.5 (CH), 132.3 (CH), 132.1 (CH), 132.0 (CH), 131.3 (CH), 128.5 (CH), 124.2 (C), 121.0 (q, *J* = 320.7 Hz, OTf), 119.8 (C), 21.8 (CH₃), 18.6 (CH₃).

HRMS (ESI-TOF) *m/z*: [M-OTf]⁺ Calcd for C₁₉H₁₈NS 292.1154; Found 292.1154.

Isoquinolin-1-yl(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate **2c**



Product **2c** was synthesized via General procedure C with sulfide **1c** (1.00 g, 4.06 mmol), Ph₂IOTf (1.59 g, 3.69 mmol) and Cu(OTf)₂ (67.0 mg, 0.185 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2c** as a brown oil (1.04 g, 59%).

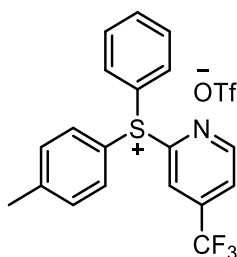
TLC: *R*_f = 0.49 (5% MeOH in CH₂Cl₂).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.83 – 8.68 (m, 1H), 8.63 (d, *J* = 5.4 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.97 – 7.84 (m, 6H), 7.74 – 7.68 (m, 1H), 7.67 – 7.57 (m, 2H), 7.50 – 7.41 (m, 2H), 2.43 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 146.5 (C), 146.0 (C), 143.1 (CH), 138.2 (C), 134.6 (CH), 133.1 (CH), 132.5 (CH), 132.2 (CH), 132.1 (CH), 131.8 (CH), 131.3 (CH), 128.4 (C), 128.1 (CH), 126.6 (CH), 124.3 (C), 124.0 (CH), 120.0 (C), 21.8 (CH₃). Signal for OTf not detected.

HRMS (ESI-TOF) m/z : $[M-OTf]^+$ Calcd for $C_{22}H_{18}NS$ 328.1154; Found 328.1154.

Phenyl(*p*-tolyl)(4-(trifluoromethyl)pyridin-2-yl)sulfonium trifluoromethanesulfonate 2d



Product **2d** was synthesized via General procedure C with sulfide **1d** (500 mg, 1.86 mmol), Ph_2IOTf (726 mg, 1.69 mmol) and $Cu(OTf)_2$ (31 mg, 0.08 mmol). Purification by FCC (5% MeOH in CH_2Cl_2) gave sulfonium salt **2d** as a yellow oil (443 mg, 53%).

TLC: R_f = 0.49 (5% MeOH in CH_2Cl_2).

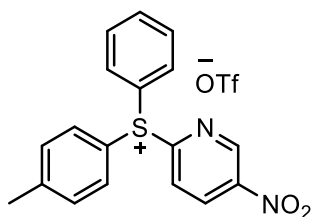
1H NMR (500 MHz, Chloroform-*d*) δ 9.04 – 8.95 (m, 1H), 8.56 (dt, J = 1.5, 0.7 Hz, 1H), 7.94 – 7.88 (m, 3H), 7.88 – 7.82 (m, 2H), 7.77 – 7.69 (m, 1H), 7.69 – 7.60 (m, 2H), 7.51 – 7.45 (m, 2H), 2.45 (s, 3H, CH_3).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.6 (CH), 149.0 (C), 147.0 (C), 142.3 (q, J = 36.1 Hz, CCF_3), 134.9 (CH), 132.3 (CH), 132.3 (CH), 131.9 (CH), 131.5 (CH), 125.4 (q, J = 3.5 Hz, CH), 124.6 (q, J = 3.3 Hz, CH), 121.5 (q, J = 274.6 Hz, CF_3), 120.9 (q, J = 320.5 Hz, OTf), 120.2 (C), 119.7 (C), 21.8 (CH_3).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -64.5, -78.3.

HRMS (ESI-TOF) m/z : $[M-OTf]^+$ Calcd for $C_{19}H_{15}F_3NS$ 346.0872; Found 346.0873.

(5-Nitropyridin-2-yl)(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate 2e



Product **2e** was synthesized via General procedure C with sulfide **1e** (1.00 g, 4.06 mmol), Ph_2IOTf (1.59 g, 3.69 mmol) and $Cu(OTf)_2$ (67.0 mg, 0.185 mmol). Purification by FCC (5% MeOH in CH_2Cl_2) gave sulfonium salt **2e** as a brown oil (1.04 g, 60%).

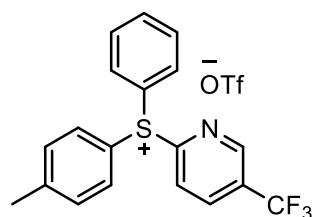
TLC: R_f = 0.35 (5% MeOH in CH_2Cl_2).

^1H NMR (500 MHz, Chloroform-*d*) δ 9.43 (dd, $J = 2.6, 0.6$ Hz, 1H), 8.78 (dd, $J = 8.7, 2.6$ Hz, 1H), 8.47 (dd, $J = 8.6, 0.7$ Hz, 1H), 7.95 – 7.89 (m, 2H), 7.88 – 7.82 (m, 2H), 7.80 – 7.73 (m, 1H), 7.72 – 7.65 (m, 2H), 7.53 – 7.47 (m, 2H), 2.46 (s, 3H, CH₃).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.3, 147.4, 146.9, 146.2, 135.8, 135.2, 132.6, 132.5, 132.2, 131.7, 130.1, 124.2, 119.7, 21.9 (CH₃). Signal for OTf not detected.

HRMS (ESI-TOF) m/z : [M-OTf]⁺ Calcd for C₁₈H₁₅N₂O₂S 323.0849; Found 323.0844.

Phenyl(*p*-tolyl)(5-(trifluoromethyl)pyridin-2-yl)sulfonium trifluoromethanesulfonate **2f**



Product **2f** was synthesized via General procedure C with sulfide **1f** (1.0 g, 3.7 mmol), Ph₂IOTf (1.45 g, 3.37 mmol) and Cu(OTf)₂ (61.0 mg, 0.168 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2f** as a brown oil (1.21 g, 72%).

TLC: $R_f = 0.35$ (5% MeOH in CH₂Cl₂).

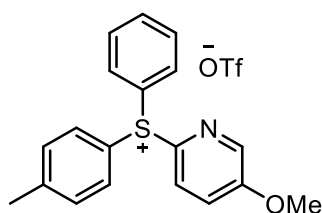
^1H NMR (400 MHz, Chloroform-*d*) δ 8.96 (dd, $J = 2.4, 1.0$ Hz, 1H), 8.63 (d, $J = 8.3$ Hz, 1H), 8.32 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.94 – 7.88 (m, 2H), 7.87 – 7.82 (m, 2H), 7.79 – 7.73 (m, 1H), 7.71 – 7.65 (m, 2H), 7.52 – 7.44 (m, 2H), 2.47 (s, 3H, CH₃).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.1, 148.8 (q, $J = 3.9$ Hz), 147.1, 138.2 (q, $J = 3.5$ Hz), 135.0, 132.4, 132.3, 131.9, 131.6, 130.94 (q, $J = 34.2$ Hz, CCF₃), 129.9, 124.3, 122.2 (q, $J = 273.8$ Hz, CF₃), 120.9 (q, $J = 320.5$ Hz, OTf), 119.9, 21.9 (CH₃).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.8, -78.3.

HRMS (ESI-TOF) m/z : [M-OTf]⁺ Calcd for C₁₉H₁₅F₃NS 346.0872; Found 346.0873.

(5-Methoxypyridin-2-yl)(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate **2g**



Product **2g** was synthesized via General procedure C with sulfide **1g** (0.80 g, 3.5 mmol), Ph₂IOTf (1.49 g, 3.46 mmol) and Cu(OTf)₂ (63 mg, 0.17 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2g** as a brown oil (1.30 g, 82%).

TLC: *R*_f = 0.21 (5% MeOH in CH₂Cl₂).

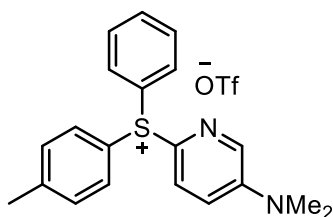
¹H NMR (500 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 3.2 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 7.77 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.65 – 7.58 (m, 2H), 7.54 (dd, *J* = 8.8, 3.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 3H, OMe), 2.42 (s, 3H, Me).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.6 (C), 146.2 (C), 142.5 (CH), 135.3 (C), 134.3 (CH), 132.0 (CH), 131.5 (CH), 131.4 (CH), 131.2 (CH), 131.0 (CH), 125.9 (C), 122.4 (CH), 121.6 (C), 120.9 (q, *J* = 320.7 Hz, OTf), 56.7 (app. d, *J* = 3.9 Hz, OMe), 21.7 (CH₃).

¹⁹F NMR (282 MHz, Chloroform-*d*) δ -78.2.

HRMS (ESI-TOF) *m/z*: [M-OTf]⁺ Calcd for C₁₉H₁₈NOS 308.1104; Found 308.1094.

(5-(Dimethylamino)pyridin-2-yl)(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate **2h**



Product **2h** was synthesized via General procedure C with sulfide **1h** (700 mg, 2.86 mmol), Ph₂IOTf (1.12 g, 2.60 mmol) and Cu(OTf)₂ (47.1 mg, 0.13 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2h** as a yellow oil (1.22 g, quantitative yield).

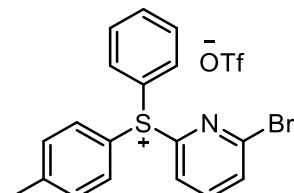
TLC: *R*_f = 0.58 (5% MeOH in CH₂Cl₂).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 3.2 Hz, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.73 – 7.70 (m, 2H), 7.69 – 7.64 (m, 1H), 7.63 – 7.58 (m, 2H), 7.45 – 7.39 (m, 2H), 7.12 (dd, *J* = 9.0, 3.2 Hz, 1H), 3.11 (s, 6H, NMe₂), 2.43 (s, 3H, CH₃).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.3 (C), 148.7 (C), 145.6 (C), 137.2 (CH), 133.9 (CH), 131.8 (CH), 131.2 (CH), 131.0 (CH), 130.8 (CH), 127.3 (C), 123.1 (C), 121.09 (q, $J = 321.0$ Hz, OTf), 119.0 (CH), 40.0 (NMe₂), 21.8 (CH₃).

HRMS (ESI-TOF) m/z : [M-OTf]⁺ Calcd for C₂₀H₂₁N₂S 321.1420; Found 321.1422.

(6-Bromopyridin-2-yl)(phenyl)(*p*-tolyl)sulfonium trifluoromethanesulfonate 2i



Product **2i** was synthesized via General procedure C with sulfide **1i** (0.77 g, 2.7 mmol), Ph₂IOTf (1.13 g, 2.61 mmol) and Cu(OTf)₂ (47 mg, 0.13 mmol). Purification by FCC (5% MeOH in CH₂Cl₂) gave sulfonium salt **2i** as a brown oil (1.05 g, 79%).

TLC: $R_f = 0.27$ (5% MeOH in CH₂Cl₂).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, $J = 7.7$ Hz, 1H), 7.98 (t, $J = 7.8$ Hz, 1H), 7.84 (dd, $J = 7.2, 1.7$ Hz, 2H), 7.82 – 7.76 (m, 3H), 7.76 – 7.71 (m, 1H), 7.69 – 7.62 (m, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 2.44 (s, 3H, CH₃).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.9 (C), 146.5 (C), 144.0 (C), 142.6 (CH), 134.9 (CH), 133.5 (CH), 132.3 (CH), 131.9 (CH), 131.5 (CH), 128.4 (CH), 124.5 (C), 120.9 (q, $J = 320.7$ Hz, OTf), 120.1 (C), 21.8 (CH₃).

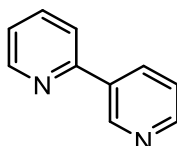
^{19}F NMR (282 MHz, Chloroform-*d*) δ -78.2.

HRMS (ESI-TOF) m/z : [M-OTf]⁺ Calcd for C₁₈H₁₅BrNS 356.0103, 358.0083; Found 356.0119, 358.0123.

6. Synthesis of bipyridines

General procedure D: Halopyridine (0.45 mmol, 1.5 equiv.) was added to an oven-dried crimp-top vial and sealed. The vial was evacuated and purged with N₂ three times. The halopyridine was dissolved in dry THF (1.5 mL) and cooled to -78 °C. *n*-BuLi (0.19 mL, 0.45 mmol, 1.5 equiv., 2.4 M in hexanes) was added dropwise to the stirring solution over 2 min. The reaction was allowed to stir for 30 min at -78 °C. Sulfonium salt (0.3 mmol, 1.0 equiv.) was added to a separate oven-dried crimp-top vial and dissolved in dry THF (1.5 mL). The solution of sulfonium salt was added dropwise down the side of the vial to the lithiated pyridine solution over 2 min. The reaction was allowed to stir for 2 h at -78 °C. Sat. aq. NH₄Cl (3 mL) was added slowly to quench any excess organolithium. The product was extracted with EtOAc (3 x 10 mL), the combined organic layers were washed with H₂O (20 mL) and brine (20 mL). The solvent was evaporated and the product was isolated by FCC.

2,3-Bipyridine 3



Product **3** was synthesized via General procedure D using 3-iodopyridine (92.3 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (80% Et₂O in pentane) gave bipyridine **3** as a colourless oil (42.1 mg, 90%).

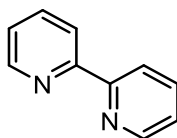
TLC: *R*_f = 0.13 (80% Et₂O in pentane).

¹H NMR (400 MHz, Chloroform-*d*) δ 9.20 (d, *J* = 2.3 Hz, 1H), 8.76 – 8.70 (m, 1H), 8.66 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.33 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.85 – 7.72 (m, 2H), 7.41 (dd, *J* = 7.9, 4.9 Hz, 1H), 7.33 – 7.26 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 154.9, 150.2, 150.0, 148.3, 137.1, 135.0, 134.5, 123.7, 123.0, 120.7.

Spectra were consistent with literature data.⁷

2,2'-Bipyridine 4



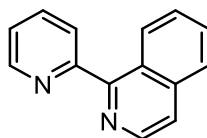
Product **4** was synthesized via General procedure D using 2-bromopyridine (42.9 μL, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (80% Et₂O in pentane) gave bipyridine **4** as a white solid (28.1 mg, 60%).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.61 (m, 2H), 8.40 (d, J = 8.0 Hz, 2H), 7.82 (td, J = 7.7, 1.8 Hz, 2H), 7.31 (ddd, J = 7.6, 4.8, 1.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.3, 149.4, 137.1, 123.9, 121.2.

Spectra are consistent with literature data.⁸

1-(Pyridin-2-yl)isoquinoline **5**



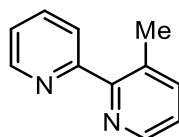
Product **5** was synthesized via General procedure D using 1-iodoisoquinoline (114.8 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (80% Et₂O in pentane) gave bipyridine **5** as a yellow oil (39.9 mg, 64%).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.80 (d, J = 1.6 Hz, 1H), 8.68 – 8.55 (m, 2H), 8.00 (dt, J = 7.9, 1.1 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.75 – 7.66 (m, 2H), 7.60 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.41 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 157.8, 148.8, 142.1, 137.3, 137.1, 130.2, 127.9, 127.8, 127.0, 126.8, 125.4, 123.4, 121.4.

Spectra are consistent with literature data.⁹

3-Methyl-2,2'-bipyridine **6**



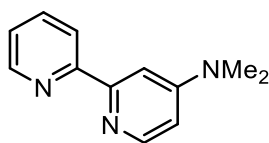
Product **6** was synthesized via General procedure D using 2-bromo-3-methylpyridine (50 μL , 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (70% Et₂O in pentane) gave bipyridine **6** as a yellow oil (41.2 mg, 81%).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.68 (dt, J = 4.9, 1.4 Hz, 1H), 8.53 (dd, J = 4.6, 1.6 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.61 (ddd, J = 7.7, 1.7, 0.8 Hz, 1H), 7.29 (ddd, J = 6.7, 4.8, 1.7 Hz, 1H), 7.22 (dd, J = 7.7, 4.7 Hz, 1H), 2.51 (s, 3H, CH₃).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.1, 156.5, 148.6, 146.9, 139.3, 136.7, 132.4, 124.3, 123.2, 122.8, 20.1 (CH₃).

Spectra are consistent with literature data.¹⁰

***N,N*-Dimethyl-[2,2'-bipyridin]-4-amine 7**



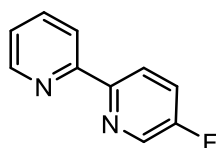
Product **7** was synthesized via General procedure D using 2-bromo-*N,N*-dimethylpyridin-4-amine (90.5 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (2% Et₃N in Et₂O) gave bipyridine **7** as a yellow oil (30.6 mg, 51%).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.66 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.38 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.32 (dd, *J* = 5.9, 0.5 Hz, 1H), 7.79 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H), 7.70 (d, *J* = 2.7 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.54 (dd, *J* = 5.9, 2.7 Hz, 1H), 3.10 (s, 6H, NMe₂).

¹³C NMR (126 MHz, Chloroform-*d*) δ 157.1, 156.3, 155.4, 149.5, 149.0, 136.9, 123.5, 121.4, 106.8, 104.0, 39.5 (NMe₂).

Spectra are consistent with literature data.¹¹

5-Fluoro-2,2'-bipyridine 8



Product **8** was synthesized via General procedure D using 2-bromo-5-fluoropyridine (79.2 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (80% Et₂O in pentane) gave bipyridine **8** as an orange oil (12.4 mg, 24%).

TLC: *R*_f = 0.38 (80% Et₂O in pentane).

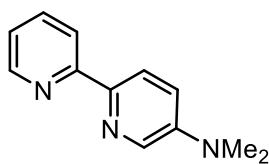
¹H NMR (500 MHz, Chloroform-*d*) δ 8.77 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 8.61 – 8.56 (m, 1H), 8.53 (d, *J* = 5.0 Hz, 1H), 8.00 (dd, *J* = 6.8, 5.0 Hz, 1H), 7.91 (ddt, *J* = 7.9, 1.9, 1.1 Hz, 1H), 7.82 (td, *J* = 7.8, 1.9 Hz, 1H), 7.36 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 157.2 (d, *J* = 256.8 Hz, CF), 150.7 (d, *J* = 2.4 Hz, C), 150.3 (CH), 146.3 (d, *J* = 5.2 Hz, CH), 139.4 (d, *J* = 26.3 Hz, CH), 136.9 (CH), 134.1 (d, *J* = 9.0 Hz, C), 125.2 (d, *J* = 10.0 Hz, CH), 124.2 (CH), 124.1 (CH).

¹⁹F NMR (282 MHz, Chloroform-*d*) δ -131.7 (d, *J* = 5.3 Hz).

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₀H₈FN₂ 175.0666; Found 175.0667.

N,N-Dimethyl-[2,2'-bipyridin]-5-amine **9**



Product **9** was synthesized via General procedure D using 6-bromo-*N,N*-dimethylpyridin-3-amine (90.5 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (40% Et₂O in pentane) gave bipyridine **9** as an off-white oil (18.5 mg, 31%).

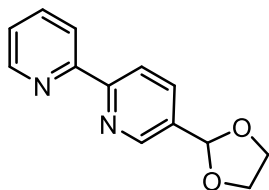
TLC: R_f = 0.10 (40% Et₂O in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.60 (ddd, J = 4.8, 1.9, 0.9 Hz, 1H), 8.25 (ddd, J = 9.8, 8.5, 0.8 Hz, 2H), 8.19 (d, J = 3.0 Hz, 1H), 7.74 (td, J = 7.7, 1.8 Hz, 1H), 7.18 (ddd, J = 7.4, 4.8, 1.2 Hz, 1H), 7.08 (dd, J = 8.9, 3.1 Hz, 1H), 3.05 (s, 6H, NMe₂).

¹³C NMR (126 MHz, Chloroform-*d*) δ 156.9 (C), 149.1 (CH), 146.3 (C), 144.6 (C), 136.8 (CH), 134.0 (CH), 122.2 (CH), 121.4 (CH), 119.8 (CH), 119.1 (CH), 40.2 (NMe₂).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₂H₁₄N₃ 200.1182; Found 200.1183.

5-(1,3-Dioxolan-2-yl)-2,2'-bipyridine **10**



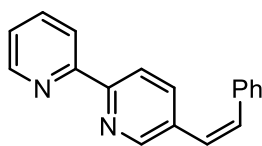
Product **10** was synthesized via General procedure D using 2-bromo-5-(1,3-dioxolan-2-yl)pyridine (103 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (40% Et₂O in pentane with 1% Et₃N) gave bipyridine **10** as an off-white solid (54.7 mg, 80%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, J = 2.2 Hz, 1H), 8.72 – 8.61 (m, 1H), 8.43 – 8.34 (m, 2H), 7.92 (dd, J = 8.2, 2.2 Hz, 1H), 7.81 (td, J = 7.7, 1.8 Hz, 1H), 7.31 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 5.93 (s, 1H), 4.16 – 4.12 (m, 2H), 4.09 – 4.04 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.1, 156.0, 149.4, 147.9, 137.1, 135.3, 133.7, 124.0, 121.4, 120.8, 102.1, 65.5.

Spectra are consistent with literature data.¹²

(Z)-5-Styryl-2,2'-bipyridine **11**



Product **11** was synthesized via General procedure D using (Z)-2-bromo-5-styrylpyridine (117.0 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (30% Et₂O in pentane) gave bipyridine **11** as a yellow oil (39.1 mg, 50%).

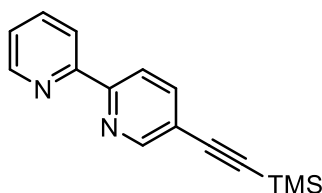
TLC: R_f = 0.14 (30% Et₂O in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.66 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.55 (d, J = 2.2 Hz, 1H), 8.35 (dt, J = 8.0, 1.1 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.66 (dd, J = 8.3, 2.2 Hz, 1H), 7.34 – 7.20 (m, 6H), 6.78 (d, J = 12.2 Hz, 1H, CH=CH), 6.60 (d, J = 12.2 Hz, 1H, CH=CH).

¹³C NMR (126 MHz, Chloroform-*d*) δ 156.1 (C), 154.6 (C), 149.8 (CH), 149.3 (CH), 137.0 (CH), 136.9 (C), 136.7 (C), 133.2 (HC=CH), 133.0 (CH), 128.9 (CH), 128.7 (CH), 127.8 (CH), 126.5 (HC=CH), 123.7 (CH), 121.2 (CH), 120.5 (CH).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₈H₁₅N₂ 259.1230; Found 259.1231.

5-((Trimethylsilyl)ethynyl)-2,2'-bipyridine **12**



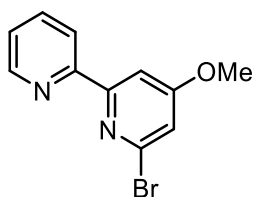
Product **12** was synthesized via General procedure D using 2-bromo-5-((trimethylsilyl)ethynyl)pyridine (114.4 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (30% Et₂O in pentane) gave bipyridine **12** as a yellow oil (38.8 mg, 51%).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.75 – 8.71 (m, 1H), 8.67 (d, J = 4.7 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 8.2 Hz, 1H), 7.86 (dd, J = 8.2, 2.1 Hz, 1H), 7.81 (td, J = 7.8, 1.8 Hz, 1H), 7.30 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 0.28 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.6, 155.1, 152.2, 149.4, 139.9, 137.1, 124.1, 121.6, 120.3, 102.0 (C \equiv C), 99.3 (C \equiv C), -0.01 (SiMe₃).

Spectra are consistent with literature data.³

6-Bromo-4-methoxy-2,2'-bipyridine **13**



Product **13** was synthesized via General procedure D at -40 °C using 2,6-dibromo-4-methoxypyridine (39.8 mg, 0.15 mmol) and sulfonium salt **2a** (42.7 mg, 0.1 mmol). Purification by FCC (50% Et₂O in pentane) gave bipyridine **13** as a white solid (5.8 mg, 22%).

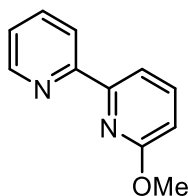
TLC: R_f = 0.50 (50% Et₂O in pentane).

¹H NMR (300 MHz, Chloroform-*d*) δ 8.65 (d, J = 4.4 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 1.9 Hz, 1H), 7.81 (m, 1H), 7.32 (dd, J = 7.4, 4.8 Hz, 1H), 7.03 (d, J = 2.3 Hz, 1H), 3.95 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 167.9, 158.4, 154.6, 149.2, 142.4, 137.1, 124.5, 121.8, 114.2, 106.2, 56.0.

Spectra were consistent with literature data.¹³

6-Methoxy-2,2'-bipyridine **14**



Product **14** was synthesized via General procedure D using 2-bromo-6-methoxypyridine (84.6 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (5% Et₂O in CH₂Cl₂) gave bipyridine **14** a colourless oil (30.3 mg, 54%).

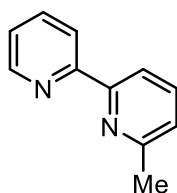
TLC: R_f = 0.12 (5% Et₂O in CH₂Cl₂).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.67 – 8.64 (m, 1H), 8.41 (dt, J = 7.9, 1.2 Hz, 1H), 8.01 (dd, J = 7.4, 0.6 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.70 (dd, J = 8.1, 7.5 Hz, 1H), 7.28 (ddd, J = 7.6, 4.9, 1.3 Hz, 1H), 6.78 (dd, J = 8.2, 0.6 Hz, 1H), 4.04 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 163.7, 156.2, 153.6, 149.2, 139.5, 136.9, 123.6, 121.1, 113.8, 111.2, 53.3.

Spectra were consistent with literature data.¹⁴

6-Methyl-2,2'-bipyridine **15**



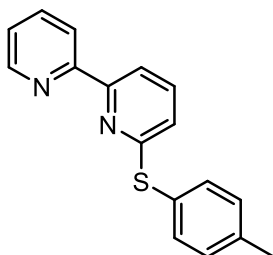
Product **15** was synthesized via General procedure D using 2-bromo-6-methylpyridine (77.4 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (40% Et₂O in pentane) gave bipyridine **15** as a yellow oil (35.7 mg, 70%).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.67 (ddd, $J = 4.8, 1.9, 0.9$ Hz, 1H), 8.40 (dt, $J = 8.0, 1.1$ Hz, 1H), 8.22 – 8.11 (m, 1H), 7.79 (td, $J = 7.7, 1.8$ Hz, 1H), 7.69 (t, $J = 7.7$ Hz, 1H), 7.28 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H), 7.18 – 7.12 (m, 1H), 2.63 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.1, 156.7, 155.7, 149.3, 137.2, 137.00, 123.6, 123.4, 121.3, 118.2, 24.8.

Spectra are consistent with literature data.¹⁵

6-(*p*-Tolylthio)-2,2'-bipyridine **16**



Product **16** was synthesized via General procedure D using 2-bromo-6-(*p*-tolylthio)pyridine **1i** (126.1 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (30% Et₂O in pentane) gave bipyridine **16** as a white solid (45.0 mg, 54%).

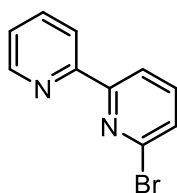
TLC: $R_f = 0.40$ (30% Et₂O in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.66 – 8.64 (m, 1H), 8.35 – 8.31 (m, 1H), 8.11 (d, $J = 7.8$ Hz, 1H), 7.78 (td, $J = 7.7, 1.7$ Hz, 1H), 7.60 – 7.55 (m, 3H), 7.32 – 7.25 (m, 3H), 6.88 (d, $J = 8.0$ Hz, 1H), 2.43 (s, 3H, CH₃).

¹³C NMR (126 MHz, Chloroform-*d*) δ 161.6 (C), 155.9 (C), 155.7 (C), 149.2 (CH), 139.6 (C), 137.6 (CH), 137.0 (CH), 135.6 (CH), 130.5 (CH), 127.4 (C), 123.9 (CH), 121.5 (CH), 120.9 (CH), 117.0 (CH), 21.5 (CH₃).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₇H₁₅N₂S 279.0950; Found 279.0944.

6-Bromo-2,2'-bipyridine **17**



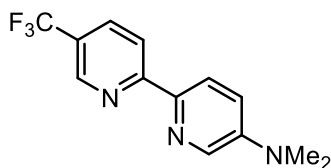
Product **17** was synthesized via General procedure D using 2,6-dibromopyridine (106.6 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (40% Et₂O in pentane) gave bipyridine **17** as a yellow solid (42.3 mg, 60%).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.65 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.46 – 8.30 (m, 2H), 7.80 (td, J = 7.7, 1.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 7.48 (dd, J = 7.8, 0.9 Hz, 1H), 7.31 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 157.5, 154.6, 149.3, 141.7, 139.3, 137.1, 128.1, 124.4, 121.6, 119.8.

Spectra are consistent with literature data.¹⁶

N,N-Dimethyl-5'-(trifluoromethyl)-[2,2'-bipyridin]-5-amine **18**



Product **18** was synthesized via General procedure D using 6-bromo-*N,N*-dimethylpyridin-3-amine (90.5 mg, 0.45 mmol) and sulfonium salt **2f** (148.6 mg, 0.3 mmol). Purification by FCC (25% Et₂O in pentane) gave bipyridine **18** as a yellow oil (32.7 mg, 41%).

TLC: R_f = 0.10 (25% Et₂O in pentane).

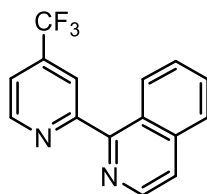
¹H NMR (500 MHz, Chloroform-*d*) δ 8.83 (dd, J = 2.2, 1.1 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 8.19 (d, J = 3.1 Hz, 1H), 7.94 (dd, J = 8.5, 2.4 Hz, 1H), 7.06 (dd, J = 8.9, 3.1 Hz, 1H), 3.07 (s, 6H, NMe₂).

¹³C NMR (126 MHz, Chloroform-*d*) δ 160.0 (C), 146.8 (C), 146.0 (q, J = 4.2 Hz, CH), 142.8 (C), 134.0 (CH), 133.8 (q, J = 3.5 Hz, CH), 124.5 (q, J = 32.8 Hz, CCF₃), 124.2 (q, J = 271.9 Hz, CF₃), 122.2 (CH), 119.2 (CH), 118.6 (CH), 40.0 (NMe₂).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.2.

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₃H₁₃F₃N₃ 268.1056; Found 268.1057.

1-(4-(Trifluoromethyl)pyridin-2-yl)isoquinoline **19**



Product **19** was synthesized via General procedure D using 1-iodoisoquinoline (114.8 mg, 0.45 mmol) and sulfonium salt **2d** (148.6 mg, 0.3 mmol). Purification by FCC (20% Et₂O in pentane) gave bipyridine **19** as a yellow solid (46.4 mg, 56%).

TLC: R_f = 0.17 (20% Et₂O in pentane).

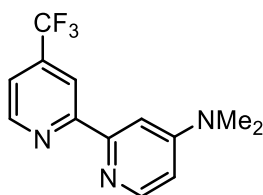
¹H NMR (400 MHz, Chloroform-*d*) δ 8.98 (dt, J = 5.1, 0.8 Hz, 1H), 8.70 (dd, J = 8.6, 1.1 Hz, 1H), 8.66 (d, J = 5.7 Hz, 1H), 8.35 (dt, J = 1.7, 0.8 Hz, 1H), 7.99 – 7.88 (m, 1H), 7.77 (dd, J = 5.6, 1.0 Hz, 1H), 7.73 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.67 – 7.60 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.0 (C), 155.9 (C), 149.6 (CH), 142.1 (CH), 139.2 (q, J = 34.2 Hz, CCF₃), 137.4 (C), 130.4 (CH), 128.2 (CH), 127.5 (CH), 127.3 (CH), 126.7 (C), 123.0 (q, J = 273.2 Hz, CF₃), 122.1 (CH), 121.3 (q, J = 3.8 Hz, CH), 118.8 (q, J = 3.4 Hz, CH).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -64.7.

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₅H₁₀F₃N₂ 275.0791; Found 275.0782.

N,N-Dimethyl-4'-(trifluoromethyl)-[2,2'-bipyridin]-4-amine **20**



Product **20** was synthesized via General procedure D using 2-bromo-*N,N*-dimethylpyridin-4-amine (90.5 mg, 0.45 mmol) and sulfonium salt **2d** (148.6 mg, 0.3 mmol). Purification by FCC (20% Et₂O in pentane) gave bipyridine **20** as a yellow solid (40.0 mg, 50%).

TLC: R_f = 0.15 (25% Et₂O in pentane).

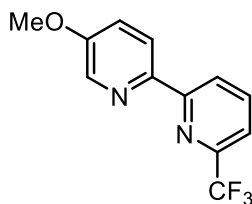
¹H NMR (500 MHz, Chloroform-*d*) δ 8.81 (d, J = 5.0 Hz, 1H), 8.67 (dt, J = 1.8, 0.9 Hz, 1H), 8.33 (d, J = 5.9 Hz, 1H), 7.73 (d, J = 2.7 Hz, 1H), 7.48 (ddd, J = 5.1, 1.8, 0.8 Hz, 1H), 6.57 (dd, J = 5.9, 2.7 Hz, 1H), 3.11 (s, 6H, NMe₂).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.6 (C), 155.4 (C), 154.9 (C), 149.8 (CH), 149.6 (CH), 139.3 (q, $J = 33.9$ Hz, CCF_3), 123.2 (q, $J = 273.3$ Hz, CF_3), 118.9 (d, $J = 3.5$ Hz, CH), 117.2 (d, $J = 3.9$ Hz, CH), 107.4 (CH), 104.2 (CH), 39.5 (NMe_2).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -64.7.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{N}_3$ 268.1056; Found 268.1058.

5-Methoxy-6'-(trifluoromethyl)-2,2'-bipyridine **21**



Product **21** was synthesized via General procedure D using 2-bromo-6-trifluoromethylpyridine (101.7 mg, 0.45 mmol) and sulfonium salt **2g** (137.2 mg, 0.3 mmol). Purification by FCC (100% CH_2Cl_2) gave bipyridine **21** as a white solid (23.4 mg, 31%).

TLC: $R_f = 0.28$ (100% CH_2Cl_2).

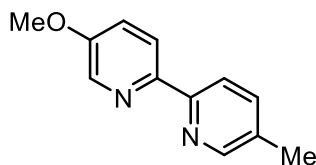
^1H NMR (500 MHz, Chloroform-*d*) δ 8.53 (d, $J = 8.0$ Hz, 1H), 8.47 (d, $J = 8.7$ Hz, 1H), 8.37 (d, $J = 2.9$ Hz, 1H), 7.94 (t, $J = 7.9$ Hz, 1H), 7.62 (d, $J = 7.7$ Hz, 1H), 7.32 (dd, $J = 8.7, 3.0$ Hz, 1H), 3.93 (s, 3H, OMe).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.8 (C), 156.6 (C), 147.7 (q, $J = 34.6$ Hz, CCF_3), 147.6 (C), 138.2 (CH), 137.2 (CH), 122.9 (CH), 122.5 (CH), 121.8 (q, $J = 274.7$ Hz, CF_3), 121.0 (CH), 119.4 (q, $J = 2.7$ Hz, CH), 55.8 (app d, $J = 1.9$ Hz, OMe).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -68.1.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{N}_2\text{O}$ 255.0740; Found 255.0741.

5-Methoxy-5'-methyl-2,2'-bipyridine **22**



Product **22** was synthesized via General procedure D using 2-fluoro-5-methylpyridine (77.4 mg, 0.45 mmol) and sulfonium salt **2g** (137.2 mg, 0.3 mmol). Purification by FCC (5% MeOH in CH_2Cl_2) gave bipyridine **22** as a yellow solid (37.6 mg, 63%).

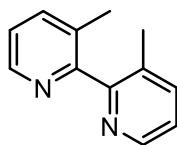
TLC: $R_f = 0.07$ (5% MeOH in CH_2Cl_2).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.46 – 8.44 (m, 1H), 8.34 (d, J = 2.9 Hz, 1H), 8.29 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 8.1 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.29 (dd, J = 8.8, 3.0 Hz, 1H), 3.89 (s, 3H, OMe), 2.36 (s, 3H, CH₃).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 153.7, 149.6, 149.3, 137.5, 136.9, 132.6, 121.5, 121.1, 120.0, 55.8 (OMe), 18.4 (CH₃).

Spectra were consistent with literature data.²⁰

3,3'-Dimethyl-2,2'-bipyridine **23**



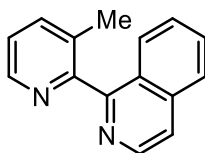
Product **23** was synthesized via General procedure D using 2-bromo-3-methylpyridine (77.4 mg, 0.45 mmol) and sulfonium salt **2b** (132.4 mg, 0.3 mmol). Purification by FCC (40% Et₂O in pentane) gave bipyridine **23** as an orange oil (50.7 mg, 92%).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, J = 4.8 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H), 7.21 (dd, J = 7.8, 4.7 Hz, 2H), 2.14 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.7, 146.7, 138.4, 131.7, 123.0, 18.6.

Spectra are consistent with literature data.²¹

1-(3-Methylpyridin-2-yl)isoquinoline **24**



Product **24** was synthesized via General procedure D using 1-iodoisoquinoline (114.8 mg, 0.45 mmol) and sulfonium salt **2b** (132.4 mg, 0.3 mmol). Purification by FCC (90% Et₂O in pentane) gave bipyridine **24** as a yellow oil (57.1 mg, 86%).

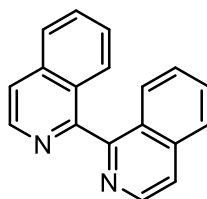
TLC: R_f = 0.20 (90% Et₂O in pentane).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.62 (d, J = 5.7 Hz, 1H), 8.59 (dd, J = 4.9, 1.6 Hz, 1H), 7.94 – 7.83 (m, 1H), 7.68 (app ddd, J = 11.2, 7.7, 5.9 Hz, 4H), 7.49 (ddd, J = 7.5, 6.9, 1.2 Hz, 1H), 7.32 (dd, J = 7.8, 4.8 Hz, 1H), 2.17 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 156.8, 146.7, 142.1, 138.6, 136.8, 132.8, 130.3, 127.5, 127.1, 127.03, 127.00, 123.3, 120.7, 18.9.

Spectra were consistent with literature data.²³

1,1'-Biisoquinoline **25**



Product **25** was synthesized via General procedure D using 1-iodoisoquinoline (114.8 mg, 0.45 mmol) and sulfonium salt **2c** (143.3 mg, 0.3 mmol). Purification by FCC (50% Et₂O in pentane) gave bipyridine **25** as a yellow oil (58.5 mg, 76%).

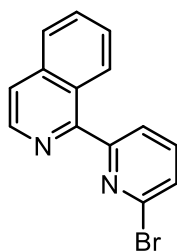
The reaction was scaled up and product **25** was synthesized via General procedure D using 1-iodoisoquinoline (2.96 g, 11.6 mmol) and sulfonium salt **2c** (3.68 g, 7.7 mmol). Purification by FCC (50% Et₂O in pentane) gave bipyridine **25** as a yellow oil (0.91 g, 46%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.73 (br s, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 5.5 Hz, 2H), 7.75 (dd, J = 8.5, 1.2 Hz, 2H), 7.69 (ddd, J = 8.2, 6.9, 1.2 Hz, 2H), 7.47 (ddd, J = 8.3, 6.9, 1.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.2 (br), 142.0, 136.9, 130.4, 128.0, 127.7, 127.3, 127.0, 121.2 (br).

Spectra are consistent with literature data.²⁴

1-(6-Bromopyridin-2-yl)isoquinoline **26**



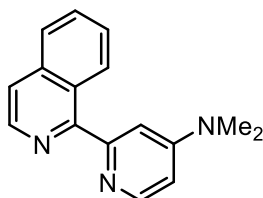
Product **26** was synthesized via General procedure D using 2,6-dibromopyridine (106.6 mg, 0.45 mmol) and sulfonium salt **2c** (143.3 mg, 0.3 mmol). Purification by FCC (40% Et₂O in pentane) gave bipyridine **26** as an off-yellow solid (44.1 mg, 52%).

TLC: R_f = 0.29 (25% Et₂O in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.66 (dd J = 8.6, 1.0 Hz, 1H), 8.61 (d, J = 5.6 Hz, 1H), 8.00 (dd, J = 7.7, 0.9 Hz, 1H), 7.88 (dt, J = 8.3, 1.0 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.64 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.60 (dd, J = 7.9, 0.9 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.3 (C), 155.6 (C), 141.8 (CH), 140.6 (C), 139.2 (CH), 137.2 (C), 130.2 (CH), 128.0 (CH), 127.7 (CH), 127.4 (CH), 127.0 (CH), 126.6 (C), 124.1 (CH), 121.8 (CH).
HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{10}\text{BrN}_2$ 285.0022, 287.0001; Found 285.0023, 287.0003.

2-(Isoquinolin-1-yl)-*N,N*-dimethylpyridin-4-amine **27**



Product **27** was synthesized via General procedure D using 2-bromo-*N,N*-dimethylpyridin-4-amine (90.5 mg, 0.45 mmol) and sulfonium salt **2c** (143.3 mg, 0.3 mmol). Purification by FCC (100% EtOAc) gave bipyridine **27** as a white solid (56.6 mg, 76%).

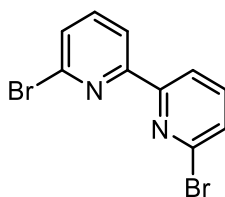
TLC: R_f = 0.20 (100% EtOAc).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.59 (d, J = 5.7 Hz, 1H), 8.54 (dd, J = 8.6, 1.1 Hz, 1H), 8.40 (dd, J = 6.0, 0.5 Hz, 1H), 7.85 (dt, J = 8.2, 1.0 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.56 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.14 (d, J = 2.6 Hz, 1H), 6.61 (dd, J = 6.0, 2.7 Hz, 1H), 3.09 (s, 6H, NMe_2).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.4, 158.6, 155.3, 149.0, 141.9, 137.2, 130.1, 128.3, 127.5, 127.0, 126.8, 121.0, 108.0, 106.3, 39.4 (NMe_2).

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3$ 250.1339; Found 250.1341.

6,6'-Dibromo-2,2'-bipyridine **28**



Product **28** was synthesized via General procedure D using 2,6-dibromopyridine (106.6 mg, 0.45 mmol) and sulfonium salt **2i** (151.9 mg, 0.3 mmol). Purification by FCC (5% Et_2O in pentane), followed by precipitation in Et_2O gave bipyridine **28** as a white solid (12.4 mg, 13%).

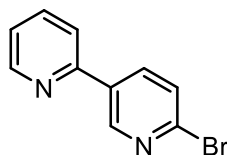
TLC: R_f = 0.59 (5% Et_2O in pentane).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.38 (dd, J = 7.8, 0.7 Hz, 2H), 7.67 (t, J = 7.8 Hz, 2H), 7.51 (dd, J = 7.8, 0.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.8, 141.7, 139.5, 128.7, 120.3.

Spectra were consistent with literature data.²⁵

6'-Bromo-2,3'-bipyridine **29**



Product **29** was synthesized via a modification to General procedure D. 2,5-Dibromopyridine (106.6 mg, 0.45 mmol) was dissolved in dry THF (0.75 mL) and added dropwise to a solution of *n*-BuLi (0.19 mL, 0.45 mmol, 1.5 equiv., 2.4 M in hexanes) in dry THF (0.75 mL) over 2 min. The solution of sulfonium salt **2a** (128.2 mg, 0.3 mmol) in dry THF (1.5 mL) was then added dropwise down the side of the vial to the lithiated pyridine solution over 2 min. Purification by FCC (10% Et₂O in CH₂Cl₂) gave bipyridine **29** as a white solid (45.0 mg, 64%).

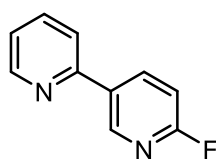
TLC: R_f = 0.11 (20% Et₂O in CH₂Cl₂).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.94 (d, J = 2.5 Hz, 1H), 8.73 – 8.69 (m, 1H), 8.20 (dd, J = 8.3, 2.6 Hz, 1H), 7.80 (td, J = 7.6, 1.8 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.31 (ddd, J = 7.3, 4.9, 0.9 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 153.7 (C), 150.3 (CH), 148.6 (CH), 142.7 (C), 137.3 (CH), 137.0 (CH), 134.3 (C), 128.3 (CH), 123.3 (CH), 120.6 (CH).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₀H₈BrN₂ 234.9865, 236.9845; Found 234.9869, 236.9834.

6'-Fluoro-2,3'-bipyridine **30**



Product **30** was synthesized via General procedure D using 2-fluoro-5-iodopyridine (100.3 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (10% Et₂O in CH₂Cl₂) gave bipyridine **30** as a white solid (36.1 mg, 69%).

TLC: R_f = 0.43 (10% Et₂O in CH₂Cl₂).

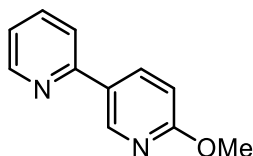
¹H NMR (500 MHz, Chloroform-*d*) δ 8.78 (d, J = 2.5 Hz, 1H), 8.70 (dd, J = 4.7, 1.6 Hz, 1H), 8.44 (td, J = 8.0, 2.5 Hz, 1H), 7.78 (td, J = 7.8, 1.8 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.28 (dd, J = 7.6, 4.7 Hz, 1H), 7.03 (dd, J = 8.5, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.1 (d, J = 240.4 Hz, CF), 153.9 (C), 150.2 (CH), 146.3 (d, J = 15.3 Hz, CH), 140.0 (d, J = 8.5 Hz, CH), 137.2 (CH), 133.3 (d, J = 4.5 Hz, C), 123.0 (CH), 120.4 (CH), 109.7 (d, J = 37.2 Hz, CH).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -68.3 (d, J = 5.7 Hz).

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{FN}_2$ 175.0666; Found 175.0667.

6'-Methoxy-2,3'-bipyridine **31**



Product **31** was synthesized via General procedure D using 5-iodo-2-methoxypyridine (105.8 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (20% EtOAc in pentane) gave bipyridine **31** as a yellow oil (32.5 mg, 58%).

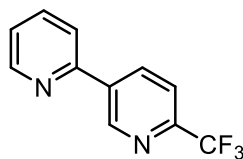
TLC: R_f = 0.25 (20% EtOAc in pentane).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, J = 2.4 Hz, 1H), 8.65 (dt, J = 5.1, 1.5 Hz, 1H), 8.23 (dd, J = 8.6, 2.7 Hz, 1H), 7.72 (td, J = 7.7, 1.8 Hz, 1H), 7.65 (dt, J = 8.2, 1.1 Hz, 1H), 7.20 (ddd, J = 7.3, 4.8, 1.2 Hz, 1H), 6.83 (d, J = 8.6 Hz, 1H), 3.98 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.8, 155.2, 149.9, 145.6, 137.5, 137.0, 128.7, 122.1, 119.9, 111.0, 53.8.

Spectra were consistent with literature data.¹⁷

6'-(Trifluoromethyl)-2,3'-bipyridine **32**



Product **32** was synthesized via General procedure D using 5-bromo-2-(trifluoromethyl)pyridine (101.7 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (20% Et₂O in pentane) gave bipyridine **32** as a yellow oil (35.8 mg, 53%).

TLC: R_f = 0.18 (25% Et₂O in pentane).

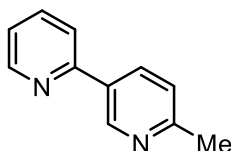
^1H NMR (500 MHz, Chloroform-*d*) δ 9.30 (d, J = 2.1 Hz, 1H), 8.77 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 8.52 (ddd, J = 8.2, 2.2, 0.8 Hz, 1H), 8.08 – 7.72 (m, 3H), 7.36 (ddd, J = 7.3, 4.8, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.4, 150.5, 148.5, 148.2 (q, $J = 34.7$ Hz), 137.6, 137.4, 135.8, 123.8, 121.8 (q, $J = 274.0$ Hz), 121.1, 120.6 (q, $J = 2.7$ Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -67.9.

Spectra were consistent with literature data.¹⁸

6'-Methyl-2,3'-bipyridine **33**



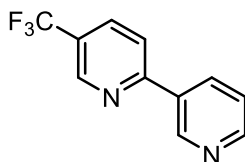
Product **33** was synthesized via General procedure D using 5-bromo-2-methylpyridine (77.4 mg, 0.45 mmol) and sulfonium salt **2a** (128.2 mg, 0.3 mmol). Purification by FCC (80% Et₂O in pentane) gave bipyridine **33** as a yellow oil (44.8 mg, 88%).

^1H NMR (400 MHz, Chloroform-*d*) δ 9.07 (d, $J = 2.4$ Hz, 1H), 8.70 (ddd, $J = 4.8, 2.5, 1.2$ Hz, 1H), 8.22 (dt, $J = 8.1, 2.6$ Hz, 1H), 7.86 – 7.64 (m, 2H), 7.25 (ddt, $J = 7.2, 3.6, 1.8$ Hz, 2H), 2.61 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.9, 155.0, 150.0, 147.6, 137.0, 134.7, 132.1, 123.3, 122.6, 120.3, 24.3.

Spectra are consistent with literature data.¹⁹

5-(Trifluoromethyl)-2,3'-bipyridine **34**



Product **34** was synthesized via General procedure D using 3-iodopyridine (92.3 mg, 0.45 mmol) and sulfonium salt **2f** (148.6 mg, 0.3 mmol). Purification by FCC (45% Et₂O in pentane) gave bipyridine **34** as a yellow oil (58.0 mg, 86%).

TLC: $R_f = 0.13$ (25% Et₂O in pentane).

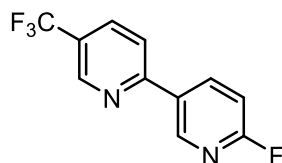
^1H NMR (500 MHz, Chloroform-*d*) δ 9.24 (d, $J = 2.3$ Hz, 1H), 8.97 (d, $J = 2.4$ Hz, 1H), 8.71 (d, $J = 4.6$ Hz, 1H), 8.36 (dt, $J = 8.1, 1.9$ Hz, 1H), 8.02 (dd, $J = 8.3, 2.4$ Hz, 1H), 7.88 (d, $J = 8.3$ Hz, 1H), 7.44 (dd, $J = 8.0, 4.8$ Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.2 (q, J = 1.4 Hz, C), 151.1 (CH), 148.6 (CH), 147.1 (q, J = 4.2 Hz, CH), 134.8 (CH), 134.4 (q, J = 3.5 Hz, CH), 133.6 (C), 125.7 (q, J = 33.3 Hz, CCF_3), 123.9 (CH), 123.7 (q, J = 272.3 Hz, CF_3), 120.1 (CH).

^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.4.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_2$ 225.0634; Found 225.0634.

6'-Fluoro-5-(trifluoromethyl)-2,3'-bipyridine **35**



Product **35** was synthesized via General procedure D using 2-fluoro-5-iodopyridine (127.8 mg, 0.45 mmol) and sulfonium salt **2f** (148.6 mg, 0.3 mmol). Purification by FCC (20% Et_2O in pentane) gave bipyridine **35** as a yellow solid (54.8 mg, 75%).

TLC: R_f = 0.29 (25% Et_2O in pentane).

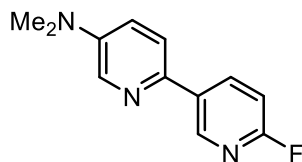
^1H NMR (500 MHz, Chloroform-*d*) δ 8.95 (dt, J = 2.1, 1.0 Hz, 1H), 8.87 – 8.84 (m, 1H), 8.50 (ddd, J = 8.6, 7.6, 2.6 Hz, 1H), 8.05 – 7.96 (m, 1H), 7.84 (dt, J = 8.3, 0.8 Hz, 1H), 7.07 (ddd, J = 8.6, 3.0, 0.7 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.7 (d, J = 242.7 Hz, CF), 157.1 (d, J = 1.5 Hz), 147.1 (q, J = 4.0 Hz), 146.9 (d, J = 15.7 Hz), 140.3 (d, J = 8.5 Hz), 134.5 (q, J = 3.6 Hz), 131.9 (d, J = 4.8 Hz), 125.8 (q, J = 33.3 Hz, CCF_3), 123.6 (q, J = 272.3 Hz, CF_3), 119.8, 110.0 (d, J = 37.6 Hz).

^{19}F NMR (470 MHz, Chloroform-*d*) δ -62.4, -66.5 (d, J = 4.6 Hz).

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_7\text{F}_4\text{N}_2$ 243.0540; Found 243.0539.

6'-Fluoro-*N,N*-dimethyl-[2,3'-bipyridin]-5-amine **36**



Product **36** was synthesized via General procedure D using 2-bromo-*N,N*-dimethylpyridin-4-amine (90.5 mg, 0.45 mmol) and sulfonium salt **2h** (148.6 mg, 0.3 mmol). Purification by FCC (40% Et_2O in pentane) gave bipyridine **36** as a yellow oil (26.7 mg, 41%).

TLC: R_f = 0.10 (40% Et_2O in pentane).

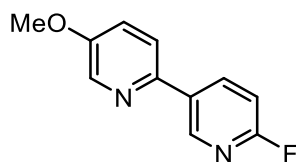
^1H NMR (500 MHz, Chloroform-*d*) δ 8.70 – 8.67 (m, 1H), 8.34 (ddd, J = 8.6, 7.8, 2.6 Hz, 1H), 8.21 (d, J = 3.1 Hz, 1H), 7.60 – 7.49 (m, 1H), 7.04 (dd, J = 8.8, 3.1 Hz, 1H), 7.00 – 6.93 (m, 1H), 3.04 (s, 6H, NMe₂).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.2 (d, J = 238.5 Hz, CF), 145.6 (C), 144.9 (d, J = 14.9 Hz, CH), 141.6 (C), 138.7 (d, J = 7.9 Hz, CH), 134.9 (CH), 133.6 (d, J = 4.4 Hz, C), 120.3 (CH), 119.2 (CH), 109.4 (d, J = 37.4 Hz, CH), 40.2 (NMe₂).

^{19}F NMR (470 MHz, Chloroform-*d*) δ -70.9 (d, J = 4.8 Hz).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₂H₁₃FN₃ 218.1088; Found 218.1090.

6'-Fluoro-5-methoxy-2,3'-bipyridine **37**



Product **37** was synthesized via General procedure D using 2-fluoro-5-iodopyridine (100.3 mg, 0.45 mmol) and sulfonium salt **2g** (137.2 mg, 0.3 mmol). Purification by FCC (50% Et₂O in pentane) gave bipyridine **37** as a white solid (49.9 mg, 82%).

TLC: R_f = 0.29 (50% Et₂O in pentane).

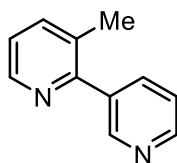
^1H NMR (400 MHz, Chloroform-*d*) δ 8.68 (d, J = 2.5 Hz, 1H), 8.35 (d, J = 2.7 Hz, 1H), 8.32 (dd, J = 8.1, 2.6 Hz, 1H), 7.61 (d, J = 8.6 Hz, 1H), 7.25 (dd, J = 8.7, 3.0 Hz, 1H), 6.96 (dd, J = 8.6, 3.0 Hz, 1H), 3.87 (s, 3H, OMe).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.6 (d, J = 239.6 Hz, CF), 155.5 (C), 146.3 (C), 145.5 (d, J = 15.2 Hz, CH), 139.4 (d, J = 8.0 Hz, CH), 137.9 (CH), 133.0 (d, J = 4.7 Hz, C), 121.3 (CH), 120.7 (CH), 109.5 (d, J = 37.4 Hz, CH), 55.8 (OMe).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -69.5 (d, J = 5.8 Hz).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₁H₁₀FN₂O 205.0772; Found 205.0774.

3-Methyl-2,3'-bipyridine **38**



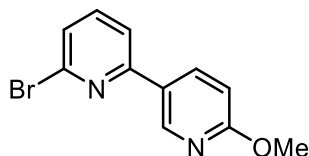
Product **38** was synthesized via General procedure D using 3-iodopyridine (92.3 mg, 0.45 mmol) and sulfonium salt **2b** (132.4 mg, 0.3 mmol). Purification by FCC (90% Et₂O in pentane) gave bipyridine **38** as a yellow oil (26.7 mg, 52%).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.81 – 8.75 (m, 1H), 8.62 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.54 (ddd, *J* = 4.7, 1.7, 0.7 Hz, 1H), 7.87 (ddd, *J* = 7.8, 2.2, 1.6 Hz, 1H), 7.60 (ddd *J* = 7.7, 1.5, 0.7 Hz, 1H), 7.38 (ddd, *J* = 7.9, 4.8, 0.9 Hz, 1H), 7.22 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 155.6, 150.0, 149.1, 147.5, 138.9, 136.6, 136.4, 131.4, 123.3, 122.9, 20.0.

Spectra were consistent with literature data.²²

6-Bromo-6'-methoxy-2,3'-bipyridine **39**



Product **39** was synthesized via General procedure D using 2-methoxy-5-iodopyridine (105.7 mg, 0.45 mmol) and sulfonium salt **2i** (151.9 mg, 0.3 mmol). Purification by FCC (30% Et₂O in pentane) gave bipyridine **39** as a white solid (26.2 mg, 33%).

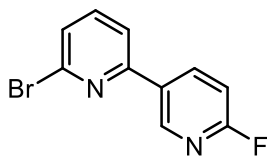
TLC: *R*_f = 0.51 (30% Et₂O in pentane).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.73 (d, *J* = 2.7 Hz, 1H), 8.26 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.40 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 4.00 (s, 3H, OMe).

¹³C NMR (101 MHz, Chloroform-*d*) δ 165.2 (C), 156.3 (C), 145.8 (CH), 142.5 (C), 139.2 (CH), 137.6 (CH), 127.2 (C), 126.3 (CH), 118.3 (CH), 111.2 (CH), 53.9 (OMe).

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₁H₁₀BrN₂O 264.9971, 266.9951; Found 264.9972, 266.9949.

6-Bromo-6'-fluoro-2,3'-bipyridine **40**



Product **40** was synthesized via General procedure D using 2-fluoro-5-iodopyridine (100.3 mg, 0.45 mmol) and sulfonium salt **2i** (151.9 mg, 0.3 mmol). Purification by FCC (30% Et₂O in pentane) gave bipyridine **40** as a white solid (32.6 mg, 43%).

TLC: R_f = 0.25 (30% Et₂O in pentane).

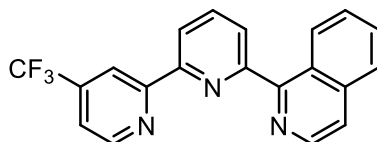
¹H NMR (500 MHz, Chloroform-*d*) δ 8.77 (dt, J = 2.7, 0.8 Hz, 1H), 8.47 (ddd, J = 8.6, 7.6, 2.6 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.48 (dd, J = 7.6, 1.1 Hz, 1H), 7.04 (ddd, J = 8.6, 3.1, 0.7 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 164.4 (d, J = 242.5 Hz, CF), 154.9 (C), 146.4 (d, J = 15.9 Hz, CH), 142.7 (C), 140.2 (d, J = 8.6 Hz, CH), 139.4 (CH), 131.7 (d, J = 4.6 Hz, C), 127.4 (CH), 118.9 (CH), 109.9 (d, J = 37.5 Hz, CH).

¹⁹F NMR (282 MHz, Chloroform-*d*) δ -67.1 (d, J = 5.7 Hz).

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₀H₇BrFN₂ 252.9771, 254.9751; Found 252.9775, 254.9738.

1-(4'-(Trifluoromethyl)-[2,2'-bipyridin]-6-yl)isoquinoline **43**



Product **43** was synthesized via General procedure D using **31** (127.8 mg, 0.45 mmol) and sulfonium salt **2d** (148.6 mg, 0.3 mmol). Purification by FCC (50% Et₂O in pentane) gave terpyridine **43** as an off-green solid (21.0 mg, 20%).

TLC: R_f = 0.18 (25% EtOAc in pentane).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.89 (d, J = 5.0 Hz, 1H), 8.79 (dd, J = 8.5, 1.0 Hz, 1H), 8.75 (dt, J = 1.6, 0.8 Hz, 1H), 8.67 (d, J = 5.6 Hz, 1H), 8.59 (dd, J = 7.7, 1.3 Hz, 1H), 8.13 (dd, J = 7.8, 1.3 Hz, 1H), 8.08 (t, J = 7.7 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.79 – 7.71 (m, 2H), 7.62 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.57 – 7.53 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 158.2 (C), 157.7 (C), 157.3 (C), 153.6 (C), 150.3 (CH), 142.1 (CH), 139.5 (q, J = 34.0 Hz, CCF₃), 138.4 (CH), 137.4 (C), 130.3 (CH), 128.0 (CH), 127.7 (CH), 127.2

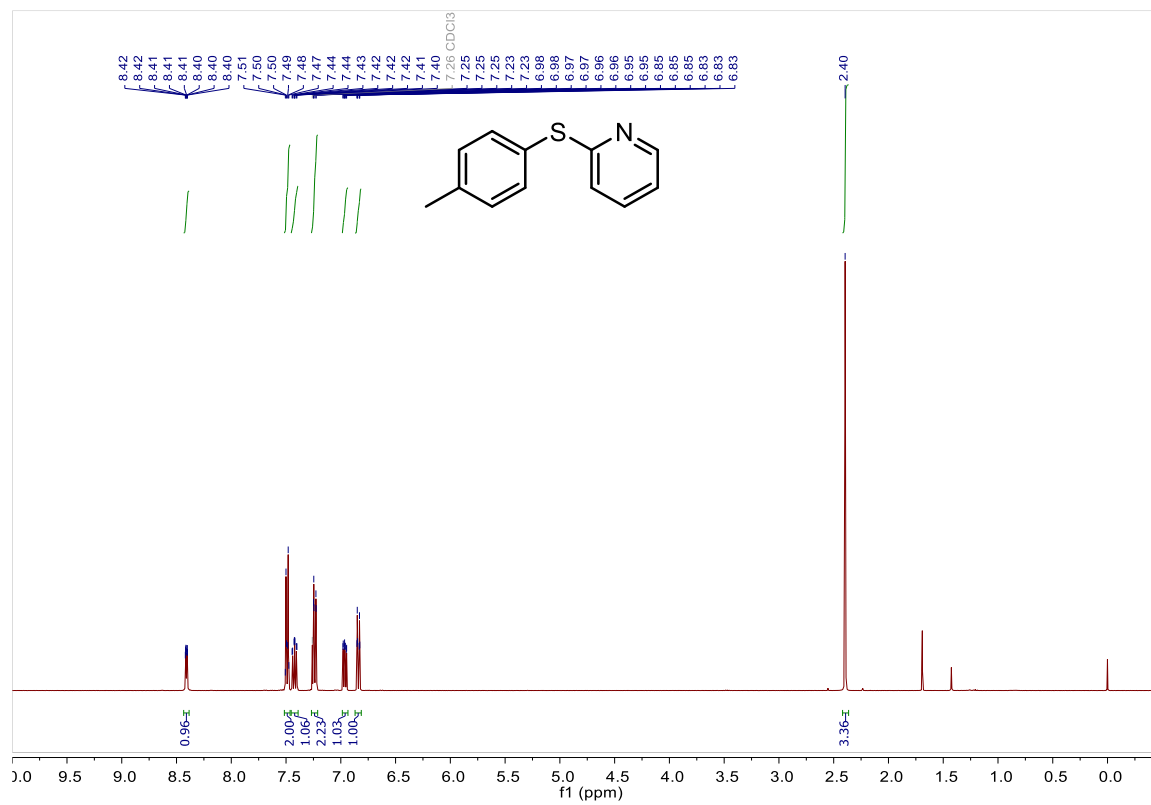
(CH), 127.0 (CH), 126.2 (C), 123.1 (q, $J = 273.2$ Hz, CF₃), 121.7 (CH), 120.8 (CH), 119.3 (q, $J = 3.7$ Hz, CH), 117.2 (q, $J = 3.7$ Hz, CH).

¹⁹F NMR (282 MHz, Chloroform-*d*) δ -64.9.

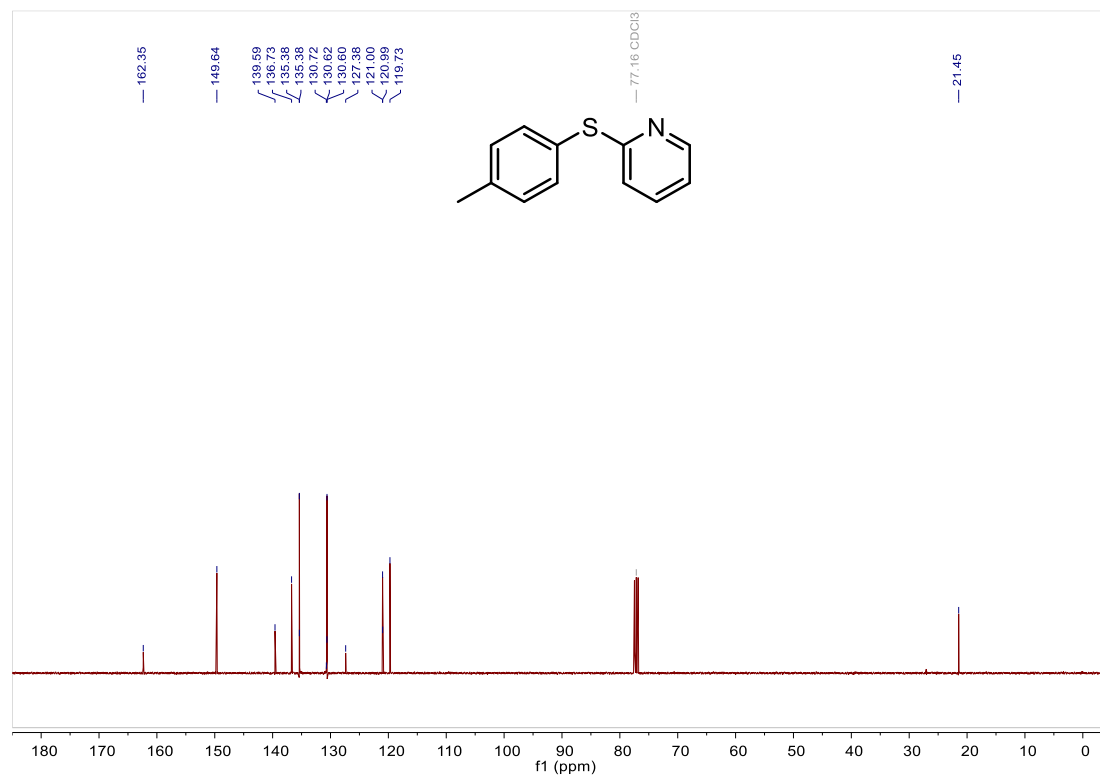
HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₂₀H₁₂F₃N₃ 352.1056; Found 352.1056.

7. NMR Spectra

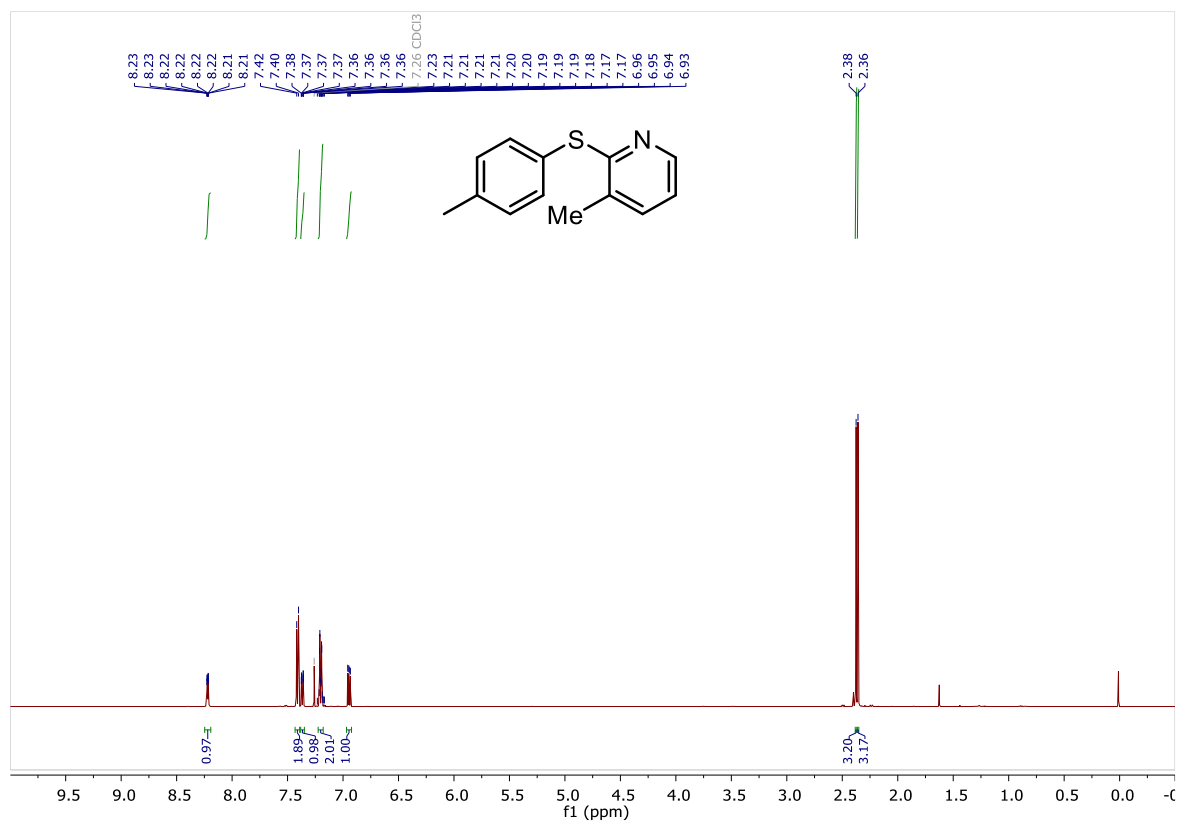
^1H NMR (400 MHz, CDCl_3): 1a



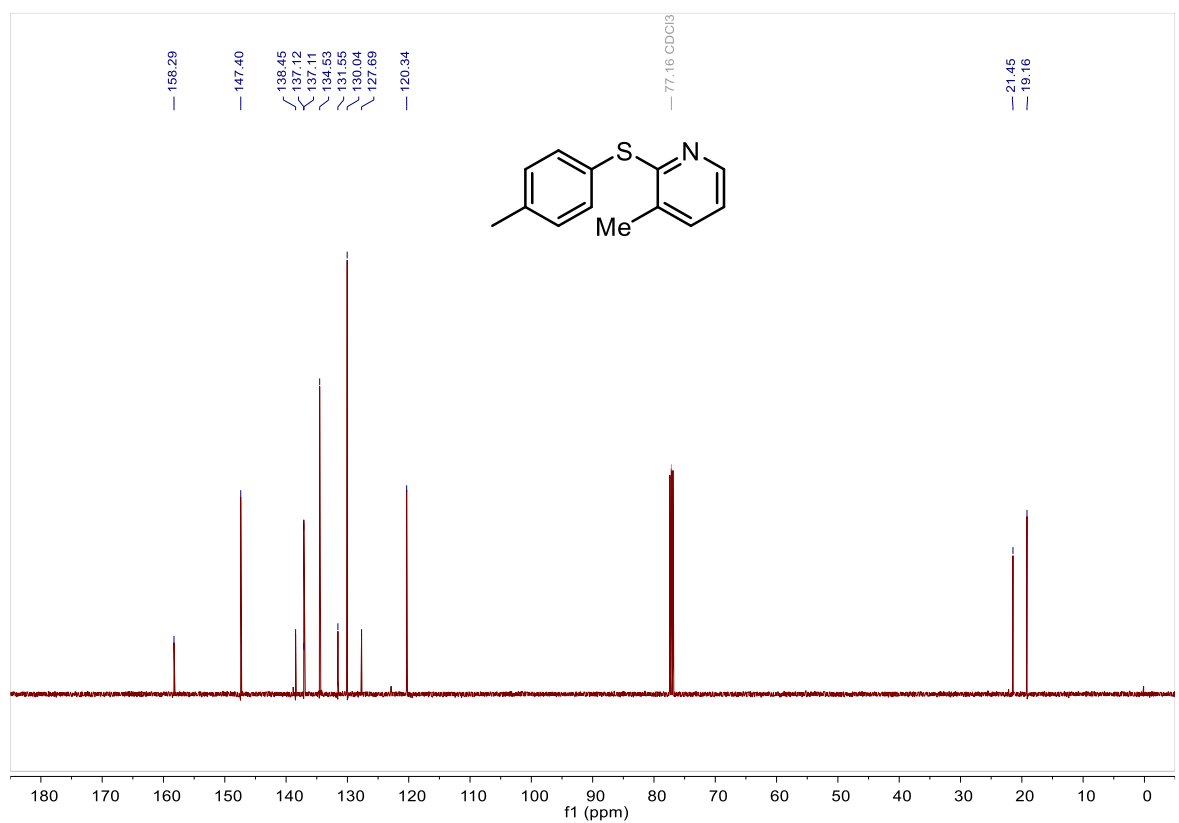
^{13}C NMR (101 MHz, CDCl_3): 1a



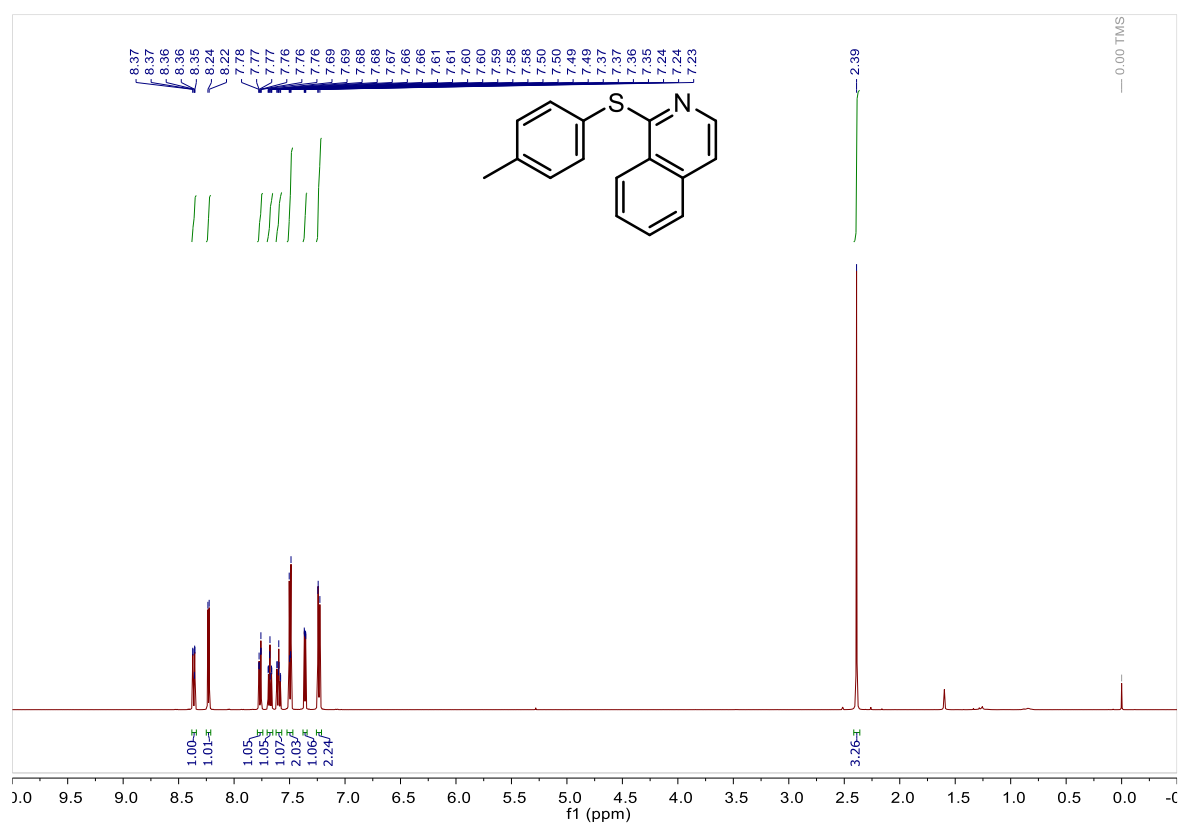
¹H NMR (400 MHz, CDCl₃): 1b



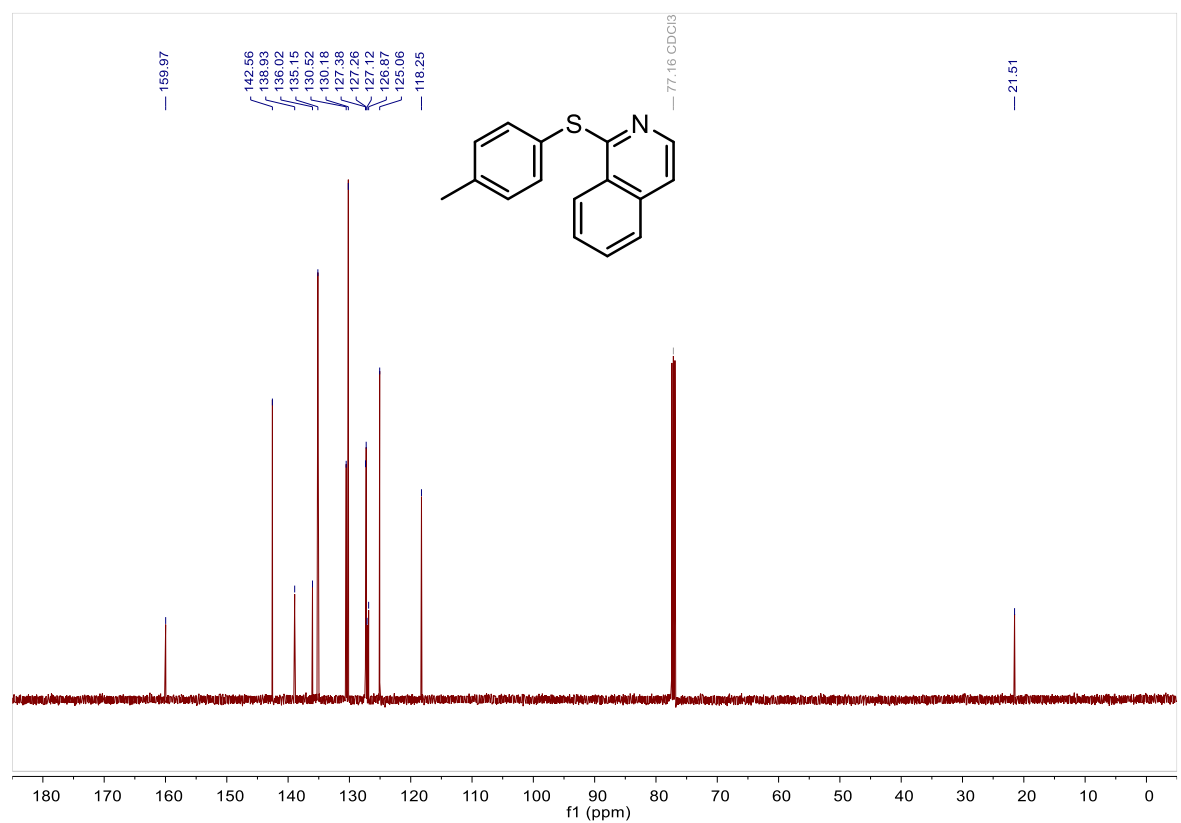
¹³C NMR (101 MHz, CDCl₃): 1b



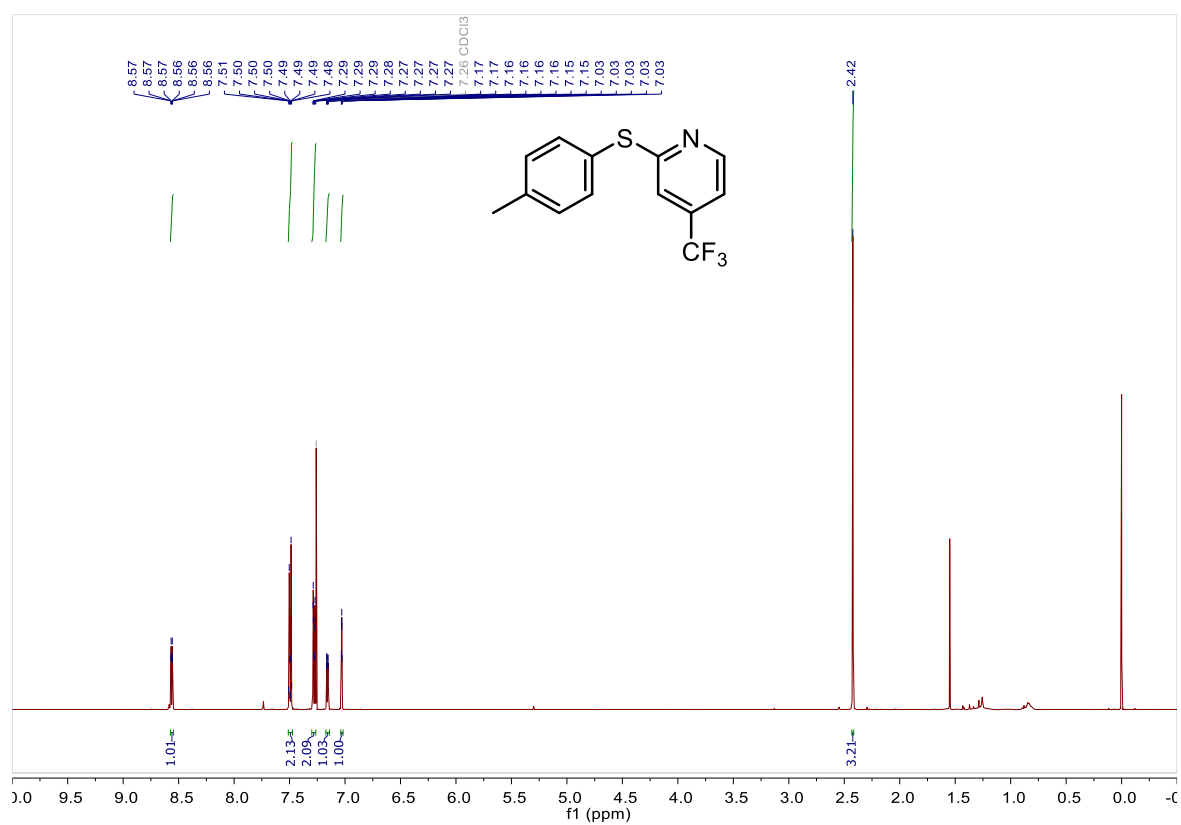
^1H NMR (500 MHz, CDCl_3): 1c



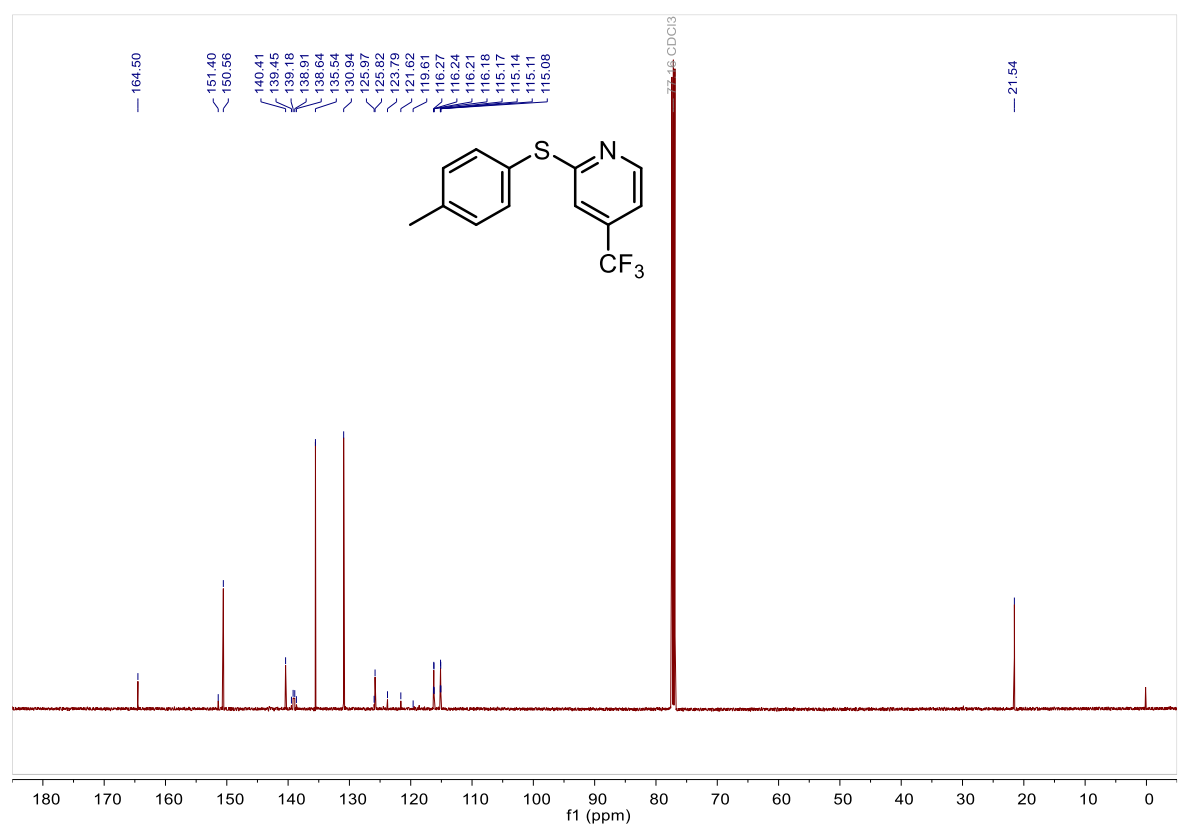
^{13}C NMR (126 MHz, CDCl_3): 1c



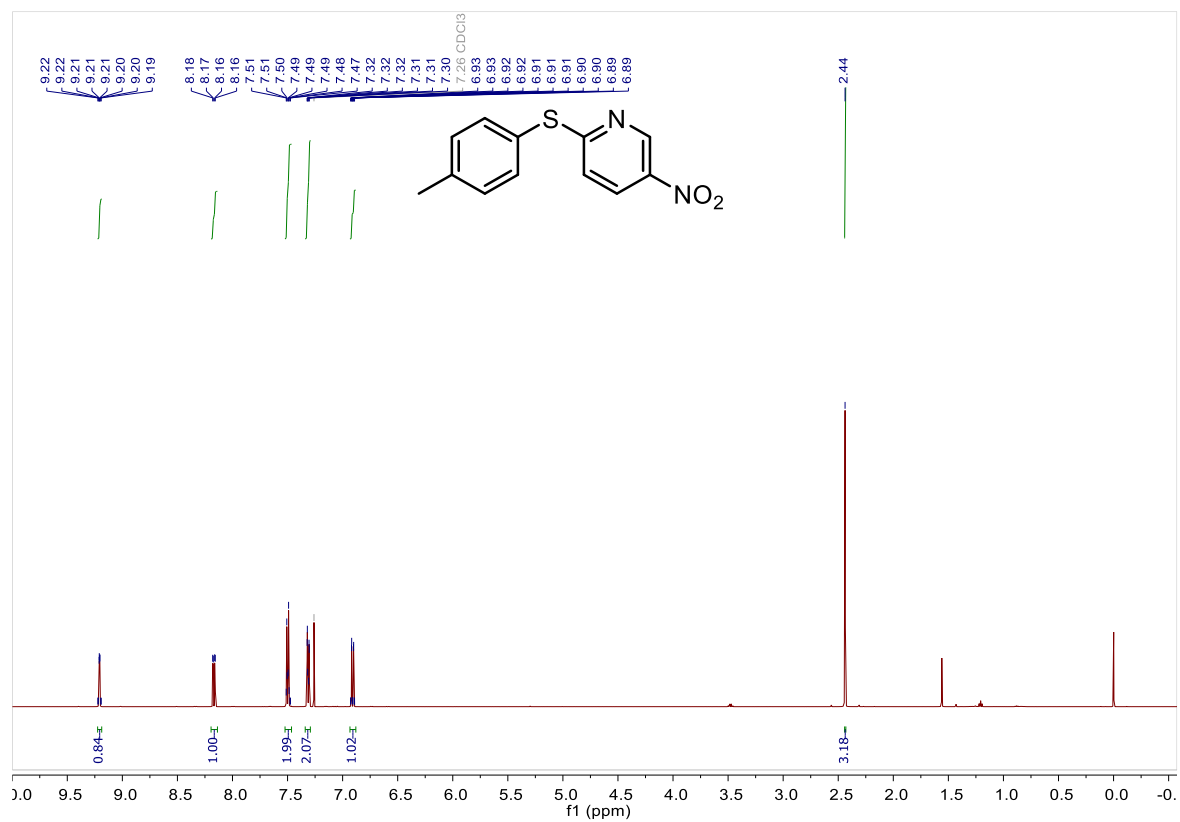
¹H NMR (500 MHz, CDCl₃): 1d



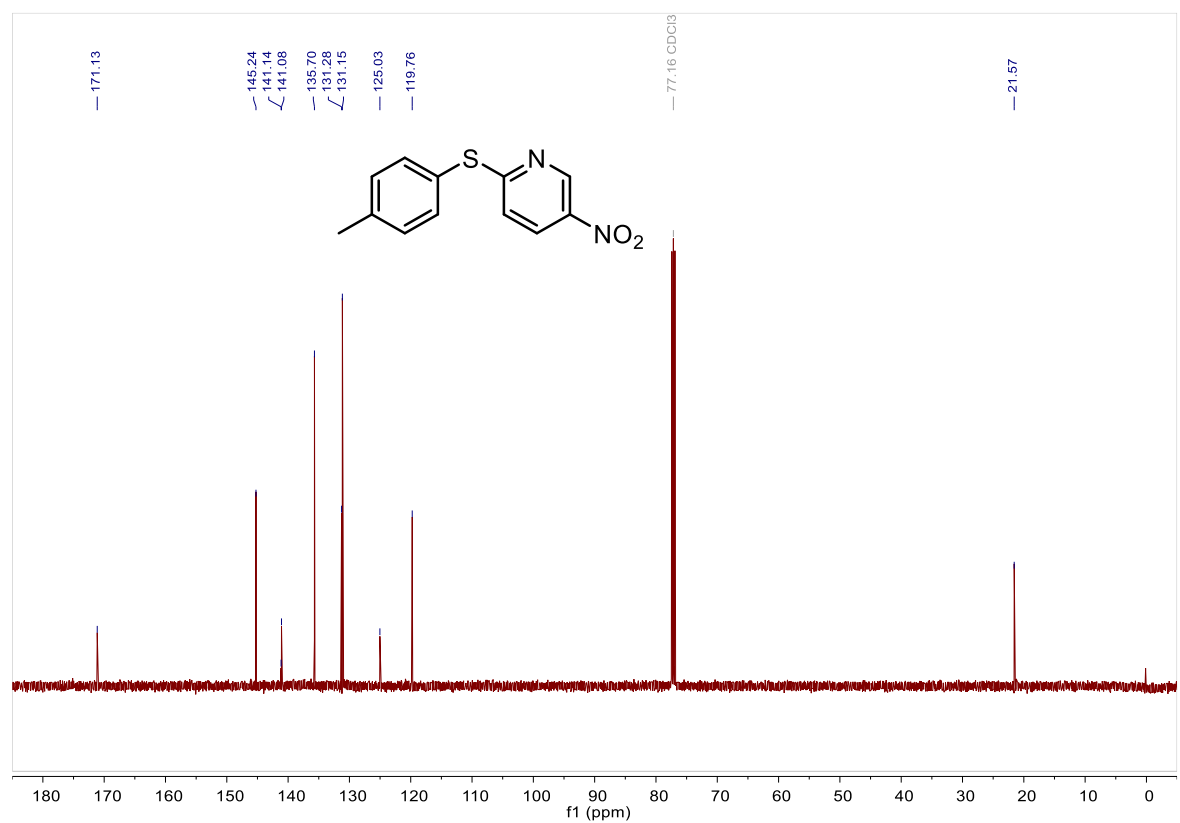
¹³C NMR (126 MHz, CDCl₃): 1d



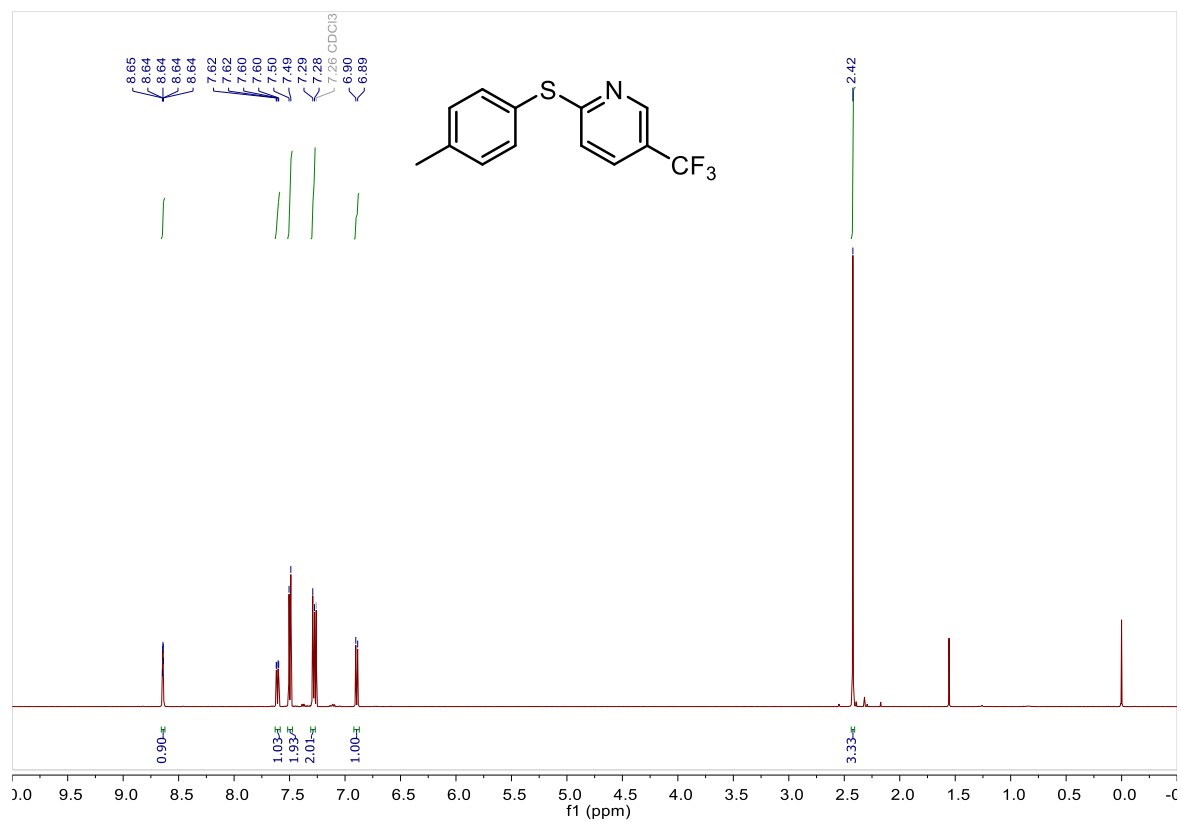
¹H NMR (500 MHz, CDCl₃): 1e



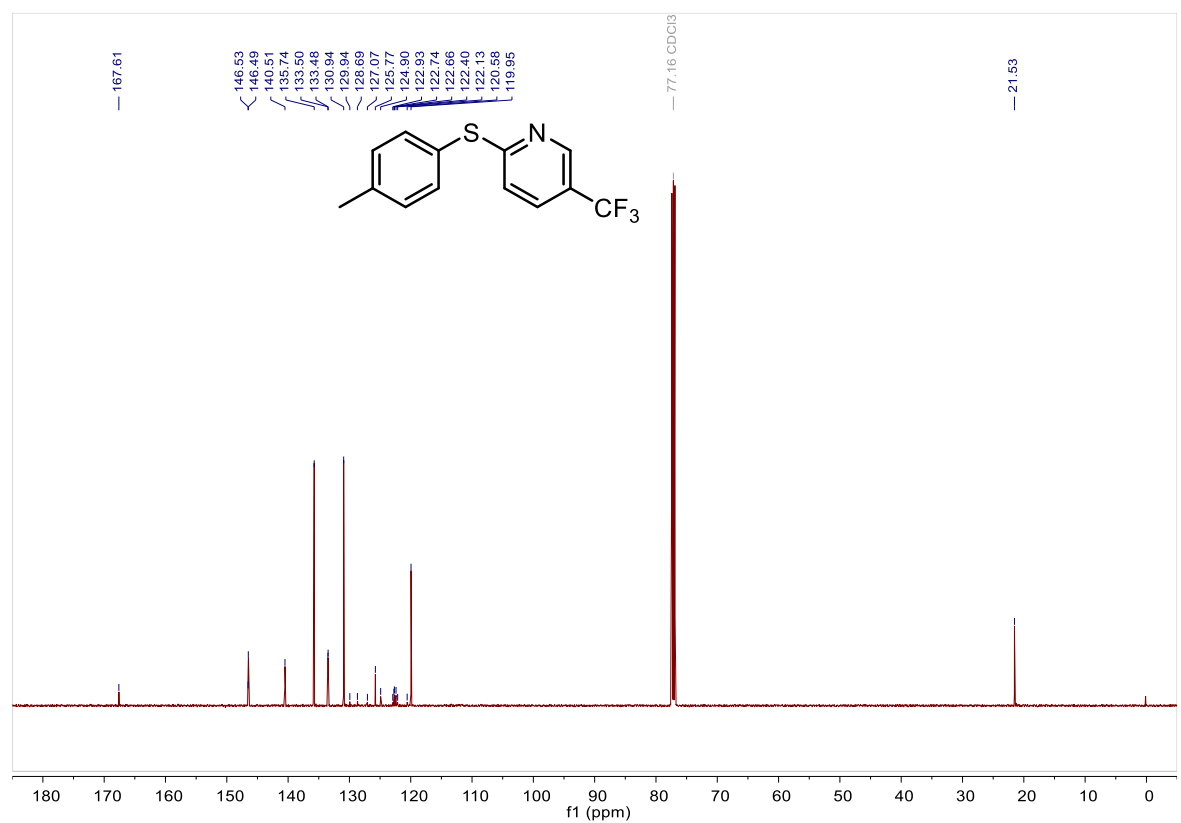
¹³C NMR (126 MHz, CDCl₃): 1e



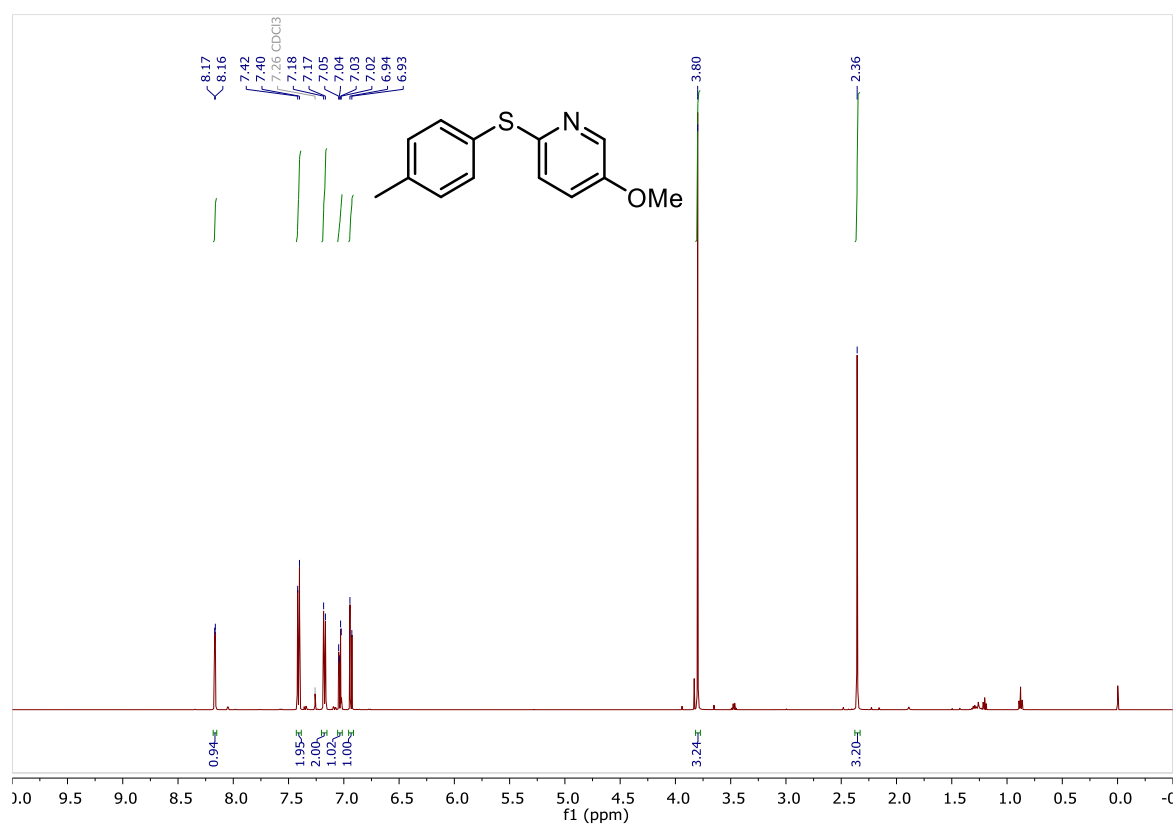
¹H NMR (500 MHz, CDCl₃): 1f



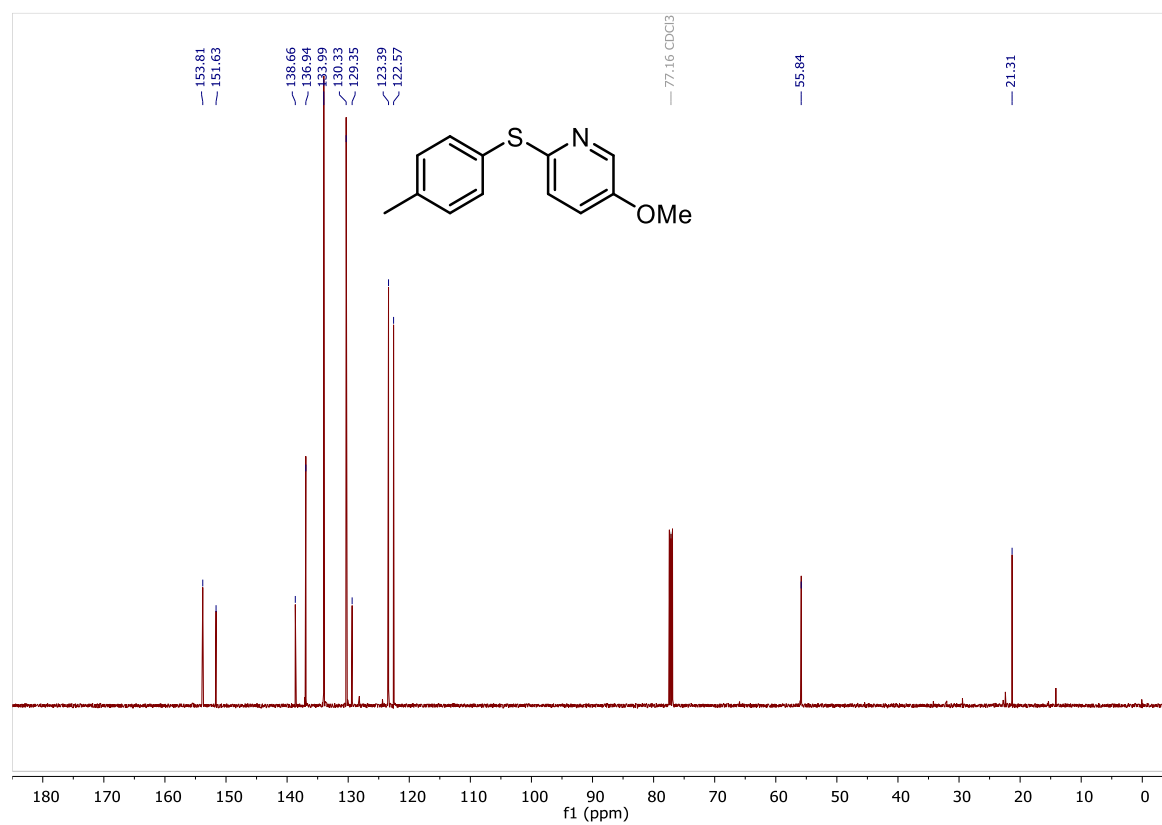
¹³C NMR (101 MHz, CDCl₃): 1f



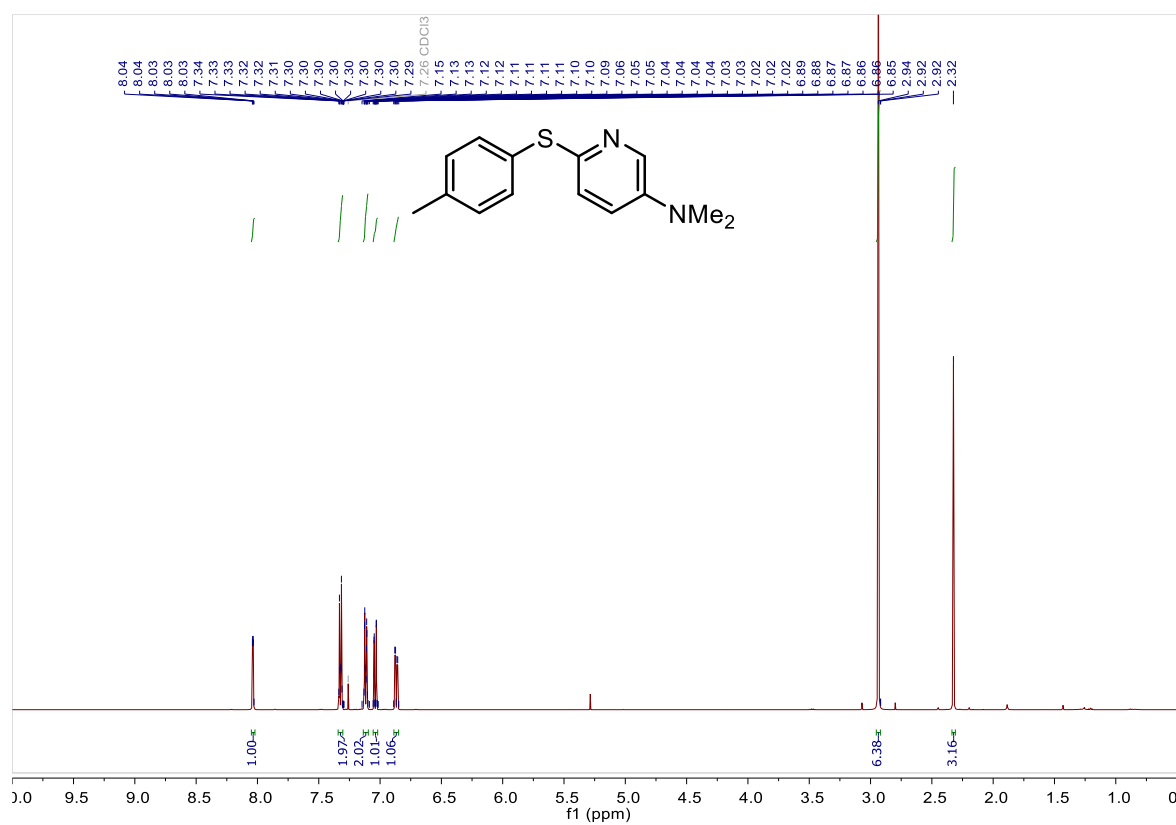
¹H NMR (500 MHz, CDCl₃): 1g



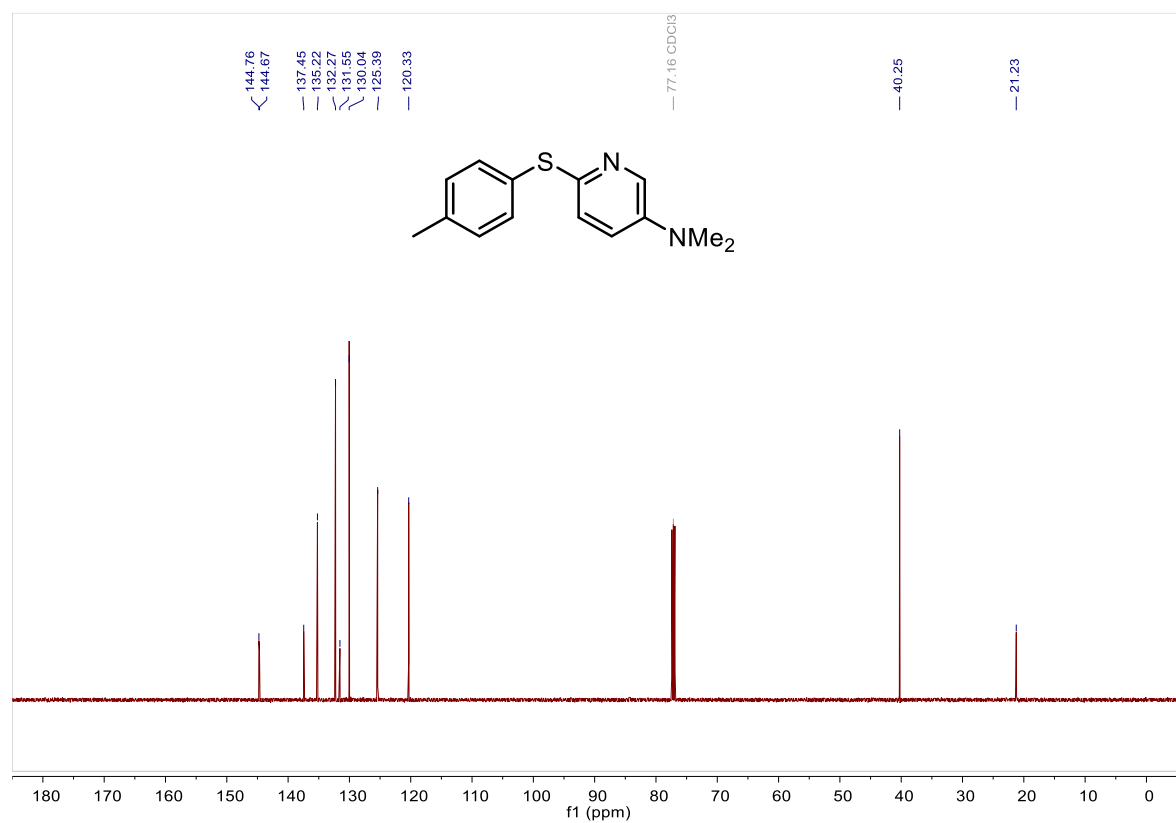
¹³C NMR (126 MHz, CDCl₃): 1g



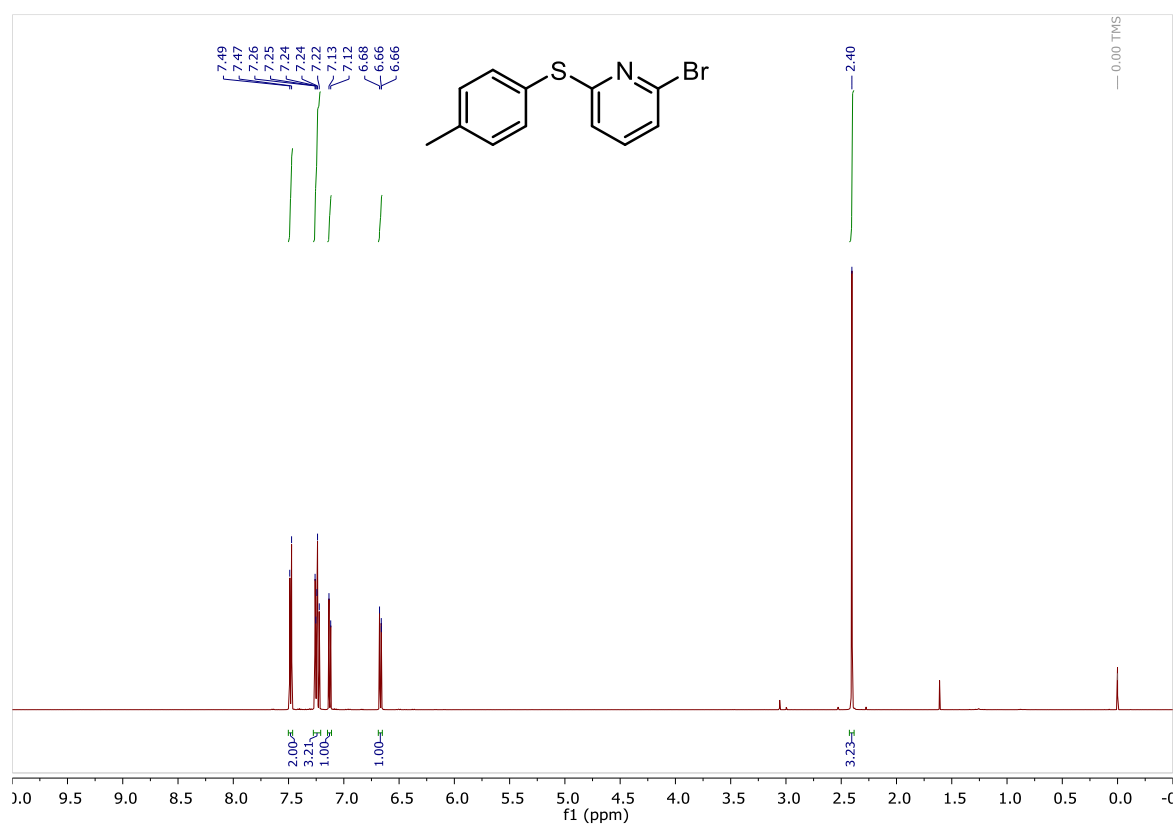
¹H NMR (500 MHz, CDCl₃): 1h



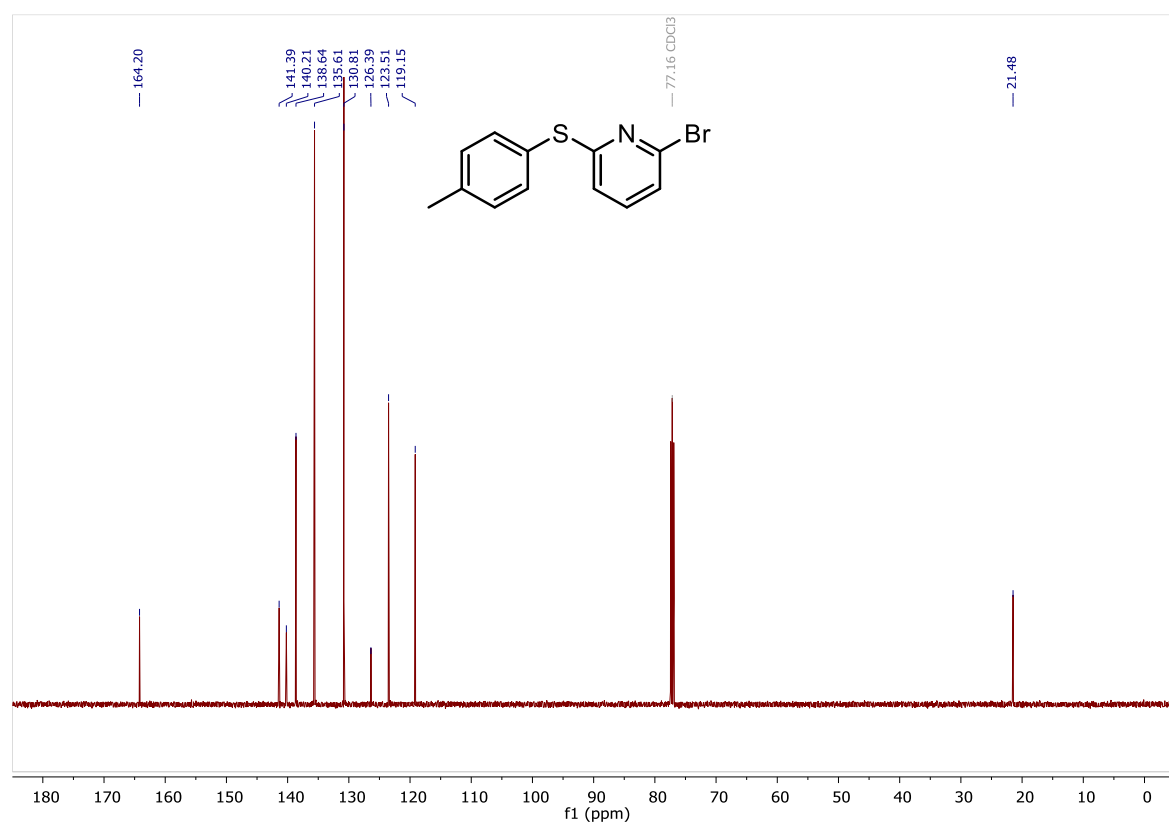
¹³C NMR (126 MHz, CDCl₃): 1h



¹H NMR (500 MHz, CDCl₃): 1i



¹³C NMR (126 MHz, CDCl₃): 1i



Chemical structure: BrC1=CC=C(C=C1)C=CC2=CC=CC=C2

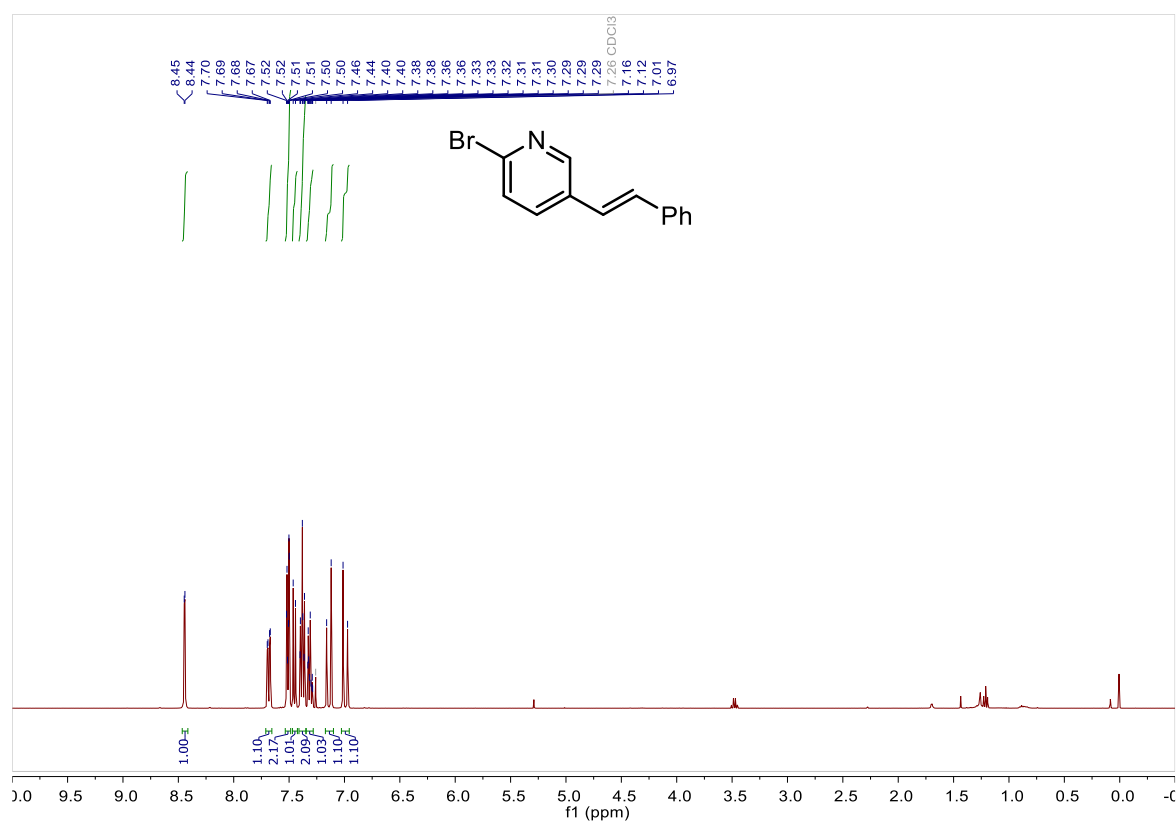
¹H NMR spectrum (CDCl₃) showing peaks from 6.44 to 8.22 ppm. Integration values are provided below the peaks: 1.00, 1.10, 4.35, 2.16, 1.14, and 1.16.

Chemical structure of 2-bromo-4-(benzyloxy)pyridine is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with the following chemical shifts (ppm) labeled above the peaks:

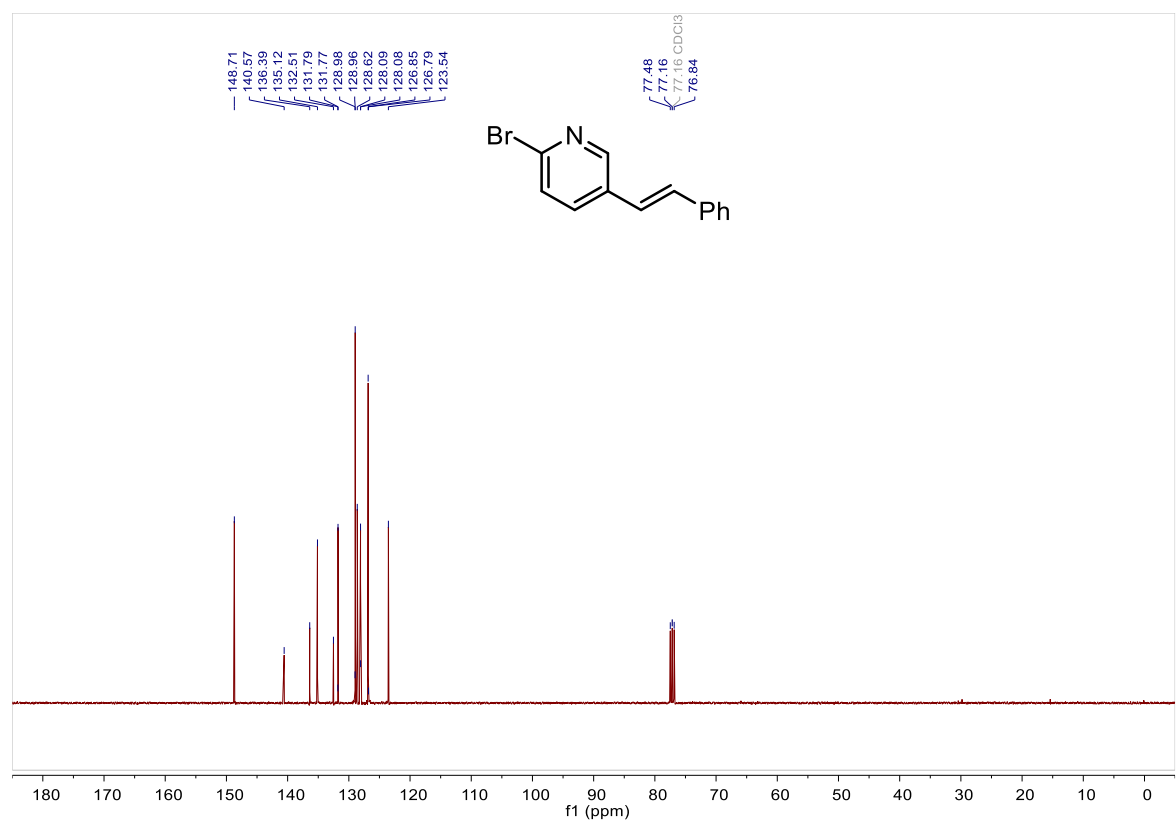
150.51, 150.49, 140.27, 138.44, 138.42, 136.24, 133.67, 133.64, 132.54, 128.78, 128.67, 127.97, 127.95, 127.57, 127.55, 125.13

The solvent peak for CDCl₃ is indicated at 77.16 ppm.

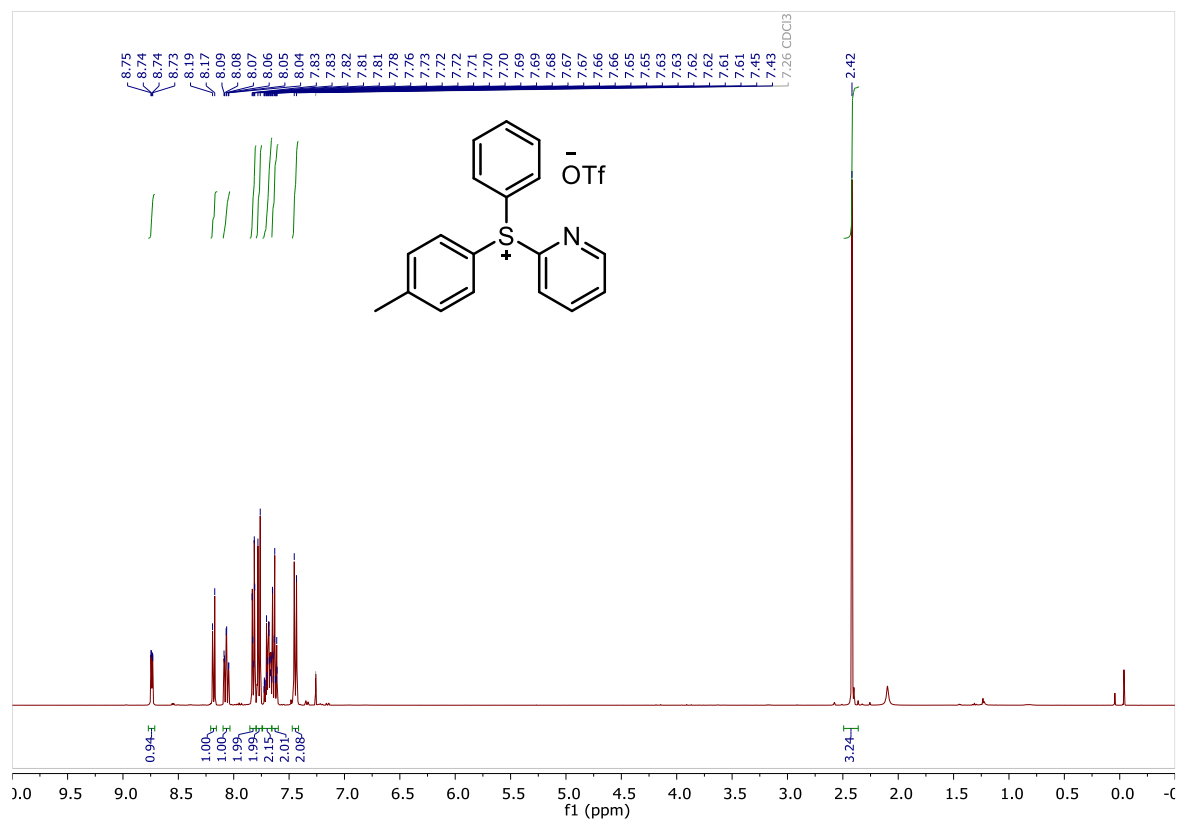
¹H NMR (400 MHz, CDCl₃): E-S1



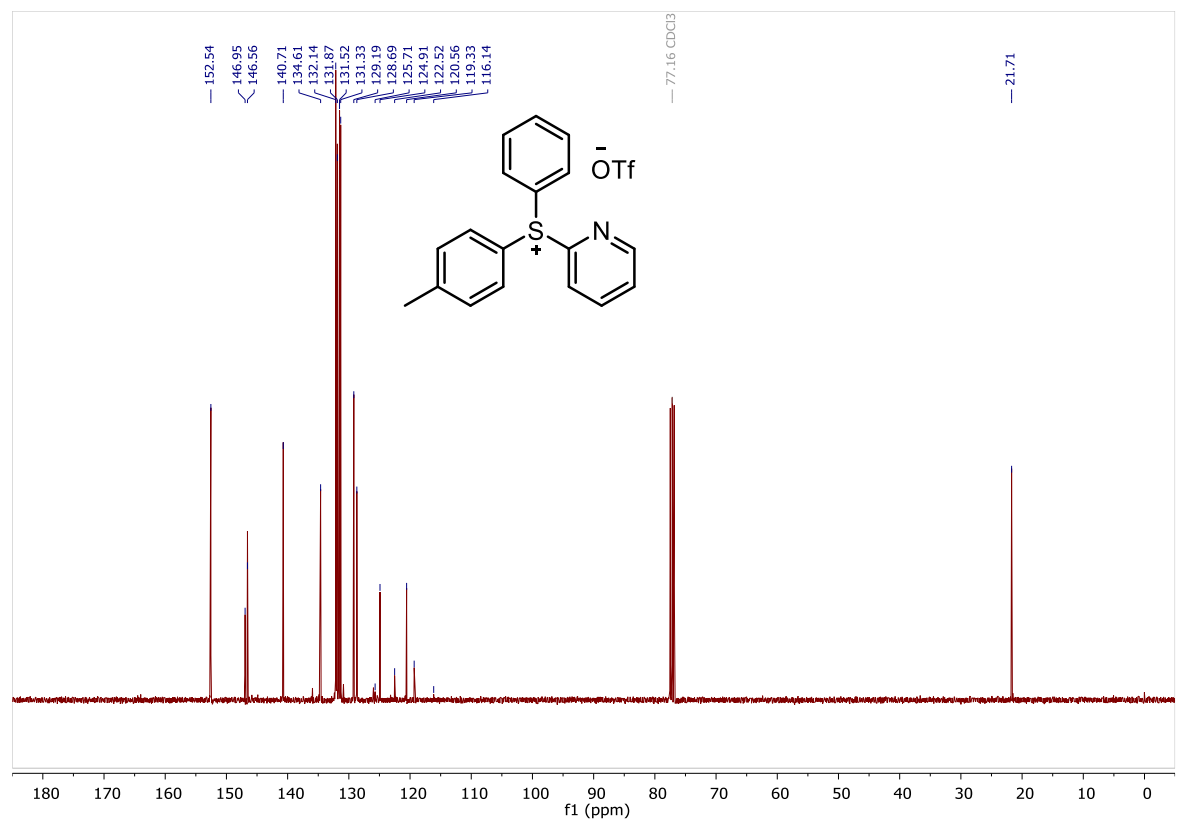
¹³C NMR (101 MHz, CDCl₃): E-S1



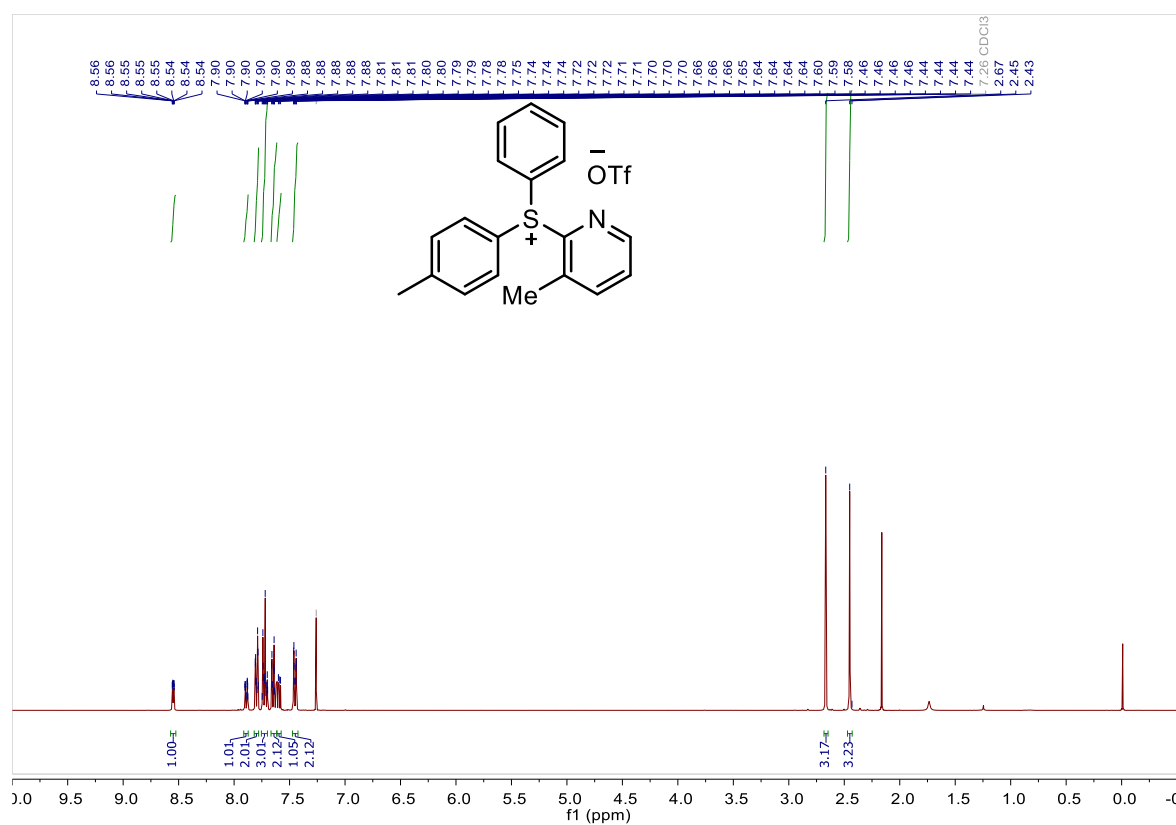
¹H NMR (400 MHz, CDCl₃): 2a



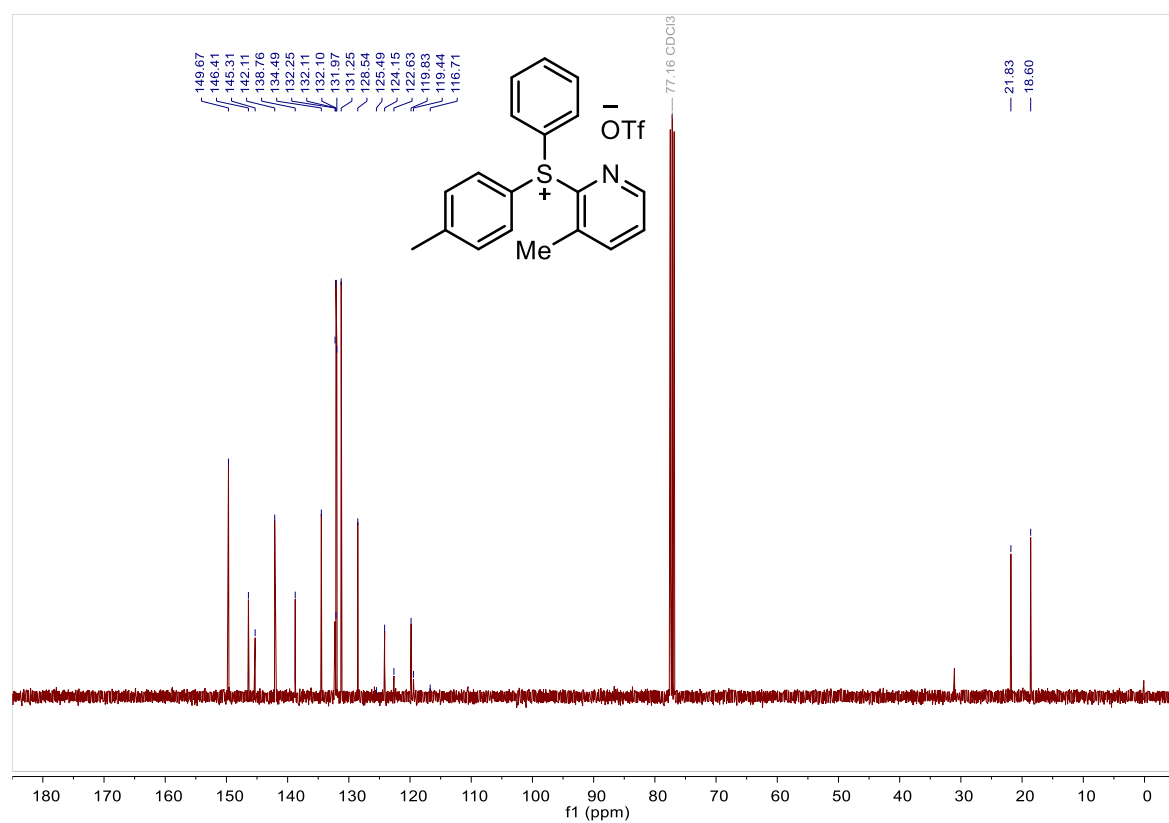
¹³C NMR (101 MHz, CDCl₃): 2a



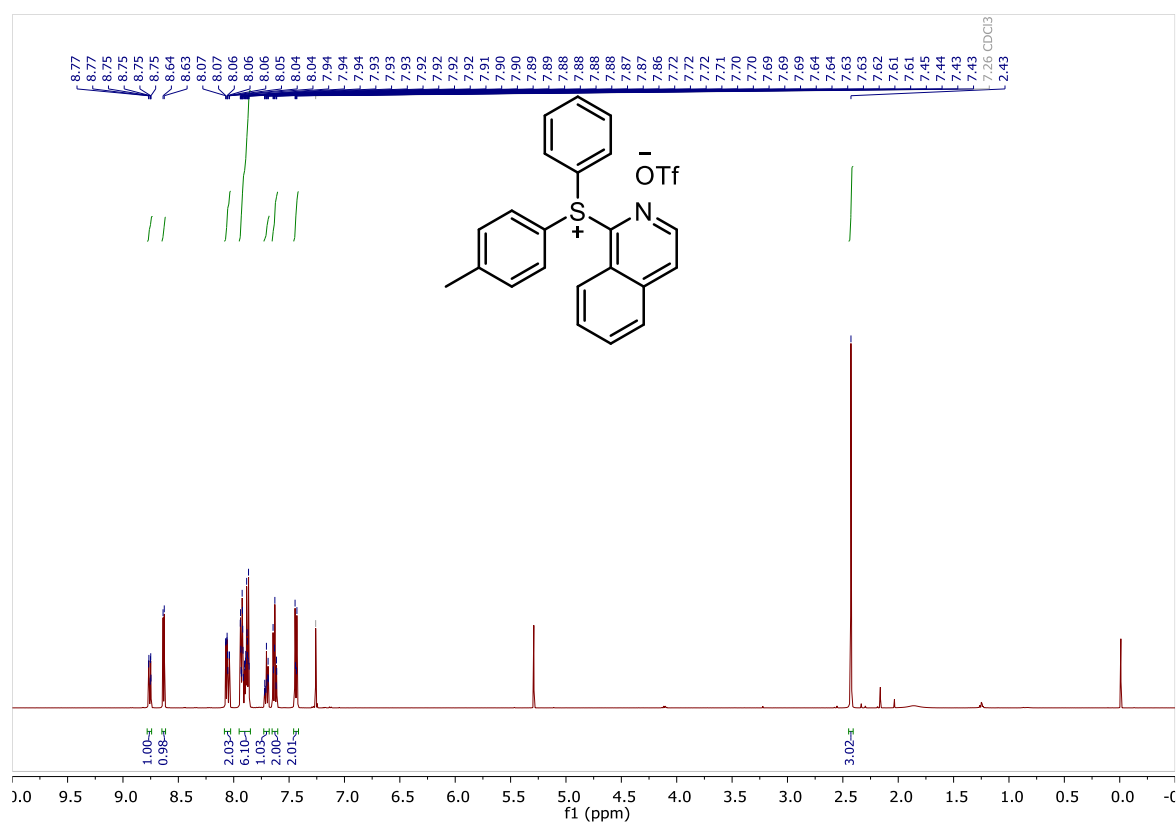
¹H NMR (400 MHz, CDCl₃): 2b



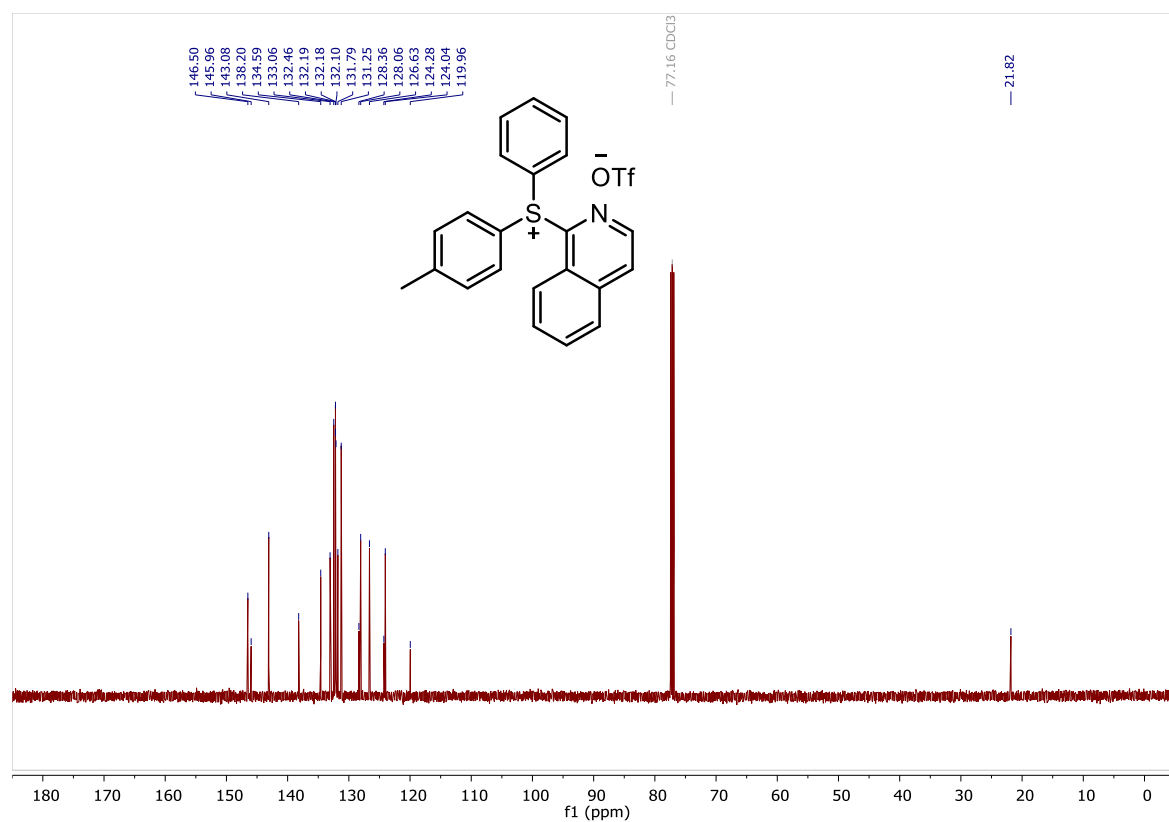
¹³C NMR (101 MHz, CDCl₃): 2b



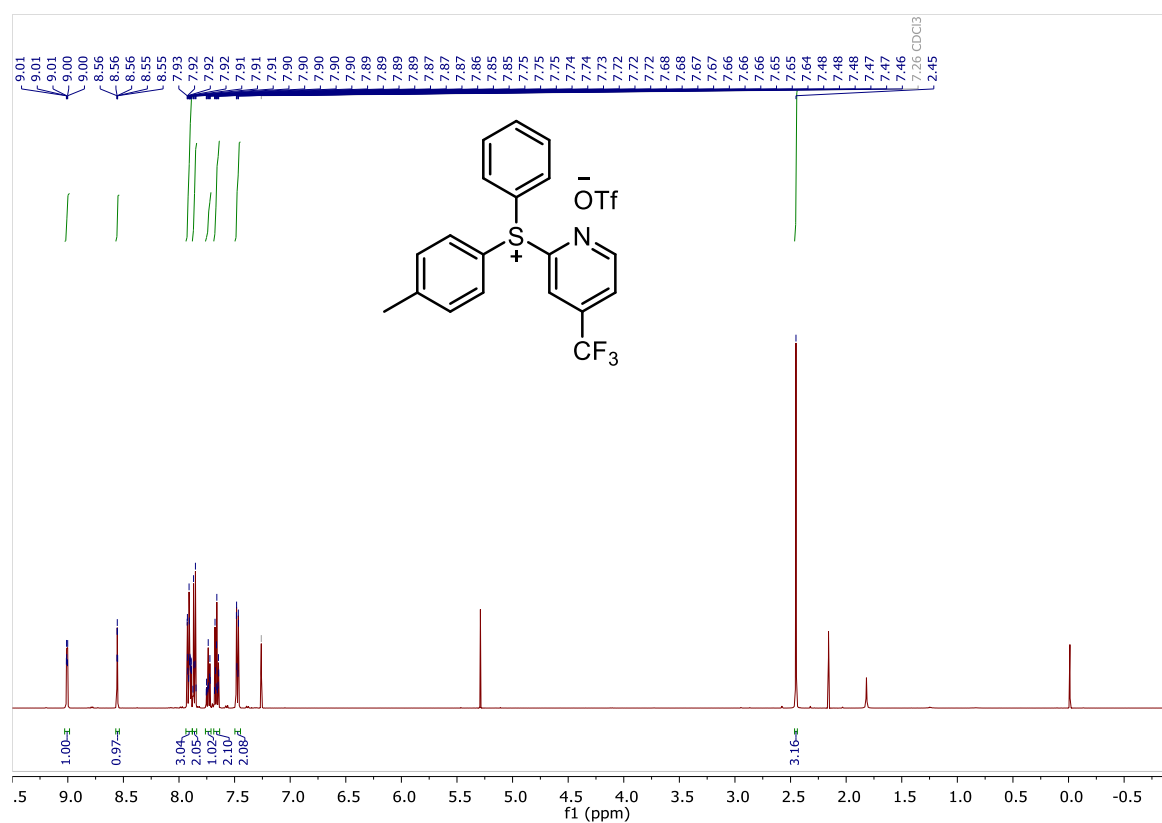
^1H NMR (500 MHz, CDCl_3): 2c



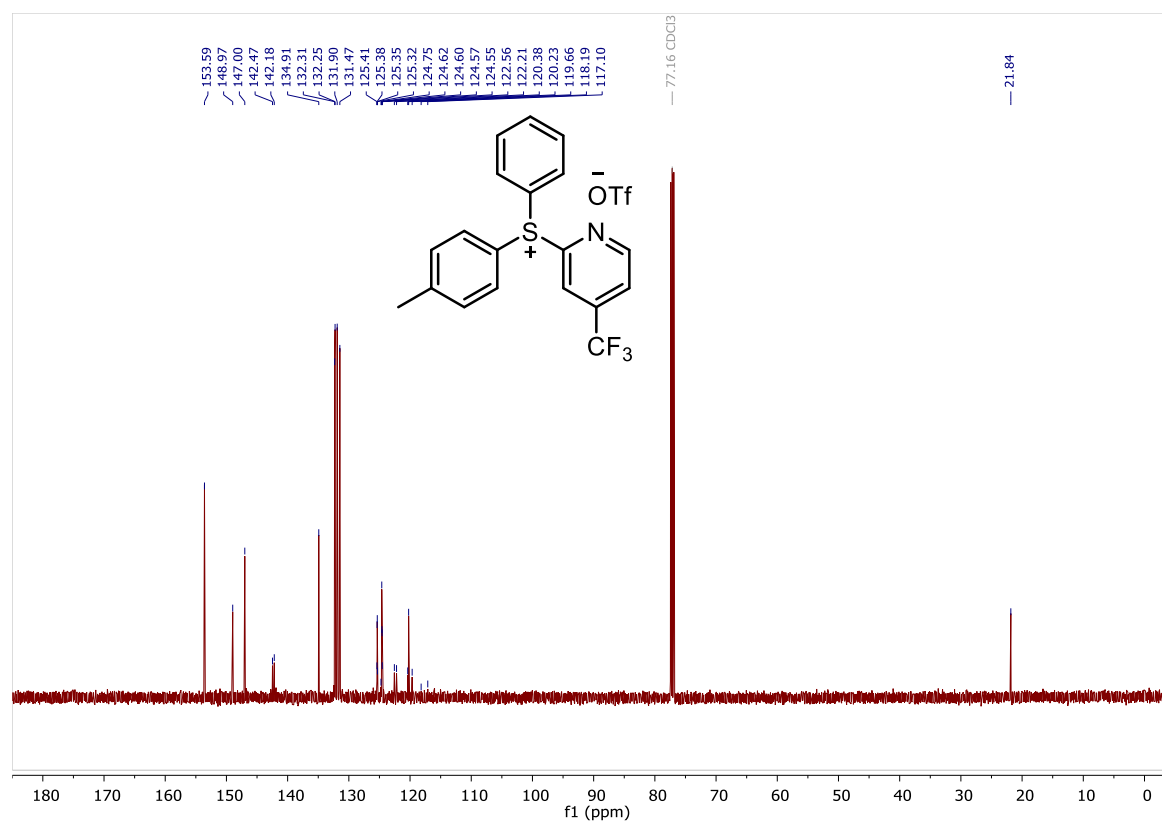
^{13}C NMR (126 MHz, CDCl_3): 2c



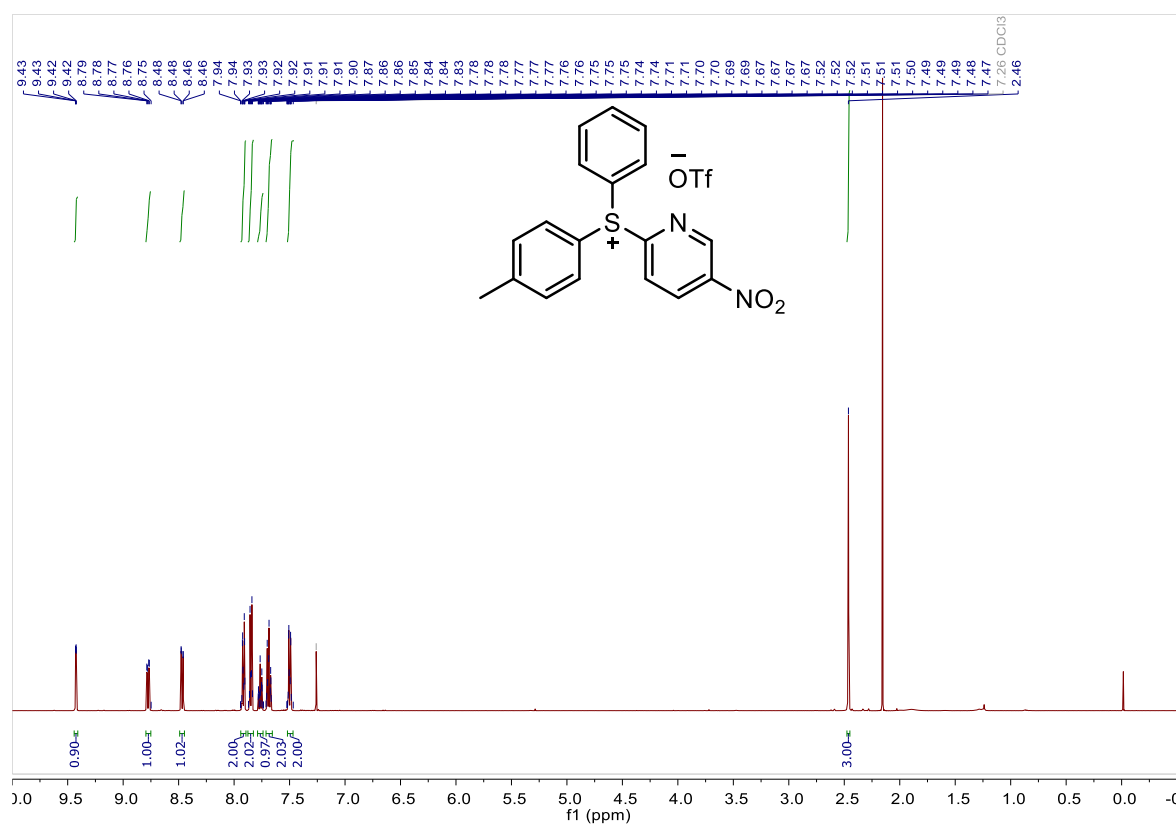
¹H NMR (500 MHz, CDCl₃): 2d



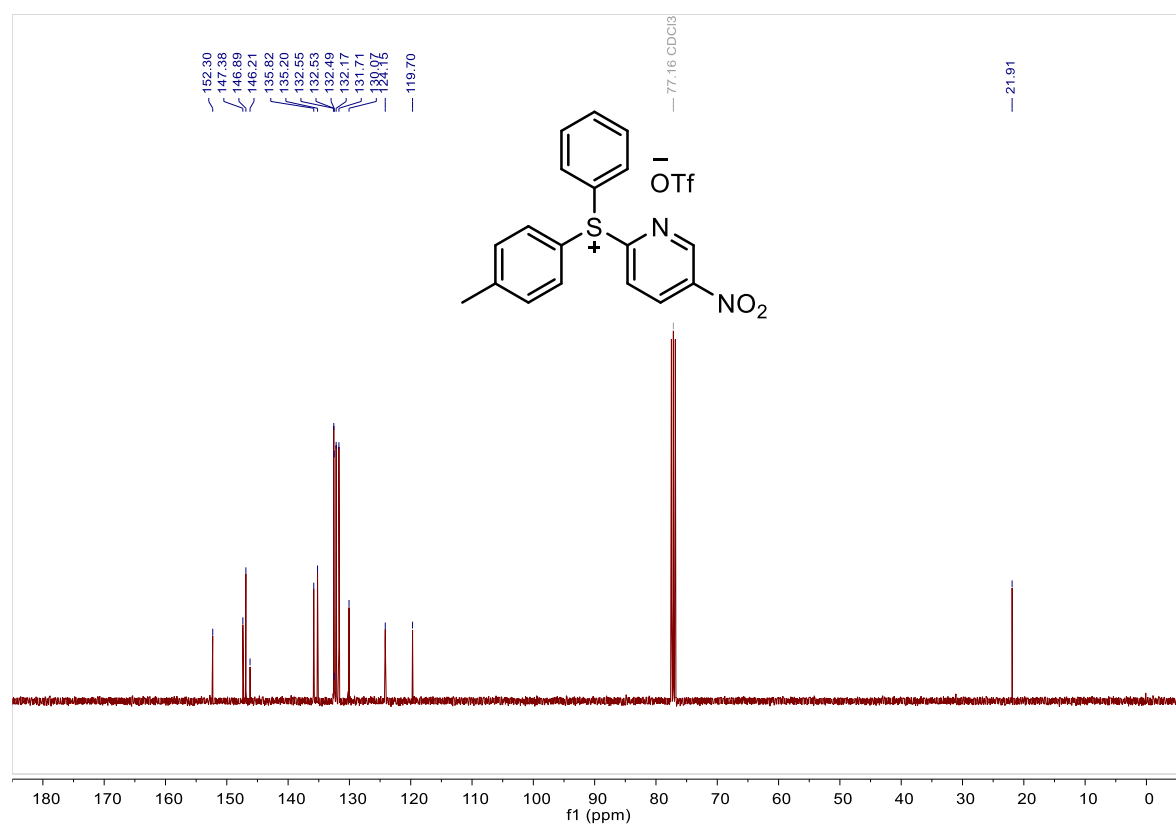
¹³C NMR (126 MHz, CDCl₃): 2d



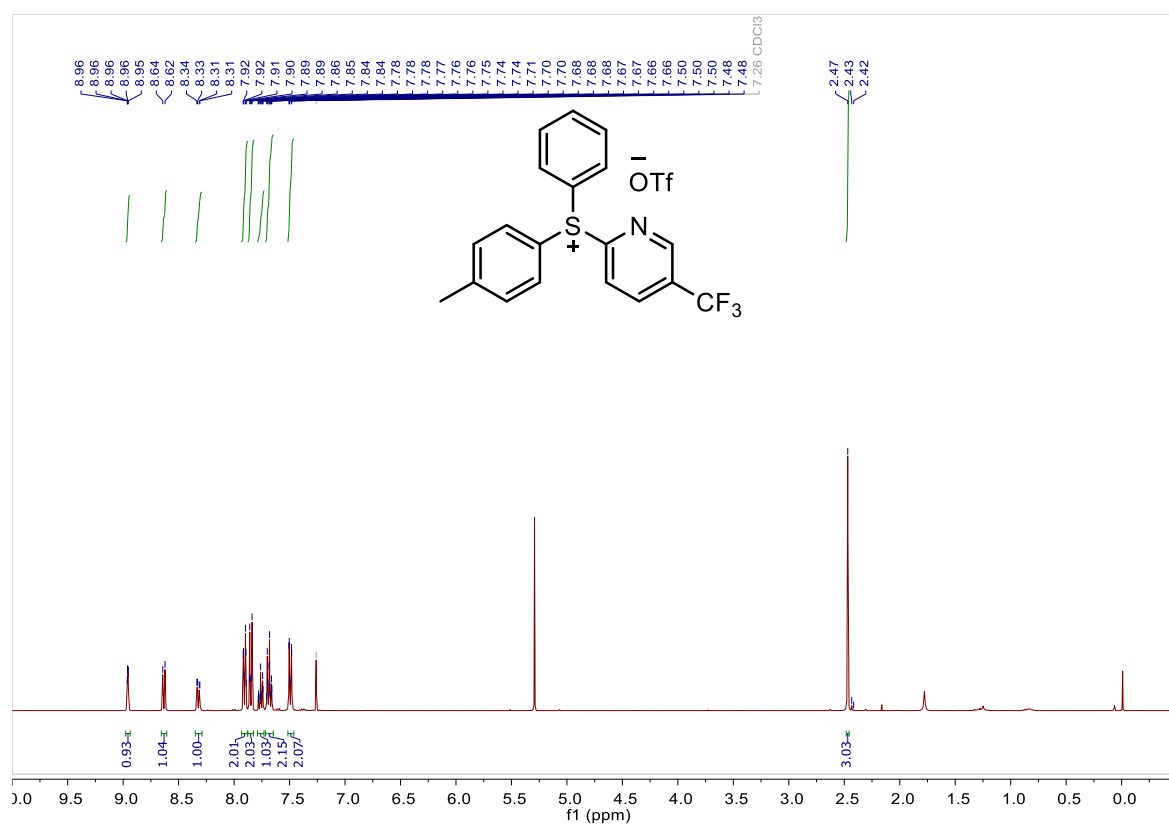
¹H NMR (500 MHz, CDCl₃): 2e



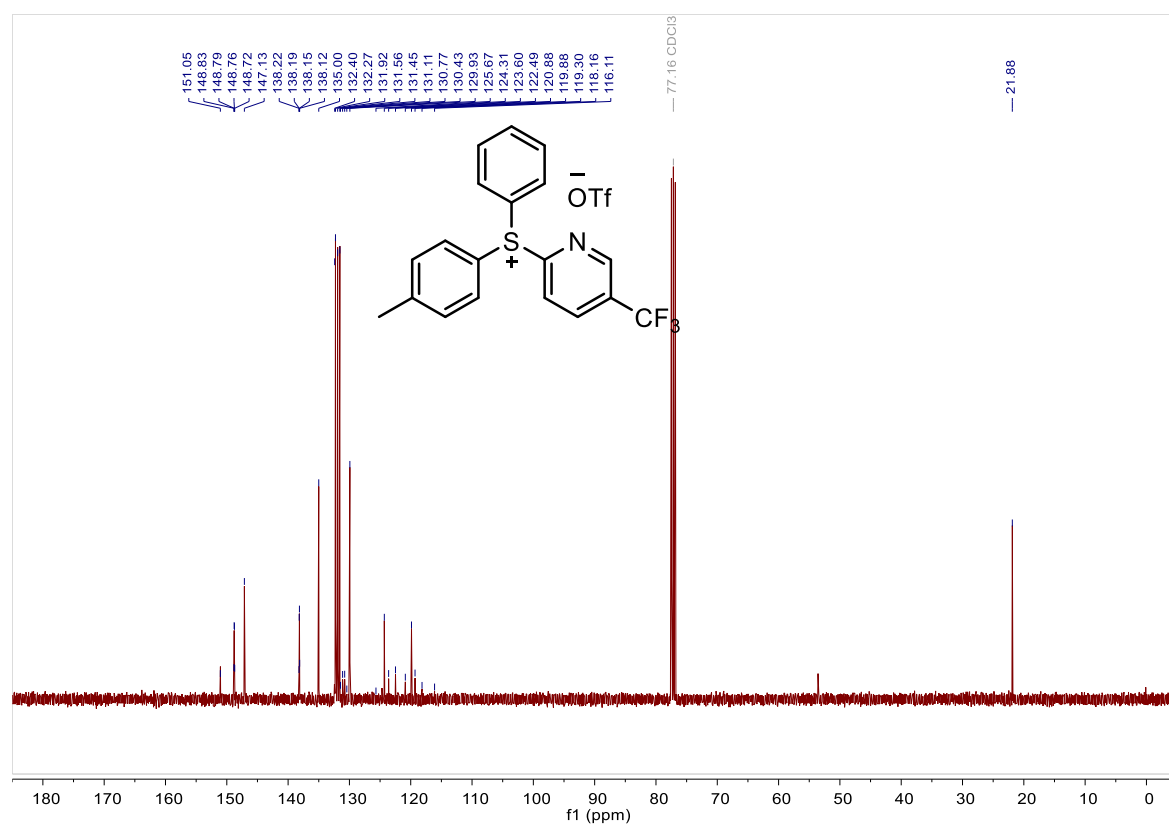
¹³C NMR (101 MHz, CDCl₃): 2e



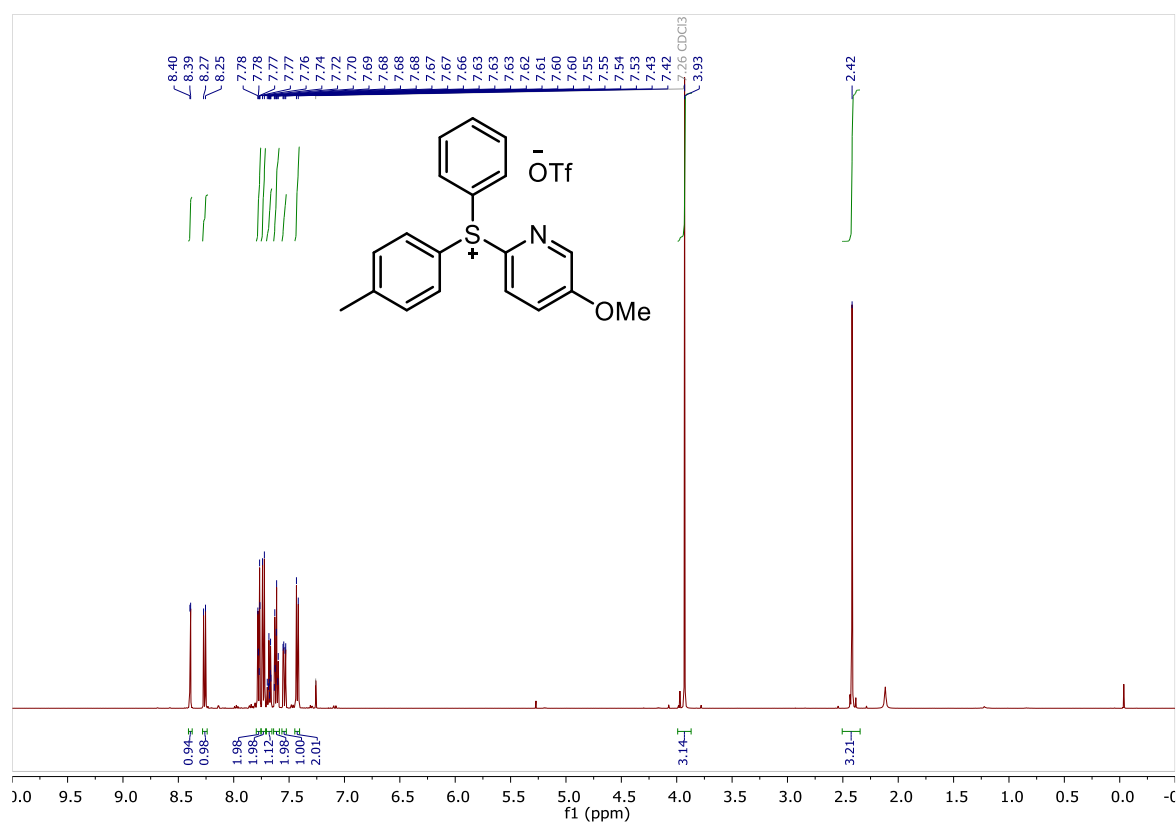
¹H NMR (400 MHz, CDCl₃): 2f



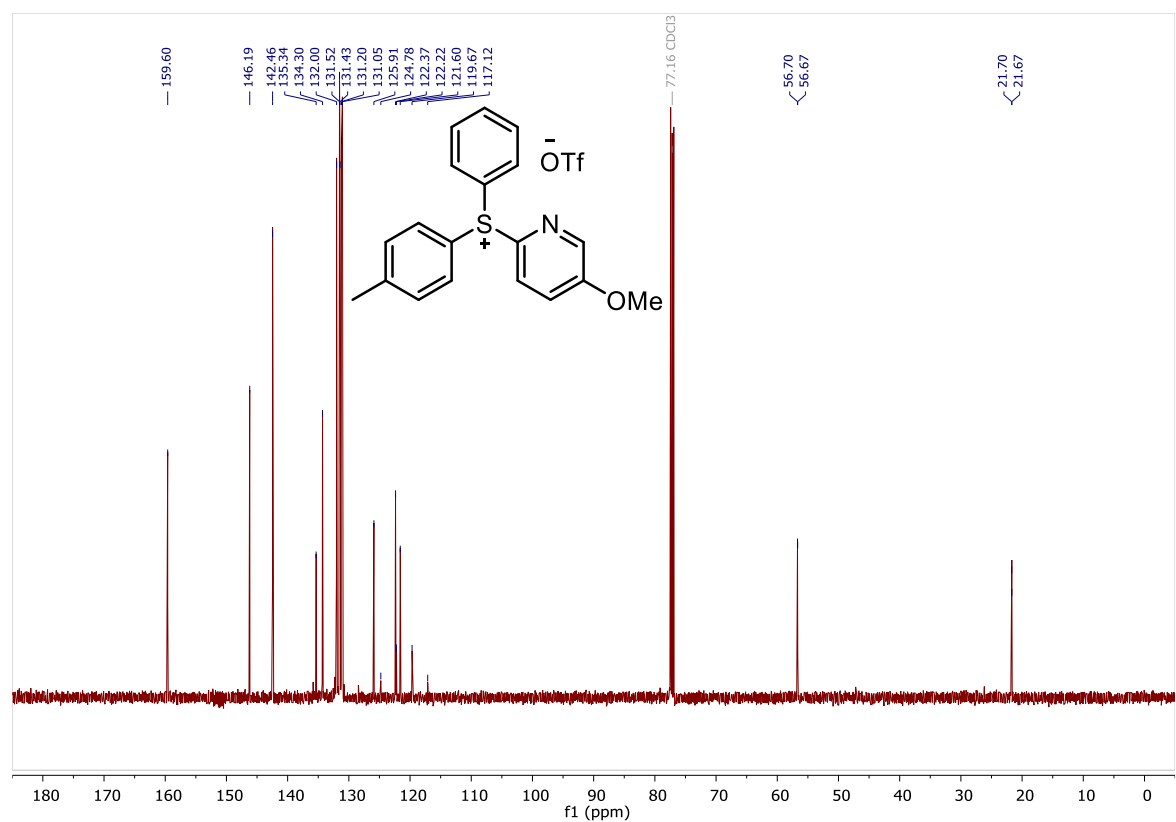
¹³C NMR (101 MHz, CDCl₃): 2f



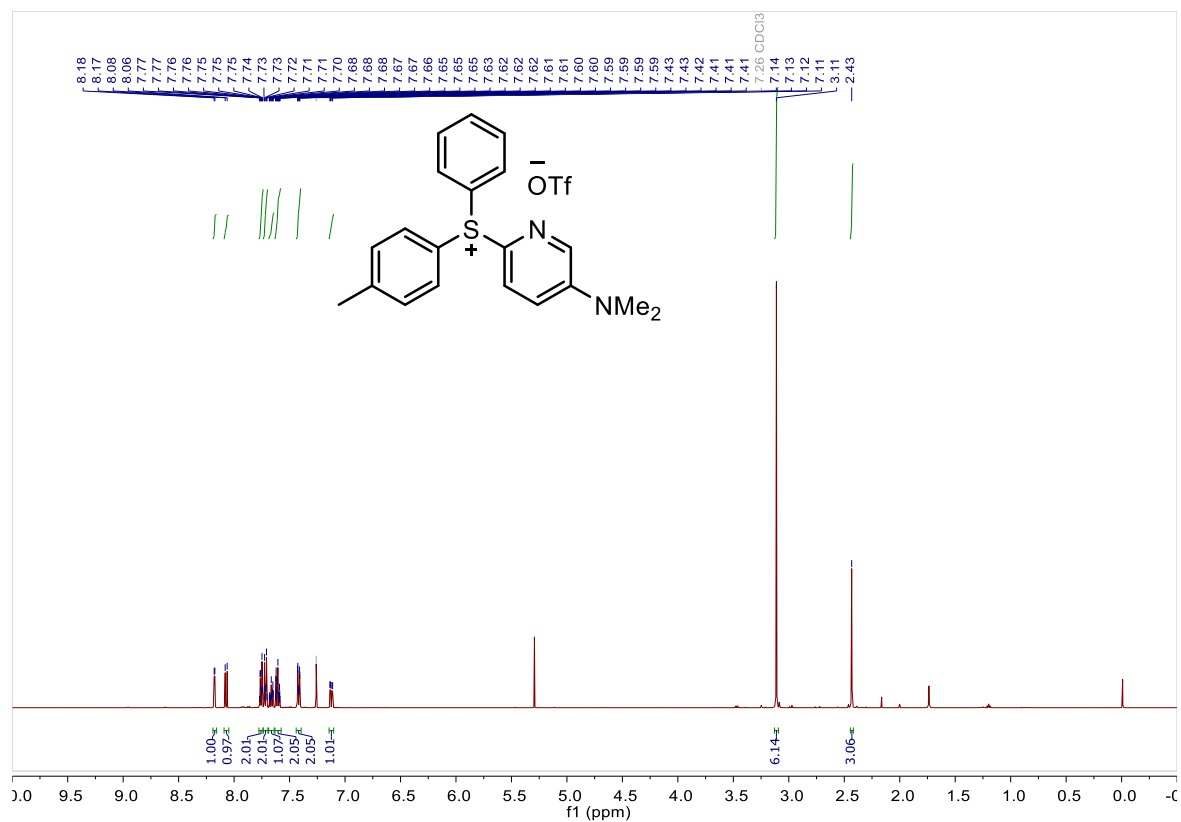
¹H NMR (500 MHz, CDCl₃): 2g



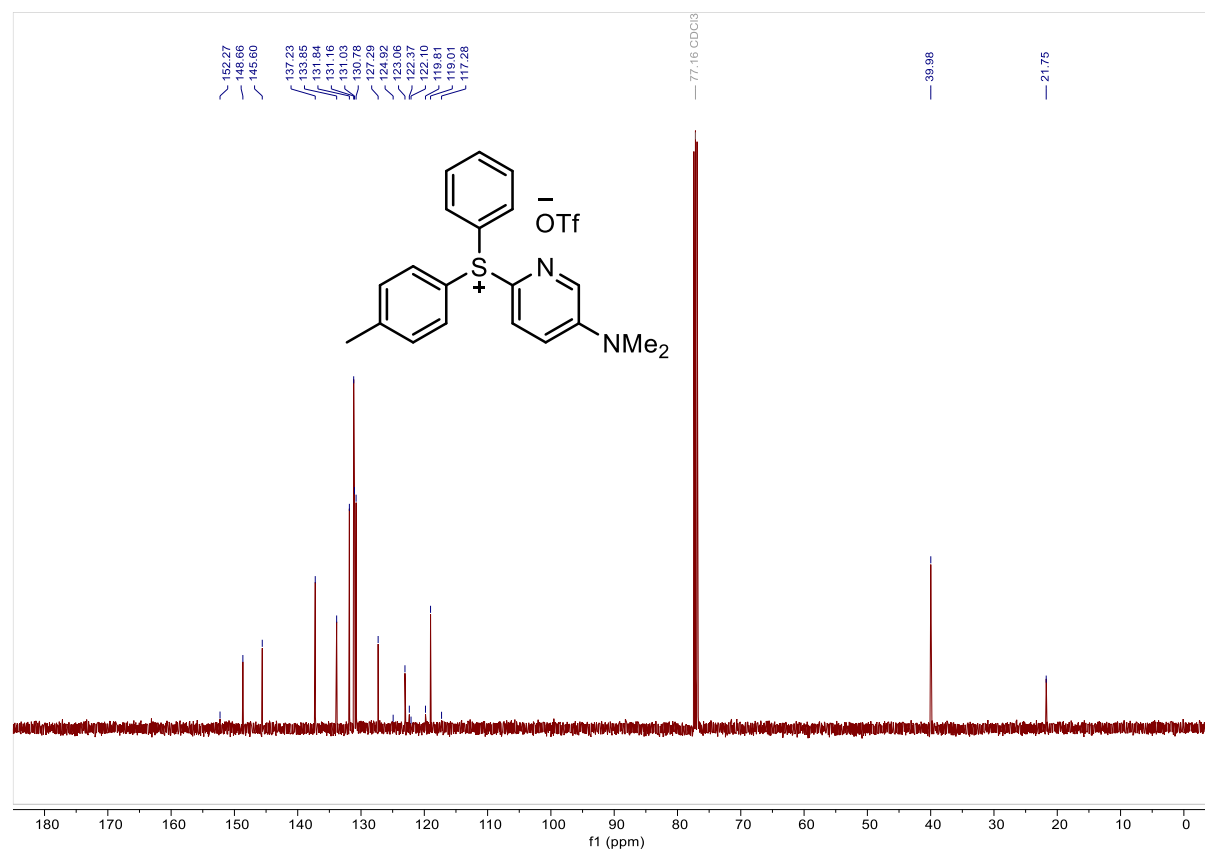
¹³C NMR (126 MHz, CDCl₃): 2g



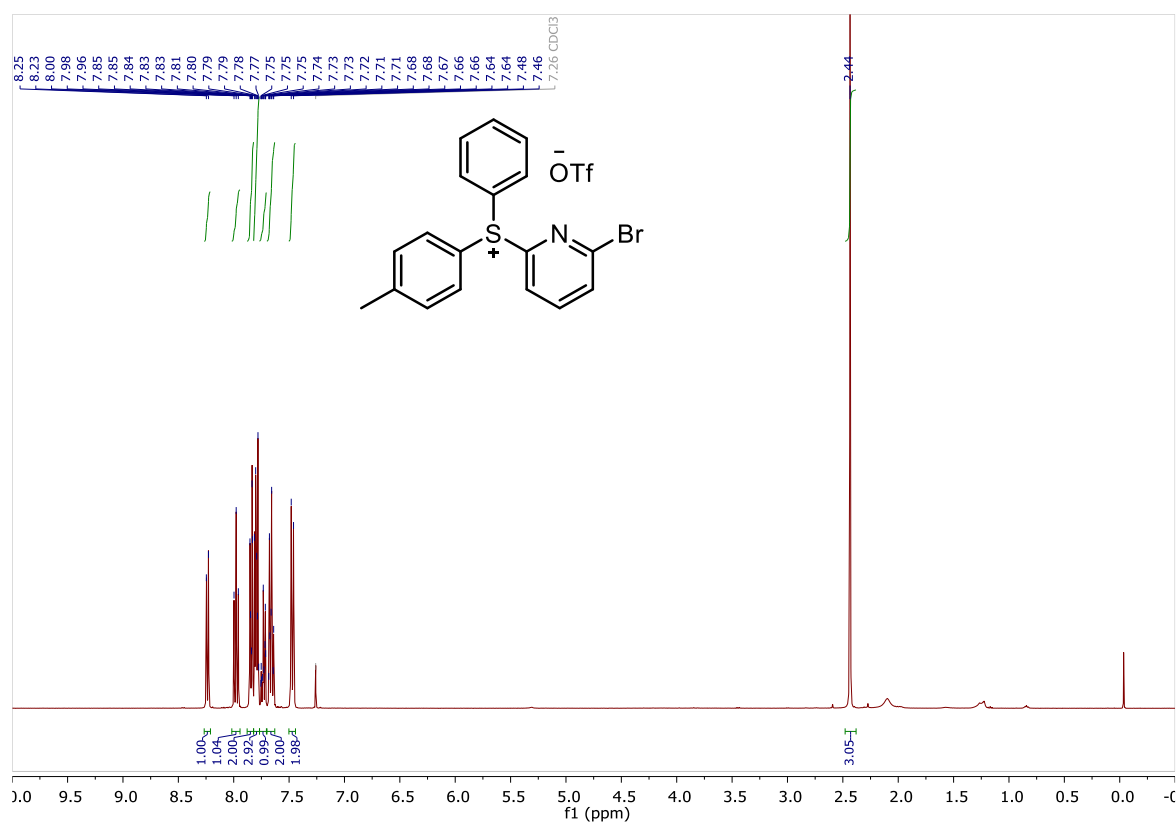
¹H NMR (500 MHz, CDCl₃): 2h



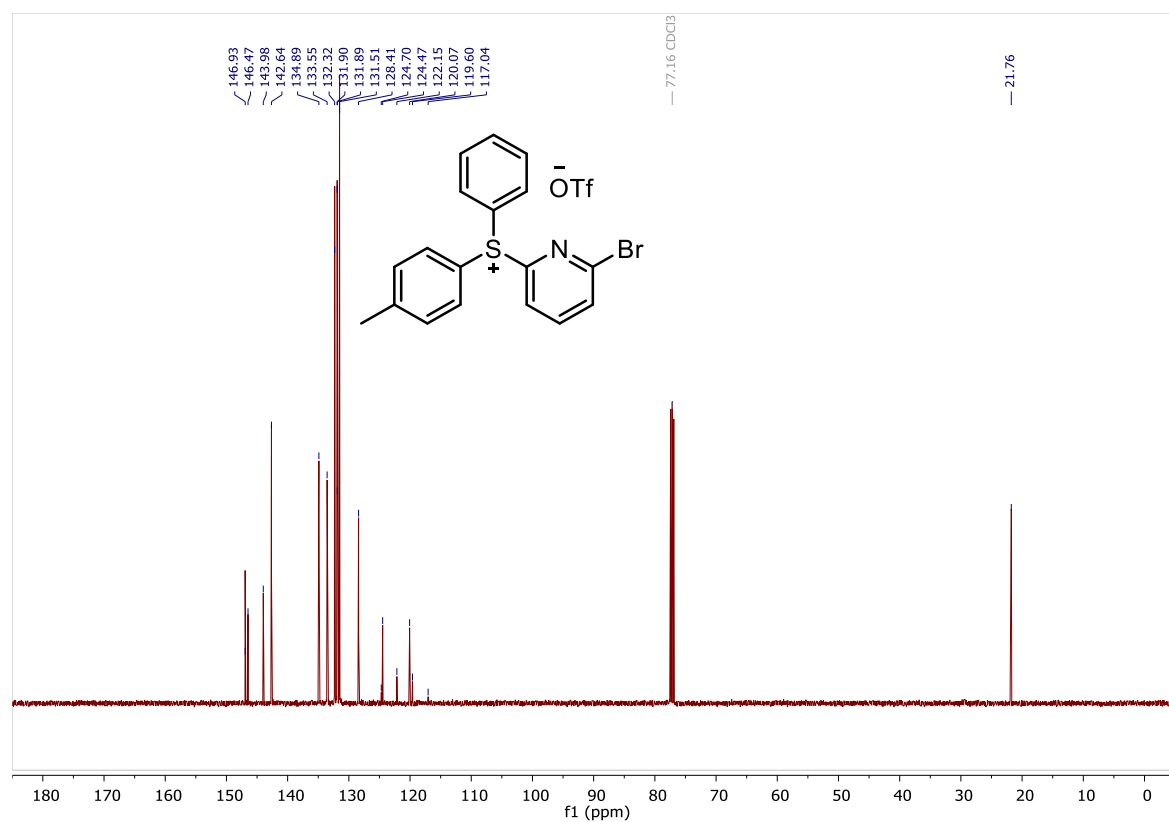
¹³C NMR (126 MHz, CDCl₃): 2h



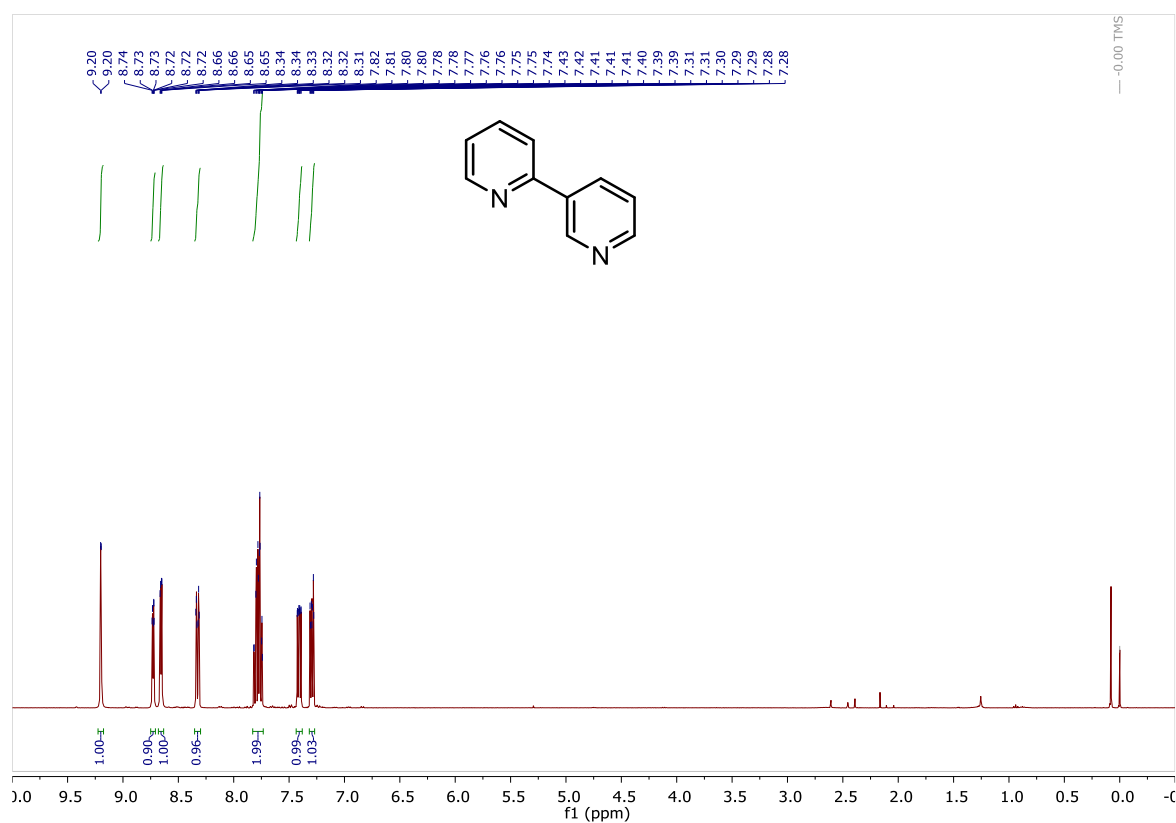
¹H NMR (400 MHz, CDCl₃): 2i



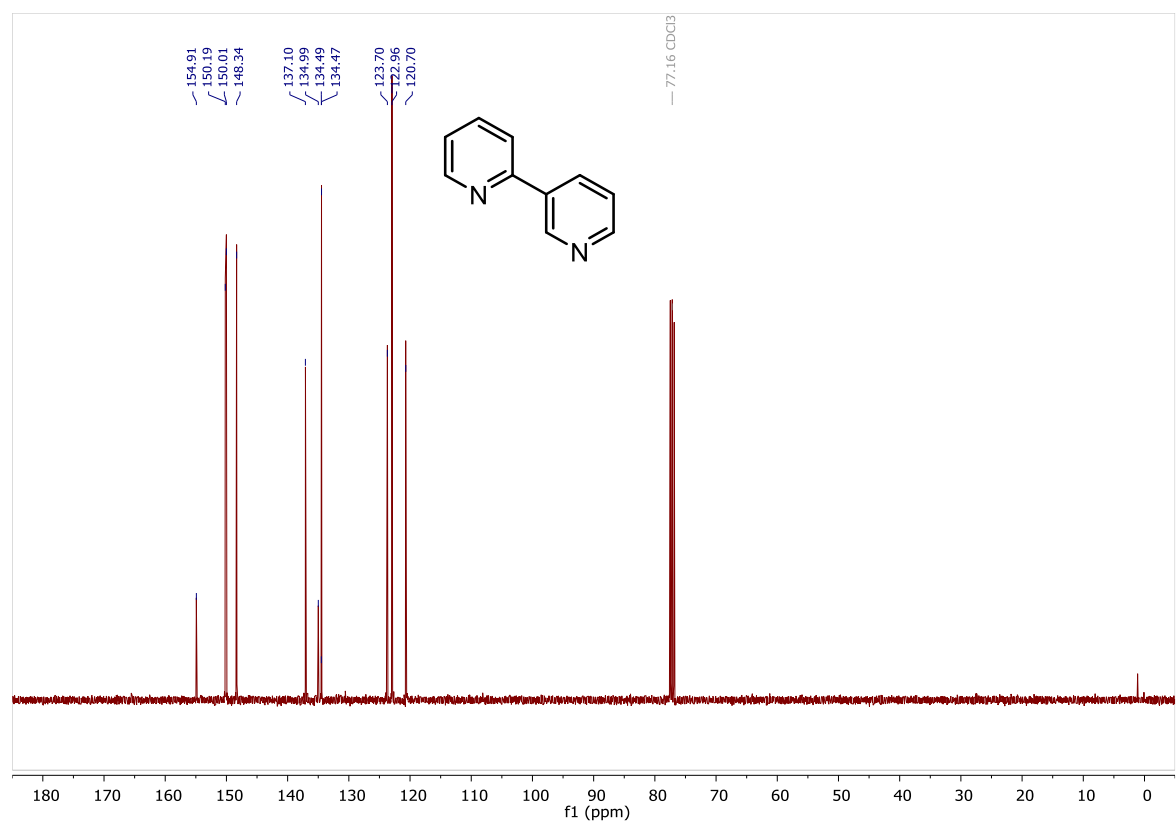
¹³C NMR (126 MHz, CDCl₃): 2i



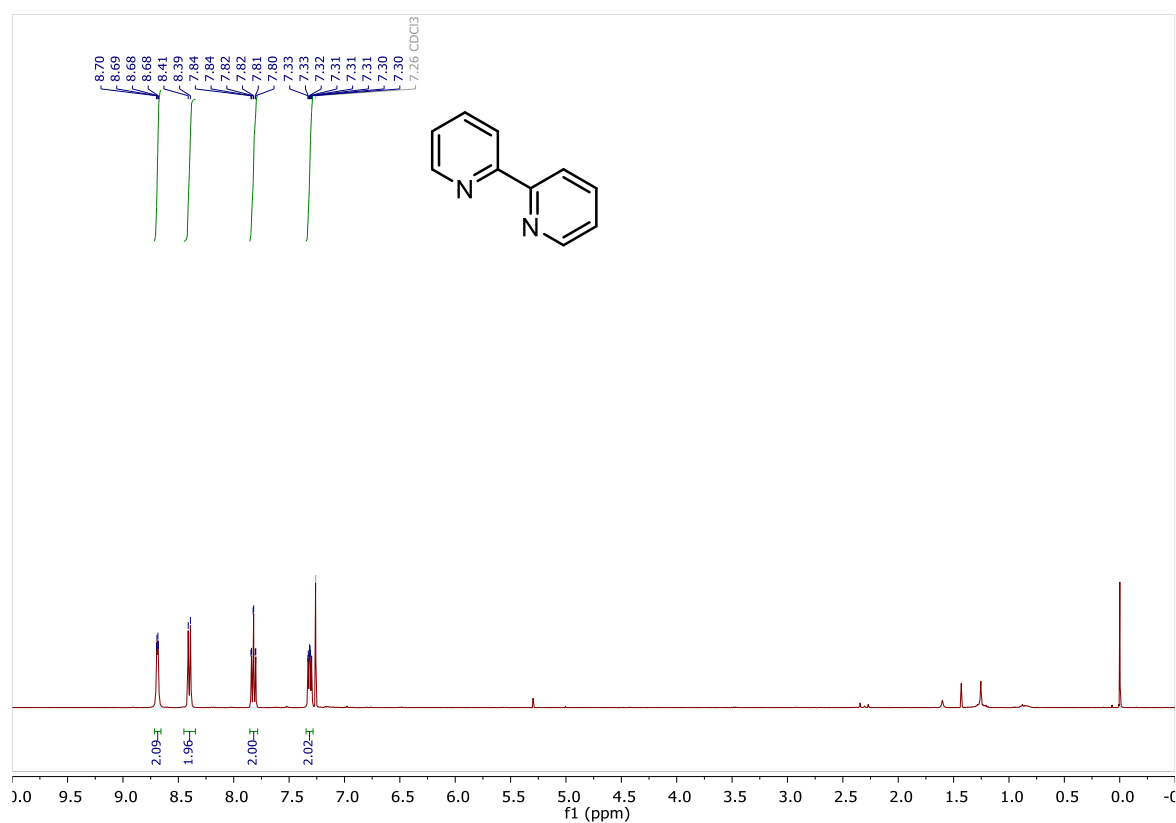
¹H NMR (400 MHz, CDCl₃): 3



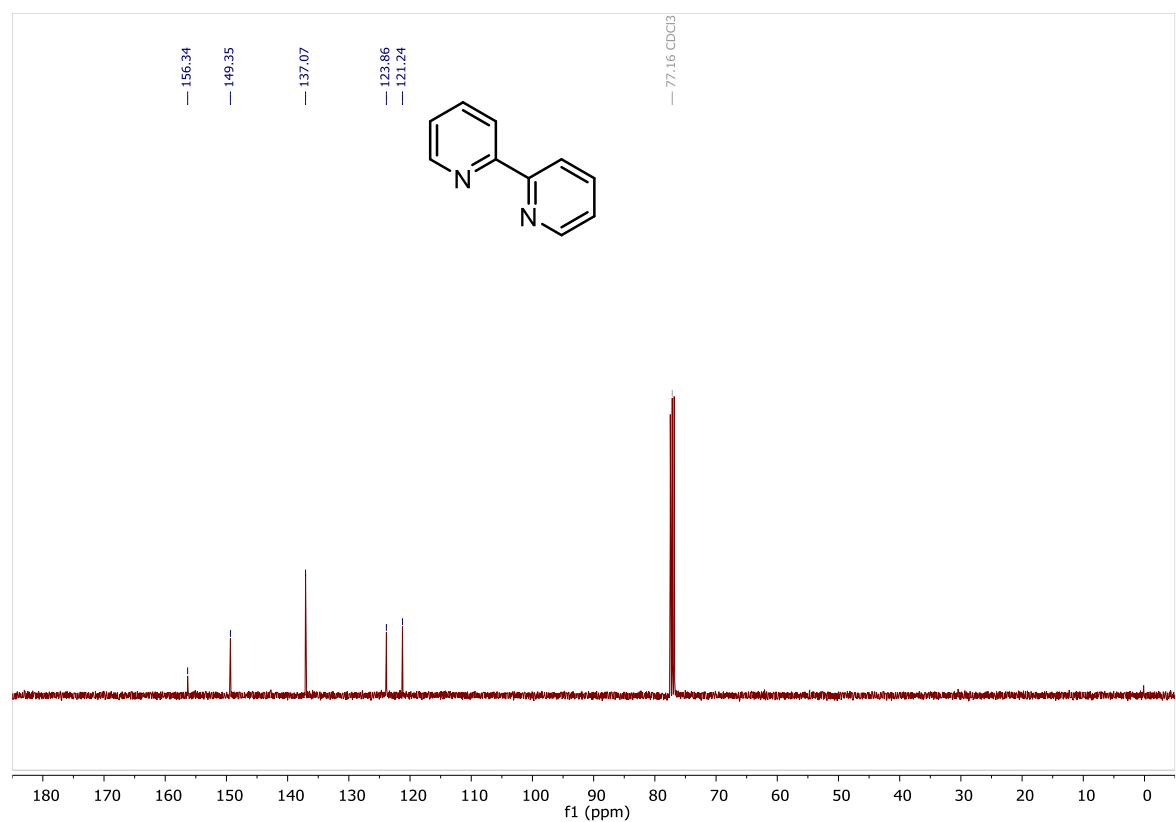
¹³C NMR (101 MHz, CDCl₃): 3



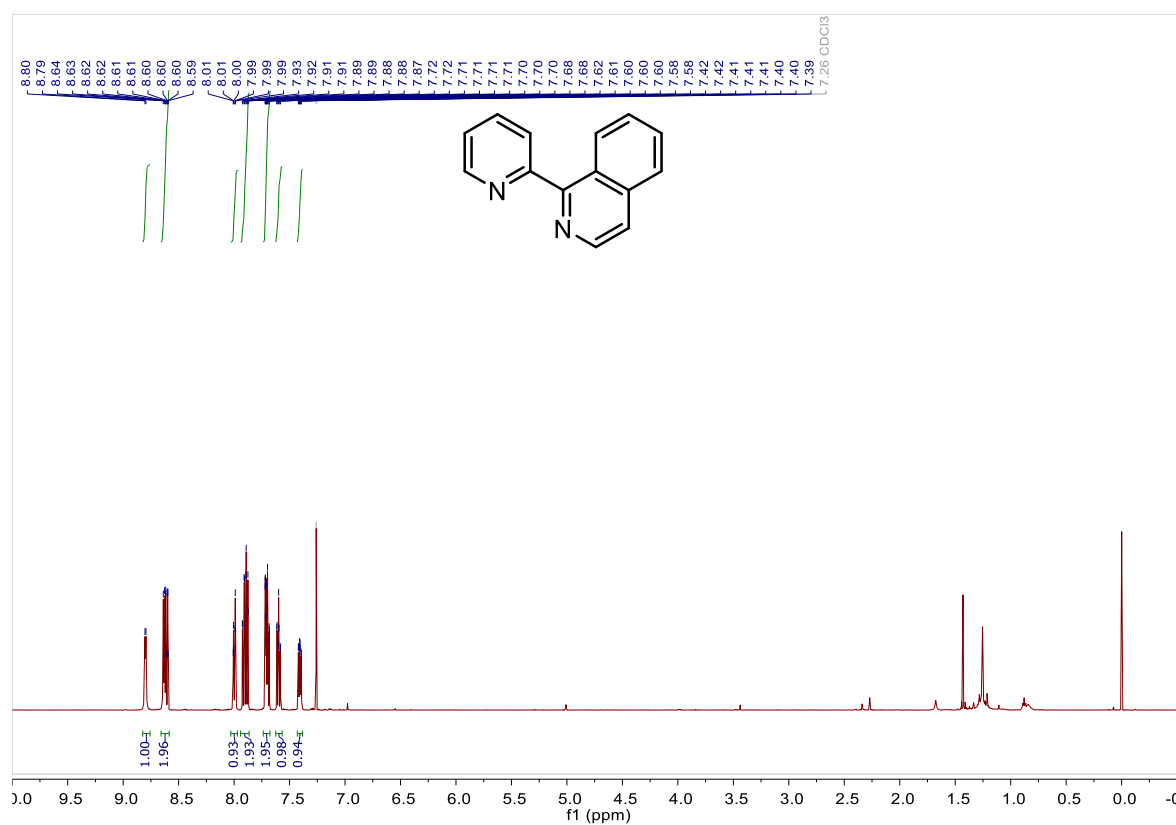
¹H NMR (400 MHz, CDCl₃): 4



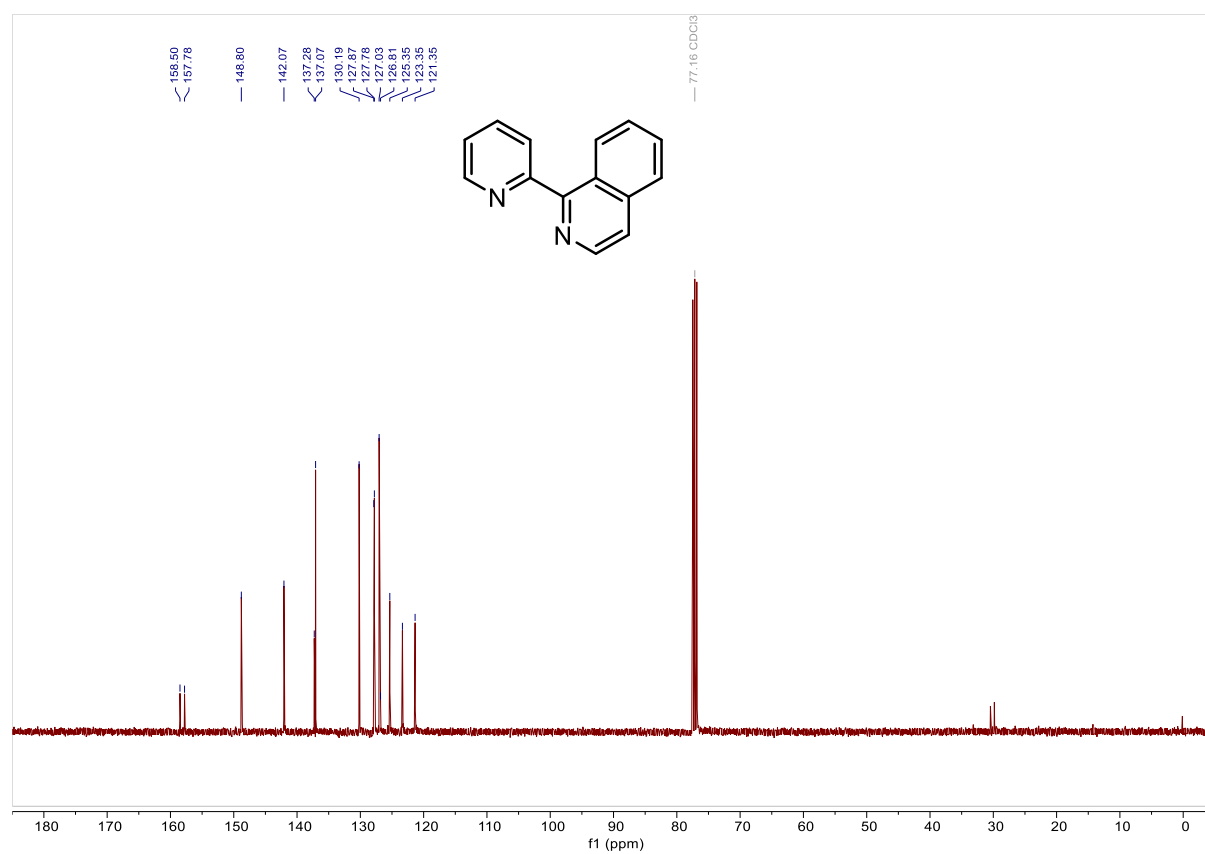
¹³C NMR (101 MHz, CDCl₃): 4



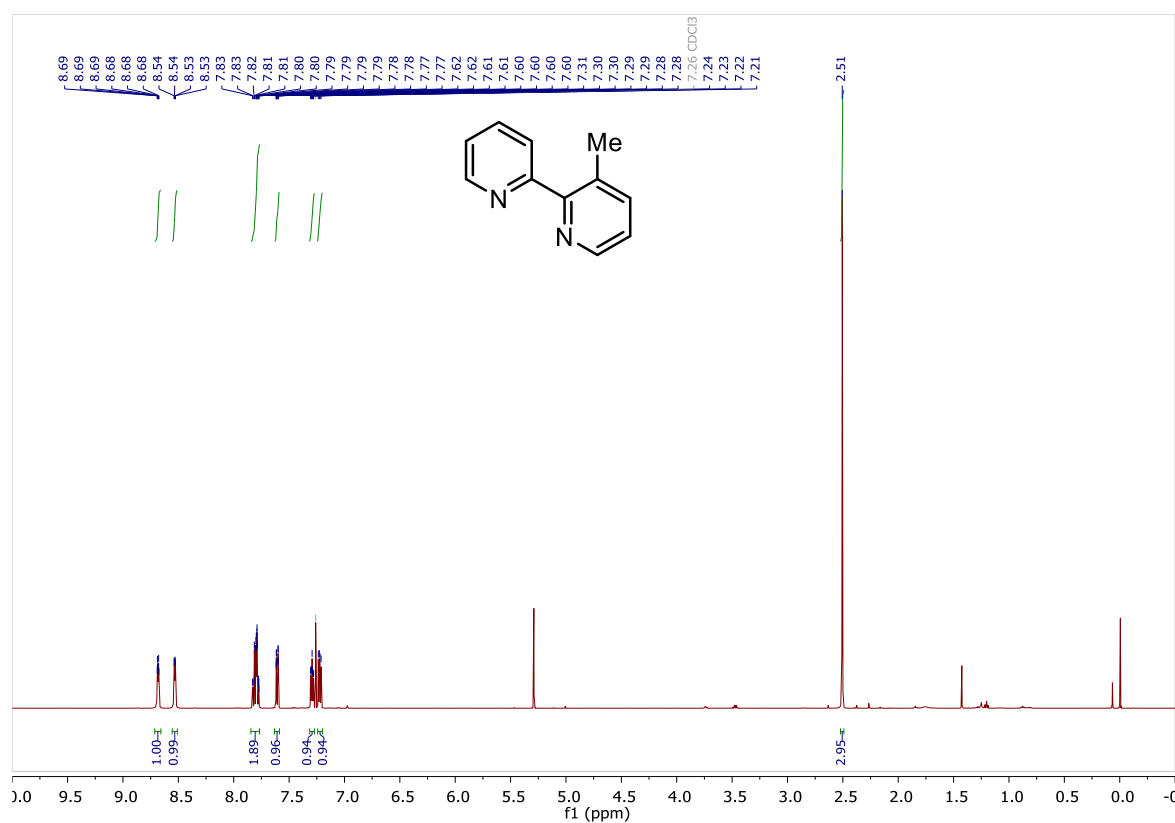
¹H NMR (500 MHz, CDCl₃): 5



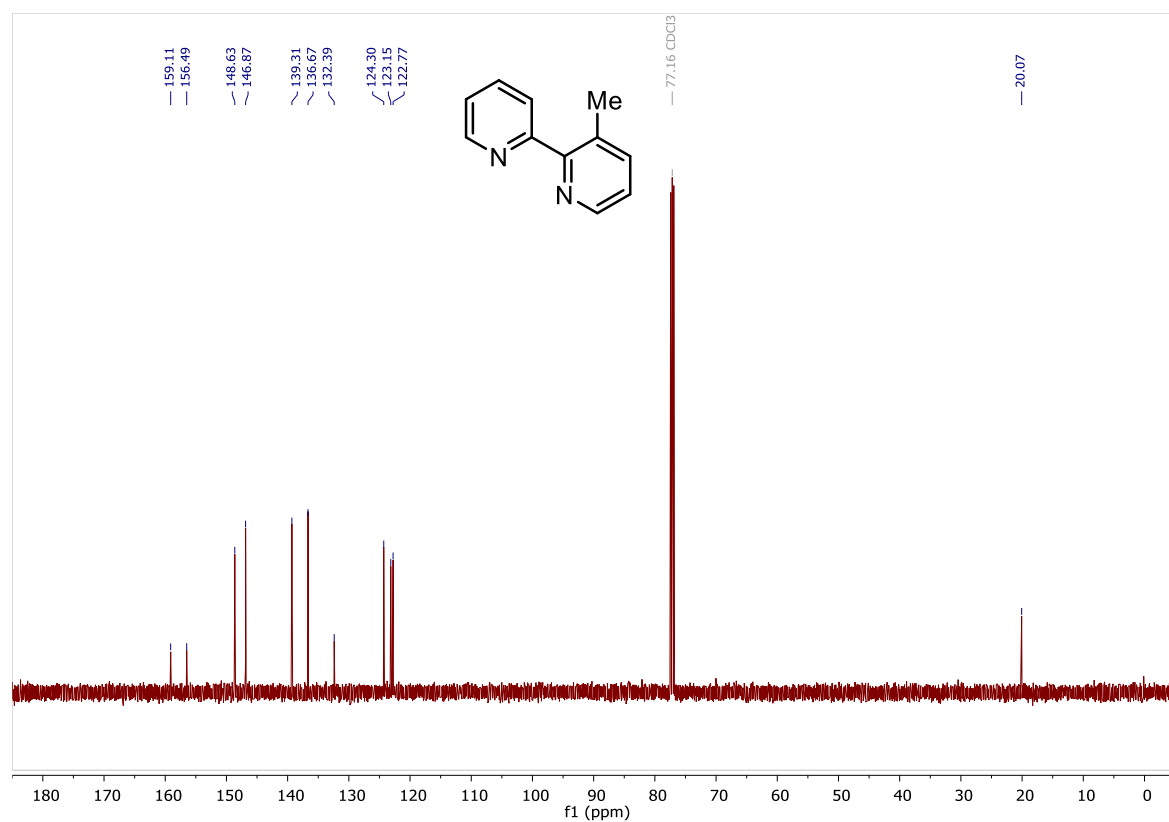
¹³C NMR (101 MHz, CDCl₃): 5



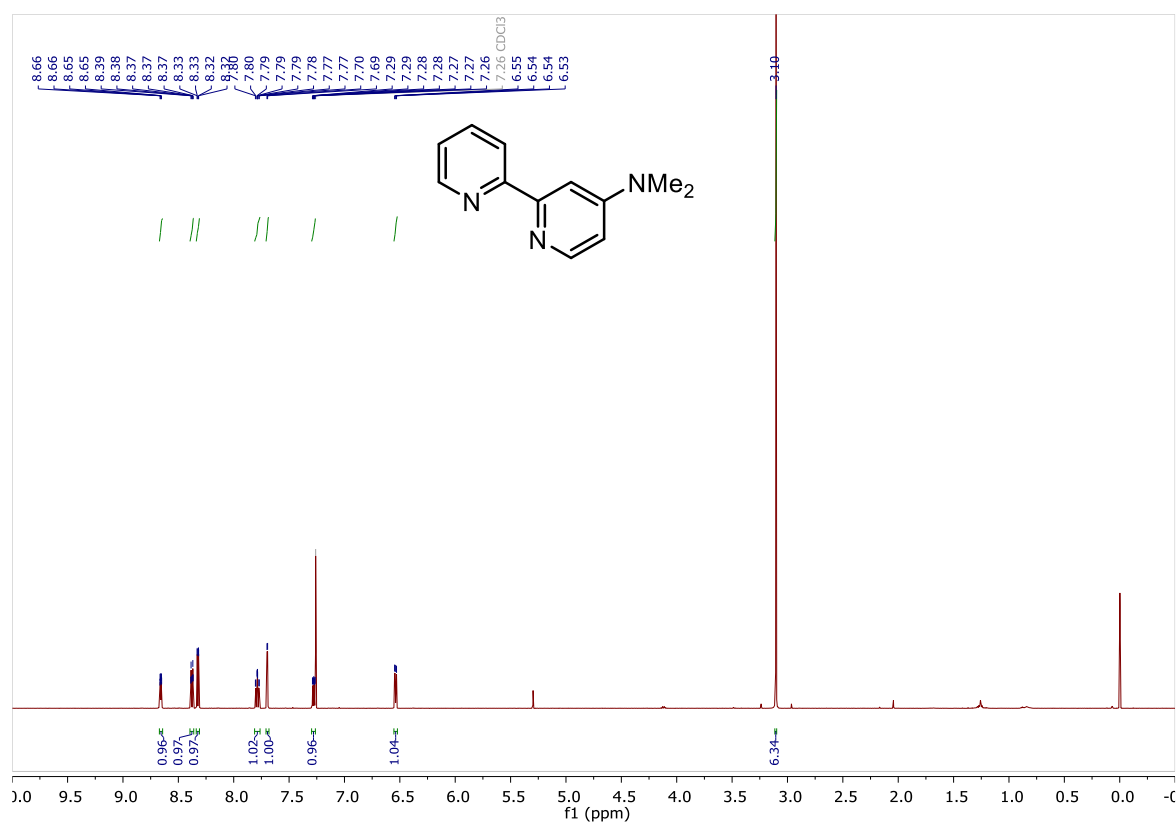
^1H NMR (500 MHz, CDCl_3): 6



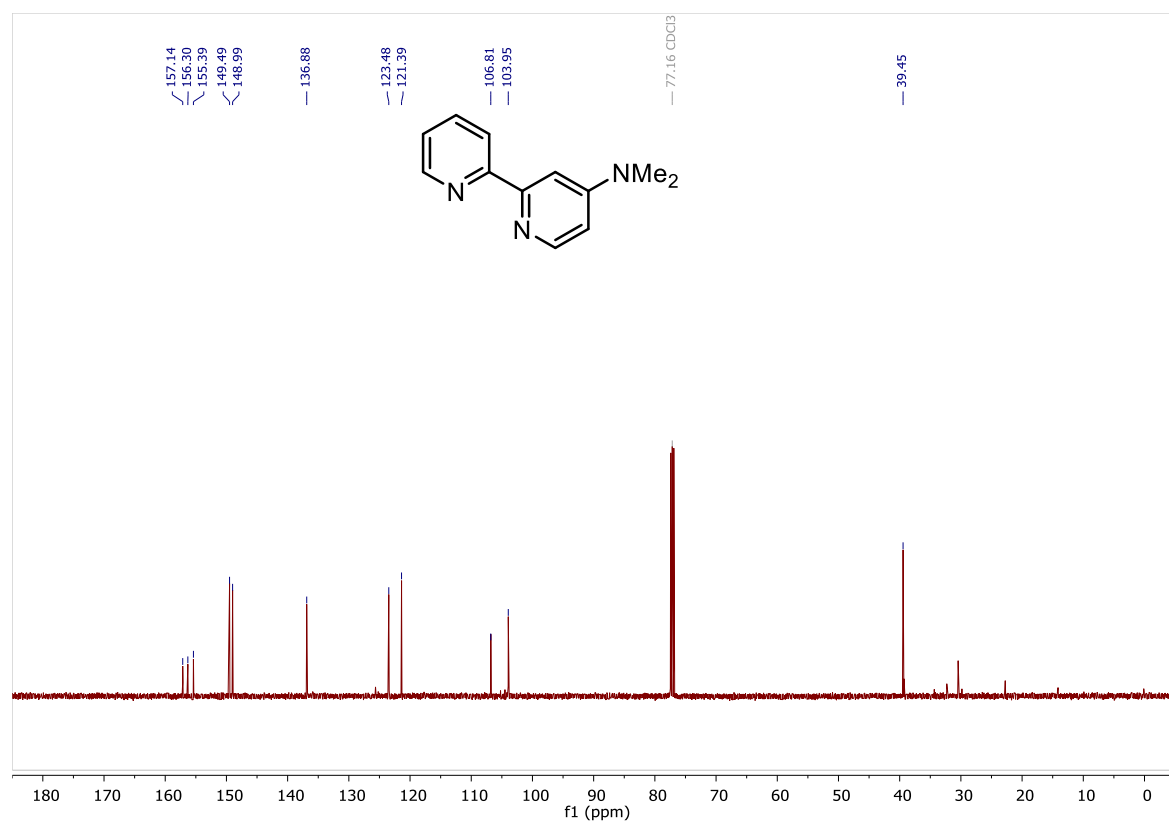
^{13}C NMR (126 MHz, CDCl_3): 6



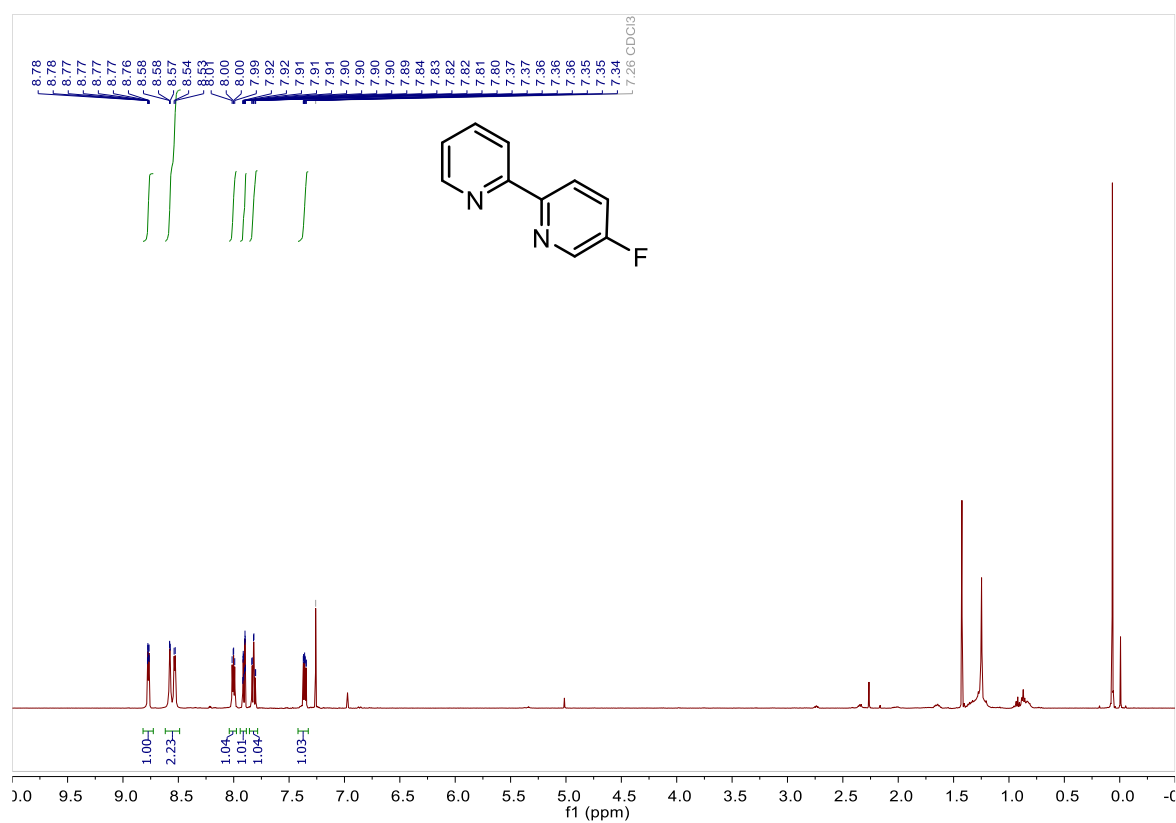
¹H NMR (500 MHz, CDCl₃): 7



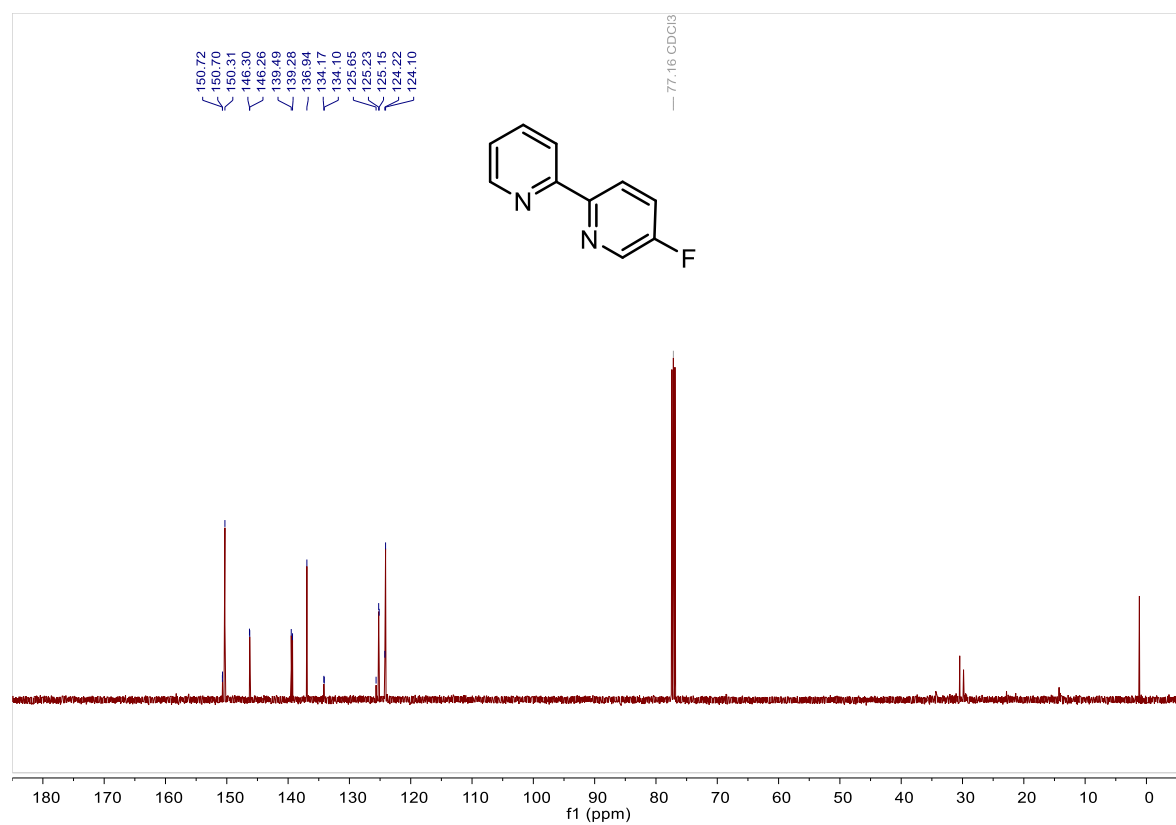
¹³C NMR (126 MHz, CDCl₃): 7



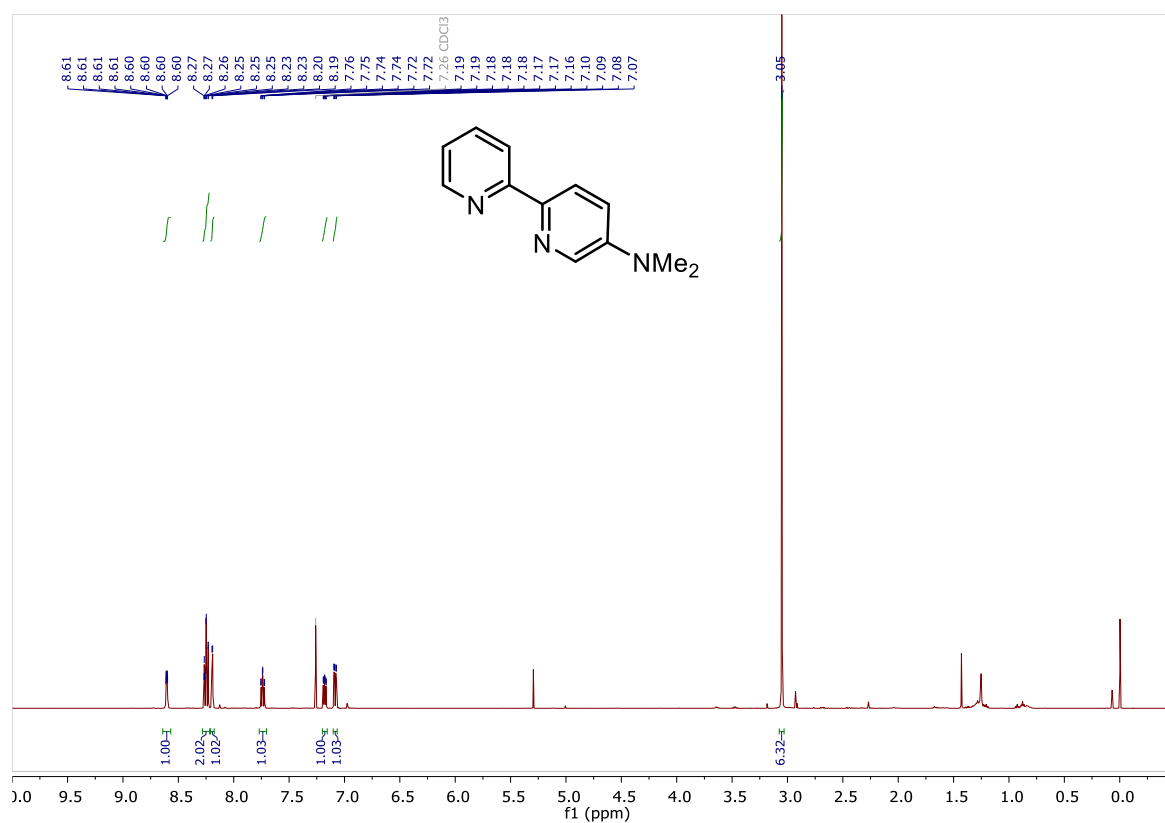
^1H NMR (500 MHz, CDCl_3): 8



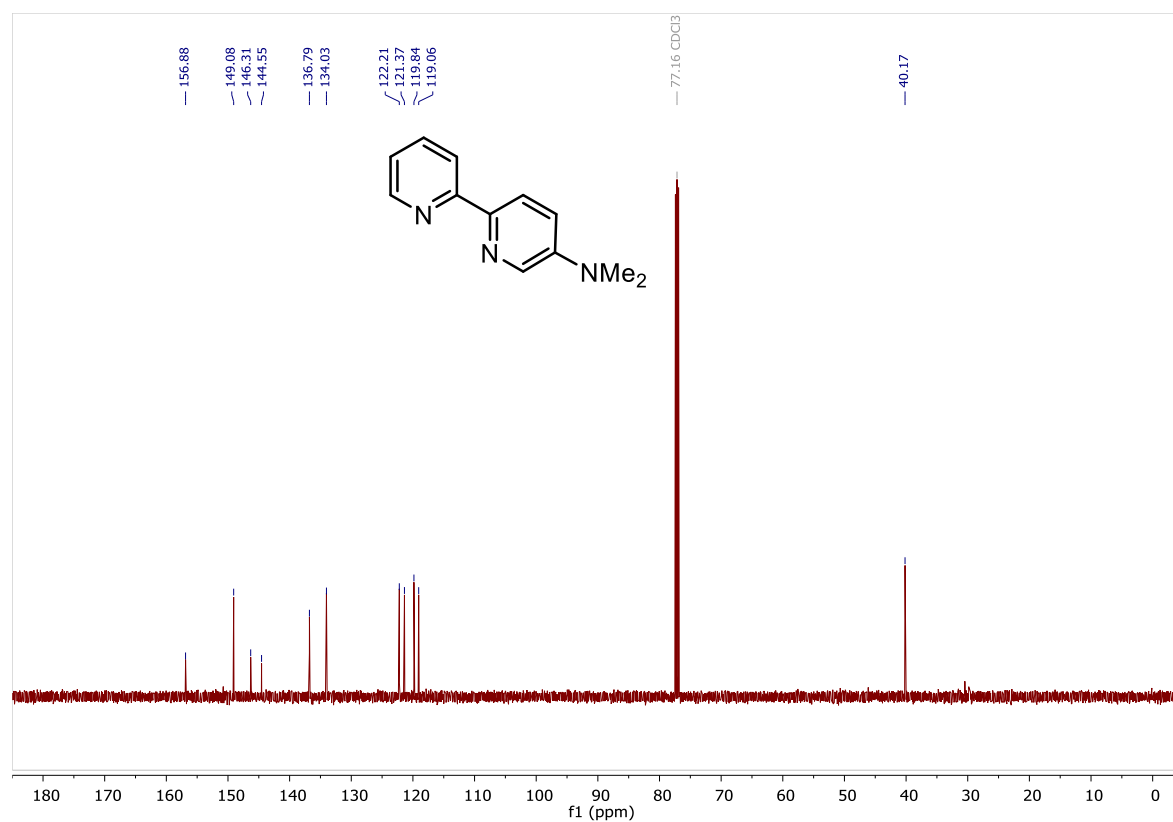
^{13}C NMR (126 MHz, CDCl_3): 8



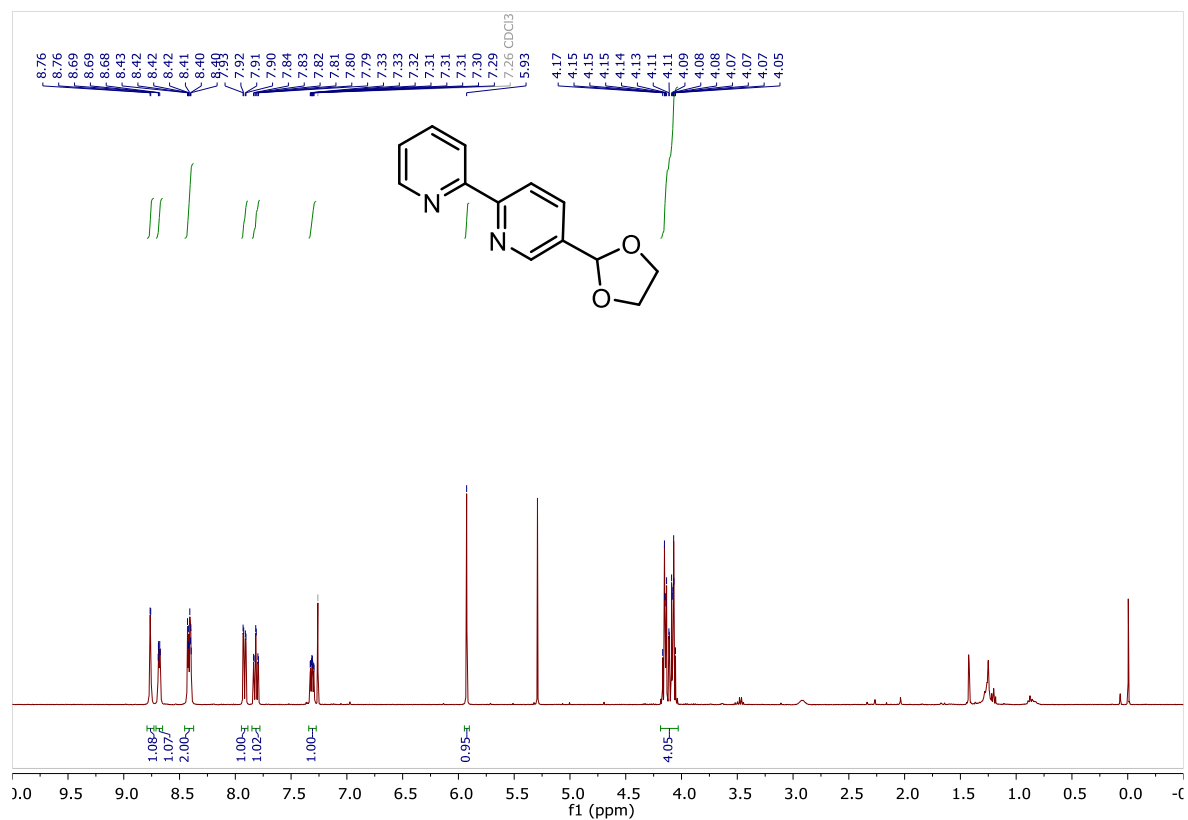
¹H NMR (500 MHz, CDCl₃): 9



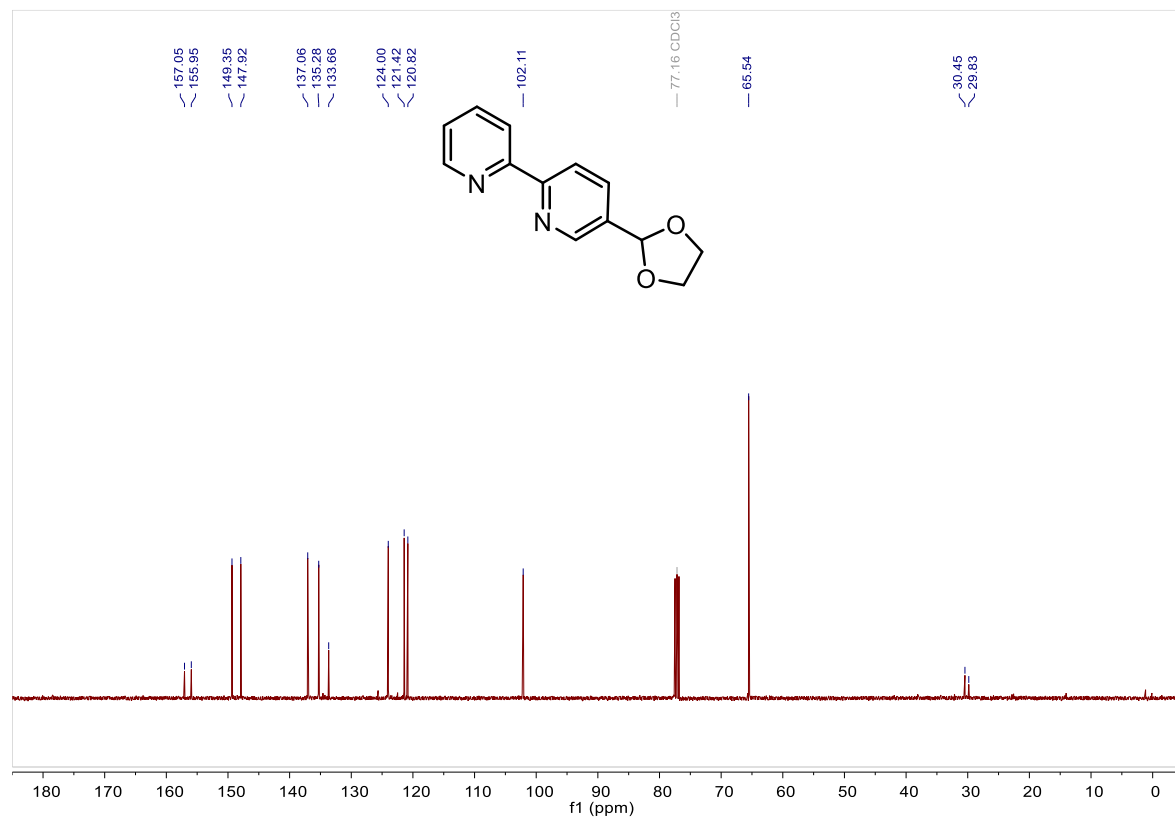
¹³C NMR (126 MHz, CDCl₃): 9



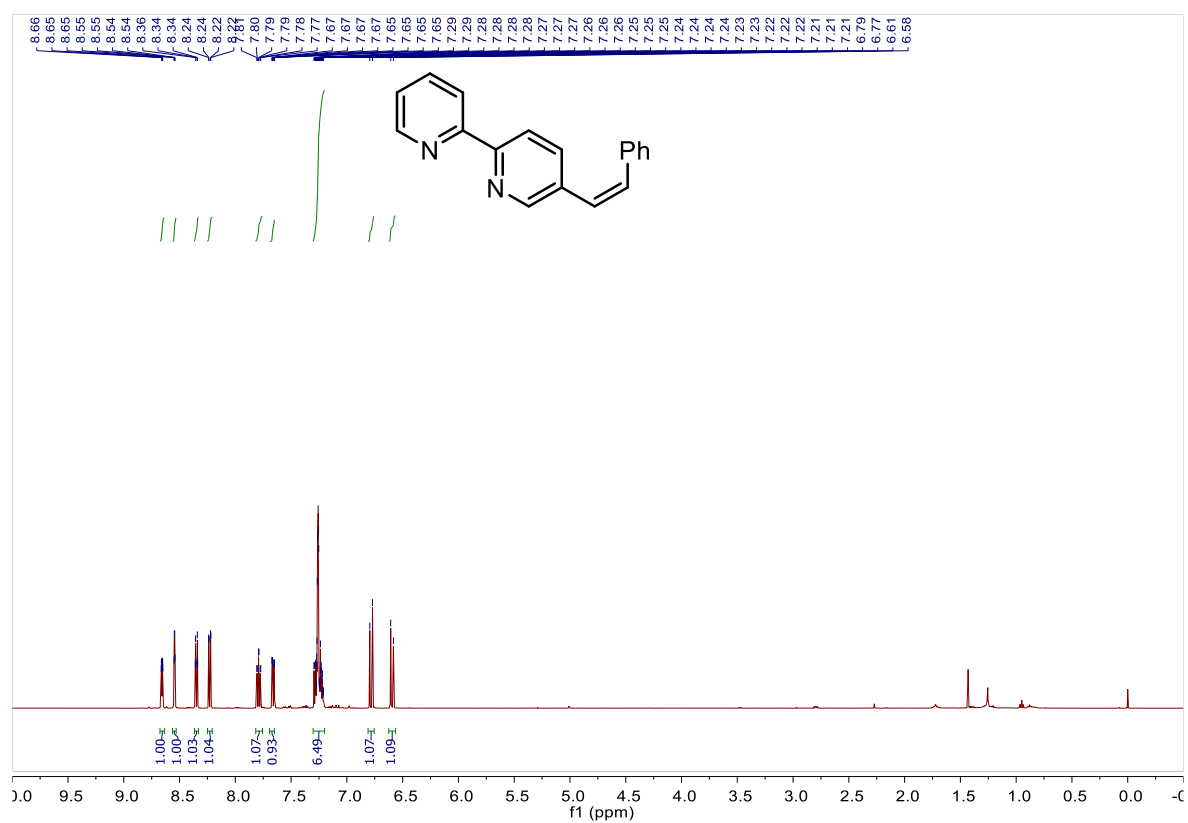
¹H NMR (400 MHz, CDCl₃): 10



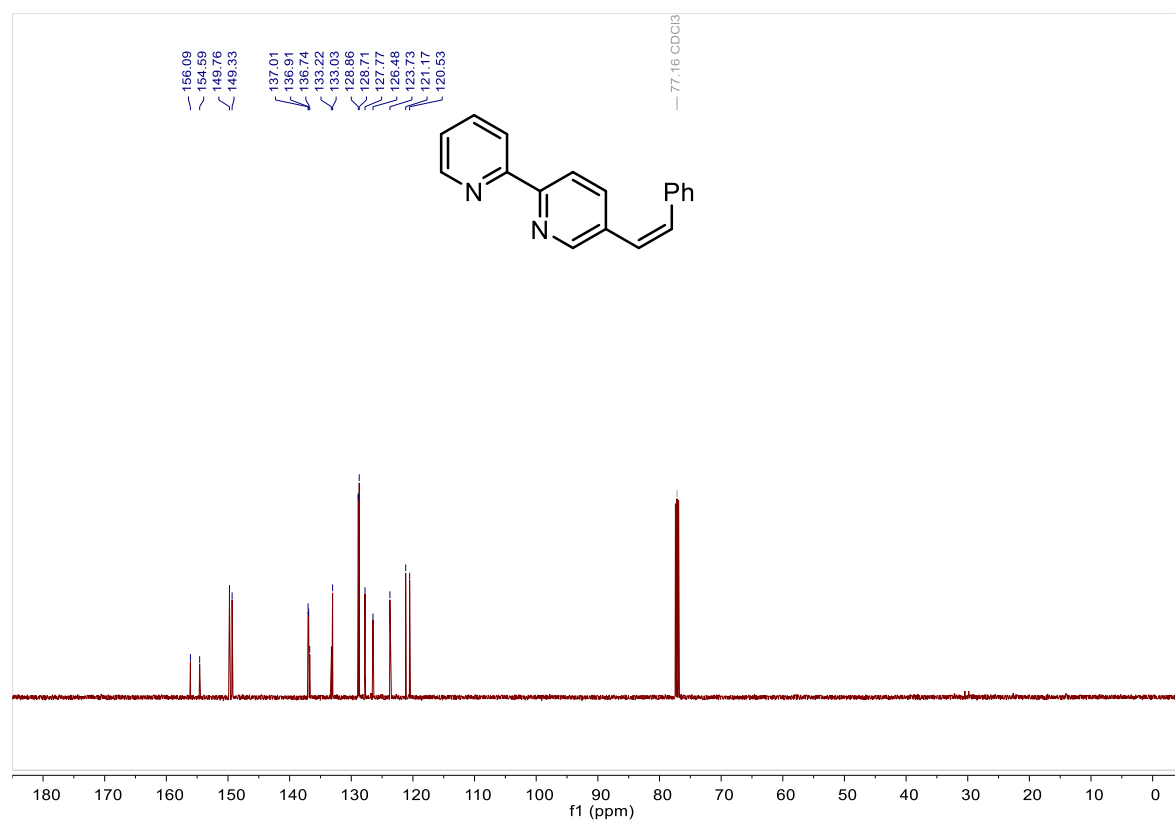
¹³C NMR (101 MHz, CDCl₃): 10



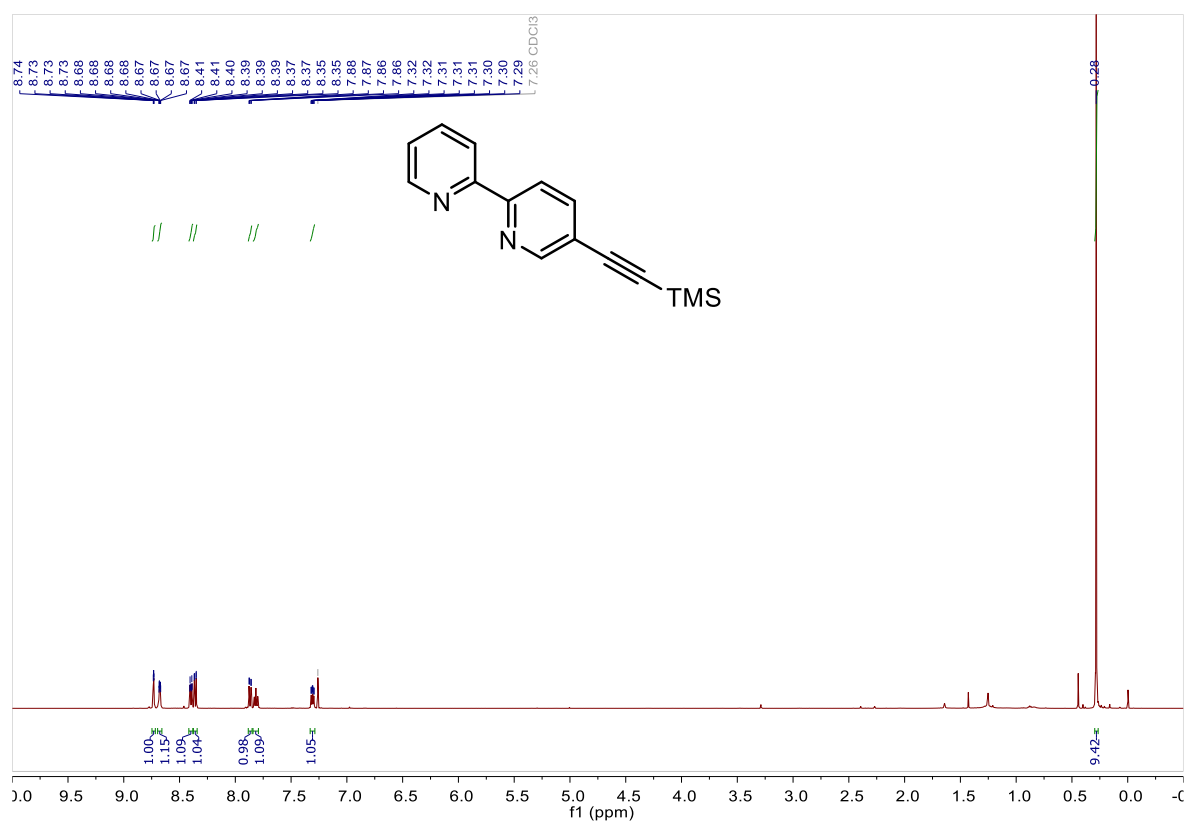
¹H NMR (500 MHz, CDCl₃): 11



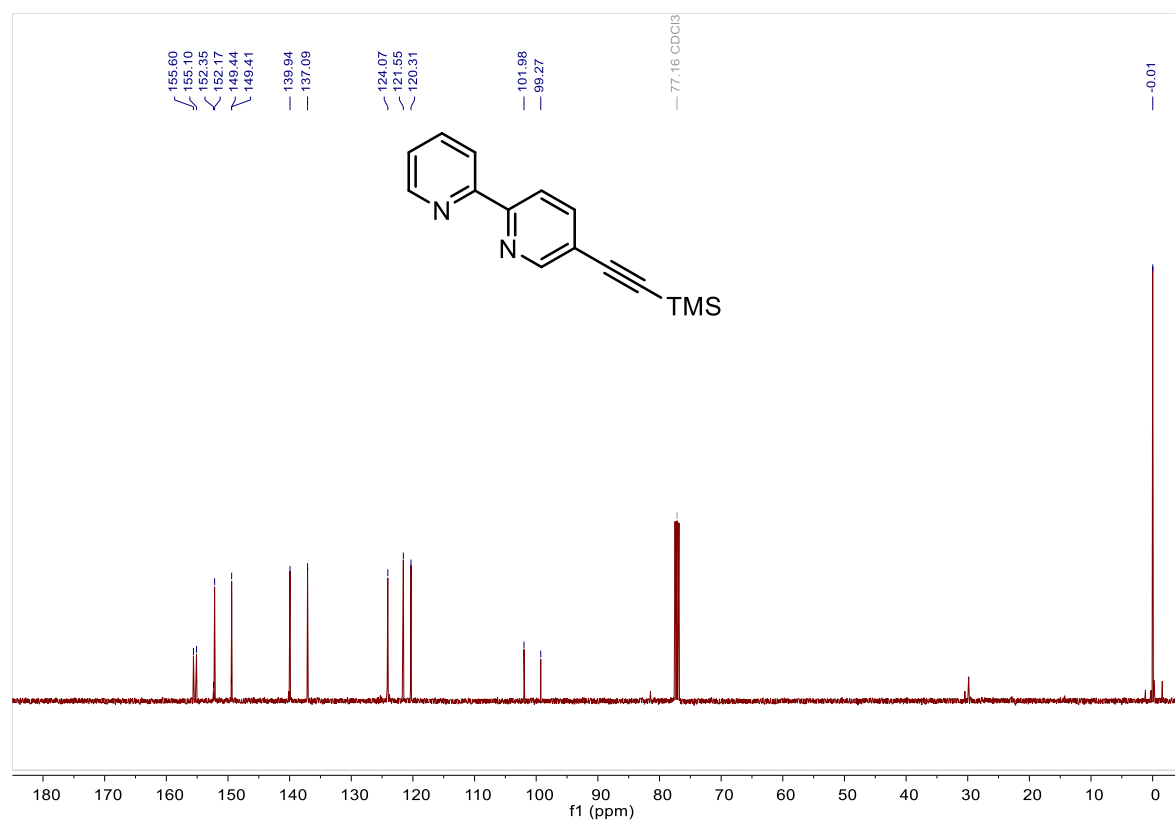
¹³C NMR (126 MHz, CDCl₃): 11



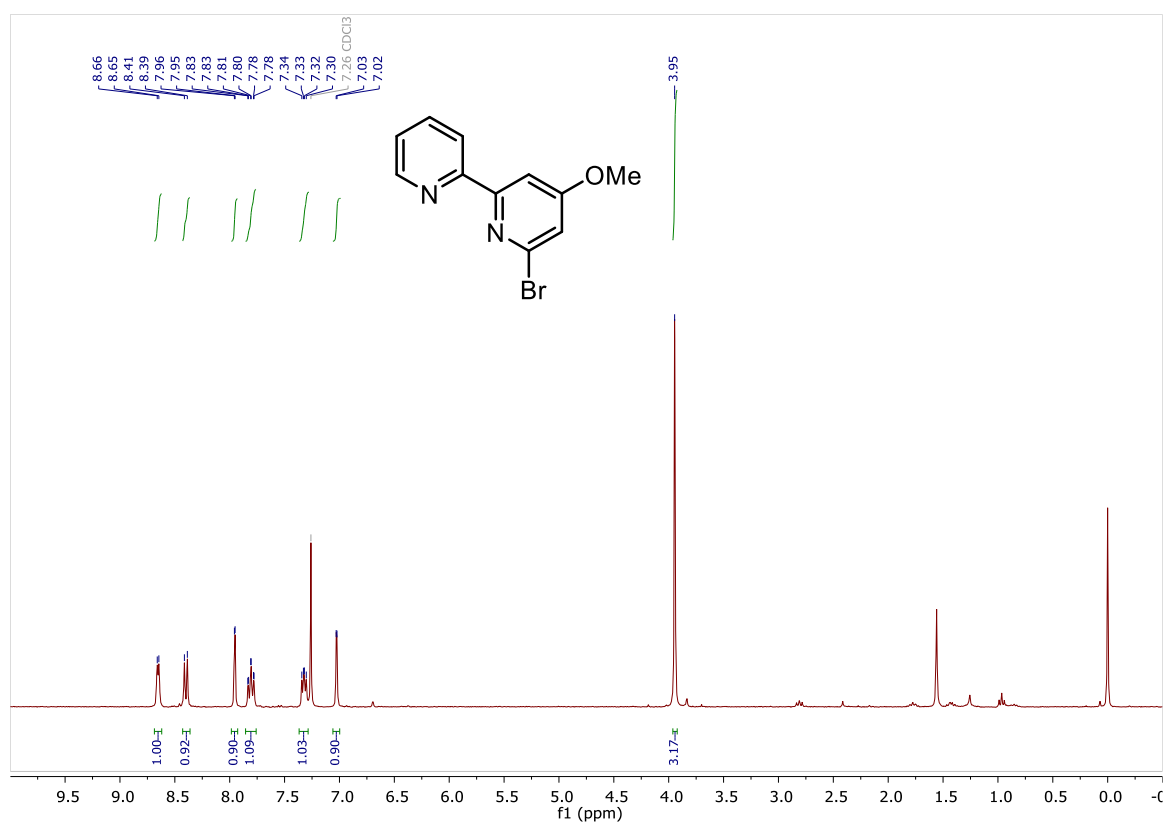
¹H NMR (500 MHz, CDCl₃): 12



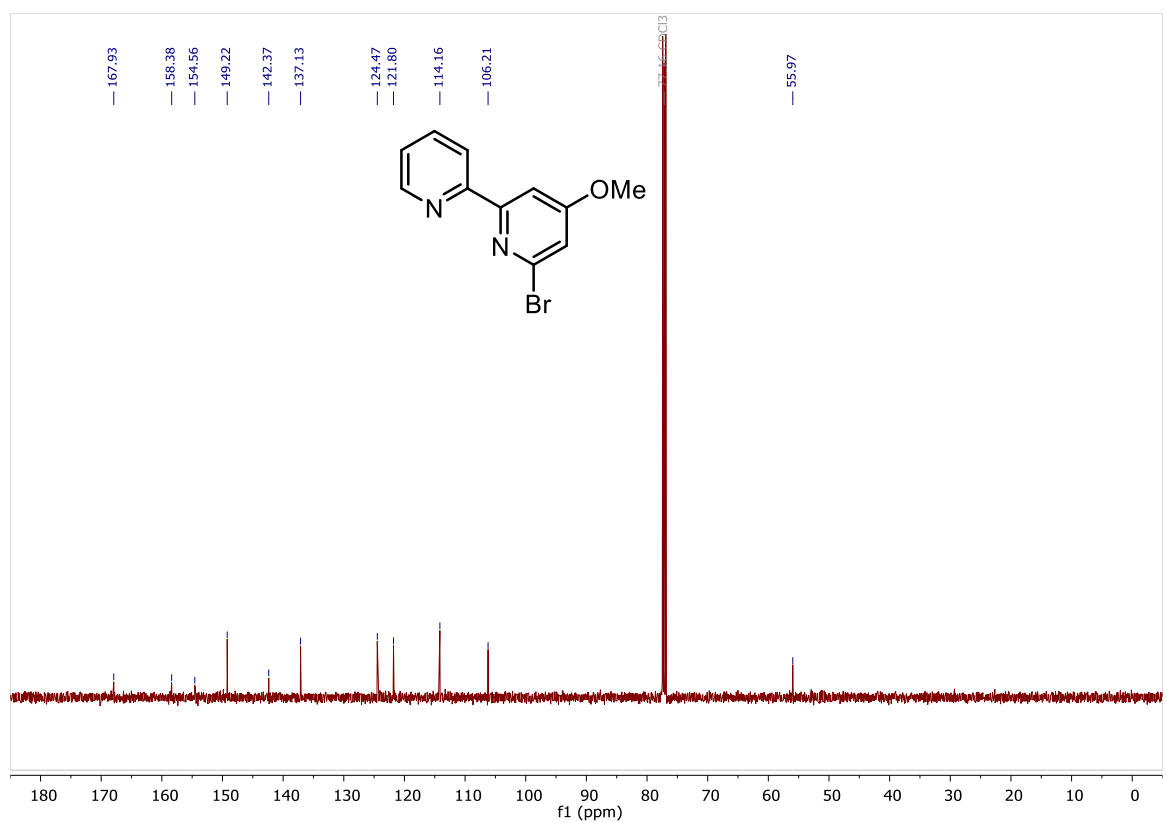
¹³C NMR (101 MHz, CDCl₃): 12



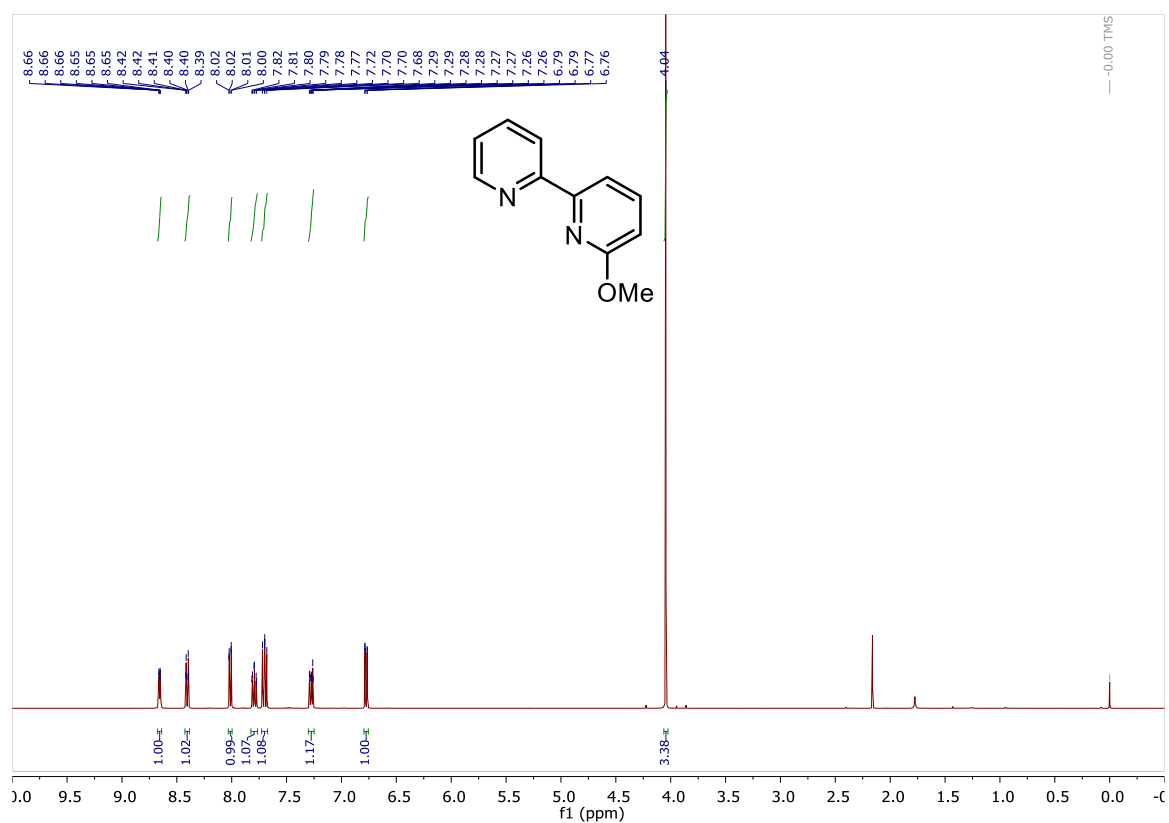
^1H NMR (300 MHz, CDCl_3): 13



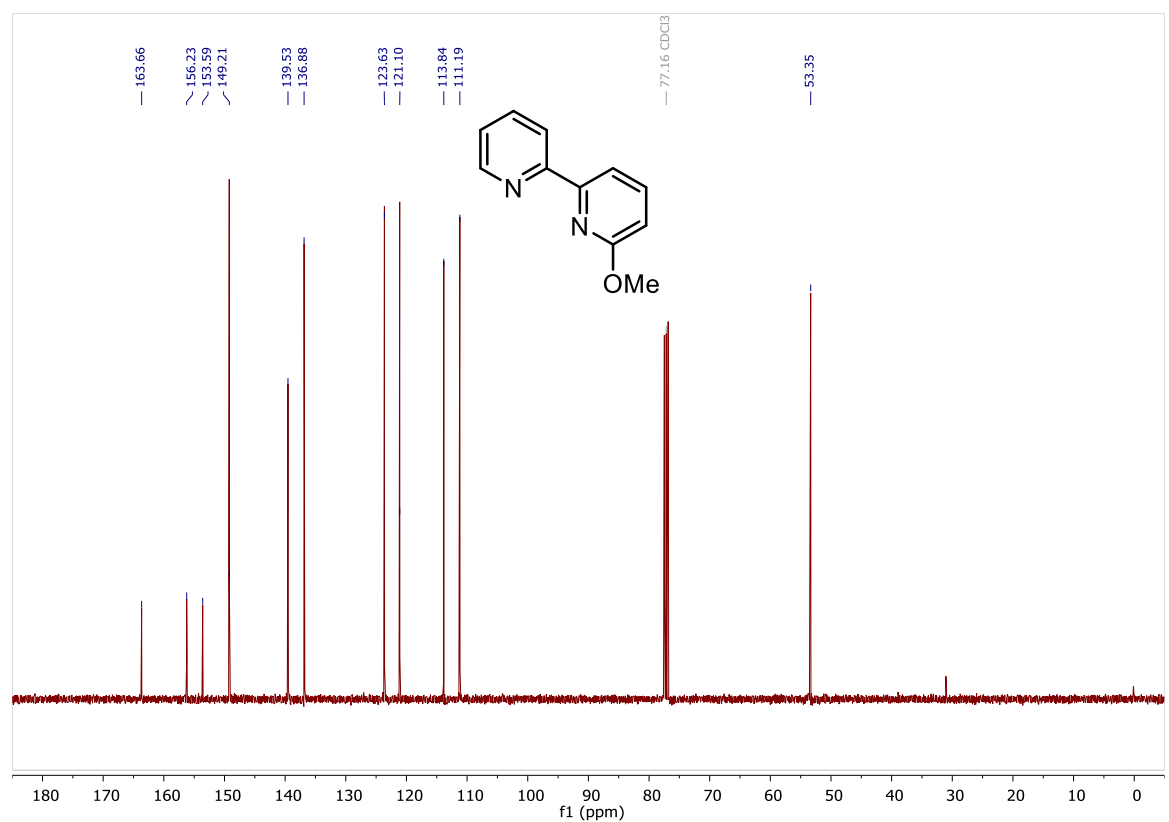
^{13}C NMR (126 MHz, CDCl_3): 13



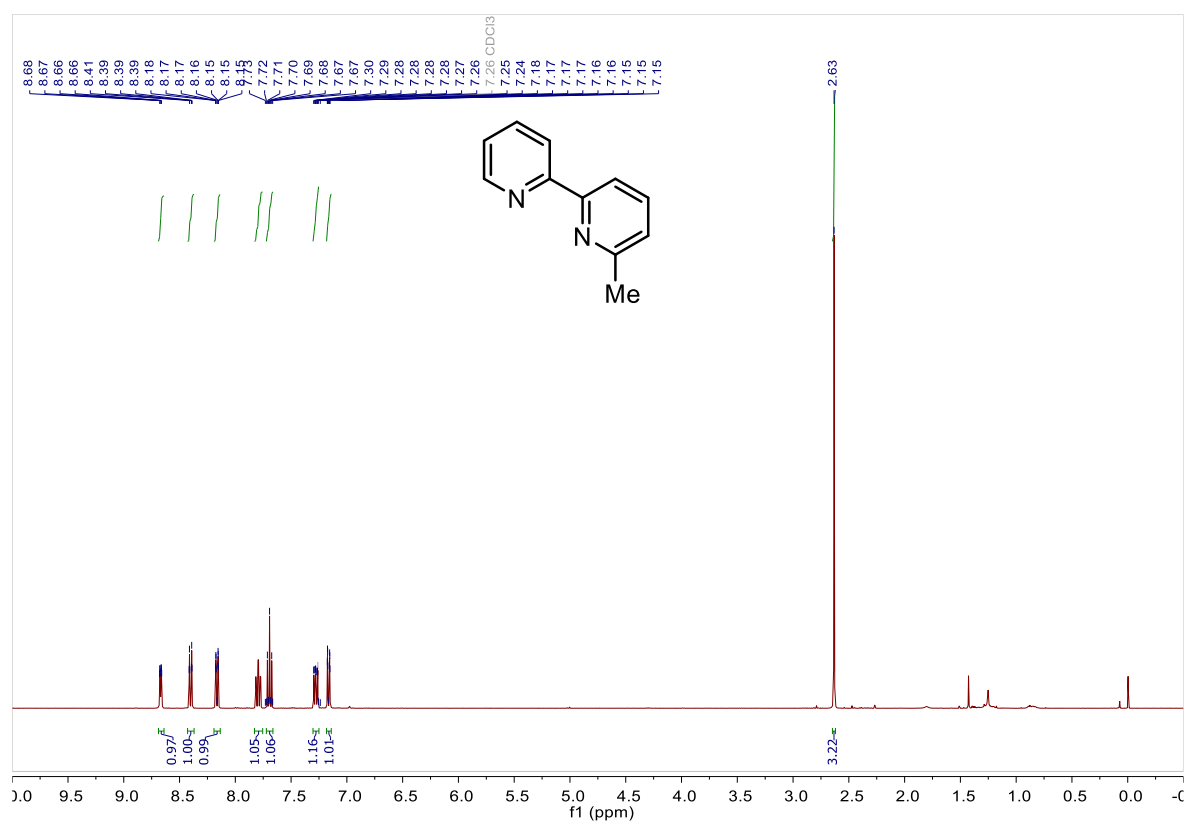
^1H NMR (400 MHz, CDCl_3): 14



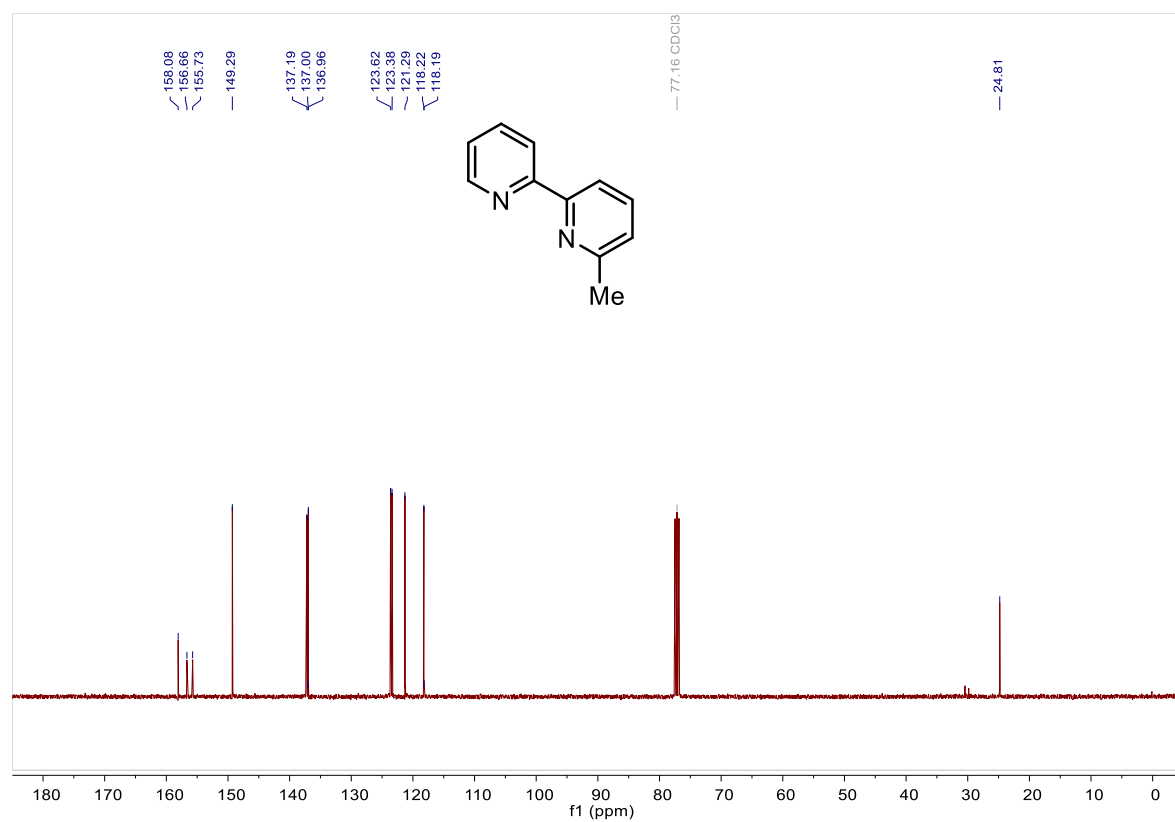
^{13}C NMR (101 MHz, CDCl_3): 14



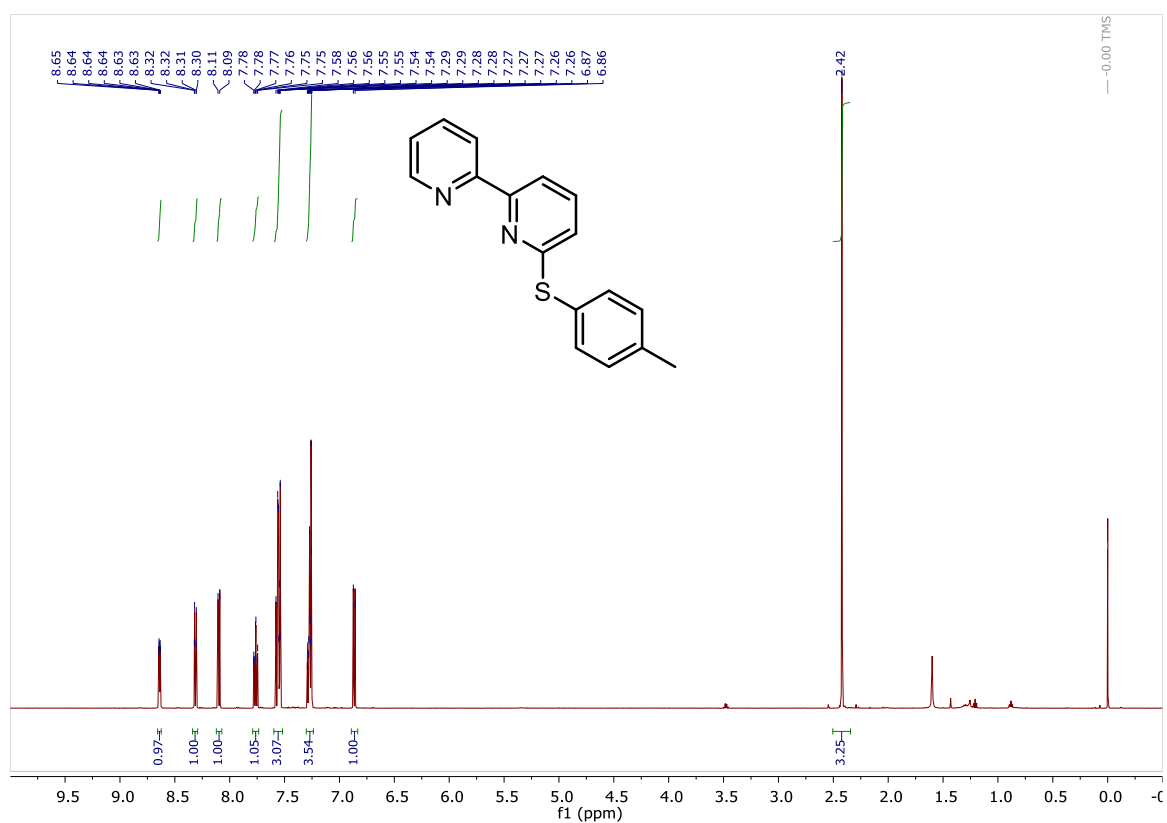
^1H NMR (500 MHz, CDCl_3): 15



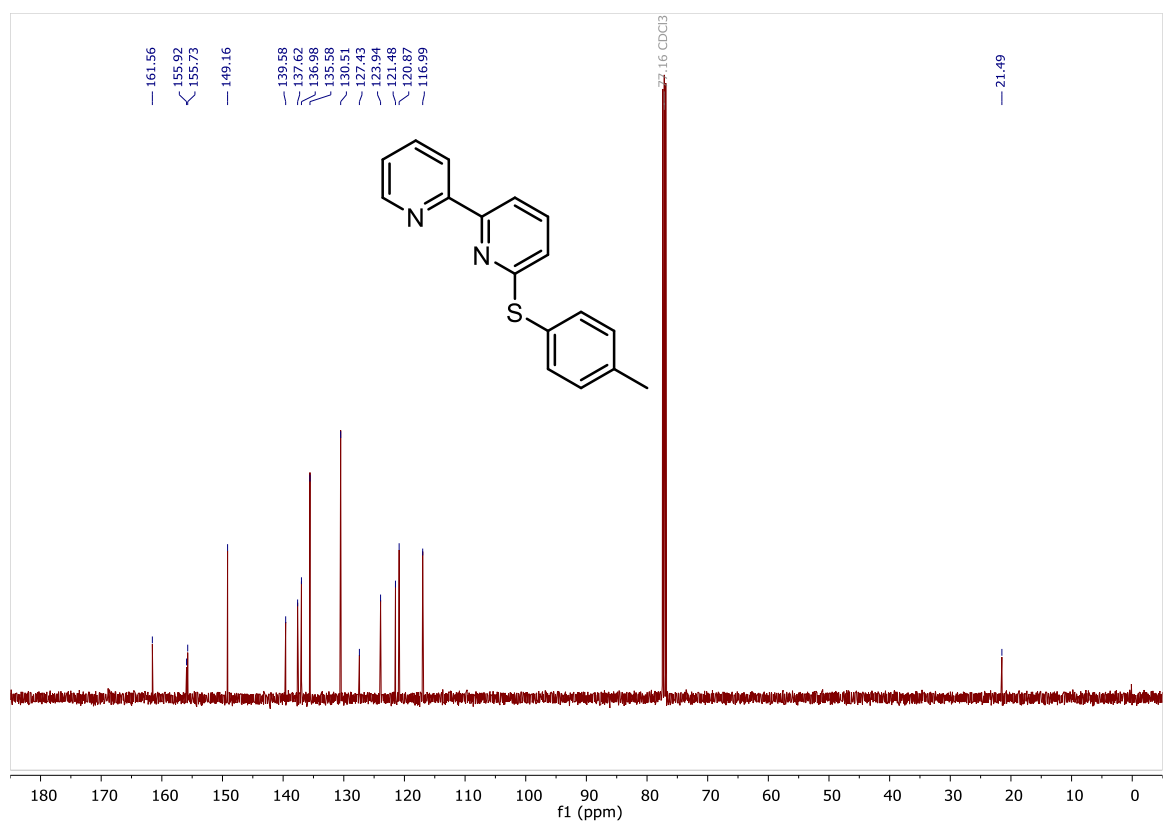
^{13}C NMR (101 MHz, CDCl_3): 15



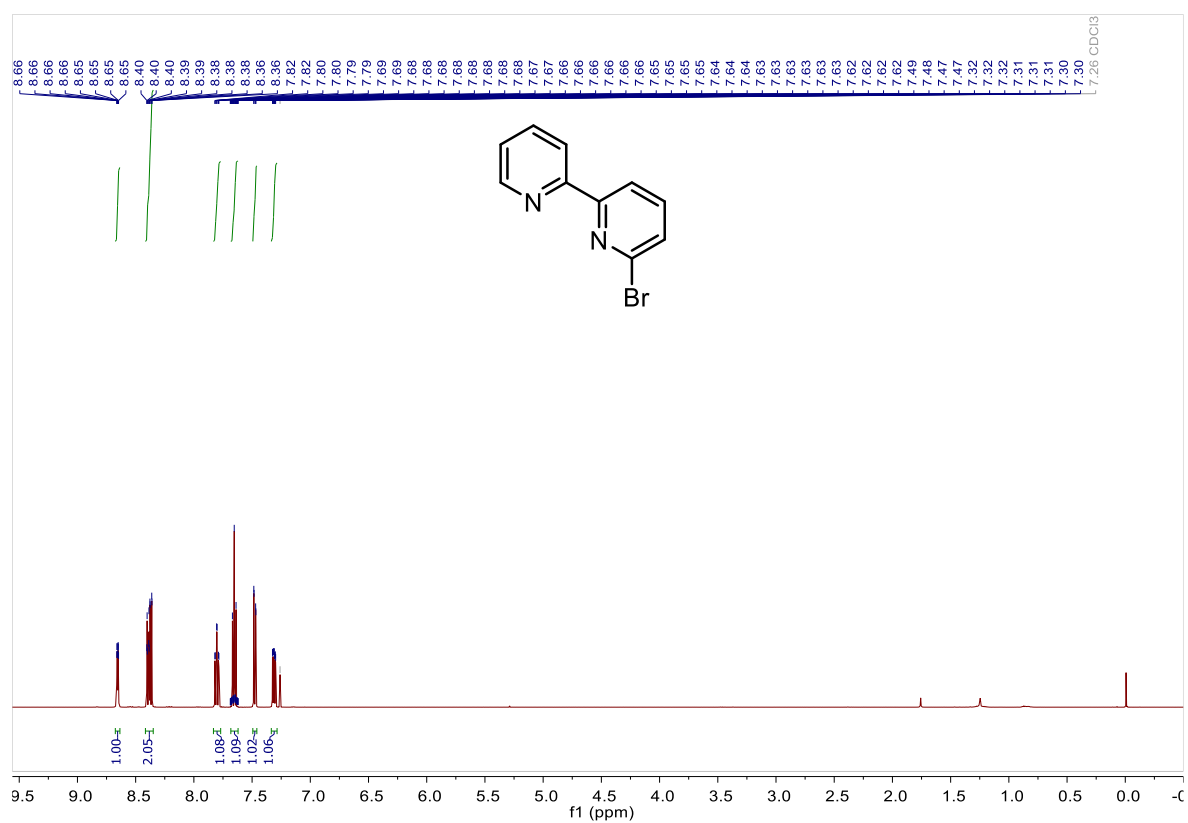
¹H NMR (500 MHz, CDCl₃): 16



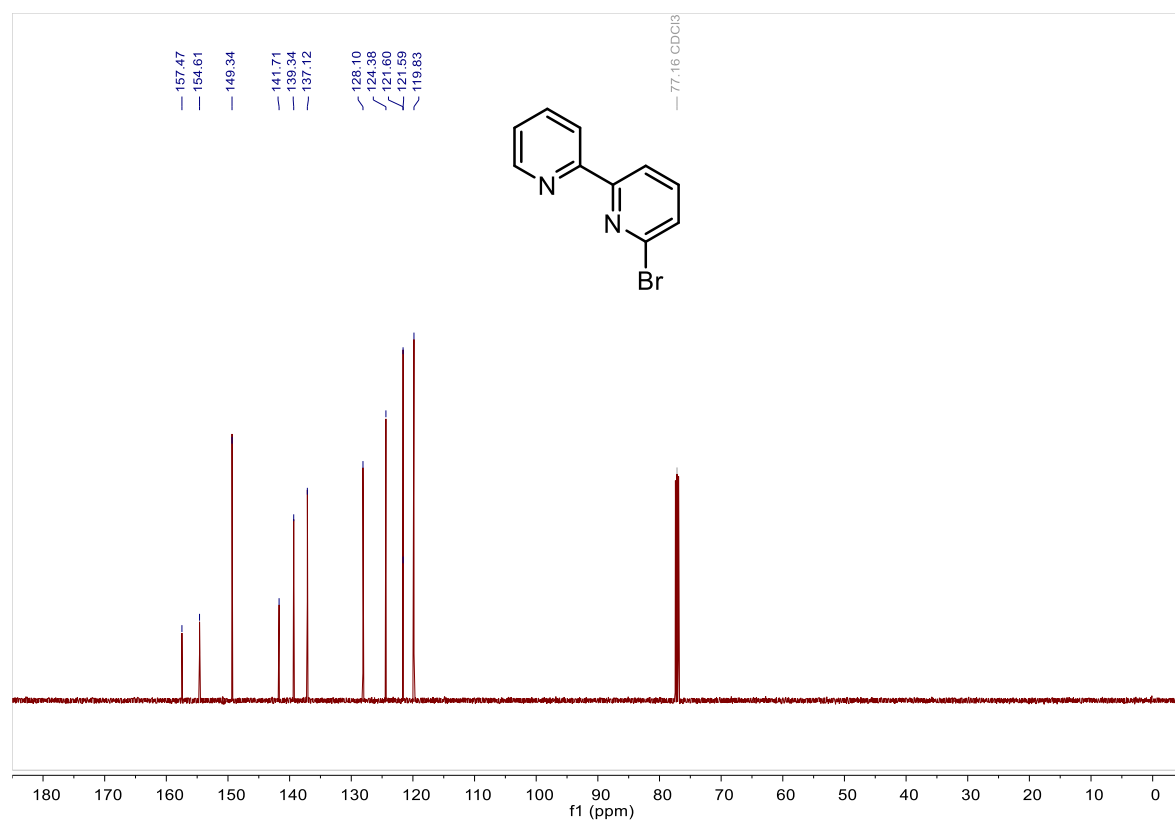
¹³C NMR (126 MHz, CDCl₃): 16



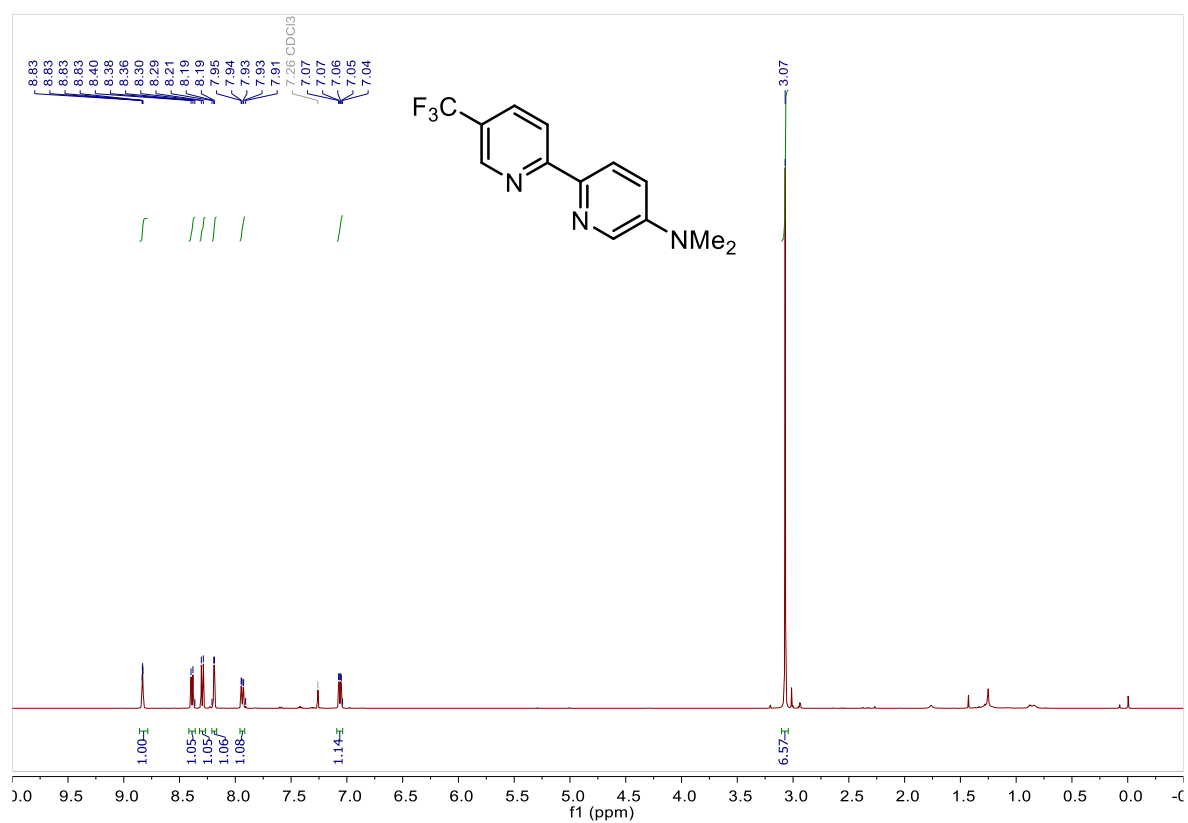
¹H NMR (500 MHz, CDCl₃): 17



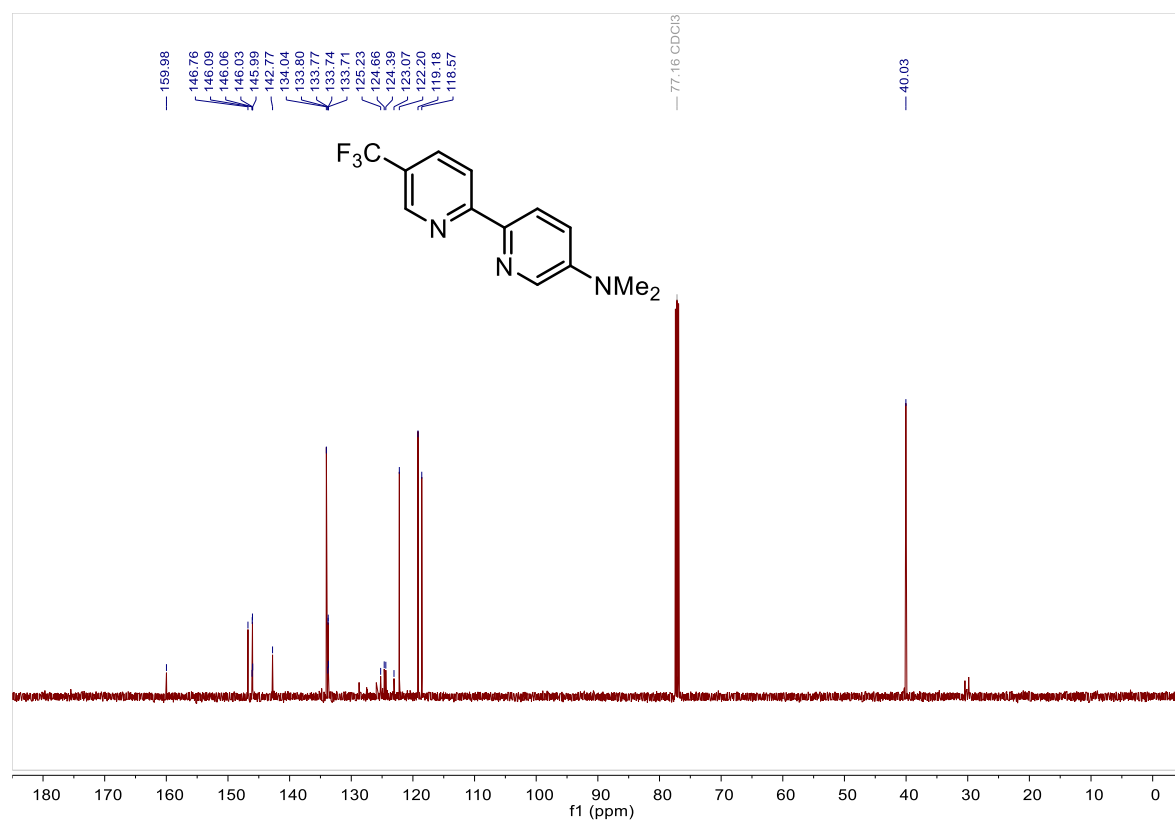
¹³C NMR (126 MHz, CDCl₃): 17



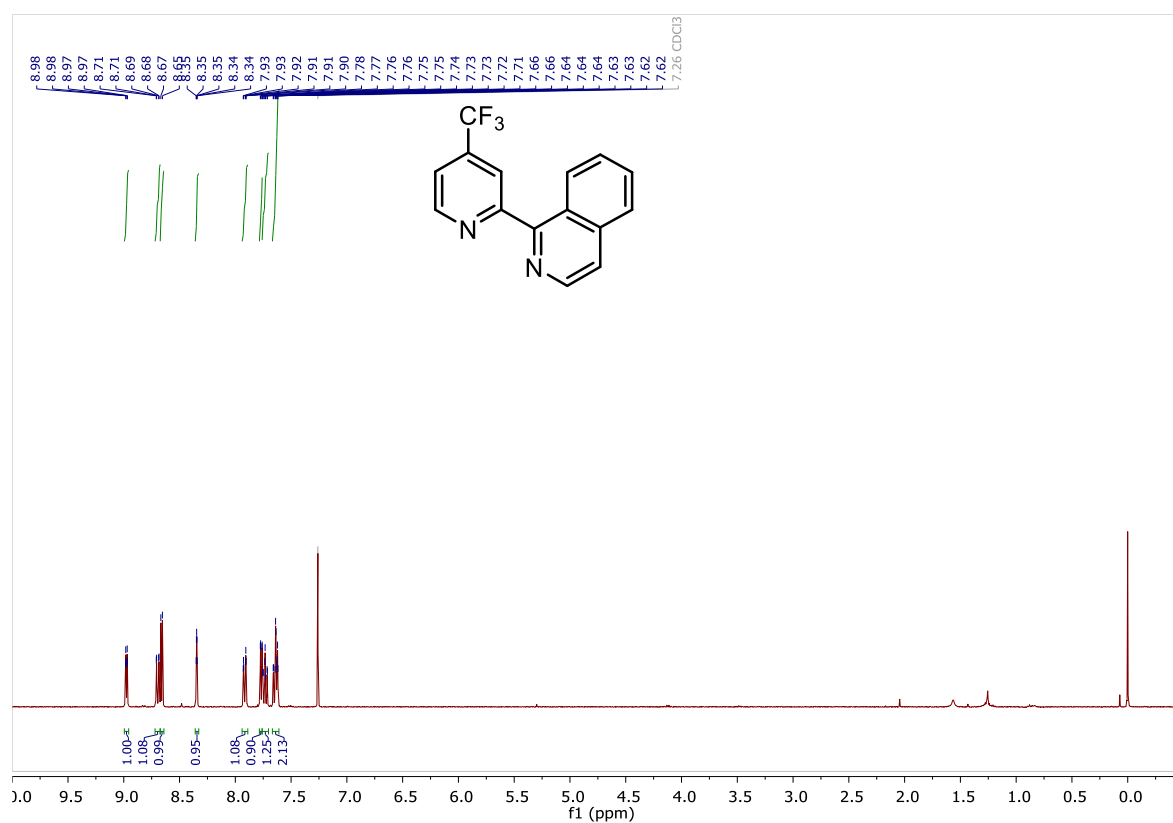
¹H NMR (500 MHz, CDCl₃): 18



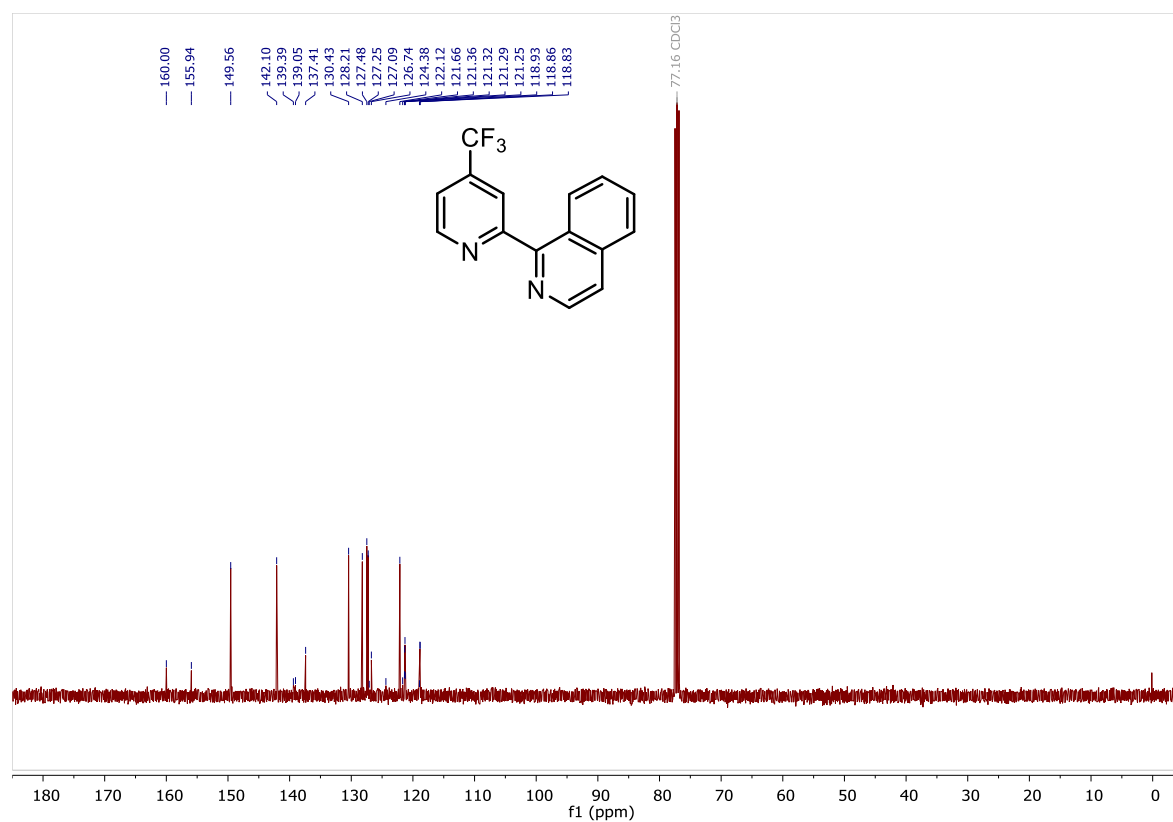
¹³C NMR (126 MHz, CDCl₃): 18



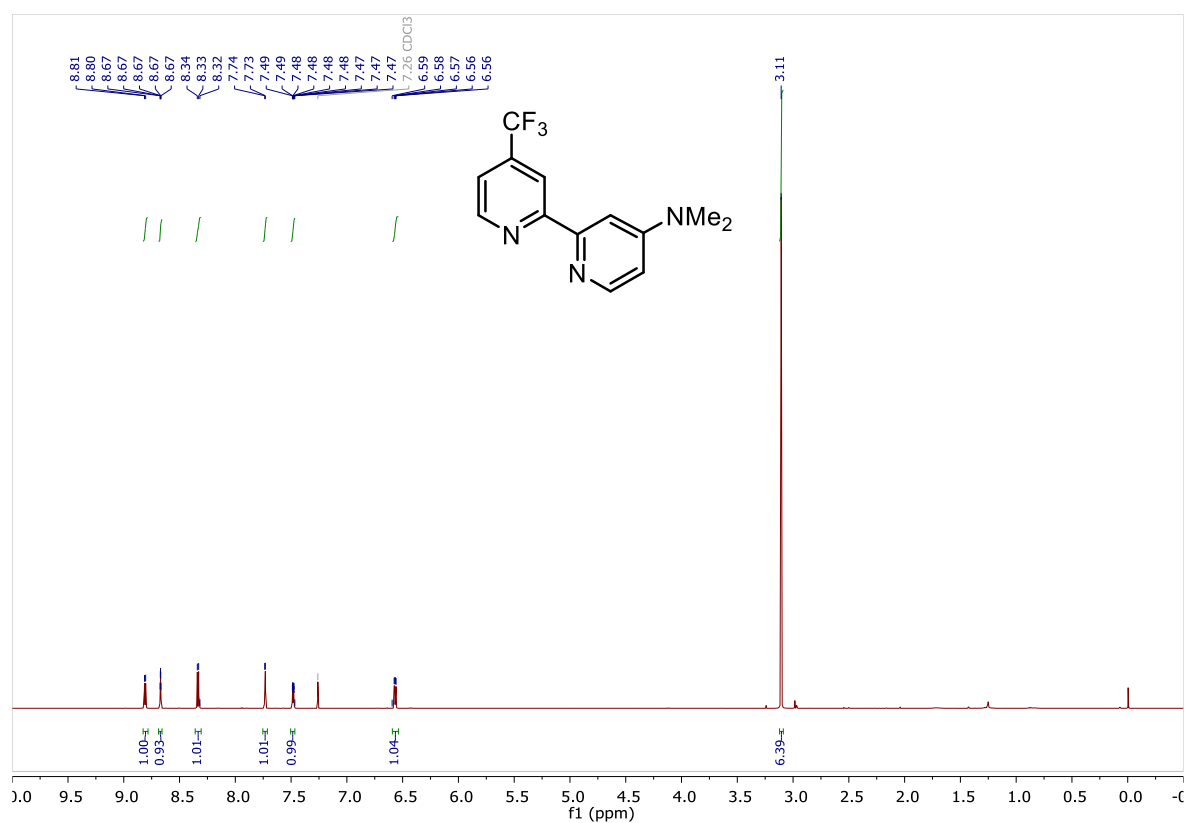
¹H NMR (400 MHz, CDCl₃): 19



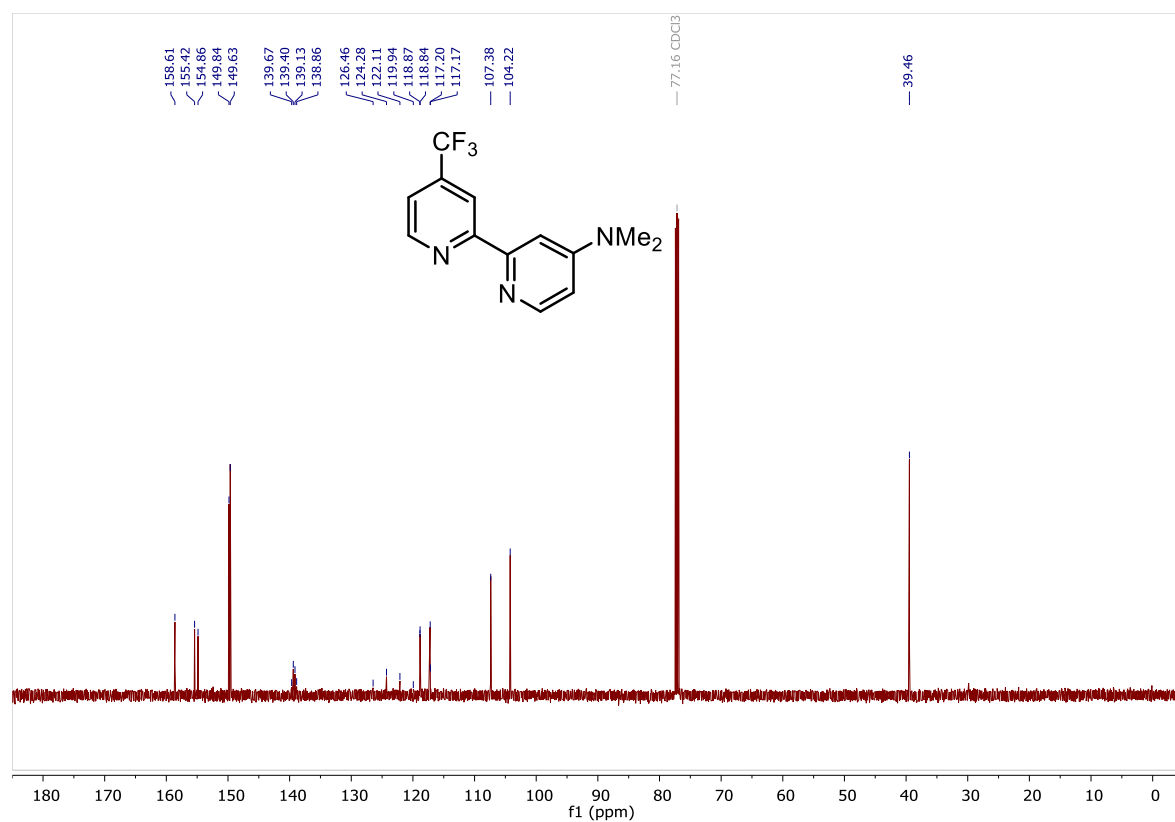
¹³C NMR (101 MHz, CDCl₃): 19



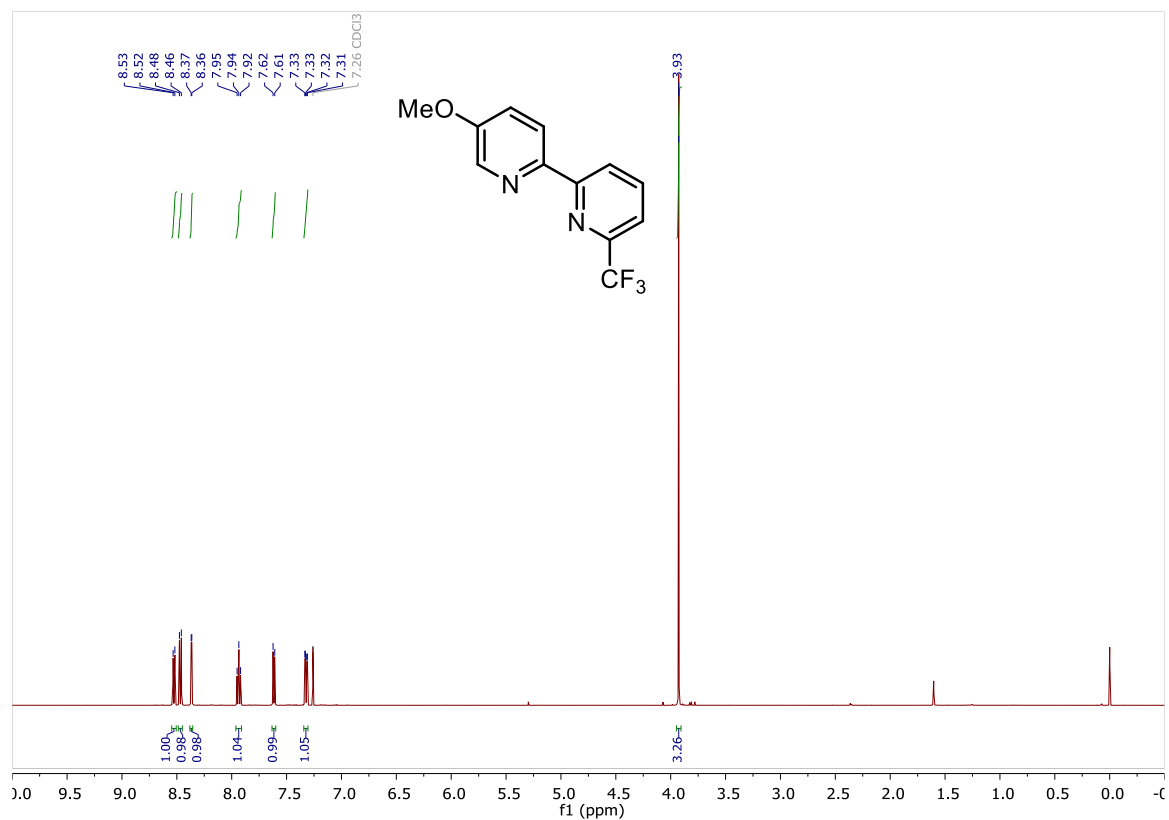
^1H NMR (500 MHz, CDCl_3): 20



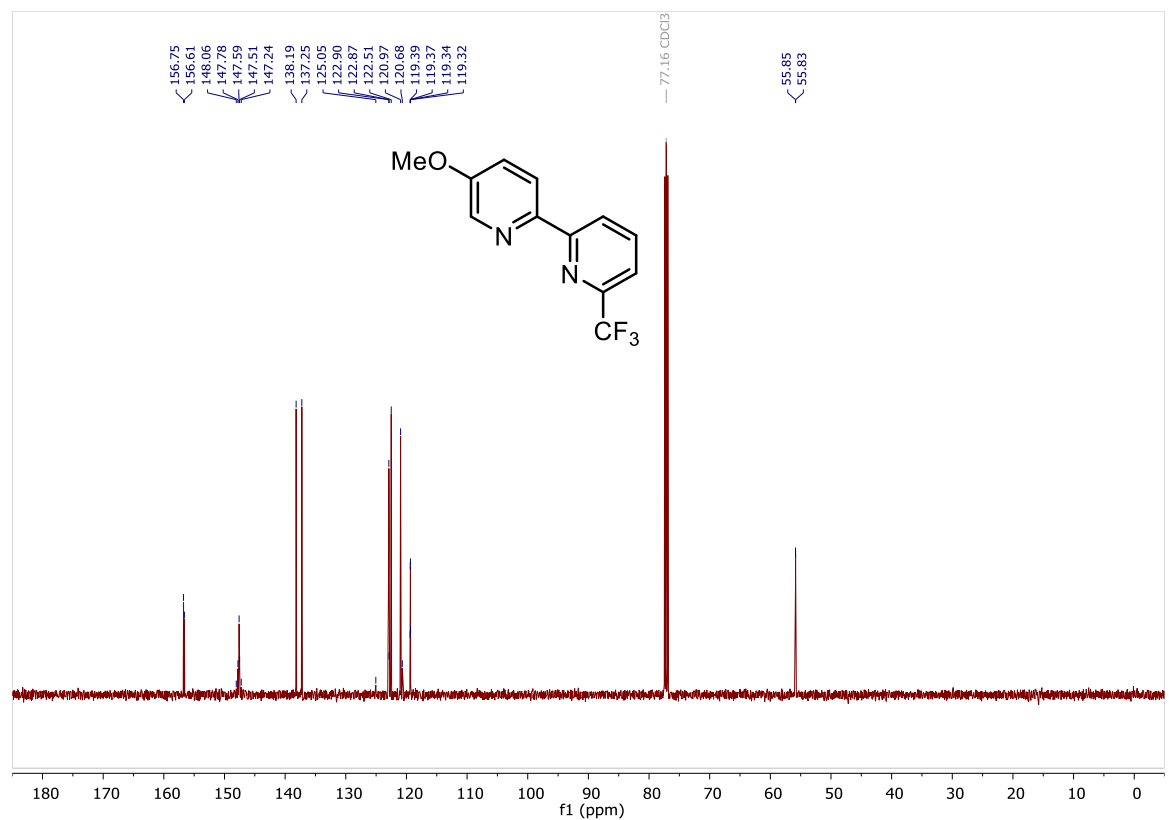
^{13}C NMR (126 MHz, CDCl_3): 20



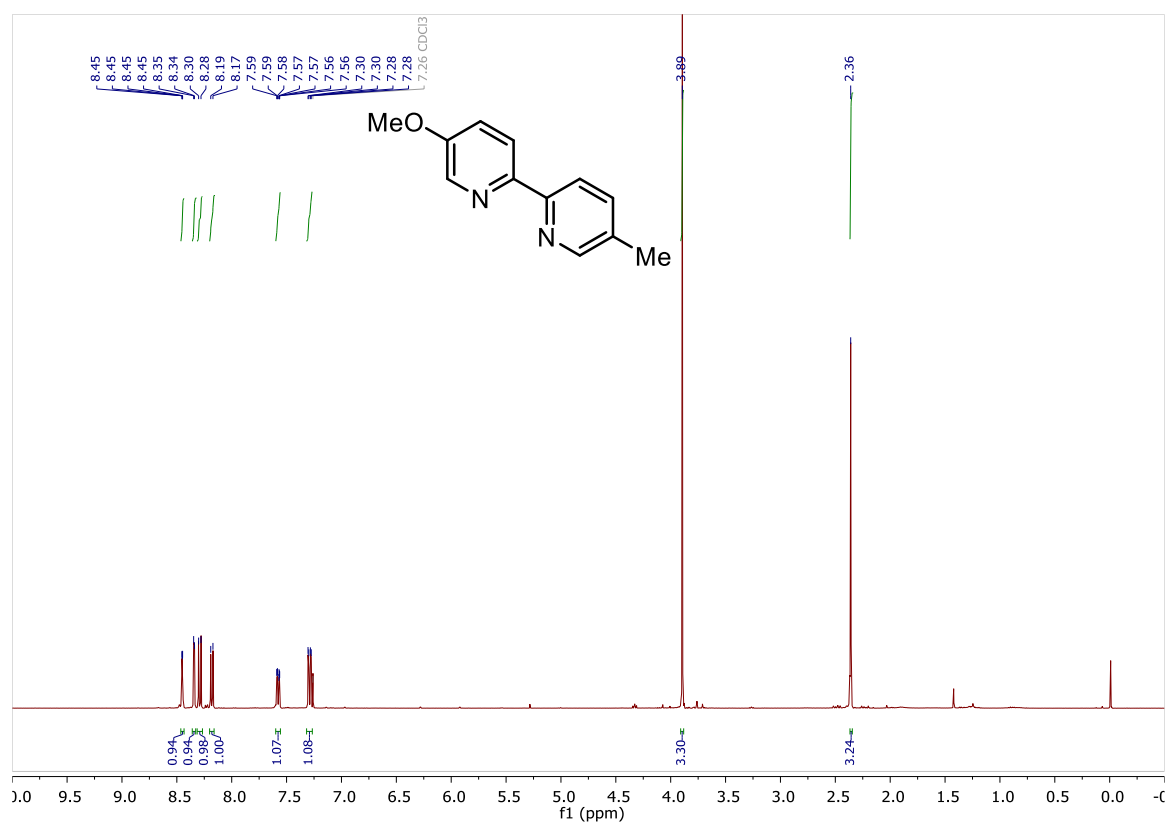
¹H NMR (500 MHz, CDCl₃): 21



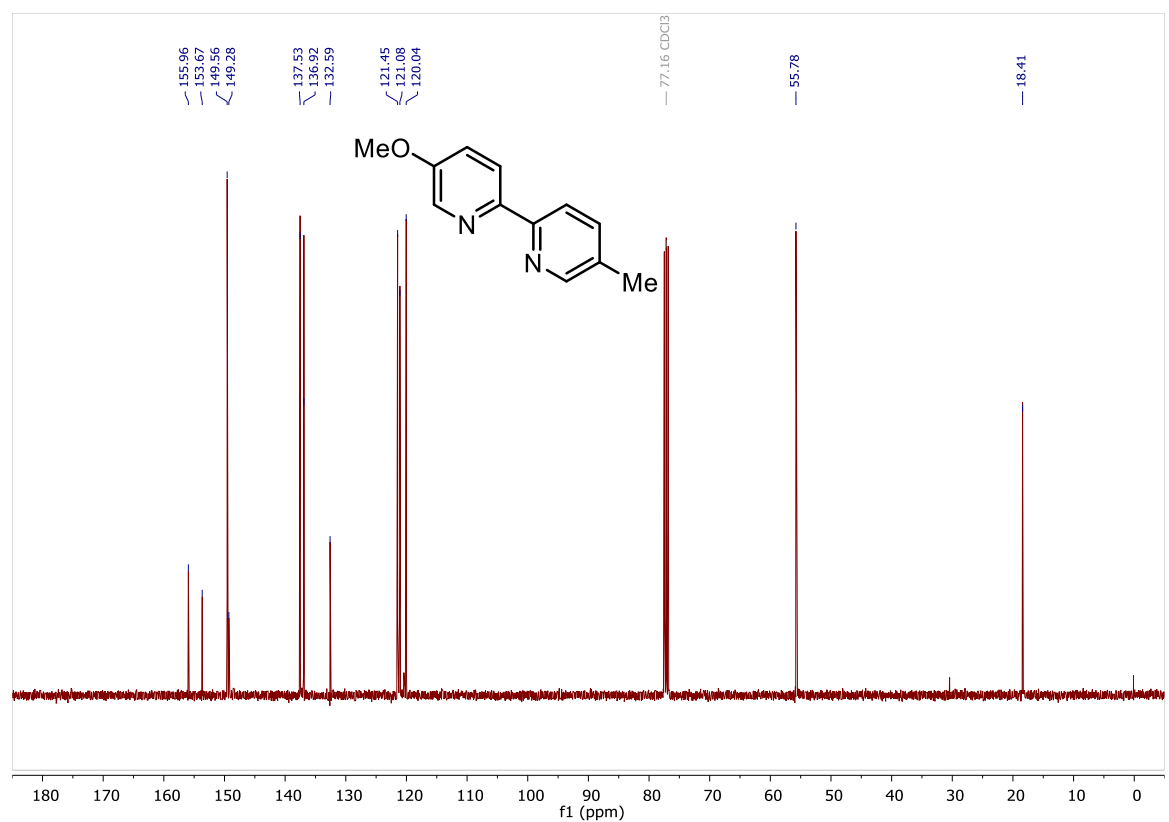
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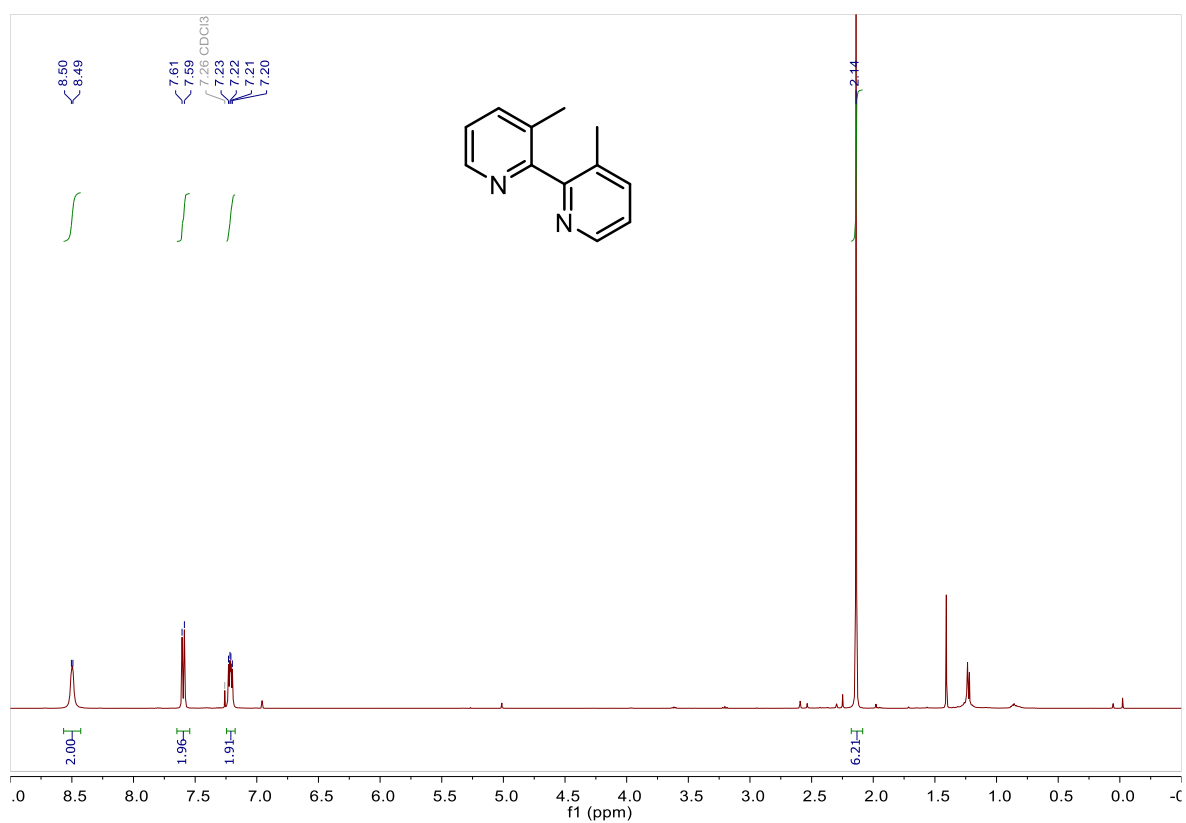
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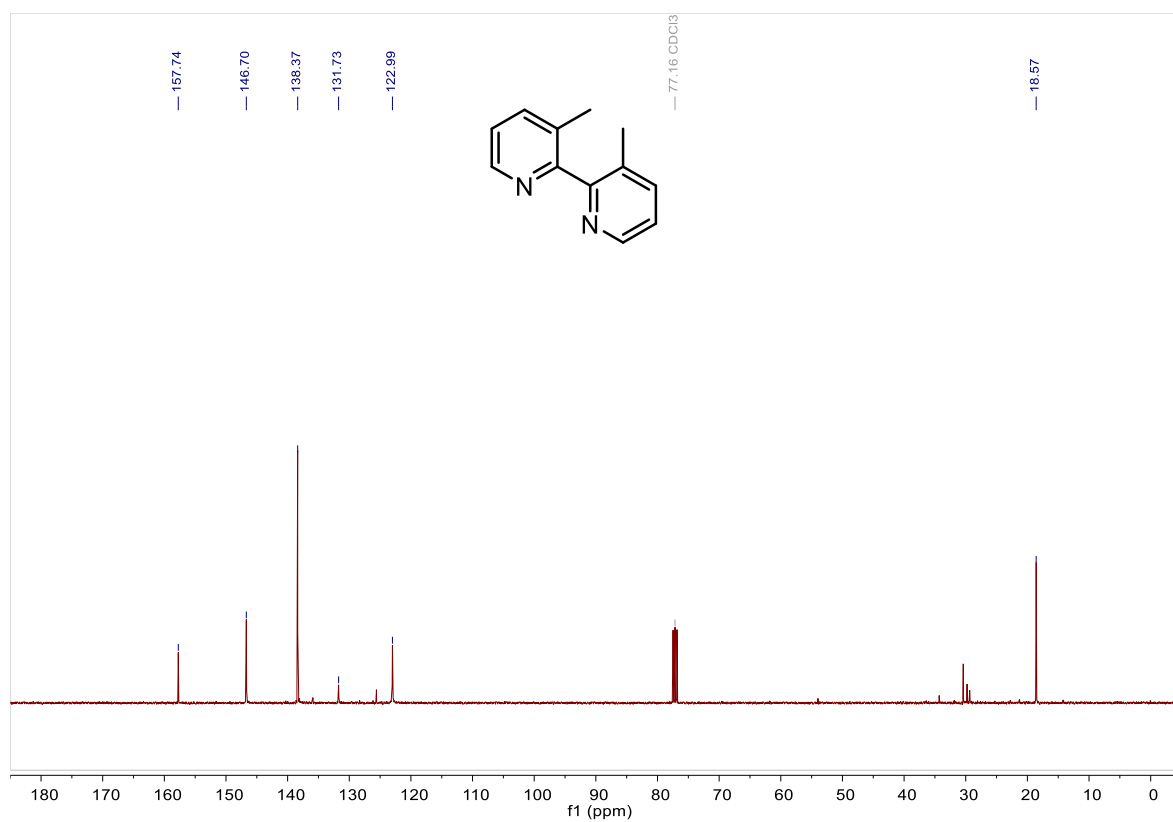
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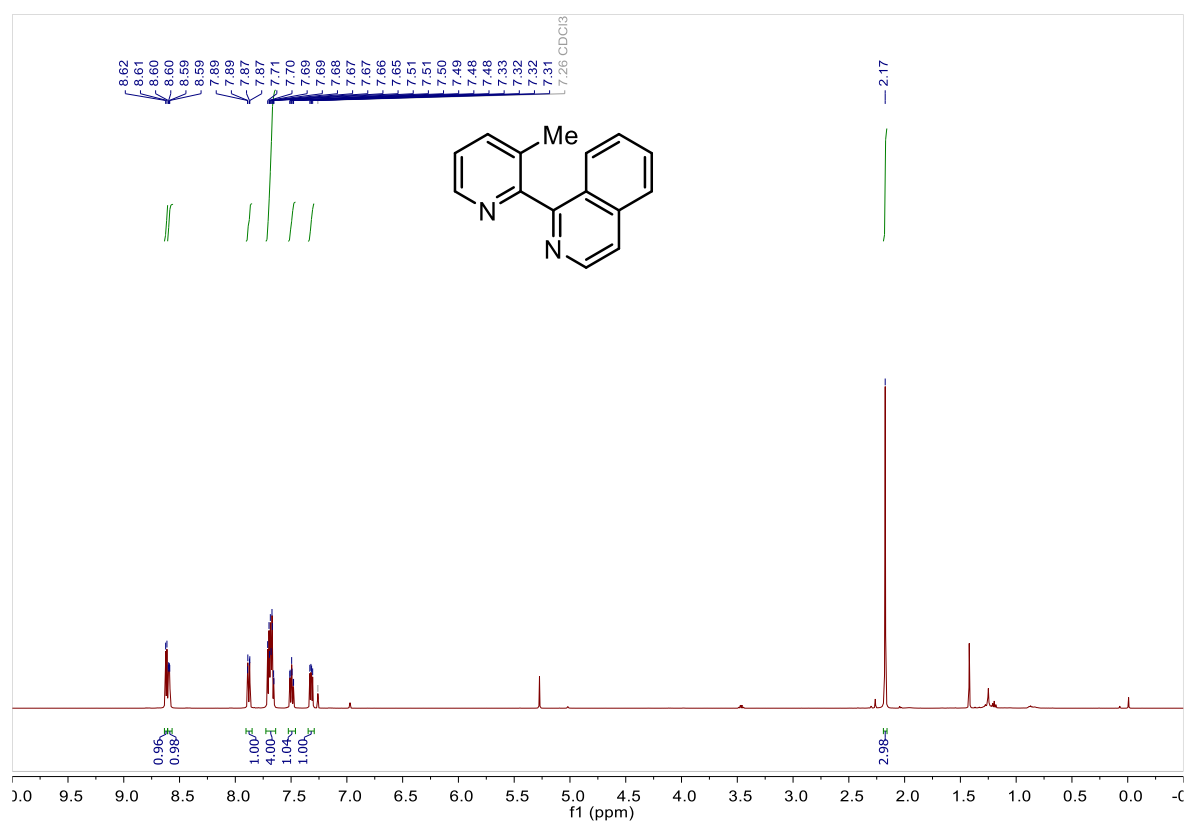
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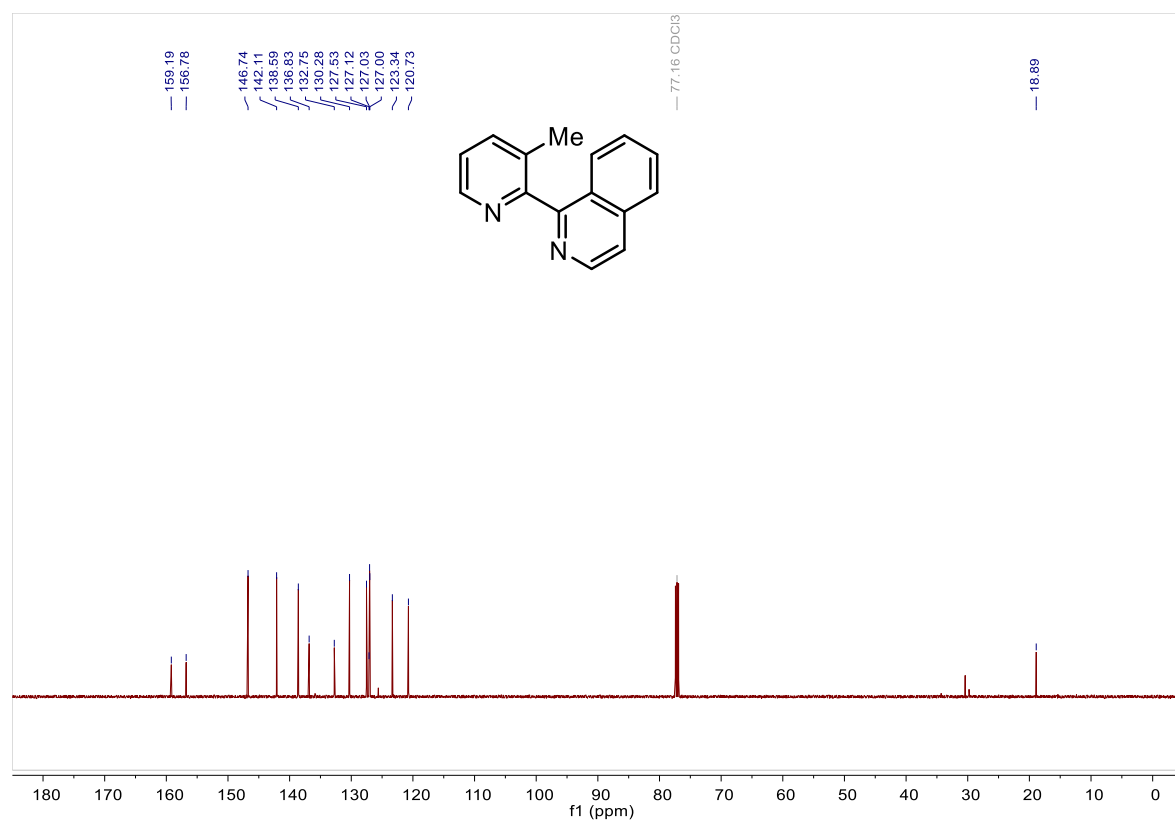
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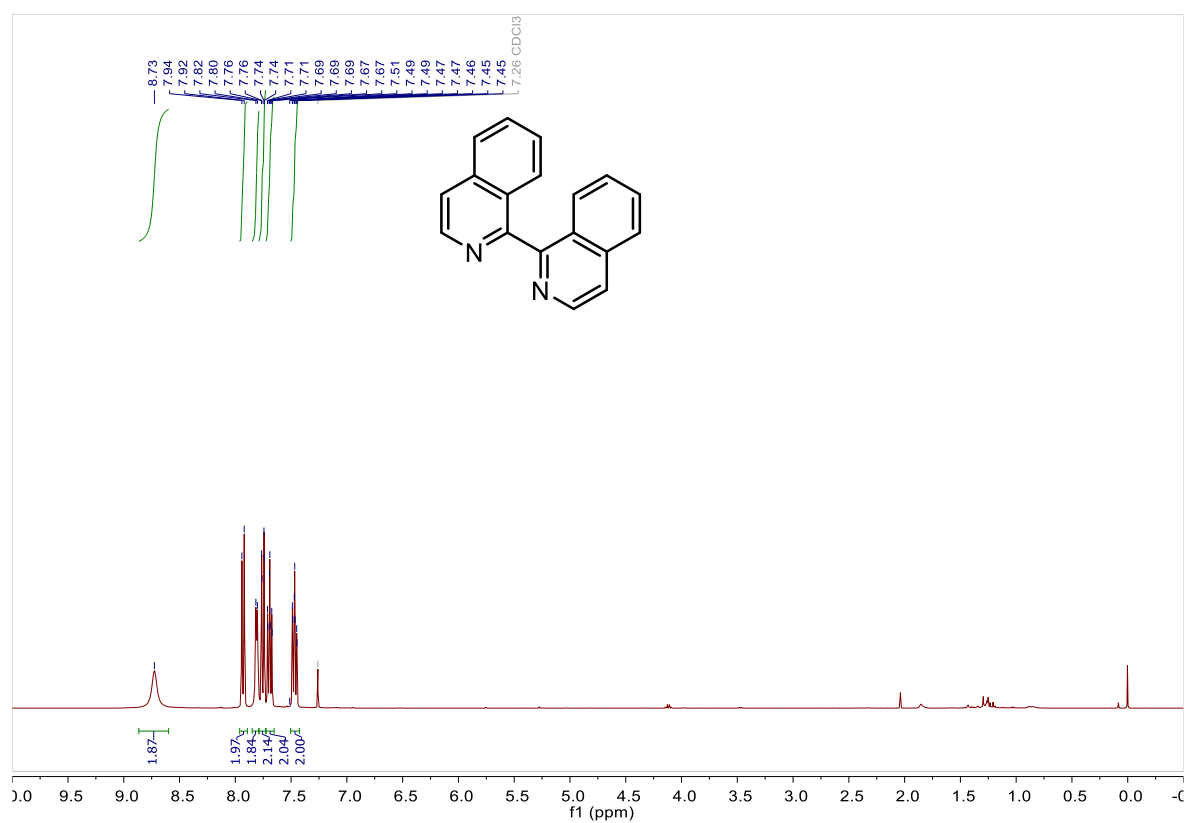
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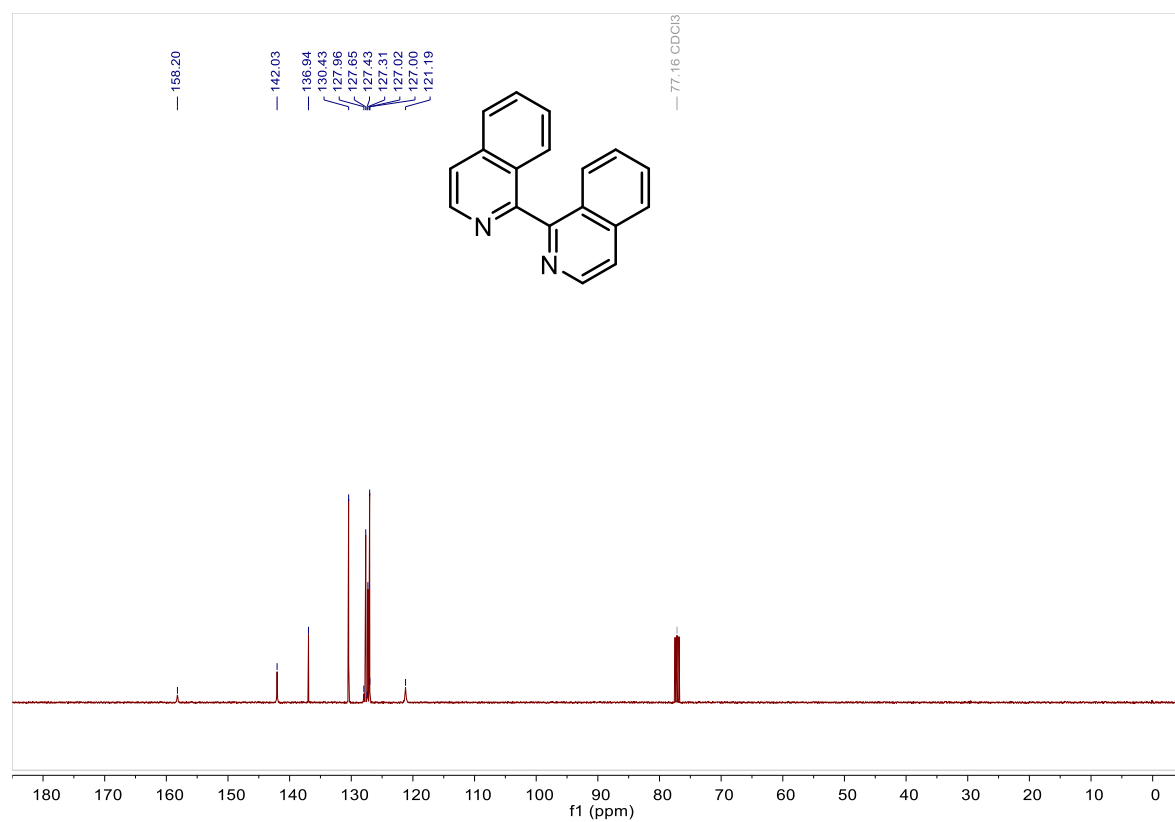
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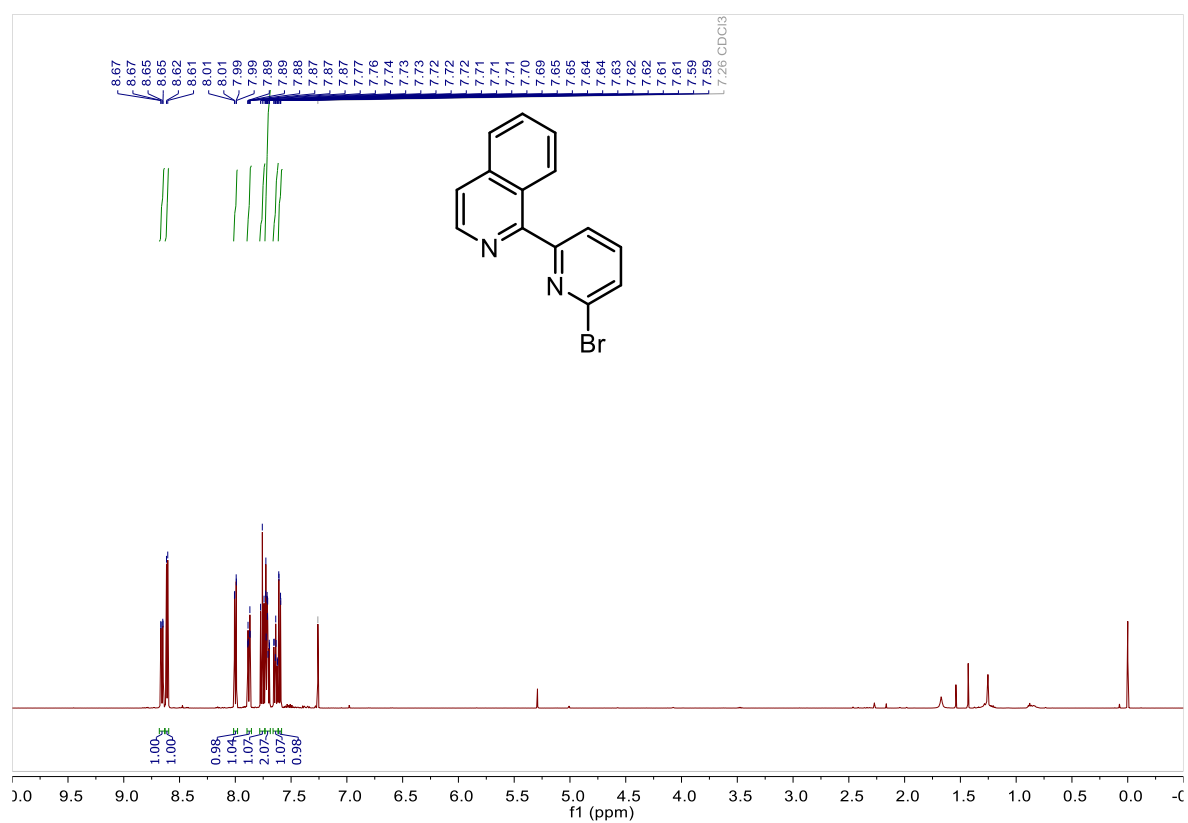
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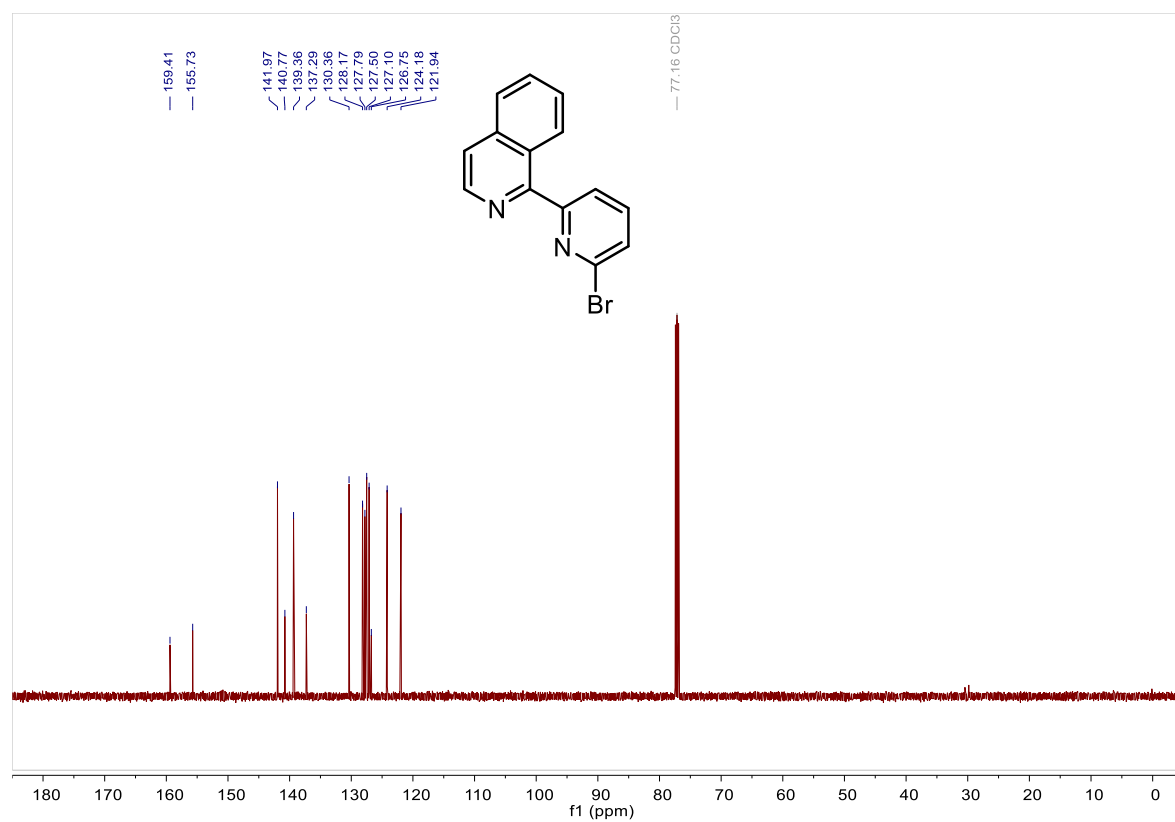
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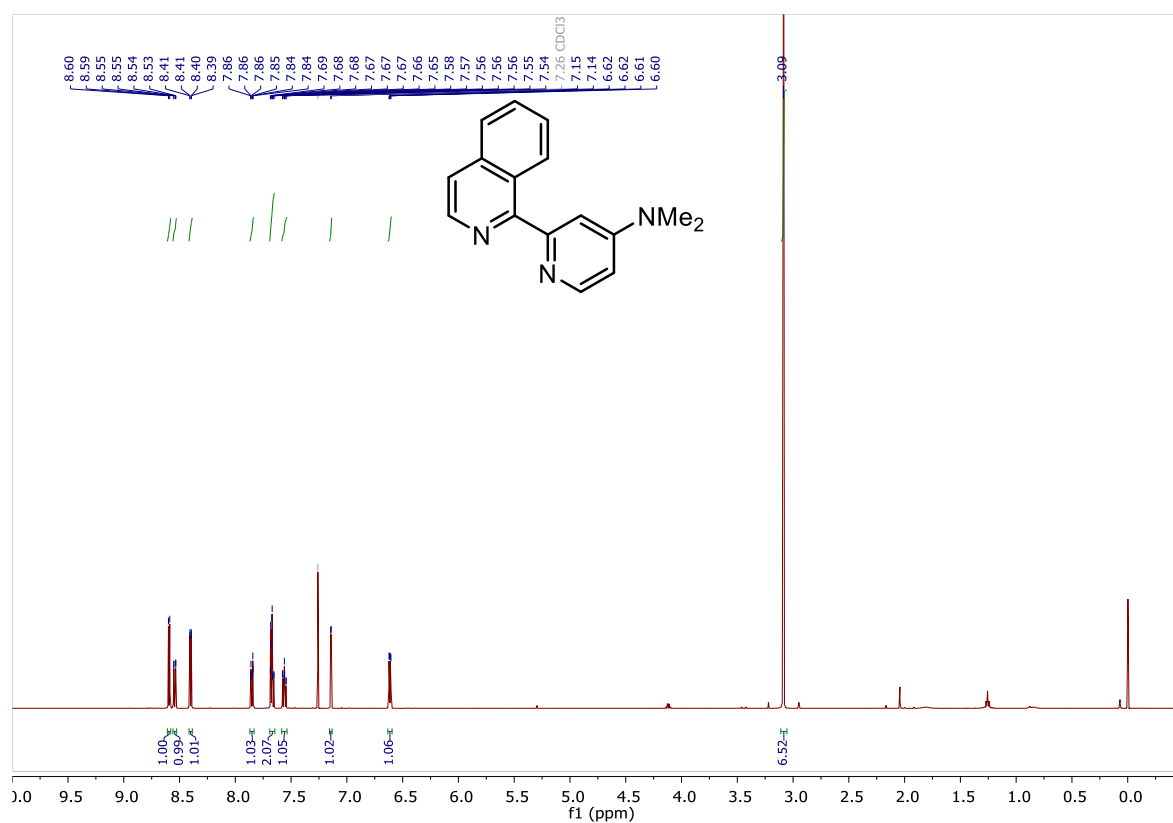
^1H NMR (500 MHz, CDCl_3): 26



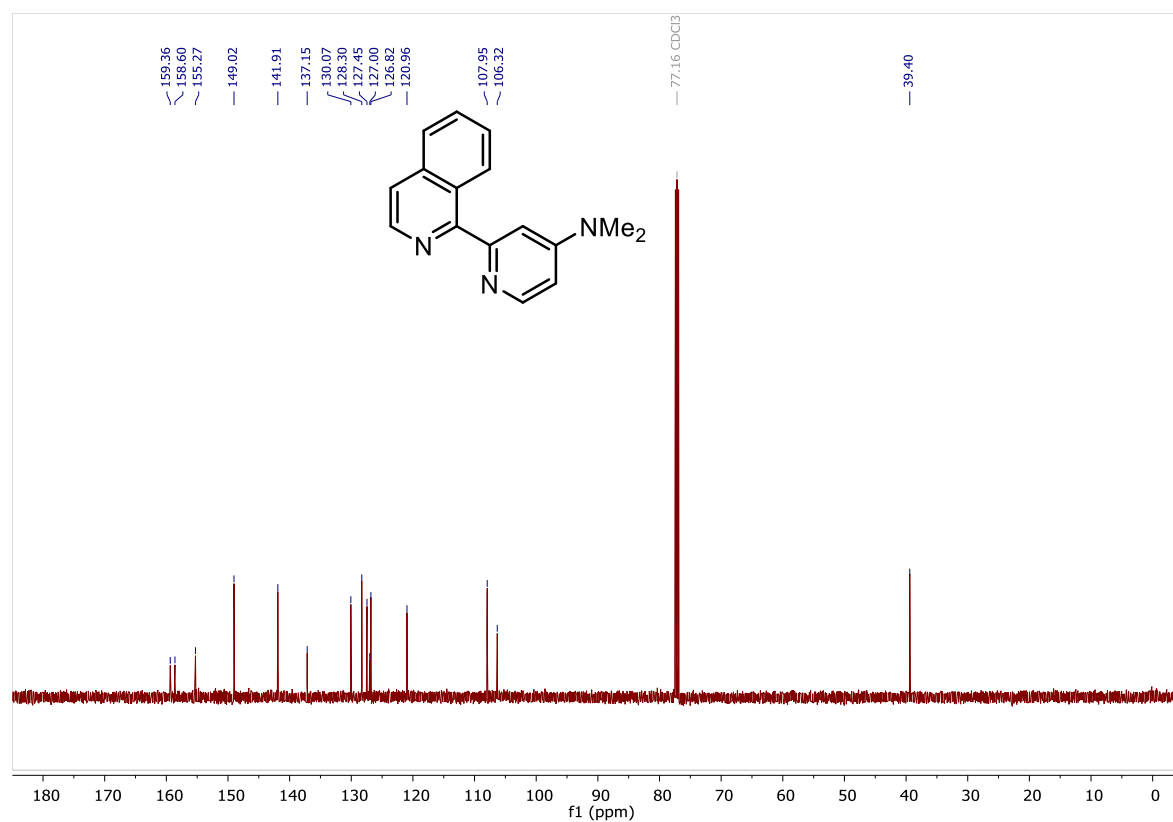
^{13}C NMR (126 MHz, CDCl_3): 26



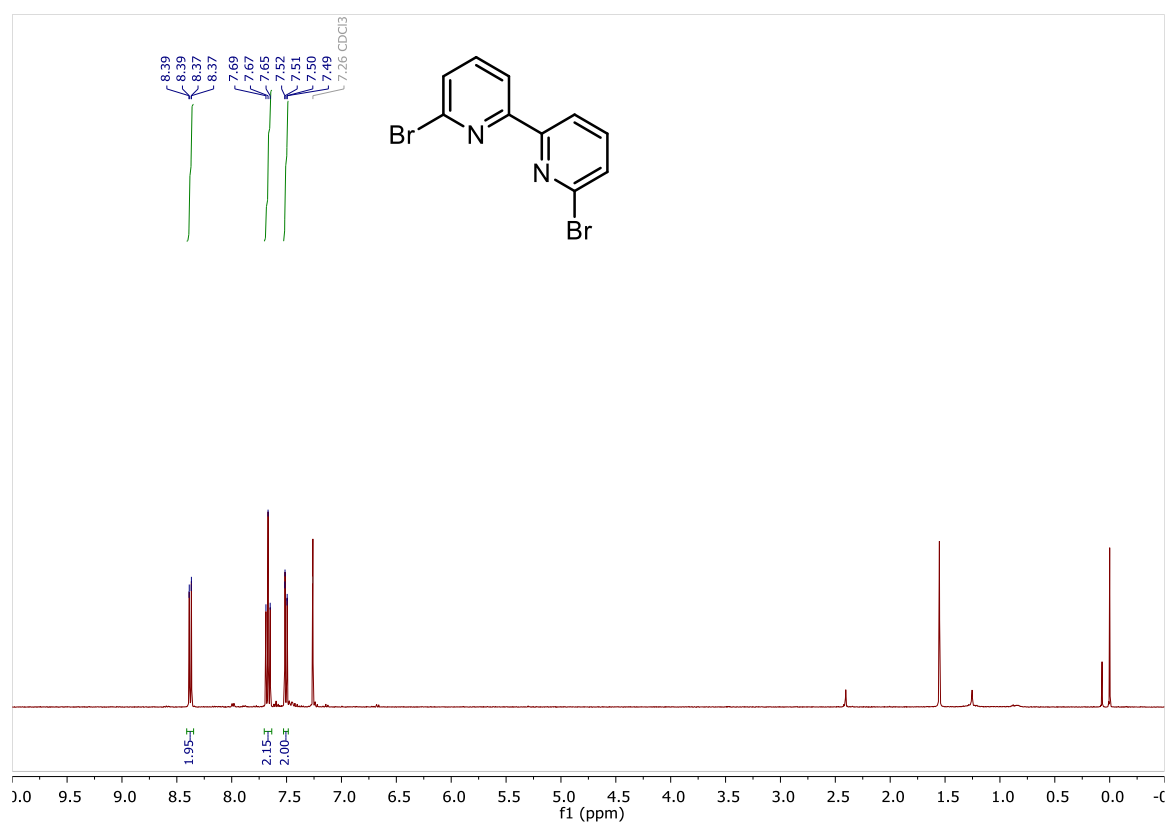
^1H NMR (500 MHz, CDCl_3): 27



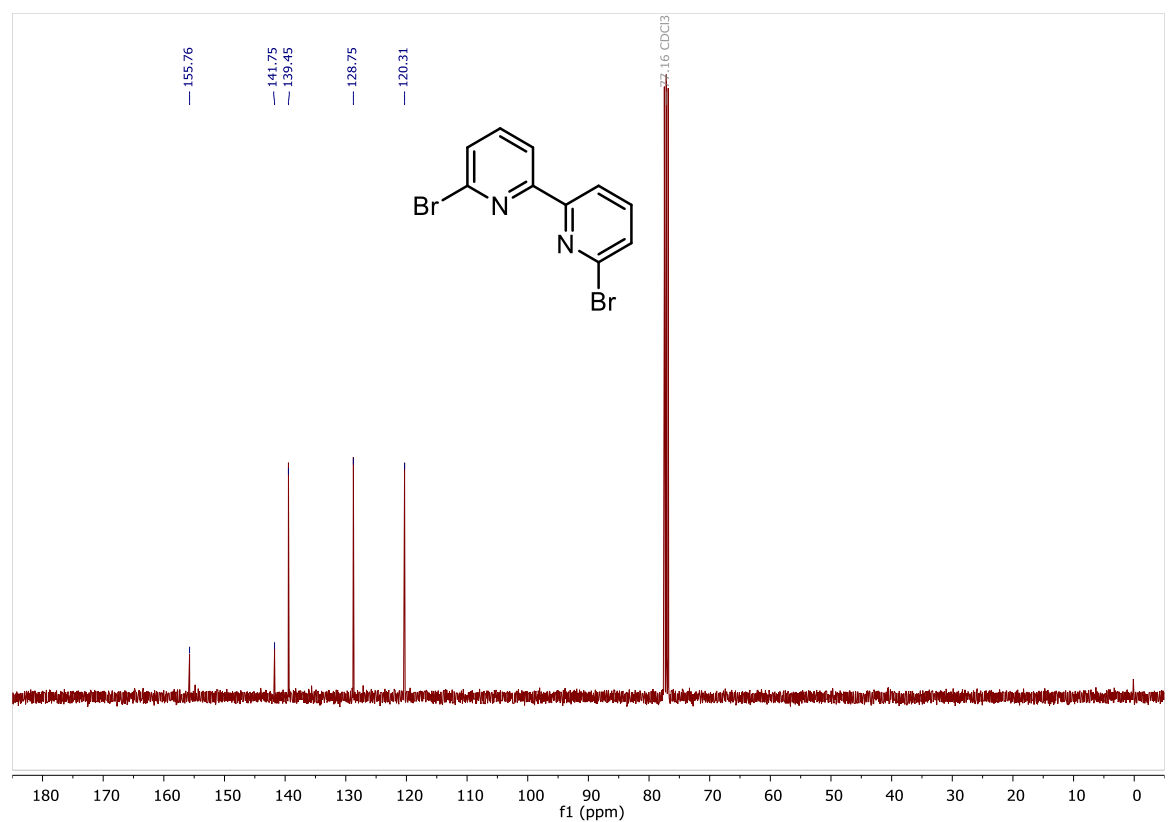
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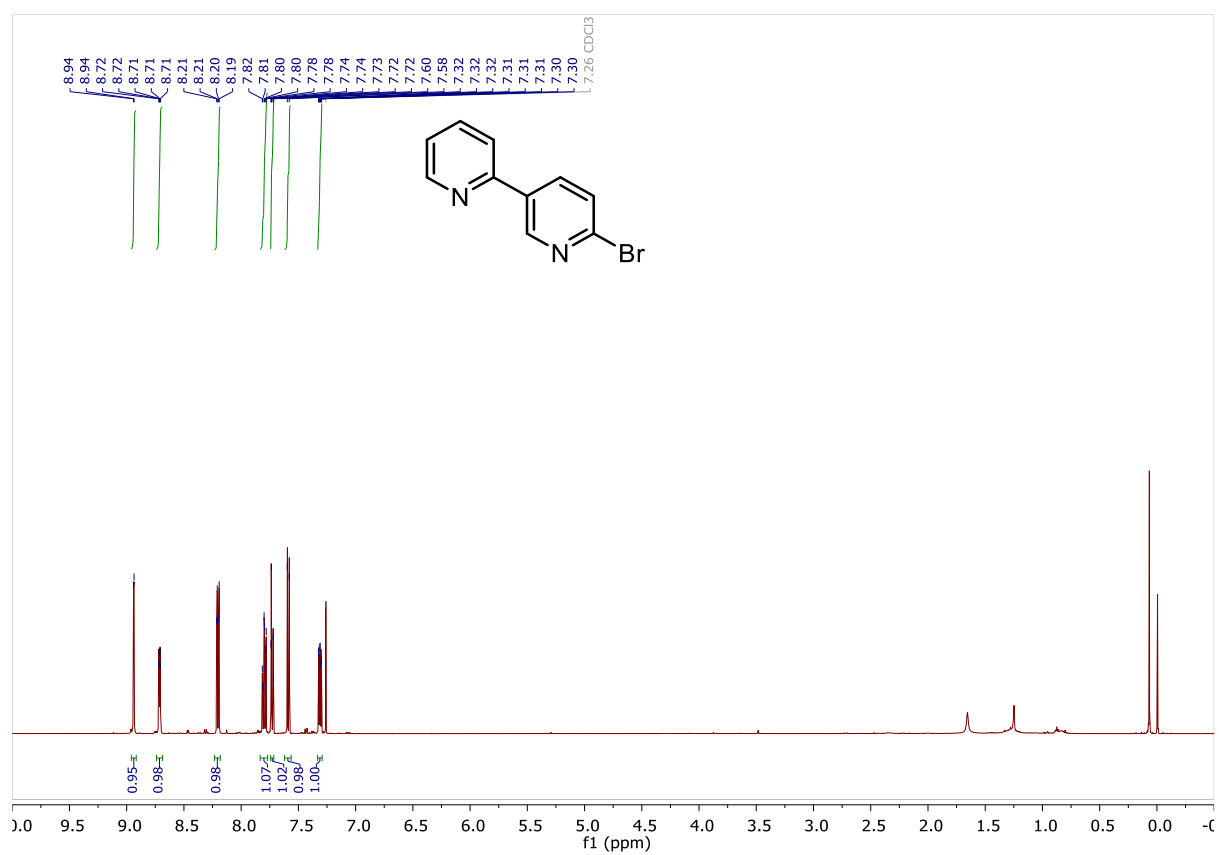
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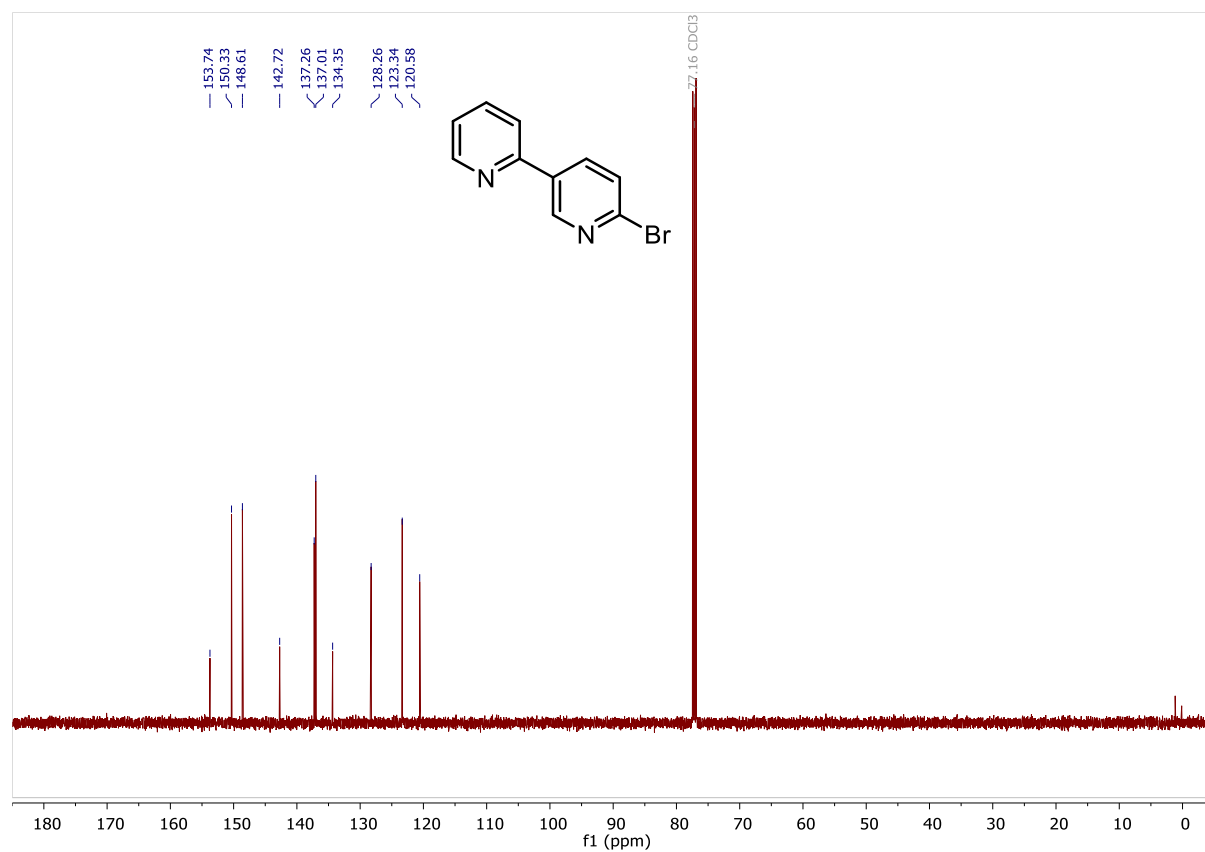
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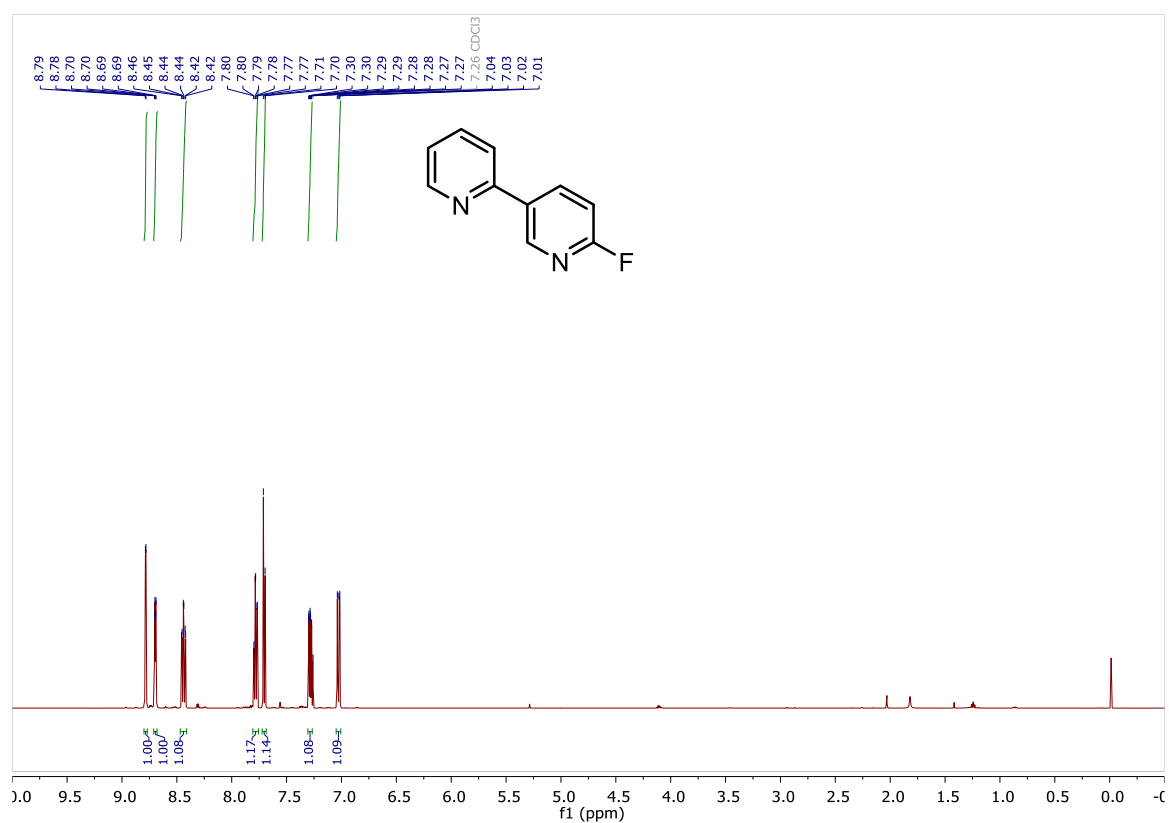
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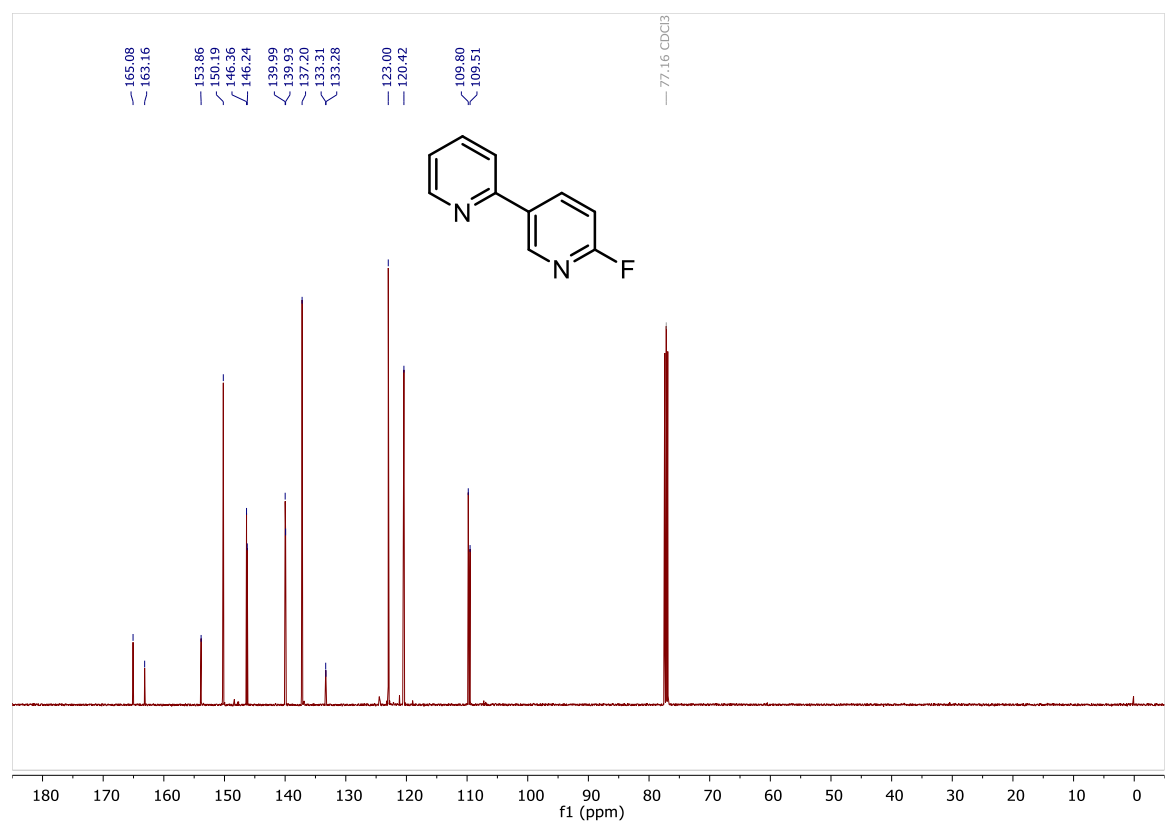
¹³C NMR (126 MHz, CDCl₃): 29



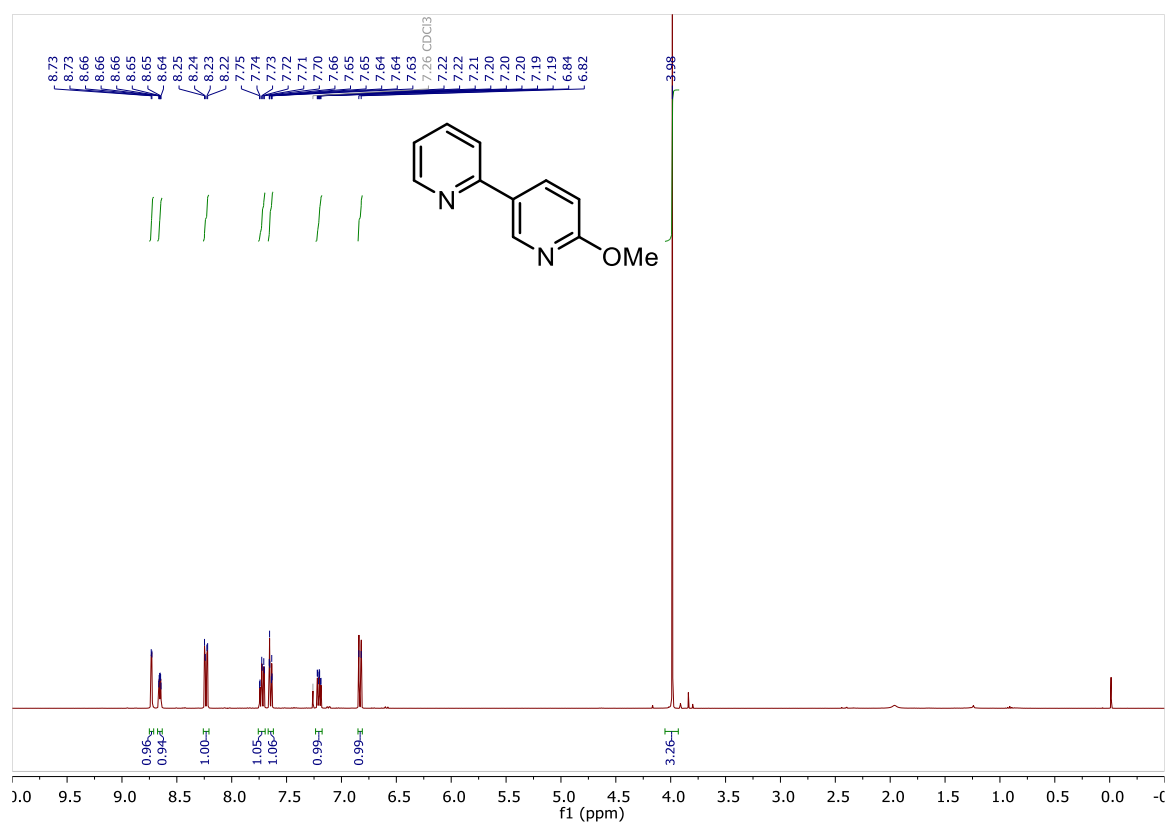
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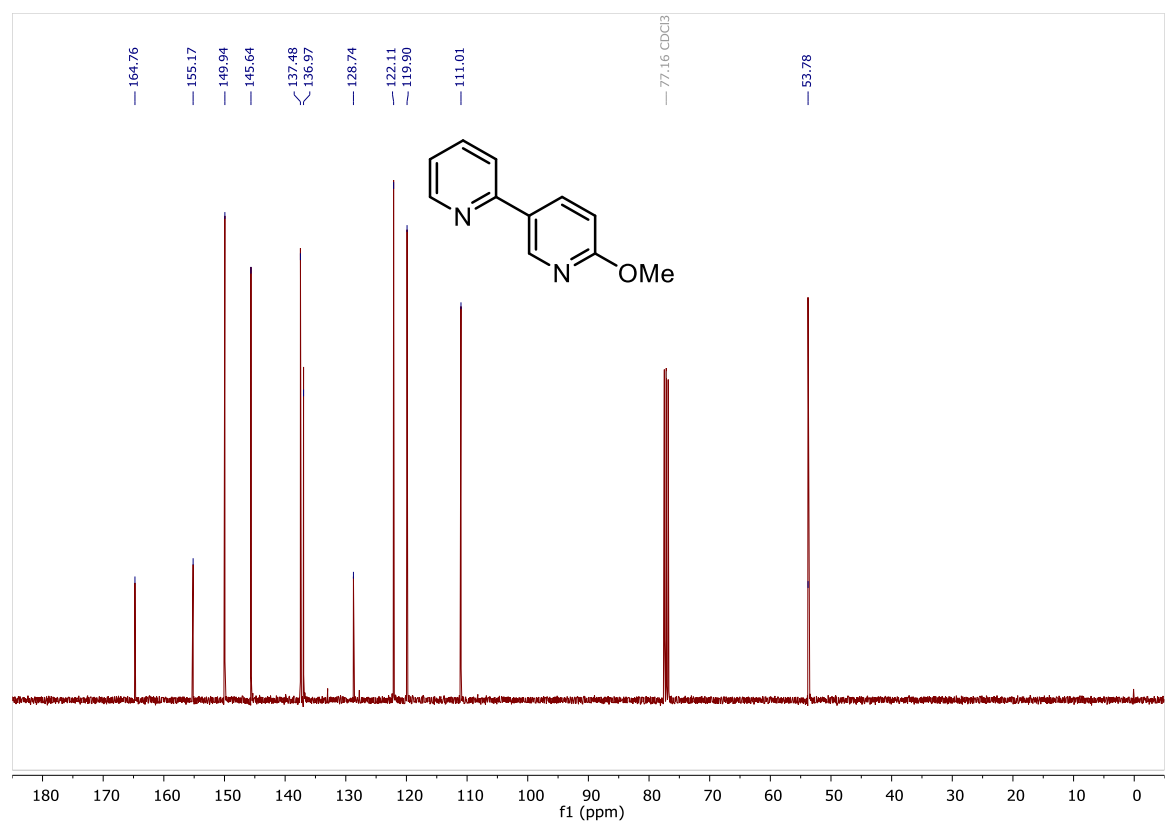
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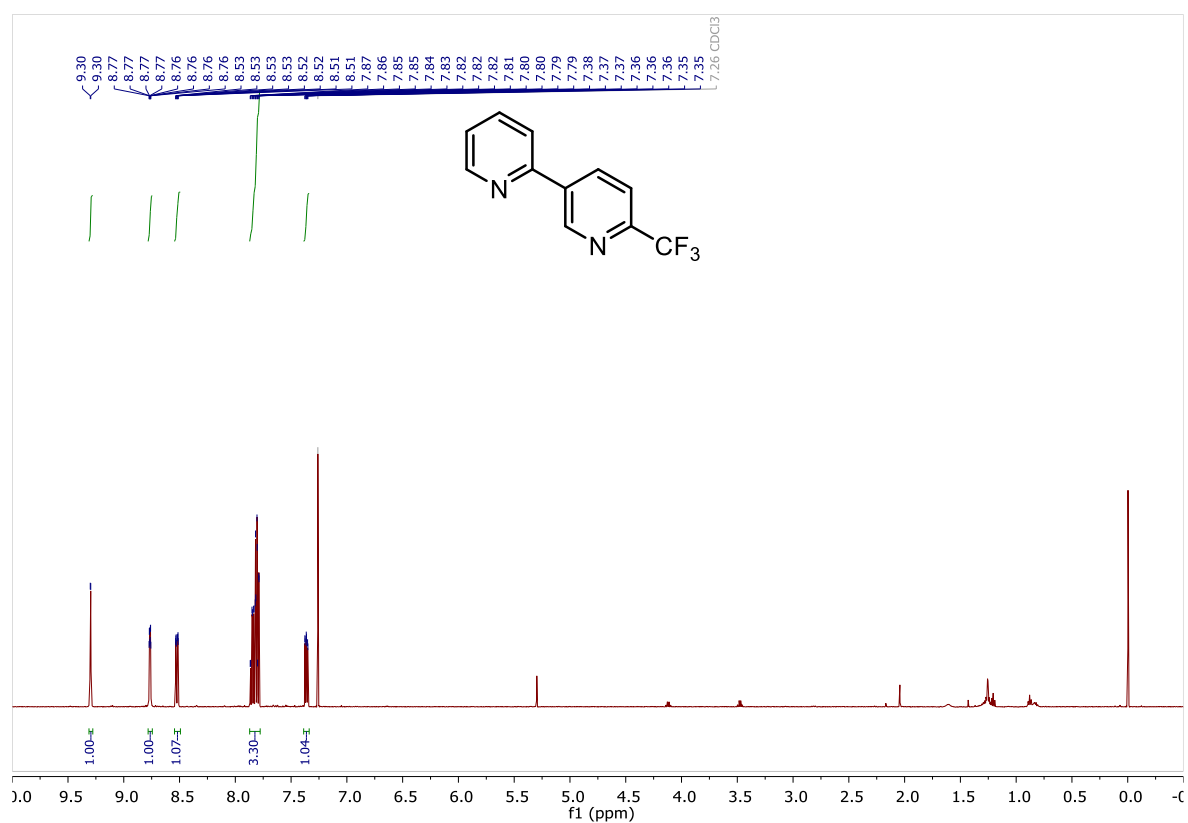
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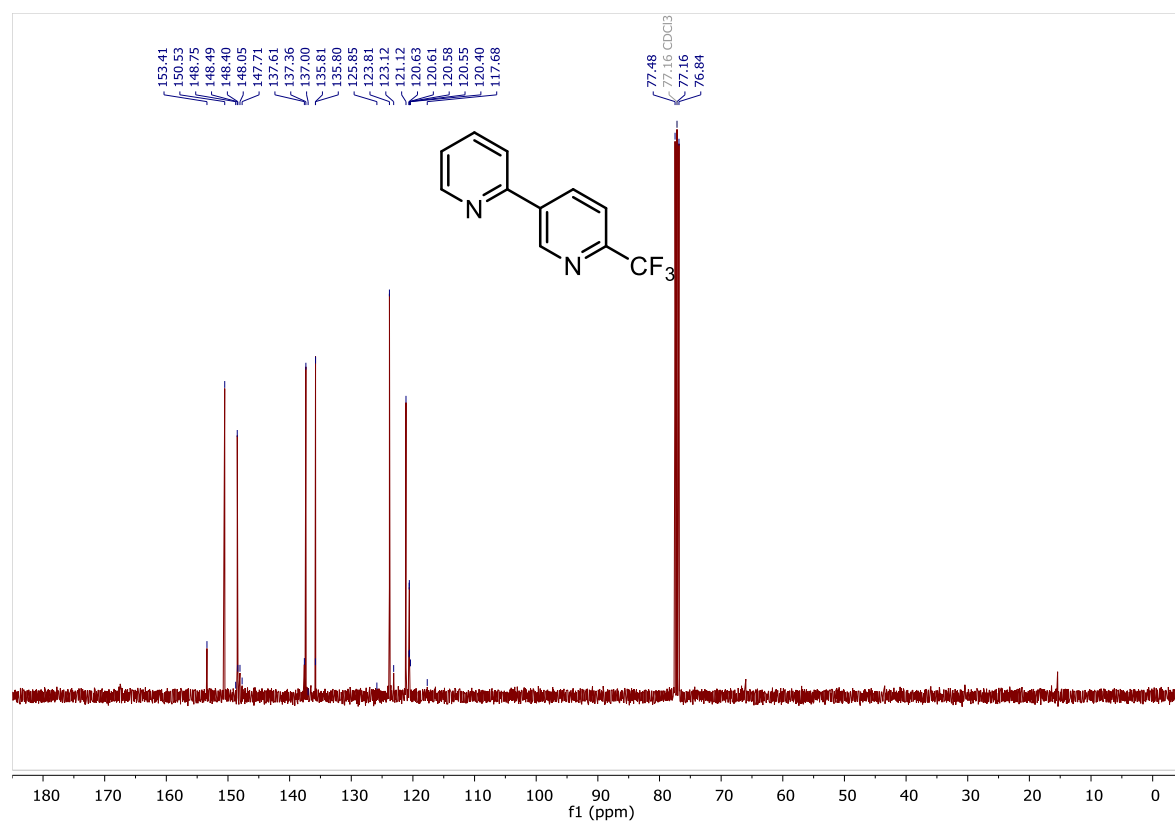
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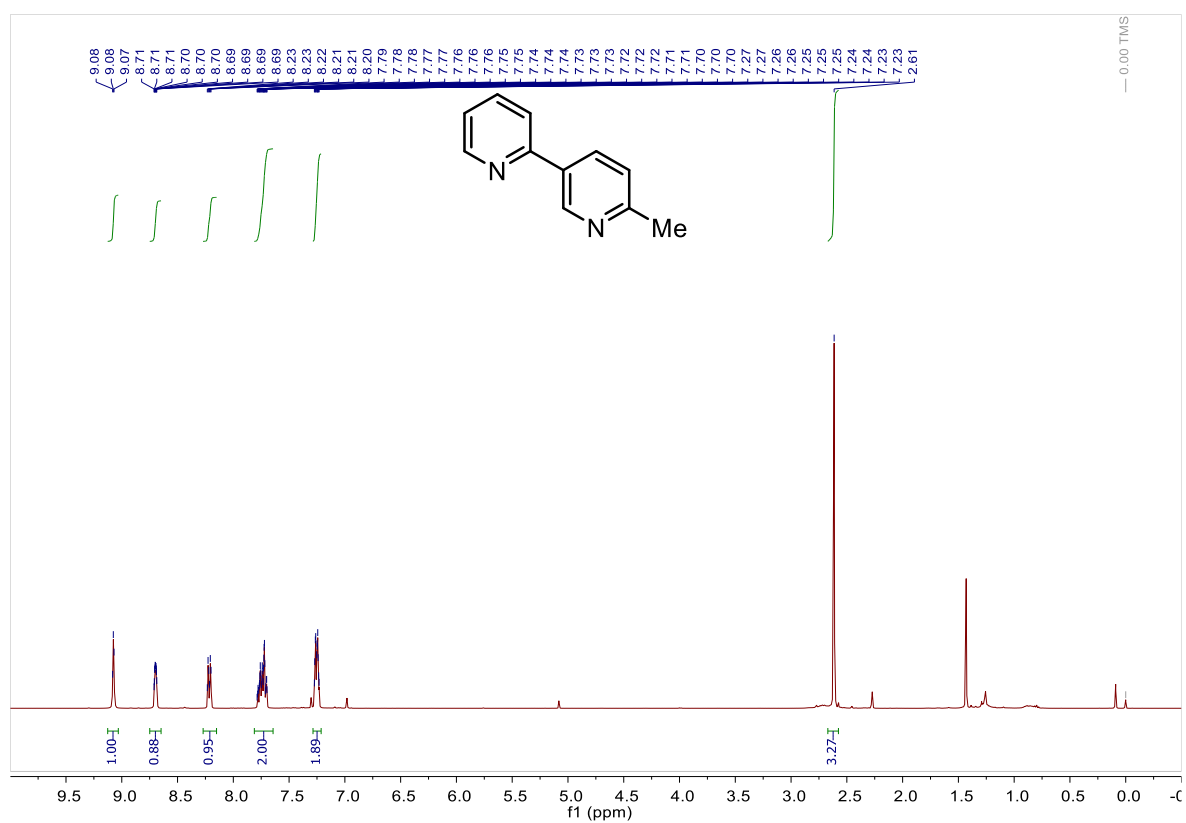
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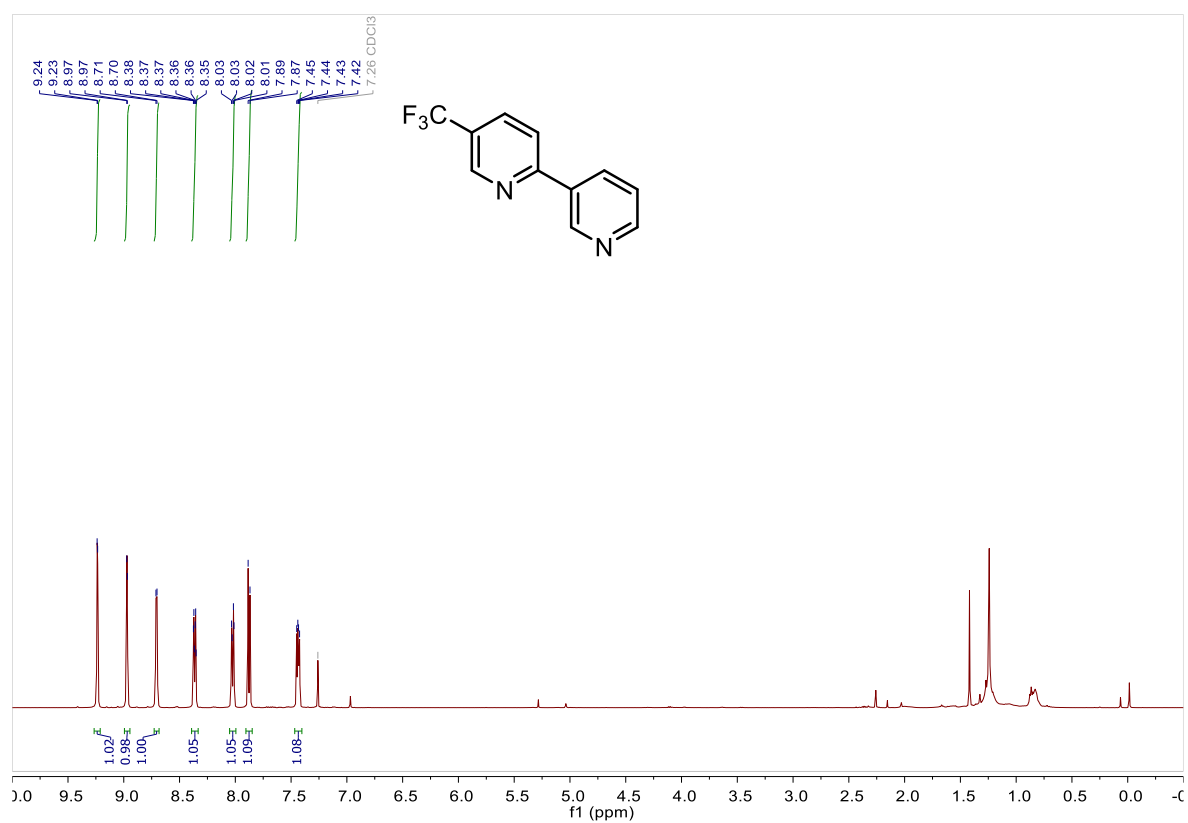
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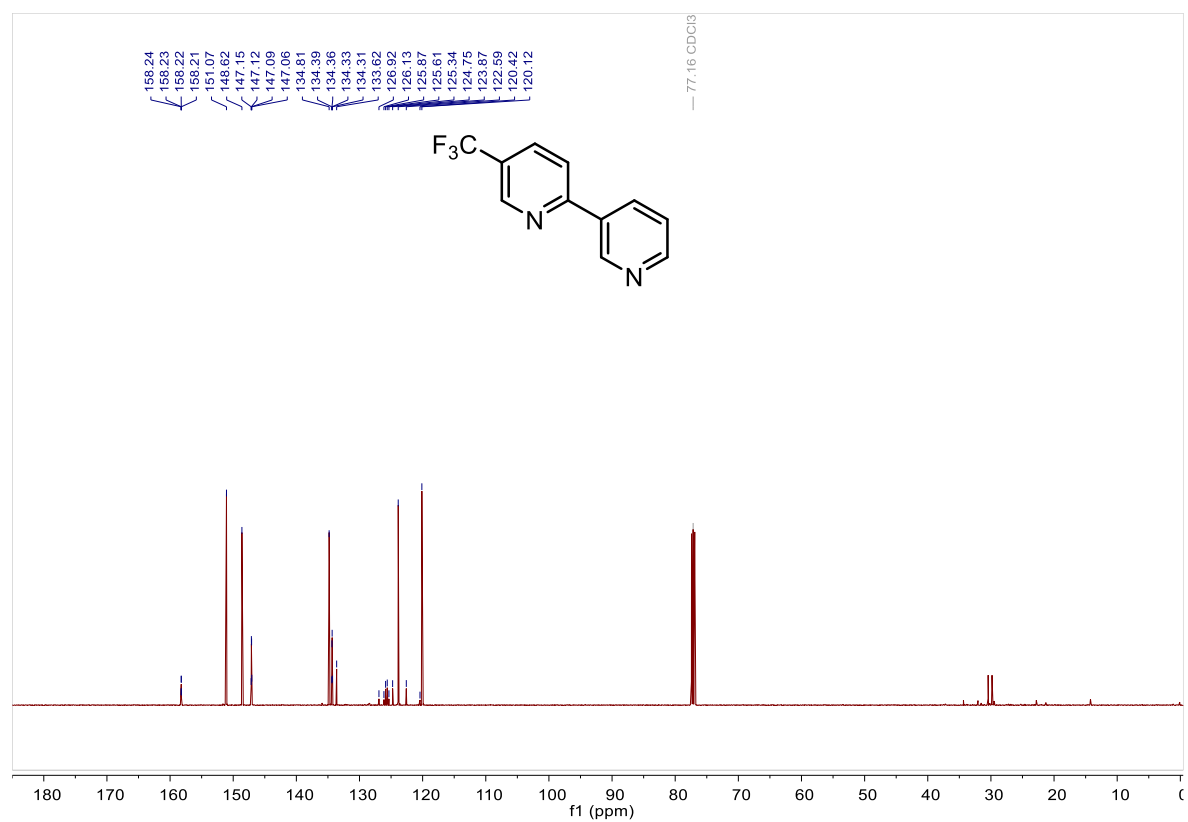
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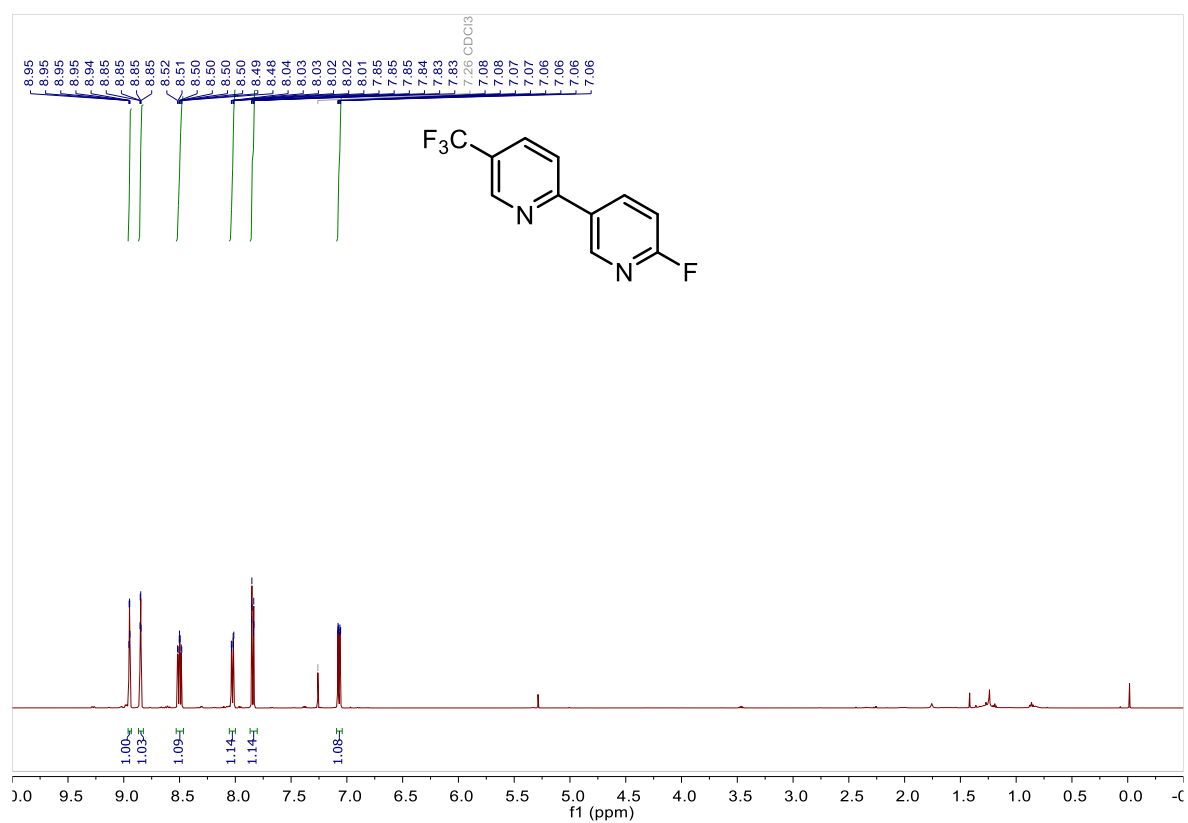
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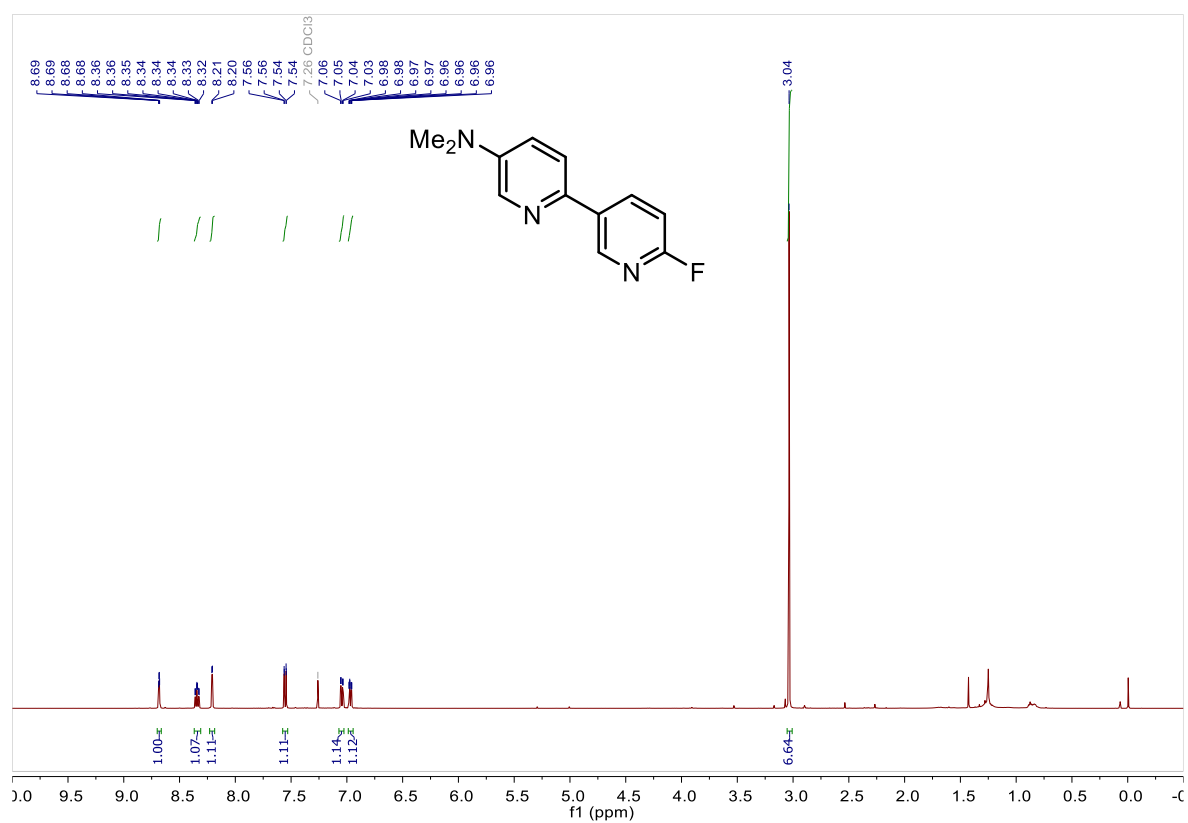
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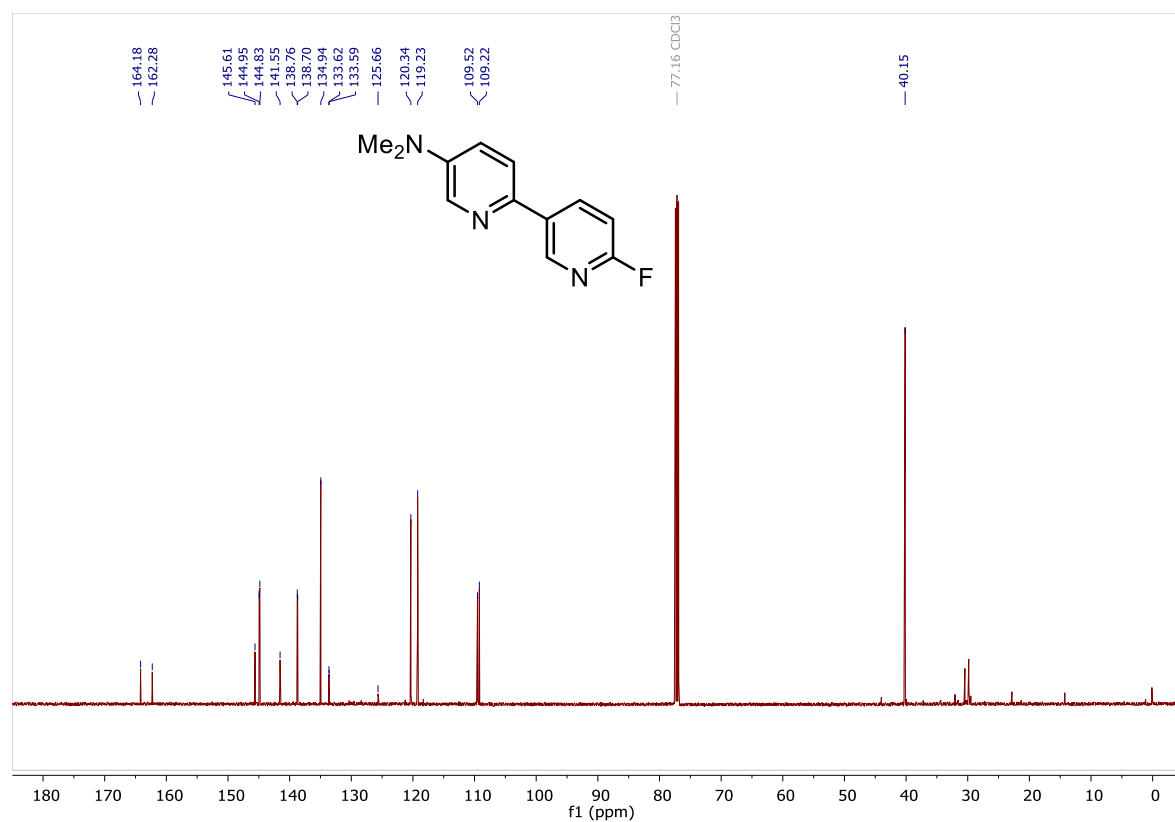
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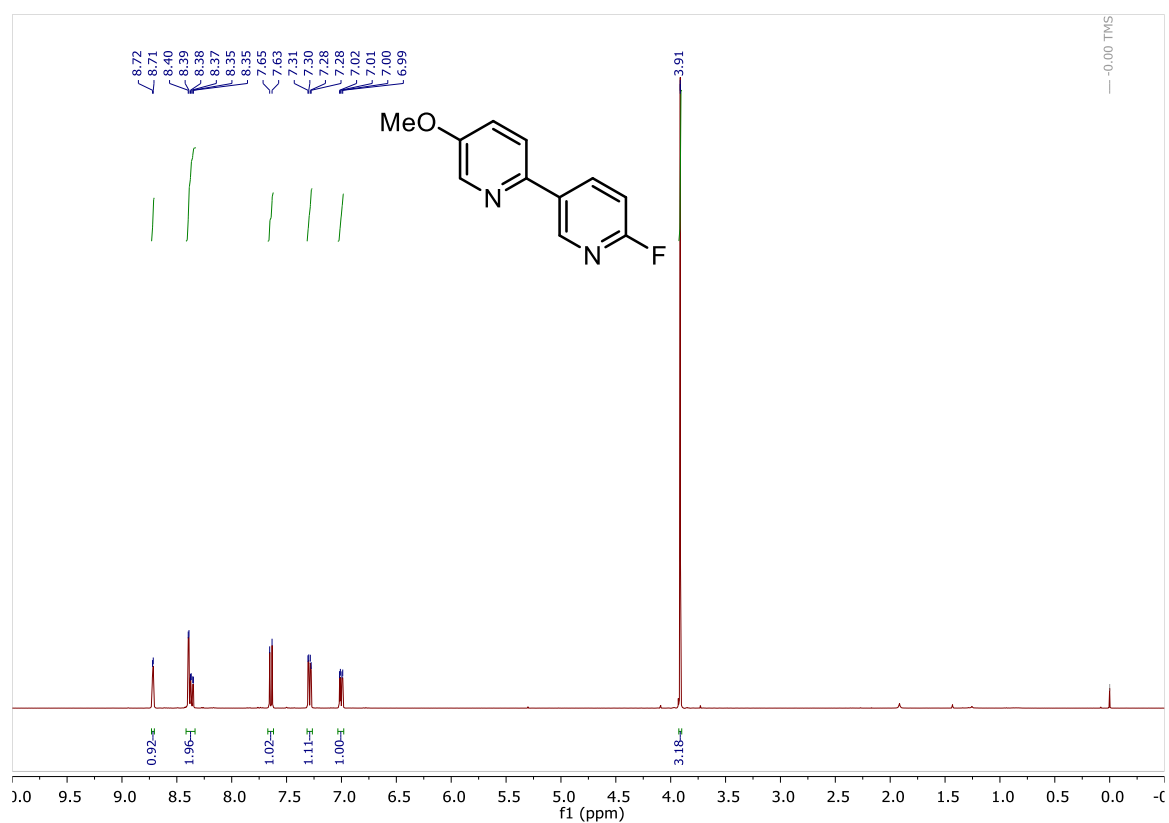
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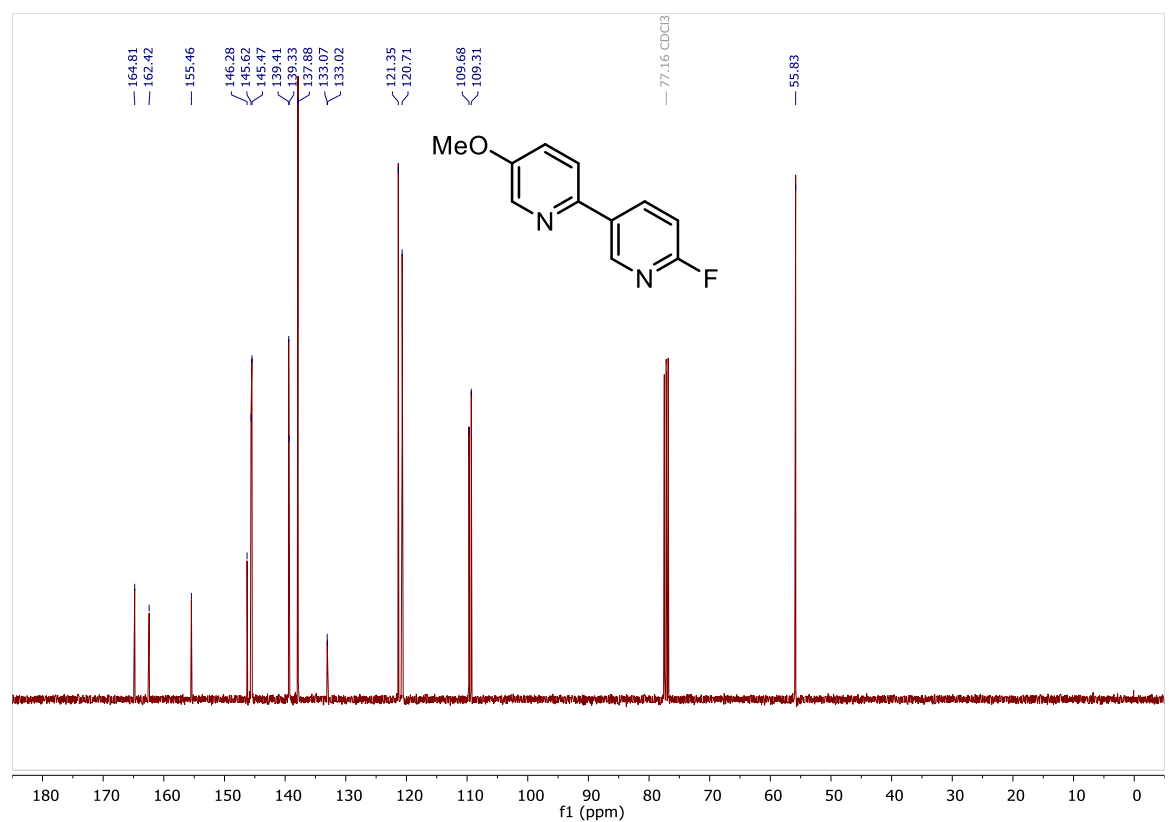
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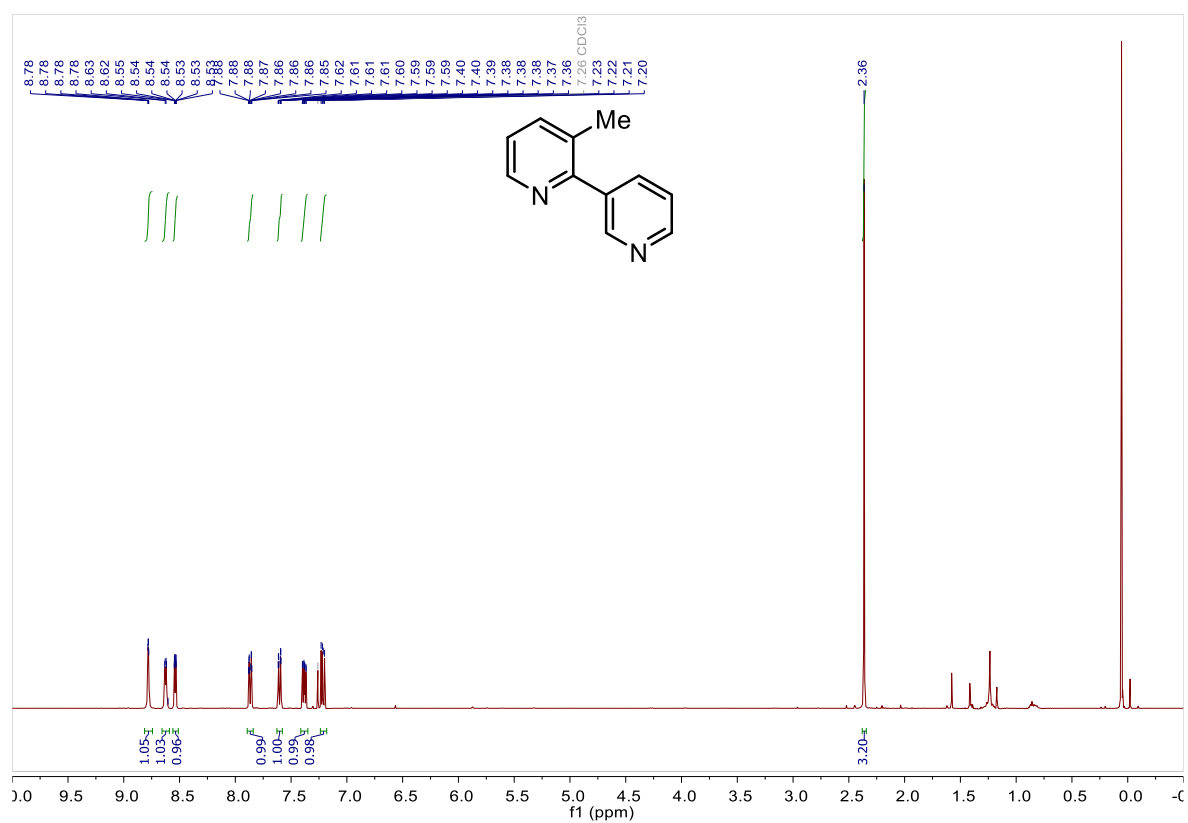
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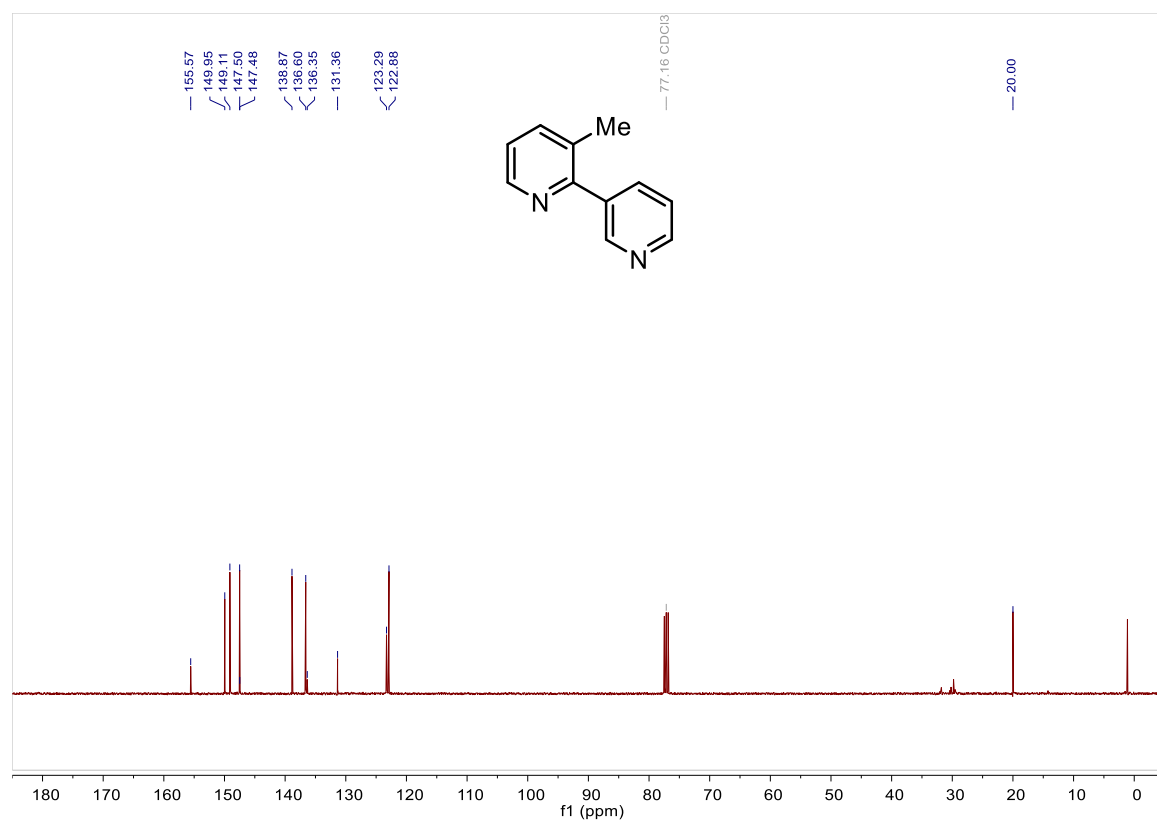
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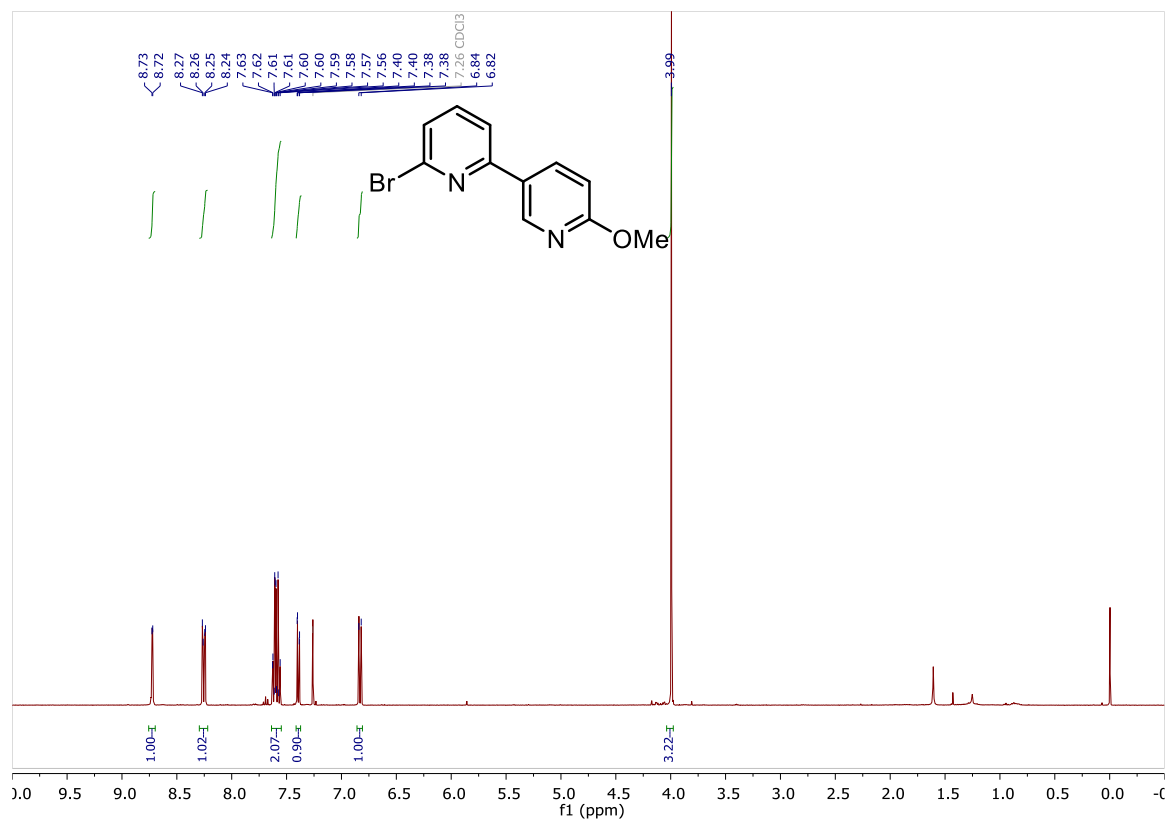
^1H NMR (400 MHz, CDCl_3): 38



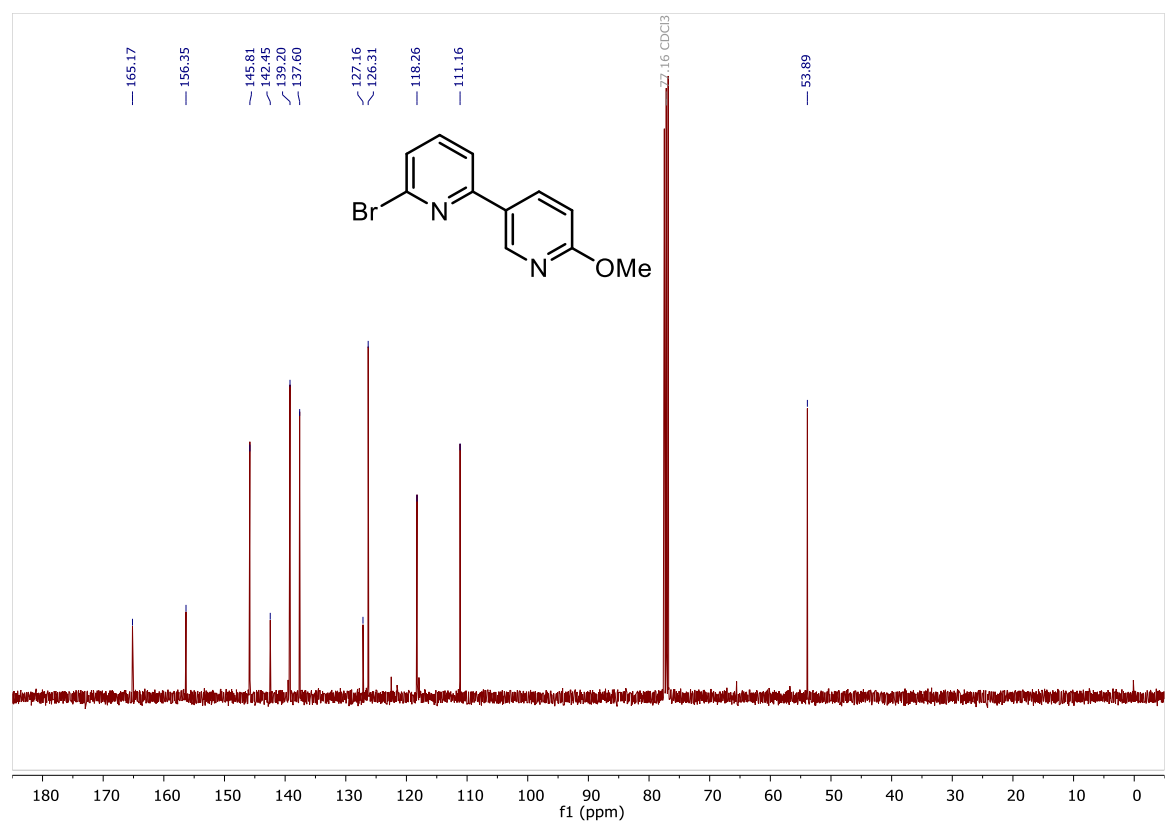
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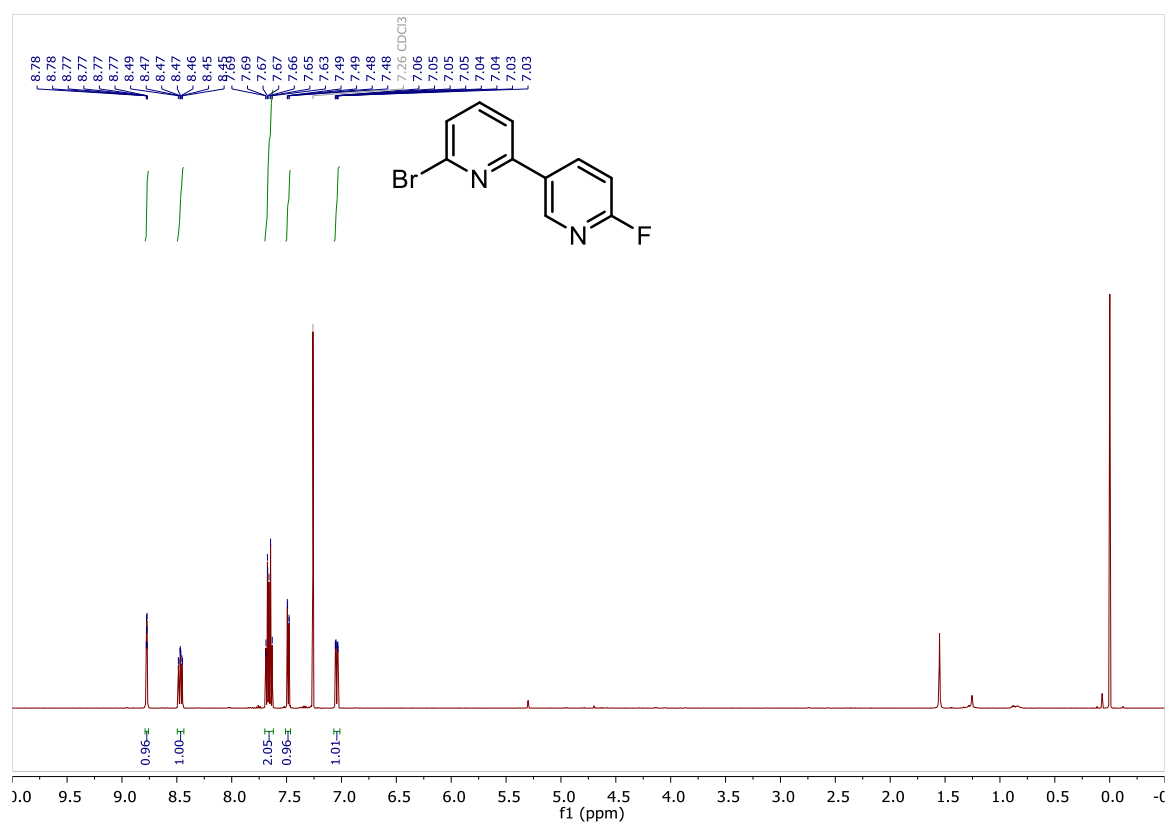
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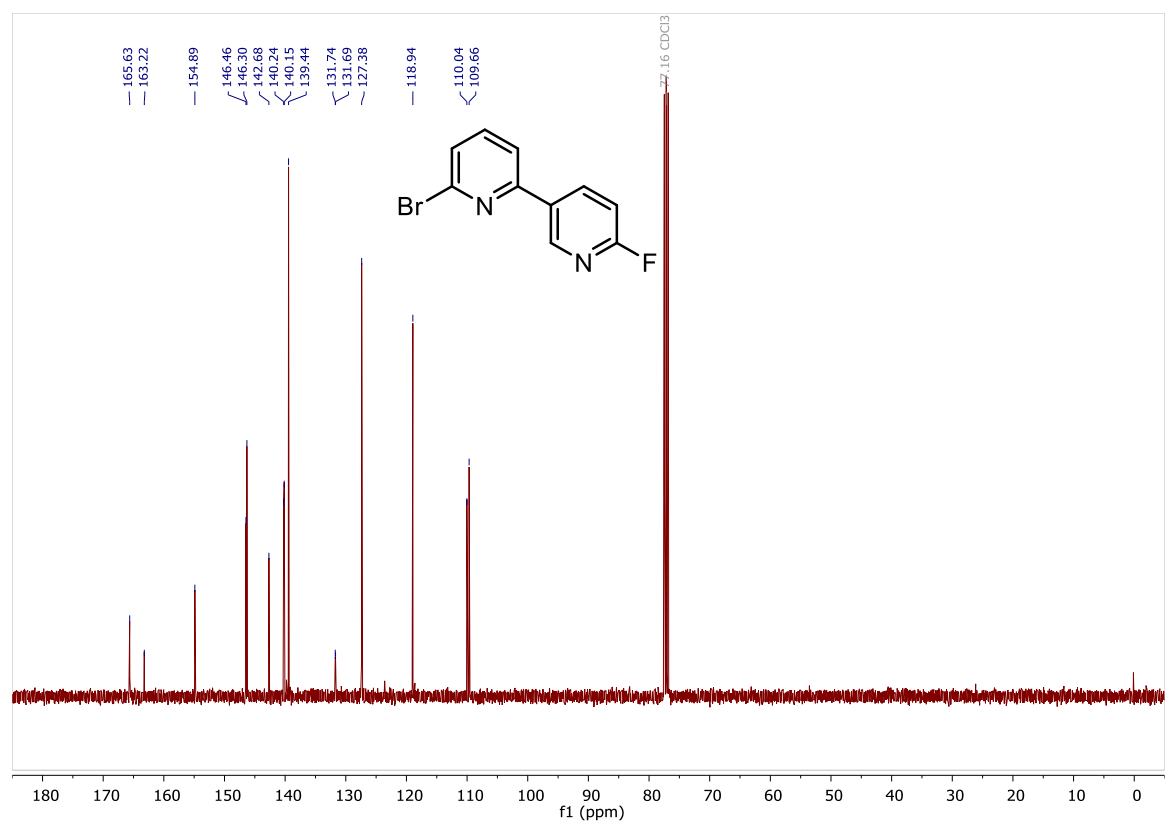
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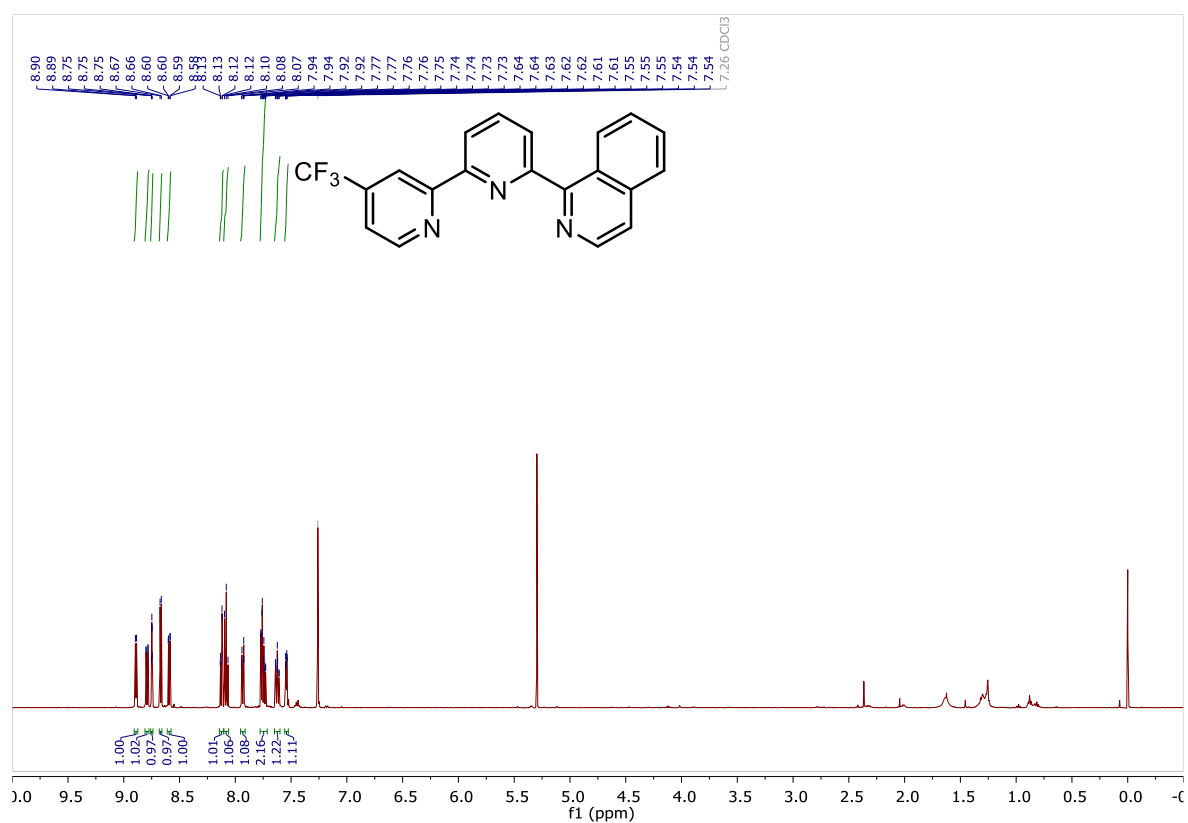
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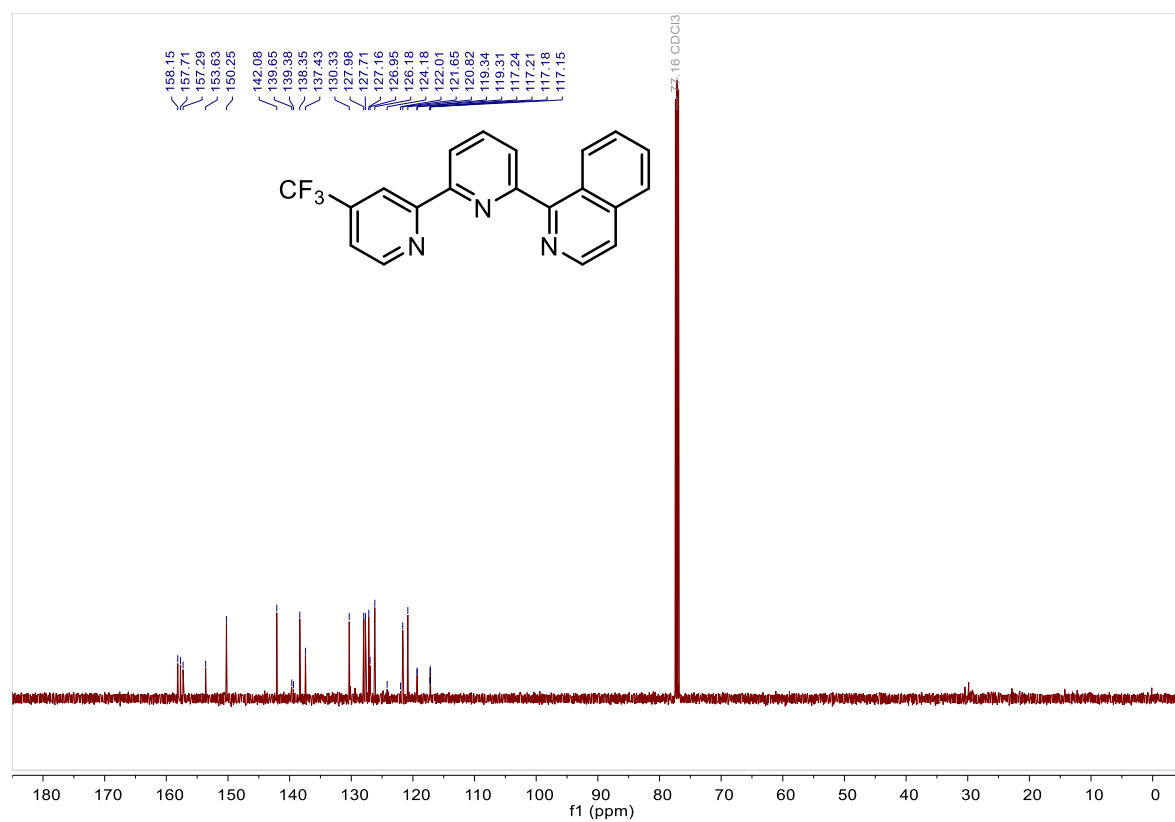
¹³C NMR (101 MHz, CDCl₃): 40



¹H NMR (500 MHz, CDCl₃): 43



¹³C NMR (126 MHz, CDCl₃): 43



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