Supporting Information

Synthesis of 1,1,1-tris(boronates) from vinylarenes by Co-catalyzed dehydrogenative borylations-hydroboration

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1. General Information

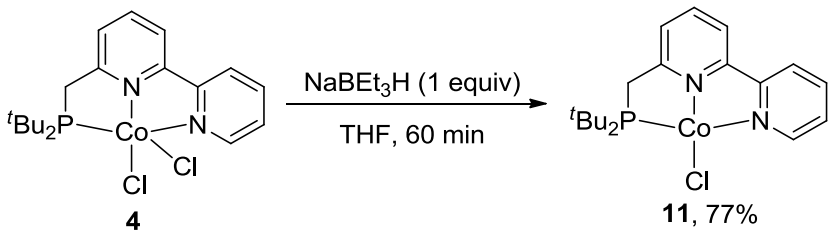
a. Materials

All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Pentane was distilled from sodium benzophenone ketyl prior to use. The following chemicals were purchased and used as received: $CoCl_2$ (Aldrich), $NaBEt_3H$ (1.0 M in THF) (Acros), bis(pinacolato)diboron (99%) (TCI), CD_3I (Innochem), vinylarenes (TCI, Alfa-Aesar, or aldrich). Complexes (^{t}Bu^{t}PNN)$FeCl_2$ **2**,[1] (^{i}Pr^{i}PNN)$FeCl_2$ **3**,[2] (^{t}Bu^{t}PNN)$CoCl_2$ **4**[2], (^{i}Pr^{i}PNN)$CoCl_2$ **5**[2] and PPh_3CD_3I[3] were prepared according to previously reported procedures. All other reagents and solvents were purchased from commercial sources and used without purification.

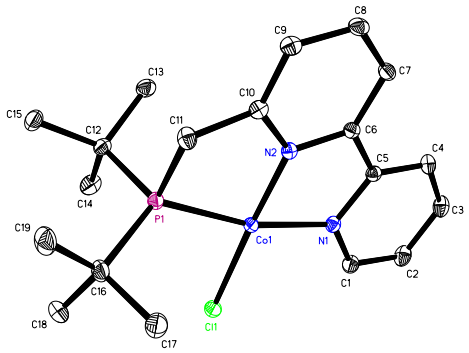
b. Analytical Methods

NMR spectra were recorded on Agilent 400 MHz or Agilent 600 MHz. ^{1}H NMR chemical shifts were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts were referenced to the solvent resonance. ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. ^{11}B NMR chemical shifts were referenced to an external BF_3-Et_2O standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Due to quadrupolar relaxation of boron, the carbon bearing the boron is missing for all hydroboration products in the ^{13}C NMR spectra. Elemental analyses and high resolution mass spectrometer (HR-MS) were carried out by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

2. Preparation of Co(I) Complexes **11** and **13**, and Stoichiometric Experiments



($^{t\mathrm{Bu}}$PNN)CoCl (11): In a nitrogen filled glovebox, the Co(II) dichloride complex ($^{t\mathrm{Bu}}$PNN)$CoCl_2$ **4** (222.0 mg, 0.5 mmol) and THF (5 mL) were added to a 50 mL Schlenk tube equipped with a magnetic stir bar. The resulting mixture was chilled in the freezer to −35 ℃, and $NaBEt_3H$ (0.5 mL, 1.0 M in THF) was then added dropwisely. The reaction solution was stirred for 60 min at ambient temperature, and then diluted with pentane (3 mL). The resulting solution was filtered through a plug of celite and the volatiles were removed in vacuo. The residue was washed with pentane (3 mL*5) to afford product **11** as black solid (156.9 mg, 77%). Dark purple crystals suitable for X-ray diffraction analysis were obtained by recrystallization of the product from a diethyl ether solution at −35 °C. ^{1}H NMR (400 MHz, C_6D_6) δ = 13.25 (d, *J* = 5.3 Hz, 1H, aryl-*H*), 9.33 (td, *J* = 7.5, 3.3 Hz, 1H, aryl-*H*), 8.27 (t, *J* = 6.4 Hz, 1H, aryl-*H*), 7.80 (t, *J* = 7.5 Hz, 1H, aryl-*H*), 7.07 (d, *J* = 8.0 Hz, 1H, aryl-*H*), 6.56 (d, *J* = 6.8 Hz, 1H, aryl-*H*), 5.56 (d, *J* = 8.0 Hz, 1H, aryl-*H*), 3.40 (d, *J* = 9.5 Hz, 2H, PCH_2), 1.35 (d, *J* = 12.7 Hz, 18H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, C_6D_6) δ 161.7 (d, J_{PC} = 7.3 Hz, aryl-*C*), 158.3 (aryl-*C*), 156.1 (aryl-*C*), 146.2 (aryl-*C*), 133.3 (aryl-*C*), 123.20 (d, J_{PC} = 4.0 Hz, aryl-*C*)), 123.18 (aryl-*C*), 123.1 (aryl-*C*), 119.7 (aryl-*C*), 113.9 (aryl-*C*), 37.8 (d, J_{PC} = 19.1 Hz), 32.9 (d, J_{PC} = 12.2 Hz), 29.21 (C(*C*H_3)$_3$), 29.18 (C(*C*H_3)$_3$). ^{31}P{^{1}H}NMR (162 MHz, C_6D_6) δ = 45.1. Anal. Calcd for $C_{26}H_{43}B_3O_6$: C, 55.82; H, 6.66; N, 6.85. Found: C, 55.44; H, 6.33; N, 6.72.

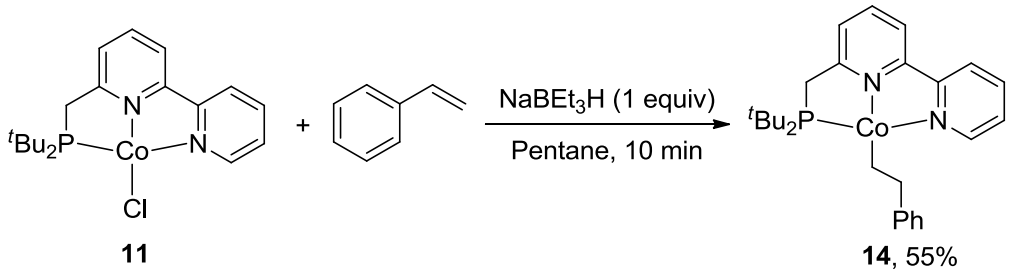


Selected Bond Length for Complex **11**

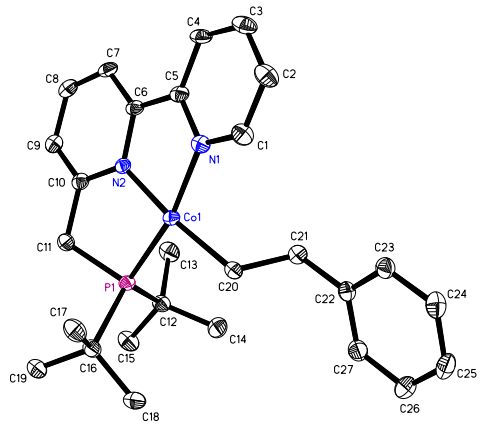
Selected Bond Length	Distance(Å)
Co1–Cl1	2.2141(5)
Co1–P1	2.1760(6)
Co1–N1	1.9354(15)
Co1–N2	1.8424(16)

Selected Bond Angles for Complex **11**

Selected Bond Angles	(deg)
P1–Co1–Cl1	96.31(2)
N1–Co1–Cl1	95.19(5)
N1–Co1–P1	167.10(6)
N2–Co1–Cl1	177.47(5)
N2–Co1–P1	86.11(5)
N2–Co1–N1	82.48(7)



($^{t\mathrm{Bu}}$PNN)CoCH$_2$CH$_2$Ph (14): In a nitrogen filled glovebox, the Co(I) monochloride complex ($^{t\mathrm{Bu}}$PNN)CoCl **11** (222.0 mg, 0.5 mmol), styrene (52.0 mg, 0.5 mmol, 1 equiv) and pentane (8 mL) were added to a 50 mL Schlenk tube equipped with a magnetic stir bar. The resulting mixture was chilled in the freezer to −35 ℃ and NaBEt$_3$H (0.5 mL, 1.0 M in THF) was added dropwisely. The reaction solution was stirred for 10 min at ambient temperature and followed by filtration through celite. The resulting dark purple solution was stored in the freezer (−35 ℃) to afford the product **14** as black solid, which was collected by filtration (131.0 mg, 55%). Dark crystals suitable for X-ray diffraction analysis were obtained by recrystallization of the product from a pentane solution at −35 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ = 15.71 (d, *J* = 5.7 Hz, 1H, aryl-*H*), 11.50 – 11.43 (m, 1H, aryl-*H*), 10.09 (t, *J* = 6.4 Hz, 1H, aryl-*H*), 9.23 (dd, *J* = 8.1, 6.9 Hz, 1H, aryl-*H*), 7.88 – 7.81 (m, 3H, aryl-*H*), 7.28 (t, *J* = 7.6 Hz, 2H, aryl-*H*), 7.20 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 7.13 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 5.36 (d, *J* = 9.1 Hz, 2H, PC*H*$_2$), 5.25 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 2.62 (t, *J* = 8.8 Hz, 2H, ArC*H*$_2$), 1.15 (d, *J* = 12.1 Hz, 18H, C(C*H*$_3$)$_3$), 0.37 – 0.29 (m, 2H, ArCH$_2$C*H*$_2$). ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 165.8 (aryl-*C*), 165.1 (d, J_{PC} = 7.9 Hz, aryl-*C*), 145.7 (d, J_{PC} = 4.0 Hz, aryl-*C*), 145.1 (d, J_{PC} = 1.9 Hz, aryl-*C*), 133.7 (d, J_{PC} = 3.9 Hz, aryl-*C*), 131.8 (aryl-*C*), 128.6 (aryl-*C*), 128.1 (aryl-*C*), 127.9 (aryl-*C*), 126.3 (aryl-*C*), 125.5 (d, J_{PC} = 2.1 Hz, aryl-*C*), 124.8 (aryl-*C*), 121.6 (d, J_{PC} = 10.1 Hz, aryl-*C*), 114.3 (d, J_{PC} = 2.0 Hz, aryl-*C*), 41.3 (d, J_{PC} = 18.1 Hz), 38.4 (Ar*C*H$_2$), 30.7 (d, J_{PC} = 11.0 Hz), 29.21 (C(*C*H$_3$)$_3$), 29.18 (C(*C*H$_3$)$_3$); Co-*C*H$_2$ not located. ^{31}P{^{1}H}NMR (162 MHz, C$_6$D$_6$) δ = 13.1. Anal. Calcd for C$_{26}$H$_{43}$B$_3$O$_6$: C, 67.77; H, 7.58; N, 5.85. Found: C, 68.12; H, 7.71; N, 5.69.

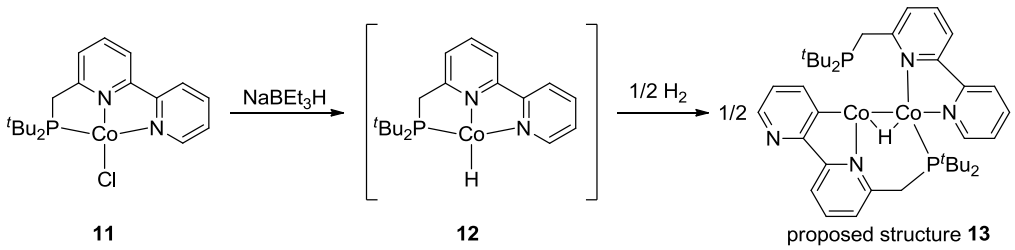


Selected Bond Length for Complex **14**

Selected Bond Length	Distance(Å)
Co1–P1	2.1558(9)
Co1–N1	1.932(2)
Co1–N2	1.865(2)
Co1–C20	1.980(3)

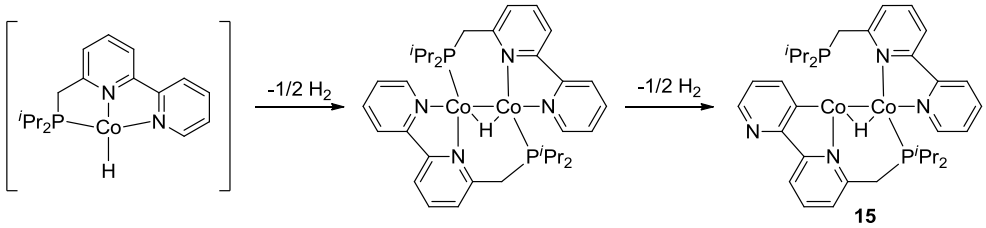
Selected Bond Angles for Complex **14**

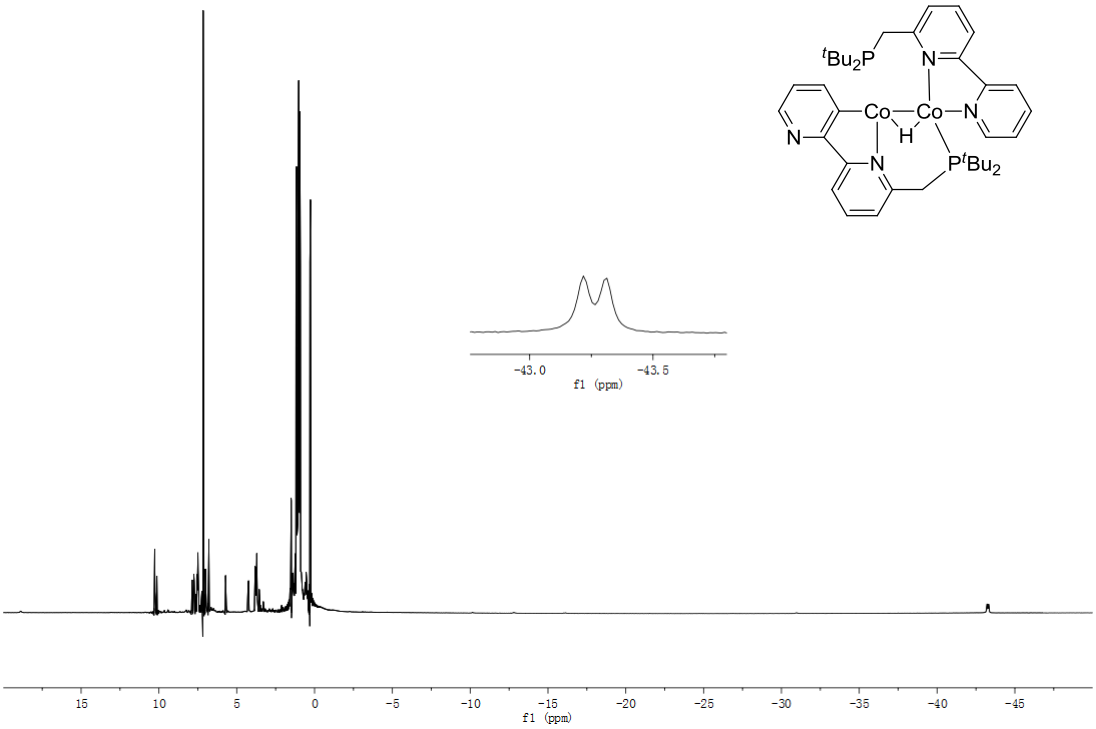
Selected Bond Angles	(deg)
N1–Co1–P1	167.64(8)
N1–Co1–C20	94.65(11)
N2–Co1–P1	86.10(7)
N2–Co1–N1	81.61(10)
N2–Co1–C20	173.45(11)
C20–Co1–P1	97.70(9)



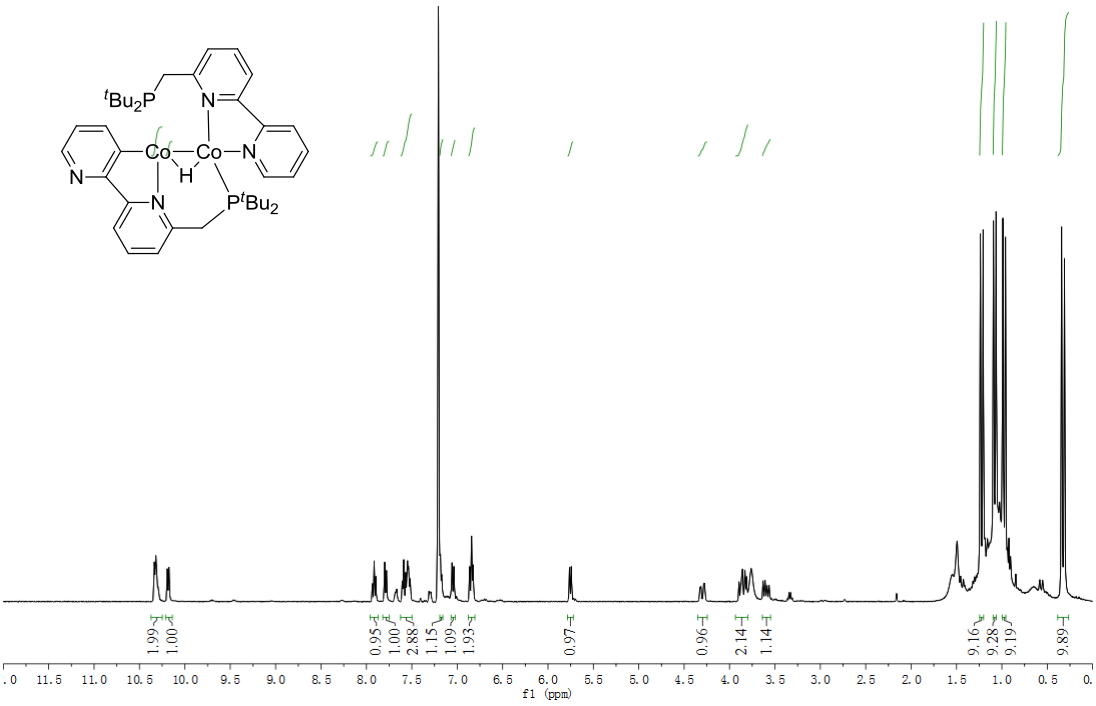
($^{t\mathrm{Bu}}$PNN)CoCl (11) + NaBEt$_3$H: In a nitrogen filled glovebox, the Co(I) monochloride complex ($^{t\mathrm{Bu}}$PNN)CoCl **11** (122.6 mg, 0.3 mmol) and pentane (6 mL) were added to a 50 mL Schlenk tube equipped with a magnetic stir bar. The resulting mixture was chilled in the freezer to −35 ℃ and NaBEt$_3$H (300 μL, 0.3 mmol, 1 equiv) was added dropwisely. The reaction solution was stirred for 15 min at ambient temperature and followed by filtration through celite. The volatiles were removed in vacuo and black solid was obtained. ^{1}H NMR analysis revealed the formation of a diamagnetic, C_1 symmetric μ-hydride dicobalt complex **13** (40%)**.** We proposed that the reaction of **11** with one equiv of NaBEt$_3$H generated a Co(I) hydride complex **12**, which was instable and decomposed under the reaction conditions to yield the μ-hydride dicobalt complex **13.** The ^{31}P and ^{1}H NMR resonances of **13** are very similar to those of a closely relevant $^{i\mathrm{Pr}}$PNN-ligated μ-hydride dicobalt complex **15** (see below). Chirik proposed a *i*Pr-substituted Co(I) hydride complex ($^{i\mathrm{Pr}}$PNN)CoH underwent loss of H_2 to form [($^{i\mathrm{Pr}}$PNN)Co]$_2$(μ_2-H), which then underwent cyclometallation of one pincer ligand to give a C_1 symmetric μ-hydride dicobalt complex **15**.[4] We proposed that our *t*Bu-substituted analogue **12** was converted to the C_1 symmetric μ-hydride dicobalt complex **13** through a similar pathway. ^{1}H NMR of complex **13** (400 MHz, C_6D_6) δ = 11.35 – 11.27 (m, 2H, aryl-*H*), 10.18 (d, *J* = 7.2 Hz, 1H, aryl-*H*), 7.91 (t, *J* = 7.6 Hz, 1H, aryl-*H*), 7.79 (d, *J* = 7.6 Hz, 1H, aryl-*H*), 7.62 – 7.51 (m, 3H, aryl-*H*), 7.18 (d, *J* = 6.7 Hz, 1H, aryl-*H*), 7.05 (d, *J* = 8.2 Hz, 1H, aryl-*H*), 6.84 (t, *J* = 7.2 Hz, 2H, aryl-*H*), 5.75 (d, *J* = 7.9 Hz, 1H, aryl-*H*), 4.30 (dd, *J* = 16.1, 4.2 Hz, 1H, PC*H*$_2$), 3.91 – 3.80 (m, 2H, PC*H*$_2$), 3.60 (dd, *J* = 17.8, 8.9 Hz, 1H, PC*H*$_2$), 1.22 (d, *J* = 12.2 Hz, 9H, C(C*H*$_3$)$_3$), 1.08 (d, *J* = 11.6 Hz, 9H, C(C*H*$_3$)$_3$), 0.97 (d, *J* =

11.5 Hz, 9H, C(C*H*$_3$)$_3$), 0.33 (d, *J* = 12.6 Hz, 9H, C(C*H*$_3$)$_3$), -43.26 (d, *J* = 36.3 Hz, 1H, Co-*H*). ^{31}P{^{1}H} NMR of complex **13** (162 MHz, C_6D_6) δ = 106.3, 71.7.

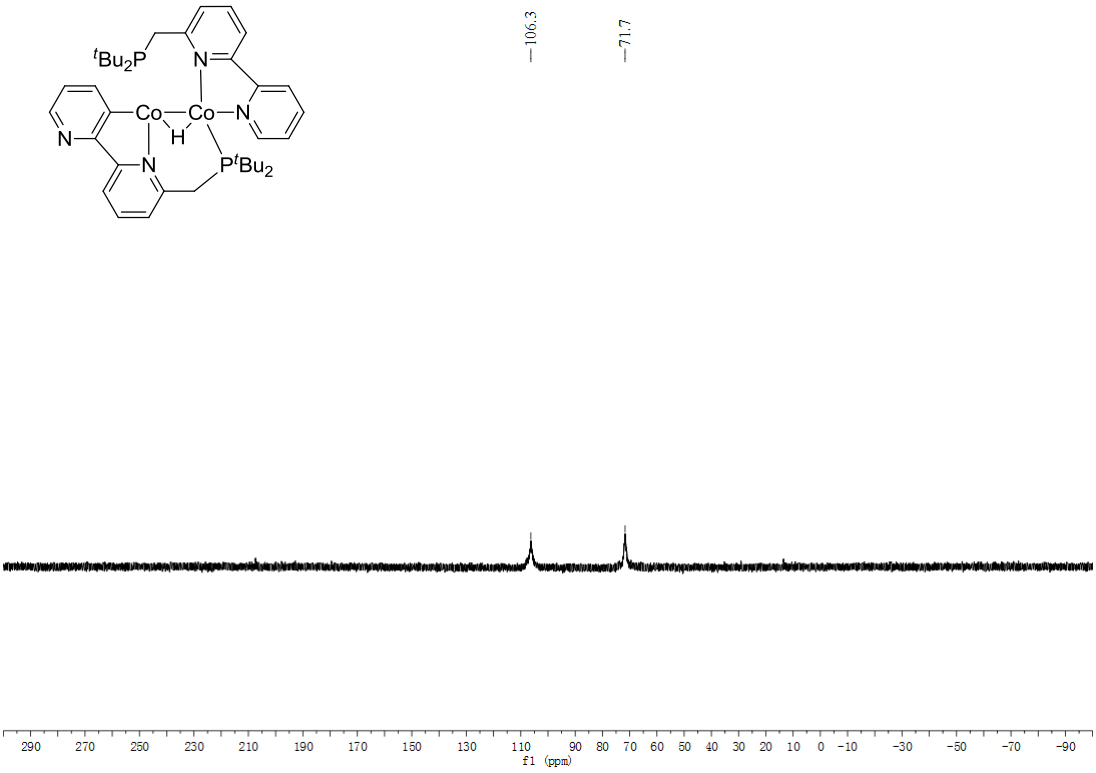




^{1}H NMR (400 MHz, C_6D_6) of **13** (From 20 to -50 ppm)



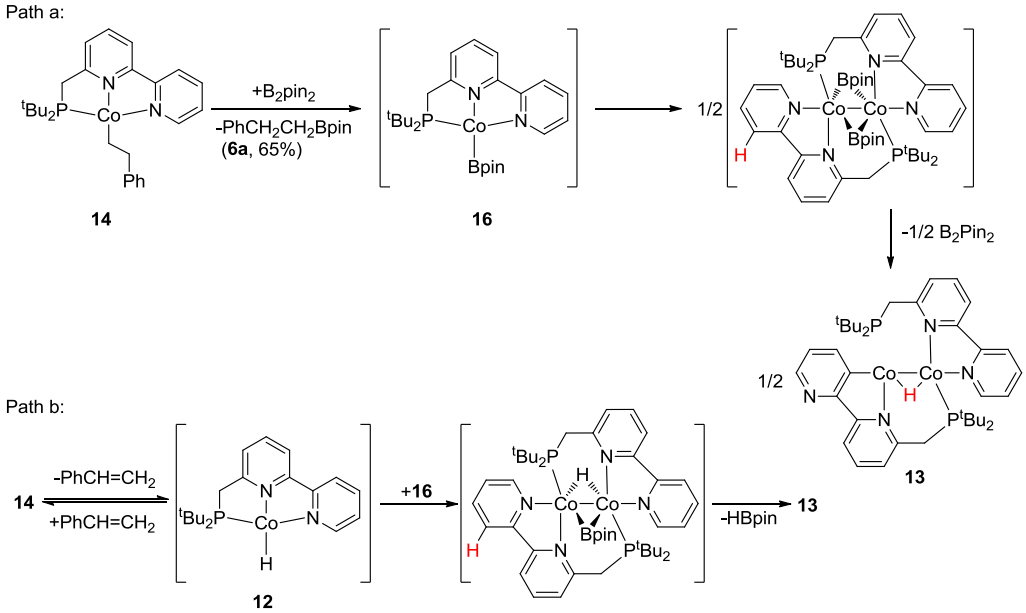
^{1}H NMR (400 MHz, C_6D_6) of **13** (From 11 to 0 ppm)



^{31}P NMR (162 MHz, C_6D_6) of **13**

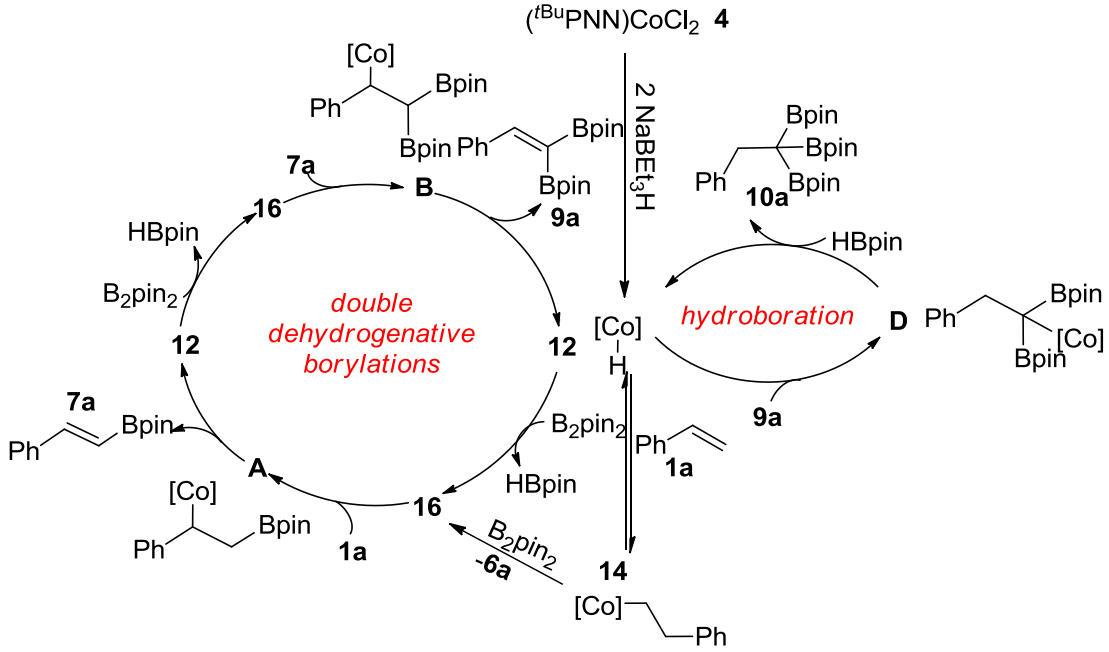
($^{t\mathrm{Bu}}$PNN)CoCH$_2$CH$_2$Ph (14) + B$_2$pin$_2$: In a nitrogen filled glovebox, the Co(I) complex ($^{t\mathrm{Bu}}$PNN)CoCH$_2$CH$_2$Ph **14** (14.4 mg, 0.03 mmol), B$_2$pin$_2$ (7.6 mg, 0.03 mmol, 1 equiv), mesitylene as an internal standard (2.7 mg) and C$_6$D$_6$ (0.5 mL) were added to a vial equipped with a magnetic stir bar. The reaction solution was stirred for 30 min at ambient temperature and followed by filtration through celite. ^{1}H NMR analysis of the resulting dark solution showed that the reaction formed **6a** (65% NMR yield), the μ-hydride dicobalt complex **13** (54% NMR yield), and other unidentified species. Based on the stoichiometry of this reaction, we proposed that the initial Co product was likely a Co(I) boryl species **16** formed via transmetallation, which was unstable and might decompose bimolecularly to form **13** (Scheme S1, path a). Alternatively, ($^{t\mathrm{Bu}}$PNN)CoBpin (**16**) may react with ($^{t\mathrm{Bu}}$PNN)CoH **12** derived from de-insertion of styrene from **14** (The deuterium labeling experiment suggests that the reaction of ($^{t\mathrm{Bu}}$PNN)CoH **12** with styrene to form **14** is reversible), to give a μ-hydride, μ-boryl dicobalt product [($^{t\mathrm{Bu}}$PNN)Co]$_2$(μ_2-H)(μ_2-Bpin). Note that the *i*Pr-substituted analogue [($^{i\mathrm{Pr}}$PNN)Co]$_2$(μ_2-H)(μ_2-Bpin) has been previously reported.[4] Complex [($^{t\mathrm{Bu}}$PNN)Co]$_2$(μ_2-H)(μ_2-Bpin) then may undergo loss of HBpin, followed by cyclometallation of the pincer ligand to give complex **13** (Scheme S1, path b).

Scheme S1. Proposed pathways for the decomposition of complex 16 and the formation of complex 13

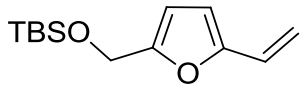


3. Alternative Mechanism

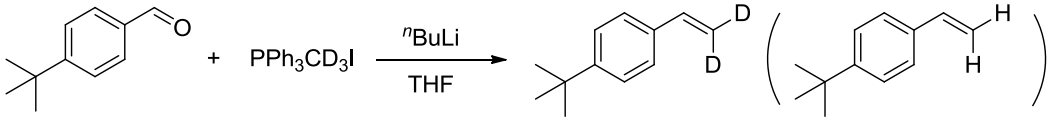
Scheme S2. Alternative Mechanism



4. Preparation of Substrates

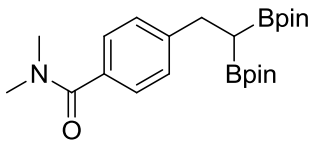


tert-butyldimethyl((5-vinylfuran-2-yl)methoxy)silane (1t). Prepared by Wittig olefination of the corresponding ketone according to a previously reported procedure.[5] Colorless oil (1.96 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.48 (dd, *J* = 17.5, 11.3 Hz, 1H, C*H*=CH_2), 6.20 (dd, *J* = 14.3, 3.2 Hz, 2H, CH=CH_2), 5.66 (dd, *J* = 17.5, 1.2 Hz, 1H, aryl-*H*), 5.14 (dd, *J* = 11.3, 1.3 Hz, 1H, aryl-*H*), 4.66 (s, 2H, ArCH_2), 0.94 (s, 9H, C(CH_3)$_3$), 0.12 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 152.8, 125.2, 112.0, 109.0, 108.9, 58.4 (Ar*C*H_2), 26.0 (C(*C*H_3)$_3$), 18.6 (*C*(CH_3)$_3$), -5.1 (Si(*C*H_3)$_2$). HRMS-EI (*m/z*): Calcd for [$C_{13}H_{22}O_2Si$+], 238.1389; found: 238.1390.



1c-*D*$_2$ Contain 11% 4-*tert*-butylstyrene **1c**

4-*tert*-butylstyrene-*β*,*β*-D$_2$ (1c-*D*$_2$). Prepared by Wittig olefination of the corresponding ketone with PPh_3CD_3I according to a previously reported procedure.[5] Colorless oil (1.23 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (s, 4H, aryl-*H*), 6.70 (s, 1H, ArC*H*), 1.34 (s, 9H, C(CH_3)$_3$).

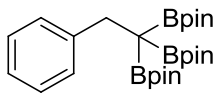


4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-N,N-dimethylbenzamide (10s'). 1,1,1-tris(boronates) **10s** (166.5 mg, 0.30 mmol), CsF (135.9 mg, 0.90 mmol, 3.0 equiv) and THF (1.5 mL) were added to a vial equipped with a magnetic stir bar. The reaction was stirred for 11 h at ambient temperature. The resulting solution was

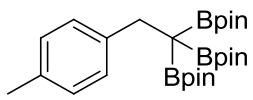
diluted with *n*-hexane (2 mL) and filtered through celite. The filter liquor was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/hexane (1:1) to give product as white solid (120.3 mg, 93%). M. P. 96-98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.24 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 3.06 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.87 (d, *J* = 8.3 Hz, 2H, ArCH_2), 1.12 (s, 24H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 (*C*=O), 146.1 (aryl-*C*), 133.2 (aryl-*C*), 128.1 (aryl-*C*), 126.8 (aryl-*C*), 83.0 (O*C*(CH_3)$_2$), 39.5 (N*C*H_3), 35.2 (N*C*H_3), 31.1 (Ar*C*H_2), 24.7 (C(*C*H_3)$_2$), 24.4 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.0. HRMS-EI (*m/z*): Calcd for [($C_{23}H_{37}B_2NO_5$+H)+], 428.3003; found: 429.2961.

5. Synthesis of 1,1,1-tris(boronates)

General procedure for synthesis of 1,1,1-tris(boronates) from vinylarenes by Co-catalyzed dehydrogenative borylations-hydroboration: In a nitrogen filled glovebox, complex **4** (4.4 mg, 0.01 mmol, 2 mol %) and B_2pin_2 (254 mg, 1 mmol, 2.0 equiv), vinylarene **1a** (52 mg, 0.5 mmol), pentane (5 mL) and $NaBEt_3H$ (20 μL, 1.0 M in THF, 4 mol %) were added to a 8 mL vial equipped with a magnetic stir bar. The reaction was stirred for 12 h at ambient temperature and quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/hexane to give product as white solid.

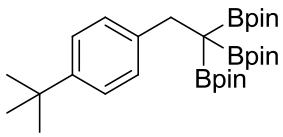


2,2',2''-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10a). White solid (224.8 mg, 93%). M. P. 95 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 7.15 (dd, *J* = 10.2, 4.7 Hz, 2H, aryl-*H*), 7.06 (t, *J* = 7.3 Hz, 1H, aryl-*H*), 3.14 (s, 2H, ArCH_2), 1.16 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2 (aryl-*C*), 129.5 (aryl-*C*), 127.2 (aryl-*C*), 125.0 (aryl-*C*), 82.9 (O*C*(CH_3)$_2$), 33.3 (Ar*C*H_2), 24.6 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.2. Anal. Calcd for $C_{26}H_{43}B_3O_6$: C, 64.51; H, 8.95. Found: C, 64.83; H, 8.95.

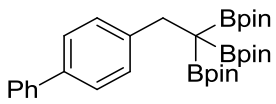


2,2',2''-(2-(p-tolyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10b). White solid (233.8 mg, 94%). M. P. 102-103 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 6.96 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 3.10 (s, 2H, ArCH_2), 2.26 (s, 3H, ArCH_3), 1.16 (s, 36H, C(CH_3)$_2$). ^{13}C

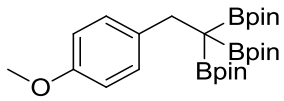
NMR (101 MHz, $CDCl_3$) δ 141.0 (aryl-*C*), 134.0 (aryl-*C*), 129.3 (aryl-*C*), 127.8 (aryl-*C*), 82.9 (O*C*$(CH_3)_2$), 32.8 (Ar*C*H_2), 24.6 (C(*C*$H_3)_2$), 21.0 (Ar*C*H_3). ^{11}B NMR (193 MHz, EtOAc) δ = 34.2. Anal. Calcd for $C_{27}H_{45}B_3O_6$: C, 65.11; H, 9.11. Found: C, 65.30; H, 9.16.



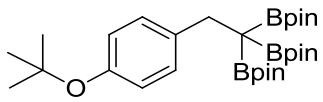
2,2',2''-(2-(4-(tert-butyl)phenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10c). White solid (252.6 mg, 94%). M. P. 120-122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.17 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 3.10 (s, 2H, ArCH_2), 1.26 (s, 9H, ArC(C$H_3)_3$), 1.16 (s, 36H, C(C$H_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7 (aryl-*C*), 141.4 (aryl-*C*), 129.3 (aryl-*C*), 124.2 (aryl-*C*), 83.0 (O*C*$(CH_3)_2$), 34.3 (Ar*C*(CH_3)), 32.8 (Ar*C*H_2), 31.6 (ArC(*C*$H_3)_3$), 24.7 (C(*C*$H_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.9. Anal. Calcd for $C_{30}H_{51}B_3O_6$: C, 66.71; H, 9.52. Found: C, 66.70; H, 9.40.



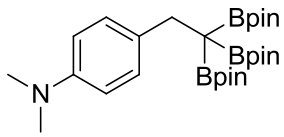
2,2'-(2-(m-tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10d). White solid (264.2 mg, 94%). M. P. 166-168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (dd, *J* = 7.6 Hz, 2H, aryl-*H*), 7.51 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.47-7.40 (m, 4H, aryl-*H*), 7.34-7.29 (m, 1H, aryl-*H*), 3.23 (s, 2H, ArCH_2), 1.21 (s, 36H, C(C$H_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (aryl-*C*), 141.6 (aryl-*C*), 137.8 (aryl-*C*), 130.0 (aryl-*C*), 128.6 (aryl-*C*), 126.9 (aryl-*C*), 126.7 (aryl-*C*), 125.9 (aryl-*C*), 83.0 (O*C*$(CH_3)_2$), 32.9 (Ar*C*H_2), 24.6 (C(*C*$H_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. Anal. Calcd for $C_{32}H_{47}B_3O_6$: C, 68.61; H, 8.46. Found: C, 68.87; H, 8.46.



2,2',2''-(2-(4-methoxyphenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10e). White solid (230.0 mg, 89%). M. P. 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 6.70 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 3.73 (s, 3H, ArOC*H*$_3$), 3.05 (s, 2H, ArC*H*$_2$), 1.15 (s, 36H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2 (aryl-*C*), 136.5 (aryl-*C*), 130.5 (aryl-*C*), 112.5 (aryl-*C*), 82.9 (O*C*(CH$_3$)$_2$), 55.2 (ArO*C*H$_3$), 32.3 (Ar*C*H$_2$), 24.6 (C(*C*H$_3$)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.4. Anal. Calcd for $C_{27}H_{47}B_3O_7$: C, 63.08; H, 8.82. Found: C, 63.22; H, 8.83.

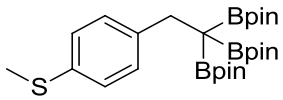


2,2',2''-(2-(4-(tert-butoxy)phenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10f). White solid (269.6 mg, 97%). M. P. 88-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 6.78 (d, *J* = 8.4 Hz, 2H, aryl-*H*), 3.07 (s, 2H, ArC*H*$_2$), 1.27 (s, 9H, ArOC(C*H*$_3$)$_3$), 1.15 (s, 36H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4 (aryl-*C*), 139.5 (aryl-*C*), 129.9 (aryl-*C*), 123.3 (aryl-*C*), 82.9 (O*C*(CH$_3$)$_2$), 32.6 (Ar*C*H$_2$), 28.8 (ArOC(*C*H$_3$)$_3$), 24.6 (C(*C*H$_3$)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.2. Anal. Calcd for $C_{30}H_{51}B_3O_7$: C, 64.79; H, 9.24. Found: C, 64.83; H, 9.11.

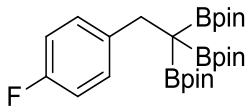


N,N-dimethyl-4-(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)aniline (10g). White solid (217.7 mg, 83%). M. P. 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 6.61 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 3.04 (s,

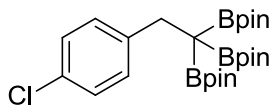
2H, ArCH_2), 2.84(s, 6H, ArN(CH_3)$_2$), 1.16 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8 (aryl-*C*), 133.3 (aryl-*C*), 130.2 (aryl-*C*), 112.7 (aryl-*C*), 82.8 (O*C*(CH_3)$_2$), 41.4 (ArN(*C*H_3)$_2$), 32.2 (Ar*C*H_2), 24.7 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. Anal. Calcd for $C_{28}H_{48}B_3NO_6$: C, 63.80; H, 9.18; N, 2.66. Found: C, 64.15; H, 9.29; N, 2.56.



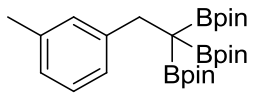
2,2',2''-(2-(4-(methylthio)phenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10h). White solid (258.4 mg, 97%). M. P. 85-86 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.09 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 3.07 (s, 2H, ArCH_2), 2.41 (s, 3H, ArSCH_3), 1.15 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9 (aryl-*C*), 133.9 (aryl-*C*), 130.2 (aryl-*C*), 126.7 (aryl-*C*), 83.0 (O*C*(CH_3)$_2$), 32.8 (Ar*C*H_2), 24.7 (C(*C*H_3)$_2$), 17.0 (ArS*C*H_3). ^{11}B NMR (193 MHz, EtOAc) δ = 34.4. Anal. Calcd for $C_{27}H_{45}B_3O_6S$: C, 61.17; H, 8.56. Found: C, 61.31; H, 8.62.



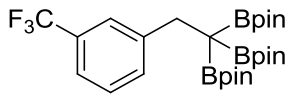
2,2',2''-(2-(4-fluorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10i). White solid (236.5 mg, 94%). M. P. 105-106 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (dd, *J* = 8.2, 5.9 Hz, 2H, aryl-*H*), 6.80 (t, *J* = 8.8 Hz, 2H, aryl-*H*), 3.05 (s, 2H, ArCH_2), 1.13 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (d, *J* = 241.8 Hz, aryl-*C*), 139.8 (d, *J* = 3.1 Hz, aryl-*C*), 131.0 (d, *J* = 7.5 Hz, aryl-*C*), 113.6 (d, *J* = 20.6 Hz, aryl-*C*), 82.9 (O*C*(CH_3)$_2$), 32.4 (Ar*C*H_2), 24.5 (C(*C*H_3)$_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -119.4. ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. Anal. Calcd for $C_{26}H_{42}B_3FO_6$: C, 62.20 H, 8.43. Found: C, 62.34; H, 8.47.



2,2',2''-(2-(4-chlorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10j). The reaction used 3 mol % of **4** and 6 mol % of $NaBEt_3H$. White solid (226.7 mg, 87%). M. P. 130-131 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.4 Hz, 2H, aryl-*H*), 7.10 (d, *J* = 8.4 Hz, 2H, aryl-*H*), 3.06 (s, 2H, ArCH_2), 1.14 (s, 36H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8 (aryl-*C*), 131.0 (aryl-*C*), 130.6 (aryl-*C*), 127.1 (aryl-*C*), 83.1 ($OC(CH_3)_2$), 32.6 ($ArCH_2$), 24.6 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.4. Anal. Calcd for $C_{26}H_{42}B_3ClO_6$: C, 60.23; H, 8.16. Found: C, 60.45; H, 8.30.

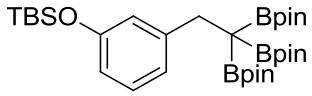


2,2',2''-(2-(m-tolyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10k). White solid (239.4 mg, 96%). M. P. 84-85 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.22-7.14 (m, 2H, aryl-*H*), 7.04 (t, *J* = 7.5 Hz, 1H, aryl-*H*), 6.88 (d, *J* = 7.4 Hz, 1H, aryl-*H*), 3.11 (s, 2H, ArCH_2), 2.26 (s, 3H, ArCH_3), 1.16 (s, 36H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2 (aryl-*C*)，136.4 (aryl-*C*)，130.2 (aryl-*C*), 127.3 (aryl-*C*), 126.7 (aryl-*C*), 125.7 (aryl-*C*), 83.0 ($OC(CH_3)_2$), 33.2 ($ArCH_2$), 24.7 ($C(CH_3)_2$), 21.0 ($ArCH_3$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. Anal. Calcd for $C_{27}H_{45}B_3O_6$: C, 65.11; H, 9.11. Found: C, 65.36; H, 9.33.

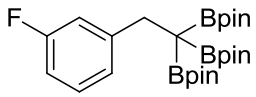


2,2',2''-(2-(3-(trifluoromethyl)phenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10l). The reaction used 5 mol % of **4** and 10 mol % of $NaBEt_3H$. White solid (204.1 mg, 74%). M. P. 132-133 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H, aryl-*H*), 7.57 (d, *J* = 7.6 Hz, 1H, aryl-*H*), 7.33 (d, *J* = 7.7 Hz, 1H, aryl-*H*), 7.25

(t, *J* = 7.7 Hz, 1H, aryl-*H*), 3.15 (s, 2H, ArCH_2), 1.15 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2 (aryl-*C*), 133.5 (aryl-*C*), 129.4 (q, *J* = 31.5 Hz, aryl-*C*), 127.3 (aryl-*C*), 126.3 (q, *J* = 3.8 Hz, aryl-*C*), 124.6 (q, *J* = 273.4 Hz, aryl-*C*), 121.8 (q, *J* = 3.9 Hz, aryl-*C*), 83.1 (O*C*(CH_3)$_2$), 33.1 (Ar*C*H_2), 24.5 (C(*C*H_3)$_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.4. ^{11}B NMR (193 MHz, EtOAc) δ = 33.9. Anal. Calcd for $C_{27}H_{42}B_3F_3O_6$: C, 58.74; H, 7.67. Found: C, 58.70; H, 7.69.

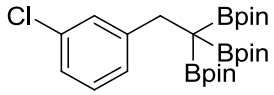


***tert*-butyldimethyl(3-(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl) phenoxy)silane (10m).** White solid (301.7 mg, 98 %). M. P. 73-74 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02-6.90 (m, 3H, aryl-*H*), 6.54 (d, *J* = 7.4 Hz, 1H, aryl-*H*), 3.07 (s, 2H, ArCH_2), 1.16 (s, 36H, C(CH_3)$_2$)，0.96 (s, 9H, SiC(CH_3)$_3$), 0.16 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (aryl-*C*)，145.9 (aryl-*C*)，127.7 (aryl-*C*), 122.7 (aryl-*C*), 121.3 (aryl-*C*), 116.0 (aryl-*C*), 82.8 (O*C*(CH_3)$_2$), 33.1 (Ar*C*H_2), 25.6 (SiC(*C*H_3)$_3$), 24.5 (C(*C*H_3)$_2$), 18.0 (Si*C*(CH_3)$_3$), -4.5 (Si(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.8. Anal. Calcd for $C_{32}H_{57}B_3O_7Si$: C, 62.56; H, 9.35. Found: C, 62.86; H, 9.46.

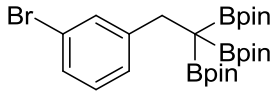


2,2',2''-(2-(3-fluorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10n). White solid (228.3 mg, 91%). M. P. 108-109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18-7.06 (m, 3H, aryl-*H*), 6.76 (t, *J* = 7.9 Hz, 1H, aryl-*H*), 3.11 (s, 2H, ArCH_2), 1.16 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 242.8 Hz, aryl-*C*), 147.1 (d, *J* = 7.2 Hz, aryl-*C*), 128.4 (d, *J* = 8.3 Hz, aryl-*C*), 125.4 (d, *J* = 2.6 Hz, aryl-*C*), 116.3 (d, *J* = 21.2 Hz, aryl-*C*), 111.7 (d, *J* = 21.0 Hz, aryl-*C*), 83.1 (O*C*(CH_3)$_2$), 33.1 (Ar*C*H_2), 24.6 (C(*C*H_3)$_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -115.7.

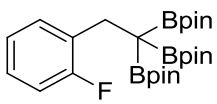
^{11}B NMR (193 MHz, EtOAc) δ = 33.4. Anal. Calcd for $C_{26}H_{42}B_3FO_6$: C, 62.20; H, 8.43. Found: C, 61.88; H, 8.61.



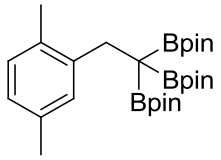
2,2',2''-(2-(3-chlorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10o). The reaction used 5 mol % of **4** and 10 mol % of $NaBEt_3H$. White solid (106.4 mg, 90%). M. P. 131-133 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (s, 1H, aryl-*H*), 7.27 (d, *J* = 8.1 Hz, 1H, aryl-*H*), 7.11-7.03 (m, 2H, aryl-*H*), 3.09 (s, 2H, ArCH_2), 1.17 (s, 36H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4 (aryl-*C*)，133.0 (aryl-*C*)， 129.7 (aryl-*C*), 128.4 (aryl-*C*), 128.1 (aryl-*C*), 125.0 (aryl-*C*), 83.1 ($OC(CH_3)_2$), 33.0 ($ArCH_2$), 24.6 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.9. Anal. Calcd for $C_{26}H_{42}B_3ClO_6$: C, 60.23; H, 8.16. Found: C, 60.04; H, 8.25.



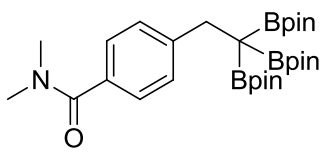
2,2',2''-(2-(3-bromophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10p). The reaction used 5 mol % of **4** and 10 mol % of $NaBEt_3H$. White solid (130.3 mg, 46%). M. P. 128-130 ^oC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (s, 1H, aryl-*H*), 7.27 (d, *J* = 7.6 Hz, 1H, aryl-*H*), 7.19 (d, *J* = 7.8 Hz, 1H, aryl-*H*), 7.01 (t, *J* = 7.8 Hz, 1H, aryl-*H*), 3.07 (s, 2H, ArCH_2), 1.17 (s, 36H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7 (aryl-*C*)，132.5 (aryl-*C*)， 128.7 (aryl-*C*), 128.5 (aryl-*C*), 127.9 (aryl-*C*), 121.4 (aryl-*C*), 83.1 ($OC(CH_3)_2$), 32.9 ($ArCH_2$), 24.6 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.9. Anal. Calcd for $C_{26}H_{42}B_3BrO_6$: C, 55.47; H, 7.52. Found: C, 55.62; H, 7.51.



2,2',2''-(2-(2-fluorophenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10q). White solid (236.0 mg, 94%). M. P. 139-140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (t, *J* = 7.4 Hz, 1H, aryl-*H*), 7.04 (dd, *J* = 13.1, 5.8 Hz, 1H, aryl-*H*), 6.96-6.86 (m, 2H, aryl-*H*), 3.14 (s, 2H, ArCH_2), 1.16 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 244.3 Hz, aryl-*C*), 131.2 (d, *J* = 15.5 Hz, aryl-*C*), 130.1 (d, *J* = 4.9 Hz, aryl-*C*), 126.2 (d, *J* = 8.2 Hz, aryl-*C*), 122.7 (d, *J* = 3.4 Hz, aryl-*C*), 114.2 (d, *J* = 23.1 Hz, aryl-*C*), 83.0 (O*C*(CH_3)$_2$), 25.1 (d, *J* = 3.6 Hz, Ar*C*H_2), 24.6 (C(*C*H_3)$_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -115.7. ^{11}B NMR (193 MHz, EtOAc) δ = 34.2. Anal. Calcd for $C_{26}H_{42}B_3FO_6$: C, 62.20; H, 8.43. Found: C, 62.25; H, 8.33.

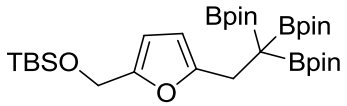


2,2',2''-(2-(2,5-dimethylphenyl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10r). White solid (239.2 mg, 93%). M. P. 96-97 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (s, 1H, aryl-*H*), 6.94 (d, *J* = 7.5 Hz, 1H, aryl-*H*), 6.79 (d, *J* = 7.5 Hz, 1H, aryl-*H*), 3.05 (s, 2H, ArCH_2), 2.28 (s, 3H, ArCH_3), 2.22 (s, 3H, ArCH_3), 1.17 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9 (aryl-*C*)，133.8 (aryl-*C*)， 133.7 (aryl-*C*), 129.1 (aryl-*C*), 128.3 (aryl-*C*), 125.1 (aryl-*C*), 82.9 (O*C*(CH_3)$_2$), 30.0 (Ar*C*H_2), 24.7 (C(*C*H_3)$_2$), 21.1 (Ar*C*H_3), 19.7 (Ar*C*H_3). ^{11}B NMR (193 MHz, EtOAc) δ = 34.6. Anal. Calcd for $C_{28}H_{47}B_3O_6$: C, 65.67; H, 9.25. Found: C, 65.98; H, 9.32.

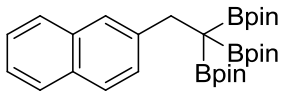


N,N-dimethyl-4-(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzamide (10s). White solid (168.0 mg, 61%). M. P. 148-150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.20 (dd, *J* = 8.2, 1.7 Hz, 2H, aryl-*H*),

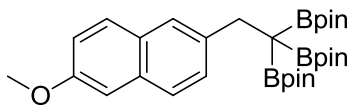
3.10 (s, 2H, ArCH_2), 3.03 (s, 3H, NCH_3), 2.91 (s, 3H, NCH_3), 1.12 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 (*C*=O), 146.1 (aryl-*C*), 132.8 (aryl-*C*), 129.3 (aryl-*C*), 126.2 (aryl-*C*), 83.0 (O*C*(CH_3)$_2$), 39.6 (N*C*H_3), 35.4 (N*C*H_3), 33.2 (Ar*C*H_2), 24.6 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.8. Anal. Calcd for $C_{29}H_{48}B_3NO_7$: C, 62.74; H, 8.72; N, 2.52. Found: C, 62.90; H, 8.44; N, 2.42.



tert-butyldimethyl((5-(2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)furan-2-yl)methoxy)silane (10t). White solid (251.0 mg, 81%). M. P. 100-101 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.03 (d, *J* = 3.0 Hz, 1H, aryl-*H*), 5.91 (d, *J* = 2.9 Hz, 1H, aryl-*H*), 4.54 (s, 2H, ArOCH_2), 3.03 (s, 2H, ArCH_2), 1.17 (s, 36H, C(CH_3)$_2$), 0.88 (s, 9H, C(CH_3)$_3$), 0.04 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (aryl-*C*)，151.2 (aryl-*C*)，107.8 (aryl-*C*), 105.4 (aryl-*C*), 83.0 (O*C*(CH_3)$_2$), 58.4 (ArOCH_2), 26.4 (Ar*C*H_2), 26.0 (C(*C*H_3)$_3$), 24.6 (C(*C*H_3)$_2$), 18.4 (*C*(CH_3)$_3$), -5.1 (Si(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.8. Anal. Calcd for $C_{31}H_{47}B_3O_7$: C, 60.22; H, 9.29. Found: C, 66.23; H, 9.28.

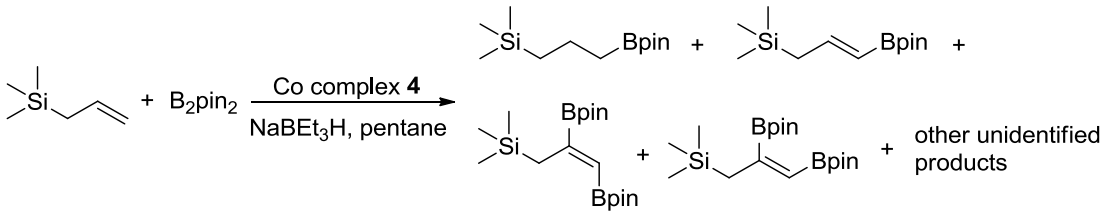


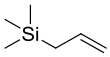
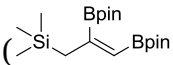
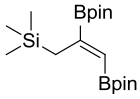
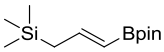
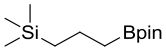
2,2',2''-(2-(naphthalen-2-yl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10v). White solid (247.4 mg, 93%). M. P. 176-178 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79-7.73 (m, 2H, aryl-*H*), 7.68 (dd, *J* = 12.8, 7.9 Hz, 2H, aryl-*H*), 7.57 (dd, *J* = 8.5, 1.4 Hz, 1H, aryl-*H*), 7.41-7.32 (m, 2H, aryl-*H*), 3.32 (s, 2H, ArCH_2), 1.17 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (aryl-*C*)，133.4 (aryl-*C*)，131.8 (aryl-*C*), 129.2 (aryl-*C*), 127.5 (aryl-*C*), 126.9 (aryl-*C*), 126.5 (aryl-*C*), 125.3 (aryl-*C*), 124.5 (aryl-*C*), 83.1 (O*C*(CH_3)$_2$), 33.6 (Ar*C*H_2), 24.7 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.5. Anal. Calcd for $C_{30}H_{45}B_3O_6$: C, 67.46; H, 8.49. Found: C, 67.38; H, 8.47.



2,2',2''-(2-(6-methoxynaphthalen-2-yl)ethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10w). White solid (266.7 mg, 95%). M. P. 142-143 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 1H, aryl-*H*), 7.61-7.51 (m, 3H, aryl-*H*), 7.08-7.02 (m, 2H, aryl-*H*), 3.89 (s, 3H, ArOCH_3), 3.28 (s, 2H, ArCH_2), 1.16 (s, 36H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (aryl-*C*)，139.5 (aryl-*C*)，129.5 (aryl-*C*), 128.8 (aryl-*C*), 128.7 (aryl-*C*), 126.8 (aryl-*C*), 125.3 (aryl-*C*), 117.9 (aryl-*C*), 105.4 (aryl-*C*), 82.9 (O*C*(CH_3)$_2$), 55.1 (ArOCH_3), 33.2 (Ar*C*H_2), 24.6 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. Anal. Calcd for $C_{31}H_{47}B_3O_7$: C, 66.00; H, 8.40. Found: C, 66.08; H, 8.38.

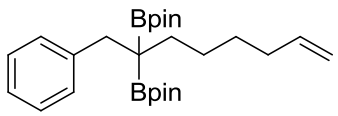
Attempted synthesis of 1,1,1-tris(boronates) from vinylalkane



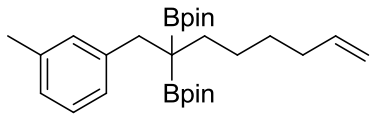
When aliphatic alkene  was used as the substrate, the products were complicated. A mixture of diborylalkene products ( (8% NMR yield),  (23% NMR yield)), monoboryl-substituted products ( (17% NMR yield),  (18% NMR yield)) and other unidentified products were observed by GC- MS and ^{1}H NMR analysis. [6]

6. Deborylative Alkylation of 1,1,1-tris(boronates)

General procedure for deborylative alkylation of 1,1,1-tris(boronates): In a nitrogen filled glovebox, 1,1,1-tris(boronates) **10a** (266.2 mg, 0.55 mmol, 1.1 equiv) and NaOMe (40.5 mg, 0.75 mmol, 1.5 equiv), THF (1 mL) and 6-bromo-1-hexene (81.5 mg, 0.5 mmol) were added to a 8 mL vial equipped with a magnetic stir bar. The reaction was stirred for 1 h at ambient temperature. The resulting solution was diluted with *n*-hexane (2 mL) and filtered through celite. The filter liquor was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/hexane to give product as white solid.

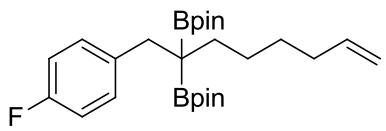


2,2'-(1-phenyloct-7-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13a). White solid (201.6 mg, 92%). M. P. 77-79 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.18 (m, 4H, aryl-*H*), 7.15-7.10 (m, 1H, aryl-*H*), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, $CH_2CH{=}CH_2$), 5.02-4.90 (m, 2H, $CH_2CH{=}CH_2$), 2.99 (s, 2H, $ArCH_2$), 2.09-2.01 (m, 2H), 1.57-1.51 (m, 2H), 1.41-1.34 (m, 4H), 1.26 (s, 12H, $C(CH_3)_2$) , 1.22 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9 (aryl-*C*), 139.3 ($CH{=}CH_2$), 129.8 (aryl-*C*), 127.8 (aryl-*C*), 125.5 (aryl-*C*), 114.1 ($CH{=}CH_2$), 83.2 ($OC(CH_3)_2$), 34.6 ($ArCH_2$), 33.9 ($CH_2CH{=}CH_2$), 29.6, 28.6, 26.8, 25.1 ($C(CH_3)_2$), 24.8 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 33.6. HRMS-ESI (*m/z*): Calcd for [($C_{26}H_{42}B_2O_4$+NH_4)+], 456.3680; found: 456.3680.

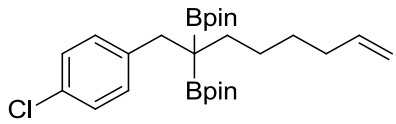


2,2'-(1-(m-tolyl)oct-7-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13b). White solid (200.9 mg, 88%). M. P. 70-72 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ =

7.14-7.09 (m, 2H, aryl-*H*), 7.03 (d, *J* = 7.6 Hz, 1H, aryl-*H*), 6.95 (d, *J* = 7.5 Hz, 1H, aryl-*H*), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, $CH_2CH{=}CH_2$), 5.09-4.91 (m, 2H, $CH_2CH{=}CH_2$), 2.97 (s, 2H, $ArCH_2$), 2.30 (s, 3H, $ArCH_3$), 2.10-2.03 (m, 2H), 1.58-1.51 (m, 2H), 1.43-1.36 (m, 4H), 1.27 (s, 12H, $C(CH_3)_2$), 1.23 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8 (aryl-*C*), 139.3 ($CH{=}CH_2$), 136.9 (aryl-*C*), 130.5 (aryl-*C*), 127.6 (aryl-*C*), 126.8 (aryl-*C*), 126.2 (aryl-*C*), 114.1 ($CH{=}CH_2$), 83.2 ($OC(CH_3)_2$), 34.4 ($ArCH_2$), 33.8 ($CH_2CH{=}CH_2$), 29.5, 28.6, 26.7, 25.1 ($C(CH_3)_2$), 24.8 ($C(CH_3)_2$), 21.4 ($ArCH_3$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. HRMS-ESI (*m/z*): Calcd for $[(C_{27}H_{44}B_2O_4+NH_4)+]$, 470.3837; found: 470.3836.

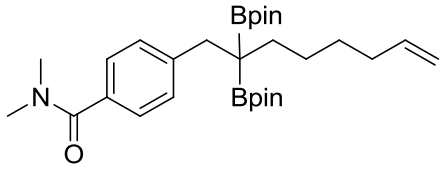


2,2'-(1-(4-fluorophenyl)oct-7-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13c). White solid (218.5 mg, 95%). M. P. 69-70 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.18 (dd, *J* = 8.5, 5.6 Hz, 2H, aryl-*H*), 6.87 (t, *J* = 8.8 Hz, 2H, aryl-*H*), 5.77 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, $CH_2CH{=}CH_2$), 4.99-4.87 (m, 2H, $CH_2CH{=}CH_2$), 2.92 (s, 2H, $ArCH_2$), 2.06-1.99 (m, 2H), 1.54-1.47 (m, 2H), 1.38-1.31 (m, 4H), 1.22 (s, 12H, $C(CH_3)_2$), 1.18 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 242.8 Hz, aryl-*C*), 139.1 ($CH{=}CH_2$), 137.5 (d, *J* = 3.2 Hz, aryl-*C*), 131.0 (d, *J* = 7.6 Hz, aryl-*C*), 114.4 ($CH{=}CH_2$), 114.2 (d, *J* = 5.0 Hz, aryl-*C*), 83.2 ($OC(CH_3)_2$), 33.8 ($CH_2CH{=}CH_2$), 29.5, 28.6, 26.7, 25.0 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -118.3. ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. HRMS-ESI (*m/z*): Calcd for $[(C_{26}H_{41}B_2FO_4+NH_4)+]$, 474.3586; found: 474.3585.

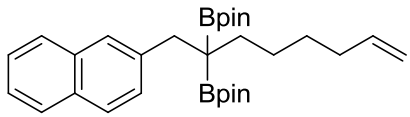


2,2'-(1-(3-chlorophenyl)oct-7-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13d). White solid (181.0 mg (0.4 mmol substrate was added in this reaction),

95%). M. P. 46-48 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (s, 4H, aryl-*H*), 5.77 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, CH_2CH=CH_2), 5.00-4.88 (m, 2H, CH_2CH=CH_2), 2.93 (s, 2H, ArCH_2), 2.07-1.99 (m, 2H), 1.53-1.46 (m, 2H), 1.37-1.31 (m, 4H), 1.23 (s, 12H, $C(CH_3)_2$), 1.19 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5 (aryl-*C*), 139.2 (*C*H=CH_2), 131.2 (aryl-*C*), 131.1 (aryl-*C*), 127.8 (aryl-*C*), 114.2 (CH=CH_2), 83.3 ($OC(CH_3)_2$), 34.0 (ArCH_2), 33.8 (CH_2CH=CH_2), 29.5, 28.6, 26.8, 25.1 ($C(CH_3)_2$), 24.8 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. HRMS-ESI (*m/z*): Calcd for [($C_{26}H_{41}B_2ClO_4$+NH_4)+], 490.3290; found: 490.3293.

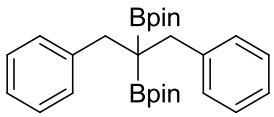


4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-yl)-N,N-dimethylbenzamide (13e). White solid (76.2 mg (0.2 mmol substrate was added in this reaction), 75%). M. P. 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.22 (m, 4H, aryl-*H*), 5.77 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.00-4.86 (m, 2H, CH_2CH=CH_2), 3.07 (s, NCH_3), 2.97 (s, 5H, ArCH_2 and NCH_3), 2.05-1.97 (m, 2H), 1.53-1.46 (m, 2H), 1.37-1.30 (m, 4H), 1.22 (s, 12H, $C(CH_3)_2$), 1.19 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9 (*C*=O), 143.7 (aryl-*C*), 139.2 (*C*H=CH_2), 133.3 (aryl-*C*), 129.6 (aryl-*C*), 126.6 (aryl-*C*), 114.1 (CH=CH_2), 83.2 ($OC(CH_3)_2$), 39.6 (NCH_3), 35.4 (NCH_3), 34.4 (ArCH_2), 33.7 (CH_2CH=CH_2), 29.4, 28.5, 26.7, 25.0 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, $CDCl_3$) δ = 33.6. HRMS-ESI (*m/z*): Calcd for [($C_{29}H_{47}B_2NO_5$+H)+], 510.3786; found: 510.3787.

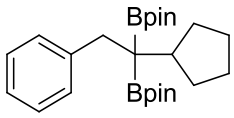


2,2'-(1-(naphthalen-2-yl)oct-7-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13f). Colorless oil (229.2 mg, 94%). M. P. 74-76 °C. ^{1}H NMR (400 MHz,

$CDCl_3$) δ = 7.85-7.75 (m, 4H, aryl-*H*), 7.51-7.40 (m, 3H, aryl-*H*), 5.88 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, $CH_2CH{=}CH_2$), 5.10-4.98 (m, 2H, $CH_2CH{=}CH_2$), 3.26 (s, 2H, $ArCH_2$), 2.17-2.10 (m, 2H), 1.70-1.64 (m, 2H), 1.57-1.43 (m, 4H), 1.33 (s, 12H, $C(CH_3)_2$), 1.28 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7 (aryl-*C*), 139.2 ($CH{=}CH_2$), 133.5 (aryl-*C*), 132.0 (aryl-*C*), 128.9 (aryl-*C*), 127.7 (aryl-*C*), 127.6 (aryl-*C*), 127.4 (aryl-*C*), 127.1 (aryl-*C*), 125.6 (aryl-*C*), 124.9 (aryl-*C*), 114.2 ($CH{=}CH_2$), 83.3 ($OC(CH_3)_2$), 34.8 ($ArCH_2$), 33.9 ($CH_2CH{=}CH_2$), 29.6, 28.7, 26.9, 25.1 ($C(CH_3)_2$), 24.8 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. HRMS-ESI (*m/z*): Calcd for [($C_{30}H_{44}B_2O_4$+NH_4)+], 506.3837; found: 506.3834.

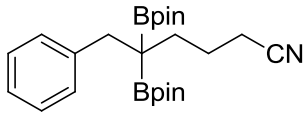


2,2'-(1,3-diphenylpropane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13g). White solid (213.8 mg, 95%). M. P. 130-132 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.26 (m, 8H, aryl-*H*), 7.24-7.18 (m, 2H, aryl-*H*), 3.14 (s, 4H, $ArCH_2$), 1.29 (s, 24H, $C(CH_3)_2$) . ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6 (aryl-*C*), 129.7 (aryl-*C*), 127.7 (aryl-*C*), 125.5 (aryl-*C*), 83.4 ($OC(CH_3)_2$), 34.6 ($ArCH_2$), 25.0 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. HRMS-ESI (*m/z*): Calcd for [($C_{27}H_{38}B_2O_4$+NH_4)+], 464.3367; found: 464.3369.

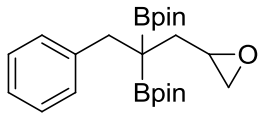


2,2'-(1-cyclopentyl-2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13h). Colorless oil (185.8 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 7.2 Hz, 2H, aryl-*H*), 7.22 (dd, *J* = 10.1, 4.7 Hz, 2H, aryl-*H*), 7.17-7.11 (m, 1H, aryl-*H*), 3.02 (s, 2H, $ArCH_2$), 2.09-1.99 (m, 1H), 1.93-1.83 (m, 2H), 1.61-1.52 (m, 2H), 1.48-1.35 (m, 4H), 1.25 (s, 12H, $C(CH_3)_2$), 1.23 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5 (aryl-*C*), 129.9 (aryl-*C*), 127.7 (aryl-*C*), 125.5 (aryl-*C*),

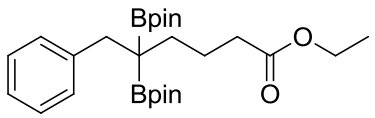
82.9 (O*C*(CH_3)$_2$), 40.9, 37.7, 31.0, 25.9, 25.1 (C(*C*H_3)$_2$), 24.9 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. HRMS-ESI (*m/z*): Calcd for [($C_{25}H_{40}B_2O_4$+NH_4)+], 442.3524; found: 442.3523.



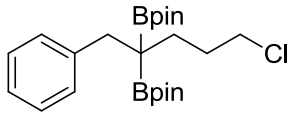
6-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanenitrile (13i). Colorless oil (198.9 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24-7.18 (m, 4H, aryl-*H*), 7.16-7.11 (m, 1H, aryl-*H*), 2.96 (s, 2H, ArC*H*$_2$), 2.20 (t, *J* = 7.3 Hz, 2H, C*H*$_2$CN), 1.75-1.66 (m, 2H), 1.60-1.54 (m, 2H), 1.24 (s, 12H, C(C*H*$_3$)$_2$) , 1.21 (s, 12H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1 (aryl-*C*), 129.5 (aryl-*C*), 127.9 (aryl-*C*), 125.7 (aryl-*C*), 119.9 (*C*N), 83.4 (O*C*(CH_3)$_2$), 35.1 (Ar*C*H_2), 28.8, 25.0 (C(*C*H_3)$_2$), 24.7 (C(*C*H_3)$_2$), 23.5, 17.6. ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. HRMS-ESI (*m/z*): Calcd for [($C_{24}H_{37}B_2NO_4$+NH_4)+], 441.3320; found: 441.3319.



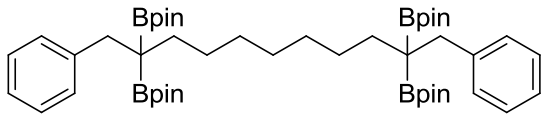
2,2'-(1-(oxiran-2-yl)-3-phenylpropane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13j). Colorless oil (143.4 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 7.20 (t, *J* = 7.4 Hz, 2H, aryl-*H*), 7.12 (t, *J* = 7.3 Hz, 1H, aryl-*H*), 3.08 (s, 2H, ArC*H*$_2$), 3.06-3.00 (m, 1H), 2.69 (dd, *J* = 5.2, 4.1 Hz, 1H), 2.44 (dd, *J* = 5.3, 2.7 Hz, 1H), 1.81-1.70 (m, 2H), 1.25 (s, 6H, C(C*H*$_3$)$_2$), 1.24 (s, 6H, C(C*H*$_3$)$_2$), 1.22 (s, 6H, C(C*H*$_3$)$_2$), 1.20 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4 (aryl-*C*), 129.9 (aryl-*C*), 127.8 (aryl-*C*), 125.6 (aryl-*C*), 83.4 (O*C*(CH_3)$_2$), 83.4 (O*C*(CH_3)$_2$), 51.6, 48.1, 36.0 (Ar*C*H_2), 32.3, 25.0 (C(*C*H_3)$_2$), 25.0 (C(*C*H_3)$_2$), 24.8 (C(*C*H_3)$_2$), 24.7 (C(*C*H_3)$_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. HRMS-ESI (*m/z*): Calcd for [($C_{23}H_{36}B_2O_5$+NH_4)+], 430.3160; found: 430.3161.



Ethyl 6-phenyl-5,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (13k). White solid (201.3 mg, 85%). M. P. 69-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 7.2 Hz, 2H, aryl-*H*), 7.18 (t, *J* = 7.4 Hz, 2H, aryl-*H*), 7.10 (t, *J* = 7.1 Hz, 1H, aryl-*H*), 4.09 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 2.97 (s, 2H, $ArCH_2$), 2.23 (t, *J* = 7.6 Hz, 2H, $COCH_2$), 1.77-1.59 (m, 2H), 1.55-1.49 (m, 2H), 1.30-1.15 (m, 27H, OCH_2CH_3 and $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7 (*C*=O), 141.6 (aryl-*C*), 129.7 (aryl-*C*), 127.7 (aryl-*C*), 125.5 (aryl-*C*), 83.3 ($OC(CH_3)_2$), 60.0 (OCH_2CH_3), 35.1, 34.6, 28.5, 25.0 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$), 22.8, 14.3. ^{11}B NMR (193 MHz, EtOAc) δ = 34.2. HRMS-ESI (*m/z*): Calcd for $[(C_{26}H_{42}B_2O_6+NH_4)+]$, 488.3578; found: 488.3577.

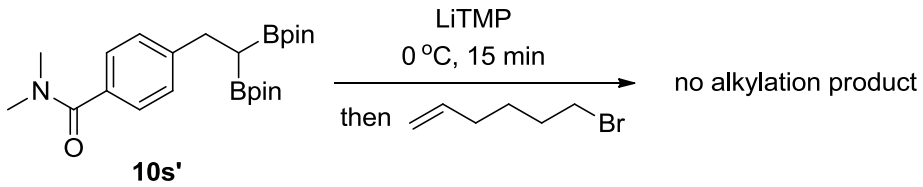


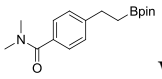
2,2'-(5-chloro-1-phenylpentane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13l). White solid (210.8 mg, 97%). M. P. 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.19 (m, 4H, aryl-*H*), 7.16-7.11 (m, 1H, aryl-*H*), 3.45 (t, *J* = 7.1 Hz, 2H, CH_2Cl), 2.98 (s, 2H, $ArCH_2$), 1.90-1.81 (m, 2H), 1.64-1.57 (m, 2H), 1.26 (s, 12H, $C(CH_3)_2$), 1.22 (s, 12H, $C(CH_3)_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3 (aryl-*C*), 129.6 (aryl-*C*), 127.8 (aryl-*C*), 125.6 (aryl-*C*), 83.3 ($OC(CH_3)_2$), 45.4 (CH_2Cl), 34.9 ($ArCH_2$), 30.9, 26.6, 25.0 ($C(CH_3)_2$), 24.7 ($C(CH_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.3. HRMS-ESI (*m/z*): Calcd for $[(C_{23}H_{41}B_2ClO_4+NH_4)+]$, 450.2977; found: 450.2977.



2,2',2'',2'''-(1,12-diphenyldodecane-2,2,11,11-tetrayl)tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13m). White solid (342.3 mg, 83%). M. P. 160-162 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27-7.18 (m, 8H, aryl-*H*), 7.15-7.09 (m, 2H, aryl-*H*), 2.99 (s, 4H, ArCH_2), 1.55-1.48 (m, 4H), 1.40-1.16 (m, 58H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0 (aryl-*C*), 129.8 (aryl-*C*), 127.7 (aryl-*C*), 125.5 (aryl-*C*), 83.2 (O*C*$(CH_3)_2$), 34.6 (Ar*C*H_2), 30.4, 29.8, 28.7, 27.3, 25.1 (C(*C*$H_3)_2$), 24.8 (C(*C*$H_3)_2$). ^{11}B NMR (193 MHz, EtOAc) δ = 34.1. Anal. Calcd for $C_{48}H_{78}B_4O_8$: C, 69.76; H, 9.51. Found: C, 69.48; H, 9.54.

Attempted Alkylation of 1,1-bis(boronate) containing an amide substitute with 6-bromo-1-hexene using Morken's method



The reaction of 1,1-bis(boronate) **17** with 6-bromo-1-hexene using Morken's[7] method did not form the desired alkylation product. In fact, a large amount of black, unidentified solid precipitated immediately when LiTMP was added to the THF solution of 1,1-bis(boronate), indicated the substrate with a tertiary amide can not tolerate LiTMP. After the reaction, only 16% of the starting material 1,1-bis(boronate) and 5% of the monoboryl side product resulting from deborylative protonation 

were detected.

7. Crystallographic Data

Table SI-1. Crystal data and structure refinement for 2,2',2''-(2-phenylethane-1,1,1-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10a)

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=9.7658(11) b=12.3604(14) c=22.998(3)
alpha=90 beta=92.758(2) gamma=90

Temperature: 130 K

	Calculated	Reported
Volume	2772.9(6)	2772.8(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C26 H43 B3 O6	C26 H43 B3 O6
Sum formula	C26 H43 B3 O6	C26 H43 B3 O6
Mr	484.03	484.03
Dx,g cm-3	1.160	1.159
Z	4	4
Mu (mm-1)	0.078	0.078
F000	1048.0	1048.0
F000'	1048.49	
h,k,lmax	14,17,33	13,17,32
Nref	8680	8598
Tmin,Tmax	0.981,0.985	0.649,0.746
Tmin'	0.981	

Correction method= # Reported T Limits: Tmin=0.649 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 30.789

R(reflections)= 0.0522(6446) wR2(reflections)= 0.1333(8598)

S = 1.009 Npar= 328

Table SI-2. Crystal data and structure refinement for (^{t}Bu^{u}PNN)CoCl (11).

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=10.9980(7) b=12.8128(9) c=13.7439(9)
alpha=90 beta=90 gamma=90

Temperature: 130 K

	Calculated	Reported
Volume	1936.7(2)	1936.7(2)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C19 H27 Cl Co N2 P	C19 H27 Cl Co N2 P
Sum formula	C19 H27 Cl Co N2 P	C19 H27 Cl Co N2 P
Mr	408.78	408.77
Dx,g cm-3	1.402	1.402
Z	4	4
Mu (mm-1)	1.110	1.110
F000	856.0	856.0
F000'	858.56	
h,k,lmax	15,18,19	15,18,19
Nref	5927[3326]	5911
Tmin,Tmax	0.819,0.895	0.654,0.746
Tmin'	0.792	

Correction method= # Reported T Limits: Tmin=0.654 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.78/1.00 Theta(max)= 30.545

R(reflections)= 0.0241(5545) wR2(reflections)= 0.0578(5911)

S = 1.019 Npar= 223

Table SI-3. Crystal data and structure refinement for (^{t}^{Bu}PNN)CoCH$_2$CH$_2$Ph (14).

Bond precision: C-C = 0.0044 A Wavelength=0.71073

Cell: a=16.925(4) b=9.297(2) c=16.995(4)
alpha=90 beta=114.388(4) gamma=90

Temperature: 130 K

	Calculated	Reported
Volume	2435.6(10)	2435.4(9)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C27 H36 Co N2 P	C27 H36 Co N2 P
Sum formula	C27 H36 Co N2 P	C27 H36 Co N2 P
Mr	478.48	478.48
Dx,g cm-3	1.305	1.305
Z	4	4
Mu (mm-1)	0.787	0.787
F000	1016.0	1016.0
F000'	1018.04	
h,k,lmax	24,13,24	24,13,24
Nref	7602	7557
Tmin,Tmax	0.790,0.821	0.641,0.746
Tmin'	0.790	

Correction method= # Reported T Limits: Tmin=0.641 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 30.747

R(reflections)= 0.0587(4212) wR2(reflections)= 0.1362(7557)

S = 0.972 Npar= 286

8. References

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(2) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 2696.
(3) Crisenza, G. E. M.; McCreanor, N. G.; Bower, J. F. *J. Am. Chem. Soc.* **2014,** *136*, 10258.
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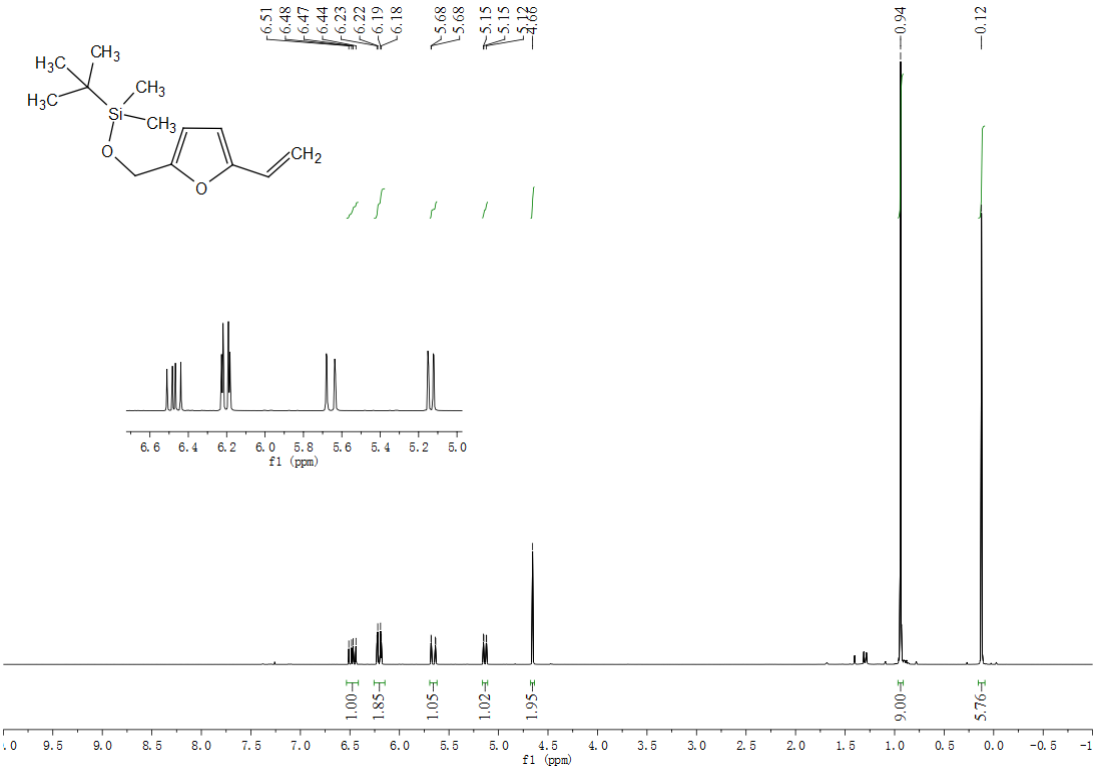
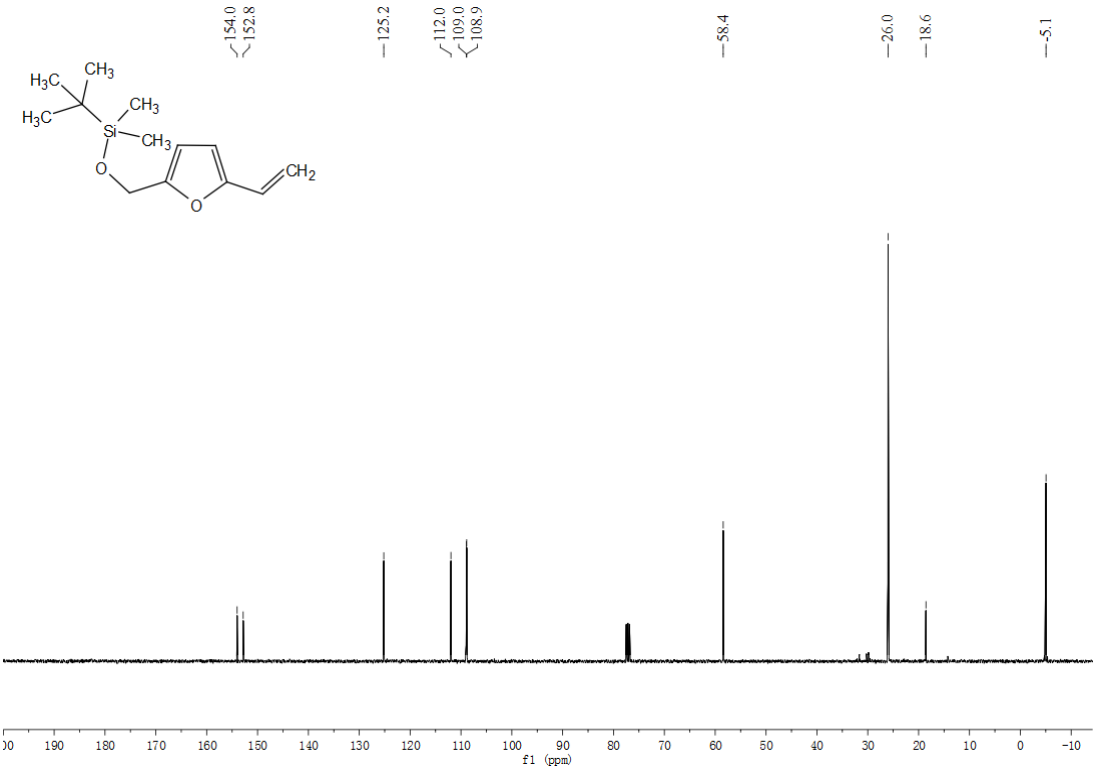
(6) Takaya, J.; Kirai, N.; Iwasawa, N. *J. Am. Chem. Soc.* **2011,** *133*, 12980.
(7) Hong, K.; Liu, X.; Morken, J. P. *J. Am. Chem. Soc.* **2014,** *136*, 10581.

9. NMR Spectra

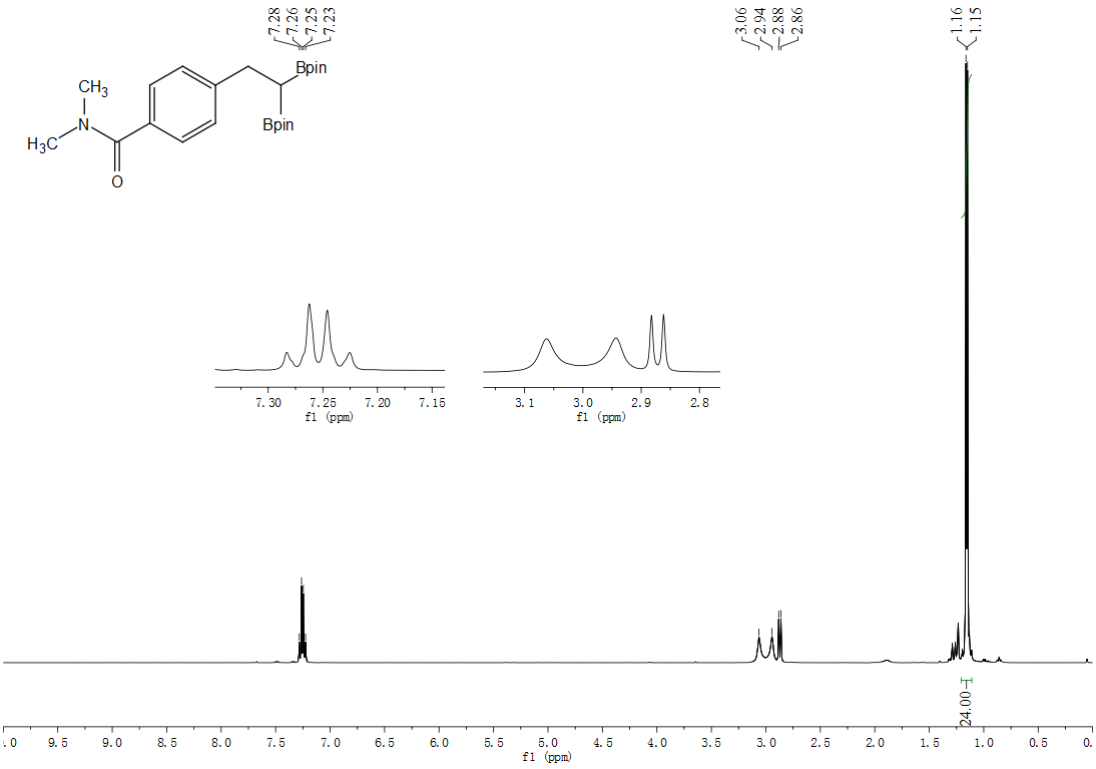


^{1}H NMR (400 MHz, $CDCl_3$) of **1t**

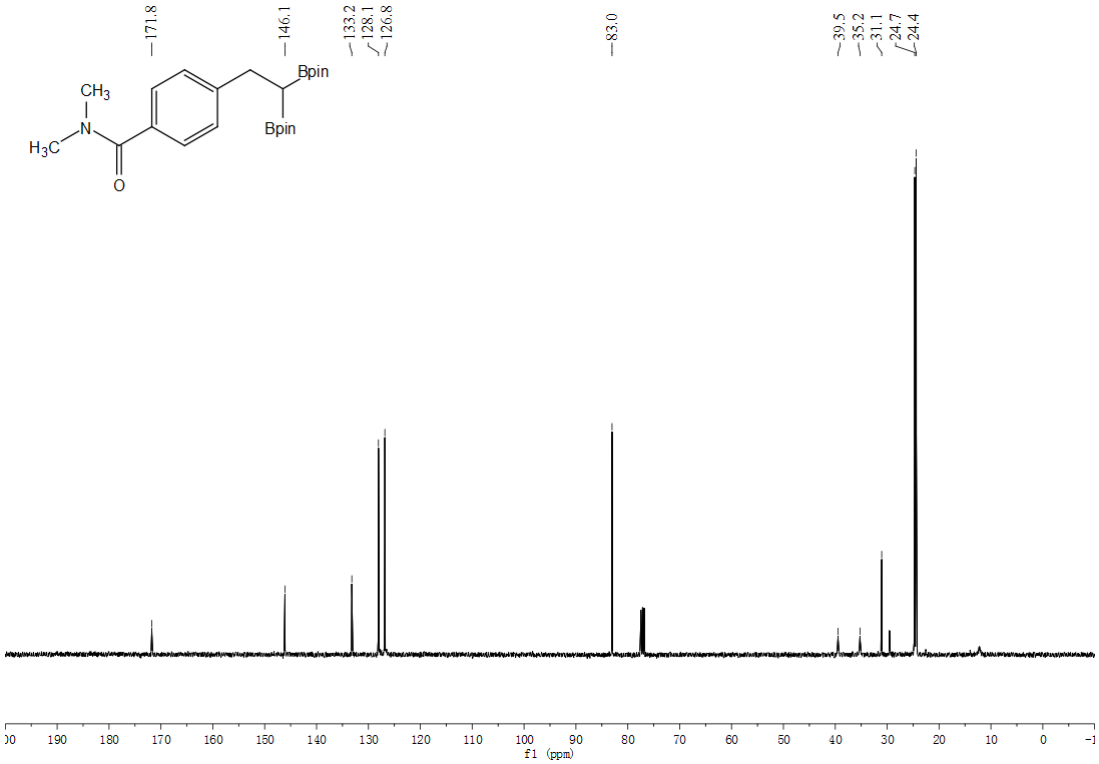


^{13}C NMR (101 MHz, $CDCl_3$) of **1t**

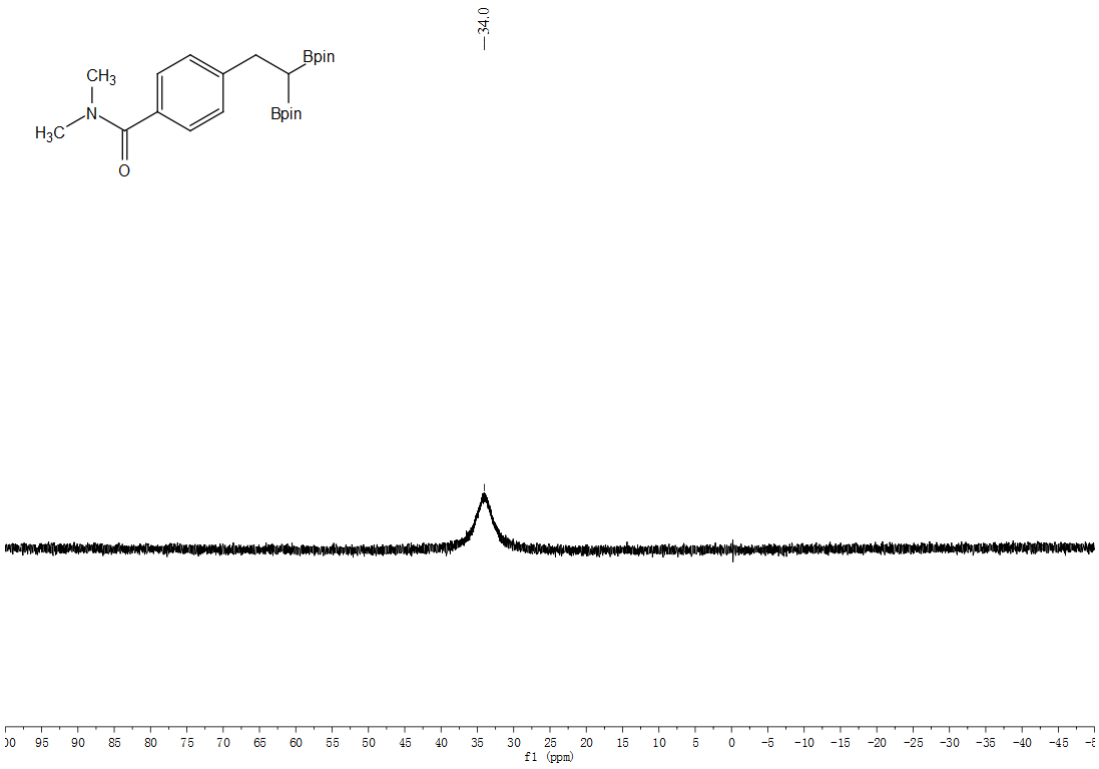
^{1}H NMR (400 MHz, $CDCl_3$) of **1c-*D*2** (1c-D_2: 1c = 89:11)



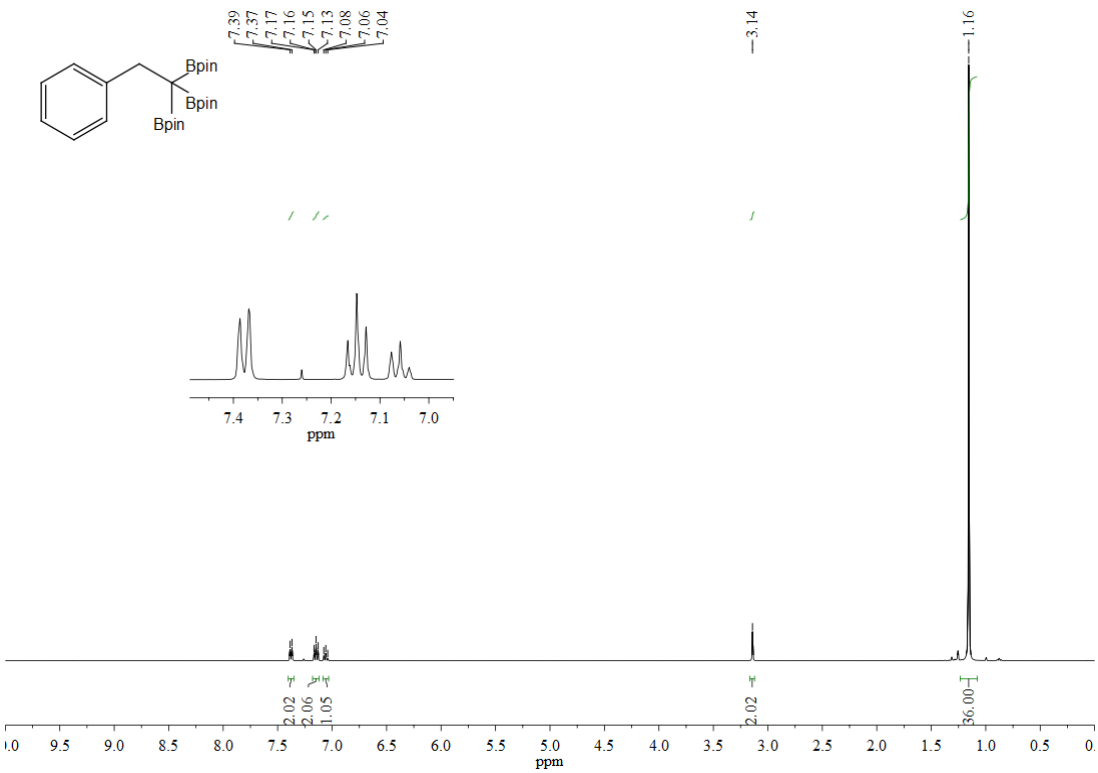
^{1}H NMR (400 MHz, $CDCl_3$) of **10s'**



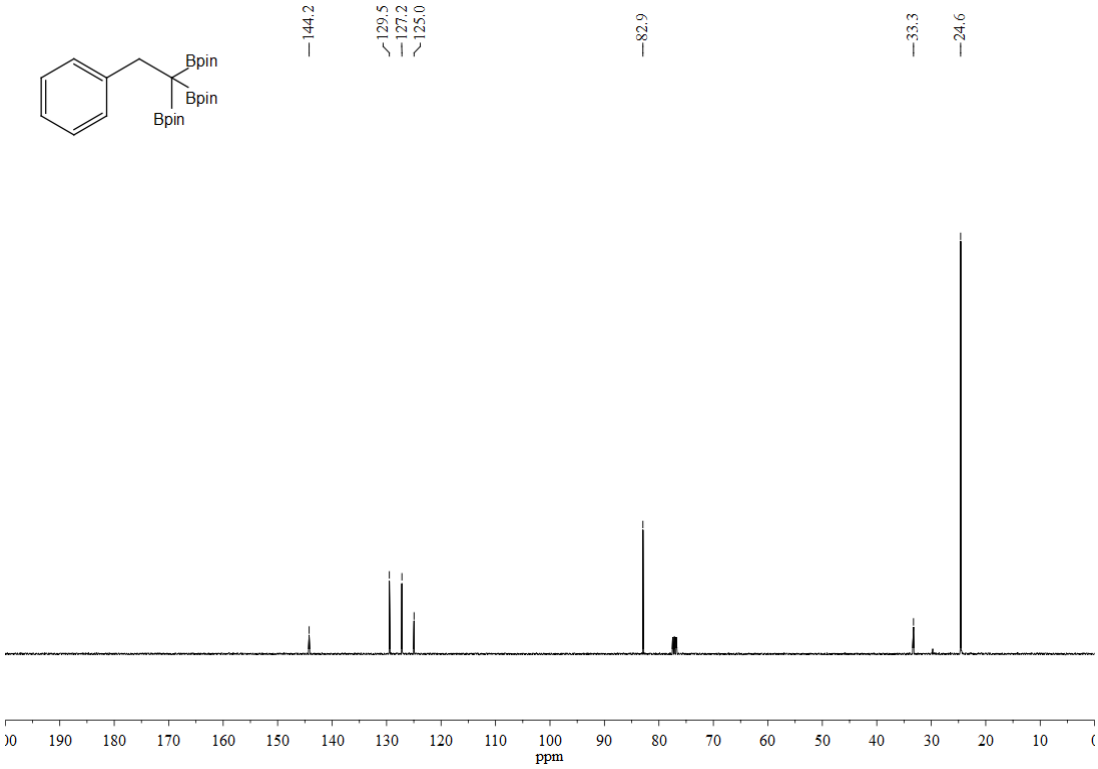
^{13}C NMR (101 MHz, $CDCl_3$) of **10s'**



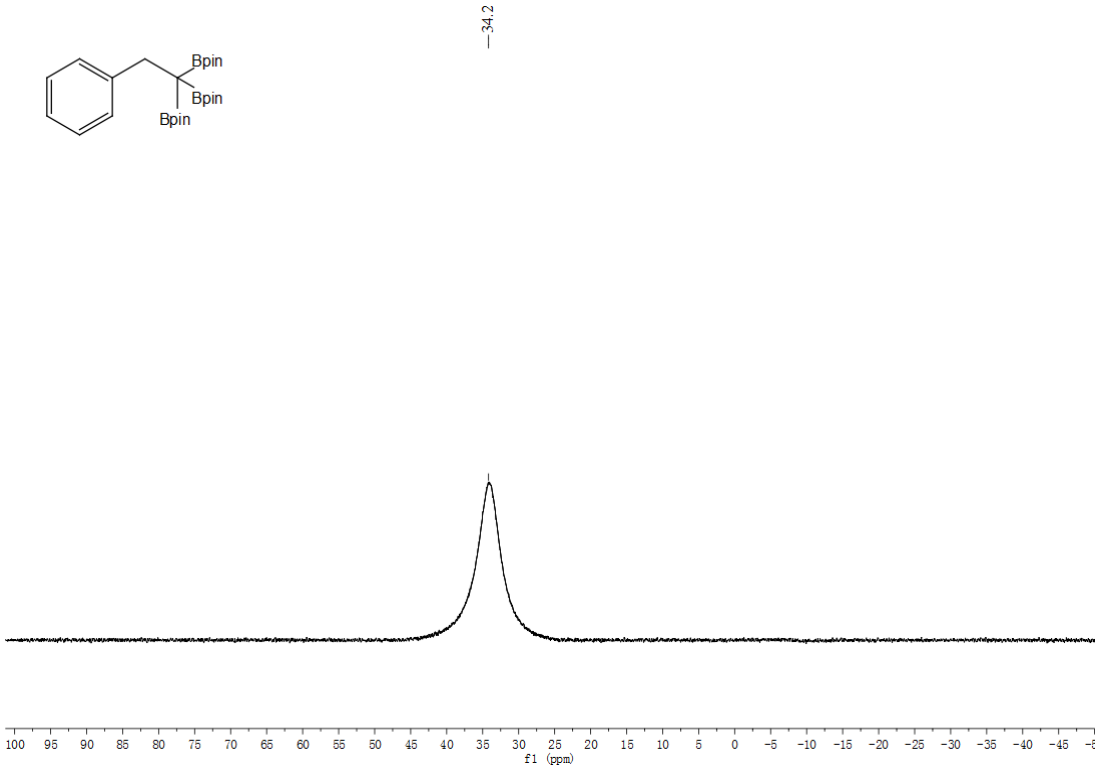
^{11}B NMR (193 MHz, EtOAc) of **10s'**



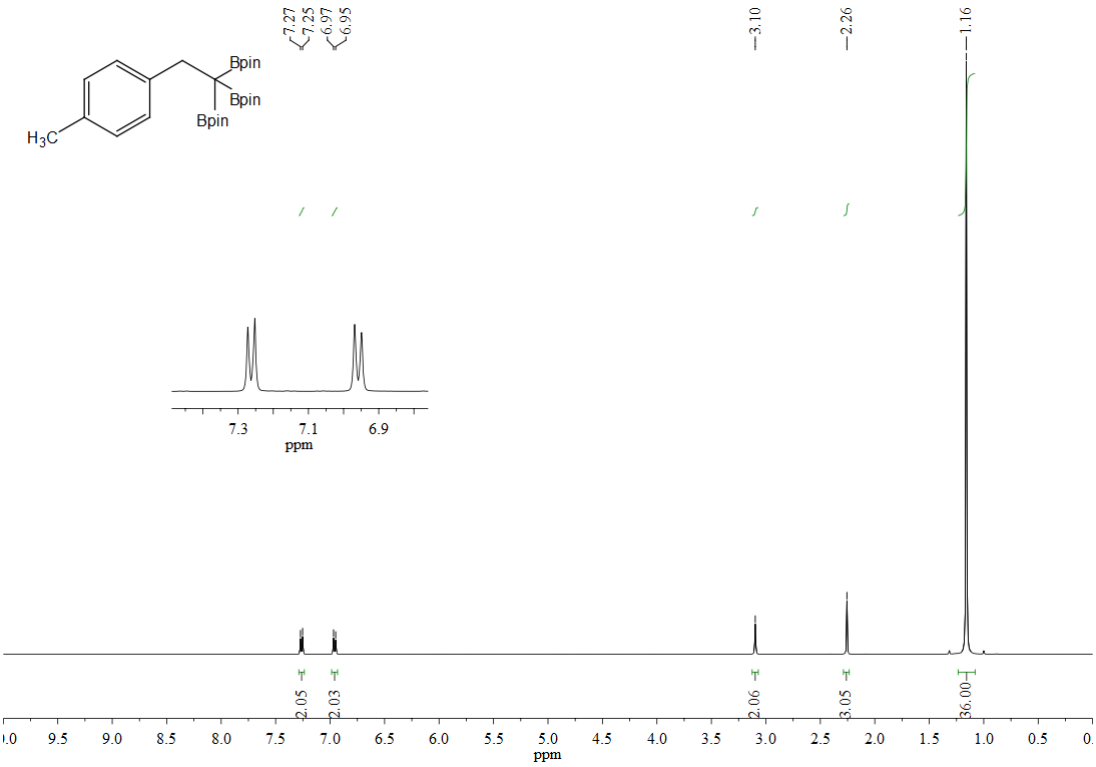
^{1}H NMR (400 MHz, $CDCl_3$) of **10a**



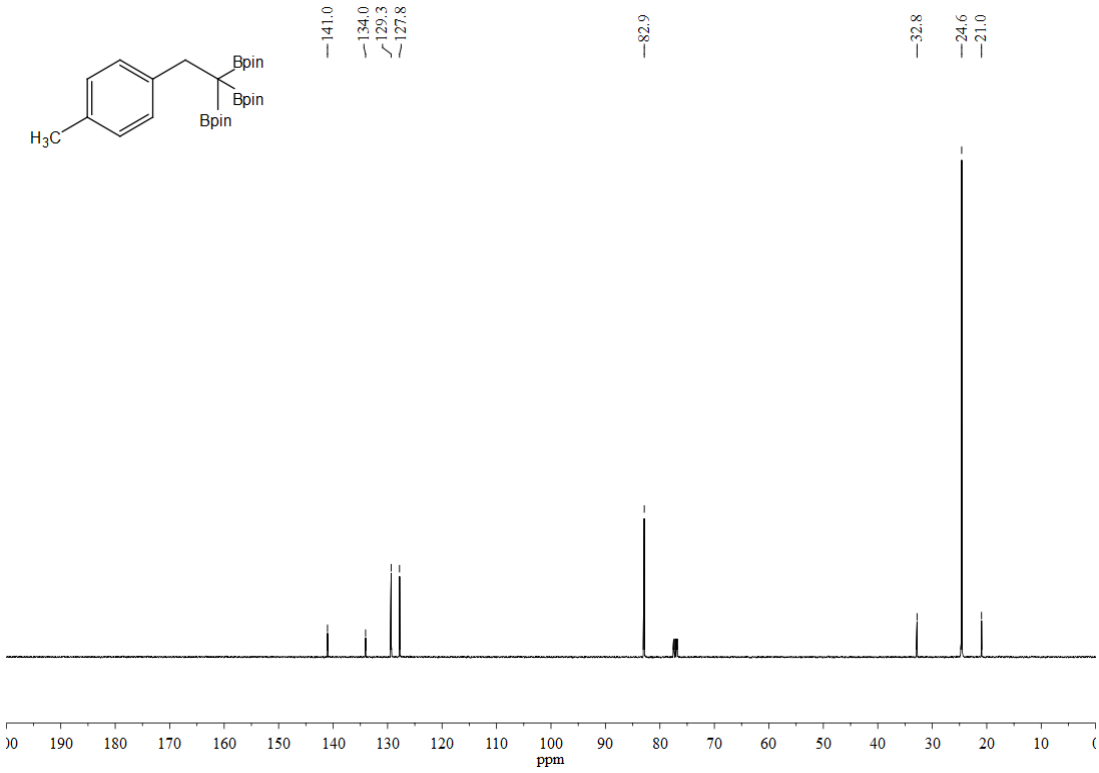
^{13}C NMR (101 MHz, $CDCl_3$) of **10a**



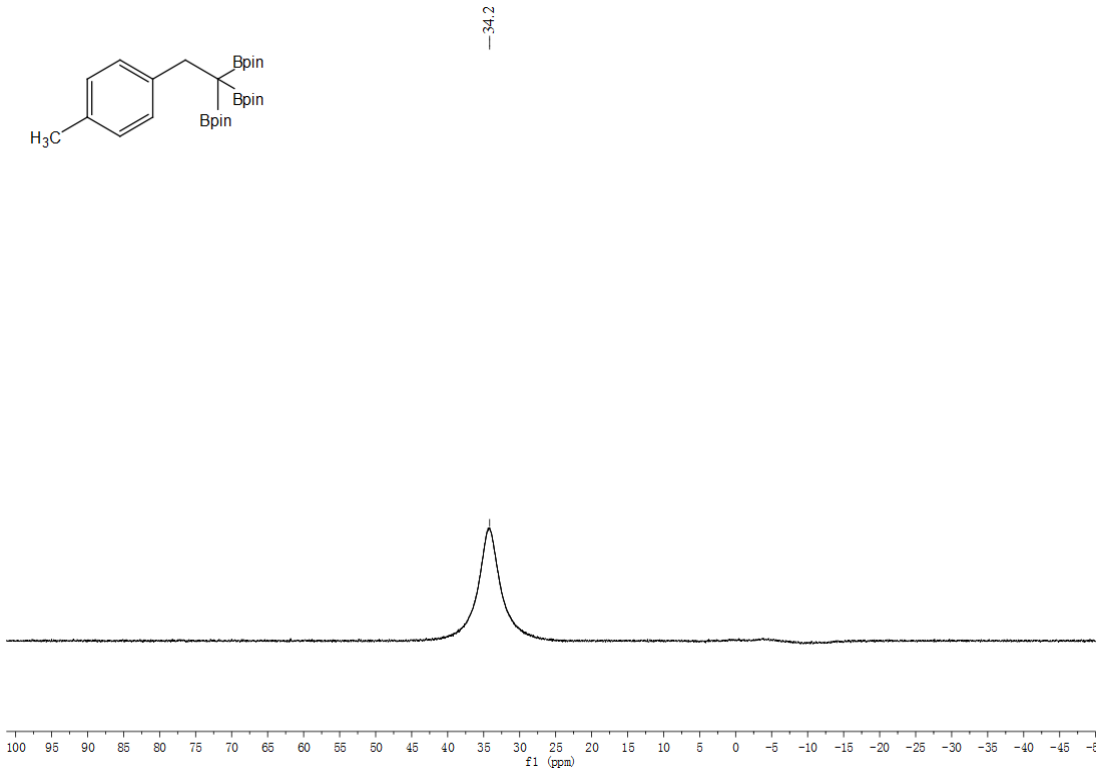
^{11}B NMR (193 MHz, EtOAc) of **10a**



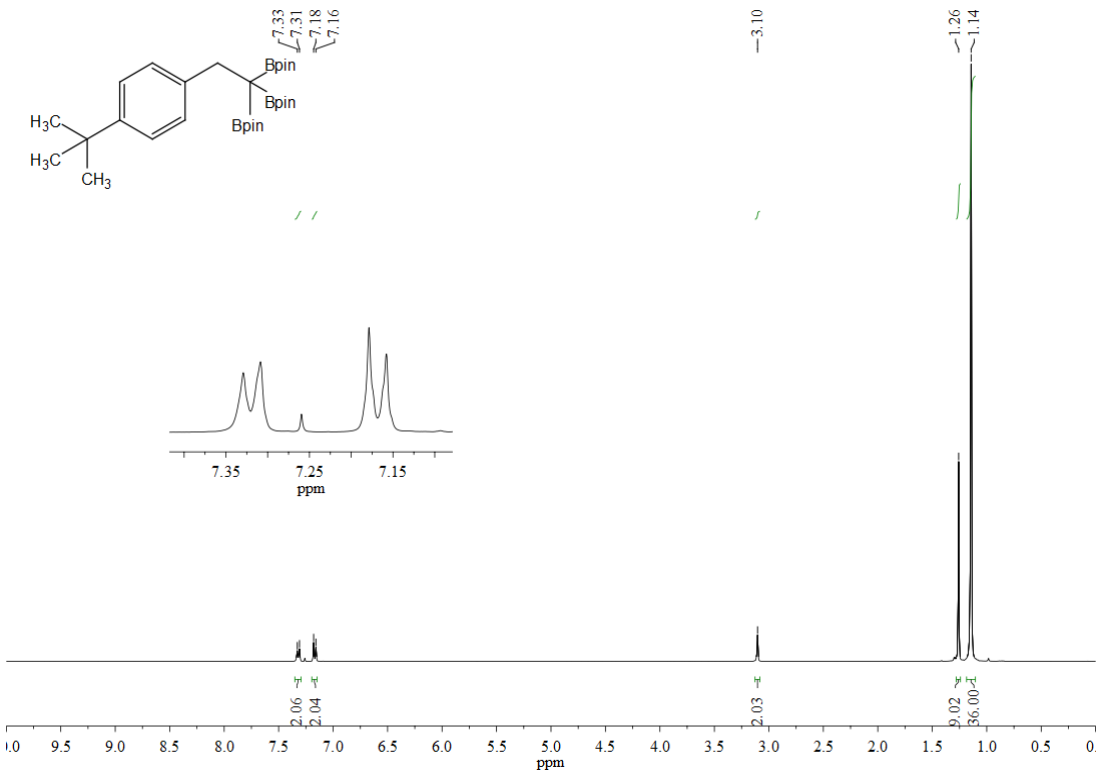
^{1}H NMR (400 MHz, $CDCl_3$) of **10b**



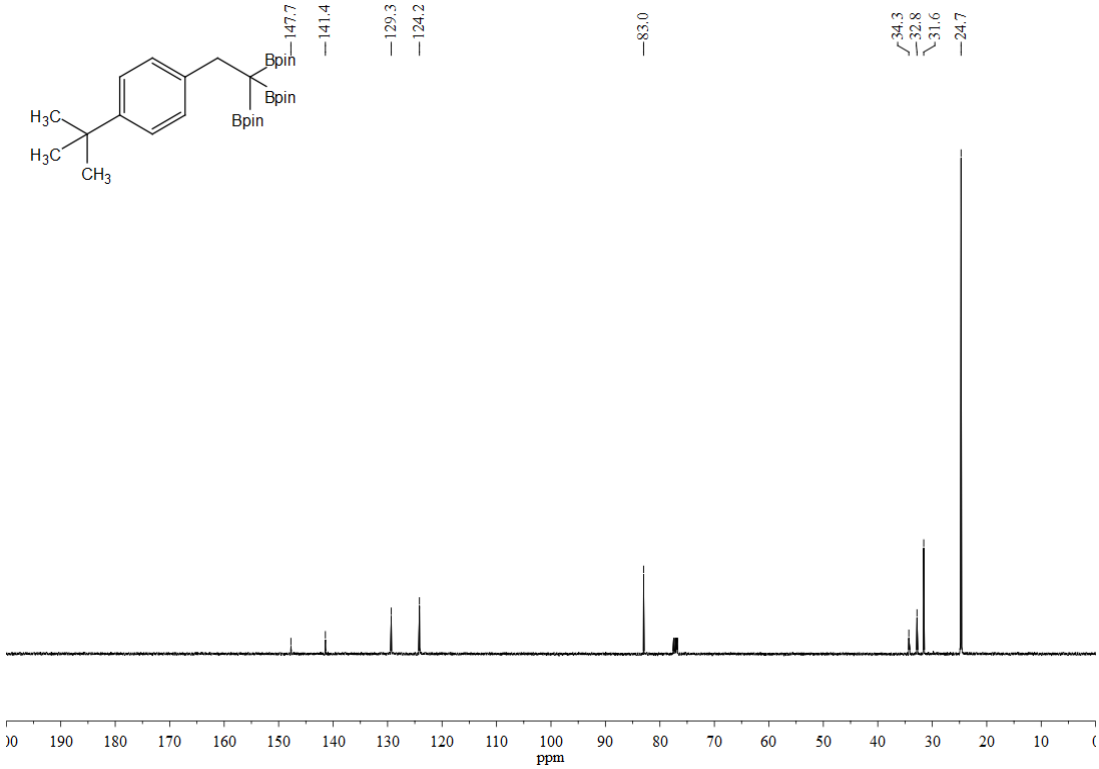
^{13}C NMR (101 MHz, $CDCl_3$) of **10b**



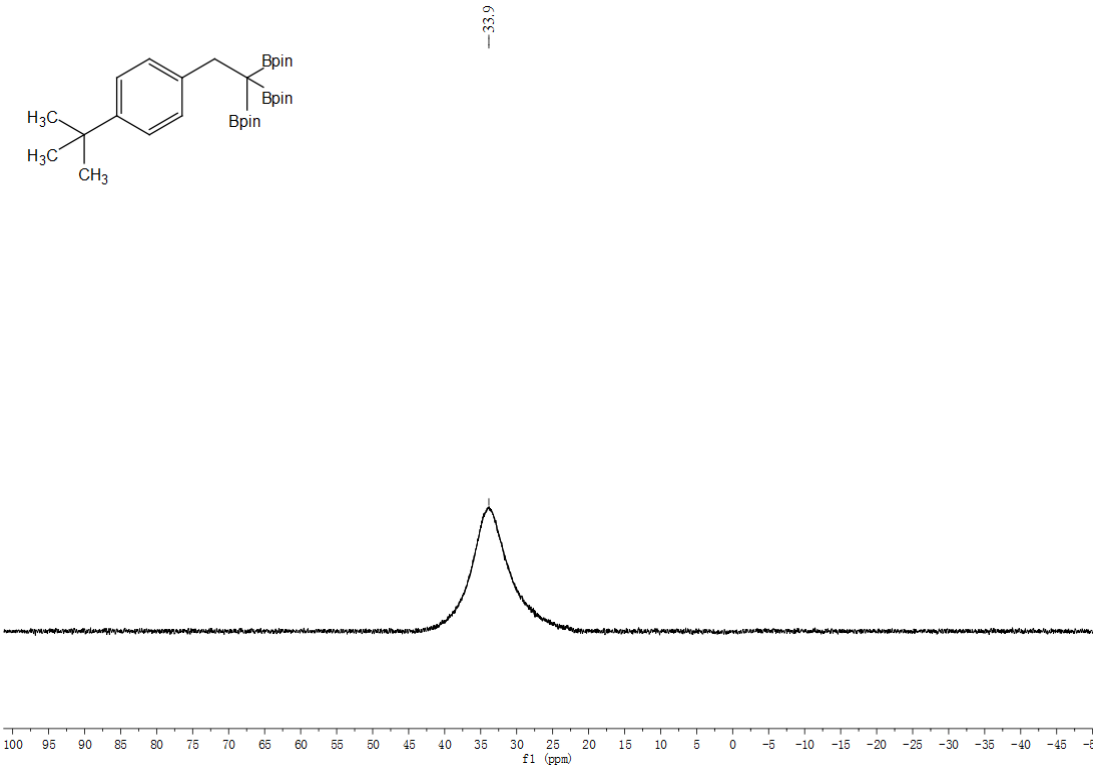
^{11}B NMR (193 MHz, EtOAc) of **10b**



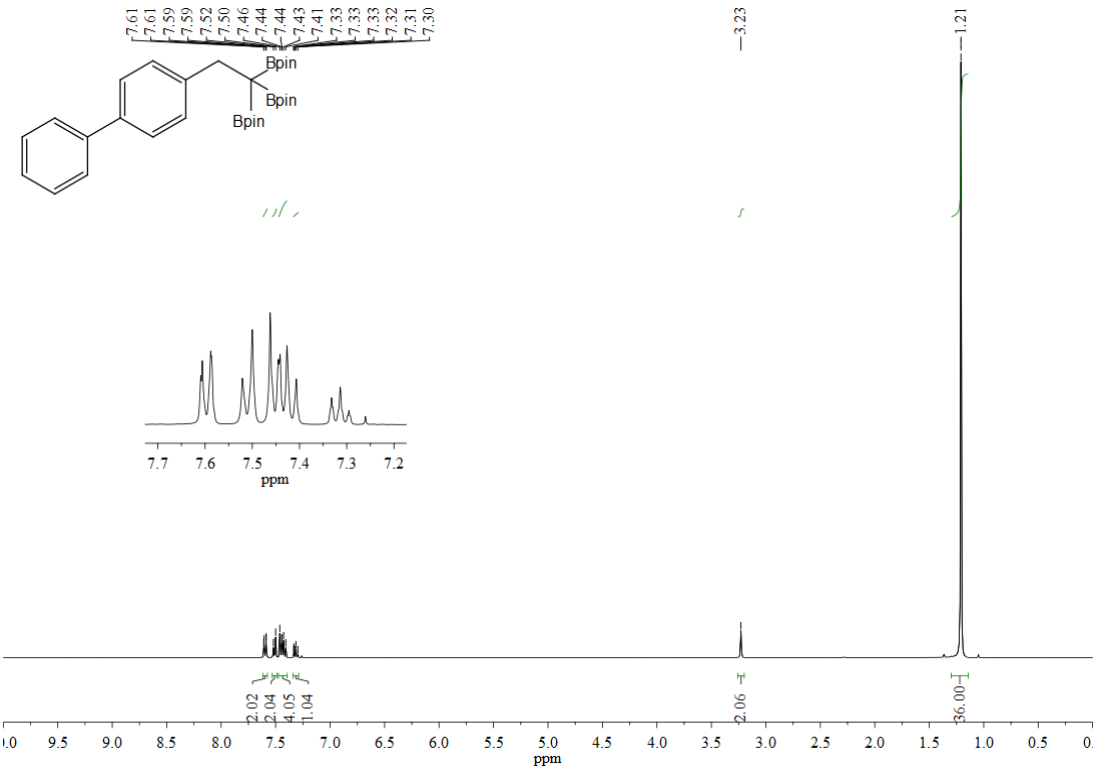
^{1}H NMR (400 MHz, $CDCl_3$) of **10c**



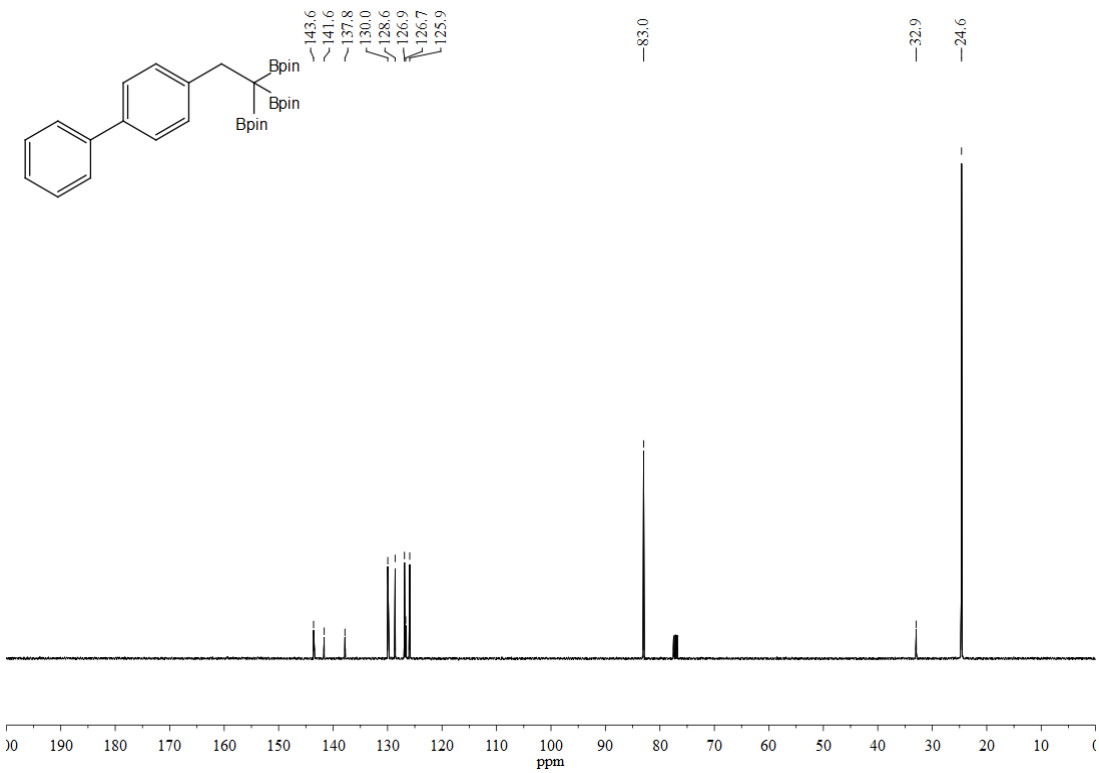
^{13}C NMR (101 MHz, $CDCl_3$) of **10c**



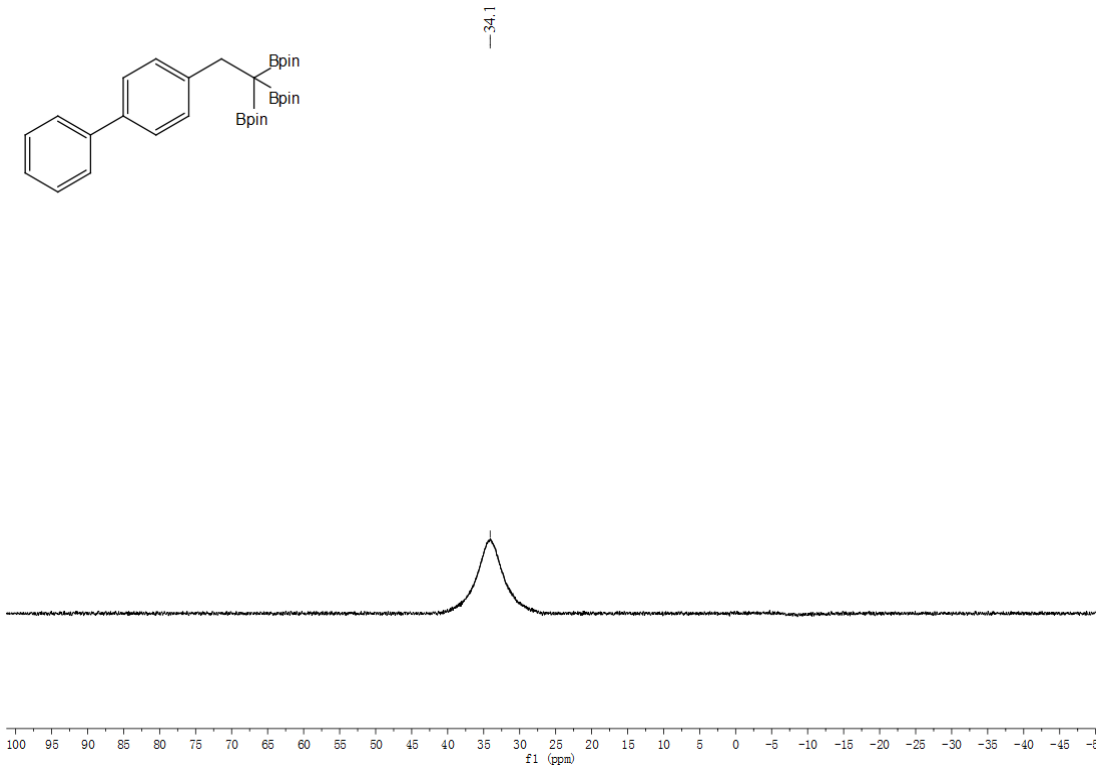
^{11}B NMR (193 MHz, EtOAc) of **10c**



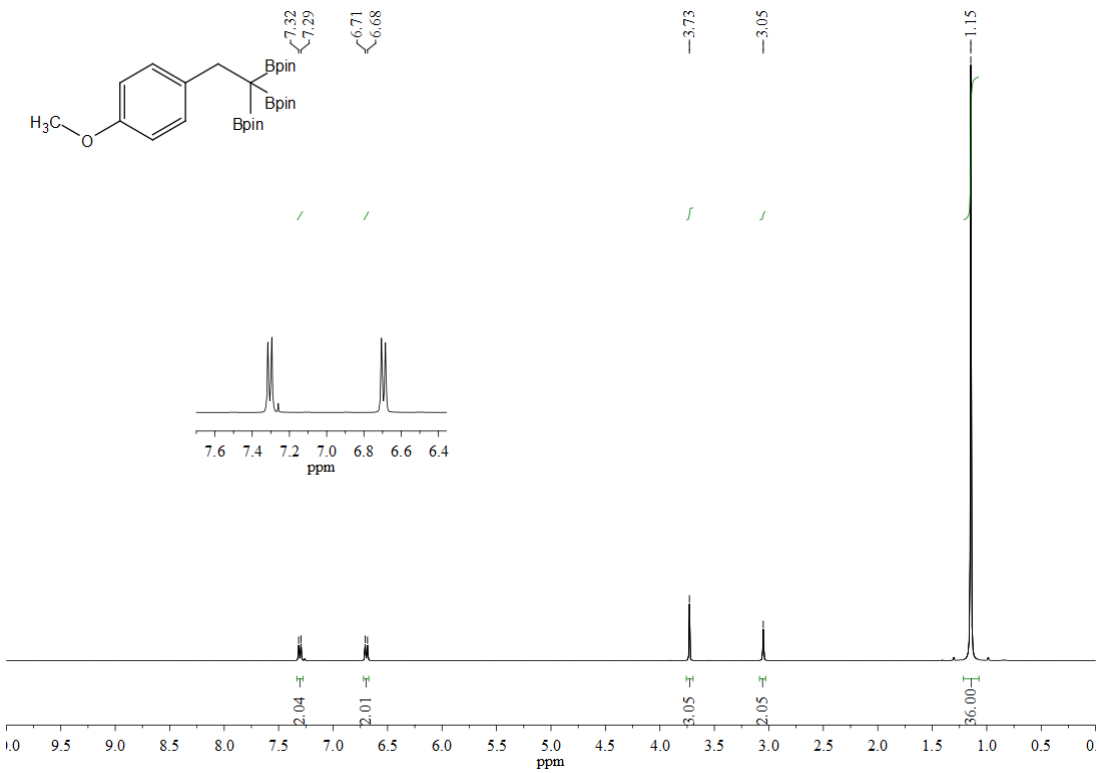
^{1}H NMR (400 MHz, $CDCl_3$) of **10d**



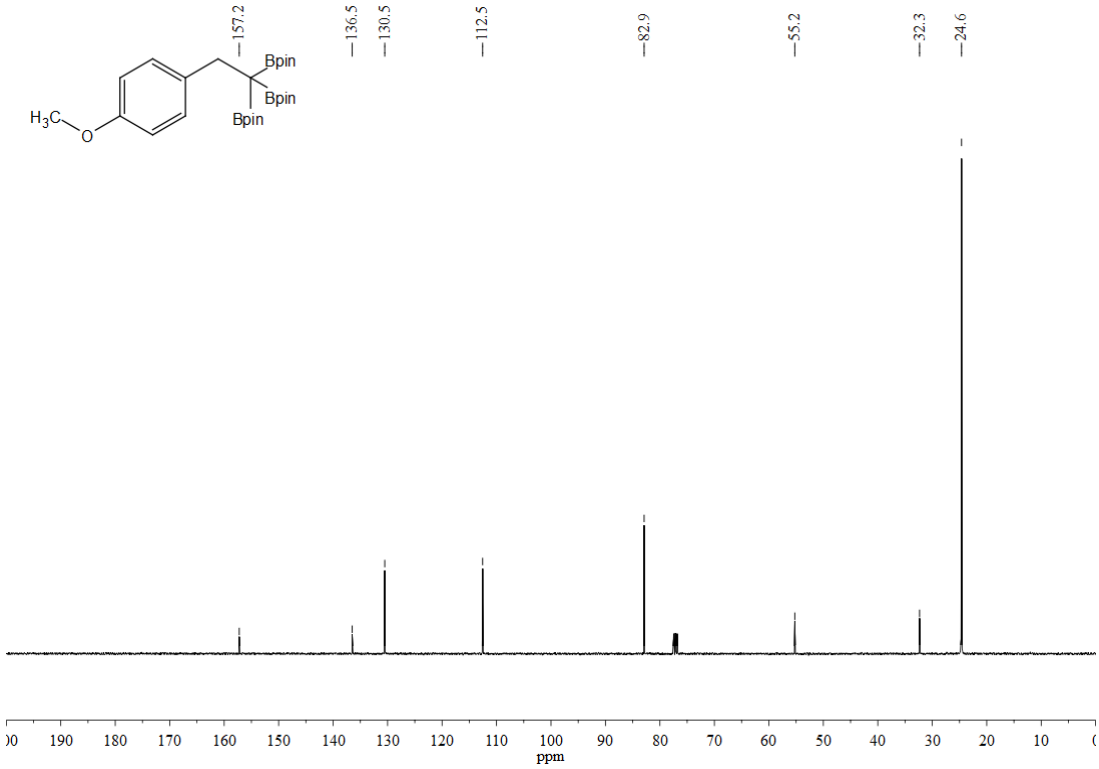
^{13}C NMR (101 MHz, $CDCl_3$) of **10d**



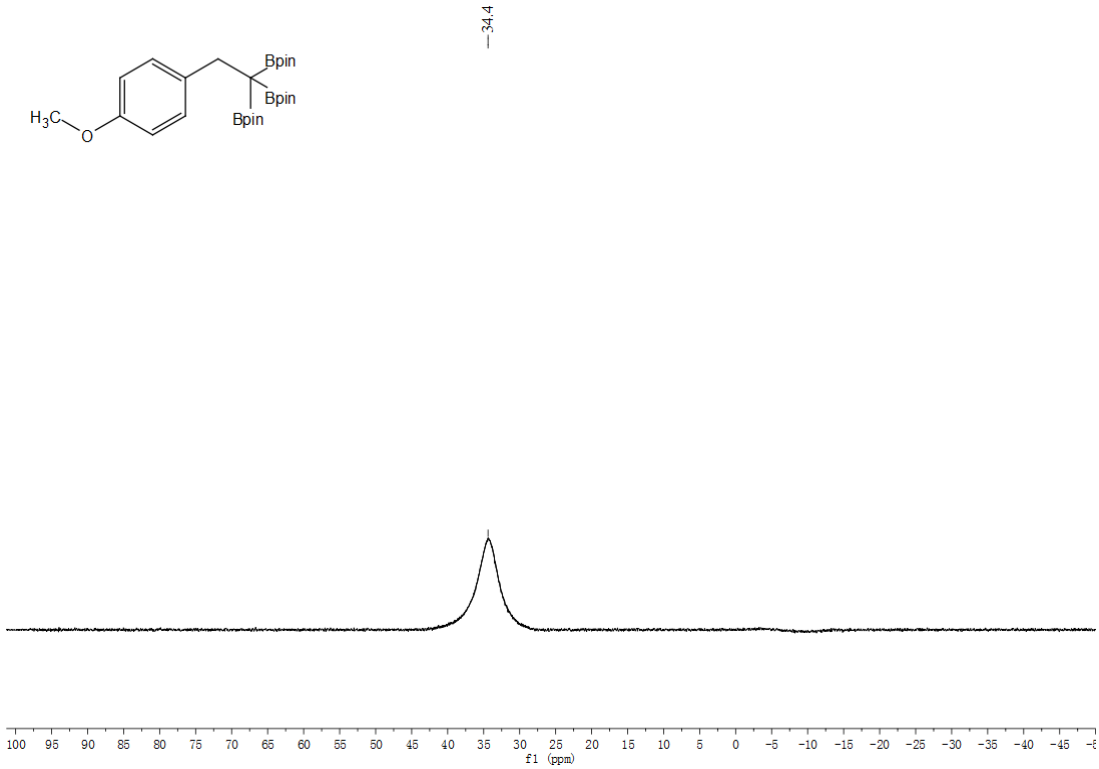
^{11}B NMR (193 MHz, EtOAc) of **10d**



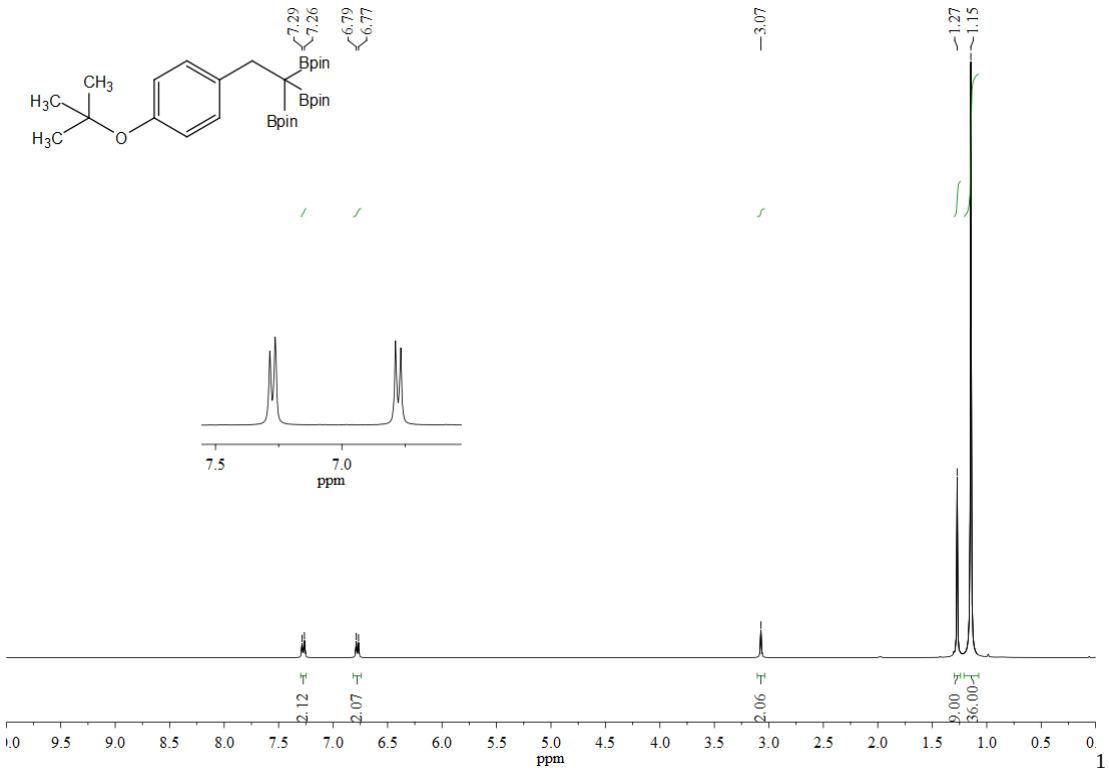
^{1}H NMR (400 MHz, $CDCl_3$) of **10e**



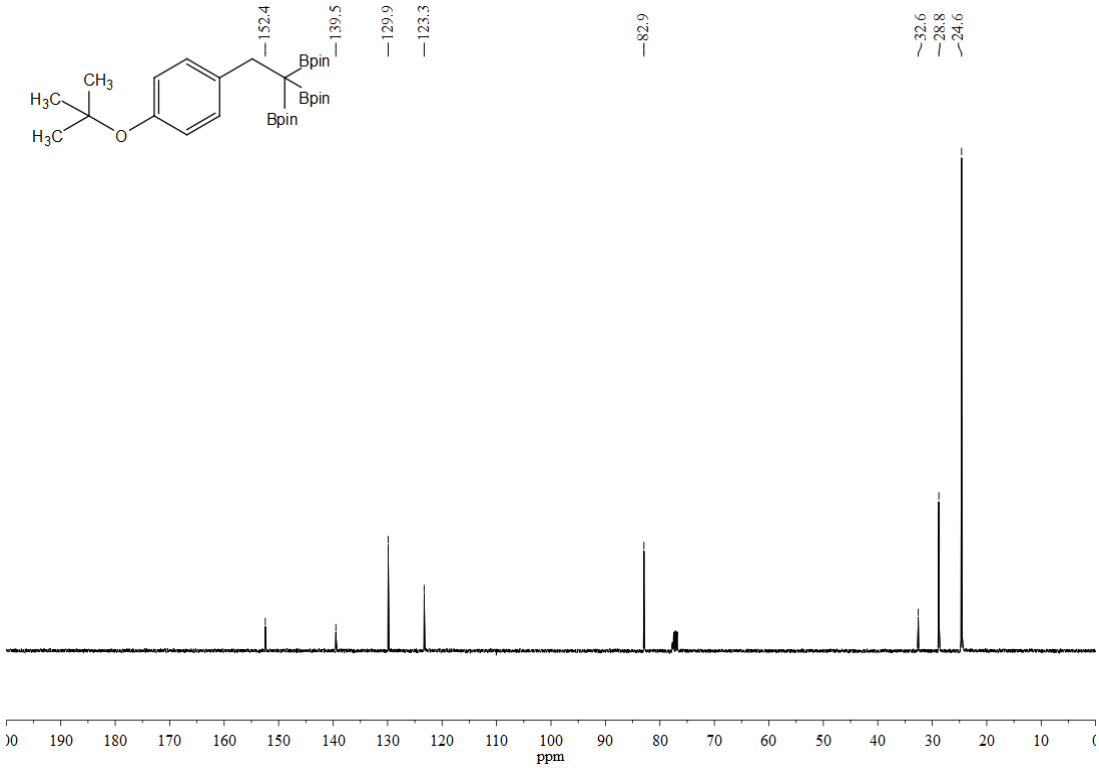
^{13}C NMR (101 MHz, $CDCl_3$) of **10e**



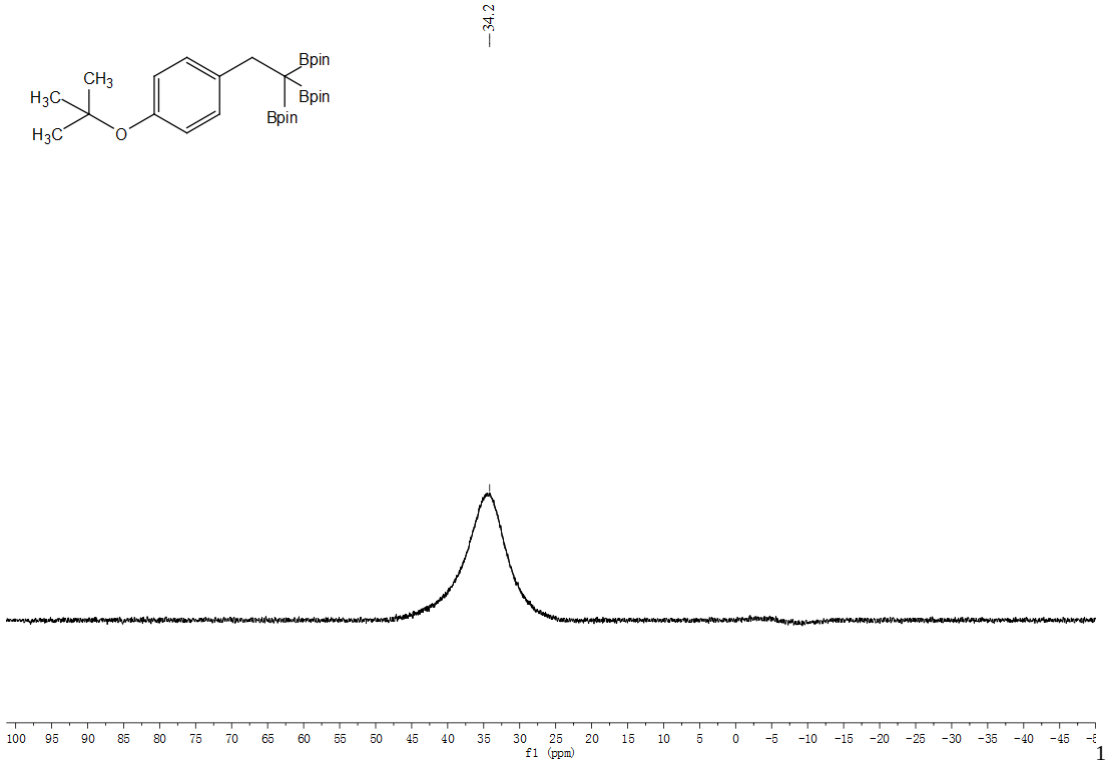
^{11}B NMR (193 MHz, EtOAc) of **10e**



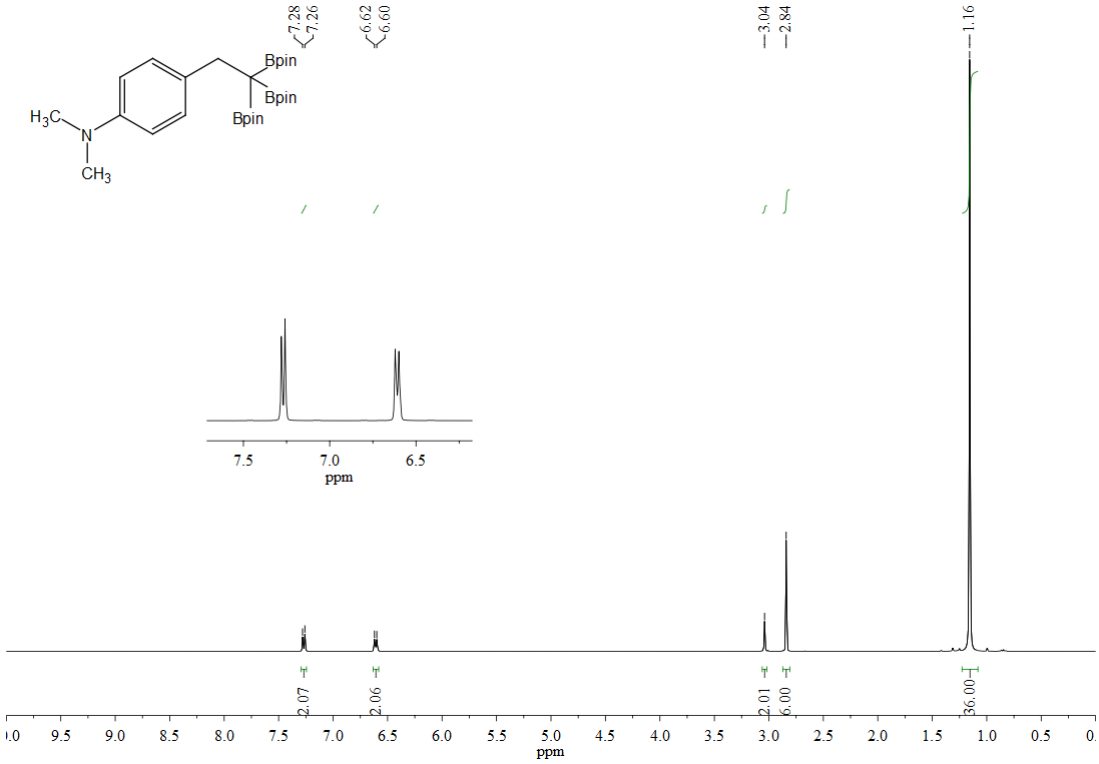
^{1}H NMR (400 MHz, $CDCl_3$) of **10f**



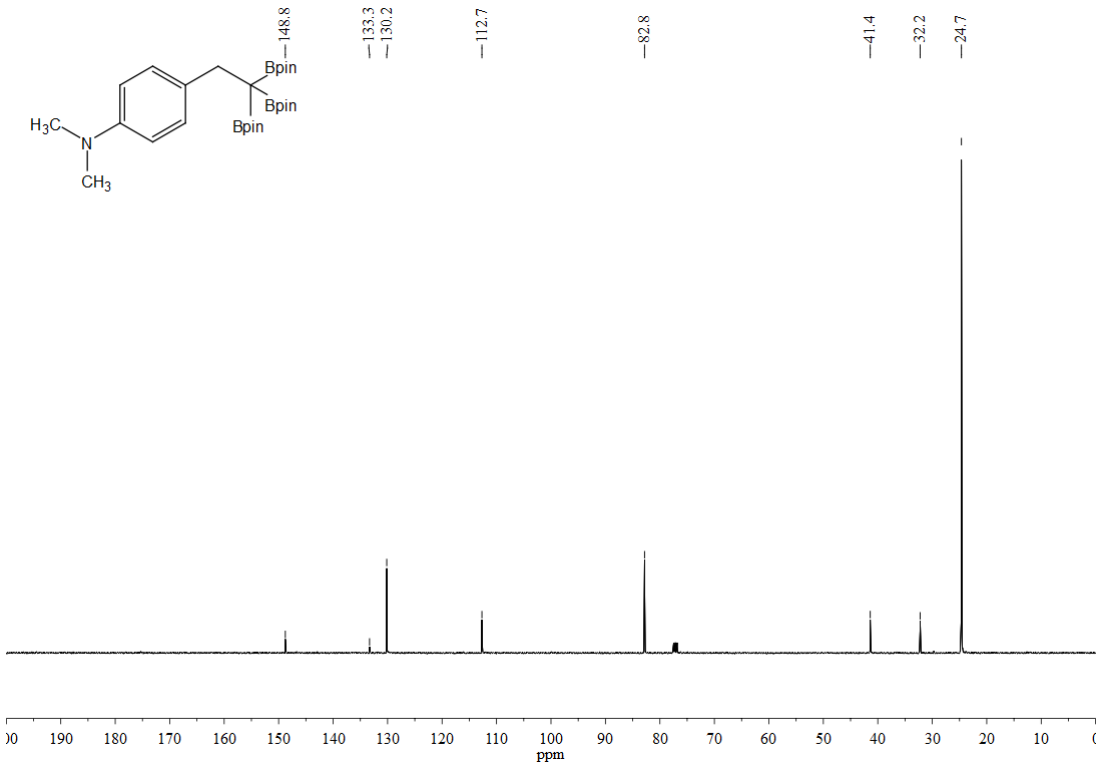
^{13}C NMR (101 MHz, $CDCl_3$) of **10f**



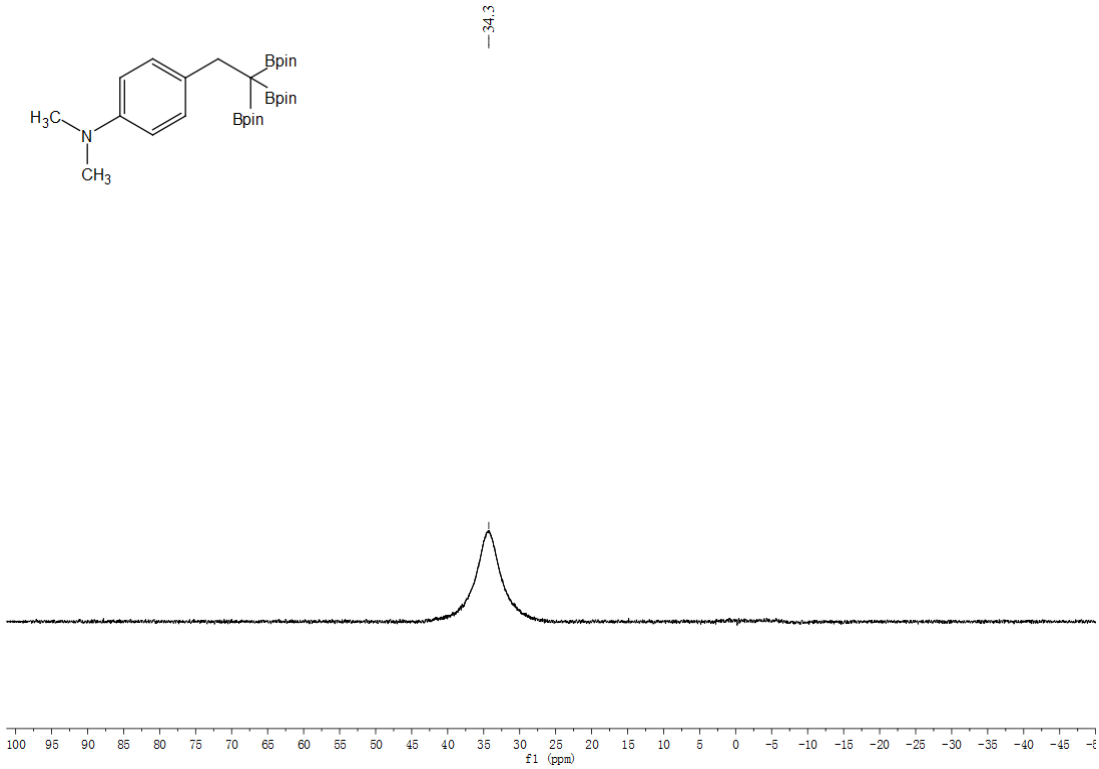
^{1}B NMR (193 MHz, EtOAc) of **10f**



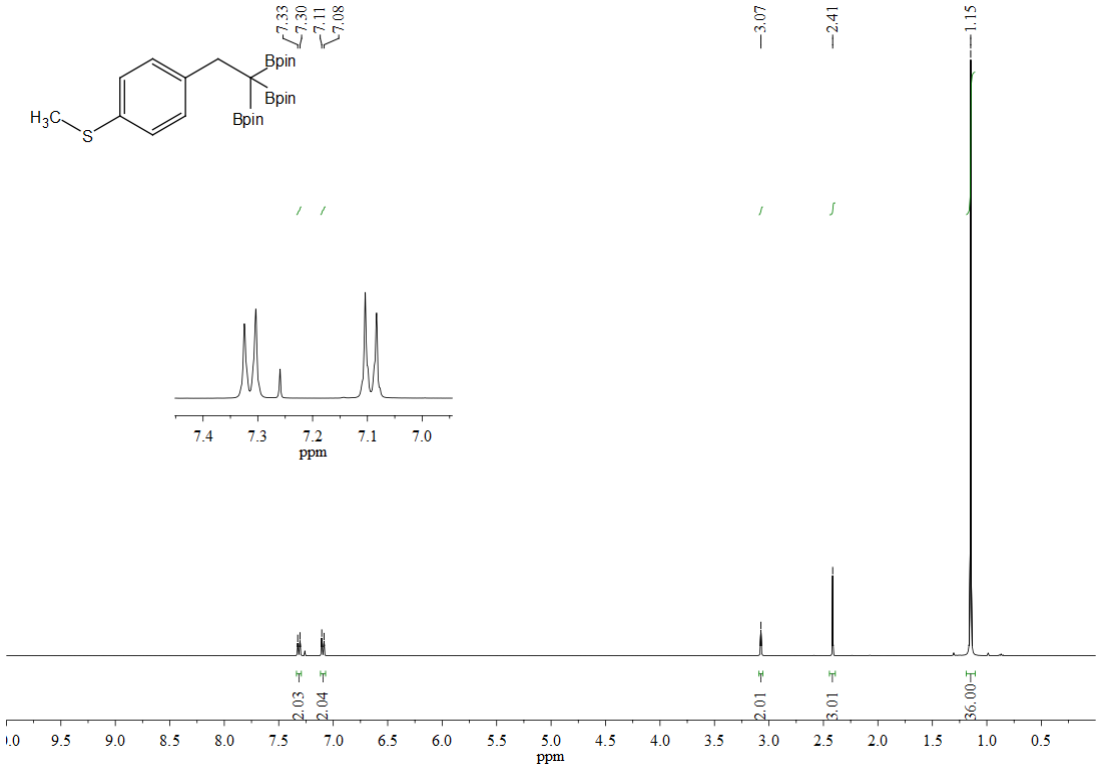
^{1}H NMR (400 MHz, $CDCl_3$) of **10g**



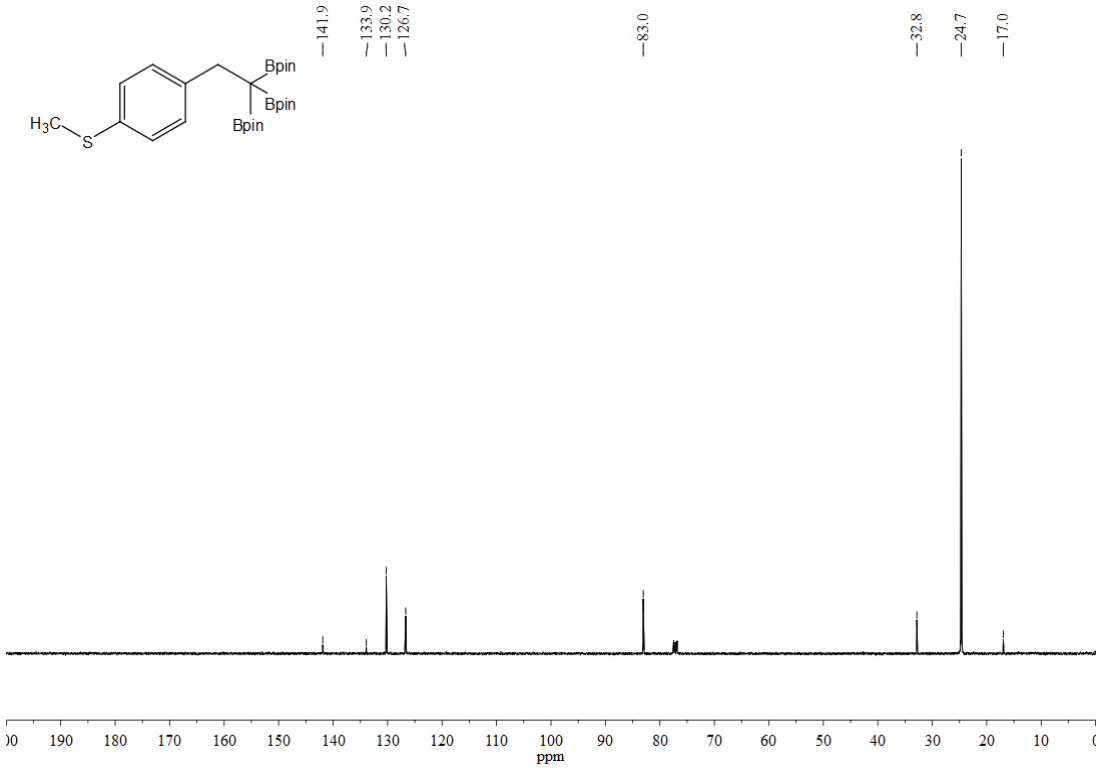
^{13}C NMR (101 MHz, $CDCl_3$) of **10g**



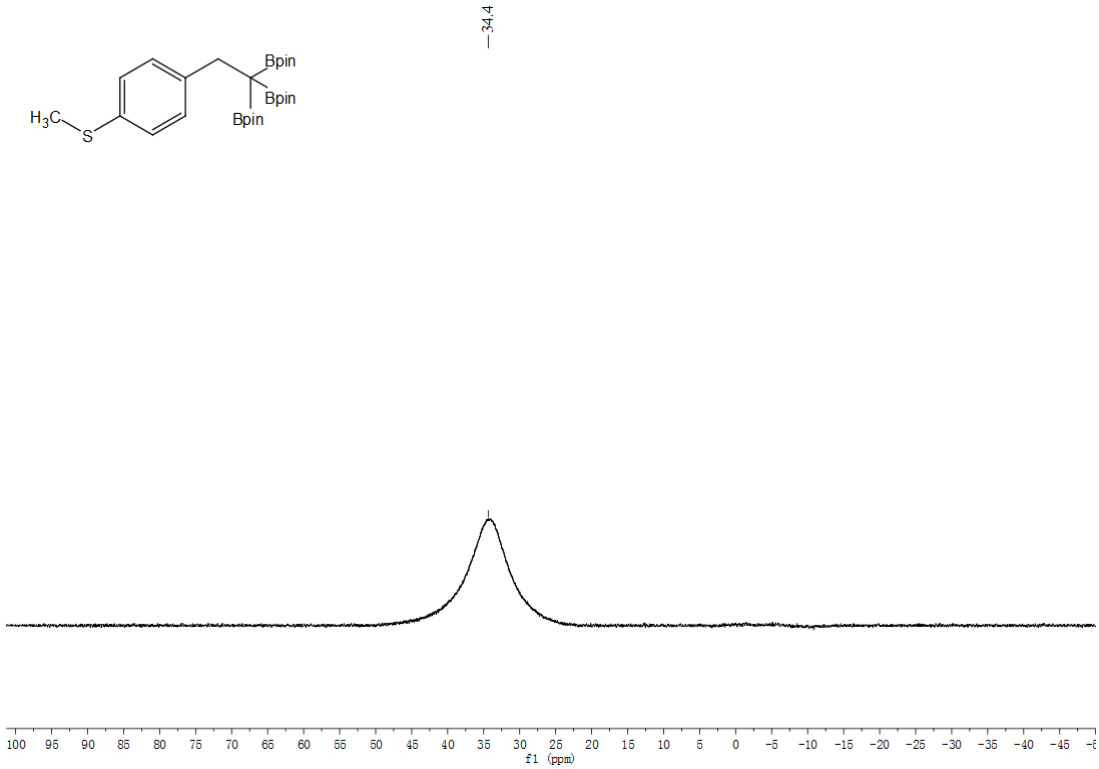
^{11}B NMR (193 MHz, EtOAc) of **10g**



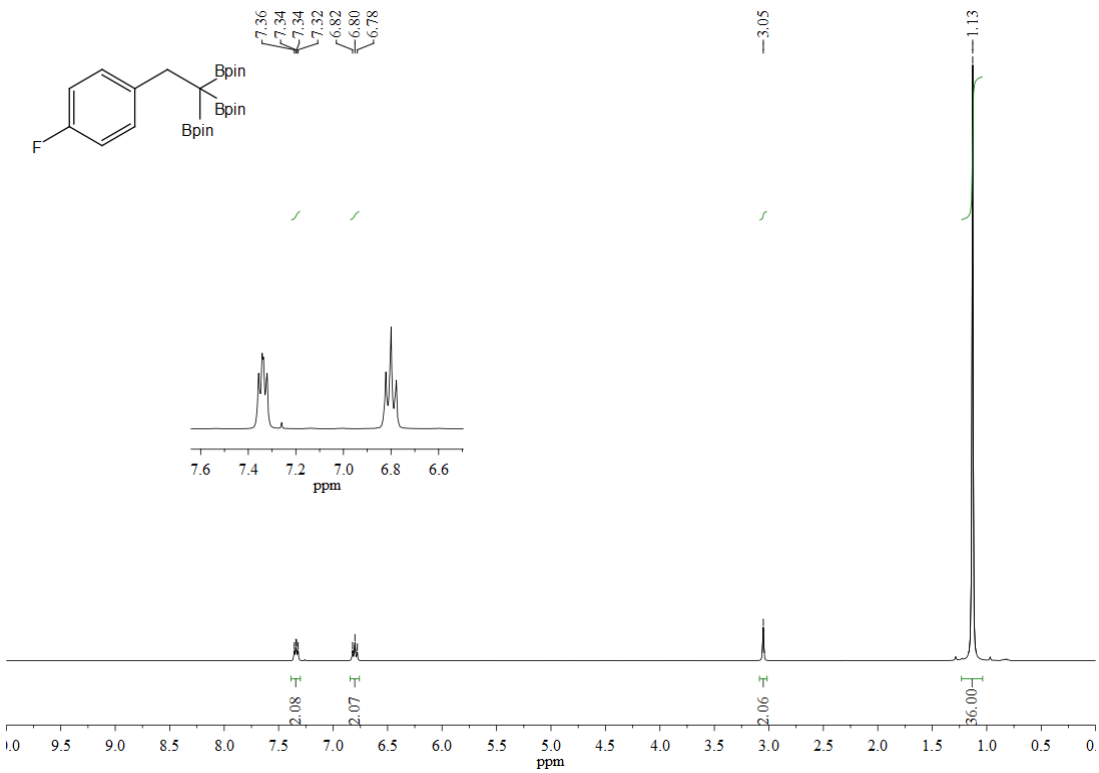
^{1}H NMR (400 MHz, $CDCl_3$) of **10h**



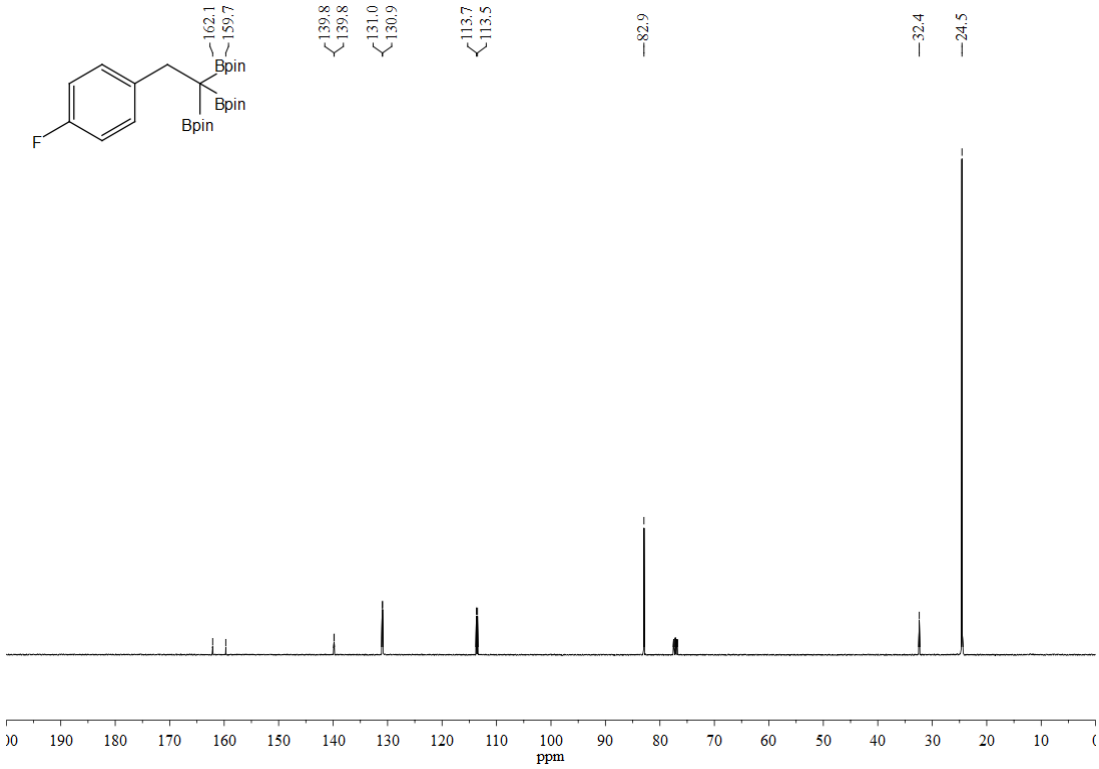
^{13}C NMR (101 MHz, $CDCl_3$) of **10h**



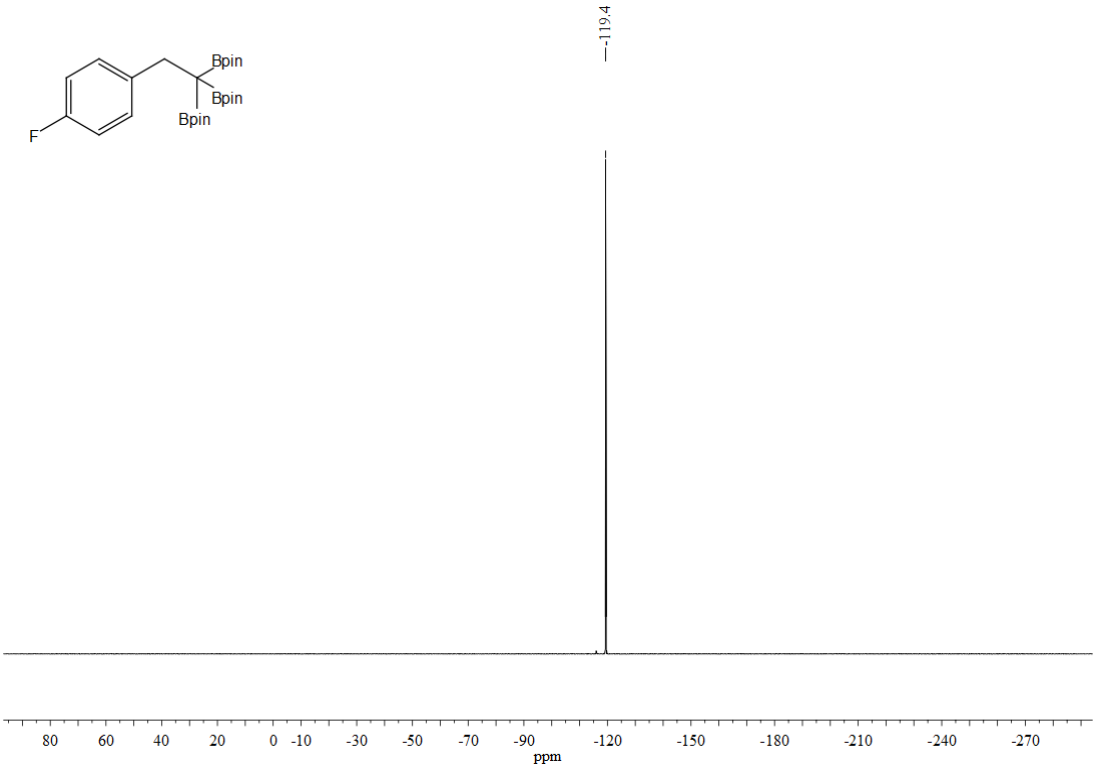
^{11}B NMR (193 MHz, EtOAc) of **10h**



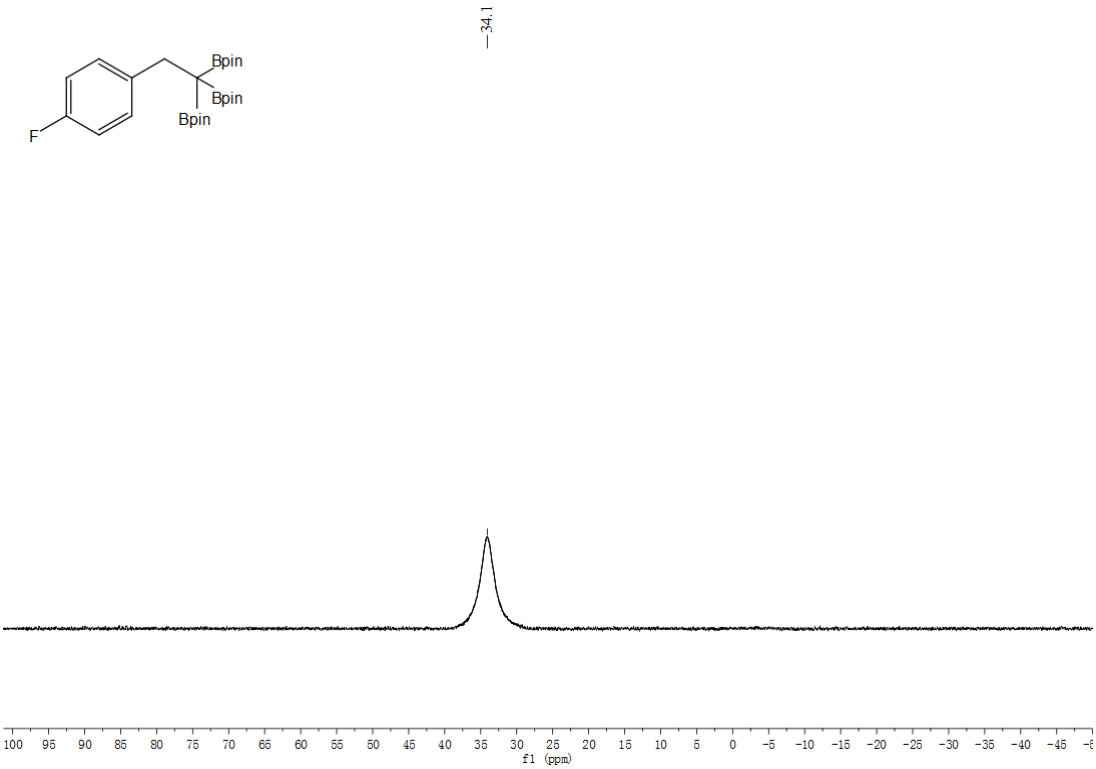
^{1}H NMR (400 MHz, $CDCl_3$) of **10i**



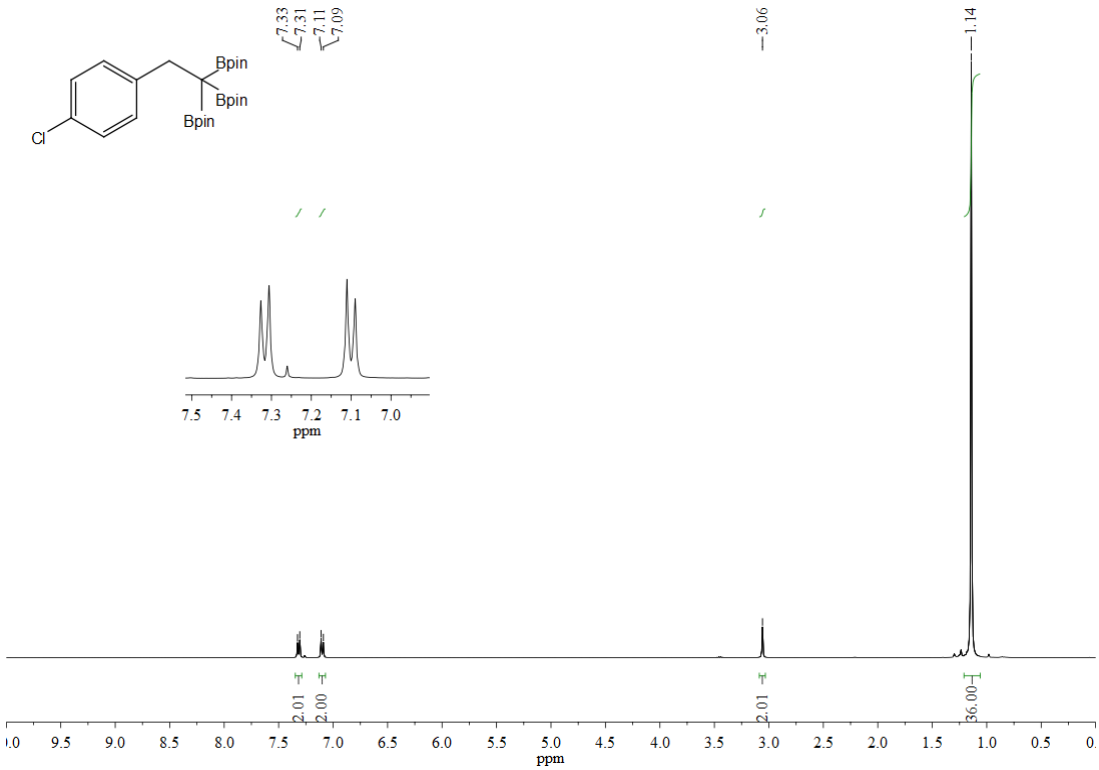
^{13}C NMR (101 MHz, $CDCl_3$) of **10i**



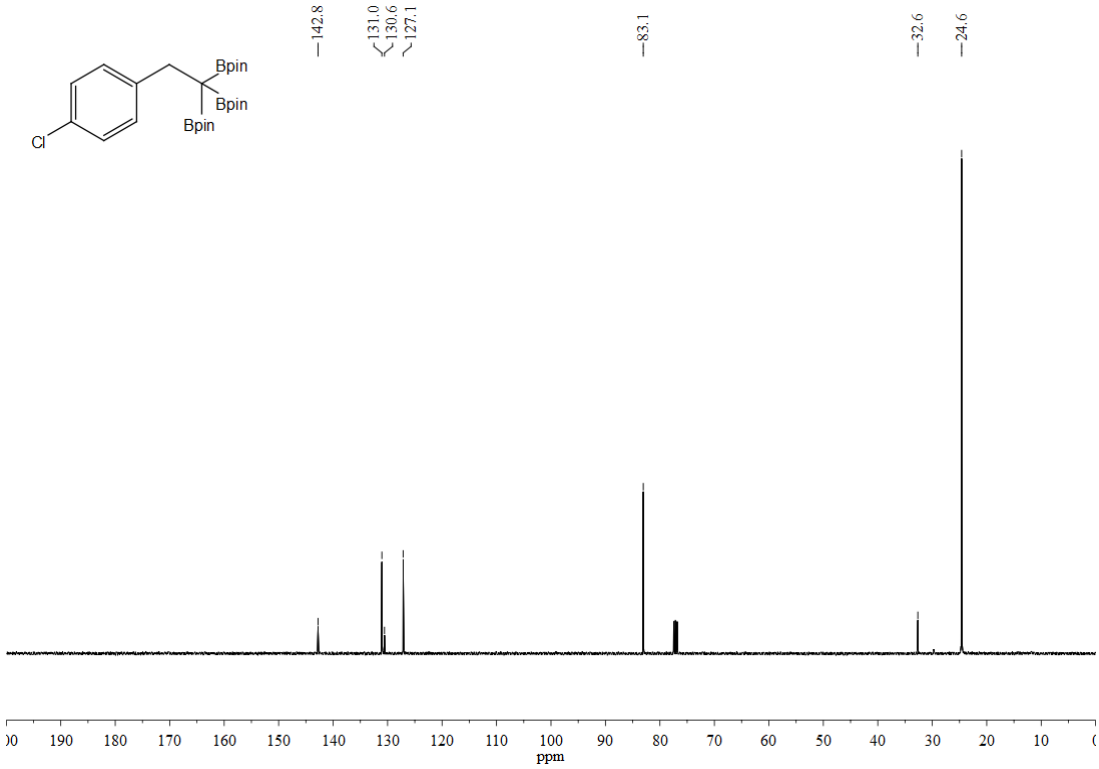
^{19}F NMR (376 MHz, $CDCl_3$) of **10i**



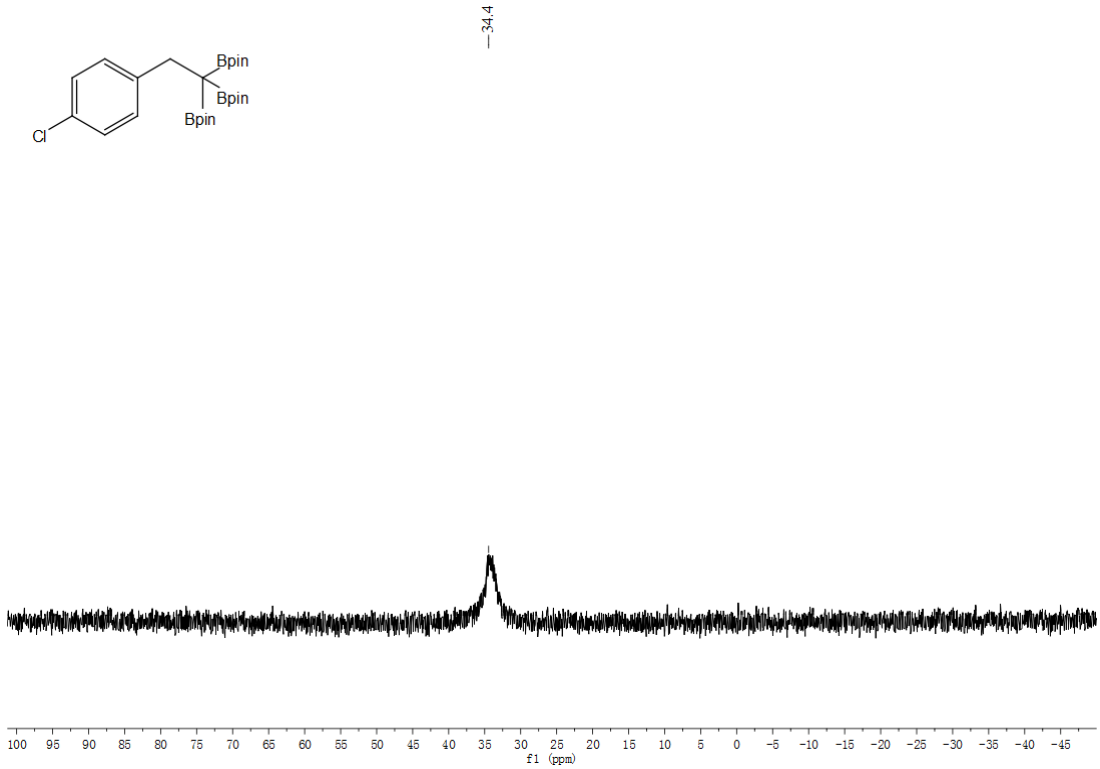
^{11}B NMR (193 MHz, EtOAc) of **10i**



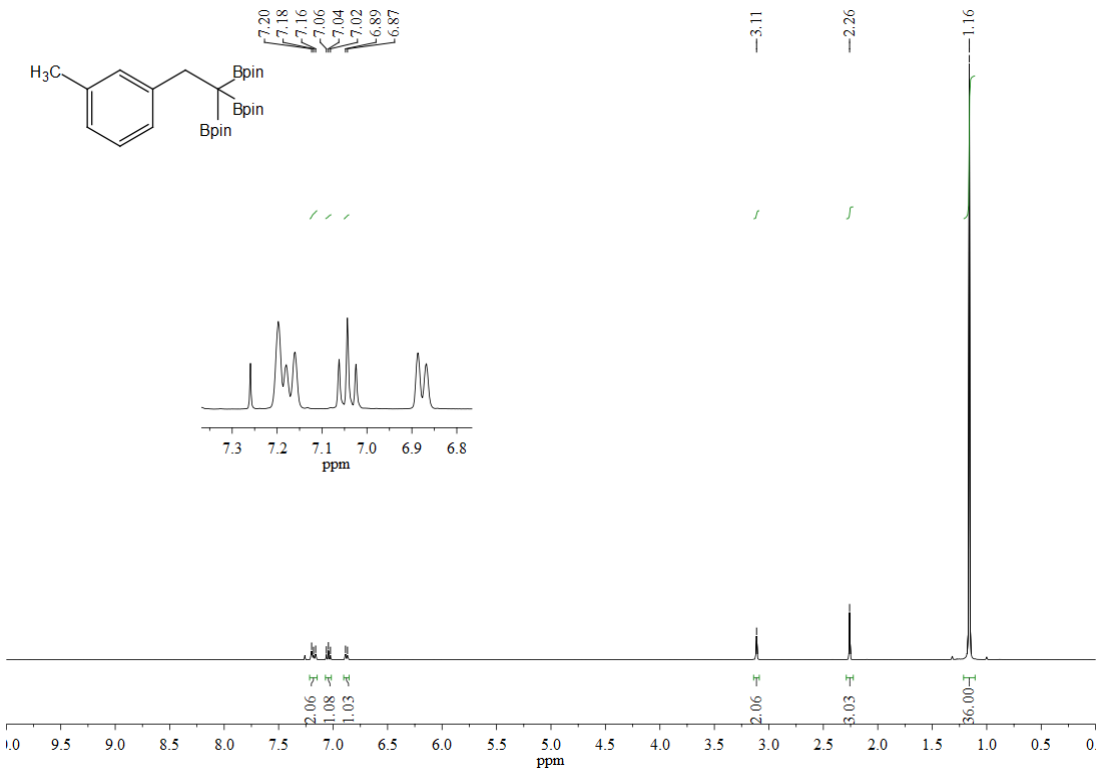
^{1}H NMR (400 MHz, $CDCl_3$) of **10j**



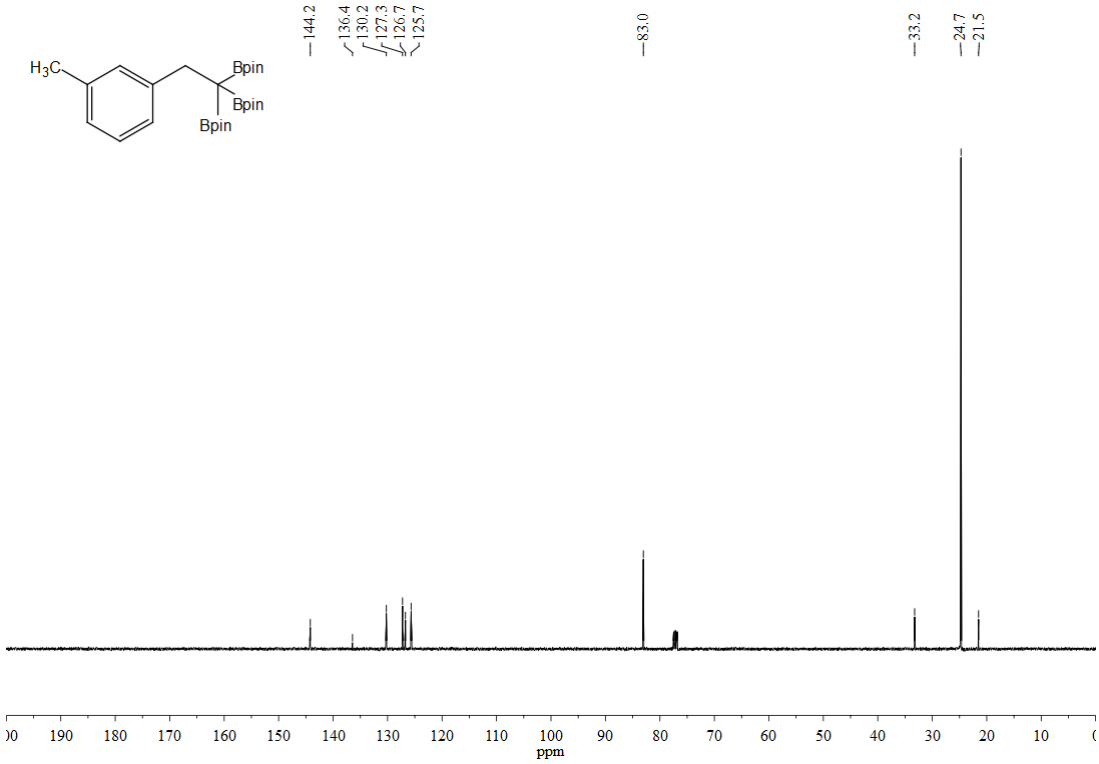
^{13}C NMR (101 MHz, $CDCl_3$) of **10j**



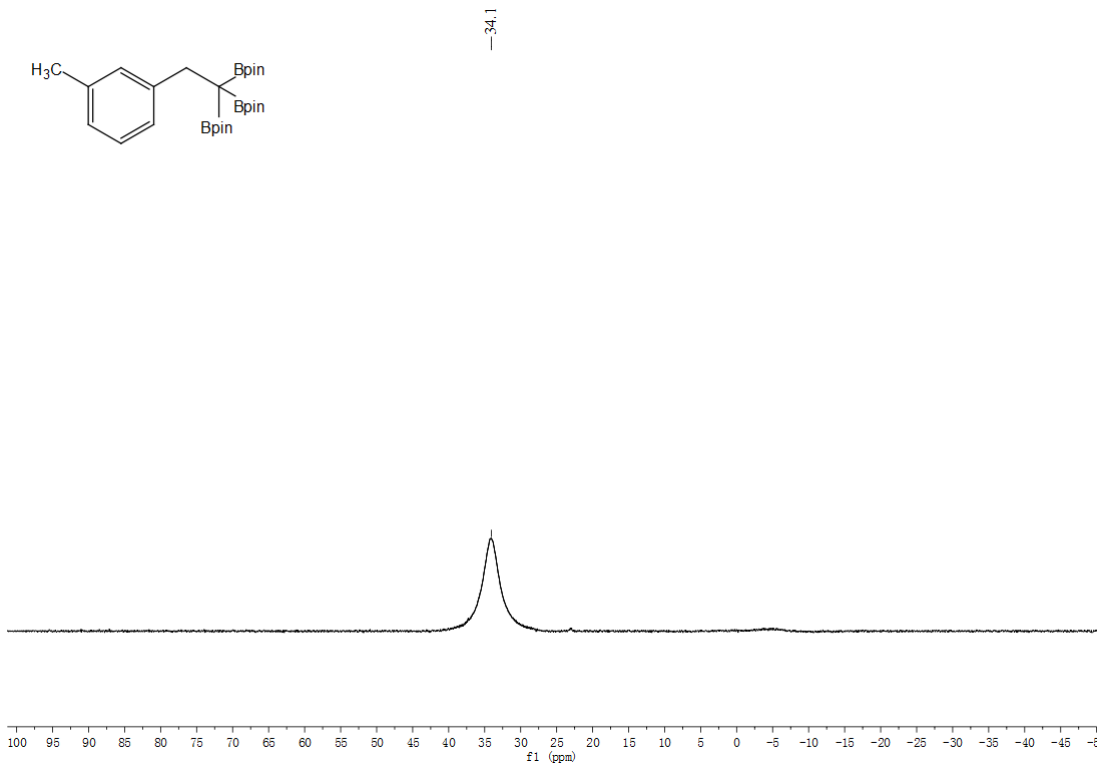
^{11}B NMR (193 MHz, EtOAc) of **10j**



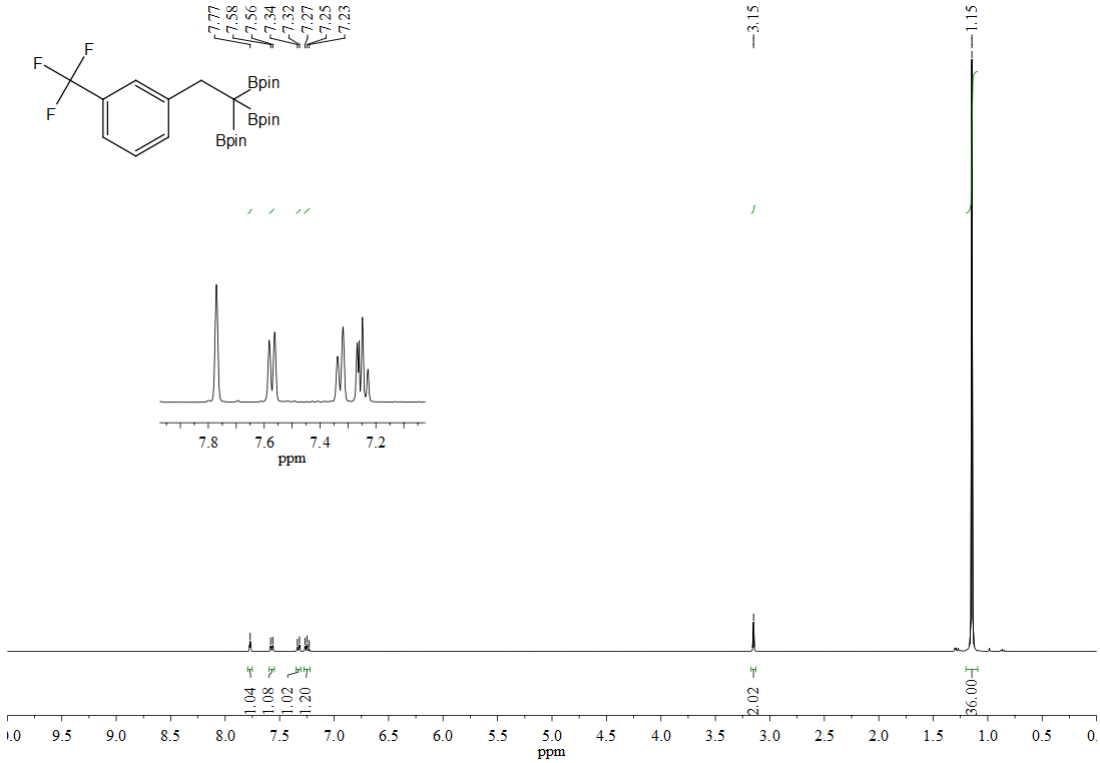
^{1}H NMR (400 MHz, $CDCl_3$) of **10k**



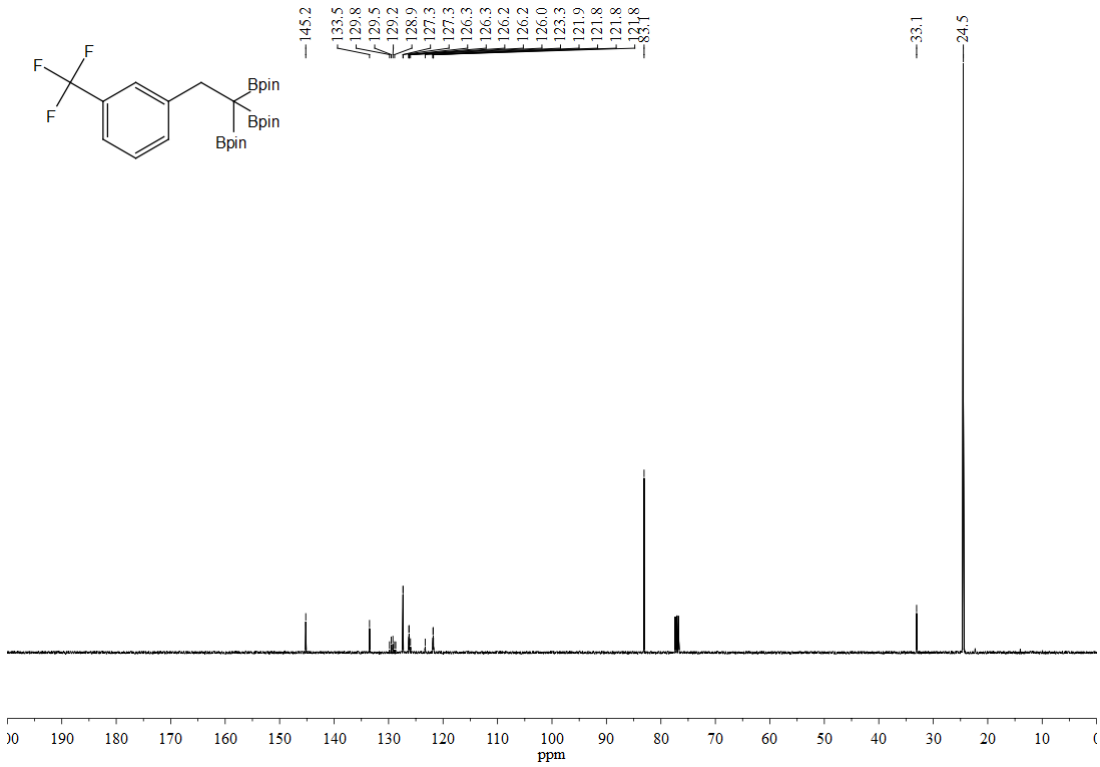
^{13}C NMR (101 MHz, $CDCl_3$) of **10k**



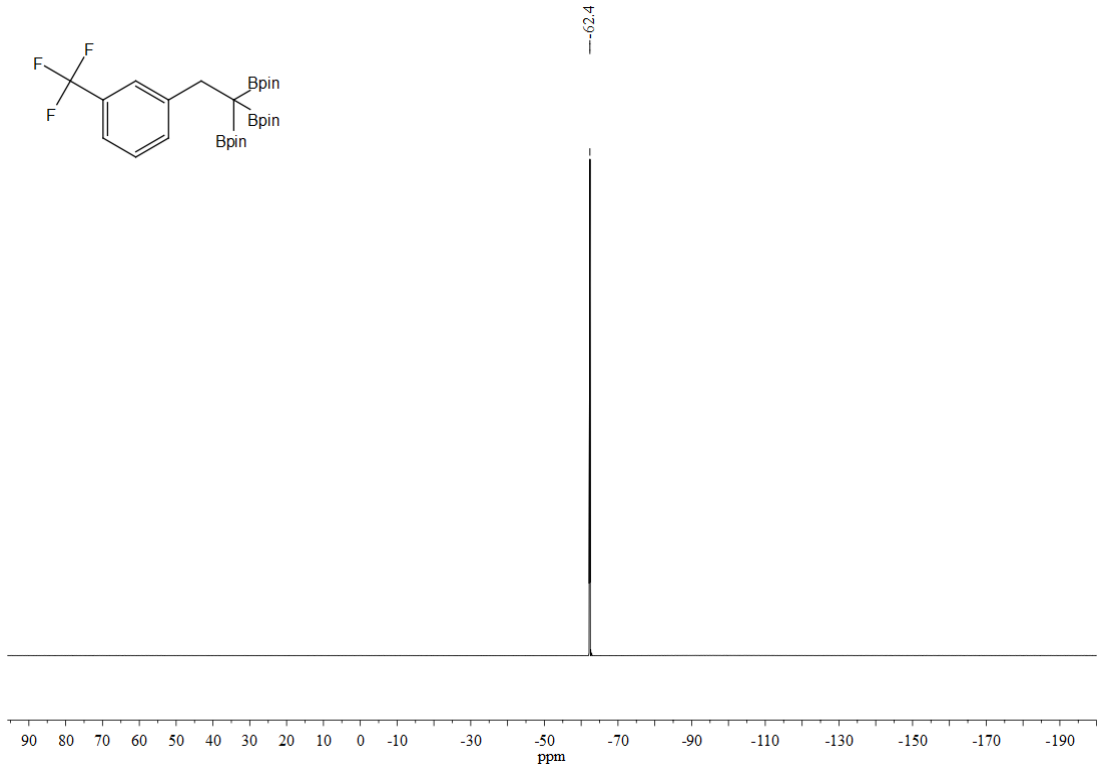
^{11}B NMR (193 MHz, EtOAc) of **10k**



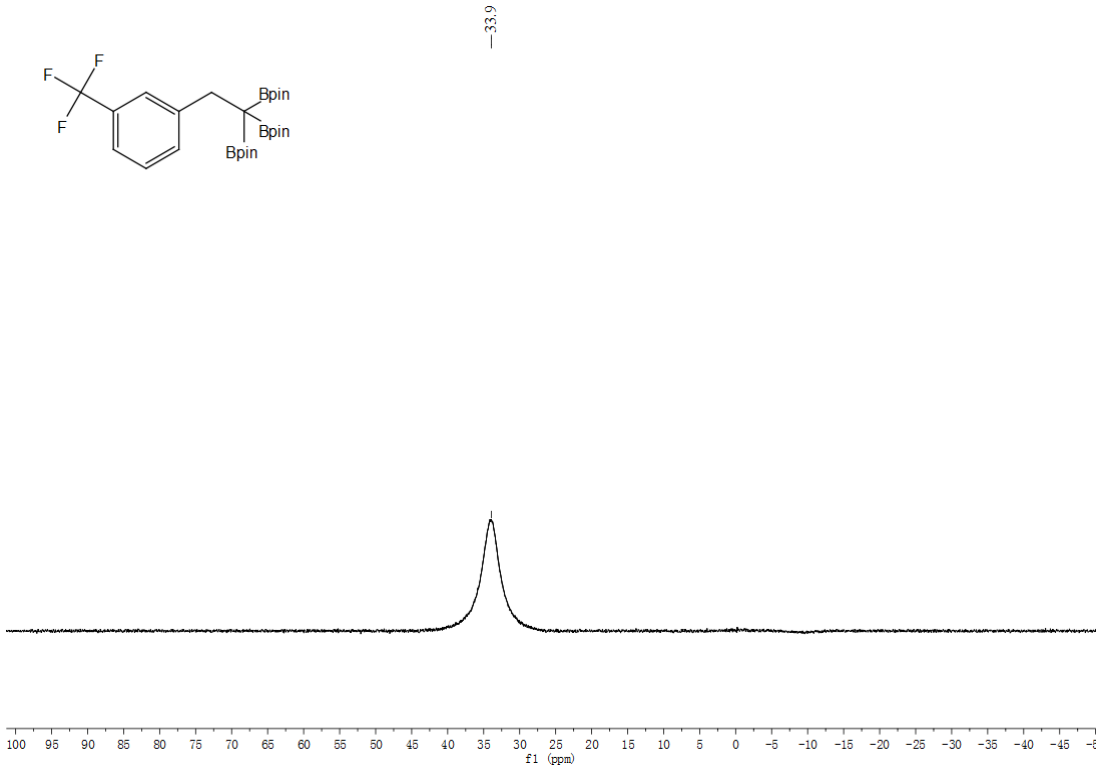
^{1}H NMR (400 MHz, $CDCl_3$) of **10l**



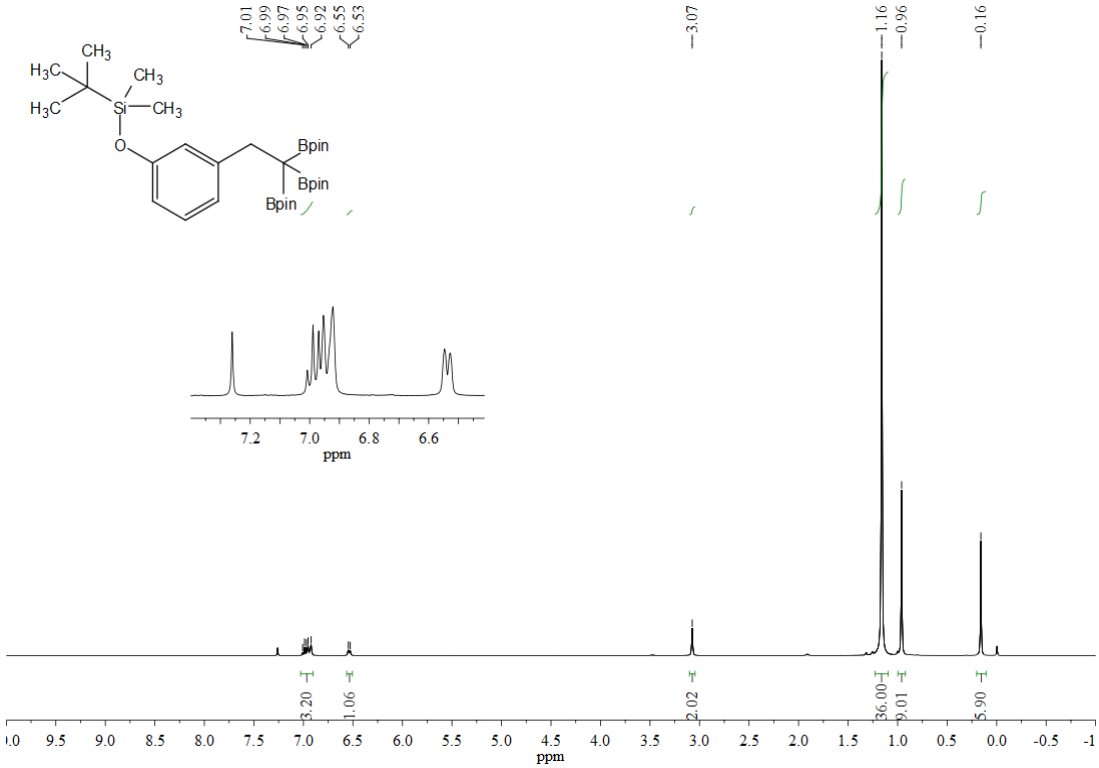
^{13}C NMR (101 MHz, $CDCl_3$) of **10l**



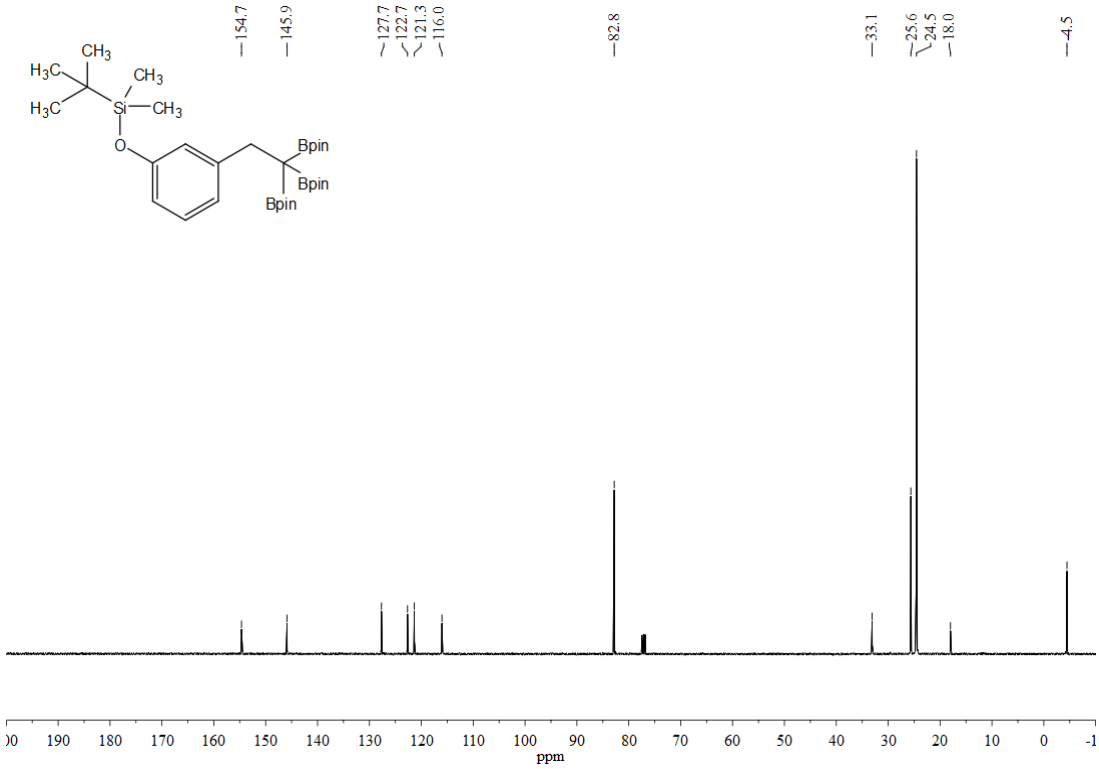
^{19}F NMR (376 MHz, $CDCl_3$) of **10l**



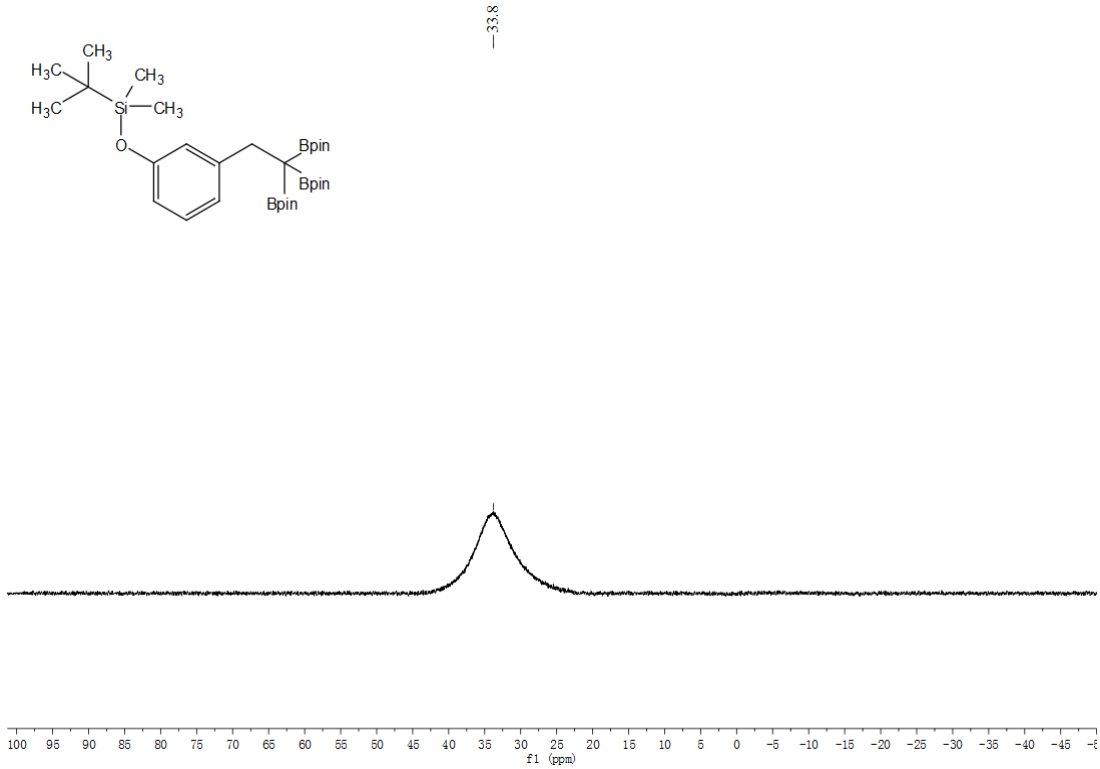
^{11}B NMR (193 MHz, EtOAc) of **10l**



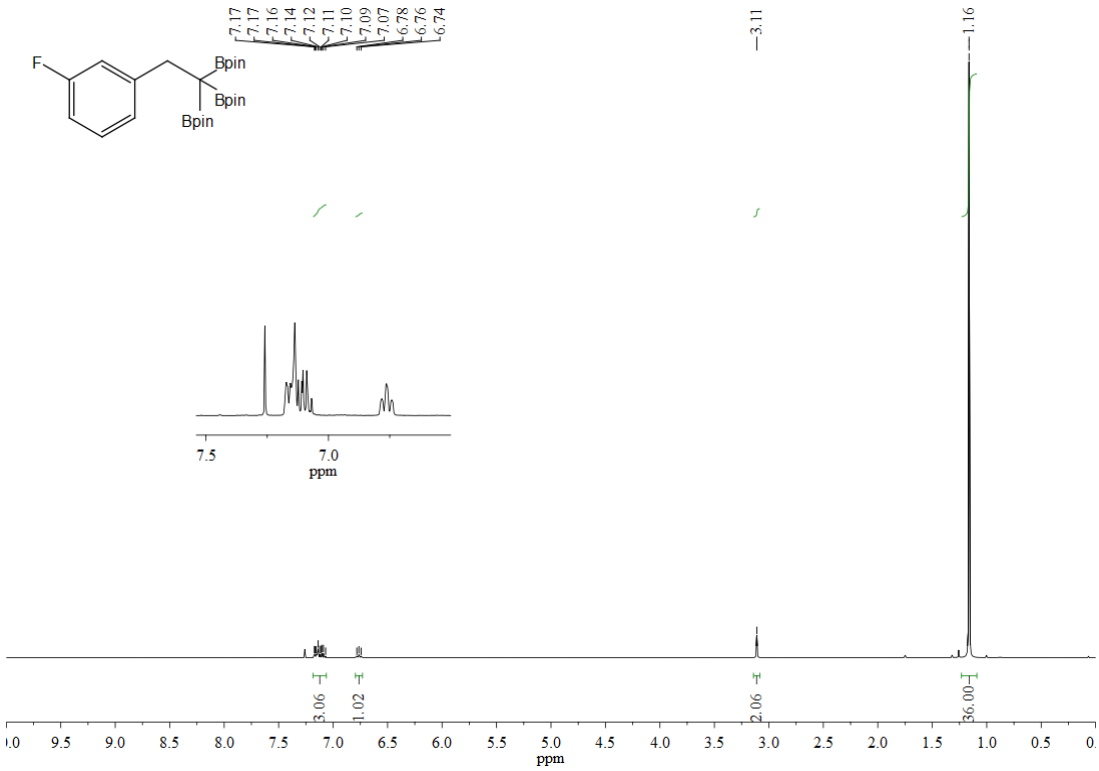
^{1}H NMR (400 MHz, $CDCl_3$) of **10m**



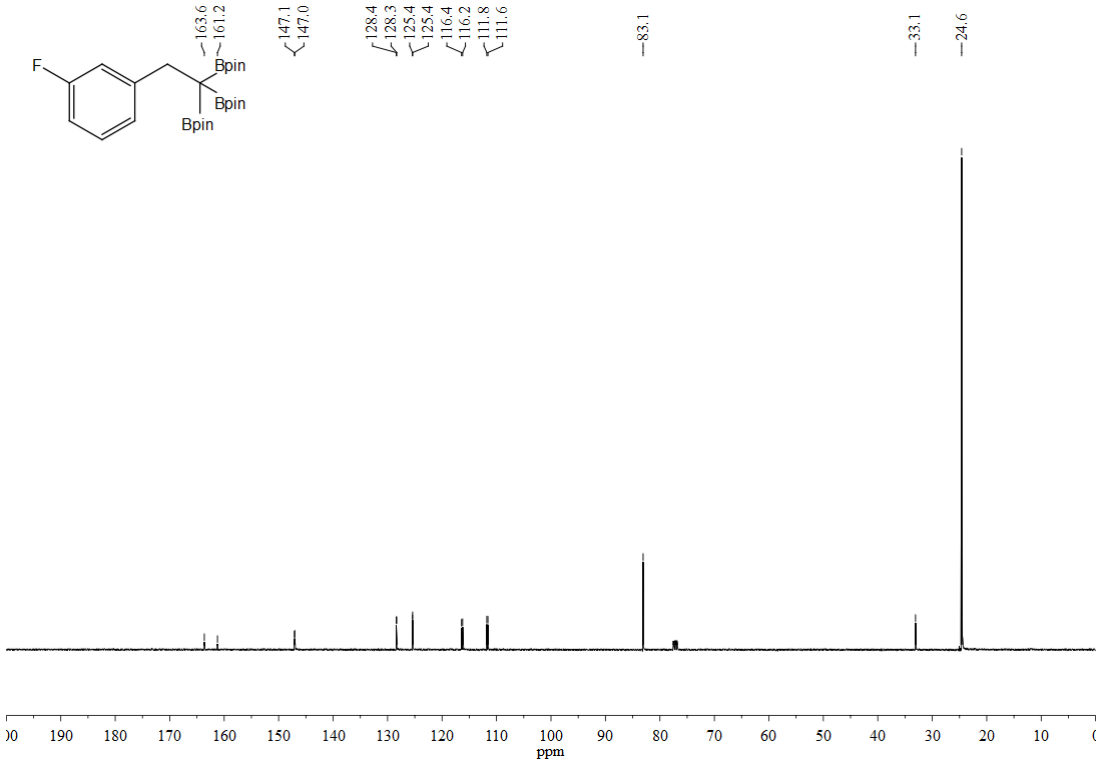
^{13}C NMR (101 MHz, $CDCl_3$) of **10m**



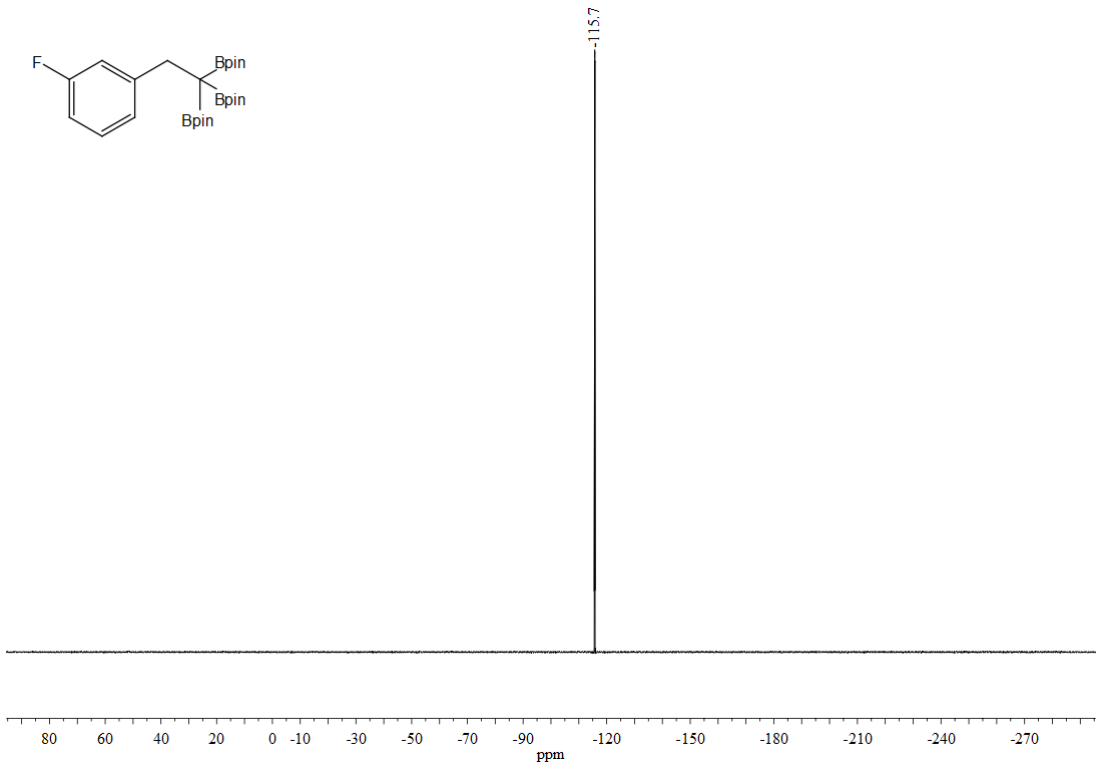
^{11}B NMR (193 MHz, EtOAc) of **10m**



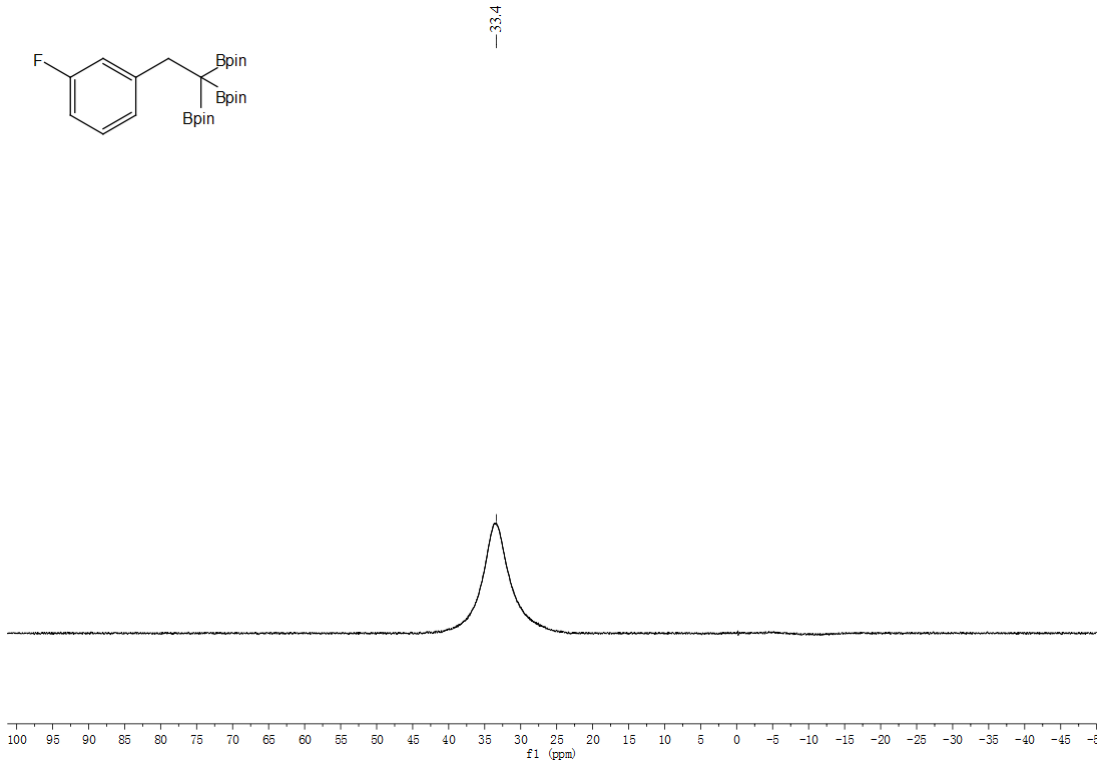
^{1}H NMR (400 MHz, $CDCl_3$) of **10n**



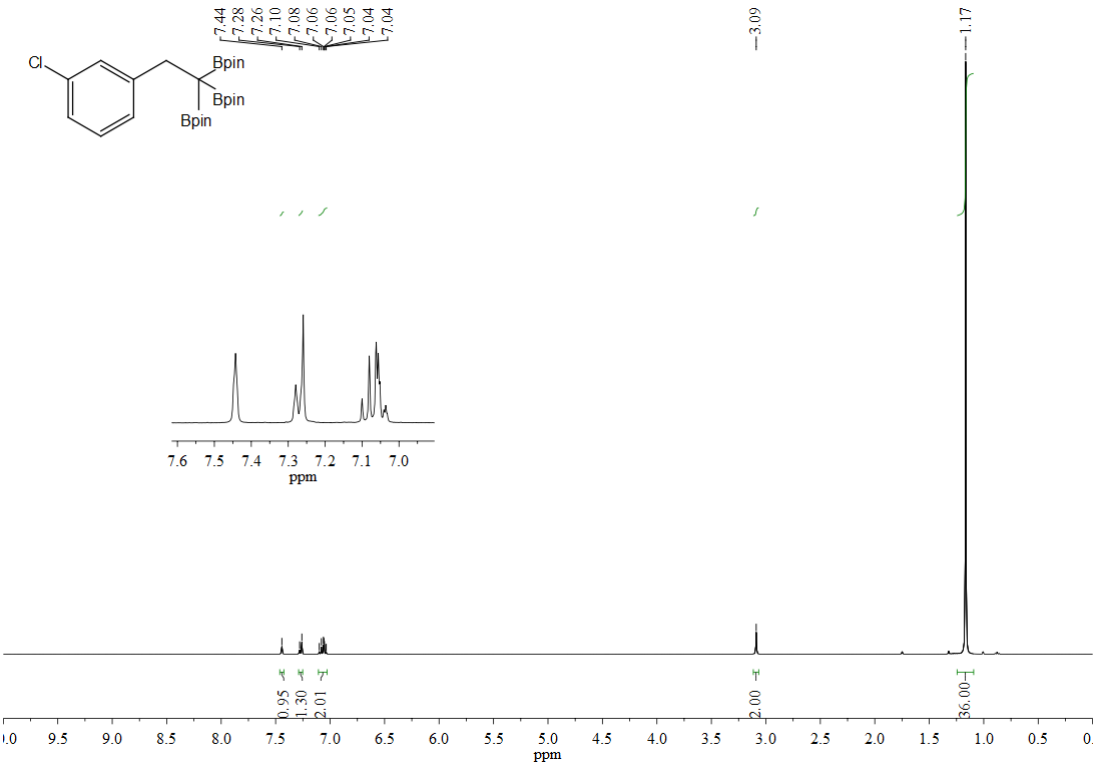
^{13}C NMR (101 MHz, $CDCl_3$) of **10n**



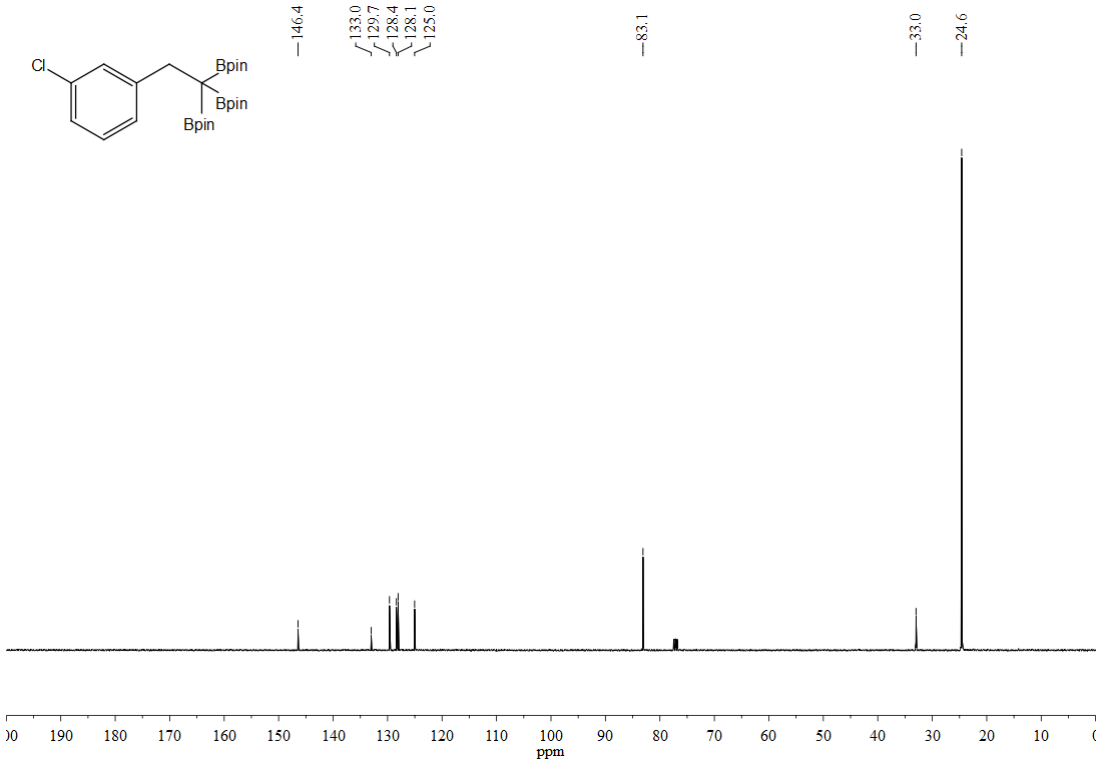
^{19}F NMR (376 MHz, $CDCl_3$) of **10n**



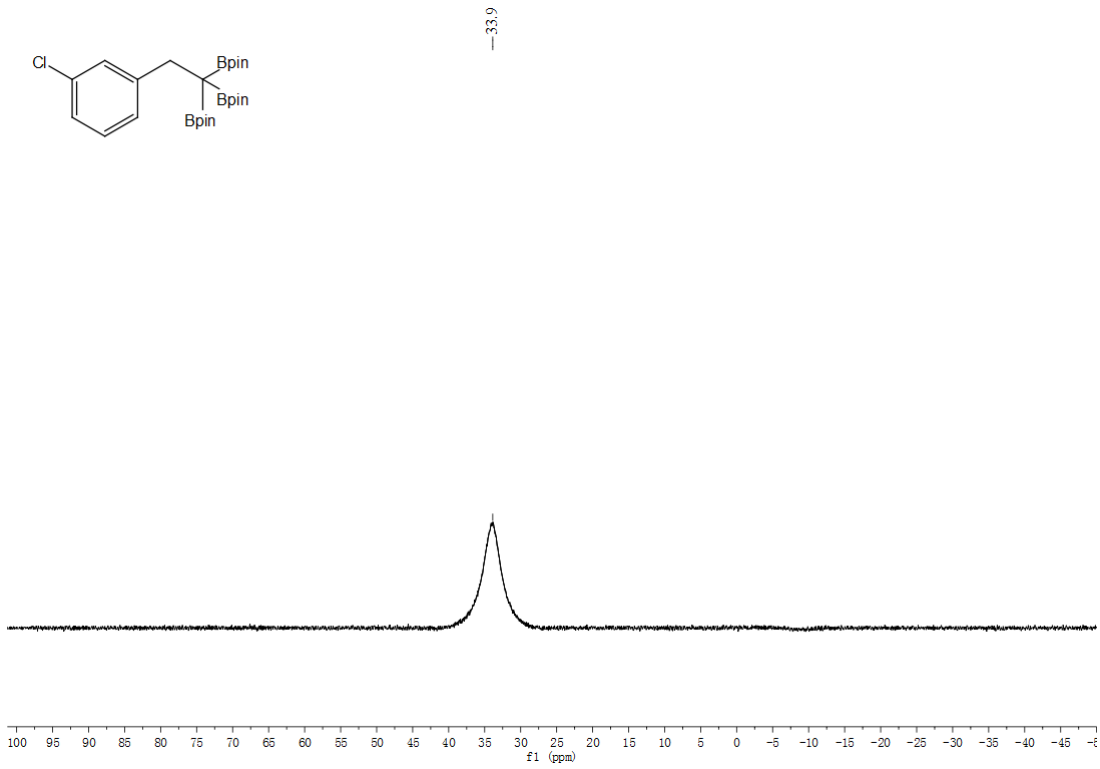
^{11}B NMR (193 MHz, EtOAc) of **10n**



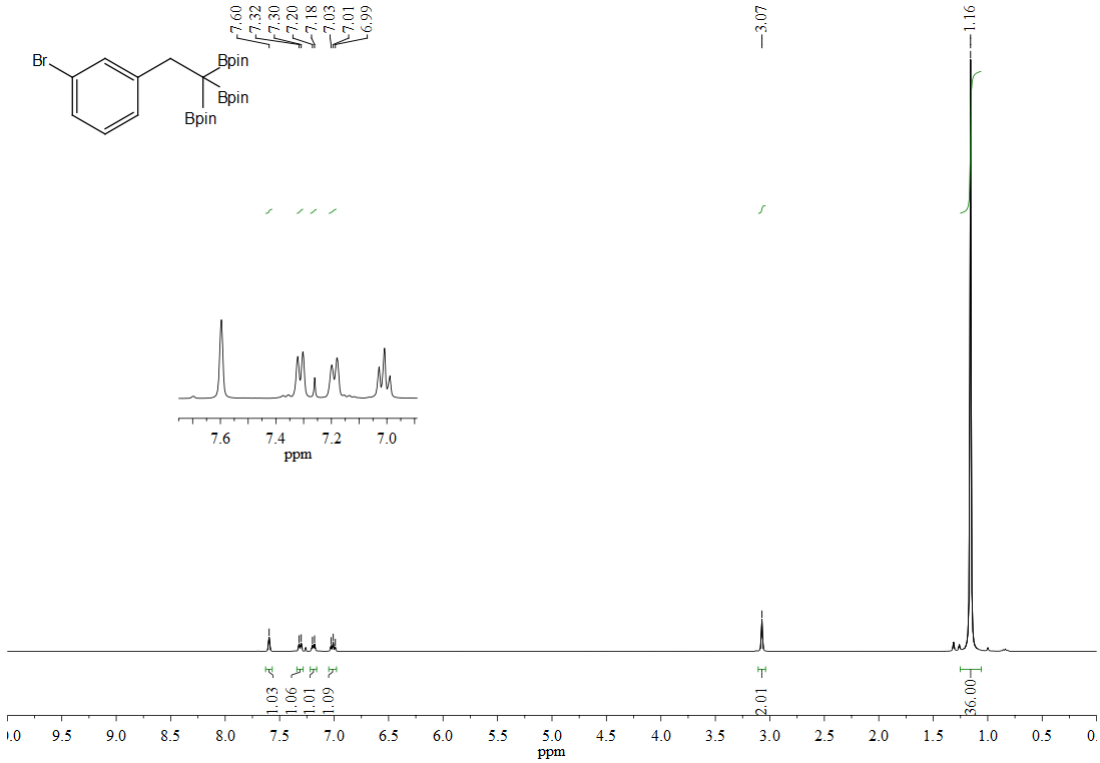
^{1}H NMR (400 MHz, $CDCl_3$) of **10o**



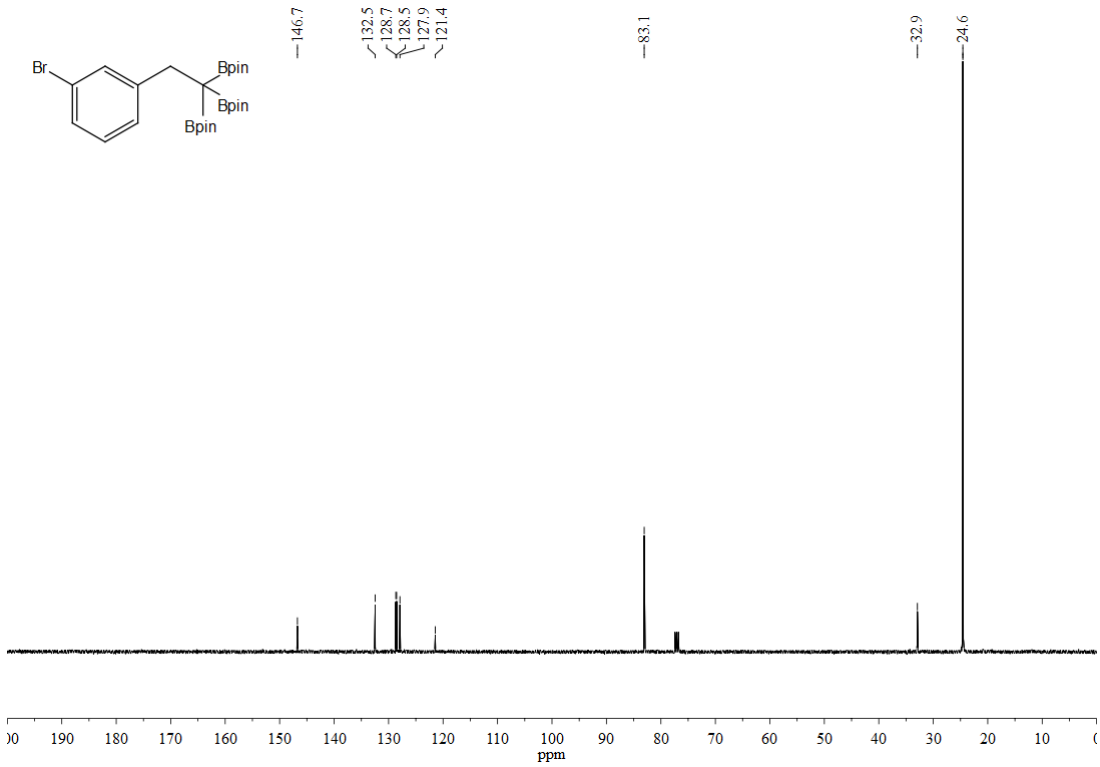
^{13}C NMR (101 MHz, $CDCl_3$) of **10o**



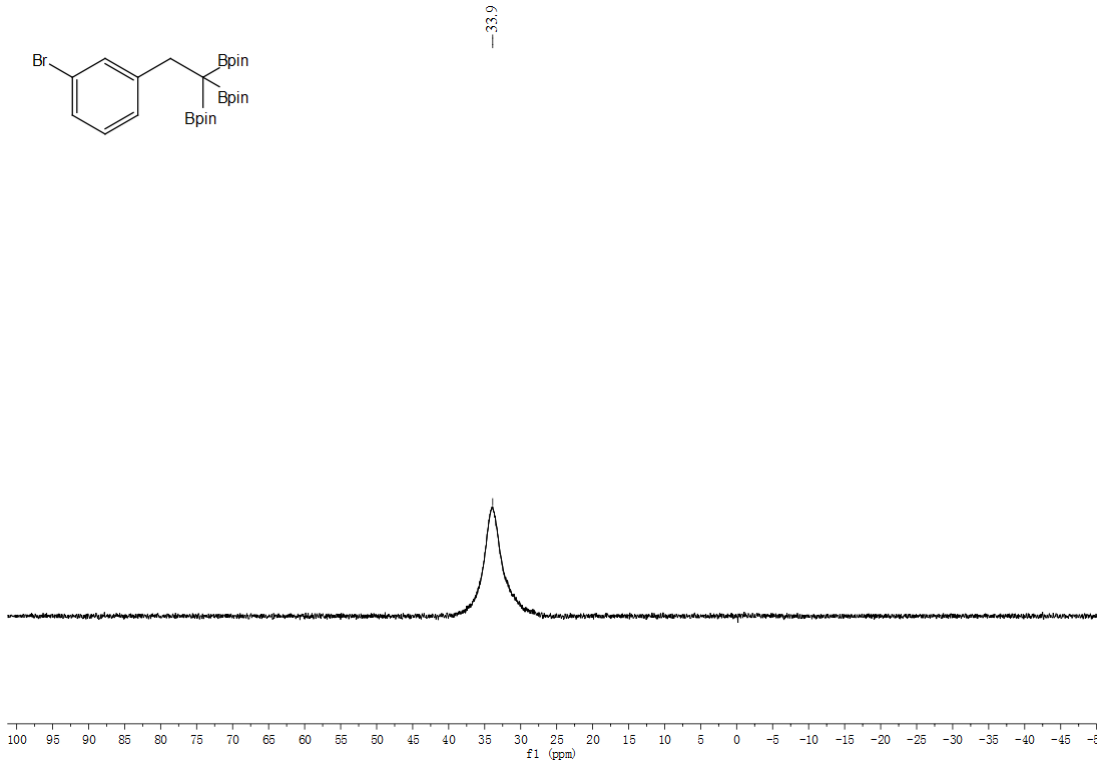
^{11}B NMR (193 MHz, EtOAc) of **10o**



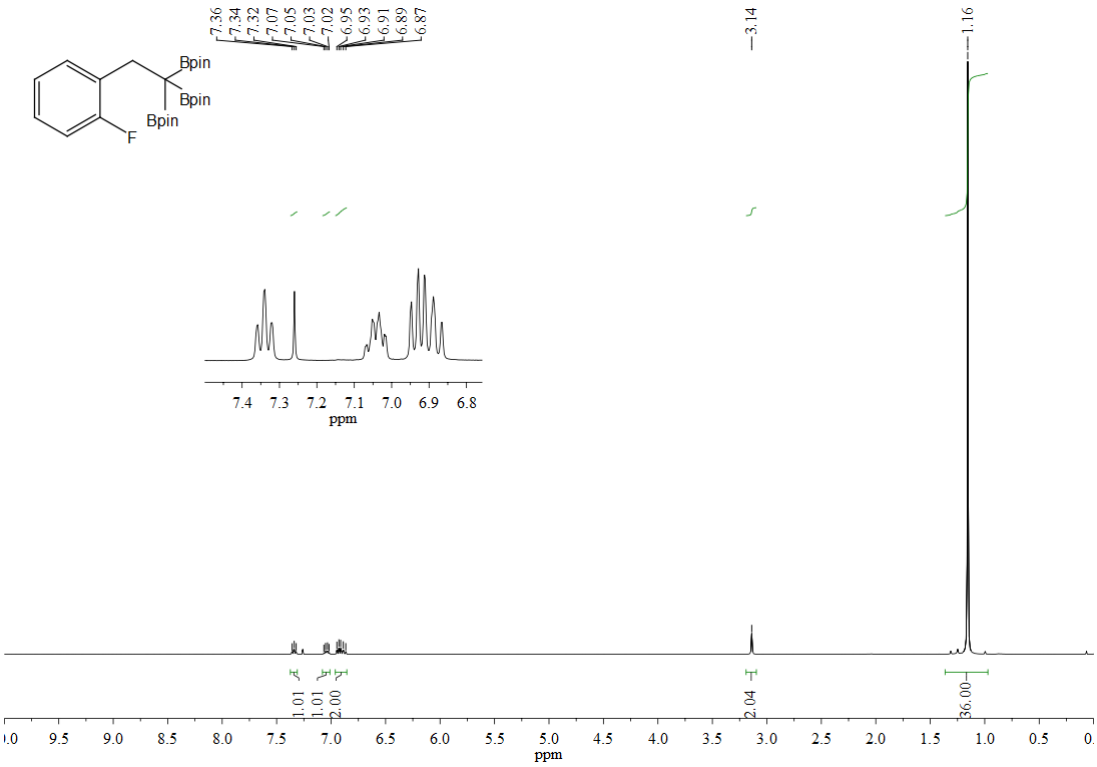
^{1}H NMR (400 MHz, $CDCl_3$) of **10p**



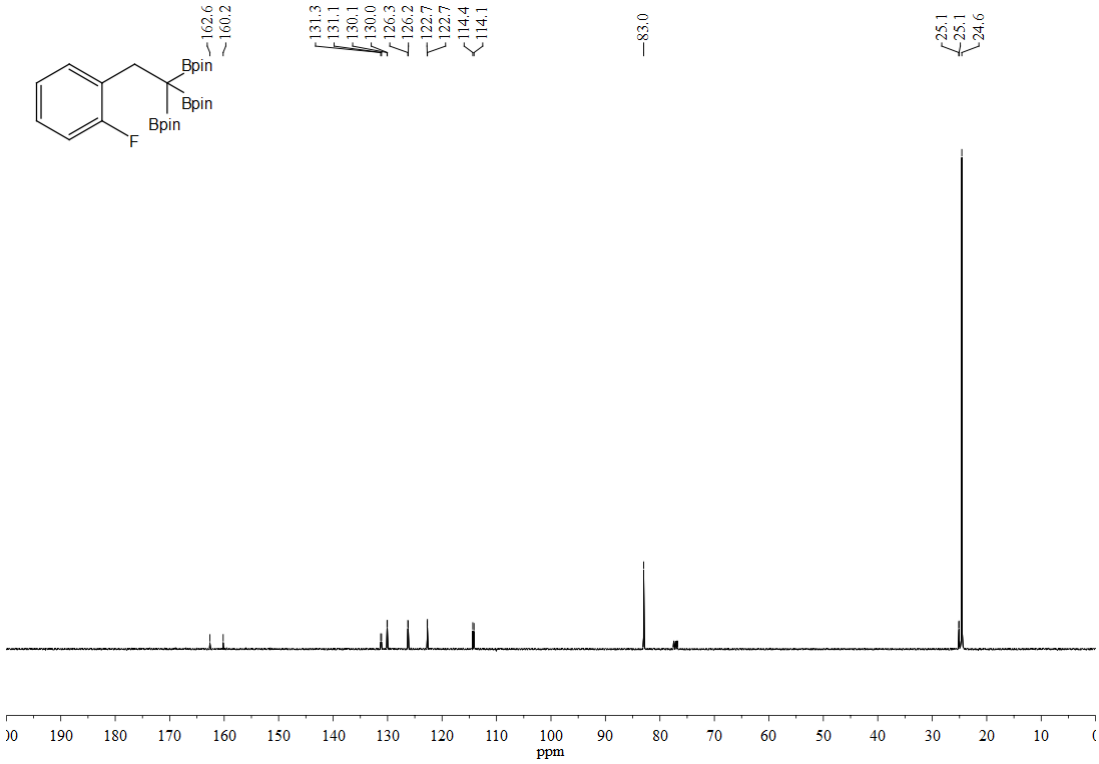
^{13}C NMR (101 MHz, $CDCl_3$) of **10p**



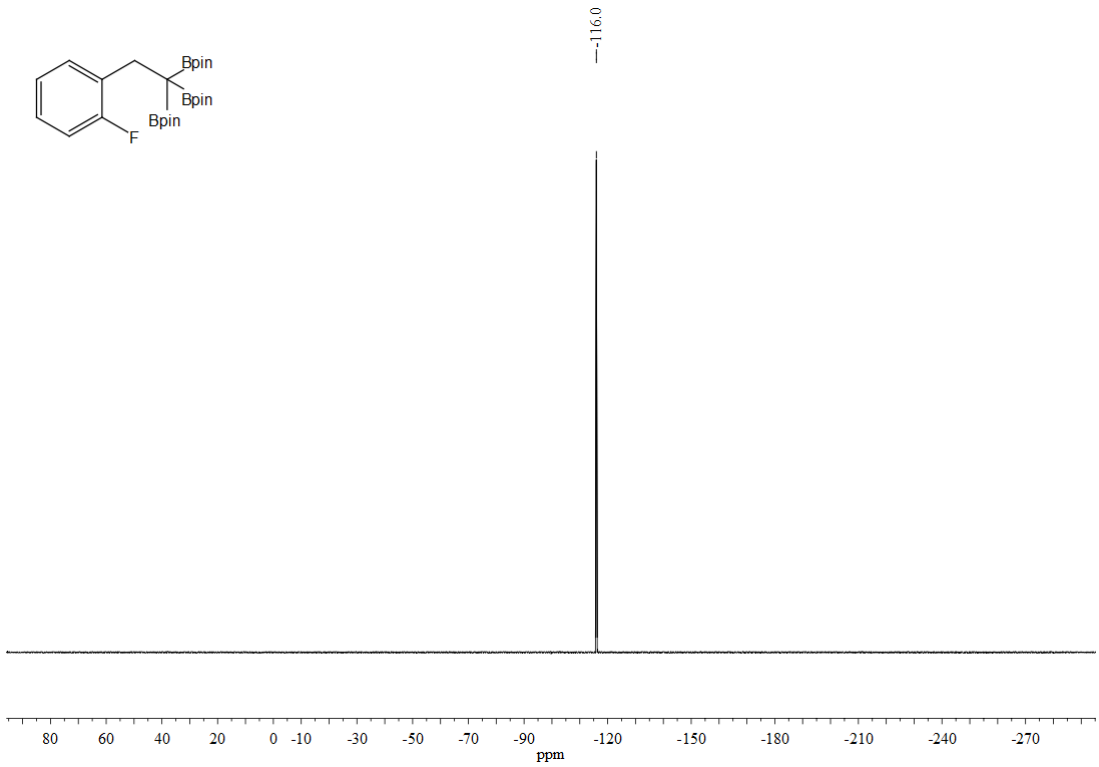
^{11}B NMR (193 MHz, EtOAc) of **10p**



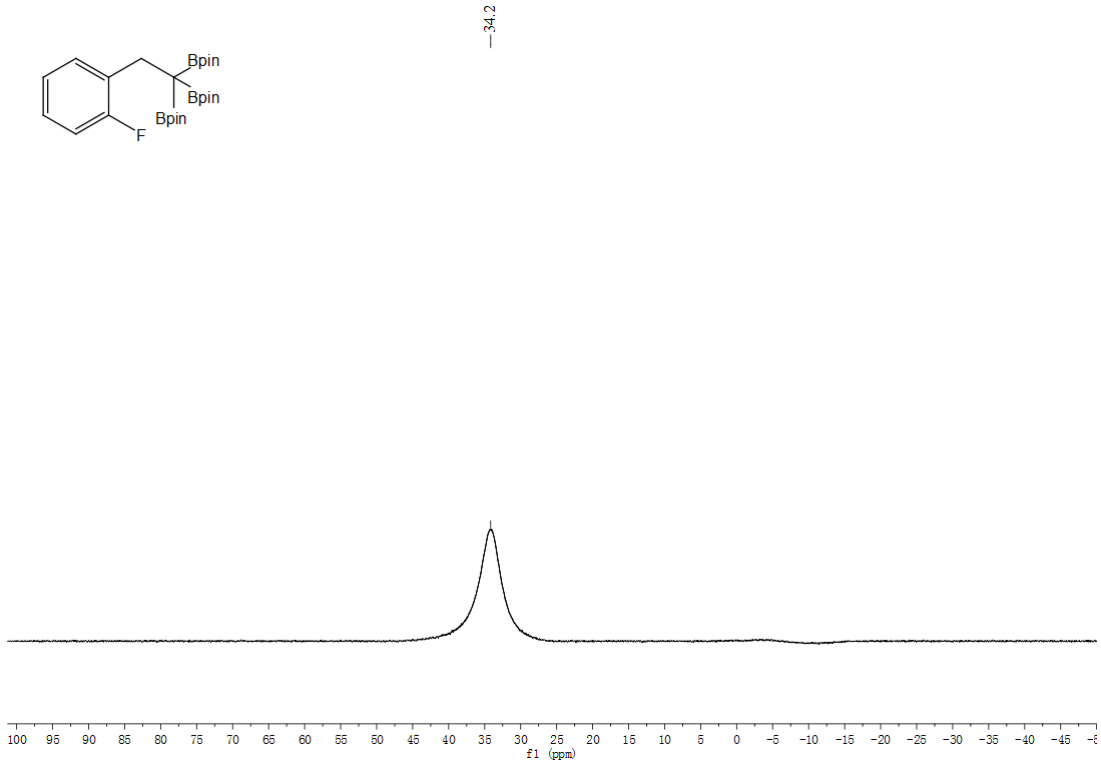
^{1}H NMR (400 MHz, $CDCl_3$) of **10q**



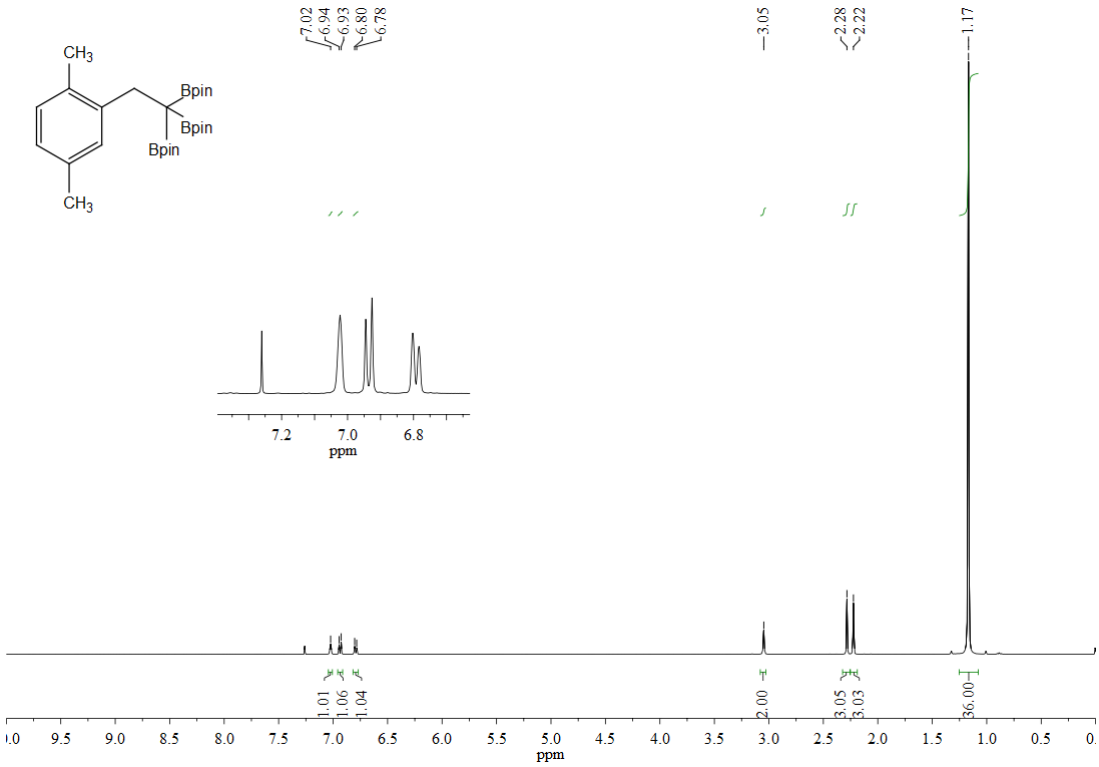
^{13}C NMR (101 MHz, $CDCl_3$) of **10q**



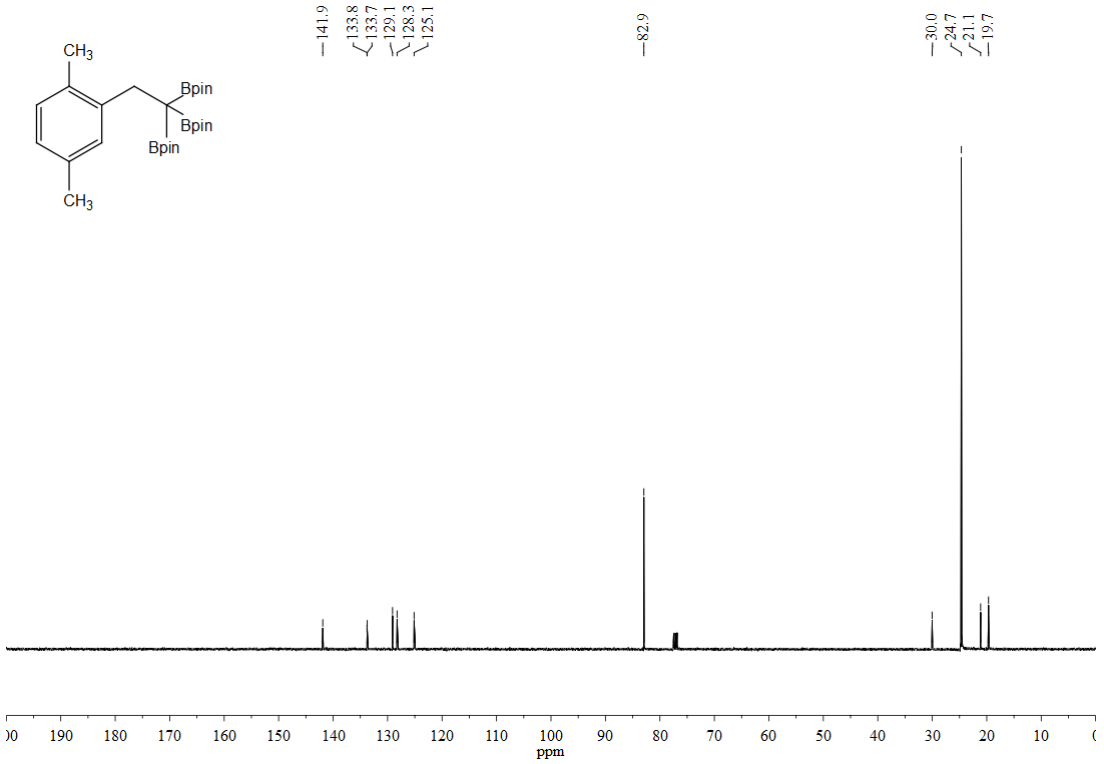
^{19}F NMR (376 MHz, $CDCl_3$) of **10q**



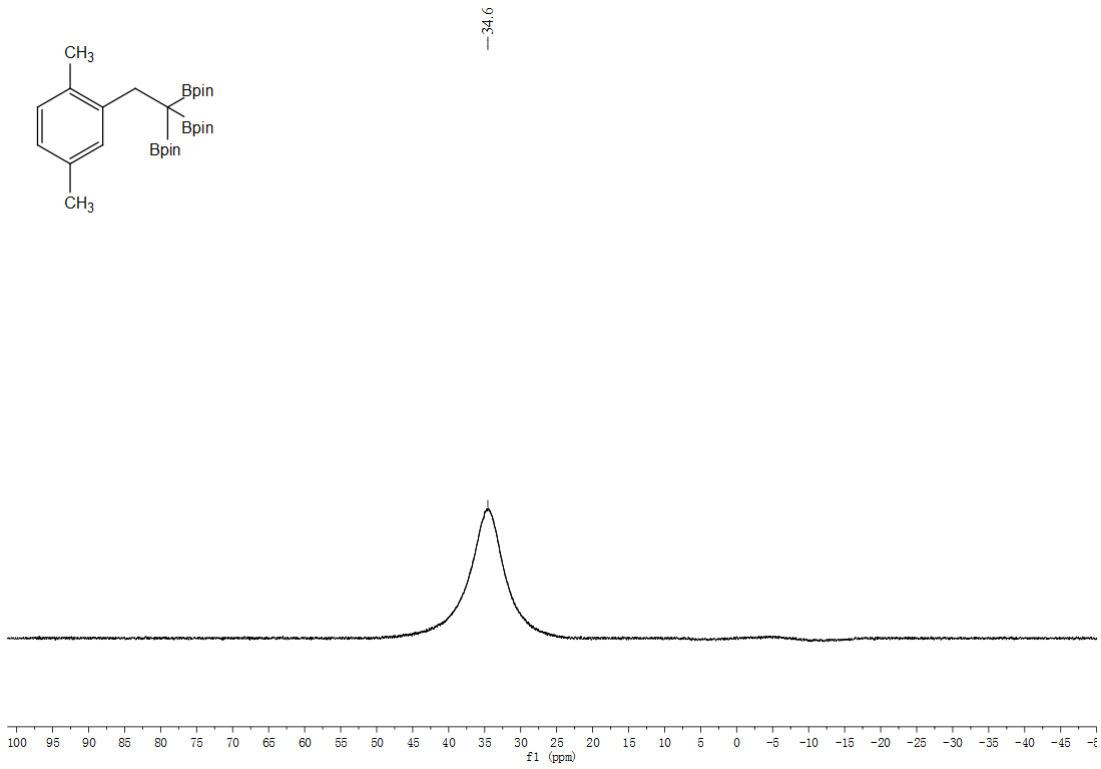
^{11}B NMR (193 MHz, EtOAc) of **10q**



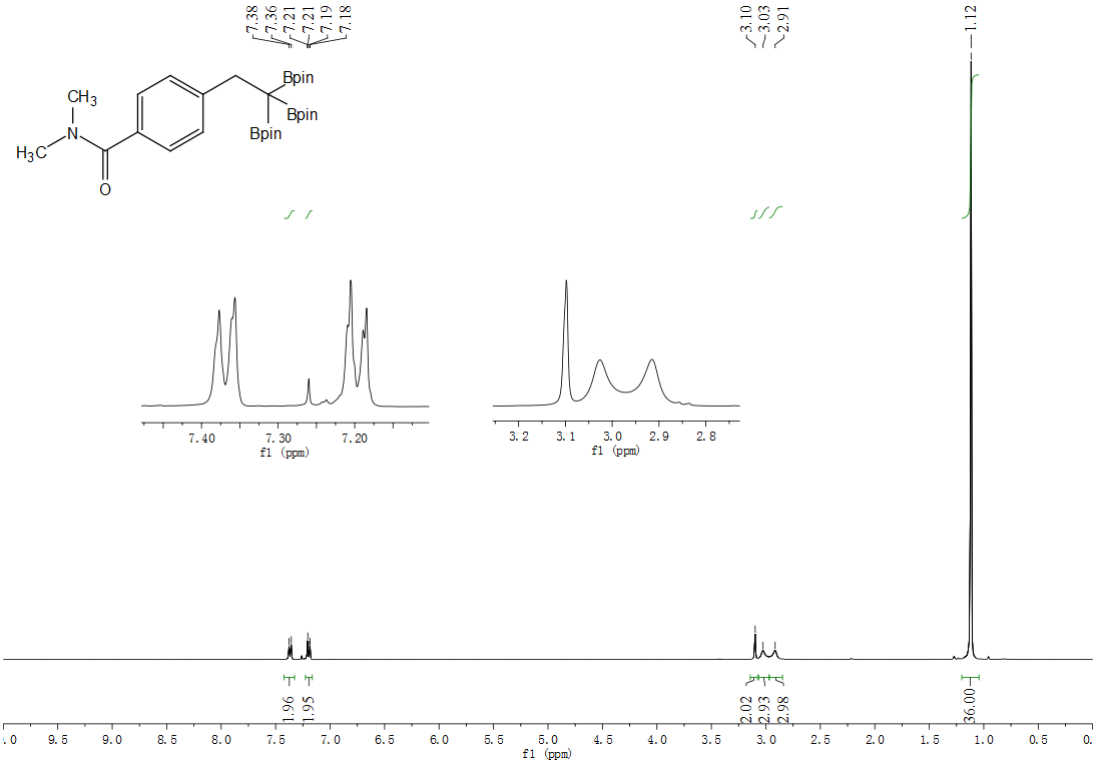
^{1}H NMR (400 MHz, $CDCl_3$) of **10r**



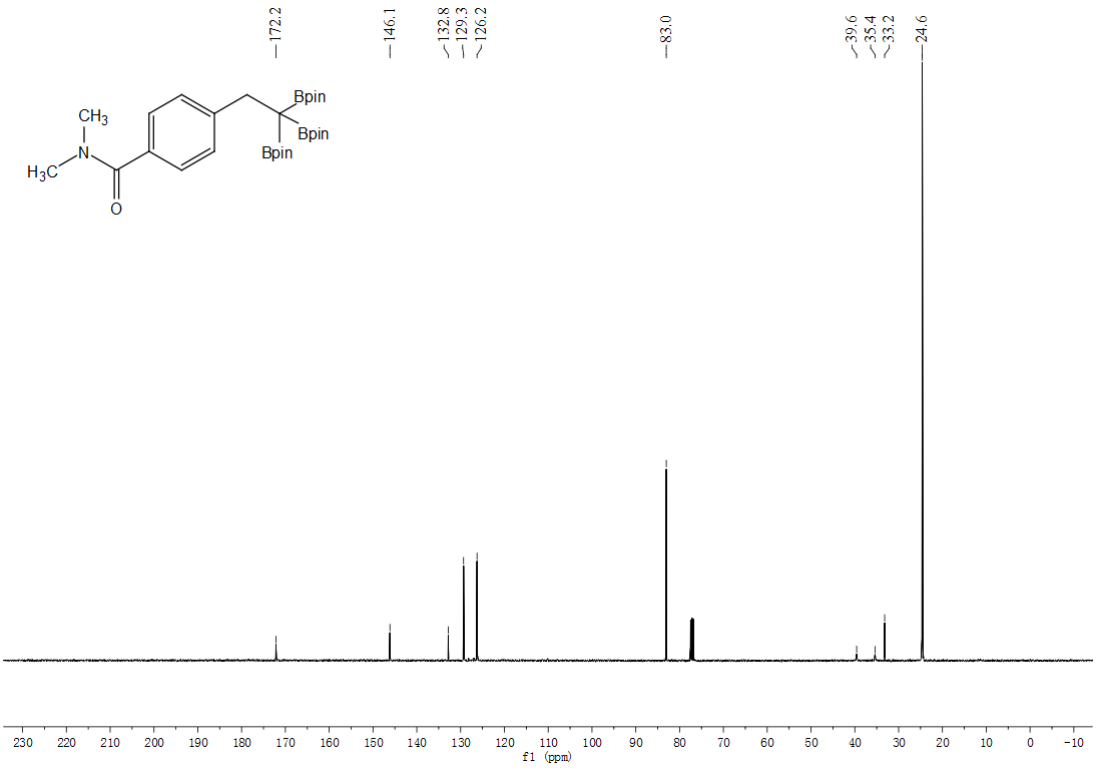
^{13}C NMR (101 MHz, $CDCl_3$) of **10r**



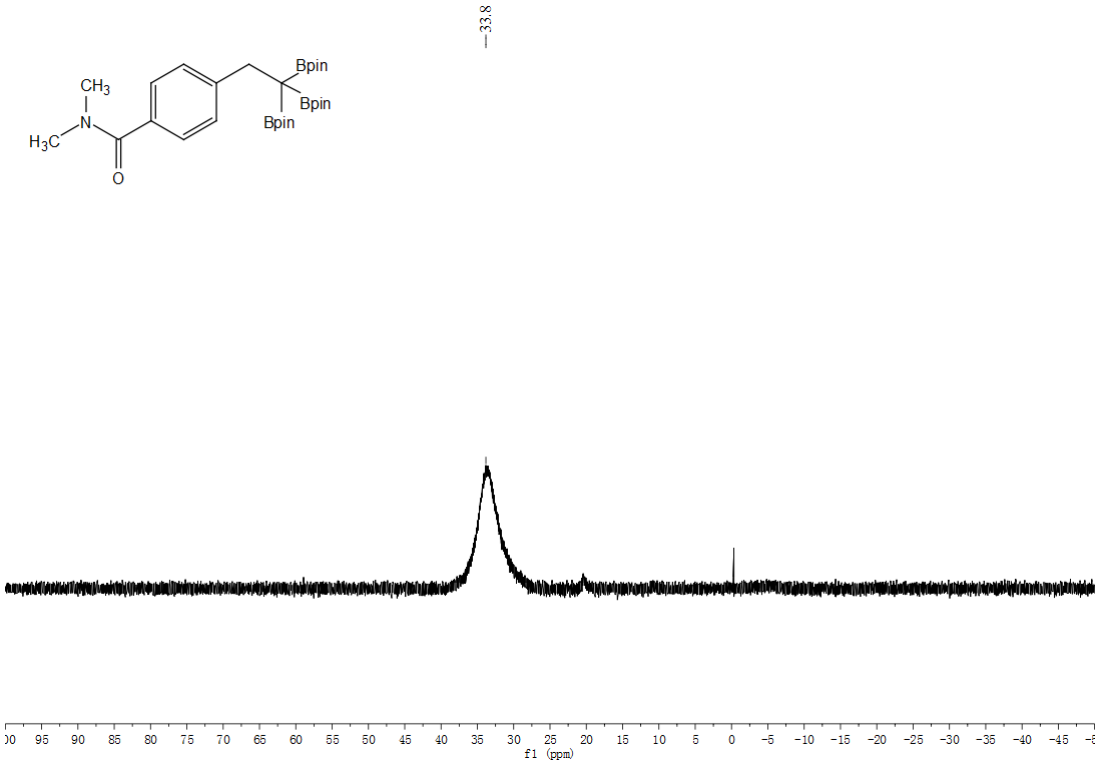
^{11}B NMR (193 MHz, EtOAc) of **10r**



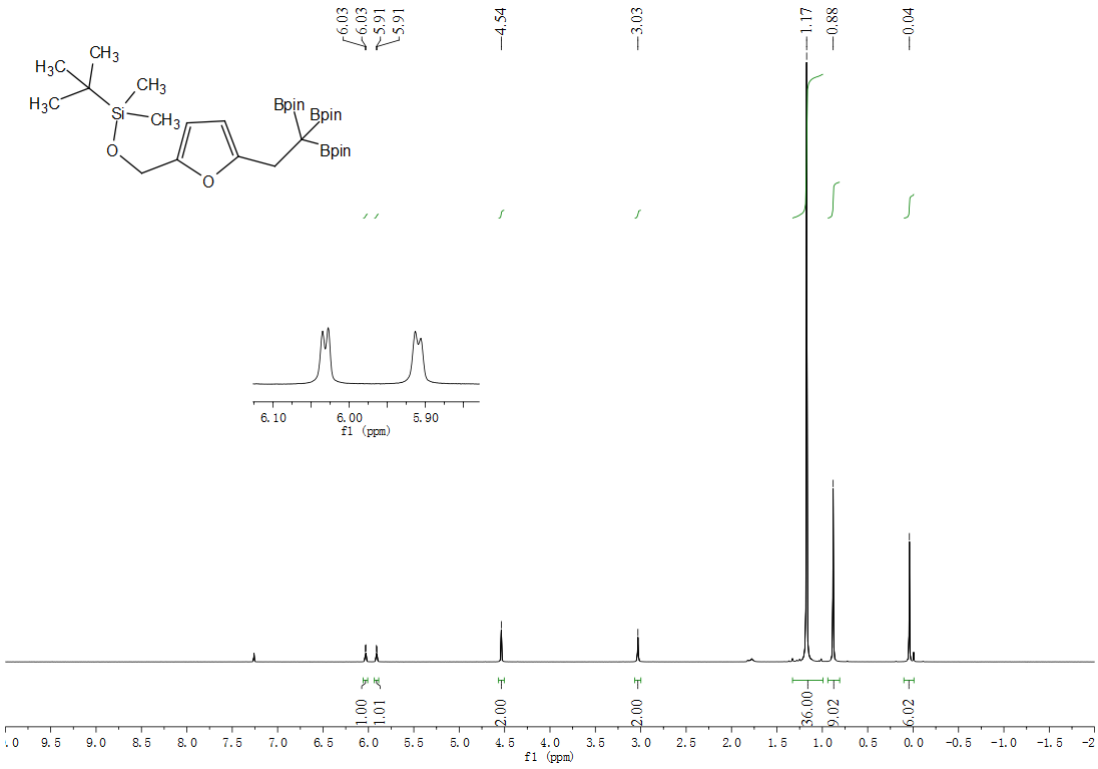
^{1}H NMR (400 MHz, $CDCl_3$) of **10s**



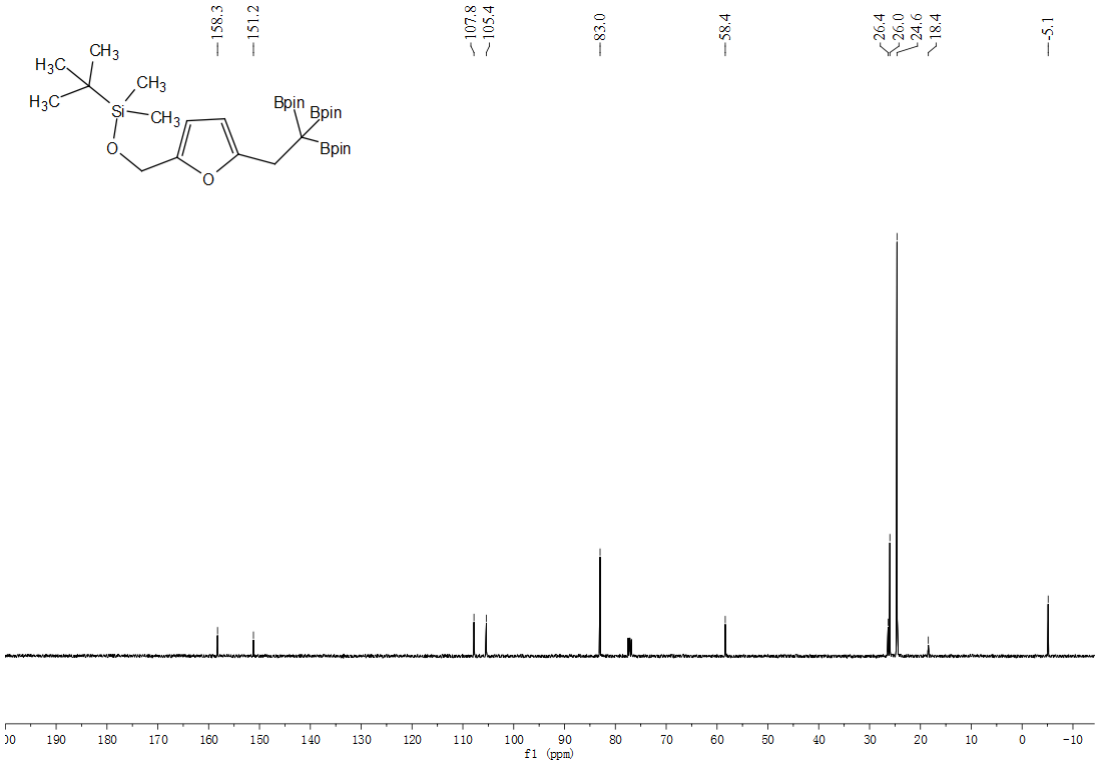
^{13}C NMR (101 MHz, $CDCl_3$) of **10s**



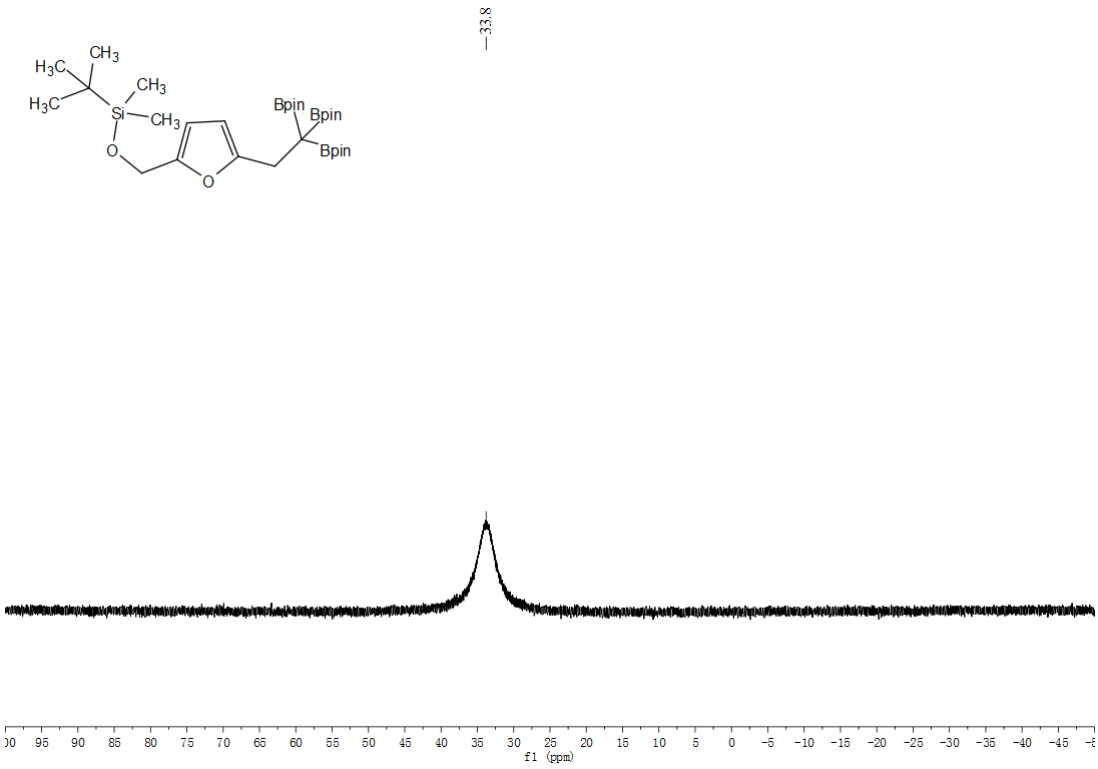
^{11}B NMR (193 MHz, EtOAc) of **10s**



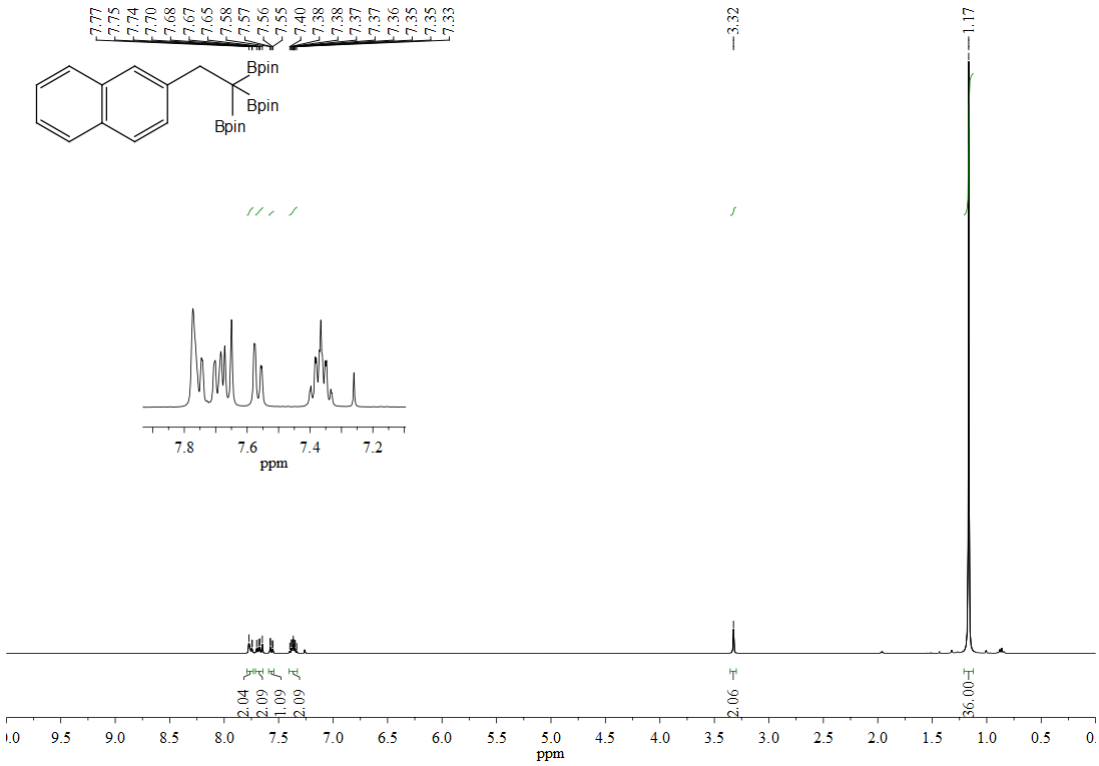
^{1}H NMR (400 MHz, $CDCl_3$) of **10t**



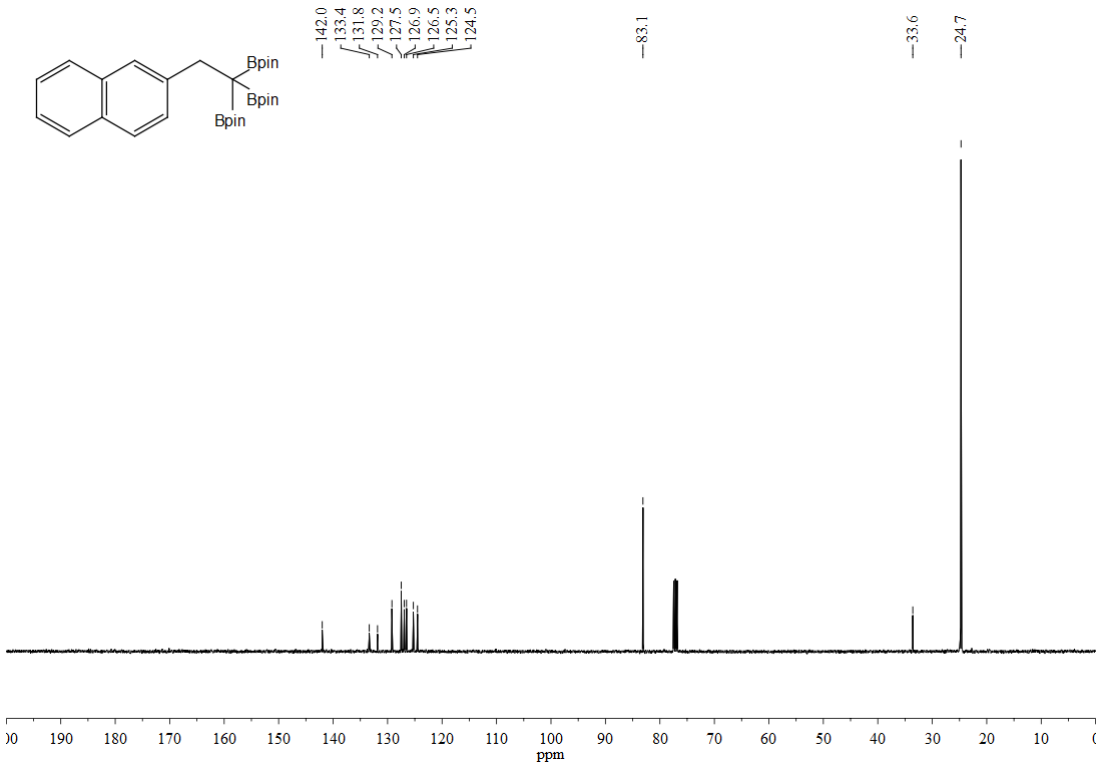
^{13}C NMR (101 MHz, $CDCl_3$) of **10t**



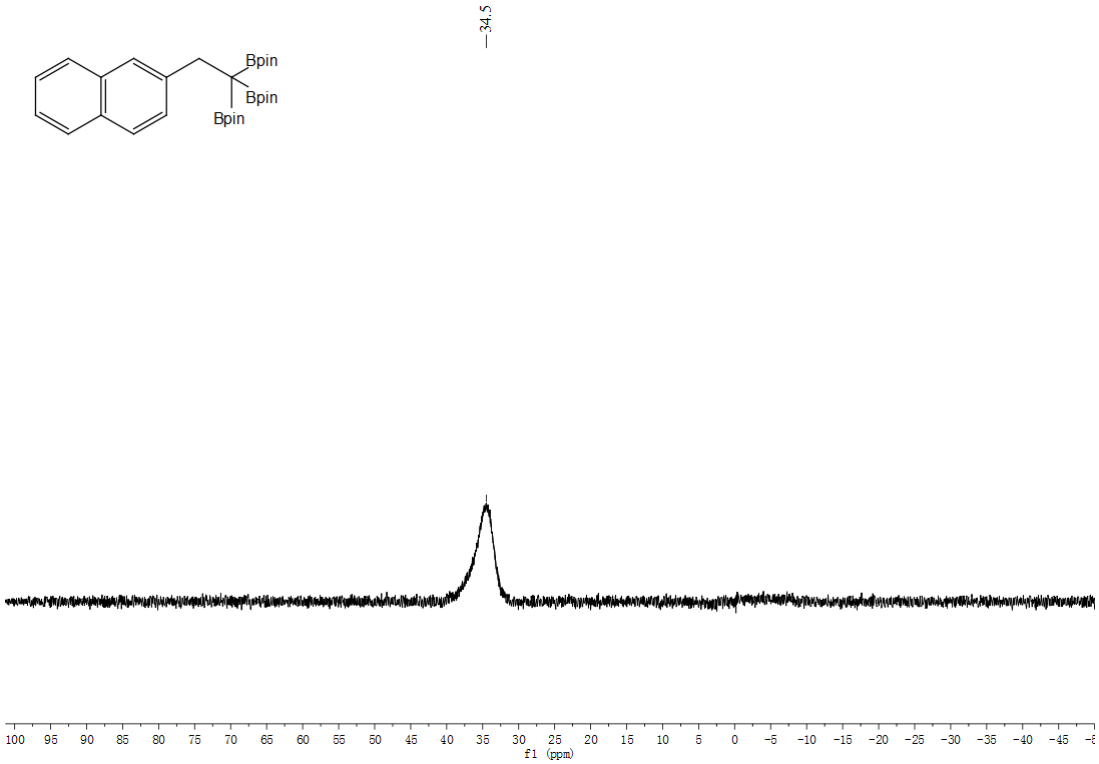
^{11}B NMR (193 MHz, EtOAc) of **10t**



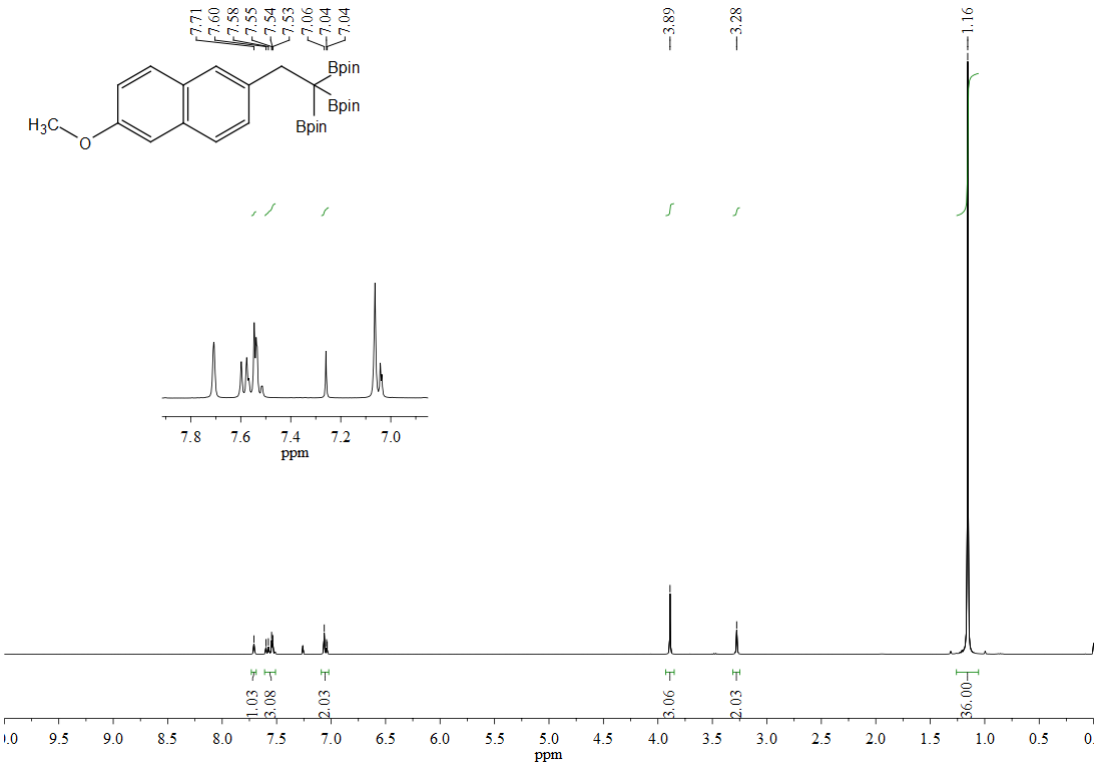
^{1}H NMR (400 MHz, $CDCl_3$) of **10v**



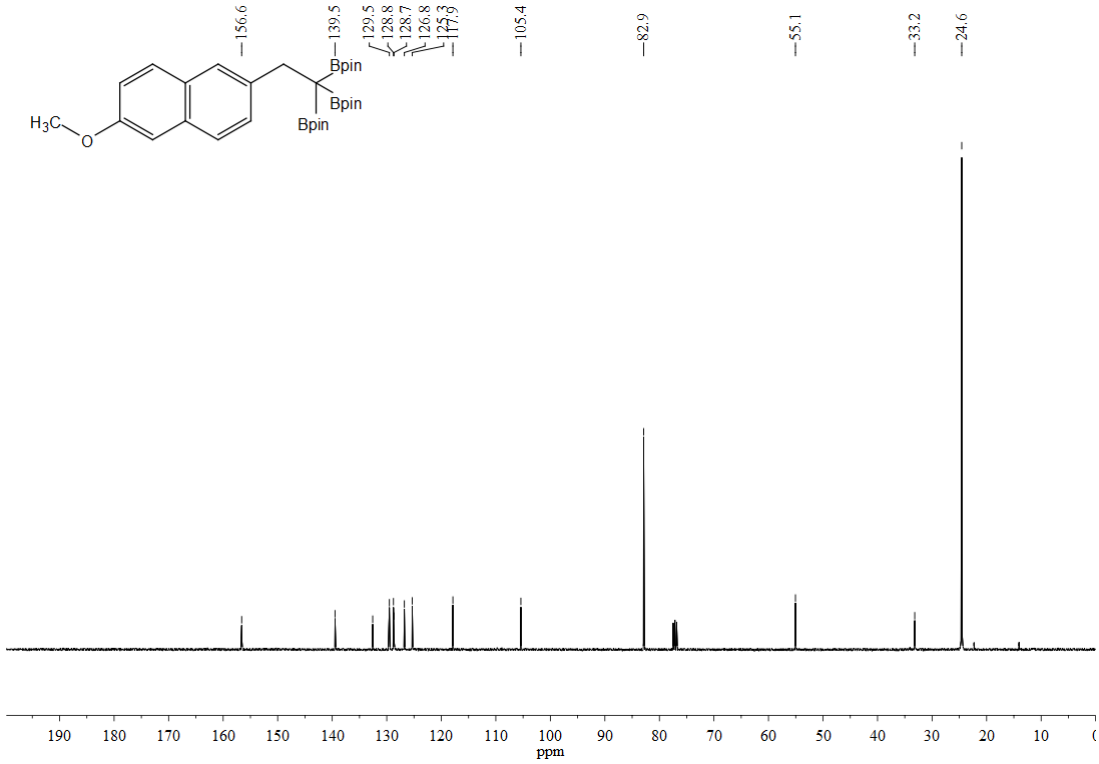
^{13}C NMR (101 MHz, $CDCl_3$) of **10v**



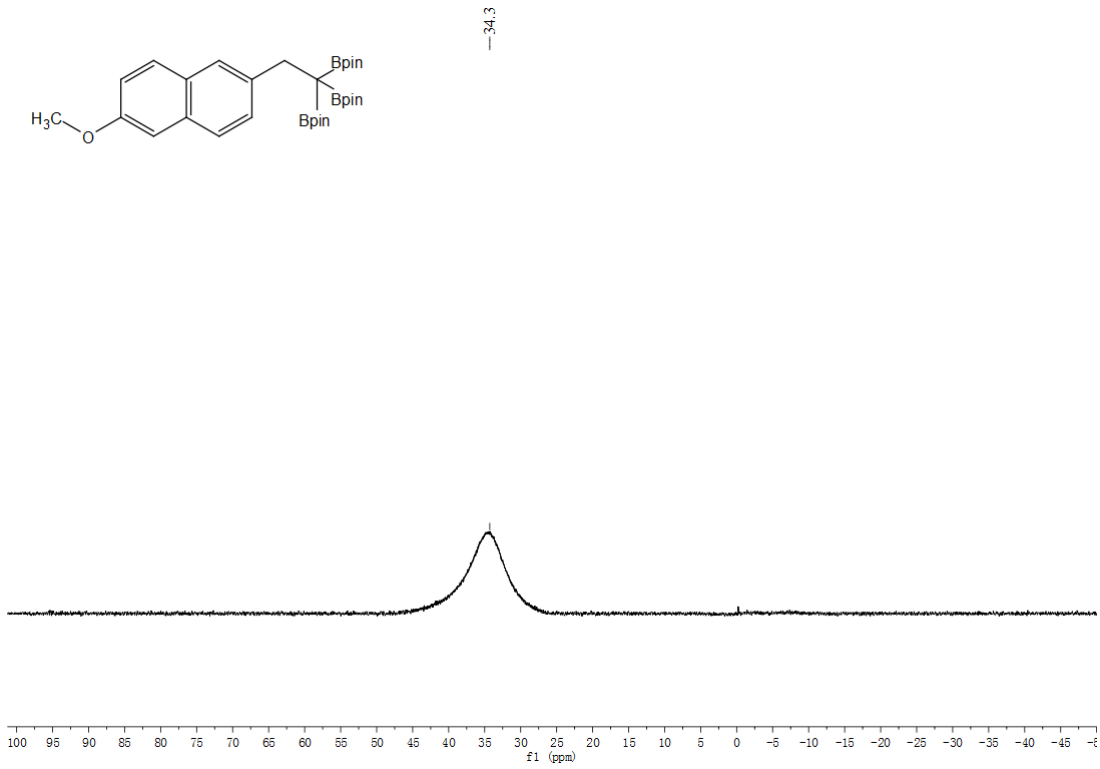
^{11}B NMR (193 MHz, EtOAc) of **10v**



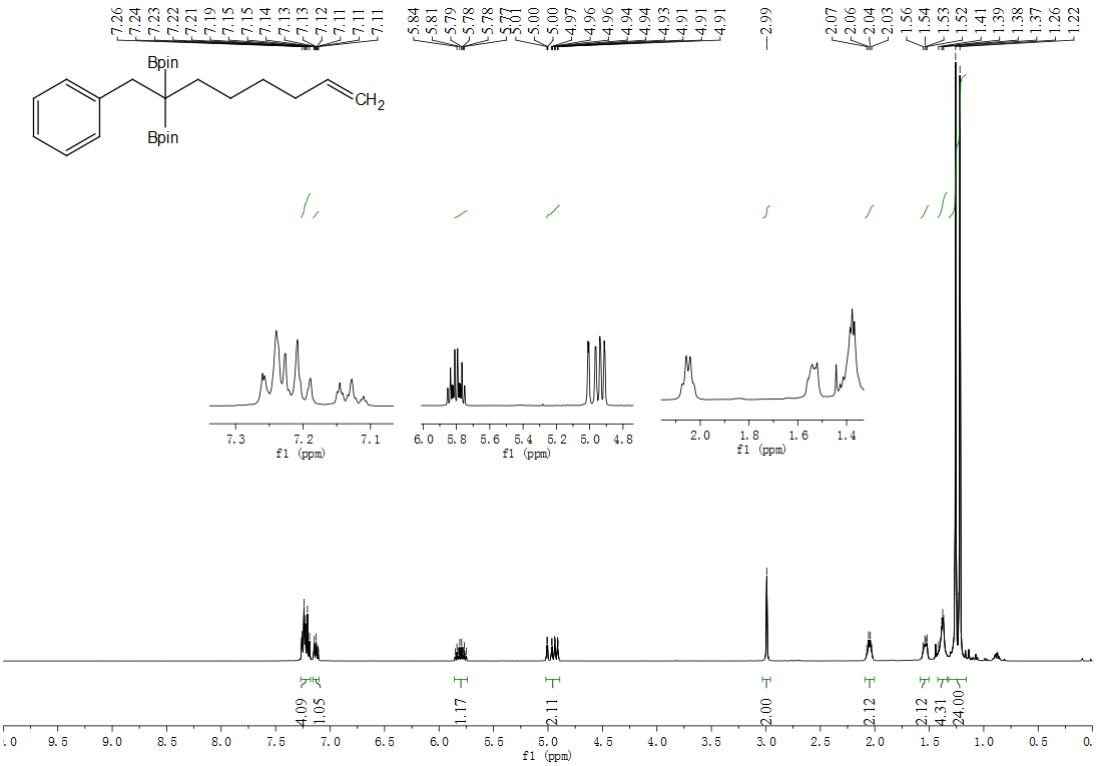
^{1}H NMR (400 MHz, $CDCl_3$) of **10w**



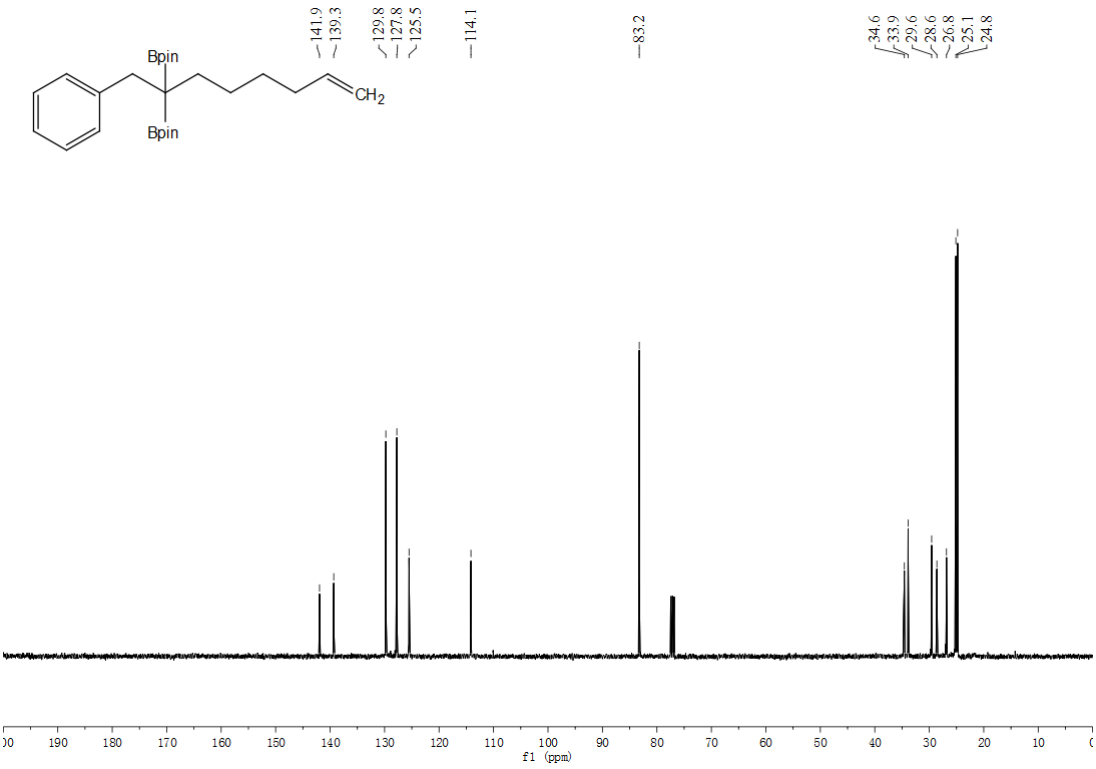
^{13}C NMR (101 MHz, $CDCl_3$) of **10w**



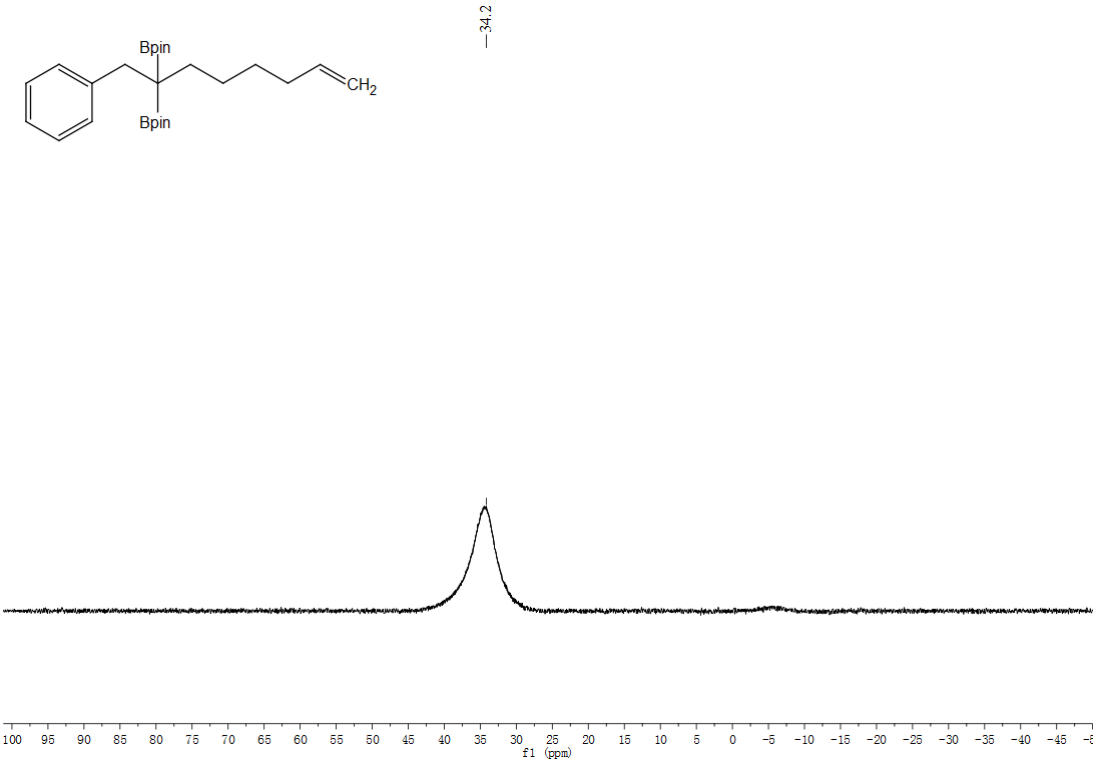
^{11}B NMR (193 MHz, EtOAc) of **10w**



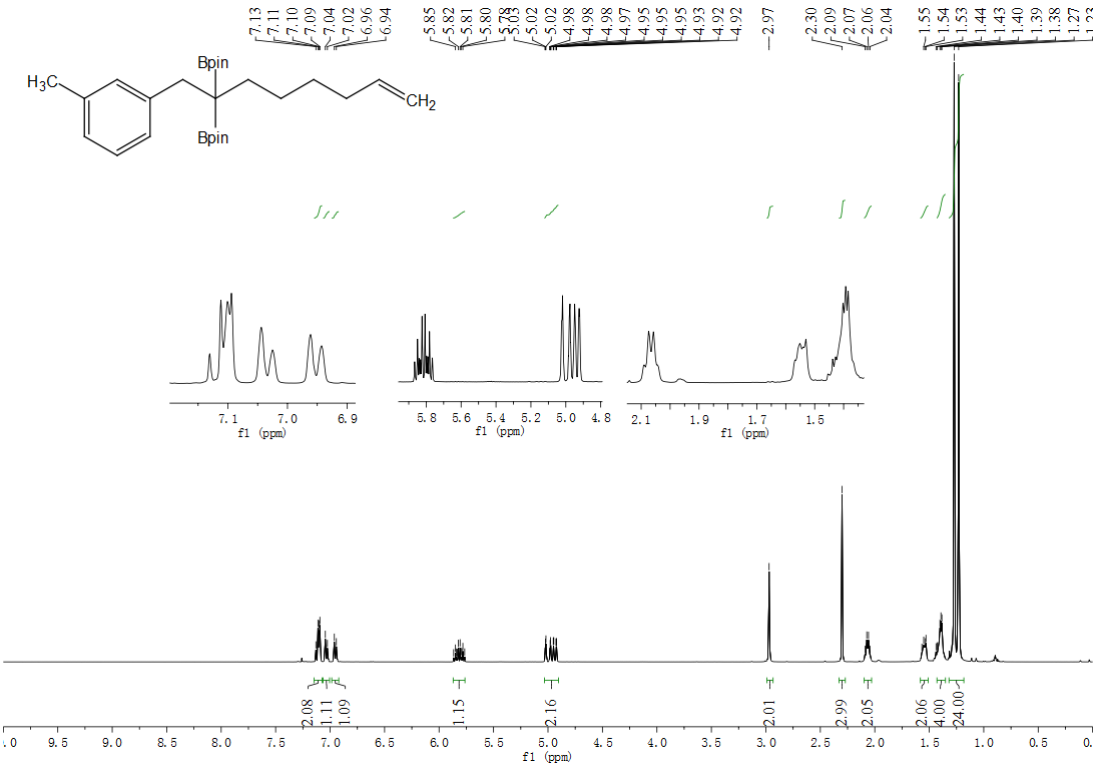
^{1}H NMR (400 MHz, $CDCl_3$) of **13a**



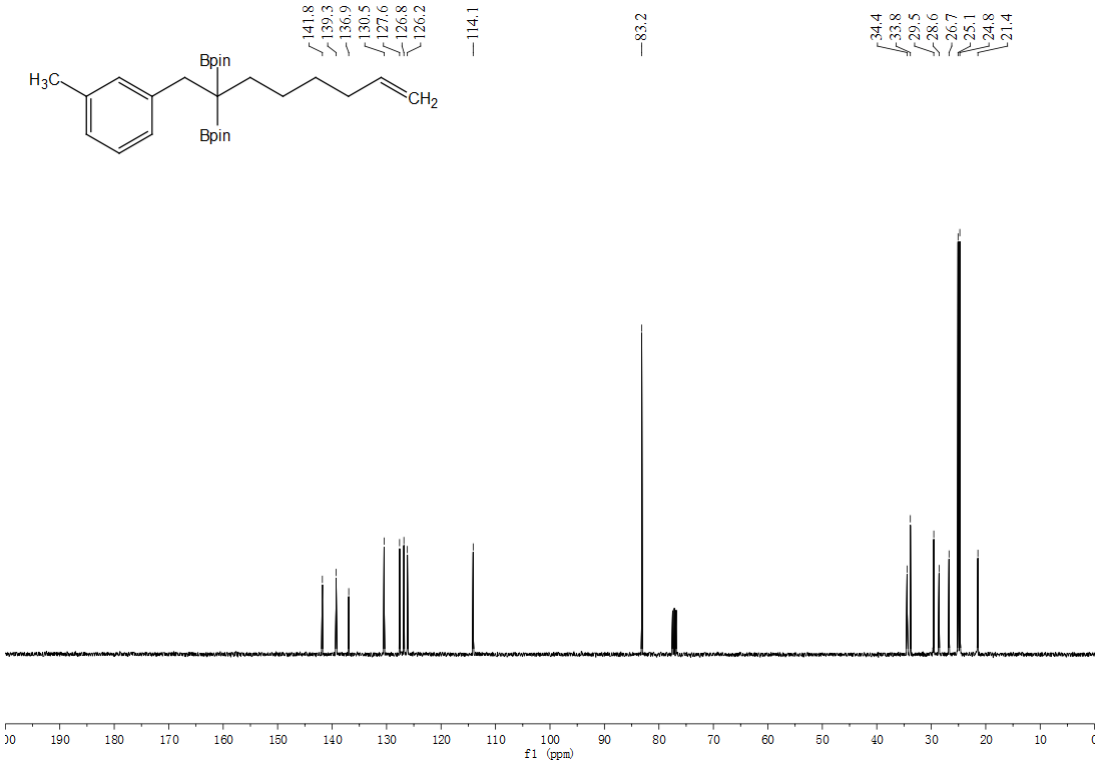
^{13}C NMR (101 MHz, $CDCl_3$) of **13a**



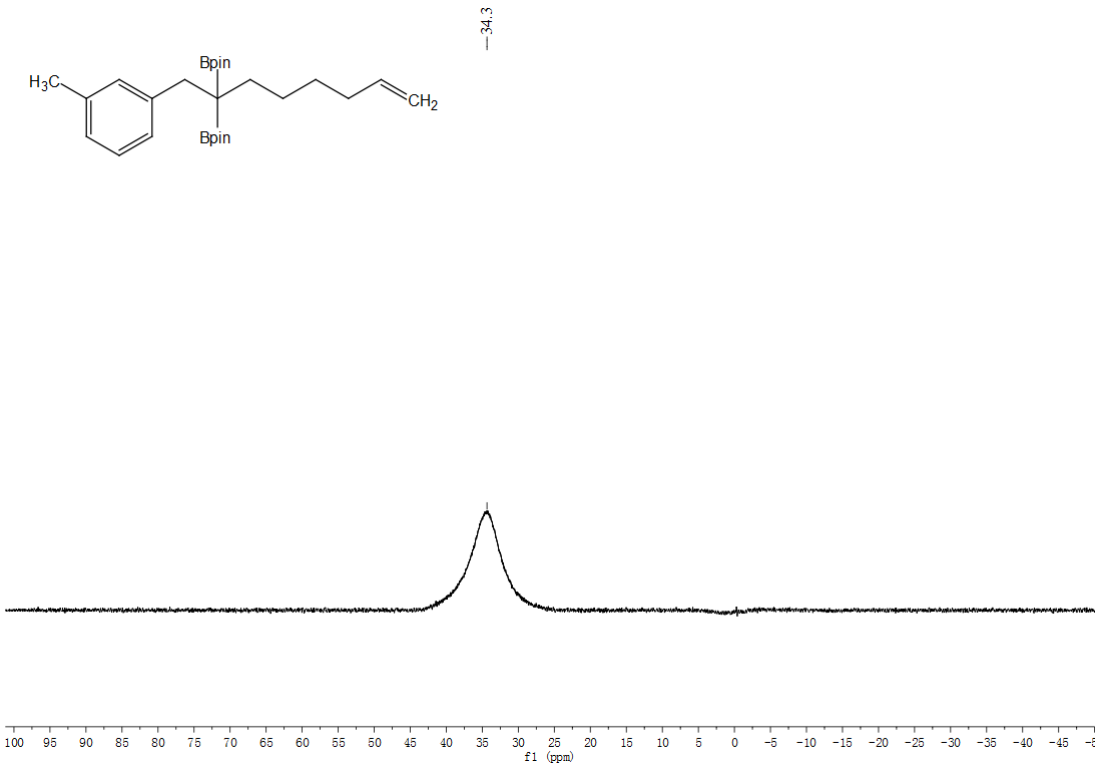
^{11}B NMR (193 MHz, EtOAc) of **13a**



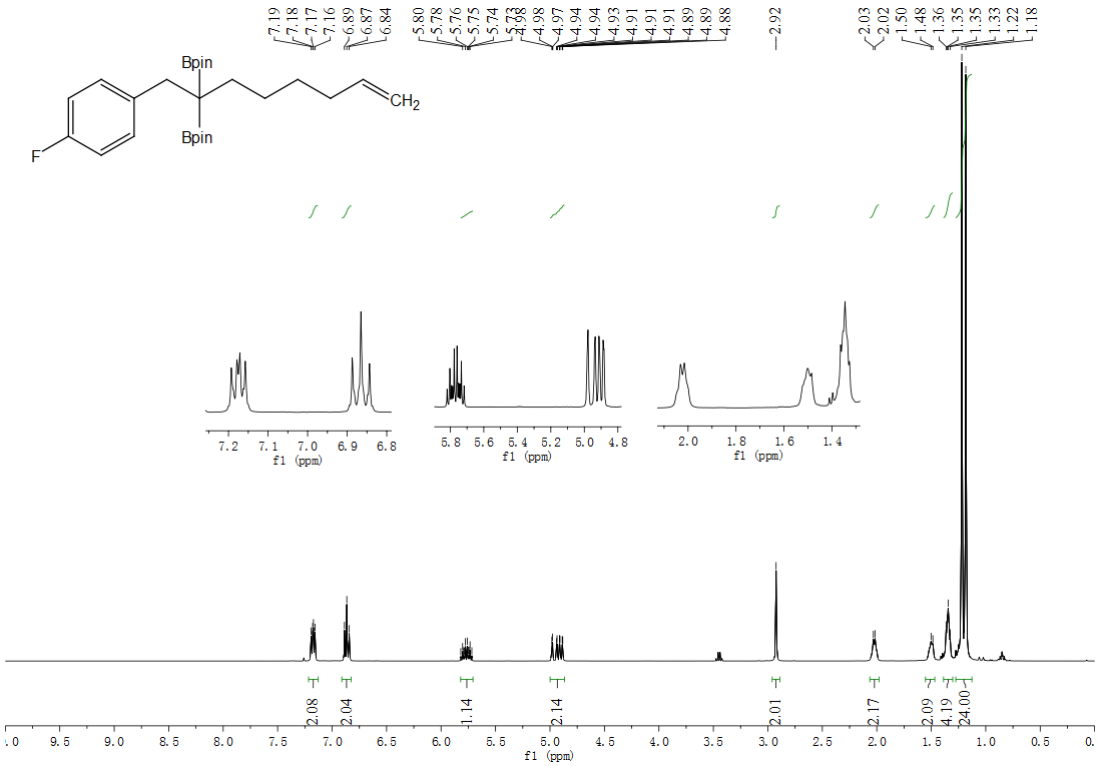
^{1}H NMR (400 MHz, $CDCl_3$) of **13b**



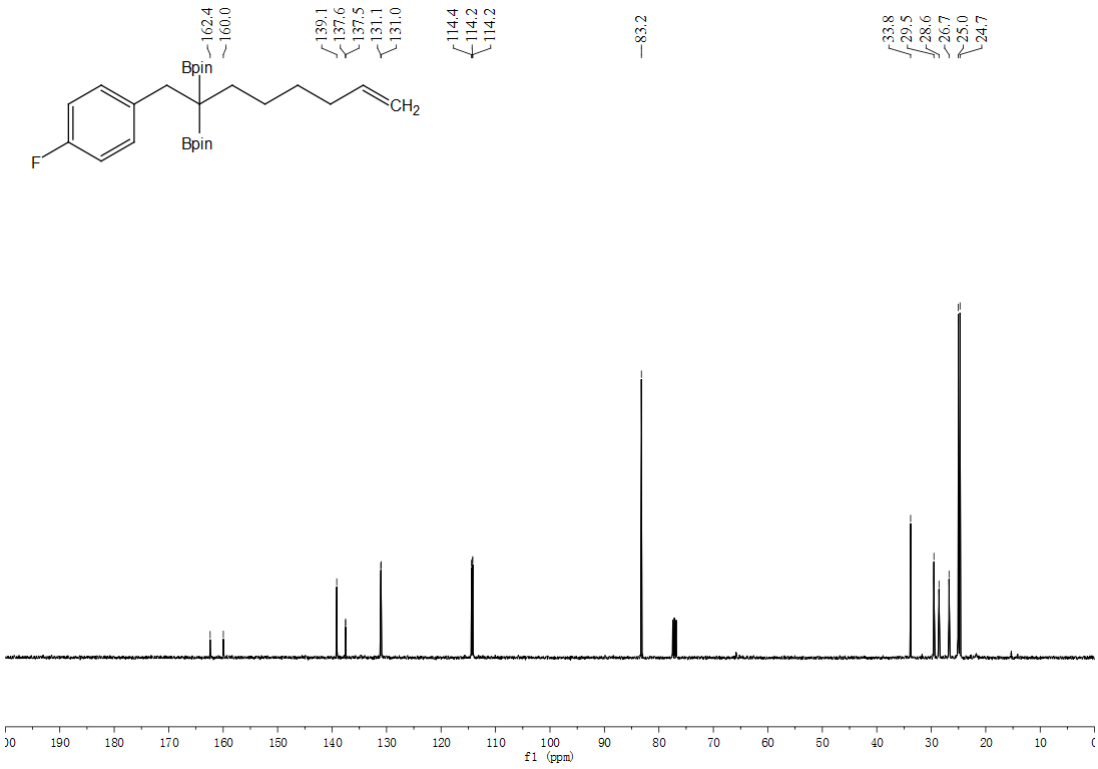
^{13}C NMR (101 MHz, $CDCl_3$) of **13b**



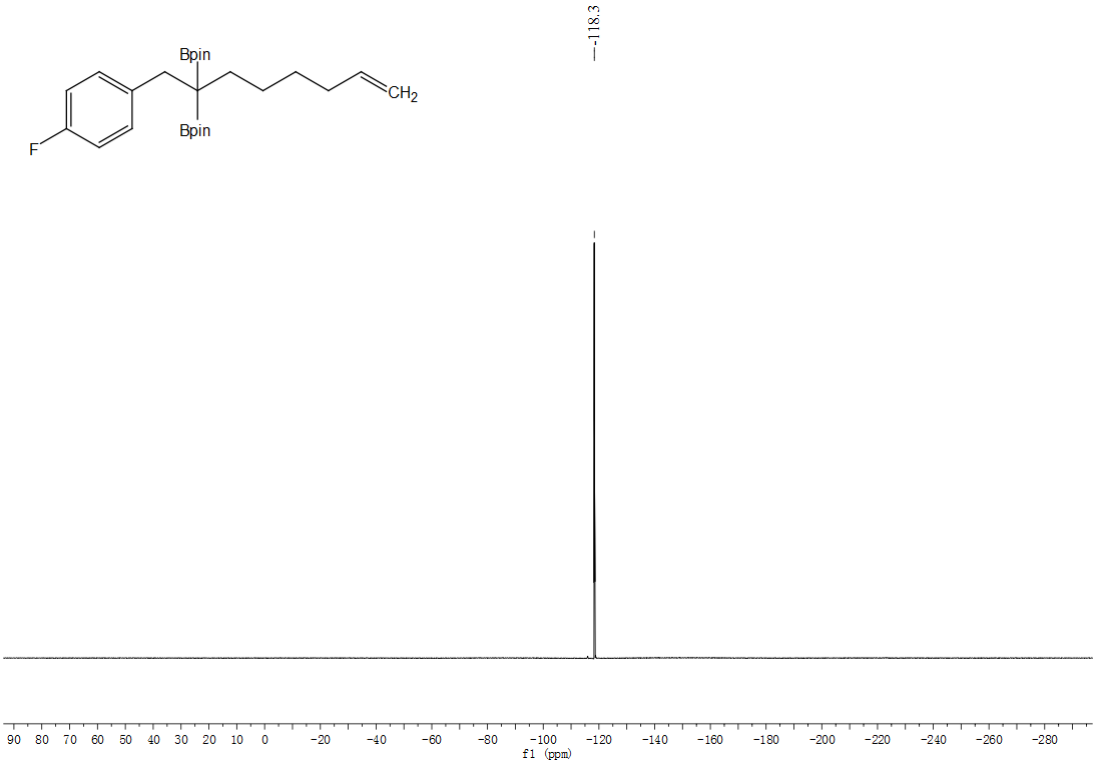
^{11}B NMR (193 MHz, EtOAc) of **13b**



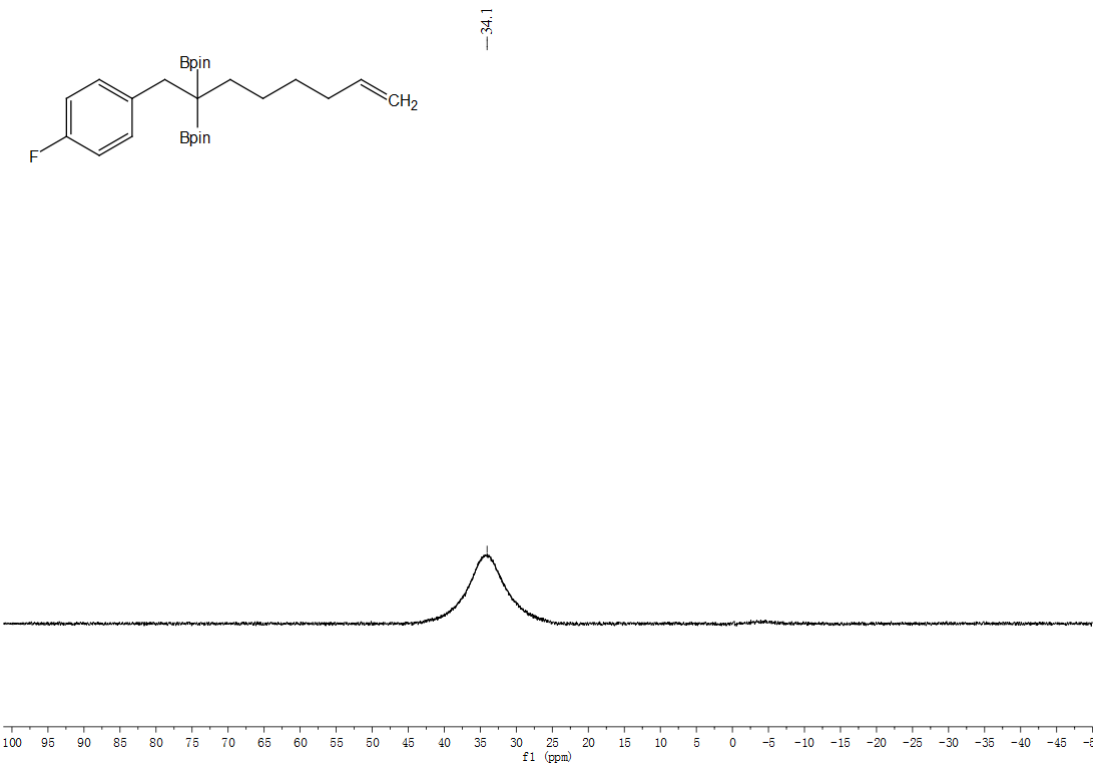
^{1}H NMR (400 MHz, $CDCl_3$) of **13c**



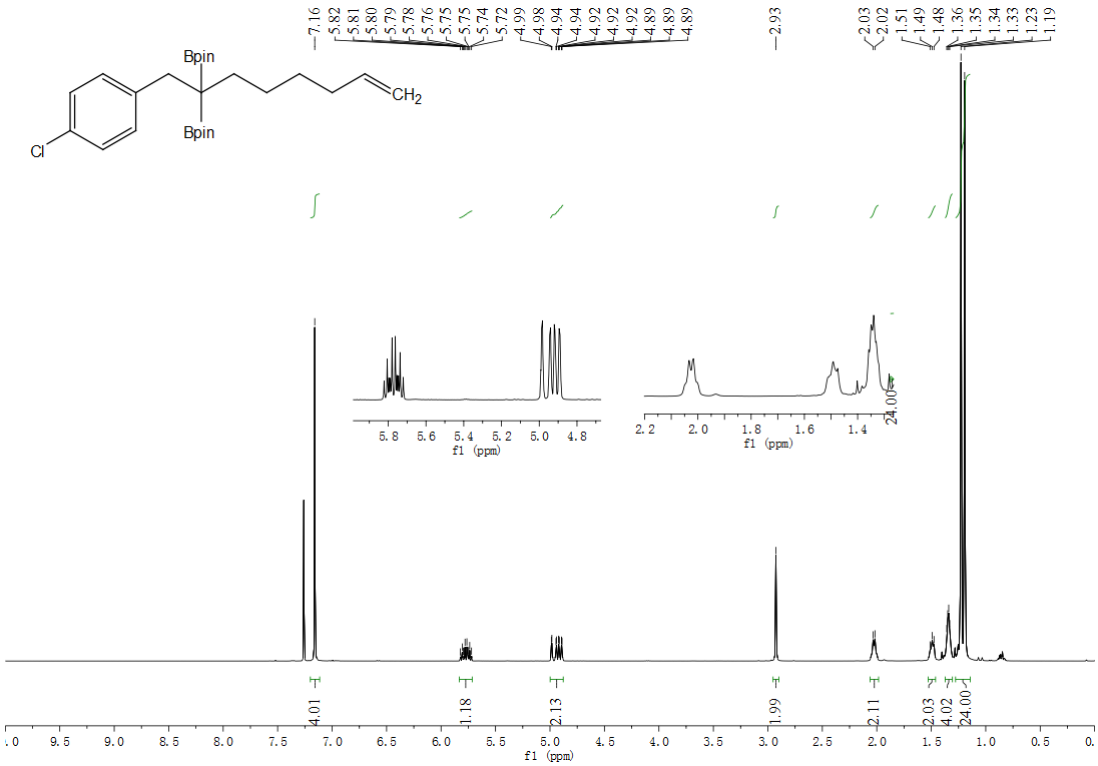
^{13}C NMR (101 MHz, $CDCl_3$) of **13c**



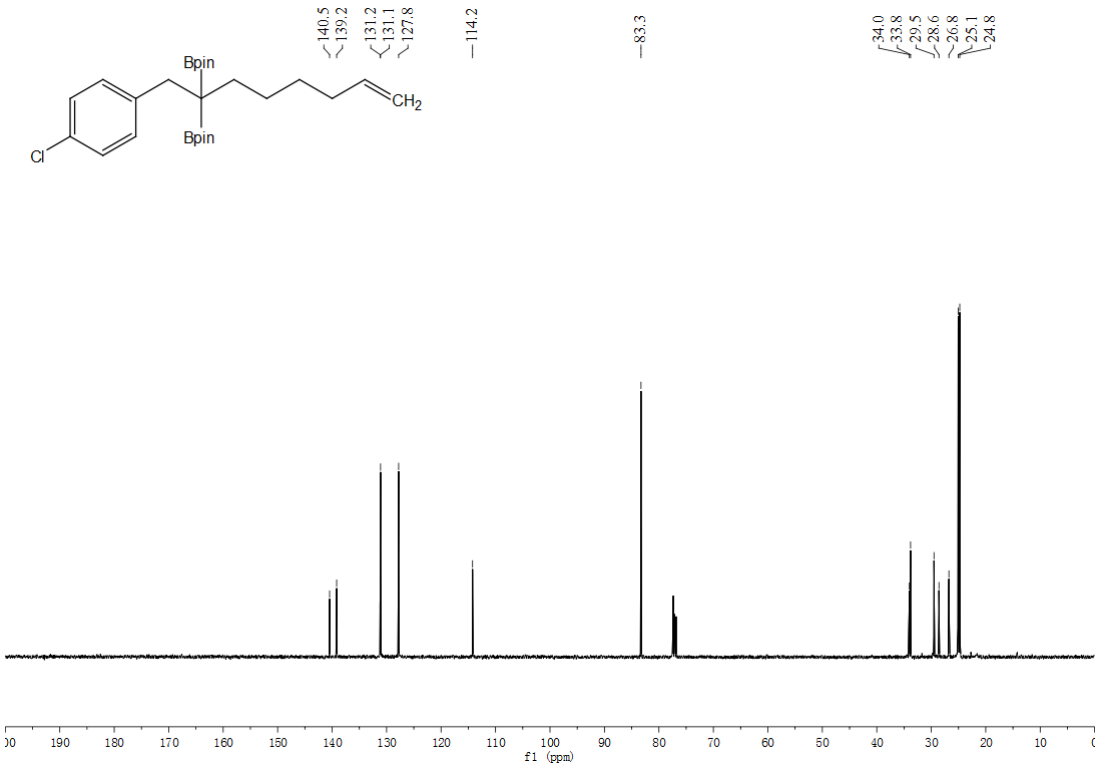
^{19}F NMR (376 MHz, $CDCl_3$) of **13c**



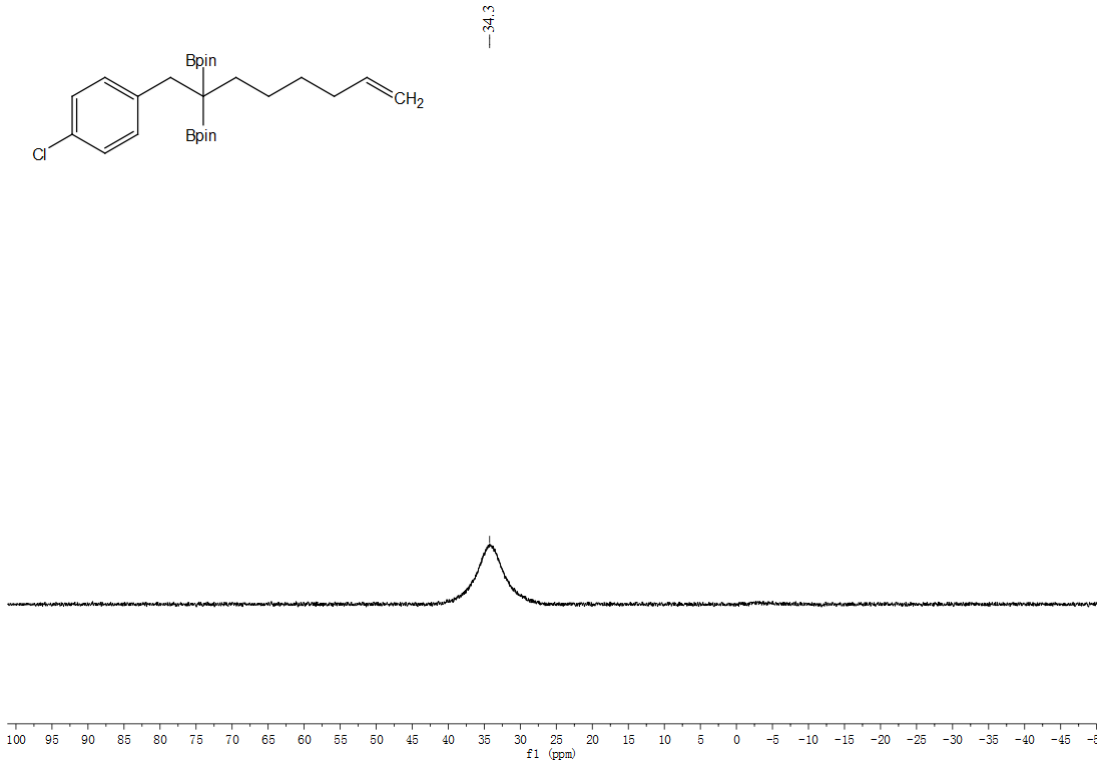
^{11}B NMR (193 MHz, EtOAc) of **13c**



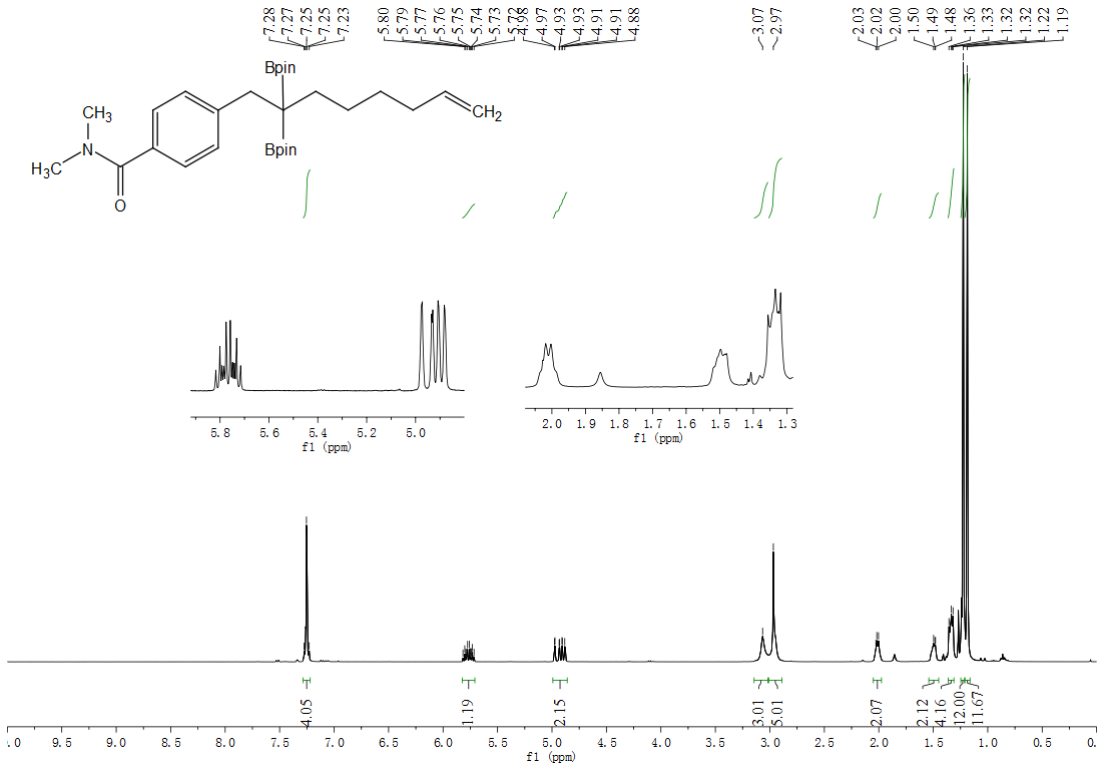
^{1}H NMR (400 MHz, $CDCl_3$) of **13d**



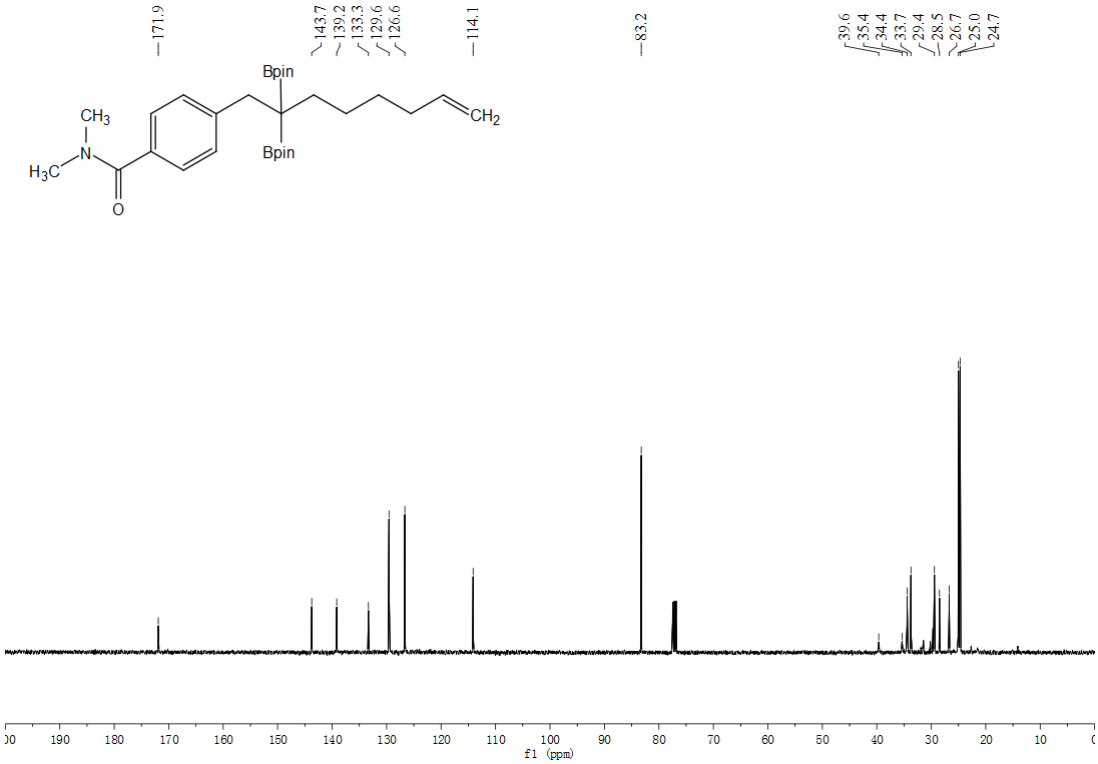
^{13}C NMR (101 MHz, $CDCl_3$) of **13d**



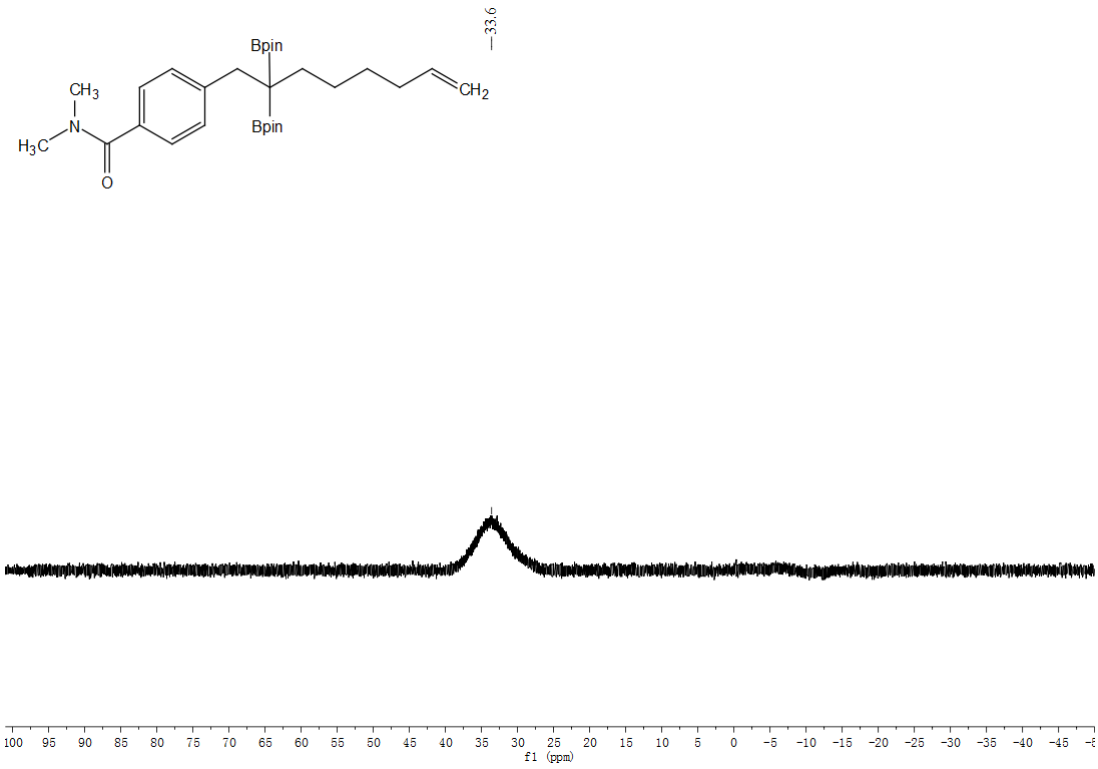
^{11}B NMR (193 MHz, EtOAc) of **13d**



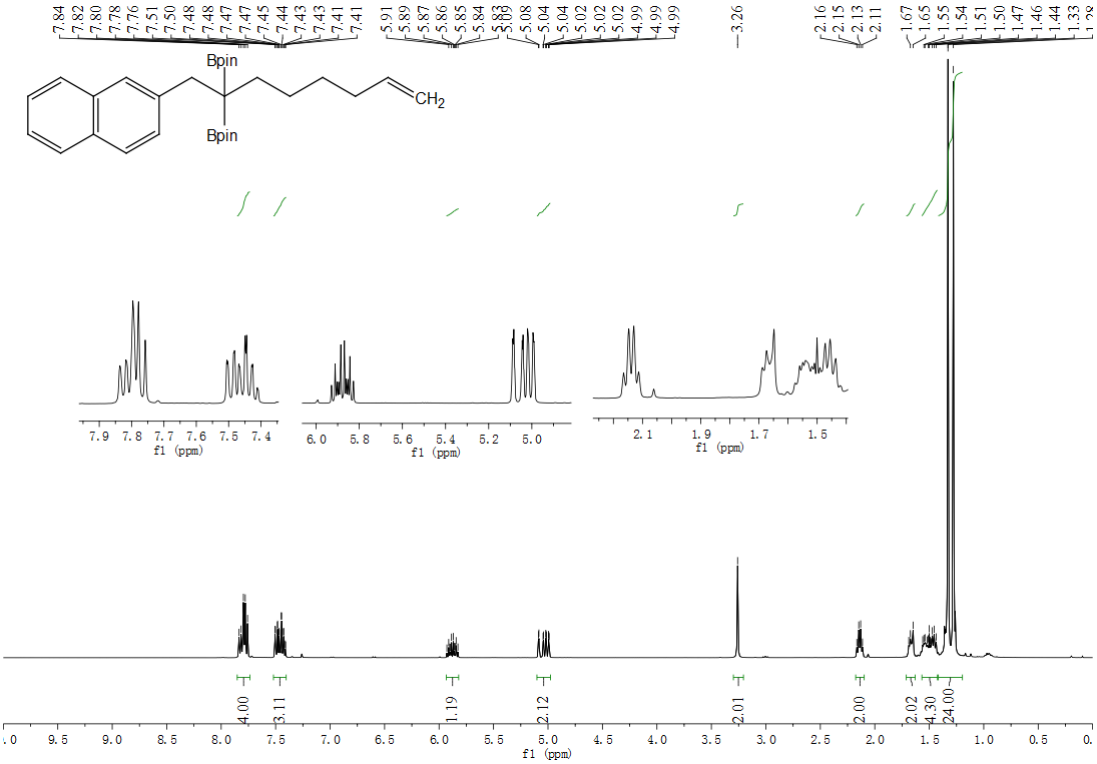
^{1}H NMR (400 MHz, $CDCl_3$) of **13e**



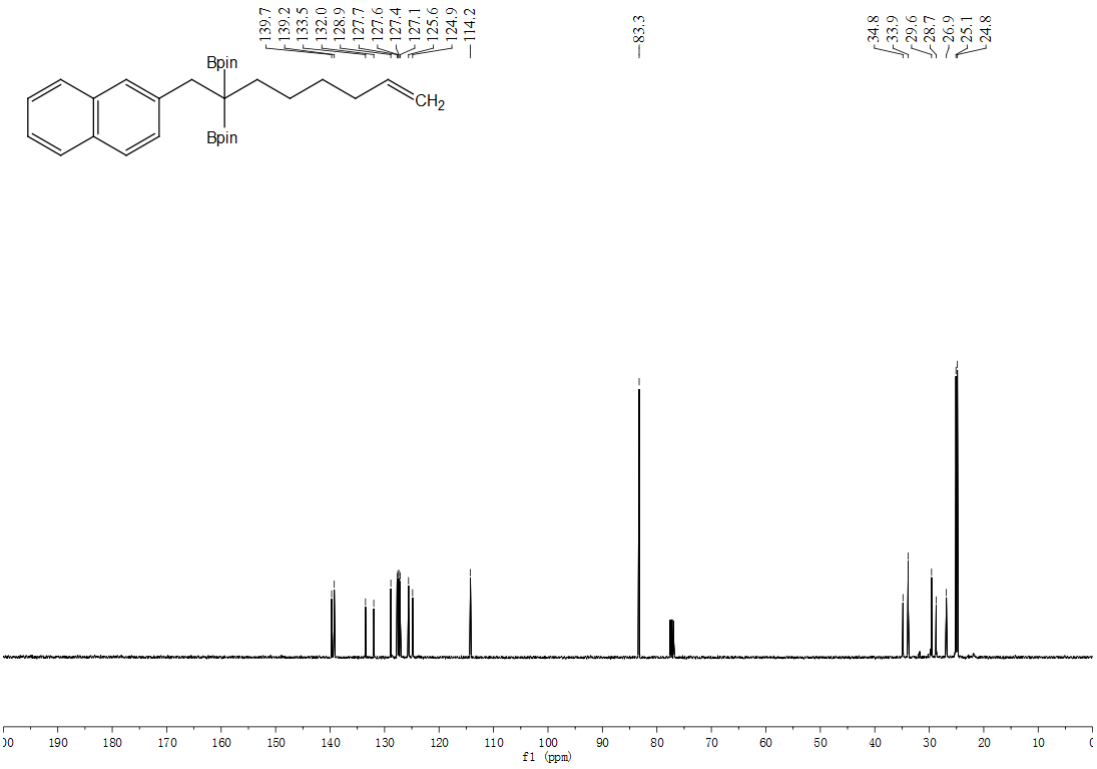
^{13}C NMR (101 MHz, $CDCl_3$) of **13e**



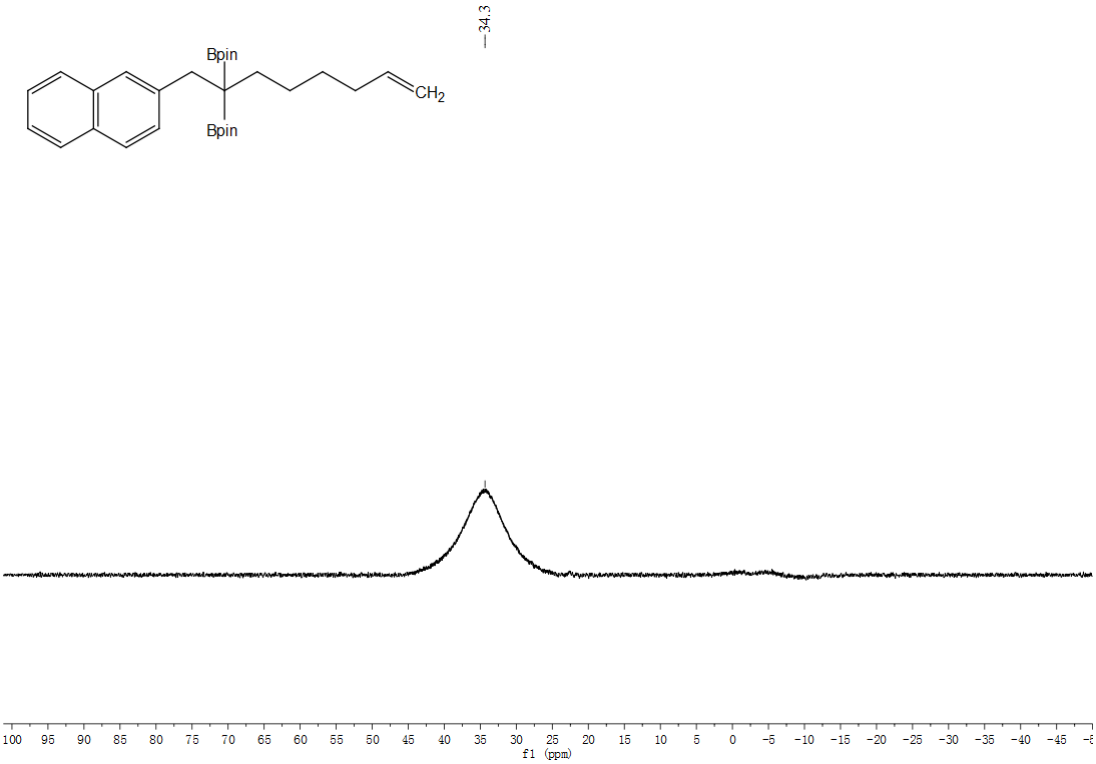
^{11}B NMR (193 MHz, EtOAc) of **13e**



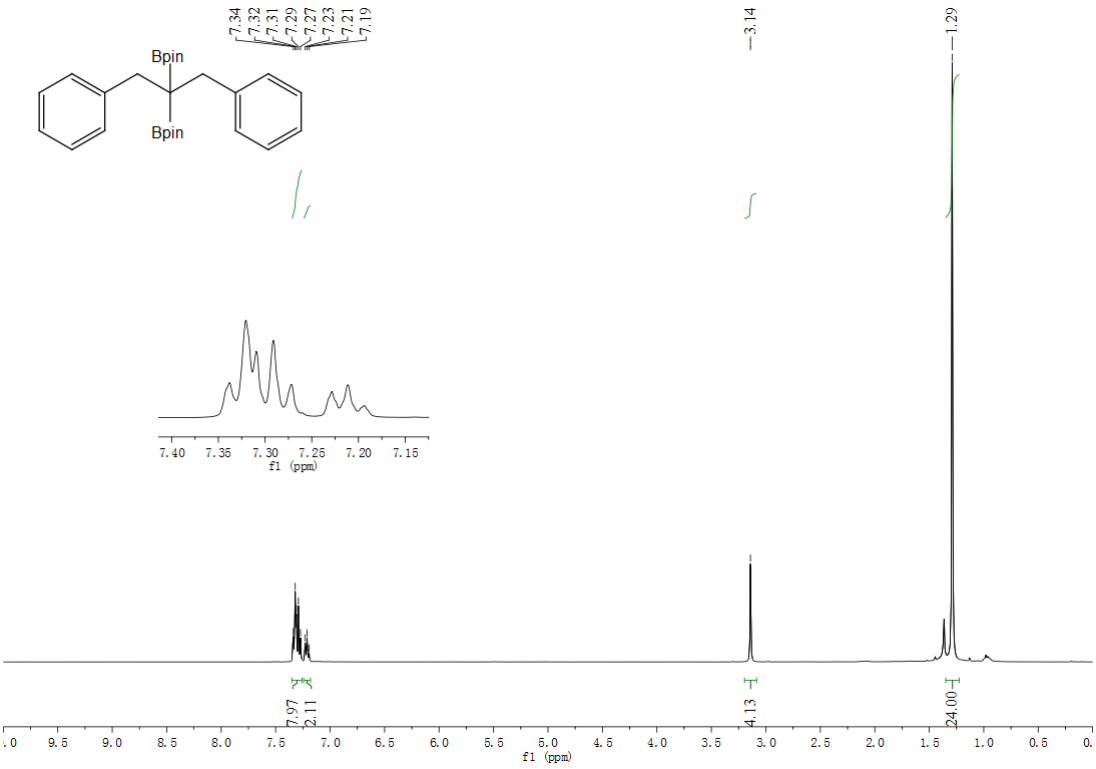
^{1}H NMR (400 MHz, $CDCl_3$) of **13f**



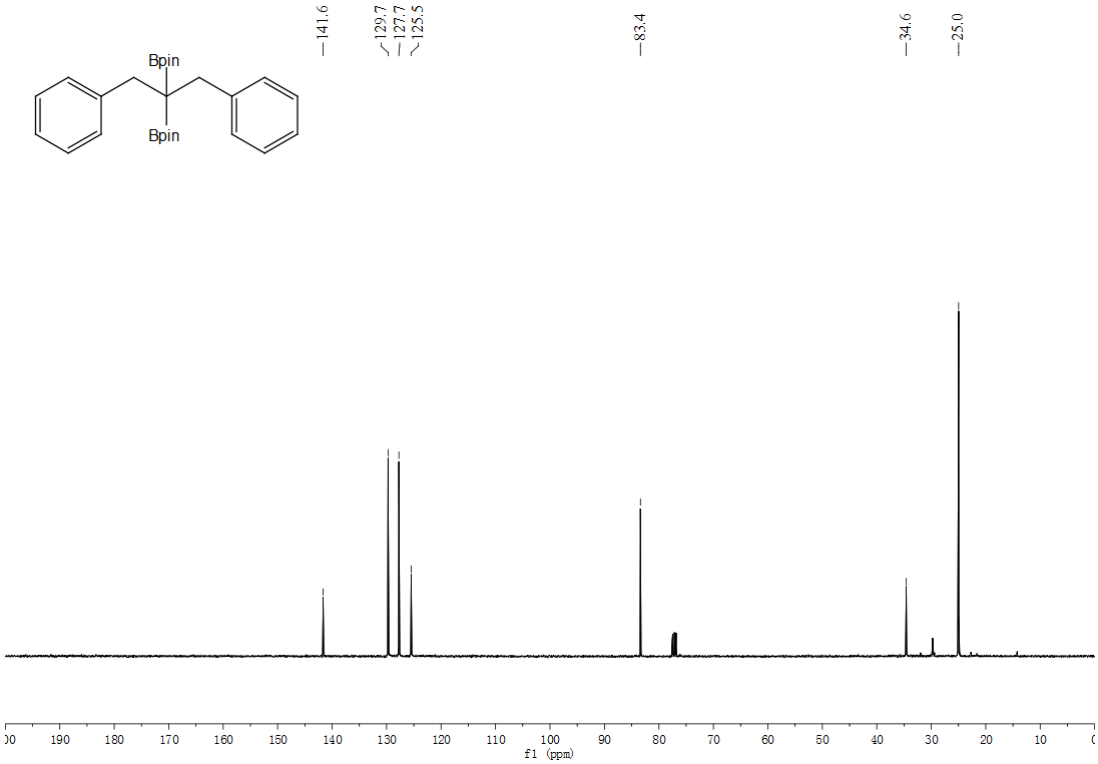
^{13}C NMR (101 MHz, $CDCl_3$) of **13f**



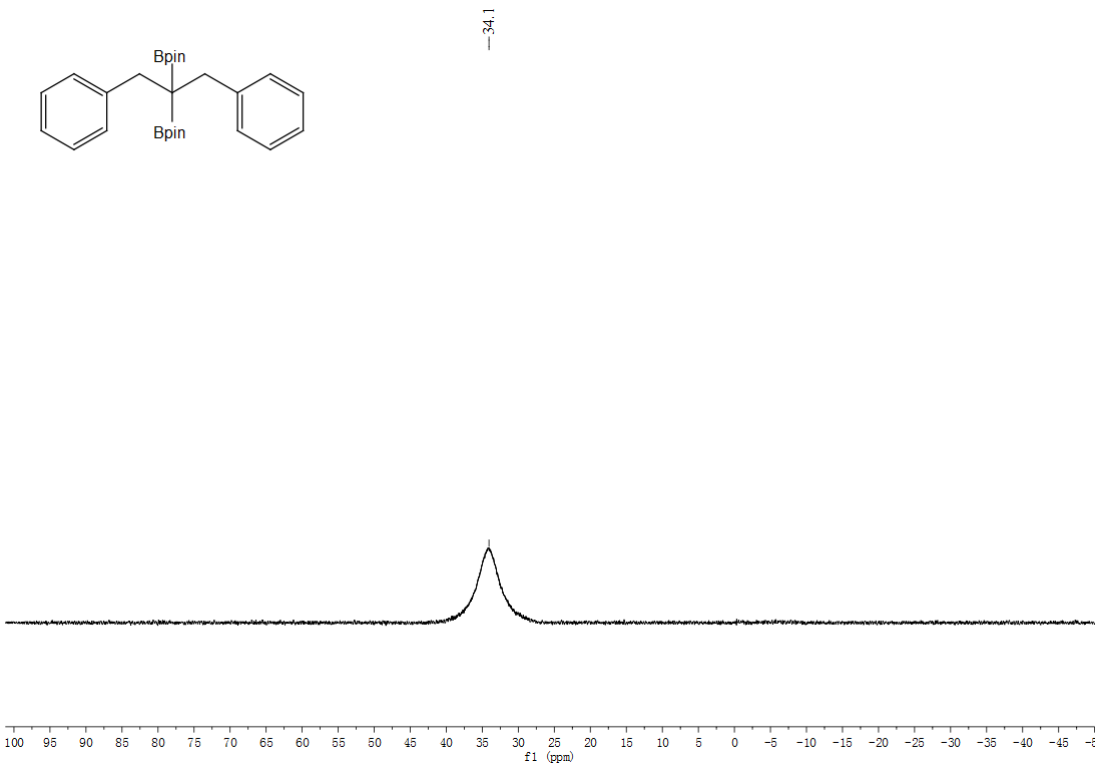
^{11}B NMR (193 MHz, EtOAc) of **13f**



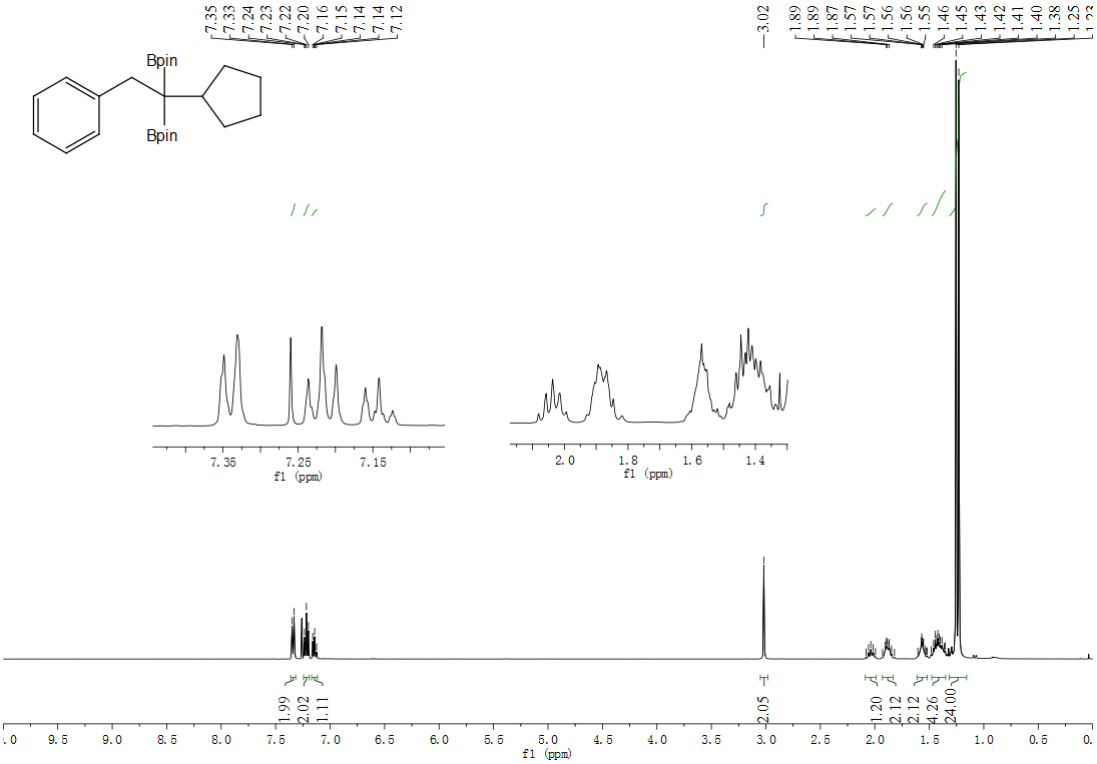
^{1}H NMR (400 MHz, $CDCl_3$) of **13g**



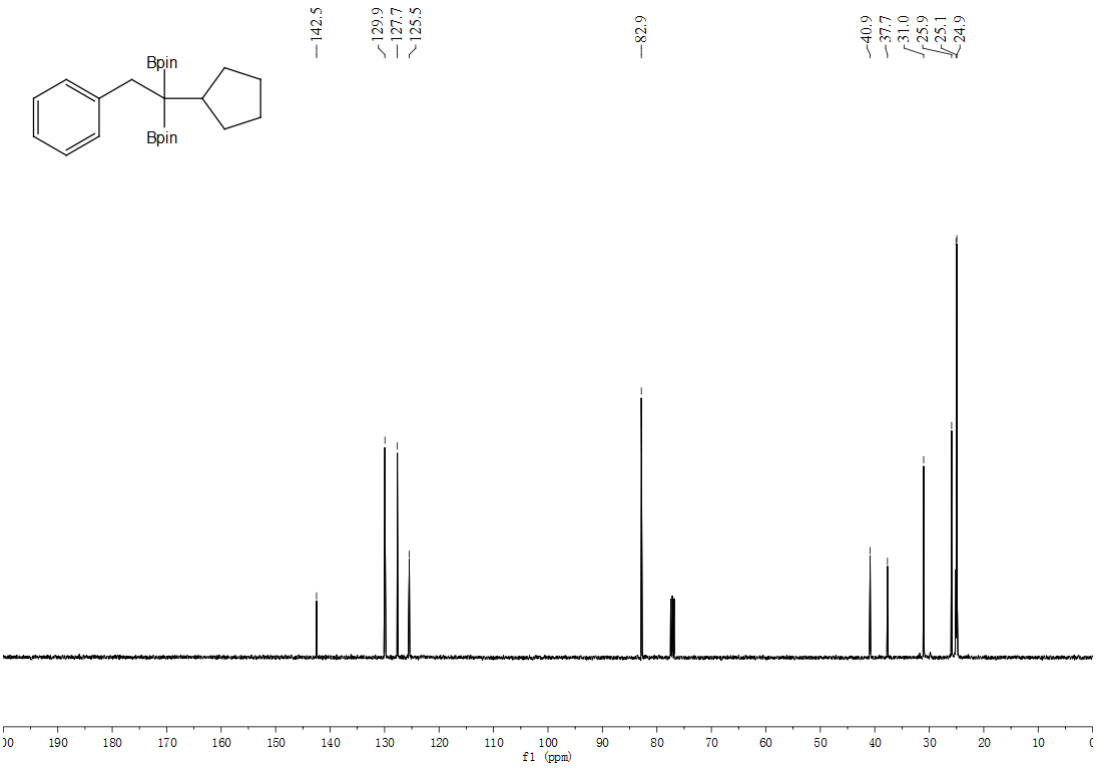
^{13}C NMR (101 MHz, $CDCl_3$) of **13g**



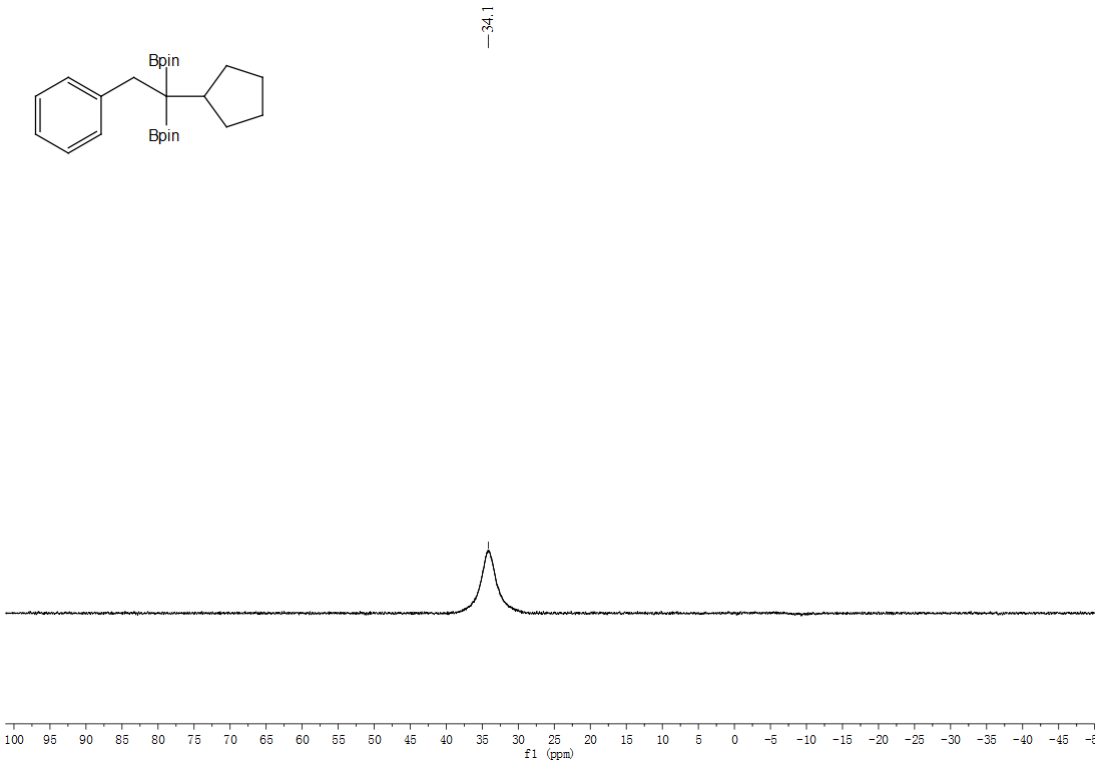
^{11}B NMR (193 MHz, EtOAc) of **13g**



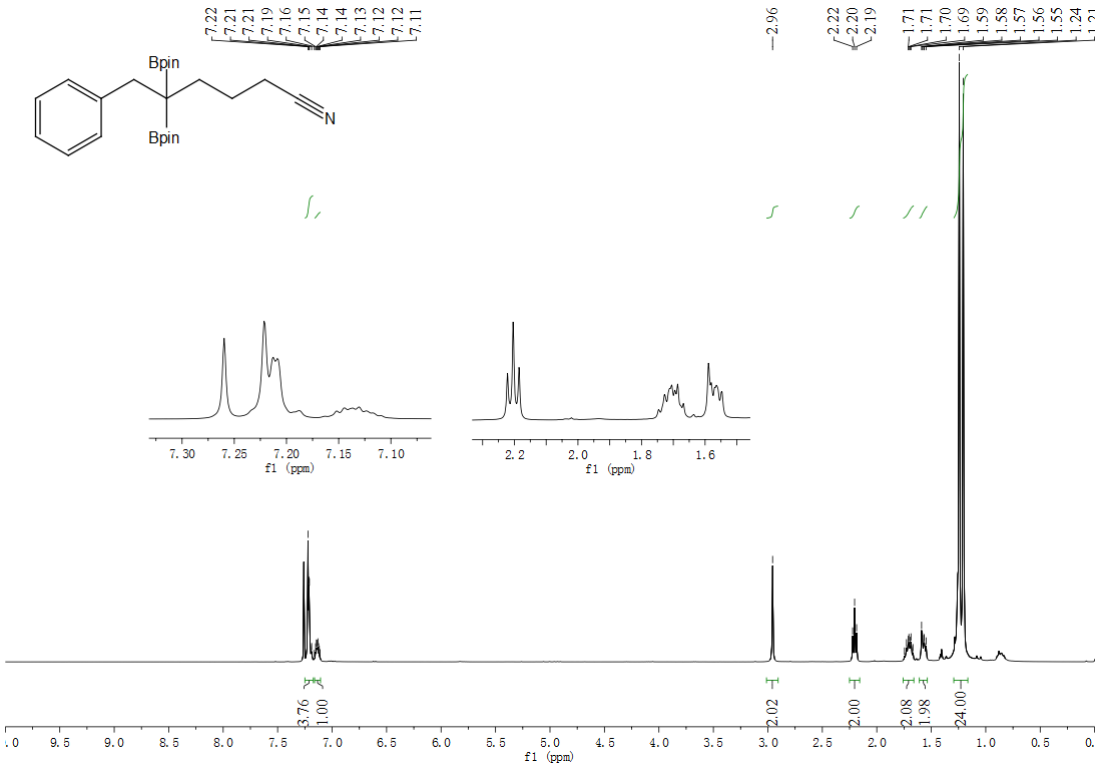
^{1}H NMR (400 MHz, $CDCl_3$) of **13h**



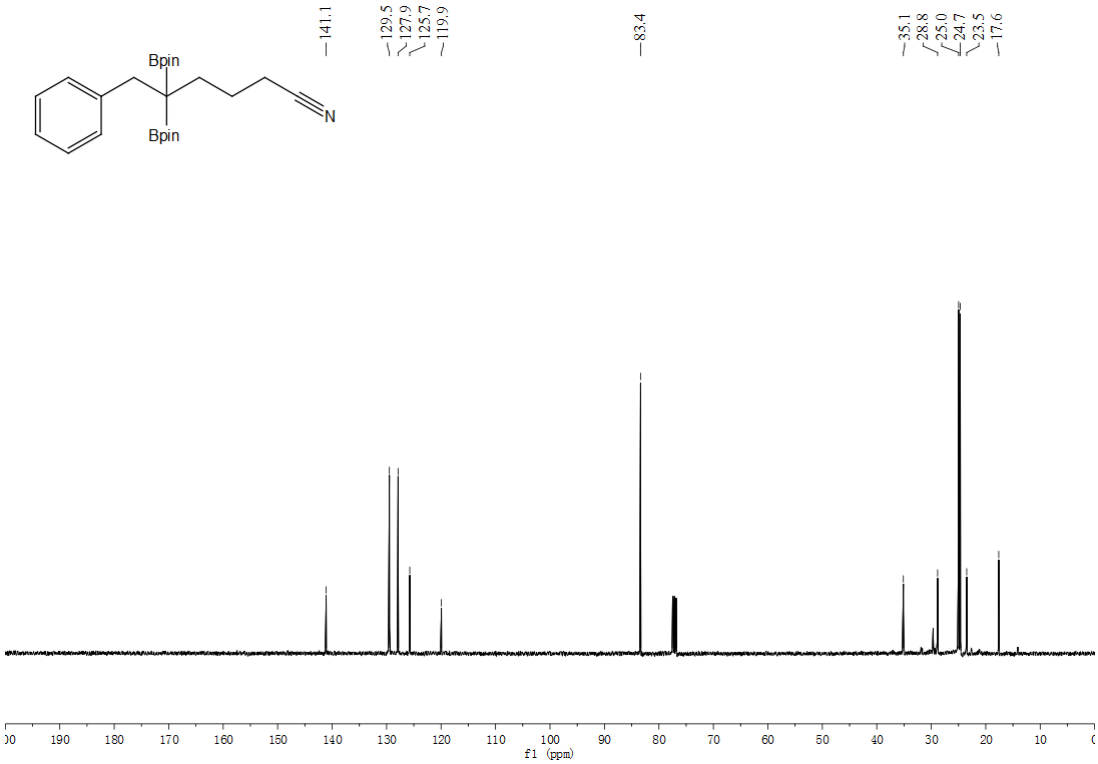
^{13}C NMR (101 MHz, $CDCl_3$) of **13h**



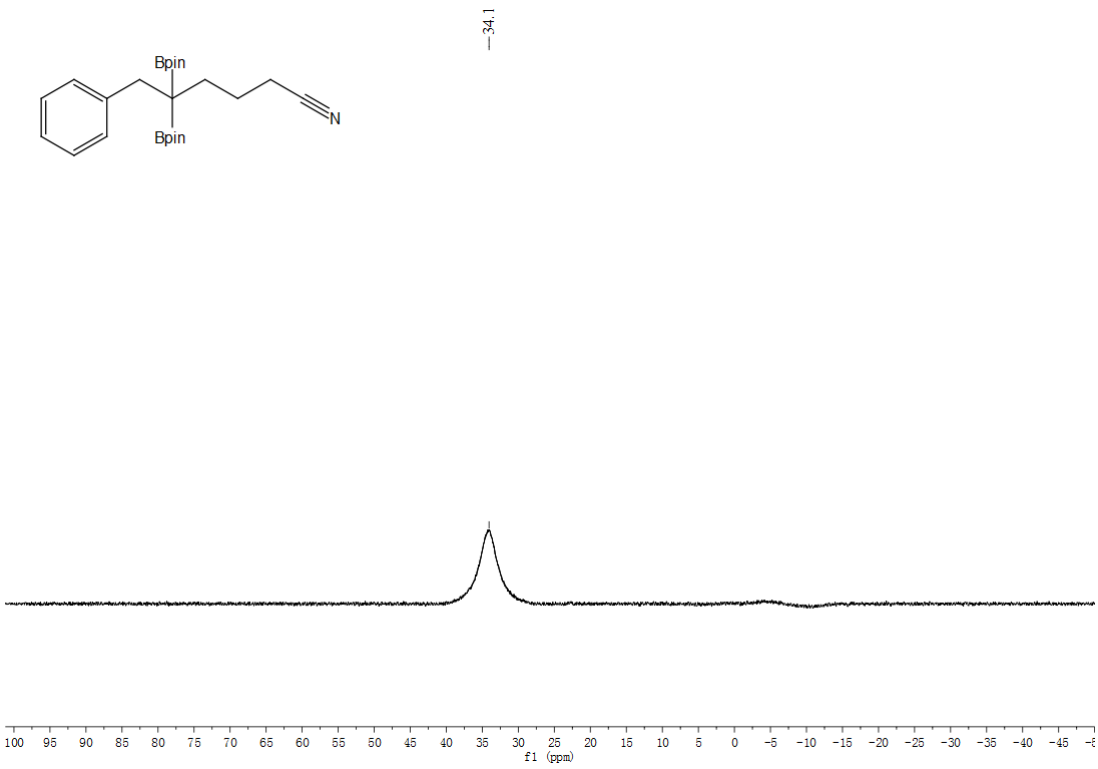
^{11}B NMR (193 MHz, EtOAc) of **13h**



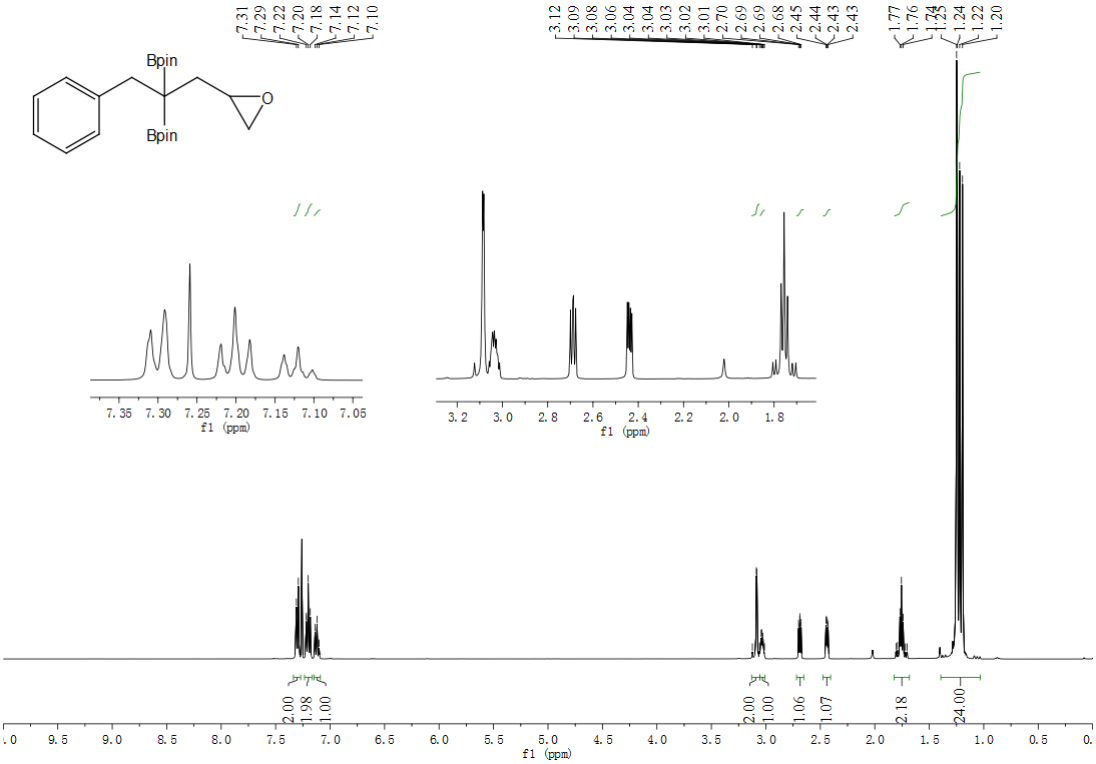
^{1}H NMR (400 MHz, $CDCl_3$) of **13i**



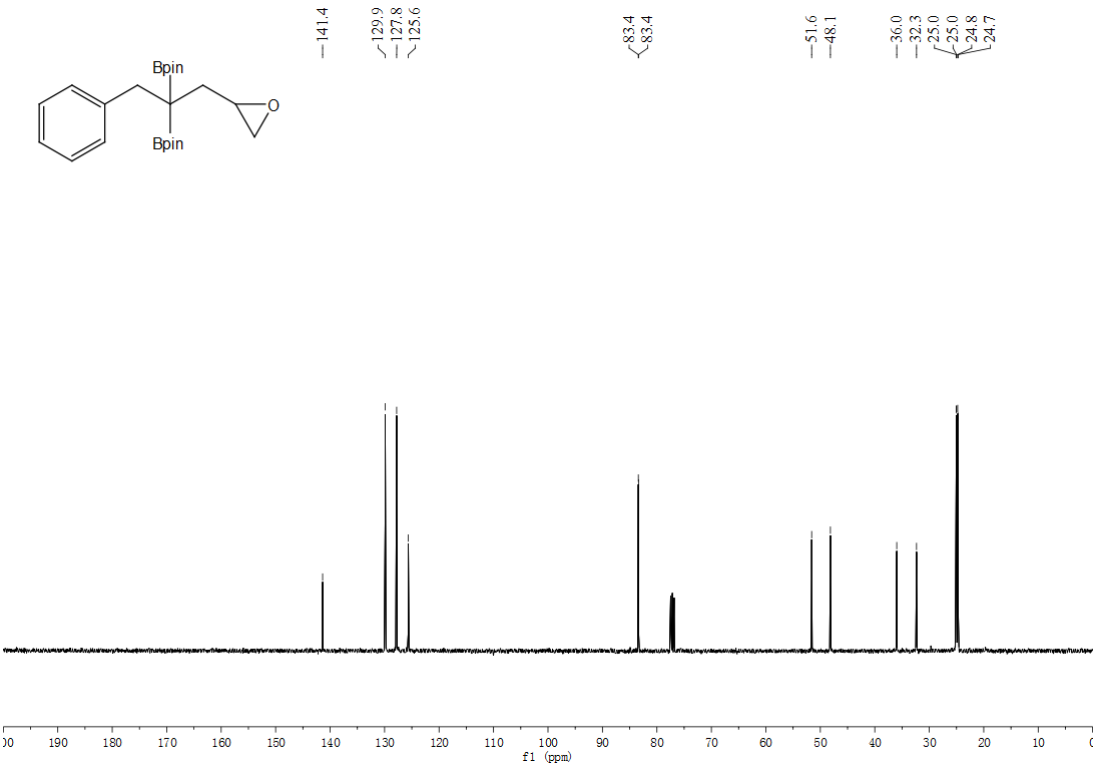
^{13}C NMR (101 MHz, $CDCl_3$) of **13i**



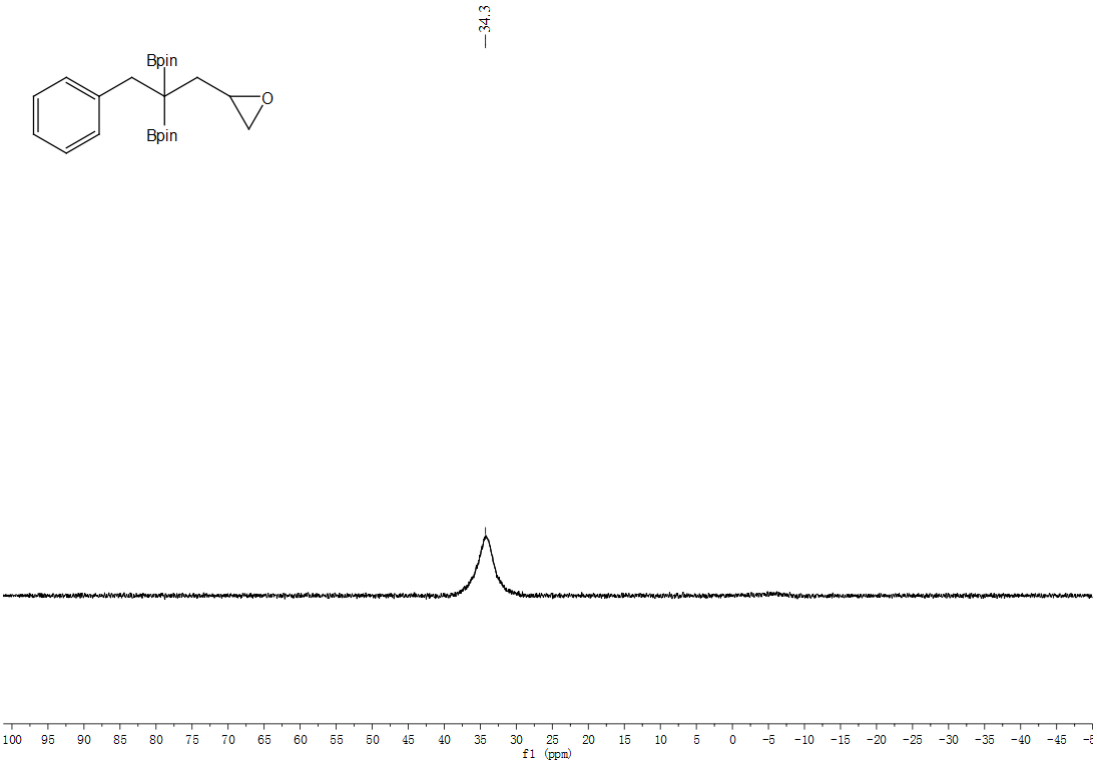
^{11}B NMR (193 MHz, EtOAc) of **13i**



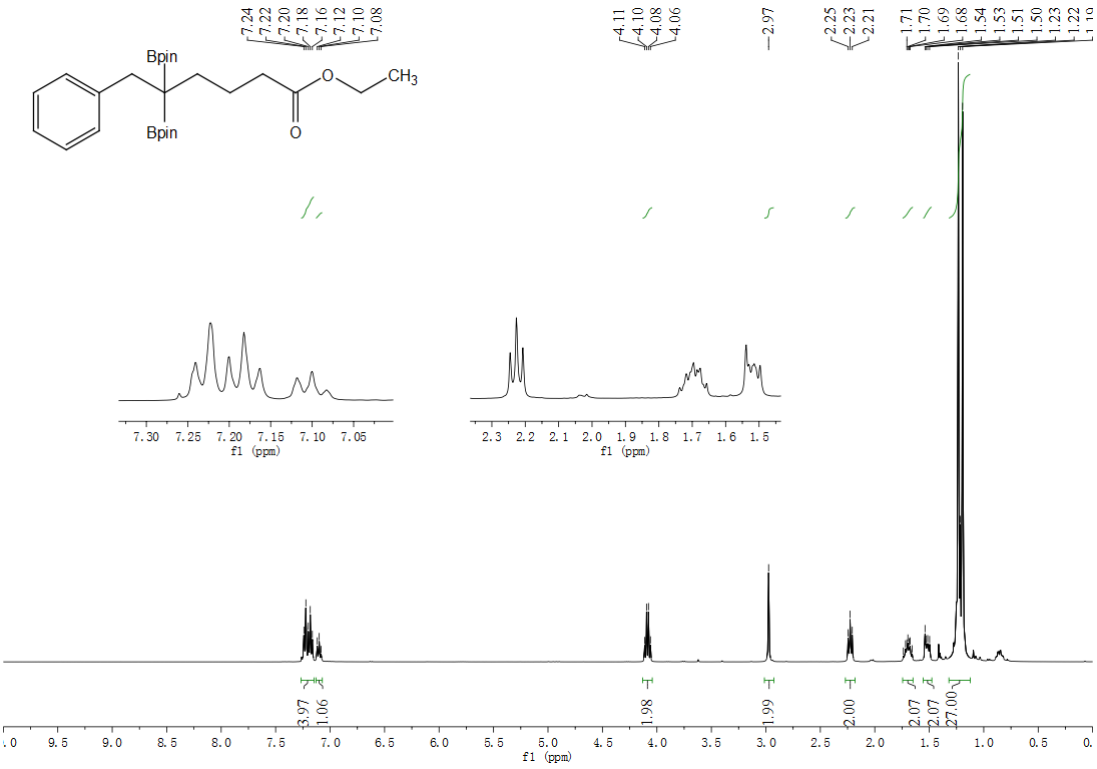
^{1}H NMR (400 MHz, $CDCl_3$) of **13j**



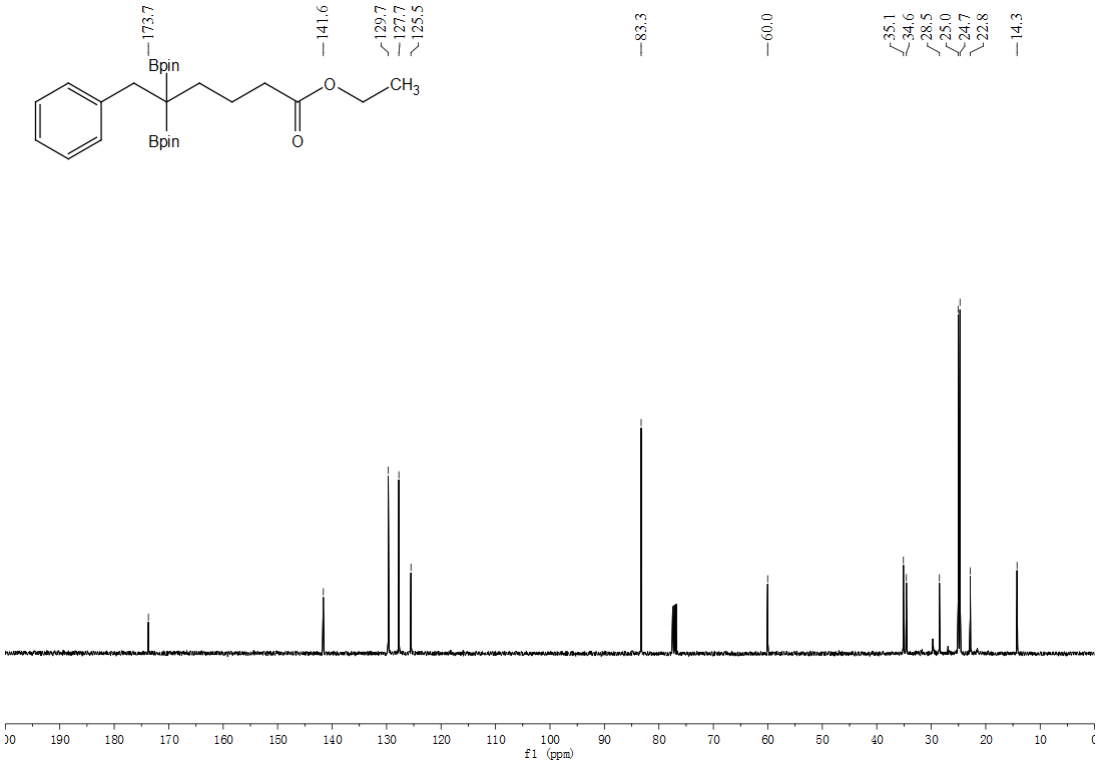
^{13}C NMR (101 MHz, $CDCl_3$) of **13j**



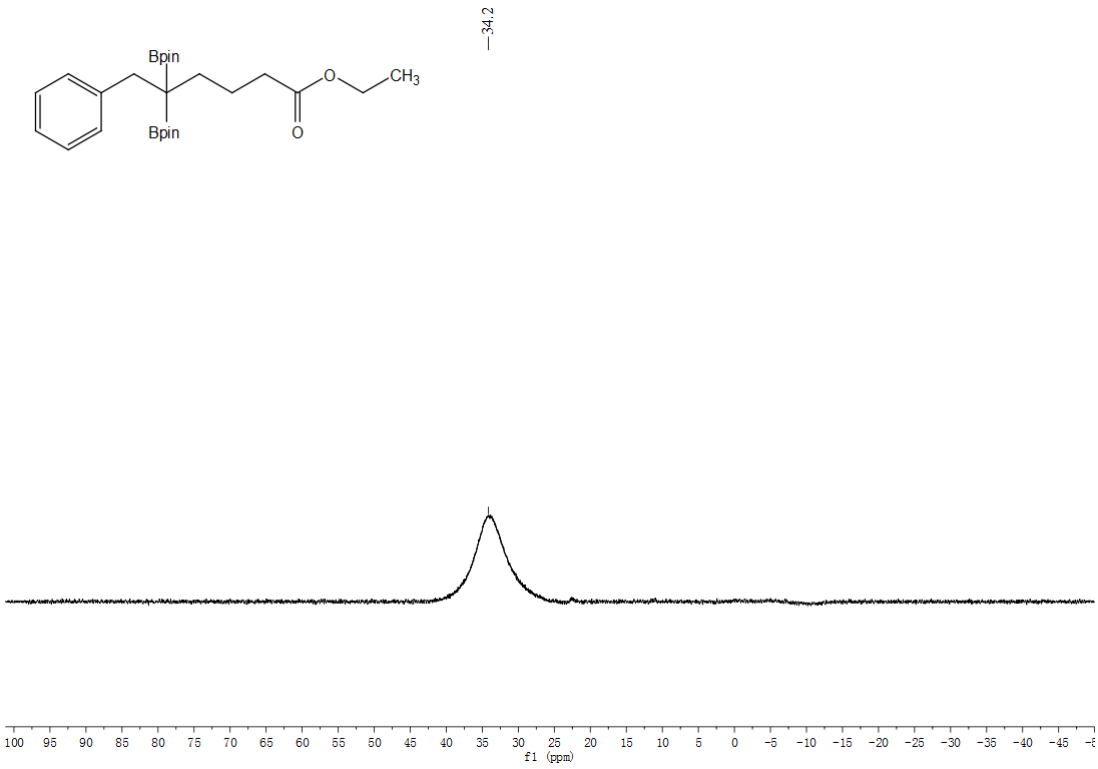
^{11}B NMR (193 MHz, EtOAc) of **13j**



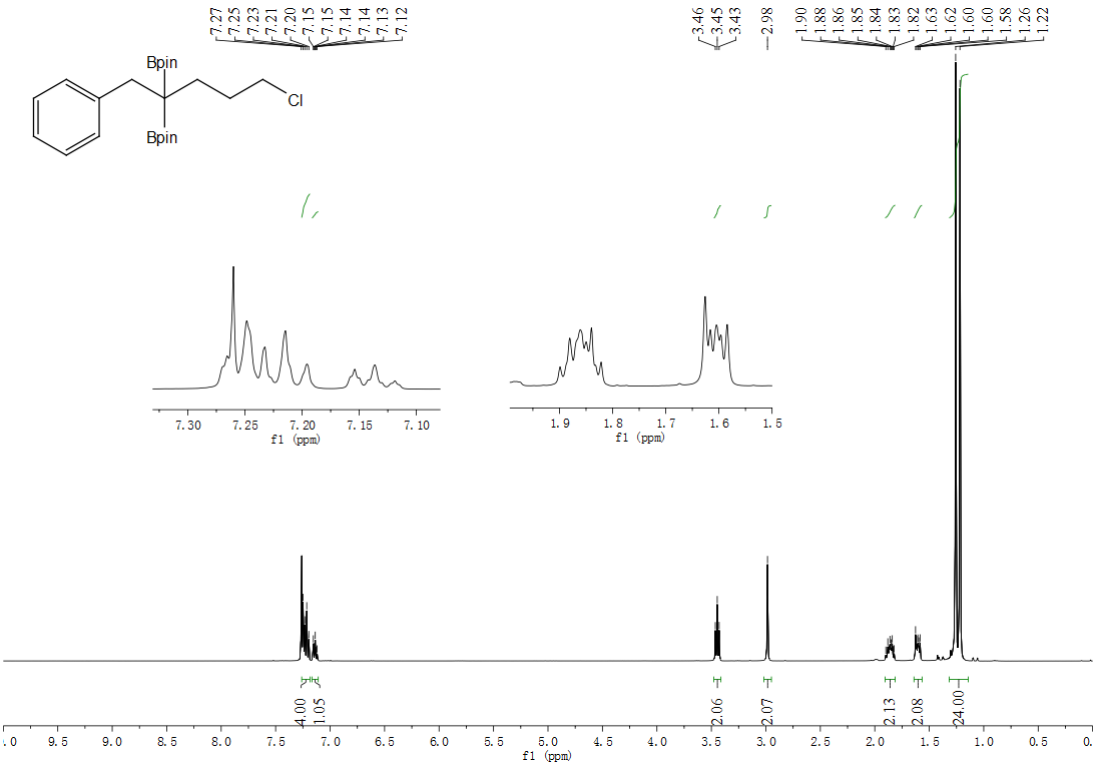
^{1}H NMR (400 MHz, $CDCl_3$) of **13k**



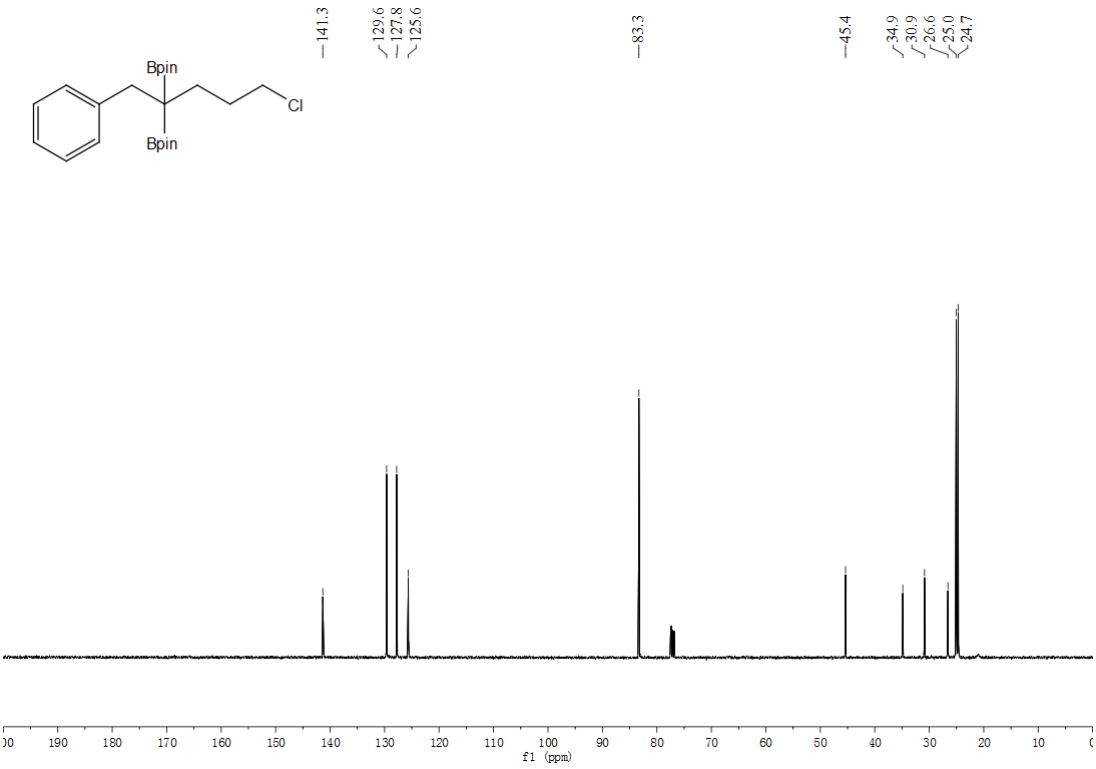
^{13}C NMR (101 MHz, $CDCl_3$) of **13k**



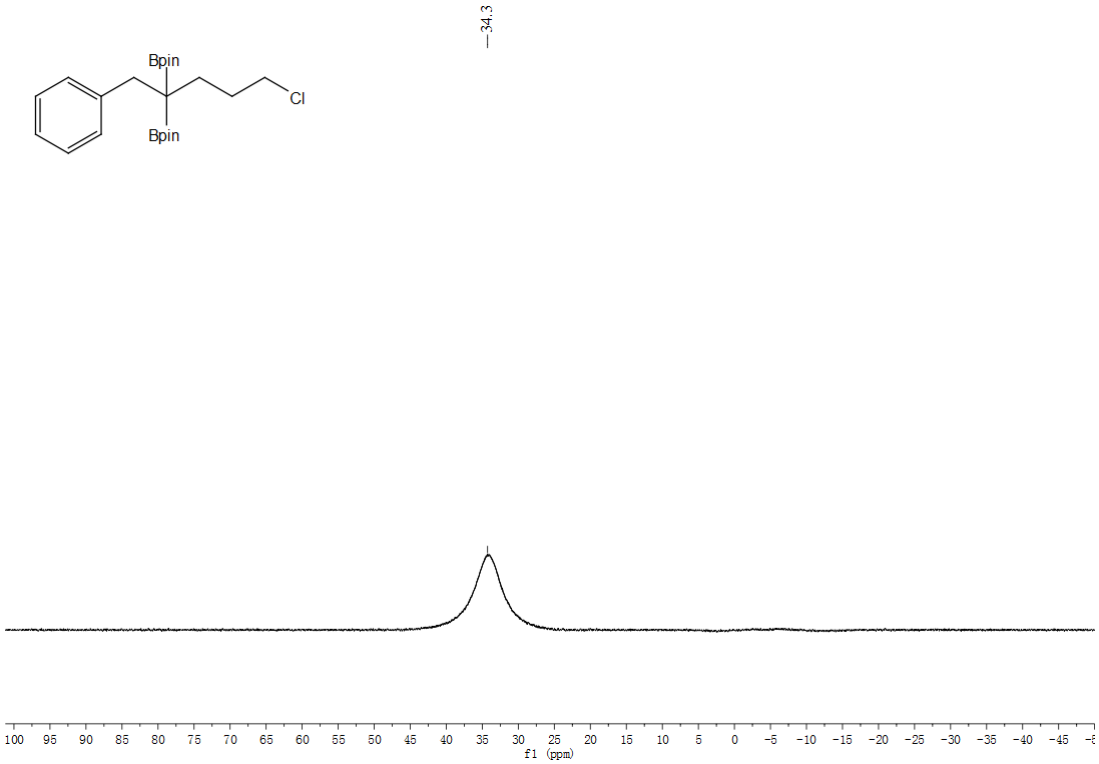
^{11}B NMR (193 MHz, EtOAc) of **13k**



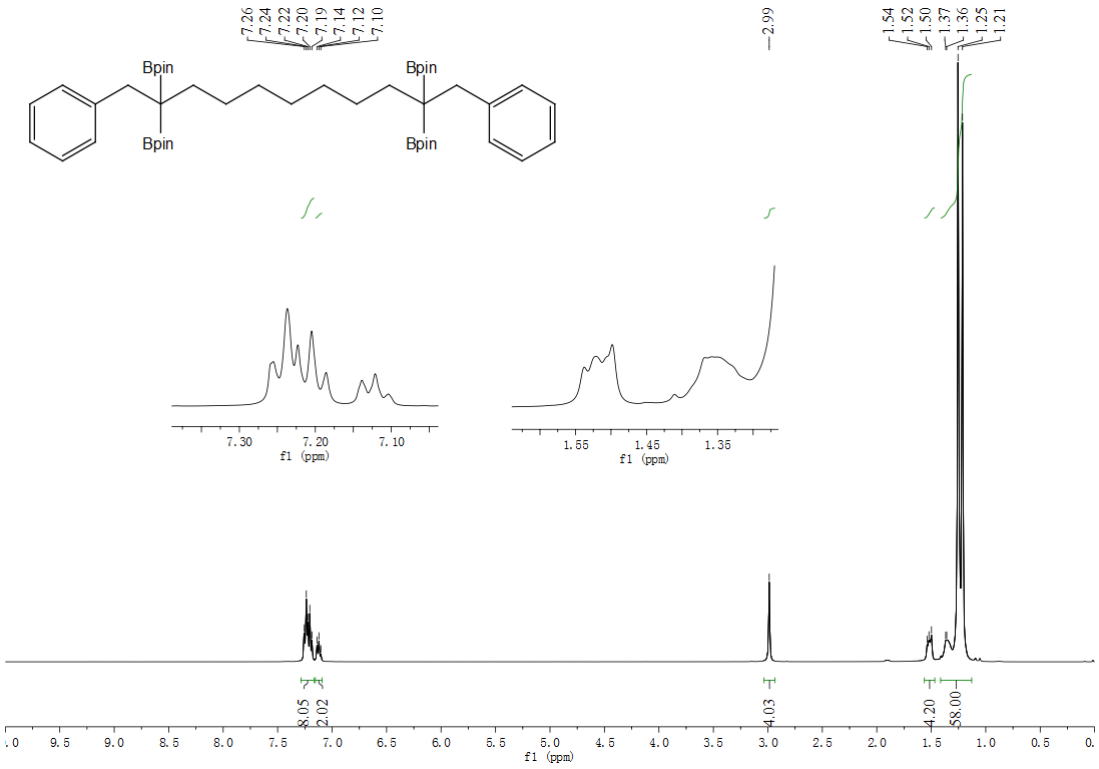
^{1}H NMR (400 MHz, $CDCl_3$) of **13l**



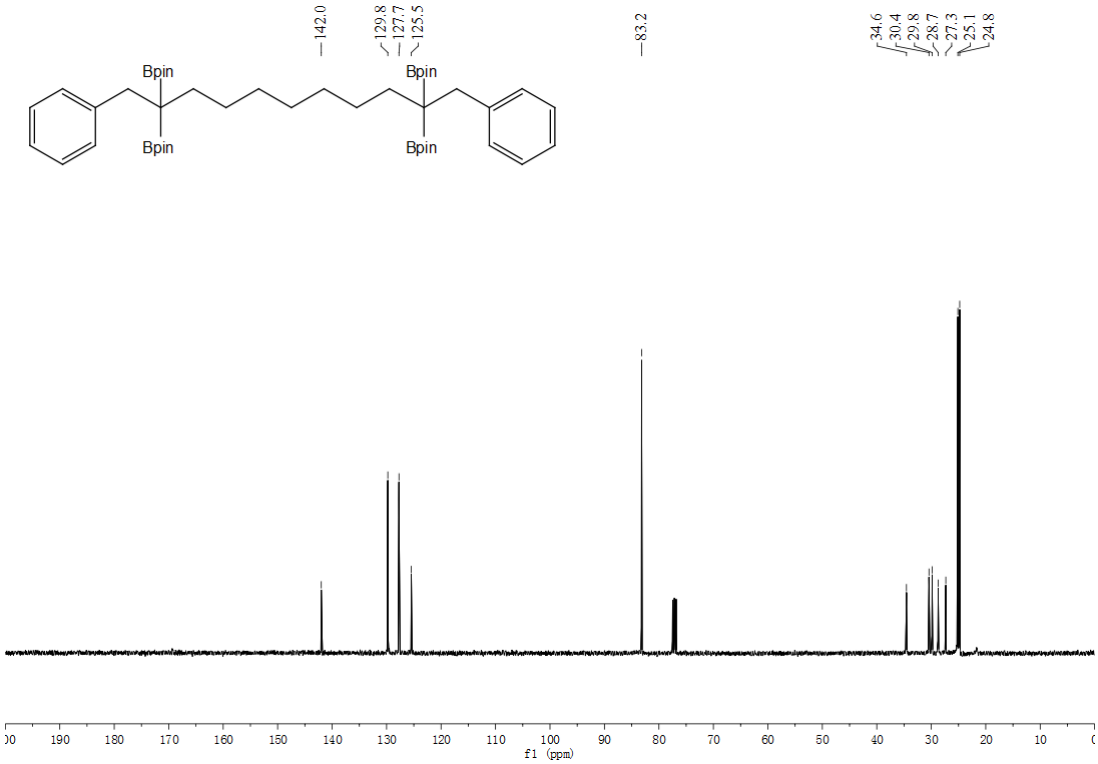
^{13}C NMR (101 MHz, $CDCl_3$) of **13l**



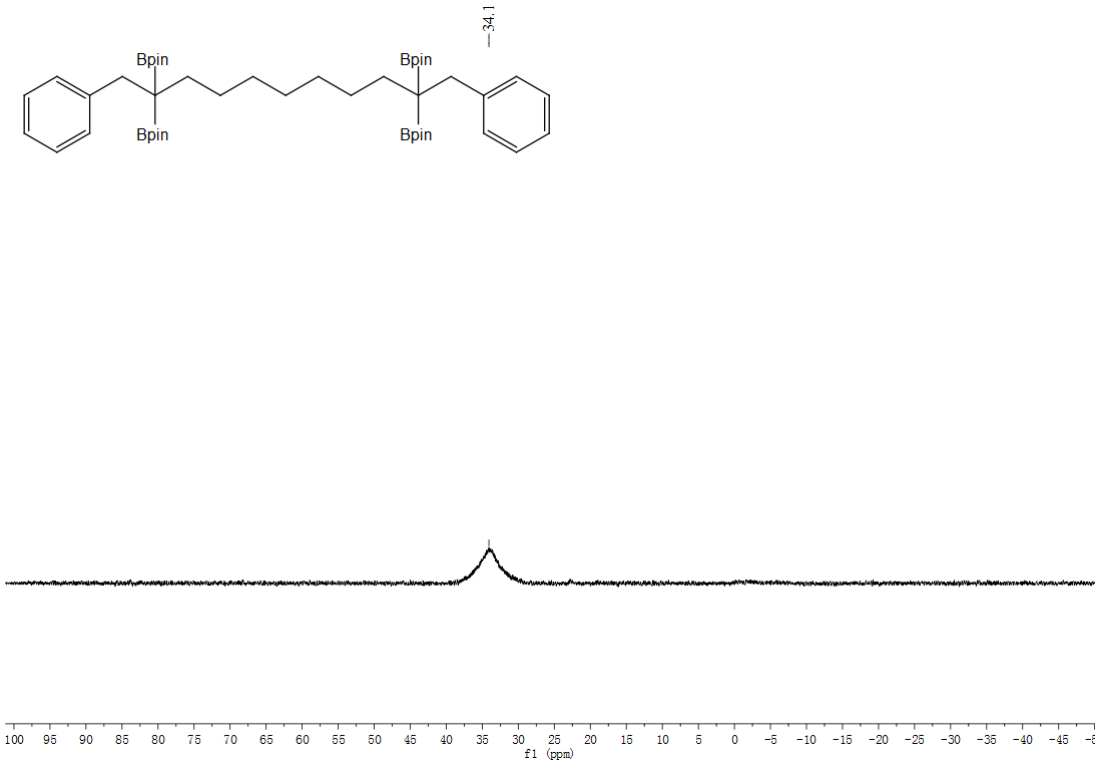
^{11}B NMR (193 MHz, EtOAc) of **13l**



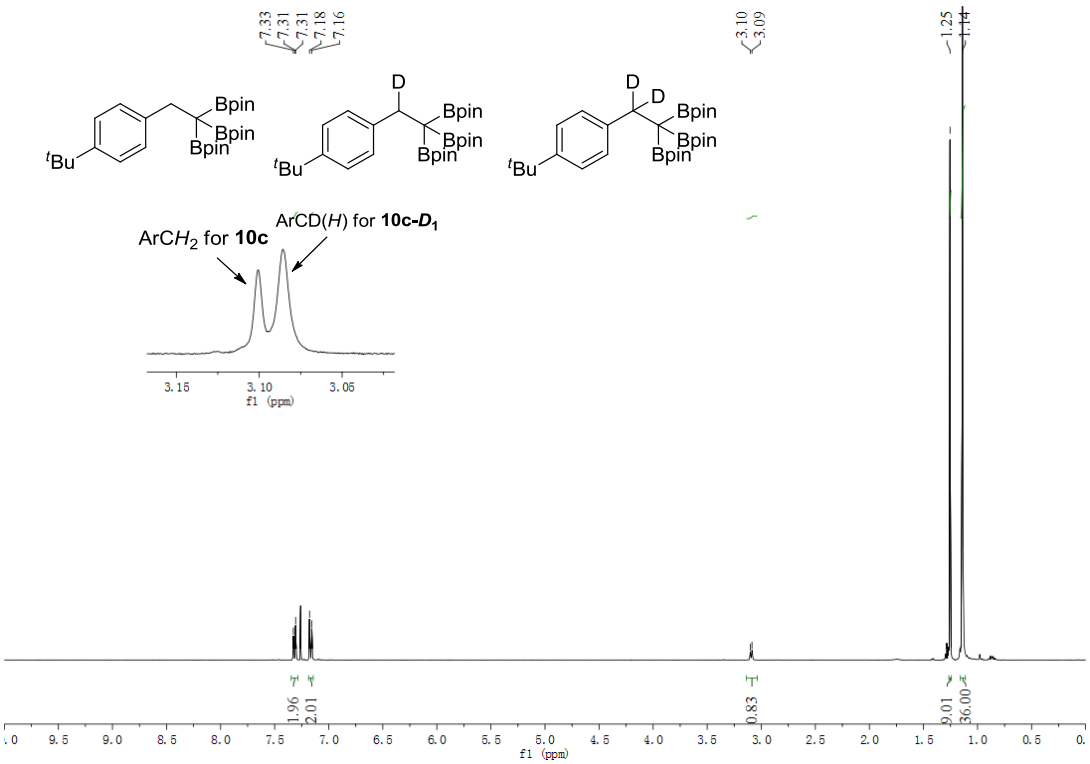
^{1}H NMR (400 MHz, $CDCl_3$) of **13m**



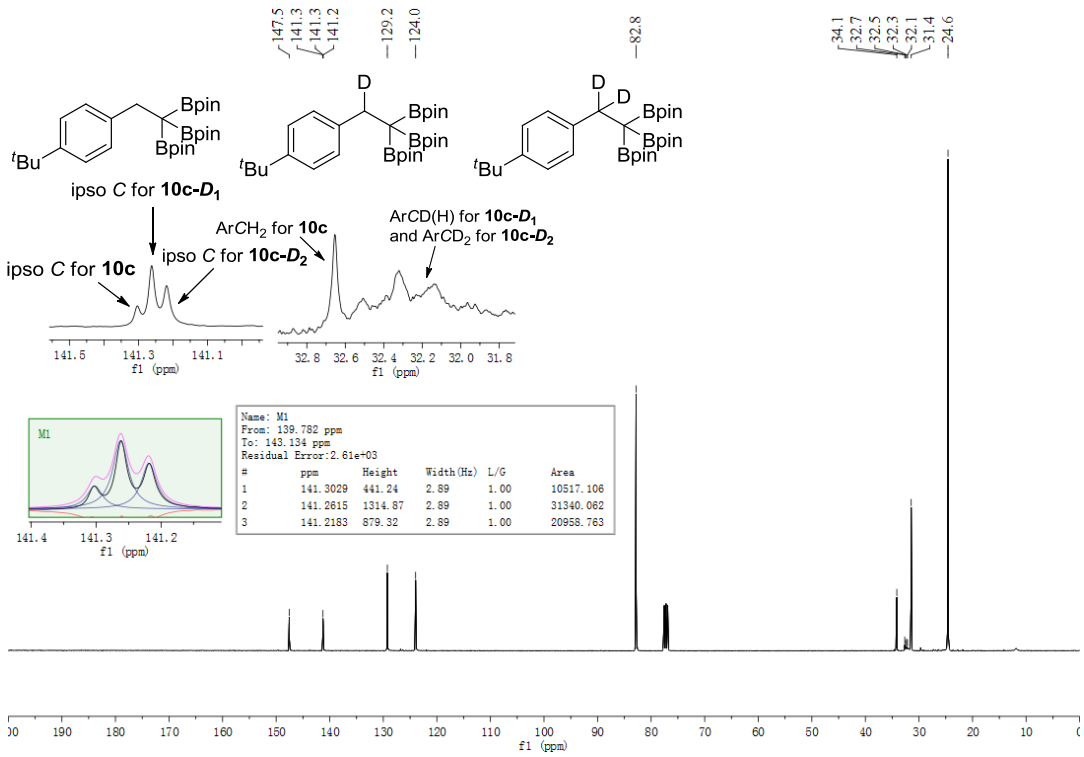
^{13}C NMR (101 MHz, $CDCl_3$) of **13m**



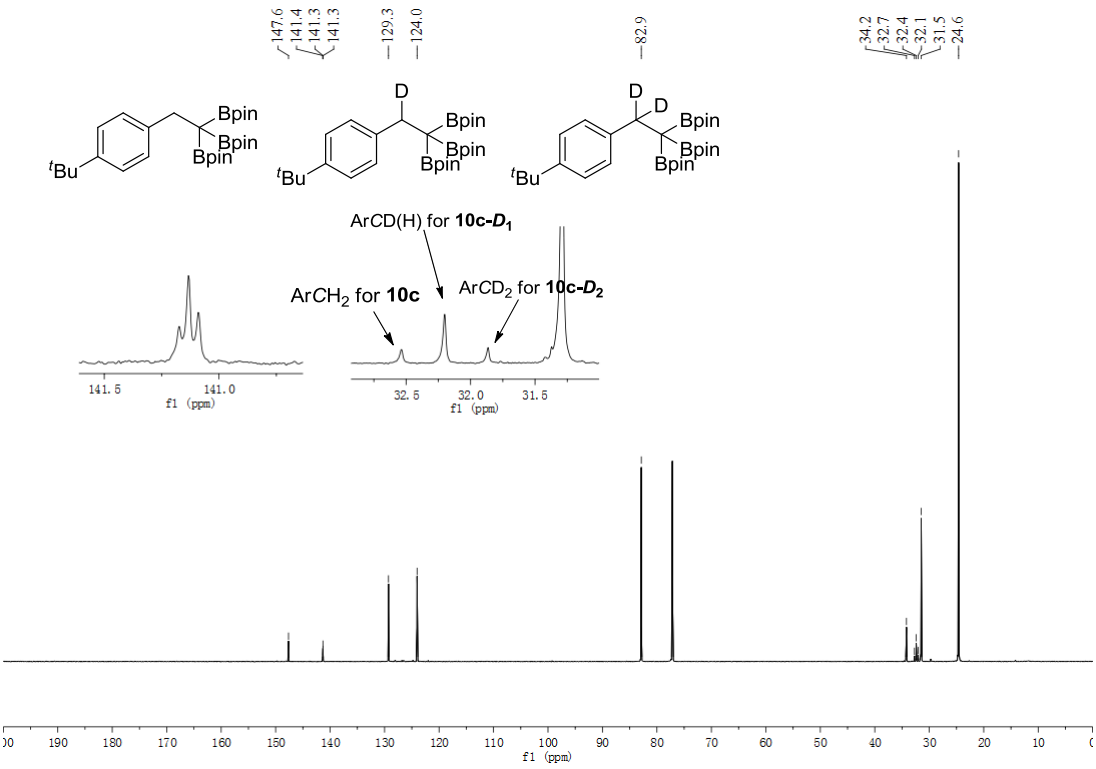
^{11}B NMR (193 MHz, EtOAc) of **13m**



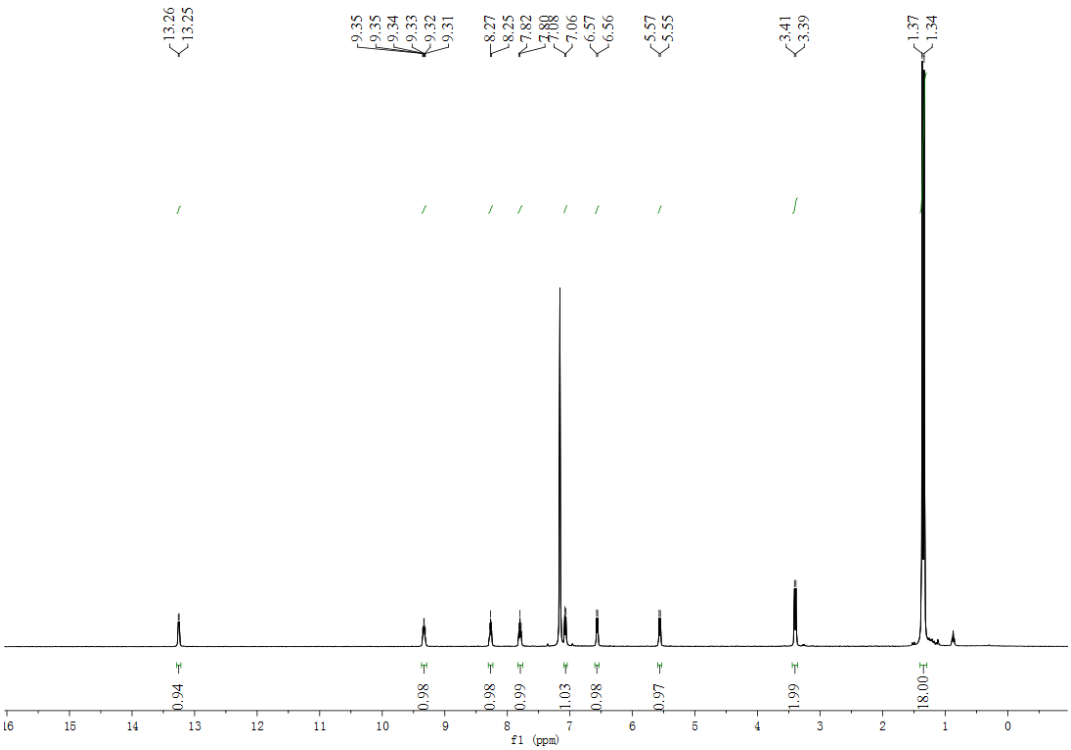
Quantitative ^{1}H NMR (400 MHz, $CDCl_3$) of **10c, 10c-D_1, 10c-D_2**



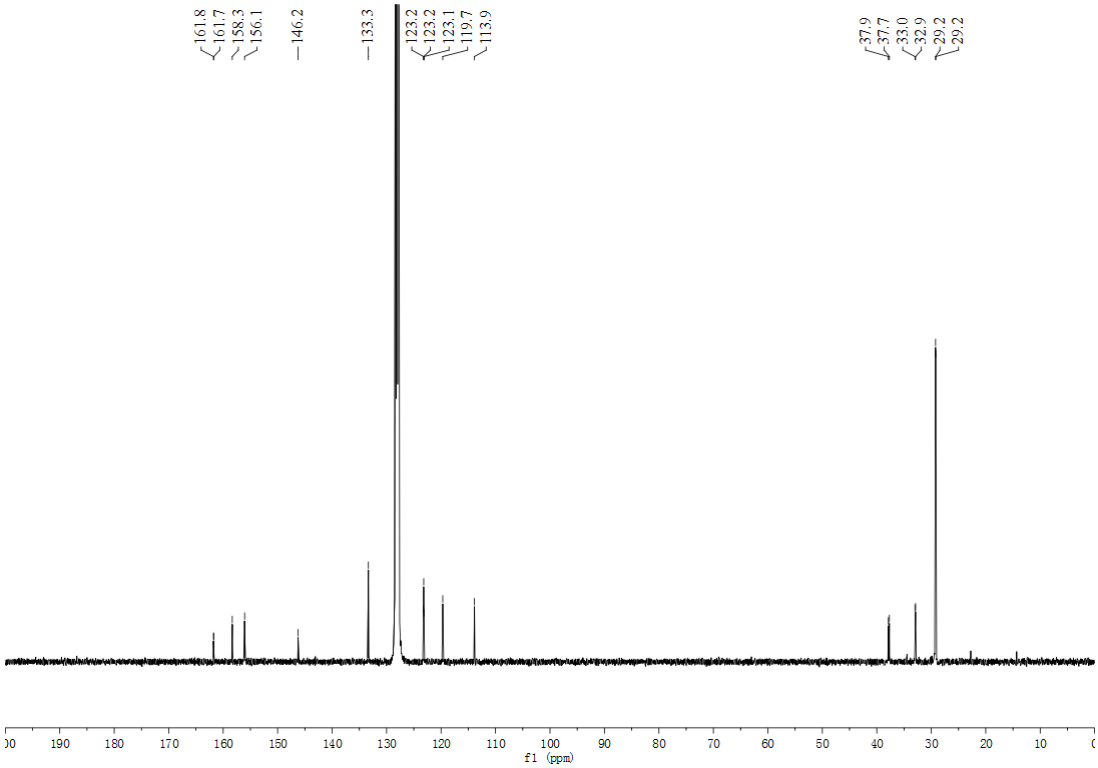
Quantitative ^{13}C NMR (101 MHz, $CDCl_3$) of **10c**, **10c-D_1**, and **10c-D_2** (The isotope effects on ^{13}C chemical shifts are highfield shifts. Also see: Aydin, R.; Guenther, H., *J. Am. Chem. Soc.* **1981,** *103*, 1301.)



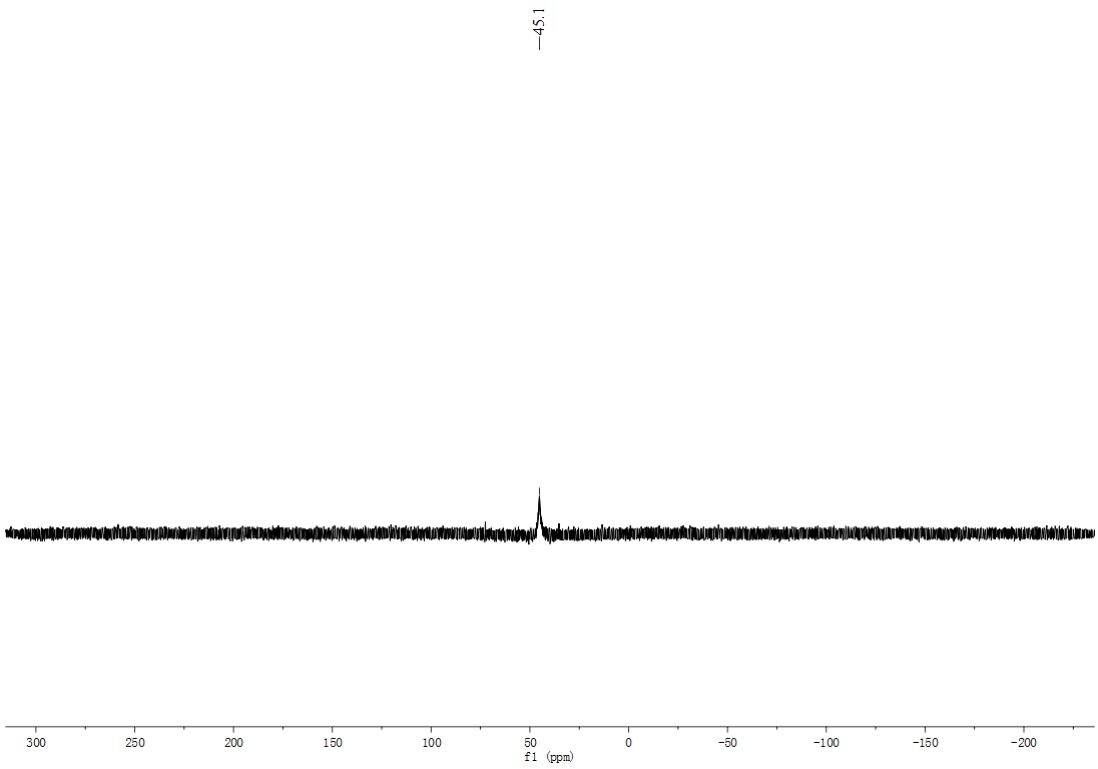
Deuterium-decoupled ^{13}C NMR (101 MHz, $CDCl_3$) of **10c**, **10c-*D*$_1$**, and **10c-*D*$_2$** (The isotope effects on ^{13}C chemical shifts are highfield shifts. Also see: Aydin, R.; Guenther, H., *J. Am. Chem. Soc.* **1981,** *103*, 1301.)



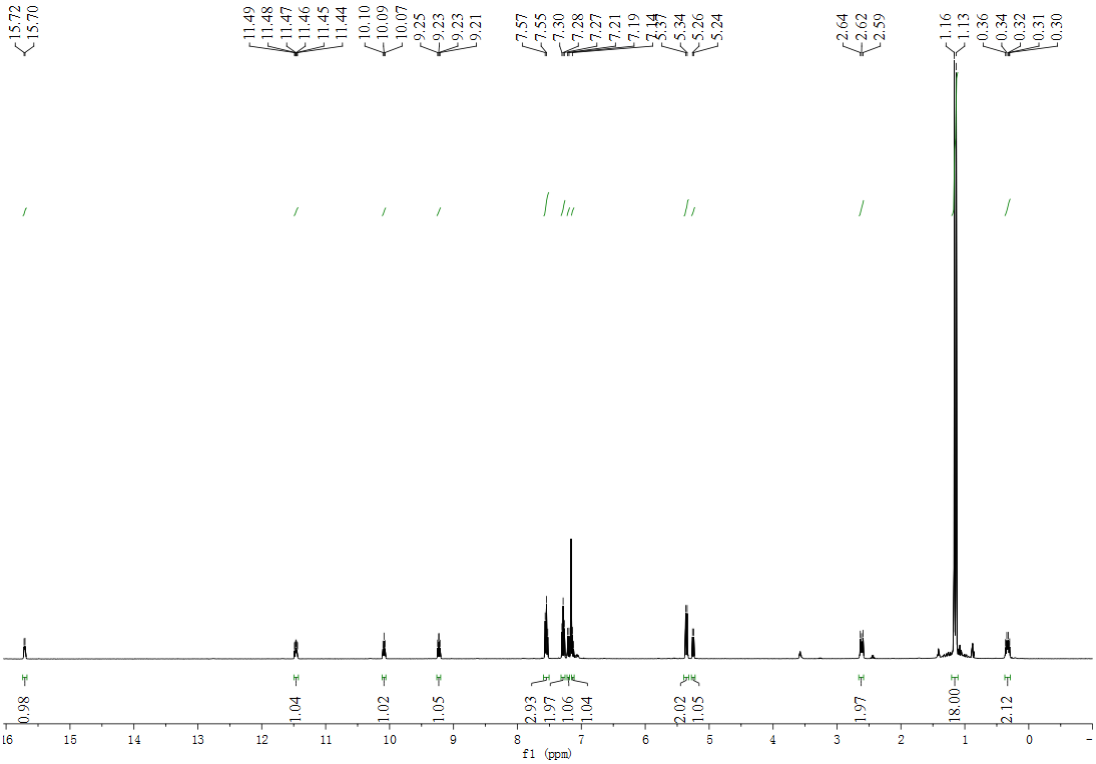
^{1}H NMR (400 MHz, C_6D_6) of **(*t*^{Bu}PNN)CoCl (11)**



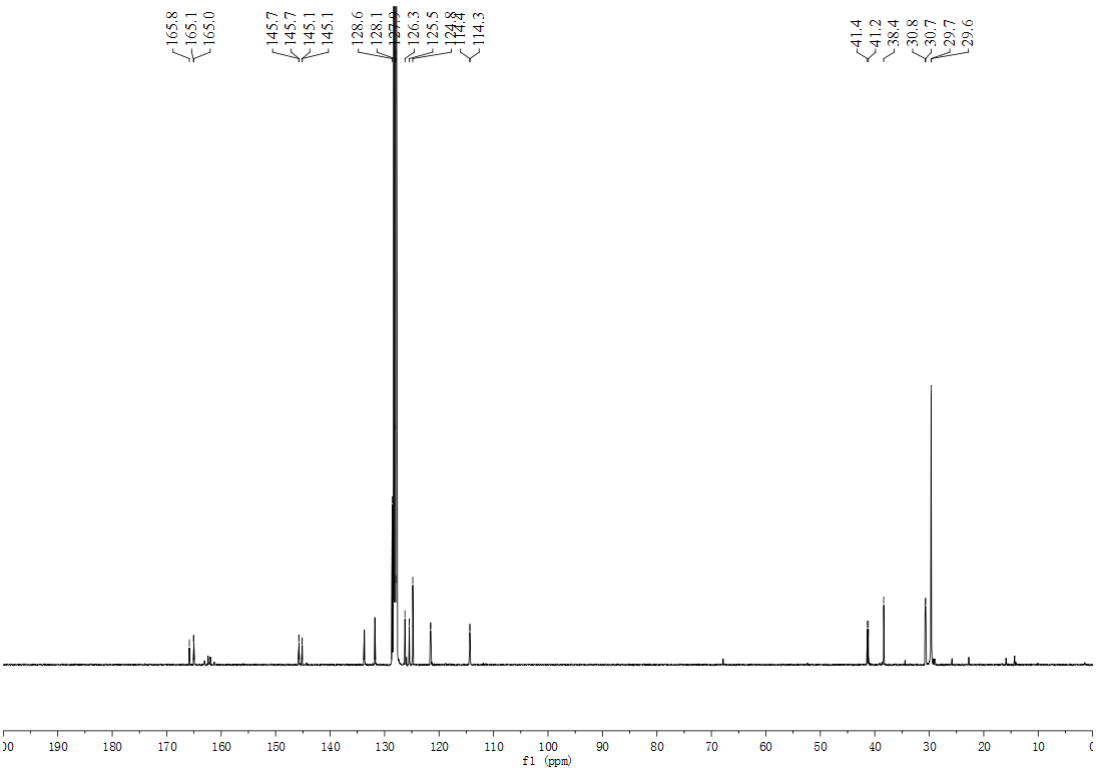
^{13}C NMR (101 MHz, C_6D_6) of **(**$^{t\mathrm{Bu}}$**PNN)CoCl** (**11)**



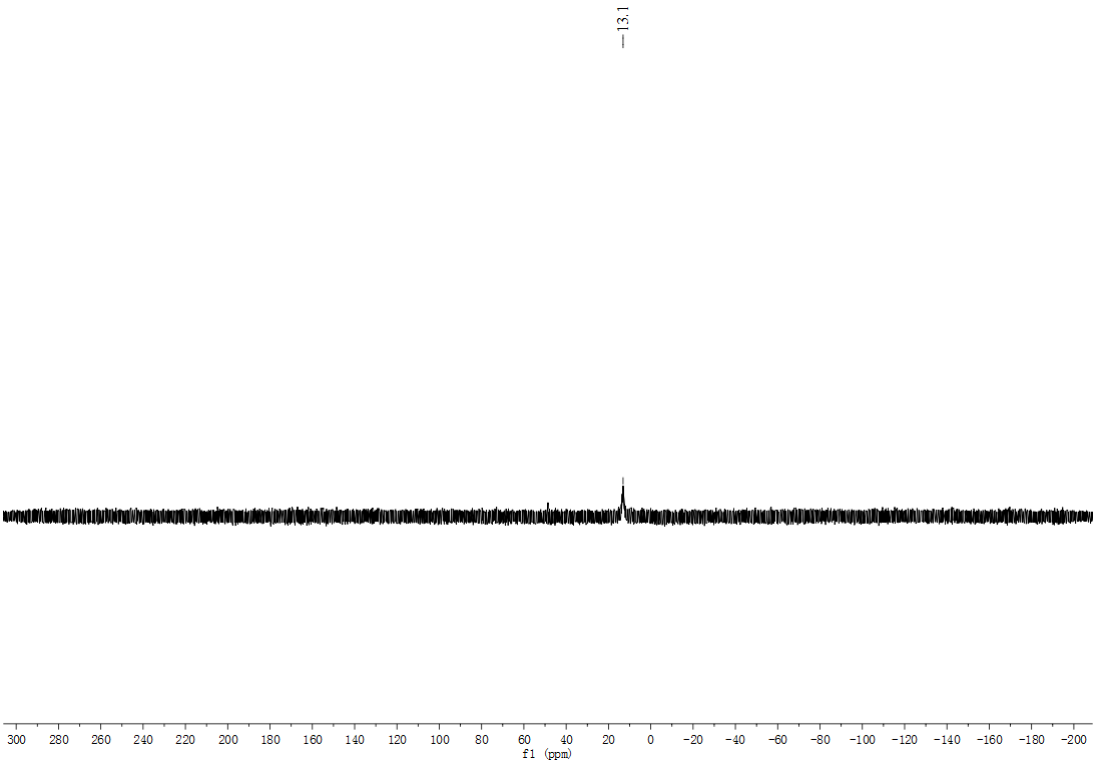
^{31}P NMR (162 MHz, C_6D_6) of **(**$^{t\mathrm{Bu}}$**PNN)CoCl** (**11)**



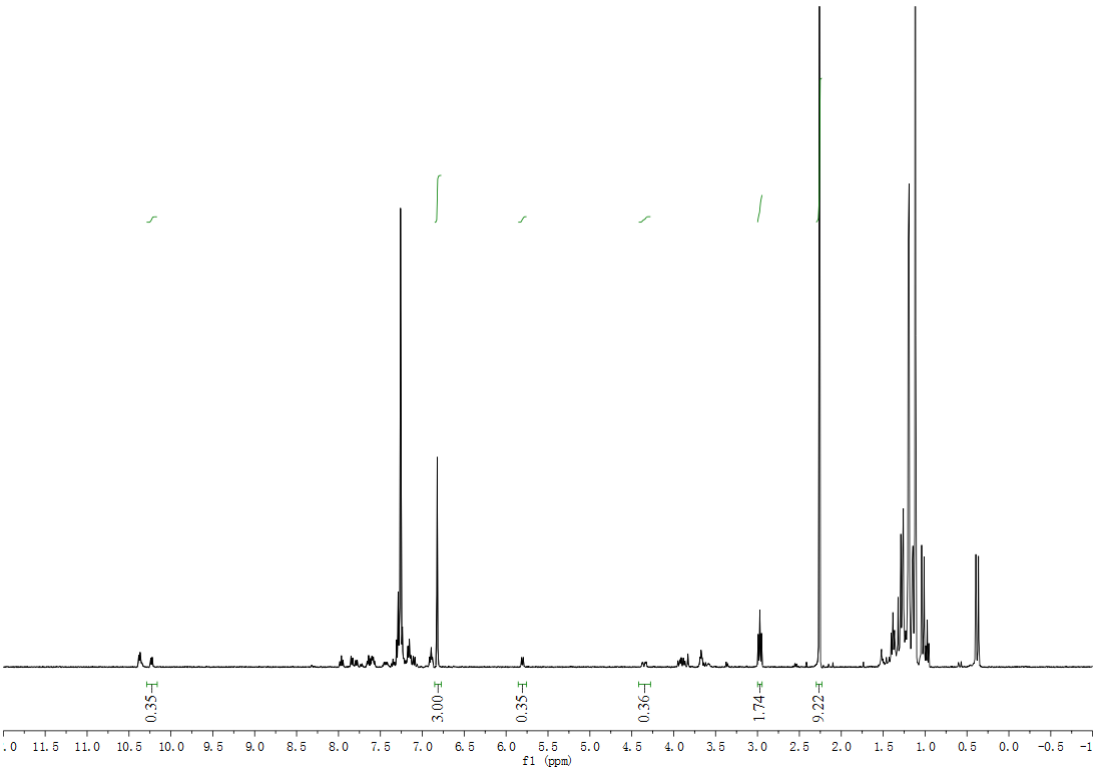
^{1}H NMR (400 MHz, C_6D_6) of **(^{t}Bu**PNN)CoCH$_2$CH$_2$Ph (14)**



^{13}C NMR (101 MHz, C_6D_6) of **(^{t}Bu**PNN)CoCH$_2$CH$_2$Ph (14)**



^{31}P NMR (162 MHz, C_6D_6) of **(^{t}Bu^{u}PNN)CoCH$_2$CH$_2$Ph (14)**



^{1}H NMR (400 MHz, C_6D_6) of **(^{t}Bu^{u}PNN)CoCH$_2$CH$_2$Ph (14) + B$_2$pin$_2$**