Formal Insertion of Imines (or Nitrogen Heteroarenes) and Arynes into the C−Cl Bond of Carbon Tetrachloride

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General Information

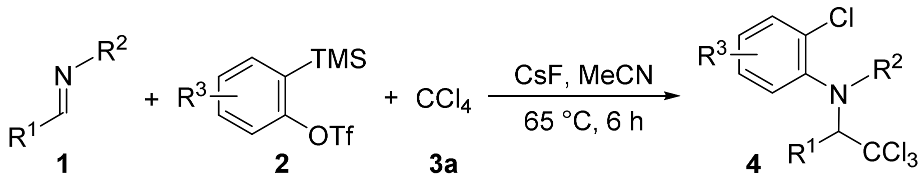
^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on an LC−TOF spectrometer (Micromass). Electron spray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Melting points were uncorrected.

Imines **1** were prepared according to literature procedures.[1] The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Energy chemical, Bide Pharmatech Ltd., Accela ChemBio Co., J&K Scientific, Meryer, Acros, Alfa Aesar, and TCI, and used as received.

Unless otherwise noted, all the reactions were performed in oven-dried glasswares with freshly distilled solvents. CsF was dried in vacuum at 130 °C for 1 h before use.

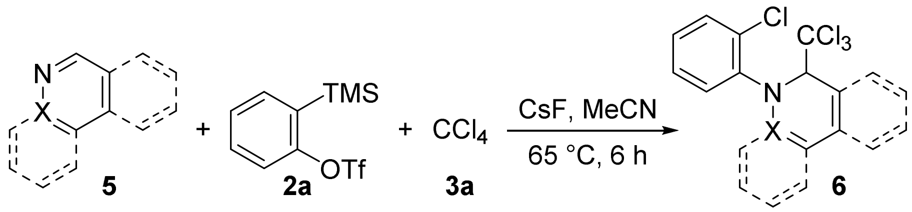
Abbreviations: PMP = *p*-methoxyphenyl, TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

General Procedure for the Three-Component Reaction of Imines, Arynes, and Carbon Tetrachloride



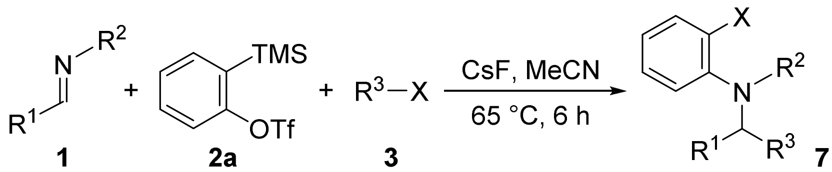
To a sealed reaction tube containing dry CsF (45.6 mg, 0.30 mmol) were sequentially added acetonitrile (0.20 mL), carbon tetrachloride (**3a**) (0.15 mL), imine **1** (0.10 mmol), and 2-(trimethylsilyl)aryl triflate **2** (0.15 mmol). The mixture was stirred at 65 °C for 6 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:30 to 0:1 v/v), to give compound **4**.

General Procedure for the Three-Component Reaction of Nitrogen Heteroarenes, Benzyne, and Carbon Tetrachloride



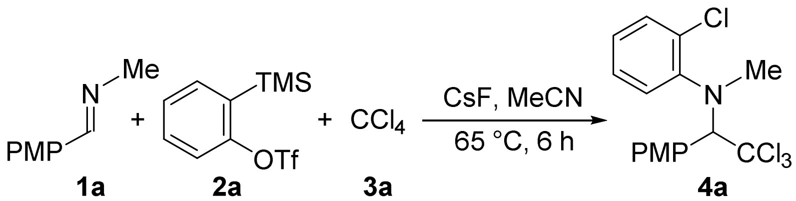
To a sealed reaction tube containing dry CsF (45.6 mg, 0.30 mmol) were sequentially added acetonitrile (0.20 mL), carbon tetrachloride (**3a**) (0.15 mL), nitrogen heteroarene **5** (0.10 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (44.8 mg, 0.15 mmol). The mixture was stirred at 65 °C for 6 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:30 to 0:1 v/v), to give compound **6**.

General Procedure for the Three-Component Reaction of Imines, Benzyne, and Organohalides



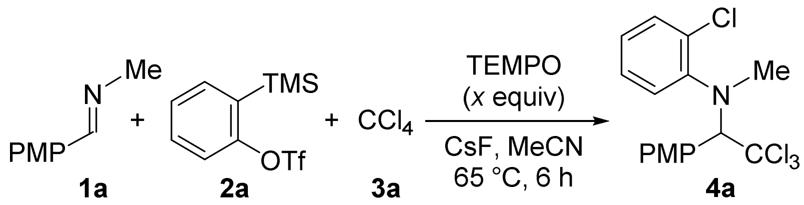
To a sealed reaction tube containing dry CsF (45.6 mg, 0.30 mmol) were sequentially added acetonitrile (0.20 mL), organohalide **3** (0.30 mmol), imine **1** (0.10 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (44.8 mg, 0.15 mmol). The mixture was stirred at 65 °C for 6 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:30 to 0:1 v/v), to give compound **7**.

Scale-Up Reaction



To a sealed reaction tube containing dry CsF (1.82 g, 12.0 mmol) were sequentially added acetonitrile (8.0 mL), carbon tetrachloride (**3a**) (6.0 mL), imine **1a** (0.60 g, 4.0 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (1.79 g, 6.0 mmol). The mixture was stirred at 65 °C for 6 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:30, v/v), to give compound **4a** (1.23 g, 81% yield) as a pale green oil.

Control Experiments

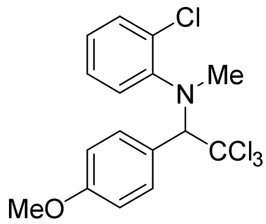


x	yield (%)
2	62
10	50

To a sealed reaction tube containing dry CsF (45.6 mg, 0.30 mmol) and TEMPO (31.2 mg, 0.20 mmol) were sequentially added acetonitrile (0.20 mL), carbon tetrachloride (**3a**) (0.15 mL), imine **1a** (14.9 mg, 0.10 mmol), and 2-(trimethylsilyl)phenyl triflate (**2a**) (44.8 mg, 0.15 mmol). The mixture was stirred at 65 °C for 6 h, cooled to room temperature, and purified directly by silica gel chromatography with the mixture eluent of ethyl acetate and petroleum ether (1:30, v/v), to give compound **4a** (23.5 mg, 62% yield) as a pale green oil.

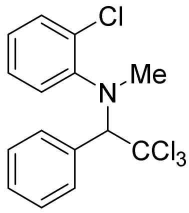
Instead, addition of 10 equiv of TEMPO gave compound **4a** (19.0 mg) in 50% yield.

Analytical Data for the Products



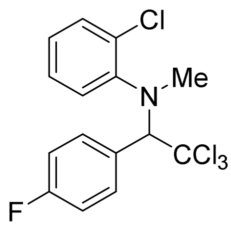
4a

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4a**). Pale green oil (33.0 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 6.8, 2.0 Hz, 2H), 7.37 (dd, J = 8.0, 1.6 Hz, 1H), 7.30 (dd, J = 8.0, 1.6 Hz, 1H), 7.20 (td, J = 7.6, 1.6 Hz, 1H), 7.01 (td, J = 7.6, 1.6 Hz, 1H), 6.95 (dd, J = 6.8, 2.0 Hz, 2H), 5.46 (s, 1H), 3.84 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 150.5, 131.7, 131.0, 130.8, 127.7, 127.1, 126.6, 125.0, 113.7, 104.5, 80.5, 55.4, 39.5; HRMS (ESI) calcd for $C_{16}H_{16}Cl_4NO^+$ $(M + H)^+$ 377.9981, found 377.9976.



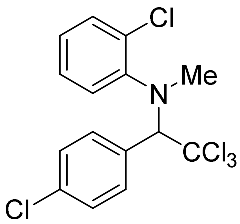
4b

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-phenylethyl)aniline (**4b**). Pale yellow solid (30.0 mg, 86% yield); m.p. 118−119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.75 (m, 2H), 7.46−7.39 (m, 3H), 7.37 (dd, J = 8.0, 1.6 Hz, 1H), 7.32 (dd, J = 8.0, 1.2 Hz, 1H), 7.20 (td, J = 8.0, 1.6 Hz, 1H), 7.01 (td, J = 7.6, 1.6 Hz, 1H), 5.52 (s, 1H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 135.1, 131.1, 130.8, 130.5, 128.7, 128.4, 127.7, 126.6, 125.1, 104.1, 81.0, 39.5; HRMS (ESI) calcd for $C_{15}H_{14}Cl_4N^+$ $(M + H)^+$ 347.9875, found 347.9877.



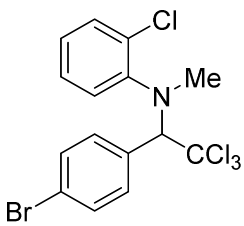
4c

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-(4-fluorophenyl)ethyl)aniline (**4c**). Yellow oil (34.9 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.71 (m, 2H), 7.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.28 (dd, J = 8.0, 1.6 Hz, 1H), 7.20 (td, J = 7.6, 1.6 Hz, 1H), 7.14−7.07 (m, 2H), 7.01 (td, J = 7.6, 1.6 Hz, 1H), 5.50 (s, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 247.1 Hz), 150.0, 132.3 (d, J = 8.0 Hz), 131.1, 131.0 (d, J = 3.6 Hz), 130.7, 127.7, 126.7, 125.2, 115.3 (d, J = 21.1 Hz), 104.0, 80.2, 39.4; HRMS (ESI) calcd for $C_{15}H_{13}Cl_4FN^+$ $(M + H)^+$ 365.9781, found 365.9785.



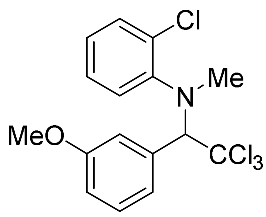
4d

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-(4-chlorophenyl)ethyl)aniline (**4d**). Yellow oil (32.6 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 6.8, 2.0 Hz, 2H), 7.41−7.37 (m, 2H), 7.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.28 (dd, J = 8.0, 1.6 Hz, 1H), 7.20 (td, J = 7.6, 1.6 Hz, 1H), 7.04−6.99 (m, 1H), 5.49 (s, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 134.6, 133.6, 131.8, 131.1, 130.6, 128.6, 127.7, 126.6, 125.2, 103.7, 80.1, 39.3; HRMS (ESI) calcd for $C_{15}H_{13}Cl_5N^+$ $(M + H)^+$ 381.9485, found 381.9490.



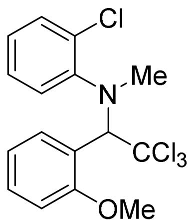
4e

N-(1-(4-bromophenyl)-2,2,2-trichloroethyl)-2-chloro-*N*-methylaniline (**4e**). Pale green oil (36.8 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, J = 6.8, 2.0 Hz, 2H), 7.57−7.52 (m, 2H), 7.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.28 (dd, J = 8.0, 1.6 Hz, 1H), 7.20 (td, J = 7.6, 1.6 Hz, 1H), 7.04−6.99 (m, 1H), 5.48 (s, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 134.1, 132.1, 131.5, 131.1, 130.6, 127.7, 126.6, 125.2, 122.9, 103.6, 80.2, 39.3; HRMS (ESI) calcd for $C_{15}H_{13}BrCl_4N^+$ $(M + H)^+$ 425.8980, found 425.8985.



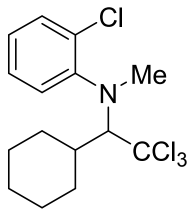
4f

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-(3-methoxyphenyl)ethyl)aniline (**4f**). Yellow oil (25.8 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.34 (m, 4H), 7.32 (dd, J = 8.0, 1.6 Hz, 1H), 7.21 (td, J = 7.6, 1.6 Hz, 1H), 7.02 (td, J = 7.6, 1.6 Hz, 1H), 6.96−6.92 (m, 1H), 5.48 (s, 1H), 3.84 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 150.4, 136.4, 131.1, 130.8, 129.3, 127.7, 126.6, 125.1, 122.9, 116.8, 113.5, 104.0, 80.7, 55.4, 39.5; HRMS (ESI) calcd for $C_{16}H_{16}Cl_4NO^+$ $(M + H)^+$ 377.9981, found 377.9985.



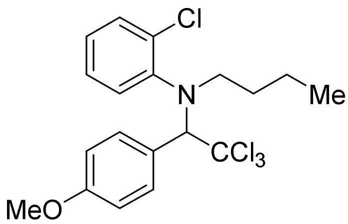
4g

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-(2-methoxyphenyl)ethyl)aniline (**4g**). Yellow oil (22.4 mg, 59% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.42−7.34 (m, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.05−6.97 (m, 3H), 6.10 (s, 1H), 3.95 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 151.3, 131.9, 130.8, 130.1, 130.0, 127.5, 126.8, 125.0, 123.2, 120.1, 111.2, 105.1, 72.4, 55.8, 40.3; HRMS (ESI) calcd for $C_{16}H_{16}Cl_4NO^+$ $(M + H)^+$ 377.9981, found 377.9985.



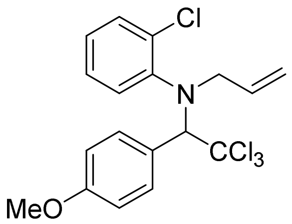
4h

2-Chloro-*N*-methyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**4h**). Colorless oil (26.3 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.26 (m, 1H), 7.17−7.11 (m, 2H), 6.88−6.81 (m, 1H), 4.43 (d, J = 8.4 Hz, 1H), 3.07 (s, 3H), 2.33−2.18 (m, 2H), 2.10−2.03 (m, 1H), 1.84−1.76 (m, 2H), 1.71−1.64 (m, 1H), 1.38−1.15 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 131.9, 127.4, 125.5, 123.2, 122.2, 105.3, 80.1, 40.6, 35.2, 32.3, 31.2, 26.9, 26.7, 26.3; HRMS (ESI) calcd for $C_{15}H_{20}Cl_4N^+$ $(M + H)^+$ 354.0344, found 354.0348.



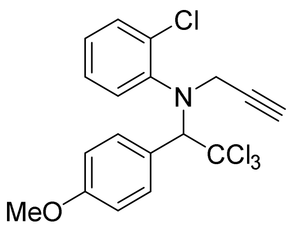
4i

N-Butyl-2-chloro-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4i**). Yellow oil (34.1 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.65 (m, 2H), 7.37−7.30 (m, 2H), 7.18 (td, J = 7.6, 1.6 Hz, 1H), 7.02 (td, J = 7.6, 1.2 Hz, 1H), 6.93−6.88 (m, 2H), 5.43 (s, 1H), 3.84 (s, 3H), 3.71 (ddd, J = 14.0, 9.2, 4.4 Hz, 1H), 3.49−3.39 (m, 1H), 1.09−0.80 (m, 4H), 0.61 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.4, 132.2, 131.6, 131.0, 129.9, 128.3, 127.2, 125.4, 113.5, 104.8, 80.8, 55.4, 49.3, 30.4, 19.9, 13.9; HRMS (ESI) calcd for $C_{19}H_{22}Cl_4NO^+$ $(M + H)^+$ 420.0450, found 420.0457.



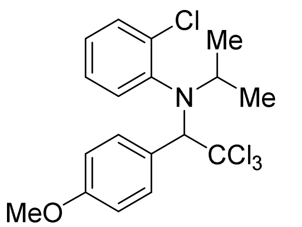
4j

N-Allyl-2-chloro-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4j**). Yellow oil (30.8 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 6.8, 2.0 Hz, 2H), 7.34 (dd, J = 8.0, 1.6 Hz, 1H), 7.25 (dd, J = 8.0, 1.6 Hz, 1H), 7.16 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 7.01 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 6.93−6.88 (m, 2H), 5.45 (s, 1H), 5.33 (dddd, J = 17.6, 10.0, 7.6, 5.2 Hz, 1H), 4.83−4.73 (m, 2H), 4.25 (dd, J = 15.6, 7.6 Hz, 1H), 4.10 (ddt, J = 15.6, 5.2, 1.6 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 146.4, 135.1, 132.4, 131.6, 130.8, 130.2, 128.1, 127.1, 125.7, 117.1, 113.6, 104.7, 80.5, 55.3, 53.3; HRMS (ESI) calcd for $C_{18}H_{18}Cl_4NO^+$ $(M + H)^+$ 404.0137, found 404.0143.



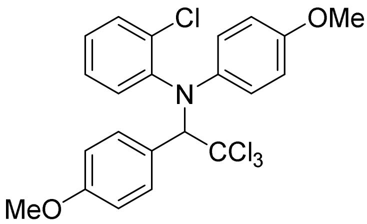
4k

2-Chloro-*N*-(prop-2-yn-1-yl)-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4k**). Yellow oil (26.6 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 6.8, 2.0 Hz, 2H), 7.30 (dd, J = 8.0, 1.6 Hz, 1H), 7.24 (dd, J = 8.0, 1.6 Hz, 1H), 7.11 (td, J = 7.6, 1.6 Hz, 1H), 7.00 (td, J = 7.6, 1.6 Hz, 1H), 6.82 (dd, J = 6.8, 2.0 Hz, 2H), 5.28 (s, 1H), 4.27 (dd, J = 18.4, 2.4 Hz, 1H), 4.08 (dd, J = 18.4, 2.4 Hz, 1H), 3.74 (s, 3H), 1.79 (t, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 146.7, 133.0, 131.7, 130.7, 130.2, 127.3, 127.2, 126.6, 113.7, 104.3, 80.5, 80.0, 72.4, 55.3, 41.8; HRMS (ESI) calcd for $C_{18}H_{16}Cl_4NO^+$ $(M + H)^+$ 401.9981, found 401.9981.



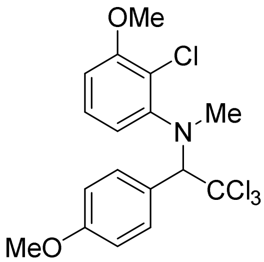
4l

2-Chloro-*N*-isopropyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4l**). Pale green oil (30.5 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.38 (m, 3H), 7.12 (td, J = 7.6, 1.6 Hz, 1H), 7.04 (td, J = 7.6, 1.6 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 6.84−6.79 (m, 2H), 5.08 (s, 1H), 4.08−4.00 (m, 1H), 3.82 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H), 0.82 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 142.0, 137.7, 137.2, 132.6, 130.7, 128.4, 127.5, 125.8, 113.1, 105.5, 82.0, 55.6, 55.3, 22.5, 20.9. HRMS (ESI) calcd for $C_{18}H_{20}Cl_4NO^+$ $(M + H)^+$ 406.0294, found 406.0300.



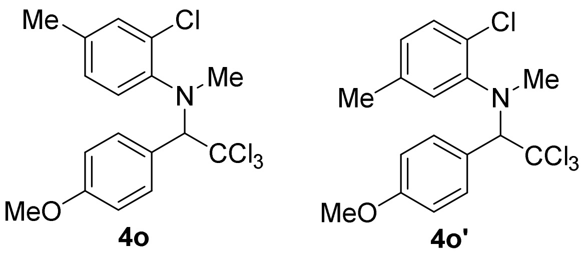
4m

2-Chloro-*N*-(4-methoxyphenyl)-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4m**). Yellow oil (30.6 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.0, 1.6 Hz, 1H), 7.28−7.16 (m, 4H), 7.13 (td, J = 7.6, 1.6 Hz, 1H), 7.05−7.01 (m, 2H), 6.75−6.70 (m, 4H), 5.94 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.3, 144.5, 141.3, 135.5, 133.0, 132.4, 131.1, 127.6, 127.2, 126.5, 125.3, 113.9, 113.1, 104.6, 79.8, 55.5, 55.2; HRMS (ESI) calcd for $C_{22}H_{20}Cl_4NO_2^+$ $(M + H)^+$ 470.0243, found 470.0244.



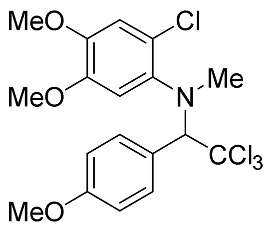
4n

2-Chloro-3-methoxy-*N*-methyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4n**). Colorless oil (37.2 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.8 Hz, 2H), 7.16 (t, J = 8.0 Hz, 1H), 6.98−6.93 (m, 3H), 6.69 (d, J = 8.0 Hz, 1H), 5.46 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 156.4, 152.2, 131.7, 127.2, 127.0, 119.4, 118.4, 113.7, 107.4, 104.5, 80.6, 56.4, 55.4, 39.5; HRMS (ESI) calcd for $C_{17}H_{18}Cl_4NO_2^+$ $(M + H)^+$ 408.0086, found 408.0082.



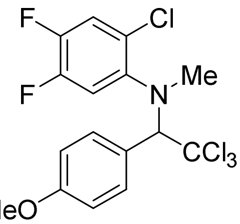
4o **4o'**

A 43:57 mixture of 2-chloro-*N*,4-dimethyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4o**) and 2-chloro-*N*,5-dimethyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4o′**) was obtained as a colorless oil (34.2 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) for amine **4o**: δ 7.66 (d, J = 8.4 Hz, 2H), 7.25−7.21 (m, 2H), 7.02−6.91 (m, 3H), 5.37 (s, 1H), 3.84 (s, 3H), 2.93 (s, 3H), 2.28 (s, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for amine **4o′**: δ 7.70 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.8 Hz, 1H), 7.09 (s, 1H), 6.97−6.91 (m, 2H), 6.82 (d, J = 8.0 Hz, 1H), 5.46 (s, 1H), 3.85 (s, 3H), 2.95 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 150.2, 148.0, 137.6, 135.2, 131.8, 131.7, 131.3, 130.8, 130.6, 128.4, 127.6, 127.3, 127.2, 126.7, 125.8, 113.7, 113.6, 104.6, 80.9, 80.4, 55.4, 39.8, 39.5, 21.2, 20.7; HRMS (ESI) calcd for $C_{17}H_{18}Cl_4NO^+$ $(M + H)^+$ 392.0137, found 392.0135.



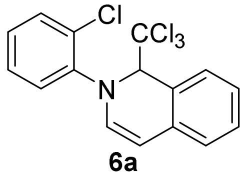
4p

2-Chloro-4,5-dimethoxy-*N*-methyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethy-l)aniline (**4p**). Colorless oil (35.6 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.83 (s, 1H), 6.76 (s, 1H), 5.19 (s, 1H), 3.84 (s, 6H), 3.80 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 147.9, 146.6, 142.8, 131.8, 127.3, 122.9, 113.6, 113.0, 111.4, 104.5, 81.5, 56.3, 56.2, 55.3, 40.8; HRMS (ESI) calcd for $C_{18}H_{20}Cl_4NO_3^+$ $(M + H)^+$ 438.0192, found 438.0191.



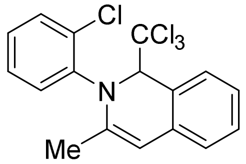
4q

2-Chloro-4,5-difluoro-*N*-methyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**4q**). Yellow oil (16.6 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.8 Hz, 2H), 7.21 (dd, J = 9.6, 8.4 Hz, 1H), 7.10 (dd, J = 11.2, 8.0 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 5.31 (s, 1H), 3.85 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 149.1 (dd, J = 248.5, 13.2 Hz), 146.8 (dd, J = 6.5, 3.5 Hz), 146.6 (dd, J = 247.4, 13.6 Hz), 131.6, 126.6, 125.8 (dd, J = 7.3, 3.3 Hz), 119.2 (dd, J = 20.2, 1.0 Hz), 115.5 (d, J = 17.8 Hz), 113.8, 104.1, 80.6, 55.4, 39.8; HRMS (ESI) calcd for $C_{16}H_{14}Cl_4F_2NO^+$ $(M + H)^+$ 413.9792, found 413.9784.



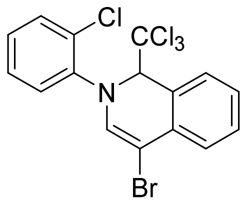
6a

2-(2-Chlorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (**6a**). Colorless oil (28.0 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.46 (m, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.27−7.20 (m, 2H), 7.15−7.08 (m, 2H), 6.61 (d, J = 7.6 Hz, 1H), 5.77 (d, J = 7.6 Hz, 1H), 5.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 133.9, 133.7, 131.2, 131.1, 130.2, 129.8, 129.3, 128.1, 127.1, 125.3, 124.1, 121.9, 105.3, 103.6, 76.2; HRMS (ESI) calcd for $C_{16}H_{12}Cl_4N^+$ $(M + H)^+$ 357.9718, found 357.9727.



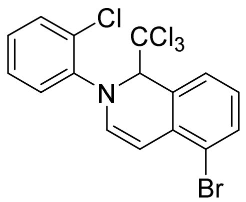
6b

2-(2-Chlorophenyl)-3-methyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (**6b**). Yellow oil (26.9 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.42−7.37 (m, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.29−7.21 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 5.79 (s, 1H), 5.26 (s, 1H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.2, 135.7, 134.5, 134.4, 130.7, 130.6, 128.9, 128.8, 126.5, 124.6, 123.4, 122.7, 105.7, 105.2, 78.3, 21.8; HRMS (ESI) calcd for $C_{17}H_{14}Cl_4N^+$ $(M + H)^+$ 371.9875, found 371.9880.



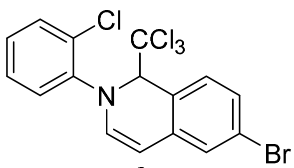
6c

4-Bromo-2-(2-chlorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (**6c**). Colorless oil (29.3 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.56 (m, 1H), 7.52 (dd, J = 8.0, 1.6 Hz, 1H), 7.50−7.45 (m, 2H), 7.42 (dd, J = 8.0, 1.2 Hz, 1H), 7.36−7.31 (m, 1H), 7.29 (td, J = 7.6, 1.6 Hz, 1H), 7.17 (td, J = 7.6, 1.6 Hz, 1H), 6.94 (d, J = 1.2 Hz, 1H), 5.69 (d, J = 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 134.2, 132.2, 131.2, 131.1, 130.2, 129.9, 129.8, 128.3, 127.7, 126.8, 123.8, 122.6, 104.0, 98.4, 76.3; HRMS (ESI) calcd for $C_{16}H_{11}BrCl_4N^+$ $(M + H)^+$ 435.8824, found 435.8828.



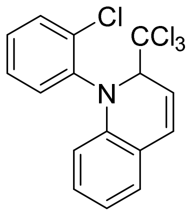
6d

5-Bromo-2-(2-chlorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (**6d**). Colorless oil (33.7 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.57 (m, 1H), 7.52 (dd, J = 8.0, 1.2 Hz, 1H), 7.44−7.39 (m, 2H), 7.27 (td, J = 8.0, 1.2 Hz, 1H), 7.15 (td, J = 8.0, 1.2 Hz, 1H), 7.07 (t, J = 8.0 Hz, 1H), 6.70 (dd, J = 8.0, 0.8 Hz, 1H), 6.13 (d, J = 7.6 Hz, 1H), 5.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 135.8, 133.4, 133.1, 131.1, 130.7, 130.0, 128.2, 127.5, 126.0, 123.3, 119.4, 104.7, 102.3, 75.9; HRMS (ESI) calcd for $C_{16}H_{11}BrCl_4N^+$ $(M + H)^+$ 435.8824, found 435.8828.



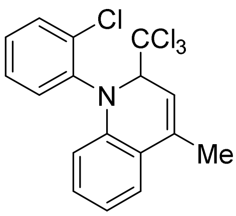
6e

6-Bromo-2-(2-chlorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (**6e**). Colorless oil (35.9 mg, 82% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.36−7.31 (m, 2H), 7.29−7.23 (m, 2H), 7.14 (t, J = 8.0 Hz, 1H), 6.62 (d, J = 7.6 Hz, 1H), 5.70−5.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 135.7, 135.2, 132.6, 131.1, 130.1, 130.0, 128.2, 128.1, 127.4, 126.7, 123.6, 120.6, 104.8, 102.5, 75.7; HRMS (ESI) calcd for $C_{16}H_{11}BrCl_4N^+$ $(M + H)^+$ 435.8824, found 435.8832.



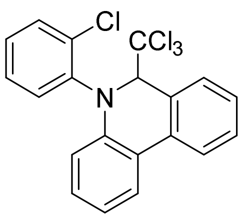
6f

1-(2-Chlorophenyl)-2-(trichloromethyl)-1,2-dihydroquinoline (**6f**). Colorless oil (28.7 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.90 (m, 1H), 7.50 (dd, J = 8.0, 1.6 Hz, 1H), 7.35 (td, J = 7.6, 1.6 Hz, 1H), 7.29 (td, J = 7.6, 1.6 Hz, 1H), 7.11 (dd, J = 7.2, 1.6 Hz, 1H), 7.04−6.97 (m, 1H), 6.91 (d, J = 9.6 Hz, 1H), 6.78 (td, J = 7.2, 1.2 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.15 (dd, J = 10.0, 5.6 Hz, 1H), 5.02−4.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.4, 137.5, 133.3, 131.3, 130.1, 129.0, 127.7, 126.5, 122.2, 119.7, 117.2, 115.3, 105.5, 74.6; HRMS (ESI) calcd for $C_{16}H_{12}Cl_4N^+$ $(M + H)^+$ 357.9718, found 357.9723.



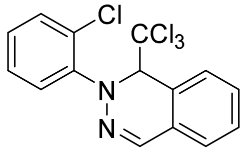
6g

1-(2-Chlorophenyl)-4-methyl-2-(trichloromethyl)-1,2-dihydroquinoline (**6g**). Colorless oil (29.1 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.82 (m, 1H), 7.45 (dd, J = 7.6, 1.6 Hz, 1H), 7.32−7.19 (m, 3H), 6.99 (t, J = 8.0 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 6.0 Hz, 1H), 4.97−4.83 (m, 1H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.3, 137.4, 135.1, 133.4, 131.3, 128.9, 128.6, 126.4, 124.3, 123.5, 119.4, 115.2, 114.7, 105.9, 74.4, 19.5; HRMS (ESI) calcd for $C_{17}H_{14}Cl_4N^+$ $(M + H)^+$ 371.9875, found 371.9882.



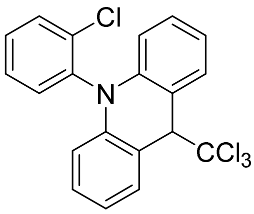
6h

5-(2-Chlorophenyl)-6-(trichloromethyl)-5,6-dihydrophenanthridine (**6h**). Pale yellow oil (25.4 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz, 1H), 7.89 (t, J = 8.0 Hz, 2H), 7.54−7.44 (m, 2H), 7.39−7.27 (m, 3H), 7.19 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 5.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 141.4, 135.6, 134.1, 132.5, 131.3, 129.2, 128.8, 126.8, 126.6, 124.5, 123.0, 122.9, 120.8, 117.9, 104.8, 77.1; HRMS (ESI) calcd for $C_{20}H_{14}Cl_4N^+$ $(M + H)^+$ 407.9875, found 407.9878.



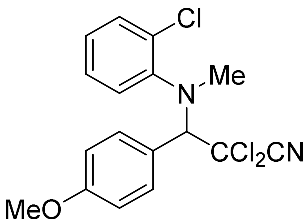
6i

2-(2-Chlorophenyl)-1-(trichloromethyl)-1,2-dihydrophthalazine (**6i**). Pale yellow oil (20.5 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.0, 1.6 Hz, 1H), 7.66 (s, 1H), 7.62−7.57 (m, 1H), 7.56−7.49 (m, 2H), 7.39−7.30 (m, 3H), 7.11 (td, J = 7.6, 1.2 Hz, 1H), 6.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 138.3, 130.8, 130.4, 130.2, 129.9, 127.9, 126.5, 126.1, 124.7, 123.6, 103.5, 71.7; HRMS (ESI) calcd for $C_{15}H_{11}Cl_4N_2^+$ $(M + H)^+$ 358.9671, found 358.9661.



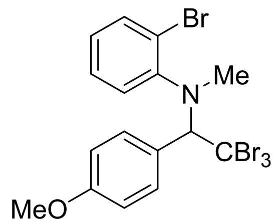
6j

10-(2-Chlorophenyl)-9-(trichloromethyl)-9,10-dihydroacridine (**6j**). Colorless oil (31.5 mg, 77% yield, major/minor isomer = 81:19); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.58 (2×m, 3H), 7.49−7.42 (2×m, 2H), 7.39−7.34 and 7.14−7.10 (2×m, 1H), 7.24−7.15 (2×m, 2H), 7.03 (2×t, J = 7.6 Hz, 2H), 6.34−6.27 (2×m, 2H), 5.08 and 5.03 (2×s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.2, 138.0, 137.2, 136.1, 135.8, 133.2, 133.1, 132.5, 131.9, 131.2, 130.5, 130.0, 129.7, 129.3, 129.2, 129.0, 120.6, 116.1, 115.9, 114.1, 105.6, 104.7, 62.3, 62.2; HRMS (ESI) calcd for $C_{20}H_{14}Cl_4N^+$ $(M + H)^+$ 407.9875, found 407.9883.



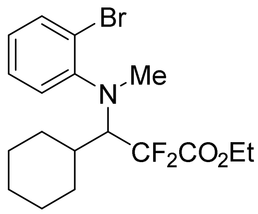
7a

2,2-Dichloro-3-((2-chlorophenyl)(methyl)amino)-3-(4-methoxyphenyl)propanenitrile (**7a**). Colorless oil (8.5 mg, 23% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.56 (m, 2H), 7.37 (dd, J = 8.0, 1.6 Hz, 1H), 7.26−7.17 (m, 2H), 7.08−7.02 (m, 1H), 6.98−6.92 (m, 2H), 5.24 (s, 1H), 3.84 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 149.5, 131.4, 131.1, 127.8, 127.0, 125.9, 125.5, 116.4, 114.0, 77.2, 72.1, 55.4, 39.6; HRMS (ESI) calcd for $C_{17}H_{16}Cl_3N_2O^+$ $(M + H)^+$ 369.0323, found 369.0324.



7b

2-Bromo-*N*-methyl-*N*-(2,2,2-tribromo-1-(4-methoxyphenyl)ethyl)aniline (**7b**). Colorless oil (16.7 mg, 30% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.71 (m, 2H), 7.59 (dd, J = 8.0, 1.6 Hz, 1H), 7.35 (dd, J = 8.0, 1.6 Hz, 1H), 7.27 (td, J = 8.0, 1.6 Hz, 1H), 7.00−6.93 (m, 3H), 5.53 (s, 1H), 3.84 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 152.9, 134.4, 131.6, 128.5, 127.8, 126.7, 125.7, 122.8, 113.7, 82.8, 55.4, 54.0, 41.4; HRMS (ESI) calcd for $C_{16}H_{16}Br_4NO^+$ $(M + H)^+$ 553.7960, found 553.7937.



7c

Ethyl-3-((2-bromophenyl)(methyl)amino)-3-cyclohexyl-2,2-difluoropropanoate (**7c**). Yellow oil (12.9 mg, 32% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 8.0, 1.6 Hz, 1H), 7.22−7.15 (m, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.81−6.74 (m, 1H), 4.23 (ddd, J = 16.4, 12.4, 9.2 Hz, 1H), 4.13 (dq, J = 10.4, 7.2 Hz, 1H), 3.91 (dq, J = 10.4, 7.2 Hz, 1H), 2.92 (s, 3H), 2.11−1.94 (m, 3H), 1.84−1.67 (m, 3H), 1.41−1.16 (m, 5H), 1.08 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (dd, J = 33.5, 31.1 Hz), 150.7, 134.8, 128.0, 123.6, 123.0, 117.3 (dd, J = 262.7, 258.1 Hz), 116.6, 66.1 (dd, J = 23.4, 20.5 Hz), 62.8, 36.6, 36.0 (d, J = 2.2 Hz), 31.0, 30.3 (d, J = 5.7 Hz), 26.7, 26.5, 13.6; HRMS (ESI) calcd for $C_{18}H_{25}BrF_2NO_2^+$ $(M + H)^+$ 404.1031, found 404.1036.

Computational Methods

DFT calculations were performed with Gaussian 09.[2] Pruned integration grids with 99 radial shells and 590 angular points per shell were used. Geometry optimizations of the stationary points were carried out in acetonitrile (MeCN) using the SMD solvation model[3] at the M06-2X[4]/6-31+G(d,p)[5] level without any constrains. Unscaled harmonic frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. Quasiharmonic corrections were applied during the entropy calculations by setting all positive frequencies that are less than 100 cm^{-1} to 100 cm^{-1}.[6] Based on the optimized structures, single-point energy calculations were carried out at the SMD(MeCN)/M06-2X/maug-cc-pVTZ[7] level. All discussed energy differences were based on Gibbs energies in MeCN at 298 K. Standard state concentrations of 18.9[8] and 1.0 mol/L were used for MeCN and all the other species, respectively. Some of the computational results have been published in our previous work.[9]

Though computational studies on polar reactions in solution are challenging, careful treatment of electronic structure, entropy, and solvation should be able to provide accurate predictions.[10] In this work, the magnitude of the computational errors could be around a few kcal/mol considering the uncertainties of entropy and solvation calculations.

Discussion on the Competing Proton Transfers

As depicted in Figure S1, the C−Cl bond formation (colored in blue) is favored over the intra- (colored in red) and intermolecular (colored in black) proton transfers.[9] The concentrations of CCl_4 and MeCN were set to 1.0 and 18.9 mol/L in such a standard Gibbs energy profile. In our experiments, 0.15 mL CCl_4 and 0.20 mL MeCN were used; thus, the molar ratio of CCl_4 to MeCN (ca. 1/2.4) is much larger than the value (1/18.9) we used in our DFT calculations.[8,11] Therefore, the predicted selectivity toward the C−Cl bond formation should be even better under our reaction conditions. These computational results are in accordance with the fact that no proton transfer products were observed during our experimental investigations.

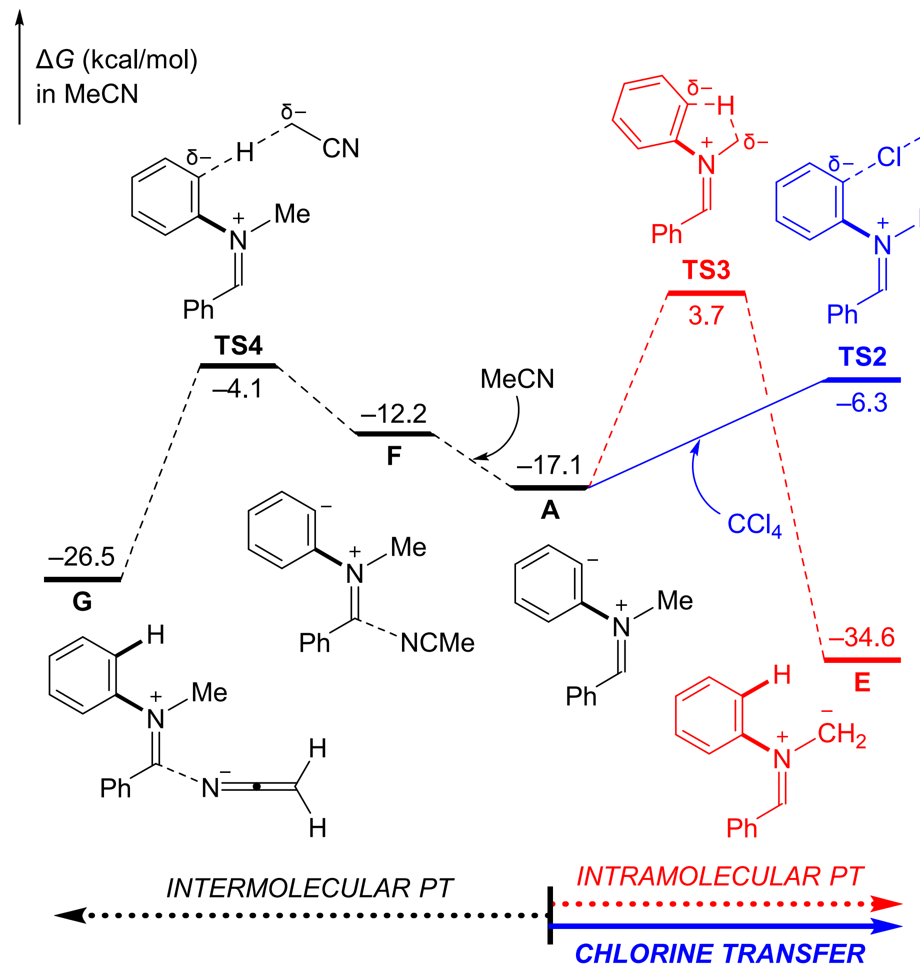


Figure S1. Competition among chlorine transfer and two proton transfers at 298 K. Computed at the SMD(MeCN)/M06-2X/maug-cc-pVTZ//SMD(MeCN)/M06-2X/6-31+G(d,p) level.

Computed Energies for the Stationary Points

Table S1. Thermal Corrections to Gibbs Energy (TCGs) and Single-Point Energies (SPEs)

	TCG[a,b] (a.u.)	SPE[a] (a.u.)	SPE[c] (a.u.)
acetonitrile (MeCN)	0.021662	−132.711320	−132.756820
benzyne	0.048297	−230.828664	−230.900117
carbon tetrachloride	−0.021168	−1878.723558	−1878.908648
1b	0.118446	−364.872032	−364.983778
4b	0.201913	−2474.601525	−2474.959480
A	0.194789	−595.756806	−595.936187
B	0.196697	−2474.488615	−2474.851496
C	0.196575	−2474.532929	−2474.893017
D	0.180376	−632.675897	−632.865580
E	0.194075	−595.782975	−595.963325
F	0.235967	−728.474985	−728.698978
G	0.234960	−728.494457	−728.720719
TS1	0.188347	−595.703411	−595.885379
TS2	0.197223	−2474.486455	−2474.848219
TS3	0.190265	−595.720013	−595.898564
TS4	0.232003	−728.458842	−728.681978
TS5	0.182840	−2511.405159	−2511.776965
TS6	0.217487	−765.376983	−765.610188

[a]Computed at the SMD(MeCN)/M06-2X/6-31+G(d,p) level.

[b]A standard state at 1 atm and 298 K was used.

[c]Computed at the SMD(MeCN)/M06-2X/maug-cc-pVTZ//SMD(MeCN)/M06-2X/6-31+G(d,p) level.

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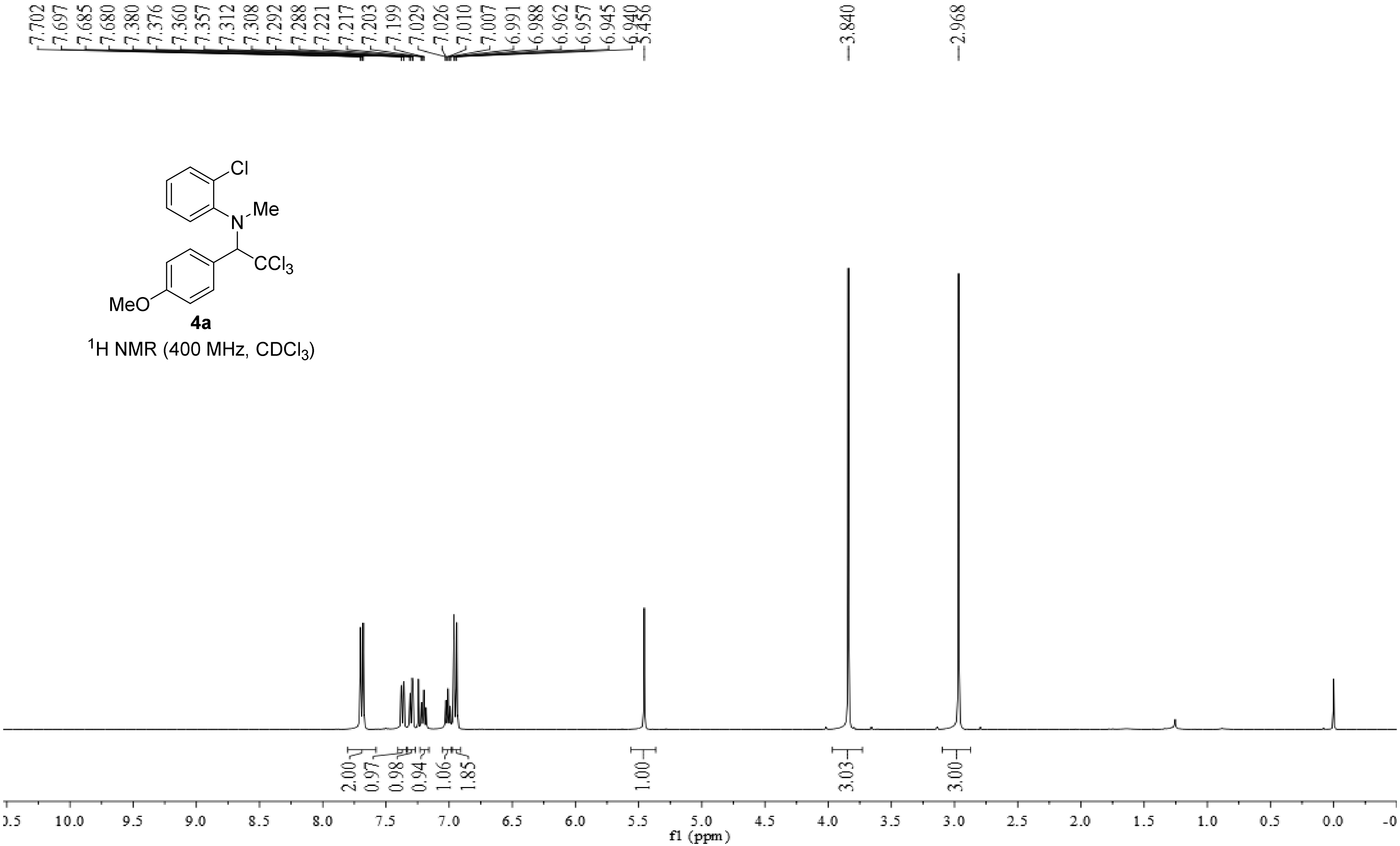
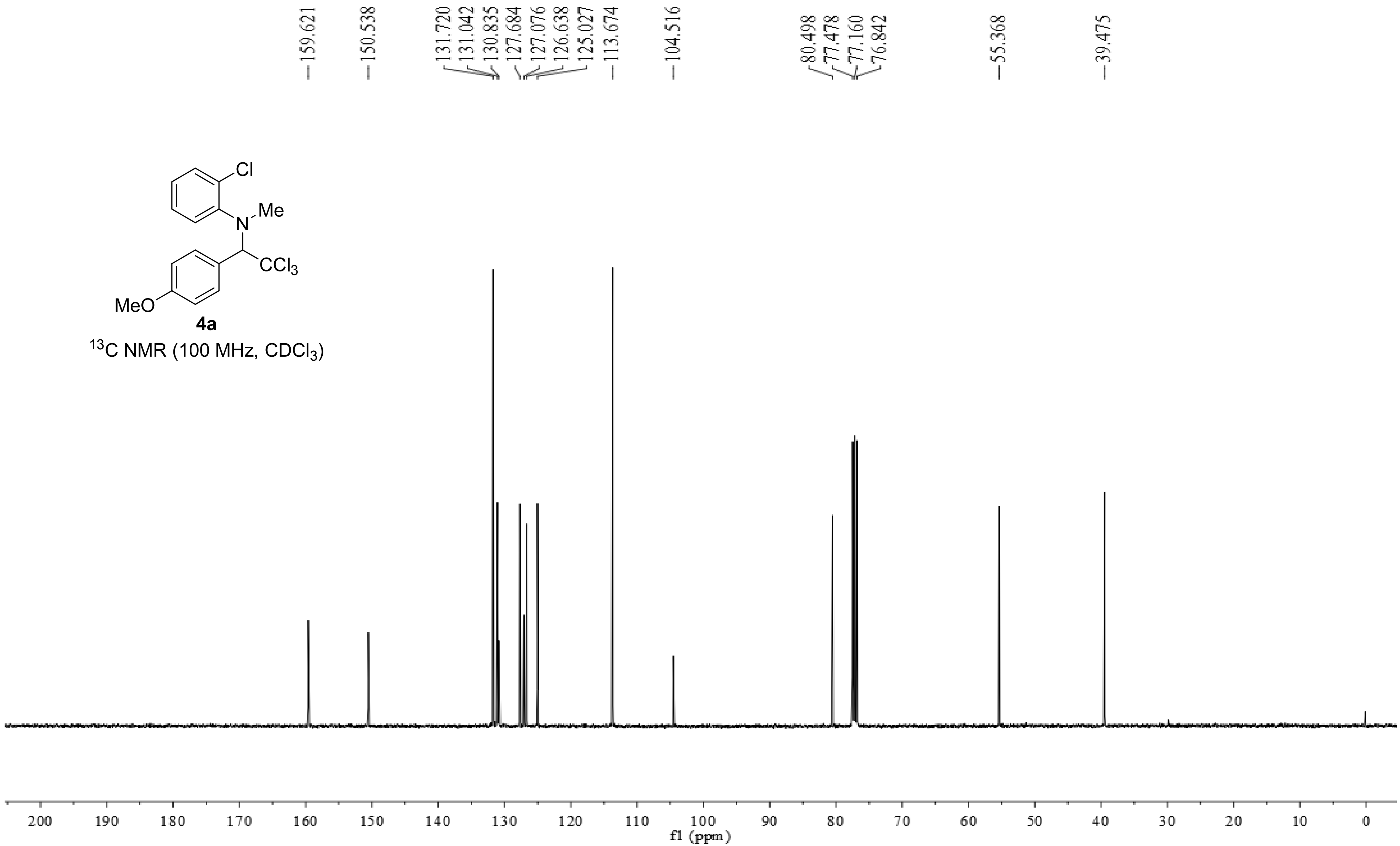
Copies of ^{1}H and ^{13}C NMR Spectra





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150.538
131.720
131.042
130.835
127.684
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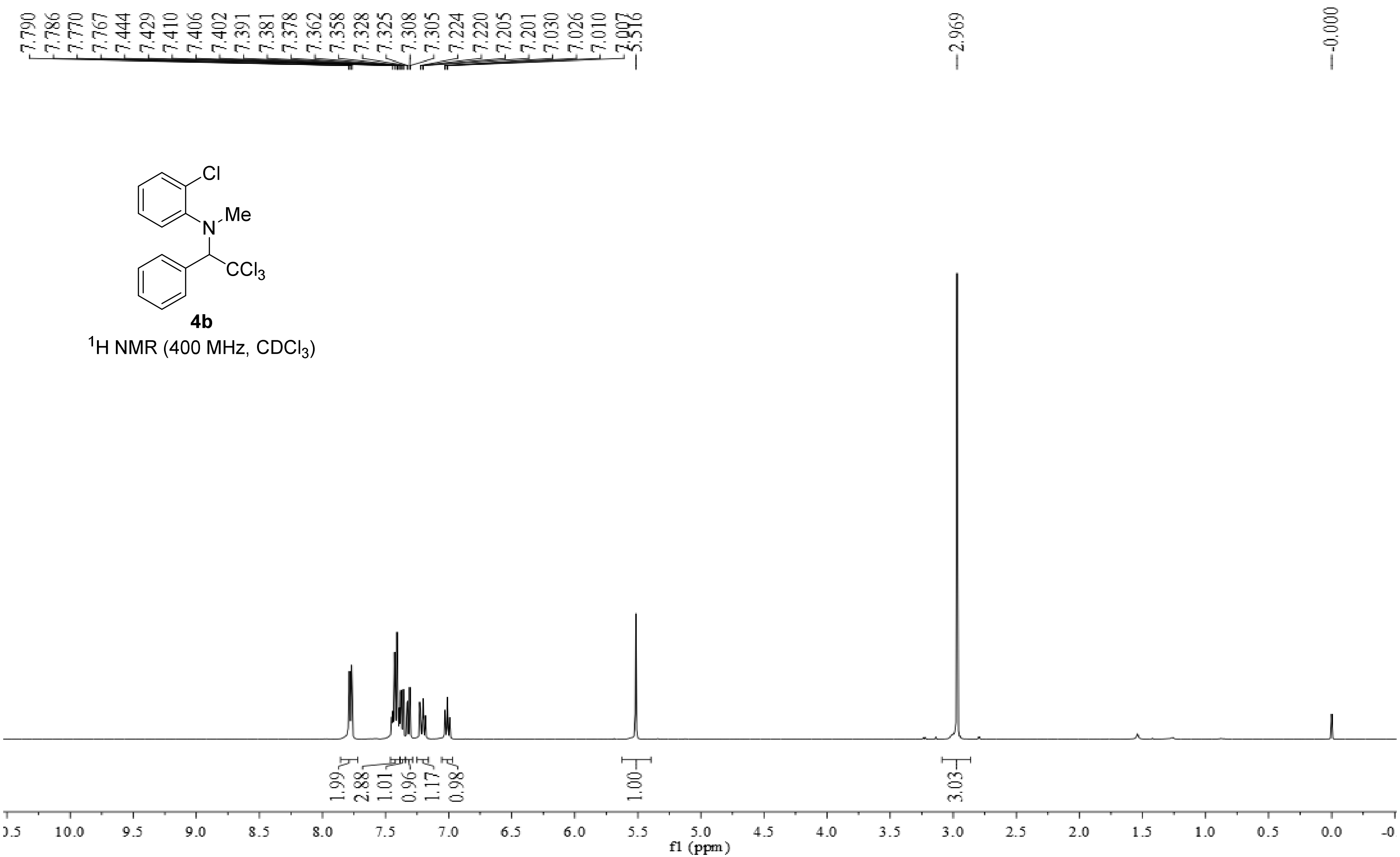
113.674
104.516
80.498
77.478
77.160
76.842
55.368
39.475
Cl
N
Me
CCl3
MeO
4a
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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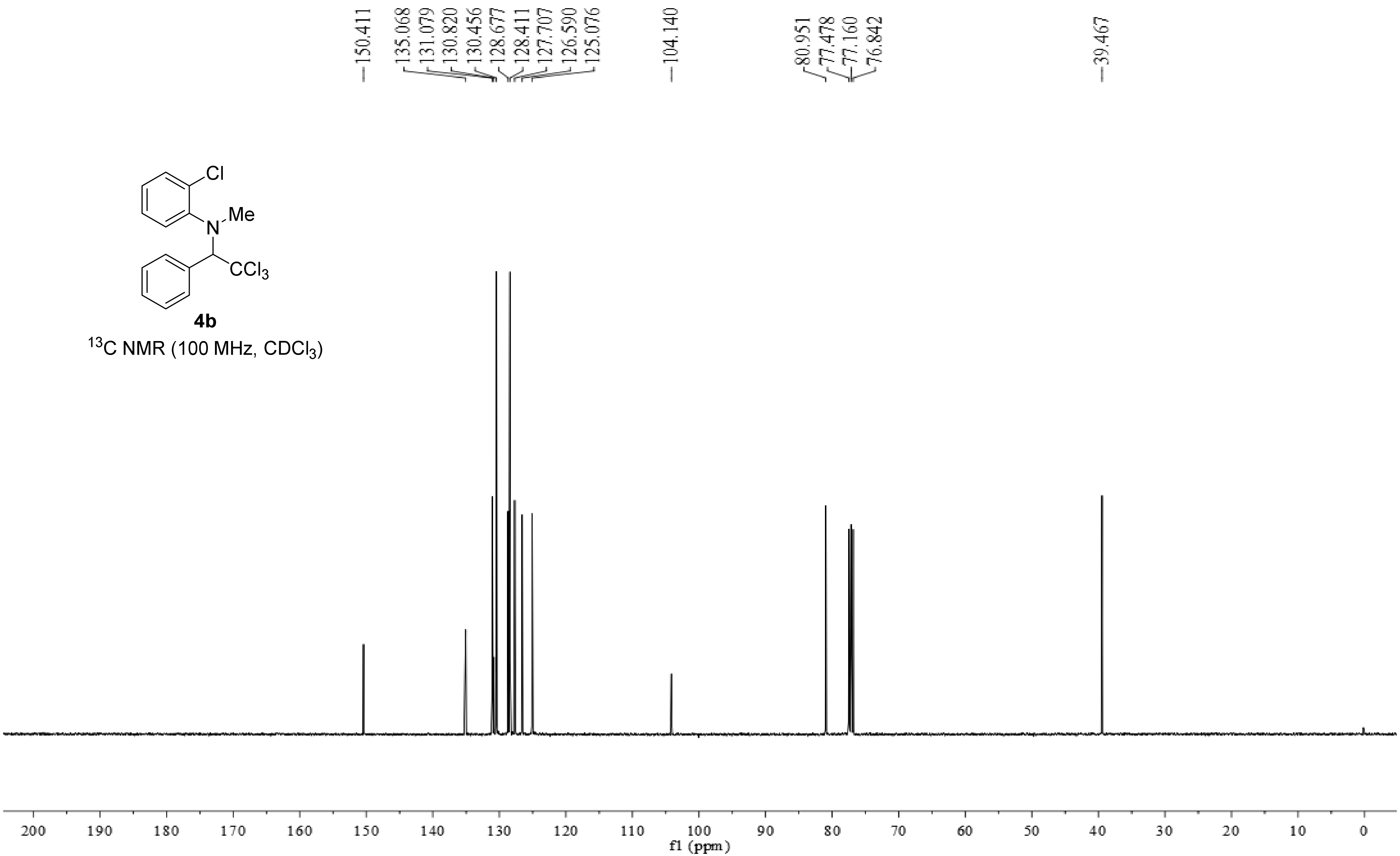
7.362
7.358
7.328
7.325
7.308
7.305
7.224
7.220
7.205
7.201
7.030
7.026
7.010
7.007
5.516
2.969
0.000
Cl
N
Me
CCl3
4b
1H NMR (400 MHz, CDCl3)
1.99
2.88
1.01
0.96
1.17
0.98
1.00
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4b

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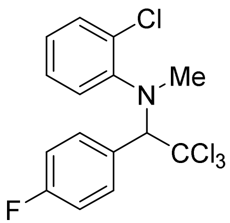
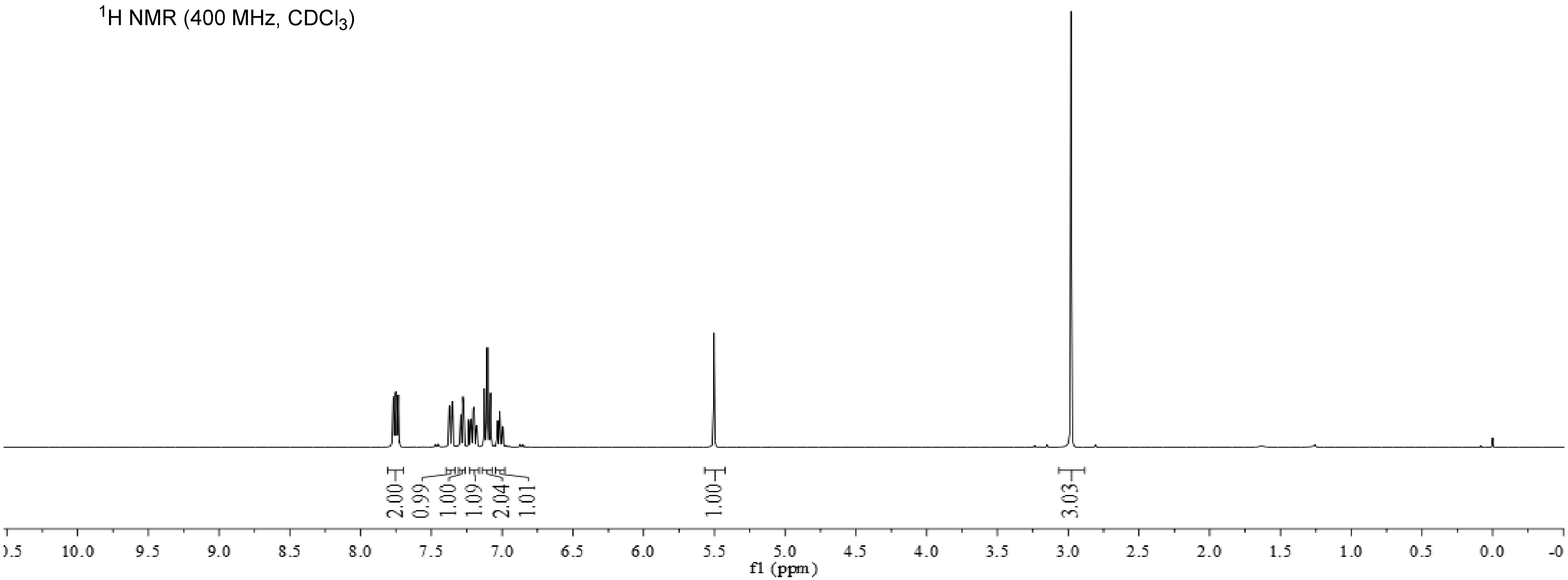
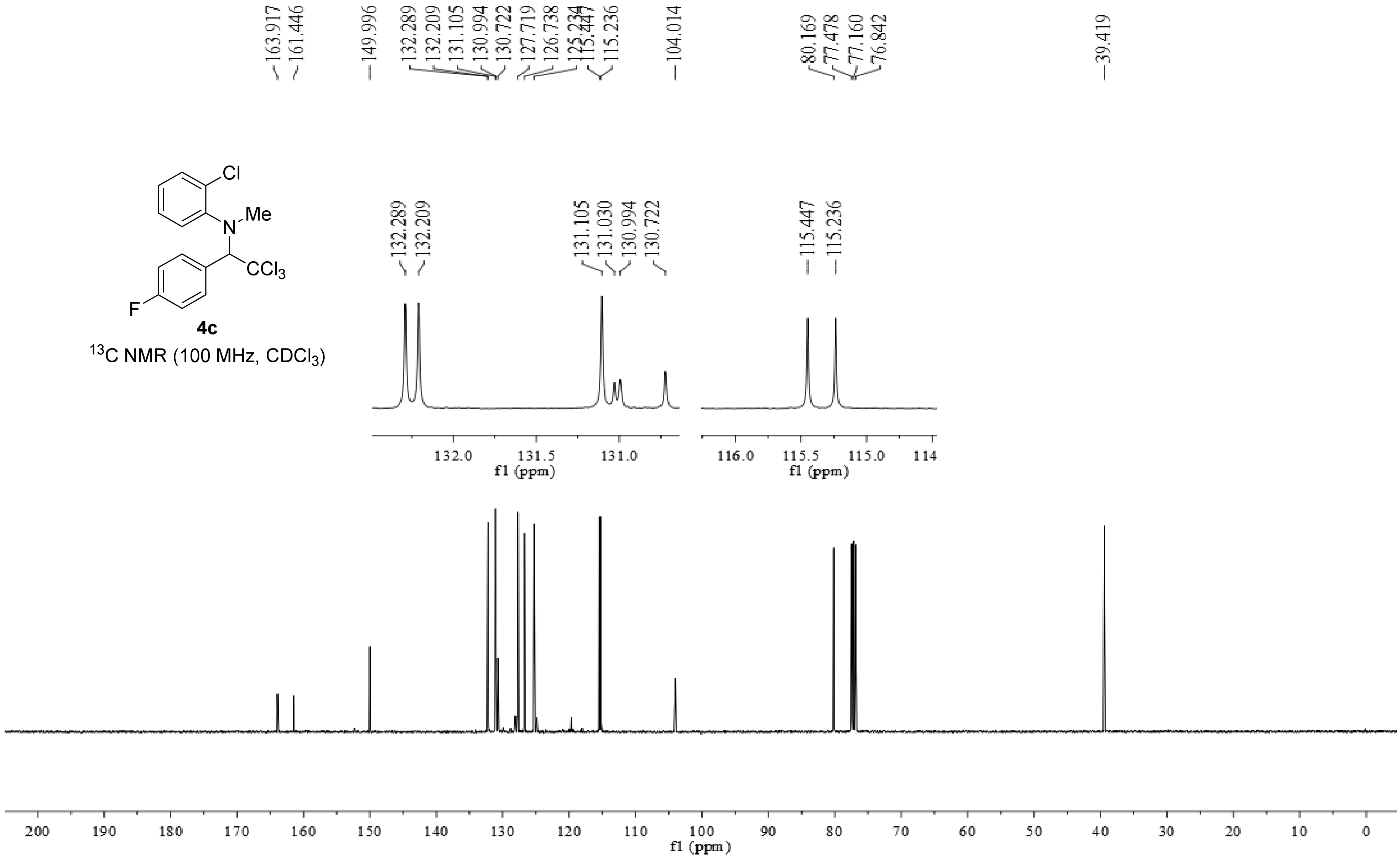


4c

^{1}H NMR (400 MHz, $CDCl_3$)

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149.996
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132.209
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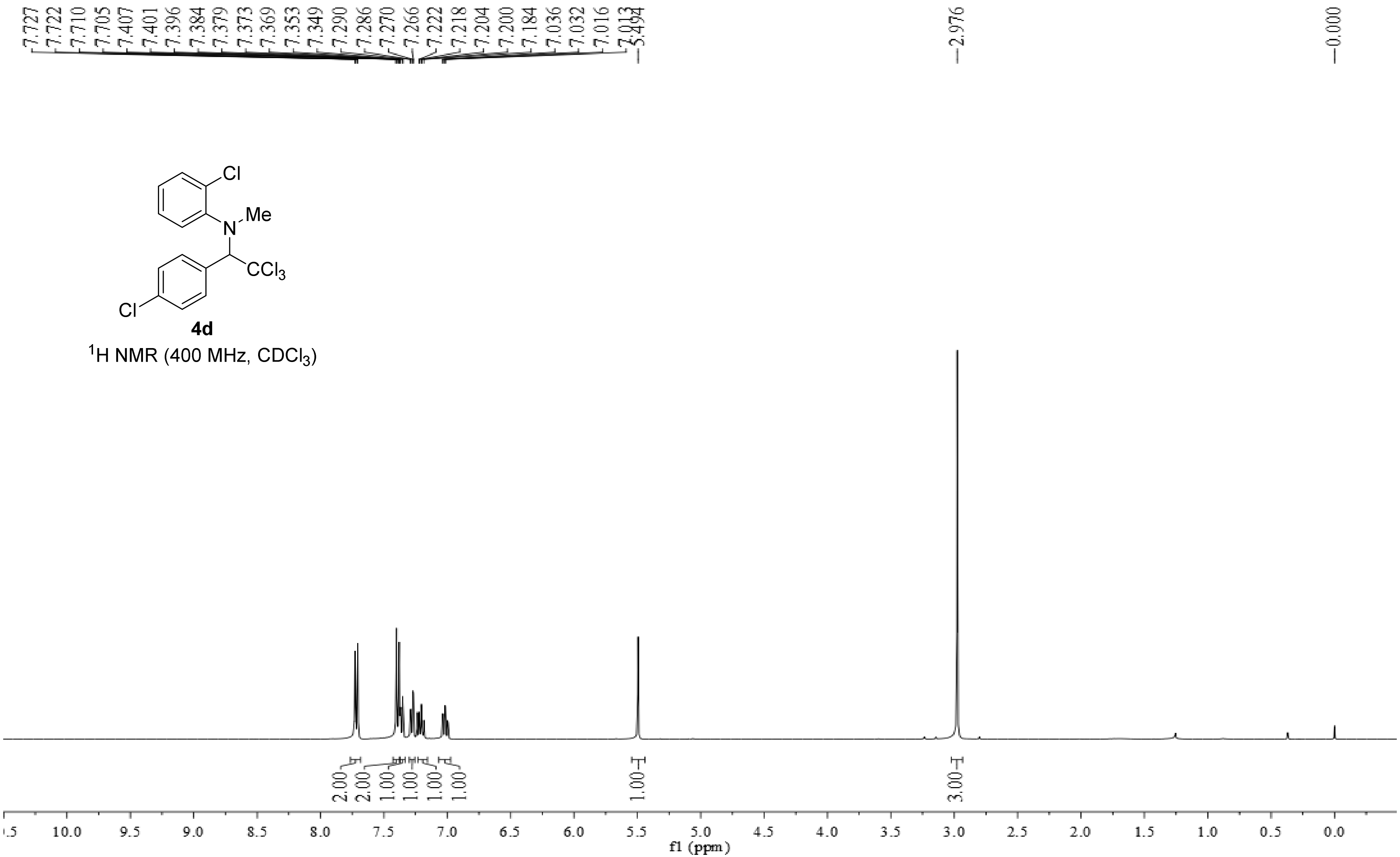
125.234
115.447
115.236
104.014
80.169
77.478
77.160
76.842
39.419
Cl
N
Me
CCl3
F
4c
13C NMR (100 MHz, CDCl3)
132.289
132.209
131.105
131.030
130.994
130.722
115.447
115.236
f1 (ppm)
f1 (ppm)
f1 (ppm)



4d

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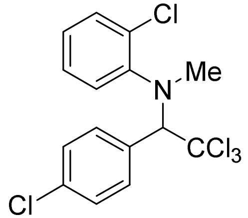

4d

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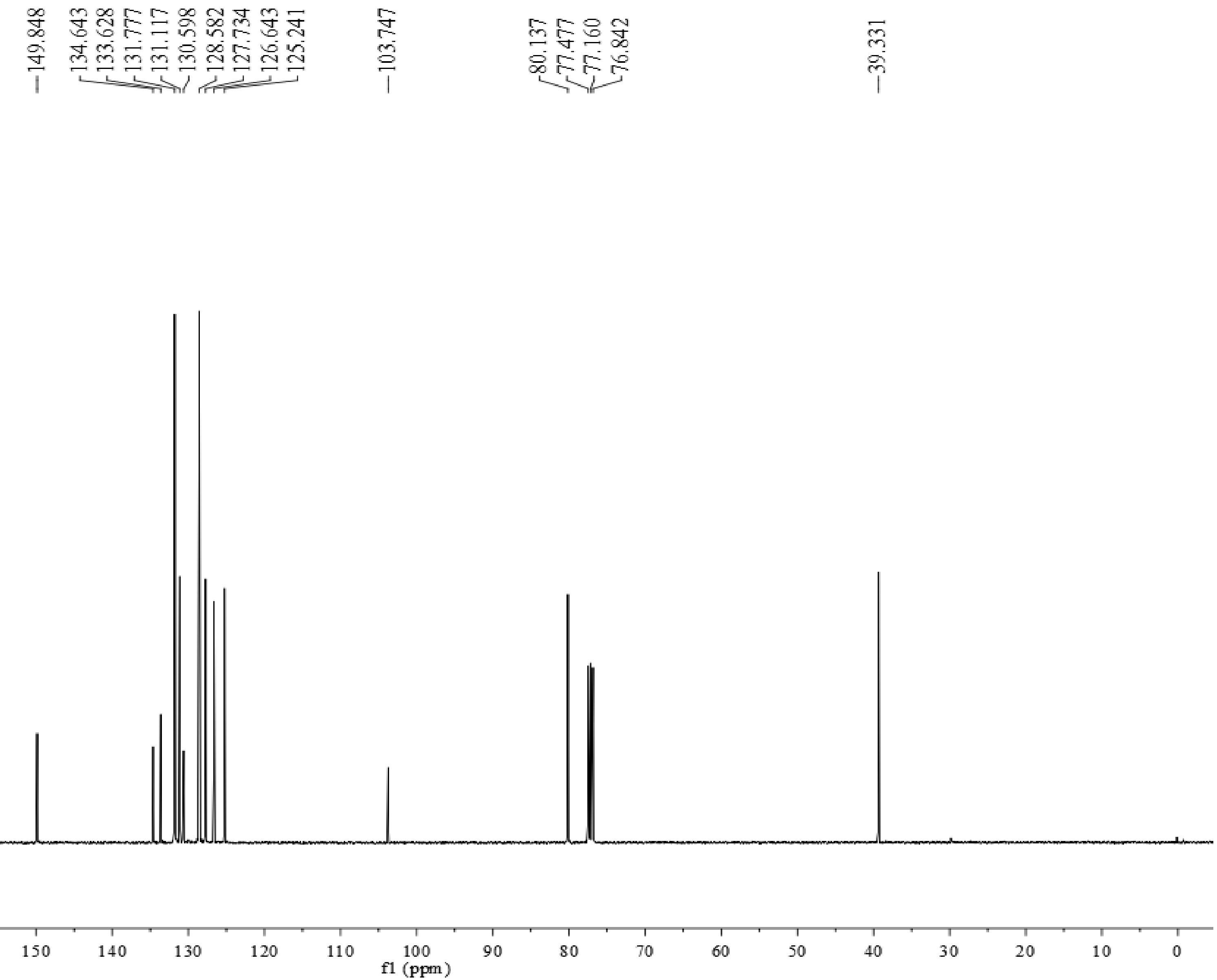

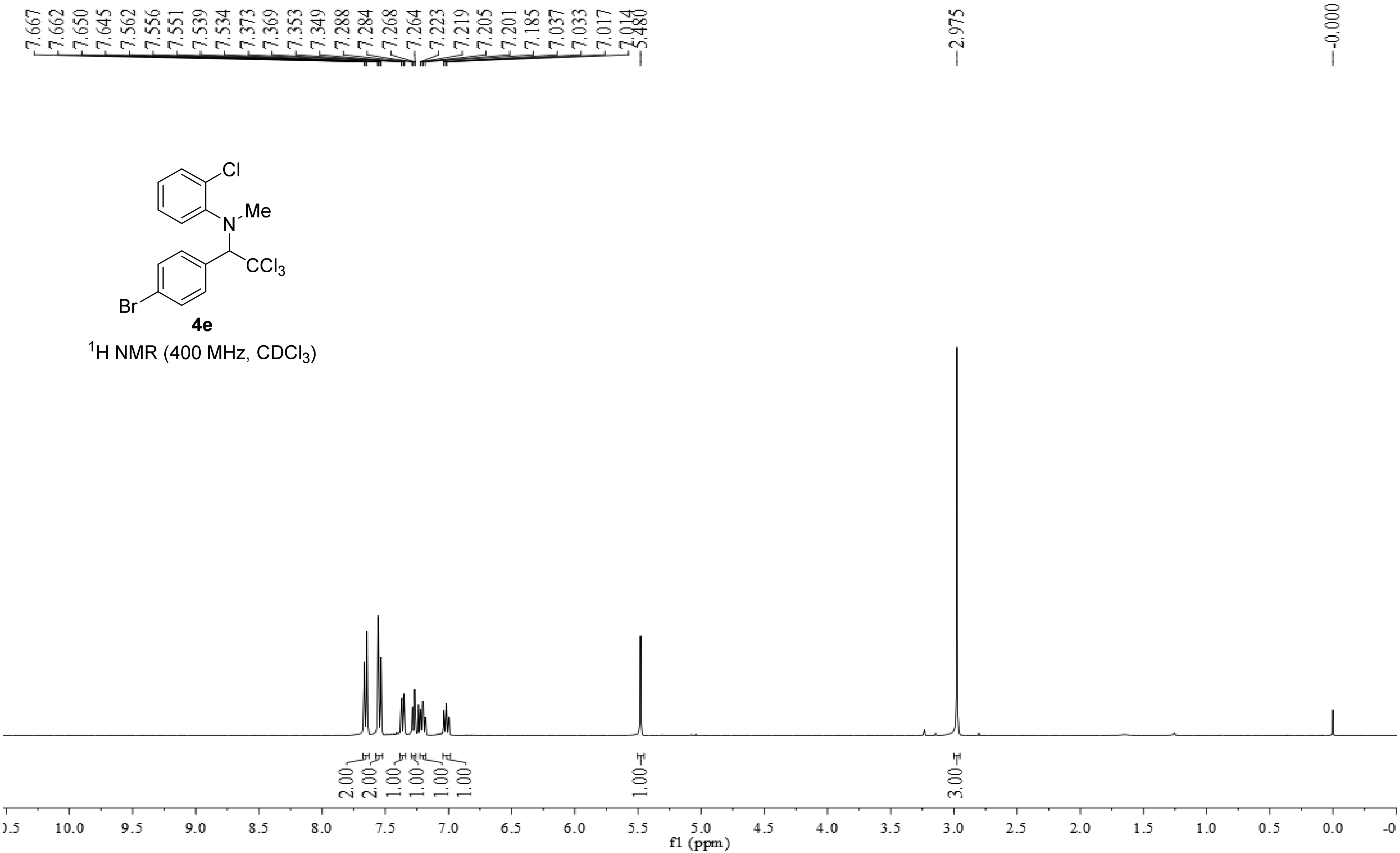

4e

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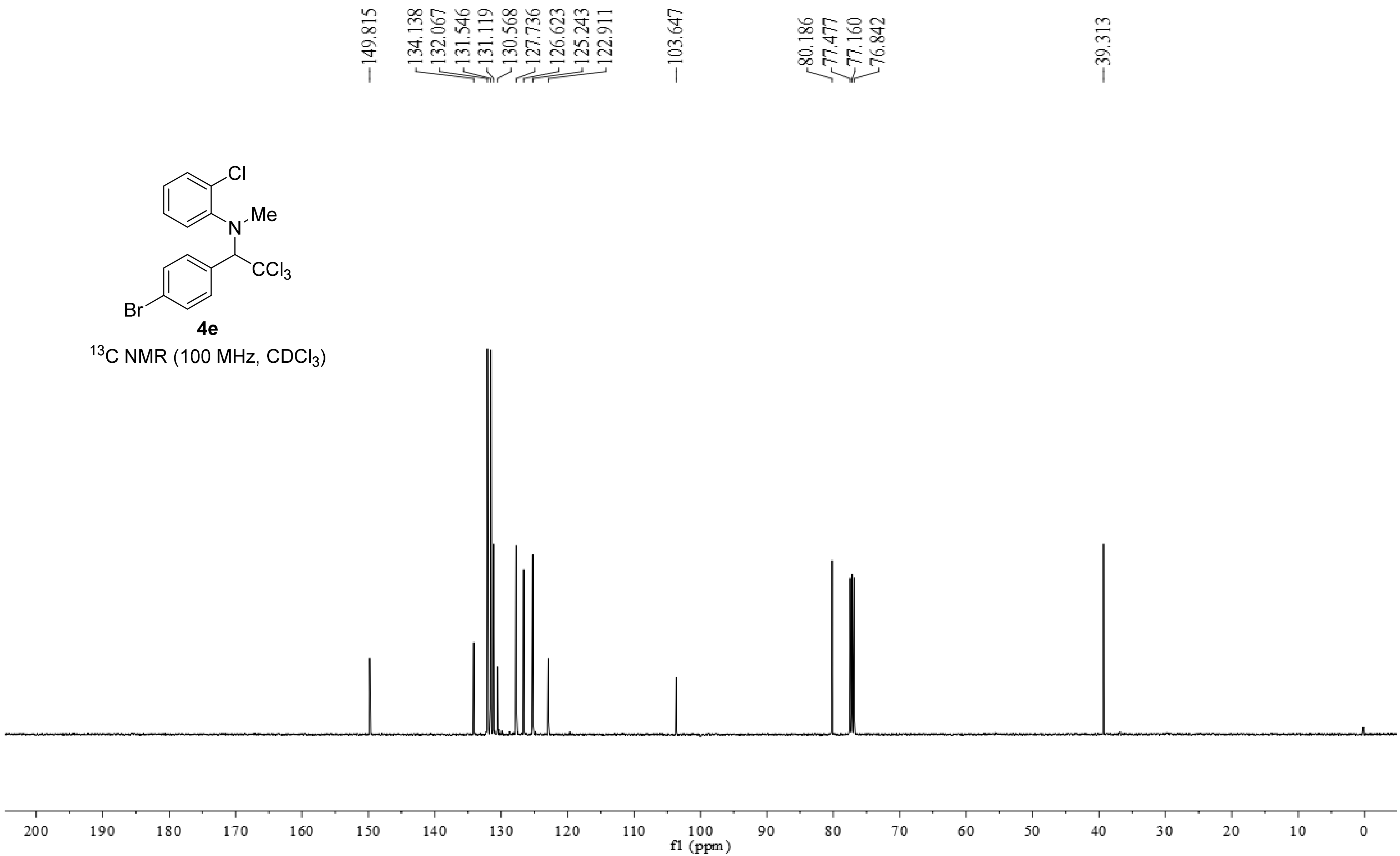
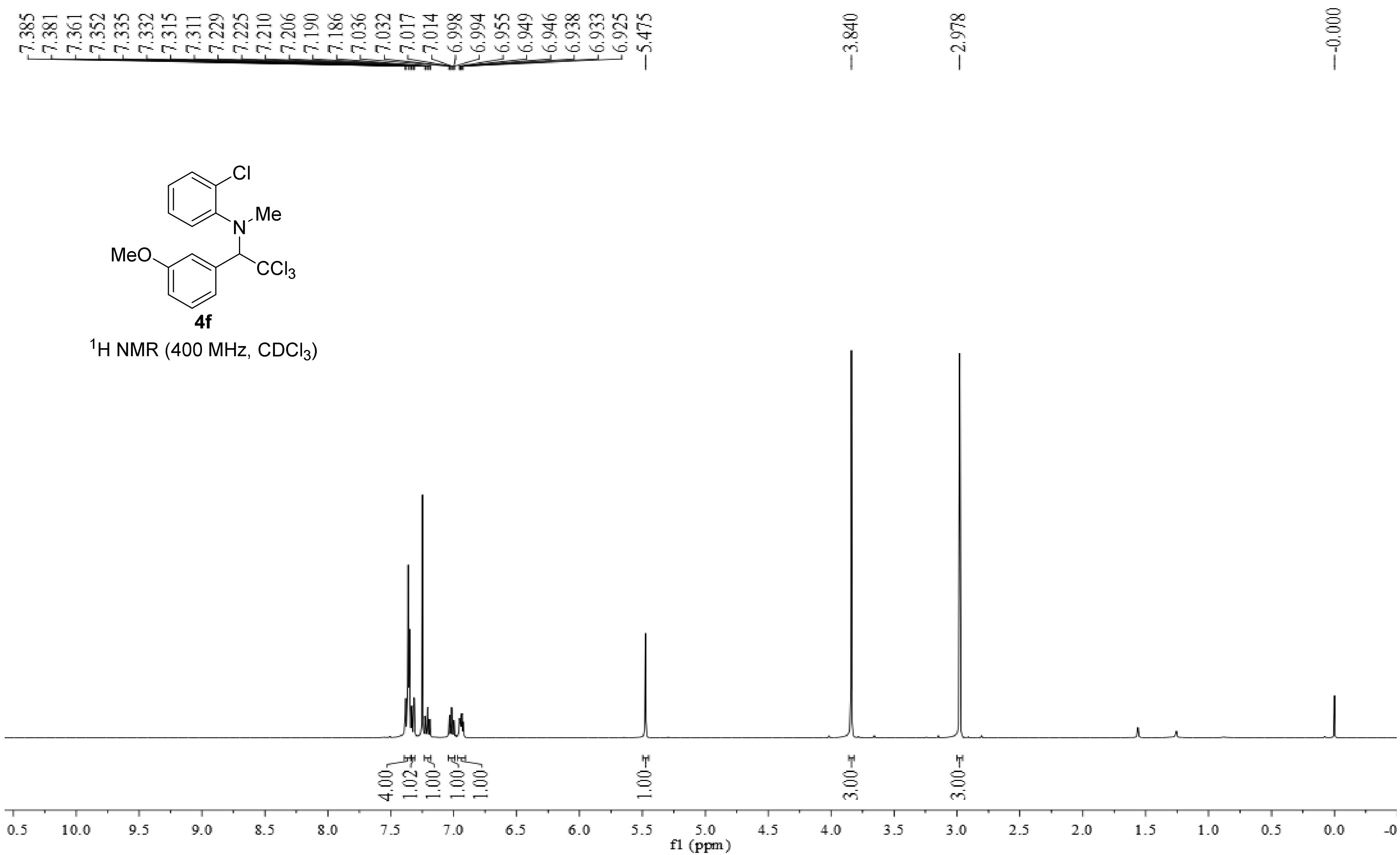


4e

^{13}C NMR (100 MHz, $CDCl_3$)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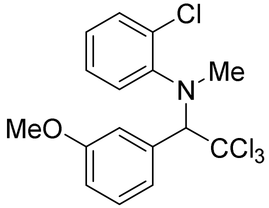
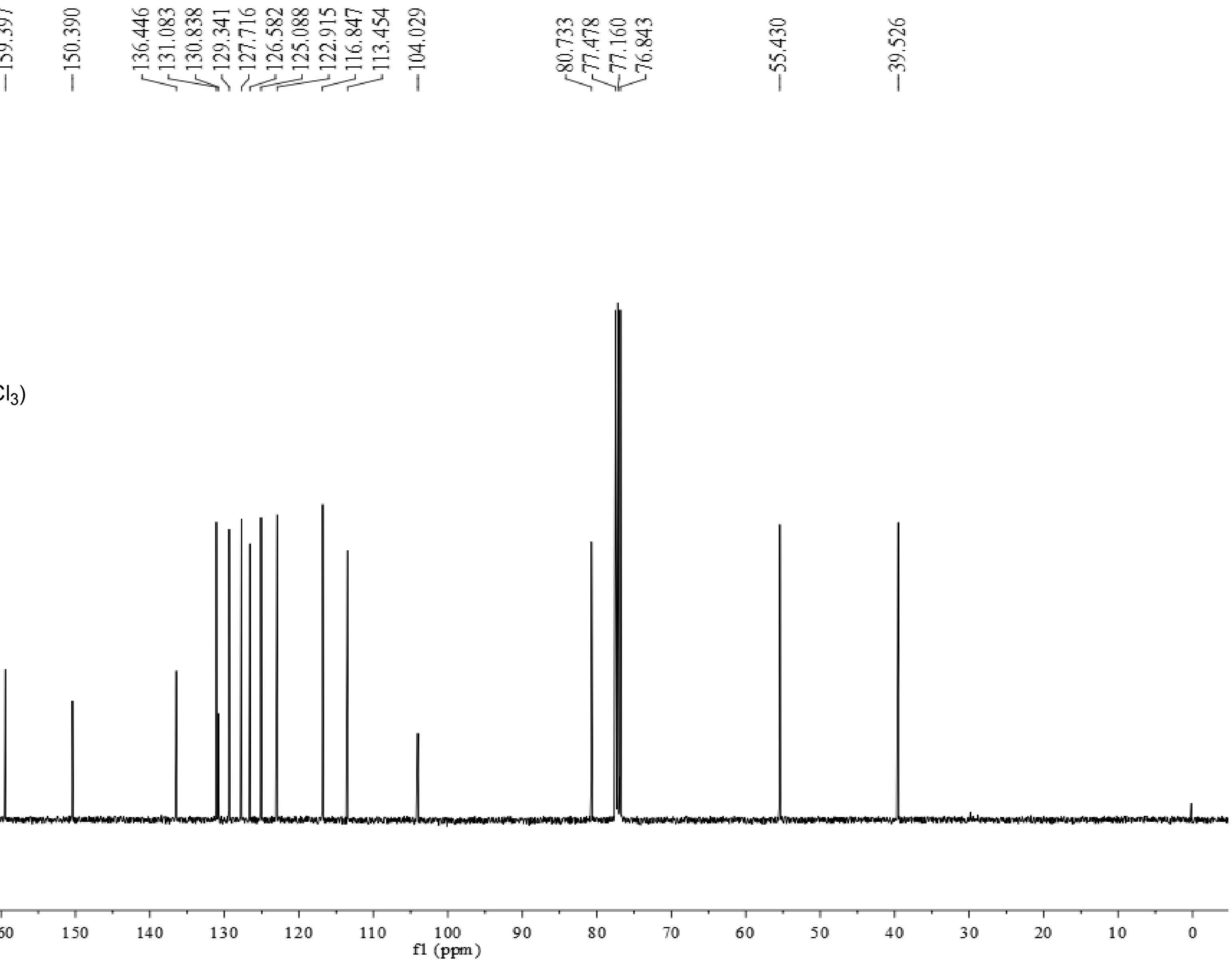
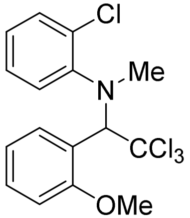
5.475
3.840
2.978
0.000
Cl
N
Me
MeO
CCl3
4f
1H NMR (400 MHz, CDCl3)
4.00 1.02 1.00 1.00 1.00
1.00
3.00
3.00
f1 (ppm)



4f

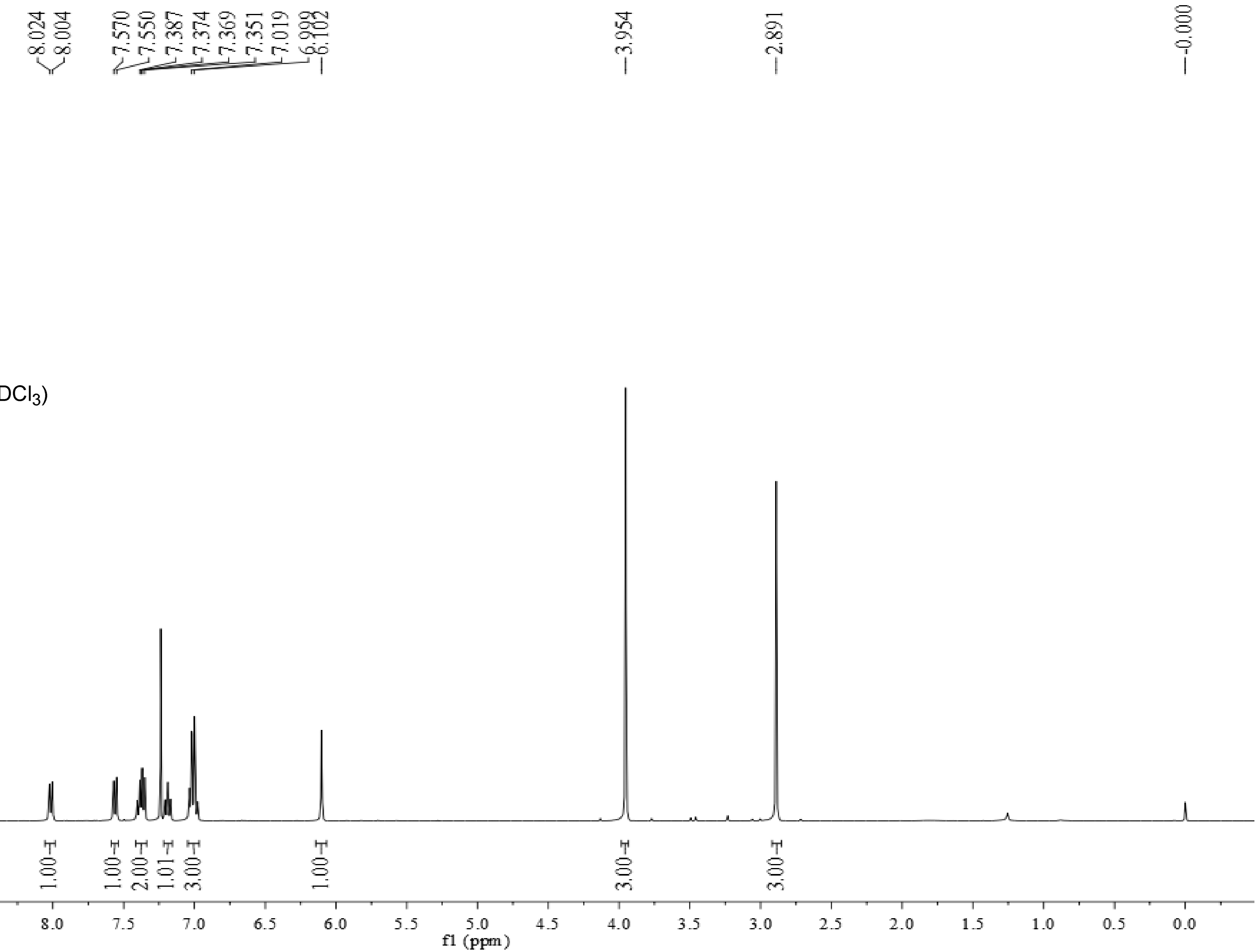
^{13}C NMR (100 MHz, CDCl$_3$)

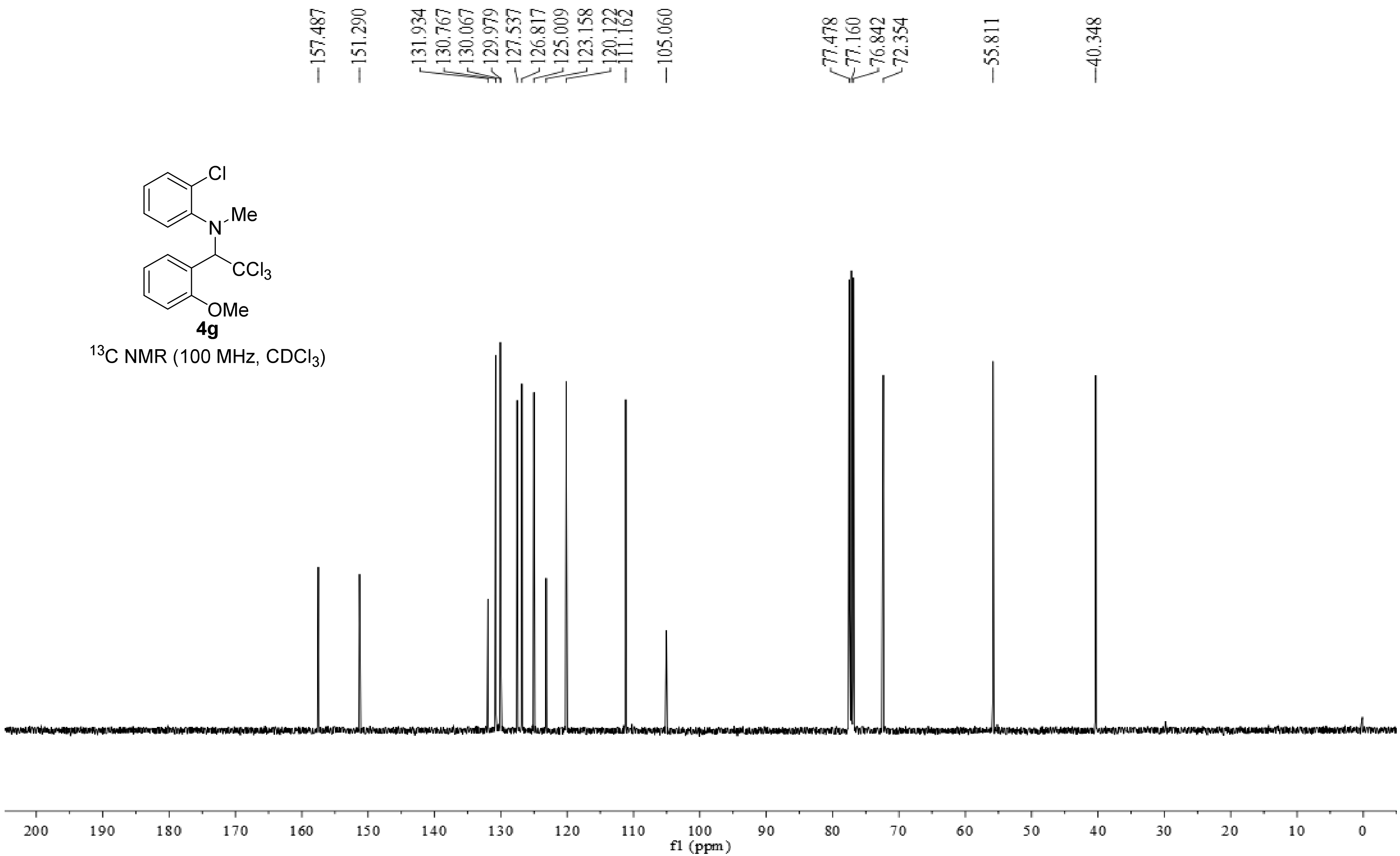




4g

^{1}H NMR (400 MHz, $CDCl_3$)

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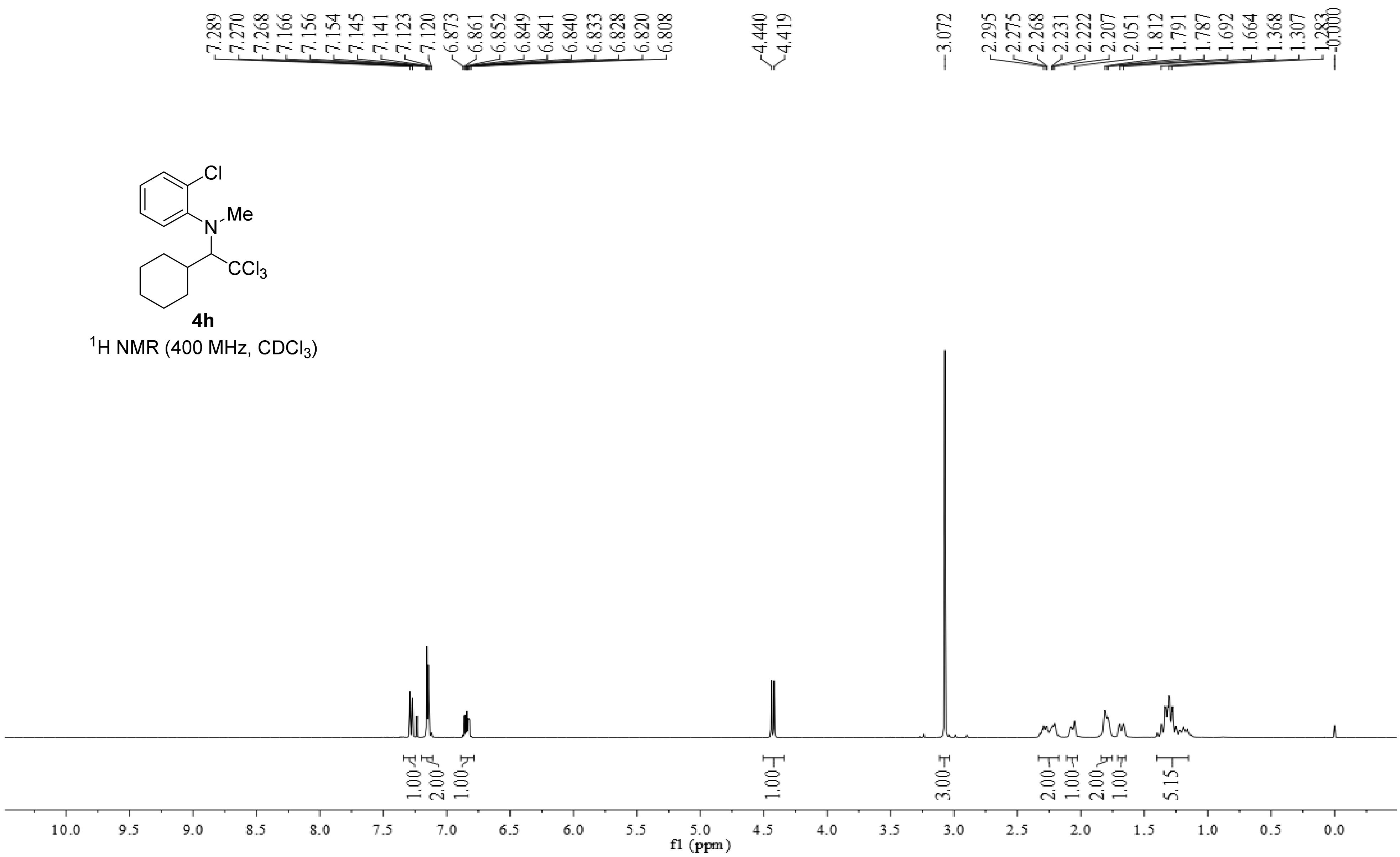
130.767
130.067
129.979
127.537
126.817
125.009
123.158
120.122
111.162
105.060
77.478
77.160
76.842
72.354
55.811
40.348
Cl
N
Me
CCl3
OMe
4g
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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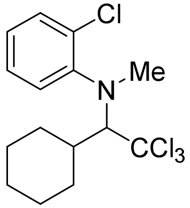
7.270
7.268
7.166
7.156
7.154
7.145
7.141
7.123
7.120
6.873
6.861
6.852
6.849
6.841
6.840
6.833
6.828
6.820
6.808
4.440
4.419
3.072
2.295
2.275
2.268
2.231
2.222
2.207
2.051
1.812
1.791
1.787
1.692
1.664
1.368
1.307
1.283
0.000
Cl
N
Me
CCl3
4h
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
1.00
3.00
2.00
1.00
2.00
1.00
5.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4h

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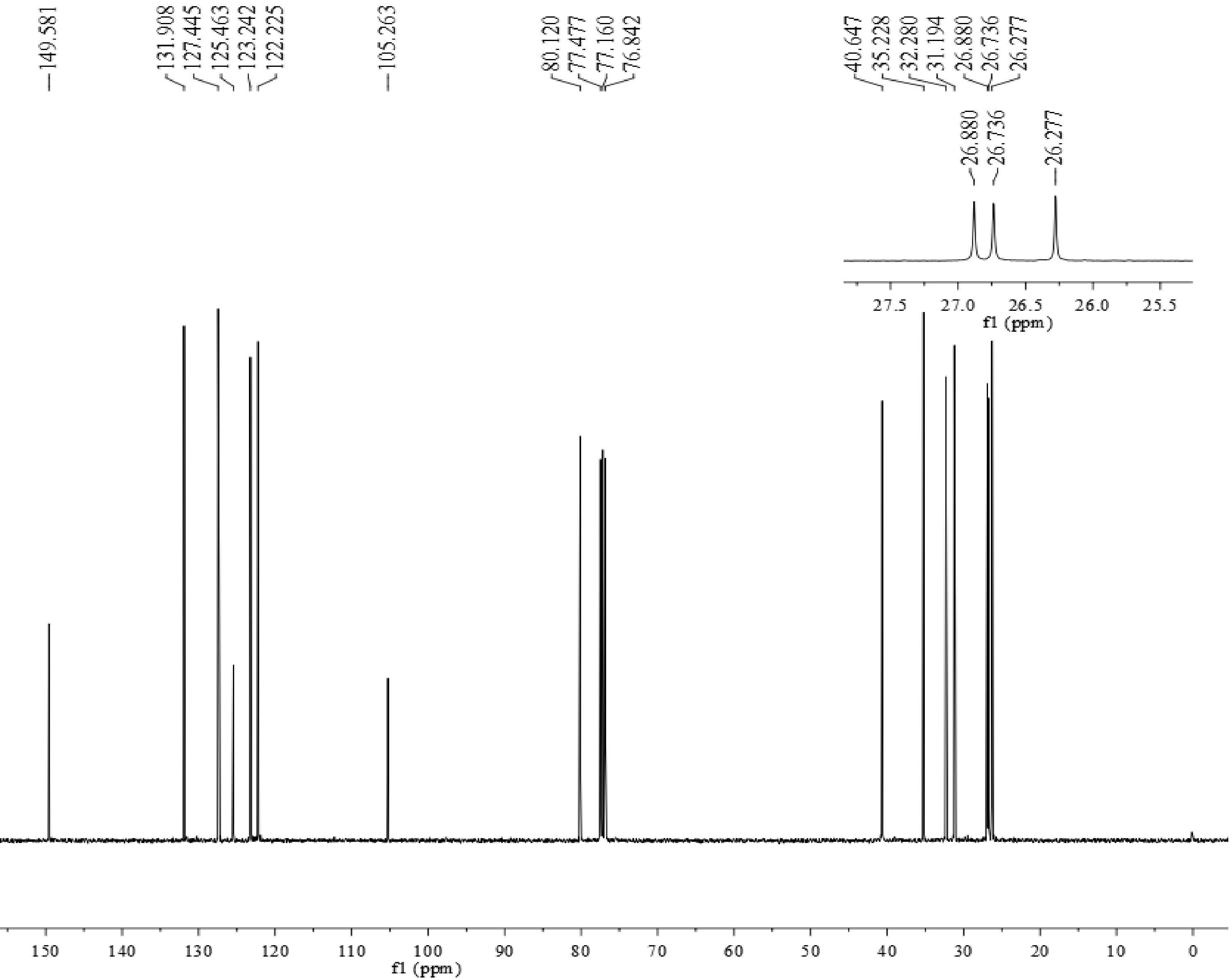
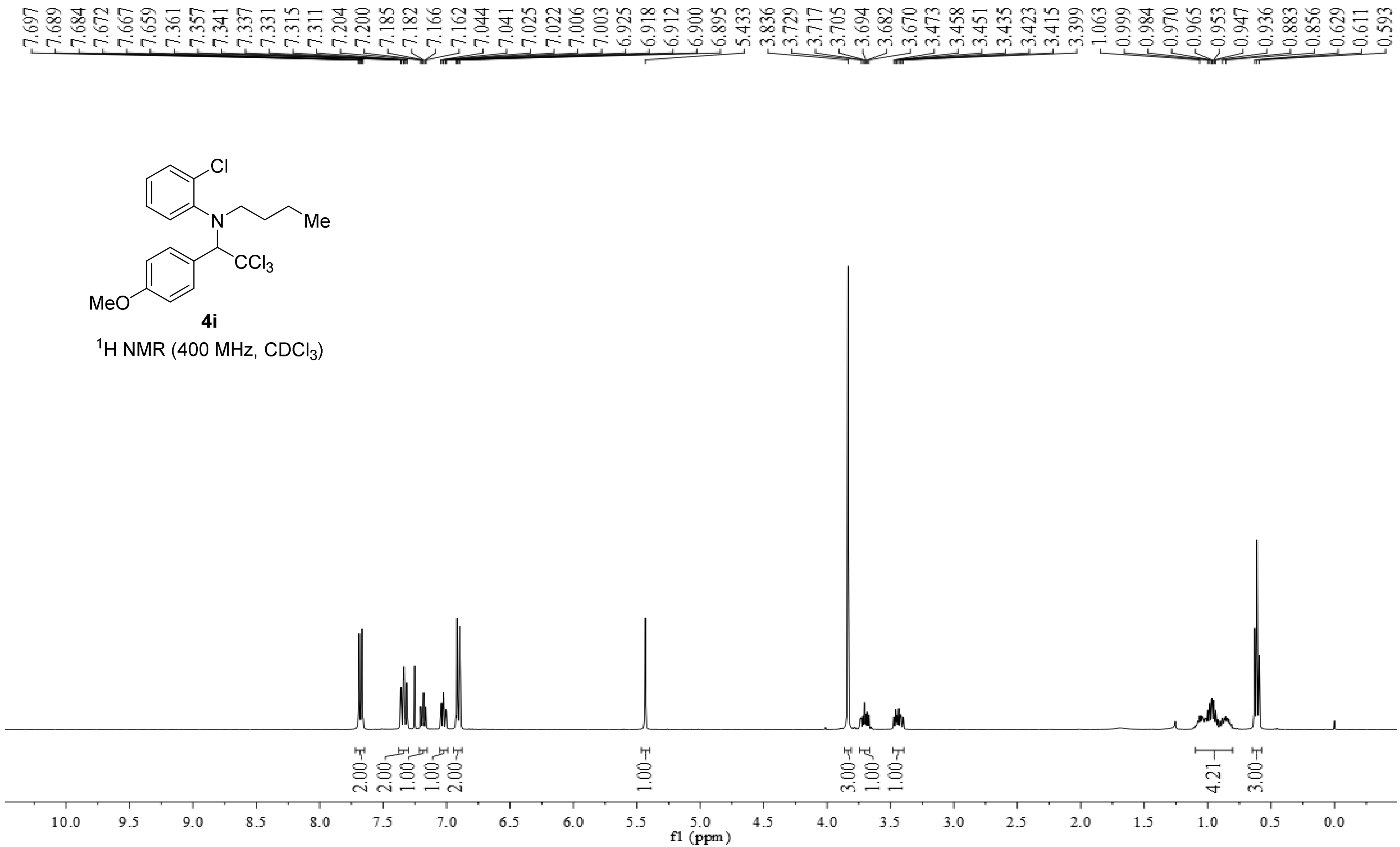
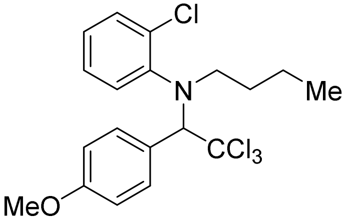
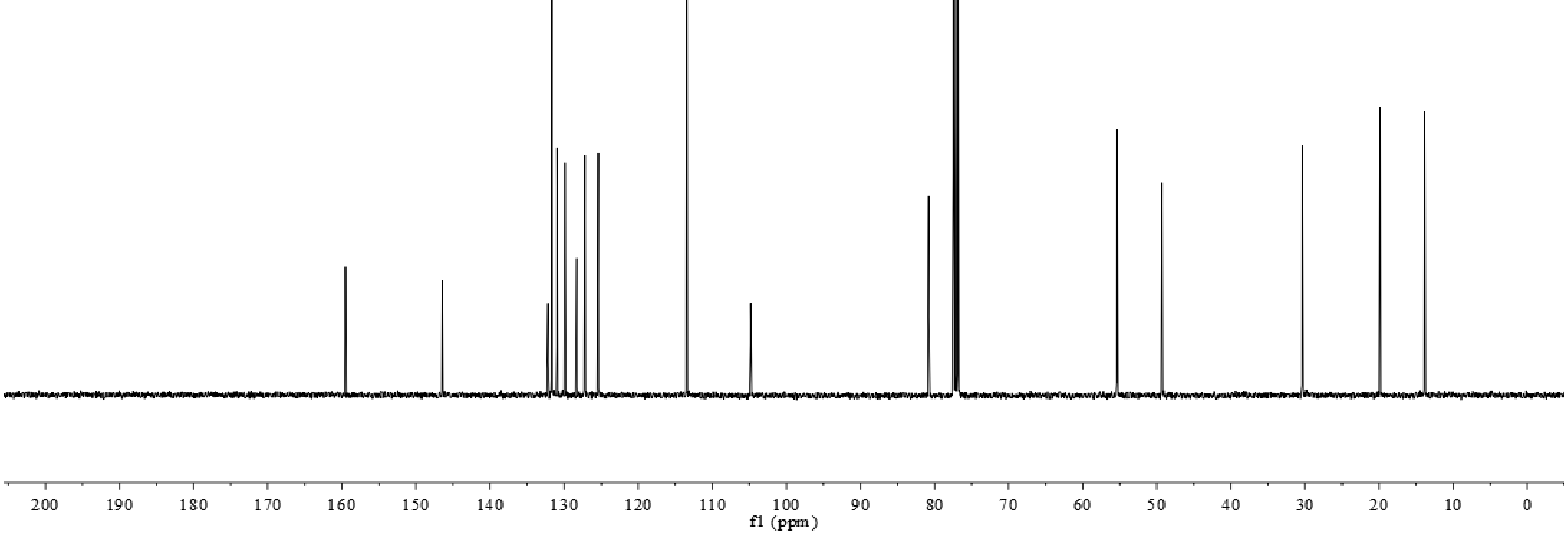


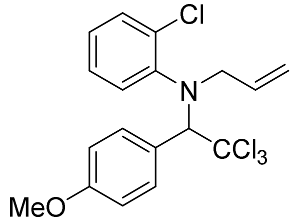

Cl
N
Me
CCl3
MeO
4i
1H NMR (400 MHz, CDCl3)
f1 (ppm)



4i

^{13}C NMR (100 MHz, $CDCl_3$)





4j

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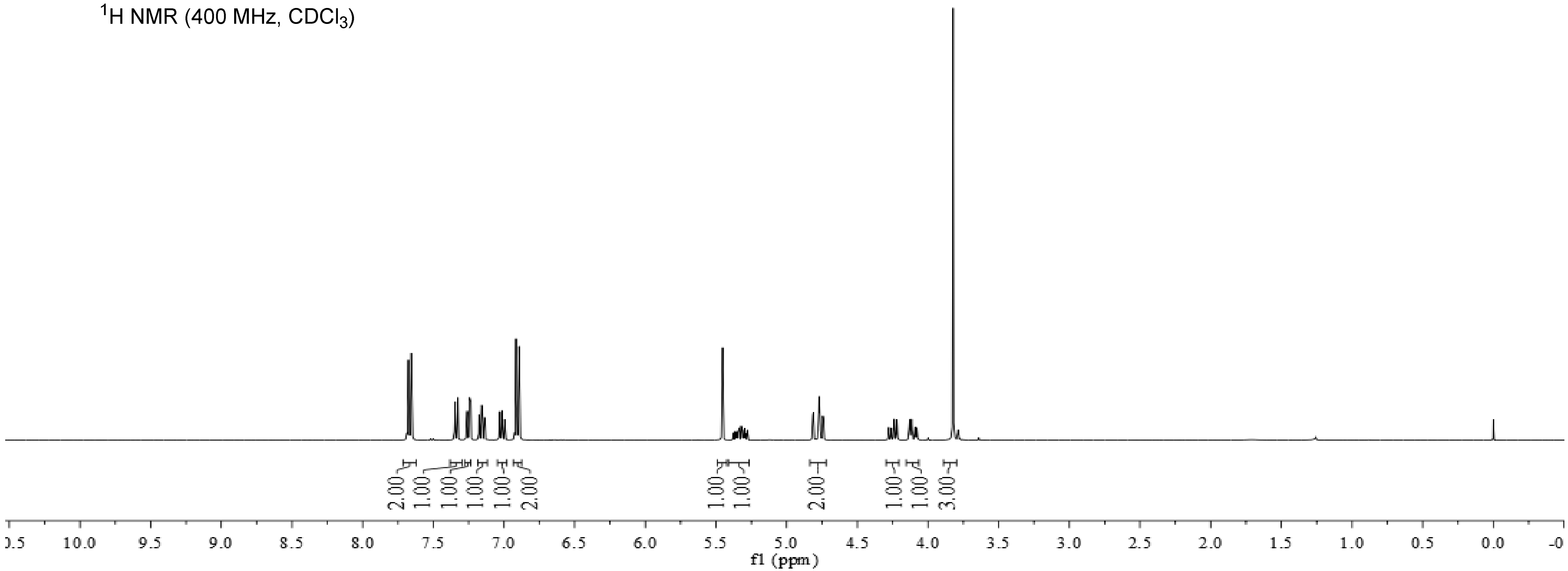
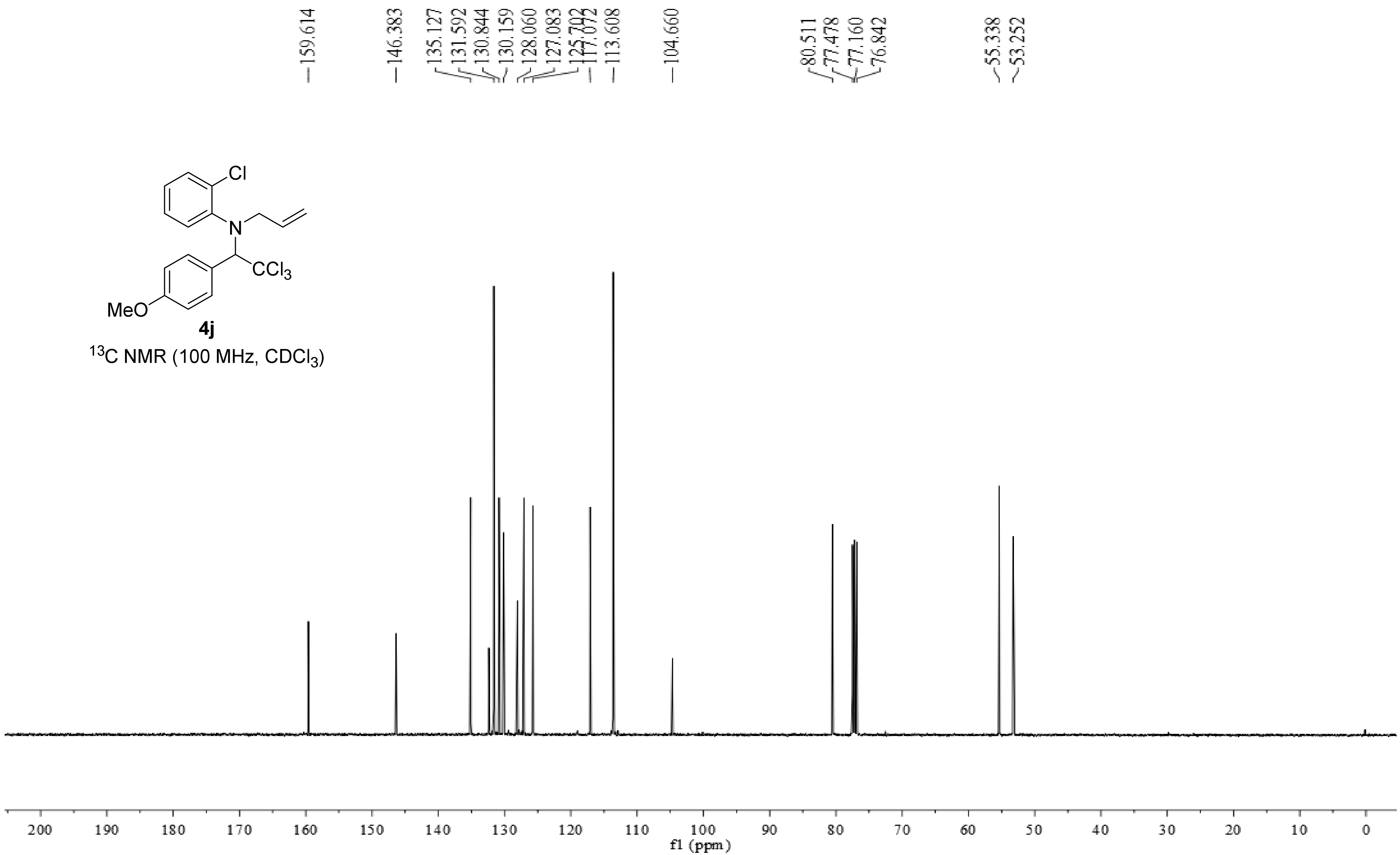
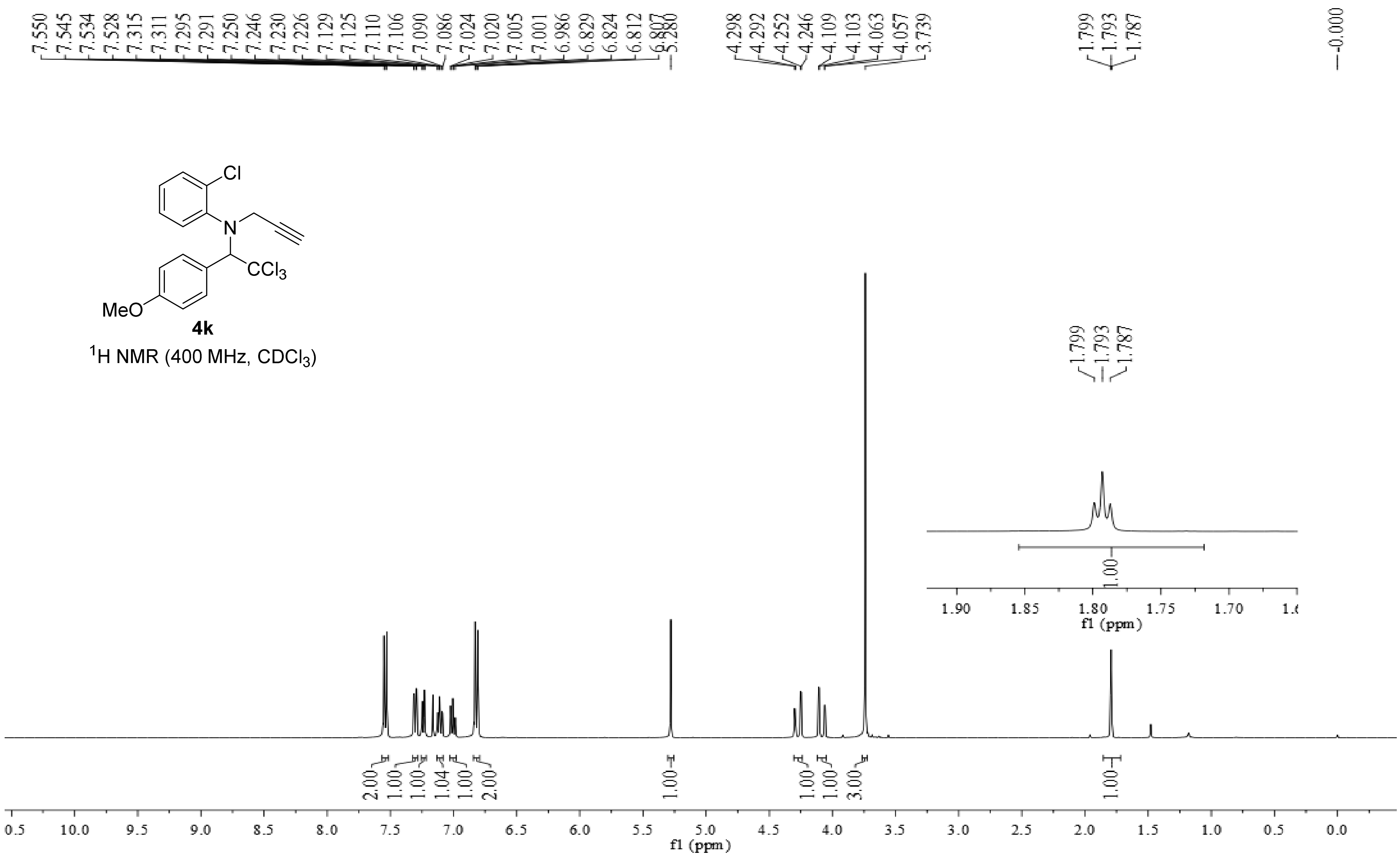




4j

^{13}C NMR (100 MHz, $CDCl_3$)


7.550
7.545
7.534
7.528
7.315
7.311
7.295
7.291
7.250
7.246
7.230
7.226
7.129
7.125
7.110
7.106
7.090
7.086
7.024
7.020
7.005
7.001
6.986
6.829
6.824
6.812
6.807
5.280
4.298
4.292
4.252
4.246
4.109
4.103
4.063
4.057
3.739
1.799
1.793
1.787
-0.000
Cl
N
CCl_3
MeO
4k
^1H NMR (400 MHz, $CDCl_3$)
2.00
1.00
1.00
1.04
1.00
2.00
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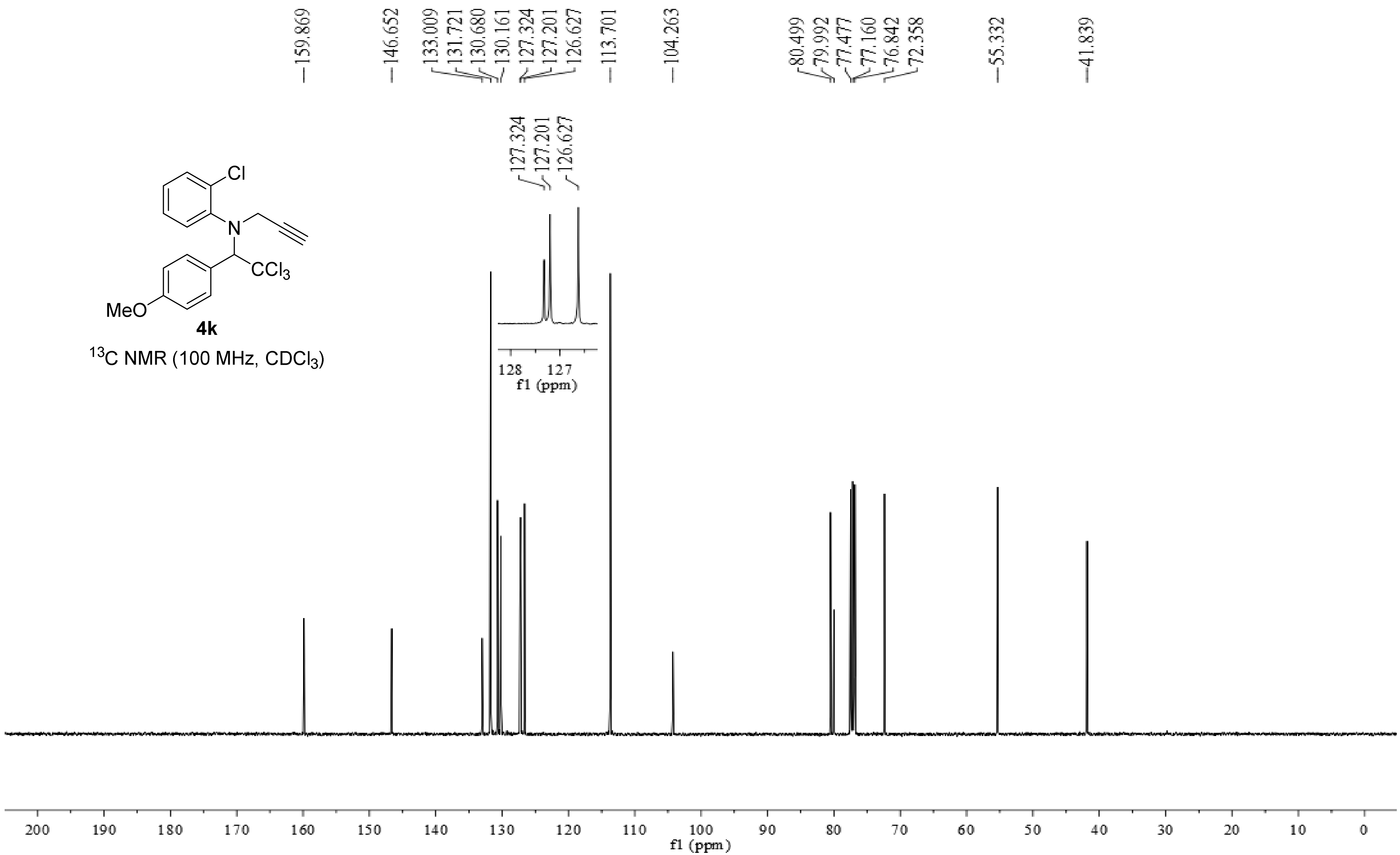
3.00
1.00
f1 (ppm)



4k

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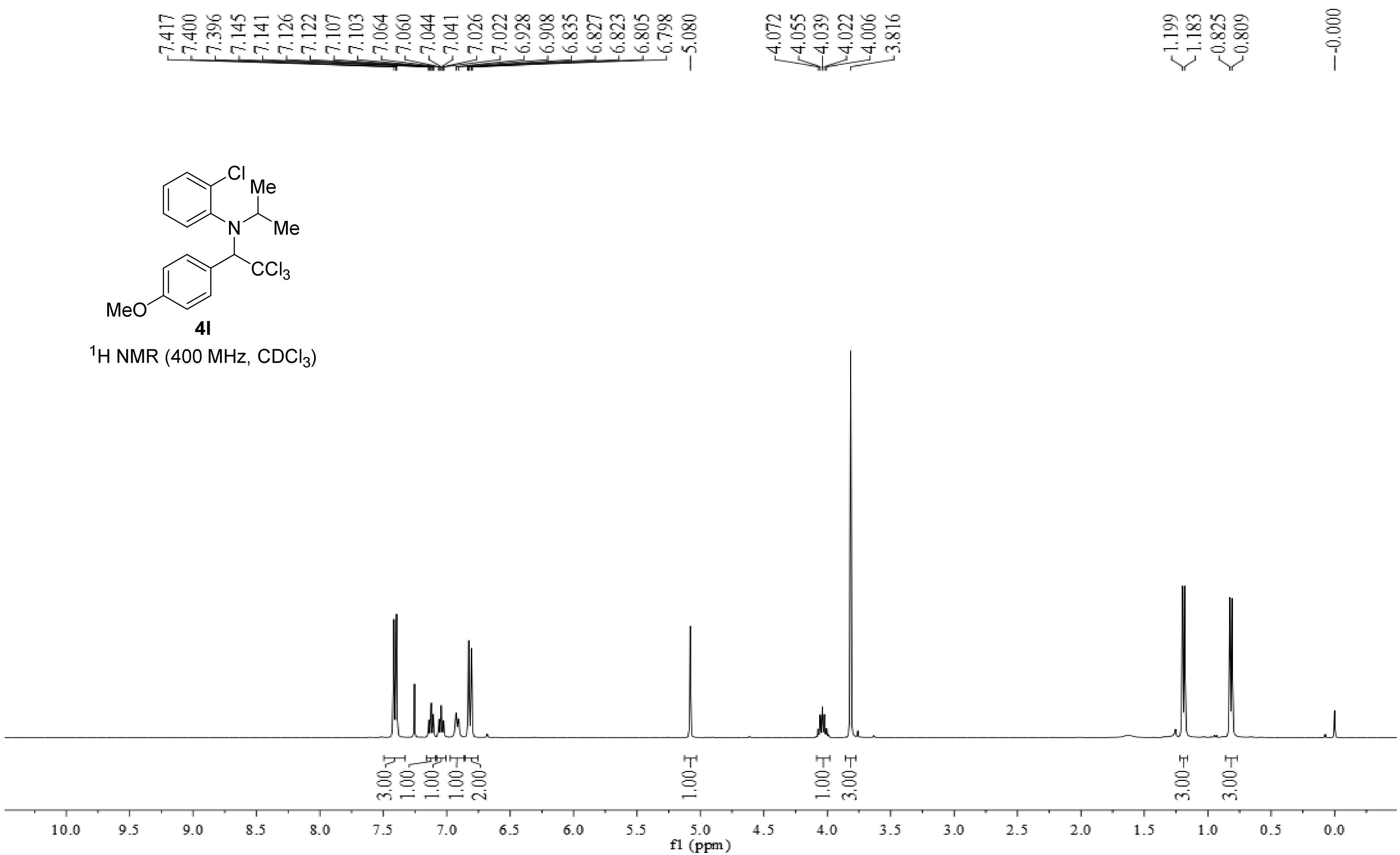

7.417
7.400
7.396
7.145
7.141
7.126
7.122
7.107
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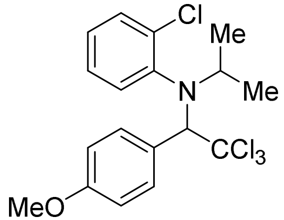
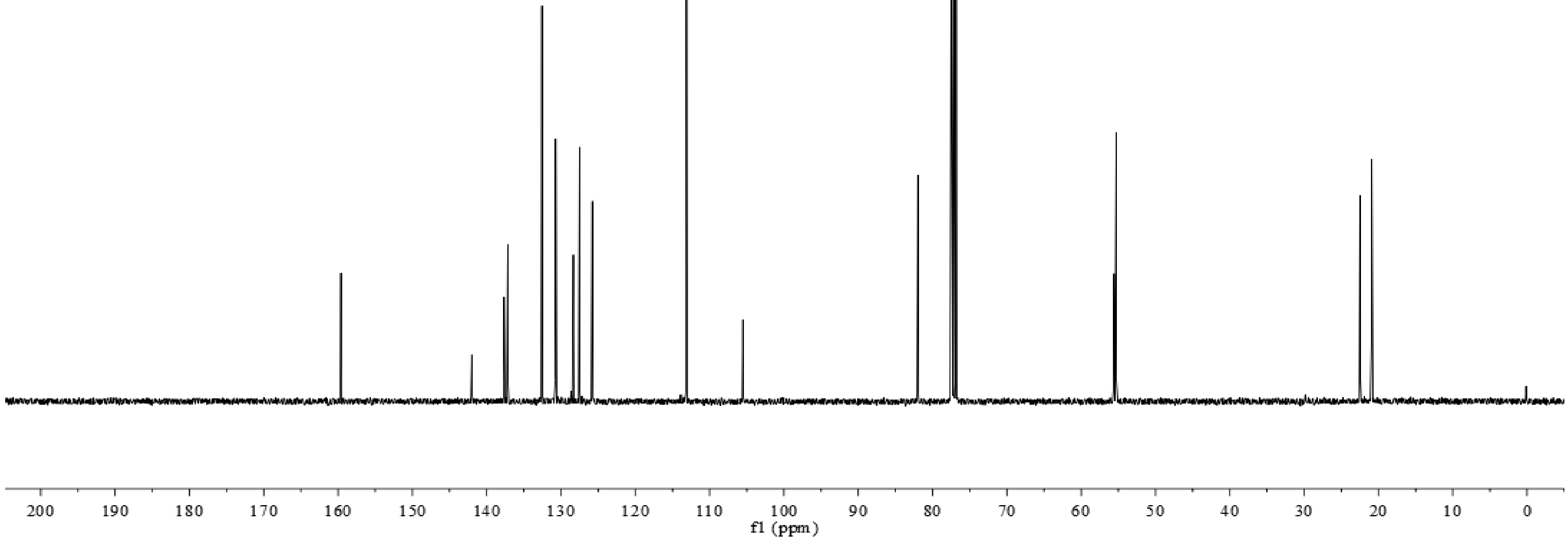
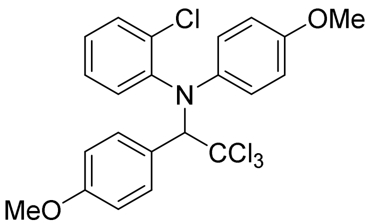
7.064
7.060
7.044
7.041
7.026
7.022
6.928
6.908
6.835
6.827
6.823
6.805
6.798
5.080
4.072
4.055
4.039
4.022
4.006
3.816
1.199
1.183
0.825
0.809
-0.000
Cl
Me
N
Me
CCl3
MeO
4l
1H NMR (400 MHz, CDCl3)
3.00
1.00
1.00
1.00
2.00
1.00
1.00
3.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



4l

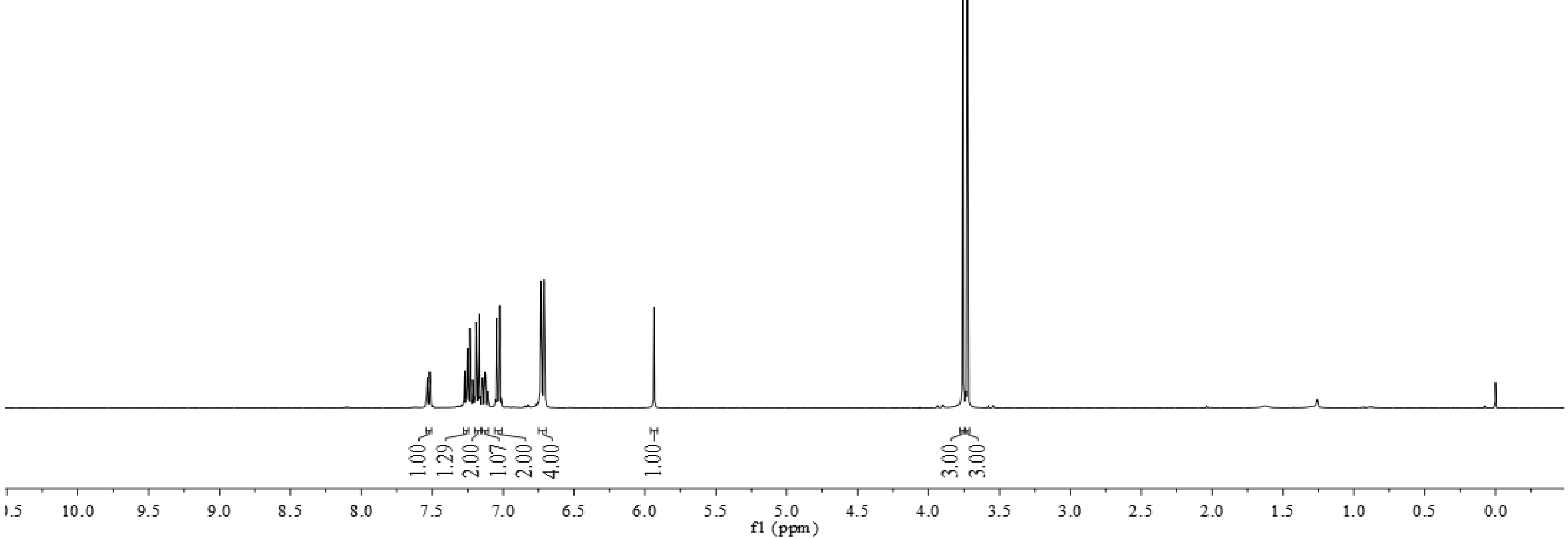
^{13}C NMR (100 MHz, $CDCl_3$)

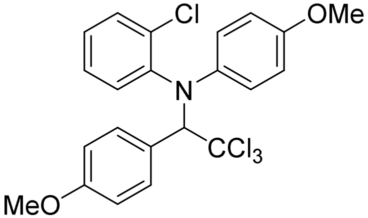




4m

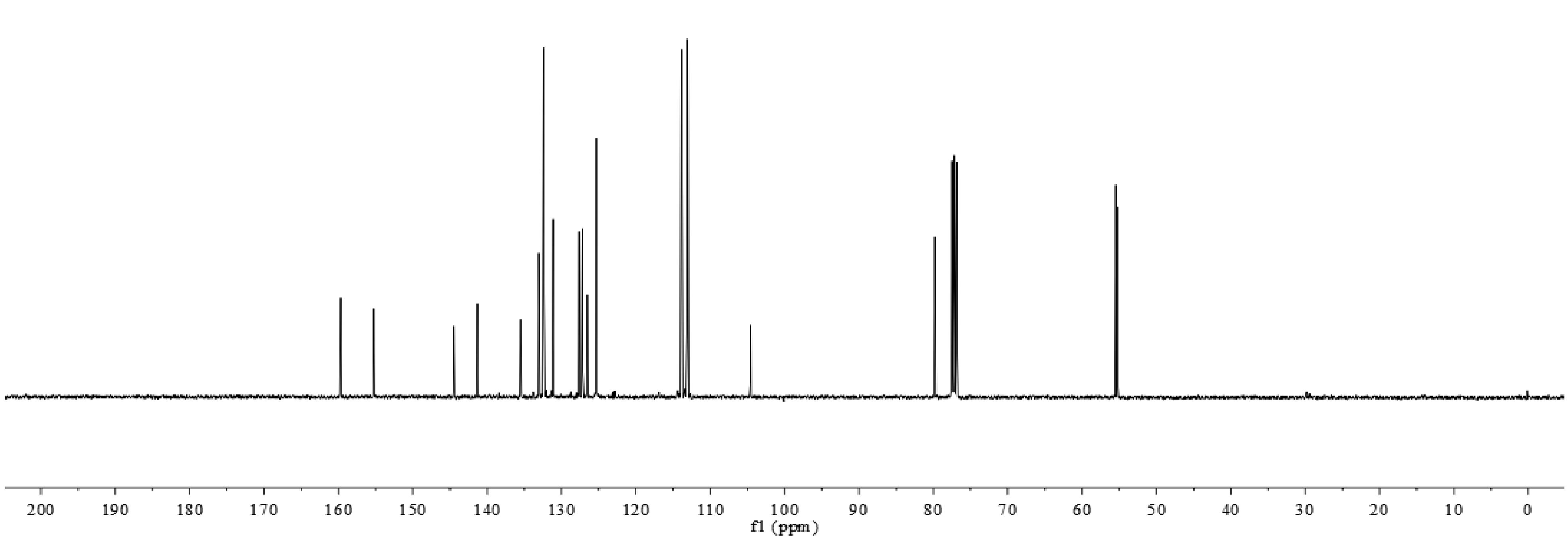
[1]H NMR (400 MHz, $CDCl_3$)

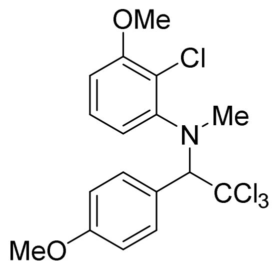




4m

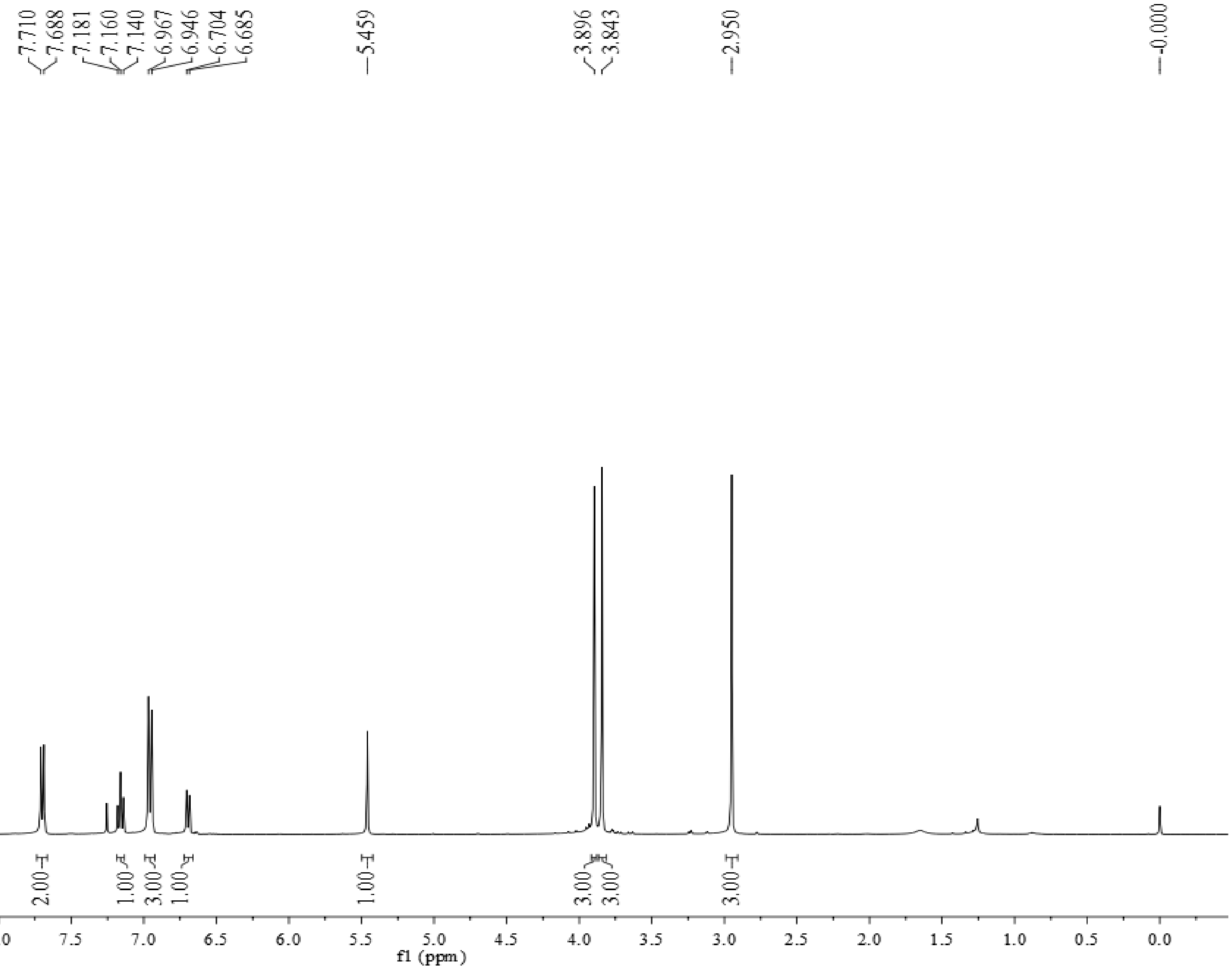
^{13}C NMR (100 MHz, $CDCl_3$)

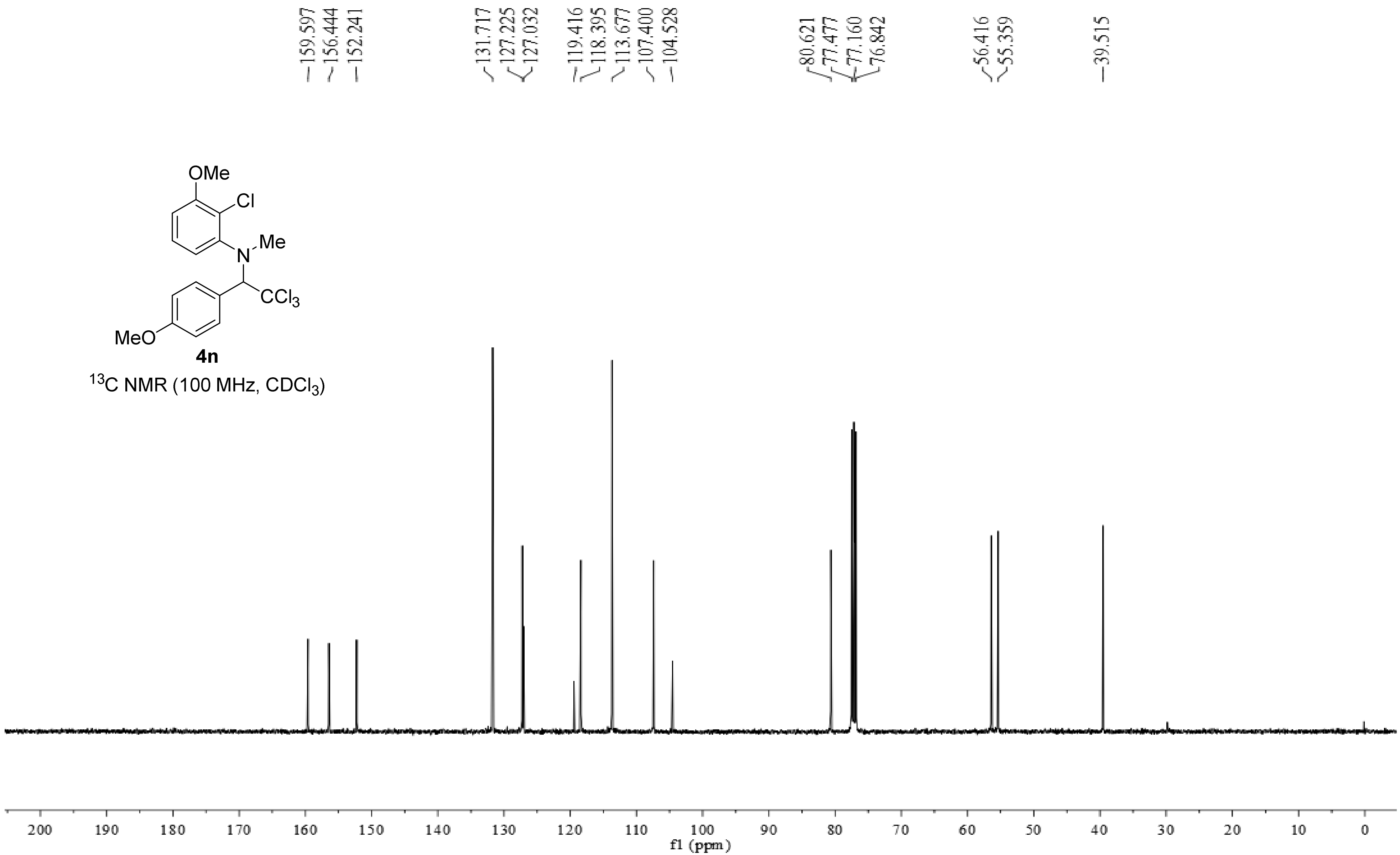


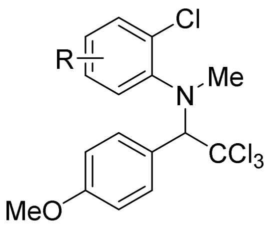


4n

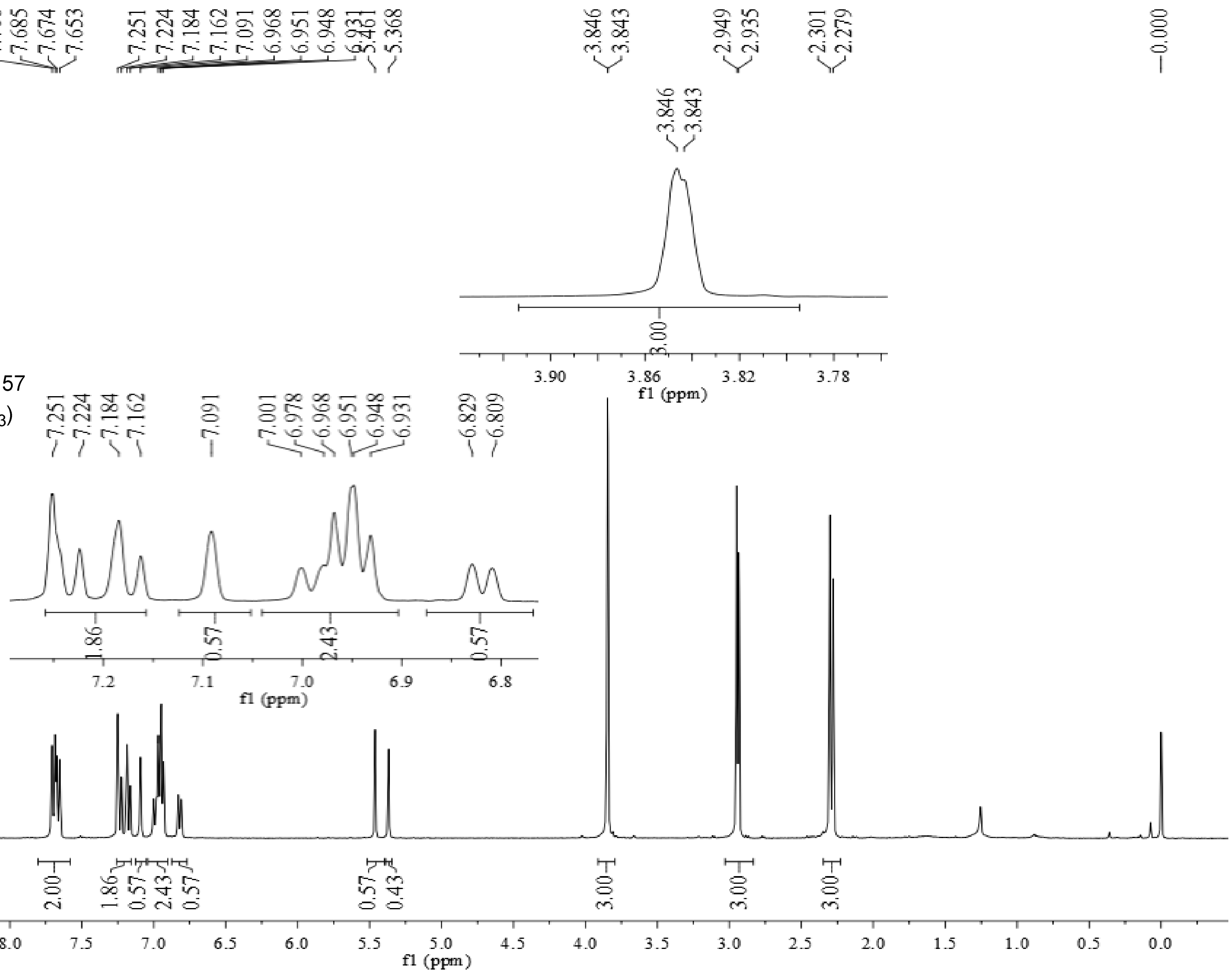
^1H NMR (400 MHz, $CDCl_3$)

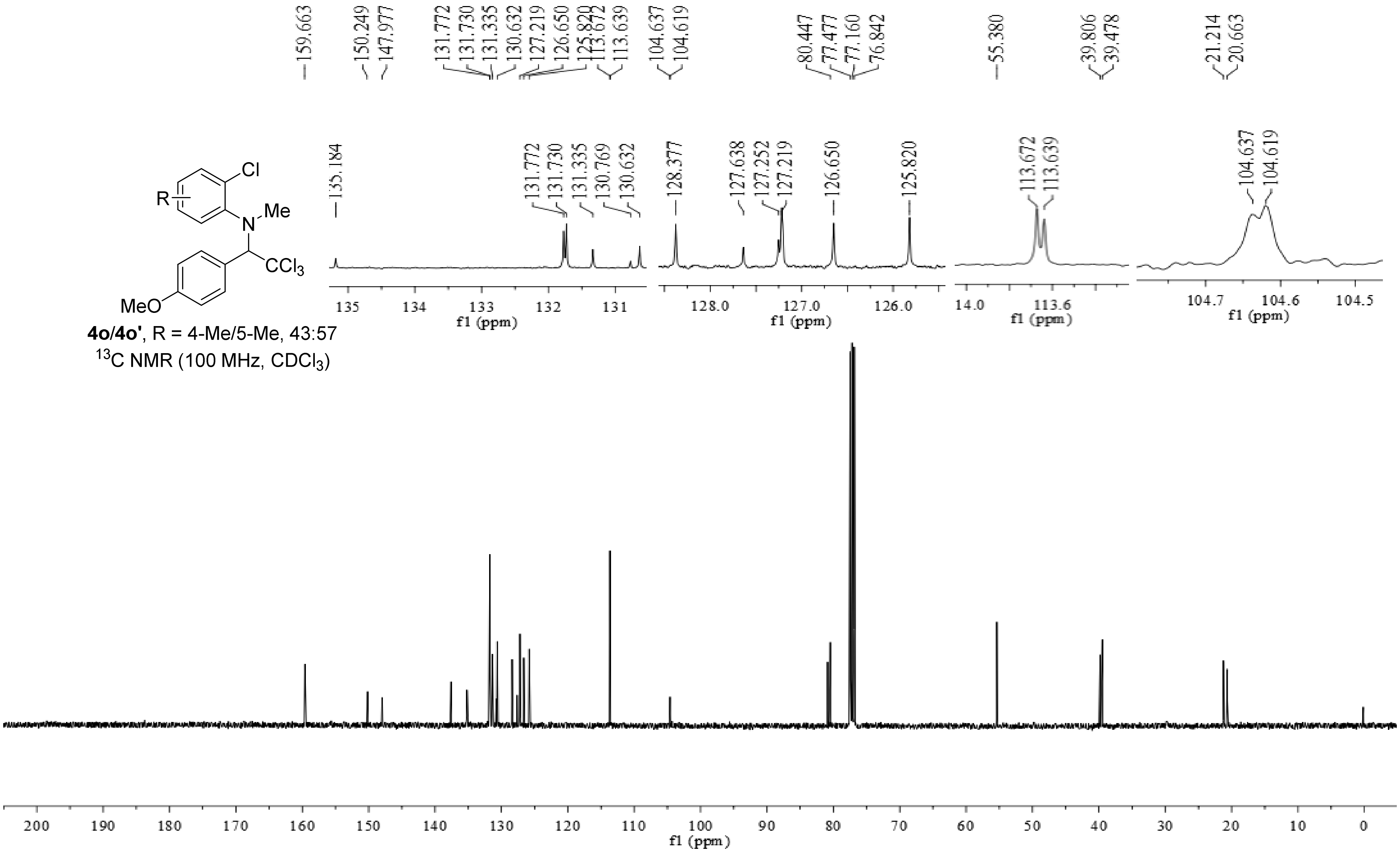


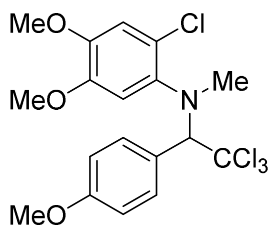

159.597
156.444
152.241
131.717
127.225
127.032
119.416
118.395
113.677
107.400
104.528
80.621
77.477
77.160
76.842
56.416
55.359
39.515
OMe
Cl
N
Me
CCl3
MeO
4n
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



4o/4o', R = 4-Me/5-Me, 43:57
^{1}H NMR (400 MHz, $CDCl_3$)

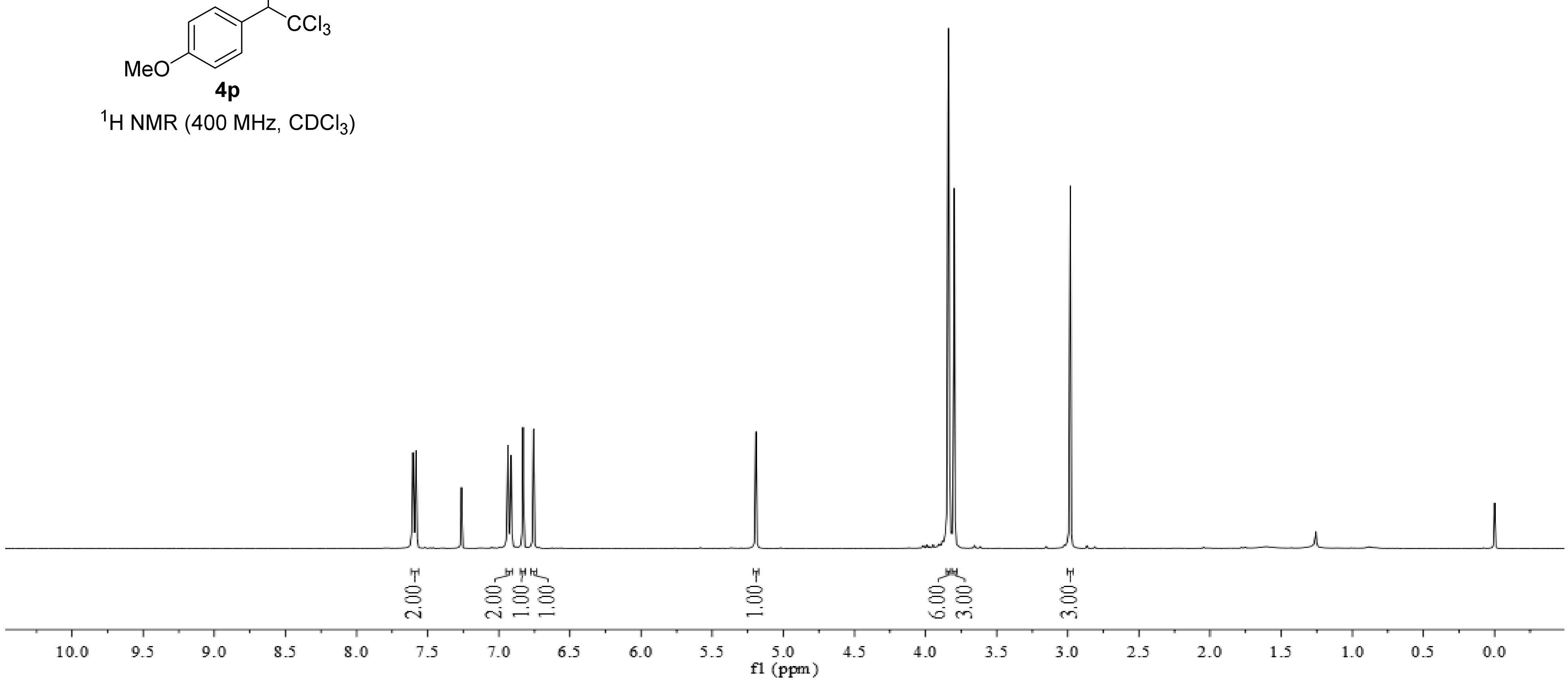


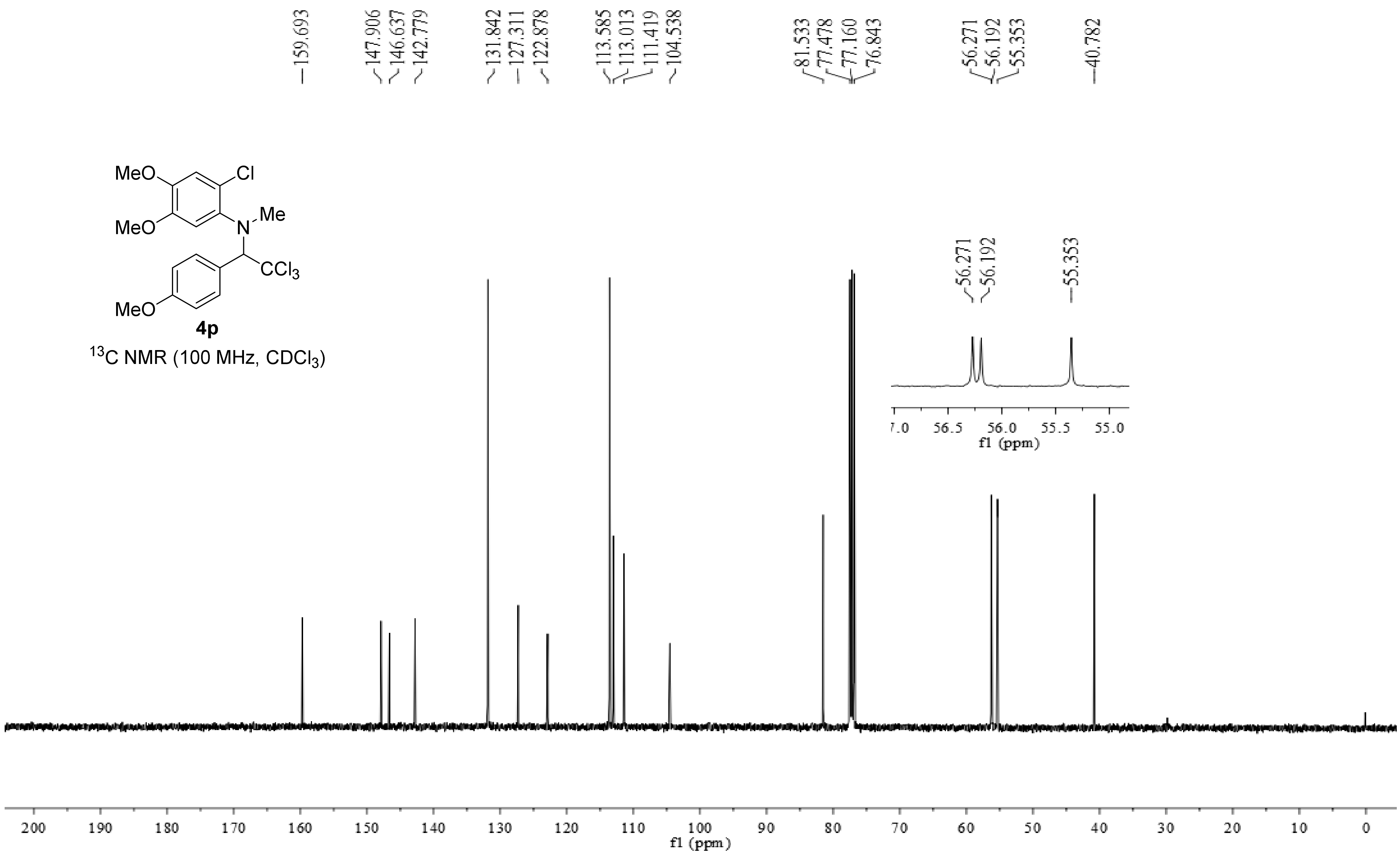

Cl
R
N
Me
CCl3
MeO
4o/4o', R = 4-Me/5-Me, 43:57
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

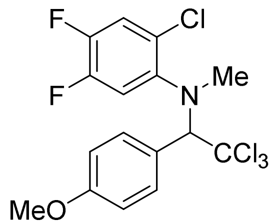


4p

^{1}H NMR (400 MHz, $CDCl_3$)

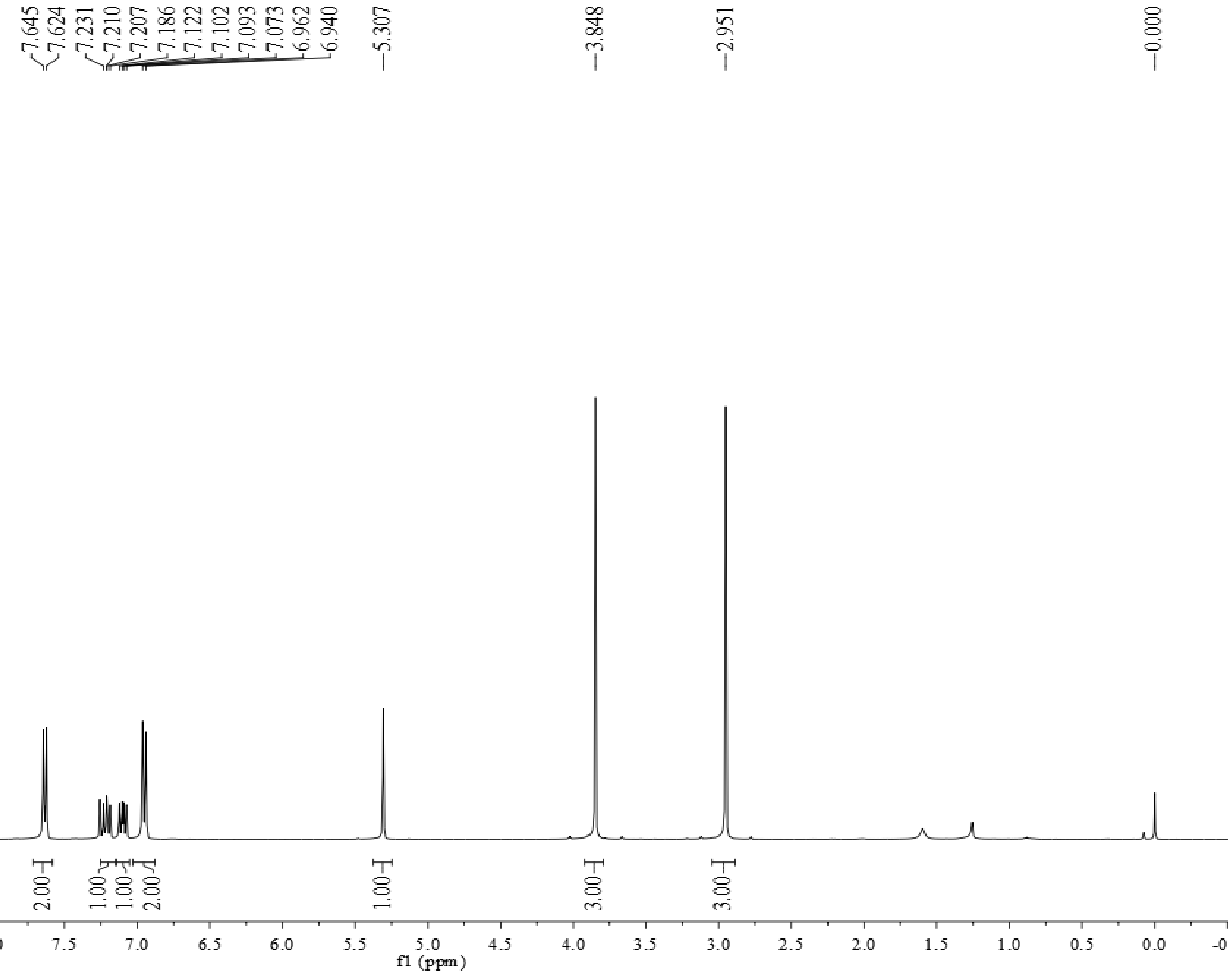


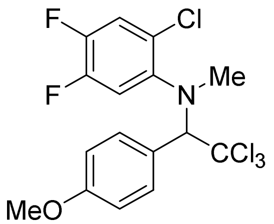

MeO
Cl
MeO
N
Me
CCl3
MeO
4p
13C NMR (100 MHz, CDCl3)
159.693
147.906
146.637
142.779
131.842
127.311
122.878
113.585
113.013
111.419
104.538
81.533
77.478
77.160
76.843
56.271
56.192
55.353
40.782
f1 (ppm)



4q

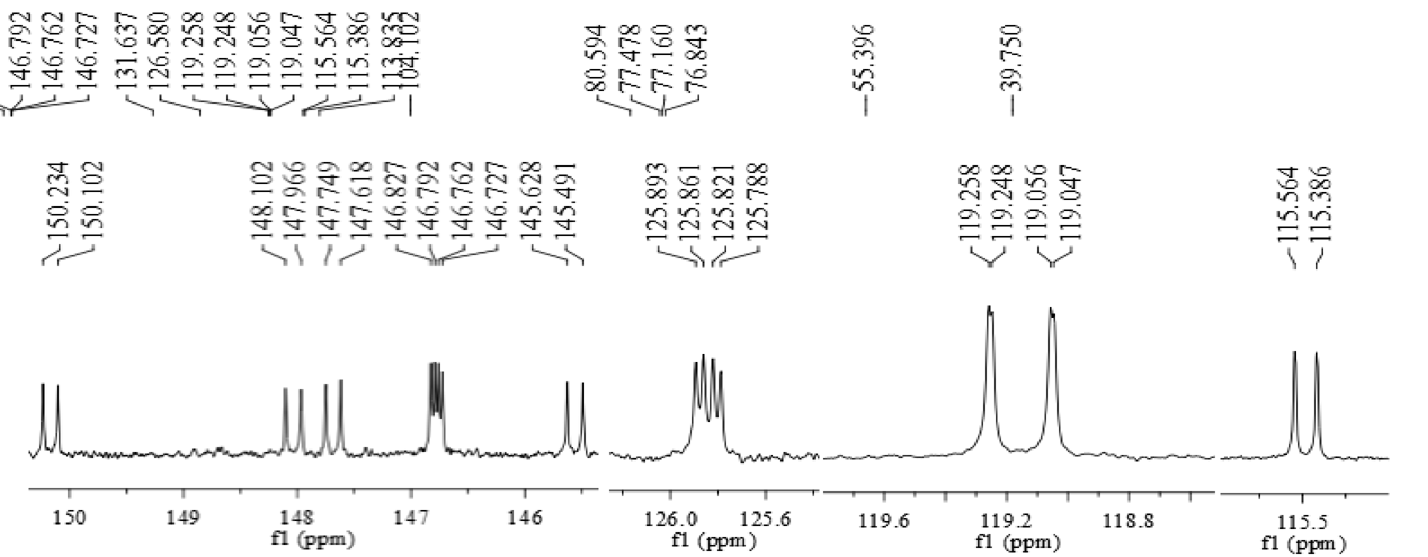
^1H NMR (400 MHz, $CDCl_3$)

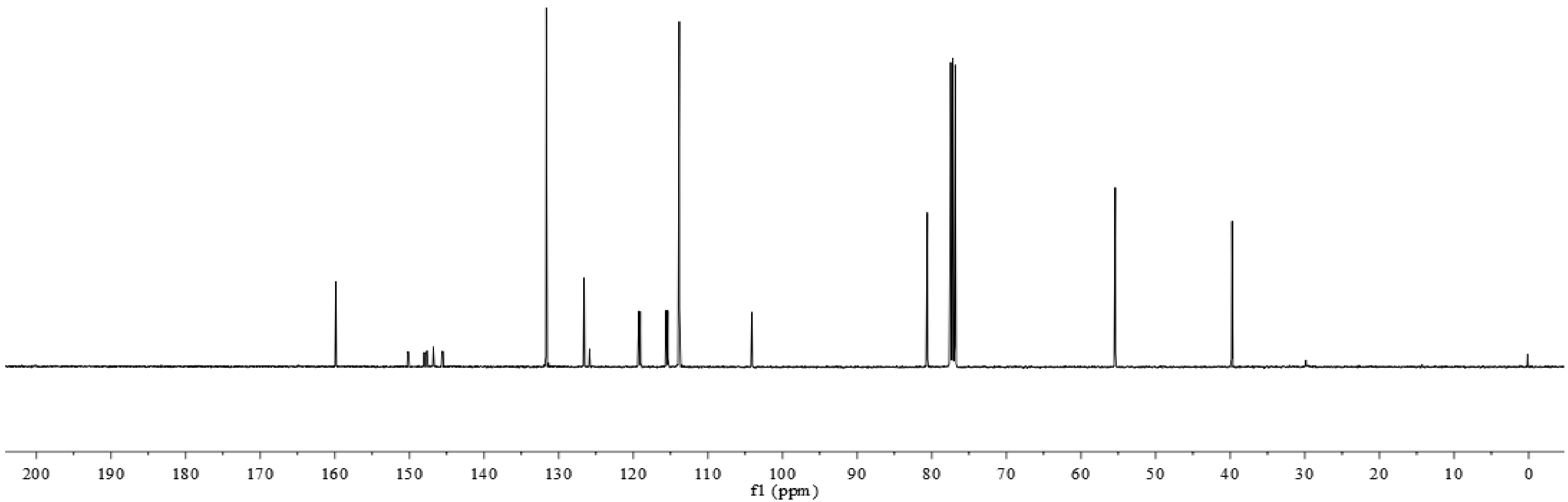


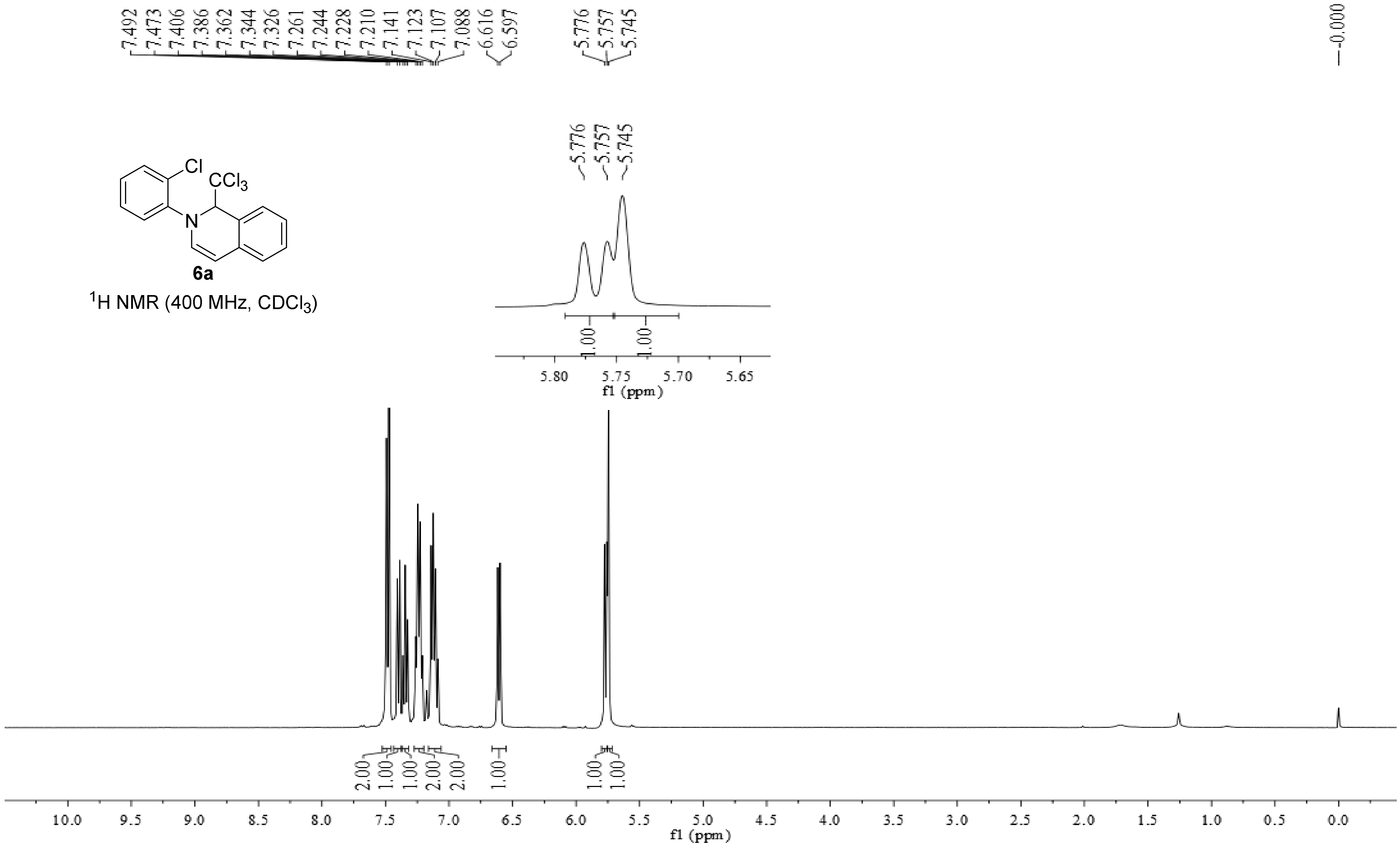


4q

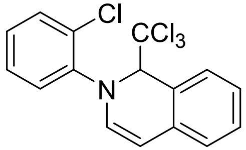
^{13}C NMR (100 MHz, $CDCl_3$)





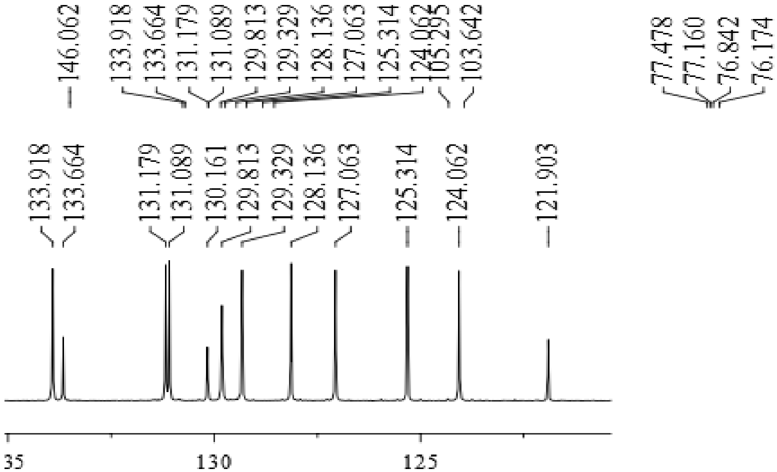
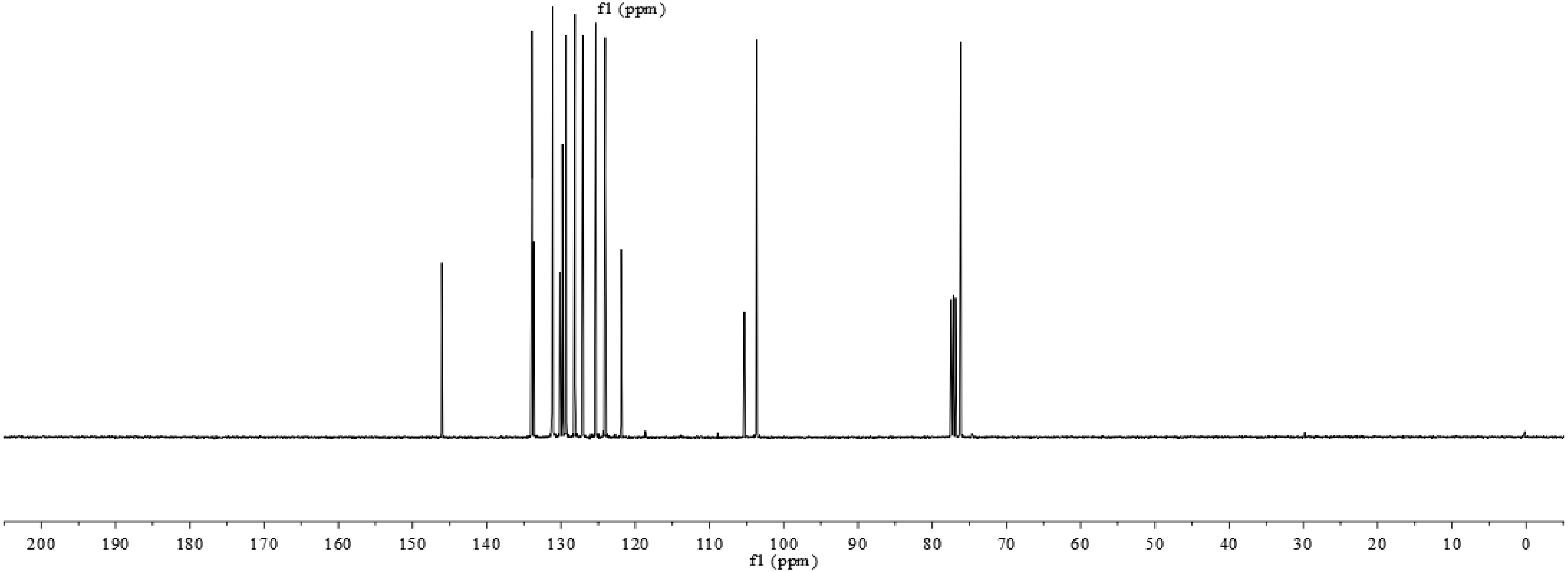


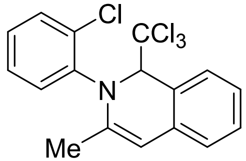
7.492
7.473
7.406
7.386
7.362
7.344
7.326
7.261
7.244
7.228
7.210
7.141
7.123
7.107
7.088
6.616
6.597
5.776
5.757
5.745
0.000
Cl
CCl3
N
6a
1H NMR (400 MHz, CDCl3)
1.00
1.00
5.80
5.75
5.70
5.65
f1 (ppm)
2.00
1.00
1.00
2.00
2.00
1.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



6a

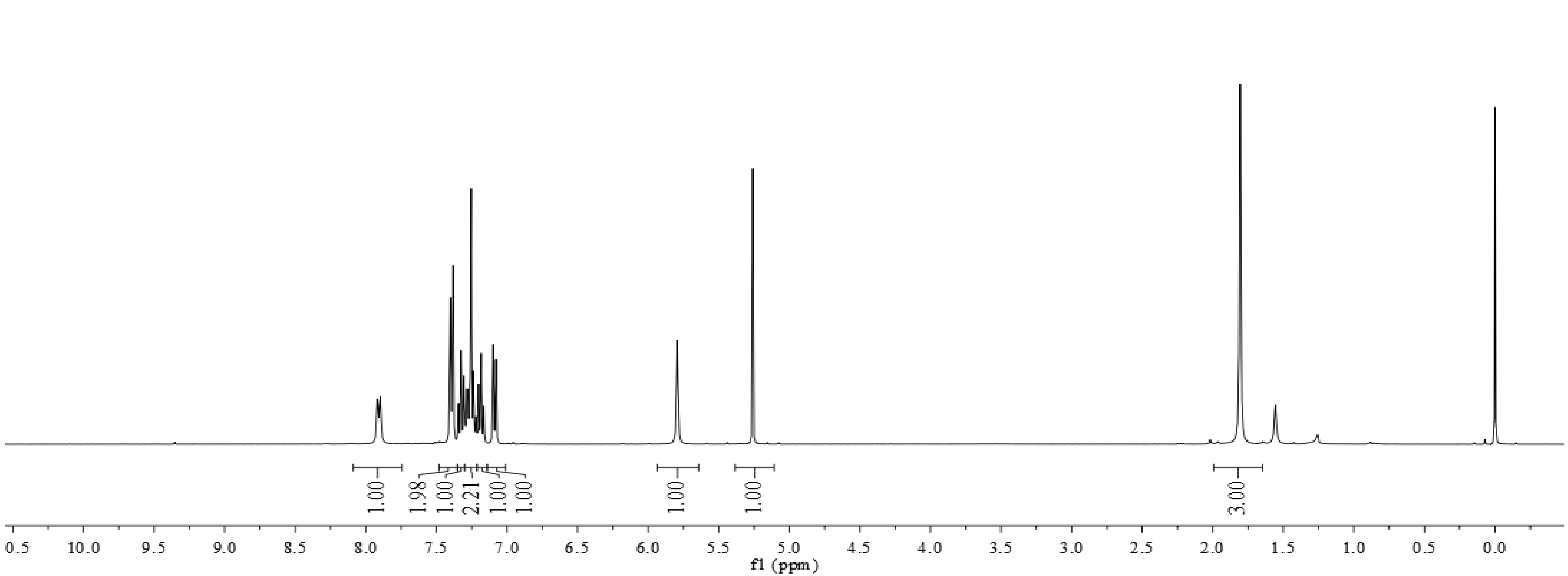
^{13}C NMR (100 MHz, $CDCl_3$)

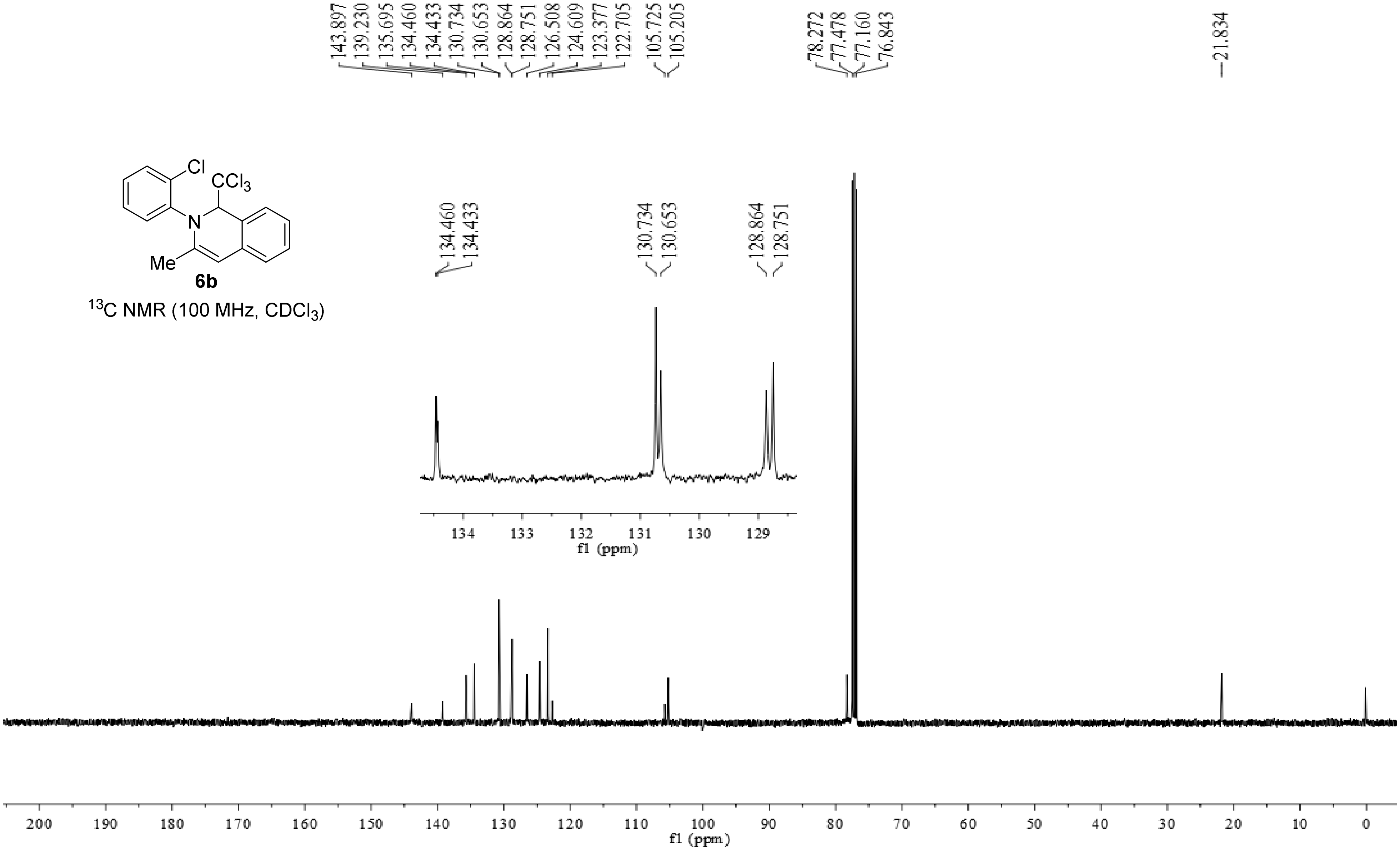





6b

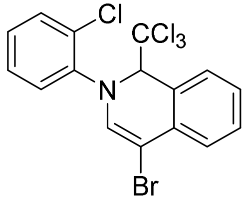
^1H NMR (400 MHz, $CDCl_3$)





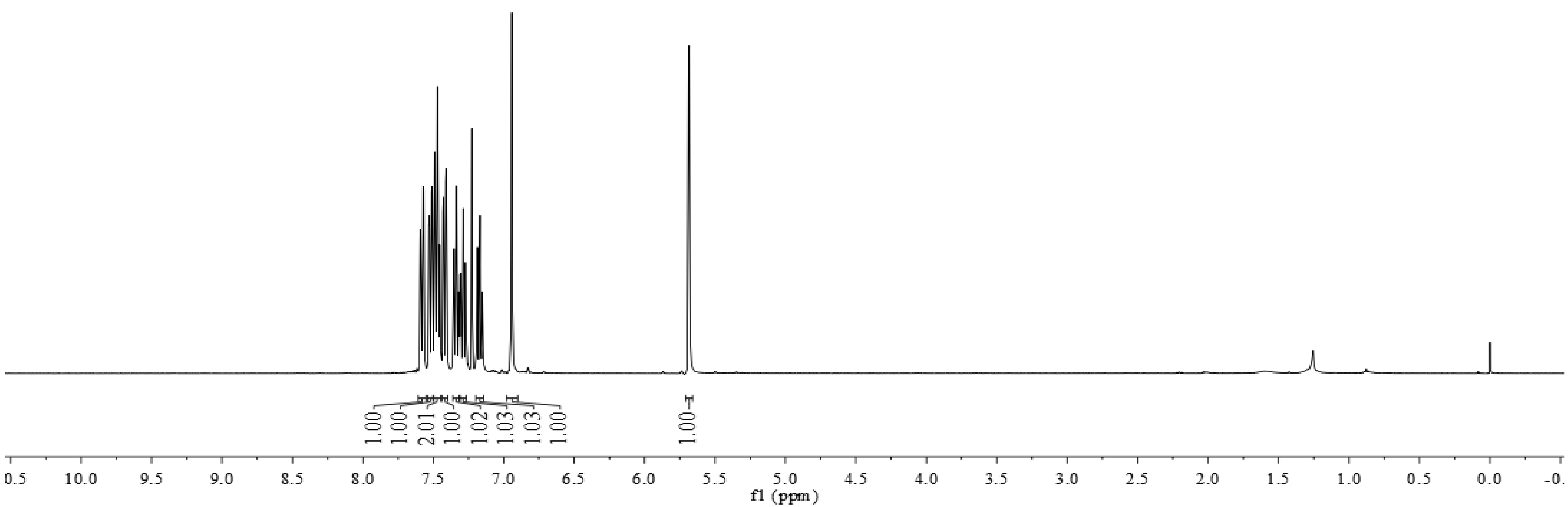
6b

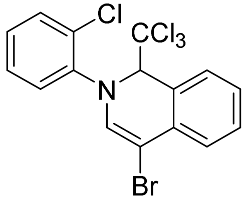
^{13}C NMR (100 MHz, $CDCl_3$)



6c

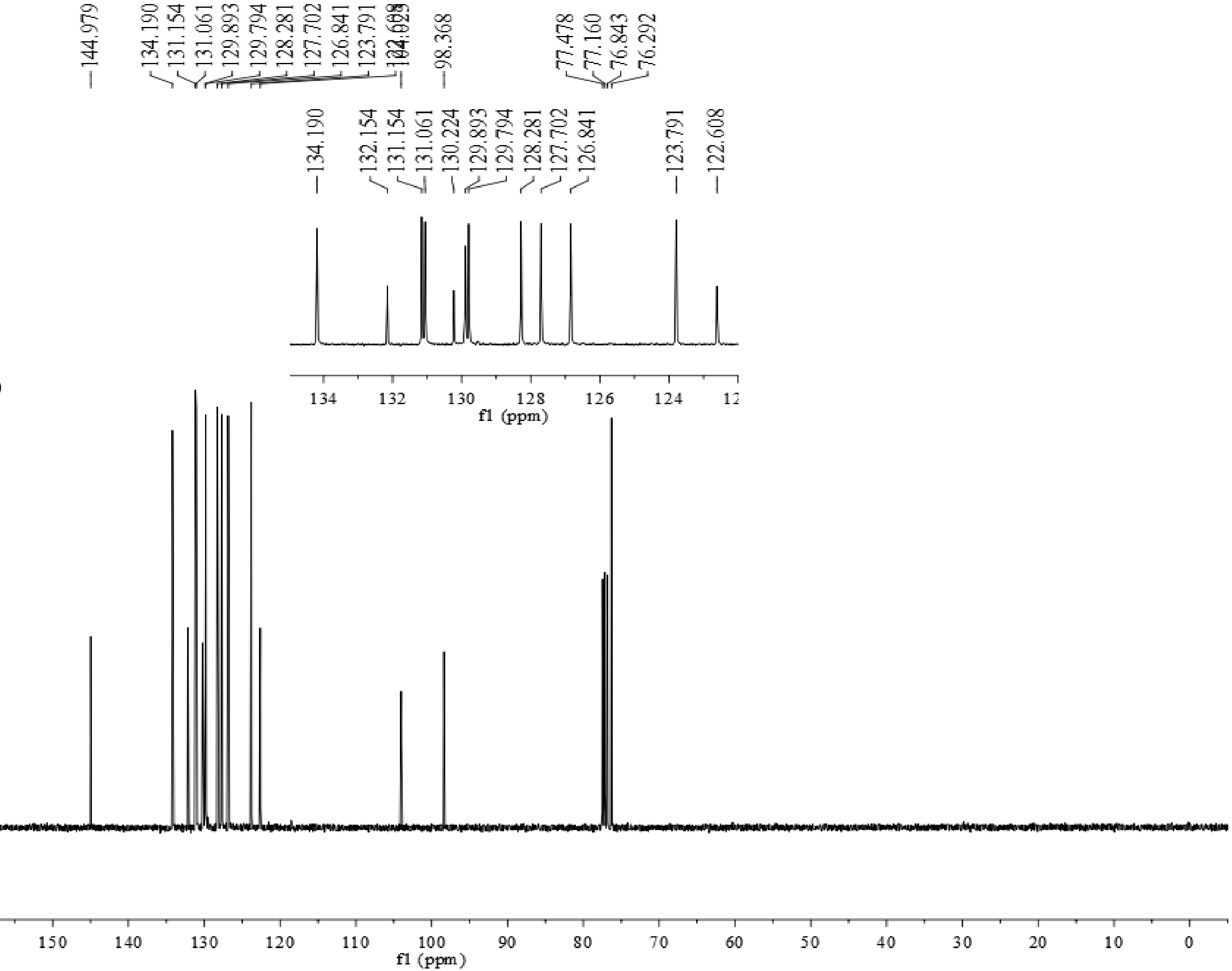
^1H NMR (400 MHz, $CDCl_3$)

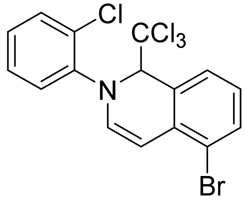




6c

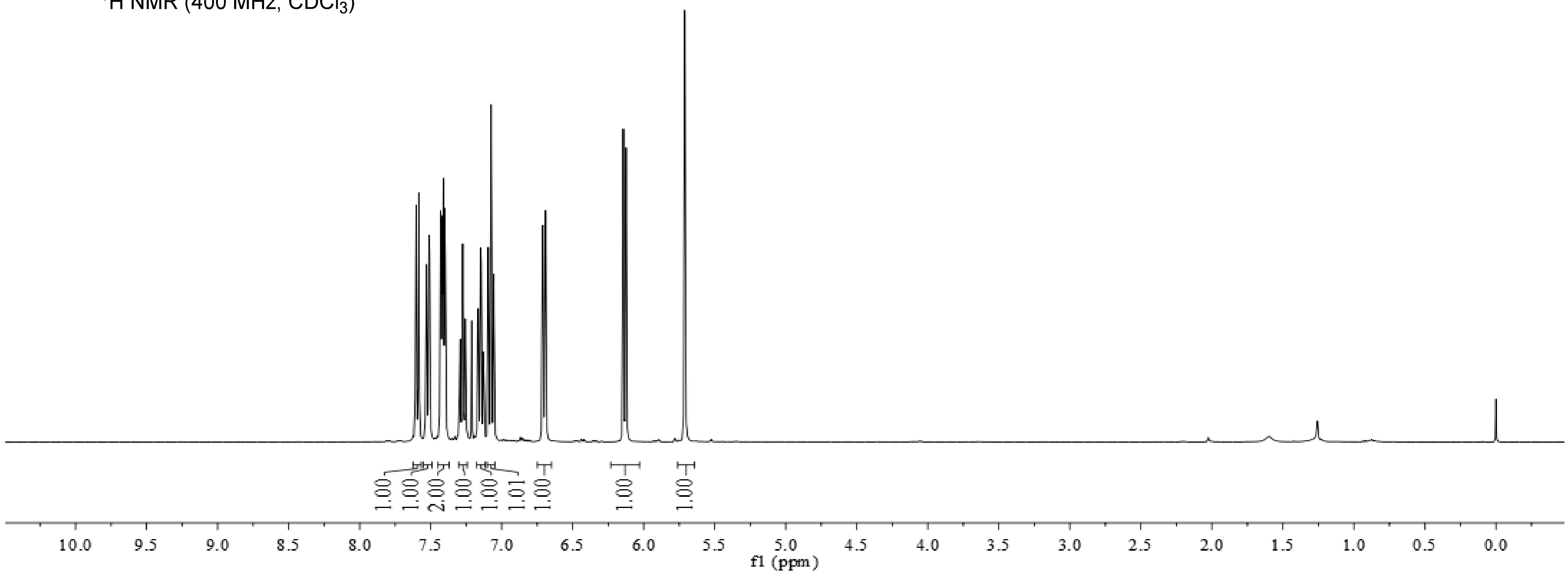
^{13}C NMR (100 MHz, $CDCl_3$)

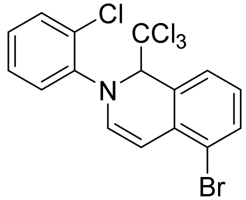




6d

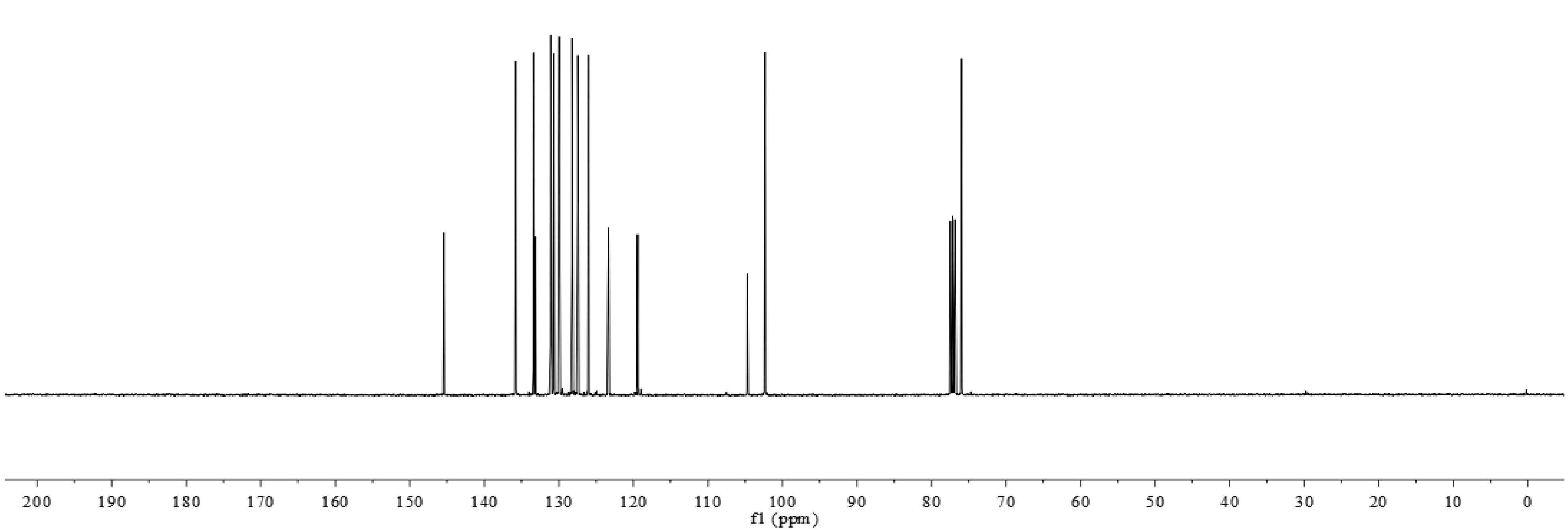
^{1}H NMR (400 MHz, $CDCl_3$)

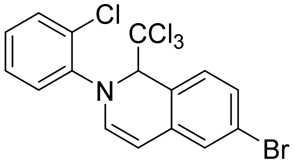




6d

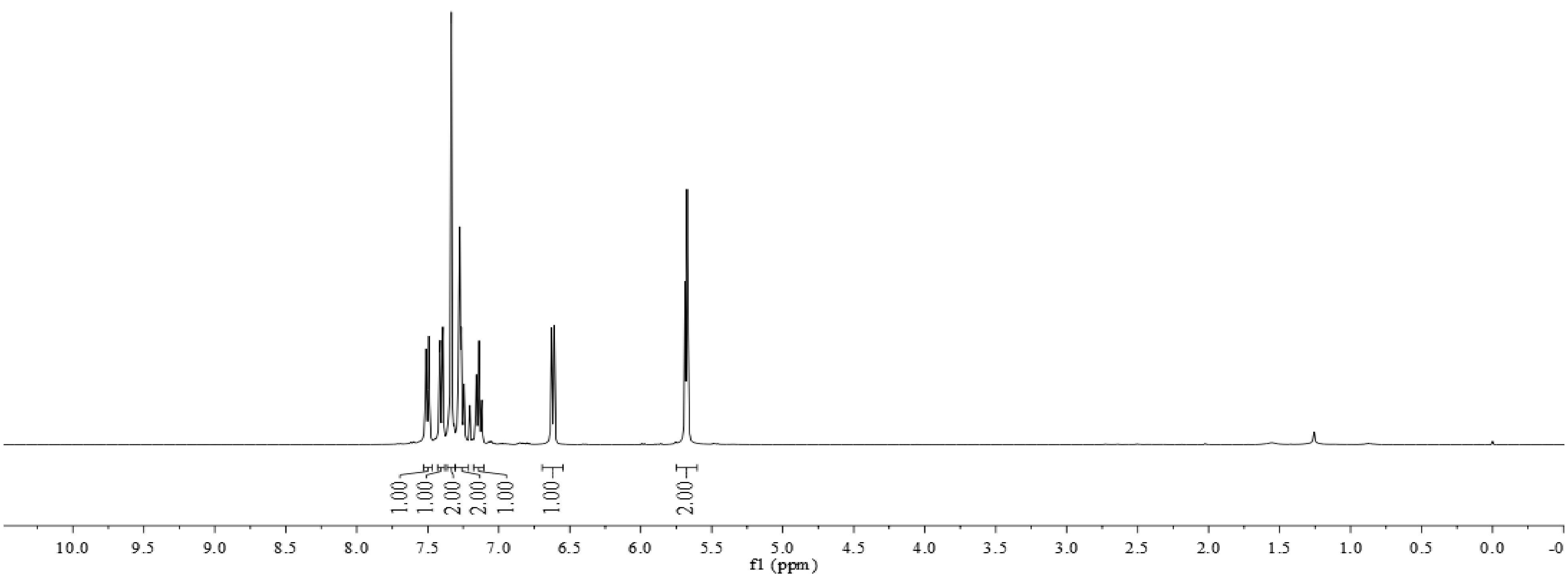
^{13}C NMR (100 MHz, $CDCl_3$)

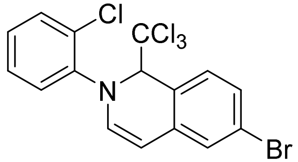




6e

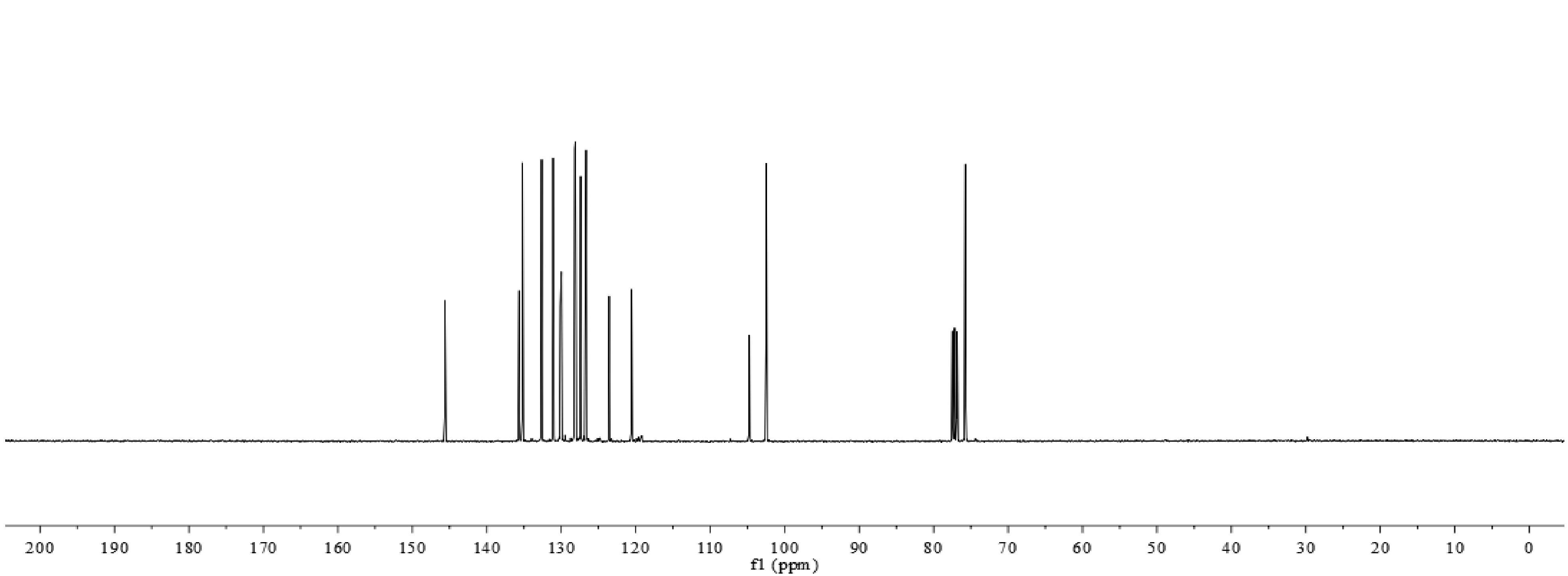
^{1}H NMR (400 MHz, $CDCl_3$)

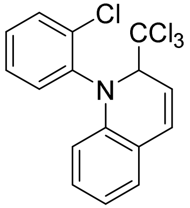




6e

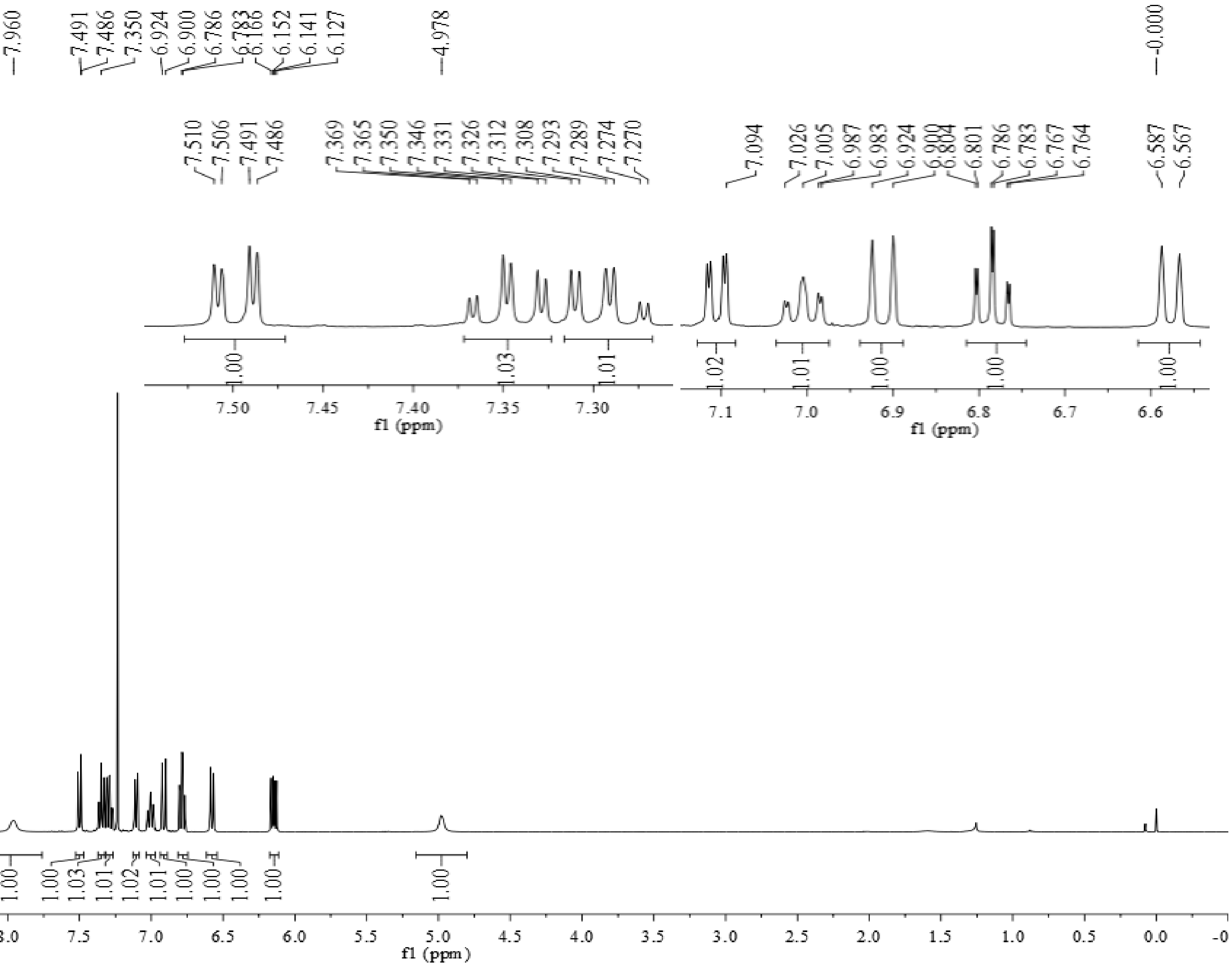
^{13}C NMR (100 MHz, $CDCl_3$)

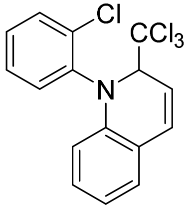




6f

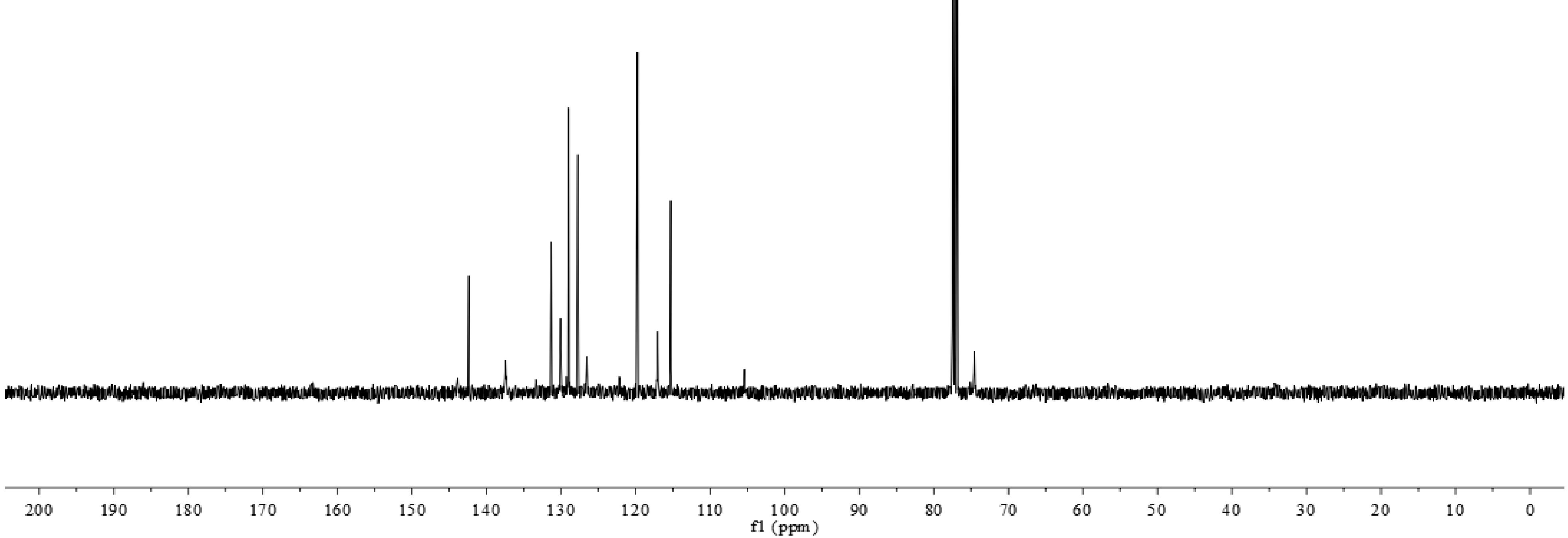
^{1}H NMR (400 MHz, $CDCl_3$)

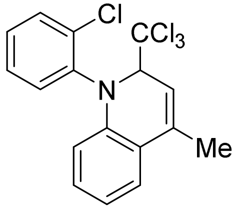




6f

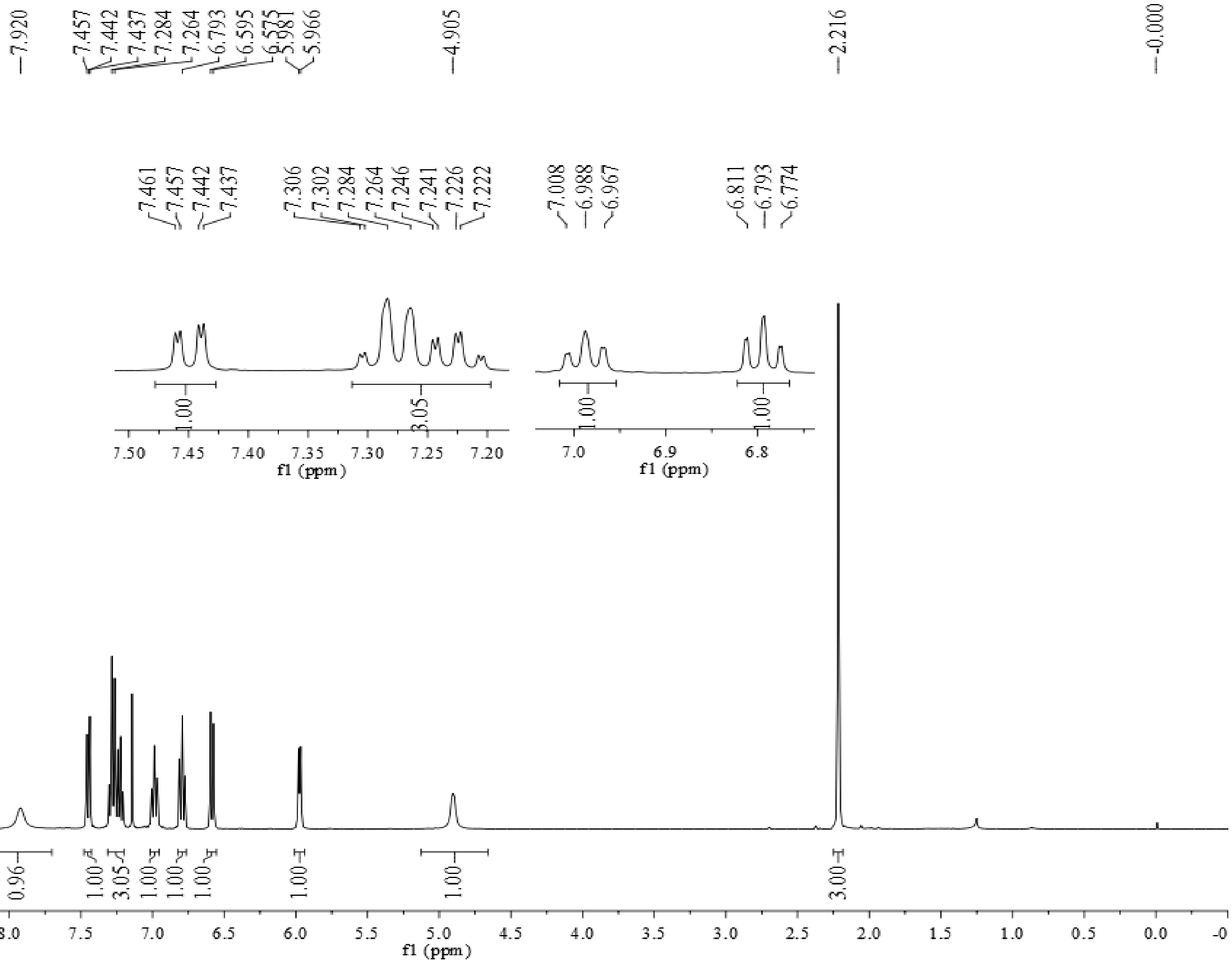
^{13}C NMR (100 MHz, $CDCl_3$)

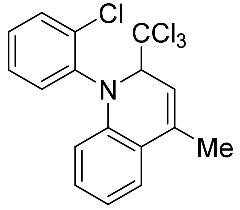




6g

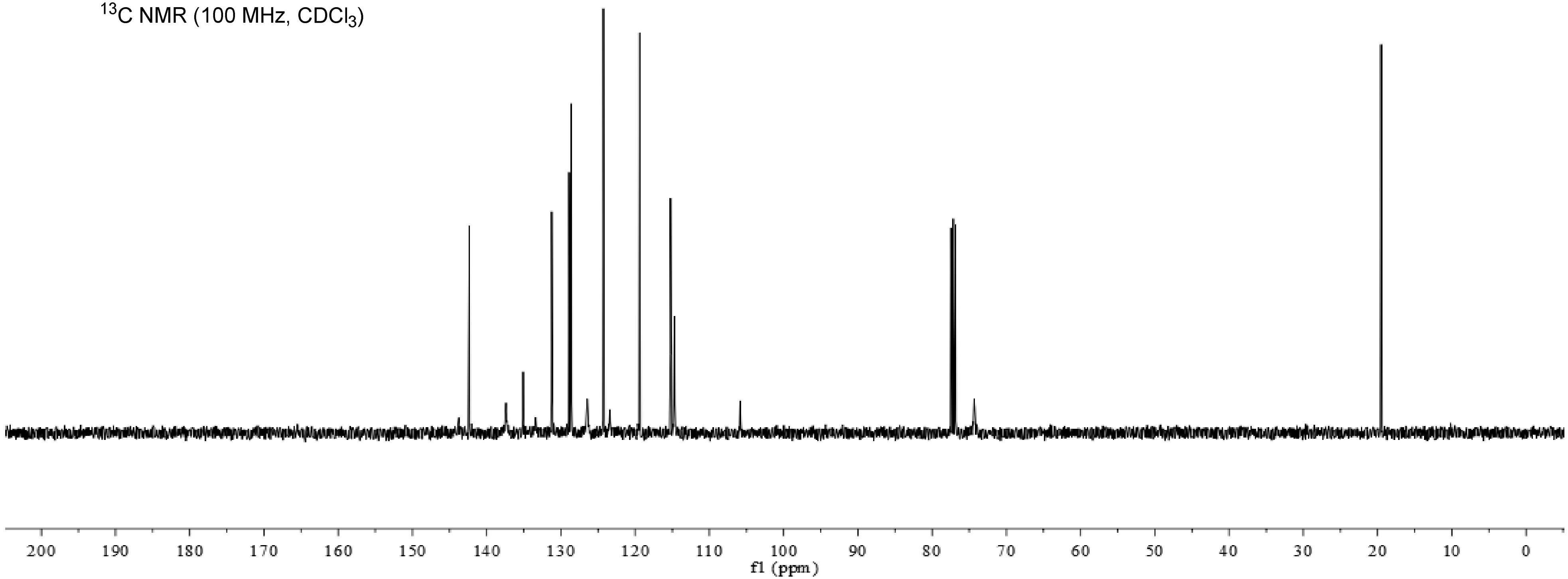
^1H NMR (400 MHz, $CDCl_3$)

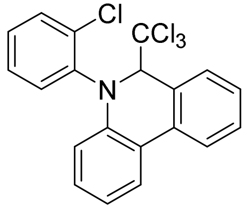




6g

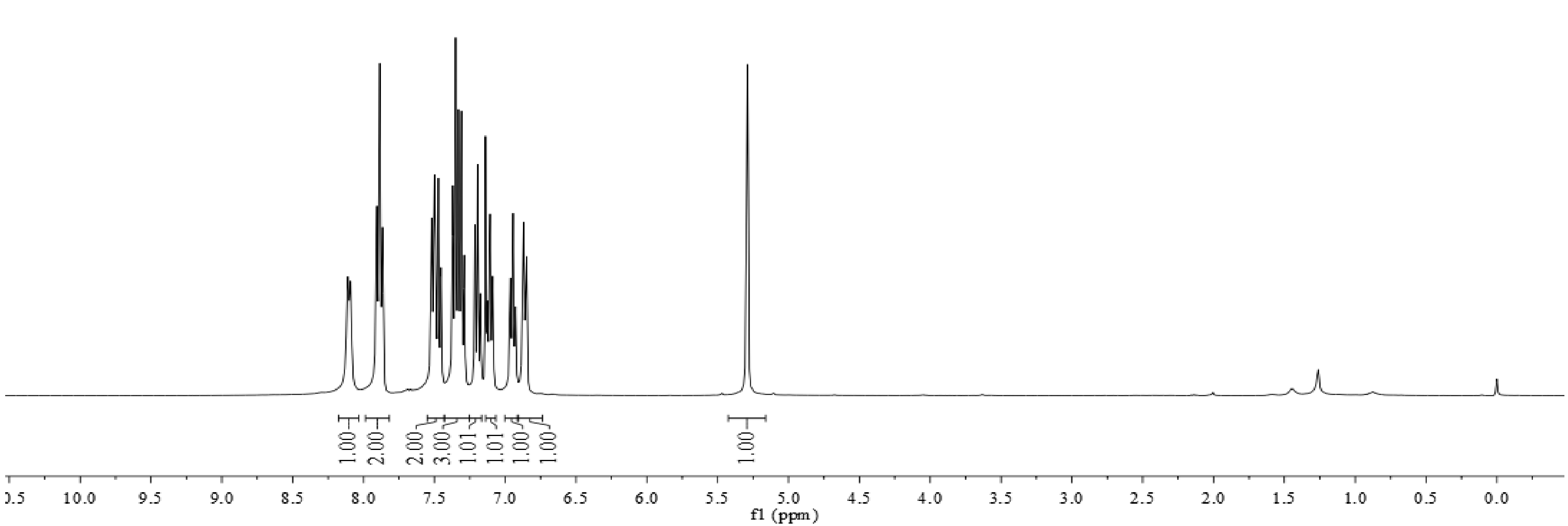
^{13}C NMR (100 MHz, $CDCl_3$)

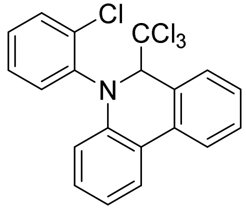




6h

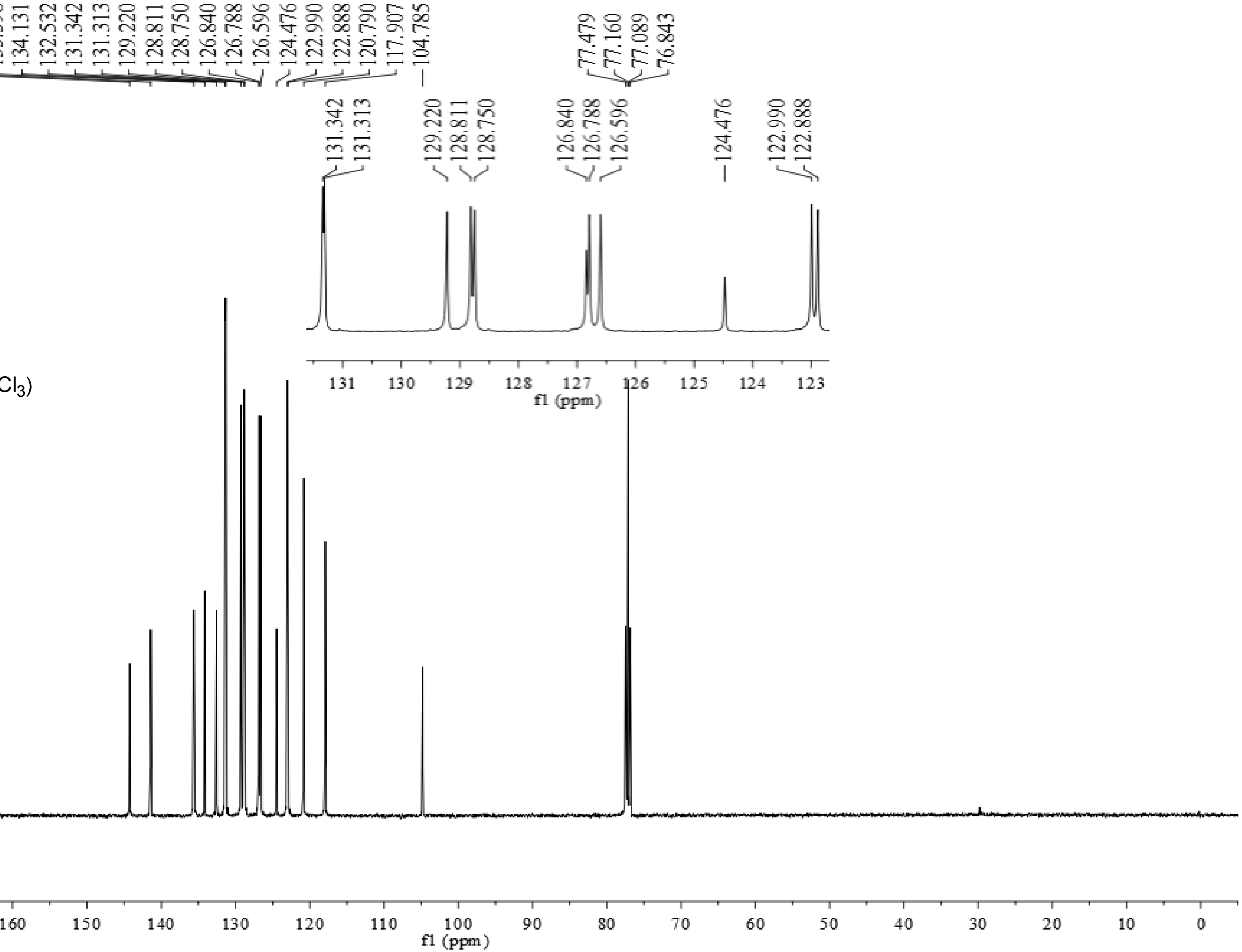
^{1}H NMR (400 MHz, $CDCl_3$)

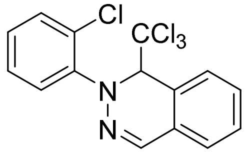




6h

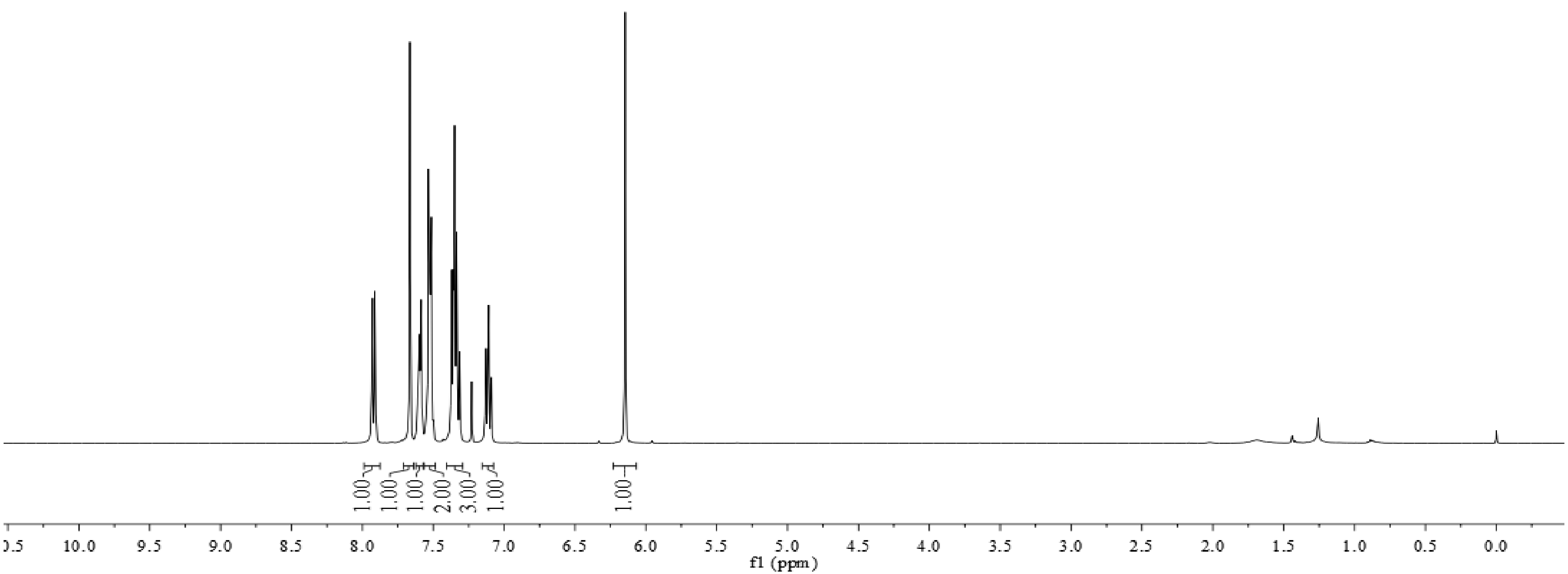
^{13}C NMR (100 MHz, $CDCl_3$)

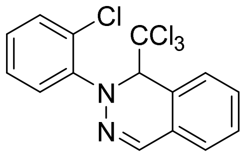




6i

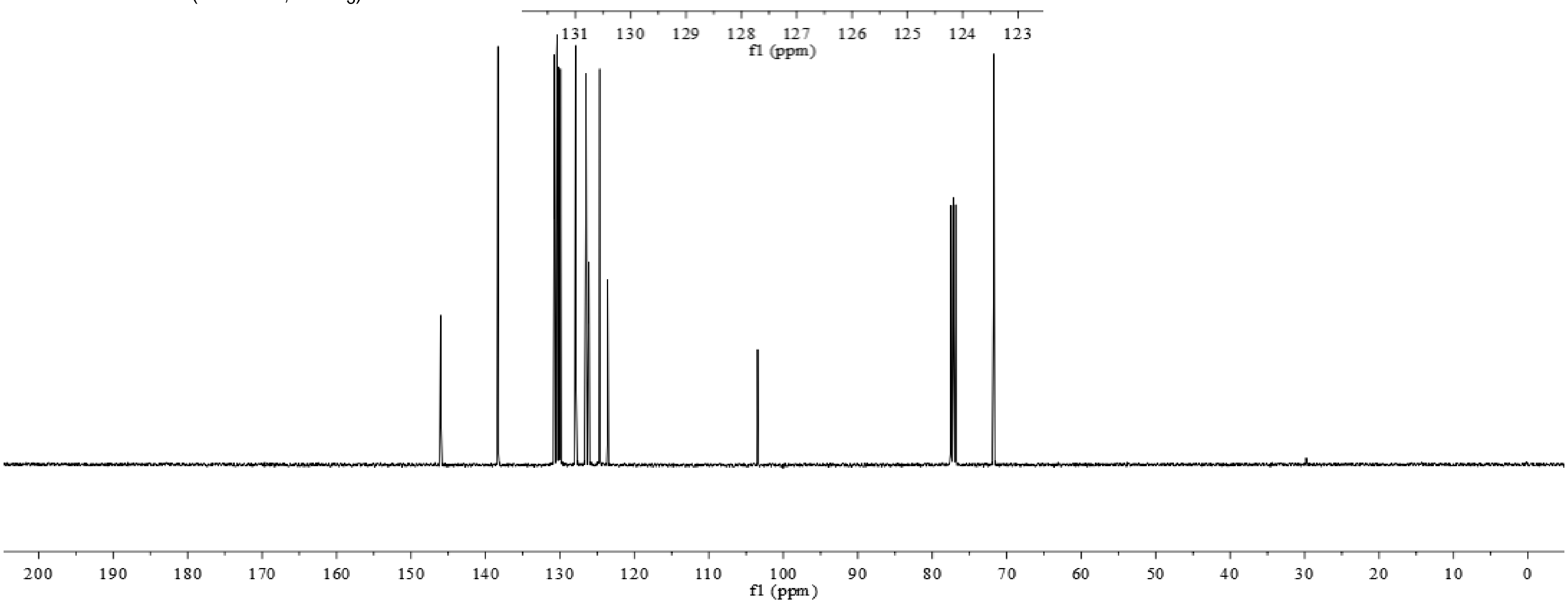
^{1}H NMR (400 MHz, $CDCl_3$)

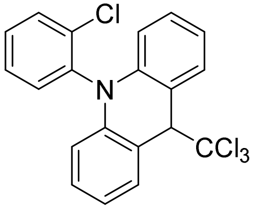




6i

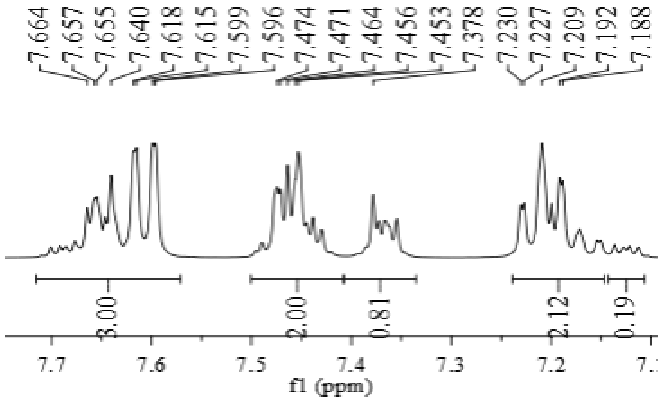
^{13}C NMR (100 MHz, $CDCl_3$)

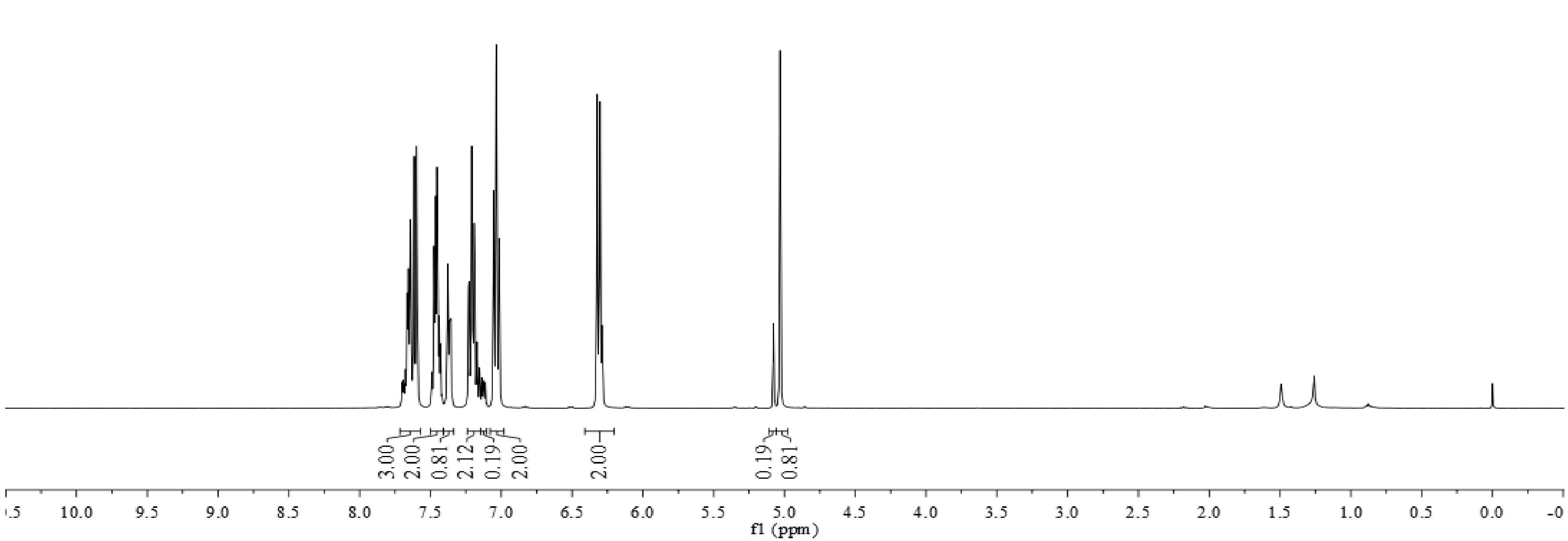


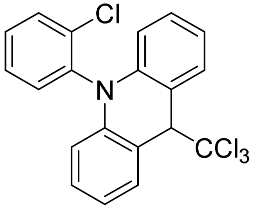


6j, major/minor isomer = 81:19

^{1}H NMR (400 MHz, $CDCl_3$)

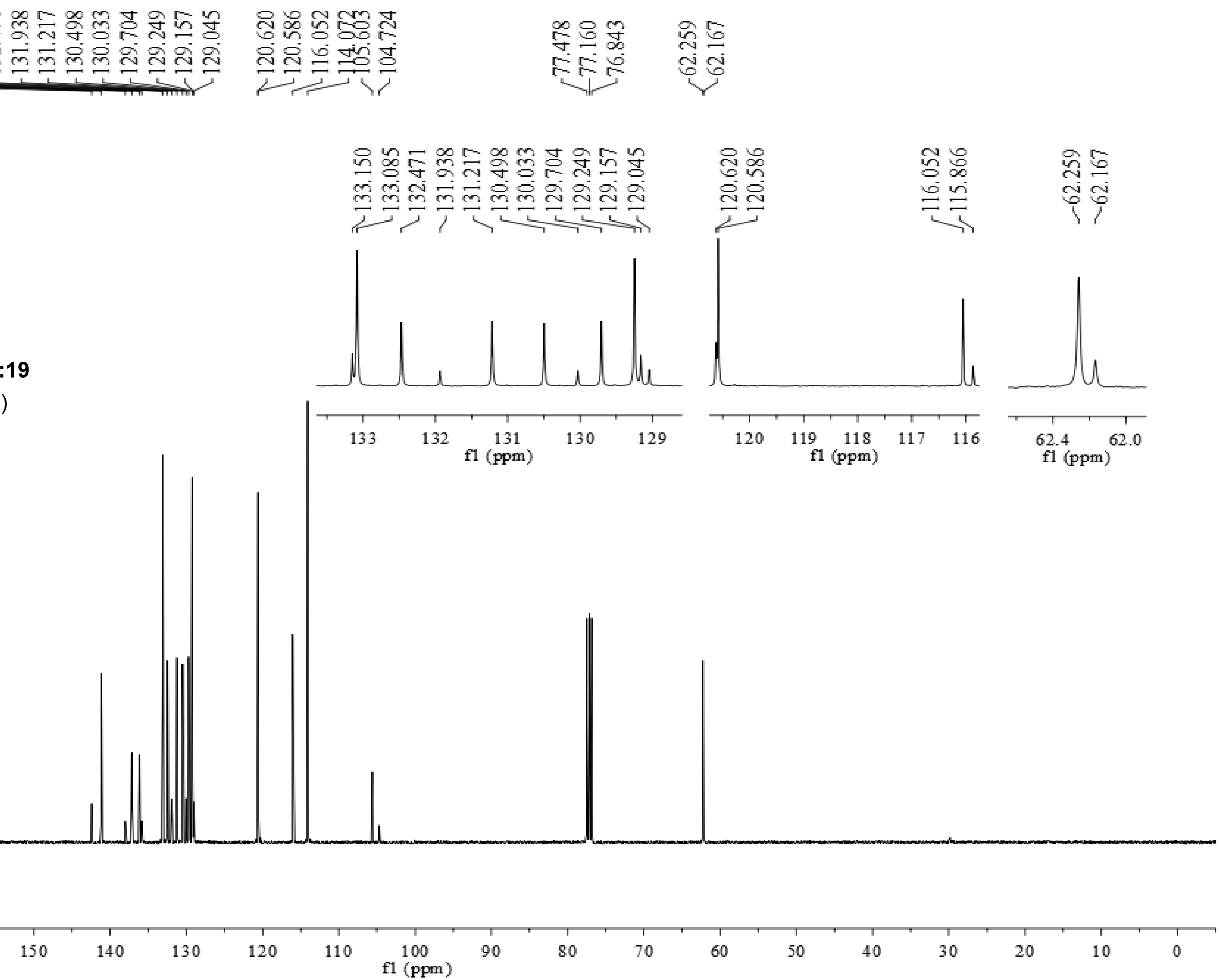


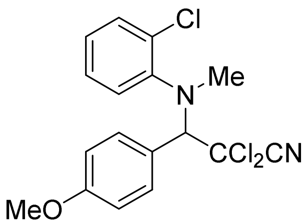




6j, major/minor isomer = 81:19

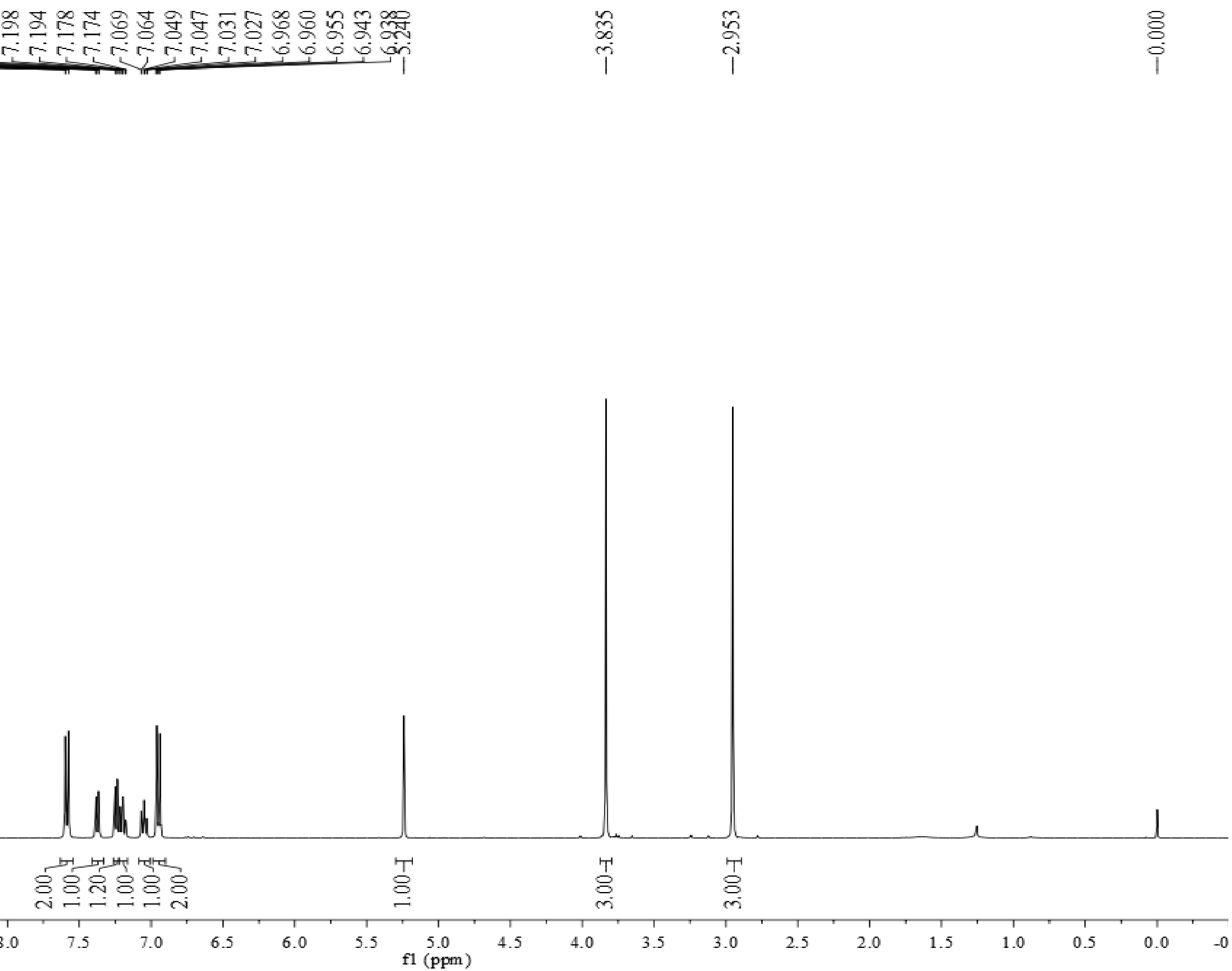
^{13}C NMR (100 MHz, $CDCl_3$)

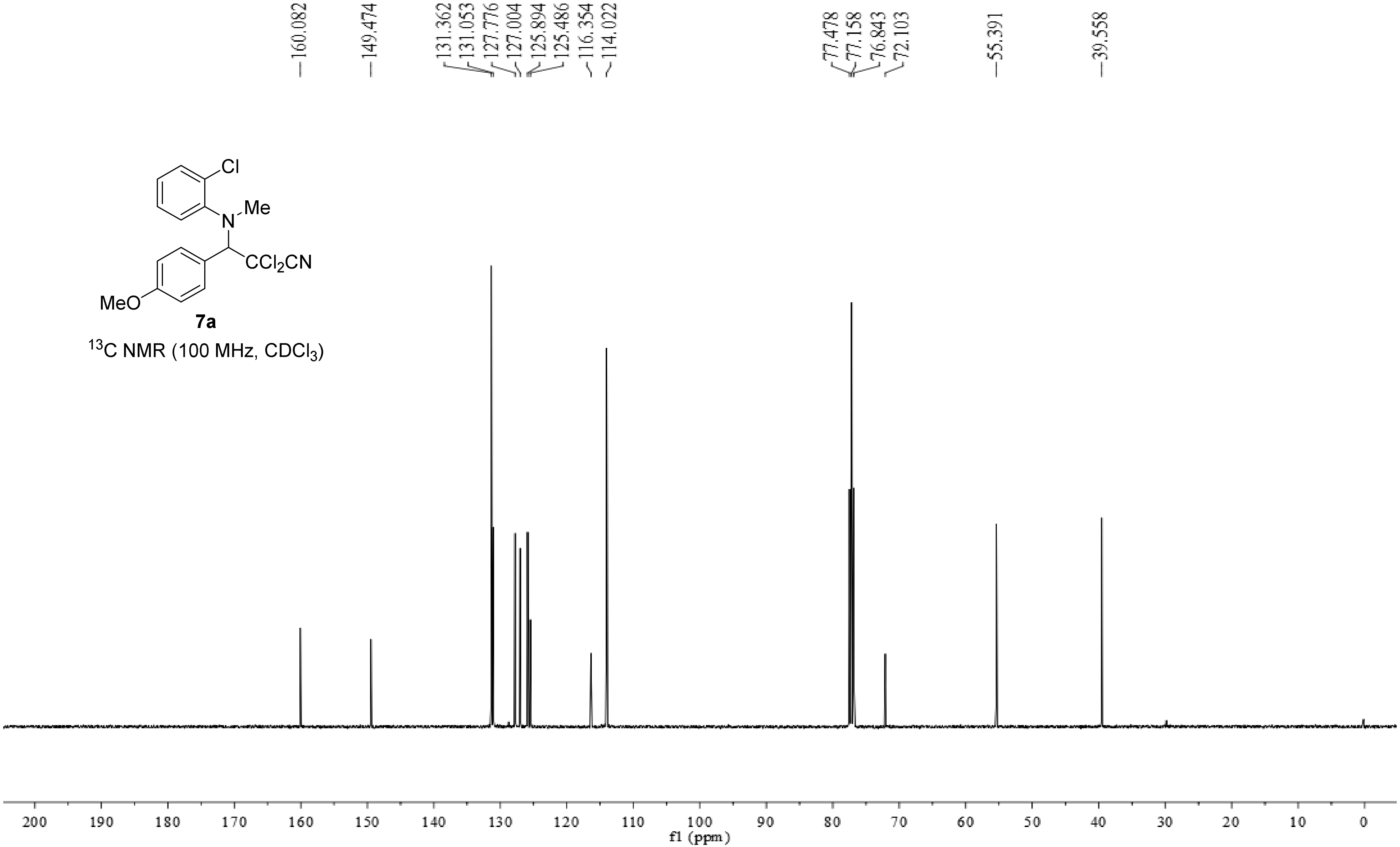




7a

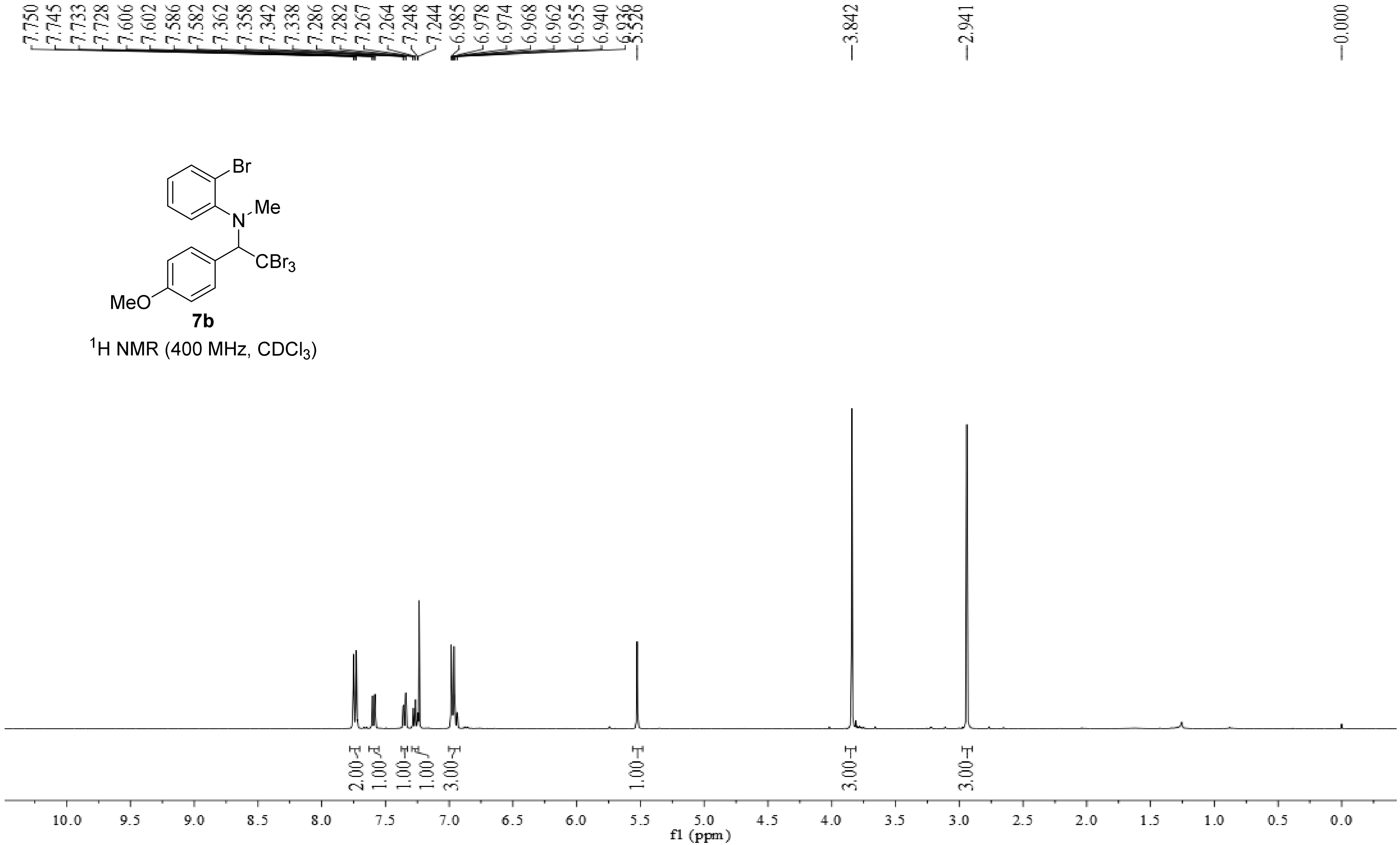
^{1}H NMR (400 MHz, $CDCl_3$)

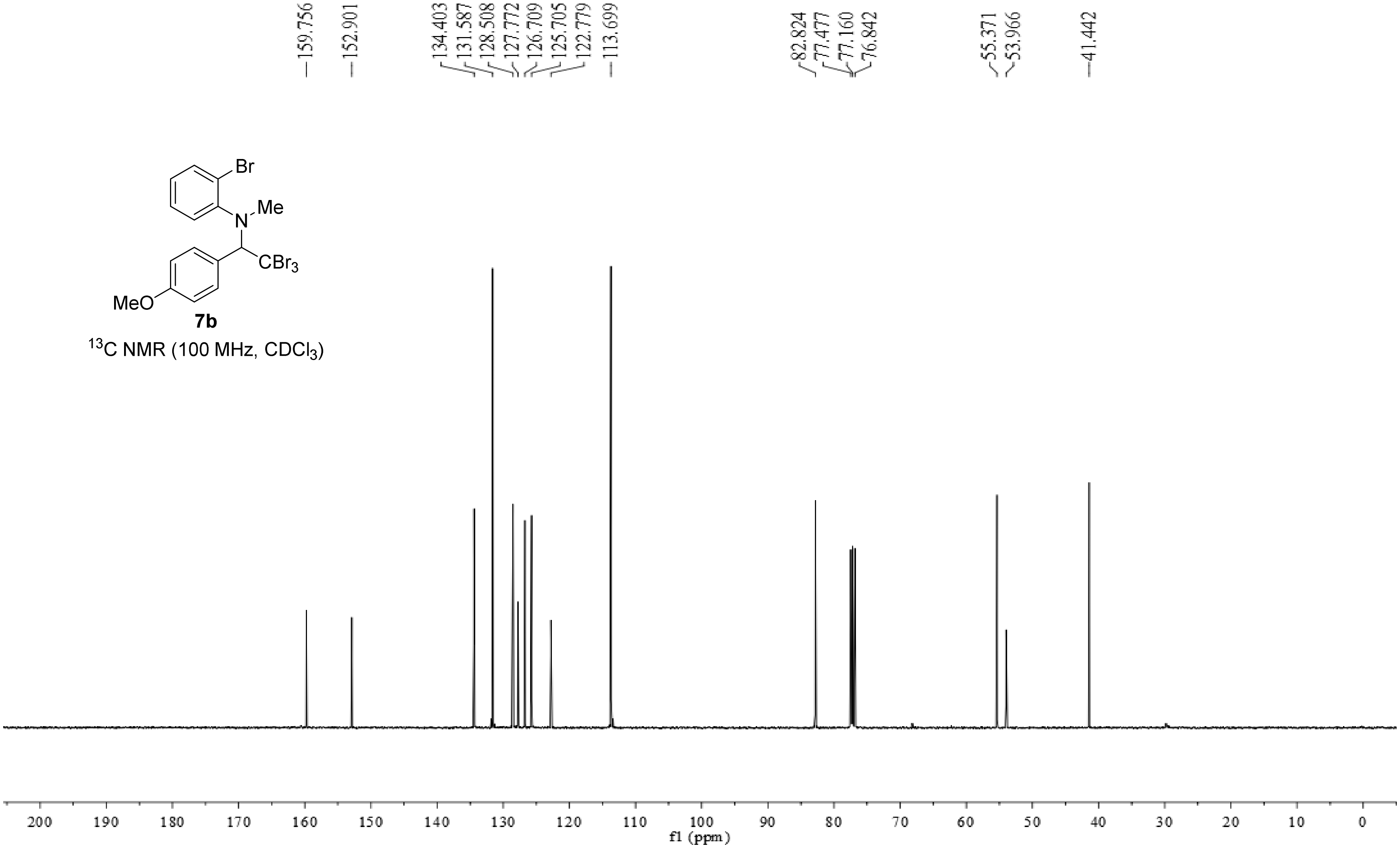




7a

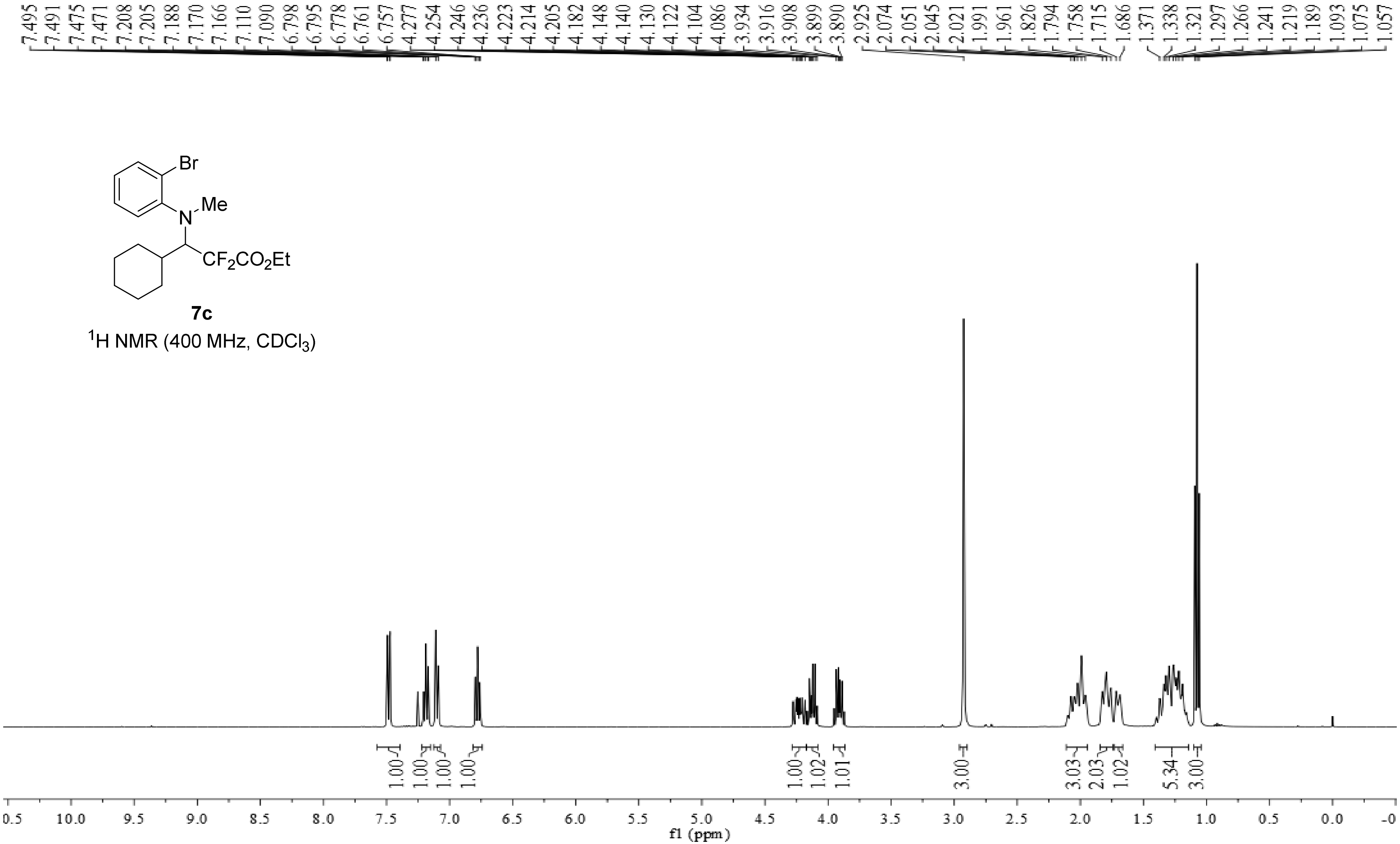
^{13}C NMR (100 MHz, $CDCl_3$)

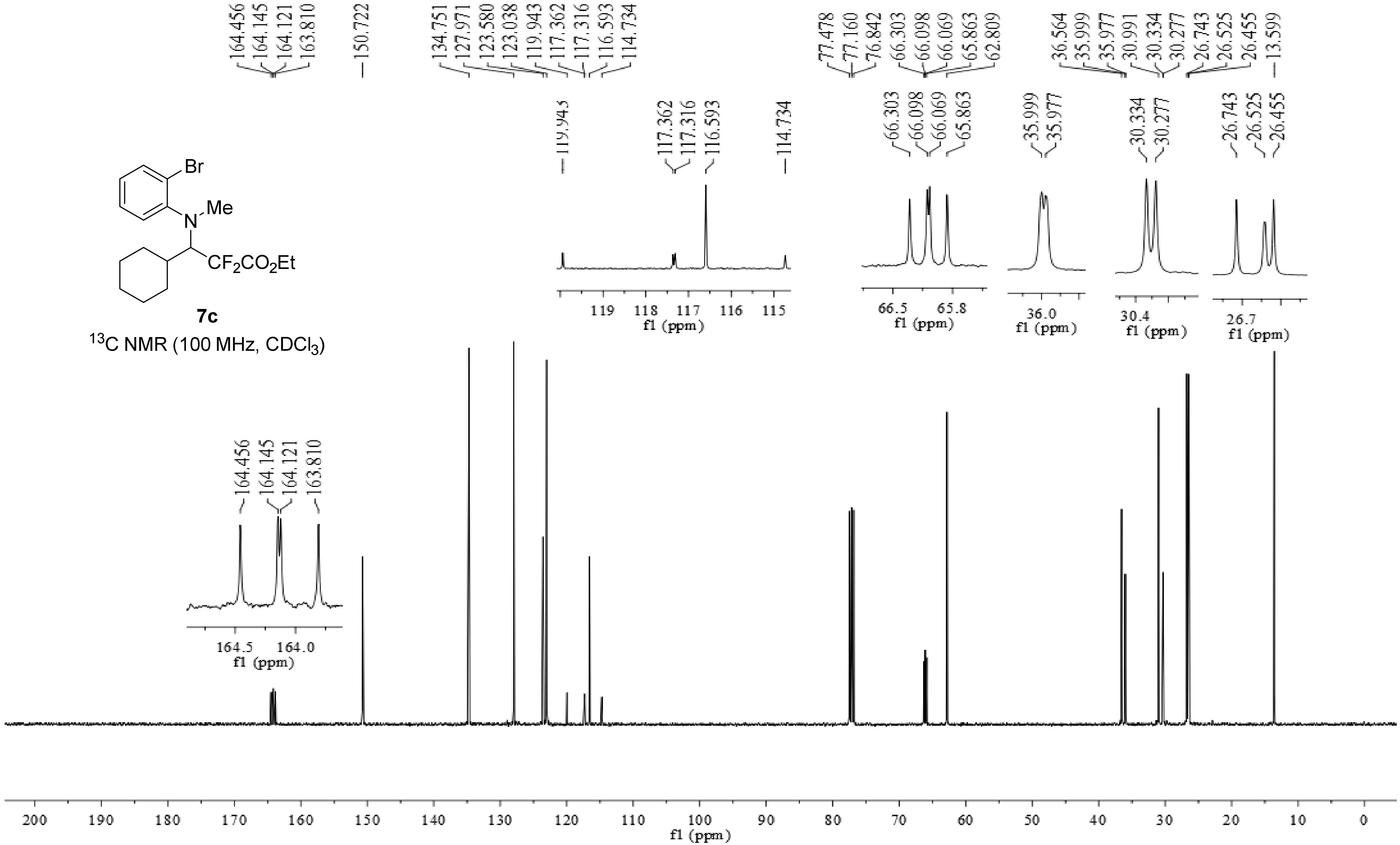

7.750
7.745
7.733
7.728
7.606
7.602
7.586
7.582
7.362
7.358
7.342
7.338
7.286
7.282
7.267
7.264
7.248
7.244
6.985
6.978
6.974
6.968
6.962
6.955
6.940
6.936
5.528
3.842
2.941
0.000
Br
N
Me
CBr3
MeO
7b
1H NMR (400 MHz, CDCl3)
2.00
1.00
1.00
1.00
3.00
1.00
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



7b

^{13}C NMR (100 MHz, $CDCl_3$)


Br
N
Me
CF2CO2Et
7c
1H NMR (400 MHz, CDCl3)
7.495
7.491
7.475
7.471
7.208
7.205
7.188
7.170
7.166
7.110
7.090
6.798
6.795
6.778
6.761
6.757
4.277
4.254
4.246
4.236
4.223
4.214
4.205
4.182
4.148
4.140
4.130
4.122
4.104
4.086
3.934
3.916
3.908
3.899
3.890
2.925
2.074
2.051
2.045
2.021
1.991
1.961
1.826
1.794
1.758
1.715
1.686
1.371
1.338
1.321
1.297
1.266
1.241
1.219
1.189
1.093
1.075
1.057
1.00
1.00
1.00
1.00
1.00
1.02
1.01
3.00
3.03
2.03
1.02
5.34
3.00
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

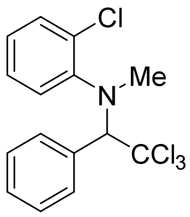


7c

^{13}C NMR (100 MHz, $CDCl_3$)

Crystal Data

The crystal of **4b** was obtained by leaving alone its solution in hexane and chloroform at room temperature in the open air for three days. The structure of compound **4b** was assigned by single crystal X-ray analysis. The crystal data of compound **4b** have been deposited in CCDC with number 1840926.



4b

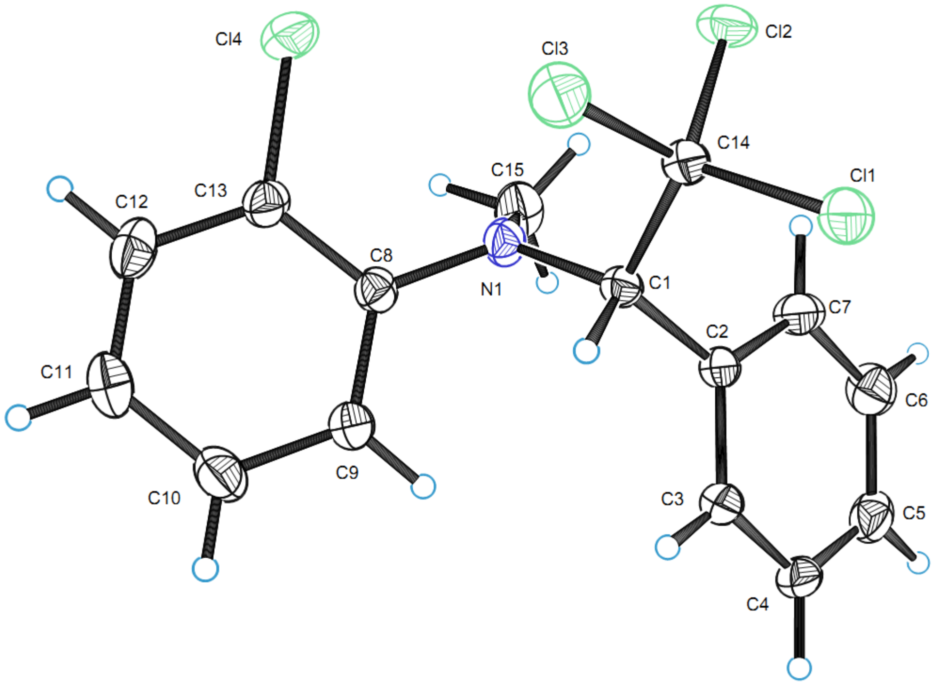


Table S2. Crystal Data and Structure Refinement for 4b

Empirical formula	$C_{15}H_{13}Cl_4N$
Formula weight	349.06
Temperature/K	292(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.6075(5)
b/Å	10.8080(6)
c/Å	12.8051(5)
α/°	90
β/°	103.278(4)
γ/°	90
Volume/Å^3	1563.50(13)

Z	4
ρ_{calc}/g cm^{-3}	1.483
μ/mm^{-1}	0.745
F(000)	712.0
Crystal size/mm^3	0.310 × 0.250 × 0.210
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.214 to 59.08
Index ranges	−15 ≤ h ≤ 11, −14 ≤ k ≤ 10, −16 ≤ l ≤ 16
Reflections collected	7774
Independent reflections	3670 [R_{int} = 0.0257, R_{sigma} = 0.0374]
Data/restraints/parameters	3670/0/182
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ(I)]	R_1 = 0.0400, wR_2 = 0.0914
Final R indexes [all data]	R_1 = 0.0627, wR_2 = 0.1046
Largest diff. peak/hole /e Å^{-3}	0.24/−0.31

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4b[a]

Atom	*x*	*y*	*z*	U(eq)
Cl2	9155.6(5)	3718.4(6)	6772.3(4)	57.55(18)
Cl1	9403.1(4)	2415.5(6)	4875.2(4)	59.16(19)
Cl3	8330.0(5)	1231.8(6)	6422.3(5)	65.05(19)
Cl4	6158.7(5)	2381.5(7)	8012.3(4)	69.7(2)
N1	6446.6(13)	3268.0(16)	5871.5(12)	41.3(4)
C1	7210.3(14)	3064.6(18)	5131.6(13)	35.5(4)
C2	7205.3(15)	4080.9(19)	4306.0(14)	36.9(4)
C8	5499.5(15)	2424.0(18)	5836.3(15)	38.1(4)
C3	6570.8(16)	3873(2)	3268.9(14)	44.5(5)
C13	5265.5(16)	1962(2)	6782.0(15)	45.1(5)
C14	8461.1(16)	2656.1(19)	5771.0(15)	41.3(5)
C9	4762.5(16)	2043(2)	4878.5(16)	47.1(5)
C4	6470.4(17)	4784(2)	2485.8(16)	55.3(6)
C7	7762.4(19)	5215(2)	4538.5(16)	52.4(5)
C12	4325.9(19)	1164(2)	6766.2(18)	55.5(6)
C10	3845.8(18)	1221(2)	4860.7(19)	58.4(6)
C11	3627.6(18)	789(2)	5806.5(19)	59.4(6)
C5	7015.5(18)	5905(2)	2738.1(18)	58.9(6)
C6	7658(2)	6115(2)	3756.3(19)	59.1(6)
C15	6269(2)	4514(2)	6236.6(19)	58.8(6)

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor.

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for 4b[a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl2	52.6(3)	72.4(4)	40.0(3)	−8.7(2)	−5.2(2)	−4.8(3)
Cl1	40.2(3)	90.0(5)	49.4(3)	−6.7(3)	14.6(2)	7.2(3)
Cl3	56.5(3)	59.9(4)	75.9(4)	23.7(3)	9.3(3)	4.1(3)
Cl4	62.5(3)	109.1(6)	38.2(3)	4.6(3)	12.9(2)	−2.2(4)
N1	40.1(8)	45.3(10)	42.0(8)	−5.6(7)	16.8(7)	−4.0(8)
C1	32.3(8)	41.6(11)	32.1(9)	−4.8(8)	6.4(7)	−2.9(8)
C2	31.6(8)	46.3(11)	33.3(9)	−0.7(8)	8.2(7)	0.2(8)
C8	32.7(8)	42.2(11)	40.7(10)	1.7(8)	10.9(8)	2.5(8)
C3	35.4(9)	62.6(14)	35.4(9)	−2.9(10)	8.0(8)	−4.2(9)
C13	38.9(9)	57.5(13)	41(1)	4(1)	13.1(8)	5(1)
C14	37.5(9)	50.5(12)	35.6(10)	0.0(9)	7.9(8)	−1.0(9)
C9	38.4(10)	60.1(14)	43.5(11)	1.2(10)	10.9(8)	−3.6(10)
C4	38.6(10)	92.5(19)	33.4(10)	9.3(11)	5.3(8)	0.6(12)
C7	59.5(12)	53.1(13)	40.1(10)	2.7(10)	2.2(9)	−10.2(11)
C12	51.7(12)	60.4(15)	62.2(14)	15.2(11)	29.4(11)	7.1(11)
C10	41.1(11)	70.6(16)	62.5(14)	−8.4(12)	9.4(10)	−10.6(11)
C11	44.8(11)	60.3(15)	78.2(16)	−0.3(13)	25.0(11)	−10.3(11)
C5	46.7(11)	78.2(18)	53.9(13)	24.8(13)	16(1)	9.7(12)
C6	62.0(13)	50.0(14)	64.3(14)	8.6(11)	12.7(11)	−5.5(11)
C15	62.6(13)	54.4(14)	66.7(14)	−17.2(11)	29.7(12)	−3.5(11)

[a]The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Table S5. Bond Lengths for 4b

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	C14	1.771(2)	C8	C9	1.387(3)
Cl1	C14	1.7762(19)	C8	C13	1.393(3)
Cl3	C14	1.774(2)	C3	C4	1.391(3)
Cl4	C13	1.736(2)	C13	C12	1.387(3)
N1	C8	1.421(2)	C9	C10	1.382(3)
N1	C1	1.455(2)	C4	C5	1.371(3)
N1	C15	1.456(3)	C7	C6	1.381(3)
C1	C2	1.524(3)	C12	C11	1.369(3)
C1	C14	1.558(2)	C10	C11	1.375(3)
C2	C3	1.381(2)	C5	C6	1.364(3)
C2	C7	1.386(3)			

Table S6. Bond Angles for 4b

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	N1	C1	117.70(15)	C8	C13	Cl4	120.02(16)
C8	N1	C15	115.99(15)	C1	C14	Cl2	114.27(14)
C1	N1	C15	120.08(16)	C1	C14	Cl3	108.83(13)
N1	C1	C2	115.92(15)	Cl2	C14	Cl3	107.23(10)
N1	C1	C14	109.52(14)	C1	C14	Cl1	109.86(12)
C2	C1	C14	115.06(15)	Cl2	C14	Cl1	108.48(10)
C3	C2	C7	118.02(18)	Cl3	C14	Cl1	107.98(11)
C3	C2	C1	117.80(17)	C10	C9	C8	121.4(2)
C7	C2	C1	124.15(16)	C5	C4	C3	119.87(19)
C9	C8	C13	117.28(18)	C6	C7	C2	120.54(19)
C9	C8	N1	122.29(17)	C11	C12	C13	119.9(2)
C13	C8	N1	120.43(17)	C11	C10	C9	120.0(2)
C2	C3	C4	121.1(2)	C12	C11	C10	119.9(2)
C12	C13	C8	121.33(19)	C6	C5	C4	119.6(2)
C12	C13	Cl4	118.65(16)	C5	C6	C7	120.9(2)

Table S7. Torsion Angles for 4b

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C8	N1	C1	C2	116.70(18)	C2	C1	C14	Cl2	75.23(18)
C15	N1	C1	C2	−34.5(2)	N1	C1	C14	Cl3	62.36(17)
C8	N1	C1	C14	−111.08(18)	C2	C1	C14	Cl3	−164.97(13)
C15	N1	C1	C14	97.7(2)	N1	C1	C14	Cl1	−179.61(13)
N1	C1	C2	C3	−102.83(19)	C2	C1	C14	Cl1	−46.95(19)
C14	C1	C2	C3	127.57(17)	C13	C8	C9	C10	−1.1(3)
N1	C1	C2	C7	74.8(2)	N1	C8	C9	C10	−180.0(2)
C14	C1	C2	C7	−54.8(2)	C2	C3	C4	C5	0.6(3)
C1	N1	C8	C9	−45.5(2)	C3	C2	C7	C6	1.4(3)
C15	N1	C8	C9	106.9(2)	C1	C2	C7	C6	−176.23(19)
C1	N1	C8	C13	135.65(18)	C8	C13	C12	C11	1.9(3)
C15	N1	C8	C13	−72.0(2)	Cl4	C13	C12	C11	−178.08(17)
C7	C2	C3	C4	−1.4(3)	C8	C9	C10	C11	1.8(3)
C1	C2	C3	C4	176.38(17)	C13	C12	C11	C10	−1.2(4)
C9	C8	C13	C12	−0.7(3)	C9	C10	C11	C12	−0.6(4)
N1	C8	C13	C12	178.21(19)	C3	C4	C5	C6	0.4(3)
C9	C8	C13	Cl4	179.24(15)	C4	C5	C6	C7	−0.4(3)
N1	C8	C13	Cl4	−1.8(3)	C2	C7	C6	C5	−0.6(3)
N1	C1	C14	Cl2	−57.44(19)					

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4b

Atom	*x*	*y*	*z*	U(eq)
H1	6881	2336	4712	43
H3	6205	3112	3091	53
H9	4888	2346	4234	57
H4	6034	4633	1792	66
H7	8210	5371	5227	63
H12	4170	885	7407	67
H10	3376	961	4208	70
H11	3006	242	5794	71
H5	6948	6519	2219	71
H6	8032	6874	3926	71
H15A	7018	4860	6593	88
H15B	5755	4484	6726	88
H15C	5917	5020	5631	88

Cartesian Coordinates for the Stationary Points

acetonitrile (MeCN)

N	1.434912	0.000018	-0.000045
C	0.278026	-0.000035	0.000106
C	-1.180397	0.000032	-0.000023
H	-1.543266	-0.348874	-0.968668
H	-1.543449	1.013279	0.182159
H	-1.543446	-0.664513	0.786322

benzyne

C	0.623355	-1.232024	0.000008
C	-0.623344	-1.232020	0.000051
C	-1.467471	-0.132172	0.000054
C	-0.703989	1.052276	0.000000
C	0.703980	1.052278	-0.000049
C	1.467471	-0.132164	-0.000048
H	-2.550983	-0.133084	0.000090
H	-1.227876	2.004550	-0.000005
H	1.227874	2.004547	-0.000090
H	2.550983	-0.133053	-0.000086

carbon tetrachloride

Cl	-0.272605	1.741186	-0.209483
Cl	-0.901501	-0.573415	1.417351
Cl	-0.559398	-0.864429	-1.445552
Cl	1.733447	-0.303348	0.237677
C	0.000160	0.000014	0.000019

1b

N	2.296776	-0.438810	0.000286
C	3.690118	-0.032311	-0.000379
C	1.417322	0.478126	0.000303
C	-0.034700	0.200839	0.000211
C	-0.539453	-1.107247	0.000148
C	-1.913324	-1.325317	-0.000109
C	-2.798177	-0.242025	-0.000162
C	-2.302415	1.061068	-0.000114
C	-0.924783	1.280322	-0.000017
H	4.185973	-0.454997	0.879144
H	3.822005	1.058231	0.000552
H	4.184648	-0.453290	-0.881494
H	1.697676	1.542090	0.000433
H	0.152470	-1.944145	0.000426
H	-2.299150	-2.340439	0.000010
H	-3.870014	-0.416745	-0.000458
H	-2.985227	1.905341	-0.000072
H	-0.533341	2.294896	0.000175

4b

Cl	-0.939538	-2.439478	0.937984
Cl	0.750057	-2.059516	-1.374612
Cl	-2.124095	-1.782539	-1.639543
Cl	3.106704	-1.043960	1.412569
N	0.529833	0.263262	0.622950
C	-0.735163	-1.481644	-0.553242
C	0.252333	0.621528	2.013682
C	-0.582767	0.053102	-0.287787
C	-1.886028	0.767424	0.054504
C	-2.729748	0.412944	1.114893
C	-3.896643	1.134789	1.362138
C	-4.239204	2.223353	0.559751
C	-3.407261	2.584012	-0.498358
C	-2.243440	1.857206	-0.747706
C	1.690378	0.880307	0.088366
C	2.962201	0.373454	0.400601
C	4.125254	0.962095	-0.087344
C	4.035894	2.074860	-0.921150
C	2.785322	2.595898	-1.249095
C	1.629853	2.009367	-0.738611
H	-0.396521	-0.120445	2.481903
H	-0.211020	1.614434	2.102359
H	1.195024	0.629106	2.563678
H	-0.290101	0.425881	-1.273632
H	-2.494223	-0.427451	1.758017
H	-4.538662	0.842622	2.187670
H	-5.148729	2.782611	0.757362
H	-3.663263	3.425063	-1.135580
H	-1.607147	2.137232	-1.583721
H	5.090315	0.540079	0.174048
H	4.942243	2.528355	-1.309209
H	2.706540	3.468135	-1.890407
H	0.657653	2.432733	-0.975763

A

N	0.717674	1.640959	-0.060273
C	1.484159	2.891812	-0.077958
C	-0.570433	1.658884	-0.055457
C	-1.512446	0.540776	-0.088894
C	-1.223958	-0.769249	-0.515184
C	-2.234535	-1.723355	-0.534312
C	-3.528725	-1.397173	-0.120281
C	-3.824635	-0.099253	0.293873
C	-2.825001	0.867953	0.293373
C	1.533048	0.417901	-0.015305
C	2.231181	0.061886	-1.171775
C	2.944411	-1.149005	-0.984869
C	2.956815	-1.884669	0.206224
C	2.243949	-1.431911	1.320668
C	1.516302	-0.250096	1.213032
H	2.082773	2.937539	0.834480
H	0.807822	3.743562	-0.140483
H	2.146884	2.863676	-0.944571
H	-1.020823	2.649248	-0.016165
H	-0.229381	-1.039068	-0.848493
H	-2.010762	-2.729374	-0.874394
H	-4.307138	-2.154249	-0.131592
H	-4.830940	0.162470	0.604238
H	-3.053665	1.886453	0.594974
H	3.527490	-1.553897	-1.814319
H	3.526611	-2.809352	0.272398
H	2.255586	-1.986085	2.254503

H	0.941033	0.135351	2.052528

B

Cl	3.661312	-1.878934	-0.903144
Cl	2.707927	-0.520637	1.478378
Cl	2.545856	0.793014	-1.101224
Cl	0.800105	-1.457693	-0.497400
N	-1.621593	-0.596368	1.550789
C	2.425875	-0.769177	-0.263613
C	-1.632622	-1.652247	2.568908
C	-0.844602	0.425177	1.672328
C	-0.589006	1.525280	0.743988
C	-0.967994	1.581447	-0.611789
C	-0.593371	2.672400	-1.385955
C	0.155348	3.715138	-0.833256
C	0.546096	3.662777	0.503752
C	0.183913	2.569325	1.283276
C	-2.546799	-0.809749	0.428761
C	-2.252975	-1.837297	-0.471336
C	-3.208742	-1.890889	-1.517154
C	-4.315454	-1.039827	-1.621288
C	-4.545568	-0.061657	-0.648350
C	-3.643548	0.057808	0.404447
H	-2.636759	-1.708845	2.995000
H	-0.895554	-1.436569	3.341903
H	-1.398404	-2.594370	2.069247
H	-0.276318	0.464889	2.600087
H	-1.530467	0.777018	-1.068646
H	-0.881460	2.706280	-2.431813
H	0.439155	4.563218	-1.449325
H	1.136788	4.463873	0.936019
H	0.499257	2.515481	2.321999
H	-3.093414	-2.640337	-2.302655
H	-5.007377	-1.141413	-2.455025
H	-5.409175	0.594016	-0.708174
H	-3.776826	0.812536	1.177176

C

Cl	4.706043	-1.409317	-0.393754
Cl	2.375756	-0.786875	1.305235
Cl	2.778699	0.653312	-1.240604
Cl	-0.216029	-1.581069	-0.983276
N	-1.424854	-0.561217	1.544285
C	2.861652	-1.061668	-0.494511
C	-1.260762	-1.656418	2.516076
C	-0.729012	0.527009	1.641966
C	-0.686087	1.698880	0.785573
C	-1.481518	1.953532	-0.350917
C	-1.289623	3.123766	-1.072749
C	-0.317699	4.050085	-0.682880
C	0.467648	3.812424	0.443996
C	0.282282	2.645204	1.174119
C	-2.367017	-0.835667	0.488566
C	-1.917511	-1.347953	-0.729008
C	-2.832763	-1.624545	-1.739924
C	-4.189335	-1.393309	-1.518614
C	-4.636102	-0.893221	-0.295293
C	-3.721720	-0.617936	0.717938
H	-2.233885	-1.871397	2.961068
H	-0.547271	-1.355910	3.281451
H	-0.897873	-2.536459	1.979203
H	-0.068752	0.557360	2.505575
H	-2.249839	1.264995	-0.676905
H	-1.903444	3.316624	-1.946354
H	-0.177550	4.959358	-1.259544
H	1.220973	4.529856	0.751582
H	0.893919	2.448692	2.050340
H	-2.480405	-2.012558	-2.689923
H	-4.899076	-1.607360	-2.311088
H	-5.693166	-0.716319	-0.128464
H	-4.040239	-0.222361	1.677804

D

N	-0.508350	0.258377	-0.079296
C	0.339521	-0.737780	0.135954
C	1.732194	-0.535125	0.106213
C	2.633623	-1.607531	0.342226
C	3.984917	-1.371054	0.310480
C	4.480678	-0.067000	0.046978
C	3.625965	0.985710	-0.181666
C	2.225763	0.772046	-0.155203
C	1.277228	1.804491	-0.382949
C	-0.056330	1.530839	-0.343865
C	-1.957918	-0.014583	-0.059211
C	-2.411124	-1.144128	-0.745704
C	-3.816364	-1.286872	-0.641255
C	-4.650982	-0.405738	0.054822
C	-4.105545	0.695492	0.720587
C	-2.729796	0.899209	0.668601
H	-0.099494	-1.708064	0.338819
H	2.236571	-2.598498	0.541305
H	4.684471	-2.181633	0.486355
H	5.553742	0.096725	0.026991
H	4.005017	1.983087	-0.382935
H	1.607491	2.813908	-0.603400
H	-0.821733	2.270929	-0.535651
H	-4.300026	-2.130501	-1.137181
H	-5.725346	-0.574968	0.084743
H	-4.736481	1.379171	1.280557
H	-2.276744	1.733348	1.199426

E

N	0.748618	1.724545	-0.050999
C	1.475078	2.816561	-0.271608
C	-0.593853	1.715680	0.153391
C	-1.503824	0.609356	-0.017167
C	-1.235084	-0.624375	-0.659612
C	-2.217910	-1.605858	-0.772459
C	-3.505633	-1.404079	-0.273822
C	-3.799068	-0.182172	0.340988
C	-2.824073	0.798251	0.466375
C	1.500568	0.486014	0.068179
C	2.313354	0.079389	-0.983593
C	3.024692	-1.114508	-0.861316

C	2.921085	-1.875624	0.302869
C	2.110607	-1.441354	1.354524
C	1.392185	-0.253665	1.241418
H	2.548466	2.749063	-0.179053
H	0.957040	3.753860	-0.425334
H	-1.012203	2.694808	0.355483
H	-0.261735	-0.817834	-1.096138
H	-1.971054	-2.538460	-1.273241
H	-4.264858	-2.173830	-0.370190
H	-4.796325	0.006570	0.729582
H	-3.070503	1.739534	0.952263
H	2.364428	0.676920	-1.888712
H	3.652955	-1.450792	-1.680106
H	3.473579	-2.805760	0.393350
H	2.039054	-2.026906	2.265661
H	0.752082	0.099319	2.044425

F

N	-1.500140	2.961374	0.733015
N	0.870714	1.156838	-1.035087
C	-1.724784	2.062820	1.427499
C	-2.000651	0.919707	2.289667
C	1.432716	2.434496	-1.484191
C	-0.366897	0.874017	-1.250003
C	-1.160157	-0.278954	-0.825699
C	-0.719541	-1.379494	-0.064737
C	-1.625087	-2.367396	0.307013
C	-2.969449	-2.278112	-0.060621
C	-3.416112	-1.193039	-0.814414
C	-2.517032	-0.202800	-1.193979
C	1.806062	0.301042	-0.291914
C	1.950556	0.544527	1.075946
C	2.861566	-0.368781	1.663539
C	3.534565	-1.376222	0.961056
C	3.341596	-1.524999	-0.415622
C	2.460755	-0.662491	-1.063769
H	-1.056895	0.435459	2.553048
H	-2.639475	0.210297	1.755832
H	-2.505965	1.259180	3.196235
H	1.778409	2.973717	-0.598926
H	0.673339	3.012067	-2.010226
H	2.282521	2.226719	-2.137952
H	-0.915497	1.625162	-1.815273
H	0.313071	-1.472548	0.243250
H	-1.277680	-3.211555	0.894015
H	-3.666247	-3.054385	0.240947
H	-4.459247	-1.116104	-1.103313
H	-2.866128	0.647846	-1.773326
H	3.064498	-0.301072	2.734061
H	4.216078	-2.045145	1.482819
H	3.865012	-2.296023	-0.973230
H	2.271553	-0.747042	-2.132085

G

N	-1.180728	2.723329	0.674153
N	0.870753	1.098938	-1.119539
C	-1.517349	2.001047	1.555941
C	-1.886893	1.119219	2.537834
C	1.512705	2.330520	-1.601621
C	-0.411119	0.935685	-1.244156
C	-1.240781	-0.197125	-0.851241
C	-0.784144	-1.476242	-0.485021
C	-1.702210	-2.471909	-0.166668
C	-3.072865	-2.208951	-0.194457
C	-3.534814	-0.944101	-0.559260
C	-2.624375	0.050558	-0.895171
C	1.728245	0.233467	-0.346468
C	1.579146	0.204614	1.037521
C	2.411496	-0.628697	1.782382
C	3.379727	-1.405185	1.143898
C	3.526925	-1.345975	-0.242976
C	2.701368	-0.516088	-1.000035
H	-2.938132	0.915840	2.704597
H	-1.163039	0.822734	3.288119
H	1.844336	2.903956	-0.732026
H	0.797864	2.907173	-2.186546
H	2.374371	2.062352	-2.215043
H	-0.924188	1.735849	-1.767884
H	0.271717	-1.716108	-0.471756
H	-1.343140	-3.459669	0.103624
H	-3.779340	-2.992110	0.063402
H	-4.599232	-0.735034	-0.587892
H	-2.976151	1.036928	-1.184578
H	0.813061	0.812338	1.509997
H	2.301463	-0.669523	2.861401
H	4.023731	-2.054726	1.728548
H	4.282460	-1.947325	-0.738383
H	2.793675	-0.463562	-2.080897

TS1

N	0.101728	1.870321	-0.193231
C	0.811141	3.108932	0.071307
C	-1.093719	1.761036	0.227776
C	-1.914298	0.554189	0.013635
C	-1.526108	-0.457111	-0.876784
C	-2.327384	-1.581655	-1.047659
C	-3.521966	-1.708616	-0.332281
C	-3.917542	-0.702660	0.549247
C	-3.118220	0.427331	0.717069
C	1.746920	0.033951	0.085221
C	1.571956	-0.900858	0.912691
C	2.635324	-1.808756	1.073618
C	3.766294	-1.554706	0.280218
C	3.825495	-0.466788	-0.610322
C	2.751865	0.434380	-0.756360
H	1.708912	2.890742	0.658996
H	0.198434	3.843594	0.609873
H	1.140390	3.542049	-0.878527
H	-1.575281	2.574439	0.789219
H	-0.601243	-0.348575	-1.435045
H	-2.024301	-2.360755	-1.740643
H	-4.144602	-2.587960	-0.468051
H	-4.847298	-0.795842	1.102125
H	-3.423413	1.217419	1.398928

H	2.613880	-2.656048	1.753378
H	4.623733	-2.218720	0.352505
H	4.720628	-0.308993	-1.205898
H	2.759520	1.284386	-1.428494

TS2

Cl	3.600562	-2.056653	-0.673340
Cl	2.841536	-0.281379	1.501144
Cl	2.726012	0.655951	-1.244835
Cl	0.725447	-1.328250	-0.295624
N	-1.699728	-0.382897	1.632001
C	2.486085	-0.755022	-0.182106
C	-1.710490	-1.303866	2.773659
C	-1.030172	0.716759	1.681441
C	-0.815031	1.738520	0.660739
C	-1.257854	1.707020	-0.676738
C	-0.929437	2.750248	-1.533962
C	-0.163346	3.829578	-1.084804
C	0.282982	3.868261	0.235027
C	-0.039170	2.827551	1.099431
C	-2.440719	-0.860127	0.457290
C	-1.770356	-1.719025	-0.410971
C	-2.562081	-2.097779	-1.515902
C	-3.882620	-1.670051	-1.701812
C	-4.489995	-0.826452	-0.766505
C	-3.758370	-0.412666	0.344856
H	-2.746576	-1.456543	3.083356
H	-1.121226	-0.889807	3.591080
H	-1.288428	-2.254422	2.439363
H	-0.534900	0.906882	2.632592
H	-1.841144	0.878477	-1.055918
H	-1.270525	2.718576	-2.563708
H	0.086124	4.636963	-1.766691
H	0.881902	4.700747	0.589559
H	0.313397	2.848810	2.126898
H	-2.138778	-2.754710	-2.277880
H	-4.443731	-1.993654	-2.575991
H	-5.515315	-0.494913	-0.900275
H	-4.189733	0.251795	1.090869

TS3

N	0.710563	1.584560	0.084192
C	1.582522	2.678122	-0.242394
C	-0.584283	1.693308	0.148655
C	-1.575245	0.626556	-0.019824
C	-1.384187	-0.471727	-0.875031
C	-2.392367	-1.416964	-1.028267
C	-3.598374	-1.282412	-0.334359
C	-3.803176	-0.182273	0.498312
C	-2.802186	0.775298	0.643636
C	1.476241	0.338228	0.135101
C	2.603139	0.375548	-0.679864
C	3.427770	-0.759338	-0.619490
C	3.107641	-1.849632	0.196328
C	1.971182	-1.815124	1.015155
C	1.138182	-0.699722	1.001776
H	2.219385	2.939965	0.606942
H	1.025720	3.520002	-0.650347
H	2.418023	1.793670	-0.930856
H	-0.960200	2.702412	0.296569
H	-0.456736	-0.575891	-1.429361
H	-2.240670	-2.258906	-1.696646
H	-4.379870	-2.026521	-0.455028
H	-4.743744	-0.064199	1.027281
H	-2.962722	1.642049	1.279443
H	4.335241	-0.812557	-1.219298
H	3.750561	-2.726508	0.212325
H	1.747923	-2.647505	1.675652
H	0.271998	-0.637137	1.655571

TS4

N	-1.349939	3.224395	0.685605
N	0.748586	1.048062	-1.114488
C	-1.220348	2.336389	1.433427
C	-0.919902	1.202889	2.244736
C	1.365860	2.282966	-1.617265
C	-0.516037	0.842299	-1.260194
C	-1.322984	-0.288286	-0.809617
C	-0.843549	-1.571698	-0.491776
C	-1.733914	-2.550398	-0.066388
C	-3.096039	-2.263860	0.061490
C	-3.580360	-0.998312	-0.267192
C	-2.699276	-0.020576	-0.717704
C	1.644384	0.178415	-0.347609
C	1.460669	0.125242	1.033833
C	2.367673	-0.730954	1.686411
C	3.359623	-1.452478	1.013269
C	3.491031	-1.338077	-0.373490
C	2.623683	-0.501106	-1.073459
H	0.211620	0.714634	1.711681
H	-1.710623	0.449649	2.184767
H	-0.728814	1.492195	3.281062
H	1.754194	2.836041	-0.758600
H	0.625678	2.876698	-2.152041
H	2.189891	2.015602	-2.281158
H	-1.061384	1.635142	-1.768060
H	0.207638	-1.813748	-0.589941
H	-1.363377	-3.542778	0.169473
H	-3.779585	-3.033443	0.407265
H	-4.638930	-0.775650	-0.181904
H	-3.068730	0.965600	-0.986381
H	2.300452	-0.849160	2.769158
H	4.033842	-2.103726	1.564783
H	4.258156	-1.892877	-0.905159
H	2.696362	-0.396105	-2.153610

TS5

Cl	2.613407	2.024606	-1.348475
Cl	2.325190	0.520276	1.119087
Cl	1.921092	3.400080	1.117539
Cl	-0.101511	1.623652	-0.187443
N	-1.694111	-1.208637	0.102511
C	1.701175	1.901617	0.178235
C	-0.783050	-1.311350	-0.854377

C	0.390815	-2.064152	-0.669411
C	1.386534	-2.122984	-1.680309
C	2.539484	-2.830525	-1.448132
C	2.732425	-3.503344	-0.213072
C	1.777769	-3.463516	0.776592
C	0.580903	-2.735308	0.568584
C	-0.438553	-2.618209	1.551587
C	-1.541617	-1.858107	1.306315
C	-2.829599	-0.293602	-0.091613
C	-2.530328	0.996192	-0.528397
C	-3.673647	1.810306	-0.661901
C	-4.971611	1.365137	-0.387586
C	-5.189372	0.051750	0.040345
C	-4.099926	-0.801611	0.194742
H	-0.982421	-0.768492	-1.771912
H	1.222430	-1.596261	-2.616106
H	3.312960	-2.878003	-2.207772
H	3.652480	-4.056553	-0.050972
H	1.927847	-3.976418	1.721815
H	-0.332220	-3.110206	2.512421
H	-2.331144	-1.698800	2.029189
H	-3.557462	2.845086	-0.988492
H	-5.817737	2.038515	-0.506194
H	-6.193685	-0.306202	0.245432
H	-4.239730	-1.832401	0.513382

TS6

N	0.722443	1.761450	2.191729
N	-0.509751	-0.679055	-0.005707
C	0.198608	2.335555	1.319872
C	-0.526826	2.904241	0.230388
C	0.319426	-0.046008	-0.826437
C	1.714164	-0.155903	-0.685566
C	2.593599	0.540883	-1.556692
C	3.949149	0.414286	-1.385191
C	4.469365	-0.407146	-0.350533
C	3.635289	-1.091923	0.501955
C	2.231625	-0.978733	0.351530
C	1.303767	-1.639700	1.199196
C	-0.034756	-1.474531	1.012510
C	-1.957032	-0.487849	-0.166532
C	-2.401293	0.816096	-0.372751
C	-3.797095	0.925889	-0.512388
C	-4.655300	-0.176371	-0.459525
C	-4.136789	-1.459184	-0.258584
C	-2.762698	-1.627646	-0.107289
H	-1.429570	1.960284	-0.134617
H	0.134779	3.127036	-0.611364
H	-1.072935	3.798092	0.542116
H	-0.136549	0.551416	-1.608825
H	2.176960	1.164841	-2.341985
H	4.633418	0.942796	-2.040792
H	5.545403	-0.491953	-0.233806
H	4.033366	-1.717898	1.294753
H	1.654286	-2.264647	2.013610
H	-0.786136	-1.924873	1.647905
H	-4.240894	1.910805	-0.663132
H	-5.728273	-0.042697	-0.575244
H	-4.793711	-2.323020	-0.227523
H	-2.338202	-2.618687	0.032968