Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photo-Induced Catalyst-Free Formal Carbon Insertion of Acylsilanes into B-B and B-Si Bonds

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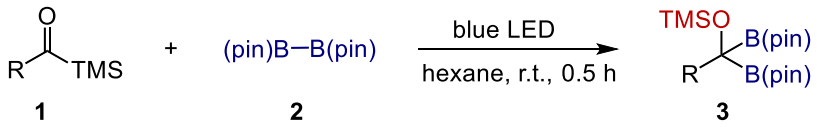
1. General information

All the chemicals were purchased from commercial suppliers, such as Bidepharm, Macklin, Energy Chemical, Adamas-beta®, and were directly used without further purification. Dry dioxane, toluene, and hexane were purchased from Energy Chemical. Acylsilanes were prepared based on reported procedures.[1-3] Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co., or was carried out on 100-200 mesh of neutral aluminum oxide purchased from Tian Jin Ke Mi Ou Chemical Industry Co. All the ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz spectrometer operating at 400 MHz, 101 MHz, and 377 MHz, respectively. Proton chemical shifts δ were given in ppm using no tetramethylsilane as the internal standard. All NMR spectra were recorded in $CDCl_3$ at room temperature (20±3 °C). High-resolution mass spectra (HRMS) were obtained *via* electrospray ionization (ESI) mode using a UPLC G2-XS Qtof mass spectrometer, or *via* an electrospray ionization (ESI) mode using Thermo Scientific Q Exactive Combined Quadrupole Orbitrap Mass Spectrometer. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), q (quartet), and brs (broad singlet) with coupling constants (*J*) in hertz (Hz).

2. General experimental procedures for the reaction of acylsilane with B(pin) derivatives

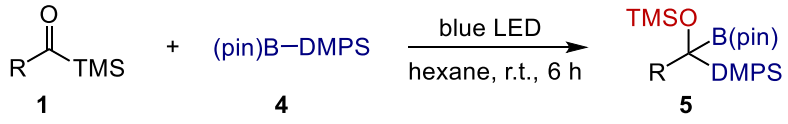
2.1 General procedure A: reaction of acylsilane with $B_2(pin)_2$



1 2 3

Acylsilane (0.1 mmol) was weighed into a 10 mL dry glass vial in a N_2-filled glovebox. 1.0 mL hexane and $B_2(pin)_2$ (33.0 mg, 0.13 mmol, 1.3 equiv.) were then added into the vial successively. The vial was capped and removed from the box. The solution was allowed to stir under 425 nm 10 W blue LED irradiation for 0.5 h. The reaction mixture was then filtrated over celite, after which the residue was purified by concentration and column chromatography on silica gel.

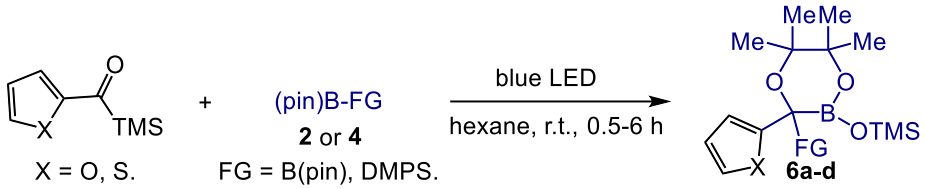
2.2 General procedure B: reaction of acylsilane with (pin)B-DMPS



1 4 5

Acylsilane (0.1 mmol) was weighed into a 10 mL dry glass vial in a N_2-filled glovebox. 1.0 mL hexane and (pin)B-DMPS (26.2 mg, 0.1 mmol, 1.0 equiv.) were then added into the vial successively. The vial was capped and removed from the box. The solution was allowed to stir under 425 nm 10 W blue LED irradiation for 6 h. The reaction mixture was then filtrated over celite, after which the residue was purified by concentration and column chromatography on silica gel.

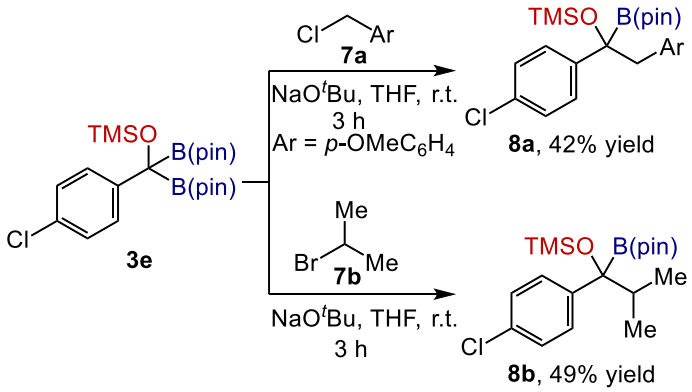
2.3 General procedure C: reaction of heteroacylsilane with $B_2(pin)_2$ and (pin)B-DMPS



Heteroacylsilane (0.1 mmol) was weighed into a 10 mL dry glass vial in a N_2-filled glovebox. 1.0 mL hexane and $B_2(pin)_2$ (33.0 mg, 0.13 mmol, 1.3 equiv.) or (pin)B-DMPS (26.2 mg, 0.1 mmol, 1.0 equiv.) were then added into the vial successively. The vial was capped and removed from the box. The solution was allowed to stir under 425 nm 10 W blue LED irradiation for 0.5 h (with $B_2(pin)_2$) or 6 h (with (pin)B-DMPS). The reaction mixture was then filtrated over celite, after which the residue was purified by concentration and column chromatography on silica gel.

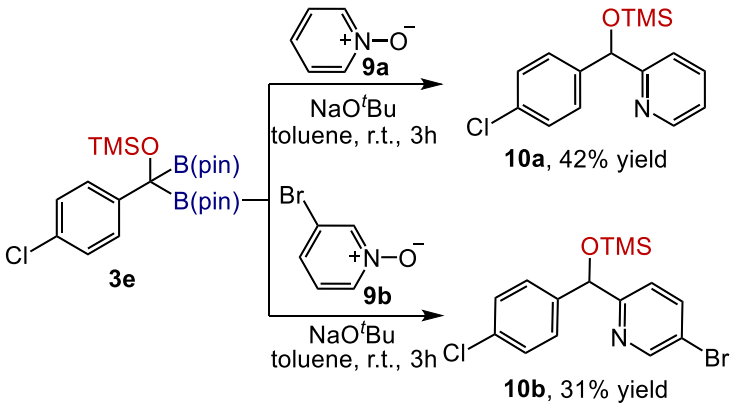
3. Application of the current method

3.1 Deborylalkylation of 3e



3e (46.7 mg, 0.1 mmol) was weighed into a 10 mL dry glass vial in an N_2-filled glovebox. 0.5 mL of THF, **7a-b** (0.13 mmol, 1.3 equiv.), and NaO^{t}Bu (28.8 mg, 0.3 mmol, 3.0 equiv.) were added to the vial successively. The vial was capped and removed from the box. The reaction mixture was allowed to stir at room temperature for 3 h. It was then filtrated over celite, after which the residue was purified by concentration and column chromatography on silica gel to afford **8a** (19.4 mg, 0.042 mmol, 42% yield) and **8b** (18.6 mg, 0.049 mmol, 49% yield), respectively.

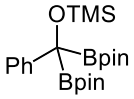
3.2 Functionalization of pyridine *N*-oxide derivatives with 3e



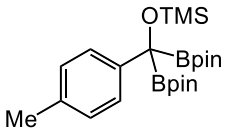
3e (93.4 mg, 0.2 mmol, 2.0 equiv.) was weighed into a 10 mL dry glass vial in an N_2-filled

glovebox. 0.5 mL of toluene, **9a-b** (0.1 mmol), and NaO^{t}Bu (19.2 mg, 0.2 mmol, 2.0 equiv.) were then added to the vial successively. The vial was capped and removed from the box. The reaction mixture was allowed to stir at room temperature for 3 h. It was then filtrated over celite, after which the residue was purified by concentration and column chromatography on silica gel to afford **10a** (12.1 mg, 0.042 mmol, 42% yield) and **10b** (11.4 mg, 0.031 mmol, 31% yield), respectively.

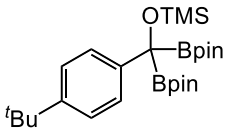
4. Characterization data for products



3a: white solid, 90%, m.p. 74.3-75.0 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58-7.55 (m, 2H), 7.25 (t, *J* = 7.1 Hz, 2H), 7.09 (t, *J* = 7.0 Hz, 1H), 1.21 (s, 12H), 1.21 (s, 12H), 0.14 (s, 9H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 143.71, 127.76, 125.89, 125.15, 84.05, 24.87, 24.73, 2.21 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, CDCl$_3$) δ 32.07 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{22}H_{39}B_2O_5Si$), requires *m/z* = 433.2753, found *m/z* = 433.2738.

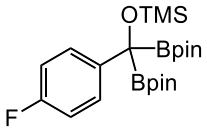


3b: white solid, 81%, m.p. 121.4-122.2 ℃. Prepared according to general procedure A.
^{1}H NMR (**400 MHz, CDCl$_3$**) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 2.28 (s, 3H), 1.22 (s, 12H), 1.21 (s, 12H), 0.11 (s, 9H).
^{13}C NMR (**101 MHz, CDCl$_3$**) δ 140.49, 134.51, 128.54, 126.07, 83.98, 24.92, 24.72, 21.16, 2.23 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, CDCl$_3$) δ 32.08 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{23}H_{40}B_2NaO_5Si$), requires *m/z* = 469.2729, found *m/z* = 469.2731.

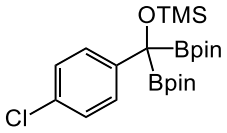


3c: white solid, 86%, m.p. 105.2-106.1 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, CDCl3) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 1.27 (s, 9H), 1.22 (s, 12H), 1.21 (s, 12H), 0.10 (s, 9H).
^{13}C NMR (101 MHz, CDCl3) δ 147.99, 140.19, 126.10, 124.77, 83.98, 34.35, 31.56, 24.96, 24.70, 2.19 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, CDCl$_3$) δ 32.08 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{26}H_{46}B_2NaO_5Si$), requires *m/z* = 511.3198,

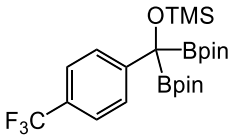
found *m/z* = 511.3200.



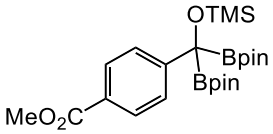
3d: white solid, 99%, m.p. 130.6-131.8 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, *J* = 8.9, 5.6 Hz, 2H), δ 6.96-6.92 (m, 2H), 1.21 (s, 24H), 0.14 (s, 9H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 161.20 (d, *J* = 242.1 Hz), 139.29 (d, *J* = 2.8 Hz), 127.33 (d, *J* = 8.0 Hz), 114.43 (d, *J* = 21.0 Hz), 84.13, 24.84, 24.72, 2.16(The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, CDCl$_3$) δ 32.03 (s).
^{19}F NMR (377 MHz, CDCl$_3$) δ -119.27 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{37}B_2NaFO_5Si$), requires *m/z* = 473.2478, found *m/z* = 473.2489.



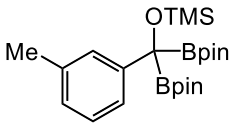
3e: white solid, 99%, m.p. 148.6-149.5 ℃. Prepared according to general procedure A.
^{1}H NMR (**400 MHz, CDCl$_3$**) δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 1.20 (s, 24H), 0.15 (s, 9H).
^{13}C NMR (**101 MHz, CDCl$_3$**) δ 142.48, 130.64, 127.76, 126.97, 84.19, 24.82, 24.74, 2.18 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, CDCl$_3$) δ 31.83 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{37}B_2NaClO_5Si$), requires *m/z* = 489.2183, found *m/z* = 489.2194.



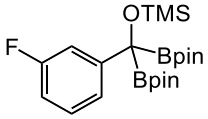
3f: white solid, 78%, m.p. 134.9-135.6 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 1.21 (s, 24H), 0.19 (s, 9H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 148.28, 127.03 (q, *J* = 31.7 Hz), 125.36, 124.87 (q, J = 90.9 Hz), 124.54 (q, *J* = 3.6 Hz), 84.33, 24.81, 24.75, 2.18 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, CDCl$_3$) δ 31.84 (s).
^{19}F NMR (377 MHz, CDCl$_3$) δ -62.00 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{23}H_{37}B_2F_3NaO_5Si$), requires *m/z* = 523.2446, found *m/z* = 523.2440.



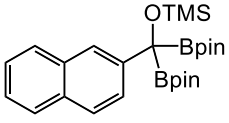
3g: white solid, 87%, m.p. 153.6-154.5 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 1.19 (s, 24H), 0.17 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.75, 149.96, 129.07, 126.73, 125.12, 84.27, 51.92, 24.75, 24.72, 2.15 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 31.55 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{24}H_{40}B_2NaO_7Si$), requires *m/z* = 513.2627, found *m/z* = 513.2626.



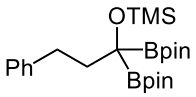
3h: white solid, 91%, m.p. 58-59 ℃Prepared according to general procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 2.31 (s, 3H), 1.22 (s, 24H), 0.13 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.36, 137.17, 127.56, 126.63, 126.01, 123.27, 84.00, 24.85, 24.72, 21.81, 2.21 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.12 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{23}H_{40}B_2NaO_5Si$), requires *m/z* = 469.2729, found *m/z* = 469.2717.



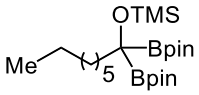
3i: white solid, 94%, m.p. 65.6-66.6℃. Prepared according to general procedure A.
^{1}H NMR (**400 MHz, $CDCl_3$**) δ 7.37 – 7.28 (m, 2H), 7.19 (td, J = 8.1, 6.2 Hz, 1H), 6.77 (t, 1H), 1.21 (s, 24H), 0.17 (s, 9H).
^{13}C NMR (**101 MHz, $CDCl_3$**) δ 162.97 (d, *J* = 242.8 Hz), 146.83 (d, *J* = 6.7 Hz), 128.84 (d, *J* = 8.5 Hz), 121.10 (d, *J* = 2.3 Hz), 112.48 (d, *J* = 22.6 Hz), 111.72 (d, *J* = 21.3 Hz), 84.21, 24.81, 24.73, 2.16 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 31.84 (s).
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.42 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{37}B_2FNaO_5Si$), requires *m/z* = 473.2478, found *m/z* = 473.2468.



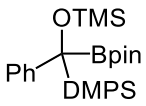
3j: white solid, 88%, m.p. 112.7-113.7 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.73 (s, 2H), 7.45–7.33 (m, 2H), 1.23 (s, 24H), 0.20 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.50, 133.73, 131.93, 128.22, 127.45, 126.85, 125.36, 125.31, 124.74, 123.36, 84.13, 24.85, 24.78, 2.27 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.22 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{26}H_{40}B_2NaO_5Si$), requires *m/z* = 505.2729, found *m/z* = 505.2727.



3k: colorless liquid, 57%. Prepared according to general procedure A.
^{1}H NMR (**400 MHz, $CDCl_3$**) δ 7.26 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 6.1 Hz, 3H), 7.14 (t, *J* = 6.9 Hz, 1H), 2.76 – 2.67 (m, 2H), 2.06 – 1.96 (m, 2H), 1.26 (s, 12H), 1.26 (s, 12H), 0.17 (s, 9H).
^{13}C NMR (**101 MHz, $CDCl_3$**) δ 143.55, 128.76, 128.28, 125.54, 83.90, 39.12, 33.33, 25.01, 24.96, 2.40 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.78 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{24}H_{42}NaB_2O_5Si$ 483.2880), requires *m/z* = 483.2885, found *m/z* = 483.2881.

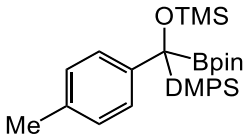


3l: white solid, 60%, m.p. 134.9-135.6 ℃. Prepared according to general procedure A.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71-1.67 (m, 2H), 1.43-1.28 (m, 9H), 1.24 (s, 12H), 1.235 (s, 12H), 0.86 (t, *J* = 6.9 Hz, 1H), 0.11 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 83.75, 36.71, 32.01, 30.14, 29.45, 26.72, 25.04, 24.87, 22.78, 14.26, 2.34 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.76 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{23}H_{49}B_2O_5SiNa$), requires *m/z* = 477.3349, found *m/z* = 477.3350.

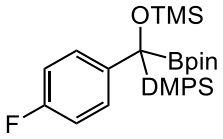


5a: colorless liquid, 48%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 3H), 7.26 (t, *J* = 7.1 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 1.17 (s, 6H), 1.09 (s, 6H), 0.26 (s, 3H), 0.18 (s, 3H), 0.08 (s, 9H).

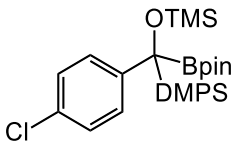
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.54, 137.18, 135.37, 129.07, 127.36, 127.02, 124.47, 124.00, 84.00, 25.37, 24.87, 2.24, -5.06, -5.76 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.36 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{38}BO_3Si_2$), requires *m/z* = 441.2447, found *m/z* = 441.2444.



5b: colorless liquid, 62%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.21–7.13 (m, 4H), 6.94 (d, *J* = 8.1 Hz, 2H), 2.23 (s, 3H), 1.08 (s, 6H), 0.99 (s, 6H), 0.17 (s, 3H), 0.09 (s, 3H), 0.00 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.39, 137.44, 135.38, 133.21, 129.01, 128.15, 127.01, 124.44, 83.92, 25.36, 24.85, 21.05, 2.27, -5.04, -5.77 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.36 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{40}BO_3Si_2$), requires *m/z* = 455.2604, found *m/z* = 455.2600.

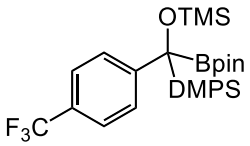


5c: colorless liquid, 55%. Prepared according to general procedure B.
^{1}H NMR (**400 MHz, $CDCl_3$**) δ 7.45 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.31 (s, 1H), 7.27–7.21 (m, 4H), 6.86 (s, 2H), 1.17 (s, 6H), 1.09 (s, 6H), 0.24 (s, 3H), 0.17 (s, 3H), 0.06 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.41 (d, *J* = 241.5 Hz), 140.12 (d, *J* = 2.3 Hz), 136.74, 135.34, 129.17, 127.06, 125.75 (d, *J* = 7.4 Hz), 114.03 (d, *J* = 21.0 Hz), 84.12, 25.38, 24.88, 2.20, -5.15, -5.78. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.19 (s).
^{19}F NMR (377 MHz, $CDCl_3$) δ -120.79 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{36}BFO_3Si_2$), requires *m/z* = 459.2353, found *m/z* = 459.2359.

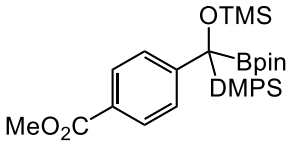


5d: colorless liquid, 59%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.6 Hz, 2H), 7.35 (s, 1H), 7.30–7.25 (m, 4H), 7.17 (d, *J* = 8.8 Hz, 2H), 1.21 (s, 6H), 1.12 (s, 6H), 0.28 (s, 3H), 0.21 (s, 3H), 0.10 (s, 9H).

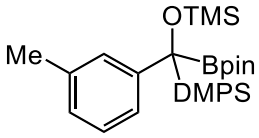
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.31, 136.53, 135.33, 129.56, 129.24, 127.43, 127.10, 125.79, 84.18, 25.39, 24.85, 2.20, -5.16, -5.81 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.32 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{37}BClO_3Si_2$), requires *m/z* = 475.2057, found *m/z* = 475.2055.



5e: colorless liquid, 52%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.38 (m, 6H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 1.21 (s, 6H), 1.12 (s, 6H), 0.28 (s, 3H), 0.20 (s, 3H), 0.09 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.22, 136.16, 135.31, 129.36, 127.13, 126.7 (q, J = 96.0 Hz), 124.90 (q, *J* = 272.3 Hz), 124.33, 124.26 (q, *J* = 3.8 Hz), 84.33, 25.42, 24.86, 2.17, -5.16, -5.81. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.00 (s).
^{19}F NMR (377 MHz, $CDCl_3$) δ -61.85 (s).
HRMS (ESI): failed after at least 4 trials with different detectors.

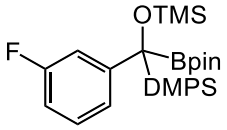


5f: colorless liquid, 45%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 6.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.33 (s, 1H), 7.24 (d, *J* = 6.9 Hz, 2H), 3.89 (s, 3H), 1.19 (s, 6H), 1.10 (s, 6H), 0.28 (s, 3H), 0.19 (s, 3H), 0.08 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.72, 150.94, 136.25, 135.31, 129.32, 128.81, 127.11, 125.79, 124.14, 84.28, 51.91, 25.39, 24.81, 2.16, -5.12, -5.78 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 33.43 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{40}BO_5Si_2$), requires *m/z* = 499.2502, found *m/z* = 499.2505.

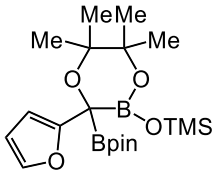


5g: colorless liquid, 56%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.8, 1.3 Hz, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 7.1 Hz, 2H), 7.13 (s, 1H), 7.07 (t, J = 7.5 Hz, 2H), 6.84 (d, J = 7.4 Hz, 1H), 2.24 (s, 3H), 1.15 (s, 6H), 1.06 (s, 6H), 0.24 (s, 3H), 0.16 (s, 3H), 0.06 (s, 9H).

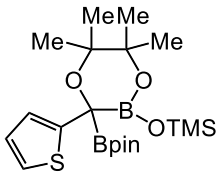
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.40, 137.30, 136.61, 135.39, 129.02, 127.18, 126.96, 125.44, 124.72, 121.56, 83.93, 25.38, 24.81, 21.84, 2.26, -5.09, -5.79 (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.30 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{40}BO_3Si_2$), requires *m/z* = 455.2604, found *m/z* = 455.2603.



5h: colorless liquid, 51%. Prepared according to general procedure B.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.41 (m, 2H), 7.31 (s, 1H), 7.24 (t, J = 7.1 Hz, 2H), 7.09 (s, 3H), 6.79–6.64 (m, 1H), 1.17 (s, 6H), 1.08 (s, 6H), 0.26 (s, 3H), 0.18 (s, 3H), 0.07 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.80 (d, *J* = 242.8 Hz), 147.81 (d, *J* = 7.3 Hz), 136.56, 135.30, 129.27, 128.56 (d, *J* = 8.3 Hz), 127.09, 120.04 (d, *J* = 2.2 Hz), 111.36 (d, *J* = 23.2 Hz), 110.65 (d, *J* = 21.2 Hz), 84.21, 25.39, 24.84, 2.17, -5.11, -5.77. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.79 (s).
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.46 (s).
HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{37}BFO_3Si_2$), requires *m/z* = 459.2353, found *m/z* = 459.2352.

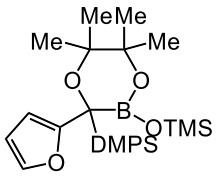


6a: pale yellow liquid, 88%. Prepared according to general procedure C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.26 (s, 1H), 6.20 (s, 1H), 1.32 (s, 3H), 1.25-1.18 (m, 18H), 1.08 (s, 3H), 0.14 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.33, 110.09, 107.59, 83.87, 79.20, 76.40, 25.82, 24.98, 24.64, 24.55, 24.44, 24.17, 1.15. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 32.16 (s), 27.44 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{20}H_{36}B_2O_6NaSi$), requires *m/z* = 445.2365, found *m/z* = 445.2378.

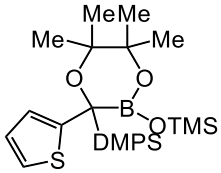


6b: pale yellow liquid, 82%. Prepared according to general procedure C.

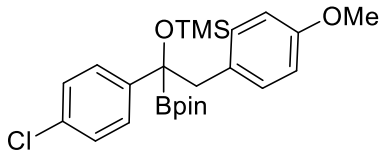
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.98 (d, *J* = 2.8 Hz, 1H), 6.91 (dd, *J* = 5.0, 3.6 Hz, 1H), 1.28 (s, 6H), 1.20 (s, 3H), 1.16 (s, 9H), 1.15 (s, 6H), 0.21 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 126.57, 122.01, 120.76, 83.95, 79.16, 77.55, 26.12, 25.08, 24.68, 24.31, 1.23. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 31.19 (s), 27.67 (s).
HRMS (ESI) m/z: exact mass calculated for $[M+H]^+$ ($C_{20}H_{37}B_2O_5SSi$), requires *m/z* = 439.2317, found *m/z* = 439.2327.



6c: pale yellow liquid, 28%. Prepared according to general procedure C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.34–7.27 (m, 4H), 6.23 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.96 (d, *J* = 3.2 Hz, 1H), 1.08 (s, 3H), 1.02 (s, 3H), 0.88 (s, 3H), 0.80 (s, 3H), 0.39 (s, 3H), 0.25 (s, 9H), 0.22 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.46, 140.15, 134.89, 129.00, 127.21, 110.06, 104.18, 78.81, 76.79, 26.14, 25.25, 24.41, 20.93, 1.15, -3.73, -5.07. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 27.46 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{35}BO_4NaSi_2$), requires *m/z* = 453.2065, found *m/z* = 453.2066.



6d: pale yellow liquid, 83%. Prepared according to general procedure C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.35–7.26 (m, 3H), 7.01 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.83 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.78 (dd, *J* = 3.5, 1.1 Hz, 1H), 1.12 (s, 3H), 1.04 (s, 3H), 0.96 (s, 3H), 0.86 (s, 3H), 0.36 (s, 3H), 0.30 (s, 9H), 0.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.06, 135.08, 127.09, 125.85, 121.25, 78.85, 77.61, 26.37, 25.19, 24.35, 21.48, 1.17, -3.69, -5.76. (The carbon attached to boron was not observed due to quadrupolar relaxation).
^{11}B NMR (128 MHz, $CDCl_3$) δ 28.34 (s).
HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{22}H_{35}BO_3SNaSi_2$), requires *m/z* = 469.1836, found *m/z* = 469.1842.



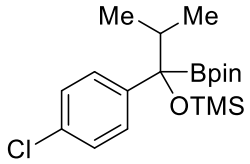
8a: colorless liquid, 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 3.77 (s, 3H), 3.10 (d, *J* = 13.5 Hz, 1H), 2.84 (d, *J* = 13.6 Hz, 1H), 1.24-1.04 (m, 12H), 0.01 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.10, 145.40, 131.82, 131.55, 130.65, 127.79, 126.89, 112.83, 84.42, 55.22, 47.91, 24.80, 24.69, 2.12. (The carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.56 (s).

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{24}H_{34}BClO_4NaSi$), requires *m/z* = 483.1906, found *m/z* = 483.1920.



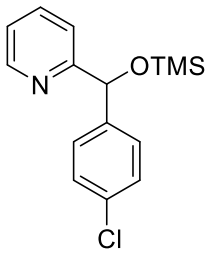
8b: colorless liquid, 49%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 2.09–2.01 (m, 1H), 1.25-1.19 (m, 12H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.55 (d, *J* = 6.6 Hz, 3H), 0.15 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.87, 131.11, 127.55, 127.07, 84.21, 38.16, 24.79, 24.70, 19.69, 15.33, 2.35. (The carbon attached to boron was not observed due to quadrupolar relaxation).

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.80 (s).

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{19}H_{32}BClO_3NaSi$), requires *m/z* = 405.1800, found *m/z* = 405.1806.



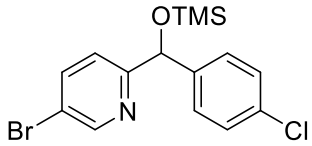
10a: colorless liquid, 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.37 (m, 1H), 7.58 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 2.8 Hz, 2H), 7.04 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 5.75 (s, 1H), -0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.56, 148.60, 142.23, 136.86, 132.98, 128.37, 127.73, 122.20, 120.20, 74.26, -0.02.

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{15}H_{18}ClNONaSi$), requires *m/z* = 314.0744,

found *m/z* = 314.0751.



10b: colorless liquid, 31%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 2H), 5.77 (s, 1H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.24, 149.64, 141.68, 139.48, 133.23, 128.48, 127.63, 121.59, 119.09, 76.49, -0.02.

HRMS (ESI): exact mass calculated for $[M+Na]^+$ ($C_{15}H_{17}BrClNONaSi$), requires *m/z* = 391.9849, found *m/z* = 391.9850.

5. References

1. Ishida K, Tobita F, Kusama H. Lewis Acid-Assisted Photoinduced Intermolecular Coupling between Acylsilanes and Aldehydes: A Formal Cross Benzoin-Type Condensation. *Chem. Eur. J*. **2018**, *24*, 543-546.
2. Yu C-J, Li R, Gu P. Intermolecular Schmidt Reaction of Alkyl Azides with Acyl Silanes. *Tetrahedron Lett.* **2016**, *57*, 3568-3570.
3. Yamamoto K, Hayashi A, Suzuki S, Tsuji, J. Preparation of Substituted Benzoyltrimethylsilanes and -Germanes by the Reaction of Benzoyl Chlorides with Hexamethyldisilane or -Digermane in the Presence of Palladium Complexes as Catalysts. *Organometallics* **1987***, 6*, 974-979.

6. NMR spectra

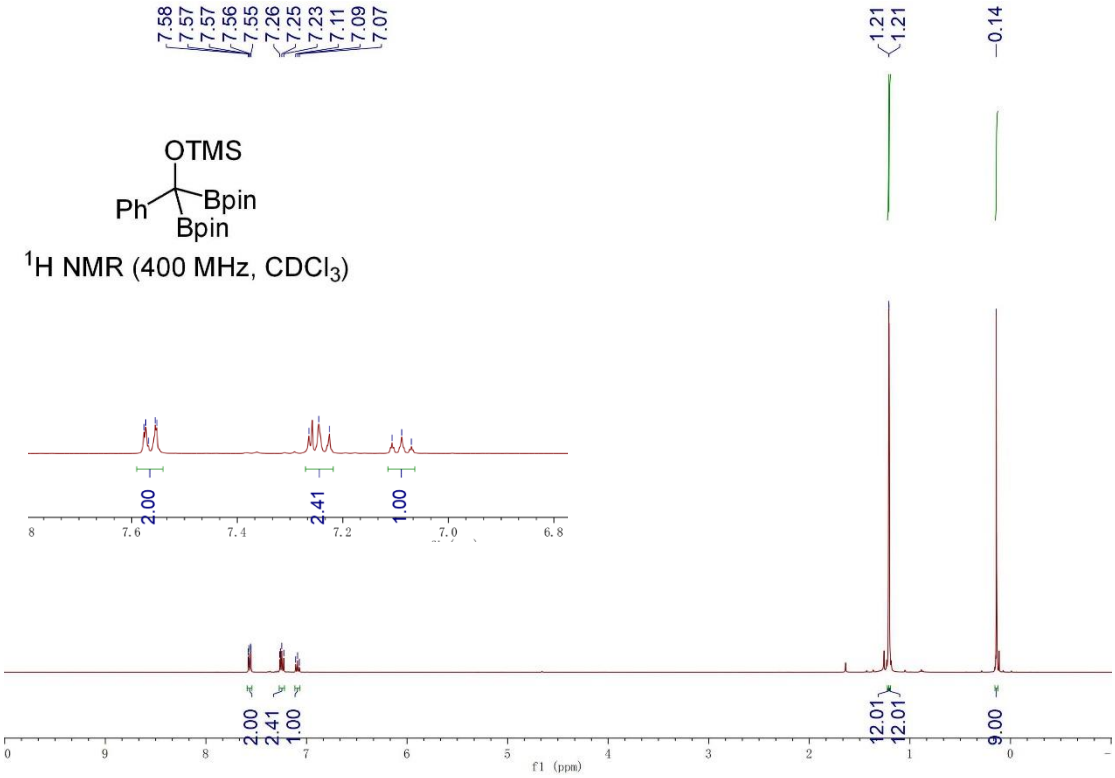


Figure S1 The ^{1}H NMR spectra of **3a**

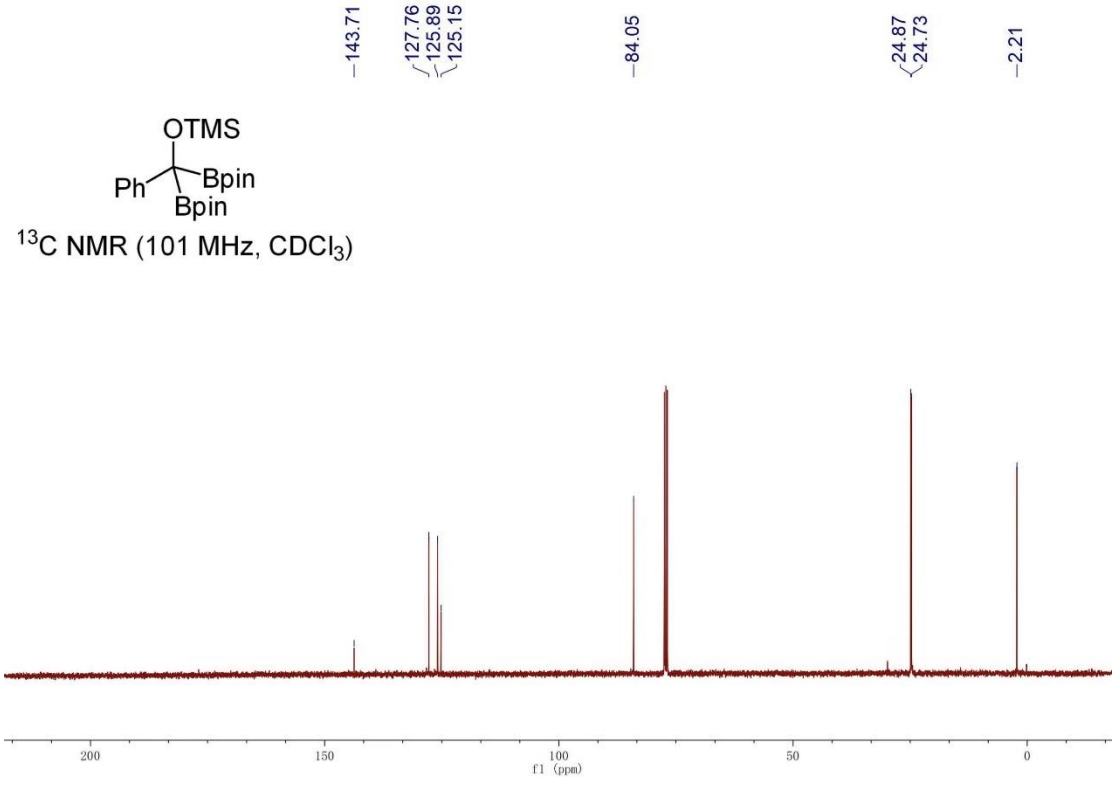


Figure S2 The ^{13}C NMR spectra of **3a**

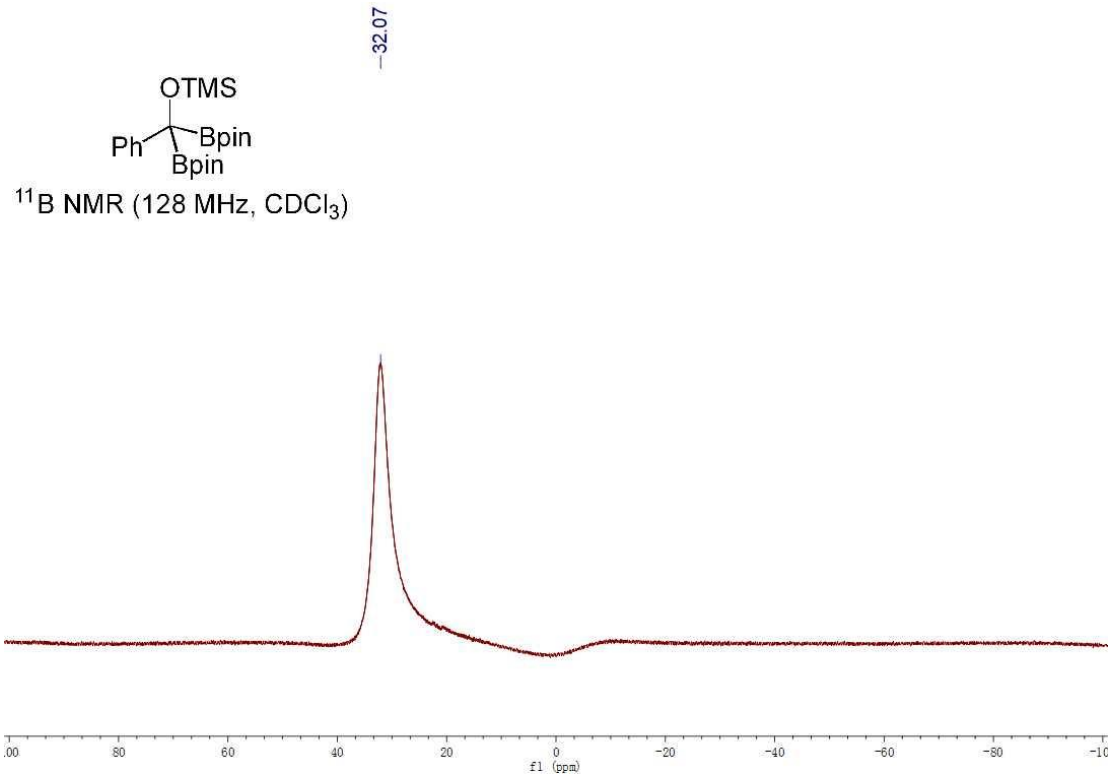


Figure S3 The ^{11}B NMR spectra of **3a**

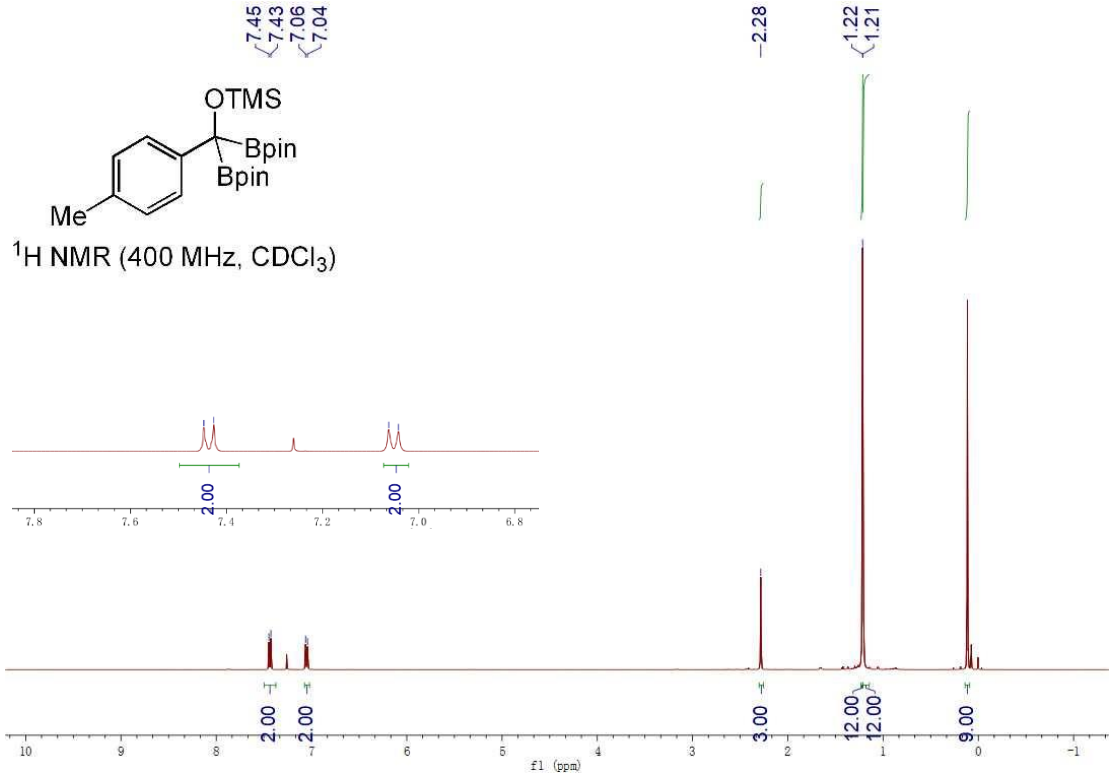


Figure S4 The ^{1}H NMR spectra of **3b**

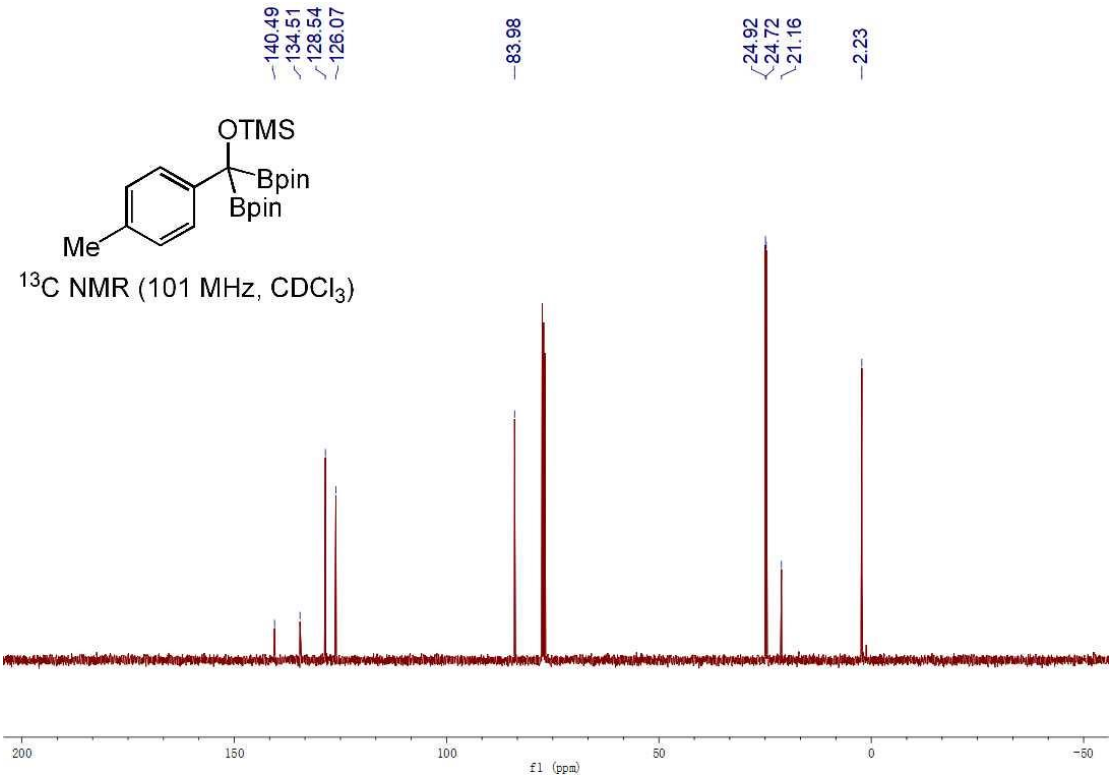


Figure S5 The ^{13}C NMR spectra of **3b**

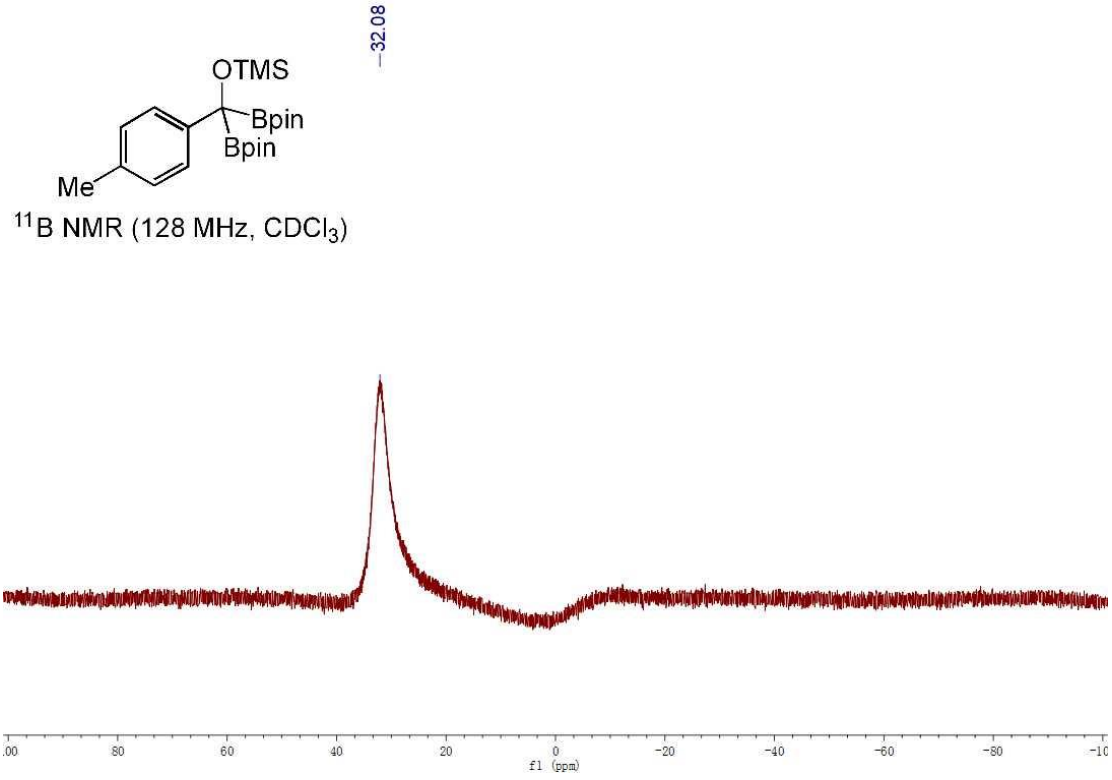


Figure S6 The ^{11}B NMR spectra of **3b**

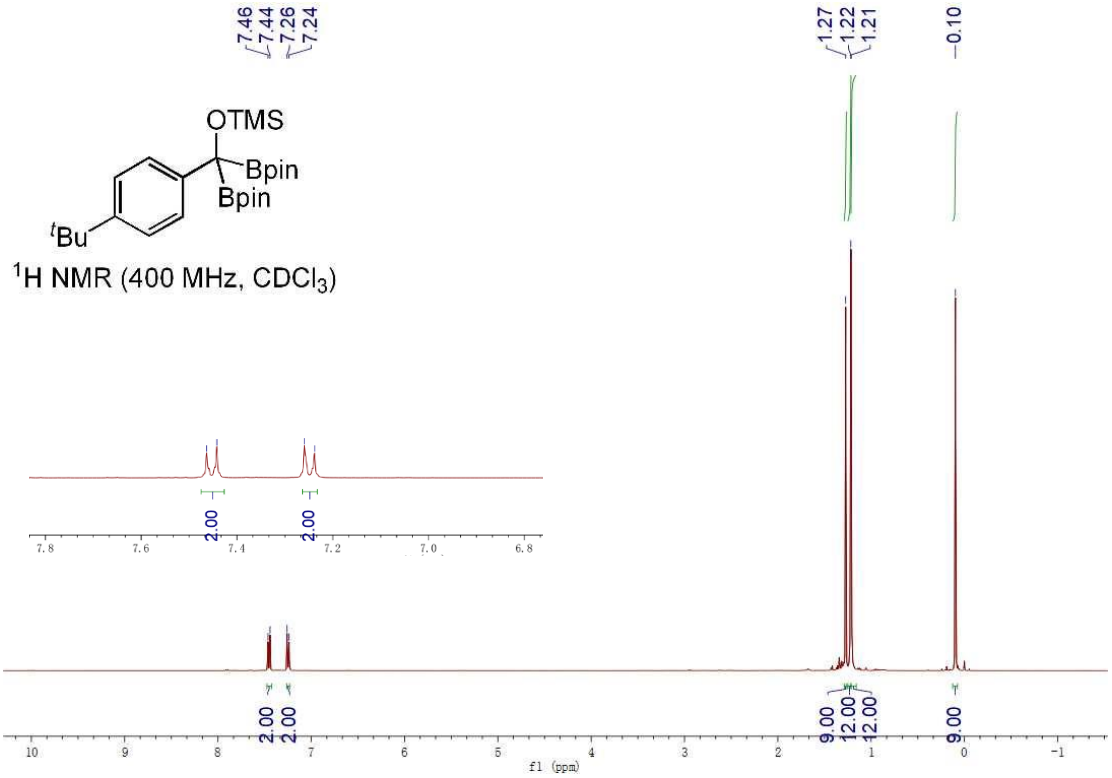


Figure S7 The ^{1}H NMR spectra of **3c**

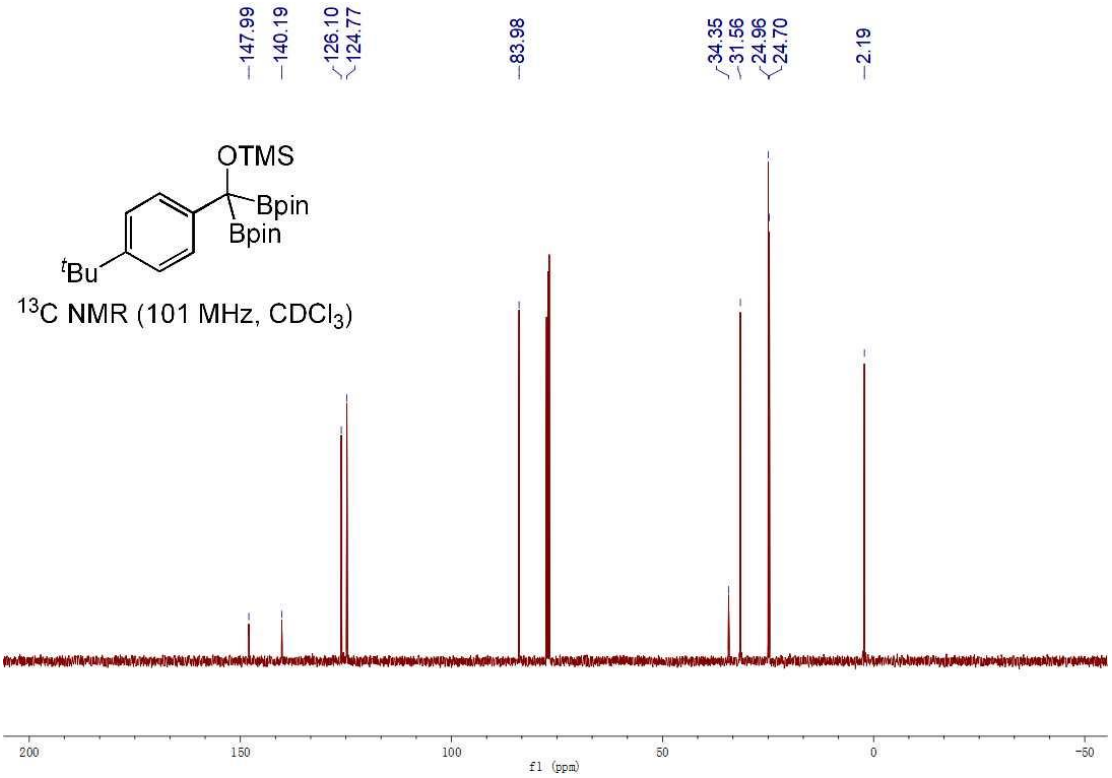


Figure S8 The ^{13}C NMR spectra of **3c**

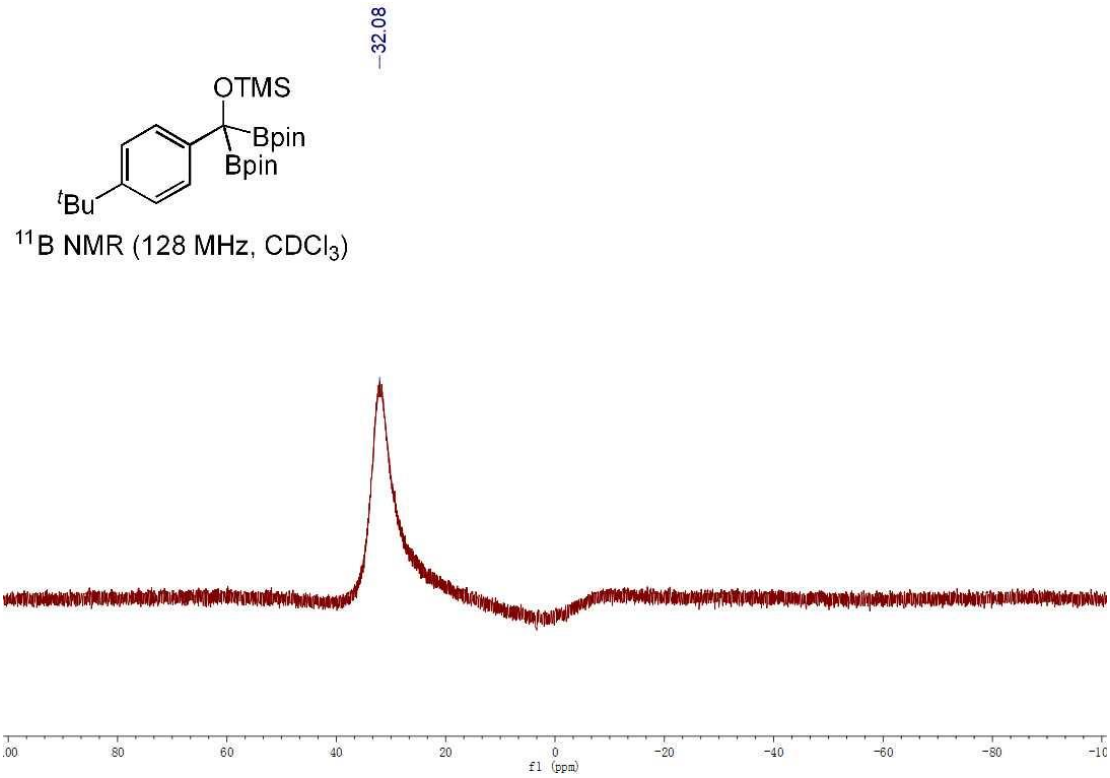


Figure S9 The ^{11}B NMR spectra of **3c**

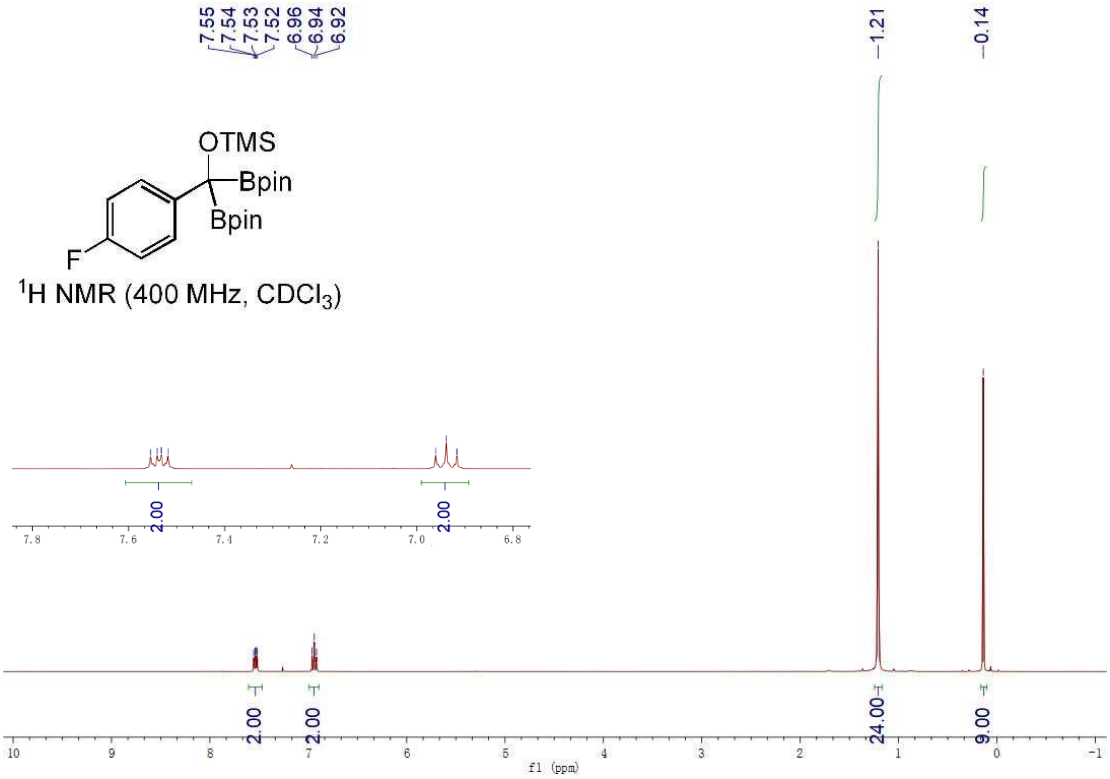


Figure S10 The ^{1}H NMR spectra of **3d**

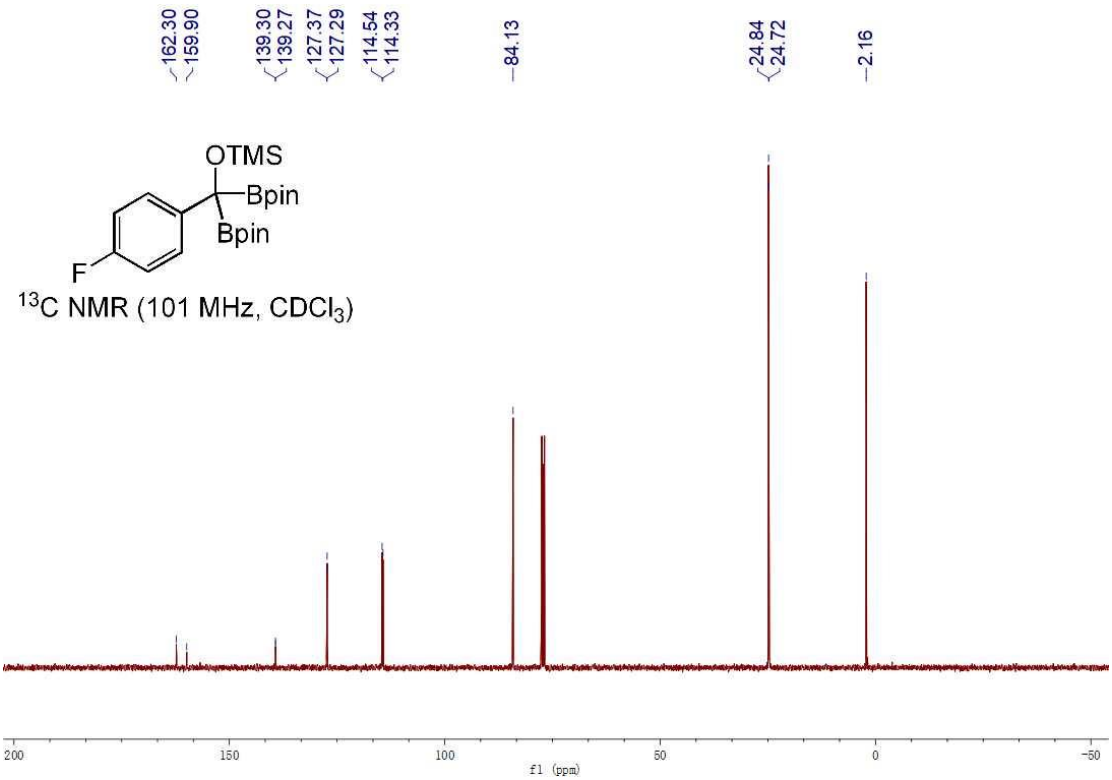


Figure S11 The ^{13}C NMR spectra of **3d**

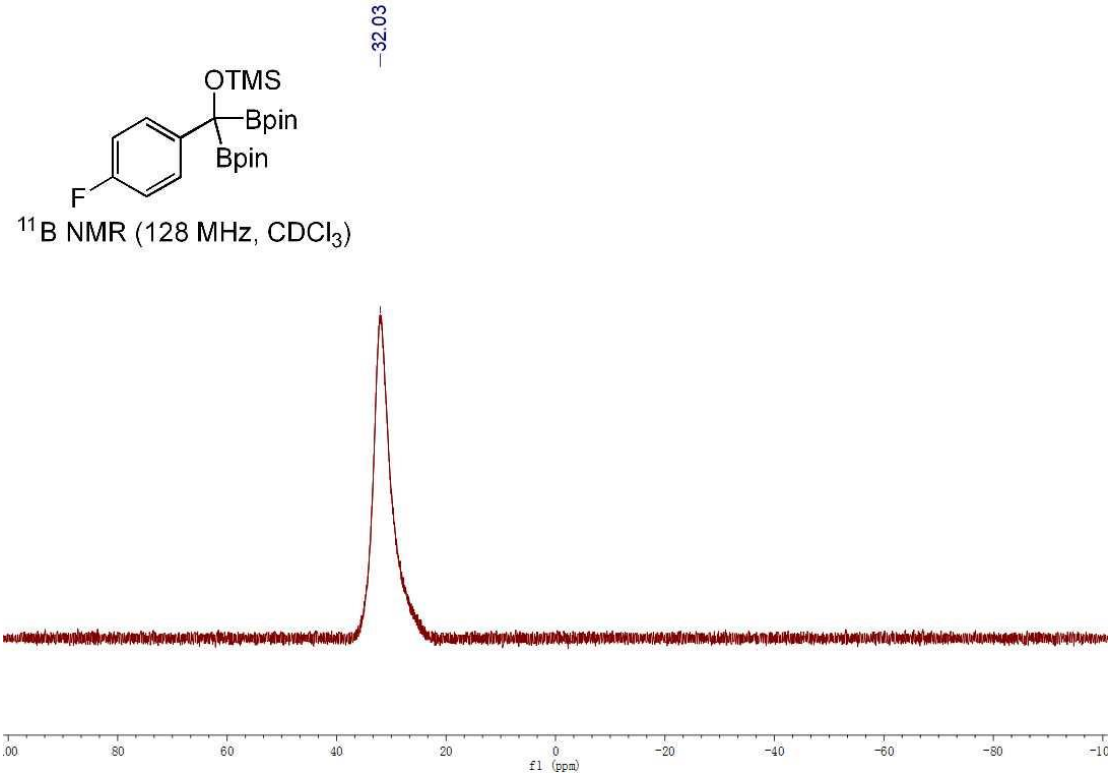


Figure S12 The ^{11}B NMR spectra of **3d**

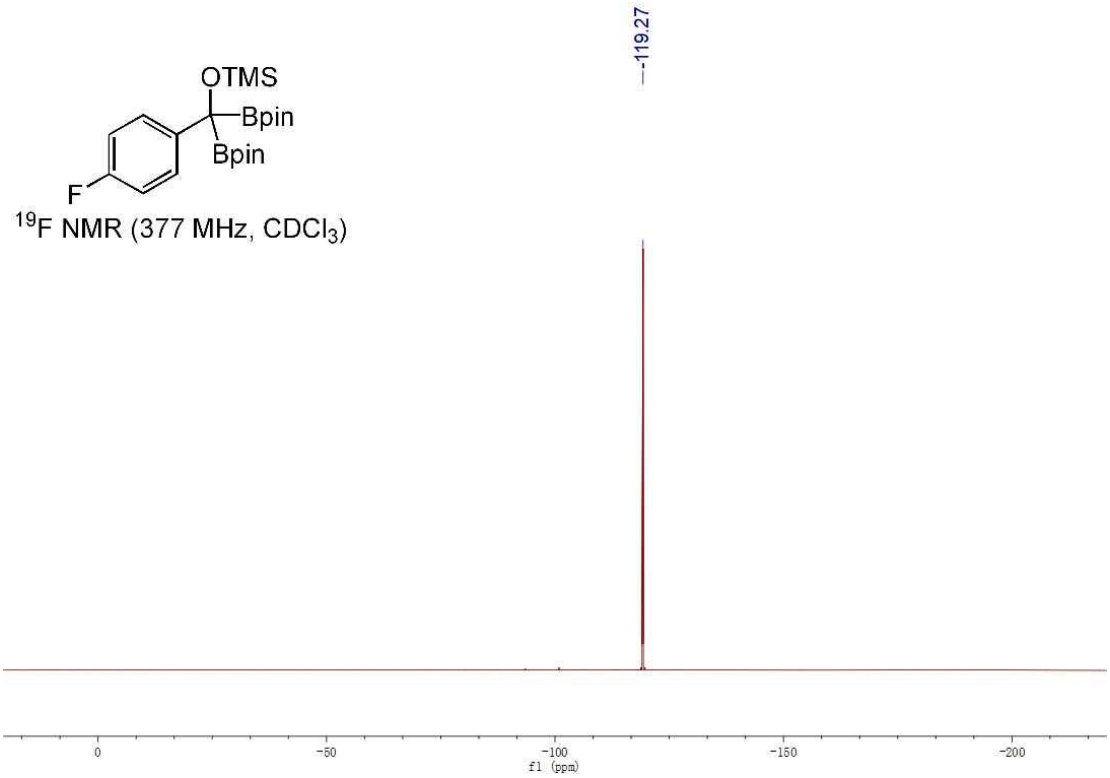


Figure S13 The ^{19}F NMR spectra of **3d**

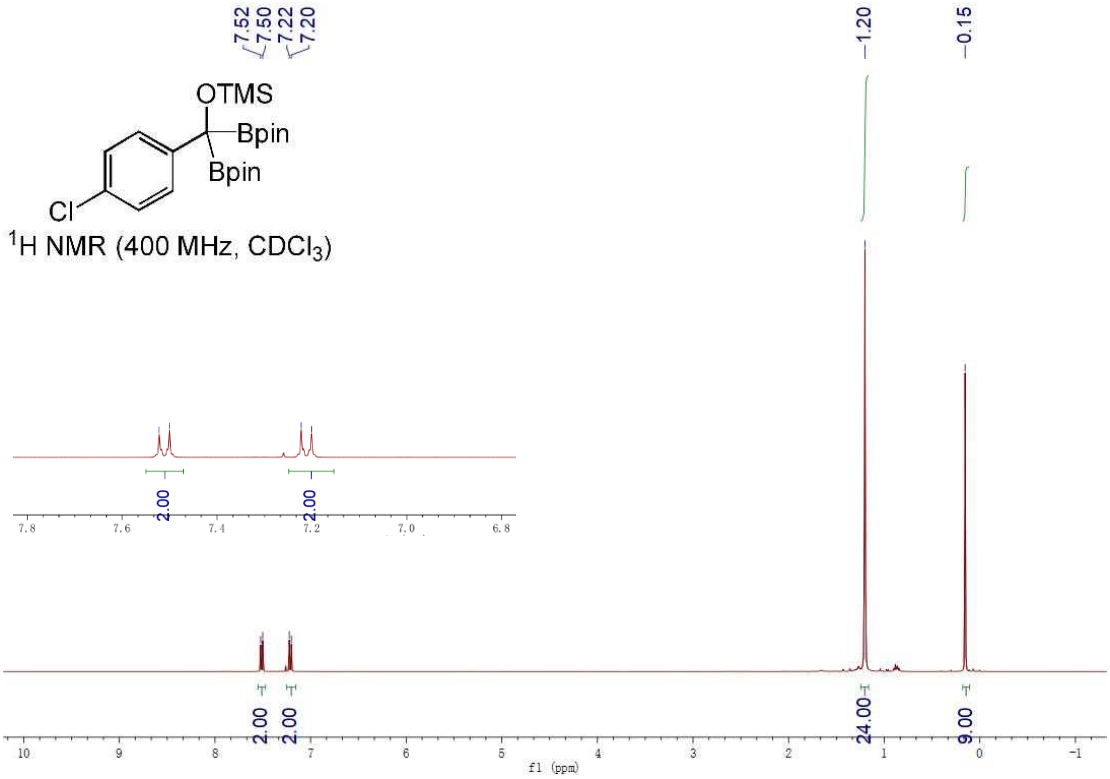


Figure S14 The ^{1}H NMR spectra of **3e**

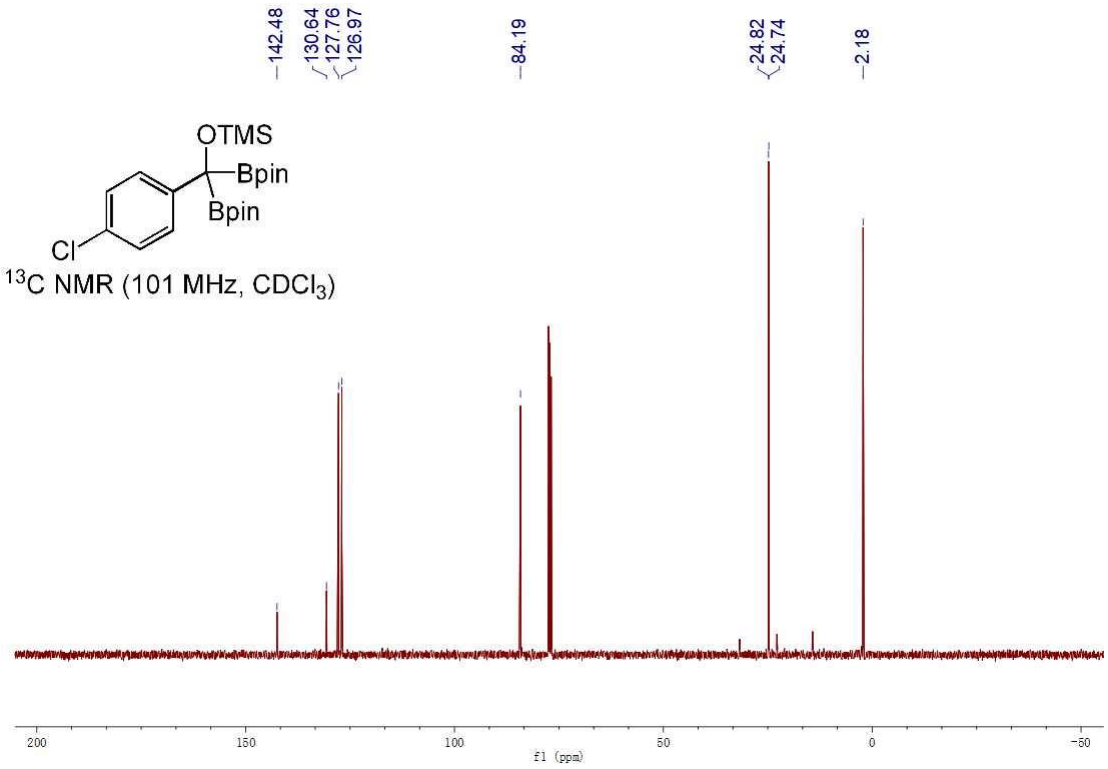


Figure S15 The ^{13}C NMR spectra of **3e**

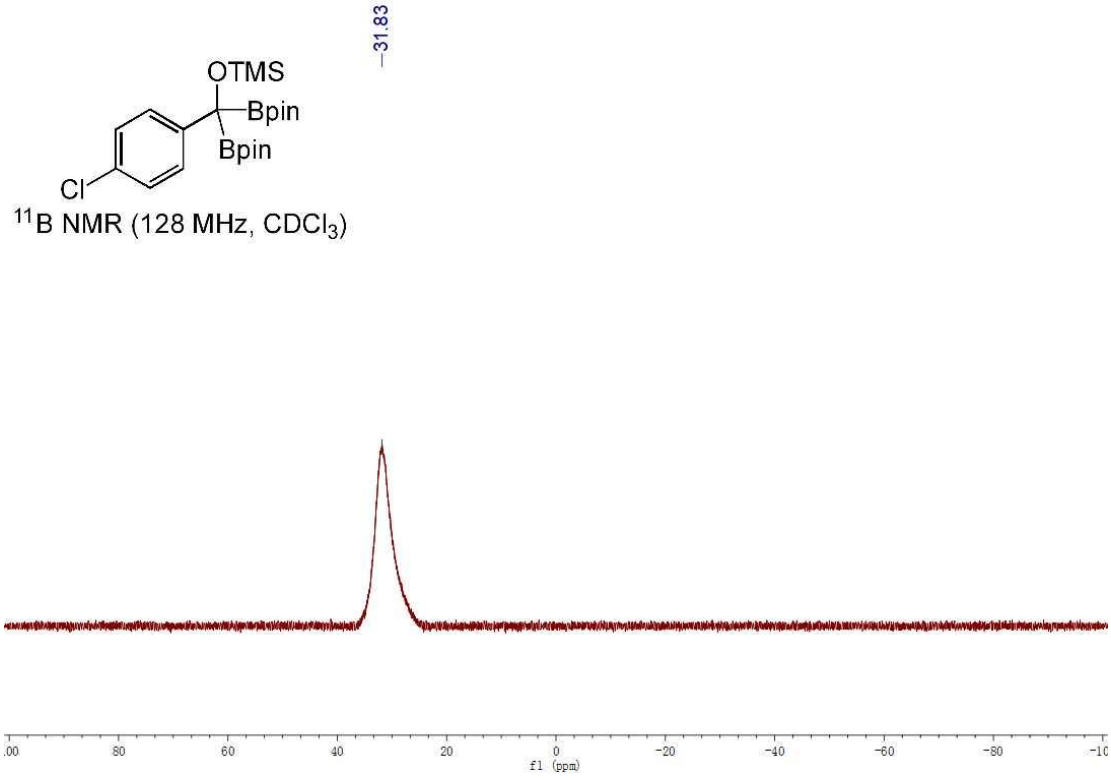


Figure S16 The ^{11}B NMR spectra of **3e**

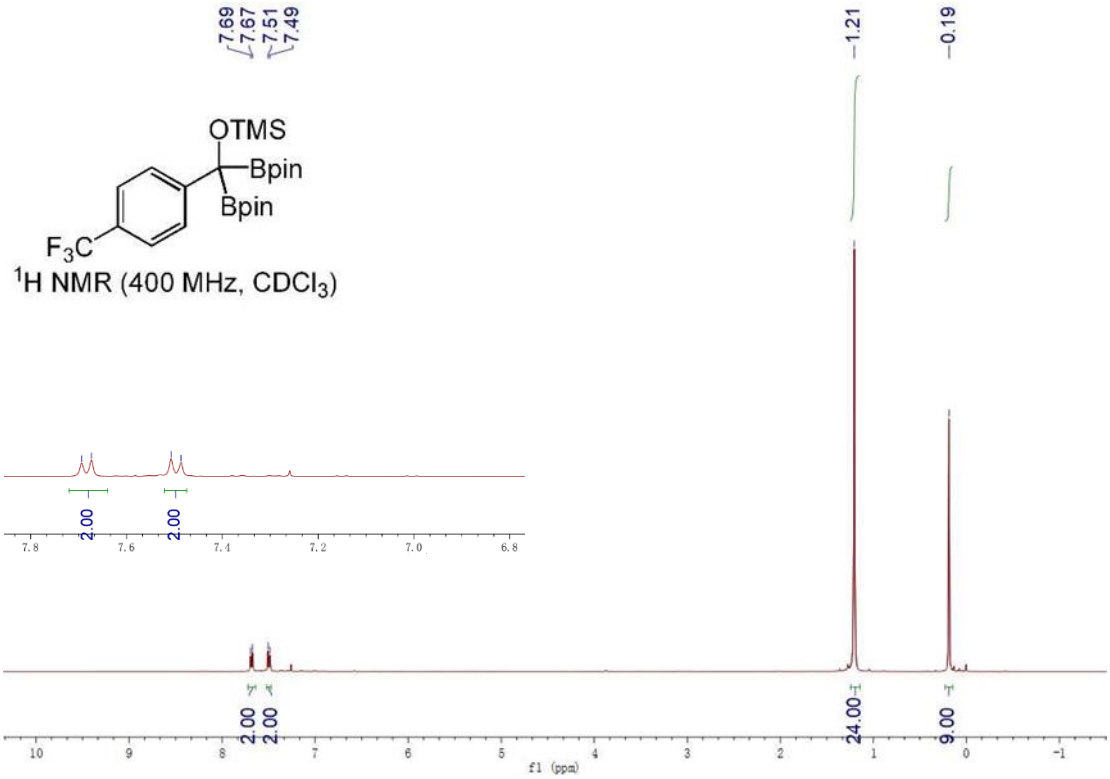


Figure S17 The ^{1}H NMR spectra of **3f**

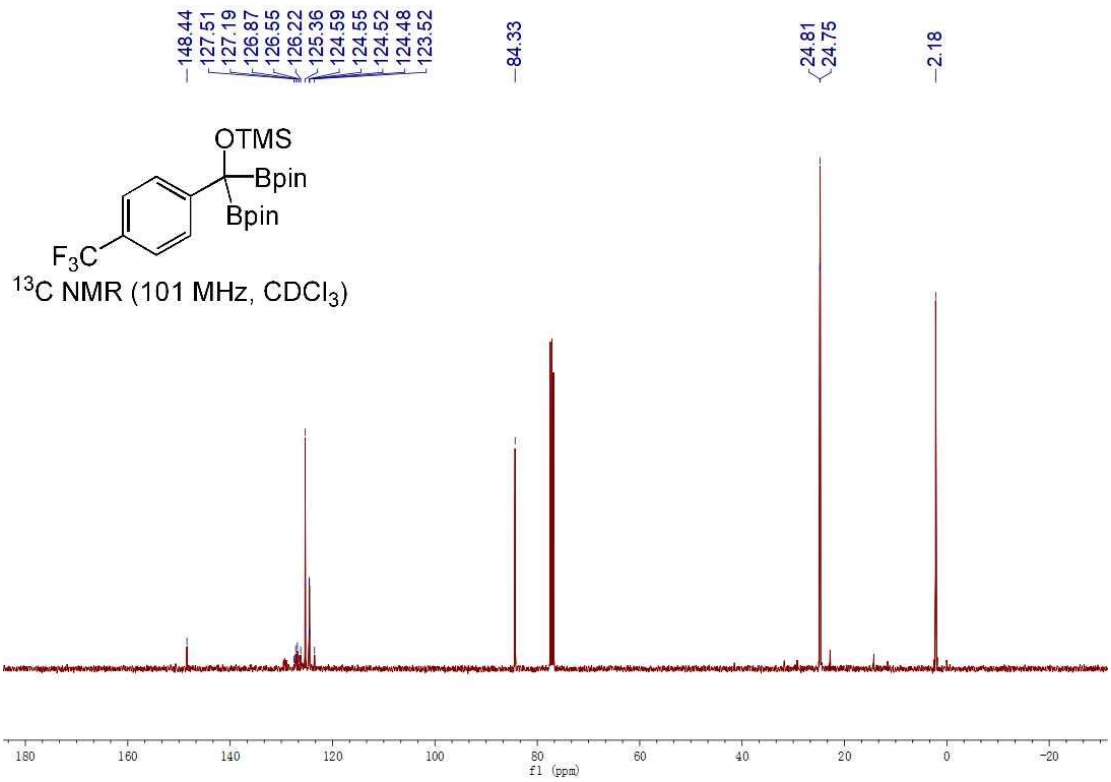


Figure S18 The ^{13}C NMR spectra of **3f**

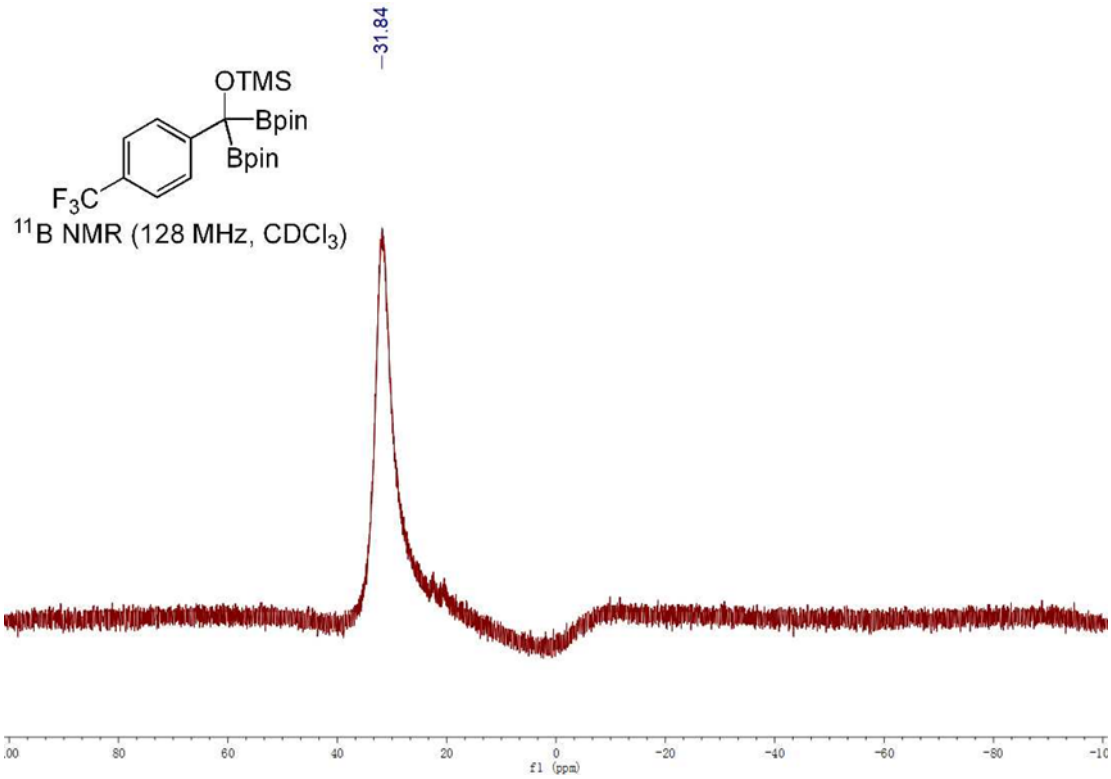


Figure S19 The ^{11}B NMR spectra of **3f**

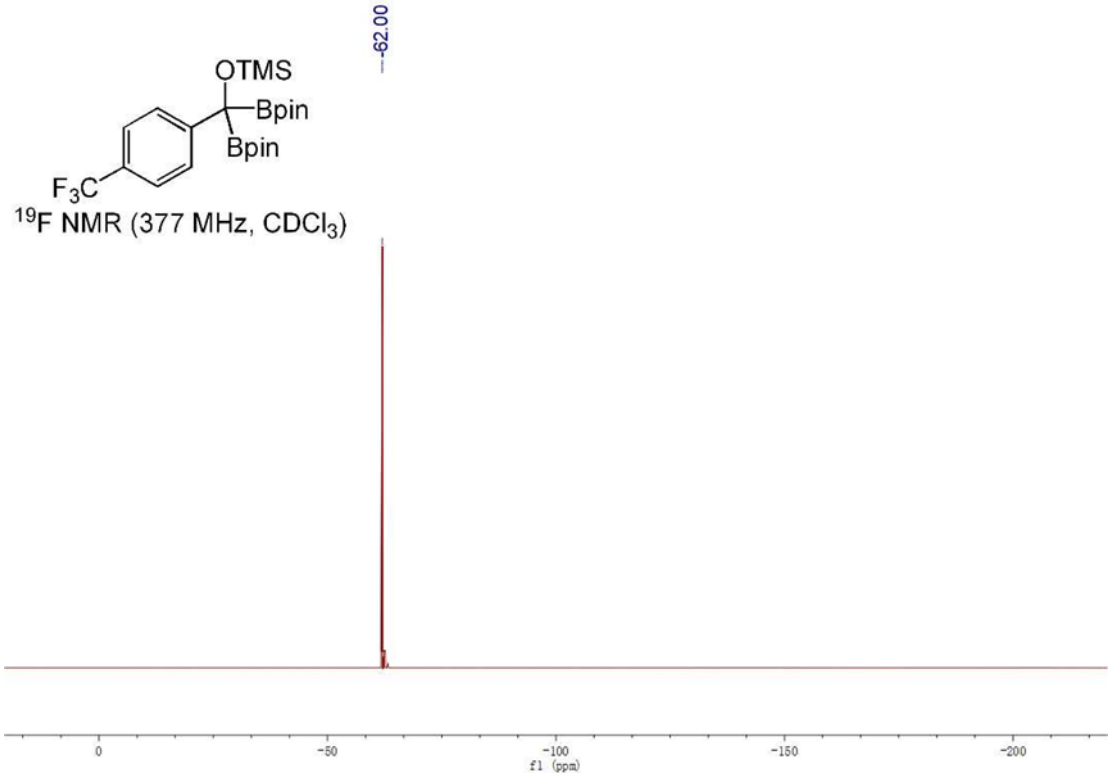


Figure S20 The ^{19}F NMR spectra of **3f**

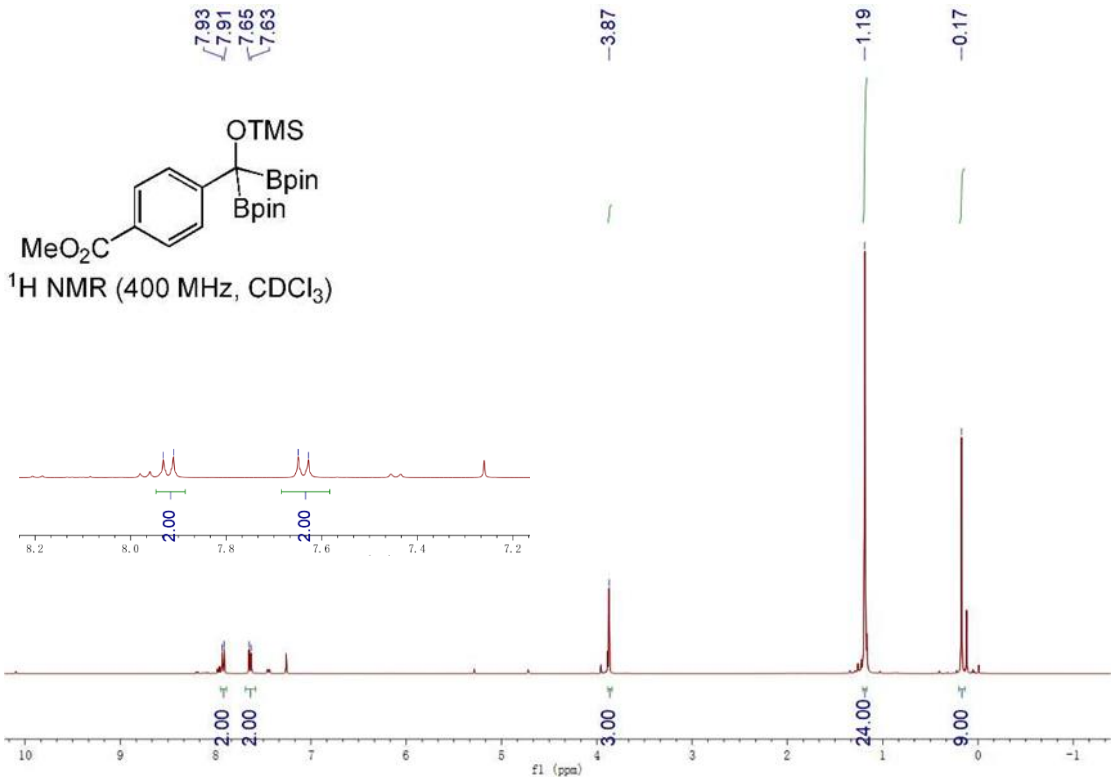


Figure S21 The ^{1}H NMR spectra of **3g**

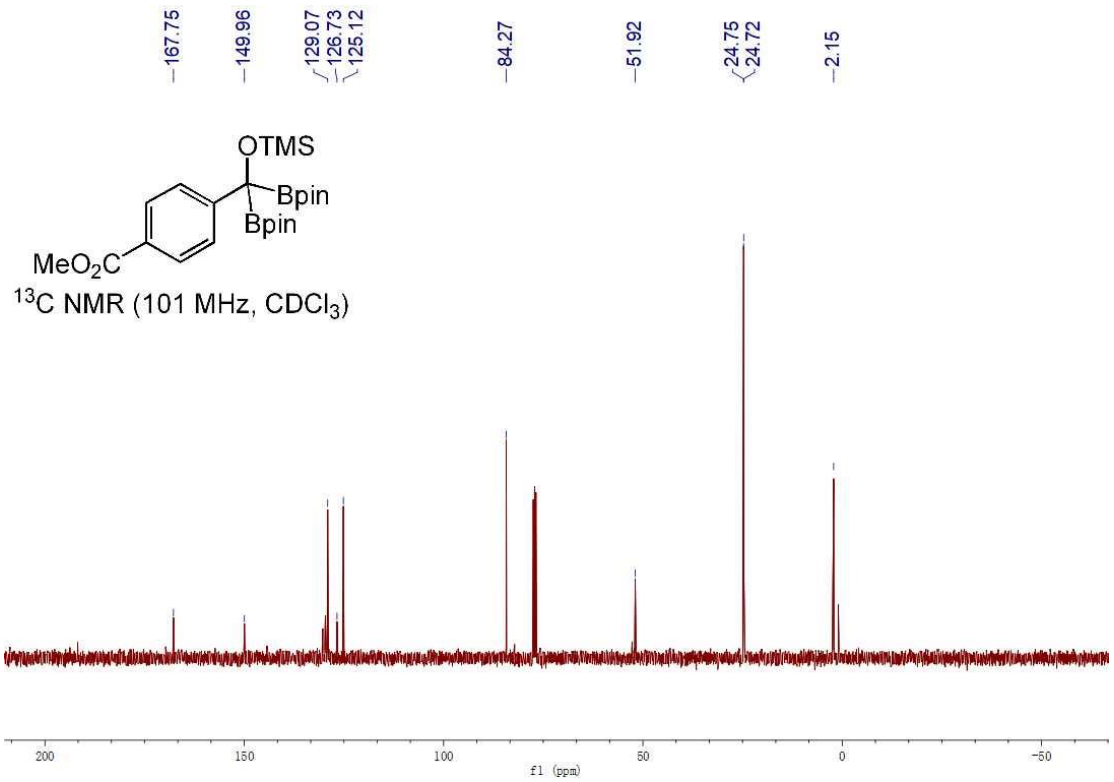


Figure S22 The ^{13}C NMR spectra of **3g**

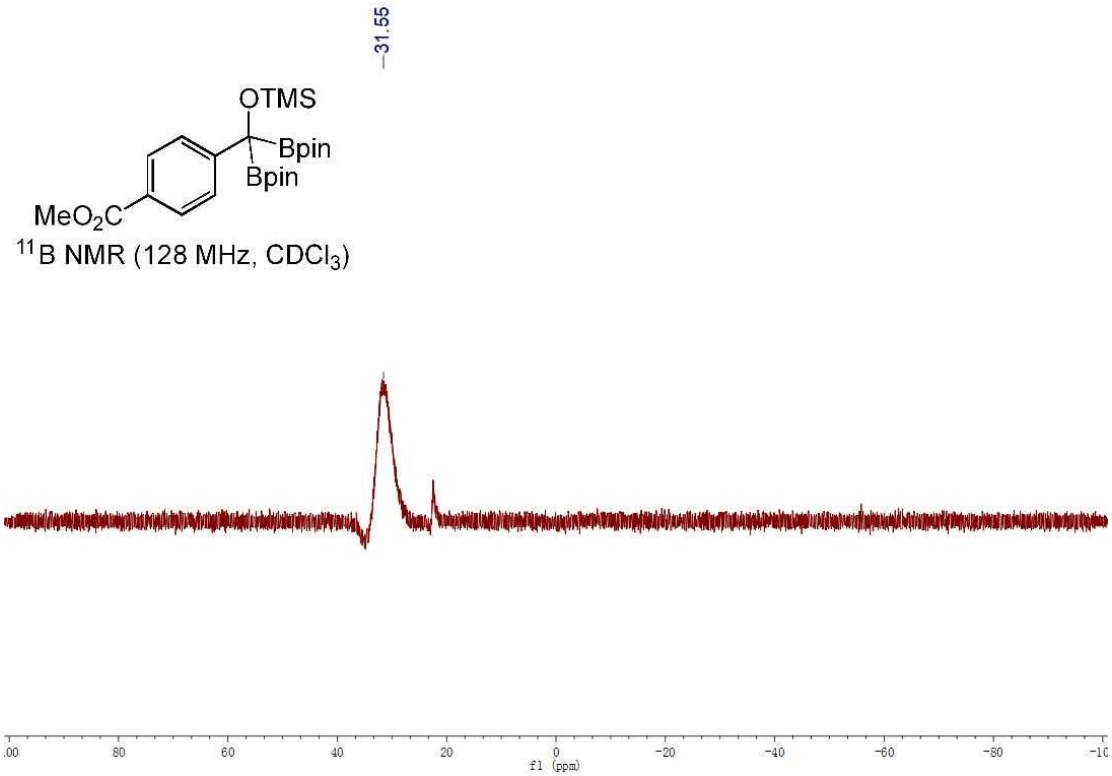


Figure S23 The ^{11}B NMR spectra of **3g**

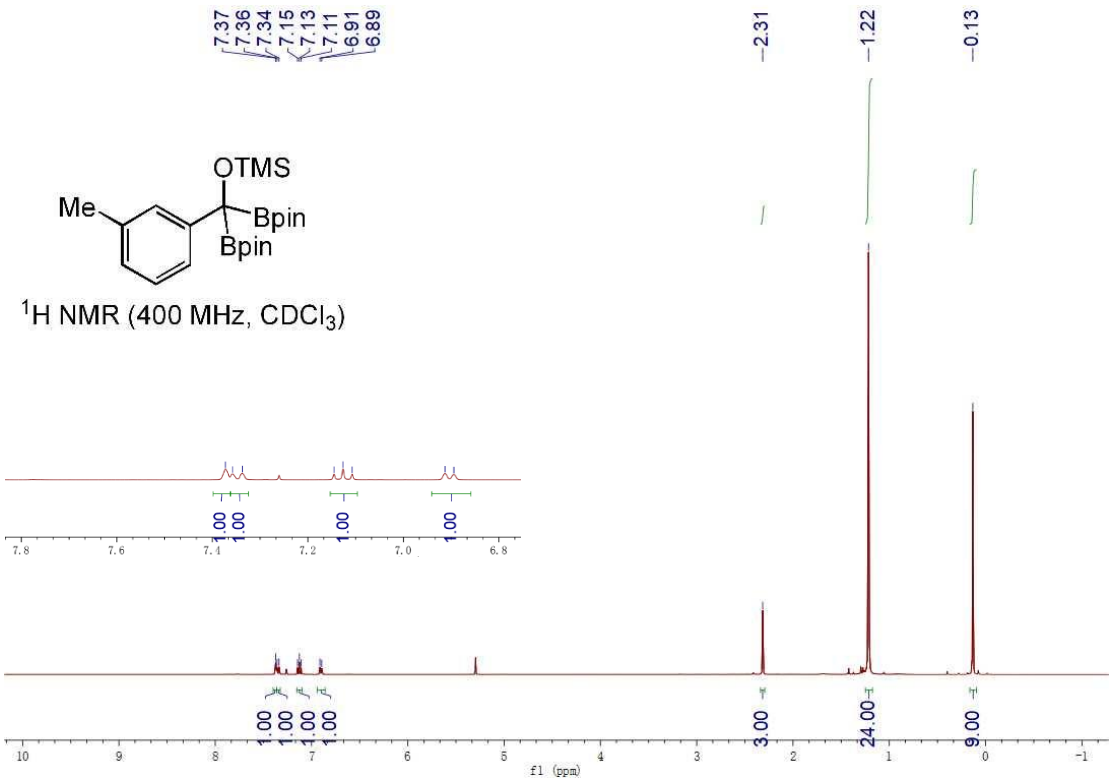


Figure S24 The ^{1}H NMR spectra of **3h**

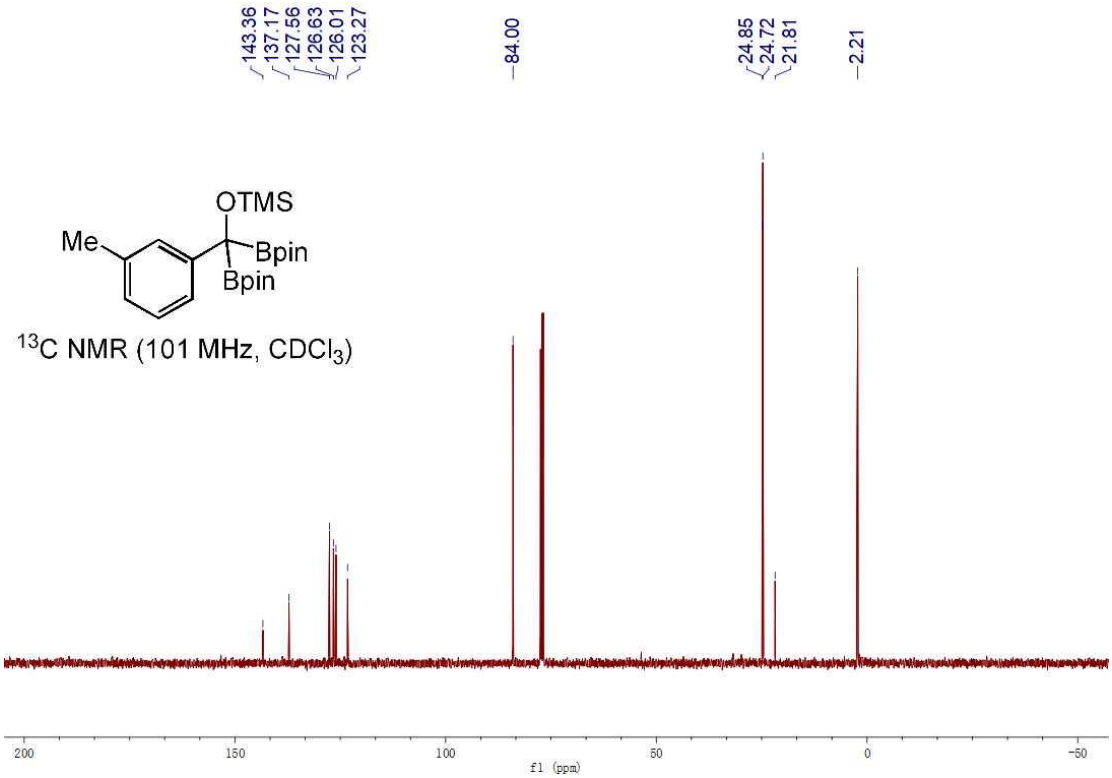


Figure S25 The ^{13}C NMR spectra of **3h**

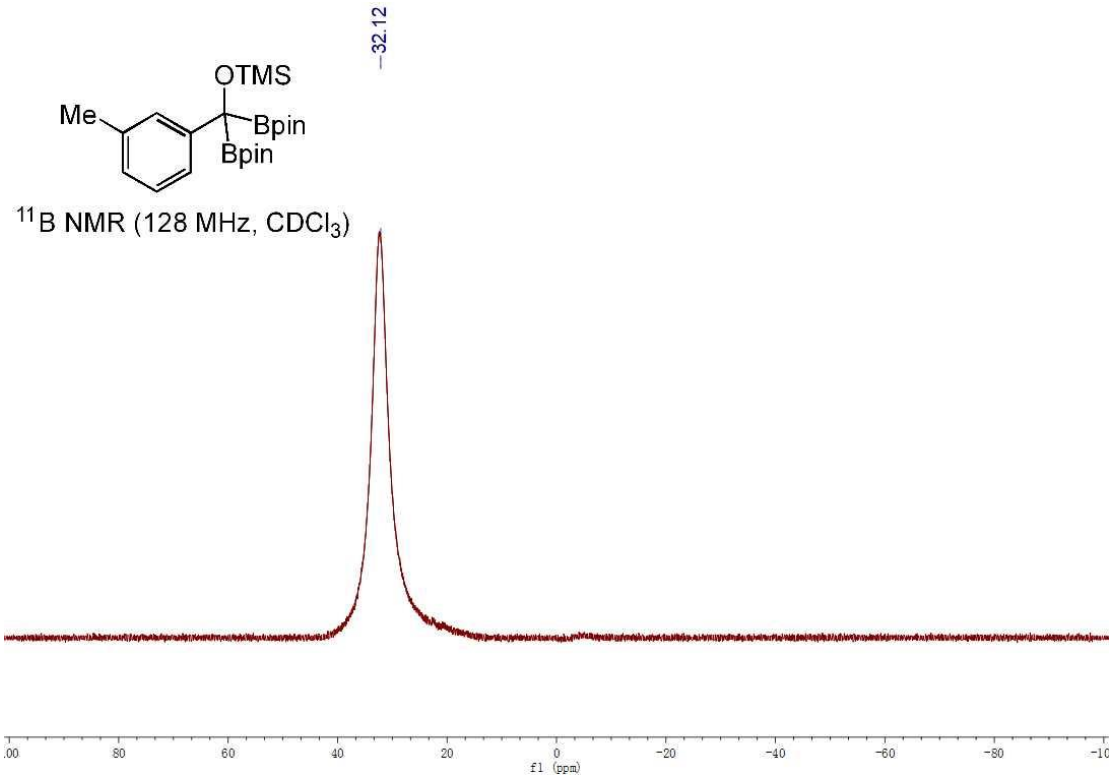


Figure S26 The ^{11}B NMR spectra of **3h**

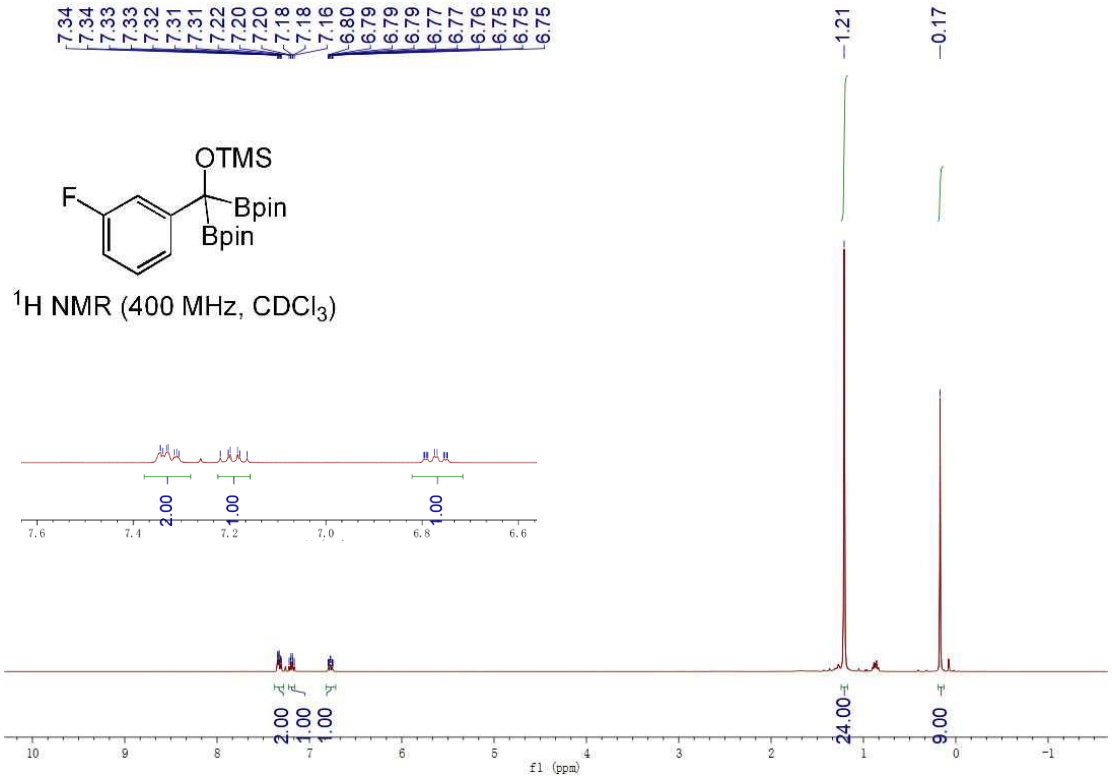


Figure S27 The ^{1}H NMR spectra of **3i**

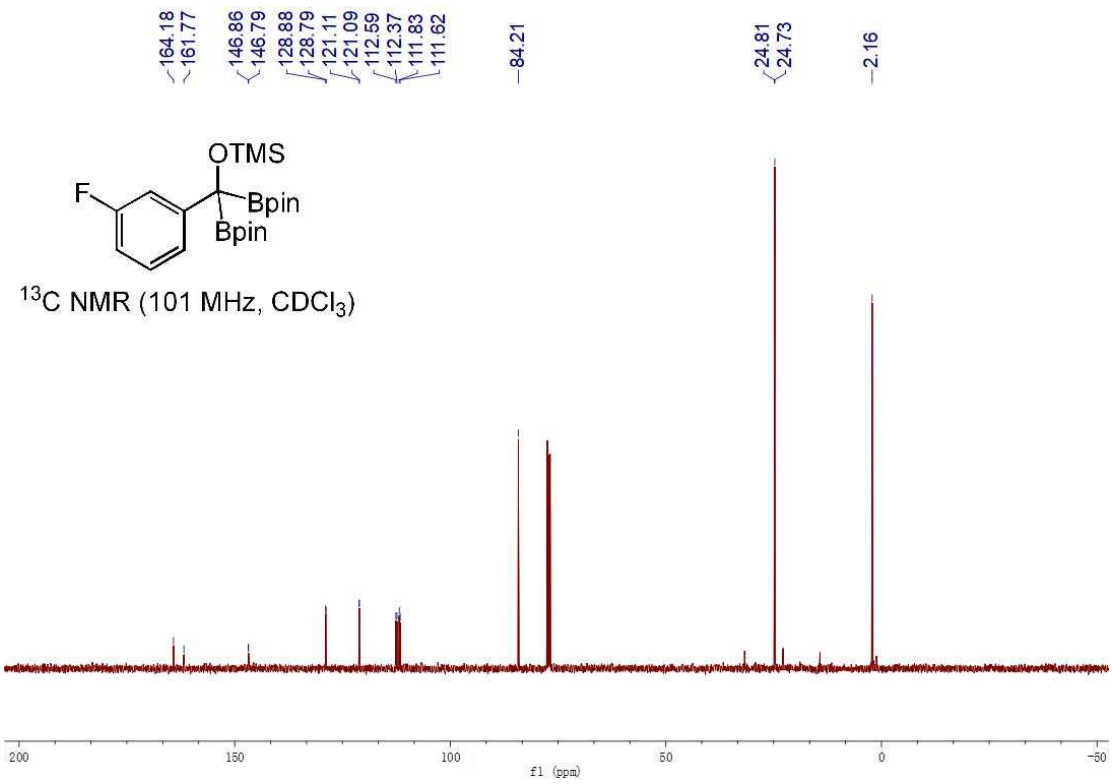


Figure S28 The ^{13}C NMR spectra of **3i**

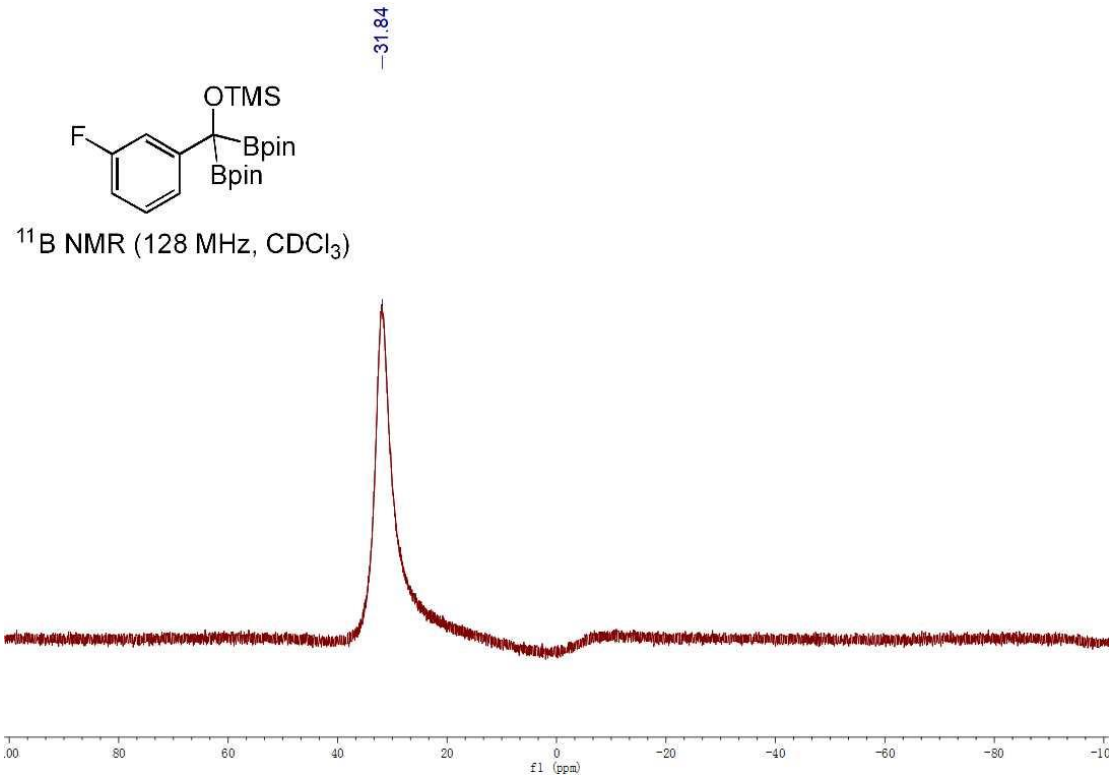


Figure S29 The ^{11}B NMR spectra of **3i**

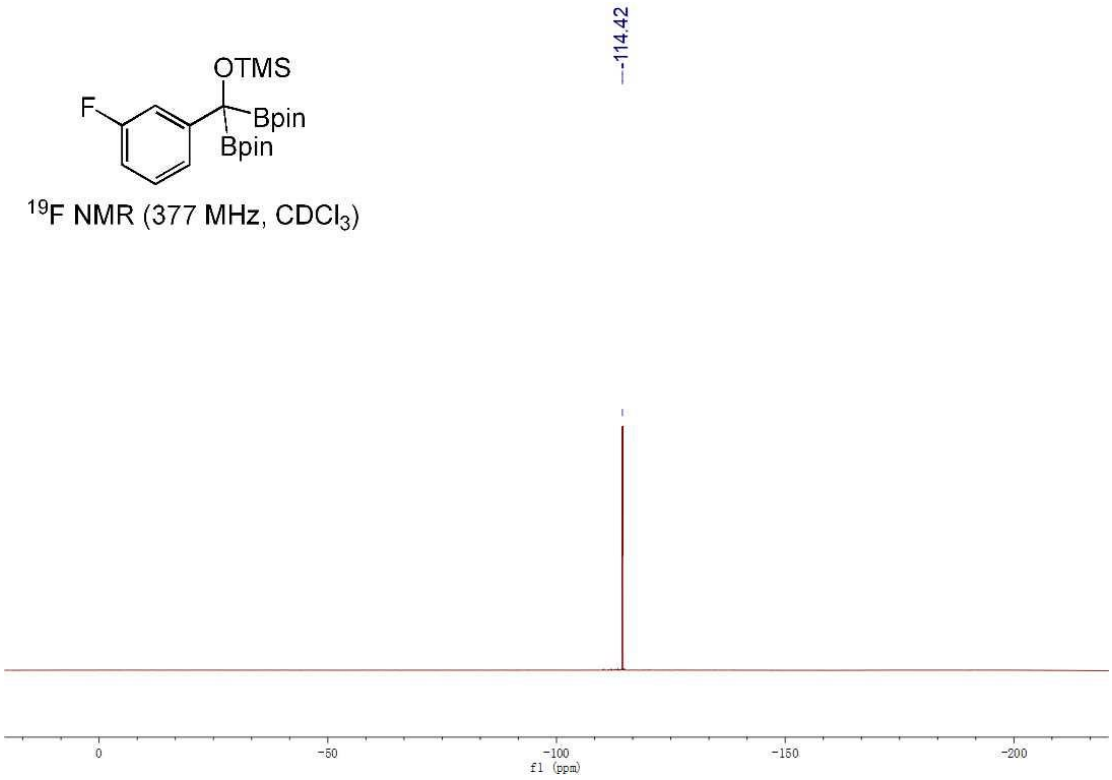


Figure S30 The^{19}F NMR spectra of **3i**

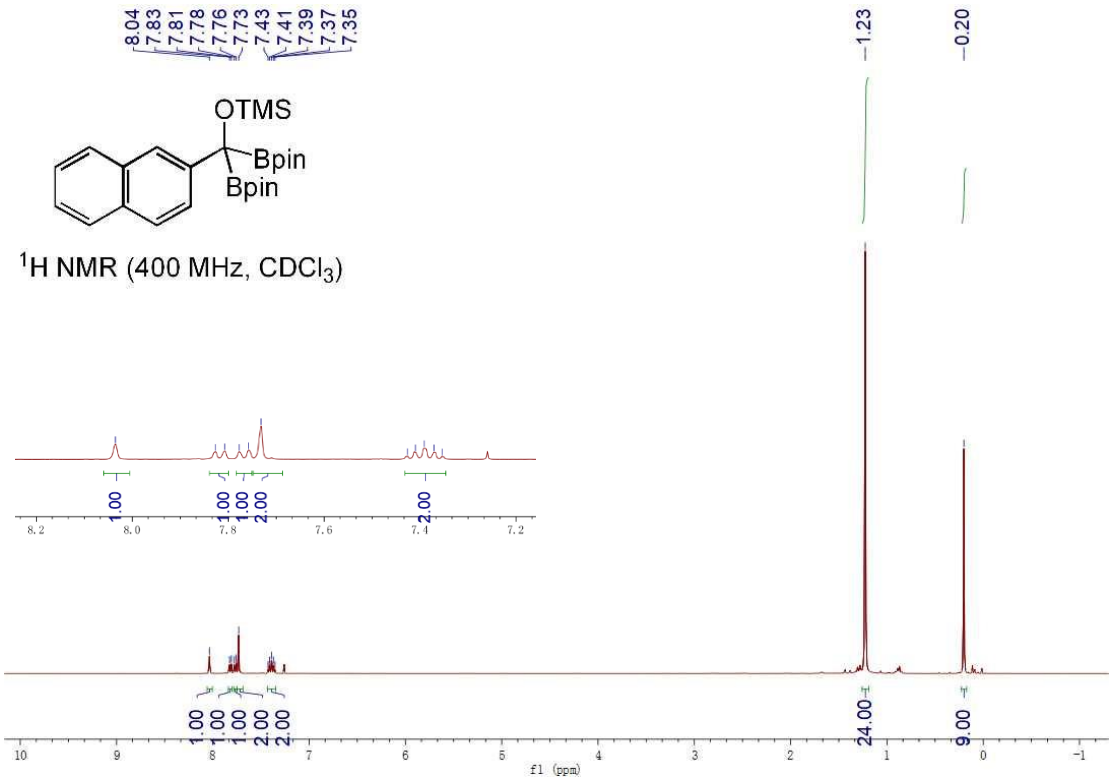


Figure S31 The ^{1}H NMR spectra of **3j**

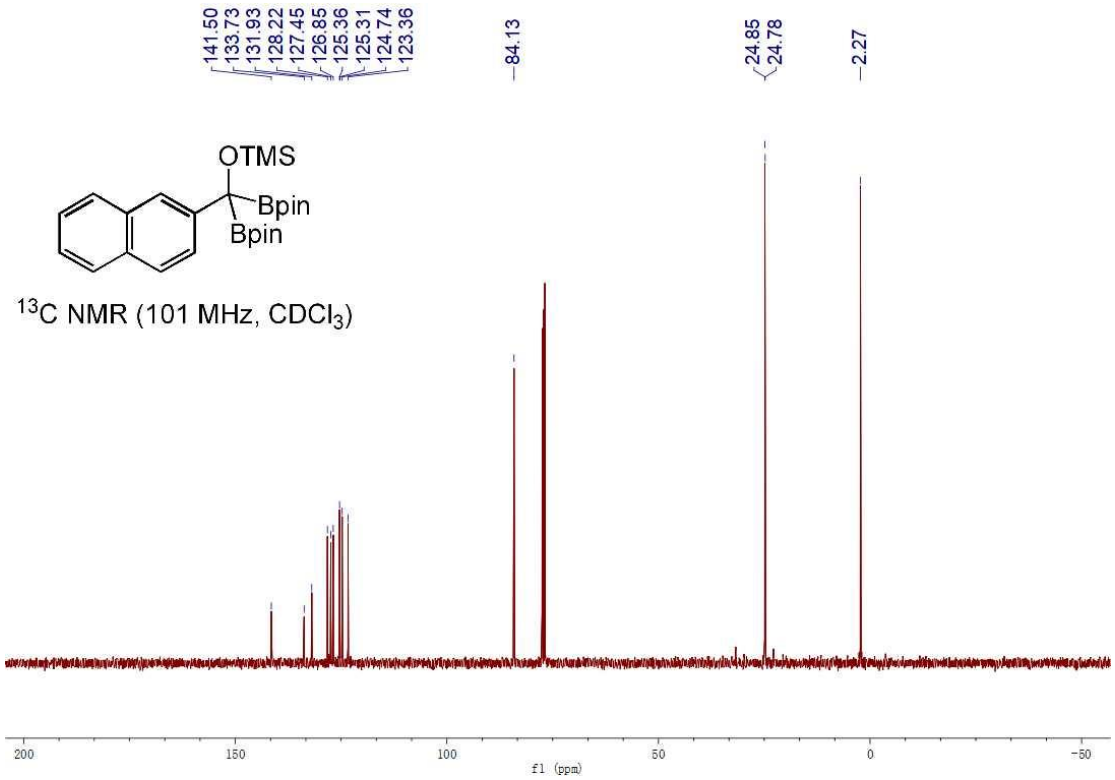


Figure S32 The ^{13}C NMR spectra of **3j**

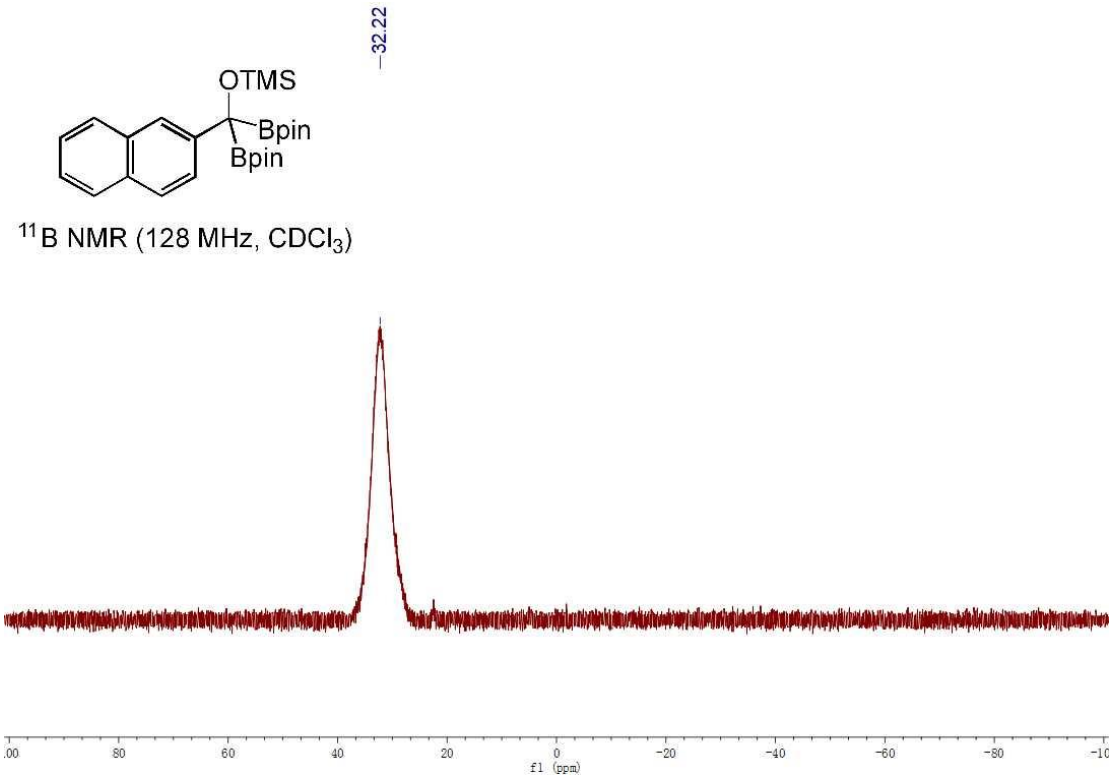


Figure S33 The ^{11}B NMR spectra of **3j**

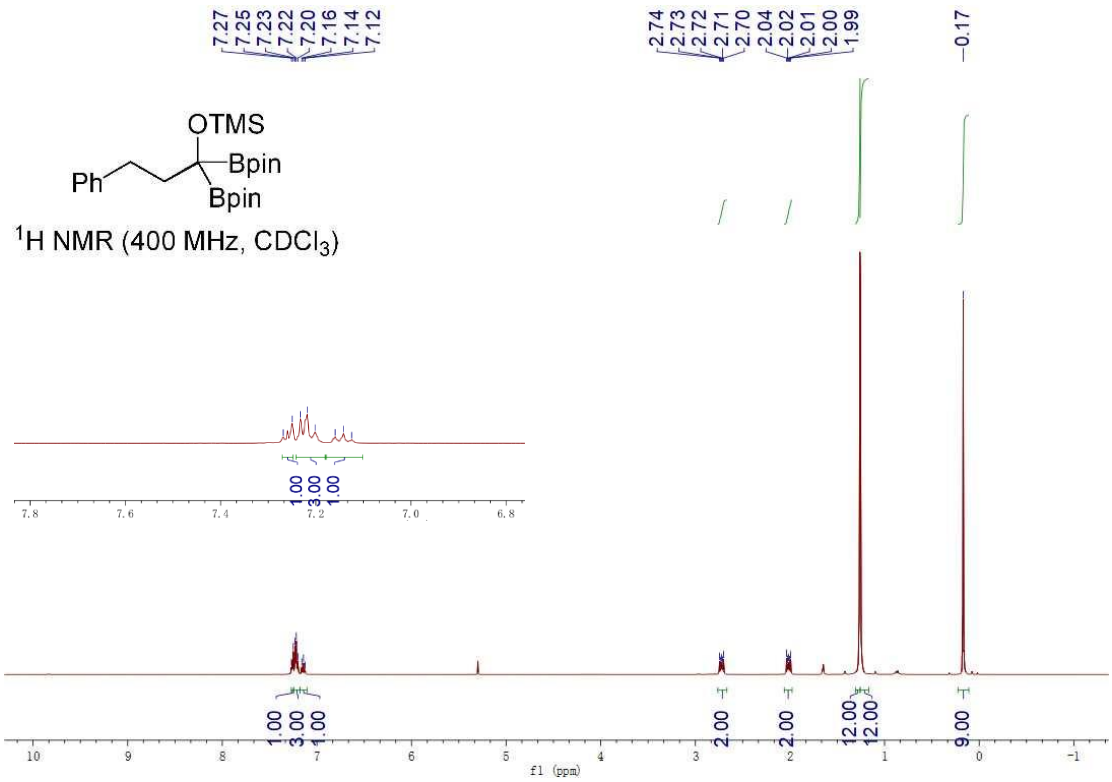


Figure S34 The ^{1}H NMR spectra of **3k**

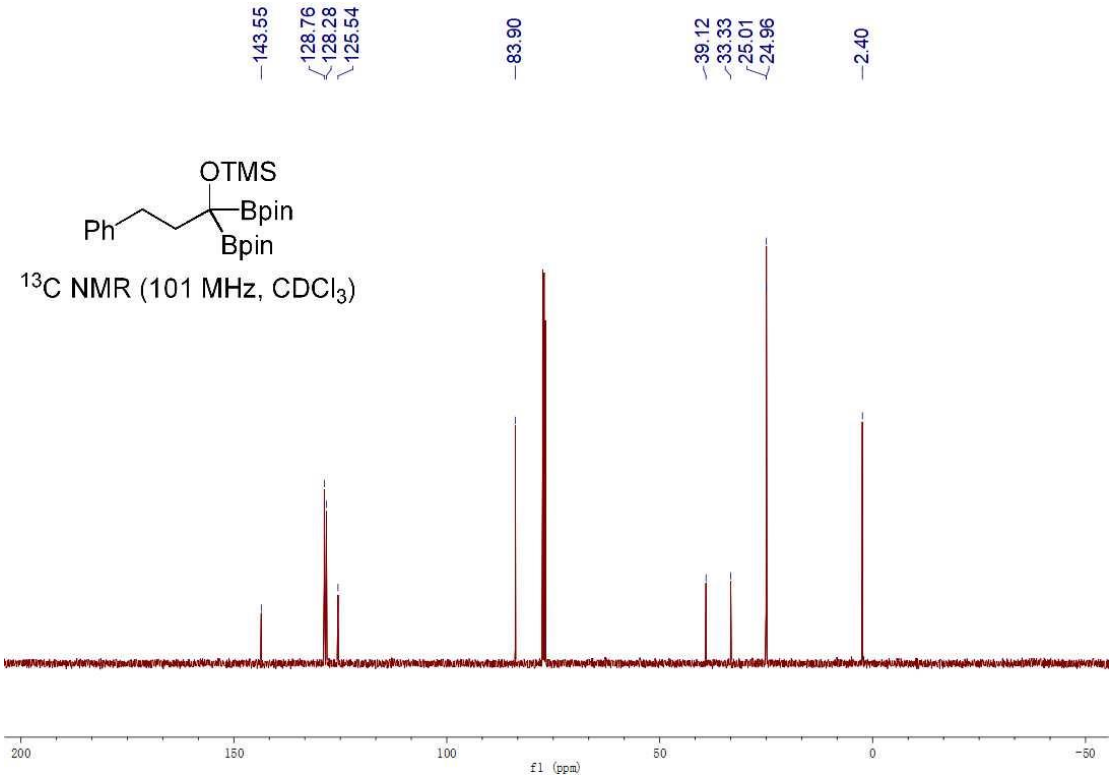


Figure S35 The ^{13}C NMR spectra of **3k**

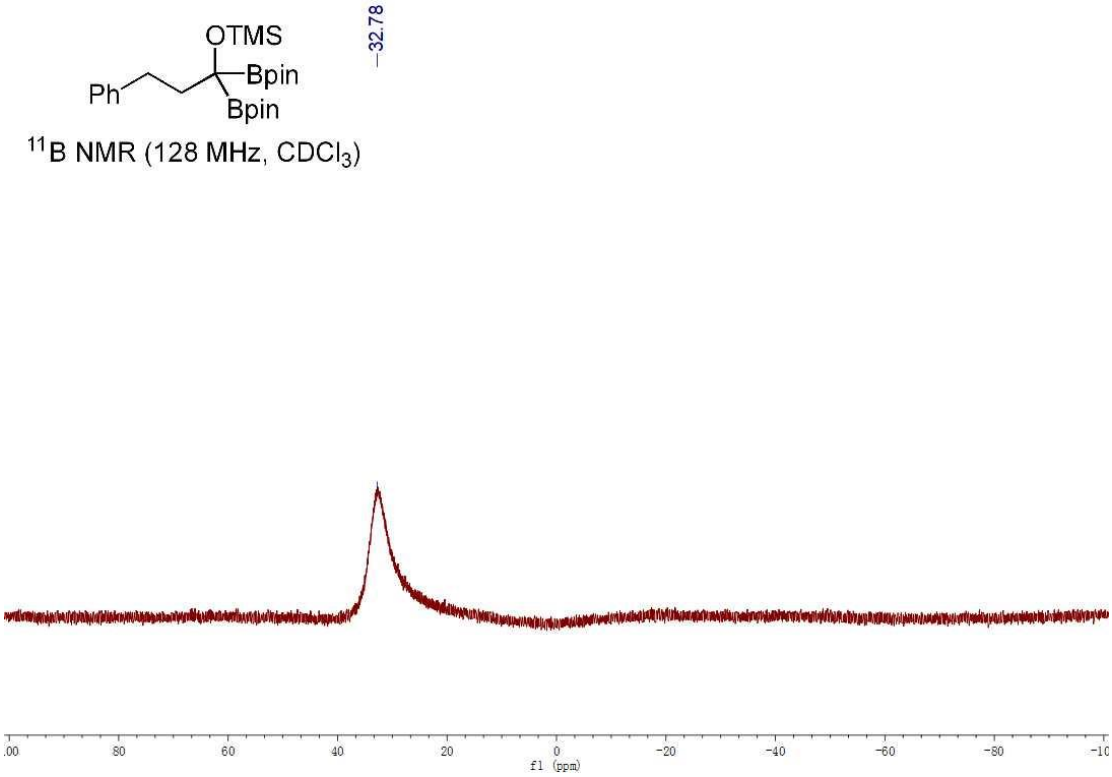


Figure S36 The ^{11}B NMR spectra of **3k**

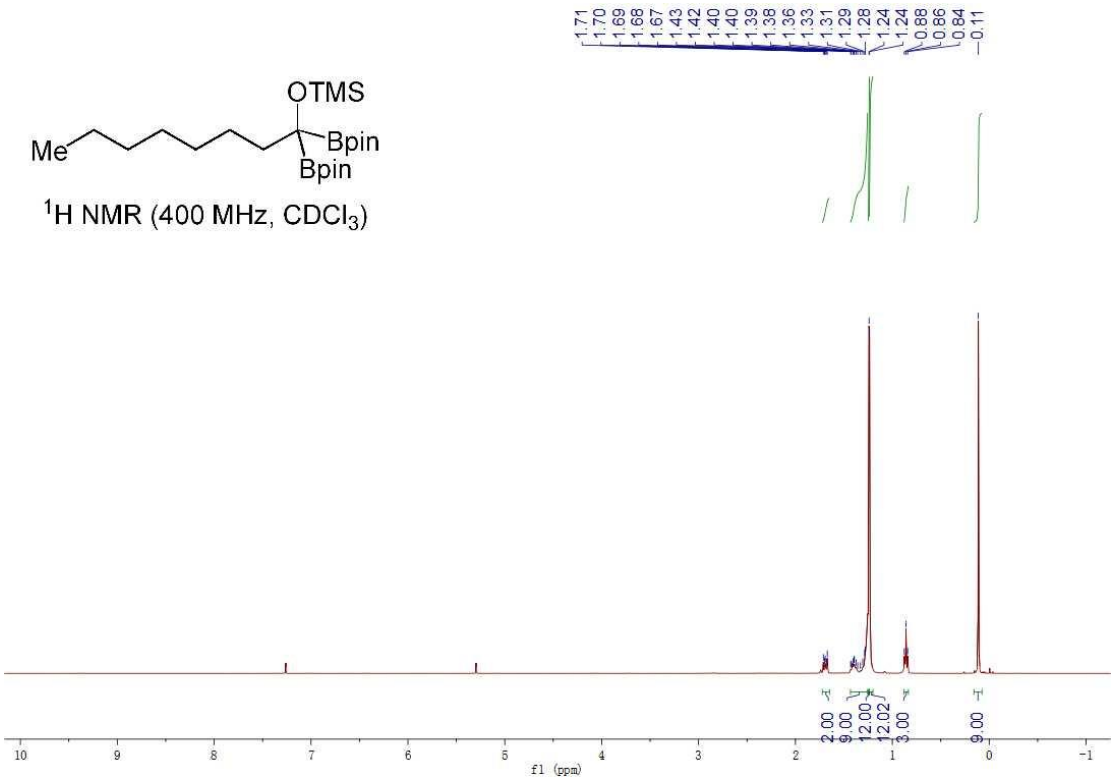


Figure S37 The ^{1}H NMR spectra of **3l**

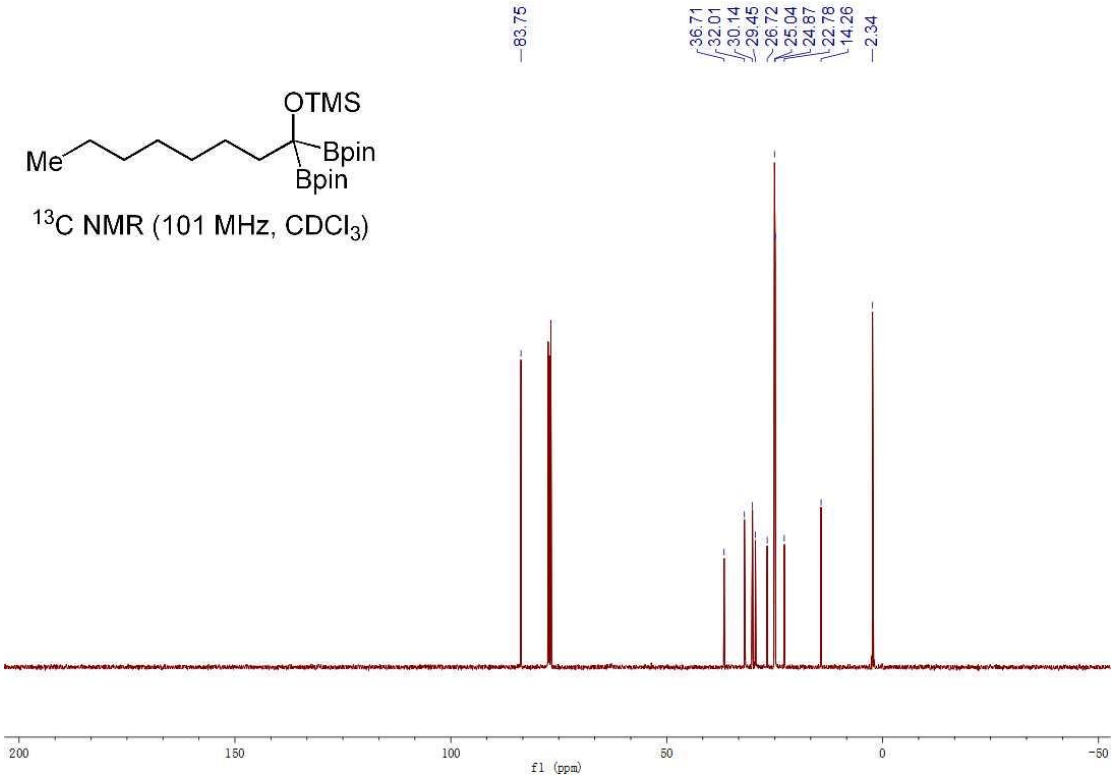


Figure S38 The ^{13}C NMR spectra of **3l**

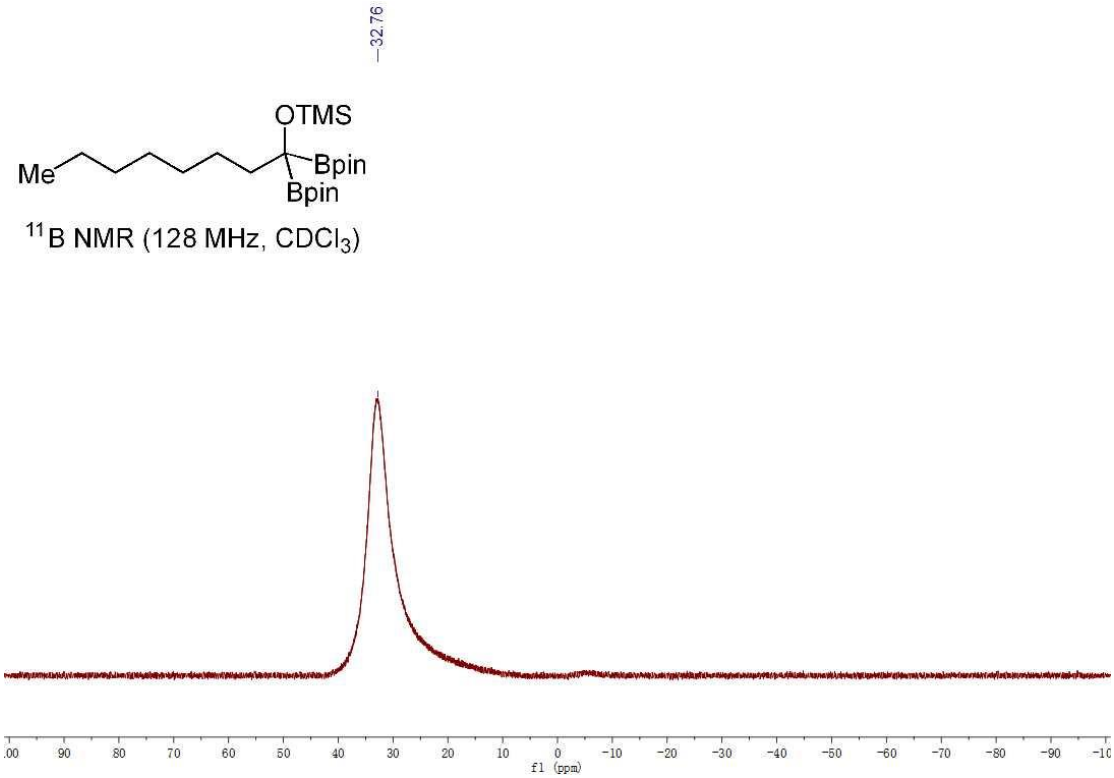


Figure S39 The ^{11}B NMR spectra of **3l**

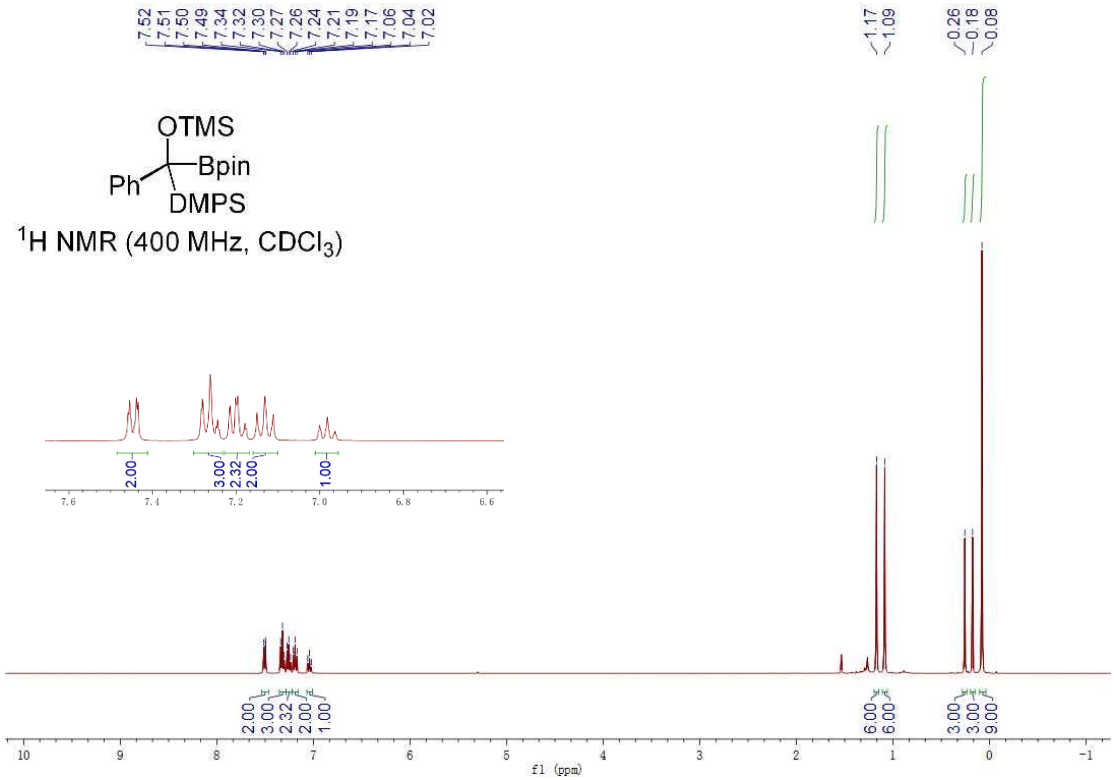


Figure S40 The ^{1}H NMR spectra of **5a**

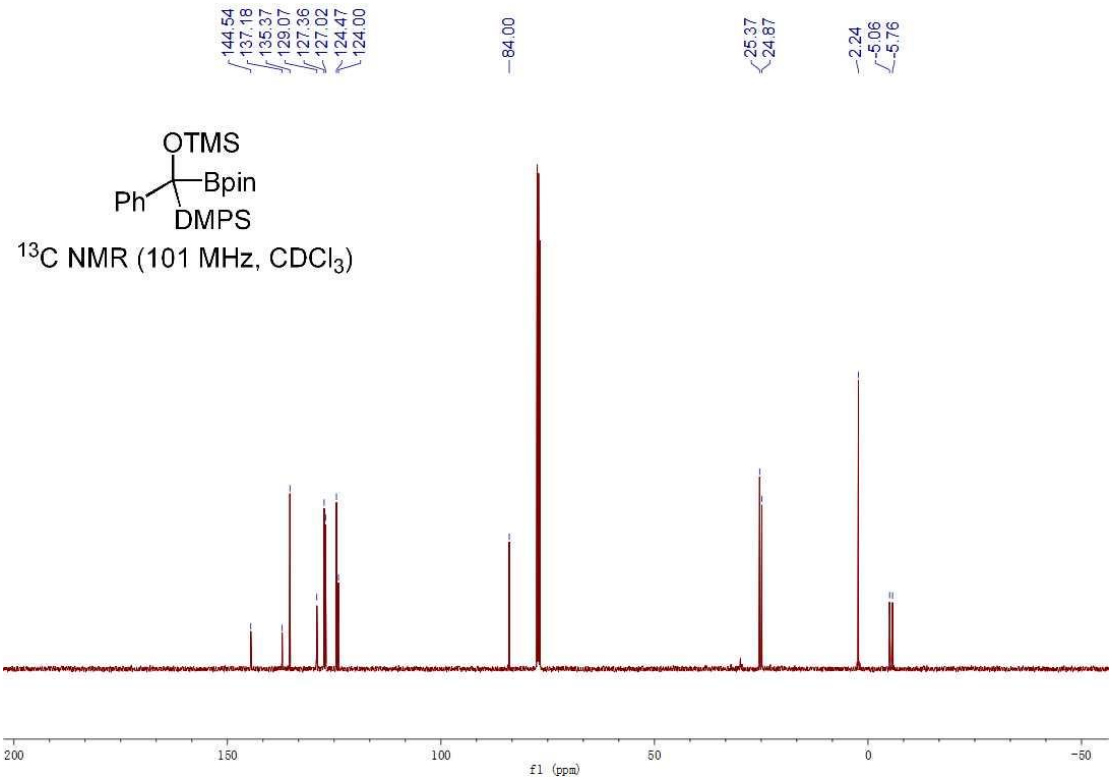


Figure S41 The ^{13}C NMR spectra of **5a**

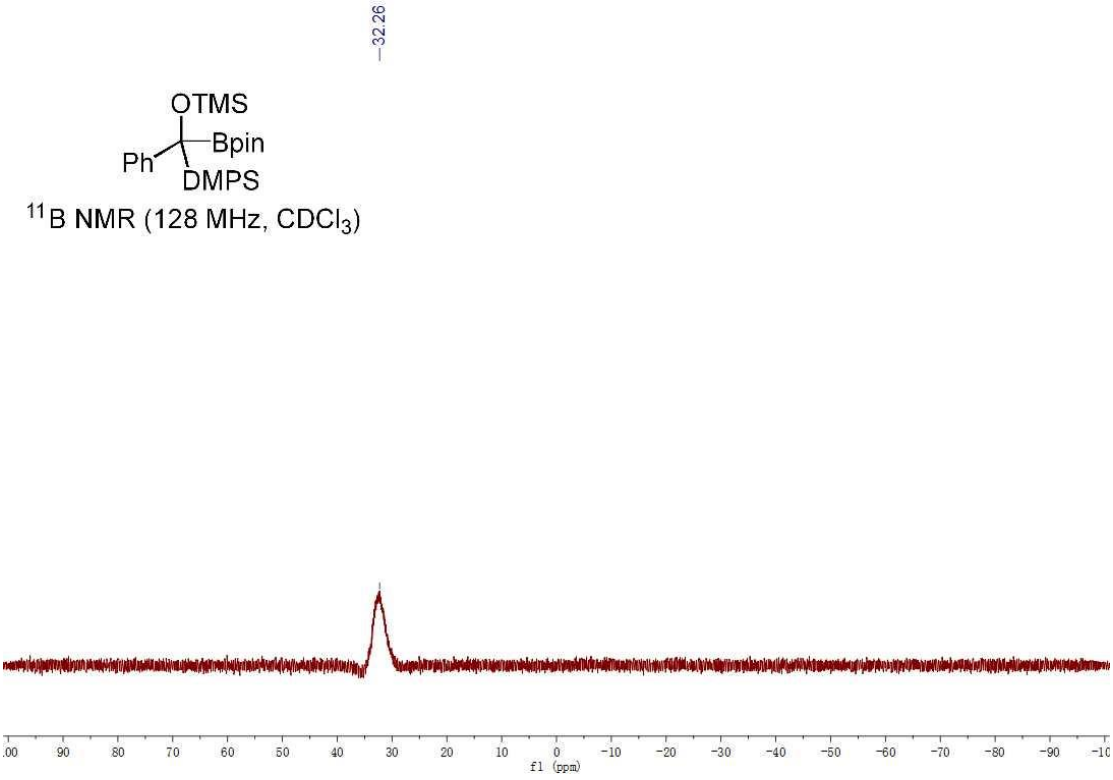


Figure S42 The ^{11}B NMR spectra of **5a**

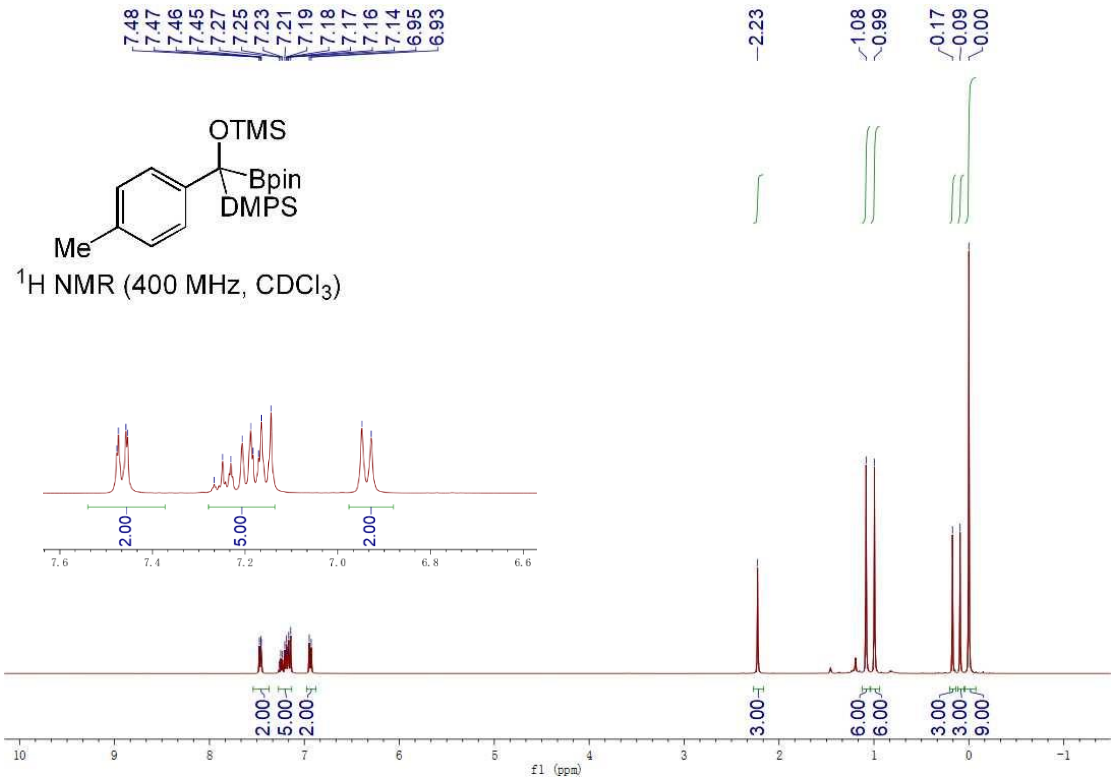


Figure S43 The ^{1}H NMR spectra of **5b**

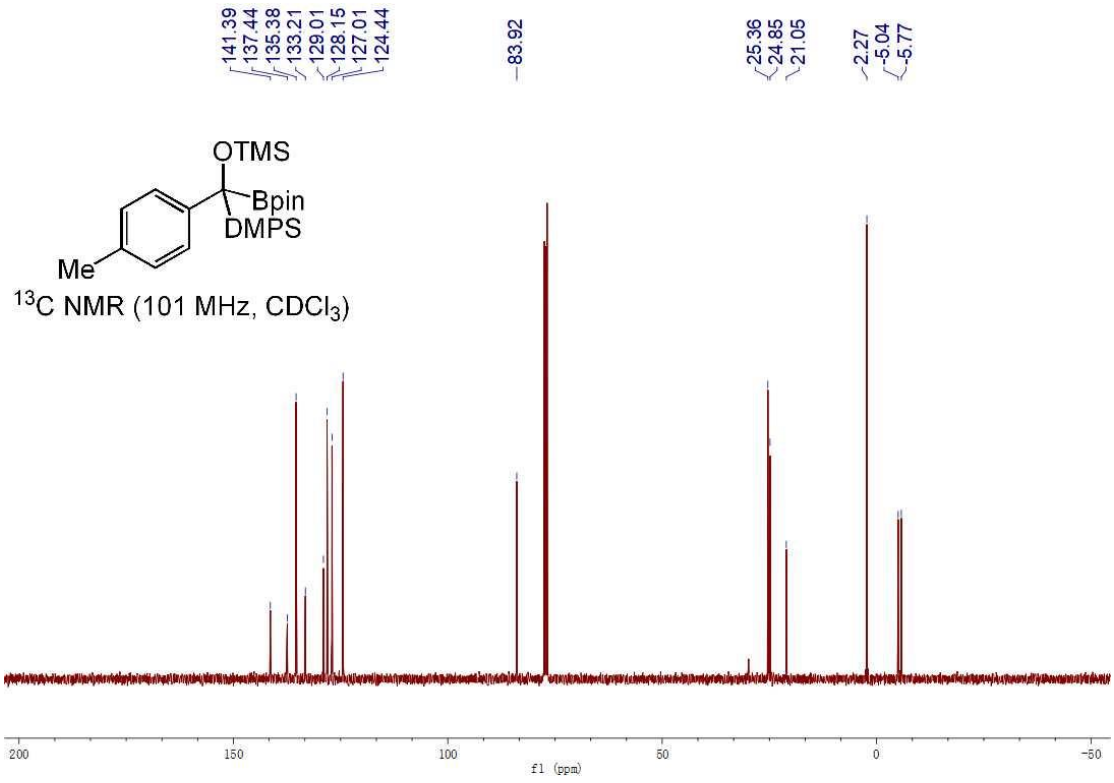


Figure S44 The ^{13}C NMR spectra of **5b**

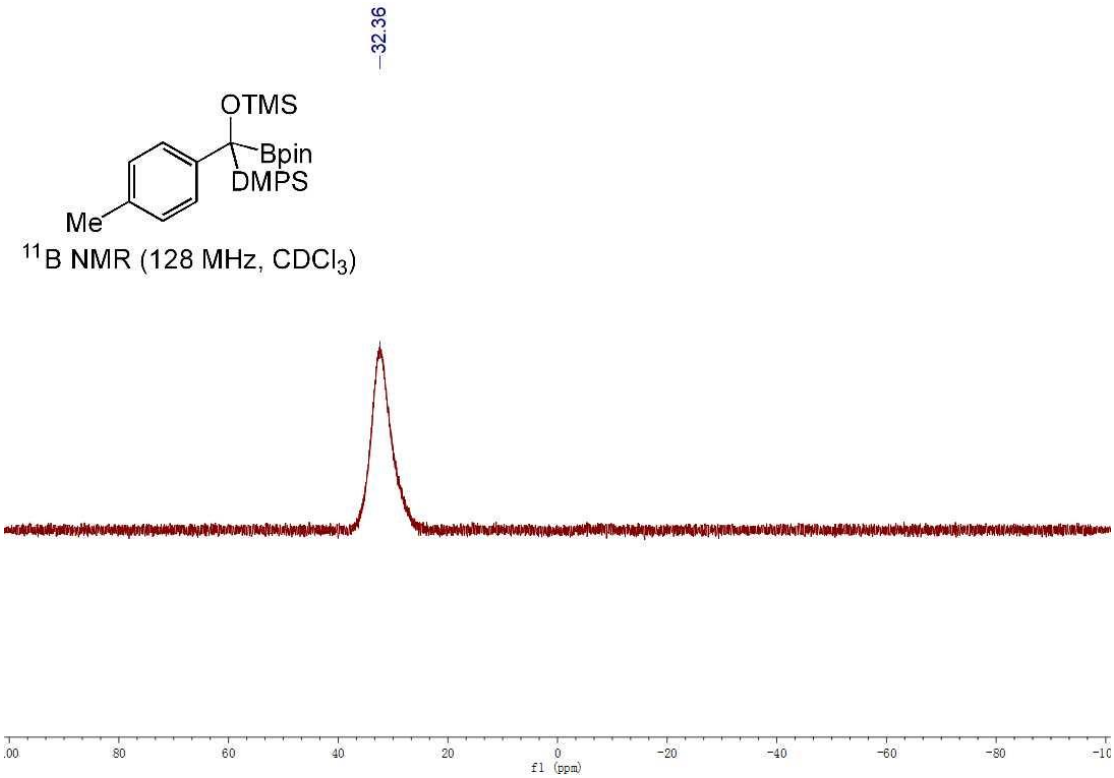


Figure S45 The ^{11}B NMR spectra of **5b**

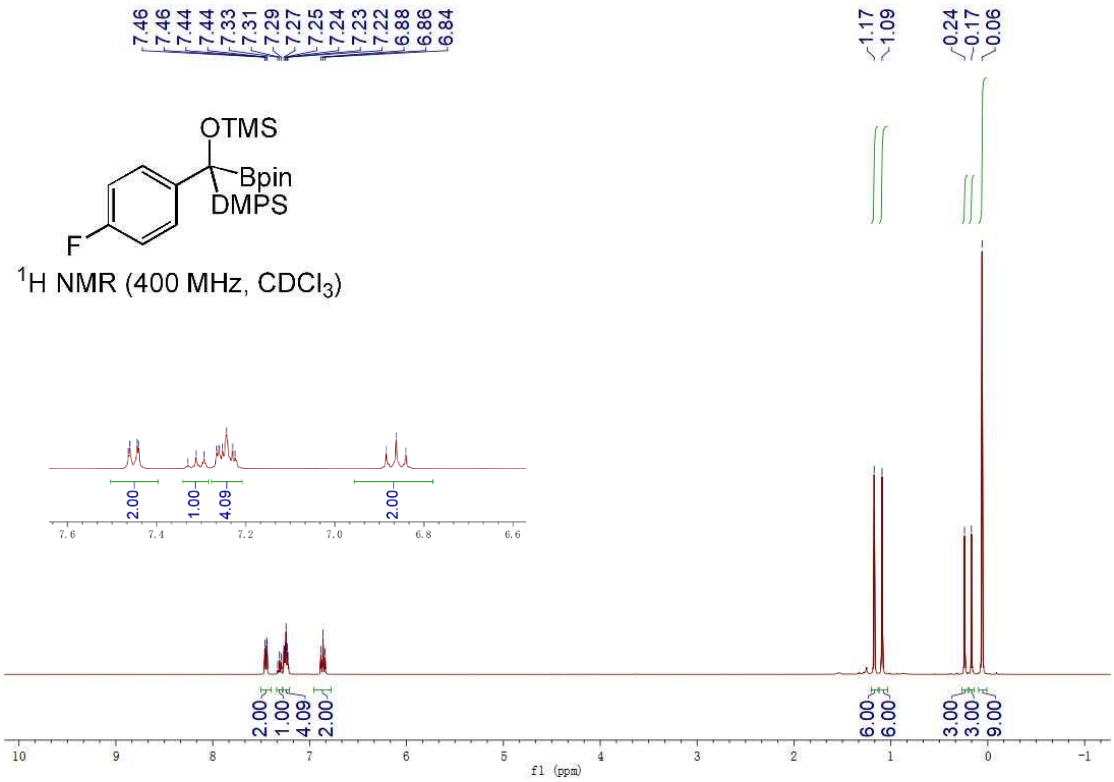


Figure S46 The ^{1}H NMR spectra of **5c**

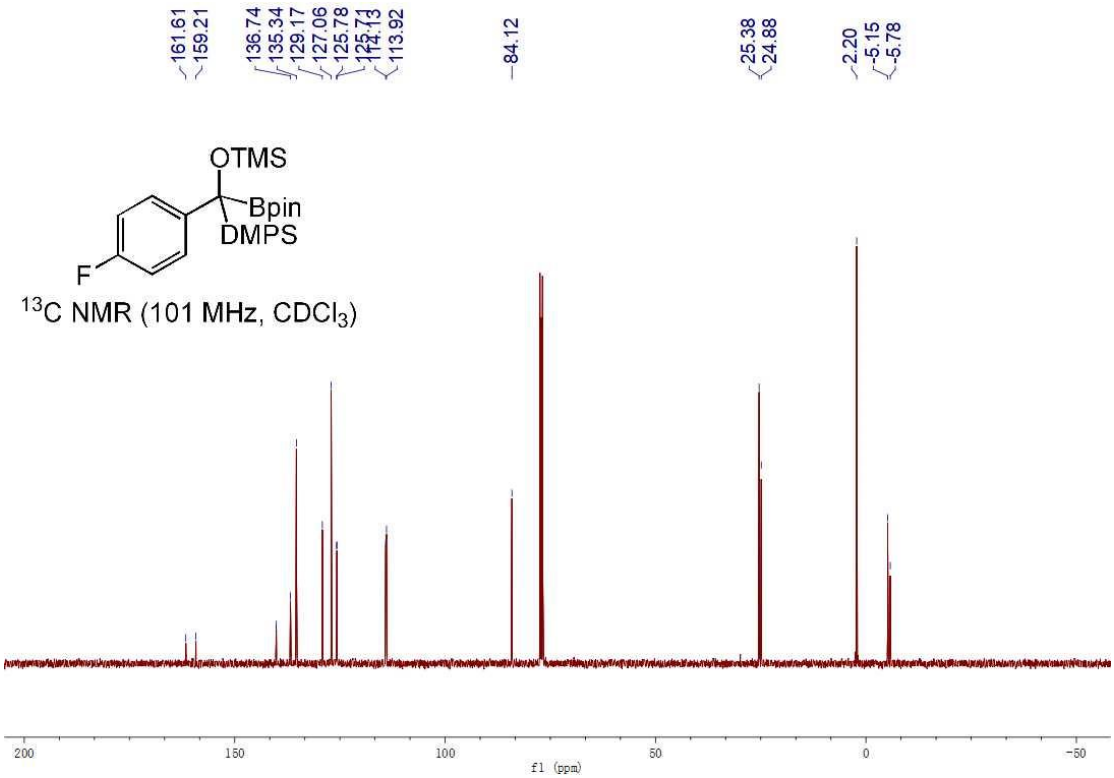


Figure S47 The ^{13}C NMR spectra of **5c**

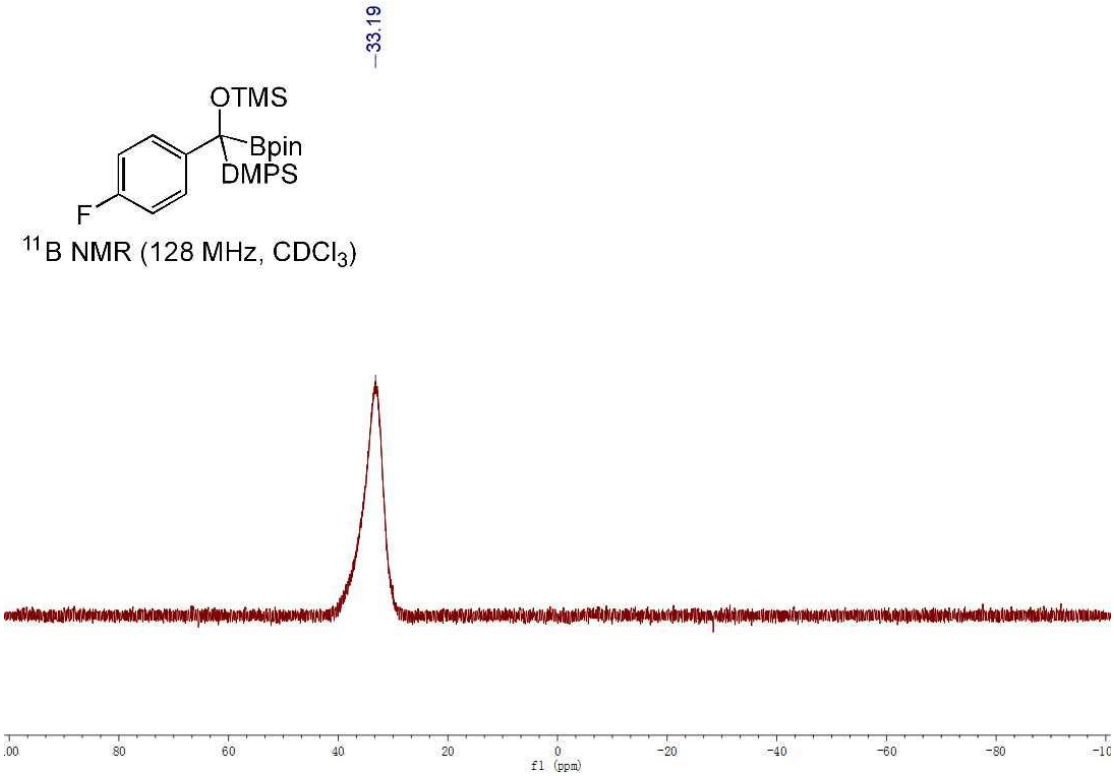


Figure S48 The ^{11}B NMR spectra of **5c**

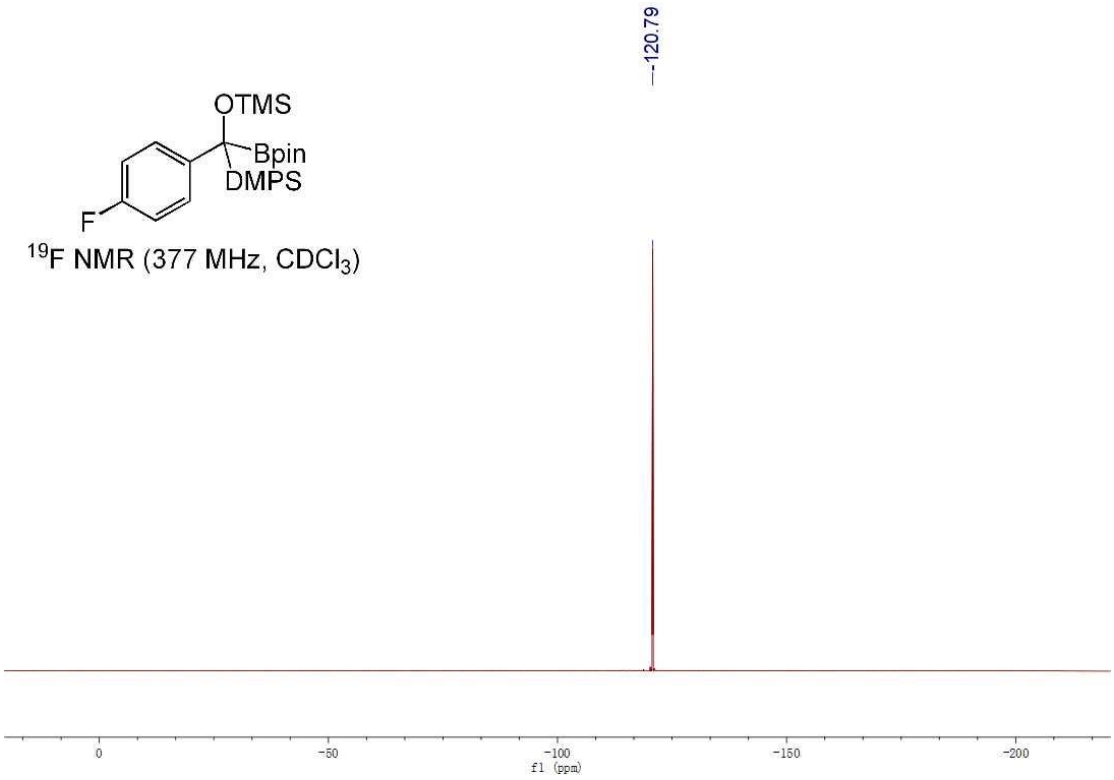


Figure S49 The ^{19}F NMR spectra of **5c**

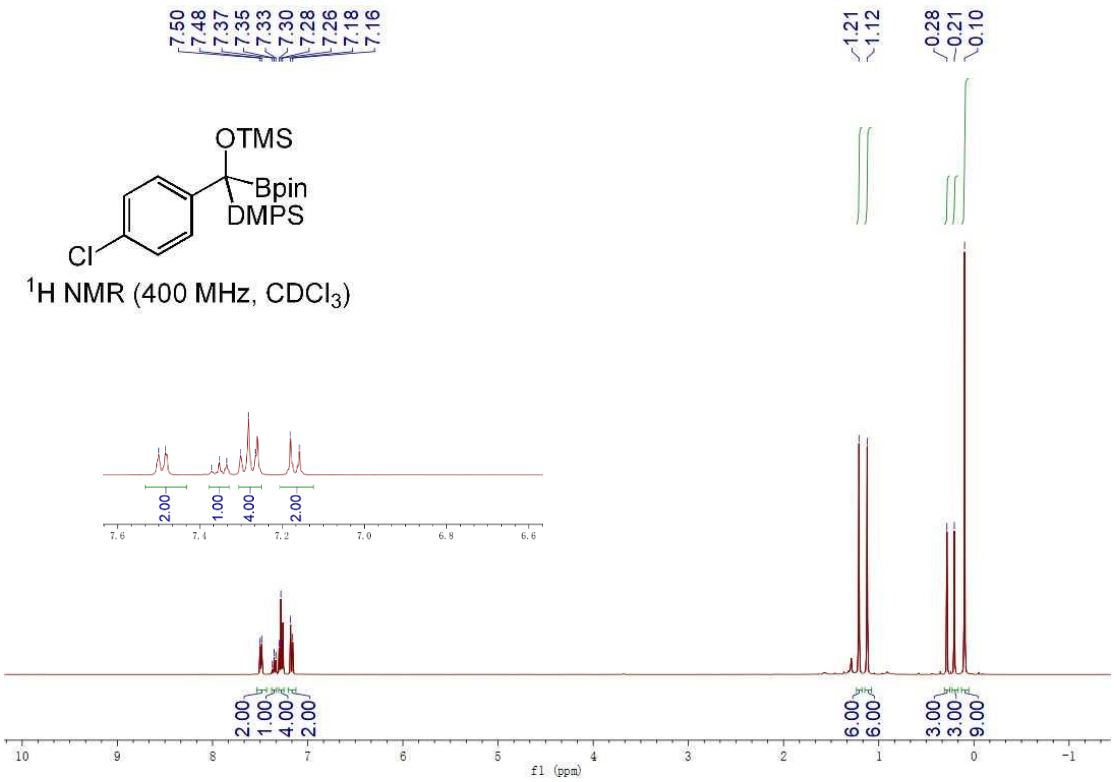


Figure S50 The ^{1}H NMR spectra of **5d**

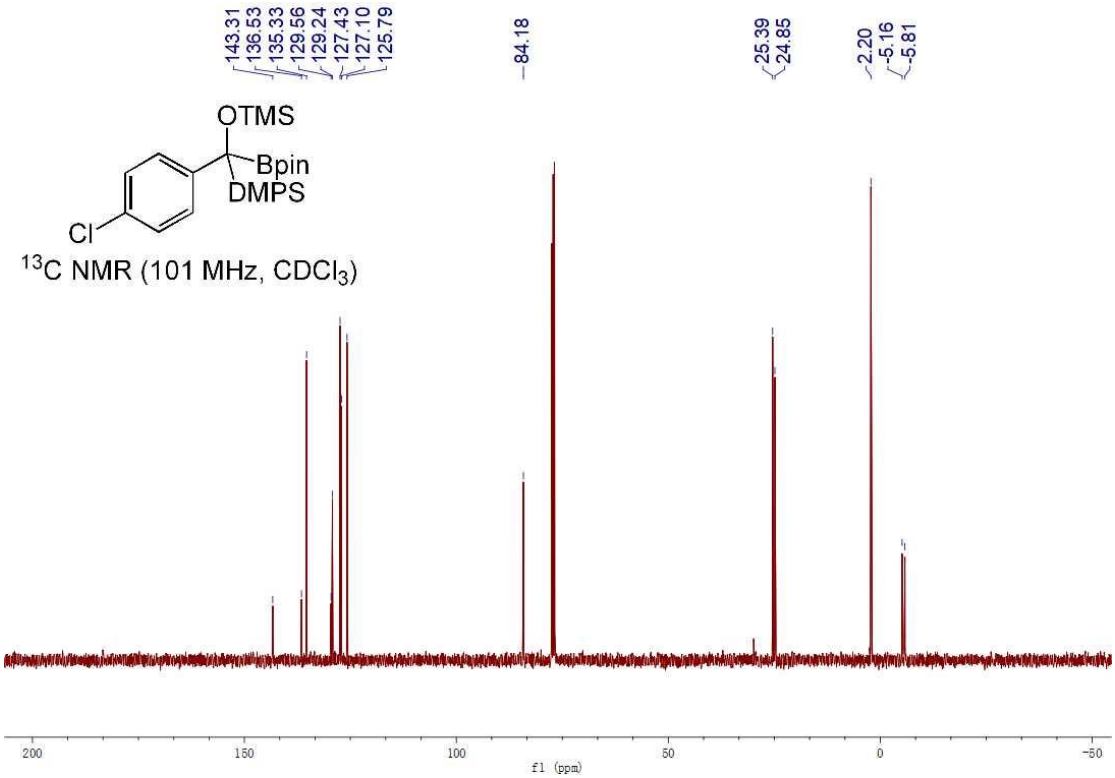


Figure S51 The ^{13}C NMR spectra of **5d**

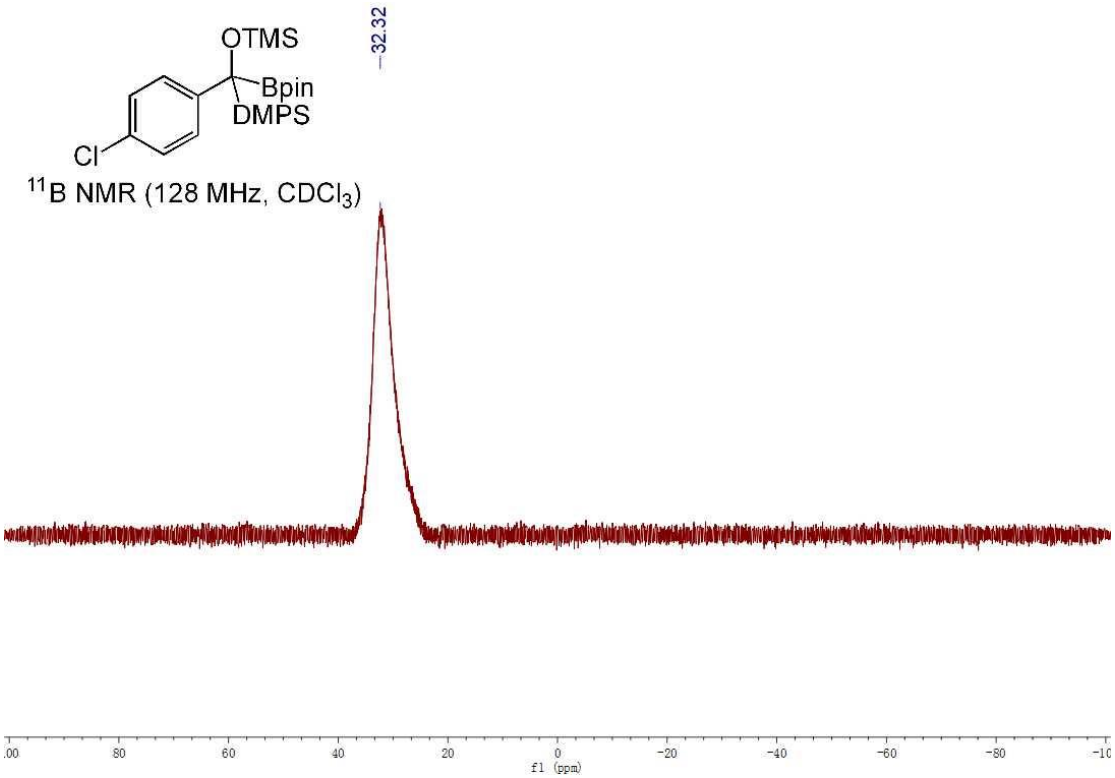


Figure S52 The ^{11}B NMR spectra of **5d**

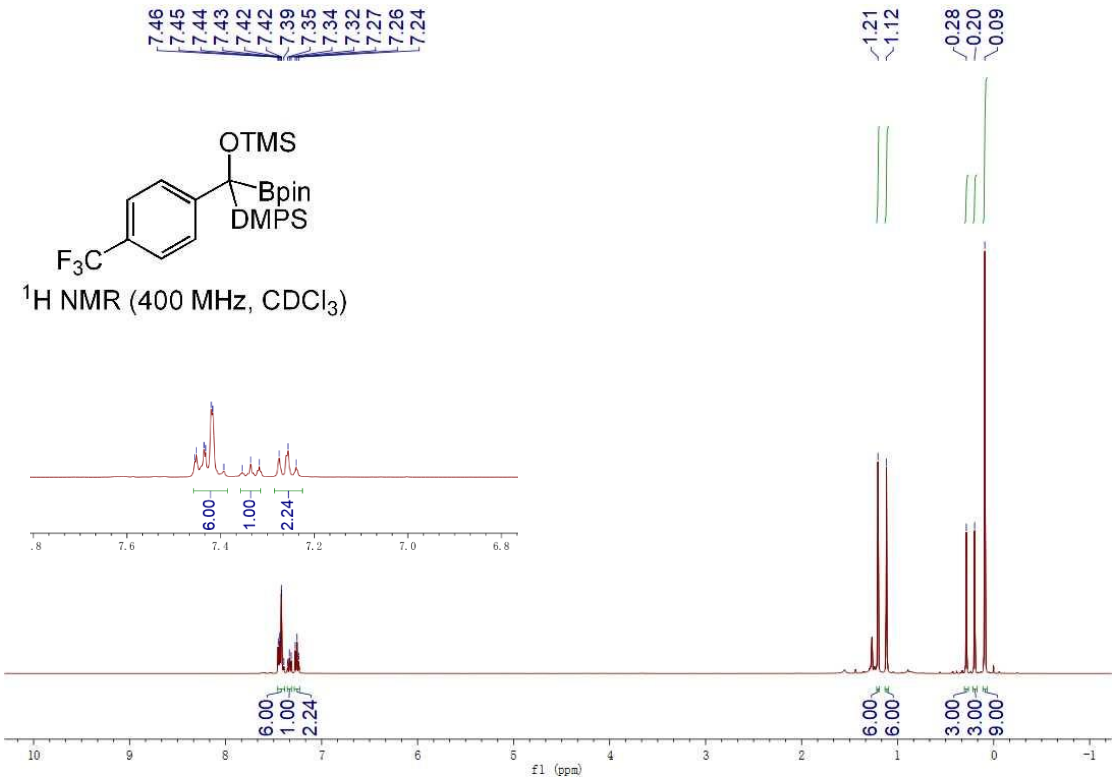


Figure S53 The ^{1}H NMR spectra of **5e**

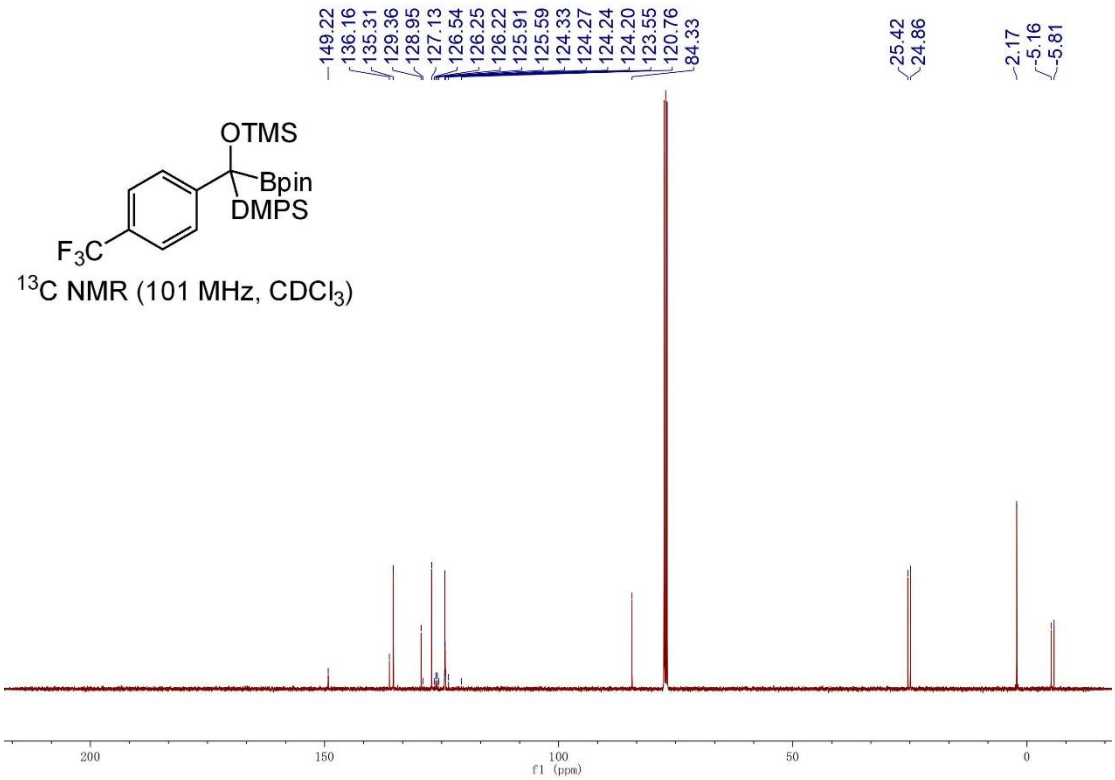


Figure S54 The ^{13}C NMR spectra of **5e**

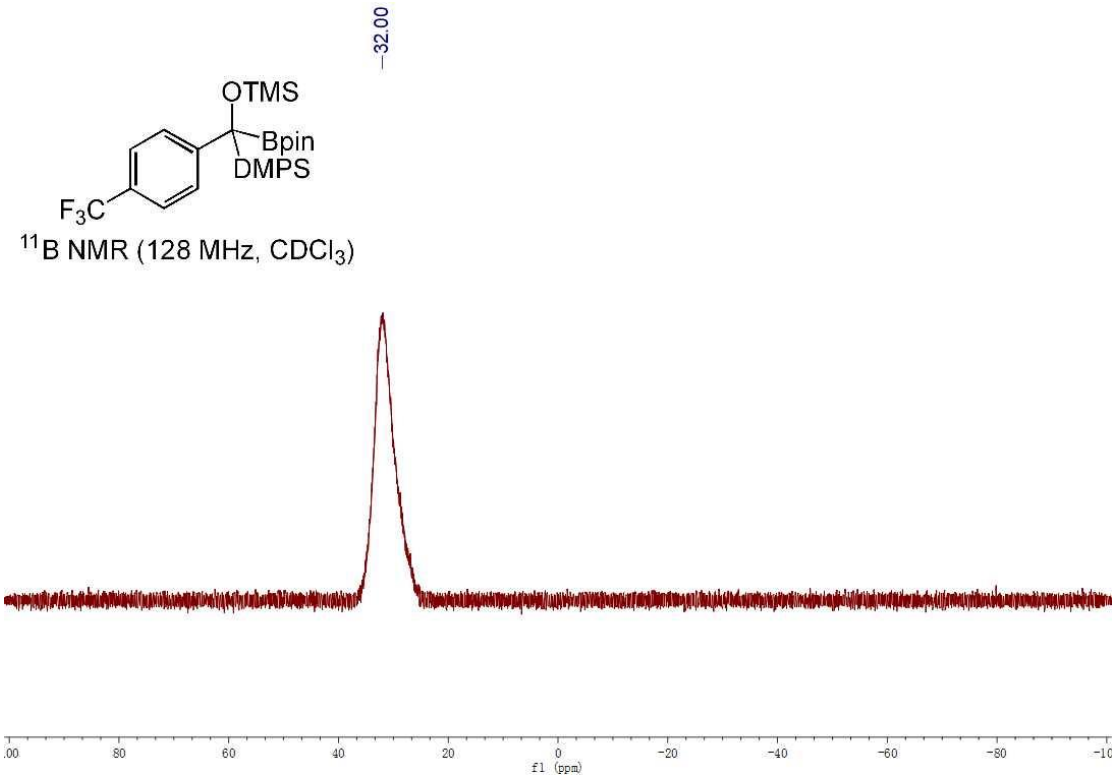


Figure S55 The ^{11}B NMR spectra of **5e**

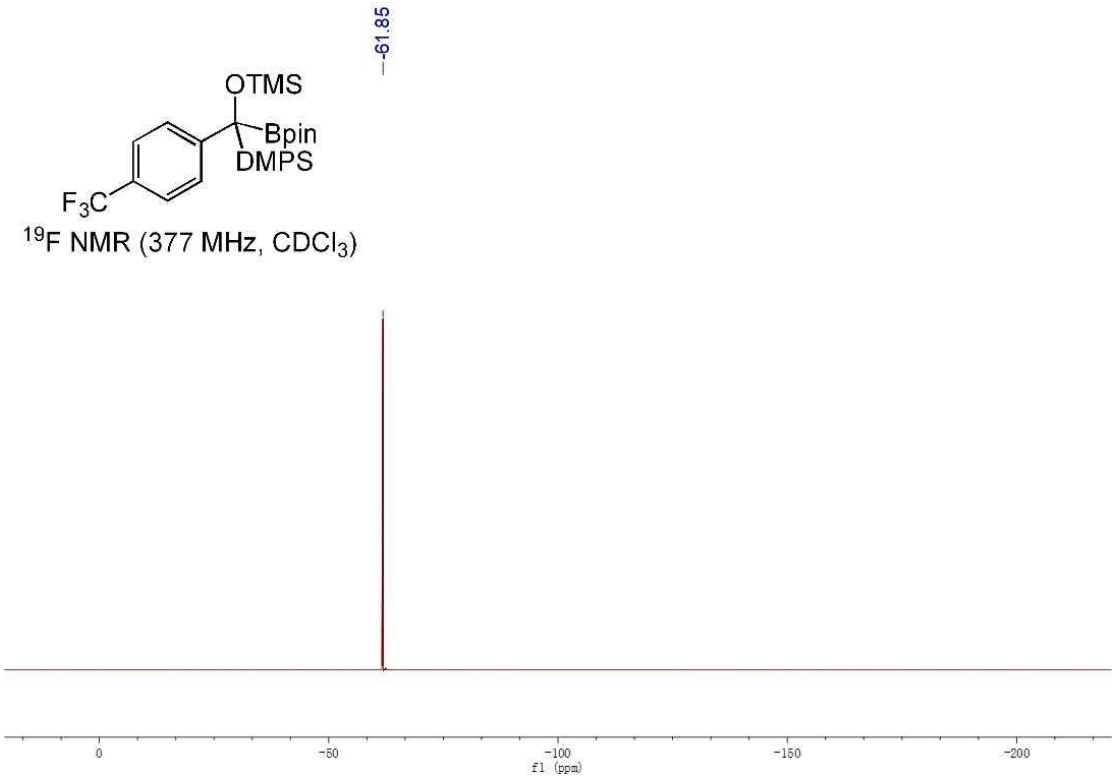


Figure S56 The ^{19}F NMR spectra of **5e**

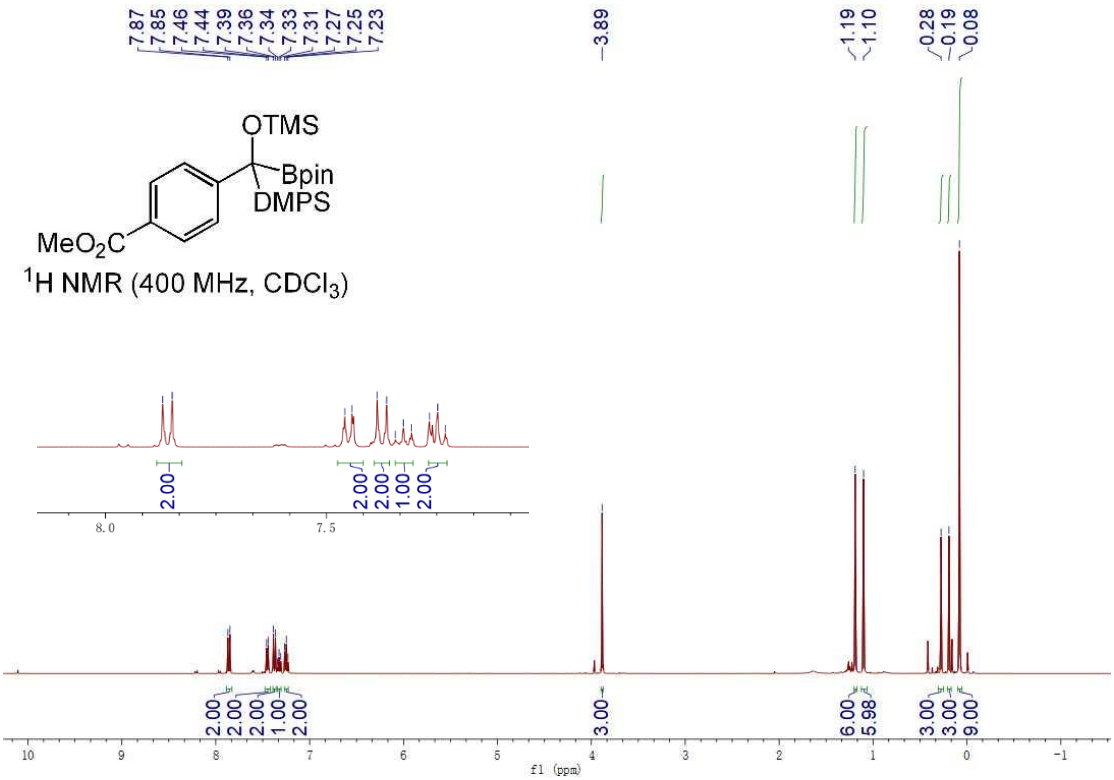


Figure S57 The ^{1}H NMR spectra of **5f**

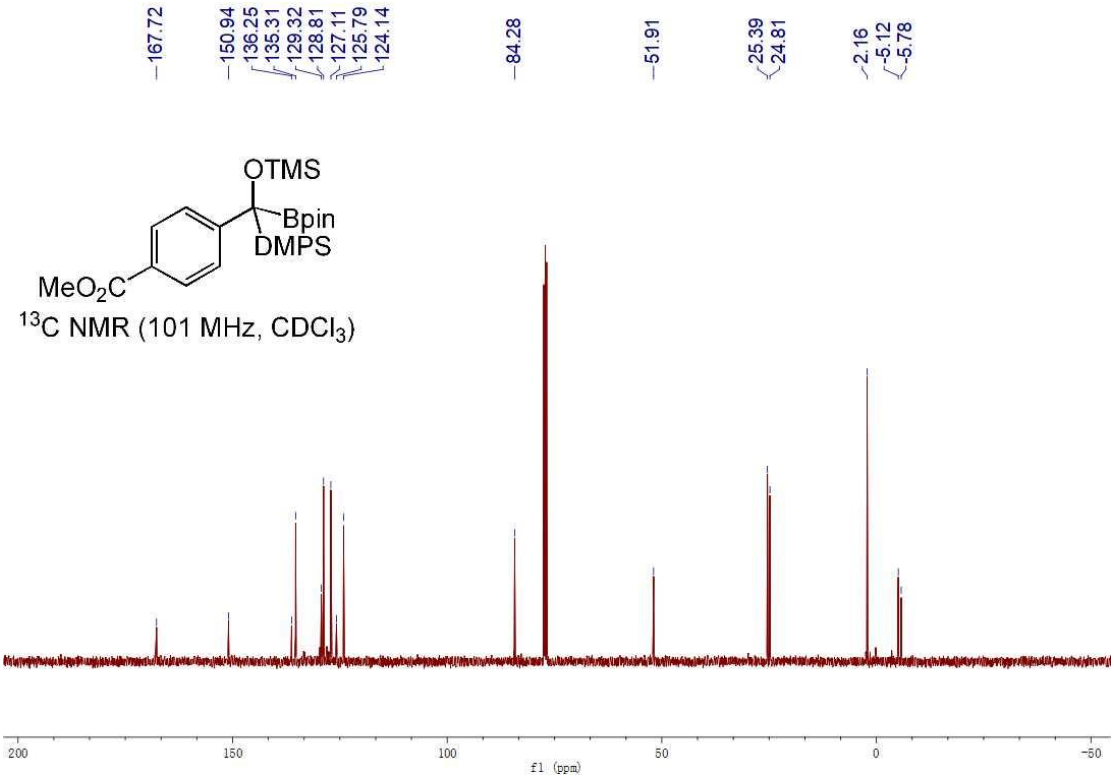


Figure S58 The ^{13}C NMR spectra of **5f**

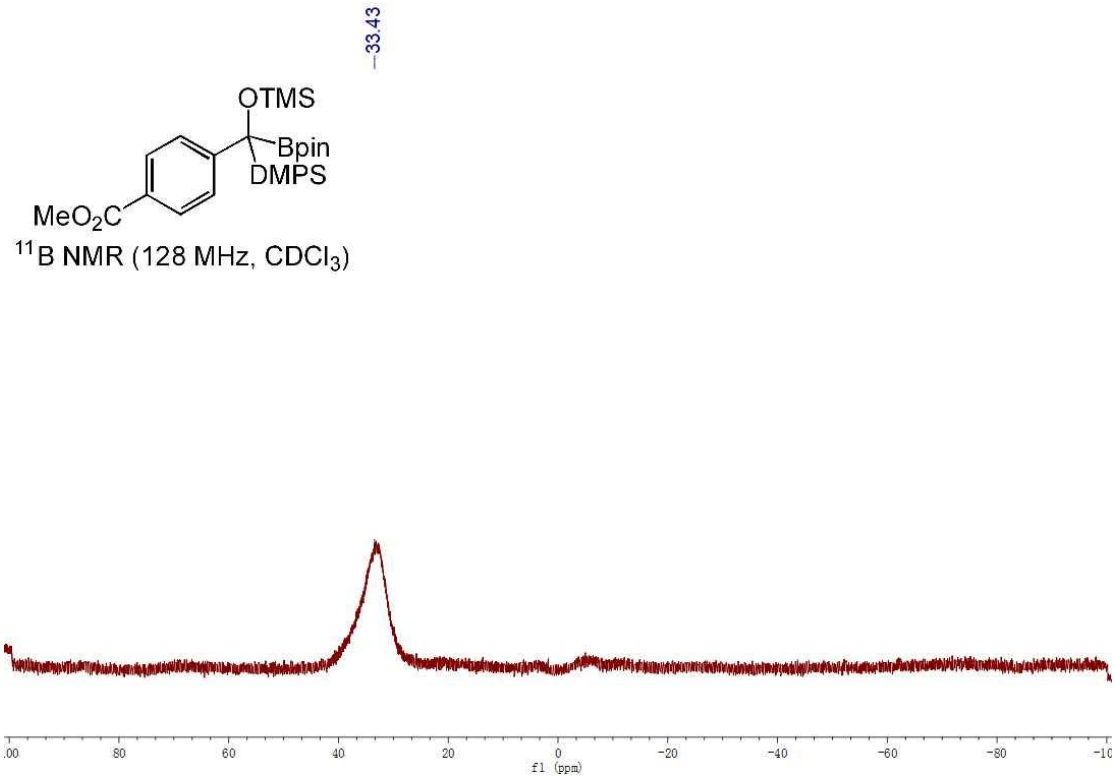


Figure S59 The ^{11}B NMR spectra of **5f**

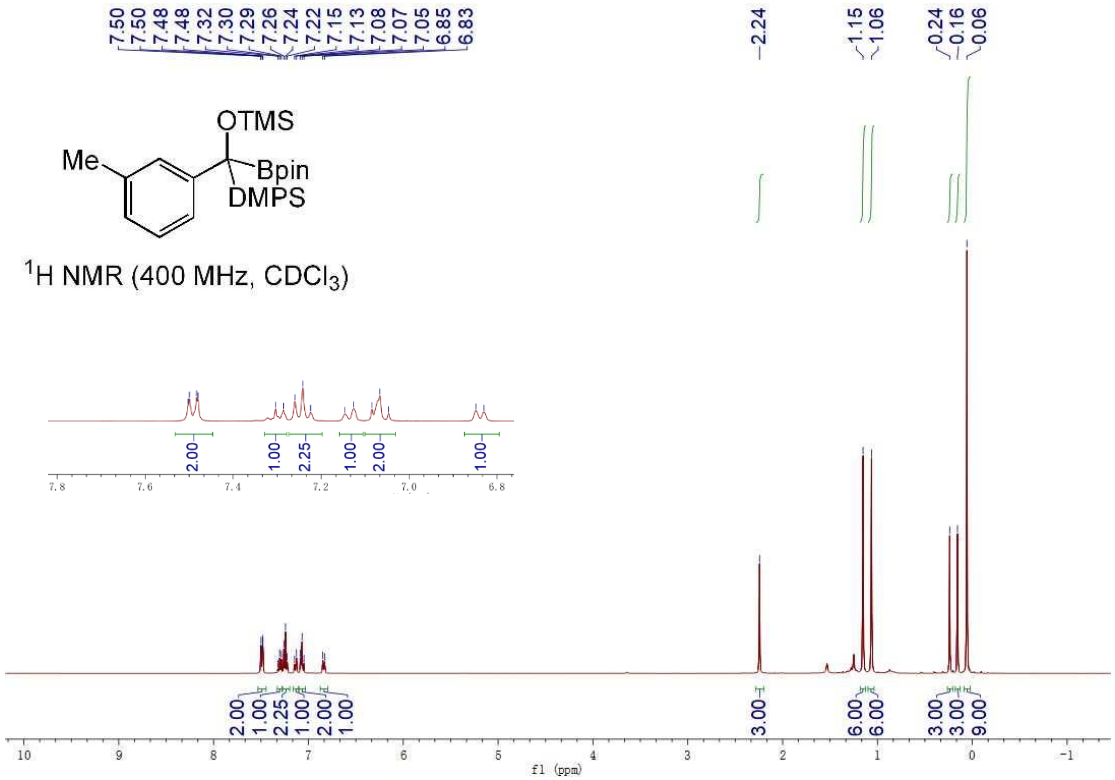


Figure S60 The ^{1}H NMR spectra of **5g**

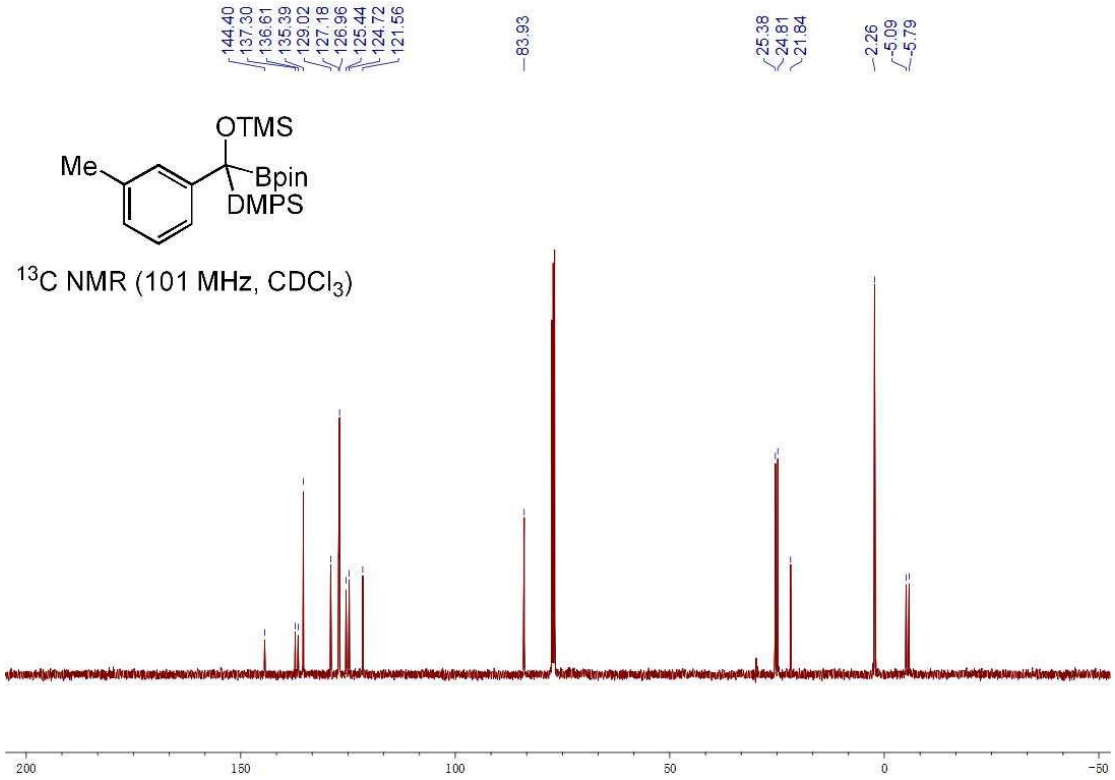


Figure S61 The ^{13}C NMR spectra of **5g**

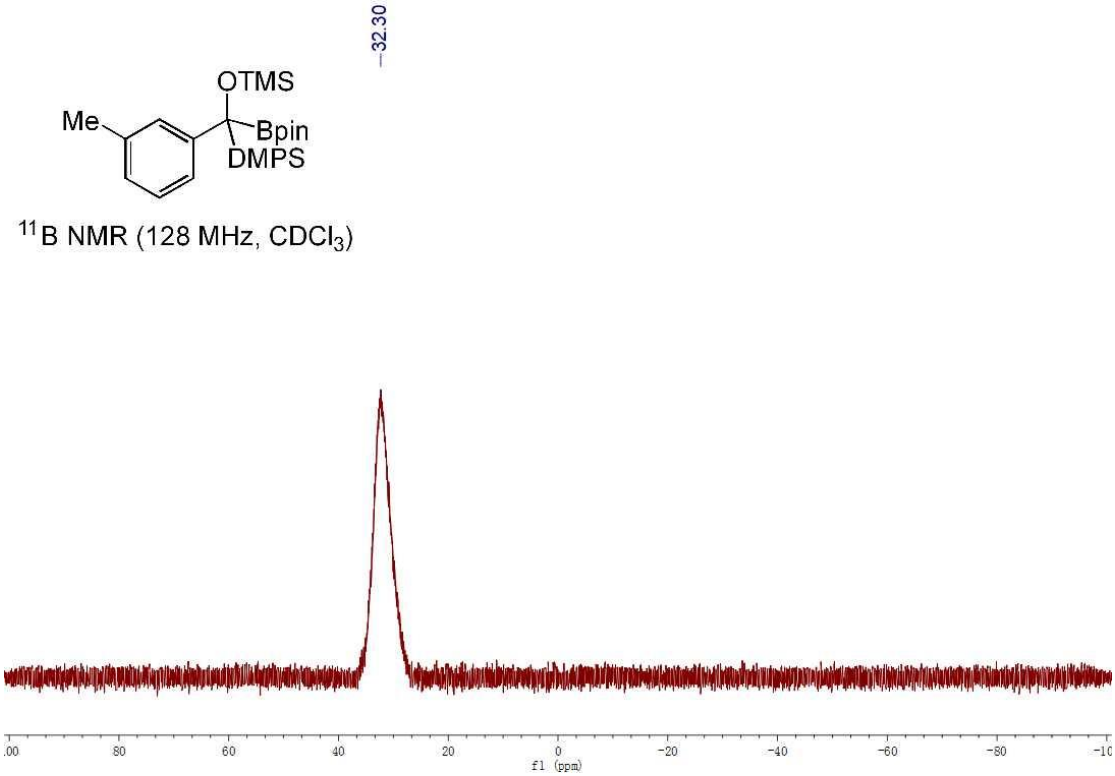


Figure S62 The ^{11}B NMR spectra of **5g**

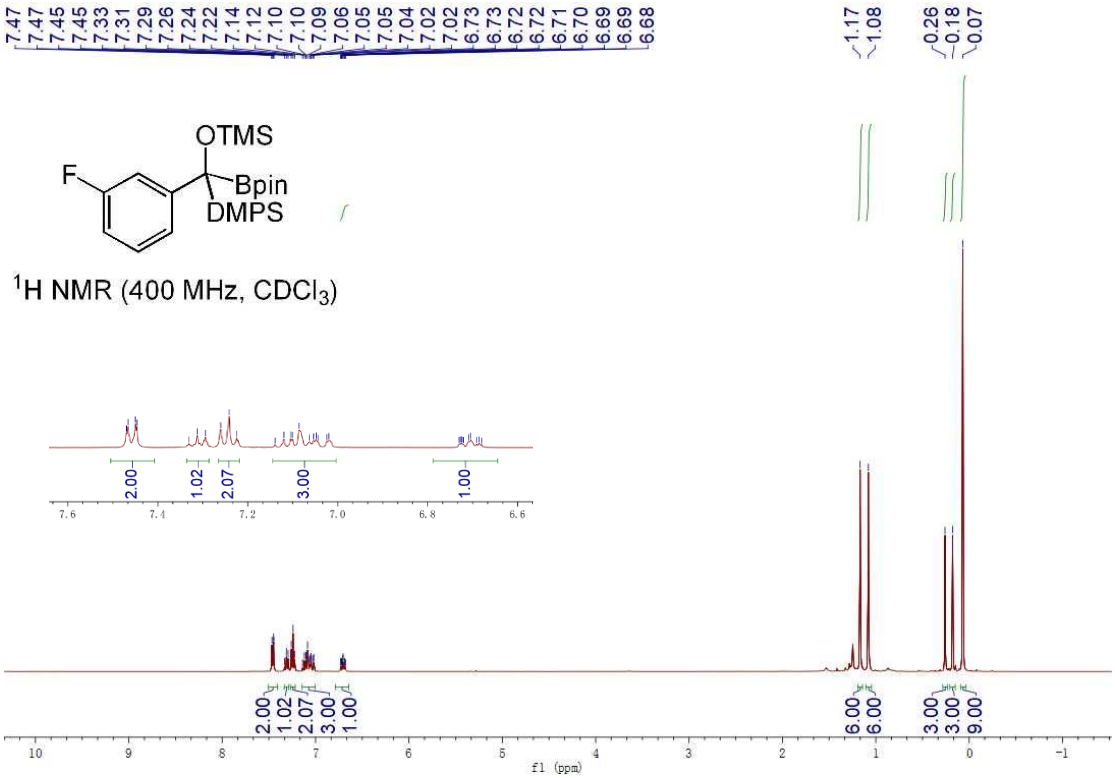


Figure S63 The ^{1}H NMR spectra of **5h**

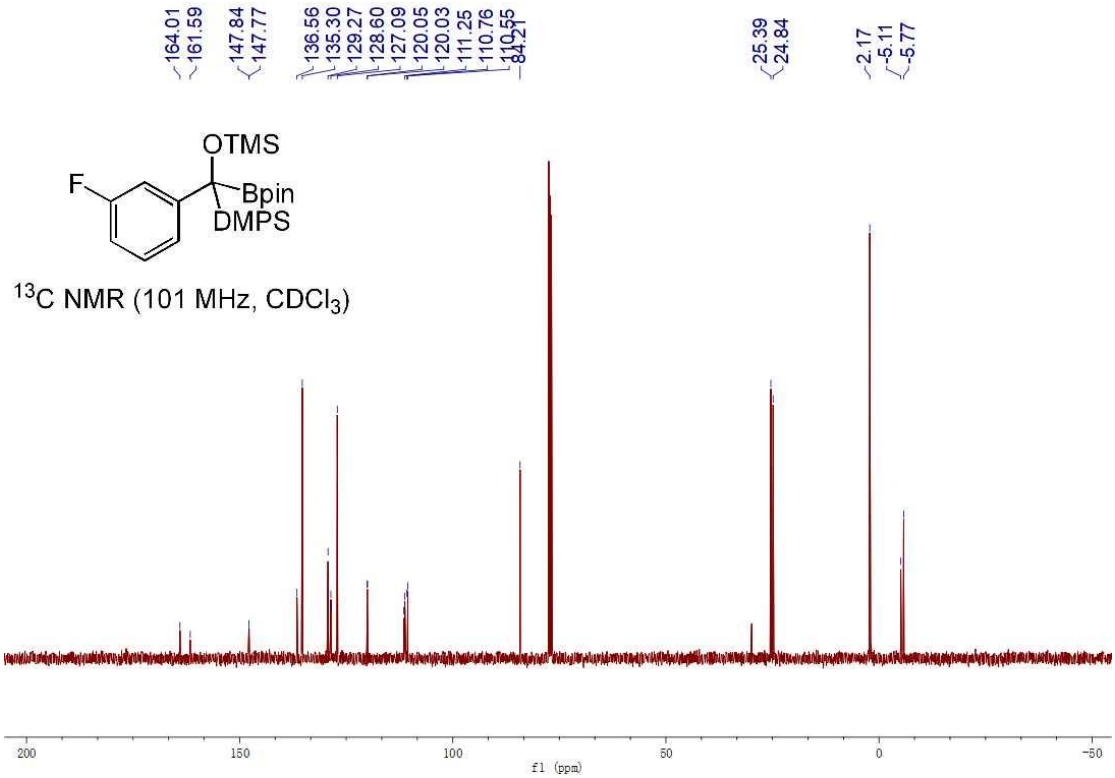


Figure S64 The ^{13}C NMR spectra of **5h**

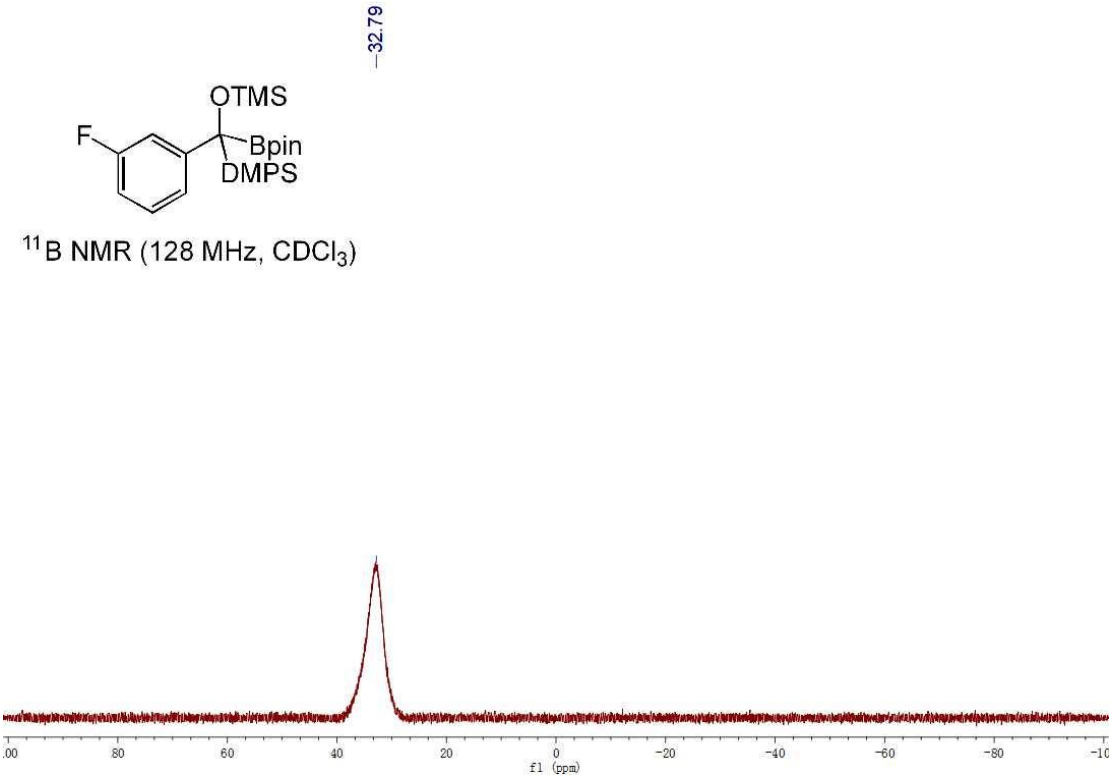


Figure S65 The ^{11}B NMR spectra of **5h**

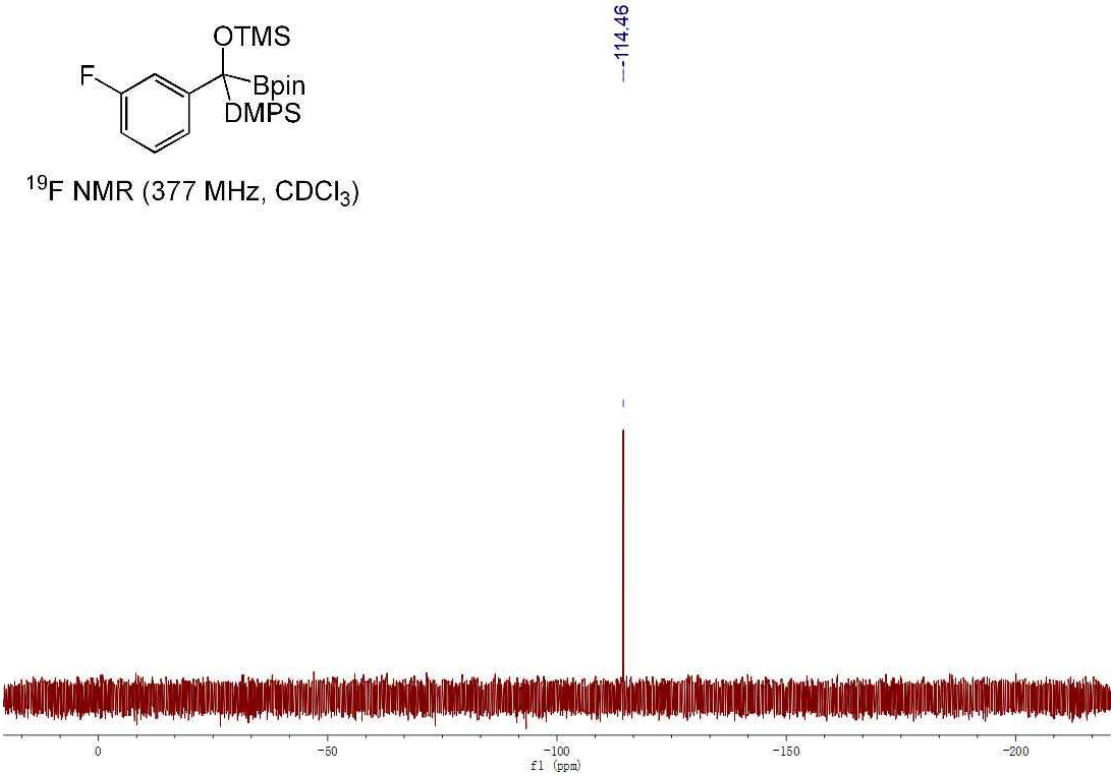


Figure S66 The ^{29}F NMR spectra of **5h**

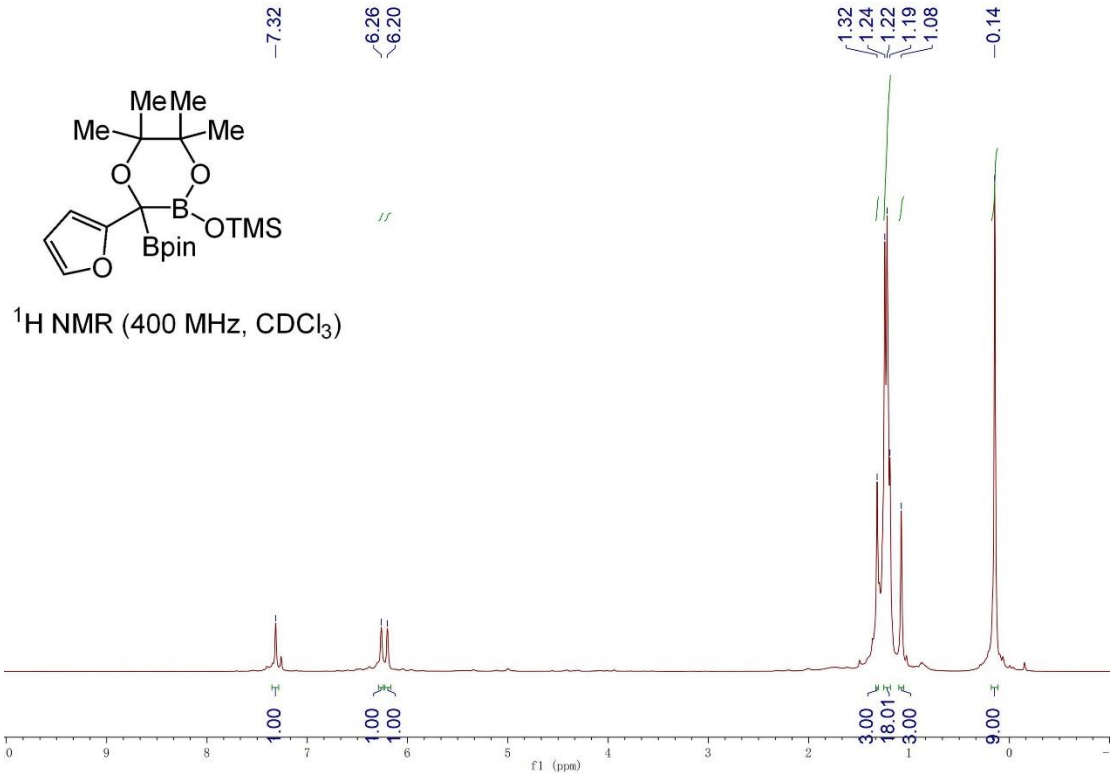


Figure S67 The ^{1}H NMR spectra of **6a**

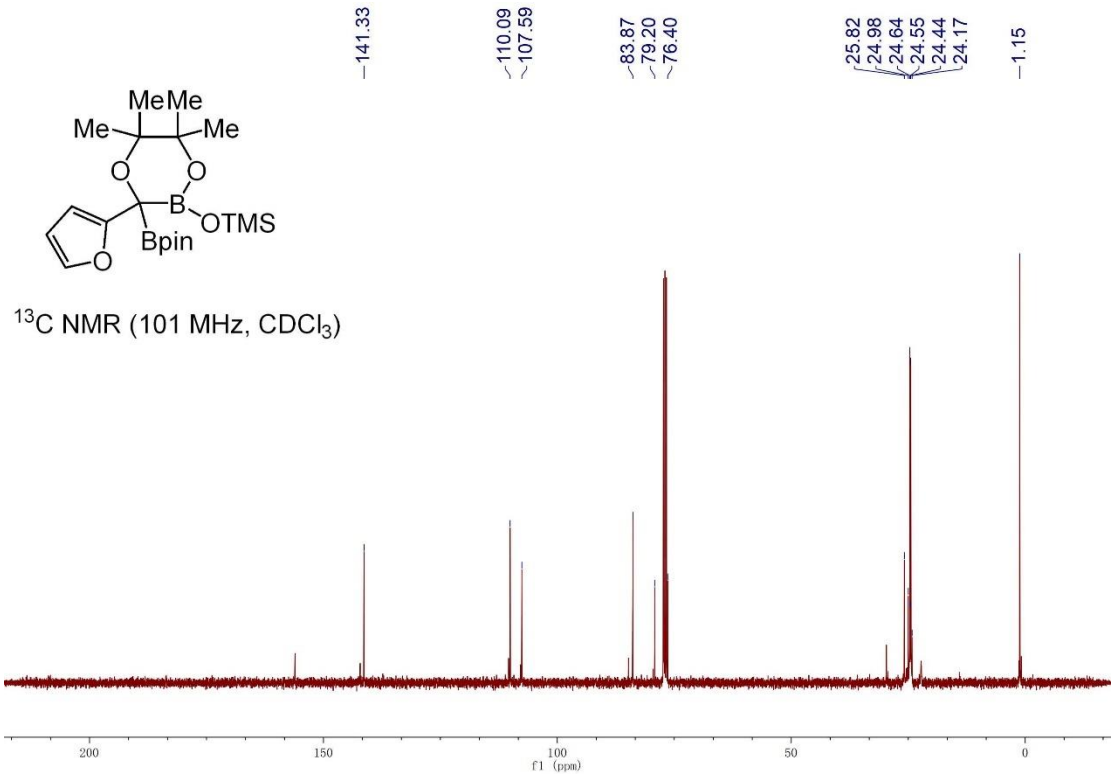


Figure S68 The ^{13}C NMR spectra of **6a**

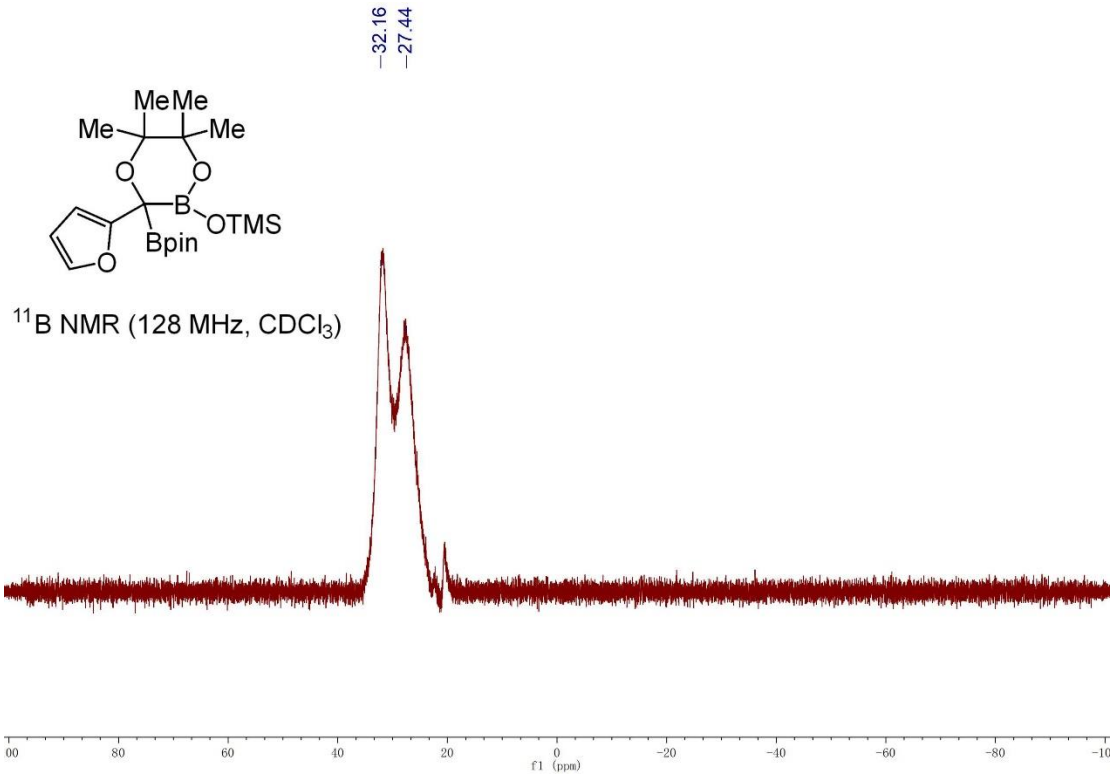


Figure S69 The ^{11}B NMR spectra of **6a**

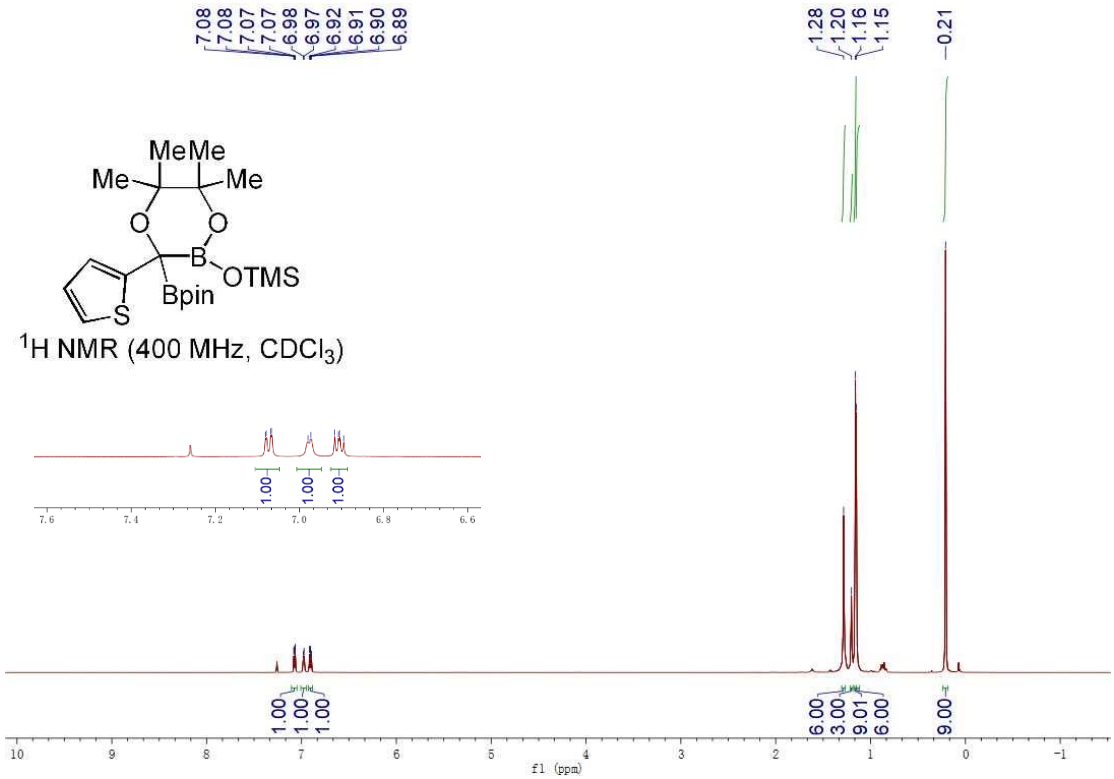


Figure S70 The ^{1}H NMR spectra of **6b**

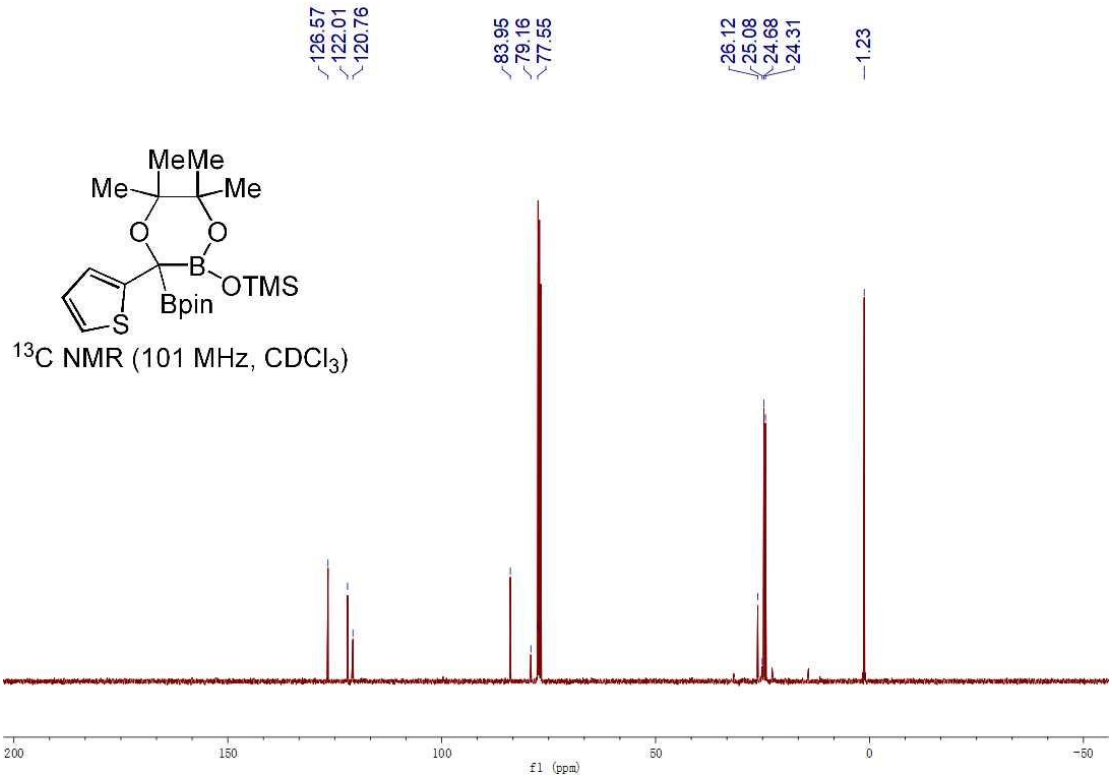


Figure S71 The ^{13}C NMR spectra of **6b**

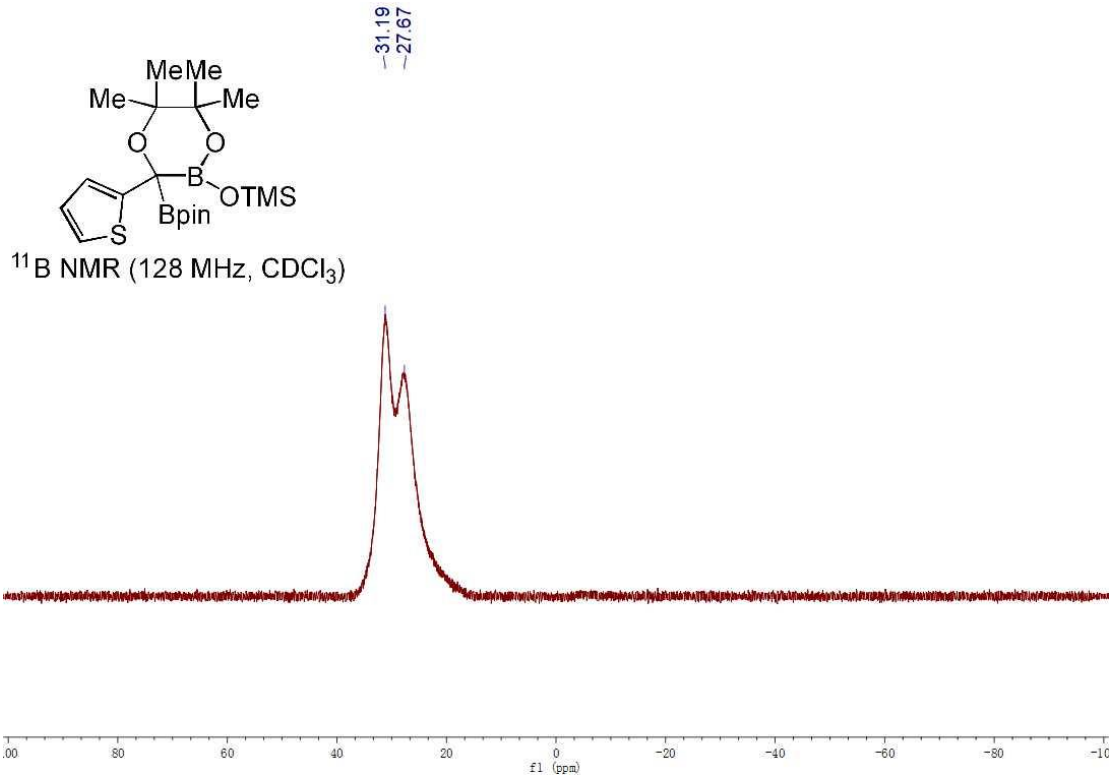


Figure S72 The ^{11}B NMR spectra of **6b**

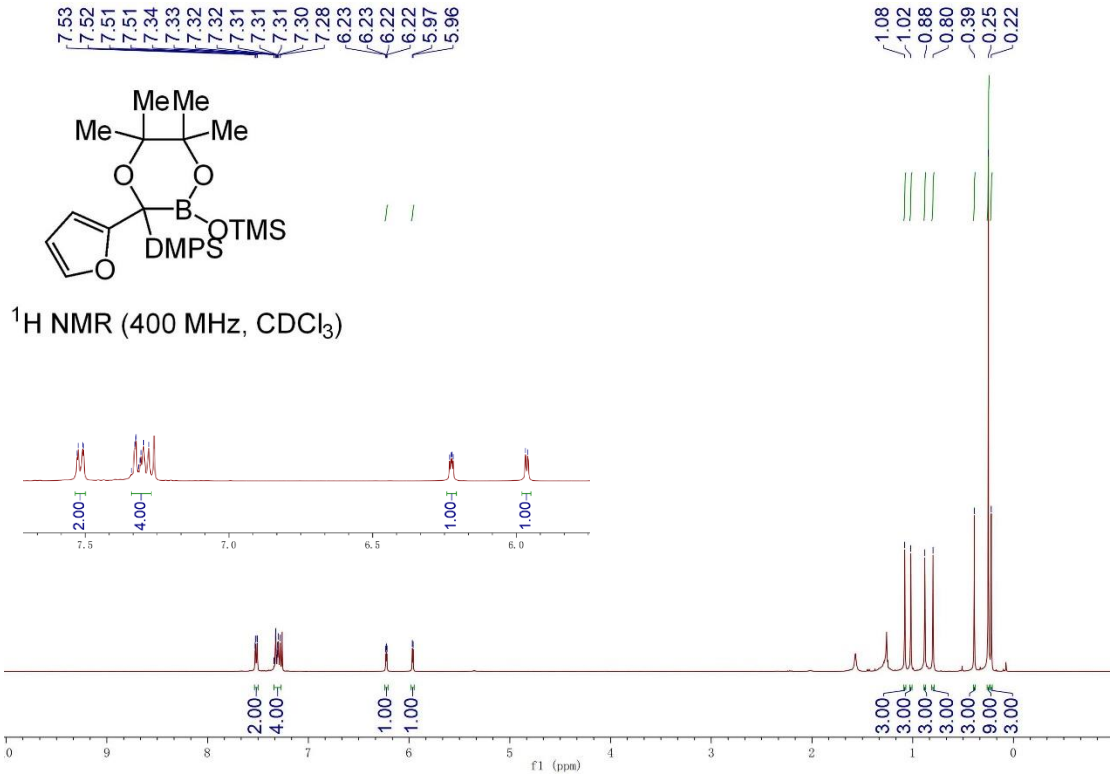


Figure S73 The ^{1}H NMR spectra of **6c**

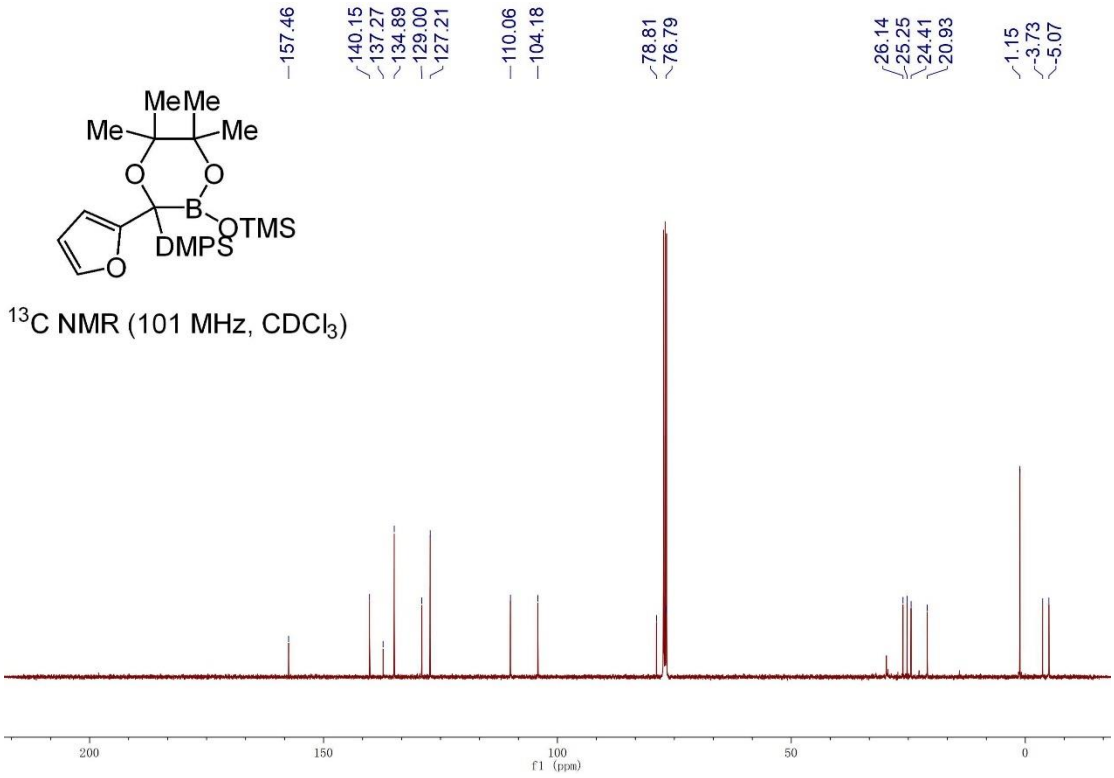


Figure S74 The ^{13}C NMR spectra of **6c**

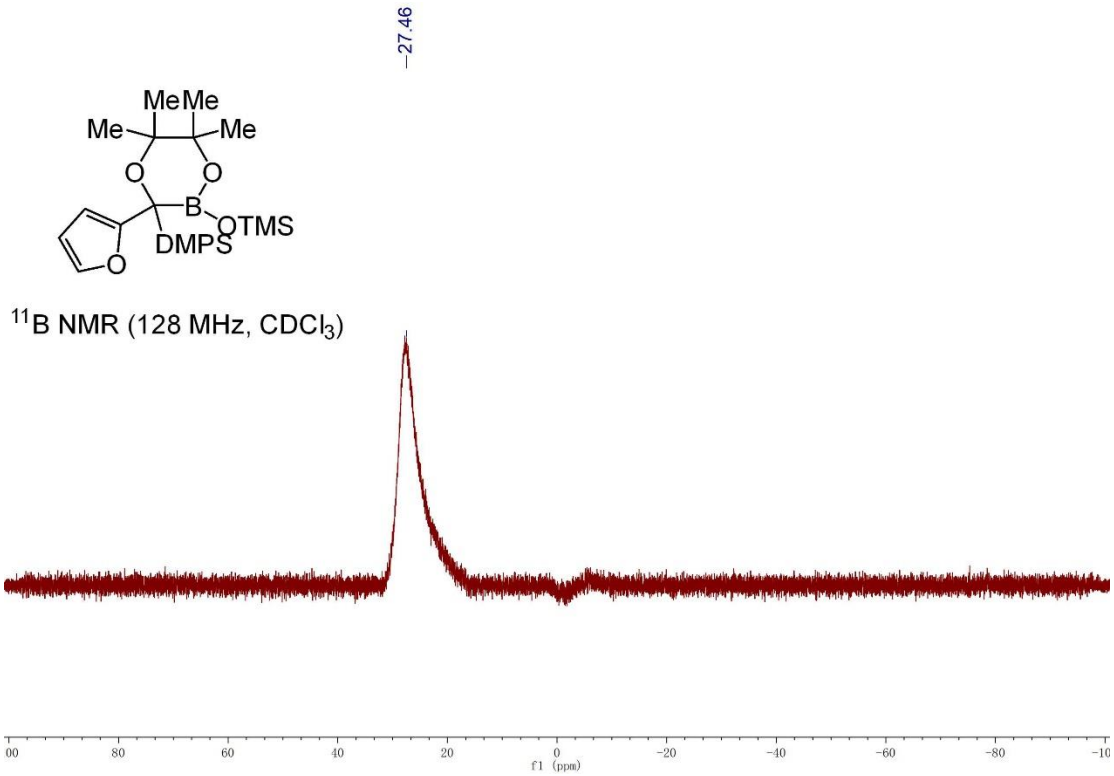


Figure S75 The ^{11}B NMR spectra of **6c**

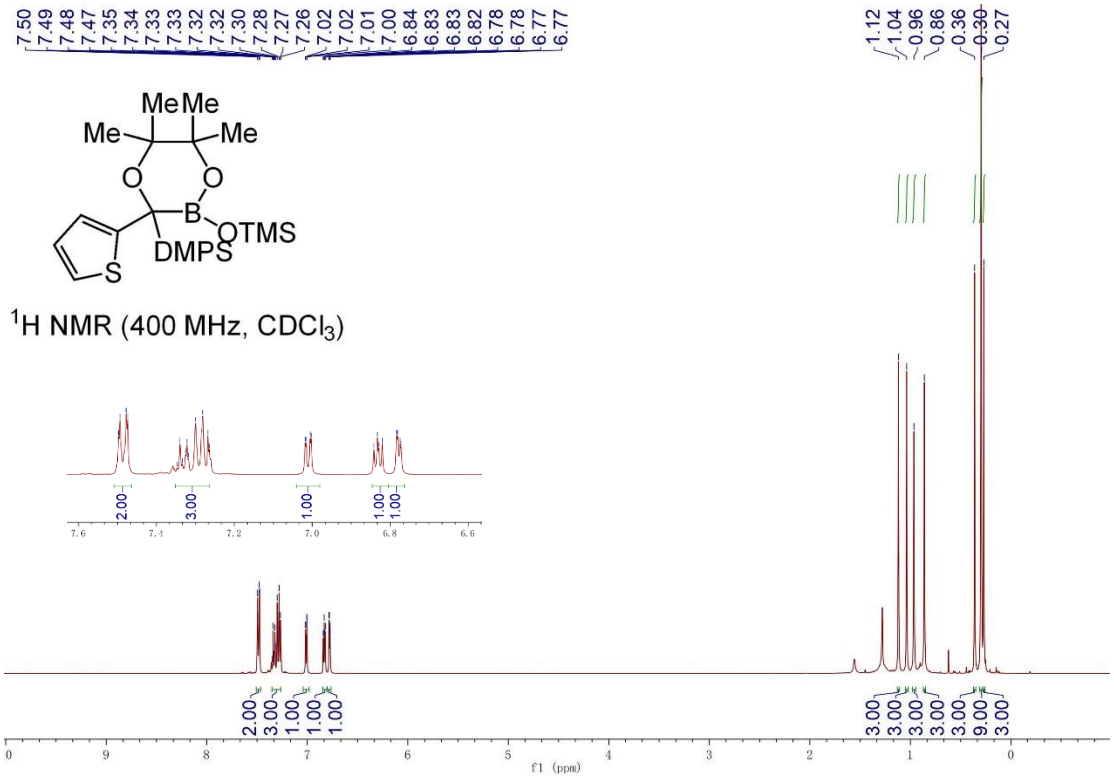


Figure S76 The ^{1}H NMR spectra of **6d**

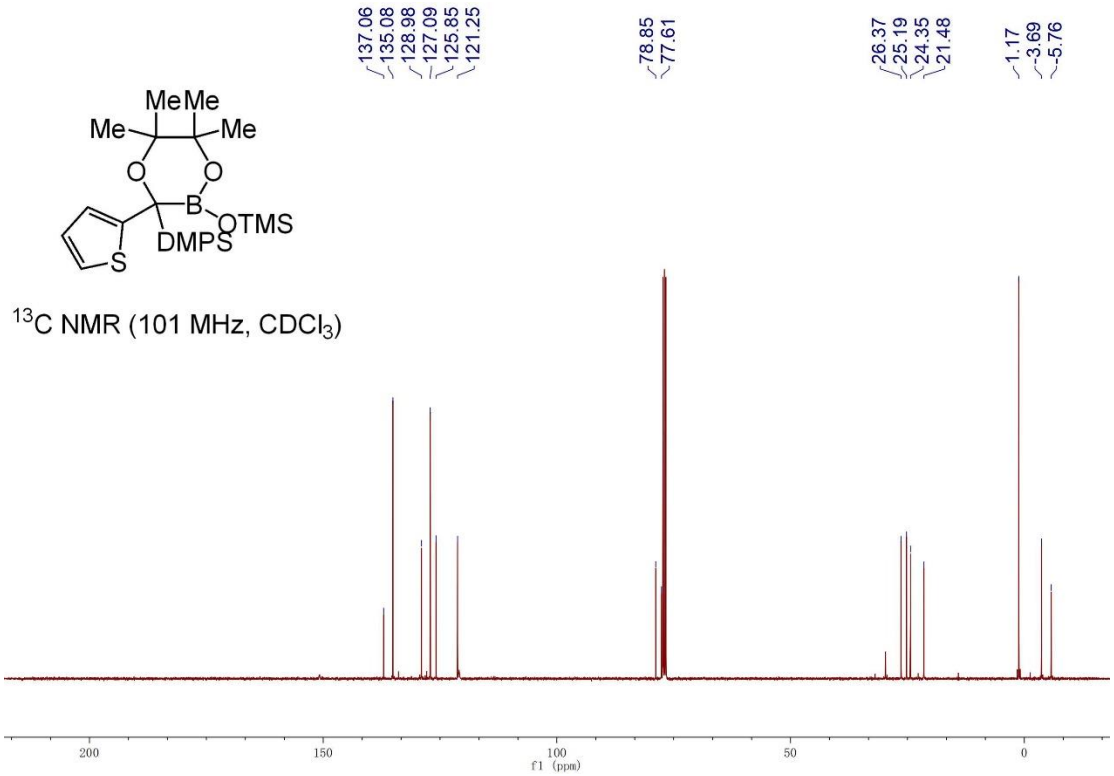


Figure S77 The ^{13}C NMR spectra of **6d**

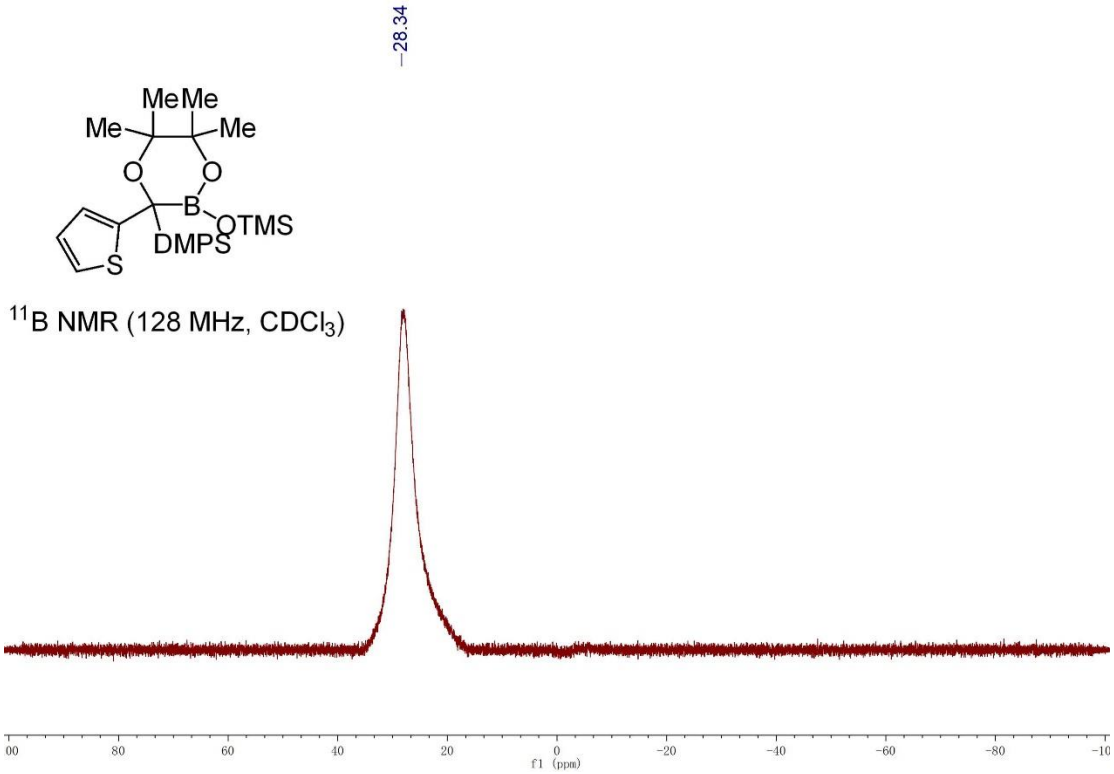


Figure S78 The ^{11}B NMR spectra of **6d**

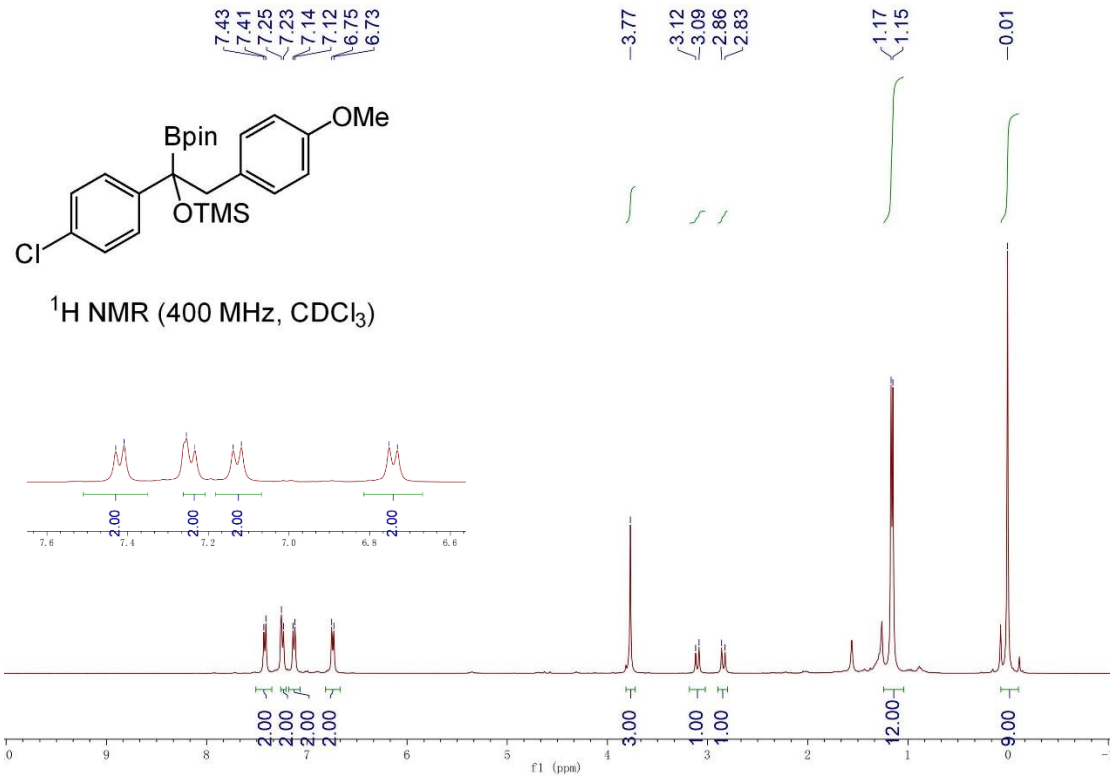


Figure S79 The ^{1}H NMR spectra of **8a**

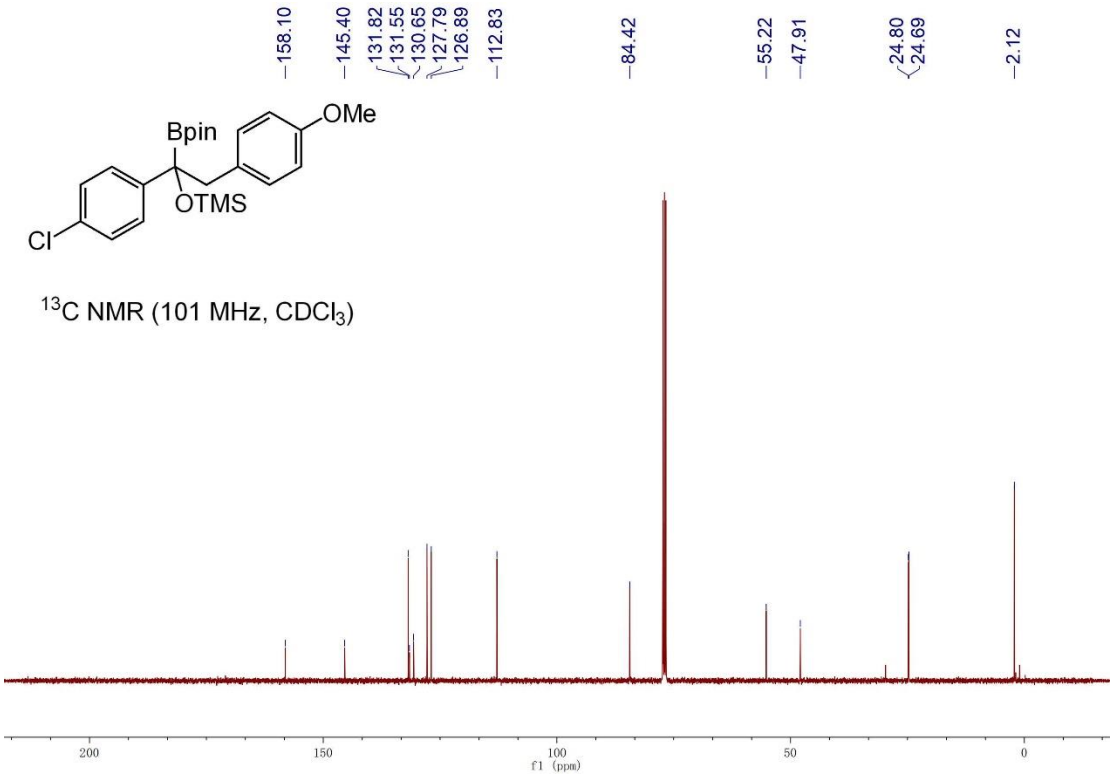


Figure S80 The ^{13}C NMR spectra of **8a**

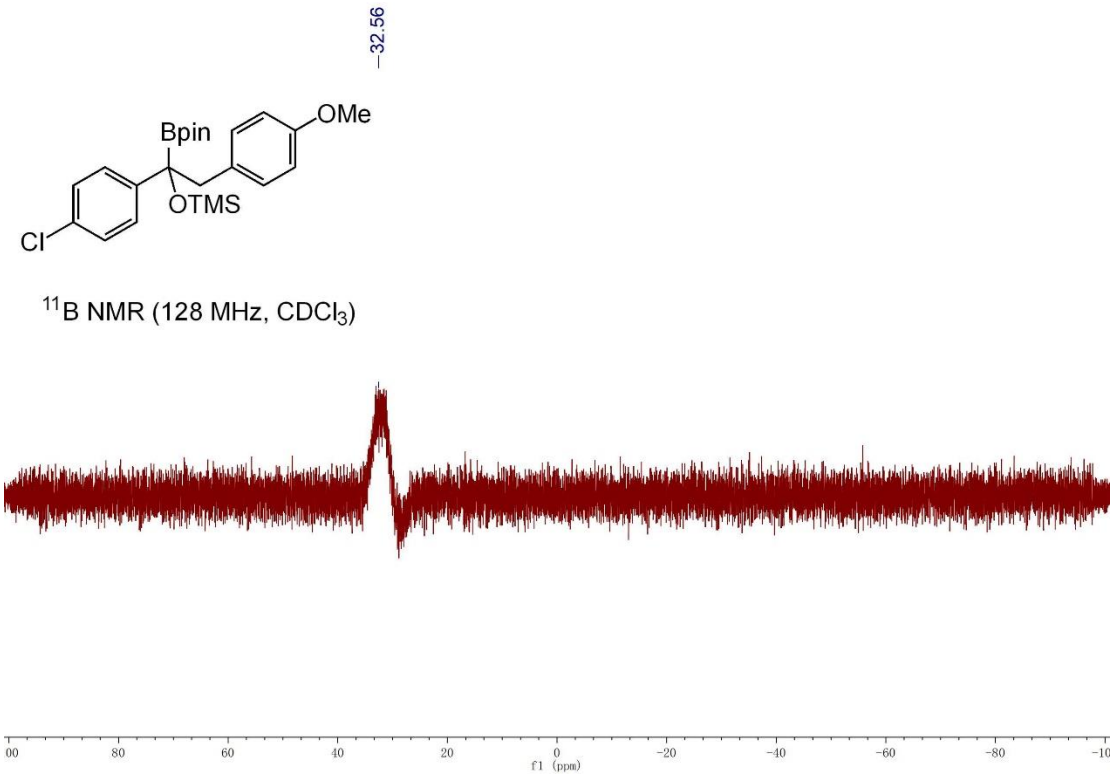


Figure S81 The ^{11}B NMR spectra of **8a**

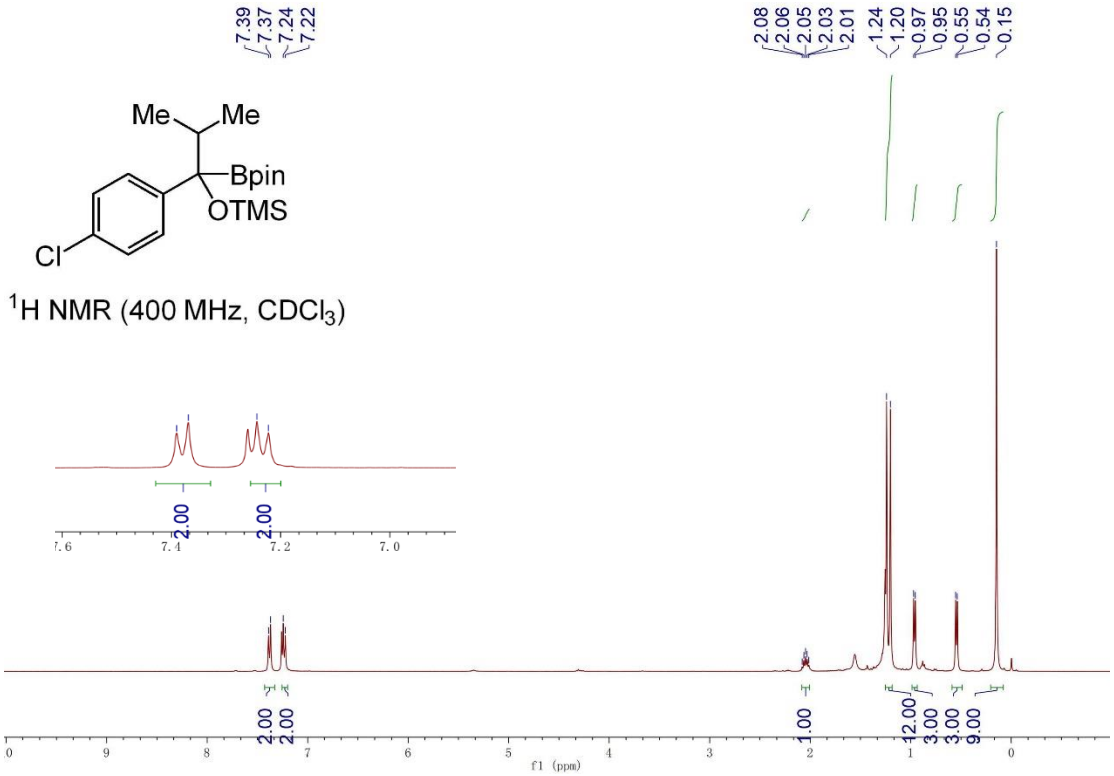


Figure S82 The ^{1}H NMR spectra of **8b**

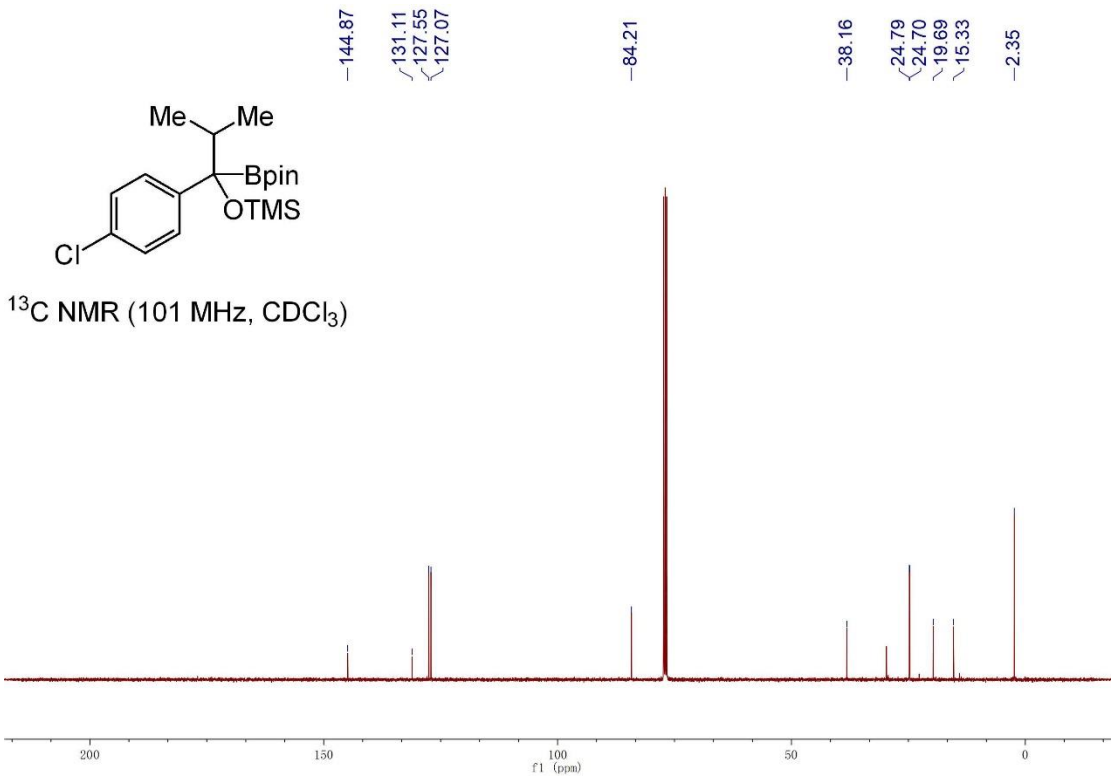


Figure S83 The ^{13}C NMR spectra of **8b**

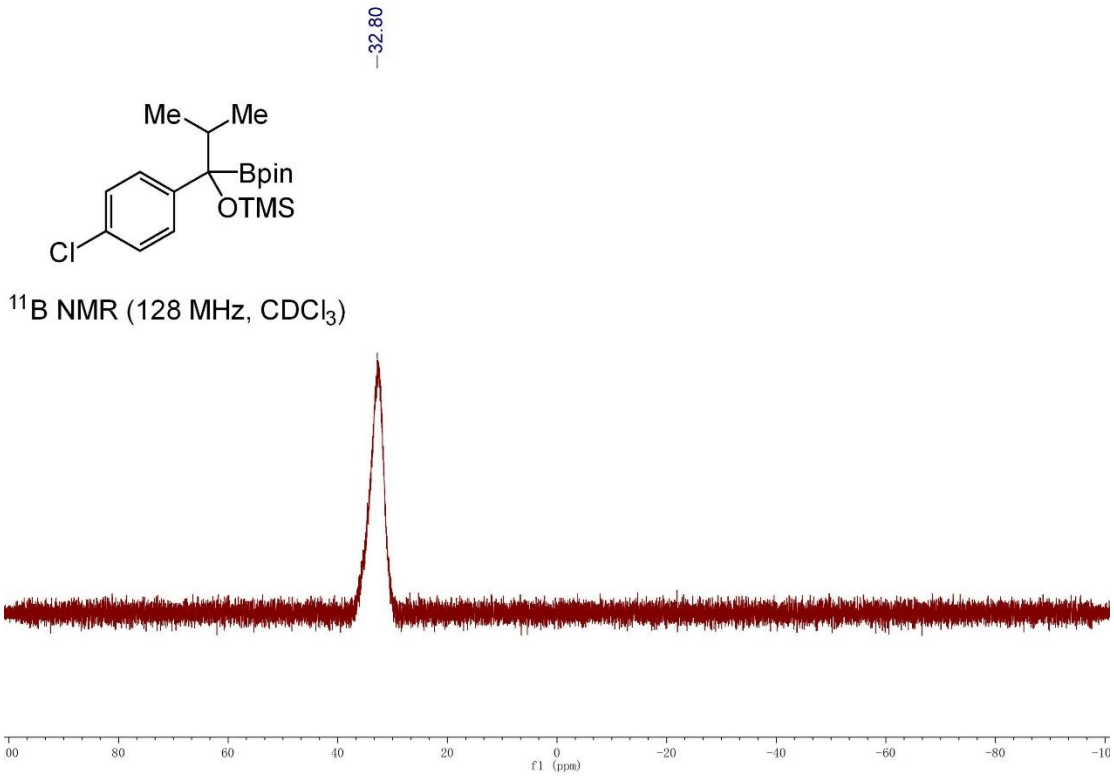


Figure S84 The ^{11}B NMR spectra of **8b**

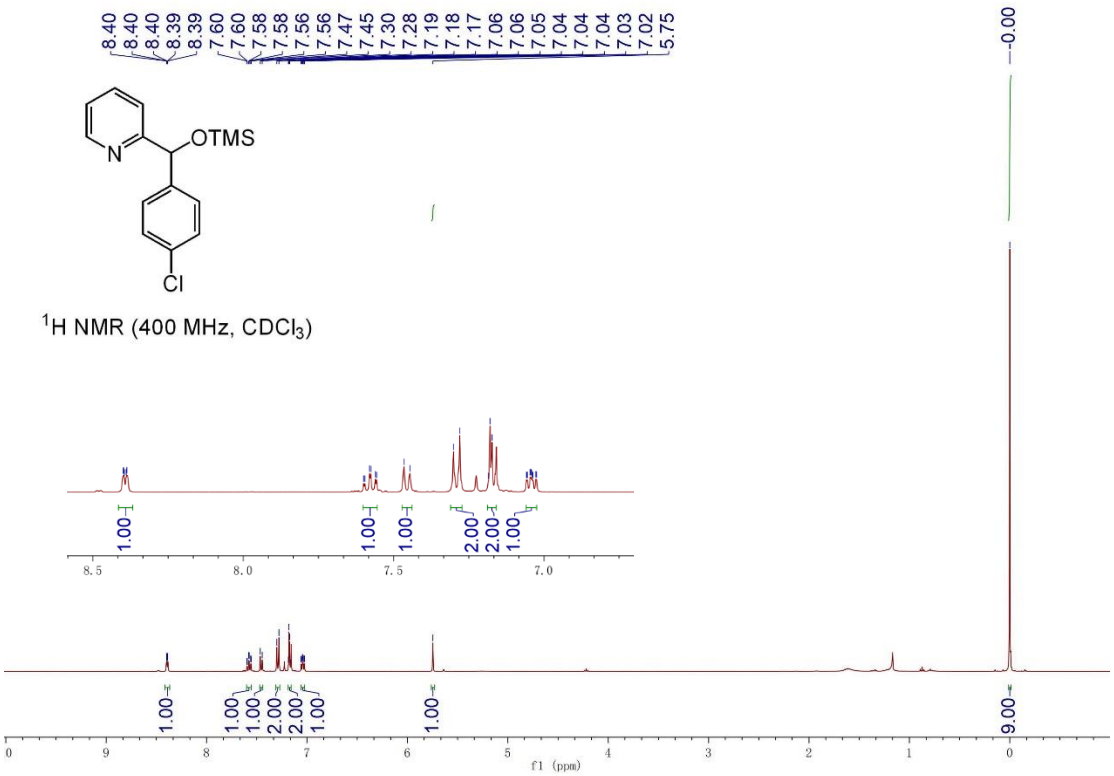


Figure S85 The ^{1}H NMR spectra of **10a**

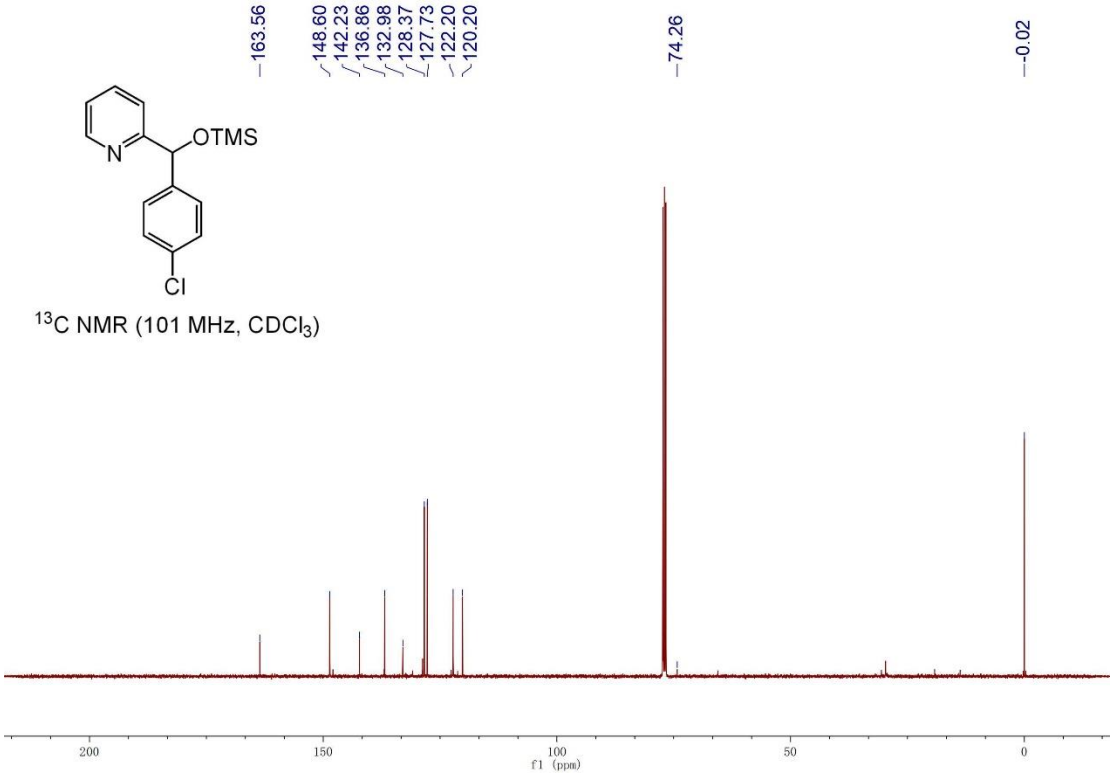


Figure S86 The ^{13}C NMR spectra of **10a**

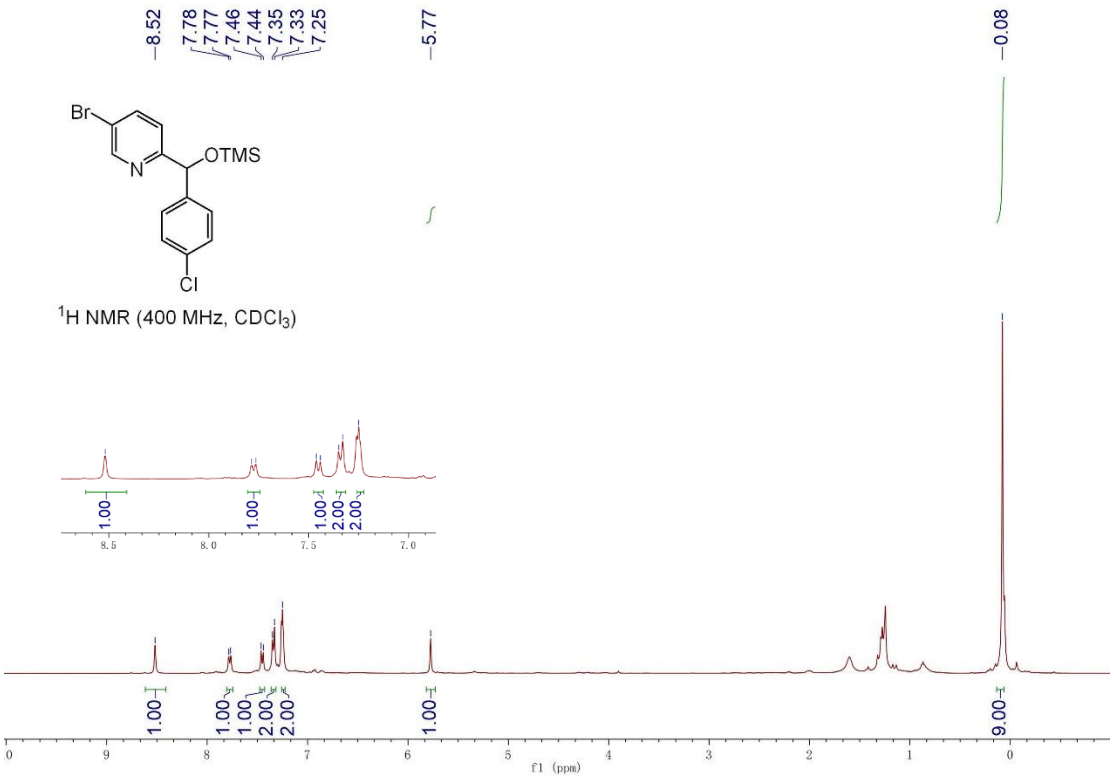


Figure S87 The ^{1}H NMR spectra of **10b**

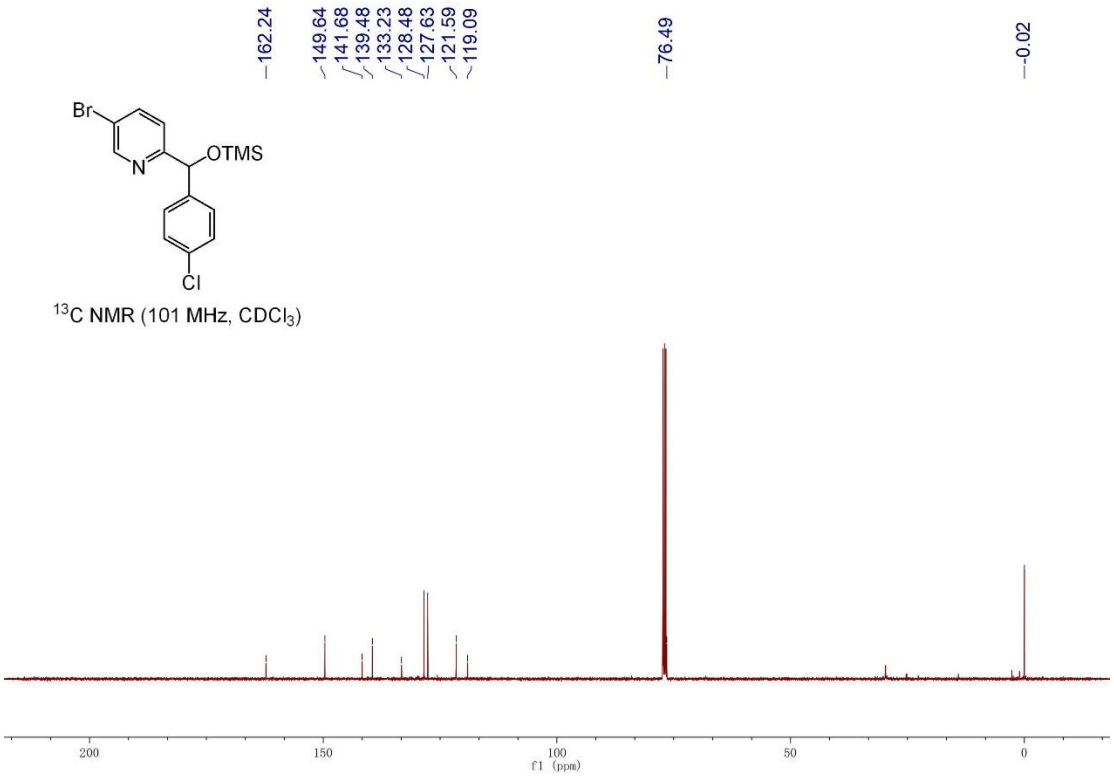


Figure S88 The ^{13}C NMR spectra of **10b**