Metal-free C−H borylation of heterocycles by merging photoredox and hydrogen atom transfer catalysis

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Supporting Information

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1. General Information

Unless stated otherwise, all reactions were performed in thoroughly oven-dried glassware. The reactions involving reagents or intermediates that are sensitive to air or moisture were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Commercially available chemicals were obtained from commercial suppliers and used as received without further purification unless otherwise stated. Anhydrous THF and CH_2Cl_2 were purchased from Energy Chemical and stored under argon. All photocatalysts were obtained from commercial suppliers and used as received.

All reactions were monitored by thin-layer chromatography (TLC) with Huanghai GF254 silica gel coated plates. TLC plates were visualized by exposure to ultraviolet light, and/or stained with the mixture of I_2 and silica gel or the solvent of potassium permanganate. Purification of reaction products were carried out by flash column chromatography using silica gel (Qingdao Haiyang Co. Ltd, 200-300 mesh). ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectra were measured in $CDCl_3$ and recorded on an Agilent DD2 400-MR or Brucker Avance-400 spectrometer at ambient temperature. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for $CDCl_3$). The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.00 ppm). Chemical shifts for ^{19}F NMR were reported in ppm downfield from $CFCl_3$ ($CFCl_3$ as outside standard) and referenced to the fluorine resonance of $CFCl_3$ (δ = 0). Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), doublet of doublet of doublets (ddd), multiplet (m), quartet (q), and broad (br). High-resolution mass spectra (HRMS) were obtained on a Waters Xevo G2-XS QTof mass spectrometer with positive mode electrospray ionization (ESI, analyzer type: TOF). Melting points (°C) are uncorrected and were recorded on a SGW X-4 apparatus.

Irradiation of reaction vessels was accomplished using 40 W Kessil® PR160L blue LED with specific wavelength (λ_{max} = 456 nm). The average intensity of PR160L blue LED in a 2×10 cm is 159 mW/cm^2. The distance from the light source to the irradiation vessel was approximate 3 cm. We did not use band pass filters. A fan was employed to ensure reactions remained at or near room temperature when using LED.

2. General Procedure for the Preparation of Reaction Substrates

2.1 Preparation of *N*-alkyl quinoxalin-2(1*H*)-ones

The quinoxalin-2(1*H*)-one substrates (**1a**-**1f**,[1] **1g**,[1] **1h**,[1] **1i**,[2] **1j**-**1o**,[1] and **1q**[1]) shown in Figure S1 are reported compounds and prepared according to the reported procedures. **1p** is commercial available.

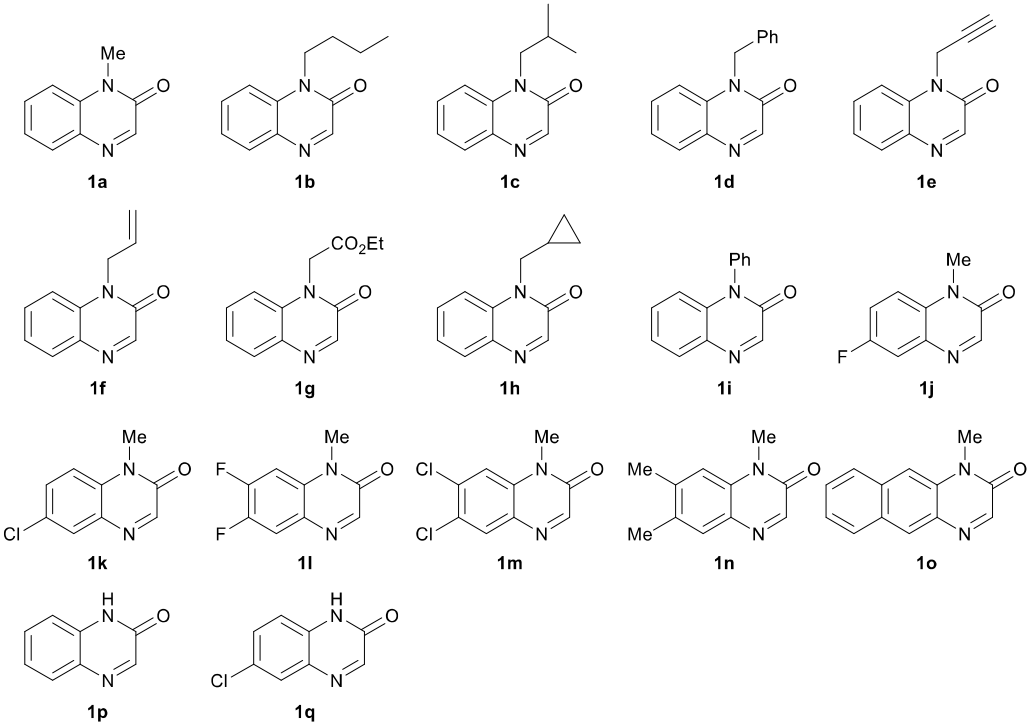


Figure S1. Quinoxalin-2(1*H*)-one substrates used in this work

2.2 Preparation of 4*H*-chromen-4-ones

Synthetic methods for the 4*H*-chromen-4-one substrates **4** (**4c**-**4e**,[3] **4f**[4]) shown in Figure S2 were reported in the literatures. **4a** and **4b** are commercial available.

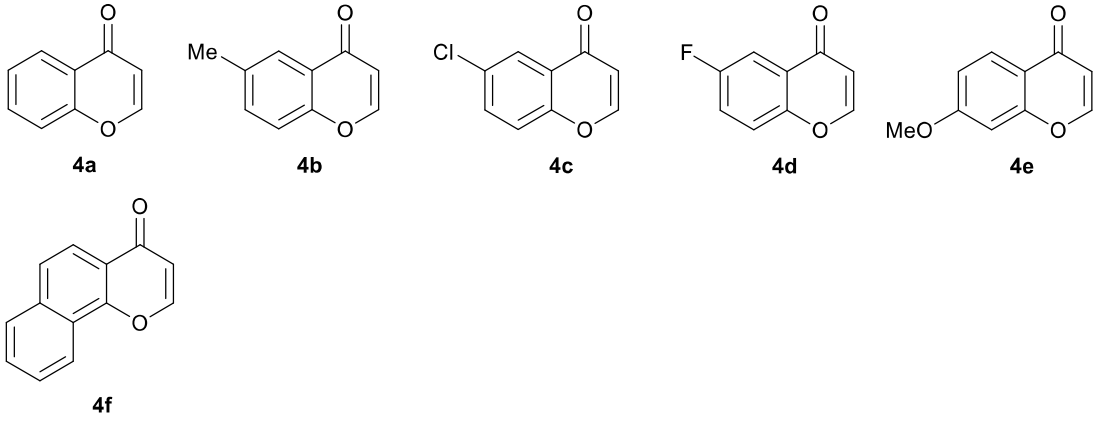


Figure S2. 4*H*-Chromen-4-one substrates used in this work

2.3 Preparation of quinazolin-4(3*H*)-ones

As shown in Figure S3, quinazolin-4(3*H*)-ones **6** (**6a**,[5] **6b**-**6n**[6]) were synthesized according to the reported procedures. Among them, quinazolin-4(3*H*)-one **6g** is a new compound and its spectra data are shown in this supporting information.

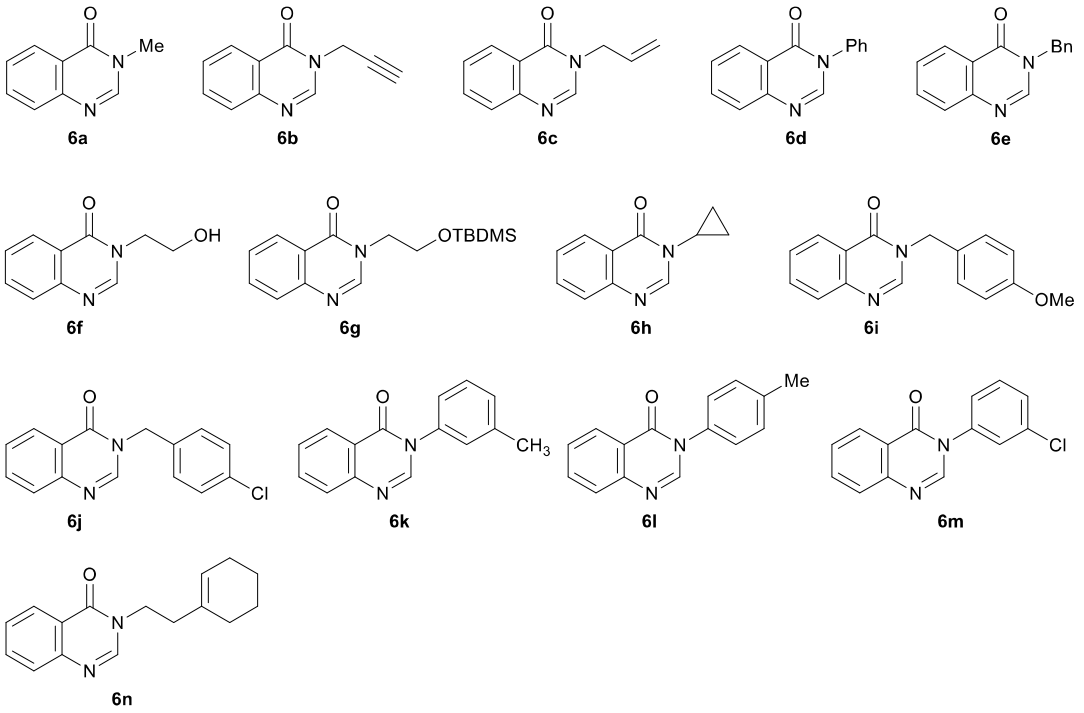


Figure S3. Quinazolin-4(3*H*)-one substrates used in this work

2.4 Preparation of azauracil substrates

The azauracil substrates **8** (**8a**-**8j**[7]) shown in Figure S4 were prepared according to the reported procedures. Among them, azauracil **8j** is a new compound and its spectra data are shown in this supporting information.

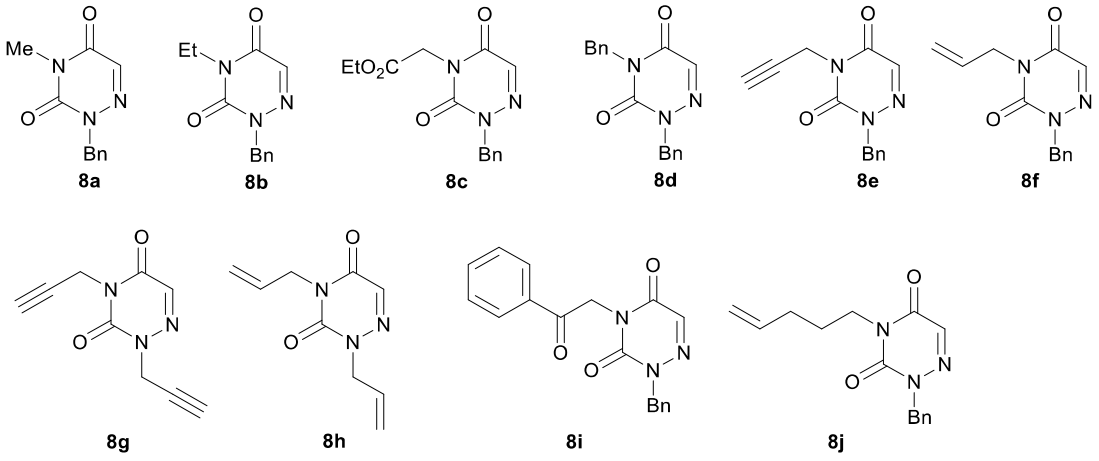
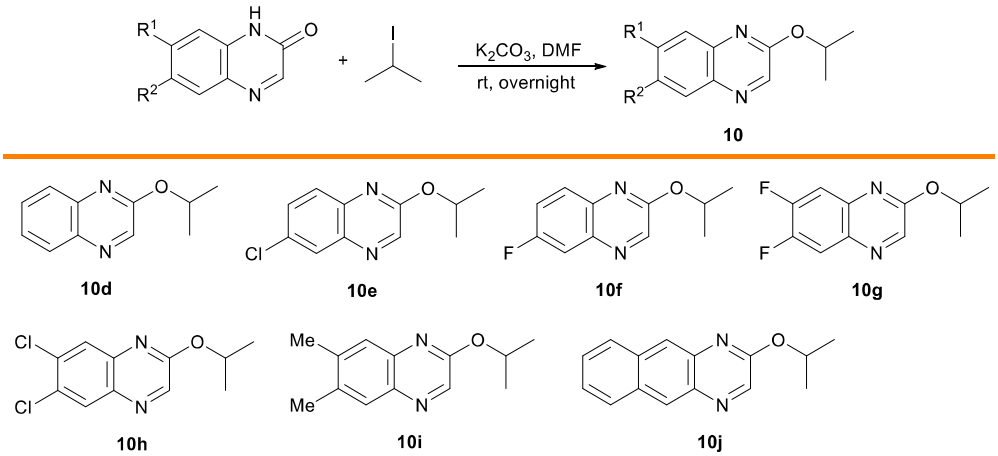


Figure S4. Azauracil substrates used in this work

2.5 General procedure for the synthesis of quinoxaline substrates

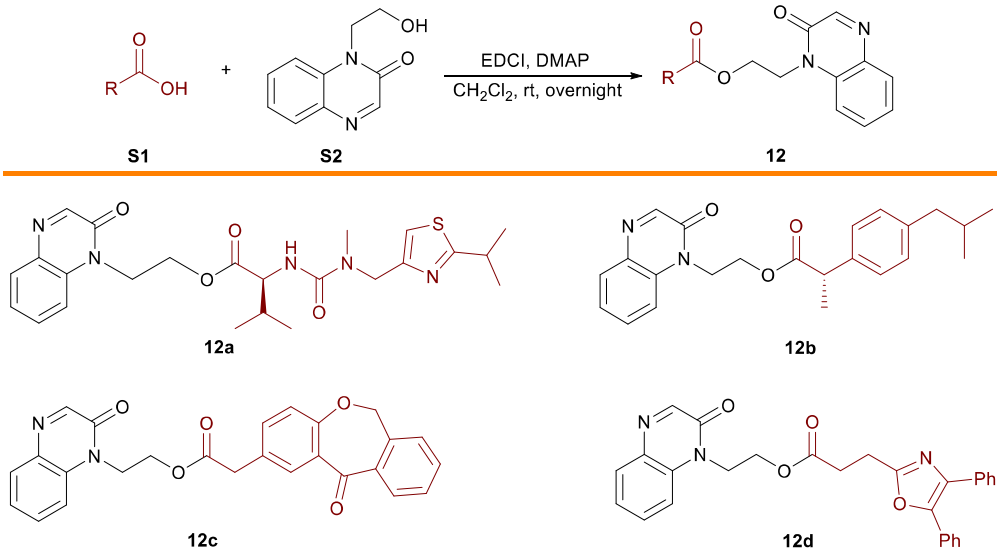


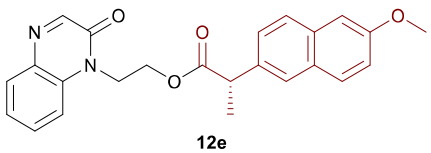
2-Isopropoxyquinoxalines **10d-10j** were prepared according to the reported procedure as follow.[8] Among them, 2-isopropoxyquinoxalines **10e-10j** are new compounds and their spectra data are shown in this supporting information.

An oven-dried round bottom flask was charged with a solution of corresponding quinoxalin-2(1*H*)-one (2.0 mmol, 1.0 equiv) in DMF (6.0 mL). To this, 2-iodopropane (0.32 mL, 3.2 mmol, 1.6 equiv) and K_2CO_3 (331.7 mg, 2.4 mmol, 1.2 equiv) were added, and the resulting mixture was stirred at room temperature overnight. After completed, the reaction mixture was diluted with H_2O, extracted with ethyl acetate, and washed with brine. The combined organic layers were died over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate) on silica gel to afford the product **10**.

2.6 Preparation of heterocyclic substrates derived from bioactive molecules

For bioactive molecules containing a carboxyl group



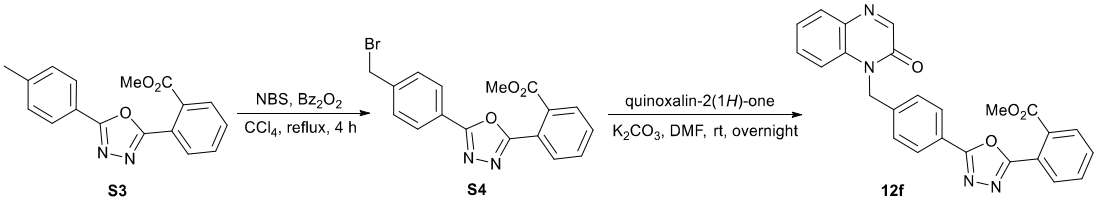


12e

According to previously reported literature,[9] quinoxalin-2(1*H*)-one derivatives **12a-12e** were conveniently synthesized under slightly modified reaction conditions. Among them, **12a**, **12d**, and **12e** are new compounds and their spectra data are shown in this supporting information.

Carboxylic acid **S1** (4.0 mmol, 2.0 equiv.), 1-(2-hydroxyethyl)quinoxalin 2(1*H*)-one **S2** (380.4 mg, 2.0 mmol, 1.0 equiv.), and DMAP (24.4 mg, 10 mol%) were mixed in an oven-dried flask with a magnetic stirring bar. Dry CH_2Cl_2 (20.0 mL) was added. The reaction mixture was stirred for 5 min before the addition of EDCI (766.8 mg, 4.0 mmol, 2.0 equiv). The resulting mixture was stirred overnight at room temperature. The reaction mixture was quenched with H_2O and extracted with EtOAc for three times. Then, the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The purification of the crude residue was achieved by flash column chromatography (eluting with petroleum ether/ethyl acetate) on silica gel to give the product **12**.

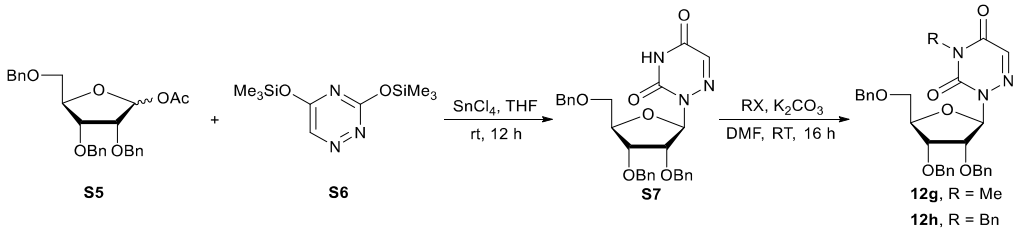
*Synthesis of **12f** (Scheme S3)*



S3 **S4** **12f**

12f was synthesized according to the previously reported procedure, and it is a known compound.[10]

For azauracil ribonucleoside substrates



S5 **S6** **S7**

Synthetic methods for acetyl ribose **S5**[11] and bis-trimethylsilyloxytriazine **S6**[12] were reported in the previous literatures.

Azauracil ribonucleosides **12g** and **12h** were prepared according to the previously reported procedures.[13] To an oven-dried round bottom flask charged with acetyl ribose **S5** (925.0 mg, 2.0 mmol, 1.0 equiv), the crude bis-trimethylsilyloxytriazine **S6** (773.0

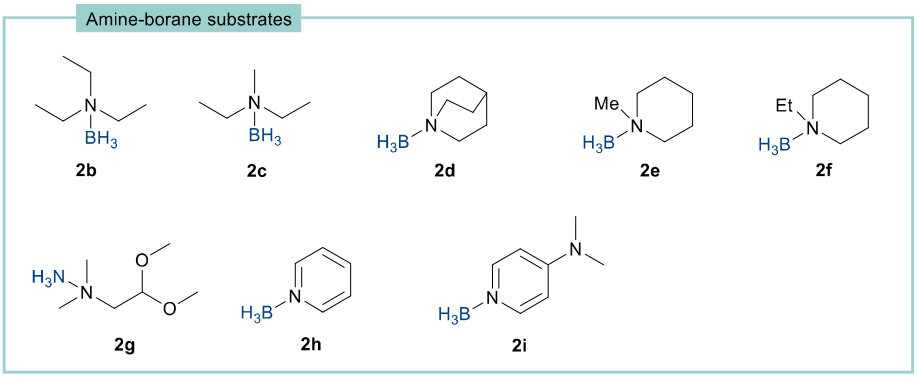
mg, 3.0 mmol, 1.5 equiv) and dry THF (20.0 mL) was added $SnCl_4$ (5.0 mL, 5.0 mmol, 2.5 equiv, 1 M solution in CH_2Cl_2) dropwise at 0 °C under nitrogen atmosphere. Then, the reaction mixture was allowed to stir at room temperature for 12 h. The reaction was quenched with aqueous $NaHCO_3$ solution and the resulting mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The purification of the crude residue was achieved by flash column chromatography (eluting with petroleum ether/ethyl acetate = 4/1, v/v) on silica gel to give the product **S7** (493.1 mg, 48% yield) as a pale yellow viscous oil.

To a solution of azauracil ribonucleoside **S7** (361.0 mg, 0.7 mmol, 1.0 equiv) and K_2CO_3 (48.5 mg, 0.35 mmol, 0.5 equiv) in DMF (7.0 mL) was added dropwise alkyl halide (0.7 mmol, 1.0 equiv). The reaction mixture was allowed to stir at room temperature for 16 h. Then, the mixture was diluted with H_2O and extracted with CH_2Cl_2 for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The purification of the crude residue was achieved by flash column chromatography (eluting with petroleum ether/ethyl acetate) on silica gel to give the corresponding *N*-alkyl azauracil ribonucleoside.

12h is new a compound and its spectra data are shown in this supporting information.

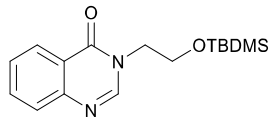
2.7 General procedure for the preparation of amine-boranes

The amine-borane substrates (**2c-2g** and **2i**)[14] shown in Figure S1 are reported compounds and prepared according to the reported procedure. **2b** and **2h** are commercial available.



2.8 Characterization data for the new substrates

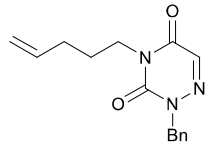
3-(2-((tert-Butyldimethylsilyl)oxy)ethyl)quinazolin-4(3H)-one (6g)



6g

White solid, m.p. 69.9–70.8 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.05 (s, 1H), 7.73 – 7.66 (m, 2H), 7.47 – 7.43 (m, 1H), 4.09 (t, *J* = 5.0 Hz, 2H), 3.88 (t, *J* = 4.7 Hz, 2H), 0.79 (s, 9H), -0.11 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 148.2, 147.6, 134.0, 127.3, 126.9, 126.5, 121.9, 60.5, 49.0, 25.7, 18.0, -5.8; **HRMS-ESI** (m/z): calcd for $C_{16}H_{25}N_2O_2Si$, $[M + H]^+$: 305.1680, found, 305.1688.

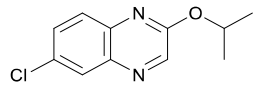
2-Benzyl-4-(pent-4-en-1-yl)-1,2,4-triazine-3,5(2H,4H)-dione (8j)



8j

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.40 (s, 1H), 7.34 – 7.29 (m, 3H), 5.83 – 5.73 (m, 1H), 5.08 (s, 2H), 5.05 – 4.96 (m, 2H), 3.97 (t, *J* = 7.3 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.88 – 1.81 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.9, 148.5, 137.0, 135.4, 134.06, 134.05, 129.4, 128.5, 128.1, 115.5, 51.4, 43.8, 30.5, 27.1; **HRMS-ESI** (m/z): calcd for $C_{15}H_{17}N_3NaO_2$, $[M + Na]^+$: 294.1213, found, 294.1222.

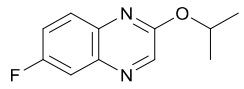
6-Chloro-2-isopropoxyquinoxaline (10e)



10e

White solid, m.p. 36.8–37.8 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.59 (dd, *J* = 8.9, 2.1 Hz, 1H), 5.53 – 5.44 (m, 1H), 1.43 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.0, 141.2, 139.0, 138.8, 131.5, 130.6, 128.2, 127.9, 69.5, 21.7; **HRMS-ESI** (m/z): calcd for $C_{11}H_{12}ClN_2O$, $[M + H]^+$: 223.0633, found, 223.0638.

6-Fluoro-2-isopropoxyquinoxaline (10f)

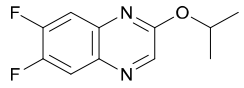


10f

White solid, m.p. 39.8–40.8 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.78 (dd, *J* = 9.1, 5.6 Hz, 1H), 7.64 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.43 (td, *J* = 8.7, 2.8 Hz, 1H), 5.53 – 5.43 (m, 1H), 1.43 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4 (d, *J* = 246.2 Hz), 156.6 (d, *J* = 2.3 Hz), 141.1, 138.8 (d, *J* = 12.3 Hz), 137.3 (d, *J* = 1.1 Hz),

128.6 (d, J = 9.4 Hz), 119.4 (d, J = 25.1 Hz), 112.9 (d, J = 21.7 Hz), 69.2, 21.7; **HRMS-ESI** (m/z): calcd for $C_{11}H_{12}FN_2O$, $[M + H]^+$: 207.0928, found, 207.0933.

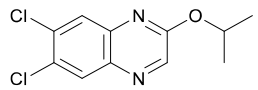
6,7-Difluoro-2-isopropoxyquinoxaline (10g)



10g

White solid, m.p. 75.7–76.4 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.74 (dd, J = 10.4, 8.4 Hz, 1H), 7.54 (dd, J = 11.0, 8.0 Hz, 1H), 5.49 – 5.41 (m, 1H), 1.42 (d, J = 6.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1 (d, J = 2.2 Hz), 152.1 (dd, J = 253.9, 15.5 Hz), 149.5 (dd, J = 250.4, 15.5 Hz), 140.3 (d, J = 3.4 Hz), 137.7 (dd, J = 11.1, 1.4 Hz), 135.0 (dd, J = 10.0, 1.6 Hz), 114.9 (dd, J = 17.4, 2.1 Hz), 113.1 (d, J = 17.8 Hz), 69.6, 21.7. **HRMS-ESI** (m/z): calcd for $C_{11}H_{11}F_2N_2O$, $[M + H]^+$: 225.0834, found, 225.0840.

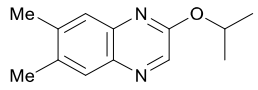
6,7-Dichloro-2-isopropoxyquinoxaline (10h)



10h

White solid, m.p. 73.9–74.5 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.98 (s, 1H), 7.82 (s, 1H), 5.47 – 5.38 (m, 1H), 1.41 (d, J = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.3, 141.4, 139.4, 137.2, 134.0, 130.0, 129.4, 127.7, 69.8, 21.6; **HRMS-ESI** (m/z): calcd for $C_{11}H_{11}Cl_2N_2O$, $[M + H]^+$: 257.0243, found, 257.0248.

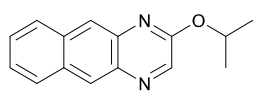
2-Isopropoxy-6,7-dimethylquinoxaline (10i)



10i

Yellow solid, m.p. 61.0–61.9 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.72 (s, 1H), 7.56 (s, 1H), 5.52 – 5.43 (m, 1H), 2.43 (s, 3H), 2.42 (s, 3H), 1.42 (d, J = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 140.0, 138.91, 138.90, 137.3, 135.8, 128.1, 126.5, 68.7, 21.8, 20.2, 19.8; **HRMS-ESI** (m/z): calcd for $C_{13}H_{17}N_2O$, $[M + H]^+$: 217.1335, found, 217.1342.

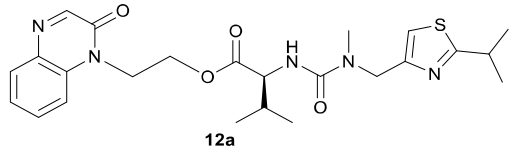
2-Isopropoxybenzo[g]quinoxaline (10j)



10j

Yellow solid, m.p. 39.7–40.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.45 (s, 1H), 8.30 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.48 (m, 2H), 5.63 – 5.54 (m, 1H), 1.48 (d, *J* = 6.2 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.8, 142.4, 137.1, 136.2, 133.9, 131.4, 128.3, 127.5, 127.4, 126.5, 125.2, 124.1, 69.1, 21.7; **HRMS-ESI** (m/z): calcd for $C_{15}H_{15}N_2O$, $[M + H]^+$: 239.1179, found, 239.1184.

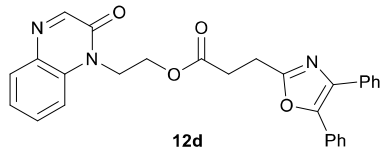
2-(2-Oxoquinoxalin-1(2H)-yl)ethyl (((2-isopropylthiazol-4-yl)methyl)(methyl) carbamoyl)-L-valinate (12a)



12a

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.37 – 7.33 (m, 1H), 6.97 (s, 1H), 6.20 (br s, 1H), 4.59 – 4.42 (m, 5H), 4.34 (d, *J* = 16.0 Hz, 1H), 4.28 (dd, *J* = 8.2, 5.2 Hz, 1H), 3.32 – 3.22 (m, 1H), 2.97 (s, 3H), 2.08 – 2.00 (m, 1H), 1.37 (d, *J* = 6.9 Hz, 6H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.4, 172.7, 158.3, 154.3, 151.7, 149.4, 133.0, 132.2, 130.9, 130.1, 123.5, 113.9, 113.8, 60.5, 58.7, 48.7, 40.1, 34.4, 32.7, 30.1, 22.7, 22.6, 18.9, 17.6; **HRMS-ESI** (m/z): calcd for $C_{24}H_{31}N_5NaO_4S$, $[M + Na]^+$: 508.1989, found, 508.1999.

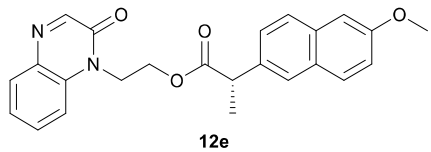
2-(2-Oxoquinoxalin-1(2H)-yl)ethyl 3-(4,5-diphenyloxazol-2-yl)propanoate (12d)



12d

Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 – 7.52 (m, 5H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.32 (m, 7H), 4.82 – 4.47 (m, 4H), 3.12 (t, *J* = 7.4 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.4, 161.0, 154.3, 149.5, 144.9, 134.6, 133.0, 132.2, 131.9, 130.7, 130.3, 128.4, 128.2, 128.1, 128.1, 127.6, 127.4, 126.0, 123.4, 113.4, 60.6, 40.1, 30.3, 22.8; **HRMS-ESI** (m/z): calcd for $C_{28}H_{23}N_3NaO_4$, $[M + Na]^+$: 488.1581, found, 488.1589.

2-(2-Oxoquinoxalin-1(2H)-yl)ethyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (12e)

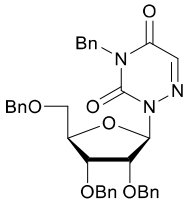


12e

Yellow solid, m.p. 115.2–116.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.81 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (t, *J* = 8.2 Hz, 2H), 7.53 (s, 1H), 7.42 – 7.30 (m, 2H), 7.29 – 7.21 (m, 2H), 7.14 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.10 (s, 1H), 4.84 – 4.26 (m, 4H),

3.92 (s, 3H), 3.74 (q, J = 7.1 Hz, 1H), 1.50 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5, 157.6, 154.7, 149.7, 134.9, 133.6, 133.2, 132.5, 130.9, 130.4, 129.1, 128.7, 127.1, 125.8, 125.8, 123.6, 119.0, 113.7, 105.4, 61.0, 55.2, 45.2, 40.5, 18.2; **HRMS-ESI** (m/z): calcd for $C_{24}H_{22}N_2NaO_4$, $[M + Na]^+$: 425.1472, found, 425.1480.

4-Benzyl-2-((2R,3R,4R,5R)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl) tetrahydrofuran-2-yl)-1,2,4-triazine-3,5(2H,4H)-dione (12h)

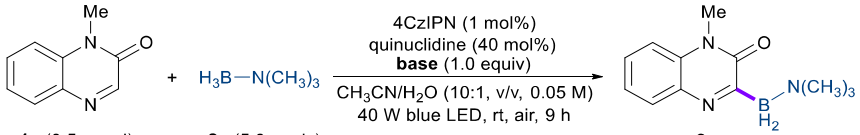


12h

Colorless viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.6, 1.8 Hz, 2H), 7.36 – 7.17 (m, 19H), 6.33 (d, J = 4.1 Hz, 1H), 5.04 (s, 2H), 4.62 (dd, J = 12.0, 4.3 Hz, 2H), 4.56 – 4.48 (m, 4H), 4.32 (q, J = 4.8 Hz, 1H), 4.28 – 4.25 (m, 1H), 4.13 (t, J = 5.3 Hz, 1H), 3.62 – 3.54 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 148.3, 138.0, 137.6, 137.2, 135.1, 134.7, 129.7, 128.5, 128.4, 128.3, 128.24, 128.22, 128.03, 127.95, 127.92, 127.85, 127.6, 127.5, 89.1, 81.5, 78.0, 76.6, 73.3, 72.4, 72.3, 69.7, 43.9; **HRMS-ESI** (m/z): calcd for $C_{36}H_{35}N_3NaO_6$, $[M + Na]^+$: 628.2418, found, 628.2427.

3. Optimization of the Reaction Conditions

Table S1. Optimization of bases

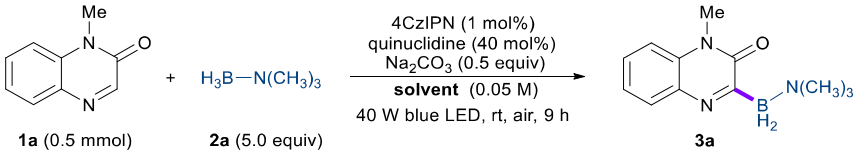


1a (0.5 mmol) **2a** (5.0 equiv) **3a**

Entry	Base	Yield (%)[a]
1	pyridine	59
2	–	58
3	$NaHCO_3$	55
4	K_2CO_3	60
5	K_3PO_4	53
6	NaOAc	39
7	Na_2CO_3	68
8[b]	**Na_2CO_3**	**68**

[a]Isolated yields are given. [b]0.5 equiv of Na_2CO_3 was used.

Table S2. Optimization of solvents

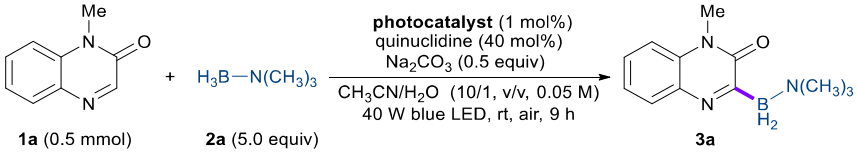


1a (0.5 mmol) **2a** (5.0 equiv) **3a**

Entry	Solvent	Yield (%)[a]
1	CH_3CN	41
2[b]	CH_3CN	36
2	acetone	22
3	DCE	16
4	DMF	39
6	DMSO	38
7	**CH_3CN/H_2O (10/1, v/v)**	**68**
8	CH_3CN/H_2O (5/1, v/v/v)	57
9	CH_3CN/acetone/H_2O (10/10/1, v/v/v)	39

[a]Isolated yields are given. [b]With 5.0 mL of CH_3CN.

Table S3. Optimization of photocatalysts

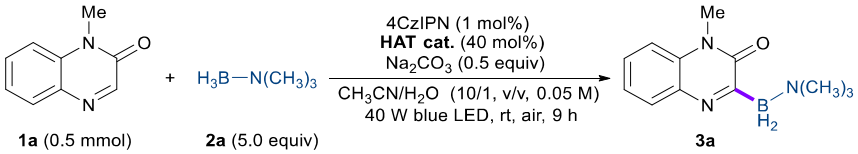


1a (0.5 mmol) **2a** (5.0 equiv) **3a**

Entry	Photocatalyst	Yield (%)[a]
1	**4CzIPN**	**68**
2	*fac*-Ir(ppy)$_3$	0
3	Ir (ppy)$_2$(dtbbpy)PF_6	11
4	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	39
5	Ir[dF(CF_3)ppy]$_2$(bpy)PF_6	37
6	3CzClIPN	48
7	Eosin Y	9
8	Eosin B	0
9	Na_2-Eosin Y	4
10	[Ru(bpz)$_3$][PF_6]$_2$	0
11	Mes-Acr$^+ClO_4^-$	9
12	Rose bengal	0
13[b]	4CzIPN	62
14[c]	4CzIPN	42

[a]Isolated yields are given. [b]2 mol% 4CzIPN was used. [c]0.5 mol% 4CzIPN was used.

Table S4. Optimization of HAT catalysts

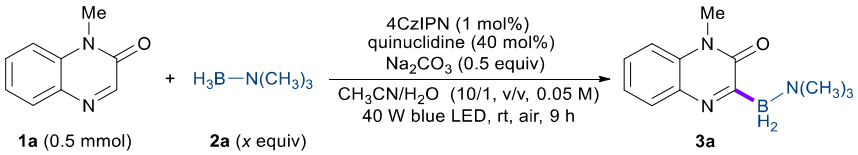


1a (0.5 mmol) **2a** (5.0 equiv) **3a**

Entry	HAT catalyst	Yield (%)[a]
1	**quinuclidine**	**68**
2	quinuclidin-3-yl acetate	40
3	DABCO	0
4[b]	quinuclidine	58
5[c]	quinuclidine	60

[a]Isolated yields are given. [b]20 mol% quinuclidine was used. [c]30 mol% quinuclidine was used.

Table S5. Optimization of equivalents of 2a

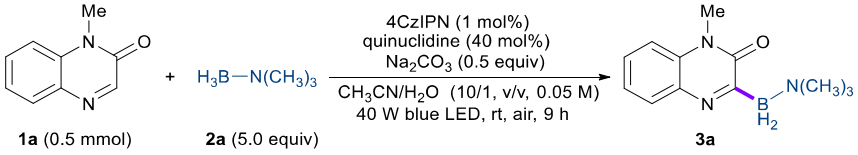


1a (0.5 mmol) **2a** (*x* equiv) **3a**

Entry	**2a** (*x* equiv)	Yield (%)[a]
1	3	51
2	4	59
3	**5**	**68**
4	8	68

[a]Isolated yields are given.

Table S6. Control experiments



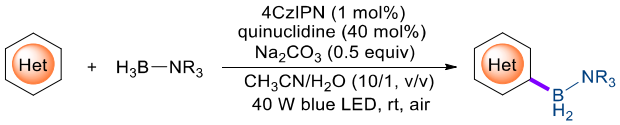
1a (0.5 mmol) **2a** (5.0 equiv) **3a**

Entry	Deviation	Yield (%)[a]
1	no PC	0
2	no HAT cat.	5
3	no light	0
4	under an Ar atmosphere	9

[a]Isolated yields are given.

4. General Procedure for the C–H Borylation of Heterocycles

General procedure for the synthesis of borylated heterocycles



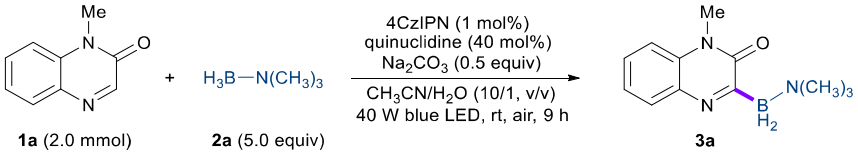
To a 50 mL oven-dried reaction tube equipped with a magnetic stir bar, heterocycle (0.5 mmol, 1.0 equiv), amine-borane (2.5 mmol, 5.0 equiv), Na_2CO_3 (27.0 mg, 0.25 mmol, 0.5 equiv), quinuclidine (22.5 mg, 40 mol%), 4CzIPN (4.0 mg, 1 mol%), and a solvent mixture of CH_3CN/H_2O (10/1, v/v, 10.0 mL) were added. Then, the reaction

mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity and an air atmosphere for 9–24 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography on silica gel using the appropriate gradient of petroleum ether and EtOAc to afford desired product.

***Note**: For 4H-chromen-4-one substrates, 10.0 equiv of amine-borane **2a** was employed.*

Scale-up experiments

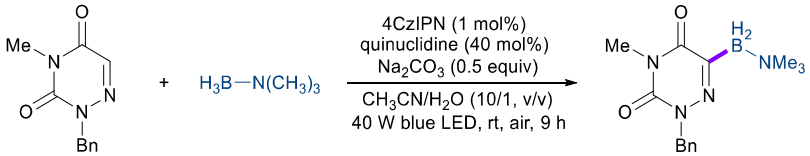
*(I) Scale-up synthesis of **3a***



1a (2.0 mmol) **2a** (5.0 equiv) **3a**

To a 100 mL oven-dried reaction tube equipped with a magnetic stir bar, heterocycle **1a** (320.4 mg, 2.0 mmol, 1.0 equiv), amine-borane **2a** (730.0 mg, 10.0 mmol, 5.0 equiv), Na_2CO_3 (106.0 mg, 1.0 mmol, 0.5 equiv), quinuclidine (89.0 mg, 40 mol%), 4CzIPN (15.8 mg, 1 mol%), and a solvent mixture of CH_3CN/H_2O (10/1, v/v, 40.0 mL) were added. Then, the reaction mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity and an air atmosphere for 9 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography on silica gel (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) to afford desired product **3a** (341.7 mg, 74% yield) as a brown oil.

*(II) Scale-up synthesis of **9a***



8a (2.0 mmol) **2a** (5.0 mmol) **9a**

To a 100 mL oven-dried reaction tube equipped with a magnetic stir bar, heterocycle **8a** (434.5 mg, 2.0 mmol, 1.0 equiv), amine-borane **2a** (730.0 mg, 10.0 mmol, 5.0 equiv), Na_2CO_3 (106.0 mg, 1.0 mmol, 0.5 equiv), quinuclidine (89.0 mg, 40 mol%), 4CzIPN (15.8 mg, 1 mol%), and a solvent mixture of CH_3CN/H_2O (10/1, v/v, 40.0 mL) were added. Then, the reaction mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity and an air atmosphere for 9 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and the filtrate was concentrated under reduced

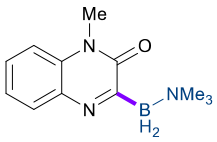
pressure. The resulting crude residue was purified via flash column chromatography on silica gel (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) to afford desired product **9a** (349.8 mg, 61% yield) as a brown oil.

*(III) Scale-up synthesis of **11b***

10b (2.0 mmol) **2a** (5.0 mmol) **11b**

To a 100 mL oven-dried reaction tube equipped with a magnetic stir bar, heterocycle **10b** (288.5 mg, 2.0 mmol, 1.0 equiv), amine-borane **2a** (730.0 mg, 10.0 mmol, 5.0 equiv), Na_2CO_3 (106.0 mg, 1.0 mmol, 0.5 equiv), quinuclidine (89.0 mg, 40 mol%), 4CzIPN (15.8 mg, 1 mol%), and a solvent mixture of CH_3CN/H_2O (10/1, v/v, 40.0 mL) were added. Then, the reaction mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity and an air atmosphere for 9 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography on silica gel (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) to afford desired product **11b** (414.4 mg, 96% yield) as a brown oil.

3-Boranyl-1-methylquinoxalin-2(1H)-one trimethylamine complex (3a)



3a

The title compound **3a** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (79.1 mg, 68% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 2:3) = 0.28;

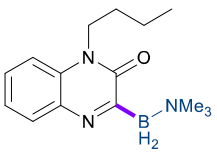
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 3.62 (s, 3H), 2.92 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 133.3, 132.5, 128.8, 127.9, 122.3, 113.3, 52.2, 28.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{12}H_{19}BN_3O$, $[M + H]^+$: 232.1616, found, 232.1619.

3-Boranyl-1-butylquinoxalin-2(1H)-one trimethylamine complex (3b)



3b

The title compound **3b** was prepared from **1b** (101.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column

chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (73.8 mg, 54% yield) as a brown oil.

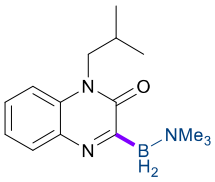
R_f (petroleum ether/EtOAc = 2:3) = 0.43;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.20 (m, 2H), 4.18 (t, *J* = 8.0 Hz, 2H), 2.92 (s, 9H), 1.75 – 1.68 (m, 2H), 1.51 – 1.42 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 133.4, 131.5, 128.9, 127.6, 121.9, 113.1, 52.0, 41.0, 29.1, 20.2, 13.7;

HRMS-ESI (m/z): calcd for $C_{15}H_{25}BN_3O$, $[M + H]^+$: 274.2085, found, 274.2095.

3-Boranyl-1-isobutylquinoxalin-2(1H)-one trimethylamine complex (3c)



3c

The title compound **3c** was prepared from **1c** (101.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (65.4 mg, 48% yield) as a brown oil.

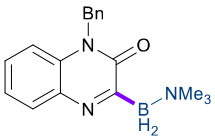
R_f (petroleum ether/EtOAc = 2:3) = 0.45;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.22 – 7.17 (m, 2H), 4.05 (d, *J* = 7.4 Hz, 2H), 2.89 (s, 9H), 2.27 – 2.17 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 133.4, 131.9, 129.0, 127.5, 121.9, 113.6, 52.1, 48.0, 27.1, 20.2.

HRMS-ESI (m/z): calcd for $C_{15}H_{25}BN_3O$, $[M + H]^+$: 274.2085, found, 274.2090.

3-Boranyl-1-benzylquinoxalin-2(1H)-one trimethylamine complex (3d)



3d

The title compound **3d** was prepared from **1d** (118.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (86.0 mg, 56% yield) as a brown solid. m.p. 143.9–144.6 °C.

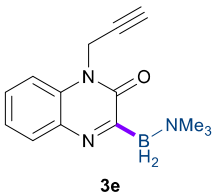
R_f (petroleum ether/EtOAc = 2:3) = 0.45;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.24 (m, 5H), 7.22 – 7.14 (m, 3H), 5.44 (s, 2H), 2.94 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 136.3, 133.5, 131.7, 128.8, 128.5, 127.7, 127.08, 127.05, 122.2, 114.0, 52.1, 45.0;

HRMS-ESI (m/z): calcd for $C_{18}H_{23}BN_3O$, $[M + H]^+$: 308.1929, found, 308.1939.

3-Boranyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one trimethylamine complex (3e)



3e

The title compound **3e** was prepared from **1e** (92.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (89.4 mg, 70% yield) as a brown solid. m.p. 125.9–126.5 °C.

R$_f$ (petroleum ether/EtOAc = 2:3) = 0.43;

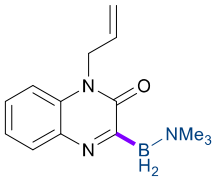
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 5.00 (d, *J* = 2.1 Hz, 2H), 2.90 (s, 9H), 2.20 (t, *J* = 2.3 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 133.4, 130.8, 128.8, 127.8, 122.6, 113.8, 77.8, 72.3, 52.1, 30.4;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.1;

HRMS-ESI (m/z): calcd for $C_{14}H_{18}BN_3NaO$, $[M + Na]^+$: 278.1435, found, 278.1445.

3-Boranyl-1-allylquinoxalin-2(1H)-one trimethylamine complex (3f)



3f

The title compound **3f** was prepared from **1f** (93.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (78.3 mg, 61% yield) as a brown oil.

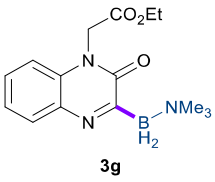
R$_f$ (petroleum ether/EtOAc = 2:3) = 0.38;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 2H), 5.95 – 5.85 (m, 1H), 5.20 – 5.12 (m, 2H), 4.83 (d, *J* = 3.8 Hz, 2H), 2.90 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 133.4, 131.60, 131.57, 128.8, 127.6, 122.2, 117.4, 113.8, 52.1, 43.6;

HRMS-ESI (m/z): calcd for $C_{14}H_{21}BN_3O$, $[M + H]^+$: 258.1772, found, 258.1779.

3-Boranyl-ethyl 2-(2-oxoquinoxalin-1(2H)-yl)acetate trimethylamine complex (3g)



3g

The title compound **3g** was prepared from **1g** (116.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (84.3 mg, 56% yield) as a brown oil.

R$_f$ (petroleum ether/EtOAc = 2:3) = 0.34;

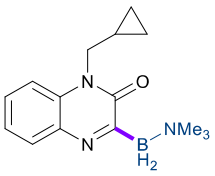
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 4.98 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 9H), 1.24 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 156.3, 133.2, 131.5, 129.0, 127.9, 122.5, 112.6, 61.5, 52.1, 42.7, 14.0;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{15}H_{22}BN_3NaO_3$, $[M + Na]^+$: 326.1646, found, 326.1652.

3-Boranyl-1-(cyclopropylmethyl)quinoxalin-2(1H)-one trimethylamine complex (3h)



3h

The title compound **3h** was prepared from **1h** (100.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (74.4 mg, 55% yield) as a brown solid. m.p. 85.6–86.1 ºC.

R_f (petroleum ether/EtOAc = 2:3) = 0.41;

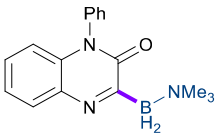
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.13 (d, *J* = 6.9 Hz, 2H), 2.91 (s, 9H), 1.29 – 1.22 (m, 1H), 0.58 – 0.54 (m, 2H), 0.52 – 0.45 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 133.4, 131.8, 129.0, 127.6, 121.9, 113.4, 52.1, 45.1, 9.5, 4.0;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{15}H_{23}BN_3O$, $[M + H]^+$: 272.1929, found, 272.1936.

3-Boranyl-1-phenylquinoxalin-2(1H)-one trimethylamine complex (3i)



3i

The title compound **3i** was prepared from **1i** (111.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (73.4 mg, 50% yield) as a brown solid. m.p. 145.3–146.2 ºC.

R_f (petroleum ether/EtOAc = 2:3) = 0.34;

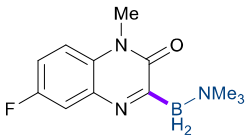
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.23 – 7.17 (m, 2H), 6.59 (dd, *J* = 7.7, 1.6 Hz, 1H), 2.95 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 136.4, 133.1, 132.9, 129.7, 128.5, 128.4, 127.4, 122.3, 114.9, 52.1;

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.7;

HRMS-ESI (m/z): calcd for $C_{17}H_{21}BN_3O$, $[M + H]^+$: 294.1772, found, 294.1782.

3-Boranyl-6-fluoro-1-methylquinoxalin-2(1H)-one trimethylamine complex (3j)



3j

The title compound **3j** was prepared from **1j** (89.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether:AcOEt:TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (65.4 mg, 53% yield) as a brown solid. m.p. 146.6–147.2 °C.

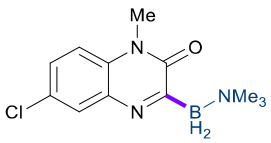
R_f (petroleum ether/EtOAc = 1:2) = 0.31;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.21 – 7.09 (m, 2H), 3.61 (s, 3H), 2.91 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (d, *J* = 240.8 Hz), 156.7, 133.6 (d, *J* = 11.0 Hz), 129.0 (d, *J* = 2.0 Hz), 115.1 (d, *J* = 23.7 Hz), 114.1 (d, *J* = 1.9 Hz), 114.0 (d, *J* = 11.2 Hz), 52.0, 28.4;

HRMS-ESI (m/z): calcd for $C_{12}H_{18}BFN_3O$, $[M + H]^+$: 250.1521, found, 250.1524.

3-Boranyl-6-chloro-1-methylquinoxalin-2(1H)-one trimethylamine complex (3k)



3k

The title compound **3k** was prepared from **1k** (97.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (79.5 mg, 60% yield) as a brown solid. m.p. 129.2–130.1 °C.

R_f (petroleum ether/EtOAc = 2:3) = 0.38;

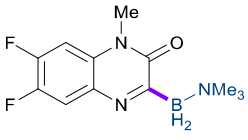
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 3.60 (s, 3H), 2.91 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 133.7, 131.2, 128.1, 127.6, 127.3, 114.4, 52.1, 28.4;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.1.

HRMS-ESI (m/z): calcd for $C_{12}H_{18}BClN_3O$, $[M + H]^+$: 266.1226, found, 266.1234.

3-Boranyl-6,7-difluoro-1-methylquinoxalin-2(1H)-one trimethylamine complex (3l)



3l

The title compound **3l** was prepared from **1l** (98.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (39.6 mg, 30% yield) as a yellow solid. m.p. 148.7–149.6 °C.

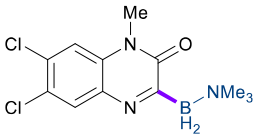
R_f (petroleum ether/EtOAc = 2:3) = 0.38;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 10.6, 8.3 Hz, 1H), 7.01 (dd, *J* = 11.7, 7.2 Hz, 1H), 3.56 (s, 3H), 2.90 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 149.5 (dd, *J* = 248.9, 14.2 Hz), 145.6 (dd, *J* = 243.8, 14.0 Hz), 129.3 (dd, *J* = 4.7, 2.0 Hz), 129.3 (dd, *J* = 3.7, 1.7 Hz), 116.0 (dd, *J* = 17.5, 1.8 Hz), 101.6 (d, *J* = 22.7 Hz), 52.0, 28.6;

HRMS-ESI (m/z): calcd for $C_{12}H_{17}BF_2N_3O$, $[M + H]^+$: 268.1427, found, 268.1435.

3-Boranyl-6,7-dichloro-1-methylquinoxalin-2(1H)-one trimethylamine complex (3m)



3m

The title compound **3m** was prepared from **1m** (114.6 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (91.0 mg, 61% yield) as a brown solid. m.p. 165.2–165.6 ºC.

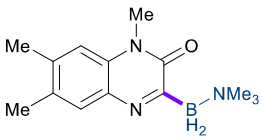
R_f (petroleum ether/EtOAc = 2:3) = 0.50;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.29 (s, 1H), 3.55 (s, 3H), 2.89 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 132.2, 131.9, 131.2, 129.4, 125.5, 114.6, 52.0, 28.4.

HRMS-ESI (m/z): calcd for $C_{12}H_{17}BCl_2N_3O$, $[M + H]^+$: 300.0836, found, 300.0845.

3-Boranyl-1,6,7-trimethylquinoxalin-2(1H)-one trimethylamine complex (3n)



3n

The title compound **3n** was prepared from **1n** (94.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (76.7 mg, 59% yield) as a brown solid. m.p. 152.3–152.8 ºC.

R_f (petroleum ether/EtOAc = 1:2) = 0.29;

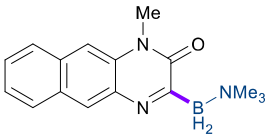
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 6.99 (s, 1H), 3.59 (s, 3H), 2.90 (s, 9H), 2.37 (s, 3H), 2.32 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 137.0, 131.8, 130.7, 130.3, 129.1, 113.8, 52.1, 28.1, 20.2, 19.0;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{14}H_{23}BN_3O$, $[M + H]^+$: 260.1929, found, 260.1935.

3-Boranyl-1-methylbenzo[g]quinoxalin-2(1H)-one trimethylamine complex (3o)



3o

The title compound **3o** was prepared from **1o** (105.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (66.1 mg, 47% yield) as a brown solid. m.p. 150.7–151.6 ºC.

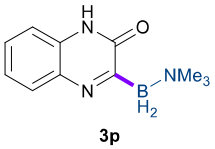
R_f (petroleum ether/EtOAc = 2:3) = 0.40;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.52 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 3.69 (s, 3H), 2.96 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 132.7, 132.5, 131.8, 129.2, 127.8, 126.90, 126.88, 126.5, 124.4, 109.1, 52.1, 28.2;

HRMS-ESI (m/z): calcd for $C_{16}H_{21}BN_3O$, $[M + H]^+$: 282.1772, found, 282.1769.

3-Boranyl-quinoxalin-2(1H)-one trimethylamine complex (3p)



3p

The title compound **3p** was prepared from **1p** (73.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (38.6 mg, 36% yield) as a brown solid. m.p. 148.1–148.7 ºC.

R_f (EtOAc) = 0.33;

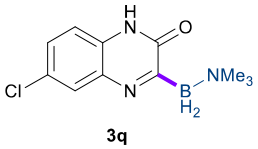
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (br s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.24 – 7.20 (m, 1H), 2.95 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 133.1, 130.2, 127.72, 127.65, 122.7, 116.1, 52.2;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{11}H_{17}BN_3O$, $[M + H]^+$: 218.1459, found, 218.1467.

3-Boranyl-6-chloroquinoxalin-2(1H)-one trimethylamine complex (3q)



3q

The title compound **3q** was prepared from **1q** (90.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (41.8 mg, 33% yield) as a brown solid. m.p. 156.3–157.1 ºC.

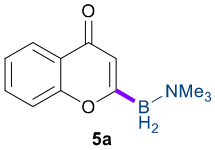
R_f (EtOAc) = 0.40;

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98 (br s, 1H), 7.75 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.29 (m, 2H), 2.95 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 133.5, 128.8, 127.8, 127.7, 127.2, 117.3, 52.2;

HRMS-ESI (m/z): calcd for $C_{11}H_{16}BClN_3O$, $[M + H]^+$: 252.1069, found, 252.1067.

2-Boranyl-4H-chromen-4-one trimethylamine complex (5a)



5a

The title compound **5a** was prepared from **4a** (73.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (365.0 mg, 5.0 mmol, 10.0 equiv) according to the *General Procedure*. Purification by flash column

chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (53.6 mg, 49% yield) as a white solid. m.p. 125.3–125.9 °C.

R_f (petroleum ether/EtOAc = 1:2) = 0.30;

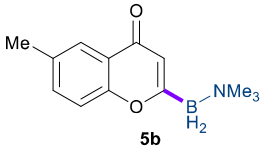
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.45 (s, 1H), 2.70 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 157.8, 132.6, 125.3, 124.0, 123.9, 120.2, 118.0, 52.8;

^{11}B NMR (128 MHz, $CDCl_3$) δ -4.6;

HRMS-ESI (m/z): calcd for $C_{12}H_{17}BNO_2$, $[M + H]^+$: 218.1347, found, 218.1347.

2-Boranyl-6-methyl-4H-chromen-4-one trimethylamine complex (5b)



5b

The title compound **5b** was prepared from **4b** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (365.0 mg, 5.0 mmol, 10.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (54.4 mg, 47% yield) as a white solid. m.p. 75.6–76.3 °C.

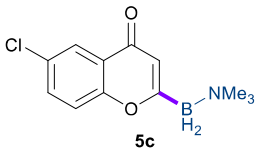
R_f (petroleum ether/EtOAc = 1:2) = 0.33;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.46 (s, 1H), 2.72 (s, 9H), 2.43 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 156.2, 133.9, 133.7, 124.7, 123.7, 120.1, 117.8, 52.8, 20.8;

HRMS-ESI (m/z): calcd for $C_{13}H_{19}BNO_2$, $[M + H]^+$: 232.1503, found, 232.1512.

2-Boranyl-6-chloro-4H-chromen-4-one trimethylamine complex (5c)



5c

The title compound **5c** was prepared from **4c** (90.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (365.0 mg, 5.0 mmol, 10.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (50.1 mg, 40% yield) as a white solid. m.p. 132.2–133.1 °C.

R_f (petroleum ether/EtOAc = 1:2) = 0.41;

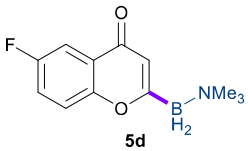
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 2.5 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 6.46 (s, 1H), 2.72 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 156.2, 132.9, 129.7, 125.1, 124.8, 120.2, 119.9, 52.9;

^{11}B NMR (128 MHz, $CDCl_3$) δ -4.8;

HRMS-ESI (m/z): calcd for $C_{12}H_{16}BClNO_2$, $[M + H]^+$: 252.0957, found, 252.0956.

2-Boranyl-6-fluoro-4H-chromen-4-one trimethylamine complex (5d)



5d

The title compound **5d** was prepared from **4d** (82.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (365.0 mg, 5.0 mmol, 10.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (54.6 mg, 47% yield) as a white solid. m.p. 124.3–125.2 °C.

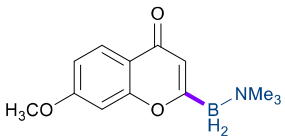
R$_f$ (petroleum ether/EtOAc = 1:2) = 0.36;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.41 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.42 (s, 1H), 2.70 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 158.8 (d, *J* = 244.8 Hz), 154.2 (d, *J* = 1.4 Hz), 125.1 (d, *J* = 7.0 Hz), 120.8 (d, *J* = 25.4 Hz), 120.1 (d, *J* = 8.0 Hz), 119.5, 110.0 (d, *J* = 23.0 Hz), 52.9;

HRMS-ESI (m/z): calcd for $C_{12}H_{15}BFNNaO_2$, $[M + Na]^+$: 258.1072, found, 258.1082.

2-Boranyl-7-methoxy-4H-chromen-4-one trimethylamine complex (5e)



5e

The title compound **5e** was prepared from **4e** (88.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (365.0 mg, 5.0 mmol, 10.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 1:1:0.01, v/v/v) on silica gel afforded the product (50.1 mg, 41% yield) as a white solid. m.p. 156.2–156.7 °C.

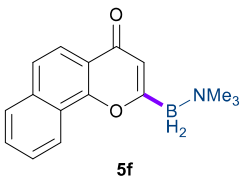
R$_f$ (petroleum ether/EtOAc = 1:2) = 0.40;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.0 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 6.40 (s, 1H), 3.87 (s, 3H), 2.71 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 163.3, 159.6, 126.7, 120.3, 118.0, 113.4, 100.0, 55.6, 52.8;

HRMS-ESI (m/z): calcd for $C_{13}H_{19}BNO_3$, $[M + H]^+$: 248.1453, found, 248.1463.

2-Boranyl-4H-benzo[h]chromen-4-one trimethylamine complex (5f)



5f

The title compound **5f** was prepared from **4f** (98.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (365.0 mg, 5.0 mmol, 10.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (49.3 mg, 37% yield) as a yellow solid. m.p. 153.5–154.3 °C.

R$_f$ (EtOAc) = 0.46;

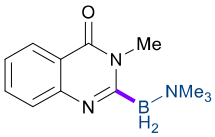
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.7 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.74–7.55 (m, 3H), 6.64 (s, 1H), 2.77 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 155.3, 135.5, 128.6, 128.0, 126.6, 124.5, 124.0, 122.3, 121.9, 121.0, 120.2, 52.8;

^{11}B NMR (128 MHz, $CDCl_3$) δ -4.5;

HRMS-ESI (m/z): calcd for $C_{16}H_{19}BNO_2$, $[M + H]^+$: 268.1503, found, 268.1513.

2-Boranyl-3-methylquinazolin-4(3H)-one trimethylamine complex (7a)



7a

The title compound **7a** was prepared from **6a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v) on silica gel afforded the product (79.7 mg, 69% yield) as a white solid. m.p. 106.5–107.3 °C.

R_f (petroleum ether/EtOAc = 2:1) = 0.31;

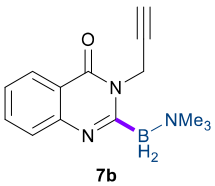
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 3.49 (s, 3H), 2.96 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 147.6, 132.8, 126.2, 126.1, 124.6, 120.1, 52.1, 30.4;

^{11}B NMR (128 MHz, $CDCl_3$) δ -8.1;

HRMS-ESI (m/z): calcd for $C_{12}H_{19}BN_3O$, $[M + H]^+$: 232.1616, found, 232.1626.

2-Boranyl-3-(prop-2-yn-1-yl)quinazolin-4(3H)-one trimethylamine complex (7b)



7b

The title compound **7b** was prepared from **6b** (92.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (82.4 mg, 65% yield) as a white solid. m.p. 160.1–160.8 °C.

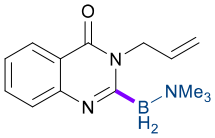
R_f (petroleum ether/EtOAc = 2:1) = 0.35;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 4.81 (s, 2H), 2.99 (s, 9H), 2.18 (t, *J* = 2.4 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 147.5, 133.3, 126.4, 126.2, 124.9, 120.3, 79.7, 69.9, 52.2, 33.1;

HRMS-ESI (m/z): calcd for $C_{14}H_{19}BN_3O$, $[M + H]^+$: 256.1616, found, 256.1624.

2-Boranyl-3-allylquinazolin-4(3H)-one trimethylamine complex (7c)



7c

The title compound **7c** was prepared from **6c** (93.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2/1/0.01, v/v/v) on silica gel afforded the product (53.4 mg, 42% yield) as a white solid. m.p. 108.9–109.5 °C.

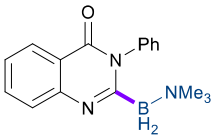
R_f (petroleum ether/EtOAc = 3:1) = 0.36;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.25 (m, 1H), 7.62 (ddd, *J* = 8.4, 7.0, 1.6 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.32 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 6.02 – 5.92 (m, 1H), 5.16 – 5.14 (m, 1H), 5.11 (t, *J* = 1.6 Hz, 1H), 4.67 (dt, *J* = 5.2, 1.5 Hz, 2H), 2.95 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 147.6, 133.3, 133.0, 126.3, 126.1, 124.7, 120.4, 116.0, 52.2, 45.6;

HRMS-ESI (m/z): calcd for $C_{14}H_{21}BN_3O$, $[M + H]^+$: 258.1772, found, 258.1785.

2-Boranyl-3-phenylquinazolin-4(3H)-one trimethylamine complex (7d)



7d

The title compound **7d** was prepared from **6d** (111.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether:AcOEt:TEA = 4:1:0.01, v/v/v) on silica gel afforded the title product (93.0 mg, 63% yield) as a white solid. m.p. 230.1–230.7 °C.

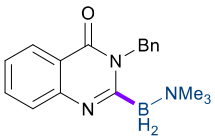
R_f (petroleum ether/EtOAc = 2:1) = 0.31;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.0 Hz, 2H), 2.87 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 147.8, 139.0, 133.4, 128.9, 128.5, 127.9, 126.6, 126.3, 125.0, 120.7, 52.2;

HRMS-ESI (m/z): calcd for $C_{17}H_{21}BN_3O$, $[M + H]^+$: 294.1772, found, 294.1779.

2-Boranyl-3-benzylquinazolin-4(3H)-one trimethylamine complex (7e)



7e

The title compound **7e** was prepared from **6e** (118.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (69.1 mg, 45% yield) as a white solid. m.p. 165.2–166.0 °C.

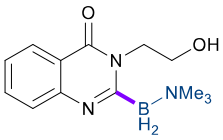
R_f (petroleum ether/EtOAc = 3:1) = 0.35;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.16 (m, 5H), 5.30 (s, 2H), 2.96 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 147.7, 138.1, 133.1, 128.1, 126.7, 126.5, 126.4, 126.2, 124.8, 120.5, 52.2, 46.9;

HRMS-ESI (m/z): calcd for $C_{18}H_{23}BN_3O$, $[M + H]^+$: 308.1929, found, 308.1935.

2-Boranyl-3-(2-hydroxyethyl)quinazolin-4(3H)-one trimethylamine complex (7f)



7f

The title compound **7f** was prepared from **6f** (95.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (76.8 mg, 59% yield) as a white solid. m.p. 131.2–132.2 °C.

R_f (petroleum ether/EtOAc = 1:2) = 0.30;

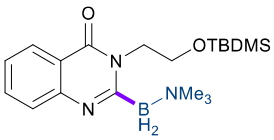
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 (td, *J* = 7.7, 7.1, 1.4 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.34 (m, 1H), 4.31 (t, *J* = 5.0 Hz, 2H), 3.95 (q, *J* = 4.9 Hz, 2H), 3.76 (s, 1H), 2.96 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 147.7, 133.4, 126.2, 126.1, 125.0, 120.0, 63.3, 52.2, 46.7;

^{11}B NMR (128 MHz, $CDCl_3$) δ -8.2;

HRMS-ESI (m/z): calcd for $C_{13}H_{20}BN_3NaO_2$, $[M + Na]^+$: 284.1541, found, 284.1545.

2-Boranyl-3-(2-((tert-butyldimethylsilyl)oxy)ethyl)quinazolin-4(3H)-one trimethylamine complex (7g)



7g

The title compound **7g** was prepared from **6g** (152.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 15:1:0.01, v/v/v) on silica gel afforded the product (106.9 mg, 57% yield) as a white solid. m.p. 111.6–112.4 °C.

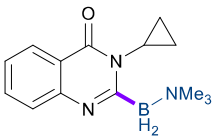
R_f (petroleum ether/EtOAc = 3:1) = 0.50;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 4.17 (t, *J* = 7.4 Hz, 2H), 3.86 (t, *J* = 7.4 Hz, 2H), 2.96 (s, 9H), 0.89 (s, 9H), 0.06 (s, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 147.6, 133.0, 126.2, 126.1, 124.7, 120.5, 60.1, 52.2, 45.2, 25.9, 18.3, -5.3;

HRMS-ESI (m/z): calcd for $C_{19}H_{35}BN_3O_2Si$, $[M + H]^+$: 376.2586, found, 376.2596.

2-Boranyl-3-cyclopropylquinazolin-4(3H)-one trimethylamine complex (7h)



7h

The title compound **7h** was prepared from **6h** (93.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (51.8 mg, 40% yield) as a white solid. m.p. 106.4–107.2 ºC.

R_f (petroleum ether/EtOAc = 2:1) = 0.34;

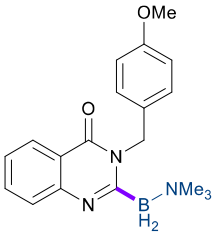
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.53 (br s, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 2.93 (s, 9H), 2.92 – 2.87 (m, 1H), 1.12 (q, *J* = 7.0 Hz, 2H), 0.86 – 0.82 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 147.1, 132.8, 126.0, 125.9, 124.7, 121.0, 52.2, 27.7, 10.4;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.4;

HRMS-ESI (m/z): calcd for $C_{14}H_{21}BN_3O$, $[M + H]^+$: 258.1772, found, 258.1772.

2-Boranyl-3-(4-methoxybenzyl)quinazolin-4(3H)-one trimethylamine complex (7i)



7i

The title compound **7i** was prepared from **6i** (133.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (66.8 mg, 40% yield) as a white solid. m.p. 147.0–147.6 ºC.

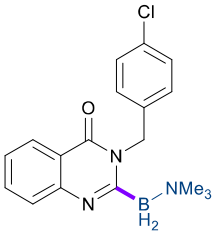
R_f (petroleum ether/EtOAc = 2:1) = 0.34;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.22 (s, 2H), 3.75 (s, 3H), 2.97 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 158.1, 147.7, 133.1, 130.3, 128.2, 126.5, 126.2, 124.7, 120.6, 113.5, 55.1, 52.2, 46.4;

HRMS-ESI (m/z): calcd for $C_{19}H_{25}BN_3O_2$, $[M + H]^+$: 338.2034, found, 338.2044.

2-Boranyl-3-(4-chlorobenzyl)quinazolin-4(3H)-one trimethylamine complex (7j)



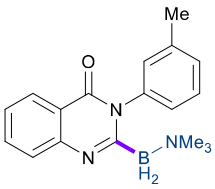
7j

The title compound **7j** was prepared from **6j** (135.4 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (107.2 mg, 63% yield) as a white solid. m.p. 147.7–148.6 ºC.

R_f (petroleum ether/EtOAc = 3:1) = 0.38;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.23 – 7.17 (m, 4H), 5.24 (s, 2H), 2.96 (s, 9H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 147.7, 136.7, 133.3, 132.1, 128.23, 128.20, 126.4, 126.3, 124.9, 120.4, 52.2, 46.3;
^{11}B NMR (128 MHz, $CDCl_3$) δ -7.9;
HRMS-ESI (m/z): calcd for $C_{18}H_{22}BClN_3O$, $[M + H]^+$: 342.1539, found, 342.1543.

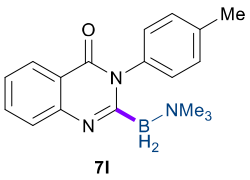
2-Boranyl 3-(m-tolyl)quinazolin-4(3H)-one triethylamine complex (7k)



7k

The title compound **7k** was prepared from **6k** (118.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (74.7 mg, 49% yield) as a white solid. m.p. 219.6–220.4 ºC.
R_f (petroleum ether/EtOAc = 3:1) = 0.35;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 2.87 (s, 9H), 2.41 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 147.8, 138.9, 138.2, 133.3, 129.5, 128.6, 128.2, 126.6, 126.2, 125.8, 124.9, 120.7, 52.1, 21.4;
^{11}B NMR (128 MHz, $CDCl_3$) δ -7.9;
HRMS-ESI (m/z): calcd for $C_{18}H_{23}BN_3O$, $[M + H]^+$: 308.1929, found, 308.1940.

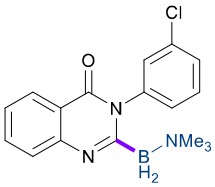
2-Boranyl-3-(p-tolyl)quinazolin-4(3H)-one trimethylamine complex (7l)



7l

The title compound **7l** was prepared from **6l** (118.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 8:1:0.01, v/v/v) on silica gel afforded the product (69.7 mg, 45% yield) as a white solid. m.p. 214.9–215.3 ºC.
R_f (petroleum ether/EtOAc = 2:1) = 0.38;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (ddd, *J* = 7.9, 1.5, 0.5 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.0, 1.6 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.36 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.87 (s, 9H), 2.42 (s, 3H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 147.7, 137.4, 136.3, 133.2, 129.1, 128.4, 126.5, 126.2, 124.8, 120.7, 52.0, 21.2;
HRMS-ESI (m/z): calcd for $C_{18}H_{23}BN_3O$, $[M + H]^+$: 308.1929, found, 308.1936.

2-Boranyl-3-(3-chlorophenyl)quinazolin-4(3H)-one trimethylamine complex (7m)



7m

The title compound **7m** was prepared from **6m** (128.4 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 8:1:0.01, v/v/v) on silica gel afforded the product (79.6 mg, 49% yield) as a white solid. m.p. 228.7–229.4 °C.

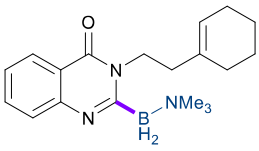
R$_f$ (petroleum ether/EtOAc = 3:1) = 0.35;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.24 (s, 1H), 7.14 – 7.11 (m, 1H), 2.87 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 147.7, 140.1, 133.9, 133.6, 129.4, 129.4, 128.2, 127.4, 126.6, 126.4, 125.2, 120.6, 52.2;

HRMS-ESI (m/z): calcd for $C_{17}H_{20}BClN_3O$, $[M + H]^+$: 328.1382, found, 328.1393.

2-Boranyl-3-(2-(cyclohex-1-en-1-yl)ethyl)quinazolin-4(3H)-one trimethylamine complex (7n)



7n

The title compound **7n** was prepared from **6n** (127.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 8:1:0.01, v/v/v) on silica gel afforded the product (63.1 mg, 39% yield) as a white solid. m.p. 109.6–110.5 °C.

R$_f$ (petroleum ether/EtOAc = 3:1) = 0.49;

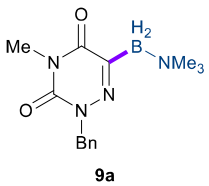
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H), 7.62 (ddd, *J* = 8.4, 7.0, 1.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.32 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 5.54 – 5.51 (m, 1H), 4.08 – 4.04 (m, 2H), 2.97 (s, 9H), 2.34 – 2.30 (m, 2H), 2.10 – 2.07 (m, 2H), 2.01 – 1.97 (m, 2H), 1.67 – 1.62 (m, 2H), 1.59 – 1.53 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 147.6, 135.4, 132.8, 126.2, 126.1, 124.6, 122.3, 120.5, 52.3, 43.0, 36.2, 28.4, 25.2, 23.0, 22.4;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.8;

HRMS-ESI (m/z): calcd for $C_{19}H_{29}BN_3O$, $[M + H]^+$: 326.2398, found, 326.2411.

6-Boranyl-1-benzyl-3-methyl-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9a)



9a

The title compound **9a** was prepared from **8a** (108.6 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (86.3 mg, 60% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 2:3) = 0.43;

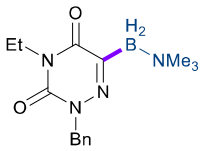
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.30 – 7.21 (m, 3H), 5.07 (s, 2H), 3.59 (s, 3H), 2.73 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 149.3, 136.5, 129.5, 128.3, 127.5, 52.5, 43.2, 39.0;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.9;

HRMS-ESI (m/z): calcd for $C_{14}H_{21}BN_4NaO_2$, $[M + Na]^+$: 311.1650, found, 311.1657.

6-Boranyl-1-benzyl-3-ethyl-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9b)



9b

The title compound **9b** was prepared from **8b** (115.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (86.9 mg, 58% yield) as a brown oil.

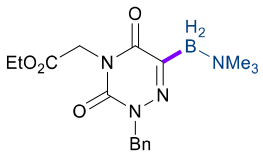
R_f (petroleum ether/EtOAc = 1:1) = 0.38;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 6.7 Hz, 2H), 7.28 – 7.19 (m, 3H), 5.06 (s, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 148.8, 136.5, 129.4, 128.2, 127.4, 52.3, 46.0, 43.0, 13.7;

HRMS-ESI (m/z): calcd for $C_{15}H_{23}BN_4NaO_2$, $[M + Na]^+$: 325.1806, found, 325.1813.

Ethyl 2-(3-benzyl-4-boranyl-2,6-dioxo-3,6-dihydro-1,3,5-triazin-1(2H)-yl)acetate trimethylamine complex (9c)



9c

The title compound **9c** was prepared from **8c** (144.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (93.3 mg, 52% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.34;

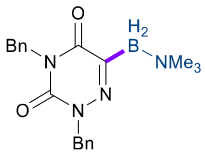
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.6 Hz, 2H), 7.30 – 7.21 (m, 3H), 5.08 (s, 2H), 4.69 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.70 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 158.8, 149.5, 136.2, 129.2, 128.3, 127.5, 61.5, 52.4, 52.1, 43.3, 14.0;

^{11}B NMR (128MHz, $CDCl_3$) δ -6.8;

HRMS-ESI (m/z): calcd for $C_{17}H_{25}BN_4NaO_4$, $[M + Na]^+$: 383.1861, found, 383.1871.

6-Boranyl-1,3-dibenzyl-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9d)



9d

The title compound **9d** was prepared from **8d** (146.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (103.9 mg, 57% yield) as a brown oil.

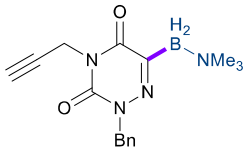
R_f (petroleum ether/EtOAc = 1:1) = 0.48;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.36 – 7.24 (m, 8H), 5.11 (s, 2H), 5.08 (s, 2H), 2.65 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 149.2, 136.8, 136.5, 129.5, 128.5, 128.4, 128.3, 127.7, 127.5, 54.4, 52.3, 43.2;

HRMS-ESI (m/z): calcd for $C_{20}H_{25}BN_4NaO_2$, $[M + Na]^+$: 387.1963, found, 387.1972.

6-Boranyl-1-benzyl-3-(prop-2-yn-1-yl)-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9e)



9e

The title compound **9e** was prepared from **8e** (120.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (76.5 mg, 49% yield) as a brown oil.

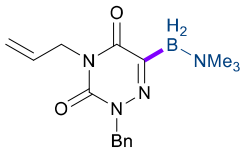
R_f (petroleum ether/EtOAc = 1:1) = 0.40;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.31 – 7.23 (m, 3H), 5.07 (s, 2H), 4.73 (d, *J* = 2.5 Hz, 2H), 2.77 (s, 9H), 2.28 (t, *J* = 2.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 148.7, 136.3, 129.6, 128.3, 127.6, 78.1, 72.5, 52.4, 43.3, 40.4;

HRMS-ESI (m/z): calcd for $C_{16}H_{21}BN_4NaO_2$, $[M + Na]^+$: 335.1650, found, 335.1660.

6-Boranyl-3-allyl-1-benzyl-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9f)



9f

The title compound **9f** was prepared from **8f** (121.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (82.6 mg, 53% yield) as a brown solid. m.p. 98.7–99.6 ºC.

R_f (petroleum ether/EtOAc = 1:1) = 0.41;

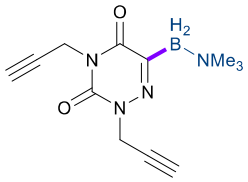
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.31 – 7.22 (m, 3H), 5.98 – 5.89 (m, 1H), 5.23 – 5.19 (m, 2H), 5.08 (s, 2H), 4.55 (d, *J* = 5.9 Hz, 2H), 2.74 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 149.0, 136.5, 132.6, 129.5, 128.3, 127.5, 117.8, 53.3, 52.4, 43.2;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.9;

HRMS-ESI (m/z): calcd for $C_{16}H_{23}BN_4NaO_2$, $[M + Na]^+$: 337.1806, found, 337.1820.

6-Boranyl-1,3-di(prop-2-yn-1-yl)-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9g)



9g

The title compound **9g** was prepared from **8g** (94.6 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (67.7 mg, 52% yield) as a brown solid. m.p 120.7–121.6 ºC.

R_f (petroleum ether/EtOAc = 1:1) = 0.33;

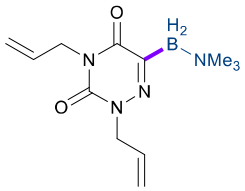
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 (d, *J* = 2.5 Hz, 2H), 4.66 (d, *J* = 2.5 Hz, 2H), 2.78 (s, 9H), 2.29 (t, *J* = 2.5 Hz, 1H), 2.16 (t, *J* = 2.5 Hz, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 147.9, 77.9, 77.5, 72.6, 70.9, 52.4, 40.3, 29.0;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.9;

HRMS-ESI (m/z): calcd for $C_{12}H_{17}BN_4NaO_2$, $[M + Na]^+$: 283.1337, found, 283.1346.

6-Boranyl-1,3-diallyl-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9h)



9h

The title compound **9h** was prepared from **8h** (96.6 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (75.1 mg, 57% yield) as a brown oil.

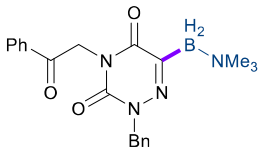
R_f (petroleum ether/EtOAc = 1:1) = 0.36;

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 – 5.79 (m, 2H), 5.39 – 5.08 (m, 4H), 4.56 (dt, *J* = 5.9, 1.4 Hz, 2H), 4.51 (dt, *J* = 6.1, 1.4 Hz, 2H), 2.74 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 148.6, 132.5, 131.1, 118.2, 117.6, 53.1, 52.3, 41.9;

HRMS-ESI (m/z): calcd for $C_{12}H_{21}BN_4NaO_2$, $[M + Na]^+$: 287.1650, found, 287.1660.

6-Boranyl-1-benzyl-3-(2-oxo-2-phenylethyl)-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9i)



9i

The title compound **9i** was prepared from **8i** (160.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (83.8 mg, 43% yield) as a white solid. m.p 168.7–169.4 °C.

R_f (petroleum ether/EtOAc = 1:1) = 0.33;

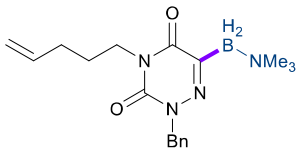
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 6.7 Hz, 4H), 7.30 – 7.23 (m, 3H), 5.40 (s, 2H), 5.10 (s, 2H), 2.66 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 158.9, 149.7, 136.3, 134.6, 133.8, 129.1, 128.8, 128.3, 127.9, 127.5, 56.8, 52.6, 43.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.7;

HRMS-ESI (m/z): calcd for $C_{21}H_{25}BN_4NaO_3$, $[M + Na]^+$: 415.1912, found, 415.1920.

6-Boranyl-1-benzyl-3-(pent-4-en-1-yl)-1,3,5-triazine-2,4(1H,3H)-dione trimethylamine complex (9j)



9j

The title compound **9j** was prepared from **8j** (135.7 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (104.7 mg, 61% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.49;

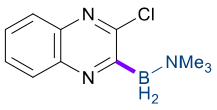
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.30 – 7.21 (m, 3H), 5.84 – 5.74 (m, 1H), 5.07 (s, 2H), 5.04 – 4.93 (m, 2H), 3.96 (t, *J* = 7.4 Hz, 2H), 2.73 (s, 9H), 2.10 (q, *J* = 7.3 Hz, 2H), 1.86 – 1.79 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 149.1, 137.4, 136.5, 129.5, 128.2, 127.5, 115.1, 52.4, 50.6, 43.2, 30.6, 27.6;

^{11}B NMR (128MHz, $CDCl_3$) δ -6.7;

HRMS-ESI (m/z): calcd for $C_{18}H_{27}BN_4NaO_2$, $[M + Na]^+$: 365.2119, found, 365.2133.

2-Boranyl-3-chloroquinoxaline trimethylamine complex (11a)



11a

The title compound **11a** was prepared from **10a** (82.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (89.4 mg, 76% yield) as a brown solid. m.p. 119.6–120.4 °C.

R_f (petroleum ether/EtOAc = 5:1) = 0.34;

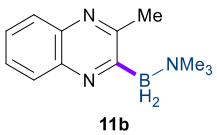
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.66 – 7.58 (m, 2H), 2.99 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 140.7, 139.5, 128.5, 128.2, 128.1, 128.0, 52.1;

^{11}B NMR (128 MHz, $CDCl_3$) δ -5.8;

HRMS-ESI (m/z): calcd for $C_{11}H_{16}BClN_3$, $[M + H]^+$: 236.1120, found, 236.1130.

2-Boranyl-3-methylquinoxaline trimethylamine complex (11b)



11b

The title compound **11b** was prepared from **10b** (72.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (102.3 mg, 95% yield) as a brown oil.

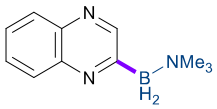
R_f (petroleum ether/EtOAc = 5:1) = 0.34;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.57 – 7.52 (m, 2H), 3.00 (s, 9H), 2.63 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 140.8, 139.4, 128.17, 128.15, 127.04, 126.98, 52.1, 23.6;

HRMS-ESI (m/z): calcd for $C_{12}H_{19}BN_3$, $[M + H]^+$: 216.1667, found, 216.1673.

2-Boranylquinoxaline trimethylamine complex (11c)



11c

The title compound **11c** was prepared from **10c** (65.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 8:1:0.01, v/v/v) on silica gel afforded the product (93.4 mg, 93% yield) as a brown oil.

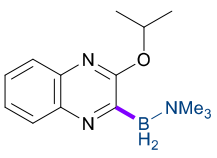
R_f (petroleum ether/EtOAc = 1:1) = 0.38;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.04 – 7.98 (m, 2H), 7.66 – 7.59 (m, 2H), 2.88 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 142.8, 140.1, 129.0, 128.9, 128.3, 127.5, 52.3.

HRMS-ESI (m/z): calcd for $C_{11}H_{17}BN_3$, $[M + H]^+$: 202.1510, found, 202.1519.

2-Boranyl-3-isopropoxyquinoxaline trimethylamine complex (11d)



11d

The title compound **11d** was prepared from **10d** (94.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 10:1:0.01, v/v/v) on silica gel afforded the product (112.8 mg, 87% yield) as a brown solid. m.p. 48.5–49.7 °C.

R_f (petroleum ether/EtOAc = 5:1) = 0.31;

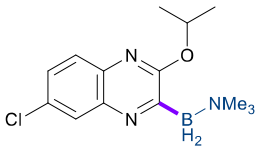
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 5.56 – 5.47 (m, 1H), 2.94 (s, 9H), 1.42 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 138.8, 138.5, 127.8, 127.1, 126.6, 124.6, 67.6, 52.7, 21.9;

^{11}B NMR (128MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{14}H_{23}BN_3O$, $[M + H]^+$: 260.1929, found, 260.1939.

3-Boranyl-6-chloro-2-isopropoxyquinoxaline trimethylamine complex (11e)



11e

The title compound **11e** was prepared from **10e** (111.4 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 20:1:0.01, v/v/v) on silica gel afforded the product (126.3 mg, 86% yield) as a brown solid. m.p. 121.3–122.1 ºC.

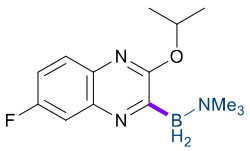
R_f (petroleum ether/EtOAc = 5:1) = 0.46;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.3 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.52 – 5.42 (m, 1H), 2.93 (s, 9H), 1.41 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 138.7, 137.4, 129.6, 127.8, 127.6, 126.9, 67.9, 52.3, 21.9;

HRMS-ESI (m/z): calcd for $C_{14}H_{22}BClN_3O$, $[M + H]^+$: 294.1539, found, 294.1548.

3-Boranyl-6-fluoro-2-isopropoxyquinoxaline trimethylamine complex (11f)



11f

The title compound **11f** was prepared from **10f** (103.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 20:1:0.01, v/v/v) on silica gel afforded the product (105.6 mg, 76% yield) as a brown solid. m.p. 44.8–45.5 ºC.

R_f (petroleum ether/EtOAc = 5:1) = 0.40;

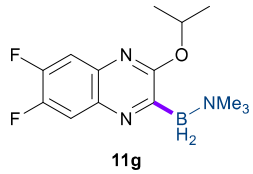
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 9.0, 5.8 Hz, 1H), 7.55 (d, *J* = 9.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 5.52 – 5.42 (m, 1H), 2.94 (s, 9H), 1.41 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 242.9 Hz), 159.2, 138.6 (d, *J* = 11.9 Hz), 135.5 (d, *J* = 1.4 Hz), 127.9 (d, *J* = 9.5 Hz), 116.1 (d, *J* = 24.6 Hz), 111.8 (d, *J* = 21.0 Hz), 67.7, 52.2, 21.9;

^{11}B NMR (128MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{14}H_{22}BFN_3O$, $[M + H]^+$: 278.1834, found, 278.1846.

2-Boranyl-6,7-difluoro-3-isopropoxyquinoxaline trimethylamine complex (11g)



11g

The title compound **11g** was prepared from **10g** (112.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 20:1:0.01, v/v/v) on silica gel afforded the product (92.9 mg, 63% yield) as a brown solid. m.p. 57.9–58.4 °C.

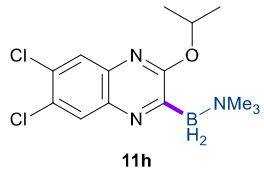
R$_f$ (petroleum ether/EtOAc = 5:1) = 0.38;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 11.0, 8.6 Hz, 1H), 7.43 (dd, *J* = 11.4, 8.2 Hz, 1H), 5.49 – 5.40 (m, 1H), 2.93 (s, 9H), 1.41 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 1.9 Hz), 150.3 (dd, *J* = 248.6, 15.2 Hz), 148.5 (dd, *J* = 246.4, 15.3 Hz), 135.7 (dd, *J* = 10.7, 1.4 Hz), 134.9 (dd, *J* = 9.9, 1.4 Hz), 113.8 (dd, *J* = 16.7, 1.7 Hz), 112.6 (dd, *J* = 17.2, 1.2 Hz), 68.0, 52.3, 21.9;

HRMS-ESI (m/z): calcd for $C_{14}H_{21}BF_2N_3O$, $[M + H]^+$: 296.1740, found, 296.1752.

2-Boranyl-6,7-dichloro-3-isopropoxyquinoxaline trimethylamine complex (11h)



11h

The title compound **11h** was prepared from **10h** (128.6 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 20:1:0.01, v/v/v) on silica gel afforded the product (111.3 mg, 68% yield) as a brown solid. m.p. 57.5–58.2 °C.

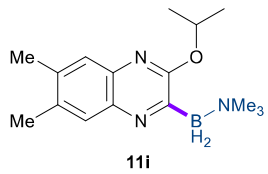
R$_f$ (petroleum ether/EtOAc = 5:1) = 0.44;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.80 (s, 1H), 5.49 – 5.40 (m, 1H), 2.93 (s, 9H), 1.41 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 138.1, 137.3, 130.6, 128.5, 127.9, 127.4, 68.3, 52.2, 21.8;

HRMS-ESI (m/z): calcd for $C_{14}H_{21}BCl_2N_3O$, $[M + H]^+$: 328.1149, found, 328.1158.

2-Boranyl-3-isopropoxy-6,7-dimethylquinoxaline trimethylamine complex (11i)



11i

The title compound **11i** was prepared from **10i** (108.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 15:1:0.01, v/v/v) on silica gel afforded the product (113.3 mg, 79% yield) as a brown solid. m.p. 85.7–86.2 °C.

R$_f$ (petroleum ether/EtOAc = 5:1) = 0.25;

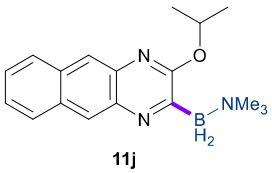
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.48 (s, 1H), 5.53 – 5.43 (m, 1H), 2.92 (s, 9H), 2.40 (s, 6H), 1.41 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 137.33, 137.25, 136.8, 133.9, 127.5, 126.2, 67.3, 52.3, 22.0, 20.0, 19.8;

^{11}B NMR (128MHz, $CDCl_3$) δ -5.8;

HRMS-ESI (m/z): calcd for $C_{16}H_{27}BN_3O$, $[M + H]^+$: 288.2242, found, 288.2251.

2-Boranyl-3-isopropoxybenzo[g]quinoxaline trimethylamine complex (11j)



11j

The title compound **11j** was prepared from **10j** (119.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 20:1:0.01, v/v/v) on silica gel afforded the product (93.1 mg, 60% yield) as a brown solid. m.p. 152.8–153.4 ºC.

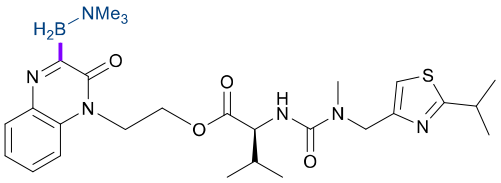
R_f (petroleum ether/EtOAc = 5:1) = 0.33;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.20 (s, 1H), 8.02 – 7.96 (m, 2H), 7.47 – 7.41 (m, 2H), 5.62 – 5.56 (m, 1H), 2.99 (s, 9H), 1.47 (d, *J* = 6.2 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 137.1, 136.8, 132.7, 131.1, 128.1, 127.6, 125.4, 125.2, 124.4, 123.3, 67.9, 52.3, 22.0;

HRMS-ESI (m/z): calcd for $C_{18}H_{25}BN_3O$, $[M + H]^+$: 310.2085, found, 310.2097.

2-(3-Boranyl-2-oxoquinoxalin-1(2H)-yl)ethyl (((2-isopropylthiazol-4-yl)methyl) (methyl)carbamoyl)-L-valinate trimethylamine complex (13a)



13a

The title compound **13a** was prepared from **12a** (242.8 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (113.1 mg, 41% yield) as a brown oil.

R_f (EtOAc) = 0.30;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.24 – 7.20 (m, 1H), 6.95 (s, 1H), 6.05 (br s, 1H), 4.51 – 4.33 (m, 7H), 3.30 – 3.23 (m, 1H), 2.97 (s, 3H), 2.91 (s, 9H), 2.10 – 2.03 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 6H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H);

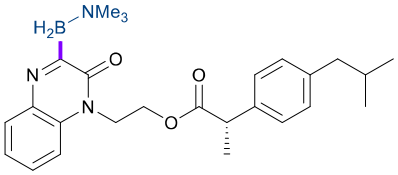
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7, 173.0, 158.5, 156.7, 152.0, 133.3, 131.7, 128.9, 128.0, 122.4, 113.8, 113.5, 61.2, 58.8, 52.0, 49.0, 39.7, 34.7, 33.1, 30.6, 23.0, 22.9, 19.1, 17.8;

^{11}B NMR (128MHz, $CDCl_3$) δ -5.7;

HRMS-ESI (m/z): calcd for $C_{27}H_{41}BN_6NaO_4S$, $[M + Na]^+$: 579.2895, found, 579.2901.

2-(3-Boranyl-2-oxoquinoxalin-1(2H)-yl)ethyl (S)-2-(4-isobutylphenyl)propanoate

trimethylamine complex (13b)



13b

The title compound **13b** was prepared from **12b** (189.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (107.6 mg, 48% yield) as a brown solid. m.p. 102.7–103.5 °C.

R_f (petroleum ether/EtOAc = 1:1) = 0.45;

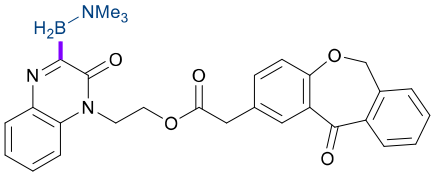
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.34 (m, 2H), 7.25 – 7.21 (m, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 4.48 – 4.33 (m, 4H), 3.60 (q, *J* = 7.1 Hz, 1H), 2.92 (s, 9H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.88 – 1.78 (m, 1H), 1.42 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 156.8, 140.4, 137.2, 133.3, 131.9, 129.2, 128.9, 127.9, 127.0, 122.3, 113.4, 61.3, 52.1, 44.89, 44.86, 39.9, 30.1, 22.3, 18.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.0;

HRMS-ESI (m/z): calcd for $C_{26}H_{36}BN_3NaO_3$, $[M + Na]^+$: 472.2742, found, 472.2751.

2-(3-Boranyl-2-oxoquinoxalin-1(2H)-yl)ethyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate trimethylamine complex (13c)



13c

The title compound **13c** was prepared from **12c** (220.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:2:0.01, v/v/v) on silica gel afforded the product (114.4 mg, 45% yield) as a colorless oil.

R_f (petroleum ether/EtOAc = 1:2) = 0.52;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.2 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.56 (td, *J* = 7.4, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.23 – 7.19 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.49 – 4.43 (m, 4H), 3.57 (s, 2H), 2.92 (s, 9H);

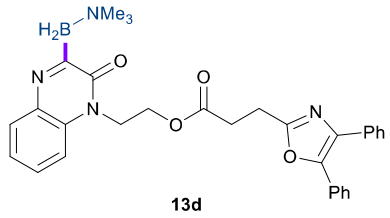
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 171.4, 160.3, 156.8, 140.3, 136.4, 135.4, 133.4, 132.7, 132.3, 131.8, 129.3, 129.1, 129.0, 127.9, 127.7, 127.3, 124.9, 122.4, 121.0, 113.2, 73.5, 61.4, 52.1, 39.9;

^{11}B NMR (128MHz, $CDCl_3$) δ -6.1;

HRMS-ESI (m/z): calcd for $C_{29}H_{30}BN_3NaO_5$, $[M + Na]^+$: 534.2171, found, 534.2179.

2-(3-Boranyl-2-oxoquinoxalin-1(2H)-yl)ethyl 3-(4,5-diphenyloxazol-2-

yl)propanoate trimethylamine complex (13d)



13d

The title compound **13d** was prepared from **12d** (232.8 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (139.2 mg, 52% yield) as a white solid. m.p. 136.3–137.4 °C.

R$_f$ (petroleum ether/EtOAc = 1:1) = 0.33;

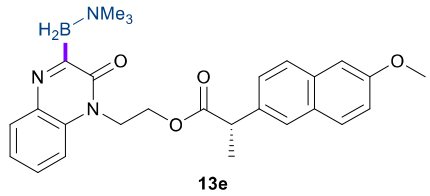
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.57 – 7.55 (m, 2H), 7.39 – 7.28 (m, 8H), 7.24 – 7.20 (m, 1H), 4.50 – 4.46 (m, 4H), 3.13 (t, *J* = 7.5 Hz, 2H), 2.92 (s, 9H), 2.85 (t, *J* = 7.5 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 161.5, 156.8, 145.3, 135.0, 133.4, 132.3, 131.9, 129.1, 128.8, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 126.4, 122.4, 113.2, 61.3, 52.1, 39.9, 30.9, 23.2;

^{11}B NMR (128MHz, $CDCl_3$) δ -6.3;

HRMS-ESI (m/z): calcd for $C_{31}H_{33}BN_4NaO_4$, $[M + Na]^+$: 559.2487, found, 559.2493.

2-(3-Boranyl-2-oxoquinoxalin-1(2H)-yl)ethyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate trimethylamine complex (13e)



13e

The title compound **13e** was prepared from **12e** (201.3 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (141.6 mg, 60% yield) as a white solid. m.p. 146.3–147.2 °C.

R$_f$ (petroleum ether/EtOAc = 1:1) = 0.31;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.7, 2.2 Hz, 2H), 7.55 (s, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 2H), 7.14 – 7.09 (m, 2H), 4.47 – 4.34 (m, 4H), 3.91 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 1H), 2.91 (s, 9H), 1.51 (d, *J* = 7.2 Hz, 3H);

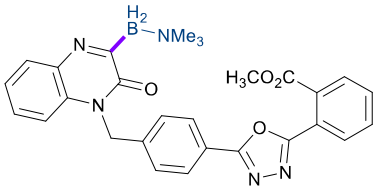
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 157.5, 156.8, 135.2, 133.6, 133.3, 131.9, 129.2, 128.9, 128.8, 127.8, 127.1, 126.1, 125.9, 122.3, 118.8, 113.4, 105.4, 61.5, 55.2, 52.1, 45.2, 40.0, 18.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.3;

HRMS-ESI (m/z): calcd for $C_{27}H_{32}BN_3NaO_4$, $[M + Na]^+$: 496.2378, found, 496.2386.

Methyl 2-(5-(4-((3-boranyl-2-oxoquinoxalin-1(2H)-yl)methyl)phenyl)-1,3,4-

oxadiazol-2-yl)benzoate trimethylamine complex (13f)



13f

The title compound **13f** was prepared from **12f** (219.2 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (109.2 mg, 43% yield) as a white solid. m.p. 168.9–169.3 °C.

R_f (EtOAc) = 0.54;

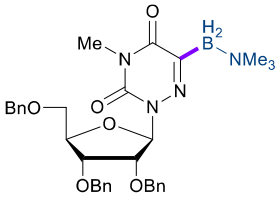
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.93 – 7.90 (m, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 5.51 (s, 2H), 3.80 (d, *J* = 1.1 Hz, 3H), 2.96 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 164.6, 163.7, 156.8, 140.5, 133.4, 131.6, 131.39, 131.36, 131.3, 130.2, 129.8, 129.0, 127.9, 127.8, 127.1, 123.4, 122.55, 122.52, 113.7, 52.6, 52.1, 44.8;

^{11}B NMR (128 MHz, $CDCl_3$) δ -6.1;

HRMS-ESI (m/z): calcd for $C_{28}H_{29}BN_5O_4$, $[M + H]^+$: 510.2307, found, 510.2313.

2-((2R,3R,4R,5R)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)tetrahydrofuran-2-yl)-6-boranyl-4-methyl-1,2,4-triazine-3,5(2H,4H)-dione trimethylamine complex (13g)



13g

The title compound **13g** was prepared from **12g** (264.8 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (134.9 mg, 45% yield) as a colorless oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.36;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 15H), 6.38 (d, *J* = 3.1 Hz, 1H), 4.67 (dd, *J* = 12.2, 6.4 Hz, 2H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 12.3 Hz, 1H), 4.46 (s, 2H), 4.32 – 4.29 (m, 2H), 4.18 – 4.15 (m, 1H), 3.69 (dd, *J* = 10.8, 3.5 Hz, 1H), 3.59 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.27 (s, 3H), 2.39 (s, 9H);

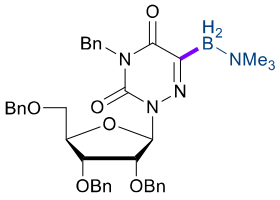
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 149.2, 137.9, 137.7, 137.1, 128.34, 128.30, 128.25, 128.0, 127.84, 127.76, 127.7, 127.6, 89.5, 80.2, 77.7, 75.7, 73.3, 72.0, 71.8, 69.3, 52.0, 26.4;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.2;

HRMS-ESI (m/z): calcd for $C_{33}H_{41}BN_4NaO_6$, $[M + Na]^+$: 623.3011, found, 623.3020.

4-Benzyl-2-((2R,3R,4R,5R)-3,4-bis(benzyloxy)-5-((benzyloxy)methyl)

tetrahydrofuran-2-yl)-6-boranyl-1,2,4-triazine-3,5(2H,4H)-dione trimethylamine complex (13h)



13h

The title compound **13h** was prepared from **12h** (302.9 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 3:1:0.01, v/v/v) on silica gel afforded the product (140.8 mg, 42% yield) as a colorless oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.49;

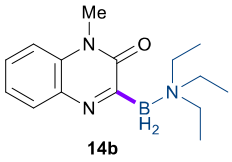
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.32 – 7.21 (m, 18H), 6.40 (d, *J* = 2.9 Hz, 1H), 5.05 (s, 2H), 4.66 (dd, *J* = 12.2, 2.7 Hz, 2H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 12.3 Hz, 1H), 4.45 (s, 2H), 4.31 – 4.27 (m, 1H), 4.24 – 4.22 (m, 1H), 4.15 – 4.12 (m, 1H), 3.69 (dd, *J* = 10.9, 3.2 Hz, 1H), 3.58 (dd, *J* = 10.9, 4.5 Hz, 1H), 2.35 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 149.0, 137.9, 137.7, 137.0, 136.2, 129.7, 128.32, 128.29, 128.25, 128.2, 128.0, 127.9, 127.7, 127.61, 127.56, 89.2, 80.2, 77.7, 75.7, 73.3, 71.9, 71.8, 69.3, 52.0, 43.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.0;

HRMS-ESI (m/z): calcd for $C_{39}H_{45}BN_4NaO_6$, $[M + Na]^+$: 699.3324, found, 699.3329.

3-Boranyl-1-methylquinoxalin-2(1H)-one triethylamine complex (14b)



14b

The title compound **14b** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2b** (287.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 8:1:0.01, v/v/v) on silica gel afforded the product (84.5 mg, 62% yield) as a yellow solid. m.p. 90.8–91.5 ºC.

R_f (petroleum ether/EtOAc = 1:1) = 0.40;

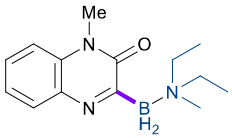
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 2H), 3.60 (s, 3H), 3.27 (q, *J* = 7.3 Hz, 6H), 1.15 (t, *J* = 7.3 Hz, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 133.1, 132.5, 128.7, 127.5, 122.0, 113.1, 49.7, 28.2, 8.2;

^{11}B NMR (128 MHz, $CDCl_3$) δ -11.2;

HRMS-ESI (m/z): calcd for $C_{15}H_{25}BN_3O$, $[M + H]^+$: 274.2085, found, 274.2093.

***3-Boranyl-1-methylquinoxalin-2(1H)-one N*-ethyl-*N*-methylethanamine complex (14c)**



14c

The title compound **14c** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2c** (250.0 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (75.3 mg, 58% yield) as a brown oil.

R$_f$ (petroleum ether/EtOAc = 1:1) = 0.37;

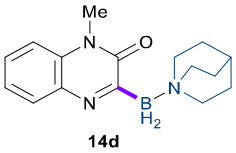
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 2H), 3.62 (s, 3H), 3.39 – 3.30 (m, 2H), 3.28 – 3.19 (m, 2H), 2.80 (s, 3H), 1.19 (t, *J* = 7.3 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 133.2, 132.5, 128.8, 127.7, 122.2, 113.2, 52.8, 45.8, 28.2, 8.4;

^{11}B NMR (193 MHz, $CDCl_3$) δ -8.9.

HRMS-ESI (m/z): calcd for $C_{14}H_{23}BN_3O$, $[M + H]^+$: 260.1929, found, 260.1939.

3-Boranyl-1-methylquinoxalin-2(1H)-one quinuclidine complex (14d)



14d

The title compound **14d** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2d** (312.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (95.5 mg, 67% yield) as a brown oil.

R$_f$ (petroleum ether/EtOAc = 1:1) = 0.30;

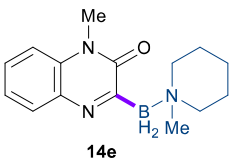
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 2H), 3.60 (s, 3H), 3.44 – 3.40 (m, 6H), 2.05 – 2.03 (m, 1H), 1.82 – 1.77 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 133.2, 132.5, 128.9, 127.8, 122.1, 113.1, 51.5, 28.2, 24.8, 20.5;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.4;

HRMS-ESI (m/z): calcd for $C_{16}H_{23}BN_3O$, $[M + H]^+$: 284.1929, found, 284.1939.

3-Boranyl-1-methylquinoxalin-2(1H)-one 1-methylpiperidine complex (14e)



14e

The title compound **14e** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2e** (282.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (85.9 mg, 63% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.33;

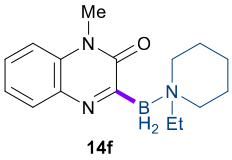
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.1 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 2H), 3.62 (s, 3H), 3.50 – 3.44 (m, 2H), 3.10 – 3.05 (m, 2H), 2.92 (s, 3H), 1.91 – 1.83 (m, 2H), 1.75 – 1.54 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 133.2, 132.5, 128.8, 127.8, 122.2, 113.2, 58.5, 45.6, 28.2, 22.9, 20.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.0;

HRMS-ESI (m/z): calcd for $C_{15}H_{23}BN_3O$, $[M + H]^+$: 272.1929, found, 272.1938.

3-Boranyl-1-methylquinoxalin-2(1H)-one 1-ethylpiperidine complex (14f)



14f

The title compound **14f** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2f** (317.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) on silica gel afforded the product (80.1 mg, 56% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.43;

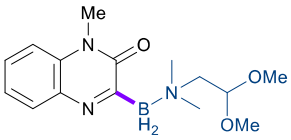
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 3.60 (s, 3H), 3.48 – 3.39 (m, 4H), 3.15 – 3.10 (m, 2H), 1.87 – 1.80 (m, 2H), 1.71 – 1.53 (m, 4H), 1.18 (t, *J* = 7.3 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 133.2, 132.5, 128.7, 127.6, 122.1, 113.1, 55.9, 49.7, 28.2, 22.8, 19.8, 8.7;

^{11}B NMR (128 MHz, $CDCl_3$) δ -9.6;

HRMS-ESI (m/z): calcd for $C_{16}H_{25}BN_3O$, $[M + H]^+$: 286.2085, found, 286.2094.

3-Boranyl-1-methylquinoxalin-2(1H)-one 2,2-dimethoxy-N,N-dimethylethan-1-amine complex (14g)



14g

The title compound **14g** was prepared from **1a** (80.1 mg, 0.5 mmol, 1.0 equiv) and amine-borane **2g** (367.5 mg, 2.5 mmol, 5.0 equiv) according to the *General Procedure*. Purification by flash column chromatography (eluting with petroleum ether/AcOEt/TEA = 4:1:0.01, v/v/v) on silica gel afforded the product (72.3 mg, 47% yield) as a brown oil.

R_f (petroleum ether/EtOAc = 1:1) = 0.27;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.41 (td, *J* = 7.6, 6.9, 1.5 Hz, 1H), 7.26 – 7.22 (m, 2H), 4.83 (t, *J* = 5.0 Hz, 1H), 3.63 (s, 3H), 3.48 (d, *J* = 5.0 Hz, 2H), 3.36 (s, 6H), 2.91 (s, 6H);

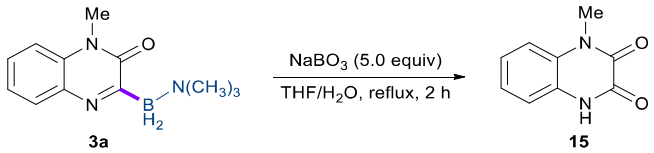
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 133.2, 132.5, 128.7, 127.9, 122.3, 113.3, 101.7, 61.9, 54.7, 51.7, 28.3;

^{11}B NMR (128 MHz, $CDCl_3$) δ -7.2;

HRMS-ESI (m/z): calcd for $C_{15}H_{25}BN_3O_3$, $[M + H]^+$: 306.1983, found, 306.1989.

5. Transformations of the Products

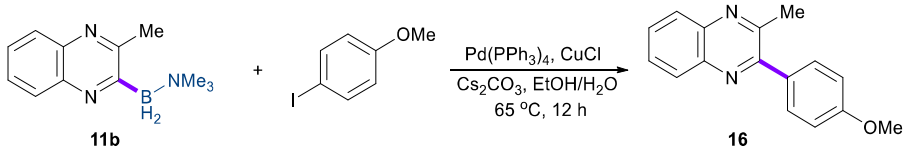
*Synthesis of **15***



A 25 mL oven-dried round bottom flask was charged with **3a** (69.5 mg, 0.3 mmol, 1.0 equiv), $NaBO_3 \cdot 4H_2O$ (230.9 mg, 1.5 mmol, 5.0 equiv), and a solvent mixture of THF/H_2O (3 mL, 1:1, v/v). The reaction mixture was heated to reflux in a heat block, and stirred for 2 h. After reaction completion, the mixture was cooled to room temperature and filtered. After the filtrate was concentrated under reduced pressure, the residue was purified via flash column chromatography on silica gel (eluting with AcOEt) to afford the desired product **15** (47.8 mg, 90% yield) as a white solid.

Product **15** is a known compound and its characterization data is consistent with the reported data in the literature.[15] **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.02 (s, 1H), 7.37 – 7.34 (m, 1H), 7.22 – 7.17 (m, 3H), 3.51 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 155.7, 154.0, 127.6, 126.0, 123.9, 123.6, 115.8, 115.4, 30.1.

*Synthesis of **16***

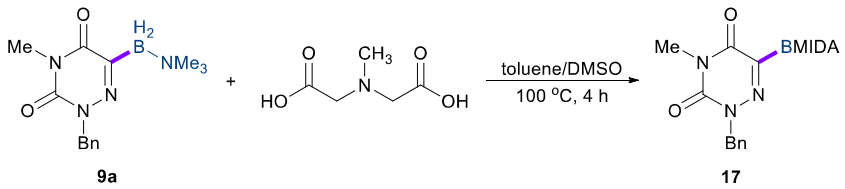


To 25 mL oven-dried round bottom flask were added **11b** (64.6 mg, 0.3 mmol, 1.0 equiv), 4-iodoanisole (281.0 mg, 1.2 mmol, 4.0 equiv), Cs_2CO_3 (391.0 mg, 1.2 mmol, 4.0 equiv), CuCl (7.5 mg, 25 mol%), and $Pd(PPh_3)_4$ (17.5 mg, 5 mol%). The flask was evacuated and backfilled with argon for three times. A degassed solvent mixture of EtOH/H_2O (3 mL, 10:1, v/v) was added via a syringe. Then, the reaction mixture was stirred at 65 °C for 12 h in a heat block. After reaction completion, the mixture was cooled to room temperature and filtered. After the filtrate was concentrated under reduced pressure, the residue was purified via flash column chromatography on silica gel (eluting with AcOEt/petroleum ether = 10:1, v/v) to give the desired product **16** (40.5 mg, 54% yield) as a white solid.

Product **16** is a known compound and its characterization data is consistent with the reported data in the literature.[16] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 1H), 8.05 – 8.03 (m, 1H), 7.75 – 7.63 (m, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 8.7 Hz,

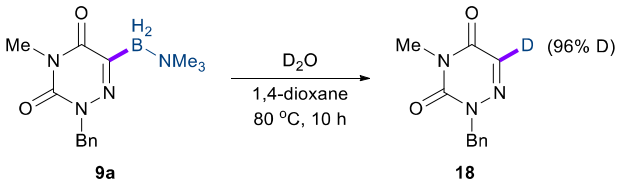
2H), 3.89 (s, 3H), 2.81 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.2, 154.5, 152.5, 142.0, 140.9, 131.3, 130.4, 129.4, 129.1, 129.0, 128.2, 113.9, 55.4, 24.5.

*Synthesis of **17***



A 25 mL oven-dried round bottom flask was charged with **9a** (86.5 mg, 0.3 mmol, 1.0 equiv), *N*-methyliminodiacetic acid (MIDA, 88.5 mg, 0.6 mmol, 2.0 equiv), and a solvent mixture of toluene/DMSO (3 mL, 5:1, v/v). The flask was evacuated and backfilled with argon for three times. Then, the reaction mixture was heated to 100 °C in a heat block, and stirred for 4 h. After reaction completion, the mixture was cooled to room temperature and filtered. After the filtrate was concentrated under reduced pressure, the residue was purified via flash column chromatography on silica gel (eluting with AcOEt) to afford the desired product **17** (63.1 mg, 57% yield) as a white solid. m.p. > 290 °C. **^{1}H NMR** (400 MHz, acetone-d_6) δ 7.38 (dd, J = 8.0, 1.5 Hz, 2H), 7.31 – 7.24 (m, 3H), 5.04 (s, 2H), 4.38 (d, J = 16.8 Hz, 2H), 4.23 (d, J = 16.8 Hz, 2H), 3.60 (s, 3H), 3.02 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 169.4, 159.1, 149.0, 136.4, 128.9, 128.2, 127.8, 63.3, 47.5, 43.3; **HRMS-ESI** (m/z): calcd for $C_{16}H_{17}BN_4NaO_6$, [M + Na]$^+$: 395.1133, found, 395.1141.

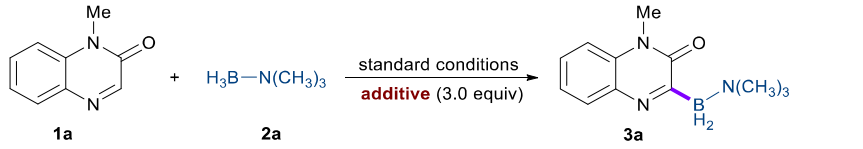
*Synthesis of **18***



Under an argon atmosphere, a 15 mL oven-dried sealed tube was charged with **9a** (86.5 mg, 0.3 mmol, 1.0 equiv), D_2O (0.2 mL), and a 1,4-dioxane (1.0 mL). The was sealed with a screw cap. Then, the reaction mixture was heated to 80 °C in a heat block, and stirred for 10 h. After reaction completion, the mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified via flash column chromatography on silica gel (eluting with AcOEt/petroleum ether = 10:1, v/v) to afford the desired product **18** (43.2 mg, 66% yield) as a white solid. m.p. 74.6–75.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.8, 1.8 Hz, 2H), 7.34 – 7.26 (m, 3H), 5.08 (s, 2H), 3.61 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 148.7, 135.3, 133.7 (t, J = 31.8 Hz), 129.4, 128.5, 128.1, 43.8, 39.6; **HRMS-ESI** (m/z): calcd for $C_{11}H_{10}DN_3NaO_2$, [M + Na]$^+$: 241.0806, found, 241.0812.

6. Experimental Procedures for the Mechanistic Studies

6.1 Radical inhibition experiments

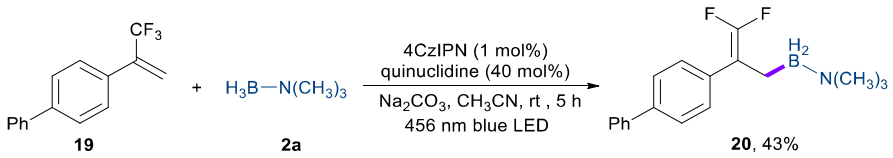


with TEMPO, 5% yield of **3a**

with 1,1-diphenylethylene, 28% yield of **3a**

To a 50 mL oven-dried reaction tube equipped with a magnetic stir bar, heterocycle **1a** (80.1 mg, 0.5 mmol, 1.0 equiv), amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv), Na_2CO_3 (27.0 mg, 0.25 mmol, 0.5 equiv), TEMPO or 1,1-diphenylethylene (1.5 mmol, 3.0 equiv), quinuclidine (22.5 mg, 40 mol%), 4CzIPN (4.0 mg, 1 mol%), and a solvent mixture of CH_3CN/H_2O (10/1, v/v, 10.0 mL) were added. Then, the reaction mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity and an air atmosphere. After 9 h, the reaction was obviously inhibited through TLC analysis.

6.2 Evidence for the presence of amine-boryl radical

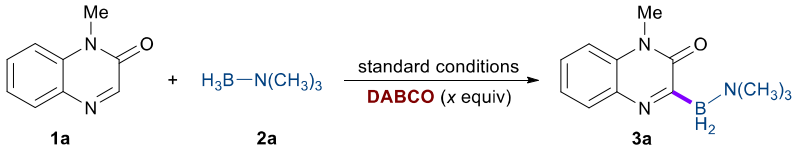


Under an argon atmosphere, a 25 mL oven-dried reaction tube equipped with a magnetic stir bar was charged with trifluoromethylalkene **19** (124.5 mg, 0.5 mmol, 1.0 equiv), amine-borane **2a** (182.5 mg ,2.5 mmol, 5.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), quinuclidine (23.0 mg, 40 mol%), 4CzIPN (4.0 mg, 1 mol%), and CH_3CN (5 mL). The resulting mixture was sealed and degassed via freeze-pump-thaw for three times. Then, the reaction mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity for 5 h. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography on silica gel (eluting with petroleum ether/AcOEt/TEA = 30:1:0.01, v/v/v) to afford desired product **20** (64.3 mg, 43% yield) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 2.59 (s, 9H), 1.59 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.1 (dd, J = 289.4, 281.8 Hz), 141.0, 138.8, 135.7 (dd, J = 5.4, 3.8 Hz), 128.63, 128.61 (dd, J = 4.1, 3.3 Hz), 127.0, 126.9, 126.5, 94.8 (dd, J = 23.7, 8.9 Hz), 51.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -94.2 (d, J = 53.8 Hz, 1F), -95.05 (d, J = 53.8 Hz, 1F); **^{11}B NMR** (128 MHz, $CDCl_3$) δ -3.5. **HRMS-ESI** (m/z): calcd for $C_{18}H_{22}BF_2NNa$, $[M + Na]^+$: 324.1706,

found, 324.1714.

According to previous literature reports on visible-light-induced defluoroborylation of trifluoromethylalkenes with NHC–boranes,[17] the formation of defluoroborylated product **20** supports the presence of boryl radicals during the reaction process. This result revealed that amine-borane **2a** could serve as an efficient radical candidate for the generation of corresponding boryl radical by merging organophotoredox and HAT catalysis.

6.3 $^1O_2$ inhibition experiment



DABCO (*x* equiv)	Yield for **3a**
2.0	20%
3.0	9%

To a 50 mL oven-dried reaction tube equipped with a magnetic stir bar, heterocycle **1a** (80.1 mg, 0.5 mmol, 1.0 equiv), amine-borane **2a** (182.5 mg, 2.5 mmol, 5.0 equiv), Na_2CO_3 (27.0 mg, 0.25 mmol, 0.5 equiv), quinuclidine (22.5 mg, 40 mol%), 4CzIPN (4.0 mg, 1 mol%), DABCO (*x* equiv), and a solvent mixture of CH_3CN/H_2O (10/1, v/v, 10.0 mL) were added. Then, the reaction mixture was stirred at room temperature under the irradiation of a 40 W Kessil blue LED (λmax = 456 nm, distance app. 3 cm) with 50% intensity and an air atmosphere. After 9 h, the reaction was obviously inhibited through TLC analysis. Then, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting crude residue was purified via flash column chromatography on silica gel (eluting with petroleum ether/AcOEt/TEA = 2:1:0.01, v/v/v) to afford product **3a**. The results indicated that the reaction was considerably inhibited when adding DABCO to the reaction mixture.

7. The X-ray Crystallographic Data of Compounds 3d and 11e

Crystals of compound **3d** or **11e** were obtained through slow evaporation technique at room temperature from the solution in a petroleum ether/CH_2Cl_2 mixture over 2 days. A suitable crystal was selected and recorded on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 122(3) K during data collection.

The X-ray crystallographic structure for **3d** was shown at 50% ellipsoid contour present probability level. This crystal structure has been deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2338977.

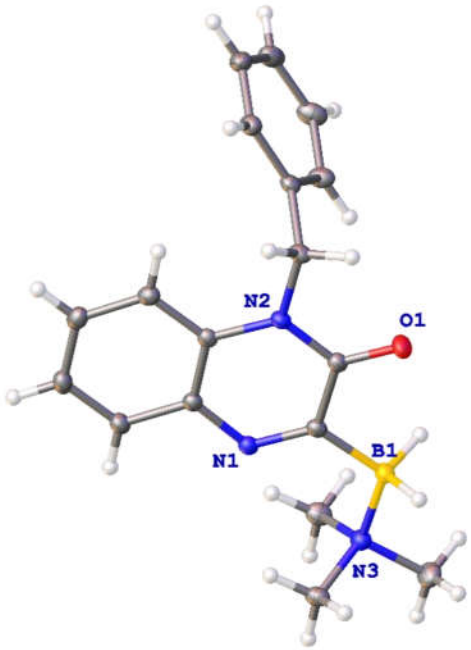


Figure S5. Ellipsoid plot (probability level 50%) of **3d**

Table S7. Crystal data and structure refinement for **3d**

Identification code	**3d**
Empirical formula	$C_{18}H_{22}BN_3O$
Formula weight	307.19
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.6346(2)
b/Å	16.4923(3)
c/Å	19.0206(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3336.00(10)
Z	8
ρ_{calc}g/cm^3	1.223
μ/mm^{-1}	0.599
F(000)	1312.0
Crystal size/mm^3	0.15 × 0.14 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.3 to 147.764
Index ranges	-12 ≤ h ≤ 13, -20 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	8510
Independent reflections	3303 [R_{int} = 0.0196, R_{sigma} = 0.0182]

Data/restraints/parameters	3303/0/220
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0972
Final R indexes [all data]	R_1 = 0.0406, wR_2 = 0.1005
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.16

The X-ray crystallographic structure for **11e** was shown at 50% ellipsoid contour present probability level. This crystal structure has been deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2338978.

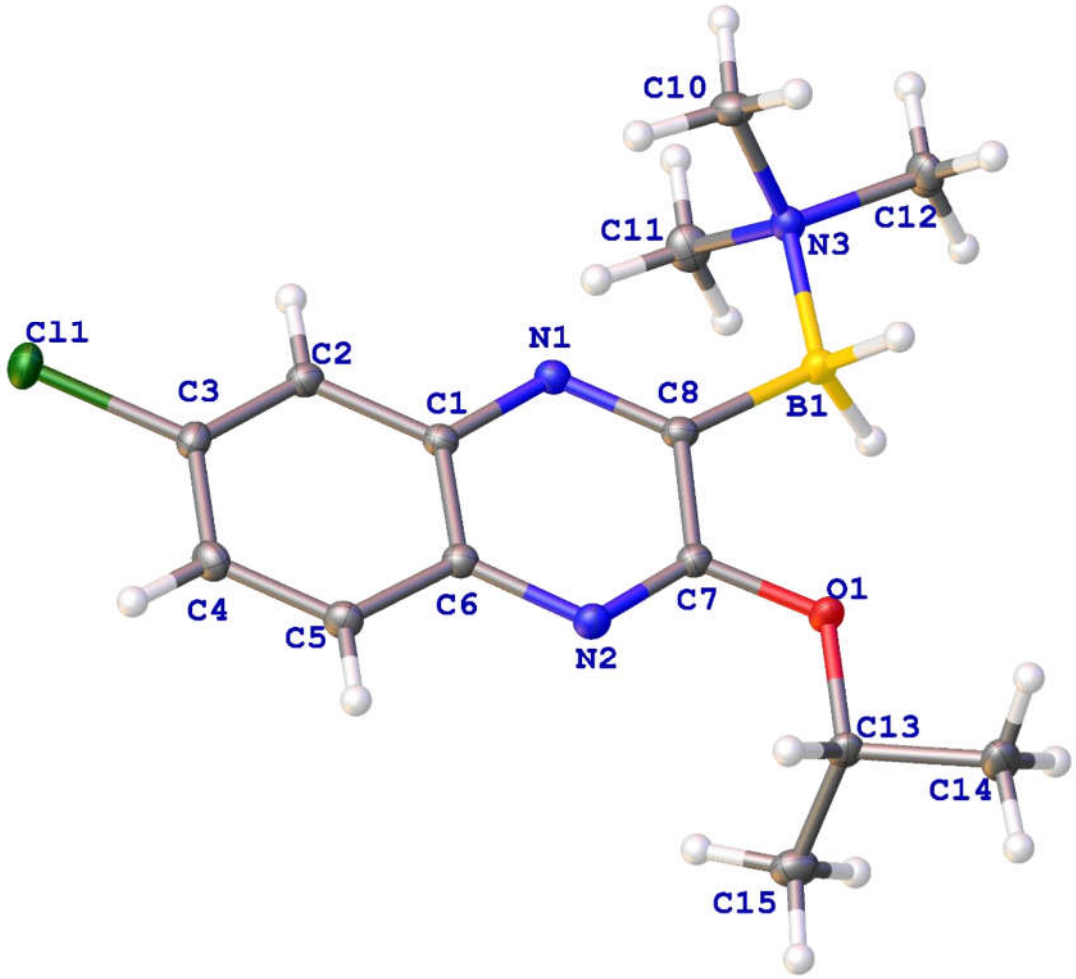


Figure S6. Ellipsoid plot (probability level 50%) of **11e**

Table S8. Crystal data and structure refinement for **11e.**

Identification code	**11e**
Empirical formula	$C_{14}H_{21}BClN_3O$
Formula weight	293.60
Temperature/K	149.99(10)
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	10.6770(3)
b/Å	10.0066(3)
c/Å	14.9641(5)
α/°	90
β/°	100.593(3)
γ/°	90
Volume/Å^3	1571.52(8)
Z	4
ρ_{calc}g/cm^3	1.241
μ/mm^{-1}	2.132
F(000)	624.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.424 to 148.208
Index ranges	$-13 \leq h \leq 12$, $-10 \leq k \leq 12$, $-11 \leq l \leq 18$
Reflections collected	5662
Independent reflections	3087 [R_{int} = 0.0206, R_{sigma} = 0.0277]
Data/restraints/parameters	3087/0/194
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0359, wR_2 = 0.0992
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.1026
Largest diff. peak/hole / e Å^{-3}	0.32/-0.34

8. References

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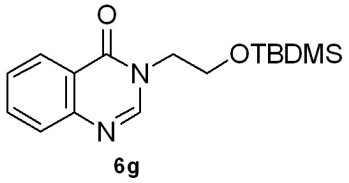
9. ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR Spectra of Products

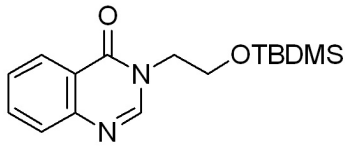
^{1}H NMR (400 MHz, $CDCl_3$)



6g

161.06
148.16
147.62
134.11
127.40
126.97
126.52
121.96
77.39
77.07
76.75
60.56
49.06
25.72
18.06
-5.70

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



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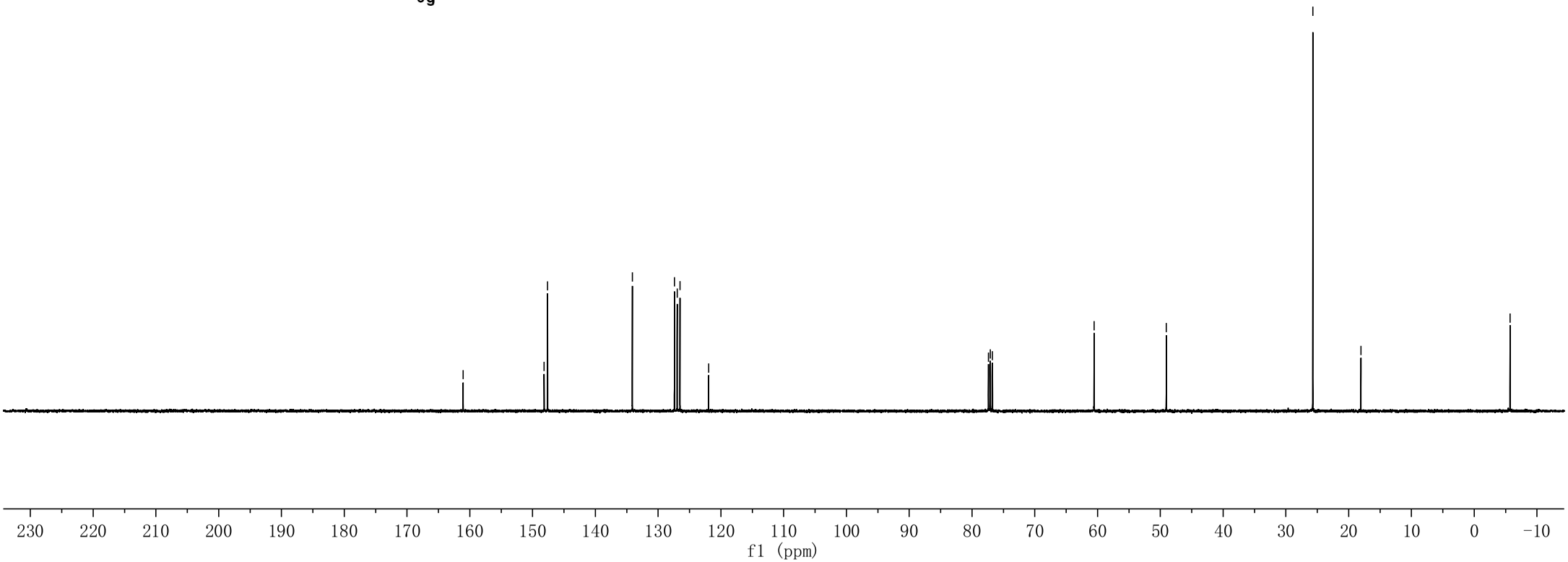
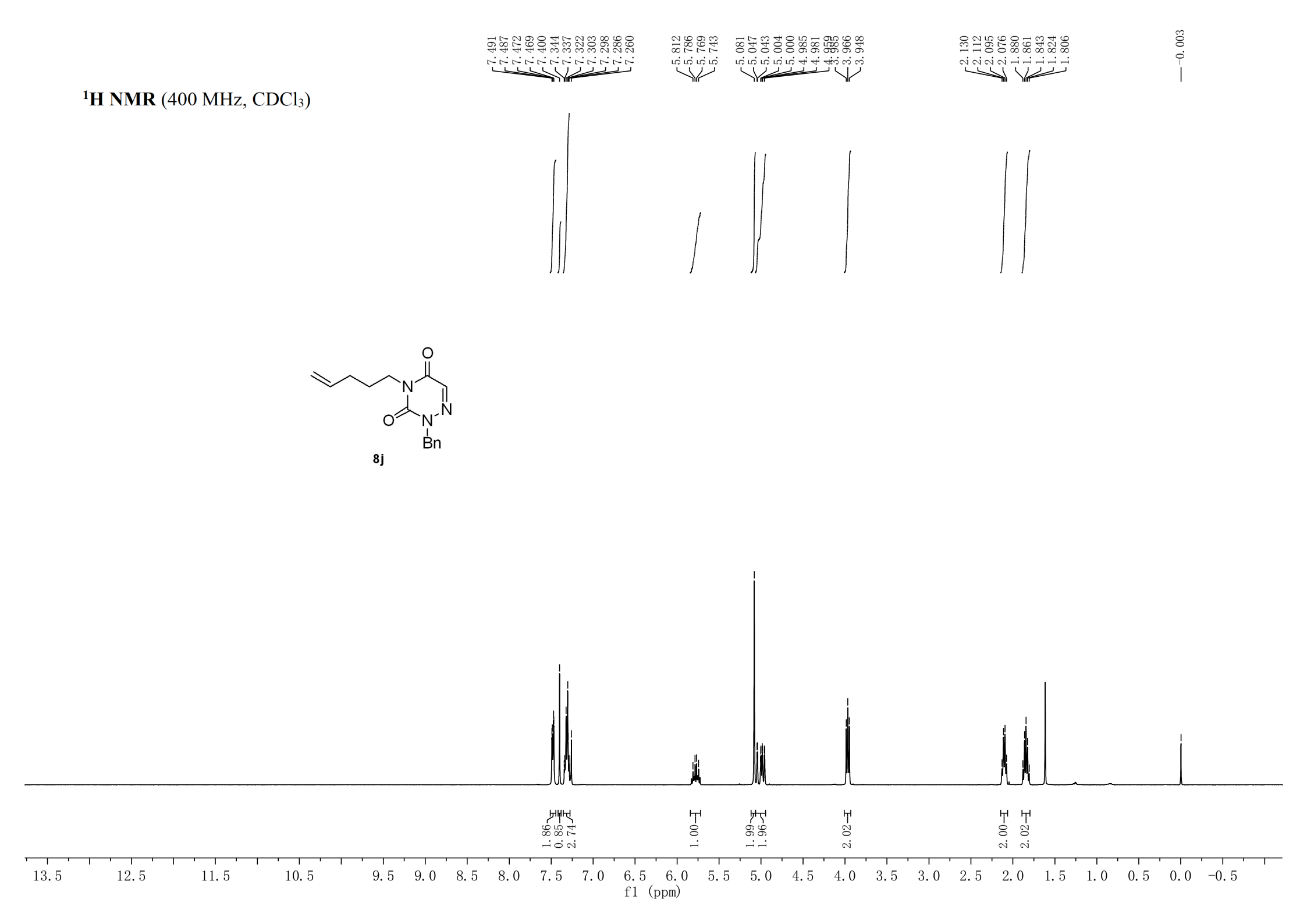


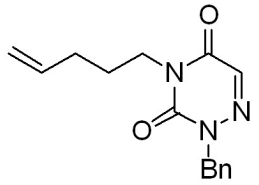
^{1}H NMR (400 MHz, $CDCl_3$)



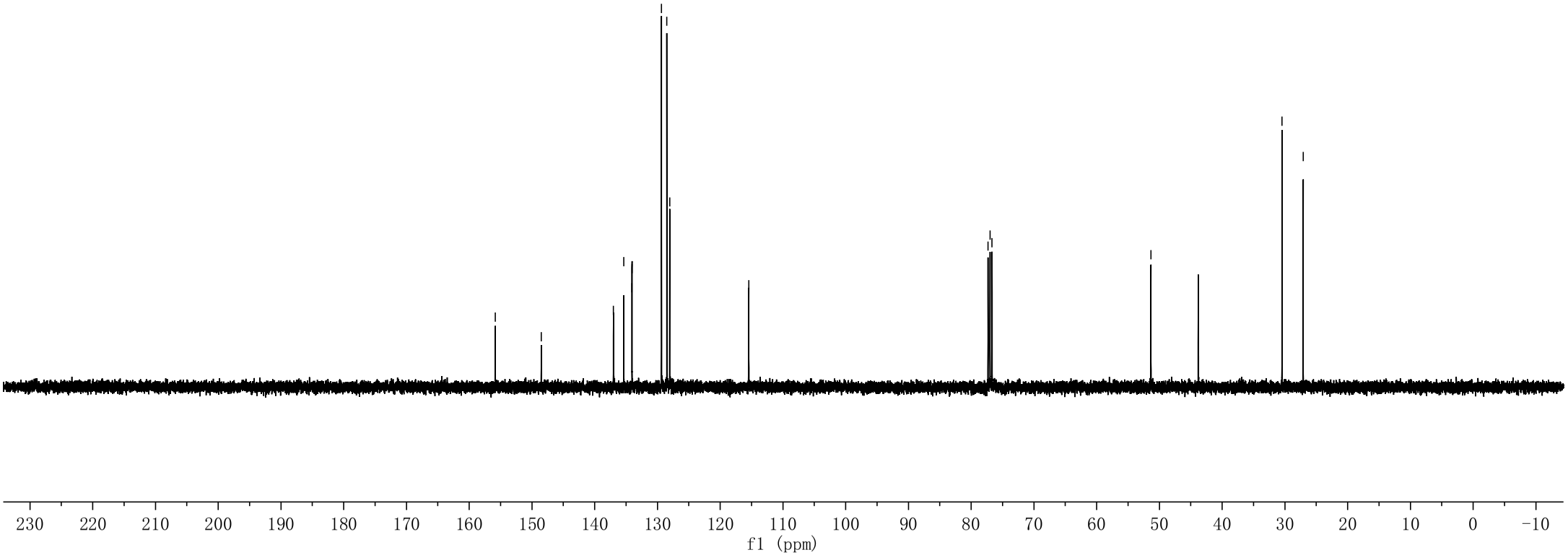
8j

155.86
148.52
137.01
135.37
134.06
134.05
129.36
128.50
128.05
115.46
77.32
77.00
76.68
51.36
43.80
30.47
27.09

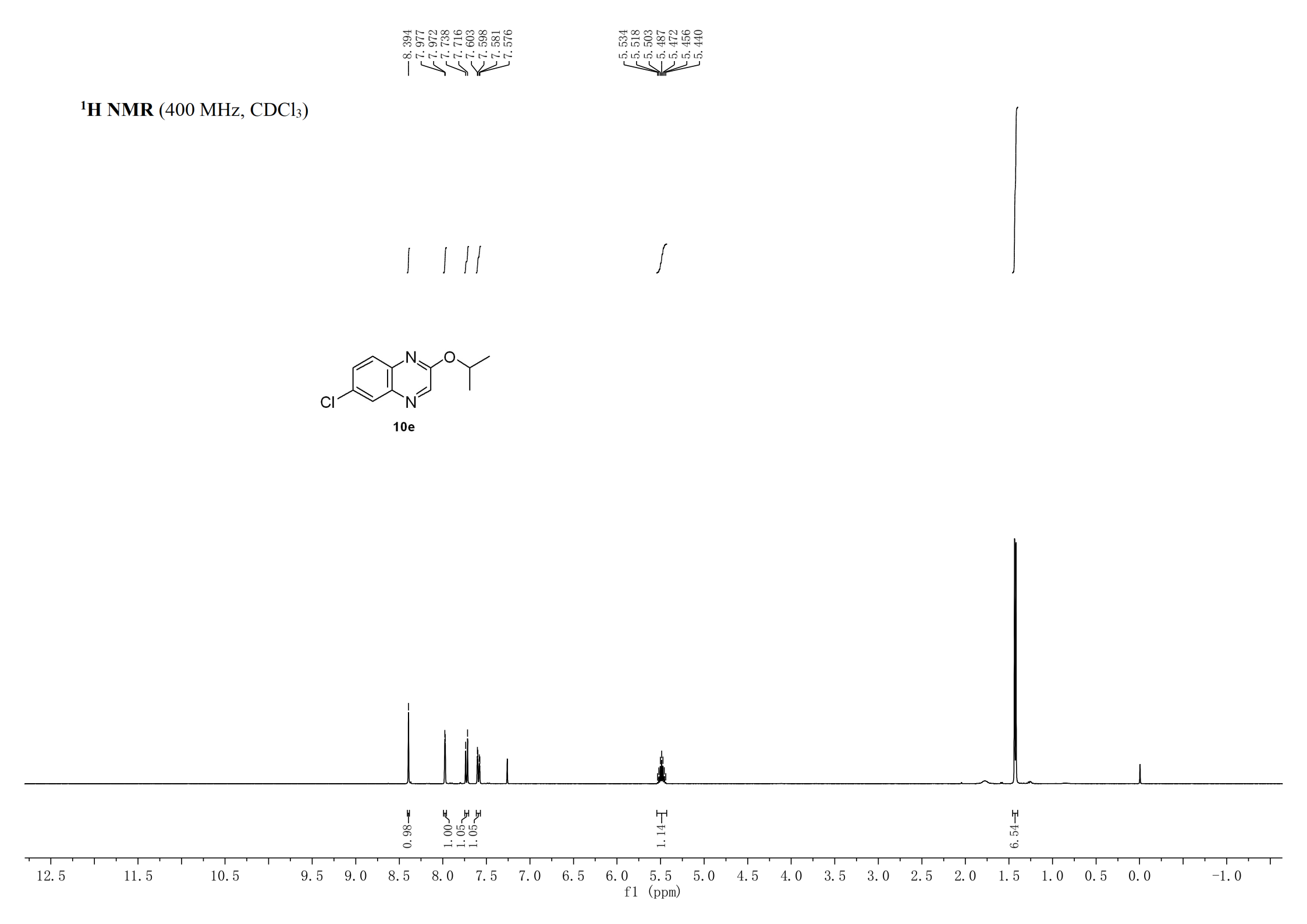
^{13}C NMR (101 MHz, $CDCl_3$)



8j

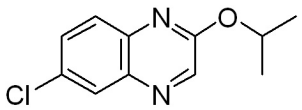


^{1}H NMR (400 MHz, $CDCl_3$)

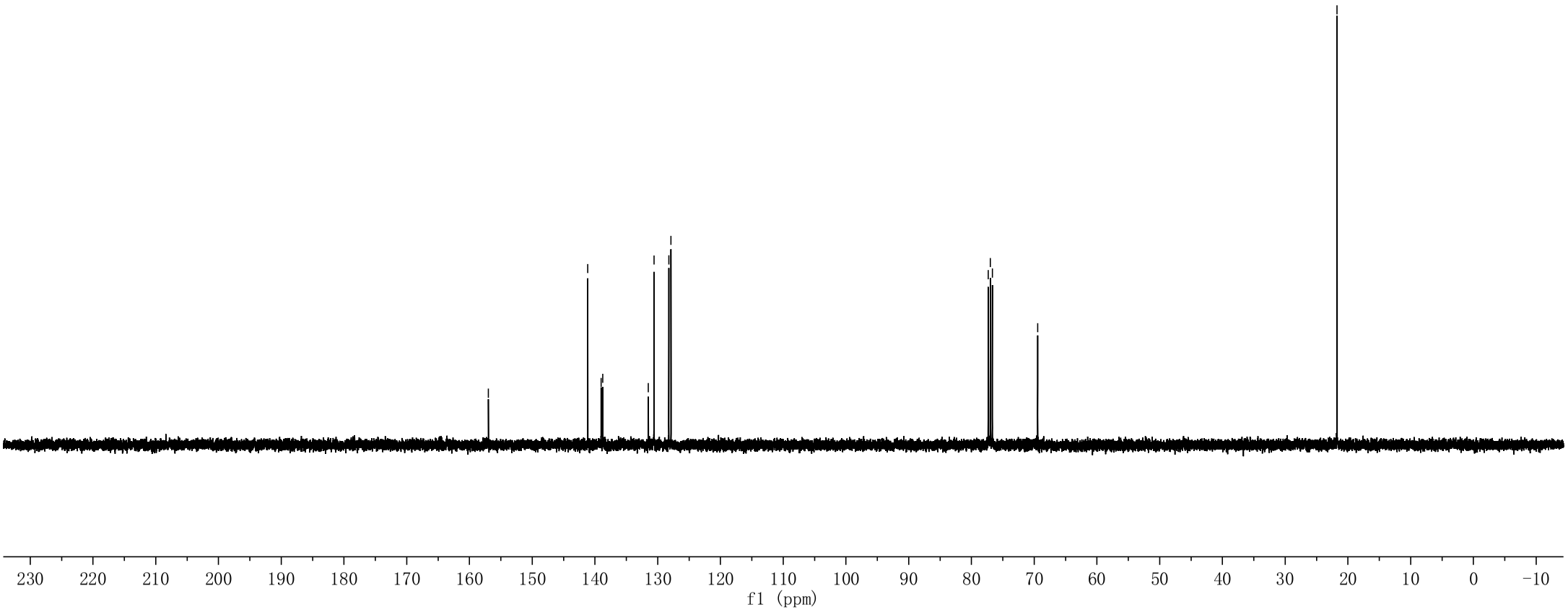


156.98
141.15
139.02
138.77
131.49
130.58
128.24
127.88
77.32
77.00
76.68
69.45
21.73

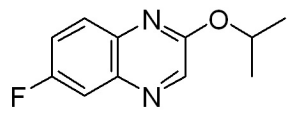
^{13}C NMR (101 MHz, $CDCl_3$)



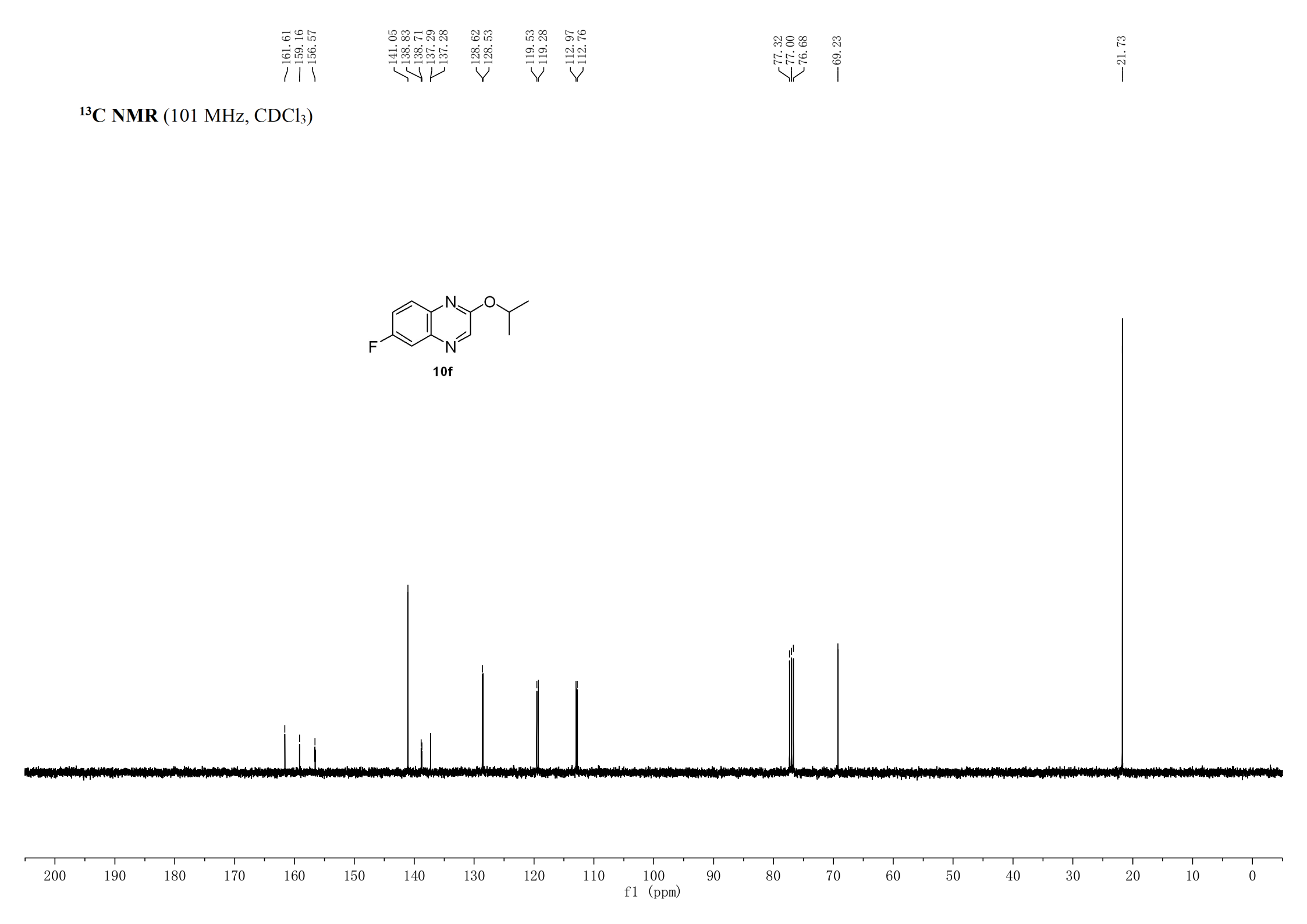
10e



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

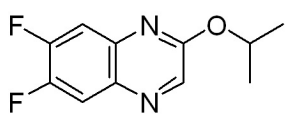


10f



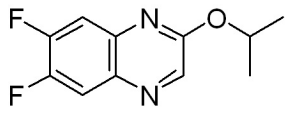
^{13}C NMR (101 MHz, $CDCl_3$)

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



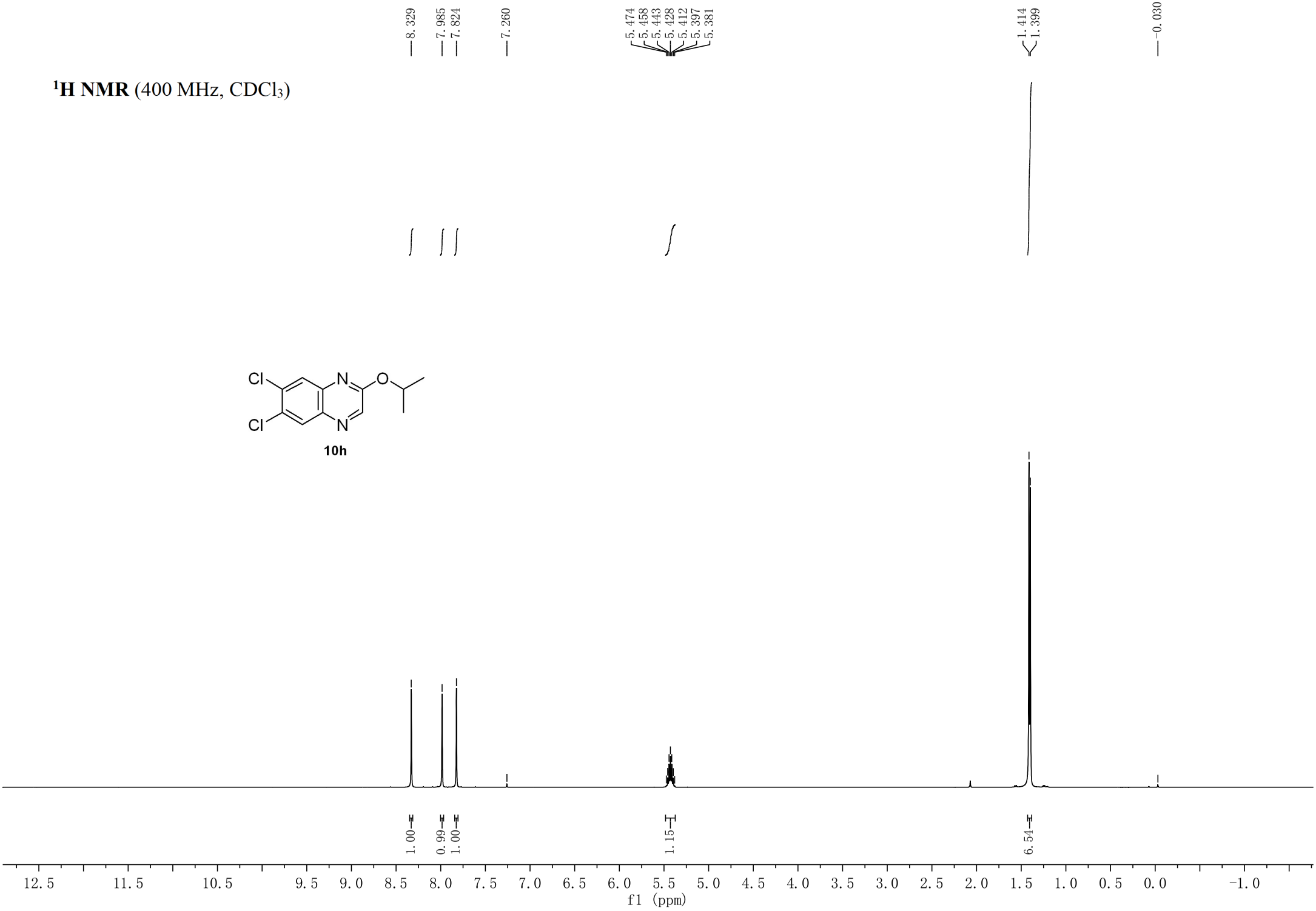
10g

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



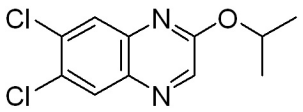
10g

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



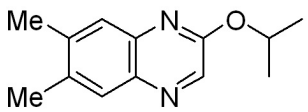
157.30
141.36
139.37
137.15
134.04
129.99
129.36
127.73
77.32
77.00
76.68
69.83
21.64

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



10h

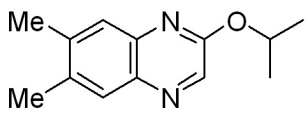
^{1}H NMR (400 MHz, $CDCl_3$)



10i

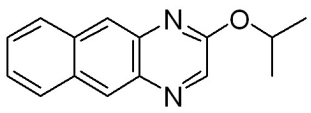
156.60
140.00
138.91
138.90
137.25
135.84
128.10
126.50
77.32
77.00
76.68
68.65
21.76
20.18
19.82

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



10i

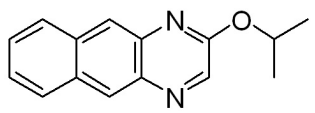
^{1}H NMR (400 MHz, $CDCl_3$)



10j

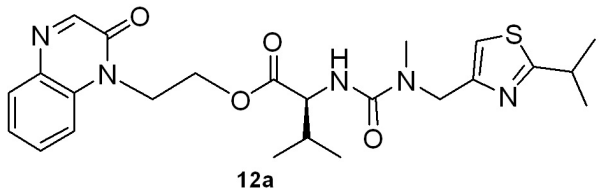
155.83
142.44
137.14
136.24
133.86
131.36
128.34
127.51
127.40
126.51
125.20
124.06
77.32
77.00
76.68
69.14
21.69

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



10j

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



12a

178.42
172.74
158.34
154.31
151.66
149.35
132.96
132.16
130.87
130.09
123.45
113.85
113.75
77.32
77.20
77.00
76.68
60.52
58.69
48.71
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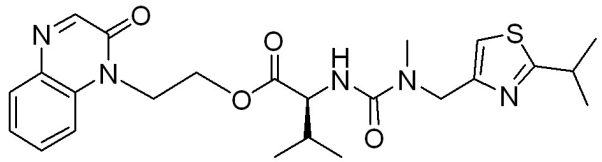
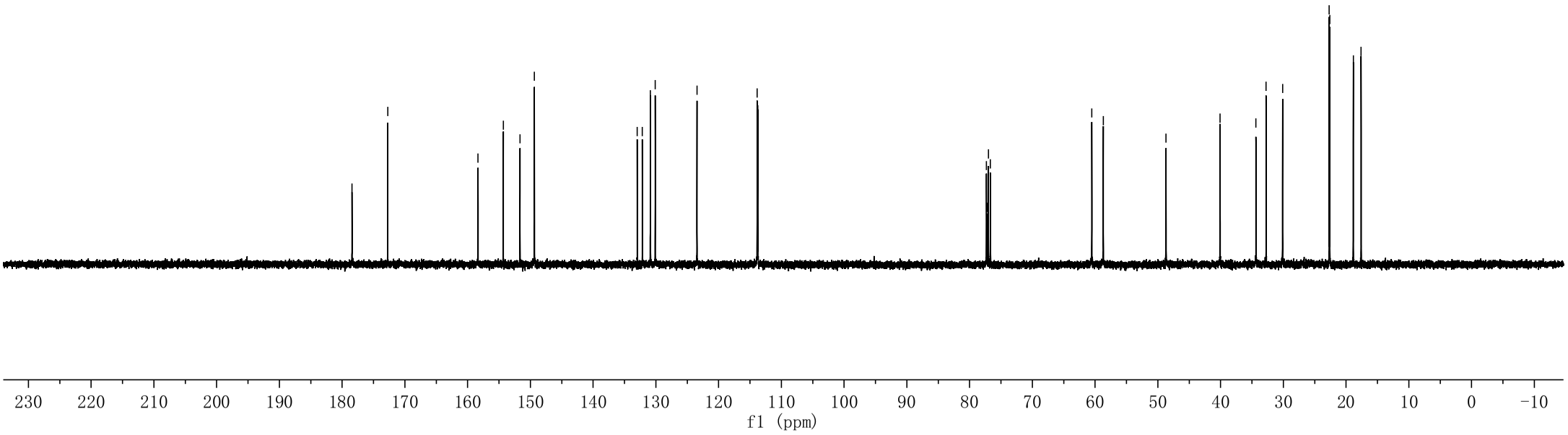
32.74
30.12
22.68
22.61
18.85
17.60

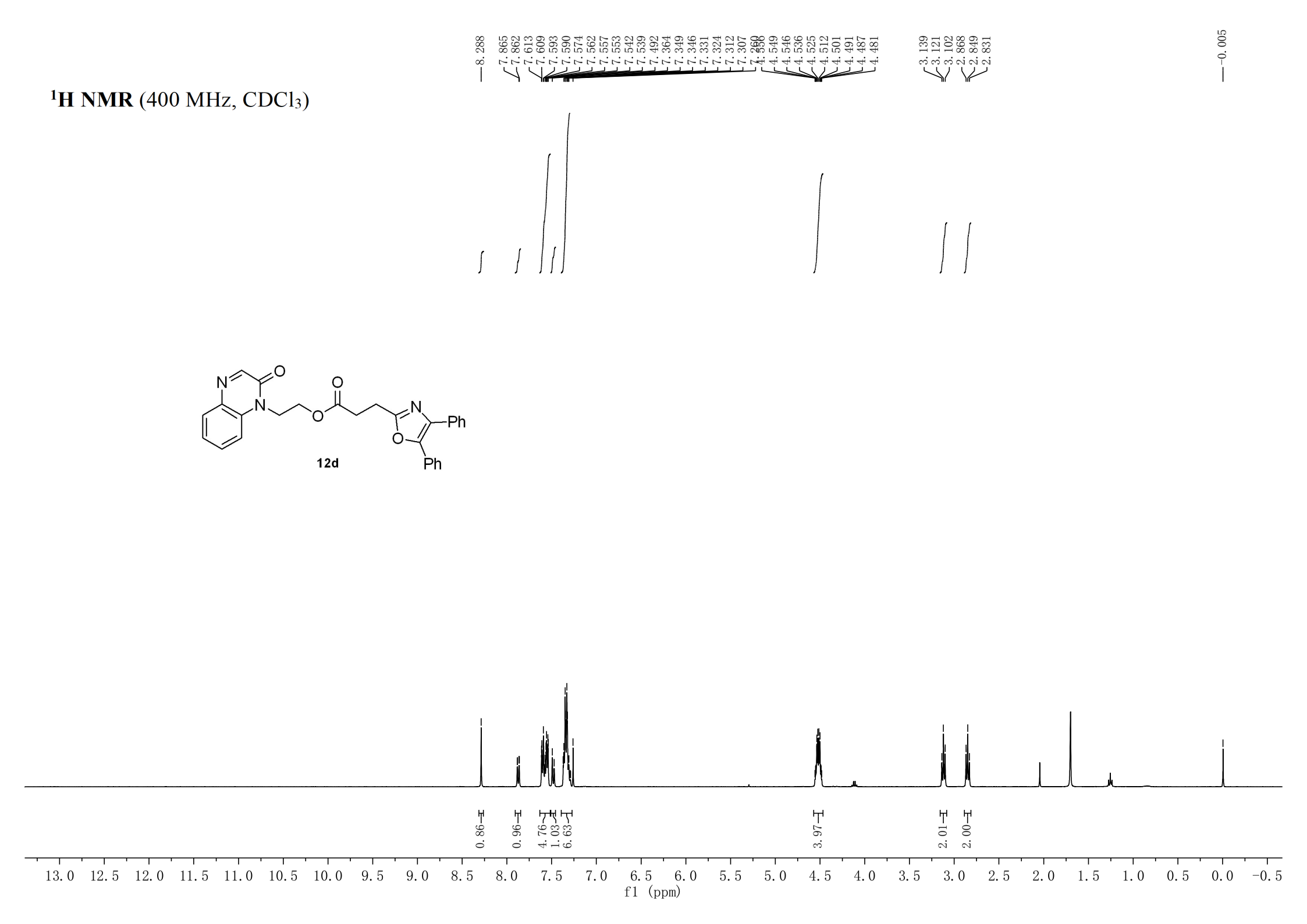
^{13}C NMR (101 MHz, $CDCl_3$)



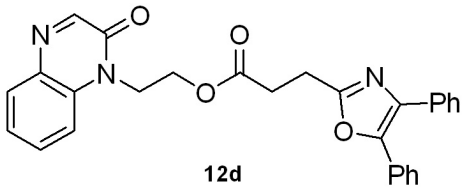
12a



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

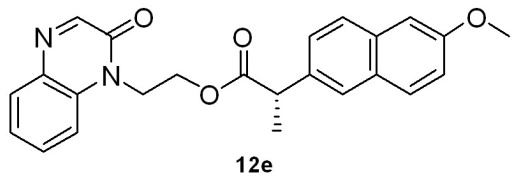


^{13}C NMR (101 MHz, $CDCl_3$)



12d

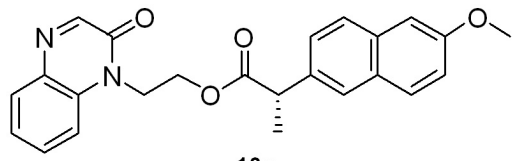
^{1}H NMR (400 MHz, $CDCl_3$)



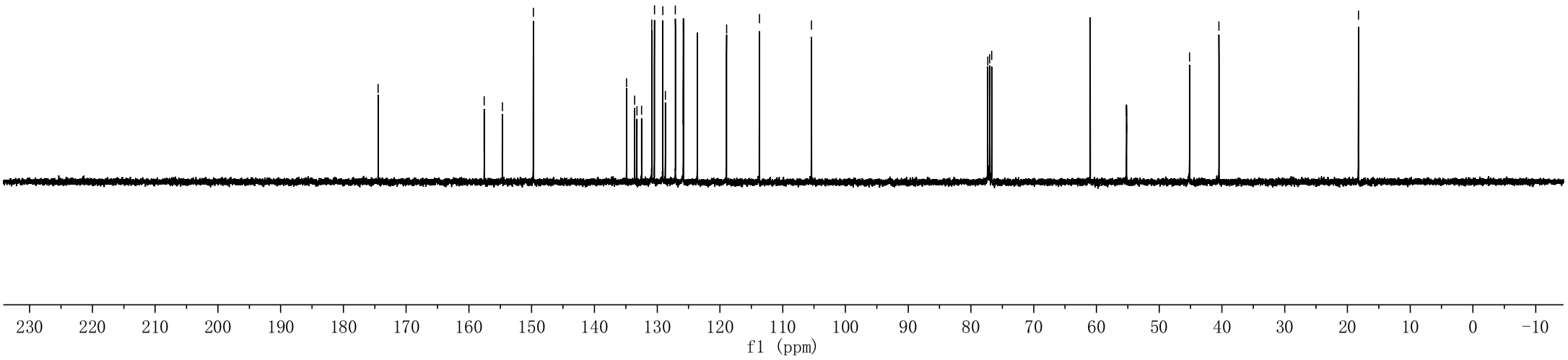
12e

174.47
157.56
154.67
149.73
134.88
133.58
133.23
132.48
130.85
130.44
129.11
128.70
127.09
125.83
125.80
123.60
118.95
113.71
105.41
77.32
77.00
76.68
60.99
55.21
55.19
45.15
40.46
18.24

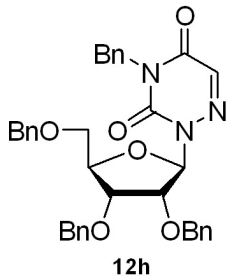
^{13}C NMR (101 MHz, $CDCl_3$)



12e



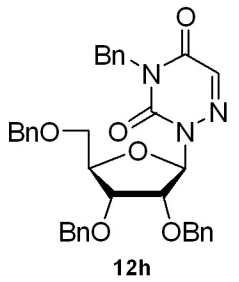
^{1}H NMR (400 MHz, $CDCl_3$)



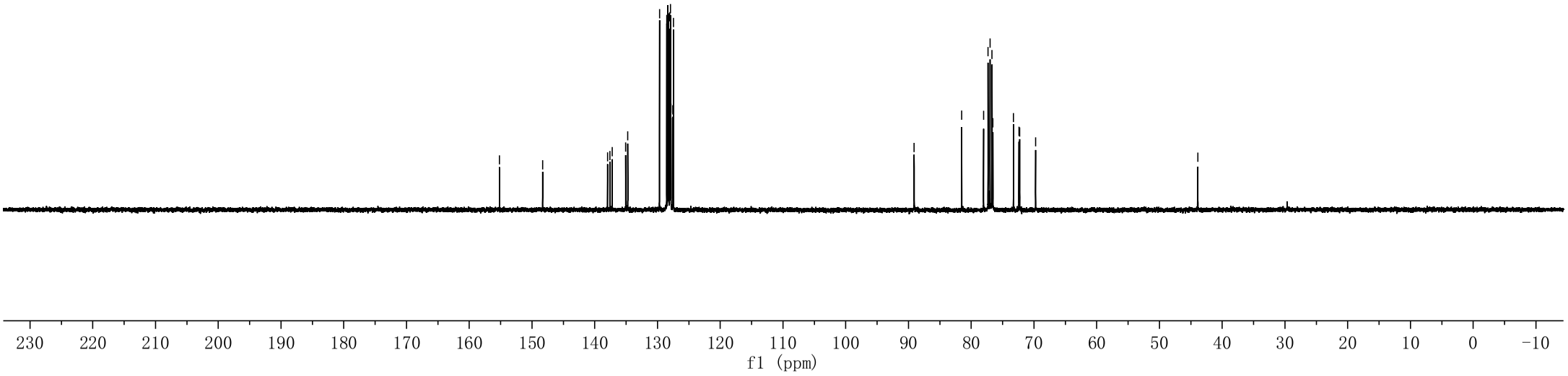
12h

155.17
148.30
137.95
137.56
137.21
135.06
134.74
129.68
128.53
128.36
128.34
128.24
128.22
128.03
127.95
127.92
127.85
127.56
127.45
89.09
81.52
78.04
77.32
77.00
76.68
76.55
73.27
72.40
72.28
69.74
43.89

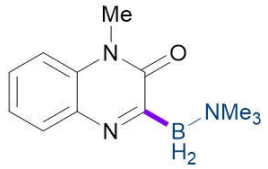
^{13}C NMR (101 MHz, $CDCl_3$)



12h



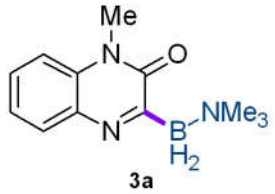
^{1}H NMR (400 MHz, $CDCl_3$)



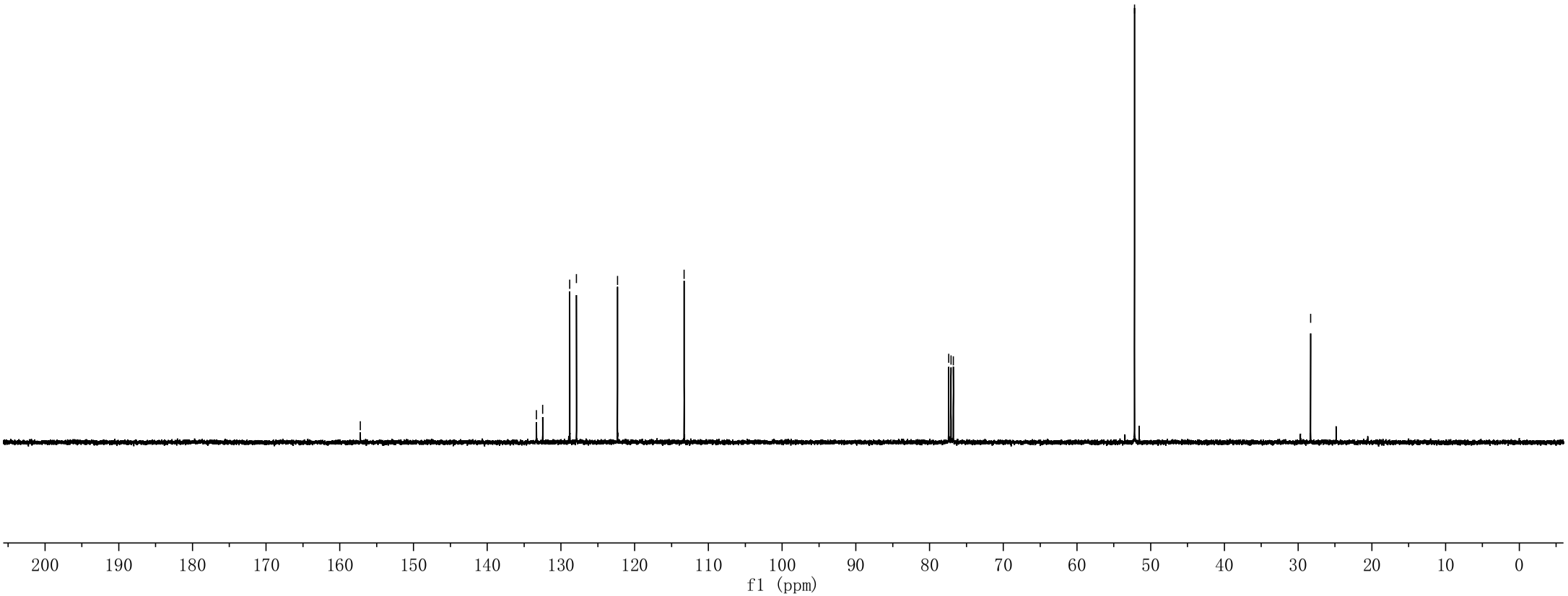
3a

157.22
133.32
132.48
128.80
127.90
122.33
113.29
77.41
77.09
76.78
52.19
28.31

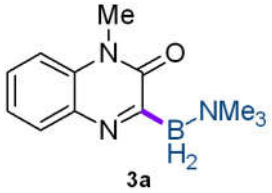
^{13}C NMR (101 MHz, $CDCl_3$)



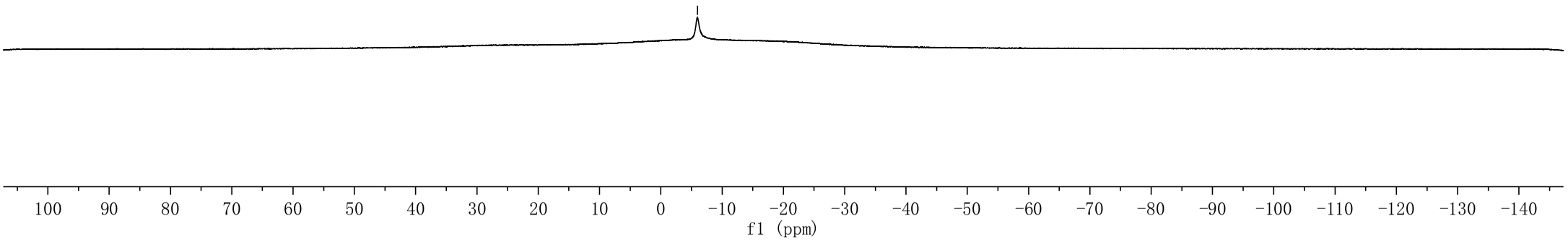
3a



^{11}B NMR (128 MHz, $CDCl_3$)



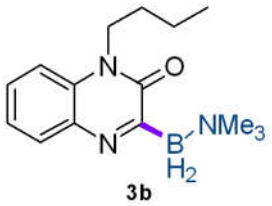
3a



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

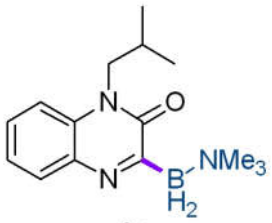
3b

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



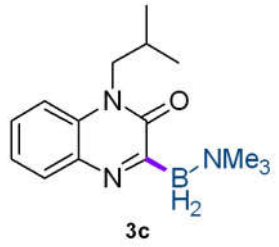
3b

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



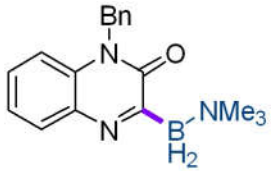
3c

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



3c

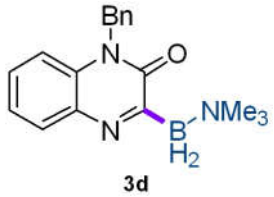
^{1}H NMR (400 MHz, $CDCl_3$)



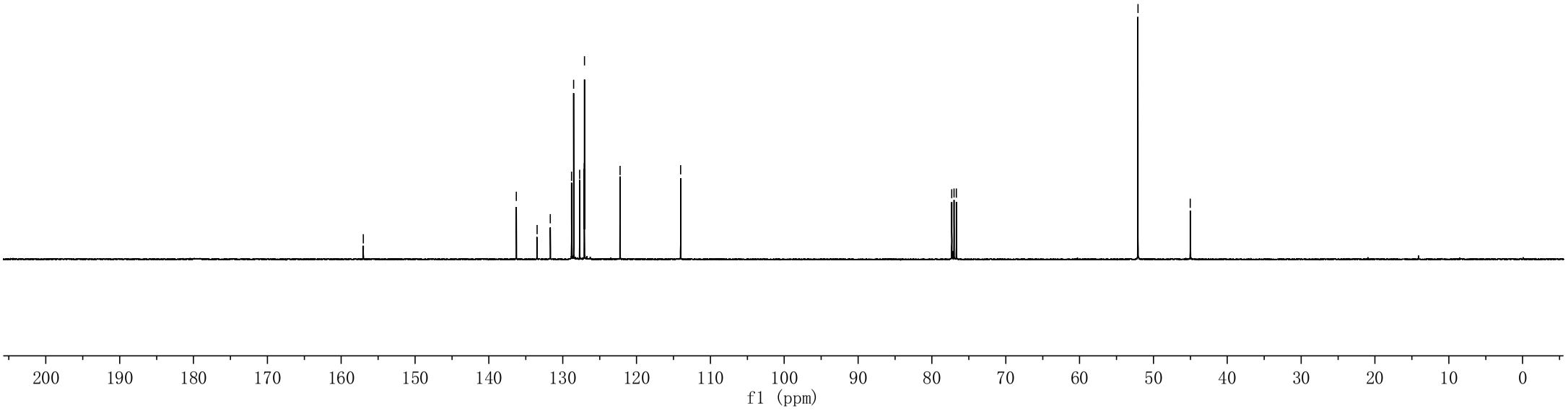
3d

157.00
136.27
133.48
131.68
128.81
128.52
127.71
127.08
127.05
122.24
114.03
77.32
77.00
76.68
52.11
45.01

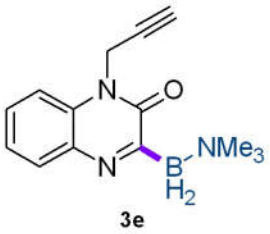
^{13}C NMR (101 MHz, $CDCl_3$)



3d



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

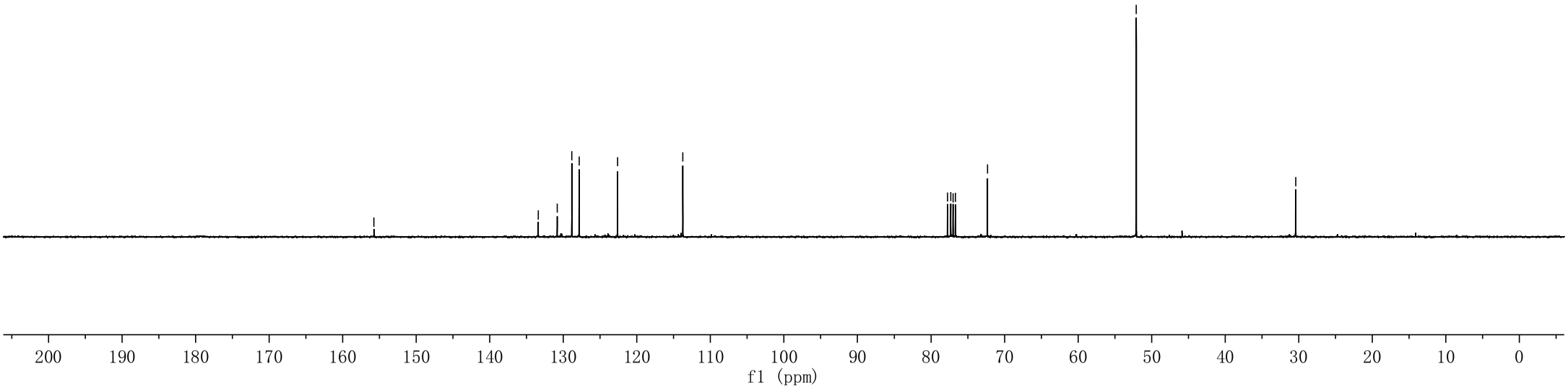


3e

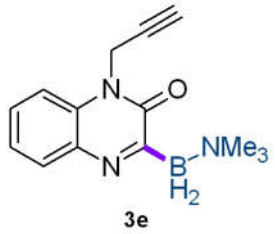
155.74
133.42
130.82
128.84
127.84
122.63
113.75
77.76
77.32
77.00
76.68
72.33
52.08
30.42

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

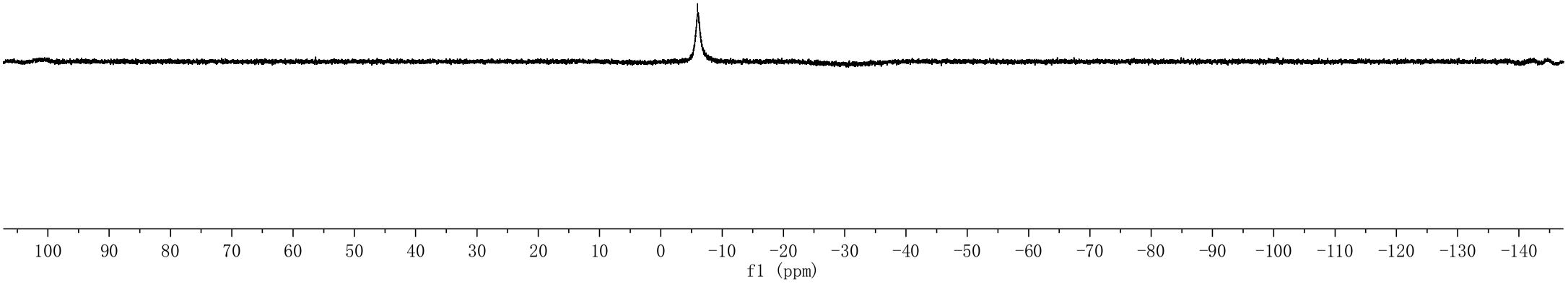
3e



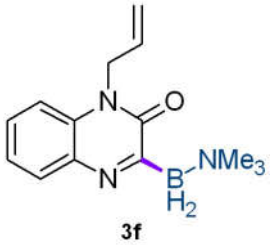
^{11}B NMR (128 MHz, $CDCl_3$)



3e

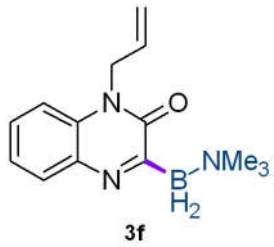


^{1}H NMR (400 MHz, $CDCl_3$)



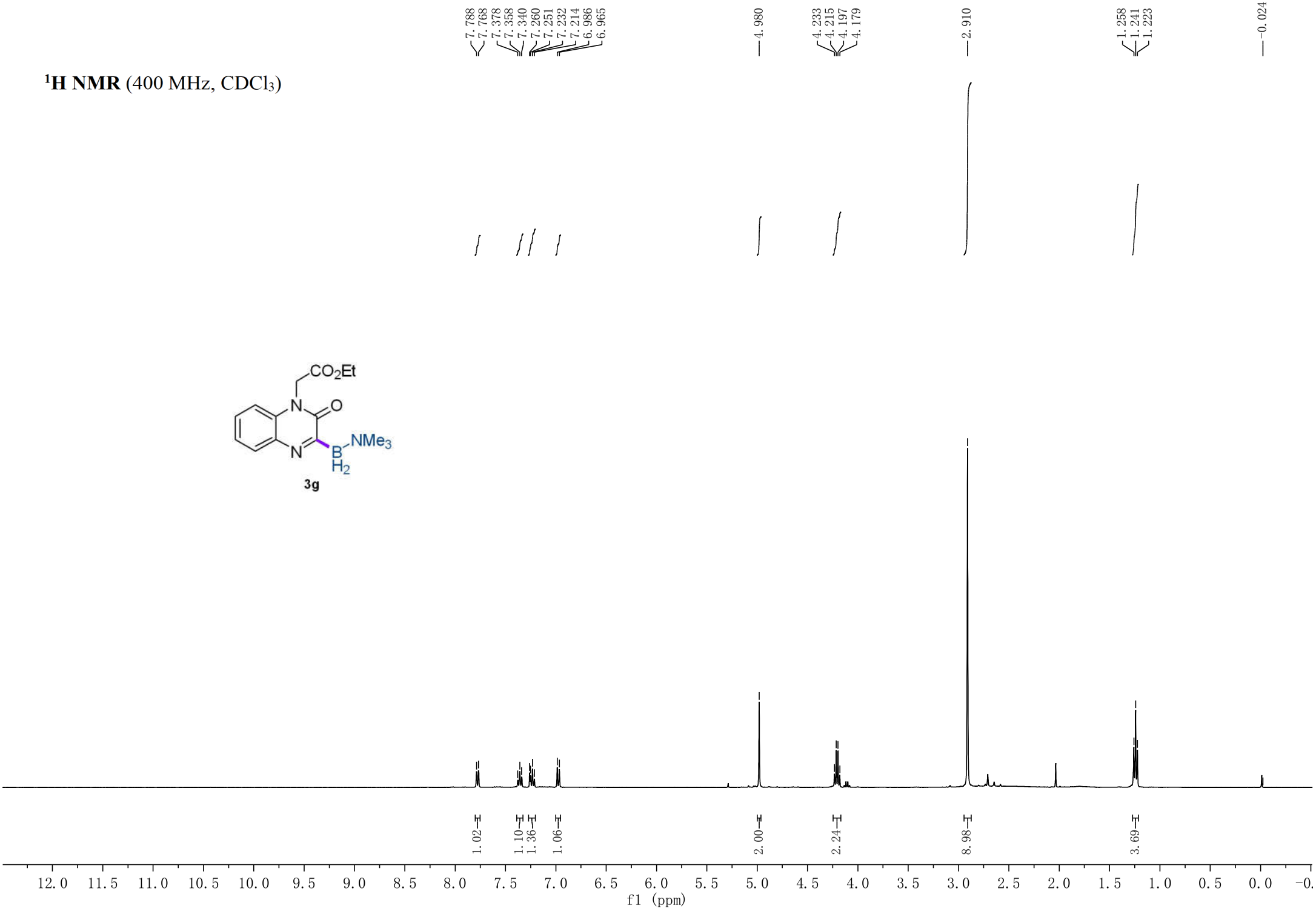
3f

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



3f

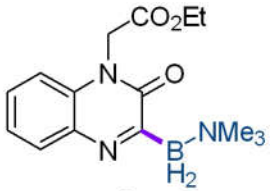
^{1}H NMR (400 MHz, $CDCl_3$)



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

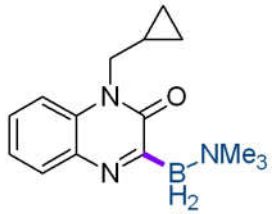
3g

^{11}B NMR (128 MHz, $CDCl_3$)



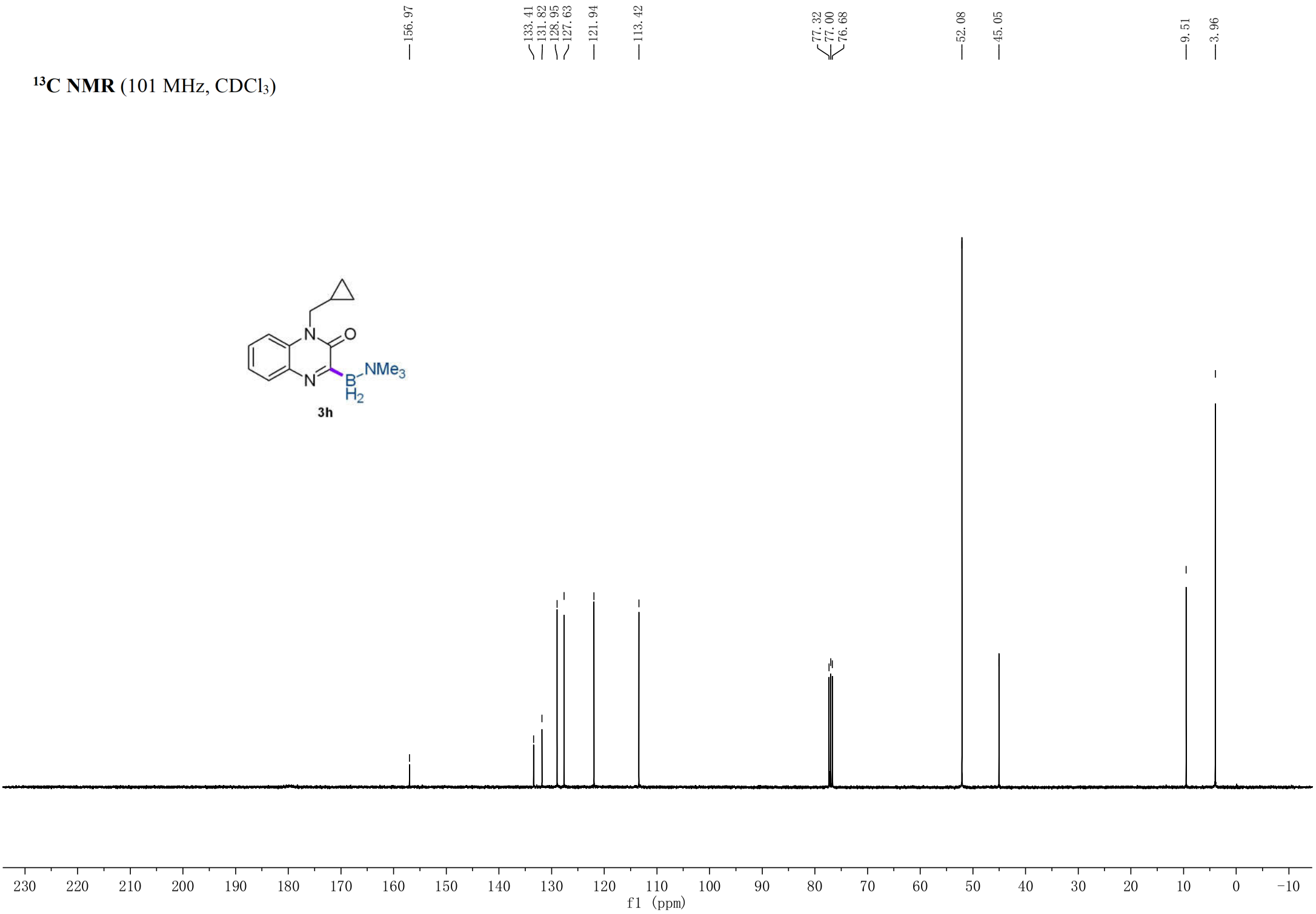
3g

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



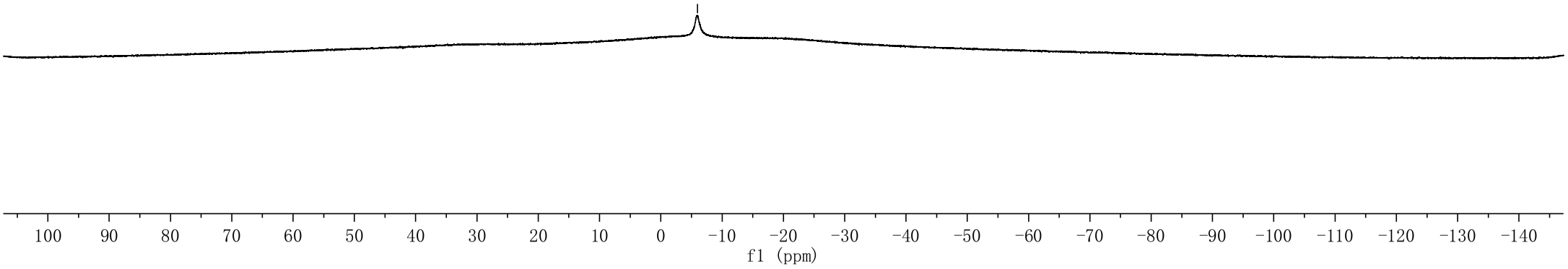
3h

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

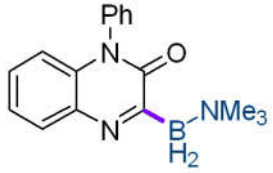


^{11}B NMR (128 MHz, $CDCl_3$)

3h



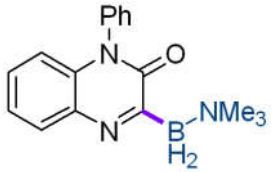
^{1}H NMR (400 MHz, $CDCl_3$)



3i

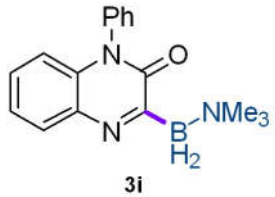
156.60
136.44
133.14
132.90
129.68
128.51
128.37
127.38
122.34
114.88
77.32
77.00
76.68
52.13

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

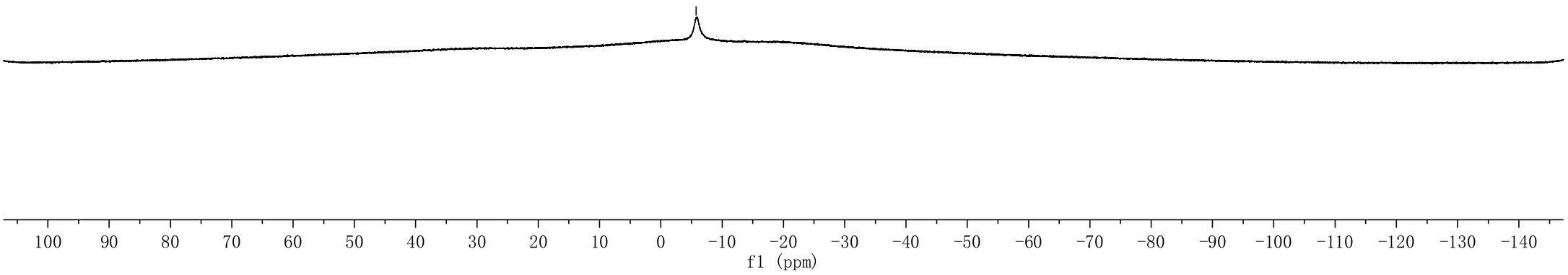


3i

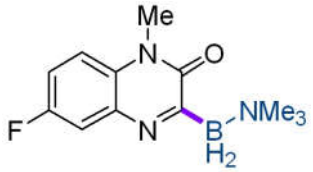
^{11}B NMR (128 MHz, $CDCl_3$)



3i



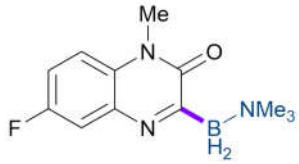
^{1}H NMR (400 MHz, $CDCl_3$)



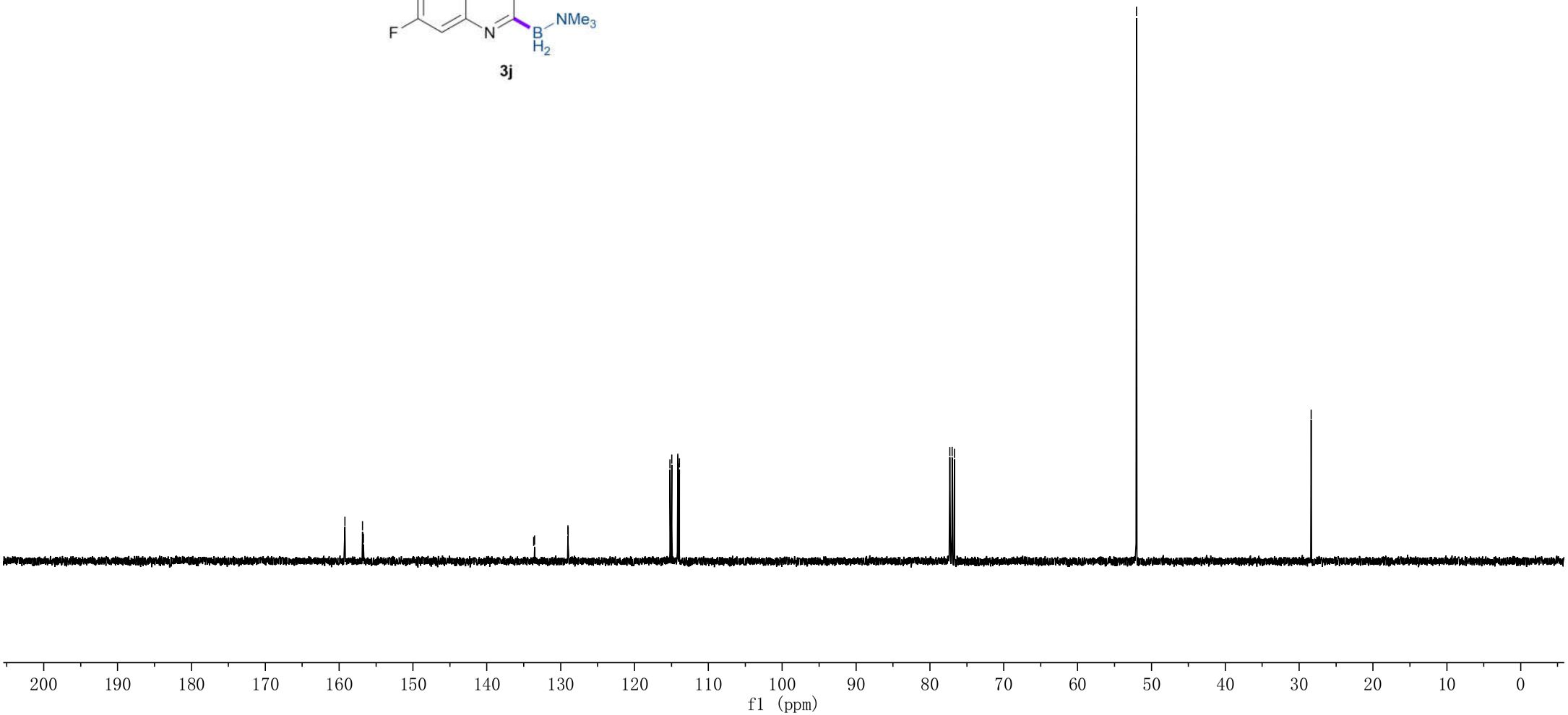
3j

159.22
156.82
156.70
133.65
133.54
129.01
128.99
115.20
114.96
114.15
114.13
114.04
113.93
77.32
77.00
76.68
52.04
28.38

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



3j

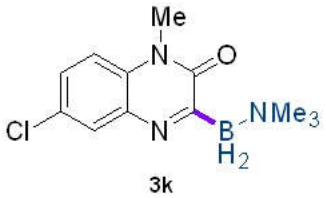


^{1}H NMR (400 MHz, $CDCl_3$)

3k

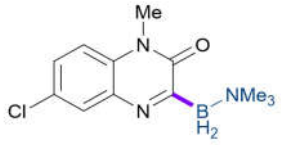
156.69
133.66
131.18
128.05
127.59
127.32
114.37
77.32
77.00
76.68
52.07
28.35

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

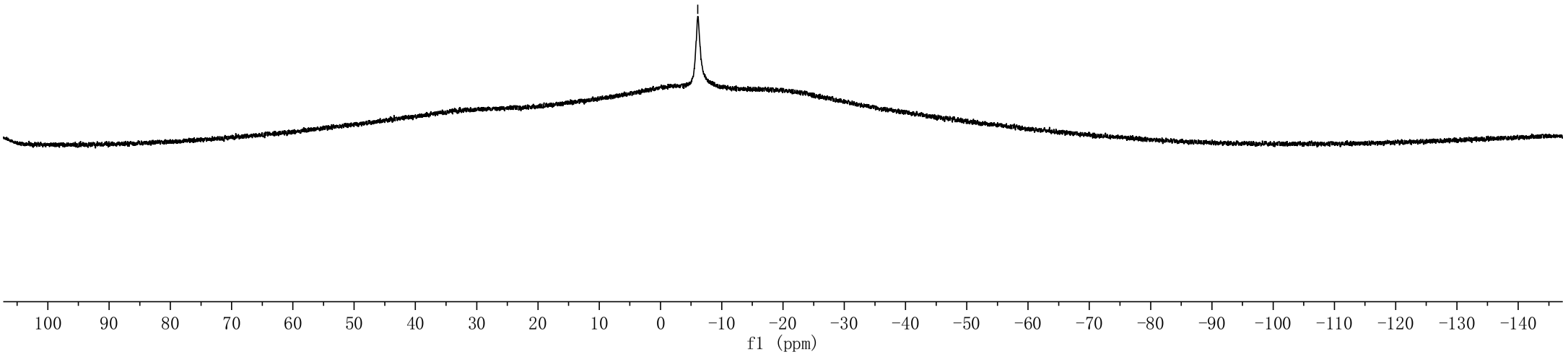


3k

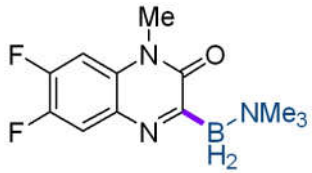
^{11}B NMR (128 MHz, $CDCl_3$)



3k



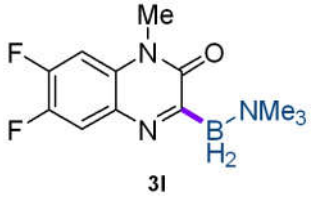
^{1}H NMR (400 MHz, $CDCl_3$)



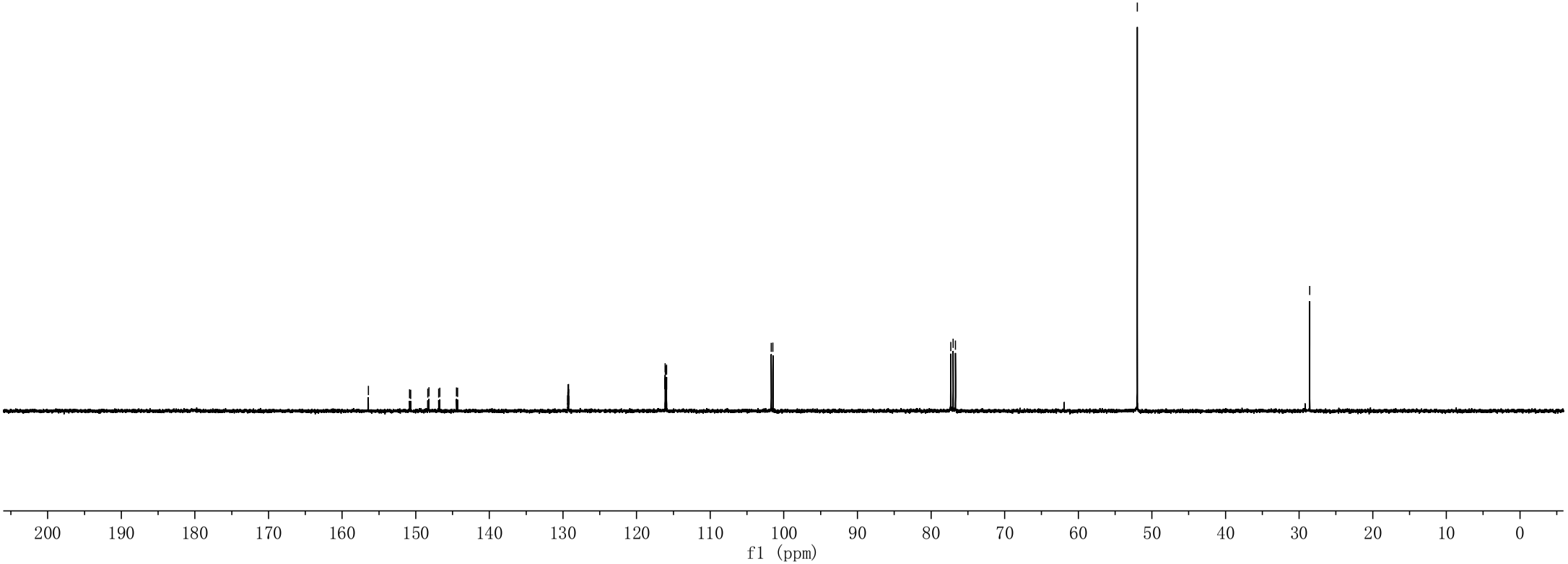
3l

156.45
150.84
150.70
148.36
148.22
146.88
146.74
144.46
144.32
129.37
129.35
129.32
129.30
129.29
129.23
116.10
115.95
115.93
101.70
101.48
77.32
77.00
76.68
51.98
28.56

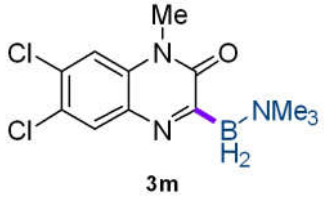
^{13}C NMR (101 MHz, $CDCl_3$)



3l



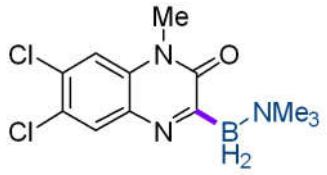
^{1}H NMR (400 MHz, $CDCl_3$)



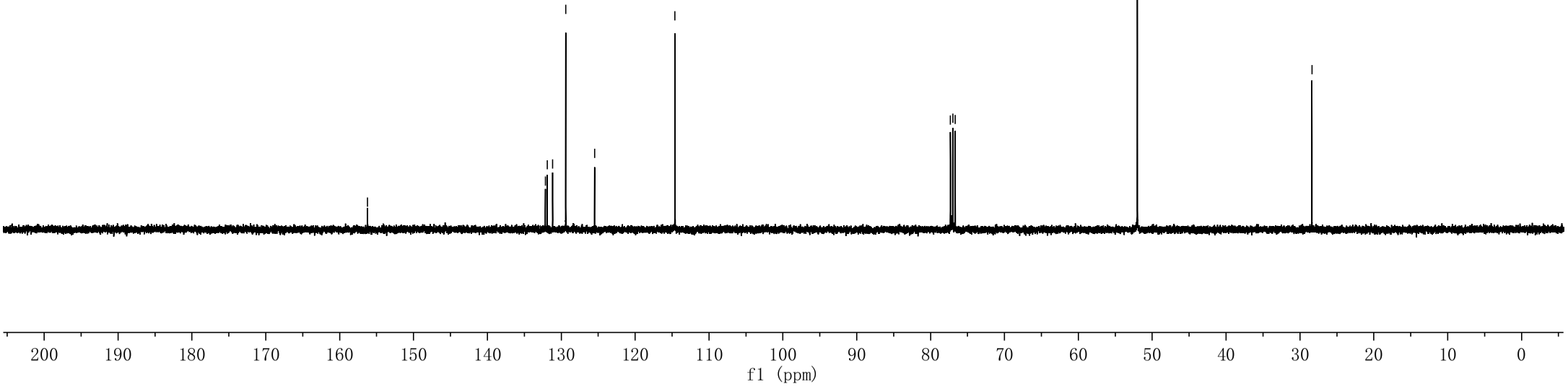
3m

156.23
132.15
131.91
131.17
129.39
125.49
114.61
77.32
77.00
76.68
52.01
28.38

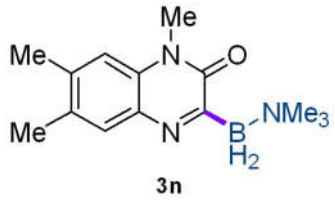
^{13}C NMR (101 MHz, $CDCl_3$)



3m



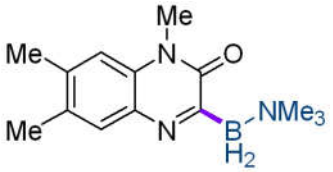
^{1}H NMR (400 MHz, $CDCl_3$)



3n

157.28
137.00
131.77
130.73
130.34
129.05
113.84
77.32
77.00
76.68
52.08
28.11
20.23
19.03

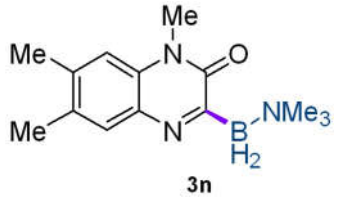
^{13}C NMR (101 MHz, $CDCl_3$)



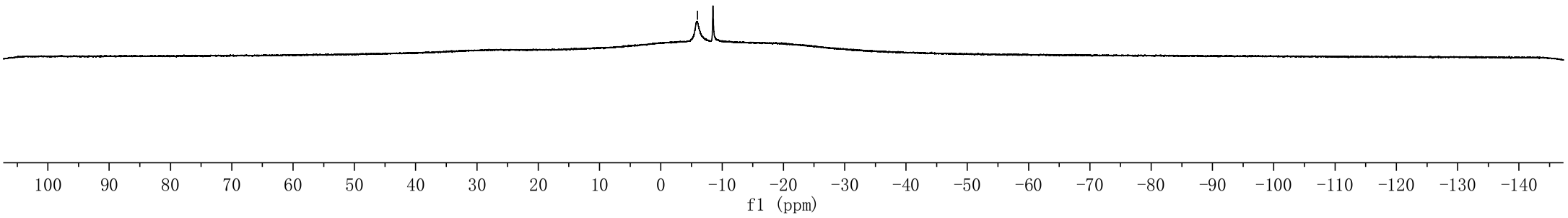
3n

—5.97

^{11}B NMR (128 MHz, $CDCl_3$)



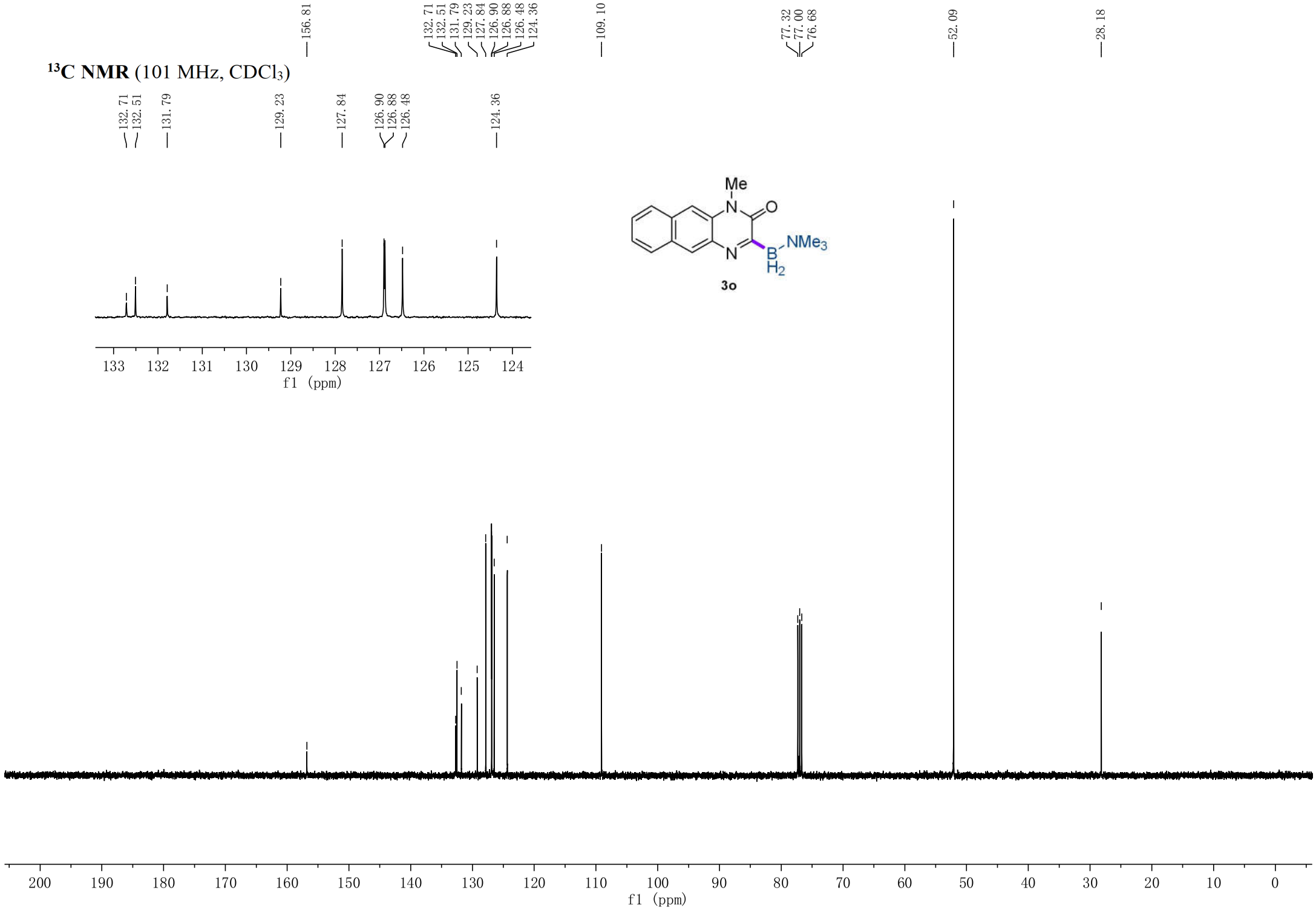
3n



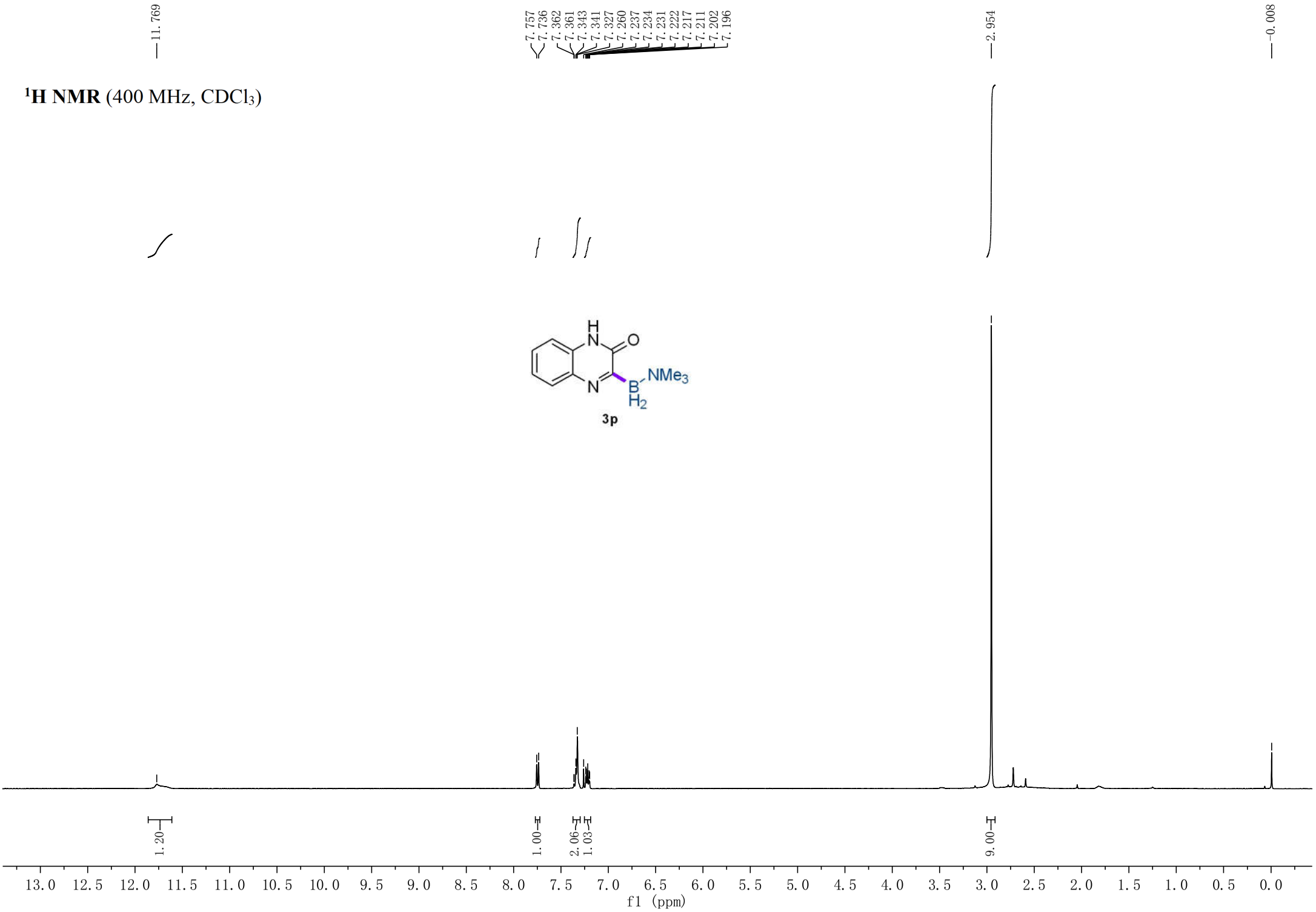
^{1}H NMR (400 MHz, $CDCl_3$)

3o

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



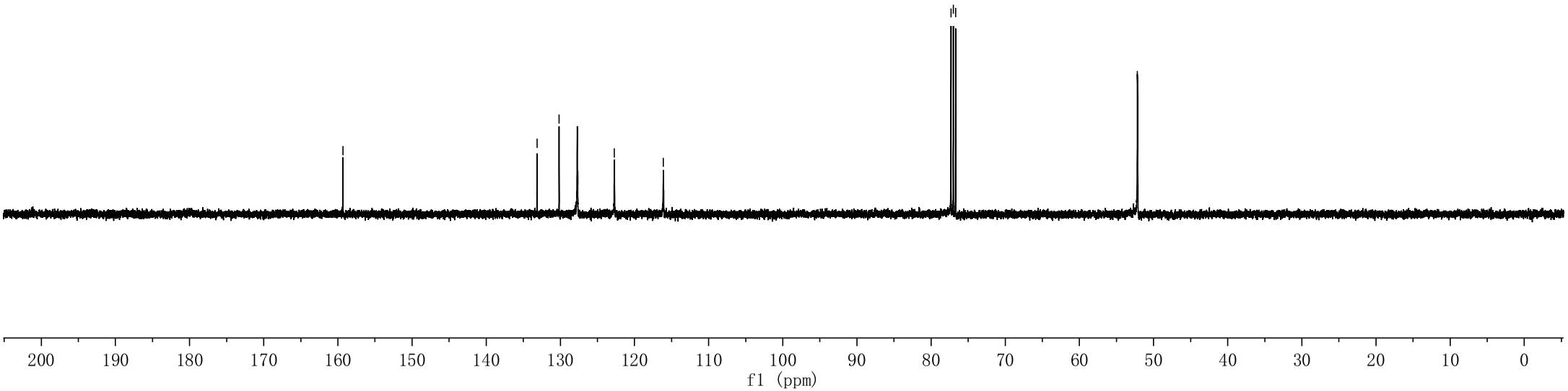
^{1}H NMR (400 MHz, $CDCl_3$)



159.33
133.14
130.16
127.72
127.65
122.71
116.11
77.32
77.00
76.68
52.18

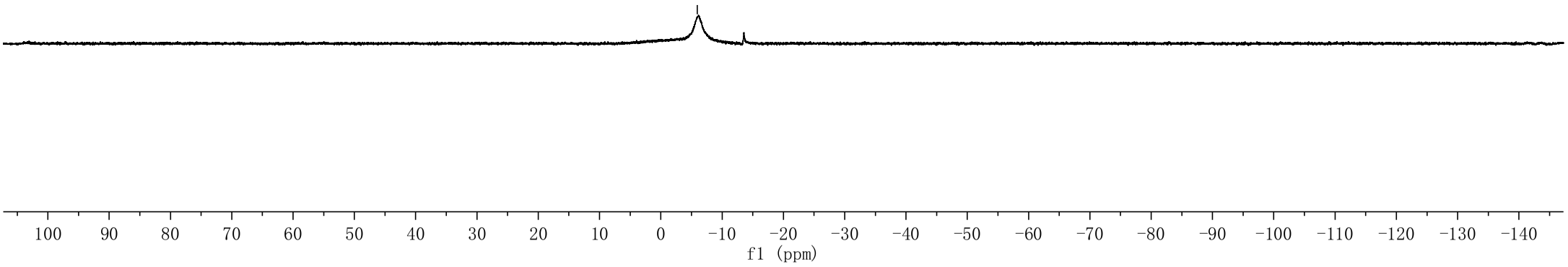
^{13}C NMR (101 MHz, $CDCl_3$)

3p

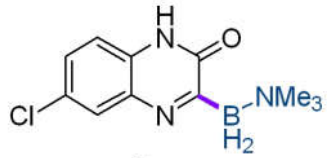


^{11}B NMR (128 MHz, $CDCl_3$)

3p



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

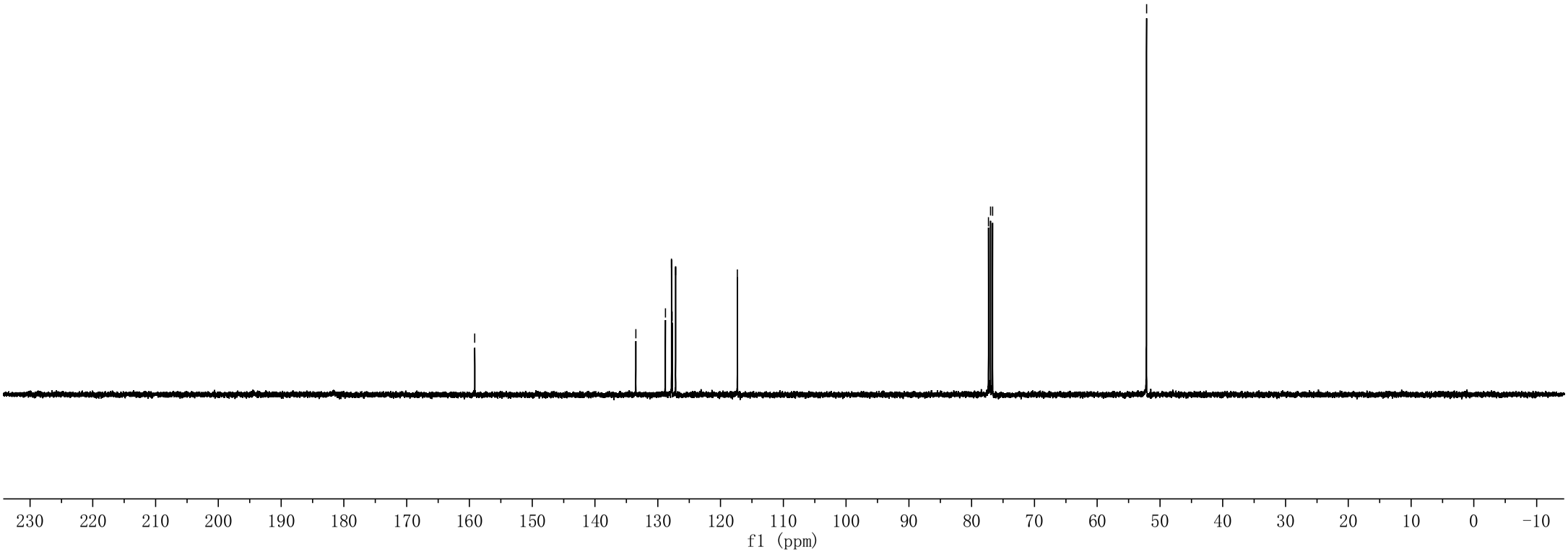


3q

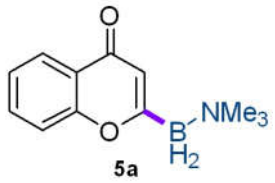
159.15
133.50
128.80
127.82
127.70
127.16
117.32
77.32
77.00
76.68
52.15

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

3q



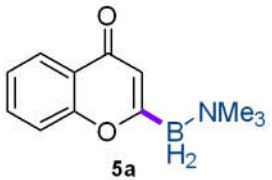
^{1}H NMR (400 MHz, $CDCl_3$)



5a

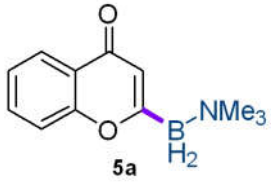
177.98
157.83
132.62
125.26
124.04
123.89
120.18
118.01
77.32
77.00
76.68
52.77

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

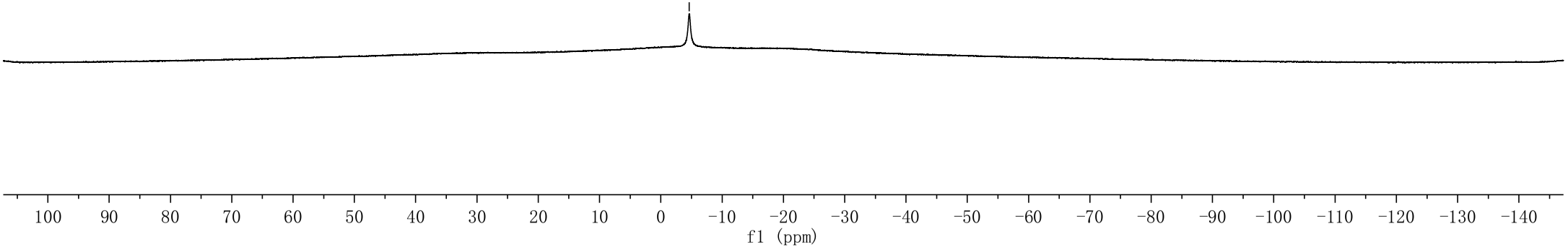


5a

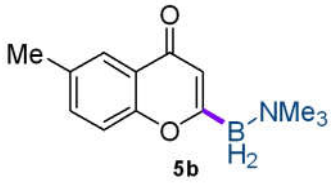
^{11}B NMR (128 MHz, $CDCl_3$)



5a



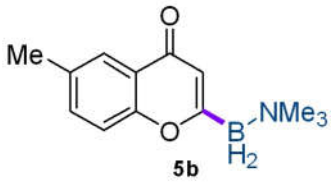
^{1}H NMR (400 MHz, $CDCl_3$)



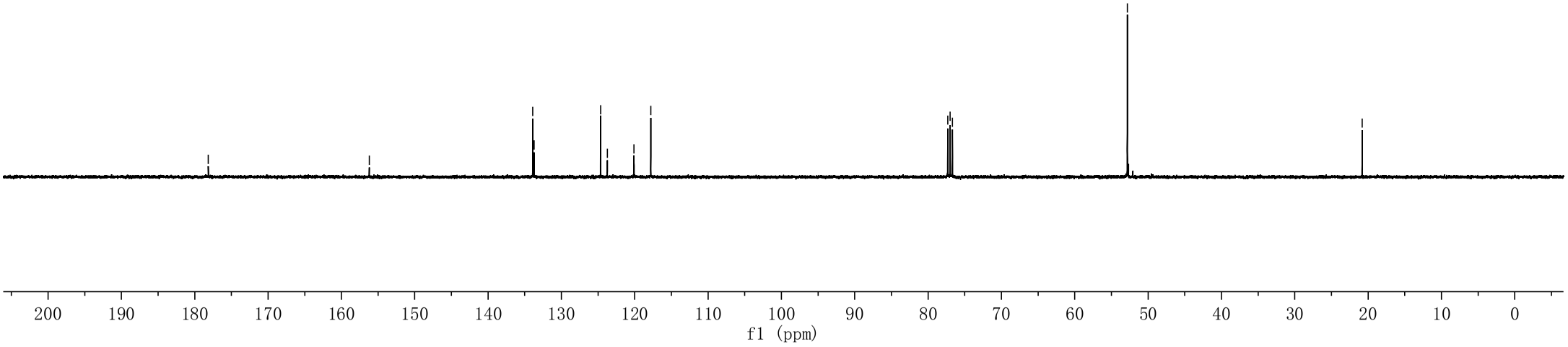
5b

178.15
156.20
133.90
133.71
124.66
123.74
120.11
117.81
77.32
77.00
76.68
52.83
20.81

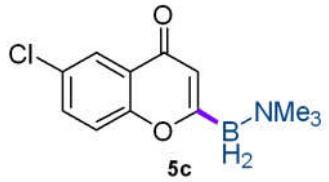
^{13}C NMR (101 MHz, $CDCl_3$)



5b



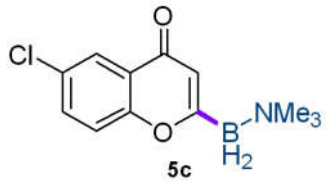
^{1}H NMR (400 MHz, $CDCl_3$)



5c

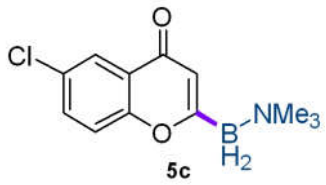
176.82
156.24
132.85
129.72
125.05
124.78
120.16
119.85
77.32
77.00
76.68
52.88

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

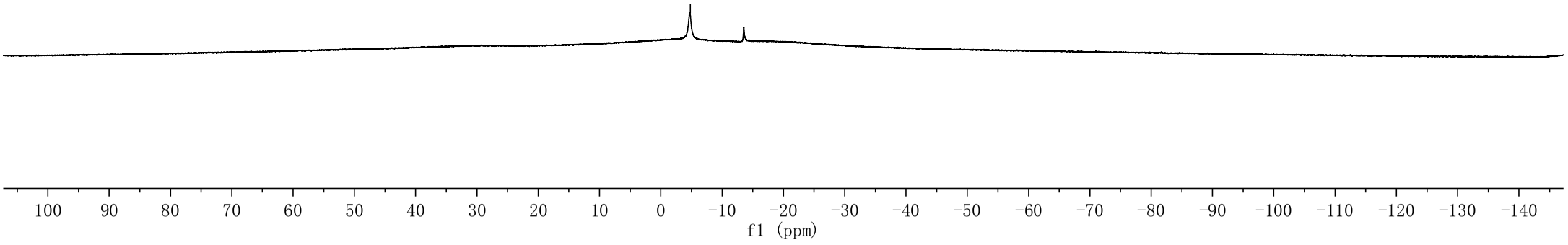


5c

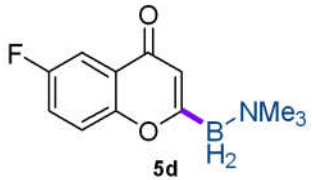
^{11}B NMR (128 MHz, $CDCl_3$)



5c

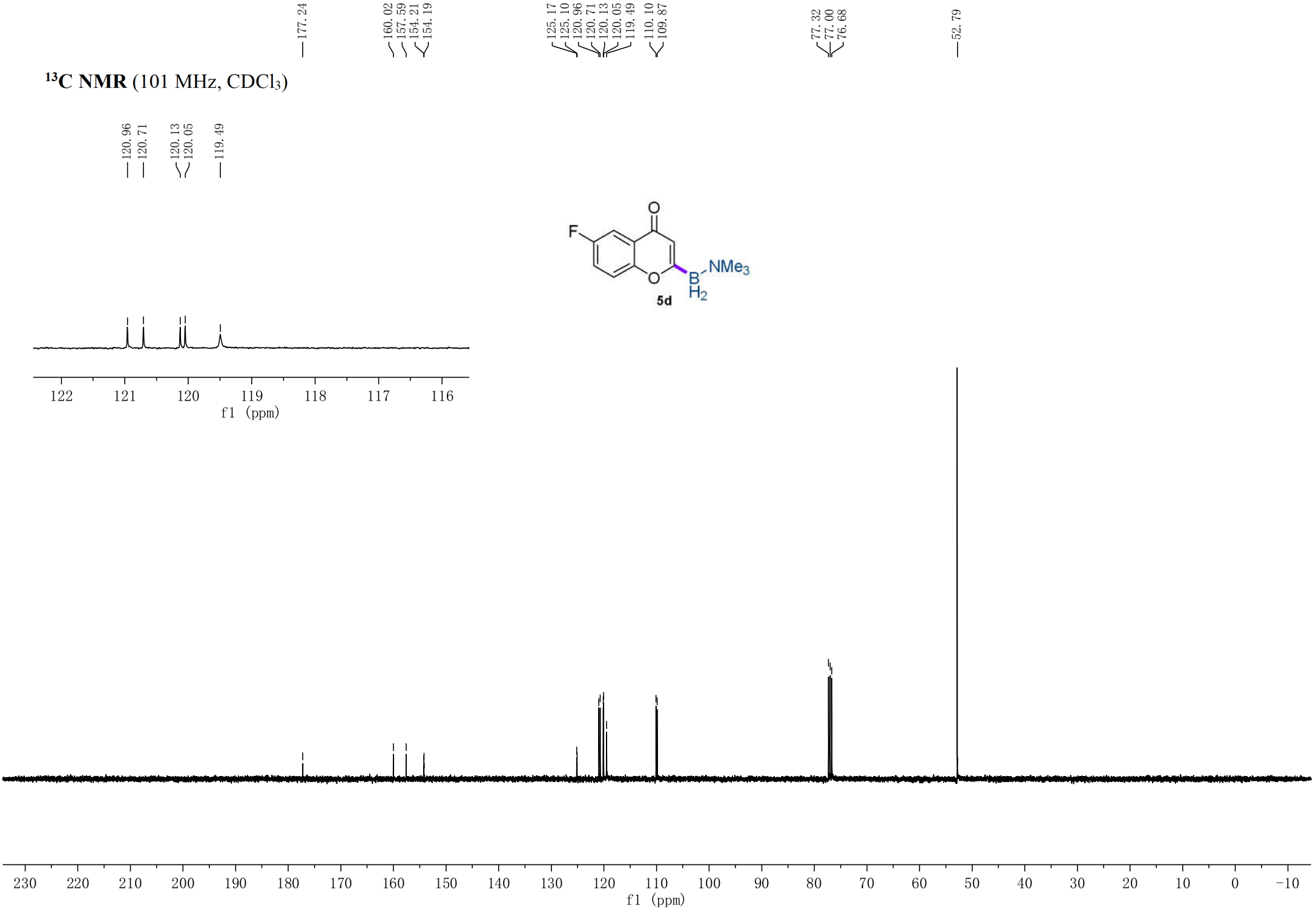


^{1}H NMR (400 MHz, $CDCl_3$)

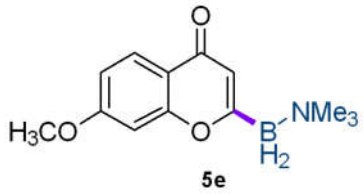


5d

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



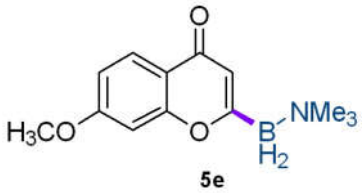
^{1}H NMR (400 MHz, $CDCl_3$)



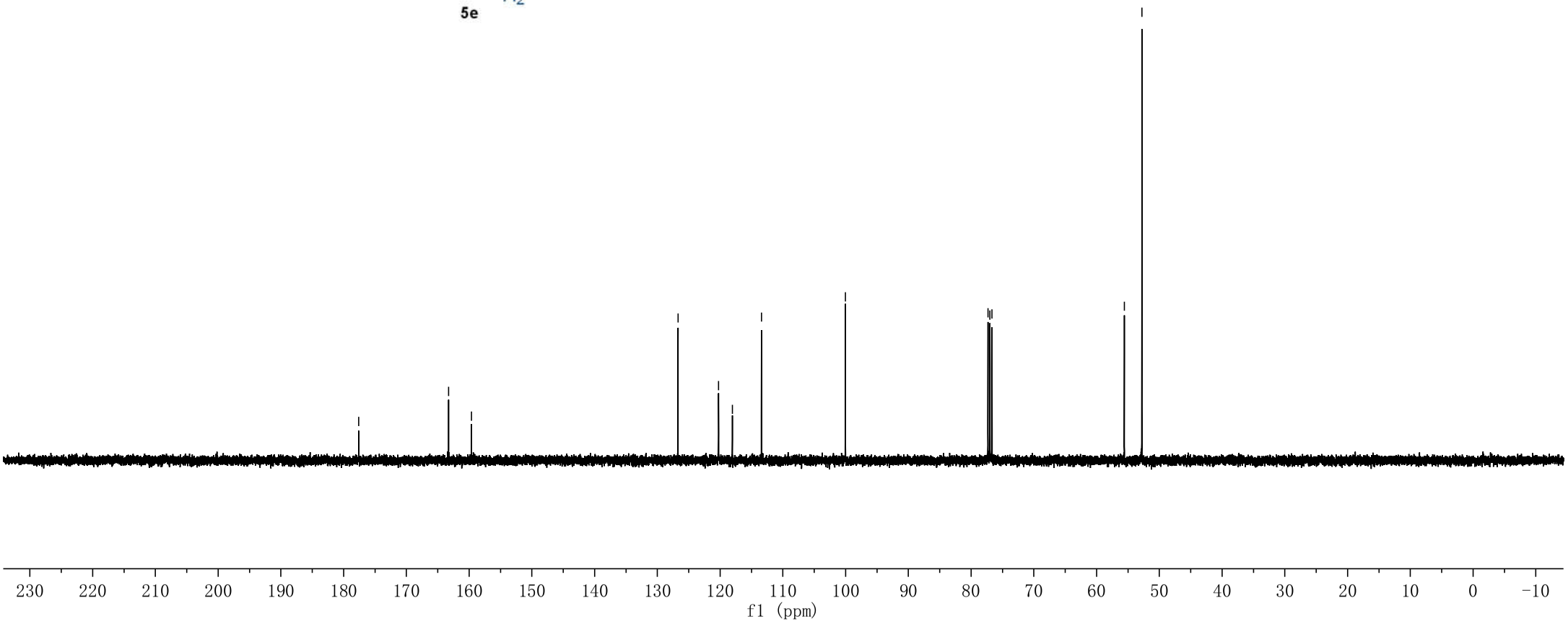
5e

177.59
163.28
159.64
126.71
120.25
118.04
113.42
100.04
77.32
77.00
76.68
55.58
52.79

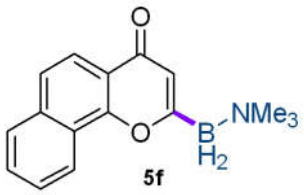
^{13}C NMR (101 MHz, $CDCl_3$)



5e

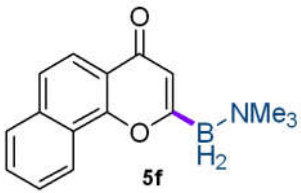


^{1}H NMR (400 MHz, $CDCl_3$)



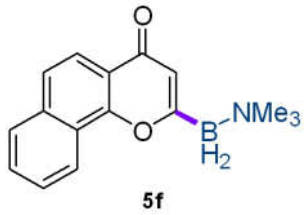
5f

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

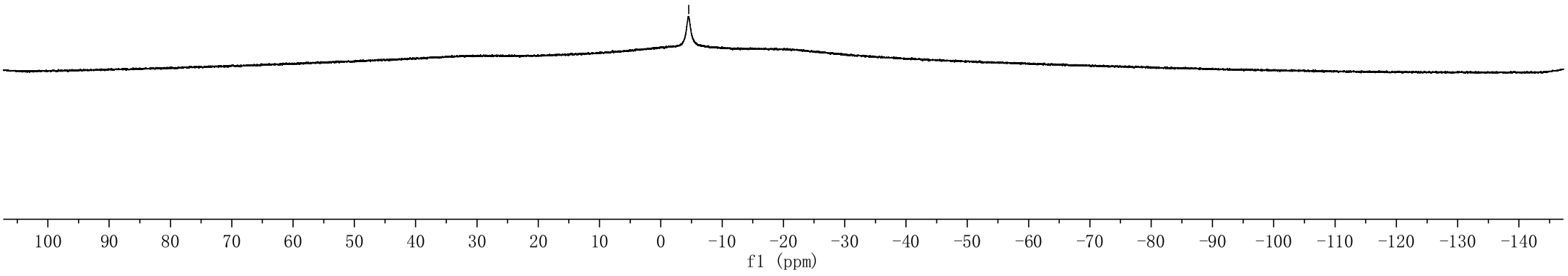


5f

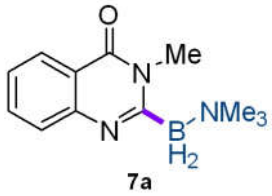
^{11}B NMR (128 MHz, $CDCl_3$)



5f

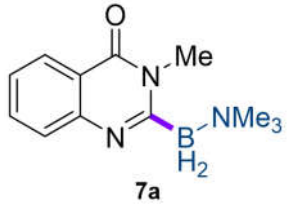


^{1}H NMR (400 MHz, $CDCl_3$)



7a

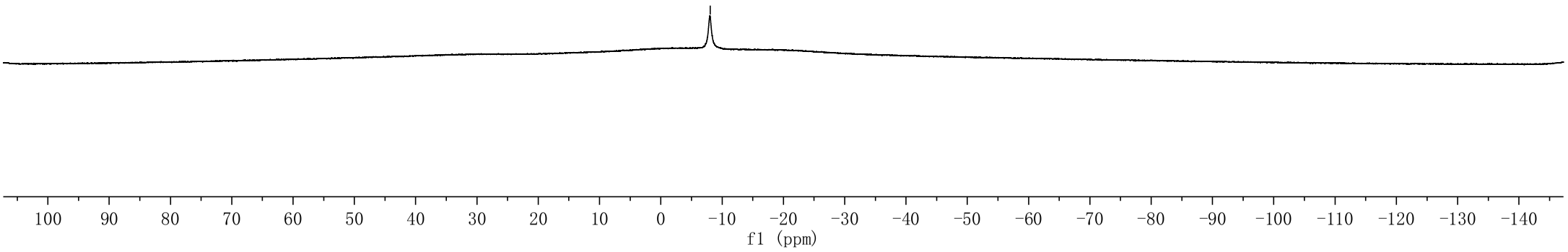
^{13}C NMR (101 MHz, $CDCl_3$)



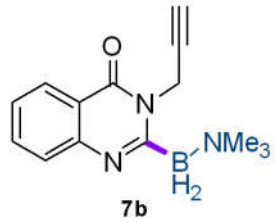
7a

^{11}B NMR (128 MHz, $CDCl_3$)

7a

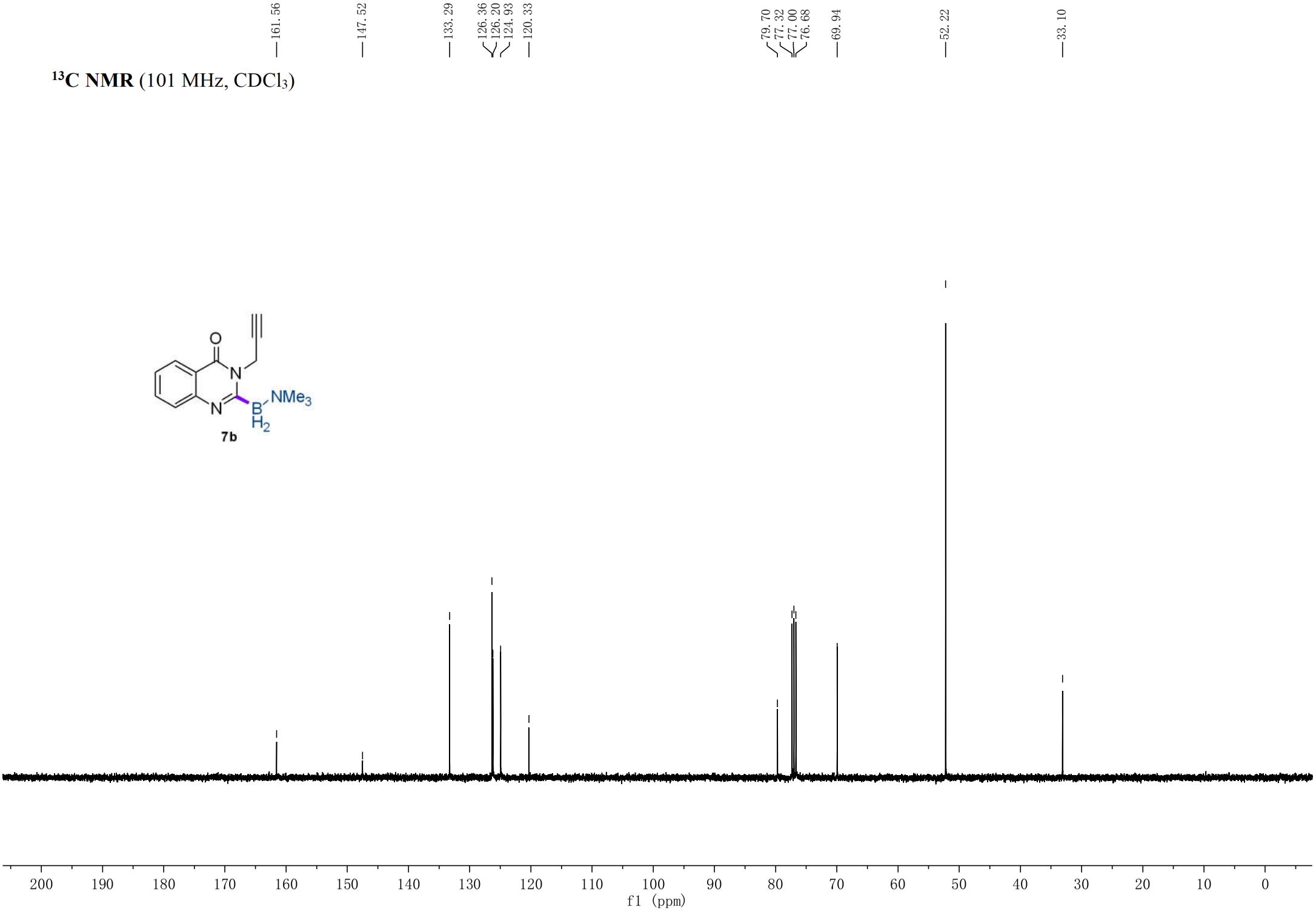


^{1}H NMR (400 MHz, $CDCl_3$)

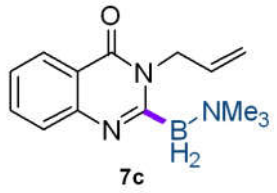


7b

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

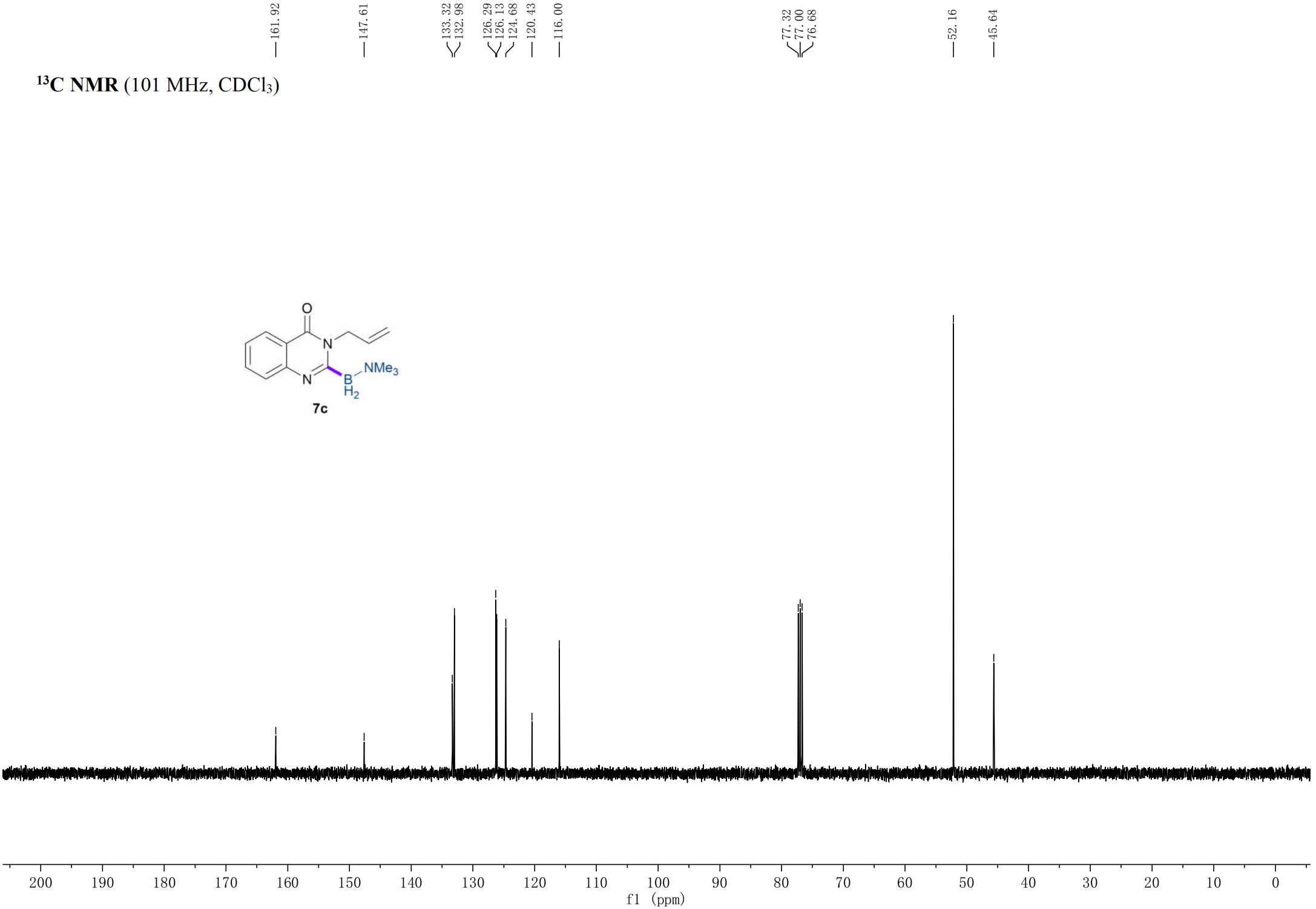


^{1}H NMR (400 MHz, $CDCl_3$)

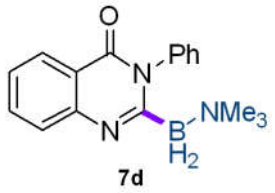


7c

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

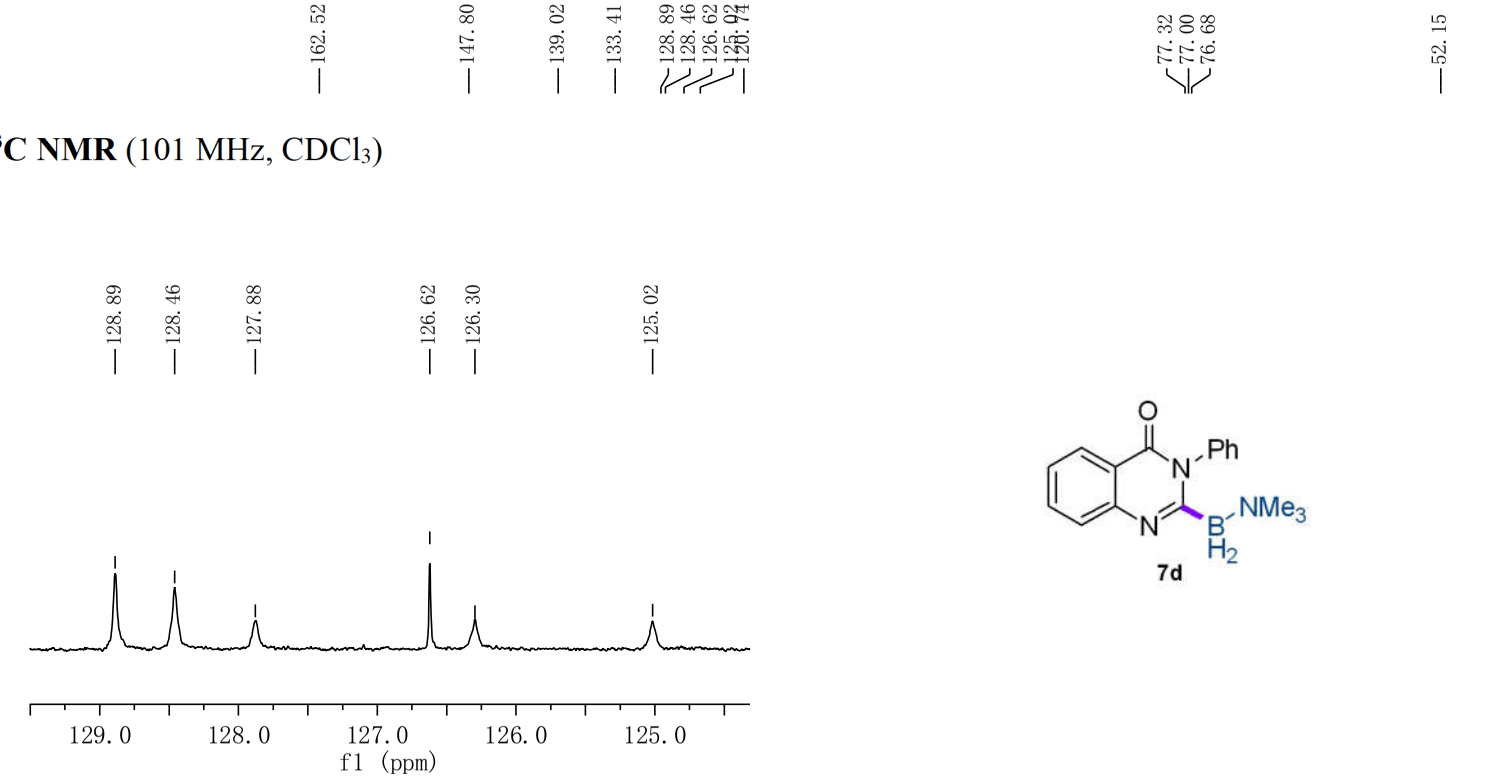


^{1}H NMR (400 MHz, $CDCl_3$)

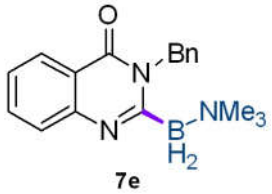


7d

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

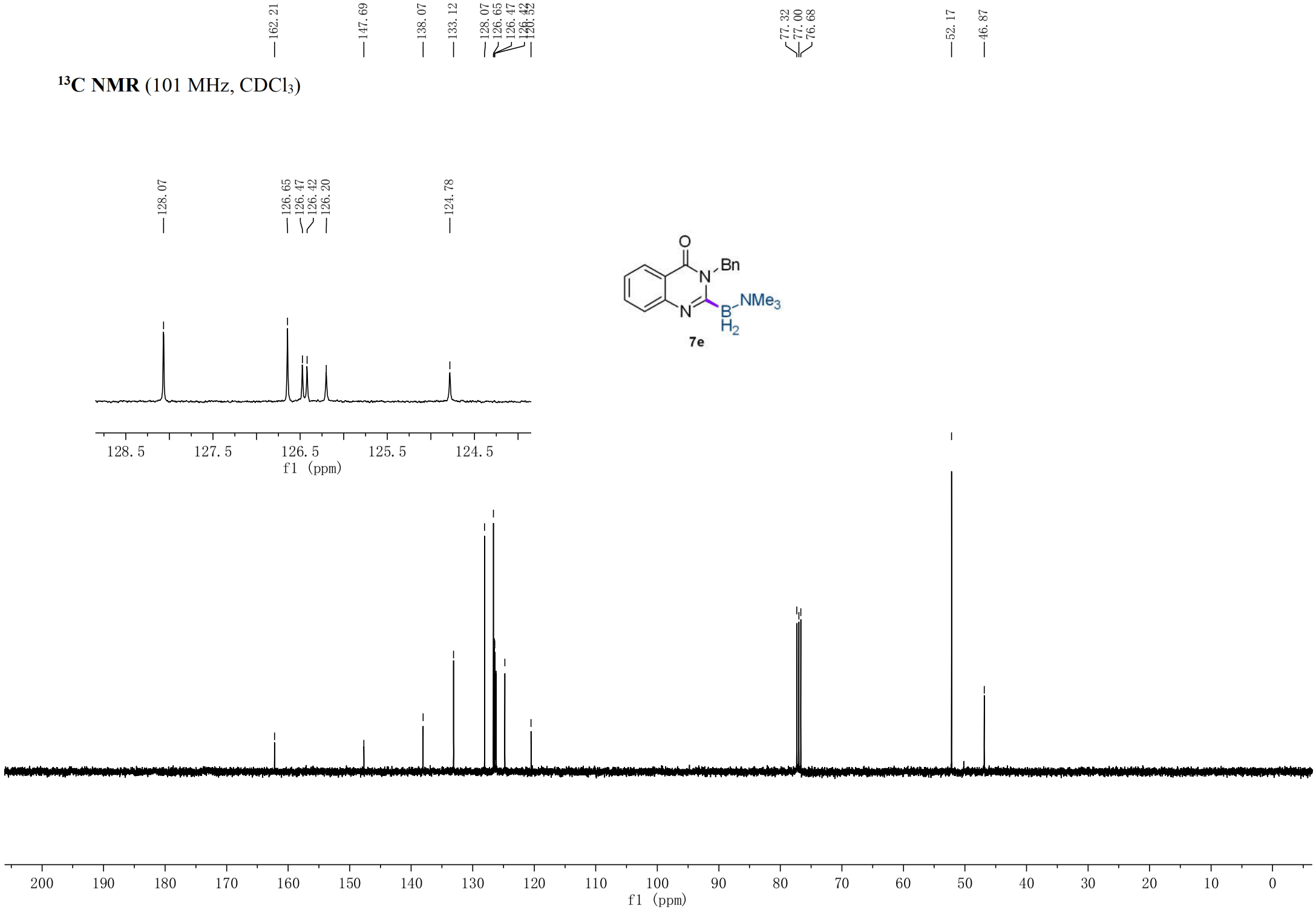


^{1}H NMR (400 MHz, $CDCl_3$)

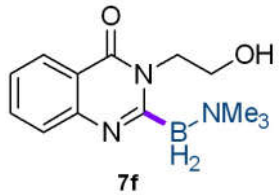


7e

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



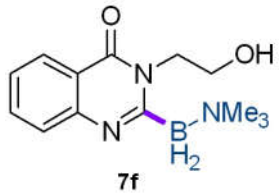
^{1}H NMR (400 MHz, $CDCl_3$)



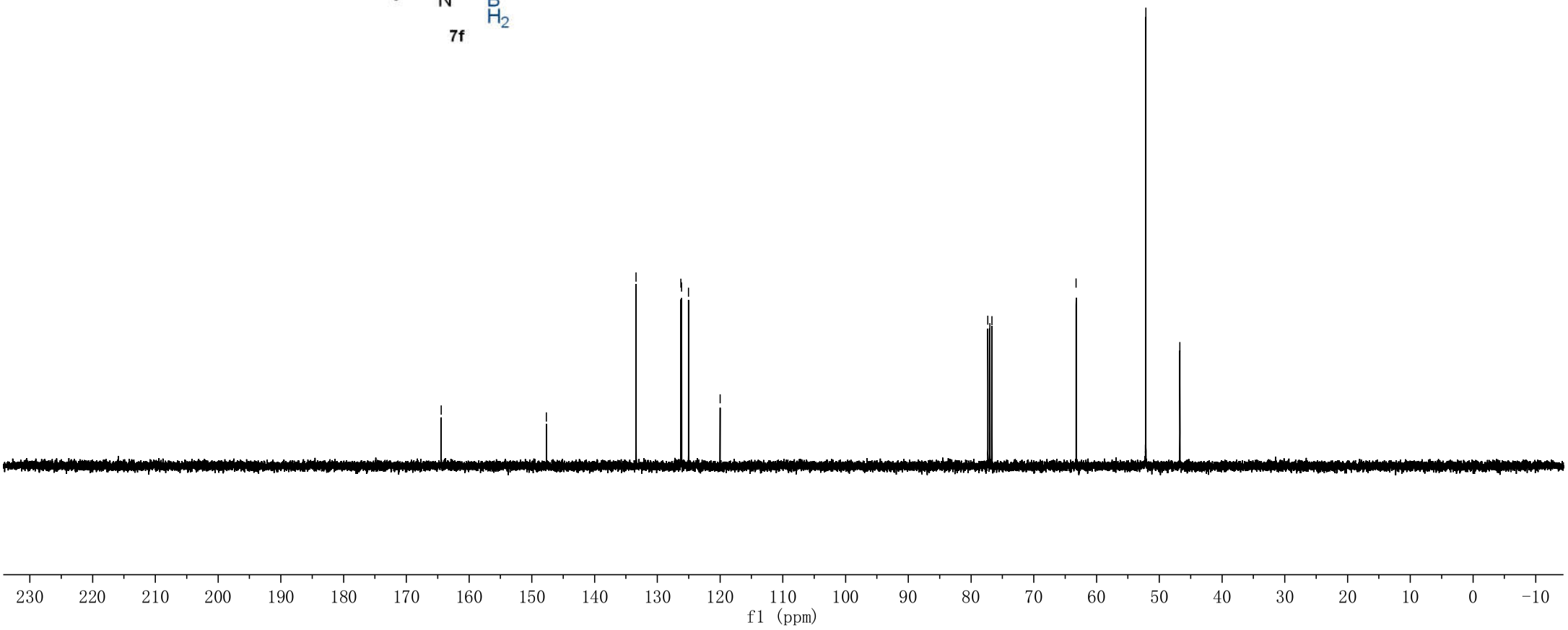
7f

164.46
147.67
133.39
126.24
126.12
125.02
120.00
77.32
77.00
76.68
63.25
52.16
46.72

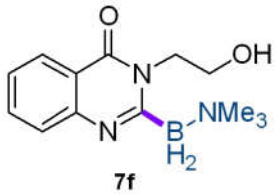
^{13}C NMR (101 MHz, $CDCl_3$)



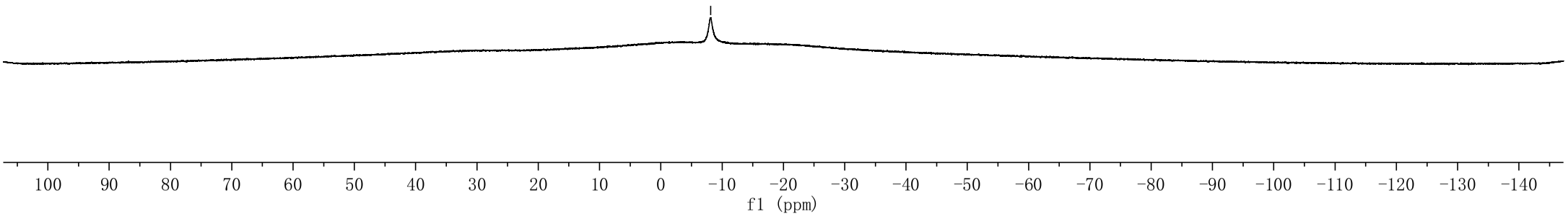
7f



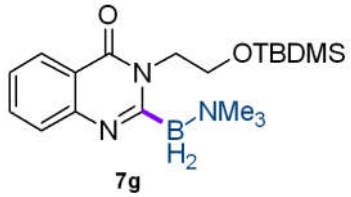
^{11}B NMR (128 MHz, $CDCl_3$)



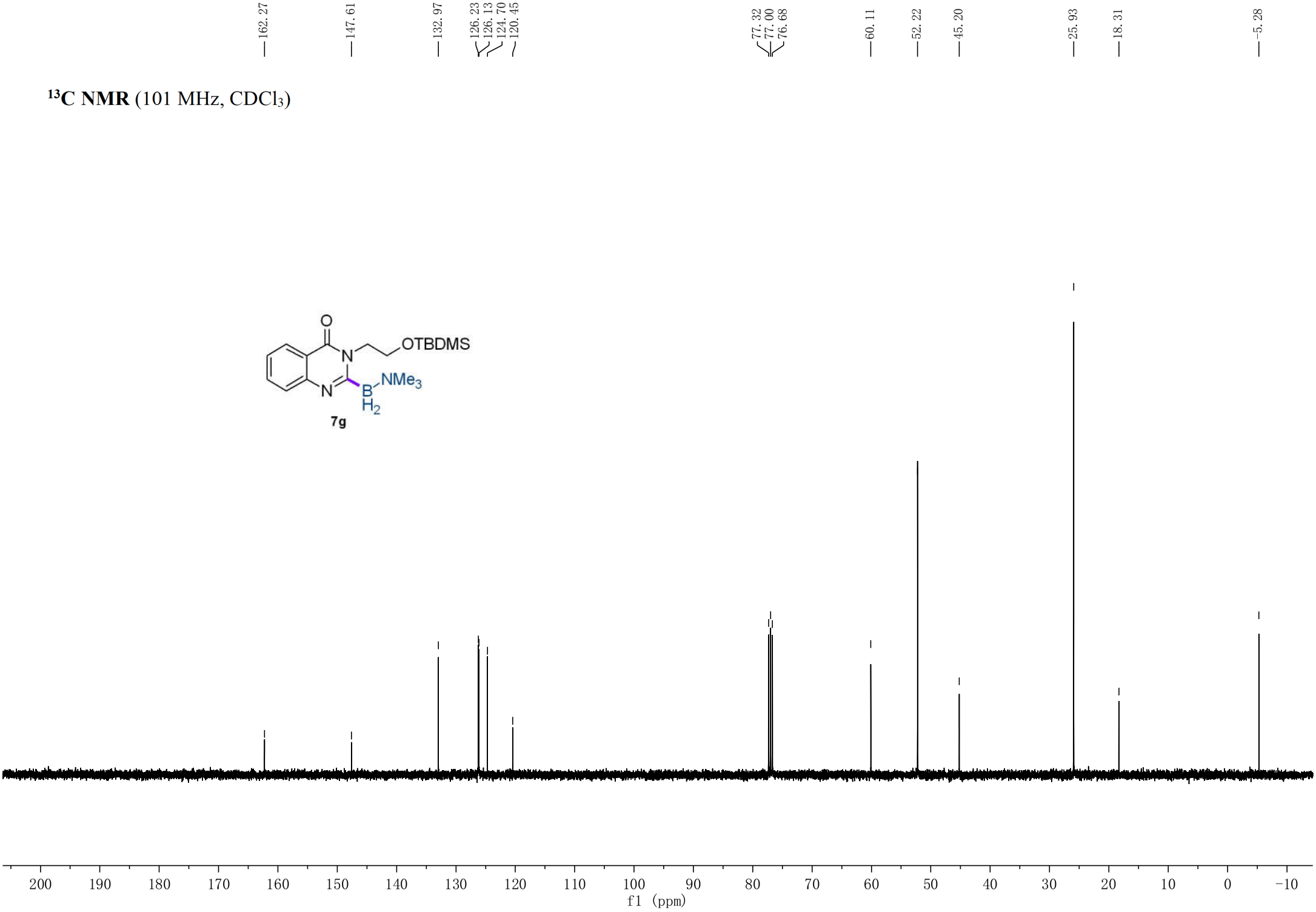
7f



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

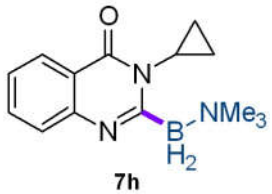


7g



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

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

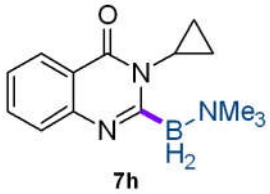


7h

f1 (ppm)

163.49
147.08
132.83
126.04
125.94
124.66
120.99
77.32
77.00
76.68
52.24
27.67
10.39

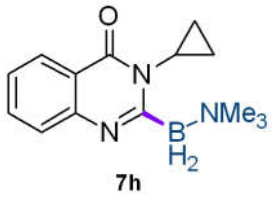
^{13}C NMR (101 MHz, $CDCl_3$)



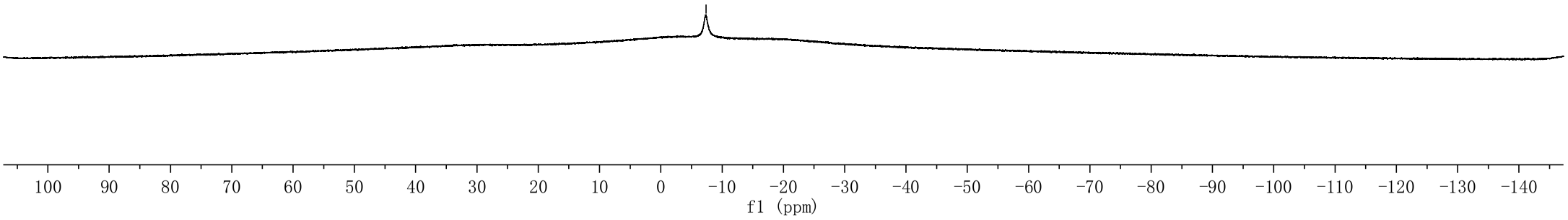
7h

—7.39

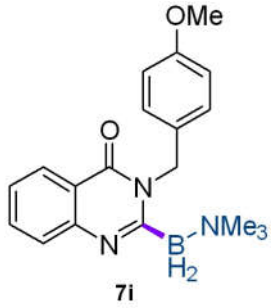
^{11}B NMR (128 MHz, $CDCl_3$)



7h

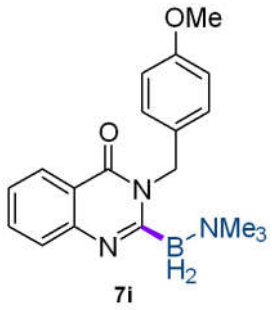


^{1}H NMR (400 MHz, $CDCl_3$)

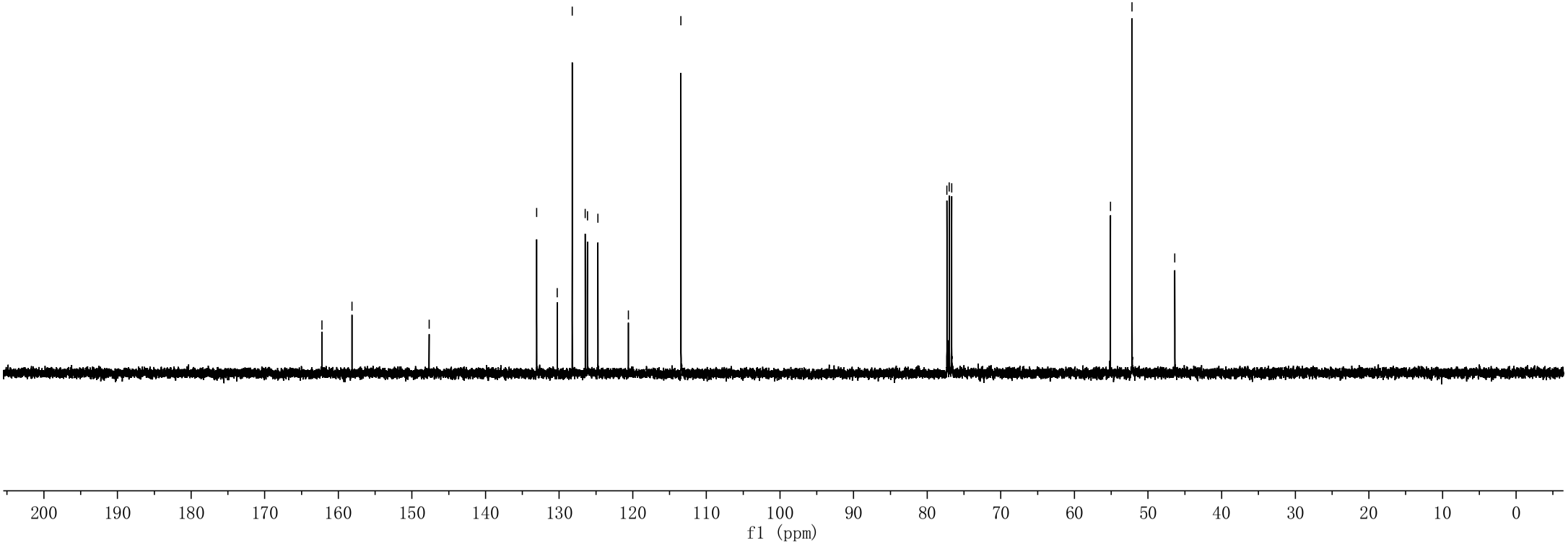


7i

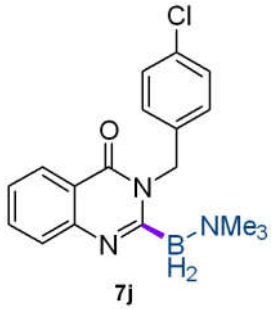
^{13}C NMR (101 MHz, $CDCl_3$)



7i



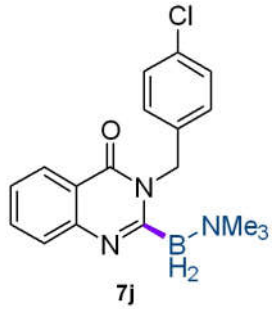
^{1}H NMR (400 MHz, $CDCl_3$)



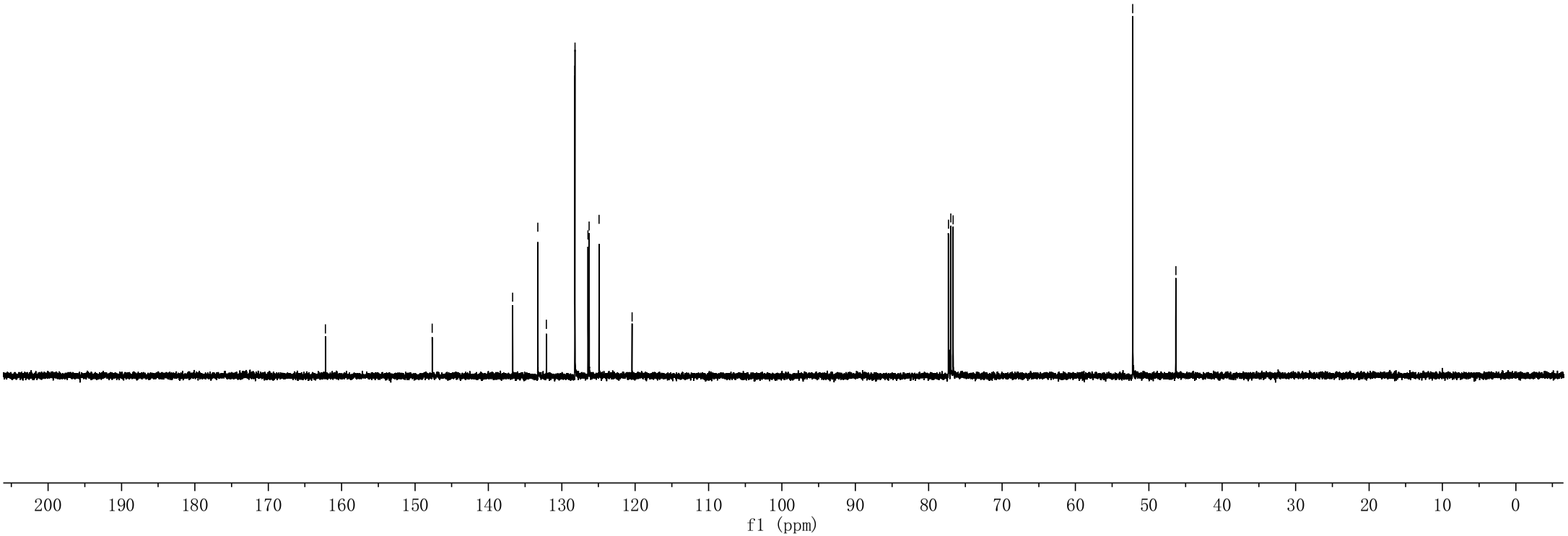
7j

162.20
147.65
136.68
133.26
132.10
128.23
128.20
126.43
126.26
124.93
120.43
77.32
77.00
76.68
52.19
46.33

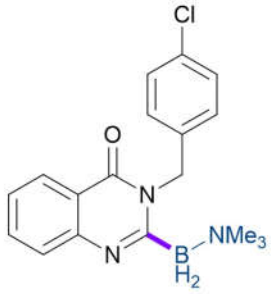
^{13}C NMR (101 MHz, $CDCl_3$)



7j

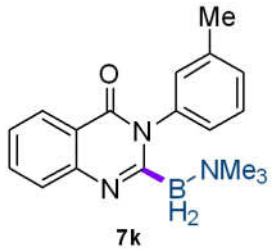


^{11}B NMR (128 MHz, $CDCl_3$)

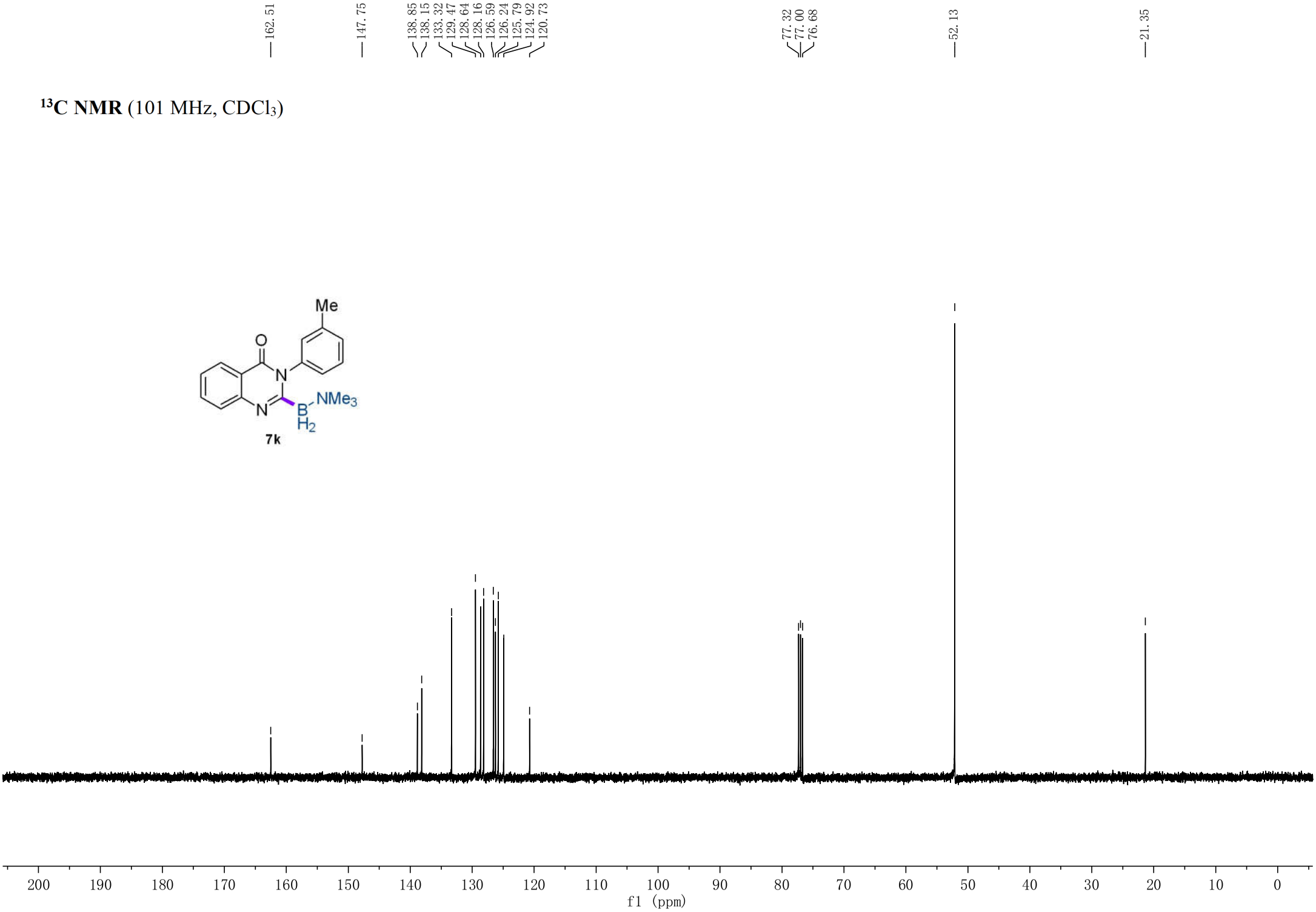


7j

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

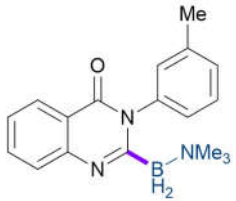


7k

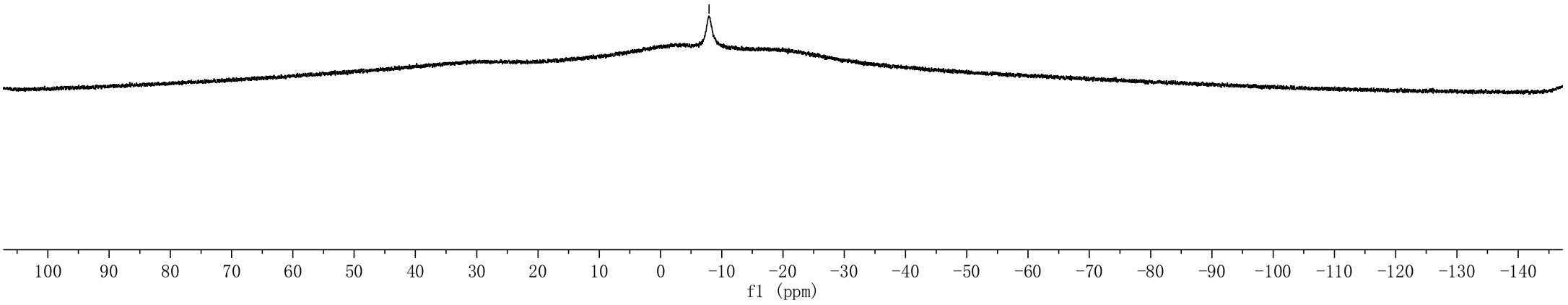


^{13}C NMR (101 MHz, $CDCl_3$)

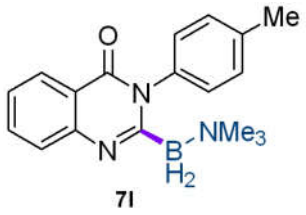
^{11}B NMR (128 MHz, $CDCl_3$)



7k

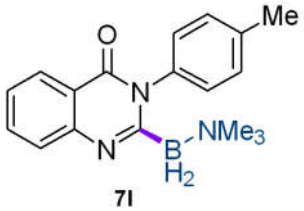


^{1}H NMR (400 MHz, $CDCl_3$)

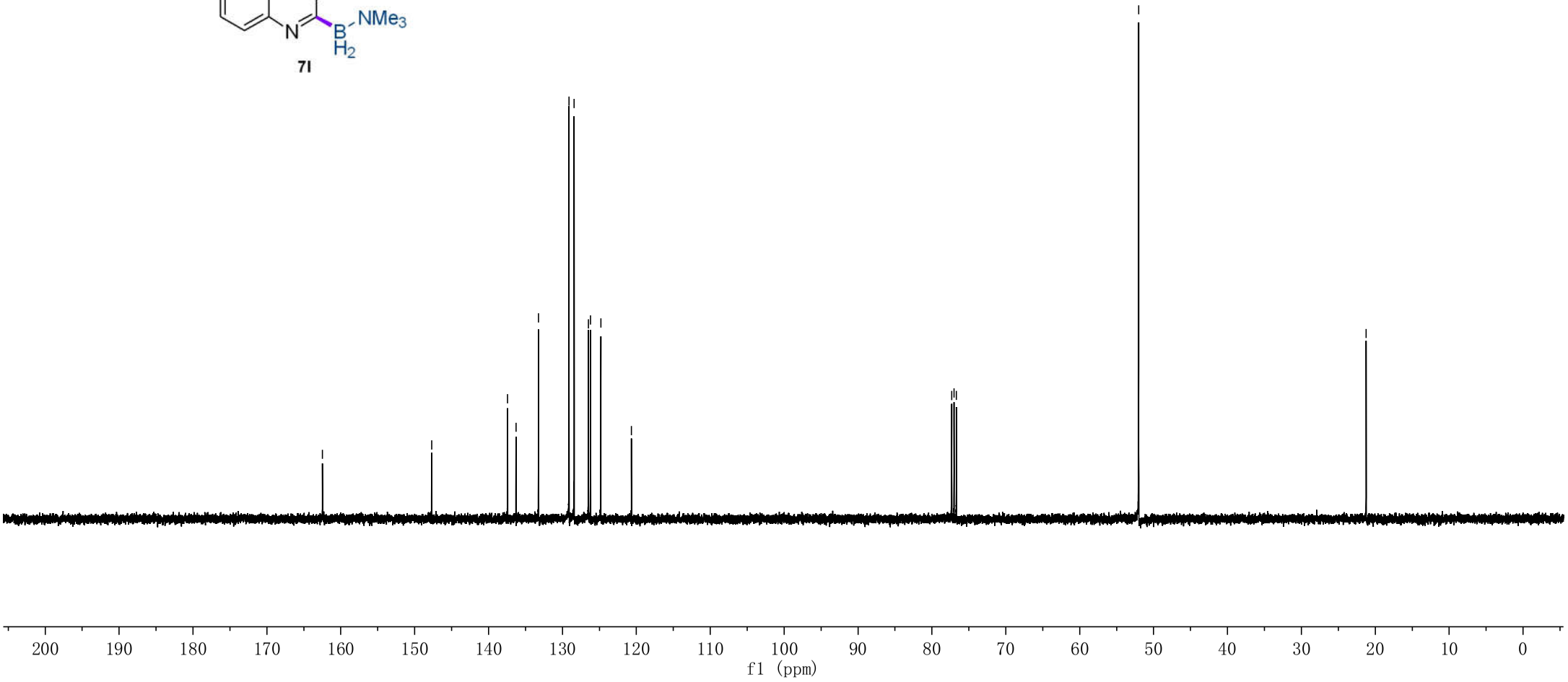


7l

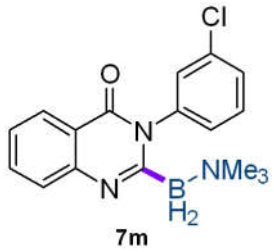
^{13}C NMR (101 MHz, $CDCl_3$)



7l

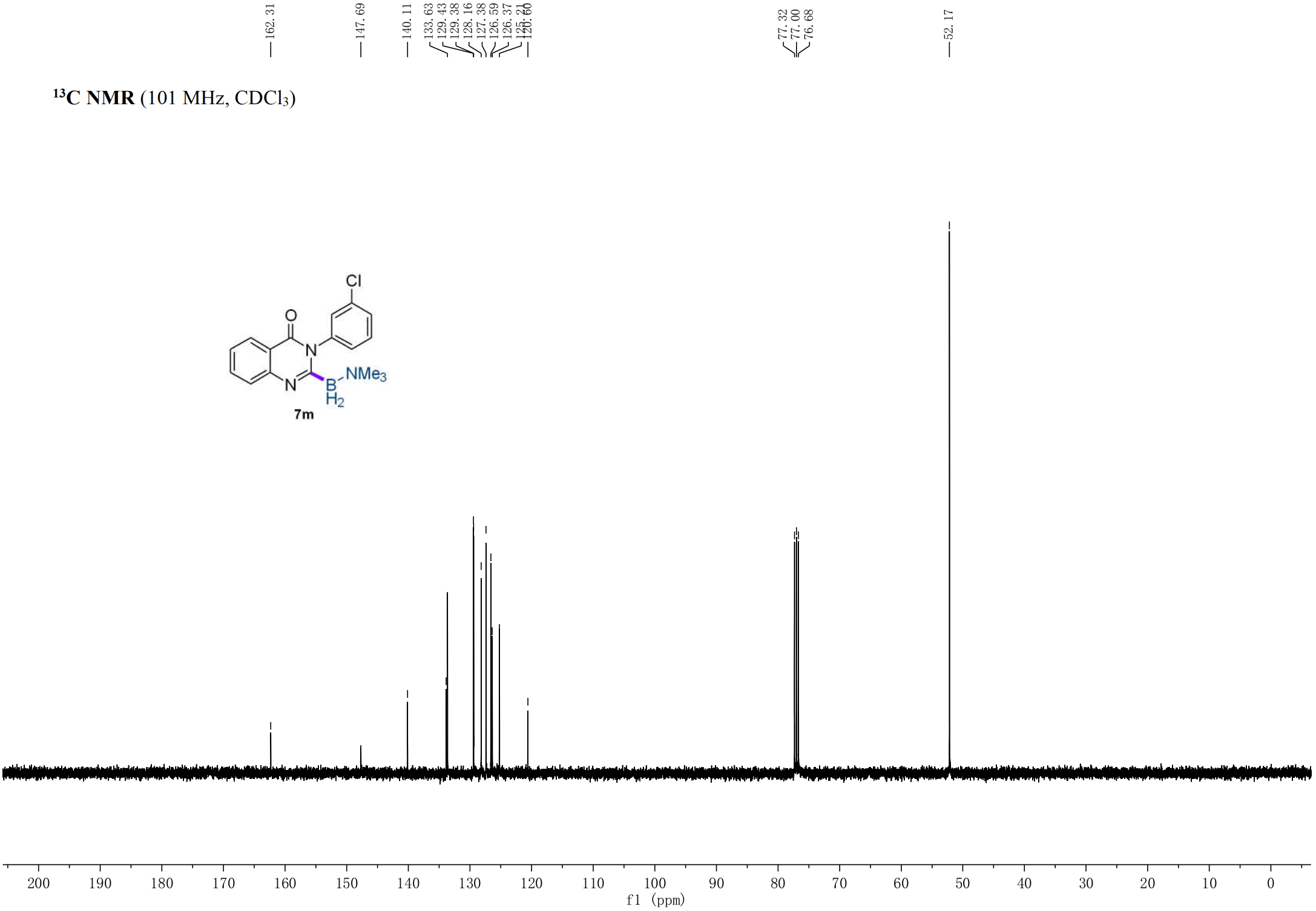


^{1}H NMR (400 MHz, $CDCl_3$)

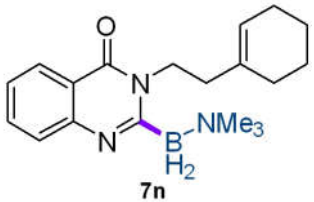


7m

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

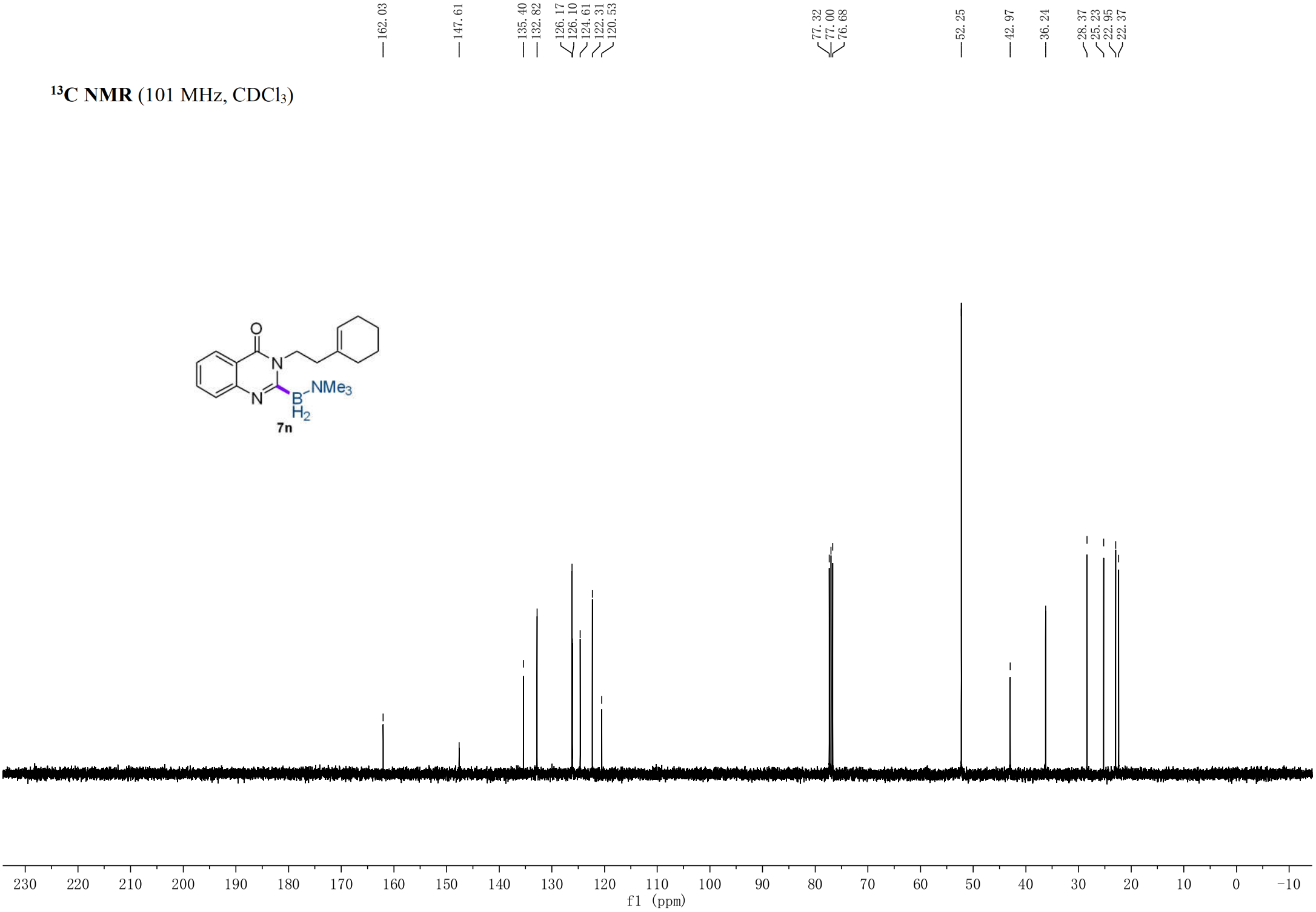


^{1}H NMR (400 MHz, $CDCl_3$)

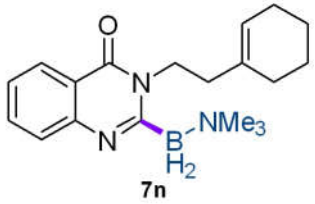


7n

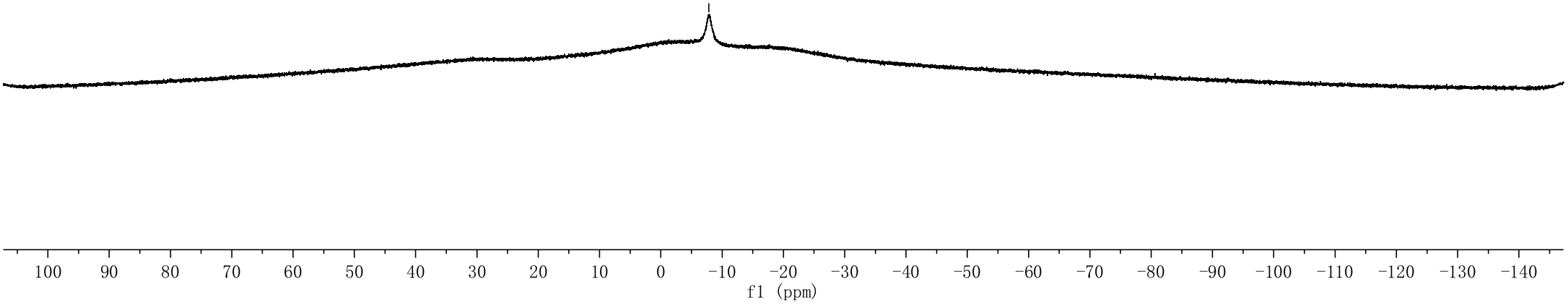
^{13}C NMR (101 MHz, $CDCl_3$)



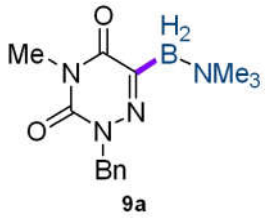
^{11}B NMR (128 MHz, $CDCl_3$)



7n



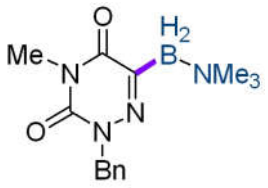
^{1}H NMR (400 MHz, $CDCl_3$)



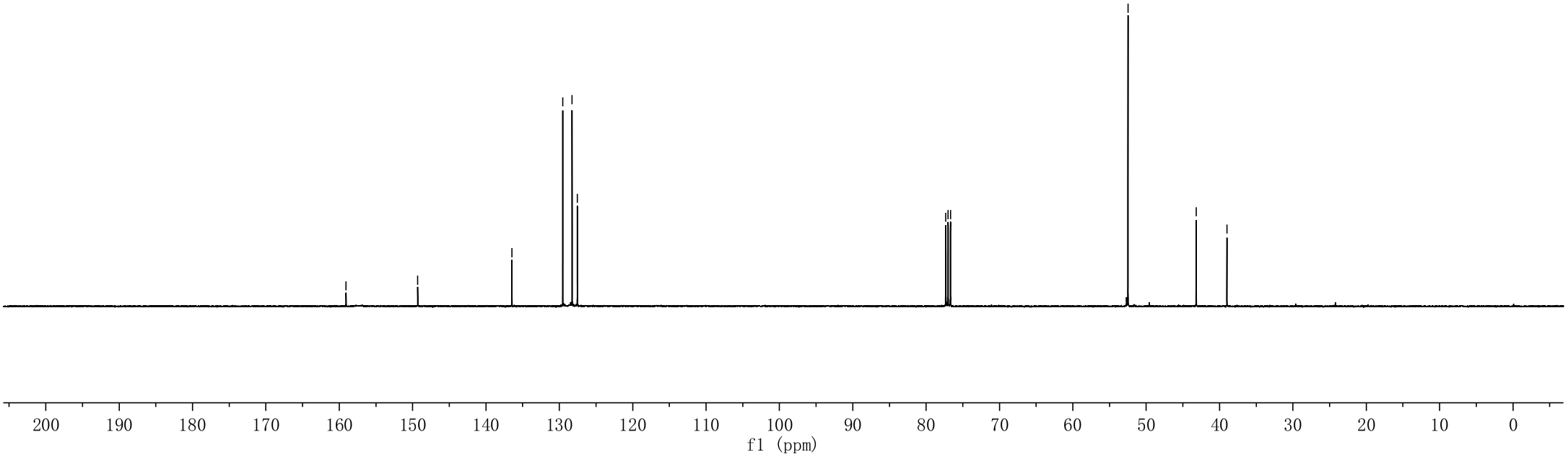
9a

159.07
149.30
136.46
129.53
128.26
127.54
77.32
77.00
76.68
52.49
43.18
38.99

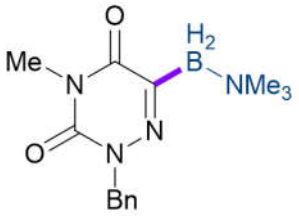
^{13}C NMR (101 MHz, $CDCl_3$)



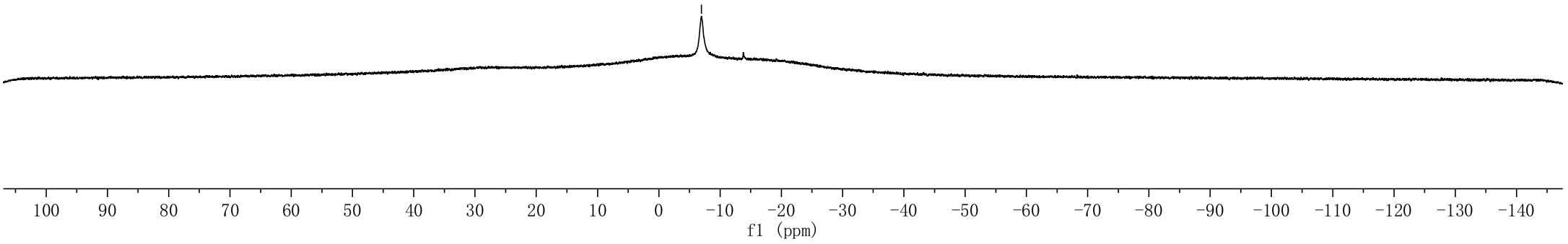
9a



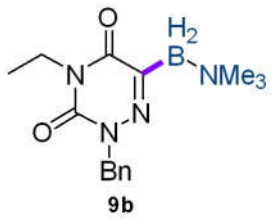
^{11}B NMR (128 MHz, $CDCl_3$)



9a



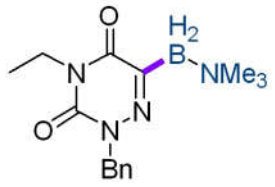
^{1}H NMR (400 MHz, $CDCl_3$)



9b

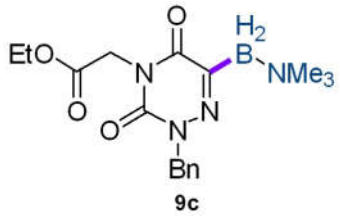
158.80
148.77
136.46
129.41
128.15
127.39
77.32
77.00
76.68
52.32
45.97
43.04
13.65

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



9b

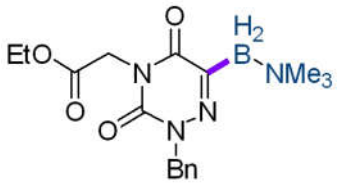
^{1}H NMR (400 MHz, $CDCl_3$)



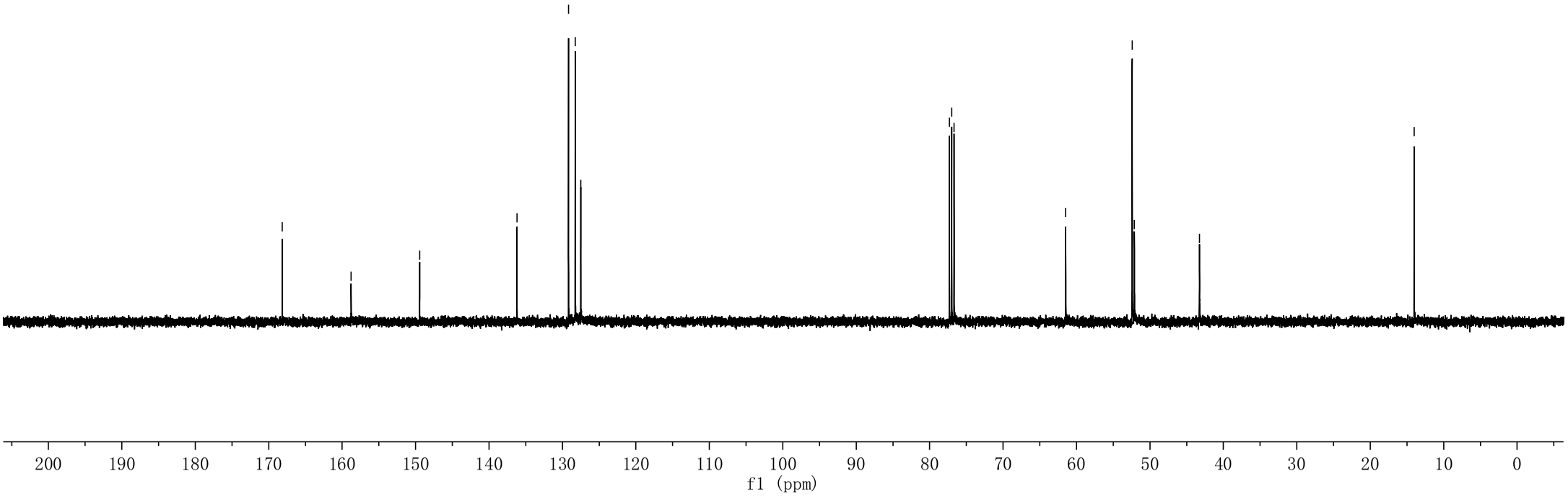
9c

168.17
158.78
149.45
136.19
129.17
128.26
127.51
77.32
77.00
76.68
61.47
52.43
52.12
43.26
14.02

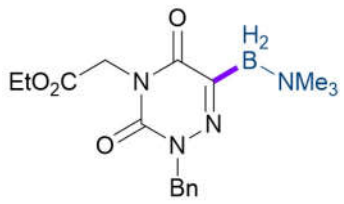
^{13}C NMR (101 MHz, $CDCl_3$)



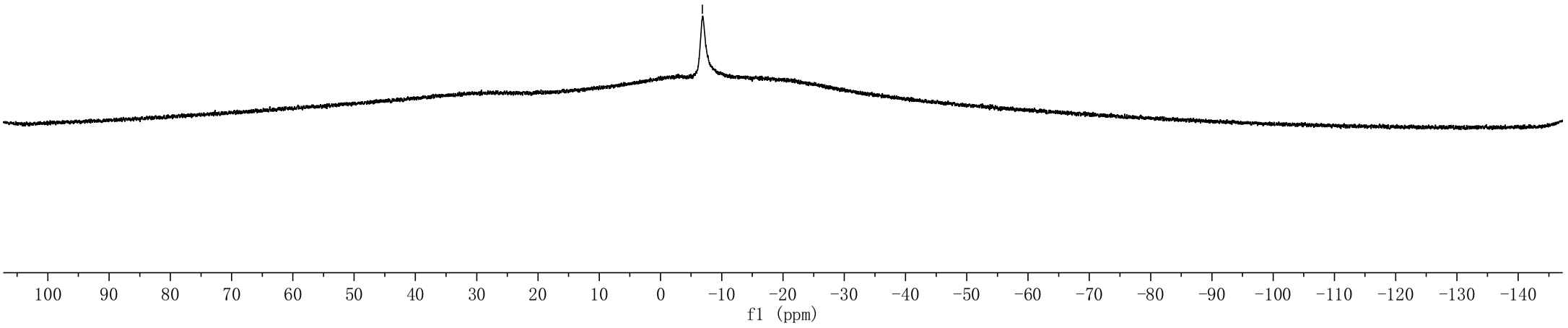
9c



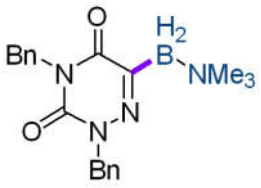
^{11}B NMR (128 MHz, $CDCl_3$)



9c



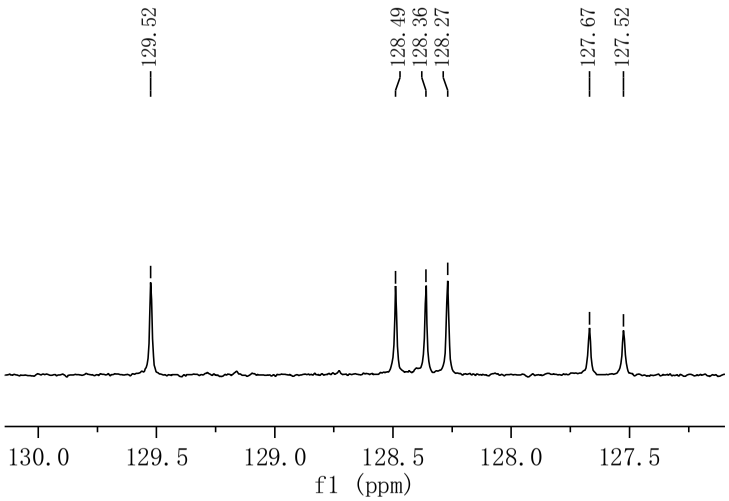
^{1}H NMR (400 MHz, $CDCl_3$)

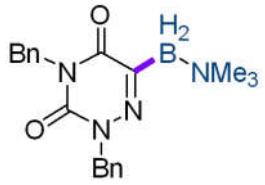


9d

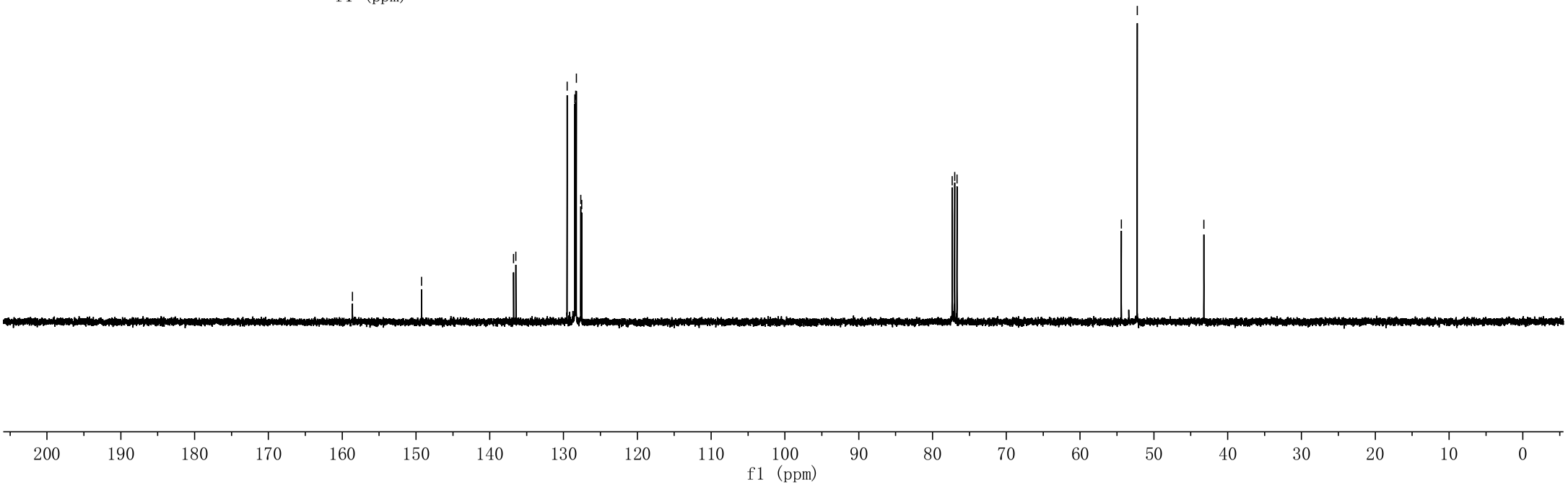
158.61
149.24
136.77
136.46
129.52
128.49
128.36
128.27
127.67
127.52
77.32
77.00
76.68
54.41
52.26
43.23

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

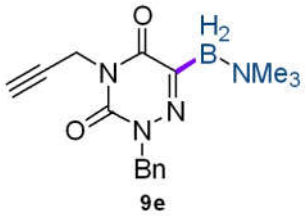




9d



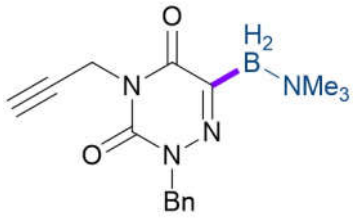
^{1}H NMR (400 MHz, $CDCl_3$)



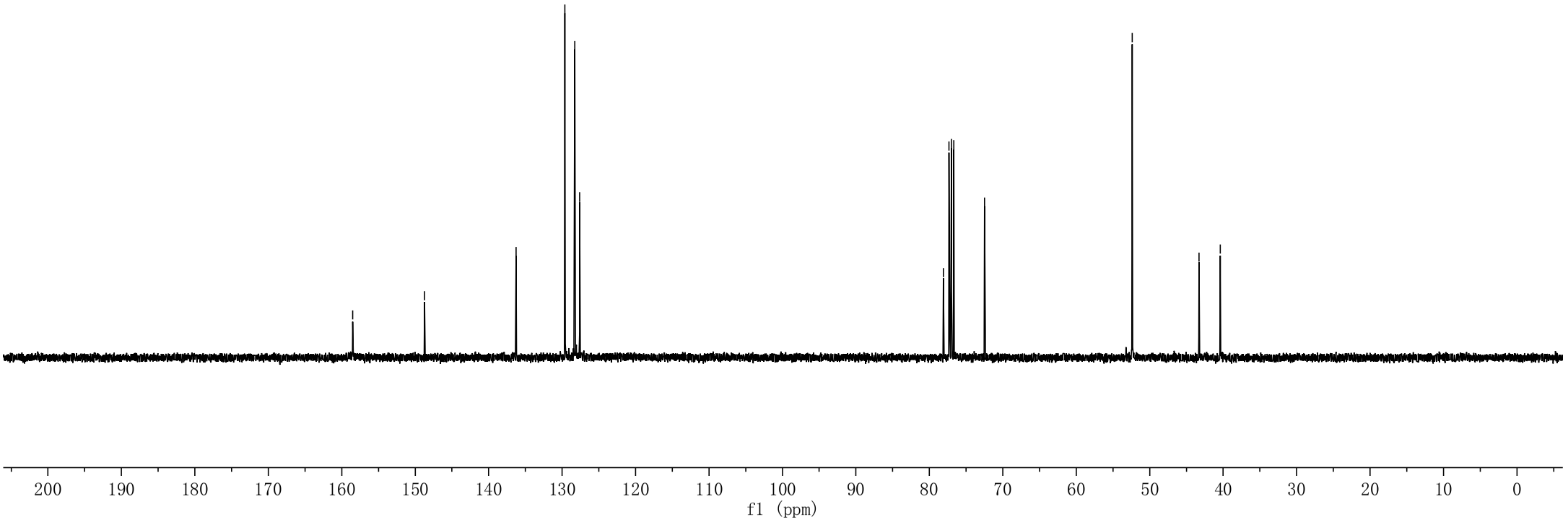
9e

158.51
148.73
136.27
129.61
128.27
127.60
78.09
77.32
77.00
76.68
72.48
52.39
43.28
40.38

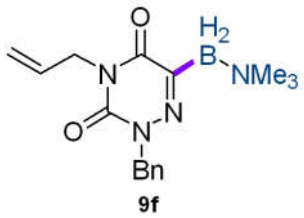
^{13}C NMR (101 MHz, $CDCl_3$)



9e



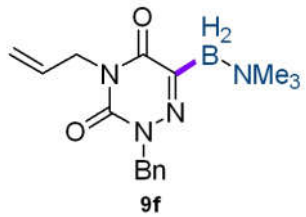
^{1}H NMR (400 MHz, $CDCl_3$)



9f

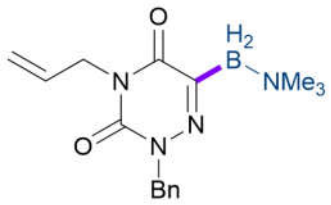
158.71
149.00
136.47
132.62
129.53
128.25
127.51
117.79
77.32
77.00
76.68
53.26
52.36
43.18

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



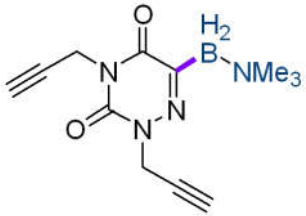
9f

^{11}B NMR (128 MHz, $CDCl_3$)



9f

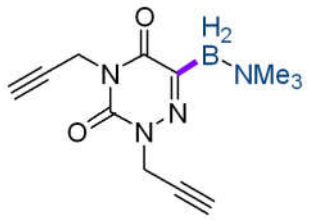
^{1}H NMR (400 MHz, $CDCl_3$)



9g

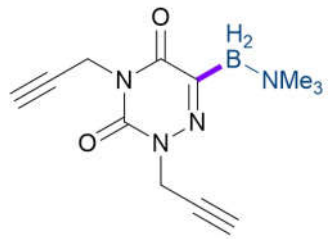
157.50
147.90
77.91
77.46
77.32
77.00
76.68
72.60
70.86
52.40
40.26
29.03

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

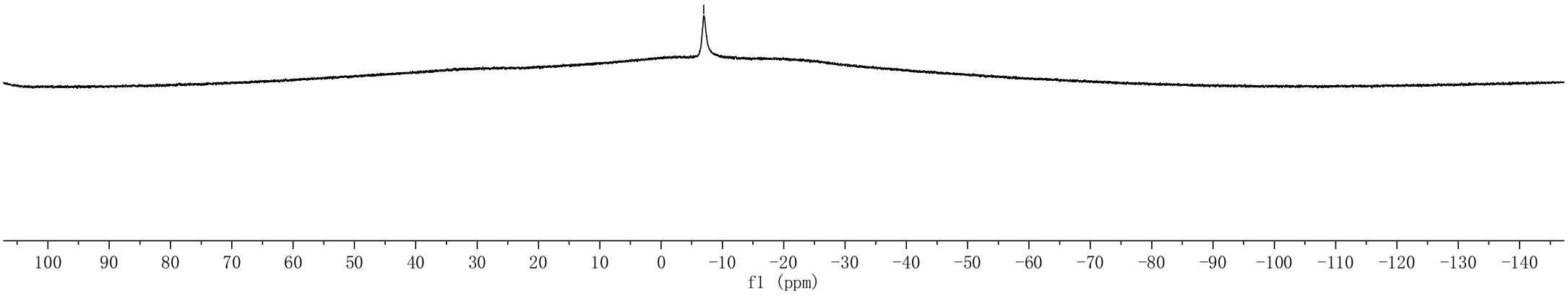


9g

^{11}B NMR (128 MHz, $CDCl_3$)



9g



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

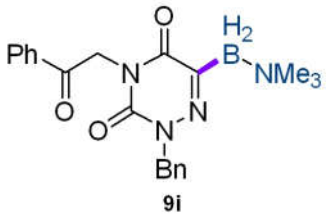
9h

158.36
148.64
132.50
131.06
118.21
117.63
77.32
77.00
76.68
53.05
52.28
41.89

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

9h

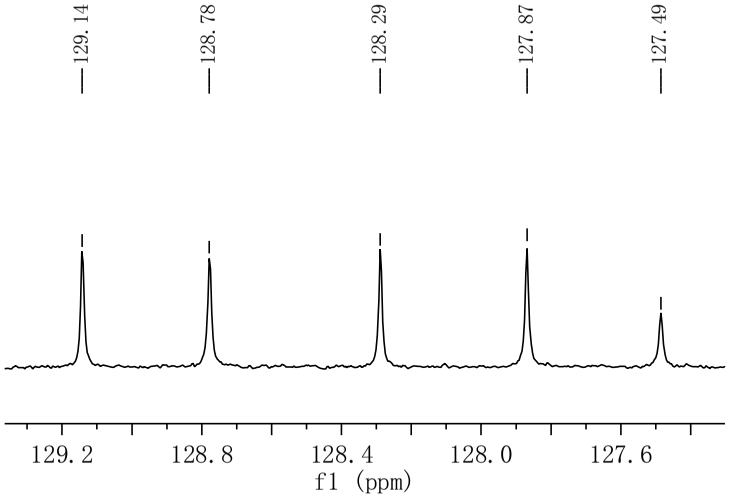
^{1}H NMR (400 MHz, $CDCl_3$)

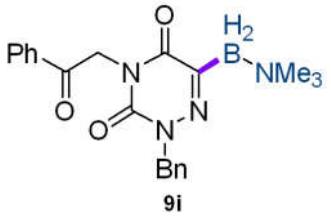


9i

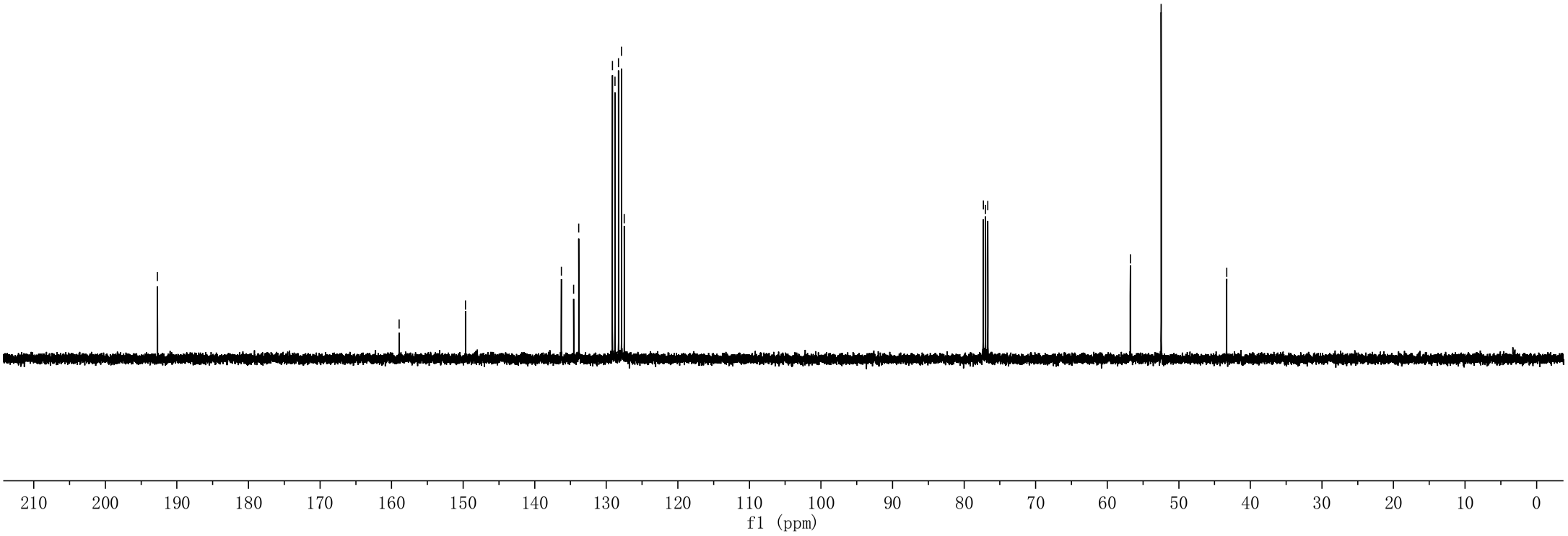
192.72
158.93
149.68
136.29
134.56
133.84
129.14
128.78
128.29
127.87
127.49
77.32
77.00
76.68
56.78
52.46
43.32

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



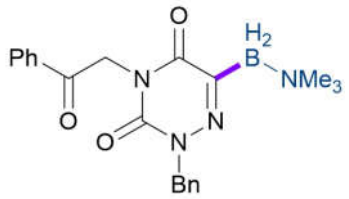


9i

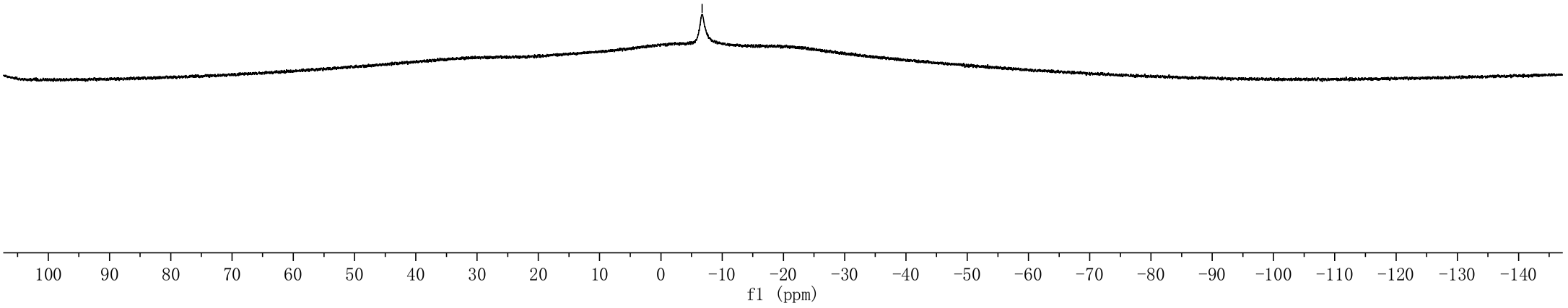


—6.72

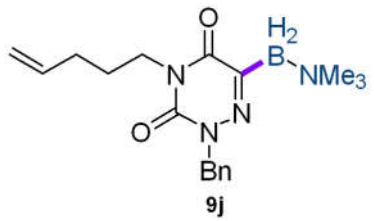
^{11}B NMR (128 MHz, $CDCl_3$)



9i



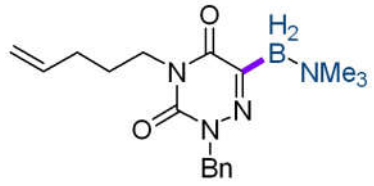
^{1}H NMR (400 MHz, $CDCl_3$)



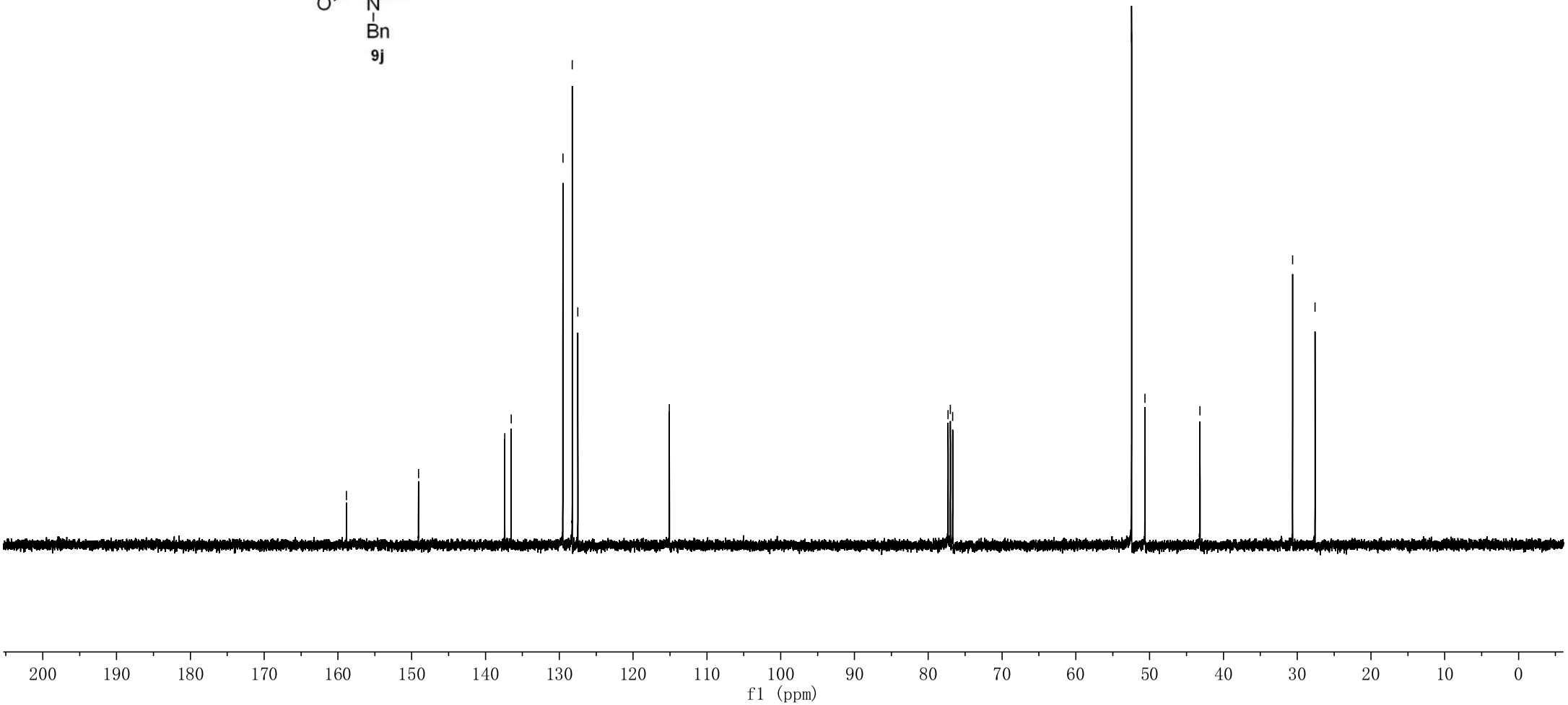
9j

158.84
149.08
137.40
136.52
129.51
128.24
127.49
115.09
77.32
77.00
76.68
52.44
50.63
43.18
30.63
27.58

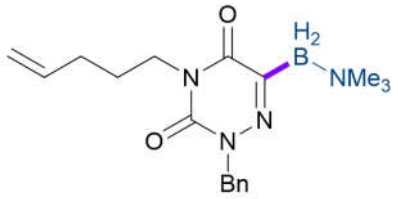
^{13}C NMR (101 MHz, $CDCl_3$)



9j

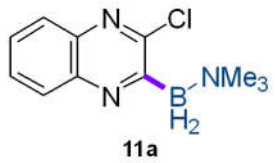


^{11}B NMR (128 MHz, $CDCl_3$)



9j

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



11a

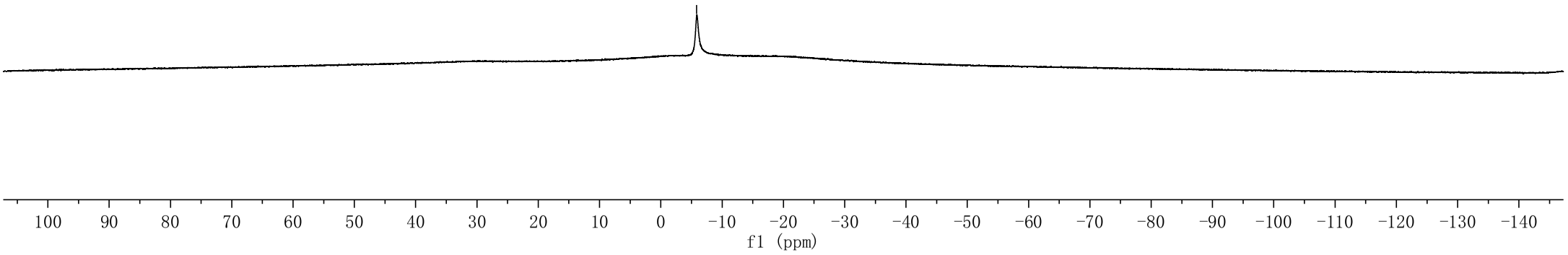
^{13}C NMR (101 MHz, $CDCl_3$)

11a

-5.81

^{11}B NMR (128 MHz, $CDCl_3$)

11a



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

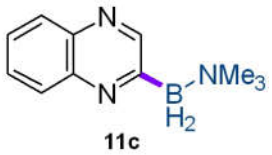
11b

158.13
140.75
139.37
128.17
128.15
127.04
126.98
77.32
77.00
76.68
52.14
23.59

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

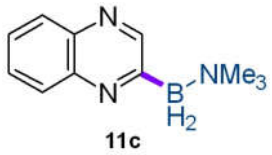
11b

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



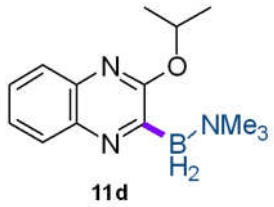
11c

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



11c

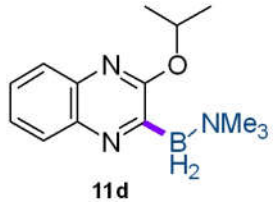
^{1}H NMR (400 MHz, $CDCl_3$)



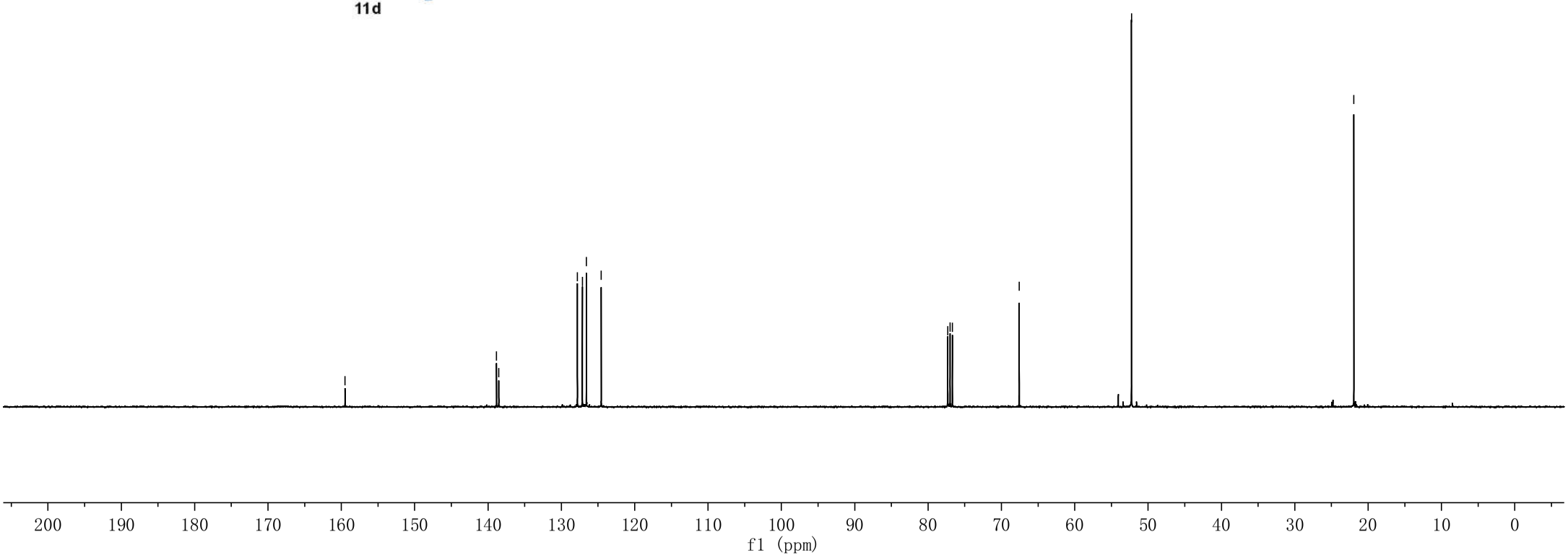
11d

159.49
138.84
138.53
127.81
127.13
126.58
124.56
77.32
77.00
76.68
67.57
52.27
21.94

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

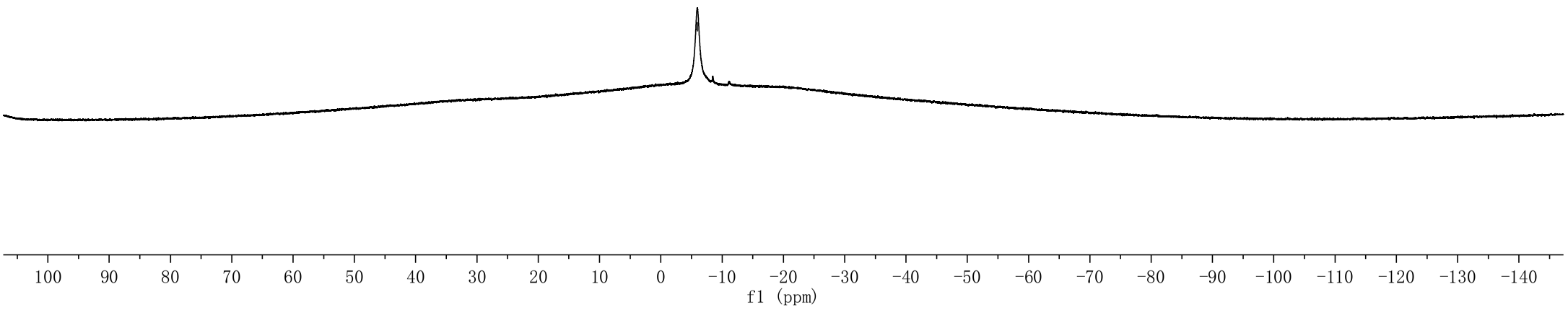


11d



^{11}B NMR (128 MHz, $CDCl_3$)

11d

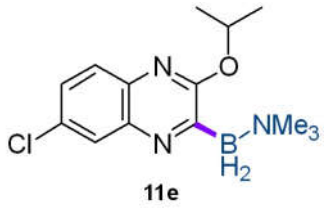


^{1}H NMR (400 MHz, $CDCl_3$)

11e

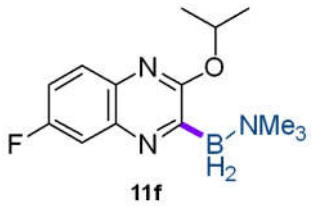
159.57
138.69
137.41
129.59
127.80
127.59
126.91
77.32
77.00
76.68
67.91
52.25
21.92

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



11e

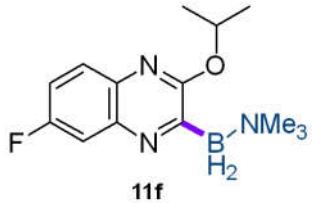
^{1}H NMR (400 MHz, $CDCl_3$)



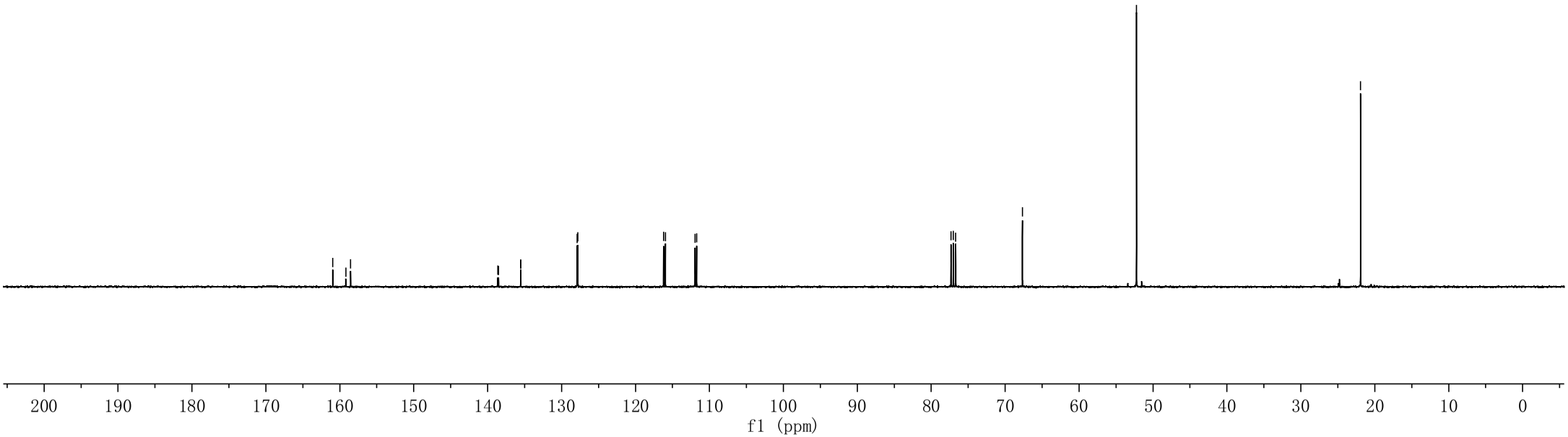
11f

160.96
159.17
158.54
138.64
138.52
135.53
135.52
127.91
127.81
116.21
115.96
111.95
111.74
77.32
77.00
76.68
67.67
52.24
21.92

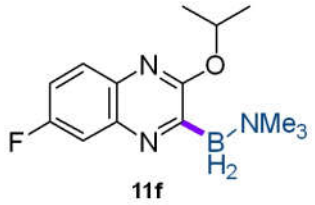
^{13}C NMR (101 MHz, $CDCl_3$)



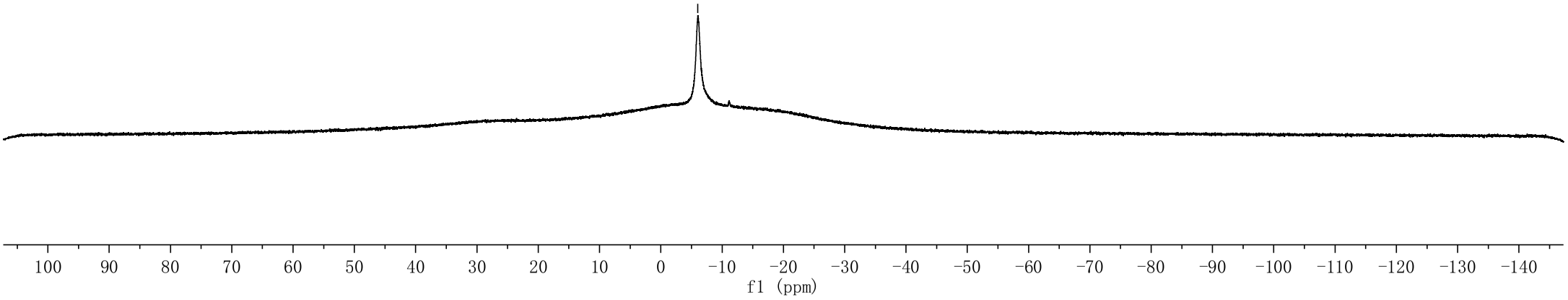
11f



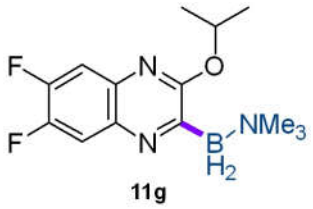
^{11}B NMR (128 MHz, $CDCl_3$)



11f

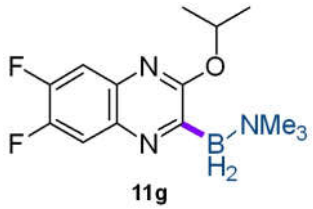


^{1}H NMR (400 MHz, $CDCl_3$)



11g

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



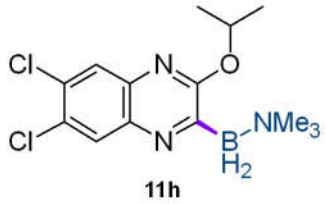
11g

159.74
159.72
151.59
149.77
149.62
149.12
147.32
147.17
135.72
135.70
135.61
135.60
134.95
134.86
113.87
113.72
113.71
112.64
112.63
112.47
112.46
77.32
77.00
76.68
67.99
52.26
21.87

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

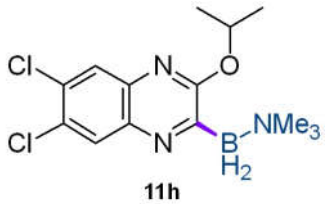
^{1}H NMR (400 MHz, $CDCl_3$)



11h

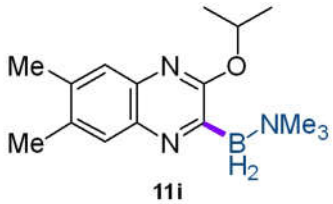
159.88
138.05
137.23
130.57
128.46
127.87
127.38
77.32
77.00
76.68
68.26
52.20
21.82

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



11h

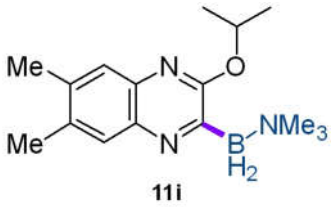
^{1}H NMR (400 MHz, $CDCl_3$)



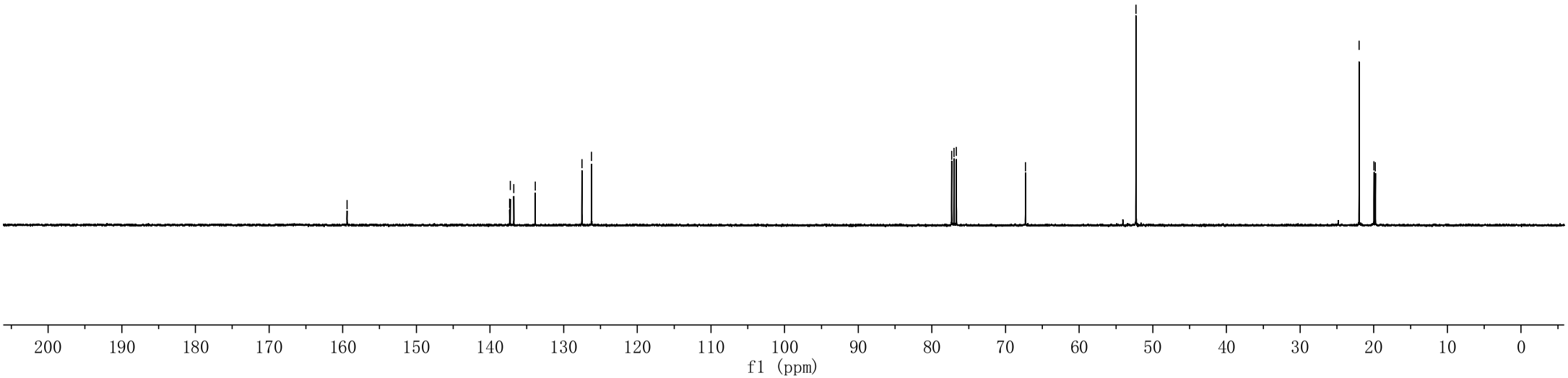
11i

159.41
137.33
137.25
136.77
133.86
127.52
126.21
77.32
77.00
76.68
67.29
52.28
21.98
19.97
19.78

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



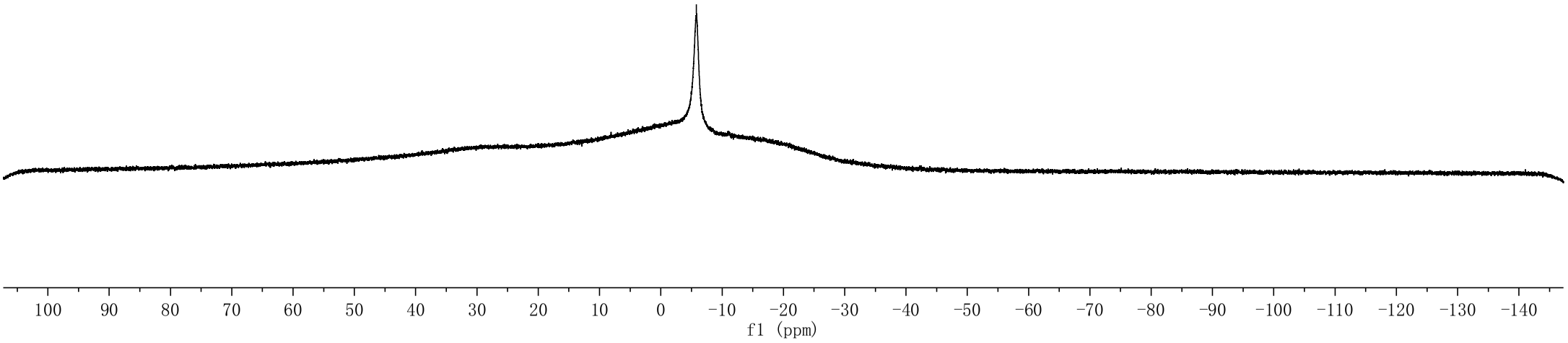
11i



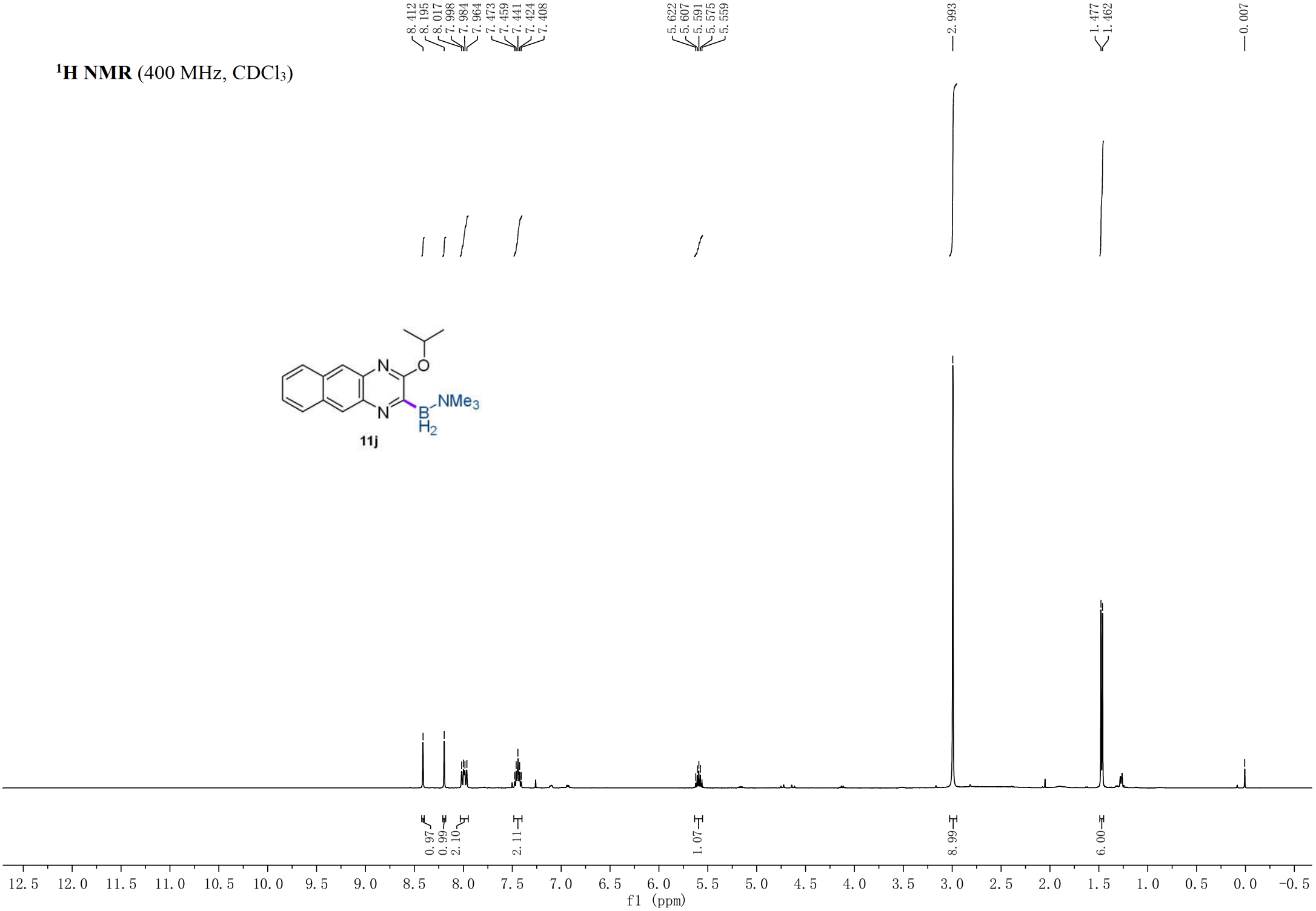
—5.80

^{11}B NMR (128 MHz, $CDCl_3$)

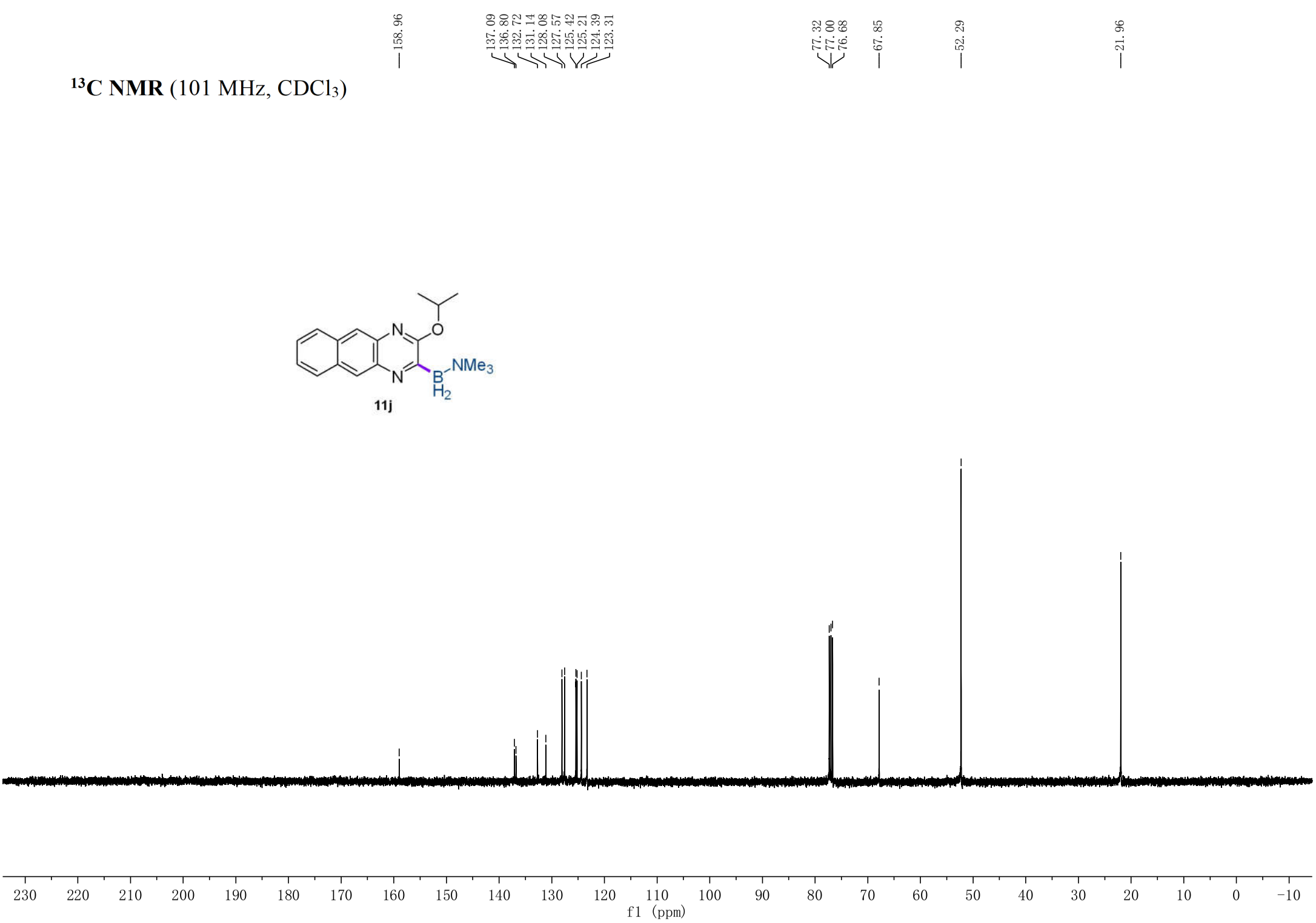
11i



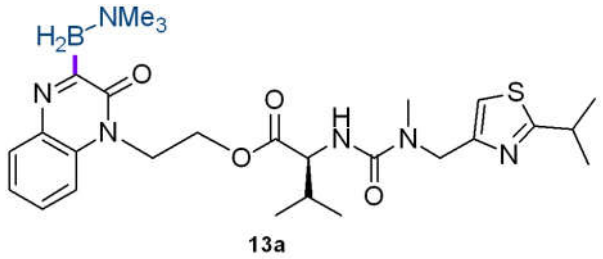
^{1}H NMR (400 MHz, $CDCl_3$)



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



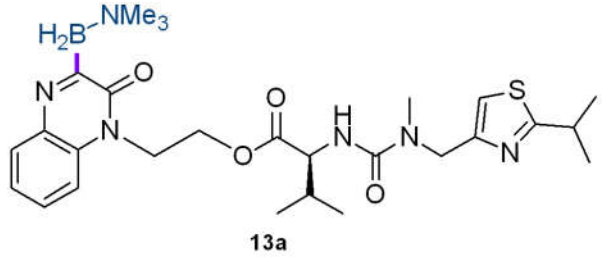
^{1}H NMR (400 MHz, $CDCl_3$)



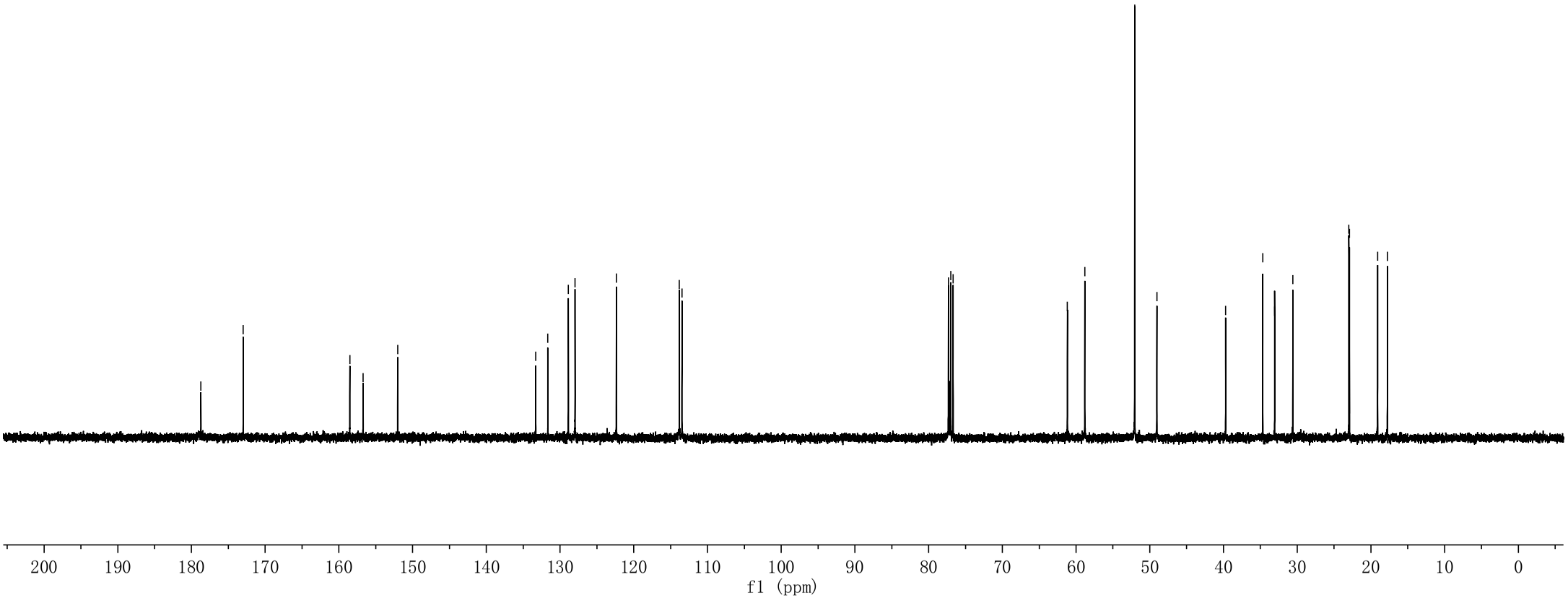
13a

178.72
172.98
158.52
156.71
152.03
133.30
131.66
128.87
127.97
122.36
113.82
113.46
77.32
77.00
76.68
61.18
58.81
52.04
49.03
39.71
34.67
33.06
30.59
22.99
22.90
19.09
17.76

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

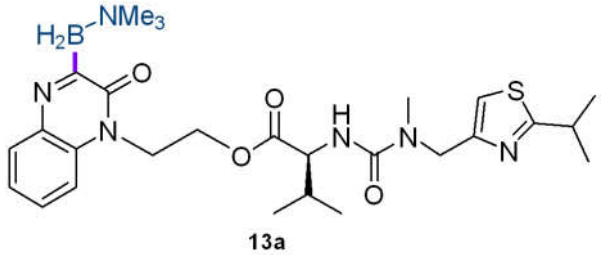


13a

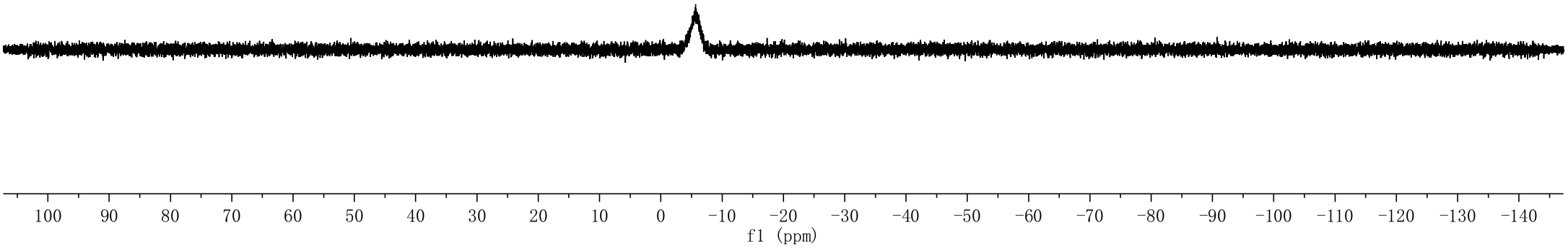


—5.68

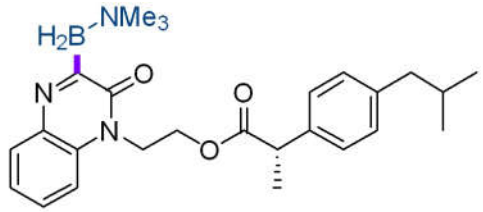
^{11}B NMR (128 MHz, $CDCl_3$)



13a



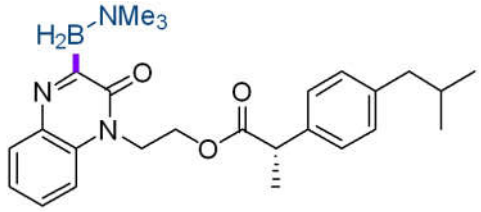
^{1}H NMR (400 MHz, $CDCl_3$)



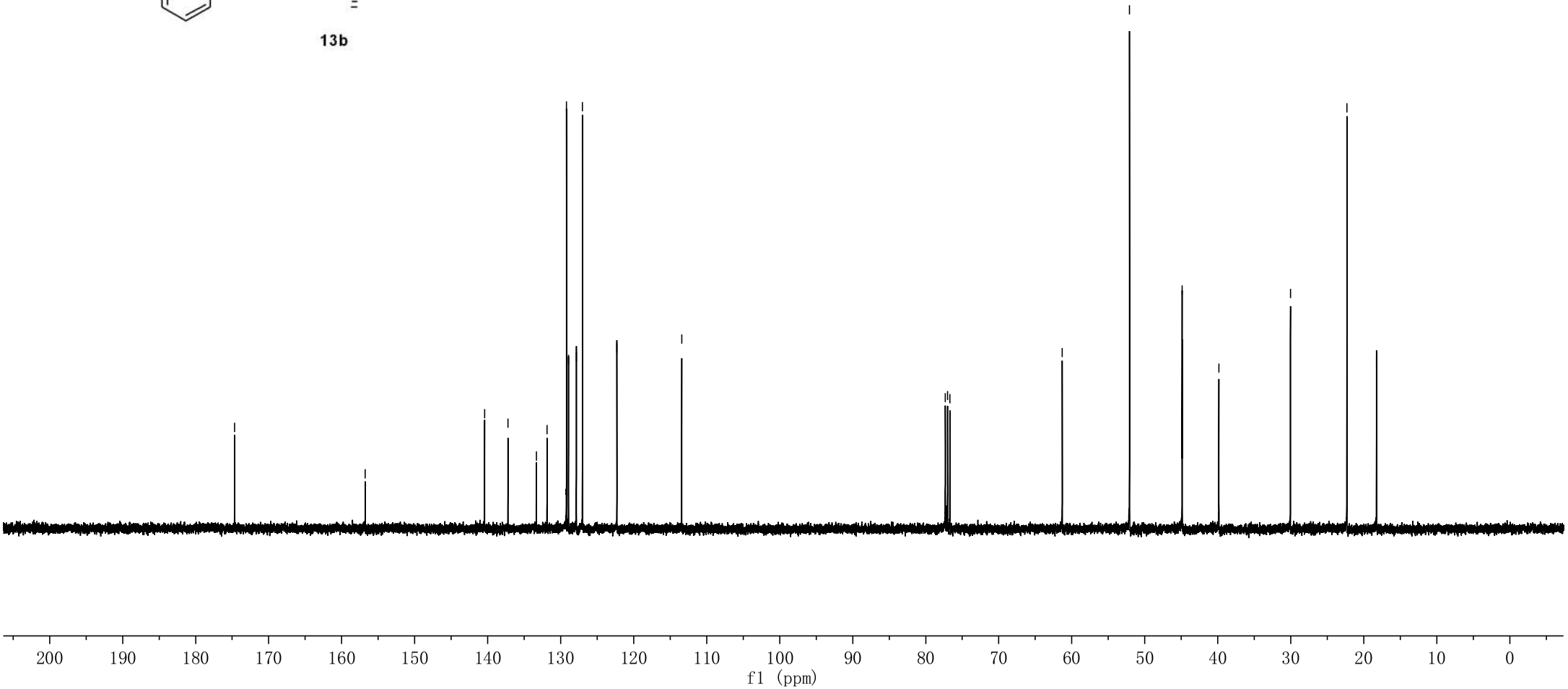
13b

174.66
156.77
140.42
137.22
133.34
131.87
129.20
128.93
127.85
127.02
122.30
113.42
77.32
77.00
76.68
61.30
52.08
44.89
44.86
39.85
30.05
22.31
18.26

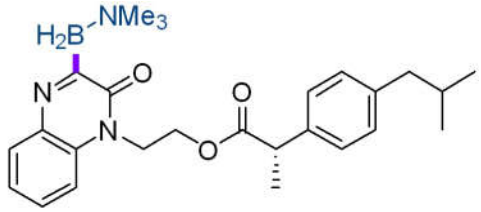
^{13}C NMR (101 MHz, $CDCl_3$)



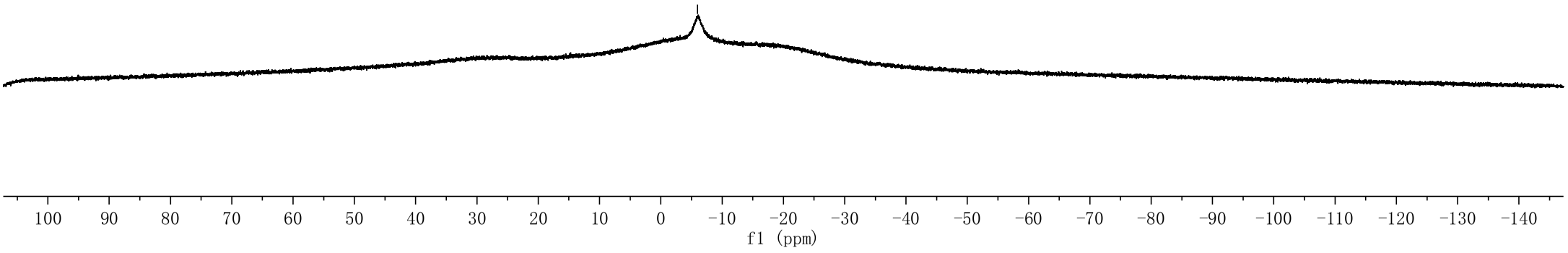
13b



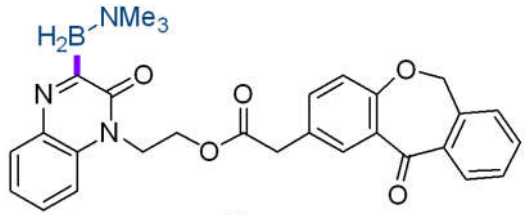
^{11}B NMR (128 MHz, $CDCl_3$)



13b



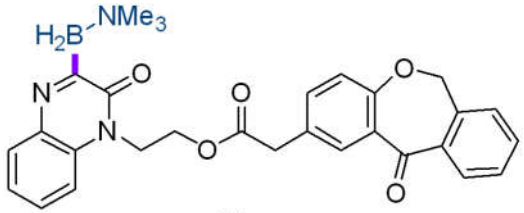
^{1}H NMR (400 MHz, $CDCl_3$)



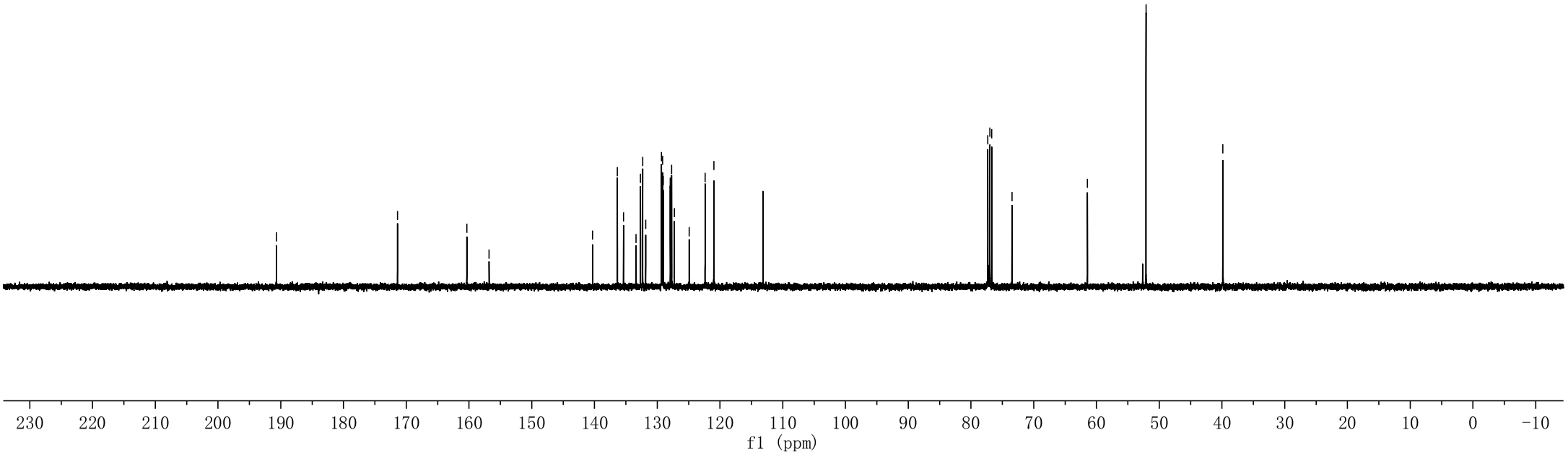
13c

190.69
171.40
160.34
156.80
140.30
136.35
135.38
133.36
132.67
132.33
131.84
129.33
129.13
129.04
127.93
127.70
127.28
124.91
122.38
120.97
113.15
77.32
77.00
76.68
73.46
61.44
52.11
39.85

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

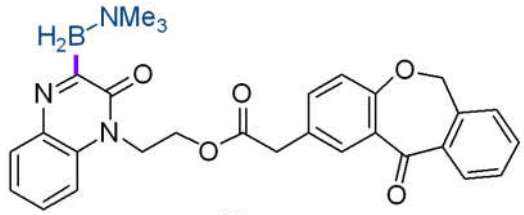


13c

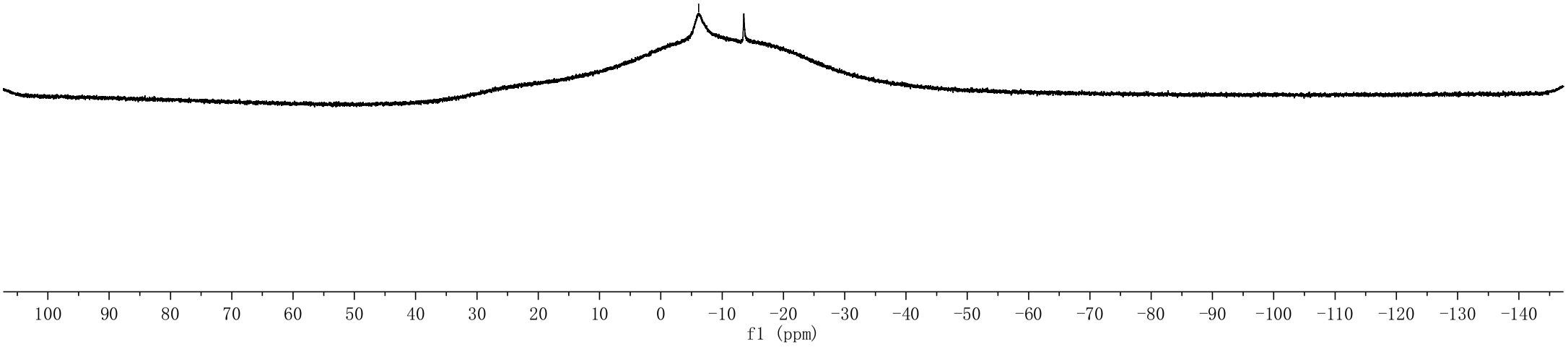


—6.16

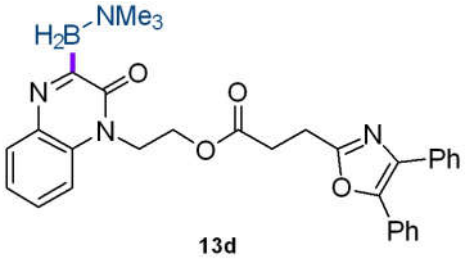
^{11}B NMR (128 MHz, $CDCl_3$)



13c

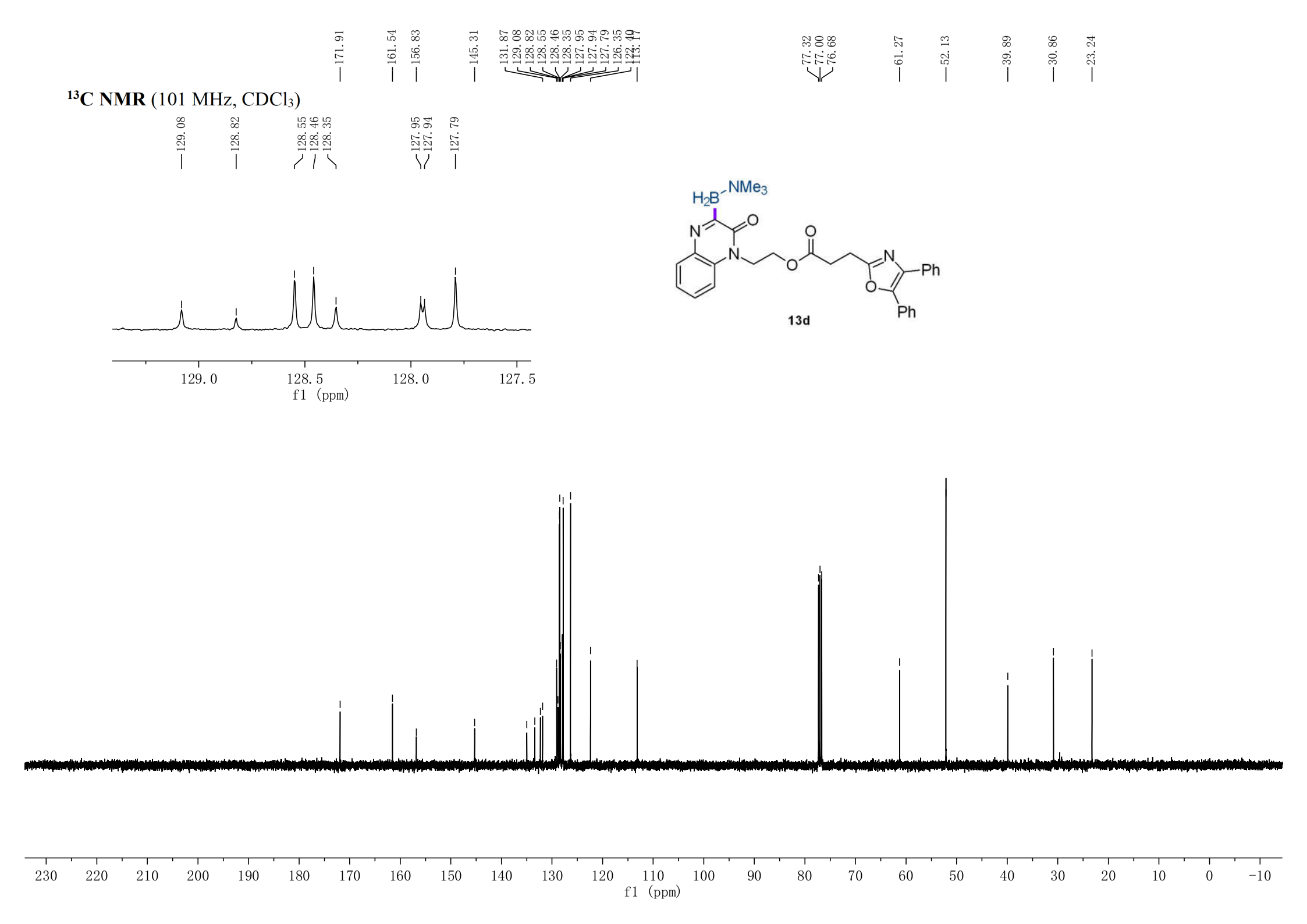


^{1}H NMR (400 MHz, $CDCl_3$)



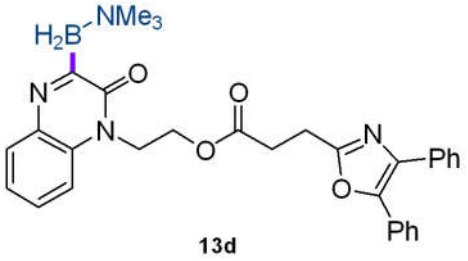
13d

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

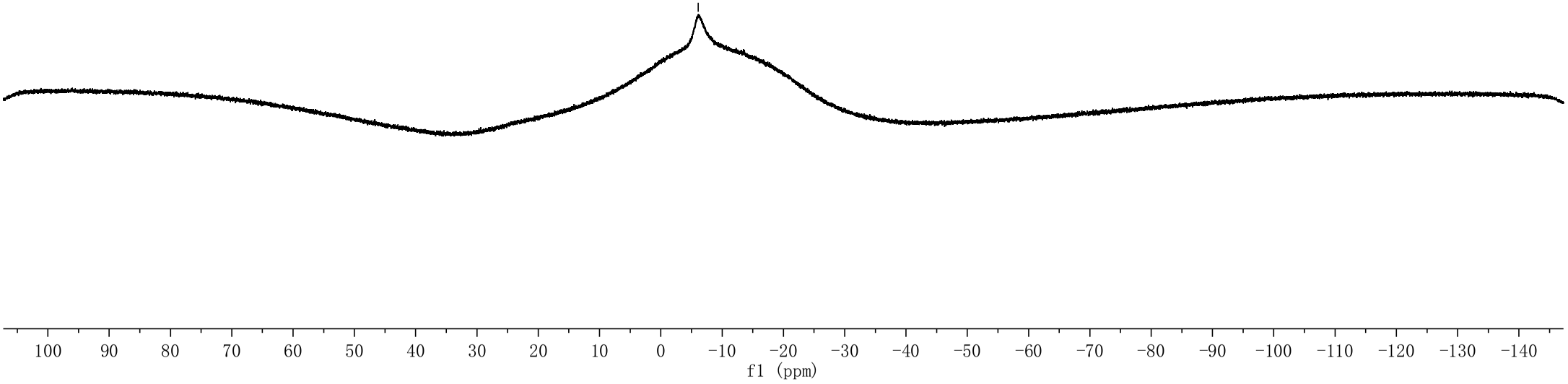


—6.10

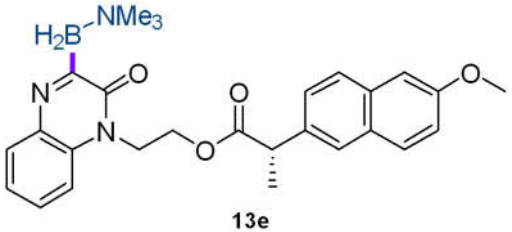
^{11}B NMR (128 MHz, $CDCl_3$)



13d

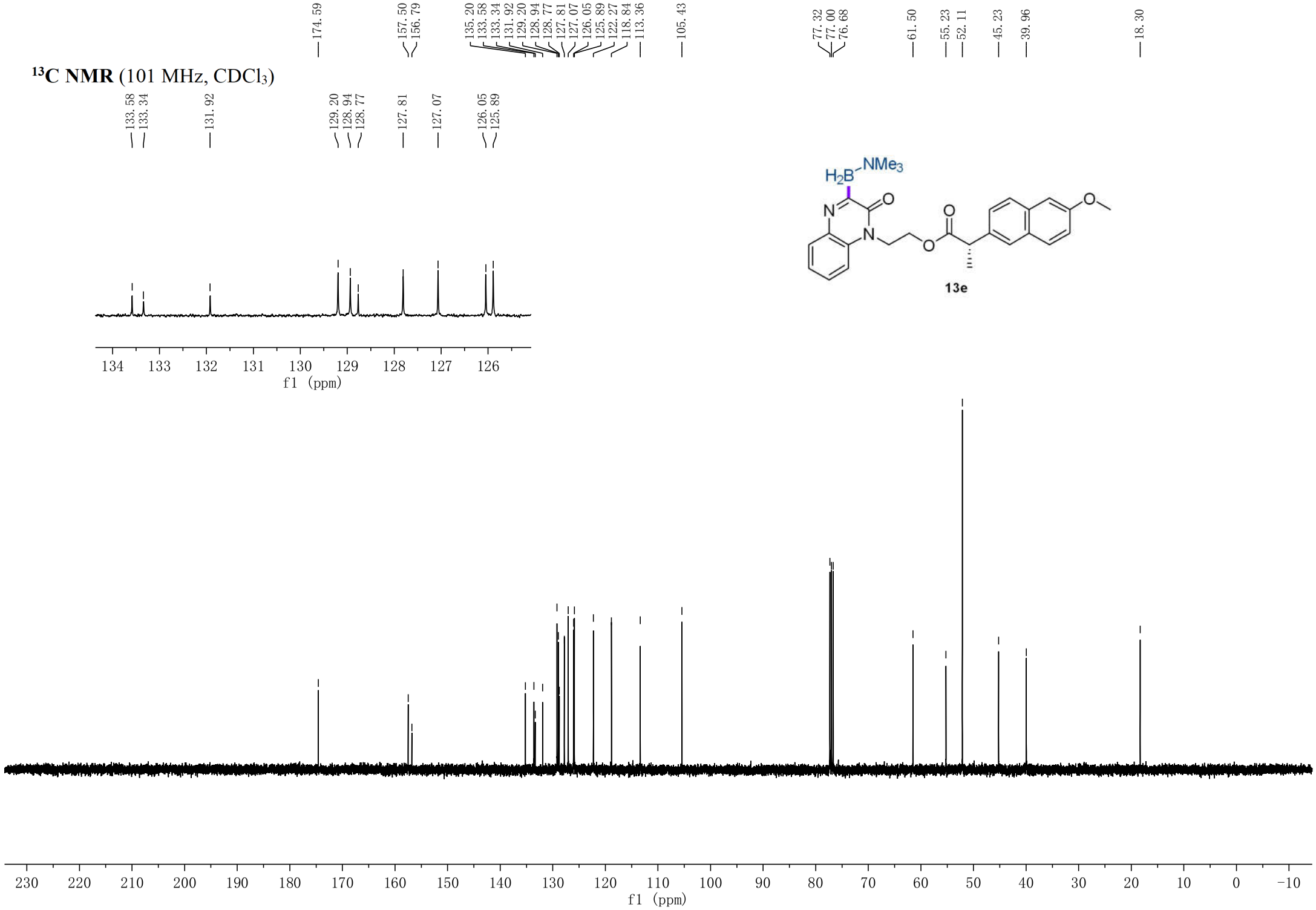


^{1}H NMR (400 MHz, $CDCl_3$)

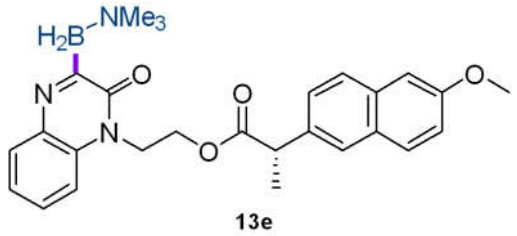


13e

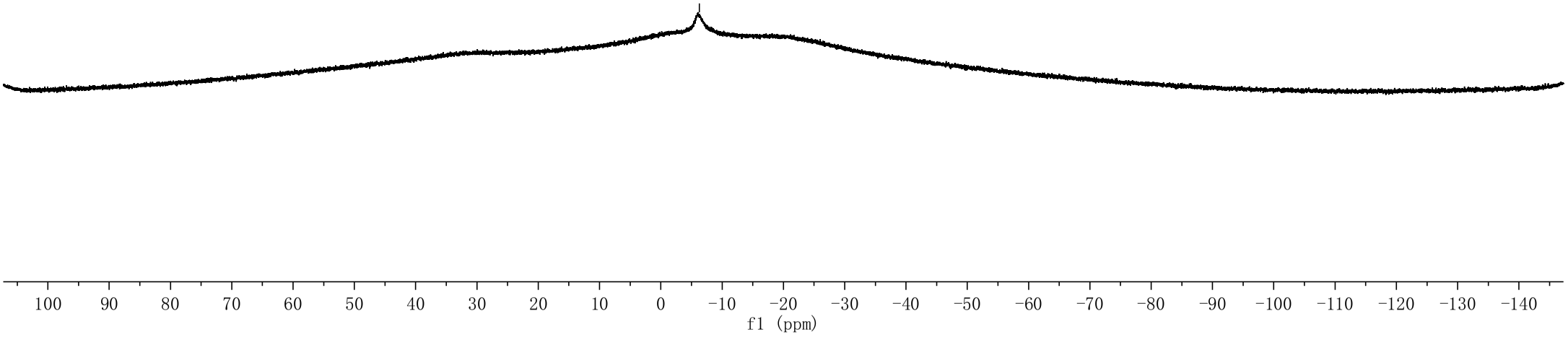
^{13}C NMR (101 MHz, $CDCl_3$)



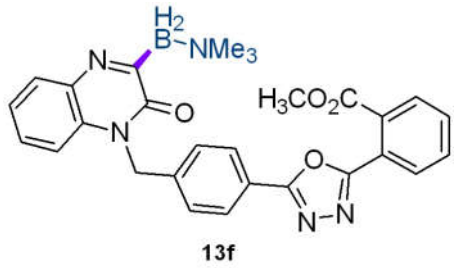
^{11}B NMR (128 MHz, $CDCl_3$)



13e



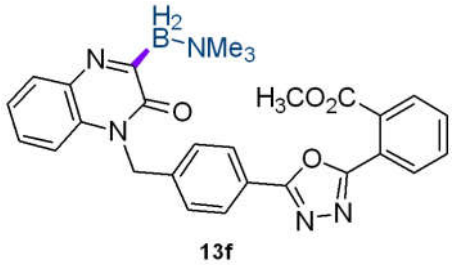
^{1}H NMR (400 MHz, $CDCl_3$)



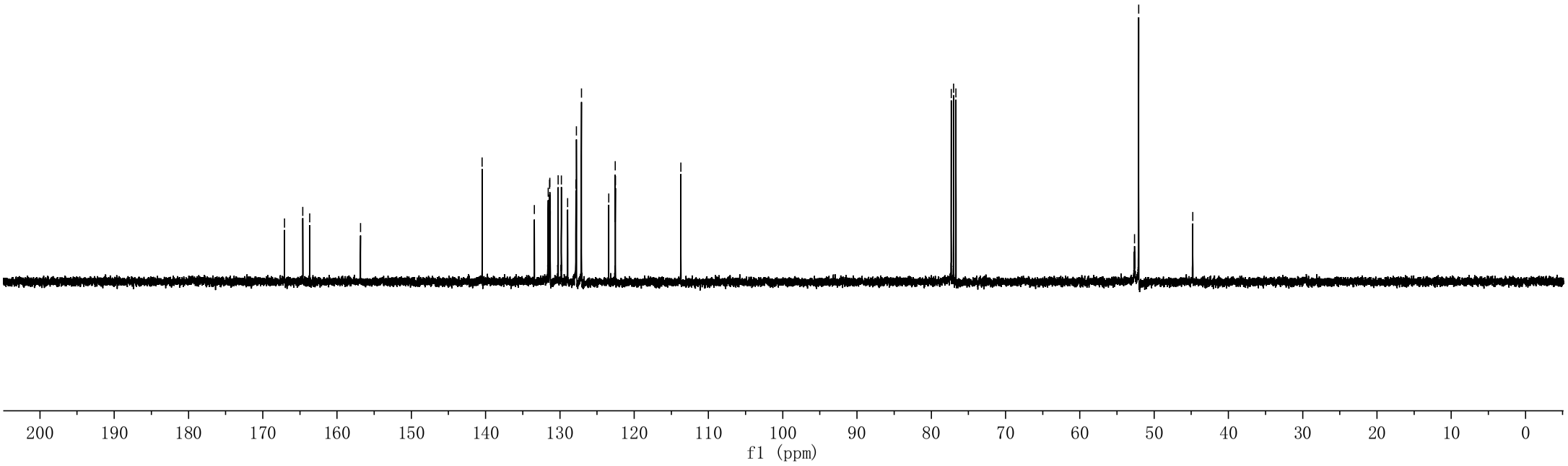
13f

167.08
164.60
163.68
156.84
140.47
131.59
131.39
131.36
130.23
129.80
127.85
127.77
127.11
123.42
122.54
77.32
77.00
76.68
52.62
52.08
44.80

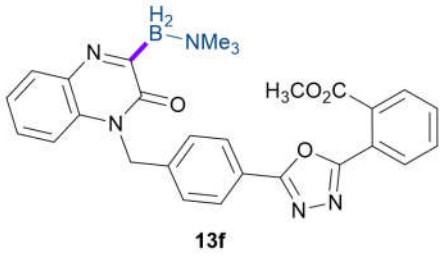
^{13}C NMR (101 MHz, $CDCl_3$)



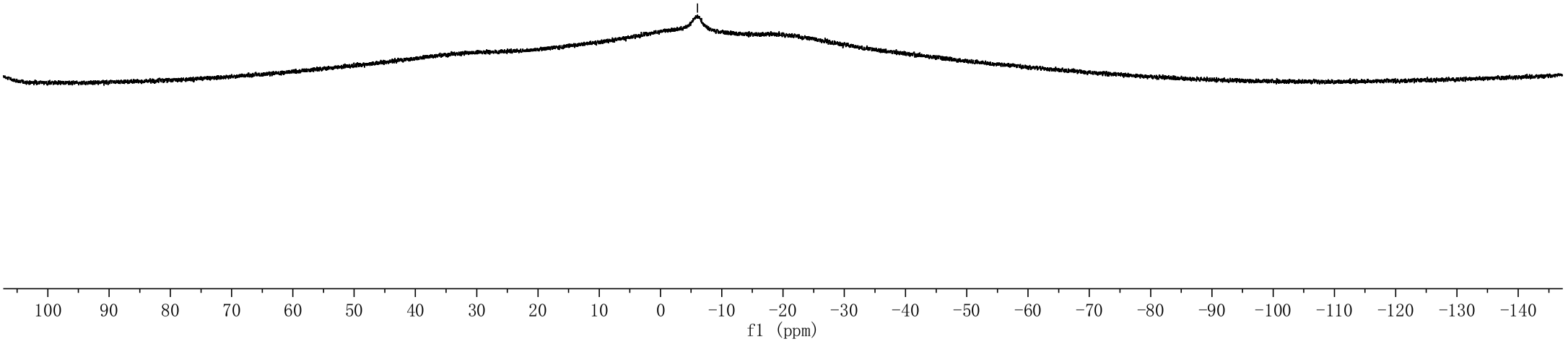
13f



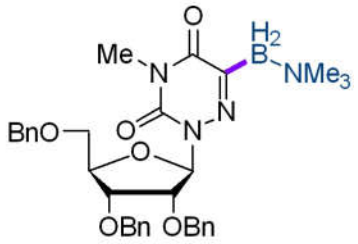
^{11}B NMR (128 MHz, $CDCl_3$)



13f



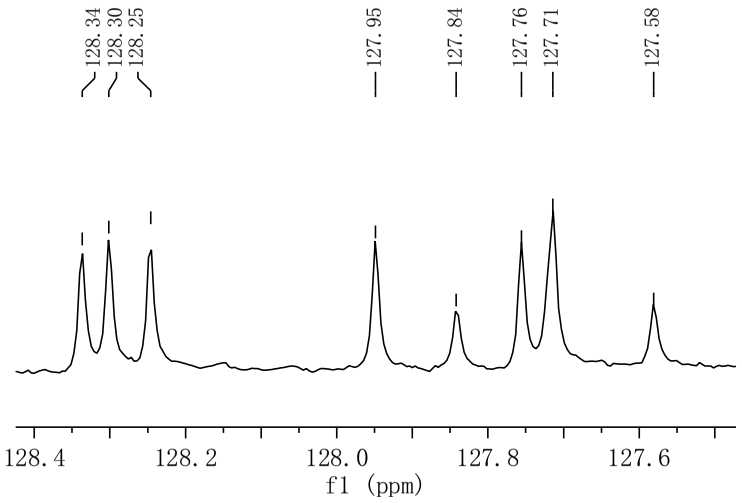
^{1}H NMR (400 MHz, $CDCl_3$)

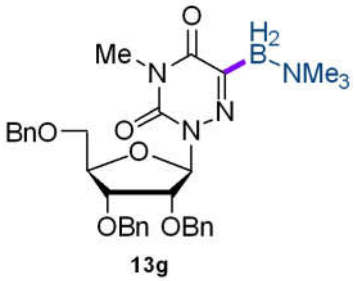


13g

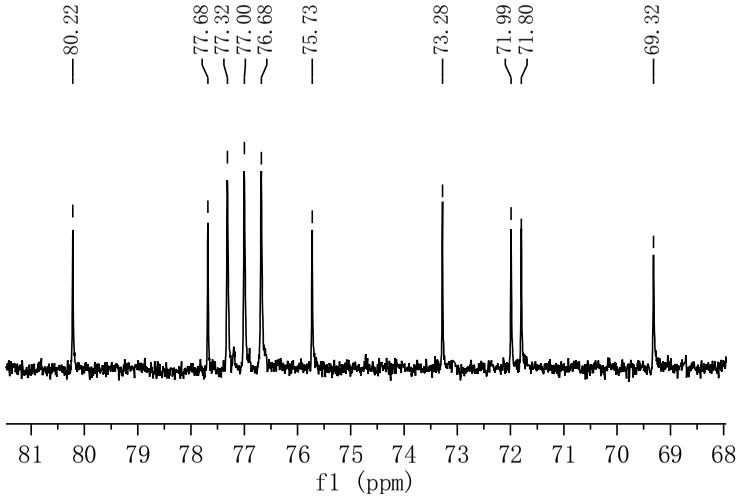
158.63
149.17
137.86
137.67
137.12
128.34
128.30
128.25
127.95
127.84
127.76
127.71
127.58
89.54
80.22
77.68
77.32
77.00
76.68
75.73
73.28
71.99
71.80
69.32
52.04
26.41

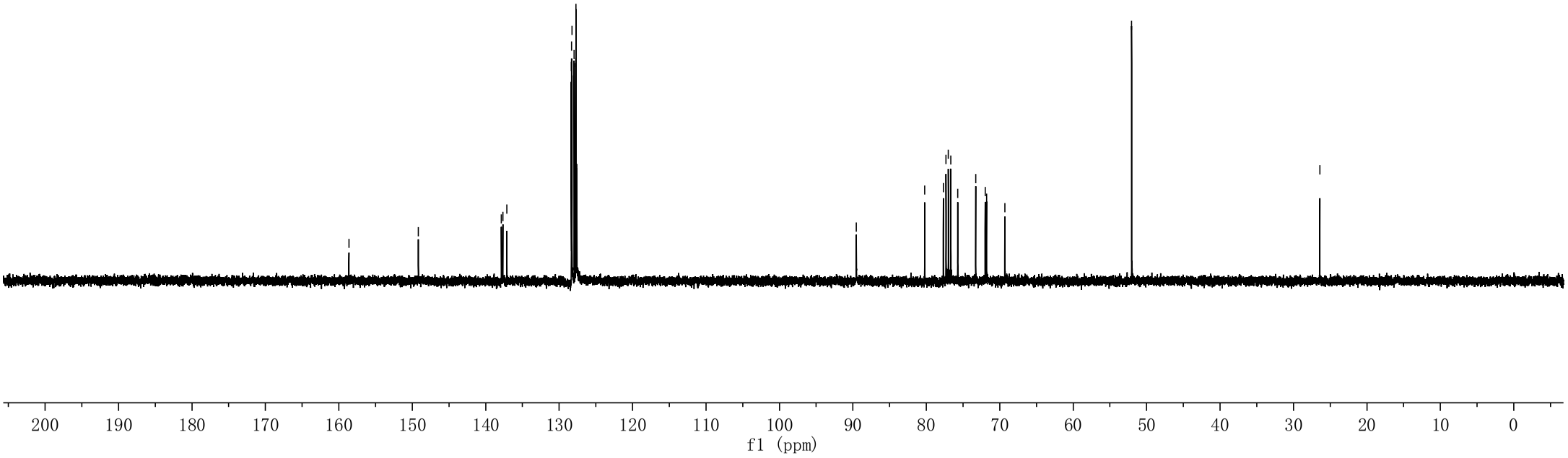
^{13}C NMR (101 MHz, $CDCl_3$)





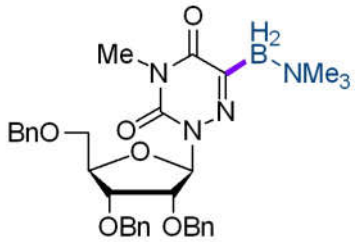
13g



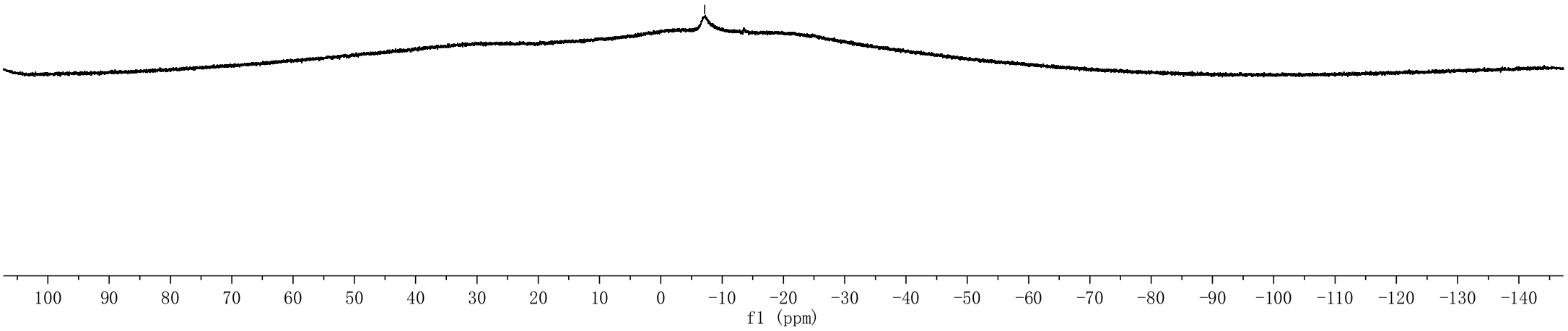


—7.16

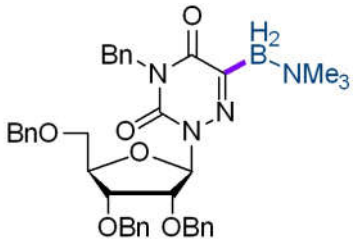
^{11}B NMR (128 MHz, $CDCl_3$)



13g

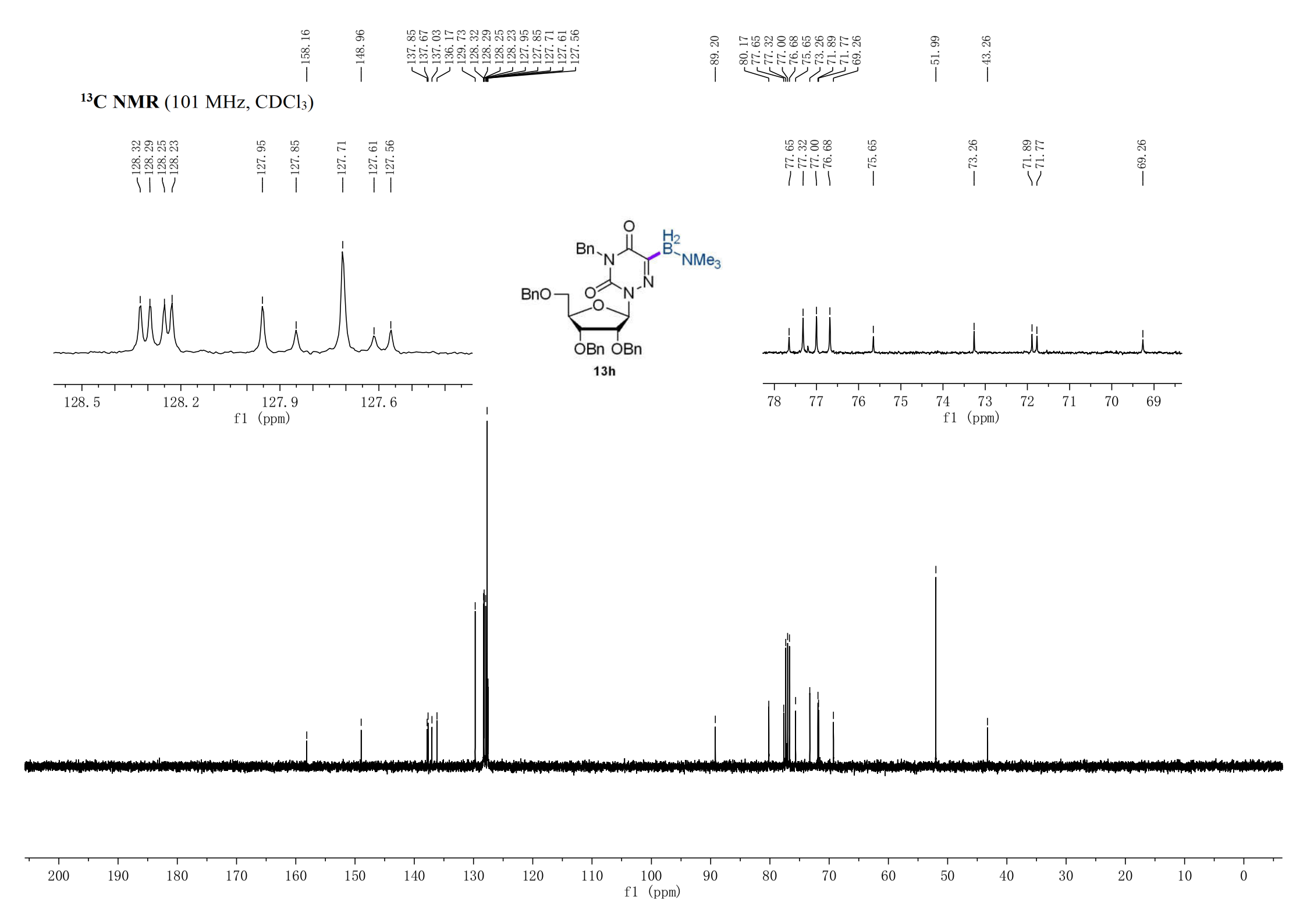


^{1}H NMR (400 MHz, $CDCl_3$)

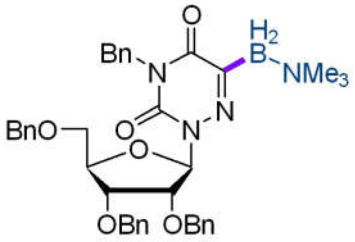


13h

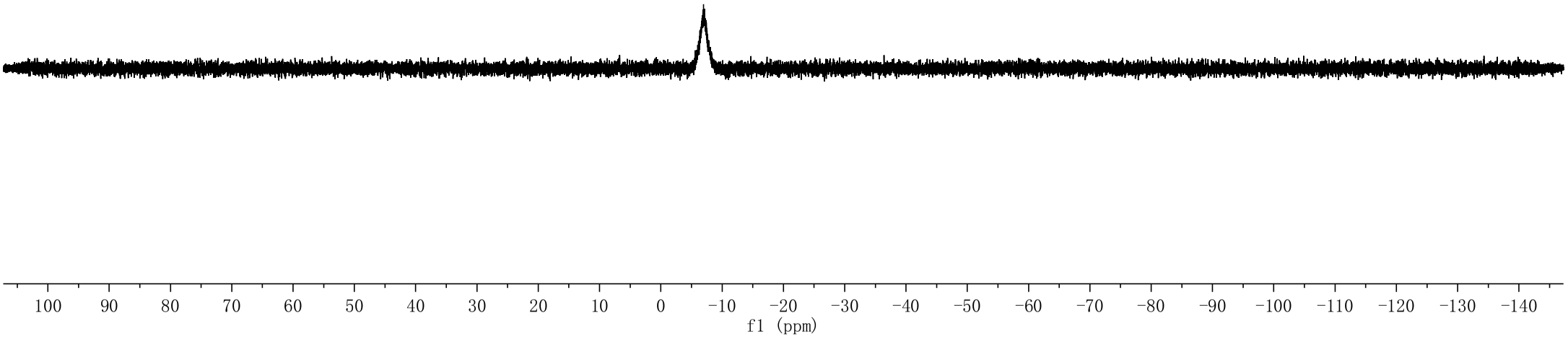
^{13}C NMR (101 MHz, $CDCl_3$)



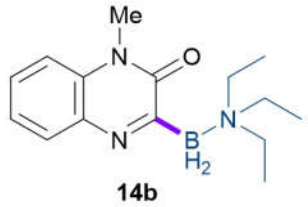
^{11}B NMR (128 MHz, $CDCl_3$)



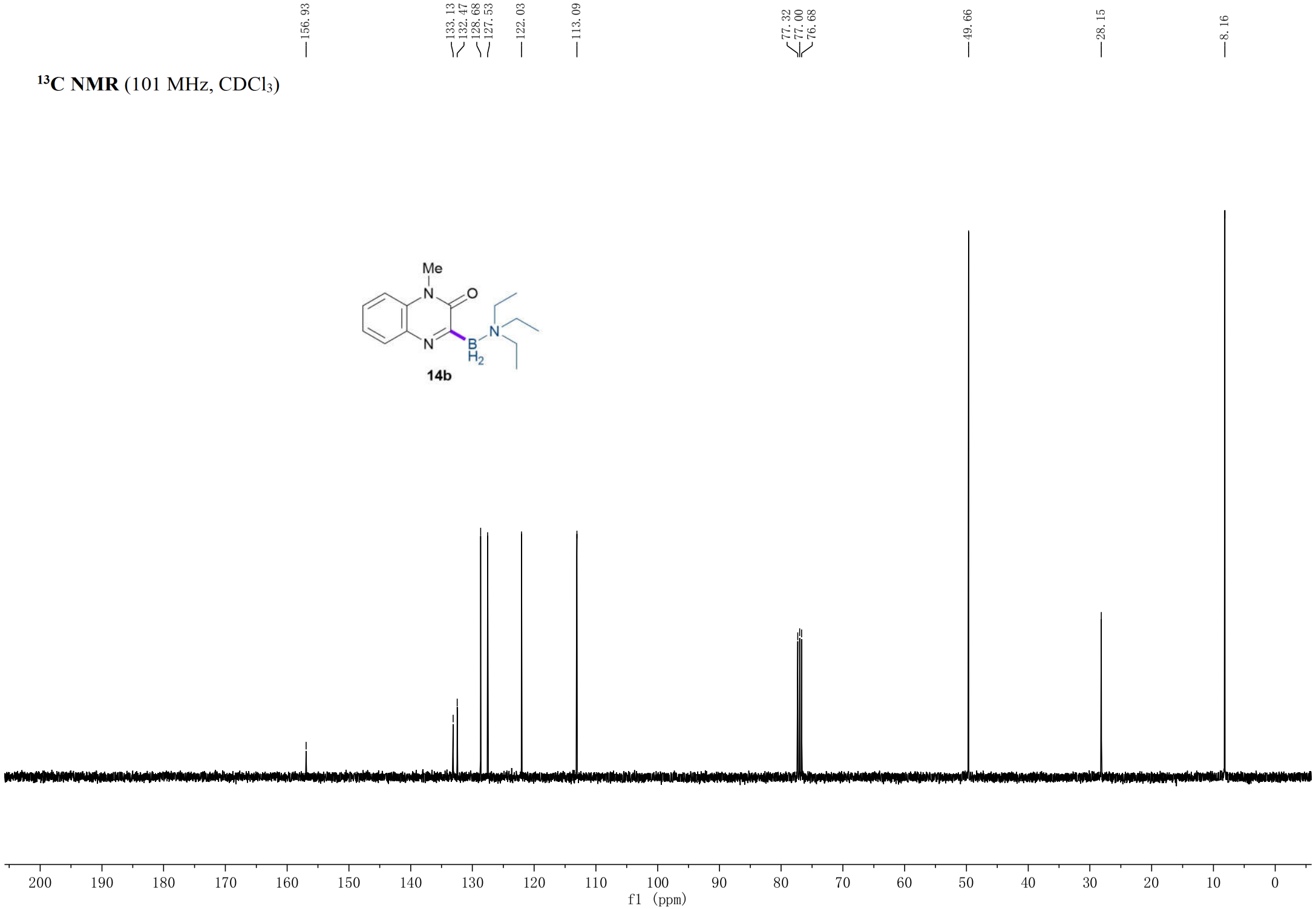
13h



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



14b

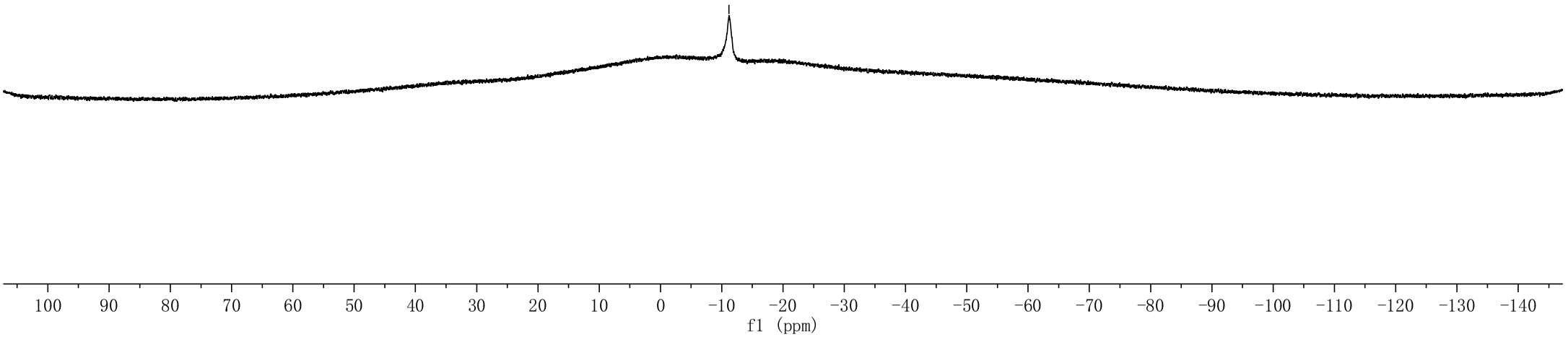


^{13}C NMR (101 MHz, $CDCl_3$)

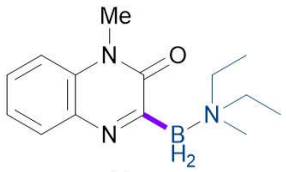
—11.17

^{11}B NMR (128 MHz, $CDCl_3$)

14b



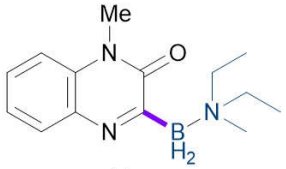
^{1}H NMR (400 MHz, $CDCl_3$)



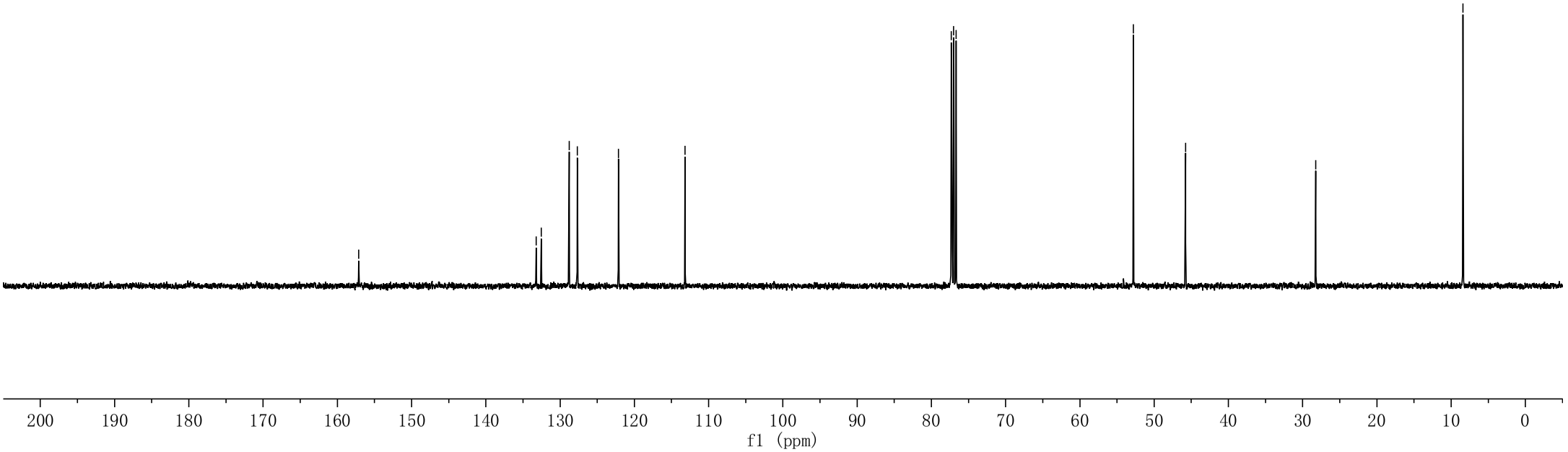
14c

157.13
133.23
132.54
128.78
127.70
122.15
113.17
77.32
77.00
76.68
52.80
45.77
28.23
8.41

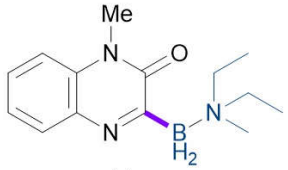
^{13}C NMR (101 MHz, $CDCl_3$)



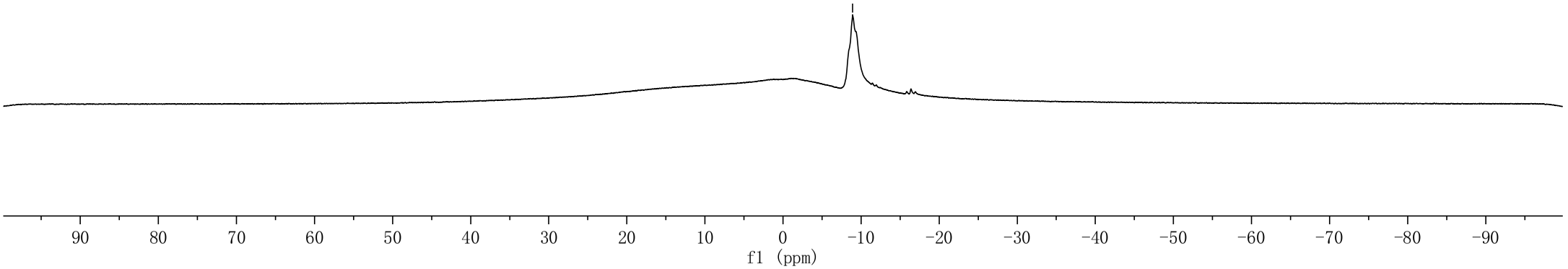
14c



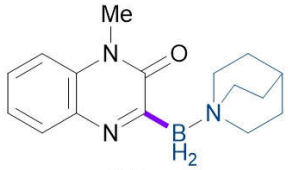
^{11}B NMR (193 MHz, $CDCl_3$)



14c



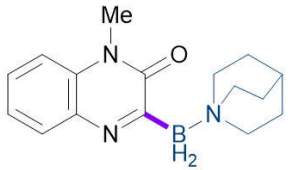
^{1}H NMR (400 MHz, $CDCl_3$)



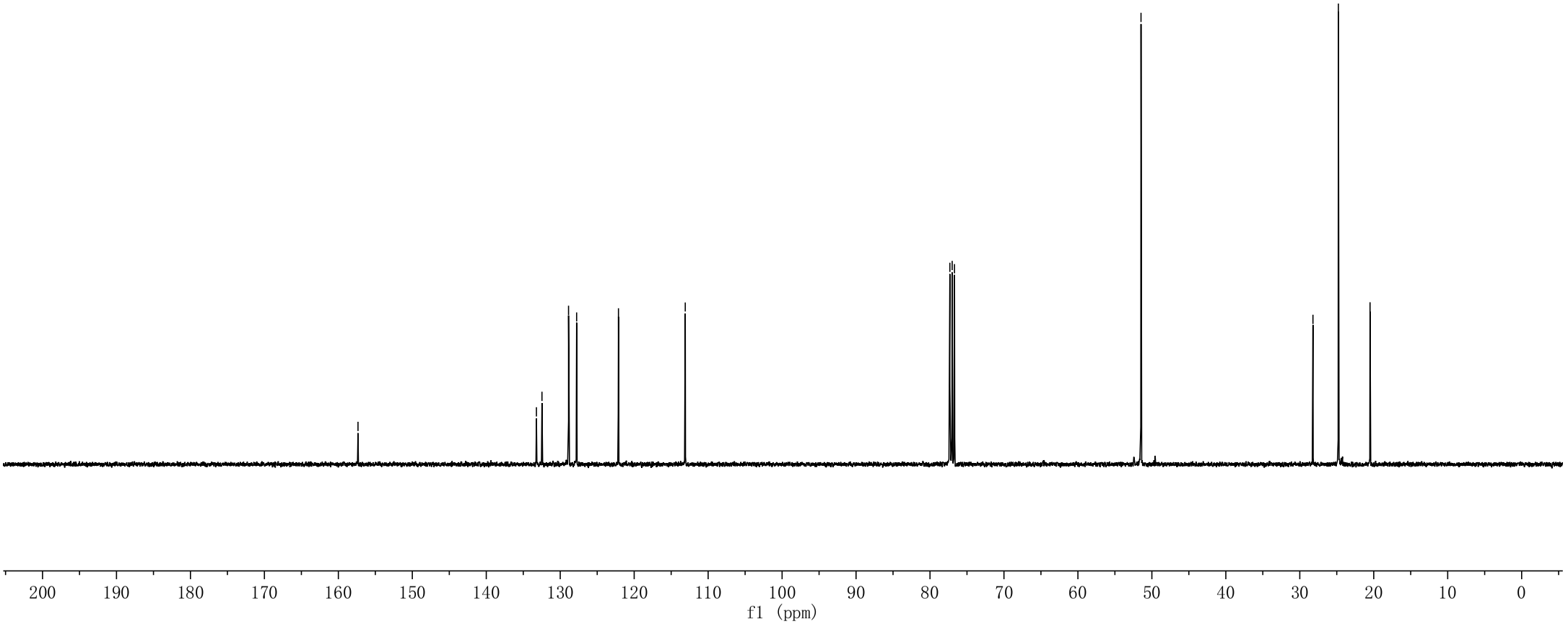
14d

157.33
133.21
132.47
128.86
127.77
122.12
113.10
77.32
77.00
76.68
51.47
28.22
24.77
20.49

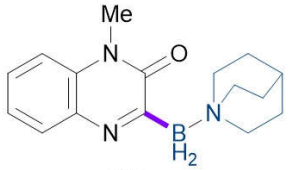
^{13}C NMR (101 MHz, $CDCl_3$)



14d

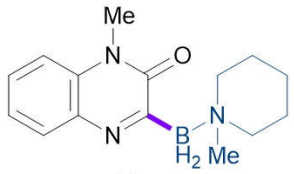


^{11}B NMR (128 MHz, $CDCl_3$)



14d

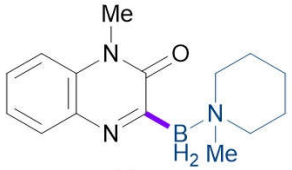
^{1}H NMR (400 MHz, $CDCl_3$)



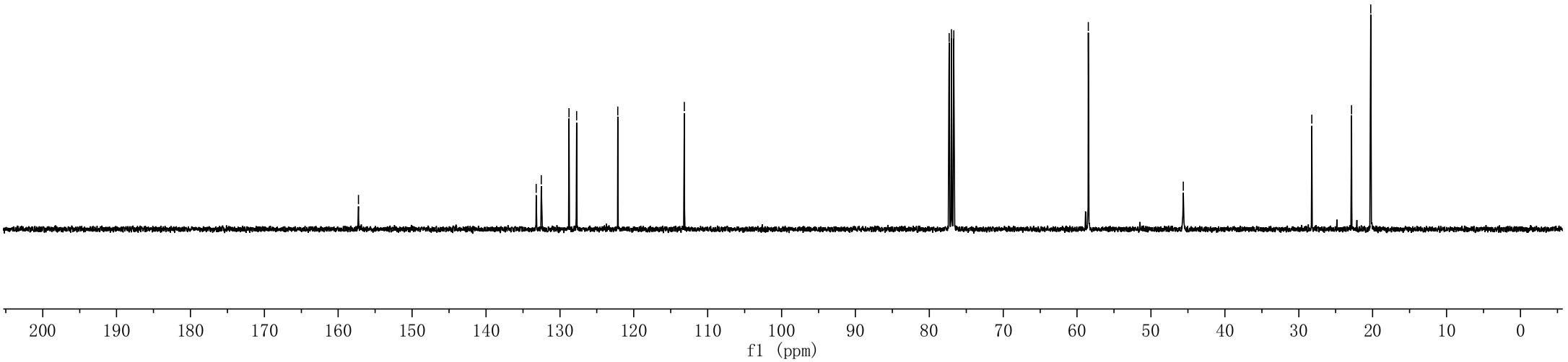
14e

157.26
133.21
132.50
128.77
127.75
122.16
113.15
77.32
77.00
76.68
58.48
45.63
28.24
22.86
20.25

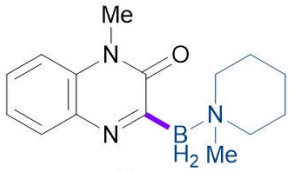
^{13}C NMR (101 MHz, $CDCl_3$)



14e

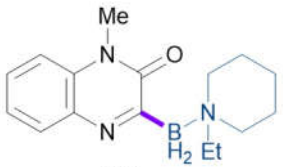


^{11}B NMR (128 MHz, $CDCl_3$)



14e

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

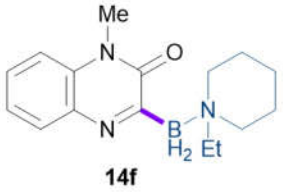


14f

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

14f

^{11}B NMR (128 MHz, $CDCl_3$)



14f

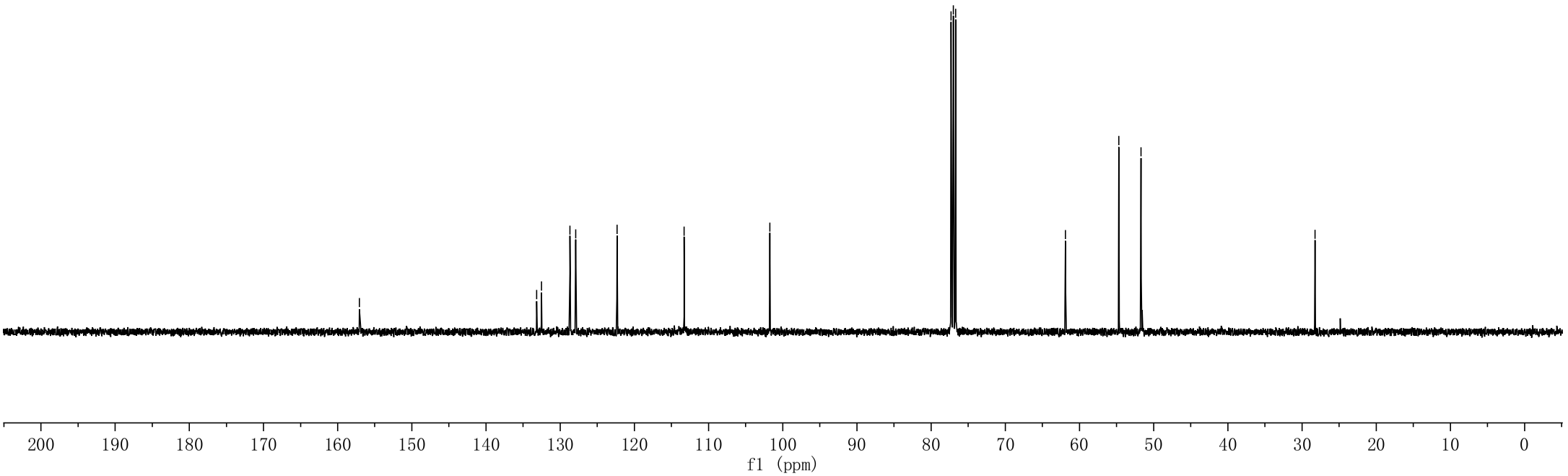
^{1}H NMR (400 MHz, $CDCl_3$)

14g

157.06
133.16
132.53
128.68
127.91
122.34
113.29
101.74
77.32
77.00
76.68
61.89
54.69
51.69
28.25

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

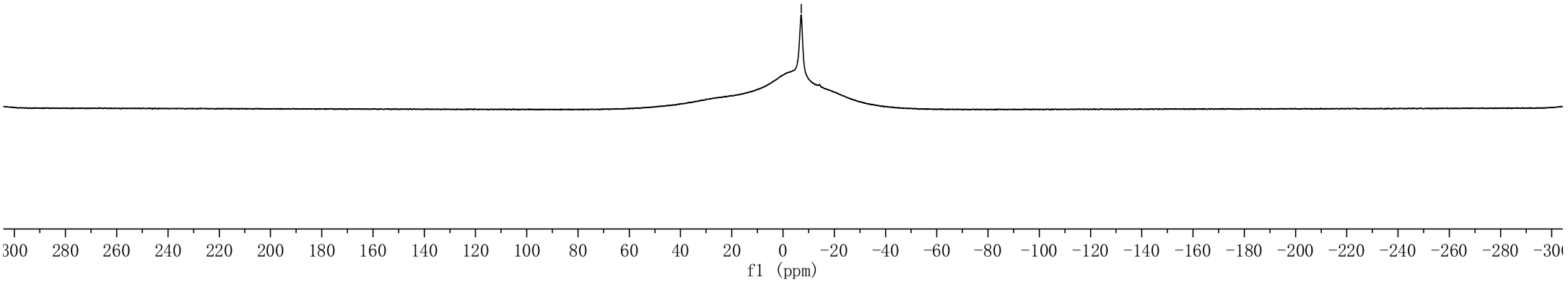
14g



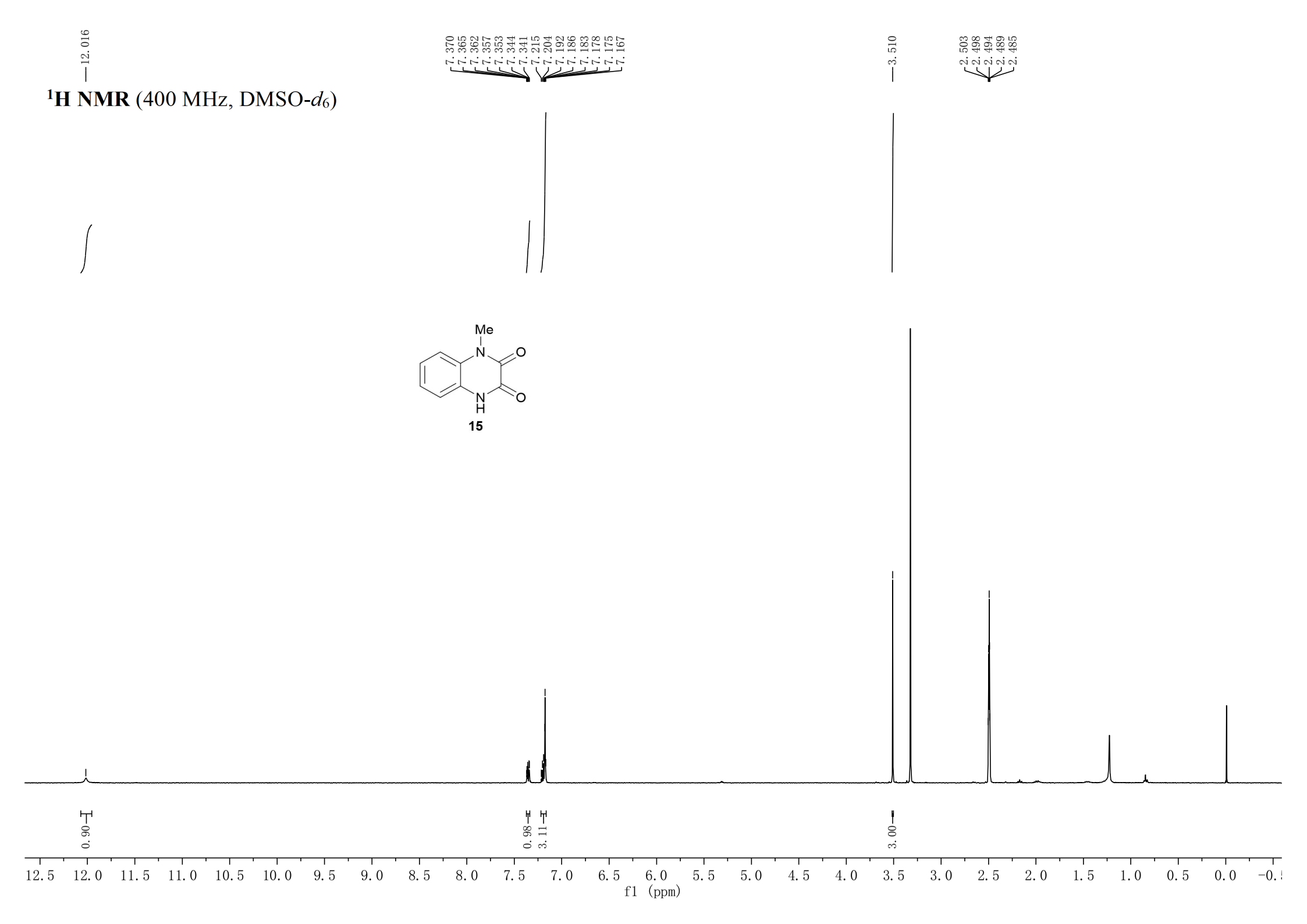
7.15

^{11}B NMR (128 MHz, $CDCl_3$)

14g

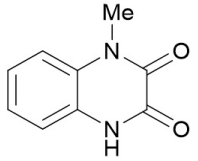


^{1}H NMR (400 MHz, DMSO-d_6)

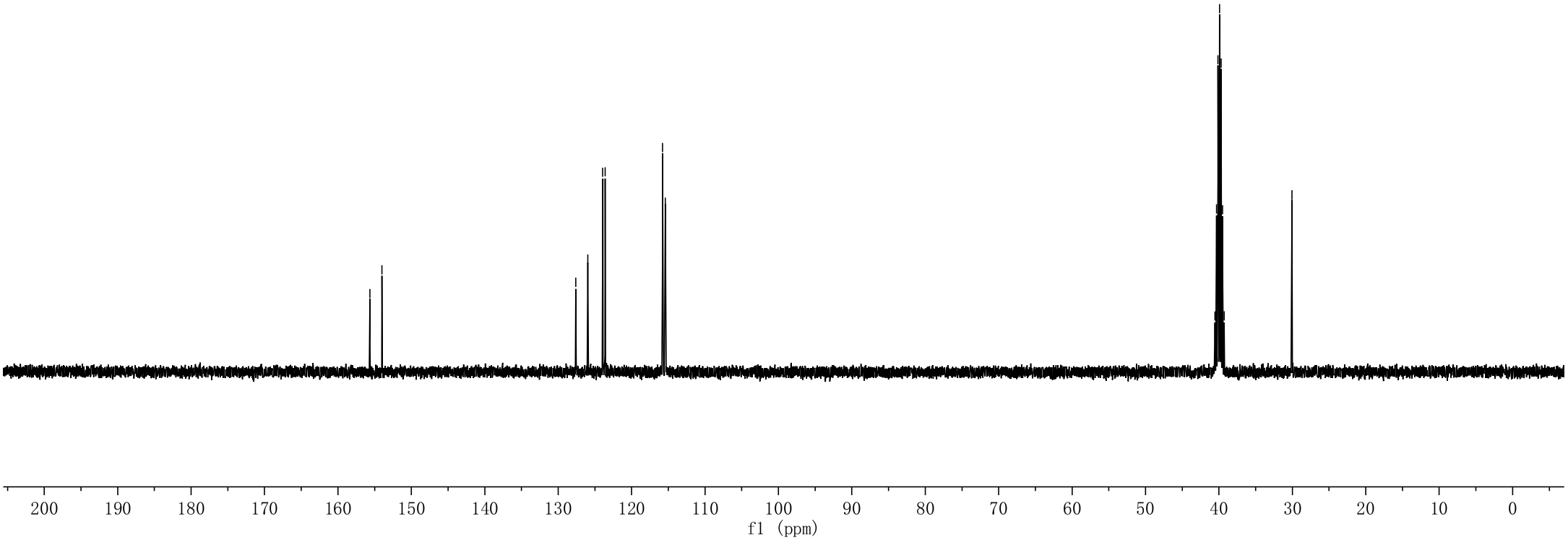


155.66
153.99
127.59
125.95
123.94
123.60
115.79
115.41
40.54
40.33
40.12
39.91
39.71
39.50
39.29
30.07

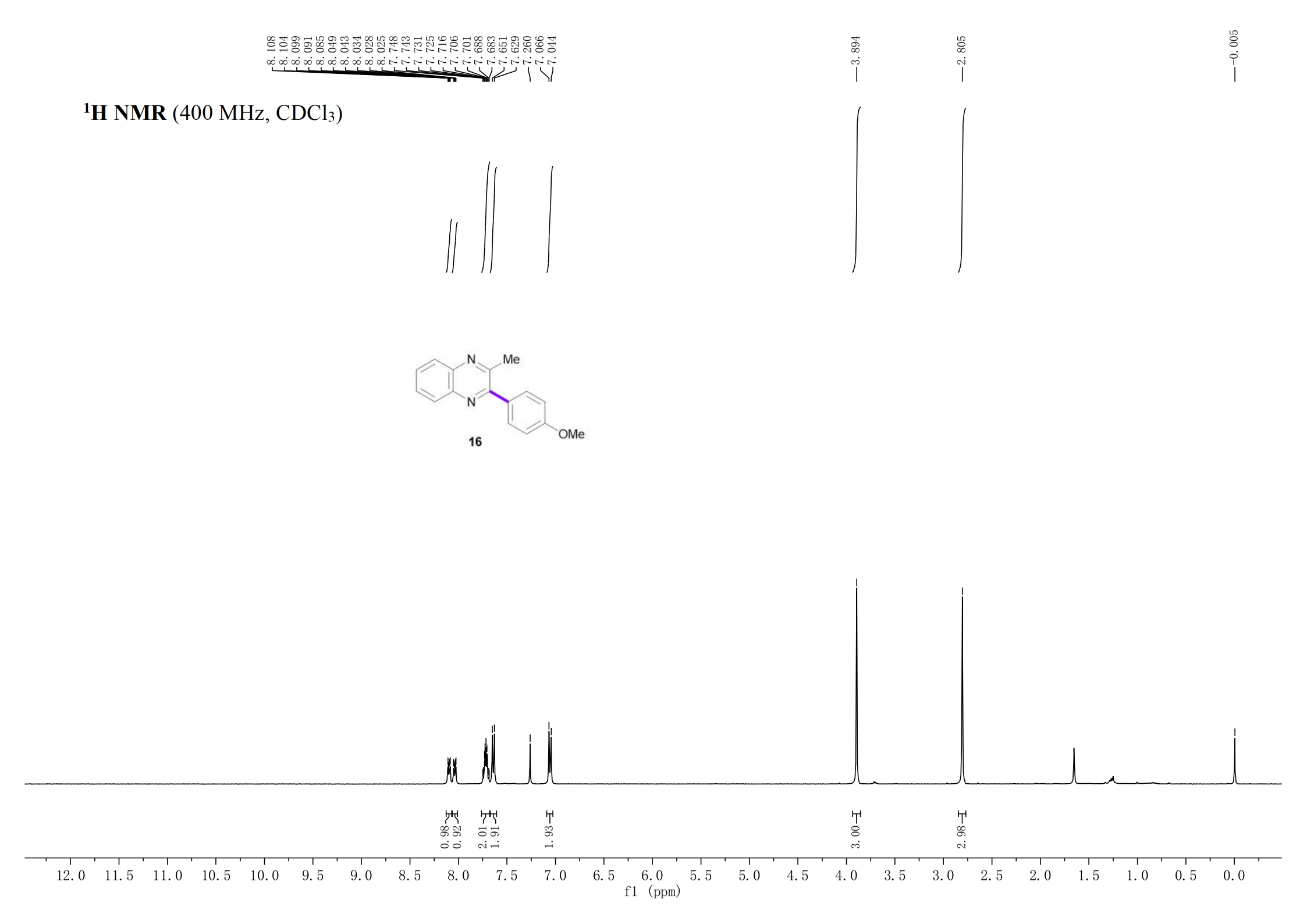
^{13}C NMR (101 MHz, DMSO-d_6)



15

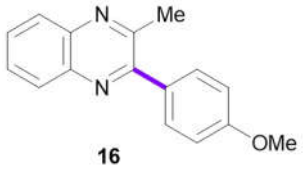


^{1}H NMR (400 MHz, $CDCl_3$)

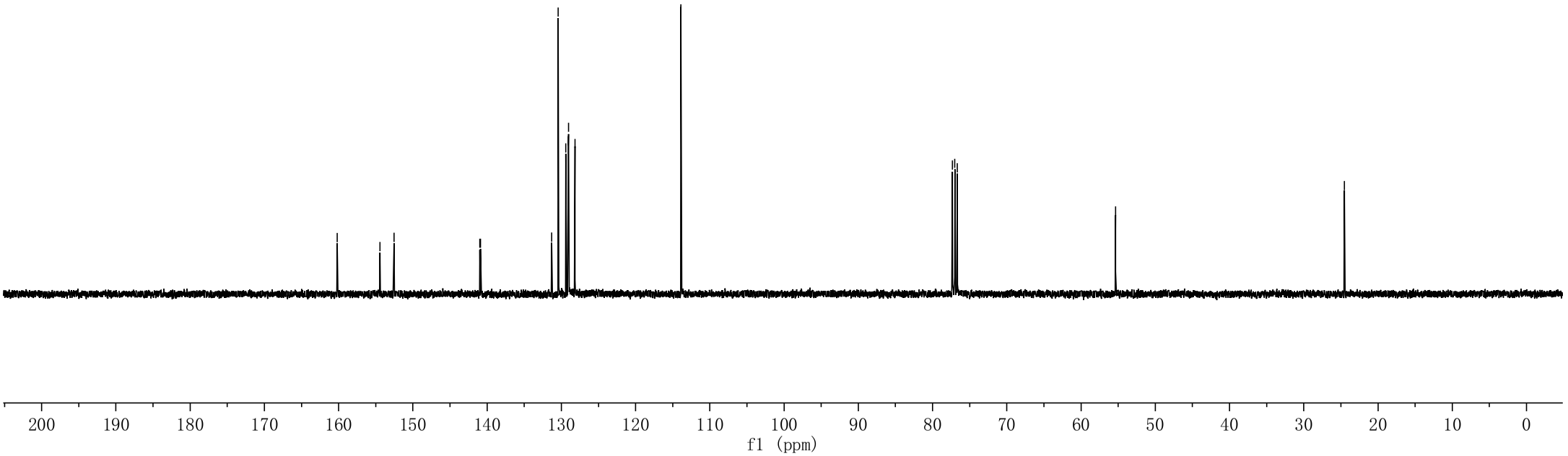


160.20
154.45
152.53
140.98
140.90
131.30
130.42
129.39
129.07
129.03
128.17
113.91
77.32
77.00
76.68
55.35
24.54

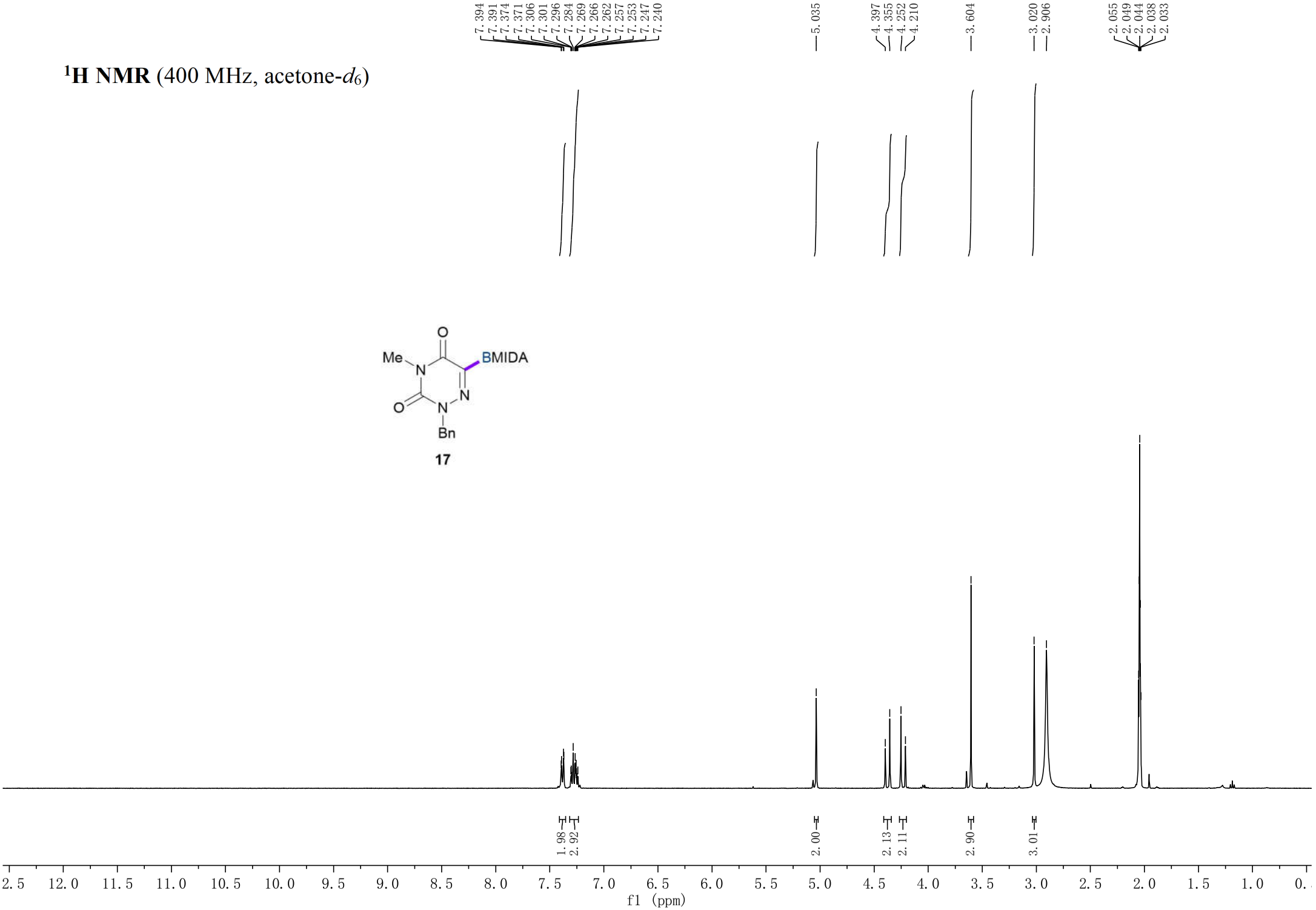
^{13}C NMR (101 MHz, $CDCl_3$)



16

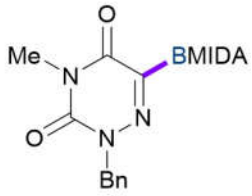


^{1}H NMR (400 MHz, acetone-d_6)

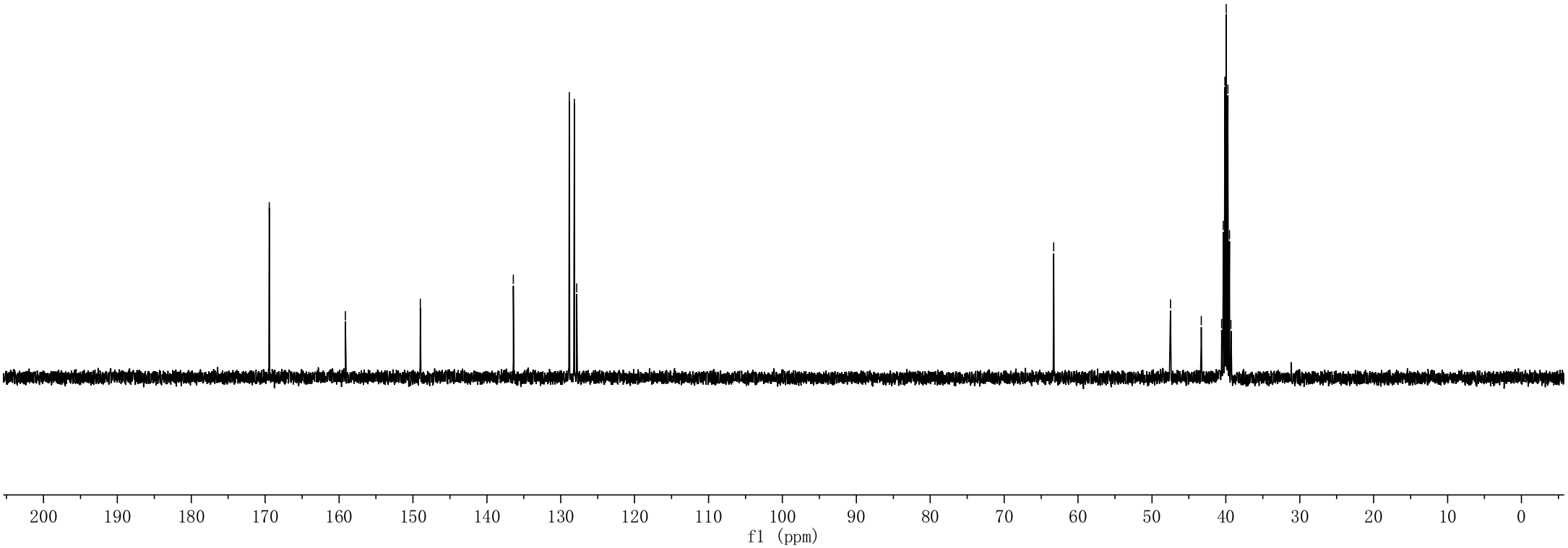


169.44
159.14
148.99
136.42
128.86
128.17
127.83
63.29
47.50
43.34
40.56
40.35
40.14
39.95
39.93
39.72
39.52
39.30

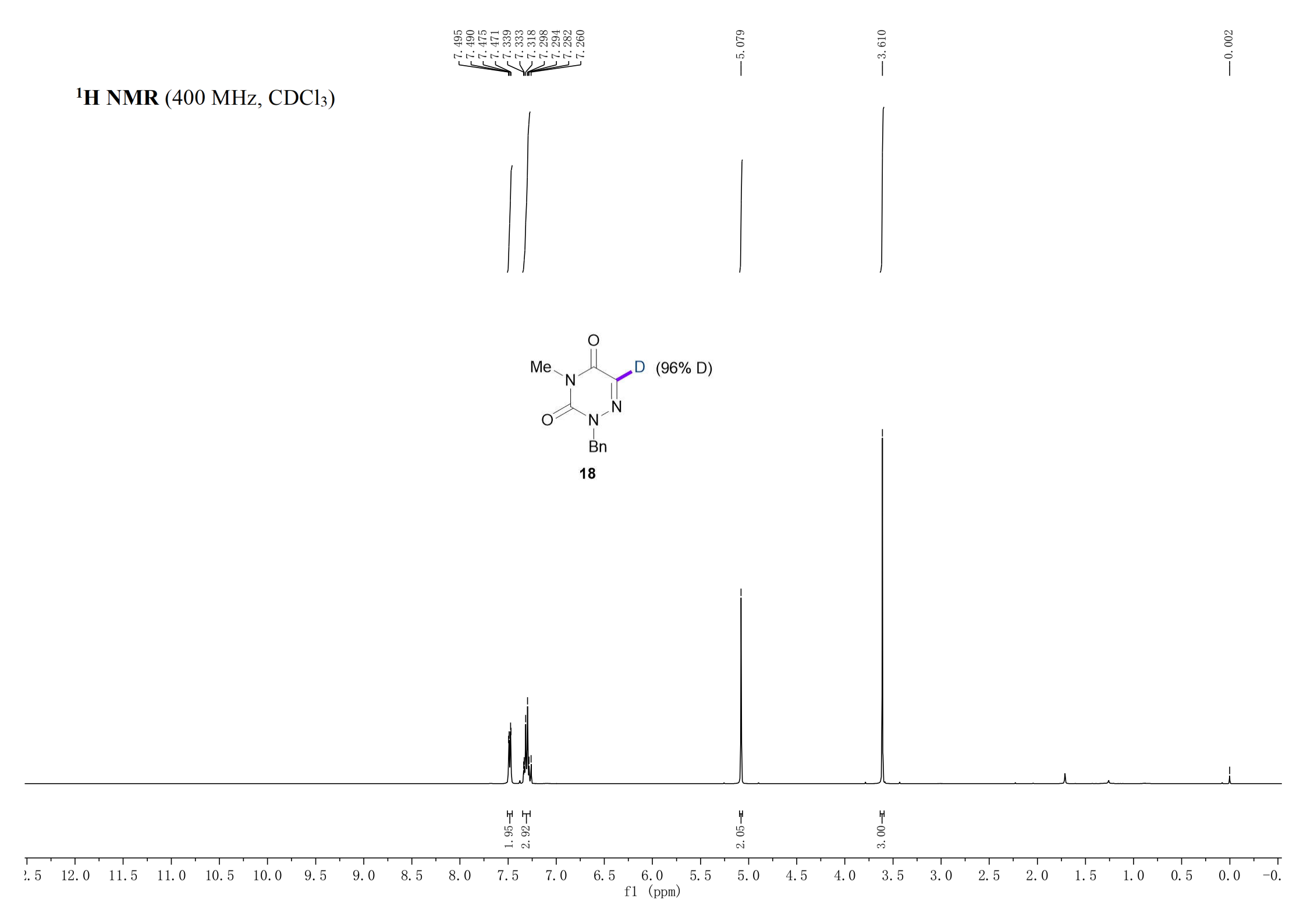
^{13}C NMR (101 MHz, DMSO-d_6)



17

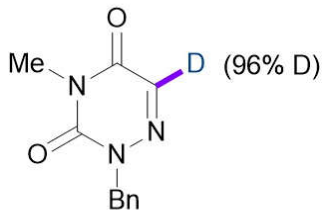


^{1}H NMR (400 MHz, $CDCl_3$)

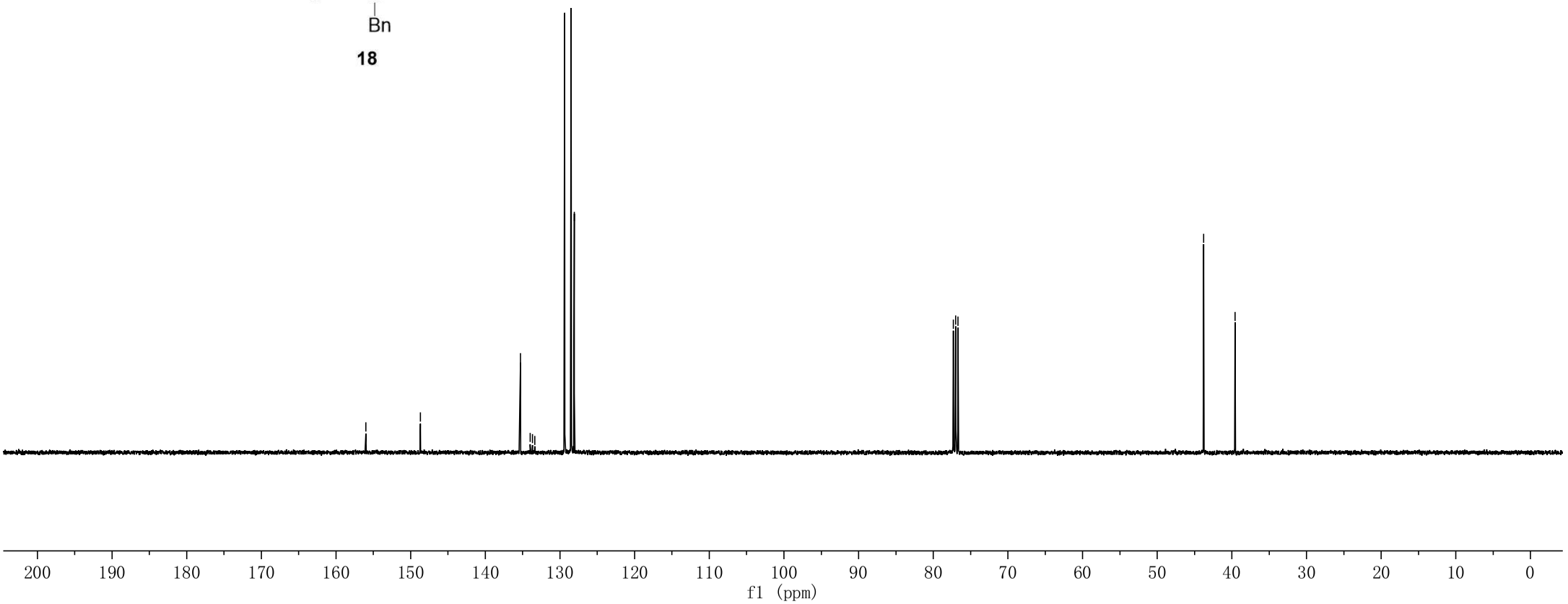


156.00
148.70
135.29
133.98
133.67
133.37
129.38
128.50
128.08
77.32
77.00
76.68
43.78
39.57

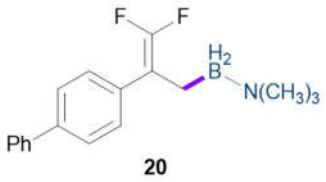
^{13}C NMR (101 MHz, $CDCl_3$)



18



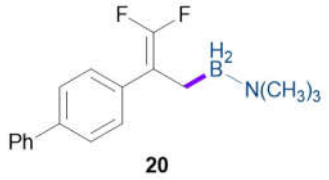
^{1}H NMR (400 MHz, $CDCl_3$)



20

154.91
152.10
152.04
149.24
140.95
138.81
135.78
135.74
135.72
135.69
128.63
128.61
128.60
128.57
126.97
126.92
126.53
94.97
94.88
94.74
94.65
77.32
77.00
76.68
51.84

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



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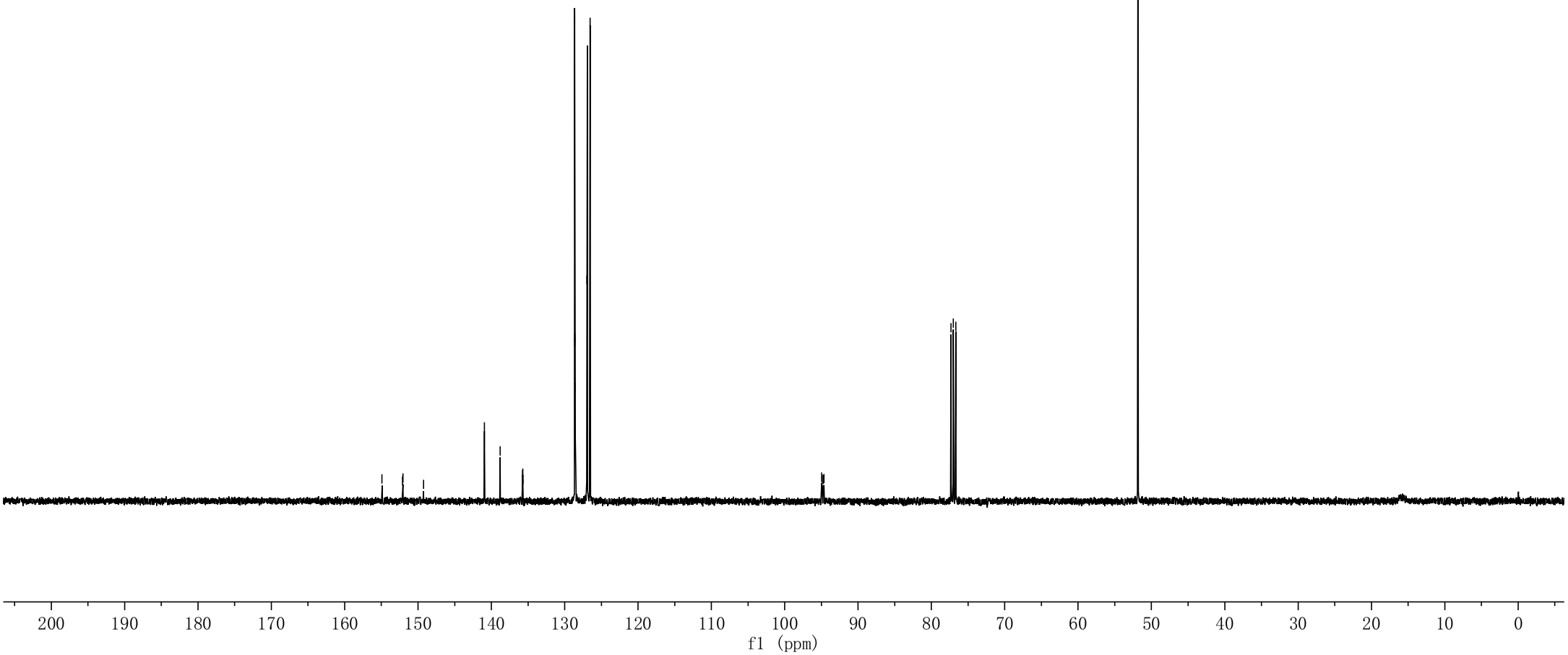
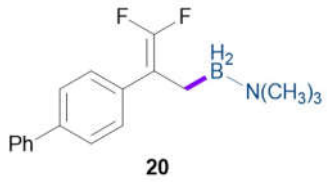


^{19}F NMR (376 MHz, $CDCl_3$)



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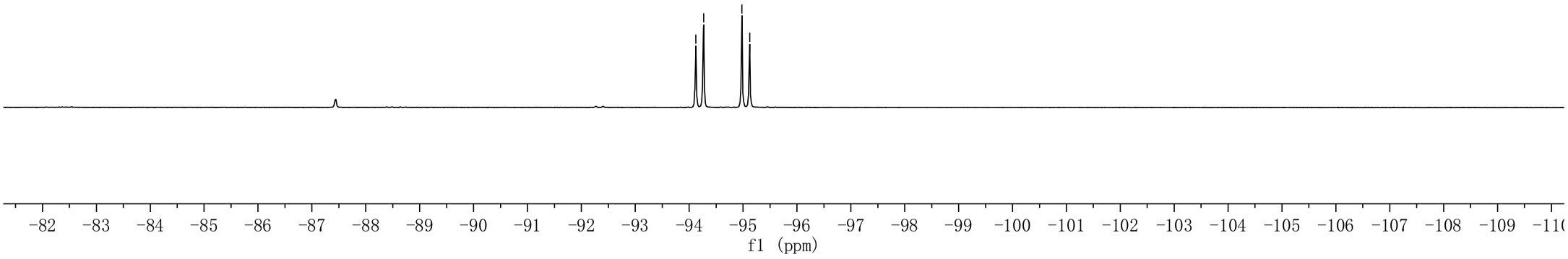
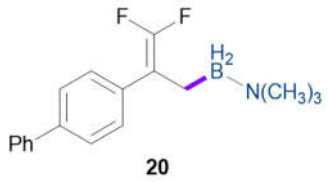


^{11}B NMR (128 MHz, $CDCl_3$)



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