Three-component carboarylation of unactivated imines with arynes and carbon nucleophiles

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Supporting information

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General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT spectrometer (400 MHz 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 a LC-TOF spectrometer (Micromass). Electrospray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. Matrix assisted laser desorption ionization (MALDI) mass spectra were recorded on a MALDI-TOF spectrometer equipped with a MALDI source.

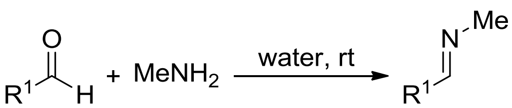
The preparation of imines **1a**, **1b**, **1h**, **1i**, **1n**, and **1u** was shown below, and the rest of imines **1**[1] and 2-(trimethylsilyl)aryl triflates **2b-g**[2] were prepared according to literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, Alfa Aesar, and TCI.

Unless otherwise noted, all the reactions were performed in oven-dried glassware under a nitrogen atmosphere with freshly distilled solvents. Toluene, 1,2-dichloroethane, chloroform, and acetonitrile were dried and distilled from calcium hydride. Tetrahydrofuran was dried and distilled from metal sodium and benzophenone. CsF was dried in vacuum at 130 ^{o}C for 2 h before use.

Abbreviations: TBAF = tetrabutylammonium fluoride, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran, TMS = trimethylsilyl.

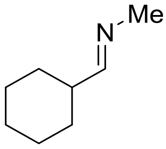
Preparation of imines

(1) Preparation of imines **1a**, **1b**, **1h**, and **1u**



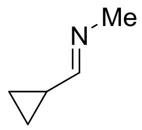
1a, **1b**, **1h**, or **1u**

A flask containing an aldehyde (3.0 mmol) and aqueous solution of methylamine (0.19 mol, 40 wt.%, 15 mL) was stirred at room temperature for 10 h. The mixture was extracted with dichloromethane (10 mL × 3), washed with brine, and dried over potassium hydroxide. After filtration, all volatiles were removed under reduced pressure to give crude imines, which were used in the following three-component reaction without further purification.



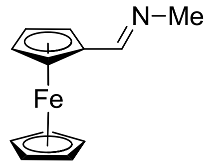
1a

(E)-1-Cyclohexyl-N-methylmethanimine (**1a**). Colorless oil (0.353 g, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 3.7 Hz, 1H), 3.24 (s, 3H), 2.19-2.07 (m, 1H), 1.85-1.62 (m, 5H), 1.34-1.13 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 48.0, 43.5, 29.6, 26.1, 25.6; IR (film): ν 2927, 2848, 1676, 1453, 1401 cm^{-1}; HRMS (ESI) calcd for $C_8H_{16}N^+$ (M+H)$^+$ 126.1277, found 126.1273.



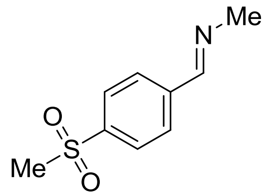
1b

(*E*)-1-Cyclopropyl-*N*-methylmethanimine (**1b**). Colorless oil (0.127 g, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 7.5 Hz, 1H), 3.22 (s, 3H), 1.71-1.59 (m, 1H), 0.90-0.81 (m, 2H), 0.71-0.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 47.6, 16.3, 5.8; IR (film): ν 2973, 2921, 2848, 1670, 1394 cm^{-1}; HRMS (ESI) calcd for $C_5H_{10}N^+$ $(M+H)^+$ 84.0808, found 84.0803.



1h

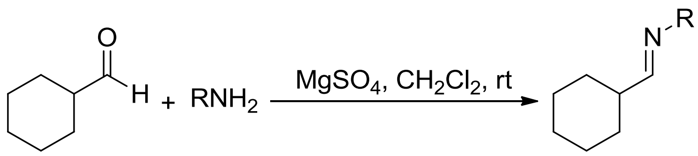
(*E*)-1-Ferrocenyl-*N*-methylmethanimine (**1h**). Red oil (0.627 g, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 4.61 (s, 2H), 4.35 (s, 2H), 4.18 (s, 5H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 80.8, 70.3, 69.1, 68.3, 48.5; IR (film): ν 3097, 2927, 2881, 2770, 1683, 1650, 1460, 1401 cm^{-1}; MS (MALDI) calcd for $C_{12}H_{13}FeN^+$ $(M)^+$ 227.04, found 227.01.



1u

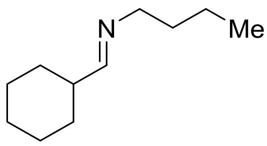
(*E*)-*N*-Methyl-1-(4-(methylsulfonyl)phenyl)methanimine (**1u**). Yellow solid (0.533 g, 90% yield); m.p. 170-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 1.6 Hz, 1H), 7.99 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 3.58 (d, J = 1.6 Hz, 3H), 3.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 141.9, 141.1, 128.7, 127.9, 48.6, 44.6; IR (film): ν 2960, 2926, 2861, 1643, 1453, 1401 cm^{-1}; HRMS (ESI) calcd for $C_9H_{12}NO_2S^+$ $(M+H)^+$ 198.0583, found 198.0575.

(2) Preparation of imines **1i** and **1n**



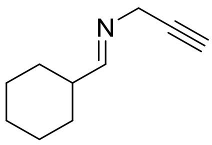
1i or **1n**

A flask containing cyclohexanecarbaldehyde (0.337 g, 3.0 mmol), an amine (6.0 mmol), dichloromethane (20 mL), and magnesium sulfate (1.20 g) was stirred at room temperature for 10 h. After filtration, all volatiles were removed under reduced pressure to give crude imines, which were used in the following three-component reaction without further purification.



1i

(*E*)-*N*-Butyl-1-cyclohexylmethanimine (**1i**). Colorless oil (0.462 g, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 5.1 Hz, 1H), 3.33 (t, J = 7.0 Hz, 2H), 2.23-2.09 (m, 1H), 1.83-1.71 (m, 4H), 1.69-1.63 (m, 1H), 1.61-1.51 (m, 2H), 1.36-1.16 (m, 7H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 61.2, 43.6, 33.0, 29.9, 26.1, 25.6, 20.4, 14.0; IR (film): ν 2926, 2855, 1670, 1453, 1381 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{22}N^+$ $(M+H)^+$ 168.1747, found 168.1742.

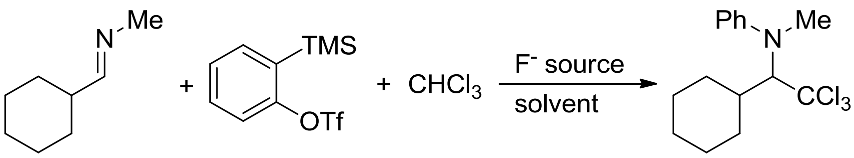


1n

(*E*)-*1*-Cyclohexyl-*N*-(prop-2-yn-1-yl)methanimine (**1n**). Colorless oil (0.394 g, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 1H), 4.27-4.23 (m, 2H), 2.43 (t, J = 2.5 Hz, 1H), 2.28-2.17 (m, 1H), 1.87-1.73 (m, 4H), 1.72-1.64 (m, 1H), 1.37-1.17 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 79.5, 75.0, 47.2, 43.6, 29.6, 26.1, 25.6; IR (film): ν 3313, 2927, 2849, 1670, 1447, 1375 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{16}N^+$ $(M+H)^+$ 150.1277, found 150.1273.

Optimization of the reaction conditions[a]

For the procedure, see below. The results were summarized in the following table.



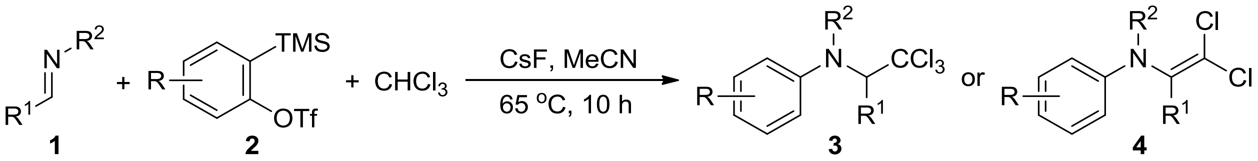
1a **2a** **3a**

Entry	F⁻ source	Solvent	Temperature (°C)	Yield[b] (%)
1	NaF	MeCN	50	0
2	KF	MeCN	50	trace
3	KF/18-crown-6	MeCN	50	37
4	CsF	MeCN	50	45
5	TBAF[c]	MeCN	50	32
6	CsF	toluene	50	0
7	CsF	1,2-dichloroethane	50	0
8	CsF	$CHCl_3$	50	0

9	CsF	THF	50	trace
10	CsF	MeCN	65	68
11	CsF	MeCN	80	61
12[d]	CsF	MeCN	65	77
13[d,e]	CsF	MeCN	65	81

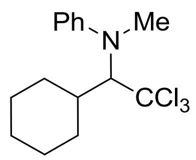
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), chloroform (0.5 mL), F^- source (0.48 mmol), solvent (0.5 mL), 50 °C, 10 h. [b] Isolated yields. [c] 1 M in THF. [d] **2a** (0.30 mmol), F^- source (0.60 mmol). [e] Chloroform (0.3 mL), MeCN (0.3 mL).

General procedure for the three-component reaction of imines, arynes, and chloroform (Schemes 2 and 3)



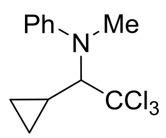
A flask containing dry CsF (91.1 mg, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)aryl triflate **2** (0.30 mmol), imine **1** (0.20 mmol), acetonitrile (0.30 mL), and chloroform (0.30 mL). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:20 to 0:1 v/v), to give amine **3** or enanime **4**.

Analytical data for the products (Schemes 2 and 3)



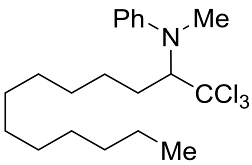
3a

N-Methyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3a**). Colorless oil (52.0 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 2H), 6.84-6.72 (m, 3H), 4.40 (d, J = 9.2 Hz, 1H), 2.97 (s, 3H), 2.38-2.15 (m, 2H), 1.87-1.79 (m, 1H), 1.76-1.61 (m, 3H), 1.39-0.97 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 129.3, 117.7, 112.9, 104.8, 77.0, 40.3, 31.9, 31.5, 31.4, 26.5, 26.2; IR (film): ν 3060, 3031, 2930, 2850, 1605, 1501, 1450, 1371, 816, 747, 687 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}NCl_3^+$ $(M+H)^+$ 320.0734, found 320.0728.



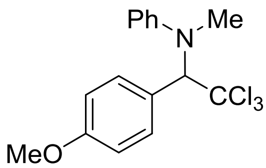
3b

N-Methyl-*N*-(2,2,2-trichloro-1-cyclopropylethyl)aniline (**3b**). Colorless oil (40.7 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.21 (m, 2H), 6.89 (d, J = 8.2 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 3.84 (d, J = 8.7 Hz, 1H), 3.17 (s, 3H), 1.58-1.46 (m, 1H), 1.07-0.94 (m, 1H), 0.83-0.73 (m, 1H), 0.72-0.60 (m, 1H), 0.29-0.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 129.1, 118.1, 113.4, 104.9, 78.5, 33.7, 11.5, 10.1, 2.6; IR (film): ν 3071, 3018, 2927, 2822, 1604, 1505, 1362, 817, 746, 687 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{15}NCl_3^+$ $(M+H)^+$ 278.0265, found 278.0259.



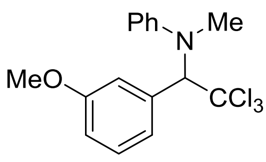
3c

N-Methyl-*N*-(1,1,1-trichlorotridecan-2-yl)aniline (**3c**). Colorless oil (59.7 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 2H), 6.90 (d, J = 8.3 Hz, 2H), 6.79 (t, J = 7.3 Hz, 1H), 4.59 (dd, J = 10.3, 3.4 Hz, 1H), 3.01 (s, 3H), 2.21-2.02 (m, 2H), 1.44-1.13 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 129.2, 118.1, 113.7, 105.0, 73.1, 32.1, 31.5, 29.7, 29.5, 28.0, 26.5, 22.8, 14.3; IR (film): ν 3031, 2920, 2855, 1597, 1505, 1460, 1381, 785, 752, 693 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{33}NCl_3^+$ $(M+H)^+$ 392.1673, found 392.1663.



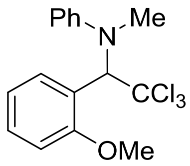
3d

N-Methyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**3d**). Yellow oil (49.6 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.47 (m, 2H), 7.35-7.26 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.93-6.82 (m, 3H), 5.86 (s, 1H), 3.81 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 150.5, 130.3, 129.4, 127.1, 118.9, 114.2, 113.8, 102.8, 76.3, 55.4, 34.7; IR (film): ν 3064, 3038, 2953, 2926, 2842, 1597, 1512, 1460, 1348, 798, 746, 693 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}NOCl_3^+$ $(M+H)^+$ 344.0370, found 344.0366.



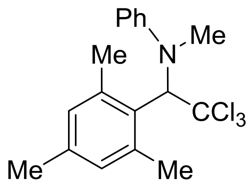
3e

N-Methyl-*N*-(2,2,2-trichloro-1-(3-methoxyphenyl)ethyl)aniline (**3e**). Yellow oil (43.4 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 3H), 7.21-7.12 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.89-6.83 (m, 2H), 5.88 (s, 1H), 3.78 (s, 3H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 150.4, 136.5, 129.5, 129.4, 121.4, 118.9, 115.4, 114.1, 113.1, 102.4, 76.3, 55.4, 34.8; IR (film): ν 3029, 2931, 2832, 1599, 1507, 1488, 1460, 806, 748, 689 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}NOCl_3^+$ $(M+H)^+$ 344.0370, found 344.0367.



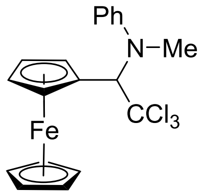
3f

N-Methyl-*N*-(2,2,2-trichloro-1-(2-methoxyphenyl)ethyl)aniline (**3f**). Yellow oil (45.5 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.9, 1.5 Hz, 1H), 7.38-7.26 (m, 3H), 7.14 (d, J = 8.1 Hz, 2H), 7.03-6.98 (m, 1H), 6.88 (dd, J = 8.2, 0.7 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 6.40 (s, 1H), 3.57 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 150.6, 129.5, 129.1, 128.7, 123.8, 111.9, 118.3, 114.4, 111.1, 103.4, 69.2, 55.6, 34.9; IR (film): ν 3063, 2923, 2858, 1606, 1505, 1464, 1379, 800, 753, 688 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}NOCl_3^+$ $(M+H)^+$ 344.0370, found 344.0365.



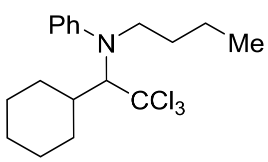
3g

N-Methyl-*N*-(2,2,2-trichloro-1-mesitylethyl)aniline (**3g**). Yellow oil (50.7 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 2H), 7.14-7.08 (m, 2H), 6.96-6.89 (m, 1H), 6.84 (s, 1H), 6.78 (s, 1H), 6.03 (s, 1H), 3.04 (s, 3H), 2.61 (s, 3H), 2.49 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 139.0, 138.0, 137.7, 132.1, 131.9, 129.9, 128.8, 122.0, 120.8, 104.1, 78.9, 41.6, 23.9, 23.2, 20.8; IR (film): ν 3062, 3020, 2957, 2919, 2865, 1599, 1494, 1449, 1377, 815, 748, 695, 651 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{21}NCl_3^+$ $(M+H)^+$ 356.0734, found 356.0725.



3h

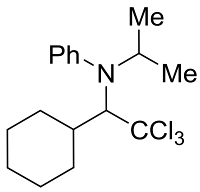
N-Methyl-*N*-(2,2,2-trichloro-1-ferrocenylethyl)aniline (**3h**). Red oil (57.3 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.85 (t, J = 7.3 Hz, 1H), 5.94 (s, 1H), 4.70 (s, 1H), 4.38 (s, 1H), 4.26 (s, 1H), 4.21 (s, 1H), 4.13 (s, 5H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 129.5, 118.3, 113.5, 103.2, 83.2, 73.9, 71.3, 69.6, 69.2, 68.1, 67.8, 34.1; IR (film): ν 3088, 2954, 2924, 2859, 1594, 1502, 1458, 814, 752, 693 cm^{-1}; MS (MALDI) calcd for $C_{19}H_{18}FeNCl_3^+$ $(M)^+$ 420.98, found 420.99.



3i

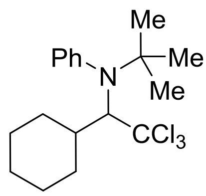
N-Butyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3i**). Colorless oil (55.9 mg, 77% yield);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 7.8 Hz, 2H), 6.82 (d, J = 8.2 Hz, 2H), 6.76 (t, J = 7.2 Hz, 1H), 4.33 (d, J = 9.3 Hz, 1H), 3.46 (t, J = 8.0 Hz, 2H), 2.33-2.27 (m, 1H), 2.23-2.13 (m, 1H), 1.88-1.80 (m, 2H), 1.76-1.48 (m, 4H), 1.41-1.00 (m, 7H), 0.95 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 129.2, 117.9, 114.7, 105.1, 79.0, 43.5, 41.1, 32.1, 32.0, 29.0, 26.6, 26.5, 26.3, 20.7, 14.1; IR (film): ν 3064, 3031, 2960, 2927, 2855, 1601, 1500, 1446, 1368, 811, 746, 693 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{27}NCl_3^+$ $(M+H)^+$ 362.1204, found 362.1197.



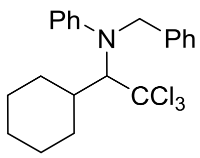
3j

N-Isopropyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3j**). Colorless oil (42.5 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 2H), 7.02 (d, J = 8.1 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H), 4.27 (d, J = 9.5 Hz, 1H), 4.24-4.13 (m, 1H), 2.36-2.30 (m, 1H), 2.17-2.07 (m, 1H), 2.05-1.99 (m, 1H), 1.87-1.81 (m, 1H), 1.75-1.64 (m, 2H), 1.45 (d, J = 6.8 Hz, 3H), 1.38 (d, J = 6.9 Hz, 3H), 1.35-1.15 (m, 4H), 1.12-0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 128.7, 119.0, 105.6, 80.4, 41.3, 32.8, 32.4, 26.9, 26.4, 22.5, 21.5; IR (film): ν 3058, 2932, 2851, 1600, 1505, 1450, 1368, 801, 752, 699 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}NCl_3^+$ $(M+H)^+$ 348.1047, found 348.1041.



3k

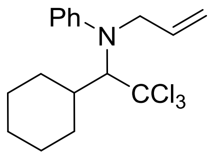
N-(*tert*-Butyl)-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3k**). Colorless oil (37.0 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m 2H), 7.30-7.22 (m, 3H), 4.04 (d, J = 8.3 Hz, 1H), 2.49-2.40 (m, 1H), 2.14-2.05 (m, 1H), 1.90-1.82 (m, 1H), 1.79-1.63 (m, 3H), 1.36-1.06 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 135.5, 127.4, 126.5, 106.7, 77.1, 56.9, 41.9, 34.2, 32.5, 30.3, 27.3, 27.0, 26.6; IR (film): ν 3051, 2927, 2848, 1597, 1453, 1492, 1401, 1362, 804, 752, 707 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{27}NCl_3^+$ $(M+H)^+$ 362.1204, found 362.1196.



3l

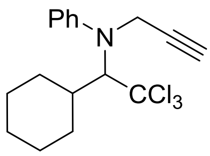
N-Benzyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3l**). Colorless oil (50.8 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.19 (m, 4H), 7.18-7.10 (m, 3H), 6.85 (d, J = 8.4 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 4.87 (s, 2H), 4.54 (d, J = 7.7 Hz, 1H), 2.32-2.14 (m, 3H), 1.89-1.81 (m, 1H), 1.76-1.63 (m, 2H), 1.55-1.43 (m, 1H), 1.35-1.16 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 138.4, 128.9, 128.4, 127.4, 126.5, 119.1, 116.7, 104.7, 80.6, 48.6, 41.5, 32.6, 31.9, 26.9, 26.6, 26.3;

IR (film): *ν* 3057, 3031, 2930, 2855, 1604, 1499, 1453, 1322, 811, 753, 698 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}NCl_3^+$ $(M+H)^+$ 396.1047, found 396.1040.



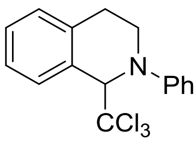
3m

N-Allyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3m**). Colorless oil (45.1 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.18 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 5.94-5.78 (m, 1H), 5.29-5.13 (m, 2H), 4.41 (d, *J* = 9.1 Hz, 1H), 4.20 (d, *J* = 5.7 Hz, 2H), 2.33-2.27 (m, 1H), 2.25-2.12 (m, 1H), 1.96-1.78 (m, 2H), 1.75-1.63 (m, 2H), 1.39-1.04 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 135.6, 129.1, 118.3, 117.2, 115.2, 104.9, 78.8, 46.8, 41.1, 32.1, 31.8, 26.6, 26.4, 26.2; IR (film): *ν* 3071, 2926, 2855, 1603, 1500, 1450, 817, 752, 687 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{23}NCl_3^+$ $(M+H)^+$ 346.0891, found 346.0883.



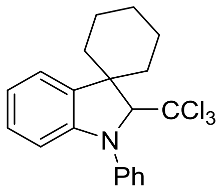
3n

N-(Prop-2-yn-1-yl)-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3n**). Colorless oil (37.2 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 4.50 (dd, *J* = 18.5, 2.4 Hz, 1H), 4.44 (d, *J* = 9.4 Hz, 1H), 4.08 (dd, *J* = 18.5, 2.4 Hz, 1H), 2.40-2.17 (m, 3H), 2.14-2.05 (m, 1H), 1.90-1.80 (m, 1H), 1.74-1.64 (m, 2H), 1.40-1.14 (m, 4H), 1.10-0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 129.3, 118.7, 113.8, 104.2, 80.0, 77.2, 77.0, 72.3, 41.1, 34.3, 32.1, 31.9, 26.6, 26.2, 26.1; IR (film): *ν* 3310, 3044, 2926, 2855, 1597, 1504, 1453, 1388, 814, 746, 686 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{21}NCl_3^+$ $(M+H)^+$ 344.0734, found 344.0730.



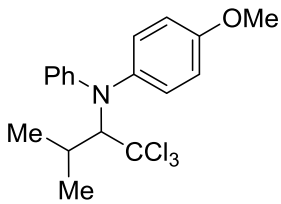
3o

2-Phenyl-1-(trichloromethyl)-1,2,3,4-tetrahydroisoquinoline (**3o**). White solid (52.3 mg, 80% yield); m.p. 100-101 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.34-7.17 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 5.64 (s, 1H), 4.13-4.05 (m, 1H), 3.67-3.59 (m, 1H), 3.23-3.15 (m, 1H), 3.12-3.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 136.5, 131.8, 129.9, 129.3, 128.9, 128.8, 125.8, 119.4, 116.0, 106.4, 74.3, 43.0, 27.5; IR (film): *ν* 3064, 3031, 2923, 2855, 1597, 1499, 1401, 803, 746, 687 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{15}NCl_3^+$ $(M+H)^+$ 326.0265, found 326.0260.



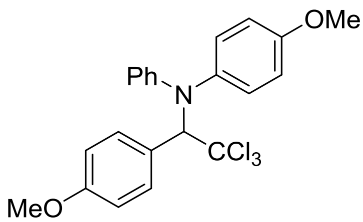
3p

1'-Phenyl-2'-(trichloromethyl)spiro[cyclohexane-1,3'-indoline] (**3p**). Yellow oil (54.8 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.9 Hz, 2H), 7.36-7.26 (m, 3H), 7.21-7.12 (m, 2H), 7.02 (t, J = 7.3 Hz, 1H), 6.98-6.90 (m, 1H), 4.57 (s, 1H), 2.50-2.40 (m, 1H), 2.30-2.20 (m, 1H), 2.08-1.87 (m, 2H), 1.73-1.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 145.8, 141.0, 129.3, 127.2, 123.0, 122.4, 121.9, 118.8, 114.6, 102.2, 85.8, 51.8, 41.3, 28.3, 25.8, 23.8, 22.6; IR (film): ν 3038, 2926, 2858, 1597, 1492, 1473, 1460, 1355, 820, 746, 699 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}NCl_3^+$ $(M+H)^+$ 380.0734, found 380.0726.



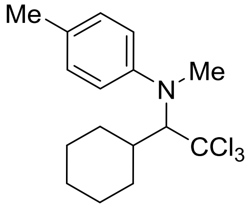
3q

4-Methoxy-*N*-phenyl-*N*-(1,1,1-trichloro-3-methylbutan-2-yl)aniline (**3q**). Yellow oil (44.7 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.2 Hz, 2H), 7.20-7.13 (m, 2H), 6.92-6.86 (m, 2H), 6.85-6.67 (m, 3H), 4.69 (d, J = 9.8 Hz, 1H), 3.82 (s, 3H), 2.43-2.31 (m, 1H), 1.33 (d, J = 6.7 Hz, 3H), 1.23 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 129.0, 117.7, 114.4, 105.0, 78.5, 55.5, 31.6, 23.1, 21.9; IR (film): ν 3005, 2960, 2933, 2842, 1597, 1505, 788, 759, 693 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{21}ONCl_3^+$ $(M+H)^+$ 372.0683, found 372.0678.

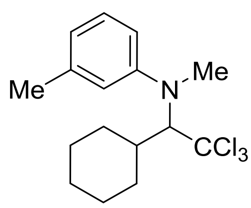


3r

4-Methoxy-*N*-phenyl-*N*-(2,2,2-trichloro-1-(4-methoxyphenyl)ethyl)aniline (**3r**). Yellow oil (45.4 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.21-7.15 (m, 2H), 6.89 -6.74 (m, 9H), 6.13 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 158.2, 150.5, 135.7, 133.4, 132.0, 129.0, 127.4, 119.7, 117.3, 114.0, 113.3, 103.7, 76.0, 55.5, 55.3; IR (film): ν 3011, 2933, 2842, 1612, 1501, 1459, 792, 746, 693 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}O_2NCl_3^+$ $(M+H)^+$ 436.0632, found 436.0624.

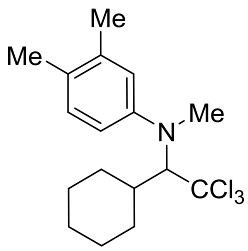


3s



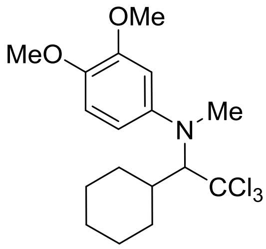
3s'

A 40:60 mixture of *N*,4-dimethyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3s**) and *N*,3-dimethyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3s'**) was obtained as a colorless oil (49.5 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) for amine **3s**: δ 7.06 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 8.2 Hz, 2H), 4.35 (d, J = 9.3 Hz, 1H), 2.96 (s, 3H), 2.27-2.17 (m, 5H), 1.86-1.80 (m, 1H), 1.76-1.62 (m, 3H), 1.39-0.96 (m, 5H); ^{1}H NMR (400 MHz, $CDCl_3$) for amine **3s'**: δ 7.14 (t, J = 7.9 Hz, 1H), 6.65-6.56 (m, 3H), 4.38 (d, J = 9.3 Hz, 1H), 2.96 (s, 3H), 2.39-2.28 (m, 5H), 1.86-1.80 (m, 1H), 1.76-1.62 (m, 3H), 1.39-0.96 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.4, 138.9, 129.7, 129.0, 126.6, 118.5, 113.4, 112.8, 110.1, 104.9, 104.7, 77.2, 76.9, 40.2, 31.8, 31.4, 31.3, 31.2, 26.4, 26.3, 26.1, 20.2; IR (film): ν 2926, 2849, 1604, 1519, 1492, 1302, 804, 759 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}NCl_3^+$ $(M+H)^+$ 334.0891, found 334.0888.



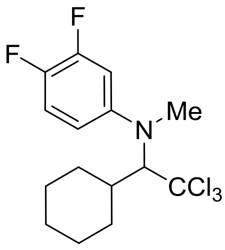
3t

N,3,4-Trimethyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3t**). Colorless oil (53.7 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J = 8.2 Hz, 1H), 6.63-6.53 (m, 2H), 4.35 (d, J = 9.3 Hz, 1H), 2.95 (s, 3H), 2.38-2.14 (m, 8H), 1.87-1.79 (m, 1H), 1.77-1.56 (m, 3H), 1.37-0.96 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 137.4, 130.4, 125.6, 114.3, 110.4, 105.1, 77.1, 40.4, 32.0, 31.5, 31.4, 26.5, 26.2, 20.6, 18.7; IR (film): ν 2923, 2860, 1617, 1505, 1450, 1381, 804, 752, 704 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}NCl_3^+$ $(M+H)^+$ 348.1047, found 348.1040.



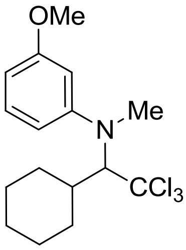
3u

3,4-Dimethoxy-*N*-methyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3u**). Colorless oil (57.1 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, J = 8.8, 1H), 6.40 (d, J = 2.9 Hz, 1H), 6.33 (dd, J = 8.8, 2.9 Hz, 1H), 4.25 (d, J = 9.1 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.97 (s, 3H), 2.34-2.17 (m, 2H), 1.88-1.64 (m, 4H), 1.38-0.98 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 146.1, 141.6, 112.9, 105.1, 104.8, 99.1, 78.2, 56.6, 56.1, 40.4, 32.0, 31.9, 31.5, 26.5, 26.2; IR (film): *ν* 2920, 2855, 1600, 1512, 1450, 804, 759 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}NO_2Cl_3^+$ $(M+H)^+$ 380.0945, found 380.0944.



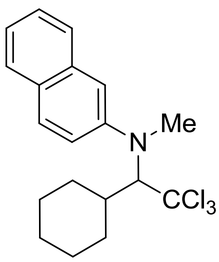
3v

3,4-Difluoro-*N*-methyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3v**). Colorless oil (27.8 mg, 39% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-6.97 (m, 1H), 6.63-6.51 (m, 1H), 6.50-6.40 (m, 1H), 4.21 (d, J = 9.2 Hz, 1H), 2.94 (s, 3H), 2.37-2.14 (m, 2H), 1.88-1.79 (m, 1H), 1.78-1.62 (m, 3H), 1.37-0.96 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (dd, J = 243.0, 13.2 Hz), 148.0 (d, J = 8.2 Hz), 143.1 (dd, J = 236.8, 13.1 Hz), 117.4 (dd, J = 17.6, 1.8 Hz), 108.1 (dd, J = 5.4, 2.9 Hz), 104.3, 102.1 (d, J = 21.5 Hz), 77.7, 40.3, 31.9, 31.4, 26.4, 26.1; IR (film): *ν* 2926, 2855, 1604, 1520, 1446, 811, 759, 703 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{19}NCl_3F_2^+$ $(M+H)^+$ 356.0546, found 356.0538.



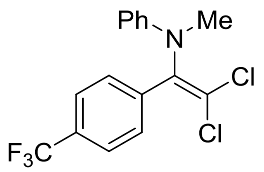
3w

3-Methoxy-*N*-methyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)aniline (**3w**). Colorless oil (59.6 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, J = 8.3 Hz, 1H), 6.47-6.40 (m, 1H), 6.36-6.30 (m, 2H), 4.37 (d, J = 9.3 Hz, 1H), 3.79 (s, 3H), 2.95 (s, 3H), 2.35-2.15 (m, 2H), 1.88-1.78 (m, 1H), 1.75-1.61 (m, 3H), 1.37-0.97 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 152.1, 130.0, 106.1, 104.6, 101.9, 100.0, 77.01, 55.3, 40.3, 31.9, 31.6, 31.3, 26.4, 26.1; IR (film): *ν* 2926, 2848, 1610, 1578, 1447, 1302, 799, 765 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}NOCl_3^+$ $(M+H)^+$ 350.0840, found 350.0835.



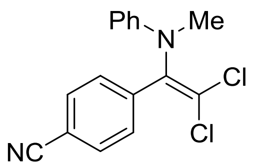
3x

N-Methyl-*N*-(2,2,2-trichloro-1-cyclohexylethyl)naphthalen-2-amine (**3x**). Colorless oil (53.4 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.64 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.26-7.16 m, 2H), 7.01 (s, 1H), 4.54 (d, J = 9.1 Hz, 1H), 3.09 (s, 3H), 2.42-2.22 (m, 2H), 1.88-1.82 (m, 1H), 1.79-1.64 (m, 3H), 1.45-0.97 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 135.0, 129.0, 127.6, 127.3, 126.6, 126.5, 122.7, 115.9, 107.2, 104.8, 76.8, 40.4, 31.9, 31.4, 26.5, 26.2; IR (film): ν 3054, 2926, 2855, 1636, 1603, 1512, 1482, 1388, 804, 759, 706 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{23}NCl_3^+$ $(M+H)^+$ 370.0891, found 370.0885.



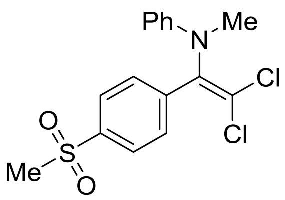
4a

N-(2,2-Dichloro-1-(4-(trifluoromethyl)phenyl)vinyl)-*N*-methylaniline (**4a**). Yellow oil (35.3 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.57 (m, 4H), 7.29-7.22 (m, 2H), 6.83 (t, J = 7.3 Hz, 1H), 6.81-6.75 (m, 2H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.6, 139.0, 131.1, 130.8, 130.1, 129.4, 125.4 (q, J = 3.8 Hz), 121.0, 119.2, 114.0, 37.6; IR (film): ν 2966, 2926, 2861, 1604, 1518, 1459, 1381, 746 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}NF_3Cl_2^+$ $(M+H)^+$ 346.0372, found 346.0361.



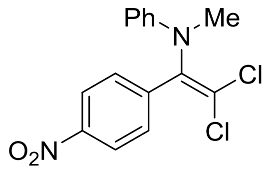
4b

4-(2,2-Dichloro-1-(methyl(phenyl)amino)vinyl)benzonitrile (**4b**). Yellow oil (38.8 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (m, 4H), 7.28-7.21 (m, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.79-6.73 (m, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 140.4, 140.1, 132.2, 130.4, 129.5, 121.8, 119.4, 118.5, 114.1, 112.6, 37.7; IR (film): ν 2928, 2859, 2226, 1593, 1490, 748, 694 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}N_2Cl_2^+$ $(M+H)^+$ 303.0450, found 303.0451.



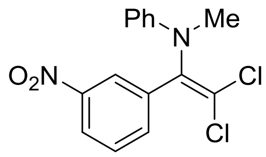
4c

N-(2,2-Dichloro-1-(4-(methylsulfonyl)phenyl)vinyl)-*N*-methylaniline (**4c**). Yellow solid (28.5 mg, 40% yield); m.p. 189-190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.25 (t, J = 7.8 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.1 Hz, 2H), 3.11 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 141.1, 140.7, 140.3, 130.6, 129.5, 127.5, 121.9, 119.4, 114.1, 44.5, 37.7; IR (film): ν 3019, 2921, 2846, 1593, 1498, 1395, 1313, 1150, 748, 686 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}NO_2SCl_2^+$ $(M+H)^+$ 356.0273, found 356.0271.



4d

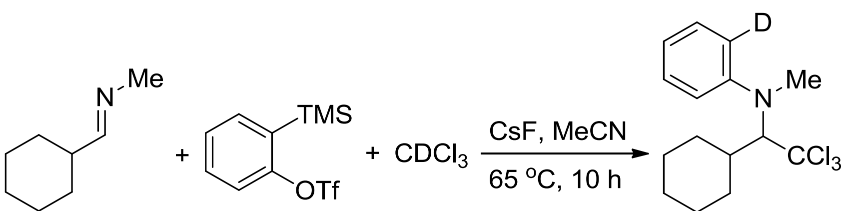
N-(2,2-Dichloro-1-(4-nitrophenyl)vinyl)-*N*-methylaniline (**4d**). Yellow oil (31.7 mg, 49% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.25 (t, J = 7.9 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 8.1 Hz, 2H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.1, 142.0, 140.2, 130.7, 129.5, 123.7, 122.2, 119.5, 114.2, 37.8; IR (film): ν 2960, 2921, 2853, 1600, 1511, 1340, 748, 693 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2Cl_2^+$ $(M+H)^+$ 323.0349, found 323.0344.



4e

N-(2,2-Dichloro-1-(3-nitrophenyl)vinyl)-*N*-methylaniline (**4e**). Yellow oil (31.0 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, J = 2.0 Hz, 1H), 8.17 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.83 (ddd, J = 7.8, 1.7, 1.1 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.29-7.21 (m, 2H), 6.87-6.76 (m, 3H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 146.1, 140.0, 137.3, 135.5, 129.5, 124.7, 124.0, 121.4, 119.5, 114.3, 37.8; IR (film): ν 3084, 2928, 2819, 1600, 1532, 1497, 1348, 816, 749, 693 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2Cl_2^+$ $(M+H)^+$ 323.0349, found 323.0346.

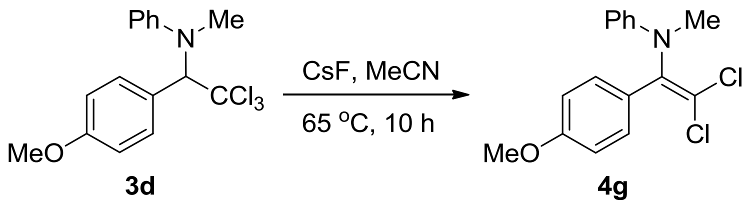
Reaction of imine 1a, benzyne precursor 2a, and deuterated chloroform (Equation 2)



1a **2a** **3a-D1**

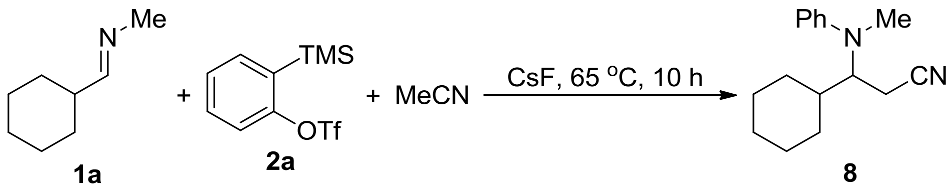
A flask containing dry CsF (91.1 mg, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol), imine **1a** (25.0 mg, 0.20 mmol), acetonitrile (0.30 mL), and deuterated chloroform (0.30 mL). The mixture was stirred at 65 °C for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with petroleum ether, to give *N*-methyl-*N*-(2,2,2-trichloro-1-cyclohexyl-ethyl)aniline-2-*d* (**3a-D1**) as a colorless oil (47.0 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 6.84-6.73 (m, 2H), 4.39 (d, J = 9.2 Hz, 1H), 2.97 (s, 3H), 2.38-2.16 (m, 2H), 1.88-1.79 (m, 1H), 1.77-1.60 (m, 3H), 1.38-0.96 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 129.3, 129.2, 117.7, 112.9, 104.8, 77.0, 40.3, 31.9, 31.5, 31.4, 26.5, 26.2; IR (film): ν 2921, 2848, 1591, 1479, 1450, 1375, 818, 752 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{20}DNCl_3^+$ $(M+H)^+$ 321.0797, found 321.0791.

Elimination of HCl from 2,2,2-trichloroethanamine 3d (Equation 3)



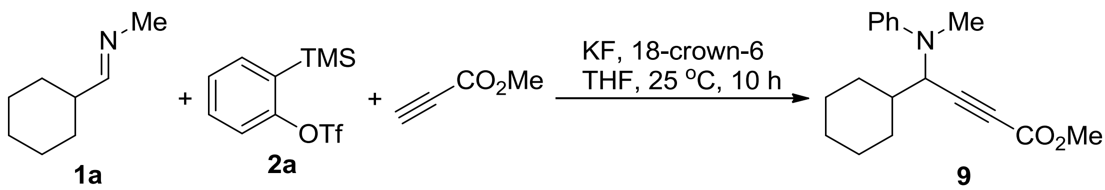
A reaction tube containing dry CsF (30.4 mg, 0.20 mmol) was evacuated and purged with nitrogen gas three times. A solution of 2,2,2-trichloroethanamine **3d** (34.5 mg, 0.10 mmol) in acetonitrile (0.5 mL) was added via syringes. The mixture was stirred at 65 ℃ for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with petroleum ether, to give *N*-(2,2-dichloro-1-(4-methoxyphenyl)vinyl)-*N*-methylaniline (**4g**) as a colorless oil (25.0 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) for the major tautomer: δ 7.46 (dd, *J* = 9.3, 2.4 Hz, 2H), 7.27-7.20 (m, 2H), 6.88-6.83 (m, 2H), 6.82-6.75 (m, 3H), 3.80 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major tautomer: δ 160.1, 146.8, 141.5, 132.4, 131.2, 129.3, 127.2, 118.6, 113.9, 113.8, 55.4, 37.5; IR (film): ν 2934, 2835, 1600, 1498, 1348, 843, 749, 693 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{16}ONCl_2^+$ $(M+H)^+$ 308.0604, found 308.0606.

Reaction of imine 1a, benzyne precursor 2a, and acetonitrile (Scheme 5)



A flask containing dry CsF (91.1 mg, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol), imine **1a** (25.0 mg, 0.20 mmol), acetonitrile (0.60 mL). The mixture was stirred at 65 ℃ for 10 h, cooled to room temperature, and purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5 v/v), to give 3-cyclohexyl-3-(methyl(phenyl)amino)propanenitrile (**8**) as a colorless oil (28.6 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-71.9 (m, 2H), 6.84-6.70 (m, 3H), 3.83-3.74 (m, 1H), 2.85 (s, 3H), 2.62-2.56 (m, 2H), 1.88-1.59 (m, 6H), 1.37-0.82 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 129.4, 118.6, 117.6, 113.5, 60.6, 40.1, 31.2, 30.7, 30.5, 26.2, 26.1, 25.9, 18.9; IR (film): ν 2928, 2853, 2242, 1629, 1600, 1504 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}N_2^+$ $(M+H)^+$ 243.1856, found 243.1854.

Reaction of imine 1a, benzyne precursor 2a, and methyl propiolate (Scheme 5)

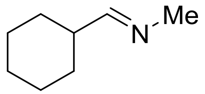


A reaction tube containing dry KF (34.9 mg, 0.60 mmol) and 18-crown-6 (0.159 g, 0.60 mmol) was evacuated and purged with nitrogen gas three times. To the flask were added 2-(trimethylsilyl)phenyl triflate (**2a**) (89.5 mg, 0.30 mmol), imine **1a** (25.0 mg, 0.20 mmol), tetrahydrofuran (0.5 mL) via syringes. The mixture was stirred at room temperature for 10 h. The mixture was purified directly by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5 v/v), to give methyl 4-cyclohexyl-4-(methyl(phenyl)amino)but-2-ynoate (**9**) as a colorless oil (30.8 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.20 (m, 2H), 6.91-6.74 (m, 3H), 4.21 (d, J = 9.9 Hz, 1H), 3.74 (s, 3H), 2.85 (s, 3H), 2.10-2.03 (m, 1H), 1.94-1.61 (m, 5H), 1.35-0.85 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 150.3, 129.3, 118.7, 114.9, 86.5, 77.1, 58.5, 52.8, 40.7, 33.6, 30.7, 30.1, 26.4, 26.0, 25.9; IR (film): ν 2928, 2853, 2226, 1716, 1600, 1504, 1436 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{24}NO_2^+$ $(M+H)^+$ 286.1802, found 286.1799.

References

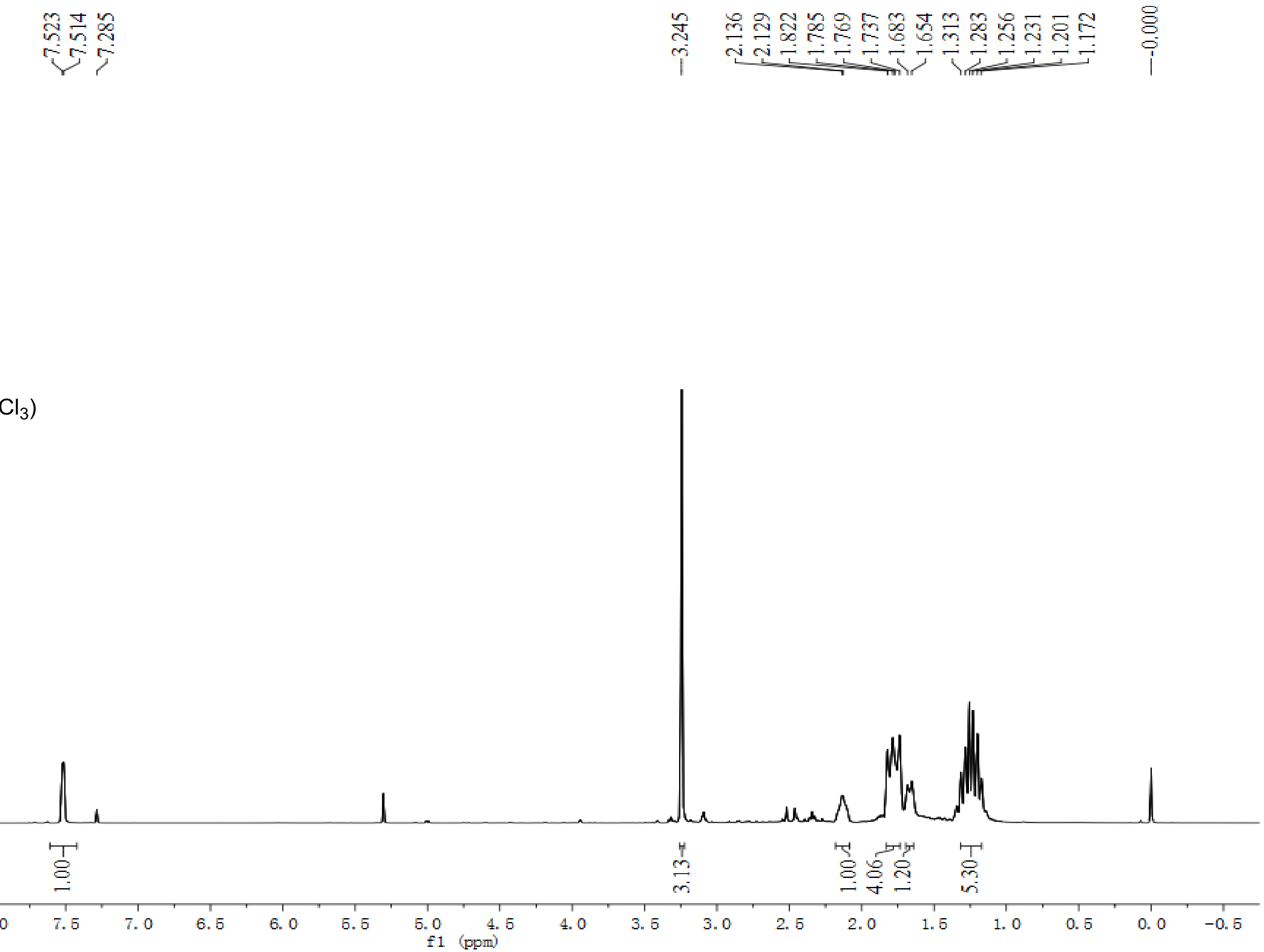
1 (*a*) S. Andersson, R. E. Carter and T. Drakenberg, *Acta. Chem. Scand. B.*, 1984, **38**, 579; (*b*) D. Cuvinot, P. Mangeney, A. Alexakis and J.-F. Normant, *J. Org. Chem.*, 1989, **54**, 2420; (*c*) G. D. Joly and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2004, **126**, 4102; (*d*) H. Rodríguez-Solla, C. Concellón, N. Alvaredo and R. G. Soengas, *Tetrahedron*, 2012, **68**, 1736; (*e*) N. S. Radulović, A. B. Miltojević and R. D. Vukićević, *C. R. Chimie*, 2013, **16**, 257; (*f*) D.-J. Cheng and S.-K. Tian, *Adv. Synth. Catal.*, 2013, **355**, 1715; (*g*) Y. Qin, L. Zhang, J. Lv, S. Luo and J.-P. Cheng, *Org. Lett.*, 2015, **17**, 1469; (*h*) B. M. Trost, S. Mahapatra and M. Hansen, *Angew. Chem. Int. Ed.*, 2015, **54**, 6032; (*i*) J.-C. Castillo, J. Quiroga, R. Abonia, J. Rodriguez and Y. Coquerel, *J. Org. Chem.*, 2015, **80**, 9767; (*j*) H. Nagae, Y. Shibata, H. Tsurugi and K. Mashima, *J. Am. Chem. Soc.*, 2015, **137**, 640.

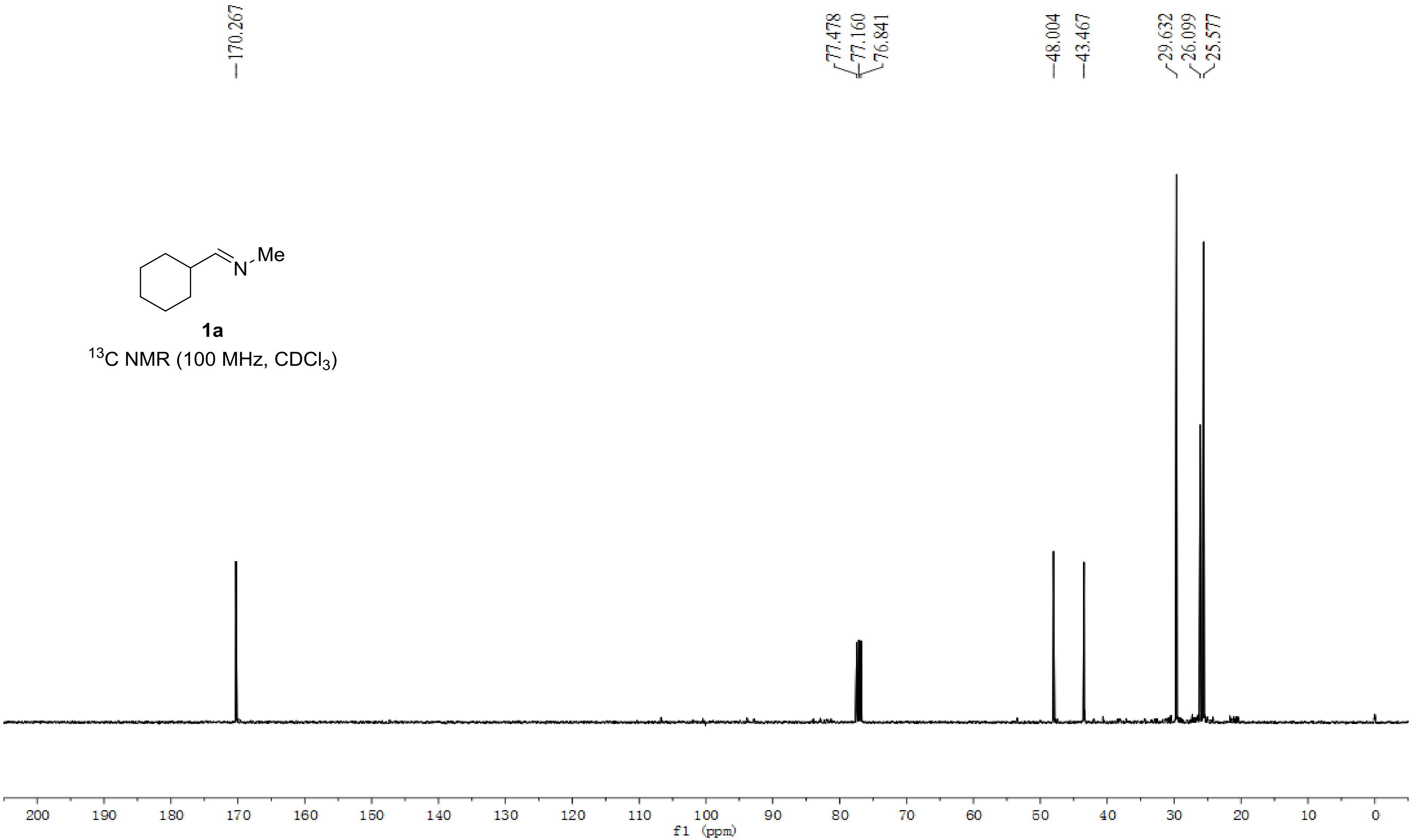
2 (*a*) B. Michel and M. F. Greaney, *Org. Lett.*, 2014, **16**, 2684; (*b*) B. S. Shaibu, R. K. Kawade and R.-S. Liu, *Org. Biomol. Chem.*, 2012, **10**, 6834.



1a

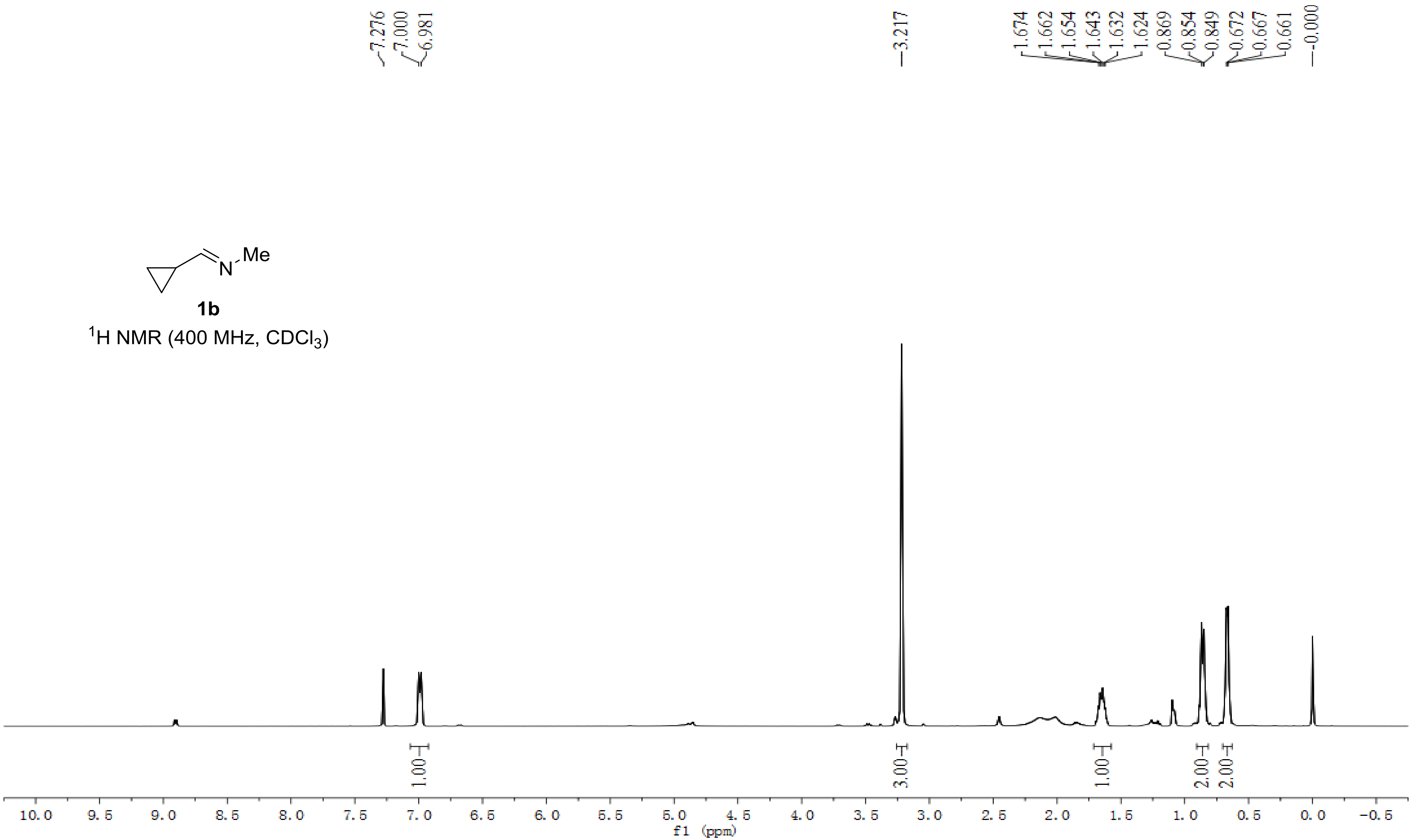
^{1}H NMR (400 MHz, $CDCl_3$)



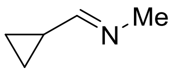


1a

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

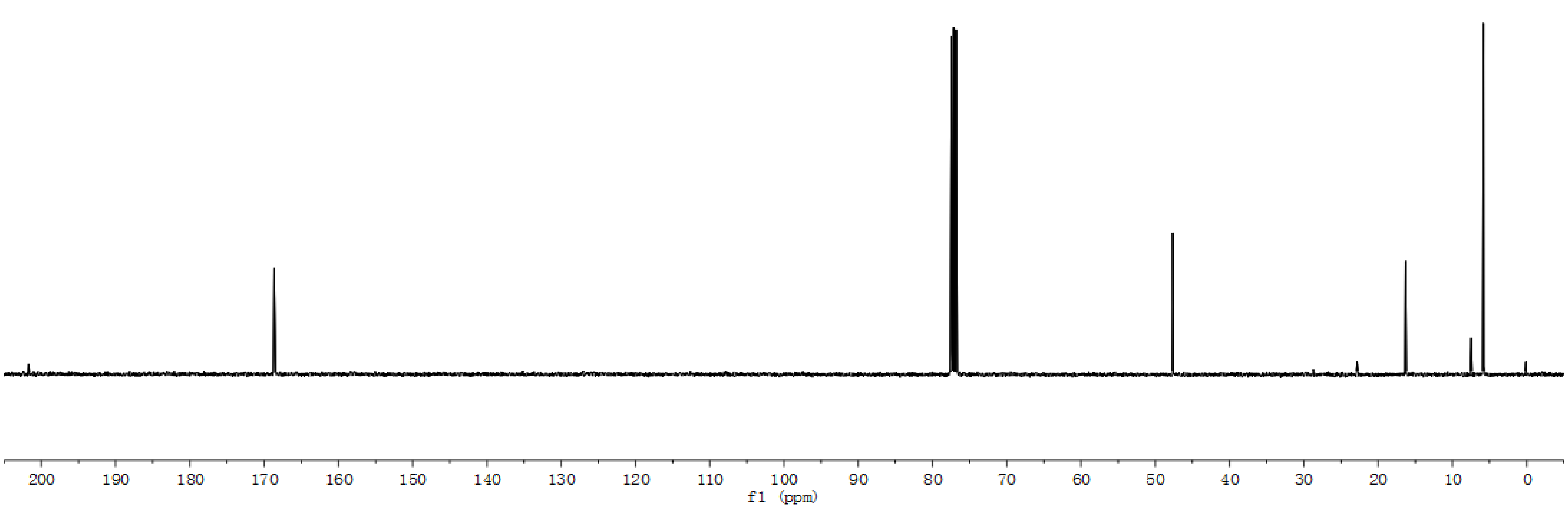


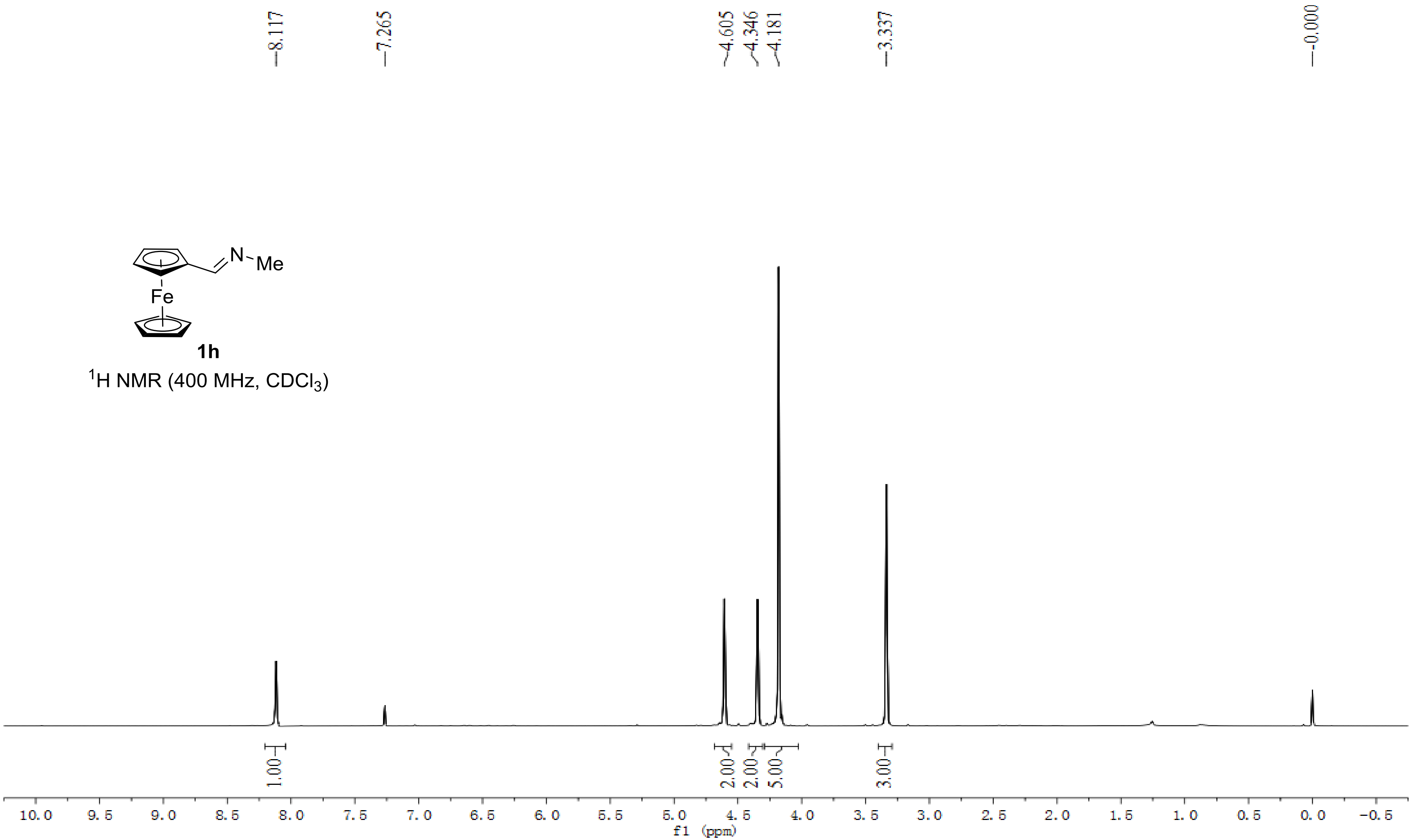
^{1}H NMR (400 MHz, $CDCl_3$)



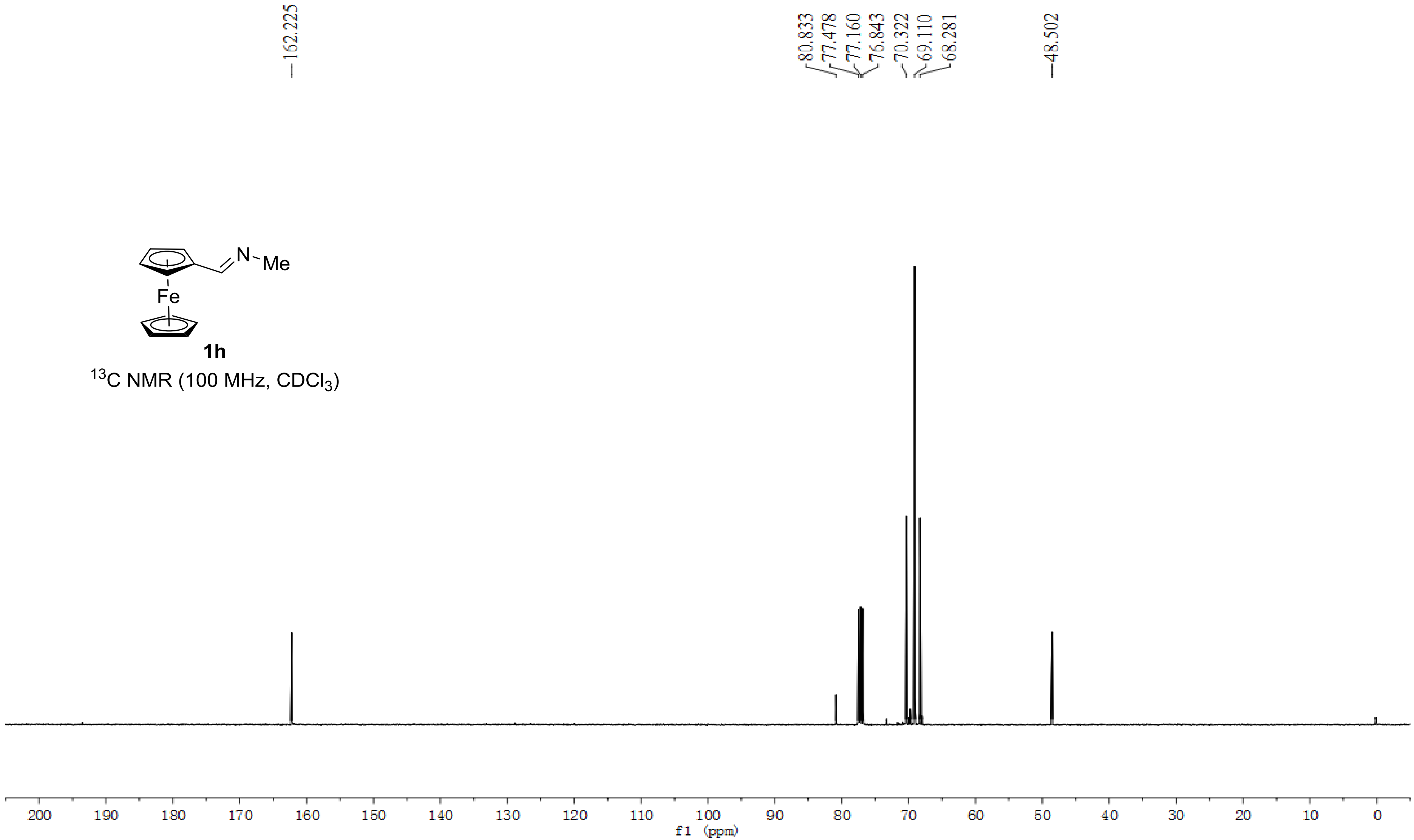
1b

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



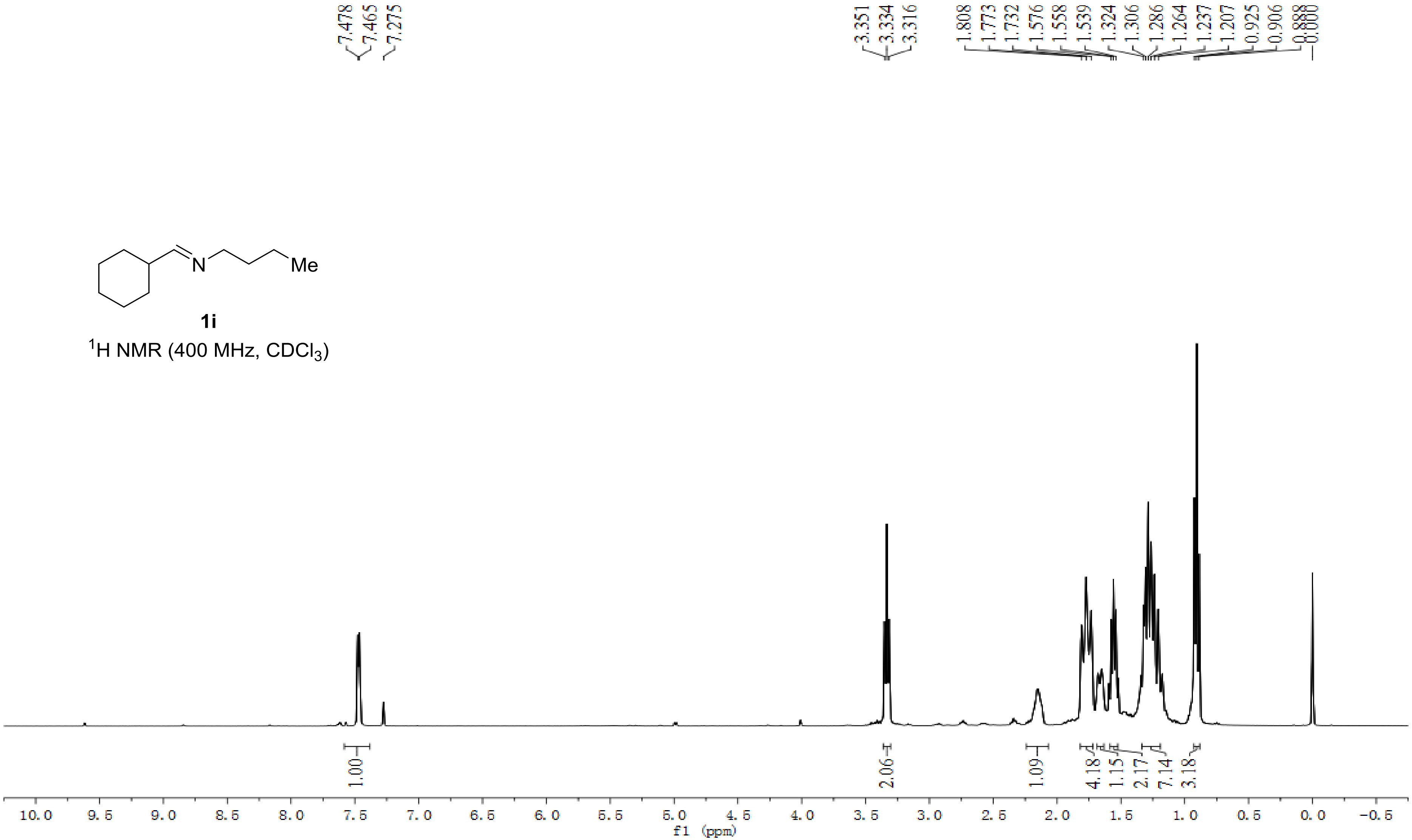


8.117
7.265
4.605
4.346
4.181
3.337
0.000
N
Me
Fe
1h
1H NMR (400 MHz, CDCl3)
1.00
2.00
2.00
5.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

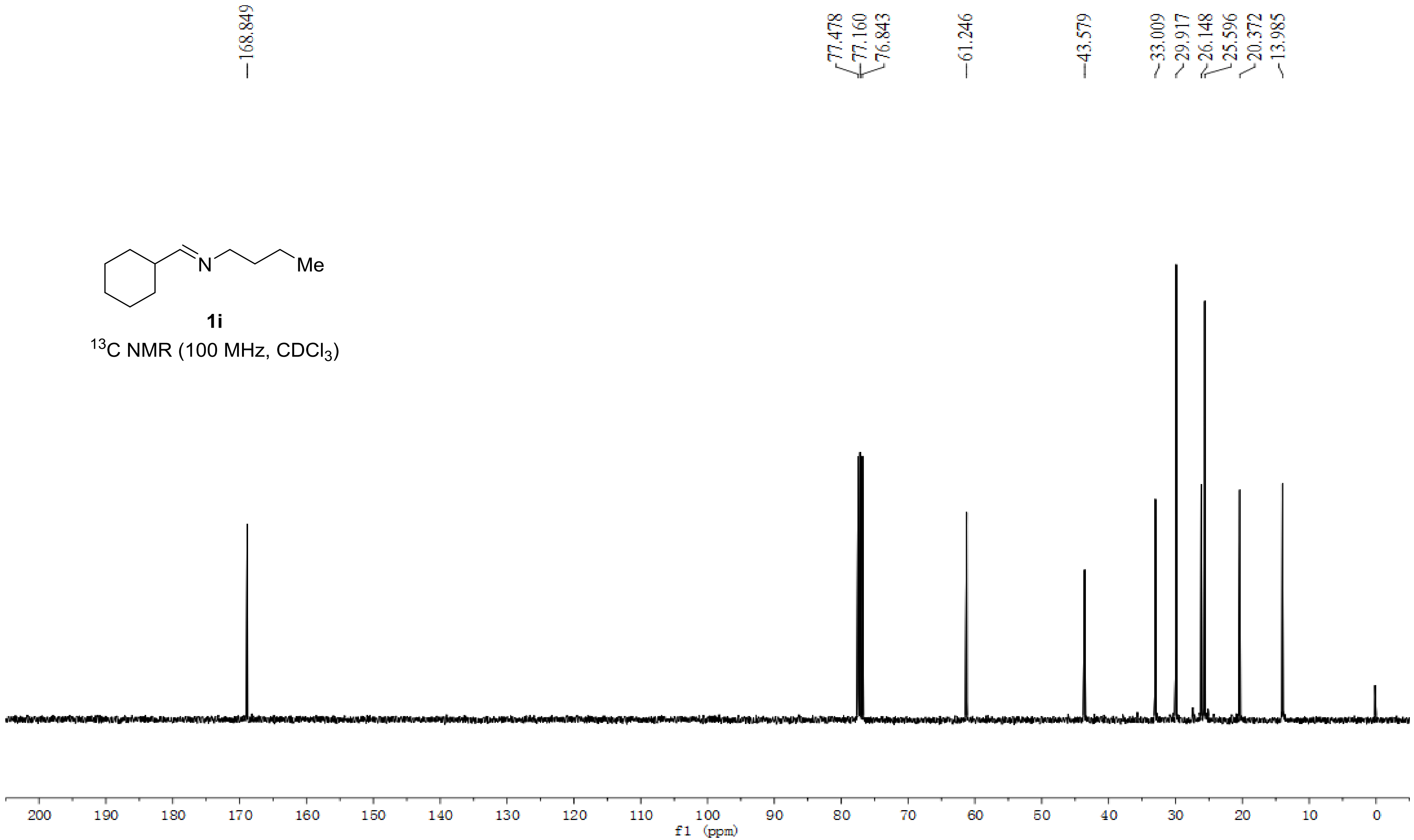


1h

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

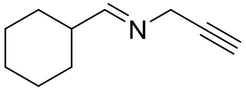


1i
^{1}H NMR (400 MHz, CDCl$_3$)
Me
N
7.478
7.465
7.275
3.351
3.334
3.316
1.808
1.773
1.732
1.576
1.558
1.539
1.324
1.306
1.286
1.264
1.237
1.207
0.925
0.906
0.888
0.000
1.00
2.06
1.09
4.18
1.15
2.17
7.14
3.18
f1 (ppm)



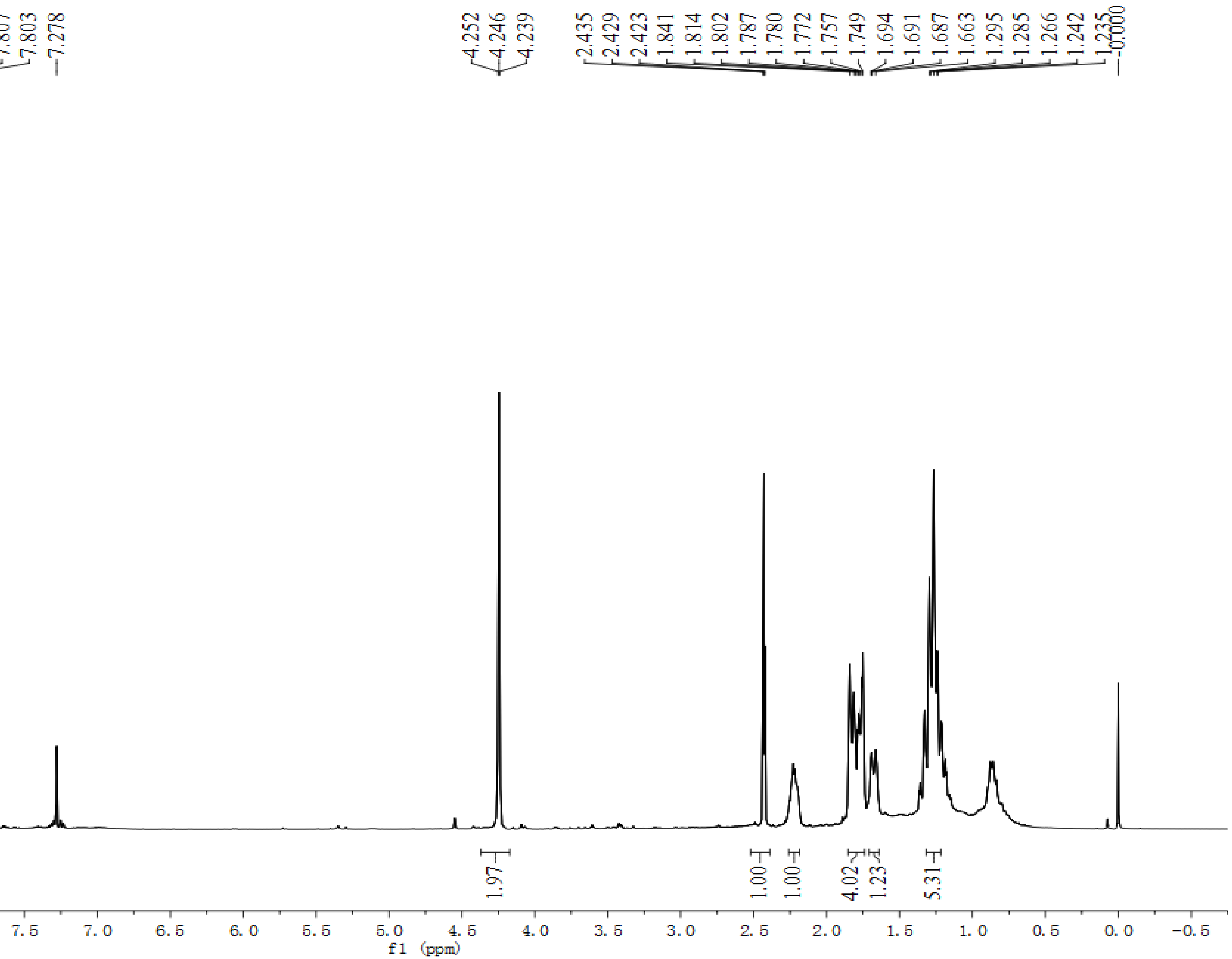
1i

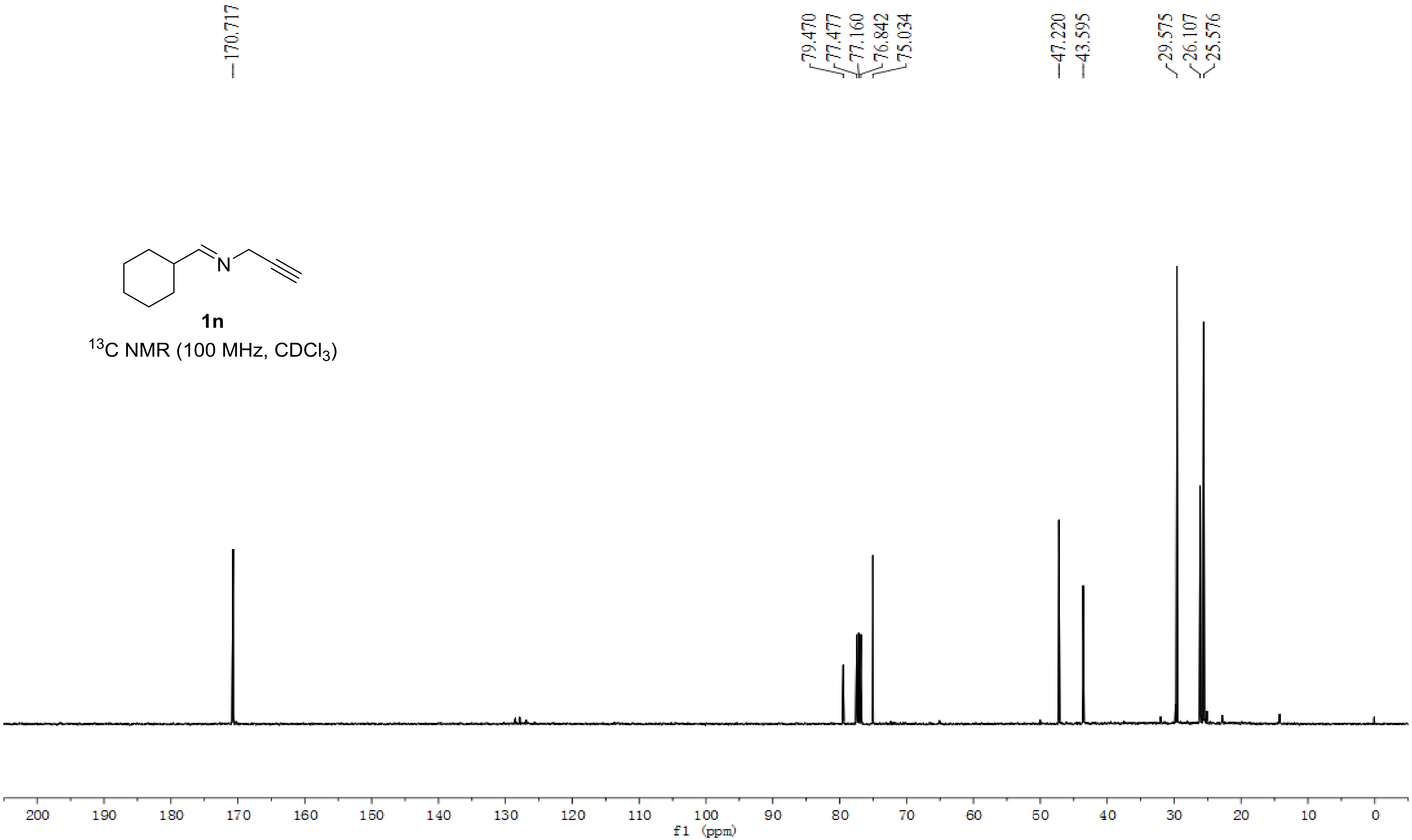
^{13}C NMR (100 MHz, $CDCl_3$)



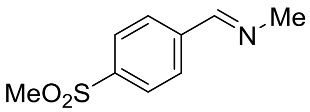
1n

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



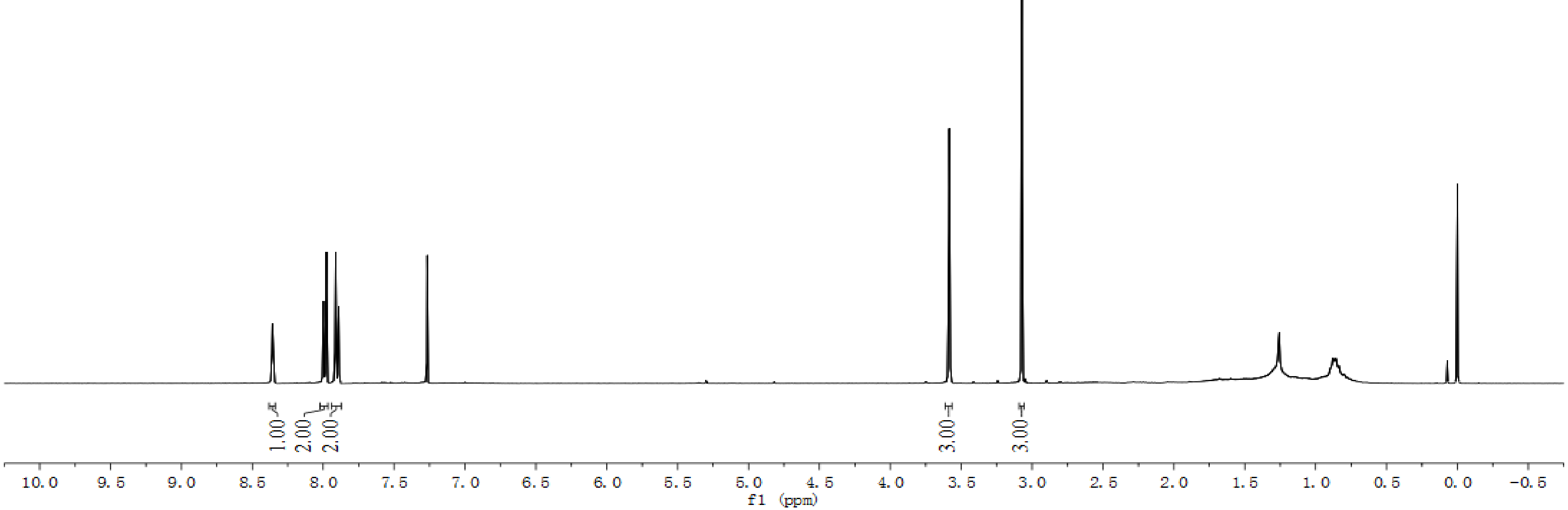


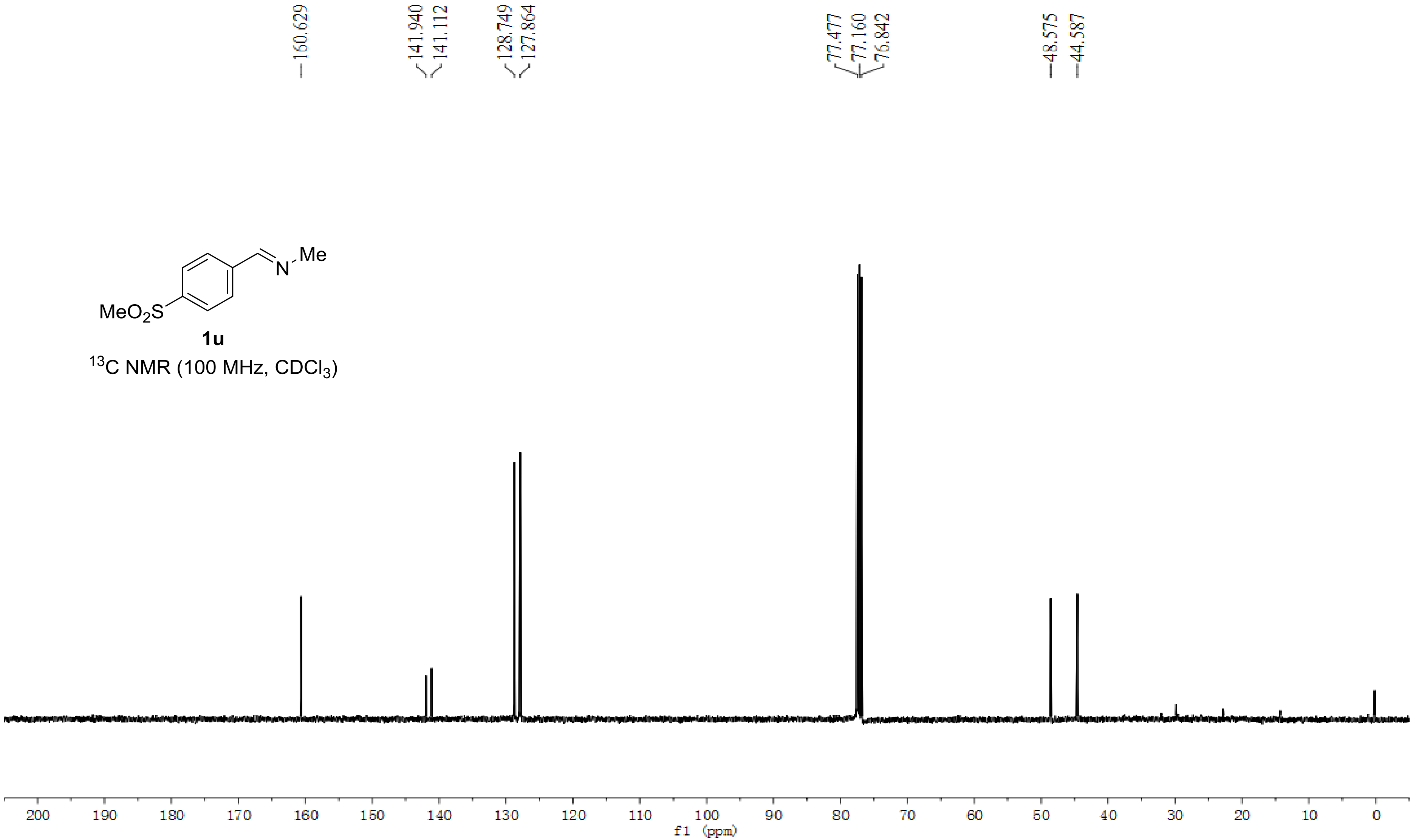
^{13}C NMR (100 MHz, $CDCl_3$)



1u

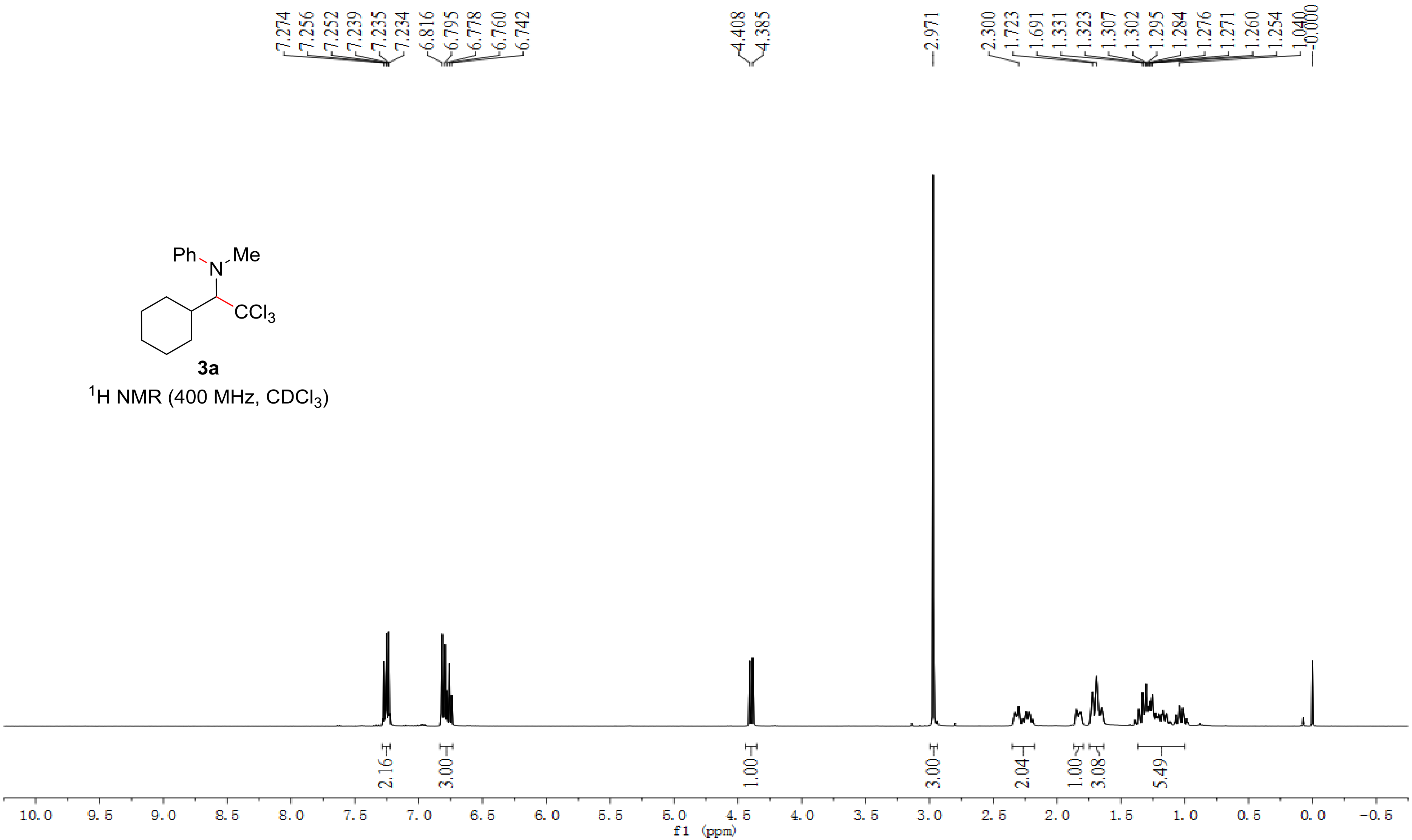
^{1}H NMR (400 MHz, $CDCl_3$)





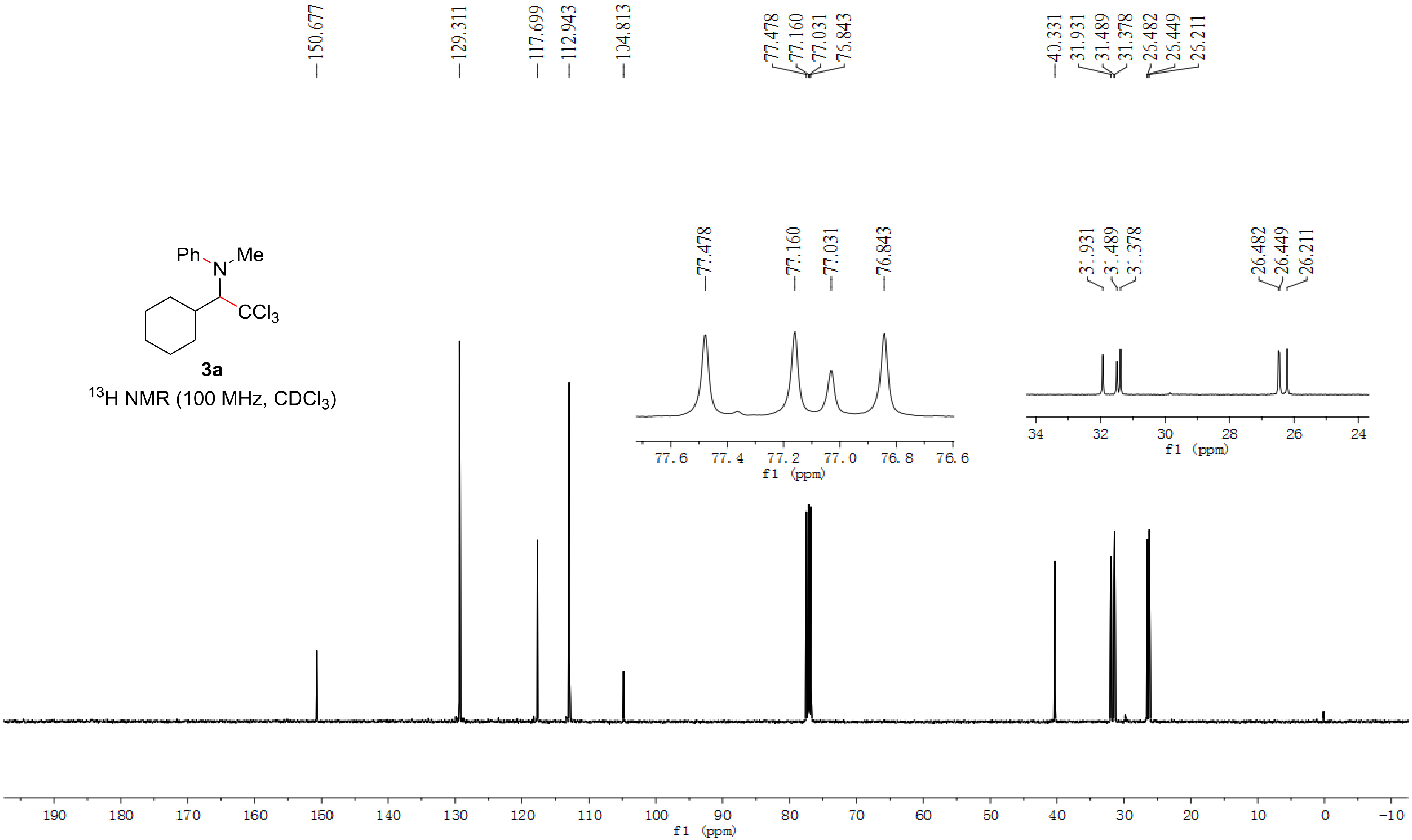
1u

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



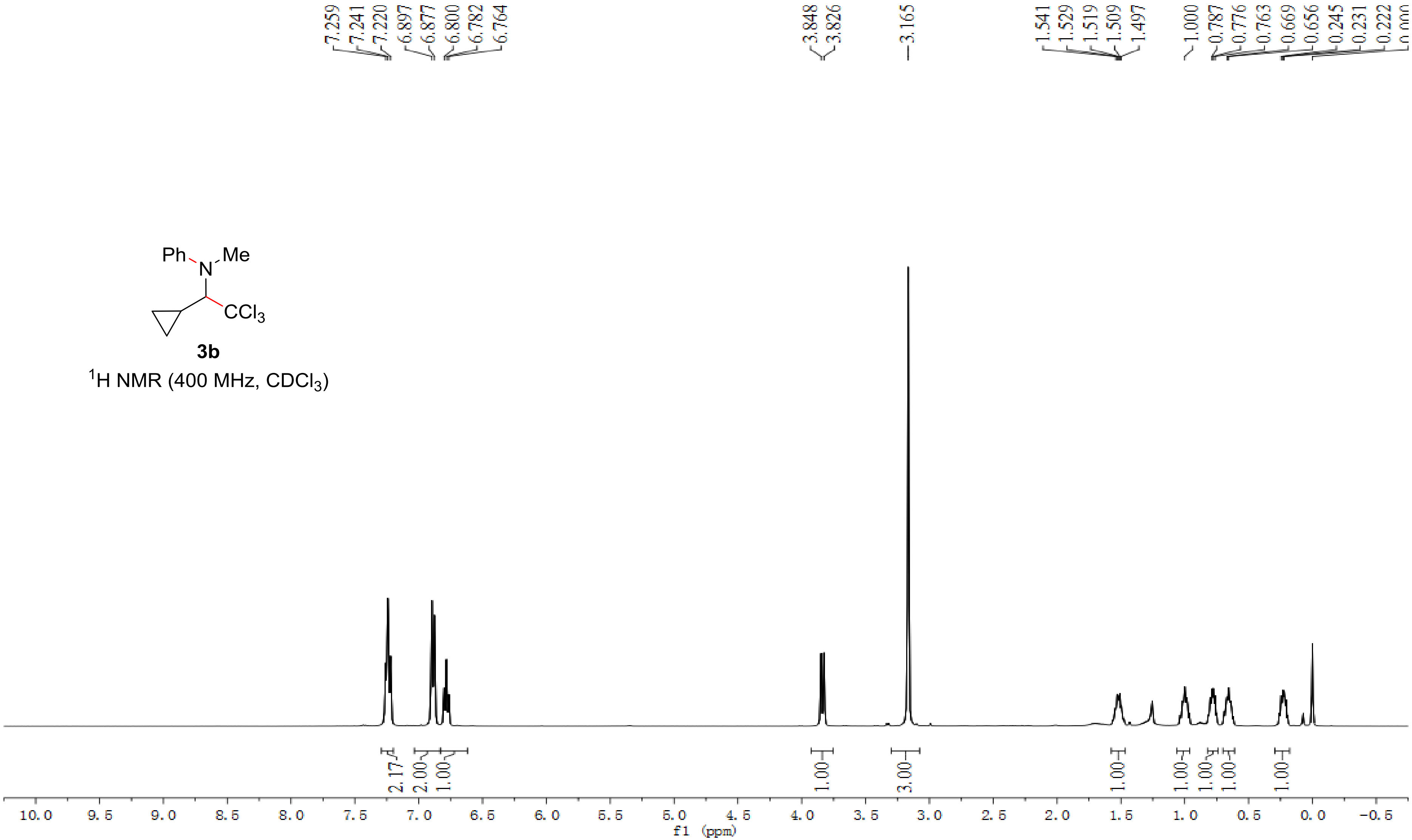
3a

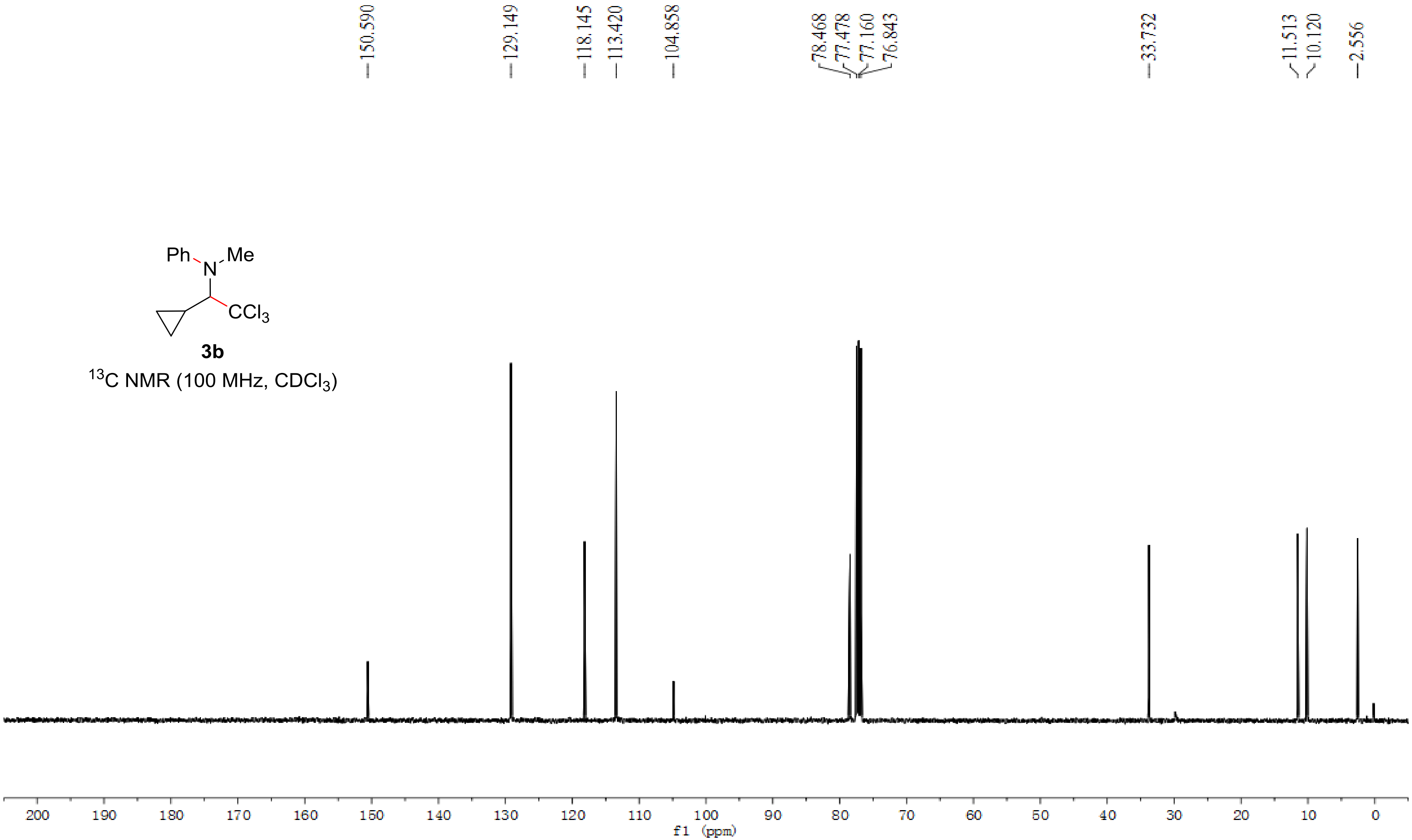
^{1}H NMR (400 MHz, $CDCl_3$)

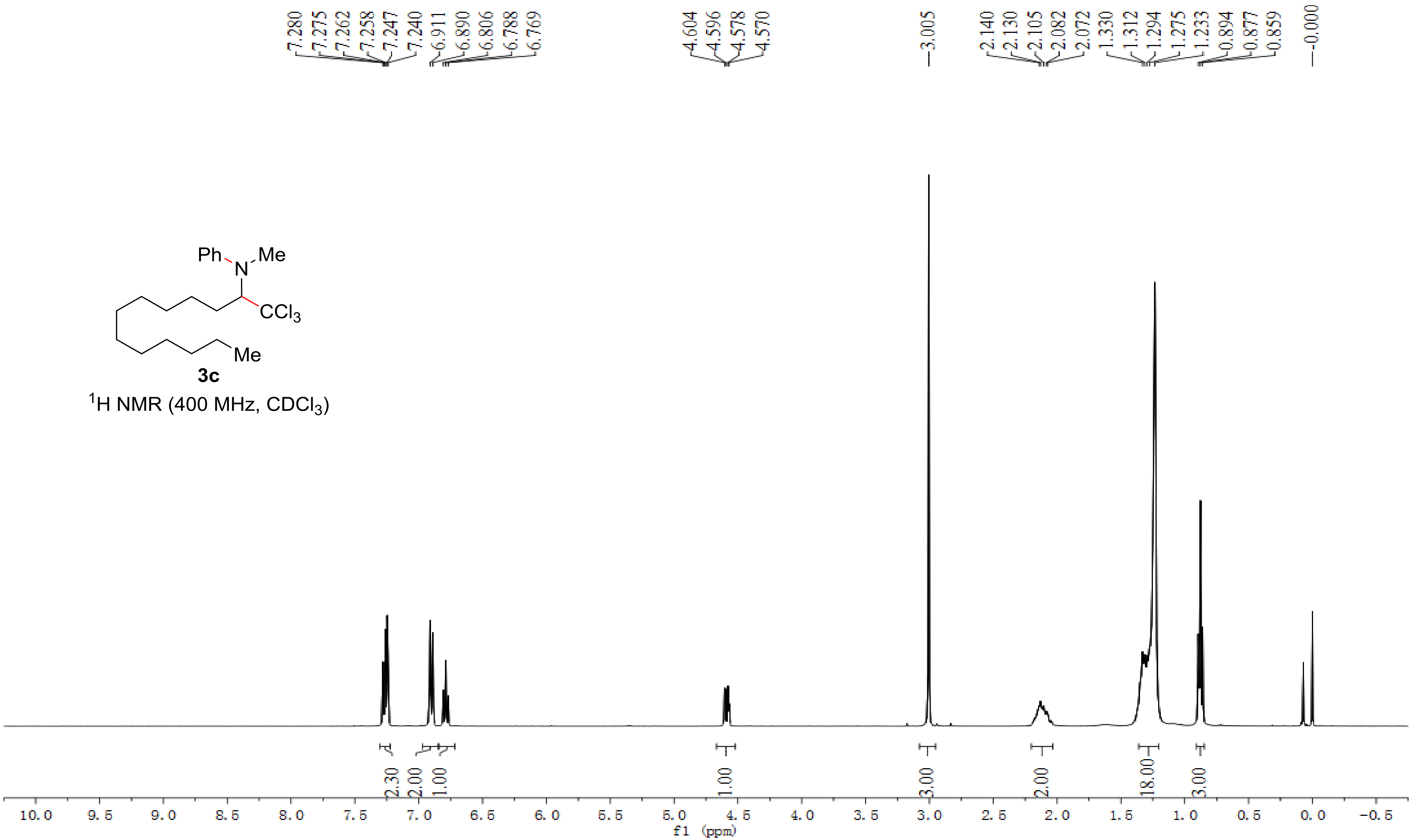


3a

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

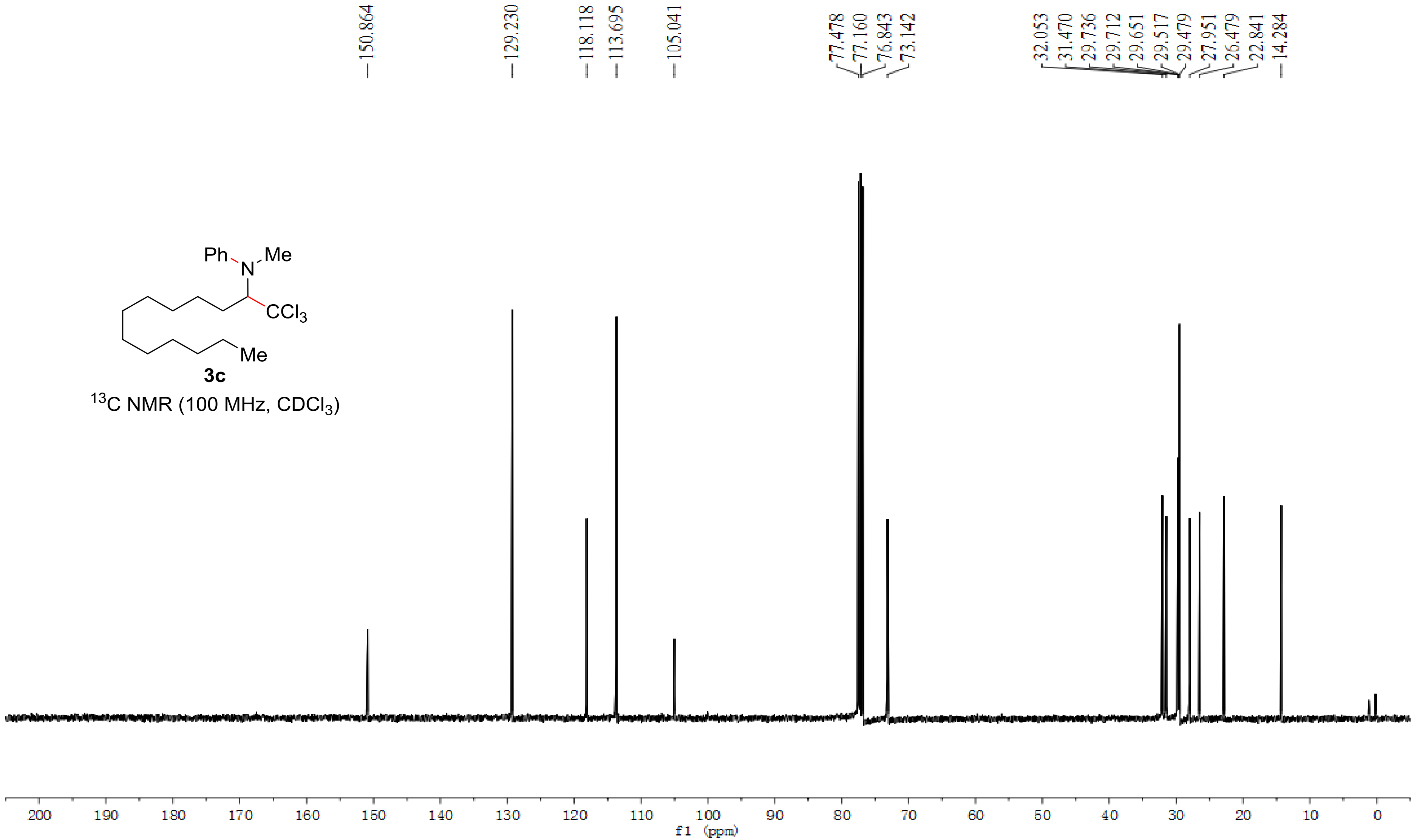

Ph
N
Me
CCl3
3b
1H NMR (400 MHz, CDCl3)
7.259
7.241
7.220
6.897
6.877
6.800
6.782
6.764
3.848
3.826
3.165
1.541
1.529
1.519
1.509
1.497
1.000
0.787
0.776
0.763
0.669
0.656
0.245
0.231
0.222
0.000
2.17
2.00
1.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

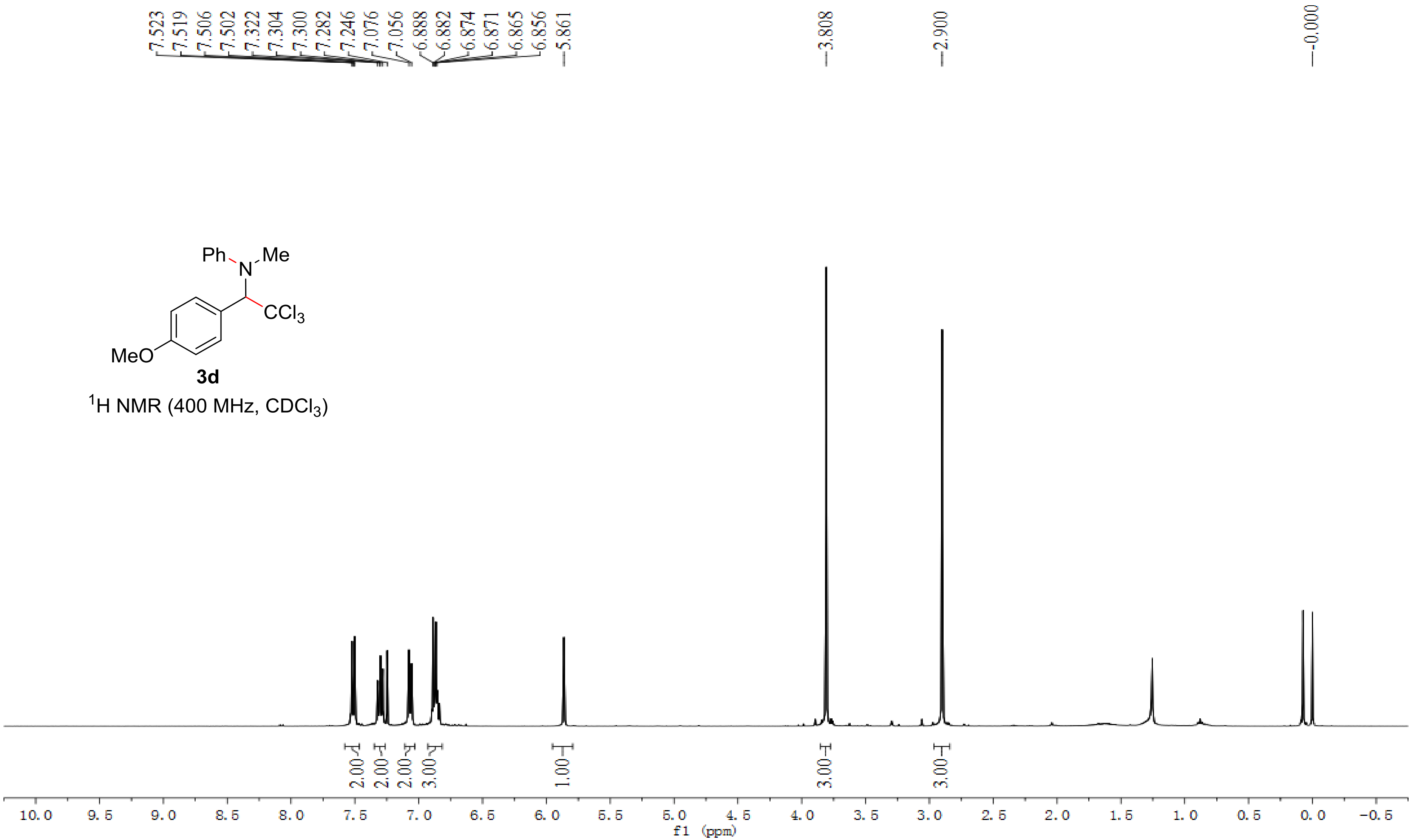

150.590
129.149
118.145
113.420
104.858
78.468
77.478
77.160
76.843
33.732
11.513
10.120
2.556
Ph
N
Me
CCl3
3b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

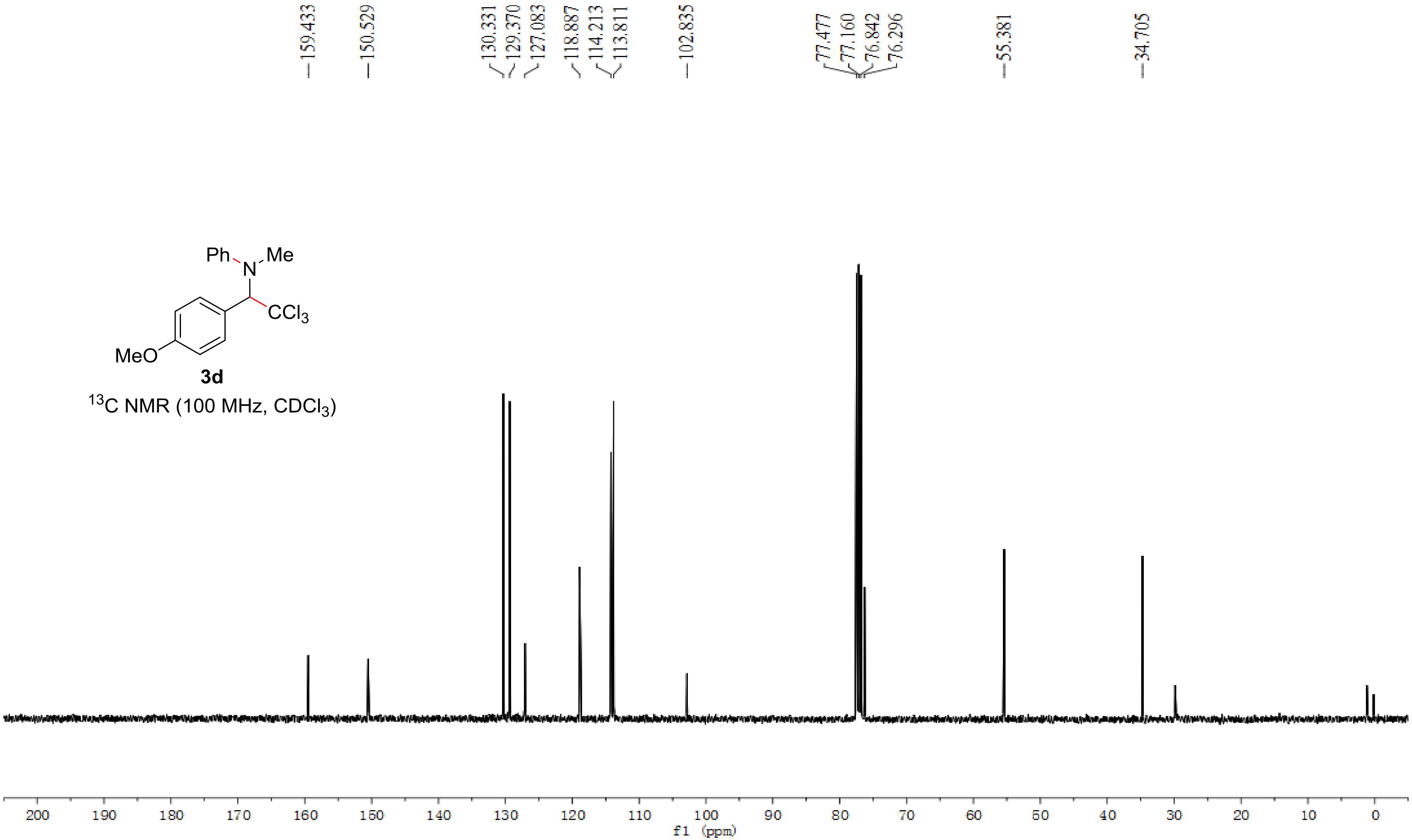


3c

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

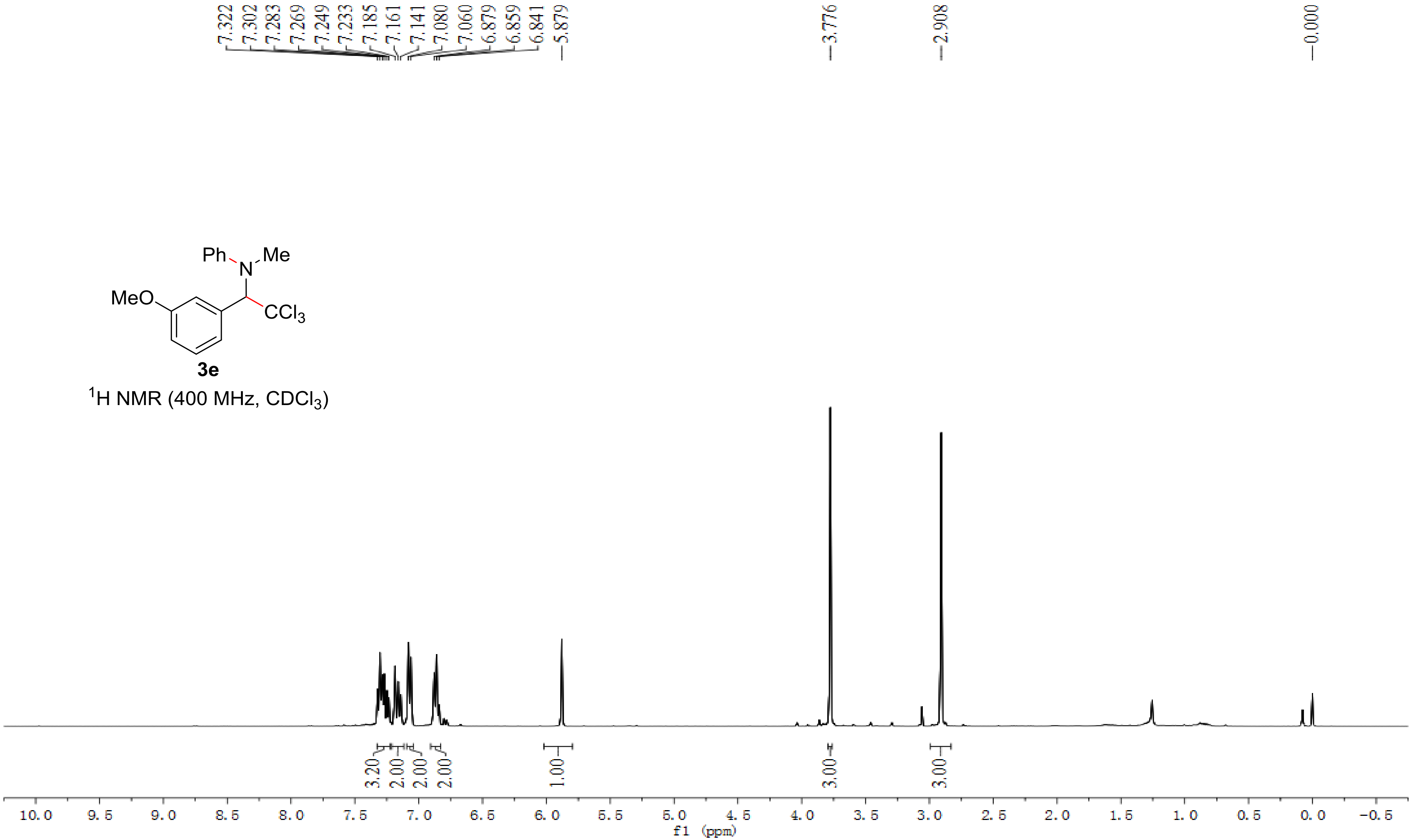

150.864
129.230
118.118
113.695
105.041
77.478
77.160
76.843
73.142
32.053
31.470
29.736
29.712
29.651
29.517
29.479
27.951
26.479
22.841
14.284
Ph
N
Me
CCl3
Me
3c
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.523
7.519
7.506
7.502
7.322
7.304
7.300
7.282
7.246
7.076
7.056
6.888
6.882
6.874
6.871
6.865
6.856
5.861
3.808
2.900
0.000
Ph
N
Me
CCl3
MeO
3d
1H NMR (400 MHz, CDCl3)
2.00
2.00
2.00
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
-0.5
f1 (ppm)

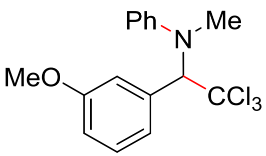


3d

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

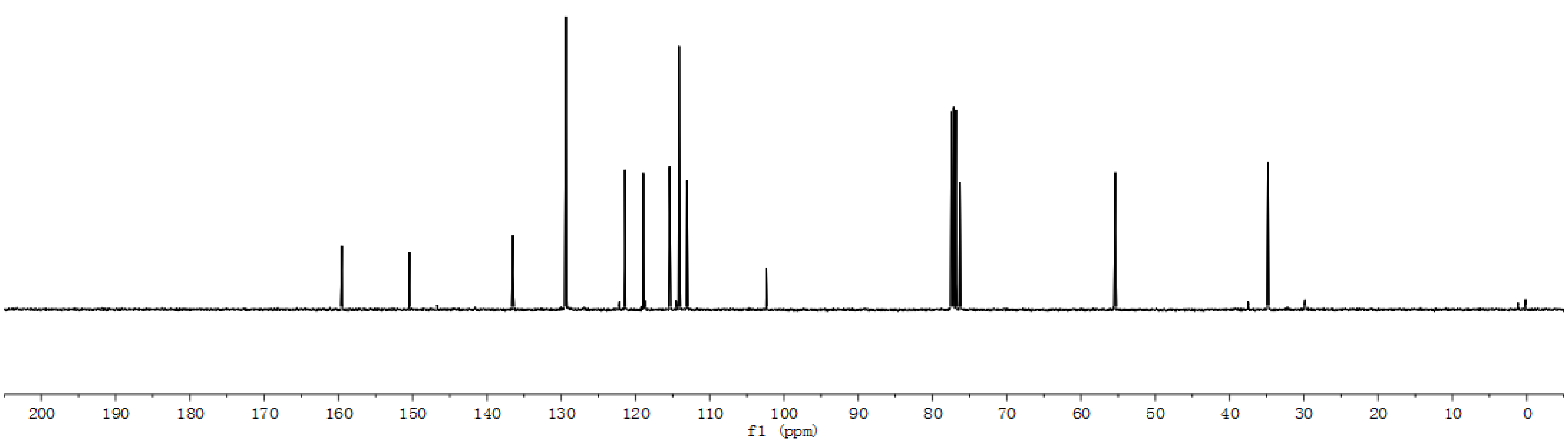


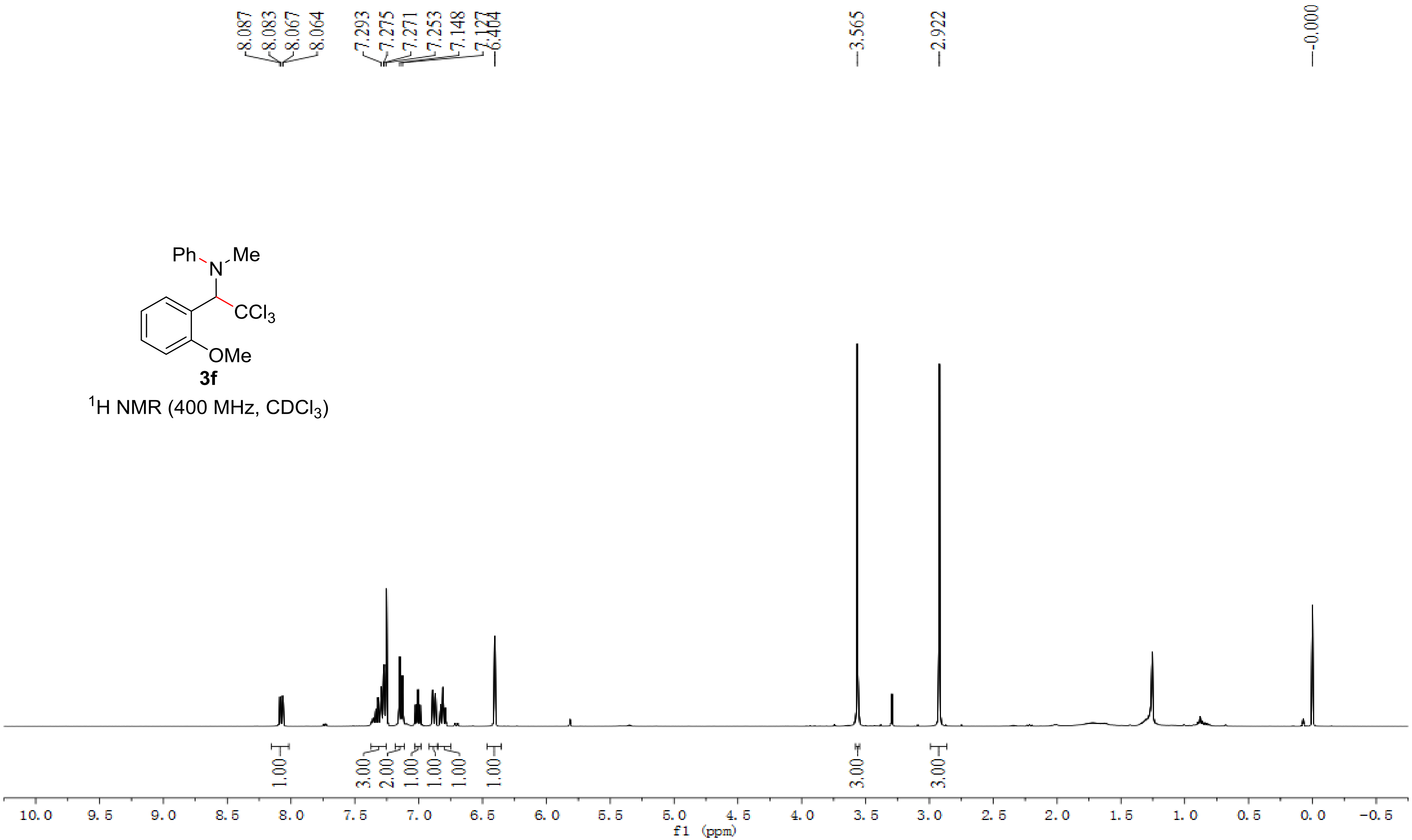
7.322
7.302
7.283
7.269
7.249
7.233
7.185
7.161
7.141
7.080
7.060
6.879
6.859
6.841
5.879
3.776
2.908
0.000
Ph
N
Me
MeO
CCl3
3e
1H NMR (400 MHz, CDCl3)
3.20
2.00
2.00
2.00
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



3e

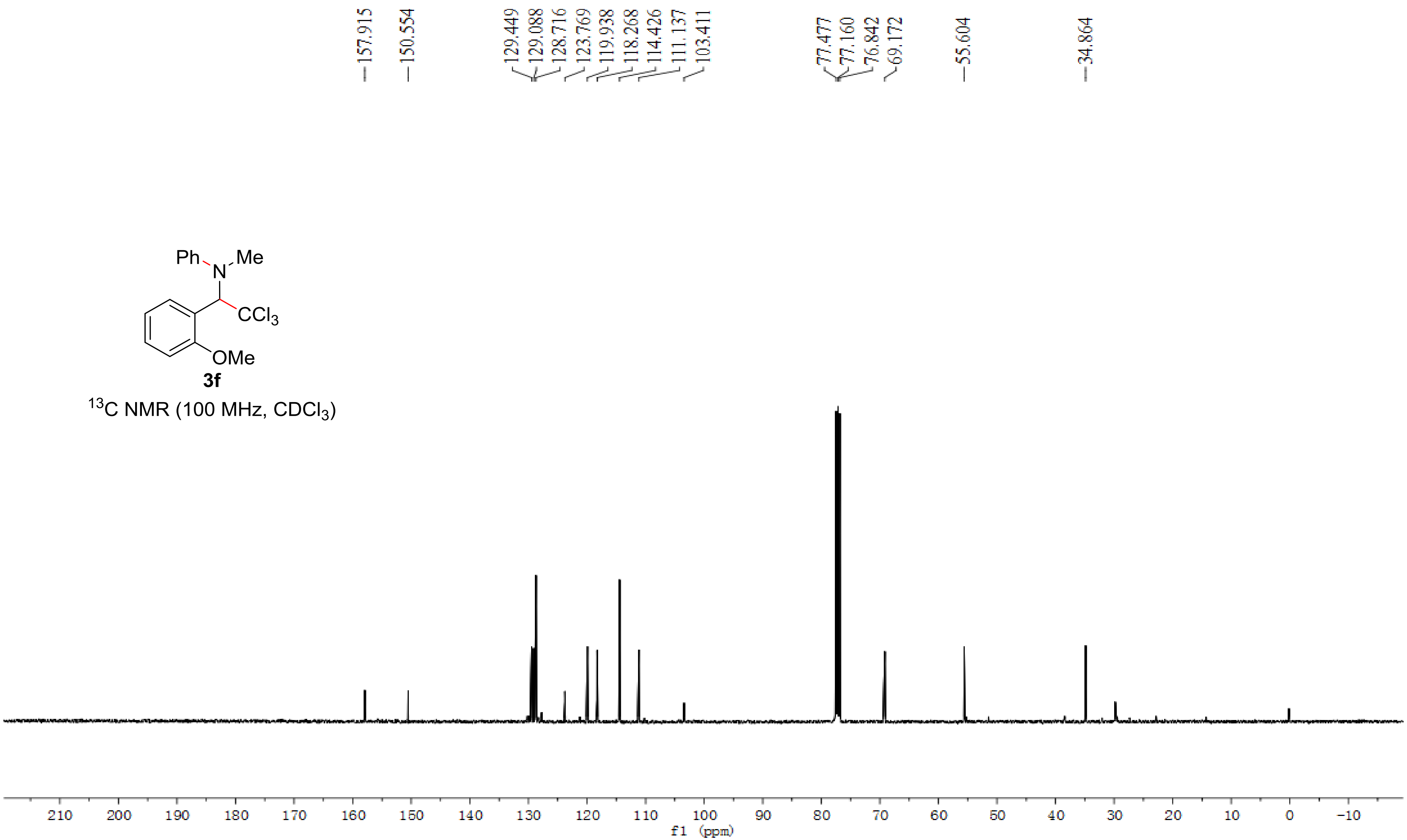
^{13}C NMR (100 MHz, $CDCl_3$)





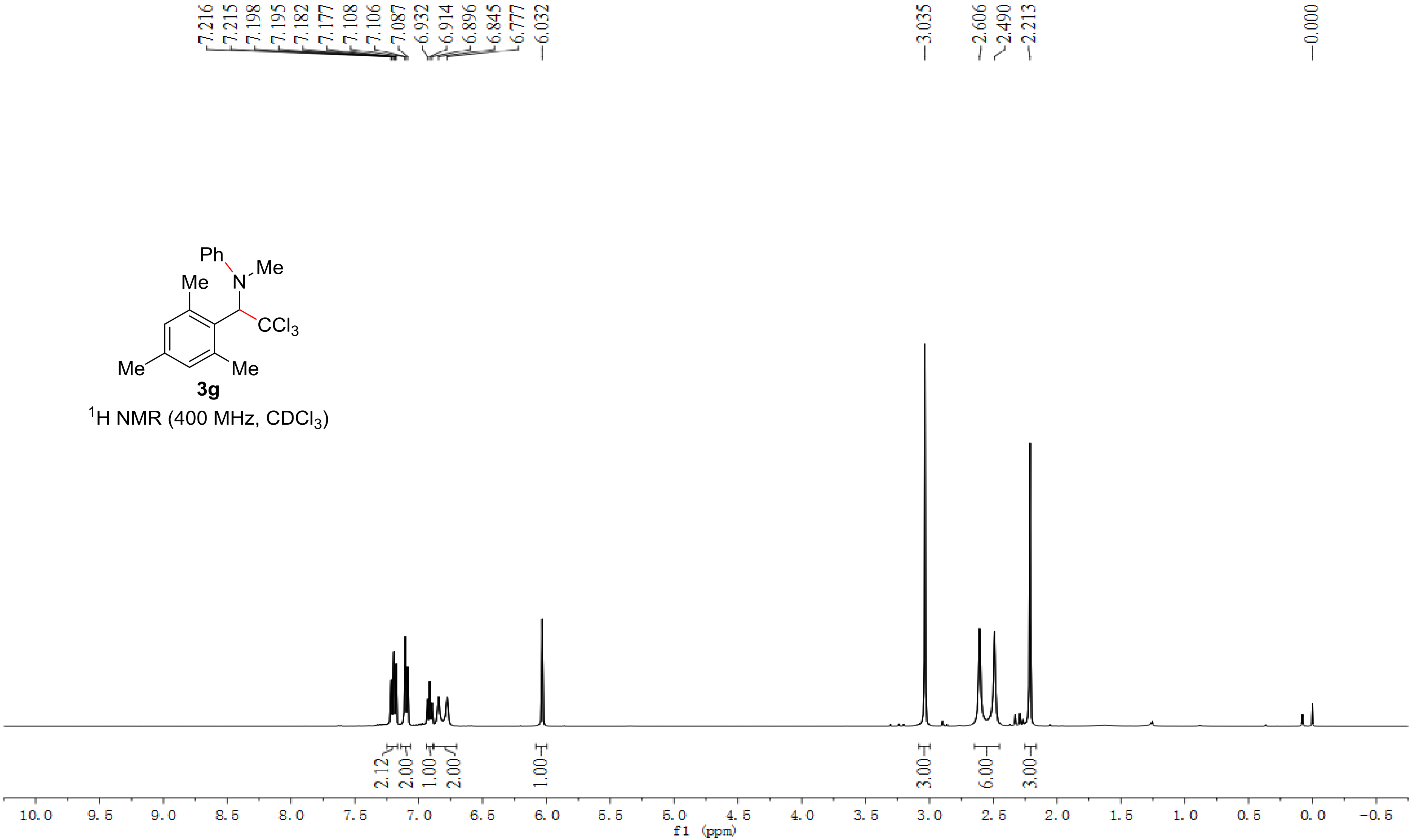
3f

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



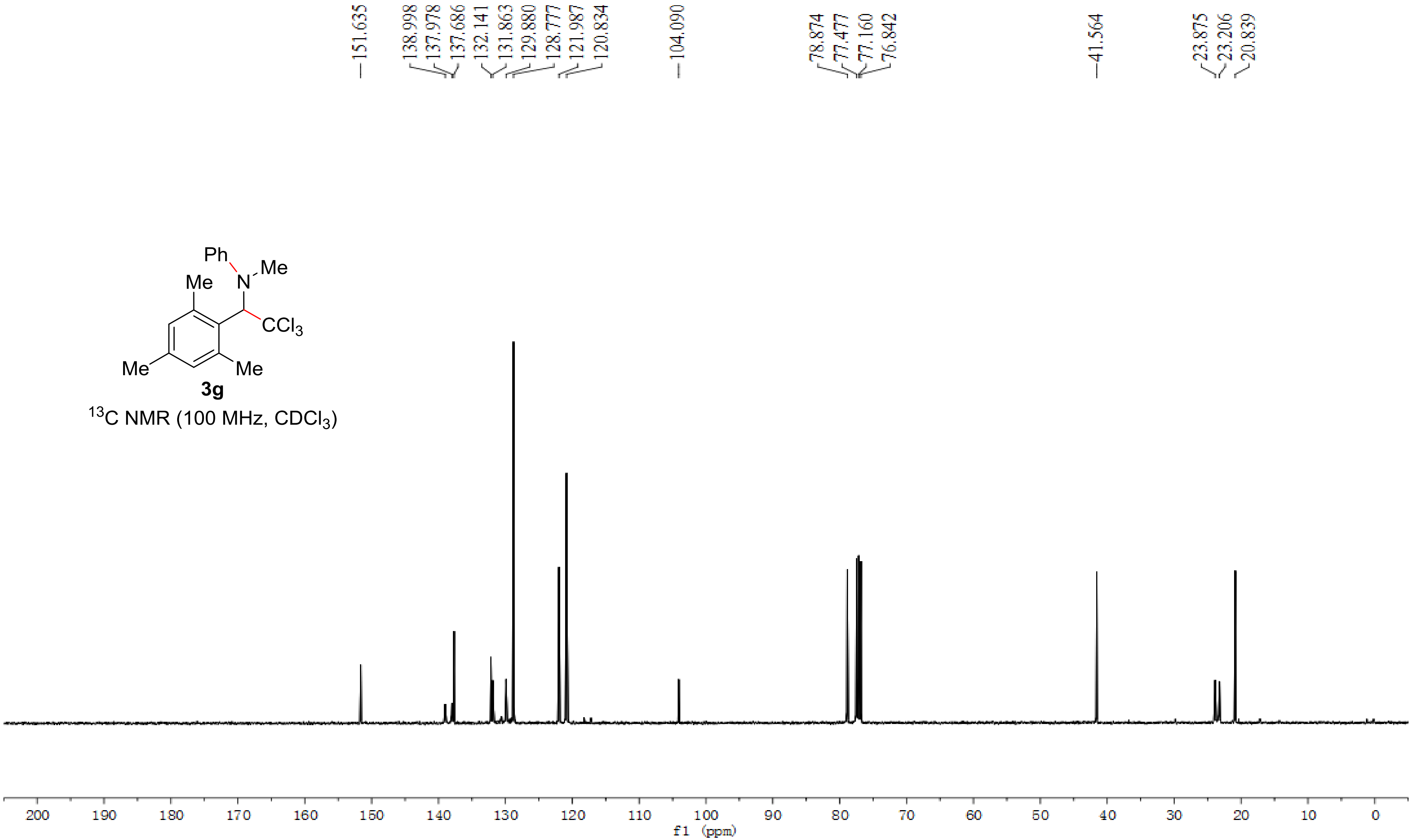
3f

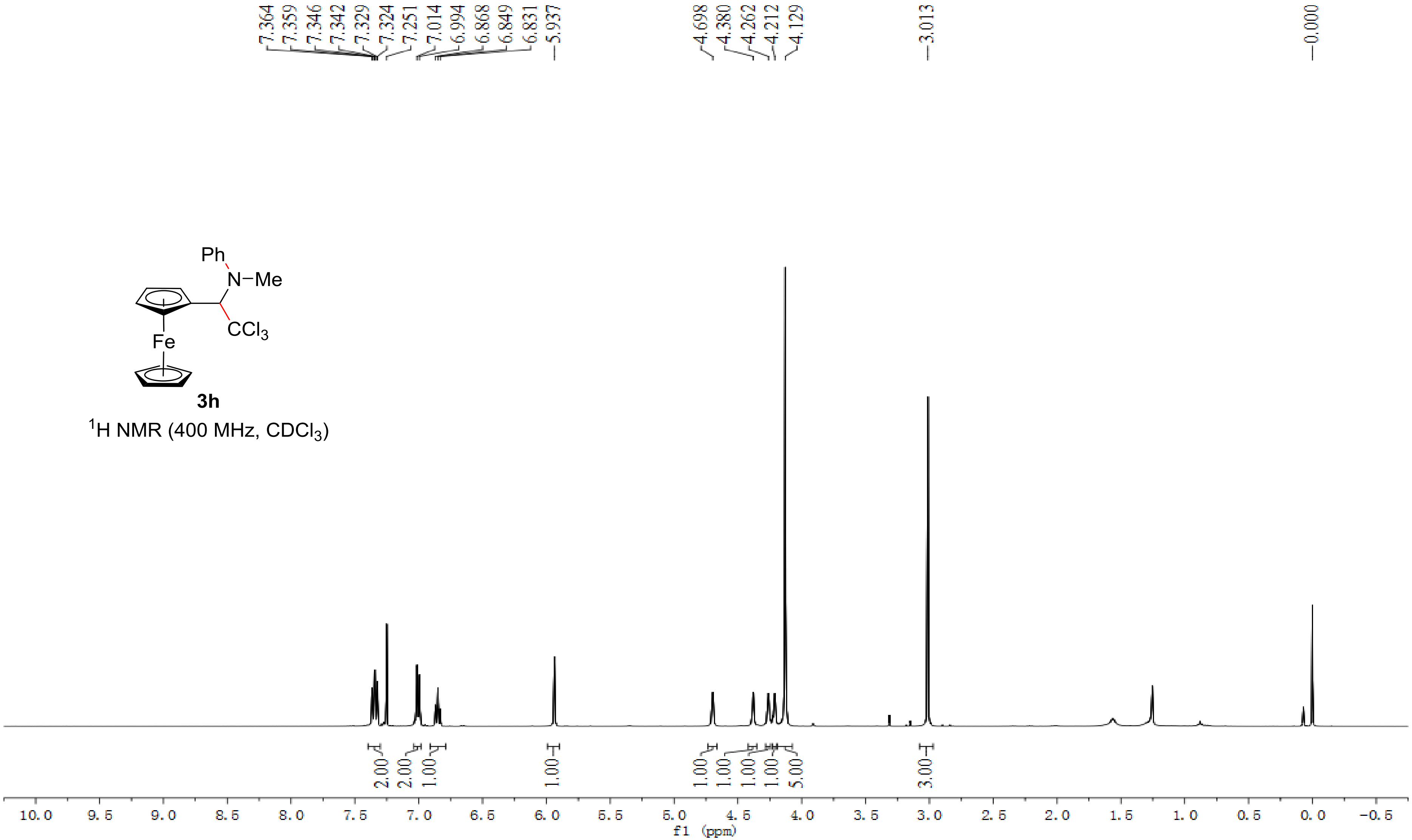
^{13}C NMR (100 MHz, $CDCl_3$)



3g

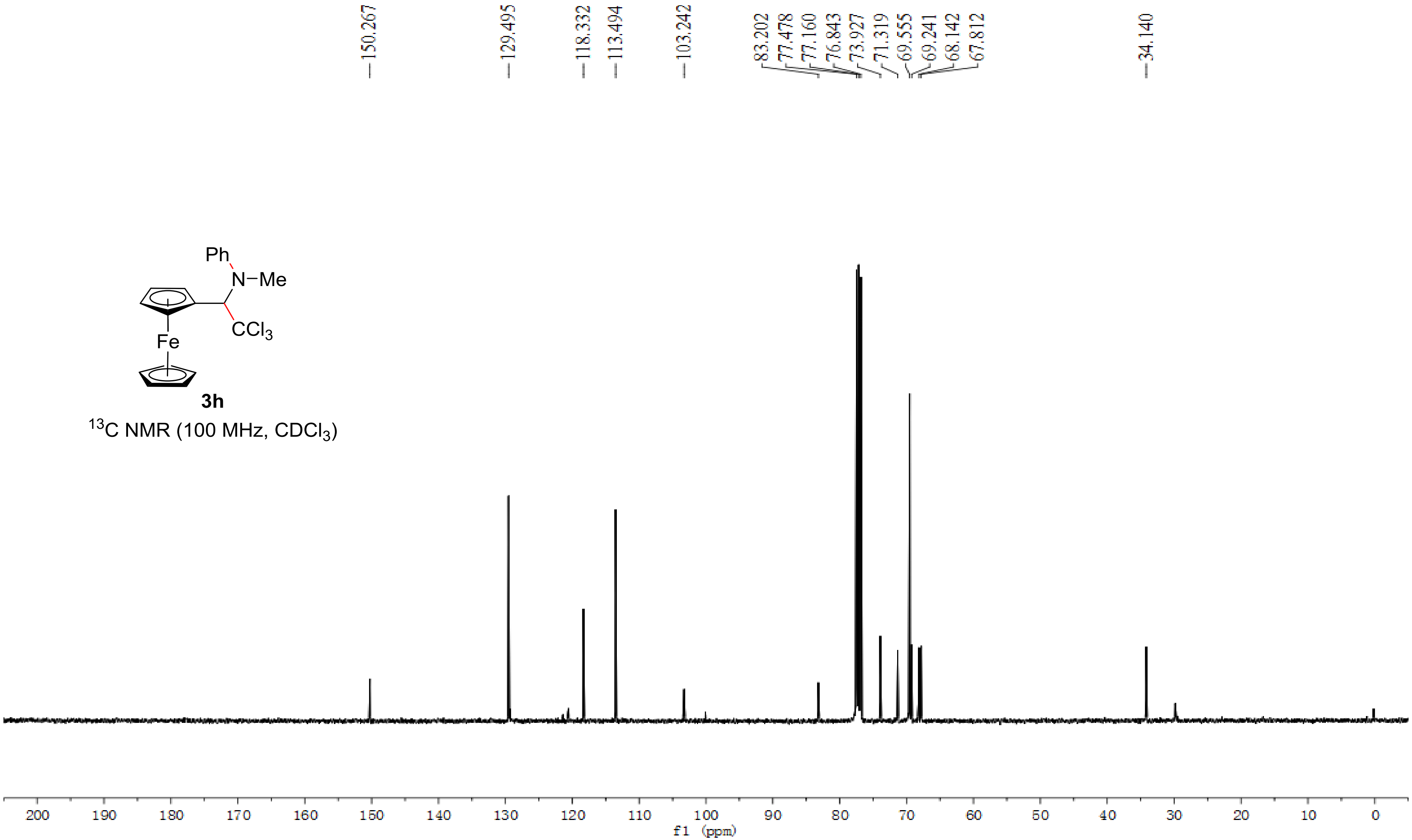
^{1}H NMR (400 MHz, $CDCl_3$)


151.635
138.998
137.978
137.686
132.141
131.863
129.880
128.777
121.987
120.834
104.090
78.874
77.477
77.160
76.842
41.564
23.875
23.206
20.839
Ph
N
Me
Me
CCl3
Me
Me
3g
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)



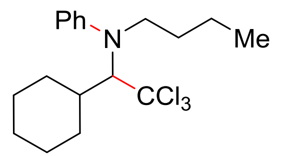
3h

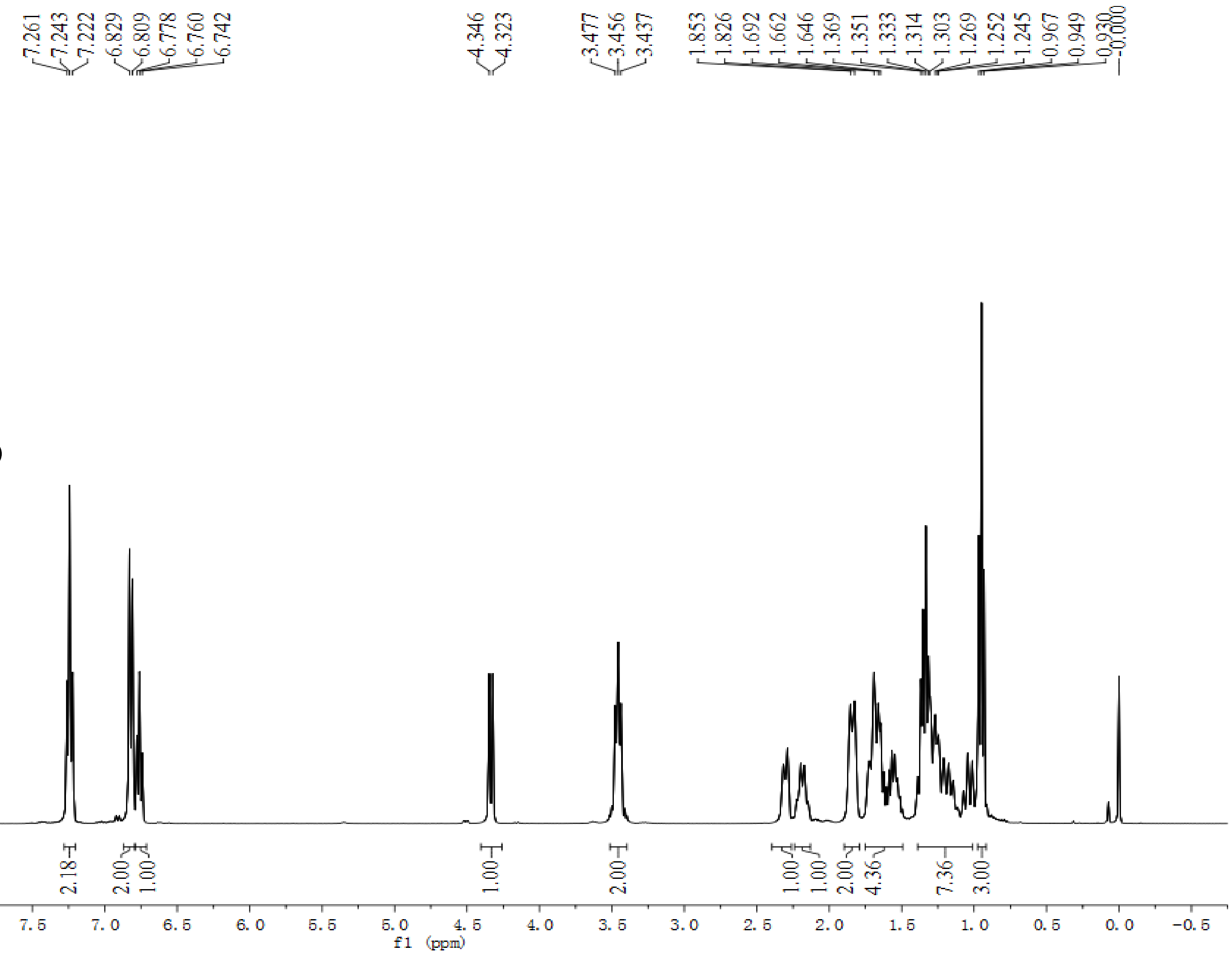
^1H NMR (400 MHz, $CDCl_3$)



3h

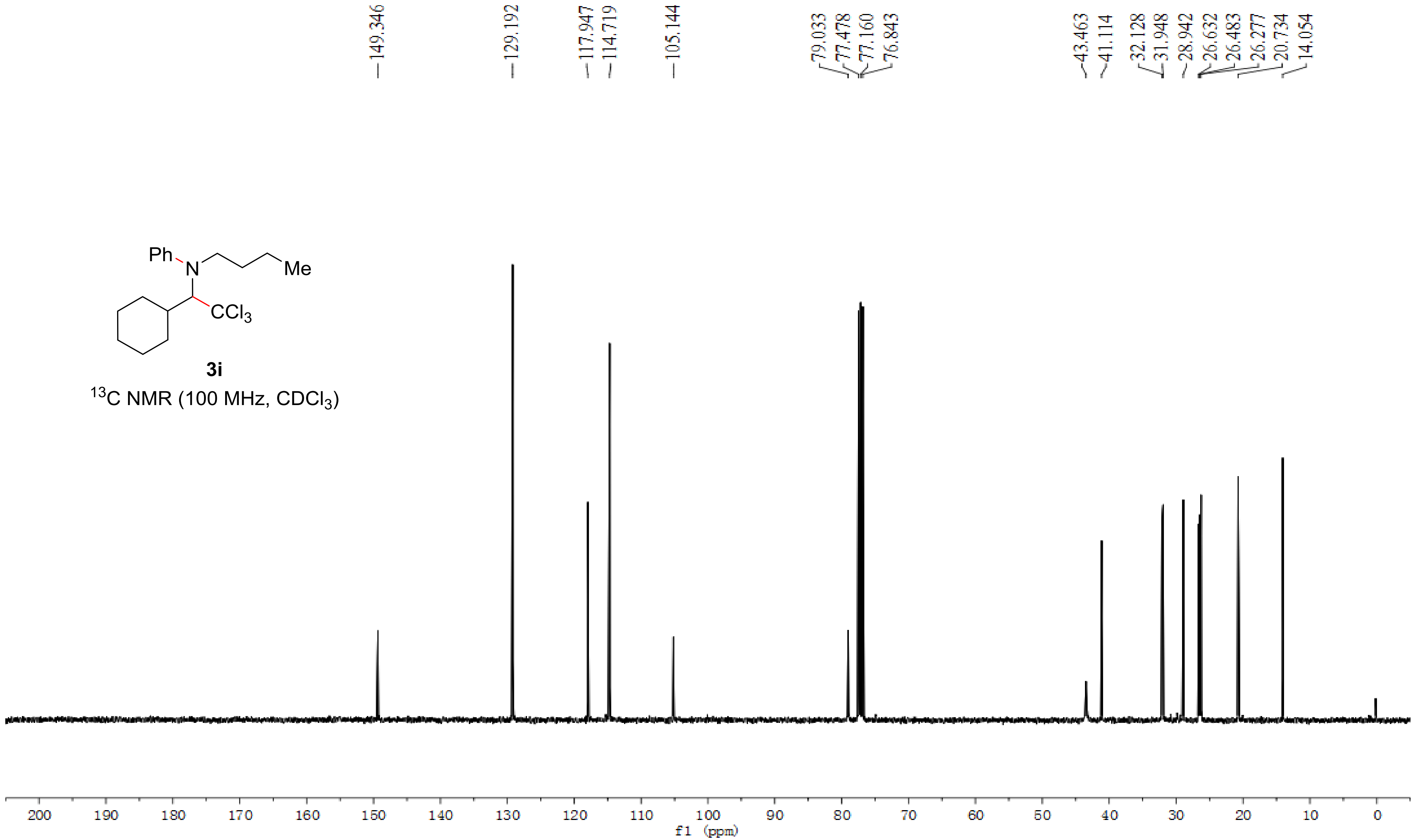
^{13}C NMR (100 MHz, $CDCl_3$)

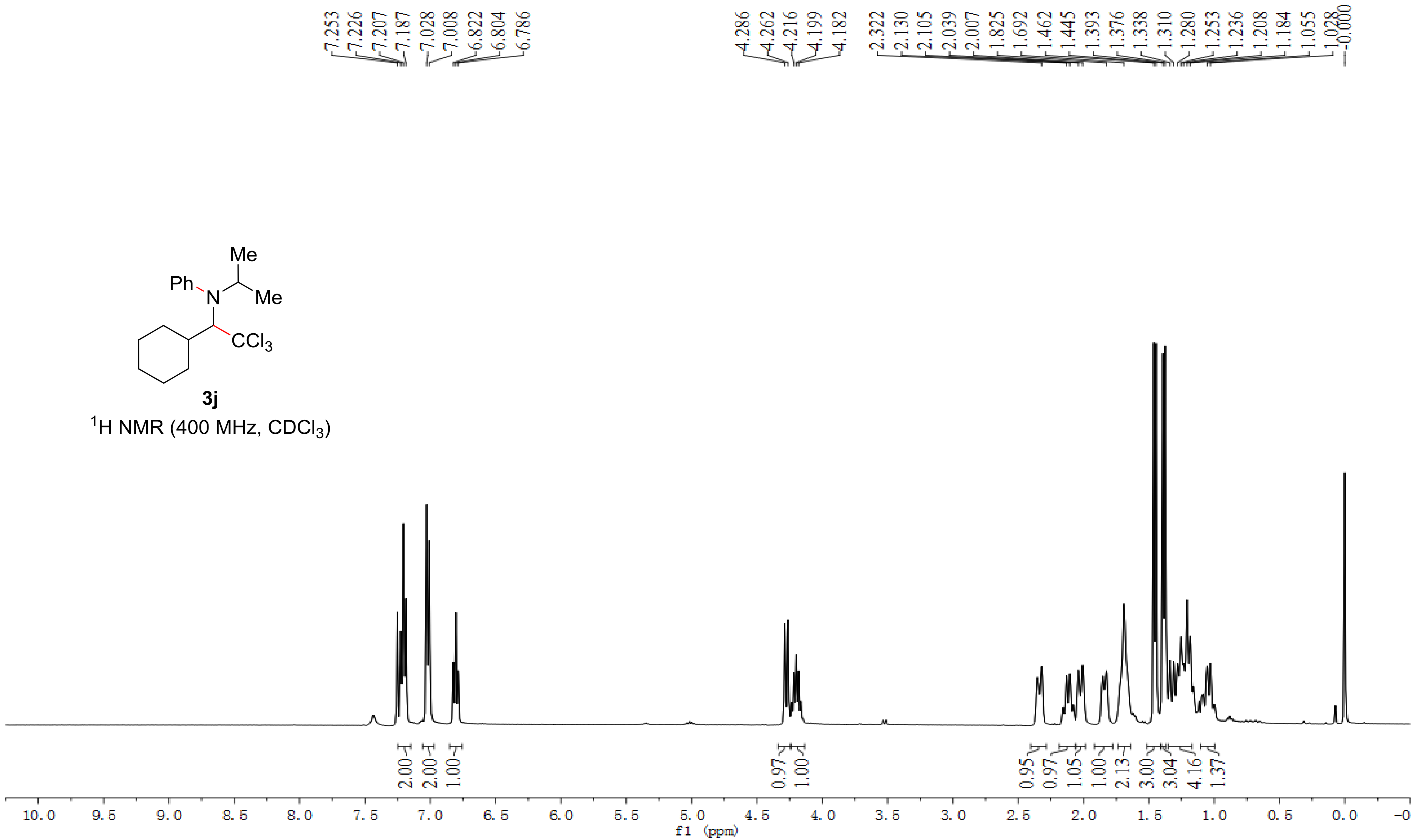




3i

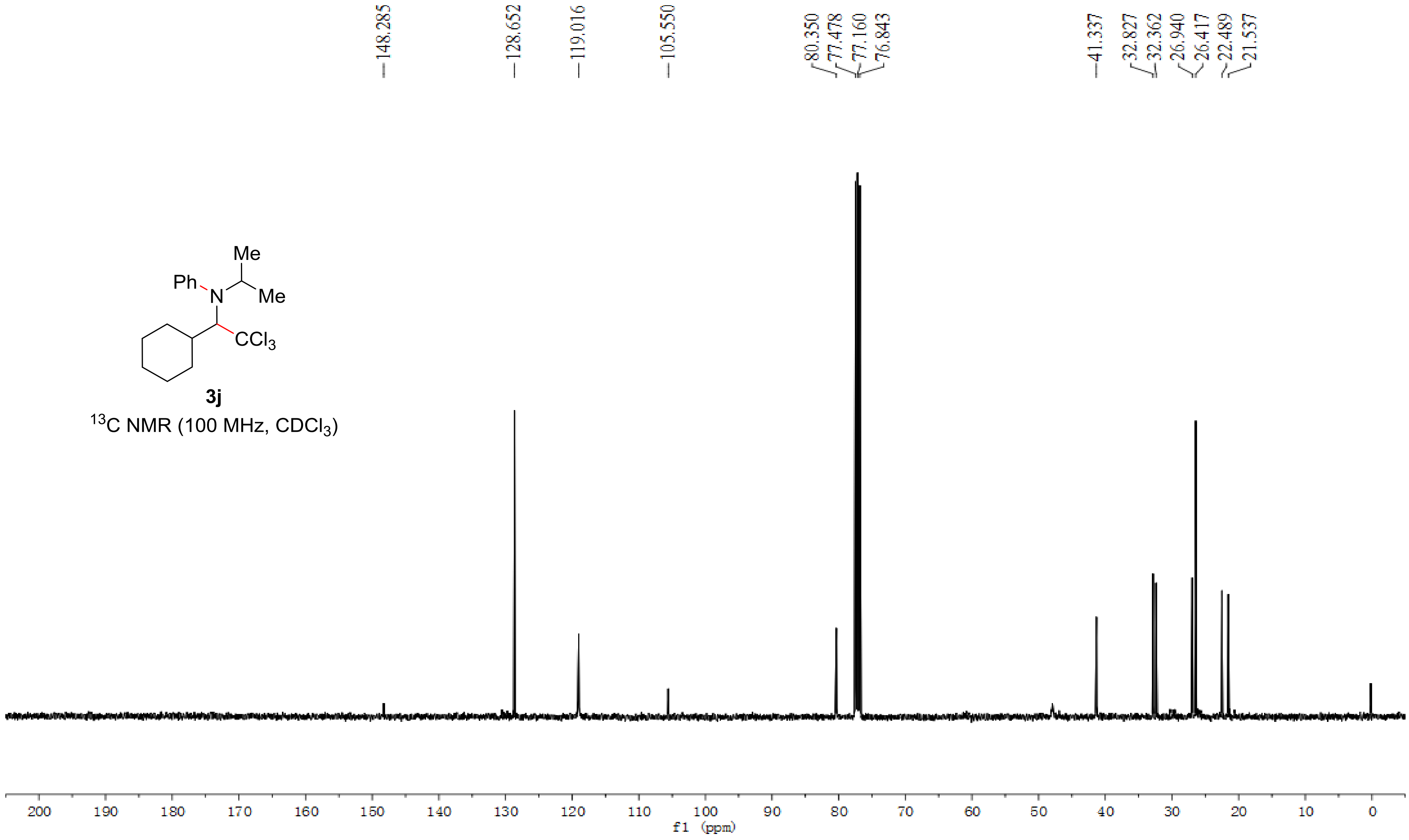
^{1}H NMR (400 MHz, $CDCl_3$)

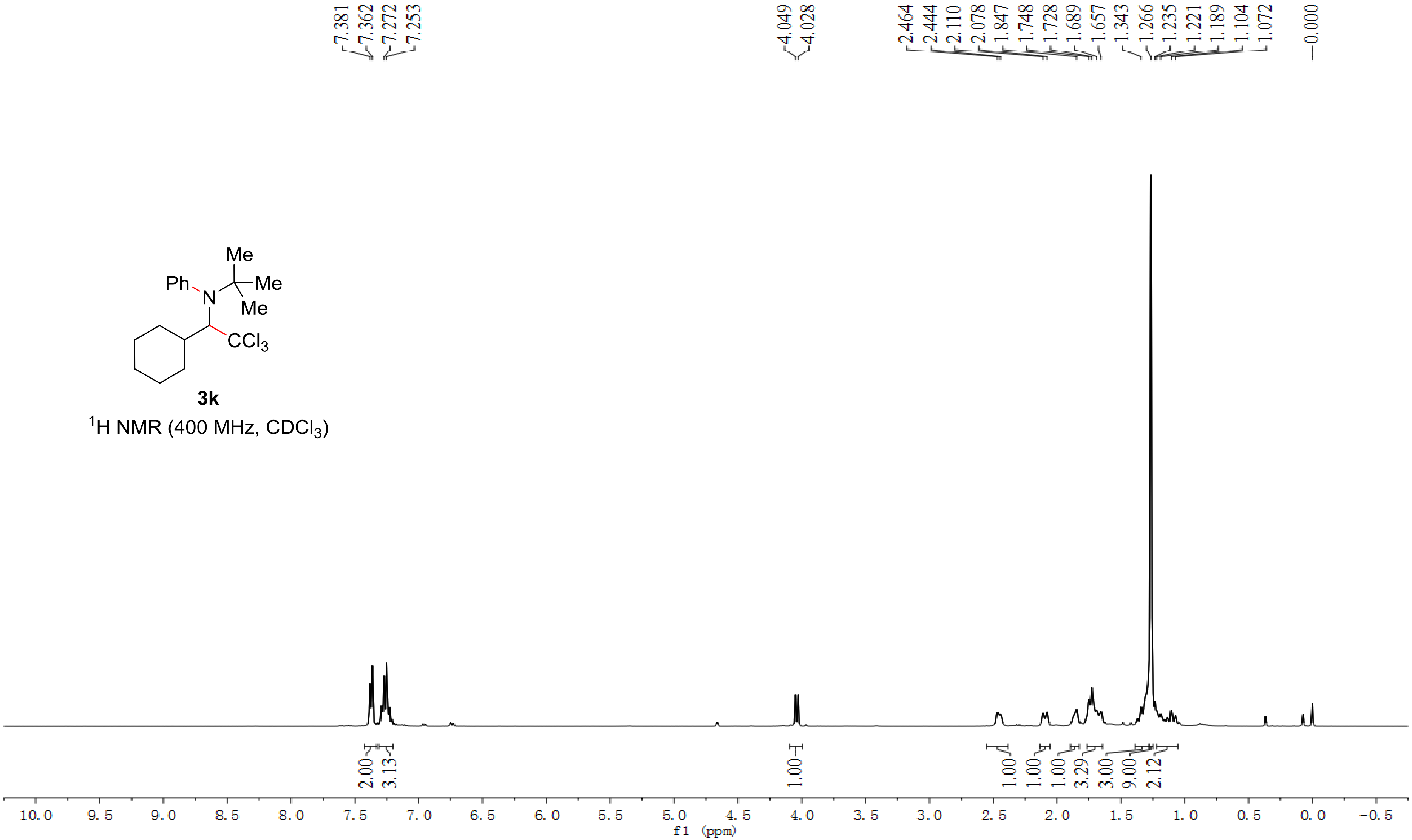

149.346
129.192
117.947
114.719
105.144
79.033
77.478
77.160
76.843
43.463
41.114
32.128
31.948
28.942
26.632
26.483
26.277
20.734
14.054
Ph
N
Me
CCl3
3i
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3j

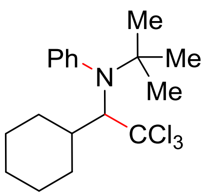
^{1}H NMR (400 MHz, $CDCl_3$)


148.285
128.652
119.016
105.550
80.350
77.478
77.160
76.843
41.337
32.827
32.362
26.940
26.417
22.489
21.537
Ph
N
Me
Me
CCl3
3j
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)



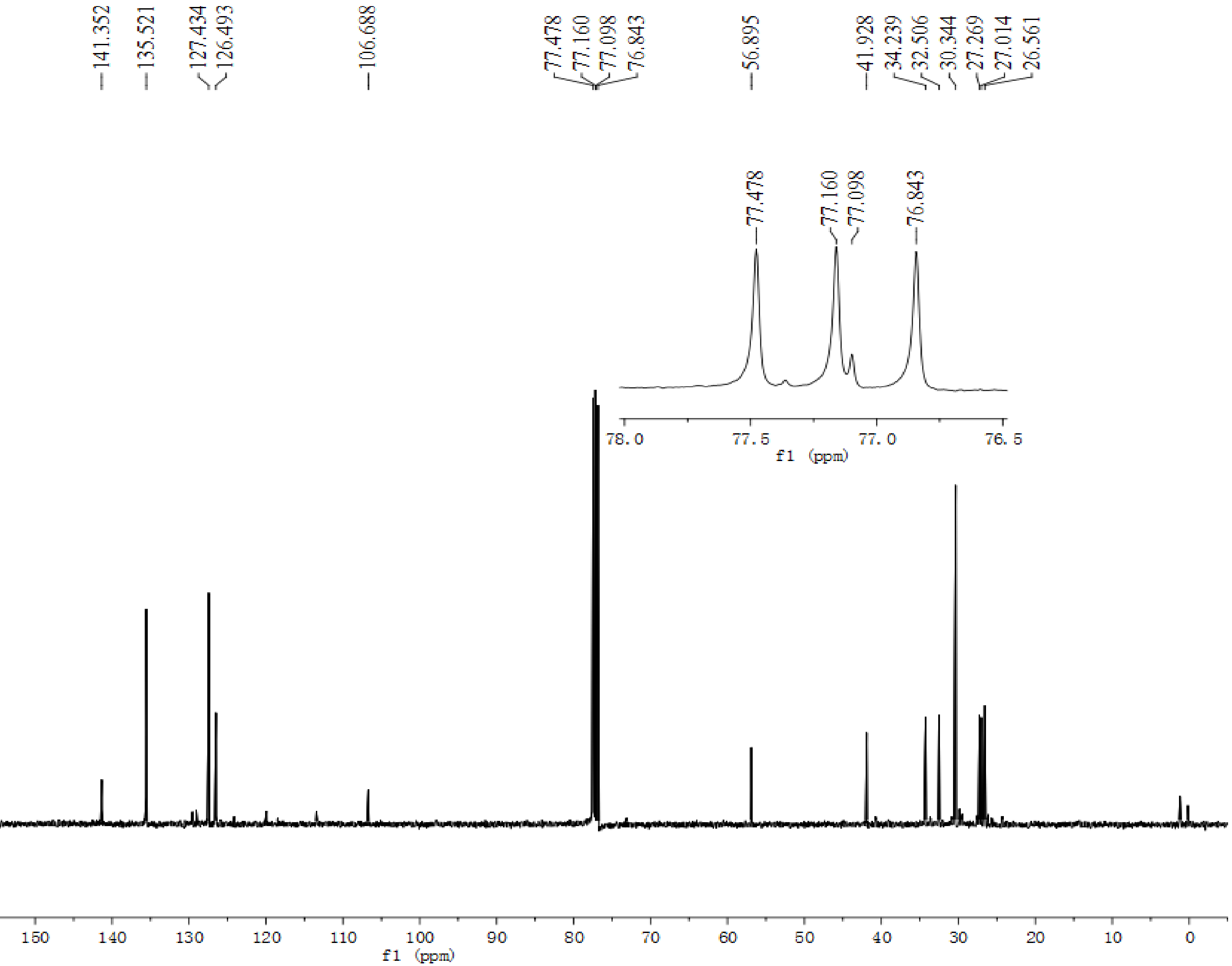
3k

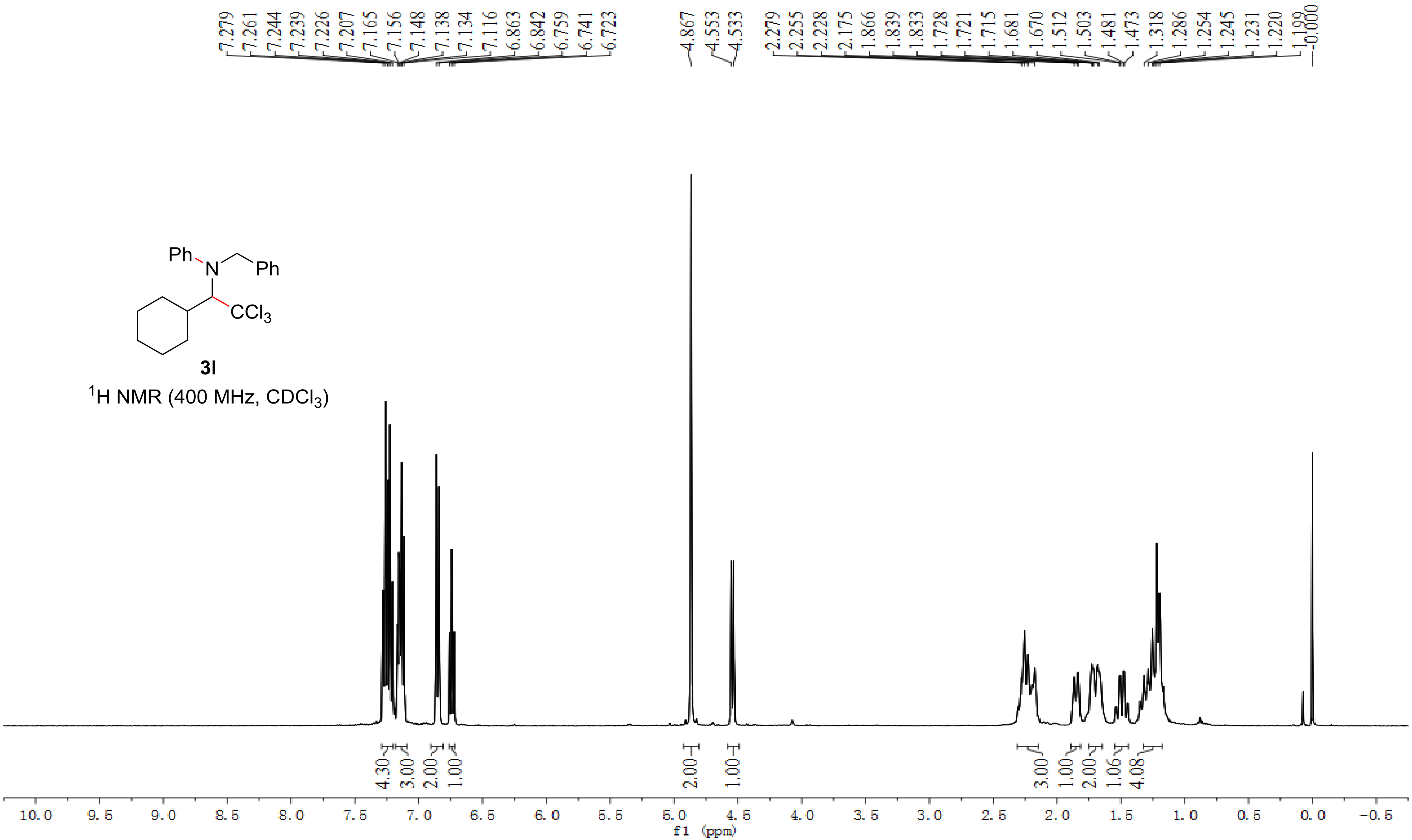
^{1}H NMR (400 MHz, $CDCl_3$)



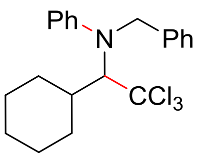
3k

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



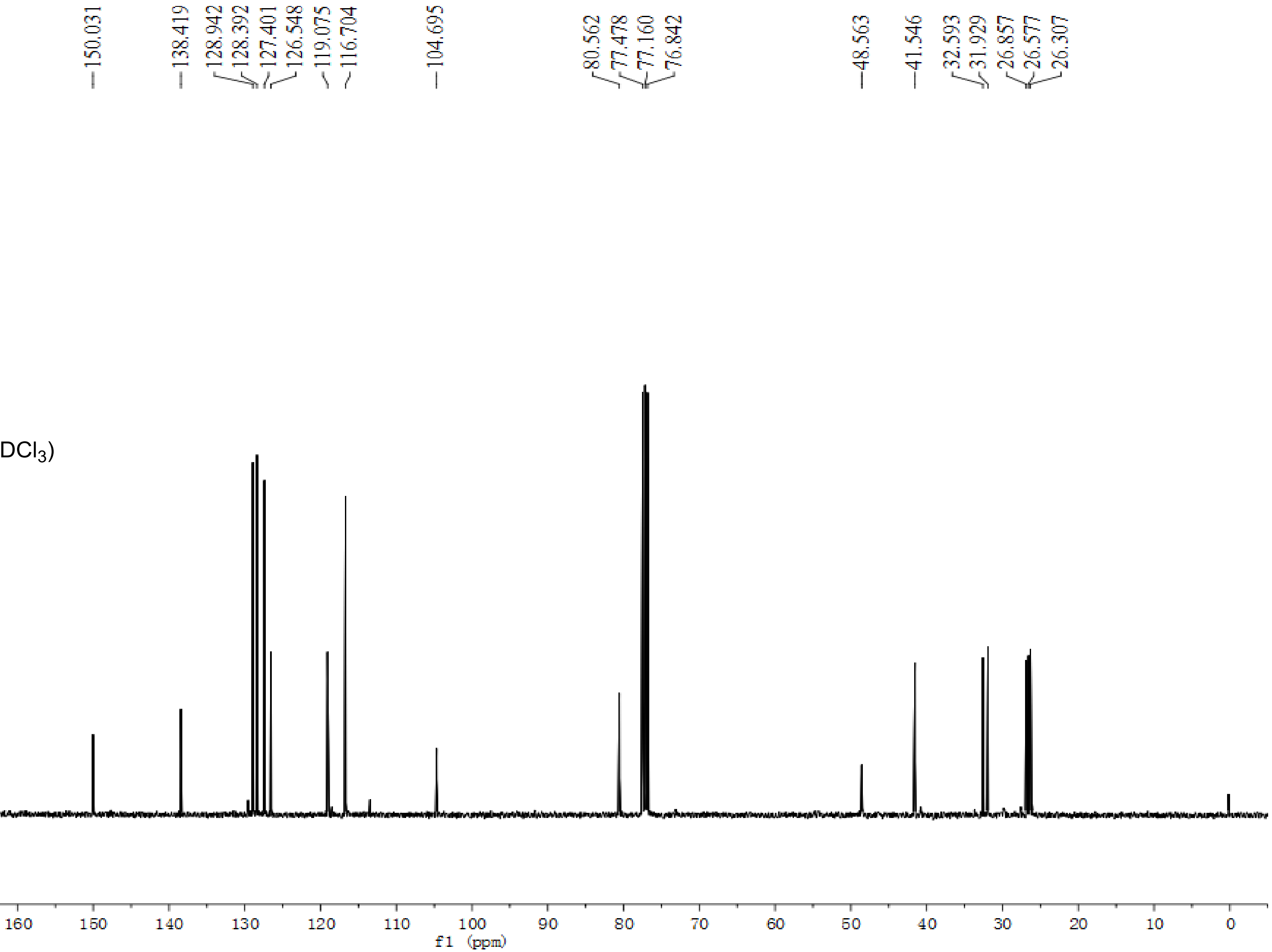


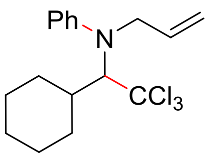
7.279
7.261
7.244
7.239
7.226
7.207
7.165
7.156
7.148
7.138
7.134
7.116
6.863
6.842
6.759
6.741
6.723
4.867
4.553
4.533
2.279
2.255
2.228
2.175
1.866
1.839
1.833
1.728
1.721
1.715
1.681
1.670
1.512
1.503
1.481
1.473
1.318
1.286
1.254
1.245
1.231
1.220
1.199
0.000
Ph
N
Ph
CCl3
3l
1H NMR (400 MHz, CDCl3)
4.30
3.00
2.00
1.00
2.00
1.00
3.00
1.00
2.00
1.06
4.08
f1 (ppm)



3l

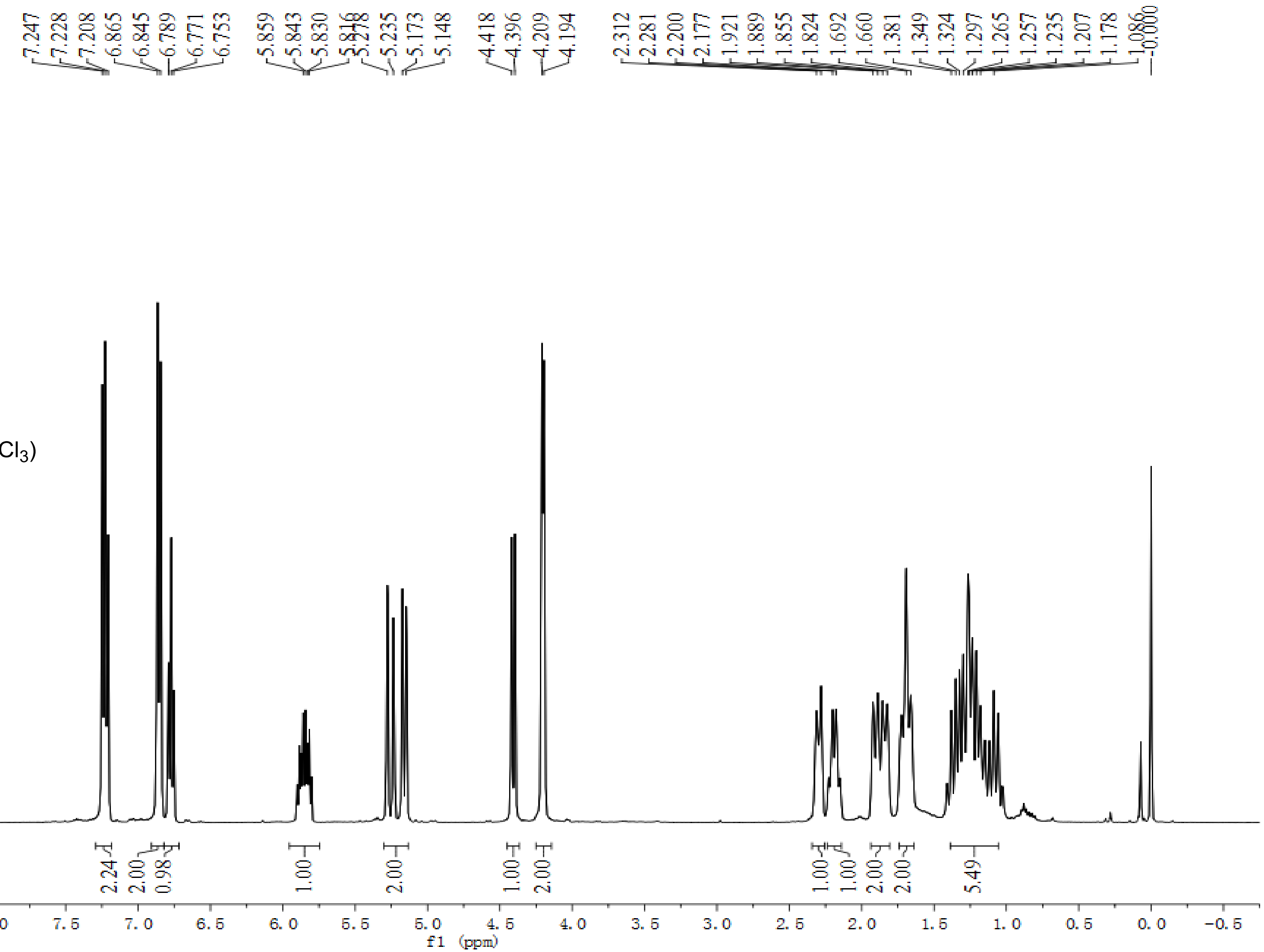
^{13}C NMR (100 MHz, $CDCl_3$)

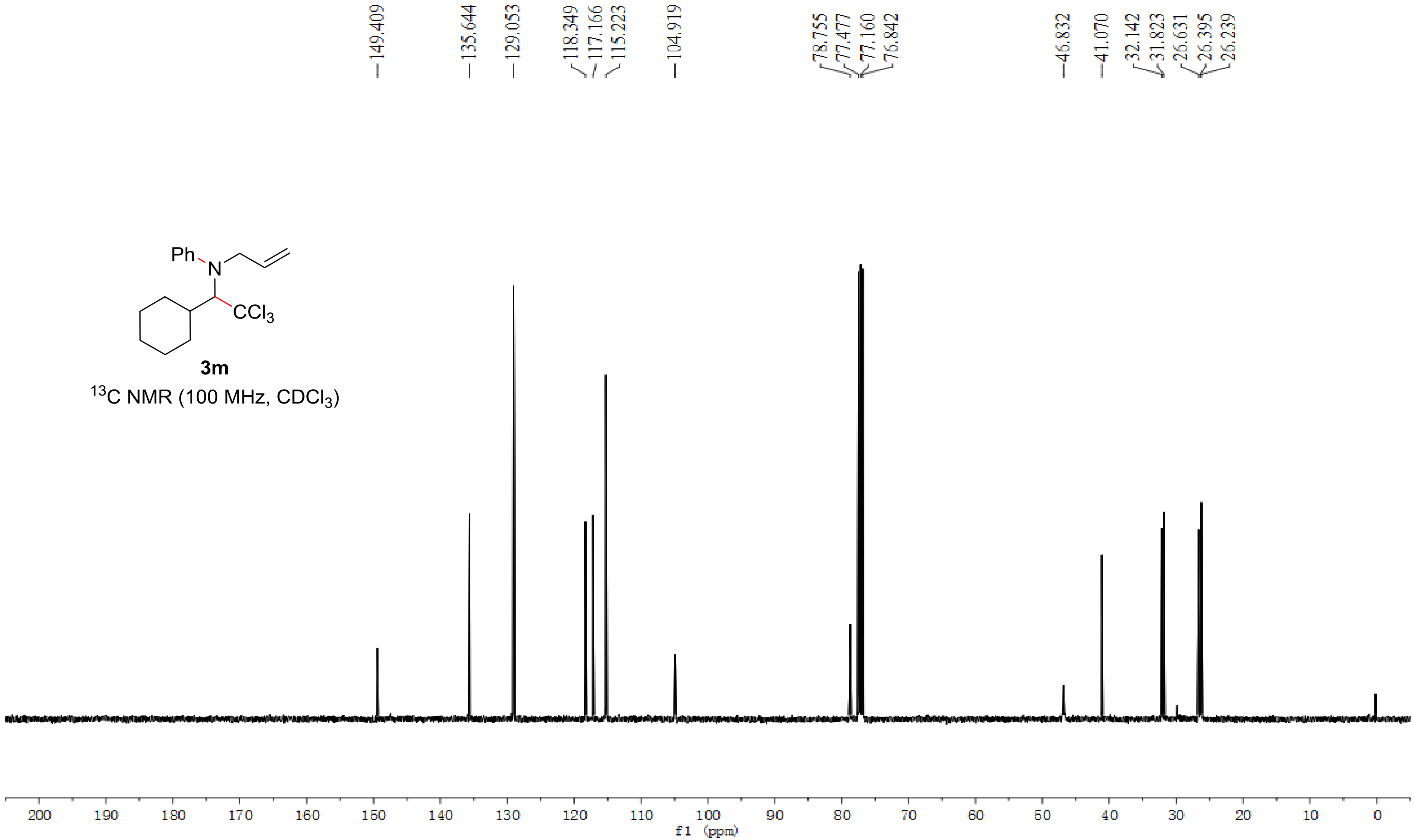




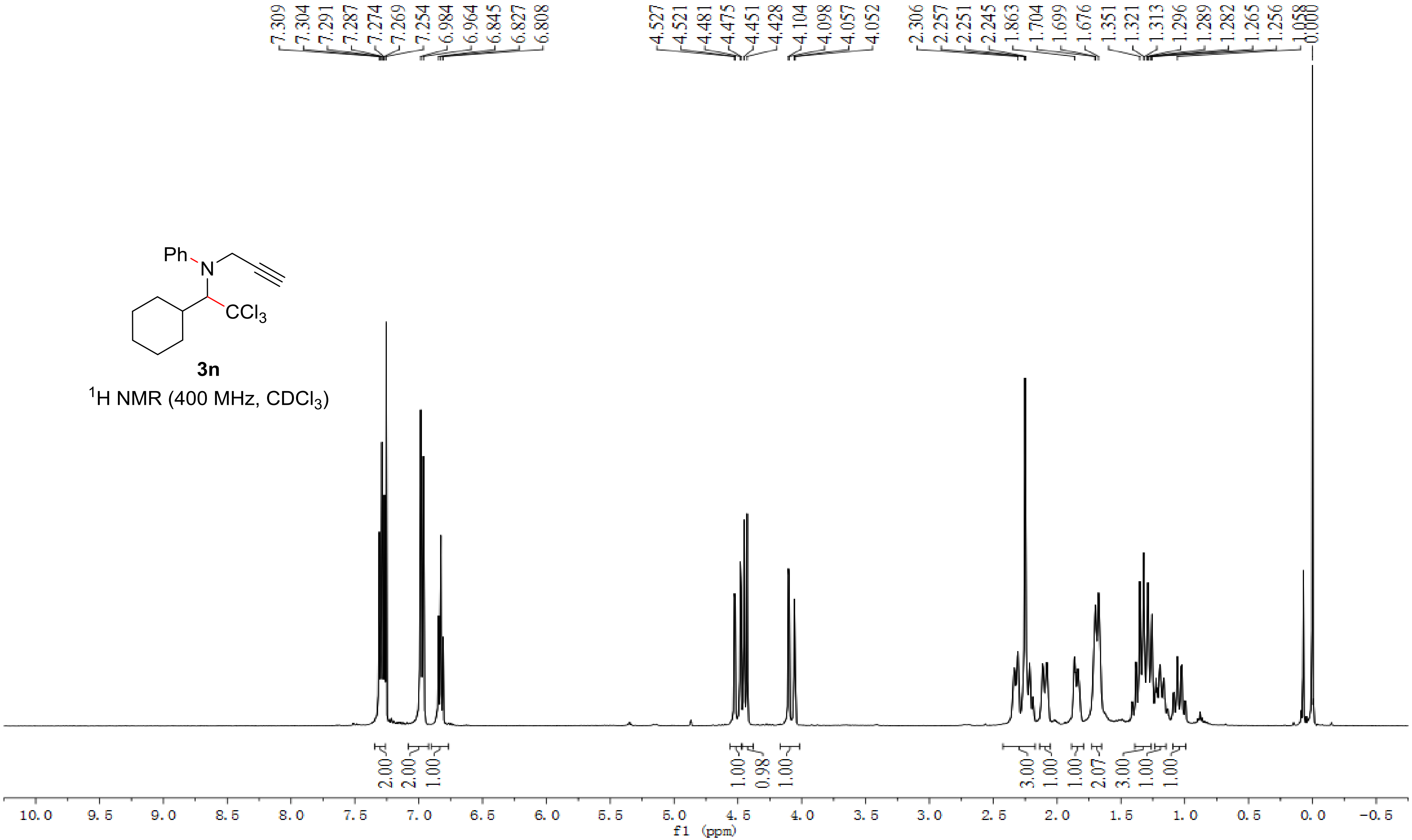
3m

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

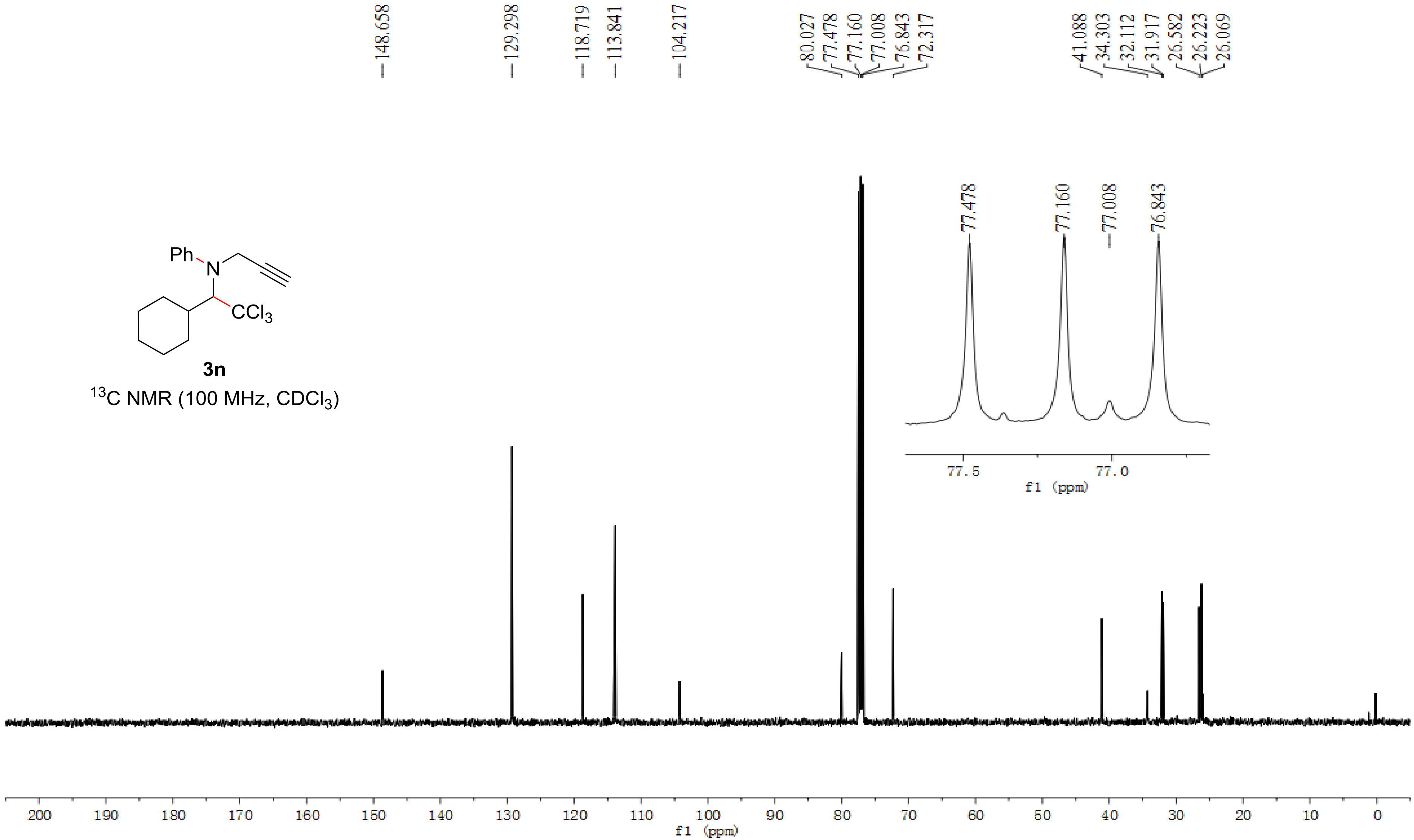


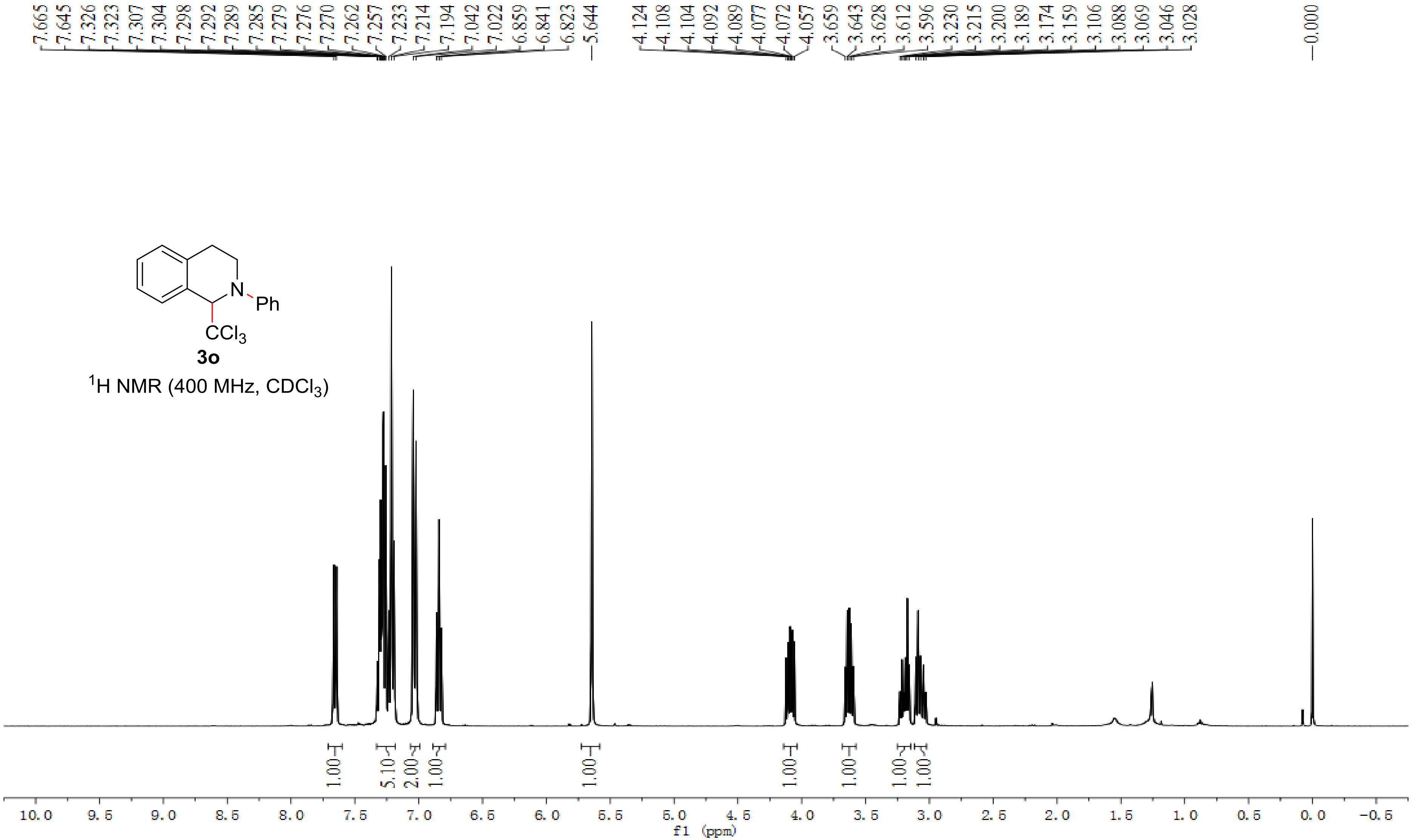


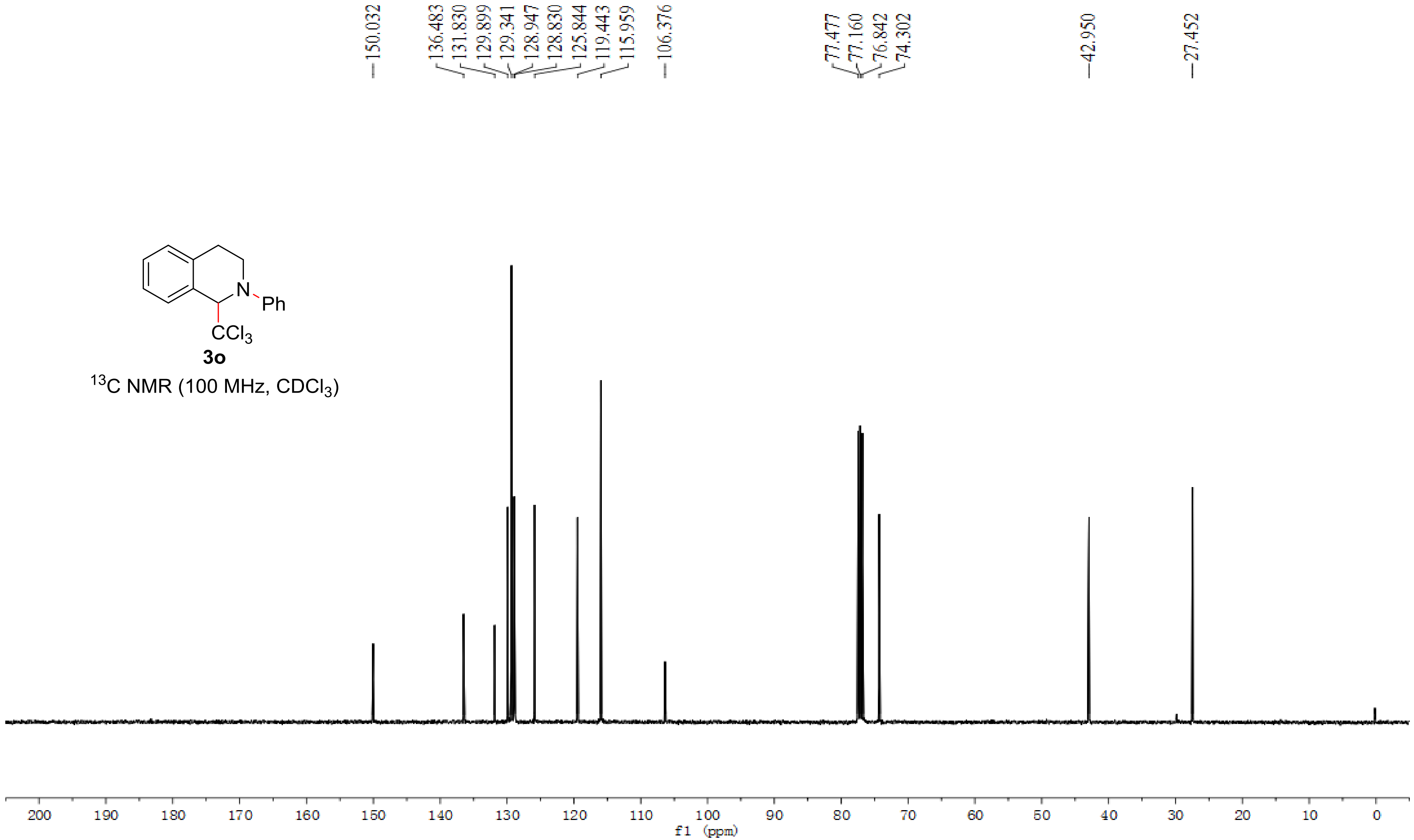
Ph
N
CCl3
3m
13C NMR (100 MHz, CDCl3)
149.409
135.644
129.053
118.349
117.166
115.223
104.919
78.755
77.477
77.160
76.842
46.832
41.070
32.142
31.823
26.631
26.395
26.239
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Ph
N
CCl3
3n
1H NMR (400 MHz, CDCl3)
7.309
7.304
7.291
7.287
7.274
7.269
7.254
6.984
6.964
6.845
6.827
6.808
4.527
4.521
4.481
4.475
4.451
4.428
4.104
4.098
4.057
4.052
2.306
2.257
2.251
2.245
1.863
1.704
1.699
1.676
1.351
1.321
1.313
1.296
1.289
1.282
1.265
1.256
1.058
0.000
2.00
2.00
1.00
1.00
0.98
1.00
3.00
1.00
1.00
2.07
3.00
1.00
1.00
f1 (ppm)

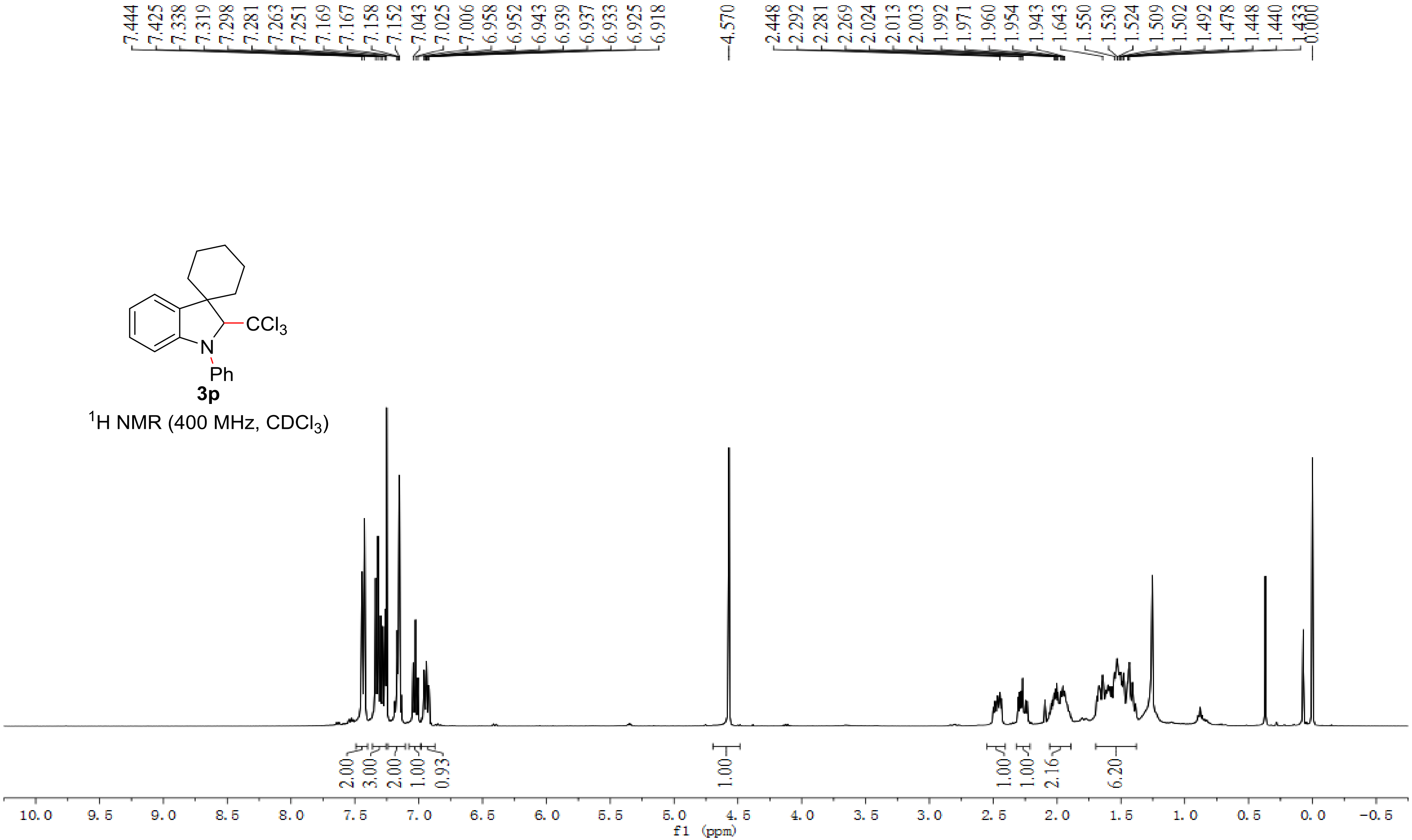

148.658
129.298
118.719
113.841
104.217
80.027
77.478
77.160
77.008
76.843
72.317
41.088
34.303
32.112
31.917
26.582
26.223
26.069
Ph
N
CCl3
3n
13C NMR (100 MHz, CDCl3)
77.478
77.160
77.008
76.843
77.5
77.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

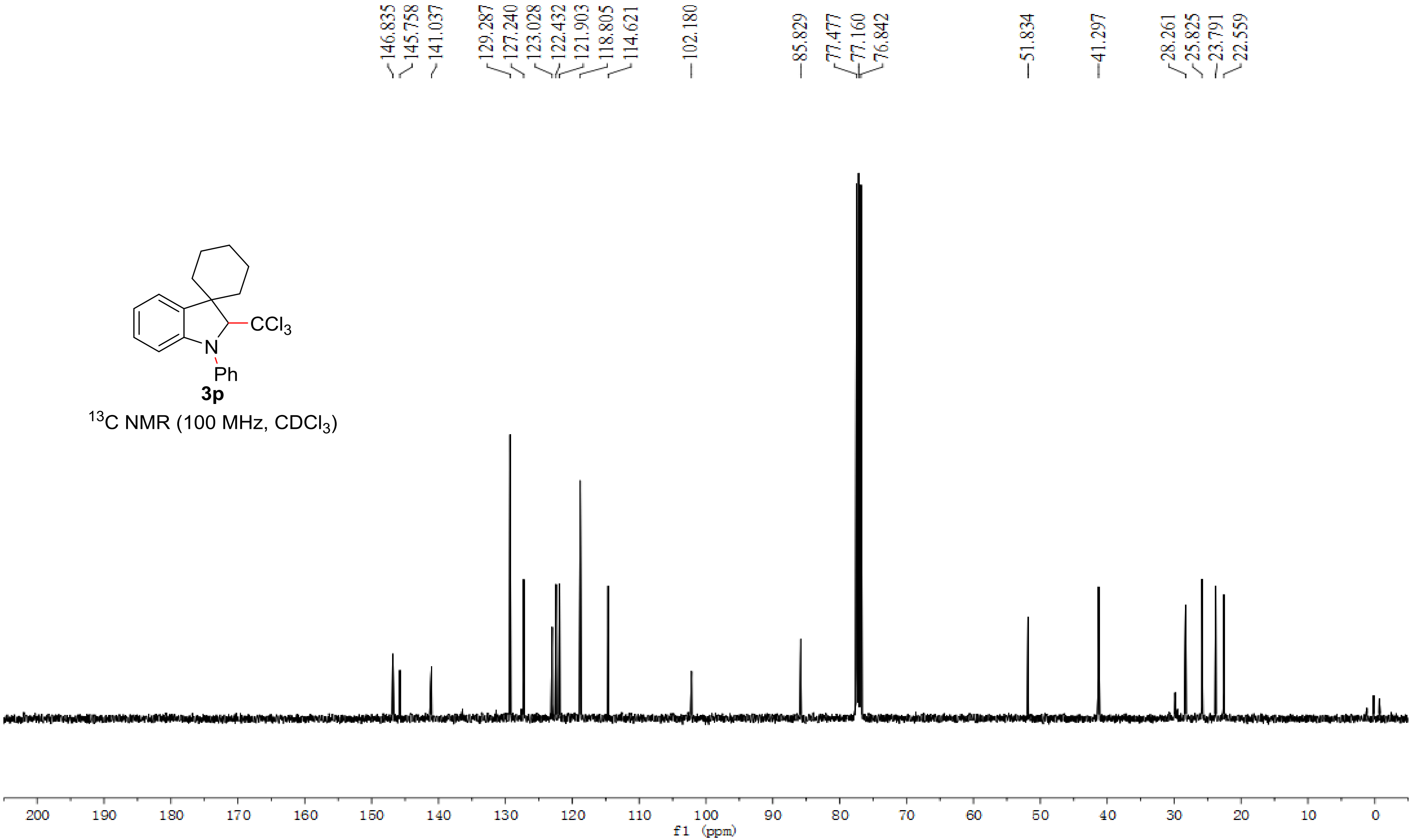

7.665
7.645
7.326
7.323
7.307
7.304
7.298
7.292
7.289
7.285
7.279
7.276
7.270
7.262
7.257
7.233
7.214
7.194
7.042
7.022
6.859
6.841
6.823
5.644
4.124
4.108
4.104
4.092
4.089
4.077
4.072
4.057
3.659
3.643
3.628
3.612
3.596
3.230
3.215
3.200
3.189
3.174
3.159
3.106
3.088
3.069
3.046
3.028
0.000
N
Ph
CCl3
3o
1H NMR (400 MHz, CDCl3)
1.00
5.10
2.00
1.00
1.00
1.00
1.00
1.00
1.00
f1 (ppm)

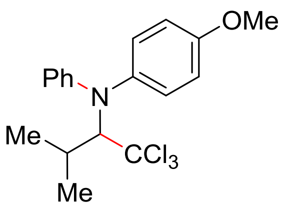


3o

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

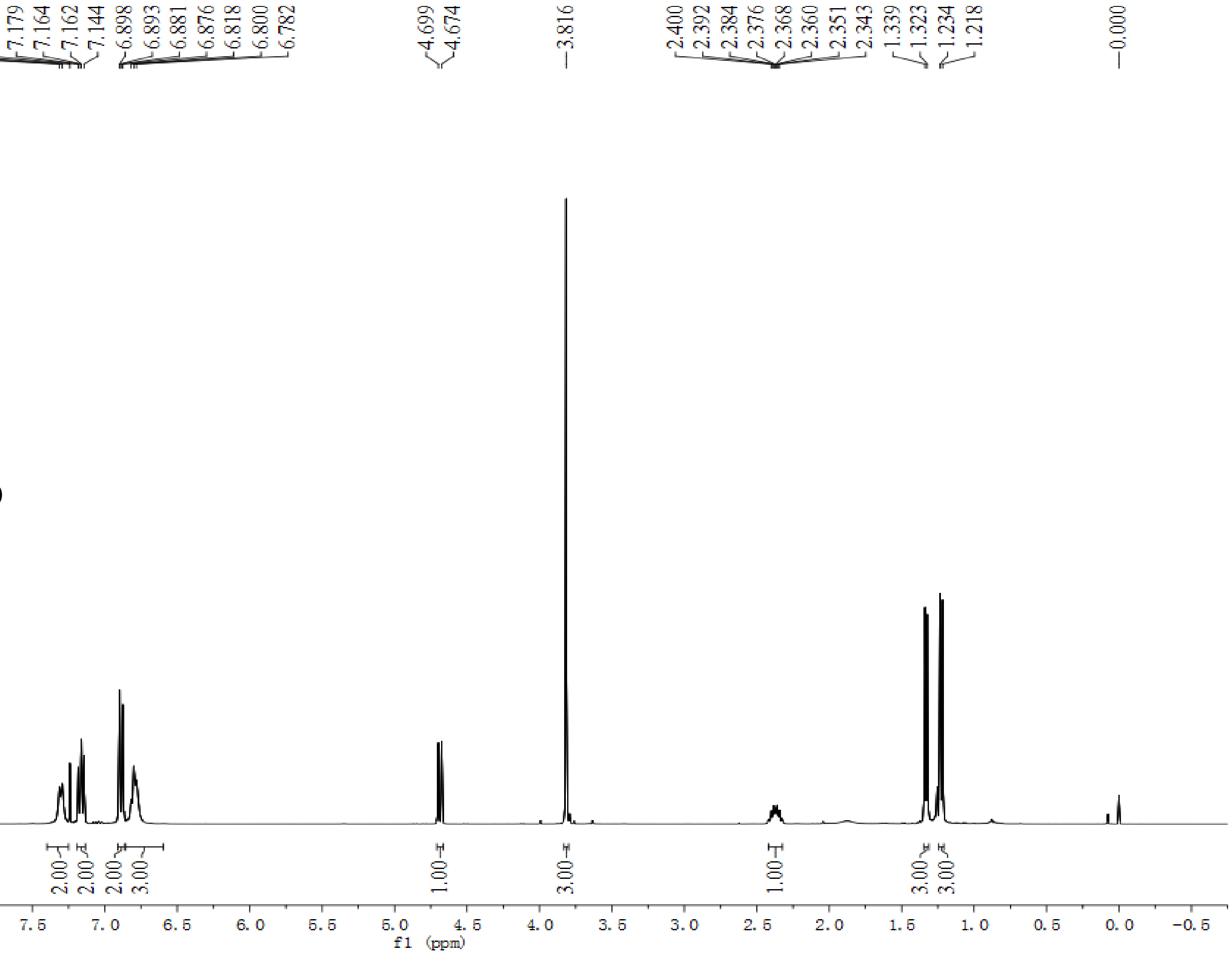

CCl3
N
Ph
3p
1H NMR (400 MHz, CDCl3)
f1 (ppm)

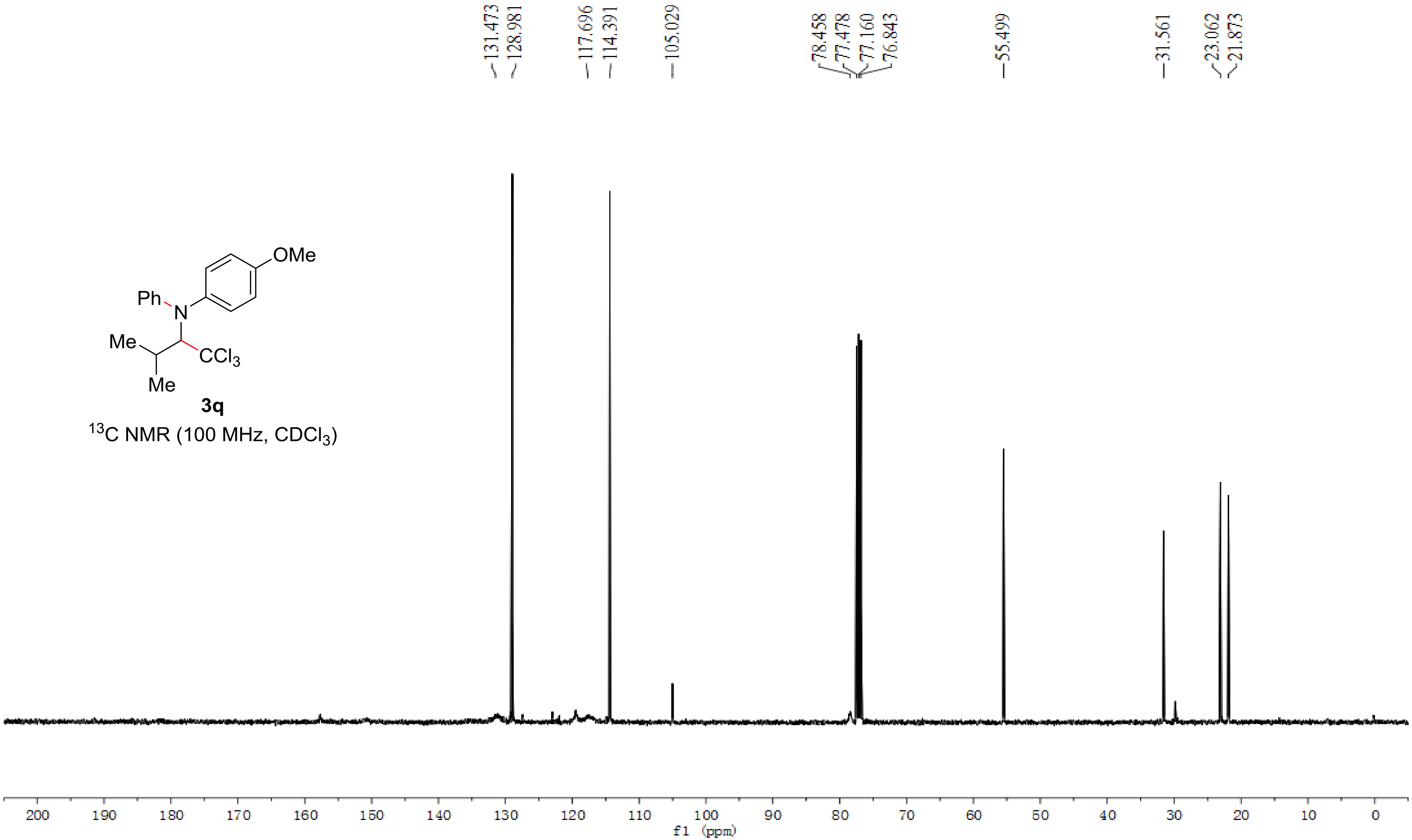

146.835
145.758
141.037
129.287
127.240
123.028
122.432
121.903
118.805
114.621
102.180
85.829
77.477
77.160
76.842
51.834
41.297
28.261
25.825
23.791
22.559
CCl3
N
Ph
3p
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3q

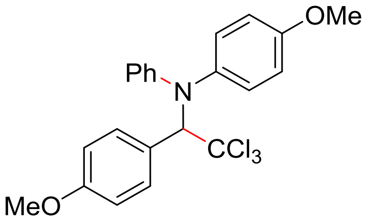
^{1}H NMR (400 MHz, $CDCl_3$)





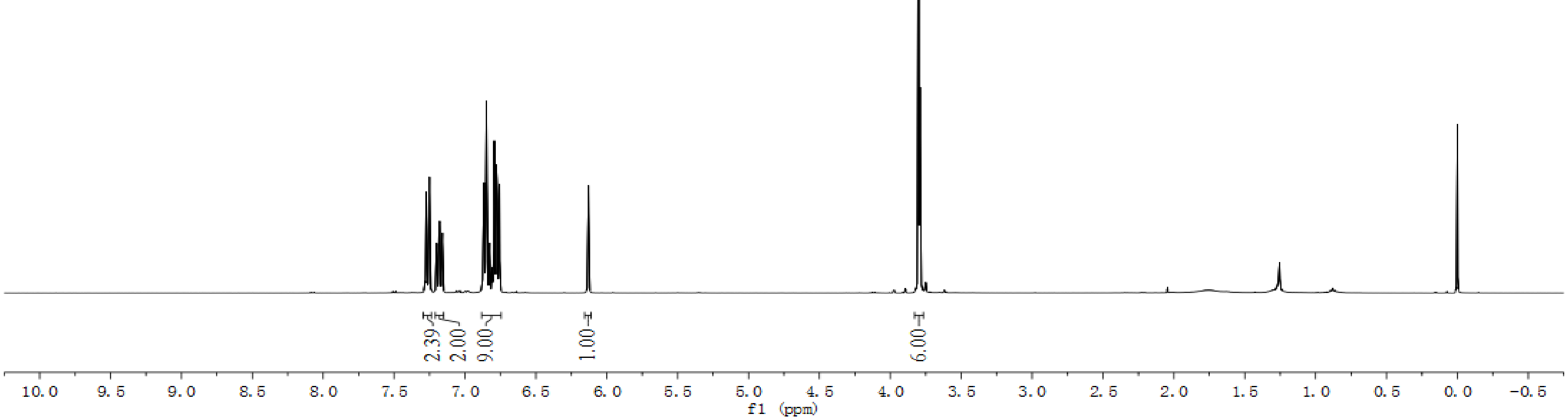
3q

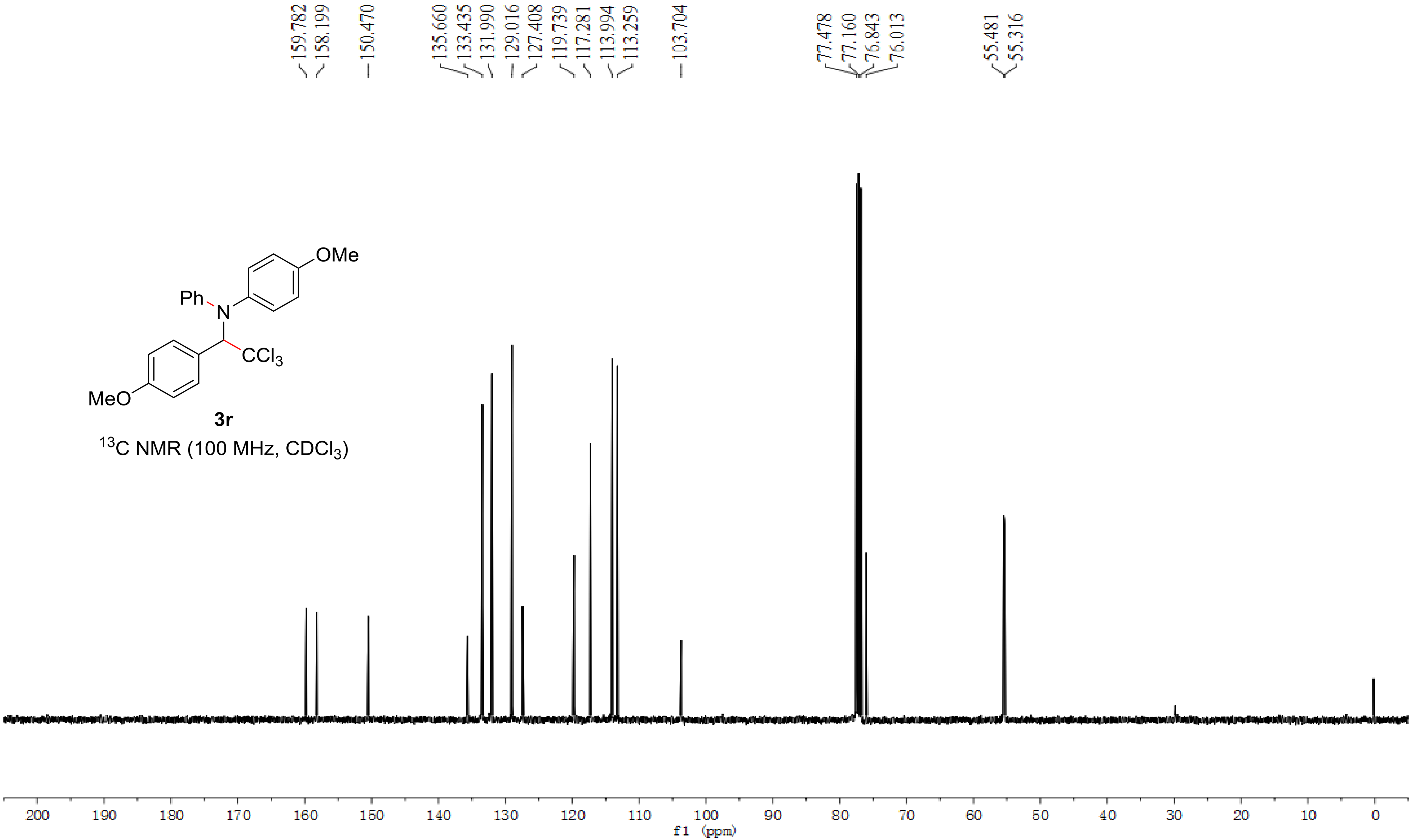
^{13}C NMR (100 MHz, $CDCl_3$)

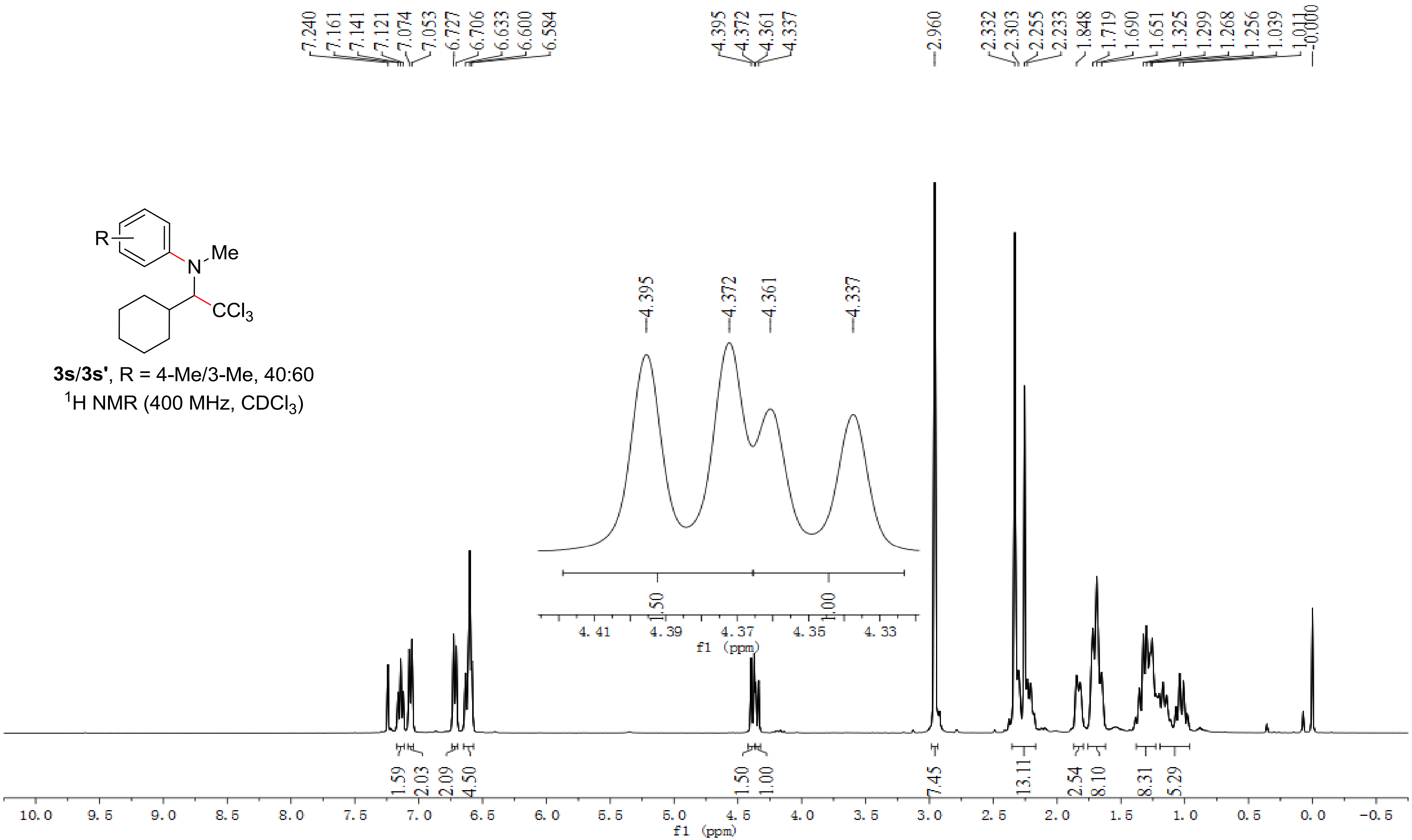


3r

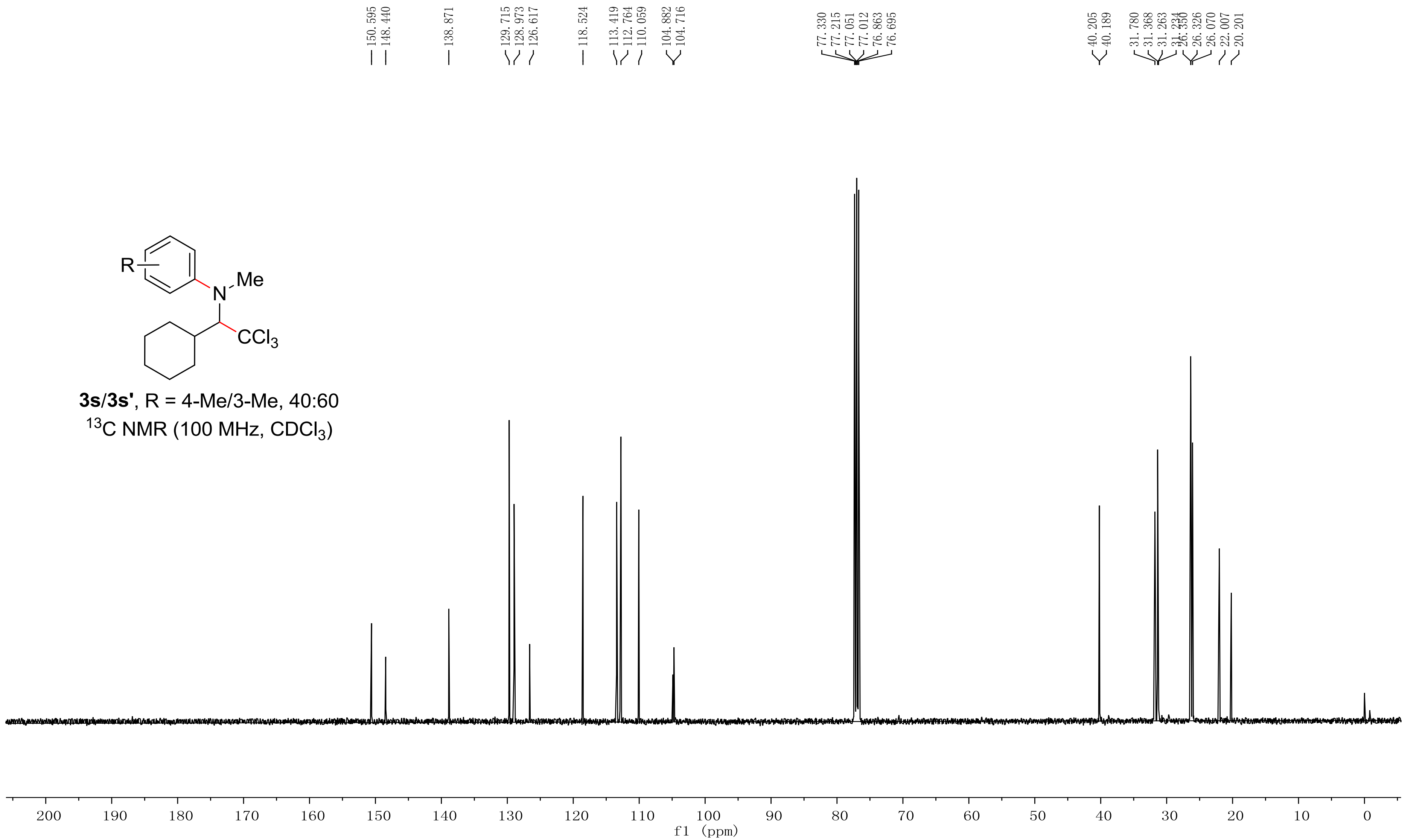
^{1}H NMR (400 MHz, $CDCl_3$)

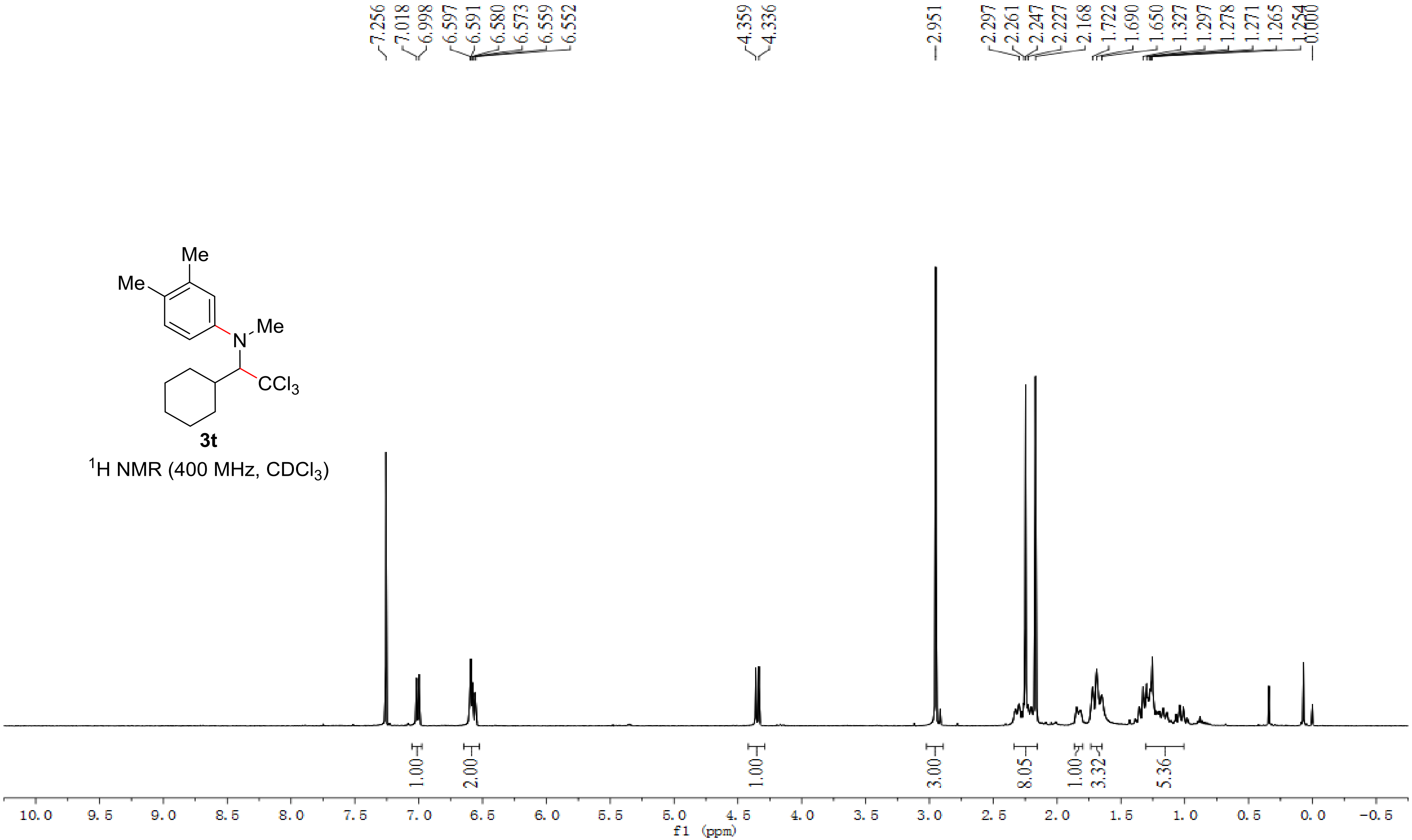



159.782
158.199
150.470
135.660
133.435
131.990
129.016
127.408
119.739
117.281
113.994
113.259
103.704
77.478
77.160
76.843
76.013
55.481
55.316
OMe
Ph
N
CCl3
MeO
3r
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

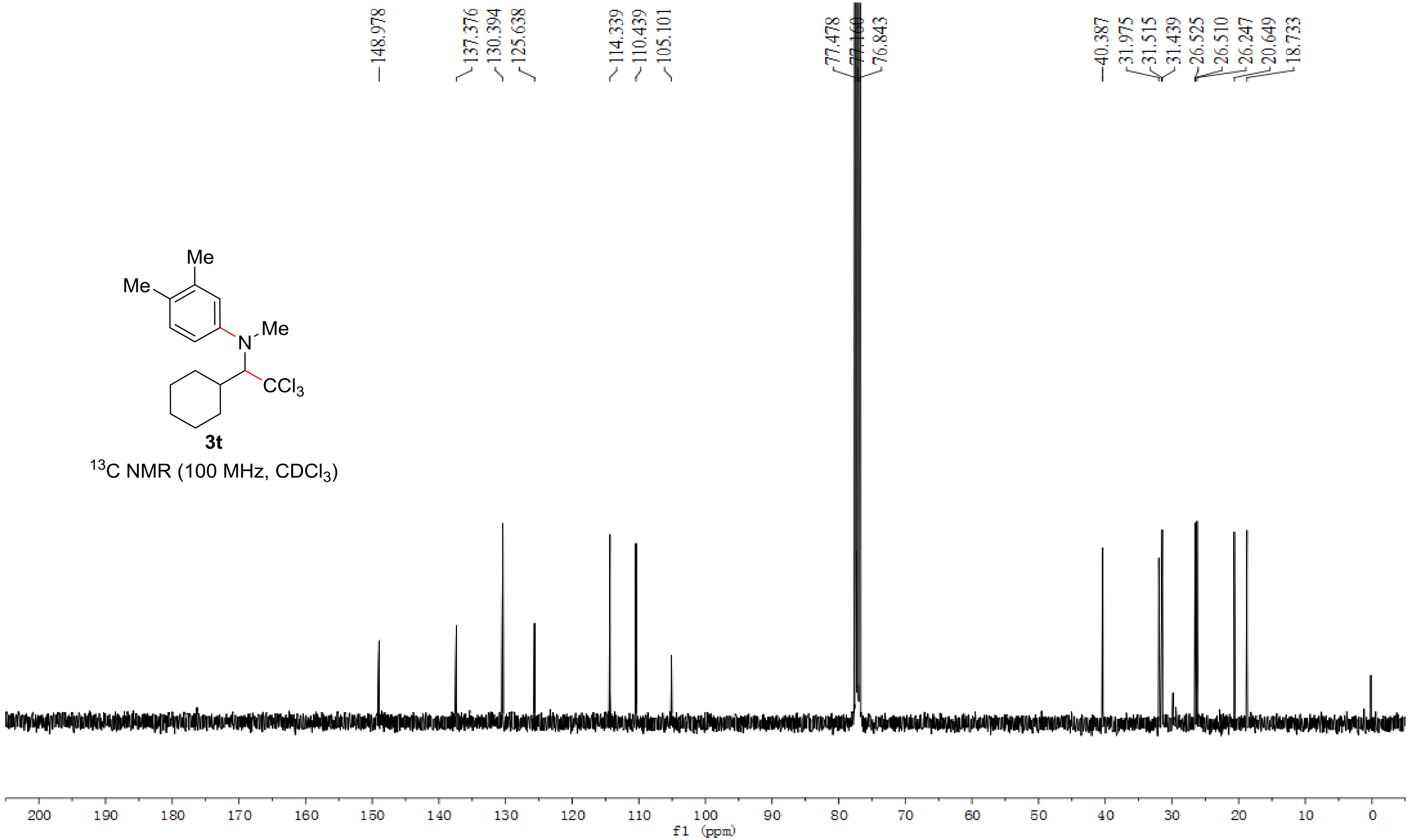


3s/**3s'**, R = 4-Me/3-Me, 40:60
^{1}H NMR (400 MHz, $CDCl_3$)


150.595
148.440
138.871
129.715
128.973
126.617
118.524
113.419
112.764
110.059
104.882
104.716
77.330
77.215
77.051
77.012
76.863
76.695
40.205
40.189
31.780
31.368
31.263
31.234
26.350
26.326
26.070
22.007
20.201
R
N
Me
CCl_3
3s/**3s'**, R = 4-Me/3-Me, 40:60
^{13}C NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

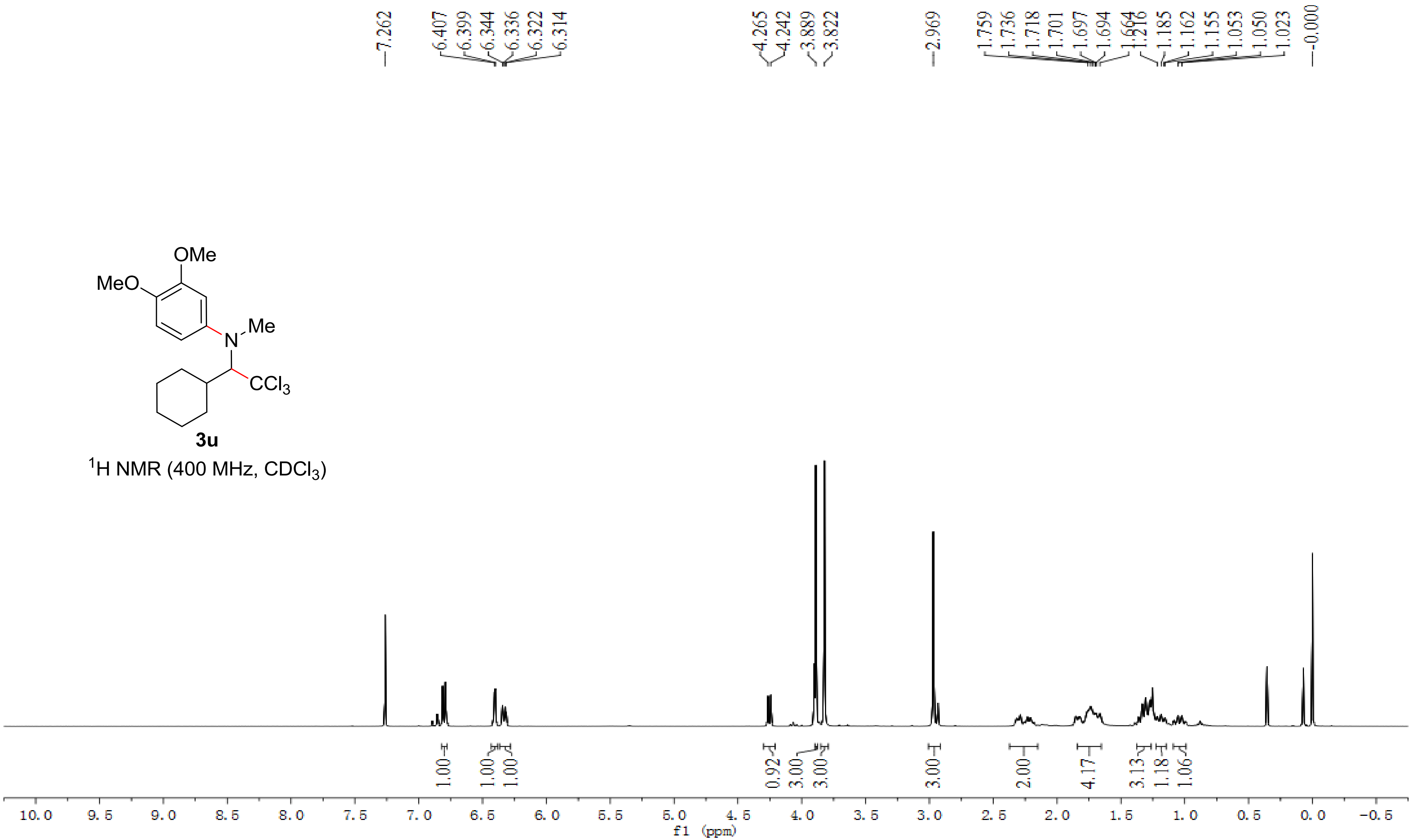


7.256
7.018
6.998
6.597
6.591
6.580
6.573
6.559
6.552
4.359
4.336
2.951
2.297
2.261
2.247
2.227
2.168
1.722
1.690
1.650
1.327
1.297
1.278
1.271
1.265
1.254
0.000
Me
Me
N
Me
CCl3
3t
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
3.00
8.05
1.00
3.32
5.36
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

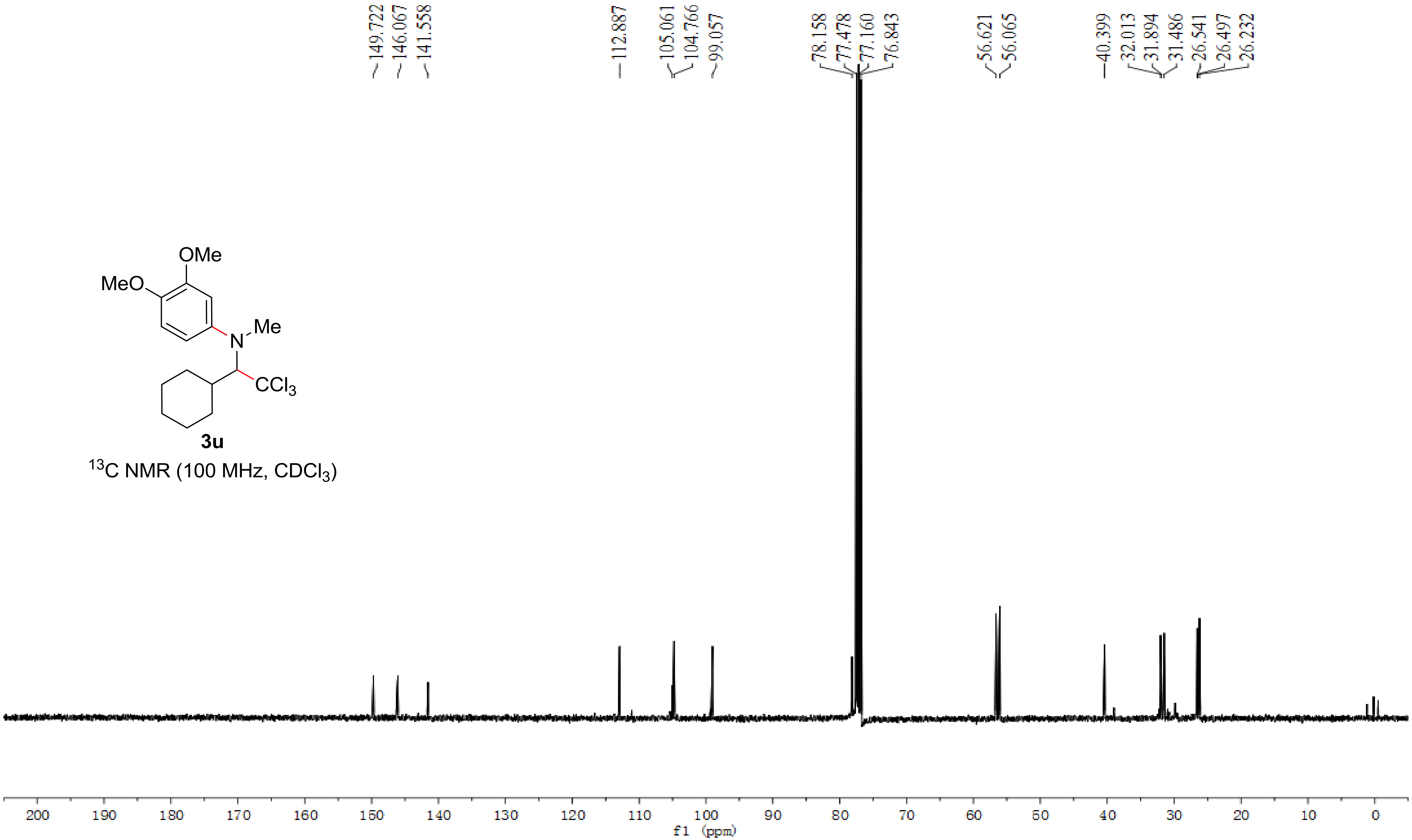


3t

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

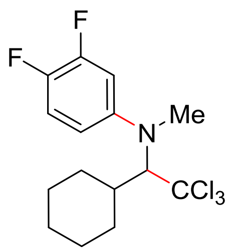


7.262
6.407
6.399
6.344
6.336
6.322
6.314
4.265
4.242
3.889
3.822
2.969
1.759
1.736
1.718
1.701
1.697
1.694
1.664
1.216
1.185
1.162
1.155
1.053
1.050
1.023
-0.000
OMe
MeO
N
Me
CCl3
3u
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
0.92
3.00
3.00
3.00
2.00
4.17
3.13
1.18
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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
-0.5
f1 (ppm)



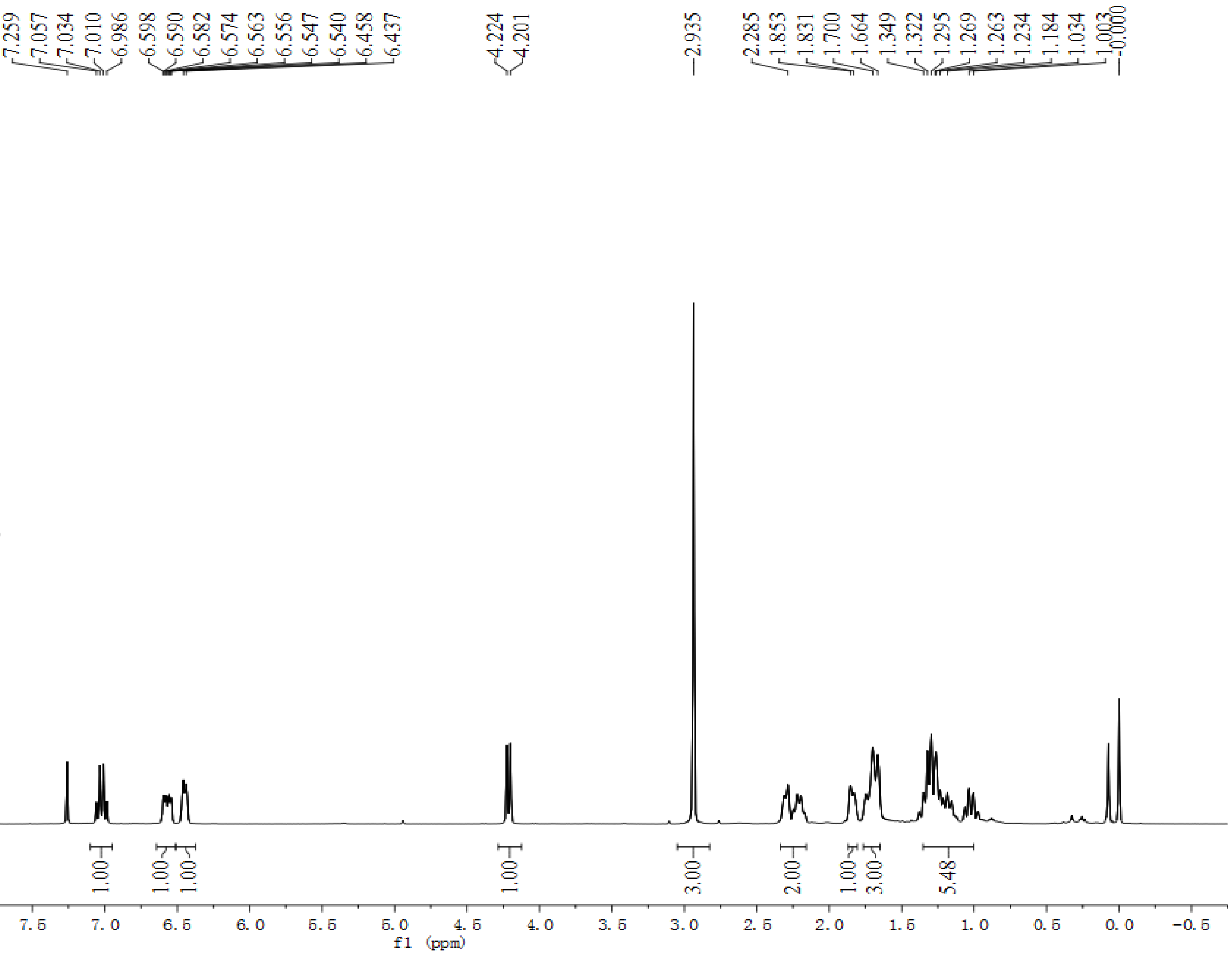
3u

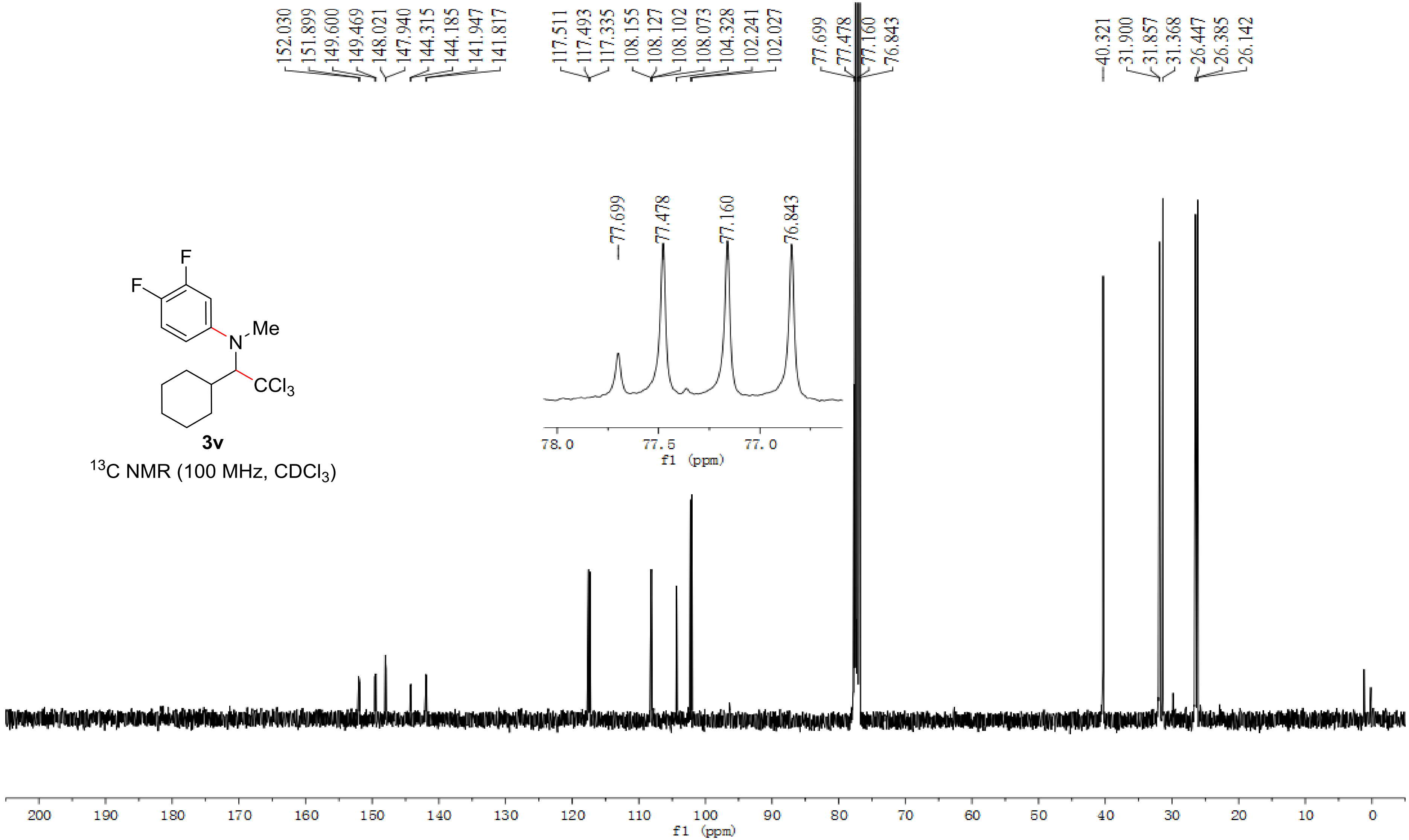
^{13}C NMR (100 MHz, $CDCl_3$)



3v

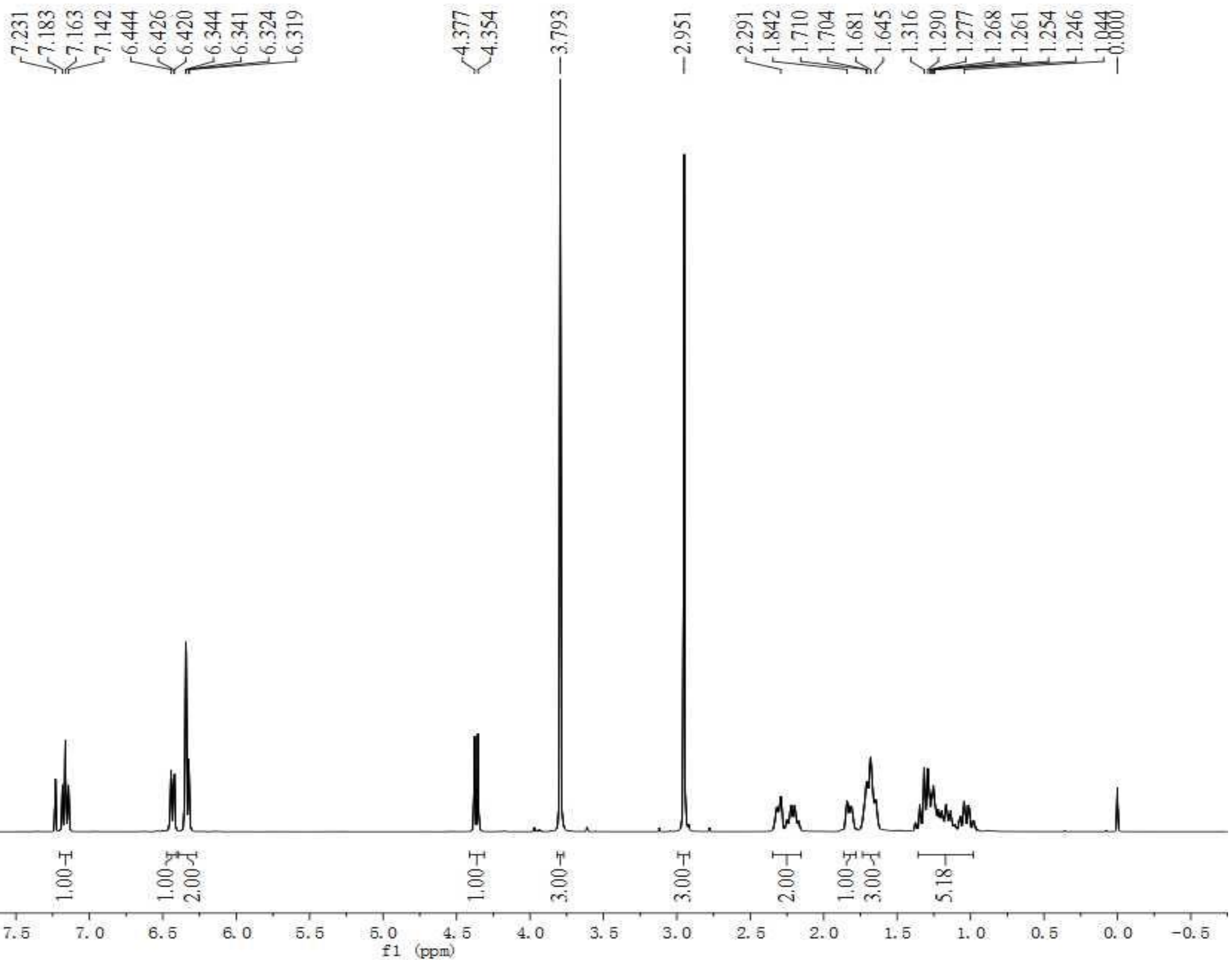
^{1}H NMR (400 MHz, $CDCl_3$)

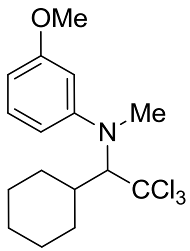




3v

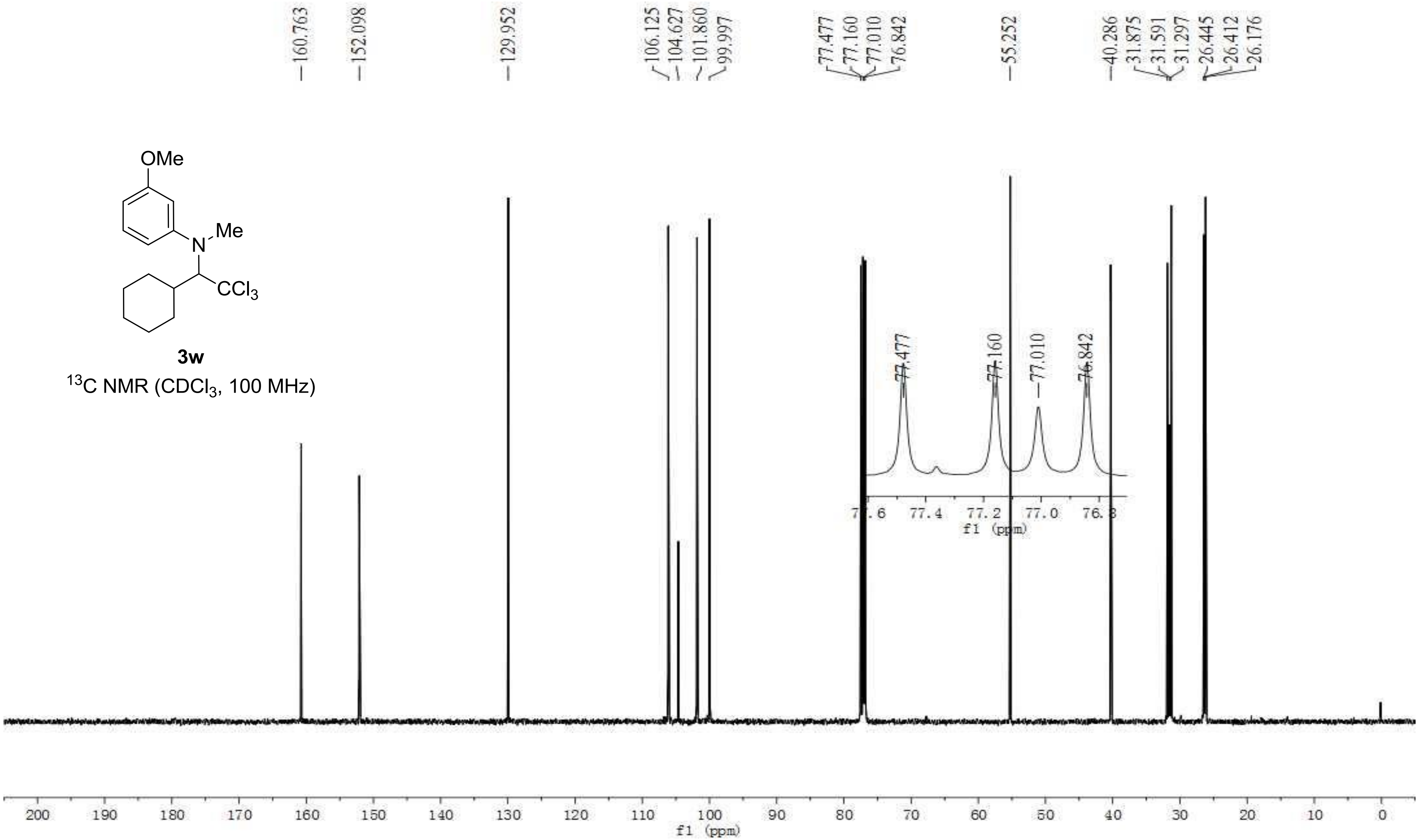
^{13}C NMR (100 MHz, $CDCl_3$)





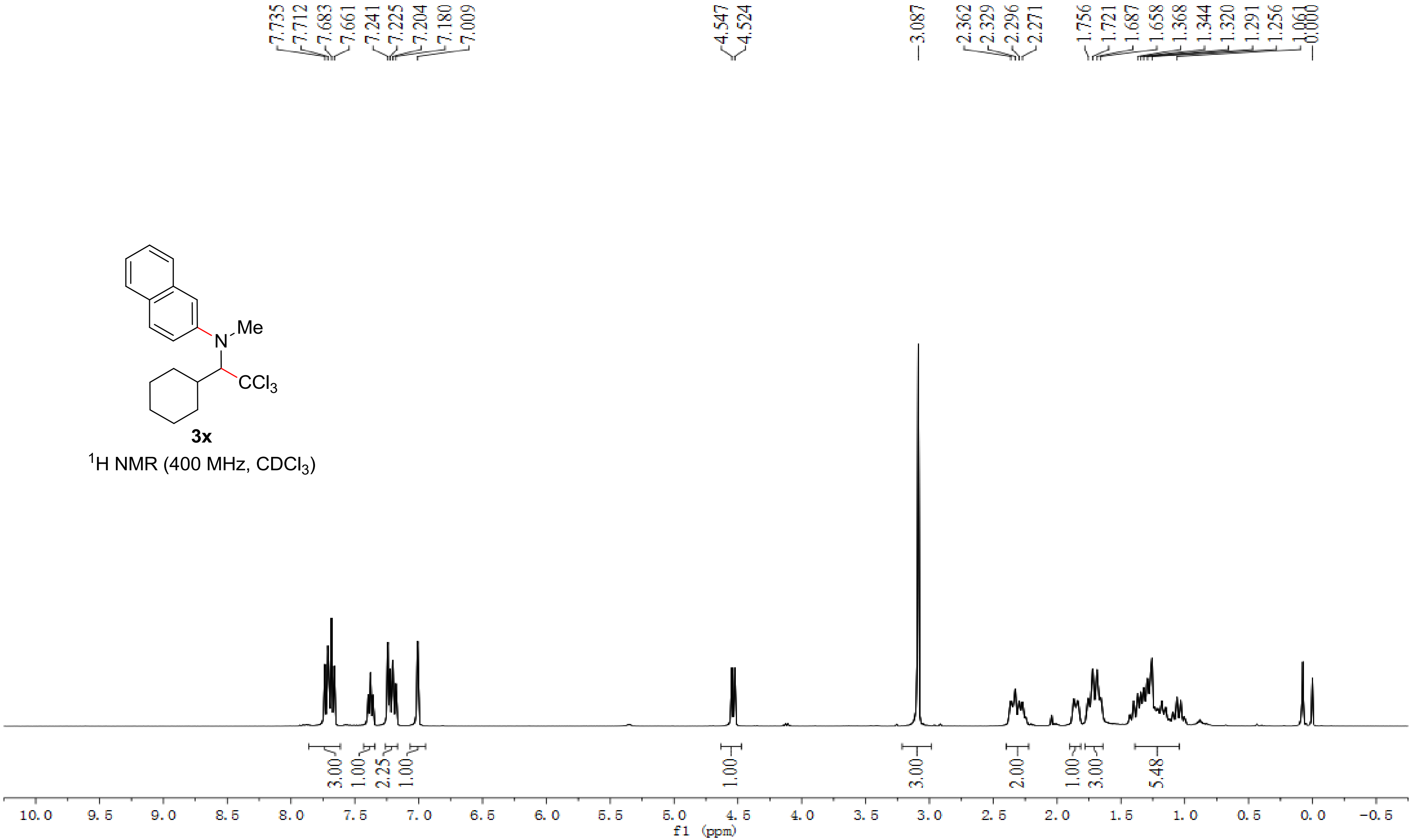
3w

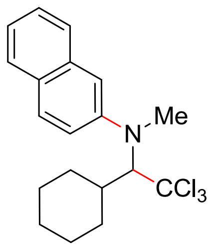
^{1}H NMR ($CDCl_3$, 400 MHz)



3w

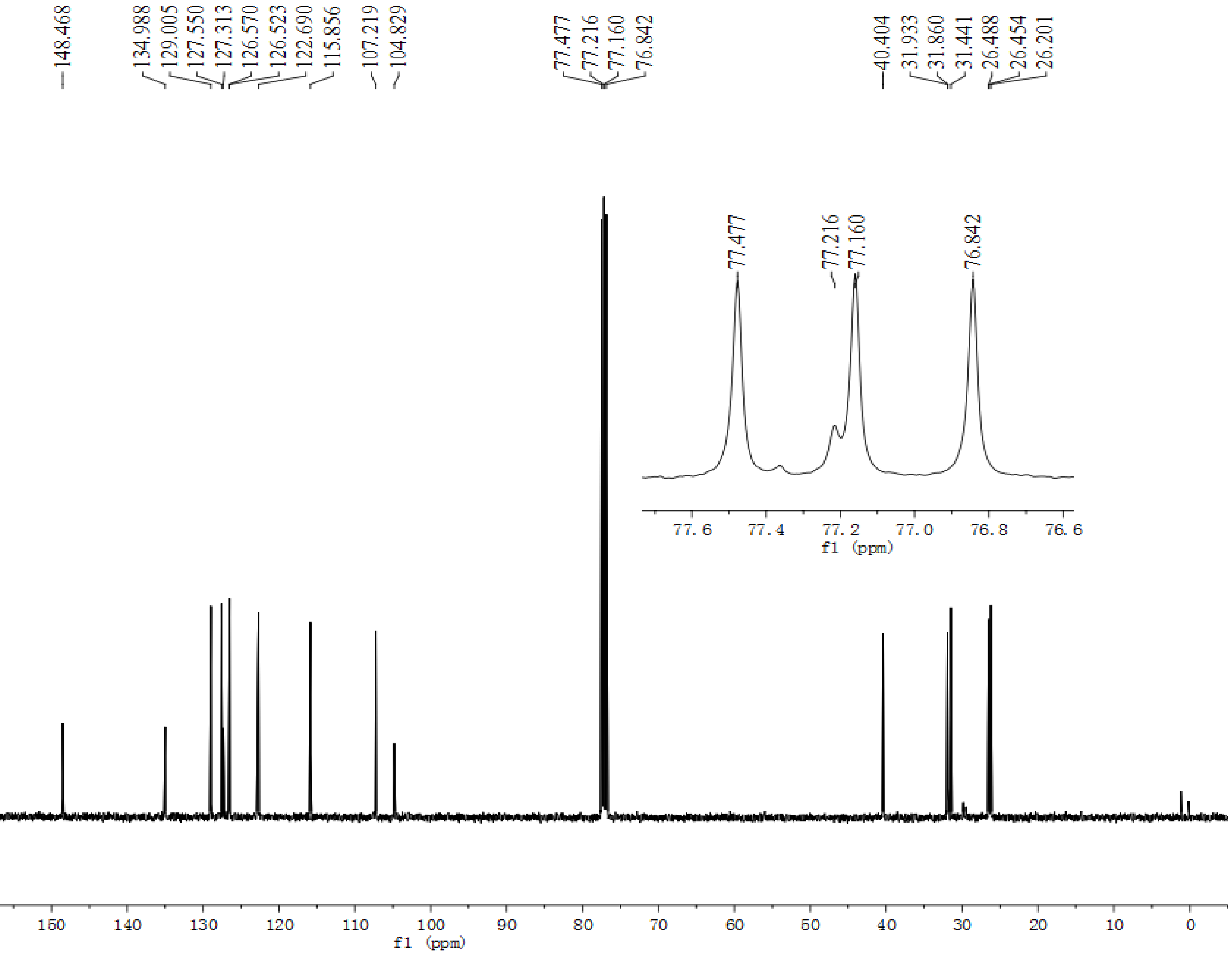
^{13}C NMR ($CDCl_3$, 100 MHz)

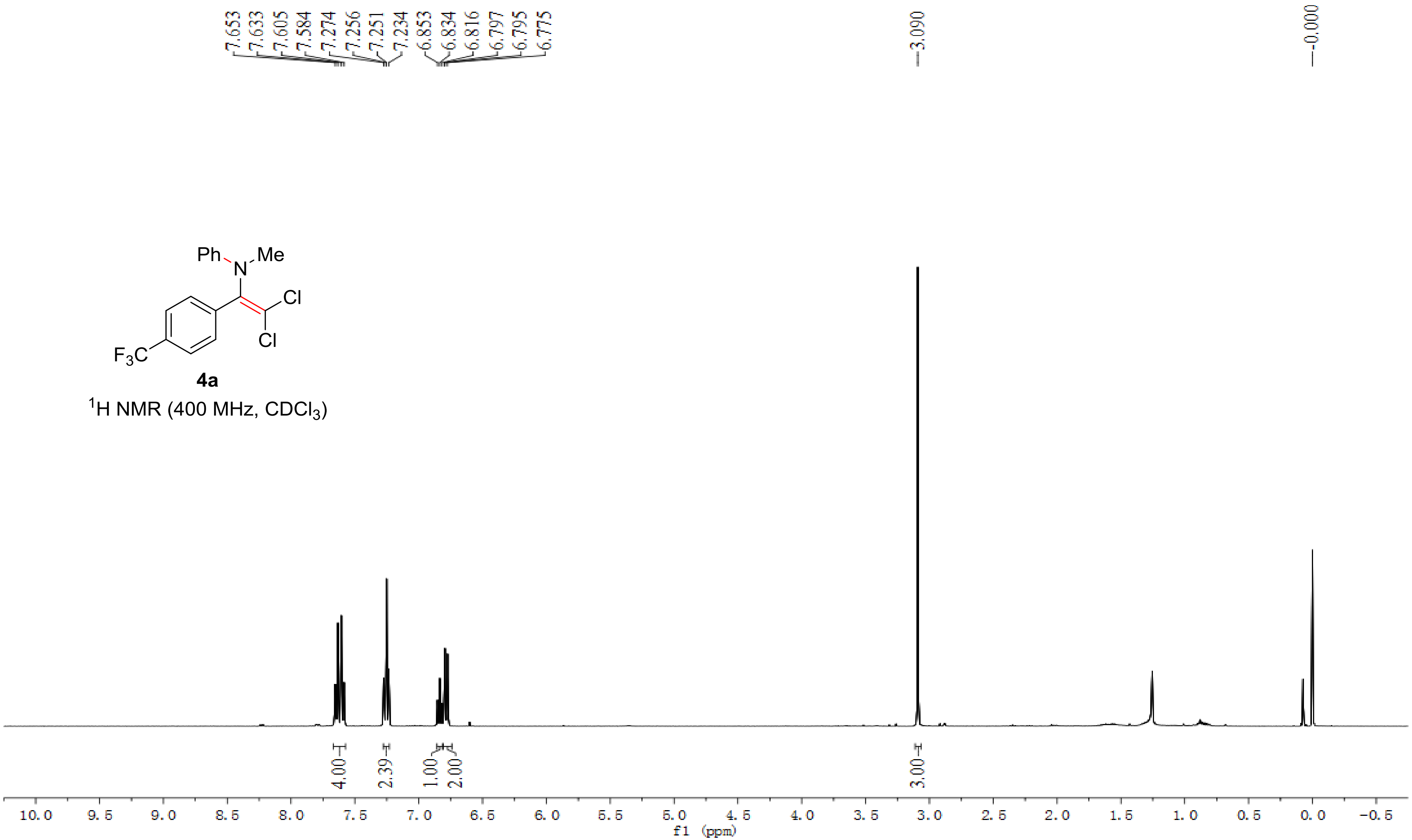

7.735
7.712
7.683
7.661
7.241
7.225
7.204
7.180
7.009
4.547
4.524
3.087
2.362
2.329
2.296
2.271
1.756
1.721
1.687
1.658
1.368
1.344
1.320
1.291
1.256
1.061
0.000
Me
N
CCl_3
3x
^1H NMR (400 MHz, $CDCl_3$)
3.00
1.00
2.25
1.00
1.00
3.00
2.00
1.00
3.00
5.48
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

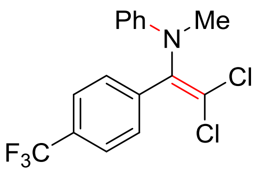


3x

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

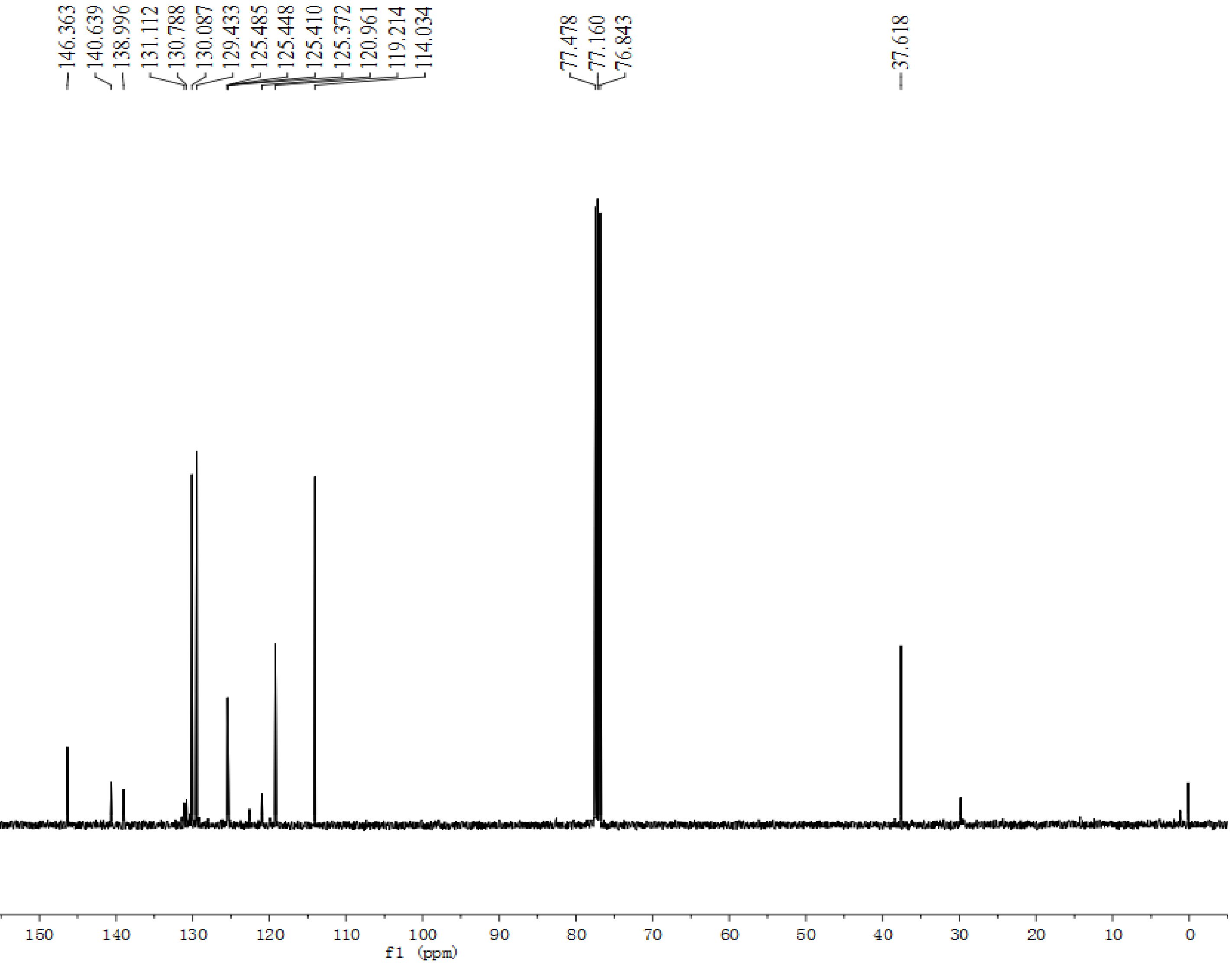


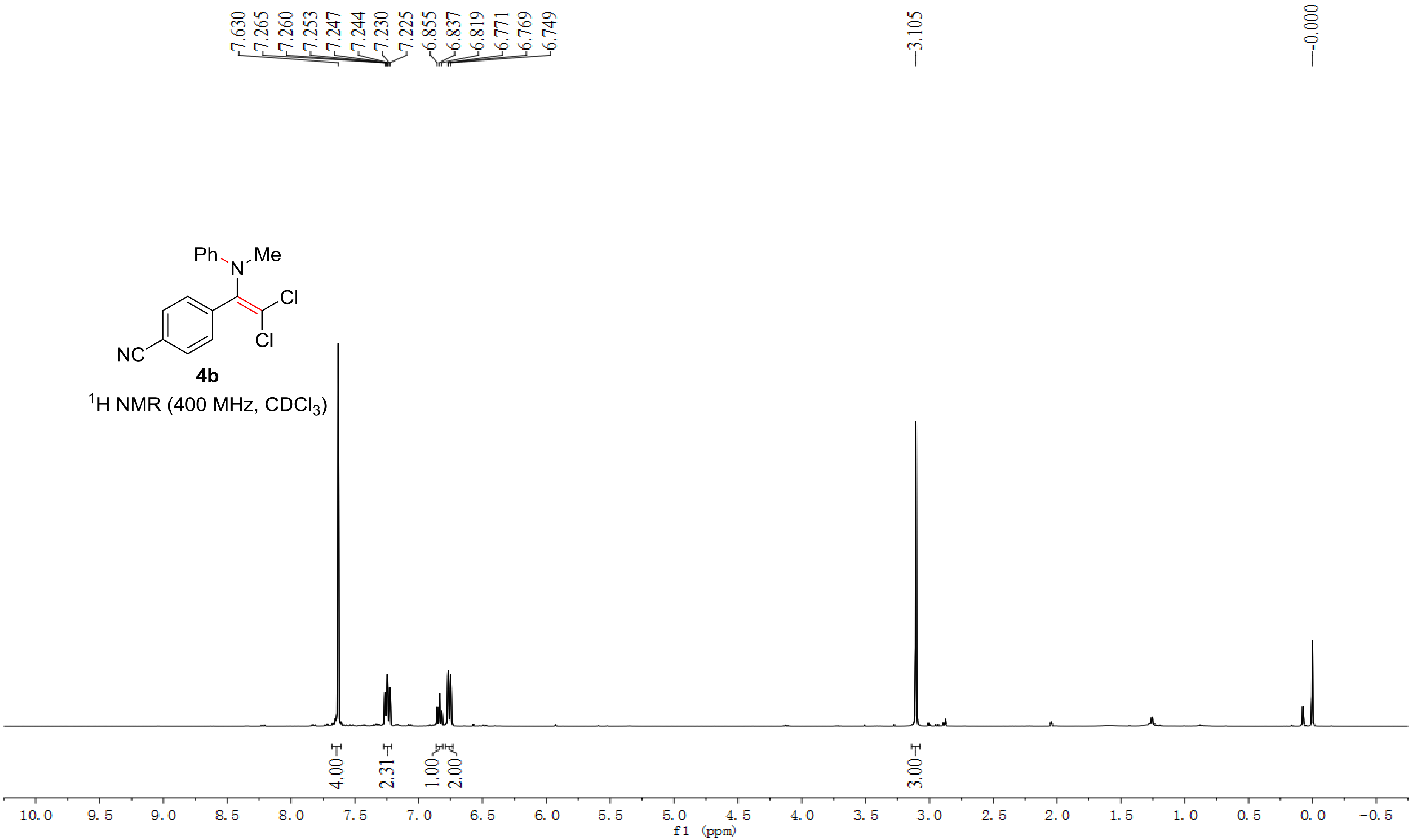

7.653
7.633
7.605
7.584
7.274
7.256
7.251
7.234
6.853
6.834
6.816
6.797
6.795
6.775
3.090
-0.000
Ph
N
Me
Cl
Cl
F3C
4a
1H NMR (400 MHz, CDCl3)
4.00
2.39
1.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



4a

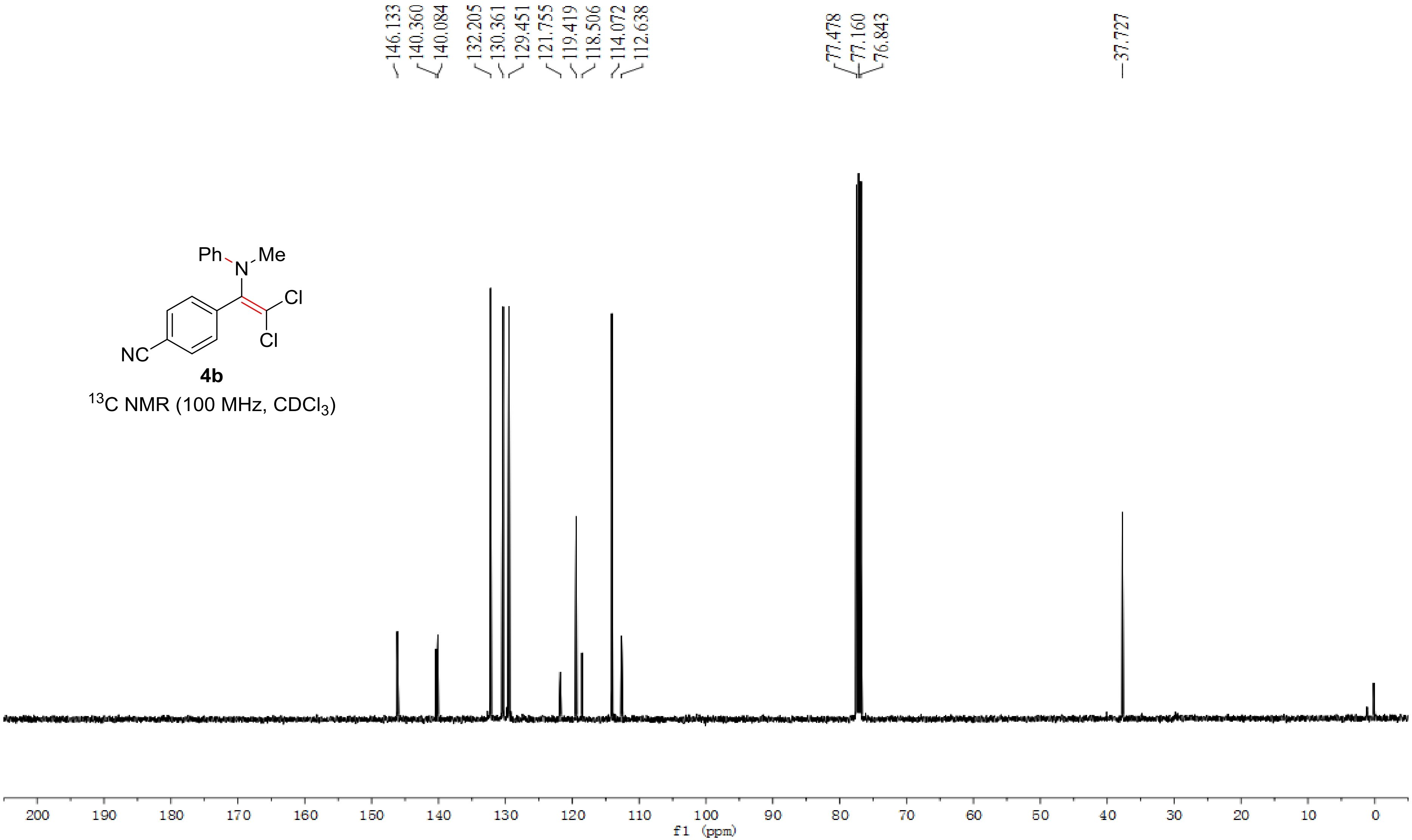
^{13}C NMR (100 MHz, $CDCl_3$)

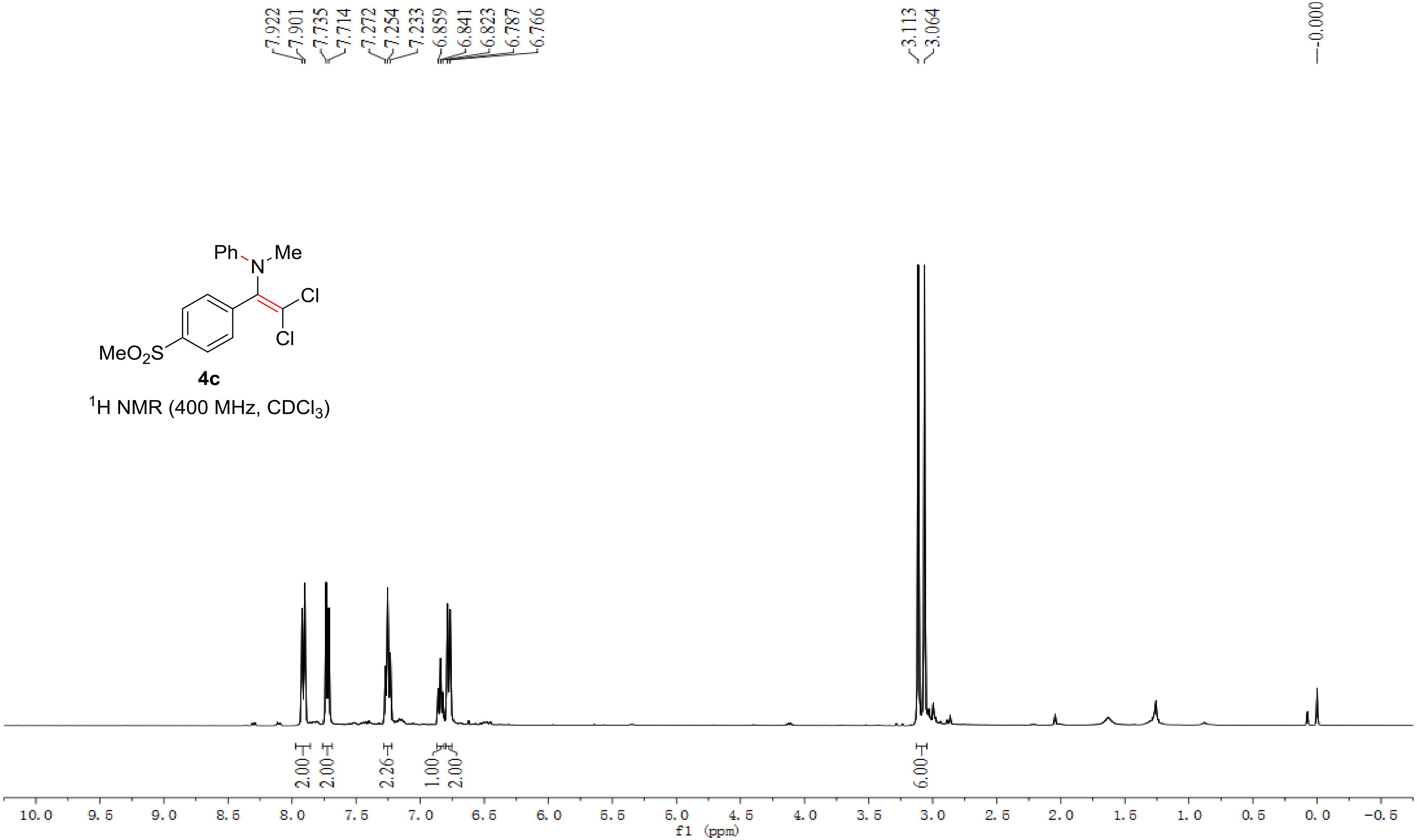


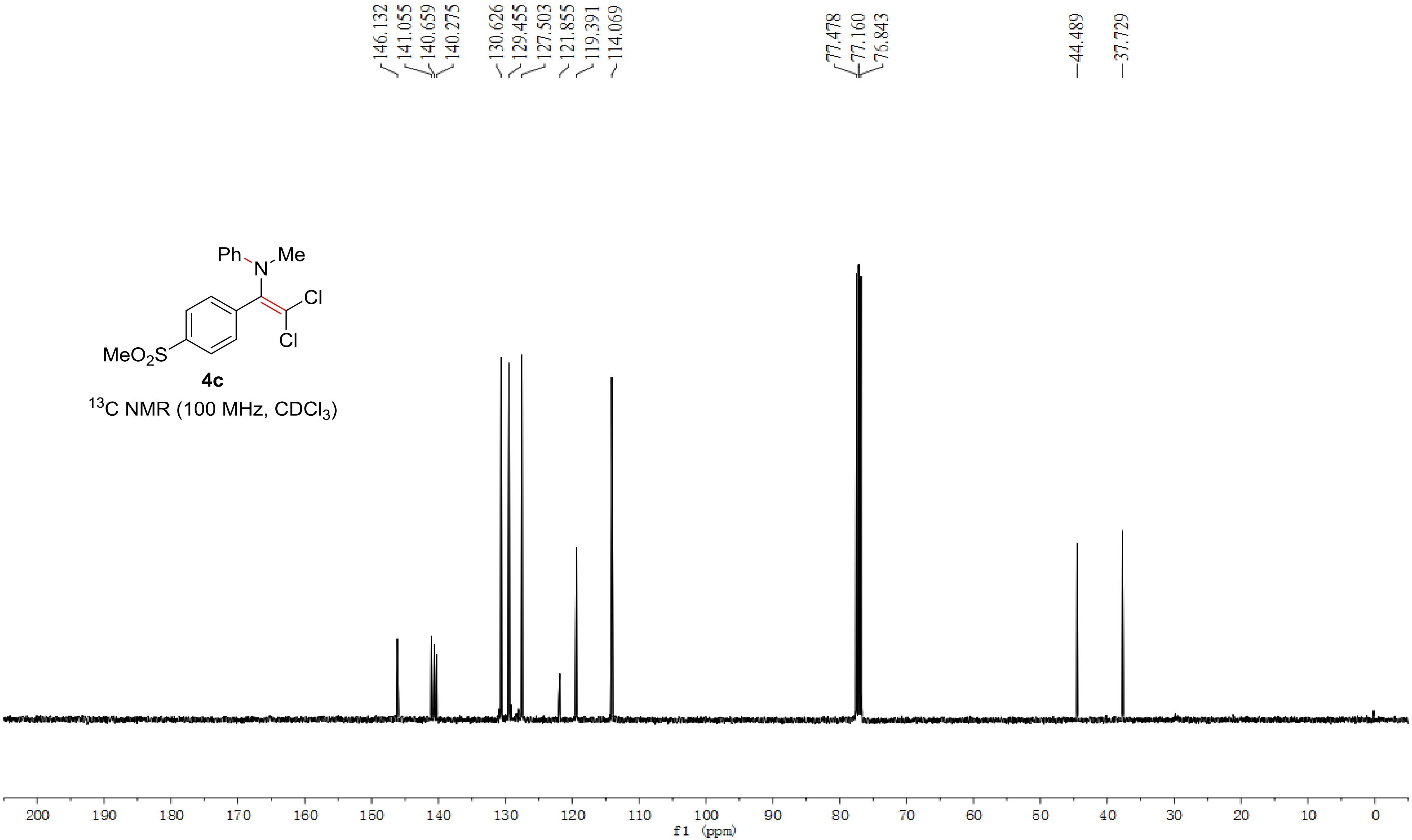


4b

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

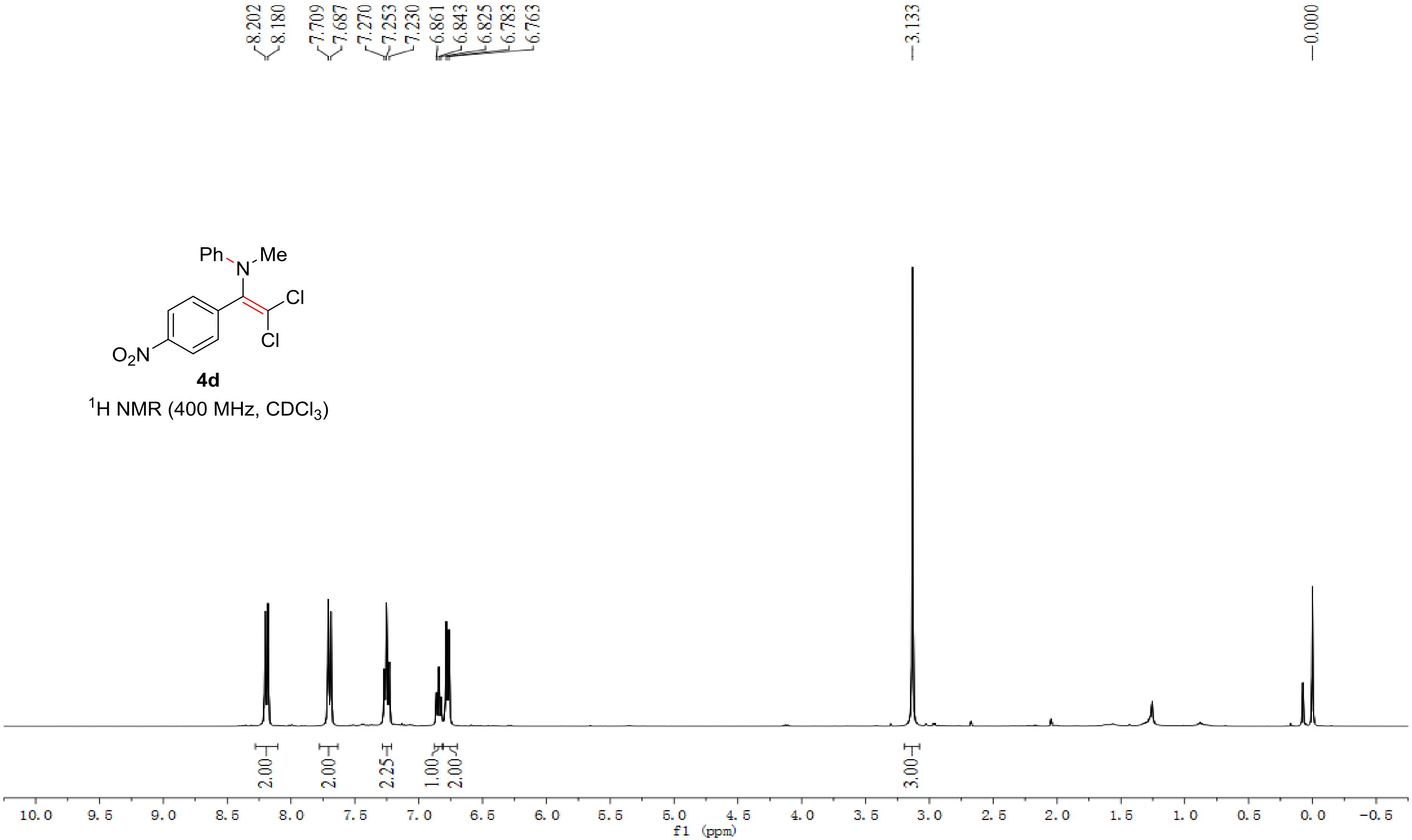

146.133
140.360
140.084
132.205
130.361
129.451
121.755
119.419
118.506
114.072
112.638
77.478
77.160
76.843
37.727
Ph
N
Me
Cl
Cl
NC
4b
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

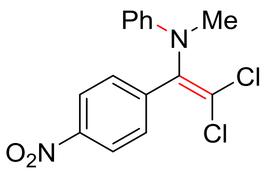

7.922
7.901
7.735
7.714
7.272
7.254
7.233
6.859
6.841
6.823
6.787
6.766
3.113
3.064
0.000
Ph
N
Me
Cl
Cl
MeO2S
4c
1H NMR (400 MHz, CDCl3)
2.00
2.00
2.26
1.00
2.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



4c

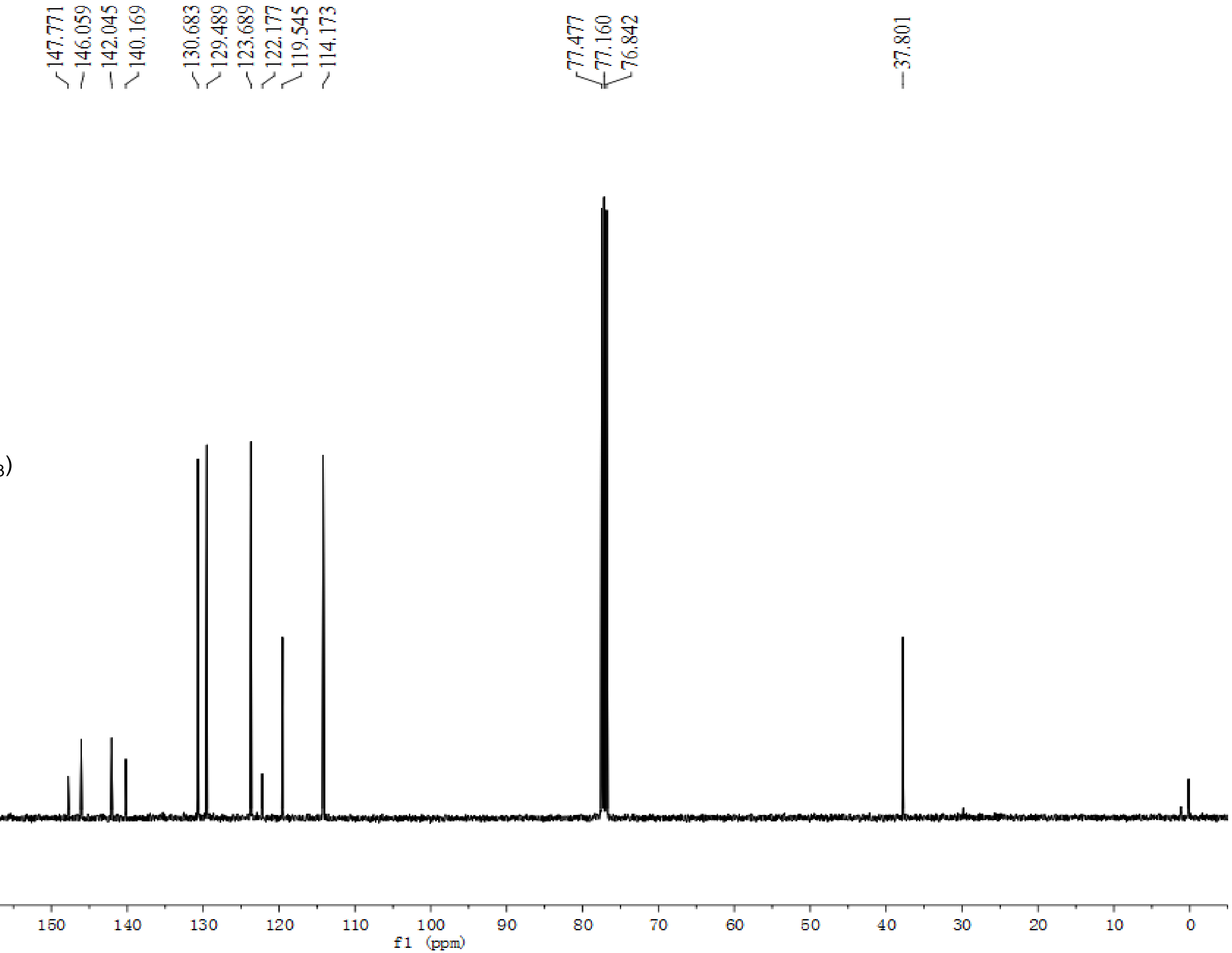
^{13}C NMR (100 MHz, $CDCl_3$)

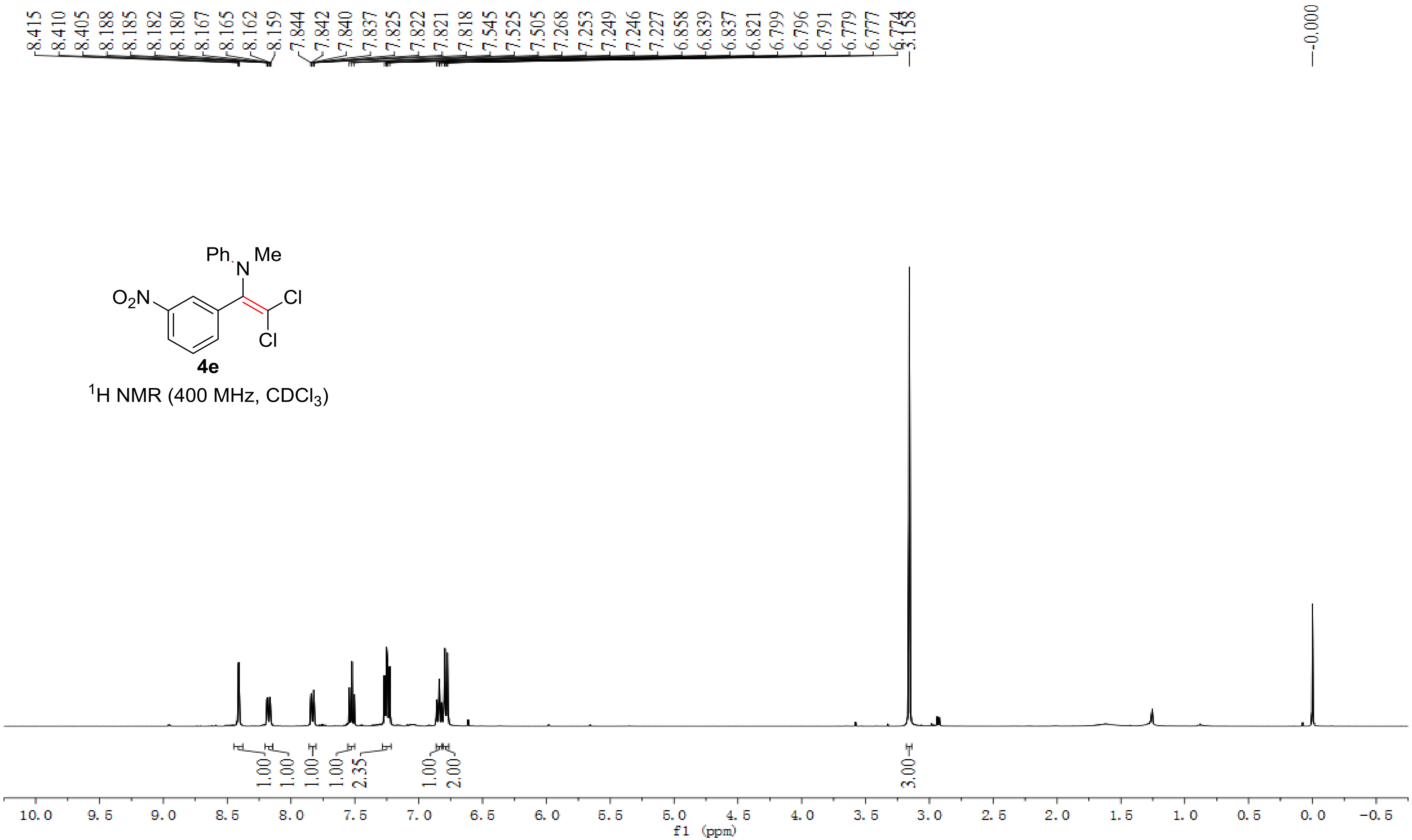

8.202
8.180
7.709
7.687
7.270
7.253
7.230
6.861
6.843
6.825
6.783
6.763
3.133
0.000
Ph
N
Me
Cl
Cl
O2N
4d
1H NMR (400 MHz, CDCl3)
2.00
2.00
2.25
1.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



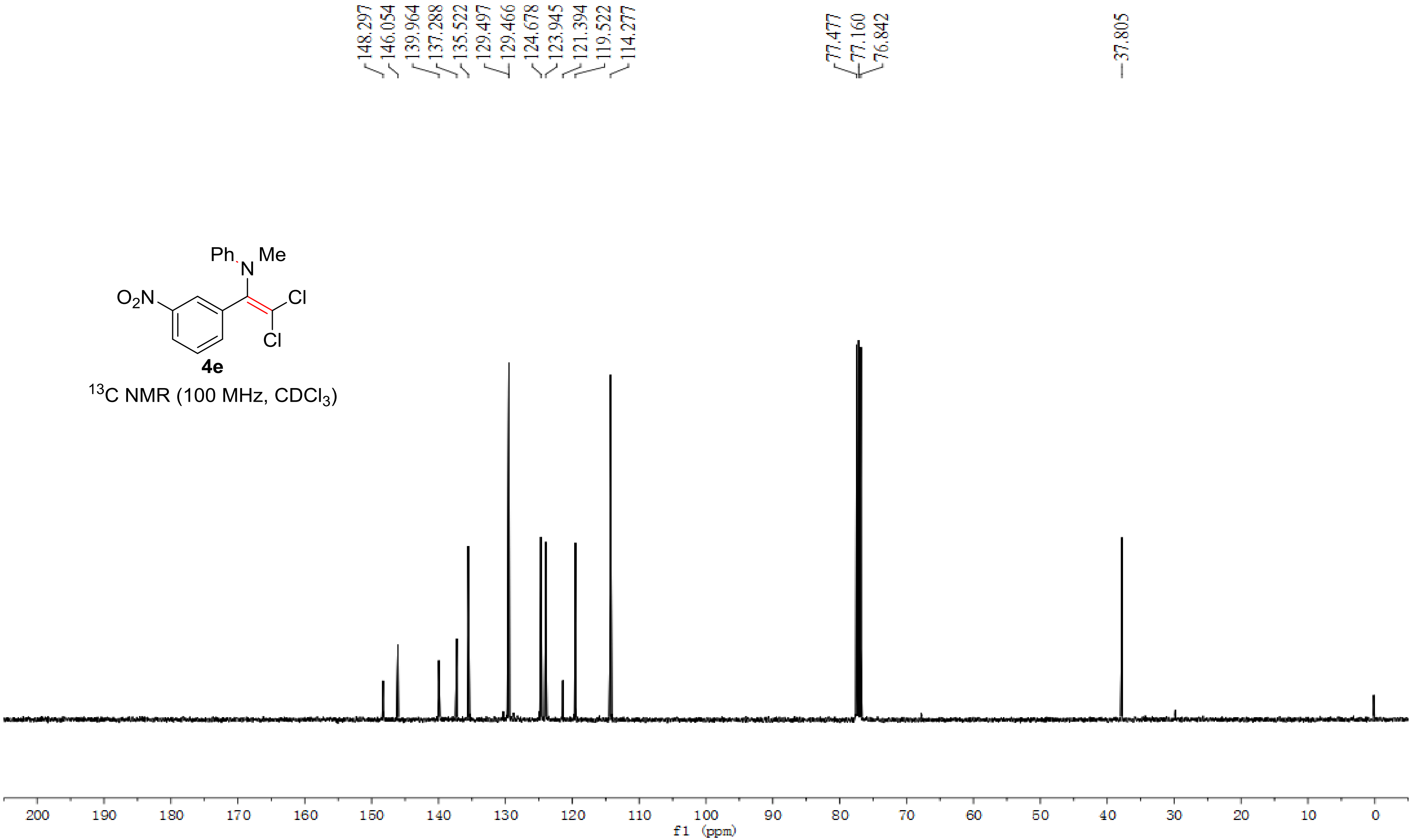
4d

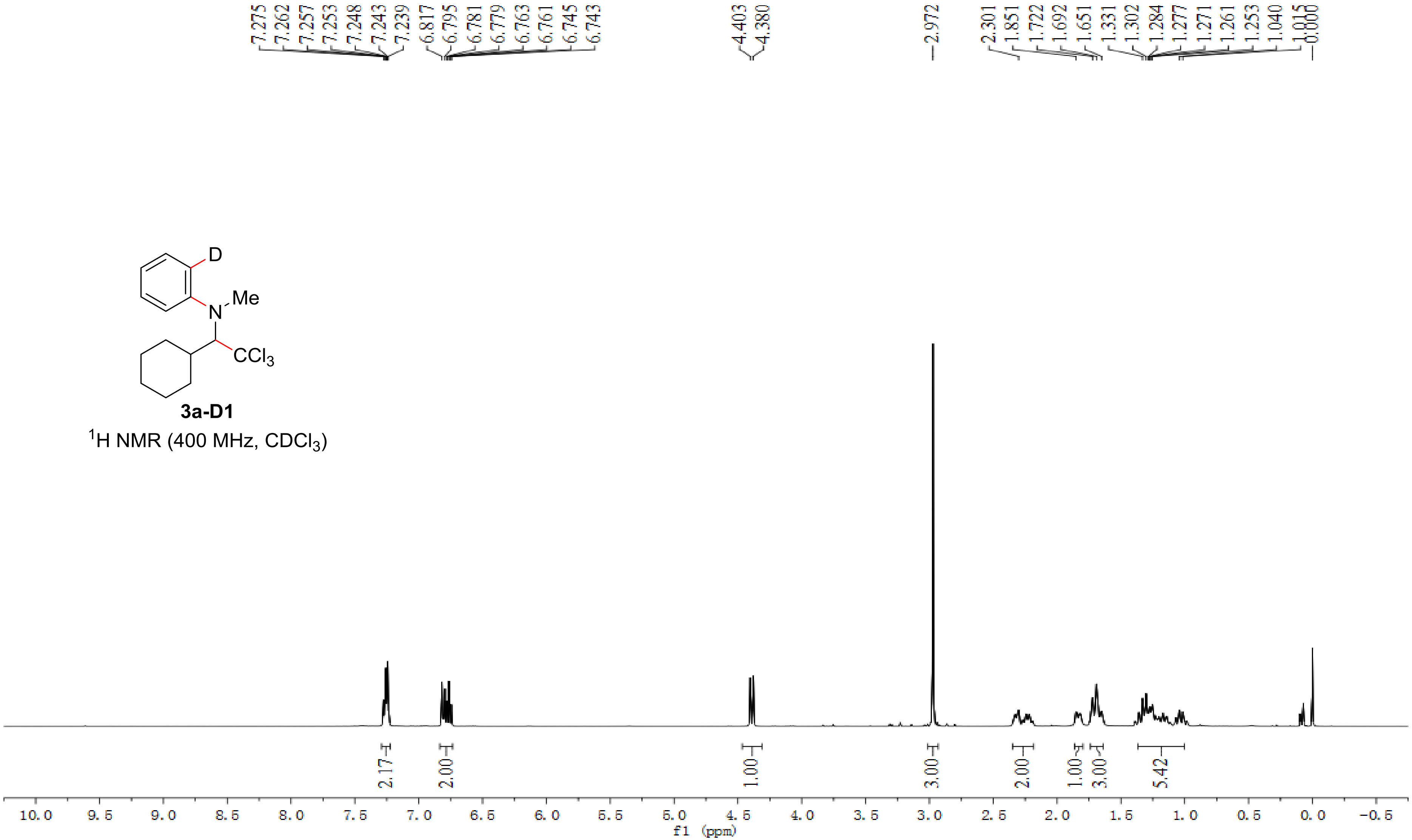
^{13}C NMR (100 MHz, $CDCl_3$)





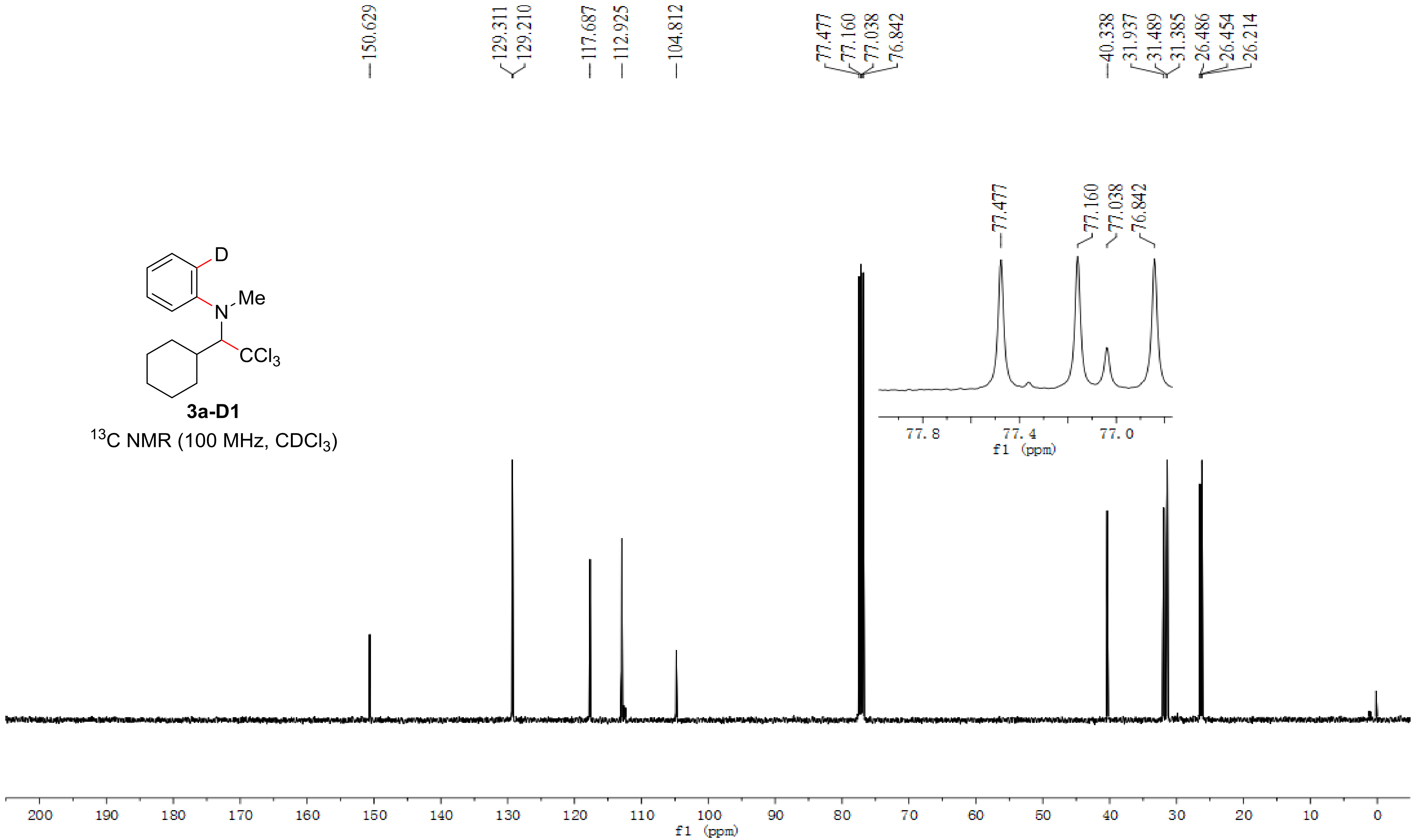
8.415
8.410
8.405
8.188
8.185
8.182
8.180
8.167
8.165
8.162
8.159
7.844
7.842
7.840
7.837
7.825
7.822
7.821
7.818
7.545
7.525
7.505
7.268
7.253
7.249
7.246
7.227
6.858
6.839
6.837
6.821
6.799
6.796
6.791
6.779
6.777
6.774
3.158
-0.000
Ph
N
Me
O2N
Cl
Cl
4e
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
1.00
2.35
1.00
2.00
3.00
f1 (ppm)

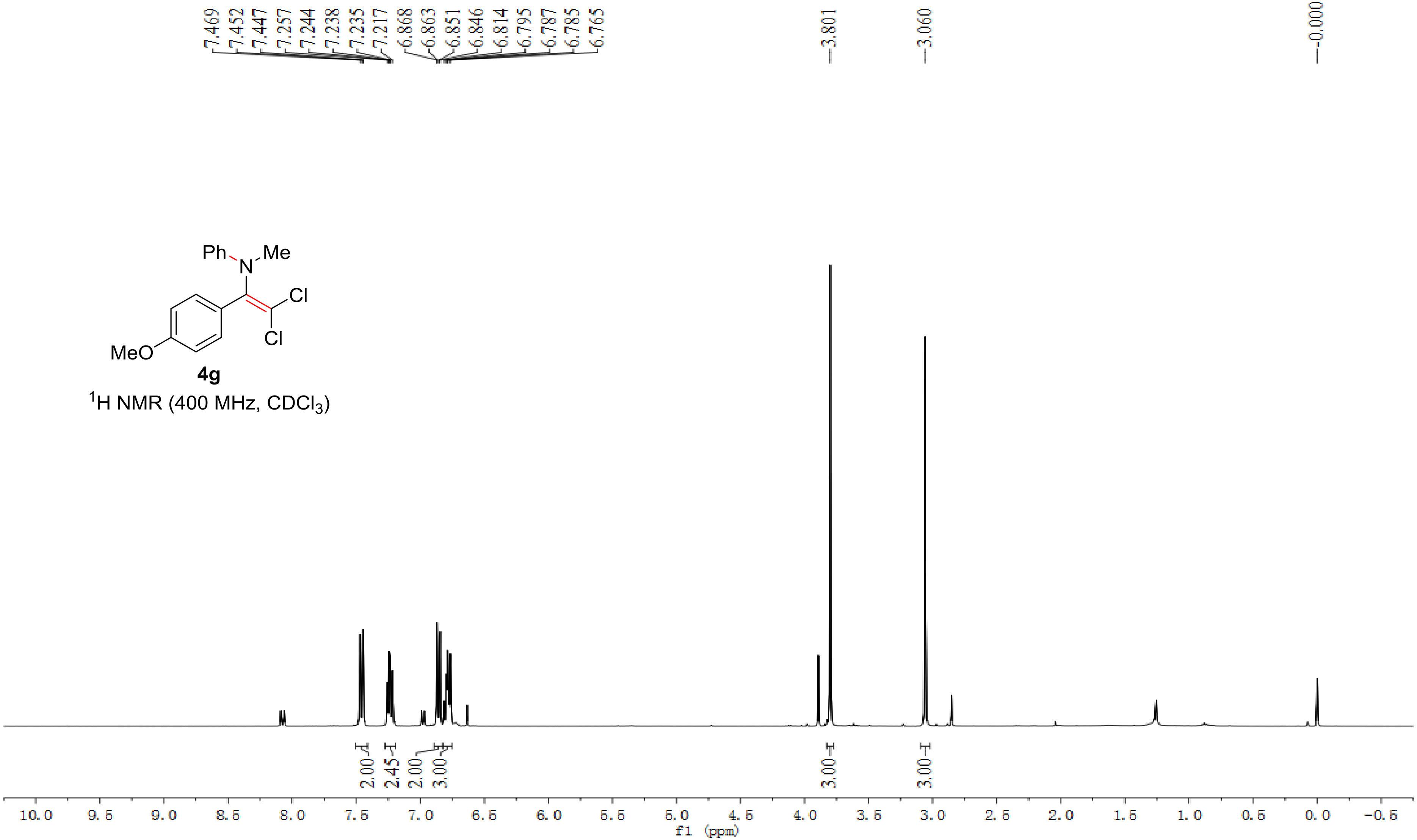

148.297
146.054
139.964
137.288
135.522
129.497
129.466
124.678
123.945
121.394
119.522
114.277
77.477
77.160
76.842
37.805
Ph
N
Me
O2N
Cl
Cl
4e
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3a-D1

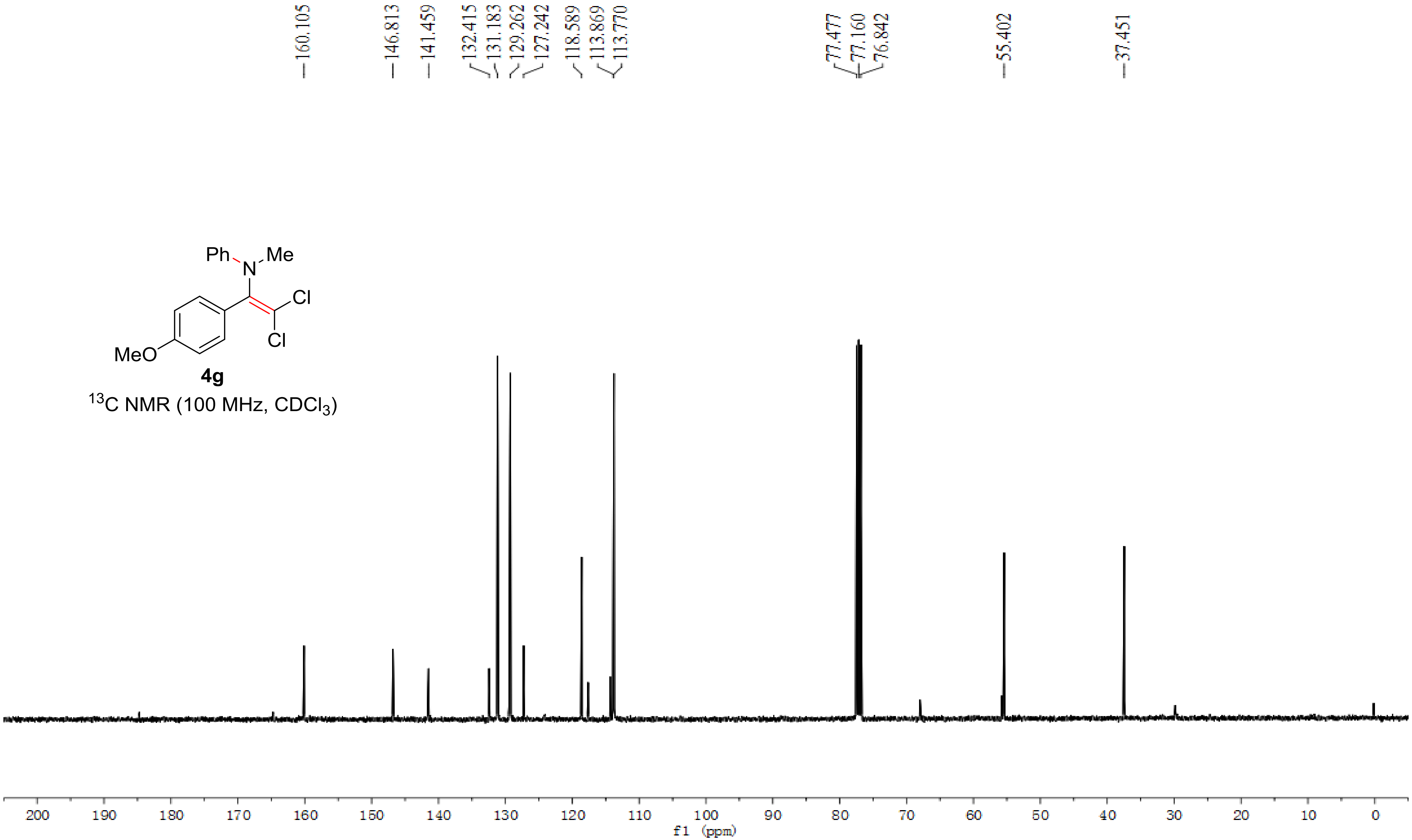
^{1}H NMR (400 MHz, $CDCl_3$)


150.629
129.311
129.210
117.687
112.925
104.812
77.477
77.160
77.038
76.842
40.338
31.937
31.489
31.385
26.486
26.454
26.214
D
N
Me
CCl3
3a-D1
13C NMR (100 MHz, CDCl3)
77.8
77.4
77.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



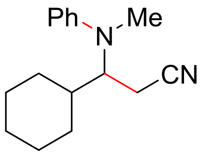
4g

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



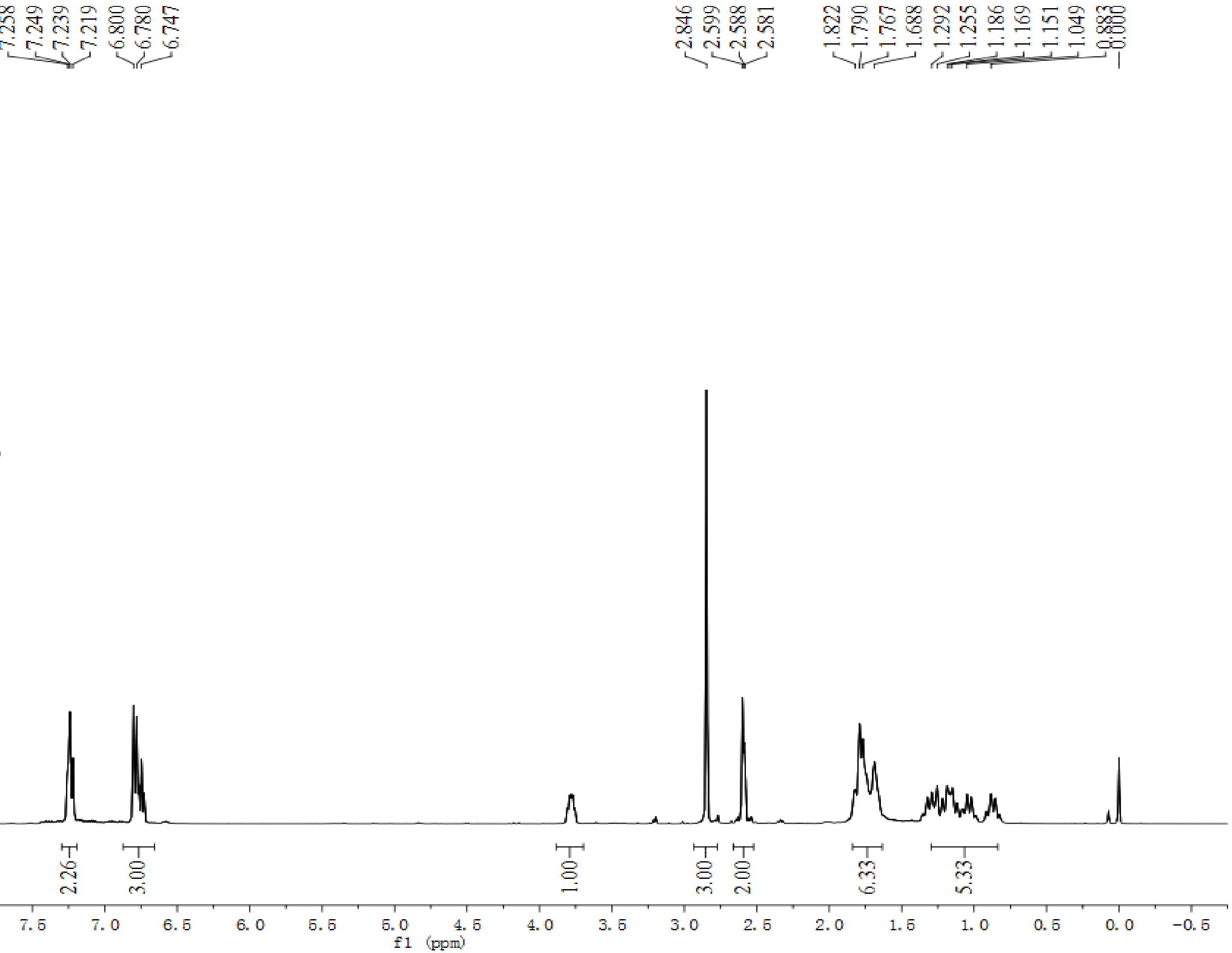
4g

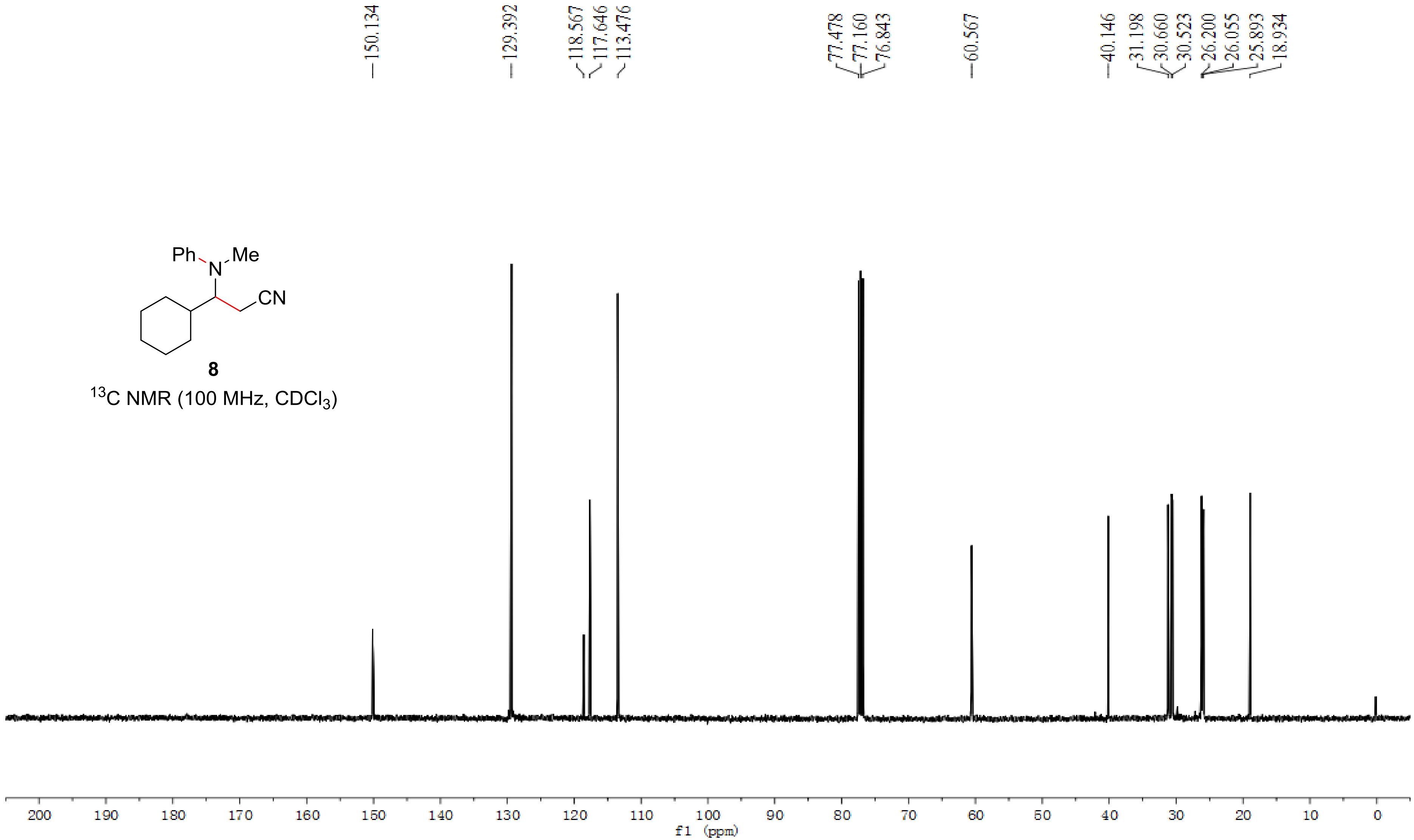
^{13}C NMR (100 MHz, $CDCl_3$)



8

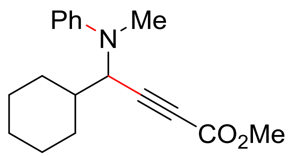
^{1}H NMR (400 MHz, $CDCl_3$)





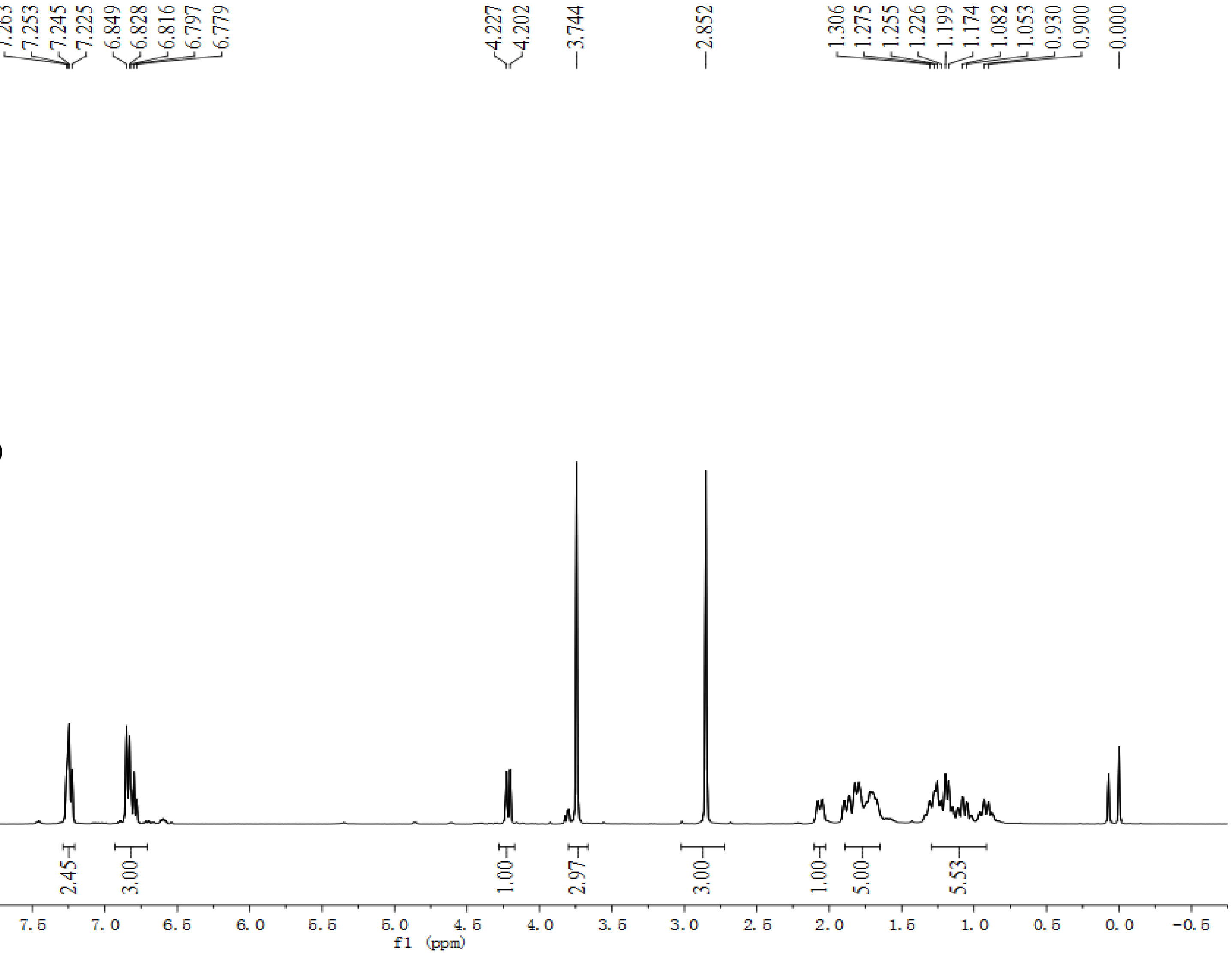
8

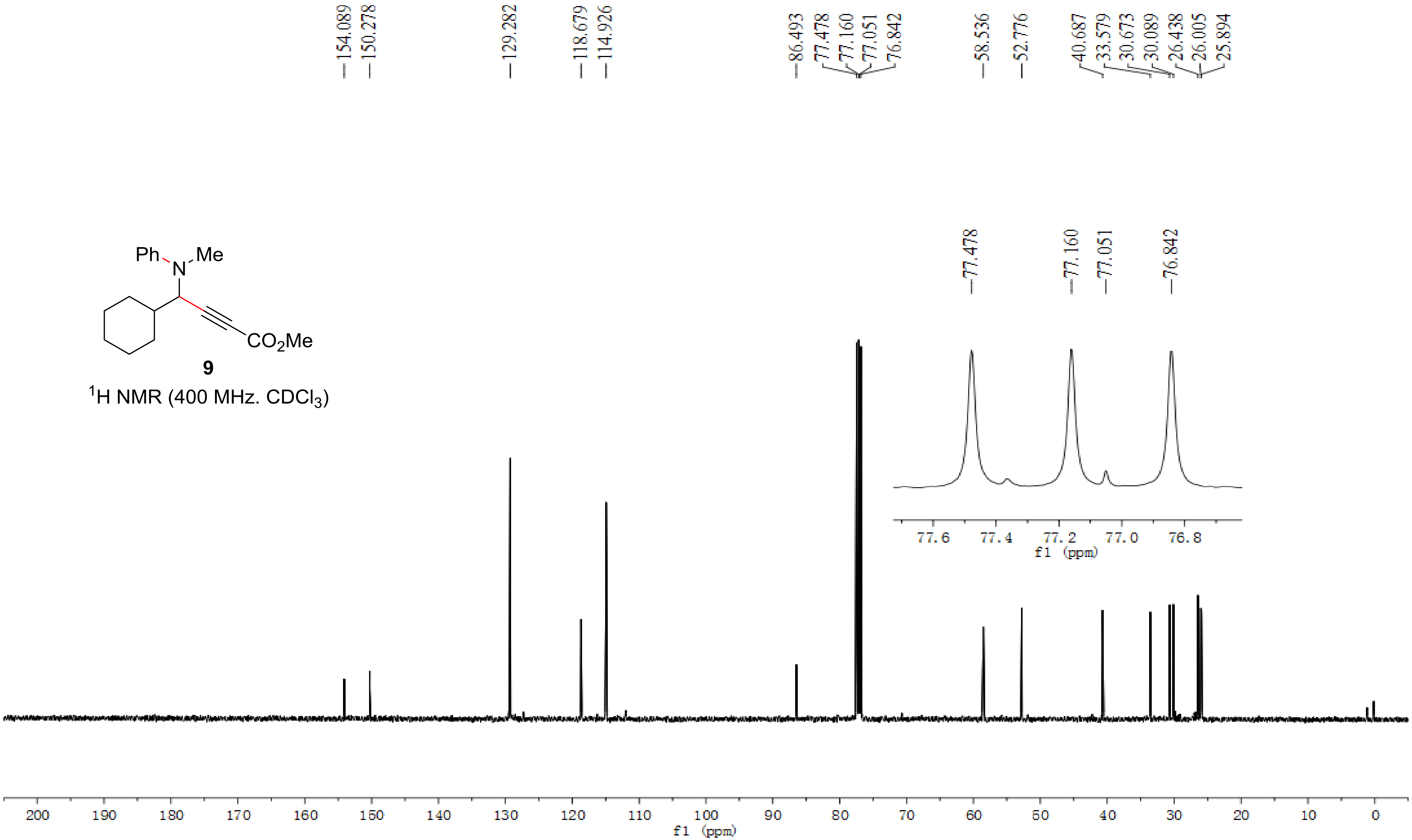
^{13}C NMR (100 MHz, $CDCl_3$)



9

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





9

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