Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of 1,1-Diboronate Esters by Cobalt-Catalyzed Sequential Hydroboration of Terminal Alkynes

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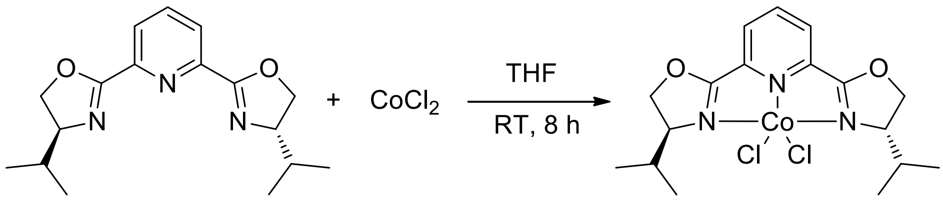
Table of Contents

1. General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification**.** All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Tetrahydrofuran (THF), dioxane and toluene were distilled from sodium benzophenone ketyl prior to use. The following compounds were prepared according to the related literature procedures: [(*S*)-*i*Pr-IPO]$FeBr_2$ ((*S*)-**4a**).[1] [(*S*)-*i*Pr-IPO]$CoCl_2$ ((*S*)-**4b**),[2] ($^{i\text{Pr}}$PDI)$CoCl_2$ (**4c**).[3]

NMR spectra were recorded on Agilent 400 MHz or Varian Mercury 400 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. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, quint = quintuplet, sext = sextuplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Elemental analyses and high resolution mass spectrometer (HR-MS) were carried out by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

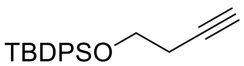
2. Synthesize [(*S*)-*i*Pr-Pybox]$CoCl_2$ ((*S*)-4d)



4d

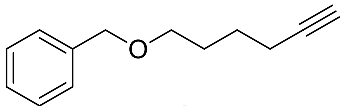
Preparation of [(*S*)-*i*Pr-Pybox]$CoCl_2$ ((*S*)-4d). To a solution of (*S*)-^{iPr}Pybox (60 mg, 0.199 mmol) in approximately 15 mL of THF, 26 mg (0.199 mmol) of $CoCl_2$ were added. The resulting mixture was stirred at room temperature for 8 hours. The solvent was removed under vacuum and the resulting solid was washed with diethyl ether, collected by filtration and dried under vacuum to yield 71 mg (85%) of a blue solid identified as (*S*)-**4d**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 71.82, 11.17, 2.98, -11.26, -11.64, -17.92, -21.00, -40.89, -41.71. Anal. Calcd. ($C_{17}H_{23}Cl_2CoN_3O_2$): C, 47.35; H, 5.38; N, 9.74. Found: C, 46.96; H, 5.58; N, 9.58.

3. Procedure for prepare of terminal alkynes



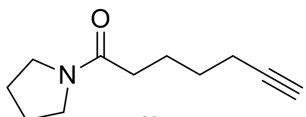
1f

(but-3-yn-1-yloxy)(tert-butyl)diphenylsilane (1f). Compound **1f** was prepared according to the literature.[4] The product was purified with silica gel chromatography (PE/EA = 100/1) as colorless oil (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 4H), 7.43 – 7.31 (m, 6H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.43 (td, *J* = 7.0, 2.6 Hz, 2H), 1.90 (t, *J* = 2.6 Hz, 1H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 133.6, 129.8, 127.8, 81.5, 69.6, 62.4, 26.9, 22.7, 19.3. These spectroscopic data correspond to reported data.[4]



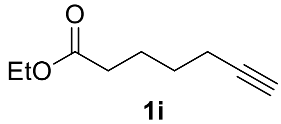
1g

((hex-5-yn-1-yloxy)methyl)benzene (1g). Compound **1g** was prepared according to the literature.[5] The product was purified with silica gel chromatography (PE/EA = 100/1) as colorless oil (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.30 – 7.21 (m, 1H), 4.49 (s, 2H), 3.48 (t, J = 6.2 Hz, 2H), 2.21 (td, J = 7.0, 2.6 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 1.77 – 1.68 (m, 2H), 1.68 – 1.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 128.4, 127.7, 127.6, 84.4, 72.9, 69.8, 68.5, 28.8, 25.3, 18.3. These spectroscopic data correspond to reported data.[5]



1h

1-(pyrrolidin-1-yl)hept-6-yn-1-one (1h). A solution of pyrrolidine (2.54 g, 35.67 mol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C to a solution of hept-6-ynoyl chloride (1.71 g, 11.9 mmol) in 20 mL of CH_2Cl_2. The reaction mixture was allowed to warm to room temperature and was stirred for 1.5 hours. Then 2 M HCl (15 mL) was slowly added at that temperature. The resulting mixture was extracted with CH_2Cl_2 (3×20 mL). Combined organic phase was washed with saturated aq. $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:2) to give the title compound **1h** (1.68 g, 79%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 – 3.35 (m, 4H), 2.25 (t, J = 7.5 Hz, 2H), 2.19 (td, J = 7.1, 2.6 Hz, 2H), 1.96 – 1.88 (m, 3H), 1.85 – 1.79 (m, 2H), 1.78 – 1.69 (m, 2H), 1.60 – 1.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 84.3, 68.5, 46.7, 45.7, 34.2, 28.3, 26.2, 24.5, 24.0, 18.3. HRMS-ESI (*m/z*): Calc. for $C_{11}H_{18}NO$ $[M+H]^+$ 180.1383 , found 180.1384.

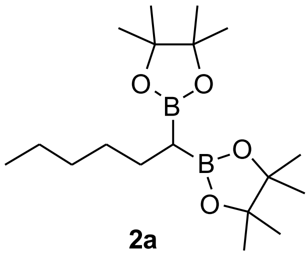


1i

ethyl hept-6-ynoate (1i). Compound **1i** was prepared according to the literature.[6] The product was purified with silica gel chromatography (PE/EA = 30/1) as colorless oil

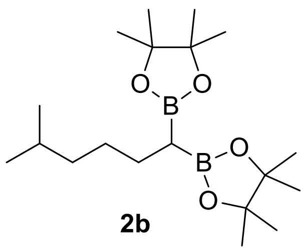
(80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (q, J = 7.1 Hz, 2H), 2.29 (t, J = 7.4 Hz, 2H), 2.18 (td, J = 7.0, 2.6 Hz, 2H), 1.93 (t, J = 2.6 Hz, 1H), 1.78 – 1.66 (m, 2H), 1.58 – 1.48 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 84.0, 68.7, 60.4, 33.8, 27.9, 24.1, 18.2, 14.3. These spectroscopic data correspond to reported data.[6]

4. Procedure for Dihydroboration of Terminal Alkynes



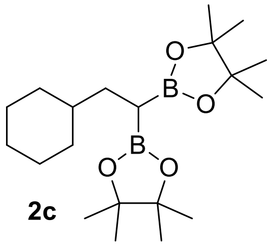
2a

Representative procedure for dihydroboration with cobalt complex. **2,2'-(hexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2a).** In a nitrogen filled glovebox, to a solution of cobalt complex (*S*)-**4a** (0.015mmol, 7.8 mg) in 2 mL of THF, a solution (1.0 M in THF) of $NaBHEt_3$ (30 μL, 0.03 mmol) was slowly added at 25 ºC. After stirring for 1 min, HBpin (128 mg, 1.0 mmol, 2 equiv), 1-hexyne **1a** (41.0 mg, 0.5 mmol) were sequentially added. The reaction mixture stirred for 12 h at 25 ºC and then was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by silica gel column chromatography (5% EtOAc in hexane) to give the product **2a** as colorless oil (156 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 – 1.48 (m, 2H), 1.32 – 1.23 (m, 6H), 1.22 (s, 12H), 1.21 (s, 12H), 0.84 (t, *J* = 6.7 Hz, 3H), 0.70 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 32.3, 31.9, 25.7, 24.9, 24.6, 22.6, 14.1. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. These spectroscopic data correspond to reported data.[7]



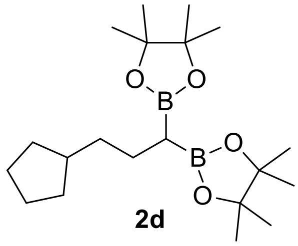
2b

2,2'-(5-methylhexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2b). Colorless oil (168 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 – 1.46 (m, 3H), 1.30 – 1.23 (m, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 1.16 – 1.09 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 6H), 0.71 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 39.1, 30.4, 27.8, 26.0, 25.0, 24.6, 22.7. ^{11}B NMR (192 MHz, EtOAc) δ 34.3. HRMS-EI (*m/z*): Calc. for $C_{18}H_{35}B_2O_4$ [M^+- CH_3] 335.2794 , found 335.2796.



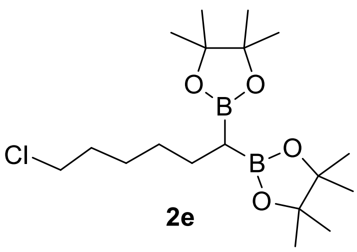
2c

2,2'-(2-cyclohexylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2c). Colorless oil (159 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 – 1.53 (m, 5H), 1.43 (t, *J* = 7.4 Hz, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 1.14 – 0.98 (m, 4H), 0.84 – 0.71 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 39.9, 33.2, 33.0, 26.8, 26.6, 24.9, 24.7. ^{11}B NMR (192 MHz, EtOAc) δ 34.5. These spectroscopic data correspond to reported data.[8]



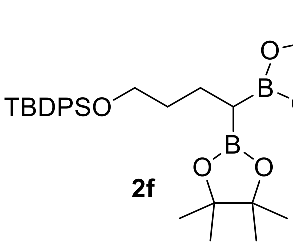
2d

2,2'-(3-cyclopentylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2d). Colorless oil (152 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 – 1.64 (m, 1H), 1.60 – 1.48 (m, 1H), 1.48 – 1.39 (m, 1H), 1.29 – 1.23 (m, 1H), 1.22 (s, 1H), 1.21 (s, 1H), 1.10 – 0.99 (m, 1H), 0.68 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.9, 40.2, 39.5, 32.8, 25.3, 25.0, 24.9, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.0. HRMS-EI (*m/z*): Calc. for $C_{19}H_{35}B_2O_4$ [M^+- CH_3] 347.2794 , found 347.2786.



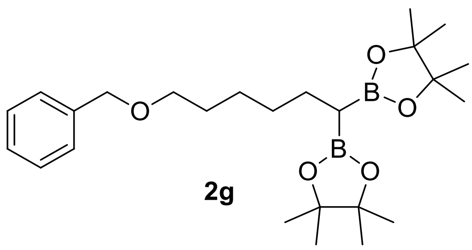
2e

2,2'-(6-chlorohexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2e). Colorless oil (156 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 (t, J = 6.8 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.53 (dd, J = 15.5, 7.8 Hz, 2H), 1.44 – 1.35 (m, 2H), 1.33 – 1.25 (m, 2H), 1.21 (s, 6H), 1.20 (s, 8H), 0.70 (t, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.1, 45.2, 32.5, 31.7, 26.9, 25.5, 25.0, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{17}H_{32}B_2O_4Cl$ [M^+- CH_3] 355.2248 , found 355.2242.



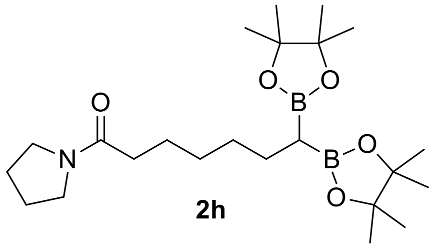
2f

(4,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)(tert-butyl)diphenylsilane (2f). Colorless oil (251 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.43 – 7.34 (m, 3H), 3.66 (t, J = 6.1 Hz, 1H), 1.65 – 1.59 (m, 2H), 1.23 (s, 3H), 1.22 (s, 3H), 0.73 (t, J = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 134.4, 129.5, 127.6, 83.0, 64.2, 35.5, 27.0, 24.9, 24.6, 21.9, 19.3. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{31}H_{47}B_2O_5Si$ [M^+- CH_3] 547.3452, found 547.3449.



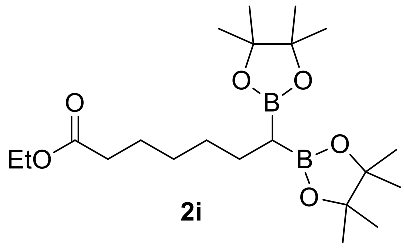
2g

2,2'-(6-(benzyloxy)hexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2g). Colorless oil (189 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 1H), 7.29 – 7.23 (m, 1H), 4.48 (s, 1H), 3.44 (t, J = 6.7 Hz, 1H), 1.65 – 1.51 (m, 1H), 1.39 – 1.28 (m, 1H), 1.22 (s, 3H), 1.21 (s, 3H), 0.71 (t, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $cdcl_3$) δ 138.9, 128.4, 127.7, 127.5, 83.0, 73.0, 70.7, 32.5, 29.8, 26.3, 25.8, 25.00, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{24}H_{39}B_2O_5$ [M^+-CH_3] 427.3056, found 427.3058.



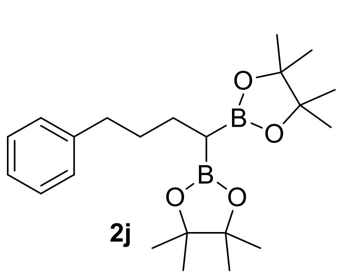
2h

1-(pyrrolidin-1-yl)-7,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-one (2h). Colorless oil (191 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (dt, *J* = 18.5, 6.8 Hz, 4H), 2.18 (t, *J* = 8.0 Hz, 2H), 1.94 – 1.85 (m, 2H), 1.84 – 1.75 (m, 2H), 1.64 – 1.54 (m, 2H), 1.54 – 1.45 (m, 2H), 1.28 – 1.24 (m, 4H), 1.18 (s, 12H), 1.17 (s, 12H), 0.66 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 82.9, 46.7, 45.6, 34.9, 32.4, 29.6, 26.2, 25.6, 25.0, 24.9, 24.6, 24.5. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{23}H_{43}NB_2O_4$ $[M]^+$ 433.3400 , found 433.3389.



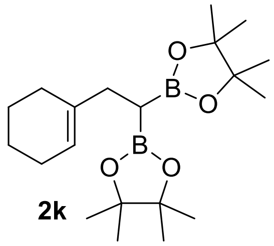
2i

ethyl 7,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (2i). Light yellow oil (160 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (q, *J* = 7.1 Hz, 2H), 2.24 (t, *J* = 7.9 Hz 2H), 1.62 – 1.47 (m, 4H), 1.30 – 1.24 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 3H, $COOCH_2CH_3$, the "CH_3" signals were partially overlappled by the intensive signal of four Me groups), 1.20 (s, 12H), 1.19 (s, 12H), 0.68 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 83.0, 60.2, 34.5, 32.2, 29.2, 25.6, 25.0, 24.9, 24.6, 14.4. ^{11}B NMR (192 MHz, EtOAc) δ 34.3. HRMS-EI (*m/z*): Calc. for $C_{20}H_{37}B_2O_6$ $[M^+- CH_3]$ 393.2849, found 393.2844.



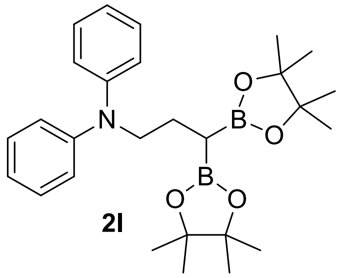
2j

2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2j). Colorless oil (185 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 1H), 7.18 – 7.12 (m, 2H), 2.59 (t, *J* = 7.0 Hz, 1H), 1.66 – 1.59 (m, 2H), 1.23 (s, 4H), 1.22 (s, 6H), 0.77 (t, *J* = 6.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 128.5, 128.3, 125.5, 83.1, 36.2, 34.5, 25.7, 25.0, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. These spectroscopic data correspond to reported data.[7]



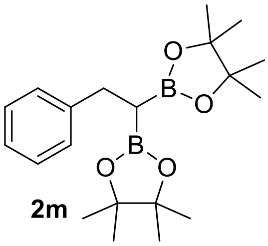
2k

2,2'-(2-(cyclohex-1-en-1-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2k). Colorless oil (99 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.35 (m, 1H), 2.15 (d, *J* = 8.2 Hz, 2H), 1.95 – 1.85 (m, 4H), 1.60 – 1.44 (m, 4H), 1.19 (s, 12H), 1.18 (s, 12H), 0.96 (t, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 119.6, 83.0, 33.4, 28.6, 25.3, 24.9, 24.6, 23.2, 22.8. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{20}H_{36}B_2O_4$ $[M]^+$ 360.2872, found 360.2870.



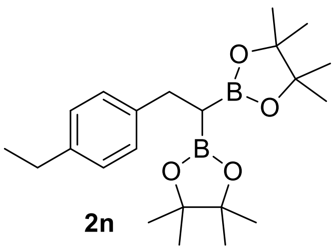
2l

N-(3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-N-phenylaniline (2l). White solid (108 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 4H), 7.13 – 7.03 (m, 4H), 6.96 – 6.84 (m, 2H), 3.65 (t, *J* = 8.0 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.24 (s, 12H), 1.23 (s, 12H), 0.68 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 129.2, 120.9, 120.8, 83.3, 54.8, 25.01, 24.7, 23.3. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{27}H_{39}NB_2O_4$ $[M]^+$ 461.3138, found 461.3136.



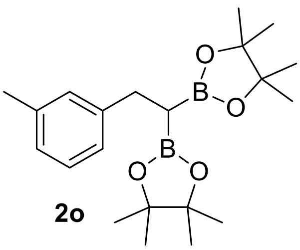
2m

2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2m). Colorless oil (155 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 4H), 7.15 – 7.09 (m, 1H), 2.89 (d, *J* = 8.4 Hz, 2H), 1.19 (s, 12H), 1.18 (s, 13H, $C(C\mathit{H}_3)_2$ and $CH_2\mathit{CH}$, the "CH" signals were overlappled by the intensive signal of four Me groups). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 128.4, 128.0, 125.4, 83.2, 31.4, 24.9, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.0. These spectroscopic data correspond to reported data.[9]



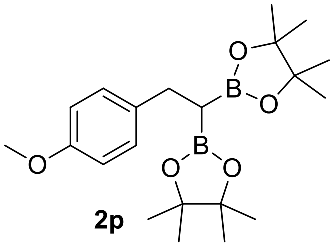
2n

2,2'-(2-(4-ethylphenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan e) (2n). Light yellow oil (182 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.85 (d, *J* = 8.3 Hz, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 8.0 Hz, 3H, $PhCH_2\mathit{CH}_3$, the "CH_3" signals were partially overlappled by the intensive signal of four Me groups), 1.18 (s, 12H), 1.17 (s, 12H), 1.15 (t, *J* = 8.4 Hz, 1H, $PhCH_2\mathit{CH}B_2$, the "CH" signals were partially overlappled by the intensive signal of four Me groups). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 141.2, 128.3, 127.5, 83.1, 31.0, 28.5, 24.9, 24.6, 15.9. ^{11}B NMR (192 MHz, EtOAc) δ 34.4. HRMS-EI (*m/z*): Calc. for $C_{22}H_{36}B_2O_4$ $[M]^+$ 384.2872 , found 384.2868.



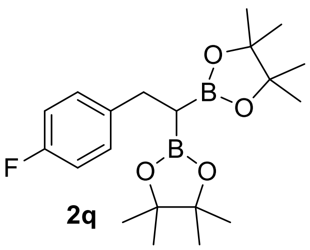
2o

2,2'-(2-(m-tolyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2o). Colorless oil (155 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.00 (m, 3H), 6.93 (d, J = 7.2 Hz, 1H), 2.84 (d, J = 8.3 Hz, 2H), 2.29 (s, 3H), 1.19 (s, 12H), 1.18 (s, 12H), 1.13 (t, J = 8.3 Hz,1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 137.4, 129.3, 128.0, 126.1, 125.4, 83.2, 31.3, 24.9, 24.6, 21.5. ^{11}B NMR (192 MHz, EtOAc) δ 34.3. HRMS-EI (m/z): Calc. for $C_{21}H_{34}B_2O_4$ $[M]^+$ 370.2716, found 370.2711.



2p

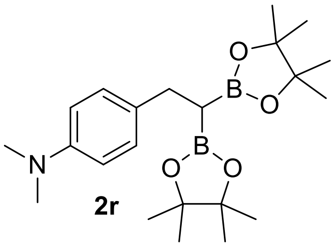
2,2'-(2-(4-methoxyphenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2p). Colorless oil (170 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 3.73 (s, 3H), 2.80 (d, J = 8.3 Hz, 2H), 1.16 (s, 12H), 1.15 (s, 12H), 1.11 (t, J = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 136.7, 129.2, 113.3, 83.1, 55.2, 30.4, 24.8, 24.5. ^{11}B NMR (192 MHz, EtOAc) δ 34.3. These spectroscopic data correspond to reported data.[9]



2q

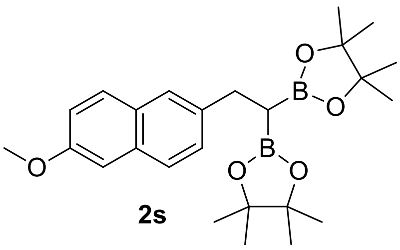
2,2'-(2-(4-fluorophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2q). White solid (147 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 2H), 6.89 (t, J = 8.6 Hz, 2H), 2.83 (d, J = 8.3 Hz, 2H), 1.17 (s, 12H), 1.16 (s, 12H), 1.12 (t, J = 8.0 Hz, 1H, $PhCH_2\mathit{CH}B_2$, the "CH" signals were partially overlappled by the intensive signal of four Me groups). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (s), 159.9 (s), 140.2(d, J = 3.1 Hz), 129.7 (d, J = 7.7 Hz), 114.7 (d, J = 20.9 Hz), 83.3 (s), 30.6 (s), 24.9 (s), 24.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.67. ^{11}B NMR (192

MHz, EtOAc) δ 34.9. HRMS-EI (*m/z*): Calc. for $C_{20}H_{31}FB_2O_4$ $[M]^+$ 374.2465, found 374.2469.



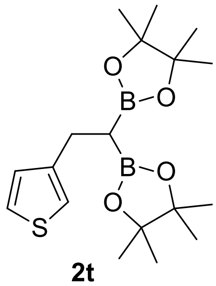
2r

4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-N,N-dimethylaniline (2r). Yellow solid (175 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 2.87 (s, 6H), 2.80 (d, *J* = 8.3 Hz, 2H), 1.19 (s, 12H), 1.18 (s, 12H), 1.12 (t, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 133.3, 128.9, 113.2, 83.1, 41.3, 30.4, 24.9, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.1. HRMS-EI (*m/z*): Calc. for $C_{22}H_{37}NB_2O_4$ $[M]^+$ 399.2981, found 399.2987.



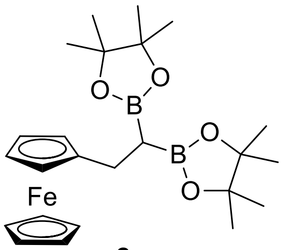
2s

2,2'-(2-(6-methoxynaphthalen-2-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2s). White solid (173 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.12 – 7.06 (m, 2H), 3.89 (s, 3H), 3.02 (d, *J* = 8.2 Hz, 2H), 1.17 (s, 25H, $C(CH_3)_2$ and CH_2CH, the "CH" signals were overlappled by the intensive signal of four Me groups). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 139.9, 132.9, 129.1, 129.0, 128.2, 126.5, 126.0, 118.4, 105.7, 83.2, 55.3, 31.4, 24.9, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{25}H_{36}B_2O_5$ $[M]^+$ 436.2822, found 399.2987.



2t

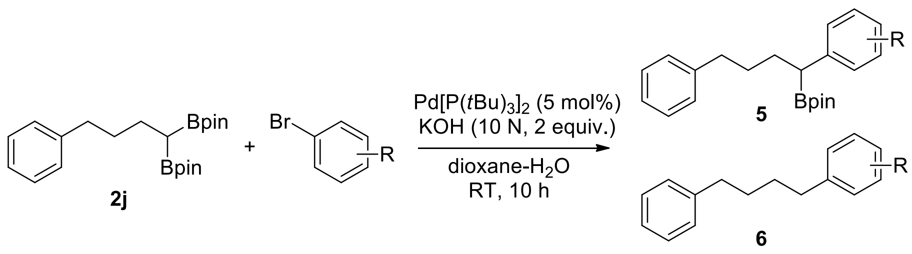
2,2'-(2-(thiophen-3-yl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2t). White solid (132 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 1H), 6.97 – 6.93 (m, 2H), 2.88 (d, J = 8.3 Hz, 2H), 1.19 (s, 12H), 1.17 (s, 13H, $C(CH_3)_2$ and CH_2CH, the "CH" signals were overlappled by the intensive signal of four Me groups). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 128.6, 124.8, 119.8, 83.2, 26.1, 24.9, 24.6. ^{11}B NMR (192 MHz, EtOAc) δ 34.2. HRMS-EI (*m/z*): Calc. for $C_{18}H_{30}B_2O_4$ $[M]^+$ 362.2124, found 362.2129.



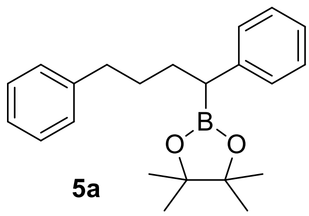
2u

2,2'-(2-ferrocenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2u). Brown solid (168 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 – 4.06 (m, 7H), 3.97 – 3.95 (m, 2H), 2.59 (d, J = 7.8 Hz, 21H), 1.21 (s, 24H), 0.98 (t, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 91.8, 83.2, 68.5, 68.4, 66.9, 25.6, 24.9, 24.8. ^{11}B NMR (192 MHz, EtOAc) δ 34.0. HRMS-EI (*m/z*): Calc. for $C_{24}H_{36}B_2O_4Fe$ $[M]^+$ 462.2268, found 462.2260.

5. General procedure for coupling reactions of 1,1-diboronate 2j with aryl bromides

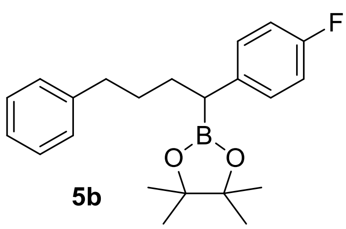


To a solution of 1,1-diborylalkane **2j** (0.2 mmol, 1.1 equiv), aryl bormide (0.2 mmol), and Pd[P(*t*Bu)$_3$]$_2$ (5 mol %) in dioxane 1 mL was added 10 N KOH aq. (0.4 mmol, 40 μL) at room temperature. The mixture was stirred at room temperature for 10 h and filtered through a pad of silica gel with ether. Concentration gave the residue which was purified by silica gel column chromatography (1% EtOAc in petroleum ether) to gave the product **5** or the protodeborylation product **6**.



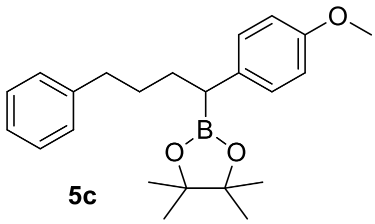
5a

2-(1,4-diphenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a). Colorless oil (152 mg, 90%, his case was carried out in 0.5 mmol scale). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 – 7.18 (m, 6H), 7.17 – 7.09 (m, 4H), 2.67 – 2.51 (m, 2H), 2.33 (t, *J* = 7.8 Hz, 1H), 1.91 (dt, *J* = 14.6, 7.8 Hz, 1H), 1.77 – 1.66 (m, 1H), 1.60 (dt, *J* = 11.3, 5.6 Hz, 2H), 1.20 (s, 6H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.3, 142.8, 128.5, 128.4, 128.3, 125.7, 125.3, 83.4, 36.1, 32.4, 31.2, 24.8, 24.7. HRMS-EI (*m/z*): Calc. for $C_{22}H_{29}BO_2$ [M]$^+$ 335.2297 , found 335.2291.



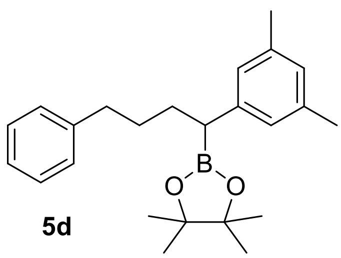
5b

2-(1-(4-fluorophenyl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b). Colorless oil (61 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.13 (m, 5H), 6.99 – 6.91 (m, 2H), 2.71 – 2.54 (m, 2H), 2.33 (t, *J* = 7.8 Hz, 1H), 1.96 – 1.83 (m, 1H), 1.78 – 1.66 (m, 1H), 1.66 – 1.55 (m, 2H), 1.22 (s, 6H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 159.8, 142.7, 138.8 (d, *J* = 3.1 Hz), 129.7 (d, *J* = 7.6 Hz), 128.4 (d, *J* = 11.3 Hz), 125.7, 115.2, 114.9, 83.5, 36.0, 32.5, 31.1, 24.8, 24.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.73 (m). HRMS-EI (*m/z*): Calc. for $C_{22}H_{28}BO_2F$ $[M]^+$ 353.2203, found 353.2207.



5c

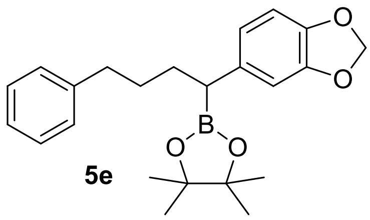
2-(1-(4-methoxyphenyl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c). Colorless oil (67 mg, 91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.0, 6.8 Hz, 2H), 7.20 – 7.10 (m, 5H), 6.84 – 6.80 (m, 2H), 3.79 (s, 3H), 2.71 – 2.54 (m, 2H), 2.30 (t, *J* = 7.7 Hz, 1H), 1.95 – 1.83 (m, 1H), 1.71 (dt, *J* = 12.6, 6.4 Hz, 1H), 1.66 – 1.56 (m, 2H), 1.23 (s, 6H), 1.20 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 142.8, 135.3, 129.3, 128.5, 128.3, 125.6, 113.8, 83.4, 55.3, 36.1, 32.7, 31.2, 24.8, 24.7.These spectroscopic data correspond to reported data.[7]



5d

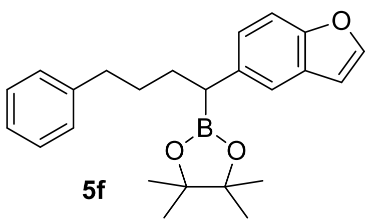
2-(1-(3,5-dimethylphenyl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d). Colorless oil (65 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 6.86 – 6.72 (m, 3H), 2.69 – 2.52 (m, 2H), 2.29 – 2.21 (m, 7H, Ph(CH_3)$_2$ and Ph*CH*B-, the "CH" signals were overlappled by the intensive signal of two Me groups of the phenyl ring), 1.92 – 1.81 (m, 1H), 1.73 – 1.55 (m, 3H), 1.20

(s, 6H), 1.18 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.9, 137.6, 128.5, 128.3, 127.0, 126.3, 125.6, 83.3, 36.1, 32.6, 31.3, 24.7, 21.5. HRMS-EI (*m/z*): Calc. for $C_{24}H_{33}BO_2$ $[M]^+$ 363.2610 , found 363.2614.



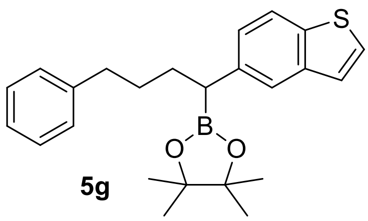
5e

2-(1-(benzo[d][1,3]dioxol-5-yl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e). Colorless oil (65 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.11 (m, 5H), 6.75 – 6.60 (m, 3H), 5.89 (s, 2H), 2.70 – 2.48 (m, 2H), 2.24 (t, *J* = 7.7 Hz, 1H), 1.92 – 1.78 (m, 1H), 1.70 – 1.51 (m, 3H), 1.20 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.2, 142.8, 137.1, 128.5, 128.3, 125.7, 121.3, 108.9, 108.2, 100.7, 83.4, 36.1, 32.7, 31.1, 24.8, 24.7. HRMS-EI (*m/z*): Calc. for $C_{23}H_{29}BO_4$ $[M]^+$ 379.2195, found 375.2191.



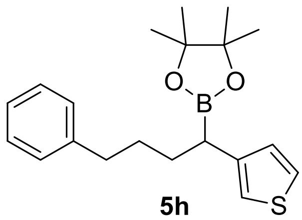
5f

2-(1-(benzofuran-5-yl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f). Colorless oil (67 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 1.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.19 – 7.12 (m, 4H), 6.71 (d, *J* = 1.5 Hz, 1H), 2.72 – 2.55 (m, 2H), 2.45 (t, *J* = 7.9 Hz, 1H), 1.97 (dt, *J* = 13.9, 7.7 Hz, 1H), 1.83 – 1.71 (m, 1H), 1.68 – 1.58 (m, 2H), 1.23 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 144.9, 142.8, 137.6, 128.5, 128.3, 127.6, 125.7, 125.0, 120.5, 111.0, 106.6, 83.4, 36.1, 32.9, 31.2, 24.8, 24.7. HRMS-EI (*m/z*): Calc. for $C_{24}H_{29}BO_3$ $[M]^+$ 375.2246, found 375.2243.



5g

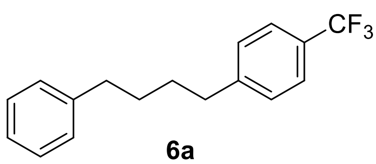
2-(1-(benzo[b]thiophen-5-yl)-4-phenylbutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g). White solid (158 mg, 86%; this case was carried out in 0.47 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 1H), 7.66 (s, 1H), 7.38 (d, *J* = 5.4 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 3H), 2.72 – 2.55 (m, 2H), 2.47 (t, *J* = 7.8 Hz, 1H), 1.99 (dt, *J* = 14.2, 7.7 Hz, 1H), 1.80 (dt, *J* = 15.4, 8.0 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.22 (d, *J* = 5.3 Hz, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 140.1, 139.4, 136.9, 128.5, 128.3, 126.2, 125.7, 125.5, 123.9, 123.1, 122.3, 83.4, 36.1, 32.7, 31.2, 24.8, 24.7. HRMS-EI (*m/z*): Calc. for $C_{24}H_{29}BO_2S$ $[M]^+$ 391.2018, found 391.2015.



5h

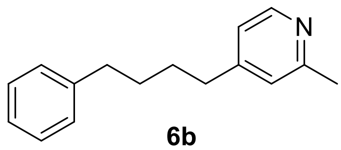
4,4,5,5-tetramethyl-2-(4-phenyl-1-(thiophen-3-yl)butyl)-1,3,2-dioxaborolane (5h). Colorless oil (38 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.20 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.18 – 7.13 (m, 3H), 6.95 (dd, *J* = 4.9, 1.2 Hz, 1H), 6.93 – 6.91 (m, 1H), 2.65 – 2.56 (m, 2H), 2.48 (t, *J* = 7.7 Hz, 1H), 1.91 – 1.81 (m, 1H), 1.76 – 1.66 (m, 1H), 1.65 – 1.57 (m, 2H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 142.7, 128.5, 128.4, 128.3, 125.7, 124.9, 119.5, 83.5, 36.0, 32.1, 31.2, 24.8, 24.7. HRMS-EI (*m/z*): Calc. for $C_{20}H_{27}BO_2S$ $[M]^+$ 341.1861, found 341.1858.

The protodeborylation product **6a** and **6b**



6a

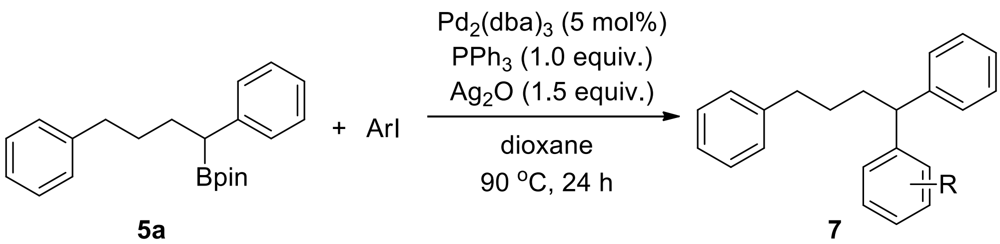
1-(4-phenylbutyl)-4-(trifluoromethyl)benzene (6a). Colorless oil (45 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.20 – 7.13 (m, 3H), 2.68 (t, *J* = 7.0 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 1.70 – 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7 (s), 142.4 (s), 128.8 (s), 128.5 (s), 128.4 (s), 125.9 (s), 125.3 (q, *J* = 3.8 Hz), 35.9 (s), 35.8 (s), 31.1 (s), 30.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3. HRMS-EI (*m/z*): Calc. for $C_{17}H_{17}F_3$ $[M]^+$ 278.1282, found 278.1279.



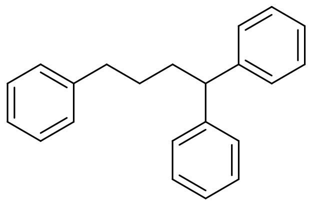
6b

2-methyl-4-(4-phenylbutyl)pyridine (6b). Pale yellow oil (40 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 5.1 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.94 (s, 1H), 6.88 (d, *J* = 5.0 Hz, 1H), 2.63 (t, *J* = 6.7 Hz, 2H), 2.57 (t, *J* = 6.7 Hz, 2H), 2.51 (s, 3H), 1.68 – 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 151.7, 148.9, 142.3, 128.5, 128.4, 125.8, 123.5, 121.1, 35.8, 35.1, 31.0, 29.9, 24.4. HRMS-EI (*m/z*): Calc. for $C_{16}H_{19}N$ $[M]^+$ 225.1517, found 225.1517.

6. General procedure for subsequential coupling reactions of 5a with aryl iodides

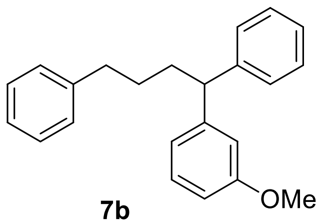


To a solution of **5a** (0.2 mmol), aryl iodide (0.24 mmol, 1.2 equiv.) in dioxane 1 mL was added sequentially $Pd_2(dba)_3$ (5 mol %), PPh_3 (0.2 mmol, 1.0 equiv.), and Ag_2O (0.3 mmol, 1.5 equiv.) at room temperature. The mixture was stirred at 90 °C for 24 h and filtered through a pad of silica gel with ether. Concentration gave the residue which was purified by silica gel column chromatography to gave the product **7**.



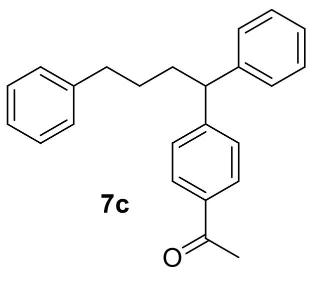
7a

butane-1,1,4-triyltribenzene (7a). Colorless oil (42 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.08 (m, 15H), 3.90 (t, *J* = 7.8 Hz, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.14 – 2.02 (m, 2H), 1.64 – 1.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 142.4, 128.5, 128.4, 127.9, 126.2, 125.8, 51.4, 35.9, 35.3, 29.9. HRMS-EI (*m/z*): Calc. for $C_{22}H_{22}$ $[M]^+$ 286.1722, found 286.1274.



7b

(1-(3-methoxyphenyl)butane-1,4-diyl)dibenzene (7b). Pale yellow oil (47 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.08 (m, 11H), 6.84 – 6.66 (m, 3H), 3.87 (t, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.11 – 2.01 (m, 2H), 1.64 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 146.8, 145.0, 142.4, 129.4, 128.5, 128.4, 127.9, 126.2, 125.8, 120.4, 114.1, 111.0, 55.2, 51.4, 35.9, 35.3, 29.9. HRMS-EI (*m/z*): Calc. for $C_{23}H_{24}O$ $[M]^+$ 316.1827, found 316.1825.



7c

1-(4-(1,4-diphenylbutyl)phenyl)ethanone (7c). Pale yellow oil (32 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.09 (m, 12H), 3.96 (t, *J* = 7.8 Hz, 1H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.55 (s, 3H), 2.16 – 2.05 (m, 2H), 1.65 – 1.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 150.8, 144.1, 142.2, 135.3, 128.8, 128.7, 128.5, 128.4, 128.2, 127.9, 126.5, 125.9, 51.4, 35.9, 35.0, 29.8, 26.7. HRMS-EI (*m/z*): Calc. for $C_{24}H_{24}O$ $[M]^+$ 328.1827, found 328.1830.

6. **References**

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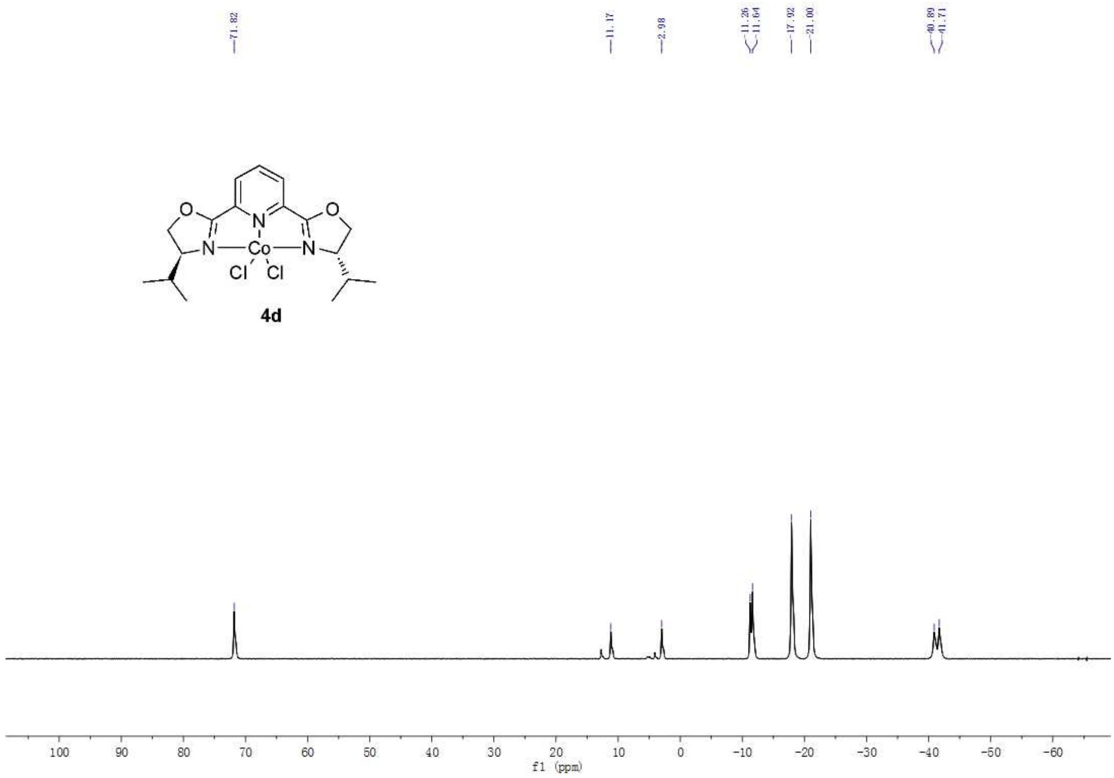
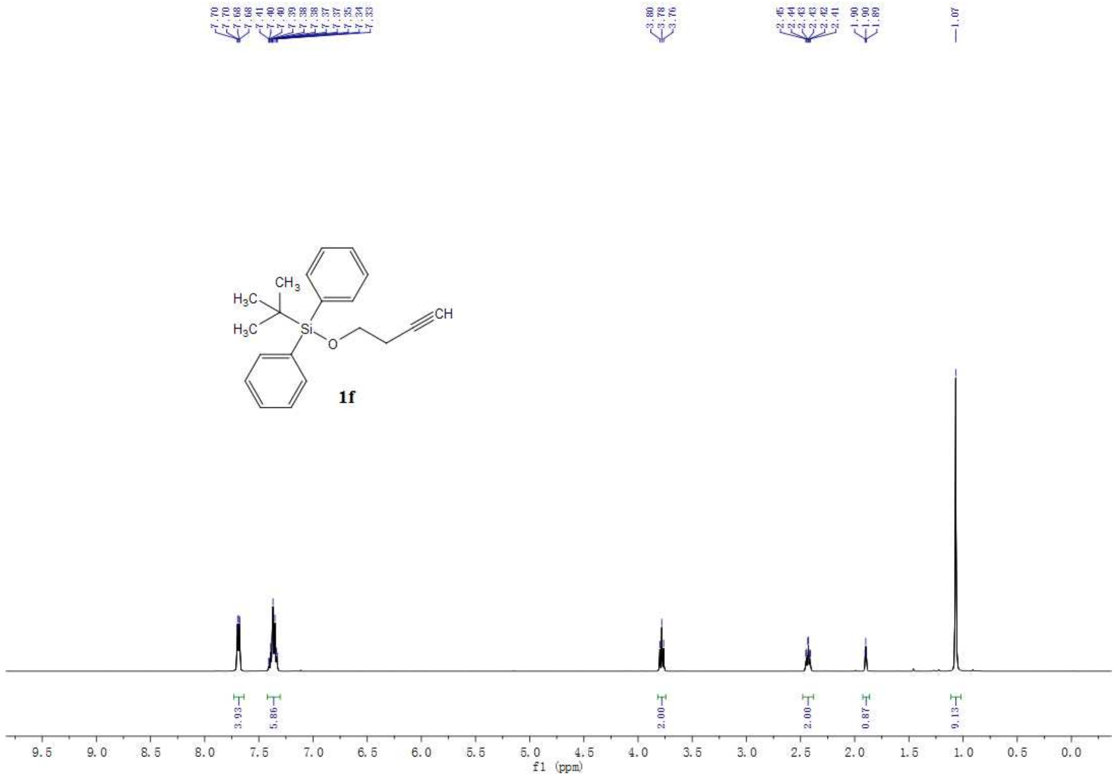
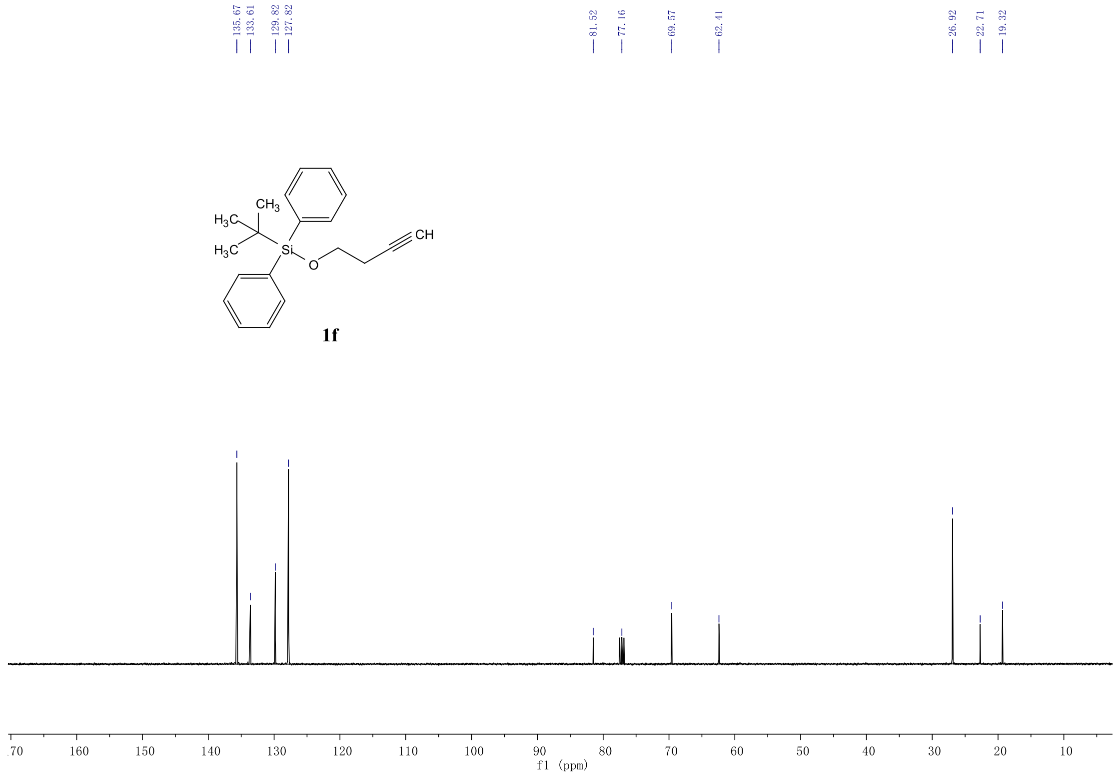
7. NMR Spectra



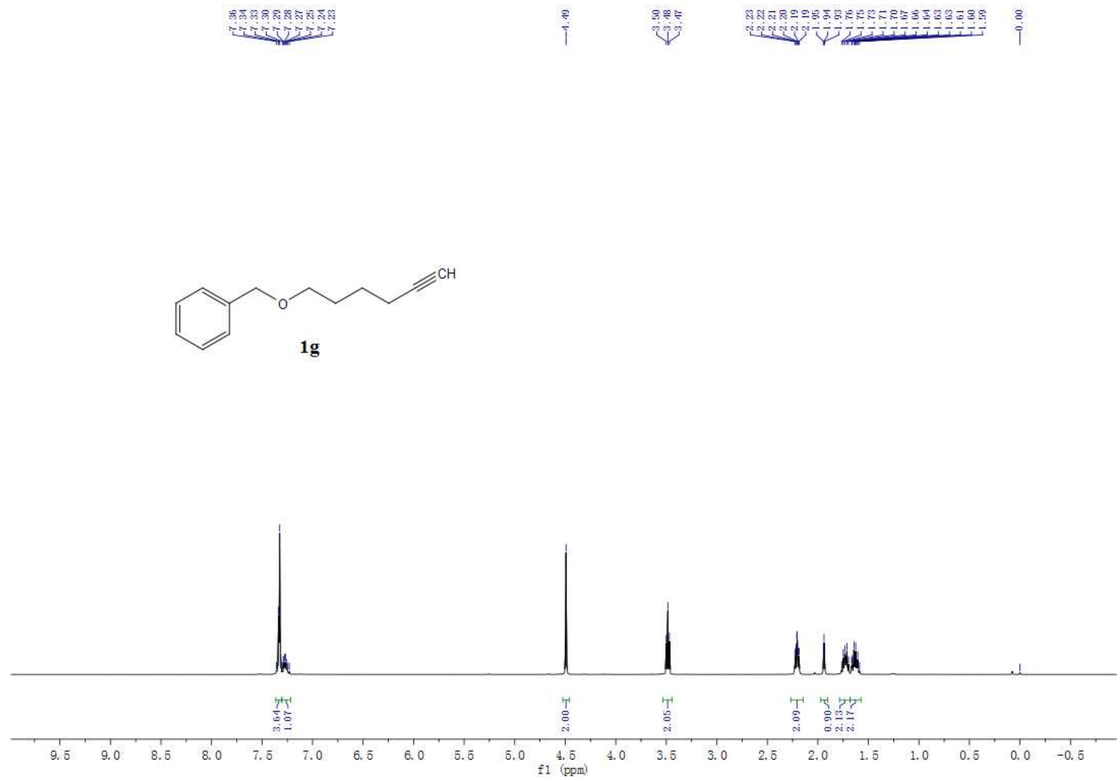
[1]H NMR (400 M, $CDCl_3$) spectrum of **4d**



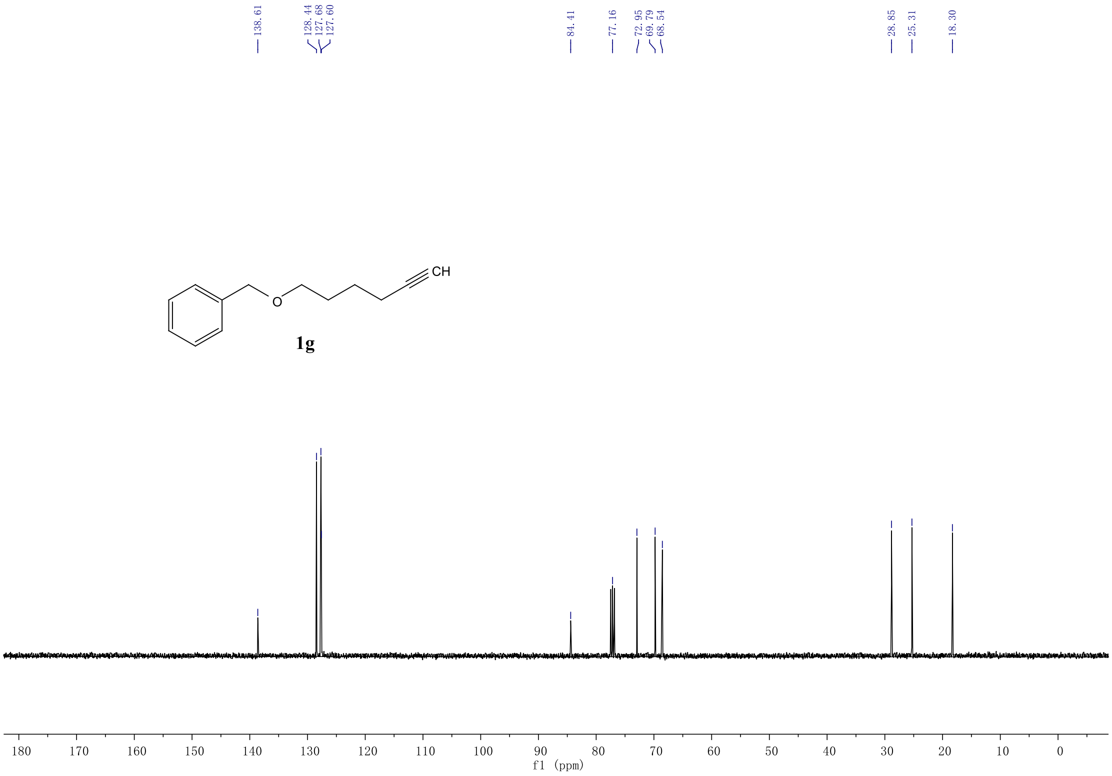
[1]H NMR (400 M, $CDCl_3$) spectrum of **1f**



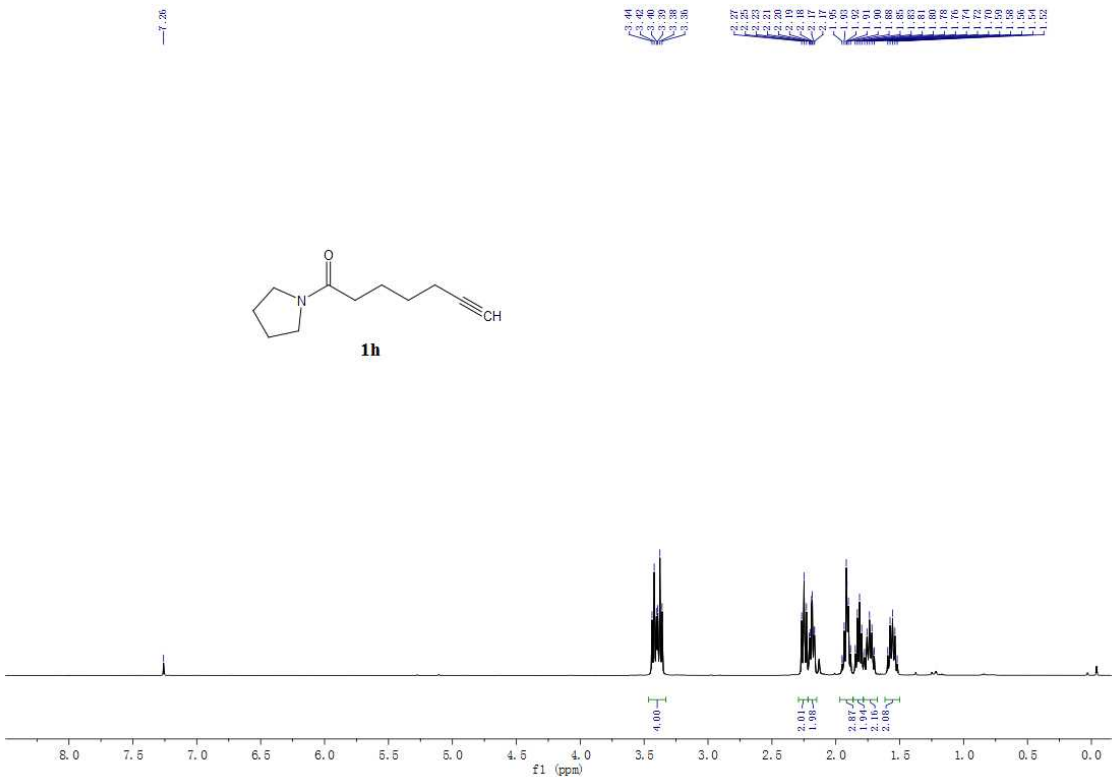
^{13}C NMR (101 M, $CDCl_3$) spectrum of **1f**



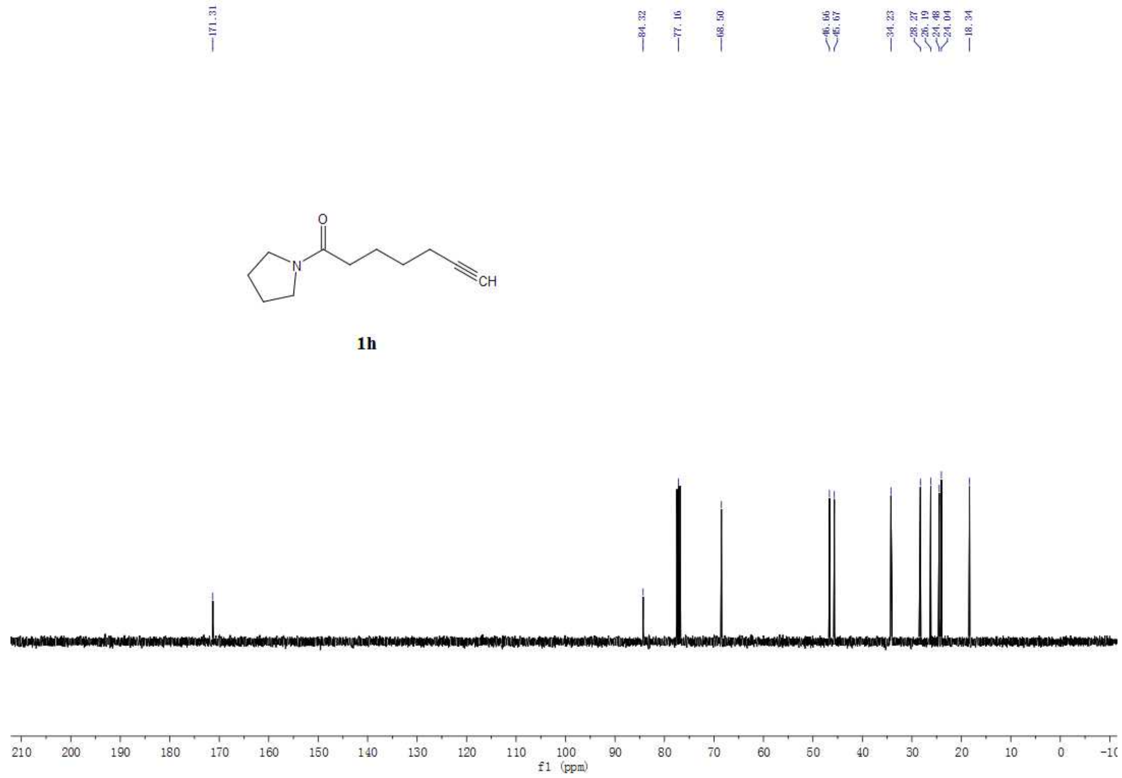
^{1}H NMR (400 M, $CDCl_3$) spectrum of **1g**



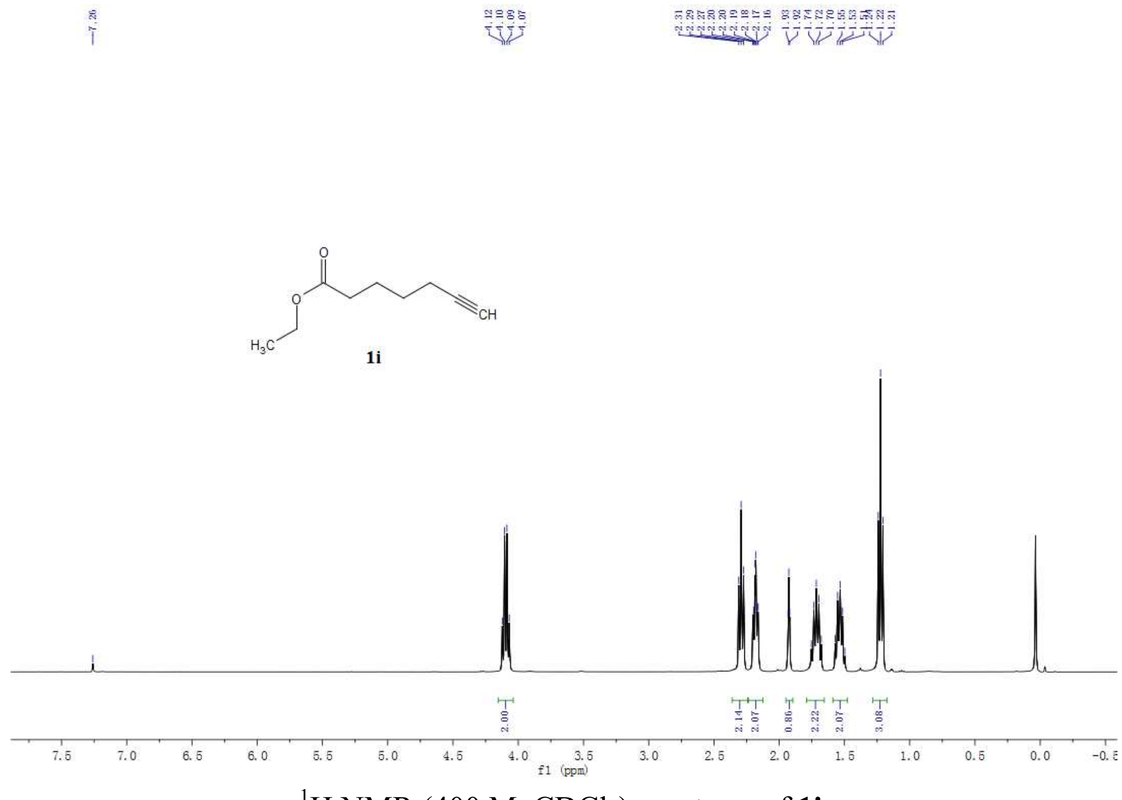
^{13}C NMR (101 M, $CDCl_3$) spectrum of **1g**



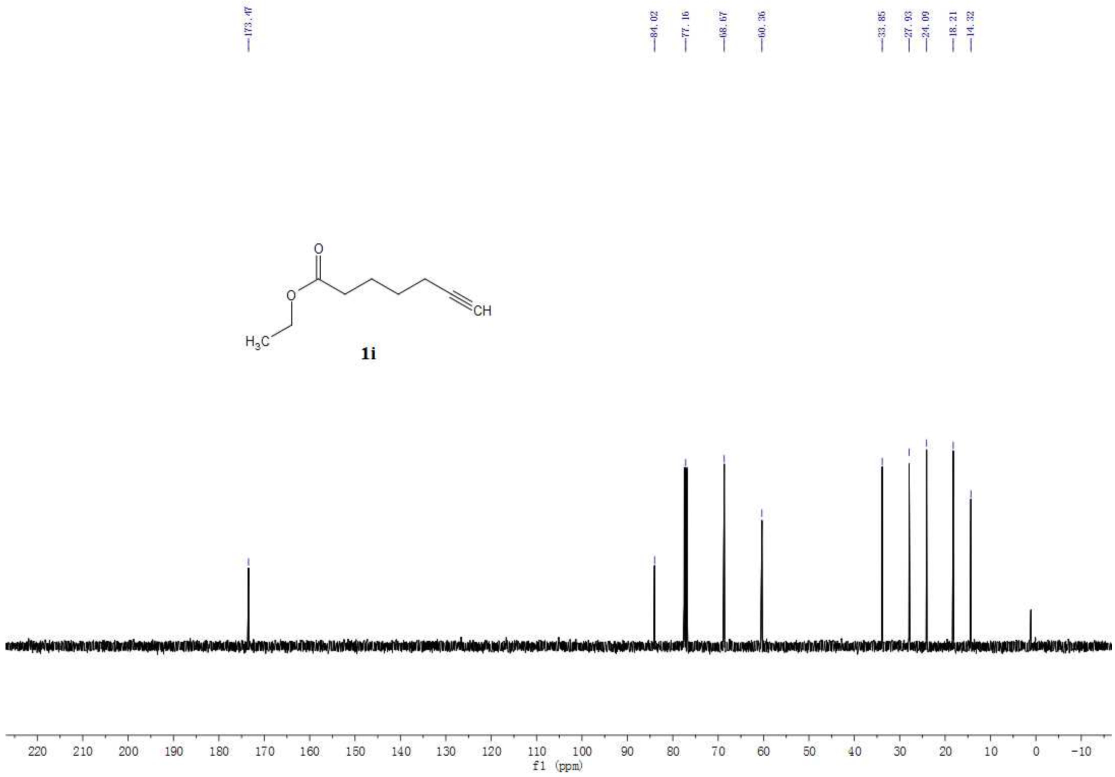
^{1}H NMR (400 M, $CDCl_3$) spectrum of **1h**



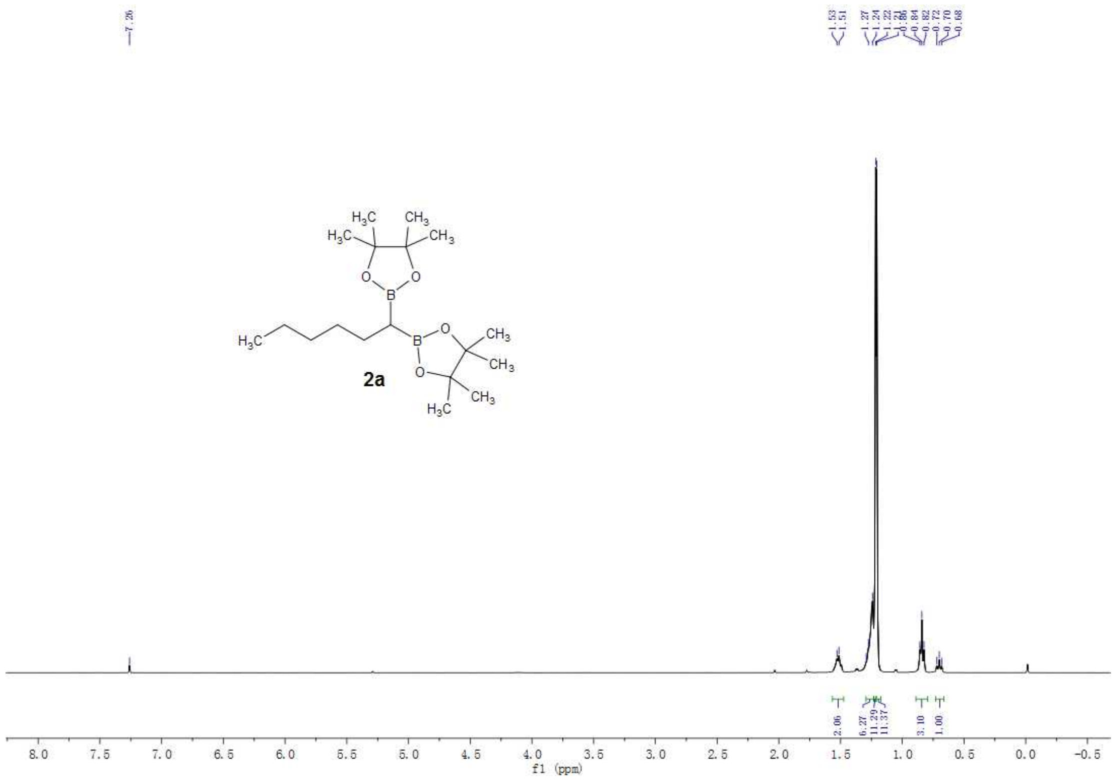
^{13}C NMR (101 M, $CDCl_3$) spectrum of **1h**



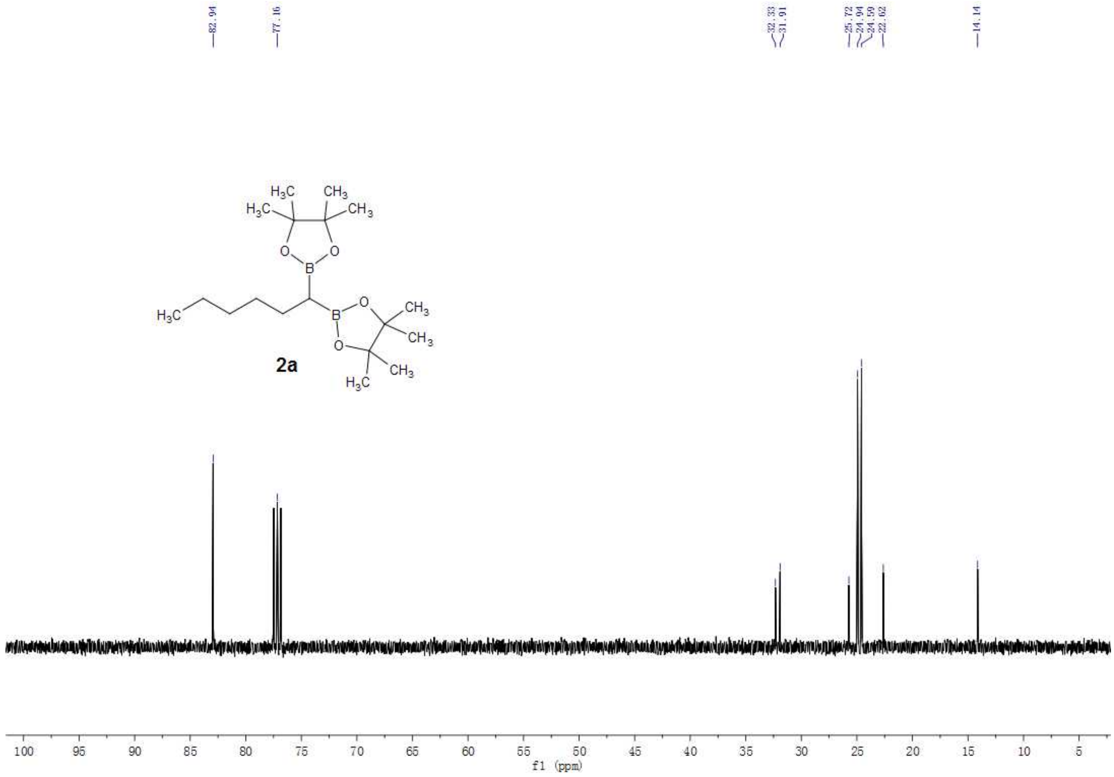
^{1}H NMR (400 M, $CDCl_3$) spectrum of **1i**



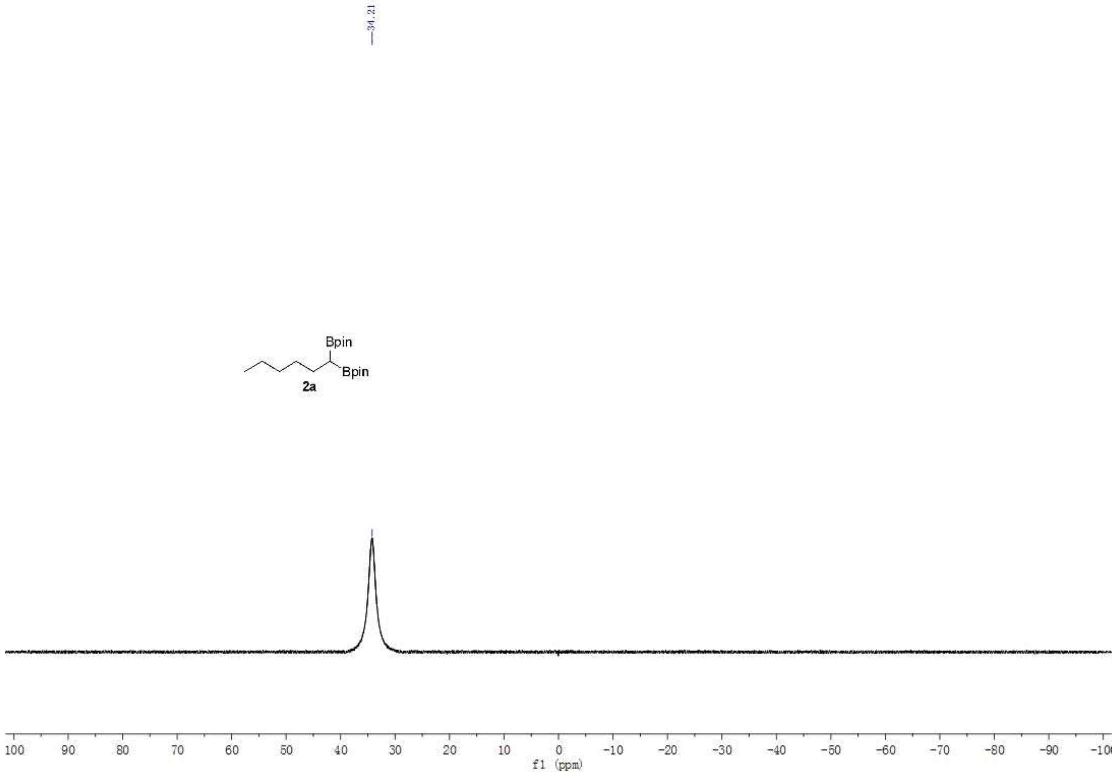
^{13}C NMR (101 M, $CDCl_3$) spectrum of **1i**



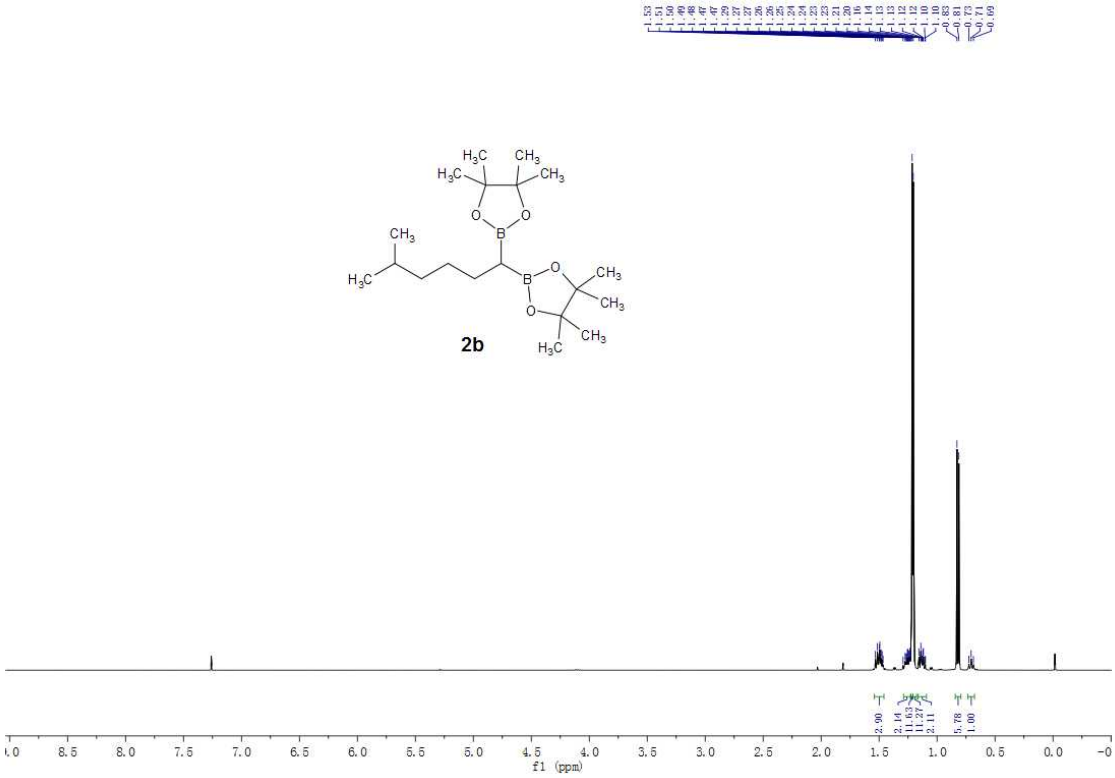
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2a**



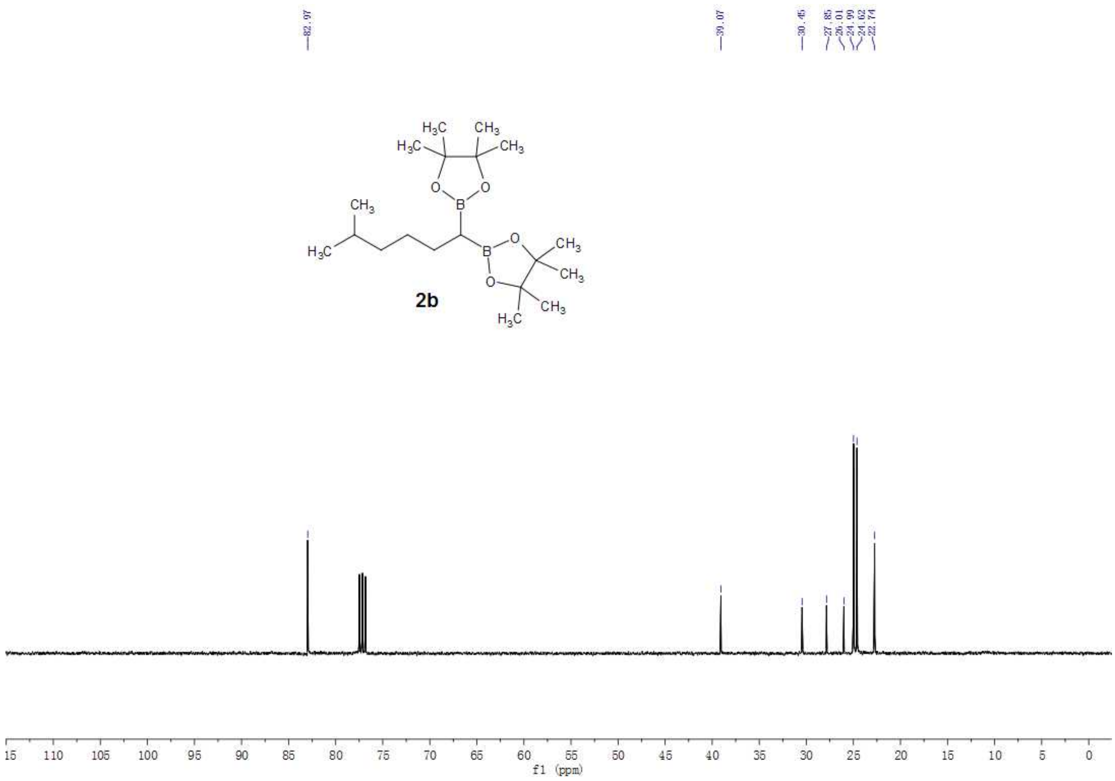
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2a**



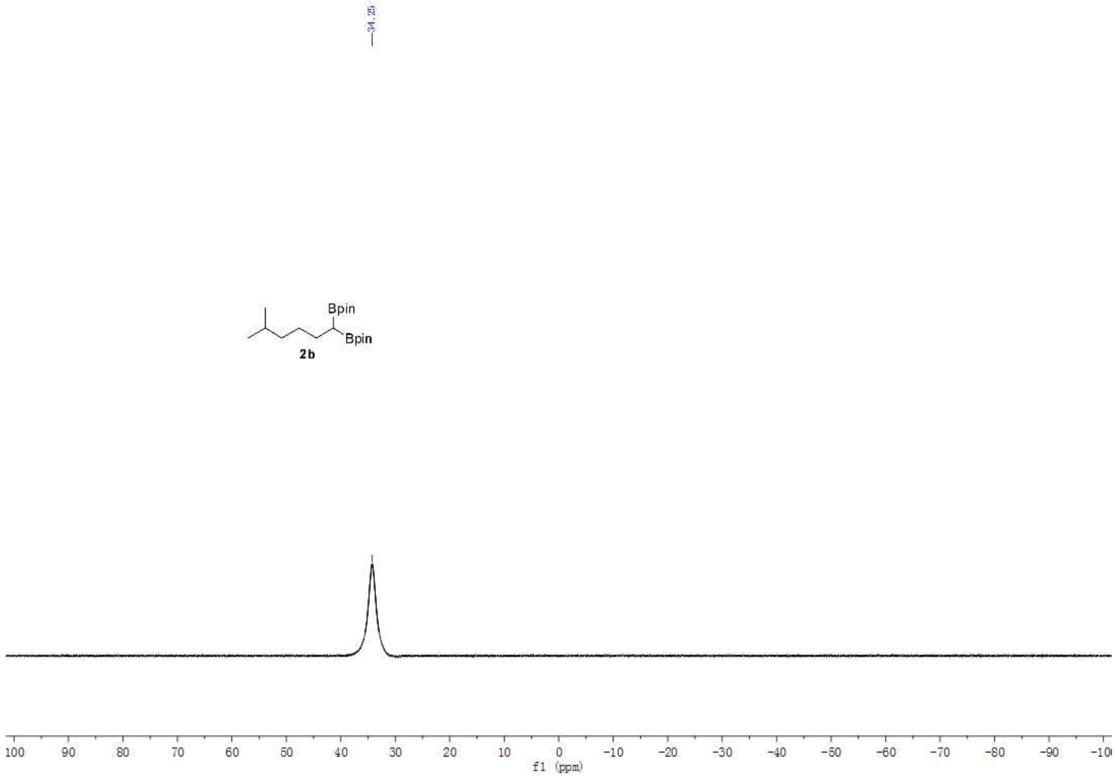
^{11}B NMR (192 MHz, EtOAc) spectrum of **2a**



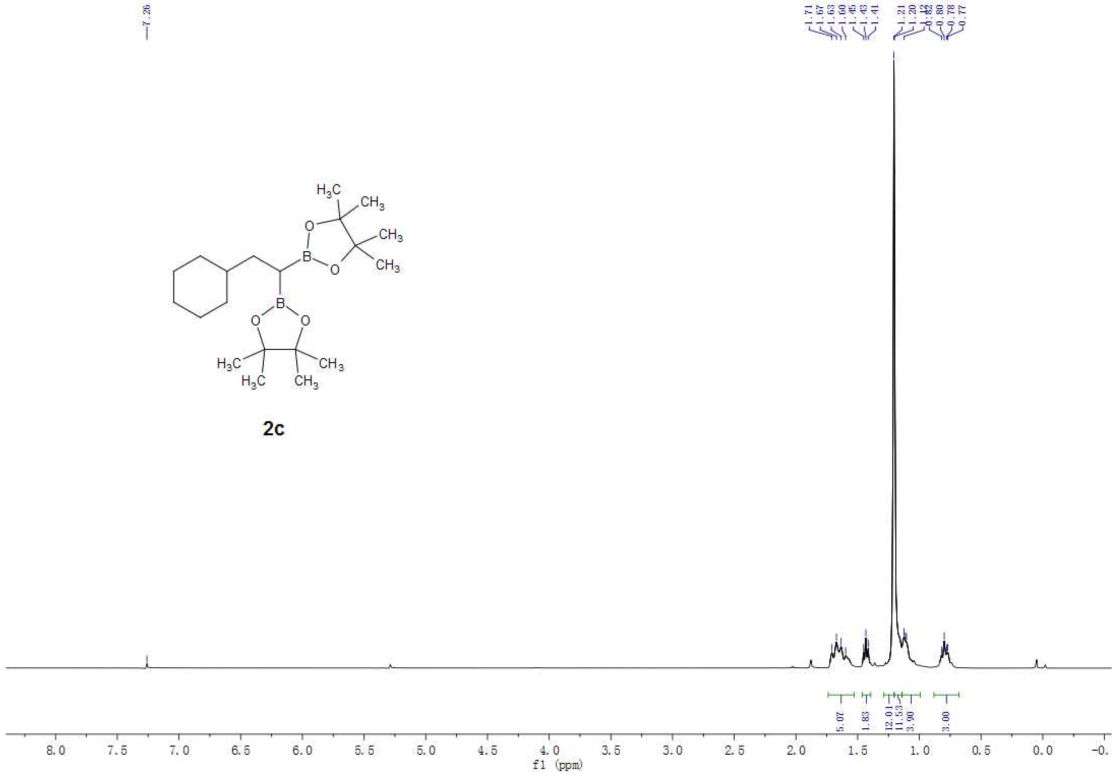
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2b**



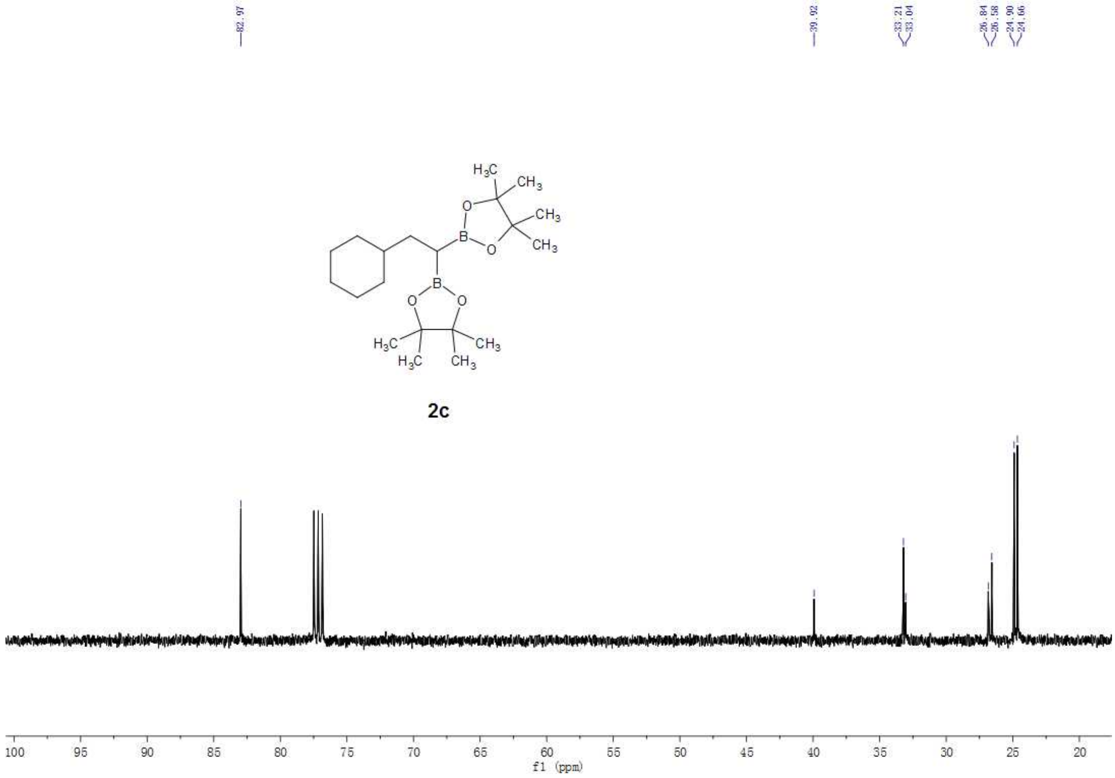
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2b**



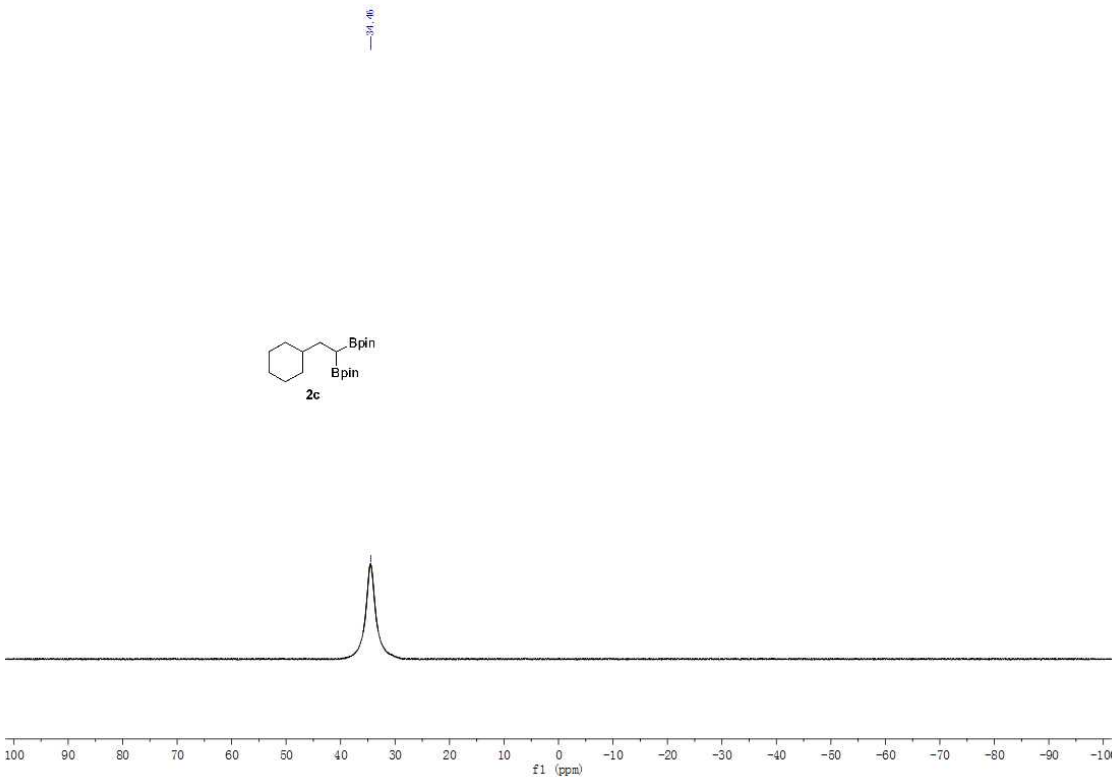
^{11}B NMR (192 MHz, EtOAc) spectrum of **2b**



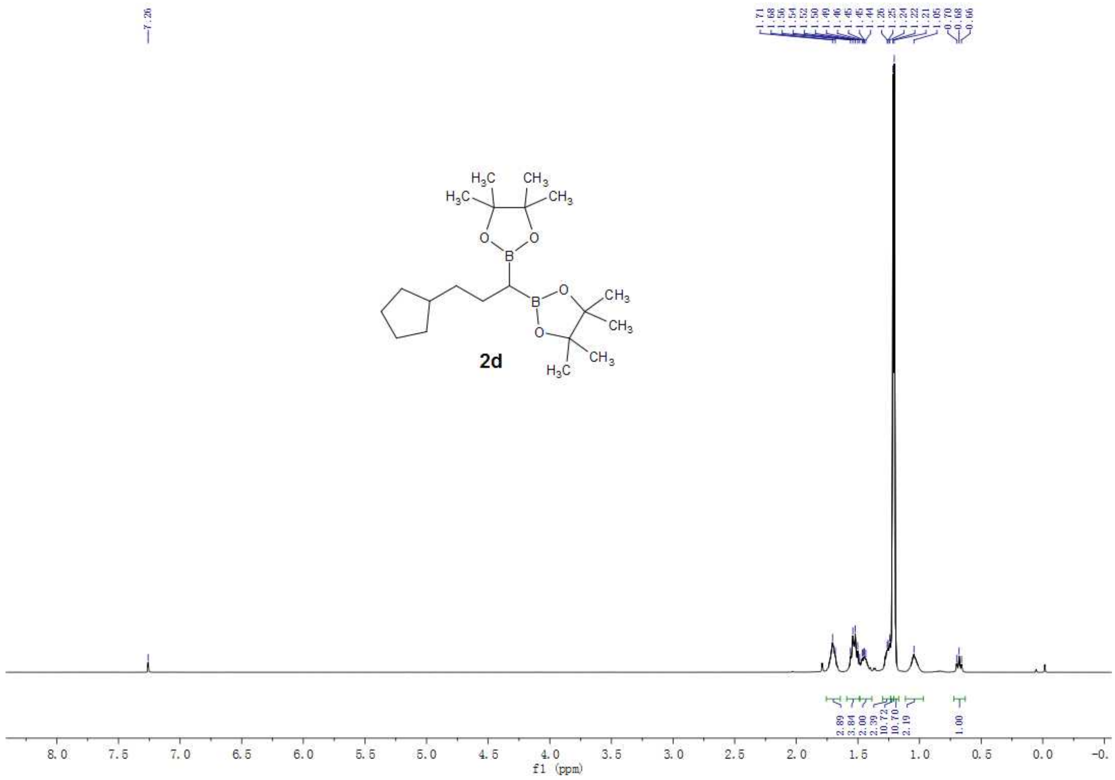
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2c**



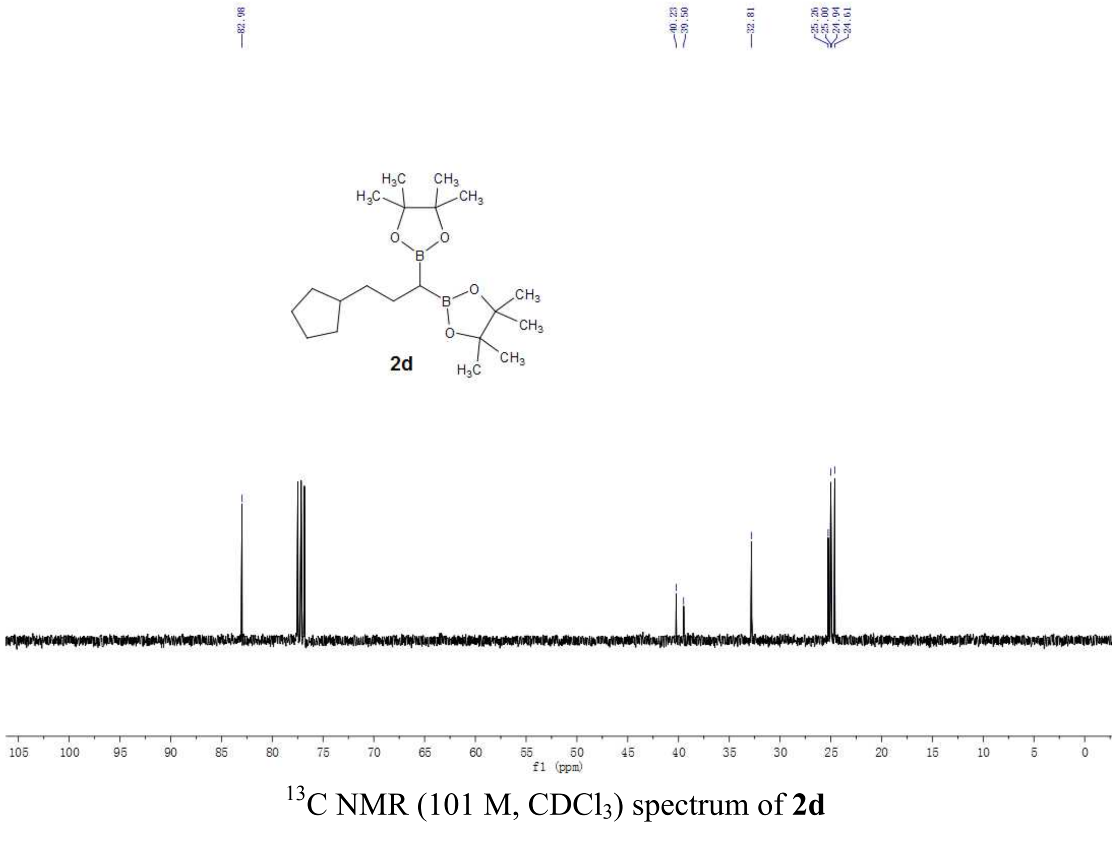
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2c**



^{11}B NMR (192 MHz, EtOAc) spectrum of **2c**



^{1}H NMR (400 M, $CDCl_3$) spectrum of **2d**



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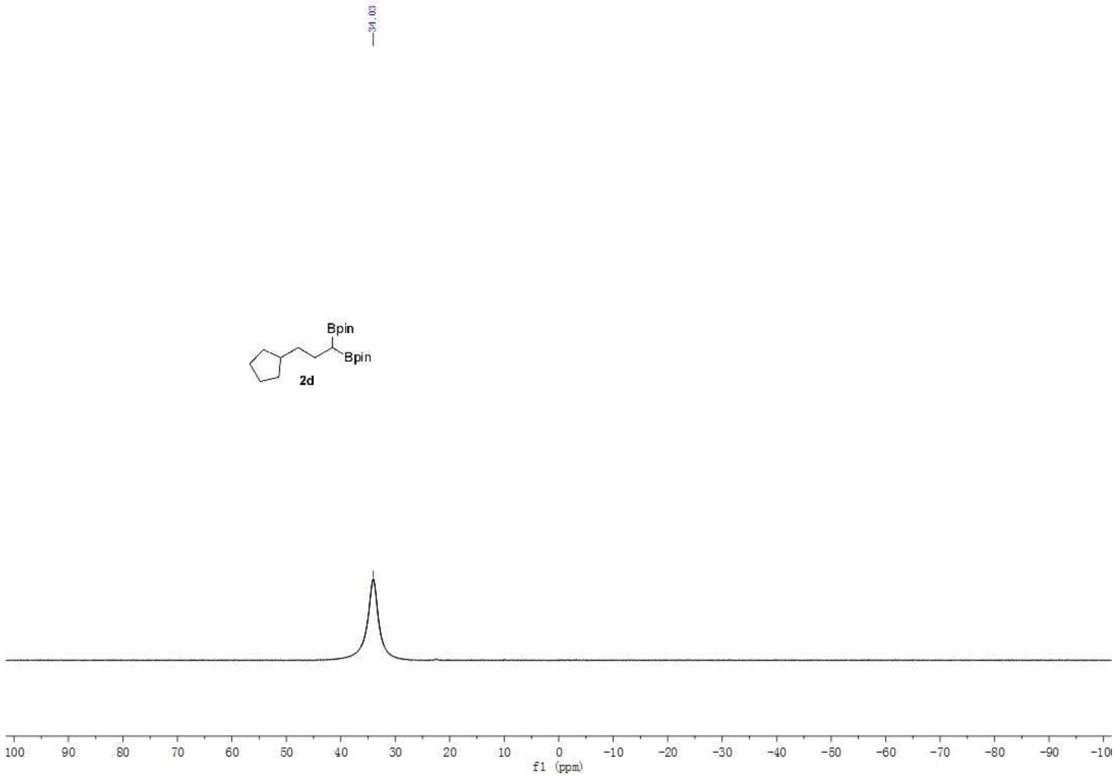
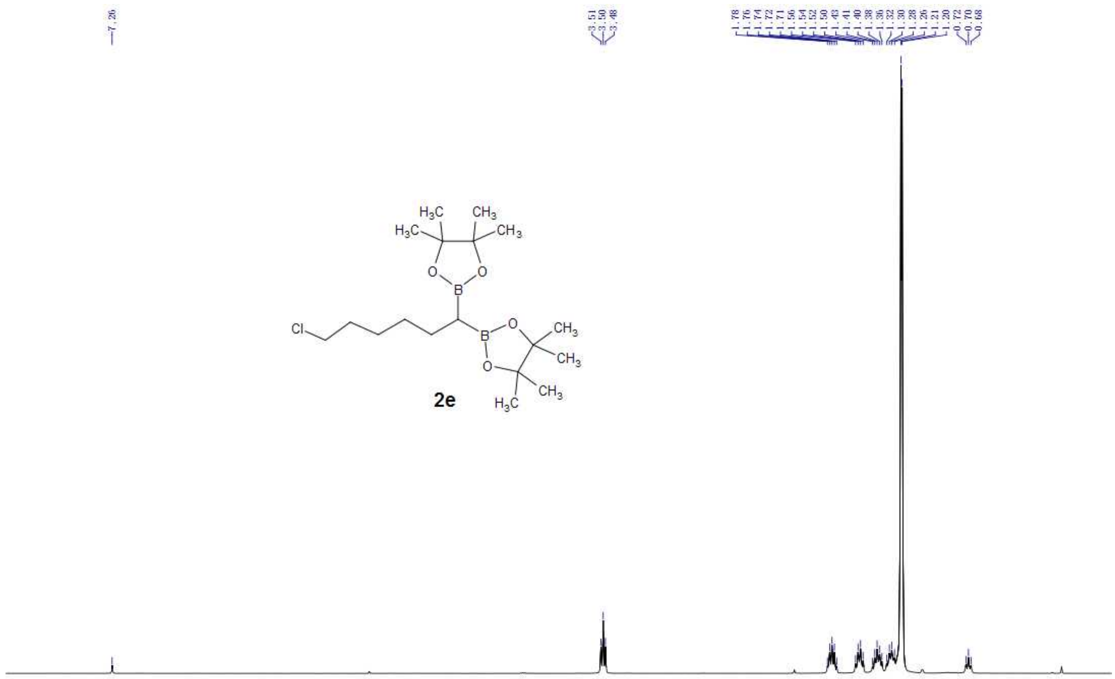
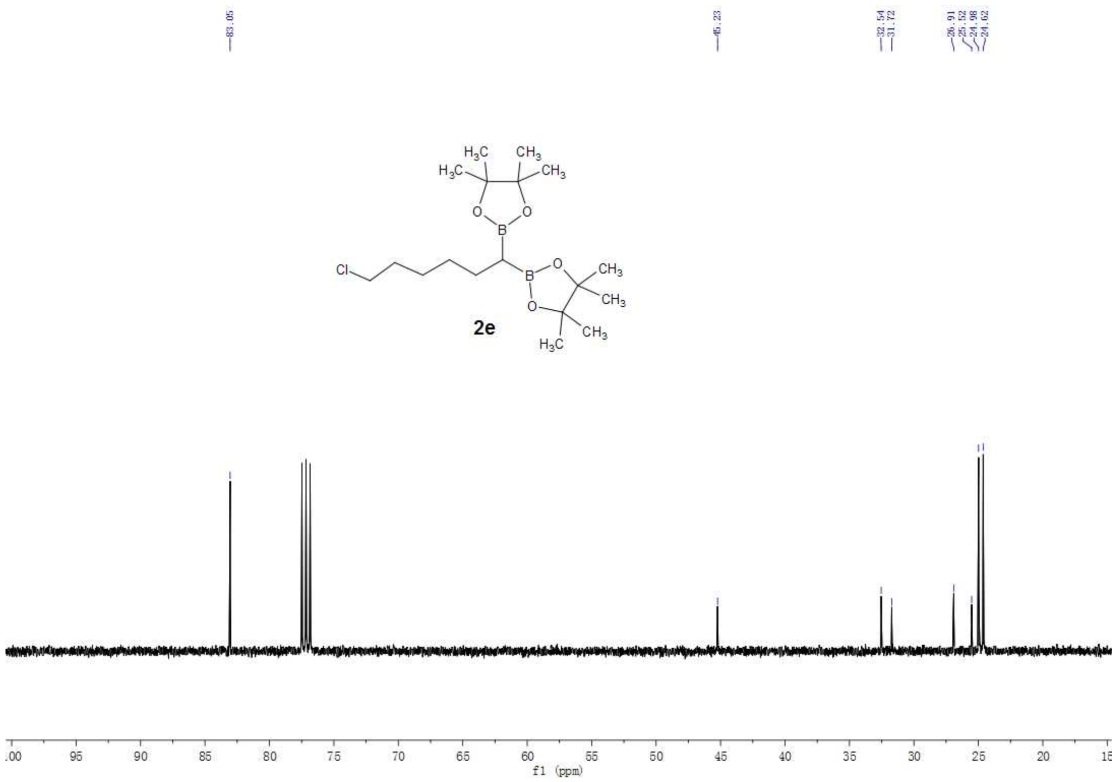


^{11}B NMR (192 MHz, EtOAc) spectrum of **2d**



^{1}H NMR (400 M, $CDCl_3$) spectrum of **2e**



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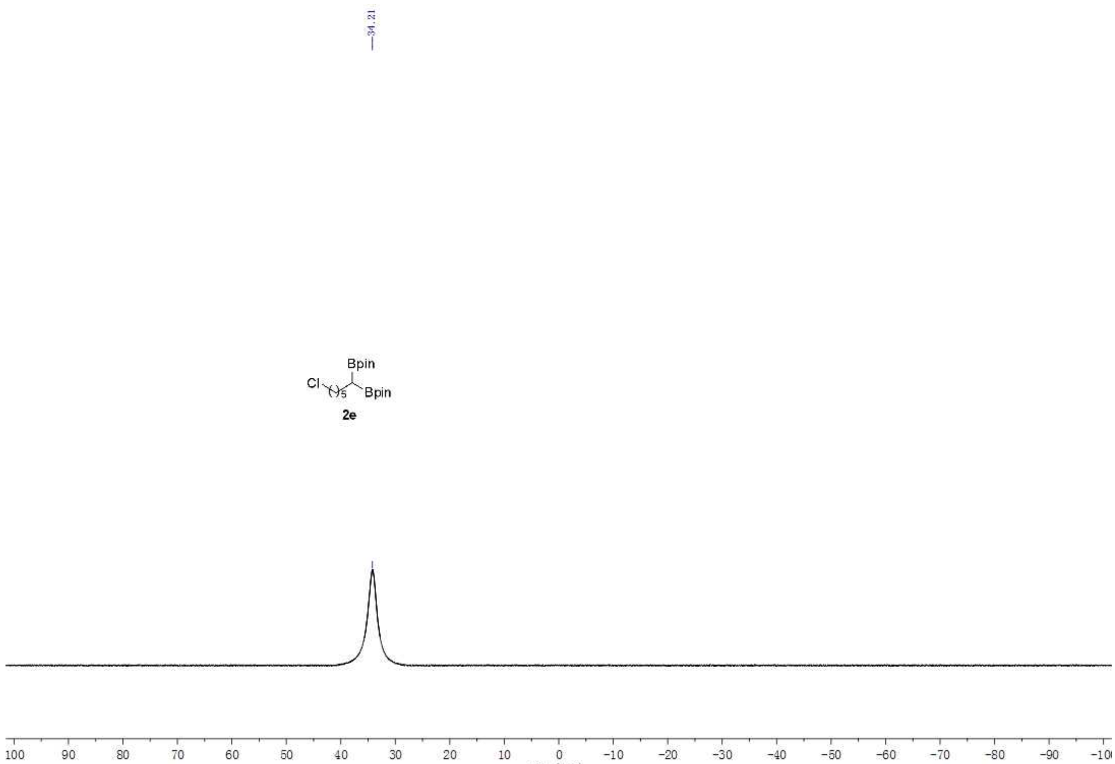

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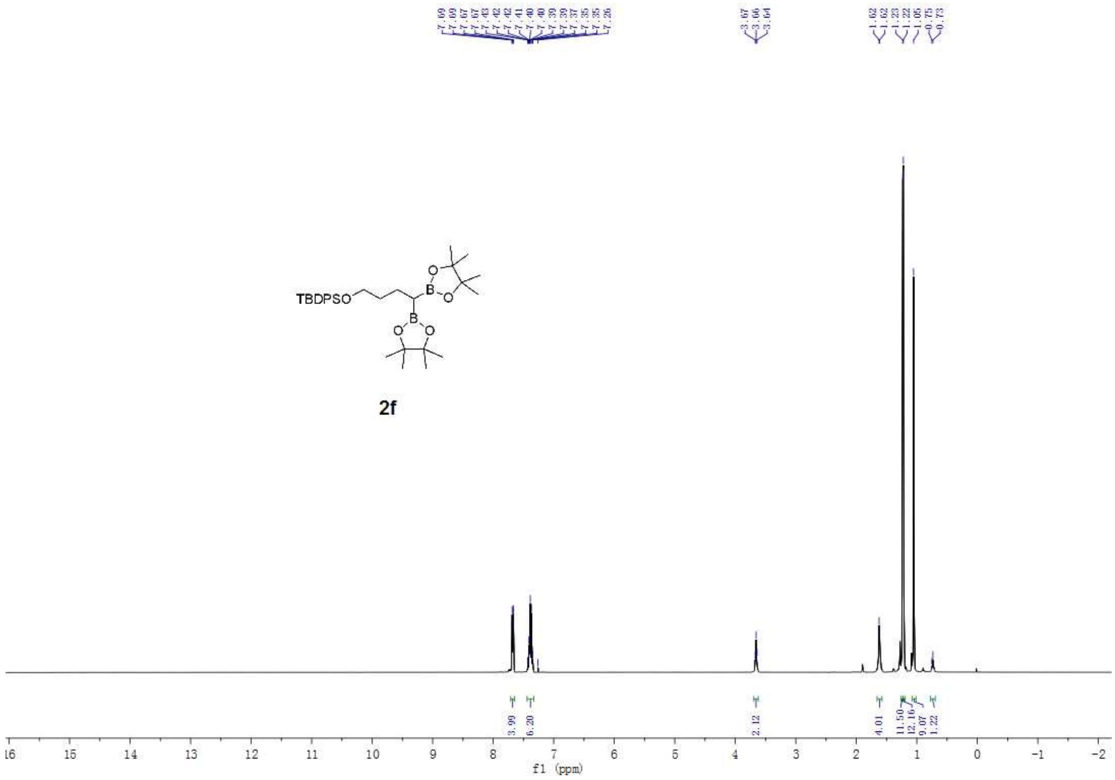

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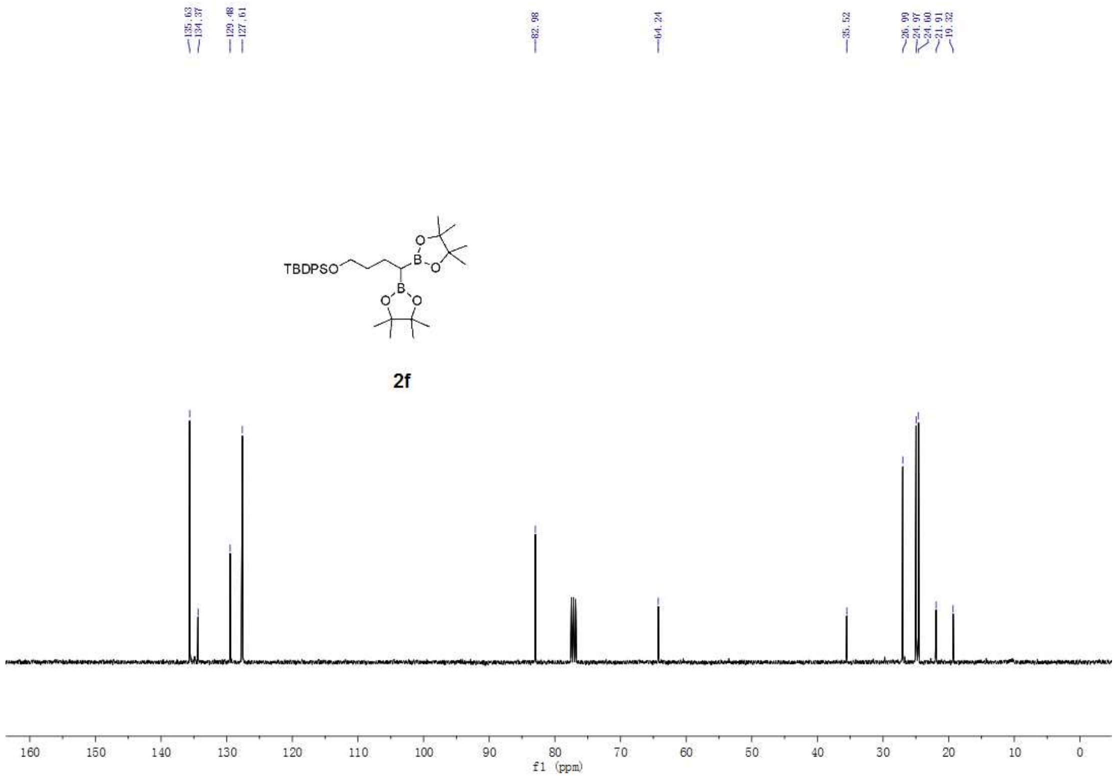

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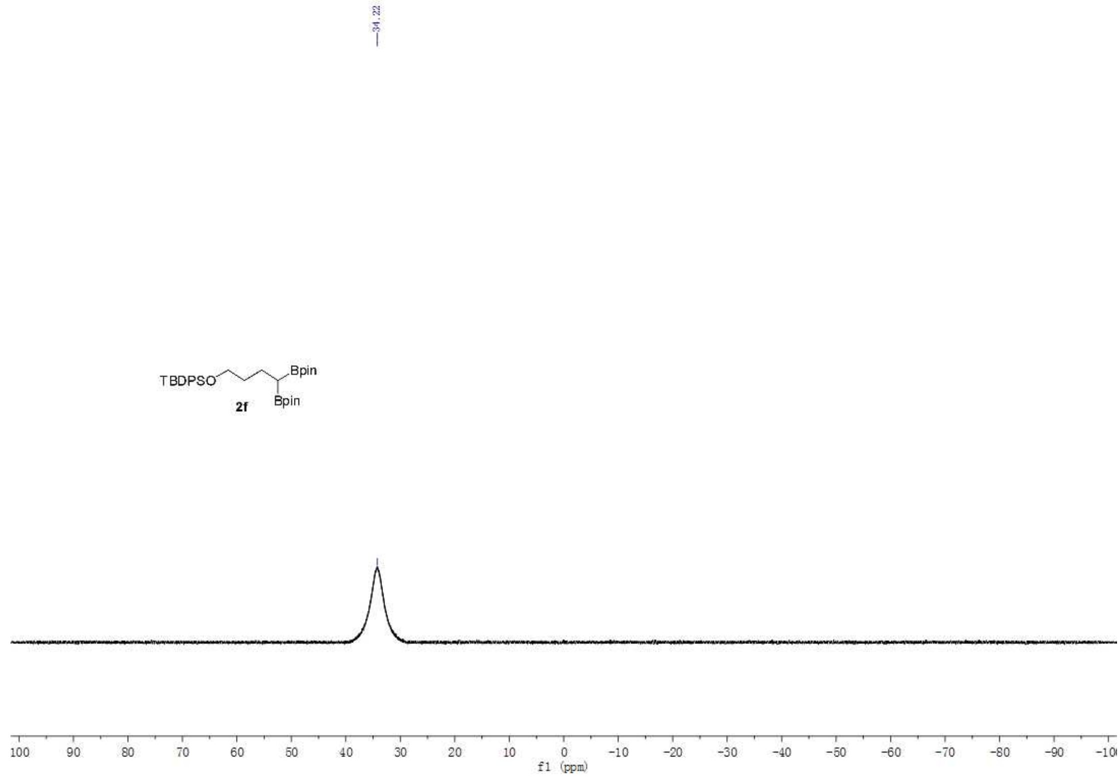

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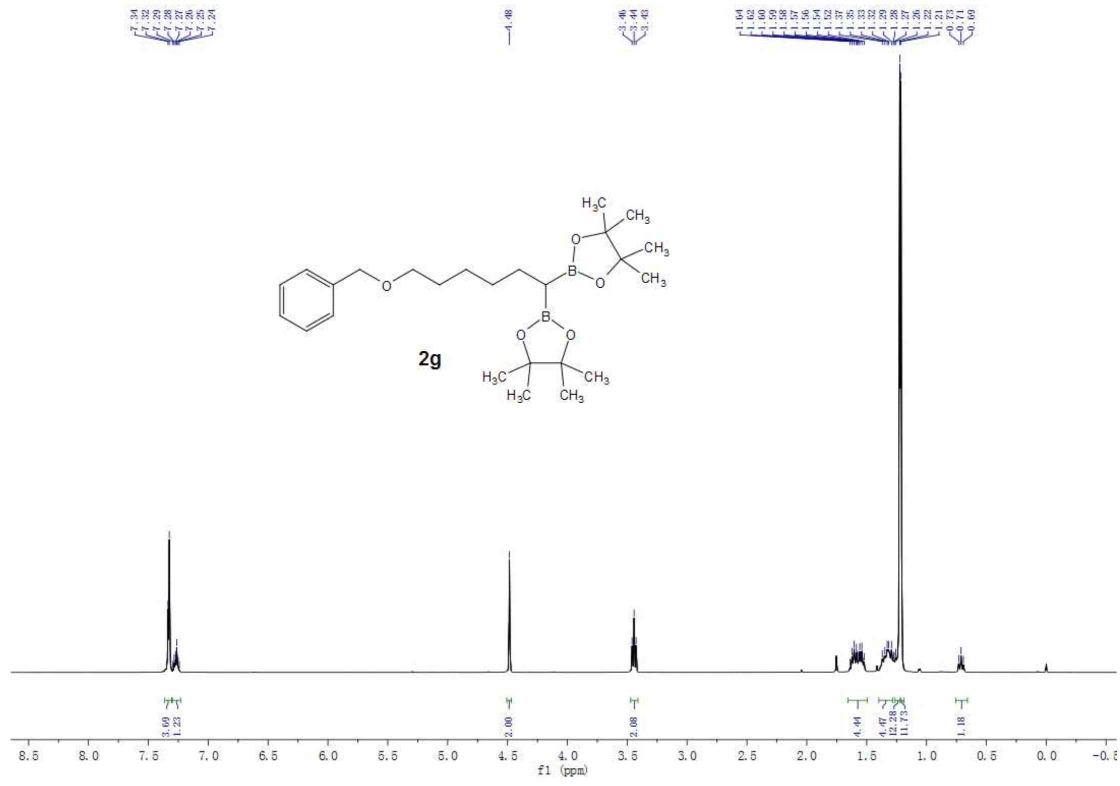

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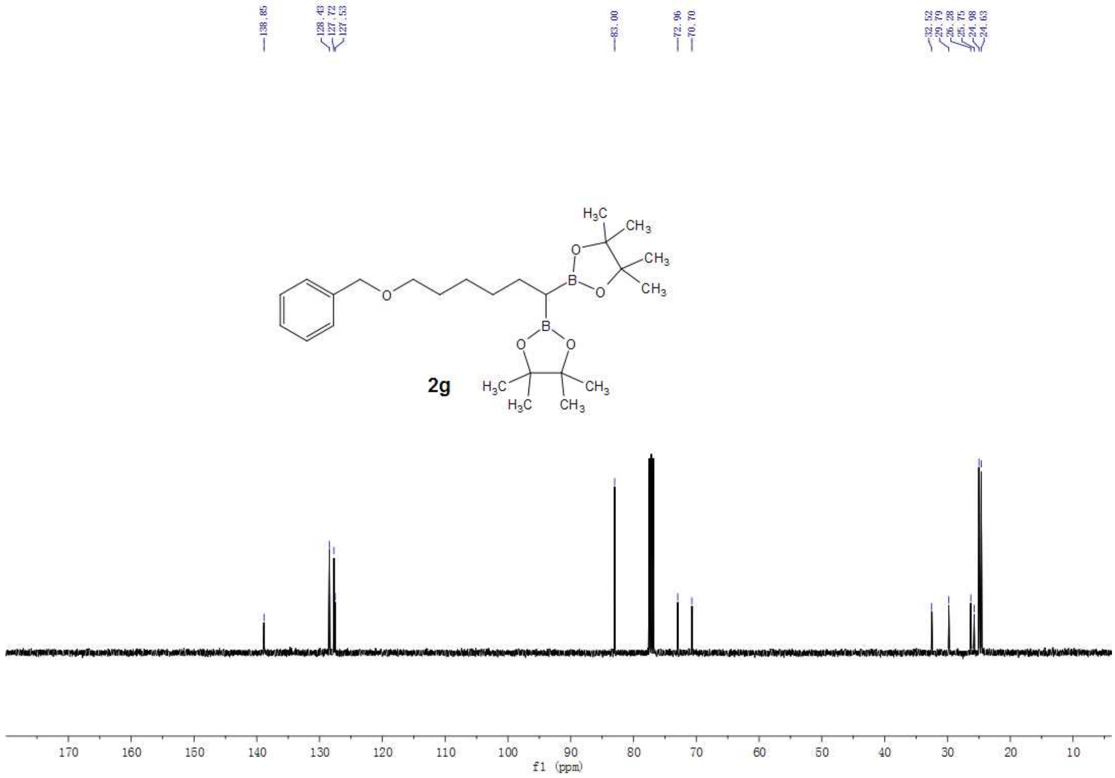

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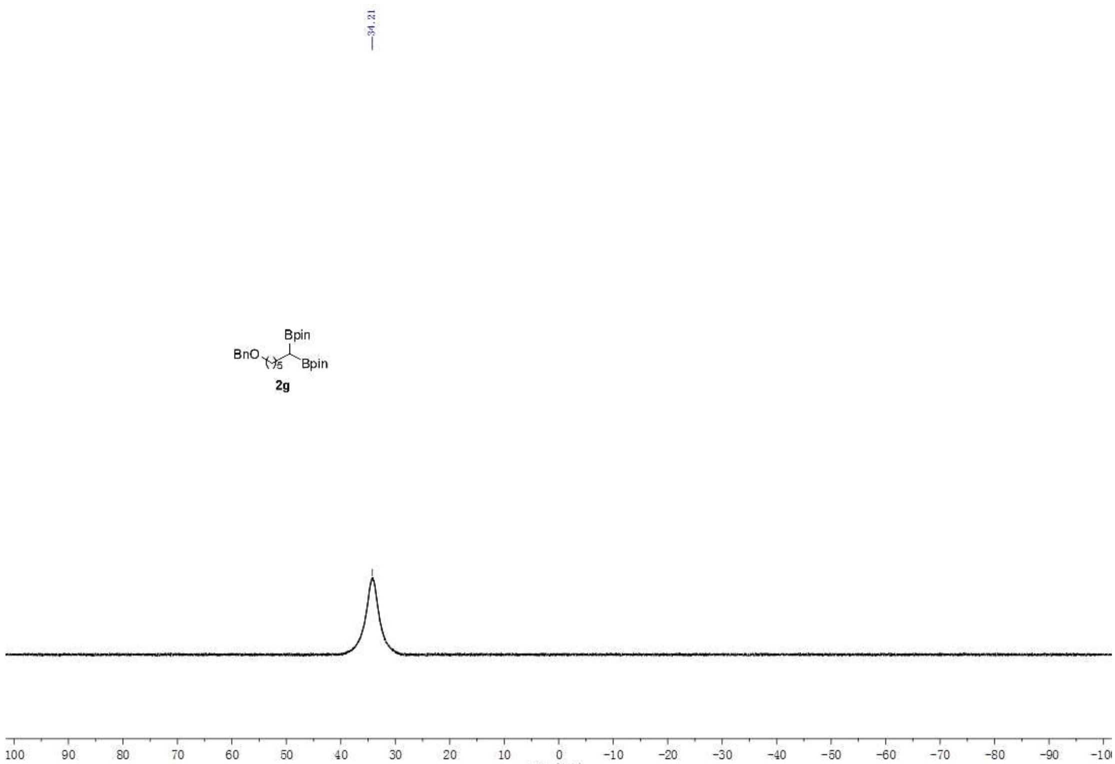

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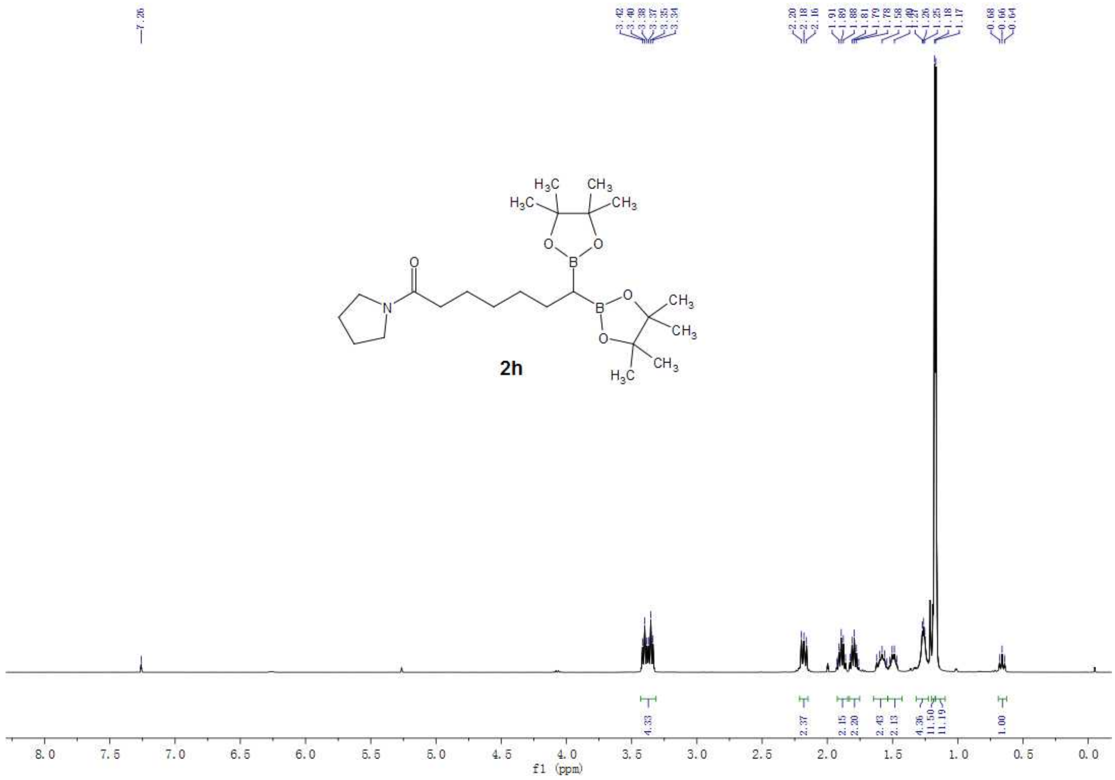

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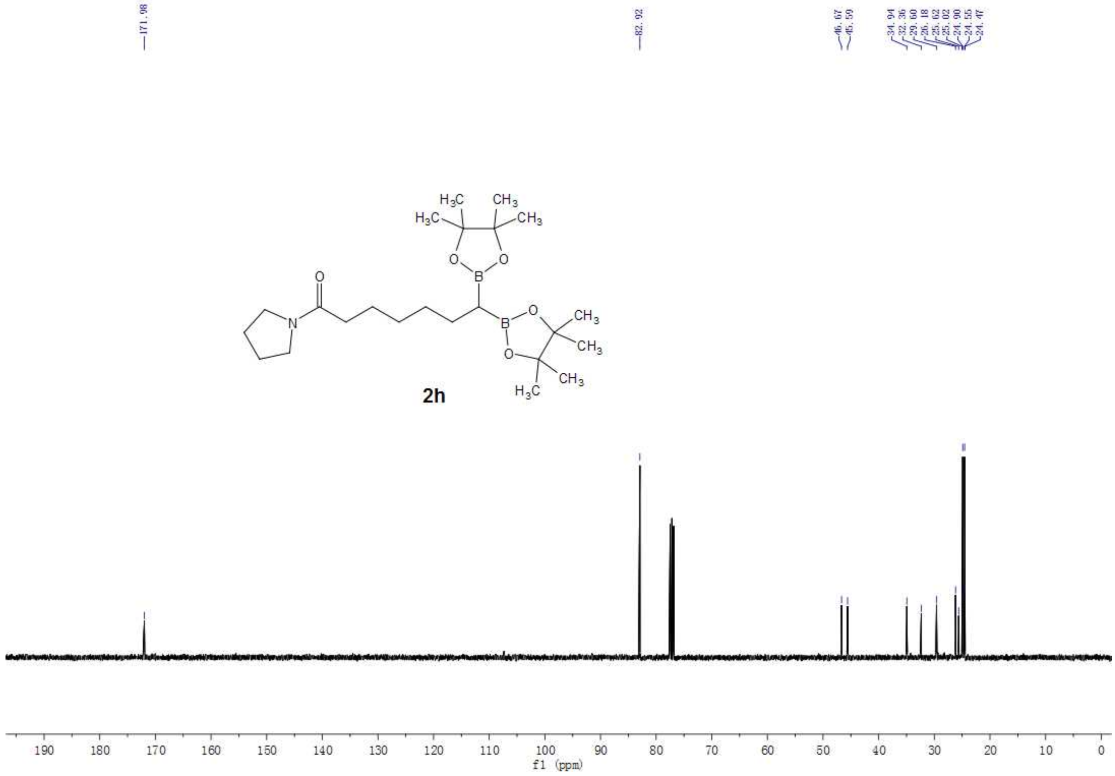
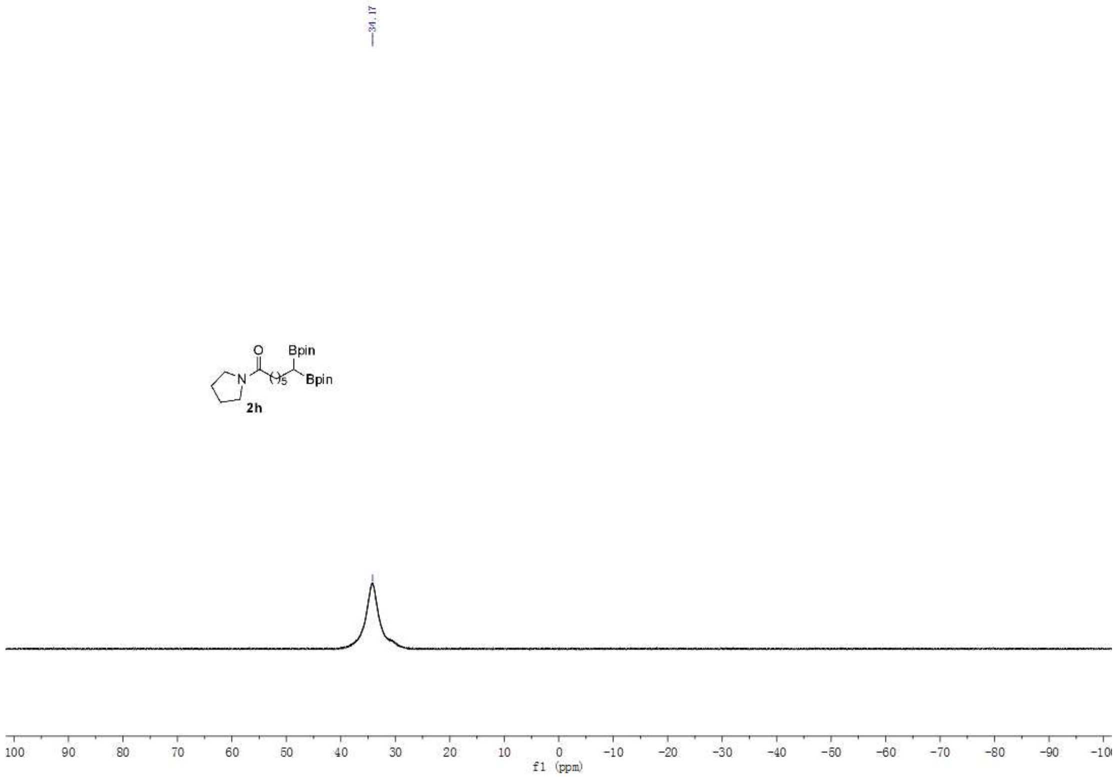


^{13}C NMR (101 M, $CDCl_3$) spectrum of **2h**



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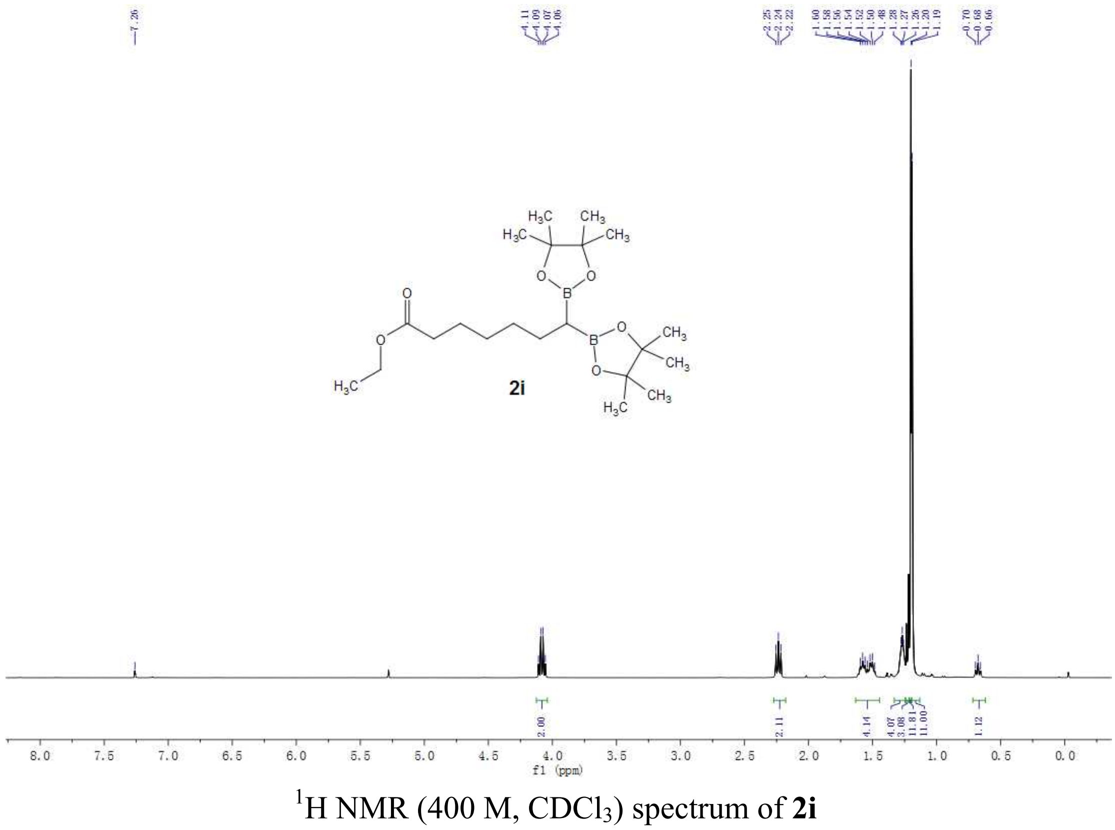

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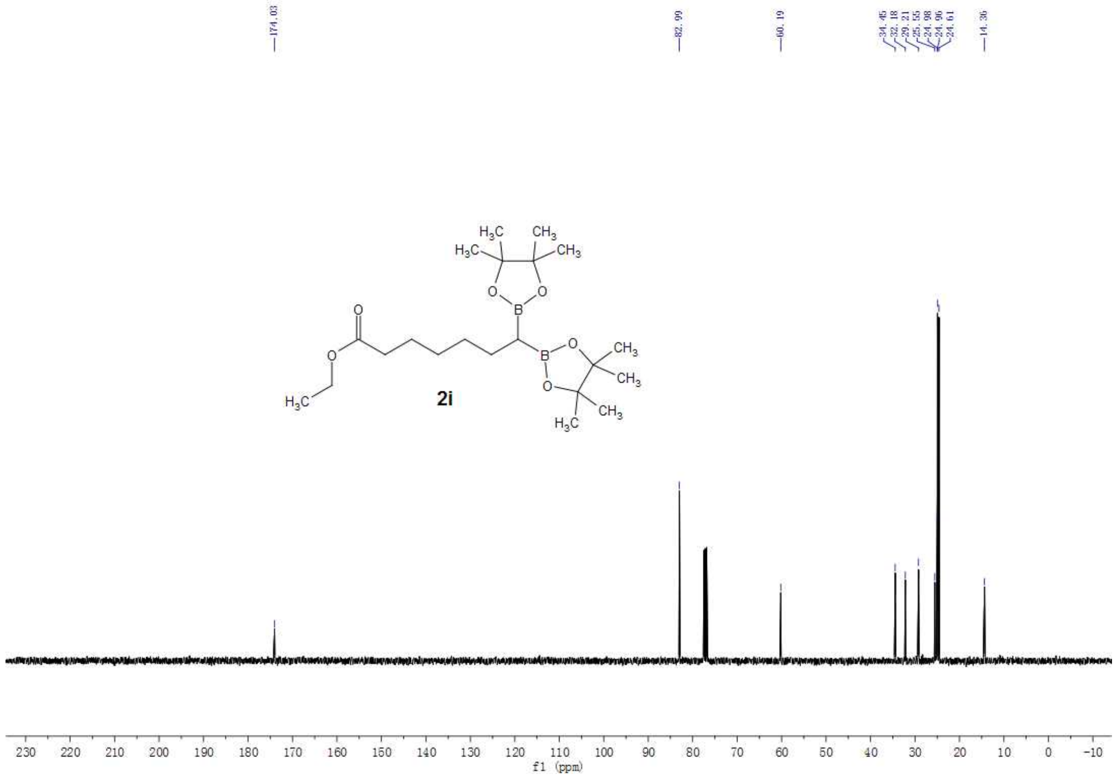

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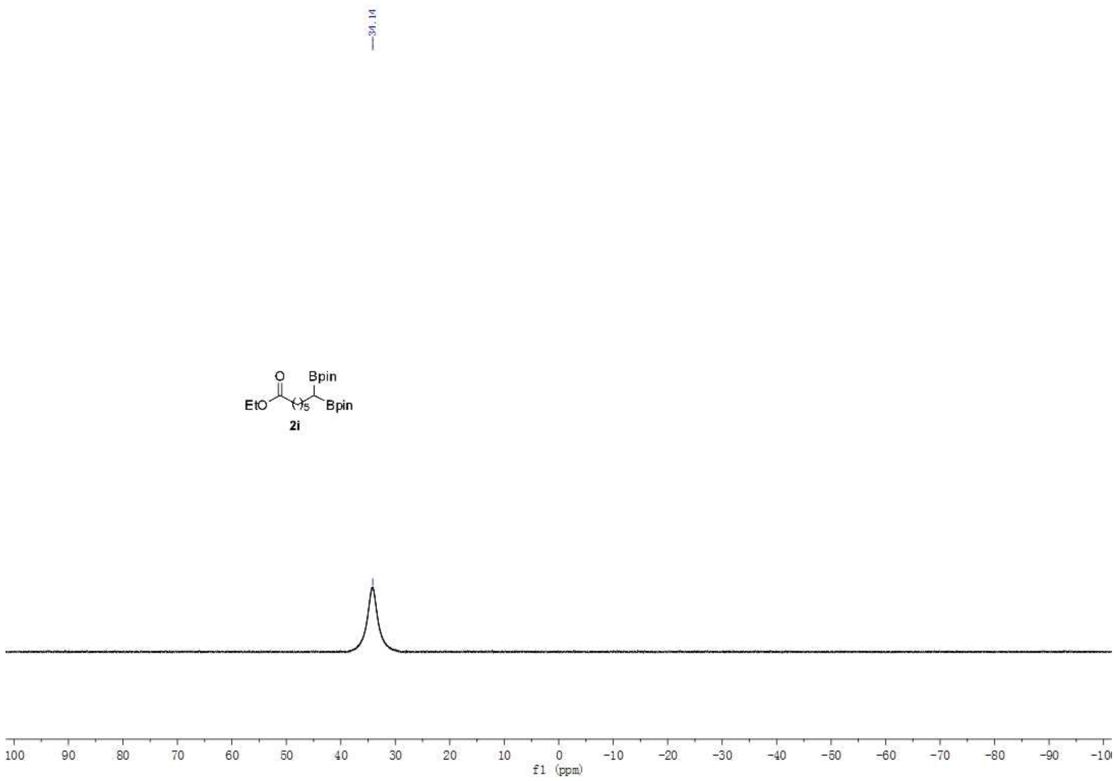

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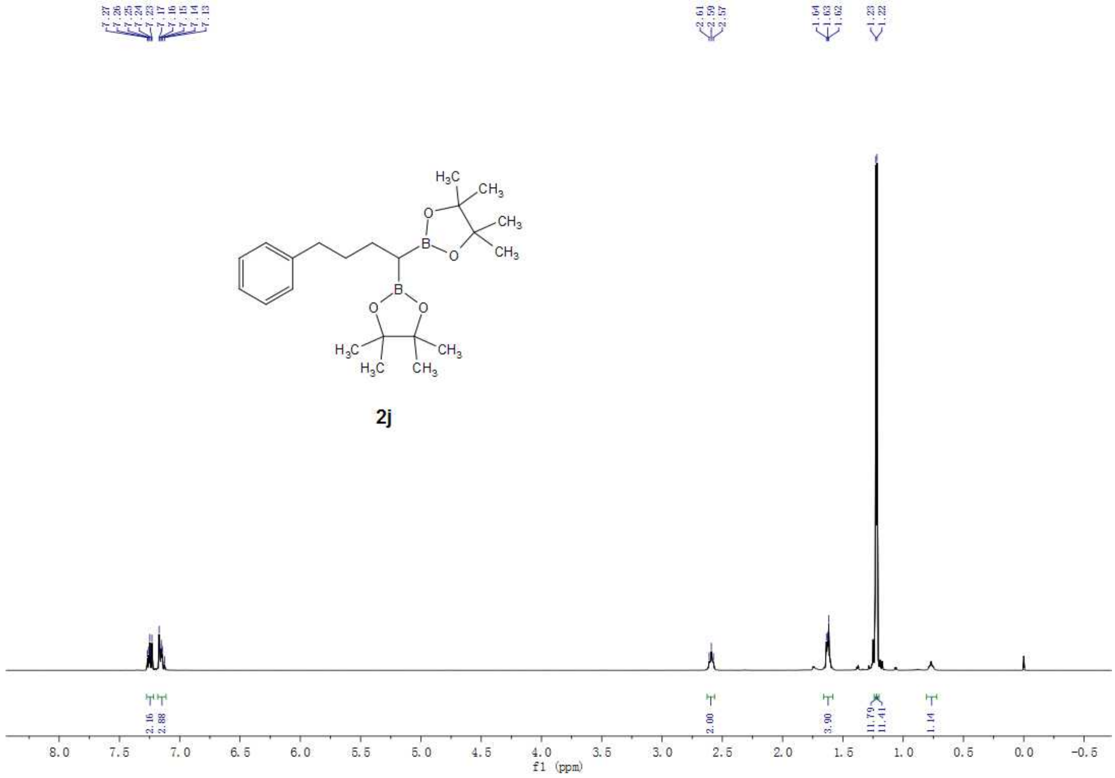

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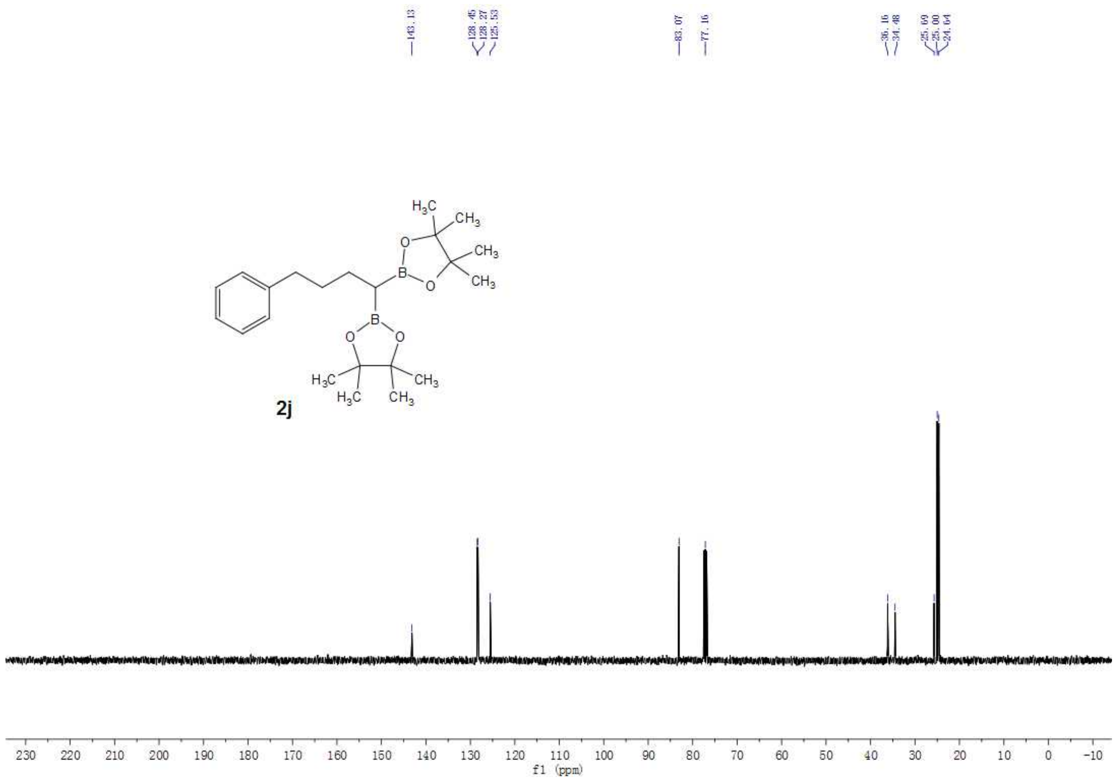

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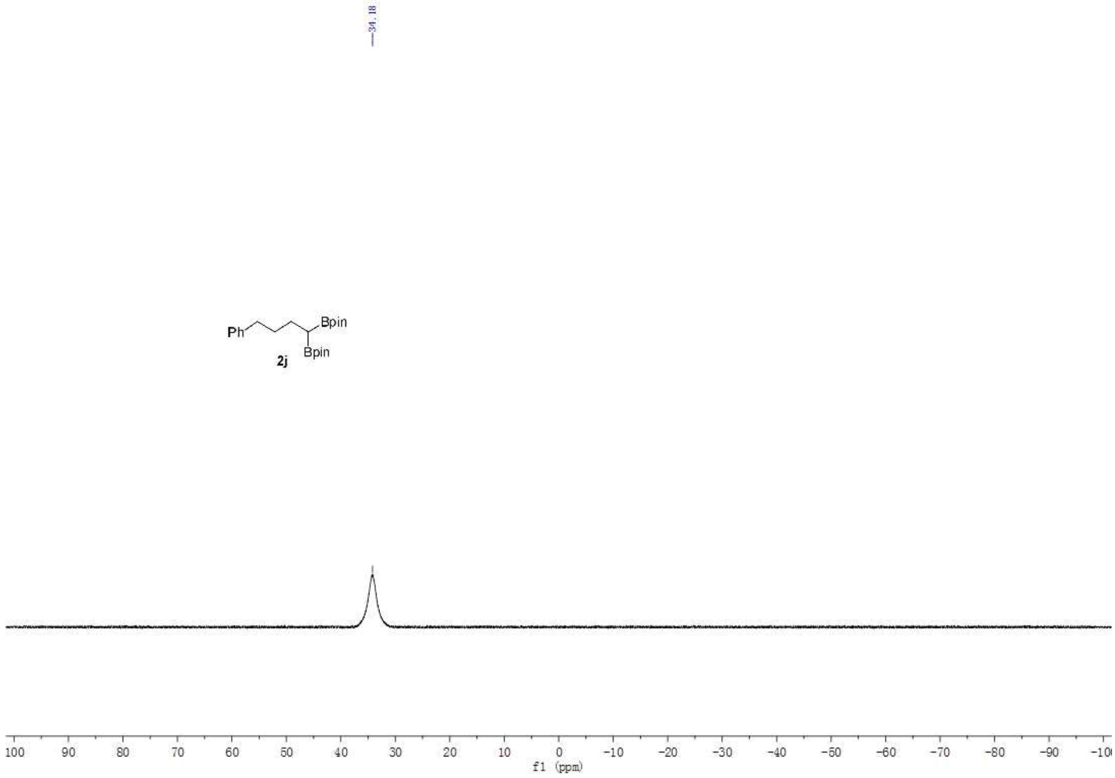

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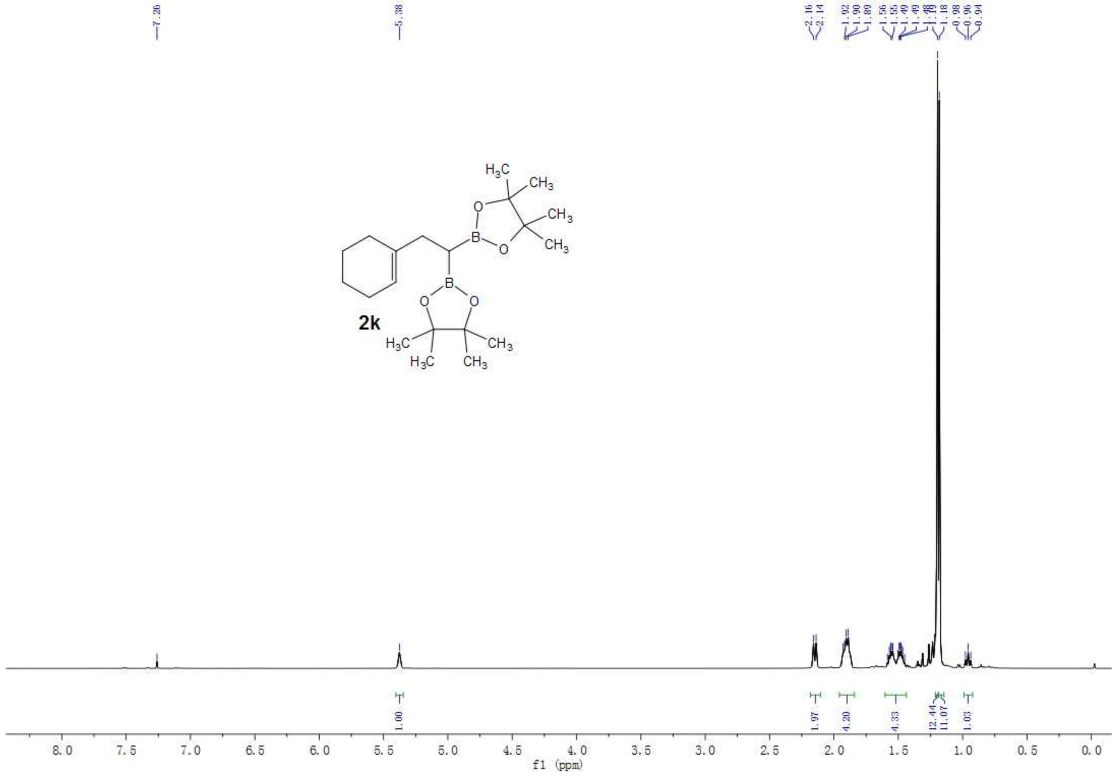

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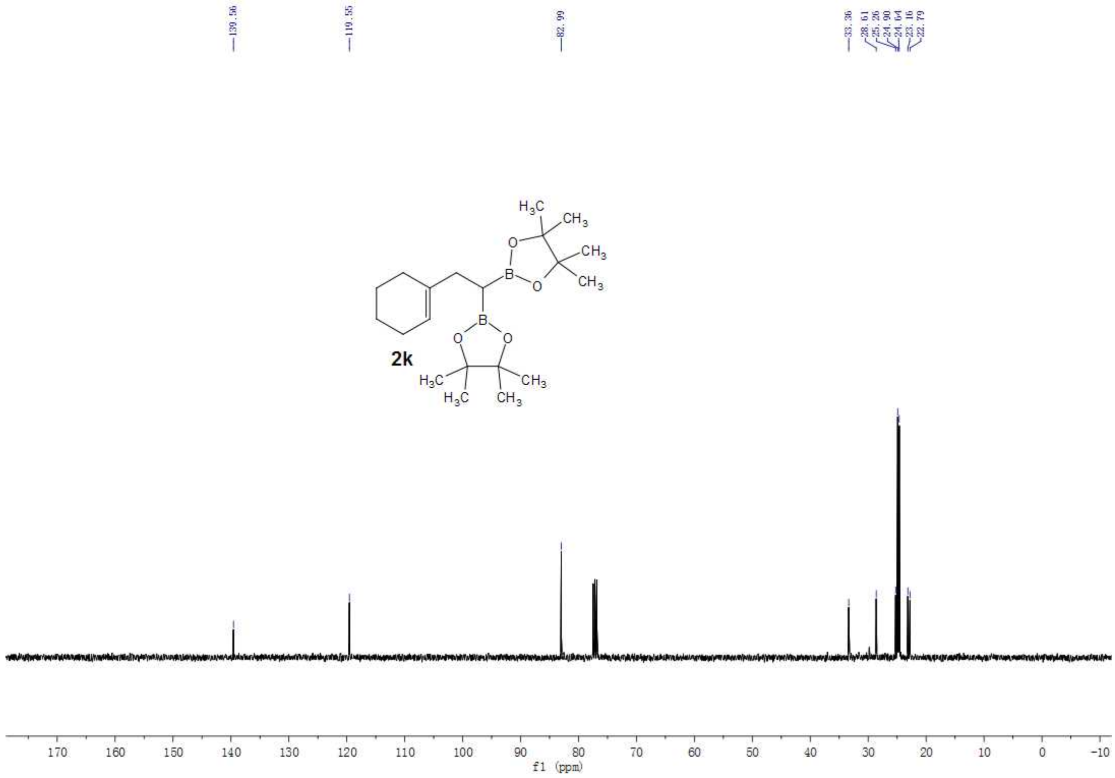

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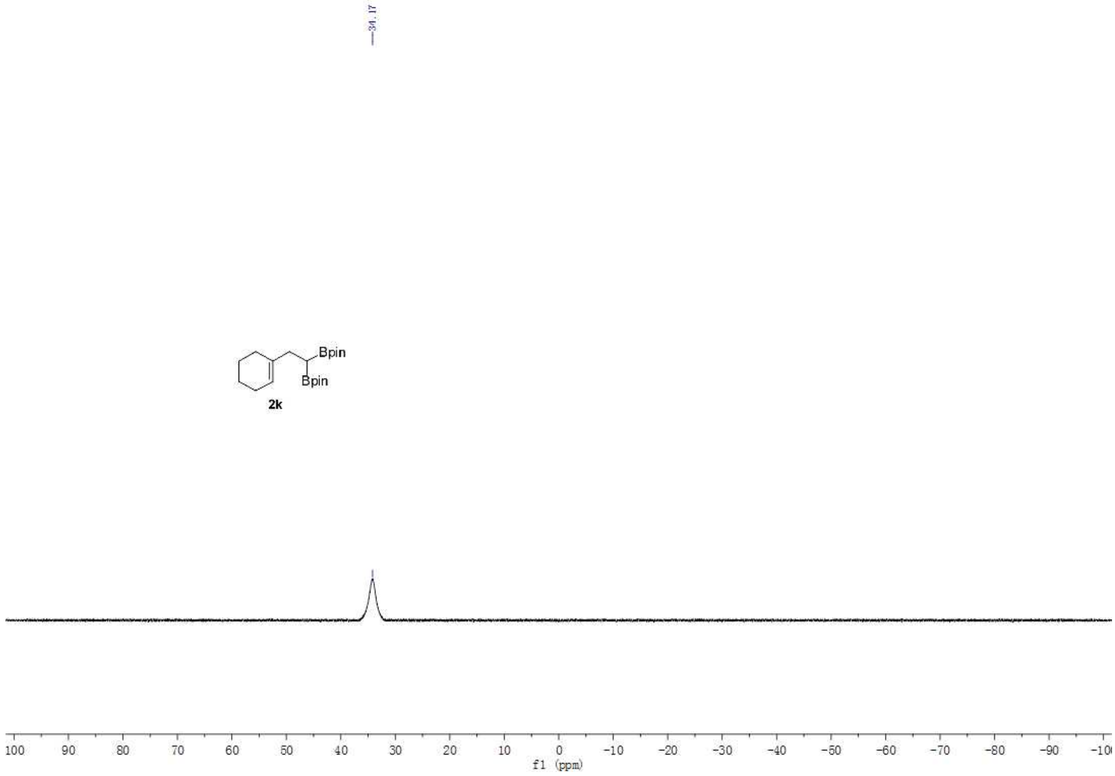

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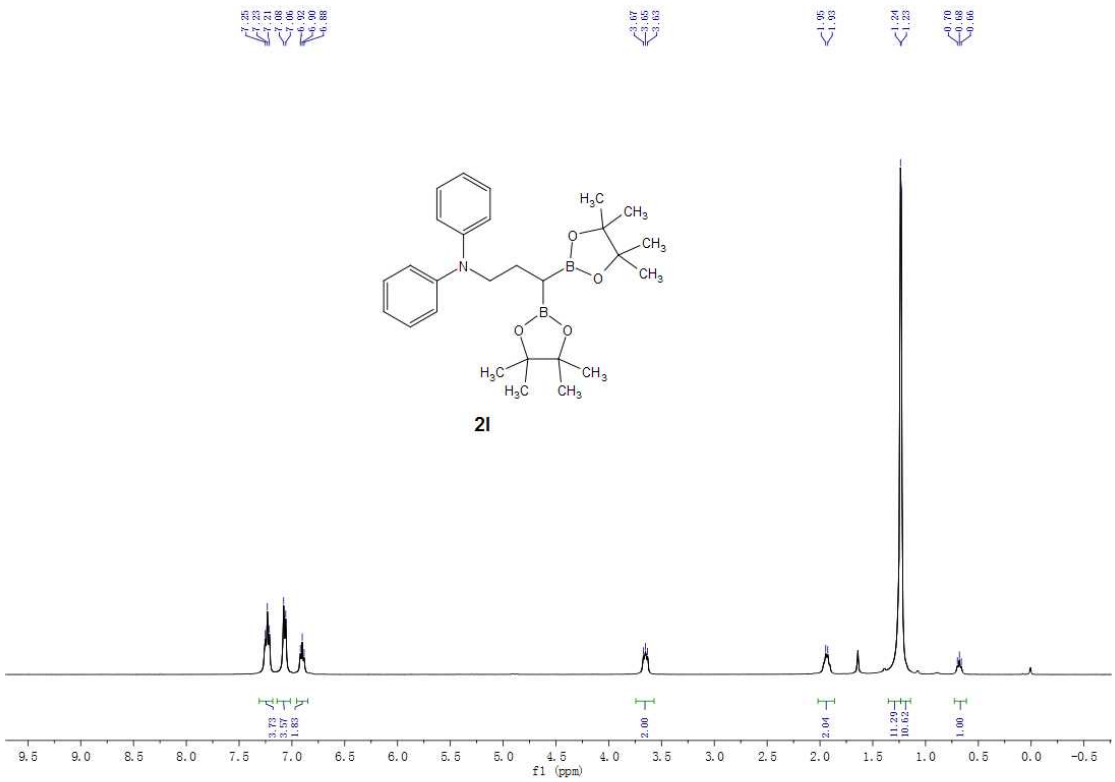

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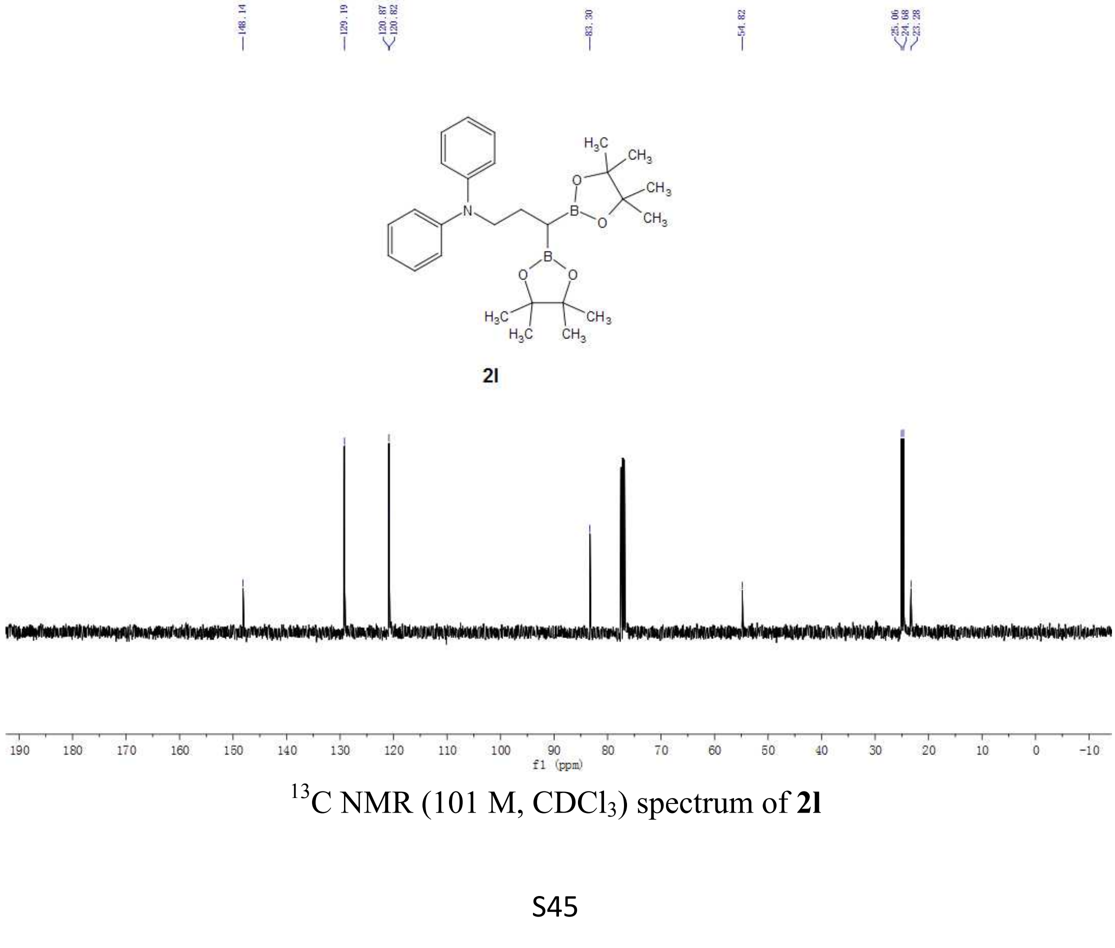
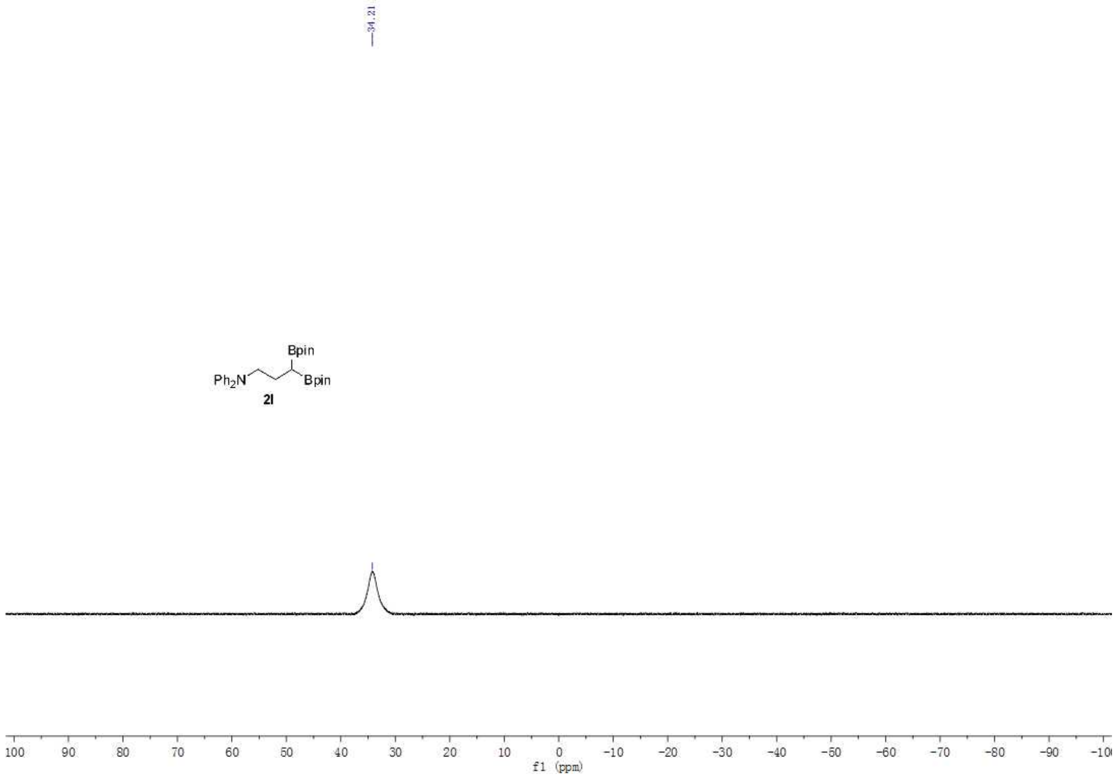


^{13}C NMR (101 M, $CDCl_3$) spectrum of **2l**



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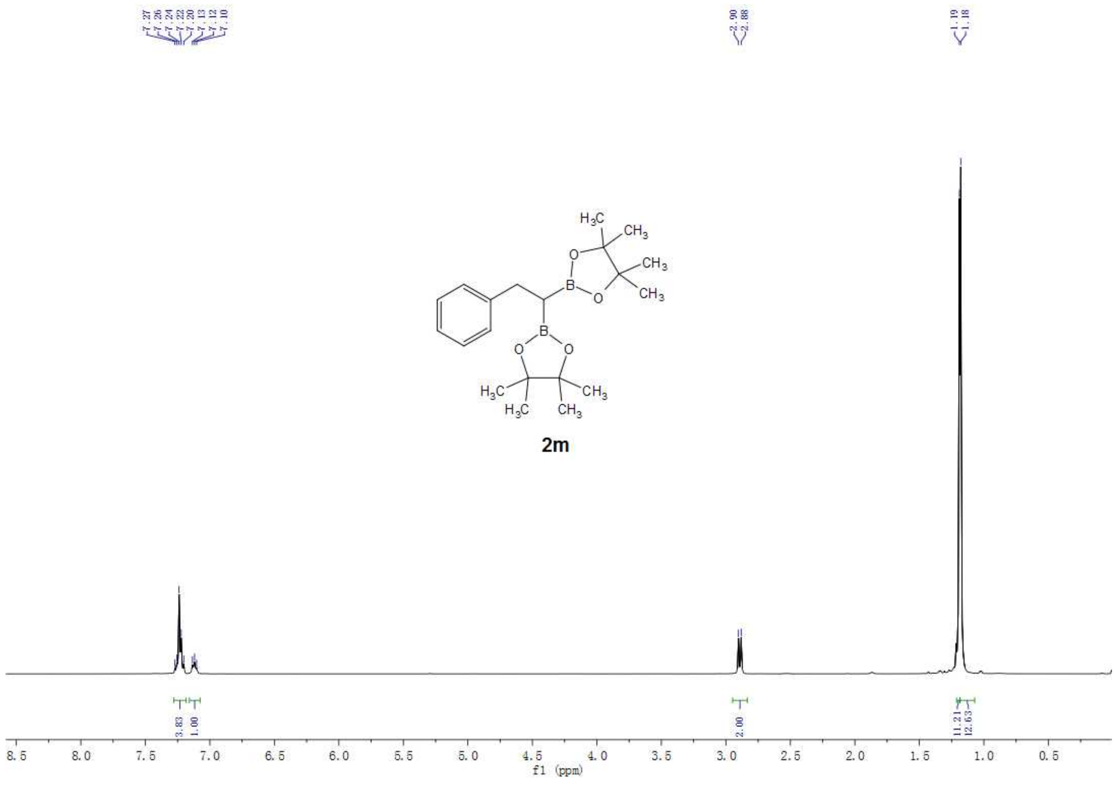

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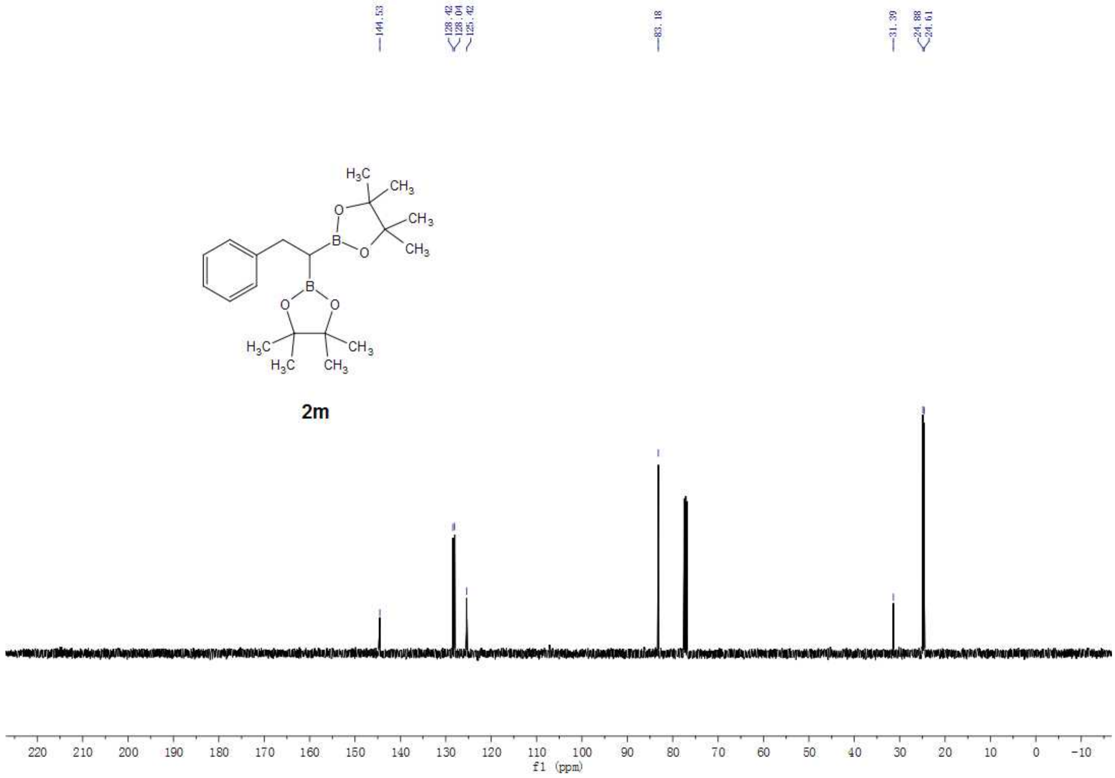
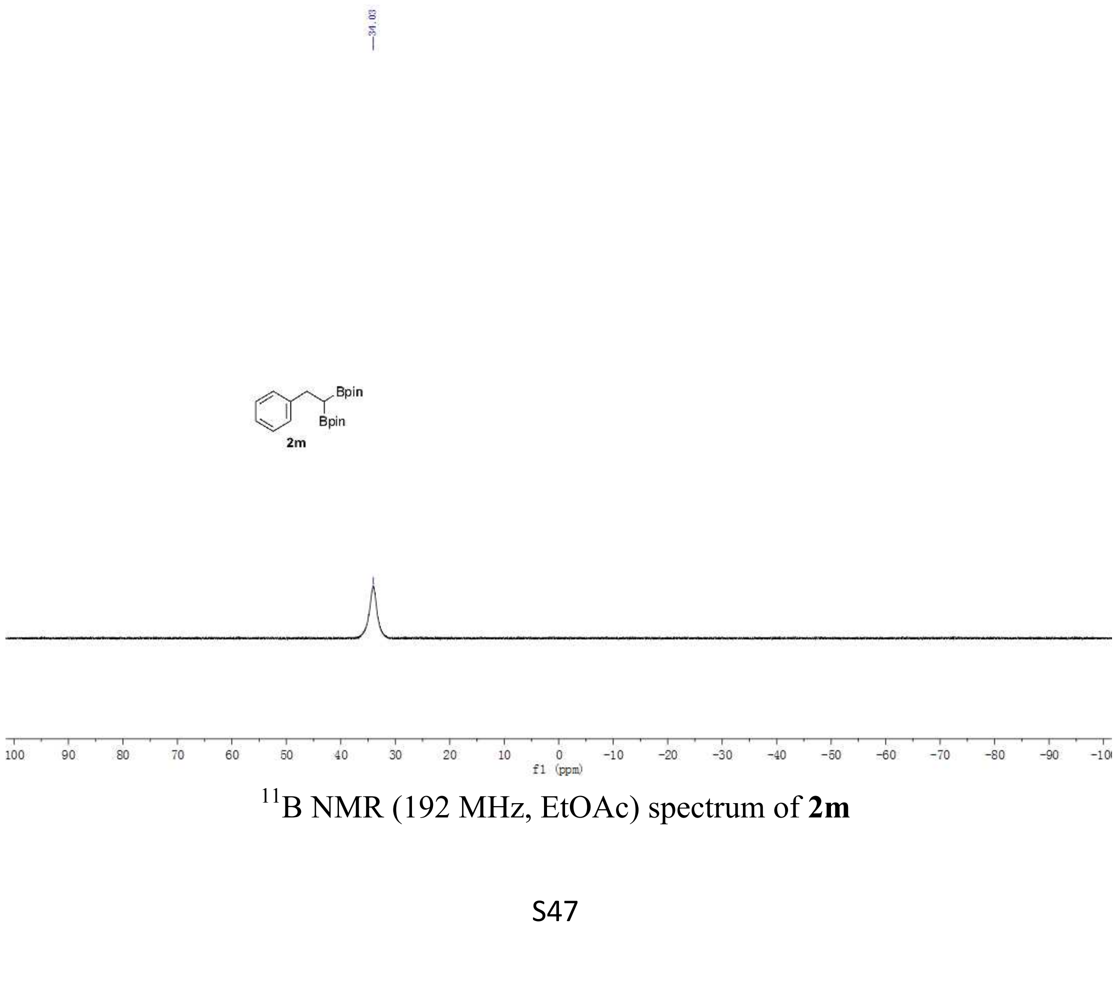
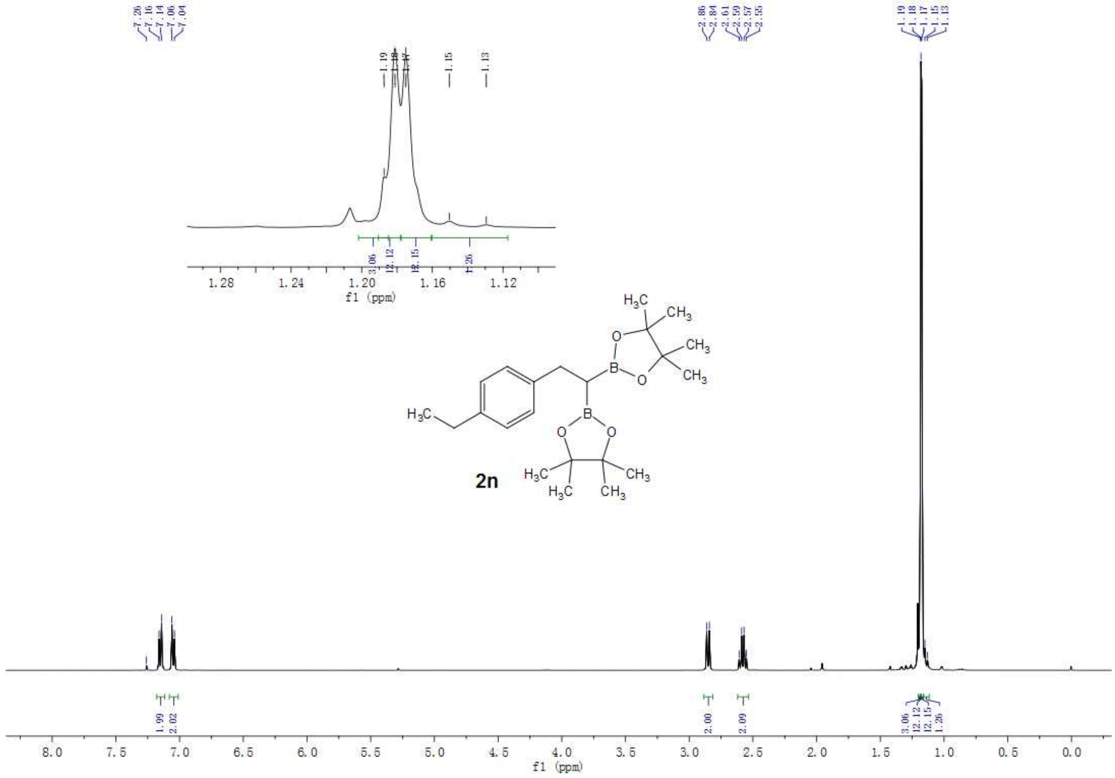


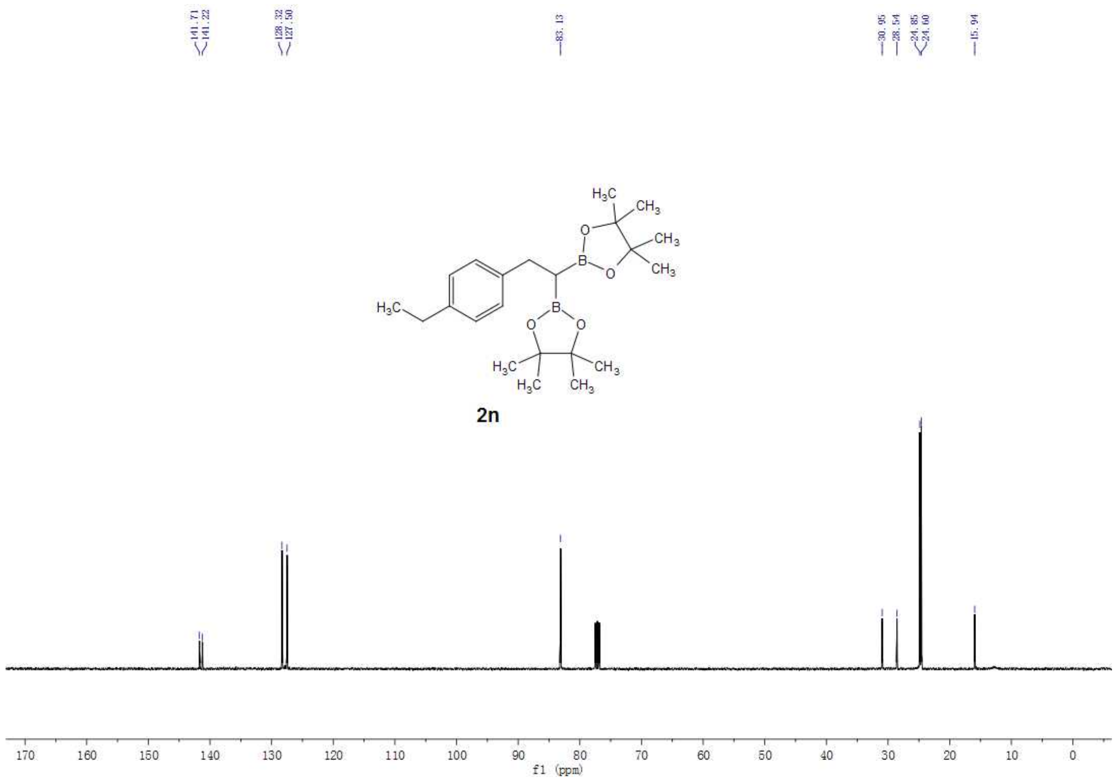
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2m**



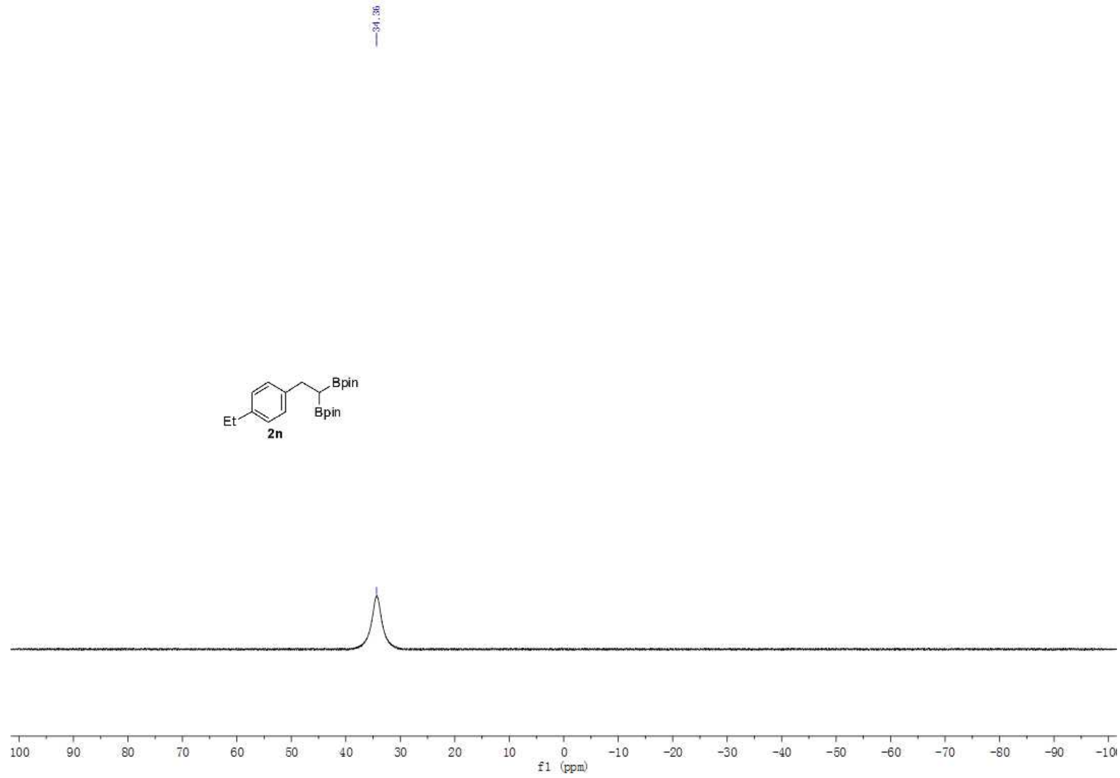
^{11}B NMR (192 MHz, EtOAc) spectrum of **2m**



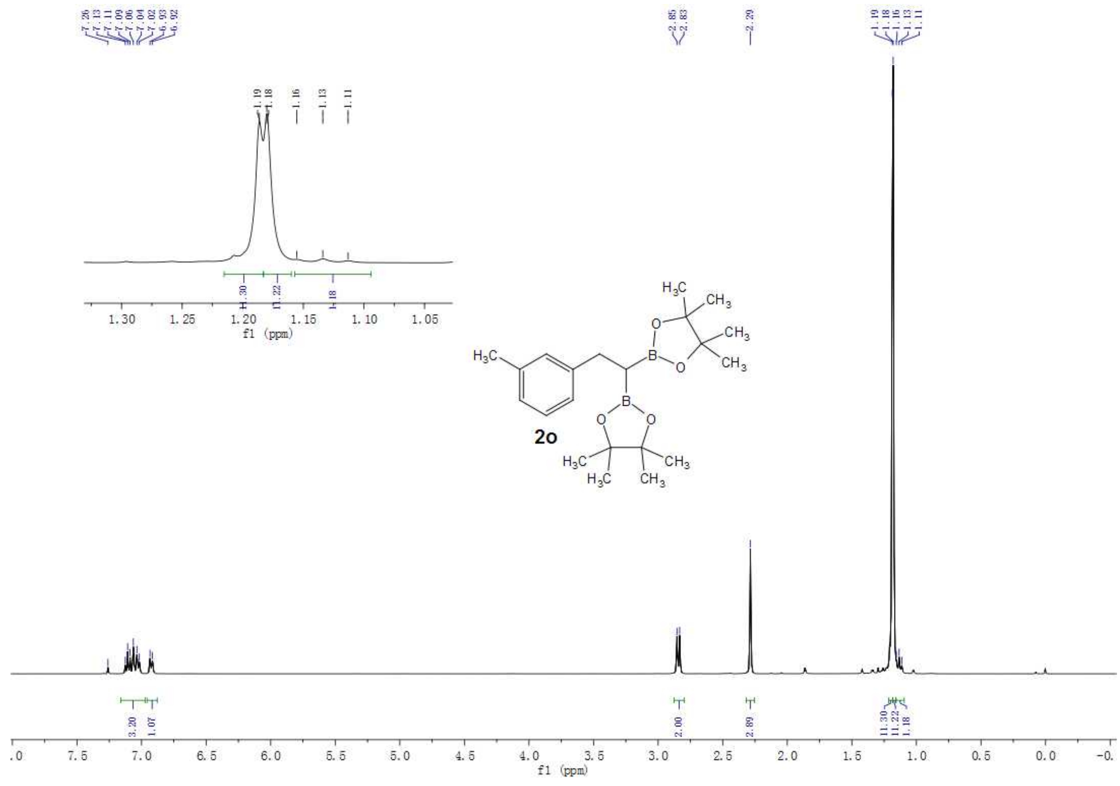
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2n**



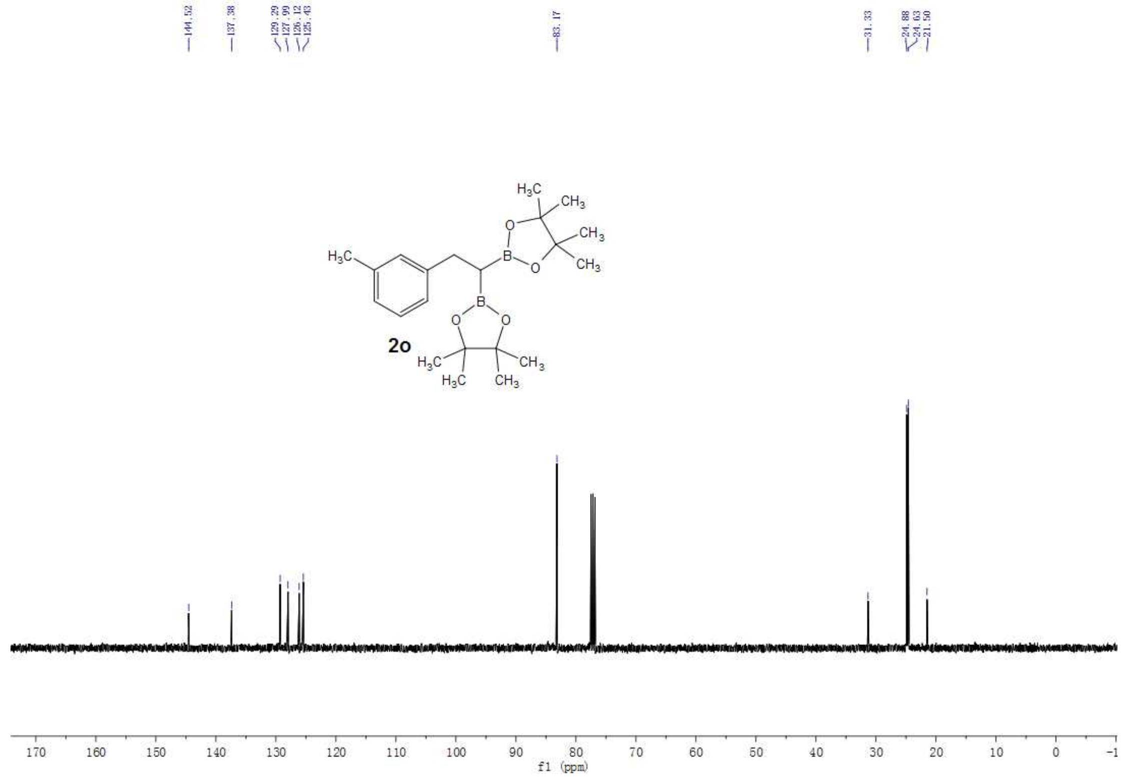
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2n**



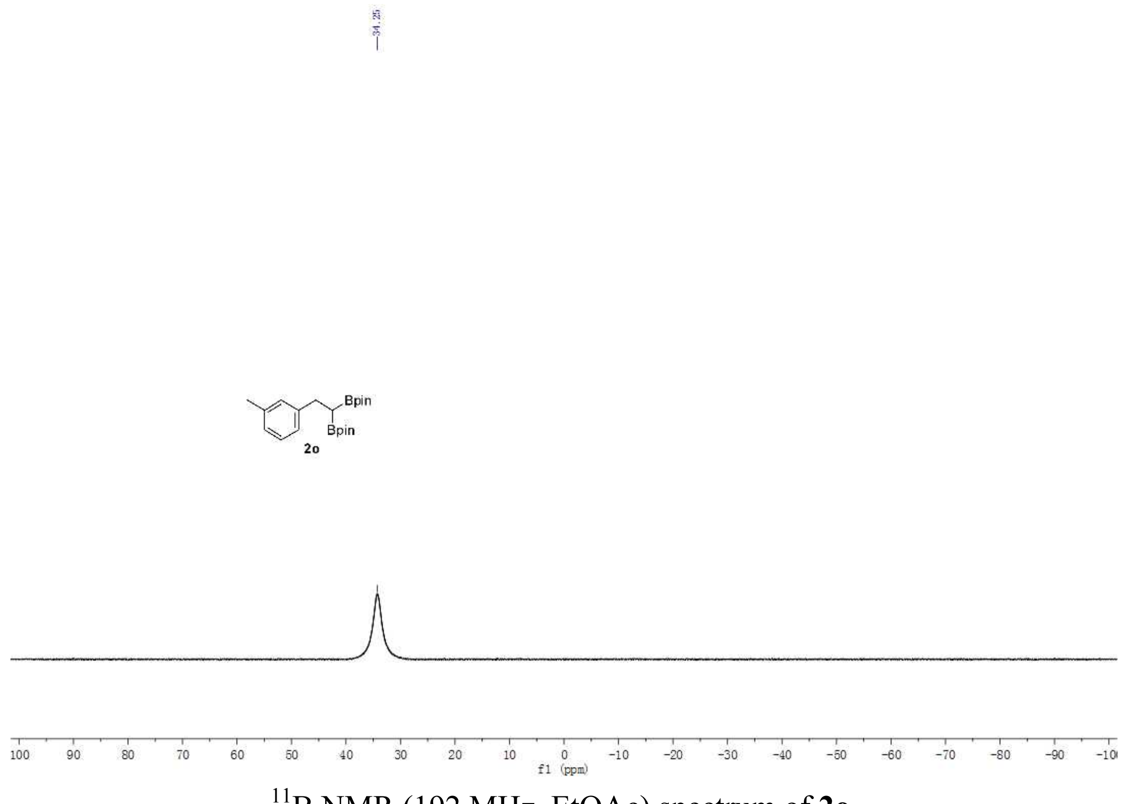
^{11}B NMR (192 MHz, EtOAc) spectrum of **2n**



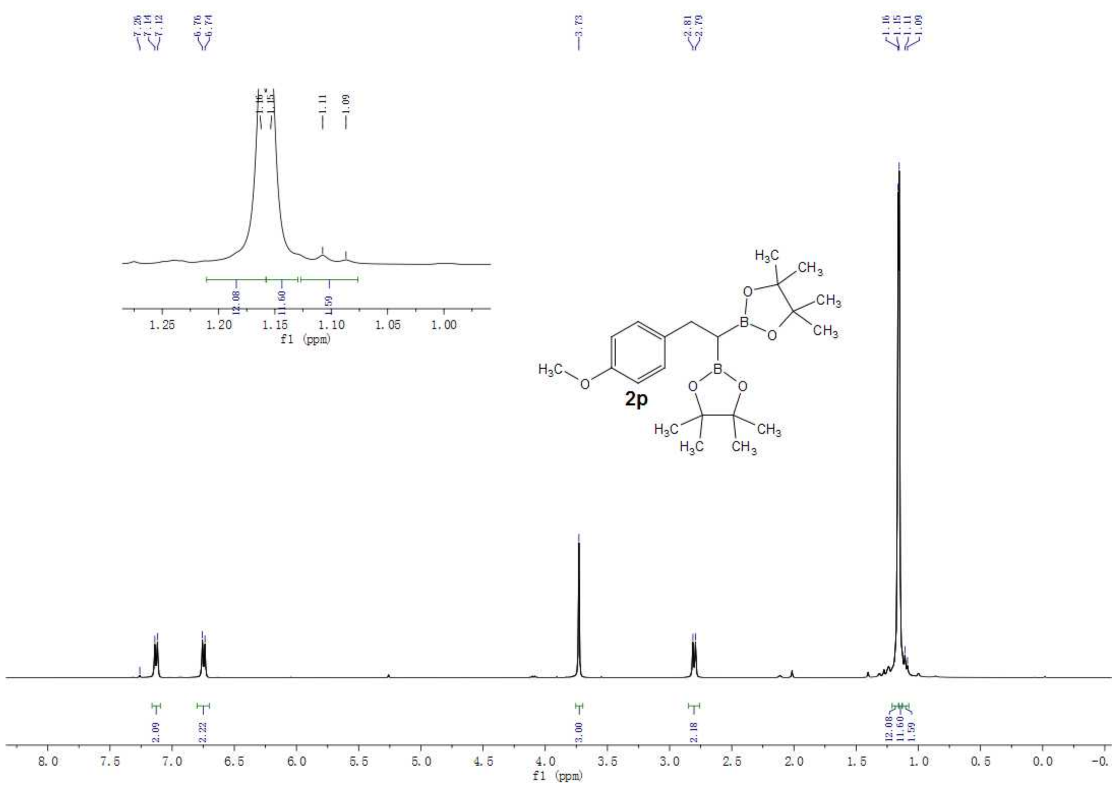
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2o**



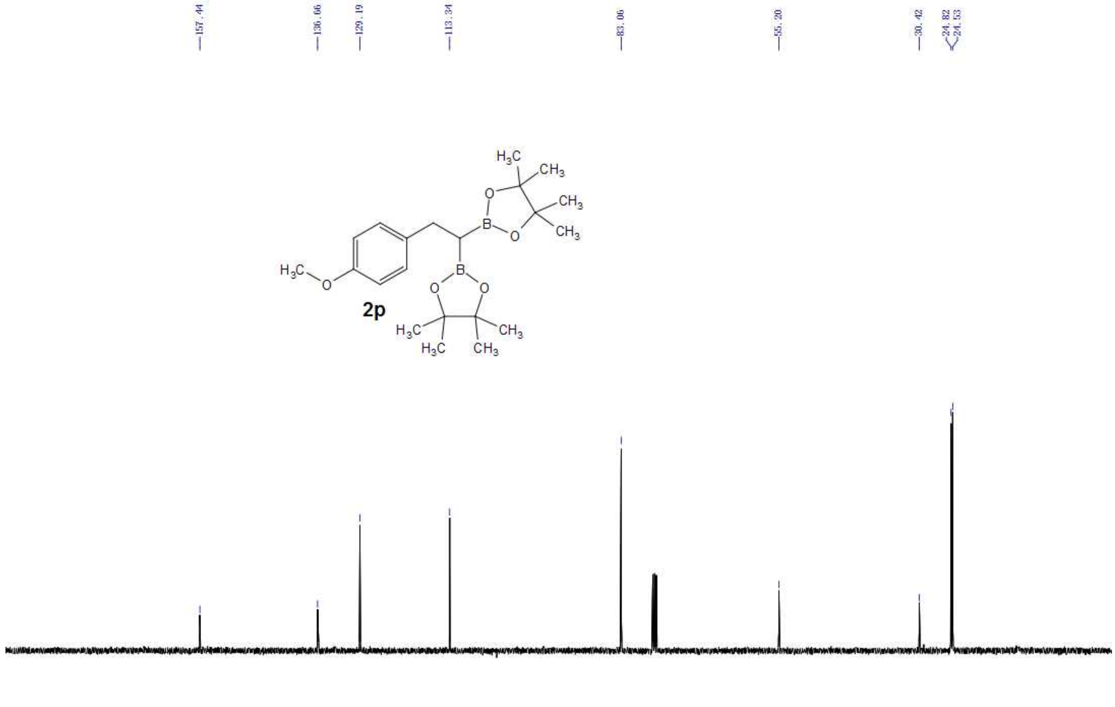
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2o**



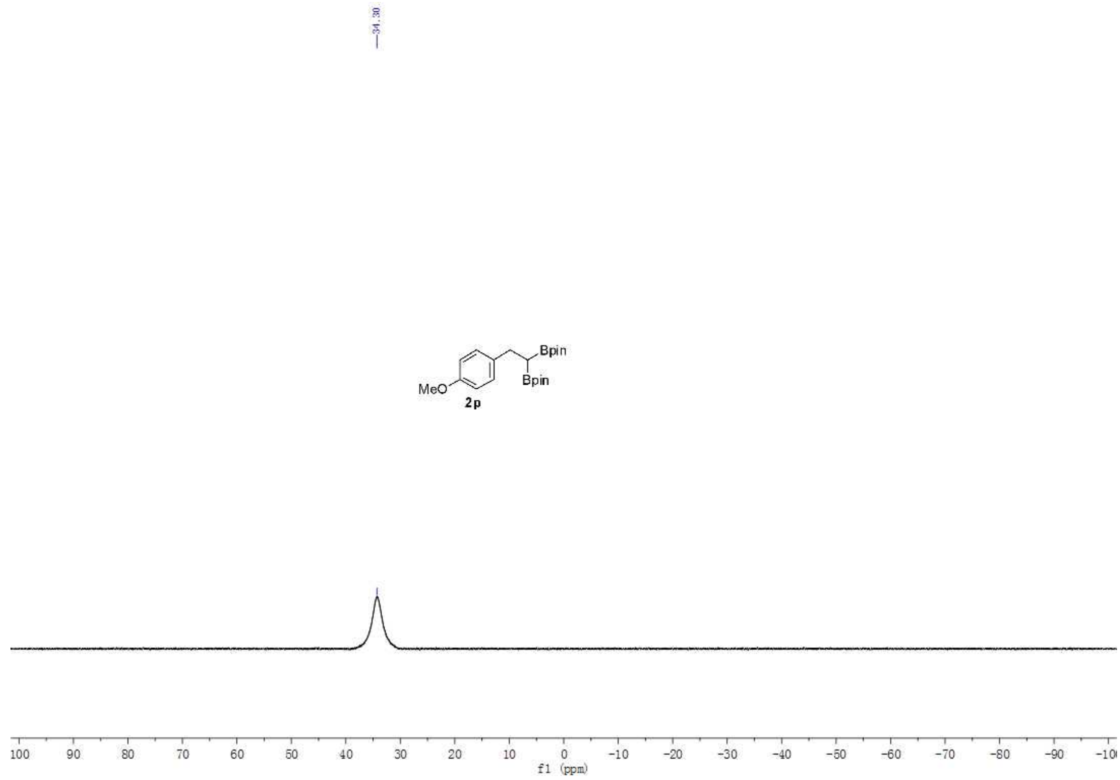
^{11}B NMR (192 MHz, EtOAc) spectrum of **2o**



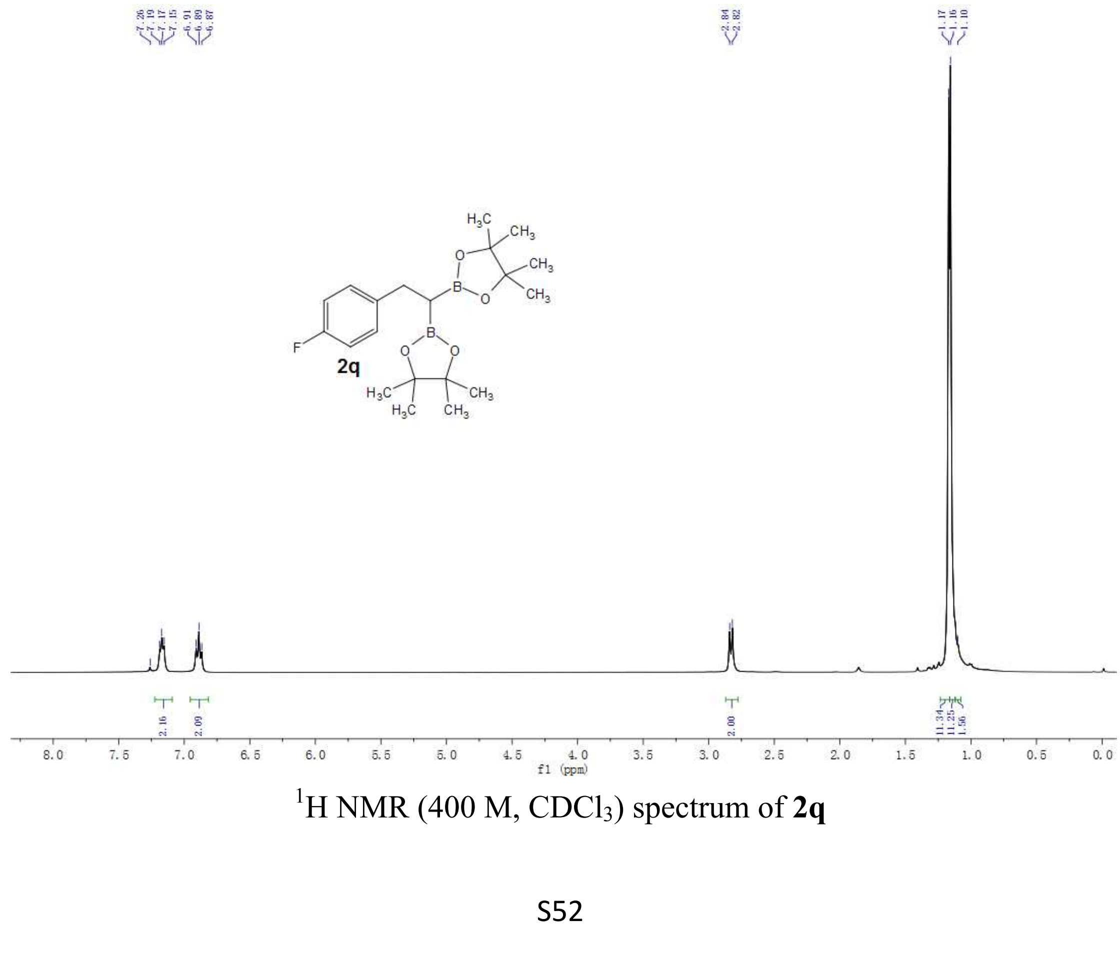
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2p**



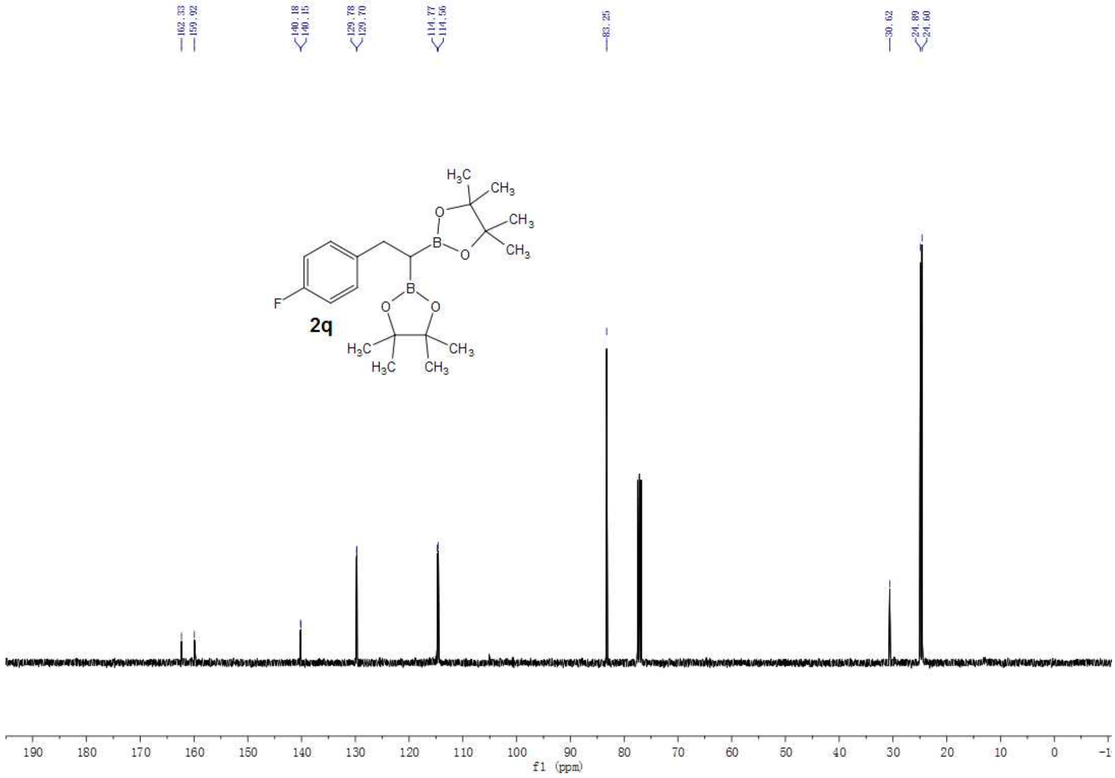
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2p**



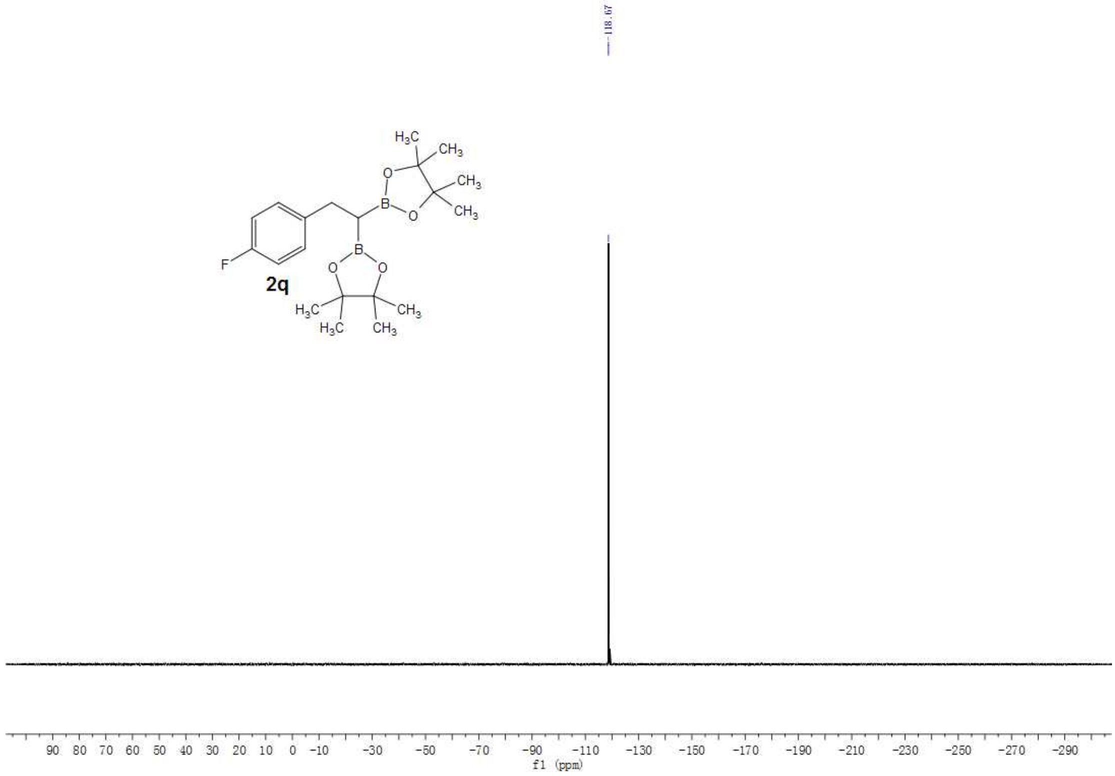
^{11}B NMR (192 MHz, EtOAc) spectrum of **2p**



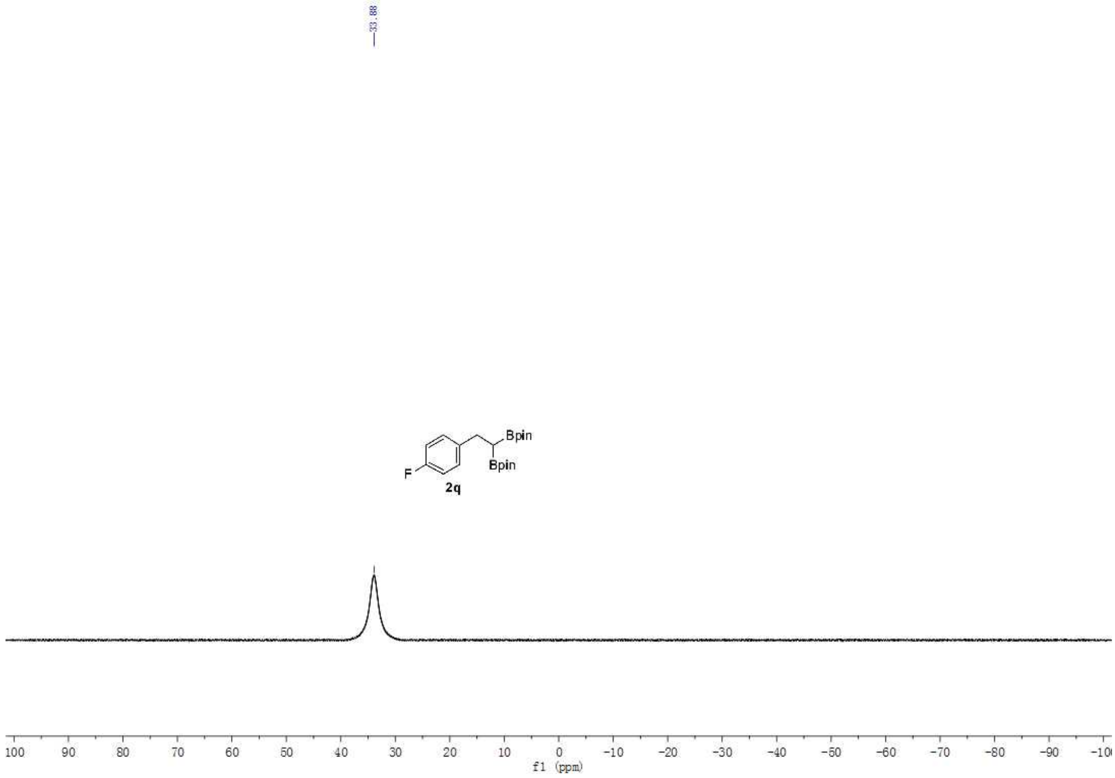
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2q**



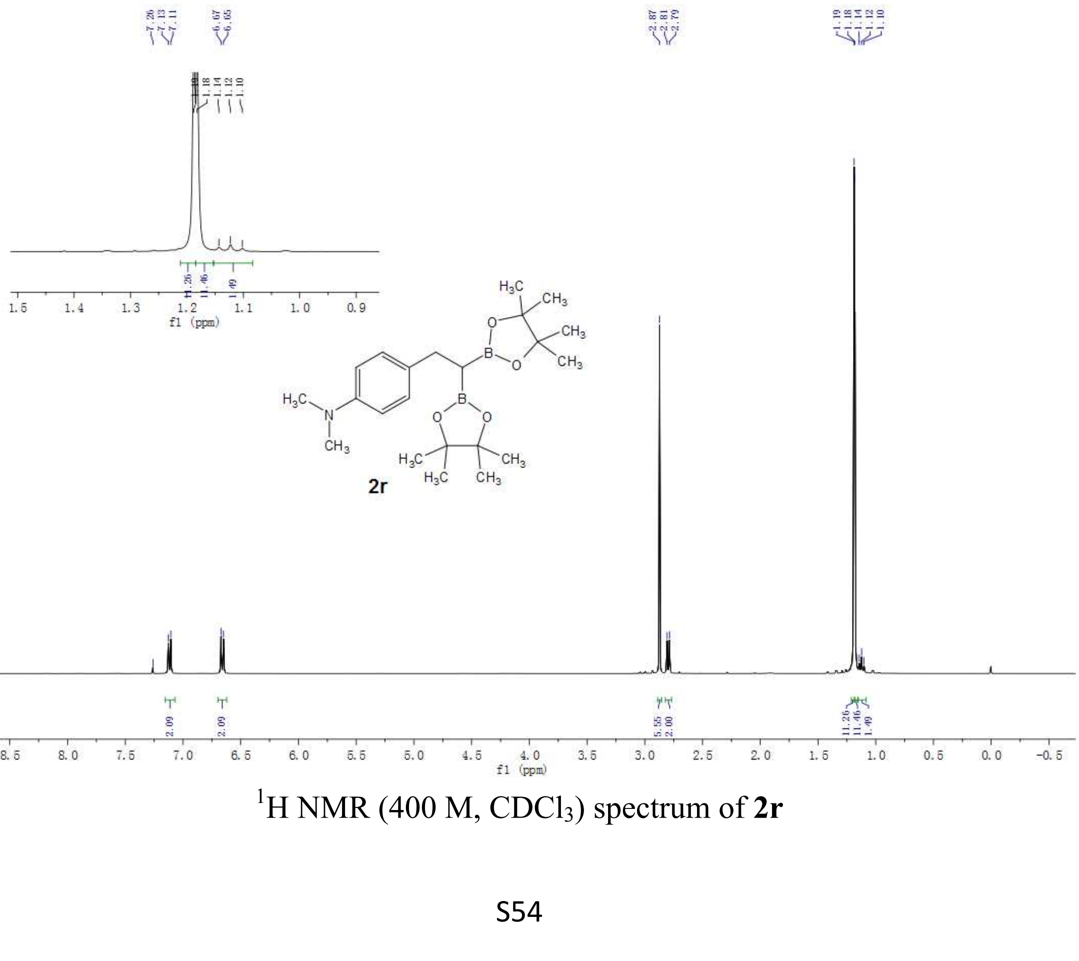
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2q**



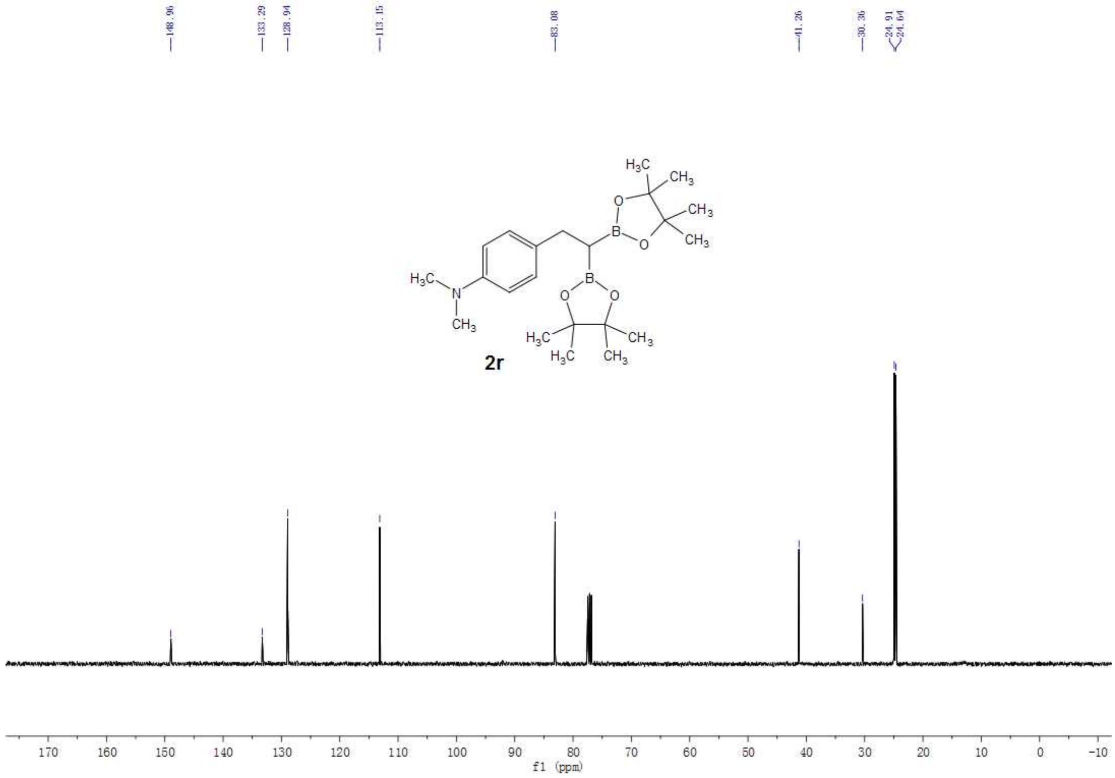
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2q**



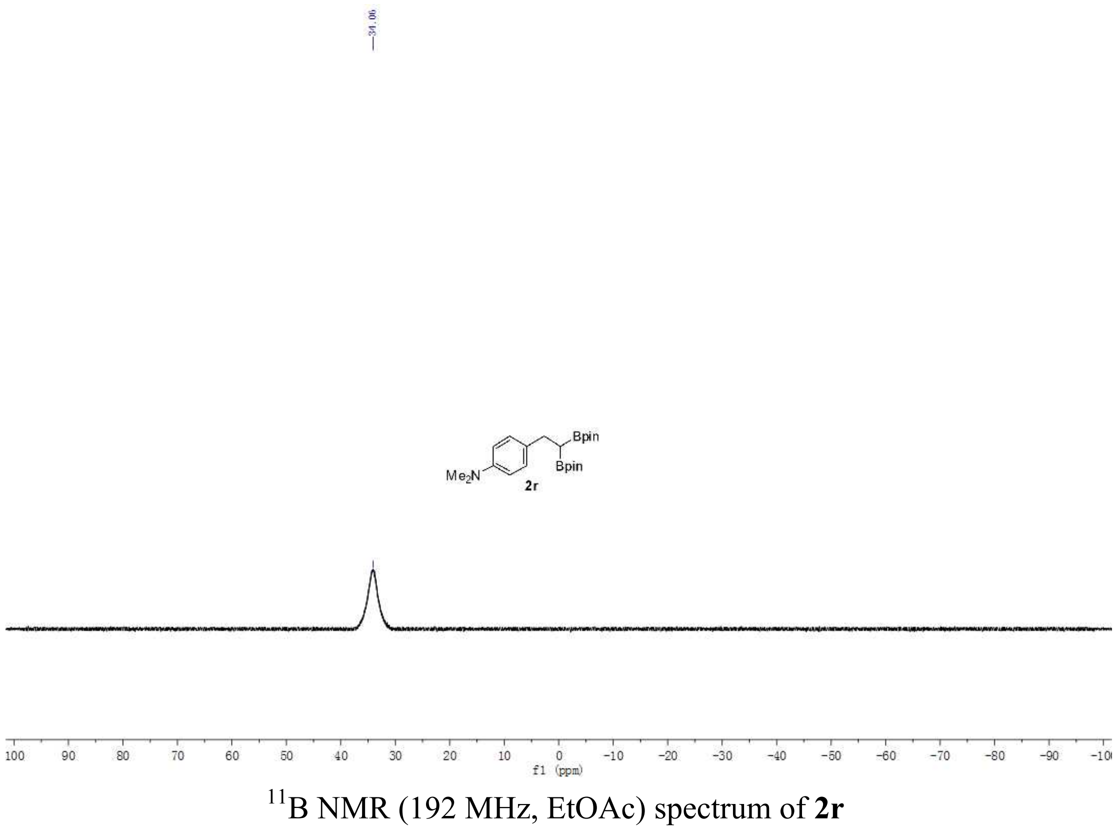
^{11}B NMR (192 MHz, EtOAc) spectrum of **2q**



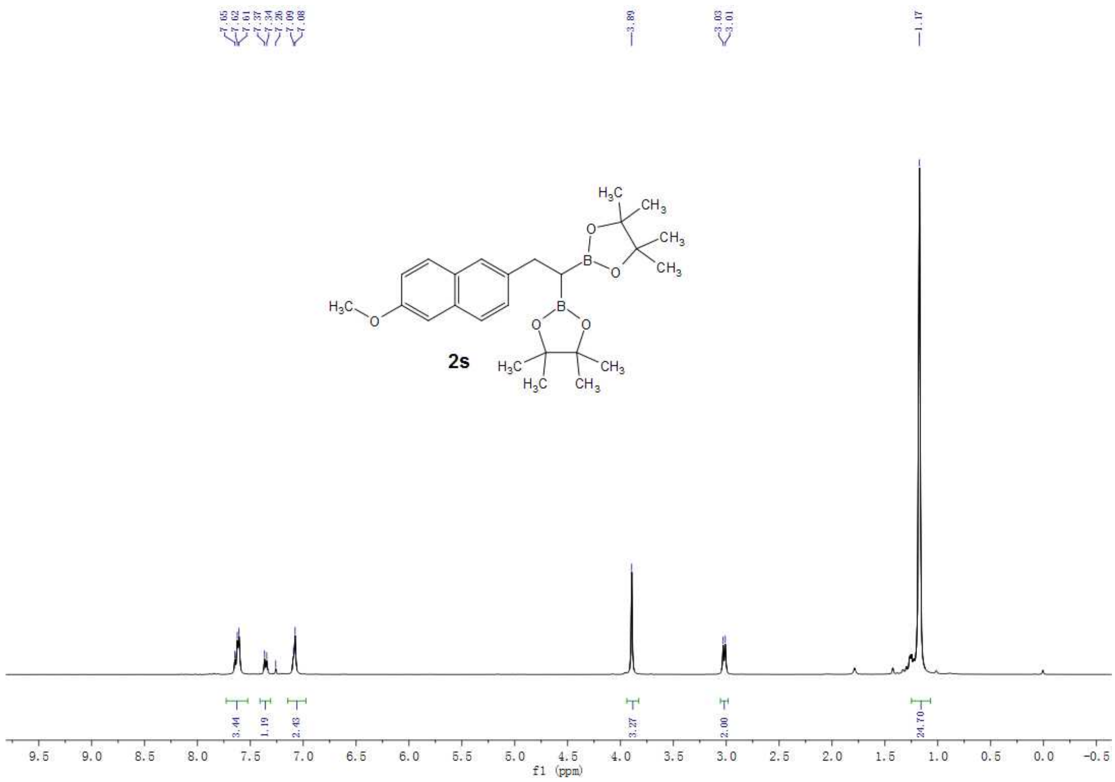
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2r**



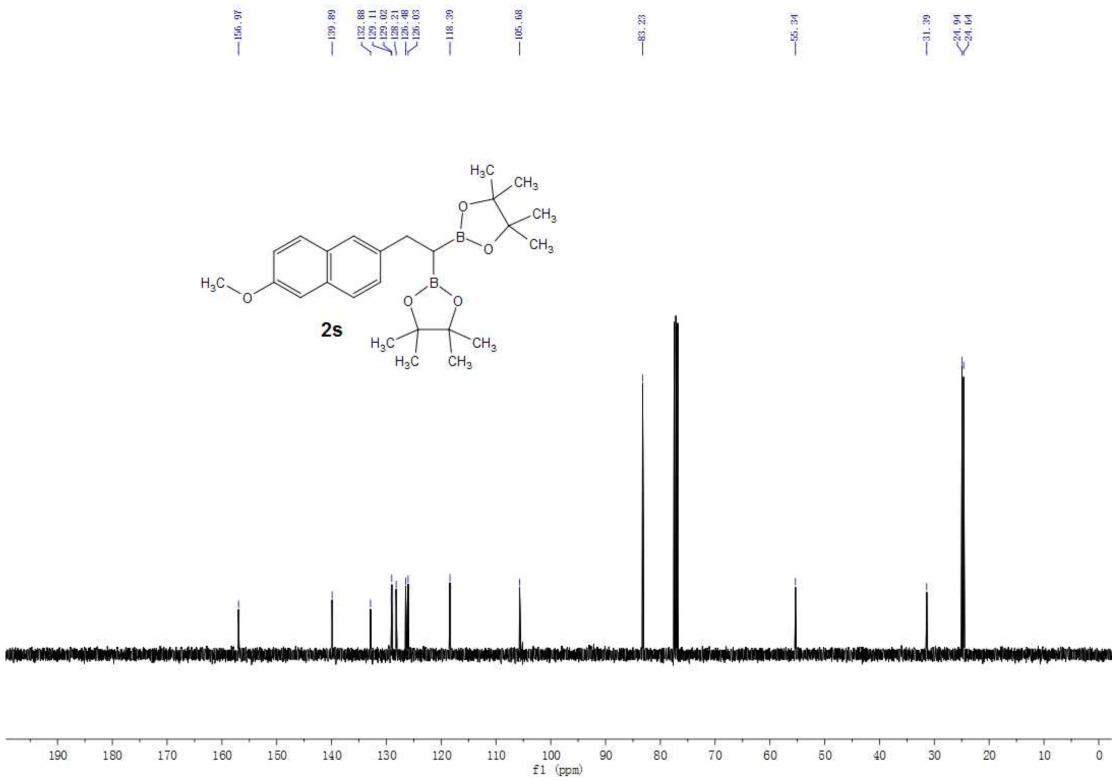
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2r**



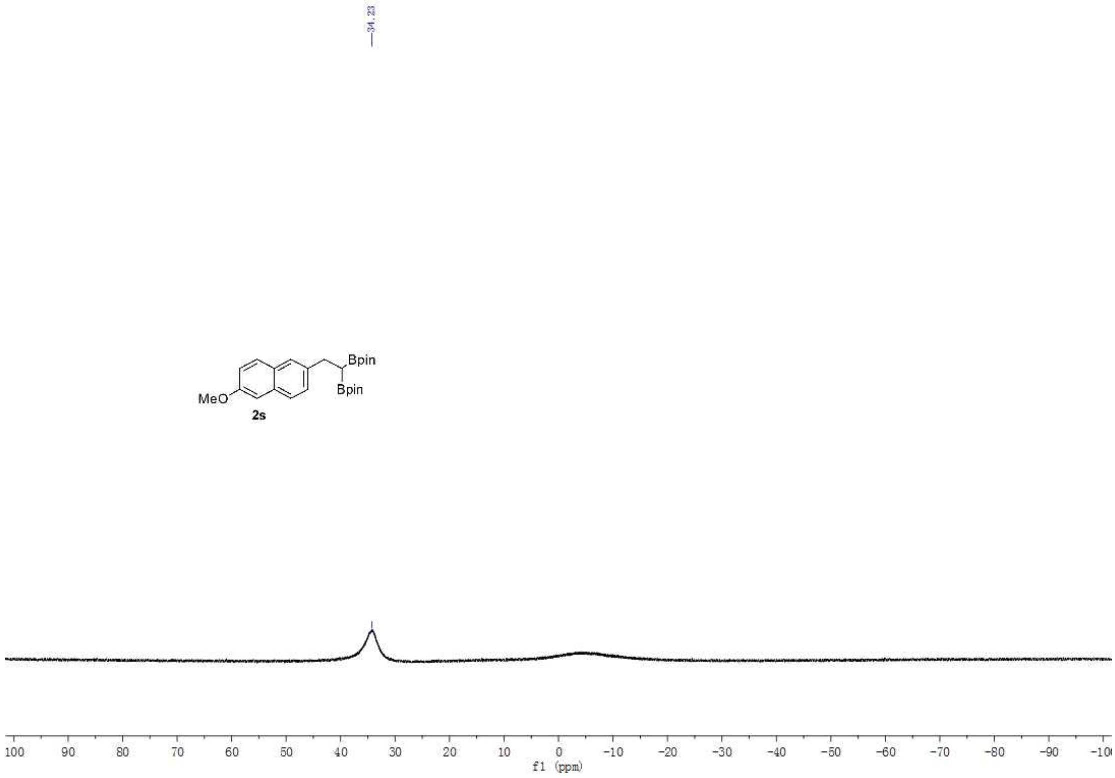
^{11}B NMR (192 MHz, EtOAc) spectrum of **2r**



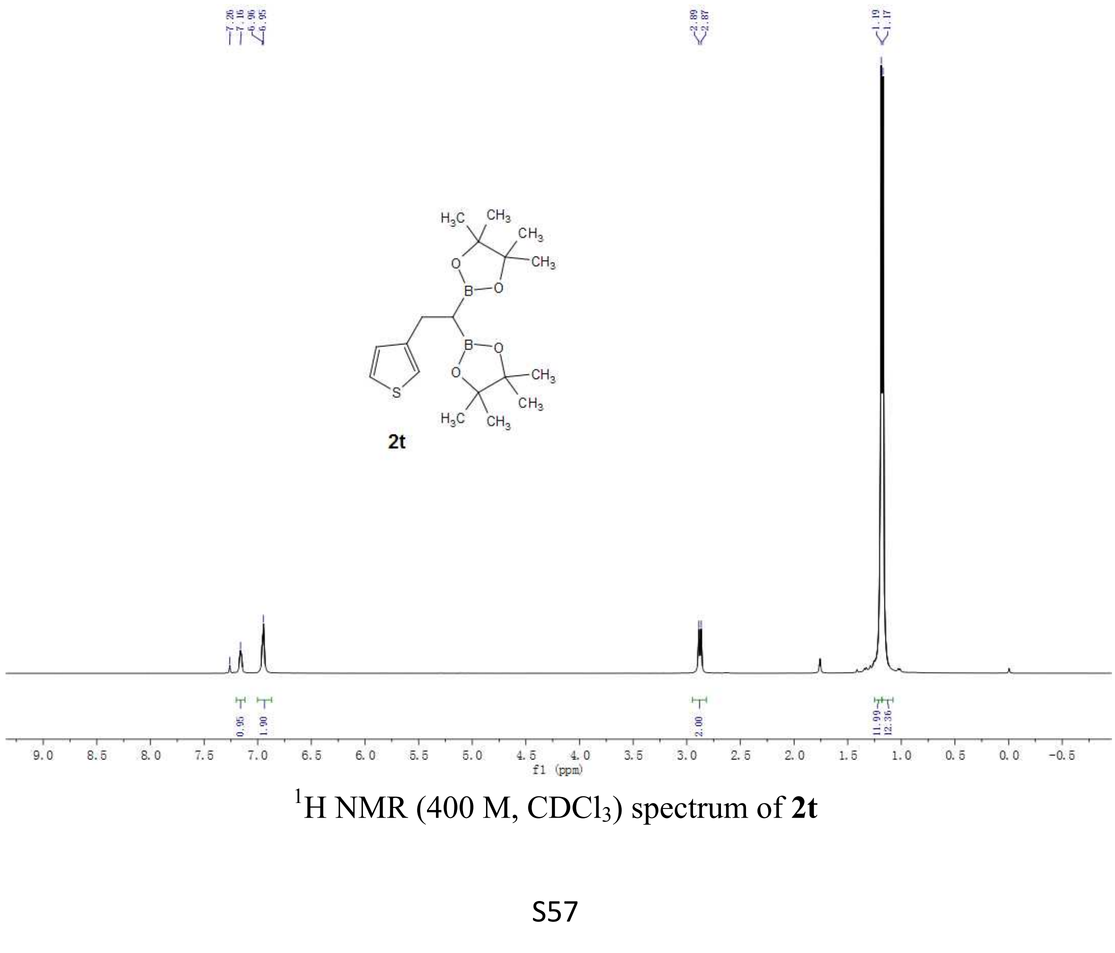
^1H NMR (400 M, $CDCl_3$) spectrum of **2s**



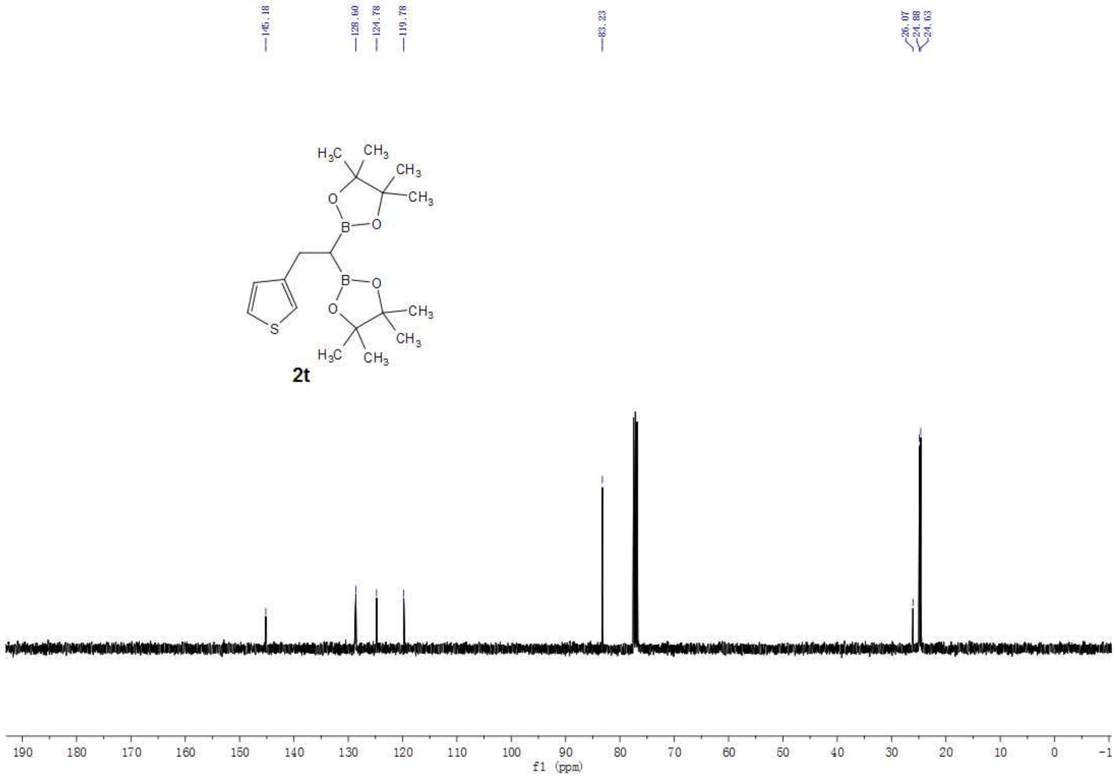
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2s**



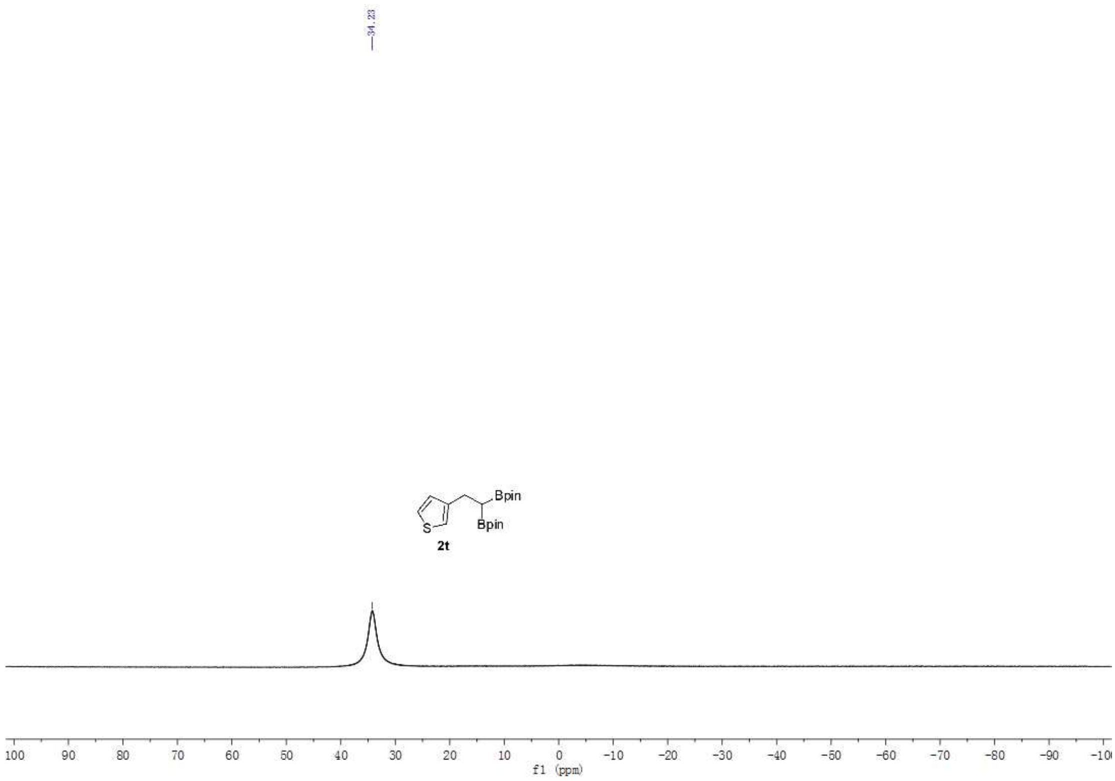
^{11}B NMR (192 MHz, EtOAc) spectrum of **2s**



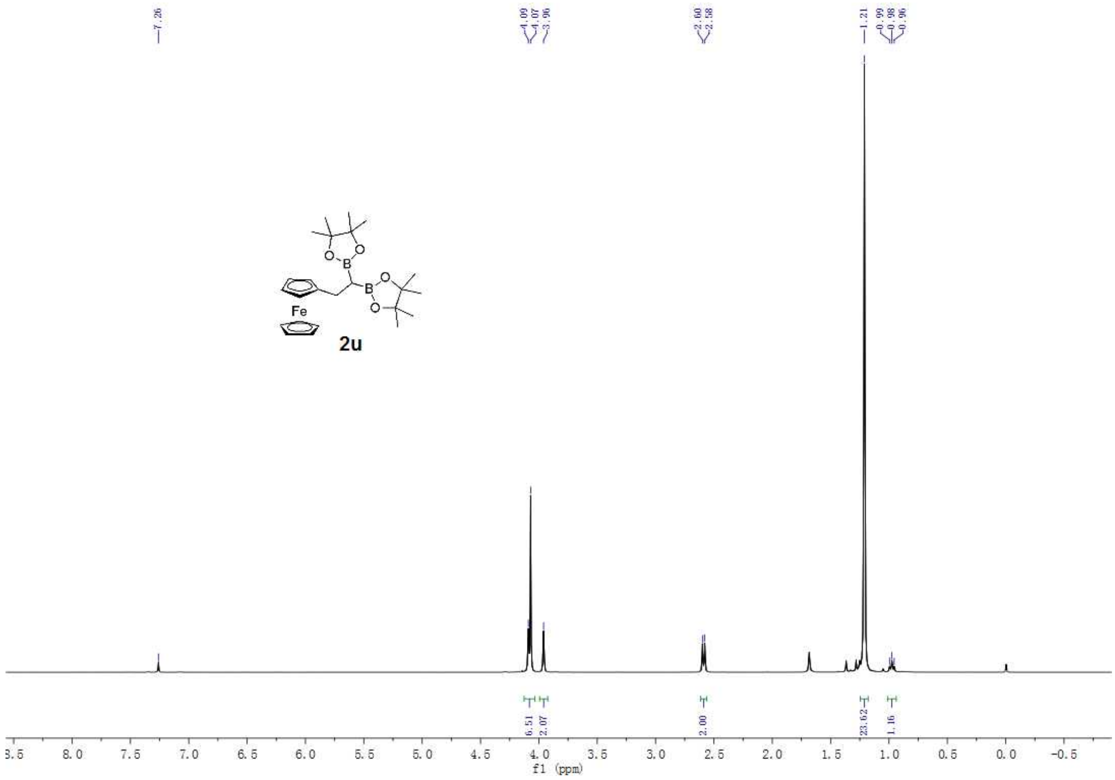
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2t**



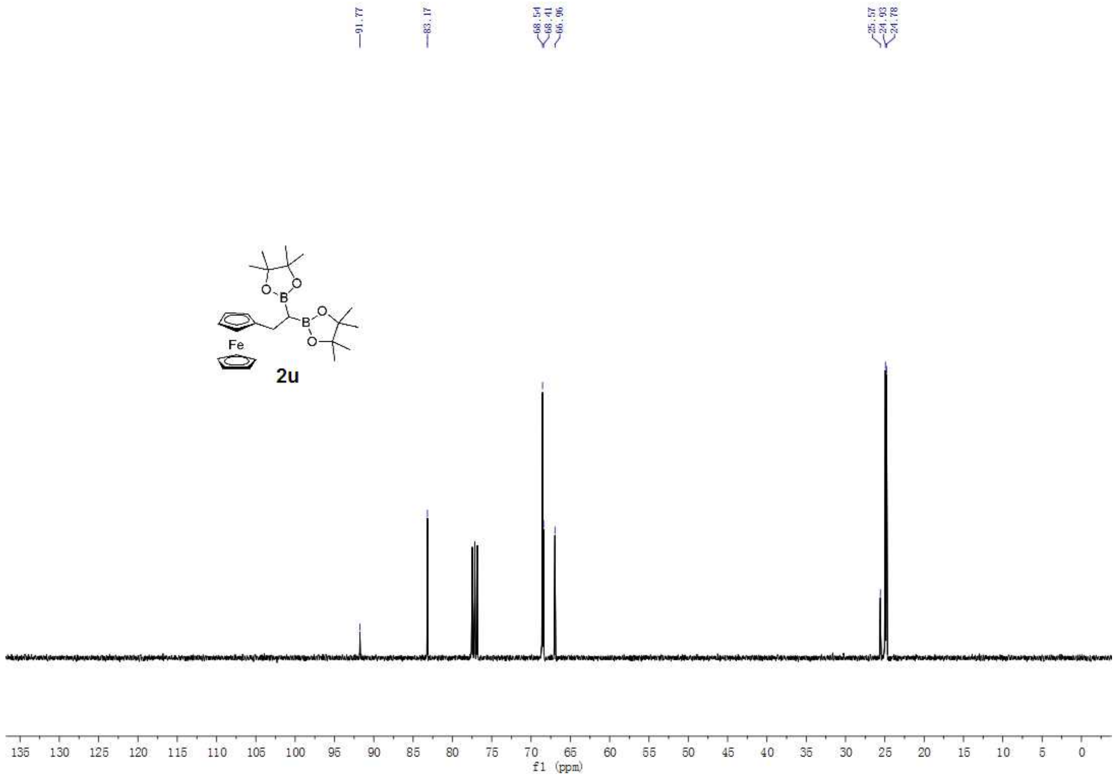
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2t**



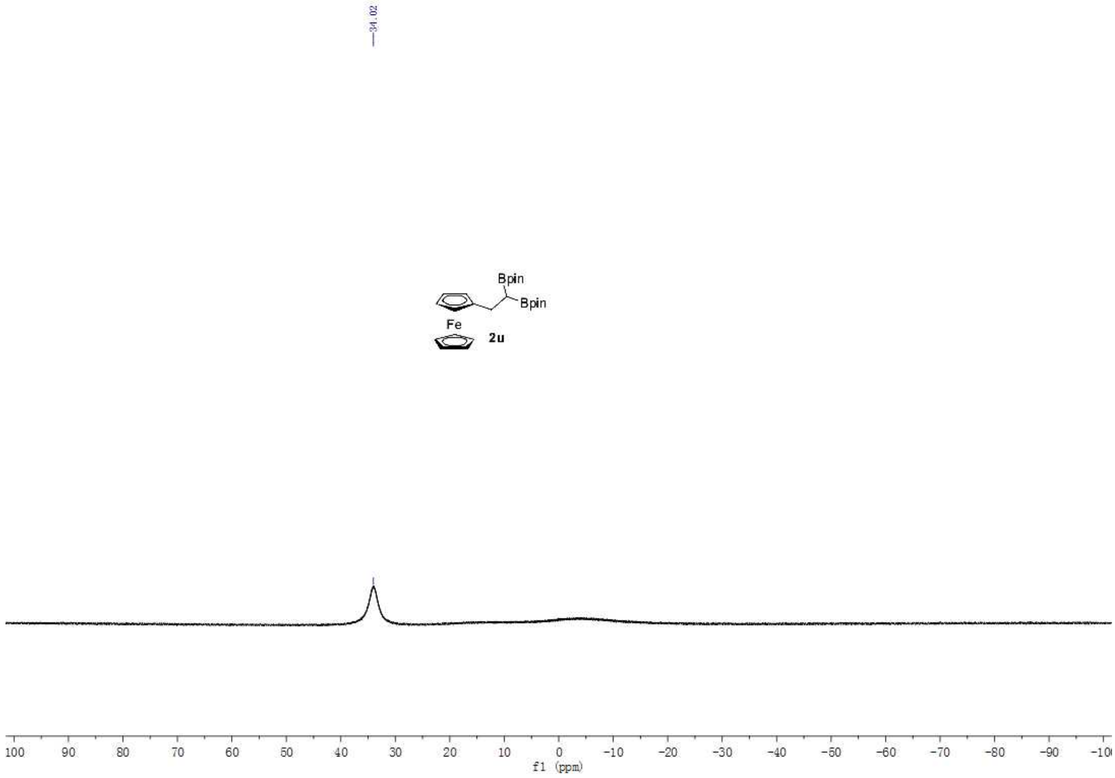
^{11}B NMR (192 MHz, EtOAc) spectrum of **2t**



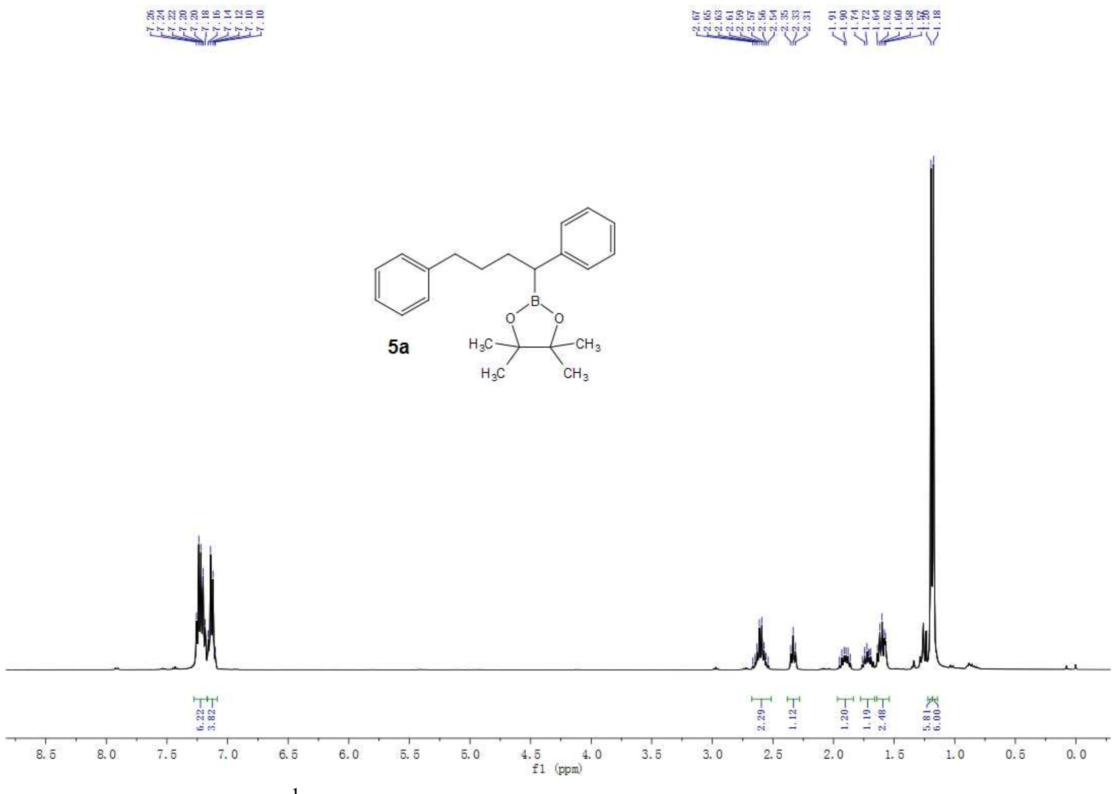
^{1}H NMR (400 M, $CDCl_3$) spectrum of **2u**



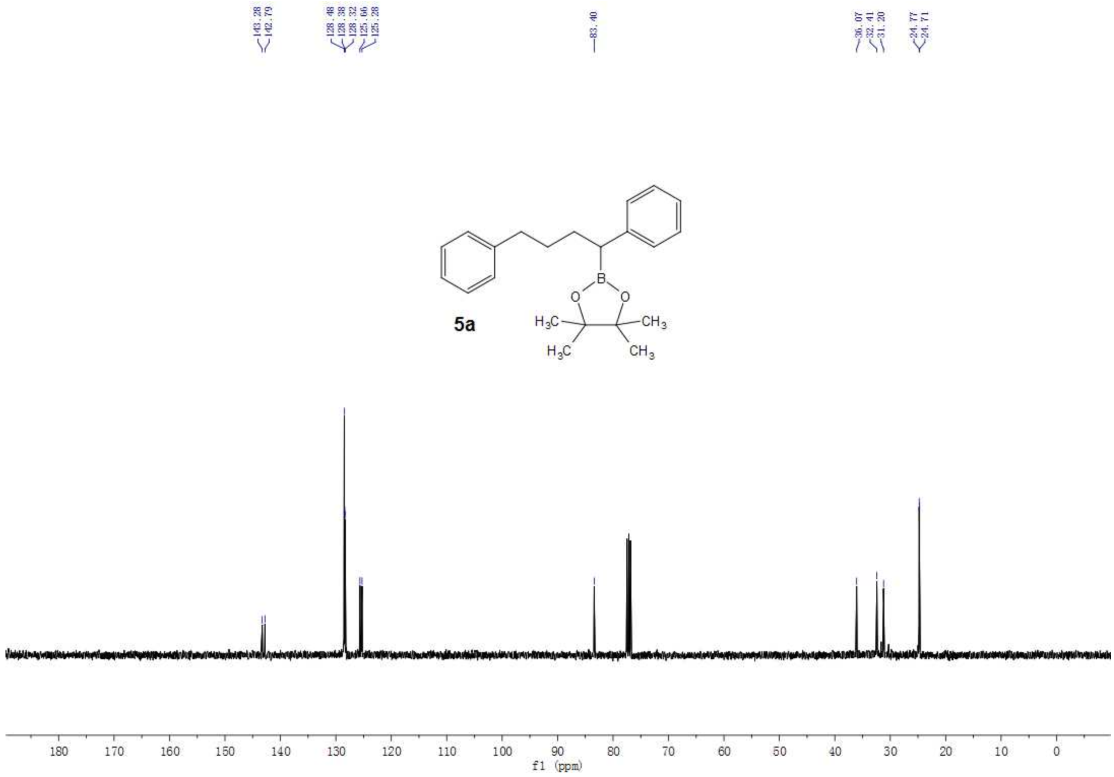
^{13}C NMR (101 M, $CDCl_3$) spectrum of **2u**



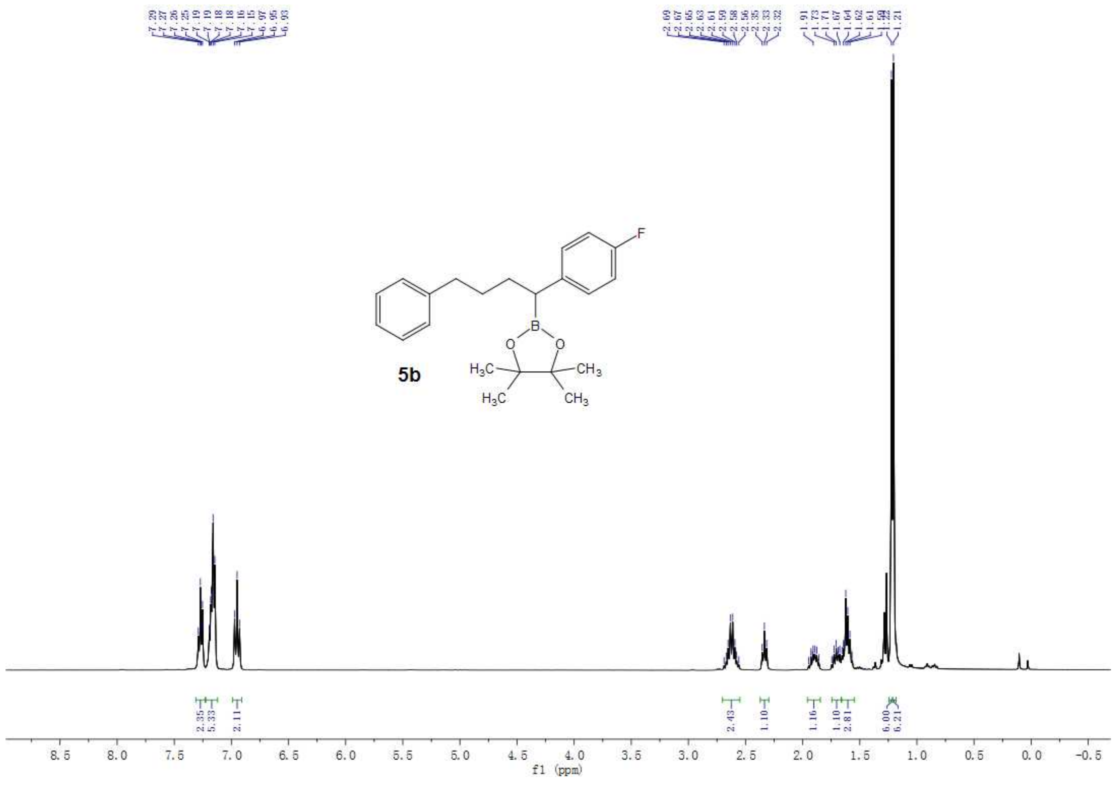
^{11}B NMR (192 MHz, EtOAc) spectrum of **2u**



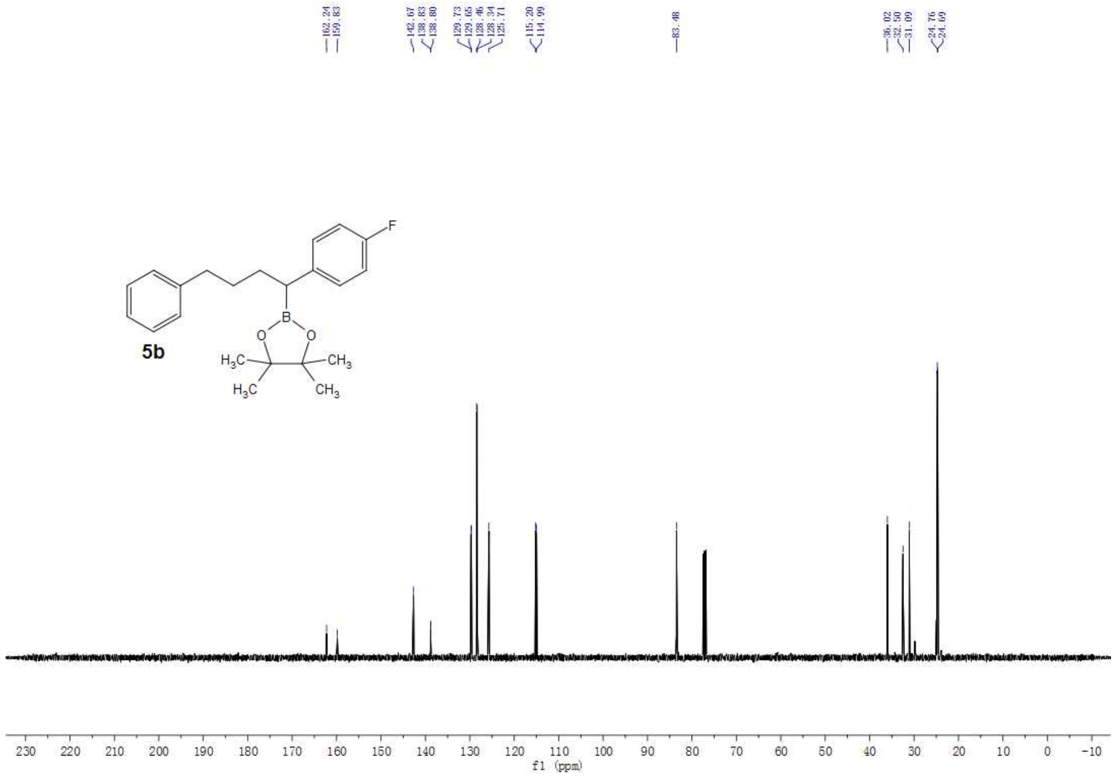
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5a**



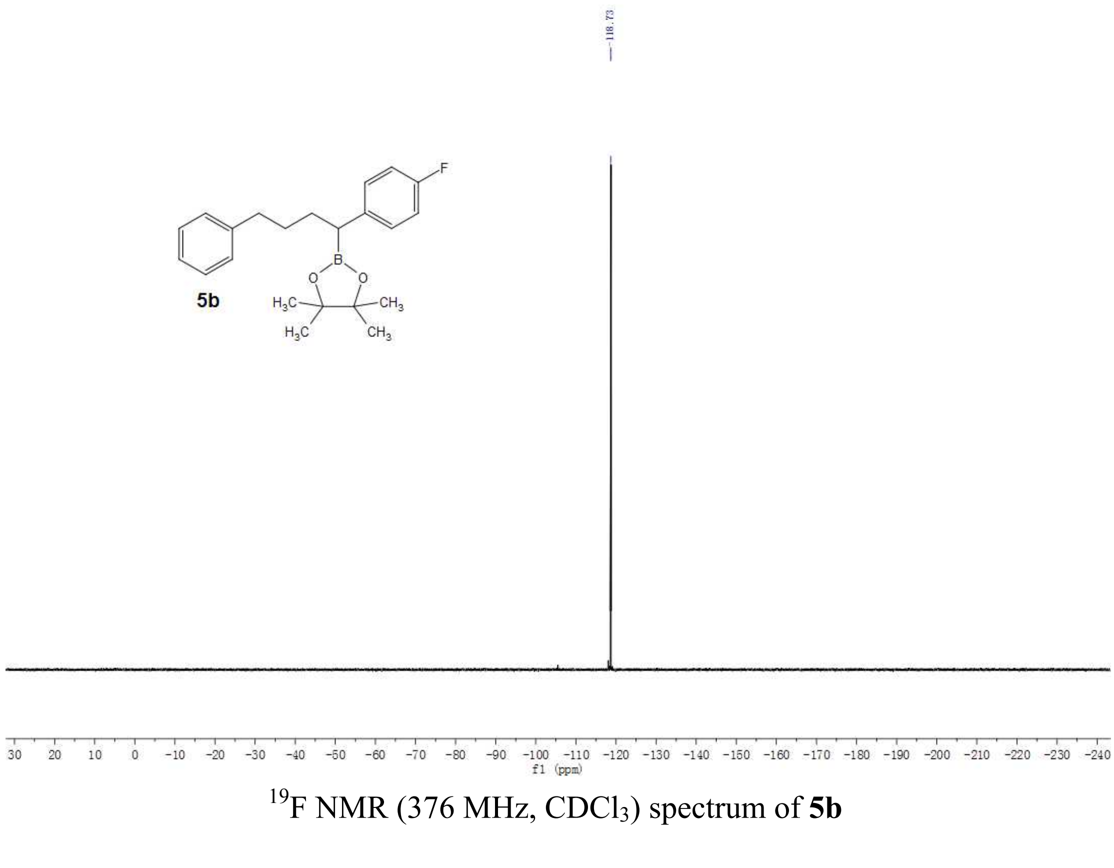
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5a**



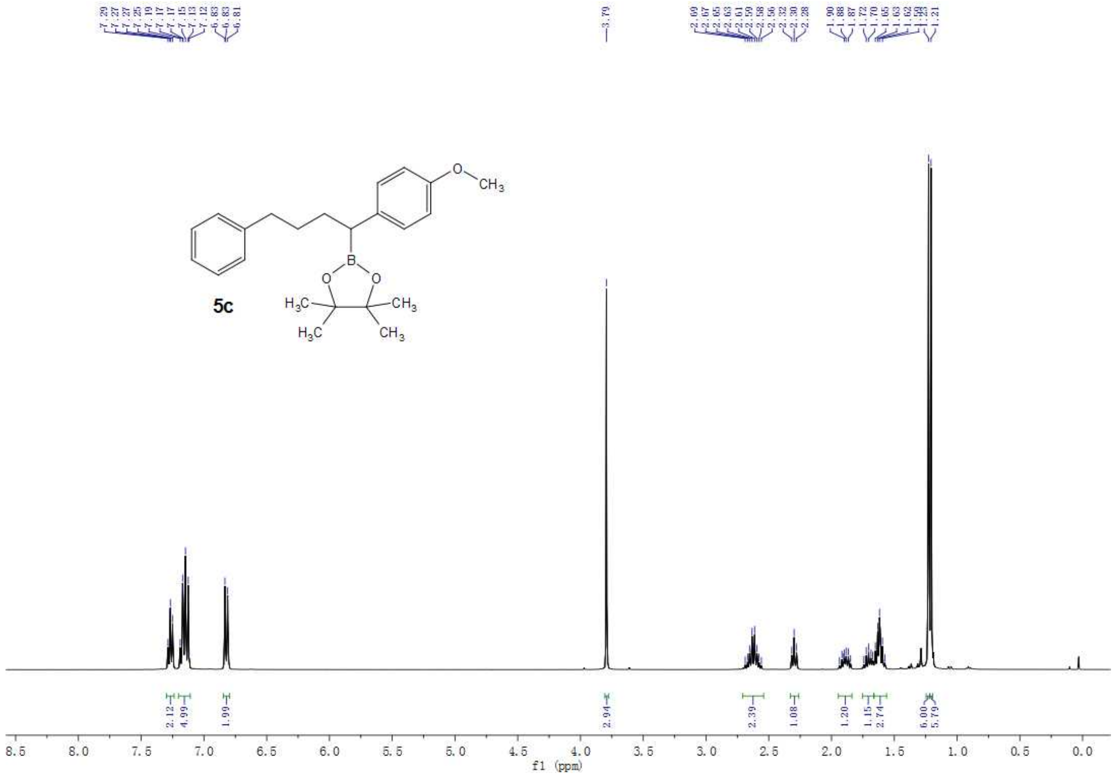
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5b**



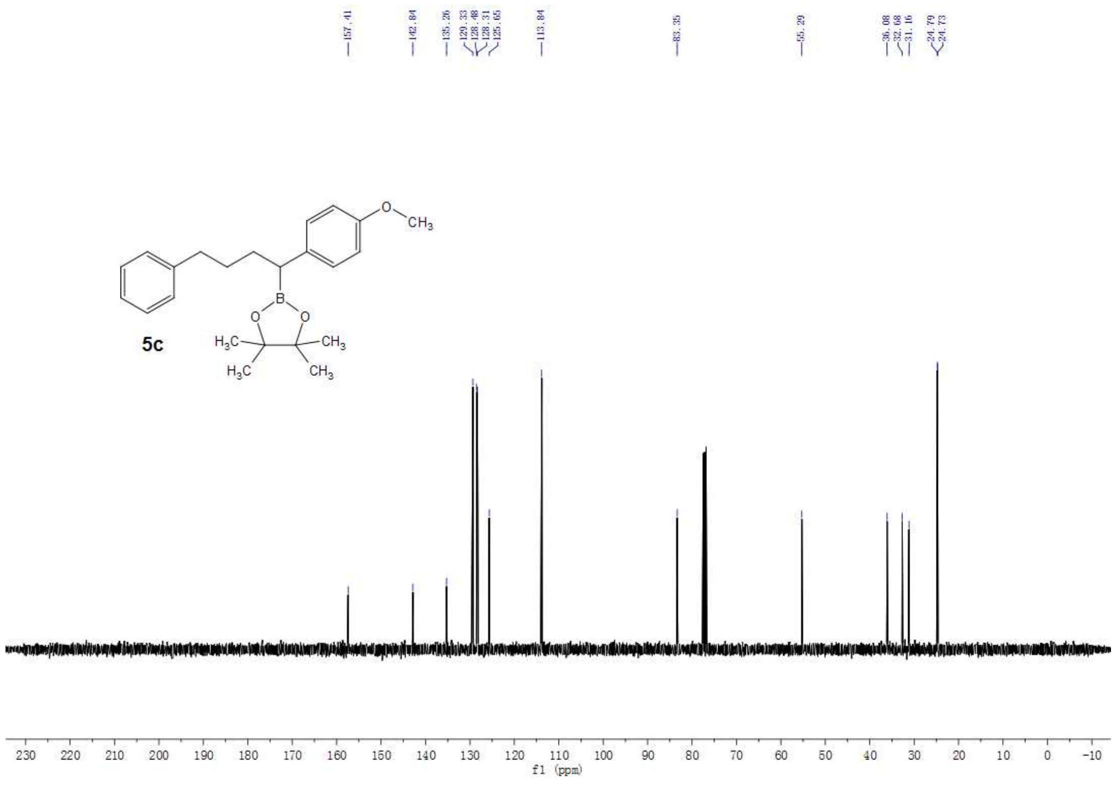
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5b**



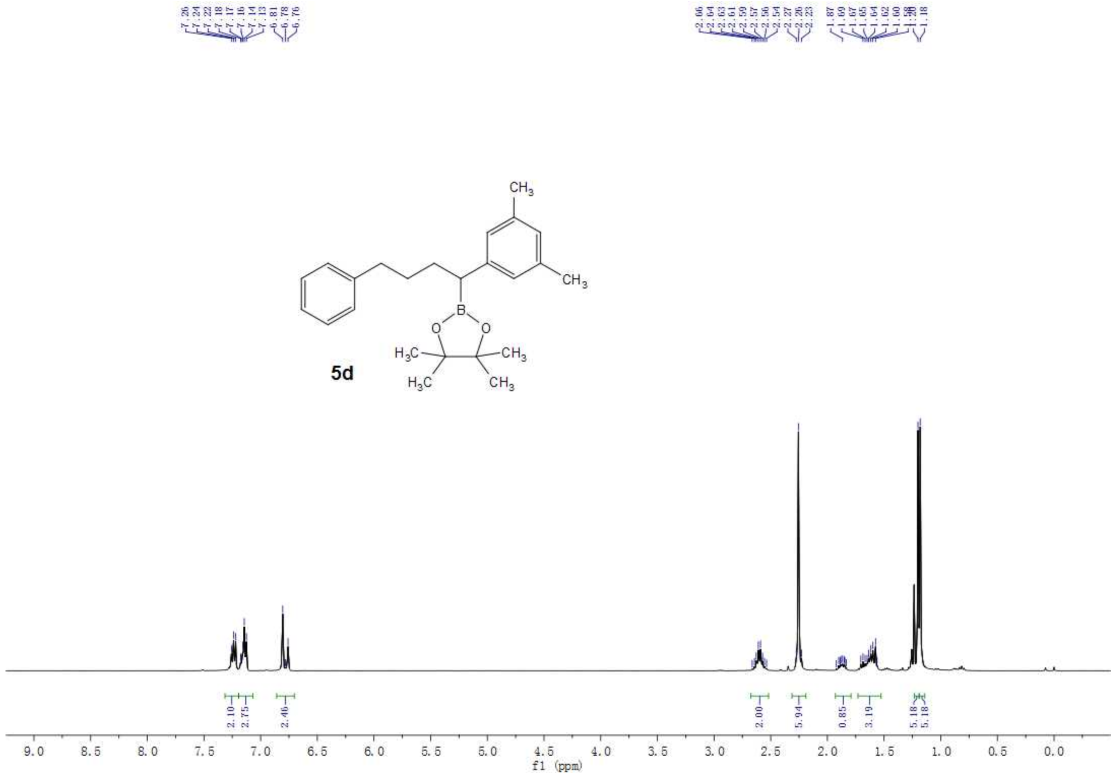
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **5b**



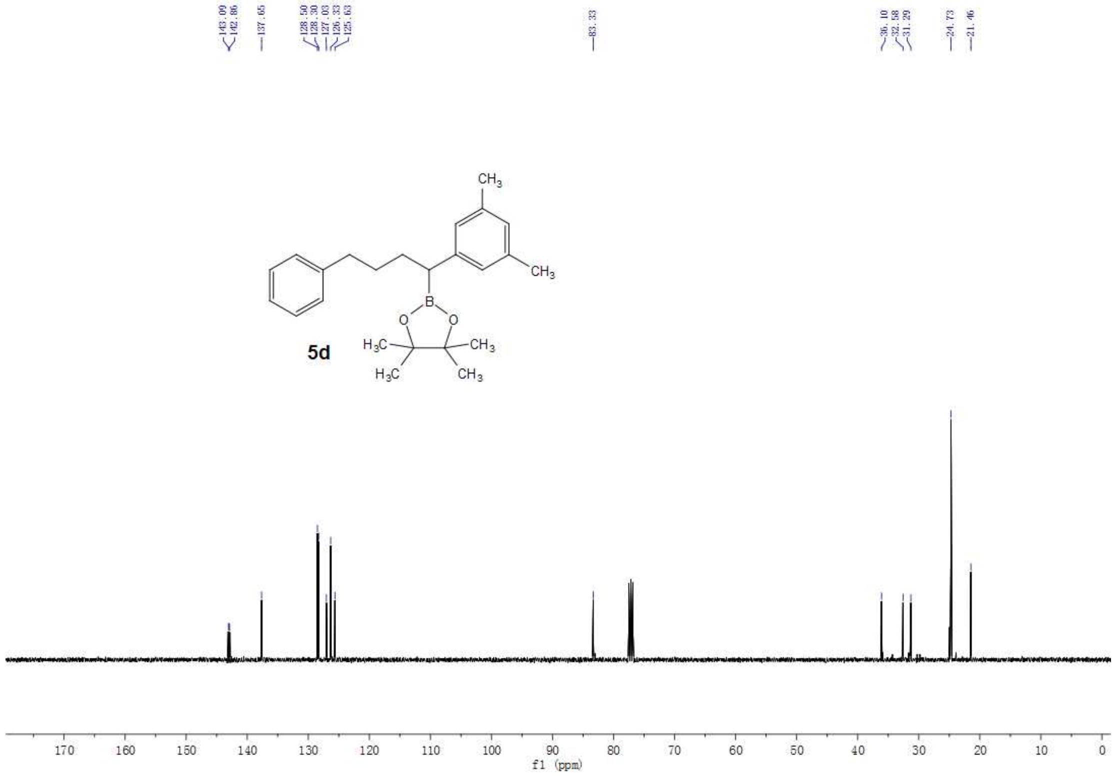
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5c**



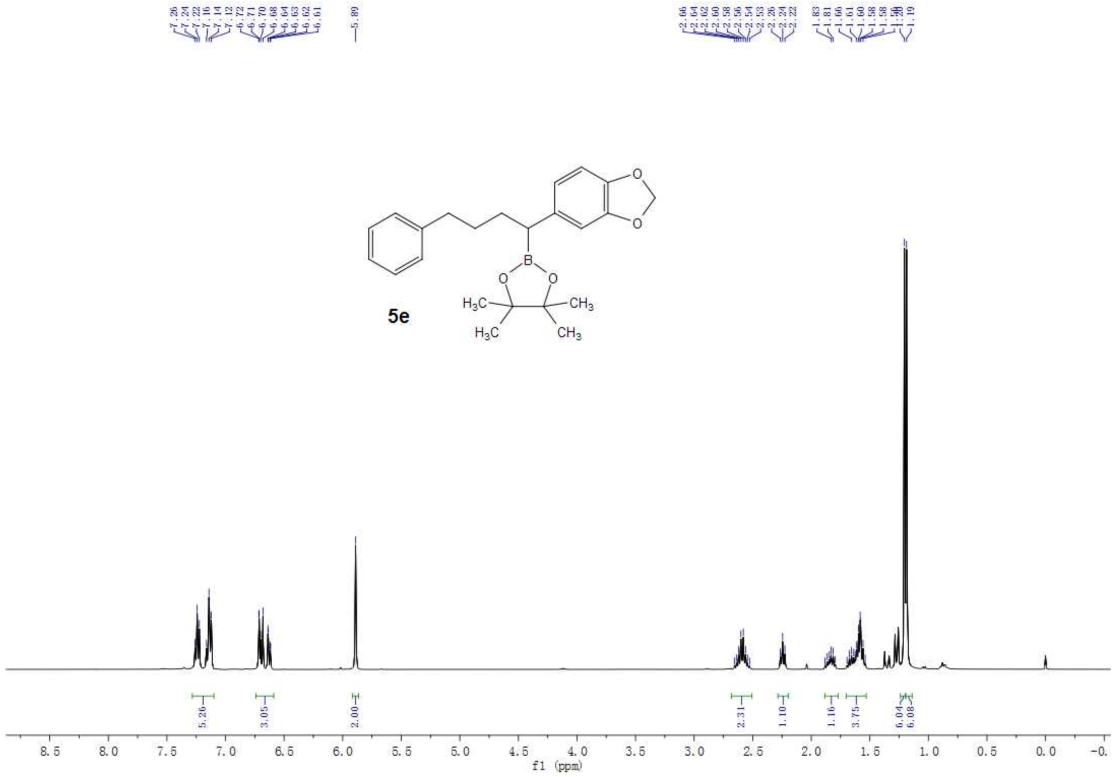
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5c**



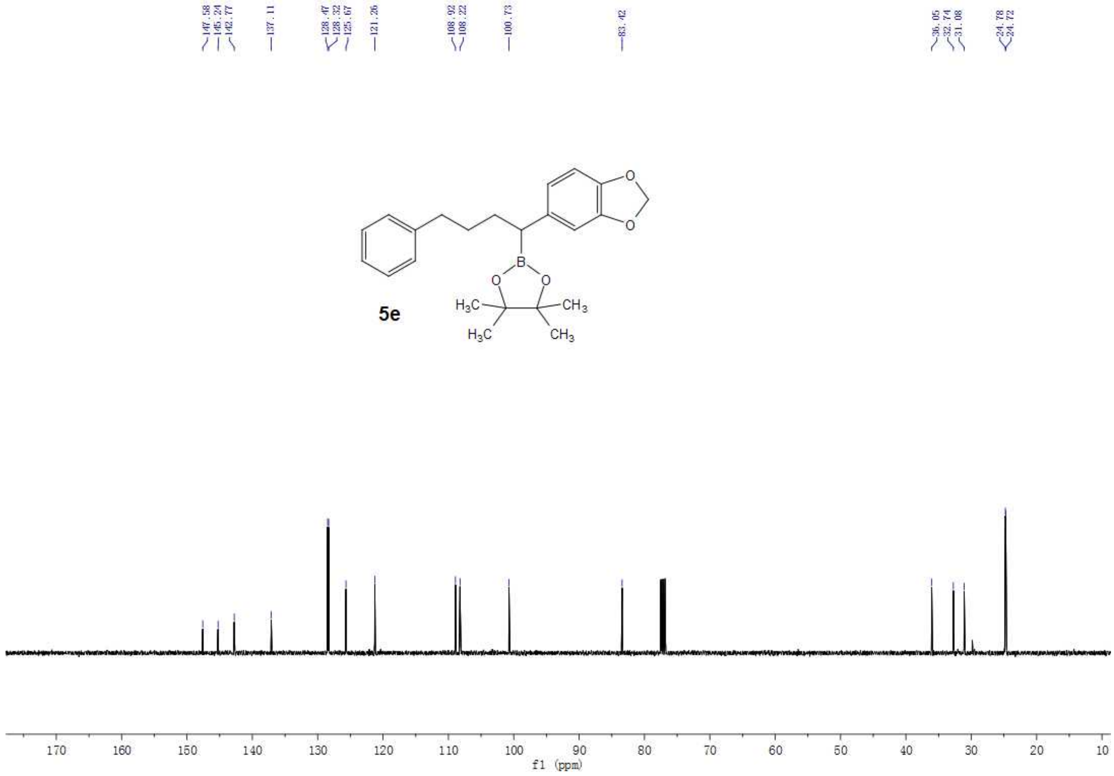
[1]H NMR (400 M, $CDCl_3$) spectrum of **5d**



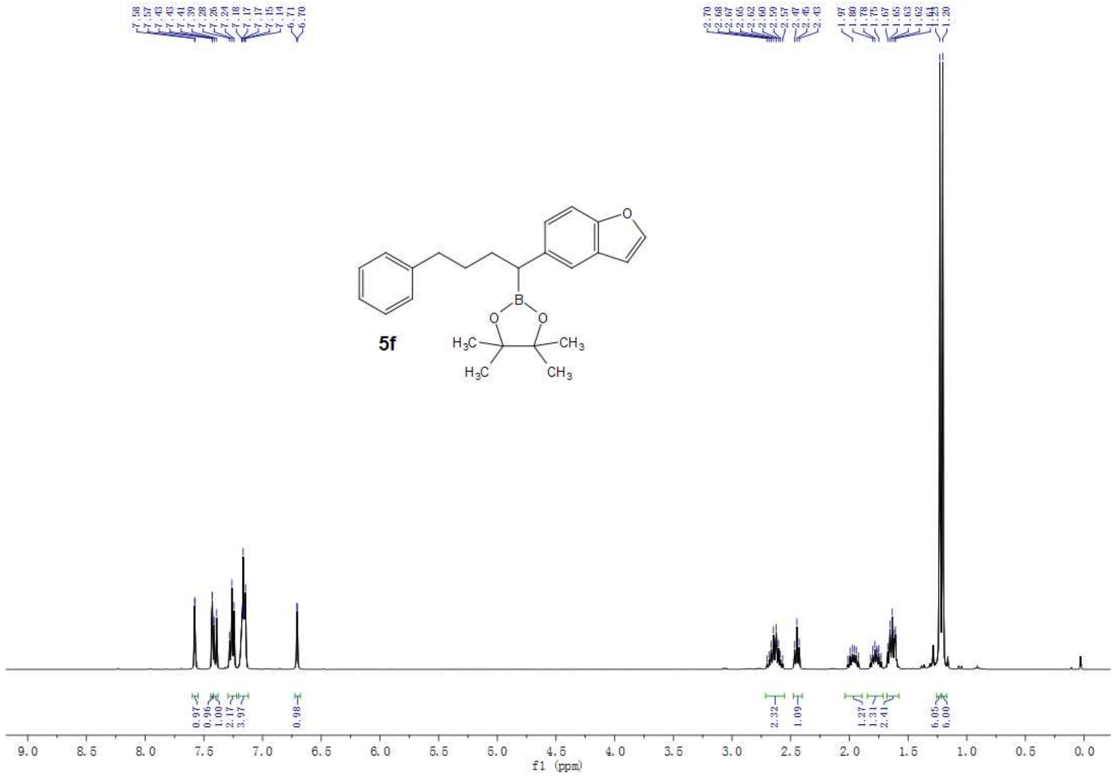
[13]C NMR (101 M, $CDCl_3$) spectrum of **5d**



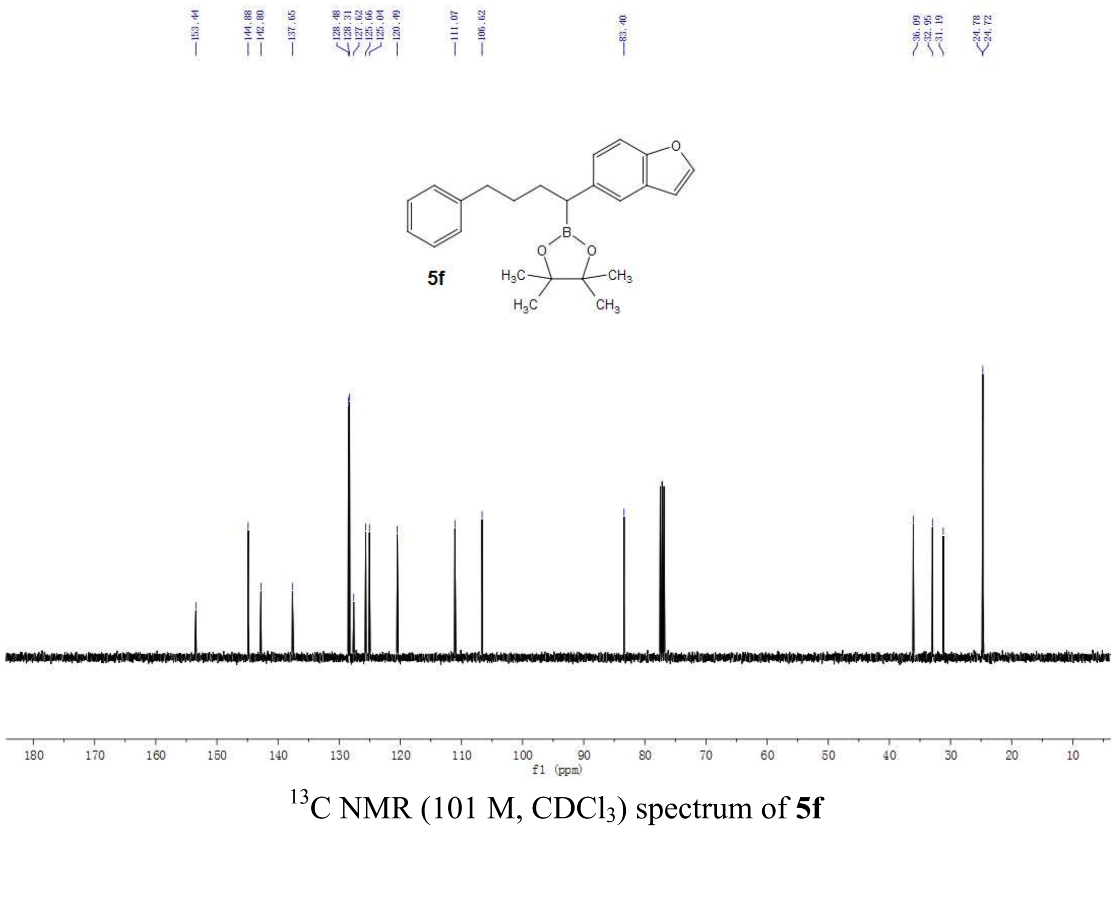
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5e**



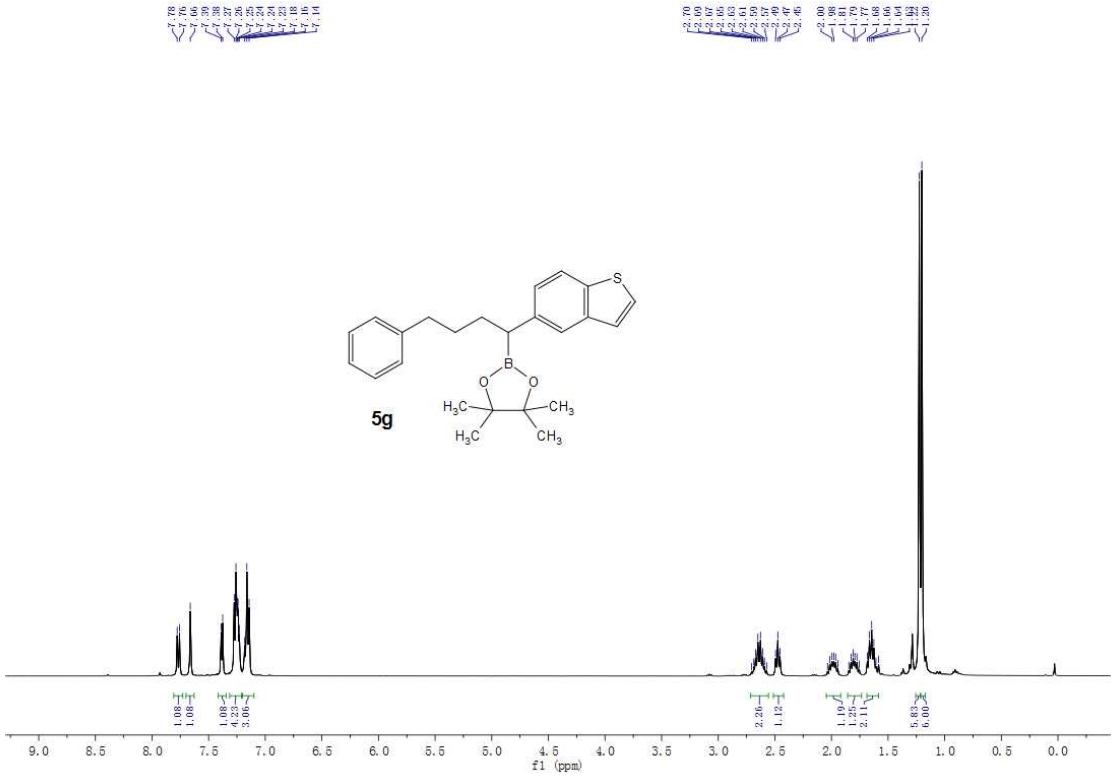
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5e**



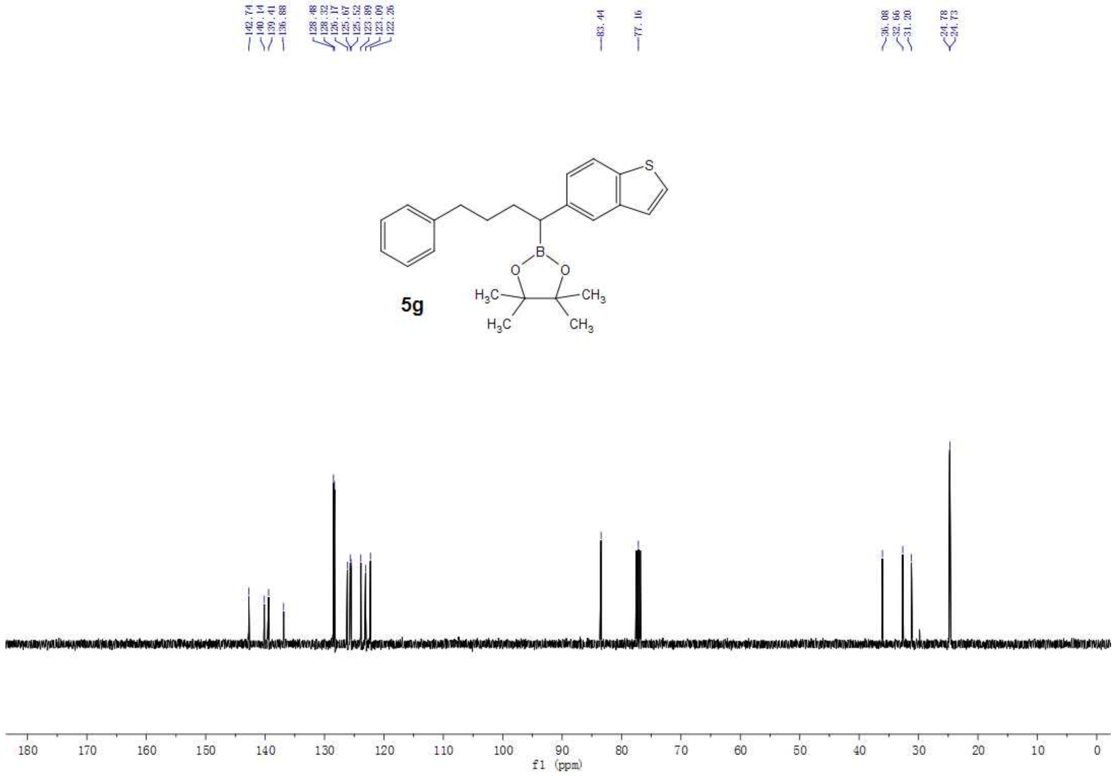
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5f**



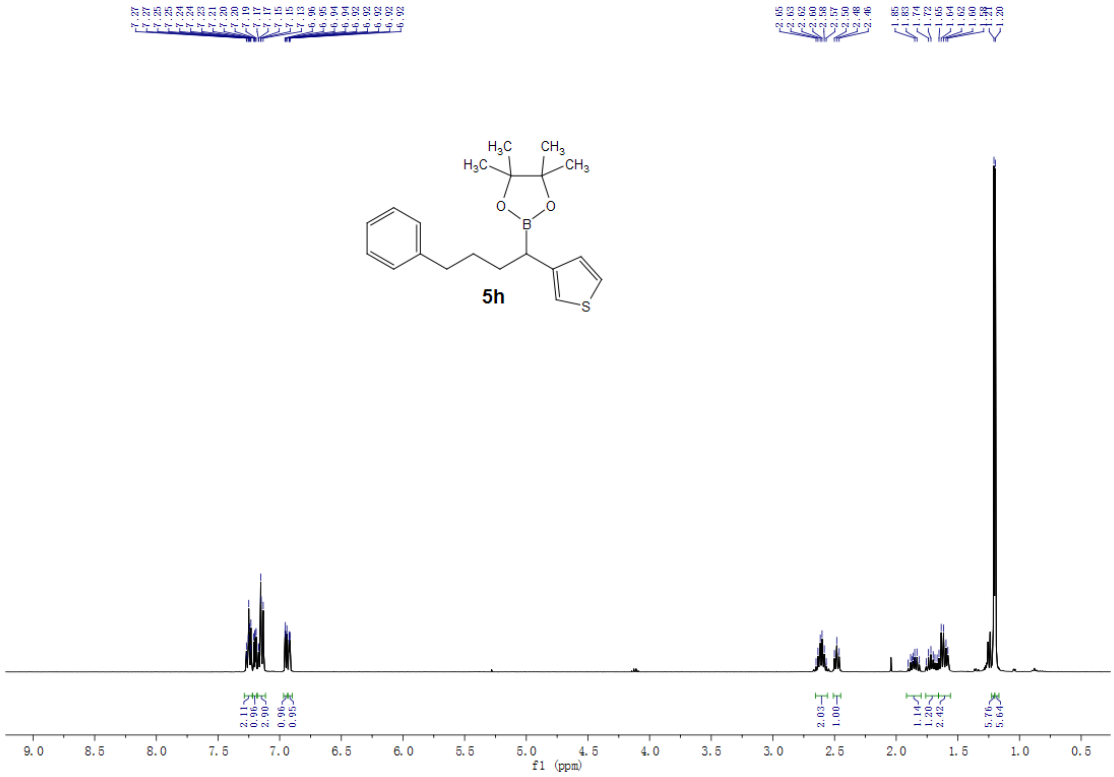
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5f**



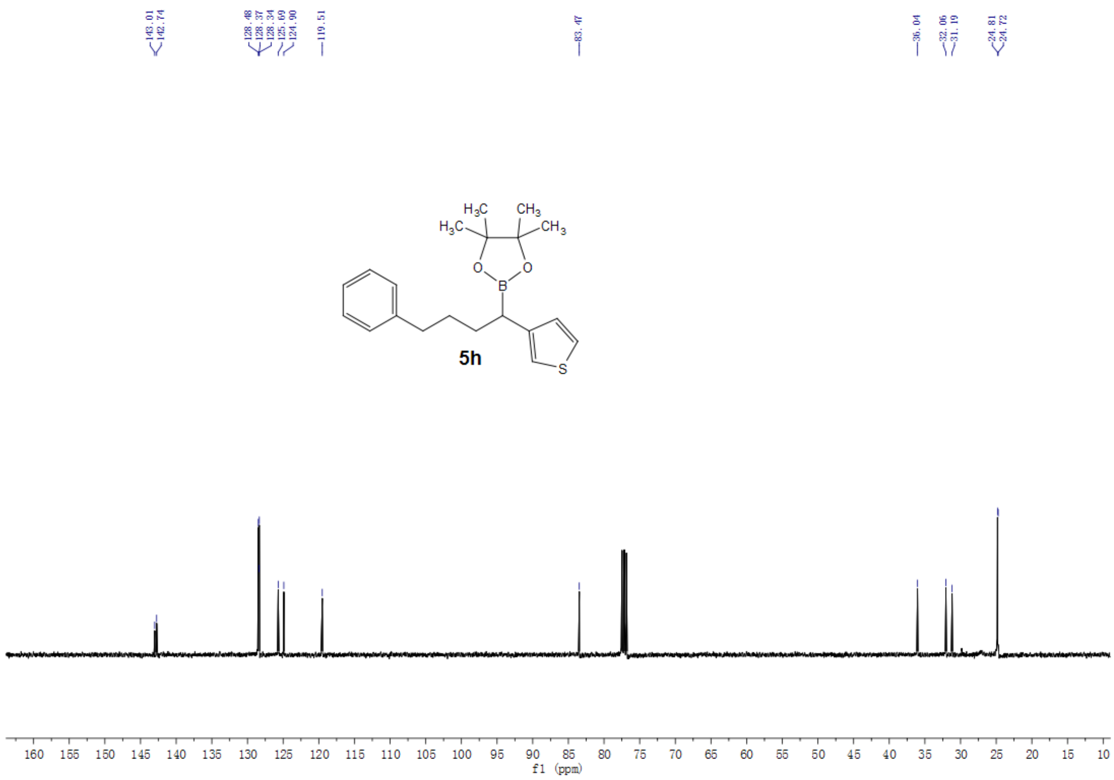
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5g**



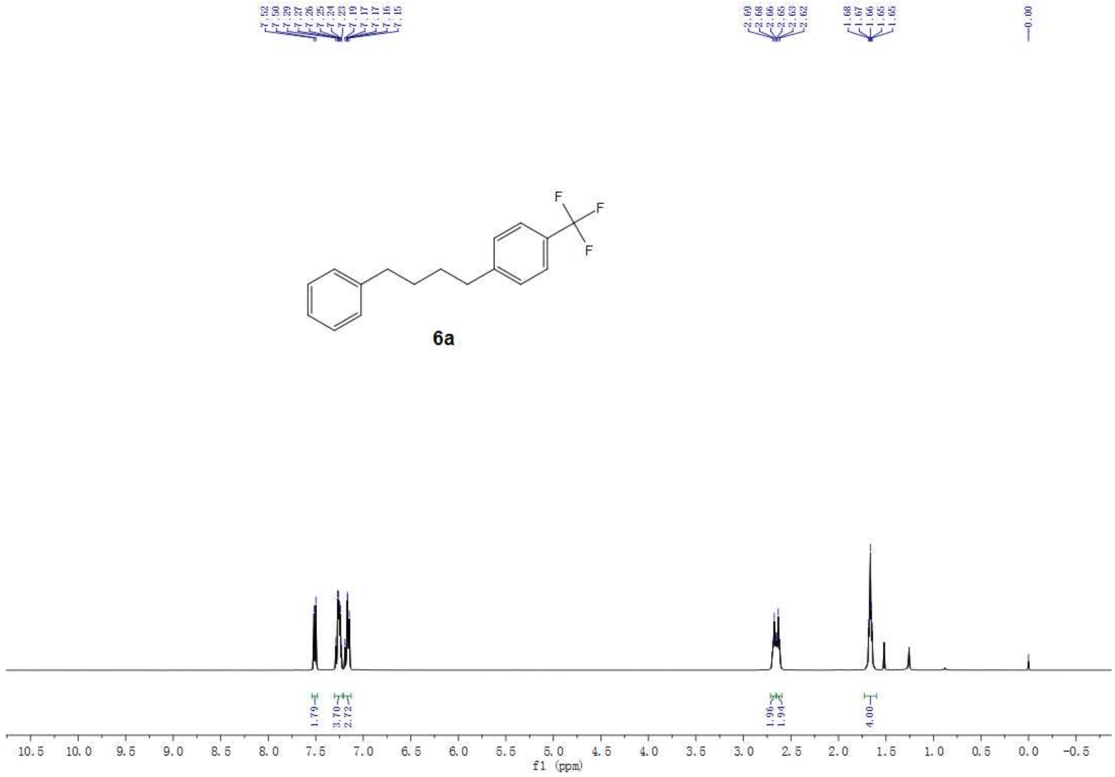
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5g**



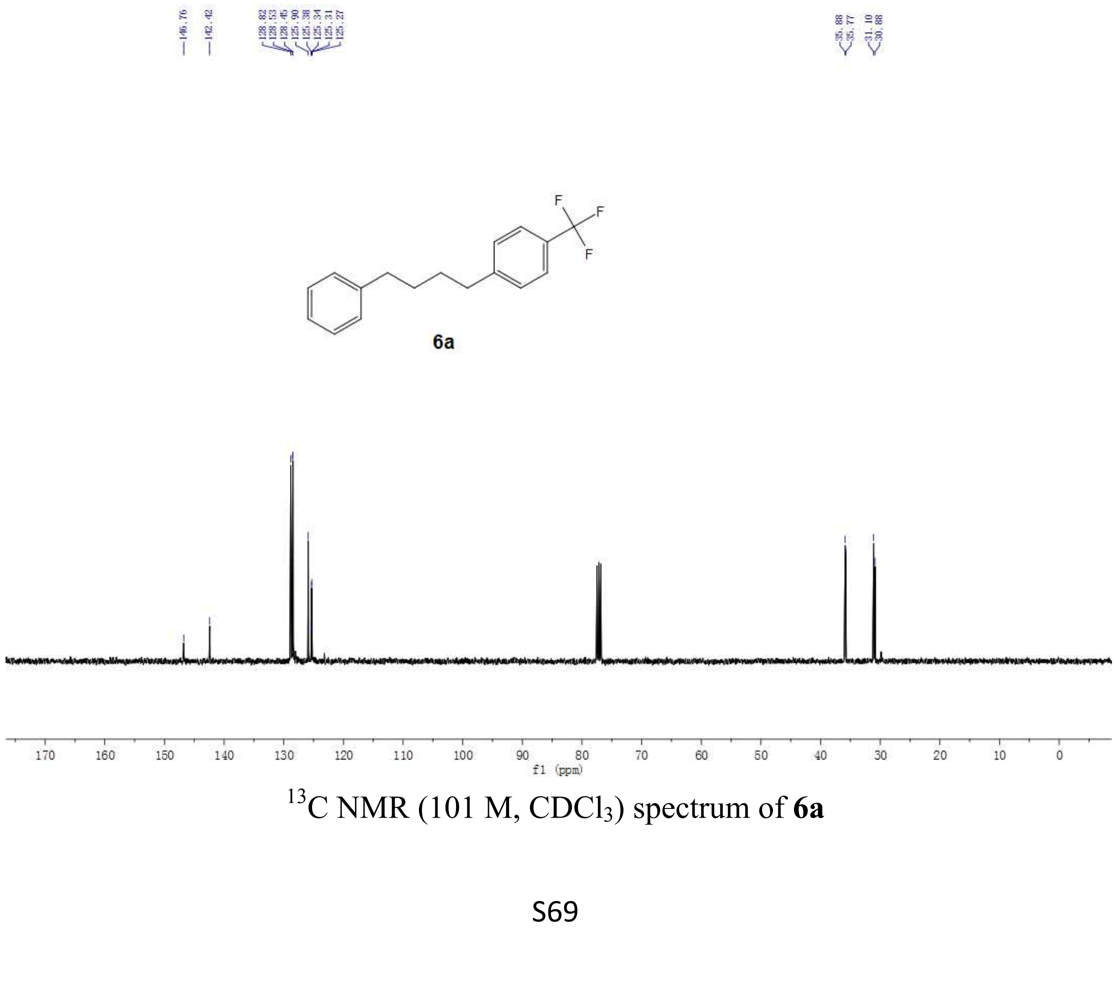
^{1}H NMR (400 M, $CDCl_3$) spectrum of **5h**



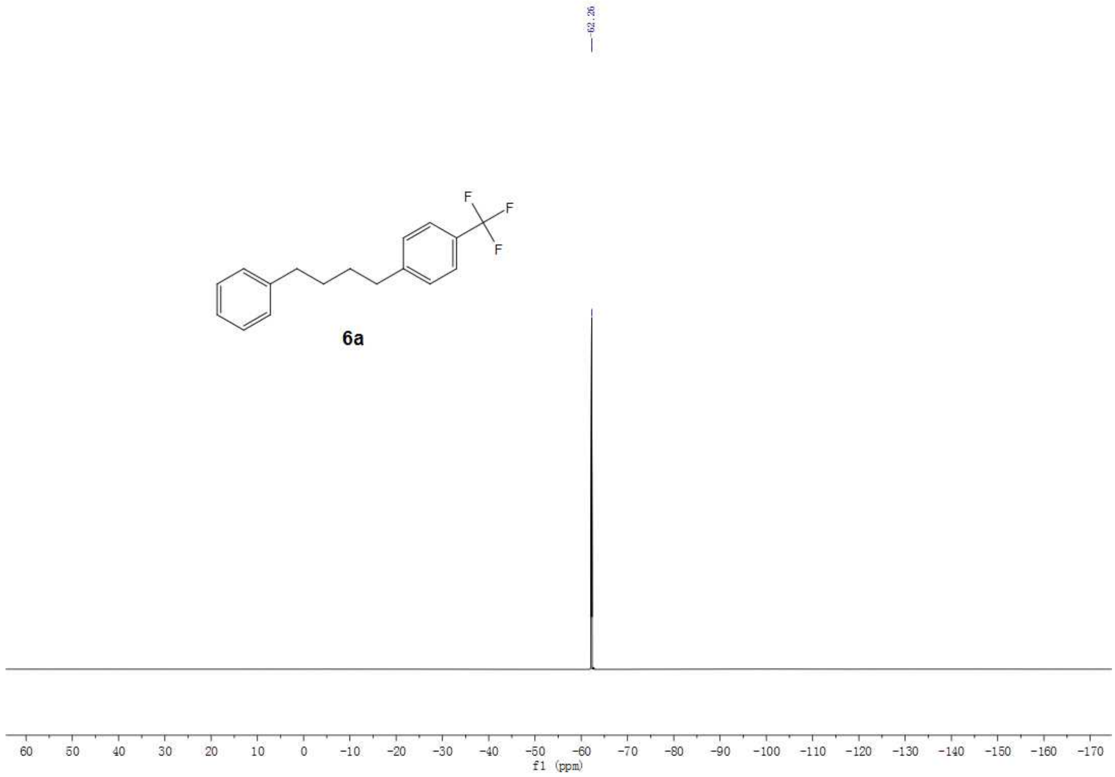
^{13}C NMR (101 M, $CDCl_3$) spectrum of **5h**



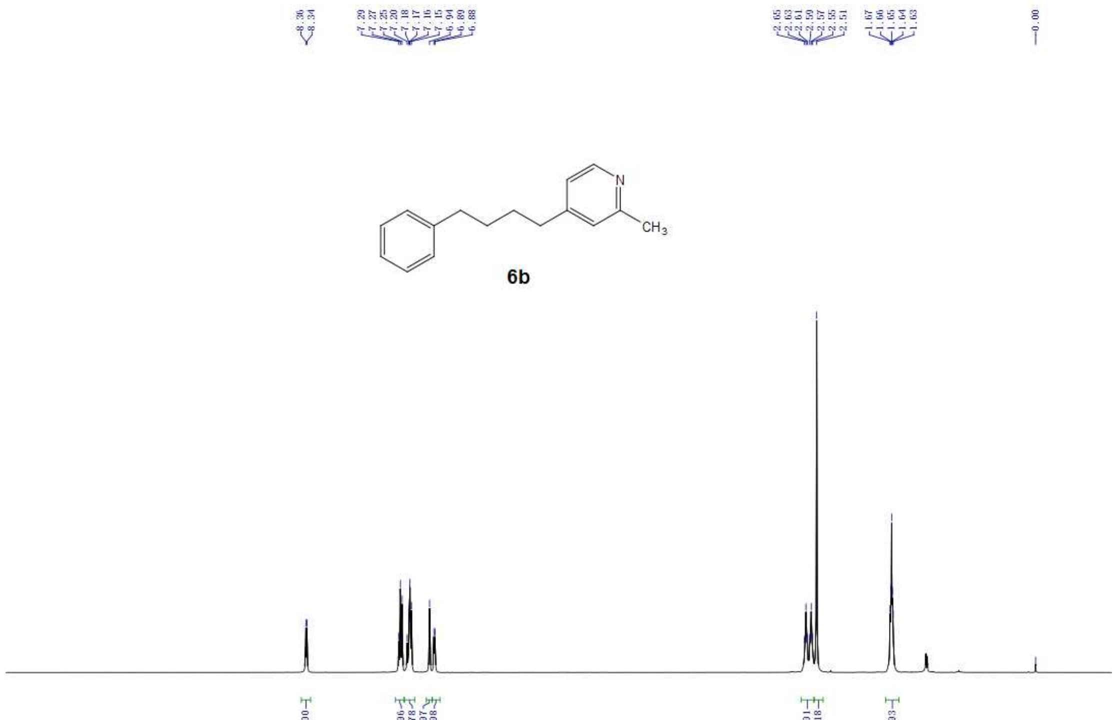
^{1}H NMR (400 M, $CDCl_3$) spectrum of **6a**



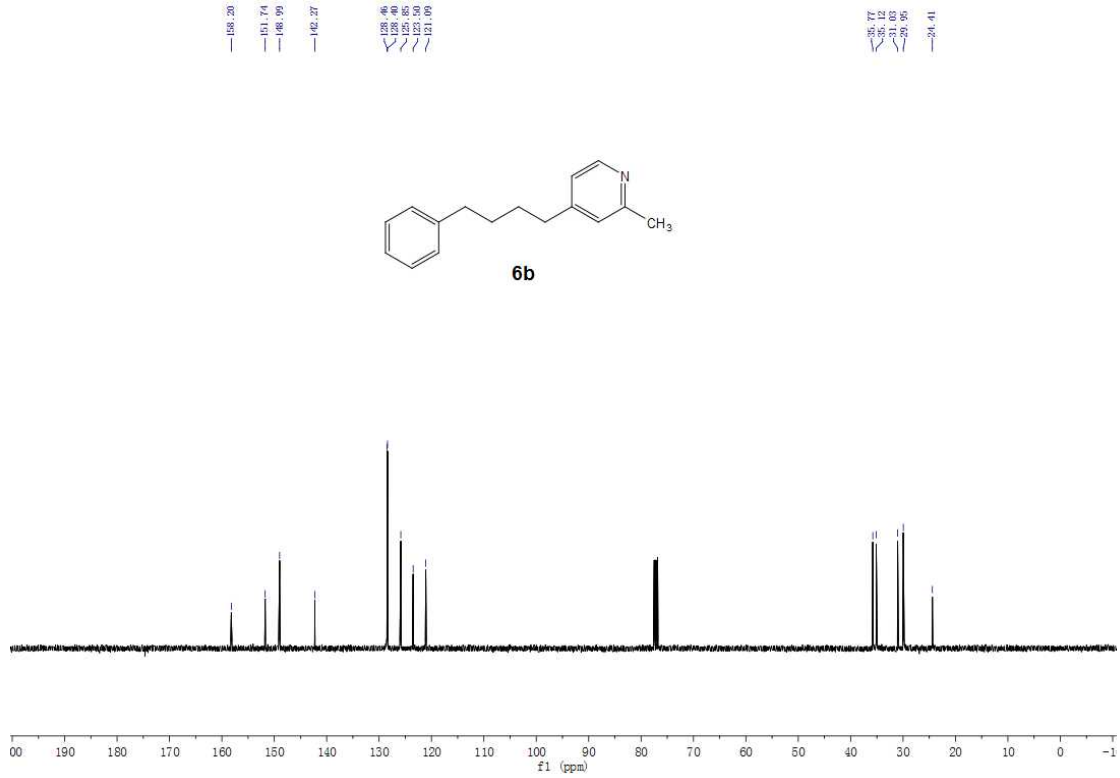
^{13}C NMR (101 M, $CDCl_3$) spectrum of **6a**



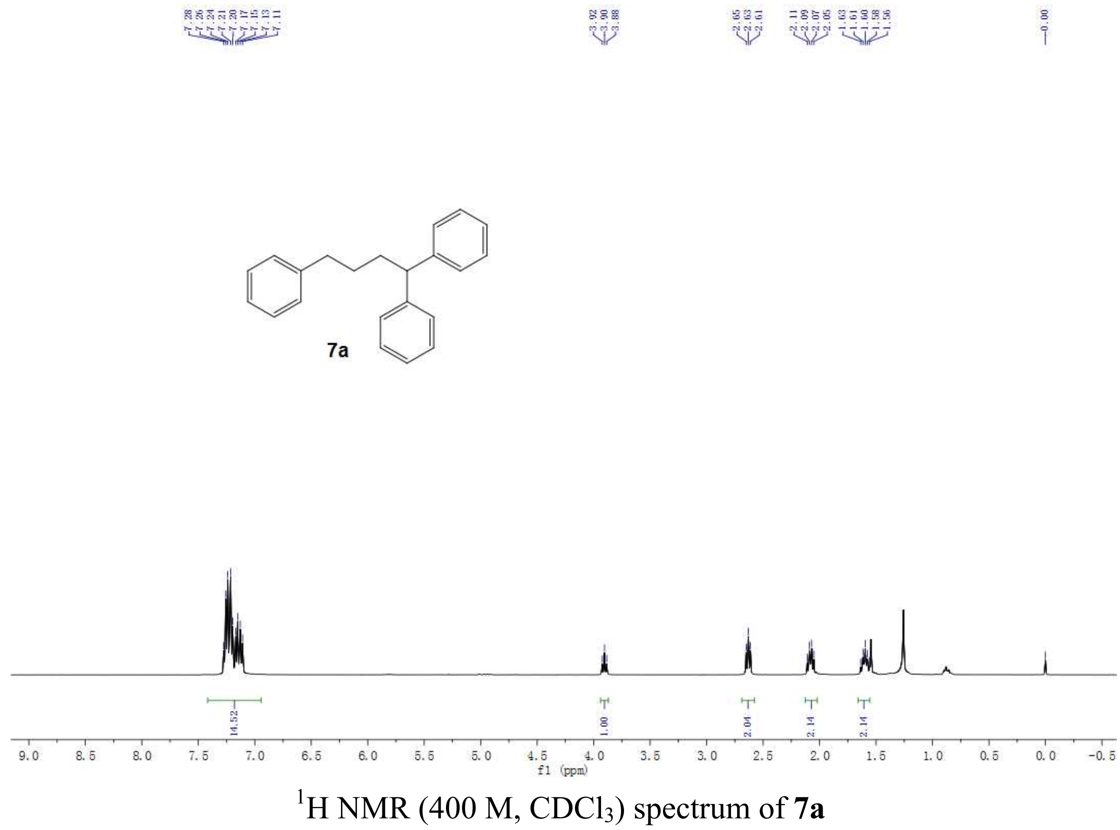
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **6a**



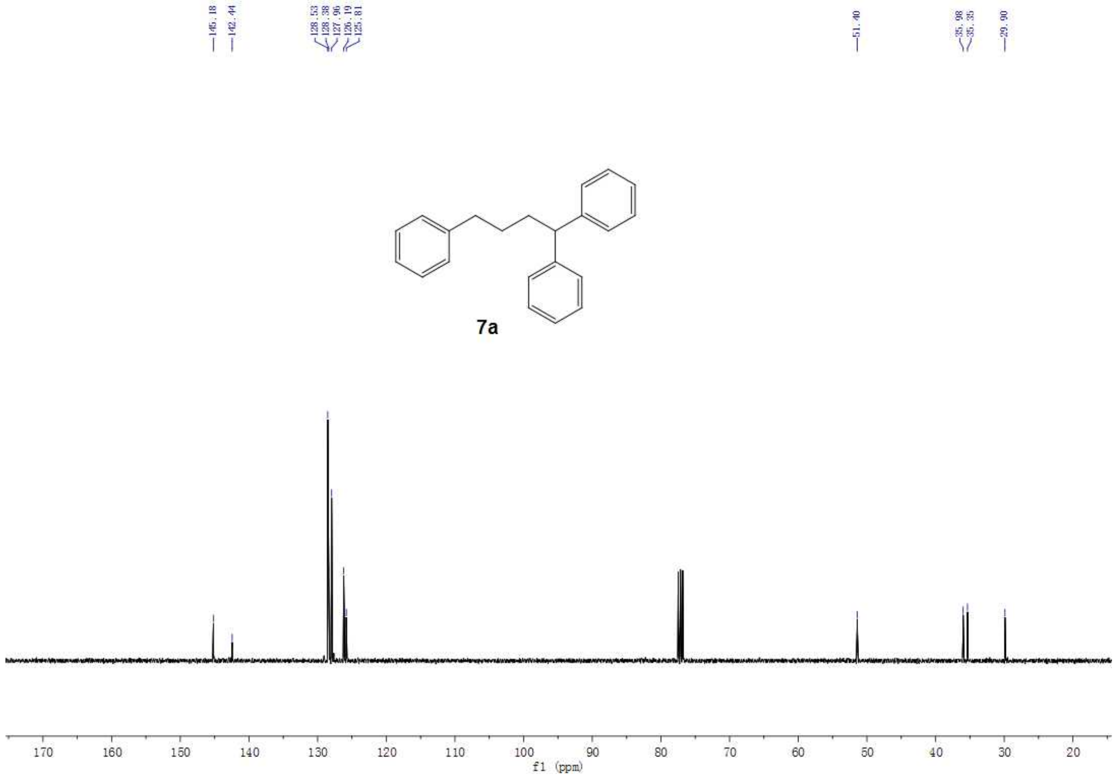
^{1}H NMR (400 M, $CDCl_3$) spectrum of **6b**



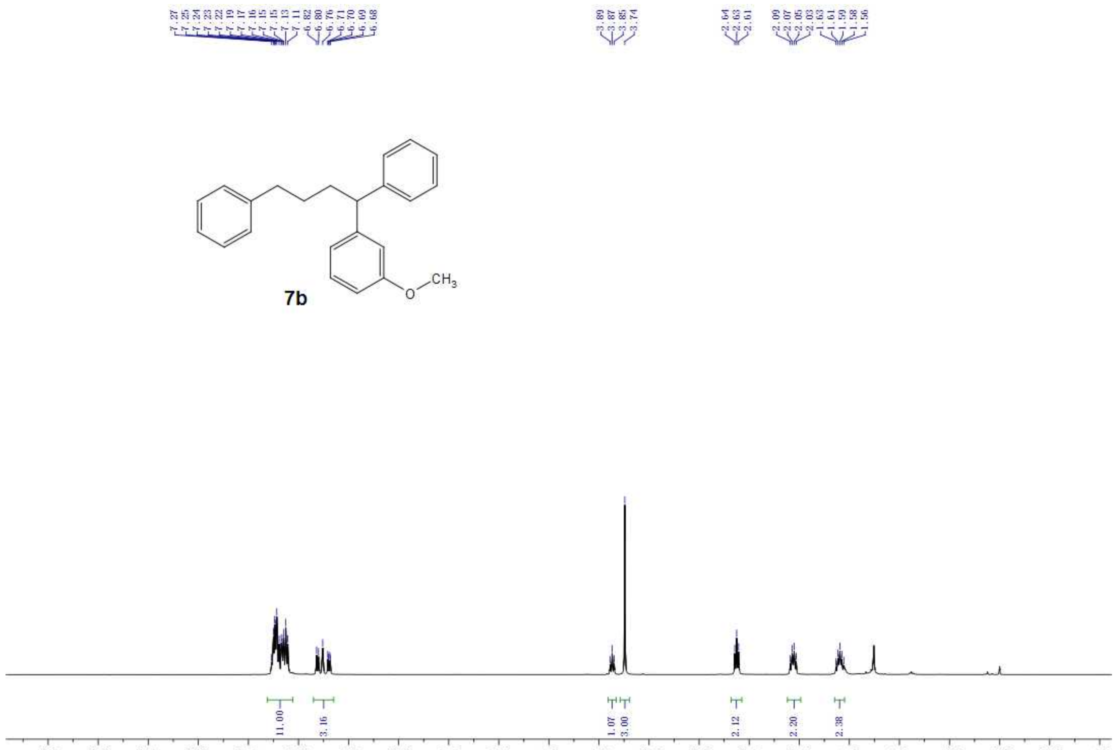
^{13}C NMR (101 M, $CDCl_3$) spectrum of **6b**



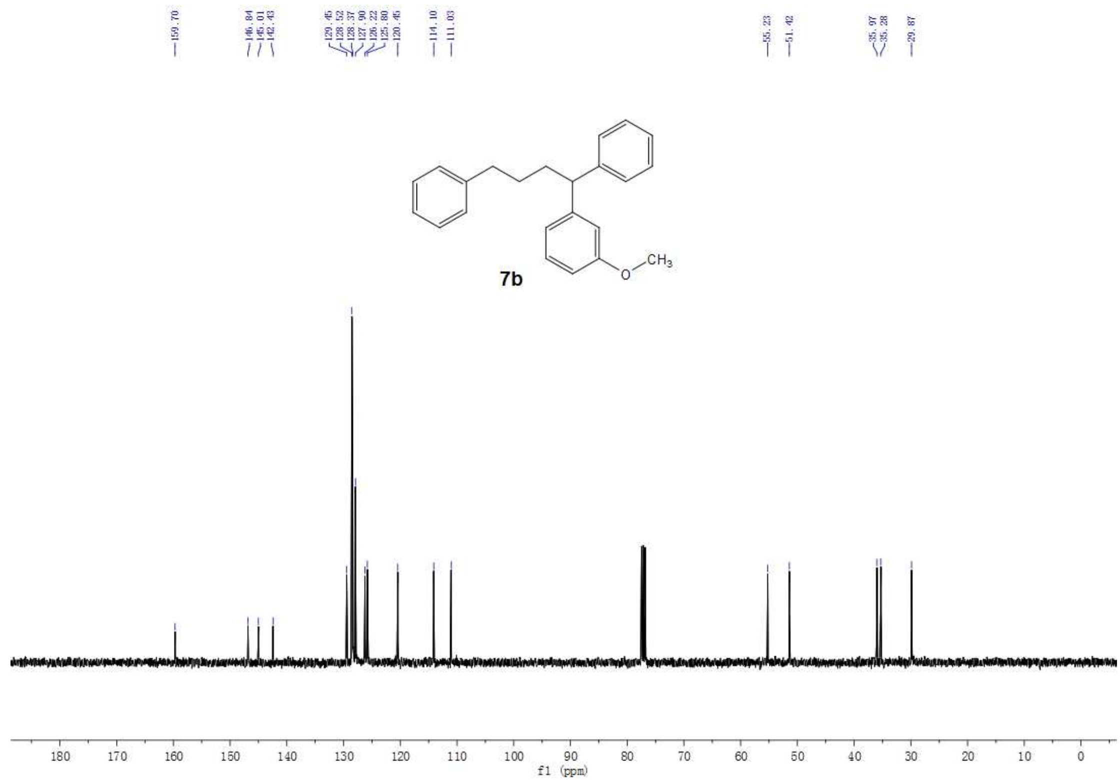
^{1}H NMR (400 M, $CDCl_3$) spectrum of **7a**



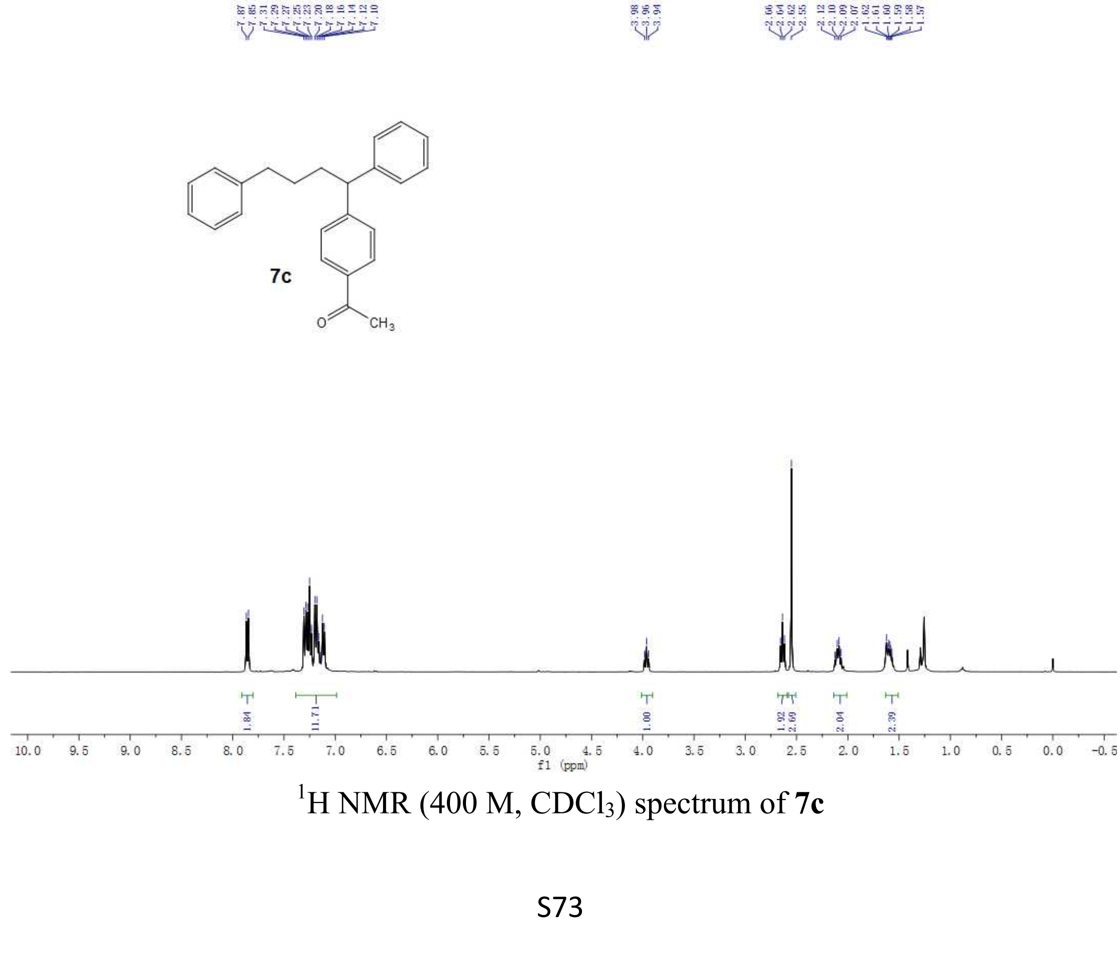
^{13}C NMR (101 M, $CDCl_3$) spectrum of **7a**



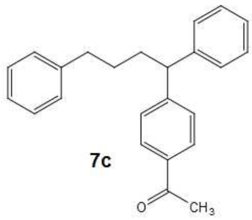
^{1}H NMR (400 M, $CDCl_3$) spectrum of **7b**



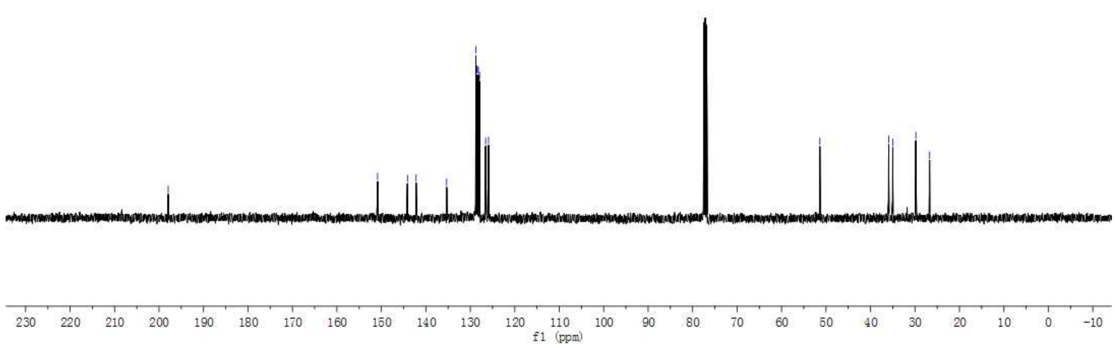
^{13}C NMR (101 M, $CDCl_3$) spectrum of **7b**



^{1}H NMR (400 M, $CDCl_3$) spectrum of **7c**



7c



^{13}C NMR (101 M, $CDCl_3$) spectrum of **7c**