Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Fluoro-Benzoxazepines via I(III)/BF_3·Et_2O Enabled 1,2-Aryl Migration/Fluorination Cascade

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Supporting Information

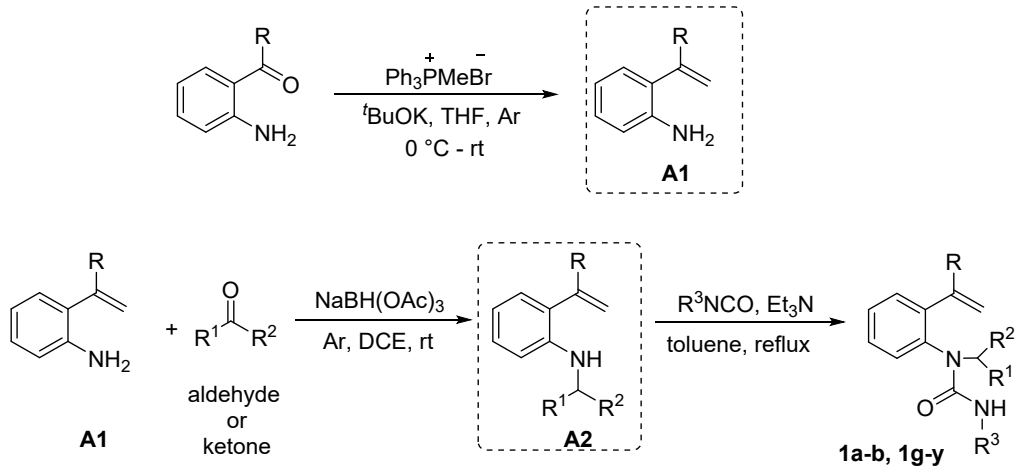
I. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer at 25 °C. $CDCl_3$ and DMSO-d_6 were used as NMR solvents. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J*, are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) data were recorded on Q Exactive HF (Q Exactive™ HF/UltiMate™ 3000 RSLCnano) using electron spray ionization (ESI) in positive (or negative) mode. Melting points were determined with a Micromelting point apparatus. TLC plates were visualized by exposure to ultraviolet light. Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 70 °C for 3 h before used. Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate (EtOAc) and petroleum ether (PE).

II. Experimental Procedures and Spectroscopic Data

1. Synthesis of Starting Materials

General procedure for preparation of substrates 1a-b, 1g-1y, 1ab and 1ac.[1-5]



Method A:

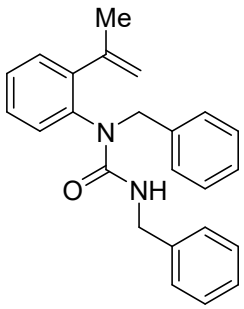
A1: To a suspension of methyltriphenylphosphonium bromide (1.5 equiv) in anhydrous THF (200 mL), potassium *tert*-butoxide (2.0 equiv) was added portion-wisely at 0 ℃ under argon atmosphere. The mixture was stirred at 0 ℃ for 1 h. Then 2-amino ketone (1.0 equiv.) was added at the same temperature. The mixture was allowed to warm overnight to ambient temperature. The reaction was quenched by the addition of an aqueous saturated solution of NH_4Cl. The aqueous phase was extracted with EtOAc (30 mL×3). The combined organic layer weas washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1/15) to give the product 2-alkenyl aniline **A1**.

A2: 2-Alkenyl aniline (A1, 1.0 equiv) and aldehyde or ketone (1.2 equiv) were mixed in 1,2-dichloroethane (DCE) and then treated with $NaBH(OAc)_3$ (1.5 equiv). The mixture was stirred at room temperature under a nitrogen atmosphere for 4-6 h. The reaction mixture was then quenched by addition of aqueous saturated $NaHCO_3$. The aqueous phase was extracted with EtOAc (30 mL×3). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum.

The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1/30) to give the product **A2**.

1a-b, 1g-y: To a solution of compound **A2** (500 mg, 1.0 equiv) in toluene (10.0 mL) were added benzyl isocyanate (1.5 equiv) and Et_3N (2.0 equiv) at room temperature. The mixture was heated to reflux and maintained at this temperature for 12 h. The solvent was evaporated under reduced pressure and the residue was quenched by addition of brine (30 mL). The aqueous phase was extracted with EtOAc (30 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1/7 ~ 1/5) to give the compound **1a-b, 1g-y**.

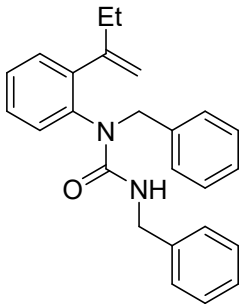
1,3-Dibenzyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1a (614 mg, 77% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 12H), 7.10 (td, *J* = 7.6, 1.7 Hz, 1H), 6.79 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.55 (d, *J* = 14.6 Hz, 1H), 5.21 – 5.19 (m, 1H), 5.02 – 5.00 (m, 1H), 4.58 (s, 1H), 4.41 (t, *J* = 5.4 Hz, 2H), 4.00 (d, *J* = 14.7 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 143.4, 142.7, 139.5, 138.5, 137.6, 130.9, 130.5, 128.9, 128.5, 128.3, 128.3, 128.2, 127.5, 127.1, 127.1, 116.7, 52.0, 44.9, 23.1. HRMS (ESI) calcd for $C_{24}H_{24}N_2NaO^+$ [M + Na^+] 379.1781, found 379.1783.

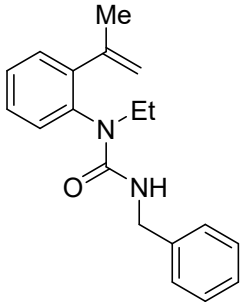
1,3-Dibenzyl-1-(2-(but-1-en-2-yl)phenyl)urea



1b (648 mg, 83% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 12H), 7.16 (td, *J* = 7.5, 2.0 Hz, 1H), 6.89 – 6.85 (m, 1H), 5.62 (d, *J* = 14.7 Hz, 1H), 5.28 (d, *J* = 1.5 Hz, 1H), 5.09 (s, 1H), 4.71 (t, *J* = 5.8 Hz, 1H), 4.52 (t, *J* = 7.3 Hz, 1H), 4.47 – 4.39 (m, 1H), 4.08 (d, *J* = 14.7 Hz, 1H), 2.43 (dq, *J* = 32.1, 7.3 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 149.7, 142.6, 139.6, 138.6, 137.6, 131.1, 130.9, 128.9, 128.5, 128.3, 128.3, 127.6, 127.2, 127.1, 114.4, 65.9, 52.0, 44.9, 29.1, 12.9. HRMS (ESI) calcd for $C_{25}H_{26}N_2NaO^+$ [M + Na^+] 393.1937, found 393.1935.

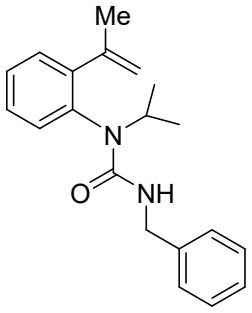
3-Benzyl-1-ethyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1g (484 mg, 53% yield, a white solid, mp: 76 – 78 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 5H), 7.24 – 7.15 (m, 4H), 5.17 – 5.12 (m, 1H), 4.97 (s, 1H), 4.50 (t, *J* = 5.9 Hz, 1H), 4.39 (d, *J* = 4.8 Hz, 2H), 4.20 (dq, *J* = 14.7, 7.3 Hz, 1H), 3.06 (dq, *J* = 14.3, 6.9 Hz, 1H), 2.01 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 143.4, 142.9, 139.7, 137.9, 130.7, 130.6, 128.5, 128.3, 127.5, 127.1, 116.5, 44.7, 43.2, 23.0, 13.7. HRMS (ESI) calcd for $C_{19}H_{22}N_2NaO^+$ [M + Na^+] 317.1624, found 317.1620.

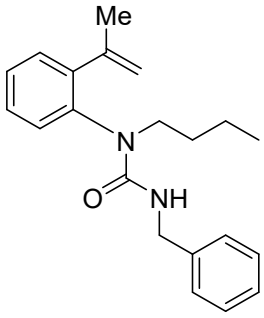
3-Benzyl-1-isopropyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1h (581 mg, 66% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.33 – 7.25 (m, 3H), 7.24 – 7.19 (m, 3H), 7.17 – 7.12 (m, 1H), 5.18 – 5.15 (m, 1H), 5.03 (s, 1H), 4.53 (hept, *J* = 6.7 Hz, 1H), 4.38 (m, 3H), 2.06 (s, 3H), 1.26 (d, *J* = 6.2 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 144.1, 143.7, 139.7, 136.3, 131.6, 130.5, 128.5, 128.4, 128.3, 127.5, 127.0, 117.1, 49.8, 44.6, 23.4, 22.0, 20.3. HRMS (ESI) calcd for $C_{20}H_{24}N_2NaO^+$ [M + Na^+] 331.1781, found 331.1783.

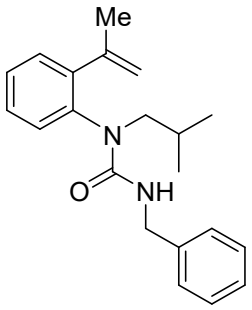
3-Benzyl-1-butyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1i (605 mg, 71% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 5H), 7.25 – 7.16 (m, 4H), 5.18 – 5.14 (m, 1H), 4.97 (s, 1H), 4.51 (t, *J* = 5.5 Hz, 1H), 4.41 – 4.36 (m, 2H), 4.15 (m, 1H), 3.01 – 2.91 (m, 1H), 2.01 (s, 3H), 1.59 (m, 1H), 1.48 – 1.35 (m, 1H), 1.30 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 143.3, 142.7, 139.7, 138.1, 130.7, 130.6, 128.4, 128.4, 128.2, 127.5, 127.1, 116.5, 48.2, 44.7, 30.6, 23.0, 20.2, 13.9. HRMS (ESI) calcd for $C_{21}H_{26}N_2NaO^+$ [M + Na^+] 345.1937, found 345.1933.

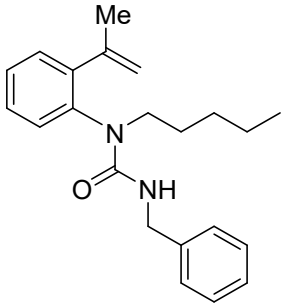
3-Benzyl-1-isobutyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1j (451 mg, 53% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 5H), 7.23 – 7.17 (m, 4H), 5.15 (s, 1H), 4.97 (s, 1H), 4.58 (s, 1H), 4.38 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.02 (m, 1H), 2.82 (m, 1H), 1.99 (s, 3H), 1.70 (m, 1H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 143.3, 142.5, 139.8, 138.2, 130.8, 130.8, 128.4, 128.3, 128.2, 127.5, 127.1, 116.6, 55.0, 44.8, 27.4, 22.9, 20.4, 20.2. HRMS (ESI) calcd for $C_{21}H_{26}N_2NaO^+$ [M + Na^+] 345.1937, found 345.1939.

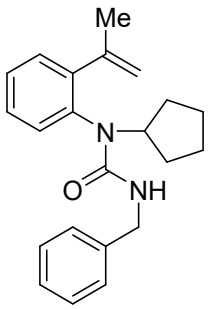
3-Benzyl-1-pentyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1k (472 mg, 57% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 3H), 7.27 – 7.24 (m, 2H), 7.22 – 7.14 (m, 4H), 5.17 – 5.12 (m, 1H), 4.96 (s, 1H), 4.50 (t, *J* = 5.6 Hz, 1H), 4.38 (d, *J* = 5.8 Hz, 2H), 4.12 (m, 1H), 3.01 – 2.90 (m, 1H), 2.00 (s, 3H), 1.65 – 1.37 (m, 2H), 1.24 (m, 4H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 143.4, 142.7, 139.7, 138.1, 130.6, 128.4, 128.4, 128.2, 127.5, 127.0, 116.5, 48.4, 44.7, 29.1, 28.1, 23.0, 22.5, 14.1. HRMS (ESI) calcd for $C_{22}H_{28}N_2NaO^+$ [M + Na^+] 359.2094, found 359.2097.

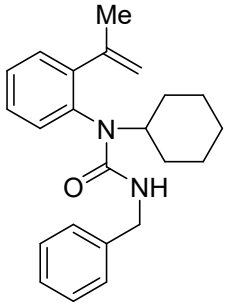
3-Benzyl-1-cyclopentyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1l (540 mg, 66% yield, a white solid, mp: 72 - 74 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.29 – 7.27 (m, 1H), 7.26 – 7.22 (m, 2H), 7.21 – 7.16 (m, 3H), 7.13 (dt, *J* = 7.1, 2.7 Hz, 1H), 5.15 – 5.12 (m, 1H), 4.99 (s, 1H), 4.47 – 4.39 (m, 1H), 4.38 – 4.31 (m, 3H), 2.07 (s, 1H), 2.03 (s, 3H), 1.87 – 1.76 (m, 1H), 1.51 (m, 5H), 1.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 143.9, 143.5, 139.7, 137.1, 131.3, 130.4, 128.5, 128.5, 128.4, 127.5, 127.0, 117.0, 60.0, 44.6, 31.0, 29.5, 23.5, 23.3, 23.2. HRMS (ESI) calcd for $C_{22}H_{26}N_2NaO^+$ [M + Na^+] 357.1937, found 357.1934.

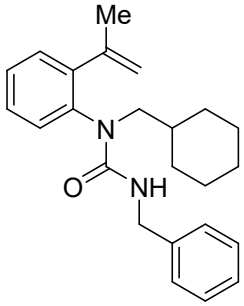
3-Benzyl-1-cyclohexyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1m (542 mg, 67% yield, a white solid, mp: 95 - 97 °C).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.25 (m, 5H), 7.24 – 7.19 (m, 3H), 7.15 – 7.11 (m, 1H), 5.16 – 5.14 (m, 1H), 5.03 (s, 1H), 4.38 (m, 2H), 4.31 (d, *J* = 9.6 Hz, 1H), 4.18 (m, 1H), 2.05 (s, 3H), 2.02 (s, 1H), 1.88 (d, *J* = 10.8 Hz, 1H), 1.78 – 1.65 (m, 2H), 1.57 (d, *J* = 12.8 Hz, 1H), 1.31 (m, 3H), 1.15 – 1.05 (m, 1H), 0.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 144.2, 143.7, 139.7, 136.3, 131.9, 130.4, 128.4, 128.4, 128.2, 127.5, 127.0, 117.1, 57.7, 44.6, 32.3, 30.8, 26.1, 25.6, 23.5. HRMS (ESI) calcd for $C_{23}H_{28}N_2NaO^+$ [M + Na^+] 371.2094, found 371.2097.

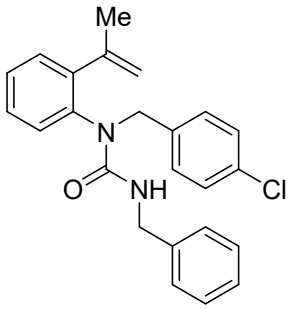
3-Benzyl-1-(cyclohexylmethyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1n (506 mg, 64% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 5H), 7.23 – 7.16 (m, 4H), 5.16 – 5.13 (m, 1H), 4.96 (s, 1H), 4.56 (t, *J* = 5.5 Hz, 1H), 4.38 (d, *J* = 5.8 Hz, 2H), 4.05 (m, 1H), 2.81 (dd, *J* = 13.8, 5.2 Hz, 1H), 1.98 (s, 3H), 1.86 (m, 1H), 1.72 (s, 1H), 1.67 – 1.50 (m, 3H), 1.49 – 1.40 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 1H), 1.11 (m, 3H), 0.92 – 0.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 143.3, 142.5, 139.8, 138.4, 130.8, 130.7, 128.4, 128.4, 128.1, 127.5, 127.0, 116.6, 54.1, 44.8, 36.9, 31.1, 30.9, 26.6, 26.0, 25.9, 23.0. HRMS (ESI) calcd for $C_{24}H_{30}N_2NaO^+$ [M + Na^+] 385.2250, found 385.2246.

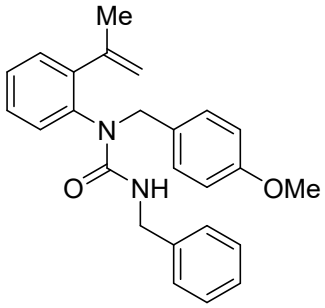
3-Benzyl-1-(4-chlorobenzyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1o (515 mg, 68% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.25 – 7.20 (m, 5H), 7.18 – 7.12 (m, 3H), 6.78 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.50 (d, *J* = 14.8 Hz, 1H), 5.24 – 5.20 (m, 1H), 5.02 (s, 1H), 4.60 (t, *J* = 5.3 Hz, 1H), 4.46 – 4.39 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 143.3, 142.6, 139.4, 137.4, 137.0, 133.0, 130.7, 130.6, 130.3, 128.5, 128.4, 128.4, 127.5, 127.2, 116.8, 51.3, 44.9, 23.0. HRMS (ESI) calcd for $C_{24}H_{23}{}^{35}ClN_2NaO^+$ [M + Na^+] 413.1391, found 413.1394.

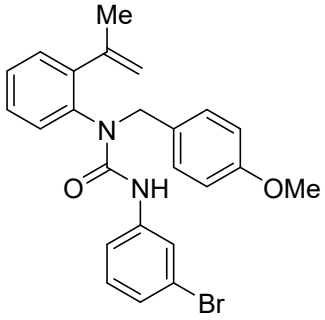
3-Benzyl-1-(4-methoxybenzyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1p (519 mg, 68% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.10 (m, 7H), 7.08 – 6.99 (m, 3H), 6.72 – 6.65 (m, 3H), 5.41 (d, *J* = 14.5 Hz, 1H), 5.13 – 5.09 (m, 1H), 4.92 (s, 1H), 4.47 (t, *J* = 5.6 Hz, 1H), 4.33 (dd, *J* = 9.6, 5.8 Hz, 2H), 3.85 (m, 1H), 3.68 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 157.1, 143.4, 142.7, 139.6, 137.6, 131.0, 130.7, 130.5, 130.2, 128.5, 128.3, 127.5, 127.1, 116.7, 113.6, 55.2, 51.3, 44.9, 23.1. HRMS (ESI) calcd for $C_{25}H_{26}N_2NaO_2^+$ [M + Na^+] 409.1886, found 409.1889.

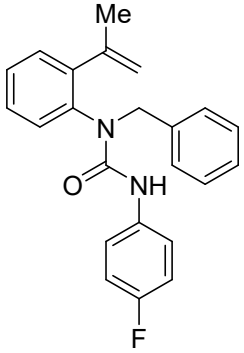
3-(3-Bromophenyl)-1-(4-methoxybenzyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1q (454 mg, 51% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.42 – 7.32 (m, 2H), 7.21 (td, *J* = 7.6, 1.6 Hz, 1H), 7.16 (dt, *J* = 6.3, 2.4 Hz, 3H), 7.12 – 7.03 (m, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.19 (s, 1H), 5.51 (d, *J* = 14.6 Hz, 1H), 5.25 (s, 1H), 5.06 (s, 1H), 3.98 (m, 1H), 3.76 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 154.0, 143.0, 142.7, 140.2, 137.1, 130.8, 130.6, 130.2, 130.0, 130.0, 129.0, 128.7, 125.8, 122.5, 122.1, 117.8, 117.1, 113.7, 55.2, 51.5, 23.2. HRMS (ESI) calcd for $C_{24}H_{23}{}^{79}BrN_2NaO_2^+$ [M + Na^+] 473.0835, found 473.0837.

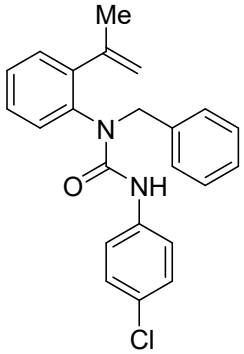
1-Benzyl-3-(4-fluorophenyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1r (540 mg, 67% yield, a white solid, mp: 115 - 116 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.25 (d, *J* = 3.5 Hz, 4H), 7.24 – 7.17 (m, 4H), 6.96 – 6.86 (m, 3H), 6.13 (s, 1H), 5.57 (d, *J* = 14.7 Hz, 1H), 5.27 – 5.24 (m, 1H), 5.06 (s, 1H), 4.03 (d, *J* = 14.7 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, (d, $^{1}J_{C\text{-}F}$ = 242.8 Hz), 154.6, 143.1, 142.8, 138.0, 137.4, 134.8, (d, $^{4}J_{C\text{-}F}$ = 2.7 Hz), 130.8, 130.6, 128.9, 128.7, (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 128.3, 127.3, 121.5, (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 117.0, 115.5, 115.3, 52.1, 23.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.1. HRMS (ESI) calcd for $C_{23}H_{21}FN_2NaO^+$ [M + Na^+] 383.1530, found 383.1532.

1-Benzyl-3-(4-chlorophenyl)-1-(2-(prop-1-en-2-yl)phenyl)urea

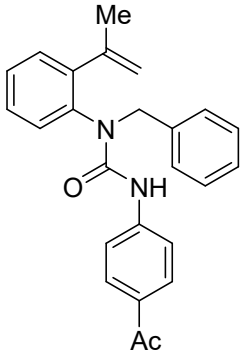


1s (397 mg, 47% yield, a white solid, mp: 87 - 89 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.31 (m, 8H), 7.26 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.26 (s, 1H), 5.64 (d, *J* = 14.7 Hz, 1H), 5.32 (s, 1H), 5.12 (s, 1H), 4.10 (d, *J* = 14.7 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 143.0, 142.7, 137.9, 137.4, 137.2, 130.8, 130.5, 129.0, 128.9, 128.8, 128.7, 128.4, 127.9, 127.4, 120.7, 117.1, 52.1, 23.2. HRMS (ESI) calcd for $C_{23}H_{21}{}^{35}ClN_2NaO^+$ [M + Na^+]

399.1235, found 399.1238.

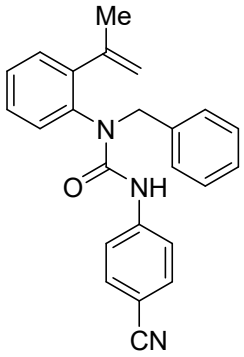
3-(4-Acetylphenyl)-1-benzyl-1-(2-(prop-1-en-2-yl)phenyl)urea



1t (594 mg, 69% yield, a brown solid, mp: 110 - 112 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.25 (td, *J* = 7.5, 1.2 Hz, 1H), 7.19 – 7.13 (m, 5H), 7.11 (dd, *J* = 7.3, 1.8 Hz, 1H), 6.82 – 6.75 (m, 1H), 6.39 (s, 1H), 5.49 (d, *J* = 14.7 Hz, 1H), 5.17 – 5.13 (m, 1H), 4.96 (s, 1H), 3.96 (d, *J* = 14.7 Hz, 1H), 2.42 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 153.8, 143.4, 142.8, 142.6, 137.7, 137.0, 131.7, 130.8, 130.4, 129.7, 129.1, 128.9, 128.8, 128.4, 127.5, 118.1, 117.2, 52.3, 26.4, 23.2. HRMS (ESI) calcd for $C_{25}H_{24}N_2NaO_2^+$ [M + Na^+] 407.1730, found 407.1726.

1-Benzyl-3-(4-cyanophenyl)-1-(2-(prop-1-en-2-yl)phenyl)urea

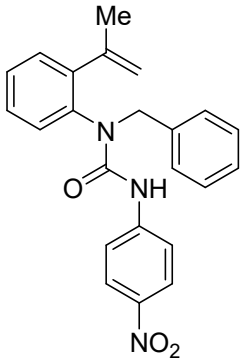


1t (510 mg, 62% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.35 (m, 4H), 7.24 (m, 5H), 7.23 – 7.19 (m, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.47 (s, 1H), 5.56 (d, *J* = 14.7 Hz, 1H), 5.25 (s, 1H), 5.04 (s, 1H), 4.05 (m, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 143.1, 142.8, 142.6, 137.5, 136.8, 133.1, 130.9, 130.3, 129.2, 128.9, 128.8, 128.5, 127.6, 119.1, 118.8, 117.2, 105.5, 52.4, 23.2. HRMS (ESI) calcd for

$C_{24}H_{21}N_3NaO_2^+$ [M + Na^+] 390.1577, found 390.1573.

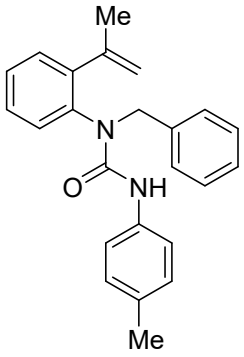
1-Benzyl-3-(4-nitrophenyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1v (625 mg, 72% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.2 Hz, 2H), 7.51 (d, *J* = 9.2 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.43 – 7.39 (m, 1H), 7.34 – 7.25 (m, 6H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.64 (s, 1H), 5.62 (d, *J* = 14.7 Hz, 1H), 5.31 (s, 1H), 5.09 (s, 1H), 4.11 (m, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 145.0, 142.7, 142.6, 142.5, 137.4, 136.7, 131.0, 130.2, 129.3, 128.9, 128.9, 128.5, 127.6, 125.0, 118.1, 117.3, 52.4, 23.2. HRMS (ESI) calcd for $C_{23}H_{21}N_3NaO_3^+$ [M + Na^+] 410.1475, found 410.1471.

1-Benzyl-1-(2-(prop-1-en-2-yl)phenyl)-3-(*p*-tolyl)urea

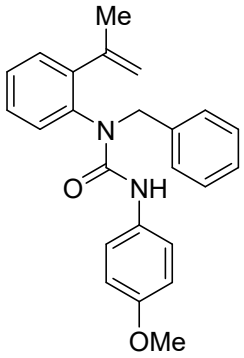


1w (559 mg, 70% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H), 7.26 – 7.20 (m, 5H), 7.19 – 7.14 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.87 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.12 (s, 1H), 5.58 (d, *J* = 14.7 Hz, 1H), 5.25 – 5.22 (m, 1H), 5.06 (s, 1H), 4.03 (d, *J* = 14.7 Hz, 1H), 2.25 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 143.2, 142.8, 138.3, 137.5, 136.3, 132.6, 130.7, 130.7, 129.4, 128.9, 128.8, 128.6, 128.3, 127.3, 119.7, 117.0, 52.0, 23.2, 20.8. HRMS (ESI) calcd for

$C_{24}H_{24}N_2NaO^+$ [M + Na^+] 379.1781, found 379.1778.

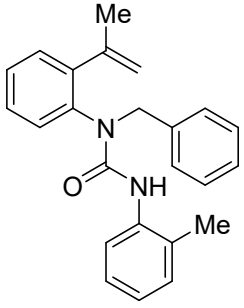
1-Benzyl-3-(4-methoxyphenyl)-1-(2-(prop-1-en-2-yl)phenyl)urea



1x (609 mg, 73% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.17 – 7.05 (m, 9H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 2H), 5.97 (s, 1H), 5.49 (d, *J* = 14.6 Hz, 1H), 5.16 (s, 1H), 4.98 (s, 1H), 3.94 (m, 1H), 3.63 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 154.9, 143.2, 142.8, 138.3, 137.6, 131.9, 130.7, 130.7, 128.9, 128.7, 128.6, 128.3, 127.3, 121.8, 117.0, 114.1, 55.5, 52.0, 23.2. HRMS (ESI) calcd for $C_{24}H_{24}N_2NaO_2^+$ [M + Na^+] 395.1730, found 395.1733.

1-Benzyl-1-(2-(prop-1-en-2-yl)phenyl)-3-(*o*-tolyl)urea

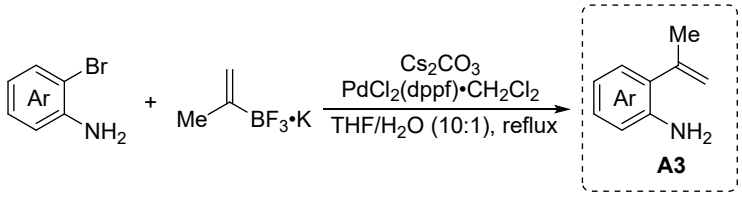


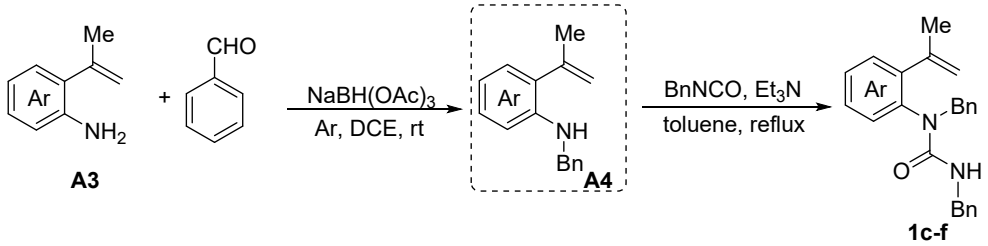
1y (493 mg, 58% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.32 – 7.26 (m, 5H), 7.23 (t, *J* = 6.5 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.15 (s, 1H), 5.66 (d, *J* = 14.7 Hz, 1H), 5.32 (m, 1H), 5.15 (s, 1H), 4.09 (d, *J* = 14.7 Hz, 1H), 2.18 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 143.1, 142.9, 138.2, 137.4, 137.1, 130.8, 130.8, 130.1, 129.0, 128.9, 128.5, 128.3, 127.3, 127.0, 126.9, 123.3, 121.0, 117.0, 51.7, 23.3, 17.3. HRMS

(ESI) calcd for $C_{24}H_{24}N_2NaO^+$ [M + Na^+] 379.1781, found 379.1784.

General procedure for preparation of substrates 1c - 1f. [4]



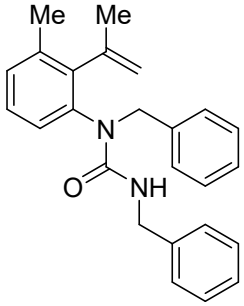


Method B:

A3: To a suspension of potassium isopropenyltrifluoroborate (1.1 equiv), Cs_2CO_3 (3.0 equiv), $PdCl_2(dppf)\cdot CH_2Cl_2$ (9.0 mol%) in a solvent mixture (THF/H_2O = 10/1) was added 2-bromoaniline (1.0 equiv). The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with EtOAc (50 mL × 3). The combined organic layers were washed with brine (50mL) and dried over anhydrous Na_2SO_4. After filtered, the mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc/PE = 1/15) gave the compound **A3**.

1c-f: The following preparation procedure from **A3** to **1c-f** is similar to that of method A.

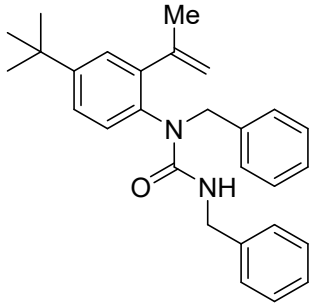
1,3-Dibenzyl-1-(3-methyl-2-(prop-1-en-2-yl)phenyl)urea



1c (569 mg, 73% yield, a white solid, mp: 97 – 99 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.05 (m, 11H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.48 (d, *J* = 7.0 Hz, 1H), 5.49 (d, *J* = 14.7 Hz, 1H), 5.20 (s, 1H), 4.71 (s, 1H), 4.33 (m, 3H), 3.88 (d, *J* = 14.7 Hz, 1H), 2.16 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 143.2, 139.7, 138.9, 138.0, 137.8, 130.4, 129.0, 128.5, 128.3, 127.6, 127.6, 127.1, 116.5, 52.9, 44.9, 23.5, 20.0. HRMS (ESI) calcd for $C_{25}H_{26}N_2NaO^+$ [M + Na^+] 393.1937, found 393.1934.

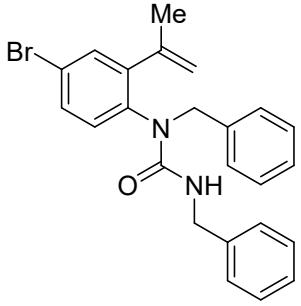
1,3-Dibenzyl-1-(4-(*tert*-butyl)-2-(prop-1-en-2-yl)phenyl)urea



1d (509 mg, 69% yield, a white solid, mp: 77 – 79 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 12H), 7.03 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 5.44 (d, *J* = 14.8 Hz, 1H), 5.13 – 5.06 (m, 1H), 4.96 – 4.88 (m, 1H), 4.58 (t, *J* = 5.8 Hz, 1H), 4.34 (p, *J* = 9.0 Hz, 2H), 3.90 (d, *J* = 14.8 Hz, 1H), 1.96 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 151.3, 144.0, 141.8, 139.8, 138.8, 135.0, 130.1, 128.7, 128.5, 128.2, 127.5, 127.4, 127.1, 127.0, 125.4, 116.4, 52.2, 44.8, 34.6, 31.3, 23.3. HRMS (ESI) calcd for $C_{28}H_{32}N_2NaO^+$ [M + Na^+] 435.2407, found 435.2403.

1,3-Dibenzyl-1-(4-bromo-2-(prop-1-en-2-yl)phenyl)urea

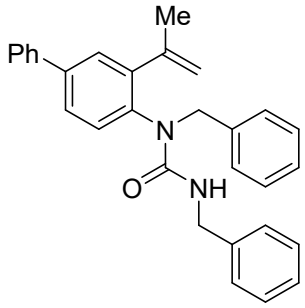


1e (540 mg, 75% yield, a white solid, mp: 104 – 106 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.2 Hz, 1H), 7.33 (m, 10H), 6.71 (d, *J* = 8.4

Hz, 1H), 5.62 (d, *J* = 14.2 Hz, 1H), 5.30 (s, 1H), 5.10 (s, 1H), 4.61 (t, *J* = 5.3 Hz, 1H), 4.48 (dd, *J* = 9.7, 5.5 Hz, 2H), 4.01 (d, *J* = 14.3 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 144.6, 142.2, 139.3, 138.1, 136.7, 133.4, 132.5, 131.4, 128.8, 128.6, 128.4, 127.6, 127.3, 127.3, 122.1, 117.7, 51.8, 45.0, 22.8. HRMS (ESI) calcd for $C_{24}H_{23}{}^{79}BrN_2NaO^+$ [M + Na^+] 457.0886, found 457.0889.

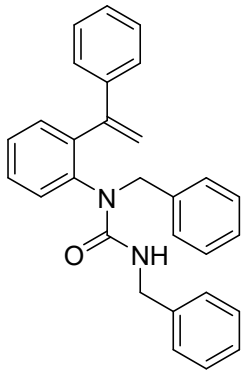
1,3-Dibenzyl-1-(3-(prop-1-en-2-yl)-[1,1'-biphenyl]-4-yl)urea



1f (491 mg, 68% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.16 (m, 11H), 6.78 (d, *J* = 8.1 Hz, 1H), 5.50 (d, *J* = 14.5 Hz, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 4.59 (t, *J* = 5.5 Hz, 1H), 4.36 (t, *J* = 4.8 Hz, 2H), 3.95 (d, *J* = 14.6 Hz, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 143.5, 142.9, 141.1, 139.8, 139.6, 138.5, 136.8, 131.2, 129.2, 128.9, 128.9, 128.5, 128.3, 127.8, 127.6, 127.2, 127.0, 126.9, 116.9, 52.1, 44.9, 23.1. HRMS (ESI) calcd for $C_{30}H_{28}N_2NaO^+$ [M + Na^+] 455.2094, found 455.2091.

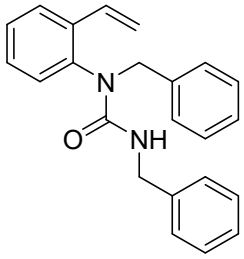
1,3-dibenzyl-1-(2-(1-phenylvinyl)phenyl)urea



1ab (447.3 mg, 61% yield, a white solid, mp: 99 – 101 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.17 (m, 13H), 7.15 (d, *J* = 7.5 Hz, 4H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 1H), 5.24 (s, 1H), 5.19 (d, *J* = 14.8 Hz, 1H), 4.32 (m, 2H), 4.09 (m, 1H), 3.65 (d, *J* = 14.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 147.5, 141.4, 140.9, 139.5, 138.8, 138.8, 132.1, 131.2, 129.0, 128.8, 128.7, 128.5, 128.4, 128.2, 128.0, 127.6, 127.1, 127.1, 126.7, 117.0, 51.4, 44.8. HRMS (ESI) calcd for $C_{29}H_{26}N_2NaO^+$ [M + Na^+] 441.1937, found 441.1935.

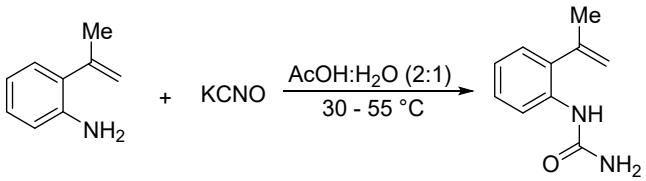
1,3-dibenzyl-1-(2-vinylphenyl)urea



1ac (303 mg, 37% yield, colorless liquid).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.21 (m, 8H), 7.19 (m, 4H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.69 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.29 (t, *J* = 10.3 Hz, 2H), 4.46 – 4.28 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 139.5, 138.3, 138.2, 136.5, 131.7, 130.3, 129.1, 129.1, 128.6, 128.4, 128.3, 127.3, 127.2, 127.0, 126.7, 116.7, 52.9, 44.7. HRMS (ESI) calcd for $C_{23}H_{22}N_2NaO^+$ [M + Na^+] 365.1624, found 365.1620.

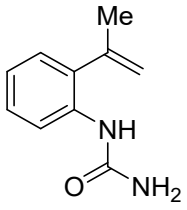
General procedure for preparation of substrates 1ad.[5]



To a solution of 2-alkenyl aniline (500 mg, 1.0 equiv) in a solvent mixture ($AcOH/H_2O$ = 2/1) was added warm KCNO solution (10 equiv of KCNO dissolved in 15 mL water) slowly at 30 °C. Then reaction mixture was heated to 55 °C and stirred at that temperature for 30 mins. The product was filtered under reduced pressure. The residue was washed with water and dried by lyophilization to obtain the corresponding

compound **1ad** as a white powder.

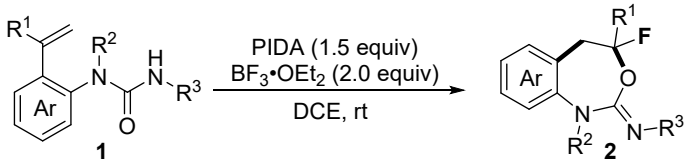
1-(2-(Prop-1-en-2-yl)phenyl)urea



1ad (423 mg, 64% yield, a white solid, mp: 168 – 169 ℃).

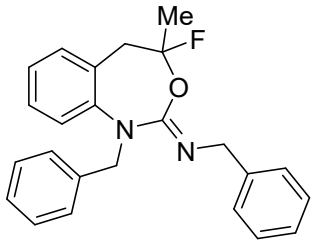
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 8.1 Hz, 1H), 7.48 (s, 1H), 7.15 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 6.93 (t, J = 7.3 Hz, 1H), 6.13 (s, 2H), 5.28 (s, 1H), 4.95 (s, 1H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.5, 143.3, 136.6, 134.0, 128.4, 127.6, 122.3, 121.7, 117.1, 24.1. HRMS (ESI) calcd for $C_{10}H_{12}N_2NaO^+$ [M + Na^+] 199.0842, found 199.0838.

2. Typical Synthetic Procedure and Spectroscopic Data of 2a-y.



To a reaction flask filled with PIDA (1.5 equiv, 0.75 mmol) in DCE (5.0 mL) was added BF_3•OEt_2 (2.0 equiv, 1mmol). The mixture was stirred at room temperature for 1 min and reactant **1** (0.5 mmol) was added. The resulting mixture was kept stirring until TLC indicated the total consumption of substrate **1**. Then the reaction mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtered, the mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 30/1~ 10/1) to afford target product **2**.

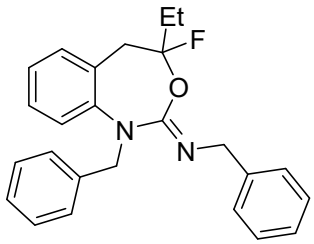
(*Z*)-*N*,1-Dibenzyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2a (154 mg, 82% yield, a pale yellow solid, mp: 88 - 90 °C).

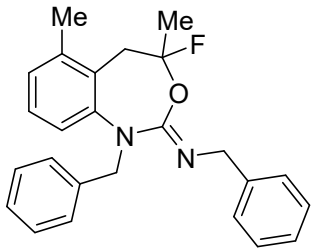
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.16 (m, 8H), 7.12 (dd, *J* = 12.4, 5.1 Hz, 5H), 7.02 (t, *J* = 7.3 Hz, 1H), 5.35 (d, *J* = 16.0 Hz, 1H), 5.05 (d, *J* = 16.0 Hz, 1H), 4.74 (d, *J* = 15.9 Hz, 1H), 4.54 (d, *J* = 15.9 Hz, 1H), 3.39 (t, *J* = 13.6 Hz, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 1.53 (d, *J* = 17.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 143.2, 142.0, 138.6, 131.0, 129.4, 128.7, (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 128.5, 128.0, 127.3, 127.1, 126.9, 125.9, 124.1, 121.2, 119.9, (d, $^{1}J_{C\text{-}F}$ = 231.7 Hz), 54.1, 50.7, 41.5, (d, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 23.2, (d, $^{2}J_{C\text{-}F}$ = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.8. HRMS (ESI) calcd for $C_{24}H_{23}FN_2NaO^+$ [M + Na^+] 397.1687, found 397.1689.

(*Z*)-*N*,1-Dibenzyl-4-ethyl-4-fluoro-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2b (155 mg, 80% yield, a white solid, mp: 56 – 57 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 7.9 Hz, 4H), 7.25 – 7.20 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.11 (dd, *J* = 14.0, 6.8 Hz, 5H), 7.01 (t, *J* = 7.3 Hz, 1H), 5.37 (d, *J* = 16.0 Hz, 1H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.74 (d, *J* = 15.8 Hz, 1H), 4.53 (d, *J* = 15.8 Hz, 1H), 3.35 (t, *J* = 14.0 Hz, 1H), 2.95 (d, *J* = 14.1 Hz, 1H), 1.93 – 1.66 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 143.3, 142.0, 138.6, 129.3, 128.7, (d, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 128.6, 128.5, 128.0, 127.3, 127.1, 126.9, 125.9, 123.9, 122.2, (d, $^{1}J_{C\text{-}F}$ = 234.9 Hz), 121.1, 54.1, 50.7, 39.8, (d, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 29.2, (d, $^{2}J_{C\text{-}F}$ = 26.2 Hz), 6.8, (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.0. HRMS (ESI) calcd for $C_{25}H_{25}FN_2NaO^+$ [M + Na^+] 411.1843, found 411.1845.

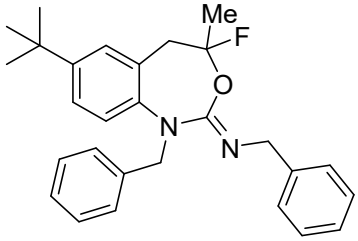
(*Z*)-*N*,1-Dibenzyl-4-fluoro-4,6-dimethyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2c (161 mg, 84% yield, a white solid, mp: 91 - 92 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 4H), 7.17 – 7.09 (m, 3H), 7.04 (m, 4H), 6.92 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 7.4 Hz, 1H), 5.22 (d, J = 15.9 Hz, 1H), 4.98 (d, J = 16.0 Hz, 1H), 4.65 (d, J = 15.9 Hz, 1H), 4.46 (d, J = 15.9 Hz, 1H), 3.12 (m, 2H), 2.27 (s, 3H), 1.46 (d, J = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 143.6, 142.1, 138.7, 135.9, 128.4, 127.9, 127.8, 127.8, (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 127.3, 127.2, 126.9, 126.1, 125.9, 119.9, (d, $^1J_{C\text{-}F}$ = 231.7 Hz), 119.4, 54.3, 50.6, 36.3, (d, $^2J_{C\text{-}F}$ = 32.5 Hz), 23.2, (d, $^2J_{C\text{-}F}$ = 28.2 Hz), 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ-84.5. HRMS (ESI) calcd for $C_{25}H_{25}FN_2NaO^+$ [M + Na^+] 411.1843, found 411.1840.

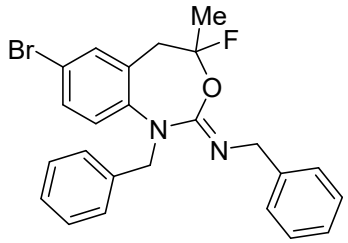
(*Z*)-*N*,1-Dibenzyl-7-(*tert*-butyl)-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2d (168 mg, 81% yield, a white solid, mp: 84 - 86 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (m, 13H), 5.32 (m, 1H), 4.86 (m, 1H), 4.55 (m, 2H), 3.34 (s, 1H), 2.81 (d, J = 12.4 Hz, 1H), 1.46 (d, J = 17.0 Hz, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 146.2, 142.1, 140.8, 138.9, 128.5, 128.0, (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 127.9, 127.3, 127.0, 126.8, 126.3, 125.8, 125.5, 120.5, 119.9, (d, $^1J_{C\text{-}F}$ = 231.2 Hz), 54.1, 50.7, 41.8, (d, $^2J_{C\text{-}F}$ = 32.4 Hz), 34.3, 31.4, 23.3, (d, $^2J_{C\text{-}F}$ = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9. HRMS (ESI) calcd for $C_{28}H_{31}FN_2NaO^+$ [M + Na^+] 453.2313, found 453.2317.

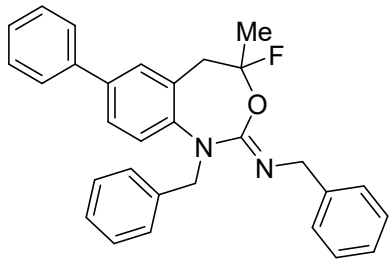
(*Z*)-*N*,1-Dibenzyl-7-bromo-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2e (188 mg, 83% yield, a white solid, mp: 112 - 113 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 7H), 7.22 (m, 5H), 7.01 (d, J = 8.5 Hz, 1H), 5.33 (d, J = 15.9 Hz, 1H), 5.08 (d, J = 15.9 Hz, 1H), 4.76 (d, J = 15.7 Hz, 1H), 4.57 (d, J = 15.7 Hz, 1H), 3.39 (t, J = 13.5 Hz, 1H), 2.88 (d, J = 13.9 Hz, 1H), 1.59 (d, J = 17.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 142.3, 141.7, 138.1, 132.0, 131.6, 130.7, (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 128.6, 128.0, 127.3, 127.1, 127.1, 126.0, 122.7, 120.5, (d, $^1J_{C\text{-}F}$ = 232.2 Hz), 116.5, 54.0, 50.7, 41.2, (d, $^2J_{C\text{-}F}$ = 33.5 Hz), 23.3, (d, $^2J_{C\text{-}F}$ = 27.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1. HRMS (ESI) calcd for $C_{24}H_{22}{}^{79}BrFN_2NaO^+$ [M + Na^+] 475.0792, found 475.0795.

(*Z*)-*N*,1-Dibenzyl-4-fluoro-4-methyl-7-phenyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine

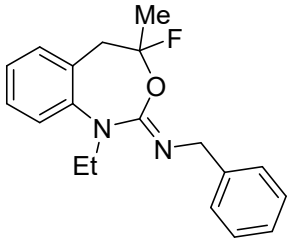


2f (171 mg, 76% yield, a white solid, mp: 107 - 108 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 3H), 7.22 (m, 16H), 5.31 (d, J = 15.8 Hz, 1H), 4.98 (d, J = 15.3 Hz, 1H), 4.68 (d, J = 15.7 Hz, 1H), 4.48 (d, J = 15.7 Hz, 1H), 3.38 (t, J = 13.0 Hz, 1H), 2.88 (d, J = 13.5 Hz, 1H), 1.50 (d, J = 17.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 142.5, 141.9, 140.1, 138.6, 136.9, 129.0, 128.9, 128.5, 128.0, 127.4, 127.3, 127.1, 127.0, 126.9, 125.9, 121.4, 119.8, (d, $^1J_{C\text{-}F}$ = 232.0 Hz), 54.1, 50.8, 41.7, (d, $^2J_{C\text{-}F}$ = 32.7 Hz), 23.4, (d, $^2J_{C\text{-}F}$ = 27.9 Hz). ^{19}F NMR (376 MHz,

$CDCl_3$) δ -84.8. HRMS (ESI) calcd for $C_{30}H_{27}FN_2NaO^+$ [M + Na^+] 473.2000, found 473.2003.

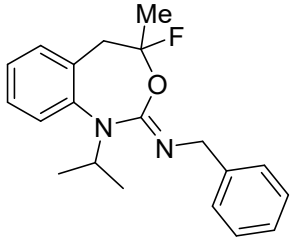
(*Z*)-*N*-Benzyl-1-ethyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2g (114 mg, 73% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.4 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.15 – 7.07 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 4.67 (d, *J* = 15.7 Hz, 1H), 4.50 (d, *J* = 15.7 Hz, 1H), 3.99 (dq, *J* = 14.0, 7.0 Hz, 1H), 3.89 (dq, *J* = 13.9, 6.9 Hz, 1H), 3.32 (t, *J* = 13.6 Hz, 1H), 2.81 (d, *J* = 13.9 Hz, 1H), 1.42 (d, *J* = 17.7 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 142.9, 142.3, 129.3, (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 129.3, 128.6, 128.1, 127.4, 126.0, 124.0, 121.5, 119.7, (d, $^1J_{C\text{-}F}$ = 231.0 Hz), 50.9, 45.6, 41.3, (d, $^2J_{C\text{-}F}$ = 32.7 Hz), 23.3, (d, $^2J_{C\text{-}F}$ = 23.3 Hz), 13.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0. HRMS (ESI) calcd for $C_{19}H_{21}FN_2NaO^+$ [M + Na^+] 335.1530, found 335.1534.

(*Z*)-*N*-Benzyl-4-fluoro-1-isopropyl-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine

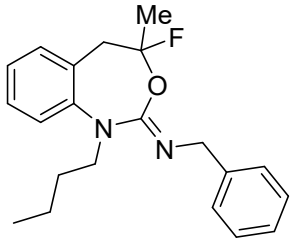


2h (135 mg, 83% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.29 (m, 3H), 7.21 (dd, *J* = 9.2, 5.6 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 4.76 (dd, *J* = 14.6, 8.7 Hz, 2H), 4.57 (d, *J* = 15.8 Hz, 1H), 3.39 (t, *J* = 13.9 Hz, 1H), 2.87 (d, *J* = 13.7 Hz, 1H), 1.56 (d, *J* = 6.5 Hz, 3H), 1.45 (d, *J* = 17.8 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 145.3, 142.6, 141.4, 131.3, (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 128.9, 128.1, 127.9, 127.4, 125.9, 124.9, 124.1, 119.1, (d, $^1J_{C\text{-}F}$ = 230.4 Hz), 51.5, 50.7, 41.2, (d, $^2J_{C\text{-}F}$ = 32.9 Hz), 23.4, (d, $^2J_{C\text{-}F}$ = 27.8 Hz), 22.2, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.2. HRMS (ESI) calcd for $C_{20}H_{23}FN_2NaO^+$ [M + Na^+] 349.1687, found 349.1684.

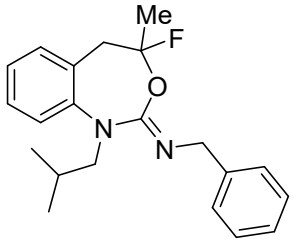
(*Z*)-*N*-Benzyl-1-butyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2i (140 mg, 82% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 5H), 7.21 – 7.08 (m, 3H), 7.04 (m, 1H), 4.77 – 4.52 (m, 2H), 4.11 (m, 1H), 3.87 – 3.77 (m, 1H), 3.39 (t, *J* = 13.6 Hz, 1H), 2.87 (d, *J* = 13.8 Hz, 1H), 1.75 – 1.63 (m, 2H), 1.48 (d, *J* = 17.7 Hz, 3H), 1.30 (m, 2H), 0.95 – 0.81 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 143.0, 142.4, 129.4, (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 129.3, 128.6, 128.1, 127.4, 126.0, 123.9, 121.6, 119.5, (d, $^1J_{C\text{-}F}$ = 231.2 Hz), 50.8, 50.3, 41.4, (d, $^2J_{C\text{-}F}$ = 32.9 Hz), 29.9, 23.3, (d, $^2J_{C\text{-}F}$ = 28.1 Hz), 20.4, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0. HRMS (ESI) calcd for $C_{21}H_{25}FN_2NaO^+$ [M + Na^+] 363.1843, found 363.1845.

(*Z*)-*N*-Benzyl-4-fluoro-1-isobutyl-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine

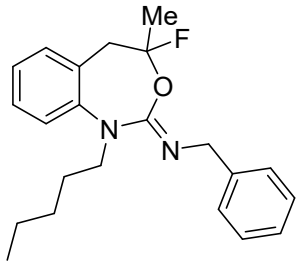


2j (131 mg, 77% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.33 (q, *J* = 8.0, 7.3 Hz, 3H), 7.25 – 7.15 (m, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 4.76 – 4.60 (m, 2H), 4.22 (m, 1H), 3.62 (m, 1H), 3.51 (m, 1H), 2.96 (m, *J* = 13.8 Hz, 1H), 2.18 (m, 1H), 1.54 (d, *J* = 17.6 Hz,

3H), 0.96 (d, J = 6.5 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 142.9, 142.4, 129.5, (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 129.4, 128.4, 128.1, 127.4, 126.0, 123.8, 121.7, 119.2, (d, $^1J_{C\text{-}F}$ = 231.4 Hz), 56.9, 50.7, 41.6, (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 26.9, 23.4, (d, $^2J_{C\text{-}F}$ = 28.1 Hz), 20.6, 20.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2. HRMS (ESI) calcd for $C_{21}H_{25}FN_2NaO^+$ [M + Na^+] 363.1843, found 363.1840.

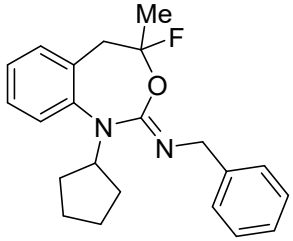
(*Z*)-*N*-Benzyl-4-fluoro-4-methyl-1-pentyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2k (145 mg, 82% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.29 (d, J = 7.1 Hz, 3H), 7.18 – 7.08 (m, 3H), 7.04 (d, J = 7.2 Hz, 1H), 4.77 – 4.54 (m, 2H), 4.08 (m, 1H), 3.82 (m, 1H), 3.40 (t, J = 13.3 Hz, 1H), 2.88 (d, J = 13.7 Hz, 1H), 1.72 (d, J = 7.4 Hz, 2H), 1.49 (d, J = 17.7 Hz, 3H), 1.37 – 1.18 (m, 4H), 0.93 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 143.1, 142.4, 129.4, 129.3, 128.6, 128.1, 127.4, 126.0, 123.9, 121.6, 119.5, (d, $^1J_{C\text{-}F}$ = 231.1 Hz), 50.8, 50.6, 41.4, (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 29.3, 27.4, 23.3, (d, $^2J_{C\text{-}F}$ = 28.1 Hz), 22.5, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0. HRMS (ESI) calcd for $C_{22}H_{27}FN_2NaO^+$ [M + Na^+] 377.2000, found 377.2003.

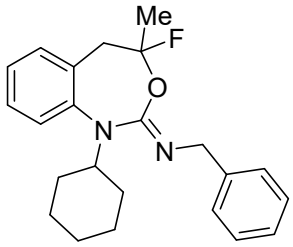
(*Z*)-*N*-Benzyl-1-cyclopentyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2l (148 mg, 84% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 6.5 Hz, 2H), 7.28 (dt, J = 14.1, 7.4 Hz, 3H), 7.17 (dd, J = 18.2, 8.7 Hz, 3H), 7.08 (t, J = 7.1 Hz, 1H), 4.76 – 4.55 (m, 3H), 3.39 (t, J = 14.1 Hz, 1H), 2.88 (d, J = 13.6 Hz, 1H), 2.11 (s, 2H), 1.98 – 1.70 (m, 4H), 1.62 – 1.51 (m, 2H), 1.45 (d, J = 17.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 142.7, 142.6, 131.3, (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 128.8, 128.1, 128.0, 127.4, 125.9, 124.8, 124.2, 118.7, (d, $^1J_{C\text{-}F}$ = 230.4 Hz), 62.2, 50.8, 41.2, (d, $^2J_{C\text{-}F}$ = 32.0 Hz), 30.5, 28.7, 24.6, 24.4, 23.5, (d, $^2J_{C\text{-}F}$ = 27.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.3. HRMS (ESI) calcd for $C_{22}H_{25}FN_2NaO^+$ [M + Na^+] 375.1843, found 375.1846.

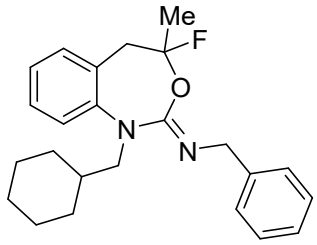
(*Z*)-*N*-Benzyl-1-cyclohexyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2m (154 mg, 84% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.22 – 7.16 (m, 1H), 7.11 (m, 2H), 4.74 (d, J = 16.1 Hz, 1H), 4.58 (d, J = 16.1 Hz, 1H), 4.35 (t, J = 10.3 Hz, 1H), 3.41 (t, J = 14.1 Hz, 1H), 2.85 (d, J = 13.6 Hz, 1H), 2.35 (d, J = 11.2 Hz, 1H), 1.87 (m, 2H), 1.69 (m, 3H), 1.50 (d, J = 11.0 Hz, 1H), 1.43 (d, J = 17.8 Hz, 3H), 1.38 – 1.31 (m, 1H), 1.28 – 1.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 142.8, 141.5, 131.6, (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 128.8, 128.0, 127.8, 127.3, 125.9, 124.9, 124.7, 119.1, (d, $^2J_{C\text{-}F}$ = 230.1 Hz), 60.3, 50.6, 41.1, (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 32.4, 30.9, 26.5, 25.9, 23.3, (d, $^2J_{C\text{-}F}$ = 27.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.3. HRMS (ESI) calcd for $C_{23}H_{27}FN_2NaO^+$ [M + Na^+] 389.2000, found 389.2004.

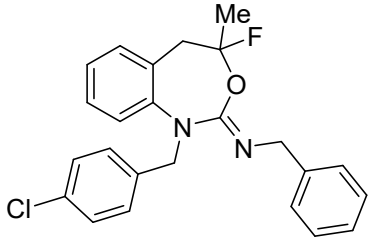
(*Z*)-*N*-Benzyl-1-(cyclohexylmethyl)-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2n (167 mg, 86% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.9 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.17 (m, 3H), 7.04 (t, *J* = 6.9 Hz, 1H), 4.64 (q, *J* = 15.7 Hz, 2H), 4.15 (m, 1H), 3.62 (m, 1H), 3.45 (t, *J* = 13.9 Hz, 1H), 2.91 (d, *J* = 13.7 Hz, 1H), 1.85 (s, 1H), 1.79 – 1.56 (m, 5H), 1.50 (d, *J* = 17.8 Hz, 3H), 1.12 (s, 3H), 1.08 – 0.96 (m, 1H), 0.87 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.2, 142.4, 129.4, 129.3, 128.4, 128.0, 127.3, 125.9, 123.7, 121.7, 119.3, (d, $^1J_{C\text{-}F}$ = 231.1 Hz), 56.0, 50.8, 41.6, (d, $^2J_{C\text{-}F}$ = 32.8 Hz), 36.3, 31.3, 31.2, 26.5, 26.0, 25.9, 23.3, (d, $^2J_{C\text{-}F}$ = 28.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2. HRMS (ESI) calcd for $C_{24}H_{29}FN_2NaO^+$ [M + Na^+] 403.2156, found 403.2159.

(*Z*)-*N*-Benzyl-1-(4-chlorobenzyl)-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]-oxazepin-2(1*H*)-imine

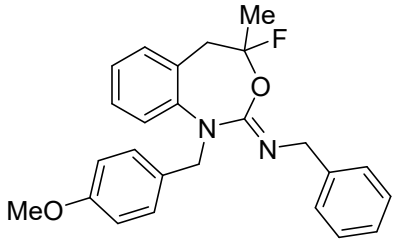


2o (162 mg, 79% yield, a white solid, mp: 127 – 128 ℃).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (m, 7H), 7.18 – 7.02 (m, 6H), 5.27 (d, *J* = 15.9 Hz, 1H), 5.02 (d, *J* = 15.4 Hz, 1H), 4.72 (d, *J* = 15.7 Hz, 1H), 4.53 (d, *J* = 15.7 Hz, 1H), 3.35 (t, *J* = 13.6 Hz, 1H), 2.90 (d, *J* = 13.9 Hz, 1H), 1.53 (d, *J* = 17.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 143.0, 141.8, 137.2, 132.7, 129.5, 128.8, (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 128.7, 128.6, 128.6, 128.0, 127.3, 126.0, 124.2, 119.9, (d, $^1J_{C\text{-}F}$ = 244.1 Hz), 53.5, 50.7, 41.4, (d, $^2J_{C\text{-}F}$ = 32.6 Hz), 23.2, (d, $^2J_{C\text{-}F}$ = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9. HRMS (ESI) calcd for $C_{24}H_{22}{}^{35}ClFN_2NaO^+$ [M + Na^+] 431.1297, found 431.1294.

(*Z*)-*N*-Benzyl-4-fluoro-1-(4-methoxybenzyl)-4-methyl-4,5-dihydrobenzo[*d*][1,3]-

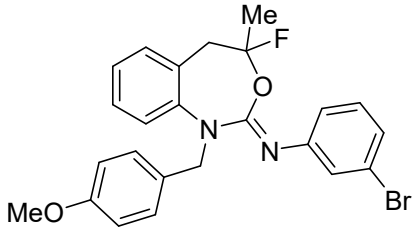
oxazepin-2(1*H*)-imine



2p (172 mg, 85% yield, a white solid, mp: 91 – 93 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.09 (m, 7H), 7.05 (m, 2H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 2H), 5.10 (d, *J* = 15.6 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.65 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 3.65 (s, 3H), 3.24 (t, *J* = 13.6 Hz, 1H), 2.75 (d, *J* = 13.9 Hz, 1H), 1.41 (d, *J* = 17.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 146.2, 143.1, 142.1, 130.7, 129.4, 129.0, (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 128.6, 128.6, 128.0, 127.4, 126.0, 124.1, 121.5, 119.9, (d, $^1J_{C\text{-}F}$ = 231.5 Hz), 113.8, 55.3, 53.4, 50.8, 41.4, (d, $^2J_{C\text{-}F}$ = 32.5 Hz), 23.3, (d, $^2J_{C\text{-}F}$ = 28.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9. HRMS (ESI) calcd for $C_{25}H_{25}FN_2NaO_2^+$ [M + Na^+] 427.1792, found 427.1788.

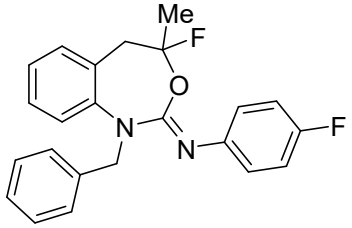
(*Z*)-*N*-(3-Bromophenyl)-4-fluoro-1-(4-methoxybenzyl)-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2q (181 mg, 77% yield, a white solid, mp: 126 – 127 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.17 (s, 1H), 7.10 (m, 4H), 6.96 – 6.89 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.24 (d, *J* = 15.2 Hz, 1H), 5.10 (d, *J* = 15.2 Hz, 1H), 3.77 (s, 3H), 3.19 (t, *J* = 13.7 Hz, 1H), 2.78 (d, *J* = 13.9 Hz, 1H), 1.34 (d, *J* = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 148.7, 146.0, 141.9, 130.1, 129.8, (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 129.7, 129.4, 129.3, 129.0, 128.7, 126.3, 125.2, 122.3, 122.0, 121.7, 119.8, (d, $^1J_{C\text{-}F}$ = 234.9 Hz), 113.9, 55.2, 53.6, 41.1, (d, $^2J_{C\text{-}F}$ = 32.3 Hz), 23.2, (d, $^2J_{C\text{-}F}$ = 27.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.5. HRMS (ESI) calcd for $C_{24}H_{22}{}^{79}BrFN_2NaO_2^+$ [M + Na^+] 491.0741, found 491.0744.

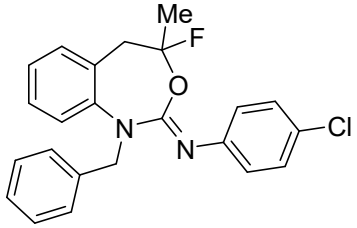
(*Z*)-1-Benzyl-4-fluoro-*N*-(4-fluorophenyl)-4-methyl-4,5-dihydrobenzo[*d*][1,3]-oxazepin-2(1*H*)-imine



2r (144 mg, 76% yield, a white solid, mp: 139 - 140 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.15 (q, J = 7.2 Hz, 2H), 6.97 (d, J = 7.0 Hz, 4H), 5.34 (d, J = 15.4 Hz, 2H), 3.33 (t, J = 14.1 Hz, 1H), 2.88 (d, J = 14.0 Hz, 1H), 1.41 (d, J = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, (d, $^1J_{C\text{-}F}$-Ar = 240.7 Hz), 145.5, 143.1, 142.3, 137.8, 129.5, (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 129.4, 128.7, 128.5, 127.4, 127.2, 124.9, 124.1, (d, $^3J_{C\text{-}F}$-Ar = 7.9 Hz), 121.9, 119.6, (d, $^1J_{C\text{-}F}$ = 234.5 Hz), 114.7, (d, $^2J_{C\text{-}F}$-Ar = 22.1 Hz), 54.2, 41.3, (d, $^2J_{C\text{-}F}$ = 32.5 Hz), 23.2, (d, $^2J_{C\text{-}F}$ = 27.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.6, -122.2. HRMS (ESI) calcd for $C_{23}H_{20}F_2N_2NaO^+$ [M + Na^+] 401.1436, found 401.1434.

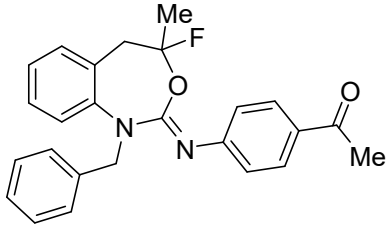
(*Z*)-1-Benzyl-*N*-(4-chlorophenyl)-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxa-zepin-2(1*H*)-imine



2s (160 mg, 81% yield, a white solid, mp: 158 - 159 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 9H), 7.16 (m, 2H), 6.96 (d, J = 8.4 Hz, 2H), 5.30 (q, J = 15.6 Hz, 2H), 3.33 (t, J = 13.7 Hz, 1H), 2.89 (d, J = 14.0 Hz, 1H), 1.42 (d, J = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 145.6, 142.2, 137.7, 129.5, (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 129.4, 128.7, 128.5, 128.2, 127.4, 127.4, 127.3, 125.0, 124.4, 121.9, 119.7, (d, $^1J_{C\text{-}F}$ = 234.6 Hz), 54.2, 41.2, (d, $^2J_{C\text{-}F}$ = 32.5 Hz), 23.2, (d, $^2J_{C\text{-}F}$ = 27.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.5. HRMS (ESI) calcd for $C_{23}H_{20}{}^{35}ClFN_2NaO^+$ [M + Na^+] 417.1140, found 417.1142.

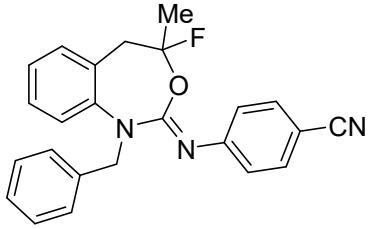
(*Z*)-1-(4-((1-Benzyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-ylidene)amino)phenyl)ethan-1-one



2t (169 mg, 84% yield, a white solid, mp: 151 - 152 °C).

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.43 – 7.24 (m, 7H), 7.15 (m, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 5.37 – 5.21 (m, 2H), 3.31 (t, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 14.0 Hz, 1H), 2.58 (s, 3H), 1.39 (d, *J* = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 151.3, 144.8, 140.9, 136.5, 130.5, 128.4, (d, $^3J_{C\text{-}F}$ = 9.1 Hz), 128.0, 127.7, 127.5, 126.4, 126.3, 124.2, 122.0, 120.9, 118.9, (d, $^1J_{C\text{-}F}$ = 235.1 Hz), 53.2, 40.1, (d, $^2J_{C\text{-}F}$ = 32.3 Hz), 25.4, 22.1, (d, $^2J_{C\text{-}F}$ = 27.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4. HRMS (ESI) calcd for $C_{25}H_{23}FN_2NaO_2^+$ [M + Na^+] 425.1636, found 425.1639.

(*Z*)-4-((1-Benzyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-ylidene)amino)benzonitrile

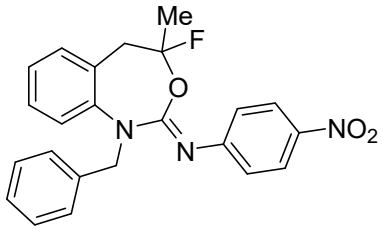


2u (144 mg, 73% yield, a white solid, mp: 161 - 162 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.22 (m, 7H), 7.14 (s, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 5.34 – 5.17 (m, 2H), 3.25 (t, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 13.9 Hz, 1H), 1.35 (d, *J* = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 146.2, 141.8, 137.3, 132.5, 129.4, (d, $^3J_{C\text{-}F}$ = 5.9 Hz), 128.9, 128.6, 127.5, 127.4, 125.5, 124.0, 122.1, 120.2, (d, $^1J_{C\text{-}F}$ = 235.4 Hz), 119.9, 105.2, 54.4, 41.1, (d, $^2J_{C\text{-}F}$ = 32.4 Hz), 23.1, (d, $^2J_{C\text{-}F}$ = 27.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0. HRMS (ESI) calcd for $C_{24}H_{20}FN_3NaO^+$ [M + Na^+] 408.1483, found 408.1485.

(*Z*)-1-Benzyl-4-fluoro-4-methyl-*N*-(4-nitrophenyl)-4,5-dihydrobenzo[*d*][1,3]-

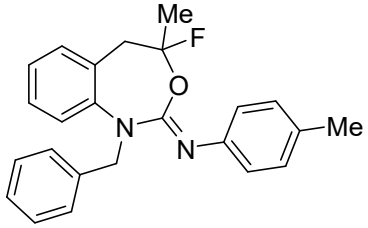
oxazepin-2(1*H*)-imine



2v (152 mg, 75% yield, a white solid, mp: 171 - 172 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.9 Hz, 2H), 7.33 (m, 7H), 7.16 (d, *J* = 4.0 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 5.27 (q, *J* = 15.6 Hz, 2H), 3.27 (t, *J* = 13.8 Hz, 1H), 2.88 (d, *J* = 14.0 Hz, 1H), 1.38 (d, *J* = 17.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 146.4, 142.7, 141.7, 137.2, 129.5, 129.4, (d, $^3J_{C\text{-}F}$ = 8.8 Hz), 128.9, 128.7, 127.5, 127.4, 125.6, 124.4, 123.5, 122.1, 120.4, (d, $^1J_{C\text{-}F}$ = 235.7 Hz), 54.4, 41.1, (d, $^2J_{C\text{-}F}$ = 32.3 Hz), 23.1, (d, $^2J_{C\text{-}F}$ = 27.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0. HRMS (ESI) calcd for $C_{23}H_{20}FN_3NaO_3^+$ [M + Na^+] 428.1381, found 428.1377.

(*Z*)-1-Benzyl-4-fluoro-4-methyl-*N*-(p-tolyl)-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine

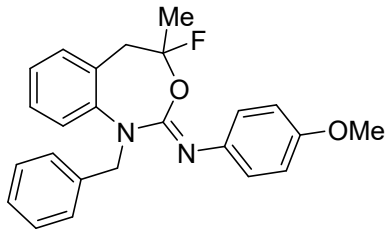


2w (152 mg, 81% yield, a white solid, mp: 108 - 109 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.31 (dd, *J* = 15.2, 7.5 Hz, 4H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 5.30 (q, *J* = 15.7 Hz, 2H), 3.34 (t, *J* = 13.6 Hz, 1H), 2.86 (d, *J* = 13.9 Hz, 1H), 2.32 (s, 3H), 1.40 (d, *J* = 17.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 138.0, 137.9, 131.5, 129.6, 129.5, 129.3, 128.8, 128.6, 128.4, 128.2, (d, $^1J_{C\text{-}F}$ = 220.7 Hz), 127.5, 124.7, 124.7, 122.8, 121.8, 54.1, 41.3, (d, $^2J_{C\text{-}F}$ = 32.4 Hz), 23.3, (d, $^2J_{C\text{-}F}$ = 27.6 Hz), 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.0. HRMS (ESI) calcd for $C_{23}H_{20}F_2N_2NaO^+$ [M + Na^+] 397.1687, found 397.1689.

(*Z*)-1-Benzyl-4-fluoro-*N*-(4-methoxyphenyl)-4-methyl-4,5-dihydrobenzo[*d*][1,3]-

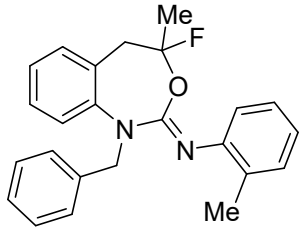
oxazepin-2(1*H*)-imine



2x (164 mg, 84% yield, a white solid, mp: 115 – 116 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.27 (m, 5H), 7.15 (m, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.40 – 5.26 (m, 2H), 3.83 (s, 3H), 3.36 (t, *J* = 13.6 Hz, 1H), 2.89 (d, *J* = 13.9 Hz, 1H), 1.44 (d, *J* = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 145.1, 142.4, 138.0, 129.5, (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 129.3, 128.6, 128.4, 127.5, 127.1, 124.7, 123.9, 121.8, 119.5, (d, $^1J_{C\text{-}F}$ = 233.6 Hz), 113.5, 55.4, 54.1, 41.3, (d, $^2J_{C\text{-}F}$ = 32.4 Hz), 23.3, (d, $^2J_{C\text{-}F}$ = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.3. HRMS (ESI) calcd for $C_{24}H_{23}FN_2NaO_2^+$ [M + Na^+] 413.1636, found 413.1632.

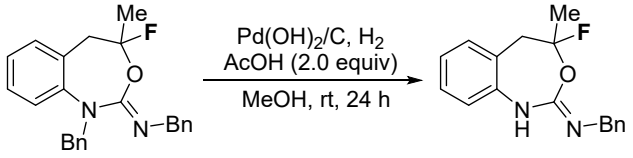
(*Z*)-1-Benzyl-4-fluoro-4-methyl-*N*-(*o*-tolyl)-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2y (108 mg, 58% yield, a colorless solid, mp: 114 – 115 ℃).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.33 – 7.22 (m, 5H), 7.08 (m, 4H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.36 (d, *J* = 15.7 Hz, 1H), 5.26 – 5.17 (m, 1H), 3.33 (t, *J* = 13.5 Hz, 1H), 2.84 (d, *J* = 13.9 Hz, 1H), 2.08 (s, 3H), 1.31 (d, *J* = 17.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 144.3, 142.6, 138.1, 130.4, 129.5, 129.4, 129.3, (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 128.7, 128.5, 127.4, 127.1, 125.5, 124.7, 122.3, 121.7, 119.2, (d, $^1J_{C\text{-}F}$ = 234.1 Hz), 54.3, 41.4, (d, $^2J_{C\text{-}F}$ = 32.5 Hz), 29.7, 23.2, (d, $^2J_{C\text{-}F}$ = 27.7 Hz), 18.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.3. HRMS (ESI) calcd for $C_{24}H_{23}FN_2NaO^+$ [M + Na^+] 397.1687, found 397.1684.

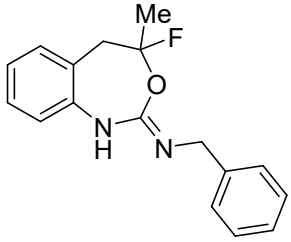
3. The Synthetic Procedure and Spectroscopic Data of 2aa.[4]



2a **2aa**

To a mixture of compound **2a** (50 mg, 1.0 equiv) and 15% palladium hydroxide on charcoal (30 mg) in MeOH (5 mL) was added AcOH (16.04 mg, 2.0 equiv). The resulting mixture was kept stirring at room temperature under a H_2 atmosphere until TLC indicated the total consumption of substrate **2a**. After filtered the palladium catalyst and washed filter cake with EtOAc, the solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel (PE/EtOAc = 10/1) to afford product **2aa**.

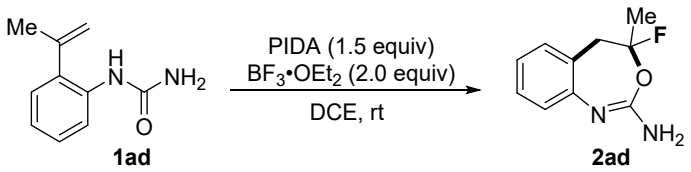
(*Z*)-*N*-Benzyl-4-fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2(1*H*)-imine



2aa (24 mg, 63% yield, colorless liquid).

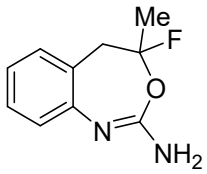
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.32 – 7.23 (m, 2H), 7.12 (d, J = 7.2 Hz, 1H), 7.06 – 6.97 (m, 2H), 4.81 (s, 1H), 4.63 – 4.50 (m, 2H), 3.27 (t, J = 13.2 Hz, 1H), 2.95 (d, J = 14.0 Hz, 1H), 1.56 (d, J = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 145.9, 138.2, 128.9, 128.7, 128.4, 127.7, 127.5, 126.9, (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 124.0, 122.9, 122.6, (d, $^1J_{C\text{-}F}$ = 230.6 Hz), 46.4, 41.8, (d, $^2J_{C\text{-}F}$ = 31.5 Hz), 23.8, (d, $^2J_{C\text{-}F}$ = 28.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.2. HRMS (ESI) calcd for $C_{17}H_{17}FN_2NaO^+$ [M + Na^+] 307.1217, found 307.1214.

4. The Synthetic Procedure and Spectroscopic Data of 2ad.



To a reaction flask filled with PIDA (1.5 equiv, 0.75 mmol) in DCE (5.0 mL) was added BF_3·OEt_2 (2.0 equiv, 1mmol). The mixture was stirred at room temperature for 1 min and reactant **1ad** (0.5 mmol) was added. The resulting mixture was kept stirring until TLC indicated the total consumption of substrate **1ad**. Then the reaction mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtered, the mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 4/1 +1% Et_3N) to afford target product **2ad**.

4-Fluoro-4-methyl-4,5-dihydrobenzo[*d*][1,3]oxazepin-2-amine



2ad (52 mg, 54% yield, a white solid, mp: 122 - 123 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, J = 6.6 Hz, 1H), 7.12 (d, J = 7.3 Hz, 1H), 7.03 – 6.95 (m, 2H), 5.29 (s, 2H), 3.29 (t, J = 12.9 Hz, 1H), 2.97 (d, J = 14.1 Hz, 1H), 1.56 (d, J = 17.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 145.2, 129.0, 128.5, 127.0, (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 123.6, 123.3, 122.2, (d, $^1J_{C\text{-}F}$ = 230.7 Hz), 41.6, (d, $^2J_{C\text{-}F}$ = 31.3 Hz), 23.9, (d, $^2J_{C\text{-}F}$ = 29.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.2. HRMS (ESI) calcd for $C_{10}H_{11}FN_2NaO^+$ [M + Na^+] 217.0748, found 217.0745.

5. Other Boron Lewis Acid Effect under Standard Conditions.

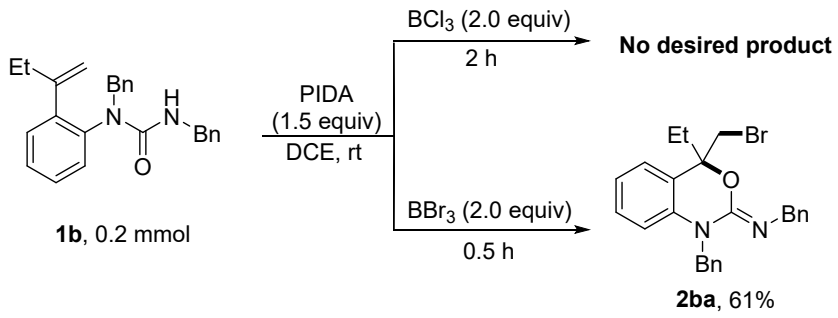
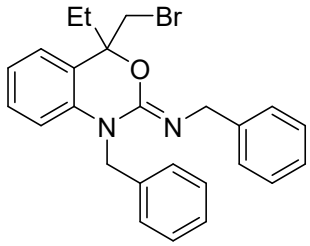


Figure. S1 The study on the effect of BCl_3 or BBr_3.

(*Z*)-*N*,1-Dibenzyl-4-(bromomethyl)-4-ethyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-imine



2ba (55 mg, 61% yield, colorless liquid).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 9H), 7.15 (q, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.45 – 5.19 (m, 2H), 4.66 (s, 2H), 3.67 – 3.54 (q, *J* = 15.4 Hz, 11.0 Hz, 2H), 2.31 (m, 1H), 2.09 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 142.4, 138.1, 137.5, 129.4, 128.6, 128.0, 127.5, 126.9, 126.7, 126.0, 124.7, 122.1, 120.8, 114.0, 81.2, 49.6, 48.1, 38.1, 29.0, 7.9. HRMS (ESI) calcd for $C_{25}H_{25}{}^{79}BrN_2NaO^+$ [M + Na^+] 471.1042, found 471.1038.

6. High Resolution Mass Spectrometry of $AcOBF_2$.

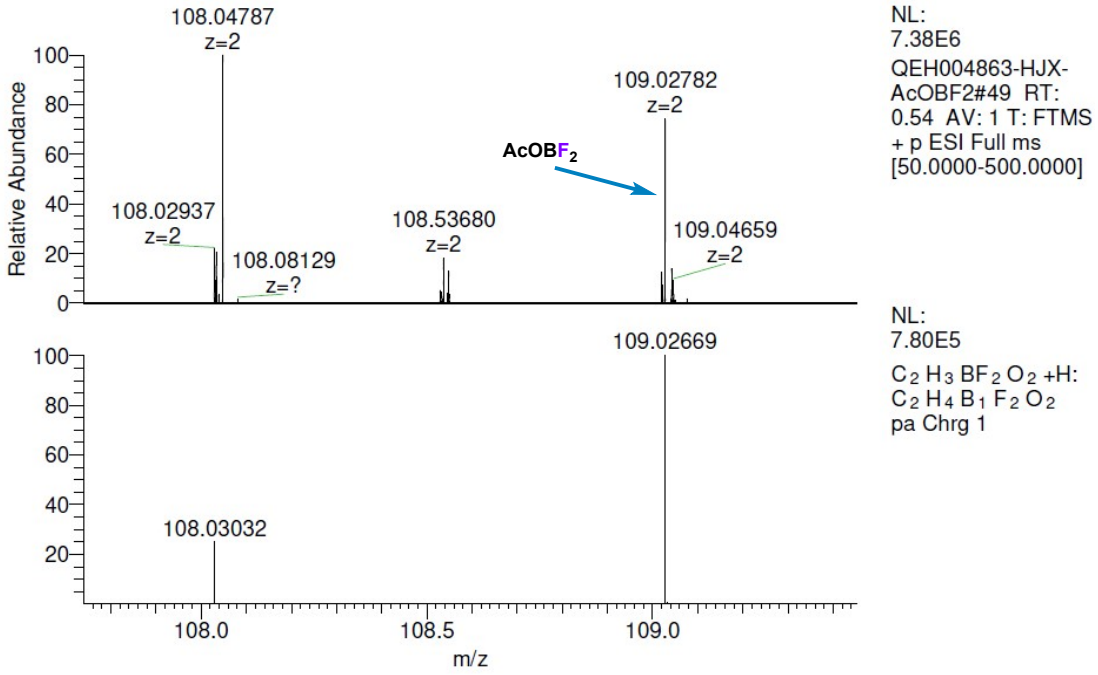


Figure. S2 High Resolution Mass Spectrometry of $AcOBF_2$

7. Solution-phase ^{1}H-NMR spectroscopy of PIDA and PIDA-BF_3 complex in $CDCl_3$.

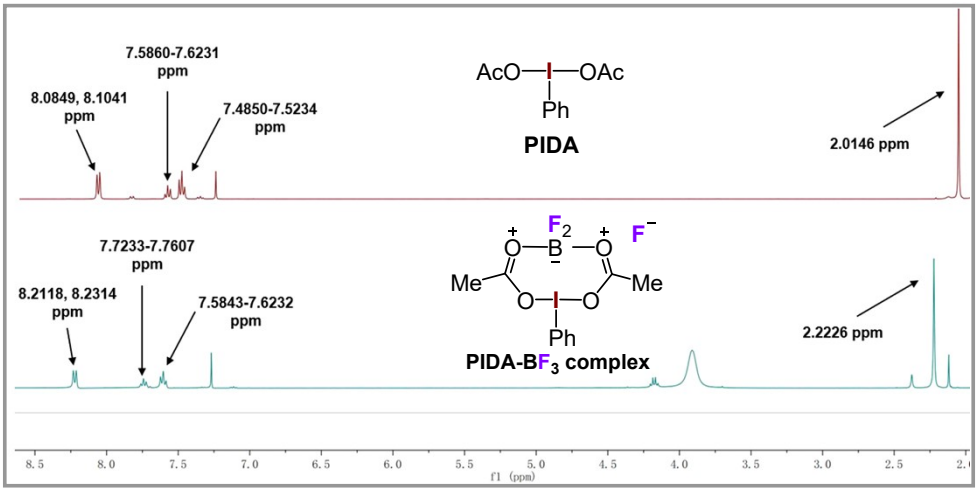
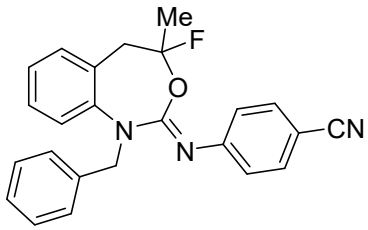


Figure. S3 Solution-phase ^{1}H-NMR spectroscopy of PIDA and PIDA-BF_3 complex in $CDCl_3$

To gain a better understanding of the process of this oxidative fluorination mediated by PIDA/BF_3·Et_2O system, the solution-phase NMR spectroscopy was conducted: (1) the ^{1}H NMR spectrum collected from a sample of phenyliodine(III) diacetate (PIDA) dissolved in $CDCl_3$; (2) the ^{1}H NMR spectrum collected from the reaction mixture of 1 equiv of PIDA with 1 equiv of BF_3.OEt_2 in $CDCl_3$ at rt for 5 min.

III. X-ray Crystal Structure and Data

Product 2u:



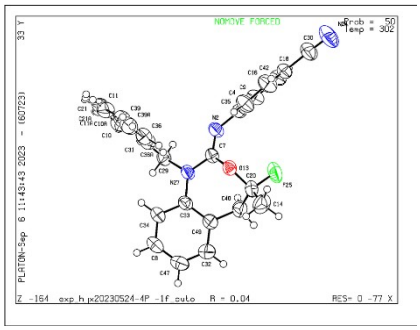


Table 1 Crystal data and structure refinement for 2u.

Identification code	2u
Empirical formula	$C_{24}H_{20}FN_3O$
Formula weight	385.43
Temperature/K	301.57(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.3241(2)
b/Å	10.9750(2)
c/Å	11.7780(2)
α/°	111.810(2)
β/°	91.382(2)
γ/°	112.051(2)
Volume/Å^3	1018.22(4)
Z	2
ρ_{calc}g/cm^3	1.257
μ/mm^{-1}	0.686
F(000)	404.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.236 to 150.272

Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 13, -14 \leq l \leq 14$
Reflections collected	35065
Independent reflections	4022 [$R_{int} = 0.0280$, $R_{sigma} = 0.0097$]
Data/restraints/parameters	4022/284/309
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	$R_1 = 0.0380$, $wR_2 = 0.1016$
Final R indexes [all data]	$R_1 = 0.0397$, $wR_2 = 0.1029$
Largest diff. peak/hole / e $Å^{-3}$	0.16/-0.17

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2u. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O13	2732.5(9)	3592.1(7)	3689.7(7)	43.40(18)
F25	589.4(10)	4036.9(10)	4103.6(8)	74.7(3)
N27	2454.5(11)	1257.9(9)	2602.4(8)	45.1(2)
N2	2131.0(12)	1975.1(10)	4640.2(8)	48.7(2)
C7	2389.7(12)	2261.2(11)	3694.6(10)	41.5(2)
C31	4170.6(14)	169.2(12)	3100.1(9)	44.7(3)
C33	2423.8(13)	1417.4(11)	1458.9(10)	44.9(2)
C29	2549.0(13)	-29.6(11)	2631.6(11)	46.1(3)
C35	2169.6(13)	3003.4(11)	5801.5(10)	43.3(2)
C9	942.8(14)	2588.3(13)	6414.1(10)	50.7(3)
C49	1456.8(14)	2005.3(13)	1155.6(11)	51.0(3)
C36	5561(8)	1425(7)	3493(11)	51.3(14)
C42	901.8(14)	3512.5(13)	7572.7(10)	52.3(3)
C40	468.6(15)	2498.1(14)	2051.8(12)	56.0(3)
C34	3313.3(16)	930.0(14)	617.0(11)	56.0(3)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2u. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C18	2125.0(15)	4866.8(13)	8162.4(10)	51.4(3)
C20	1500.0(14)	3823.2(13)	3195.1(11)	51.1(3)
C16	3394.3(16)	5266.6(14)	7583.6(12)	63.0(3)
C4	3415.3(15)	4345.5(14)	6413.3(12)	58.4(3)
C10	4224(9)	-1084(7)	3144(10)	48.3(11)
C30	2041.6(19)	5839.6(16)	9354.6(13)	67.4(4)
N24	1924(2)	6601.1(17)	10284.5(13)	98.8(5)
C32	1450(2)	2133.4(17)	29.0(12)	69.3(4)
C8	3267(2)	1054.6(17)	-506.3(12)	71.0(4)
C14	2265(2)	5184.1(15)	3011.9(16)	74.3(4)
C39	6971(9)	1411(9)	3894(9)	61.3(15)
C11	7004(9)	185(9)	3918(7)	60.6(14)
C47	2345(2)	1663.4(19)	-796.8(13)	79.6(5)
C21	5639(10)	-1059(8)	3547(10)	61.5(12)
C36A	5372(15)	1487(14)	3369(19)	63(3)
C10A	4586(19)	-822(16)	3255(18)	65(3)
C21A	6070(20)	-590(20)	3657(15)	73(3)
C11A	7269(18)	730(20)	3925(11)	76(3)
C39A	6939(15)	1790(20)	3798(16)	72(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2u. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2u. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O13	48.8(4)	36.8(4)	43.4(4)	14.5(3)	11.6(3)	18.3(3)
F25	70.1(5)	84.6(6)	69.6(5)	16.7(4)	30.4(4)	46.1(4)
N27	59.6(5)	39.7(5)	38.3(5)	13.8(4)	14.7(4)	24.7(4)
N2	62.6(6)	43.1(5)	39.8(5)	15.4(4)	15.8(4)	22.4(4)
C7	44.9(5)	37.4(5)	39.9(5)	12.9(4)	11.5(4)	17.6(4)
C31	57.0(6)	44.3(6)	32.2(5)	12.9(4)	13.5(4)	22.8(5)
C33	53.4(6)	40.8(5)	35.9(5)	11.1(4)	9.2(4)	19.3(5)
C29	54.4(6)	33.8(5)	46.1(6)	13.2(4)	13.5(5)	17.0(5)
C35	51.0(6)	42.6(5)	37.1(5)	15.7(4)	10.3(4)	20.7(5)
C9	52.6(6)	46.8(6)	40.1(6)	14.5(5)	10.0(5)	11.1(5)
C49	56.0(6)	49.7(6)	42.8(6)	12.6(5)	6.1(5)	23.8(5)
C36	51(3)	43.6(18)	50(3)	15.1(15)	12(2)	13.3(17)
C42	52.4(6)	60.0(7)	41.5(6)	19.2(5)	14.3(5)	21.5(5)
C40	51.6(6)	61.1(7)	55.8(7)	18.8(6)	8.6(5)	29.2(6)
C34	70.8(8)	59.3(7)	40.4(6)	13.7(5)	15.5(5)	36.0(6)
C18	62.5(7)	50.2(6)	38.8(6)	12.5(5)	9.2(5)	26.4(5)
C20	55.9(6)	51.8(6)	52.6(6)	18.0(5)	18.0(5)	32.4(5)
C16	64.2(8)	46.2(6)	51.0(7)	8.4(5)	8.0(6)	6.4(6)
C4	54.1(7)	54.2(7)	50.3(6)	15.8(5)	17.4(5)	10.8(5)
C10	58(2)	41.5(17)	44.8(17)	18.5(14)	3.6(18)	20.1(15)
C30	80.7(9)	61.4(8)	49.2(7)	9.3(6)	12.7(6)	31.4(7)
N24	117.0(12)	88.0(10)	61.0(8)	-3.6(7)	21.5(8)	45.0(9)
C32	93.0(10)	78.5(9)	47.7(7)	23.8(6)	8.8(7)	49.3(8)
C8	96.7(11)	82.4(10)	42.0(6)	19.8(6)	26.1(7)	50.4(9)
C14	90.5(10)	55.1(8)	87.6(10)	33.2(7)	12.2(8)	37.1(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2u. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C39	55(2)	62(3)	53(2)	15(2)	8.9(17)	19.3(18)
C11	66(3)	70(4)	41.3(15)	14(2)	2.1(19)	33(3)
C47	120.3(14)	94.8(11)	42.1(7)	29.8(7)	22.1(8)	61.4(11)
C21	75(3)	61(3)	54.1(19)	23(2)	4(2)	35(2)
C36A	53(3)	81(5)	50(4)	14(3)	7(2)	34(3)
C10A	79(6)	71(6)	52(5)	28(5)	18(4)	34(5)
C21A	86(7)	97(9)	52(5)	32(8)	8(6)	55(7)
C11A	74(4)	108(10)	52(3)	26(6)	8(3)	51(6)
C39A	60(4)	93(7)	54(3)	19(5)	10(2)	35(4)

Table 4 Bond Lengths for 2u.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O13	C7	1.3753(12)	C49	C32	1.3854(18)
O13	C20	1.4215(14)	C36	C39	1.393(7)
F25	C20	1.3884(14)	C42	C18	1.3836(17)
N27	C7	1.3683(13)	C40	C20	1.5118(17)
N27	C33	1.4221(14)	C34	C8	1.3810(19)
N27	C29	1.4611(13)	C18	C16	1.3889(19)
N2	C7	1.2700(14)	C18	C30	1.4392(17)
N2	C35	1.4021(13)	C20	C14	1.4943(19)
C31	C29	1.5036(16)	C16	C4	1.3795(17)
C31	C36	1.397(5)	C10	C21	1.377(7)
C31	C10	1.415(6)	C30	N24	1.1420(18)
C31	C36A	1.369(11)	C32	C47	1.378(2)

Table 4 Bond Lengths for 2u.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C31	C10A	1.352(11)	C8	C47	1.375(2)
C33	C49	1.3962(16)	C39	C11	1.369(6)
C33	C34	1.3914(16)	C11	C21	1.378(5)
C35	C9	1.3890(16)	C36A	C39A	1.406(11)
C35	C4	1.3872(16)	C10A	C21A	1.351(10)
C9	C42	1.3768(16)	C21A	C11A	1.363(10)
C49	C40	1.5009(17)	C11A	C39A	1.368(9)

Table 5 Bond Angles for 2u.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O13	C20	118.31(8)	C49	C40	C20	110.48(10)
C7	N27	C33	122.87(9)	C8	C34	C33	120.11(12)
C7	N27	C29	117.62(9)	C42	C18	C16	119.36(11)
C33	N27	C29	119.51(8)	C42	C18	C30	119.20(12)
C7	N2	C35	122.86(9)	C16	C18	C30	121.43(12)
N27	C7	O13	114.38(9)	O13	C20	C40	110.32(9)
N2	C7	O13	124.37(9)	O13	C20	C14	106.66(11)
N2	C7	N27	121.10(10)	F25	C20	O13	106.54(9)
C36	C31	C29	127.3(4)	F25	C20	C40	108.08(10)
C36	C31	C10	118.9(4)	F25	C20	C14	108.86(10)
C10	C31	C29	113.7(3)	C14	C20	C40	115.99(12)
C36A	C31	C29	116.6(7)	C4	C16	C18	120.54(11)
C10A	C31	C29	127.3(7)	C16	C4	C35	120.33(11)
C10A	C31	C36A	116.0(8)	C21	C10	C31	119.9(5)

Table 5 Bond Angles for 2u.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C49	C33	N27	120.33(10)	N24	C30	C18	177.67(18)
C34	C33	N27	119.72(10)	C47	C32	C49	121.27(13)
C34	C33	C49	119.90(11)	C47	C8	C34	120.19(13)
N27	C29	C31	114.85(9)	C11	C39	C36	120.7(6)
C9	C35	N2	117.14(10)	C39	C11	C21	120.4(6)
C4	C35	N2	124.02(10)	C8	C47	C32	119.84(13)
C4	C35	C9	118.58(10)	C10	C21	C11	120.5(6)
C42	C9	C35	121.27(11)	C31	C36A	C39A	121.5(11)
C33	C49	C40	119.84(10)	C21A	C10A	C31	124.6(9)
C32	C49	C33	118.65(11)	C10A	C21A	C11A	119.2(9)
C32	C49	C40	121.50(12)	C21A	C11A	C39A	119.6(10)
C39	C36	C31	119.6(6)	C11A	C39A	C36A	119.0(11)
C9	C42	C18	119.80(11)				

Table 6 Torsion Angles for 2u.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N27	C33	C49	C40	1.20(17)	C35	C9	C42	C18	-2.03(19)
N27	C33	C49	C32	-179.51(12)	C9	C35	C4	C16	-2.8(2)
N27	C33	C34	C8	178.72(12)	C9	C42	C18	C16	-1.09(19)
N2	C35	C9	C42	178.32(11)	C9	C42	C18	C30	177.93(12)
N2	C35	C4	C16	-176.72(12)	C49	C33	C34	C8	1.4(2)
C7	O13	C20	F25	77.68(11)	C49	C40	C20	O13	-50.37(14)
C7	O13	C20	C40	-39.40(13)	C49	C40	C20	F25	-166.48(10)
C7	O13	C20	C14	-166.17(10)	C49	C40	C20	C14	71.01(14)

Table 6 Torsion Angles for 2u.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	N27	C33	C49	-38.66(16)	C49	C32	C47	C8	0.0(3)
C7	N27	C33	C34	144.00(12)	C36	C31	C29	N27	-0.4(6)
C7	N27	C29	C31	-80.84(12)	C36	C31	C10	C21	-1.3(13)
C7	N2	C35	C9	134.07(12)	C36	C39	C11	C21	-0.1(15)
C7	N2	C35	C4	-51.88(17)	C42	C18	C16	C4	2.2(2)
C31	C36	C39	C11	-0.7(15)	C40	C49	C32	C47	-179.20(14)
C31	C10	C21	C11	0.6(16)	C34	C33	C49	C40	178.54(11)
C31	C36A	C39A	C11A	1(3)	C34	C33	C49	C32	-2.17(18)
C31	C10A	C21A	C11A	-1(3)	C34	C8	C47	C32	-0.8(3)
C33	N27	C7	O13	-17.25(15)	C18	C16	C4	C35	-0.3(2)
C33	N27	C7	N2	167.03(11)	C20	O13	C7	N27	84.53(11)
C33	N27	C29	C31	99.54(12)	C20	O13	C7	N2	-99.91(13)
C33	C49	C40	C20	69.16(15)	C4	C35	C9	C42	3.94(18)
C33	C49	C32	C47	1.5(2)	C10	C31	C29	N27	178.7(5)
C33	C34	C8	C47	0.2(2)	C10	C31	C36	C39	1.3(13)
C29	N27	C7	O13	163.14(9)	C30	C18	C16	C4	-176.75(13)
C29	N27	C7	N2	-12.58(16)	C32	C49	C40	C20	-110.11(14)
C29	N27	C33	C49	140.94(11)	C39	C11	C21	C10	0.1(16)
C29	N27	C33	C34	-36.40(15)	C36A	C31	C29	N27	-3.8(10)
C29	C31	C36	C39	-179.6(7)	C36A	C31	C10A	C21A	1(2)
C29	C31	C10	C21	179.5(8)	C10A	C31	C29	N27	178.1(10)
C29	C31	C36A	C39A	-179.1(14)	C10A	C31	C36A	C39A	-1(2)
C29	C31	C10A	C21A	178.6(12)	C10A	C21A	C11A	C39A	1(2)
C35	N2	C7	O13	-0.08(17)	C21A	C11A	C39A	C36A	-1(2)
C35	N2	C7	N27	175.20(10)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2u.

Atom	*x*	*y*	*z*	U(eq)
H29A	2170.99	-789.71	1796.16	55
H29B	1847.48	-348.47	3156.48	55
H9	133.53	1668.35	6034.29	61
H36	5546.31	2265.55	3487.83	62
H42	54.47	3227.27	7957.79	63
H40A	-138.84	1731.53	2295.87	67
H40B	-263.25	2716.98	1648.77	67
H34	3940.46	519.51	811.06	67
H16	4236.86	6162.5	7988.35	76
H4	4268.85	4625.69	6032.63	70
H10	3305.45	-1924.11	2901.76	58
H32	829.23	2544.54	-173.61	83
H8	3860.58	725.65	-1067.83	85
H14A	2964.38	5935.73	3768.37	111
H14B	1469.81	5459.54	2796.25	111
H14C	2851.49	5031.25	2353.42	111
H39	7898.99	2244.21	4146.96	74
H11	7953.86	190.48	4186.9	73
H47	2324.91	1757.73	-1549.09	96
H21	5672.48	-1886.3	3567.99	74
H36A	5147.12	2200.84	3266.46	76
H10A	3792.25	-1729.62	3070.75	78
H21A	6281.73	-1314.33	3750.69	87

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2u.

Atom	*x*	*y*	*z*	U(eq)
H11A	8300.75	899.15	4191.79	91
H39A	7739.2	2694.14	3991.6	86

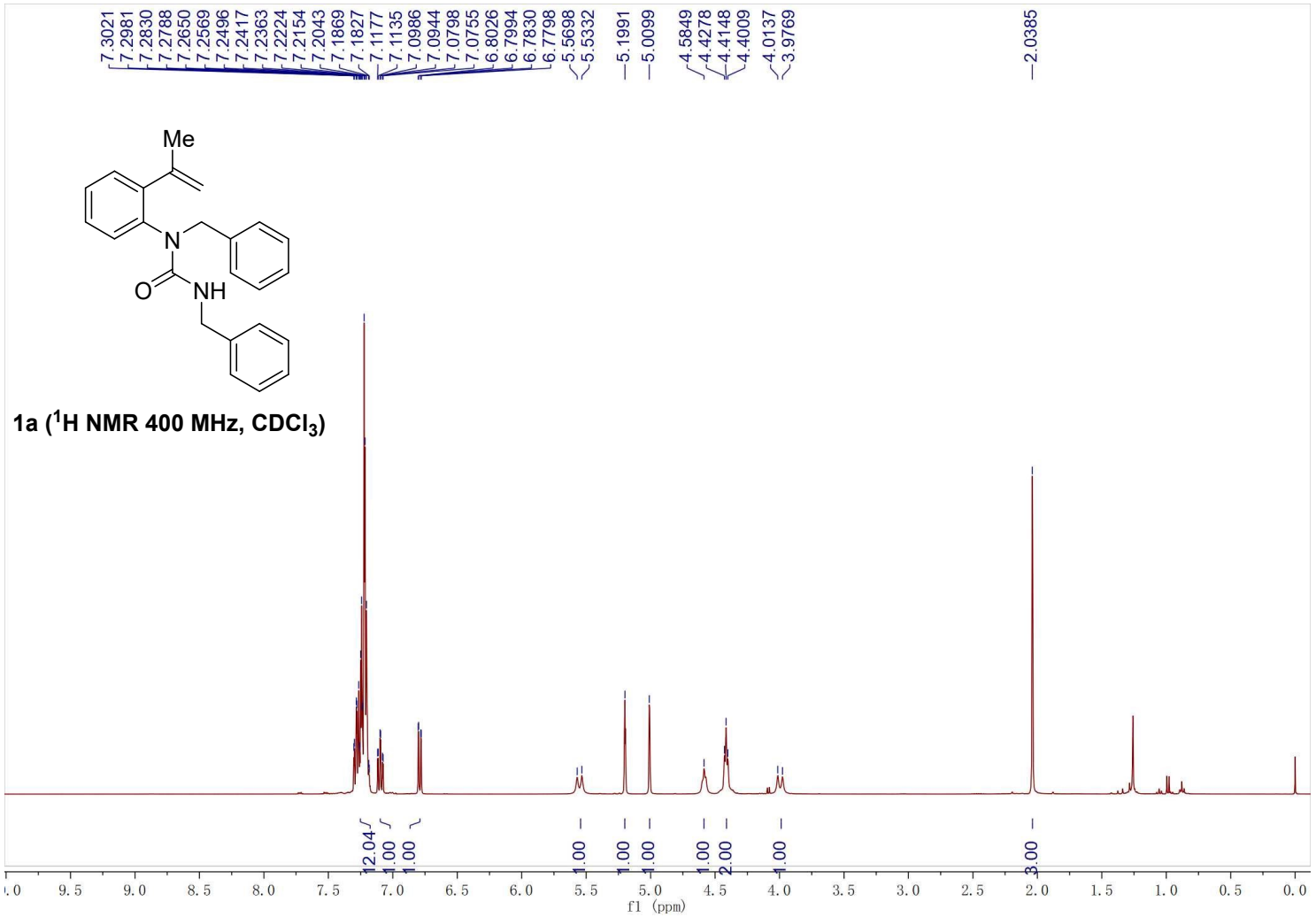
Table 8 Atomic Occupancy for 2u.

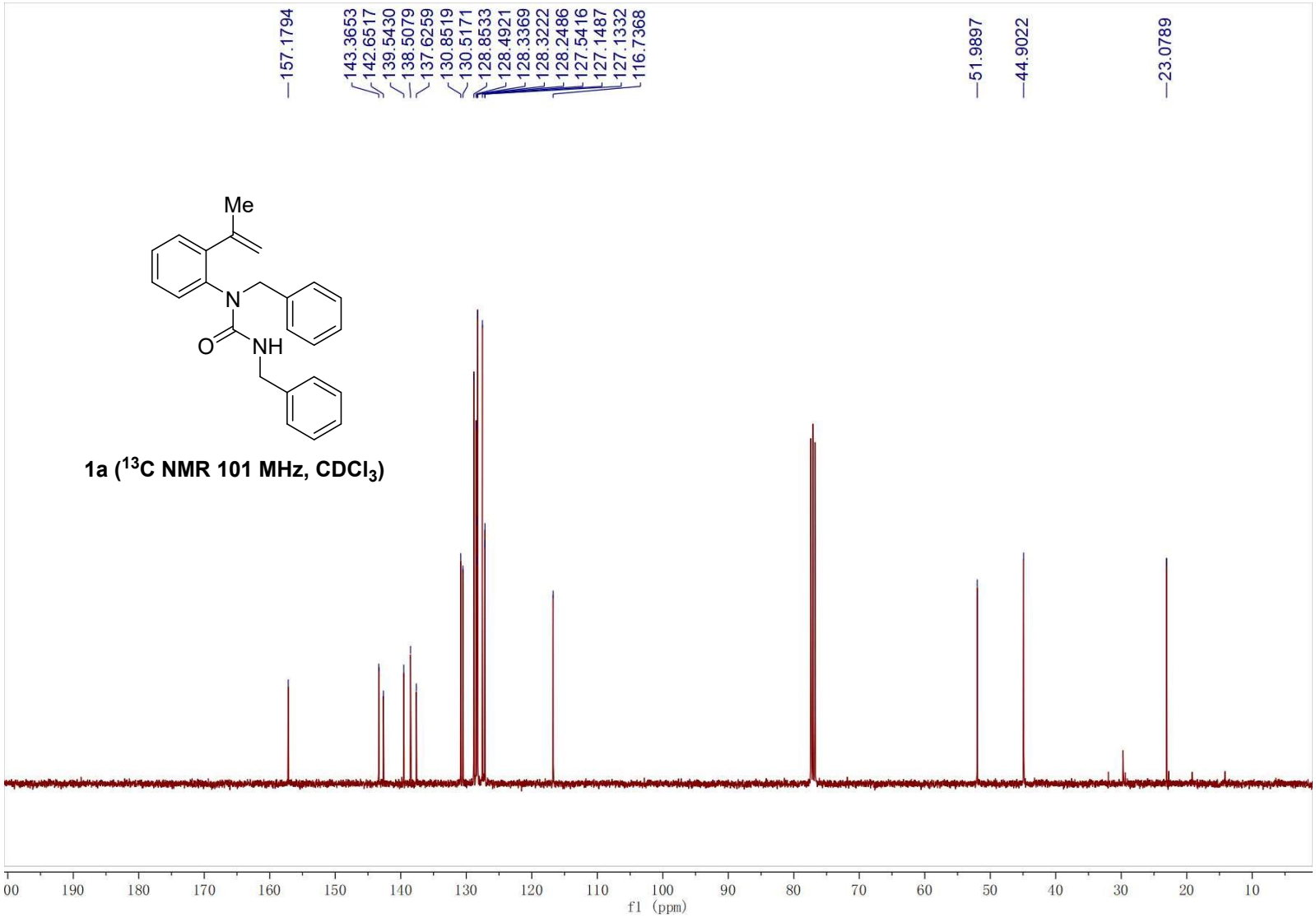
Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C36	0.61(2)	H36	0.61(2)	C10	0.61(2)
H10	0.61(2)	C39	0.61(2)	H39	0.61(2)
C11	0.61(2)	H11	0.61(2)	C21	0.61(2)
H21	0.61(2)	C36A	0.39(2)	H36A	0.39(2)
C10A	0.39(2)	H10A	0.39(2)	C21A	0.39(2)
H21A	0.39(2)	C11A	0.39(2)	H11A	0.39(2)
C39A	0.39(2)	H39A	0.39(2)		

IV. References:

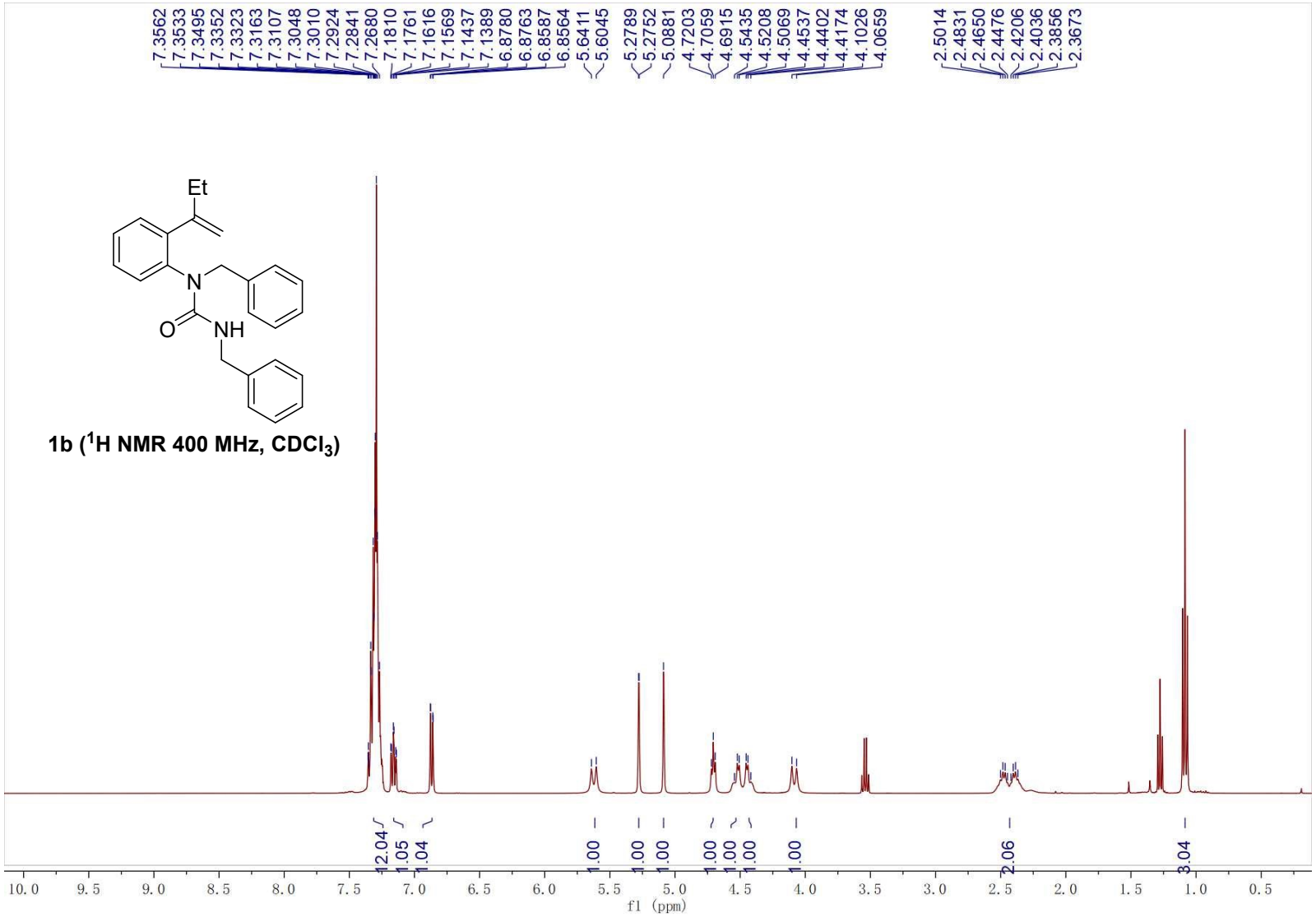
1. Fayol, A.; Fang, Y.-Q.; Lautens, M. *Org. Lett.* 2006, **8**, 4203–4206.
2. Ulmer, A.; Brunner, C.; Arnold, A. M.; Pöthig, A.; Gulder, T. *Chem. Eur. J.* 2016, **22**, 3660-3664
3. Hou, Z.-W.; Yan, H.; Song, J.-S.; Xu, H.-C. *Chin. J. Chem.* 2018, **36**, 909-915.
4. Chen, C.; Huang, Y.; Ding, J.; Liu, L.; Zhu, B. *Adv. Synth. Catal.* 2022, **364**, 794-801.
5. Babu, S. S.; Varma, A. A.; Gopinath, P. *Chem. Commun.* 2022, **58**, 1990-1993.

V. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Substrates and Products:





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



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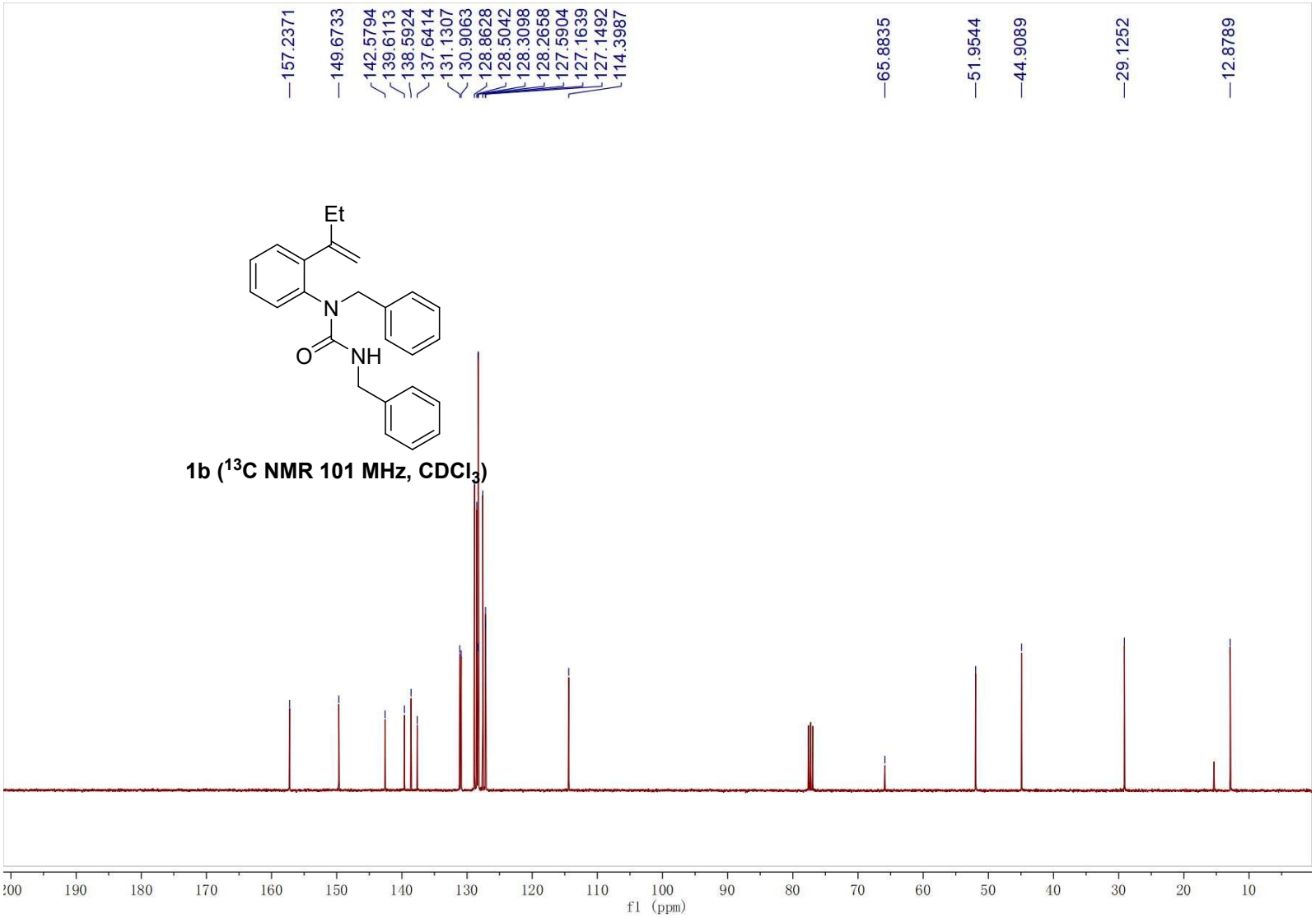

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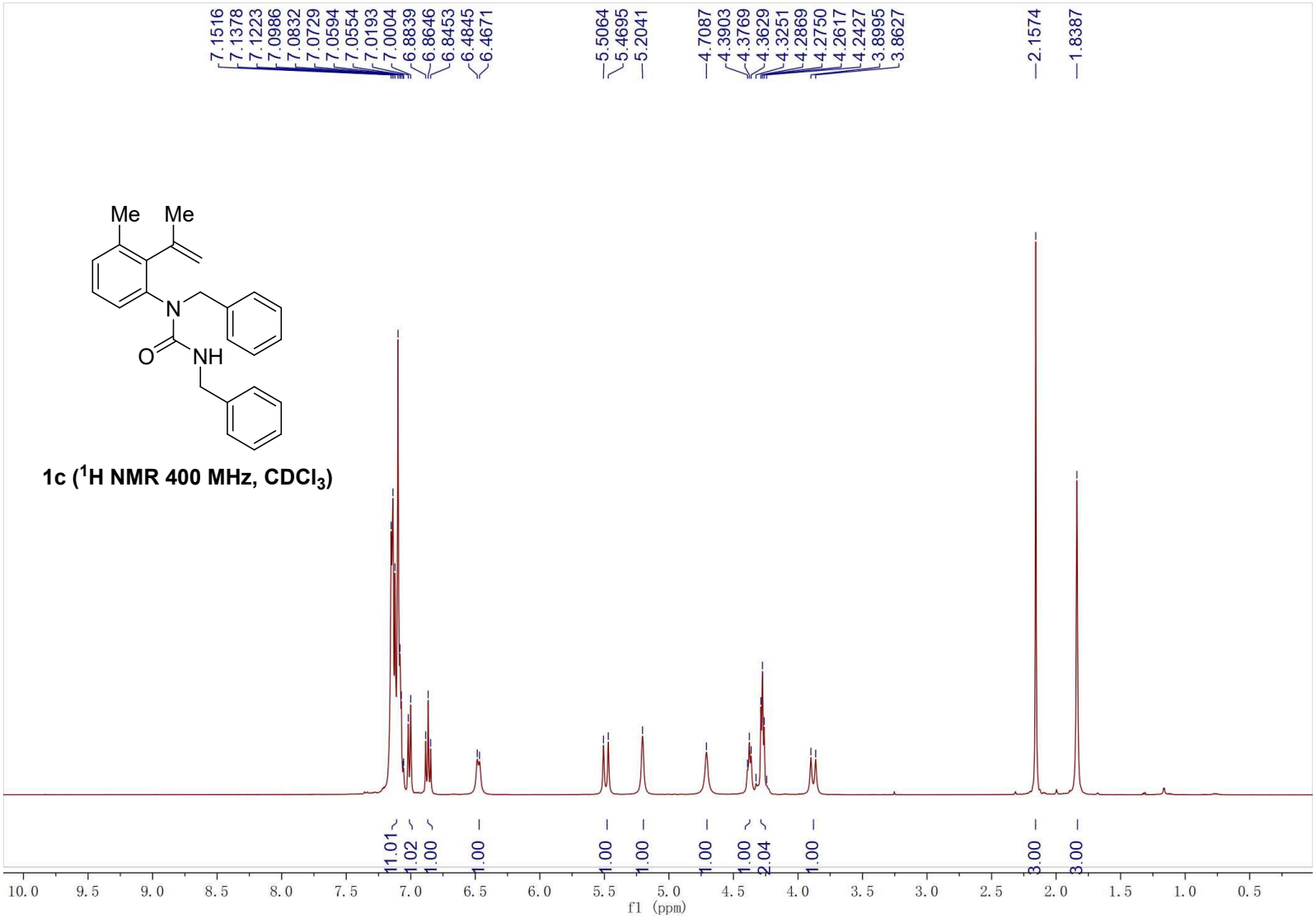
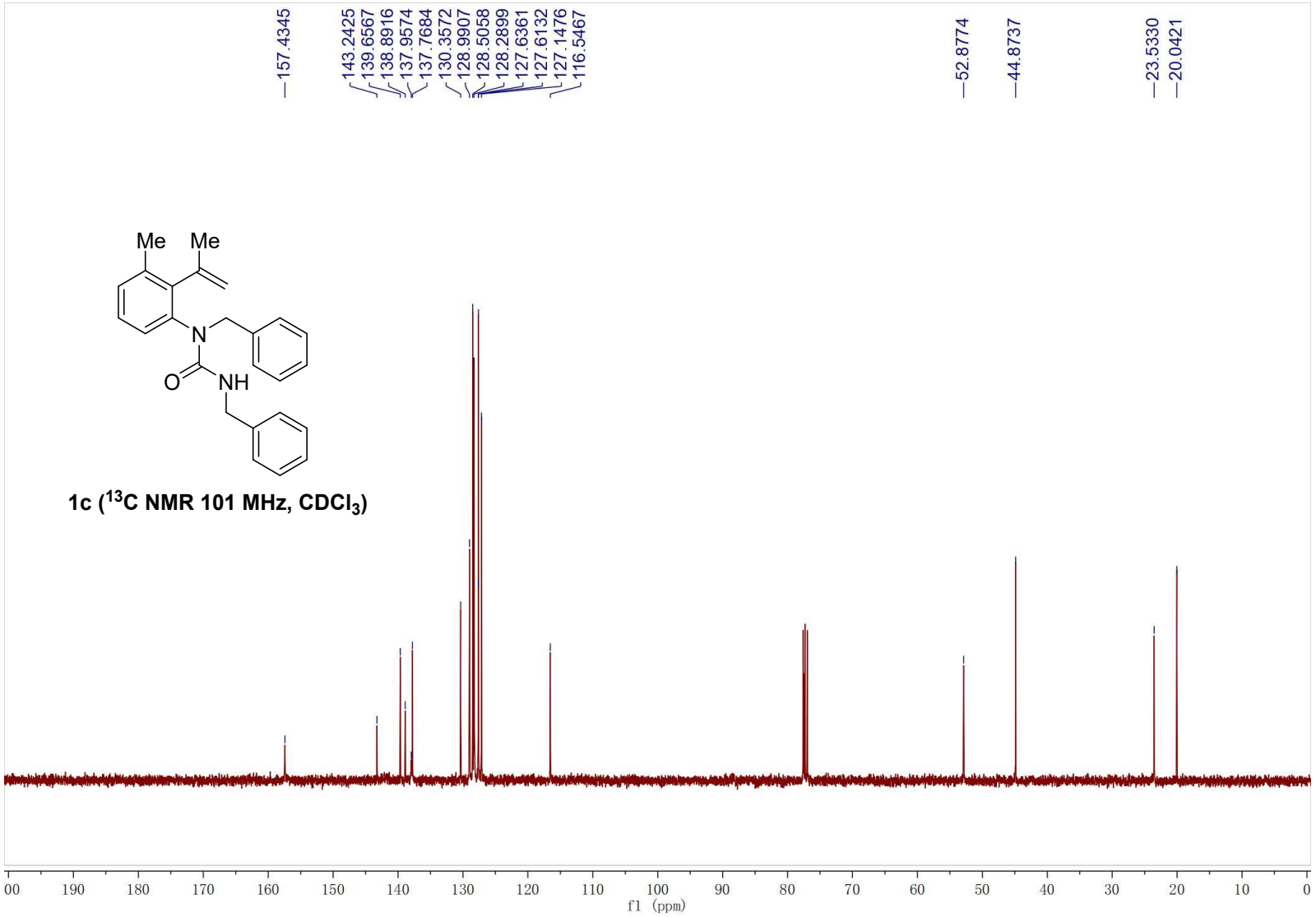


1c (^{1}H NMR 400 MHz, $CDCl_3$)



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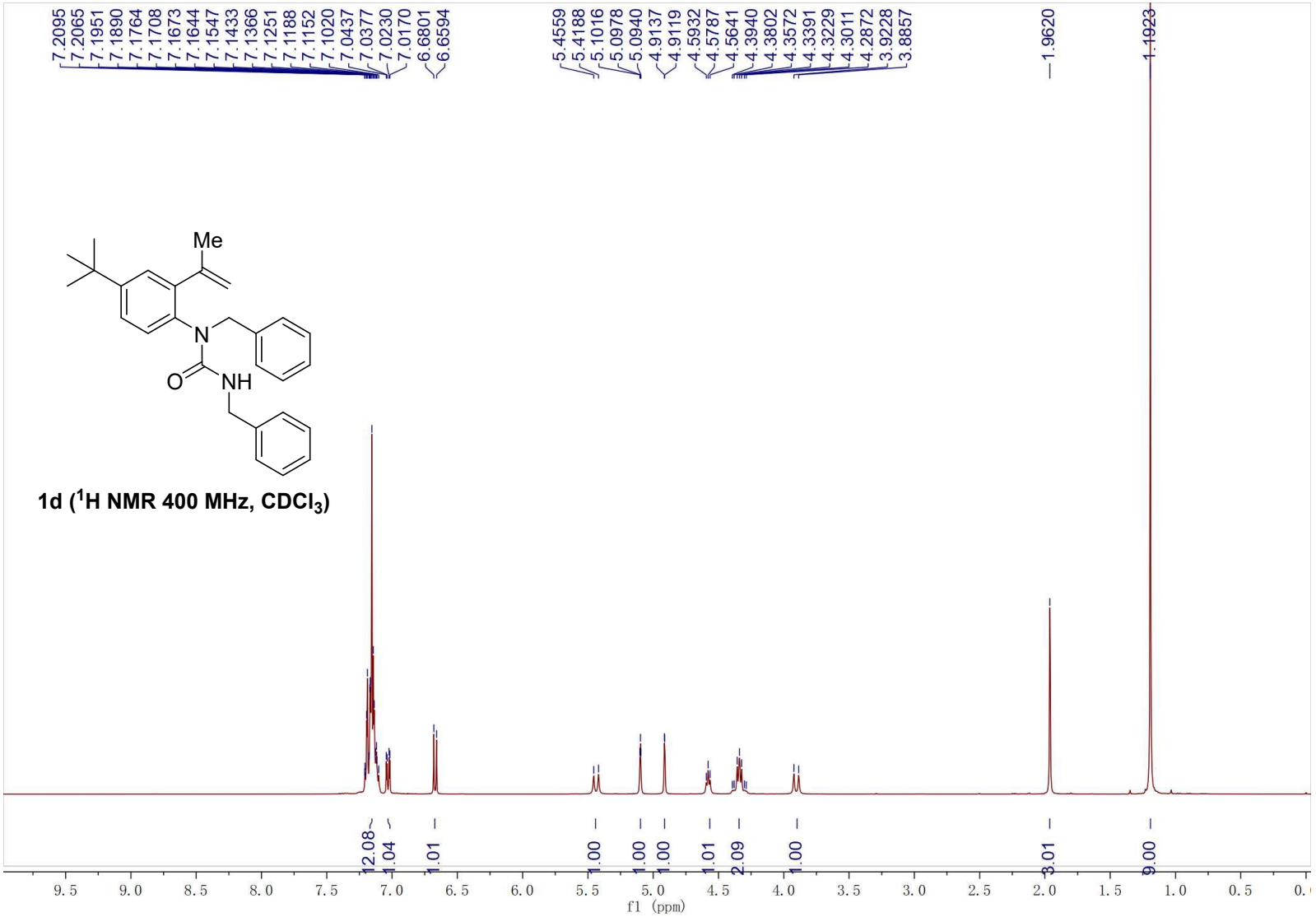

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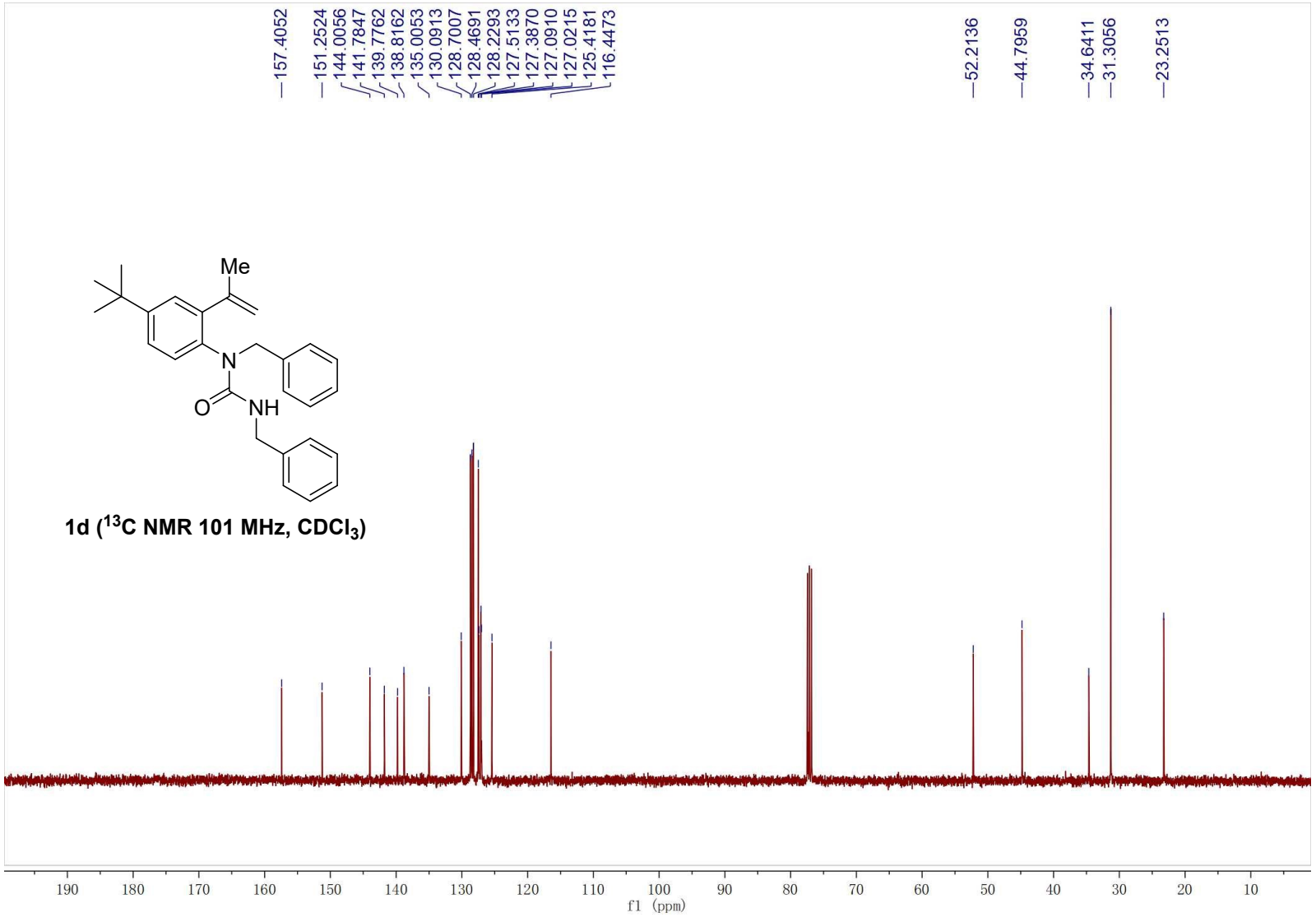
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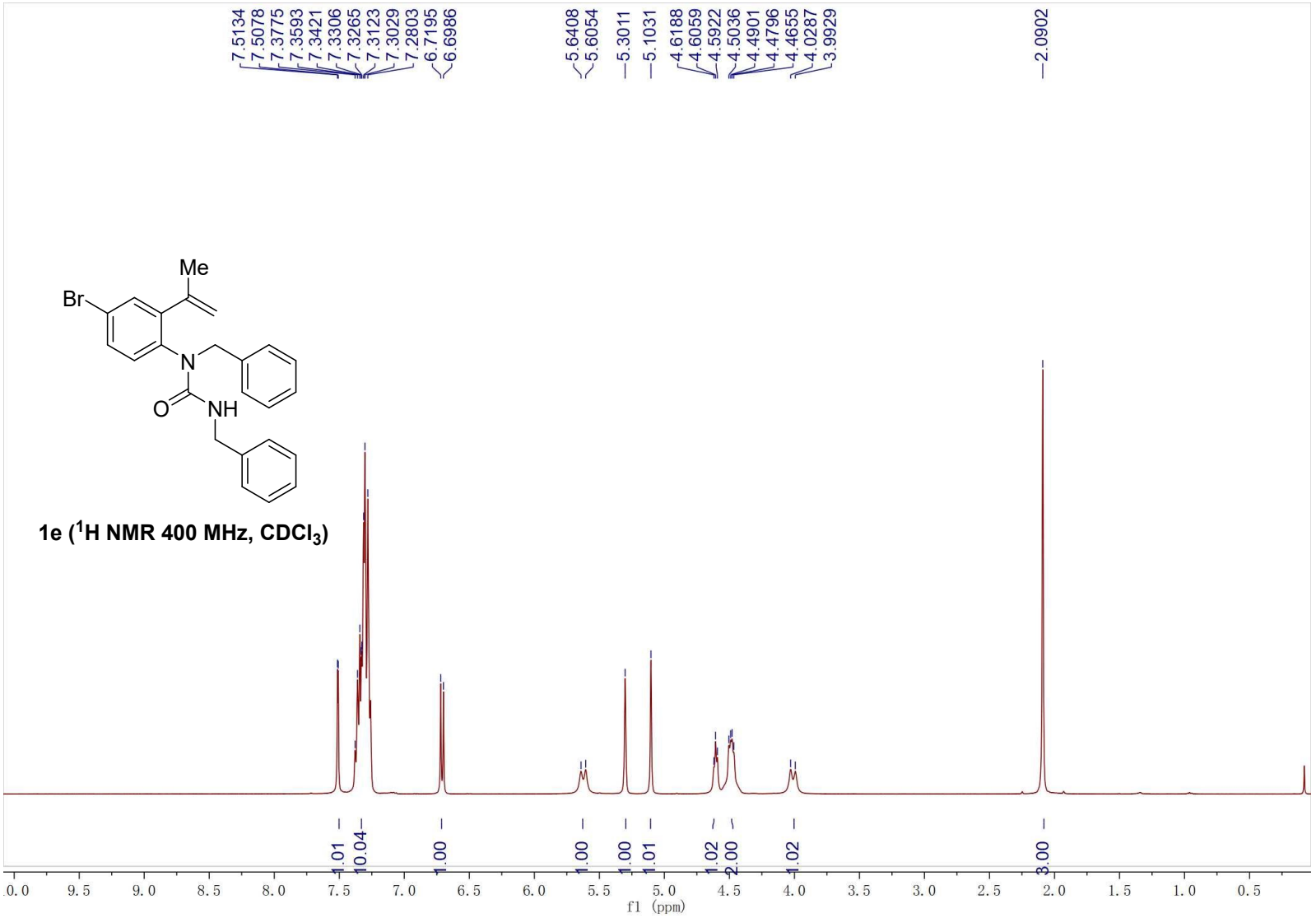
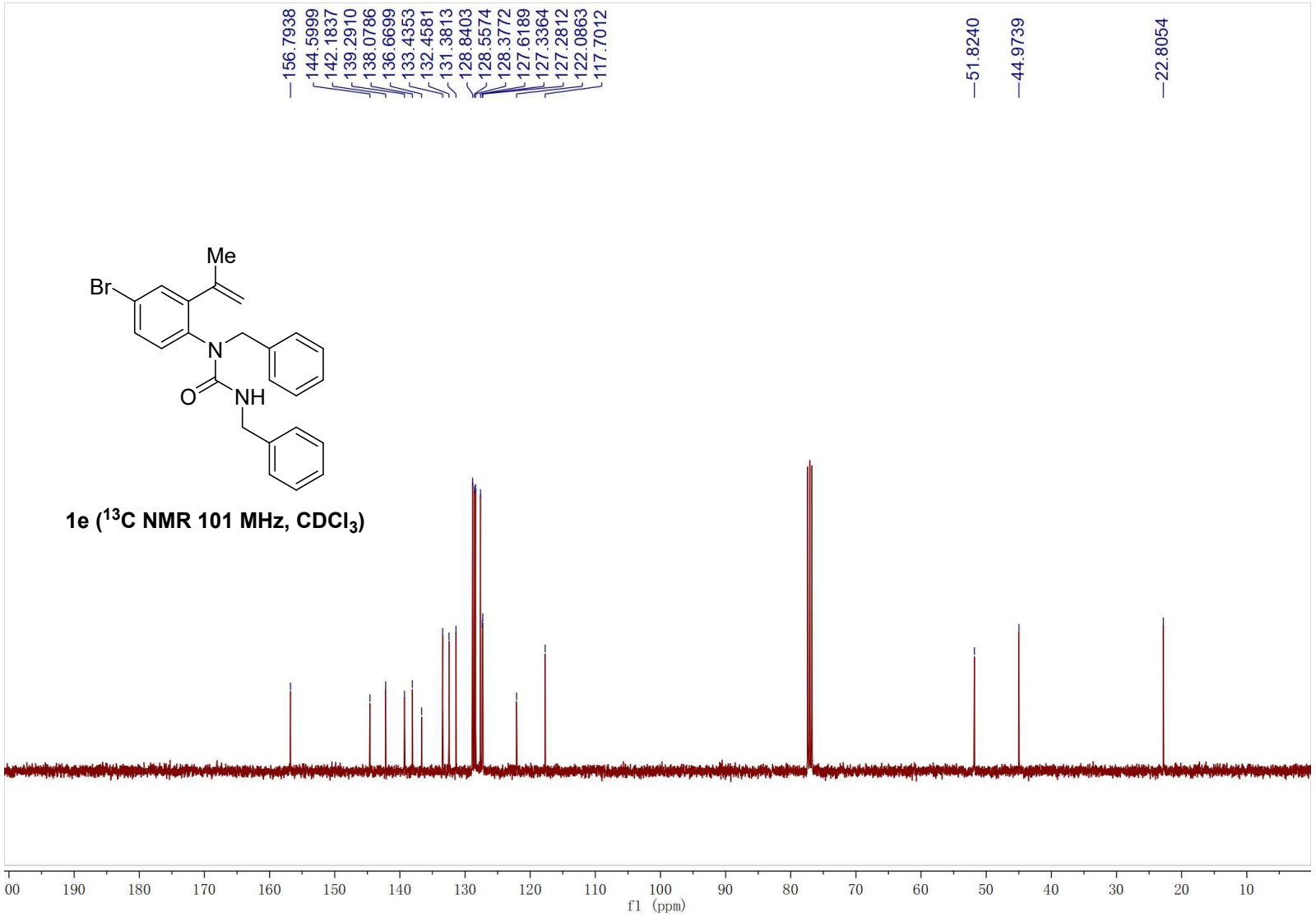
141.7847
139.7762
138.8162
135.0053
130.0913
128.7007
128.4691
128.2293
127.5133
127.3870
127.0910
127.0215
125.4181
116.4473
52.2136
44.7959
34.6411
31.3056
23.2513
Me
N
O
NH
1d (^{13}C NMR 101 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



1e (^{1}H NMR 400 MHz, $CDCl_3$)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139.2910
138.0786
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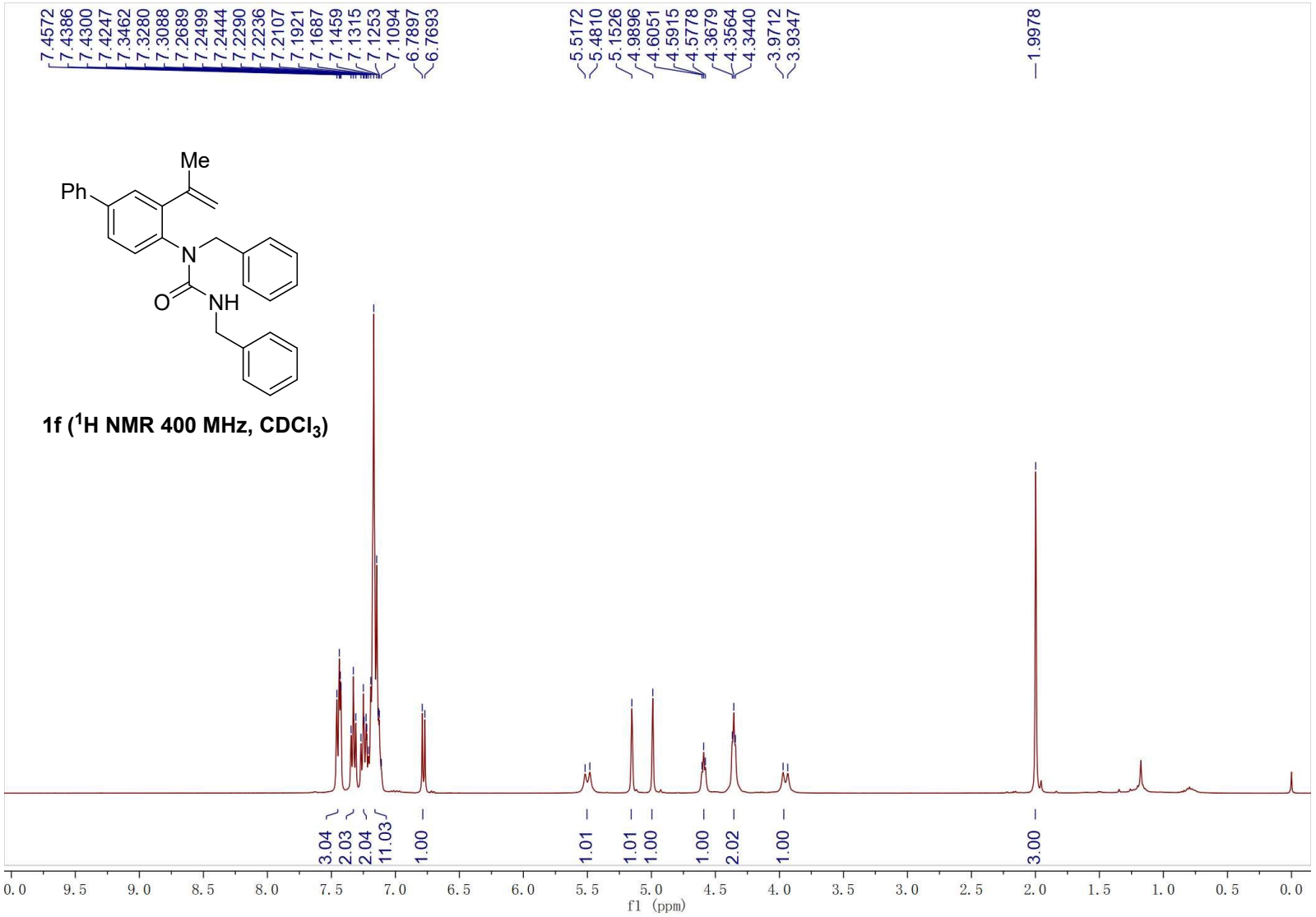
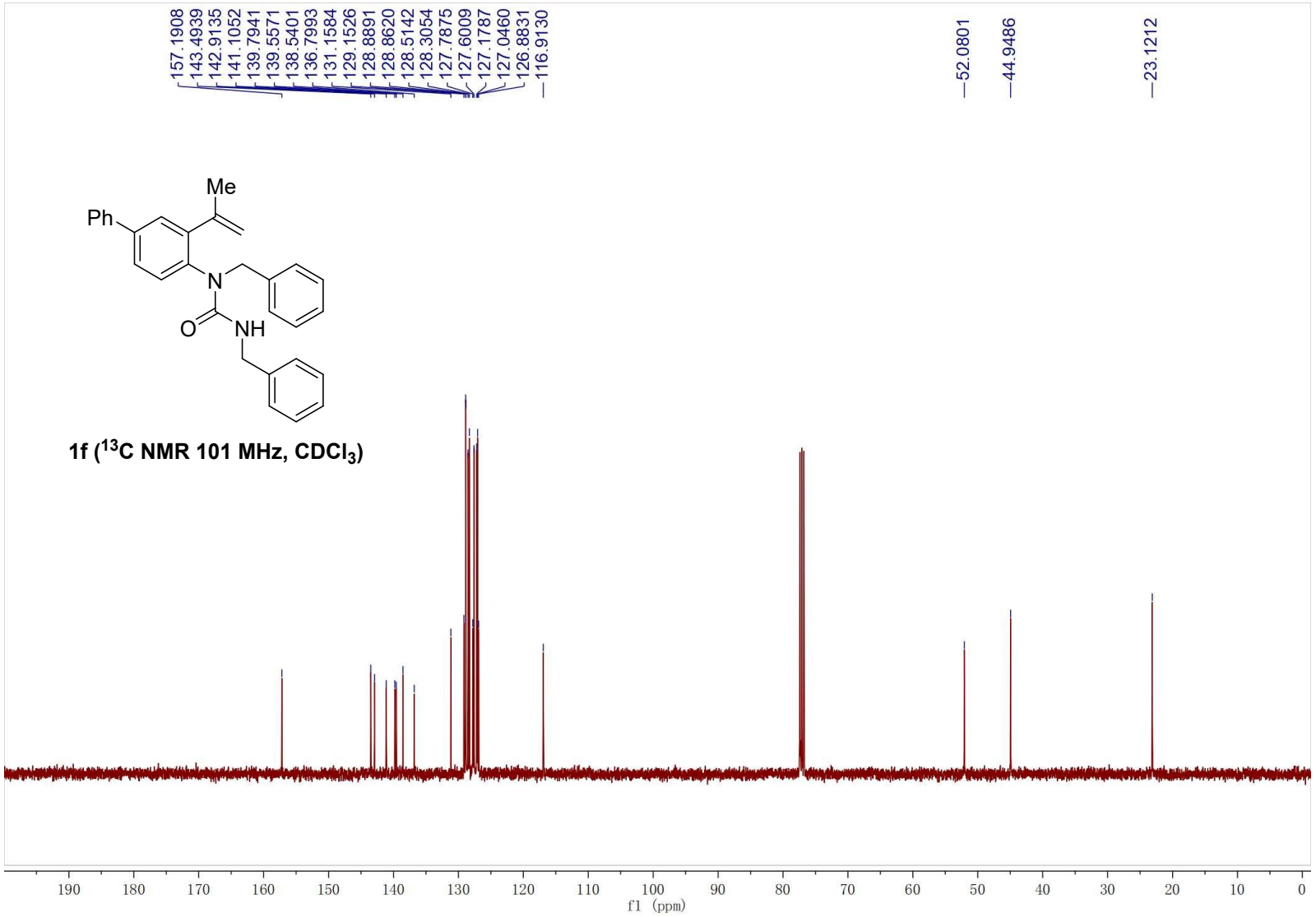
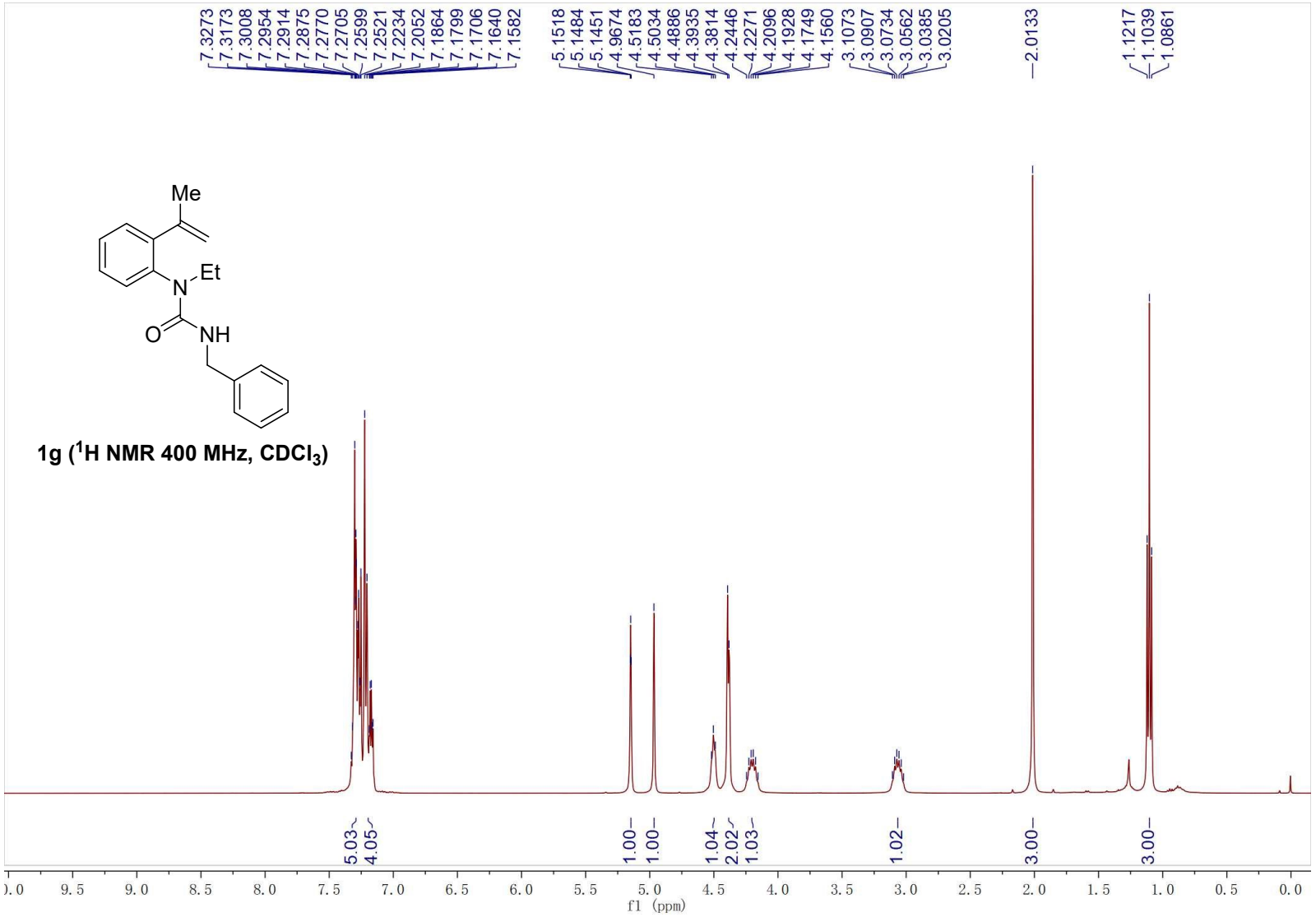
131.3813
128.8403
128.5574
128.3772
127.6189
127.3364
127.2812
122.0863
117.7012
51.8240
44.9739
22.8054
Me
Br
N
O
NH
1e (13C NMR 101 MHz, CDCl3)
f1 (ppm)



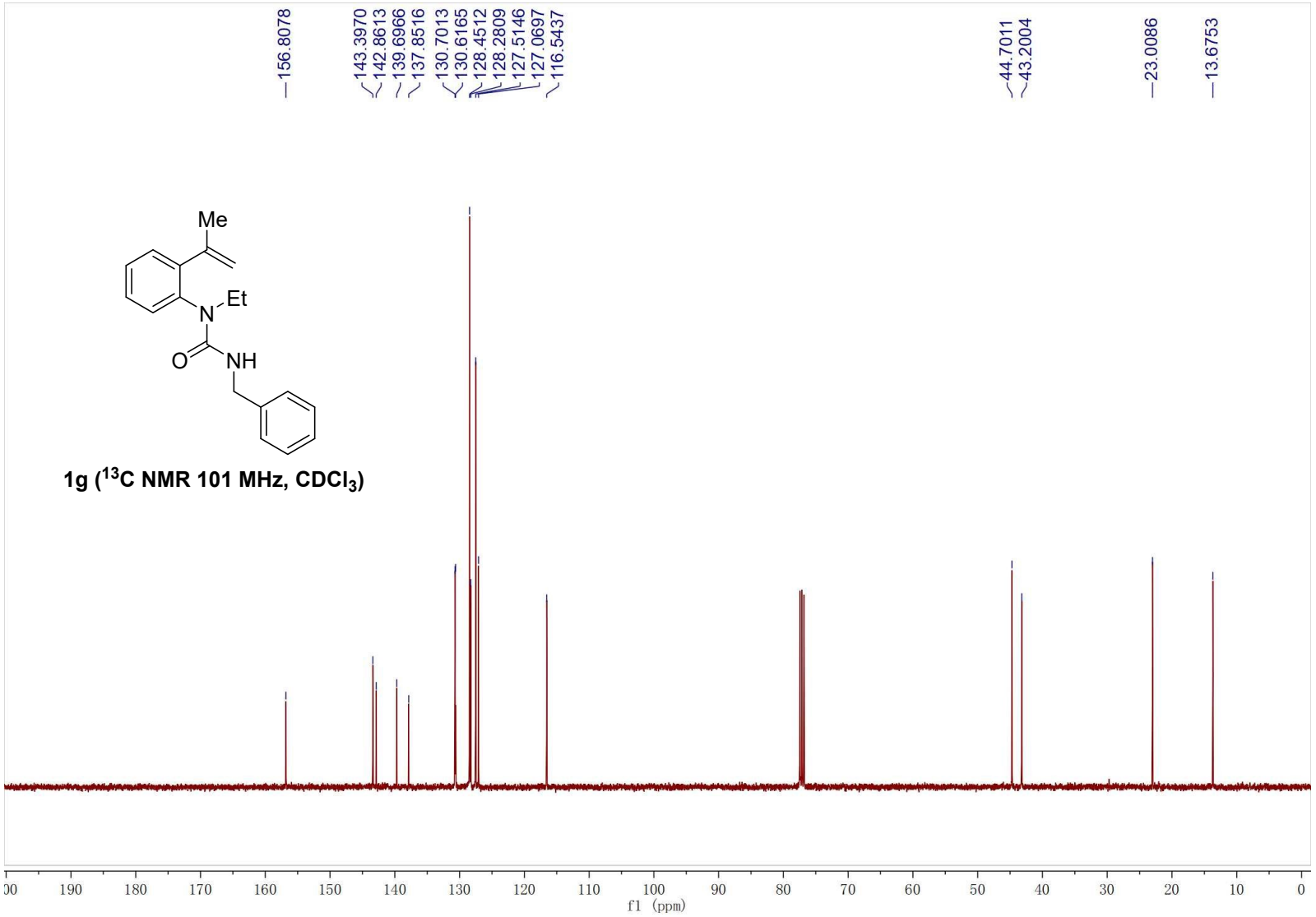
1f (^{1}H NMR 400 MHz, $CDCl_3$)



1f (^{13}C NMR 101 MHz, $CDCl_3$)



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



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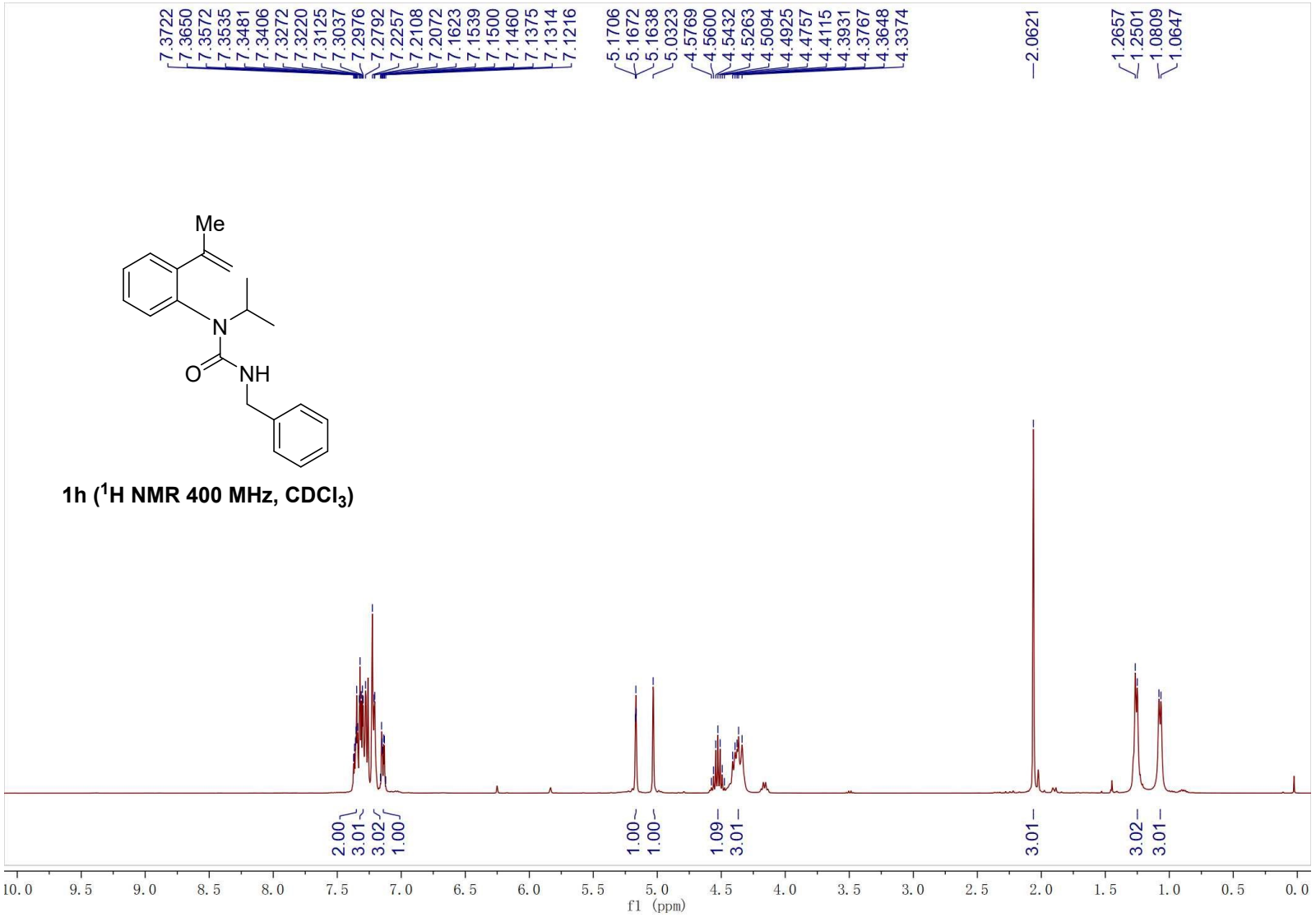
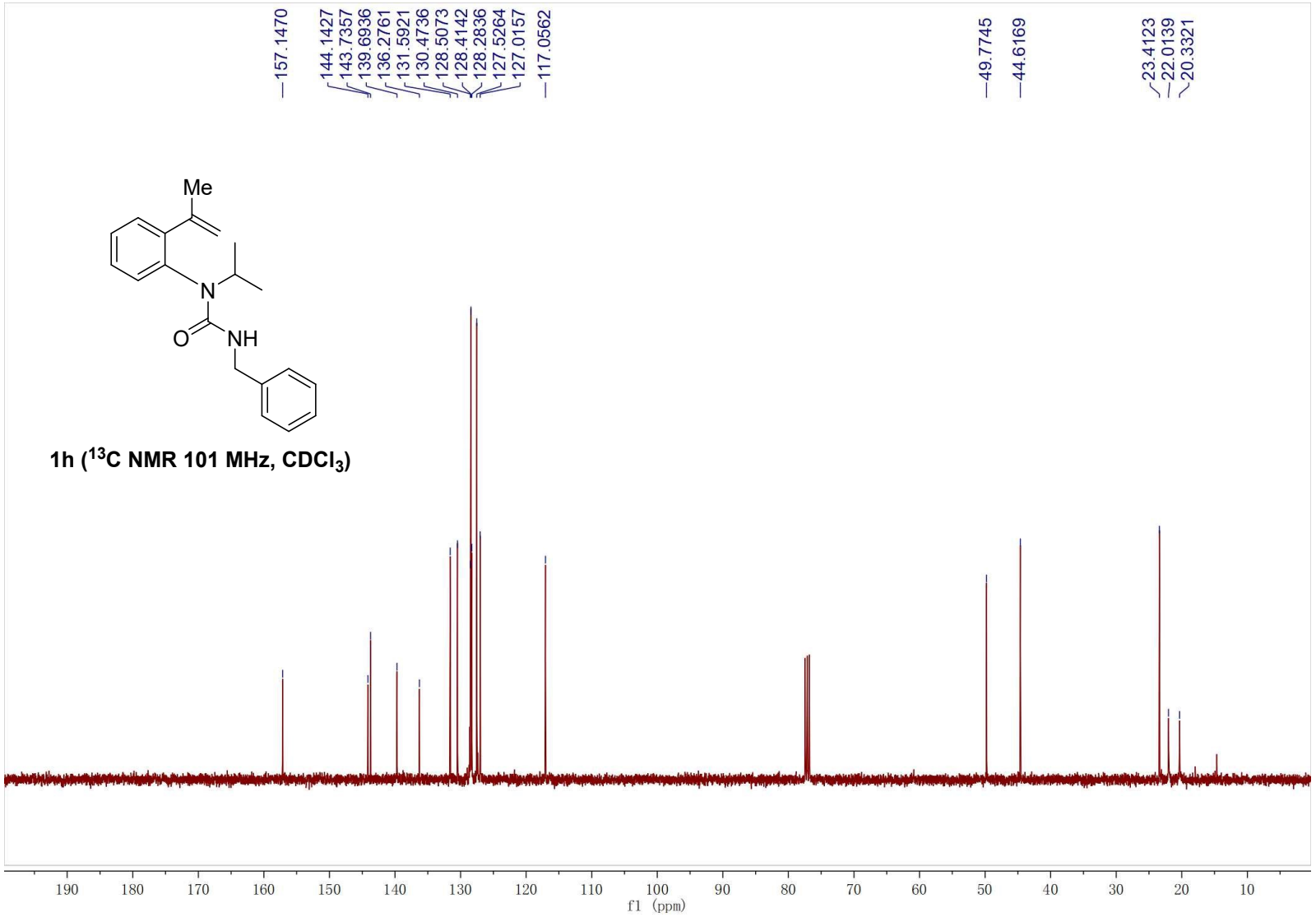


1h (^{1}H NMR 400 MHz, $CDCl_3$)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136.2761
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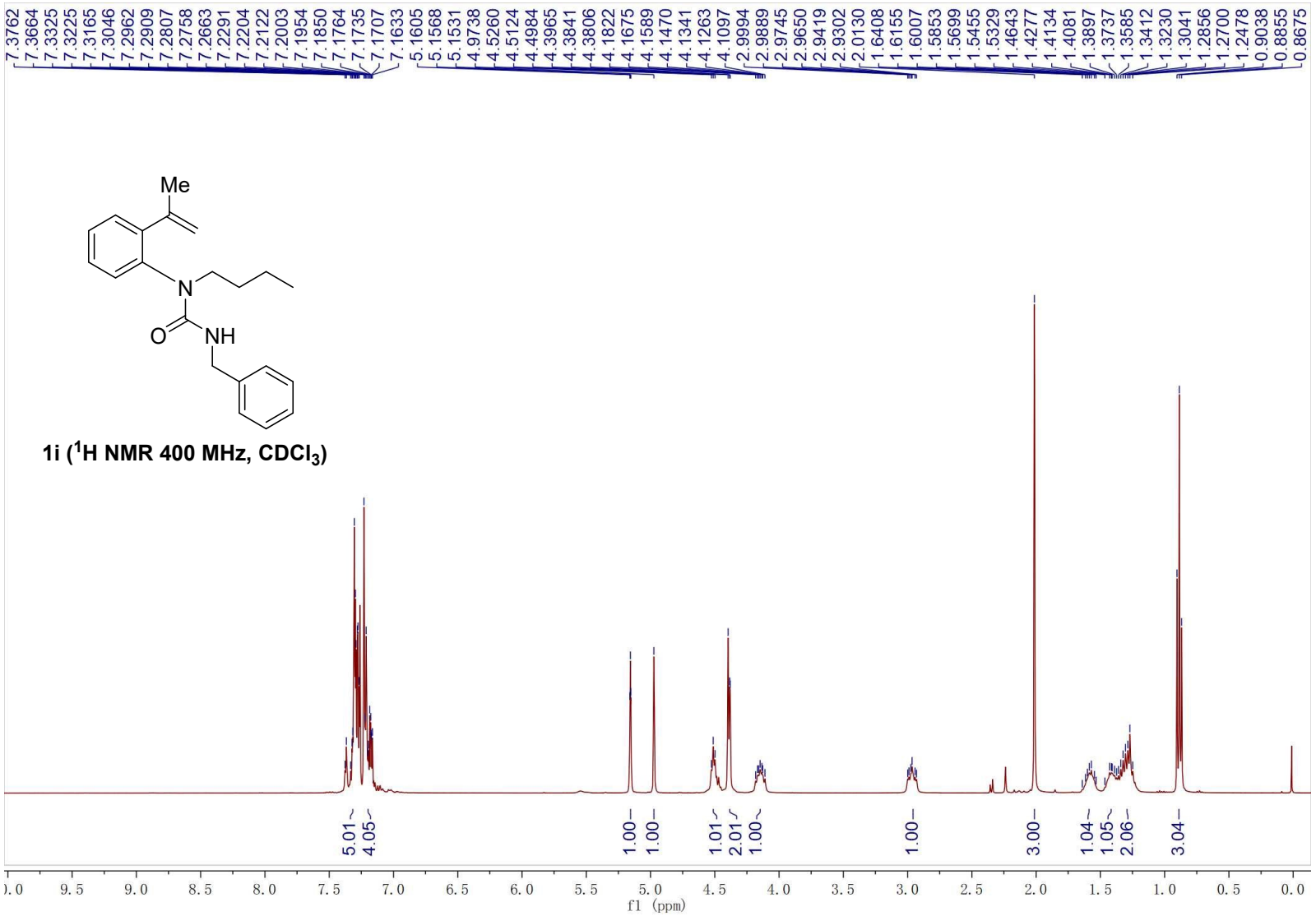
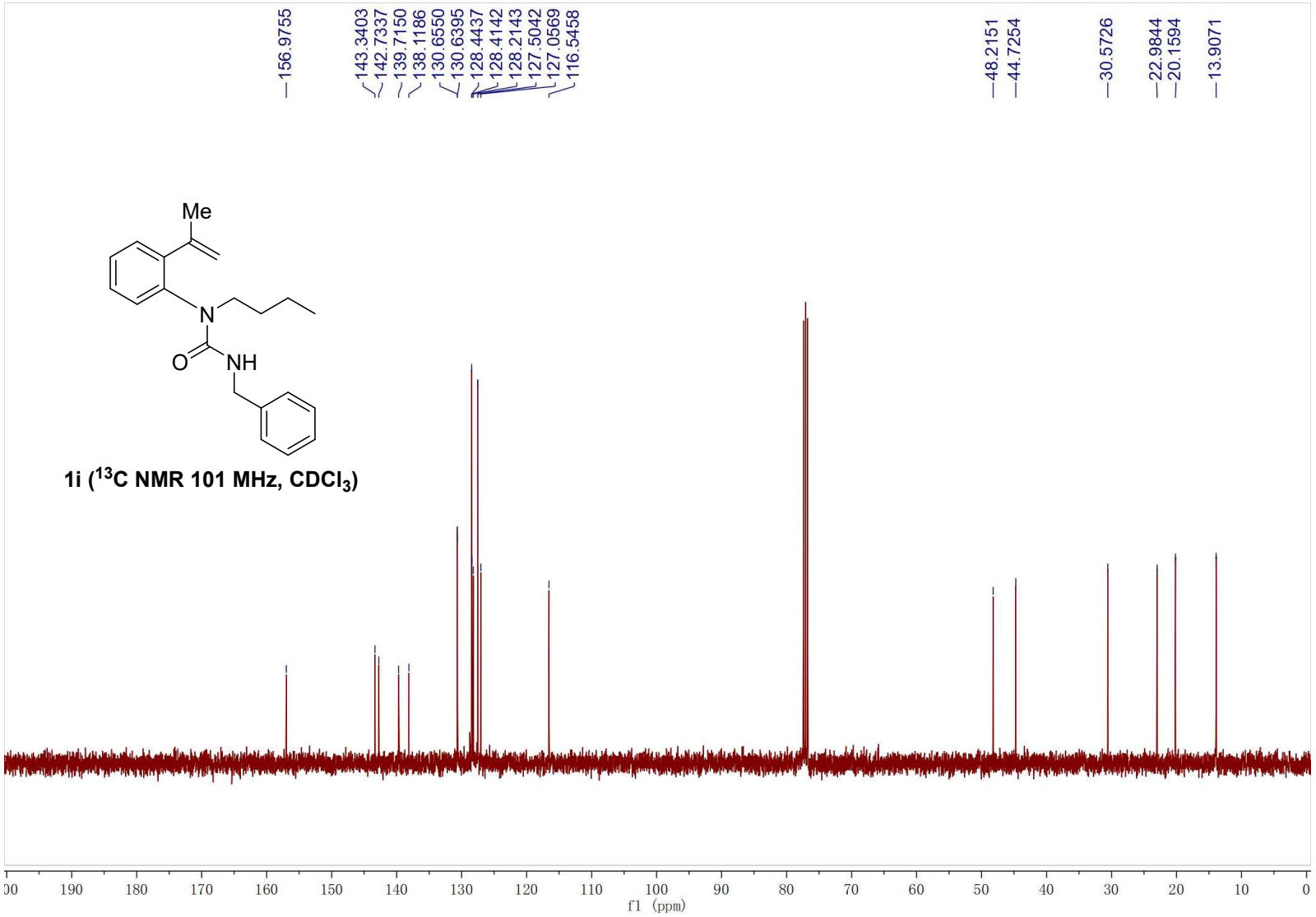
130.4736
128.5073
128.4142
128.2836
127.5264
127.0157
117.0562
49.7745
44.6169
23.4123
22.0139
20.3321
Me
N
O
NH
1h (^{13}C NMR 101 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Me
N
O
NH
1i (^{1}H NMR 400 MHz, $CDCl_3$)
f1 (ppm)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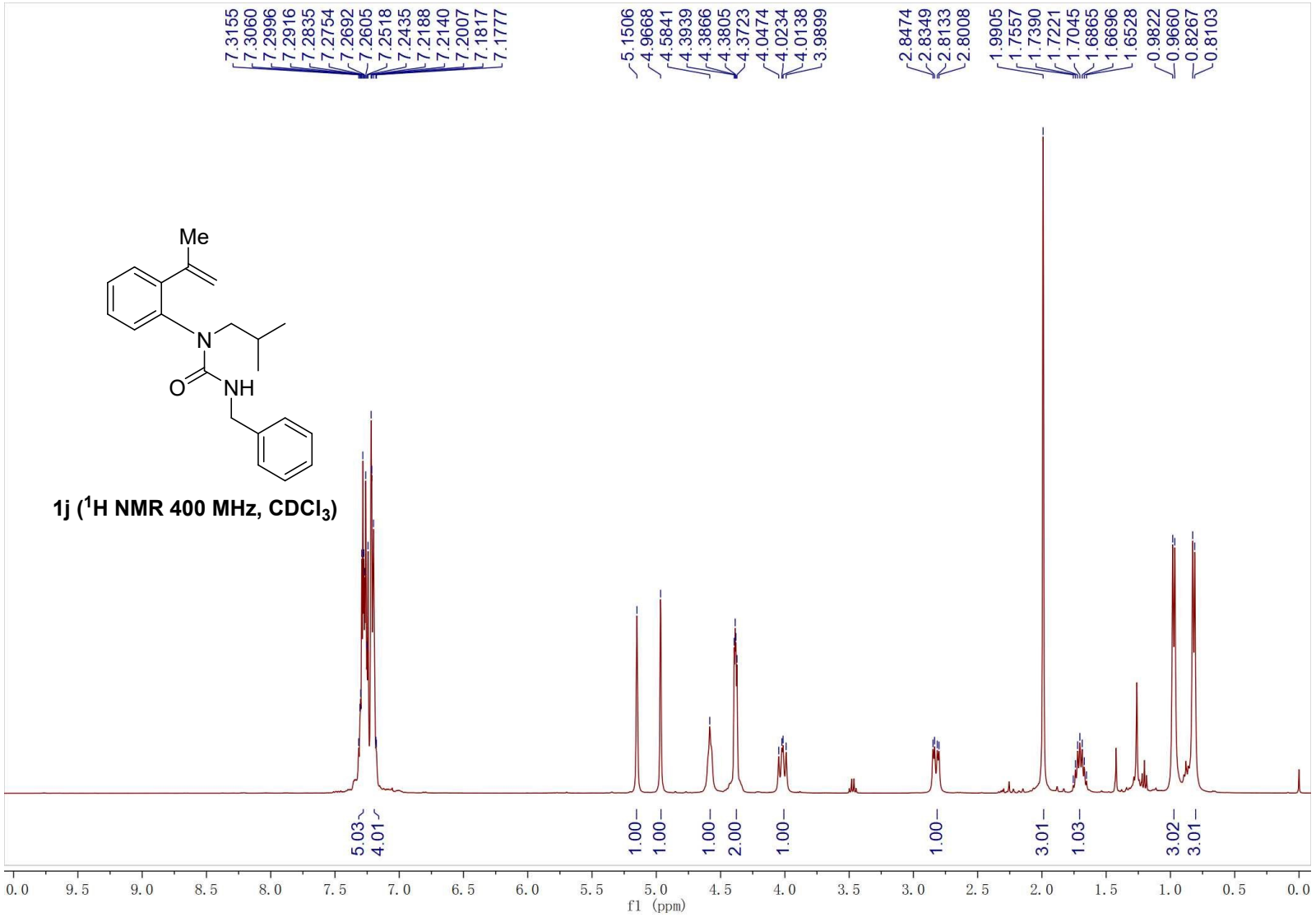
127.5042
127.0569
116.5458
48.2151
44.7254
30.5726
22.9844
20.1594
13.9071
Me
N
O
NH
1i (13C NMR 101 MHz, CDCl3)
f1 (ppm)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7.2140
7.2007
7.1817
7.1777
5.1506
4.9668
4.5841
4.3939
4.3866
4.3805
4.3723
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4.0234
4.0138
3.9899
2.8474
2.8349
2.8133
2.8008
1.9905
1.7557
1.7390
1.7221
1.7045
1.6865
1.6696
1.6528
0.9822
0.9660
0.8267
0.8103
Me
N
O
NH
1j (1H NMR 400 MHz, CDCl3)
5.03
4.01
1.00
1.00
1.00
2.00
1.00
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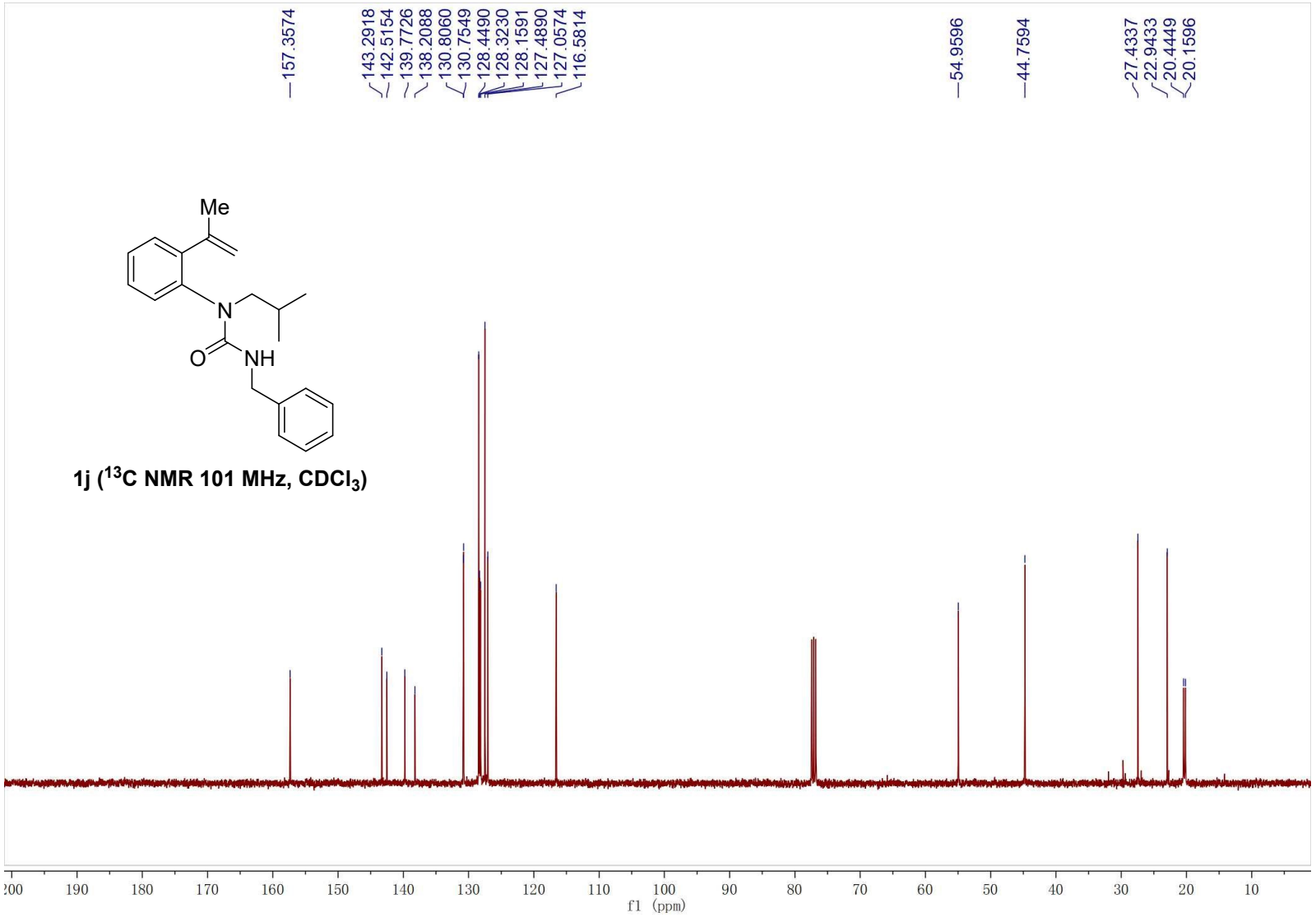
3.01
1.03
3.02
3.01
f1 (ppm)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138.2088
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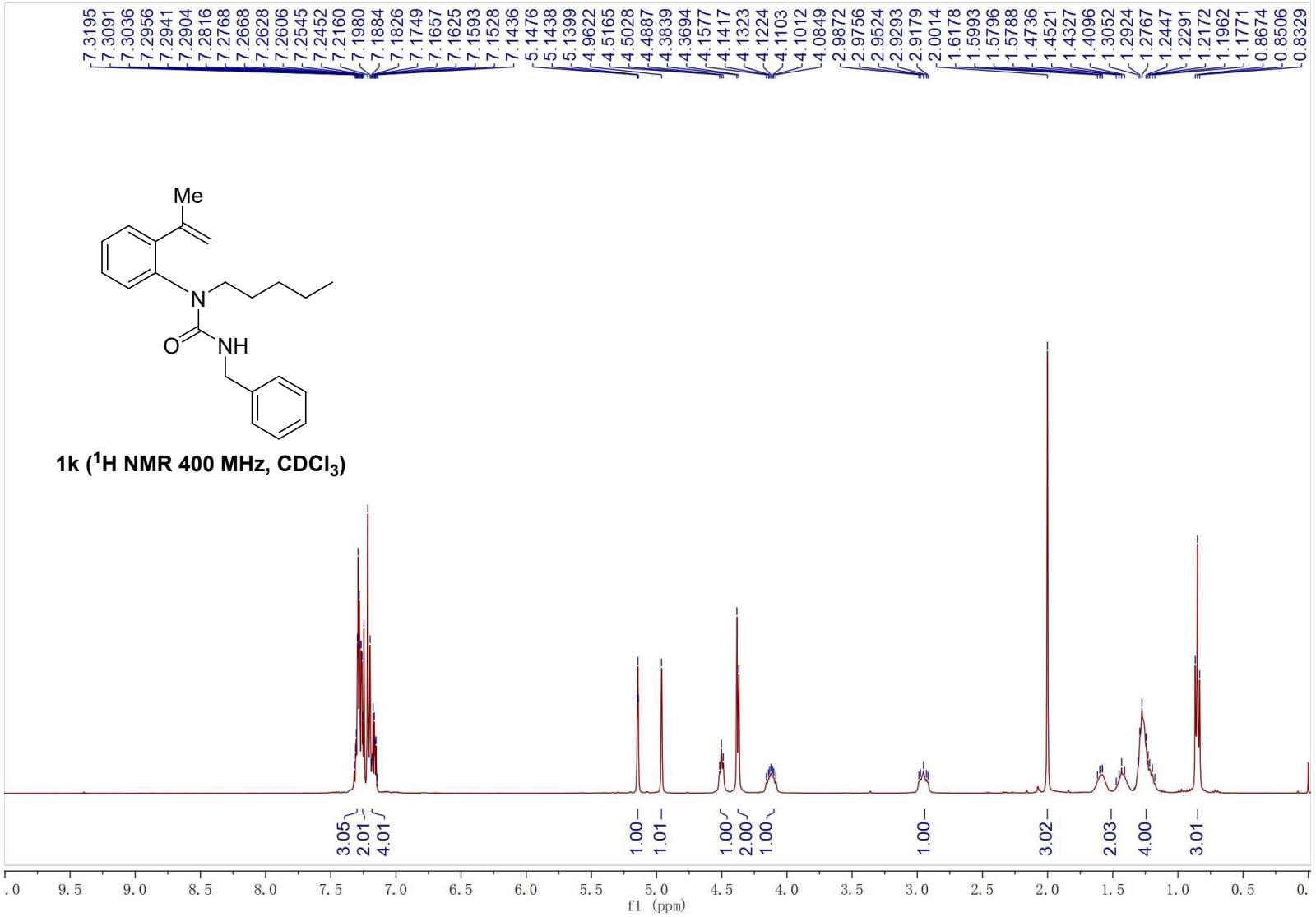
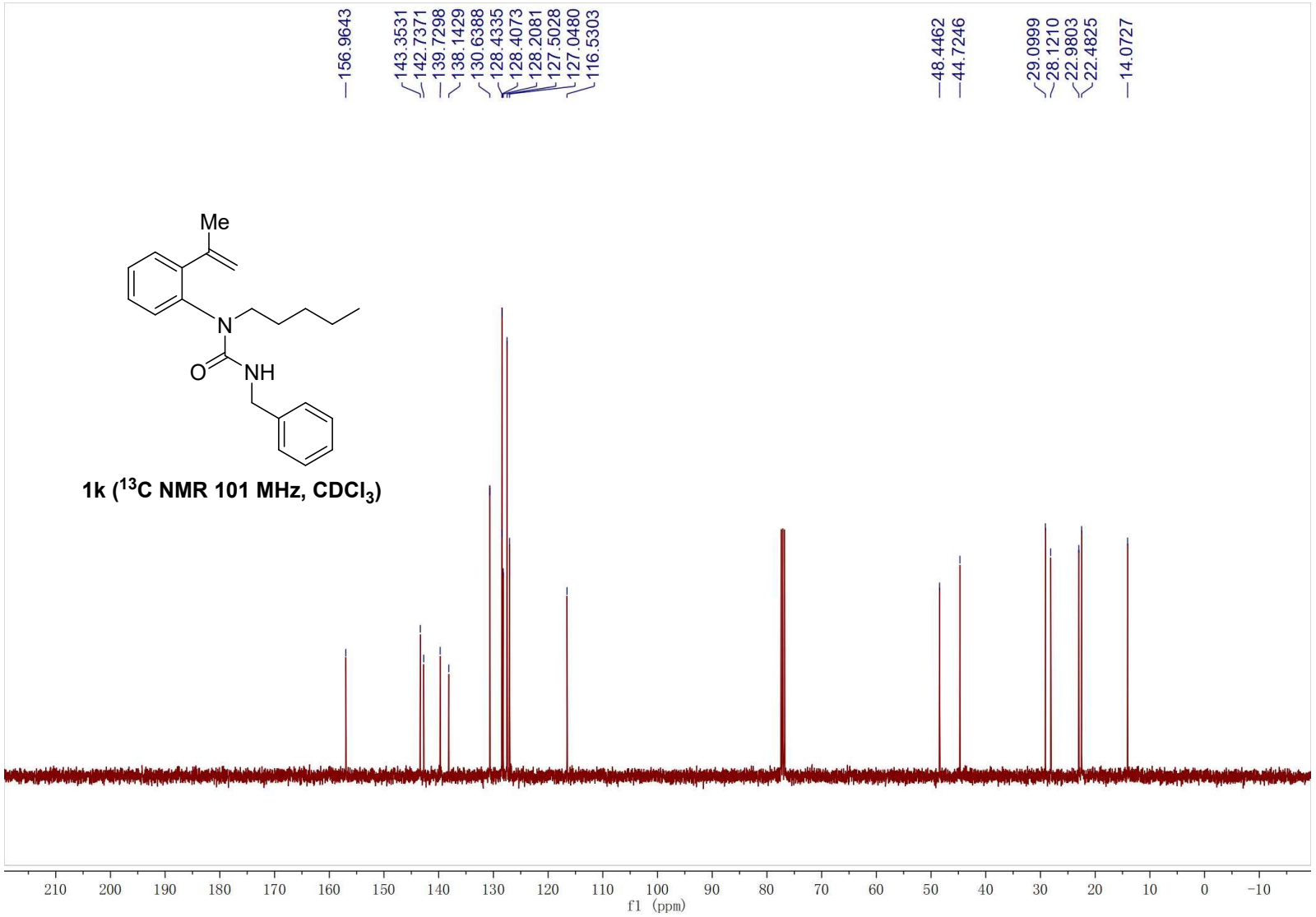
128.3230
128.1591
127.4890
127.0574
116.5814
54.9596
44.7594
27.4337
22.9433
20.4449
20.1596
Me
N
O
NH
1j (^{13}C NMR 101 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



1k (^{1}H NMR 400 MHz, $CDCl_3$)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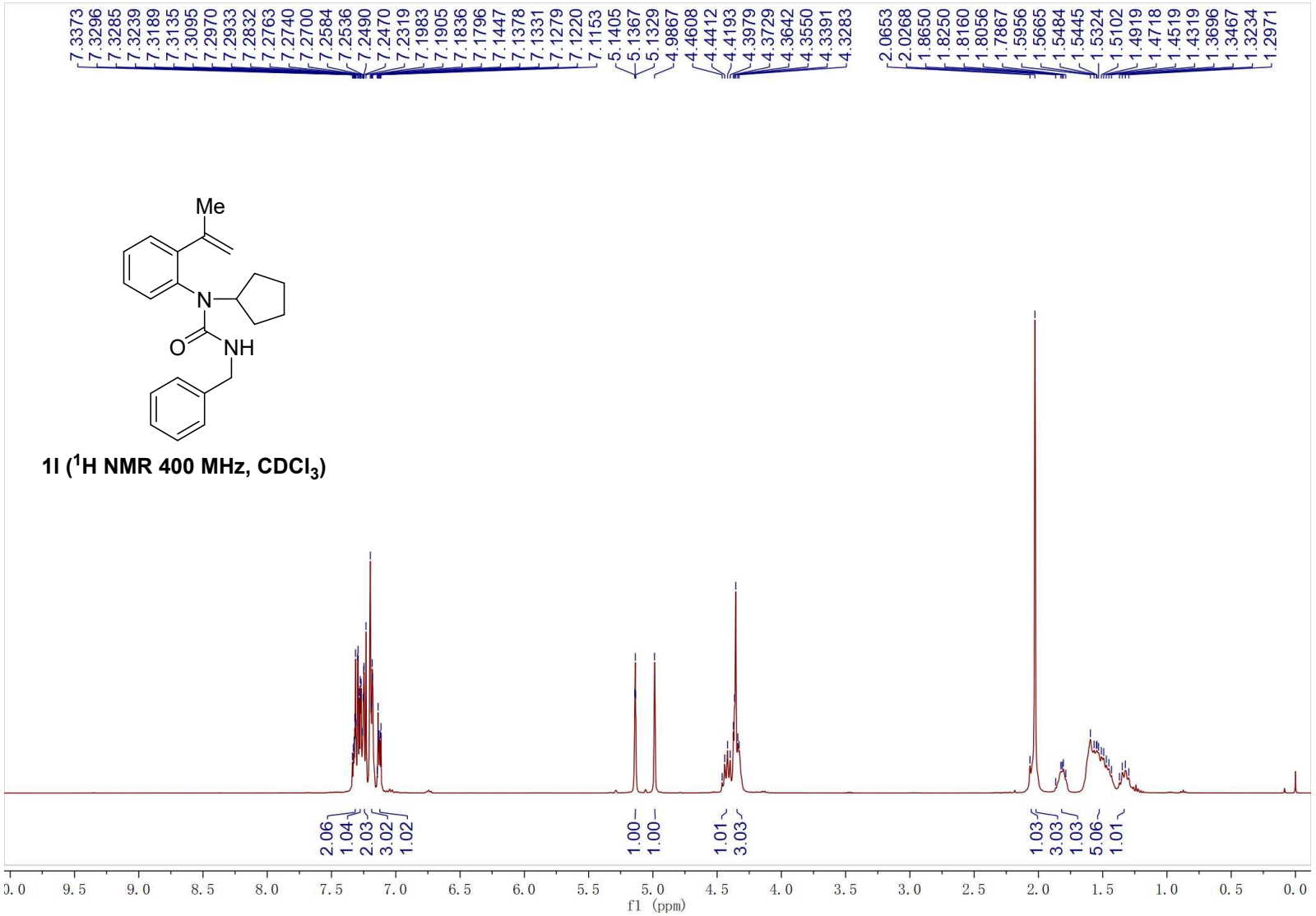
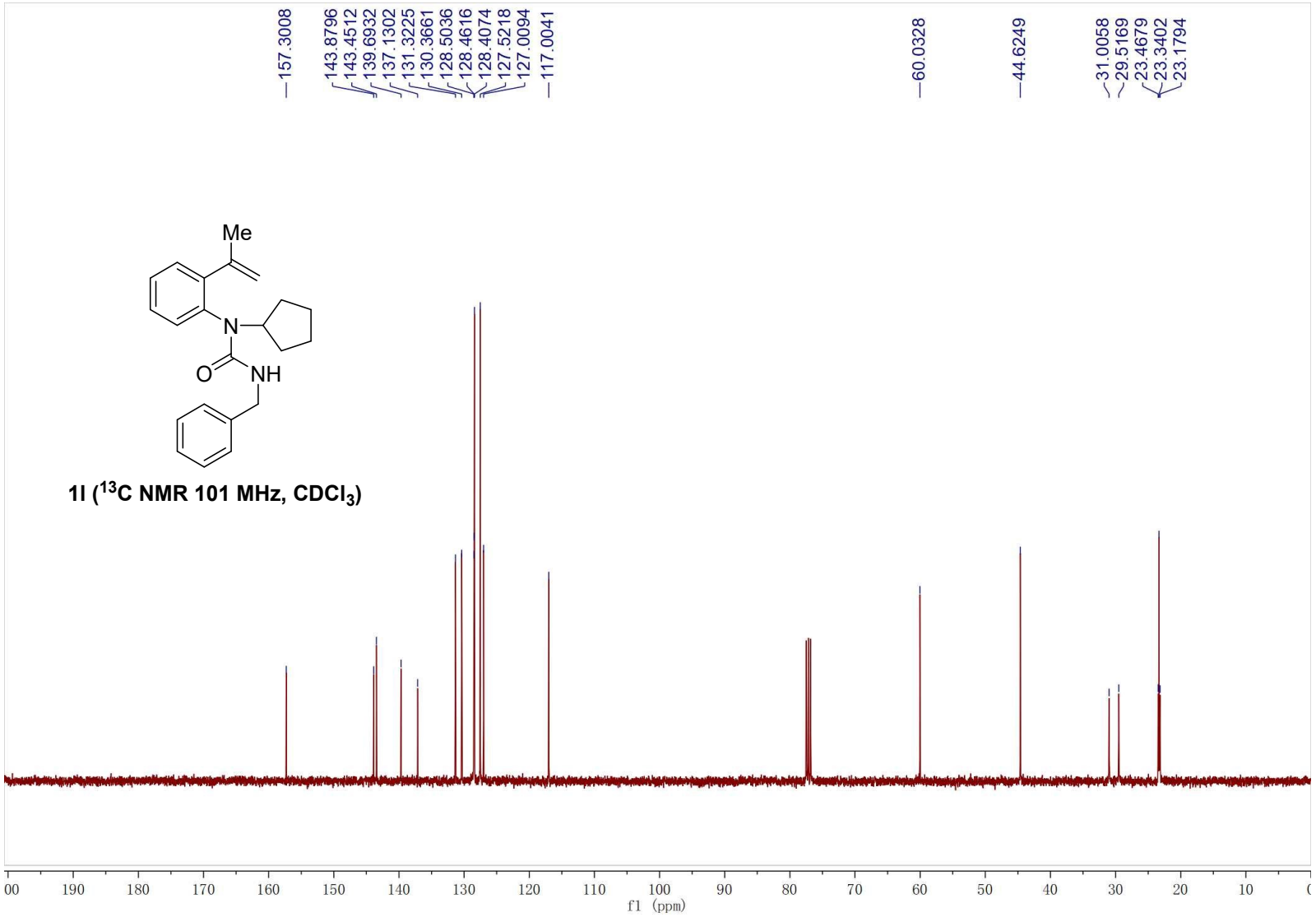
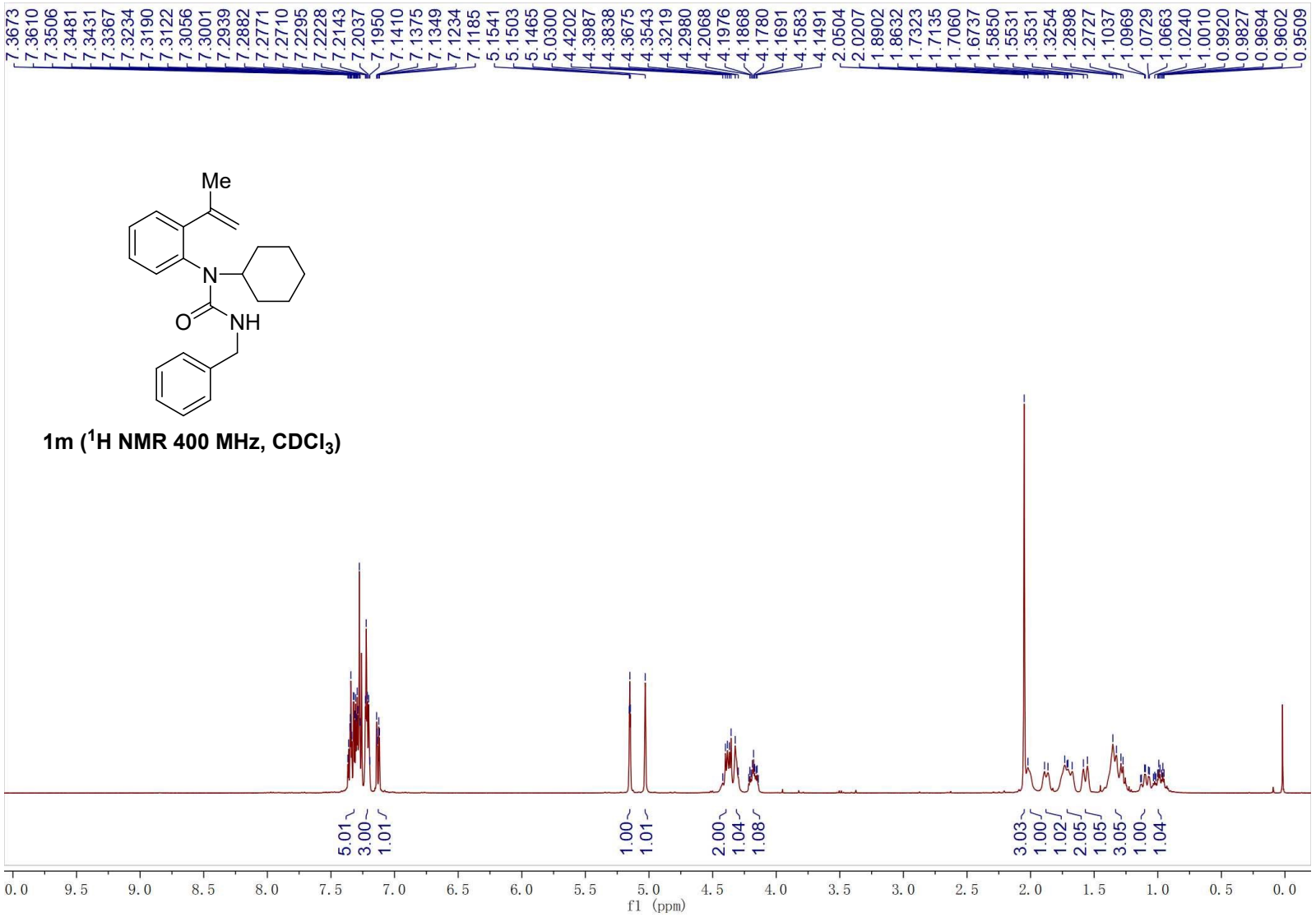
139.7298
138.1429
130.6388
128.4335
128.4073
128.2081
127.5028
127.0480
116.5303
48.4462
44.7246
29.0999
28.1210
22.9803
22.4825
14.0727
Me
N
O
NH
1k (^{13}C NMR 101 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

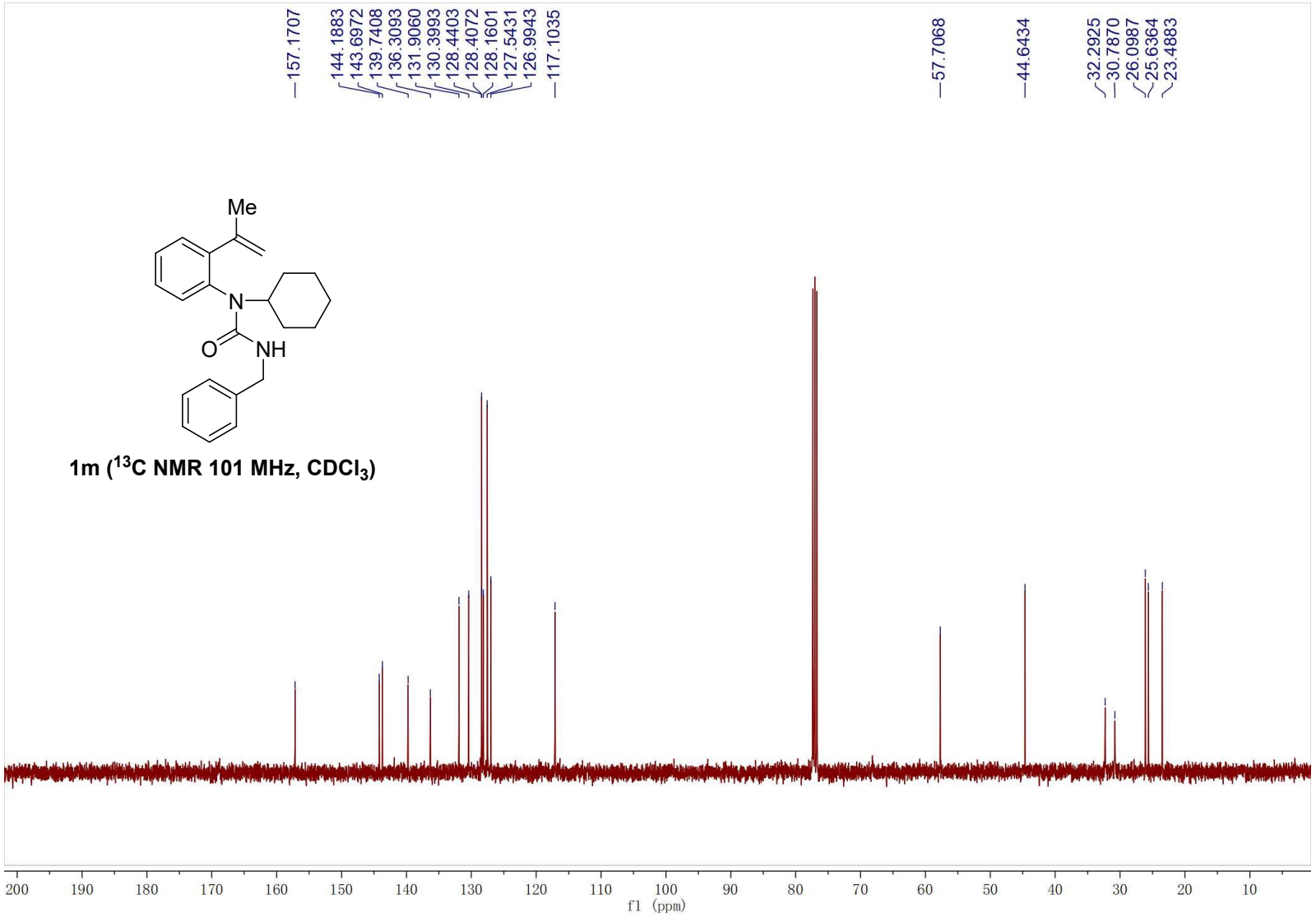


1l (^{1}H NMR 400 MHz, $CDCl_3$)

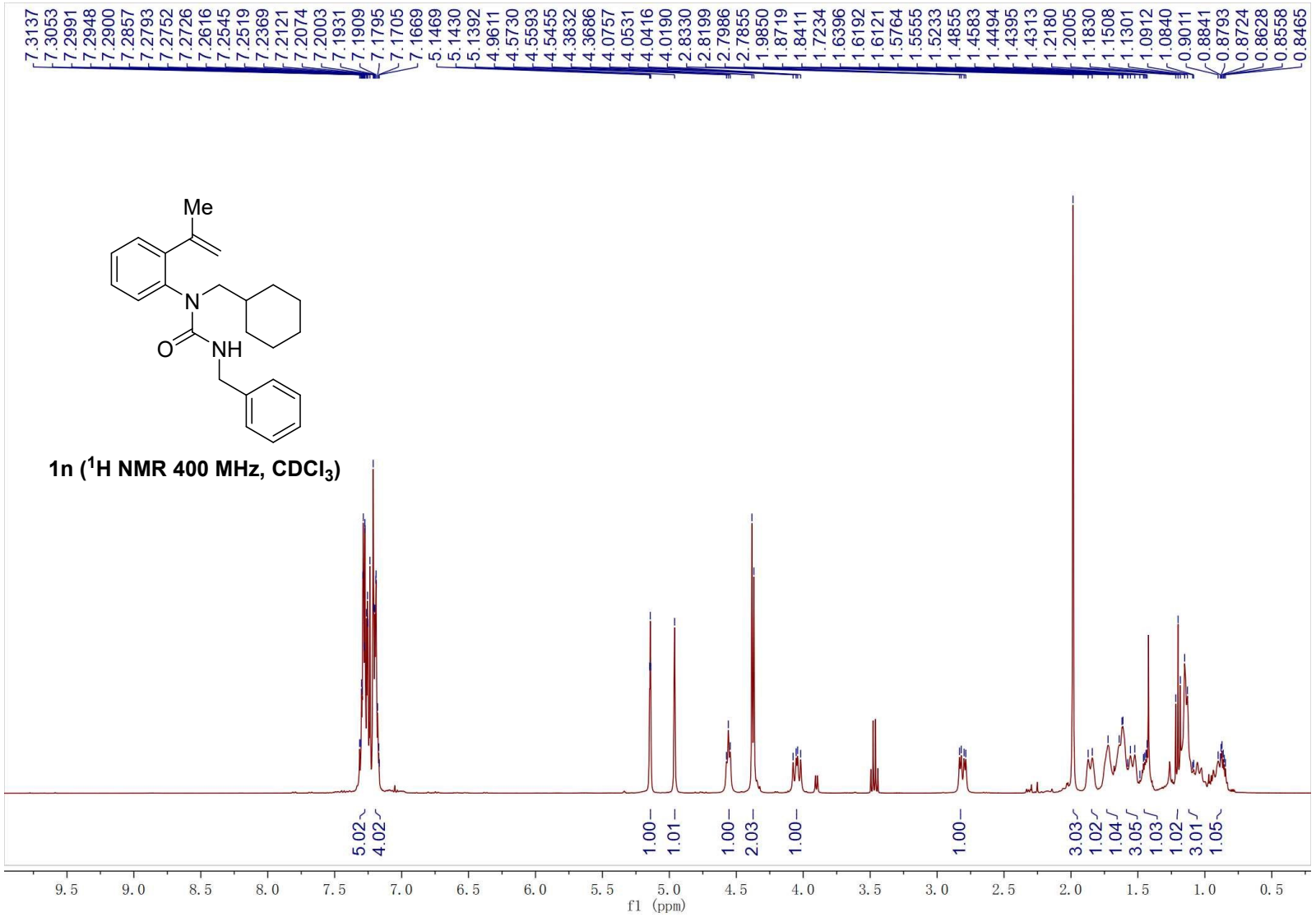


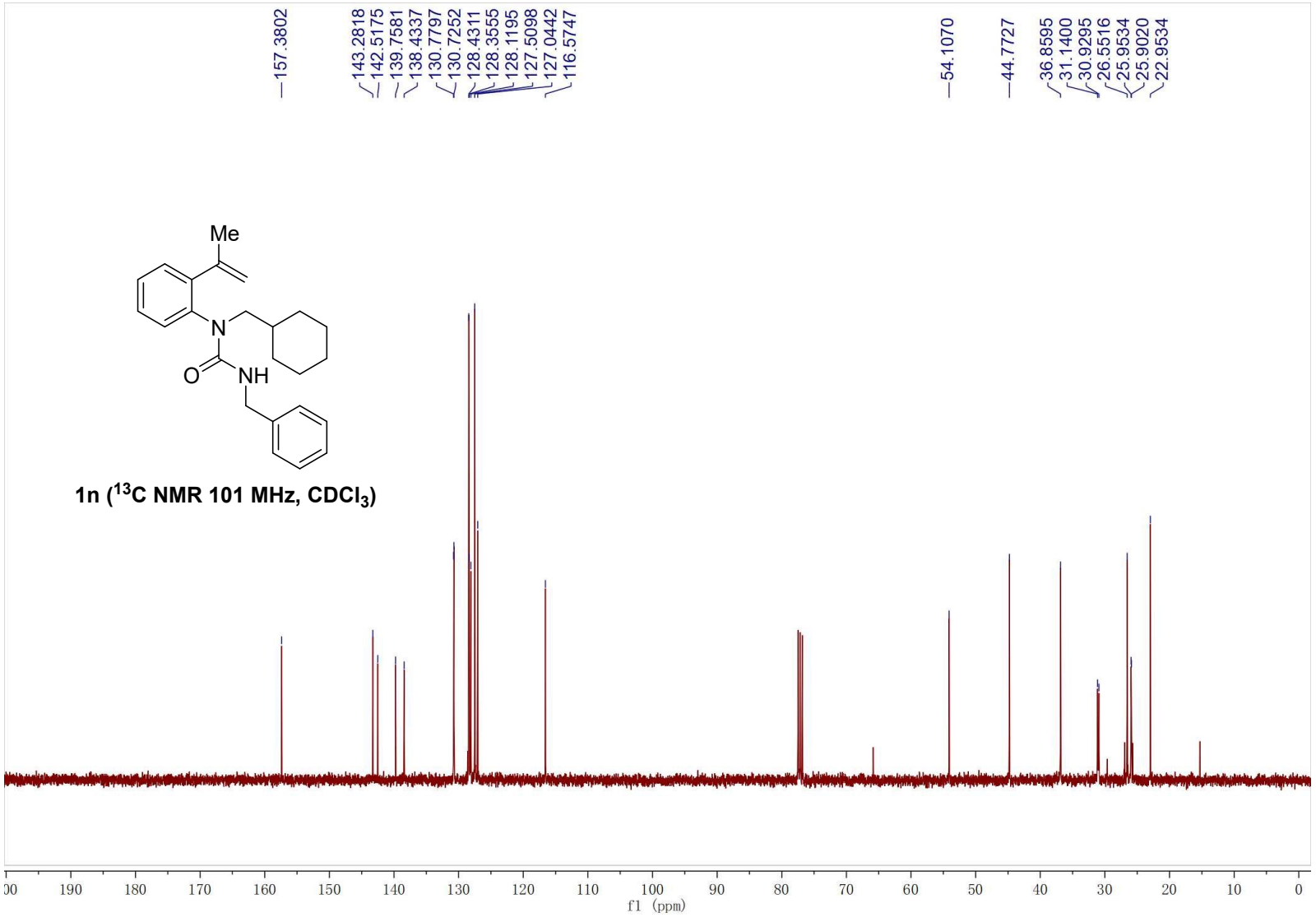
1l (^{13}C NMR 101 MHz, $CDCl_3$)

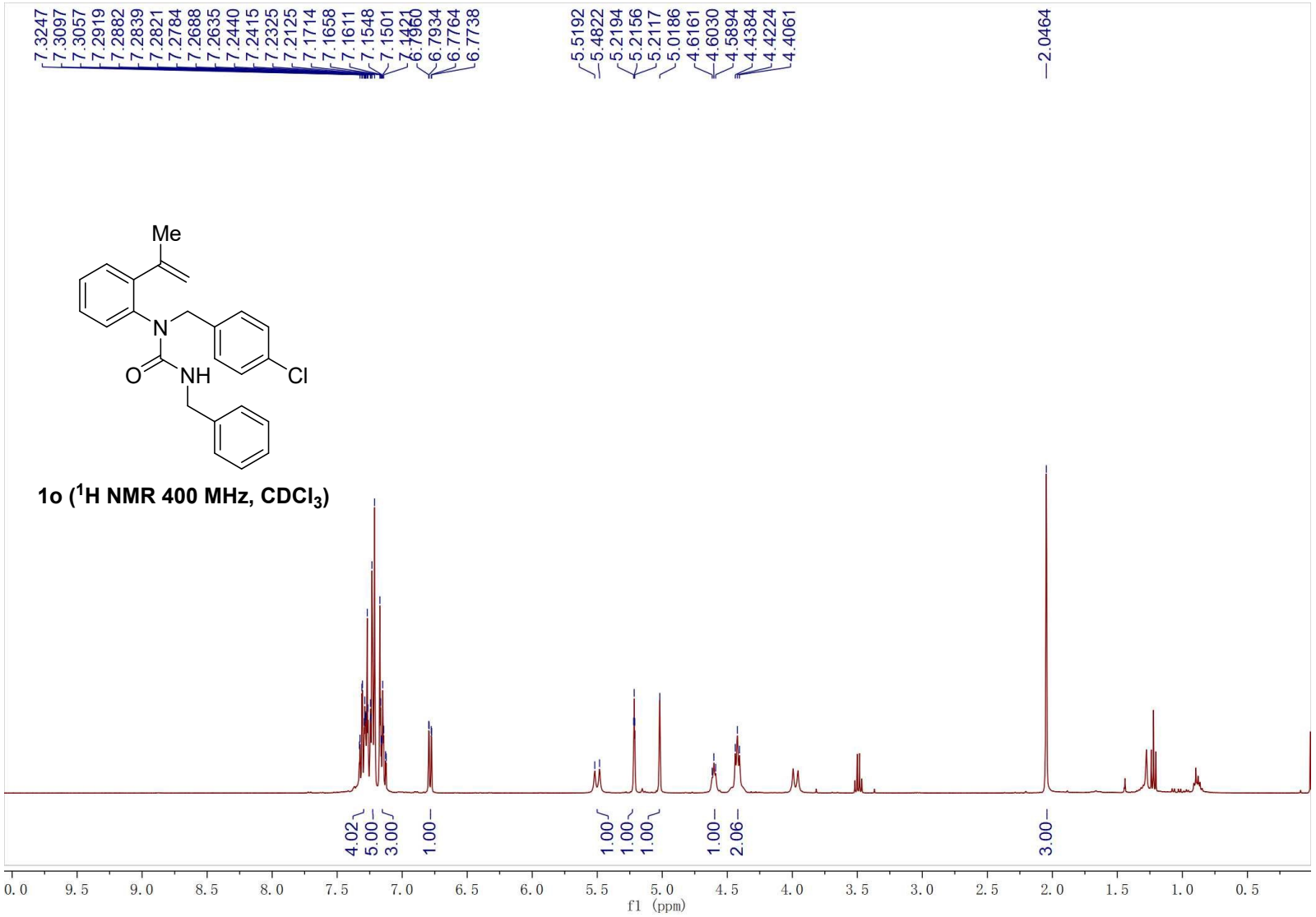

7.3673
7.3610
7.3506
7.3481
7.3431
7.3367
7.3234
7.3190
7.3122
7.3056
7.3001
7.2939
7.2882
7.2771
7.2710
7.2295
7.2228
7.2143
7.2037
7.1950
7.1410
7.1375
7.1349
7.1234
7.1185
5.1541
5.1503
5.1465
5.0300
4.4202
4.3987
4.3838
4.3675
4.3543
4.3219
4.2980
4.2068
4.1976
4.1868
4.1780
4.1691
4.1583
4.1491
2.0504
2.0207
1.8902
1.8632
1.7323
1.7135
1.7060
1.6737
1.5850
1.5531
1.3531
1.3254
1.2898
1.2727
1.1037
1.0969
1.0729
1.0663
1.0240
1.0010
0.9920
0.9827
0.9694
0.9602
0.9509
Me
N
O
NH
1m (1H NMR 400 MHz, CDCl3)
5.01
3.00
1.01
1.00
1.01
2.00
1.04
1.08
3.03
1.00
1.02
2.05
1.05
3.05
1.00
1.04
0.0
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)



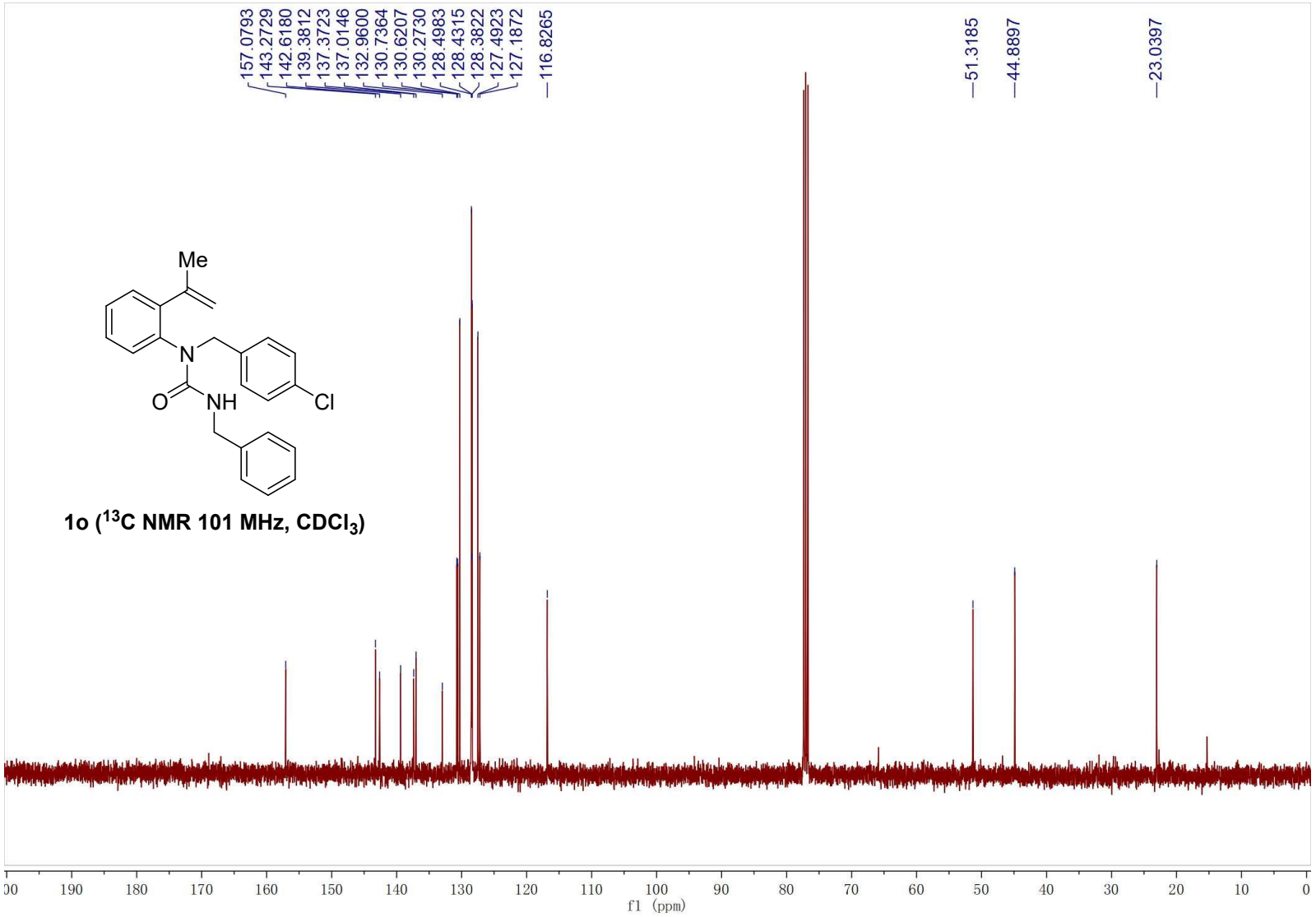
1m (^{13}C NMR 101 MHz, $CDCl_3$)

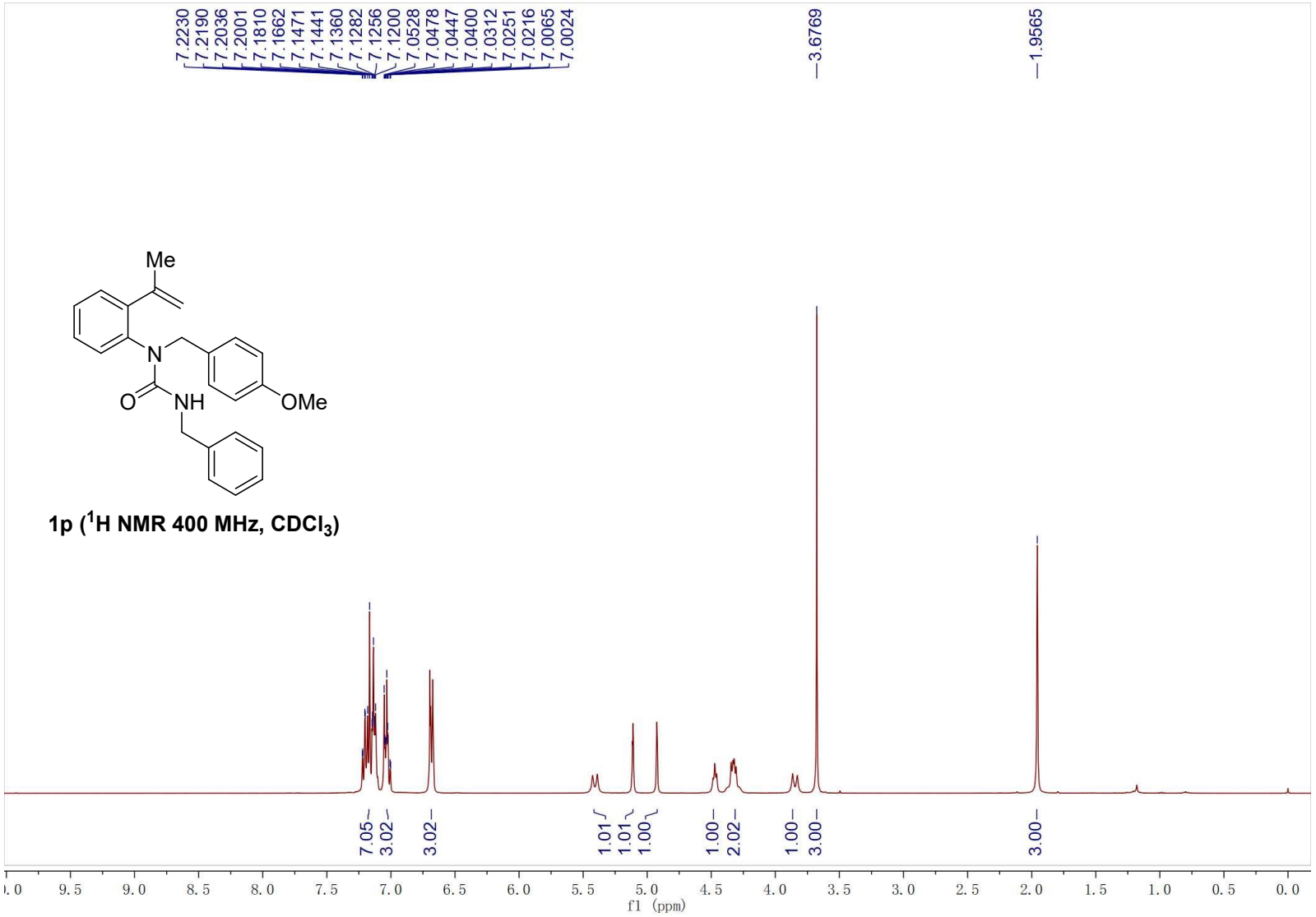

7.3137
7.3053
7.2991
7.2948
7.2900
7.2857
7.2793
7.2752
7.2726
7.2616
7.2545
7.2519
7.2369
7.2121
7.2074
7.2003
7.1931
7.1909
7.1795
7.1705
7.1669
5.1469
5.1430
5.1392
4.9611
4.5730
4.5593
4.5455
4.3832
4.3686
4.0757
4.0531
4.0416
4.0190
2.8330
2.8199
2.7986
2.7855
1.9850
1.8719
1.8411
1.7234
1.6396
1.6192
1.6121
1.5764
1.5555
1.5233
1.4855
1.4583
1.4494
1.4395
1.4313
1.2180
1.2005
1.1830
1.1508
1.1301
1.0912
1.0840
0.9011
0.8841
0.8793
0.8724
0.8628
0.8558
0.8465
Me
N
O
NH
1n (1H NMR 400 MHz, CDCl3)
5.02
4.02
1.00
1.01
1.00
2.03
1.00
1.00
3.03
1.02
1.04
3.05
1.03
1.02
3.01
1.05
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
f1 (ppm)


157.3802
143.2818
142.5175
139.7581
138.4337
130.7797
130.7252
128.4311
128.3555
128.1195
127.5098
127.0442
116.5747
54.1070
44.7727
36.8595
31.1400
30.9295
26.5516
25.9534
25.9020
22.9534
Me
N
O
NH
1n (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

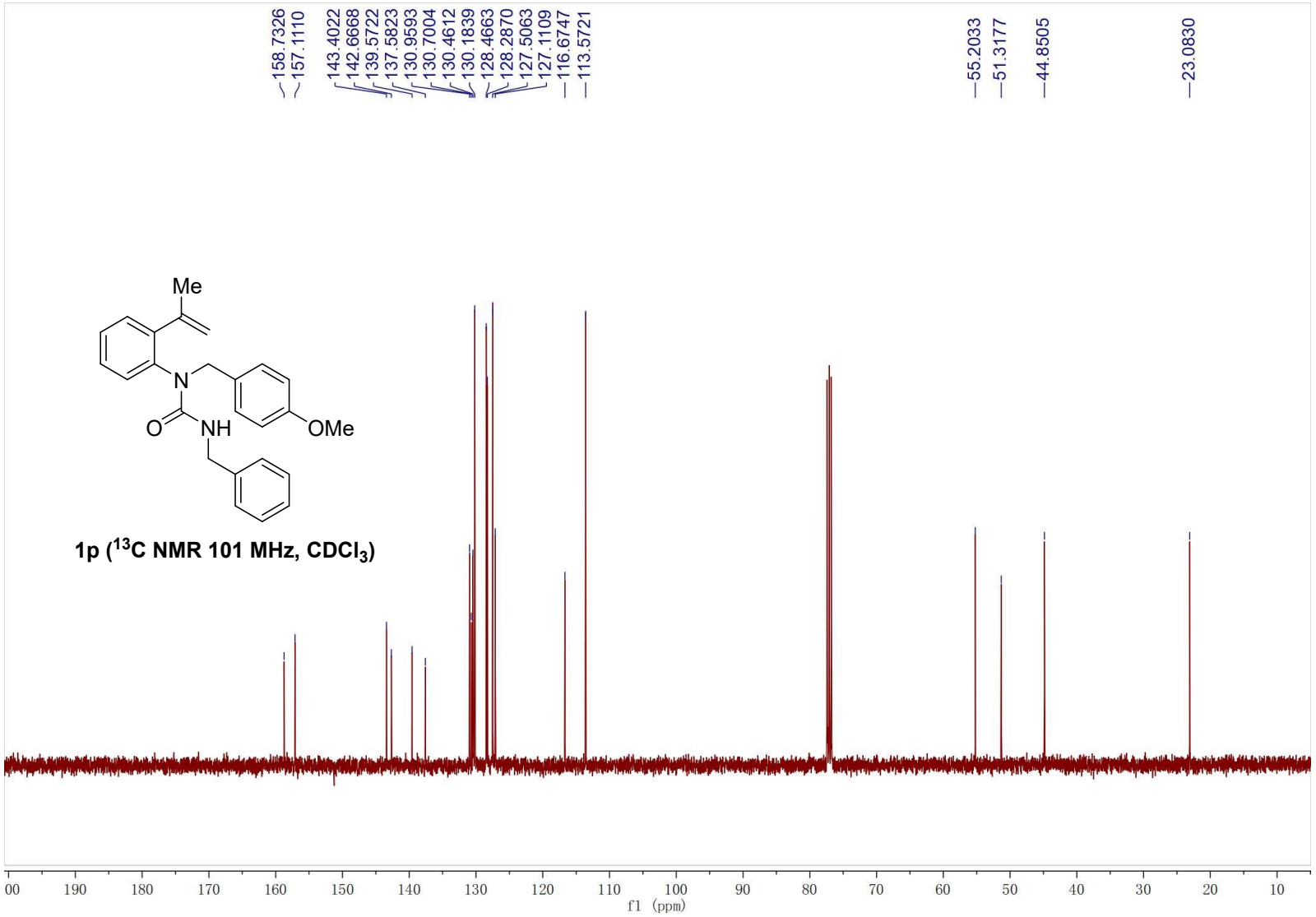


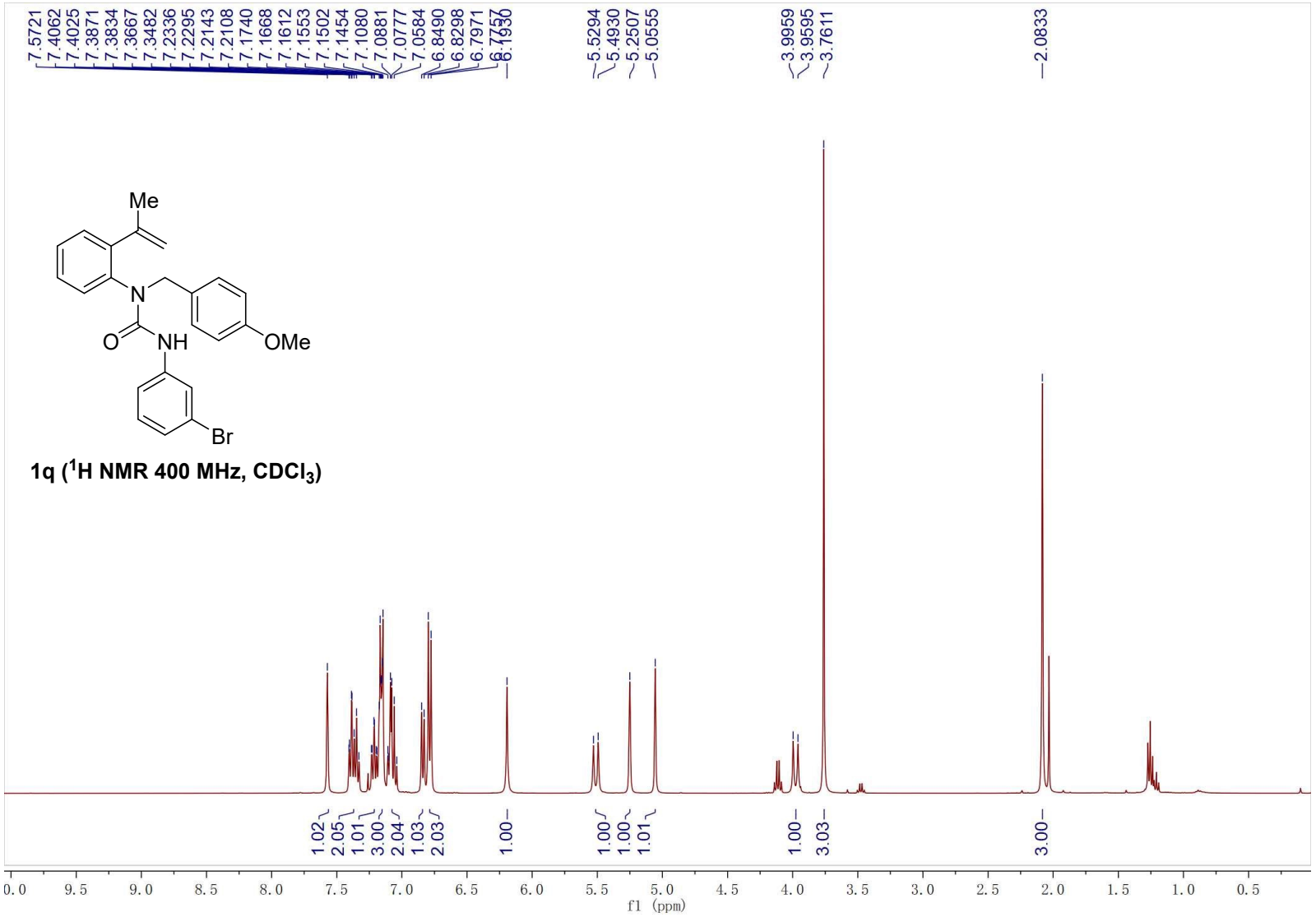
1o (^{1}H NMR 400 MHz, $CDCl_3$)


157.0793
143.2729
142.6180
139.3812
137.3723
137.0146
132.9600
130.7364
130.6207
130.2730
128.4983
128.4315
128.3822
127.4923
127.1872
116.8265
51.3185
44.8897
23.0397
Me
N
O
NH
Cl
1o (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

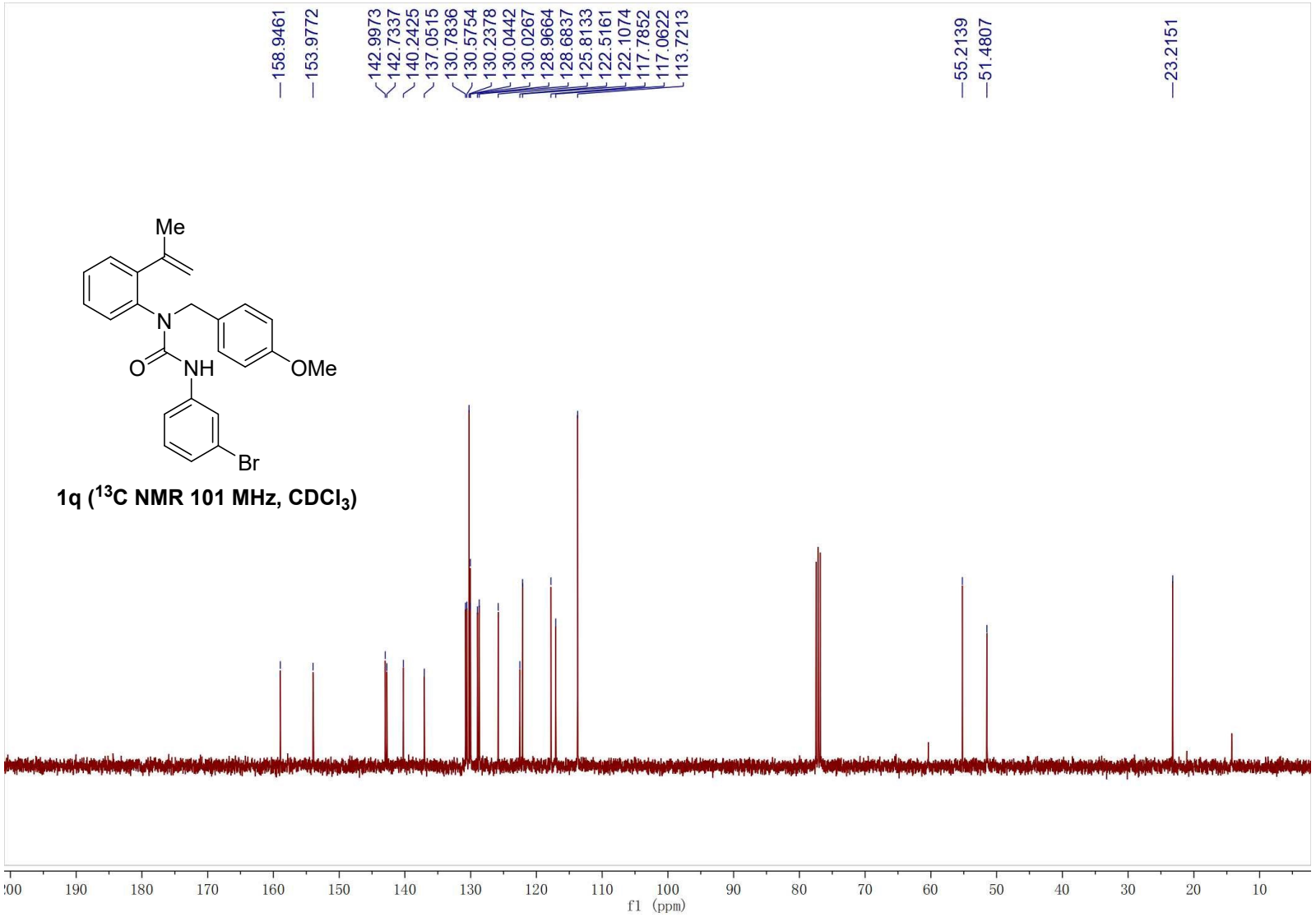


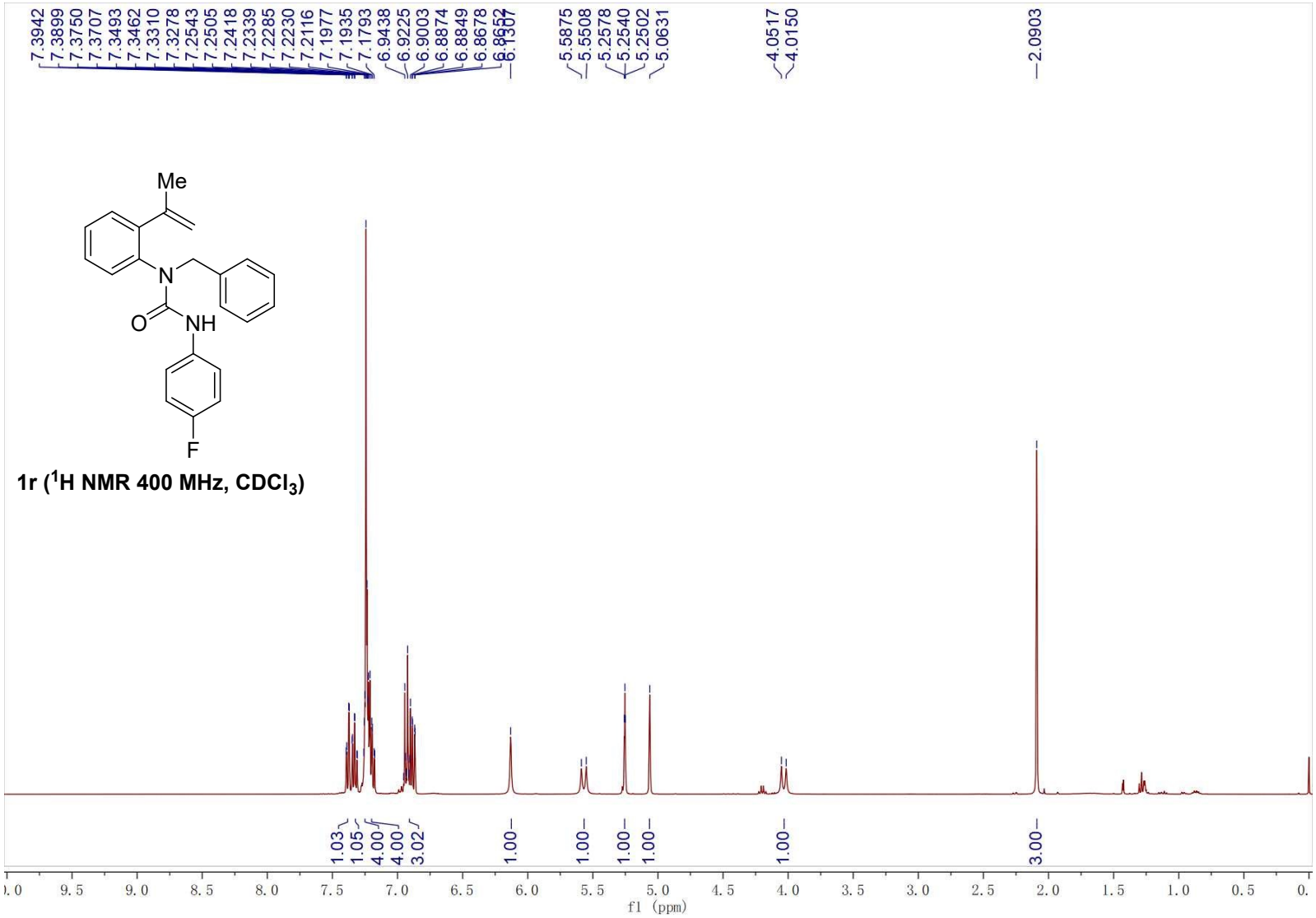
1p (^{1}H NMR 400 MHz, $CDCl_3$)


158.7326
157.1110
143.4022
142.6668
139.5722
137.5823
130.9593
130.7004
130.4612
130.1839
128.4663
128.2870
127.5063
127.1109
116.6747
113.5721
55.2033
51.3177
44.8505
23.0830
Me
N
O
NH
OMe
1p (13C NMR 101 MHz, CDCl3)
f1 (ppm)

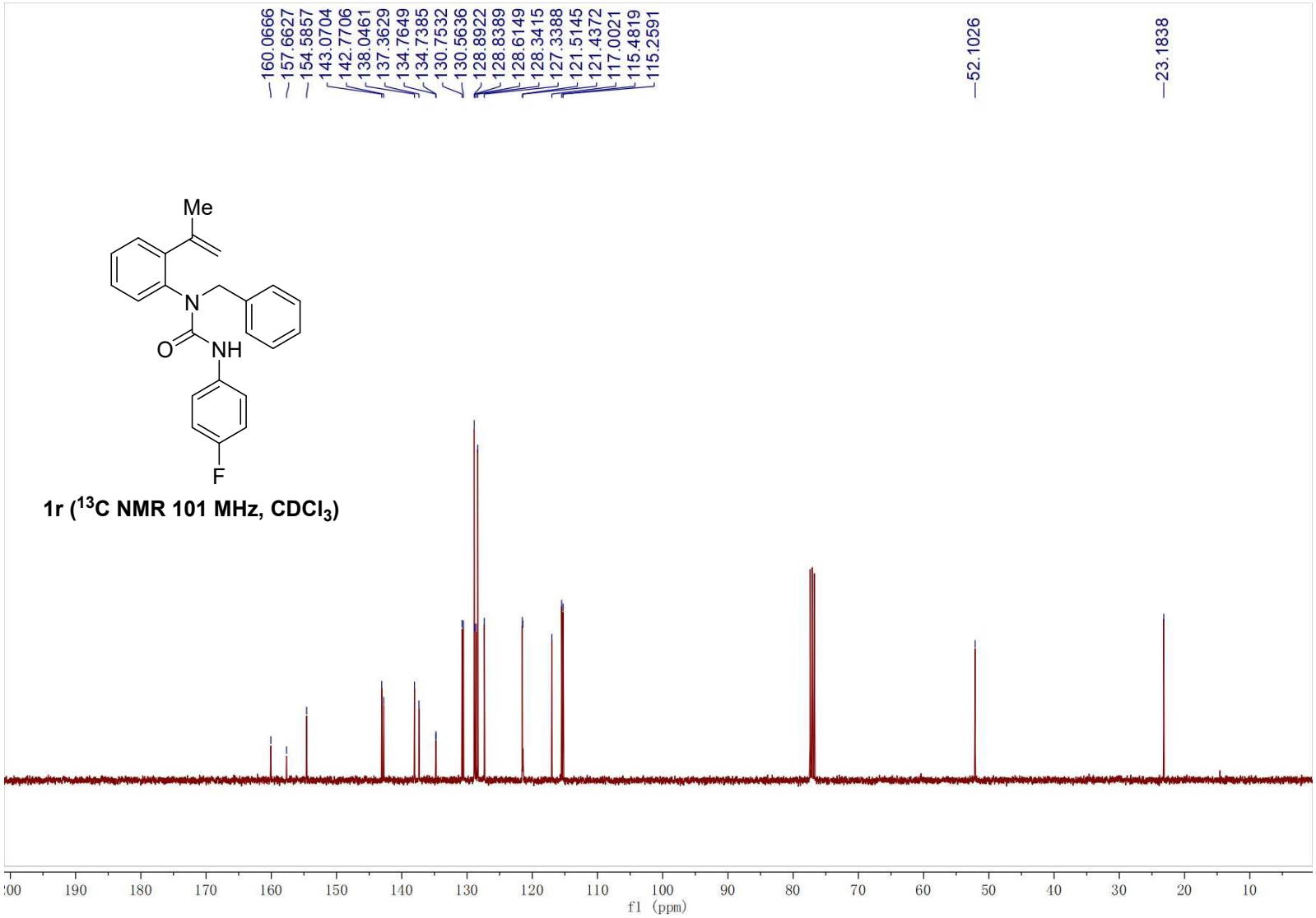


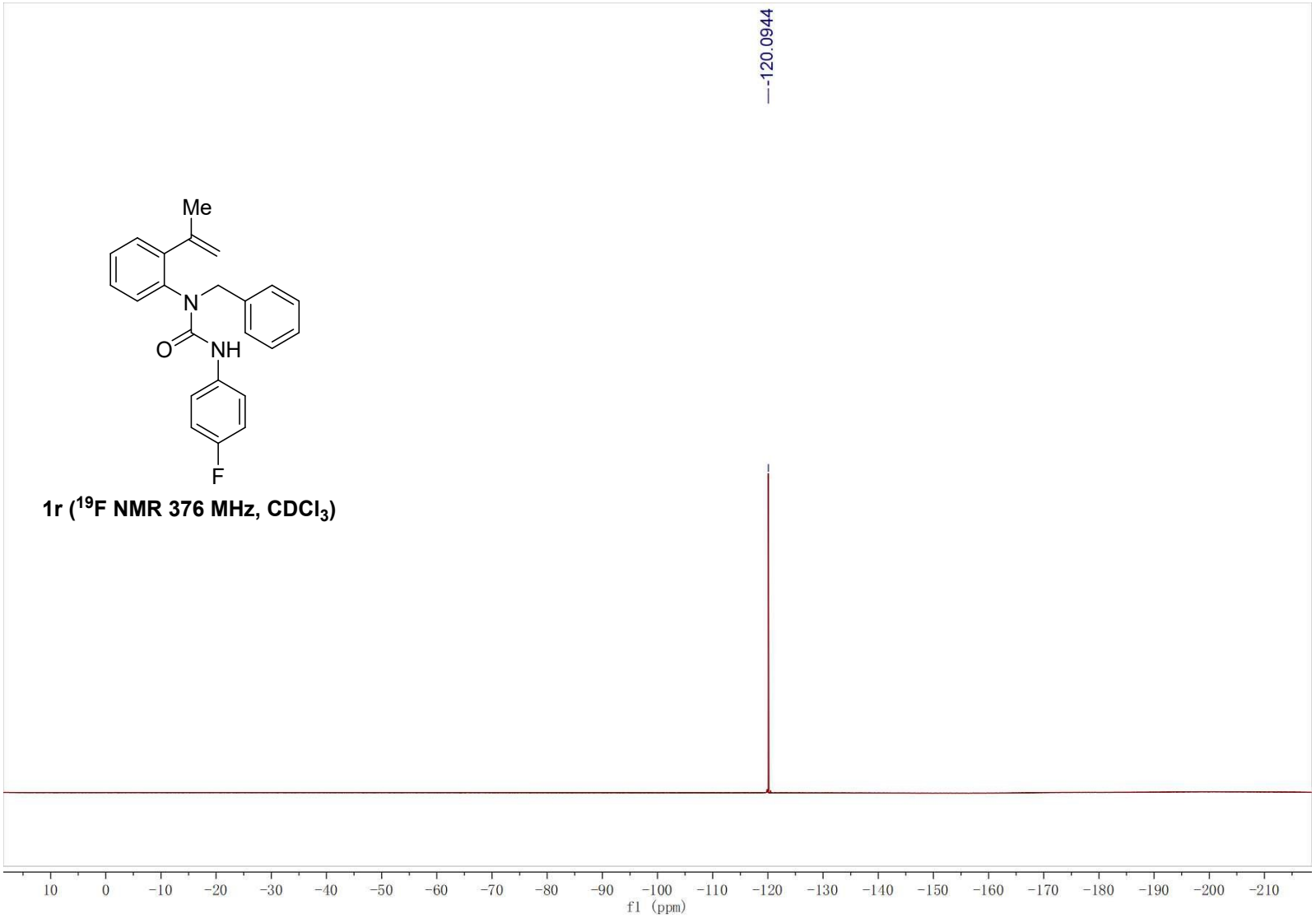
1q (^{1}H NMR 400 MHz, $CDCl_3$)


158.9461
153.9772
142.9973
142.7337
140.2425
137.0515
130.7836
130.5754
130.2378
130.0442
130.0267
128.9664
128.6837
125.8133
122.5161
122.1074
117.7852
117.0622
113.7213
55.2139
51.4807
23.2151
Me
N
O
NH
OMe
Br
1q (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

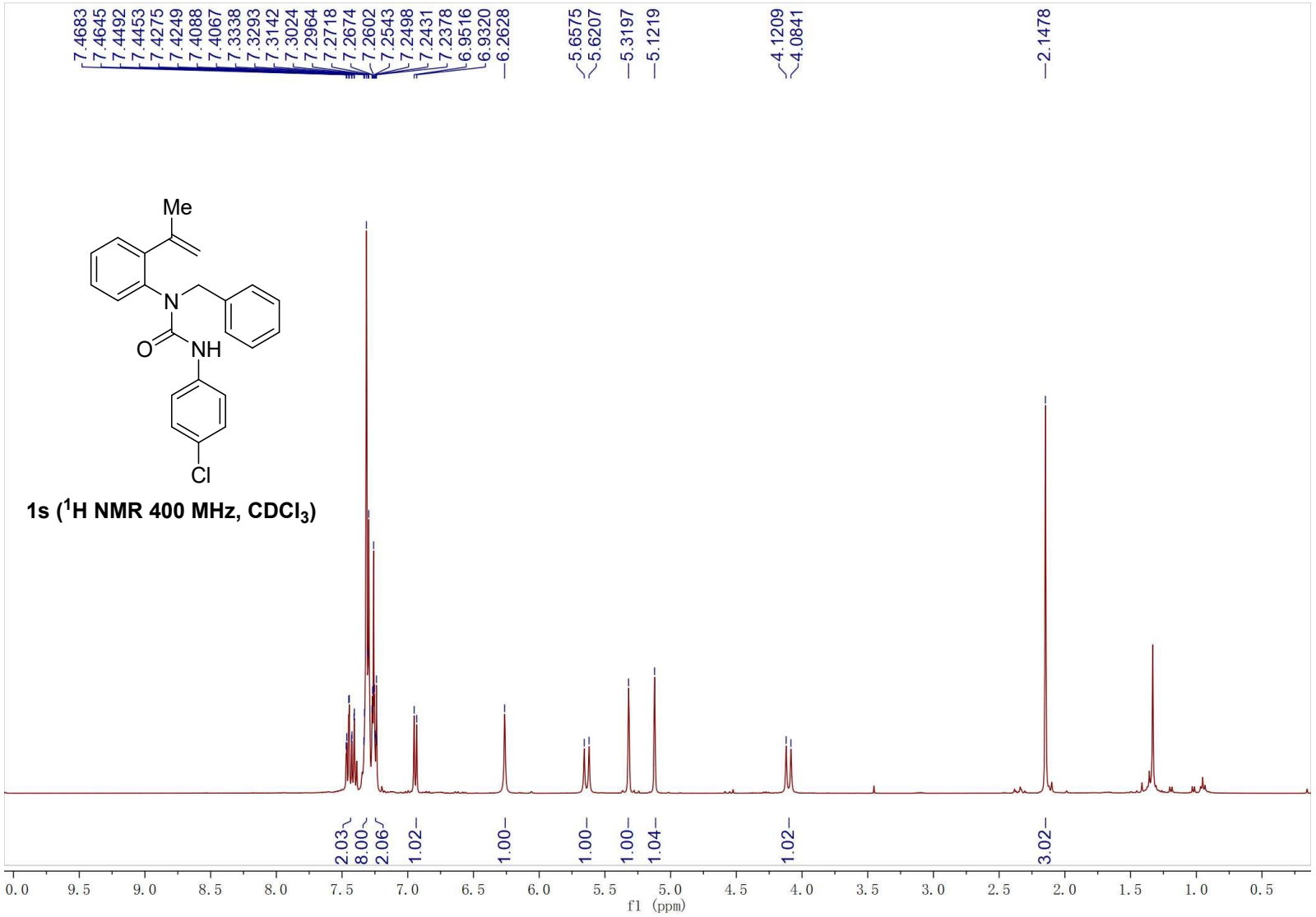


1r (^{1}H NMR 400 MHz, $CDCl_3$)

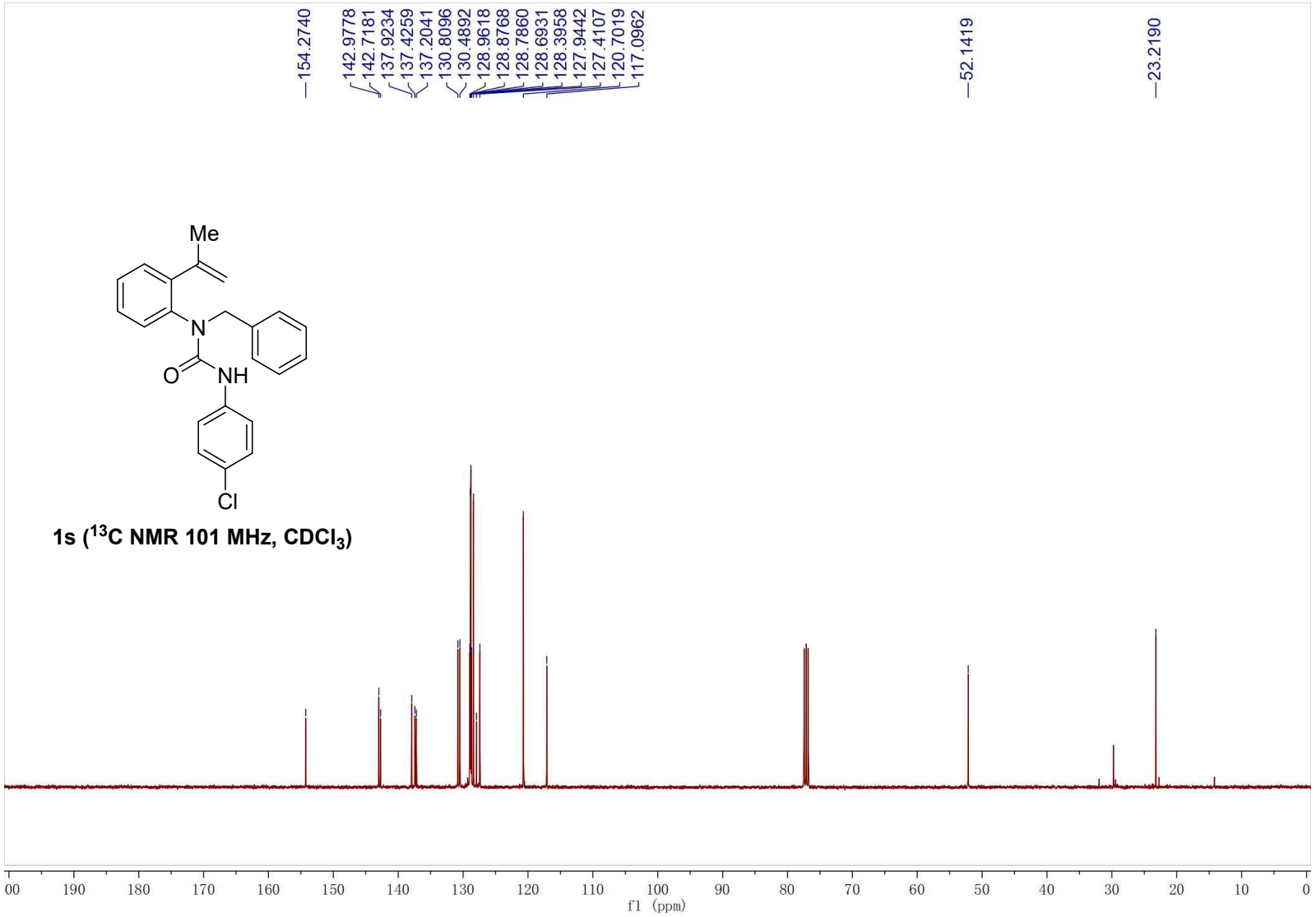

160.0666
157.6627
154.5857
143.0704
142.7706
138.0461
137.3629
134.7649
134.7385
130.7532
130.5636
128.8922
128.8389
128.6149
128.3415
127.3388
121.5145
121.4372
117.0021
115.4819
115.2591
52.1026
23.1838
Me
N
O
NH
F
1r (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

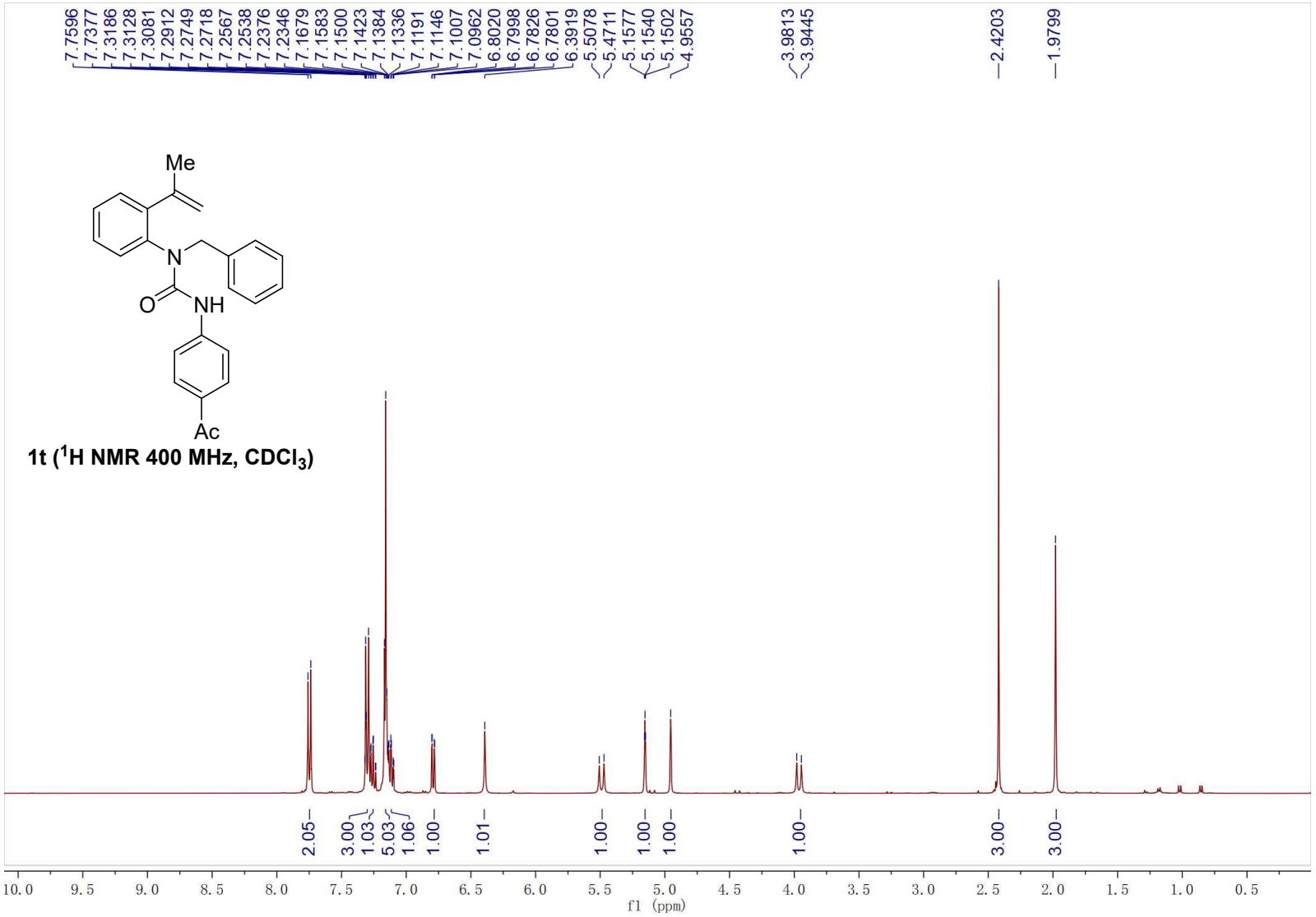


1r (^{19}F NMR 376 MHz, $CDCl_3$)

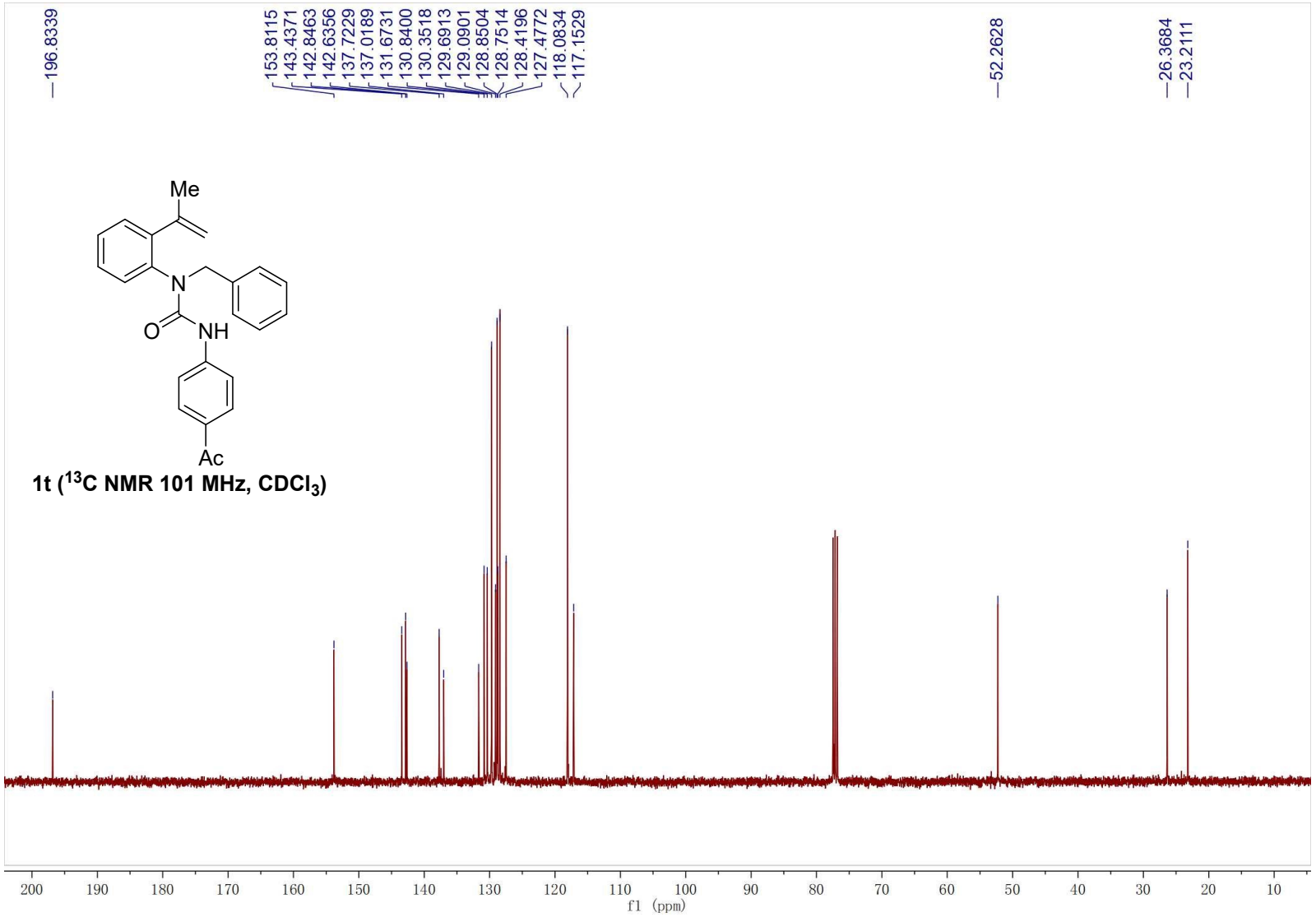


1s (^{1}H NMR 400 MHz, $CDCl_3$)

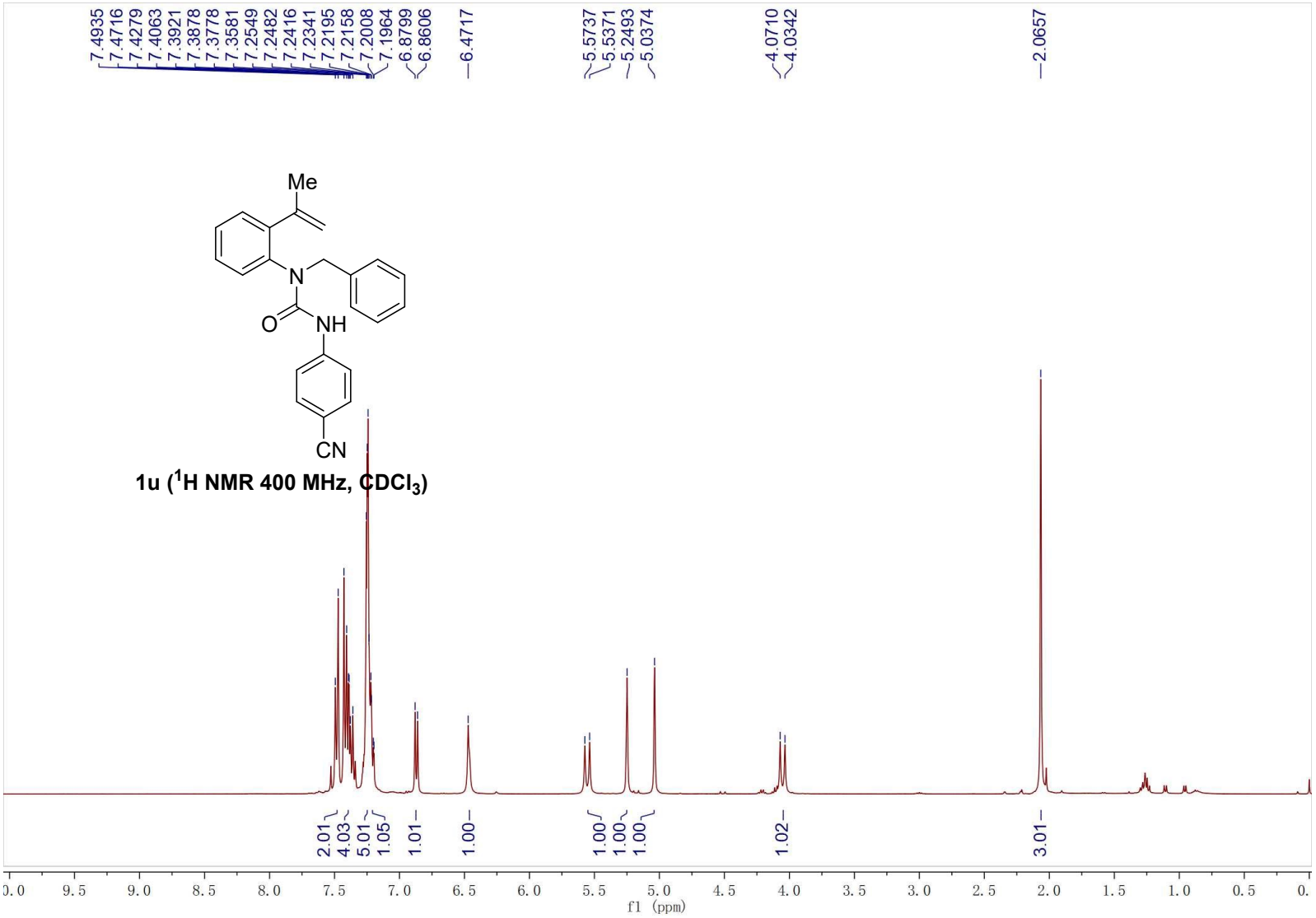

154.2740
142.9778
142.7181
137.9234
137.4259
137.2041
130.8096
130.4892
128.9618
128.8768
128.7860
128.6931
128.3958
127.9442
127.4107
120.7019
117.0962
52.1419
23.2190
Me
N
O
NH
Cl
1s (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

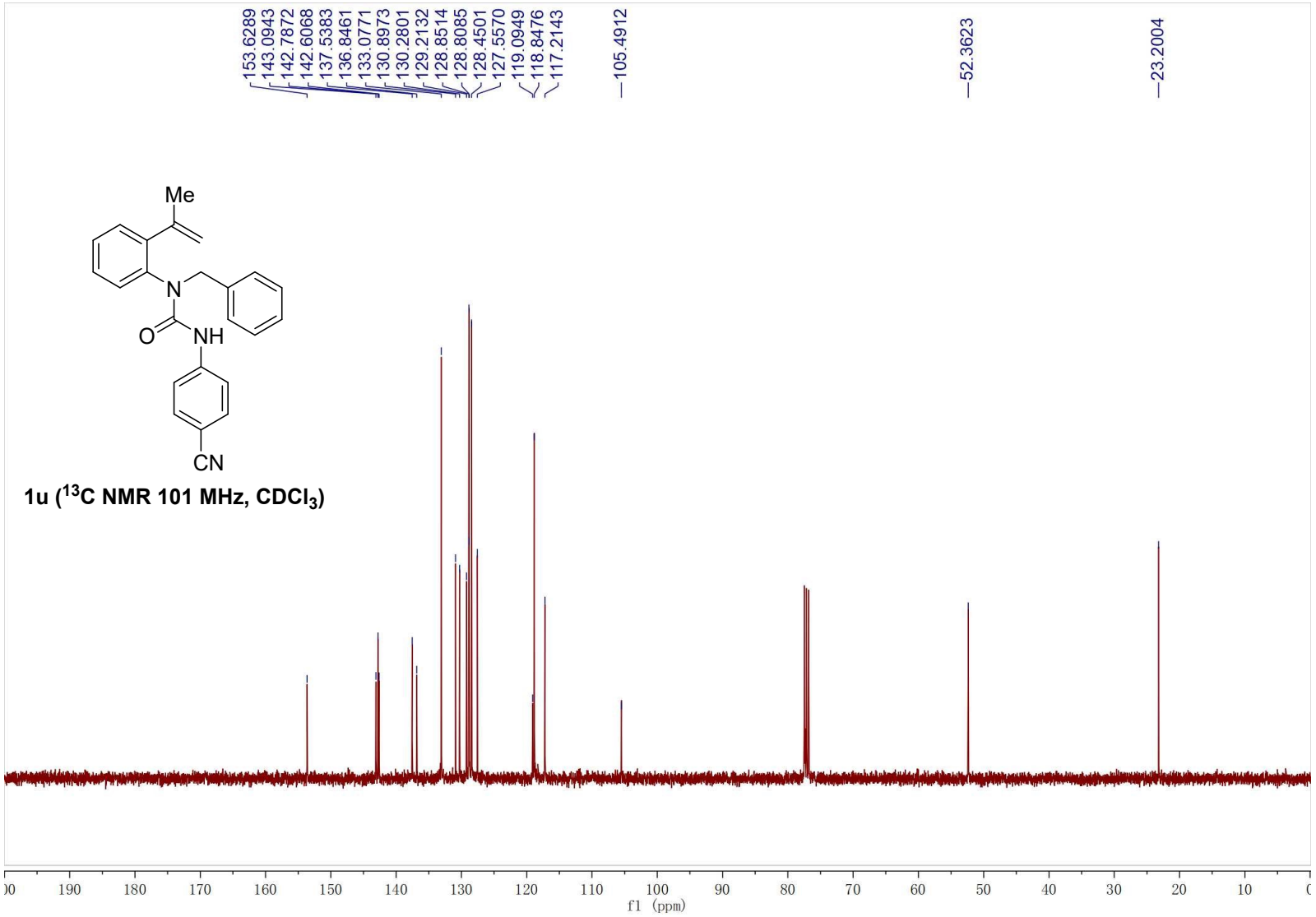


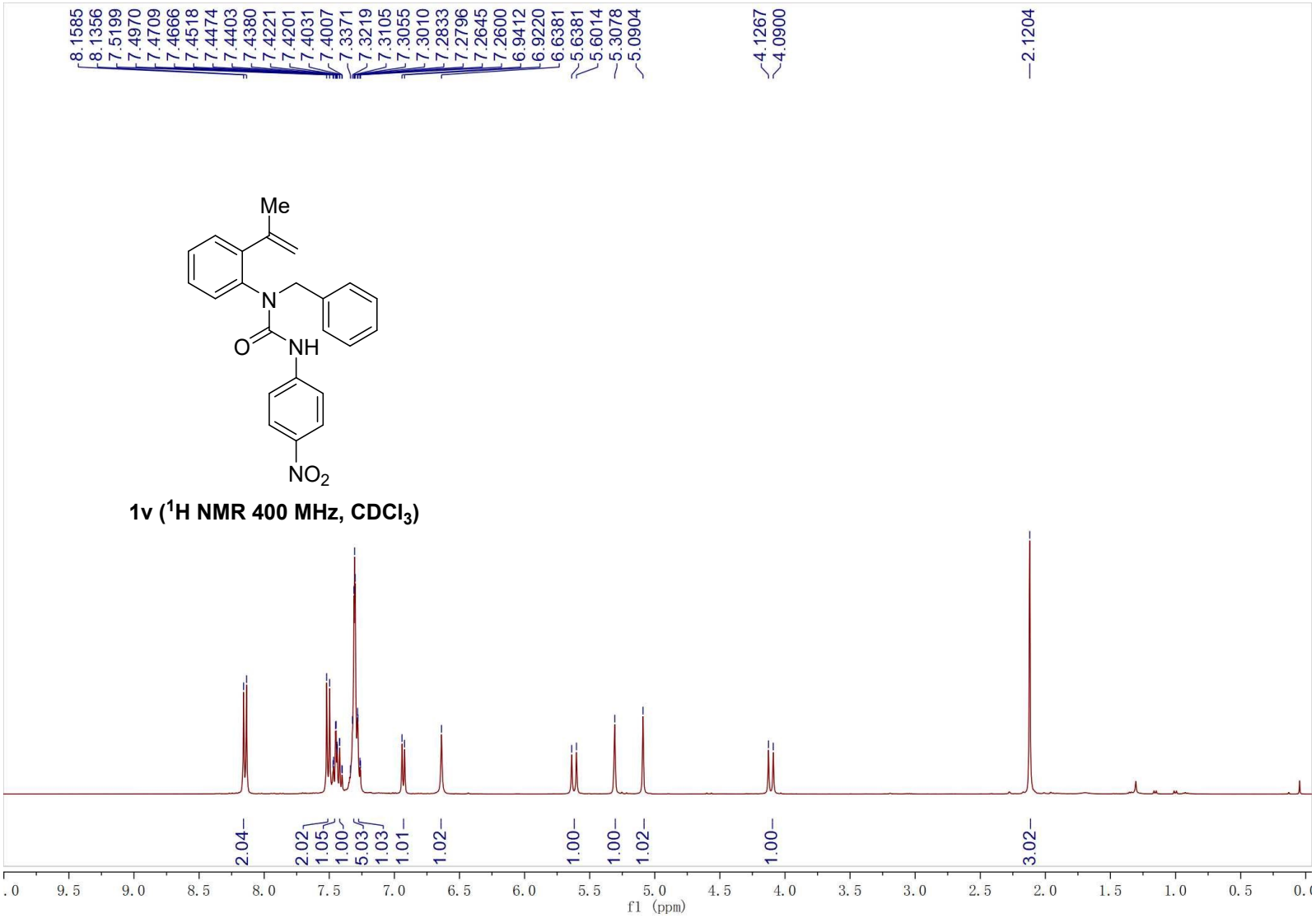
1t (^{1}H NMR 400 MHz, $CDCl_3$)



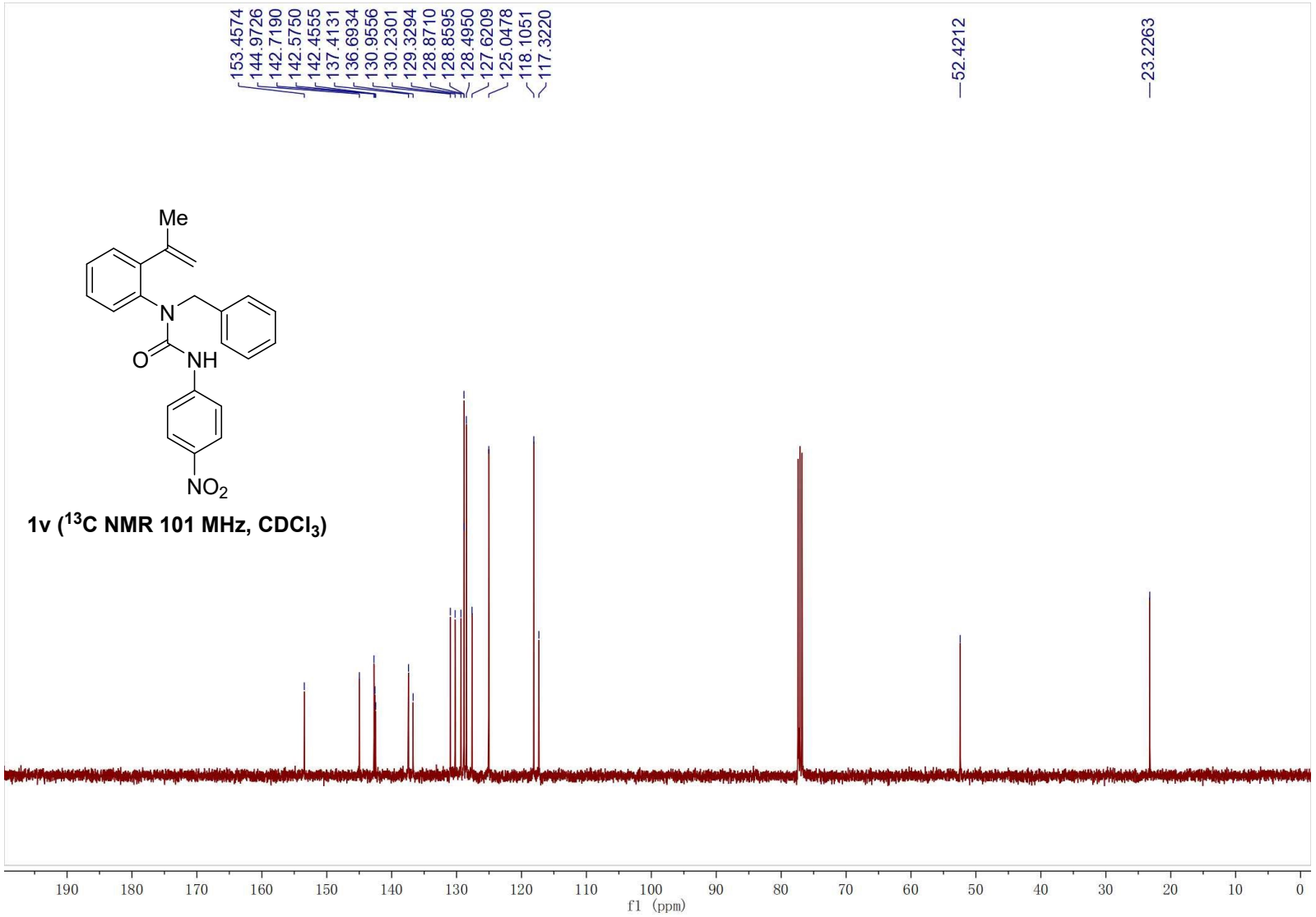
1t (^{13}C NMR 101 MHz, $CDCl_3$)


7.4935
7.4716
7.4279
7.4063
7.3921
7.3878
7.3778
7.3581
7.2549
7.2482
7.2416
7.2341
7.2195
7.2158
7.2008
7.1964
6.8799
6.8606
6.4717
5.5737
5.5371
5.2493
5.0374
4.0710
4.0342
2.0657
Me
N
O
NH
CN
1u (1H NMR 400 MHz, CDCl3)
2.01
4.03
5.01
1.05
1.01
1.00
1.00
1.00
1.00
1.02
3.01
f1 (ppm)

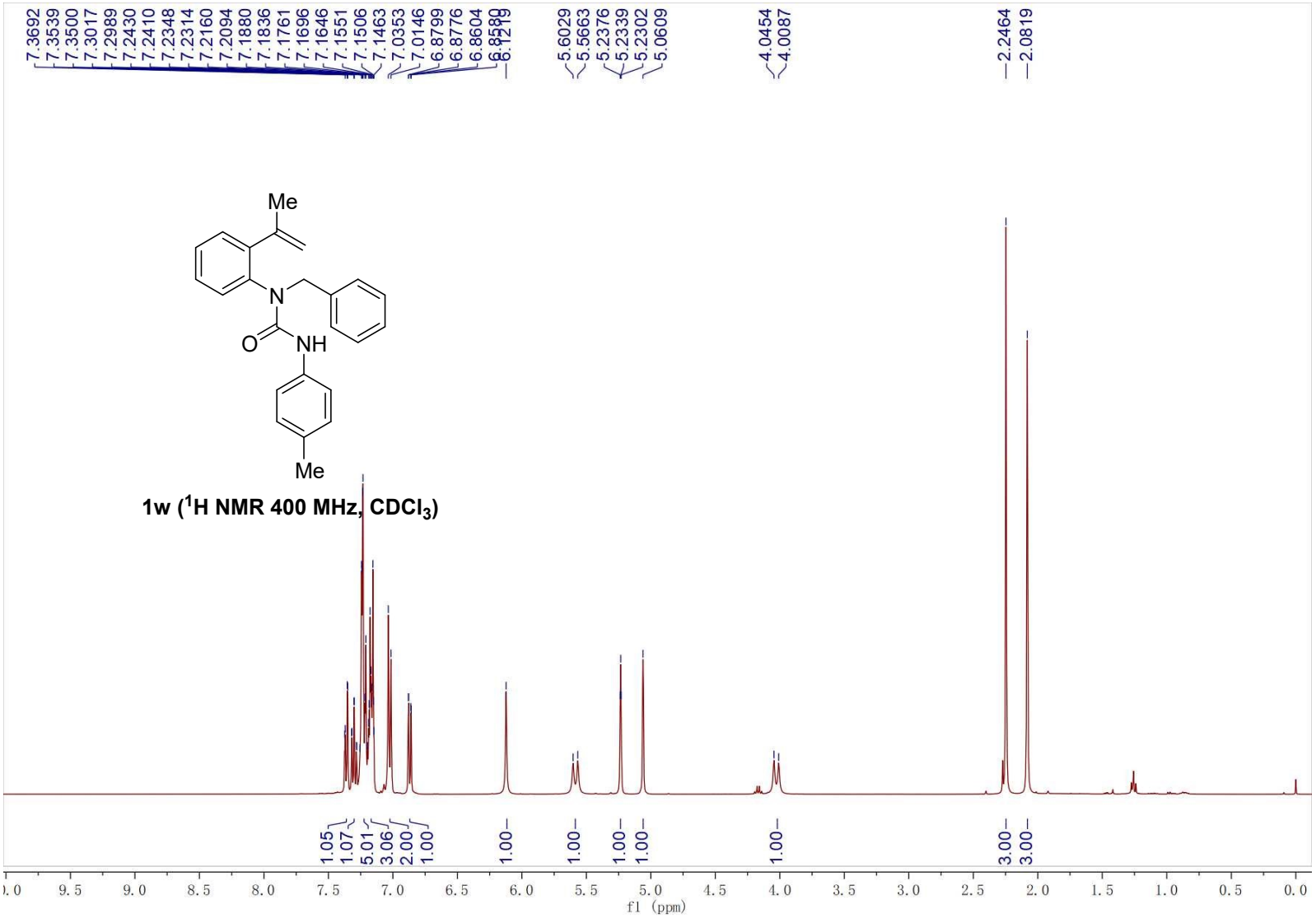

153.6289
143.0943
142.7872
142.6068
137.5383
136.8461
133.0771
130.8973
130.2801
129.2132
128.8514
128.8085
128.4501
127.5570
119.0949
118.8476
117.2143
105.4912
52.3623
23.2004
Me
N
O
NH
CN
1u (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

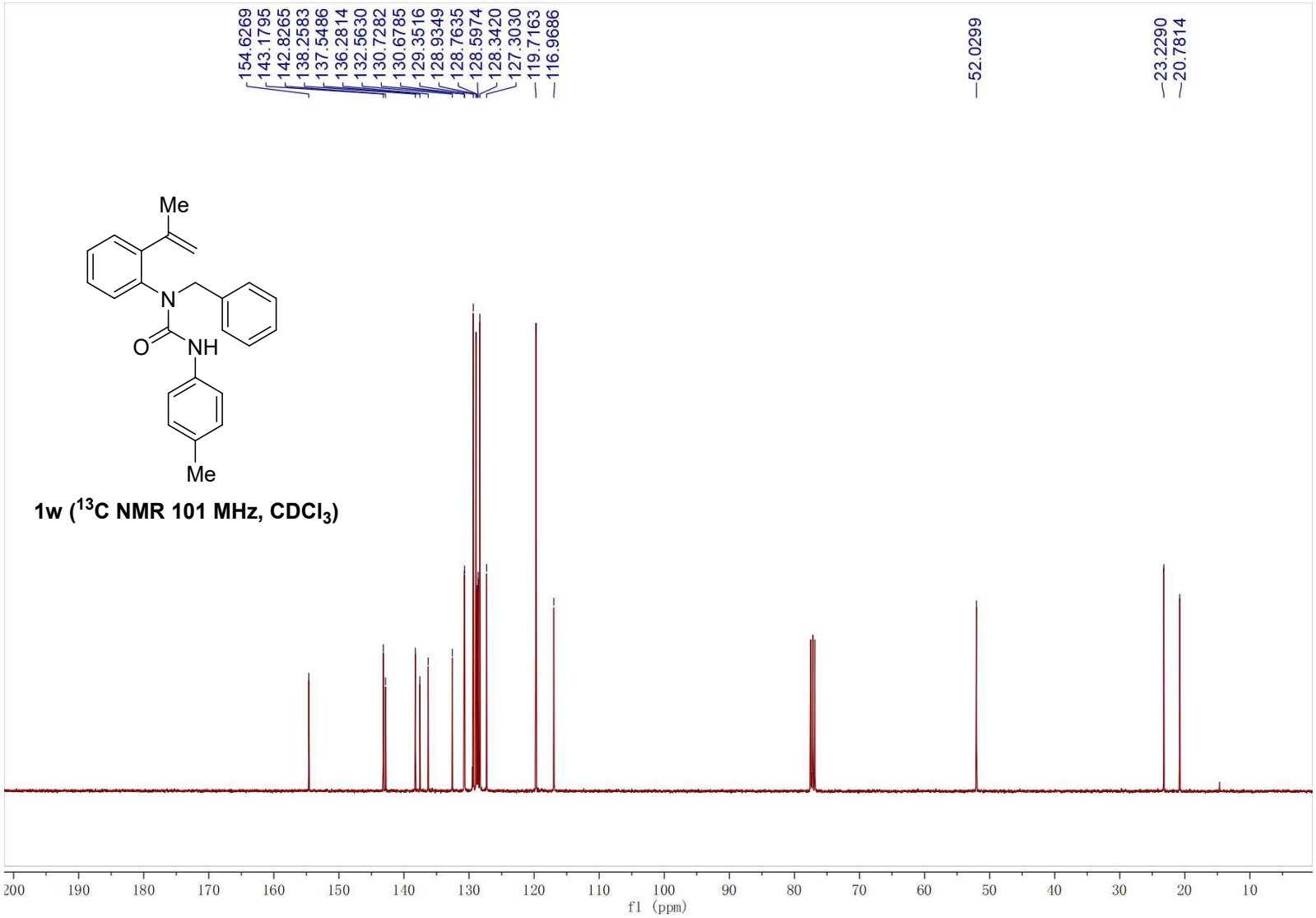


1v (^{1}H NMR 400 MHz, $CDCl_3$)

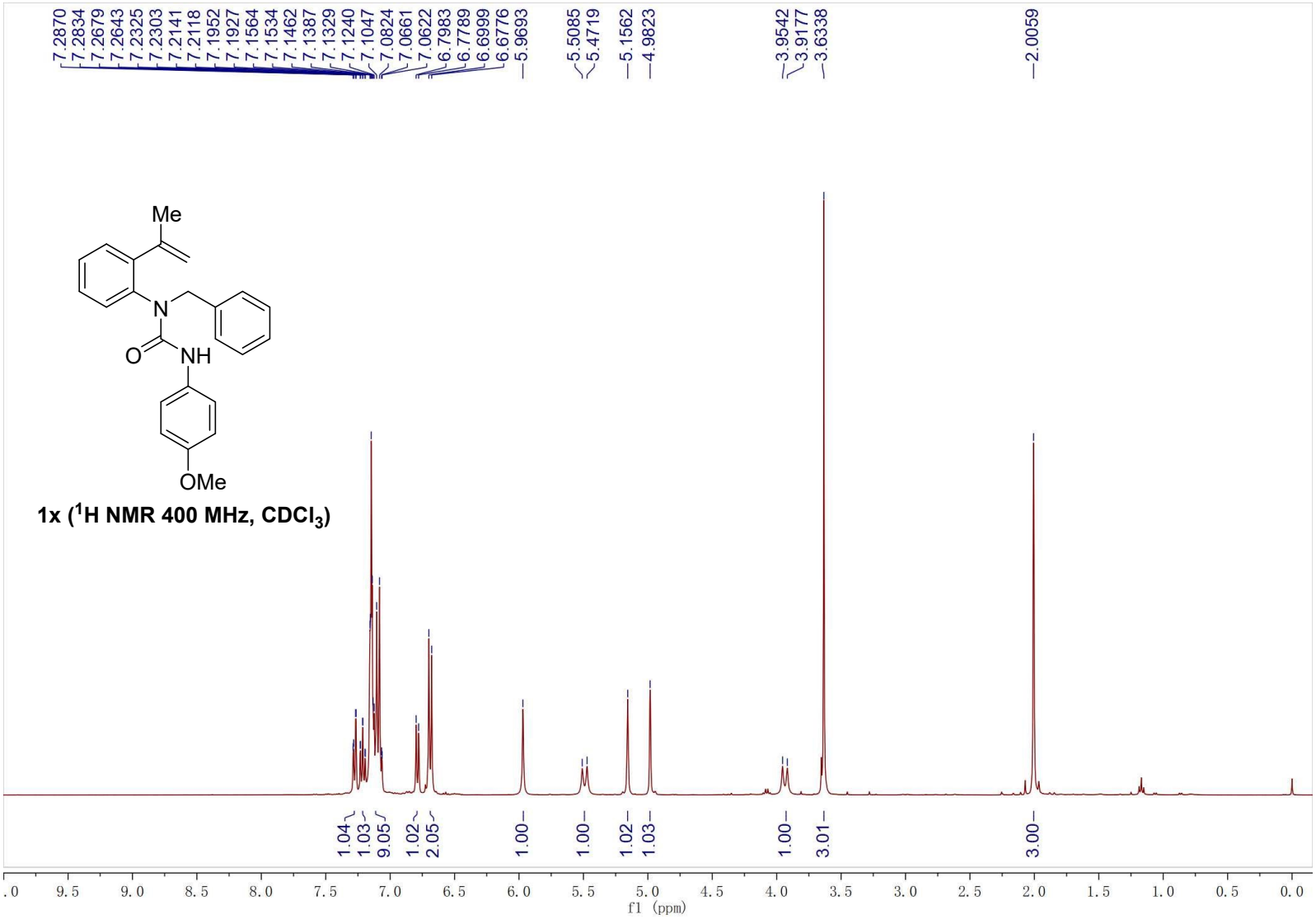


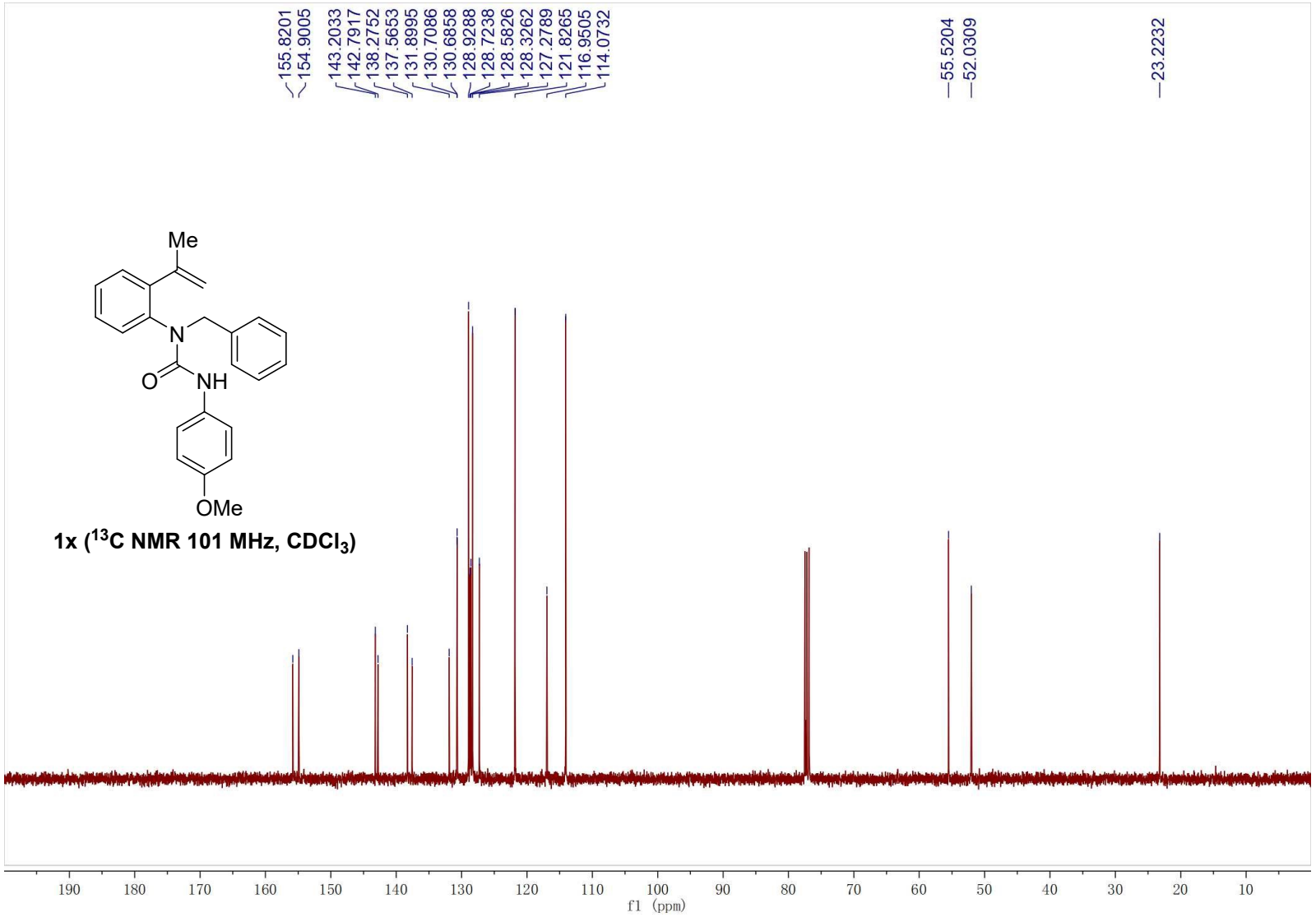
1v (^{13}C NMR 101 MHz, $CDCl_3$)


7.3692
7.3539
7.3500
7.3017
7.2989
7.2430
7.2410
7.2348
7.2314
7.2160
7.2094
7.1880
7.1836
7.1761
7.1696
7.1646
7.1551
7.1506
7.1463
7.0353
7.0146
6.8799
6.8776
6.8604
6.1219
5.6029
5.5663
5.2376
5.2339
5.2302
5.0609
4.0454
4.0087
2.2464
2.0819
Me
N
O
NH
Me
1w (1H NMR 400 MHz, CDCl3)
1.05
1.07
5.01
3.06
2.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

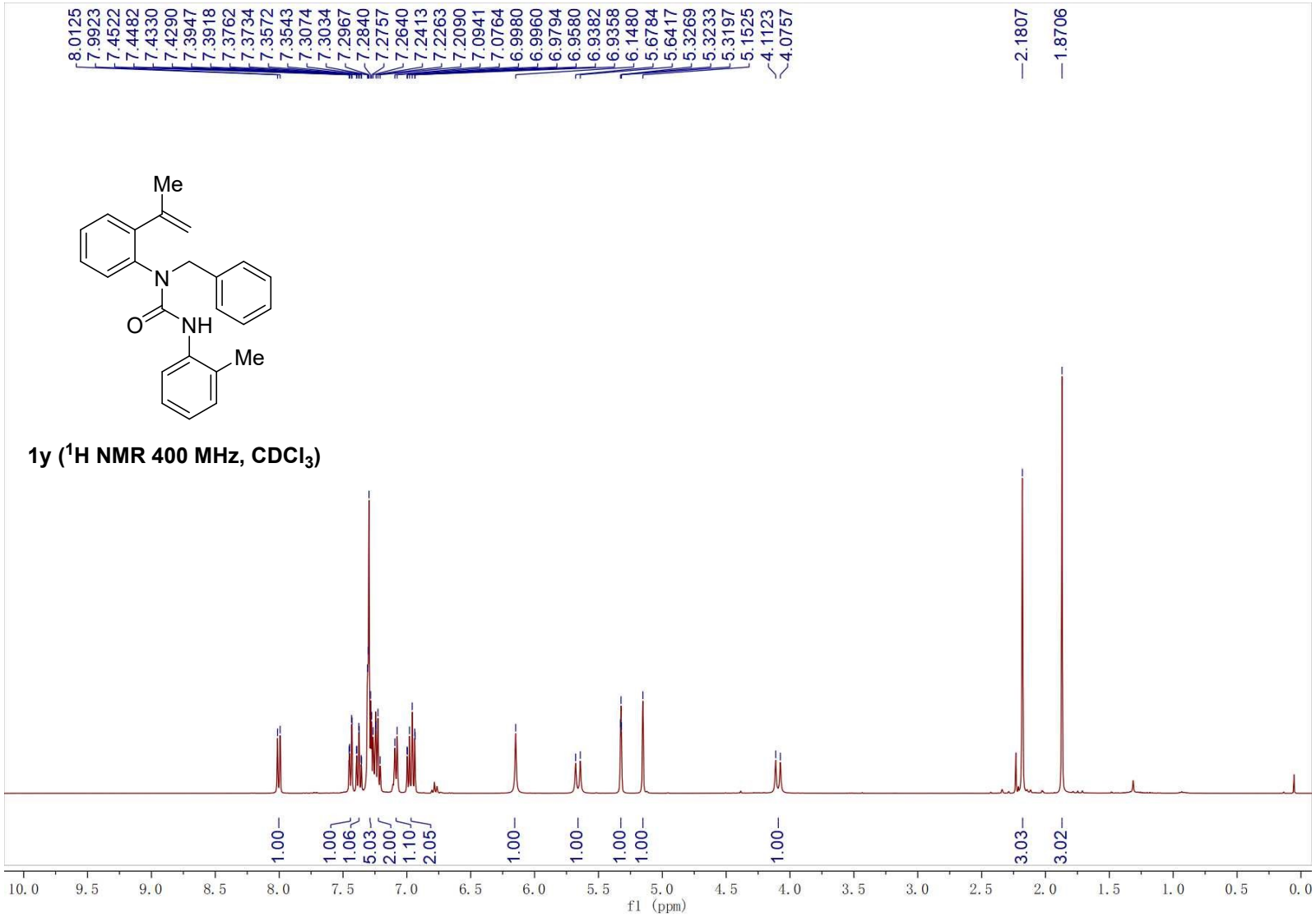


1w (^{13}C NMR 101 MHz, $CDCl_3$)

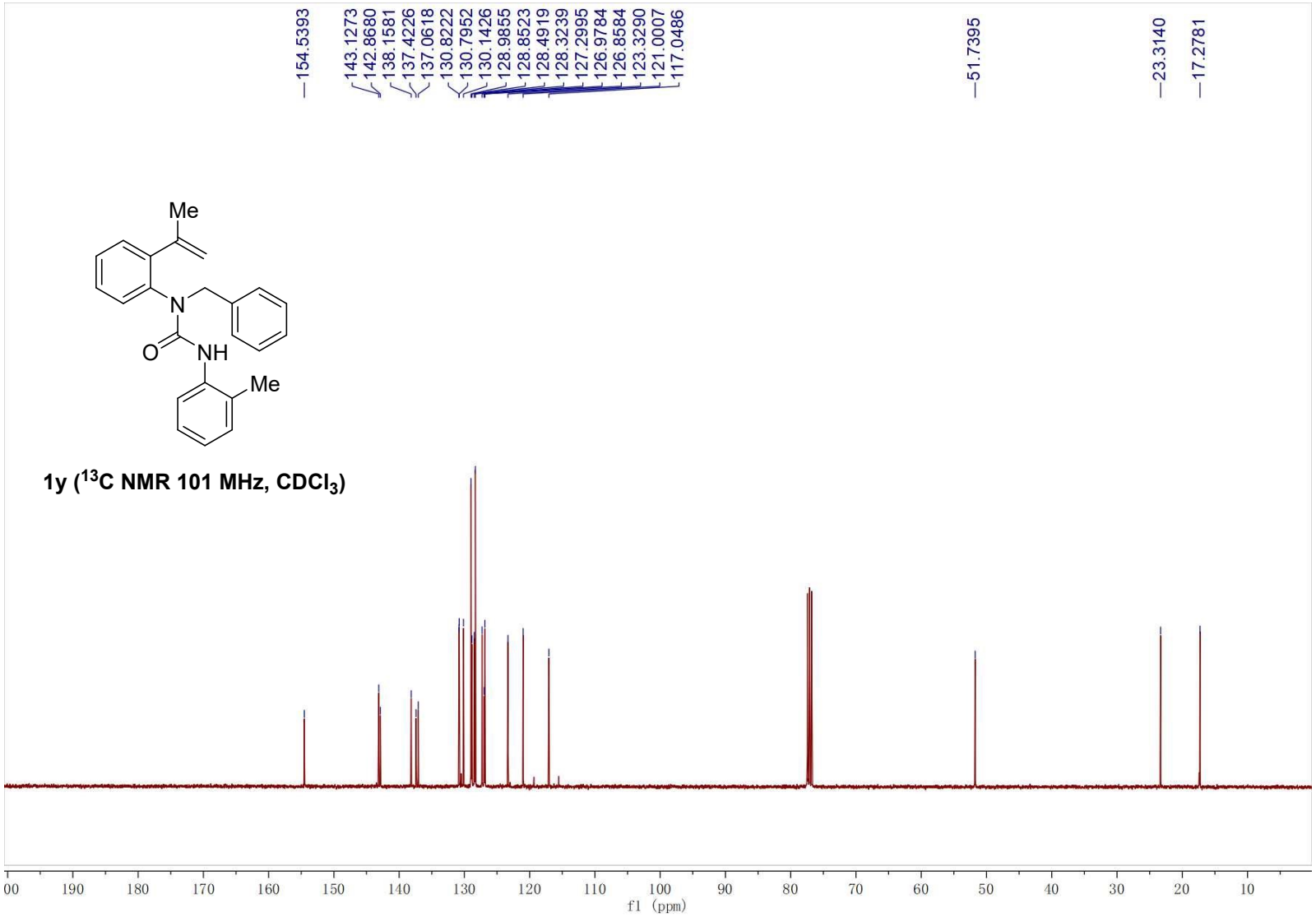

7.2870
7.2834
7.2679
7.2643
7.2325
7.2303
7.2141
7.2118
7.1952
7.1927
7.1564
7.1534
7.1462
7.1387
7.1329
7.1240
7.1047
7.0824
7.0661
7.0622
6.7983
6.7789
6.6999
6.6776
5.9693
5.5085
5.4719
5.1562
4.9823
3.9542
3.9177
3.6338
2.0059
Me
N
O
NH
OMe
1x (1H NMR 400 MHz, CDCl3)
1.04
1.03
9.05
1.02
2.05
1.00
1.00
1.02
1.03
1.00
3.01
3.00
f1 (ppm)

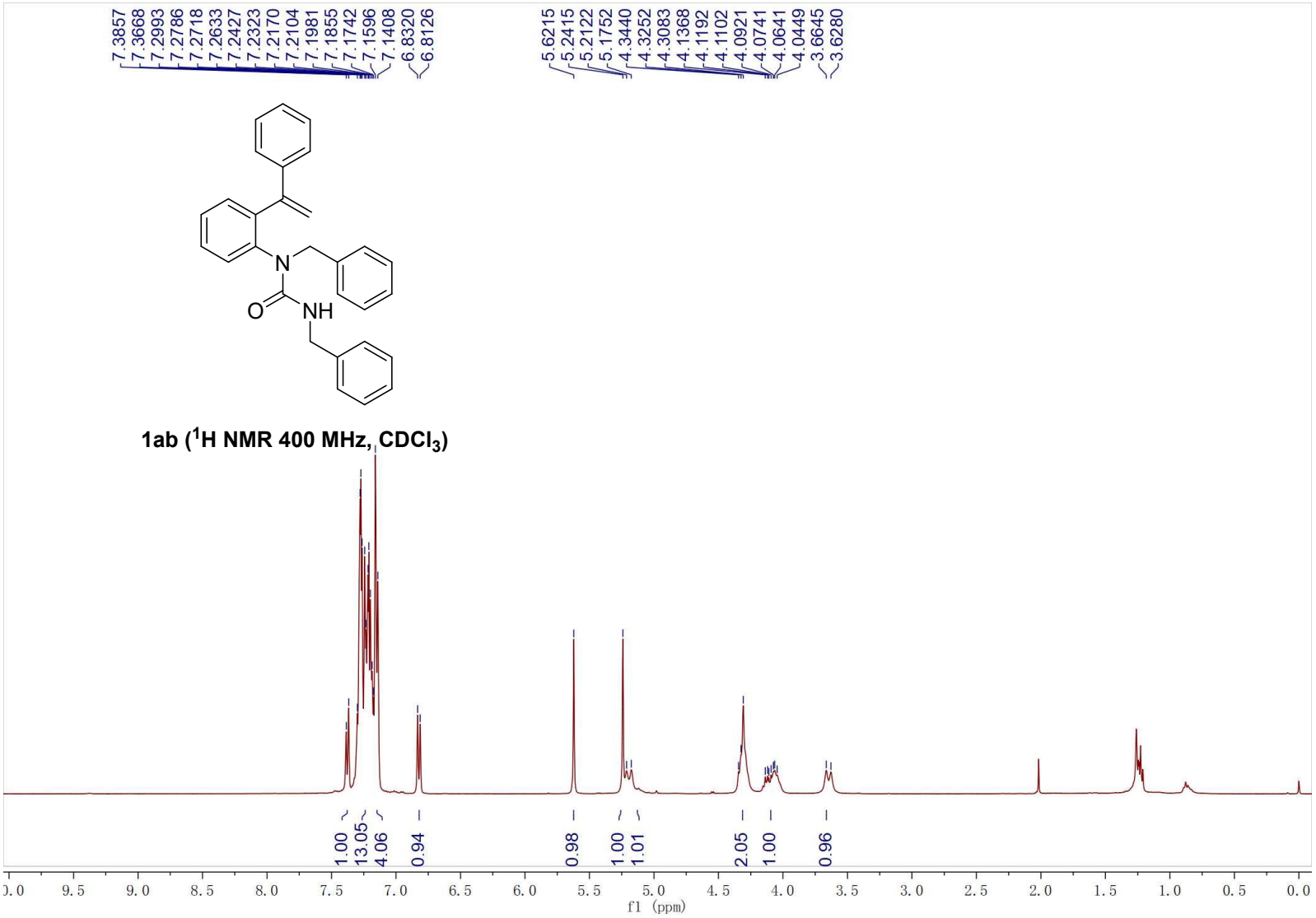


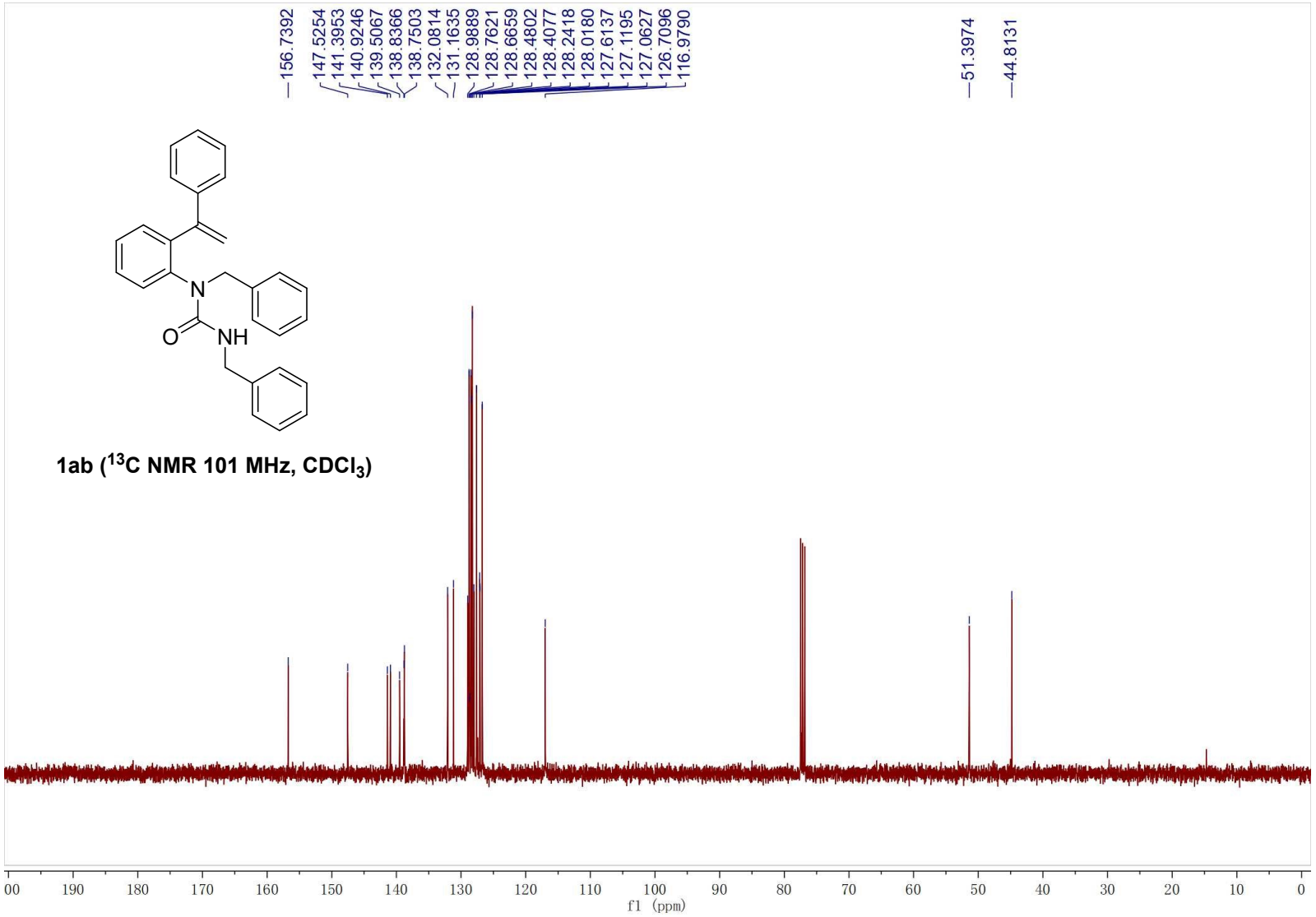
1x (^{13}C NMR 101 MHz, $CDCl_3$)



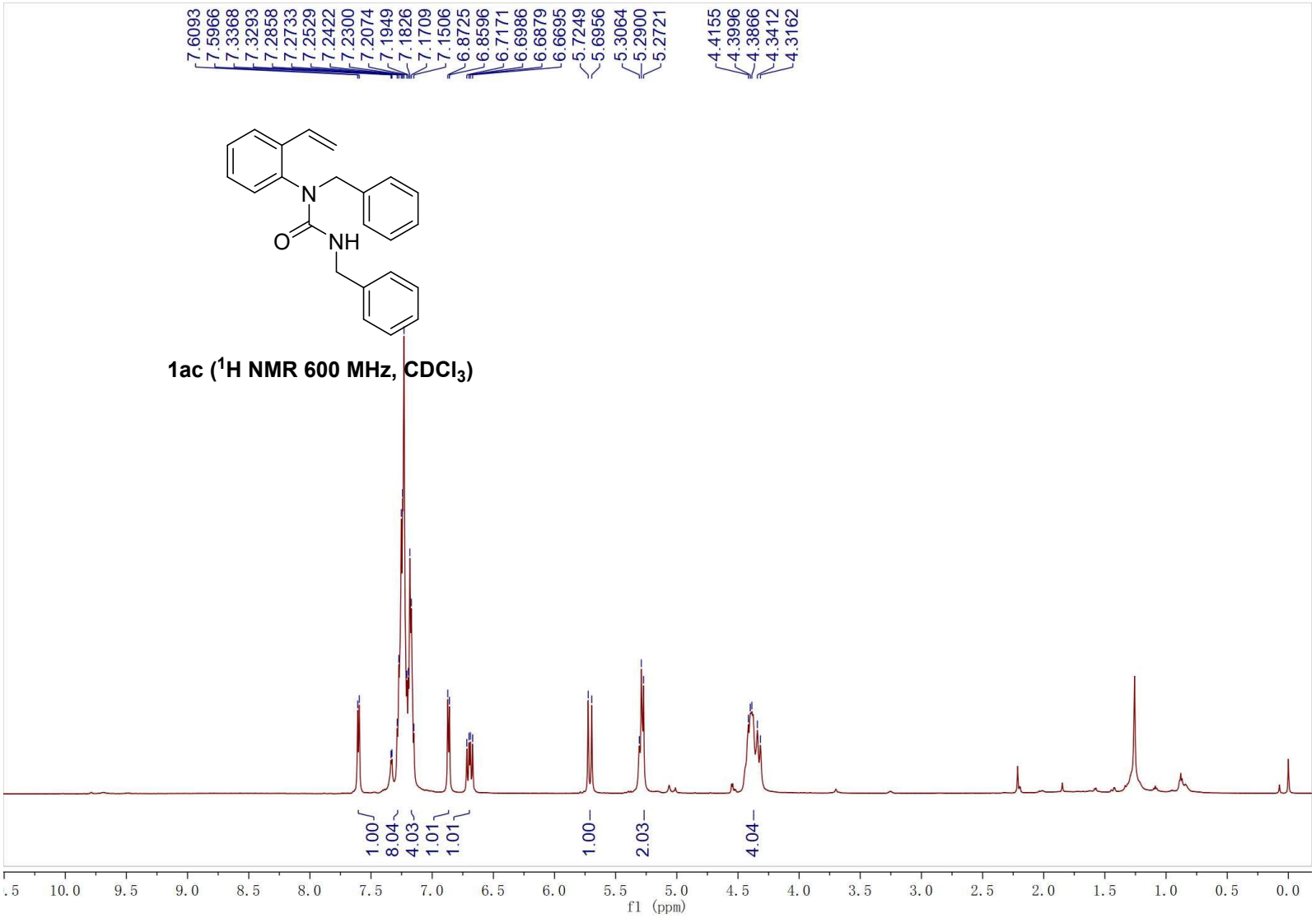
1y (^{1}H NMR 400 MHz, $CDCl_3$)

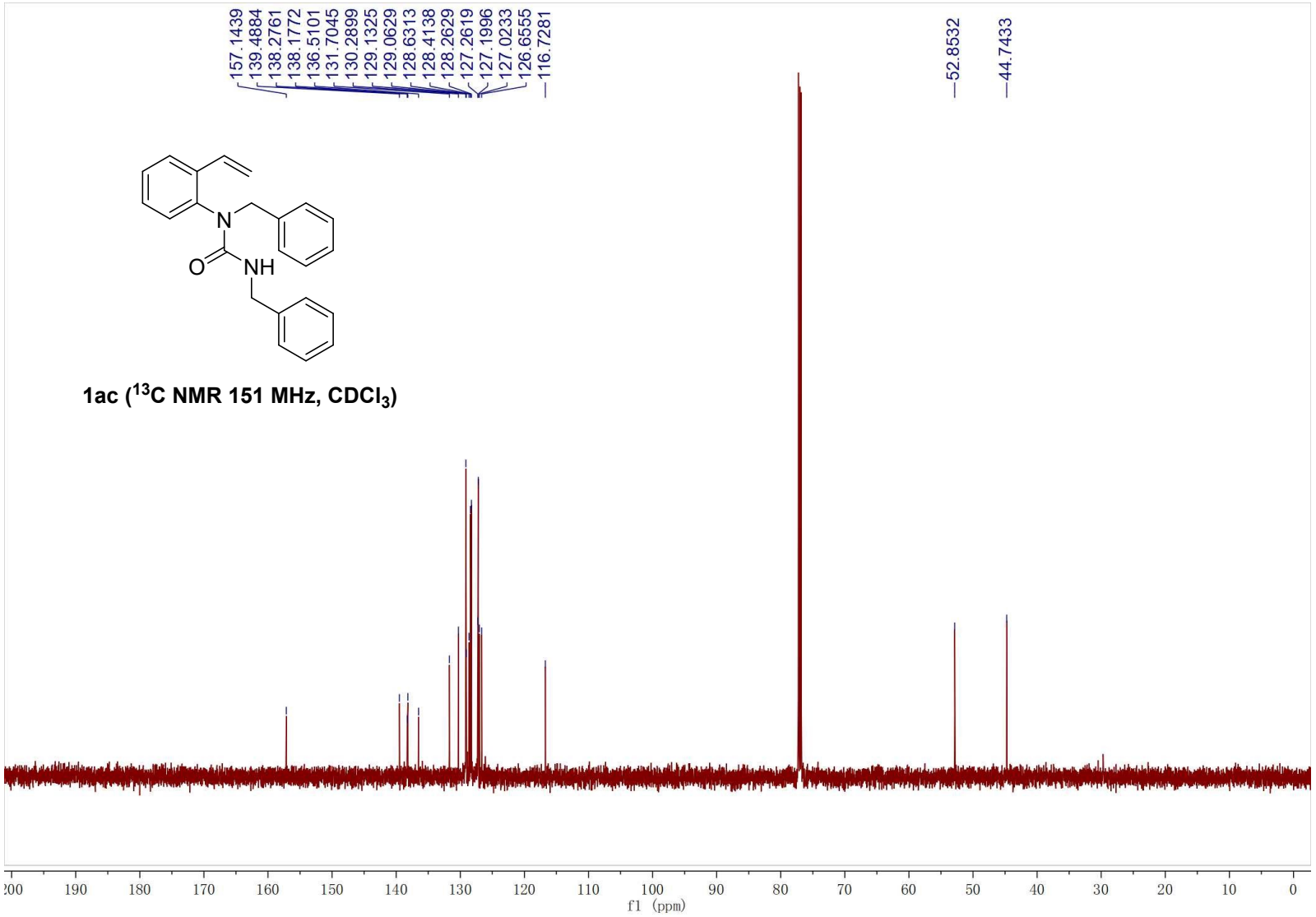

154.5393
143.1273
142.8680
138.1581
137.4226
137.0618
130.8222
130.7952
130.1426
128.9855
128.8523
128.4919
128.3239
127.2995
126.9784
126.8584
123.3290
121.0007
117.0486
51.7395
23.3140
17.2781
Me
N
O
NH
Me
1y (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)


7.3857
7.3668
7.2993
7.2786
7.2718
7.2633
7.2427
7.2323
7.2170
7.2104
7.1981
7.1855
7.1742
7.1596
7.1408
6.8320
6.8126
5.6215
5.2415
5.2122
5.1752
4.3440
4.3252
4.3083
4.1368
4.1192
4.1102
4.0921
4.0741
4.0641
4.0449
3.6645
3.6280
N
O
NH
1ab (1H NMR 400 MHz, CDCl3)
1.00
13.05
4.06
0.94
0.98
1.00
1.01
2.05
1.00
0.96
f1 (ppm)

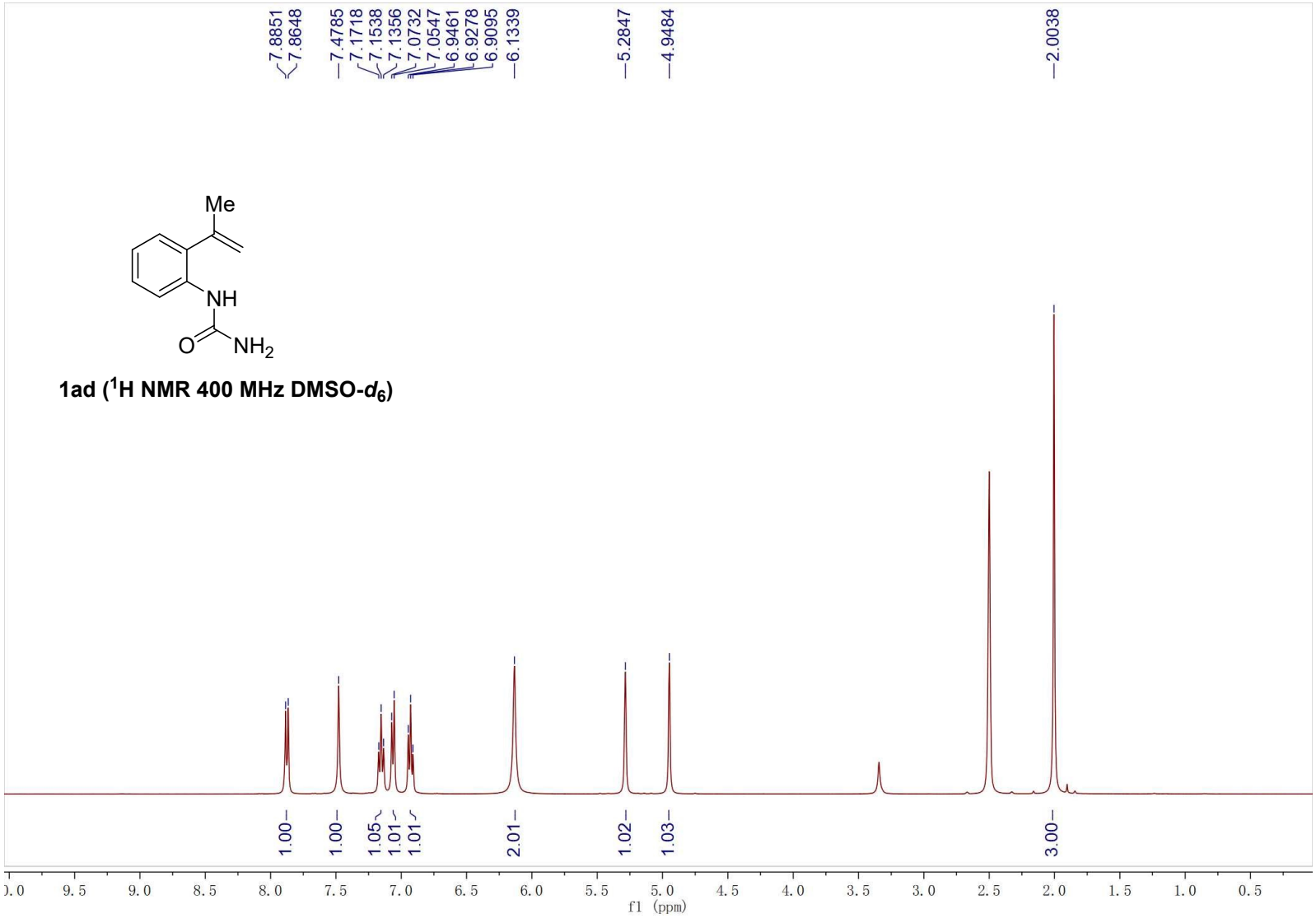


1ab (^{13}C NMR 101 MHz, $CDCl_3$)

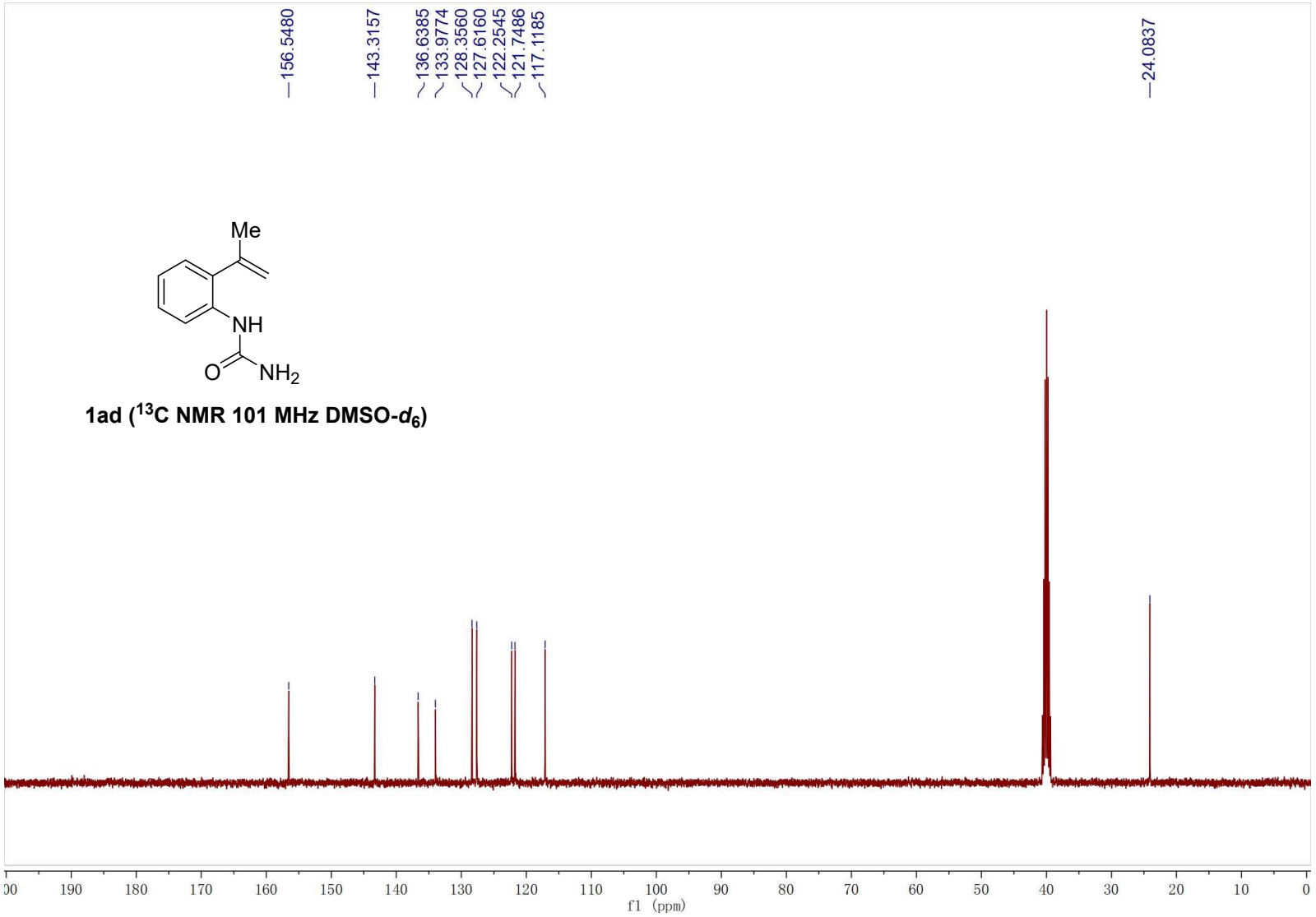

7.6093
7.5966
7.3368
7.3293
7.2858
7.2733
7.2529
7.2422
7.2300
7.2074
7.1949
7.1826
7.1709
7.1506
6.8725
6.8596
6.7171
6.6986
6.6879
6.6695
5.7249
5.6956
5.3064
5.2900
5.2721
4.4155
4.3996
4.3866
4.3412
4.3162
N
O
NH
1ac (1H NMR 600 MHz, CDCl3)
1.00
8.04
4.03
1.01
1.01
1.00
2.03
4.04
f1 (ppm)



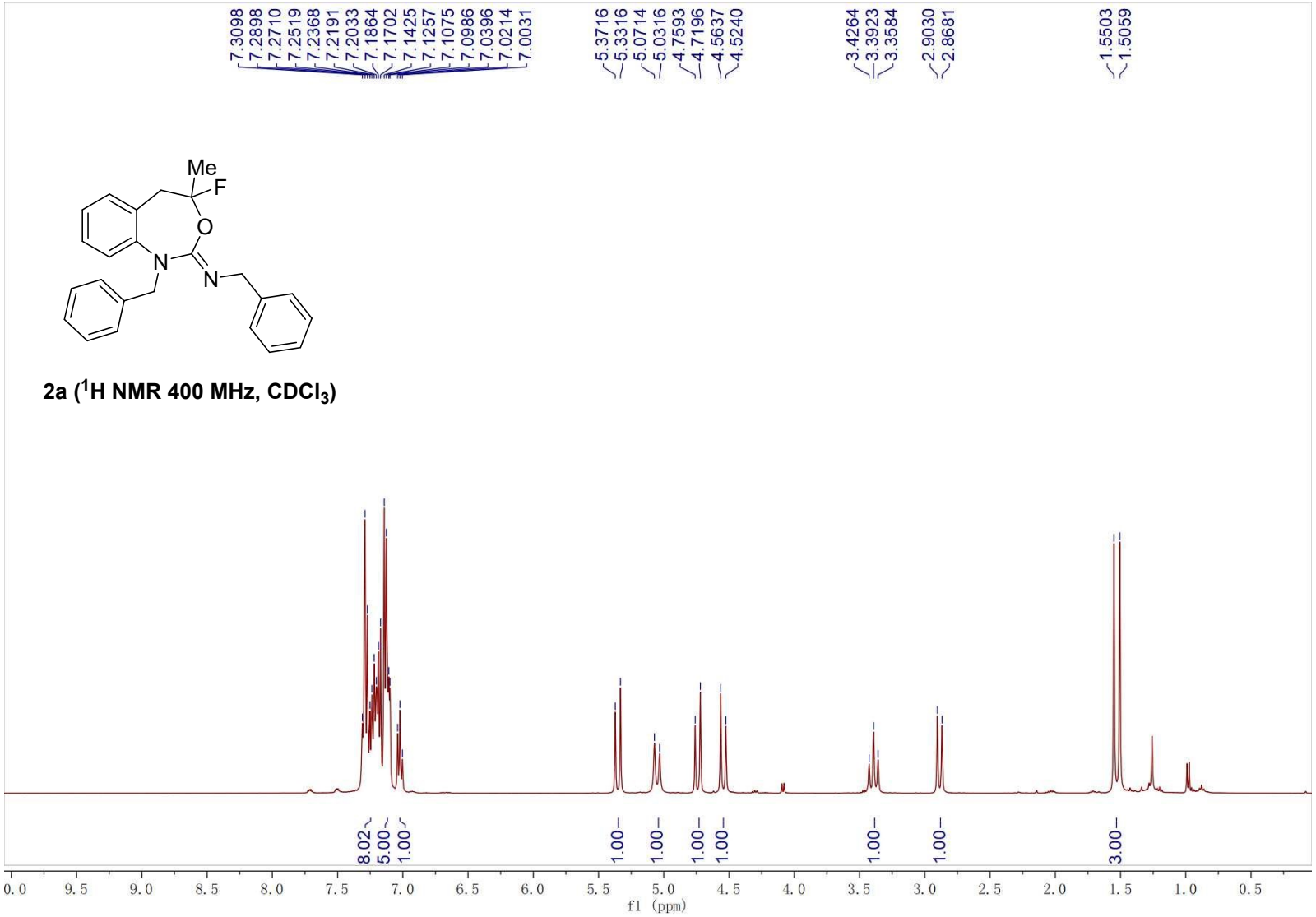
1ac (^{13}C NMR 151 MHz, $CDCl_3$)



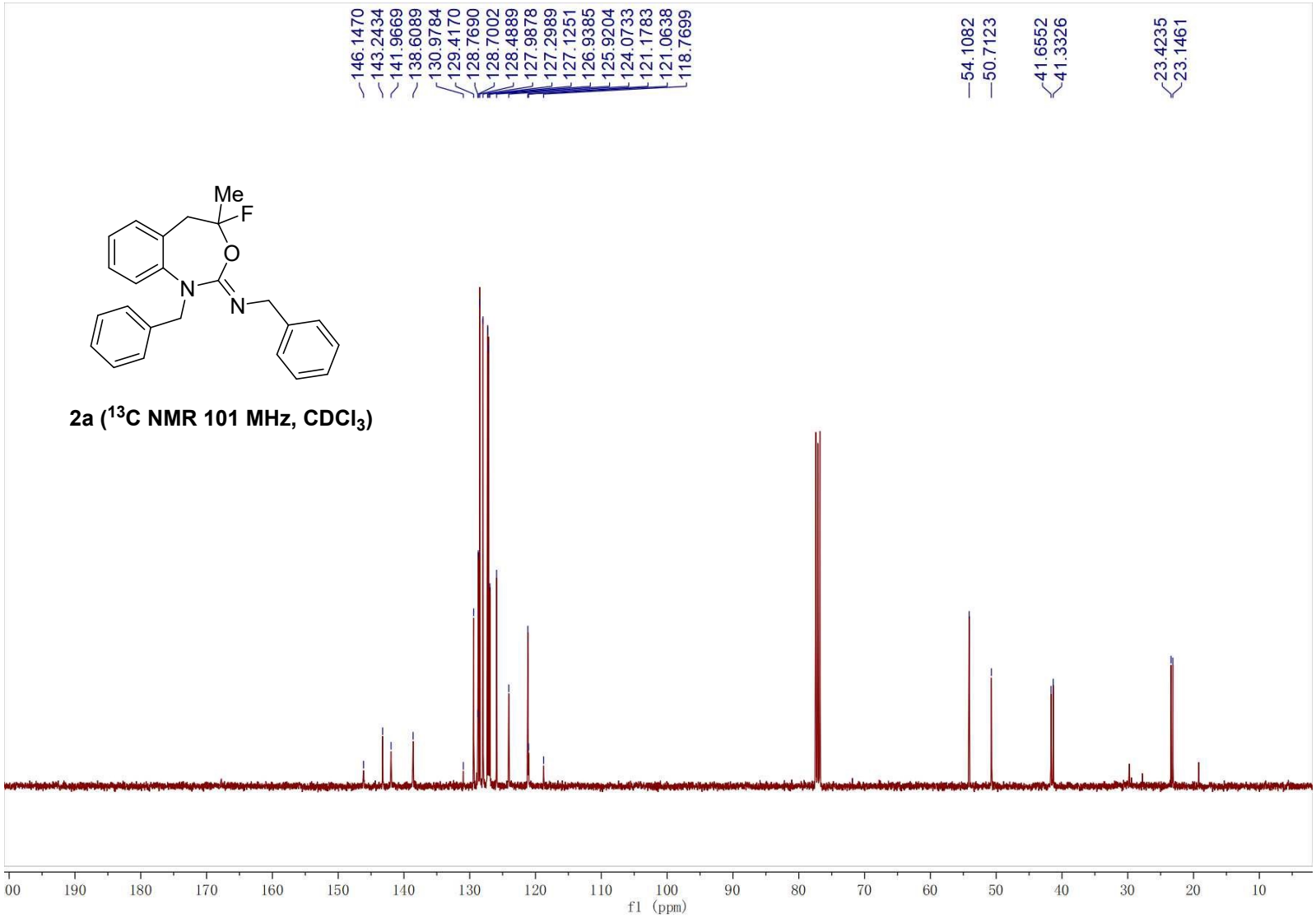
1ad (^{1}H NMR 400 MHz DMSO-d_6)



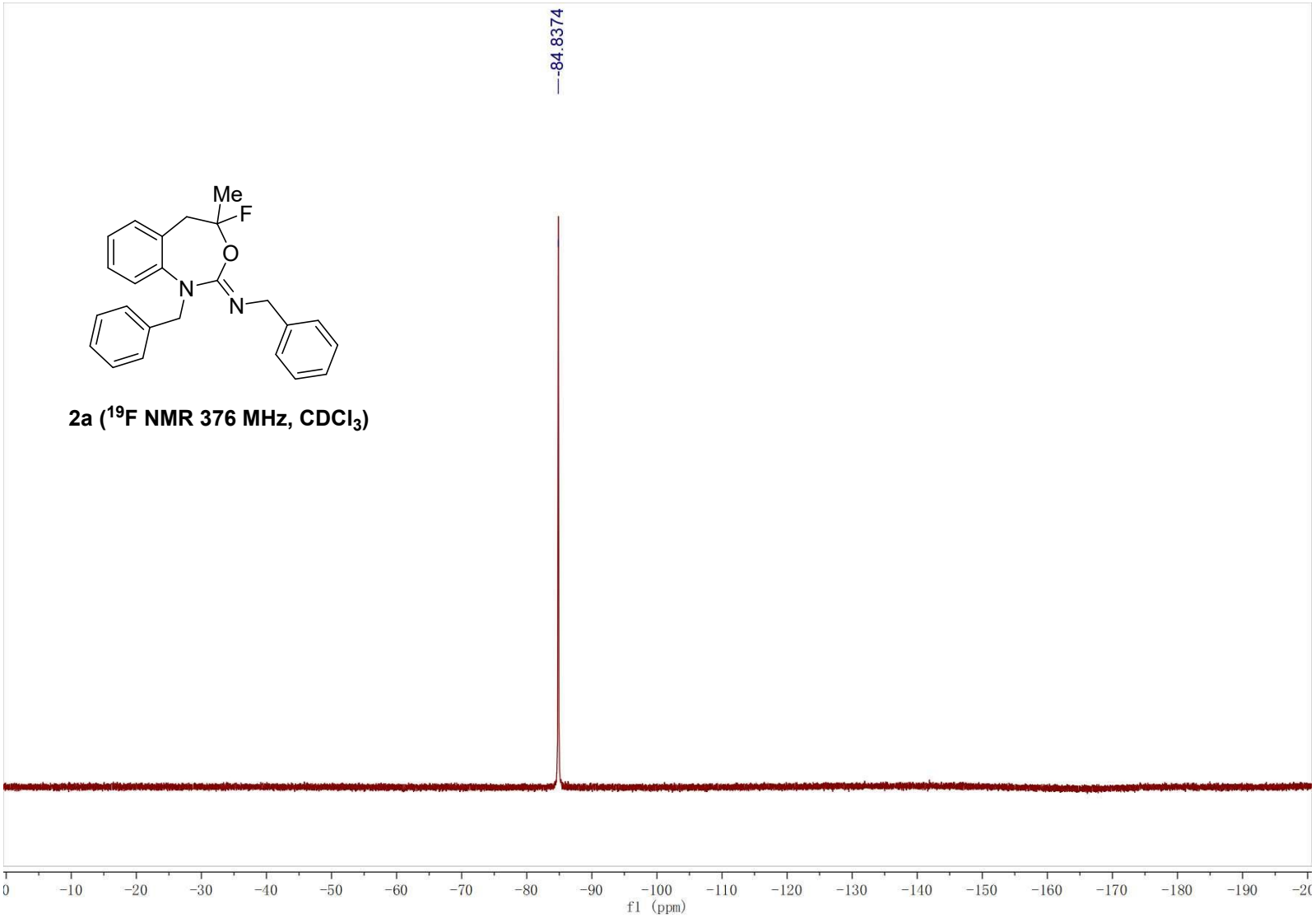
1ad (^{13}C NMR 101 MHz DMSO-d_6)



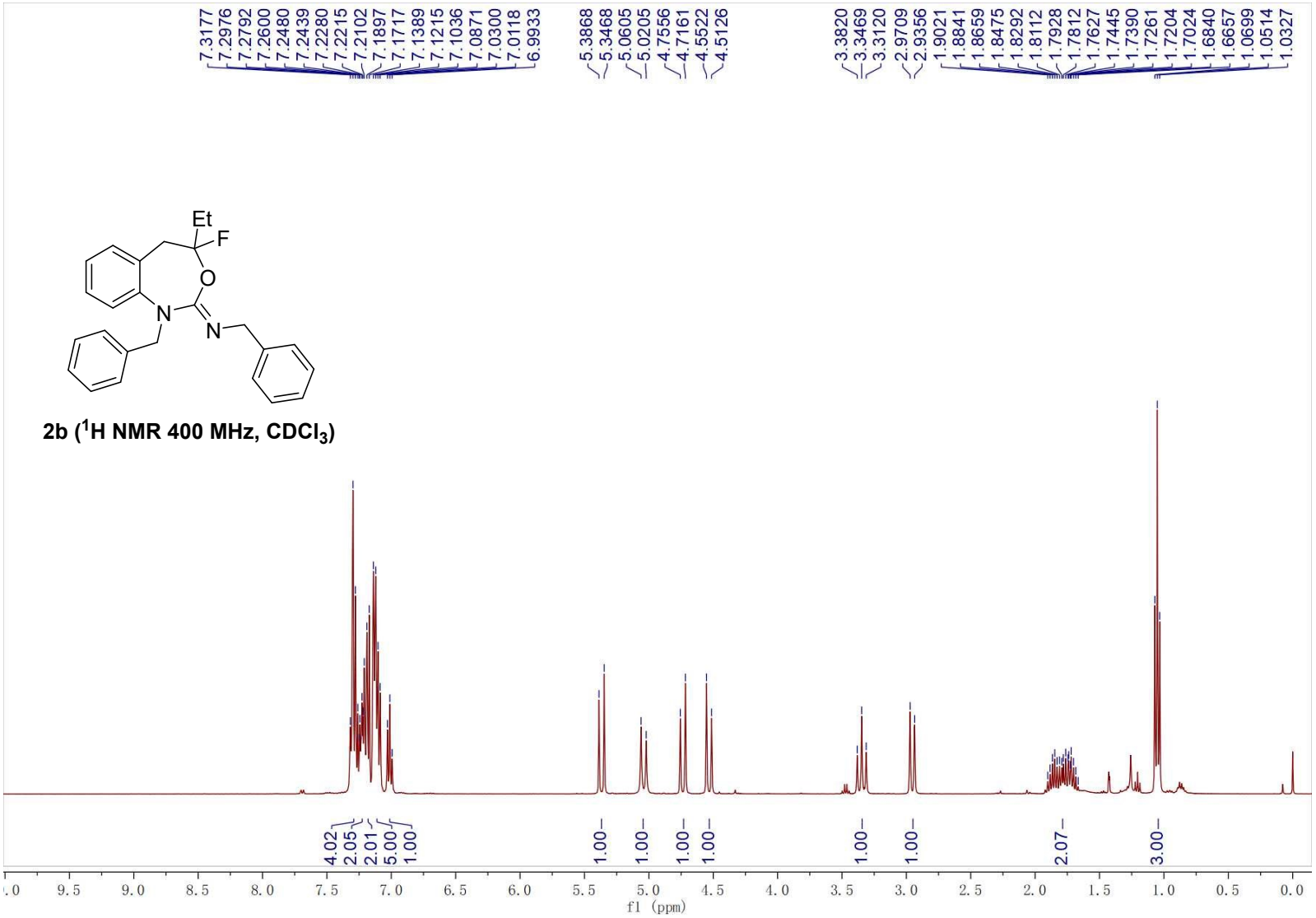
2a (^{1}H NMR 400 MHz, $CDCl_3$)



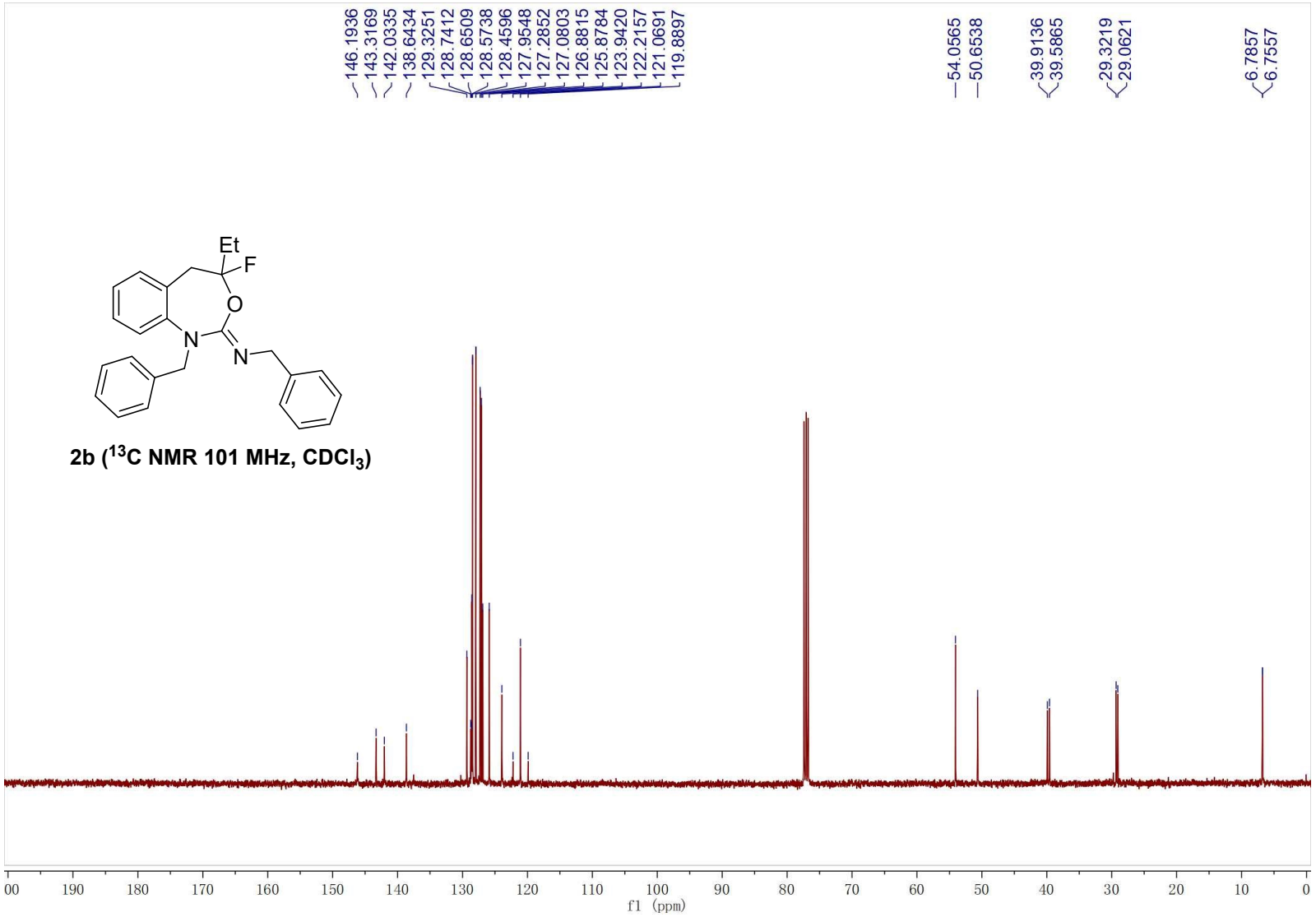
2a (^{13}C NMR 101 MHz, $CDCl_3$)



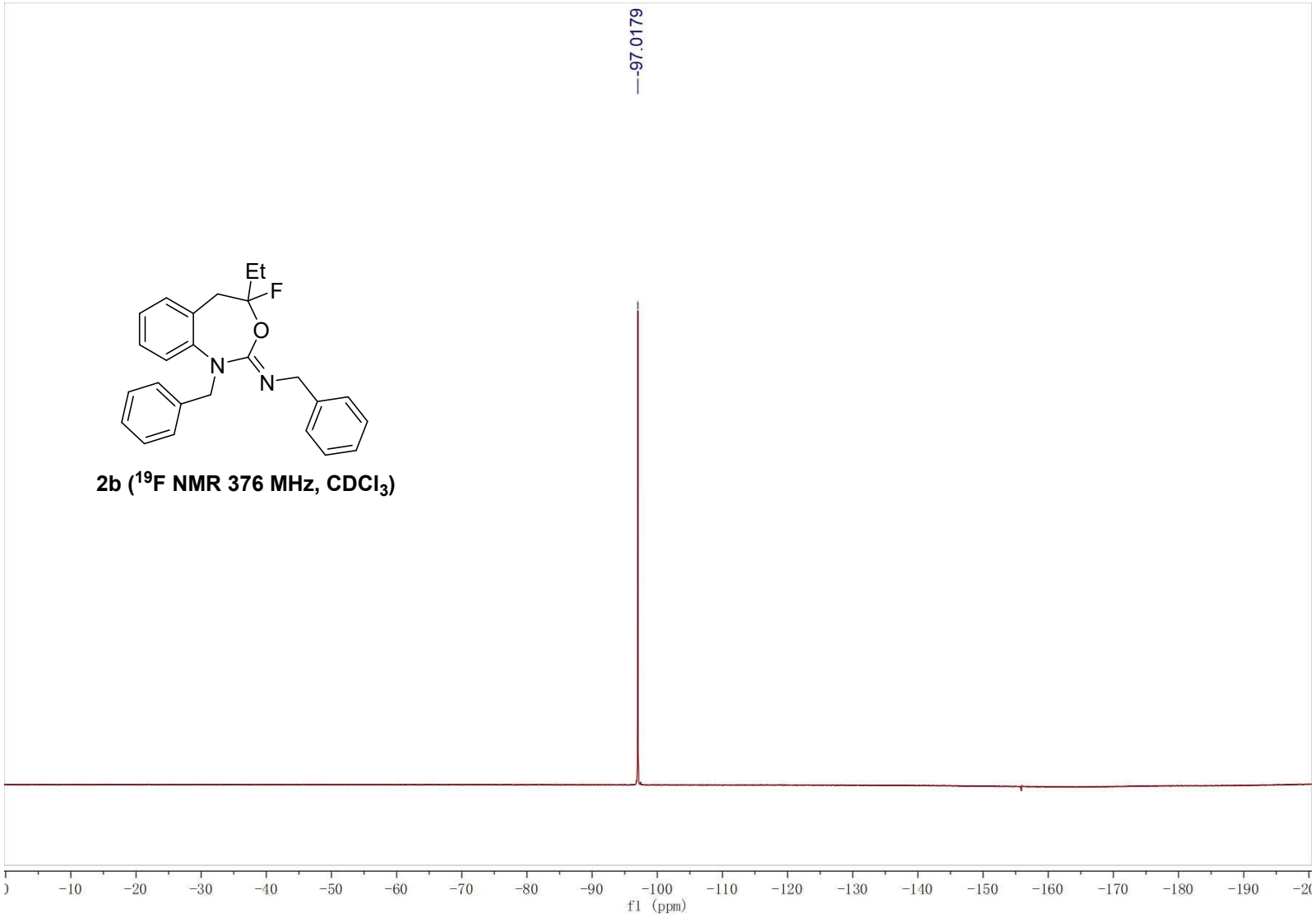
2a (^{19}F NMR 376 MHz, $CDCl_3$)



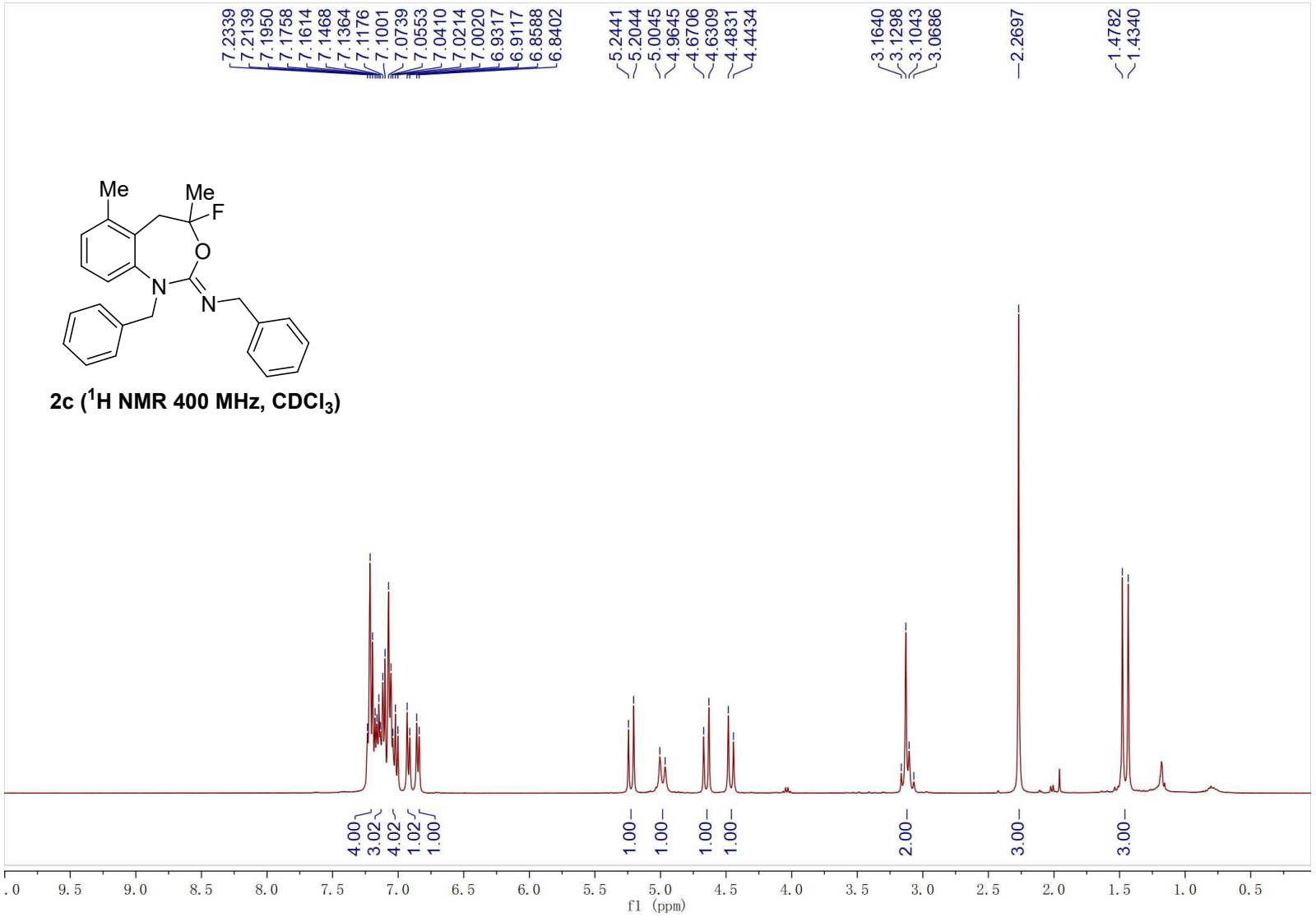
2b (^{1}H NMR 400 MHz, $CDCl_3$)



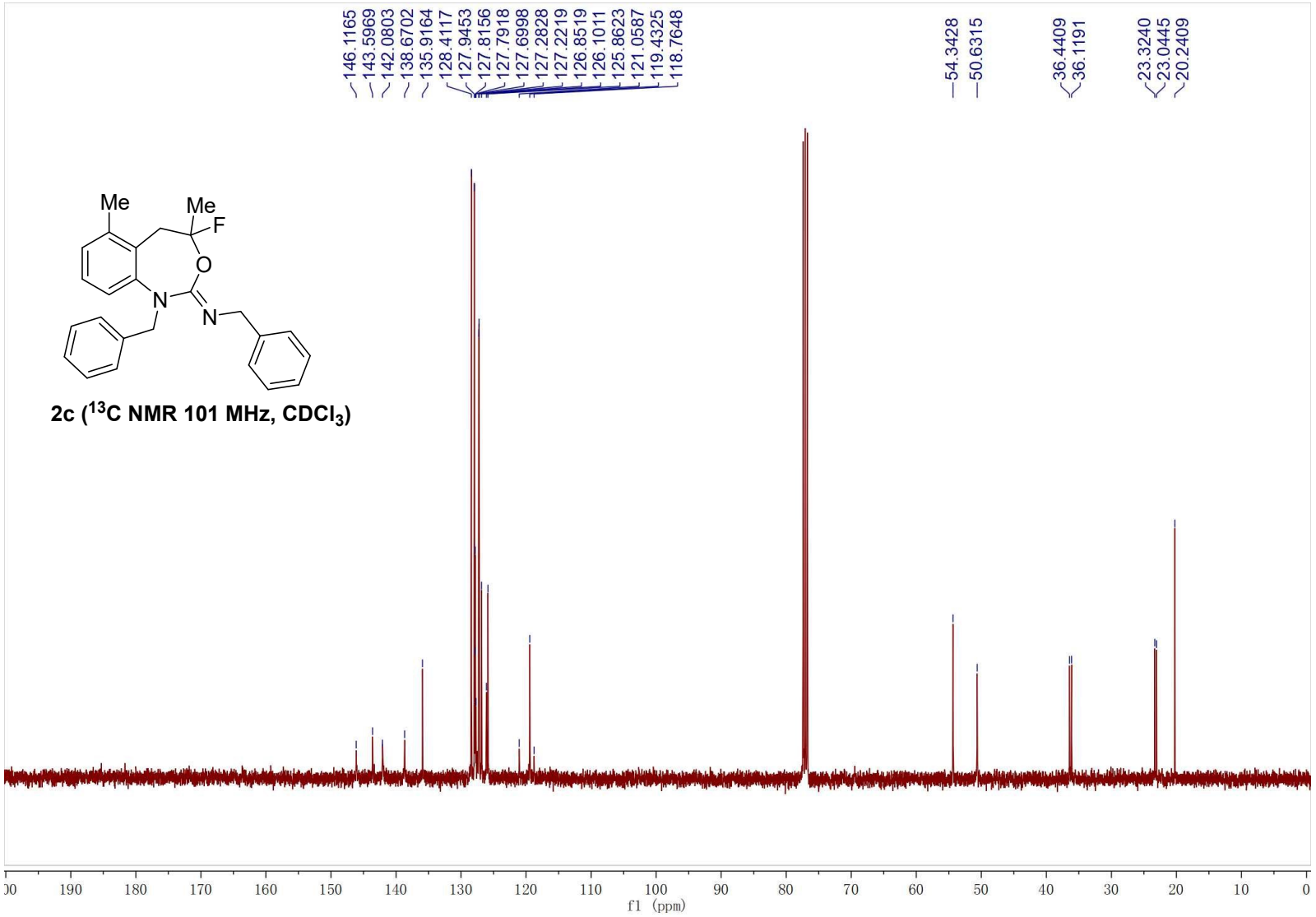
2b (^{13}C NMR 101 MHz, $CDCl_3$)



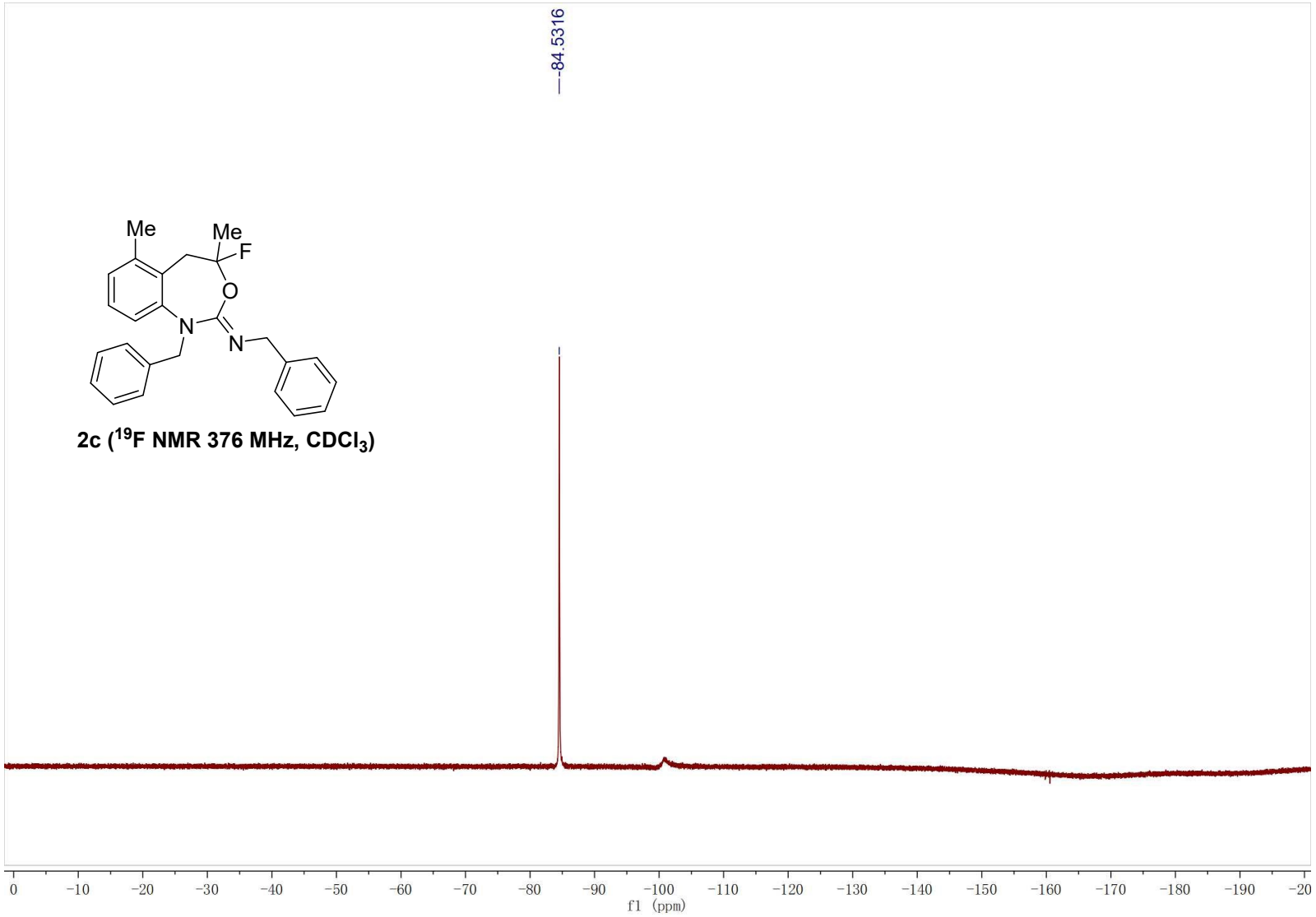
2b (^{19}F NMR 376 MHz, $CDCl_3$)



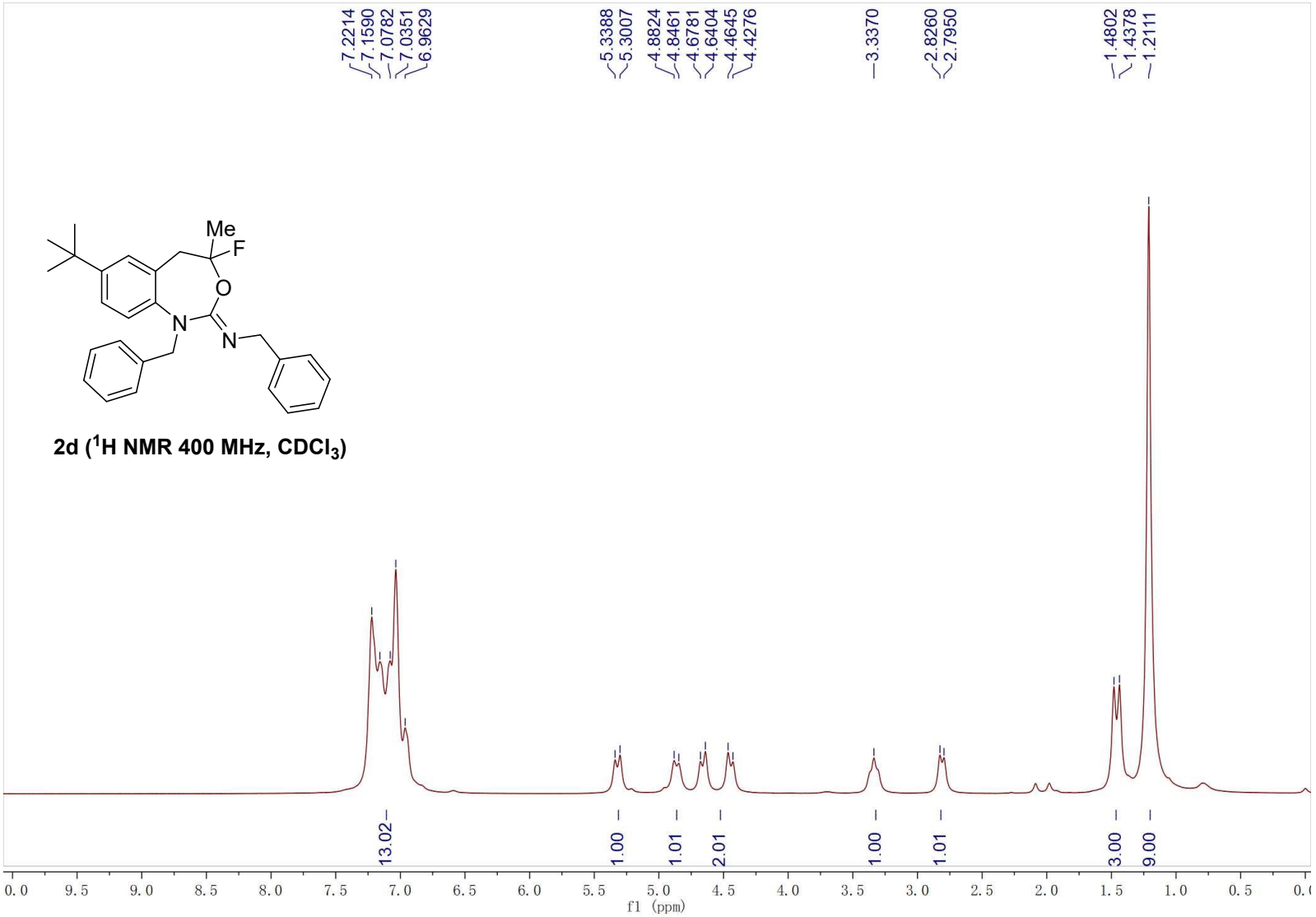
2c (^{1}H NMR 400 MHz, $CDCl_3$)



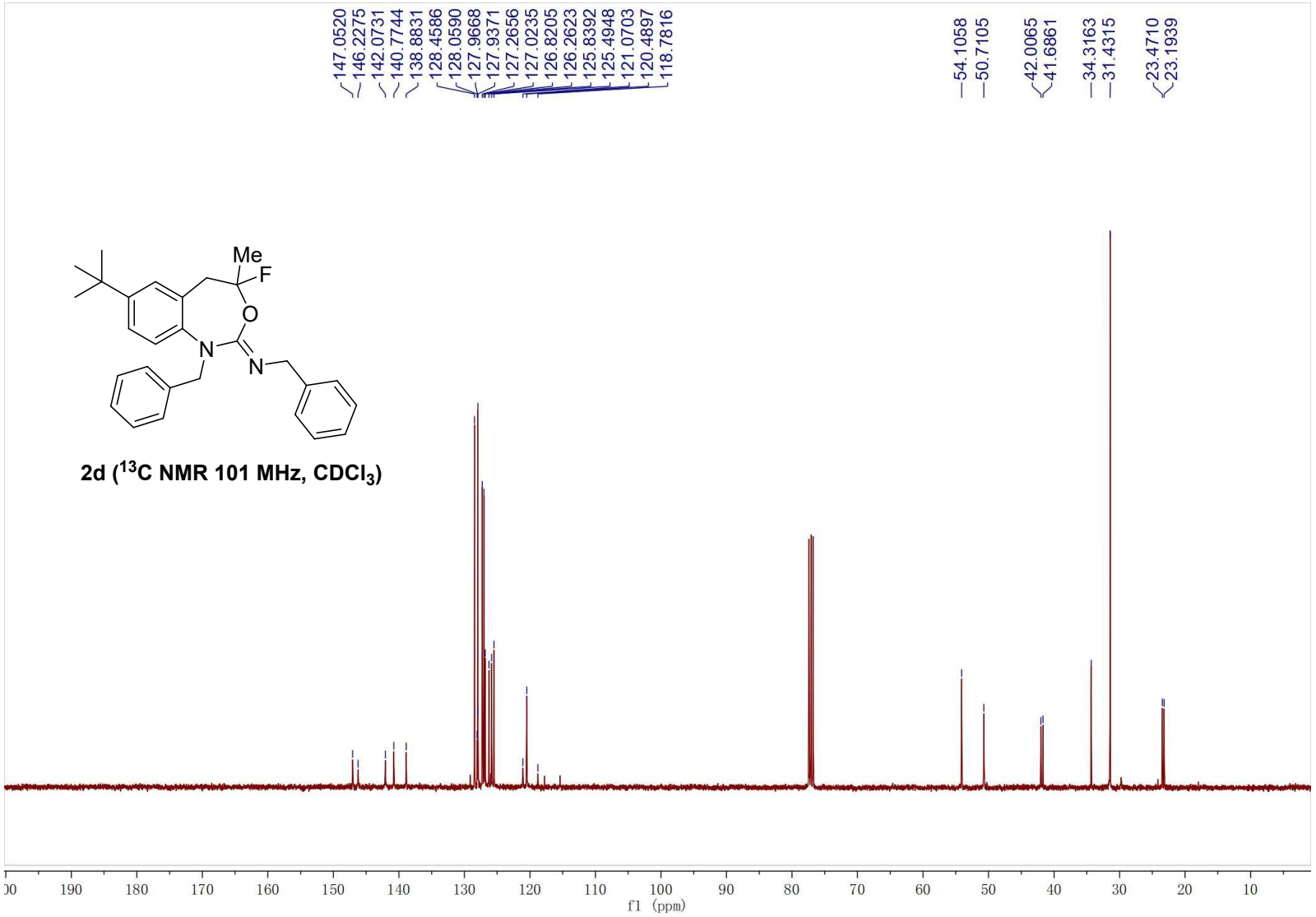
2c (^{13}C NMR 101 MHz, $CDCl_3$)

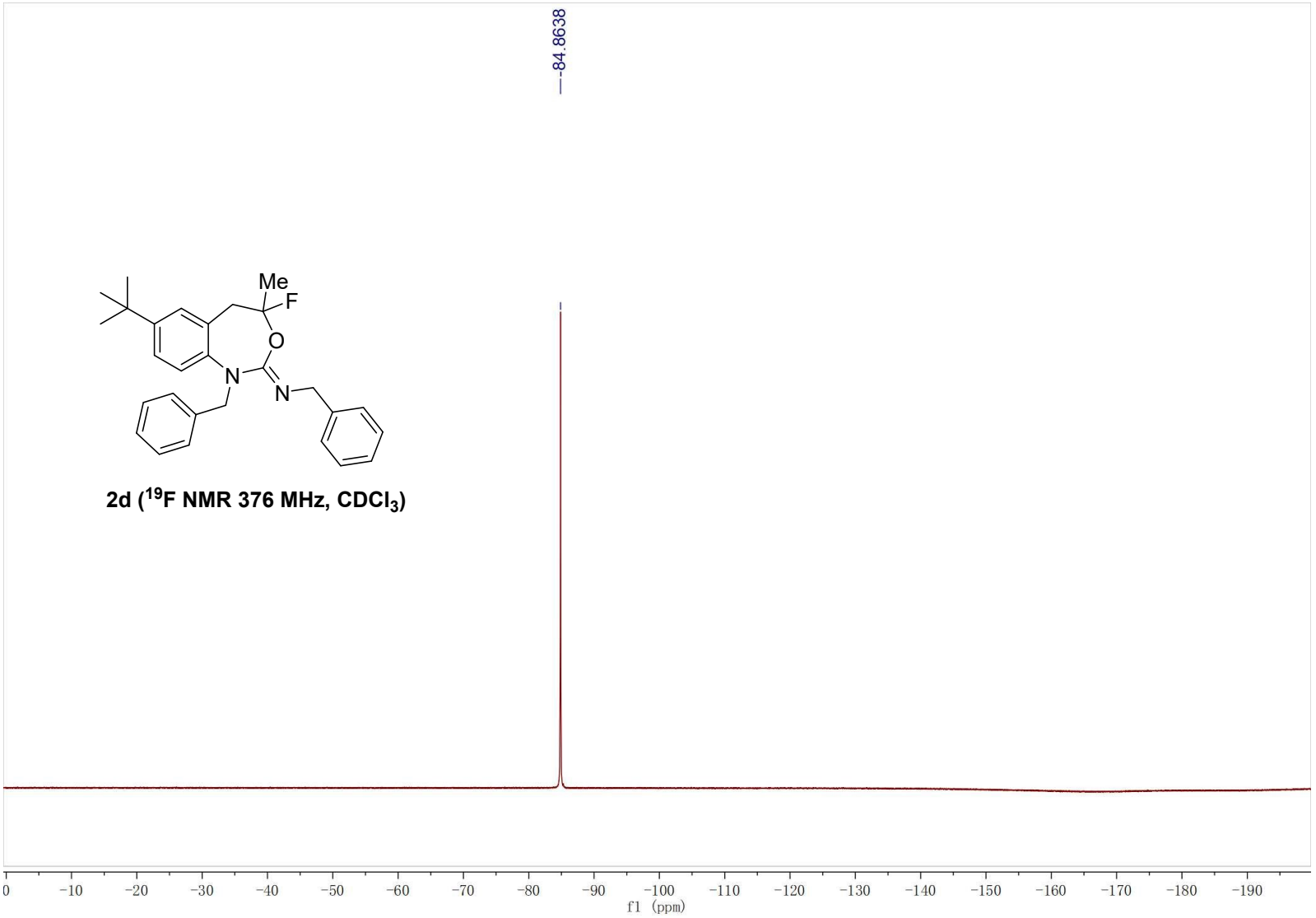


2c (^{19}F NMR 376 MHz, $CDCl_3$)

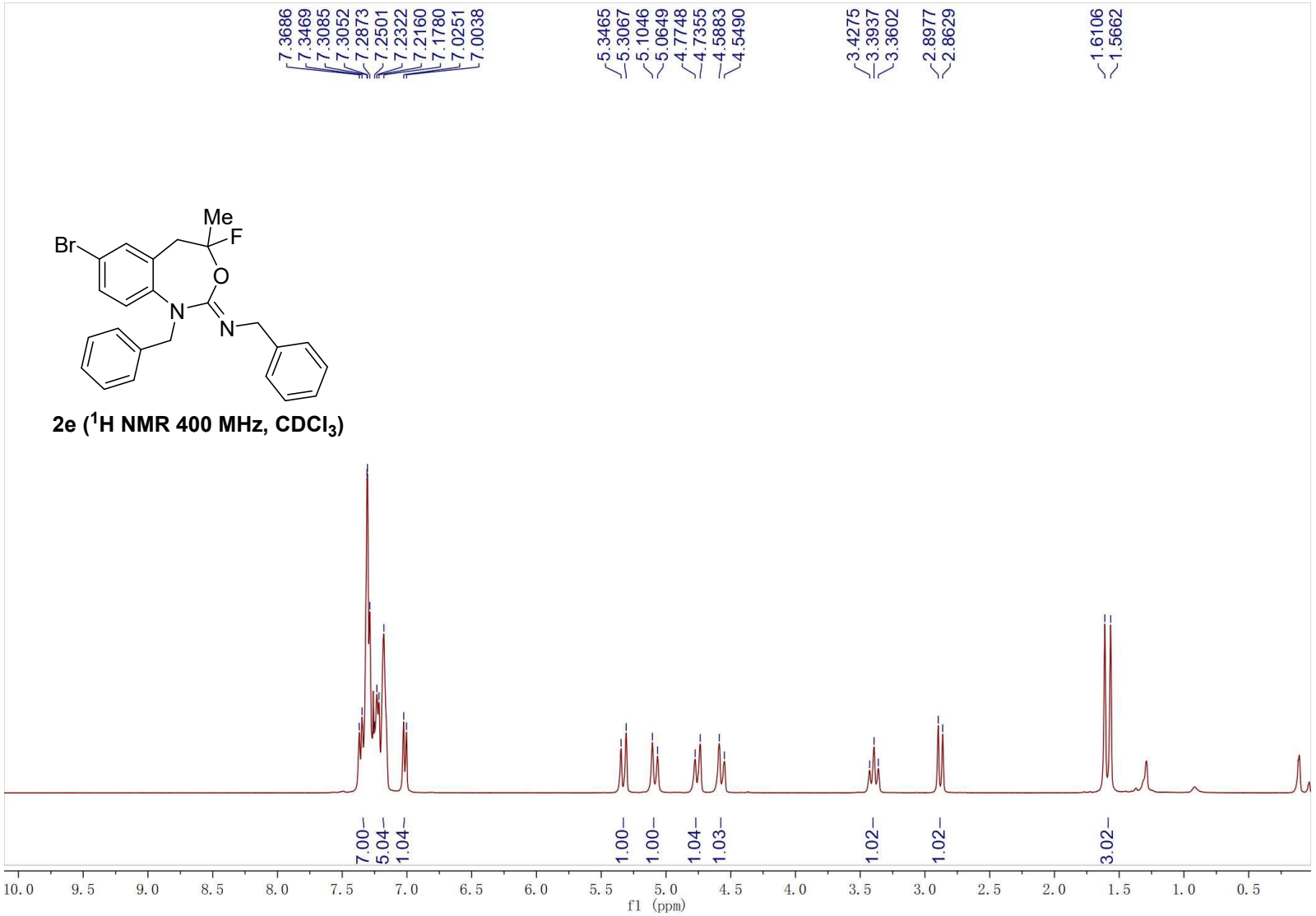


2d (^{1}H NMR 400 MHz, $CDCl_3$)

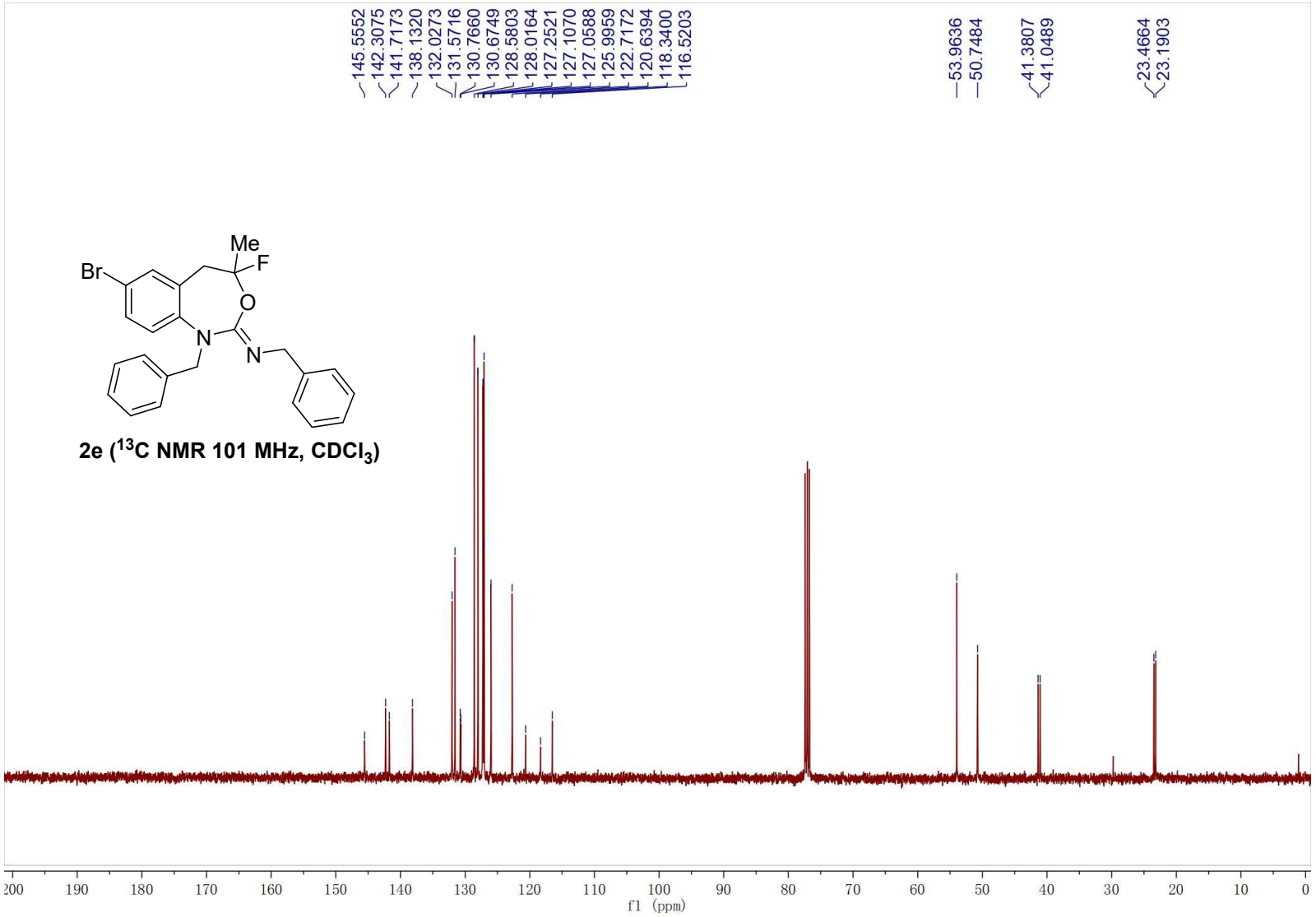

147.0520
146.2275
142.0731
140.7744
138.8831
128.4586
128.0590
127.9668
127.9371
127.2656
127.0235
126.8205
126.2623
125.8392
125.4948
121.0703
120.4897
118.7816
54.1058
50.7105
42.0065
41.6861
34.3163
31.4315
23.4710
23.1939
Me
F
O
N
N
2d (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)



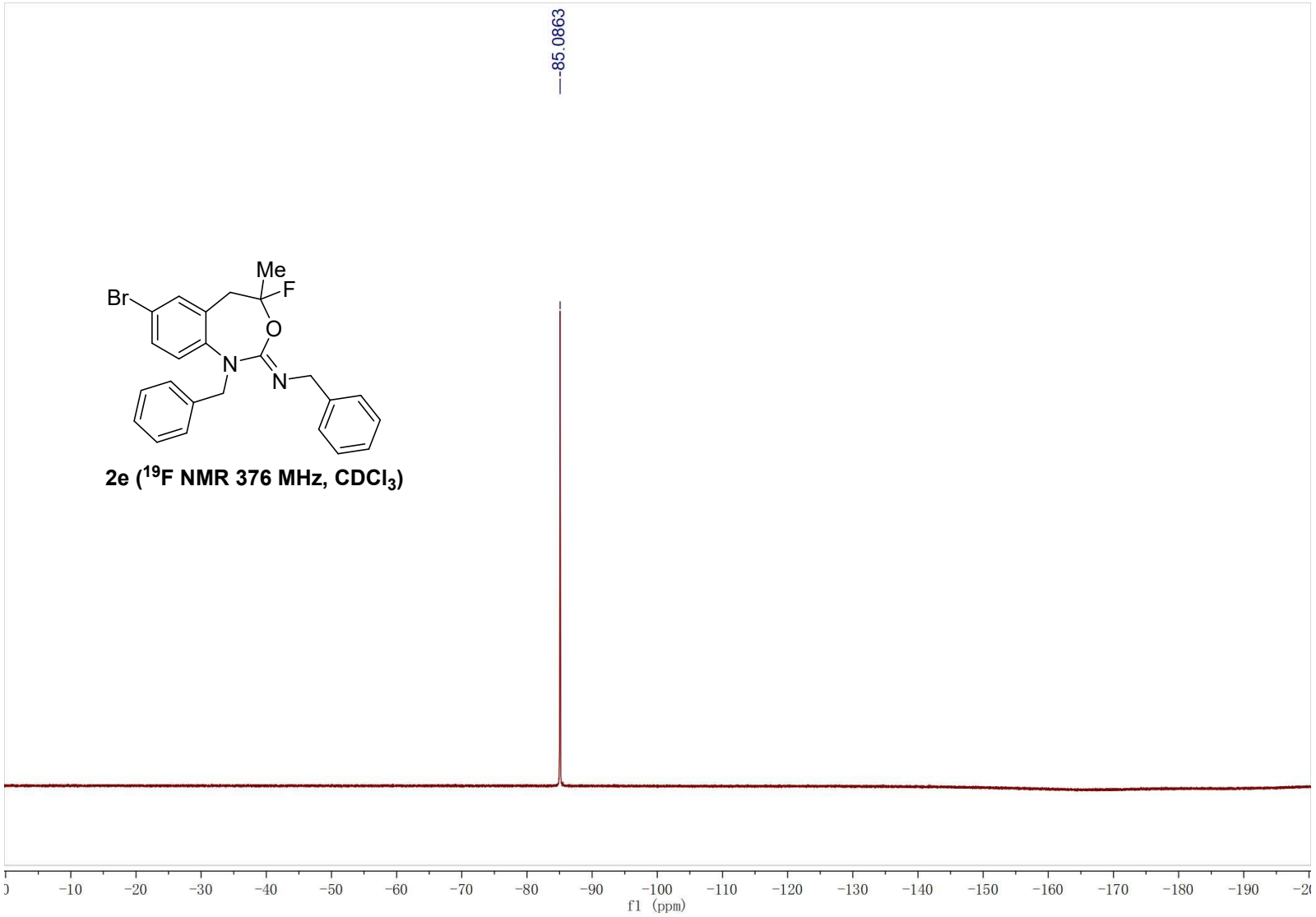
2d (^{19}F NMR 376 MHz, $CDCl_3$)



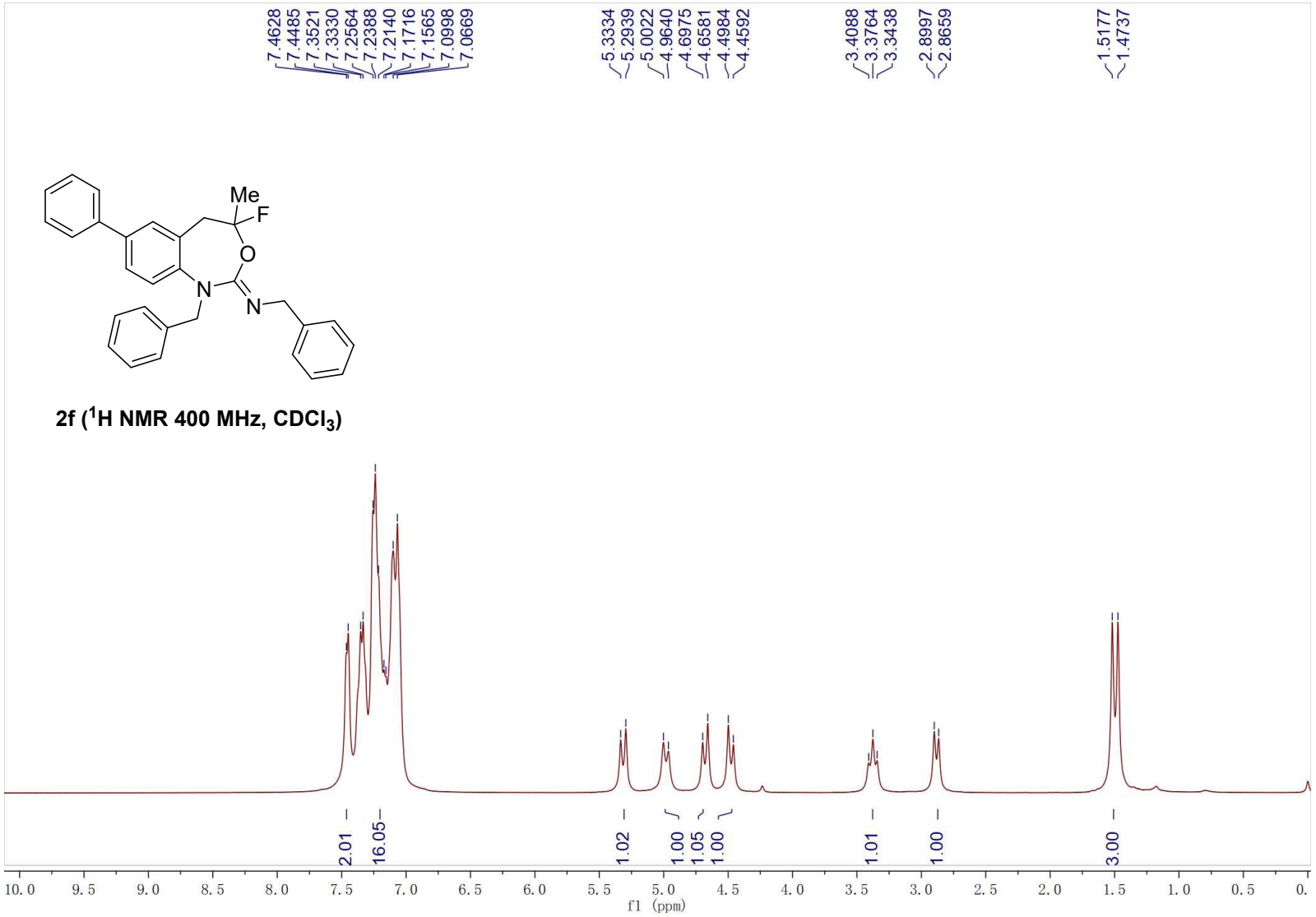
2e (^{1}H NMR 400 MHz, $CDCl_3$)



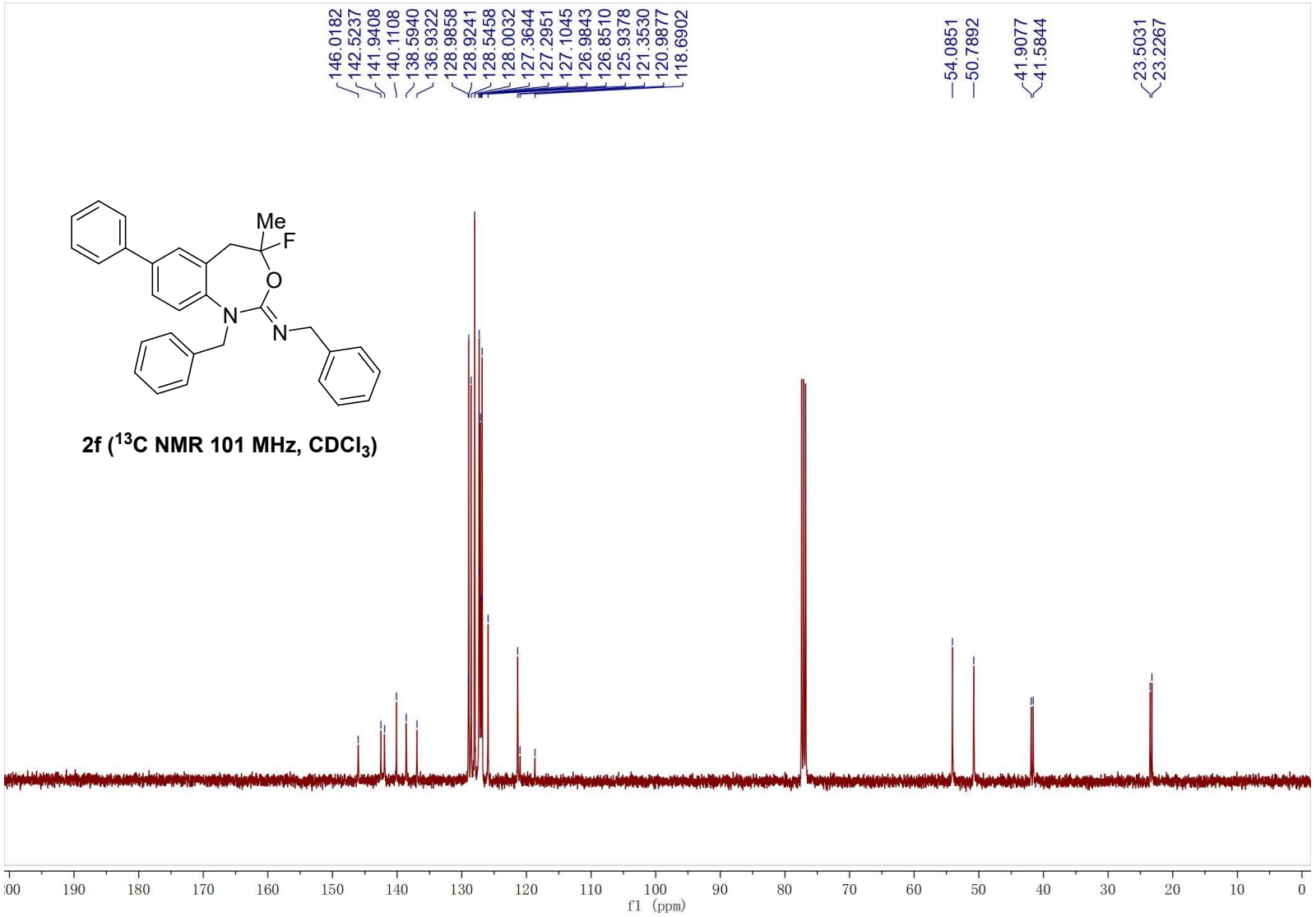
2e (^{13}C NMR 101 MHz, $CDCl_3$)



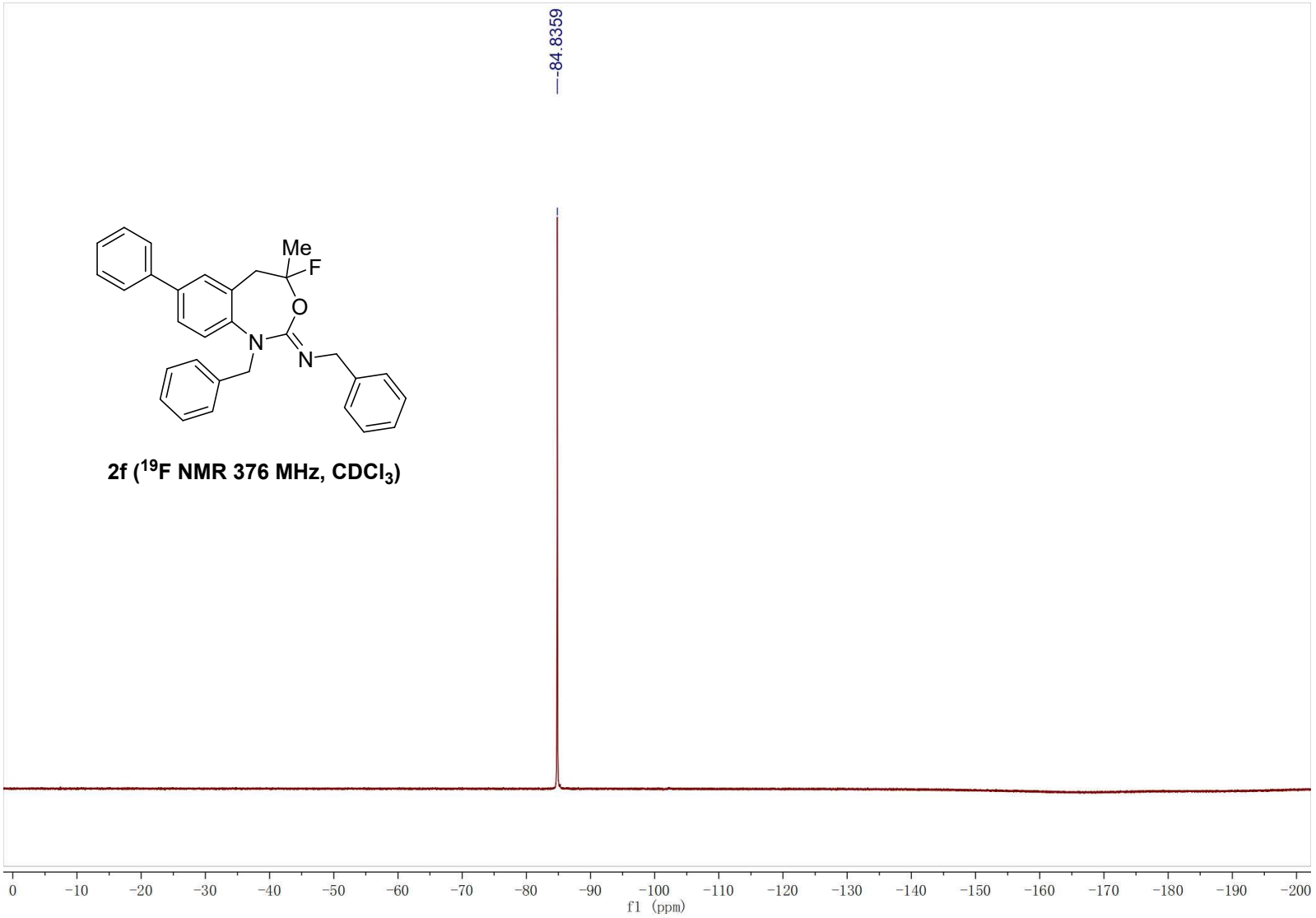
2e (^{19}F NMR 376 MHz, $CDCl_3$)



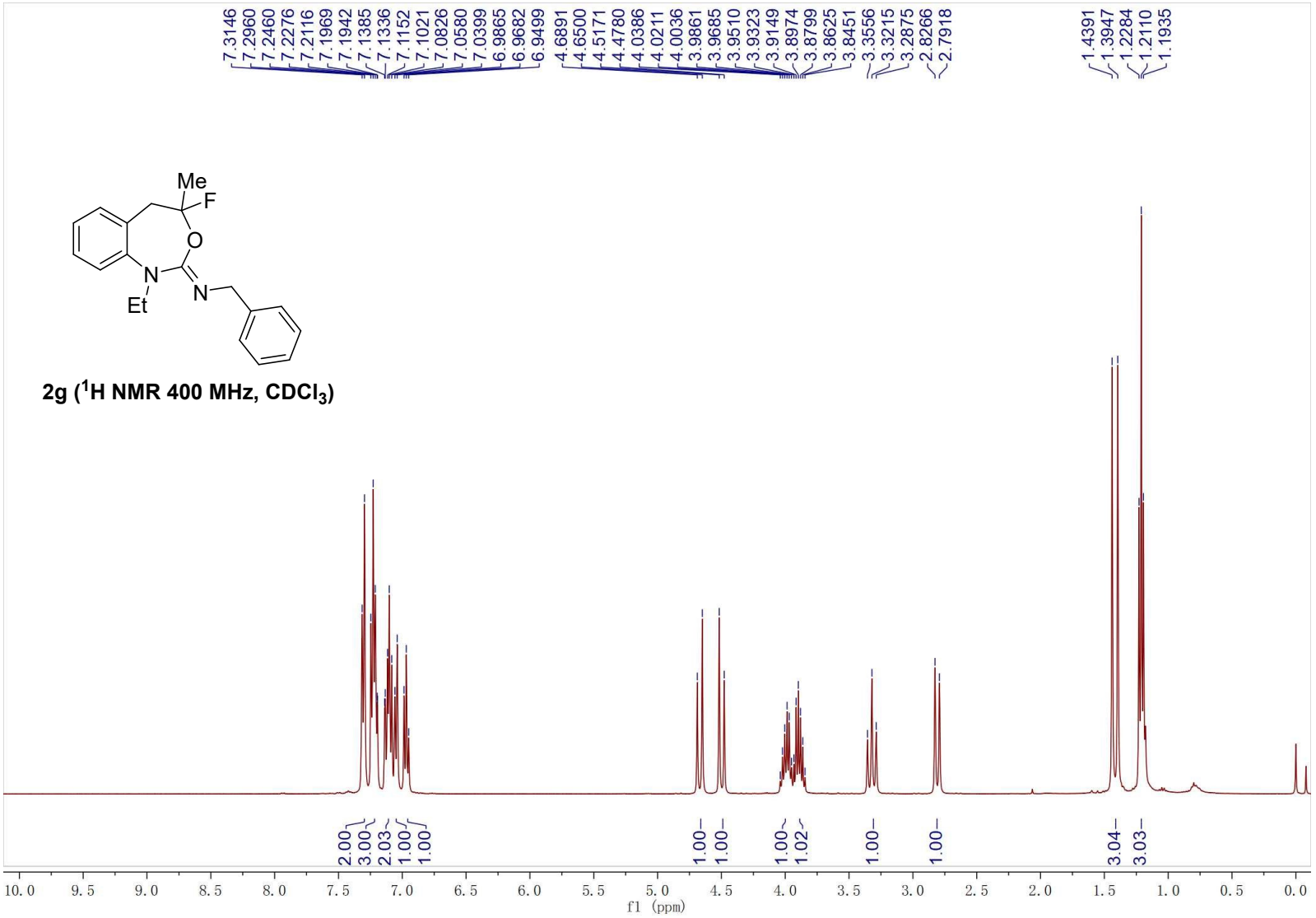
2f (^{1}H NMR 400 MHz, $CDCl_3$)



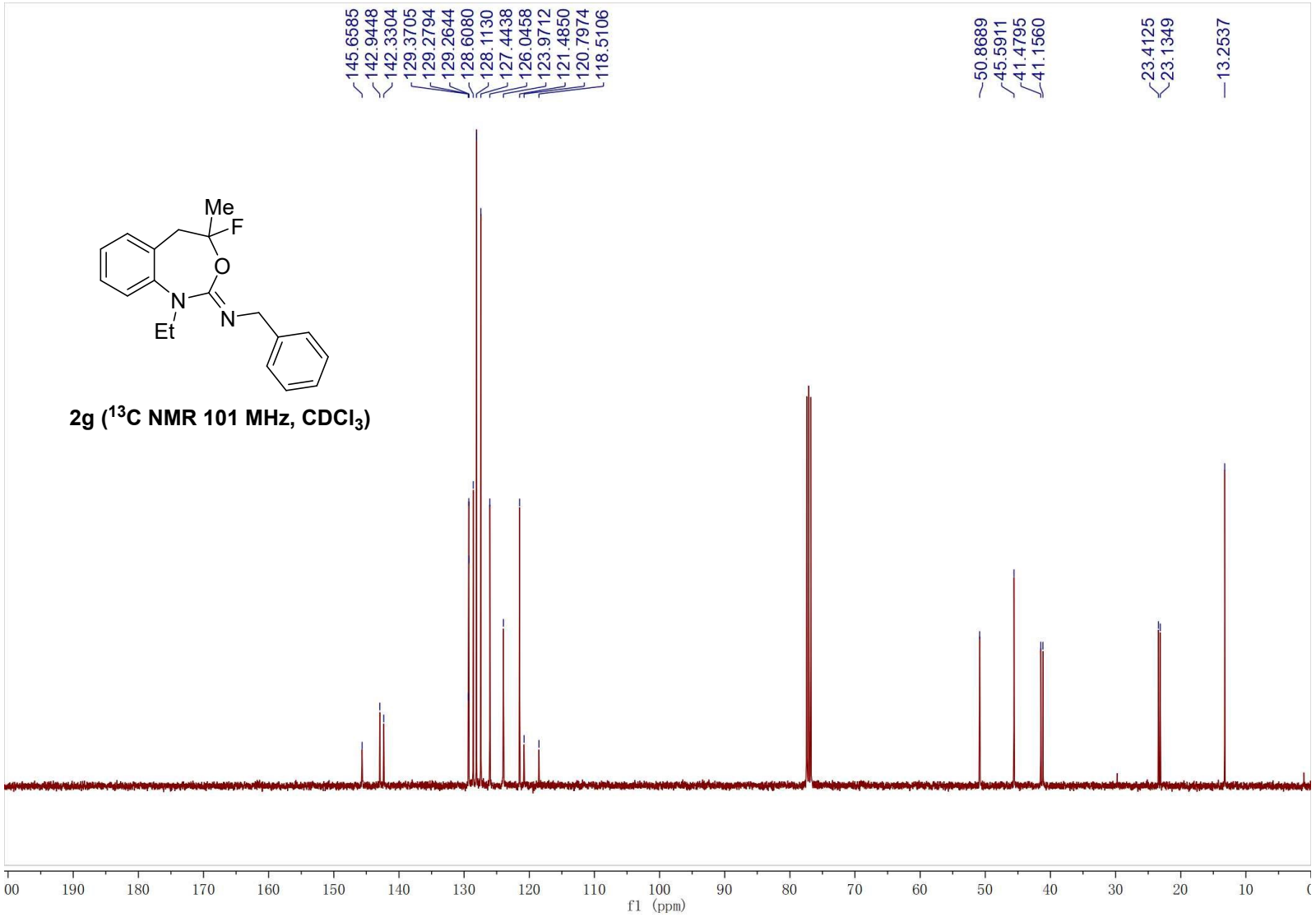
2f (^{13}C NMR 101 MHz, $CDCl_3$)



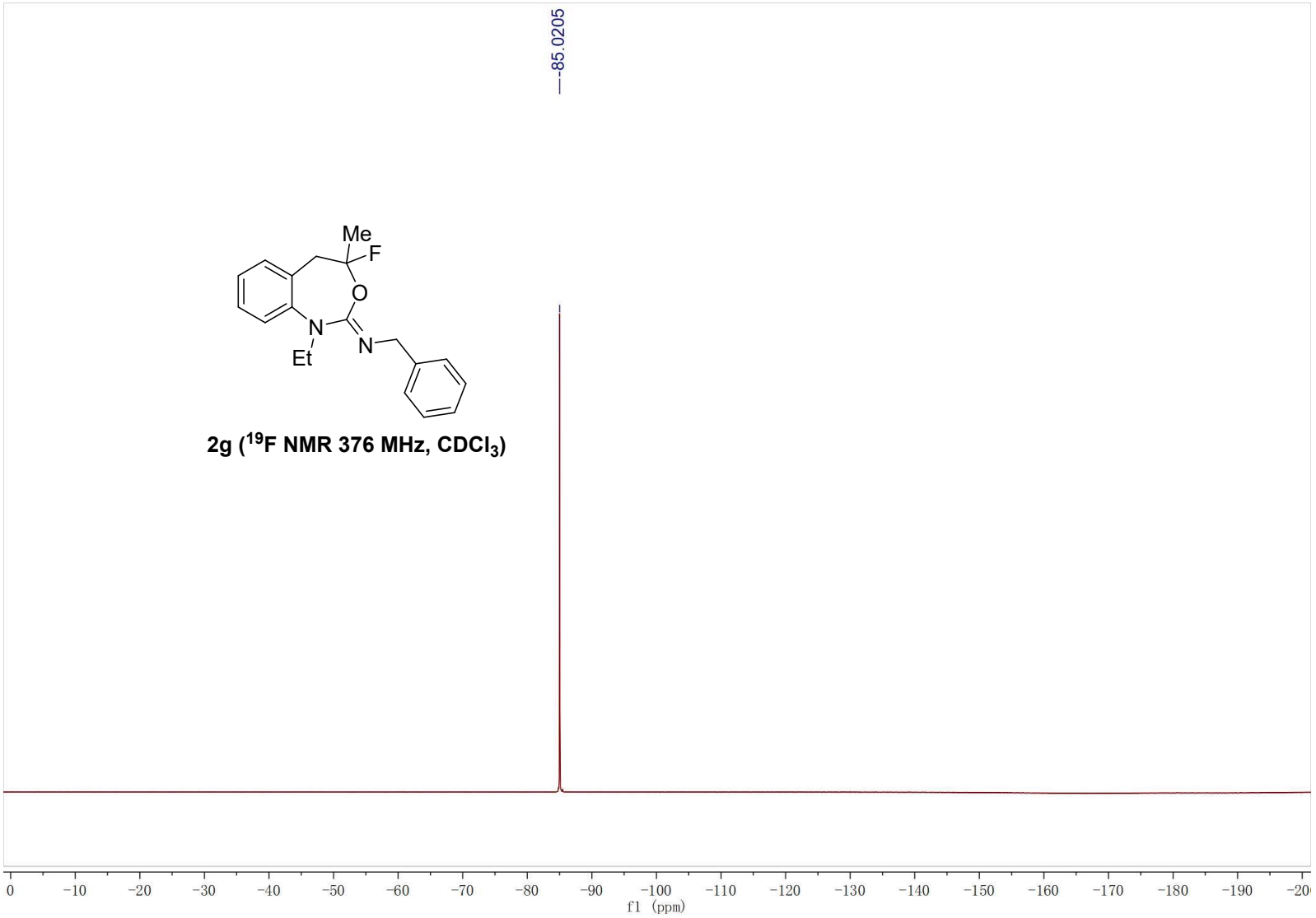
2f (^{19}F NMR 376 MHz, $CDCl_3$)



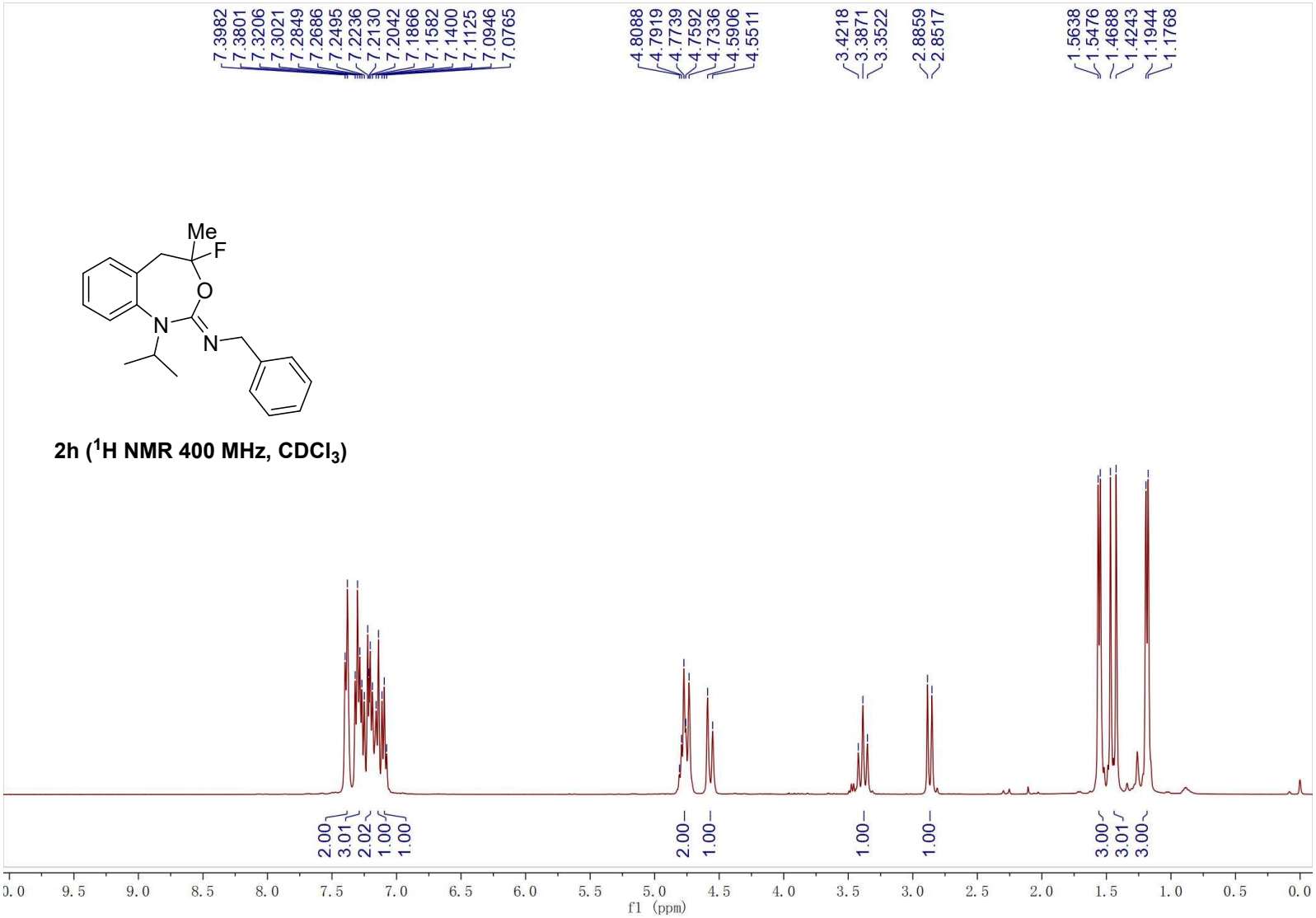
2g (^{1}H NMR 400 MHz, $CDCl_3$)



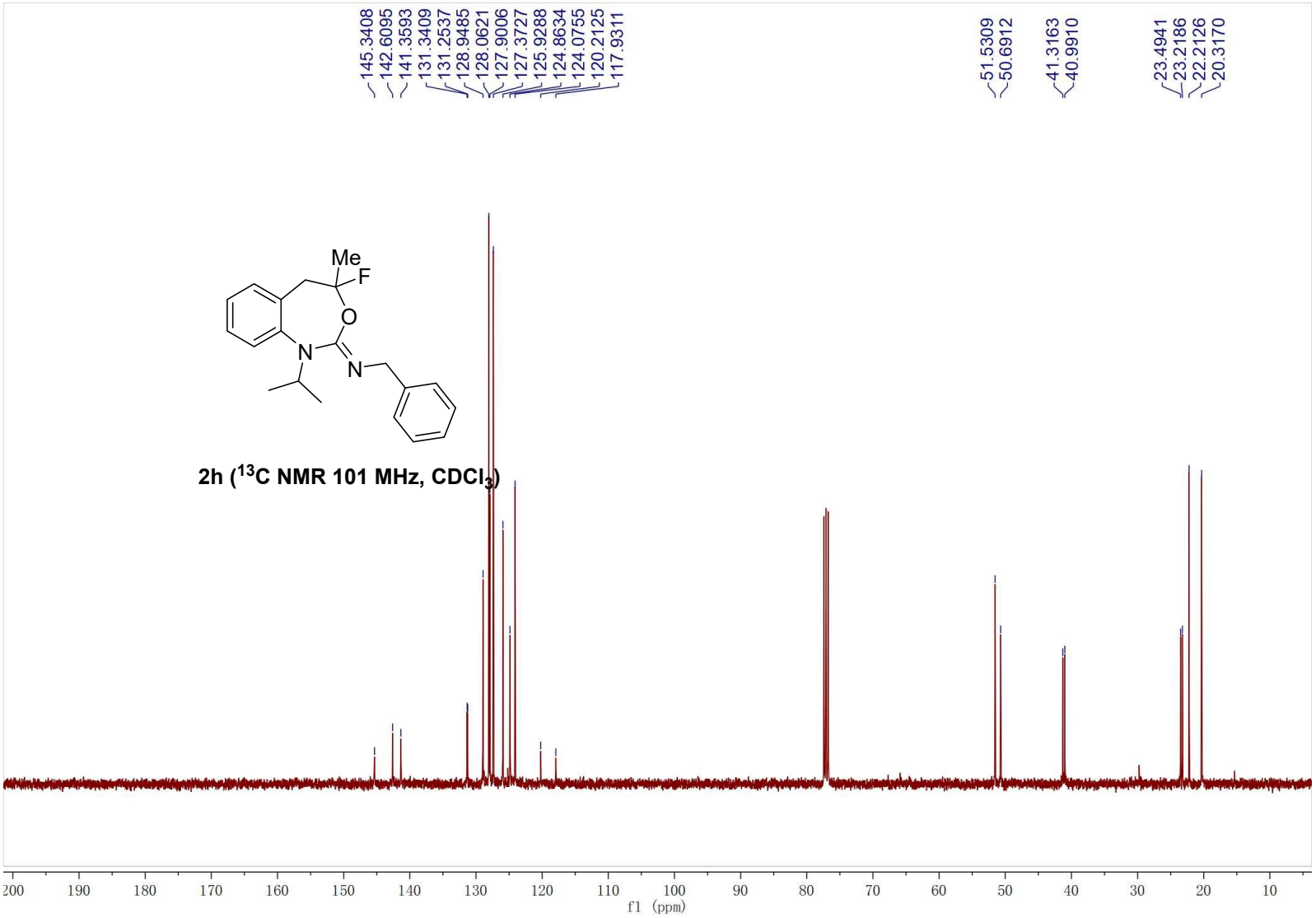
2g (^{13}C NMR 101 MHz, $CDCl_3$)

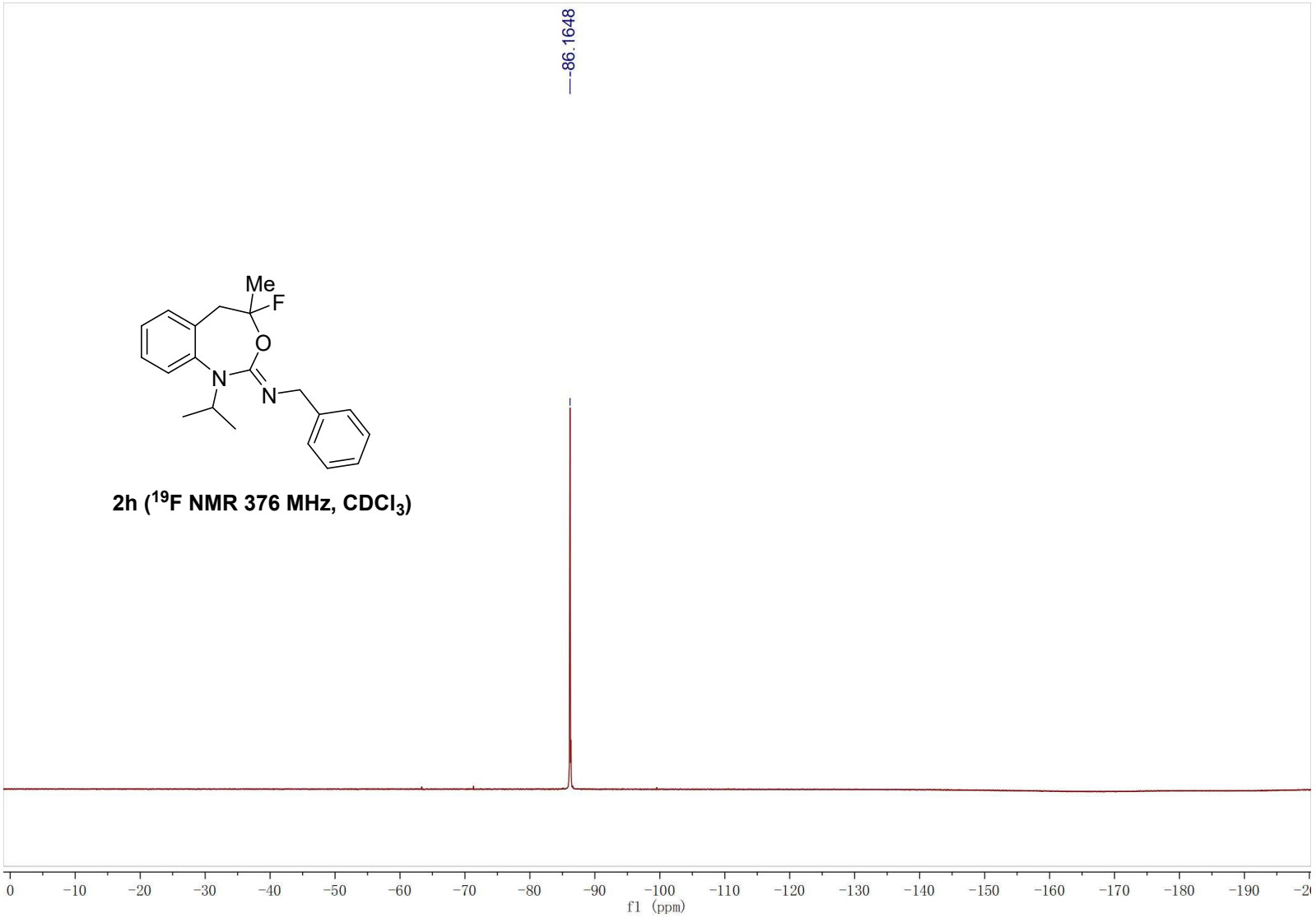


2g (^{19}F NMR 376 MHz, $CDCl_3$)

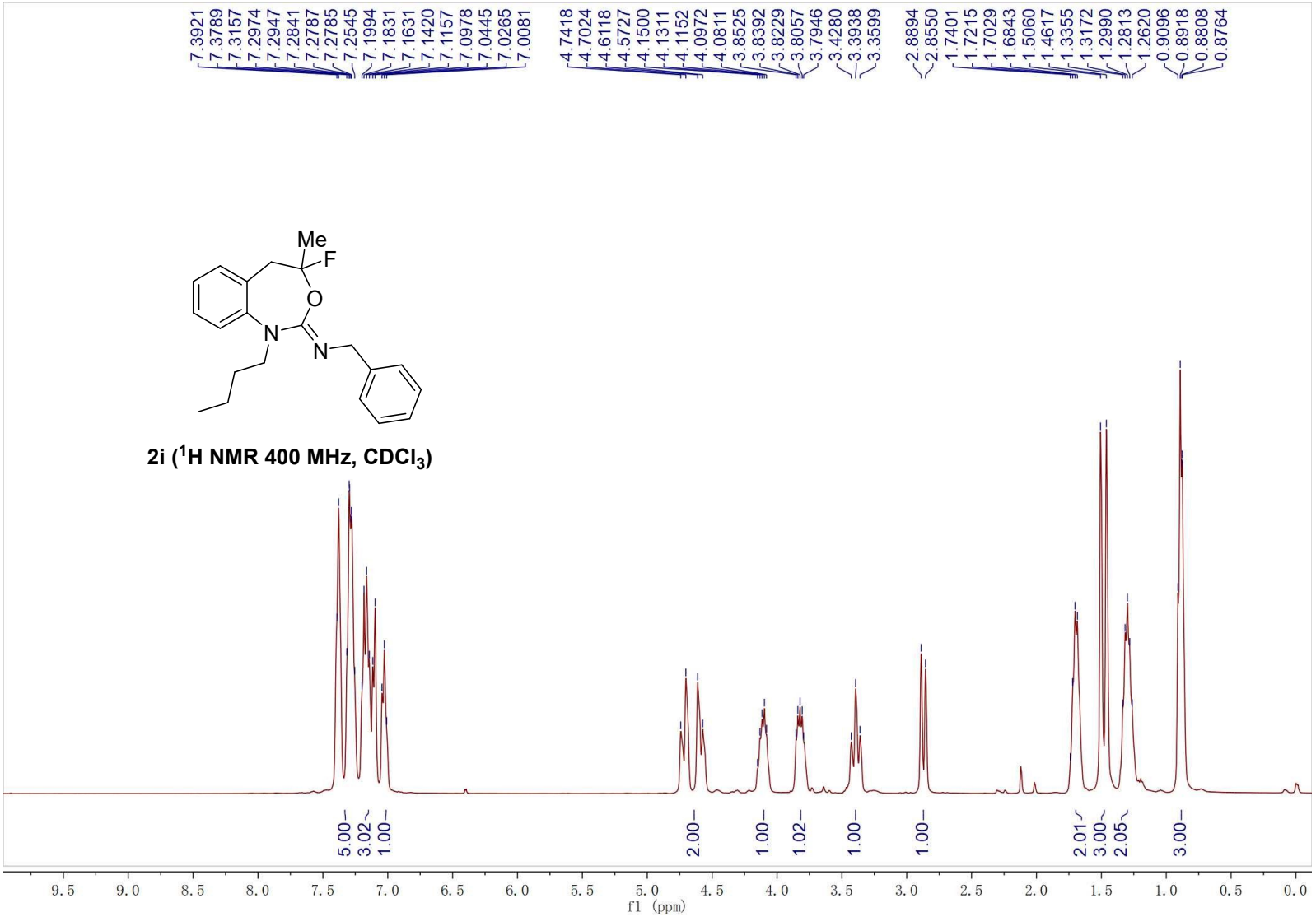


2h (^{1}H NMR 400 MHz, $CDCl_3$)

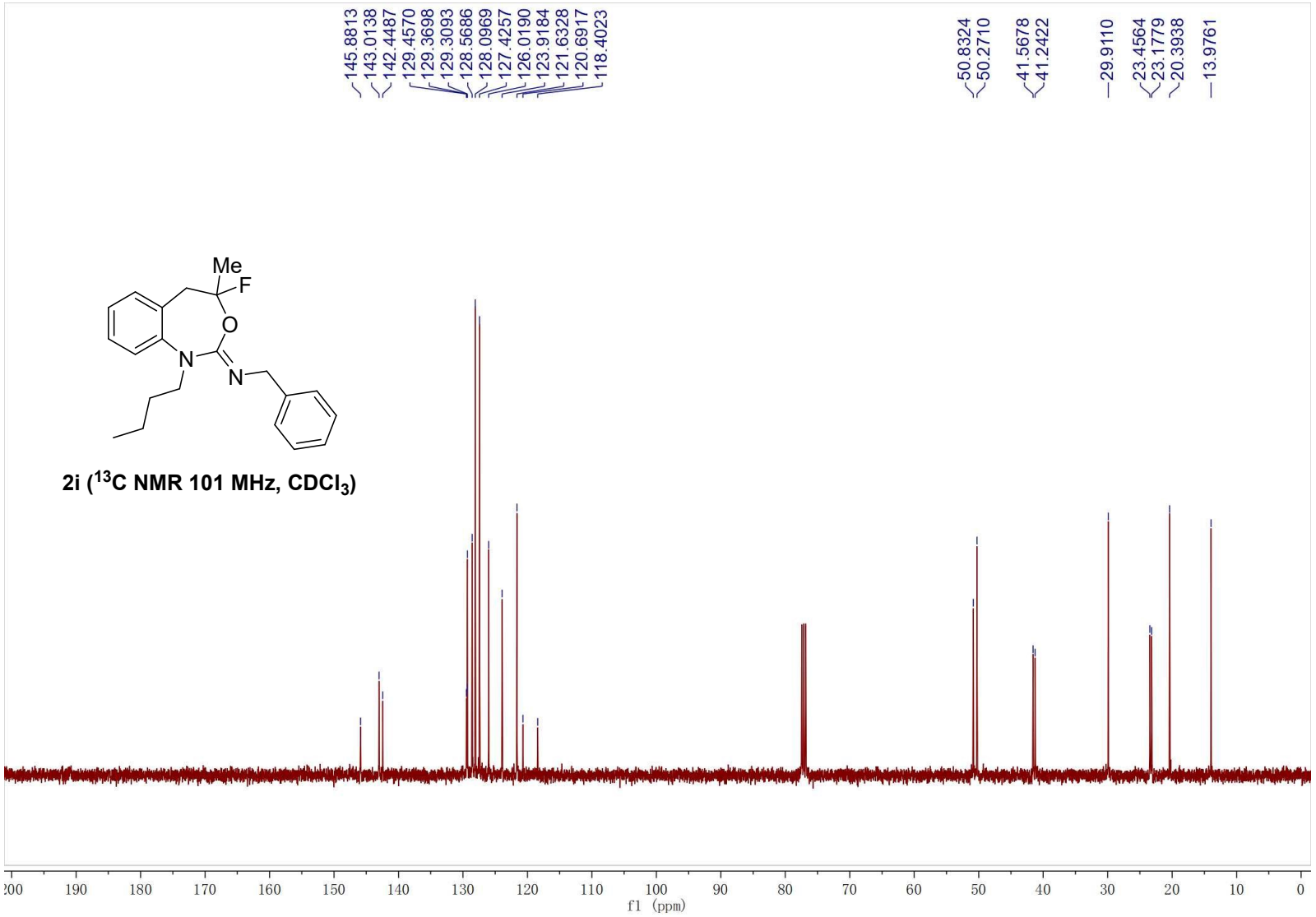

145.3408
142.6095
141.3593
131.3409
131.2537
128.9485
128.0621
127.9006
127.3727
125.9288
124.8634
124.0755
120.2125
117.9311
51.5309
50.6912
41.3163
40.9910
23.4941
23.2186
22.2126
20.3170
Me
F
O
N
N
2h (13C NMR 101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



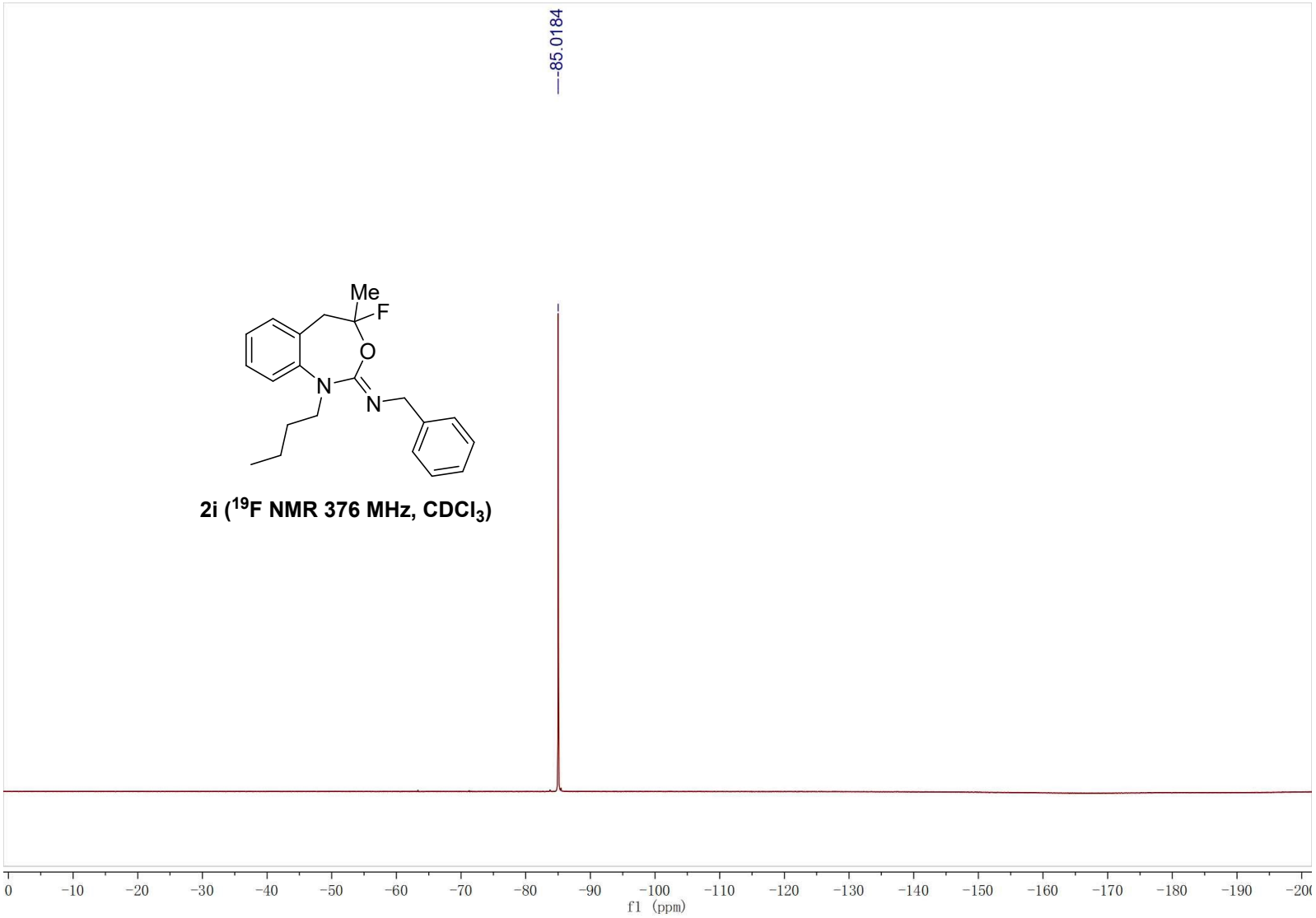
2h (^{19}F NMR 376 MHz, $CDCl_3$)



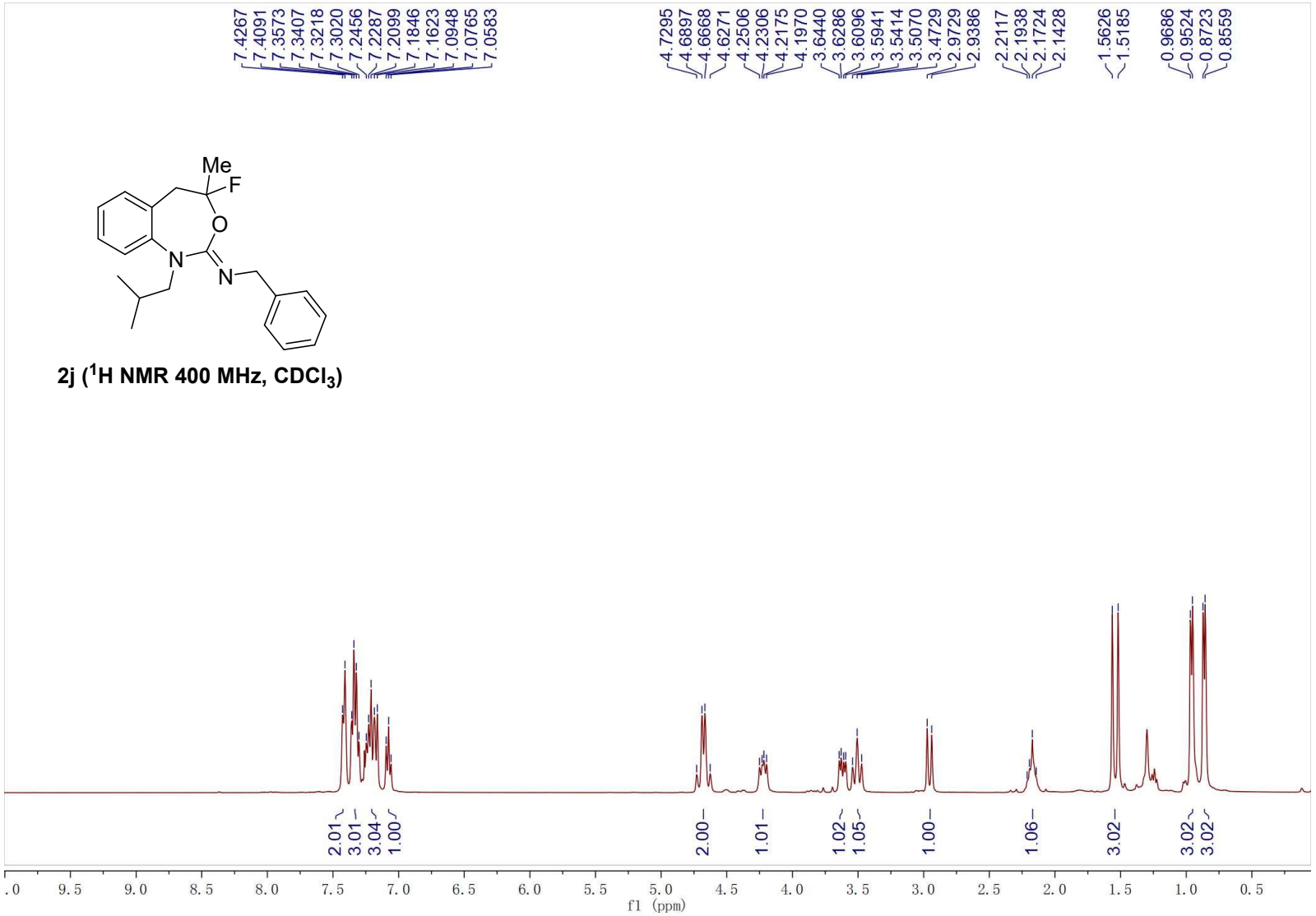
2i (^{1}H NMR 400 MHz, $CDCl_3$)



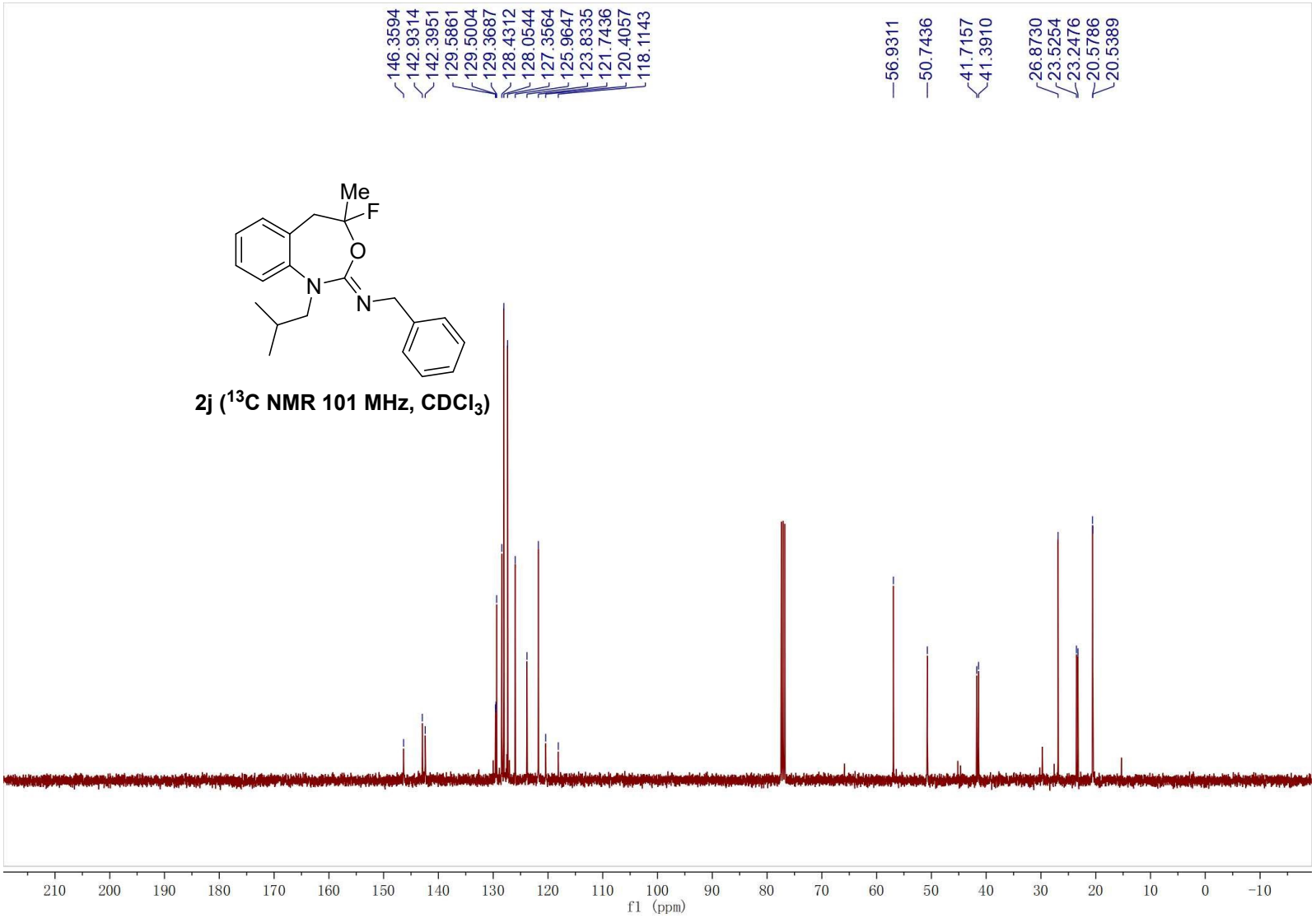
2i (^{13}C NMR 101 MHz, $CDCl_3$)



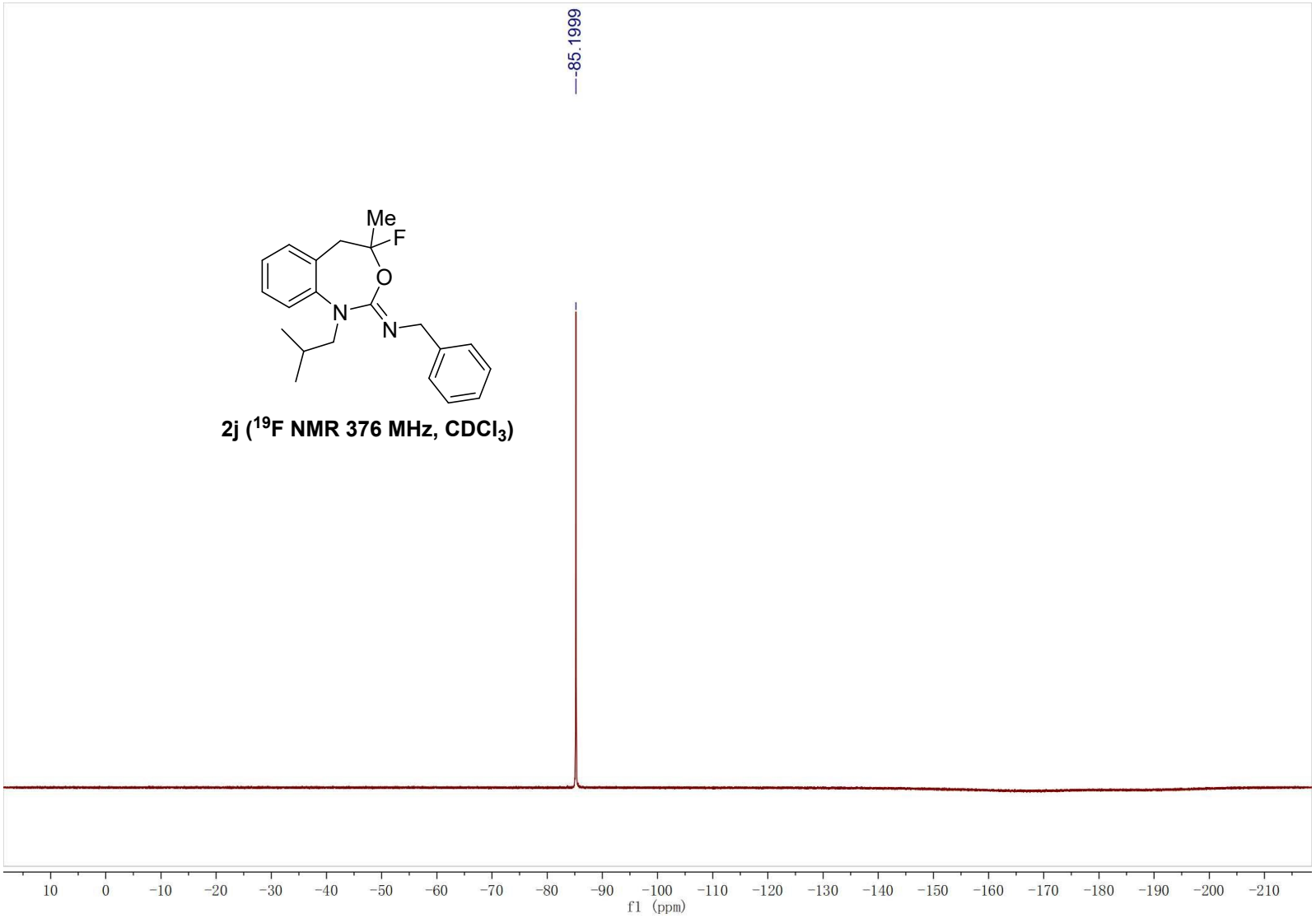
2i (^{19}F NMR 376 MHz, $CDCl_3$)



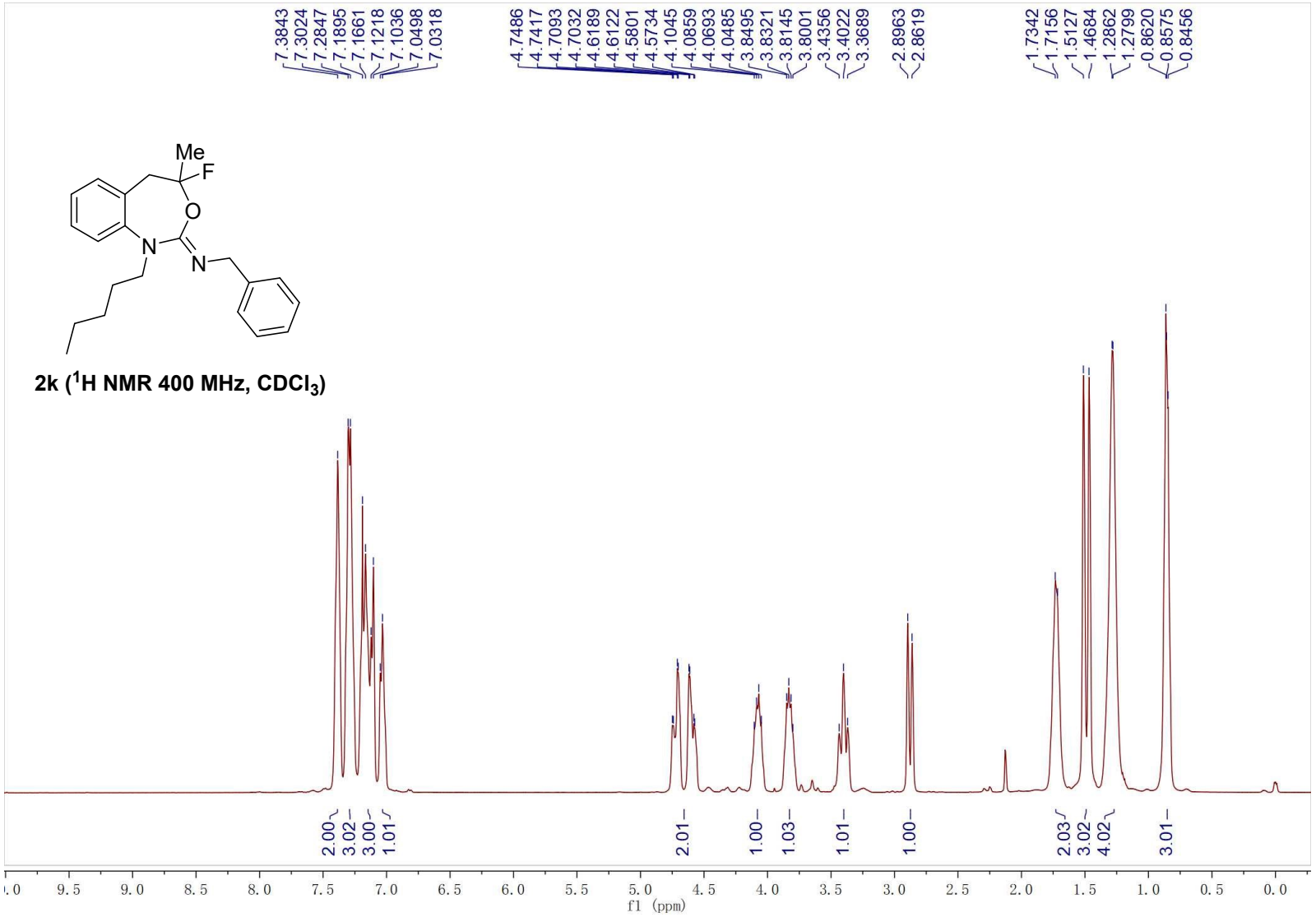
2j (^{1}H NMR 400 MHz, $CDCl_3$)

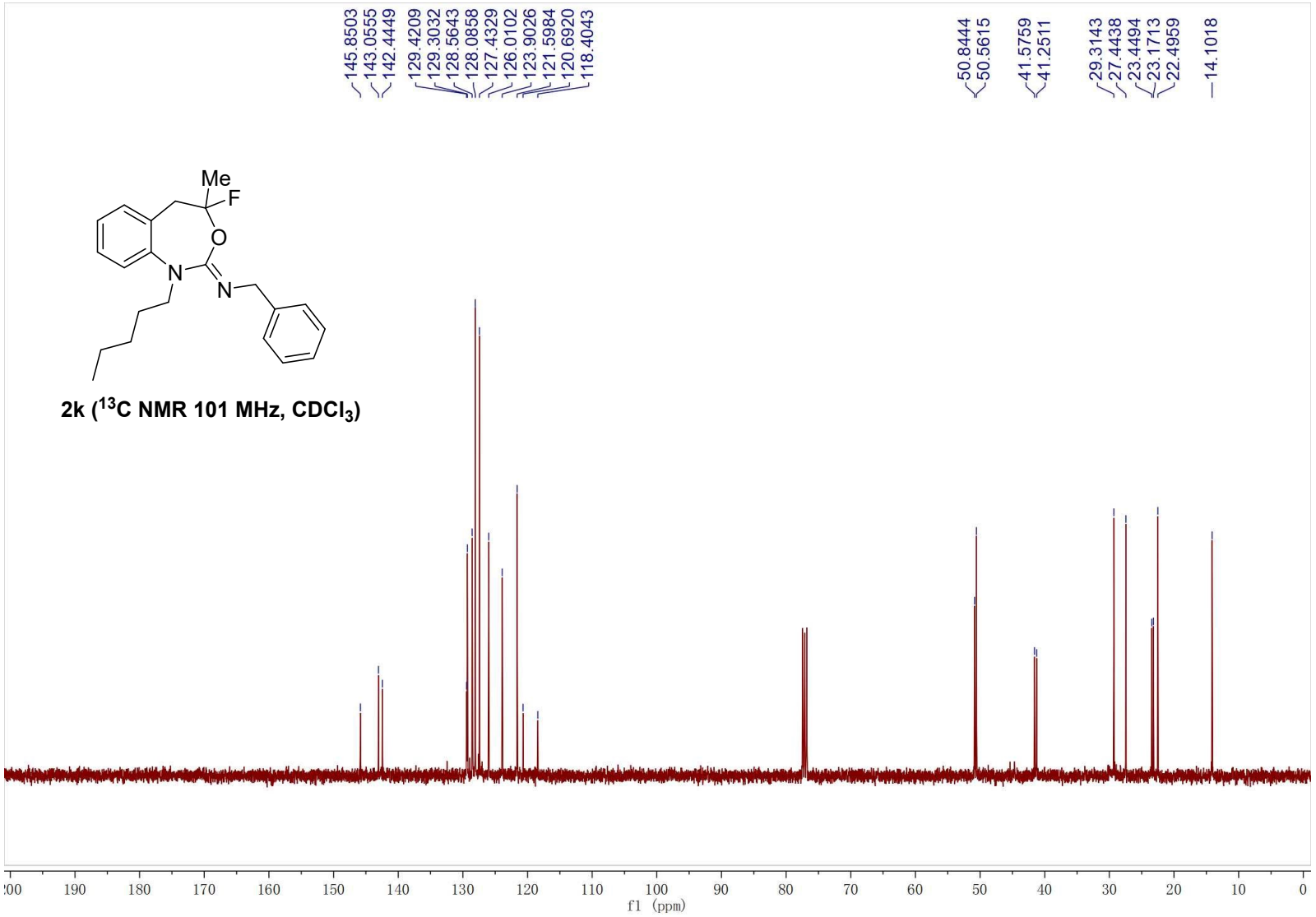


2j (^{13}C NMR 101 MHz, $CDCl_3$)

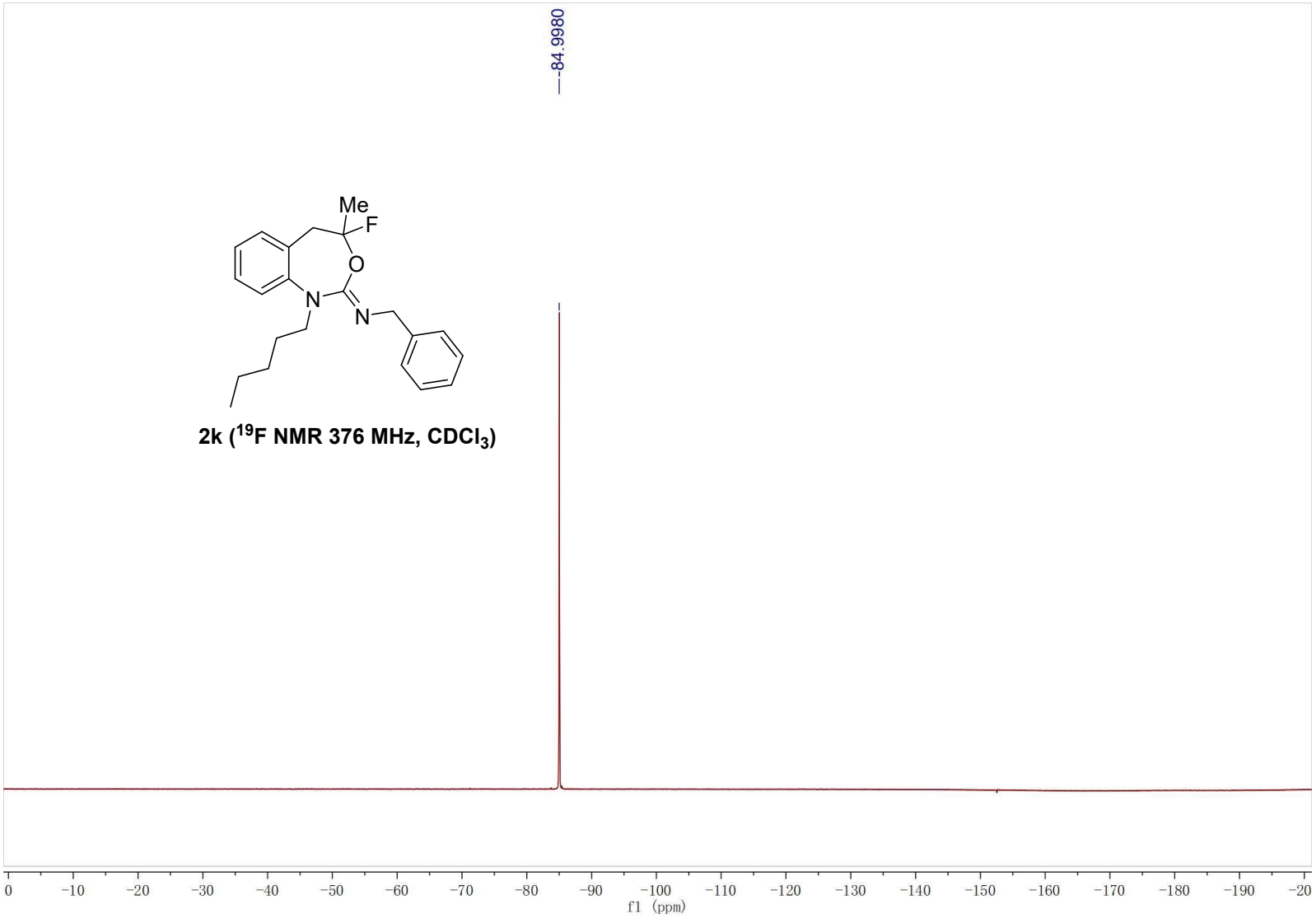


2j (^{19}F NMR 376 MHz, $CDCl_3$)

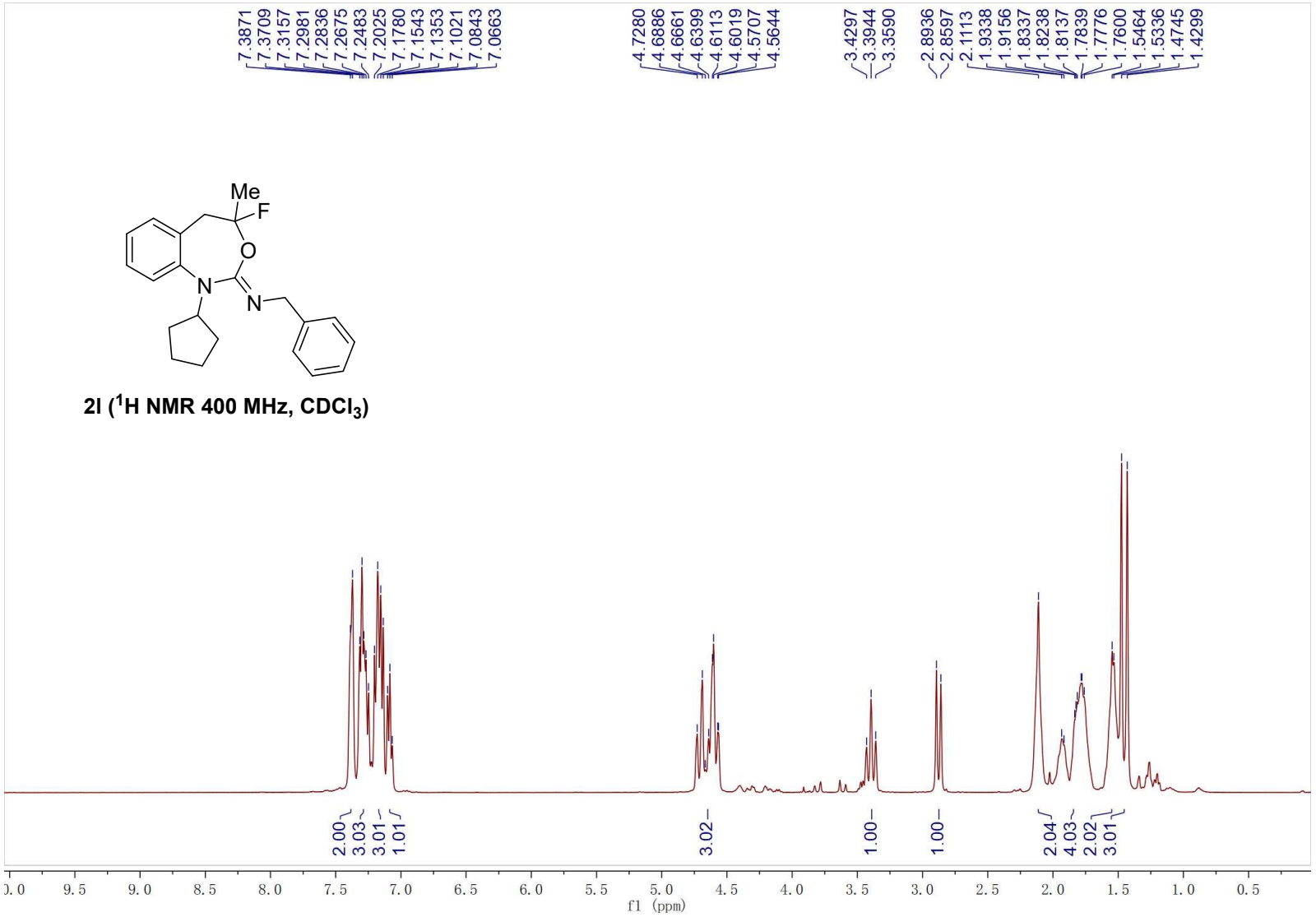

7.3843
7.3024
7.2847
7.1895
7.1661
7.1218
7.1036
7.0498
7.0318
4.7486
4.7417
4.7093
4.7032
4.6189
4.6122
4.5801
4.5734
4.1045
4.0859
4.0693
4.0485
3.8495
3.8321
3.8145
3.8001
3.4356
3.4022
3.3689
2.8963
2.8619
1.7342
1.7156
1.5127
1.4684
1.2862
1.2799
0.8620
0.8575
0.8456
Me
F
O
N
N
2k (1H NMR 400 MHz, CDCl3)
2.00
3.02
3.00
1.01
2.01
1.00
1.03
1.01
1.00
2.03
3.02
4.02
3.01
f1 (ppm)



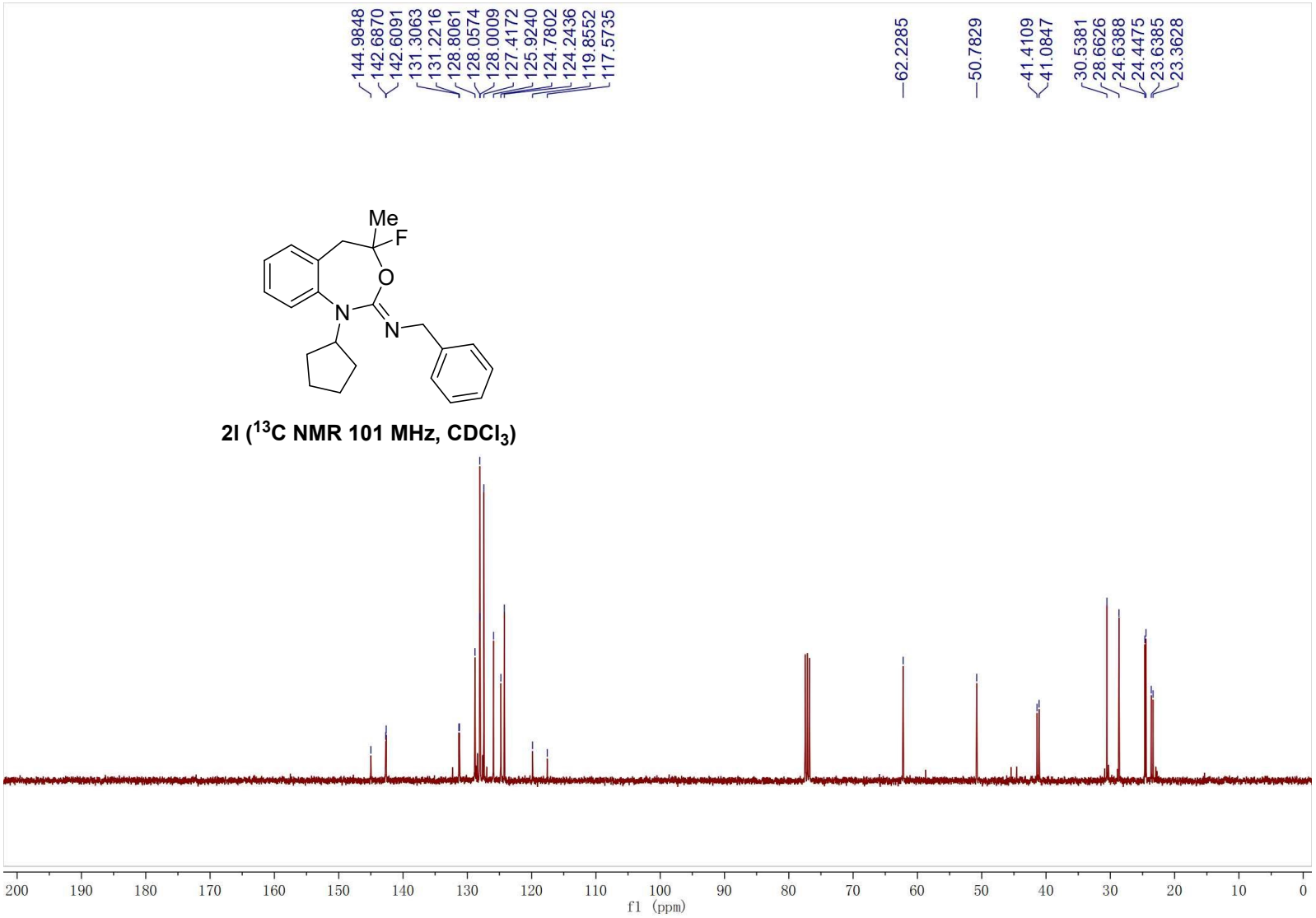
2k (^{13}C NMR 101 MHz, $CDCl_3$)



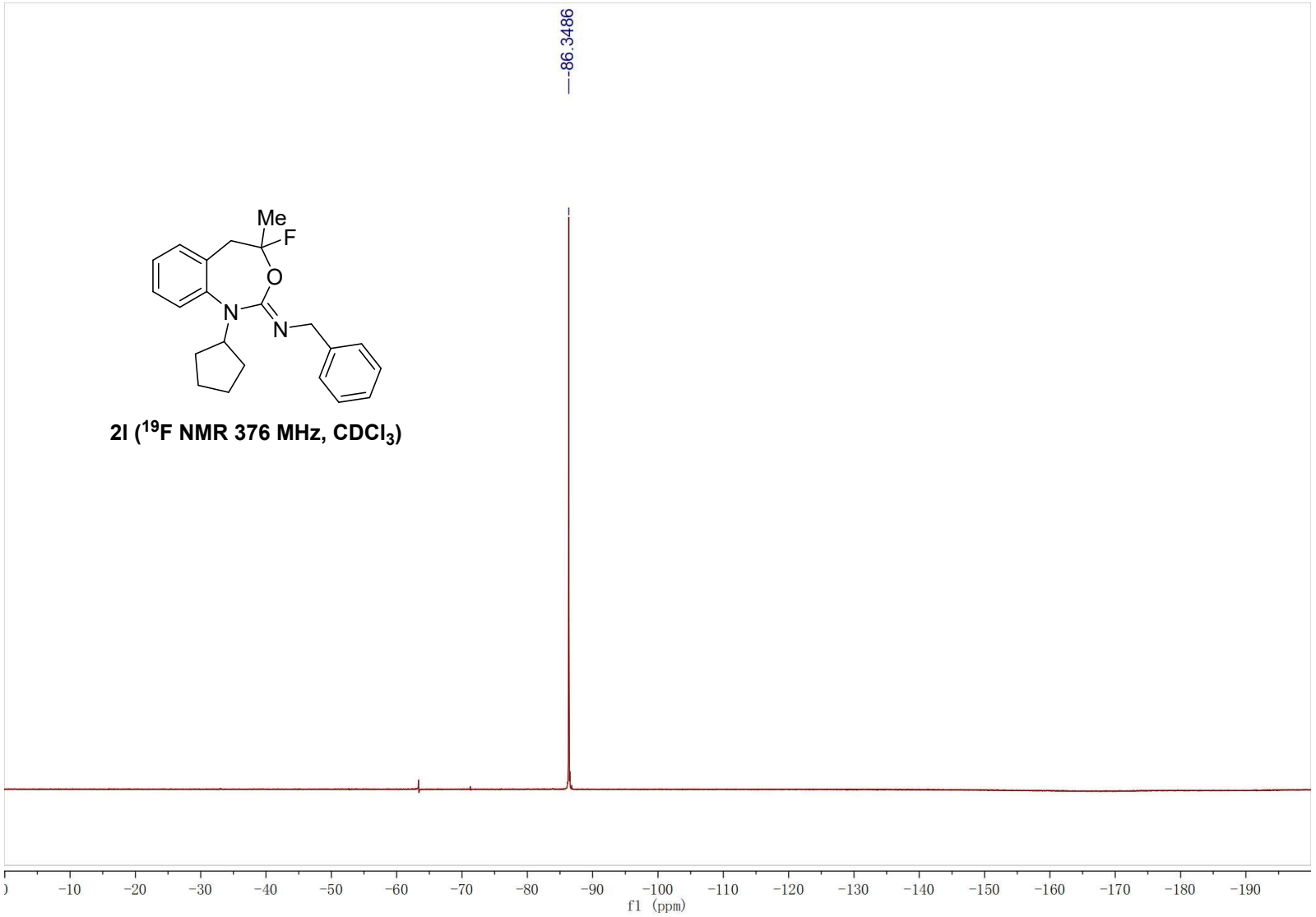
2k (^{19}F NMR 376 MHz, $CDCl_3$)



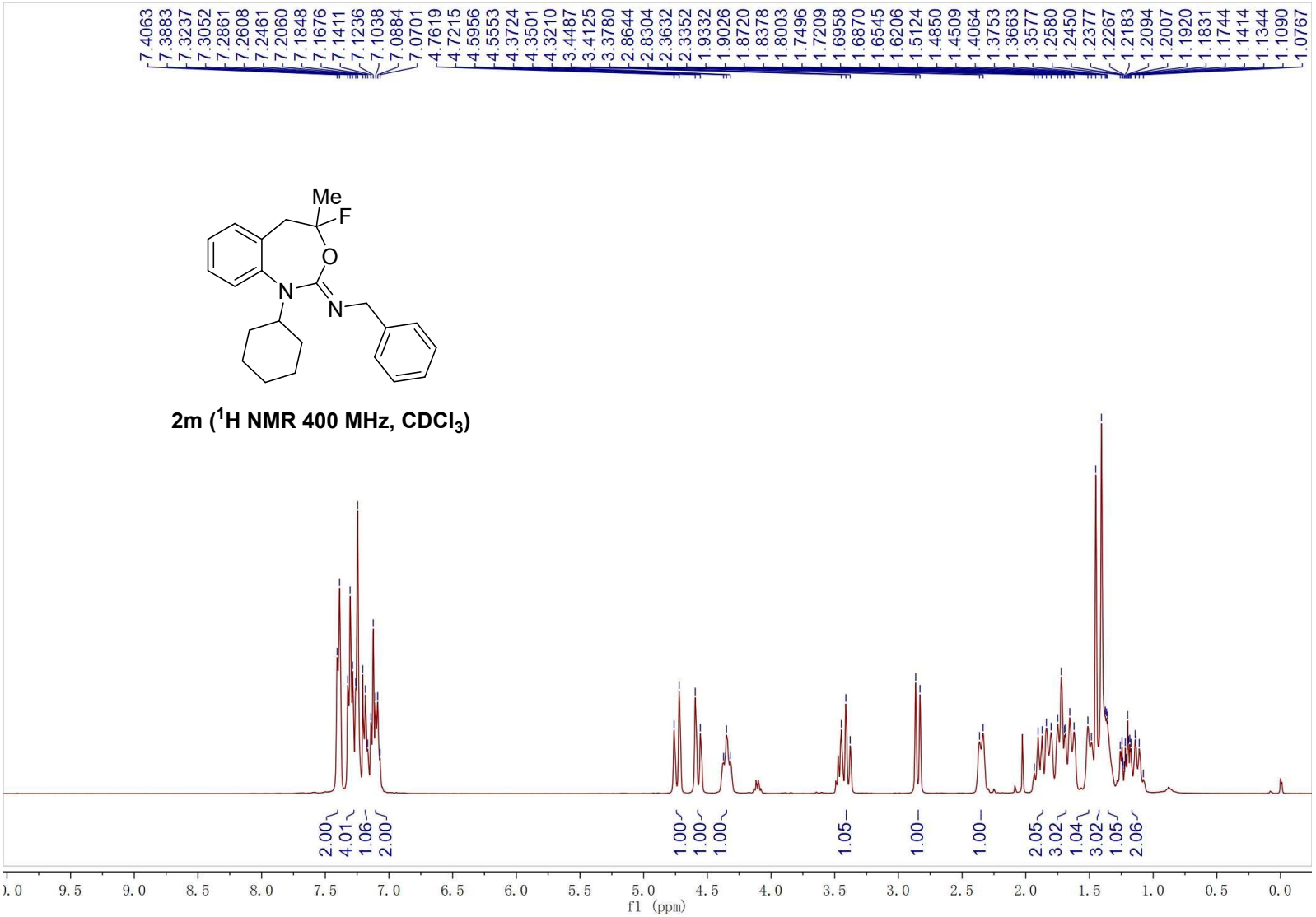
2l (^{1}H NMR 400 MHz, $CDCl_3$)

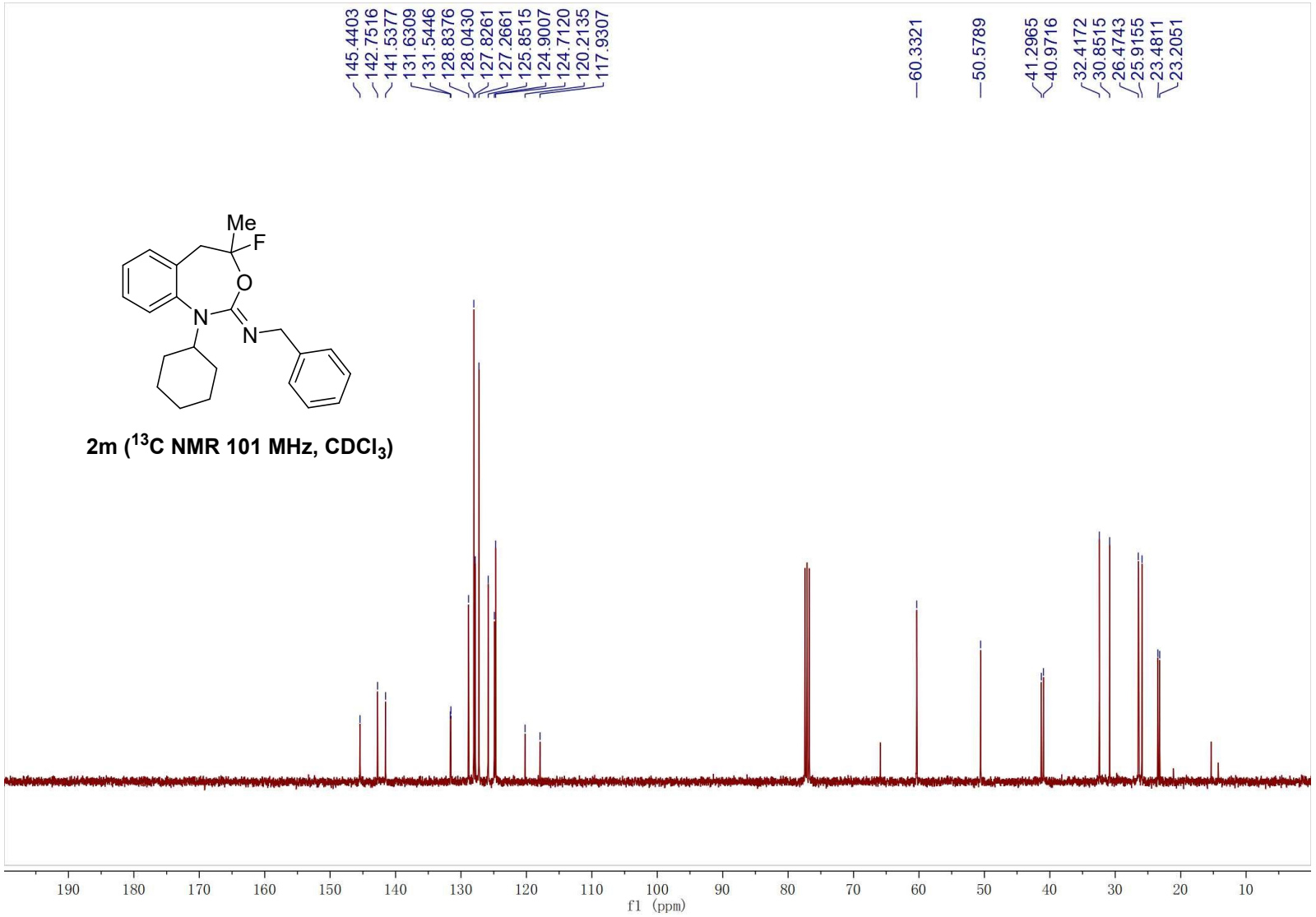


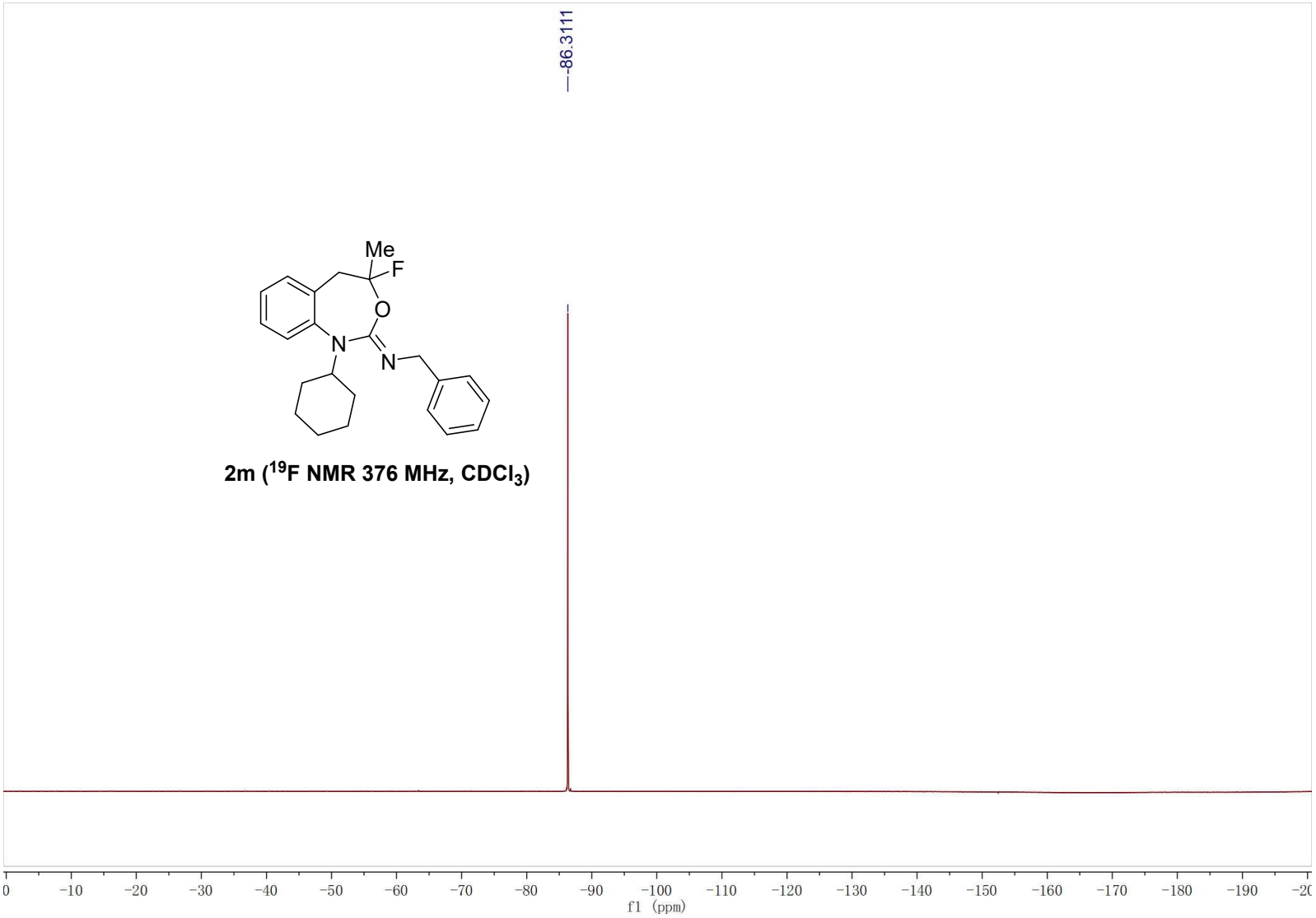
2l (^{13}C NMR 101 MHz, $CDCl_3$)



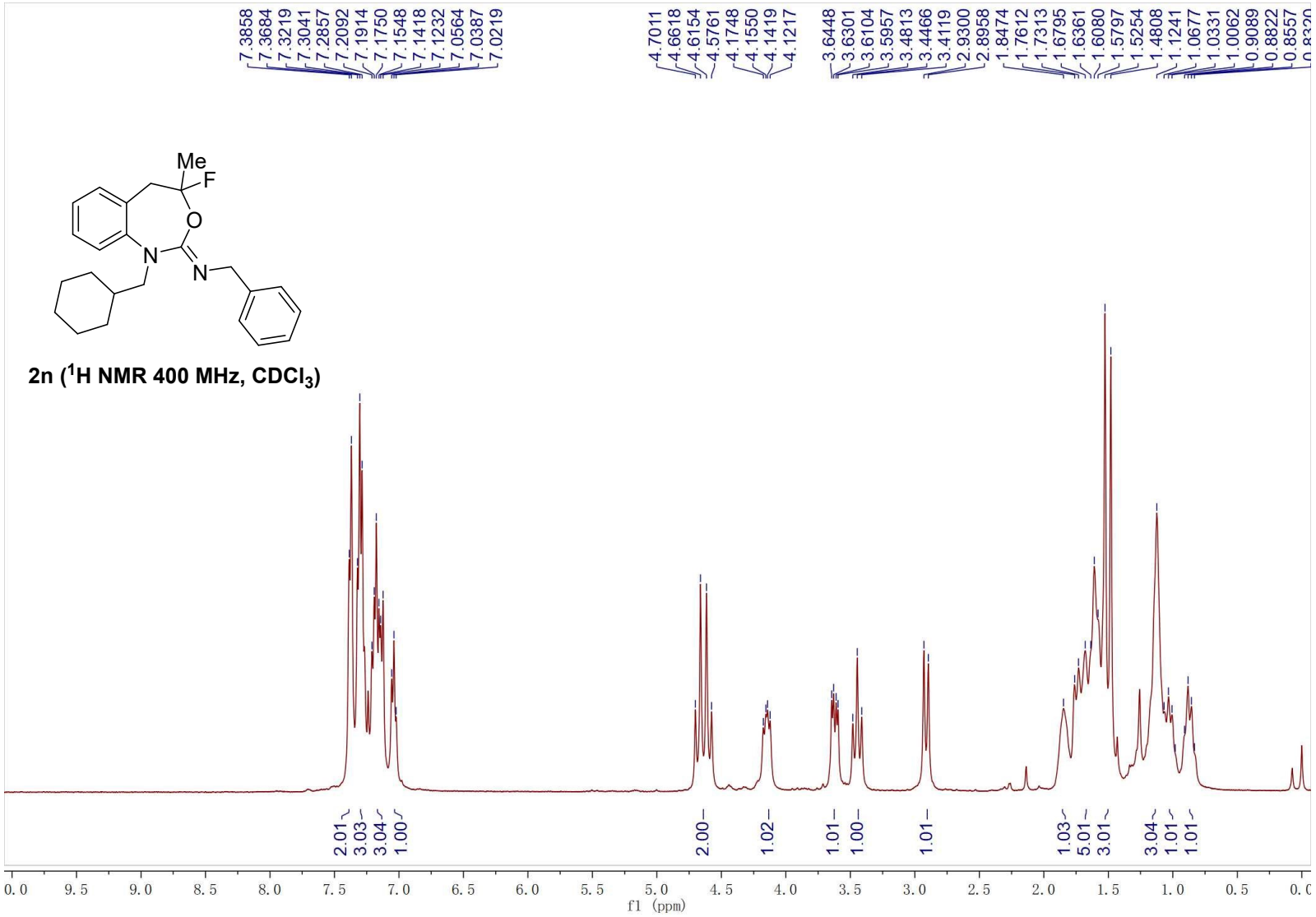
2l (^{19}F NMR 376 MHz, $CDCl_3$)

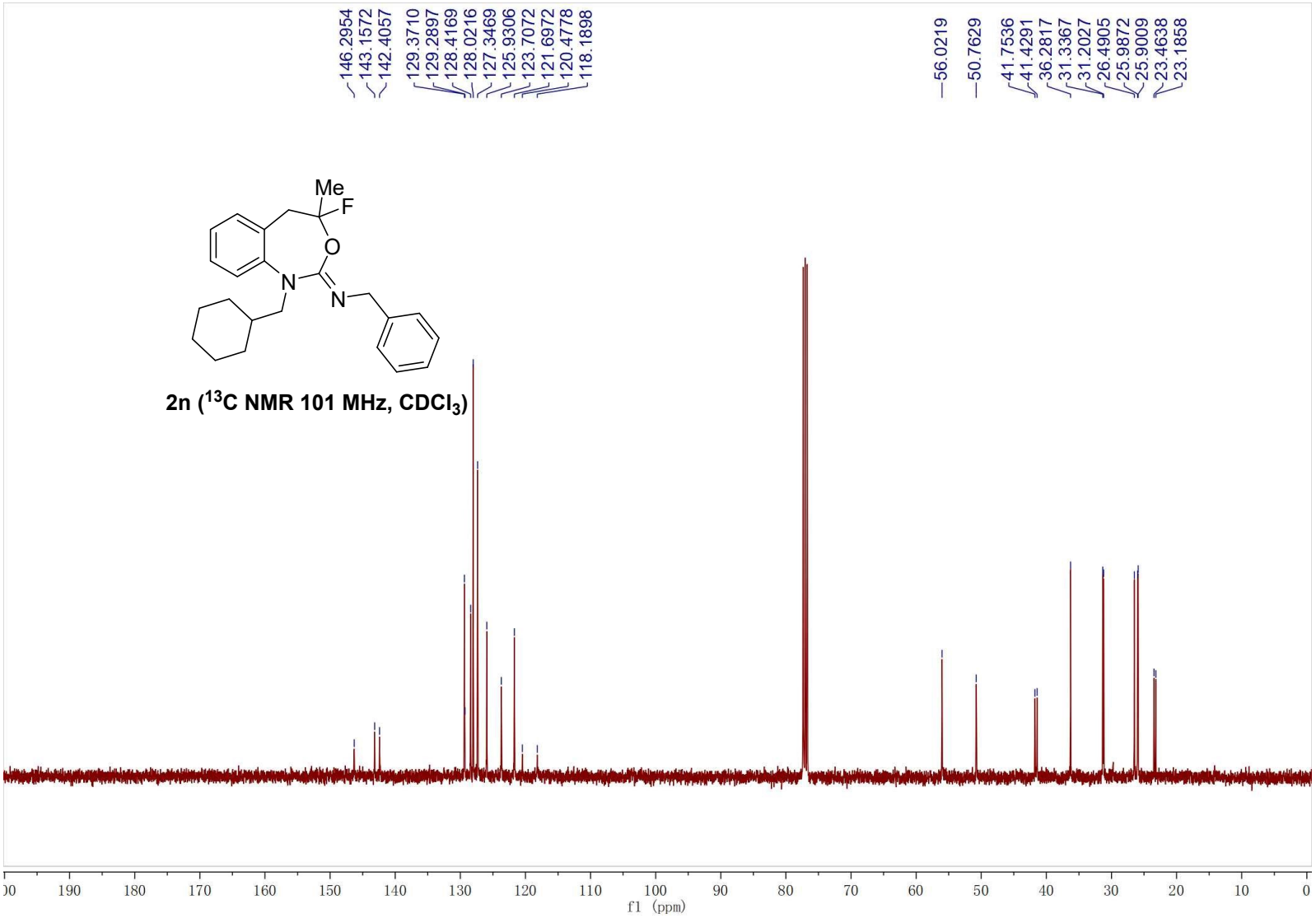

7.4063
7.3883
7.3237
7.3052
7.2861
7.2608
7.2461
7.2060
7.1848
7.1676
7.1411
7.1236
7.1038
7.0884
7.0701
4.7619
4.7215
4.5956
4.5553
4.3724
4.3501
4.3210
3.4487
3.4125
3.3780
2.8644
2.8304
2.3632
2.3352
1.9332
1.9026
1.8720
1.8378
1.8003
1.7496
1.7209
1.6958
1.6870
1.6545
1.6206
1.5124
1.4850
1.4509
1.4064
1.3753
1.3663
1.3577
1.2580
1.2450
1.2377
1.2267
1.2183
1.2094
1.2007
1.1920
1.1831
1.1744
1.1414
1.1344
1.1090
1.0767
Me
F
O
N
N
2m (^{1}H NMR 400 MHz, $CDCl_3$)
2.00
4.01
1.06
2.00
1.00
1.00
1.00
1.05
1.00
1.00
2.05
3.02
1.04
3.02
1.05
2.06
f1 (ppm)


145.4403
142.7516
141.5377
131.6309
131.5446
128.8376
128.0430
127.8261
127.2661
125.8515
124.9007
124.7120
120.2135
117.9307
60.3321
50.5789
41.2965
40.9716
32.4172
30.8515
26.4747
25.9155
23.4811
23.2051
Me
F
O
N
N
2m (^{13}C NMR 101 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

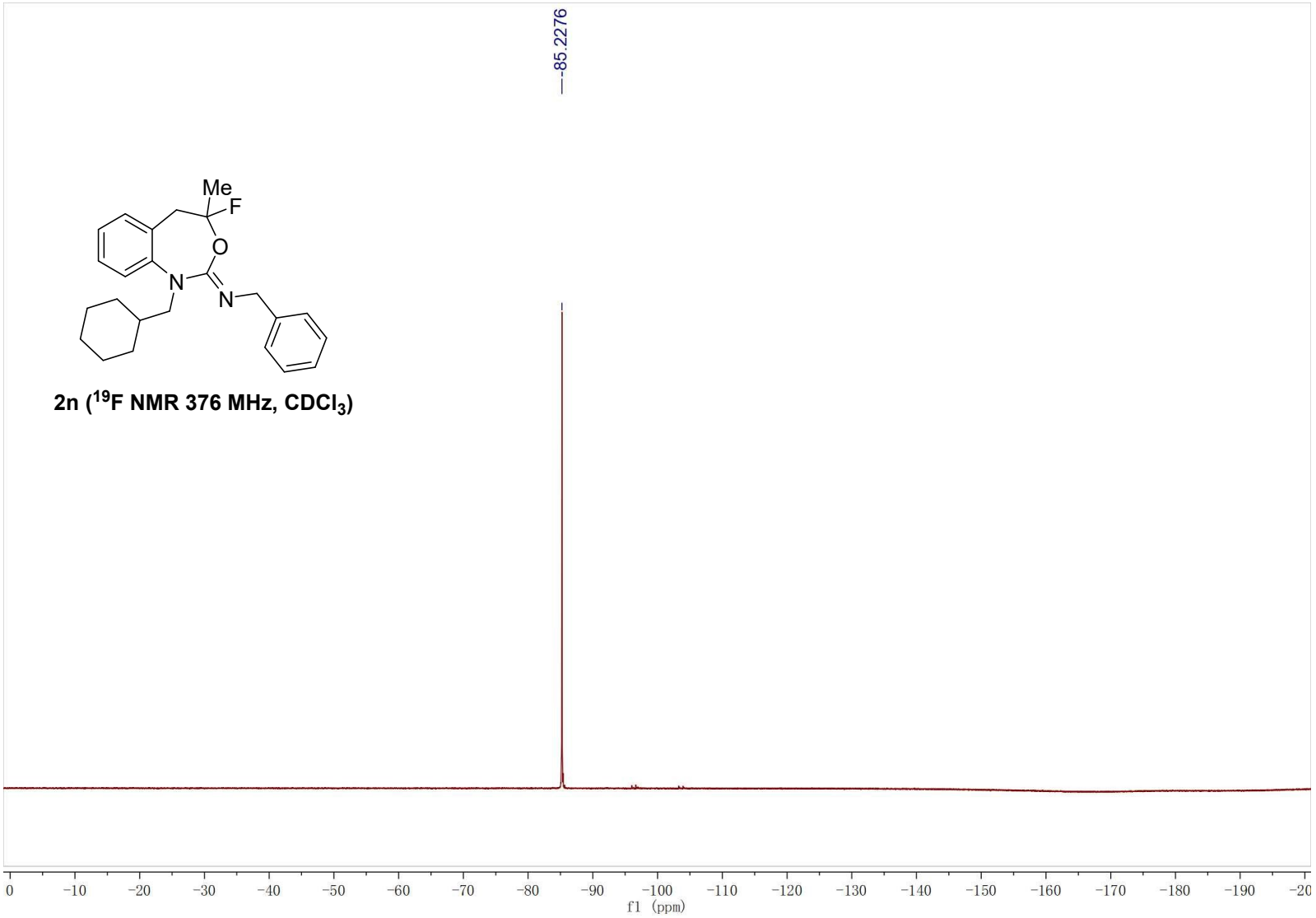


2m (^{19}F NMR 376 MHz, $CDCl_3$)

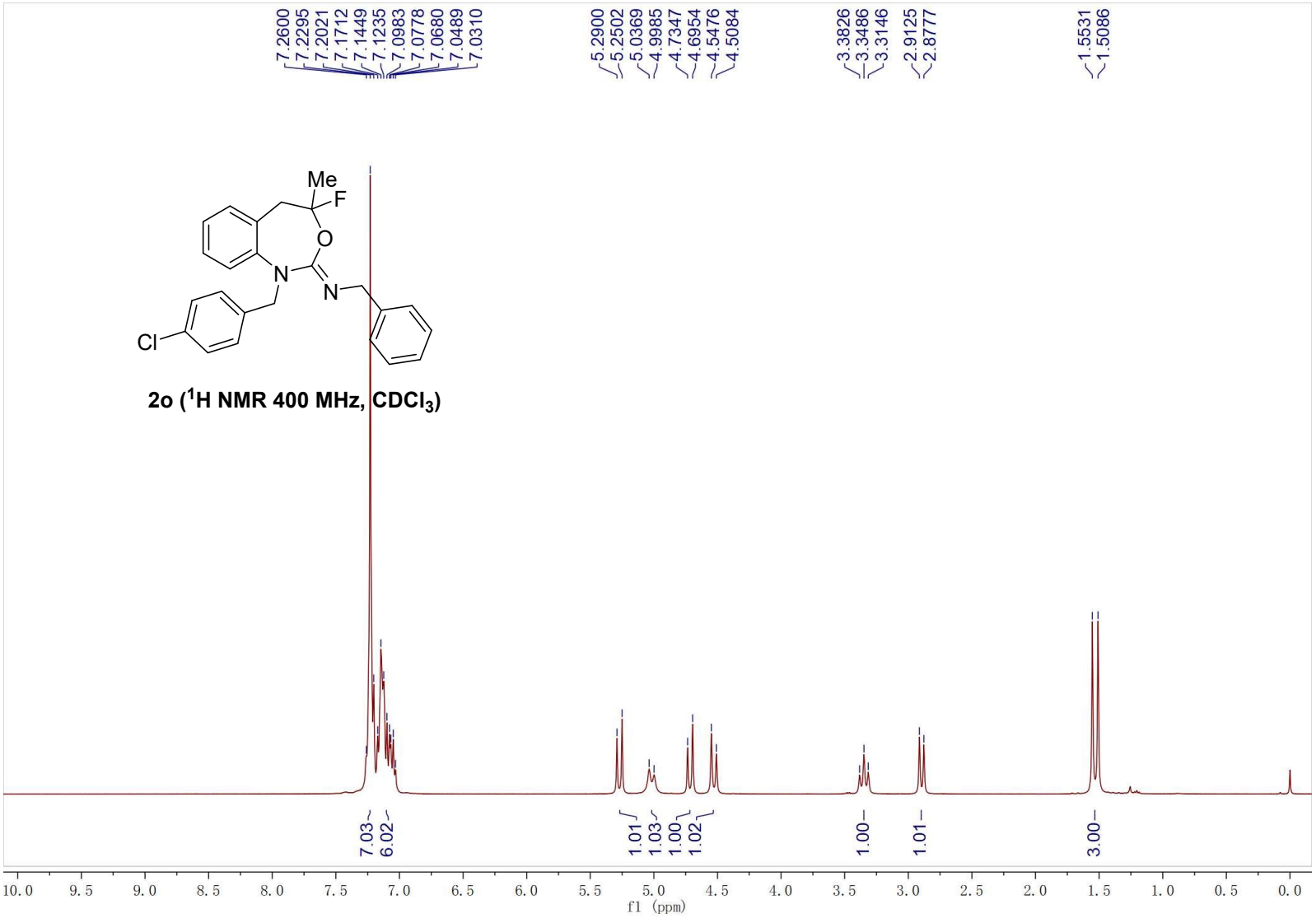

7.3858
7.3684
7.3219
7.3041
7.2857
7.2092
7.1914
7.1750
7.1548
7.1418
7.1232
7.0564
7.0387
7.0219
4.7011
4.6618
4.6154
4.5761
4.1748
4.1550
4.1419
4.1217
3.6448
3.6301
3.6104
3.5957
3.4813
3.4466
3.4119
2.9300
2.8958
1.8474
1.7612
1.7313
1.6795
1.6361
1.6080
1.5797
1.5254
1.4808
1.1241
1.0677
1.0331
1.0062
0.9089
0.8822
0.8557
Me
F
O
N
N
2n (1H NMR 400 MHz, CDCl3)
2.01
3.03
3.04
1.00
2.00
1.02
1.01
1.00
1.01
1.03
5.01
3.01
3.04
1.01
1.01
f1 (ppm)



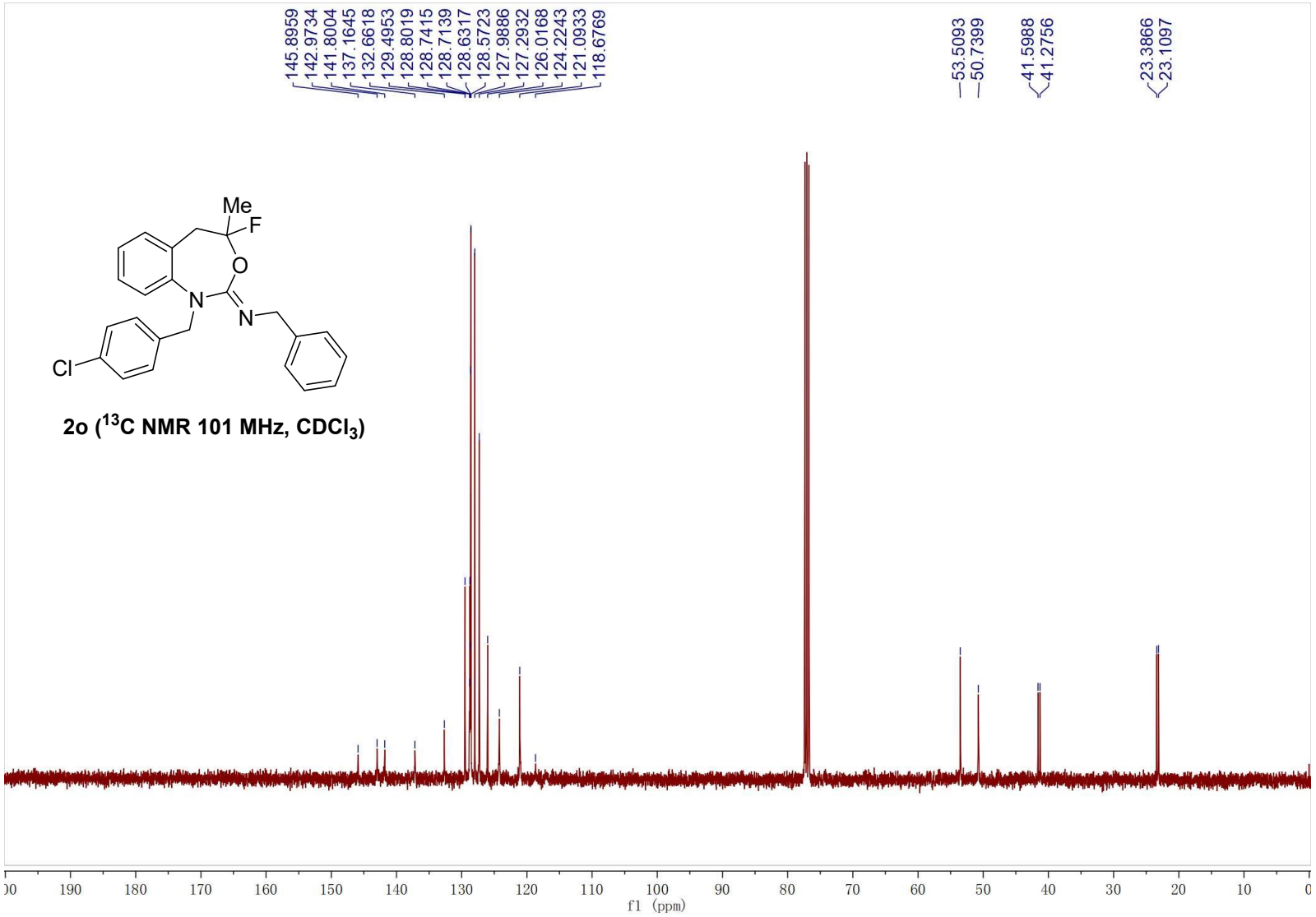
2n (^{13}C NMR 101 MHz, $CDCl_3$)



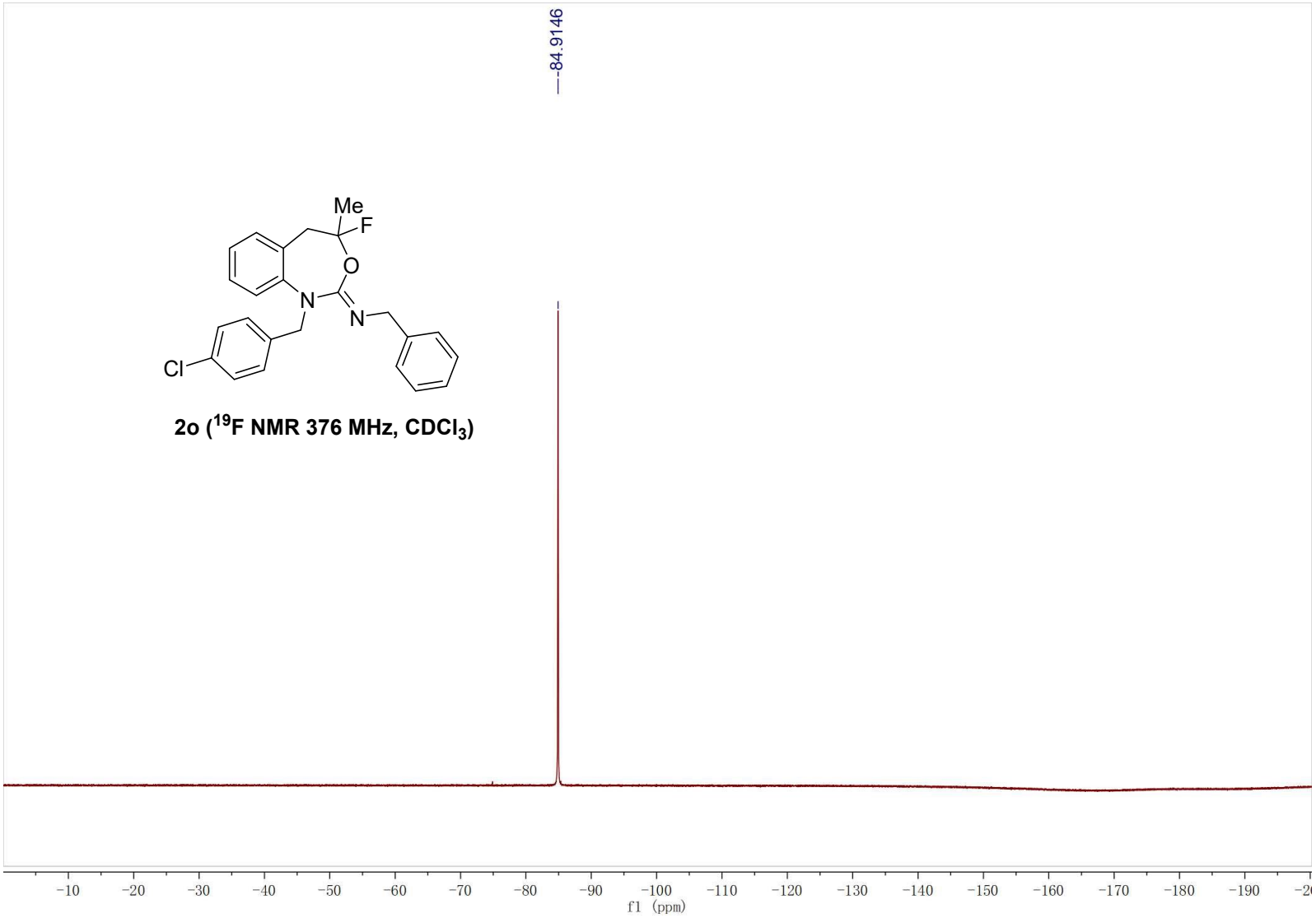
2n (^{19}F NMR 376 MHz, $CDCl_3$)



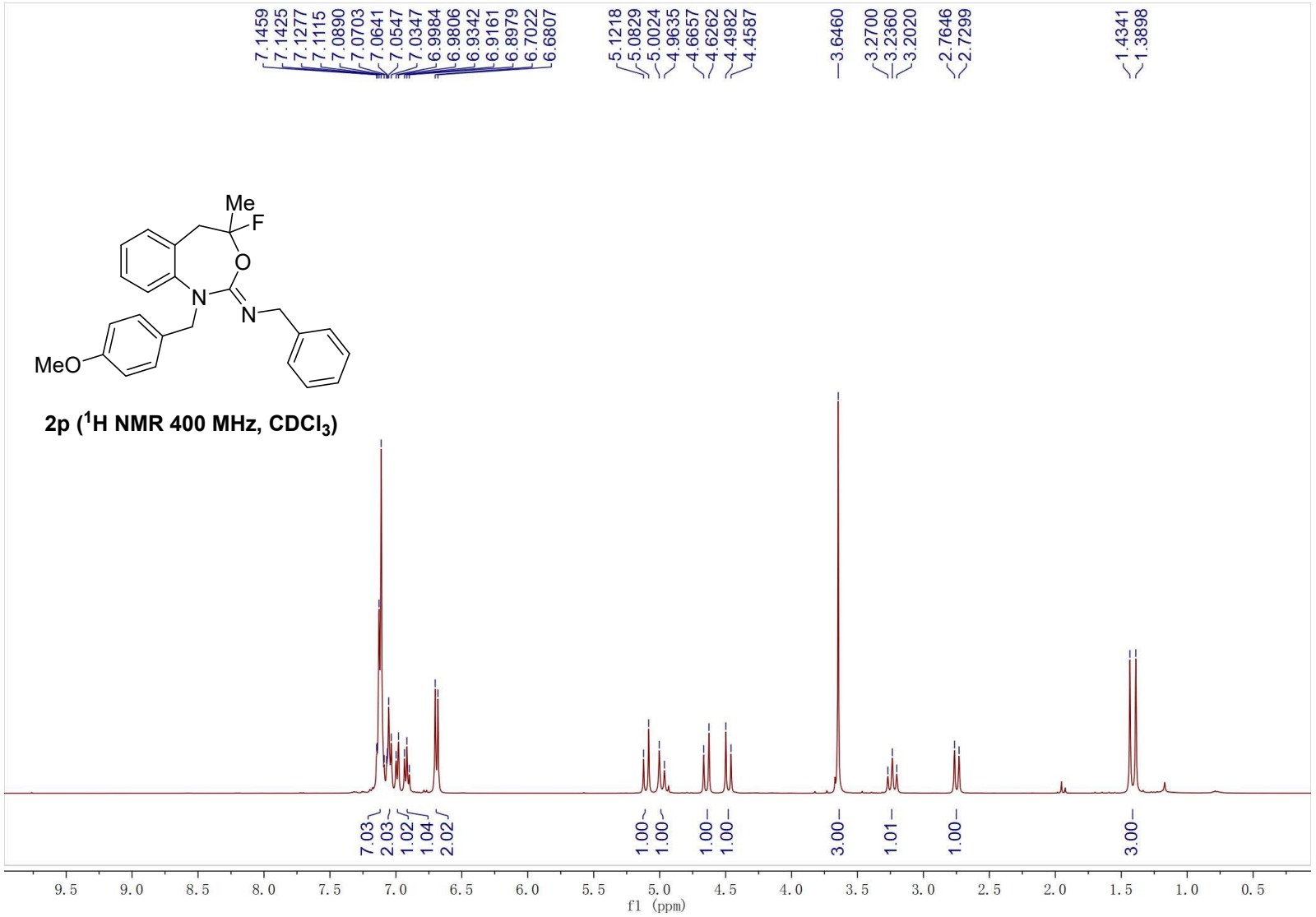
2o (^{1}H NMR 400 MHz, $CDCl_3$)

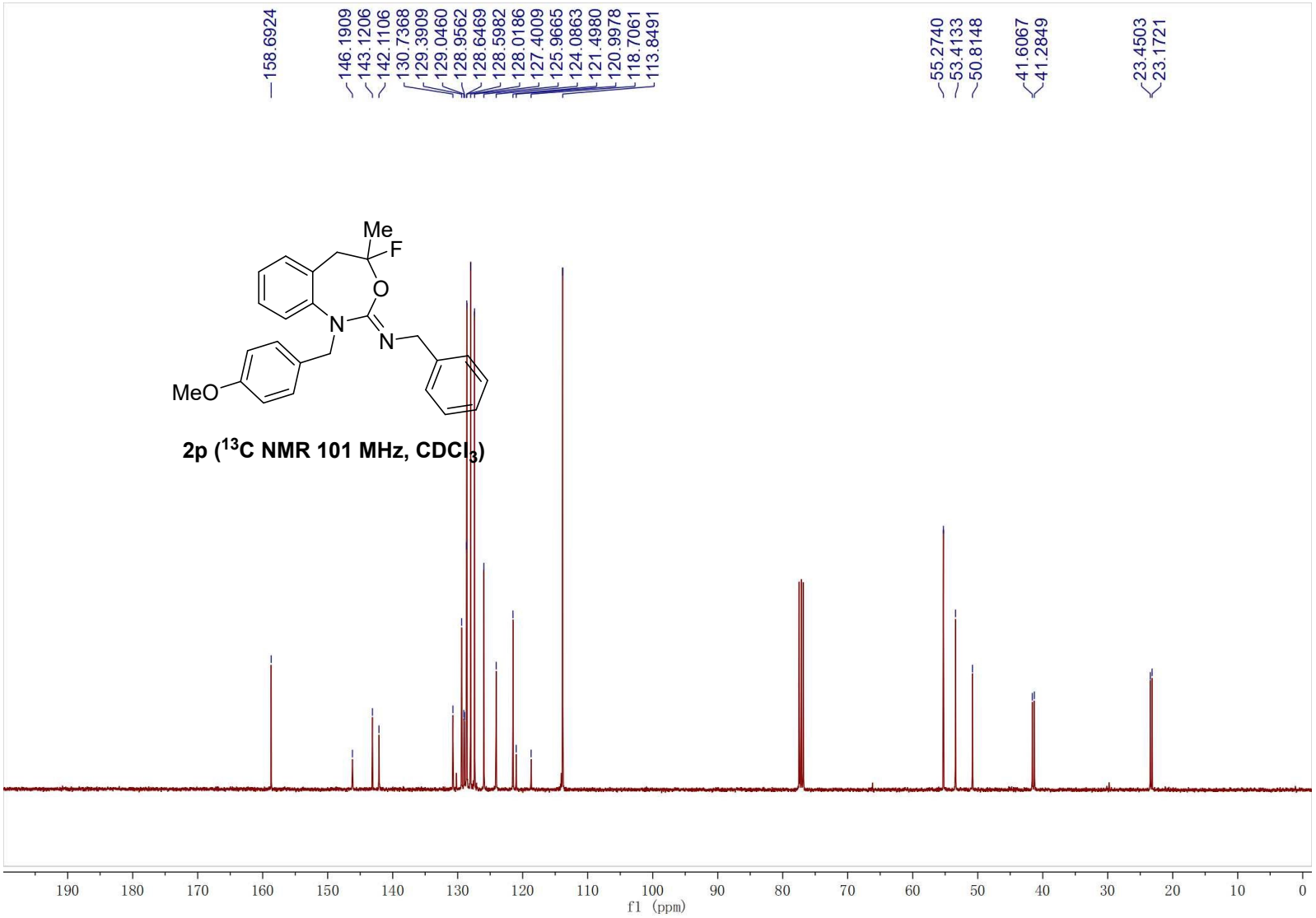


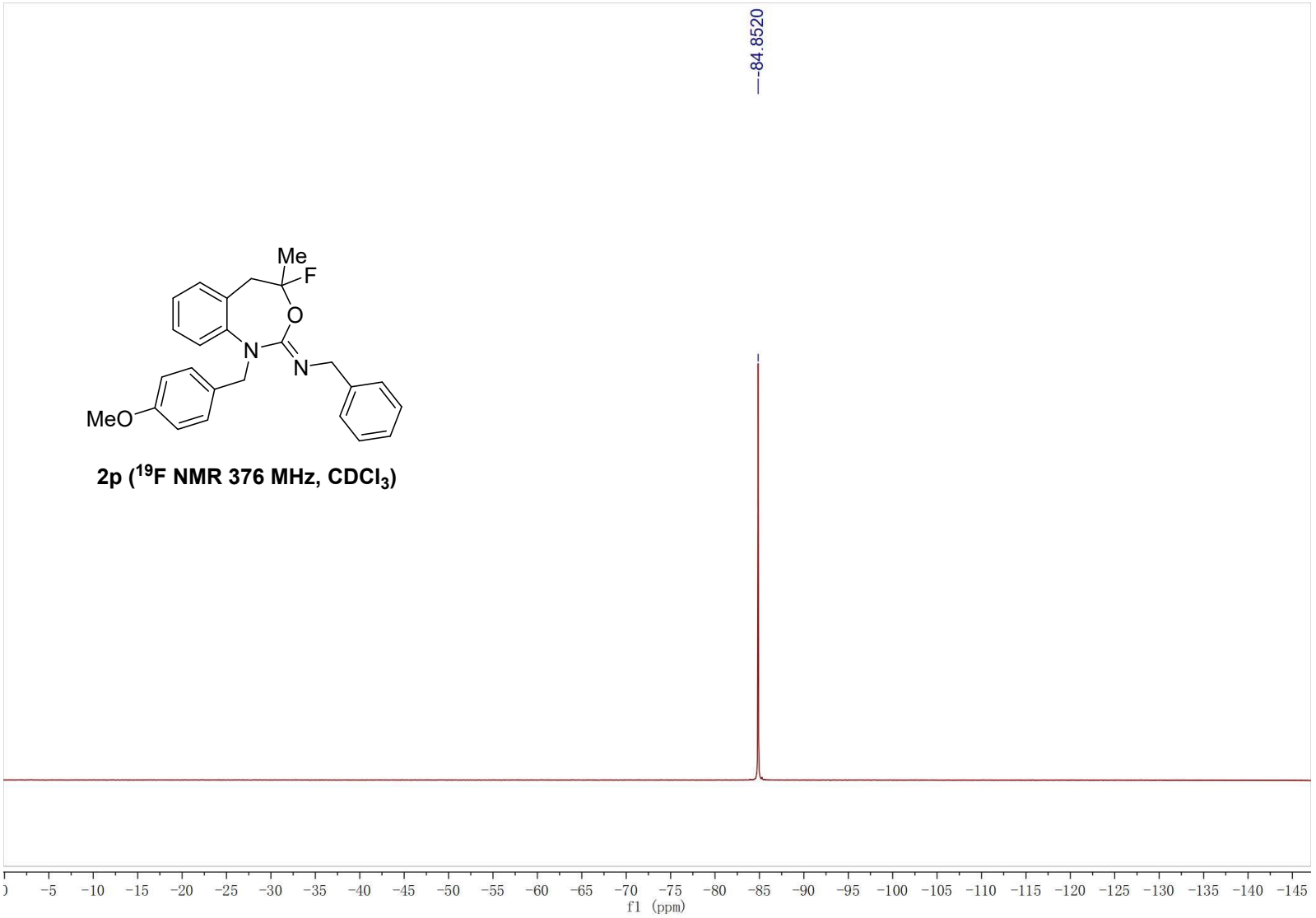
2o (^{13}C NMR 101 MHz, $CDCl_3$)



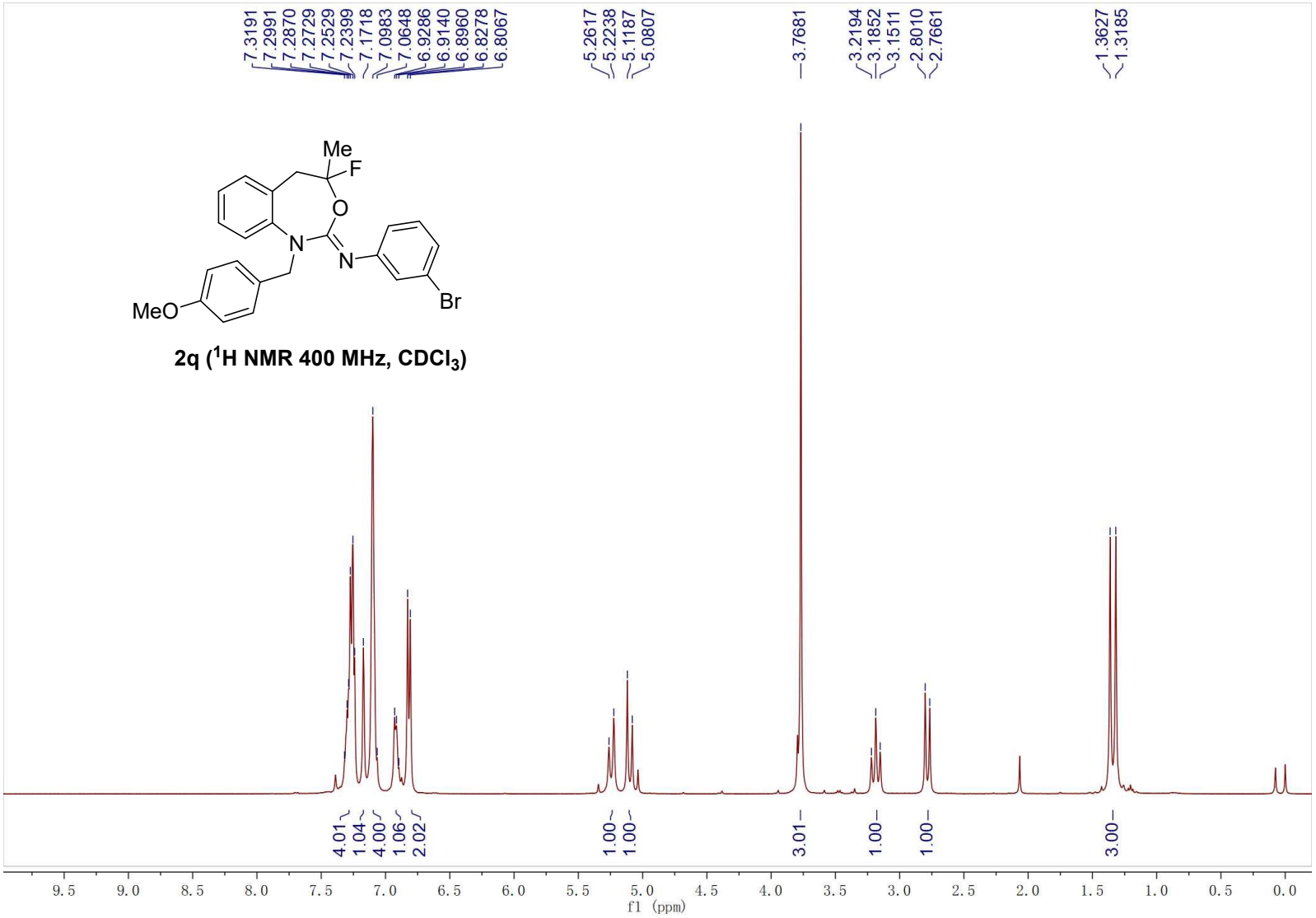
2o (^{19}F NMR 376 MHz, $CDCl_3$)


7.1459
7.1425
7.1277
7.1115
7.0890
7.0703
7.0641
7.0547
7.0347
6.9984
6.9806
6.9342
6.9161
6.8979
6.7022
6.6807
5.1218
5.0829
5.0024
4.9635
4.6657
4.6262
4.4982
4.4587
3.6460
3.2700
3.2360
3.2020
2.7646
2.7299
1.4341
1.3898
Me
F
O
N
N
MeO
2p (1H NMR 400 MHz, CDCl3)
7.03
2.03
1.02
1.04
2.02
1.00
1.00
1.00
1.00
3.00
1.01
1.00
3.00
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
f1 (ppm)

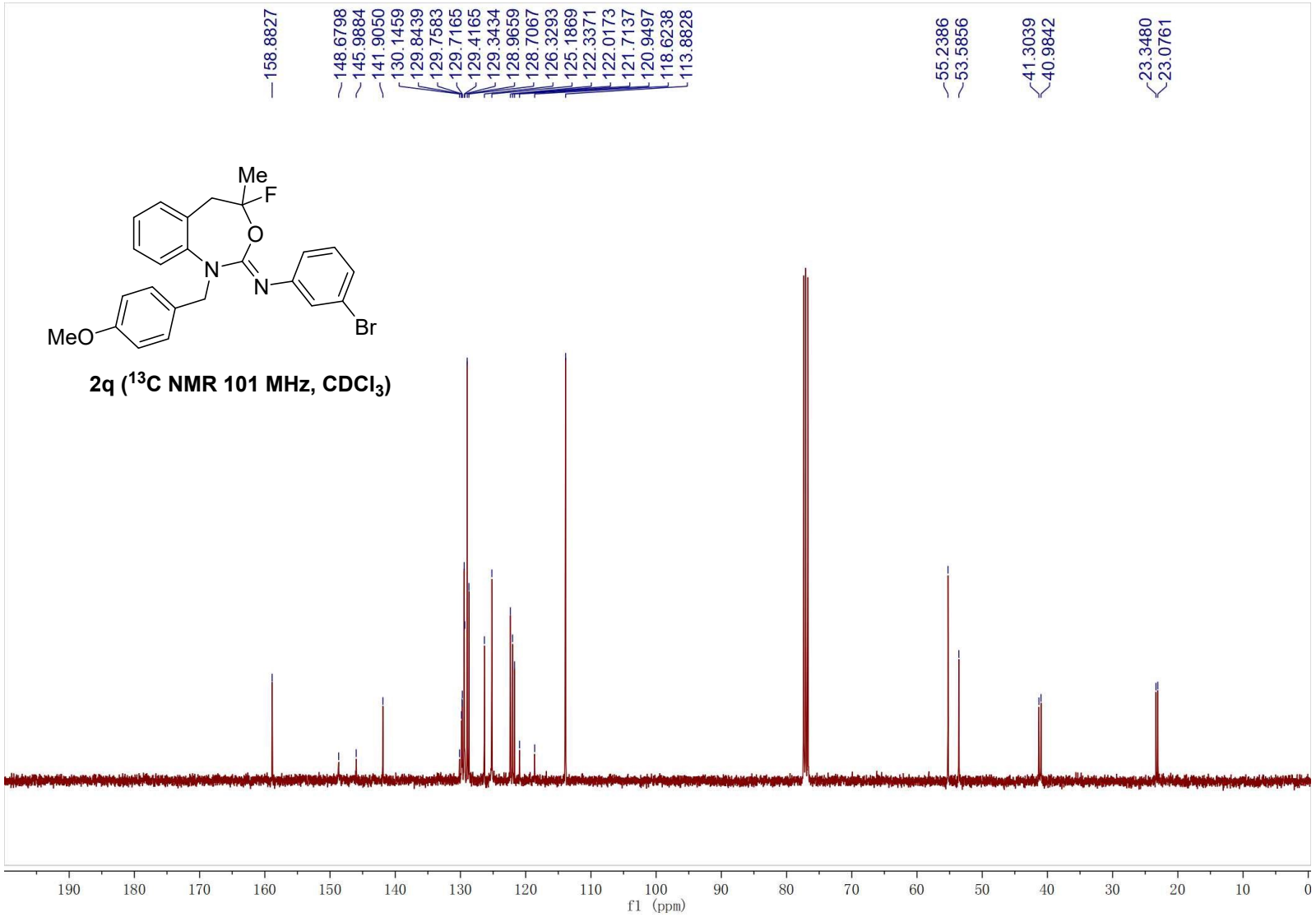

158.6924
146.1909
143.1206
142.1106
130.7368
129.3909
129.0460
128.9562
128.6469
128.5982
128.0186
127.4009
125.9665
124.0863
121.4980
120.9978
118.7061
113.8491
55.2740
53.4133
50.8148
41.6067
41.2849
23.4503
23.1721
Me
F
O
N
N
MeO
2p (^{13}C NMR 101 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

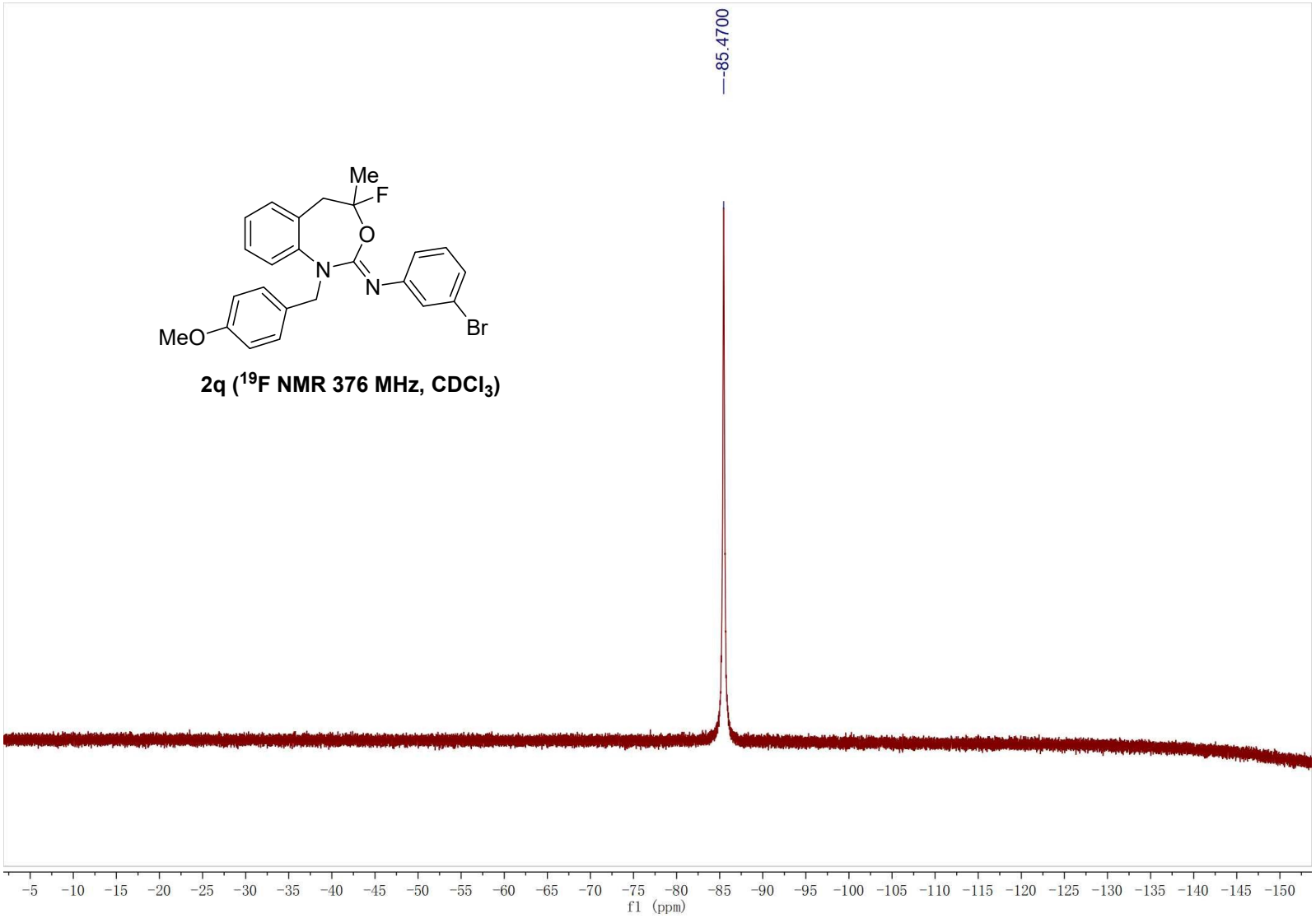


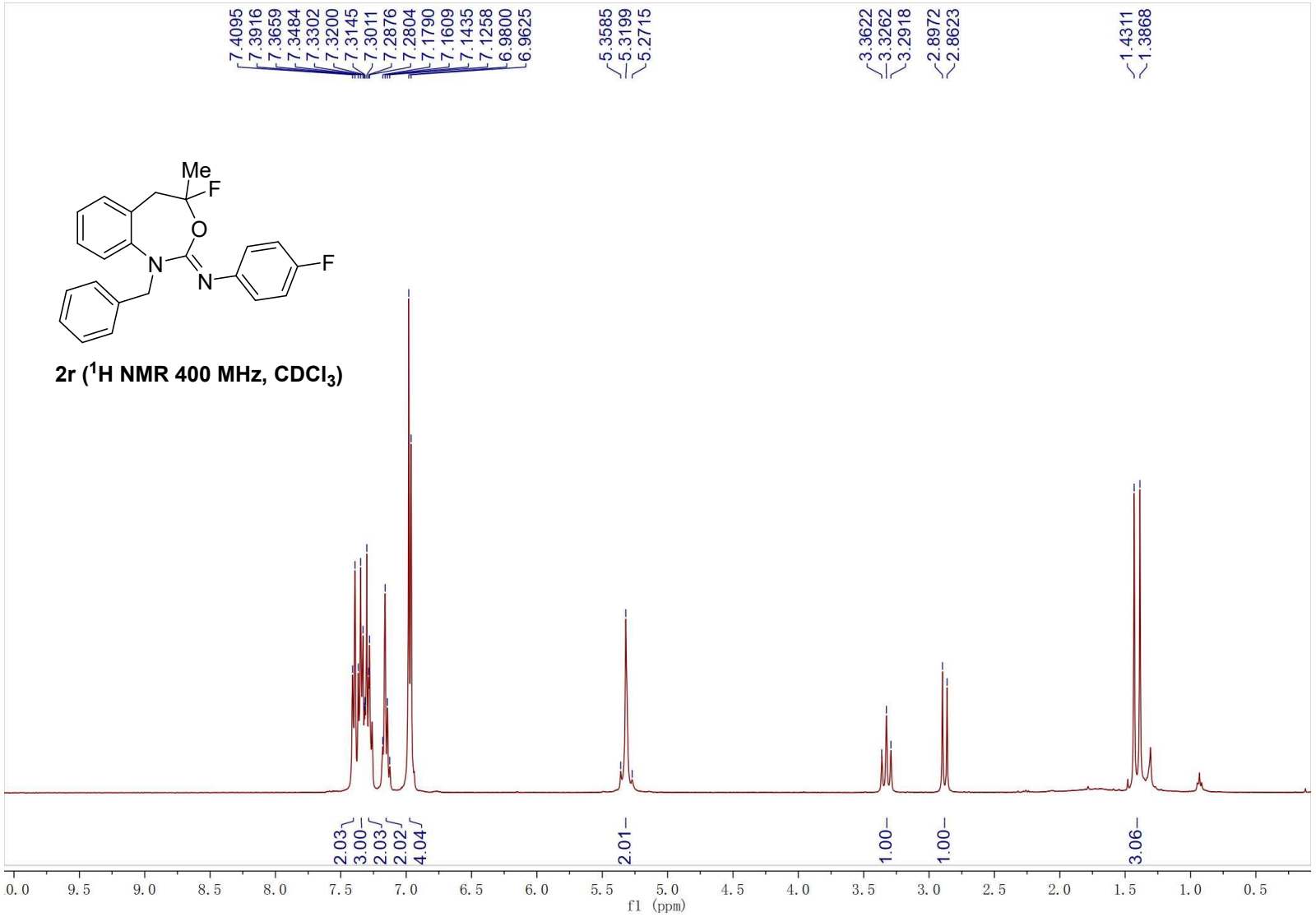
2p (^{19}F NMR 376 MHz, $CDCl_3$)

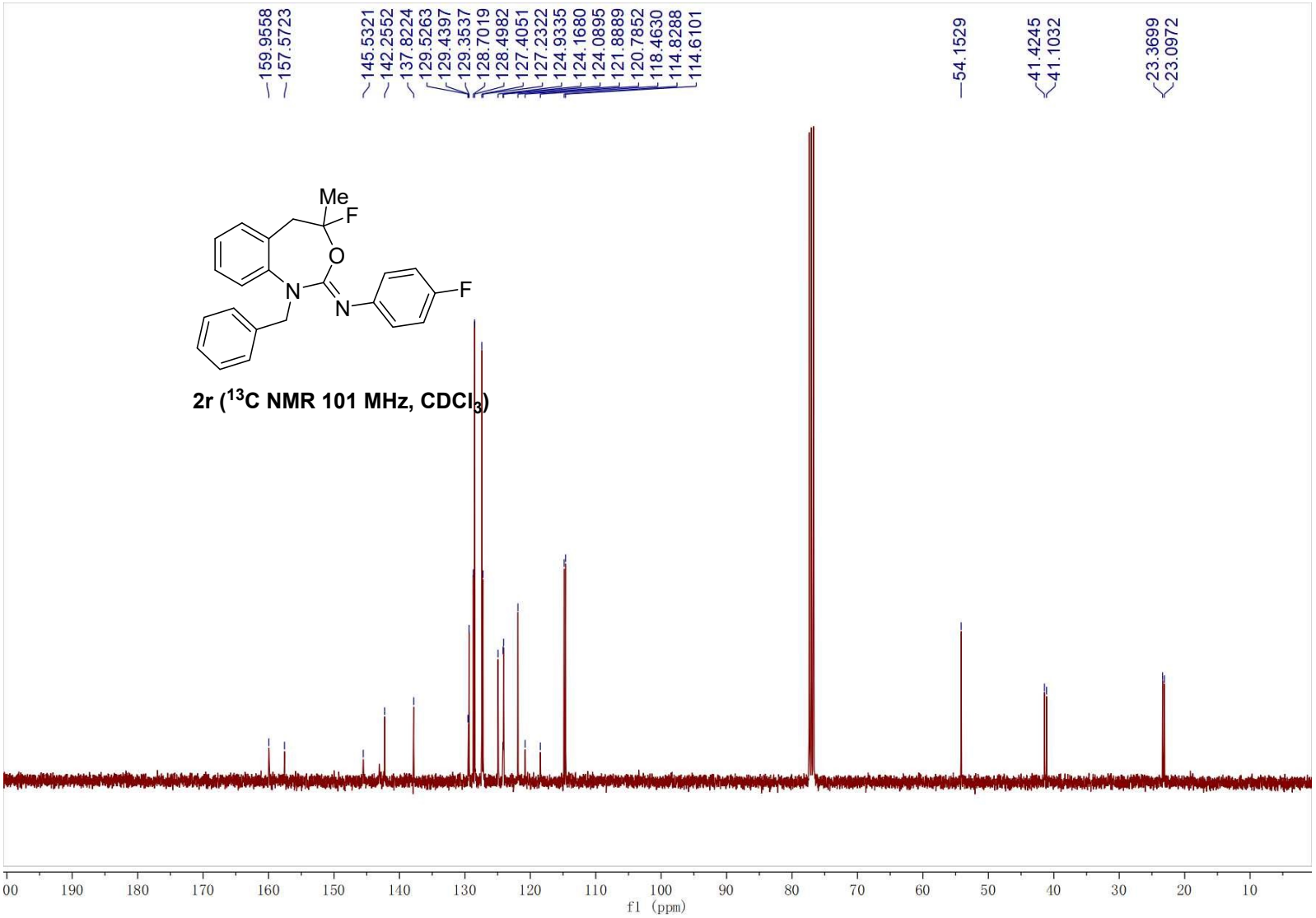


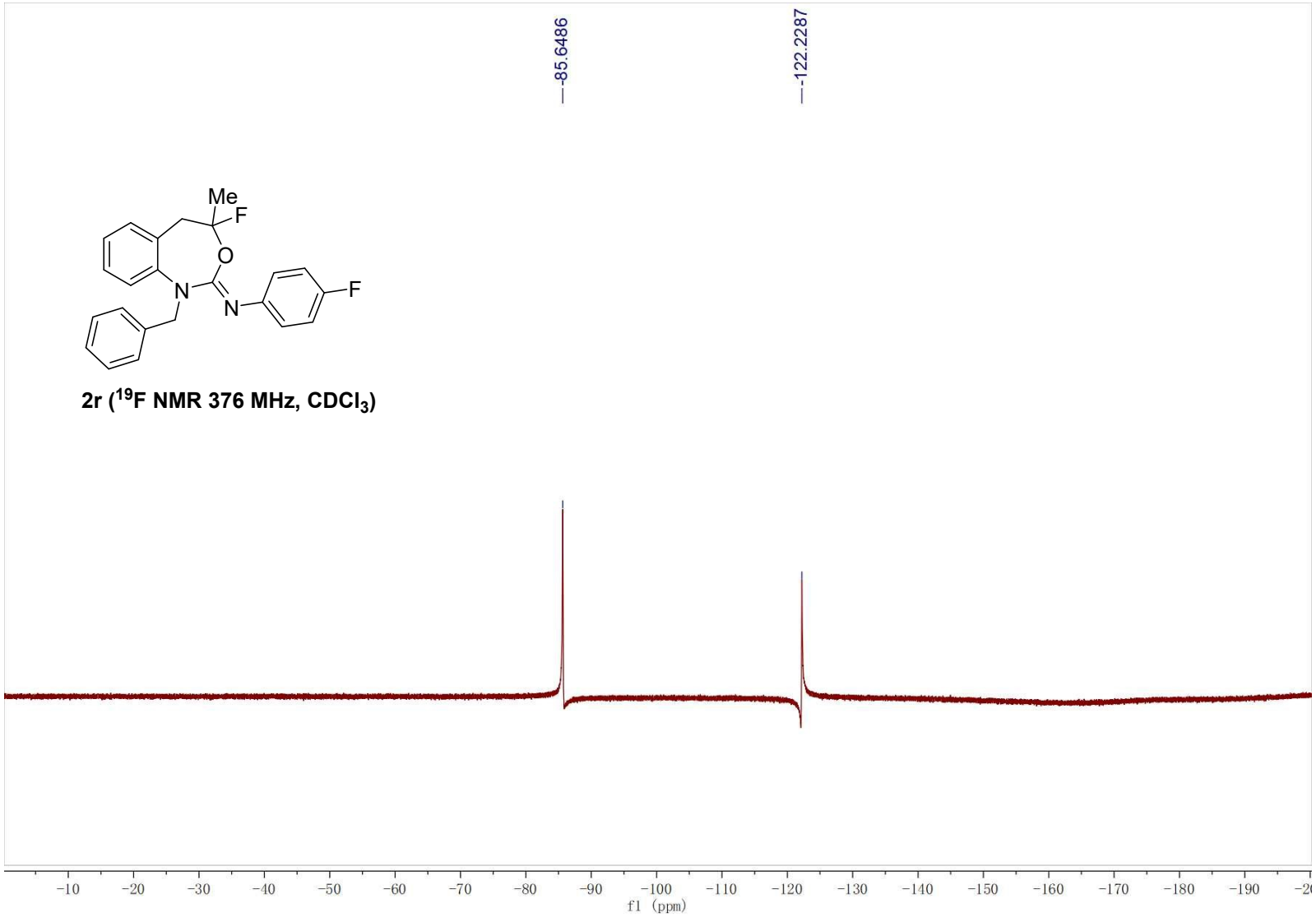
2q (^{1}H NMR 400 MHz, $CDCl_3$)


158.8827
148.6798
145.9884
141.9050
130.1459
129.8439
129.7583
129.7165
129.4165
129.3434
128.9659
128.7067
126.3293
125.1869
122.3371
122.0173
121.7137
120.9497
118.6238
113.8828
55.2386
53.5856
41.3039
40.9842
23.3480
23.0761
Me
F
O
N
N
MeO
Br
2q (^{13}C NMR 101 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

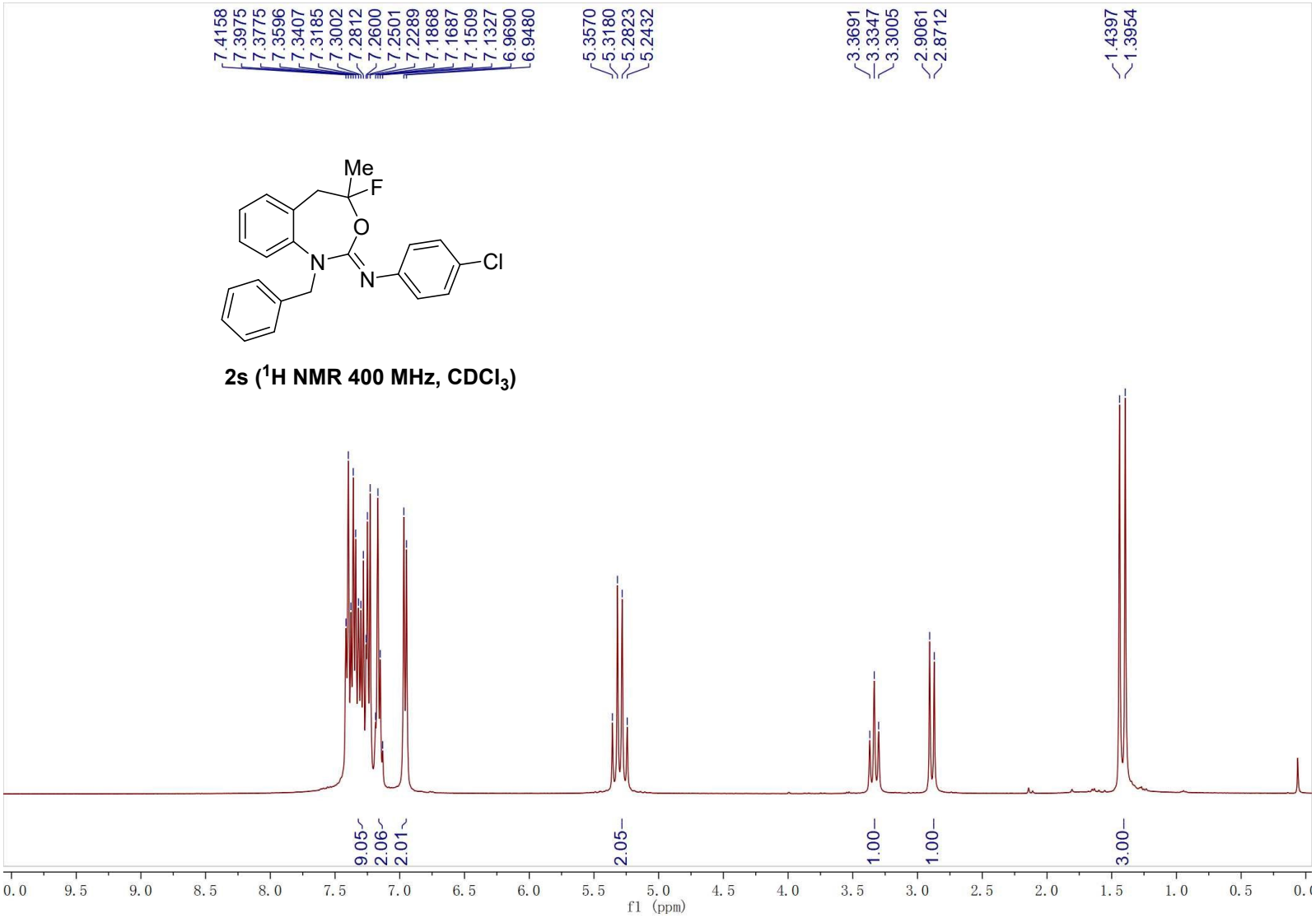

-85.4700
Me
F
O
N
N
MeO
Br
2q (^{19}F NMR 376 MHz, $CDCl_3$)
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


7.4095
7.3916
7.3659
7.3484
7.3302
7.3200
7.3145
7.3011
7.2876
7.2804
7.1790
7.1609
7.1435
7.1258
6.9800
6.9625
5.3585
5.3199
5.2715
3.3622
3.3262
3.2918
2.8972
2.8623
1.4311
1.3868
Me
F
O
N
N
F
2r (1H NMR 400 MHz, CDCl3)
2.03
3.00
2.03
2.02
4.04
2.01
1.00
1.00
3.06
f1 (ppm)

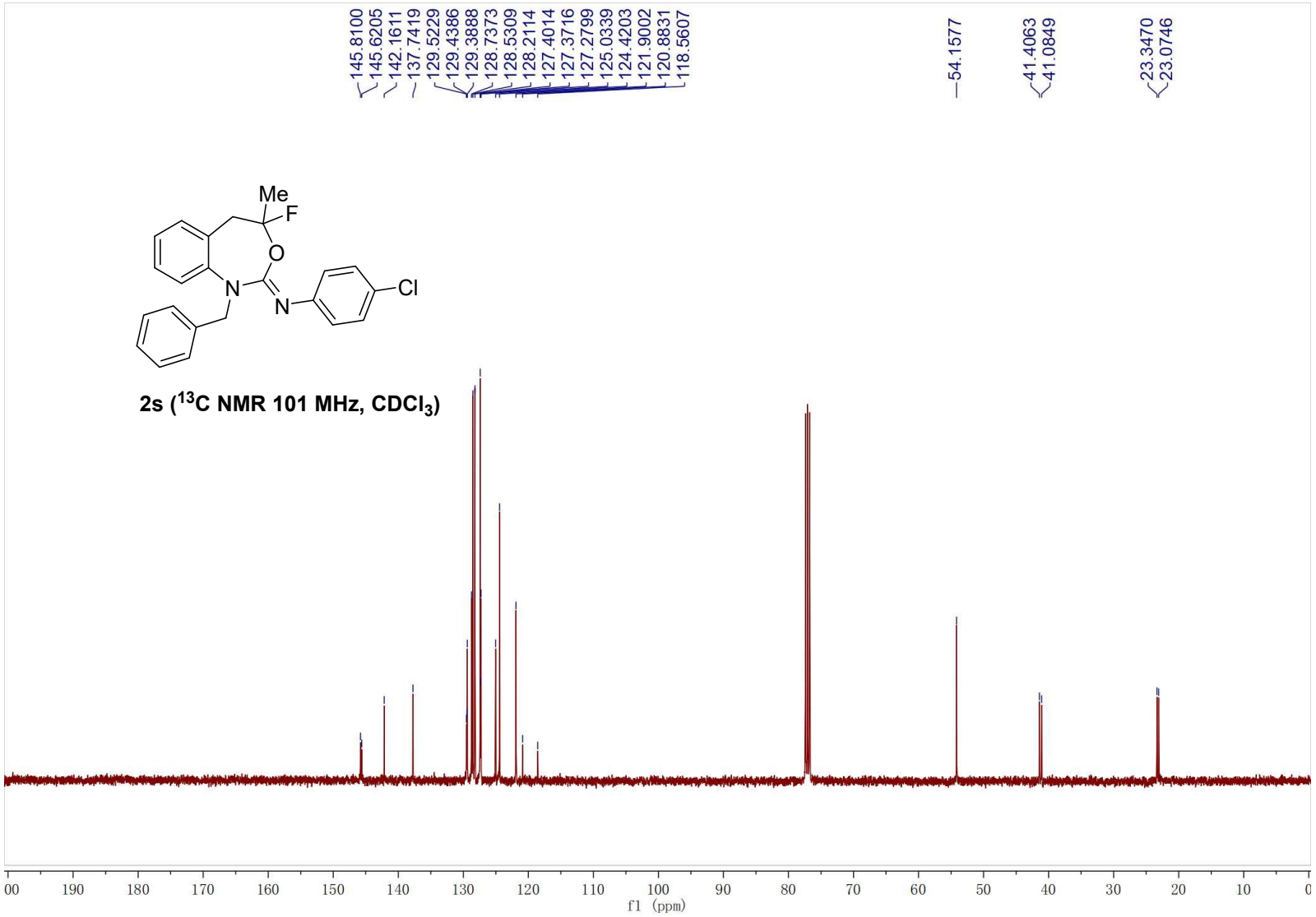

159.9558
157.5723
145.5321
142.2552
137.8224
129.5263
129.4397
129.3537
128.7019
128.4982
127.4051
127.2322
124.9335
124.1680
124.0895
121.8889
120.7852
118.4630
114.8288
114.6101
54.1529
41.4245
41.1032
23.3699
23.0972
Me
F
O
N
N
F
2r (^{13}C NMR 101 MHz, CDCl$_3$)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

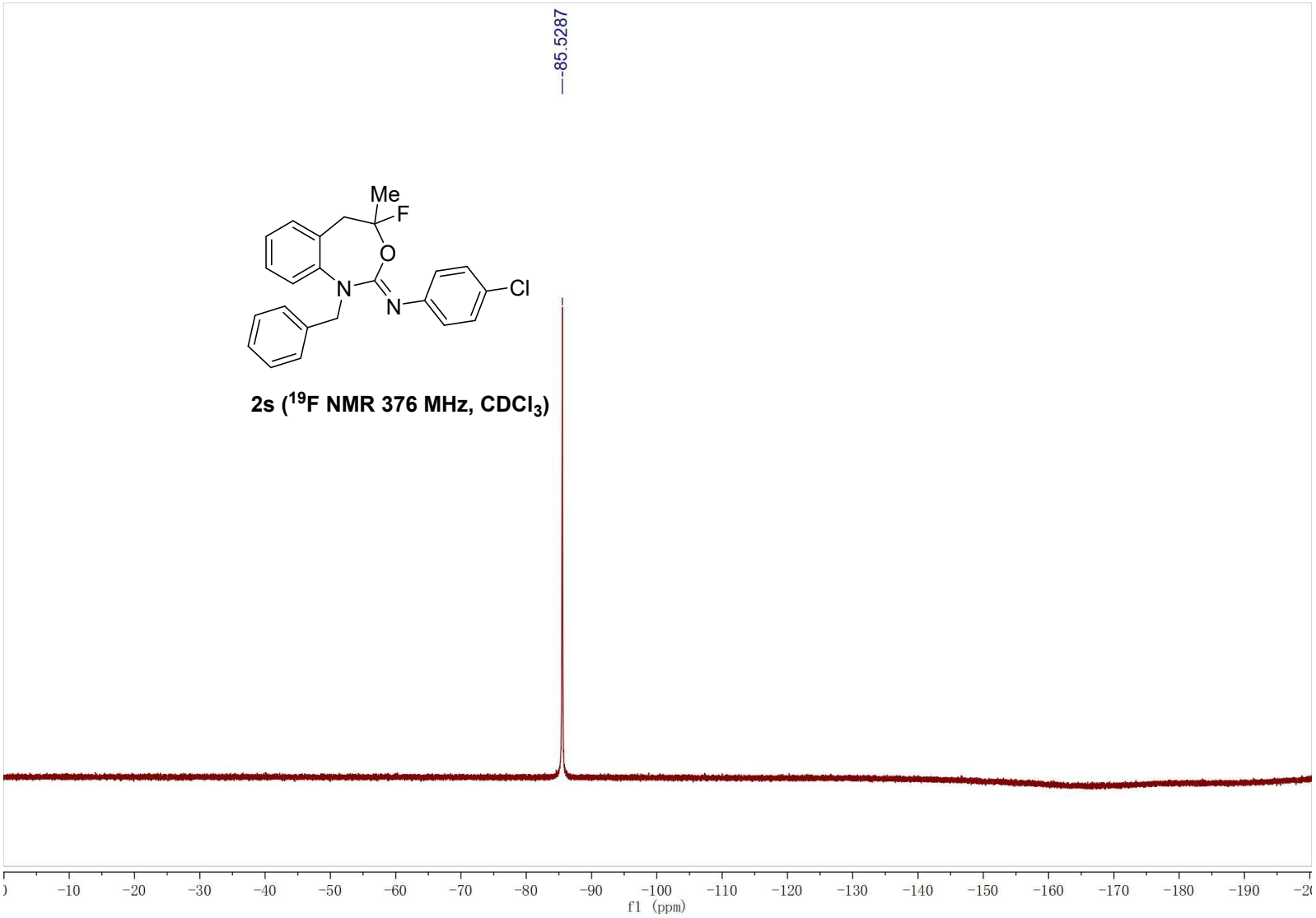


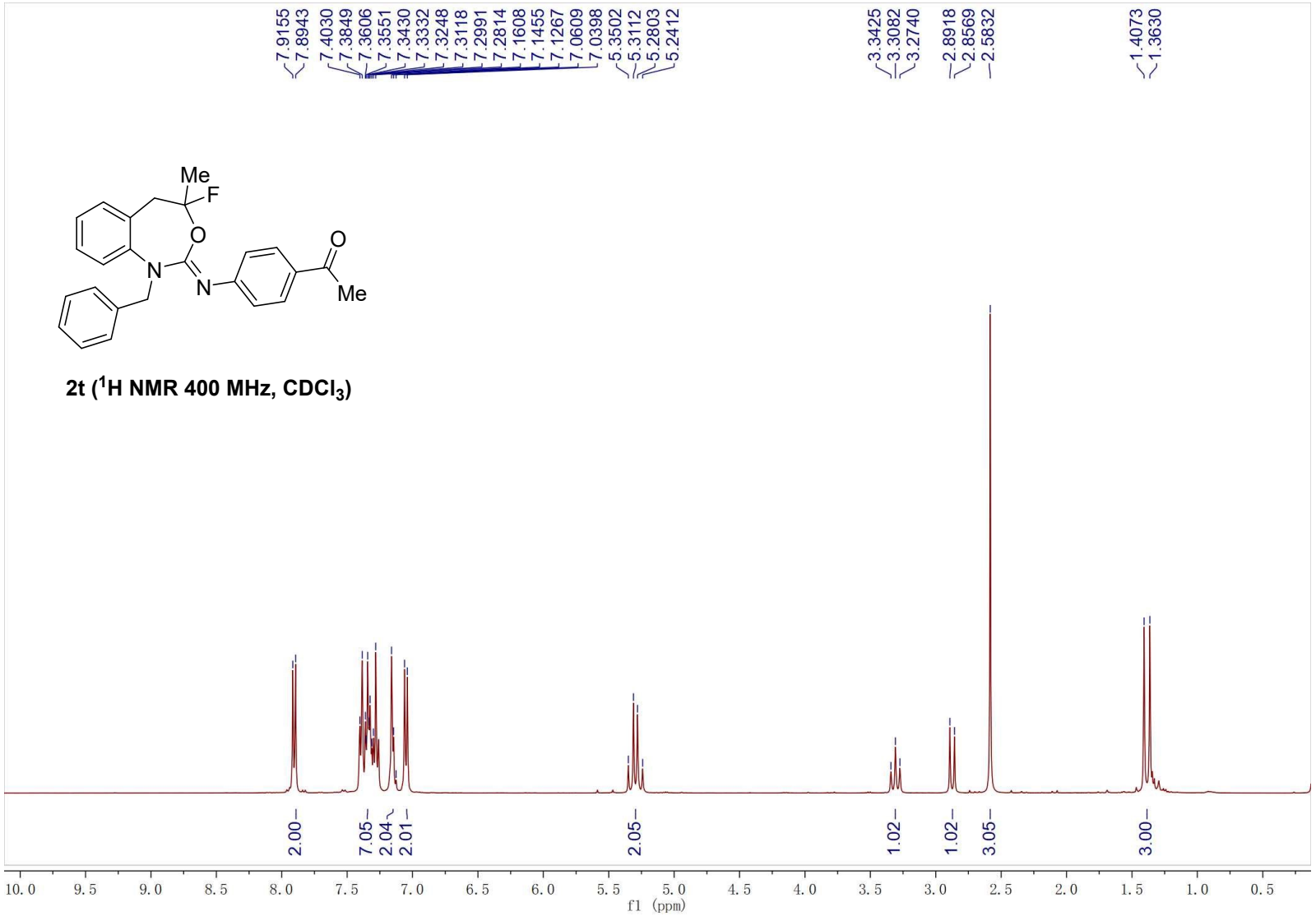
2r (^{19}F NMR 376 MHz, $CDCl_3$)



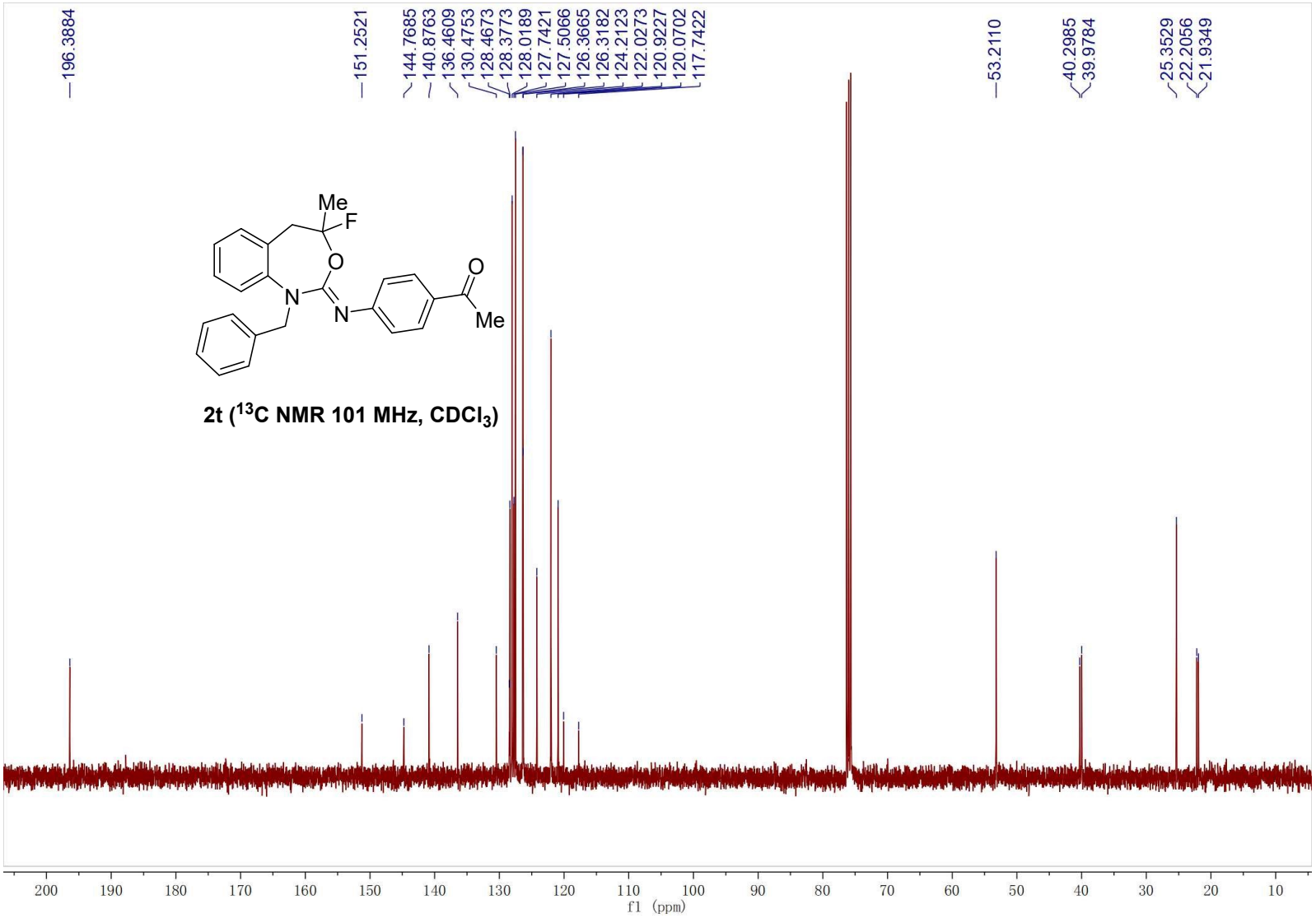
2s (^{1}H NMR 400 MHz, $CDCl_3$)

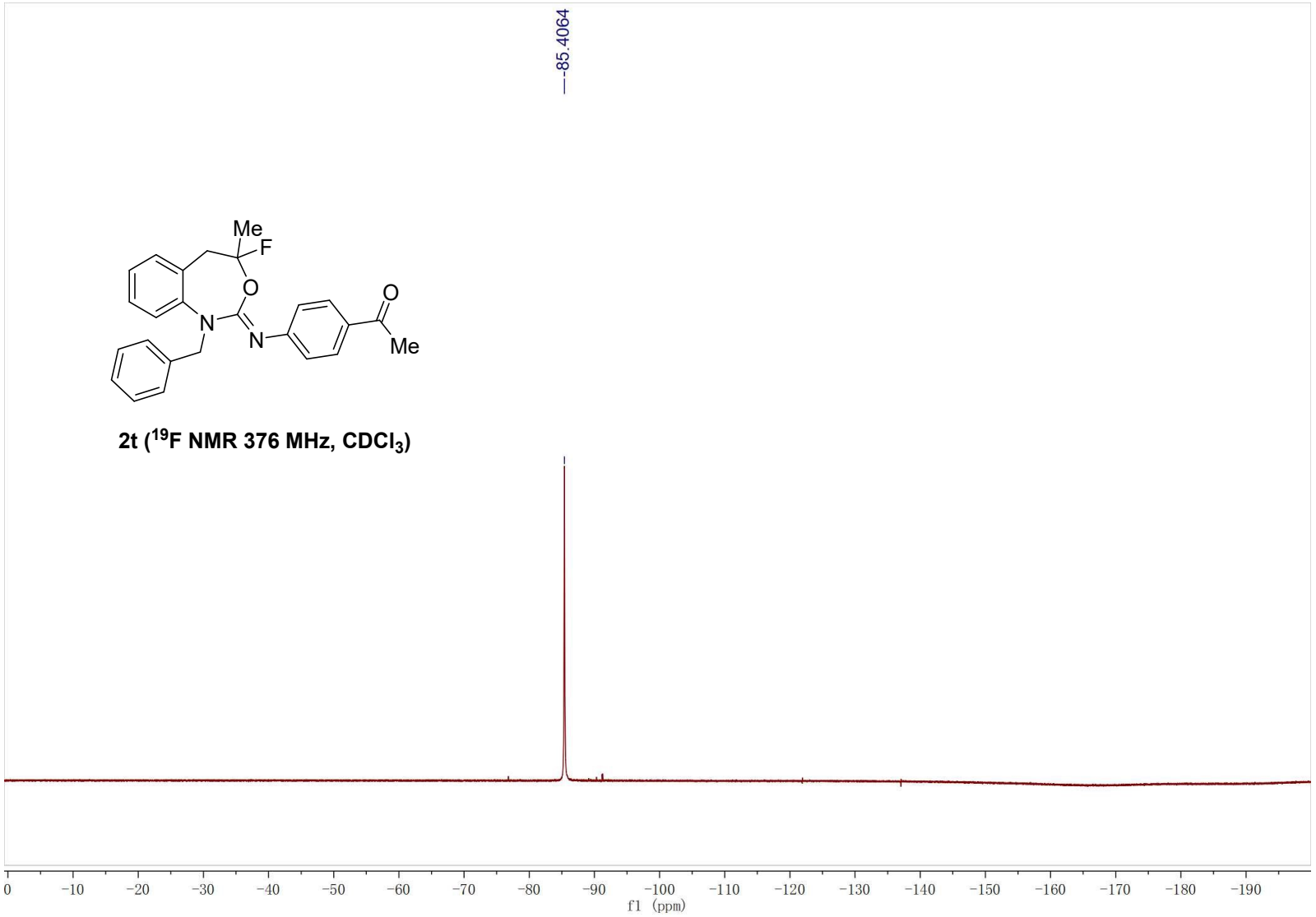

145.8100
145.6205
142.1611
137.7419
129.5229
129.4386
129.3888
128.7373
128.5309
128.2114
127.4014
127.3716
127.2799
125.0339
124.4203
121.9002
120.8831
118.5607
54.1577
41.4063
41.0849
23.3470
23.0746
Me
F
O
N
N
Cl
2s (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)


-85.5287
Me
F
O
N
N
Cl
2s (^{19}F NMR 376 MHz, $CDCl_3$)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

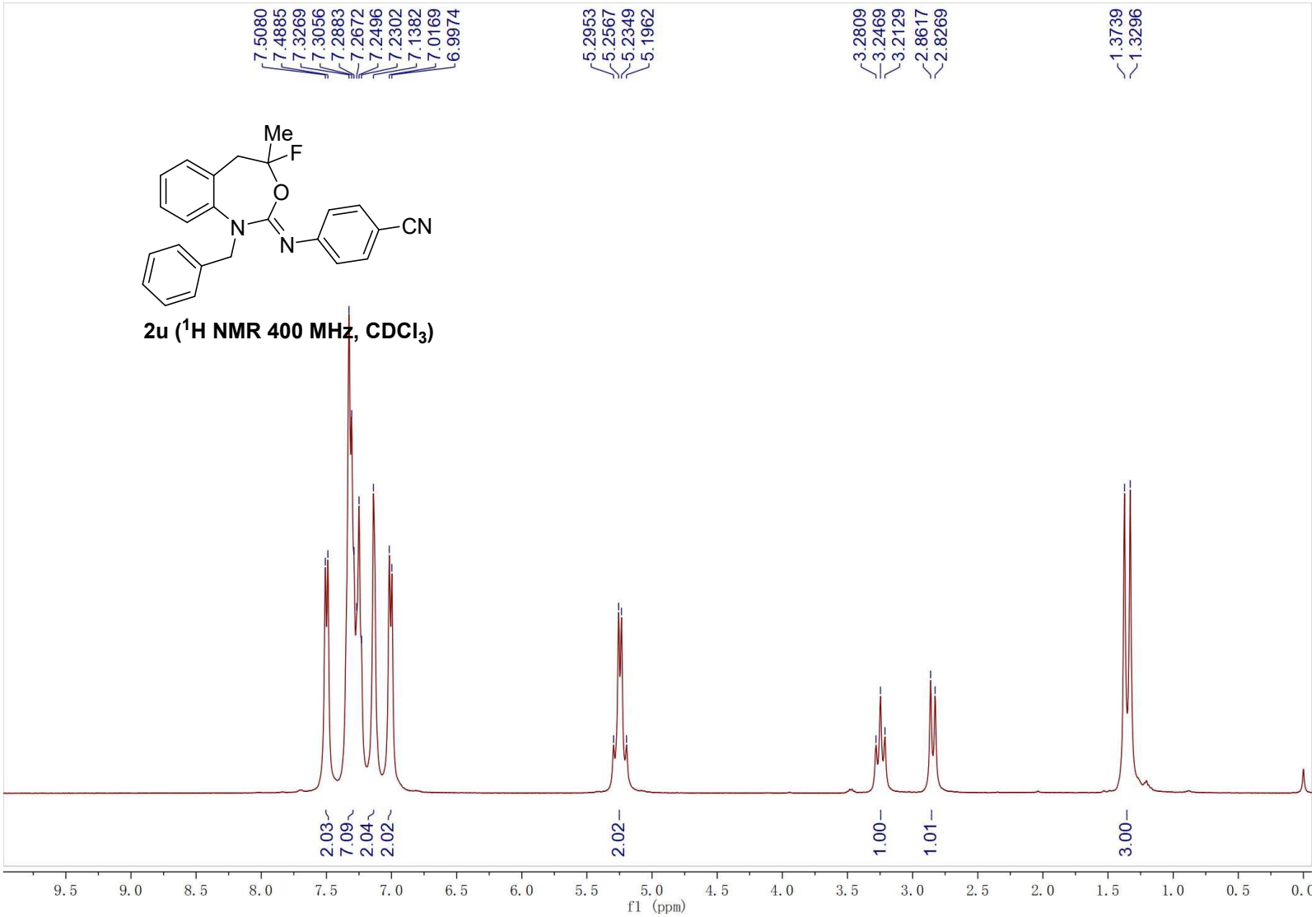


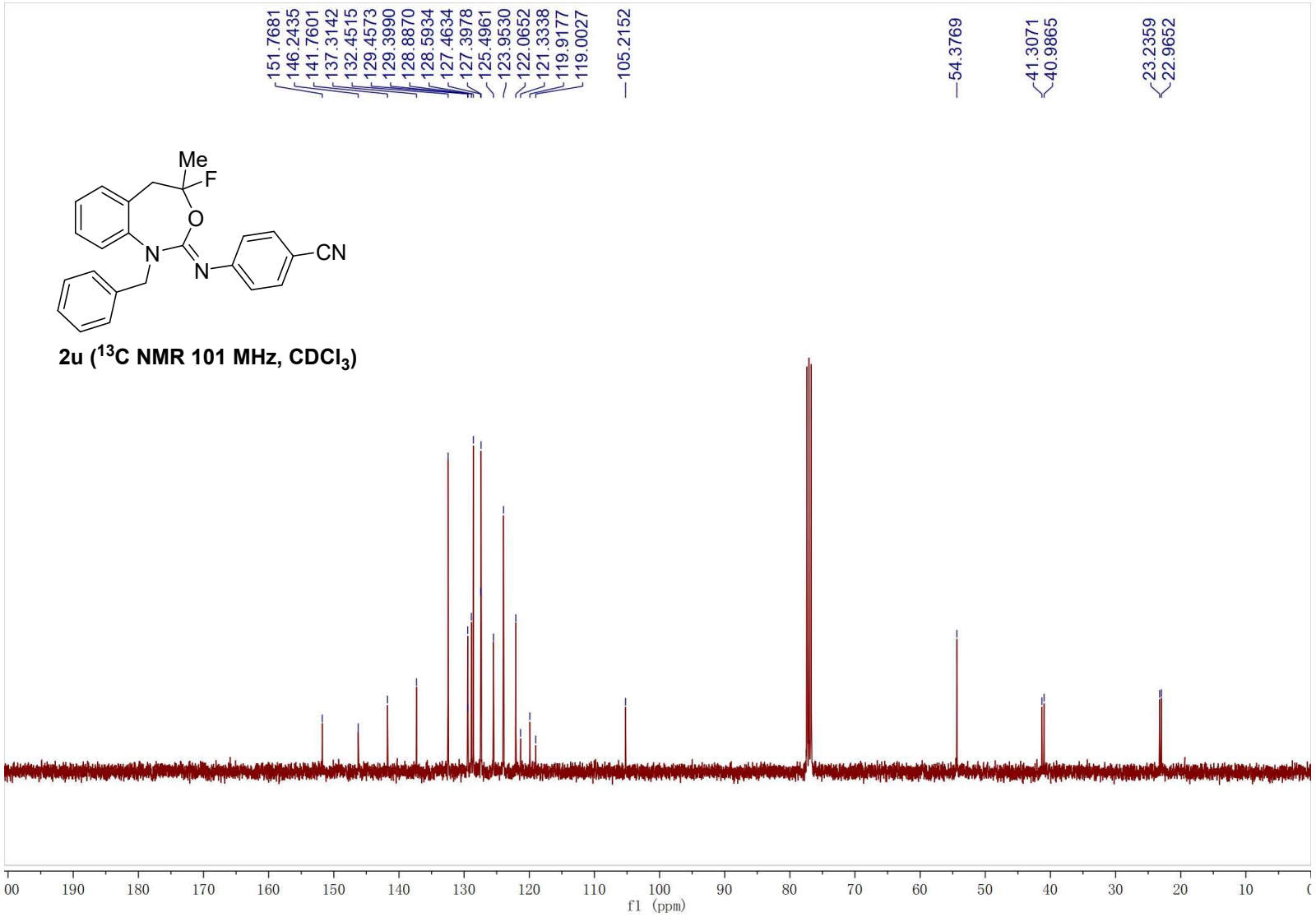
2t (^{1}H NMR 400 MHz, $CDCl_3$)

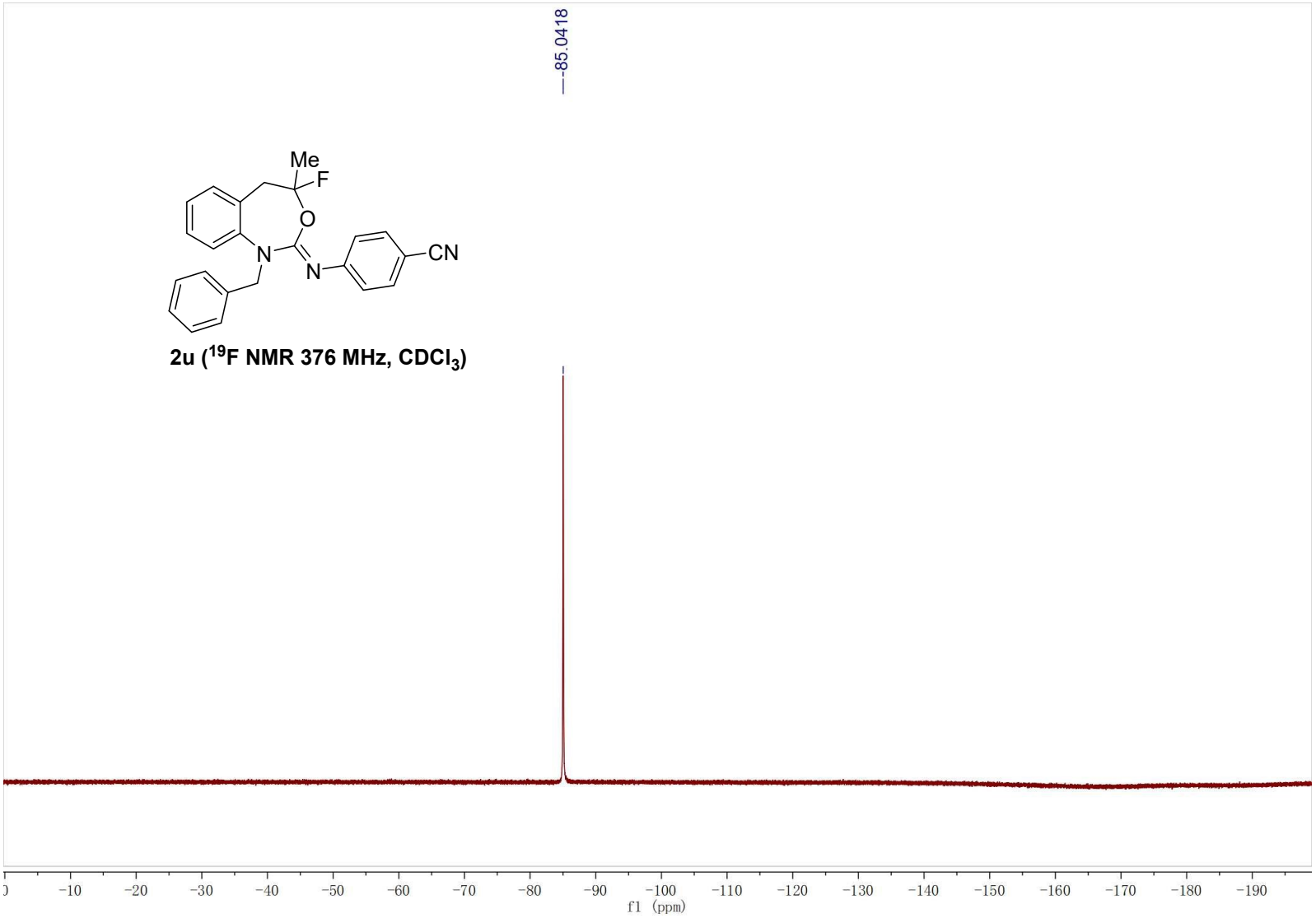

196.3884
151.2521
144.7685
140.8763
136.4609
130.4753
128.4673
128.3773
128.0189
127.7421
127.5066
126.3665
126.3182
124.2123
122.0273
120.9227
120.0702
117.7422
53.2110
40.2985
39.9784
25.3529
22.2056
21.9349
Me
F
O
N
N
O
Me
2t (^{13}C NMR 101 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

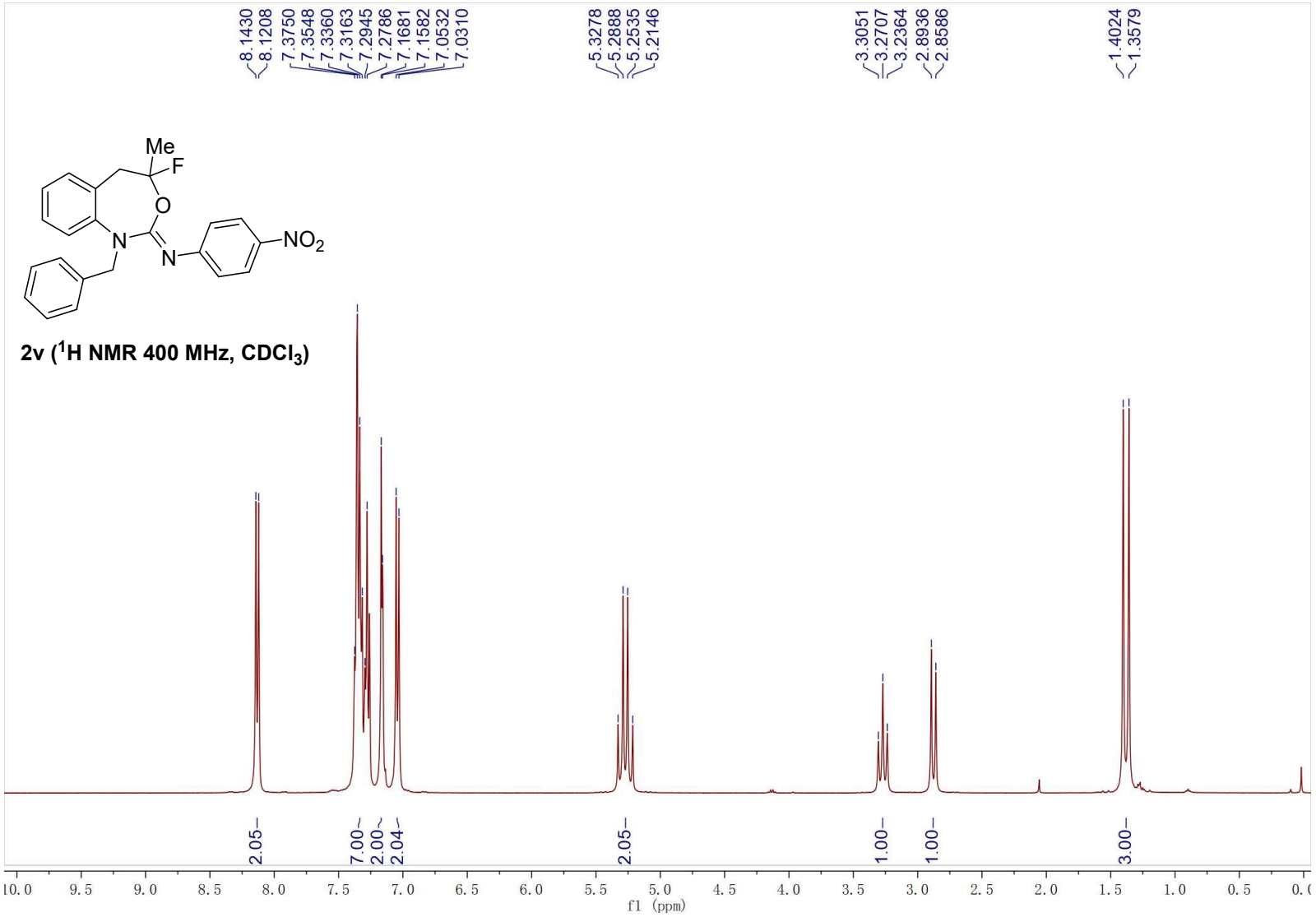


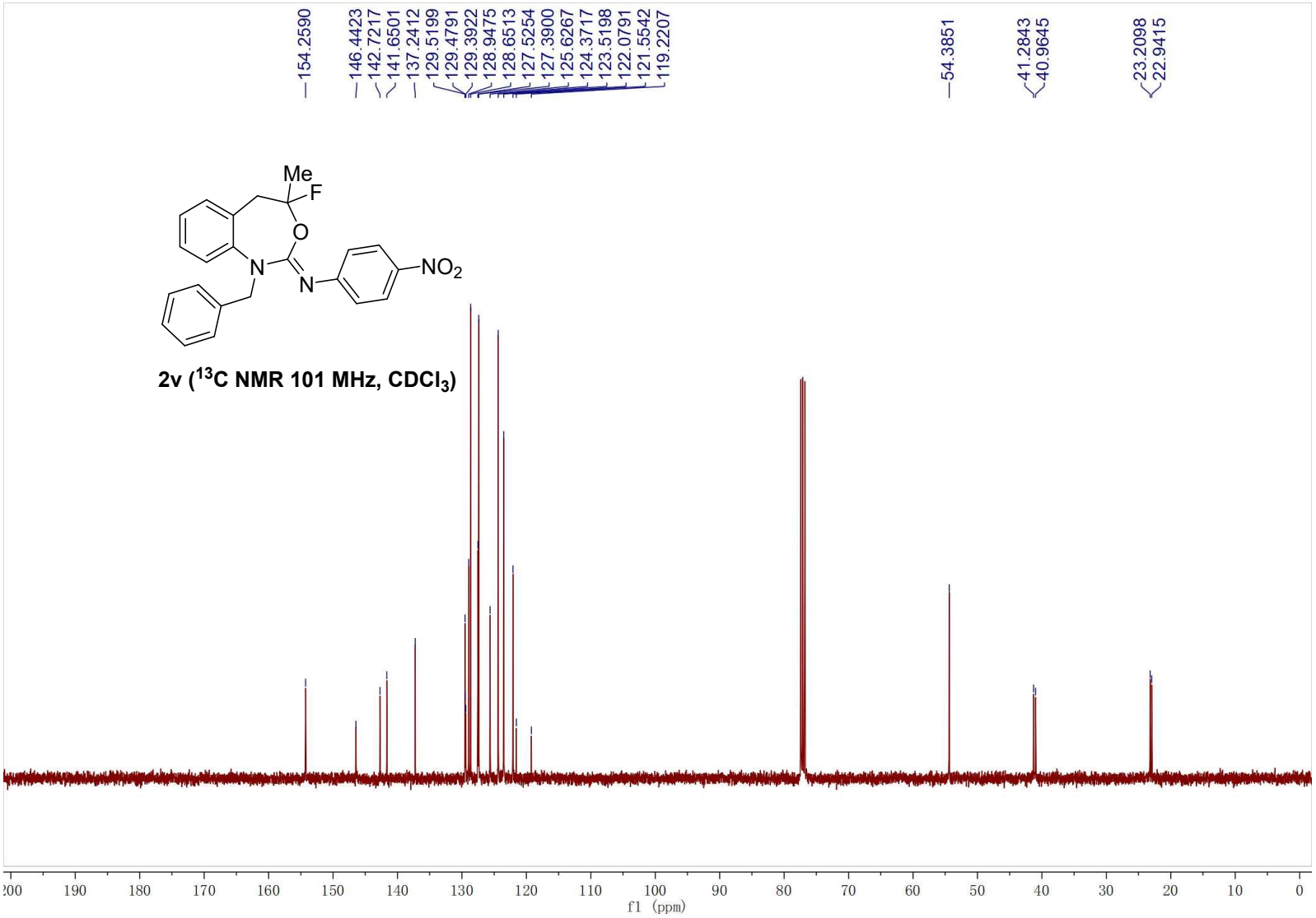
2t (^{19}F NMR 376 MHz, $CDCl_3$)

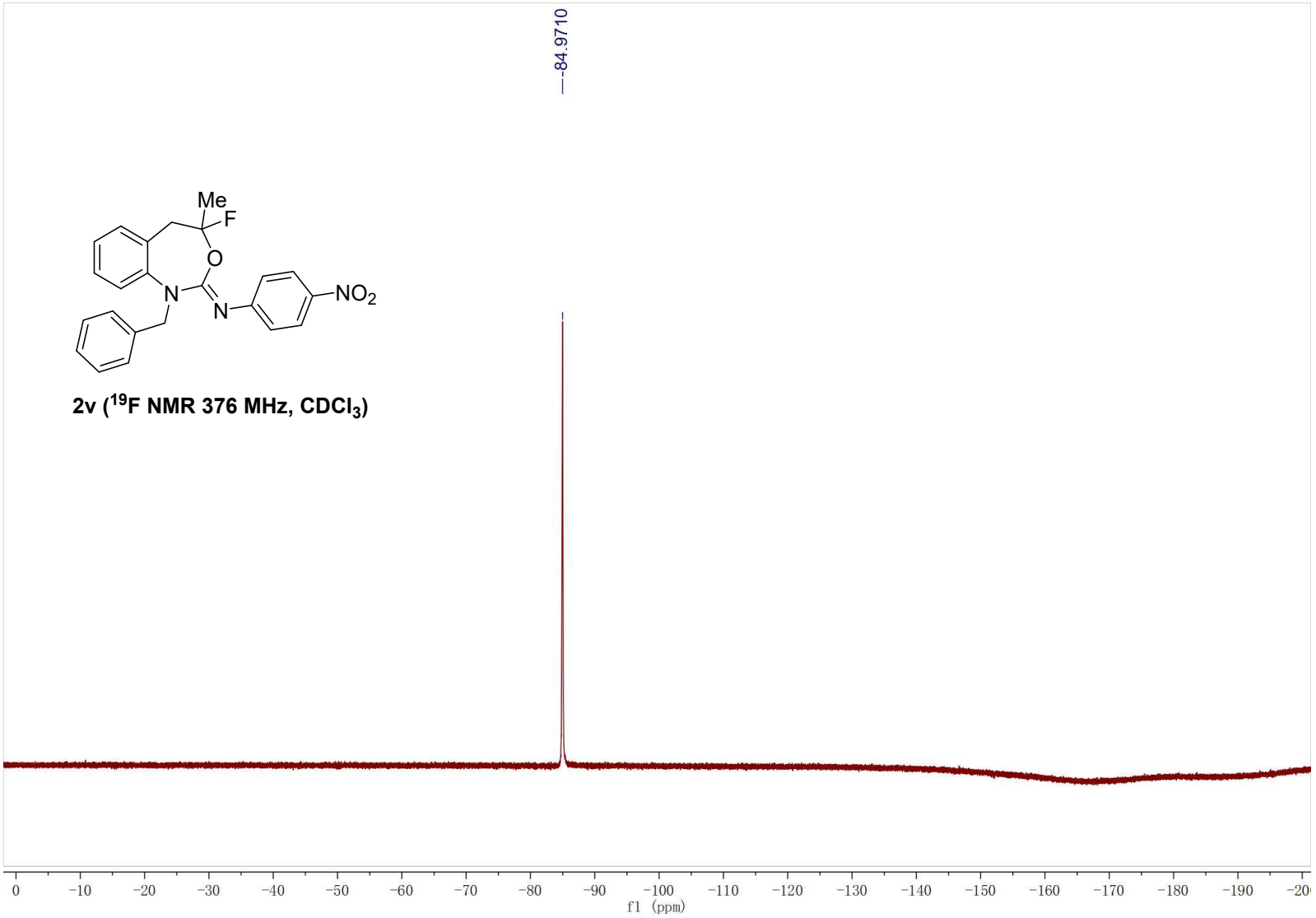

7.5080
7.4885
7.3269
7.3056
7.2883
7.2672
7.2496
7.2302
7.1382
7.0169
6.9974
5.2953
5.2567
5.2349
5.1962
3.2809
3.2469
3.2129
2.8617
2.8269
1.3739
1.3296
Me
F
O
N
N
CN
2u (1H NMR 400 MHz, CDCl3)
2.03
7.09
2.04
2.02
2.02
1.00
1.01
3.00
f1 (ppm)


151.7681
146.2435
141.7601
137.3142
132.4515
129.4573
129.3990
128.8870
128.5934
127.4634
127.3978
125.4961
123.9530
122.0652
121.3338
119.9177
119.0027
105.2152
54.3769
41.3071
40.9865
23.2359
22.9652
Me
F
O
N
N
CN
2u (^{13}C NMR 101 MHz, $CDCl_3$)
f1 (ppm)

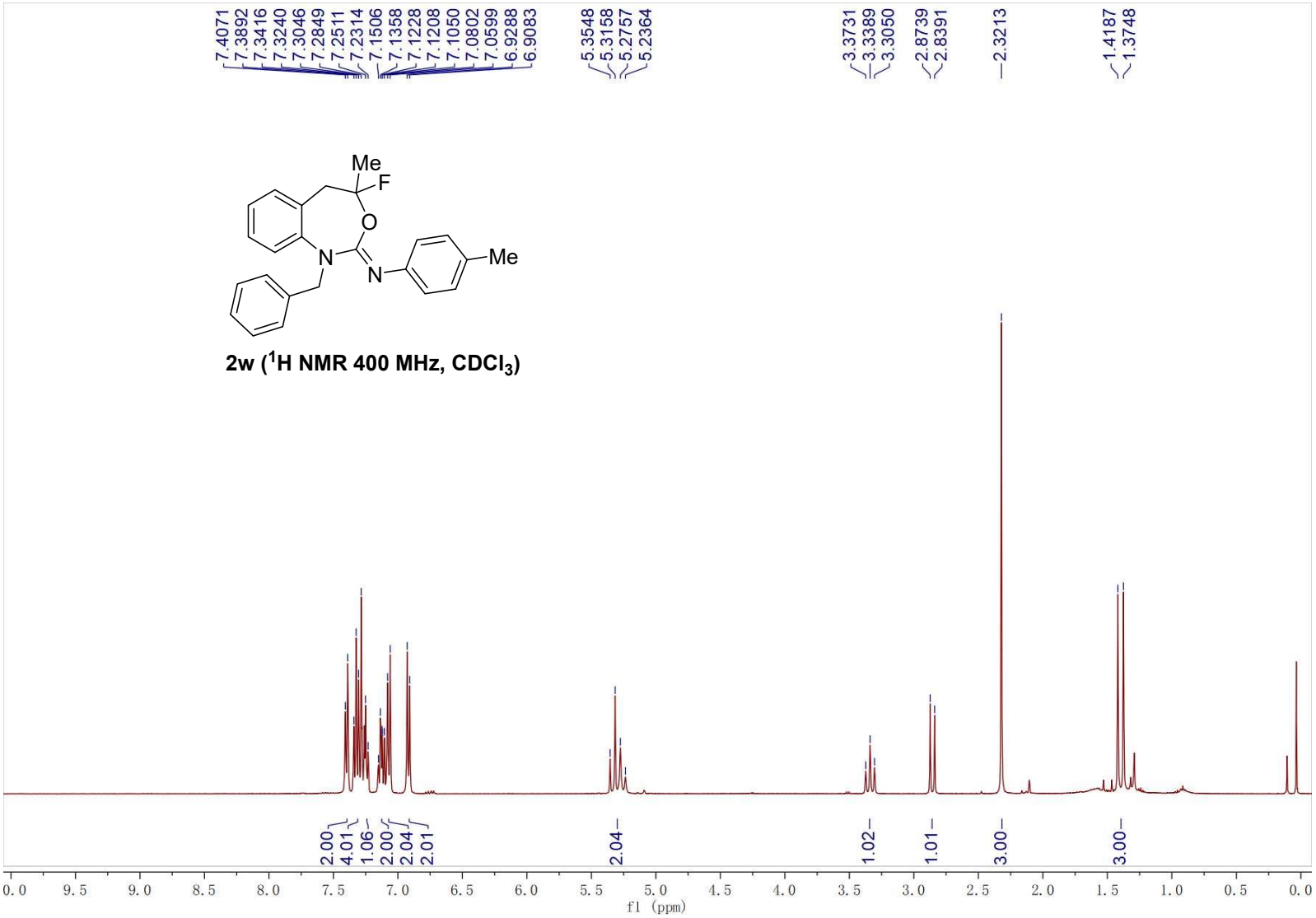

-85.0418
Me
F
O
N
N
CN
2u (^{19}F NMR 376 MHz, $CDCl_3$)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


8.1430
8.1208
7.3750
7.3548
7.3360
7.3163
7.2945
7.2786
7.1681
7.1582
7.0532
7.0310
5.3278
5.2888
5.2535
5.2146
3.3051
3.2707
3.2364
2.8936
2.8586
1.4024
1.3579
Me
F
O
N
N
NO2
2v (1H NMR 400 MHz, CDCl3)
2.05
7.00
2.00
2.04
2.05
1.00
1.00
3.00
f1 (ppm)

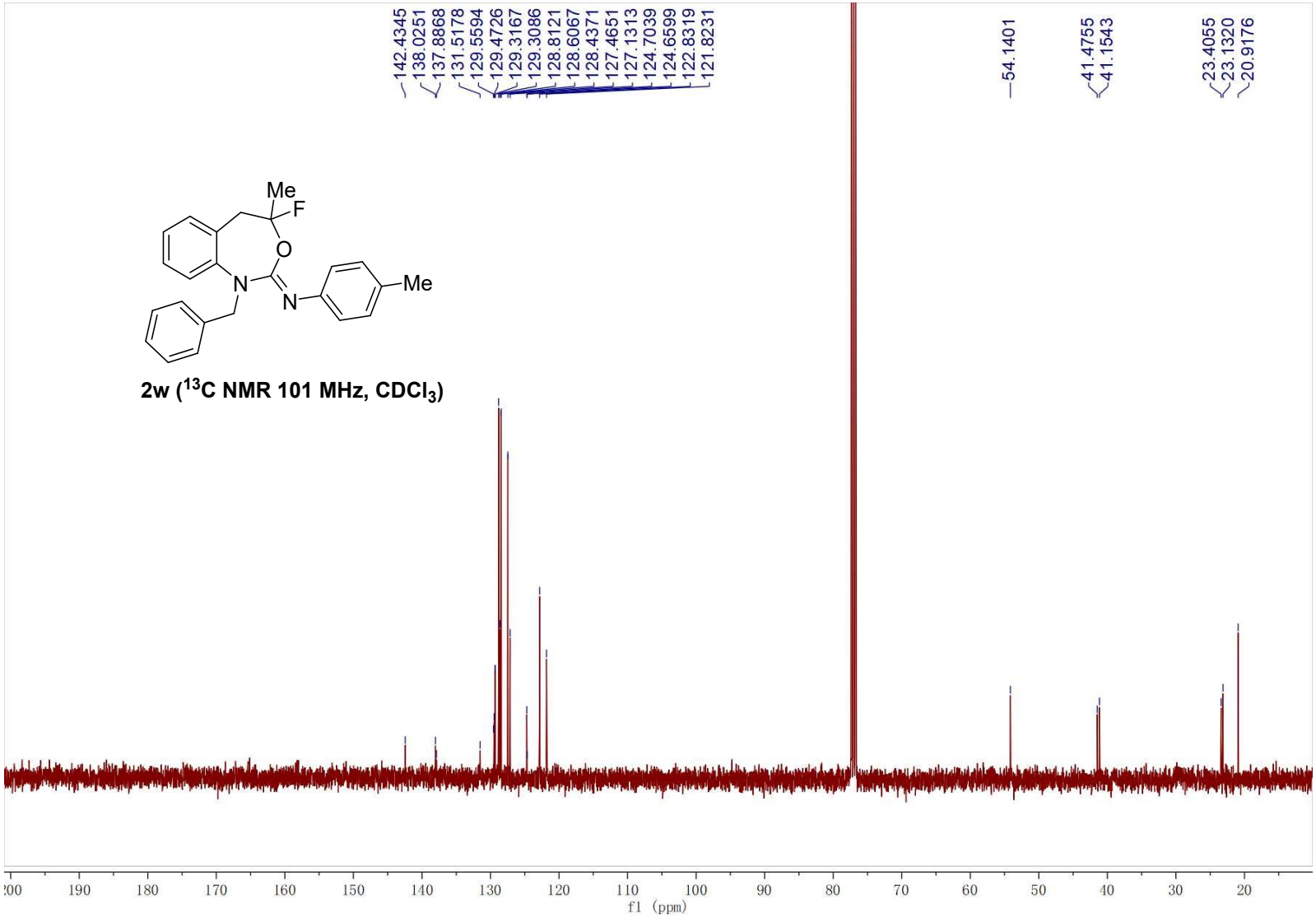

154.2590
146.4423
142.7217
141.6501
137.2412
129.5199
129.4791
129.3922
128.9475
128.6513
127.5254
127.3900
125.6267
124.3717
123.5198
122.0791
121.5542
119.2207
54.3851
41.2843
40.9645
23.2098
22.9415
Me
F
O
N
N
NO2
2v (13C NMR 101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



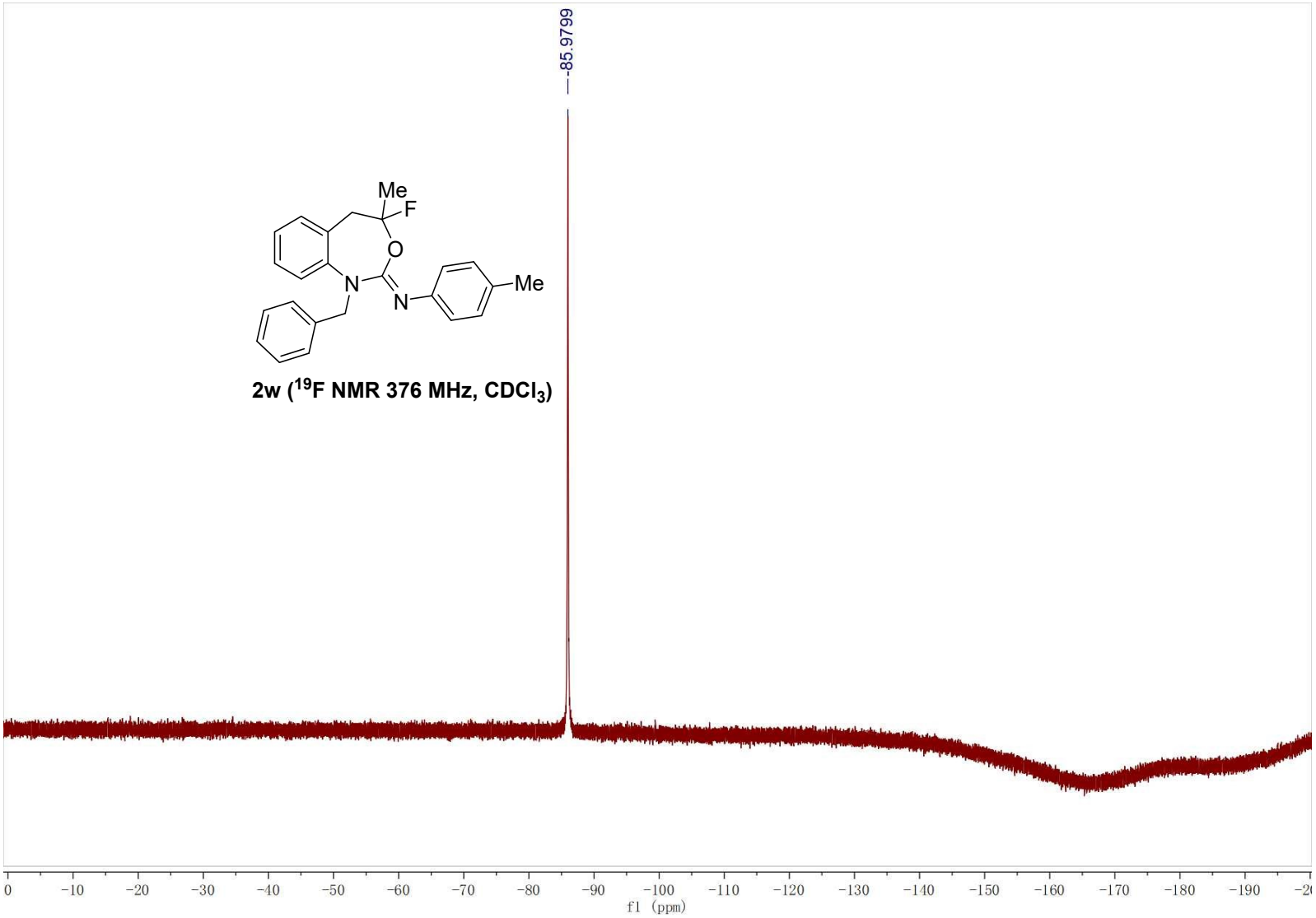
2v (^{19}F NMR 376 MHz, $CDCl_3$)



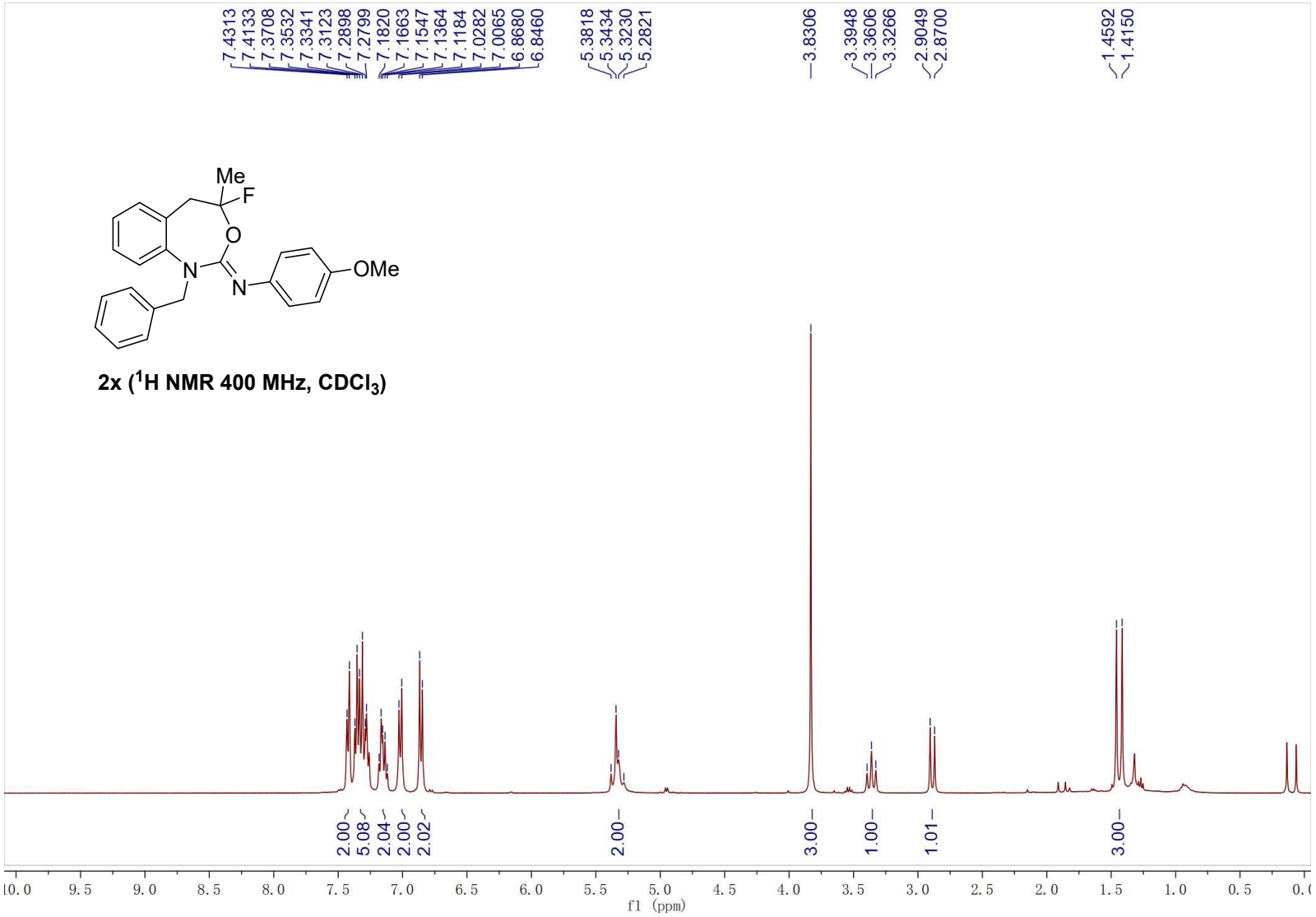
2w (^{1}H NMR 400 MHz, $CDCl_3$)



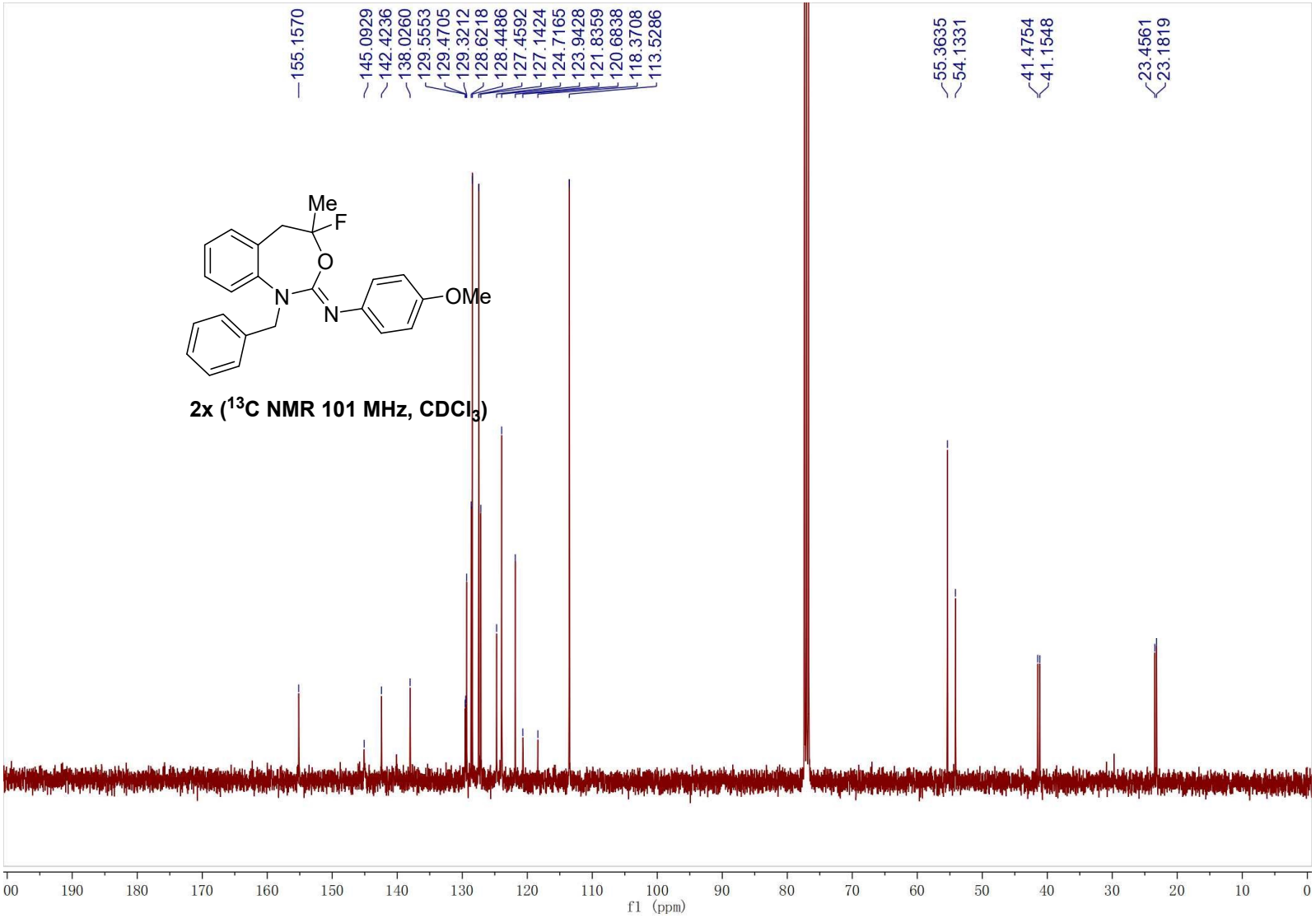
2w (^{13}C NMR 101 MHz, $CDCl_3$)



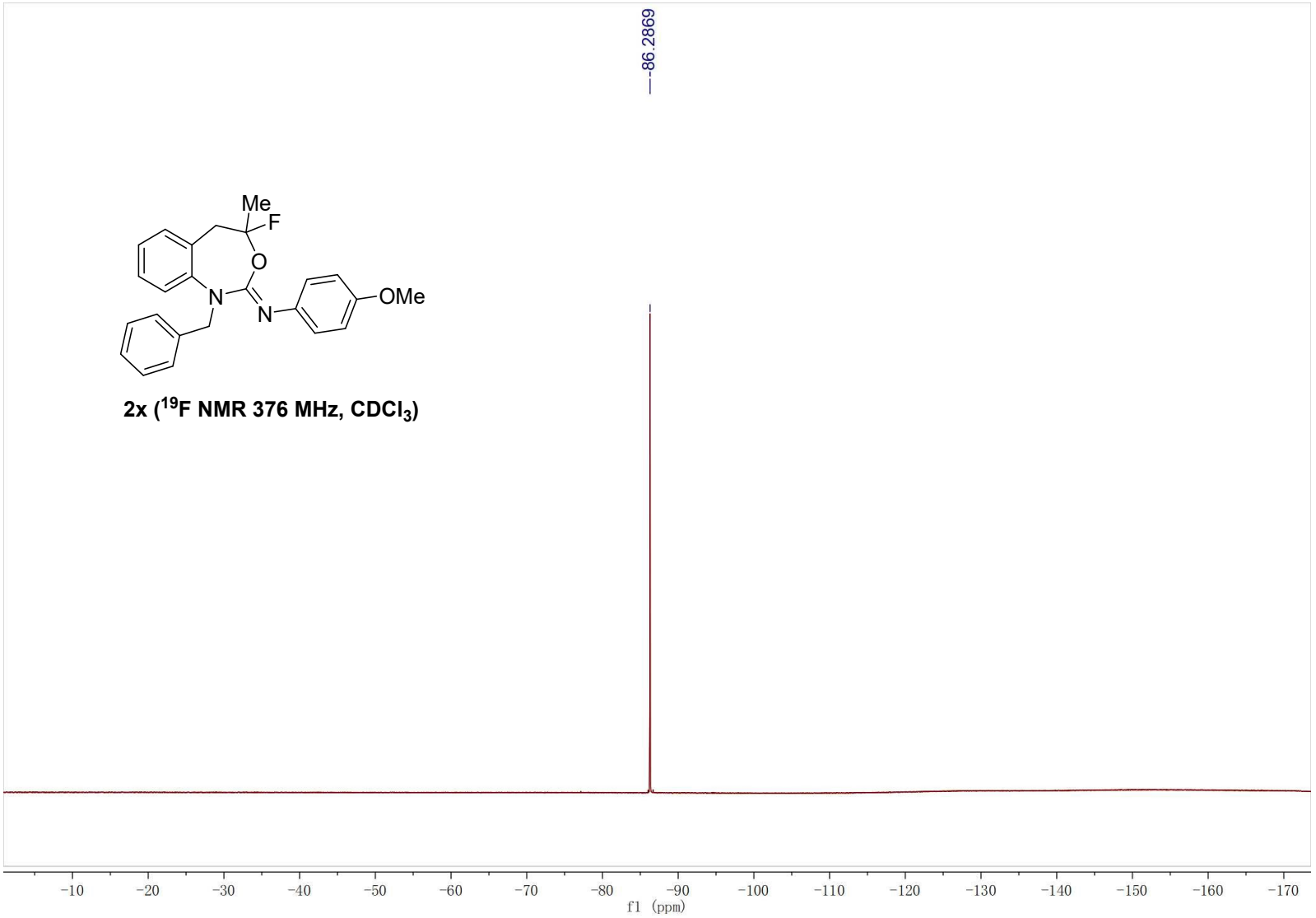
2w (^{19}F NMR 376 MHz, $CDCl_3$)



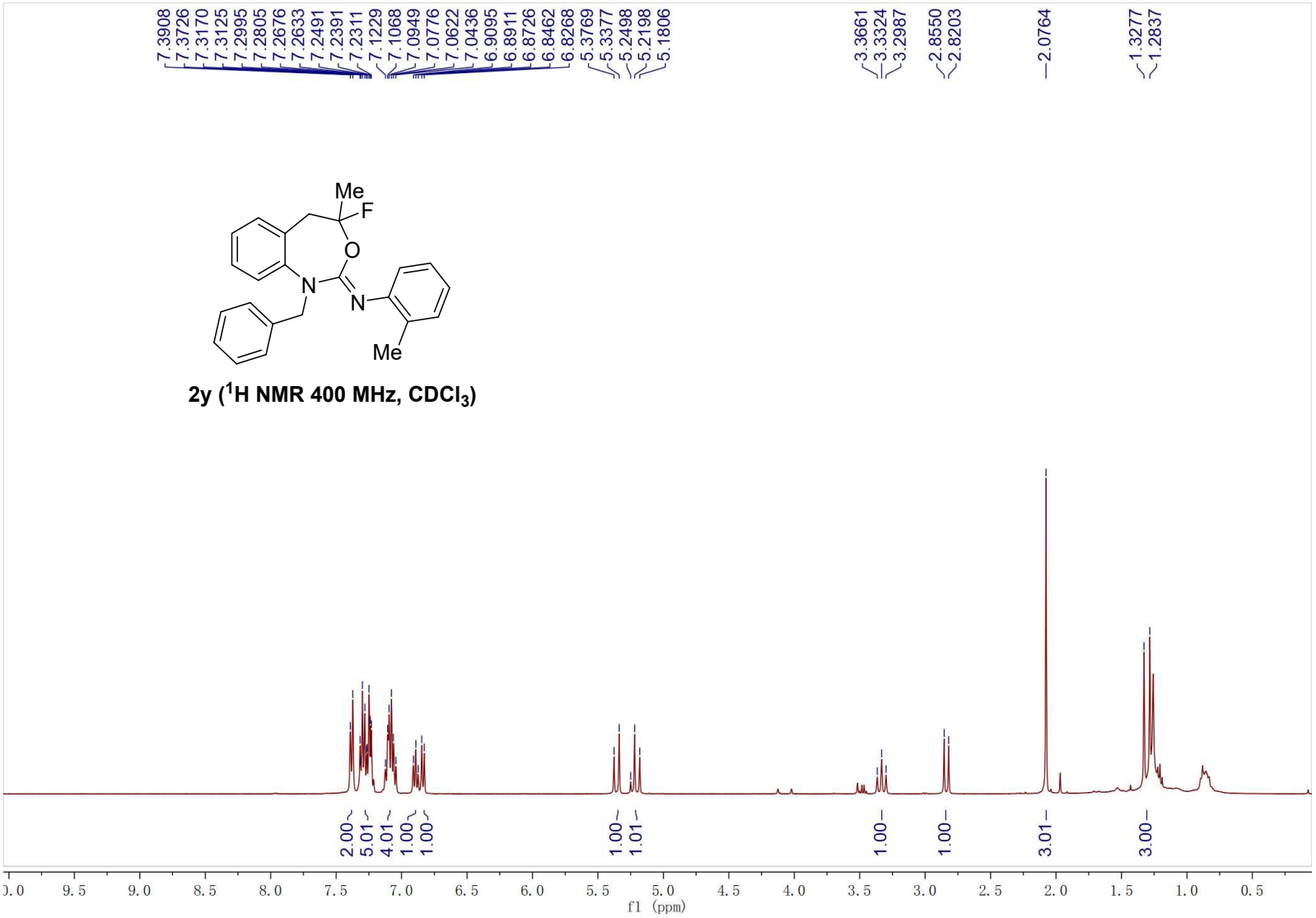
2x (^{1}H NMR 400 MHz, $CDCl_3$)



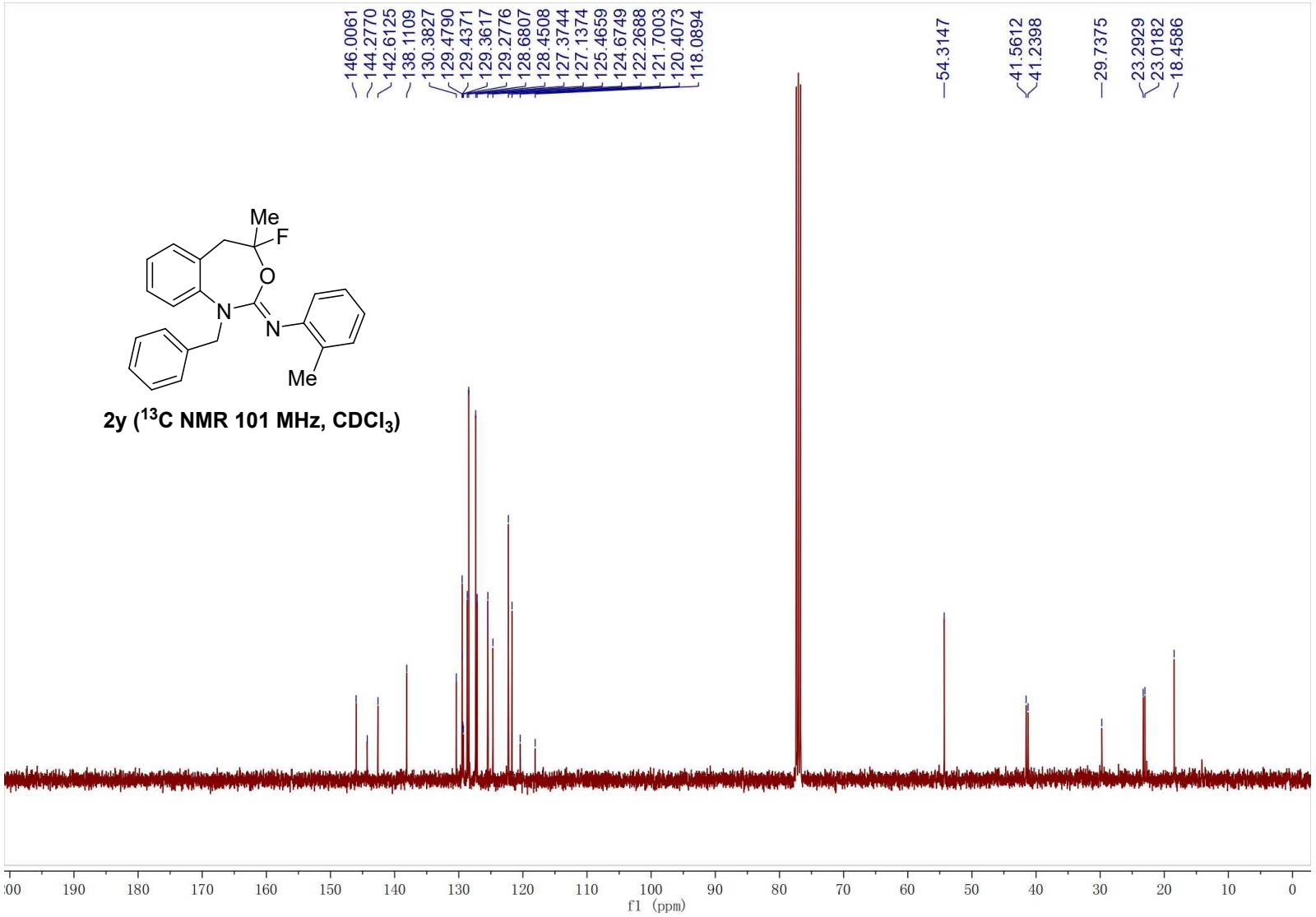
2x (^{13}C NMR 101 MHz, $CDCl_3$)

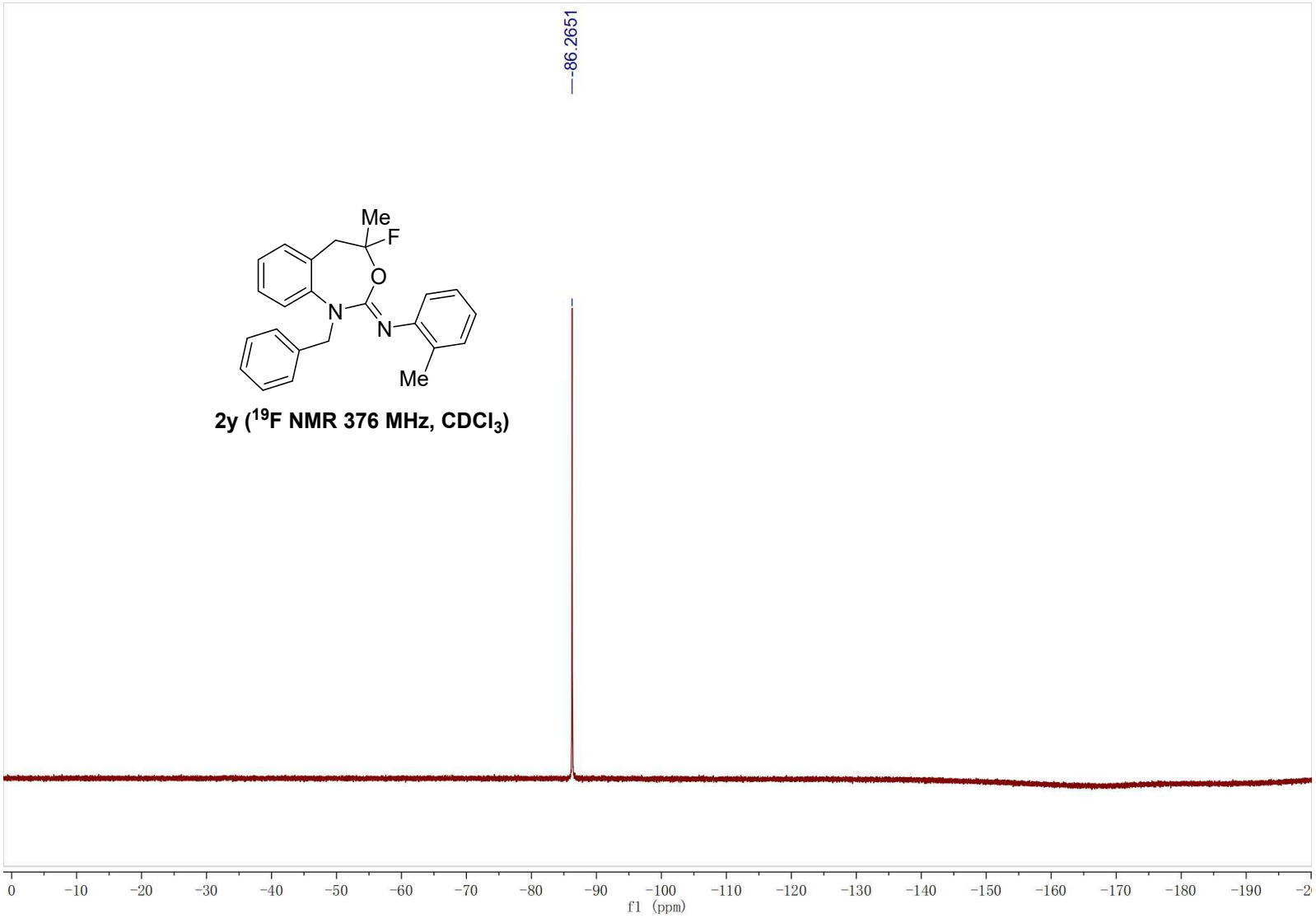


2x (^{19}F NMR 376 MHz, $CDCl_3$)

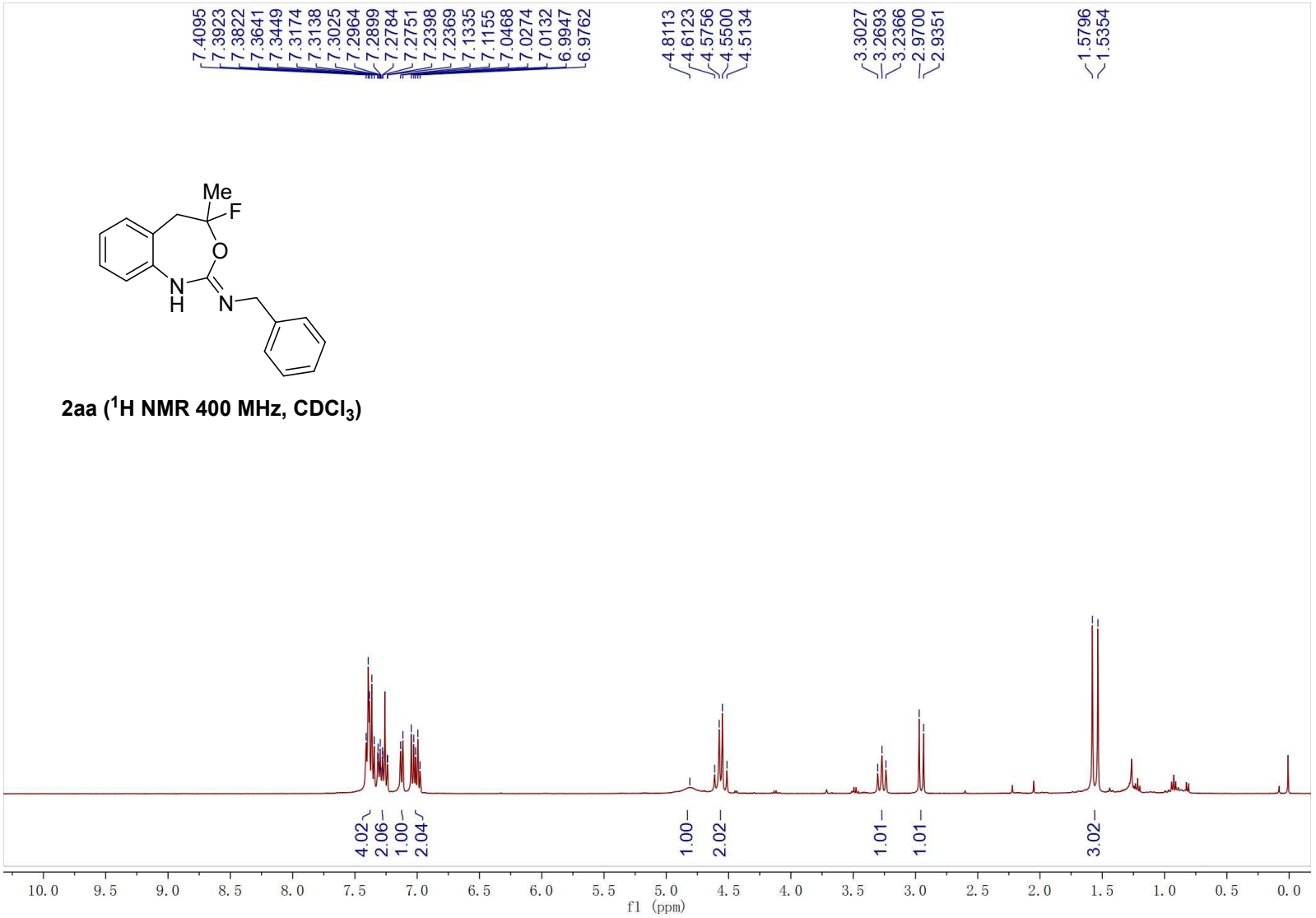


2y (^{1}H NMR 400 MHz, $CDCl_3$)

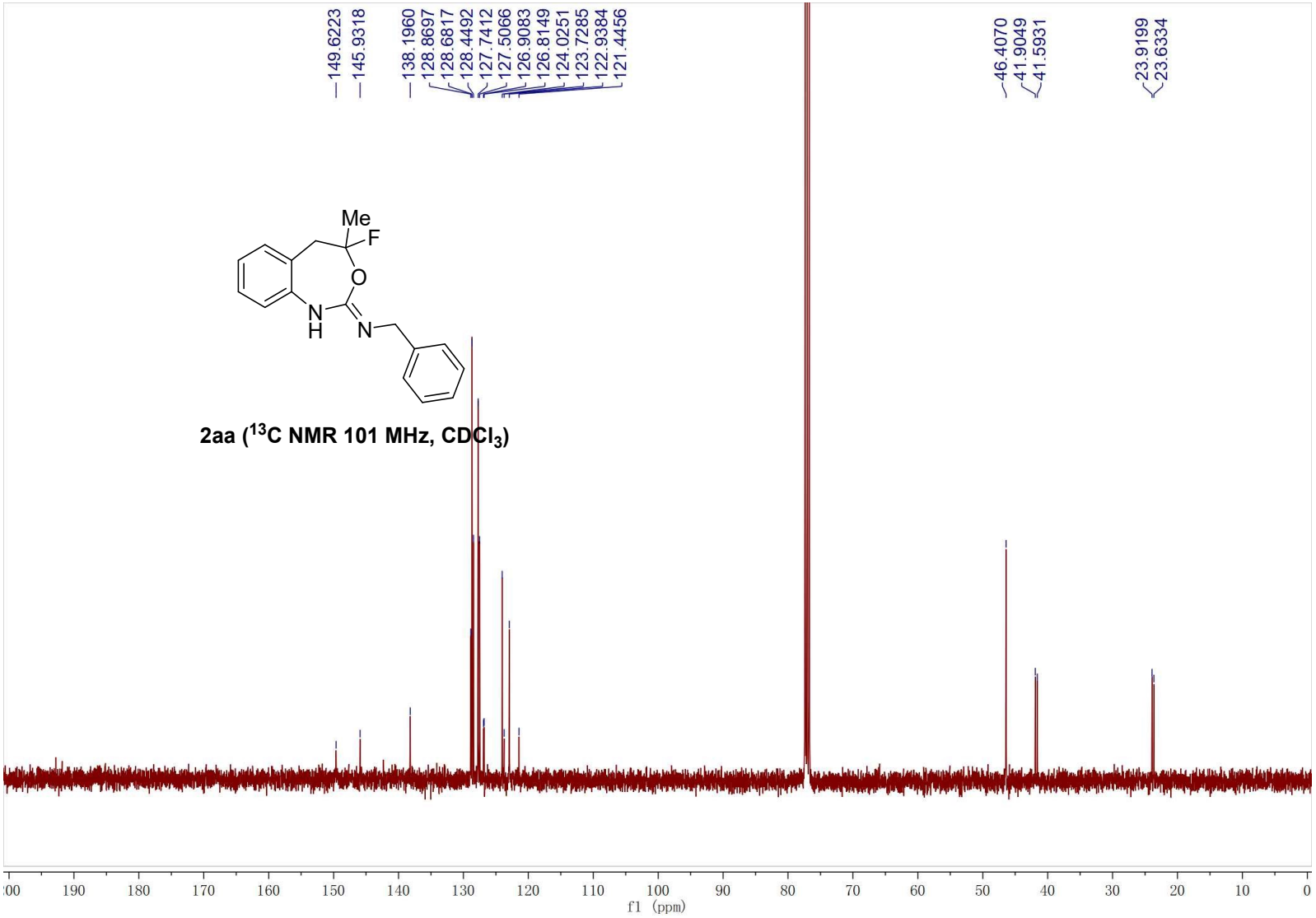

146.0061
144.2770
142.6125
138.1109
130.3827
129.4790
129.4371
129.3617
129.2776
128.6807
128.4508
127.3744
127.1374
125.4659
124.6749
122.2688
121.7003
120.4073
118.0894
54.3147
41.5612
41.2398
29.7375
23.2929
23.0182
18.4586
Me
F
O
N
N
Me
2y (^{13}C NMR 101 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



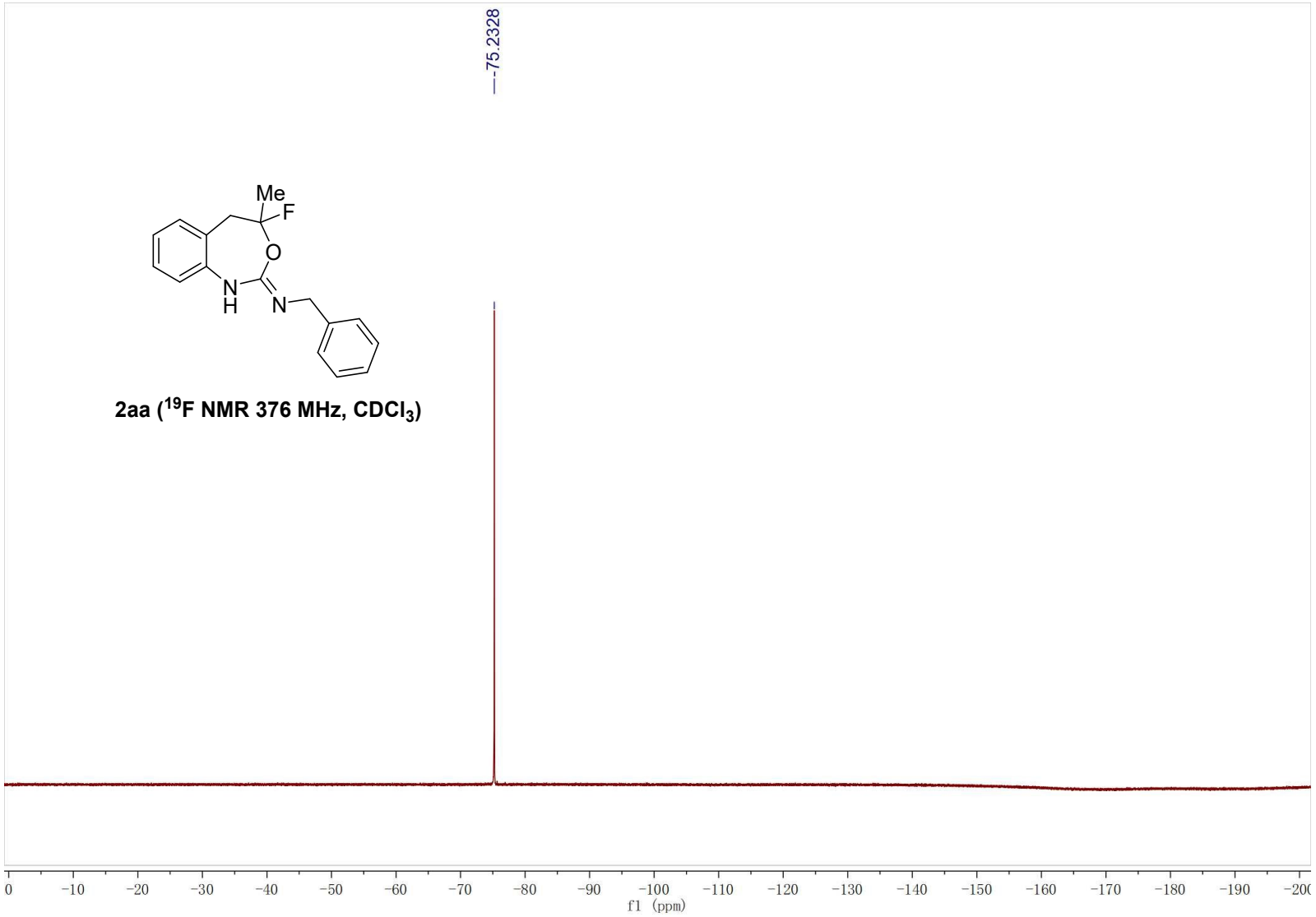
2y (^{19}F NMR 376 MHz, $CDCl_3$)



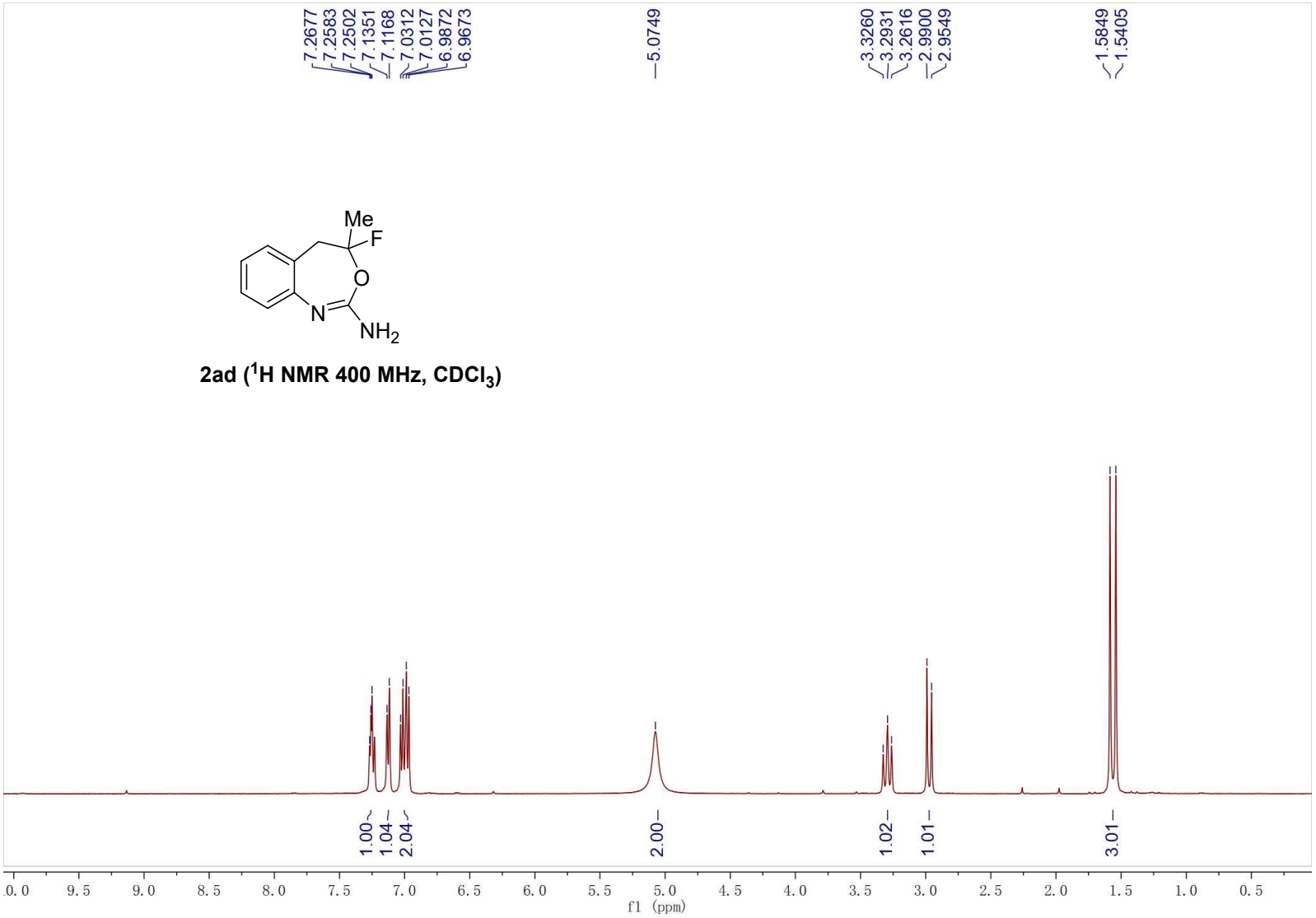
2aa (^{1}H NMR 400 MHz, $CDCl_3$)



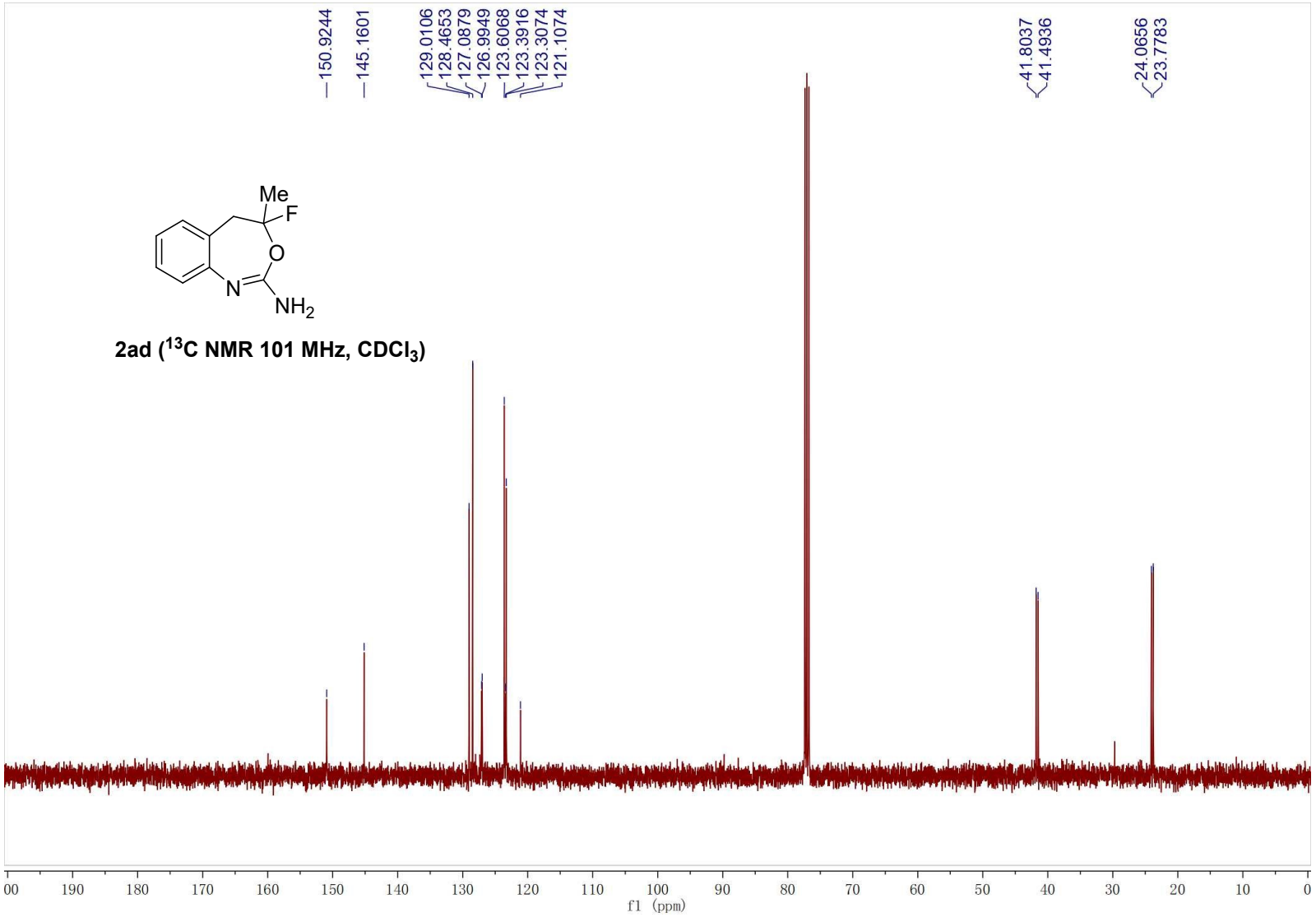
2aa (^{13}C NMR 101 MHz, $CDCl_3$)

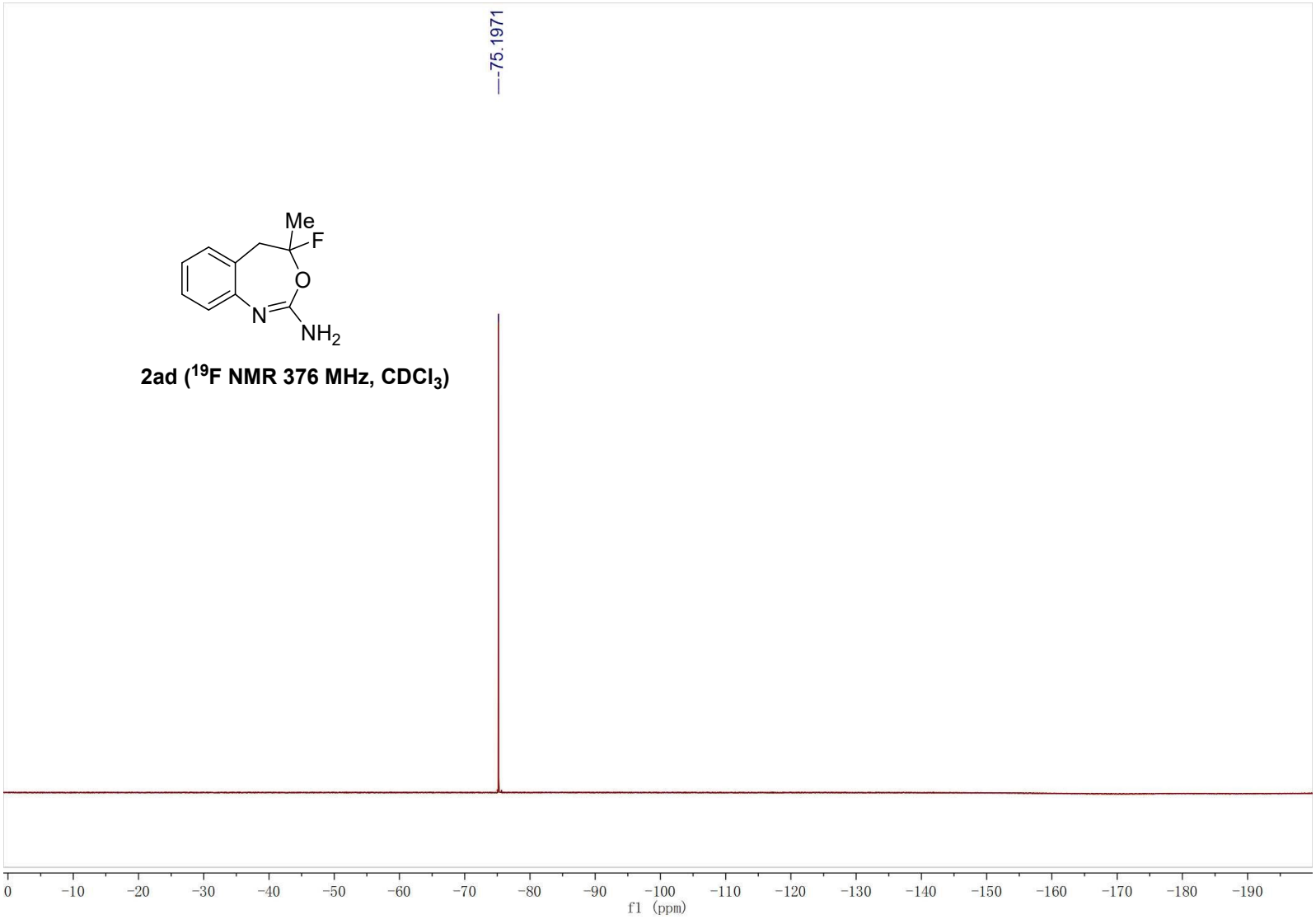


2aa (^{19}F NMR 376 MHz, $CDCl_3$)

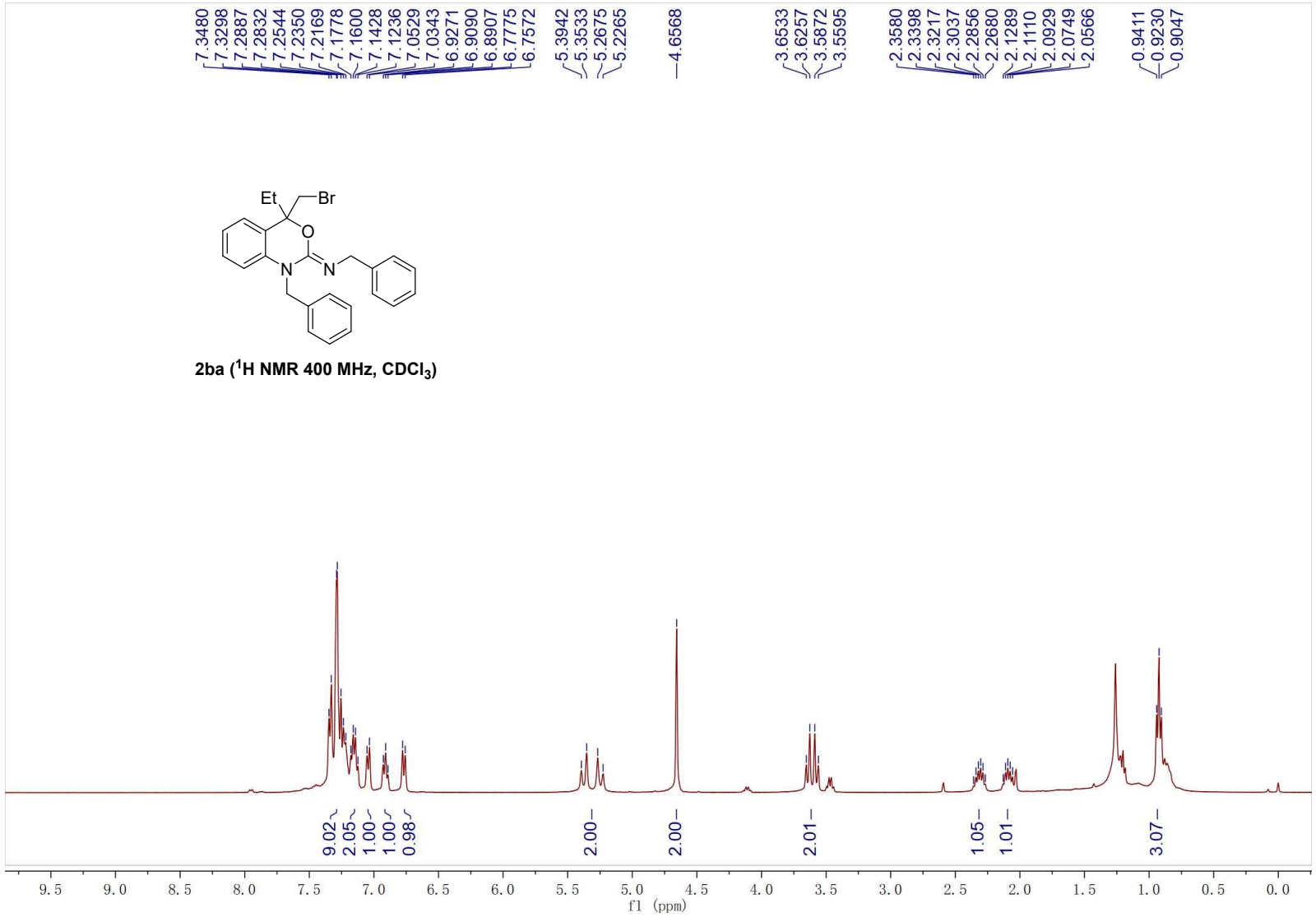


2ad (^{1}H NMR 400 MHz, $CDCl_3$)

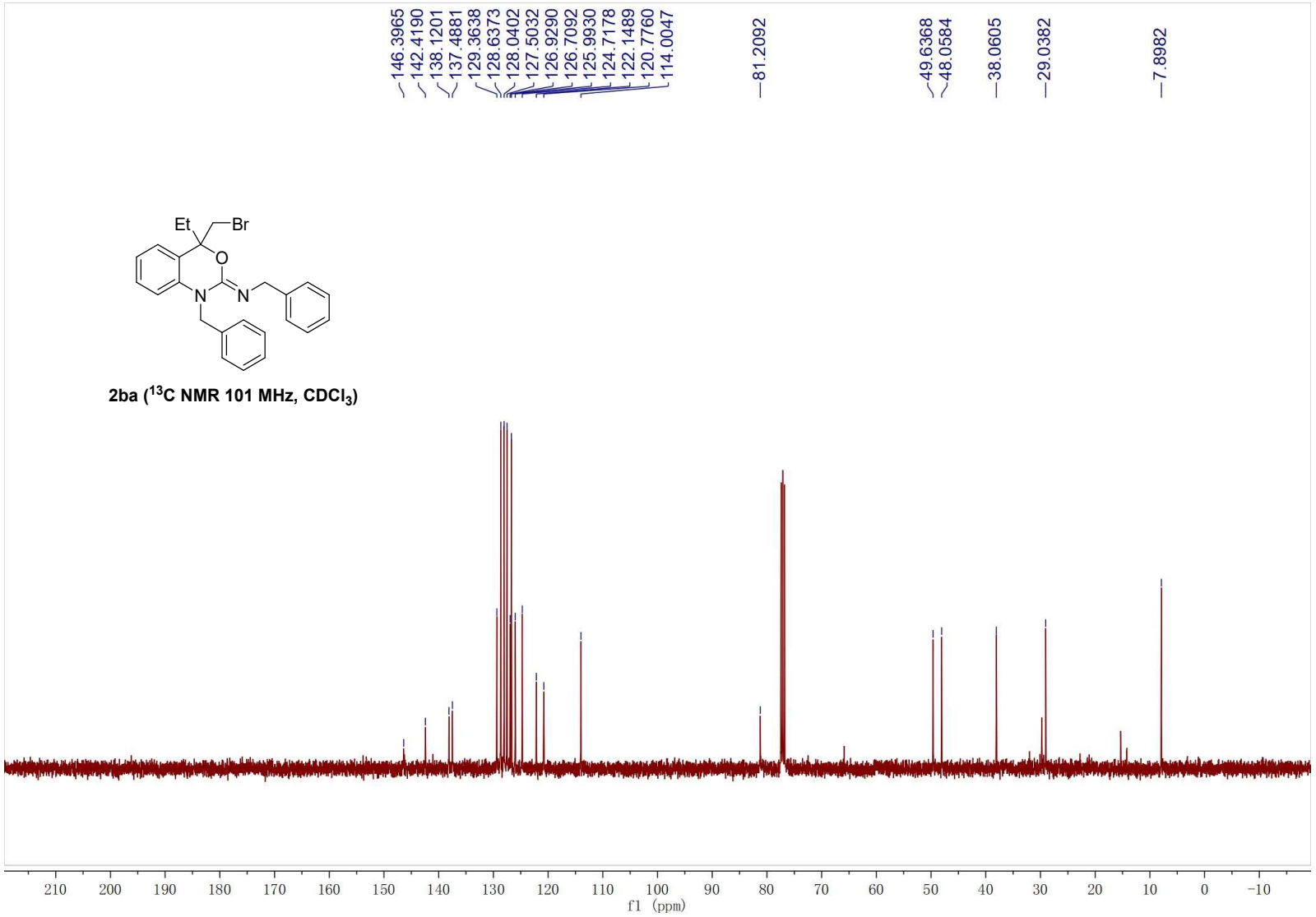

150.9244
145.1601
129.0106
128.4653
127.0879
126.9949
123.6068
123.3916
123.3074
121.1074
41.8037
41.4936
24.0656
23.7783
Me
F
O
N
NH2
2ad (13C NMR 101 MHz, CDCl3)
f1 (ppm)



2ad (^{19}F NMR 376 MHz, $CDCl_3$)



2ba (^{1}H NMR 400 MHz, $CDCl_3$)



2ba (^{13}C NMR 101 MHz, $CDCl_3$)