Supporting Information（SI）

Catalyst-Free Reductions of Nitriles to Amino-Boranes Using Sodium Amidoborane and Lithium Borohydride

Jiamin Peng, Yuwei Song, Yingying Wang, Zhenxing Liu,* Xuenian Chen*

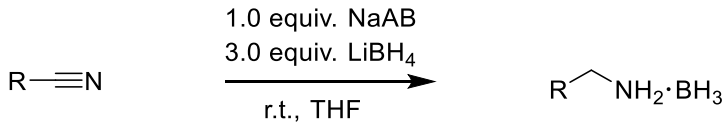
[a] College of Chemistry, Zhengzhou University, Zhengzhou, Henan 450001, China

Contents Page

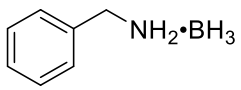
1. General methods and Materials:

All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Dry THF were obtained by distillation from Na/benzophenone. ^{1}H, $^{1}H\{^{11}B\}$, ^{13}C, ^{19}F, ^{11}B and $^{11}B\{^{1}H\}$ NMR spectra were recorded on a Bruker AV300 MHz spectrometer, Bruker AVANCENEO 400 MHz spectrometer and Bruker AVANCE 600 MHz spectrometer. The data contain properties such as chemical shift, multiplicity and coupling constants. All chemical shifts were reported in ppm units with references to the residual solvent resonance or an external standard. Coupling constants J which are reported in hertz. High-resolution mass spectra (HRMS) were obtained *via* an electrospray ionization (ESI) mode using a UPLC G2-XS Qtof mass spectrometer and the BH_3 in the products was disassociated due to electrospray ionization[1]. Sodium amino-borane was synthesized by the literature procedures[2]. All the nitriles were purchased from Energy Chemicals, Aladdin, Heowns or Royaltech. Compounds Ammonia borane and Lithium borohydride were purchased from ZhengzhouYuanli technology.

2. General procedure and spectral data of new compounds



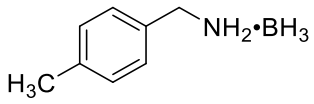
In an argon-filled glovebox, sodium amidoborane (0.2 mmol), lithium borohydride (0.6 mmol) were added in a 10-ml Schlenk flask and then the flask was removed out of the box. THF (4 ml) and nitriles (0.2 mmol) were added sequentially to the flask under N_2. Then the reaction mixture was allowed to stirred at room temperature. After completion of the reaction indicated by TLC, violates was then evaporated under reduced pressure and the residue was purified by flash chromatography on aluminum oxide. (petroleum ether: ethyl acetate = 4:1 for **2a - 2q**, **2u**, **2v**, **2y** petroleum ether: ethyl acetate = 2:1 for **2r - 2t, 2x,2w)**



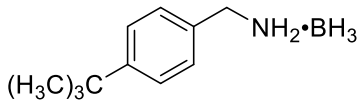
Following the general procedure, reaction time: 0.5 h.

2a[3]**:** white solid, 92%; 52-53℃;

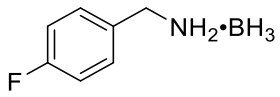
^{1}H NMR (400 MHz, DMSO) δ 7.48 - 7.22 (m, 5H), 5.67 (s, 2H), 3.72 - 3.55 (m, 2H);
^{1}H{B} NMR (400 MHz, DMSO) δ 7.55 - 7.16 (m, 5H), 5.65 (s, 2H), 3.61 (s, 2H), 1.42 (s, 3H);
^{11}B NMR (128 MHz, DMSO) δ -20.10;
^{11}B{H} NMR (101 MHz, DMSO) δ -20.00;
^{13}C NMR (101 MHz, DMSO) δ 137.81, 128.95, 128.6, 127.87, 52.19.



Following the general procedure, reaction time: 1 h.
2b[3]: white solid, 88%; melting point: 97-100℃;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 5.57 (s, 2H), 3.55 - 3.51 (m, 2H) 2.27 (s, 3H);
^{1}H{B} NMR (400 MHz, DMSO) δ 7.26 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.57 (s, 2H), 3.57 - 3.54 (m, 2H), 2.29 (s, 3H), 1.39 (t, *J* = 3.6 Hz, 3H);
^{11}B NMR (193 MHz, $CDCl_3$) δ -18.72(q, *J* = 90.7 Hz);
^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$) δ -18.90;
^{13}C NMR (151 MHz, $CDCl_3$) δ 138.87, 133.01, 129.98, 128.18, 53.09, 21.17.



Following the general procedure, reaction time: 8 h.
2c: white solid, 82%**;** melting point: 120-122℃;
^{1}H NMR (300 MHz, CD_3CN) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.34 (s, 2H), 3.75 - 3.70 (m, 2H), 1.30 (s, 9H);
^{1}H{B} NMR (600 MHz, CD_3CN) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.34 (s, 2H), 3.75 - 3.72 (m, 2H), 1.44 (t, *J* = 3.8 Hz, 3H), 1.31 (s, 9H);
^{11}B NMR (193 MHz, CD_3CN) δ -19.20 (q, *J* = 94.6Hz);
^{11}B{H} NMR (193 MHz, CD_3CN) δ -19.18;
^{13}C NMR (151 MHz, CD_3CN) δ 151.67, 134.67, 129.00, 126.21, 52.59, 34.88, 31.21.
HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_{11}H_{18}N$) requires *m/z* = 164.1439, found *m/z* = 164.1437.



Following the general procedure, reaction time: 5 min.
2d: white solid, 72%; melting point: 108-110℃;
^{1}H NMR (600 MHz, DMSO) δ 7.49 - 7.37 (m, 2H), 7.24 - 7.10 (m, 2H), 5.66 (s, 2H), 3.64 - 3.53 (m, 2H);
^{1}H{B} NMR (600 MHz, DMSO) δ 7.44 -7.41 (m, 2H), 7.17 - 7.14 (m, 2H), 5.65 (s, 2H), 3.63 - 3.55 (m, 2H), 1.38 (d, *J* = 3.3 Hz, 3H);

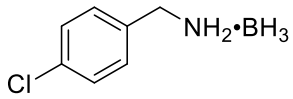
^{11}B NMR (128 MHz, DMSO) δ -18.81;

^{11}B{H} NMR (128 MHz, DMSO) δ -18.75;

^{13}C NMR (101 MHz, DMSO) δ 162 .03(d, *J* = 243.4 Hz), 134.03 (d, *J* = 3 Hz), 131.15 (d, *J* = 8.1Hz), 115.35(d, *J* =21.2 Hz), 51.29;

^{19}F{H} NMR (377 MHz, DMSO) δ -115.21.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ (C_7H_9FN) requires *m/z* = 126.0719, found *m/z* = 126.0722



Following the general procedure, reaction time: 5 min.

2e[3]: white solid, 56%; melting point: 107-110℃;

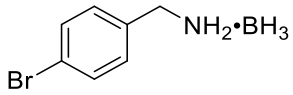
^{1}H NMR (300 MHz, DMSO) δ 7.50 - 7.31 (m, 4H), 5.69 (s, 2H), 3.65 - 3.52 (m, 2H);

^{1}H{^{11}B} NMR (600 MHz, DMSO) δ 7.42 - 7.33 (m, 3H), 5.66 (s, 2H), 3.63 - 3.52 (m, 2H), 1.36 (s, 3H);

^{11}B NMR (193 MHz, DMSO) δ -18.73 (q, *J* = 90.7 Hz);

^{11}B{^{1}H} NMR (193 MHz, DMSO) δ -18.66;

^{13}C NMR (151 MHz, DMSO) δ 136.82, 132.69, 130.94, 128.70. 51.45.



Following the general procedure, reaction time: 1 h.

2f[3]**:** white solid, 66%; melting point: 120-123℃;

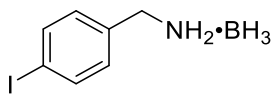
^{1}H NMR (300 MHz, DMSO) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.68 (s, 2H), 3.61 - 3.53 (m, 2H);

^{1}H{B} NMR (400 MHz, DMSO) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.68 (s, 2H), 3.64 - 3.51 (m, 2H), 1.38 (s, 3H);

^{11}B NMR (128 MHz, DMSO) δ -18.81;

^{11}B{H} NMR (128 MHz, DMSO) δ -18.81;

^{13}C NMR (151 MHz, DMSO) δ 137.14, 131.50, 131.29, 121.11, 51.33.



Following the general procedure, reaction time: 1 h.

2g: white solid 91%**;** melting point: 70-72℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.65 (s, 2H), 3.59 - 3.49 (m, 2H);

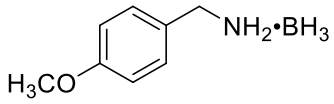
^{1}H{B} NMR (400 MHz, DMSO) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 5.67 (s, 2H), 3.62 (d, *J* = 6.9 Hz, 2H), 1.37 (s, 3H);

^{11}B NMR (128 MHz, DMSO) δ -19.02;

^{11}B{H} NMR (128 MHz, DMSO) δ -19.15;

^{13}C NMR (101 MHz, DMSO) δ 137.49, 137.38, 131.39, 93.97, 51.46.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ (C_7H_9NI) requires *m/z* = 6233.9780, found *m/z* = 233.9779.



Following the general procedure, reaction time: 20 h.

2h[3]: white solid, 85%; melting point: 80-83℃;

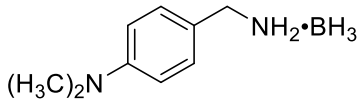
^{1}H NMR (300 MHz, CDCl3) δ 7.23 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 4.03 (s, 2H), 3.89 - 3.81 (m, 2H), 3.79 (s, 3H);

^{1}H{B} NMR (600 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 2H), 4.01 (s, 2H), 3.85 (d, *J* = 6.1 Hz, 2H), 3.79 (s, 3H), 1.62 (s, 3H);

^{11}B NMR (193 MHz, $CDCl_3$) δ -18.91 (q, *J* = 83.0 Hz);

^{11}B{H} NMR (193 MHz, $CDCl_3$) δ -18.90;

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.89, 129.78, 128.20, 114.57, 55.35, 52.62



Following the general procedure, reaction time: 24 h.

2i: white solid, 46%; melting point: 99-101℃;

^{1}H NMR (300 MHz, CD_3CN) δ 7.22 - 7.13 (m, 2H), 6.77 - 6.68 (m, 2H), 4.19 (s, 2H), 3.68 - 3.59 (m, 2H), 2.91 (s, 6H);

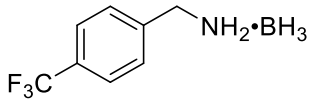
^{1}H{B} NMR (600 MHz, DMSO) δ 7.17 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 4.19 (s, 2H), 3.66 - 3.61 (m, 2H), 2.91 (s, 6H), 1.41 (s, 3H);

^{11}B NMR (193 MHz, $CDCl_3$) δ -18.82 (q, *J* = 94.6 Hz);

^{11}B{H} NMR (193 MHz, DMSO) δ -18.83;

^{13}C NMR (151 MHz, DMSO) δ 151.29, 130.26, 125.04, 112.98, 52.67, 40.37.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_9H_{15}N_2$) requires *m/z* = 151.1235, found *m/z* = 151.1236.



Following the general procedure, reaction time: 25 min.

2j[4]: white solid, 99%; melting point: 95-97 ℃;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 2H), 3.99 (dd, *J* = 8.9, 5.5 Hz, 2H);

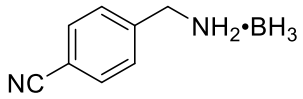
^{1}H{B} NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 4.24 (s, 2H), 4.06 - 3.90 (m, 2H), 1.64 (s, 3H);

^{11}B NMR (193 MHz, $CDCl_3$) δ -18.60 (m, *J* = 65.6 Hz);

^{11}B{H} NMR (193 MHz, $CDCl_3$) δ -18.55;

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.40, 131.17(q, *J* = 33.22), 128.84, 126.23(q, *J* = 135.9), 123.75, 52.40.

^{19}F{H} NMR (377 MHz, DMSO) δ -60.97.



Following the general procedure, reaction time: 20 h.

2k: white solid, 60%, melting point: 150-153℃;

^{1}H NMR (400 MHz, DMSO) δ 7.87 – 7.78 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 5.81 (s, 2H), 3.75 – 3.61 (m, 2H).

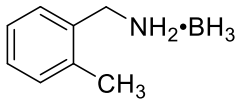
^{1}H{B} NMR (400 MHz, DMSO) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 5.80 (s, 2H), 3.75 – 3.65 (m, 2H), 1.39 (t, *J* = 3.7 Hz, 3H).

^{11}B NMR (128 MHz, DMSO) δ -18.95;

^{11}B{H} NMR (101 MHz, DMSO) δ -18.98;

^{13}C NMR (101 MHz, DMSO) δ 143.32, 132.56, 129.87, 119.25, 110.65, 51.49.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_8H_9N_2$) requires *m/z* = 133.0766, found *m/z* = 133.0766.



Following the general procedure, reaction time: 4 h.

2l[5]: white solid, 62%; melting point: 109-112℃;

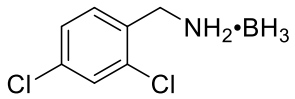
^{1}H NMR (300 MHz, DMSO) δ 7.33 - 7.28 (m, 1H), 7.17 - 7.12 (m, 3H), 5.53 (s, 2H), 3.62 - 3.54 (m, 2H), 2.27 (s, 3H);

^{1}H{B} NMR (600 MHz, DMSO) δ 7.32 (d, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 5.7 Hz, 3H), 5.52 (s, 2H), 3.62 - 3.58 (m, 2H), 2.29 (s, 3H), 1.43 (t, *J* = 3.3 Hz, 3H);

^{11}B NMR (193 MHz, DMSO) δ -18.73 (m, *J* = 86.9 Hz);

^{11}B{H} NMR (193 MHz, DMSO) δ -18.66;

^{13}C NMR (151 MHz, DMSO) δ 136.53, 135.93, 130.40, 129.36, 127.94, 126.19, 49.37, 19.24.



Following the general procedure, reaction time: 5 min.

2m: white solid, 89%; melting point: 98-100℃

^{1}H NMR (300 MHz, DMSO) δ 7.63 - 7.39 (m, 3H), 5.73 (s, 2H), 3.75 - 3.65 (m, 2H);

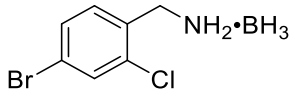
^{1}H{B} NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 5.71 (d, *J* = 11.3 Hz, 2H), 3.73 - 3.66 (m, 2H), 1.38 (s, 3H);

^{11}B NMR (193 MHz, DMSO) δ -18.88;

^{11}B{H} NMR (193 MHz, DMSO) δ -18.88;

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.93, 138.86, 138.16, 136.89, 133.75, 132.46, 53.13.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_7H_8NCl_2$) requires *m/z* = 18.0034, found *m/z* = 178.0031



Following the general procedure, reaction time: 1 h.

2n: white solid, 54%; melting point: 103-106°C;

^{1}H NMR (300 MHz, DMSO) δ 7.71 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 5.71 (s, 2H), 3.72 - 3.62 (m, 2H);

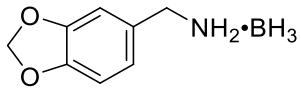
^{1}H{B} NMR (400 MHz, DMSO) δ 7.68 (d, *J* = 28.9 Hz, 1H), 7.55 (dd, *J* = 16.0, 6.9 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 5.71 (s, 2H), 3.73 - 3.66 (m, 2H), 1.40 (s, 3H).

^{11}B NMR (128 MHz, DMSO) δ -18.71.

^{11}B{H} NMR (128 MHz, DMSO) δ -18.71.

^{13}C NMR (101 MHz, DMSO) δ 134.55, 134.29, 132.42, 131.70, 130.61, 121.55, 48.45.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ (C_7H_8NClBr) requires *m/z* = 218.9529, found *m/z* = 218.9525.



Following the general procedure, reaction time: 7 h.

2o: yellow oil, 66%;

^{1}H NMR (400 MHz, DMSO) δ 6.97 (t, *J* = 3.4 Hz, 1H), 6.92 - 6.77 (m, 2H), 5.98 (s, 2H), 5.55 (s, 2H), 3.52 - 3.48 (m, 2H);

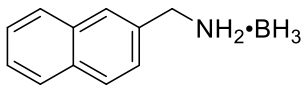
^{1}H{B} NMR (400 MHz, DMSO) δ 6.98 (d, *J* = 0.9 Hz, 1H), 6.91 – 6.81 (m, 2H), 5.98 (s, 2H), 5.53 (s, 2H), 3.52 -3.48 (m, 2H), 1.36 (t, *J* = 3.7 Hz, 3H);

^{11}B NMR (128 MHz, DMSO) δ -19.36;

^{11}B{H} NMR (128 MHz, DMSO) δ -19.39;

^{13}C NMR (101 MHz, DMSO) δ 147.52, 146.96, 131.62, 122.50, 109.49, 108.38, 101.33, 51.92.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_8H_{10}NO_2$) requires *m/z* = 152.0712, found *m/z* = 152.0712.



Following the general procedure, reaction time: 4 h.

2p: solid white, 56%; melting point: 108-110°C;

^{1}H NMR (300 MHz, DMSO) δ 7.96 - 7.76 (m, 4H), 7.62 - 7.40 (m, 3H), 5.78 (s, 2H), 3.85 - 3.70 (m, 2H);

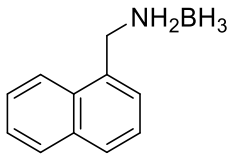
^{1}H{B} NMR (600 MHz, DMSO) δ 7.96 - 7.76 (m, 4H), 7.62 - 7.40 (m, 3H), 5.78 (s, 2H), 3.85 - 3.70 (m, 2H), 1.45(s, 3H,);

^{11}B NMR (193 MHz, DMSO) δ -18.60;

^{11}B{H} NMR (193 MHz, DMSO) δ -18.92.

^{13}C NMR (151 MHz, DMSO) δ 135.36, 133.18, 132.76, 128.19, 128.12, 127.99, 127.56, 127.15, 126.70, 126.45, 52.26.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}N$) requires *m/z* = 158.0970, found *m/z* = 158.0967.



Following the general procedure, reaction time: 16 h.

2q: white solid, 96%; melting point: 170-172℃;

^{1}H NMR (400 MHz, DMSO) δ 7.94 (dd, *J* = 50.1, 21.4 Hz, 3H), 7.69 - 7.44 (m, 4H), 5.79 (s, 2H), 4.09 (t, *J* = 19.5 Hz, 2H);

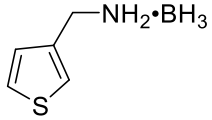
^{1}H{B} NMR (400 MHz, DMSO) δ 8.16 - 7.86 (m, 3H), 7.54 (dd, *J* = 19.6, 12.7 Hz, 4H), 5.78 (s, 2H), 4.12 (d, *J* = 4.8 Hz, 2H), 1.57 (s, 3H);

^{11}B NMR (128 MHz, DMSO) δ -18.64;

^{11}B {H} NMR (128 MHz, DMSO) δ -18.74;

^{13}C NMR (101 MHz, DMSO) δ 133.64, 133.46, 131.28, 129.00, 128.51, 126.91, 126.35, 125.79, 123.78, 49.04.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}N$) requires *m/z* = 158.0970, found *m/z* = 158.0970.



Following the general procedure, reaction time: 4 h.

2r: white solid, 88%; melting point: 135-137℃

^{1}H NMR (400 MHz, DMSO) δ 7.51 - 7.46 (m, 1H), 7.44 (s, 1H), 7.18 (d, *J* = 4.9 Hz, 1H), 5.64 (s, 2H), 3.64 - 3.57 (m, 2H);

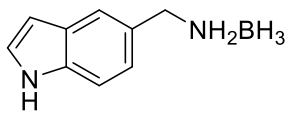
^{1}H{B} NMR (400 MHz, DMSO) δ 7.48 (d, *J* = 4.3 Hz, 1H), 7.44 (s, 1H), 7.18 (d, *J* = 4.9 Hz, 1H), 5.63 (s, 2H), 3.65 - 3.57 (m, 2H), 1.39 (s, 3H);

^{11}B NMR (128 MHz, DMSO) δ -18.77;

^{11}B{H} NMR (128 MHz, DMSO) δ -18.73;

^{13}C NMR (101 MHz, DMSO) δ 138.87, 128.60, 126.5, 123.71, 47.06.

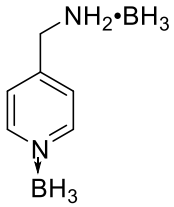
HRMS (ESI+): exact mass calculated for $[M+H]^+$ (C_5H_8NS) requires *m/z* = 114.0377, found *m/z* = 114.0381.



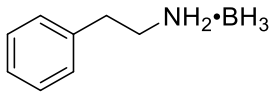
Following the general procedure, reaction time: 24 h.

2s: white solid, 39%, melting point**:** 122-123℃;

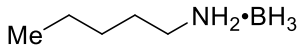
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.41 - 7.23 (m, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 4.13 - 3.98 (m, 2H), 3.85 (s, 2H);
^{1}H{B} NMR (400 MHz, DMSO) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.32 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 5.58 (s, 2H), 3.72 – 3.63 (m, 2H), 1.42 (s, 3H).;
^{11}B NMR (128 MHz, DMSO) δ -18.49;
^{11}B{H} NMR (128 MHz, DMSO) δ -18.55;
^{13}C NMR (101 MHz, DMSO) δ 130.56, 127.47, 126.07, 120.29, 120.13, 116.82, 111.98, 101.30, 52.99.
HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_9H_{11}N_2$) requires *m/z* = 147.0922, found *m/z* = 147.0921.



Following the general procedure, reaction time: 5 min.
2t: white solid, 66%; melting point: 165-168℃**;**
^{1}H NMR (400 MHz, DMSO) δ 8.55 (d, *J* = 6.5 Hz, 2H), 7.70 (d, *J* = 6.6 Hz, 2H), 5.96 (s, 2H), 3.86 - 3.74 (m, 2H);
^{1}H{B} NMR (400 MHz, DMSO) δ 8.55 (d, *J* = 6.4 Hz, 2H), 7.70 (d, *J* = 6.4 Hz, 2H), 5.95 (s, 2H), 3.82 - 3.77 (m, 2H), 2.46 (s, 3H), 1.38 (t, *J* = 3.6 Hz, 3H);
^{11}B NMR (96 MHz, DMSO) δ -19.37 (q, *J* = 94.1 Hz); -18.35 (q, *J* = 118.1Hz);
^{11}B{H} NMR (128 MHz, DMSO) δ -19.33, -18.51;
^{13}C NMR (101 MHz, DMSO) δ 150.91, 149.92, 147.27, 125.78, 123.69, 50.14.
HRMS (ESI+): exact mass calculated for $[M+Na]^+$ ($C_6H_8N_2Na$) requires *m/z* = 131.0585, found *m/z* = 131.0590.



Following the general procedure, reaction time: 10 h.
2u: yellow oil, 65%;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.2 Hz, 2H), 7.32 - 7.25 (m, 1H), 7.22 (d, *J* = 7.0 Hz, 2H), 3.63 (s, 2H), 3.10 (dt, *J* = 13.2, 6.6 Hz, 2H), 2.95 (t, *J* = 6.6 Hz, 2H);
^{1}H{B} NMR (600 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 3.64 (s, 2H), 3.11 - 3.02 (m, 2H), 2.93 (s, 2H), 1.50 (s, 3H);
^{11}B NMR (193 MHz, $CDCl_3$) δ -19.42 (q, *J* = 92.6 Hz);
^{11}B{H} NMR (193 MHz, $CDCl_3$) δ -19.43;
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.83, 129.17, 128.78, 127.29, 49.42, 34.62.
HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_8H_{12}N$) requires *m/z* = 122.0970, found *m/z* = 122.0972.



Following the general procedure, reaction time: 40 h.

2v: white solid, 61%, melting point: 103-105℃;

^{1}H NMR (400 MHz, DMSO) δ 5.08 (s, 2H), 1.51 – 1.44 (m, 2H), 1.23 (s, 6H), 0.85 (t, *J* = 5.8 Hz, 3H).

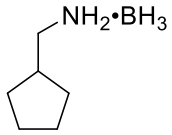
^{1}H{B} NMR (400 MHz, DMSO) δ 5.09 (s, 2H), 1.49 (s, 2H), 1.27 (s, 9H), 0.88 (dd, *J* = 13.5, 6.7 Hz, 3H).

^{11}B NMR (128 MHz, DMSO) δ -19.50 (m, *J* = 74.2 Hz);

^{11}B{H} NMR (128 MHz, DMSO) δ -19.52;

^{13}C NMR (101 MHz, DMSO) δ 48.22, 28.91, 28.11, 22.27, 14.24.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_5H_{14}N$) requires *m/z* = 88.1126, found *m/z* = 88.1126.



Following the general procedure, reaction time: 40 h.

2w: white solid, 61%; melting point: 106-107℃;

^{1}H NMR (400 MHz, DMSO) δ 5.06 (s, 2H), 2.36 (s, 2H), 2.01 (d, *J* = 7.0 Hz, 1H), 1.68 (s, 2H), 1.48 (dd, *J* = 21.2, 8.6 Hz, 4H), 1.11 (s, 2H);

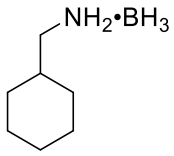
^{1}H{B} NMR (400 MHz, DMSO) δ 5.04 (s, 2H), 2.36 (s, 2H), 2.02 (s, 1H), 1.69 (s, 2H), 1.50 (d, *J* = 25.7 Hz, 4H), 1.29 (s, 3H), 1.11 (s, 2H);

^{11}B NMR (128 MHz, DMSO) δ-19.20 (m, *J* = 67.8Hz);

^{11}B{H} NMR (128 MHz, DMSO) δ -19.20;

^{13}C NMR (101 MHz, DMSO) δ 53.60, 38.99, 30.57, 25.08.

HRMS (ESI+): exact mass calculated for $[M+Na]^+$ ($C_6H_{13}NNa$) requires *m/z* = 122.0946, found *m/z* = 122.0941.



Following the general procedure, reaction time: 40 h.

2x: white solid, 65%; melting point: 90-92℃;

^{1}H NMR (400 MHz, DMSO) δ 5.02 (s, 2H), 2.26 (s, 2H), 1.67 (dd, *J* = 26.3, 11.1 Hz, 4H), 1.47 (s, 1H), 1.15 (d, *J* = 13.6 Hz, 4H), 0.83 (d, *J* = 11.5 Hz, 2H).

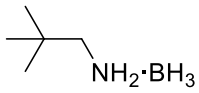
^{1}H{B} NMR (400 MHz, DMSO) δ 5.00 (s, 2H), 2.26 (s, 2H), 1.67 (dd, *J* = 25.4, 11.5 Hz, 4H), 1.48 (s, 1H), 1.28 (s, 3H), 1.23 – 0.99 (m, 4H), 0.81 (q, *J* = 11.2 Hz, 2H).

^{11}B NMR (128 MHz, DMSO) δ -19.19;

^{11}B{H} NMR (128 MHz, DMSO) δ -19.13;

^{13}C NMR (101 MHz, DMSO) δ 54.90, 36.70, 30.77, 26.35, 25.78.

HRMS (ESI+): exact mass calculated for $[M+H]^+$ ($C_7H_{16}N$) requires *m/z* = 114.1283, found *m/z* = 114.1282.



Following the general procedure, reaction time: 20 h.

2y: white solid, 59%, melting point: 130-132℃;

^{1}H NMR (400 MHz, DMSO) δ 4.93 (s, 2H), 2.35 - 2.17 (m, 2H), 0.87 (s, 9H);

^{1}H{B} NMR (400 MHz, DMSO) δ 4.93 (s, 2H), 2.35 - 2.17 (m, 2H), 1.35 (s, 3H), 0.87 (s, 9H).

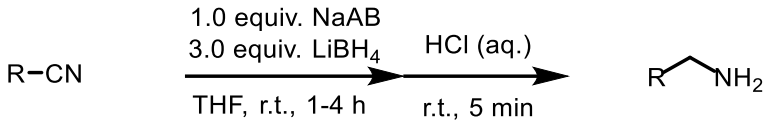
^{11}B NMR (128 MHz, DMSO) δ -18.44 (m, *J* = 85.8Hz);

^{11}B{H} NMR (128 MHz, DMSO) δ -18.43;

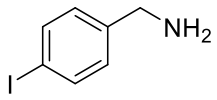
^{13}C NMR (101 MHz, DMSO) δ 60.80, 31.29, 27.67.

HRMS (ESI+): exact mass calculated for $[M+Na]^+$ ($C_5H_{13}NNa$) requires *m/z* = 110.0946, found *m/z* = 110.0945.

3. One-Pot synthesis of primary amines



In an argon-filled glovebox, sodium amidoborane (0.2 mmol), lithium borohydride (0.6 mmol) were added in a 10-ml Schlenk flask and then the flask was removed out of the box. THF (4 ml) and nitriles (0.2 mmol) were added sequentially to the flask under N_2. Then the reaction mixture was allowed to stirred at room temperature. After completion of the reaction indicated by TLC. 1 mL aqueous solution of HCl (wt%: 36%) was added to the reaction mixture. The mixture was allowed to stir for 5 minutes and then 10 mL saturated $NaHCO_3$ (aq.) was added into the mixture, followed by extraction with ethyl acetate and water. The organic mixture was concentrated under reduced pressure and purified by silica gel flash chromatography with 1:1 petroleum ether: ethyl acetate to give hydrolysis product.

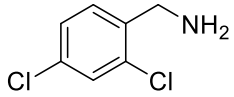


Following the general procedure, reaction time: 1 h.

3a[6]**:** white solid, 78%

^{1}H NMR (400 MHz, DMSO) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.69 (d, *J* = 24.3 Hz, 2H), 3.14 (s, 2H);

^{13}C NMR (101 MHz, DMSO) δ 144.26, 137.21, 130.02, 92.16, 45.38.

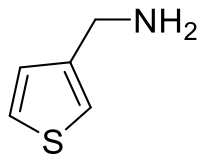


Following the general procedure, reaction time: 5 min.

3b[7]: white solid, 88%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 - 7.03 (m, 3H), 3.91 (s, 2H), 1.62 (s, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.16, 133.94, 133.13, 129.72, 129.29, 127.29, 43.90.



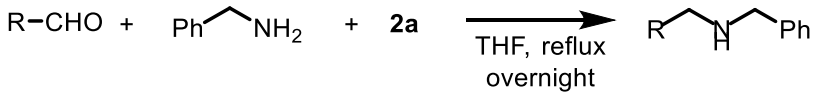
Following the general procedure, reaction time: 4h.

3c[8]: yellow oil, 77%

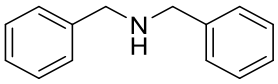
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 4.8, 2.9 Hz, 1H), 7.20 (s, 1H), 7.01 (t, *J* = 5.8 Hz, 1H), 3.78 (s, 2H), 2.18 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 127.68, 126.32, 125.86, 122.05, 47.92.

4. Synthesis of secondary amines through reductive amination



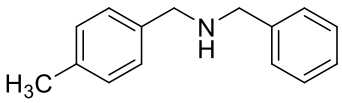
Aldehyde (0.5mmol), benzyl amine-borane (0.5 mmol) were added in a 10-ml reaction flask. THF (3 ml) and benzylamine (0.55mmol) were added sequentially to the flask. Then the reaction mixture was allowed to stirred overnight under reflux condition. After completion of the reaction indicated by TLC, violates was then evaporated under reduced pressure and the residue was purified by flash chromatography on aluminum oxide. (petroleum ether: ethyl acetate = 1:1)



4a[9]: yellow oil, 56%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.22 (m, 10H), 3.91 (s, 4H), 1.72 (s, 1H).

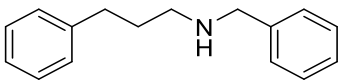
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.48, 128.50, 128.26, 127.04, 53.28.



4b[9]: yellow oil, 70%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.16 (m, 9H), 3.89 (d, *J* = 4.4 Hz, 2H), 3.86 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.44, 137.33, 136.57, 129.18, 128.48, 128.27, 128.23, 127.02, 53.16, 21.20.



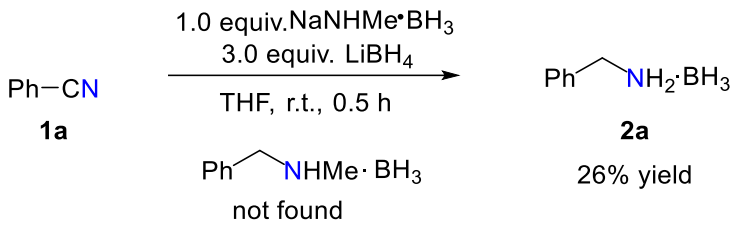
4c[10]: white solid, 70%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 -7.20 (m, 10H), 3.84 (s, 2H), 2.83 - 2.66 (m, 4H), 1.97 - 1.86 (m, 2H), 1.62 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.27, 132.01, 129.96, 128.98, 128.94, 128.50, 128.37, 126.20, 51.19, 45.99, 32.85, 28.06.

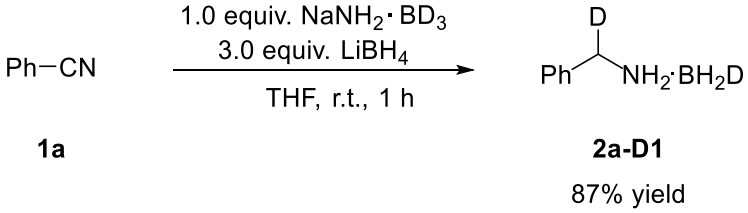
5. Preliminary mechanism study:

a) Reaction with $NaNHMe{\bullet}BH_3$



In an argon-filled glovebox, $NaNHMeBH_3$ (0.2 mmol), $LiBH_4$ (0.6 mmol) were added in a 10-ml Schlenk flask and then the flask was removed out of the box. THF (4 ml) and nitriles (0.2 mmol) were added sequentially to the flask under N_2. Then the reaction mixture was allowed to stirred at room temperature. After completion of the reaction indicated by TLC, violates was then evaporated under reduced pressure and the residue was purified by flash chromatography on aluminum oxide. (petroleum ether: ethyl acetate = 4:1)

b) Reaction with $NaNH_2{\bullet}BD_3$



In an argon-filled glovebox, sodium $NaNH_2BD_3$ (0.2 mmol), $LiBH_4$ (0.6 mmol) were added in a 10-ml Schlenk flask and then the flask was removed out of the box. THF (4 ml) and nitriles (0.2 mmol) were added sequentially to the flask under N_2. Then the reaction mixture was allowed to stirred at room temperature. After completion of the reaction indicated by TLC, violates was then evaporated under reduced pressure and the residue was purified by flash chromatography on aluminum oxide. (petroleum ether: ethyl acetate = 4:1)

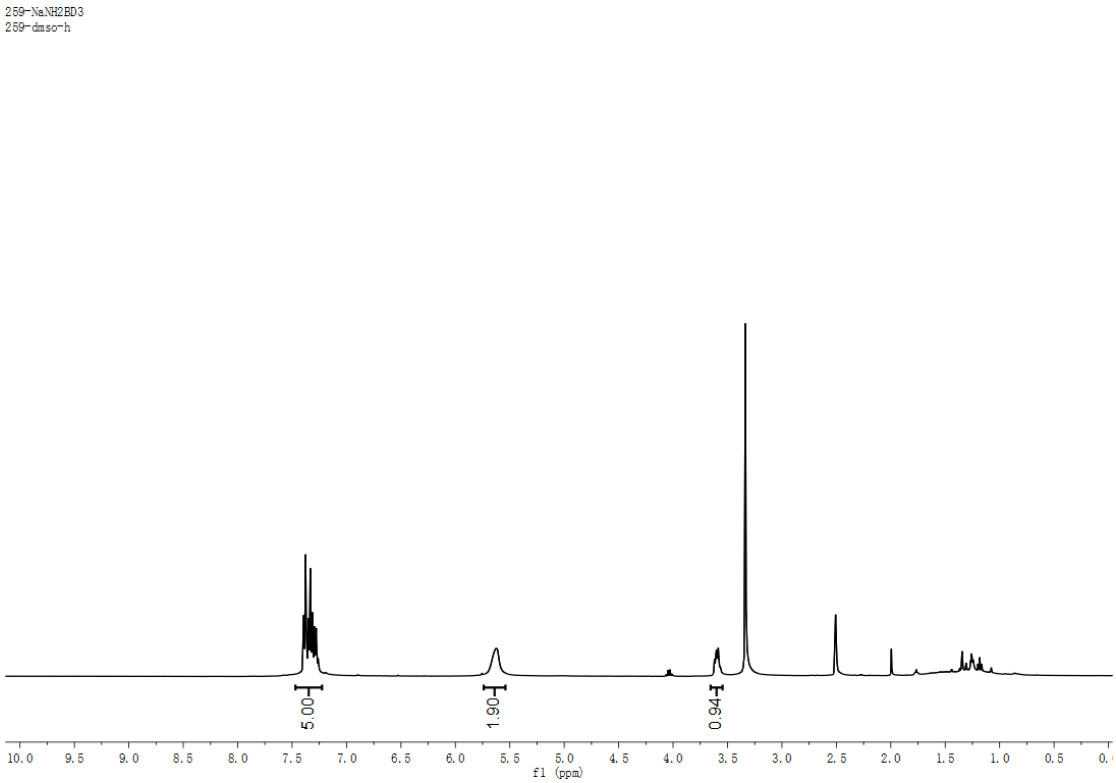


Figure S1. The ^{1}H NMR spectra of **2a-D1** in d_6-DMSO.

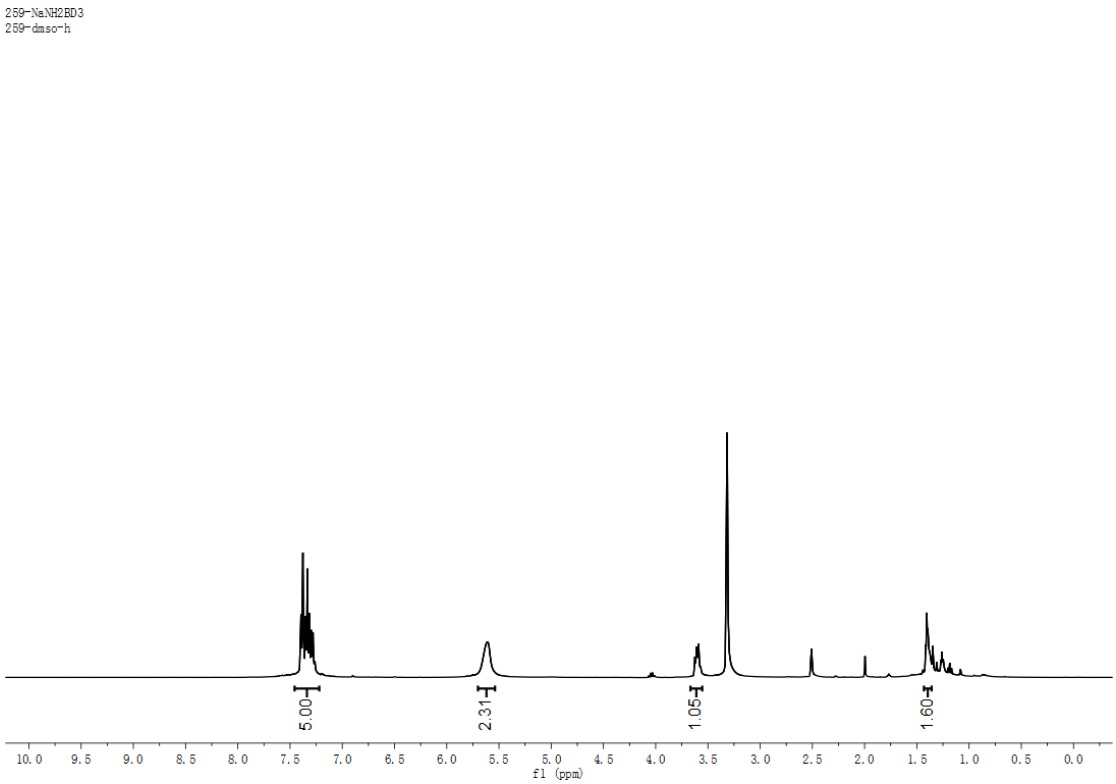
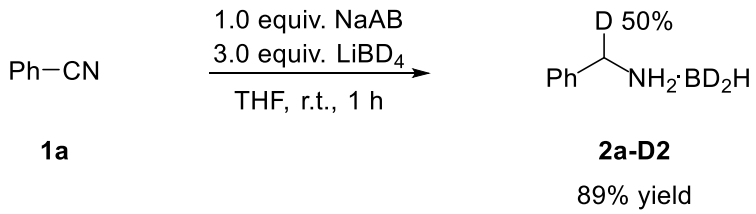


Figure S2. The ^{1}H{B} NMR spectra of **2a-D1** in d_6-DMSO.

c) Reaction with $LiBD_4$



In an argon-filled glovebox, sodium $NaNH_2BH_3$ (0.2 mmol), $LiBD_4$ (0.6 mmol) were added in a 10-ml Schlenk flask and then the flask was removed out of the box. THF (4 ml) and nitriles (0.2 mmol) were added sequentially to the flask under N_2. Then the reaction mixture was allowed to stirred at room temperature. After completion of the reaction indicated by TLC, violates was then evaporated under reduced pressure and the residue was purified by flash chromatography on aluminum oxide. (petroleum ether: ethyl acetate = 4:1)

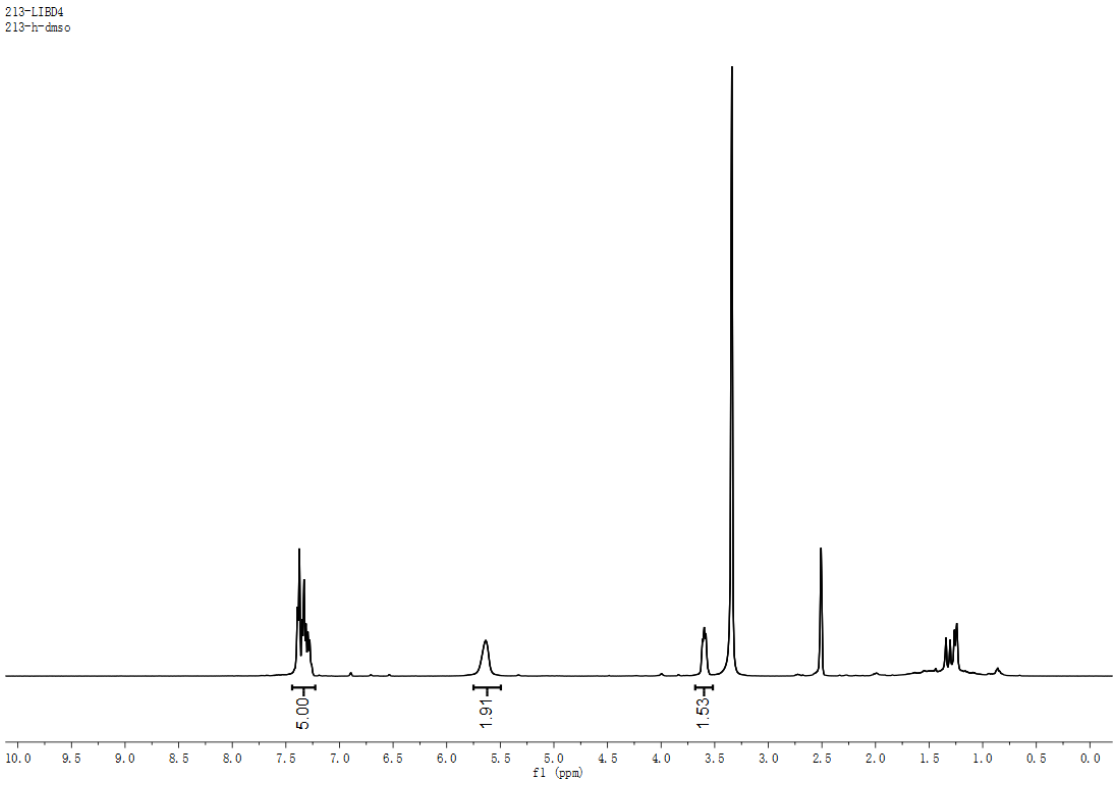


Figure S3. The ^1H NMR spectra of **2a-D2** in d_6-DMSO.

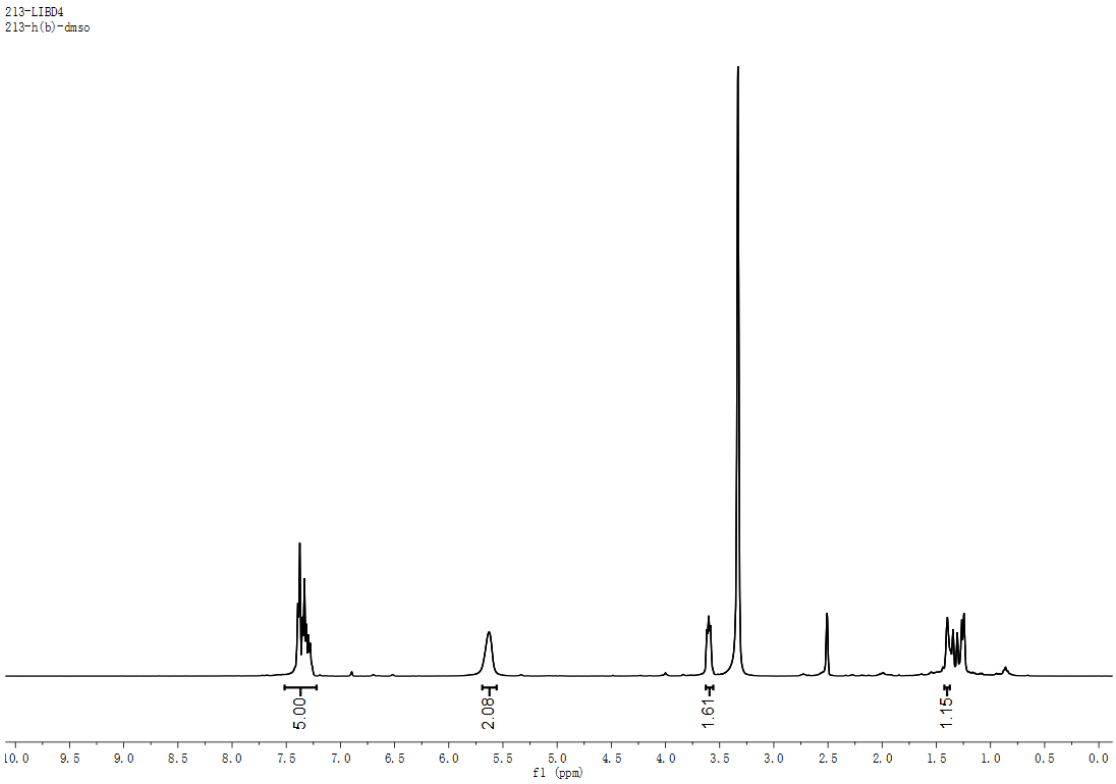
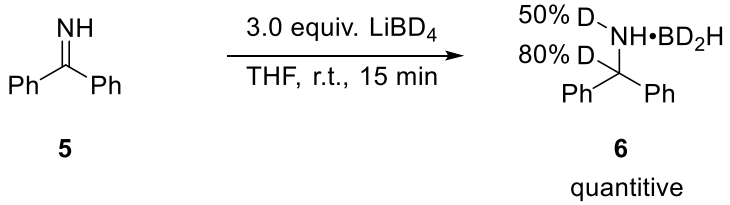


Figure S4. The $^{1}H\{B\}$ NMR spectra of **2a-D2** in d_6-DMSO.

d) Reaction of diphenylmethanimine and $LiBD_4$



5 **6**

quantitive

In an argon-filled glovebox, $LiBD_4$ (0.6 mmol) were added in a 10-ml Schlenk flask and then the flask was removed out of the box. THF (4 ml) and diphenylmethanimine (0.2 mmol) were added sequentially to the flask under N_2. Then the reaction mixture was allowed to stirred at room temperature. After completion of the reaction indicated by TLC, violates was then evaporated under reduced pressure and the residue was purified by flash chromatography on aluminum oxide. (petroleum ether: ethyl acetate = 4:1)

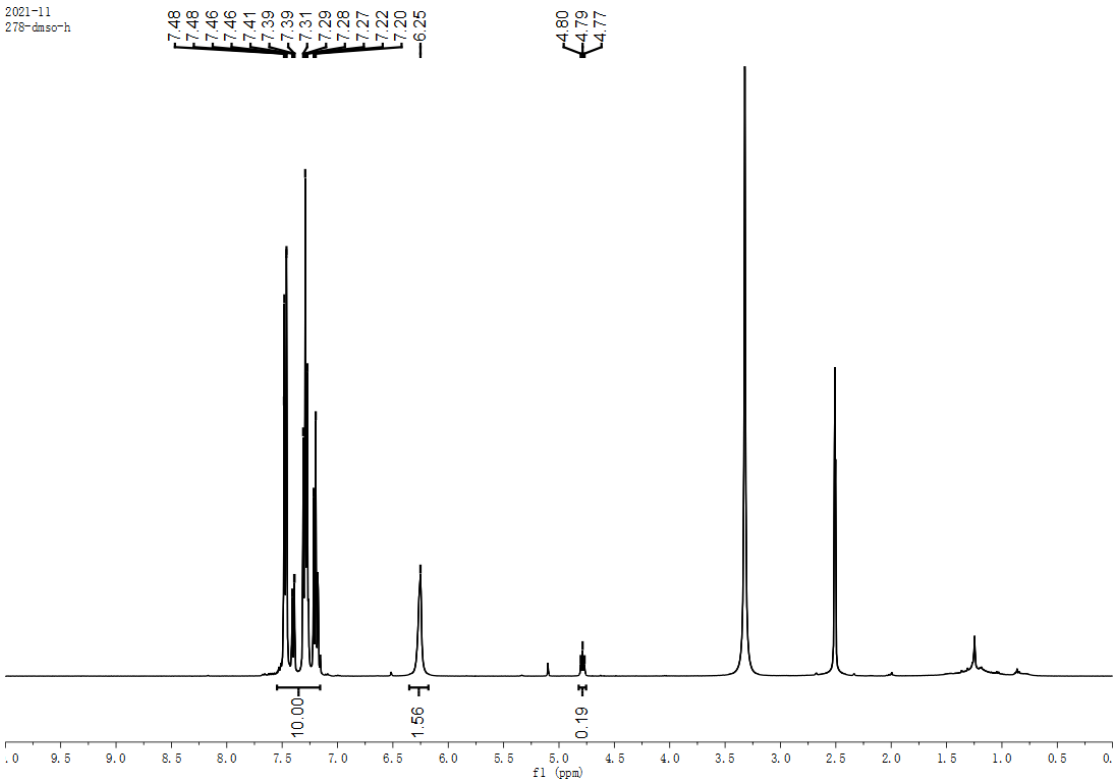


Figure S5. The ^{1}H NMR spectra of **6** in d_6-DMSO.

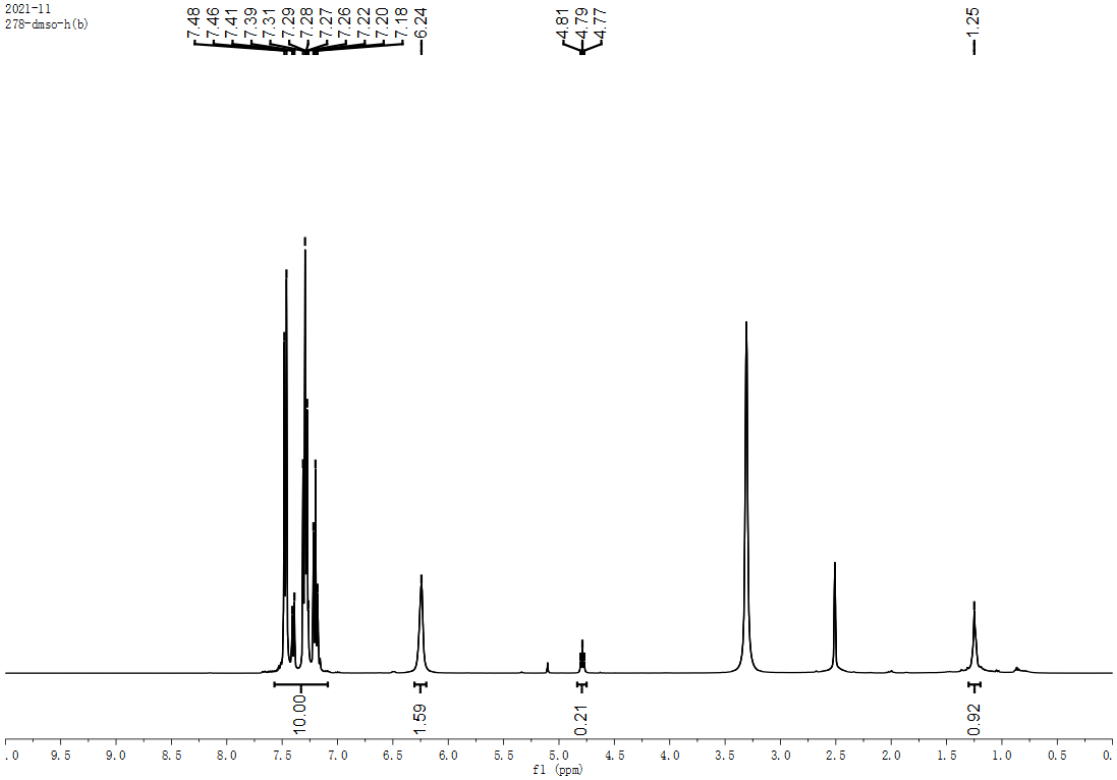


Figure S6. The ^{1}H{B} NMR spectra of **6** in d_6-DMSO.

6. References

1. J.-C. Lai, X.-Y. Jia, D.-P. Wang, Y.-B. Deng, P. Zhang, C.-H. Li, J.-L. Zuo. Z.-N. Bao, *Nature Commun*., 2019, **10**, 1164.
2. X-M. Chen, J. Wang, S. Liu, J. Zhang, D. Wei and X. Chen, *Dalton Trans.*, 2019, **48**, 14984.
3. H. C. Kelly, F. R. Marchelli and M. B. Giusto, *Inorg. Chem.,* 1964, **3**, 431.
4. K. E. Bell, C. R. Kelly, D. E. Minter and H. C. Kelly, *Inorg. Chim. Acta.,* 1993, **2**, 187.
5. K. E. Bell and H. C. Kelly, *Inorg. Chem.,* 1992, **31**, 2665.
6. S. Koushik, D. Kuhali, K. Abhishek, A. Debashi and M. Biplab, *ACS Catal.,* 2021, **11**, 2786.
7. B. Zeynizadeh, F. Mohammad Aminzadeh and H. Mousavi, *Res. Chem. Intermed.*, 2019, **45,** 3329.
8. R. Adam, E. Alberico, W. Baumann, H. J. Drexler, R. Jackstell, H. Junge and M. Beller, *Chem. Eur. J.,* 2016, **22**, 4991.
9. J. H. Cho, S. Byun, A. Cho and B. M. Kim, *Catal. Sci. Technol.,* 2020, **10**, 4201.
10. Z. Luo, Y. Pan, Z. Yao, J. Yang, X. Zhang, X. Liu, L. Xu and Q. Fan, *Green. Chem*., 2021, **23**, 5205.

7. NMR spectra:

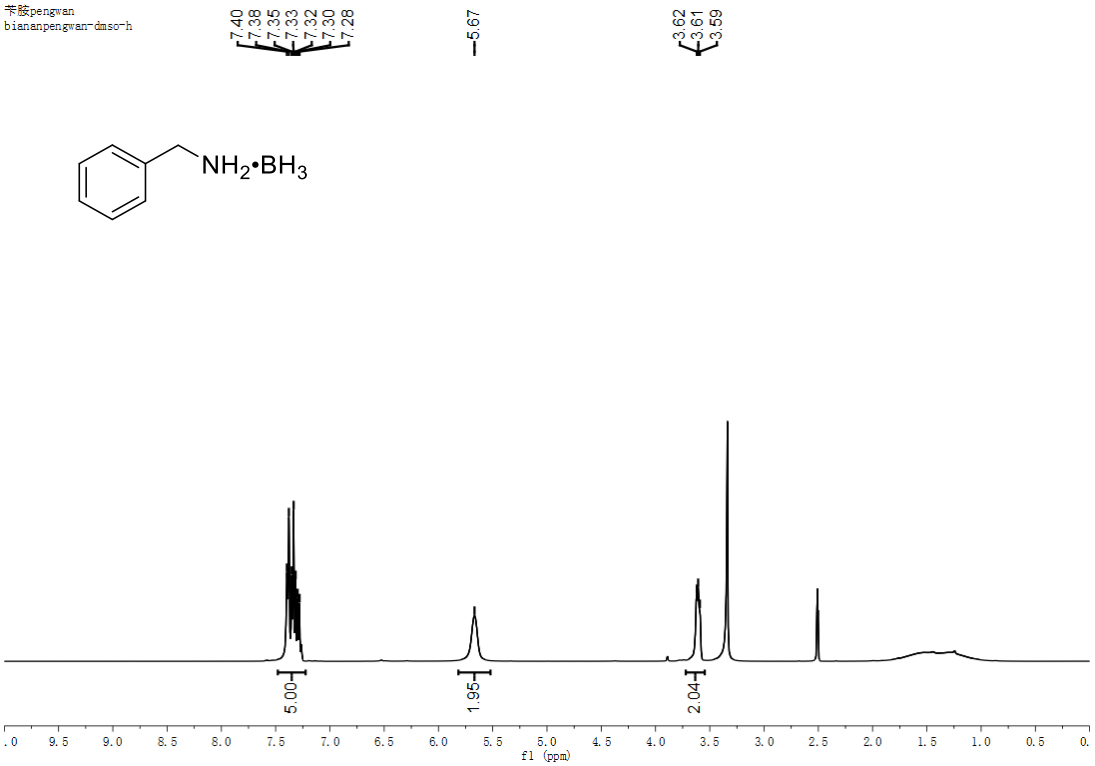


Figure S7. ^{1}H NMR spectrum of **2a** (400 MHz, DMSO)

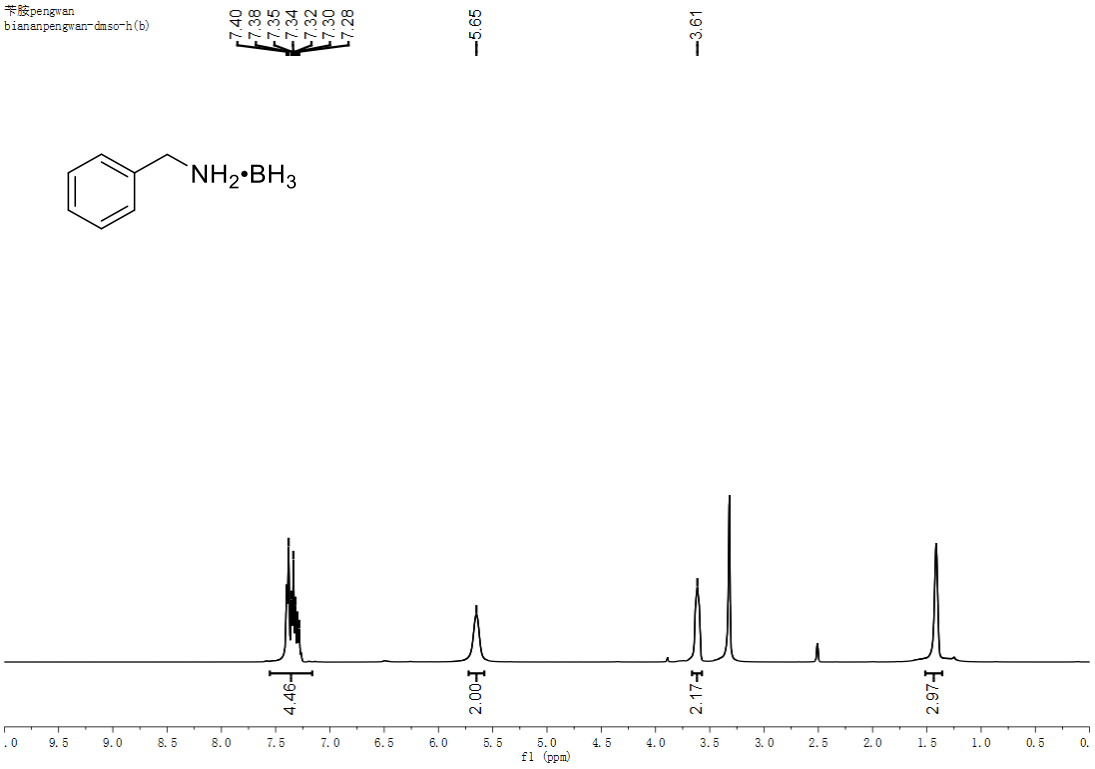


Figure S8. ^{1}H{B} NMR spectrum of **2a** (400 MHz, DMSO)

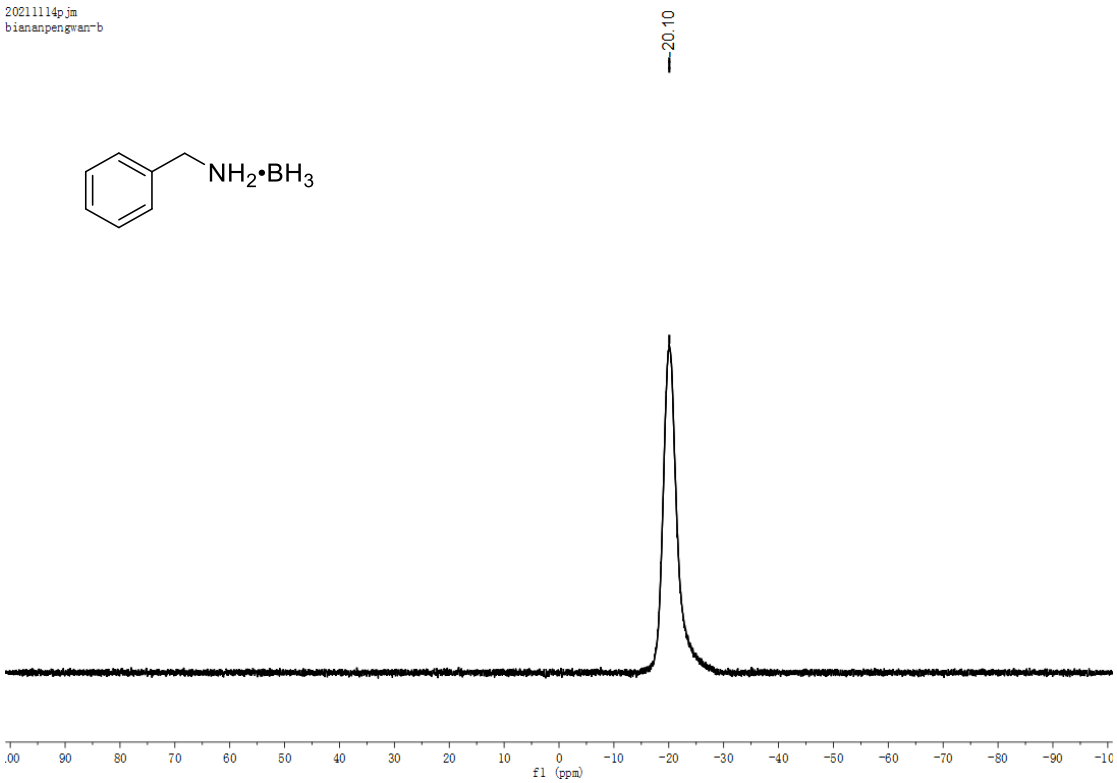


Figure S9. ^{11}B NMR spectrum of **2a** (400 MHz, DMSO)

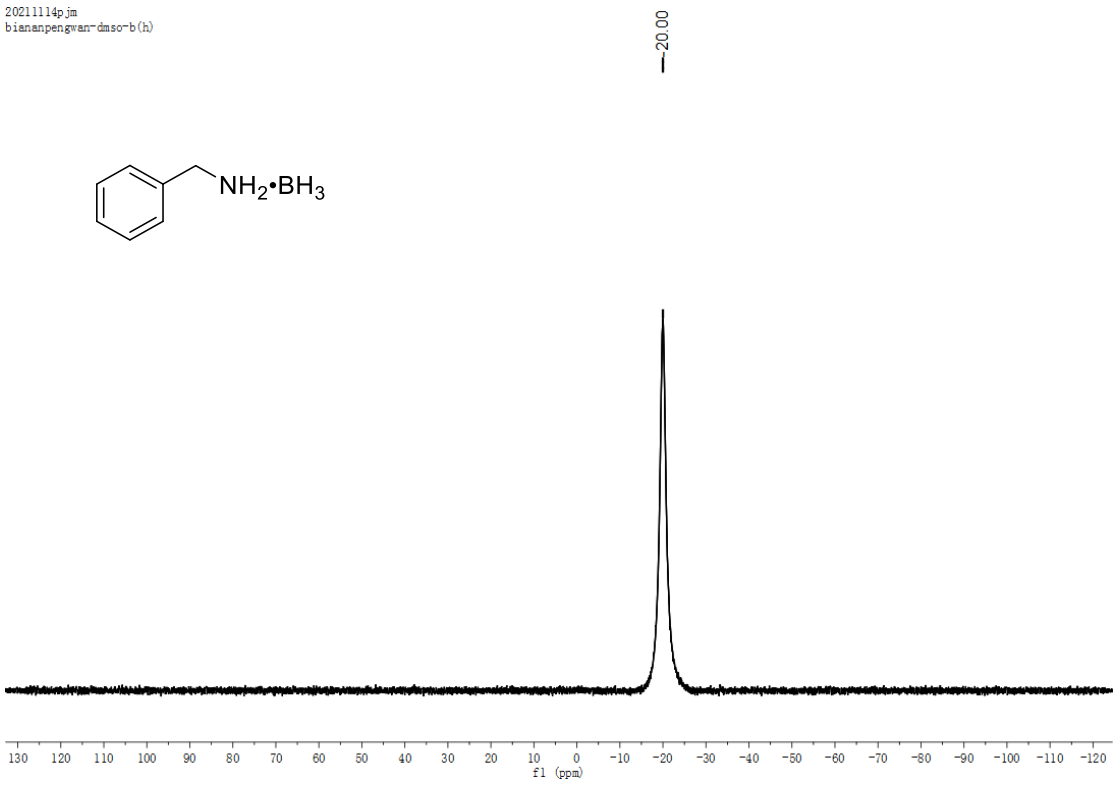


Figure S10. ^{11}B{H} NMR spectrum of **2a** (400 MHz, DMSO)

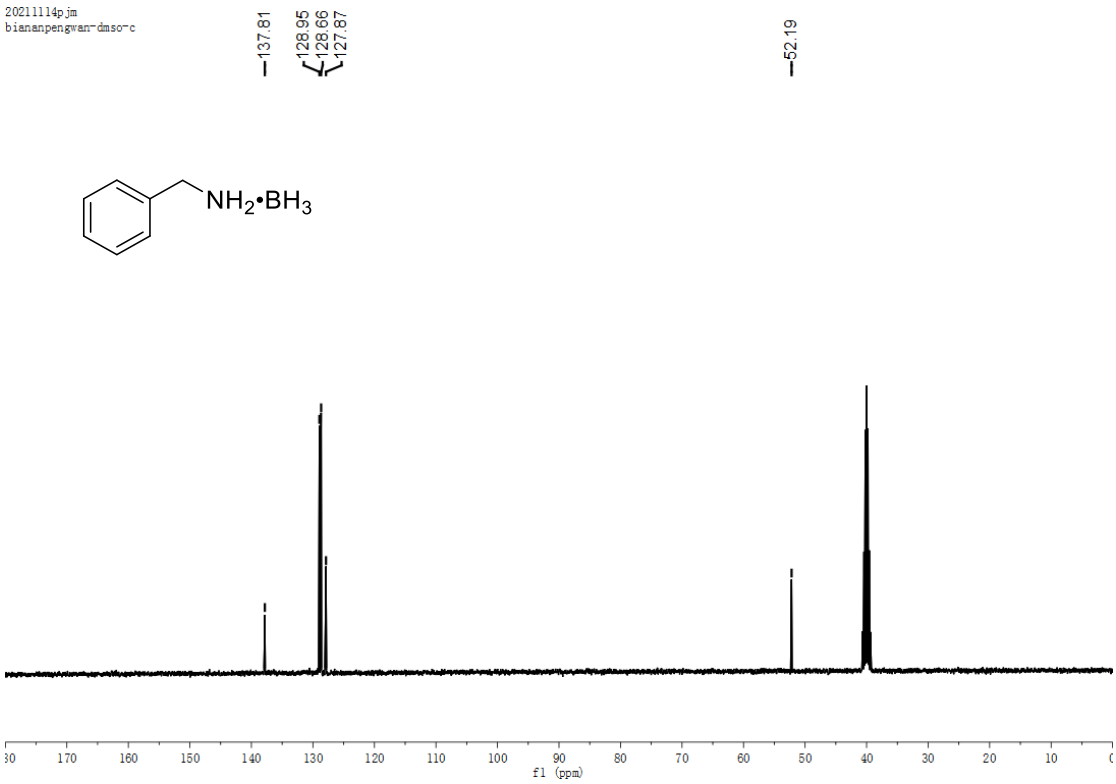


Figure S11. ^{13}C NMR spectrum of **2a** (400 MHz, DMSO)

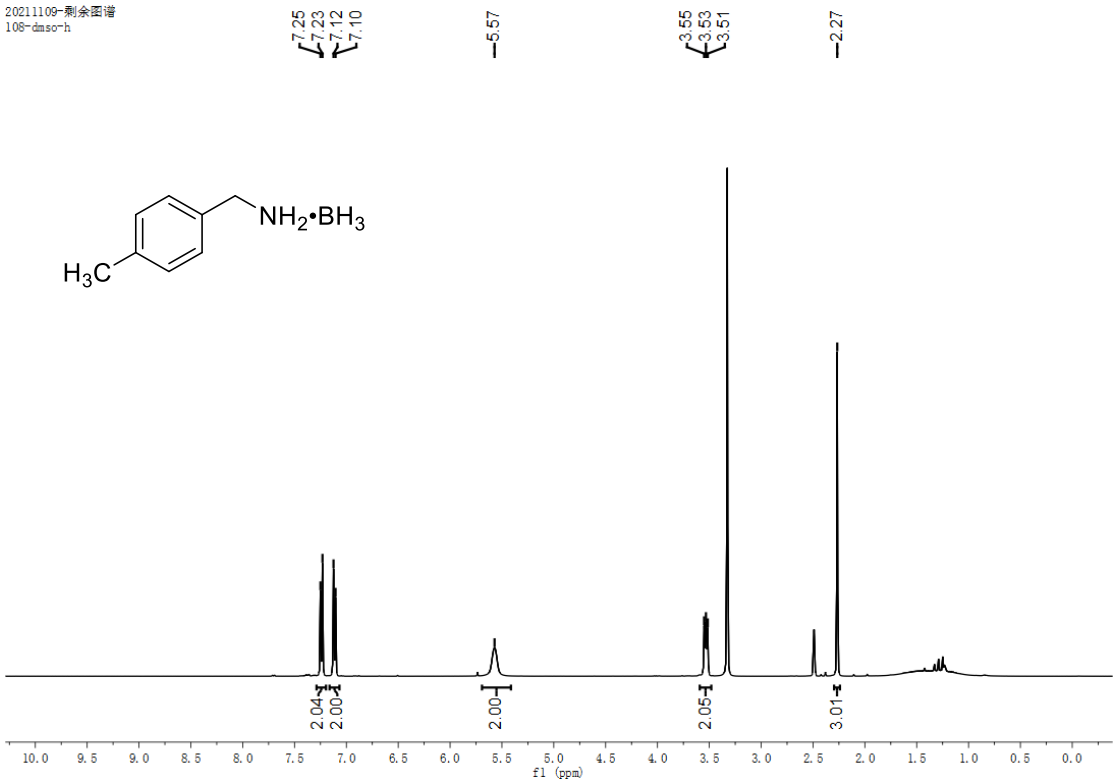


Figure S12. ^{1}H NMR spectrum of **2b** (400 MHz, DMSO)

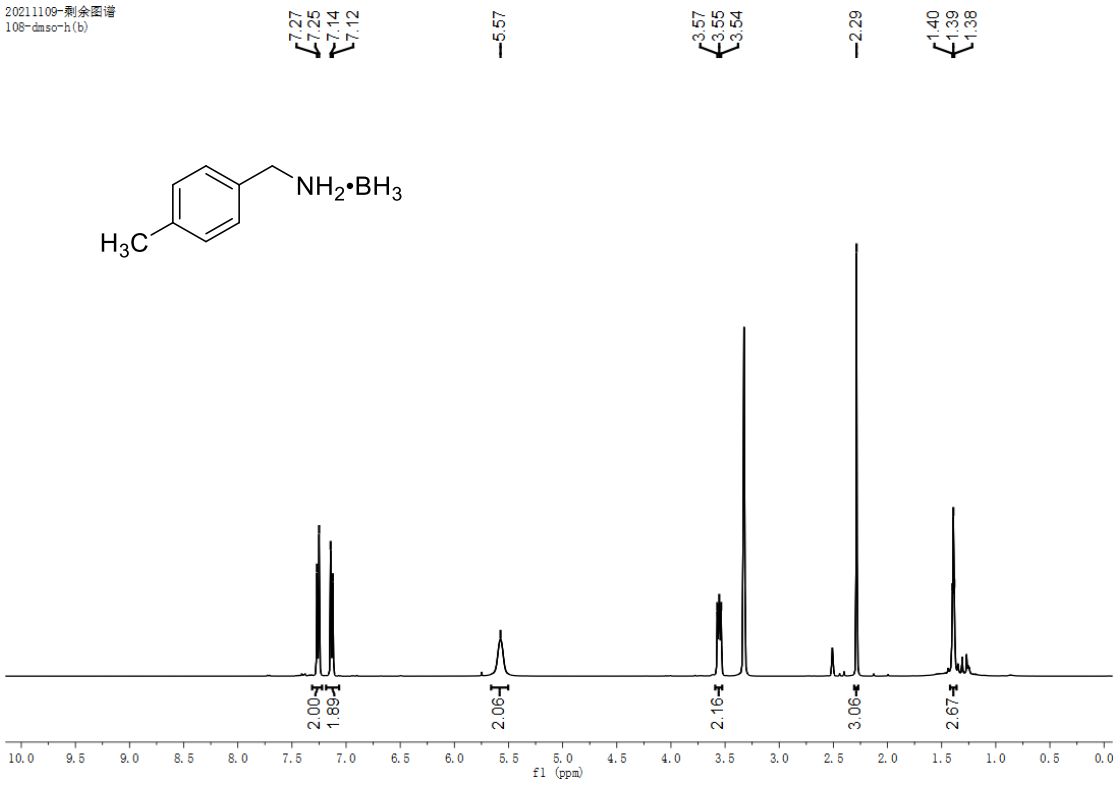


Figure S13. ^{1}H{B} NMR spectrum of **2b** (400 MHz, DMSO)

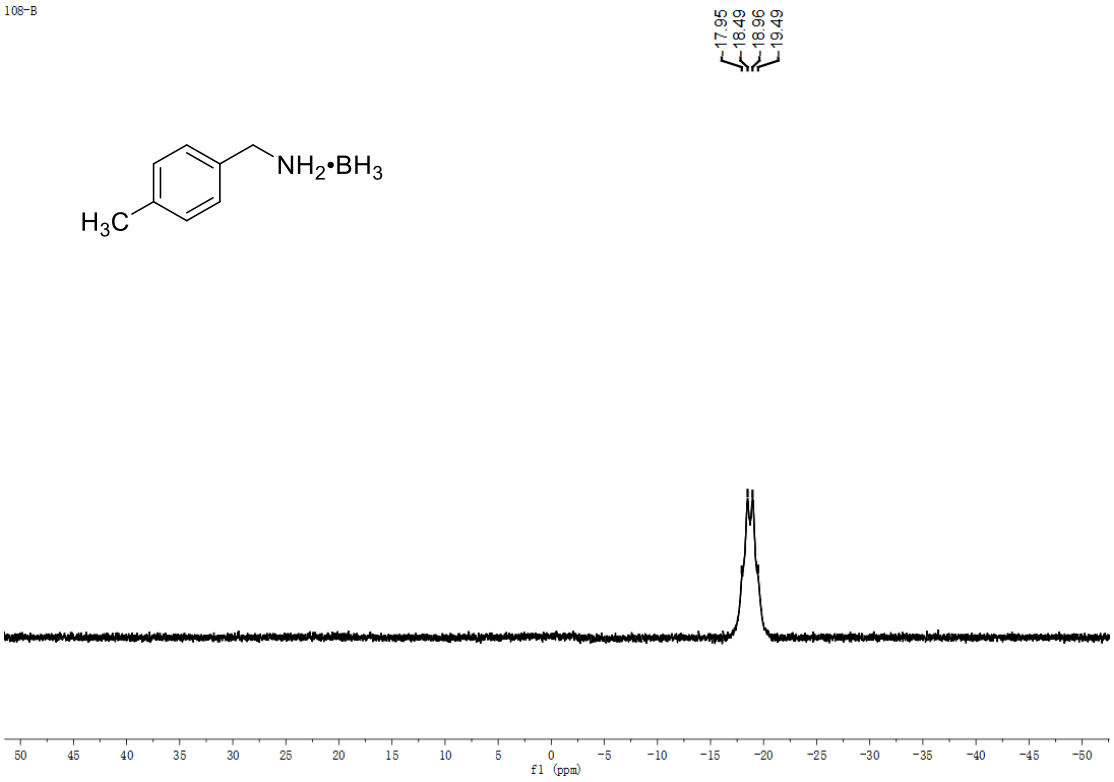


Figure S14. $^{1}H\{B\}$ NMR spectrum of **2b** (400 MHz, DMSO)

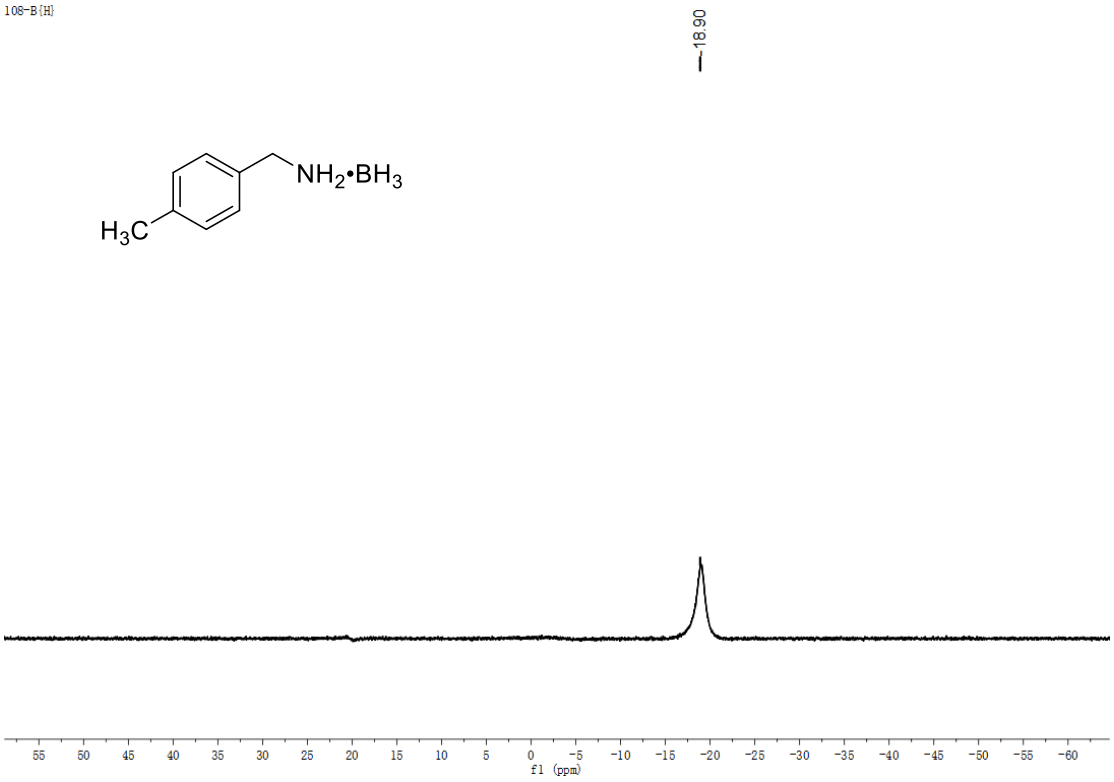


Figure S15. $^{11}B\{H\}$ NMR spectrum of **2b** (400 MHz, DMSO)

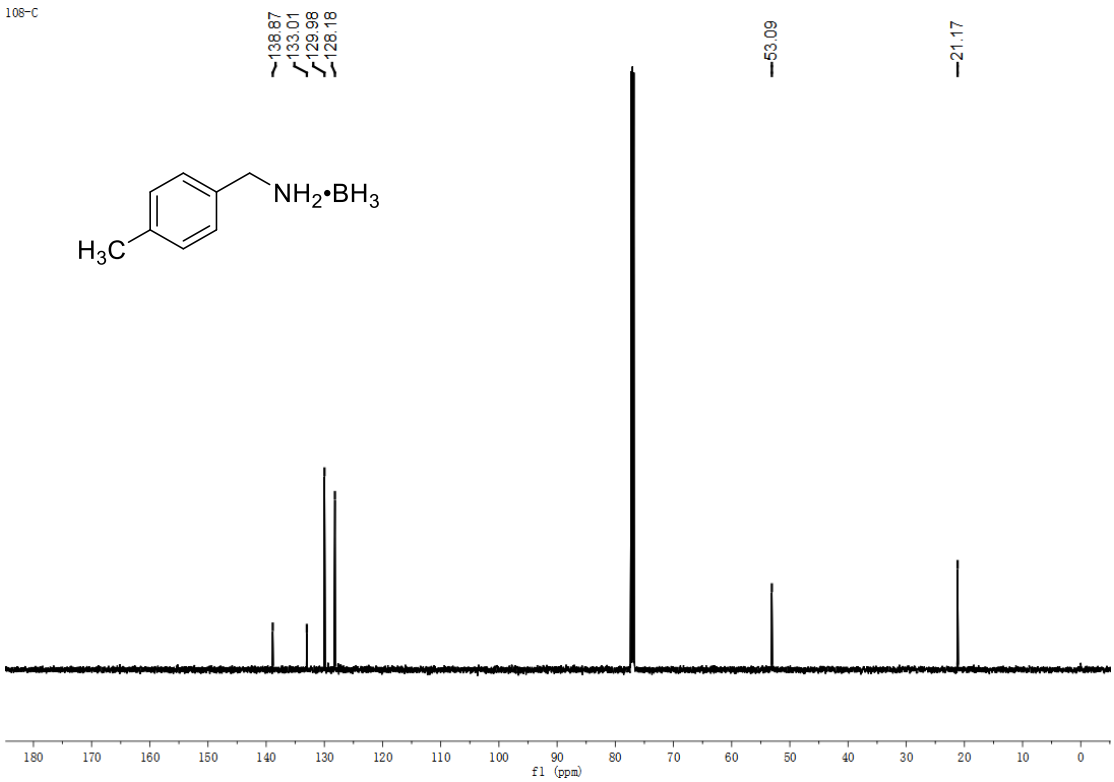


Figure S16. ^{13}C NMR spectrum of **2b** (400 MHz, DMSO)

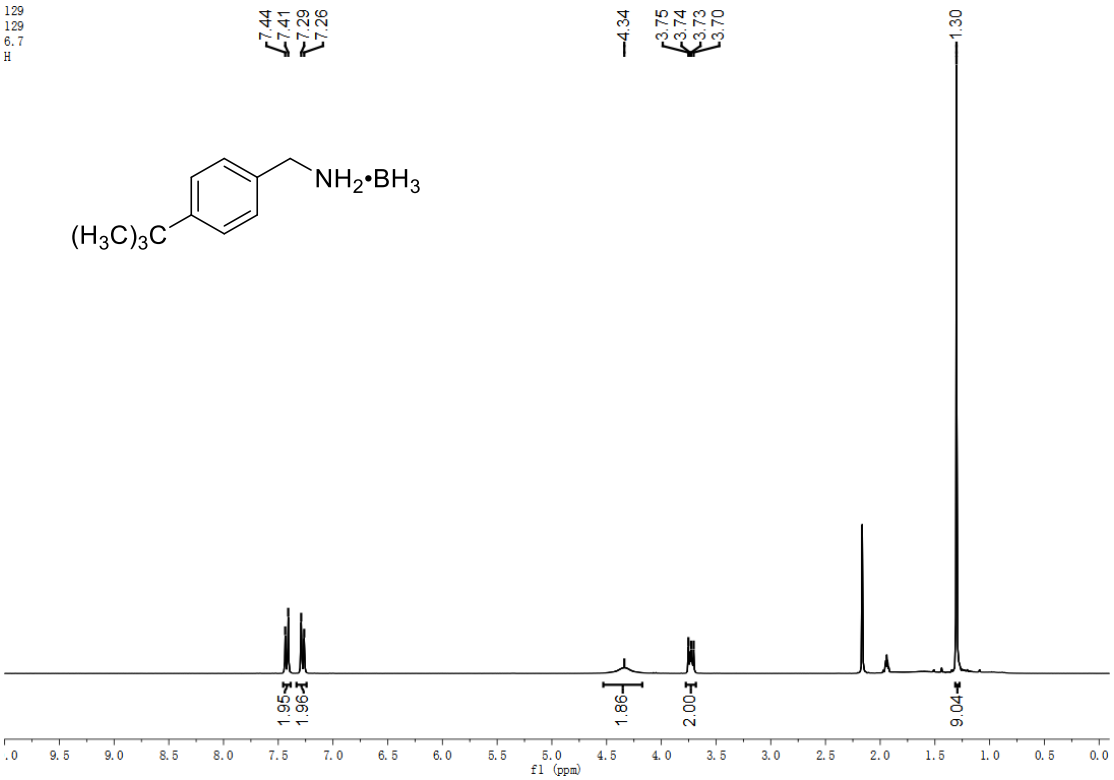


Figure S17. ^{1}H NMR spectrum of **2c** (300 MHz, DMSO)

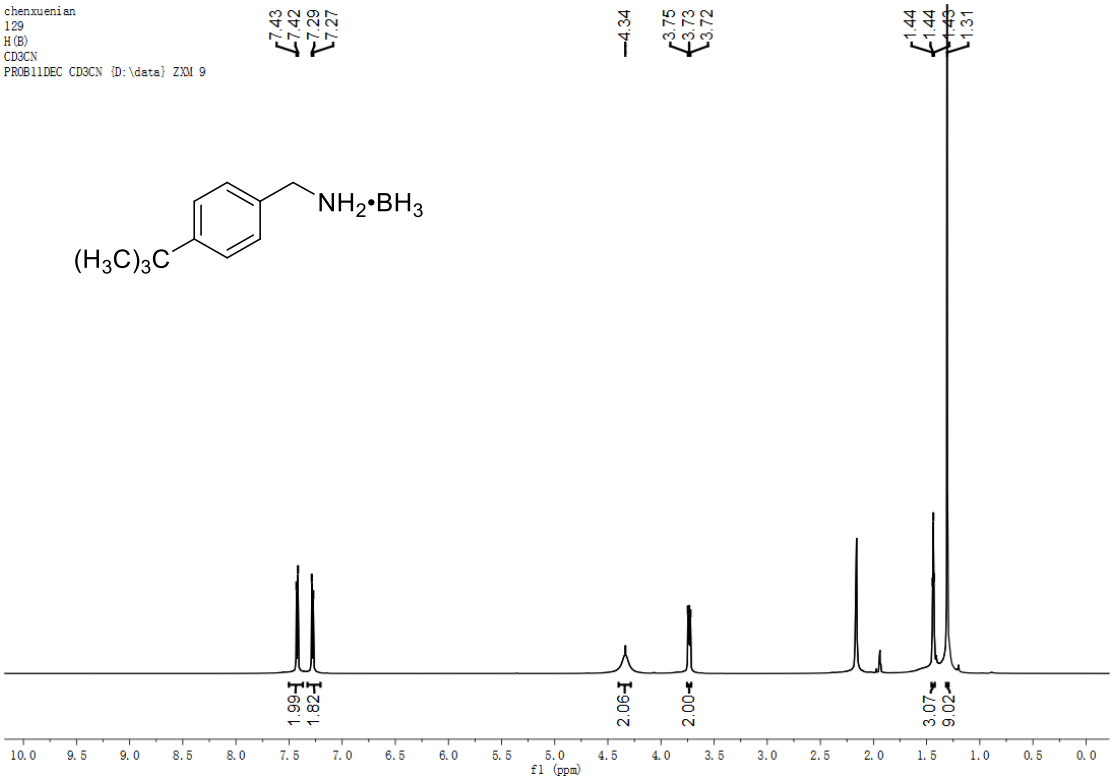


Figure S18. ^{1}H{B} NMR spectrum of **2c** (600 MHz, DMSO)

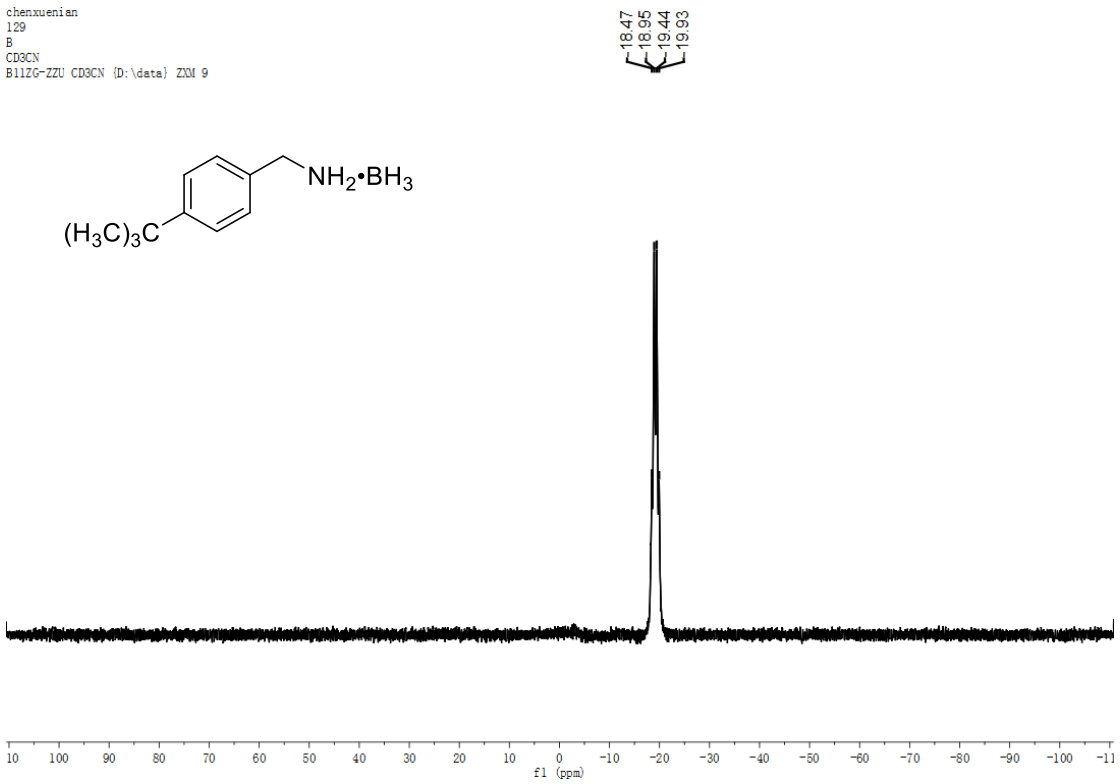


Figure S19. ^{11}B NMR spectrum of **2c** (600 MHz, DMSO)

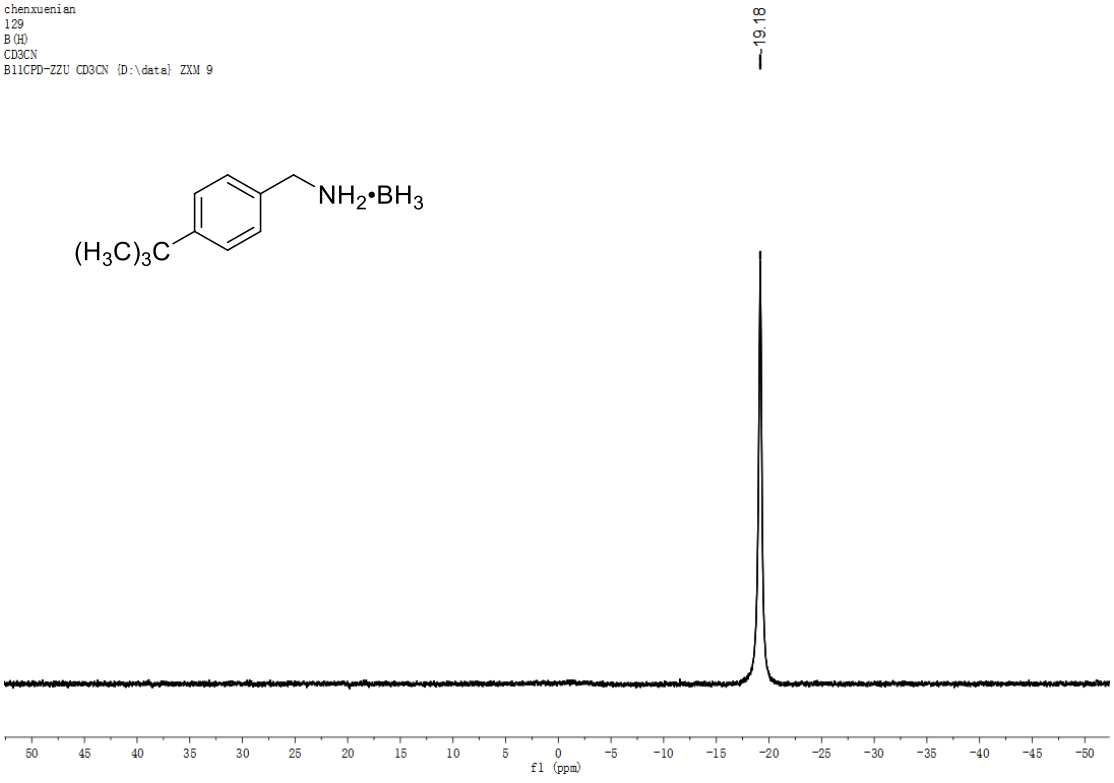


Figure S20. ^{11}B{H} NMR spectrum of **2c** (600 MHz, DMSO)

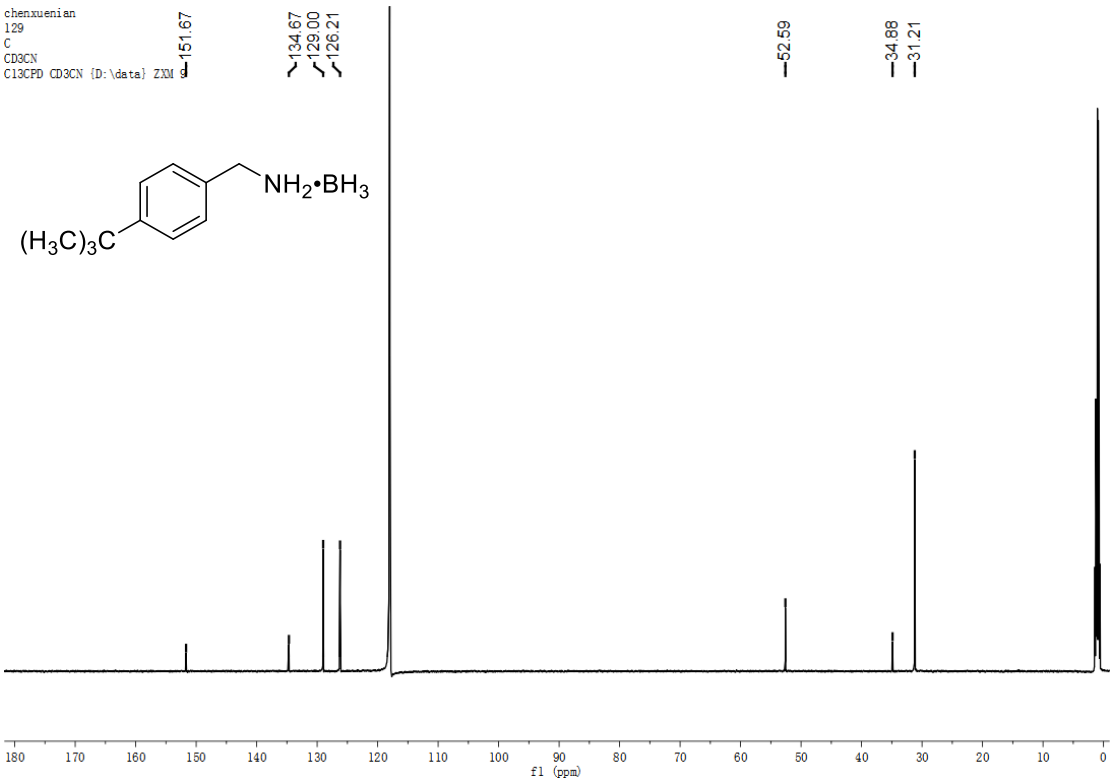


Figure S21. ^{13}C NMR spectrum of **2c** (600 MHz, DMSO)

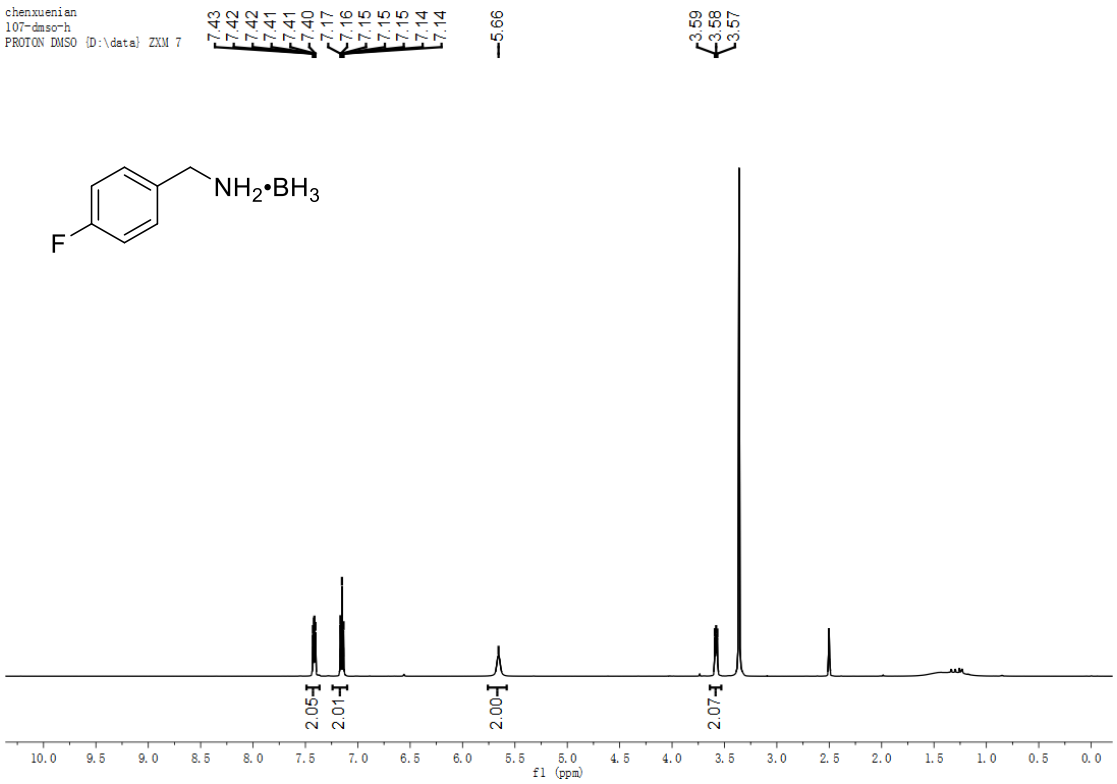


Figure S22. ^{1}H NMR spectrum of **2d** (600 MHz, DMSO)

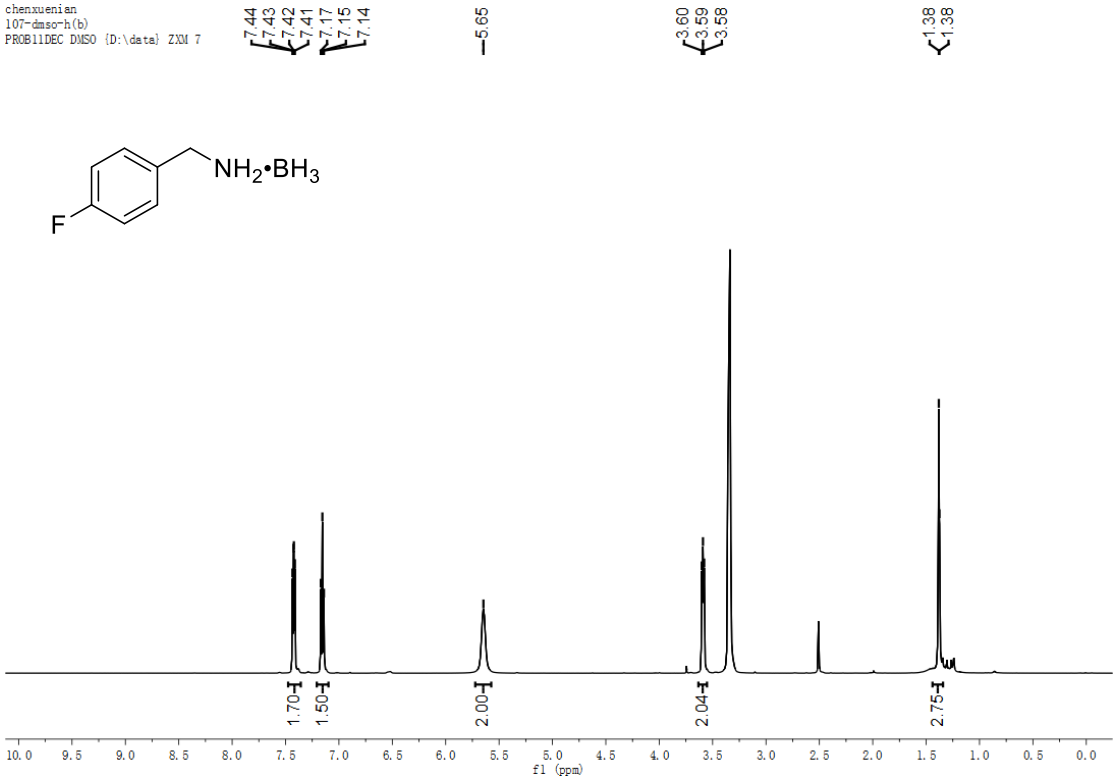


Figure S23. ^{1}H{B} NMR spectrum of **2d** (400 MHz, DMSO)

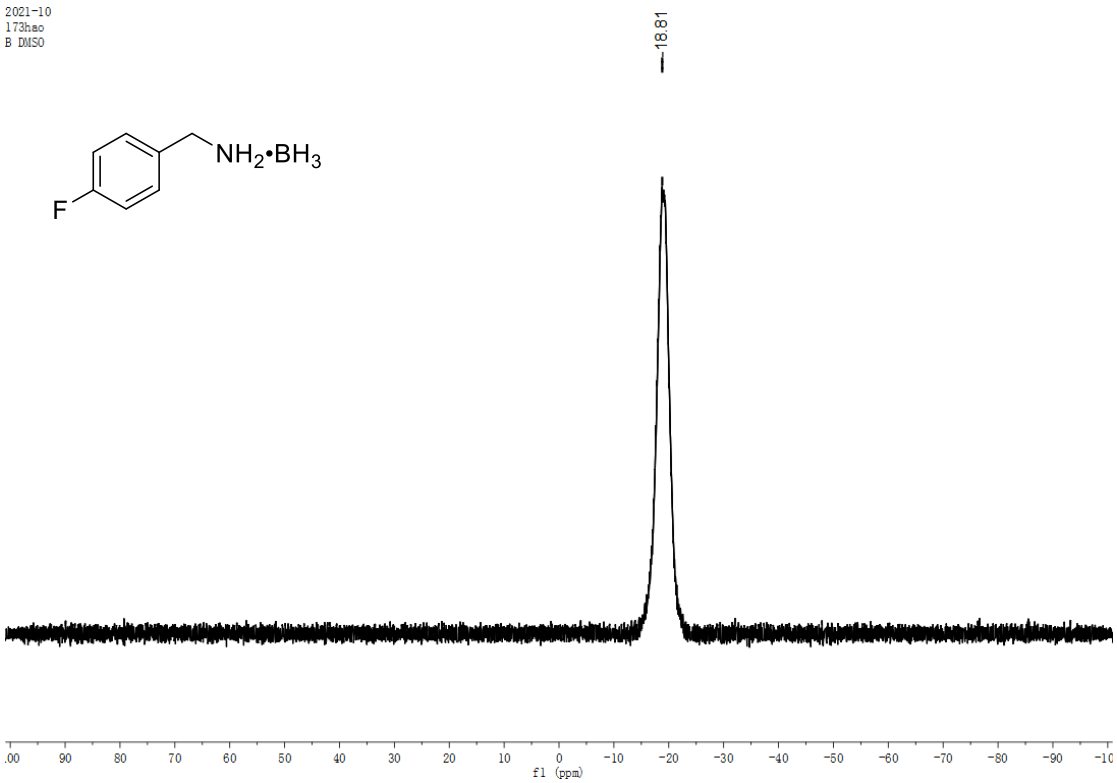


Figure S24. ^{11}B NMR spectrum of **2d** (400 MHz, DMSO)

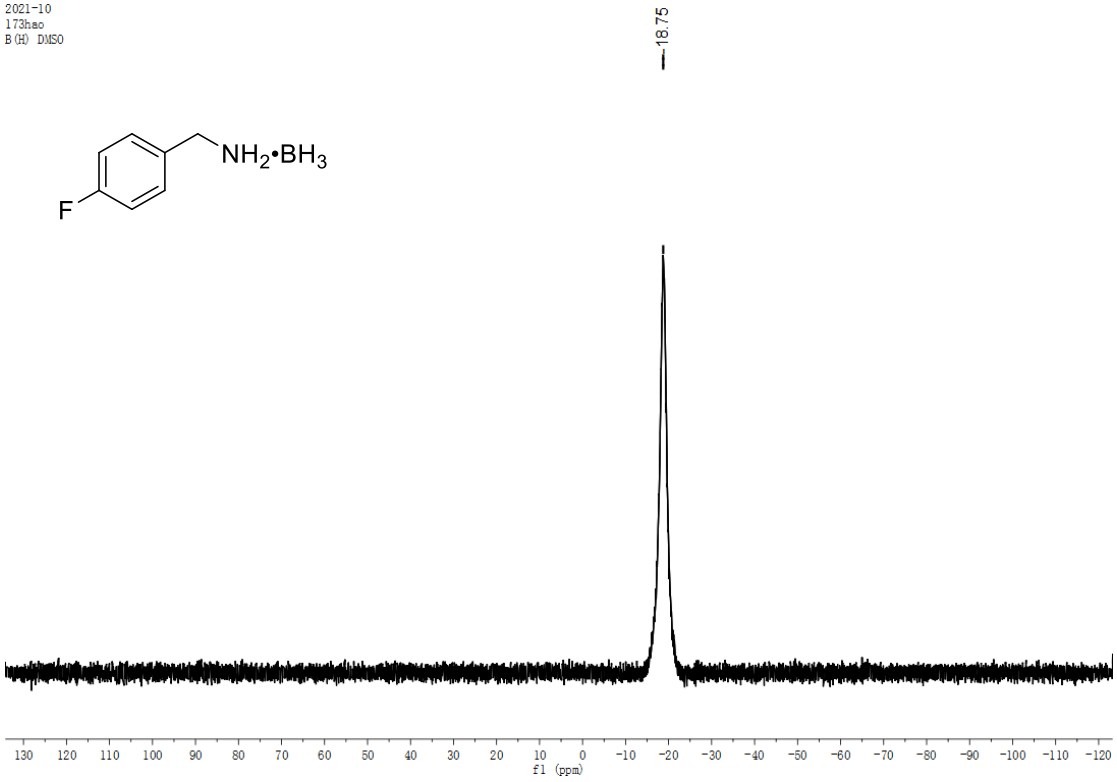


Figure S25. ^{11}B{H} NMR spectrum of **2d** (400 MHz, DMSO)

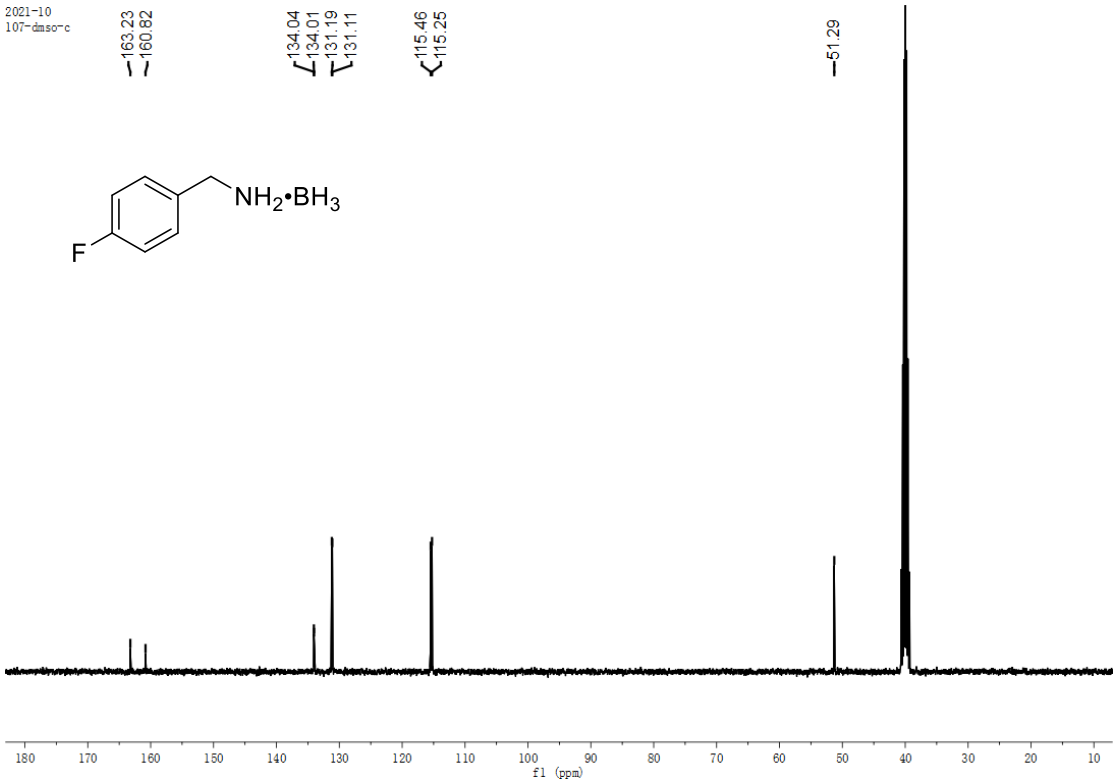


Figure S26. ^{13}C NMR spectrum of **2d** (400 MHz, DMSO)

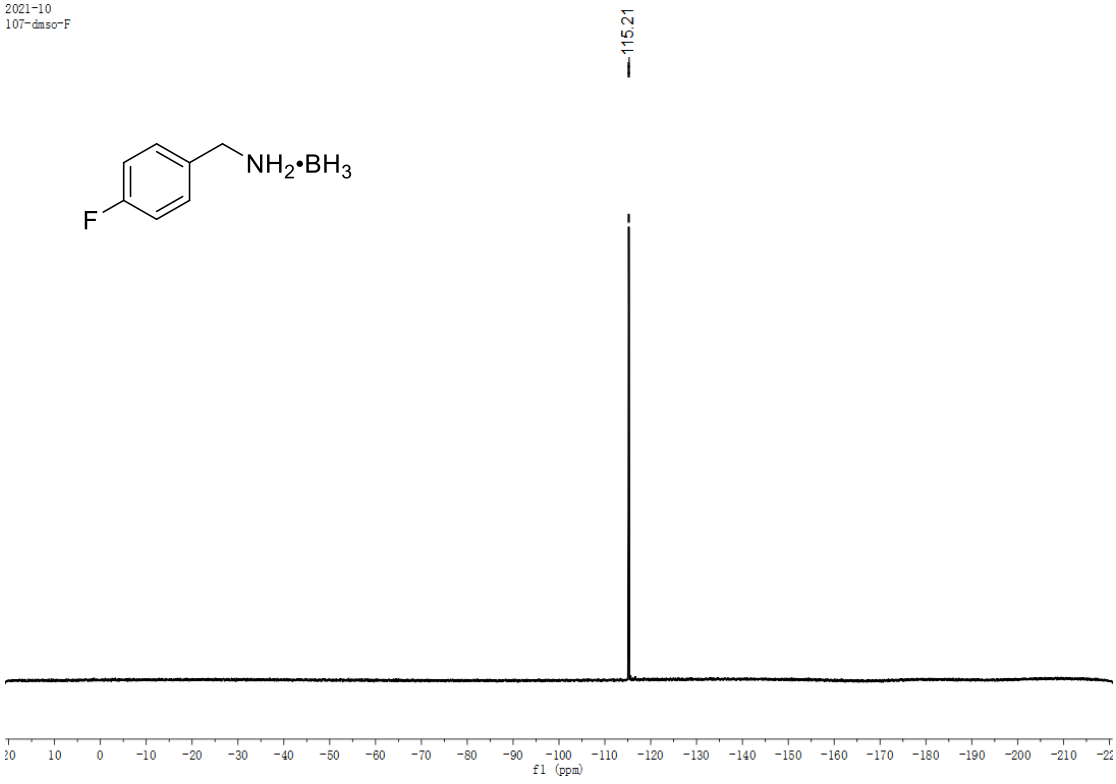


Figure S27. ^{19}F NMR spectrum of **2d** (400 MHz, DMSO)

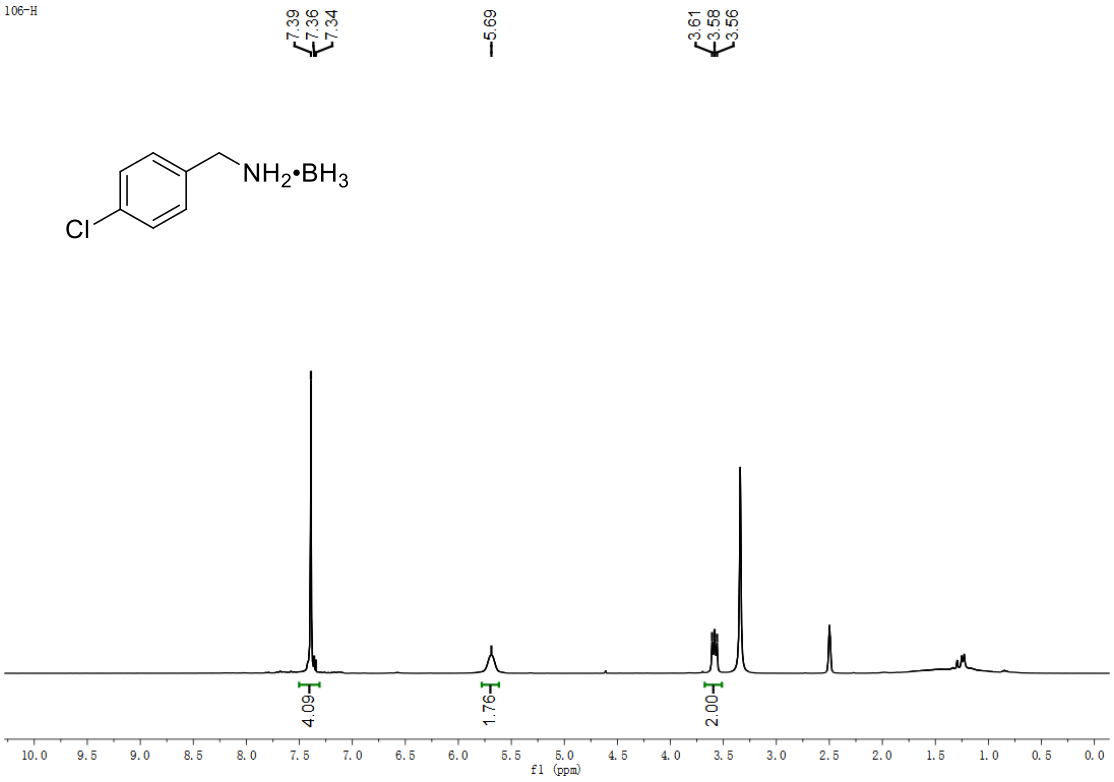


Figure S28. ^{1}H NMR spectrum of **2e** (300 MHz, DMSO)

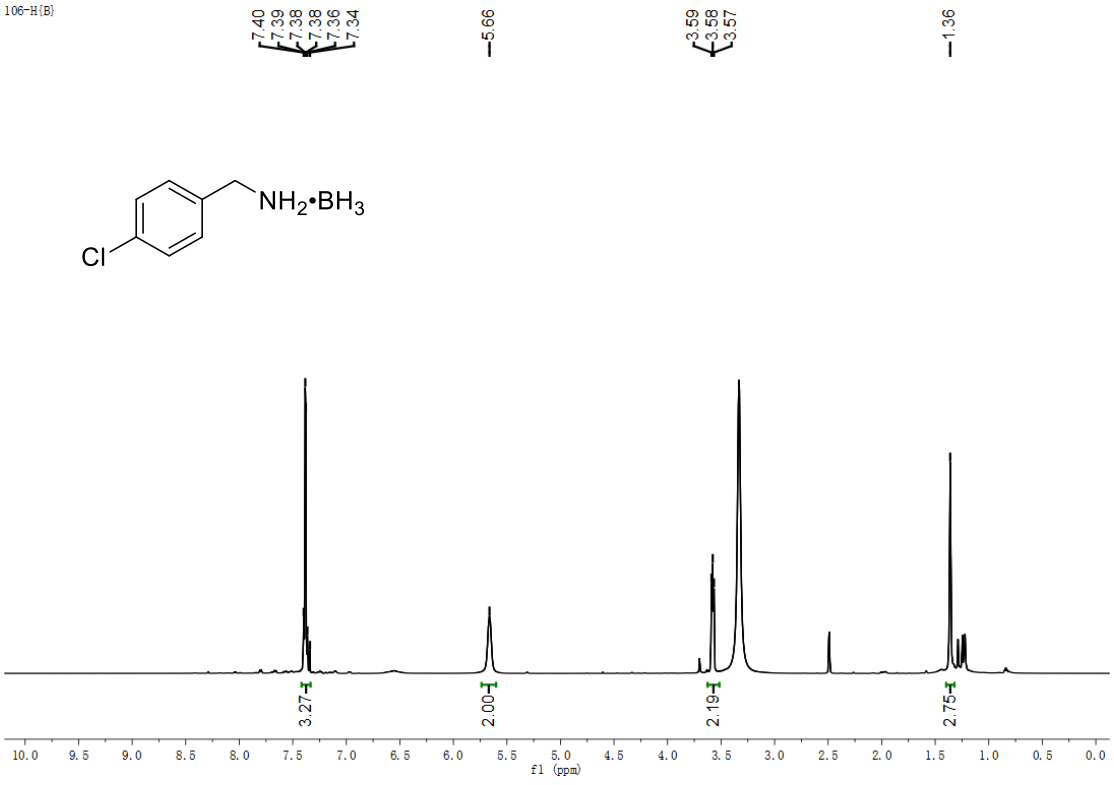


Figure S29. ^{1}H{B} NMR spectrum of **2e** (600 MHz, DMSO)

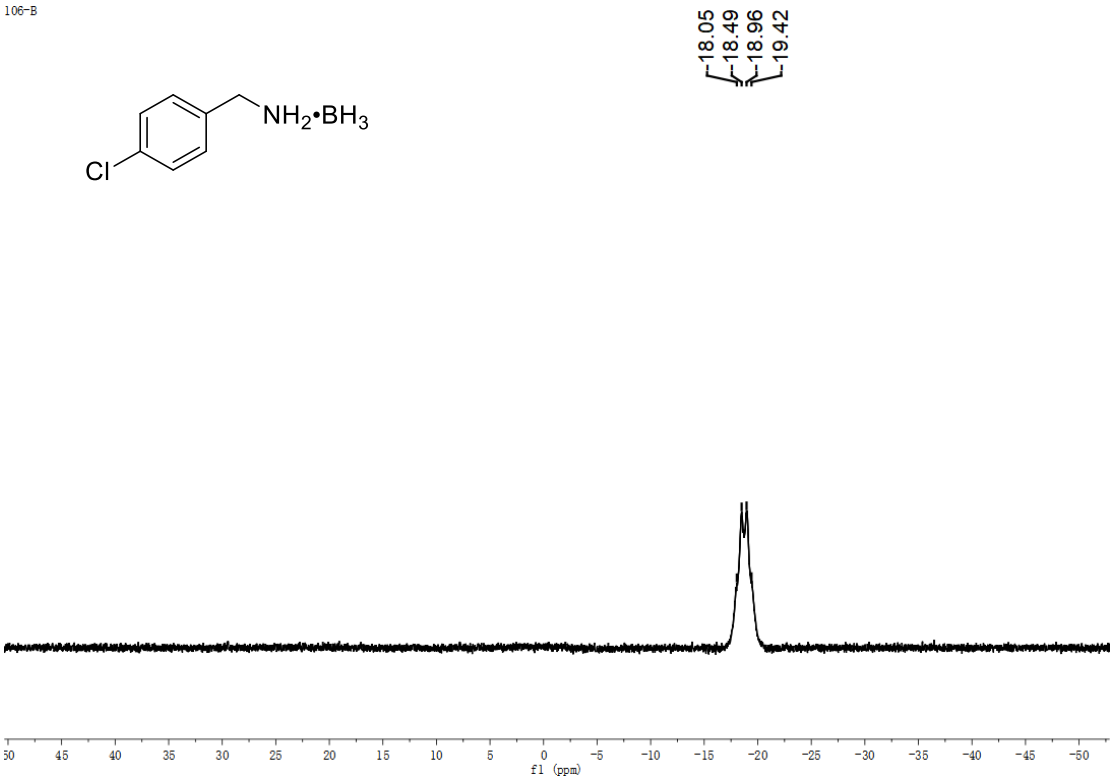


Figure S30. ^{11}B NMR spectrum of **2e** (600 MHz, DMSO)

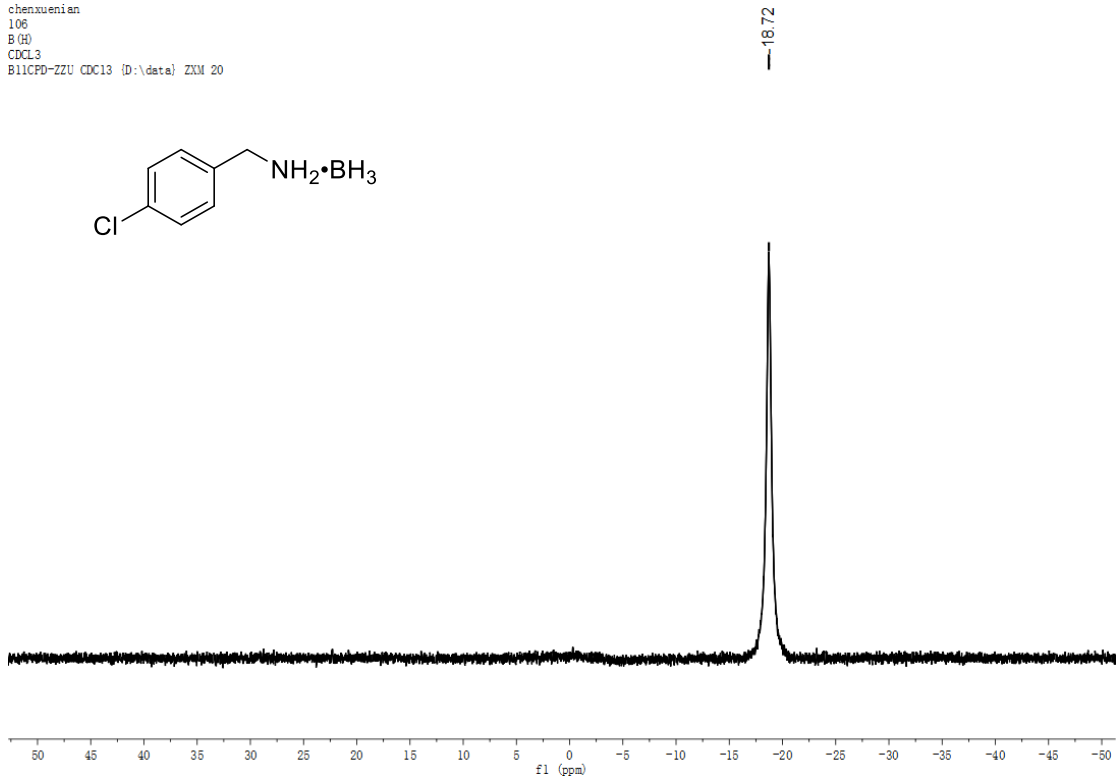


Figure S31. ^{11}B{H} NMR spectrum of **2e** (600 MHz, DMSO)

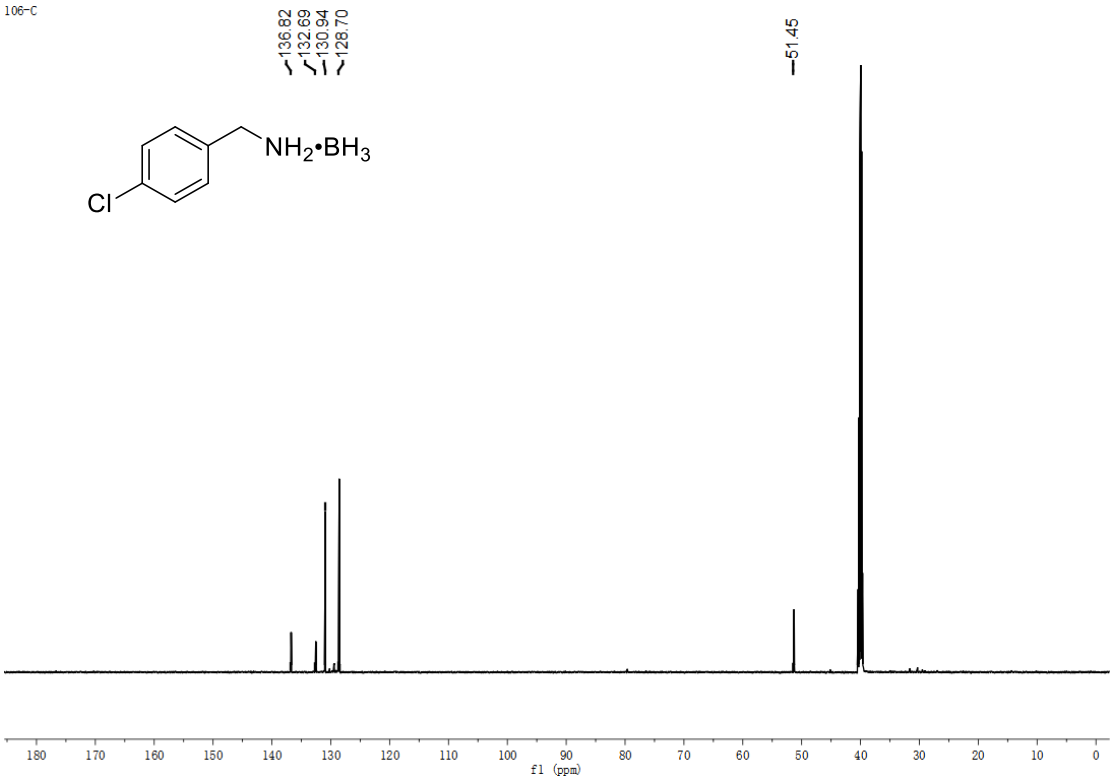


Figure S32. ^{13}C NMR spectrum of **2e** (600 MHz, DMSO)

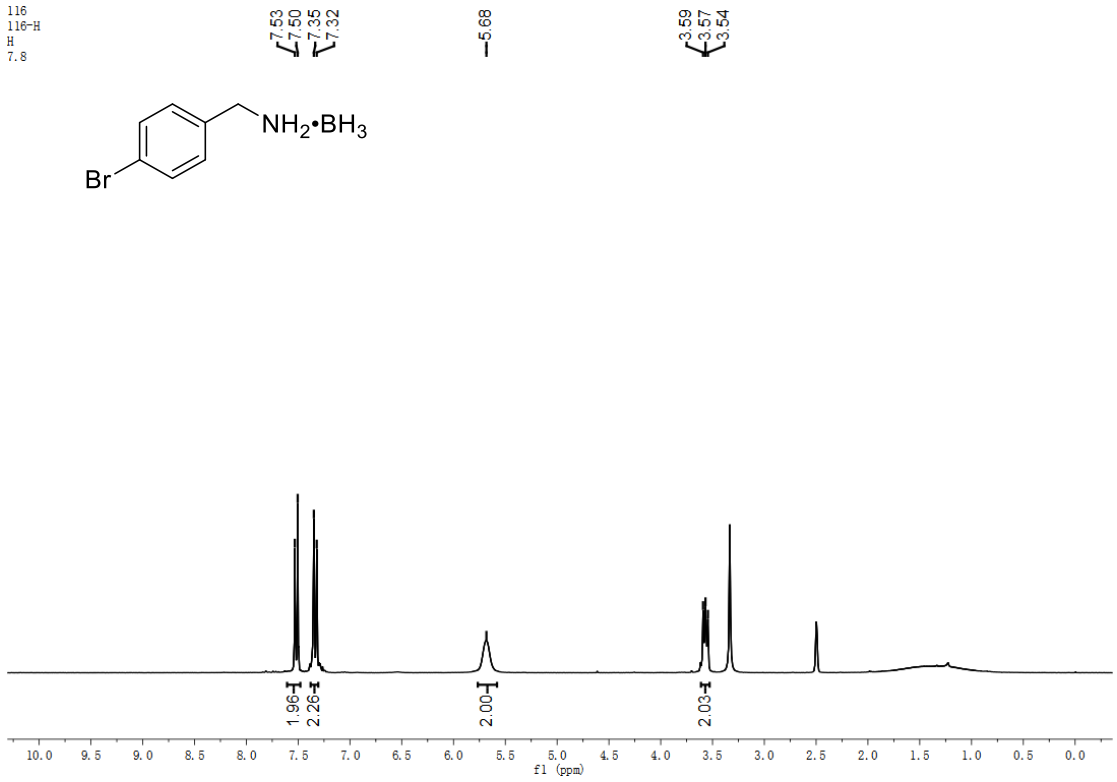


Figure S33. ^{1}H NMR spectrum of **2f** (300 MHz, DMSO)

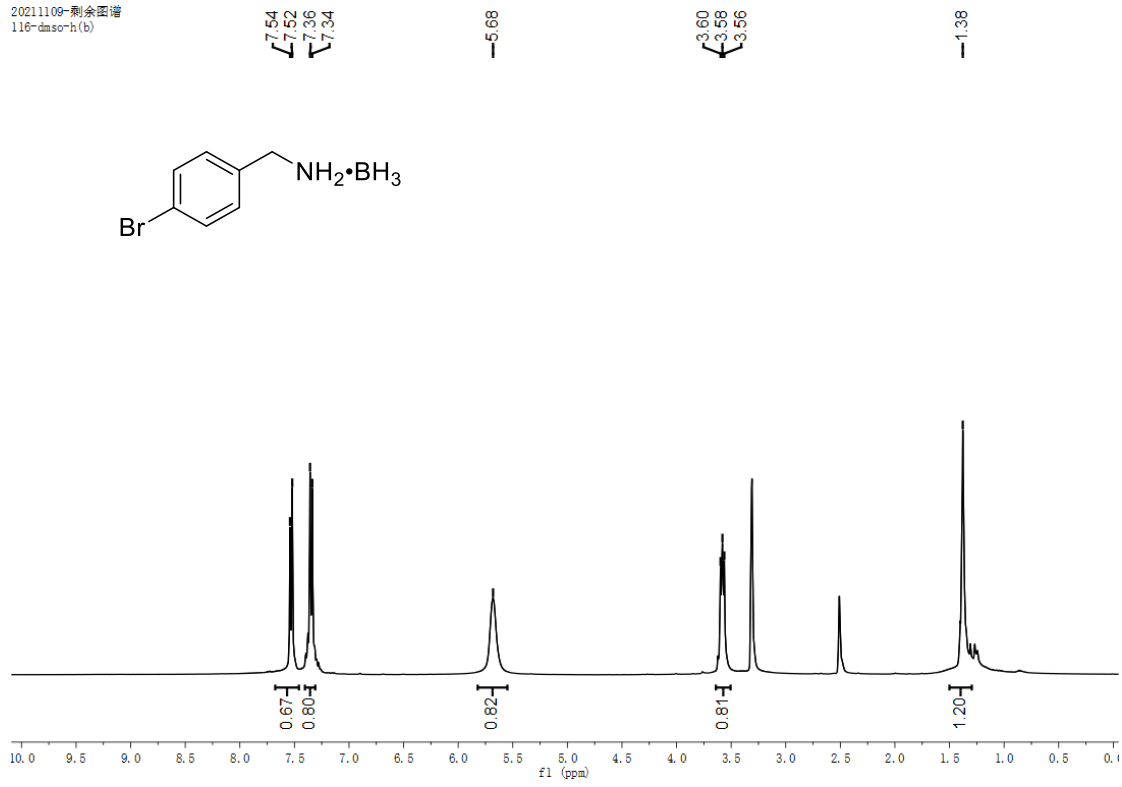


Figure S34. ^{1}H{B} NMR spectrum of **2f** (400 MHz, DMSO)

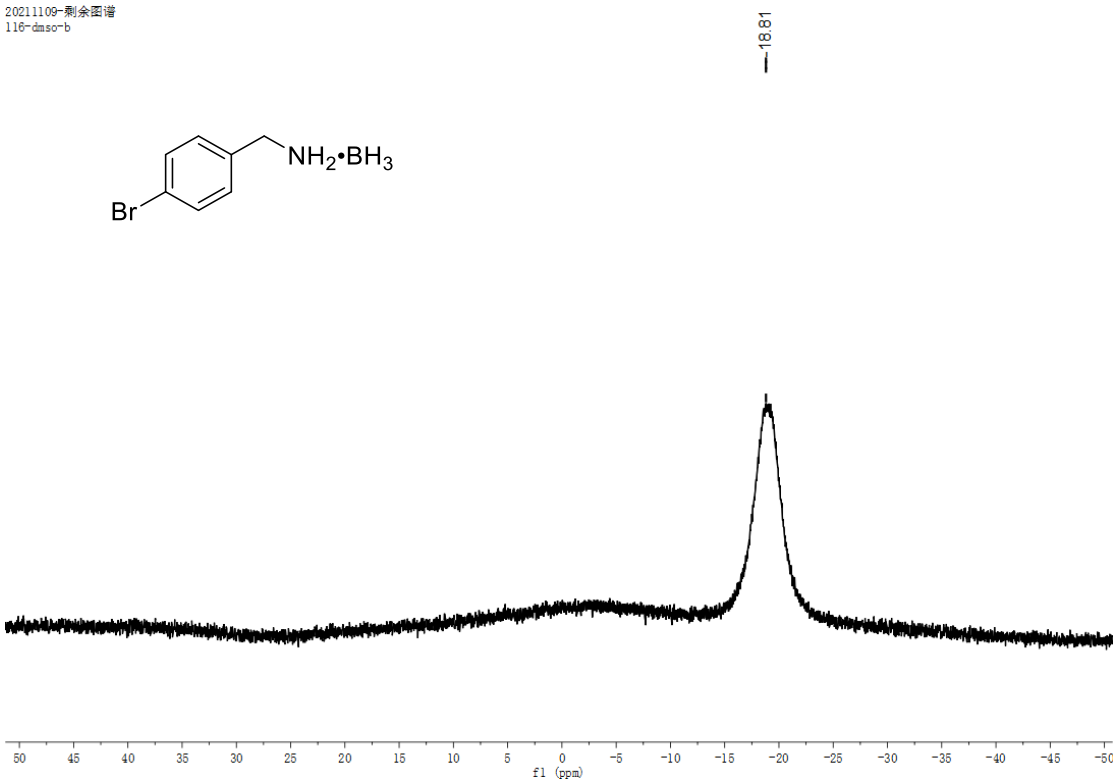


Figure S35. ^{11}B NMR spectrum of **2f** (400 MHz, DMSO)

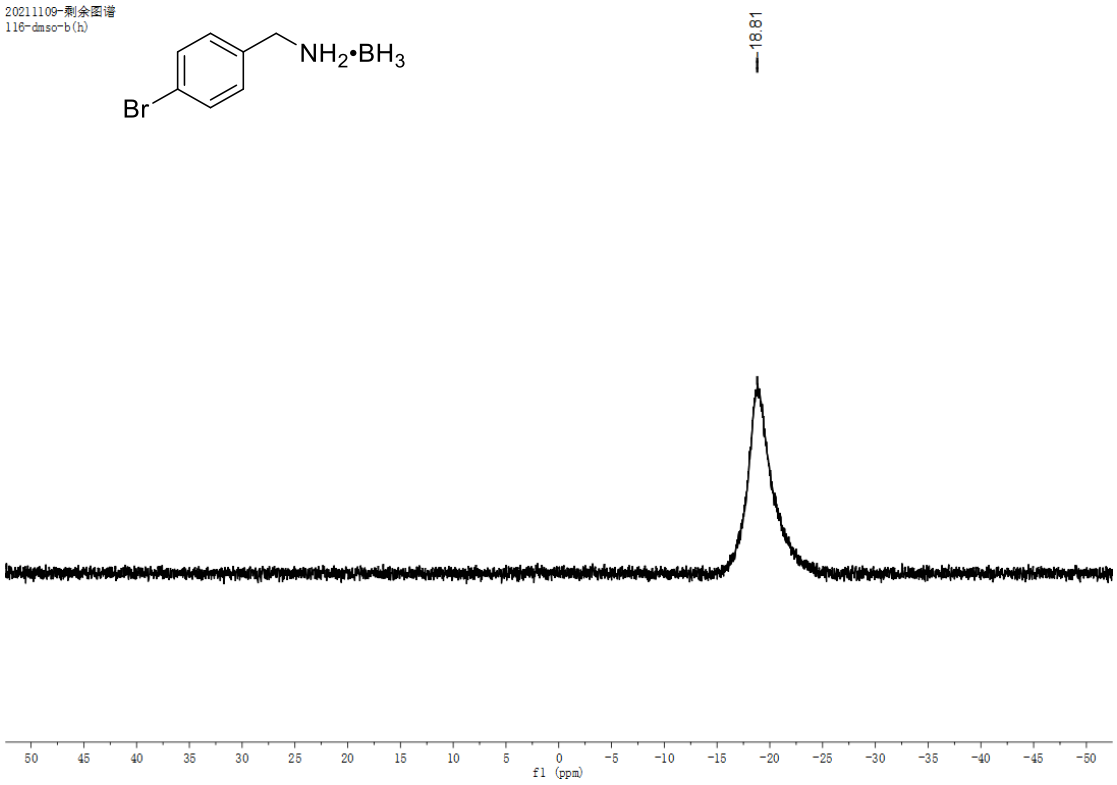


Figure S36. ^{11}B{H} NMR spectrum of **2f** (400 MHz, DMSO)

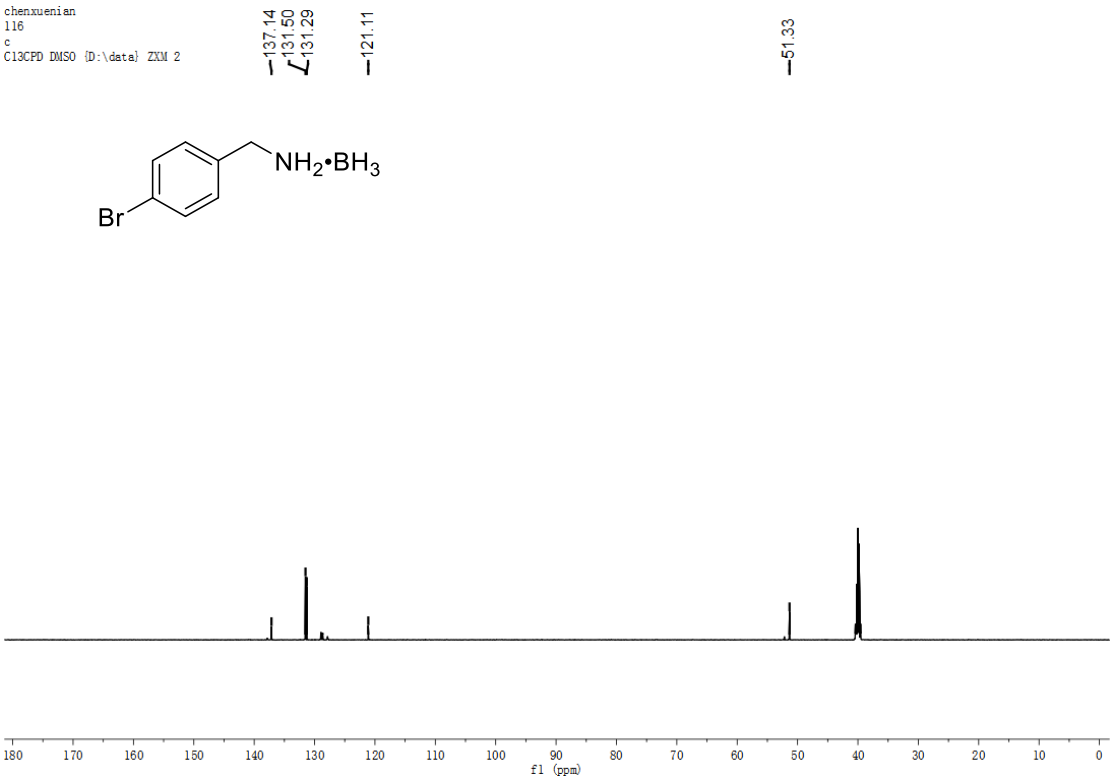


Figure S37. ^{13}C NMR spectrum of **2f** (600 MHz, DMSO)

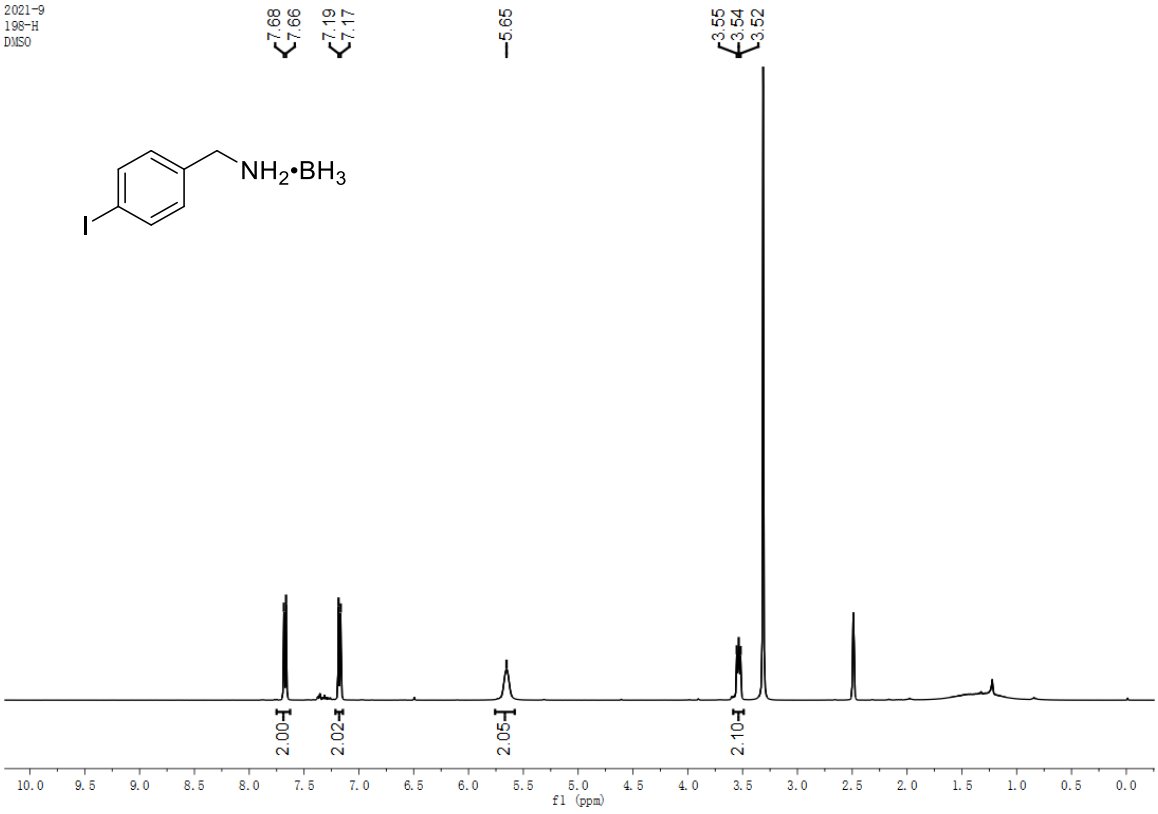


Figure S38. ^{1}H NMR spectrum of **2g** (400 MHz, DMSO)

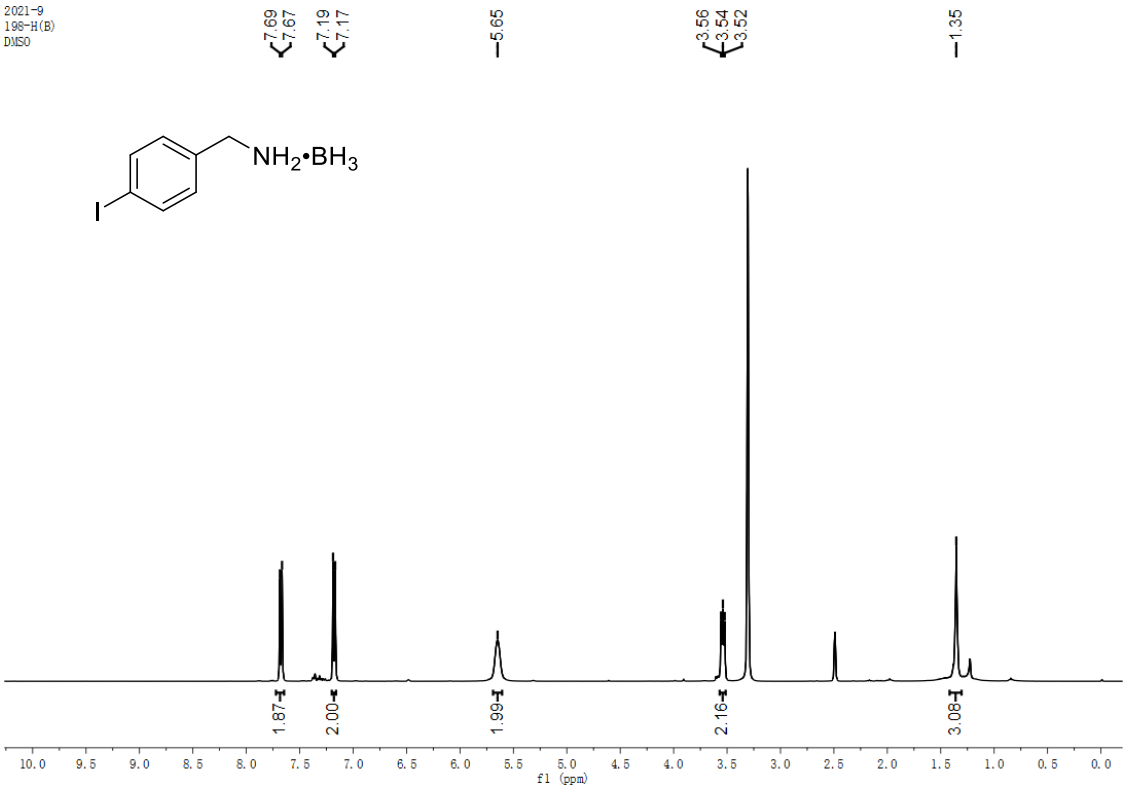


Figure S39. ^{1}H{B} NMR spectrum of **2g** (400 MHz, DMSO)

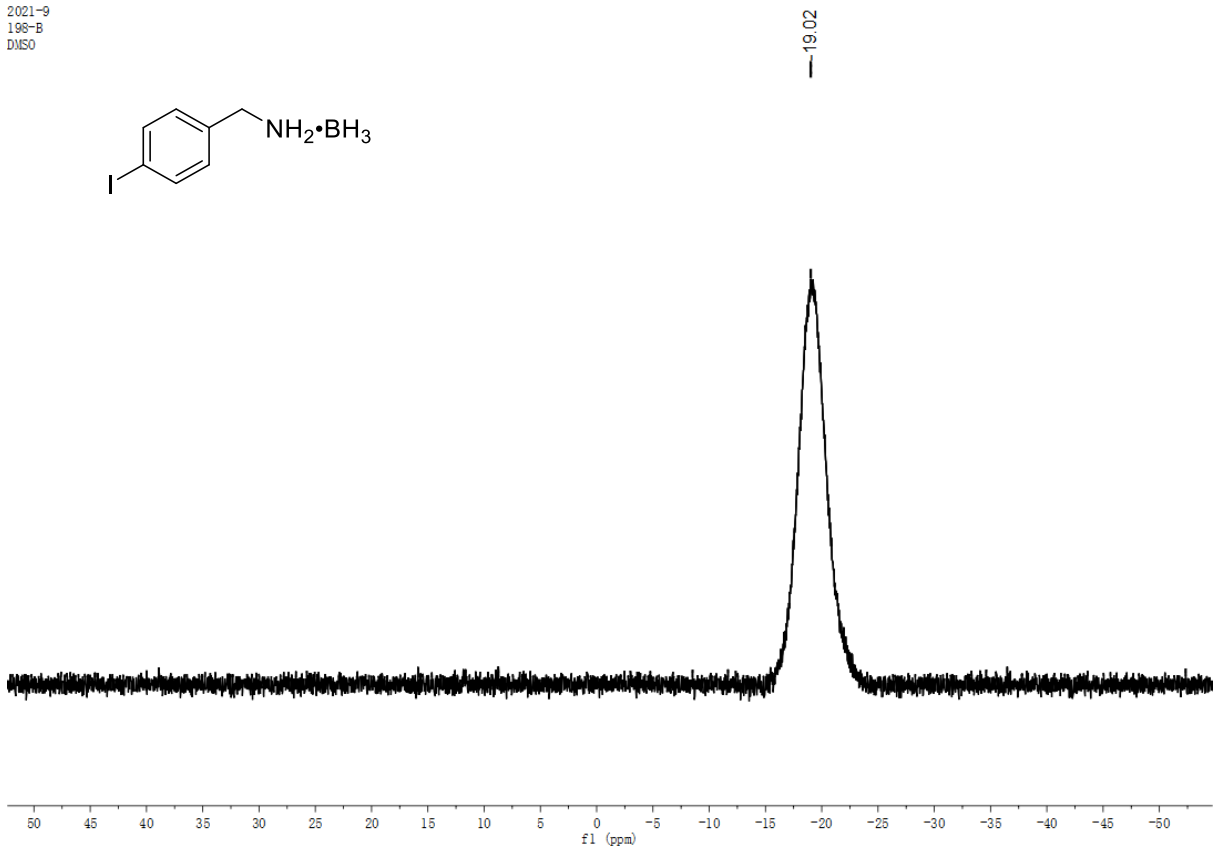


Figure S40. ^{11}B NMR spectrum of **2g** (400 MHz, DMSO)

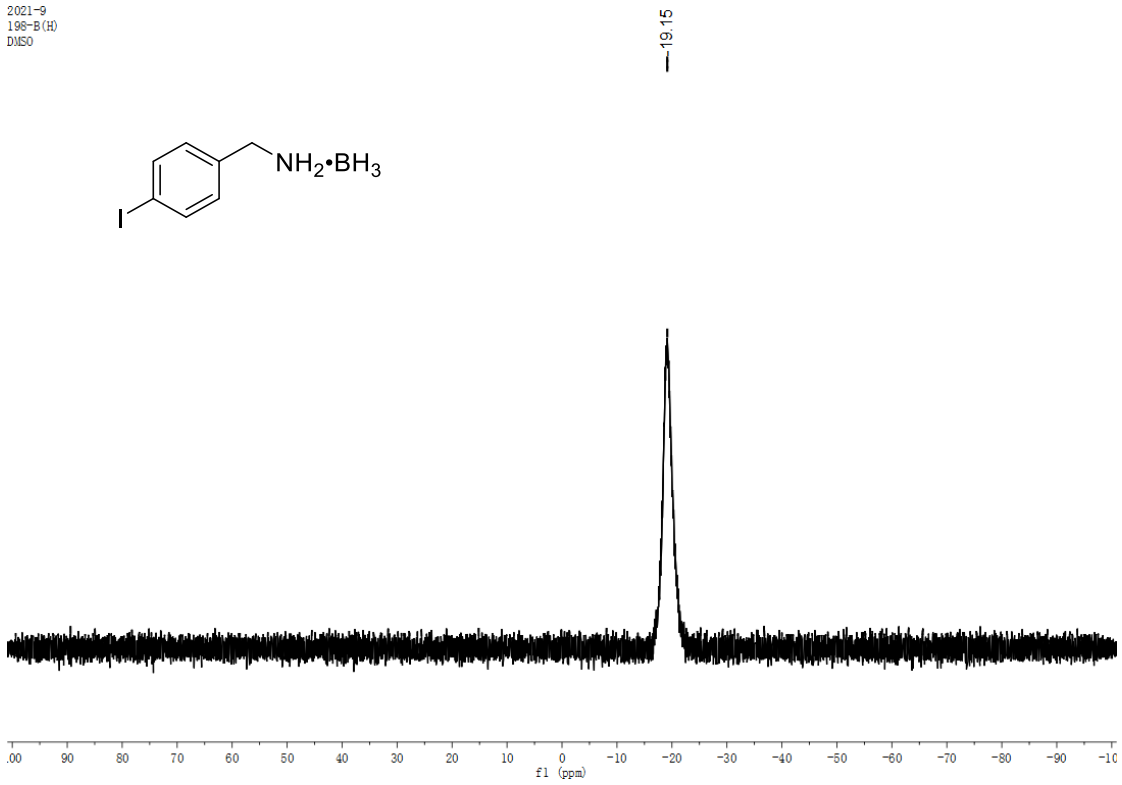


Figure S41. ^{11}B{H} NMR spectrum of **2g** (400 MHz, DMSO)

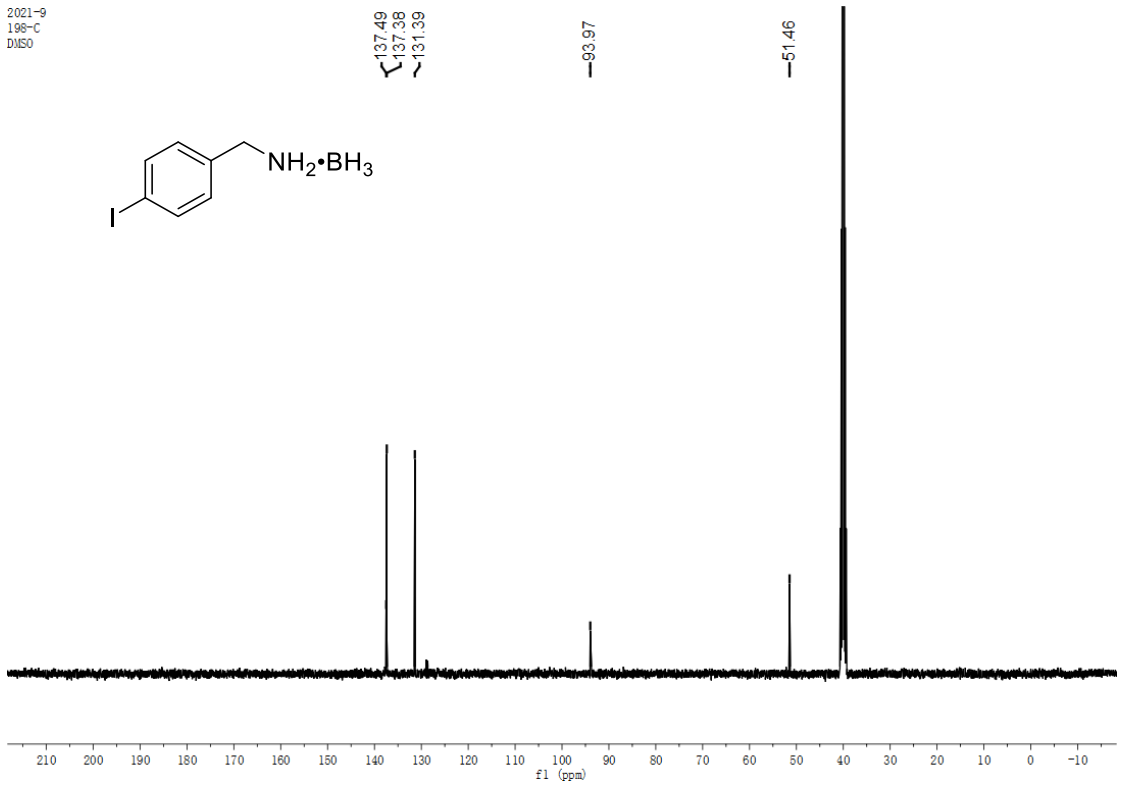


Figure S42. ^{13}C NMR spectrum of **2g** (400 MHz, DMSO)

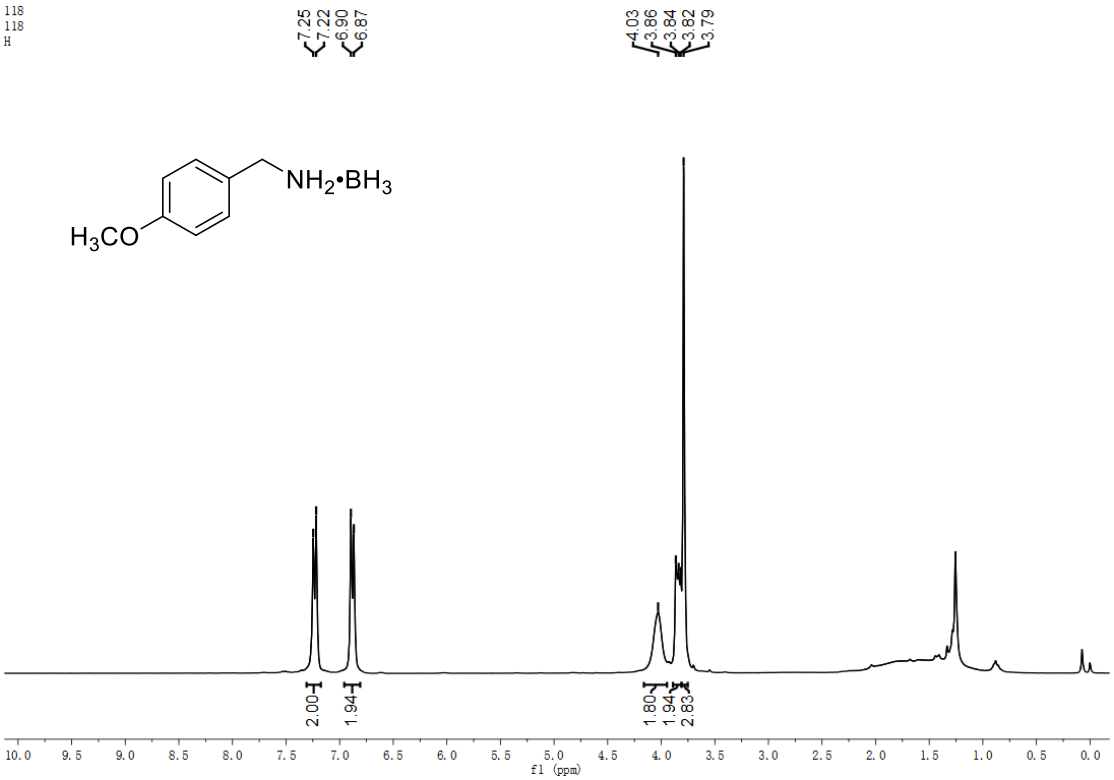


Figure S43. ^{1}H NMR spectrum of **2h** (300 MHz, $CDCl_3$)

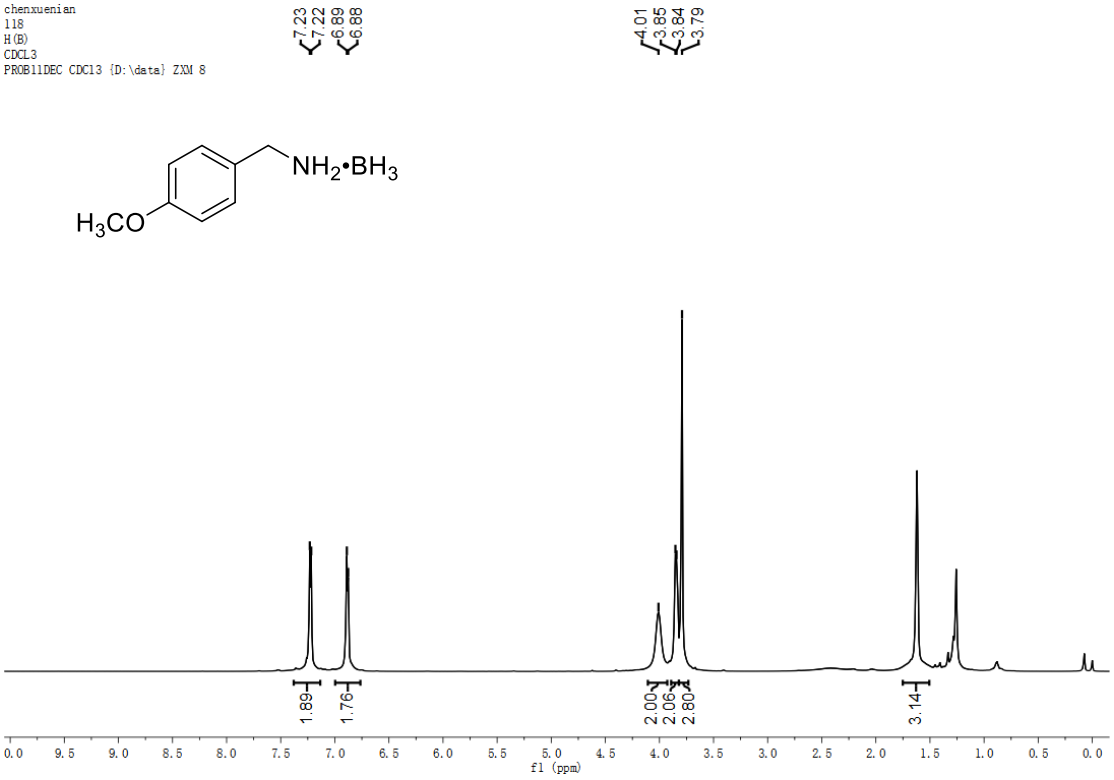


Figure S44. ^{1}H{B} NMR spectrum of **2h** (600 MHz, $CDCl_3$)

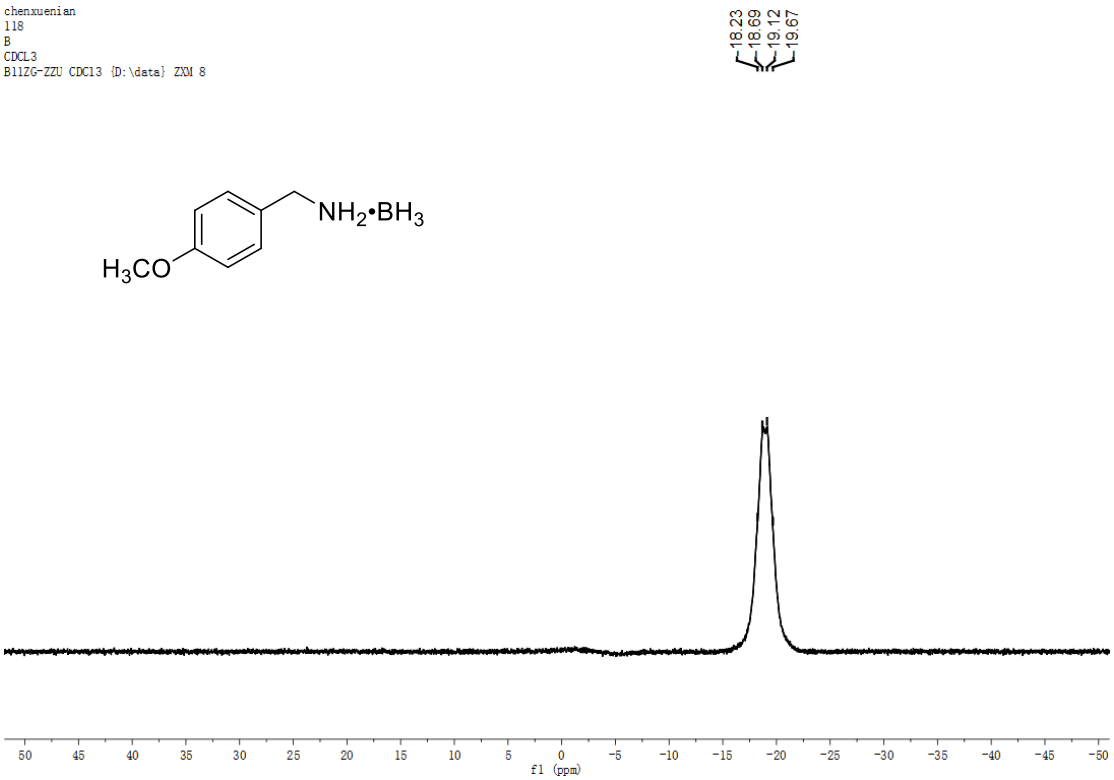


Figure S45. ^{11}B NMR spectrum of **2h** (600 MHz, $CDCl_3$)

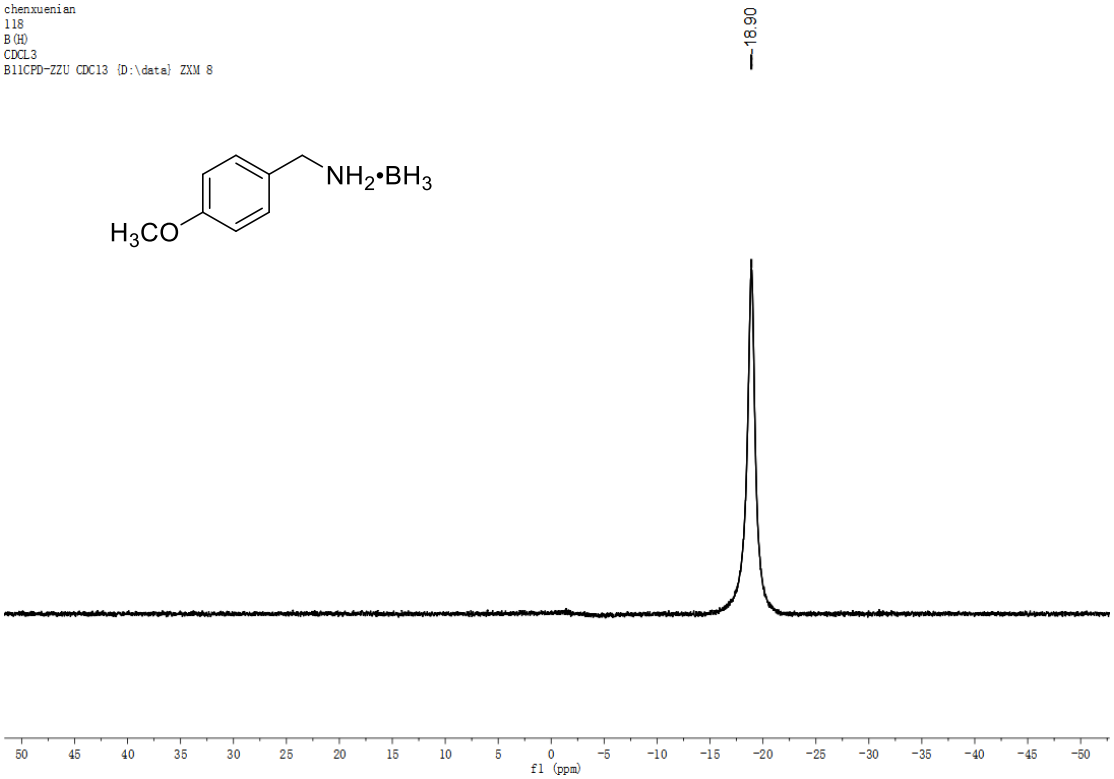


Figure S46. ^{11}B{H} NMR spectrum of **2h** (600 MHz, $CDCl_3$)

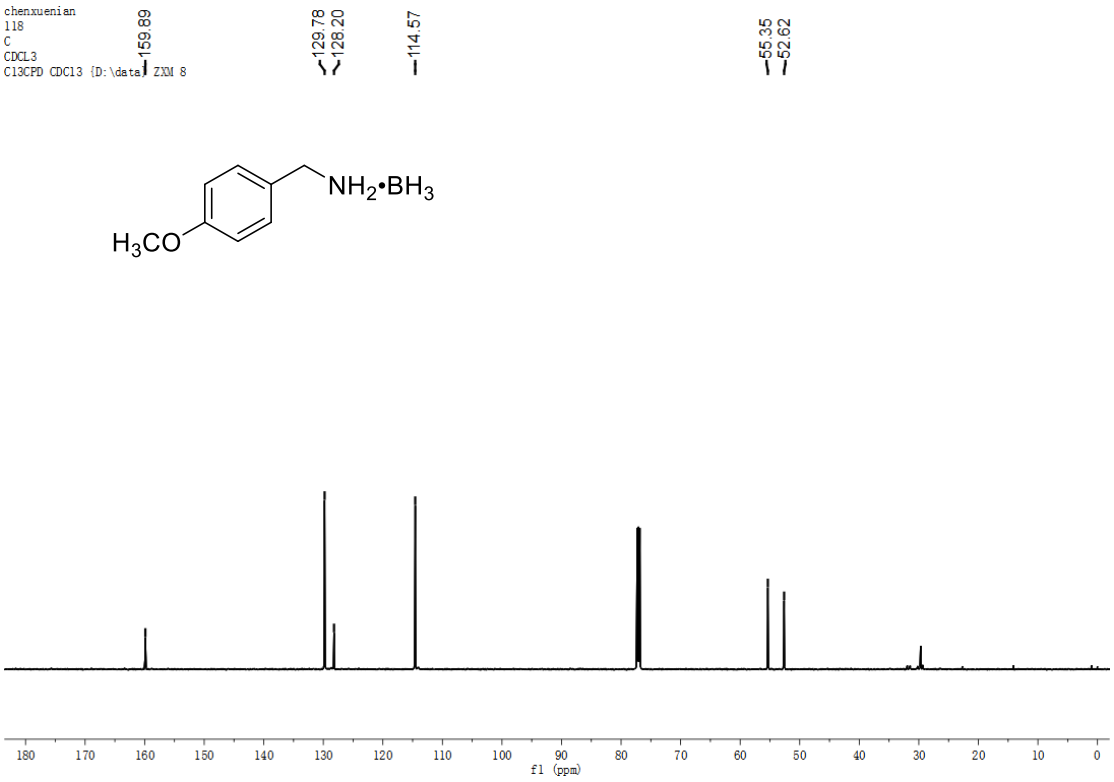


Figure S47. ^{13}C NMR spectrum of **2h** (600 MHz, $CDCl_3$)

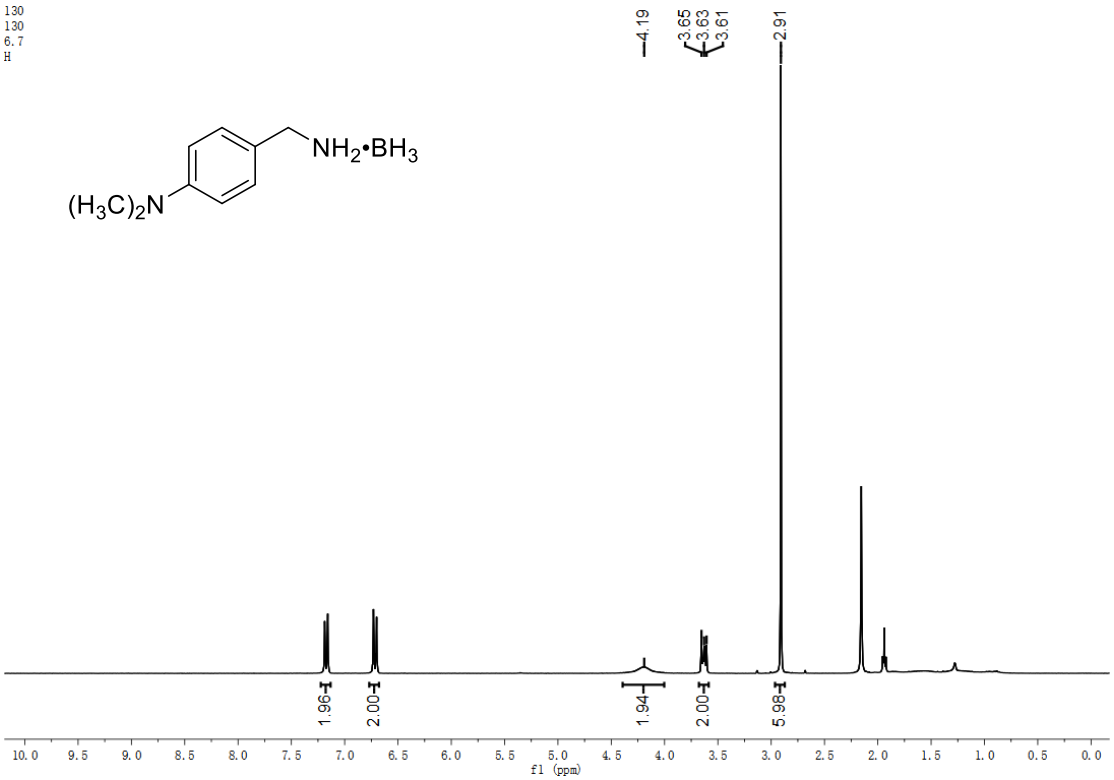


Figure S48. ^{1}H NMR spectrum of **2i** (300 MHz, CD_3CN)

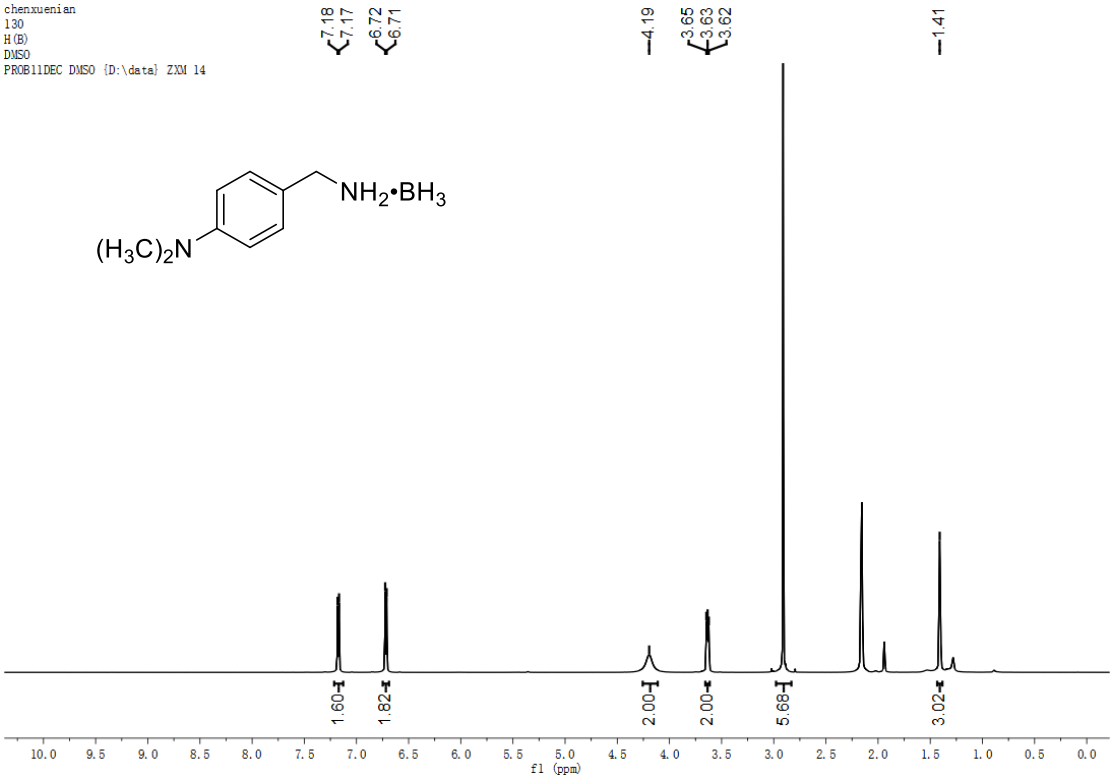


Figure S49. ^{1}H NMR spectrum of **2i** (600 MHz, CD_3CN)

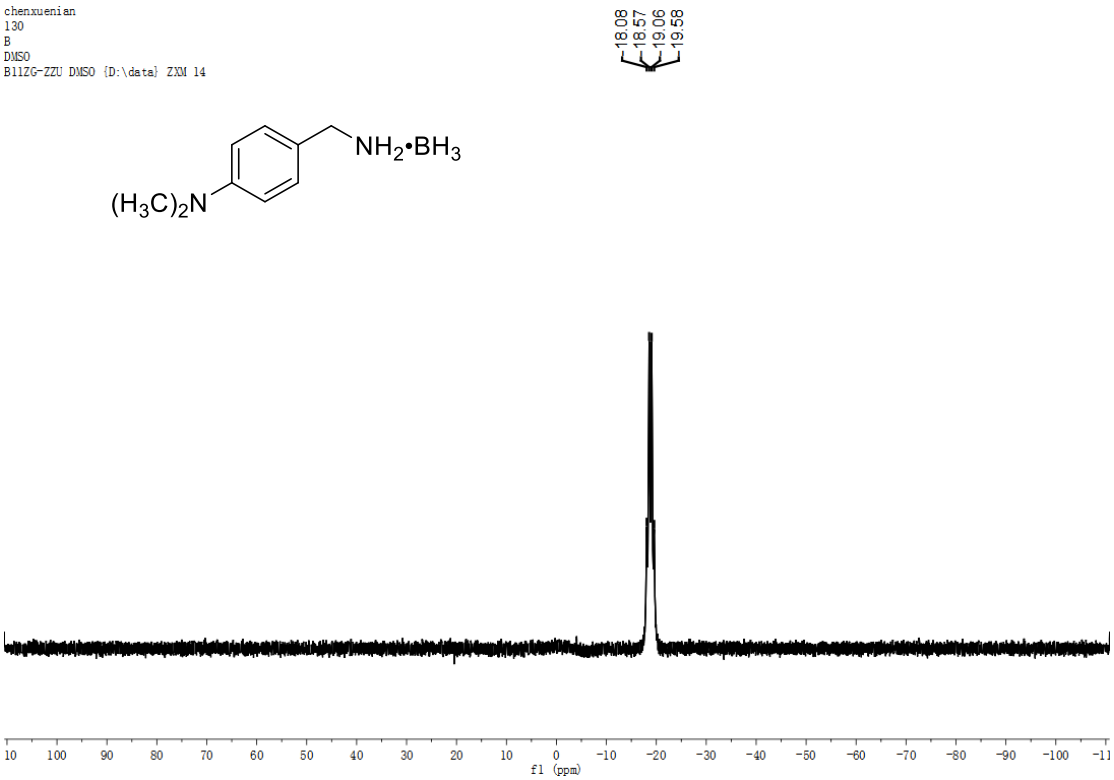


Figure S50. ^{11}B NMR spectrum of **2i** (600 MHz, CD_3CN)

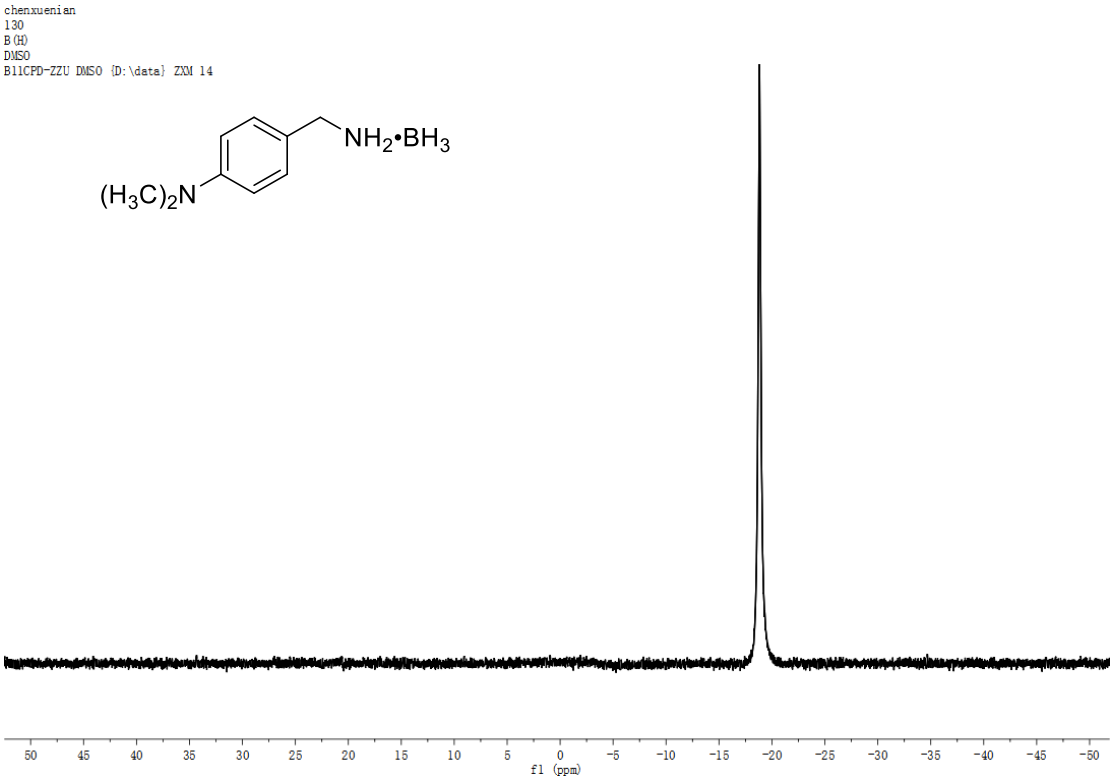


Figure S51. ^{11}B{H} NMR spectrum of **2i** (600 MHz, CD_3CN)

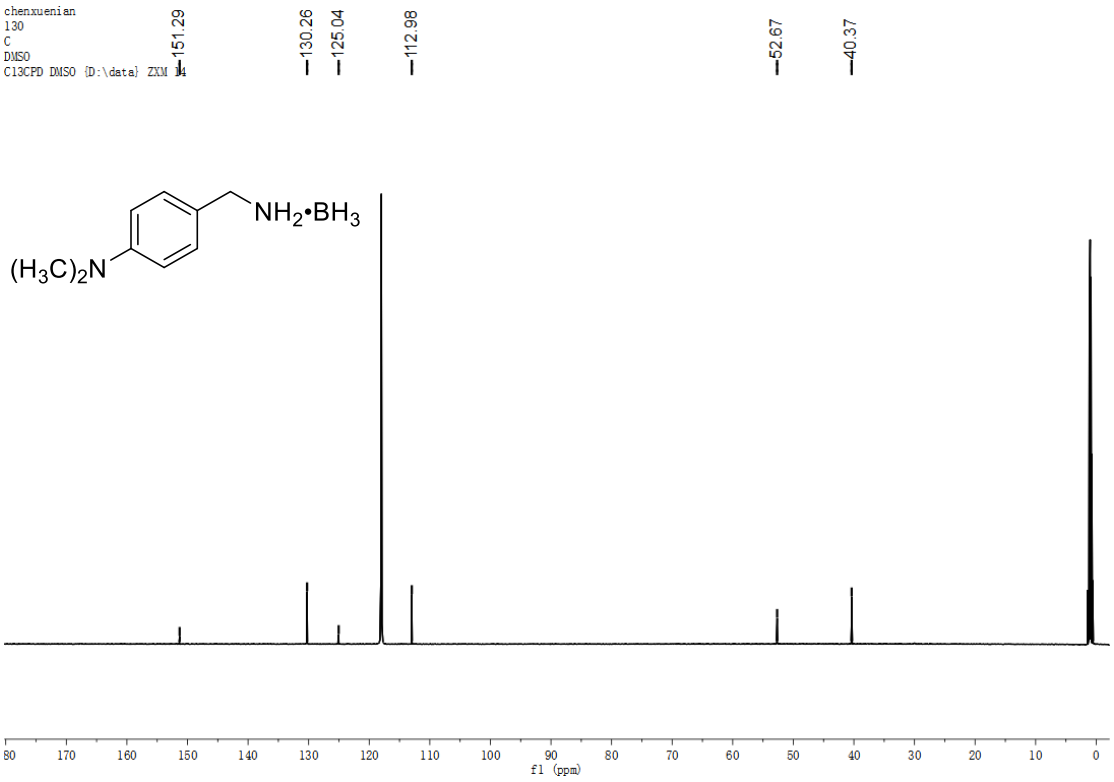


Figure S52. ^{13}C NMR spectrum of **2i** (600 MHz, CD_3CN)

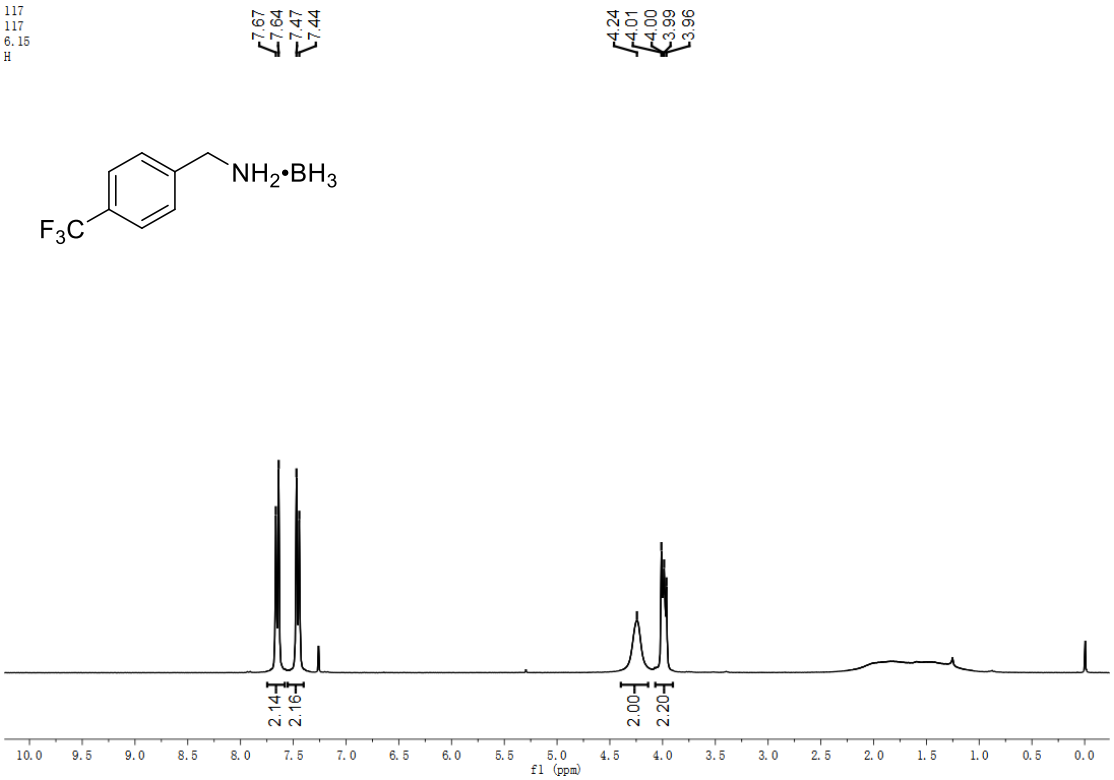


Figure S53. ^{1}H NMR spectrum of **2j** (300 MHz, $CDCl_3$)

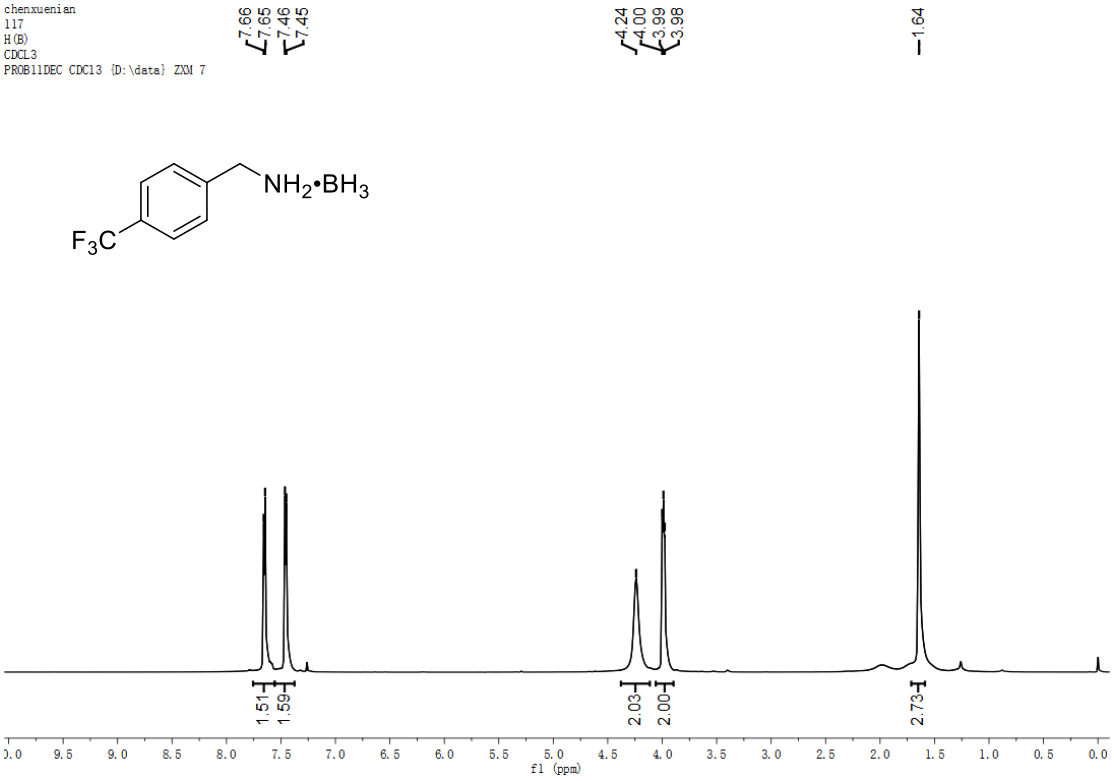


Figure S54. ^{1}H{B} NMR spectrum of **2j** (600 MHz, $CDCl_3$)

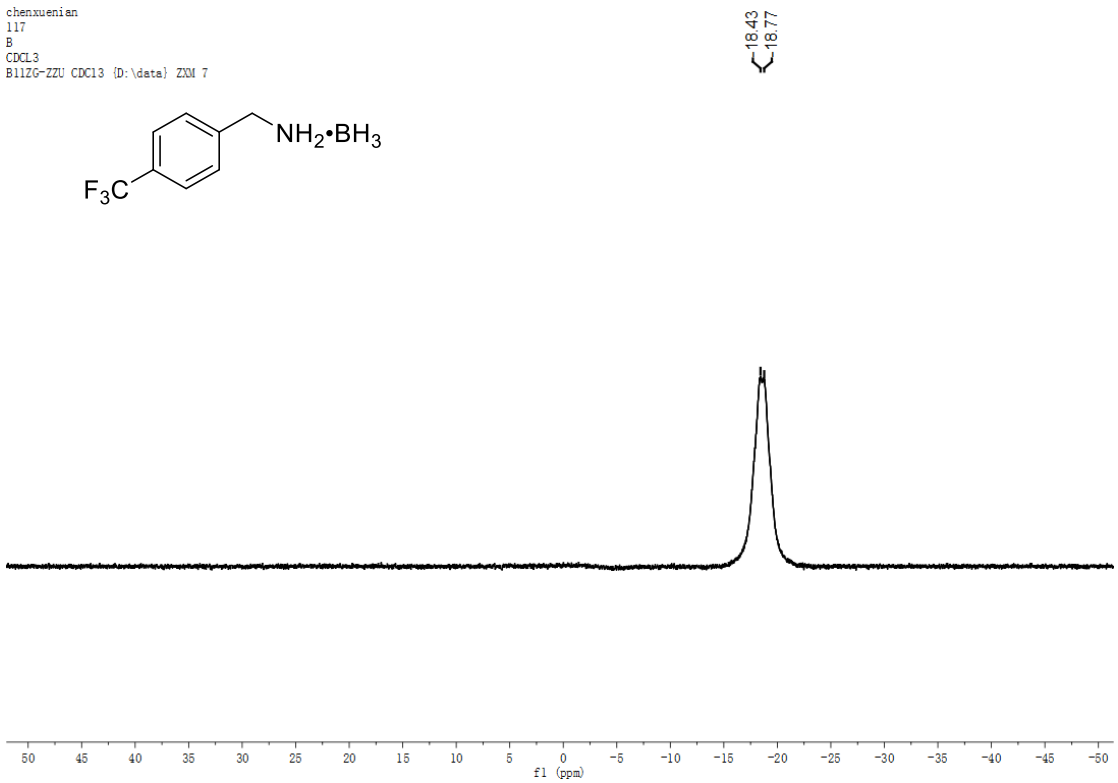


Figure S55. ^{11}B NMR spectrum of **2j** (600 MHz, $CDCl_3$)

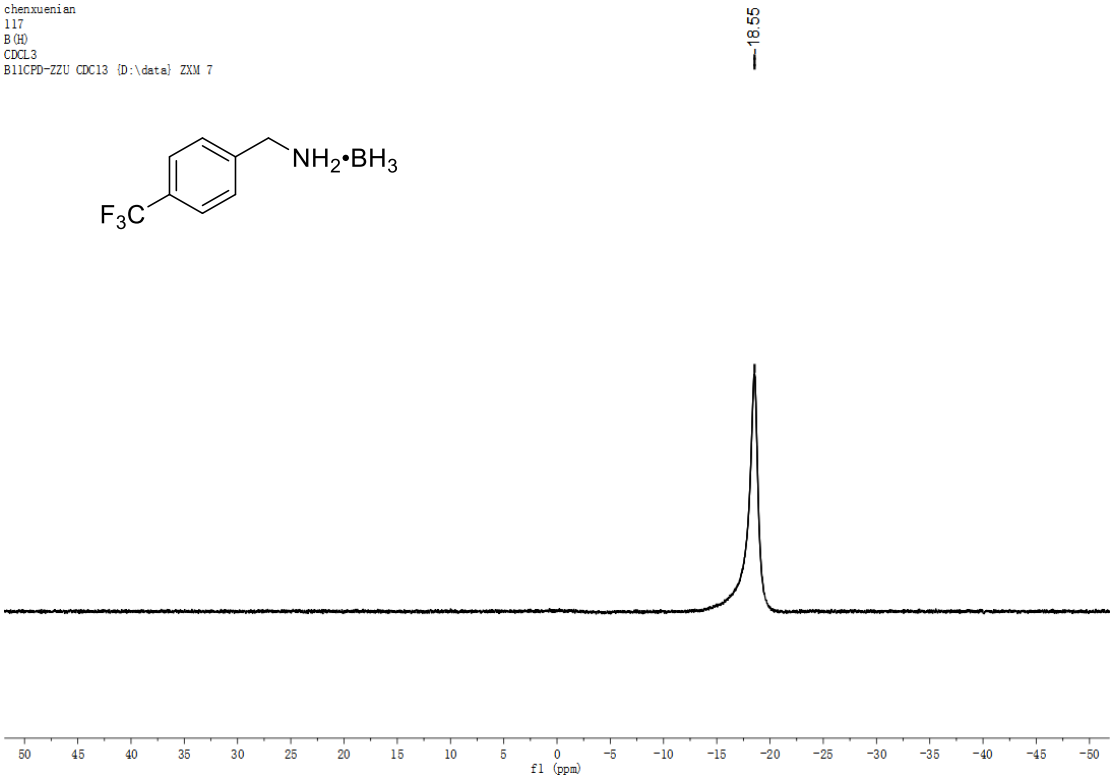


Figure S56. ^{11}B{H} NMR spectrum of **2j** (600 MHz, $CDCl_3$)

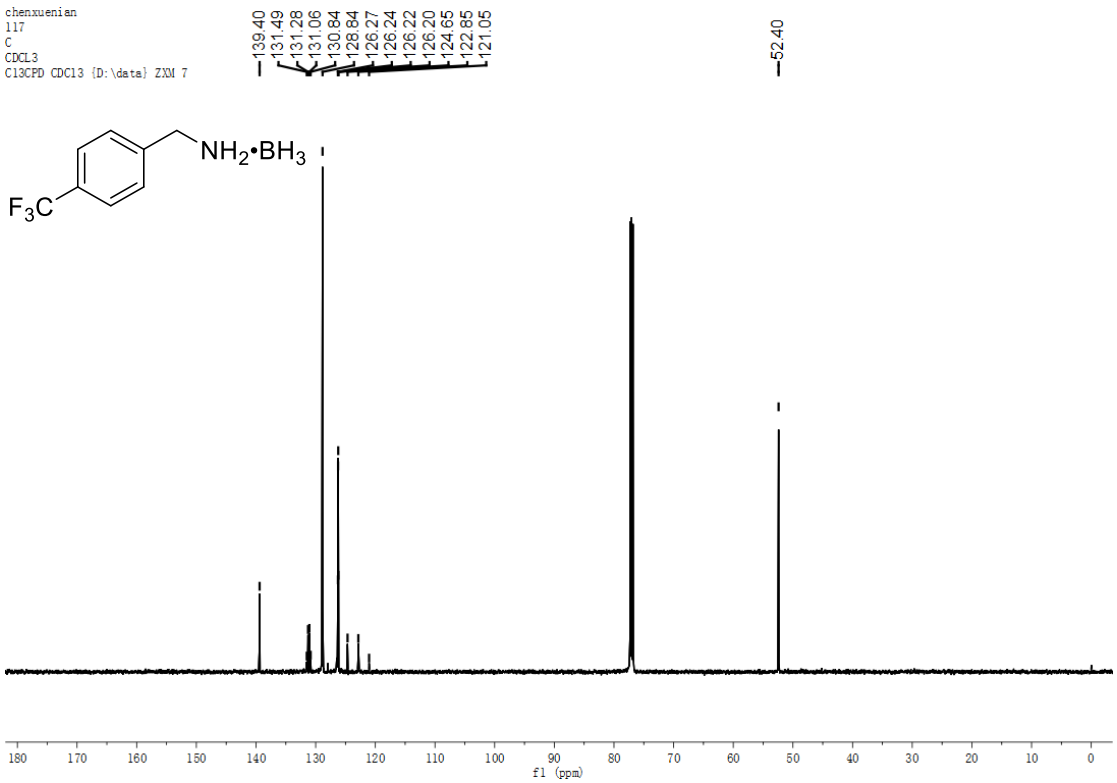


Figure S57. ^{13}C NMR spectrum of **2j** (600 MHz, $CDCl_3$)

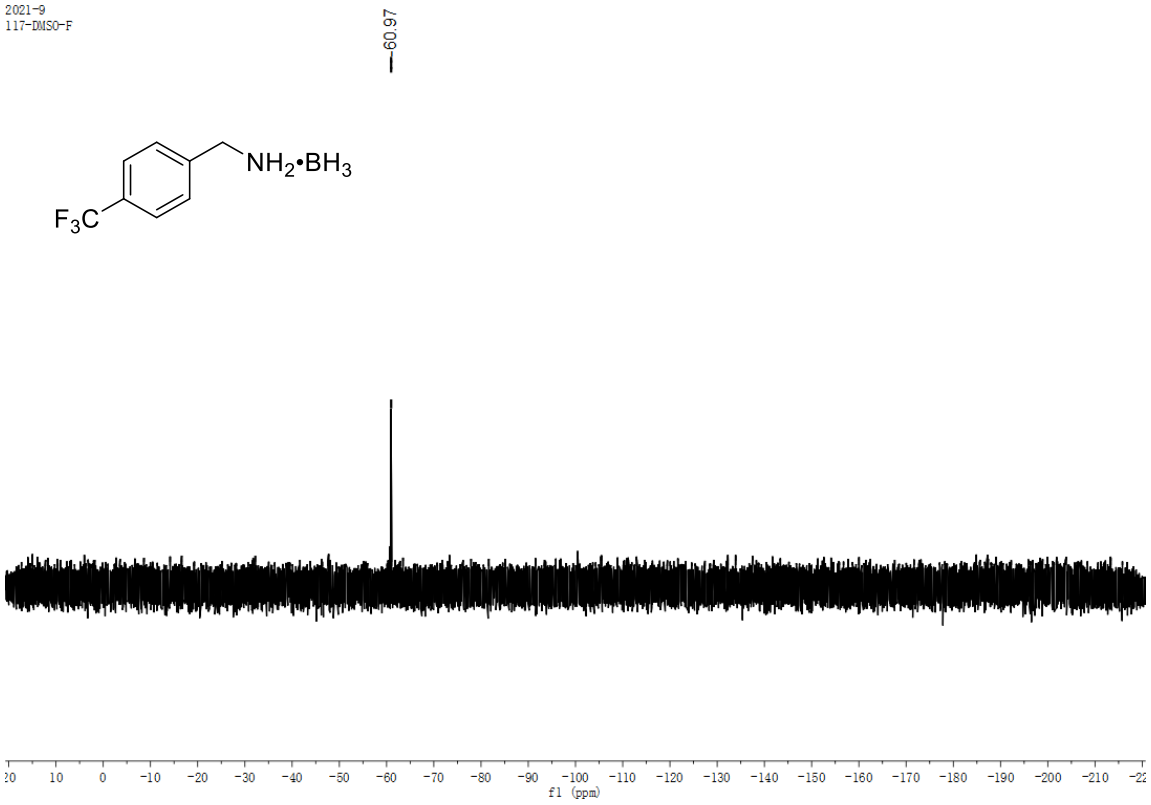


Figure S58. $^{19}F\{H\}$ NMR spectrum of **2j** (400 MHz, $CDCl_3$)

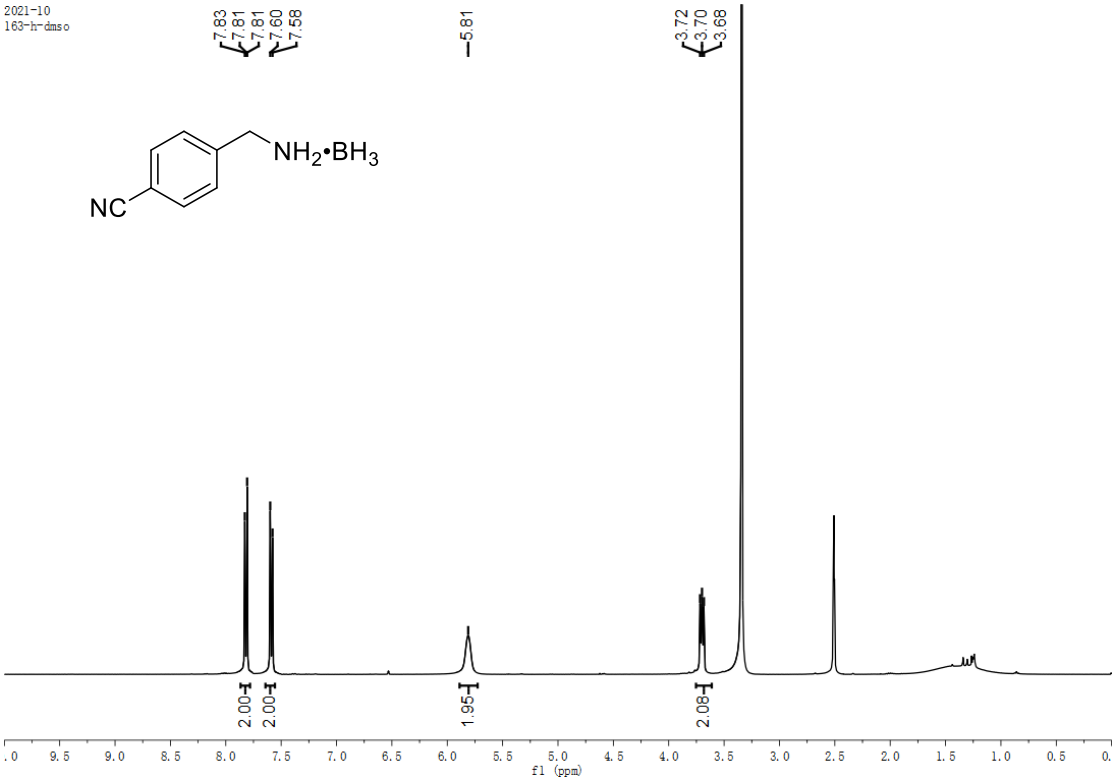


Figure S59. ^{1}H NMR spectrum of **2k** (400 MHz, DMSO)

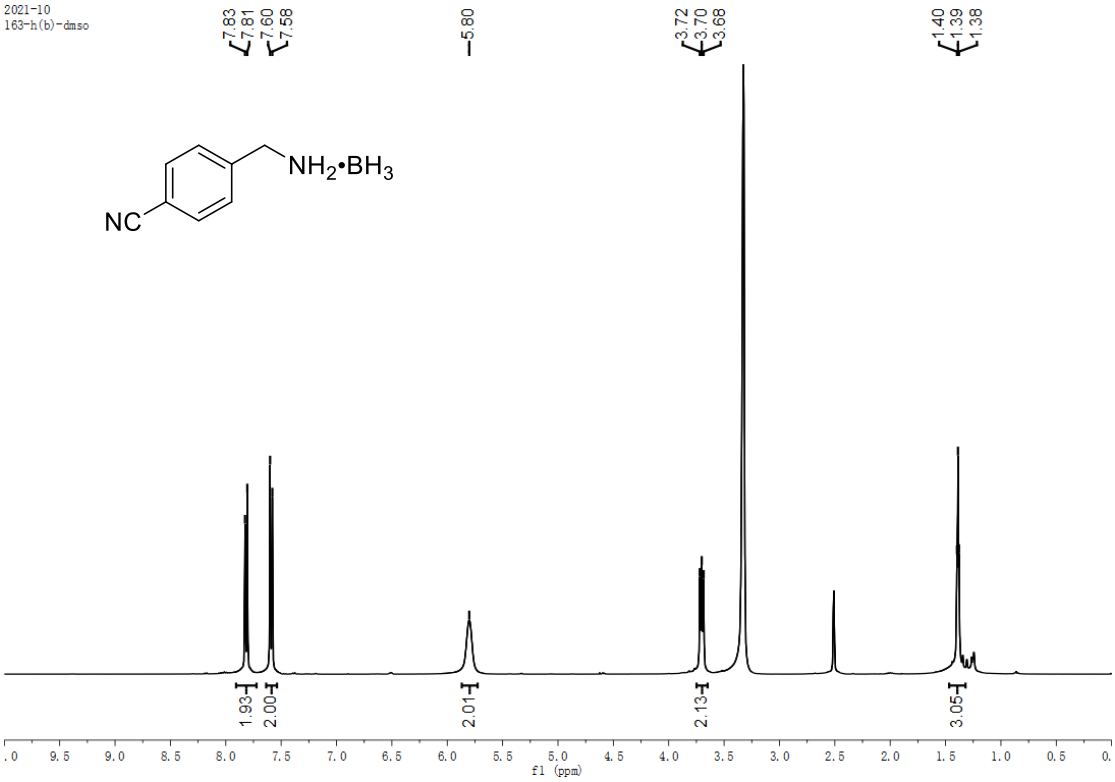


Figure S60. ^{1}H{B} NMR spectrum of **2k** (400 MHz, DMSO)

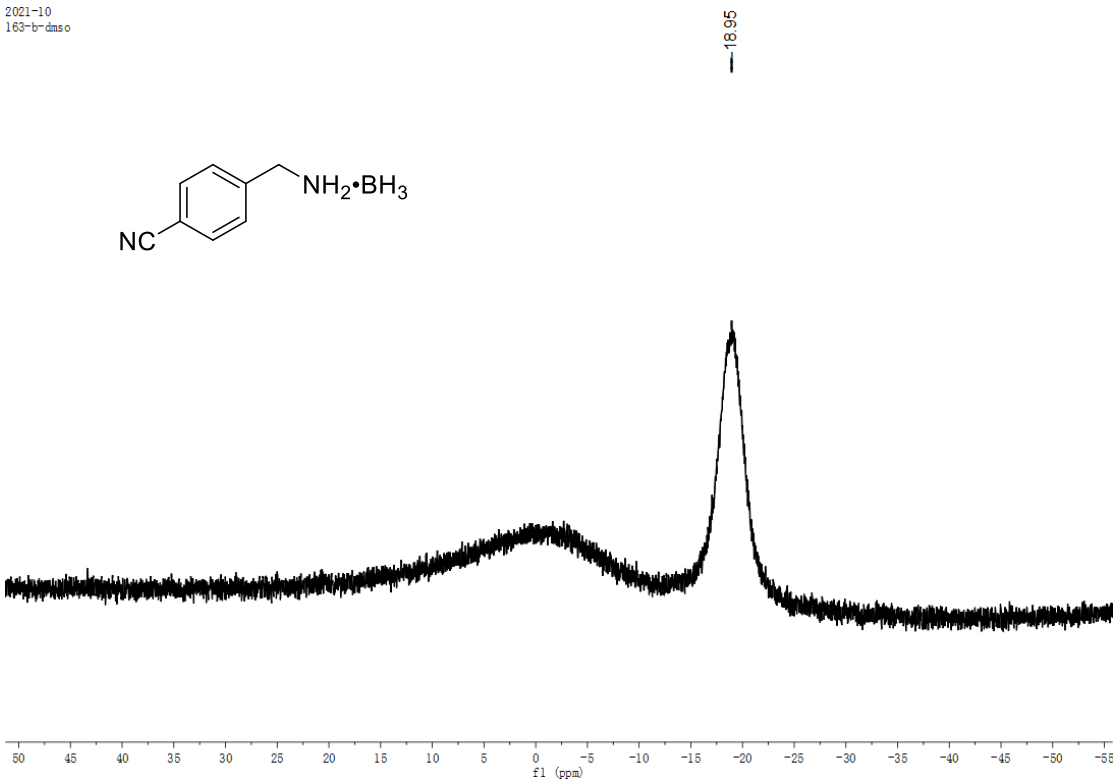


Figure S61. ^{11}B NMR spectrum of **2k** (400 MHz, DMSO)

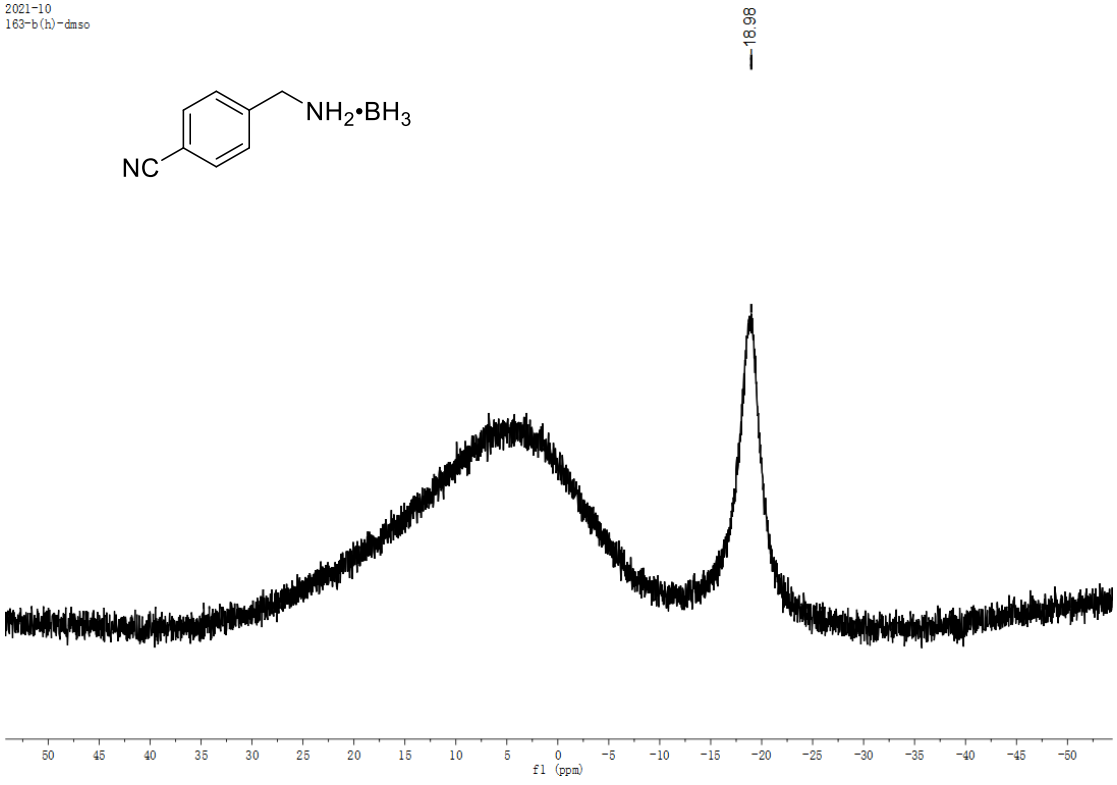


Figure S62. ^{11}B{H} NMR spectrum of **2k** (400 MHz, DMSO)

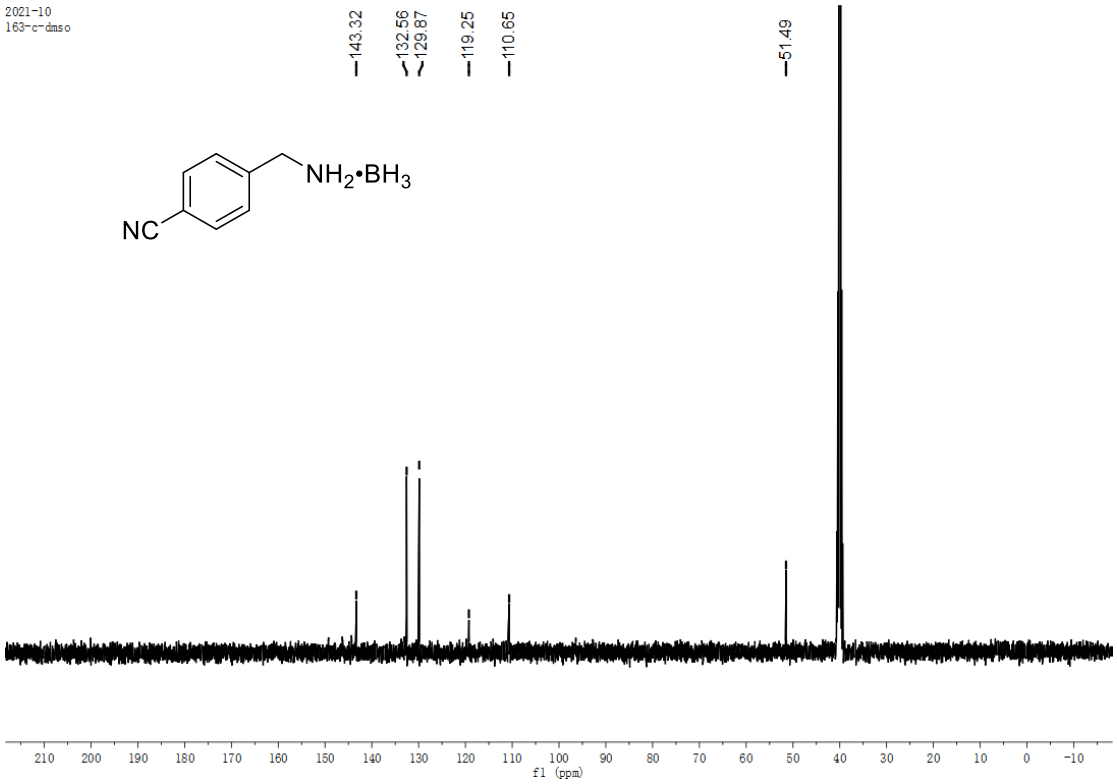


Figure S63. ^{13}C NMR spectrum of **2k** (400 MHz, DMSO)

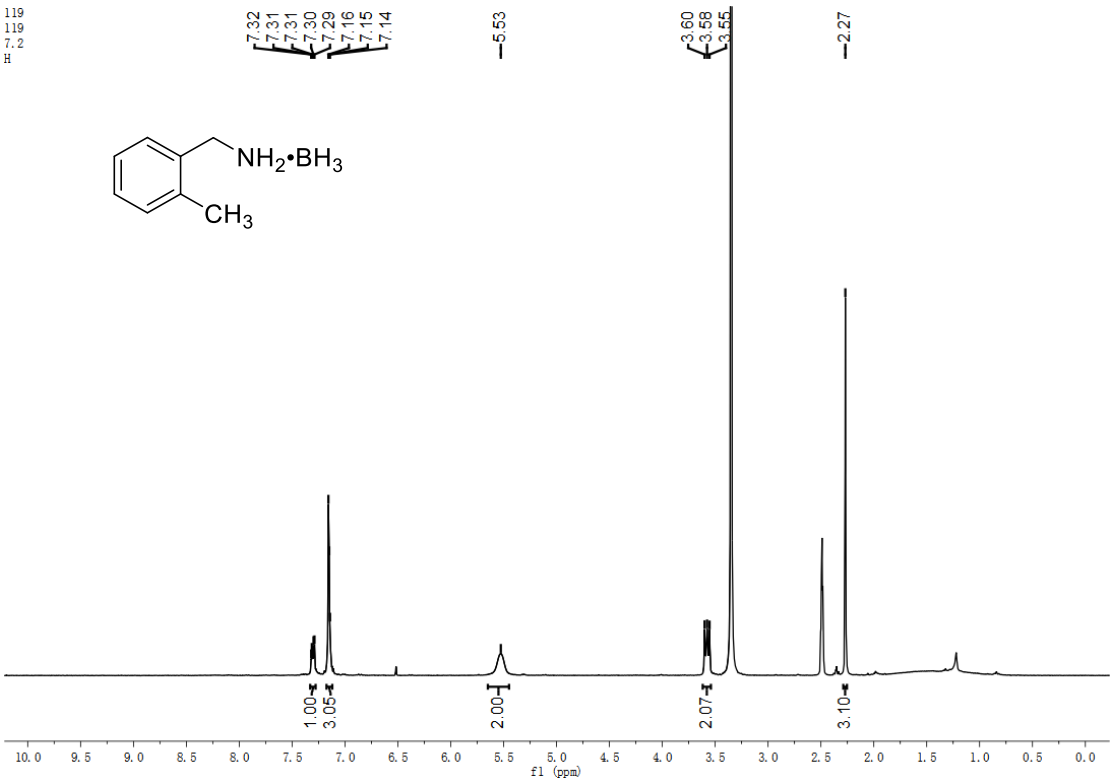


Figure S64. ^{1}H NMR spectrum of **2l** (300 MHz, DMSO)

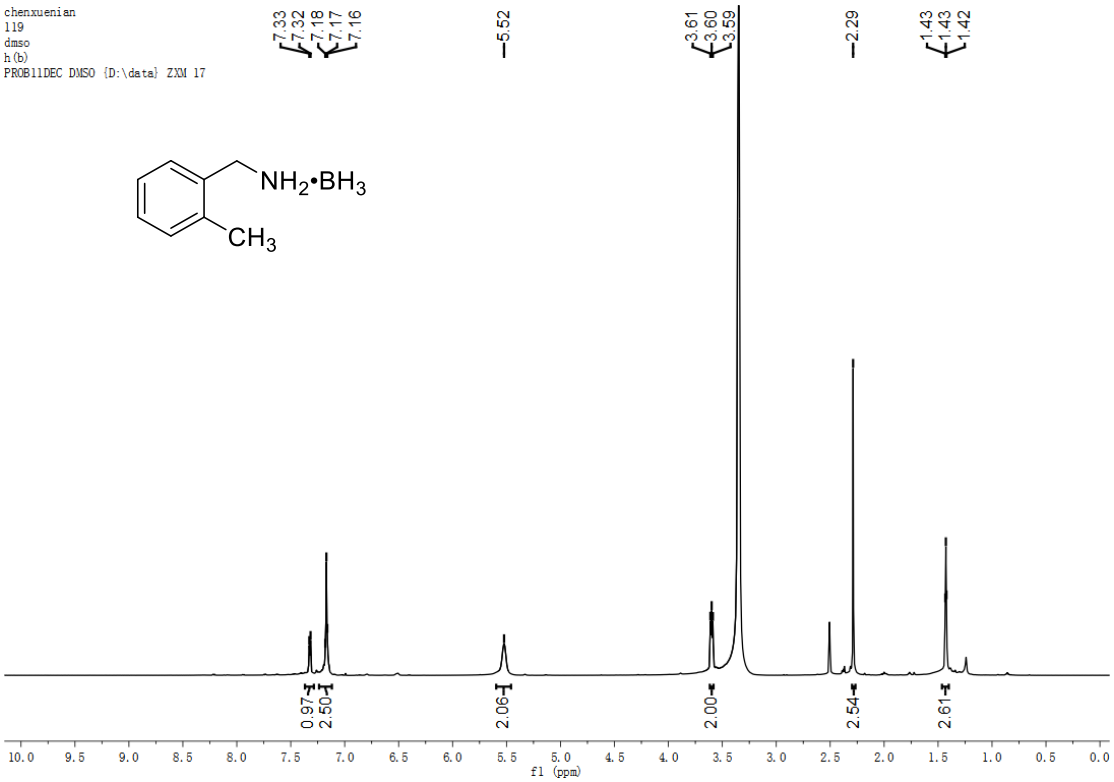


Figure S65. ^{1}H{B} NMR spectrum of **2l** (600 MHz, DMSO)

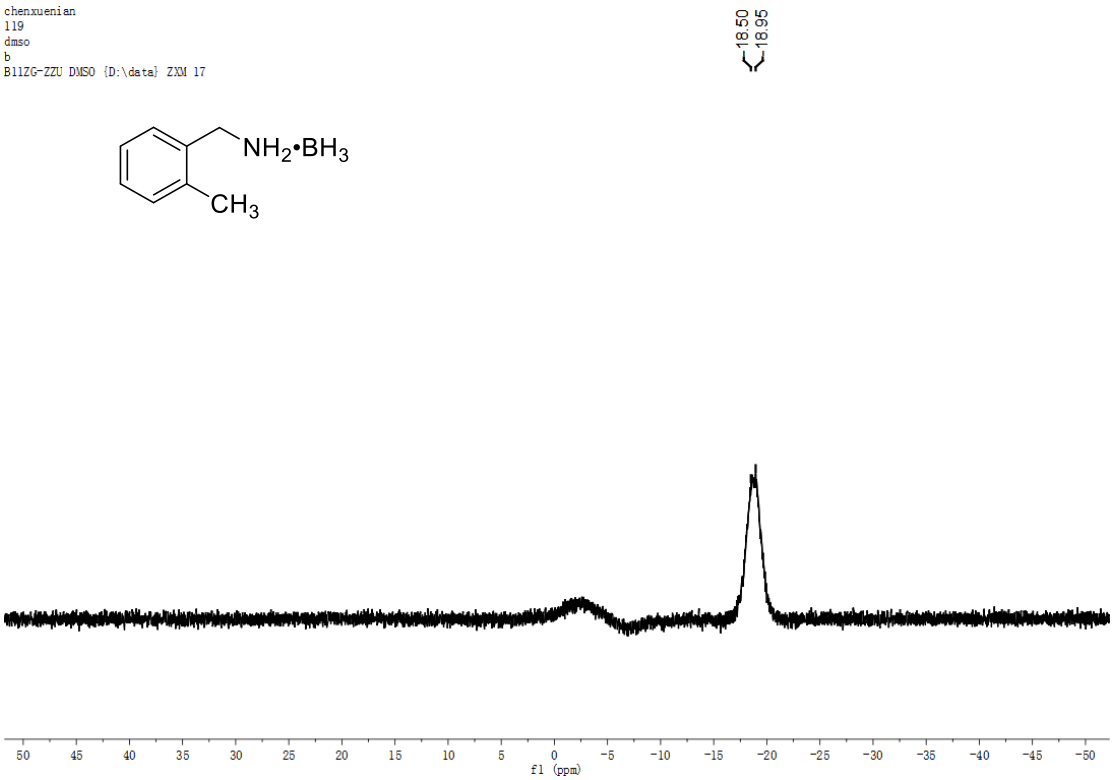


Figure S66. ^{11}B NMR spectrum of **2l** 600 MHz, DMSO)

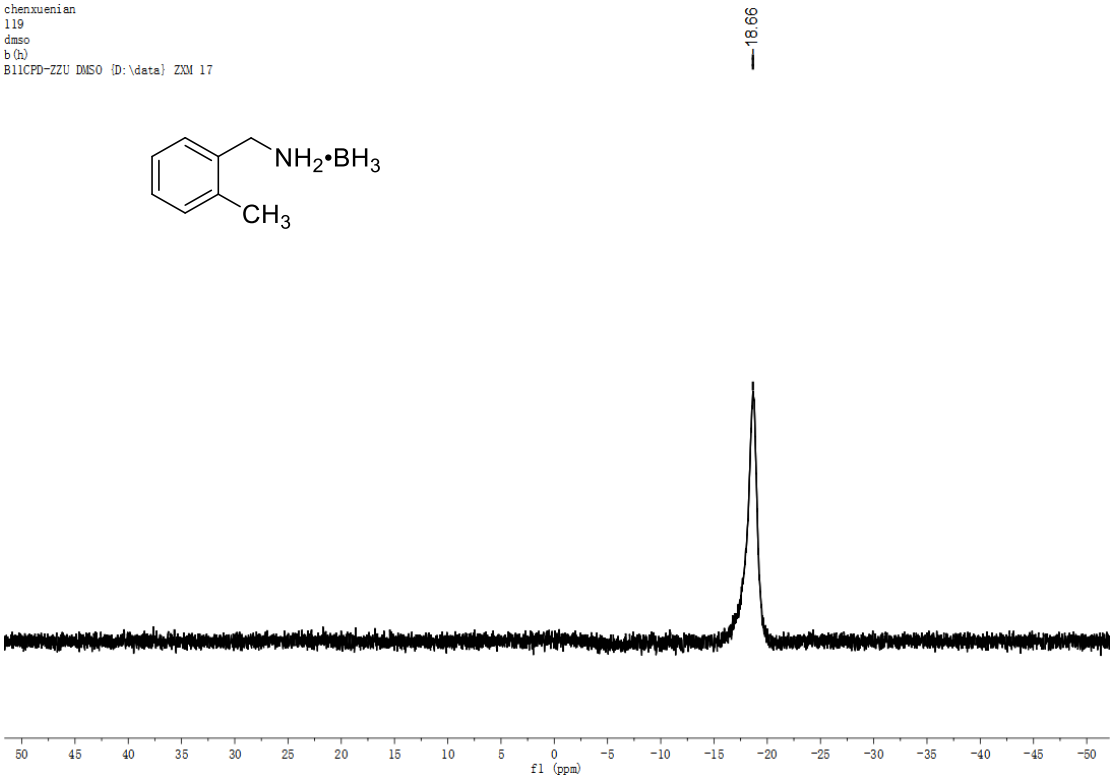


Figure S67. ^{11}B{H} NMR spectrum of **2l (**600 MHz, DMSO)

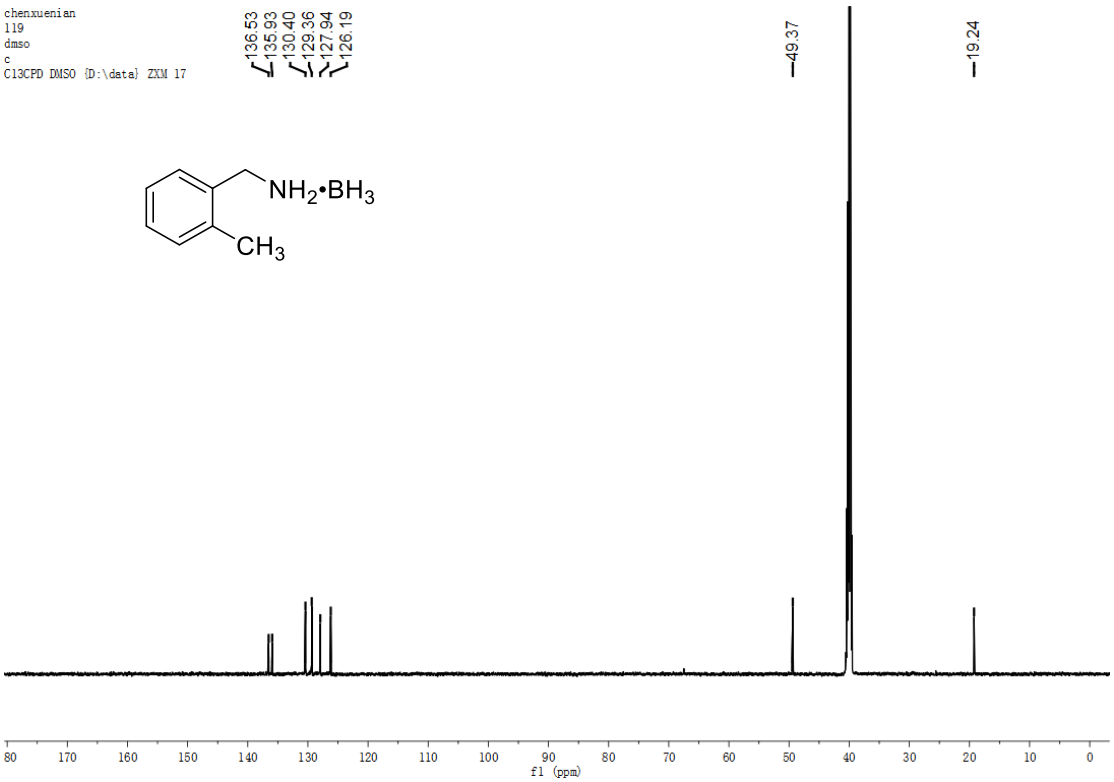


Figure S68. ^{13}C NMR spectrum of **2l (**600 MHz, DMSO)

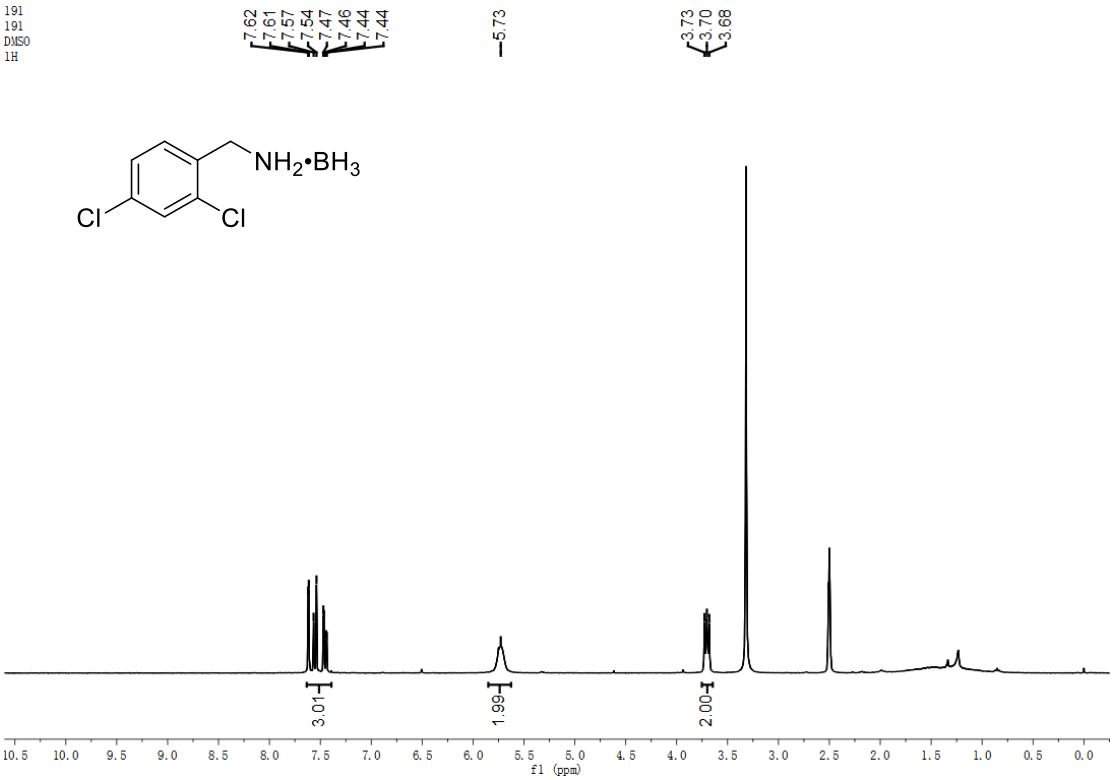


Figure S69. ^{1}H NMR spectrum of **2m (**300 MHz, DMSO)

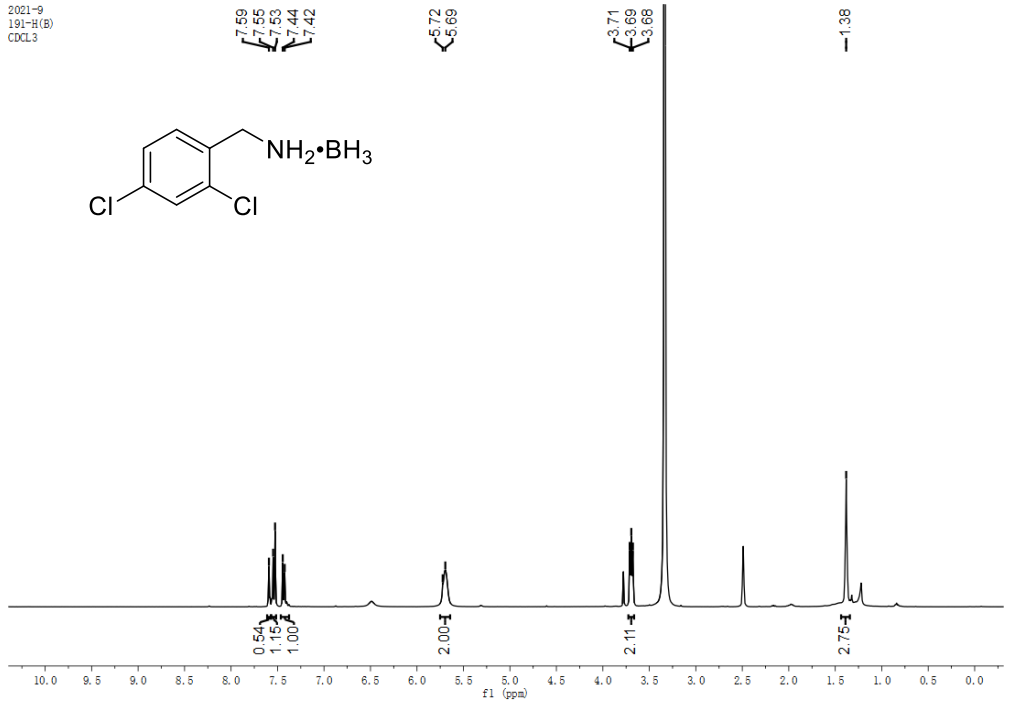


Figure S70. ^{1}H{B} NMR spectrum of **2m (**400 MHz, DMSO)

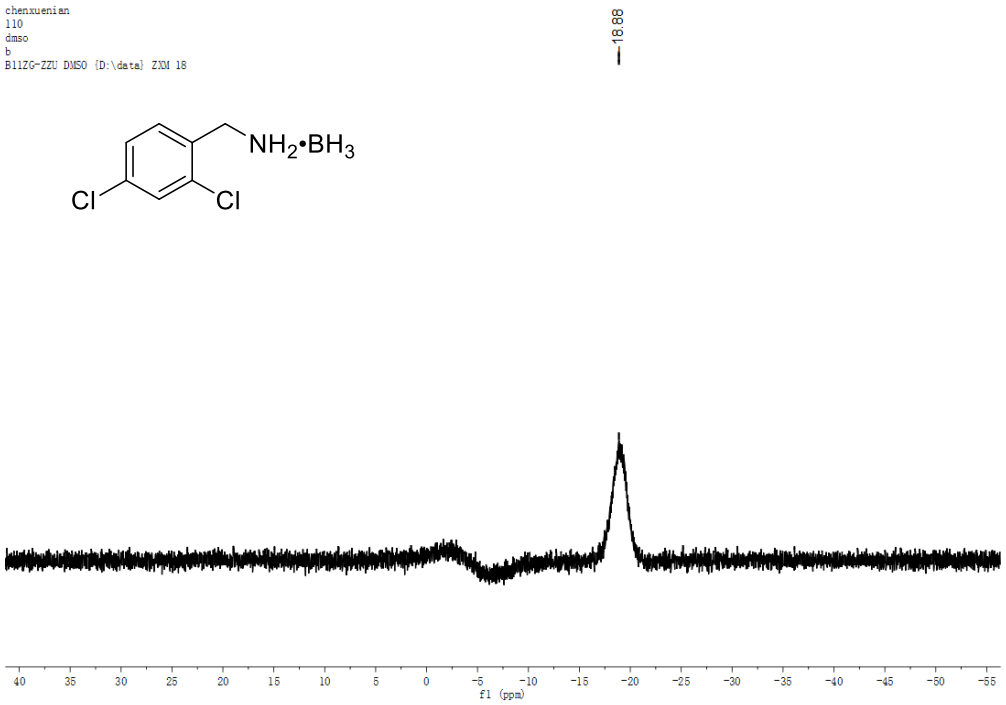


Figure S71. $^{11}B\{H\}$ NMR spectrum of **2m (**600 MHz, DMSO)

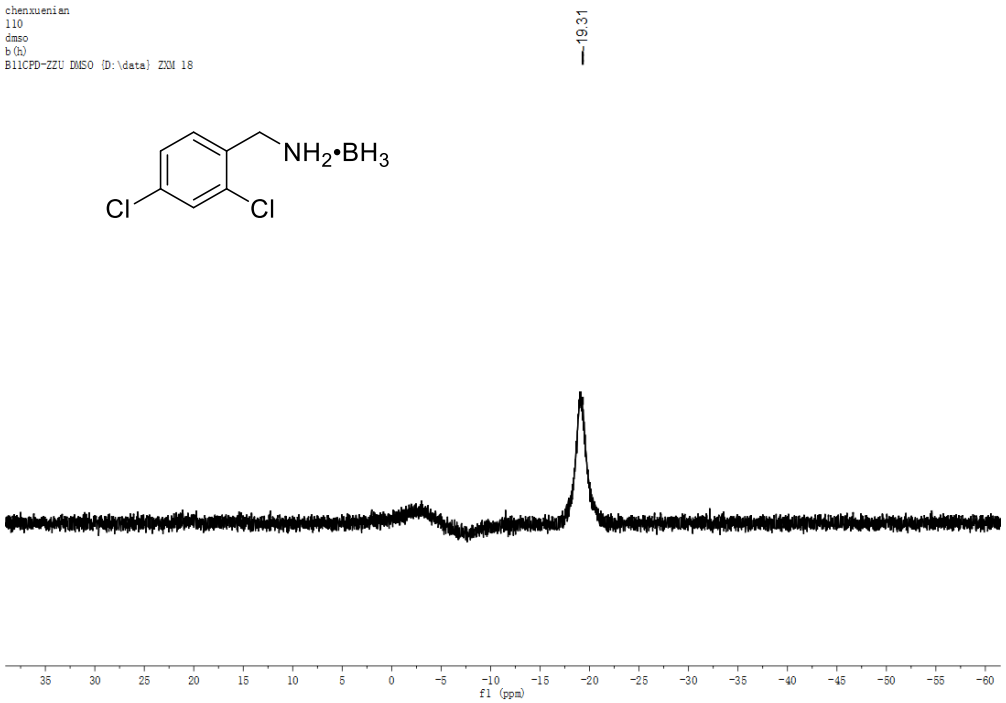


Figure S72. $^{11}B\{H\}$ NMR spectrum of **2m (**600 MHz, DMSO)

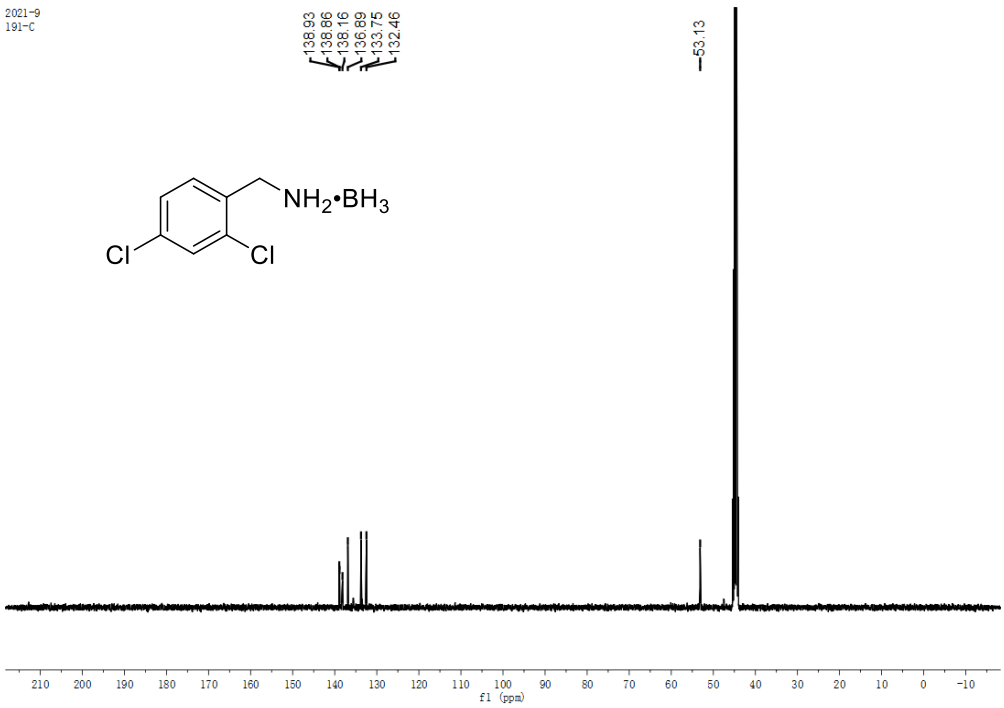


Figure S73. ^{13}C NMR spectrum of **2m (**400 MHz, DMSO)

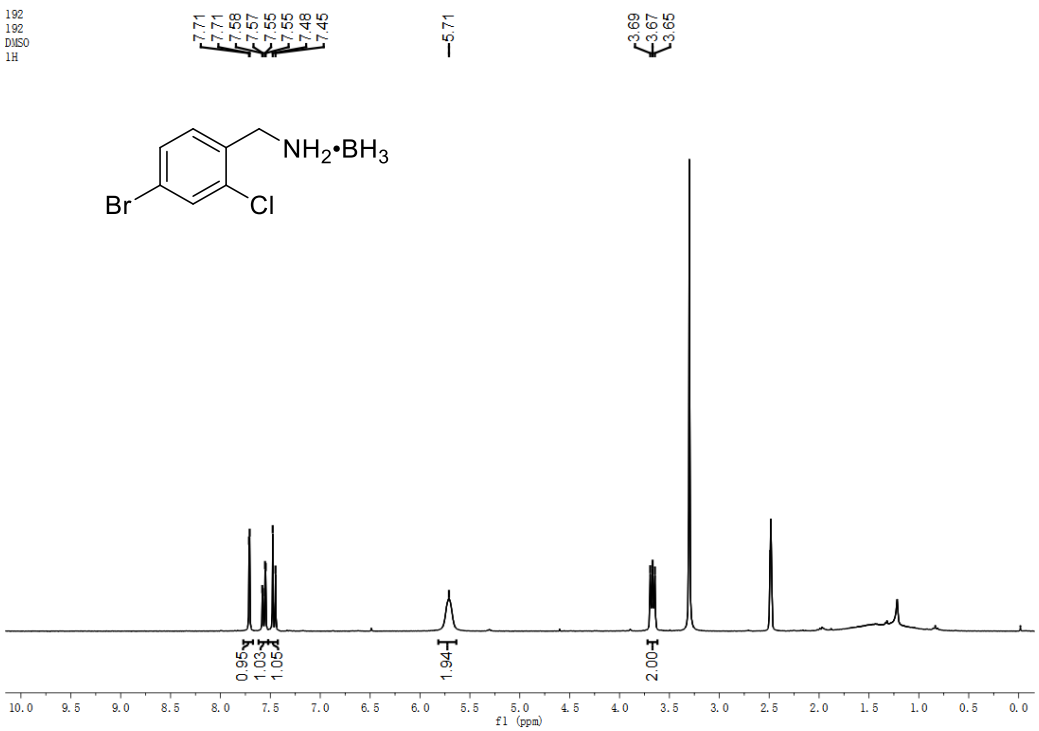


Figure S74. ^{1}H NMR spectrum of **2n (**400 MHz, DMSO)

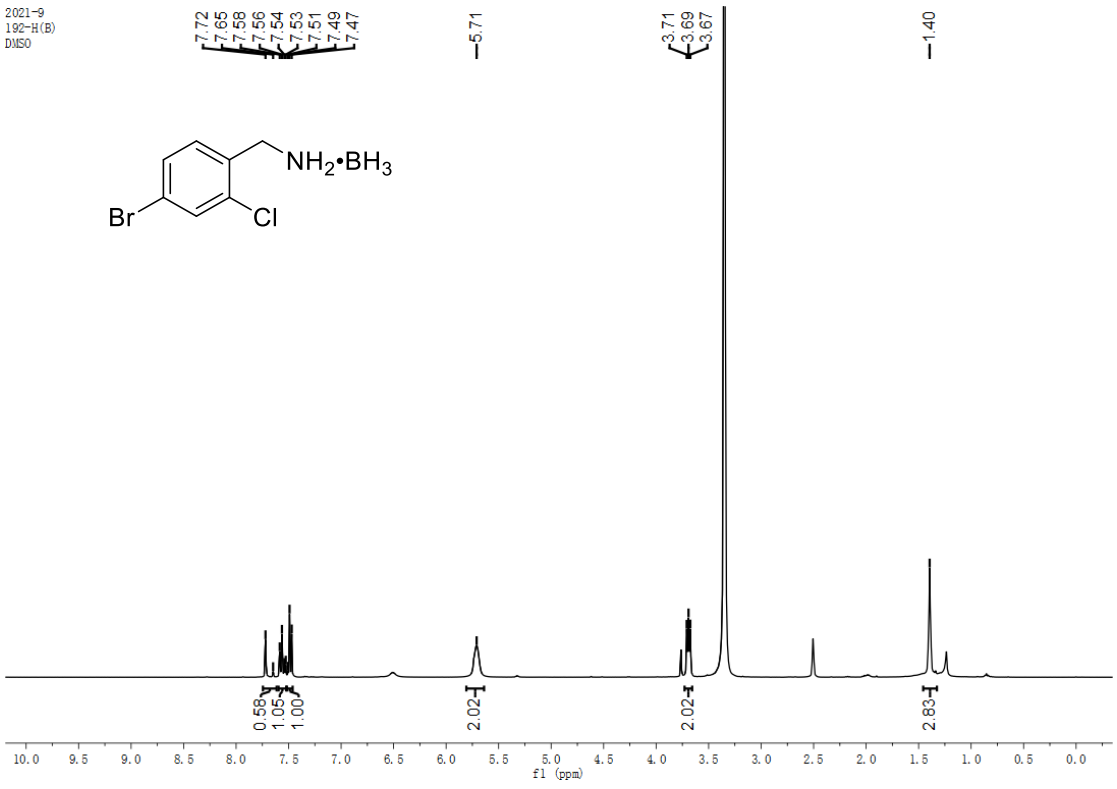


Figure S75. ^{1}H{B} NMR spectrum of **2n (**400 MHz, DMSO)

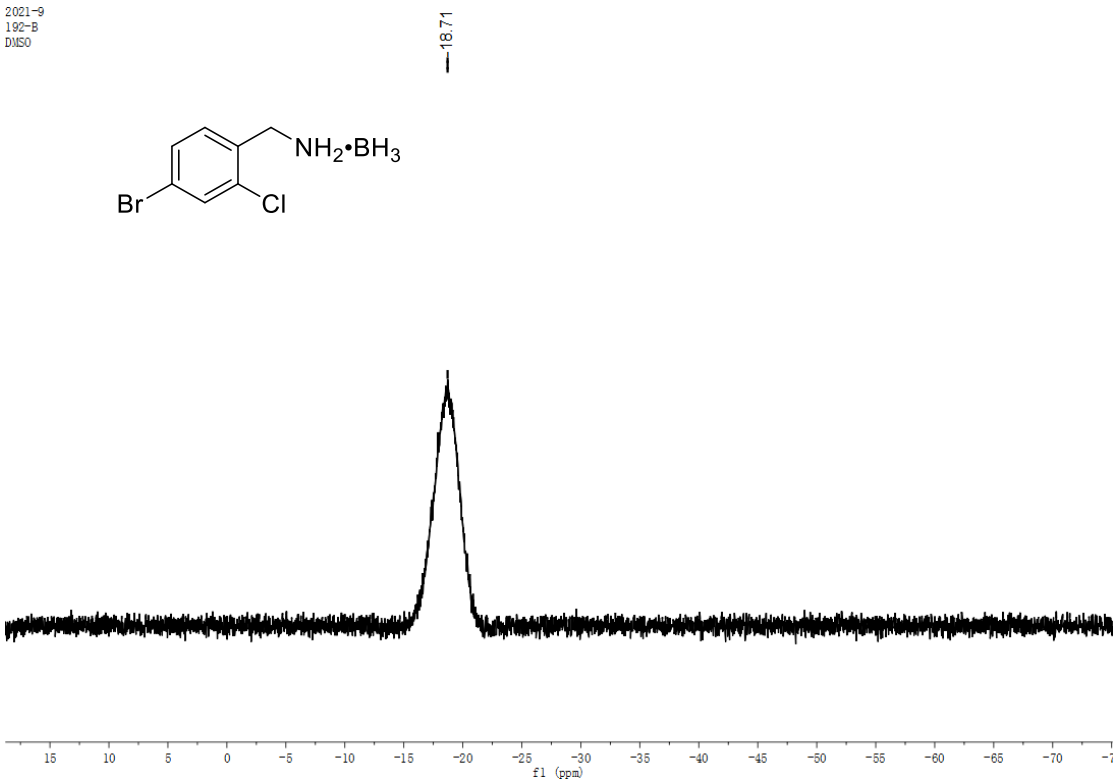


Figure S76. ^{11}B NMR spectrum of **2n (**400 MHz, DMSO)

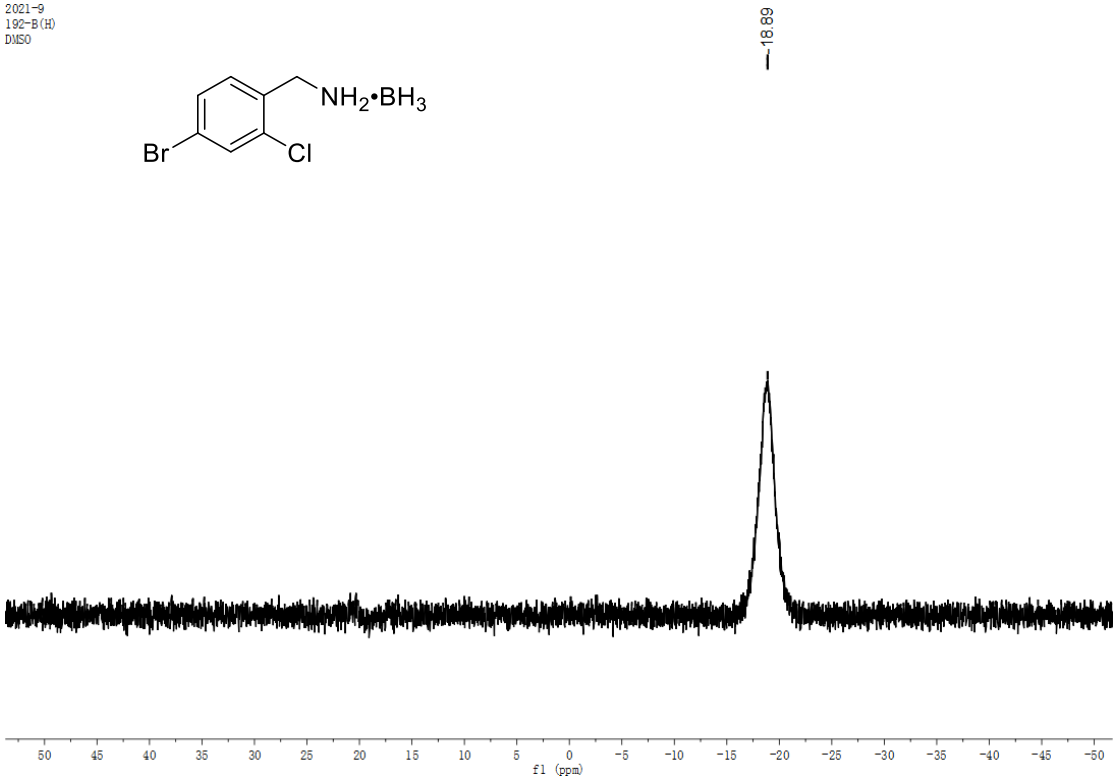


Figure S77. ^{11}B{H} NMR spectrum of **2n (**400 MHz, DMSO)

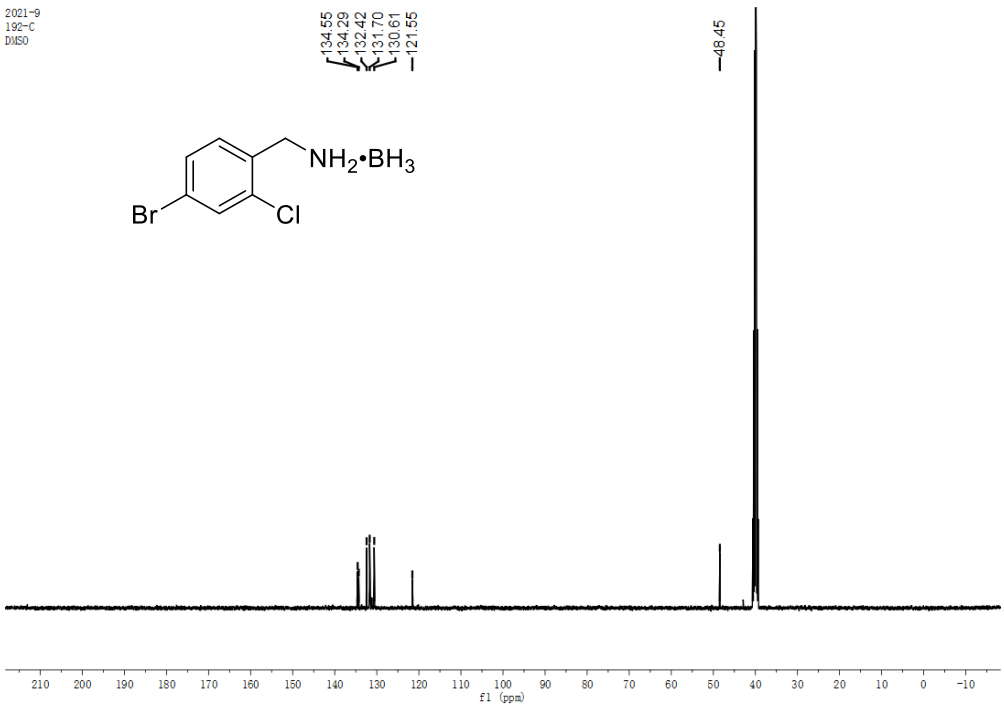


Figure S78. ^{13}C NMR spectrum of **2n (**400 MHz, DMSO)

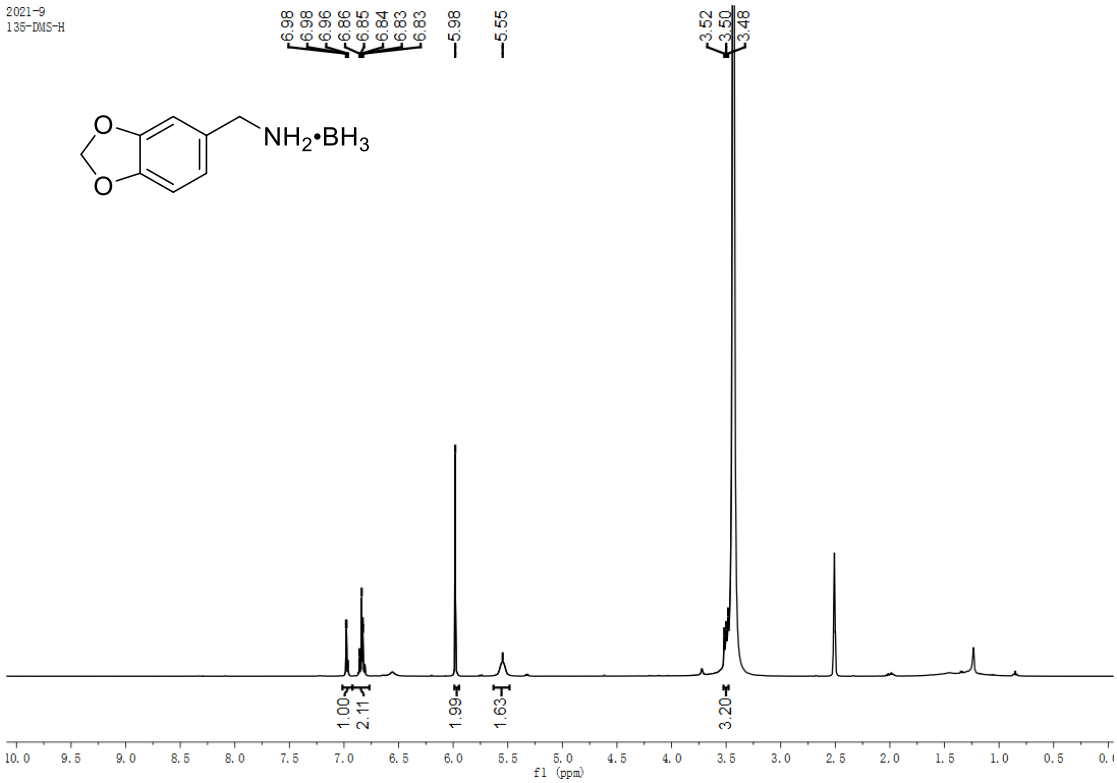


Figure S79. ^{1}H NMR spectrum of **2o (**400 MHz, DMSO)

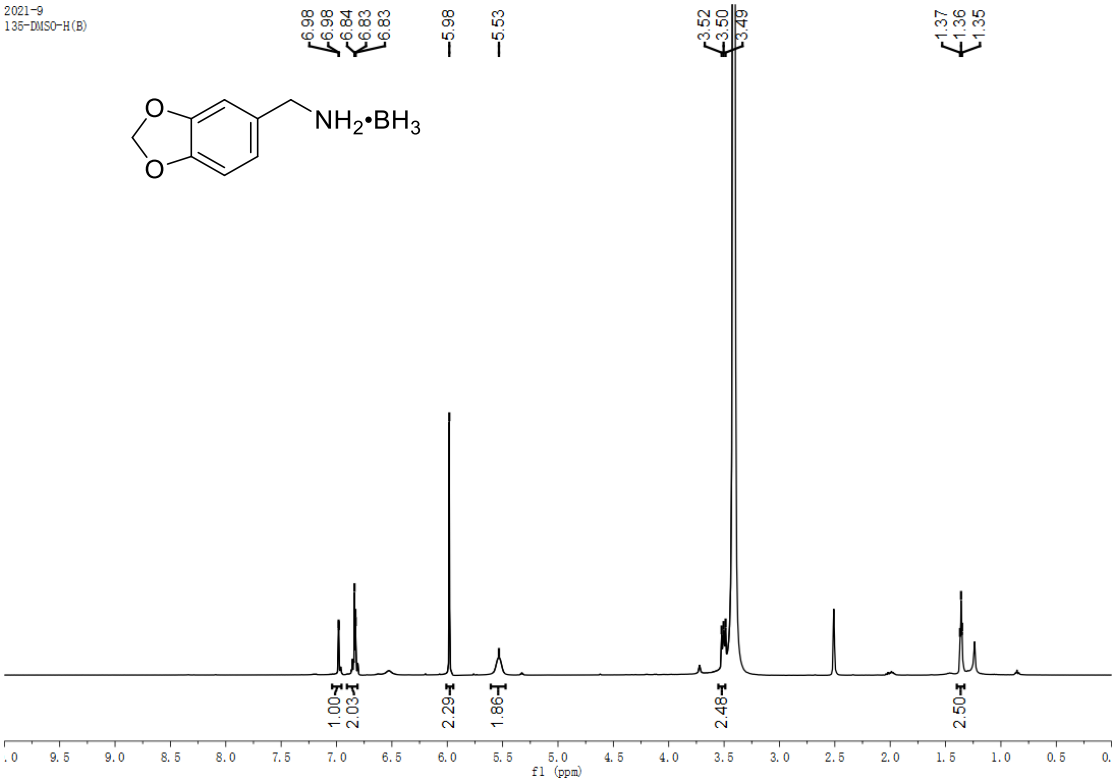


Figure S80. ^{1}H{B} NMR spectrum of **2o (**400 MHz, DMSO)

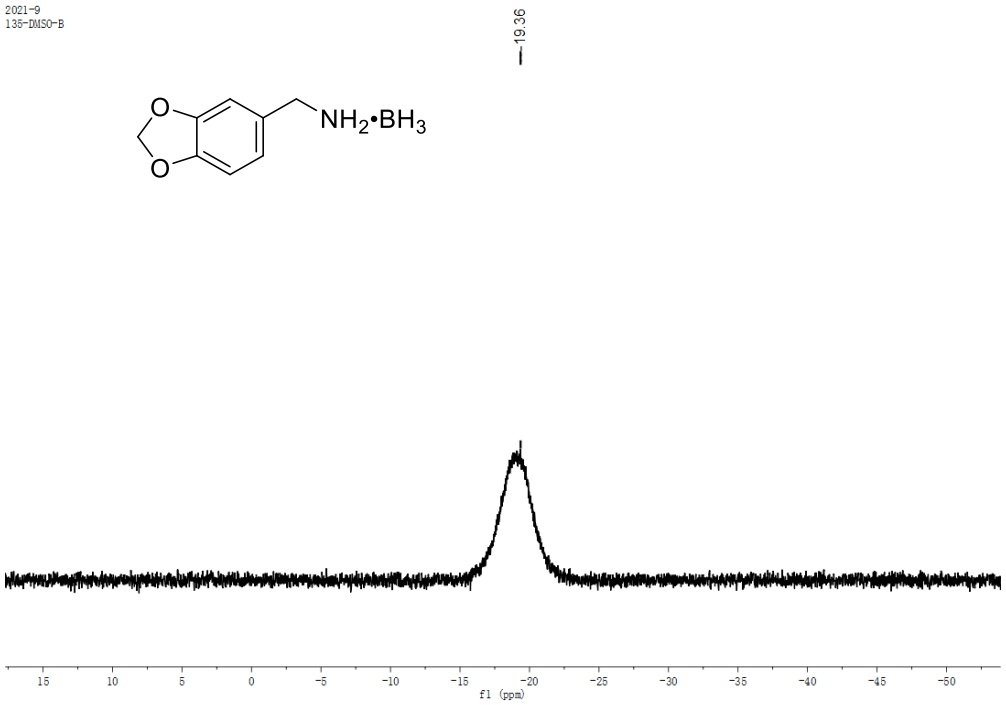


Figure S81. ^{11}BNMR spectrum of **2o (**400 MHz, DMSO)

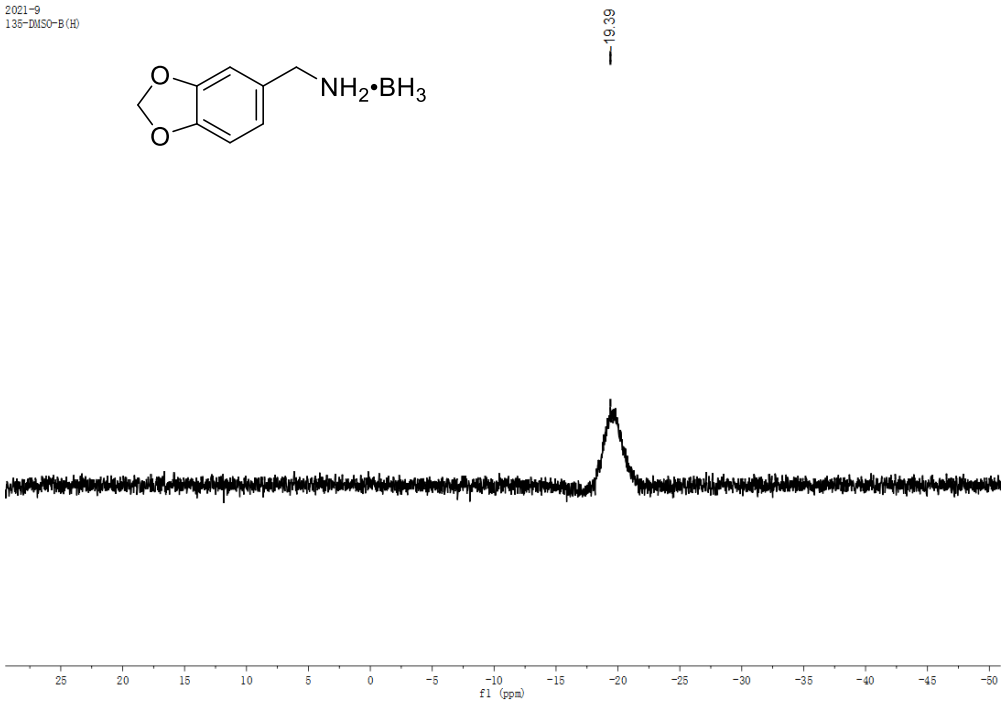


Figure S82. ^{11}B{H} NMR spectrum of **2o (**400 MHz, DMSO)

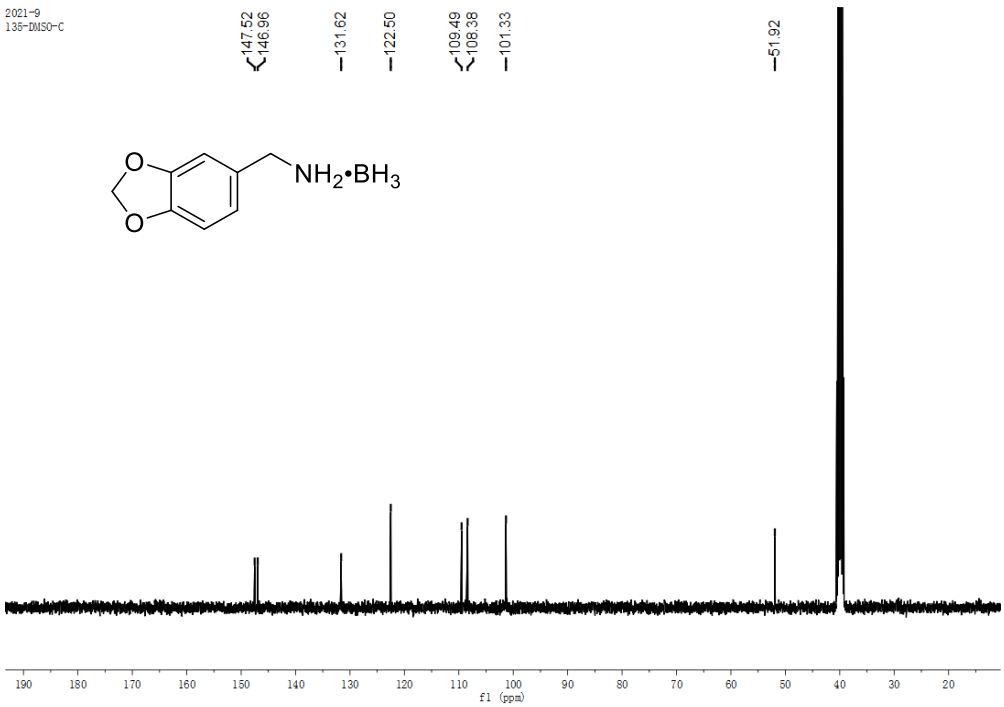


Figure S83. ^{13}C NMR spectrum of **2o (**400 MHz, DMSO)

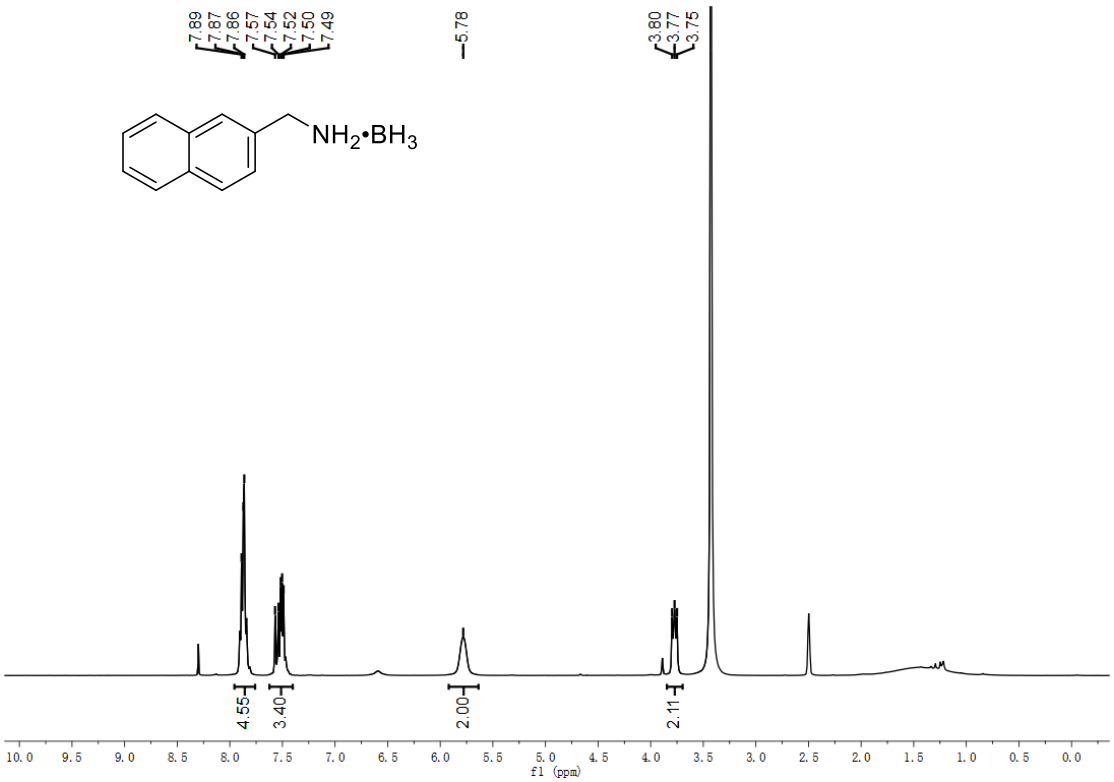


Figure S84. ^{1}H NMR spectrum of **2p (**300 MHz, DMSO)

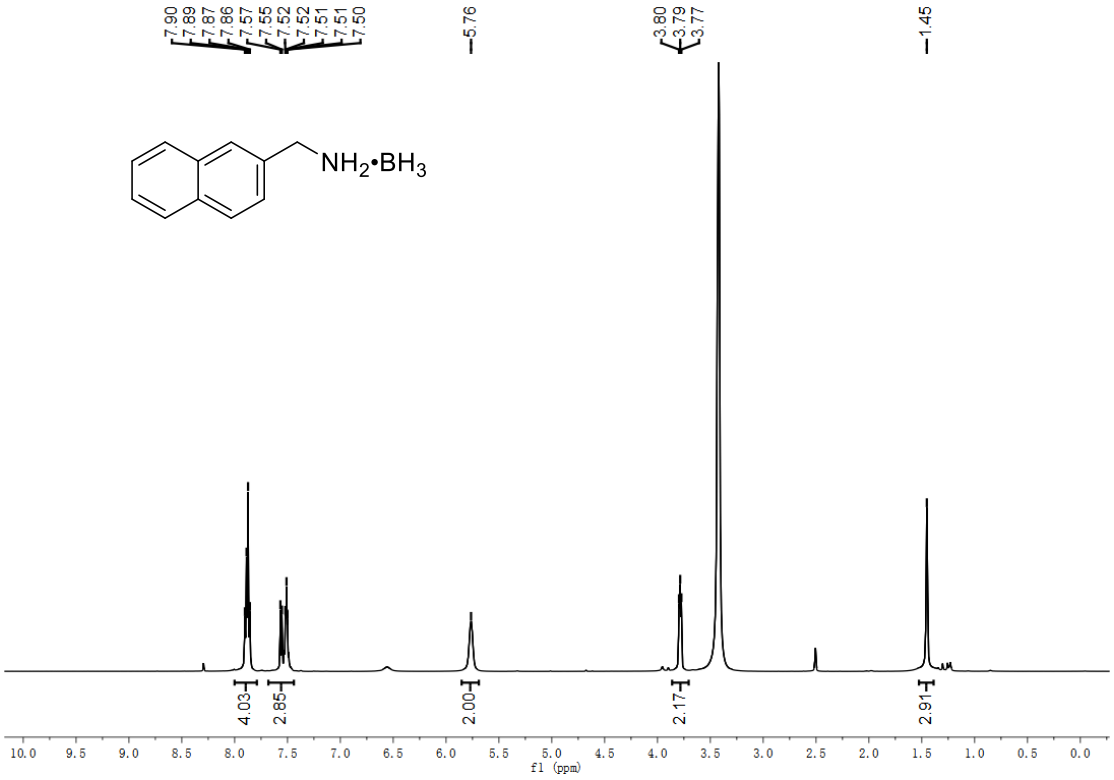


Figure S85. ^{1}H{B} NMR spectrum of **2p (**600 MHz, DMSO)

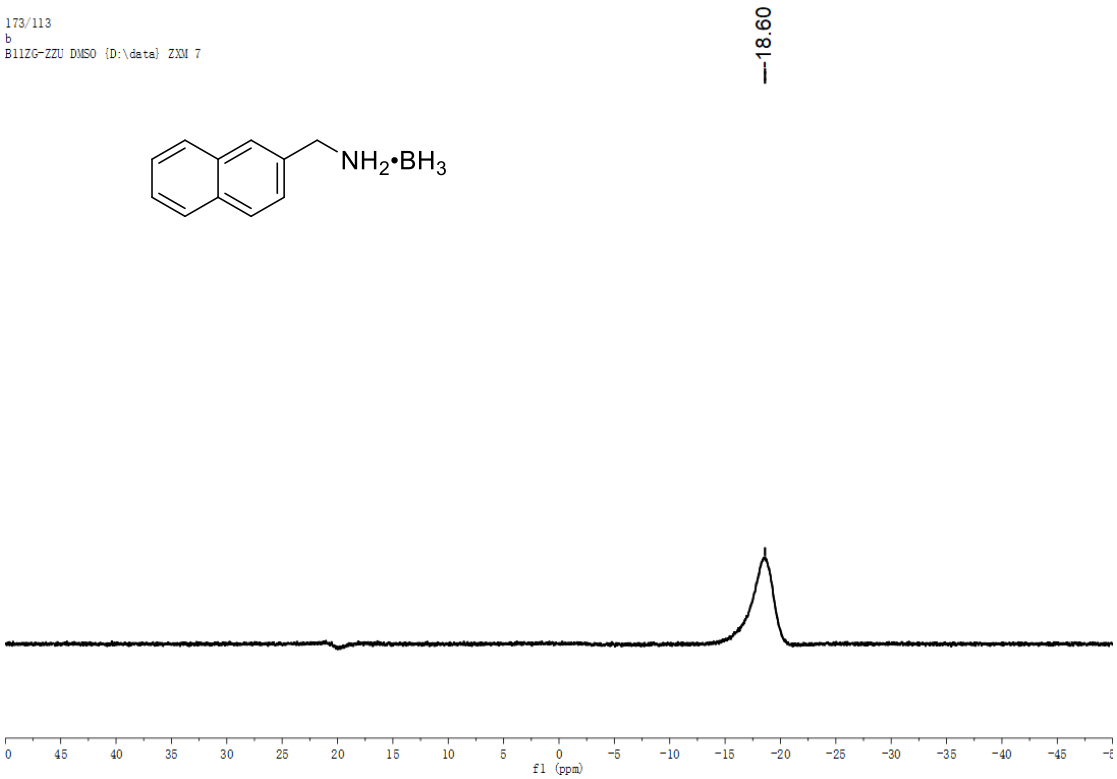


Figure S86. ^{11}B NMR spectrum of **2p (**600 MHz, DMSO)

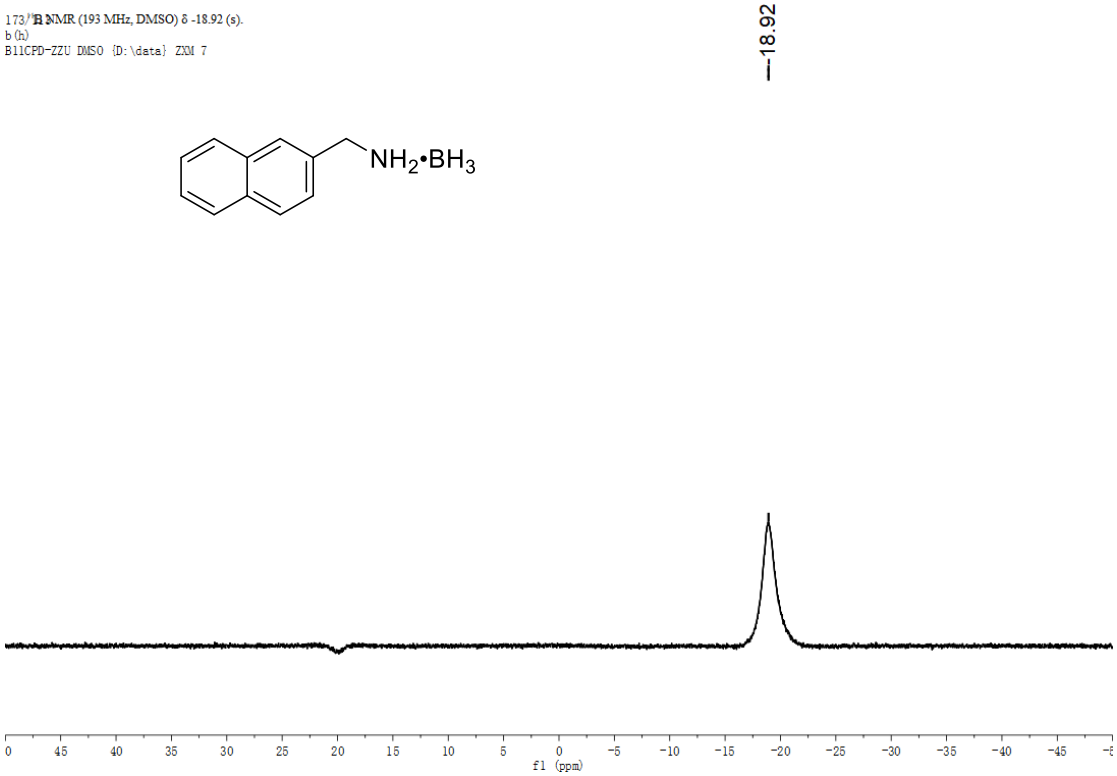


Figure S87. ^{11}B{H} NMR spectrum of **2p (**600 MHz, DMSO)

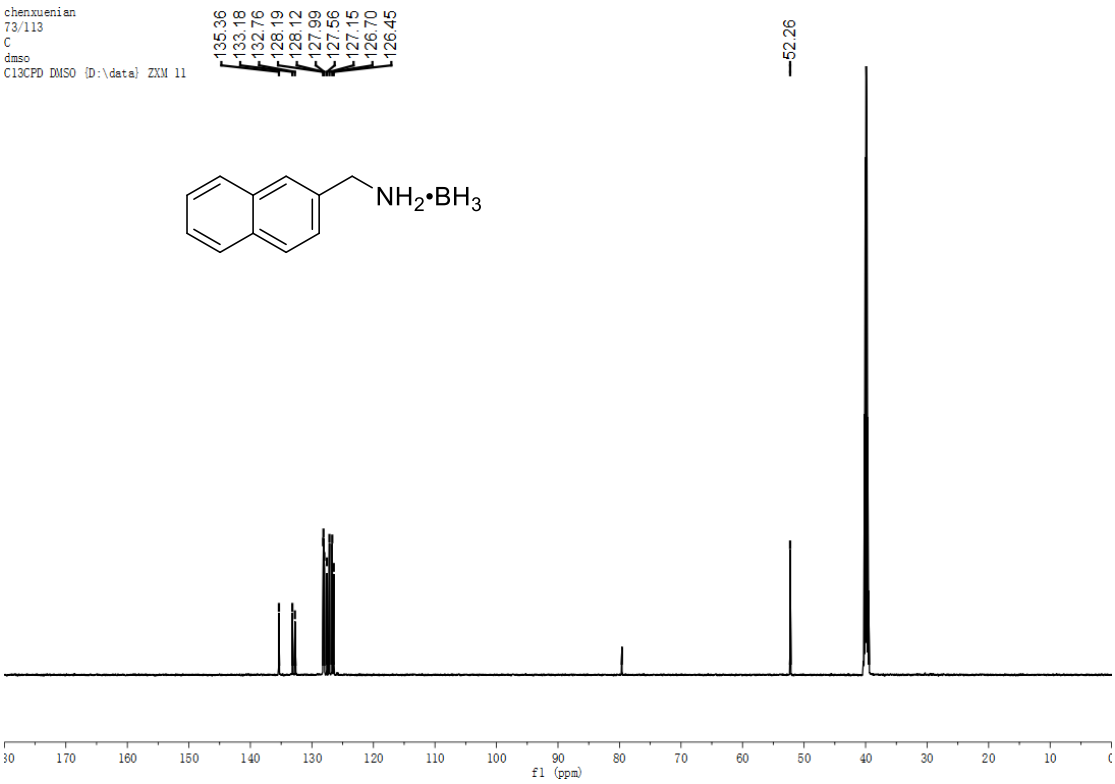


Figure S88. ^{13}C NMR spectrum of **2p (**600 MHz, DMSO)

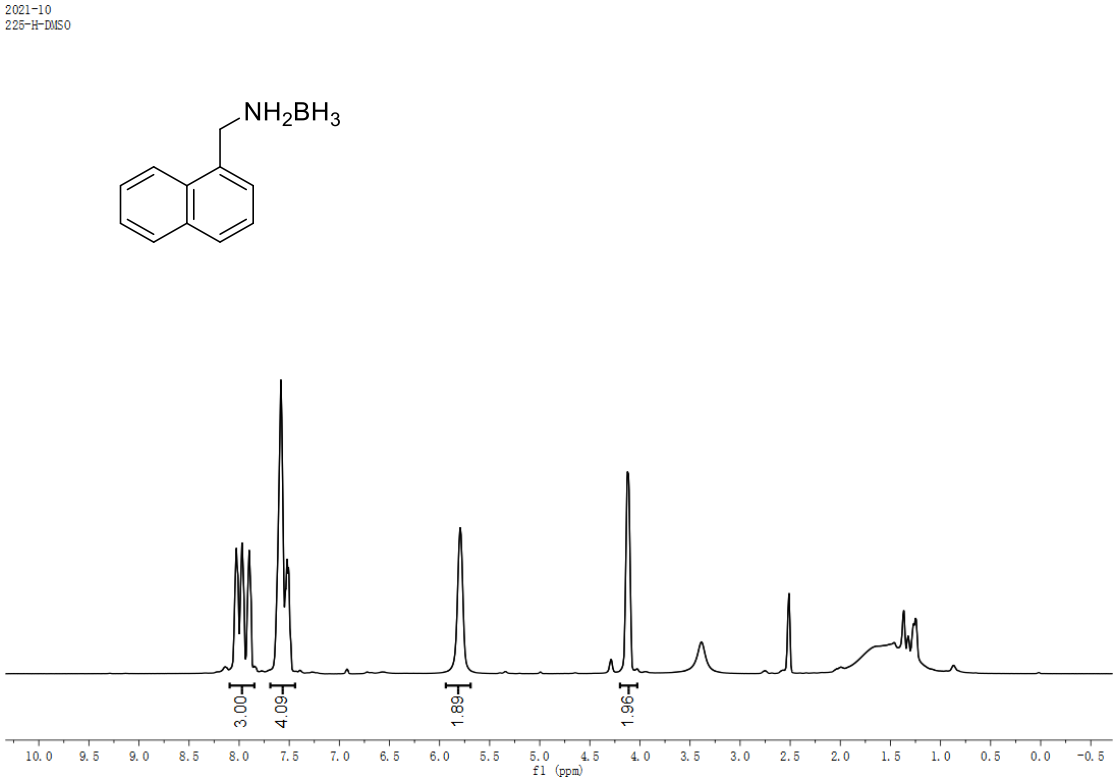


Figure S89. ^{1}H NMR spectrum of **2q** (400 MHz, DMSO)

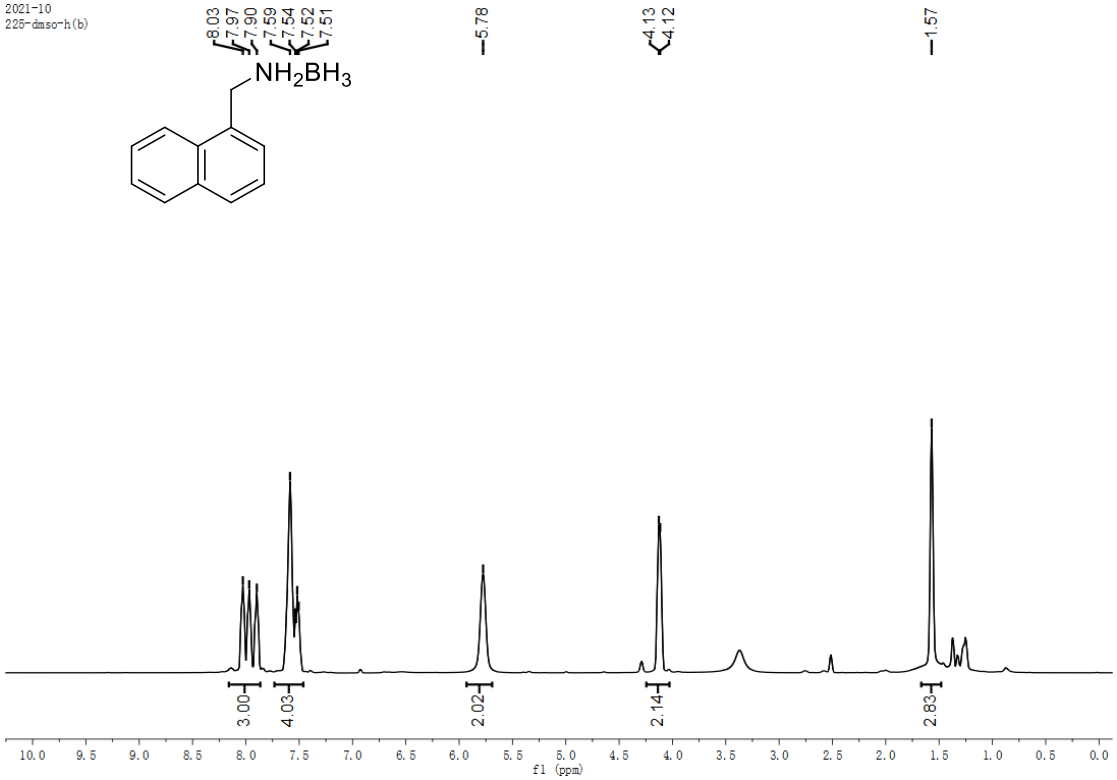


Figure S90. ^{1}H{B} NMR spectrum of **2q** (400 MHz, DMSO)

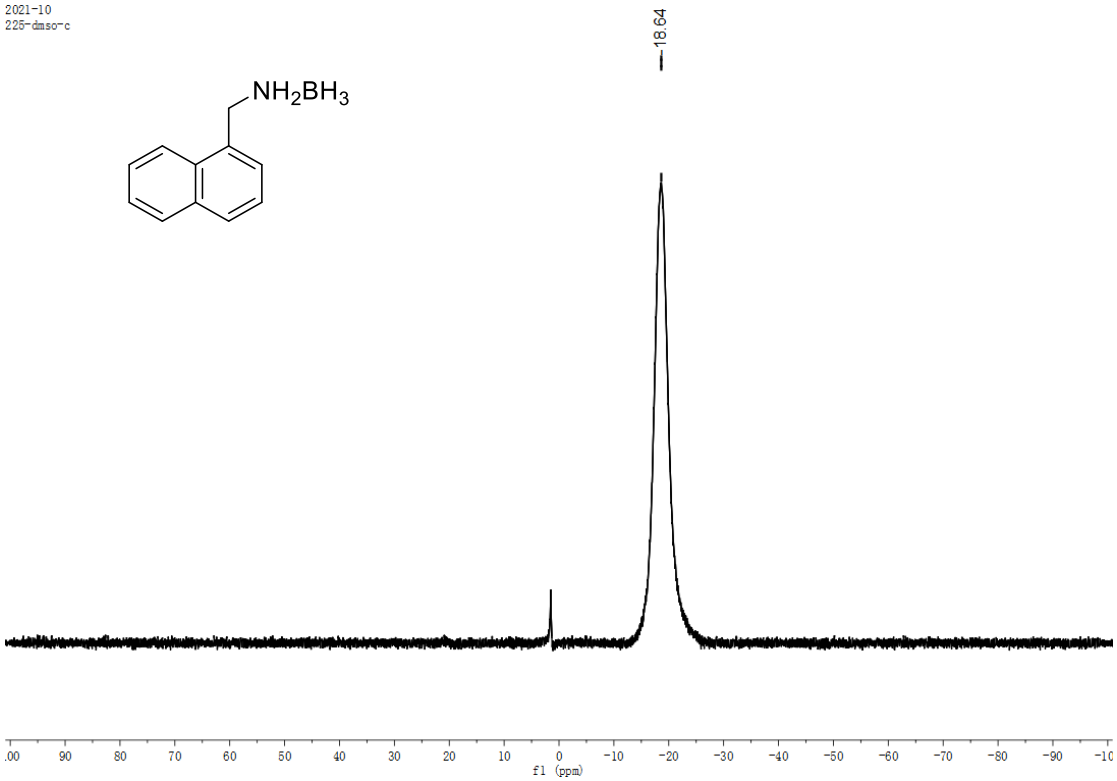


Figure S91. ^{11}B NMR spectrum of **2q** (400 MHz, DMSO)

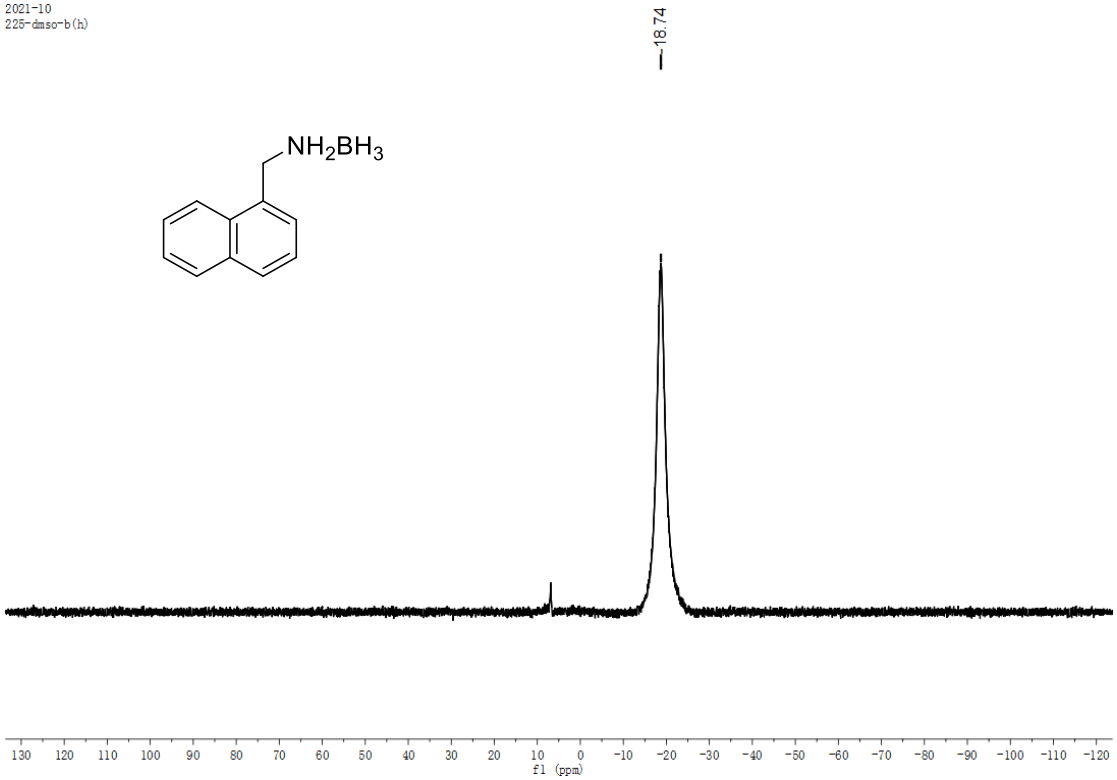


Figure S92. ^{11}B{H} NMR spectrum of **2q** (400 MHz, DMSO)

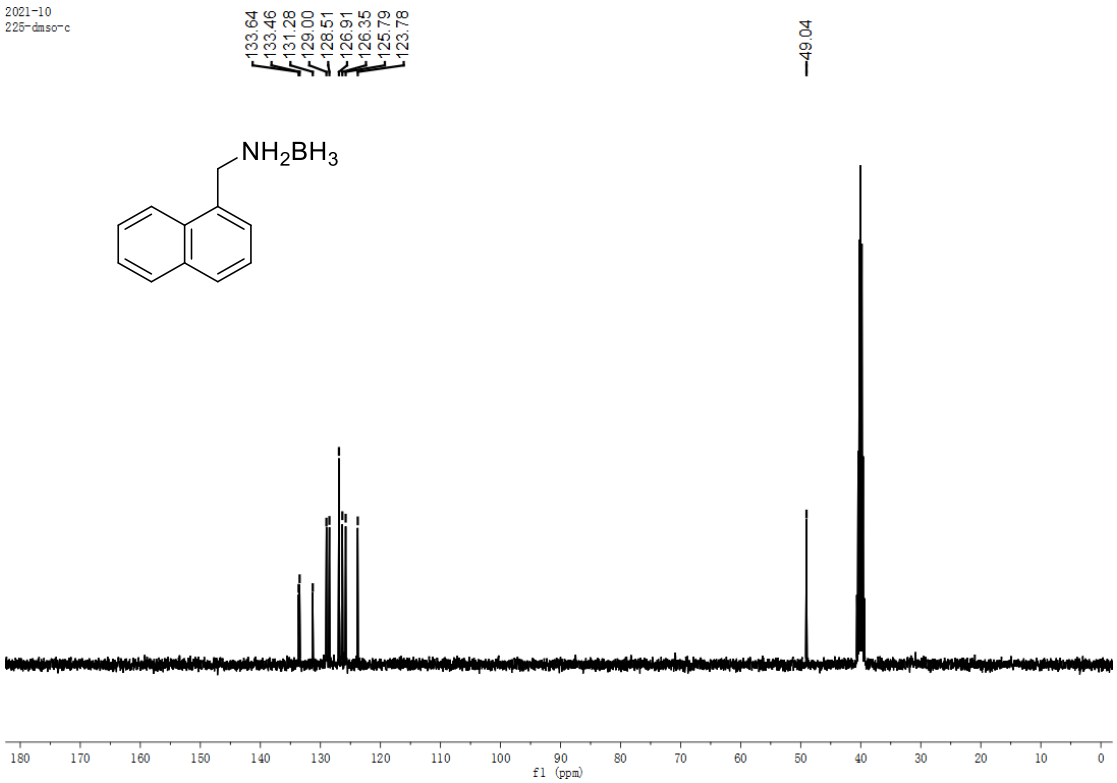


Figure S93. ^{13}C NMR spectrum of **2q** (400 MHz, DMSO)

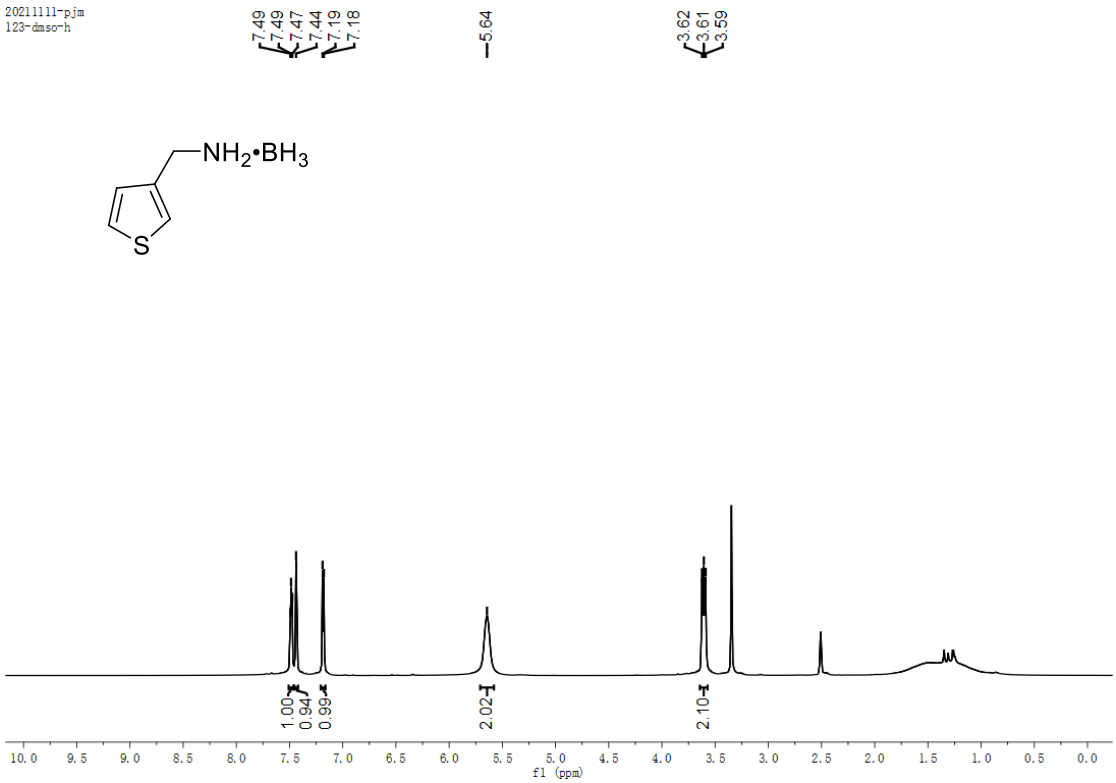


Figure S94. ^{1}H NMR spectrum of **2r** (400 MHz, DMSO)

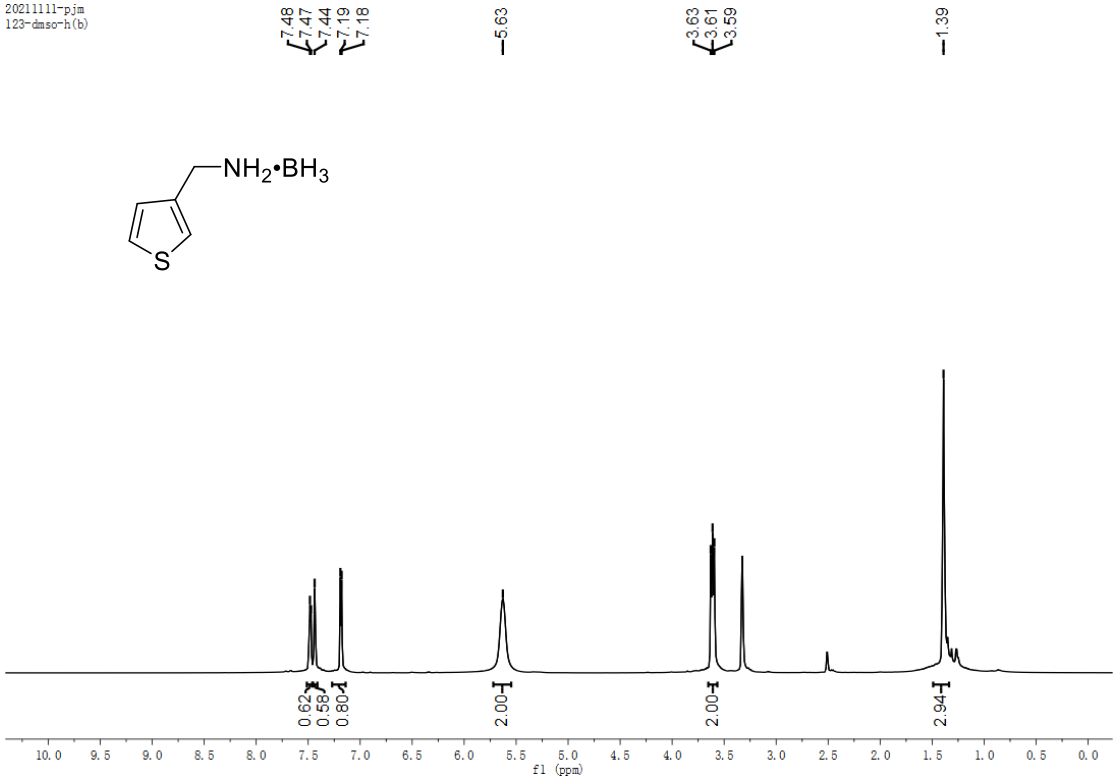


Figure S95. ^{1}H{B} NMR spectrum of **2r** (400 MHz, DMSO)

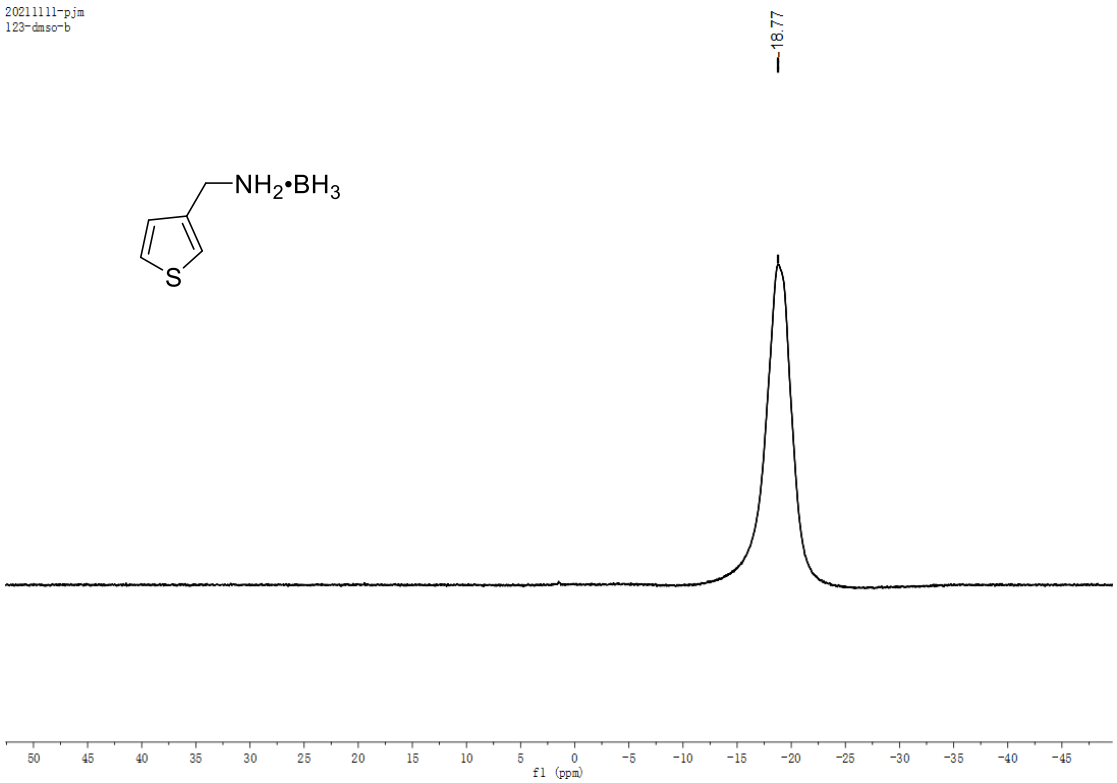


Figure S96. ^{11}B NMR spectrum of **2r** (400 MHz, DMSO)

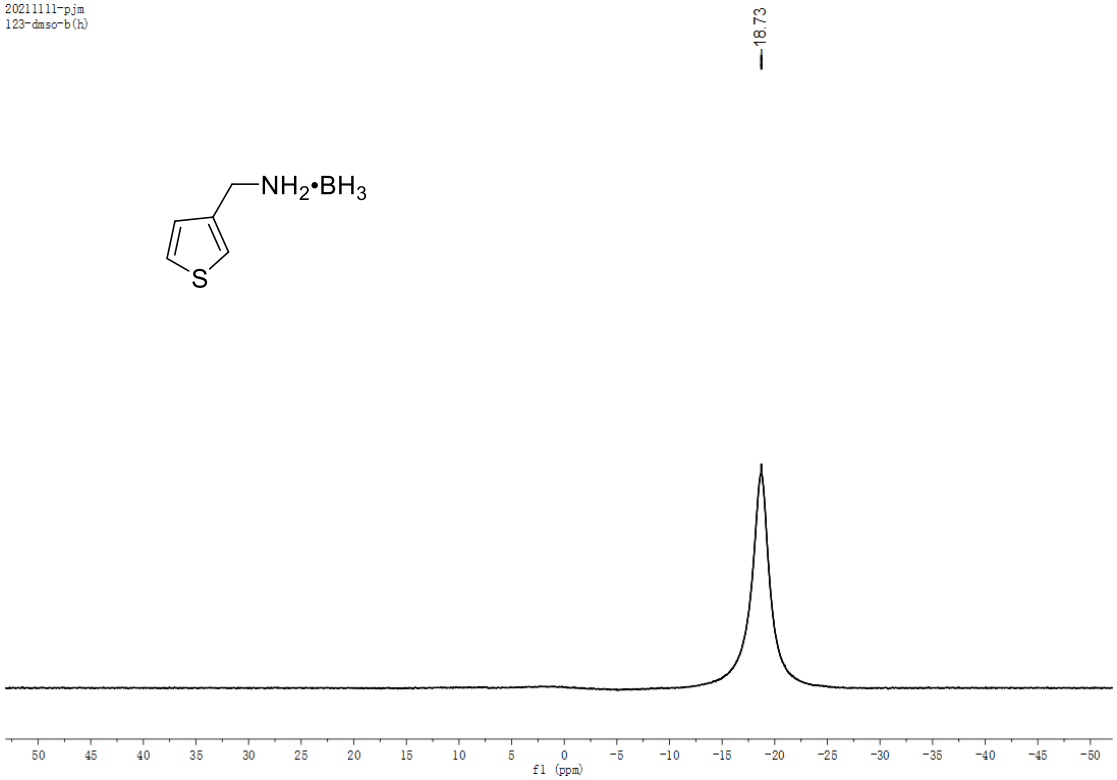


Figure S97. ^{11}B{H} NMR spectrum of **2r** (400 MHz, DMSO)

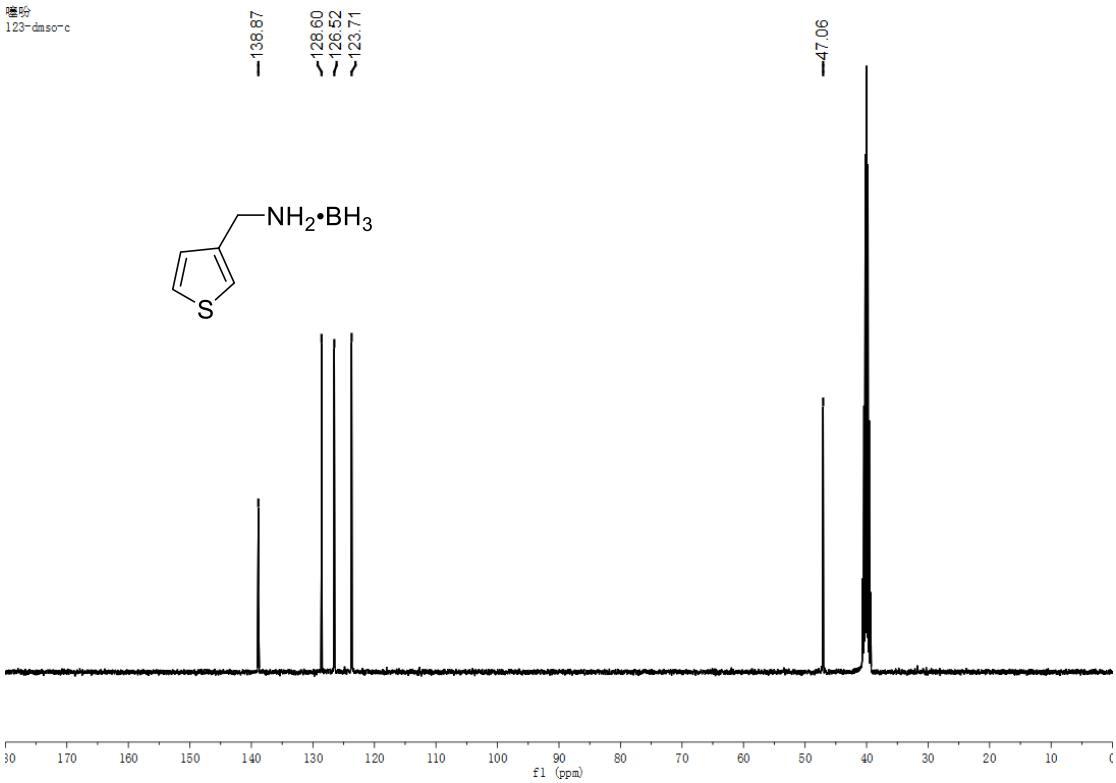


Figure S98. ^{13}C NMR spectrum of **2r** (400 MHz, DMSO)

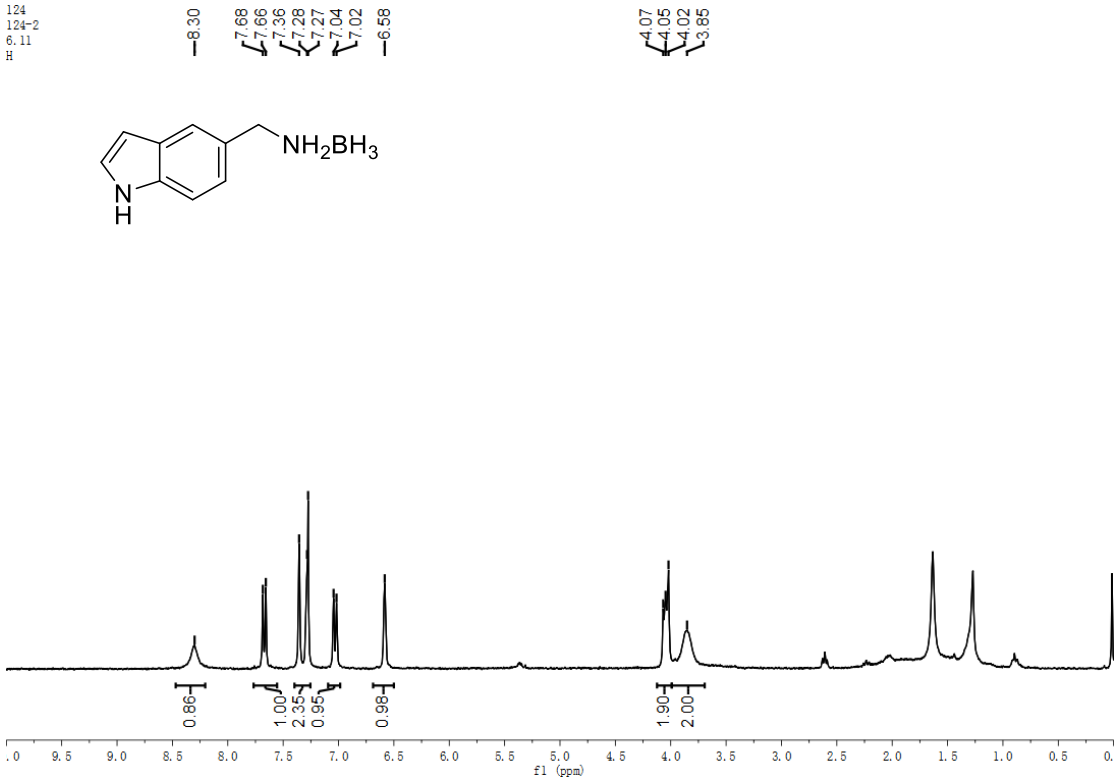


Figure S99 ^{1}H NMR spectrum of **2s** (300 MHz, DMSO)

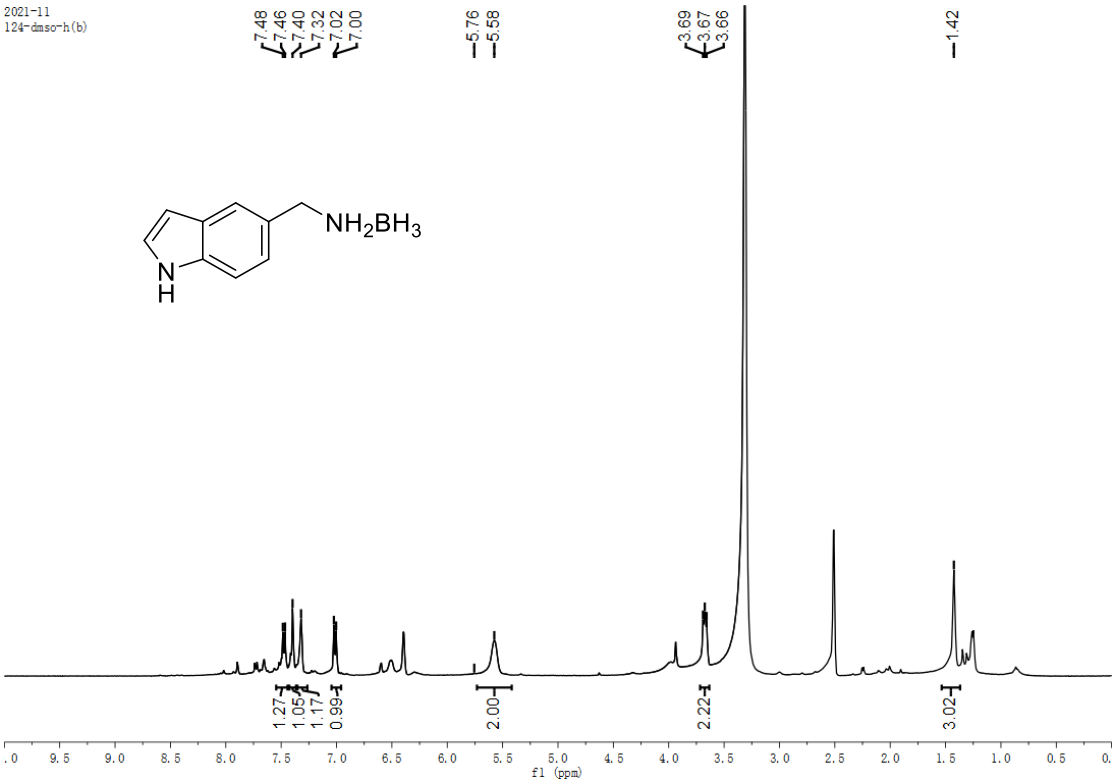


Figure S100. ^{1}H{B} NMR spectrum of **2s** (400 MHz, DMSO)

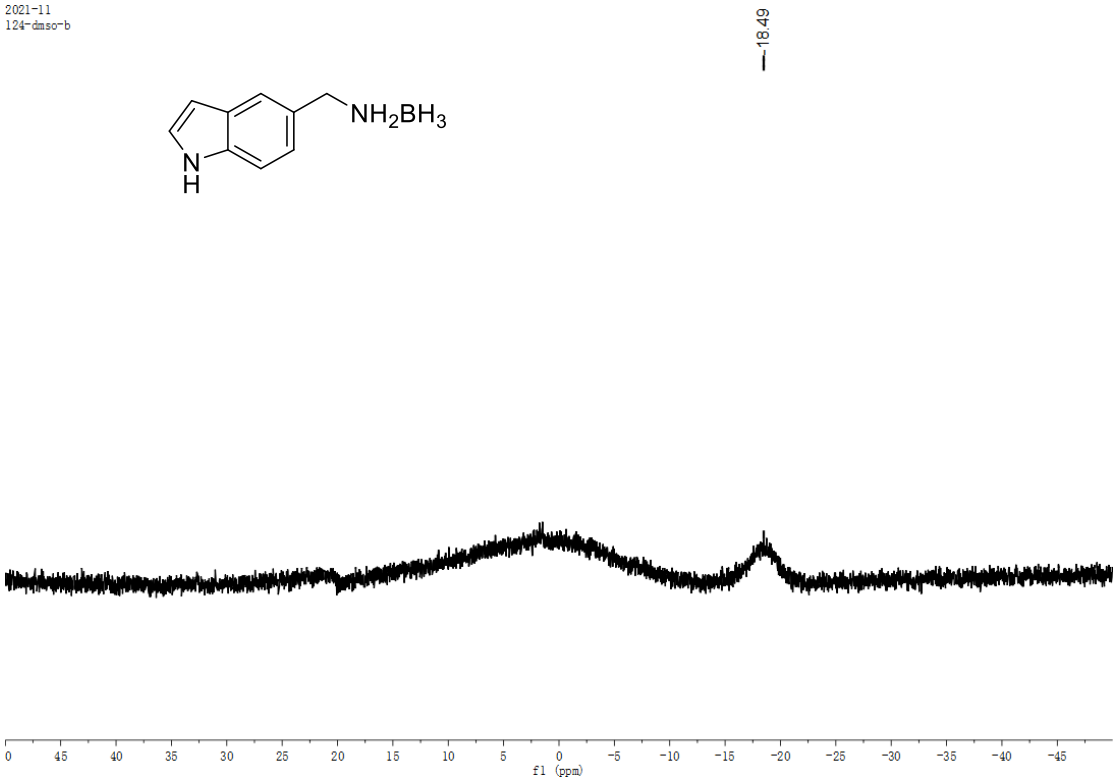


Figure S101. ^{11}B NMR spectrum of **2s** (400 MHz, DMSO)

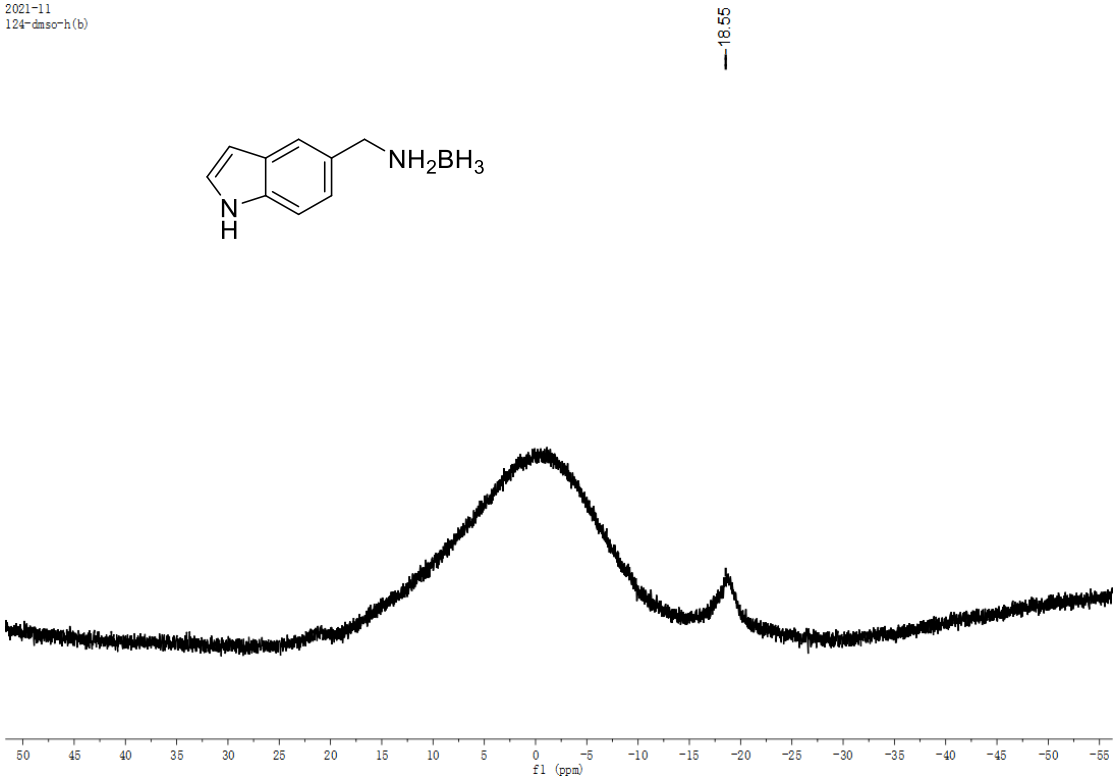


Figure S102. ^{11}B{H} NMR spectrum of **2s** (400 MHz, DMSO)

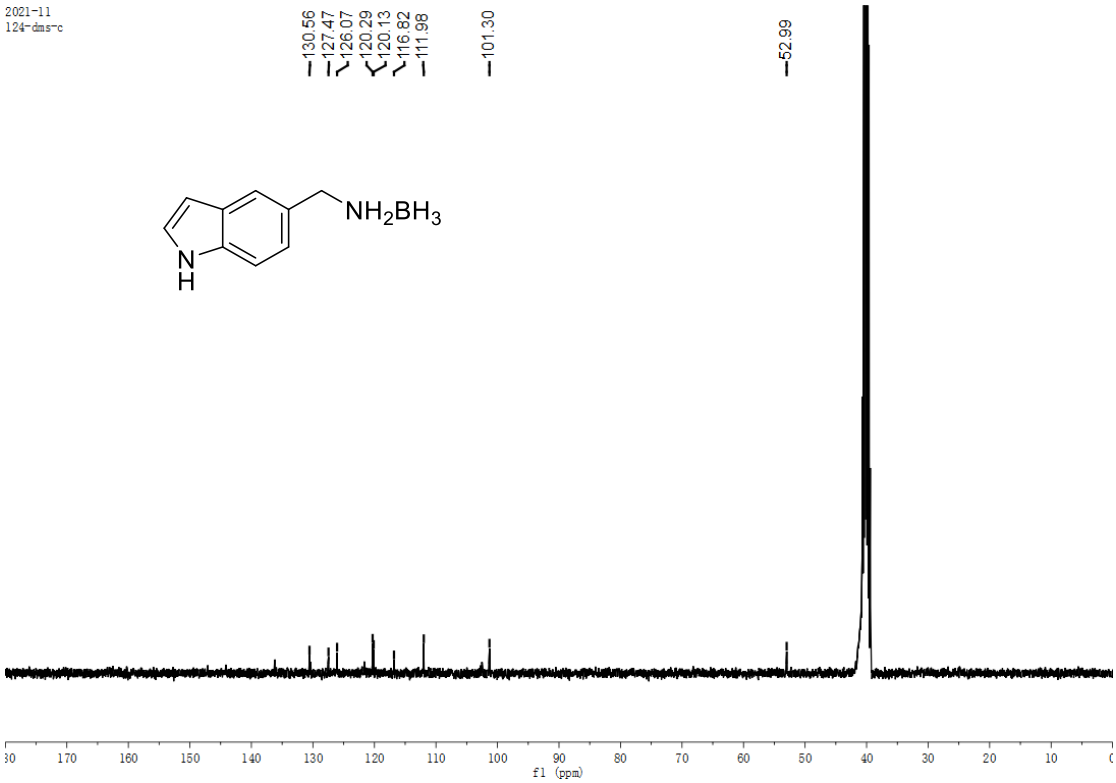


Figure S103. ^{13}C NMR spectrum of **2r** (400 MHz, DMSO)

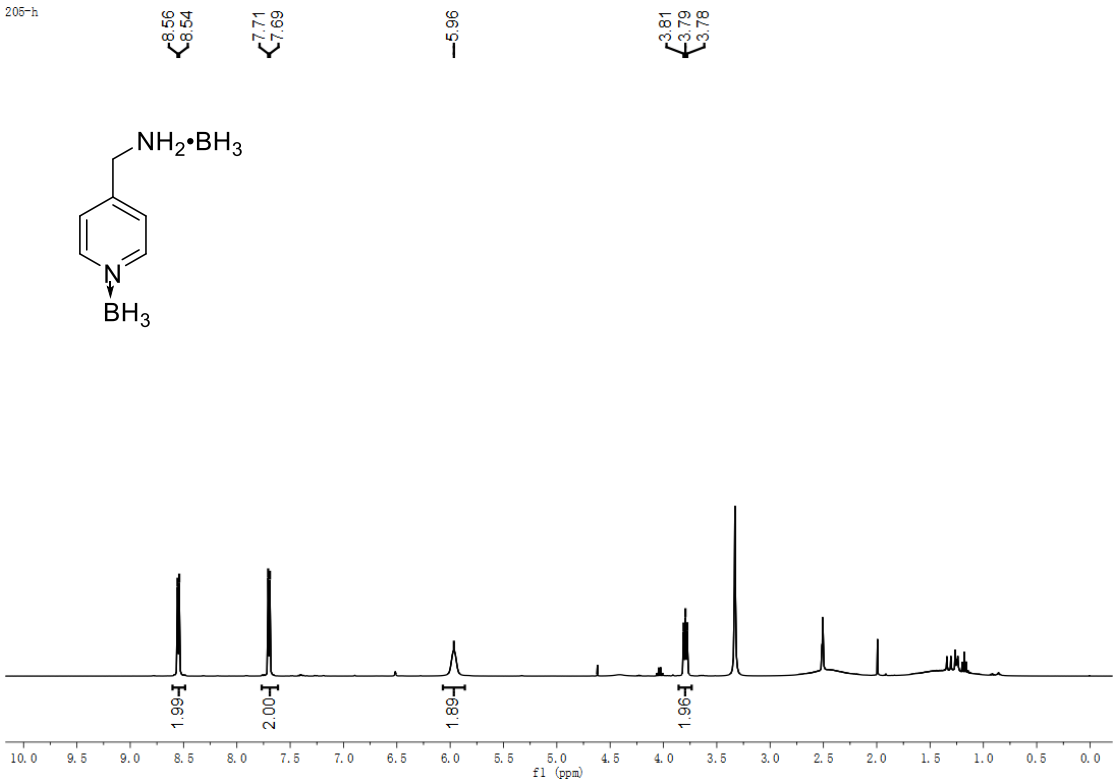


Figure S104. ^{1}H NMR spectrum of **2t** (400 MHz, DMSO)

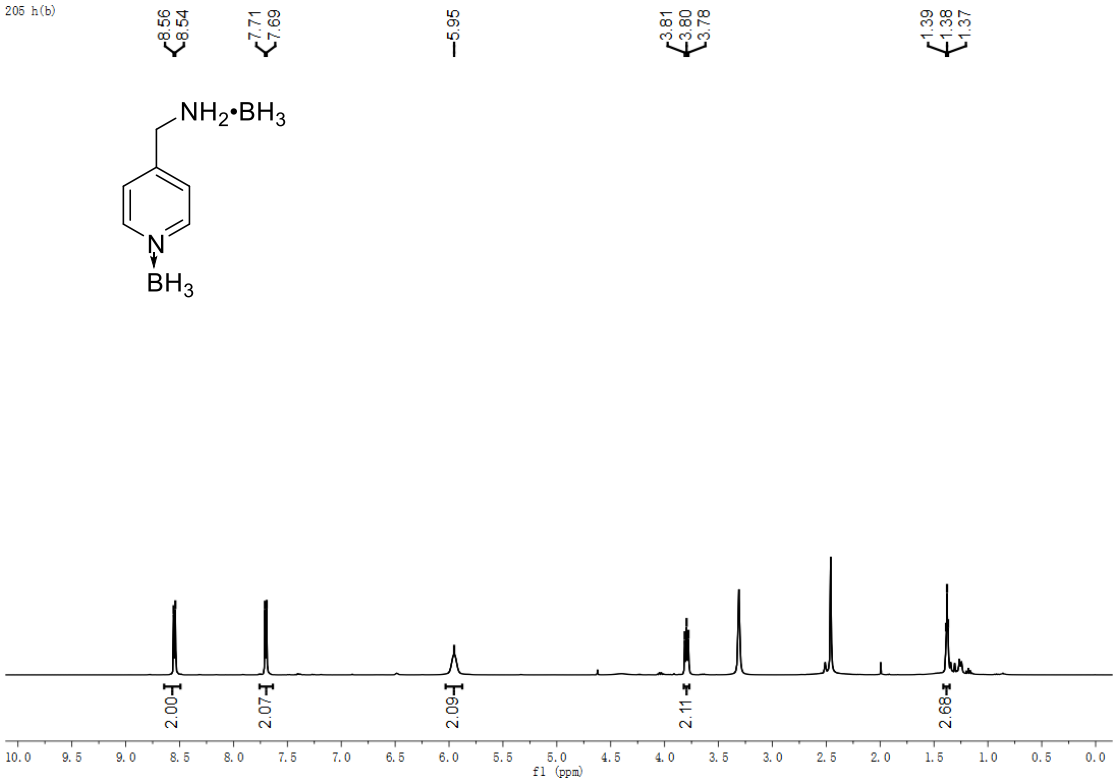


Figure S105. ^{1}H{B} NMR spectrum of **2t** (400 MHz, DMSO)

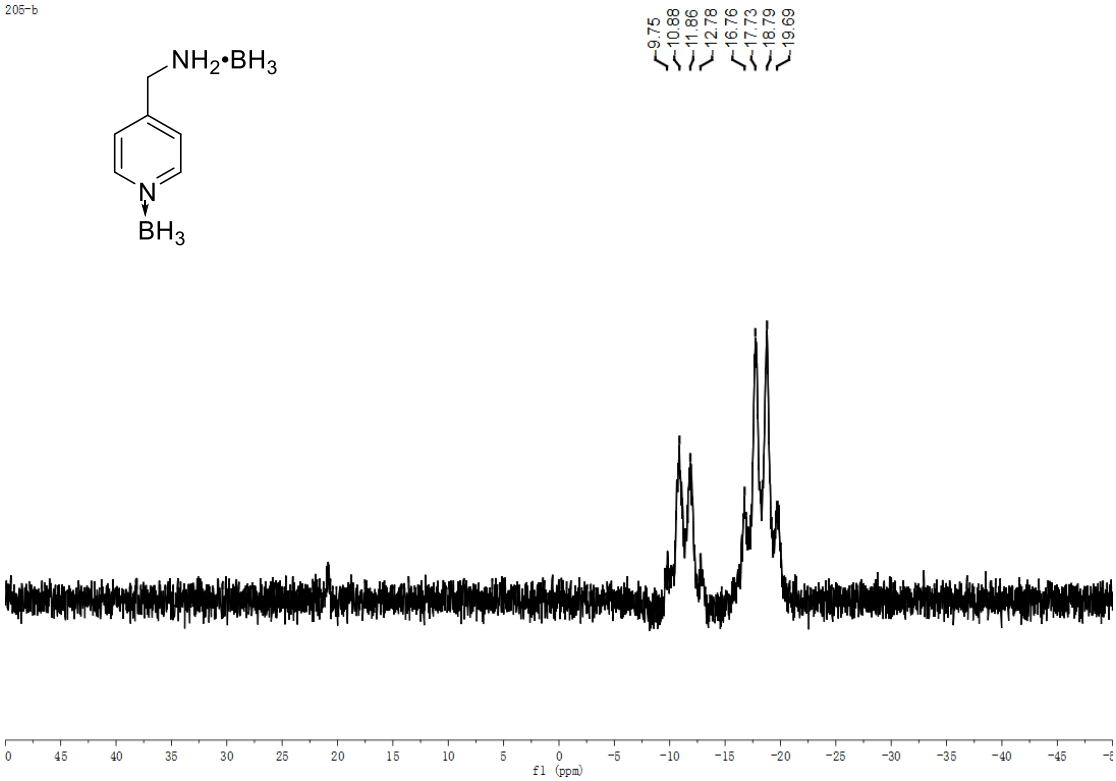


Figure S106. ^{11}B NMR spectrum of **2t** (300 MHz, DMSO)

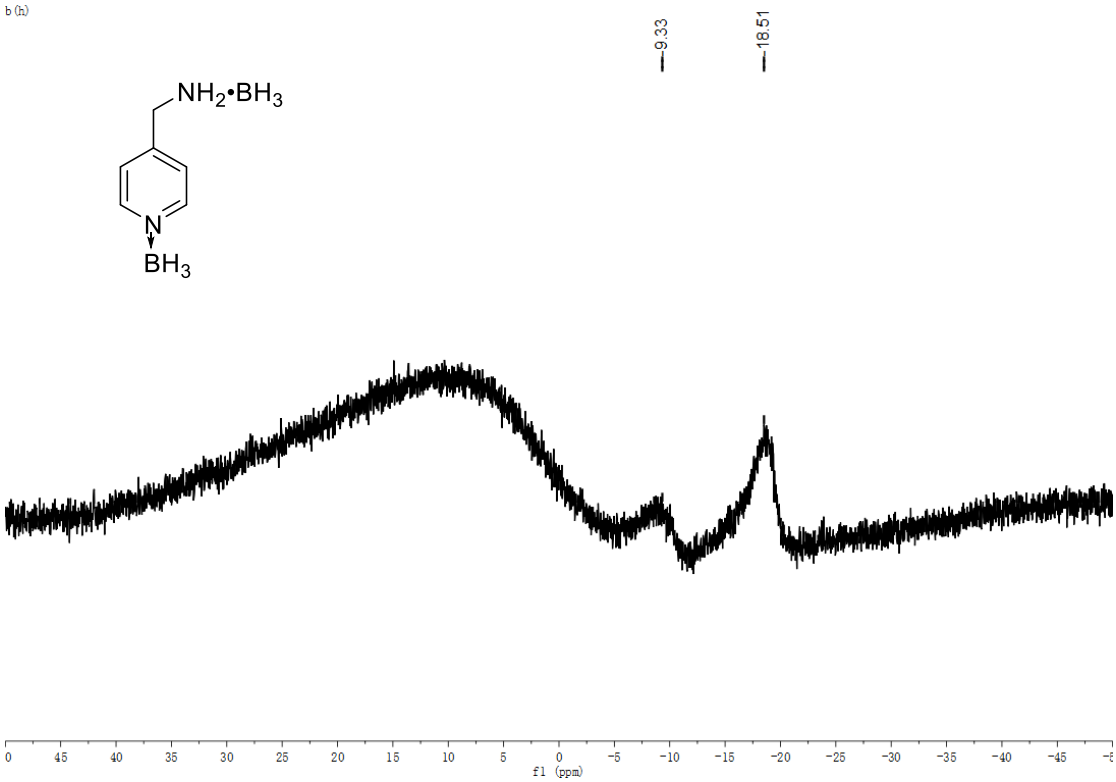


Figure S107. ^{1}H{B} NMR spectrum of **2t** (400 MHz, DMSO)

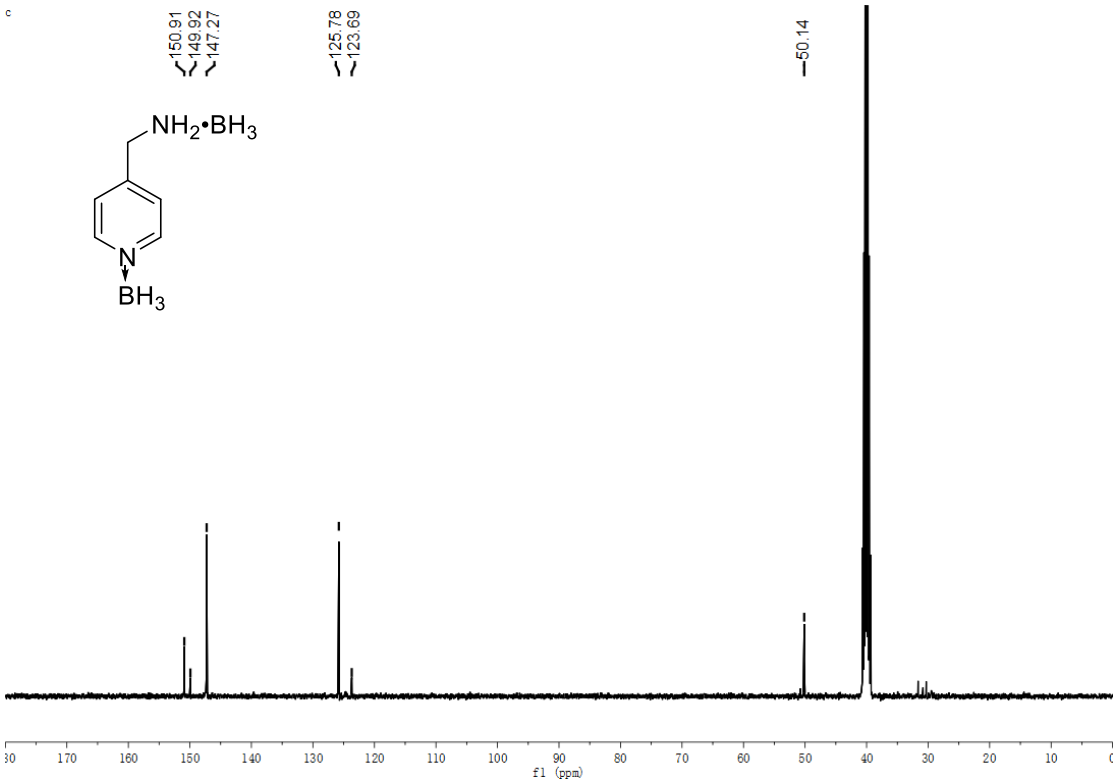


Figure S108. ^{13}C NMR spectrum of **2t** (400 MHz, DMSO)

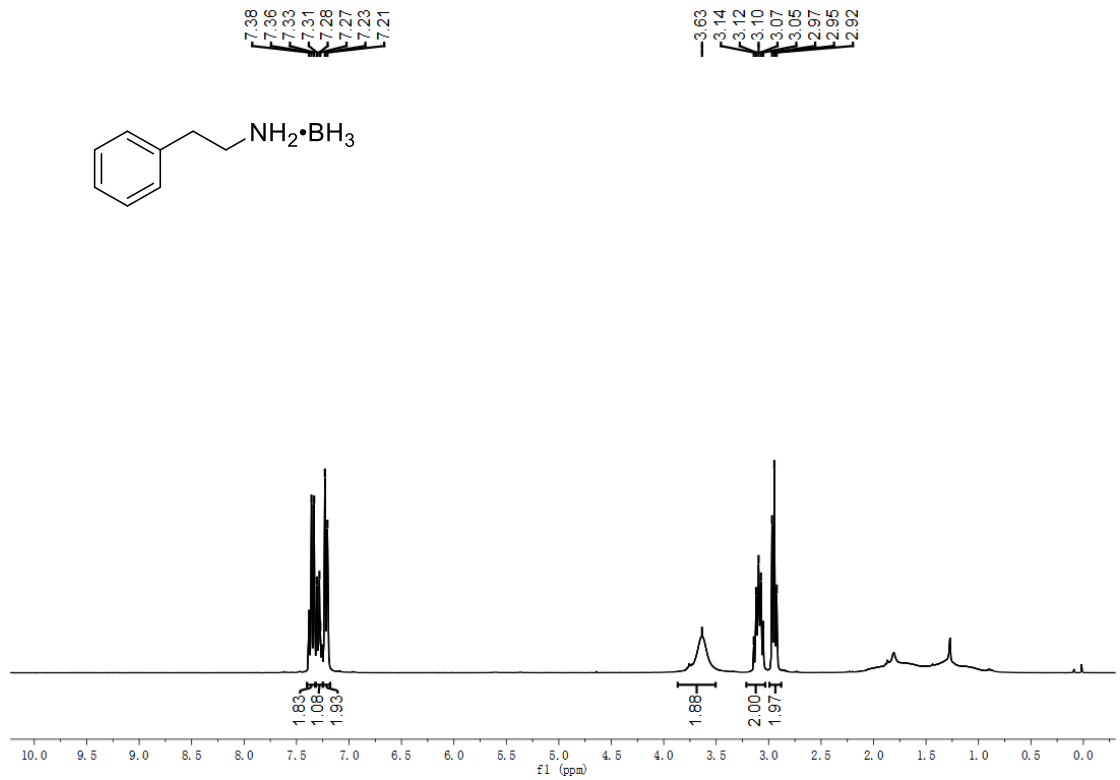


Figure 109. ^{1}H NMR spectrum of **2u** (300 MHz, DMSO)

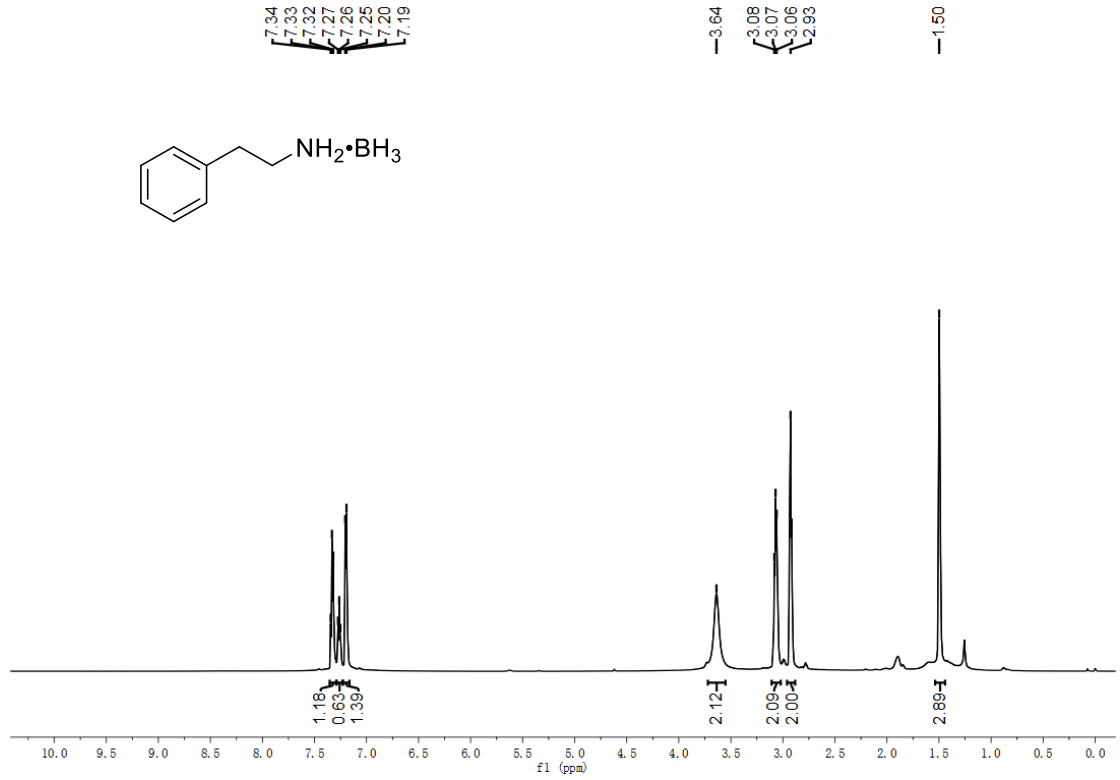


Figure S110. ^{1}H{B} NMR spectrum of **2u** (600 MHz, DMSO)

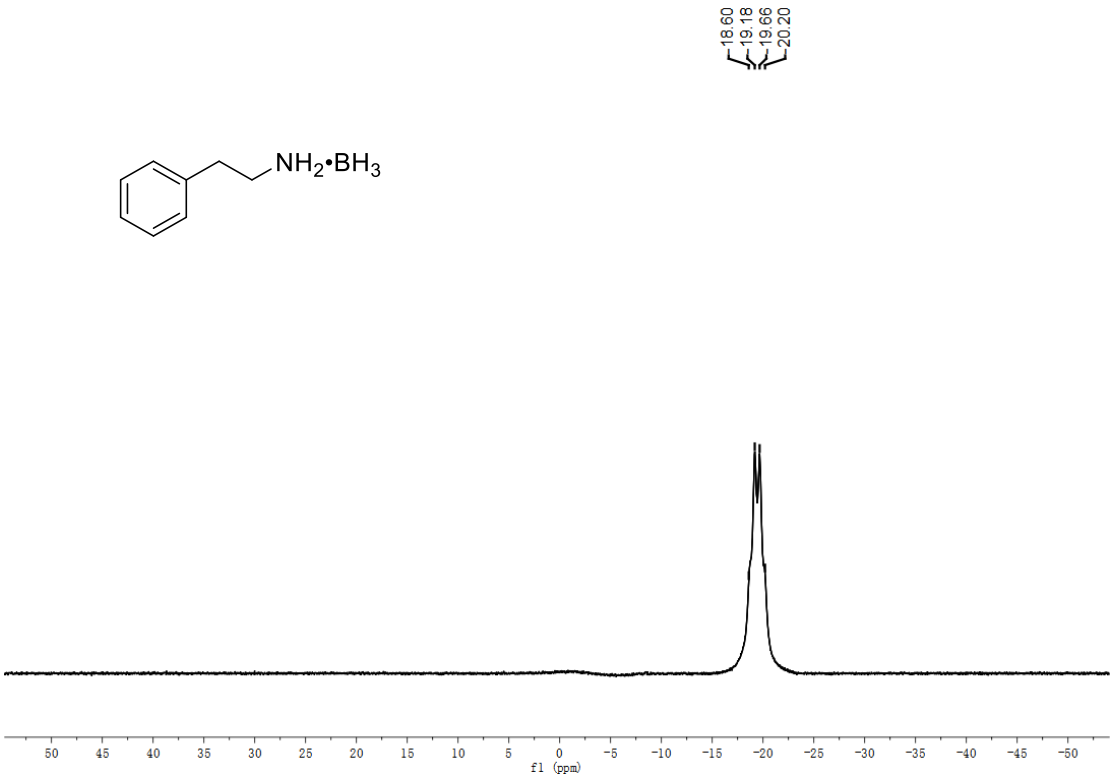


Figure S111. ^{11}B NMR spectrum of **2u** (600 MHz, DMSO)

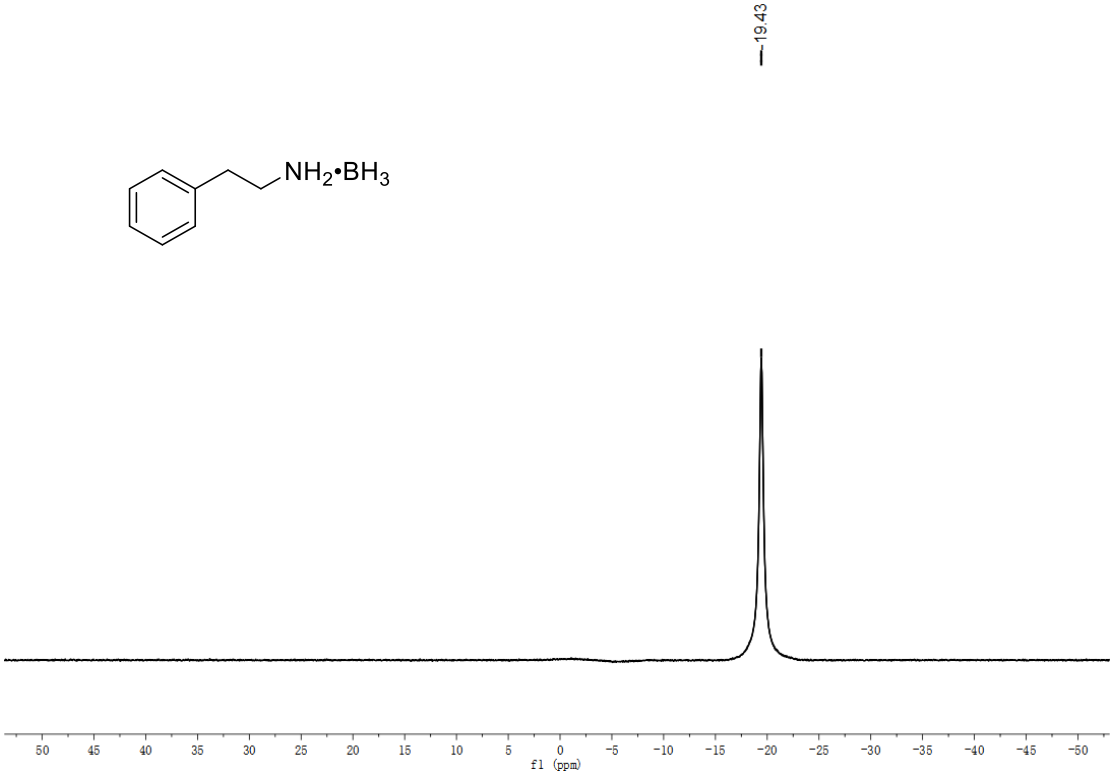


Figure S112. ^{11}B{H} NMR spectrum of **2u** (600 MHz, DMSO)

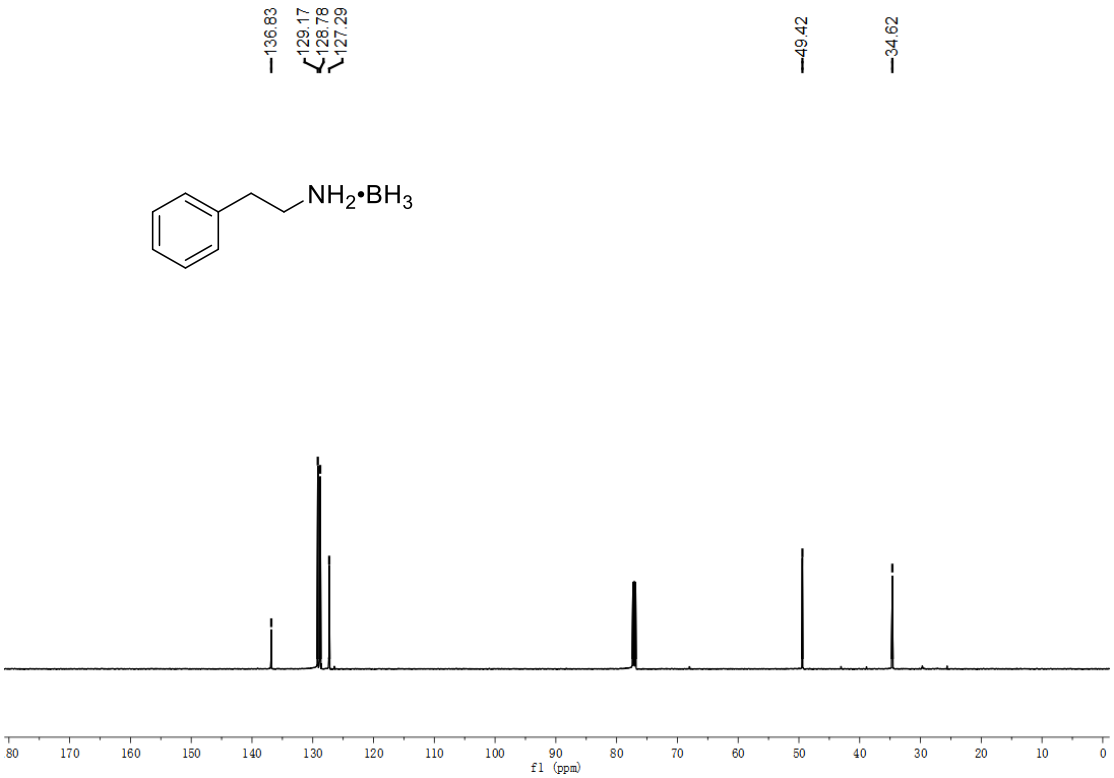


Figure S113. ^{13}C NMR spectrum of **2u** (600 MHz, DMSO)

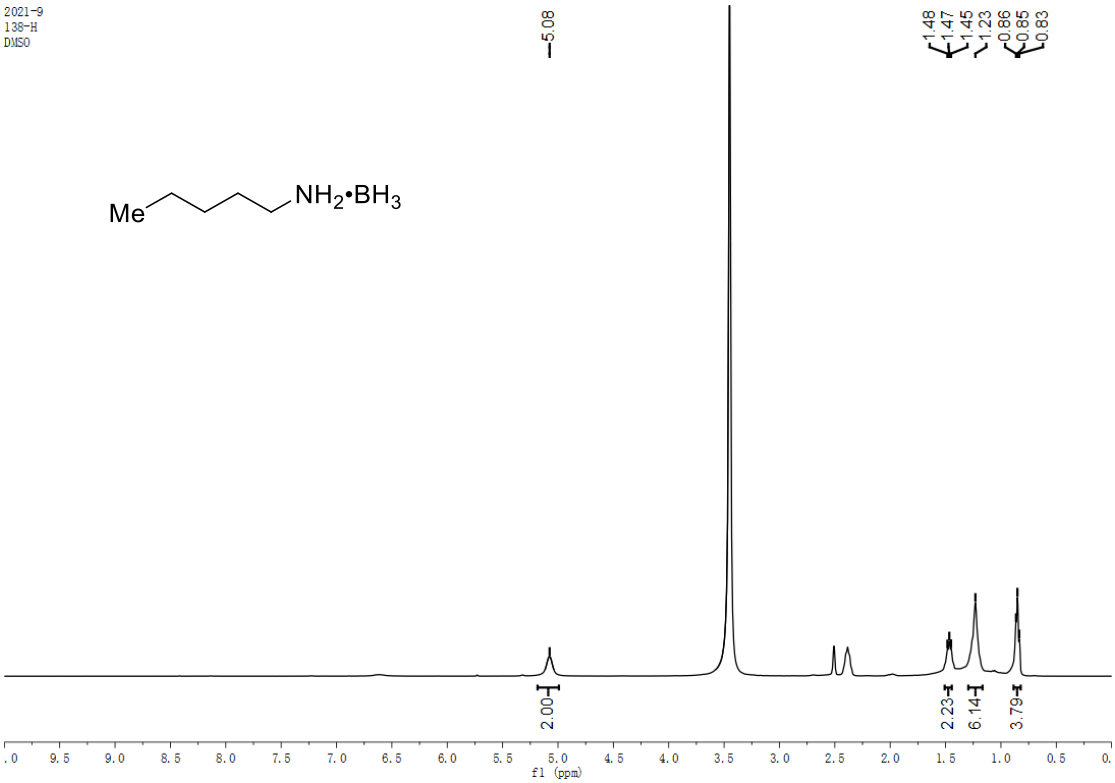


Figure S114. ^{1}H NMR spectrum of **2v** (400 MHz, DMSO)

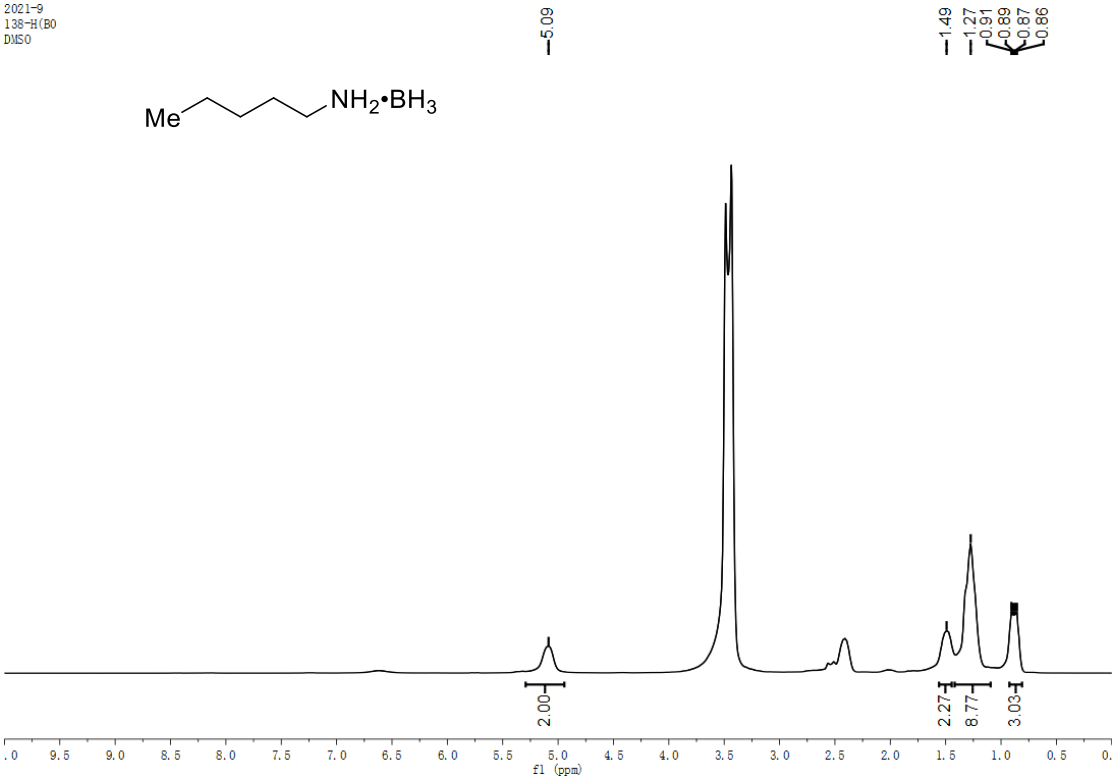


Figure S115. ^{1}H{B} NMR spectrum of **2v** (400 MHz, DMSO)

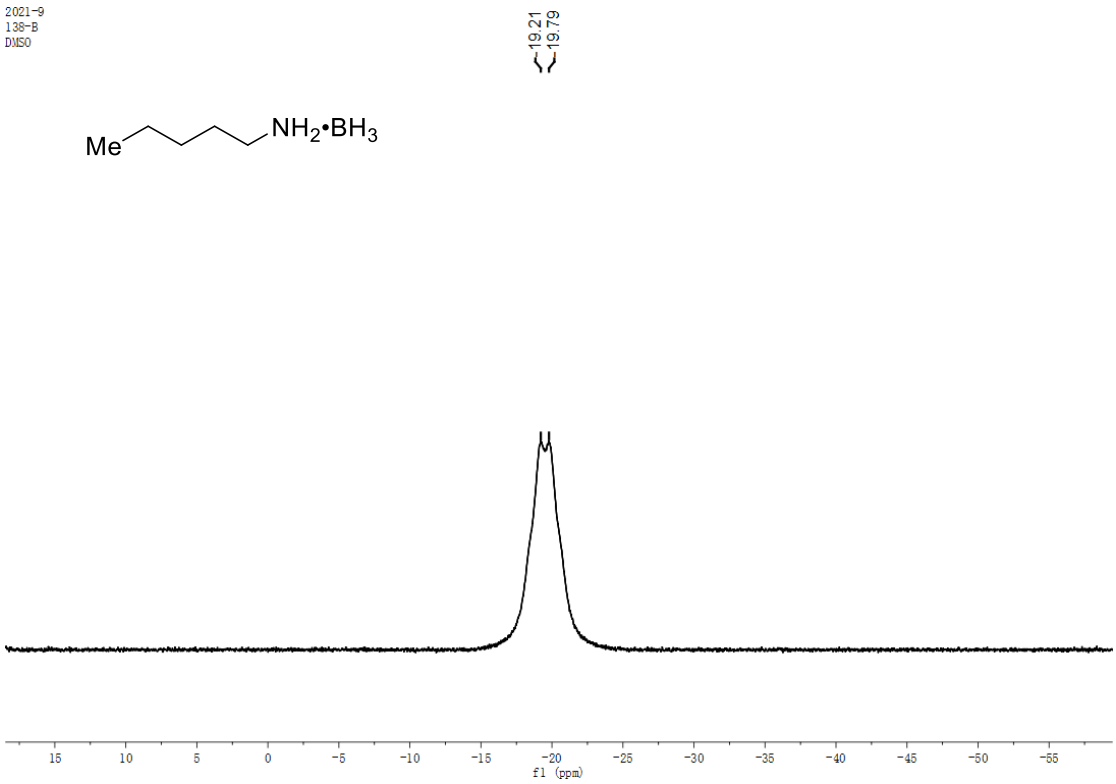


Figure S116. ^{11}B NMR spectrum of **2v** (400 MHz, DMSO)

=

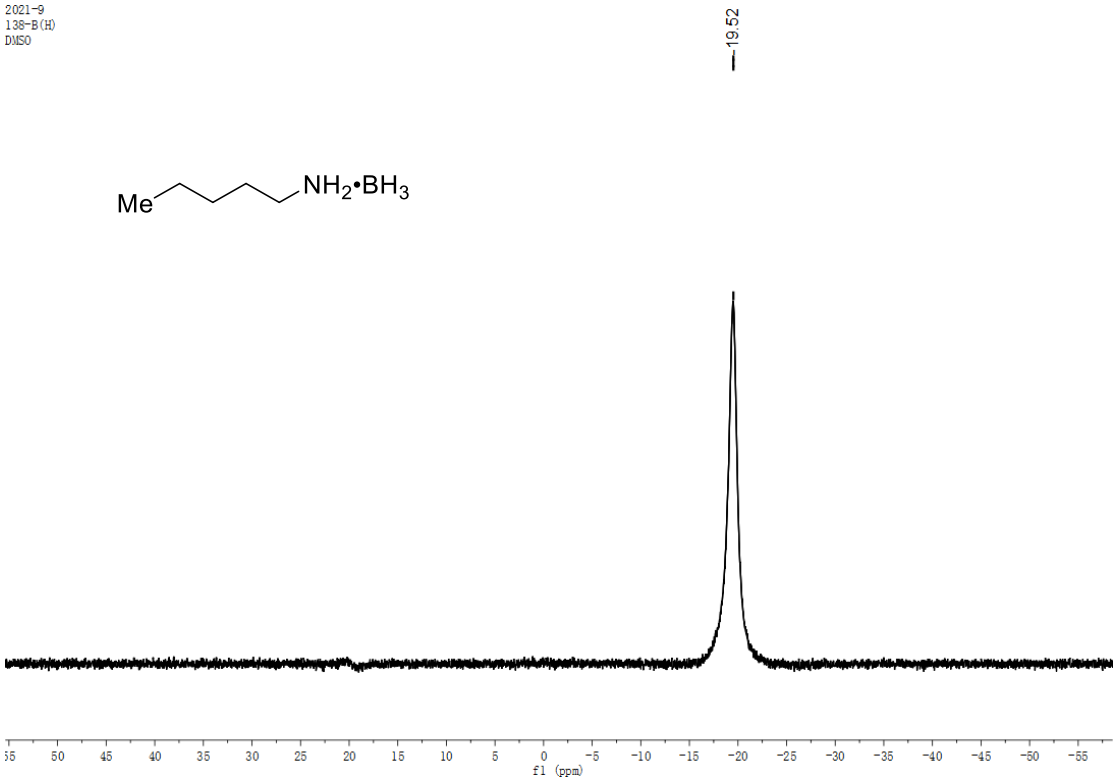


Figure S117. ^{11}B{H} NMR spectrum of **2v** (400 MHz, DMSO)

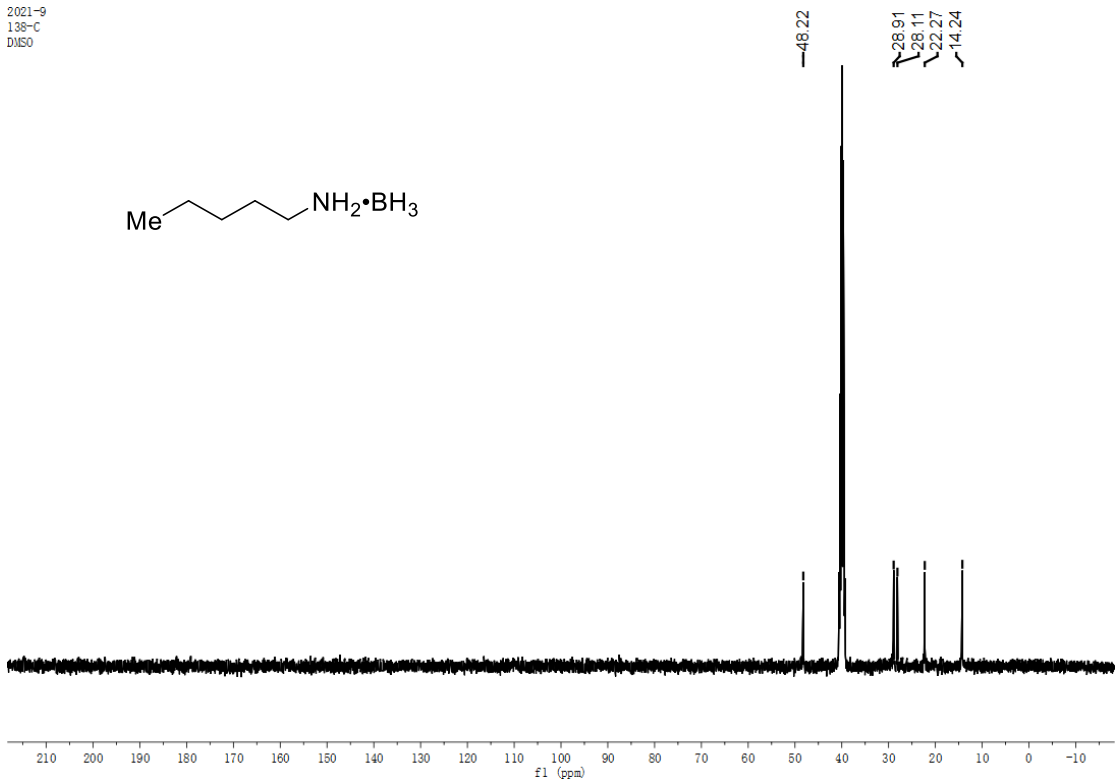


Figure S118. ^{13}C NMR spectrum of **2v** (400 MHz, DMSO)

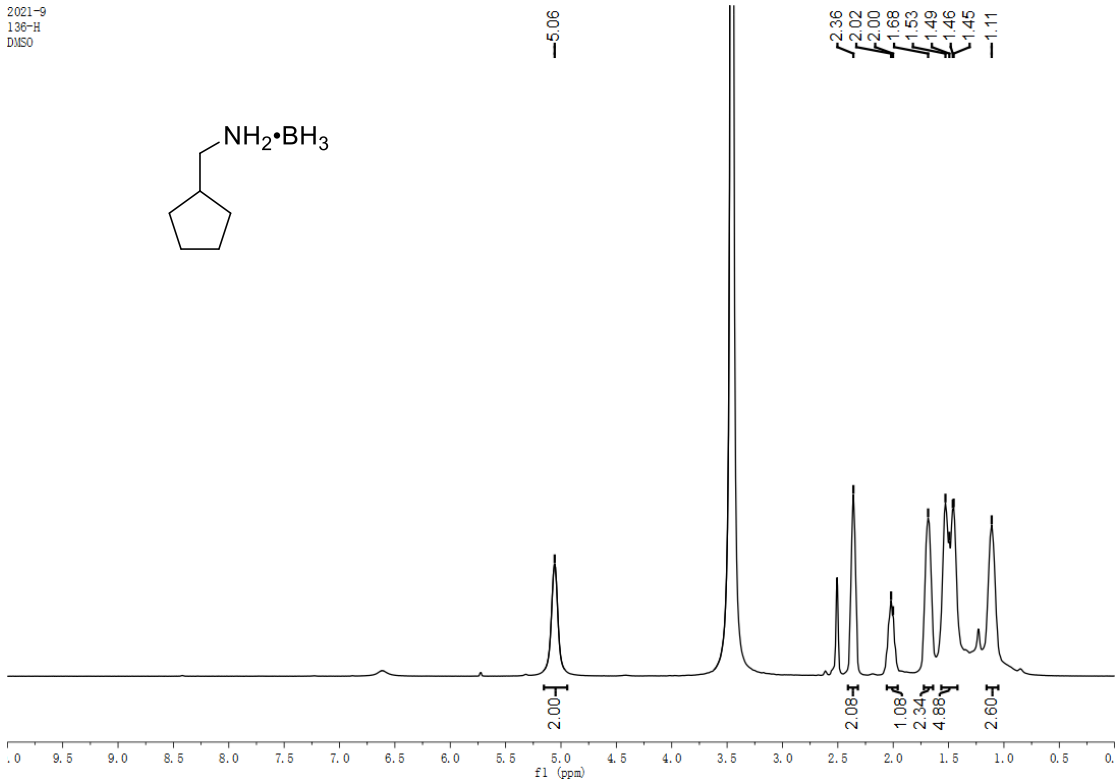


Figure S119. ^{1}H NMR spectrum of **2w** (400 MHz, DMSO)

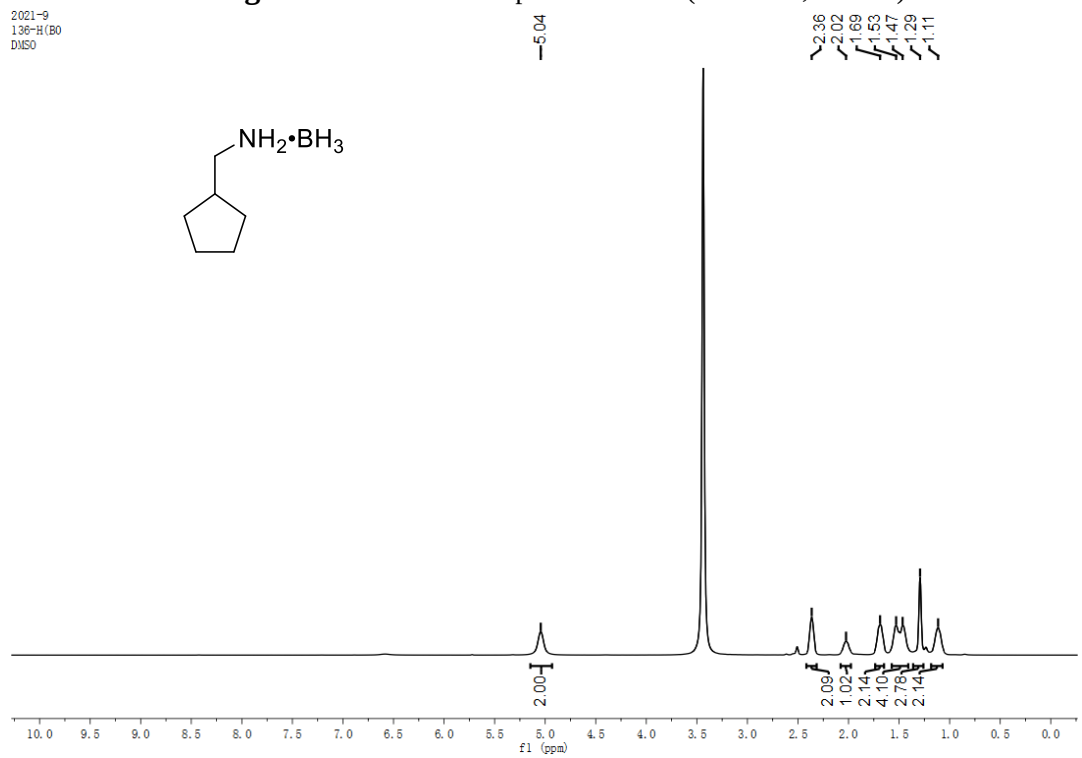


Figure S120. ^{1}H{B} NMR spectrum of **2w** (400 MHz, DMSO)

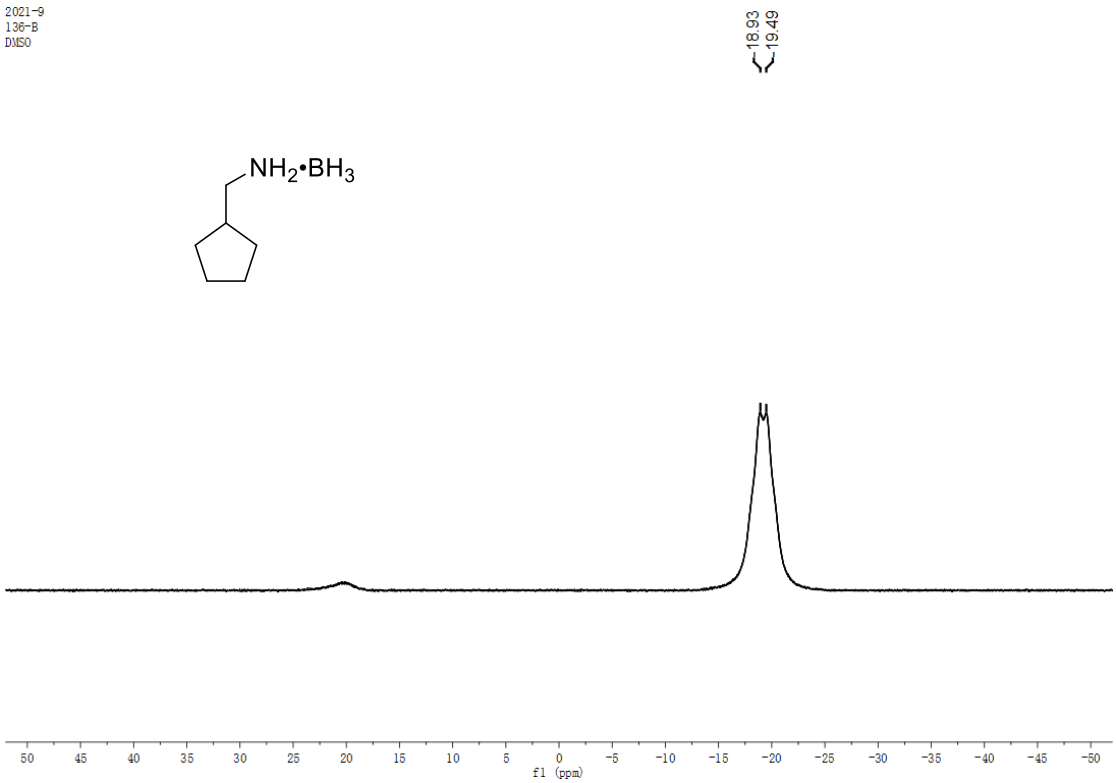


Figure S121. ^{11}B NMR spectrum of **2w** (400 MHz, DMSO)

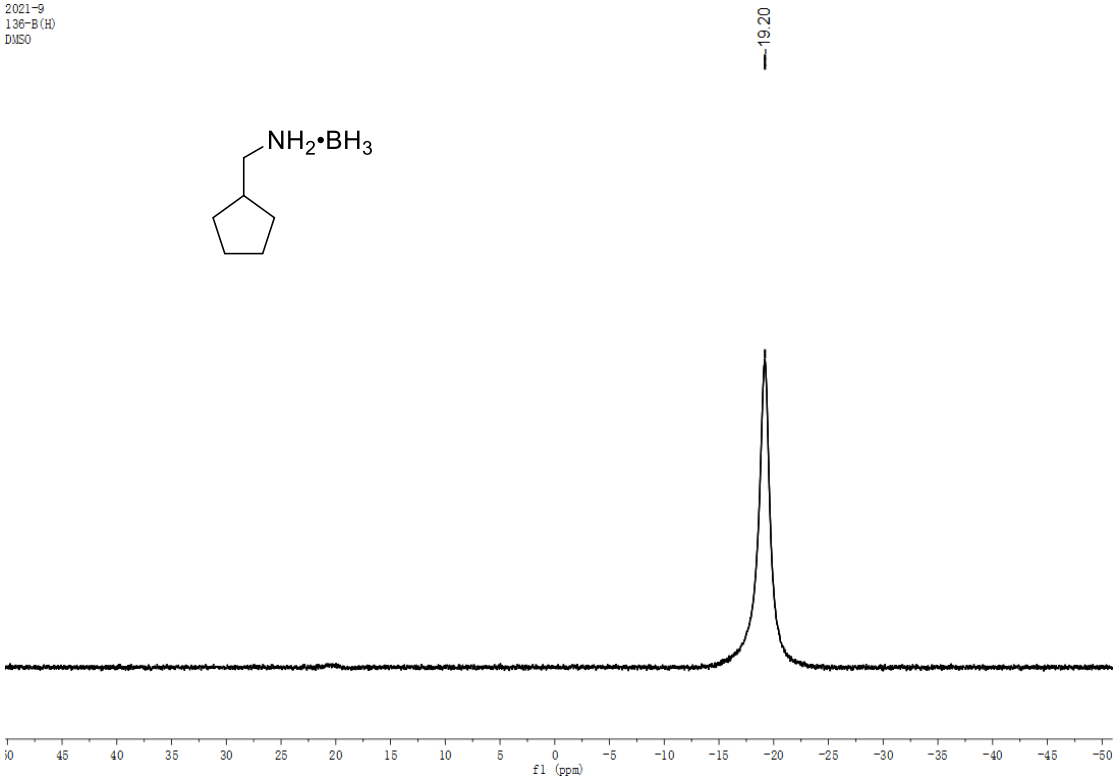


Figure S122. ^{11}B{H} NMR spectrum of **2w** (400 MHz, DMSO)

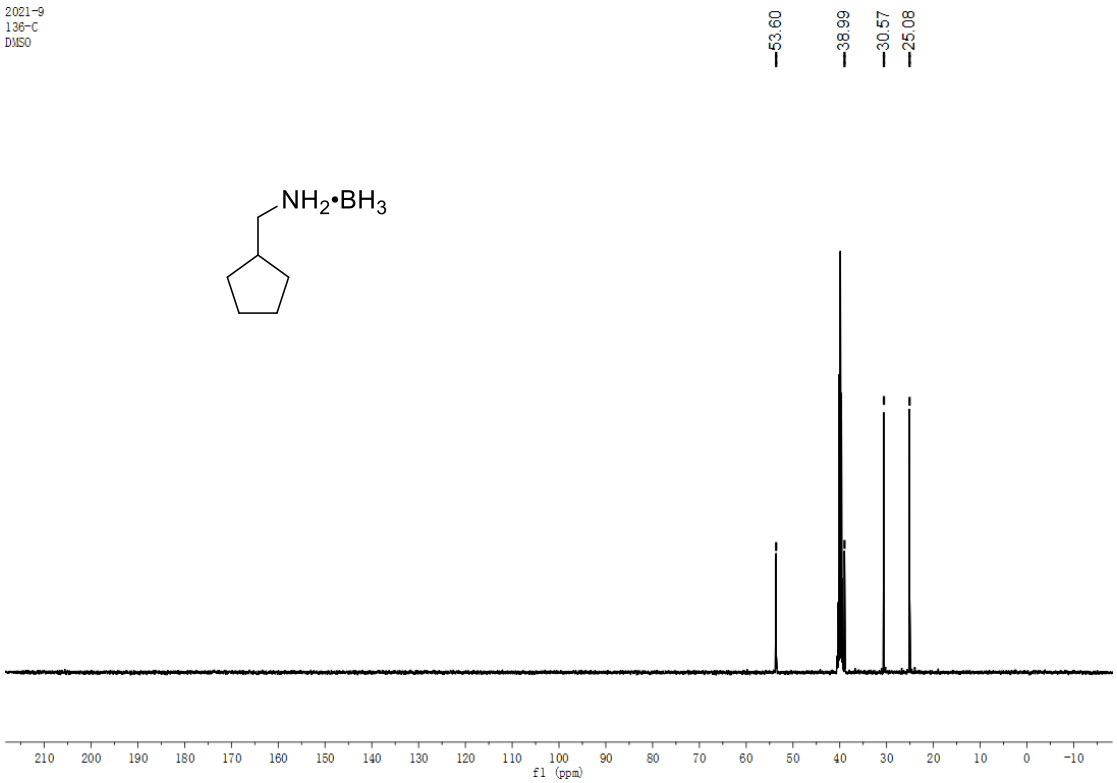


Figure S123. ^{13}C NMR spectrum of **2w** (400 MHz, DMSO)

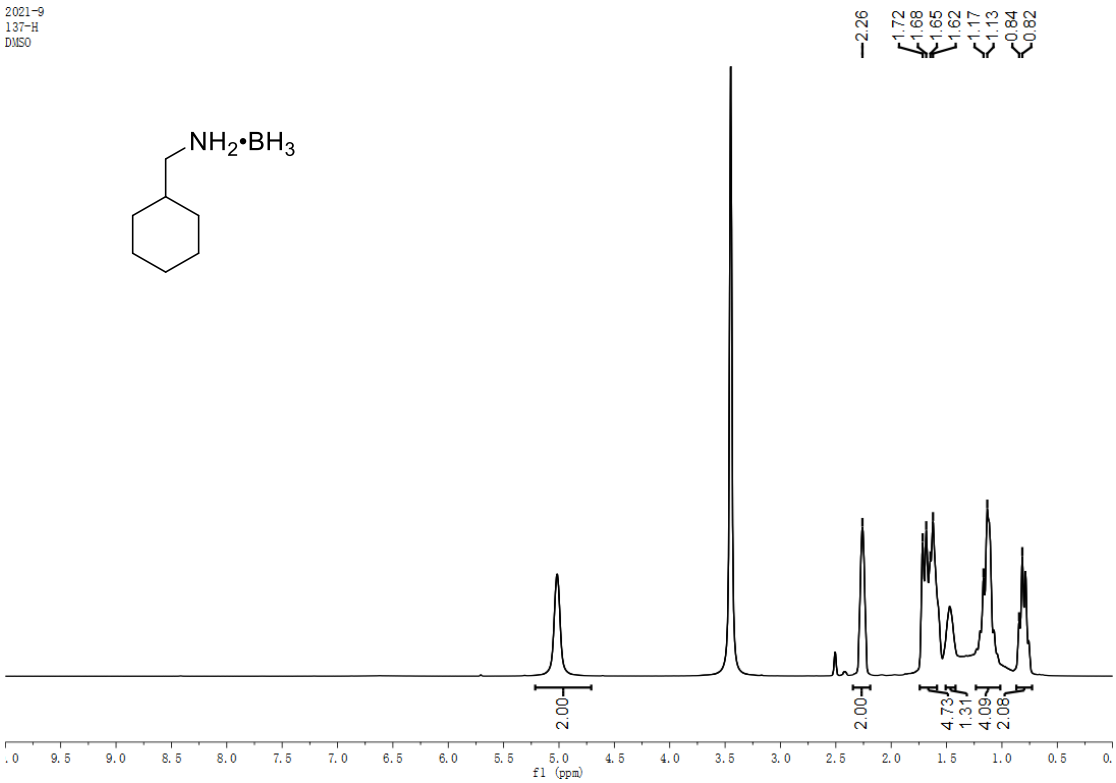


Figure S124. ^{1}H NMR spectrum of **2x** (400 MHz, DMSO)

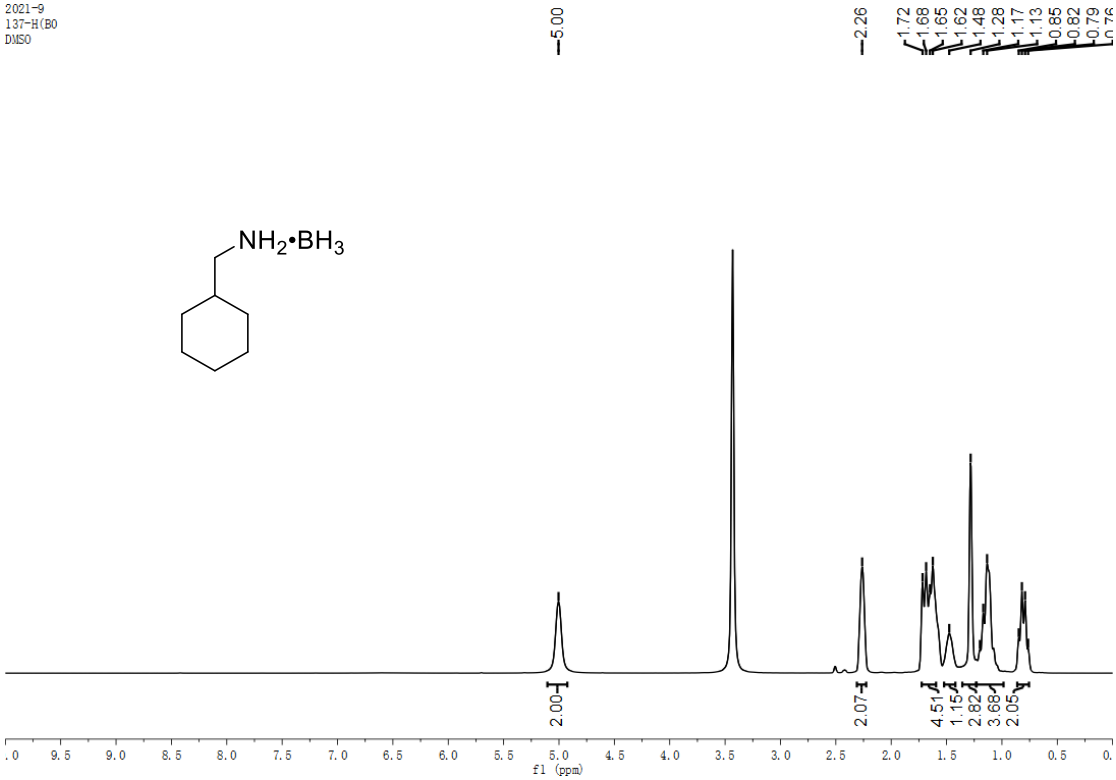


Figure S125. ^{1}H{B} NMR spectrum of **2x** (400 MHz, DMSO)

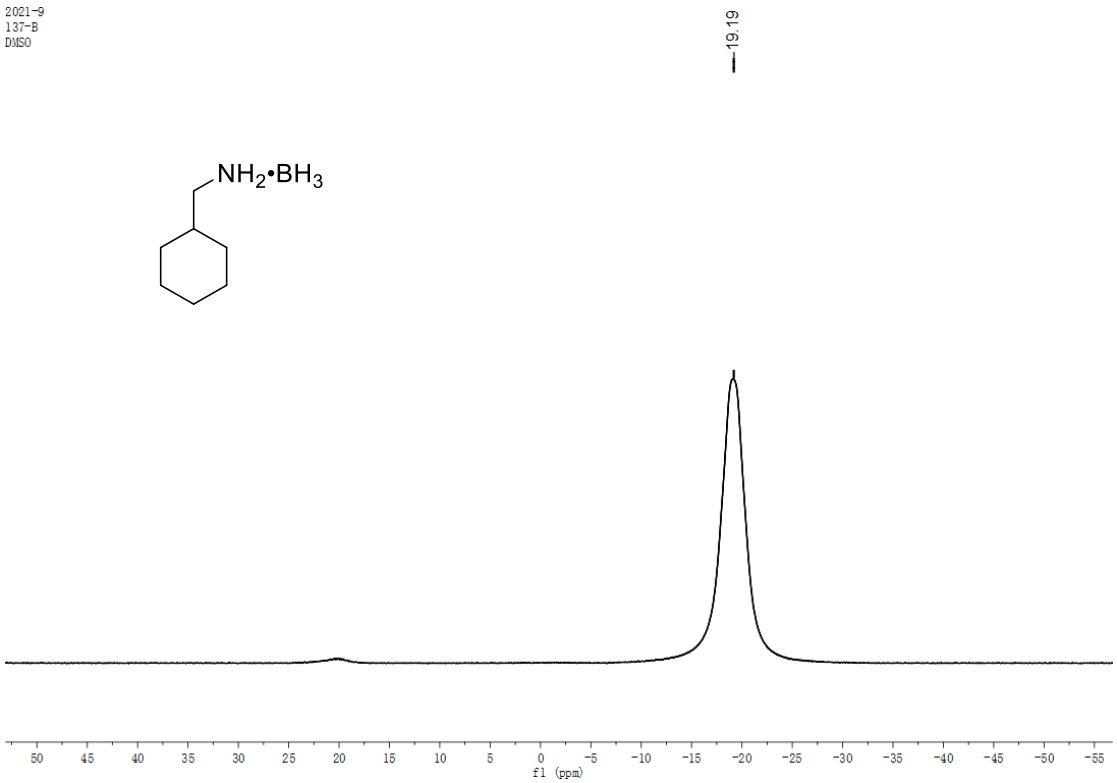


Figure S126. ^{11}B NMR spectrum of **2x** (400 MHz, DMSO)

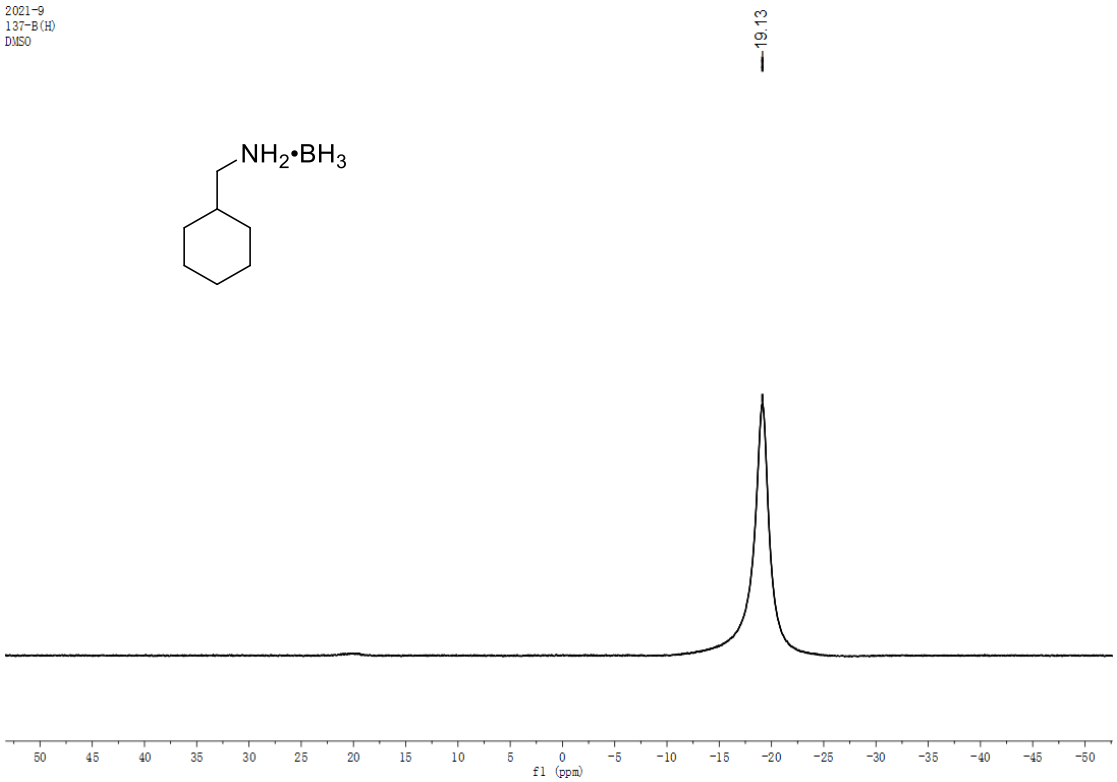


Figure S127. ^{11}B{H} NMR spectrum of **2x** (400 MHz, DMSO)

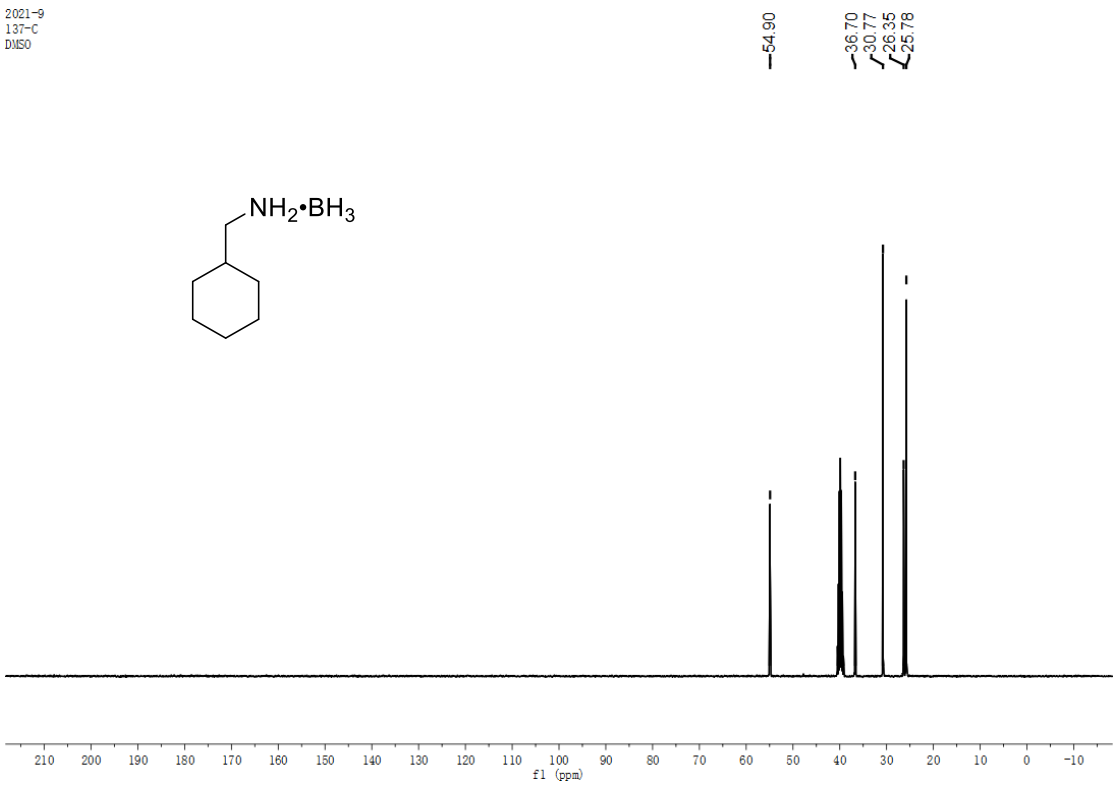


Figure S128. ^{13}C NMR spectrum of **2x** (400 MHz, DMSO)

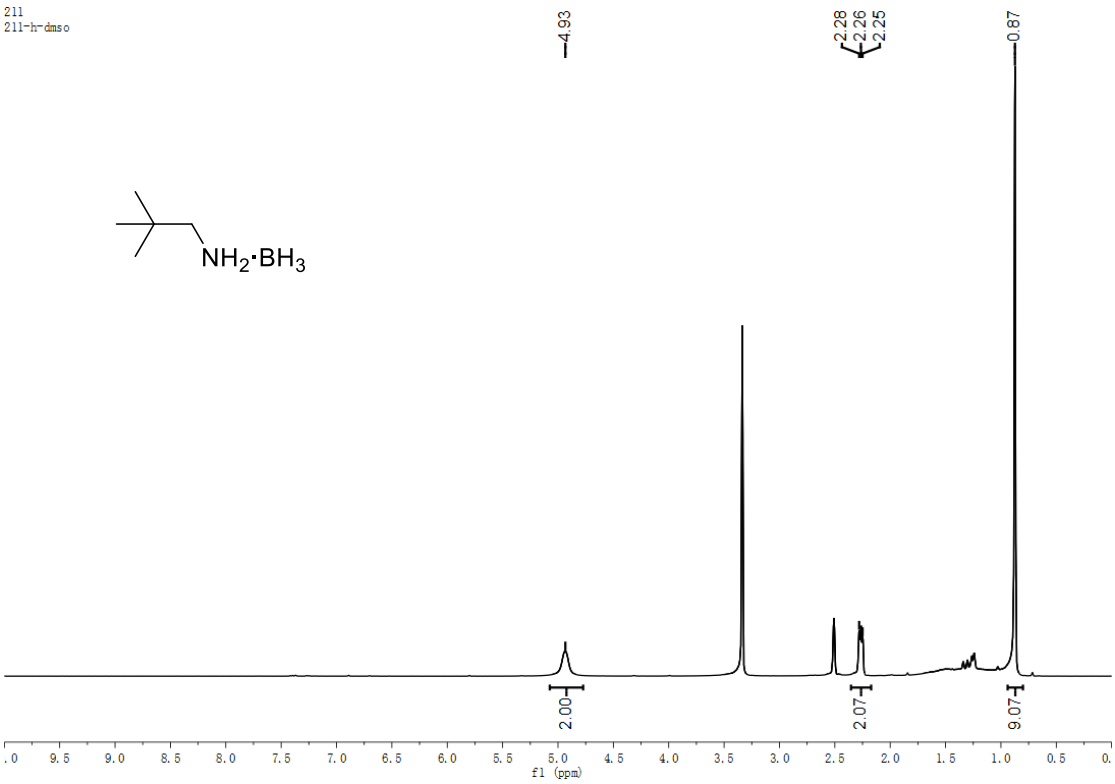


Figure S129. ^{1}H NMR spectrum of **2y** (400 MHz, DMSO)

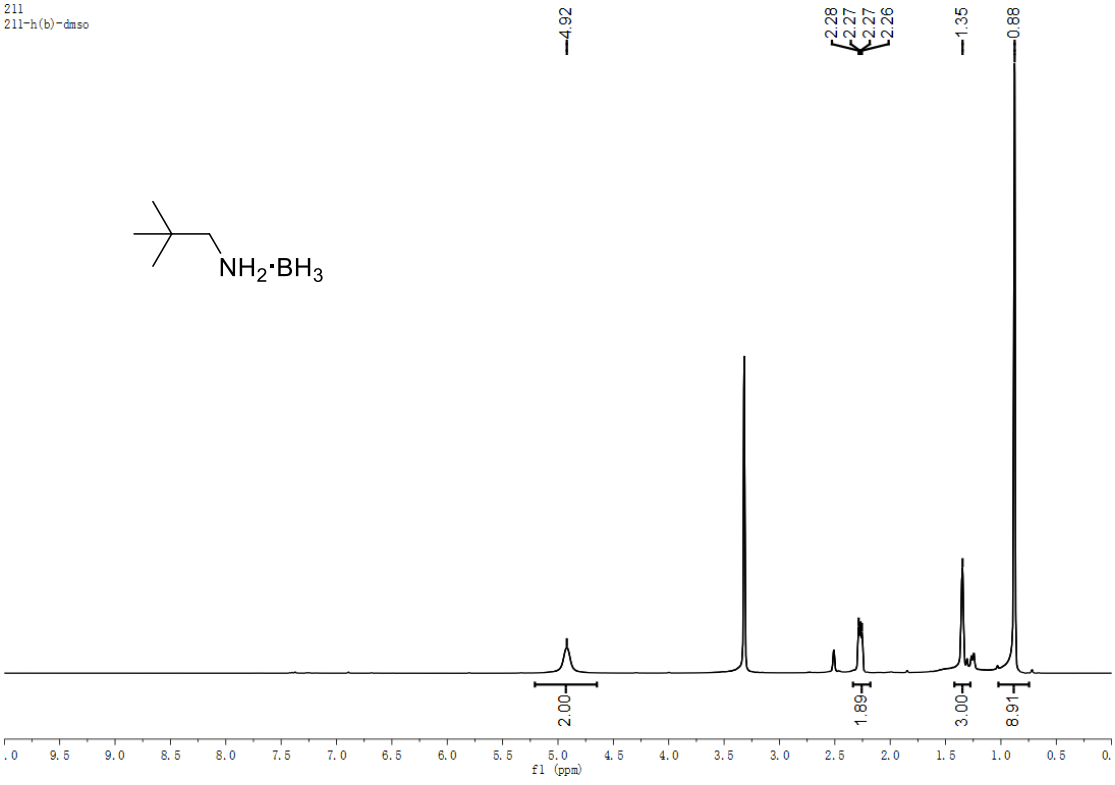


Figure S130. ^{1}H{B} NMR spectrum of **2y** (400 MHz, DMSO)

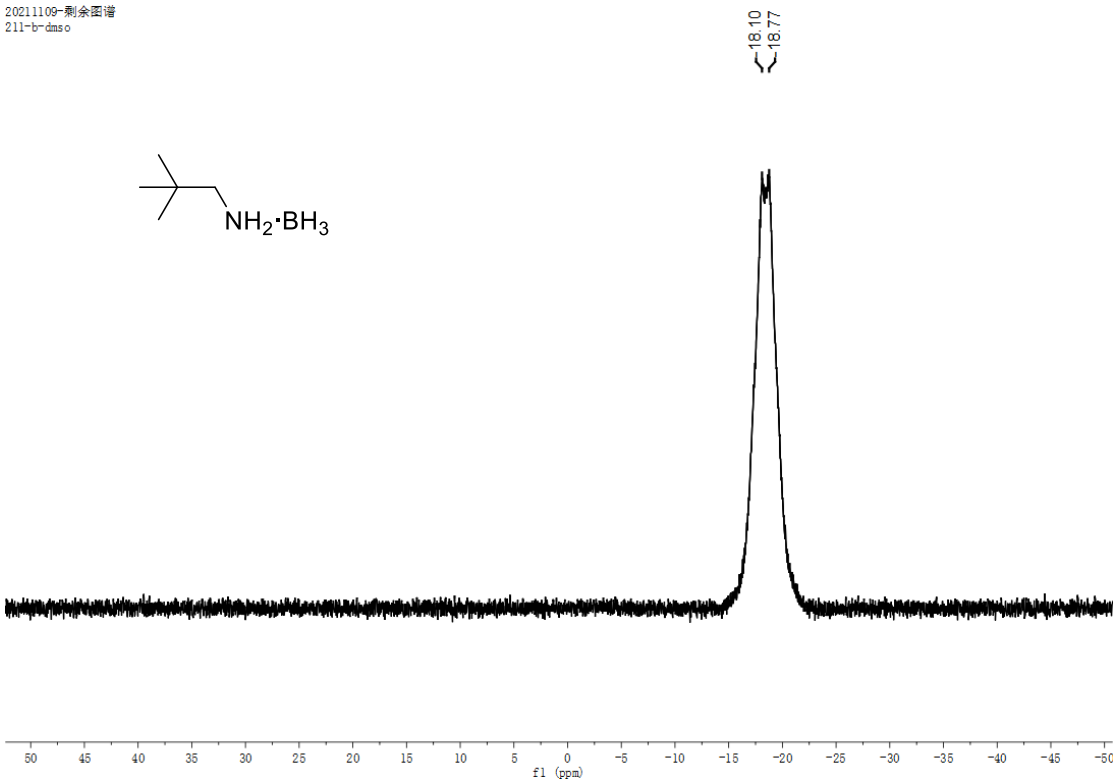


Figure S131. ^{11}B NMR spectrum of **2y** (400 MHz, DMSO)

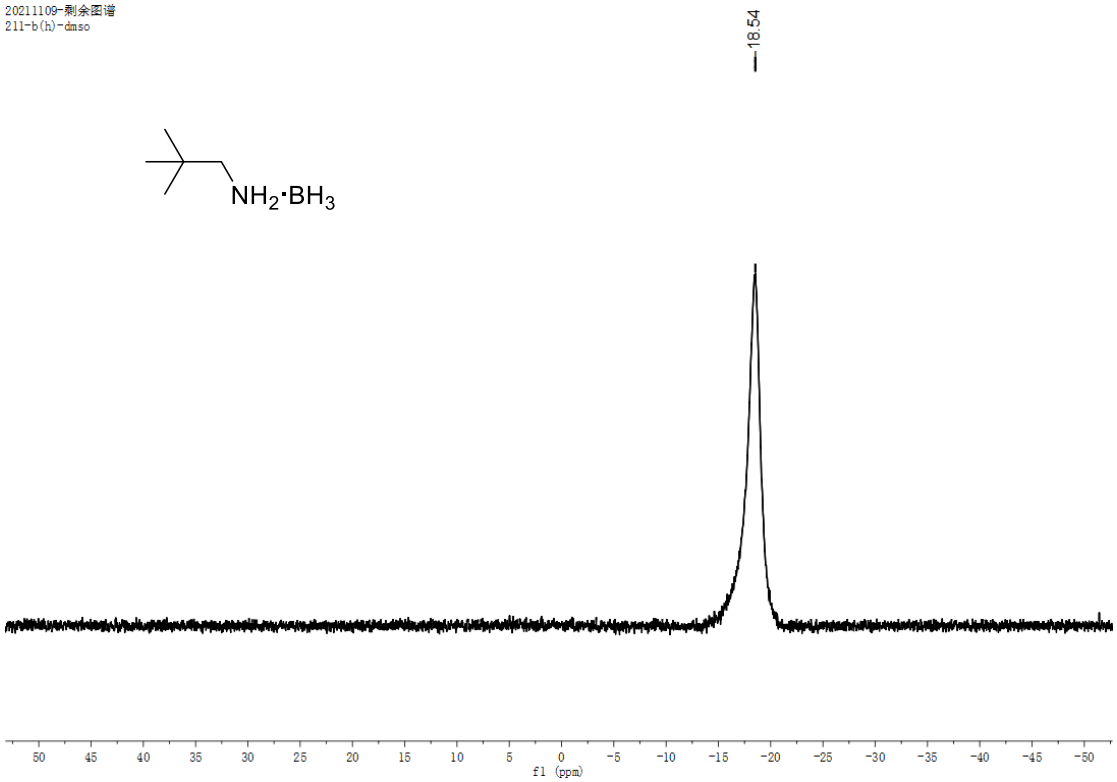


Figure S132. ^{11}B{H} NMR spectrum of **2y** (400 MHz, DMSO)

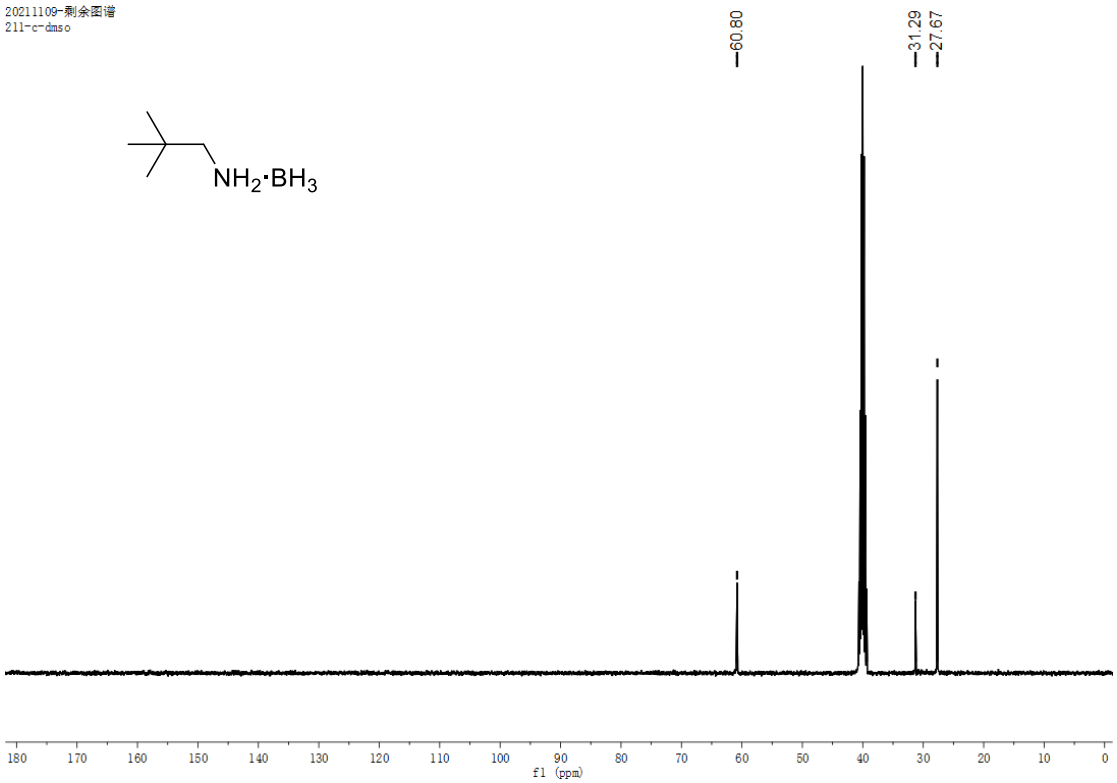


Figure S133. ^{13}C NMR spectrum of **2y** (400 MHz, DMSO)

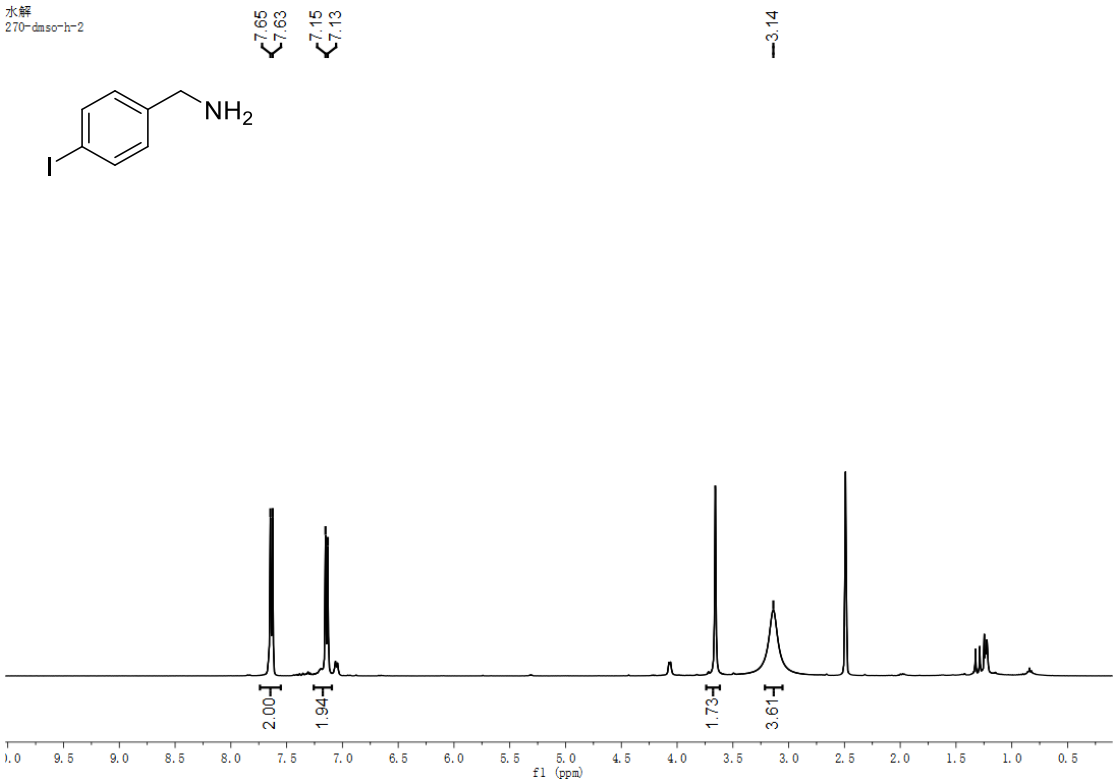


Figure S134. ^{1}H NMR spectrum of **3a** (400 MHz, DMSO)

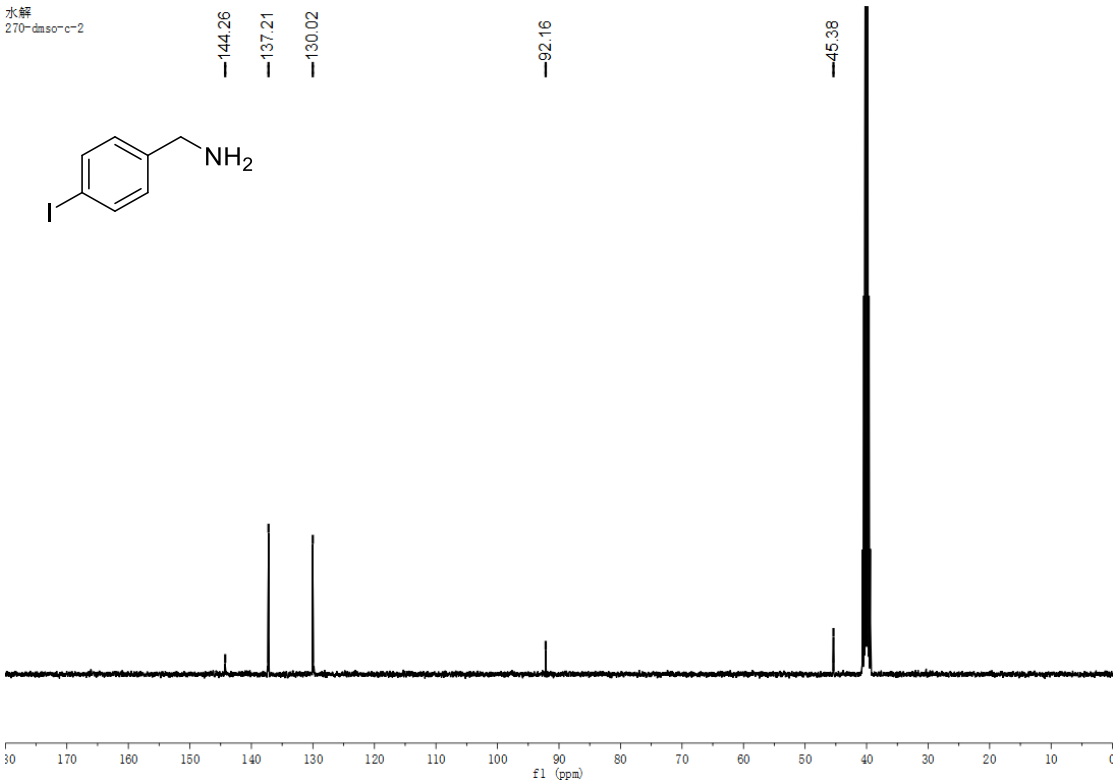


Figure S135. ^{13}C NMR spectrum of **3a** (400 MHz, DMSO)

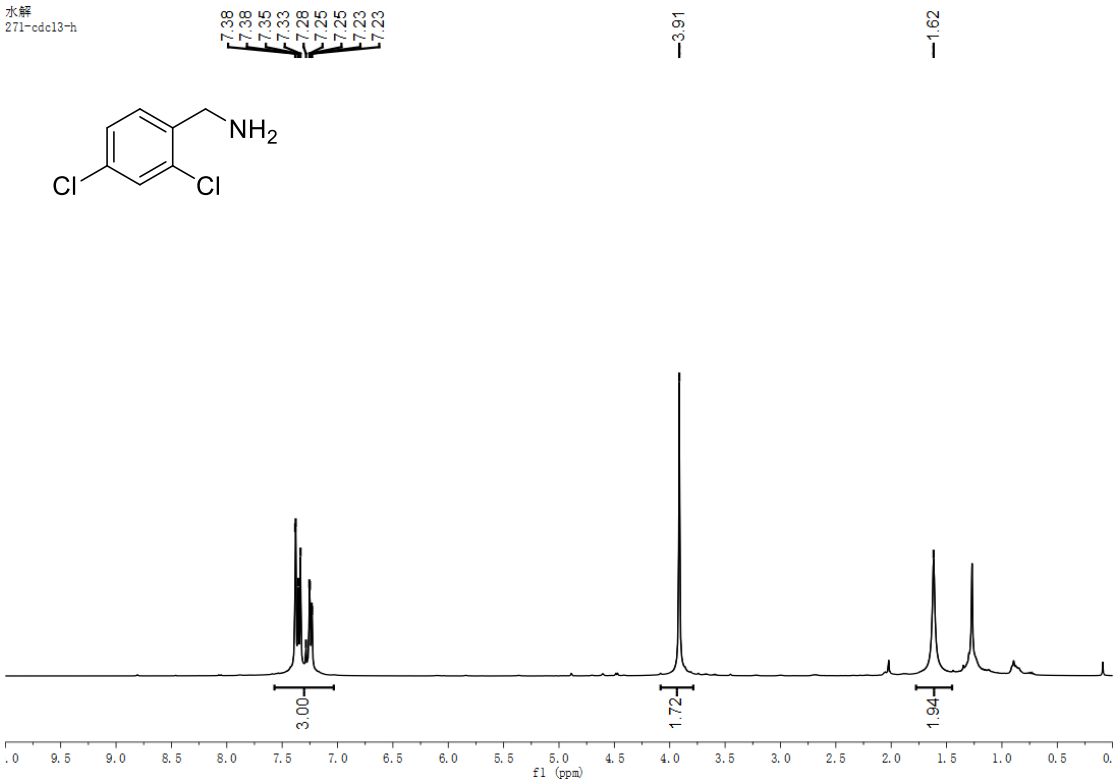


Figure S136. ^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)

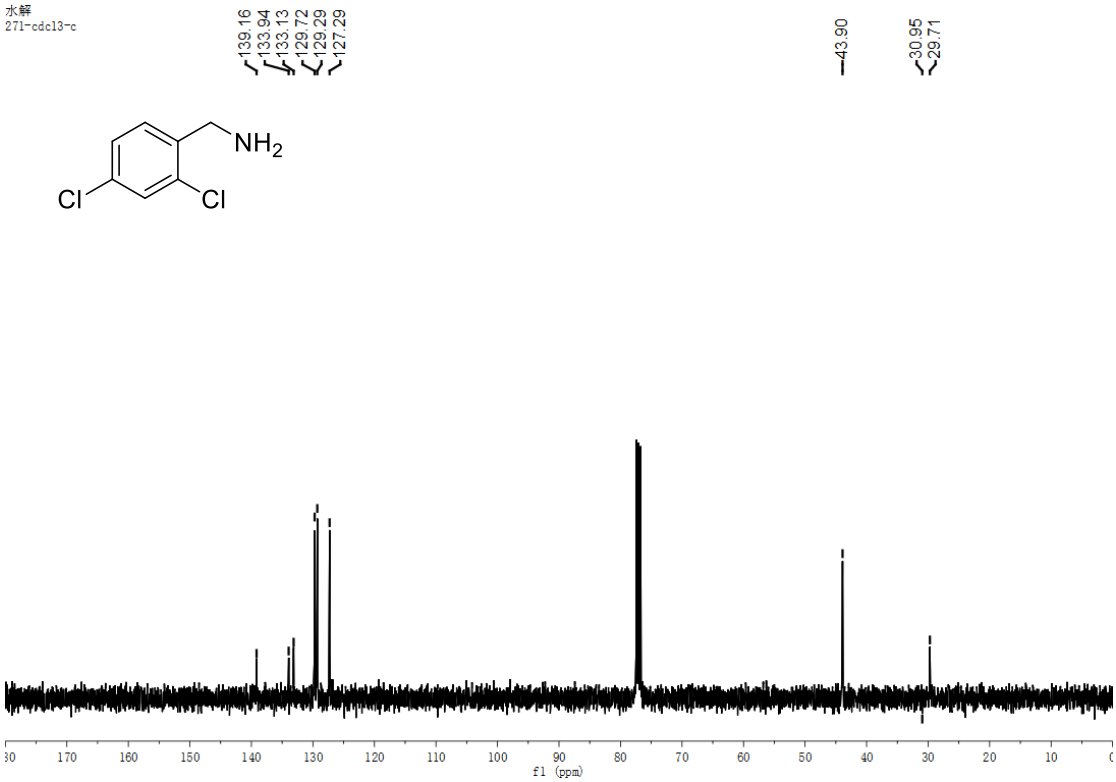


Figure S137. ^{13}C NMR spectrum of **3b** (400 MHz, $CDCl_3$)

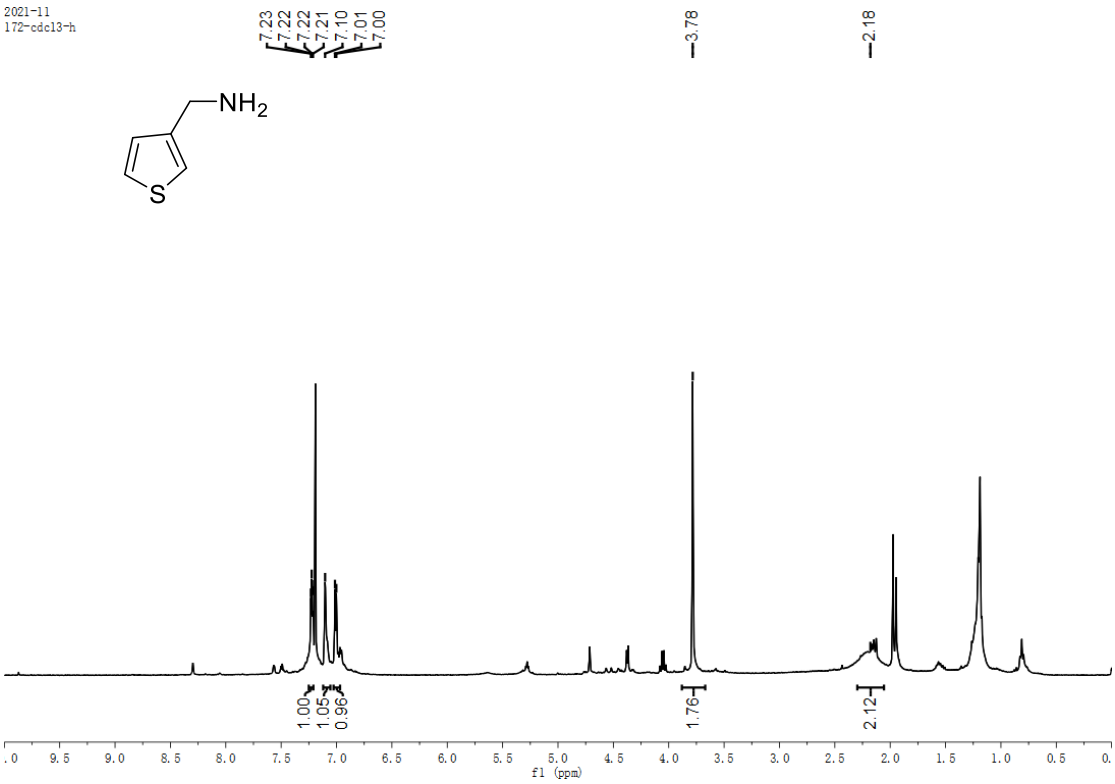


Figure S138. ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)

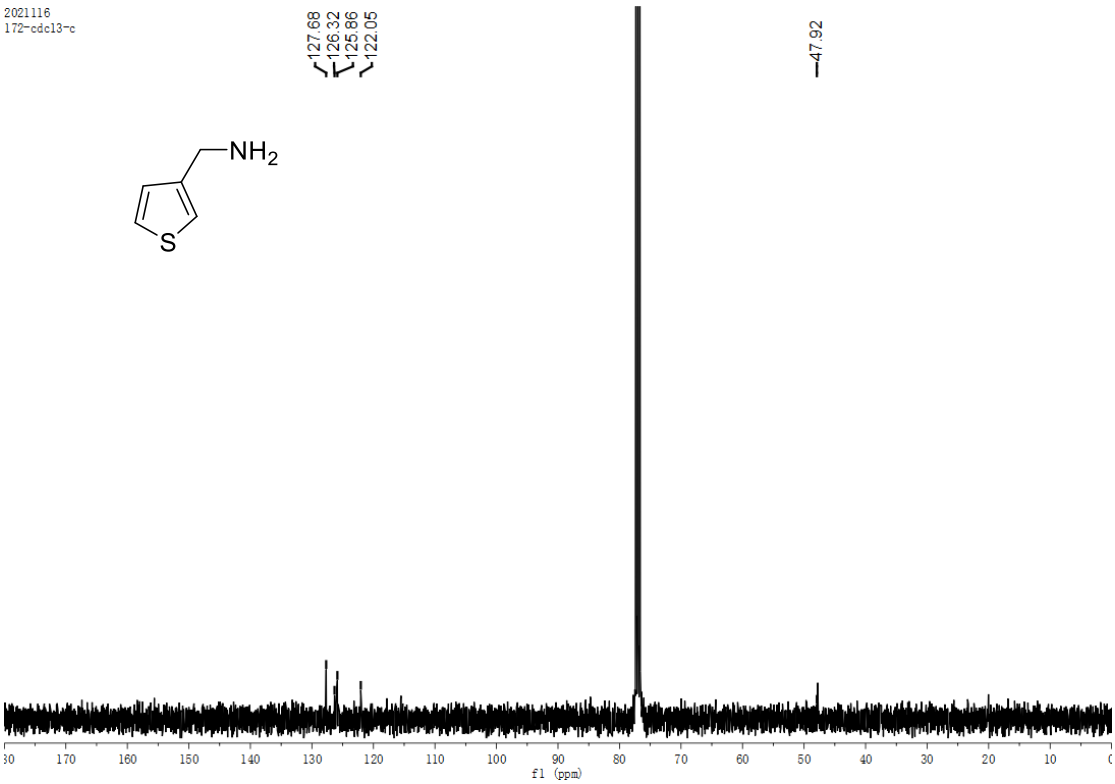


Figure S139. ^{13}C NMR spectrum of **3c** (400 MHz, $CDCl_3$)

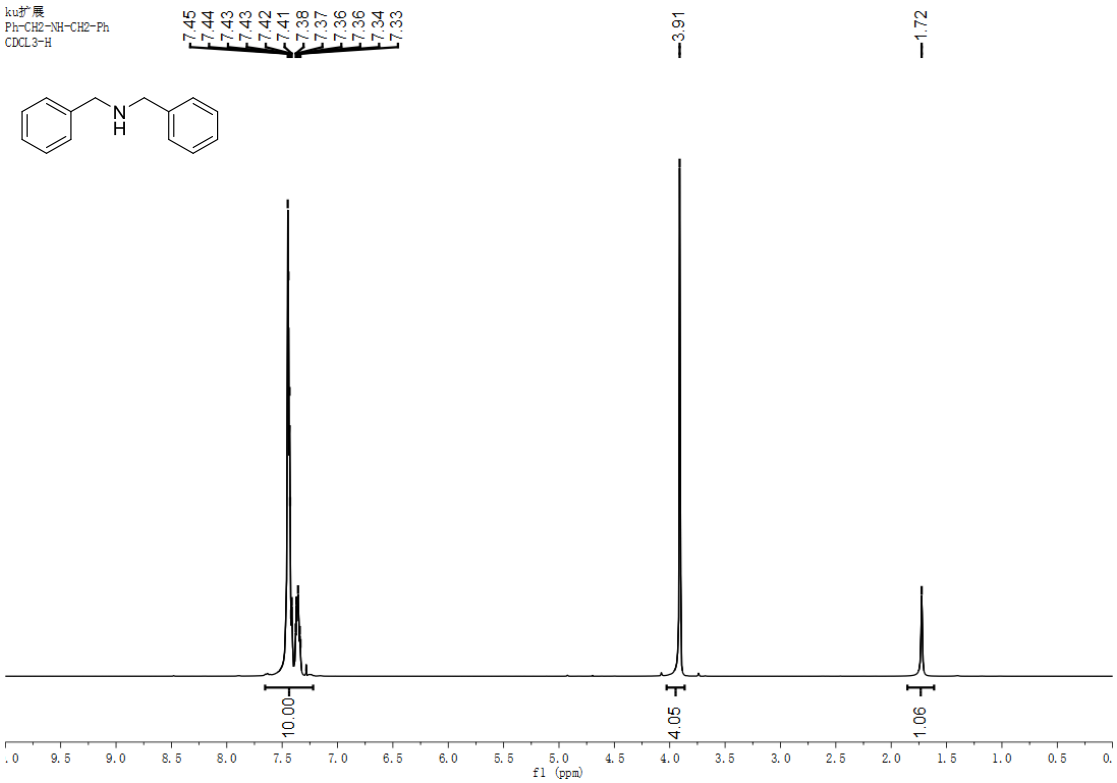


Figure S140. ^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)

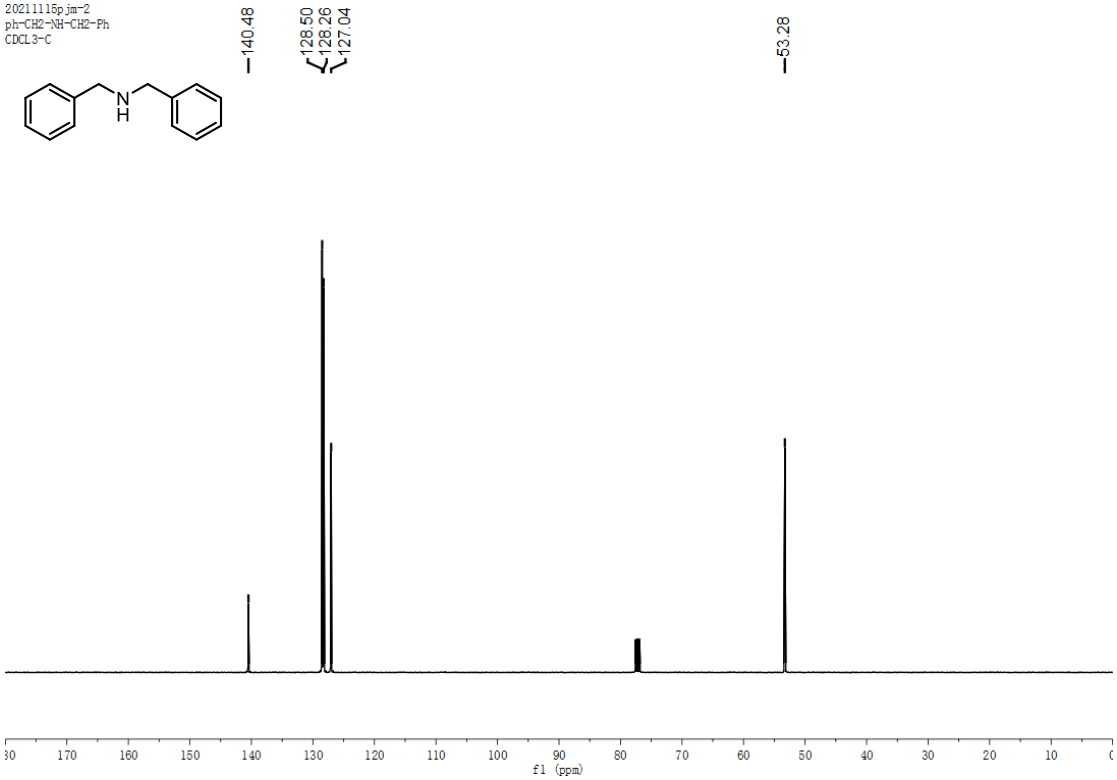


Figure S141. ^{13}CNMR spectrum of **4a** (400 MHz, $CDCl_3$)

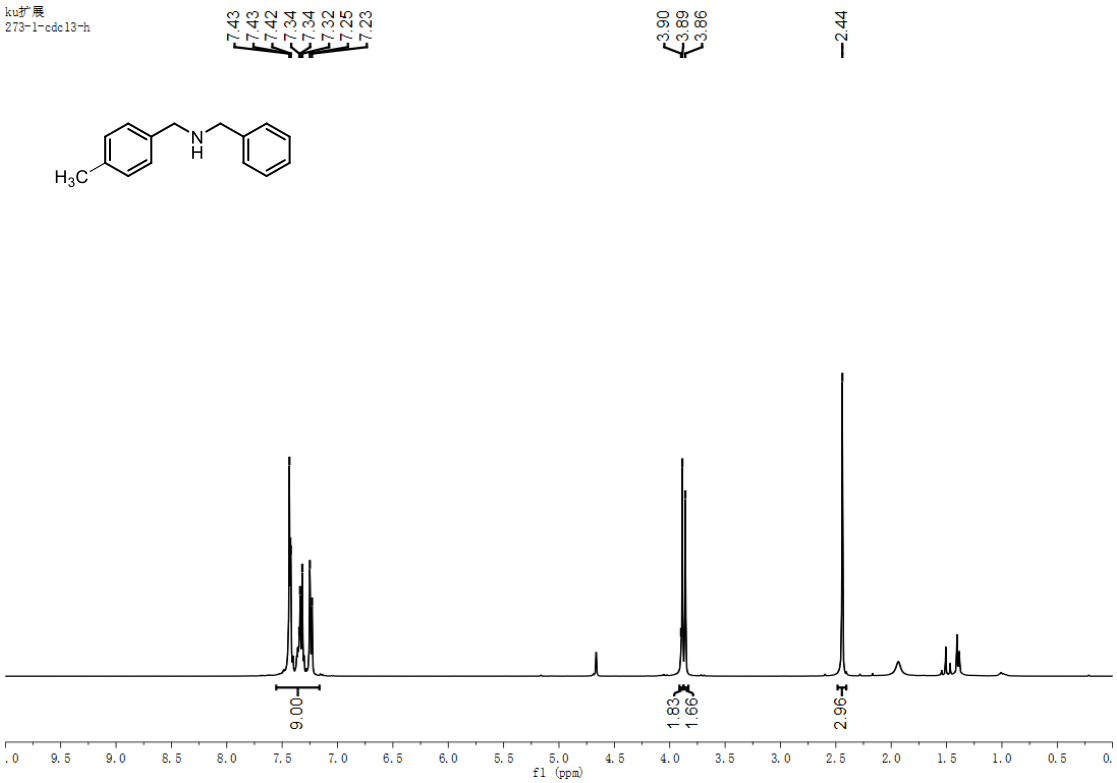


Figure S142. ^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)

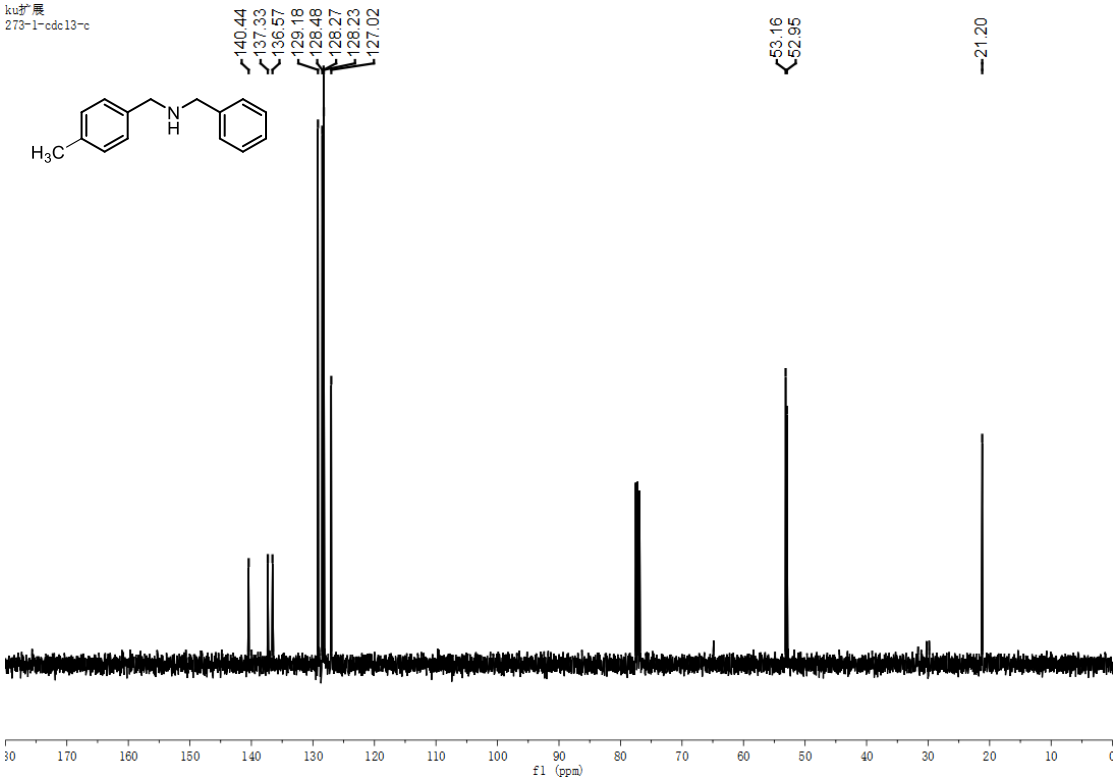


Figure S143. ^{13}C NMR spectrum of **4b** (400 MHz, $CDCl_3$)

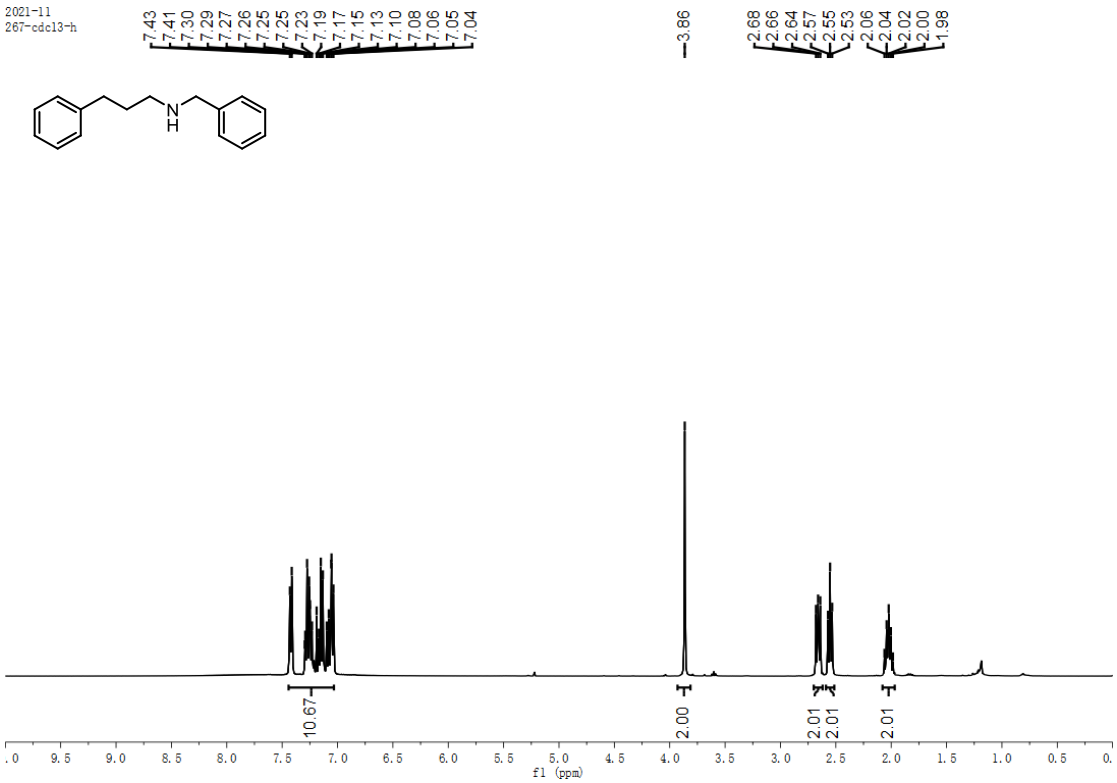


Figure S144. ^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)

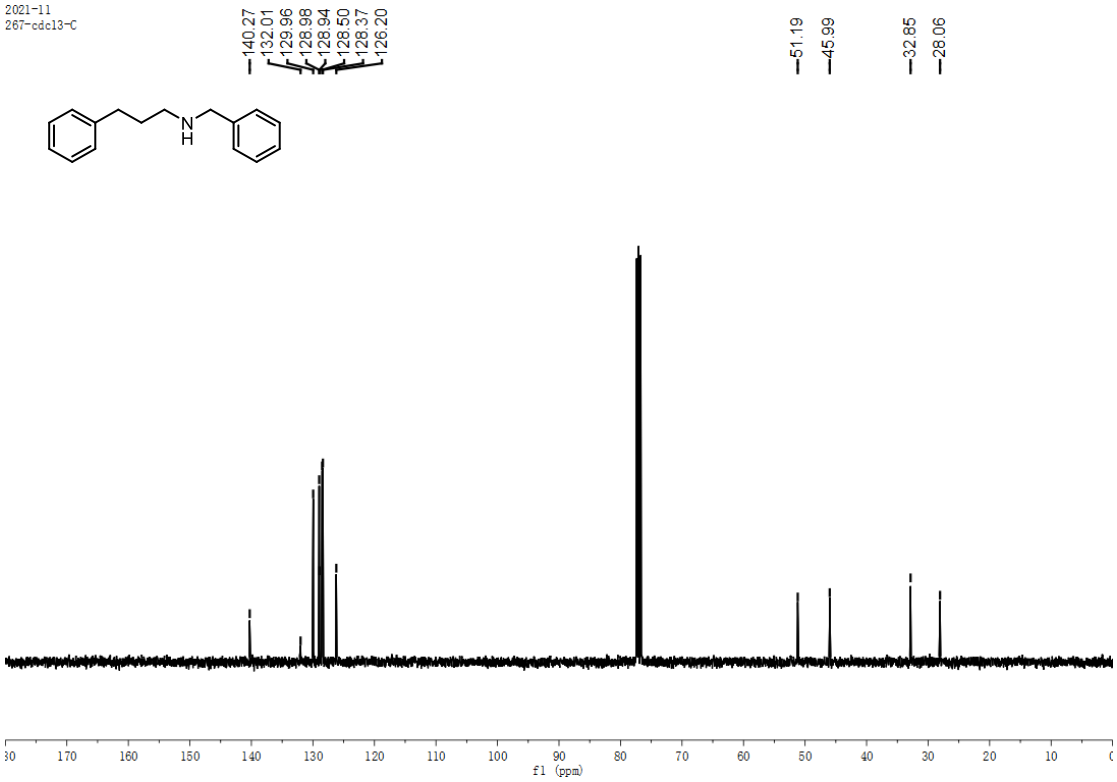


Figure S145. ^{13}C NMR spectrum of **4c** (400 MHz, $CDCl_3$)