Supporting Information

1,2-Boryl Migration Empowers Regiodivergent Synthesis of Borylated Furans

Roohollah Kazem Shiroodi, Olesja Koleda, and Vladimir Gevorgyan*

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7061, United Stated

1. General Information:

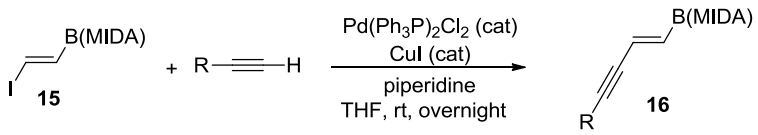
NMR spectra were recorded on Bruker DPX-400 (400 MHz) and DRX-500 (500 MHz) instruments. GC-MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). HR EI MS analysis was performed on a JEOL GCmate II mass spectrometer. Column chromatography was carried out employing Merck (Kieselgel 60, 63-200 μm), ICN (ICN SiliTech, 63-200μm), or SiliCycle (40-63 μm) silica gel. Precoated silica gel plates (0.2 mm, F-254) were used for thin-layer analytical chromatography.

Manipulations were conducted under an argon, nitrogen or ambient atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous, toluene and THF (BHT-free) was purchased from Aldrich, degassed with argon, and dried by passage through activated alumina on an Innovative Technology PureSolv system and stored over calcium hydride. Dichloroethane was purchased and stored over calcium hydride and used without further purification. All other reagents were purchased from various commercial sources and used without additional purification. Iodoalkene **15** was synthesized via the procedure developed by Burke *et al*.[1]

[1] Lee, S. J.; Anderson, T. M.; Burke, M. D. *Angew. Chem., Int. Ed*. **2010**, *49*, 8860.

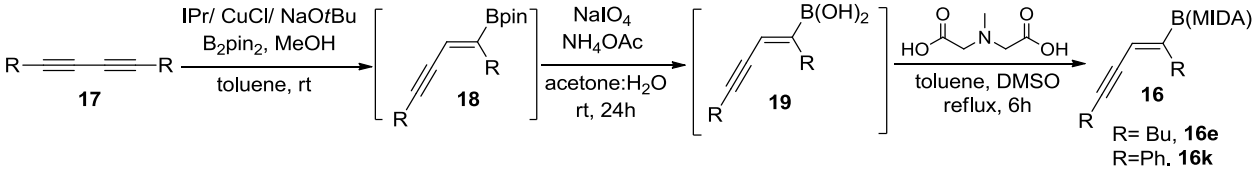
2. Synthesis of Starting Materials

Method A: General Procedure for the Synthesis of Disubstituted Enynyl Boronates.[1]



To a 10-mL round bottom flask in glove box was added $Pd(Ph_3P)_2Cl_2$ (5 mol %), CuI (10 mol%), and vinyl iodide **15**[2] (1.0 equiv). Ahydrous THF (0.2 M) was added and the reaction stirred at room temperature for 2 min. Piperidine (2.0 equiv) and terminal alkyne (1.2 equiv) were added to the solution sequentially and let the reaction stir overnight at room temperature. The reaction mixture was filtered through a short pad of silica gel and the filter was washed with EtOAc. The filtrate was concentrated under reduced pressured and purified by column chromatography on silica gel (Hex:EtOAc = 10:1 to 1:6) to afford enynyl MIDA-boronate **16**.

Method B: General Procedures for the Synthesis of Trisubstituted Enynyl Boronates.



Synthesis of Enynyl Pinacol Boronate 18:[3] To an oven dried round bottom flask in glovebox was added CuCl (2 mol %), IPr (2 mol %), and *t*BuONa (12 mol %). Toluene (0.5 M) was added and the mixture was stirred at room temperature for 15 min under argon atmosphere. B_2pin_2 (1.2 equiv) was then added to the solution in glovebox and stirred at room temperature for 5 min. Diyne **17** (1.0 equiv) and MeOH (2.0 equiv) were then added sequentially and the reaction was stirred at room temperature until completion (monitored by GC-MS). The reaction mixture was then filtrered through Celite®. The solvent was removed under reduced pressure and the crude **18** was used in the next step without any purification.

Synthesis of Enynyl Boronic Acid 19:[4] To the crude enynyl pinacol boronate **18** (1.0 equiv) acetone/water (2/1) solution (0.1 M) was added. $NaIO_4$ (3.1 equiv) and NH_4OAc (3.1 equiv) were sequentially added to the solution and the mixture was stirred at room temperature. Once completed (monitored by GC-MS), the reaction was treated with water and extracted with EtOAc. Organic layers were combined, washed with brine, dried over Na_2SO_4, and filtered. Solvents were removed under reduced pressure and the crude **19** was used in the next step without any purification.

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[1] Mohamed, Y. M.; Hansen, T. V. *Tetrahedron Lett.* **2011**, *52*, 1057 .

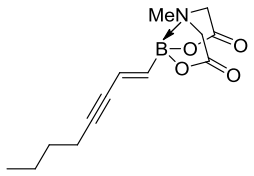
[2] Lee, S. J.; Anderson, T. M.; Burke, M. D. *Angew. Chem., Int. Ed*. **2010**, *49*, 8860.

[3] Semba, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Eur. J.* **2012**, *18*, 4179.

[4] Movassaghi, M.; Hunt, D. K.; Tjandra, M. *J. Am. Chem. Soc.* **2006**, *128*, 8126.

Synthesis of Enynyl MIDA Boronate 16e and 16k:[1] To the crude boronic acid **19** (1.0 equiv) methyliminodiacetic acid (1.1 equiv), toluene (0.3 mL), and DMSO (0.12 mL) were added. The Dean-Stark trap filled with toluene fit condenser vented to ambient atmosphere. The reaction mixture was refluxed with azeotropic removal of water for 6 hours. After 6 hours the reaction mixture was cooled down to room temperature, treated with EtOAc/acetone mixture and extracted with H_2O. Aqueous layer was washed with EtOAc/acetone mixture for two times. The organic layers were combined and washed with brine, dried over Na_2SO_4, and filtered. Solvents were removed under reduced pressure and the residue was subjected to column chromatography on silica gel (Hex:EtOAc = 10:1 to 1:6) to obtain enynyl boronate **16**.

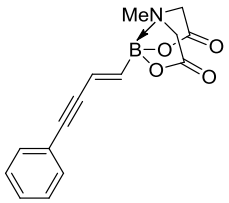
(*E*)-6-methyl-2-(oct-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16a)



Method A, (45%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.06 (d, *J*=18.9 Hz, 1 H), 5.97 (d, *J*=18.0 Hz, 1 H), 4.06 (d, *J*=16.9 Hz, 2 H), 3.72 (d, *J*=16.9 Hz, 2 H), 2.84 (s, 3 H), 2.30 (td, *J*=7.1 Hz, *J*=1.7 Hz, 2 H), 1.5 (quintet, *J*=7.0 Hz, 2 H), 1.4 (sextet, *J*=7.3 Hz, 2 H), 0.91 (t, *J*=7.3 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.4, 124.6, 92.8, 80.4, 61.6, 47.1, 30.7, 22.0, 19.1, 13.6.

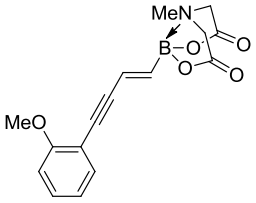
(E)-6-methyl-2-(4-phenylbut-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16b)



Method A, (61%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.44 (dd, *J*=6.4 Hz, *J*=3.1 Hz, 2 H), 7.33 – 7.31 (m, 3 H), 6.36 (d, *J*=18.0 Hz, 1 H), 6.19 (d, *J*=18.3 Hz, 1 H), 3.91 (d, *J*=16.5 Hz, 2 H), 3.73 (d, *J*=16.5 Hz, 2 H), 2.90 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.2, 131.7, 128.4, 124.3, 122.9, 889.0, 84.4, 61.6, 47.0.

(E)-2-(4-(2-methoxyphenyl)but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16c)

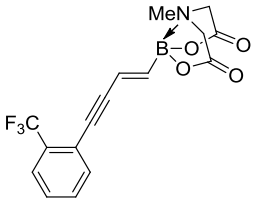


Method A, (62%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.38 (dd, *J*=7.7 Hz, *J*=1.5 Hz, 1 H), 7.24 (t, *J*=8.8 Hz, 1 H), 6.88 – 6.82 (m, 2 H), 6.34 (d, *J*=18.3 Hz, 1 H), 6.19 (d, *J*=18.0 Hz, 1 H), 4.1 (d, *J*=17.2 Hz, 2 H), 3.83 (s, 3 H), 3.77 (d, *J*=17.2 Hz, 2 H), 2.82 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.6, 159.9, 133.7, 130.1, 123.8, 120.6, 12.1, 110.8, 93.4, 87.6, 61.7, 55.8, 47.2.

[1] Gillis, E. P.; Burke, M.D. *J. Am. Chem. Soc.* **2008**, *130*, 14084.

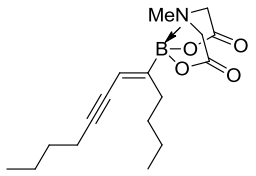
(E)-6-methyl-2-(4-(2-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16d)



Method A, (35%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.74 (d, *J*=7.7 Hz, 1 H), 7.67 – 7.63 (m, 2 H), 7.54 (t, *J*=8.3 Hz, 1 H), 6.41 (d, *J*=18.3 Hz, 1 H), 6.28 (d, *J*=18.3 Hz, 1 H), 4.28 (d, *J*=16.9 Hz, 2 H), 4.13 (d, *J*=16.9 Hz, 2 H), 3.08 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 167.9, 134.0, 132.2, 128.6, 126.0 (q, *J*=5.5 Hz), 121.1, 94.9, 85.3, 61.7, 46.7.

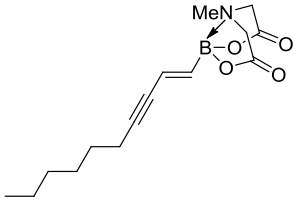
(Z)-2-(dodec-5-en-7-yn-5-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16e)



Method B, (63% over 3 steps), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.80 (s, 1 H), 4.06 (d, *J*=17.0 Hz, 2 H), 3.73 (d, *J*=16.9 Hz, 2 H), 2.77 (s, 3 H), 2.34 (dt, *J*=1.8 Hz, *J*=6.8 Hz, 2 H), 2.18 (t, *J*=7.6 Hz, 2 H), 1.51 (quintet, *J*=7.2 Hz, 2 H), 1.46 – 1.39 (m, 4 H), 1.32 (quintet, *J*=7.1 Hz, 2 H), 0.92 – 0.87 (m, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.5, 118.6, 97.3, 78.3, 61.94, 47.1, 32.4, 31.8, 30.9, 23.2, 21.9, 19.3, 13.9, 13.6.

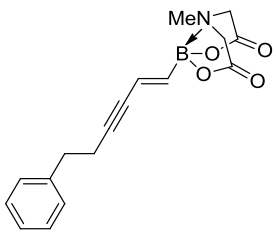
(*E*)-2-(dec-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16f)



Method A, (54%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.06 (d, *J*=18.0 Hz, 1 H), 5.97 (d, *J*=18.2 Hz, 1 H), 4.06 (d, *J*=17.1 Hz, 2 H), 3.72 (d, *J*=17.0 Hz, 2 H), 2.84 (s, 3 H), 2.3 (t, *J*=7.1 Hz, 2 H), 1.52 (quintet, *J*=7.3 Hz, 2 H), 1.37 (quintet, *J*=7.3 Hz, 2 H), 1.33 – 1.23 (m, 4 H), 0.88 (t, *J*=6.8 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm: 168.4, 124.6, 92.9, 80.4, 61.6, 47.1, 31.3, 28.6, 22.5, 19.5, 14.1.

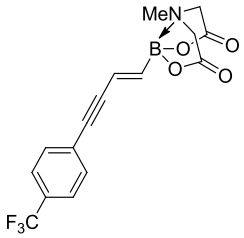
(E)-6-methyl-2-(6-phenylhex-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16g)



Method A, (68%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.30 (t, *J*=7.9 Hz, 2 H), 7.22 (d, *J*=7.0 Hz, 3 H), 6.07 (d, *J*=18.2 Hz, 1 H), 5.99 (d, *J*=18.2 Hz, 1 H), 4.02 (d, *J*=16.9 Hz, 2 H), 3.69 (d, *J*=16.8 Hz, 2 H), 2.84 (t, *J*=7.7 Hz, 2 H), 2.79 (s, 3 H), 2.60 (d, *J*=7.6 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.3, 140.6, 128.4, 126.4, 124.4, 91.9, 81.1, 61.6, 47.1, 35.0, 21.6.

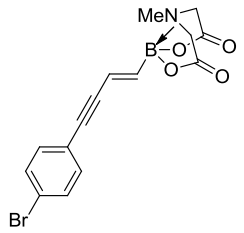
(E)-6-methyl-2-(4-(4-(trifluoromethyl)phenyl)but-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16h)



Method A, (45%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.58 (d, *J*=8.3 Hz, 2 H), 7.54 (d, *J*=8.2 Hz, 2 H), 6.38 (d, *J*=18.2 Hz, 1 H), 6.25 (d, *J*=18.2 Hz, 1 H), 3.88 (d, *J*=16.3 Hz, 2 H), 3.73 (d, *J*=16.3 Hz, 2 H), 2.92 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.5, 131.9, 125.3, 124.0, 97.1, 90.0, 61.6, 46.8.

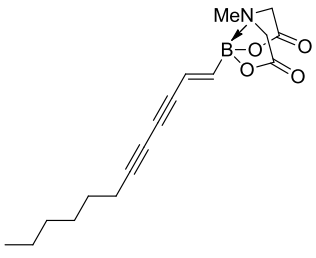
(E)-2-(4-(4-bromophenyl)but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16i)



Method A, (38%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.57 (d, *J*=8.5 Hz, 2 H), 7.39 (d, *J*=8.5 Hz, 2 H), 6.35 (d, *J*=18.2 Hz, 1 H), 6.22 (d, *J*=18.2 Hz, 1 H), 4.28 (d, *J*=16.9 Hz, 2 H), 4.11 (d, *J*=16.6 Hz, 2 H), 3.08 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 167.9, 133.1, 131.8, 122.5, 122.1, 121.3, 90.6, 88.5, 61.6, 46.7.

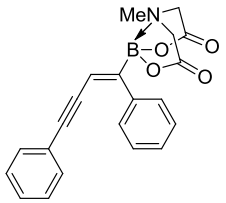
(E)-2-(dodeca-1-en-3,5-diyn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16j)



Method A, (51%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 6.39 (d, *J*=18.2 Hz, 1 H), 6.03 (d, *J*=18.3 Hz, 1 H), 4.26 (d, *J*=16.9 Hz, 2 H), 4.08 (d, *J*=16.9 Hz, 2 H), 3.05 (s, 3 H), 2.37 (t, *J*=7.0 Hz, 2 H), 1.53 (quintet, *J*=7.1 Hz, 2 H), 1.44 – 1.38 (m, 2 H), 1.34 – 1.28 (m, 4 H), 0.89 (t, *J*=6.8 Hz, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 167.9, 120.5, 85.1, 74.8, 64.9, 61.7, 46.7, 31.1, 28.3, 28.0, 22.3, 18.9, 13.4.

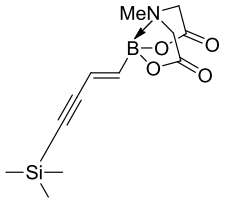
(Z)-2-(1,4-diphenylbut-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16k)



Method B, (10% over 3 steps), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.51 – 7.53 (m, 2 H), 7.40 (t, *J*=7.5 Hz, 2 H), 7.29 – 7.31 (m, 4 H), 7.21 – 7.23 (m, 2 H), 6.40 (s, 1 H), 4.25 (d, *J*=17.0 Hz, 2 H), 3.84 (d, *J*=16.3 Hz, 2 H), 2.93 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 141.1, 131.2, 128.9, 128.4, 128.3, 127.9, 126.9, 123.4, 117.9, 93.5, 88.5, 62.0, 46.8.

(E)-6-methyl-2-(5-(trimethylsilyl)pent-1-en-3-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (16'l)

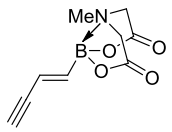


Method A, (71%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.16 (d, *J*=18.3 Hz, 1 H), 6.09 (d, *J*=19.0 Hz, 1 H), 4.06 (d, *J*=16.9 Hz, 2 H), 3.71 (d, *J*=16.9 Hz, 2 H), 2.85 (s, 3 H), 0.18 (s, 9 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.2, 124.0, 104.6, 96.6, 61.6, 47.2, -0.1.

Synthesis of (*E*)-2-(but-1-en-3-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (16l)

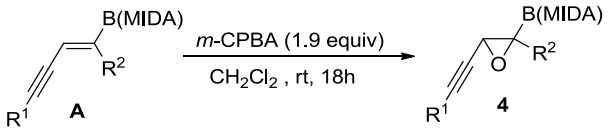
Enyne **16'l** (1.0 equiv) was dissolved in anhydrous THF (0.25 M) under argon atmosphere. The solution was cooled down to -78 °C and TBAF (1.05 equiv; 1 M sol. in THF) was added dropwise. The reaction was stirred at -78 °C for 1 hour and then warmed up to room temperature. The mixture was quenched with sat. aqueous $NaHCO_3$ and extracted with EtOAc (2 times). Organic layers were combined, washed with brine, dried over Na_2SO_4, and filtered. Solvent were removed under reduced pressure and the product was purified by column chromatography on silica gel (Hexanes:EtOAc = 10:1 to 1/6).



(72%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 6.31 (d, *J*=18.3 Hz, 1 H), 5.99 (dd, *J*=18.3 Hz, *J*=1.8 Hz, 1 H), 4.26 (d, *J*=16.9 Hz, 2 H), 4.08 (d, *J*=17.2 Hz, 2 H), 3.46 (d, *J*=2.2 Hz, 1 H), 3.04 (s, 3 H).

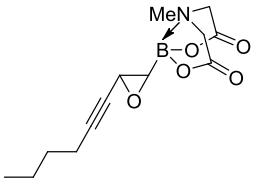
^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ 168.0, 121.0, 78.9, 61.6, 46.6.

2.3. Synthesis of Alkynyl Epoxides 4:[1]



Enynyl boronate **A** (1.0 equiv) was dissolved in dichloromethane (0.05 M) and *m*-CPBA (1.9 equiv) was added. The reaction was stirred at room temperature for 18 hours. The reaction mixture was then treated with sat. aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 times). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. Solvents were removed under reduced pressure and the crude was subjected to column chromatography on silica gel (Hex:EtOAc = 10:1 to 1:8) to obtain the desired boronated alkynyl epoxide **4**.

2-(3-(hex-1-yn-1-yl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4a)

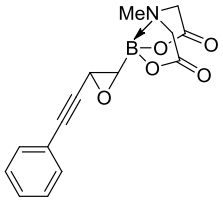


(60%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.98 (d, *J*=17.2 Hz, 1 H), 3.97 (d, *J*=16.5 Hz, 1 H), 3.84 (d, *J*=17.2 Hz, 1 H), 3.75 (d, *J*=16.1 Hz, 1 H), 3.36 (d, *J*=2.9 Hz, 1 H), 3.12 (s, 3 H), 2.45 (d, *J*=2.9 Hz, 1 H), 2.19 (t, *J*=7.2 Hz, 2 H), 1.48 (quintet, *J*=7.1 Hz, 2 H), 1.39 (sextet, *J*=7.3 Hz, 2 H), 0.90 (t, *J*=7.2 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.9, 167.5, 84.7, 77.2, 62.09, 62.02, 46.3, 44.2, 30.4, 21.9, 18.4, 13.5.

HRMS (ESI) calcd. for $C_{13}H_{18}BNO_5$ $[M+H]^+$: 280.1356, found: 280.1358.

6-methyl-2-(3-(phenylethynyl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4b)



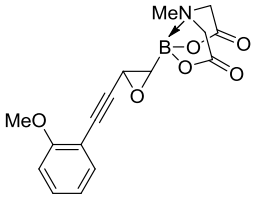
(44%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.42 (dd, *J*=7.5 Hz, *J*=1.9 Hz, 2 H), 7.31 – 7.25 (m, 3 H), 4.04 (d, *J*=17.3 Hz, 1H), 4.02 (d, *J*=16.4 Hz, 1 H), 3.88 (d, *J*=17.0 Hz, 1 H), 3.78 (d, *J*=16.4 Hz, 1 H), 3.61 (d, *J*=2.9 Hz, 1 H), 3.11 (s, 3 H), 2.61 (d, *J*=2.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.7, 167.4, 131.9, 128.8, 128.4, 121.9, 86.4, 83.5, 62.2, 62.1, 46.4, 44.4.

HRMS (ESI) calcd. for $C_{15}H_{14}BNO_5$ $[M+H]^+$: 300.1043, found: 300.1042.

[1] He, Z.; Yudin, A. K. *J. Am. Chem. Soc.* **2011**, *133*, 13770.

2-(3-((2-methoxyphenyl)ethynyl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4c)

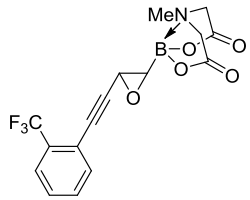


(52%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.39 (dd, *J*=7.5 Hz, *J*=1.7 Hz, 1 H), 7.31 – 7.27 (m, 1 H), 6.89 – 6.85 (m, 2 H), 3.95 (d, *J*=16.9 Hz, 2 H), 3.86 (d, *J*=16.9 Hz, 1 H), 3.86 (s, 3 H), 3.79 (d, *J*=16.1 Hz, 1 H), 3.67 (d, *J*=2.9 Hz, 1 H), 3.12 (s, 3 H), 2.64 (d, *J*2.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.2, 166.9, 160.4, 133.9, 130.3, 120.5, 111.1, 110.7, 90.3, 79.9, 62.1, 62.0, 55.8, 46.2, 44.8.

HRMS (ESI) calcd. for $C_{16}H_{16}BNO_6$ $[M+H]^+$: 330.1149, found: 330.1140

6-methyl-2-(3-((2-(trifluoromethyl)phenyl)ethynyl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4d)

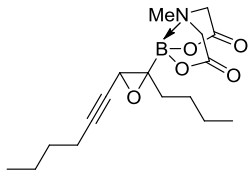


(48%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.77 (d, *J*=7.3 Hz, 1 H), 7.70 – 7.65 (m, 2 H), 7.60 (t, *J*=7.4 Hz, 1 H), 7.37 (d, *J*=17.2 Hz, 1 H), 4.30 (d, *J*=16.9 Hz, 1 H), 4.22 (d, *J*=17.2 Hz, 1 H), 4.02 (d, *J*=16.9 Hz, 1 H), 3.55 (d, *J*=2.9 Hz, 1 H), 3.33 (s, 3 H), 2.67 (d, *J*=2.9 Hz, 1 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.3, 167.3, 134.5, 132.2, 130.8 (q, *J*=31.4 Hz), 129.1, 126.0 (q, *J*=5.5 Hz), 123.7 (q, *J*=271.9 Hz), 120.2 (d, *J*=3.7 Hz), 9301, 78.1, 62.2, 62.1, 46.3, 42.9.

HRMS (ESI) calcd. for $C_{16}H_{13}BF_3NO_5$ $[M+H]^+$: 368.0917, found: 368.0913

2-(2-butyl-3-(hex-1-yn-1-yl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4e)

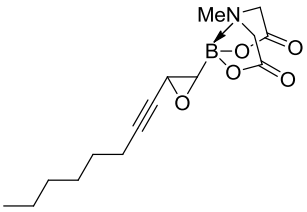


(63%) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.92 (d, *J*=17.3 Hz, 1 H), 3.87 (d, *J*=16.1 Hz, 1 H), 3.79 (d, *J*=17.0 Hz, 1 H), 3.74 (d, *J*=16.1 Hz, 1 H), 3.41 (s, 1 H), 3.07 (s, 3 H), 2.19 (t, *J*=6.7 Hz, 2 H), 1.84 – 1.77 (m, 1 H), 1.62 – 1.53 (m, 1 H), 1.53 – 1.20 (m, 8 H), 0.86 (t, *J*=7.2 Hz, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.9, 167.2, 86.6, 75.7, 62.3, 49.9, 46.1, 32.8, 30.4, 27.3, 23.4, 21.9, 18.5, 13.9, 13.5.

HRMS (ESI) calcd. for $C_{17}H_{26}BNO_5$ $[M+H]^+$: 336.1982, found 336.1977.

6-methyl-2-(3-(oct-1-yn-1-yl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4f)

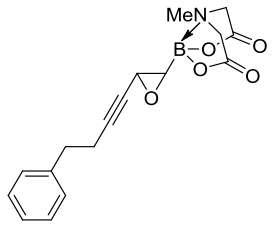


(60%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.01 (d, *J*=17.0 Hz, 1 H), 4.00 (d, *J*=16.1 Hz, 1 H), 3.85 (d, *J*=17.1 Hz, 1 H), 3.74 (d, *J*=16.3 Hz, 1 H), 3.36 (s, 1 H), 3.11 (s, 3 H), 2.45 (d, *J*=2.9 Hz, 1 H), 2.19 (t, *J*=6.6 Hz, 2 H), 1.48 (quintet, *J*=7.1 Hz, 2 H), 1.37 – 1.23 (m, 6 H), 0.87 (t, *J*=6.8 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.8, 167.4, 132.0, 128.5, 84.9, 50.9, 46.3, 44.5, 31.3, 28.6, 28.4, 22.6, 18.8, 14.2.

HRMS (ESI) calcd. for $C_{15}H_{22}BNO_5$ $[M+H]^+$: 308.1669, found: 308.1674.

6-methyl-2-(3-(4-phenylbut-1-yn-1-yl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4g)

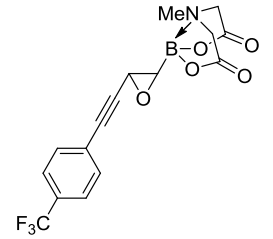


(56%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.31 – 7.28 (m, 2 H), 7.23 – 7.19 (m, 3 H), 3.97 (d, *J*=17.2 Hz, 1 H), 3.95 (d, *J*=16.1 Hz, 1 H), 3.81 (d, *J*=17.2 Hz, 1 H), 3.72 (d, *J*=16.5 Hz, 1 H), 3.36 (d, *J*=2.6 Hz, 1 H), 3.06 (s, 3 H), 2.81 (t, *J*=7.5 Hz, 2 H), 2.48 (t, *J*-7.2 Hz, 2 H), 2.44 (d, *J*=2.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.6, 167.3, 140.4, 128.5, 126.4, 83.96, 77.98, 62.08, 62.02, 46.2, 44.3, 34.71, 20.88.

HRMS (ESI) calcd. for $C_{17}H_{18}BNO_5$ $[M+H]^+$: 328.1356, found: 328.1350.

6-methyl-2-(3-((4-(trifluoromethyl)phenyl)ethynyl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4h)

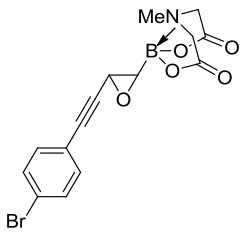


(44%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.54 – 7.50 (m, 4 H), 4.06 (d, *J*=16.9 Hz, 1 H), 4.03 (d, *J*=16.1 Hz, 1 H), 3.89 (d, *J*=17.2 Hz, 1 H), 3.81 (d, *J*=16.5 Hz, 1 H), 3.64 (d, *J*=2.9 Hz, 1 H), 3.17 (s, 3 H), 2.65 (d, *J*=2.9 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.4, 167.1, 132.1, 130.4 (q, *J*=33.3 Hz), 125.7, 125.3 (q, *J*=3.7 Hz), 123.7 (q, *J*=271.9 Hz), 88.6, 82.1, 62.2, 62.1, 46.4, 44.3.

HRMS (ESI) calcd. for $C_{16}H_{13}BF_3NO_5$ $[M+H]^+$: 368.0917, found: 368.0921.

2-(3-((4-bromophenyl)ethynyl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4i)

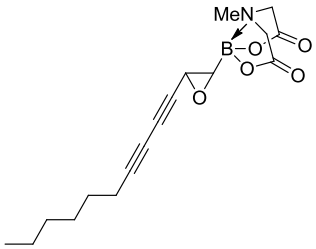


(34%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.56 (d, *J*=8.6 Hz, 2 H), 7.40 (d, *J*=8.6 Hz, 2 H), 4.36 (d, *J*=17.2 Hz, 1 H), 4.29 (d, *J*=16.9 Hz, 1 H), 4.21 (d, *J*=17.2 Hz, 1 H), 4.01 (d, *J*=16.9 Hz, 1 H), 3.50 (d, *J*=3.0 Hz, 1 H), 3.31 (s, 3 H), 2.64 (d, *J*=3.0 Hz, 1 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.3, 167.3, 133.4, 131.8, 122.6, 121.4, 88.6, 81.2, 62.2, 62.1, 46.3, 42.9.

HRMS (ESI) calcd. for $C_{15}H_{13}BBrNO_5$ $[M+H]^+$: 378.0148, found: 378.0152.

2-(3-(deca-1,3-diyn-1-yl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4j)

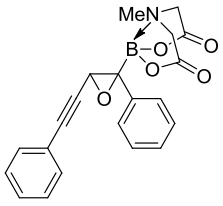


(42%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.01 (d, *J*=17.2 Hz, 1 H), 4.00 (d, *J*=16.5 Hz, 1 H), 3.87 (d, *J*=17.1 Hz, 1 H), (d, *J*=16.5 Hz, 1 H), 3.43 (d, *J*=2.7 Hz, 1 H), 3.11 (s, 3 H), 2.28 (d, *J*=2.9 Hz, 1 H), 2.28 (t, *J*=7.1 Hz, 2 H), 1.52 (quintet, *J*=7.1 Hz, 2 H), 1.49 – 1.40 (m, 2 H), 1.32 – 1.25 (m, 4 H), 0.88 (t, *J*=6.9 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.7, 167.3, 81.8, 72.9, 68.7, 64.4, 62.1, 51.1 (C-B, rough, broad), 46.5, 44.0, 31.2, 28.6, 28.1, 22.5, 19.3, 14.1.

HRMS (ESI) calcd. for $C_{17}H_{22}BNO_5$ $[M+H]^+$: 332.1669, found: 332.1669.

6-methyl-2-(2-phenyl-3-(phenylethynyl)oxiran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4k)

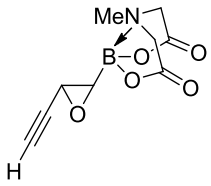


(28%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.56 – 7.54 (m, 2 H), 7.38 – 7.35 (m, 2 H), 7.30 – 7.26 (m, 2 H), 4.24 – 7.21 (m, 2 H), 7.00 – 6.98 (m, 2 H), 4.31 (d, *J*=6.8 Hz, 1 H), 4.28 (d, *J*=6.3 Hz, 1 H), 4.08 (d, *J*=16.7 Hz, 1 H), 3.93 (s, 1 H), 3.81 (d, *J*=17.2 Hz, 1 H), 2.00 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.0, 167.1, 138.7, 131.6, 128.6, 128.3, 127.7, 127.1, 126.8, 122.1, 85.4, 84.6, 62.6, 62.2, 51.1, 46.8.

HRMS (ESI) calcd. for $C_{21}H_{18}BNO_5$ $[M+H]^+$: 376.1356, found: 376.1353.

2-(3-ethynyloxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4l)

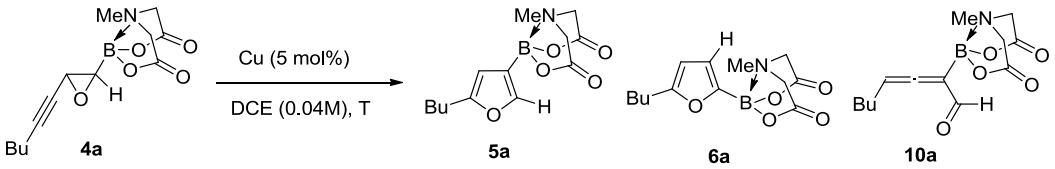


(45%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 4.34 (d, *J*=17.2 Hz, 1 H), 4.26 (d, *J*=16.9 Hz, 1 H), 4.18 (d, *J*=17.2 Hz, 1 H), 3.97 (d, *J*=16.5 Hz, 1 H), 3.29 (s, 3 H), 3.26 (dd, *J*=2.9 Hz, *J*=1.5 Hz, 1 H), 2.87 (d, *J*=1.8 Hz, 1 H), 2.52 (d, *J*=2.6 Hz, 1 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.2, 167.2, 81.7, 72.0, 62.0, 46.2, 42.3.

HRMS (ESI) calcd. for $C_9H_{10}BNO_5$ $[M+H]^+$: 224.0730, found: 224.0730.

3. Copper-Catalyzed Cycloisomerization:

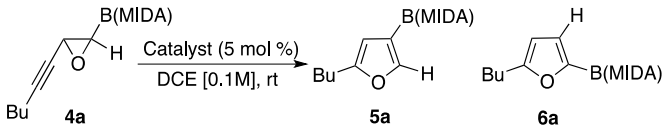


entry	Cu catalyst	T °C	Yield (**4:5:6:10**)
1	CuI	25	5 (0:88:12:0)
2	CuOAc	25	56 (38:59:3:0)
3	$[CuOTf]_2$.PhH	25	- (100:0:0:0)
4	**$[CuOTf]_2$.PhH**	**30**	**80 (0:97:3:0)**

Procedure:

To a V-shaped vial in the glovebox was added $[CuOTf]_2$.PhH (5 mol %, 2.5 mg). Dry dichloroethane (2.0 mL) was added and the mixture stirred for 2 min at room temperature. Alkynyl epoxide **4** (1.0 equiv, 0.1 mmol) as a solution in dichloroethane (0.5 mL) was added dropwise and the mixture was stirred at 30 °C overnight. The reaction mixture was then filtered through Celite® and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography on silica gel (Hexanes:EtOAc = 10:1 to 1:6) to obtain furan **5**.

4. Optimization of the Gold-Catalyzed Cycloisomerization:



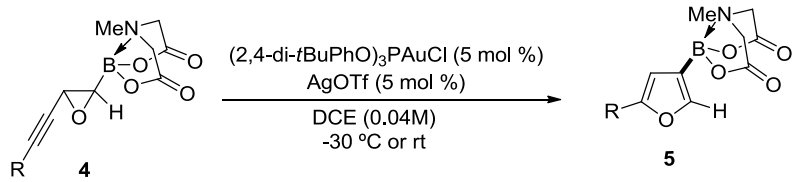
4a **5a** **6a**

Entry	Catalyst	NMR yield, %	5a:6a
1	Ph_3PAuCl	-[a]	-
2	IPrAuCl	-[a]	-
3	$AuCl_3$	96	13:87
4	$Ph_3PAuCl/ AgSbF_6$	>99	50:50
5	$Ph_3PAuCl/ AgOTf$	85	82:18
6	$(p\text{-}CF_3Ph)_3PAuCl/ AgOTf$ [b]	73	88:12
7	**$(ArO)_3PAuCl$[c]$/ AgOTf$ [b,d]**	**81**[e]	**96:4**[f]
8	$(ArO)_3PAuCl$[c]$/ AgSbF_6$ [b]	76	22:78
9	IPrAuCl/ AgOTf	79	33:67
10	**IPrAuCl/ $AgSbF_6$**	**81**	**0:100**
11	AgOTf [b]	39	87:13
12	$AgSbF_6$	39	86:14

[a] **6a** stayed intact. [b] Solution [0.04M]. [c] Ar = 2,4-di-*t*BuPh. [d] T = -30 °C. [e] 76% NMR yield at rt. [f] Ratio of 91:9 at rt.

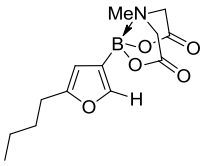
Seeking for a more general and efficient method for regioselective synthesis of borylated furans, we next examined the reaction of alkynyl epoxide **4a** in the presence of π-philic gold catalysts (Table 2). We found that substrate **4a** was unreactive in the presence of Au (I) chloride bearing both phosphine and NHC ligands (entry 1 and 2). The reaction with gold (III) chloride was high yielding though produced a 13:87 regioisomeric ratio of **5a** and **6a** (entry 3). In the presence of Ph_3PAuCl, the reaction was more regioselective for **5a** with triflate counterion (entry 5) rather than with hexafluoroantimonate (entry 4). Using a more electron deficient phosphine ligand did not improve the yield and regioselectivity (entry 6). Gratifyingly, employment of a gold catalyst possessing electron rich phosphite ligand with triflate led to furan **5a** with an excellent regioselectivity and yield (entry 7). Conversely, switching counterion to hexafluoroantimonate favored formation of **6a** (entry 8). Analogous results were obtained in the presence of IPrAuCl and triflate counterion (entry 9). Remarkably, using the same gold catalyst with hexafluoroantimonate exclusively produced furan **6a** (entry 10). Control *gold-free* experiments indicated that the reactions in the presence of silver triflate (entry 11) and silver hexafluroantimonate (entry 12) were both less efficient and regioselective.

5. Gold-Catalyzed Synthesis of C3-Borylated Furans:



To a round bottom flask in the glovebox was added (2,4-di-*t*-BuPhO)$_3$PAuCl (5 mol %, 4.4 mg), AgOTf (5 mol %, 1.3 mg). Dry dichloroethane (2.0 mL) was added and the mixture was stirred for 5 min at room temperature, which was then cooled down to -30 ºC. Alkynyl epoxide **4** (1.0 equiv, 0.1 mmol) as a solution in dichloroethane (0.5 mL) was added dropwise and the mixture was stirred at -30 ºC. After 2 hours, the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography on silica gel (Hexanes:EtOAc = 10:1 to 1:6) to obtain furan **5**.

2-(5-butylfuran-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5a)

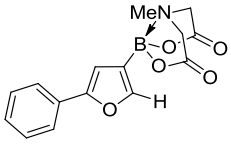


(83%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.35 (s, 1H), 5.95 (s, 1 H), 4.16 (d, *J*=16.9 Hz, 2 H), 3.79 (d, *J*=16.9 Hz, 2 H), 2.68 (s, 3 H), 2.56 (t, *J*=7.5 Hz, 2 H), 1.57 (quintet, *J*=7.6 Hz, 2 H), 1.32 (sxt, *J*=7.8 Hz, 2 H), 0.9 (t, *J*=7.3 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.9, 158.1, 145.7, 107.2, 61.4, 47.5, 30.1, 27.5, 22.3, 13.8.

HRMS (ESI) calcd. for $C_{13}H_{18}BNO_5$ $[M+H]^+$: 280.1356, found: 280.1359.

6-methyl-2-(5-phenylfuran-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (5b)



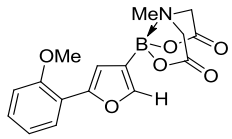
(87%) ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.72 (dd, *J*=8.3 Hz, *J*=1.3 Hz, 2 H), 7.60 (s, 1 H), 7.40 (t, *J*=7.9 Hz, 2 H), 7.28 – 7.25 (m, 1 H), 6.93 (s, 1 H), 4.33 (d, *J*=16.9 Hz, 2 H), 4.15 (d, *J*=16.9 Hz, 2 H), 2.96 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.6, 155.4, 147.0, 130.5, 128.8, 127.6, 123.9, 107.7, 61.5, 47.6.

^{11}B NMR (128 MHz, $(CD_3)_2CO$) δ ppm 10.1

HRMS (ESI) calcd. for $C_{15}H_{14}BNO_5$ $[M+H]^+$: 300.1043, 300.1042.

2-(5-(2-methoxyphenyl)furan-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5c)



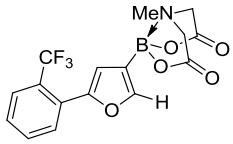
(81%) ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.80 (dd, *J*=7.7 Hz, *J*=1.5 Hz, 1 H), 7.57 (s, 1 H), 7.28 – 7.24 (m, 1 H), 7.09 (d, *J*=8.4 Hz, 7.04 (s, 1 H), 7.01 (t, *J*=7.5 Hz, 1 H), 4.31 (d, *J*=16.9 Hz, 2 H), 4.12 (d, *J*=16.9 Hz, 2 H), 3.94 (s, 3 H), 2.96 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.1, 155.3, 151.8, 146.1, 128.3, 126.0, 120.7, 119.41, 112.3, 111.0, 61.5, 55.4, 47.5.

HRMS (ESI) calcd. for $C_{16}H_{16}BNO_6$ $[M+H]^+$: 330.1149, found: 330.1139.

6-methyl-2-(5-(2-(trifluoromethyl)phenyl)furan-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (5d)

The reaction was performed at room temperature.

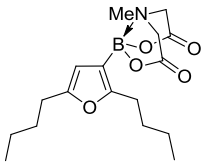


(61%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.82 (t, *J*=7.7 Hz, 2 H), 7.70 – 7.73 (m, 3 H), 7.57 (t, *J*=7.9 Hz, 1 H), 6.84 (s, 1 H), 4.34 (d, *J*=16.9 Hz, 2 H), 4.16 (d, *J*=16.9 Hz, 2 H), 2,98 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.1, 151.4, 148.0, 132.3, 130.3, 128.2, 126.5 (q, *J*=5.6 Hz), 126.1 (q, *J*=31.4 Hz), 124.3 (q, *J*=271.9 Hz), 113.4, 61.5, 47.2.

HRMS (ESI) calcd. for $C_{16}H_{13}BF_3NO_5$ $[M+H]^+$: 368.0917, found: 368.0917.

2-(2,5-dibutylfuran-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5e)

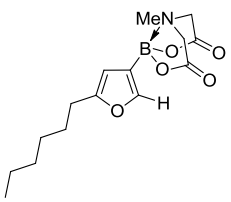


(81%) ^{1}H NMR (500 MHz, $(CDCl_3)$ δ ppm 5.77 (s, 1 H), 3.98 (d, *J*=16.9 Hz, 2 H), 3.72 (d, *J*=16.5 Hz, 2 H), 2.69 (s, 3 H), 2.60 (t, *J*=7.5 Hz, 2 H), 2.54 (t, *J*=7.5 Hz, 2 H), 1.61 – 1.54 (m. 4 H), 1.36 – 1.26 (m, 4 H), 0.92 – 0.86 (m, 6 H).

^{13}C NMR (126 MHz, $(CDCl_3)$ δ ppm 167.9, 155.3, 107.8, 61.5, 47.1, 31.5, 30.1, 27.9, 27.5, 22.4, 22.3, 13.9, 13.8.

HRMS (ESI) calcd. for $C_{17}H_{26}BNO_5$ $[M+H]^+$: 336.1982, found: 336.1976.

2-(5-hexylfuran-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5f)

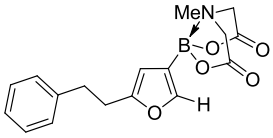


(67%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.36 (s. 1 H), 5.95 (s, 1 H), 4.09 (d, *J*=16.9 Hz, 2 H), 3.77 (d, *J*=16.9 Hz, 2 H), 2.70 (s. 3 H), 2.57 (t, *J*=7.7 Hz, 2 H), 1.60 (quintet, *J*=7.4 Hz, 2 H), 1.36 – 1.24 (m, 6 H), 0.87 (t, *J*=6.97 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.4, 158.3, 145.8, 107.1, 61.4, 47.4, 31.5, 31.5, 28.9, 28.0, 27.9, 22.6, 14.1.

HRMS (ESI) calcd. for $C_{15}H_{22}BNO_5$ $[M+H]^+$: 368.0917, found: 368.0921

6-methyl-2-(5-phenethylfuran-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (5g)

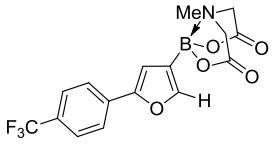


(74%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.39 (s, 1 H), 7.24 – 7.21 (m, 2 H), 7.16 – 7.11 (m, 3 H), 5.93 (s, 1 H), 4.11 (d, *J*=16.9 Hz, 2 H), 3.72 (d, *J*16.9 Hz, 2 H), 2.93 – 2.88 (m, 4 H), 2.58 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.2, 159.4, 141.0, 128.43, 128.4, 126.1, 119.9, 106.1, 61.5, 47.0, 34.5, 29.5.

HRMS (ESI) calcd. for $C_{17}H_{18}BNO_5$ $[M+H]^+$: 328.1356, found: 328.1350

6-methyl-2-(5-(4-(trifluoromethyl)phenyl)furan-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (5h)

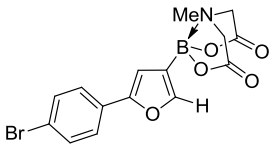


(65%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.92 (d, *J*=8.1 Hz, 2 H), 7.74 (d, *J*=8.1 Hz, 2 H), 7.70 (s, 1 H), 7.15 (s, 1 H), 4.35 (d, *J*=17.2 Hz, 2 H), 4.17 (d, *J*=16.9 Hz, 2.98 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.1, 153.0, 148.1, 134.5, 125.7 (q, *J*=3.7 Hz), 124.5 (q, *J*=270.0 Hz), 123.9, 111.2, 61.5. 47.2.

HRMS (ESI) calcd. for $C_{16}H_{13}BF_3NO_5$ $[M+H]^+$: 368.0917, found: 368.0918

2-(5-(4-bromophenyl)furan-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5i)

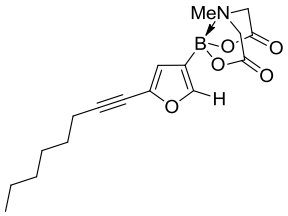


(79%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.67 (d, *J*=8.5 Hz, 2 H), 7.62 (s, 1 H), 7.58 (d. *J*=8.6 Hz, 2 H), 6.99 (s, 1 H), 4.33 (d, *J*=17.0 Hz, 2 H), 4.14 (d, *J*=16.9 Hz, 2 H), 2.96 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.0, 153.4, 147.3, 131.8, 130.2, 125.4, 120.4, 109.5, 61.5, 47.2.

HRMS (ESI) calcd. for $C_{15}H_{13}BBrNO_5$ $[M+H]^+$: 378.0148, found: 378.0154.

6-methyl-2-(5-(oct-1-yn-1-yl)furan-3-yl)-1,3,6,2-dioxazaborocane-4,8-dione (5j)

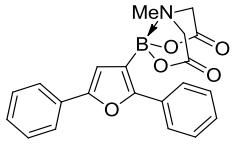


(67%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.42 (s, 1 H), 6.46 (s, 1 H), 4.11 (d, *J*=16.9 Hz, 2 H), 3.77 (d, *J*=16.7 Hz, 2 H), 2.70 (s, 3 H), 2.40 (t, *J*=7.1 Hz, 2 H), 1.88 (quintet, *J*=7.3 Hz, 2 H), 1.44 – 1.38 (m, 2 H), 1.33– 1.25 (m, 4 H), 0.89 (t, 6.8 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.3, 147.0, 139.0, 116.3, 95.6, 70.6, 61.5, 47.6, 31.3, 28.6, 28.3, 22.5, 19.5, 14.1.

HRMS (ESI) calcd. for $C_{17}H_{22}BNO_5$ $[M+H]^+$: 332.1669, found: 332.1666.

2-(2,5-diphenylfuran-3-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5k)

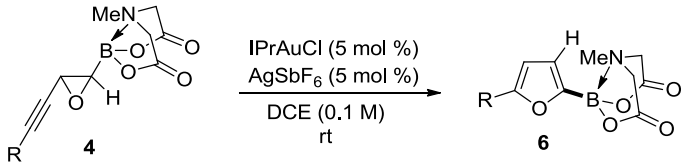


(67%) ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.82 (dd, *J*=16.3 Hz, *J*=7.9 Hz, 4 H), 7.44 – 7.41 (m, 4 H), 7.36 (t, *J*=7.34 Hz, 1 H), 7.29 (t, *J*=7.3 Hz, 1 H), 6.96 (s, 1 H), 4.28 (d, *J*=17.2 Hz, 2 H), 3.97 (d, *J*=16.9 Hz, 2 H), 2.78 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 167.9, 152.9, 132.6, 130.7, 128.8, 128.4, 128.0, 127.9, 127.3, 123.7, 112.3, 61.9, 46.9.

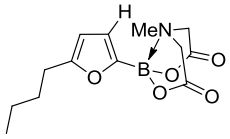
HRMS (ESI) calcd. for $C_{21}H_{18}BNO_5$ $[M+H]^+$: 376.1356, found: 376.1355.

6. Gold-Catalyzed Synthesis of C2-Borylated Furans:



To a V-shaped vial in the glovebox was added IPrAuCl (5 mol %, 3.1 mg) and $AgSbF_6$ (5 mol %, 1.7 mg). Dry dichloroethane (2.0 mL) was added and the mixture was stirred for 5 min at room temperature. Alkynyl epoxide **4** (1.0 equiv, 0.1 mmol) as a solution in dichloroethane (0.5 mL) was added dropwise and the mixture was stirred at room temperature. After 1-2 hours the reaction mixture was filtered through Celite® and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography on silica gel (Hexanes:EtOAc = 10:1 to 1:6) to obtain furan **6**.

2-(5-butylfuran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6a)

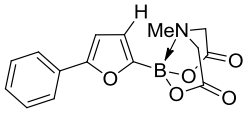


(75%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.63 (d, *J*=2.9 Hz, 1 H), 5.95 (d, *J*=2.9 Hz, 1 H), 4.13 (d, *J*=16.9 Hz, 2 H), 3.82 (d, *J*=16.9 Hz, 2 H), 2.66 (s, 3 H), 2.6 (t, *J*=7.7 Hz, 2 H), 1.57 (quintet, *J*=7.6 Hz, 2 H), 1.33 (sxt, *J*=7.4 Hz, 2 H), 0.9 (t, *J*=7.3 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.3, 160.7, 119.9, 105.4, 61.6, 47.2, 30.2, 27.8, 22.3, 13.8.

HRMS (ESI) calcd. for $C_{13}H_{18}BNO_5$ $[M+H]^+$: 280.1356, found: 280.1354.

6-methyl-2-(5-phenylfuran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (6b)



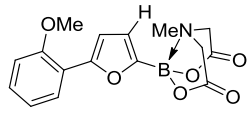
(50%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.75 (dd, *J*=8.4 Hz, *J*=1.1 Hz, 2 H), 7.39 (t, *J*=7.9 Hz, 2 H), 7.27 (t, *J*=7.3 Hz, 1 H), 6.83 (d, *J*=3.3 Hz, 1 H), 6.78 (d, *J*=3.3 Hz, 1 H), 4.39 (d, *J*=16.9 Hz, 2 H), 4.21 (d, *J*=16.9 Hz, 2 H), 2.95 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.1, 156.8, 131.1, 128.7, 127.4, 123.9, 120.0, 105.6, 61.6, 47.0.

^{11}B NMR (128 MHz, $(CD_3)_2CO$) δ ppm 9.3

HRMS (ESI) calcd. for $C_{15}H_{14}BNO_5$ $[M+H]^+$: 330.1043, found: 300,1037.

2-(5-(2-methoxyphenyl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6c)

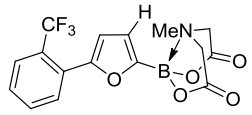


(49%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.80 (dd, *J*=7.7 Hz, *J*=1.5 Hz, 1 H), 7.20 – 7.24 (m, 1 H), 6.98 (t, *J*=7.5 Hz, 1 H), 6.93 (d, *J*=8.1 Hz, 1 H), 6.91 (d, *J*=3.3 Hz, 1 H), 6.84 (d, *J*=3.3 Hz, 1 H), 4.10 (d, *J*=4.1 Hz, 2 H), 3.90 (s, 3 H), 3.84 (d, *J*=16.5 Hz, 2 H), 2.68 (s, 3 H).

^{13}C NMR (126 MHz, $(CDCl_3)$ δ ppm 168.0, 155.35, 153.7, 128.5, 126.2, 121.2, 120.8, 119.7, 111.0, 110.4, 61.6, 55.4, 47.2.

HRMS (ESI) calcd. for $C_{16}H_{16}BNO_6$ $[M+H]^+$: 330.1149, found: 330.1145.

6-methyl-2-(5-(2-(trifluoromethyl)phenyl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (6d)

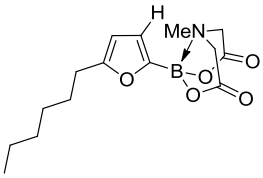


The reaction was performed at 60 °C. (42%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.84 – 7.82 (m, 2 H), 7.73 – 7.70 (m, 1 H), 7.57 (t, *J*=7.7 Hz, 6.84 (d, *J*=3.3 Hz, 1 H), 6.77 (d, *J*=3.3 Hz, 1 H), 4.4 (d, *J*=16.9 Hz, 4.16 (d, *J*=17.2 Hz, 2 H), 2.94 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 167.9, 153.9, 132.4, 131.8 (d, *J*=3.7 Hz), 130.5, 128.3, 126.6 (q, *J*=5.55 Hz), 124.4 (q, *J*=271.88 Hz), 119.7, 110.37, 64.53, 46.9.

HRMS (ESI) calcd. for $C_{16}H_{13}BF_3NO_5$ $[M+H]^+$: 368.0917, found: 368.0917.

2-(5-hexylfuran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6f)

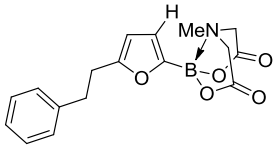


(57%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.64 (d, *J*=2.9 Hz, 1 H), 5.95 (d, *J*=3.3 Hz, 1 H), 4.07 (d, *J*=16.9 Hz, 2 H), 3.83 (d, *J*=16.9 Hz, 2 H), 2.66 (s, 3 H), 2.58 (t, *J*=7.5 Hz, 2 H), 1.58 (quintet, *J*=7.4 Hz, 2 H), 1.34 – 1.26m, 6 H), 0.87 (t, *J*=7.0 Hz, 3 H).

^{13}C NMR (126 MHz, $(CDCl_3)$ δ ppm 168.4, 160.8, 120.0, 105.4, 61.6, 47.1, 31.5, 28.9, 28.2, 28.0, 22.6, 14.1.

HRMS (ESI) calcd. for $C_{15}H_{22}BNO_5$ $[M+H]^+$: 308.1669, found: 308.1670.

6-methyl-2-(5-phenethylfuran-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (6g)

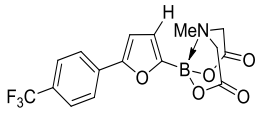


(64%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.23 – 7.26 (m, 2, H), 7.15 – 7.17 (m, 3 H), 6.62 (d, *J*=2.9 Hz, 1 H), 5.98 (d, *J*=2.9 Hz, 1 H), 4.02 (d, *J*=16.9 Hz, 2 H), 3.96 (d, *J*=16.9 Hz, 2 H), 2.98 – 2.90 (m, 4 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.2, 159.4, 141.0, 128.4, 128.4, 126.1, 119.9, 106.0, 61.5, 47.0, 34.5, 29.5.

HRMS (ESI) calcd. for $C_{17}H_{18}BNO_5$ $[M+H]^+$: 328.1356, found: 328.1352.

6-methyl-2-(5-(4-(trifluoromethyl)phenyl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (6h)

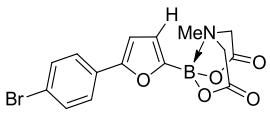


(65%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.96 (d, *J*=8.1 Hz, 2 H), 7.73 (d, *J*=8.3 Hz, 2 H), 7.05 (d, *J*=3.4 Hz, 1 H), 6.84 (d, *J*=3.4 Hz, 1 H), 4.41 (d, *J*=17.0 Hz, 2 H), 4.23 (d, *J*=17.0 Hz, 2 H), 2.97 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.0, 155.2, 134.6, 128.2 (q, *J*=32.4 Hz), 125.7 (d, *J*=3.7 Hz), 124.5 (q, *J*=271.0 Hz), 124.2, 120.3, 108.1, 61.6, 47.1.

HRMS (ESI) calcd. for $C_{16}H_{13}BF_3NO_5$ $[M+H]^+$: 368.0917, found: 368.0923.

2-(5-(4-bromophenyl)furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6i)

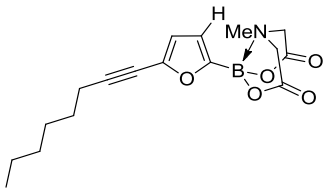


(84%), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.70 (d, *J*=8.8 Hz, 2 H), 7.57 (d, *J*=8.8 Hz, 2 H), 6.90 (d, *J*=3.3 Hz, 1 H), 6.79 (d, *J*=3.3 Hz, 1 H), 4.39 (d, *J*=16.9 Hz, 2 H), 4.21 (d, *J*=16.9 Hz, 2 H), 2.95 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.0, 155.6, 131.7, 130.3, 125.7, 120.7, 120.2, 106.5, 61.6, 47.0.

HRMS (ESI) calcd. for $C_{15}H_{13}BBrNO_5$ $[M+H]^+$: 378.0148, found: 378.0144.

6-methyl-2-(5-(oct-1-yn-1-yl)furan-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (6j)

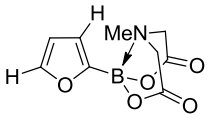


(66%), ^{1}H NMR (500 MHz, $(CDCl_3)$ δ ppm 6.71 (d, *J*=3.1 Hz, 1 H), 6.44 (d, *J*=3.1 Hz, 1 H), 4.07 (d, *J*=16.7 Hz, 2 H), 3.87 (d, *J*=16.9 Hz, 2 H), 2.71 (s, 3 H), 2.40 (t, *J*=7.1 Hz, 2 H), 1.58 (quintet, *J*=7.4 Hz, 2 H), 1.41 (dt, *J*=14.2 Hz, *J*=7.2 Hz, 2 H), 1.34– 1.22 (m, 4 H), 0.89 (t, *J*=6.7 Hz, 3 H).

^{13}C NMR (126 MHz, $(CDCl_3)$ δ ppm 168.2, 141.0, 120.0, 114.3, 95.9, 71.8, 47.3, 31.3, 28.7, 28.3, 22.5, 19.5, 14.1.

HRMS (ESI) calcd. for $C_{17}H_{22}BNO_5$ $[M+H]^+$: 332.1669, found: 332.1671.

2-(furan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6l)



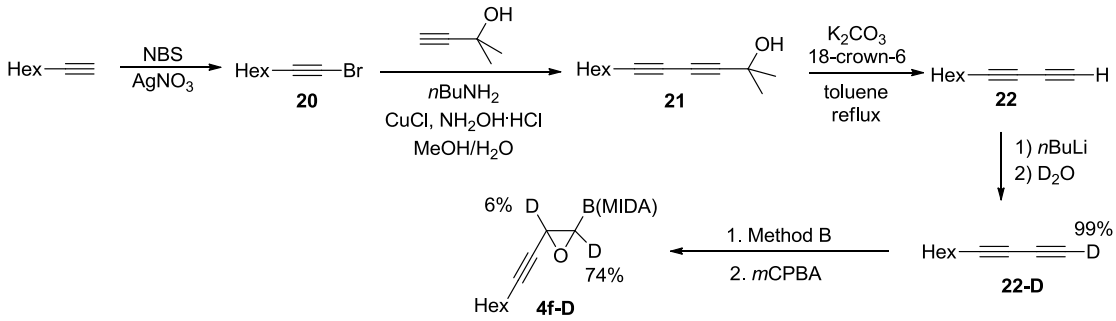
Reaction was run in anh. THF. (60% NMR yield), ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ ppm 7.59 (t, *J*=1.5 Hz, 1 H), 7.53 (s, 1 H), 6.5 (d, *J*=1.1 Hz, 1 H), 4.29 (d, *J*=17.2 Hz, 2 H), 4.09 (d, *J*=16.9 Hz, 2 H), 2.89 (s, 3 H).

^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ ppm 168.1, 147.2, 143.3, 112.7, 61.4, 47.0.

HRMS (ESI) calcd. for $C_9H_{10}BNO_5$ $[M+H]^+$: 224.0730, found: 224.0728.

7. Deuterium-Labeling Experiments:

7a. Preparation of D-labeled Alkynyl Epoxide 4f-D



Synthesis of 1-bromooct-1-yne 20: 1-Octyne (1.0 equiv, 10 mmol, 1.48 mL) was dissolved in acetone (263 mL) and the reaction flask was covered with alumina foil. $AgNO_3$ (0.3 equiv, 3 mmol, 0.51 g) and *N*-bromosuciinimide (1.4 equiv, 14 mmol, 2.5 g) were added to the reaction mixture. The reaction was stirred at room temperature for 18 h. The reaction was then quenched with H_2O and extracted with hexanes (3 times). Organic layers were combined, washed with brine, dried over Na_2SO_4, and filtered. Solvents were removed under reduced pressure and crude material was purified by column chromatography on silica gel (pure hexanes) to obtain compound **20** (85%, 8.5 mmol, 1.6 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.20 (t, *J*=7.2 Hz, 2 H), 1.54 – 1.47 (m, 2 H), 1.41 – 1.34 (m, 2 H), 1.31 – 1.25 (m, 4 H), 0.82 (t, *J*=6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 80.4, 37.4, 31.3, 28.5, 28.3, 22.6, 19.7, 14.1.

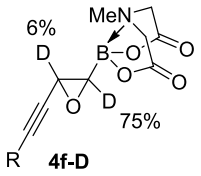
Synthesis of 2-methyldodeca-3,5-diyn-2-ol 21: The mixture of MeOH (1.80 mL), H_2O (0.88 mL), 2-methyl-3-butyne-2-ol (2.0 equiv, 14.4 mmol, 1.4 mL), CuCl (15 mol%, 1.1 mmol, 107 mg) and NH_2OH**.**HCl (0.3 equiv, 2.2 mmol, 153 mg) was cooled down to 0 ºC and **20** (1.0 equiv, 7.2 mmol, 1.36 g) as a solution in MeOH (0.9 mL) was added dropwise. The reaction was stirred at room temperature for 20 hours. The reaction mixture was then quenched with H_2O and extracted with Et_2O (2 times). Organic layers were combined, washed with brine, dried over Na_2SO_4, filtered. Solvents were removed under reduced pressure and the crude material was subjected to column chromatography on silica gel (hexane:EtOAc = 50:1 to 20:1) to obtain compound **21** (73%, 5.3 mmol, 1.0 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.36 (s_{br}, 1 H), 2.25 (t, *J*=7.2 Hz, 2 H), 1.50 (s, 3 H), 1.39 – 1.33 (m, 2 H), 1.31 – 1.23 (m, 4 H), 0.87 (t, *J*=7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 81.8, 79.8, 67.4, 65.5, 64.3, 31.3, 31.1, 28.5, 28.1, 22.5, 19.2, 14.0.

Synthesis of deca-1,3-diyne 22: Anhydrous K_2CO_3 (1.0 equiv, 7.2 mmol, 1.0 g) and 18-crown-6 (0.3 equiv, 1.6 mmol, 422 mg) were added to the Shlenk flask. Condenser was attached and the system was flushed with argon. Diyne **21** (1.0 equiv, 7.2 mmol, 1.0 g) as a solution in anhydrous toluene (38 mL) was added to the mixture under argon. The mixtures was stirred under reflux for 18 hours and then cooled down to room temperature. The reaction mixture was then quenched with H_2O and extracted with Et_2O (2 times). Organic layers were combined, washed with brine, dried over Na_2SO_4, and filtered. Solvent were removed under reduced pressure and the crude material was purified by column

chromatography on silica gel (pure hexanes) to obtain compound **22** (54%, 3.9 mmol, 522 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.24 (t, *J*=7.0 Hz, 2 H), 1.92 (s, 1 H), 1.49 1.56 (m, 2 H), 1.42 – 1.34 (m, 2 H), 1.33 – 1.25 (m, 4 H), 0.88 (t, *J*=7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 78.3, 68.5, 64.6, 64.3, 31.3, 28.5, 28.0, 22.5, 19.0, 14.0.

Synthesis of deuterated deca-1,3-diyne 22-D. Terminal diyne **22** (1.0 equiv, 3.9 mmol, 522 mg) was dissolved in anhydrous THF (5.7 mL) and the solution was cooled down to -78 °C. Then *n*BuLi (1.2 equiv, 4.9 mmol) was added dropwise. The reaction was stirred at -78 °C for 30 min then at -30 °C for 30 more min. The reaction was quenched with D_2O (10.0 equiv, 39 mmol, 706 µL), filtered through the short pad Celite®, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (pure hexanes) to obtained the desired deuterated product **22-D** (84%, 99% D-incorporation). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.26 (t, *J*=7.2 Hz, 2 H), 1.56 – 1.51 (m, 2 H), 1.42 – 1.36 (m, 2 H), 1.34 – 1.26 (m, 4 H), 0.89 (t, *J*=7.2 Hz, 3 H).

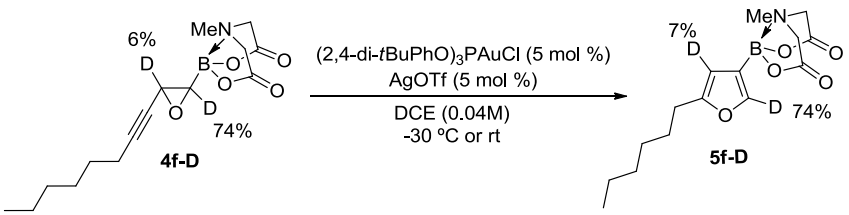
Compound **4f-D** was synthesized according to *method B* followed by epoxidation.

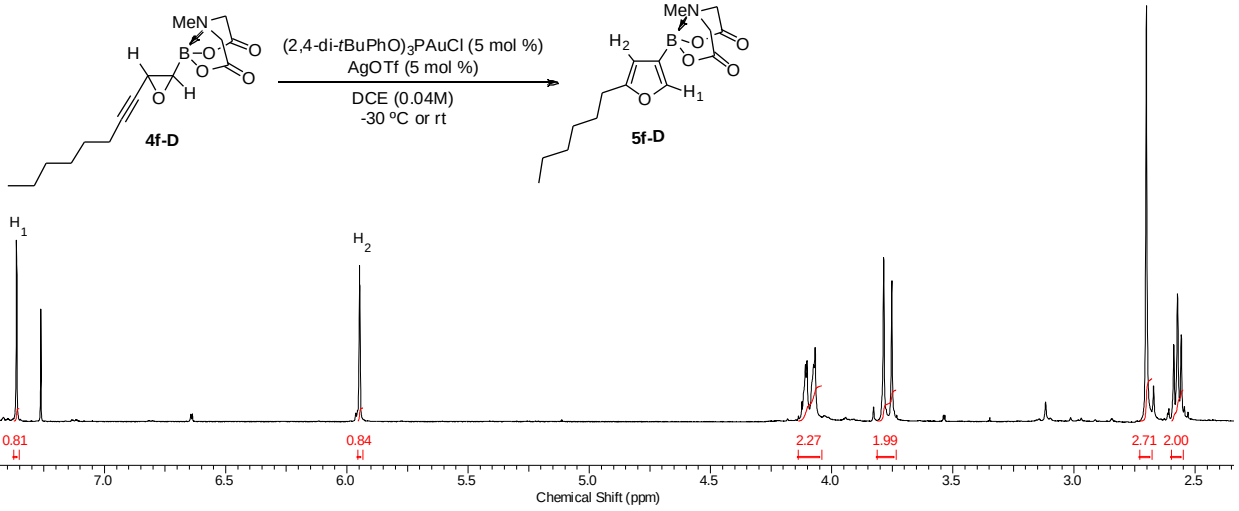


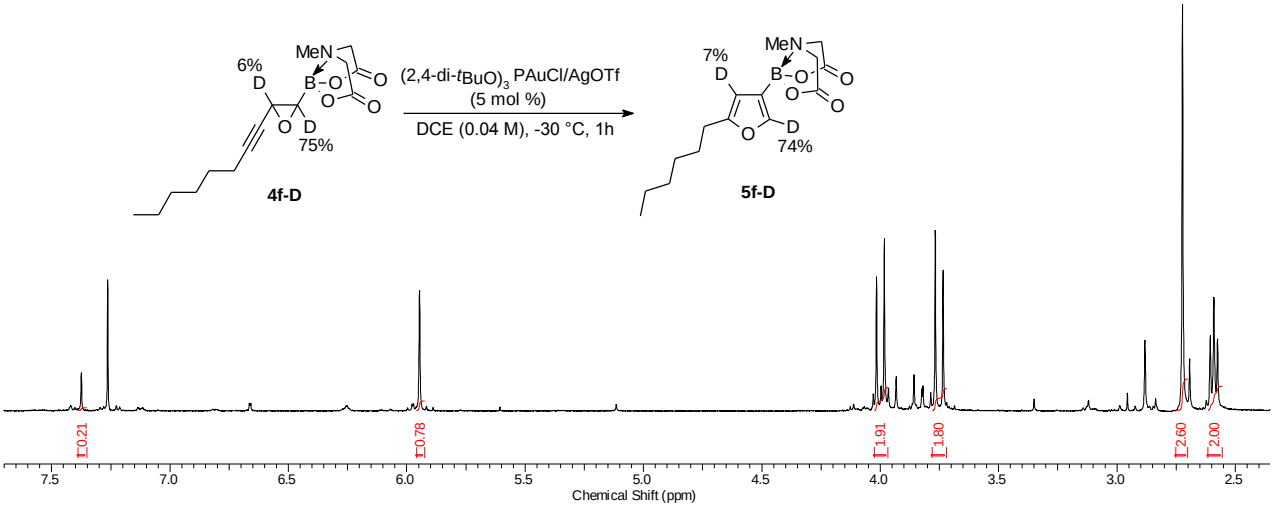
4f-D

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.01 (d, *J*=16.5 Hz, 2 H), 3.87 (d, *J*=17.2 Hz, 1 H), 3.74 (d, *J*=16.1 Hz, 1 H), 3.35 (s, 0.85 H), 3.12 (s, 3 H), 2.44 (d, *J*=2.9 Hz, 0.24 H), 2.18 (td, *J*=7.2, 1.3 Hz, 2 H), 1.51 – 1.45 (m, 2 H), 1.38 – 1.22 (m, 6 H), 0.87 (t, *J*=7.0 Hz, 3 H).

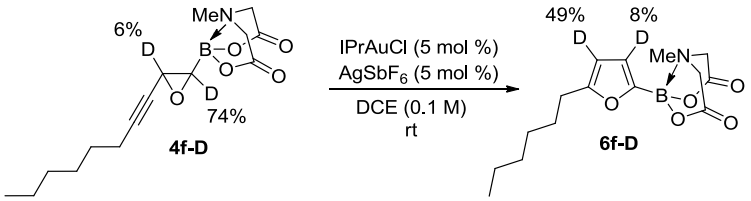
7b. Au-Catalyzed Migratory Cycloisomerization Reaction of Deuterated Alkynyl Epoxide:

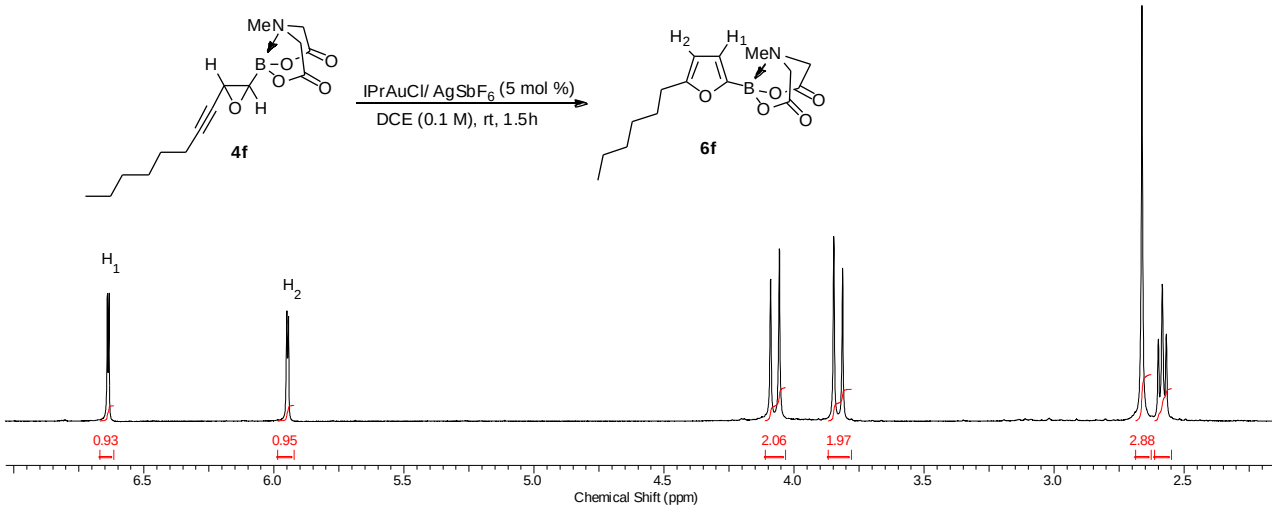


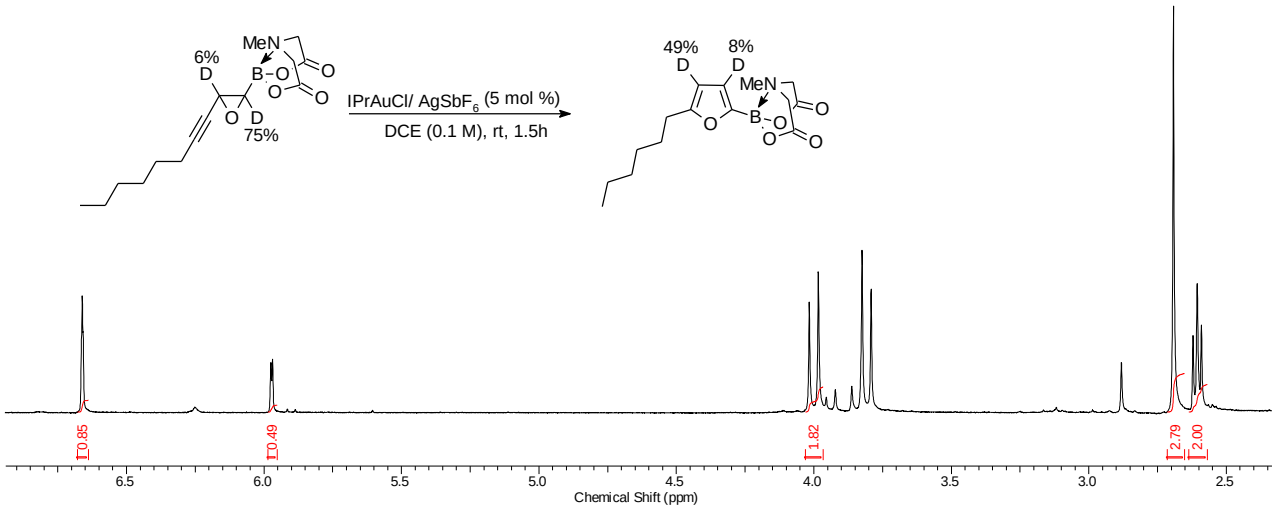




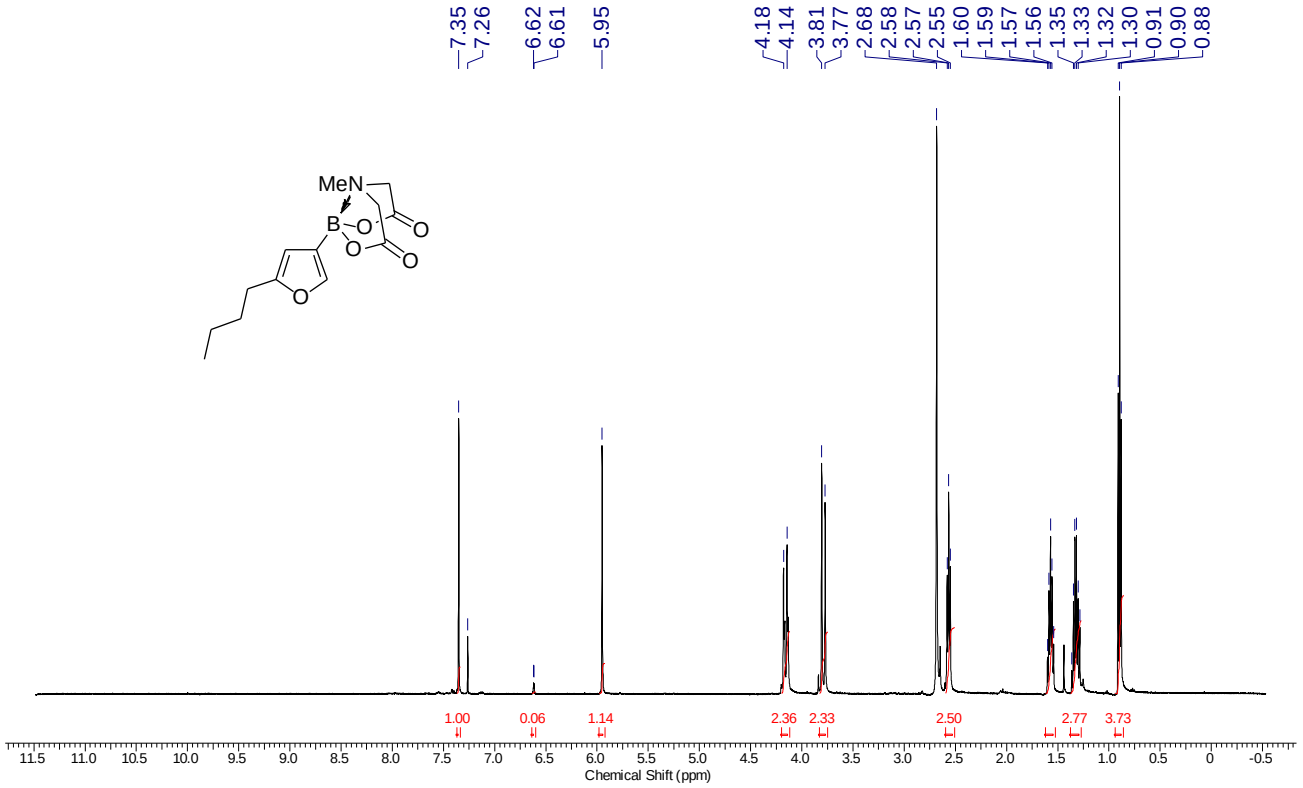
7c. Au-Catalyzed Cycloisomerization Reaction of Deuterated Alkynyl Epoxide:



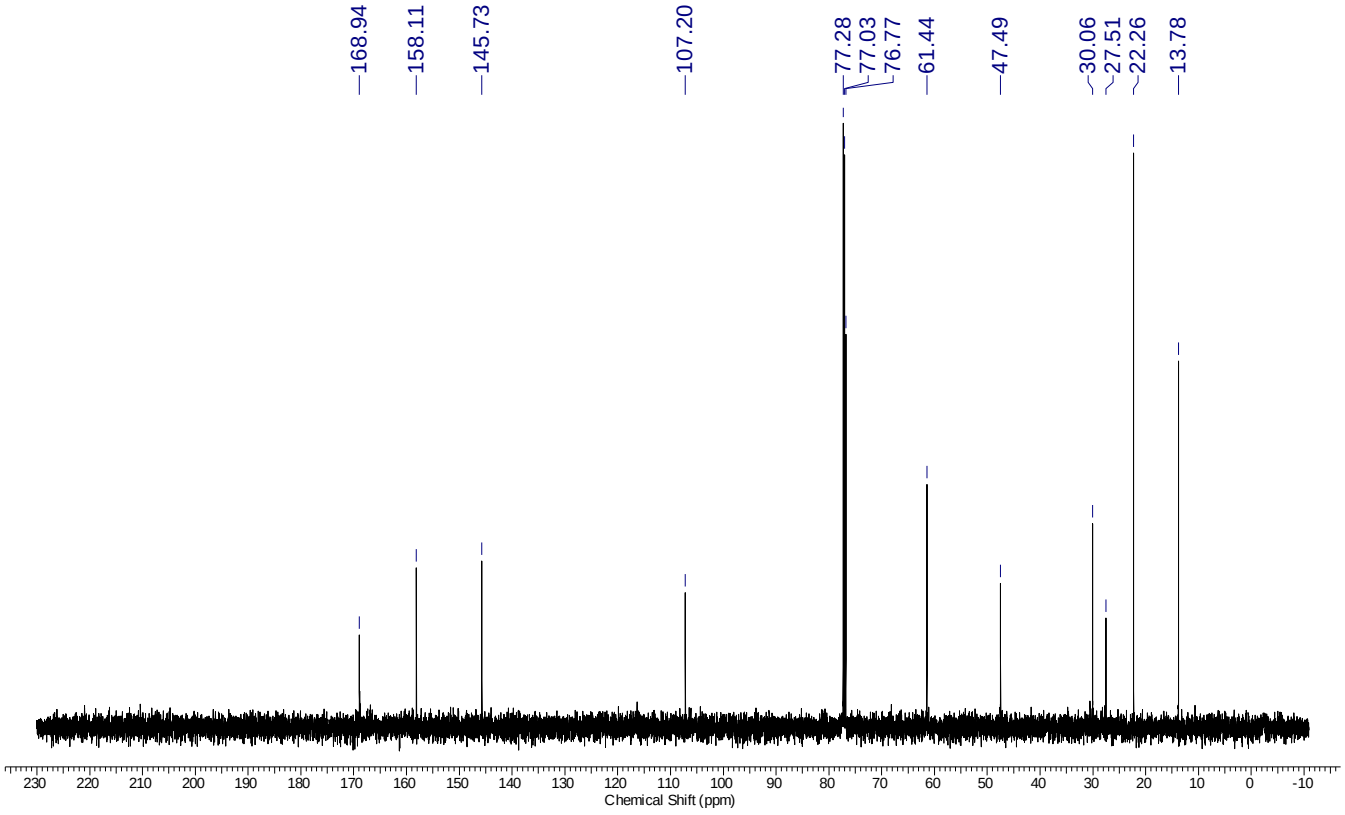




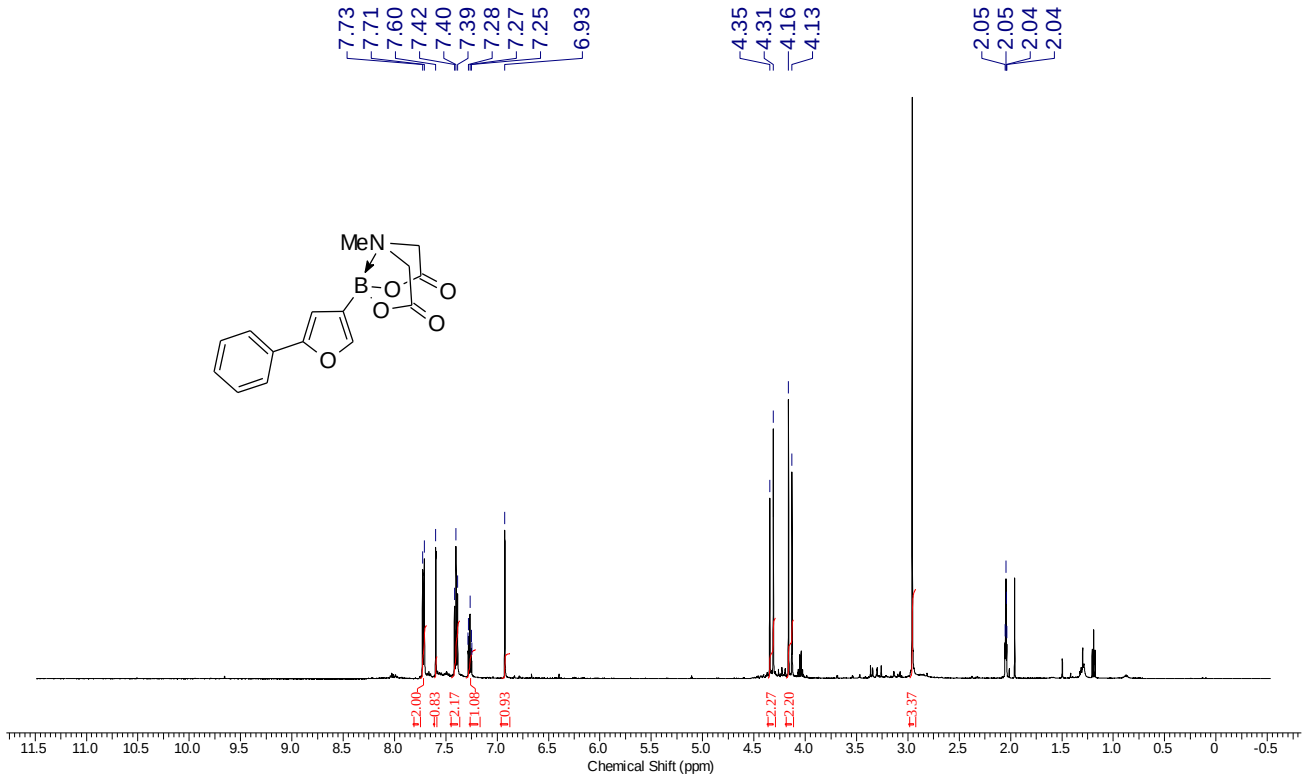
^{1}H Spectrum of **5a** in $CDCl_3$



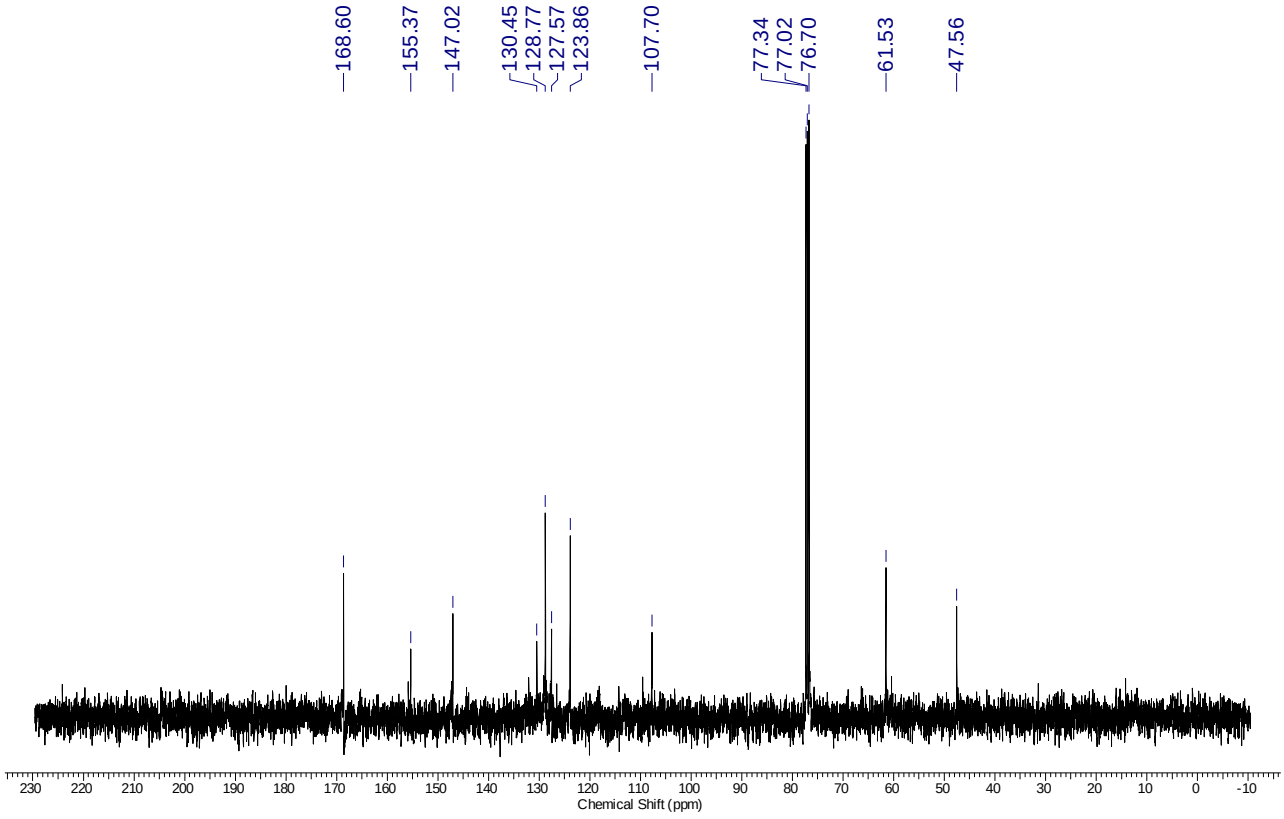
^{13}C Spectrum of **5a** in $CDCl_3$



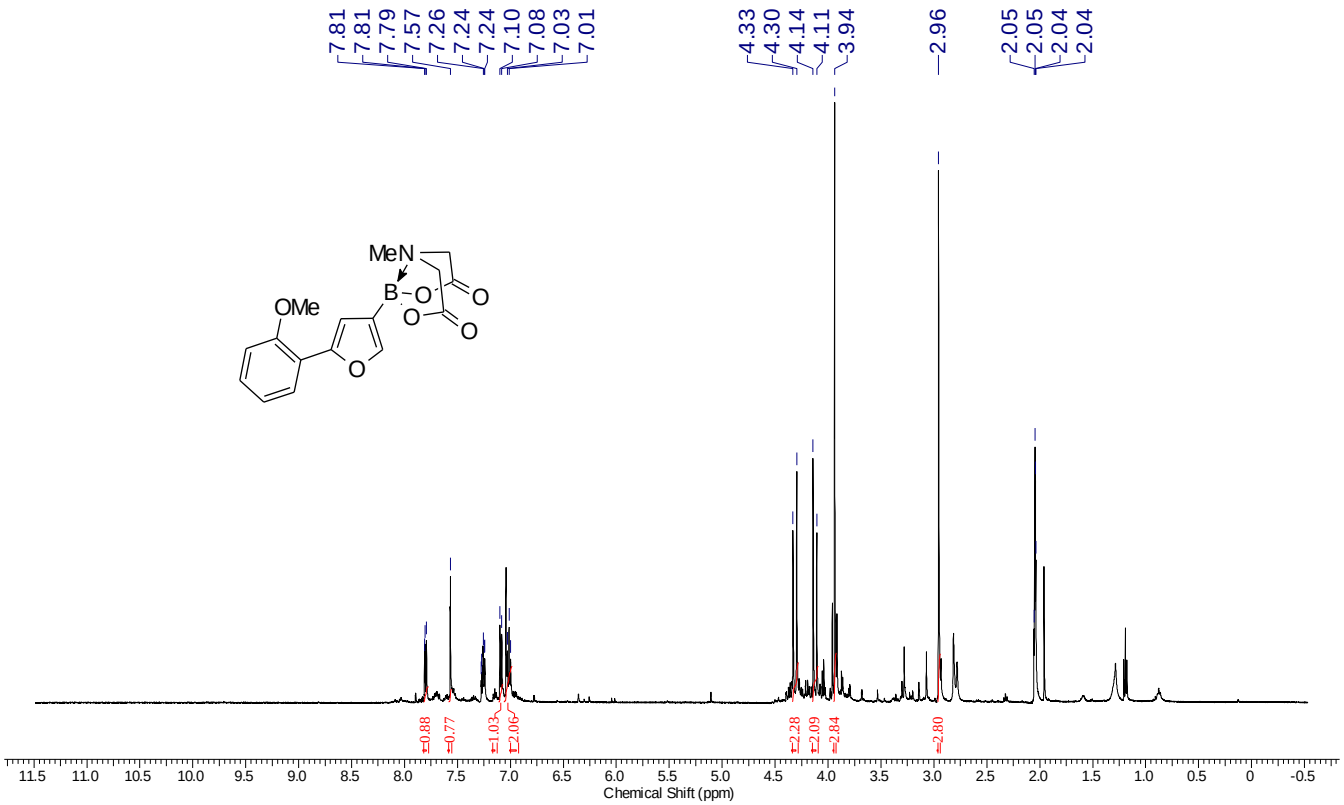
^{1}H Spectrum of **5b** in $(CD_3)_2CO$



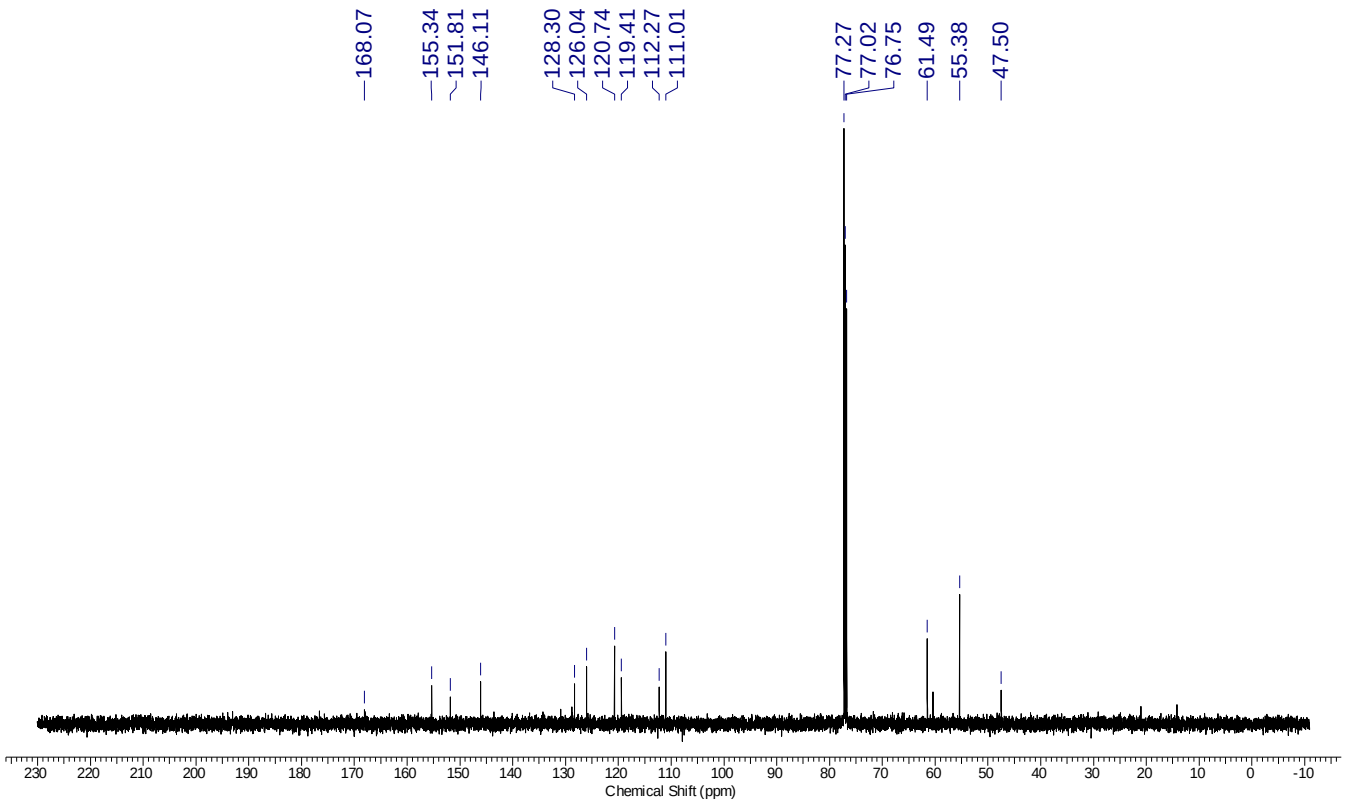
^{13}C Spectrum of **5b** in $CDCl_3$



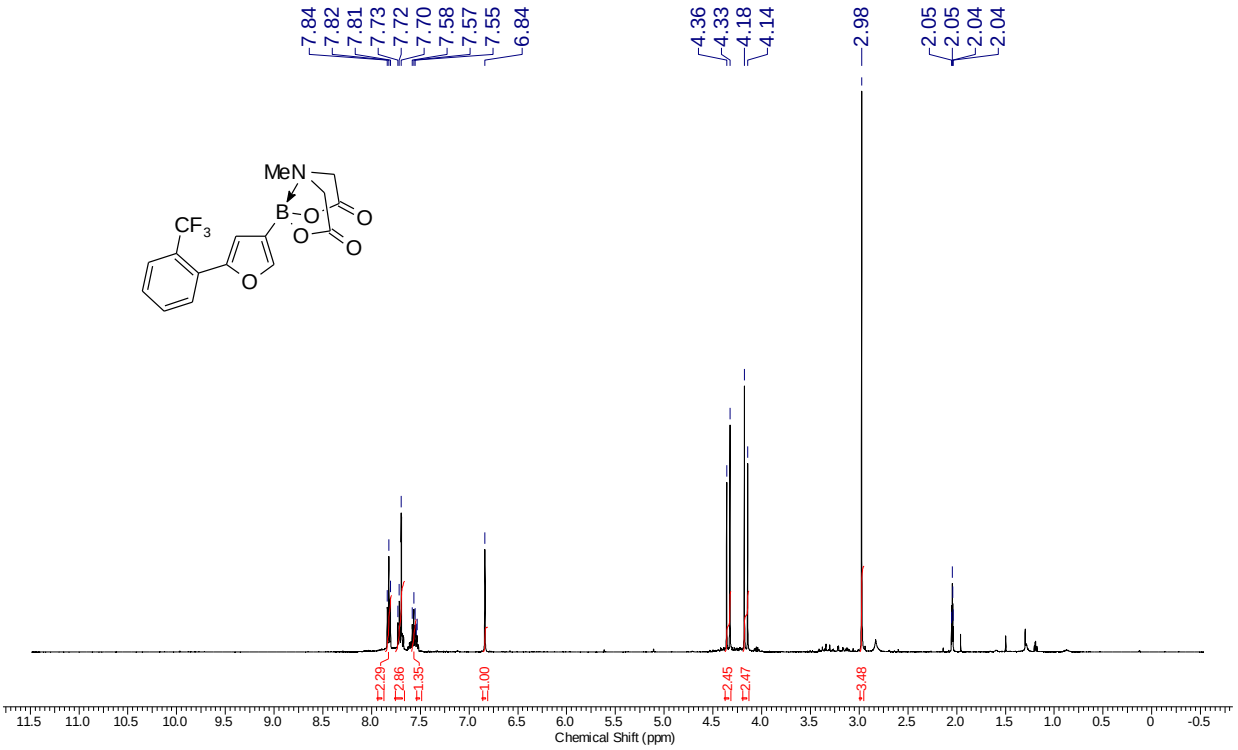
^{1}H Spectrum of **5c** in $(CD_3)_2CO$



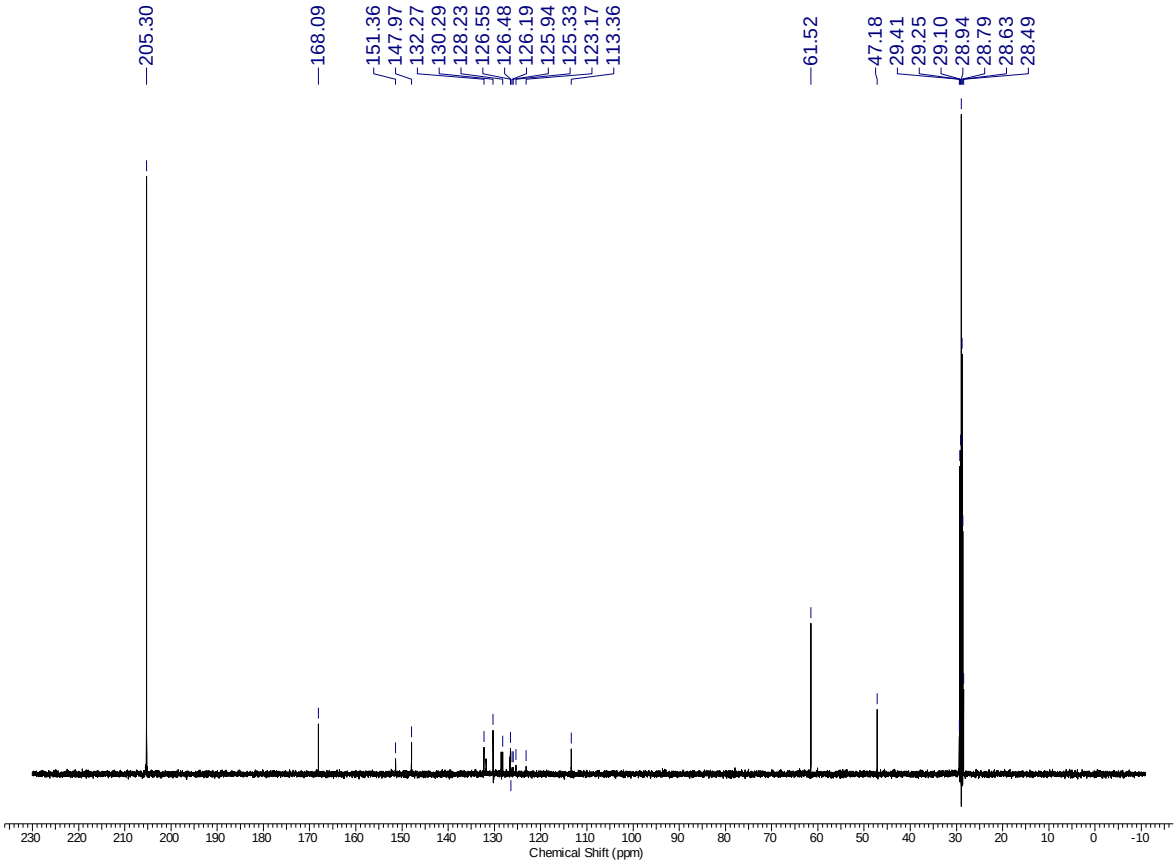
^{13}C Spectrum of **5c** in $CDCl_3$



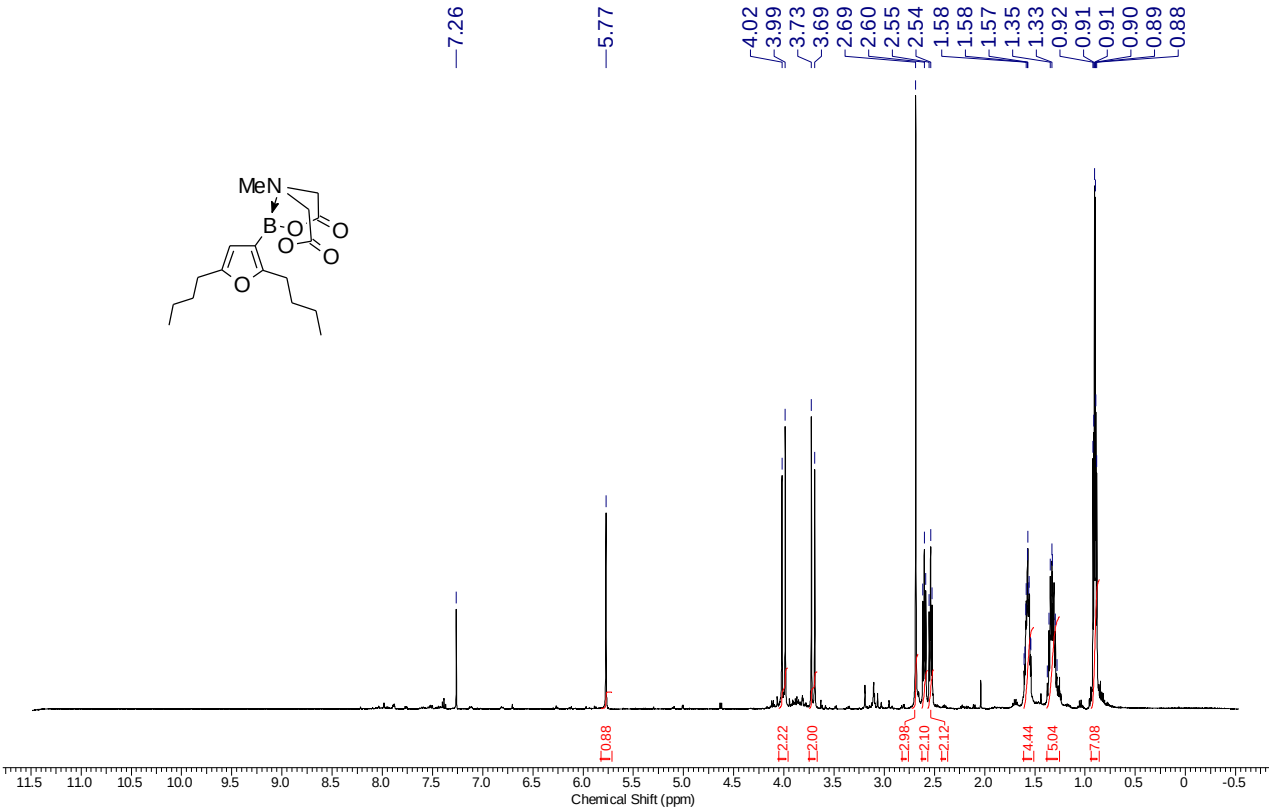
^{1}H Spectrum of **5d** in $(CD_3)_2CO$



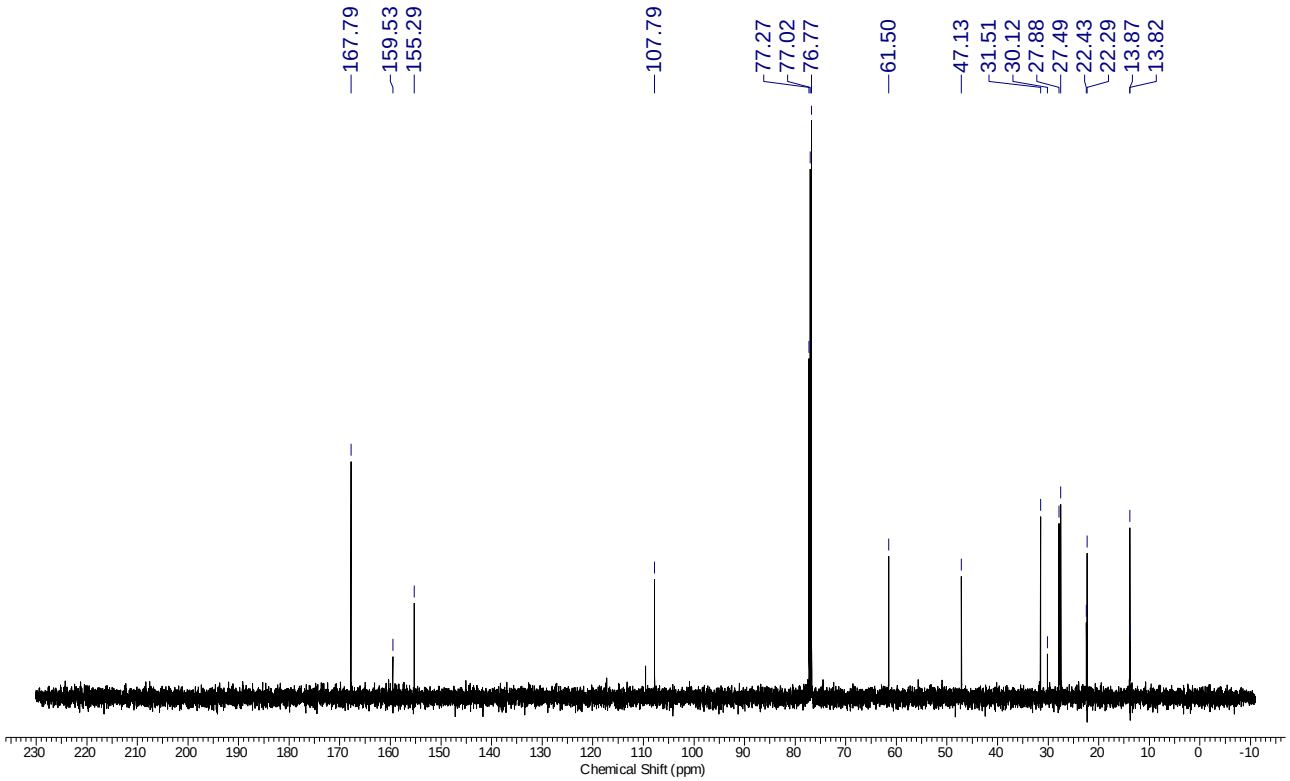
^{13}C Spectrum of **5d** in $(CD_3)_2CO$



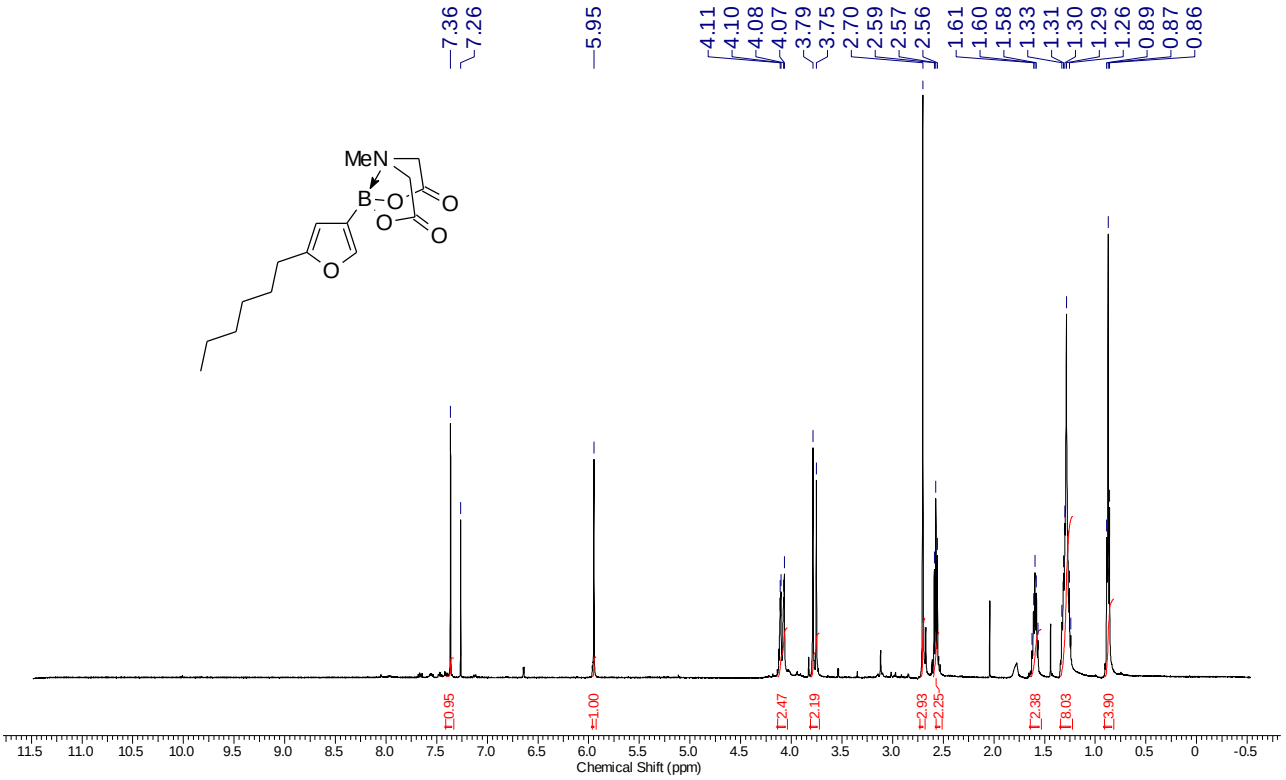
^{1}H Spectrum of **5e** in $CDCl_3$



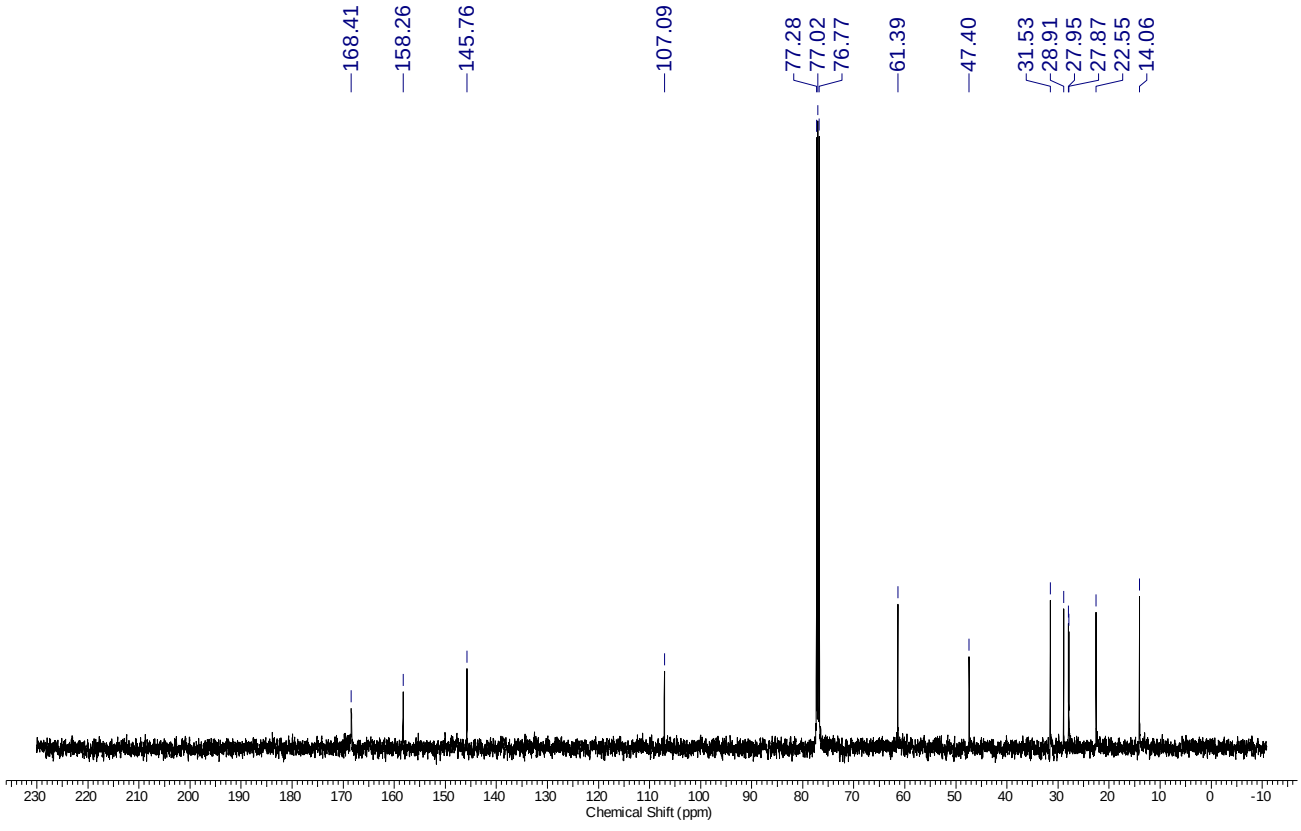
^{13}C Spectrum of **5e** in $CDCl_3$



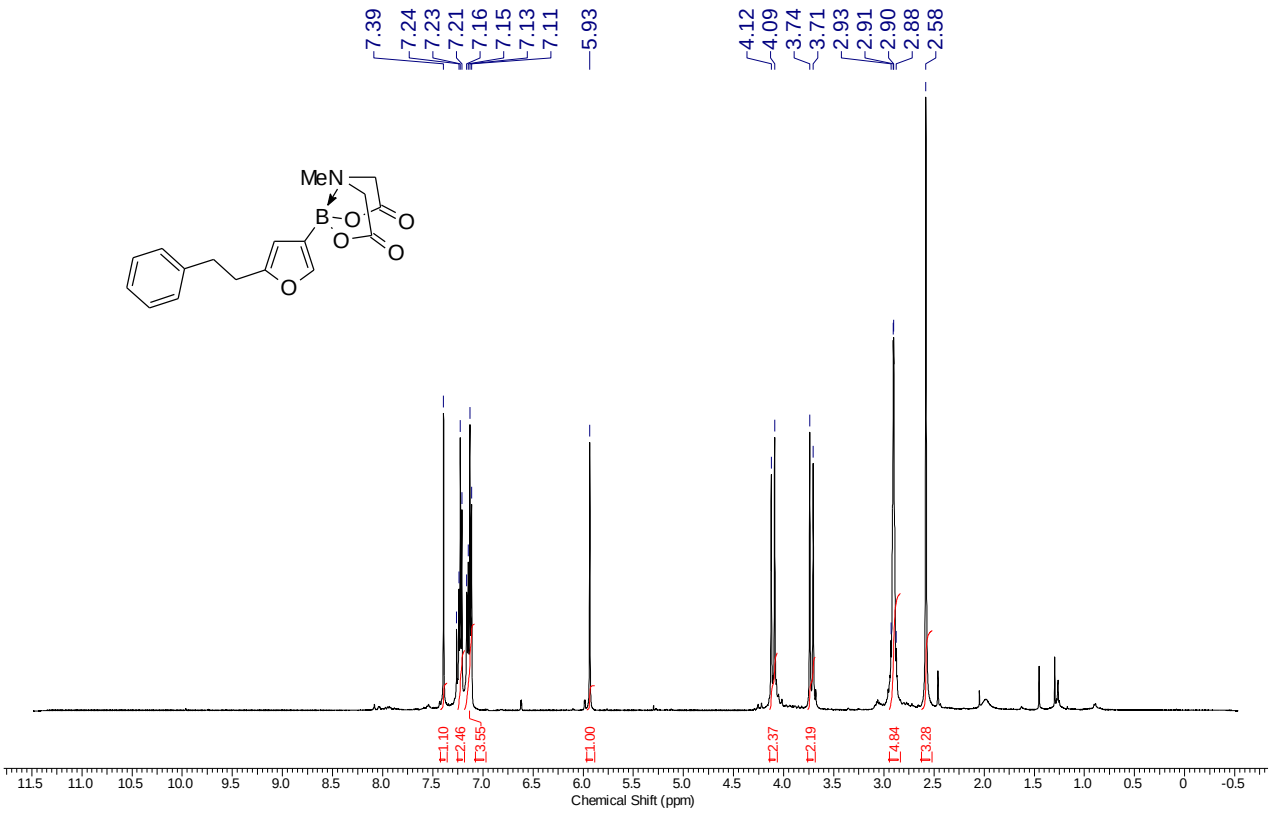
^{1}H Spectrum of **5f** in $CDCl_3$



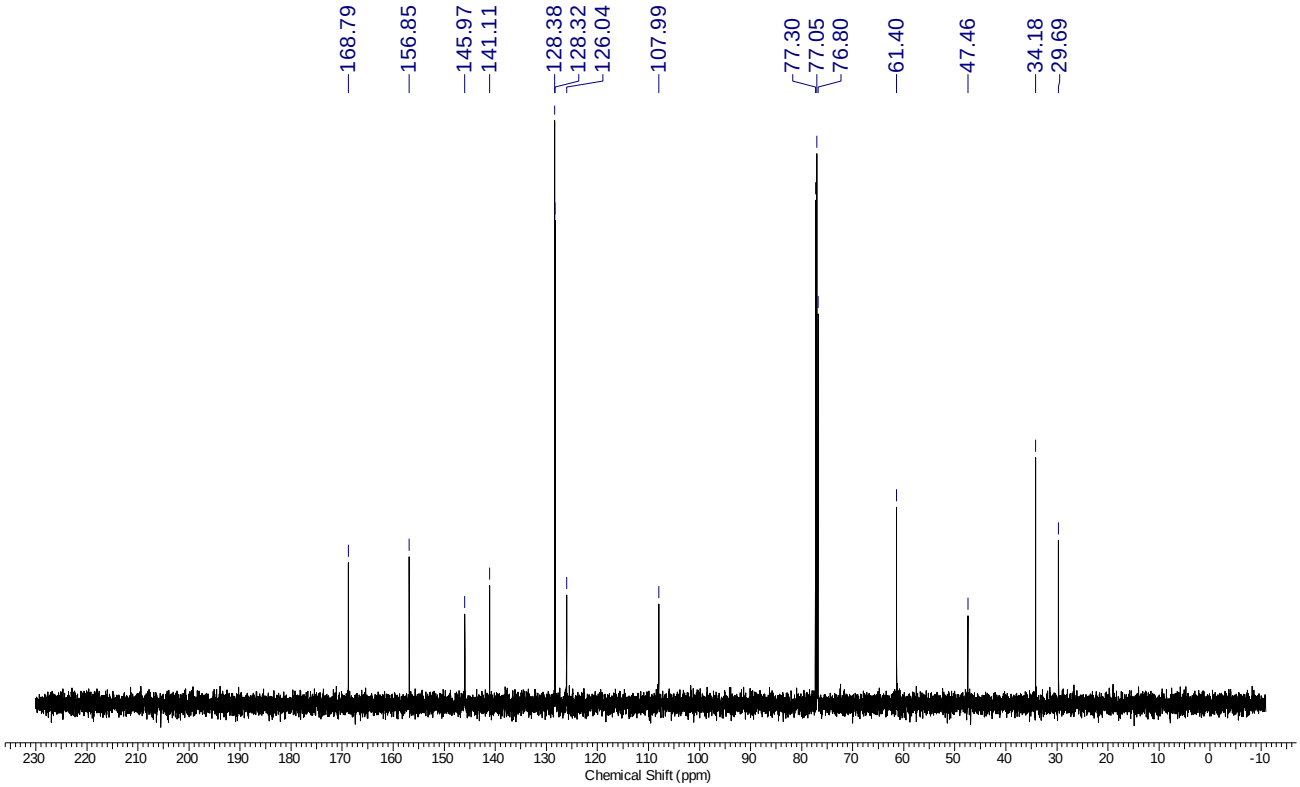
^{13}C Spectrum of **5f** in $CDCl_3$



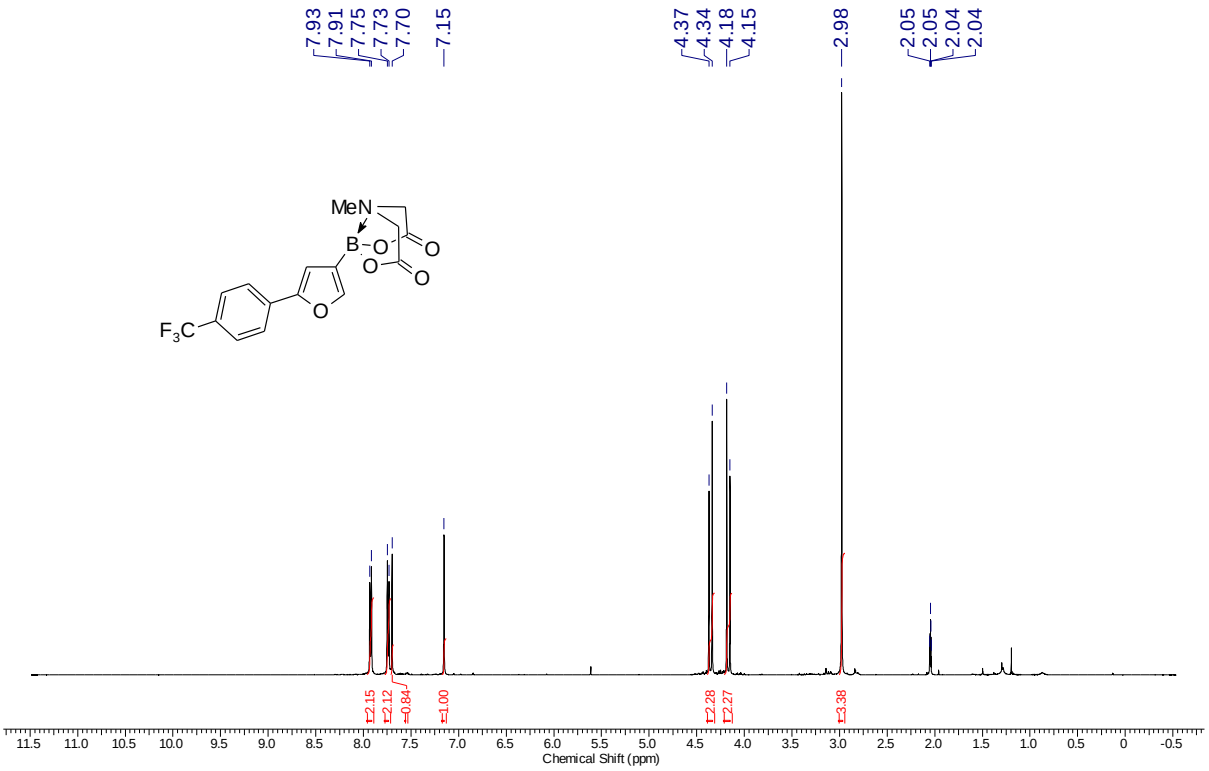
^{1}H Spectrum of **5g** in $CDCl_3$



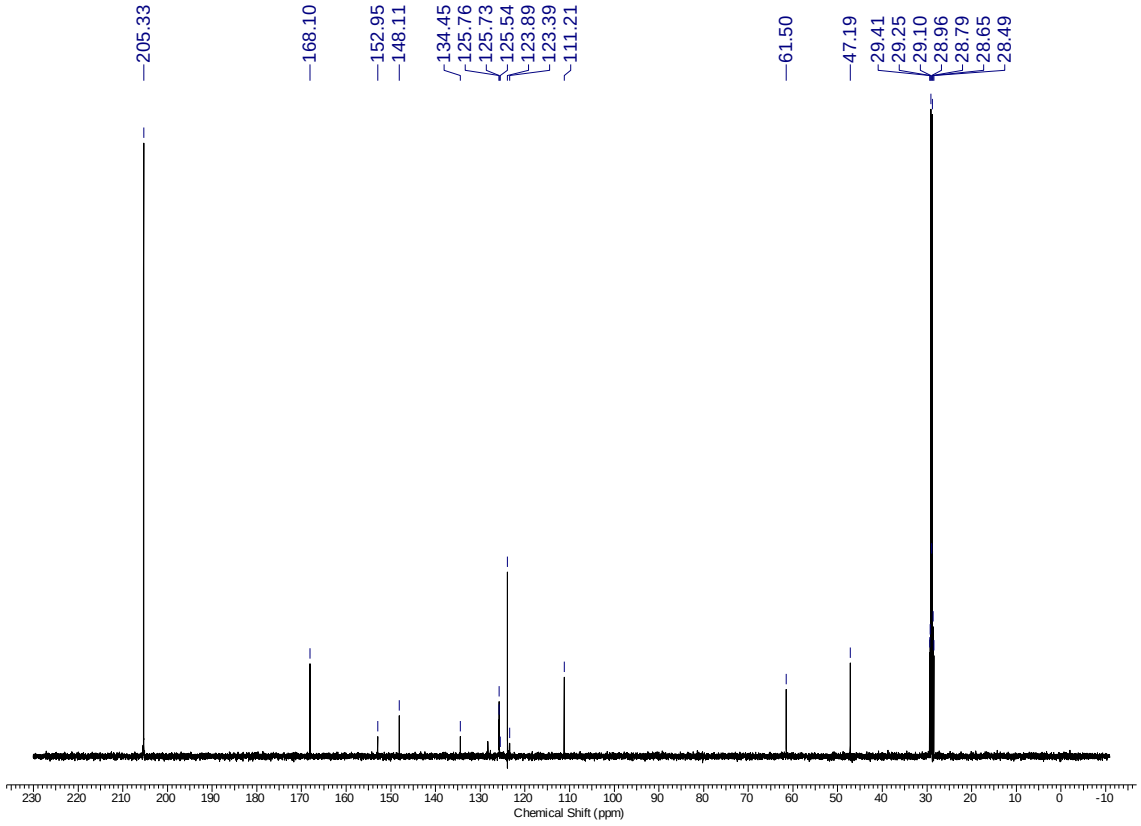
^{13}C Spectrum of **5g** in $CDCl_3$



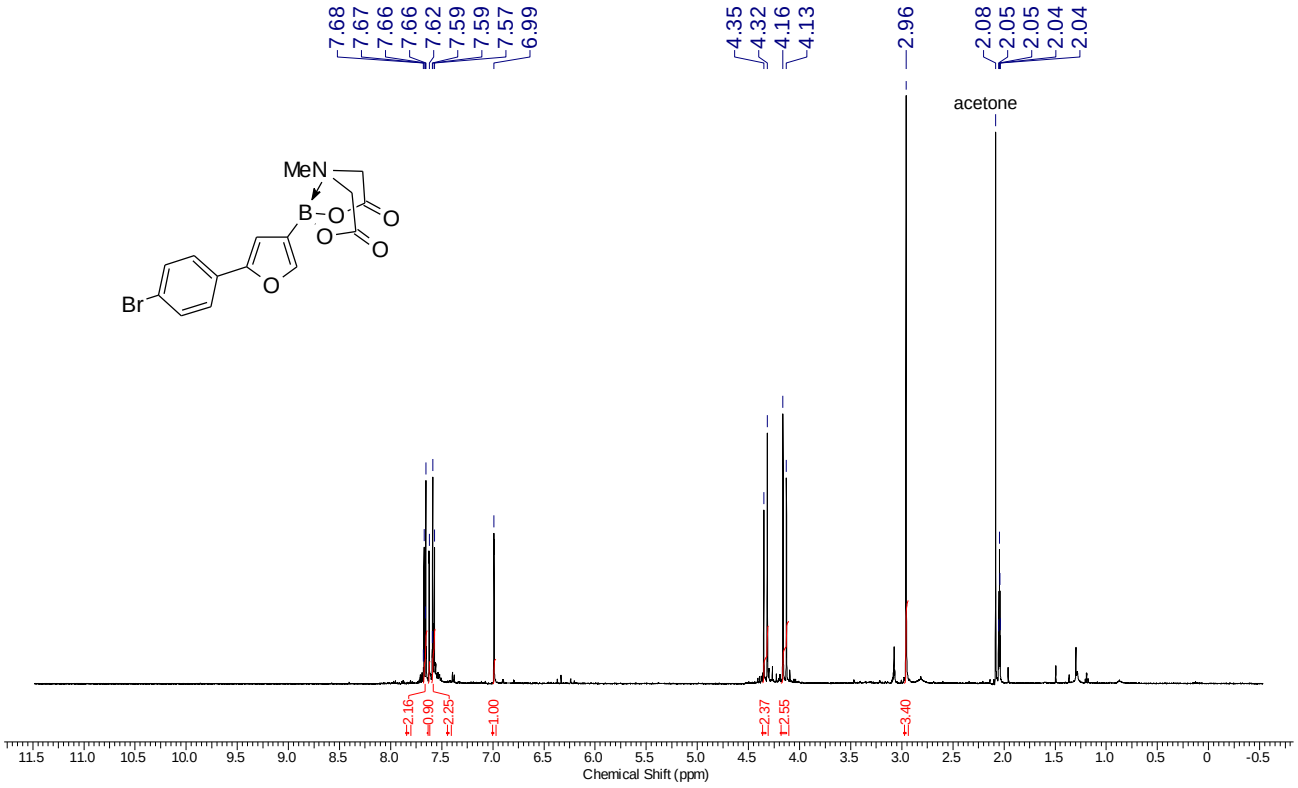
^{1}H Spectrum of **5h** in $(CD_3)_2CO$



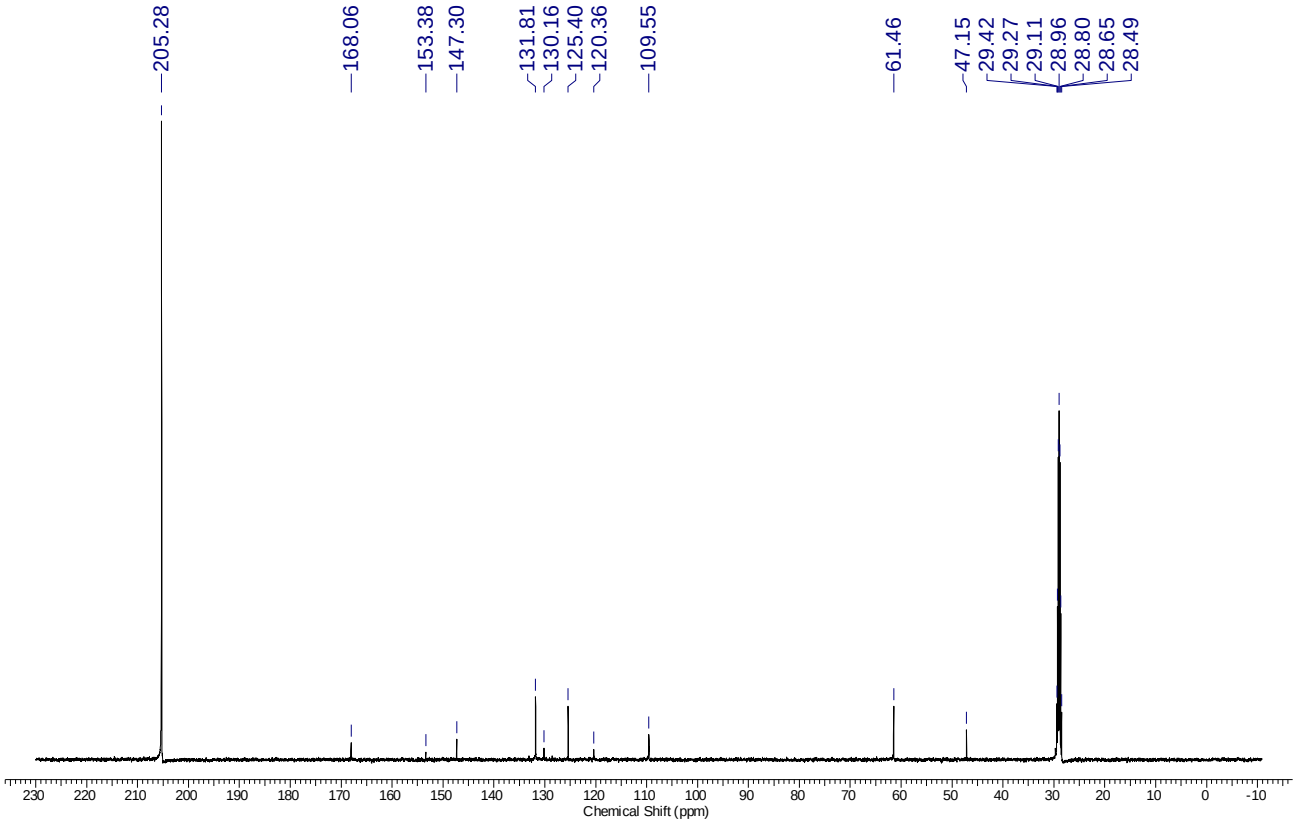
^{13}C Spectrum of **5h** in $(CD_3)_2CO$



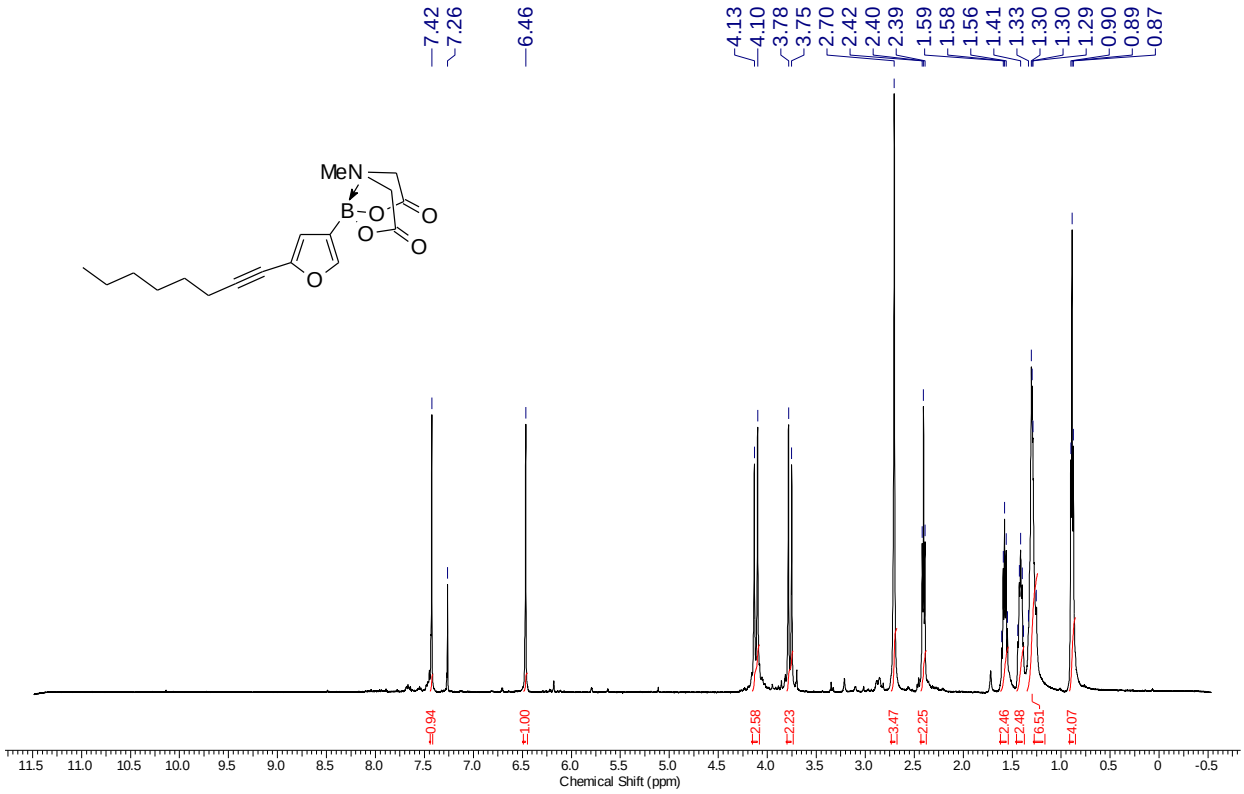
^{1}H Spectrum of **5i** in $(CD_3)_2CO$



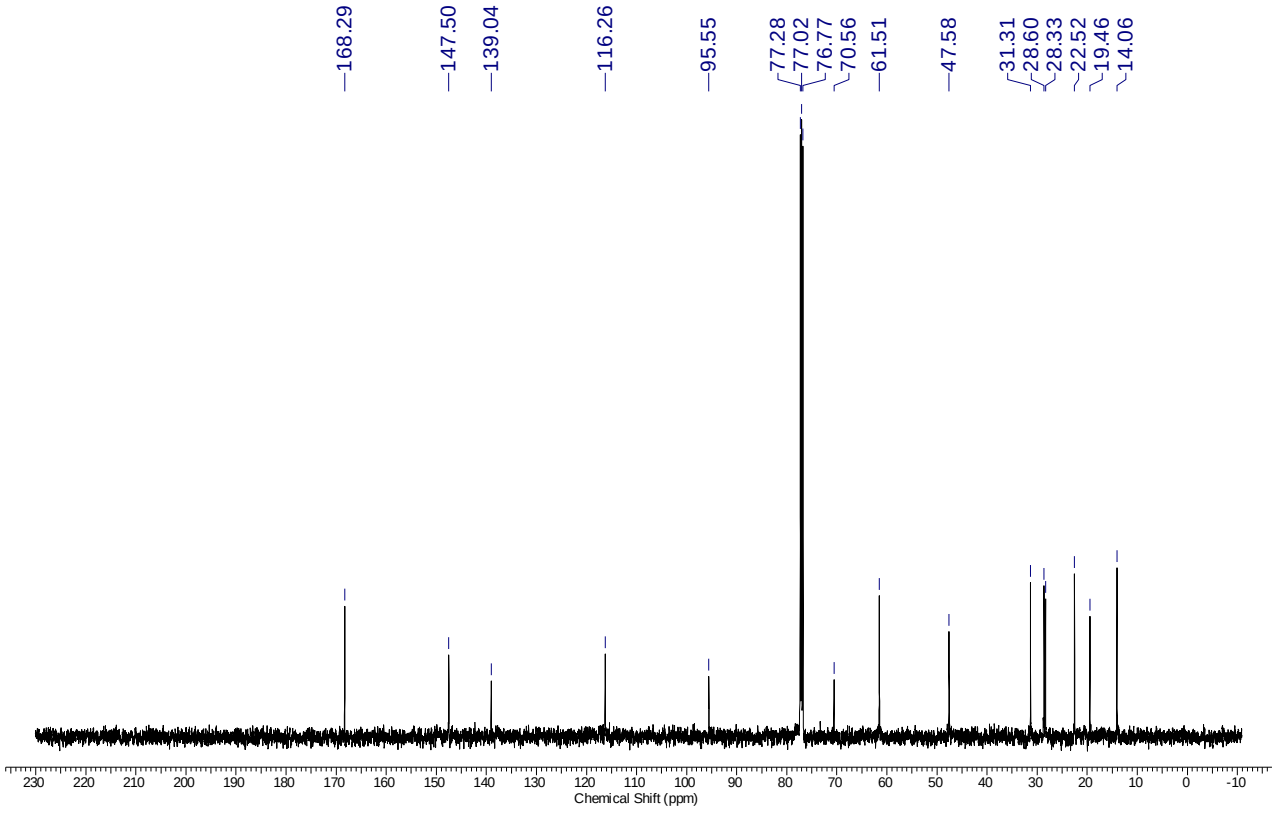
^{13}C Spectrum of **5i** in $(CD_3)_2CO$



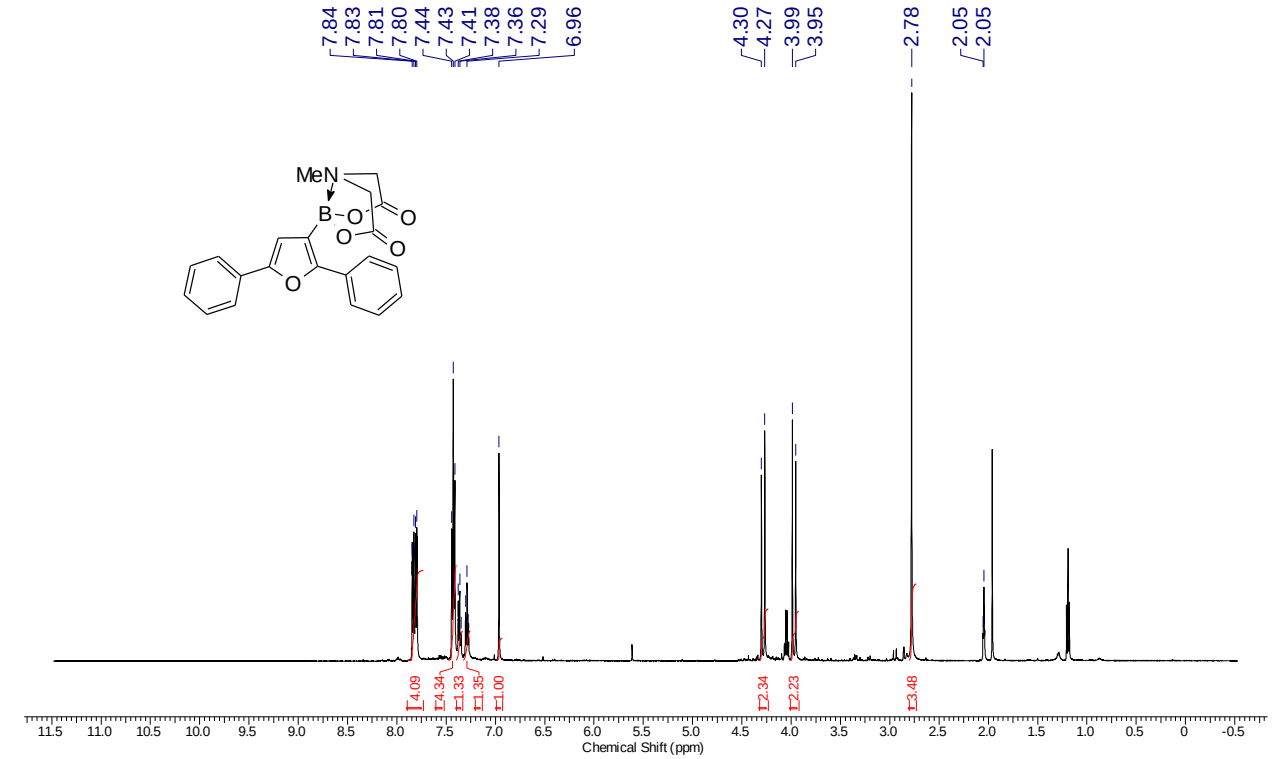
^{1}H Spectrum of **5j** in $CDCl_3$



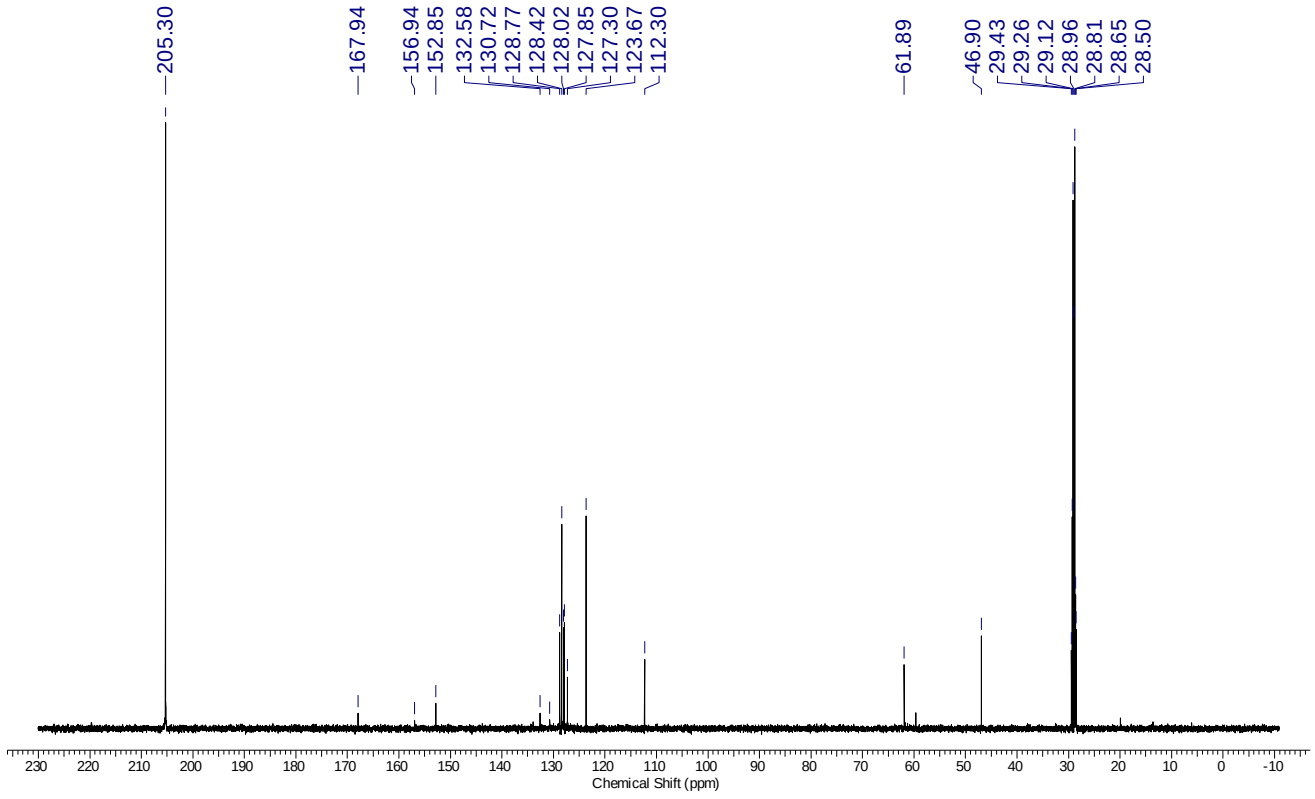
^{13}C Spectrum of **5j** in $CDCl_3$



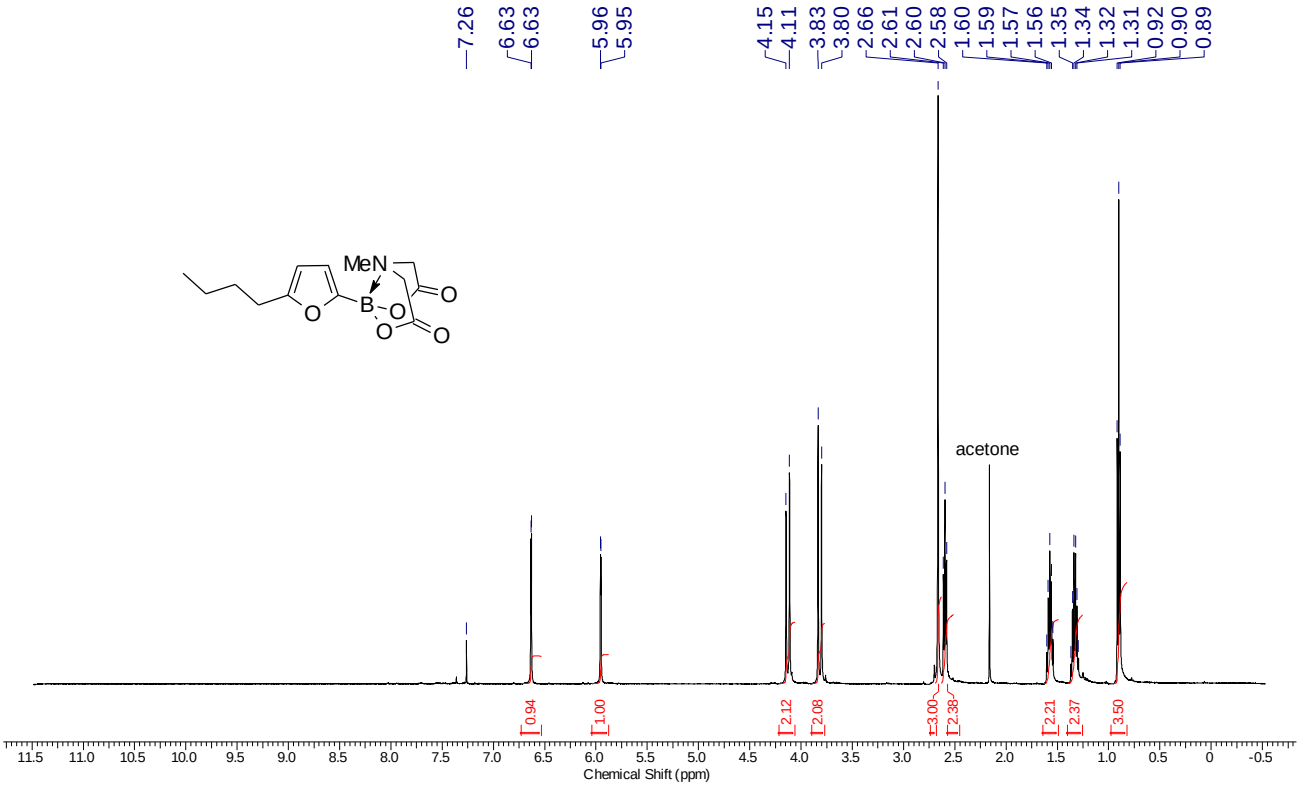
^{1}H Spectrum of **5k** in $(CD_3)_2CO$



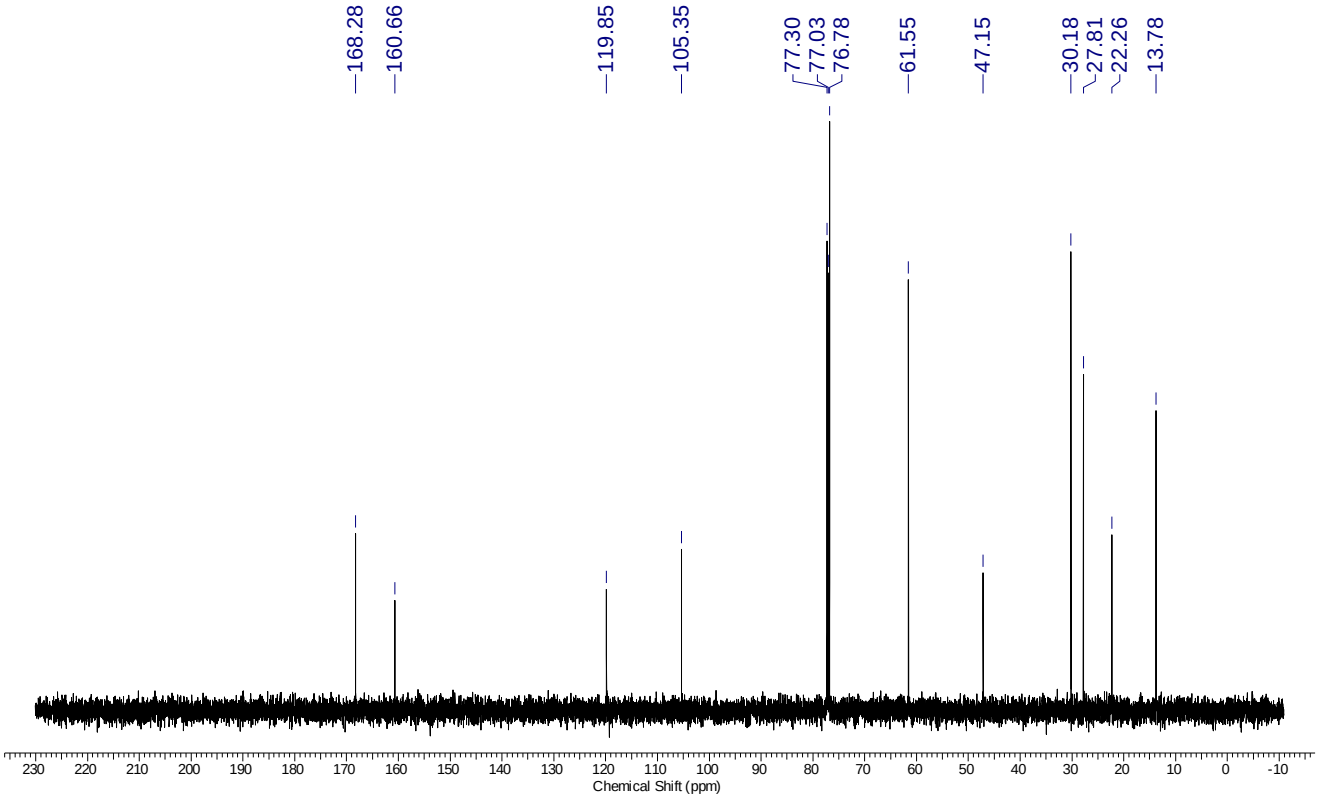
^{13}C Spectrum of **5k** in $(CD_3)_2CO$



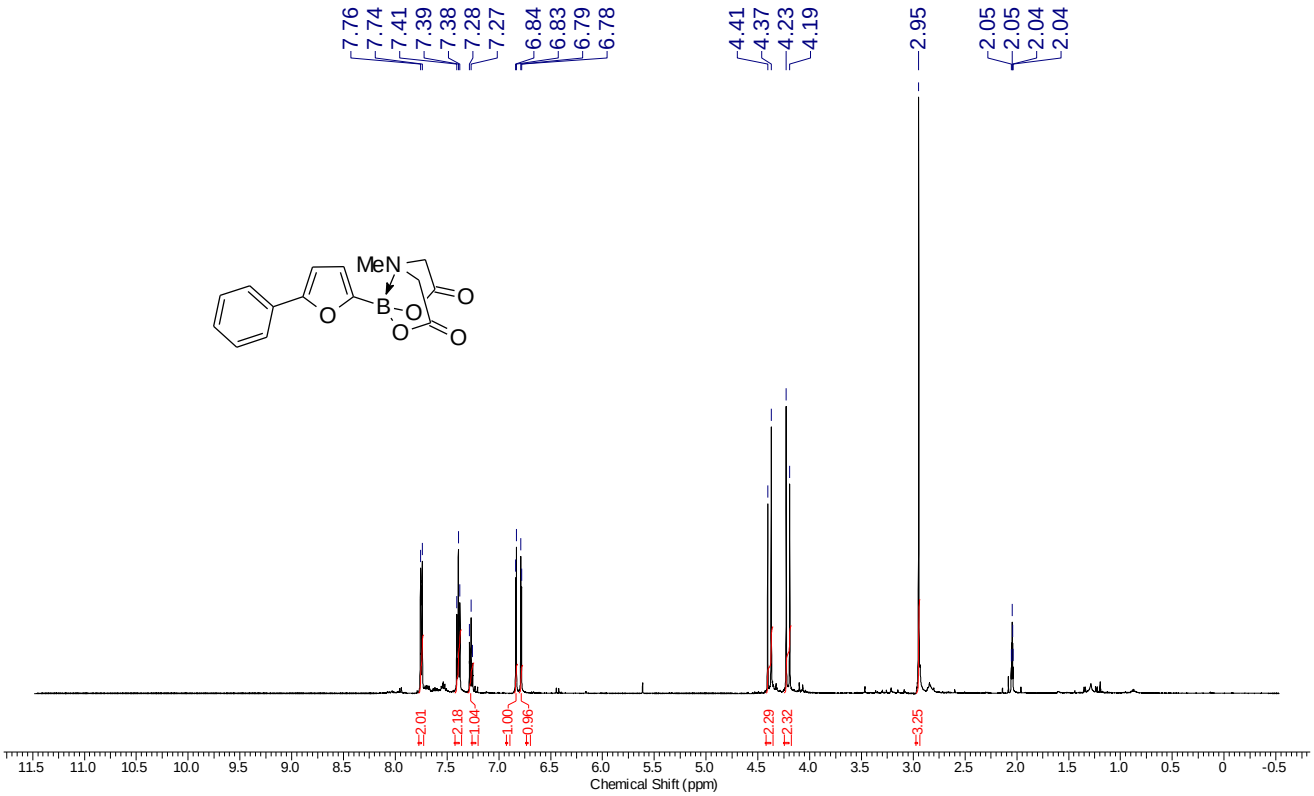
^{1}H Spectrum of **6a** in $CDCl_3$



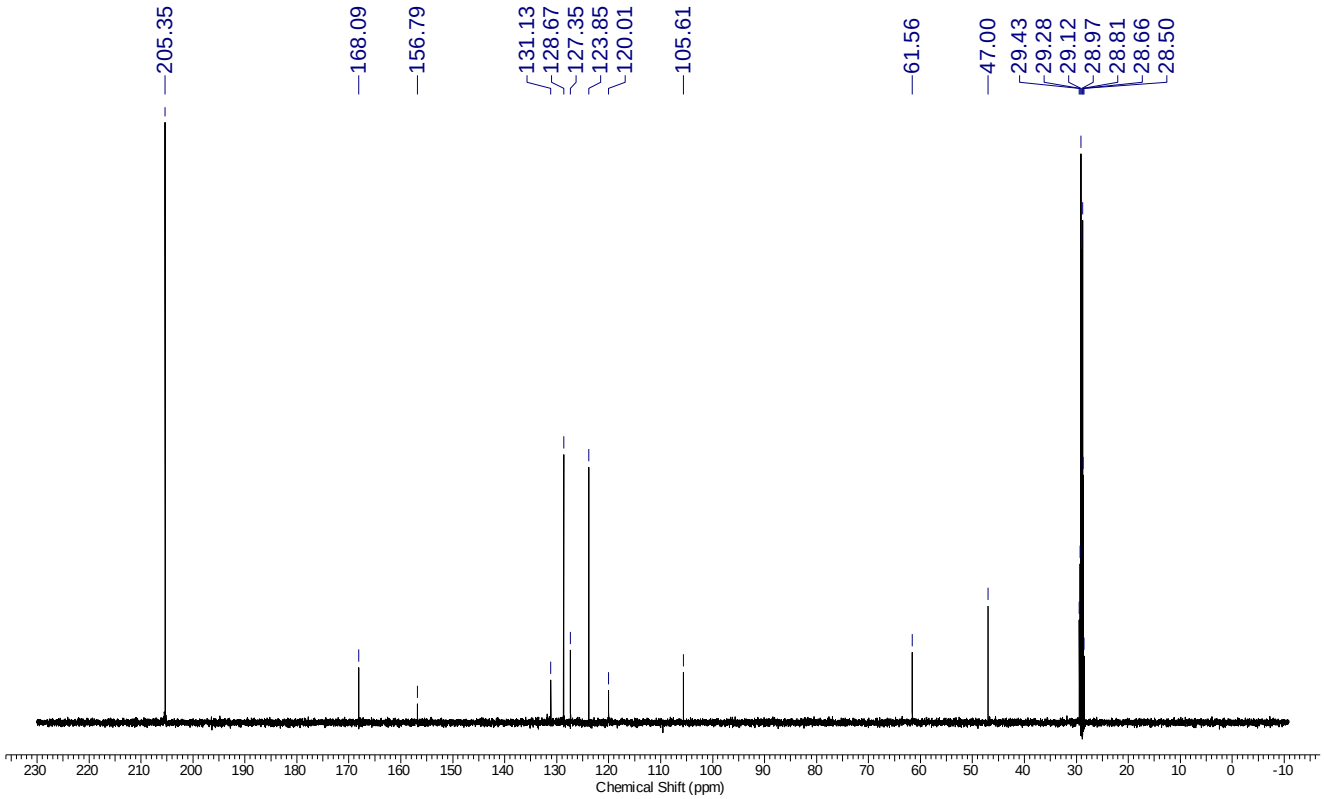
^{13}C Spectrum of **6a** in $CDCl_3$



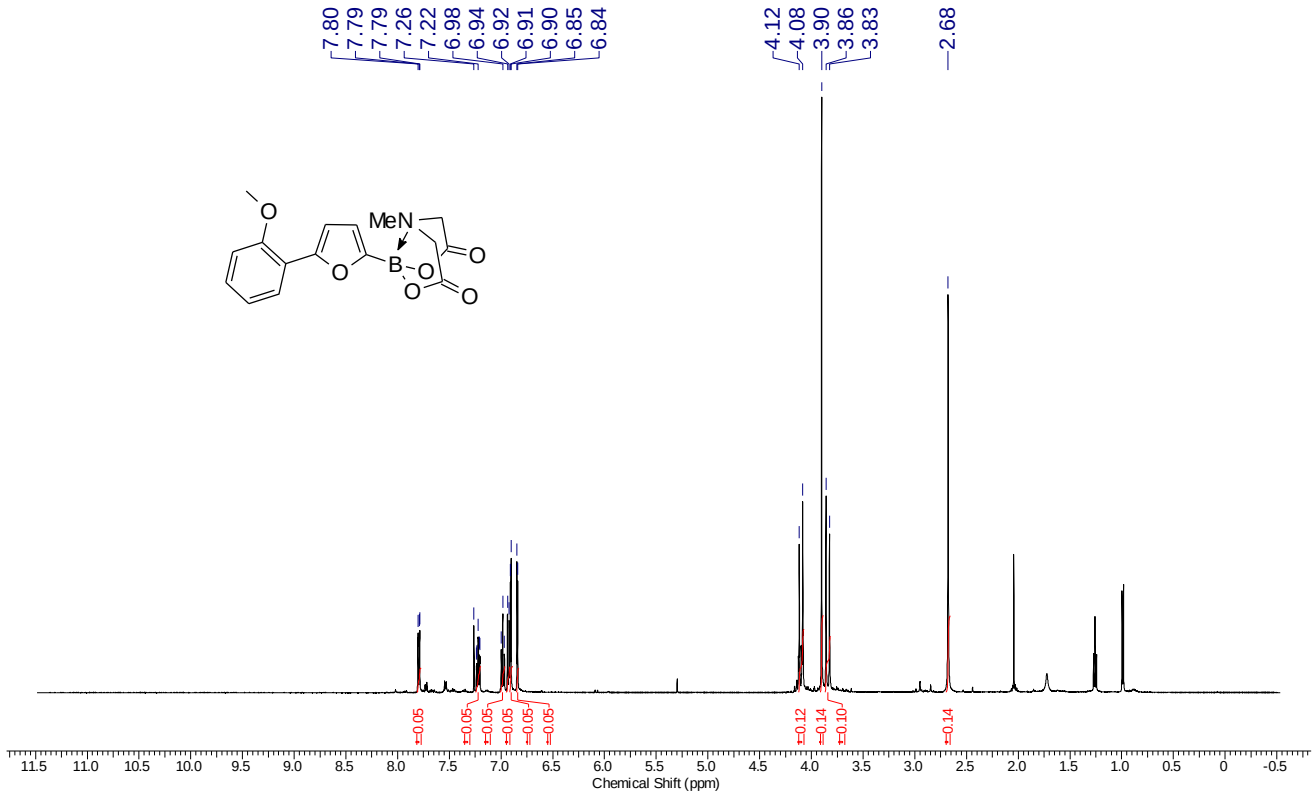
^{1}H Spectrum of **6b** in $(CD_3)_2CO$



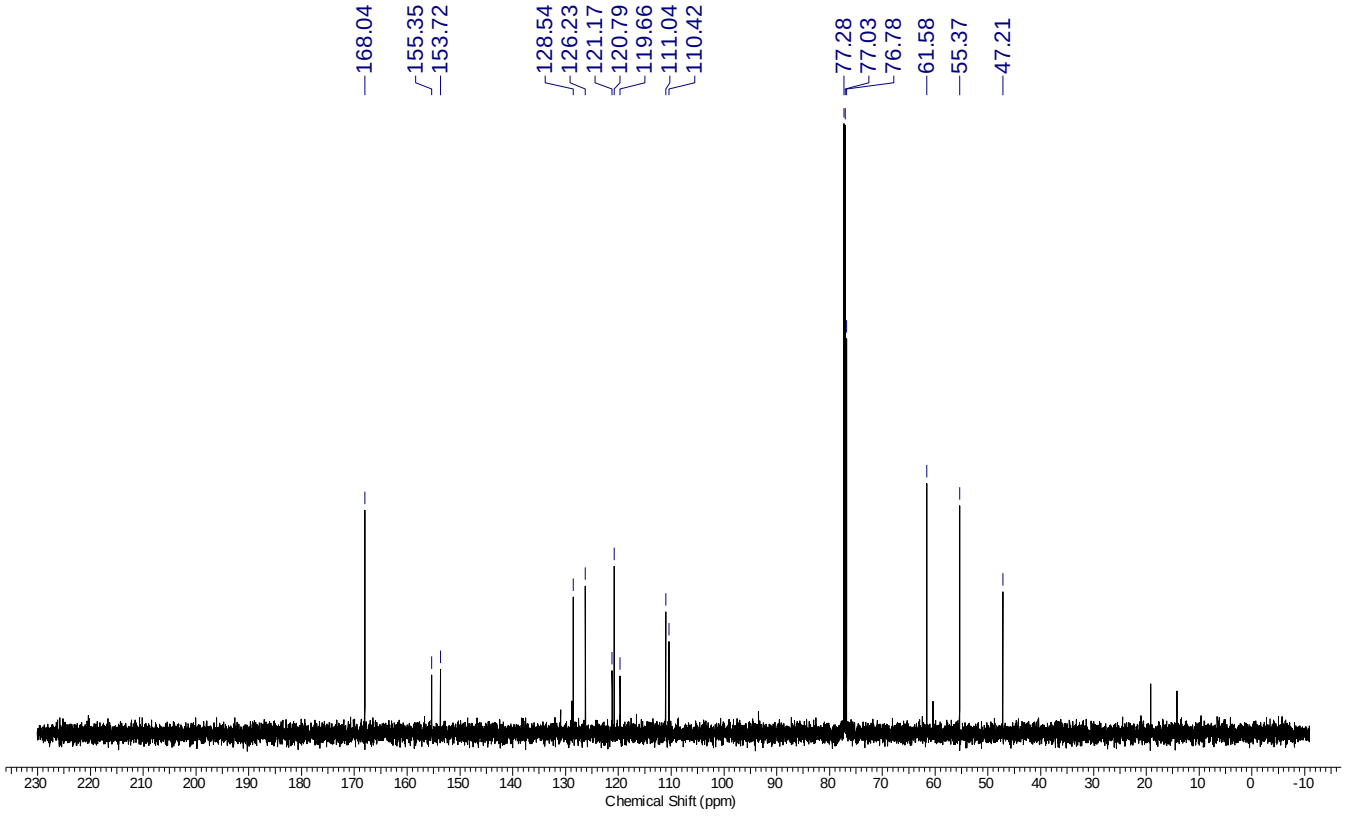
^{13}C Spectrum of **6b** in $(CD_3)_2CO$



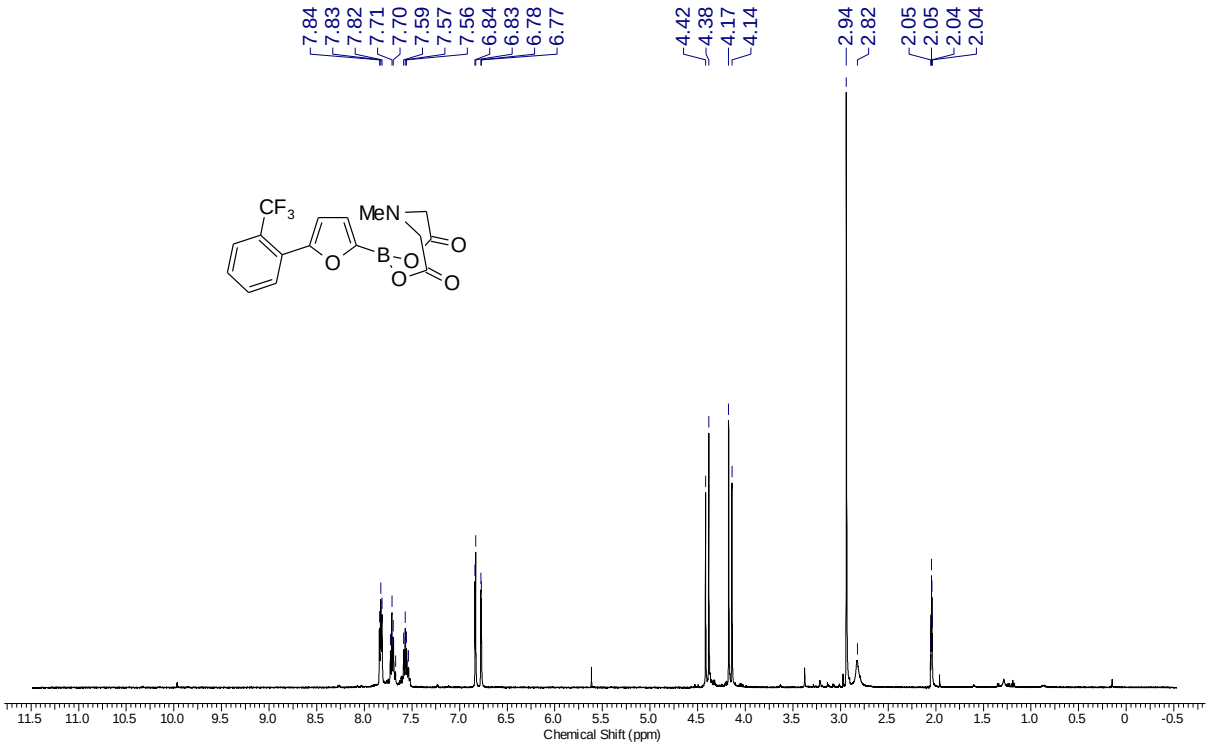
^{1}H Spectrum of **6c** in $CDCl_3$



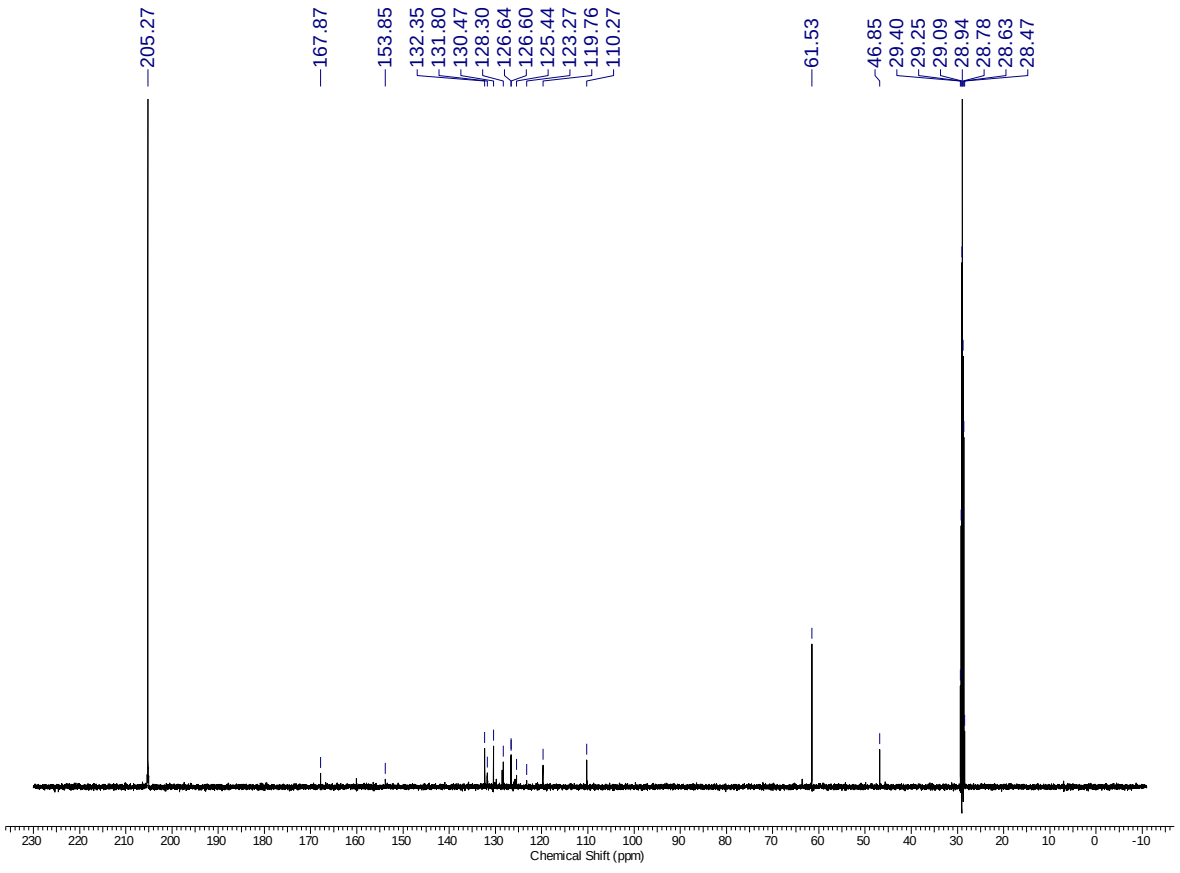
^{13}C Spectrum of **6c** in $CDCl_3$



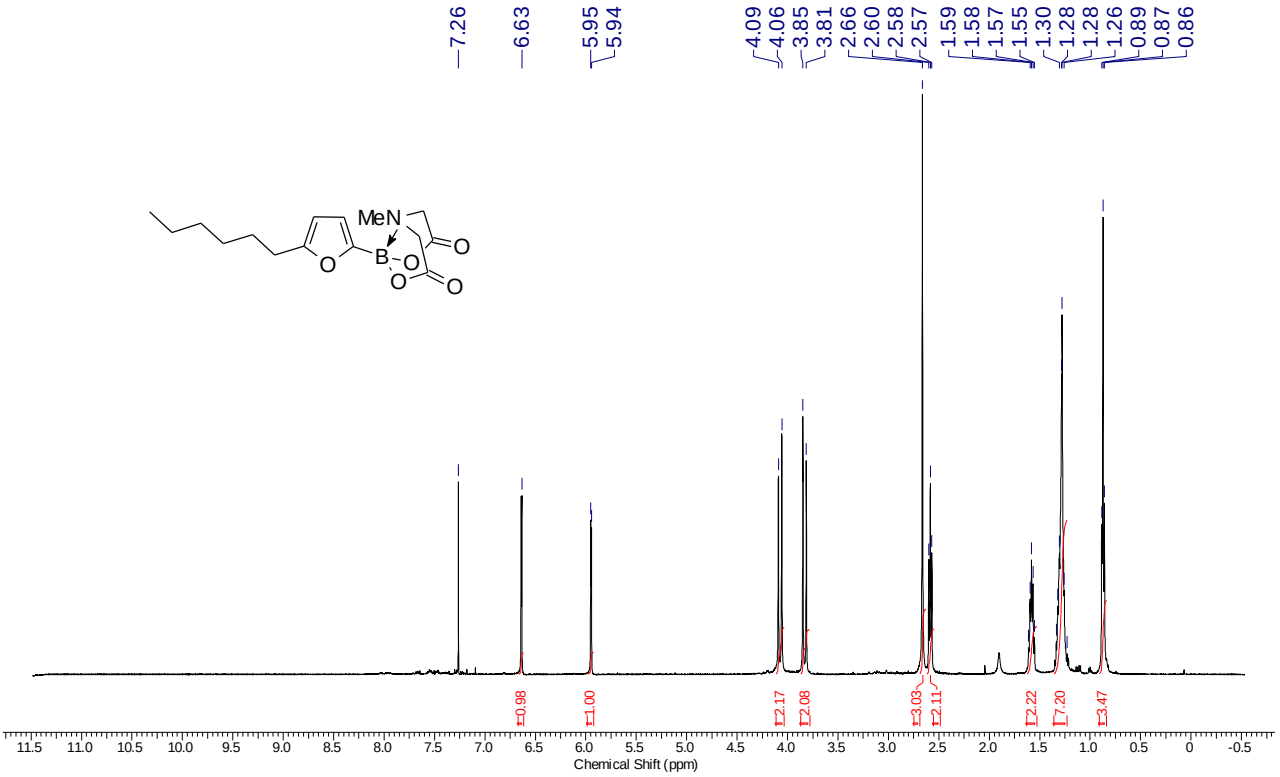
^{1}H Spectrum **6d** in $(CD_3)_2CO$



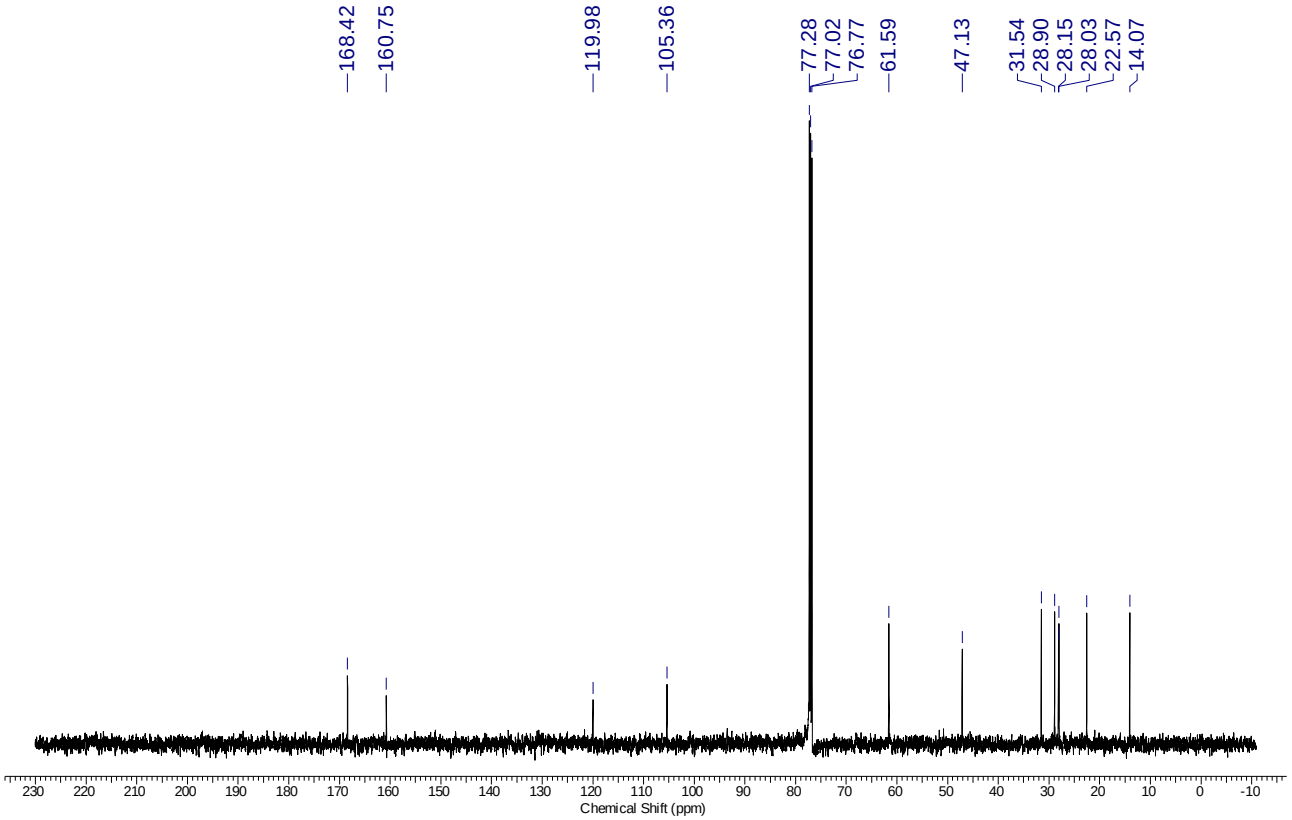
^{13}C Spectrum of **6d** in $(CD_3)_2CO$



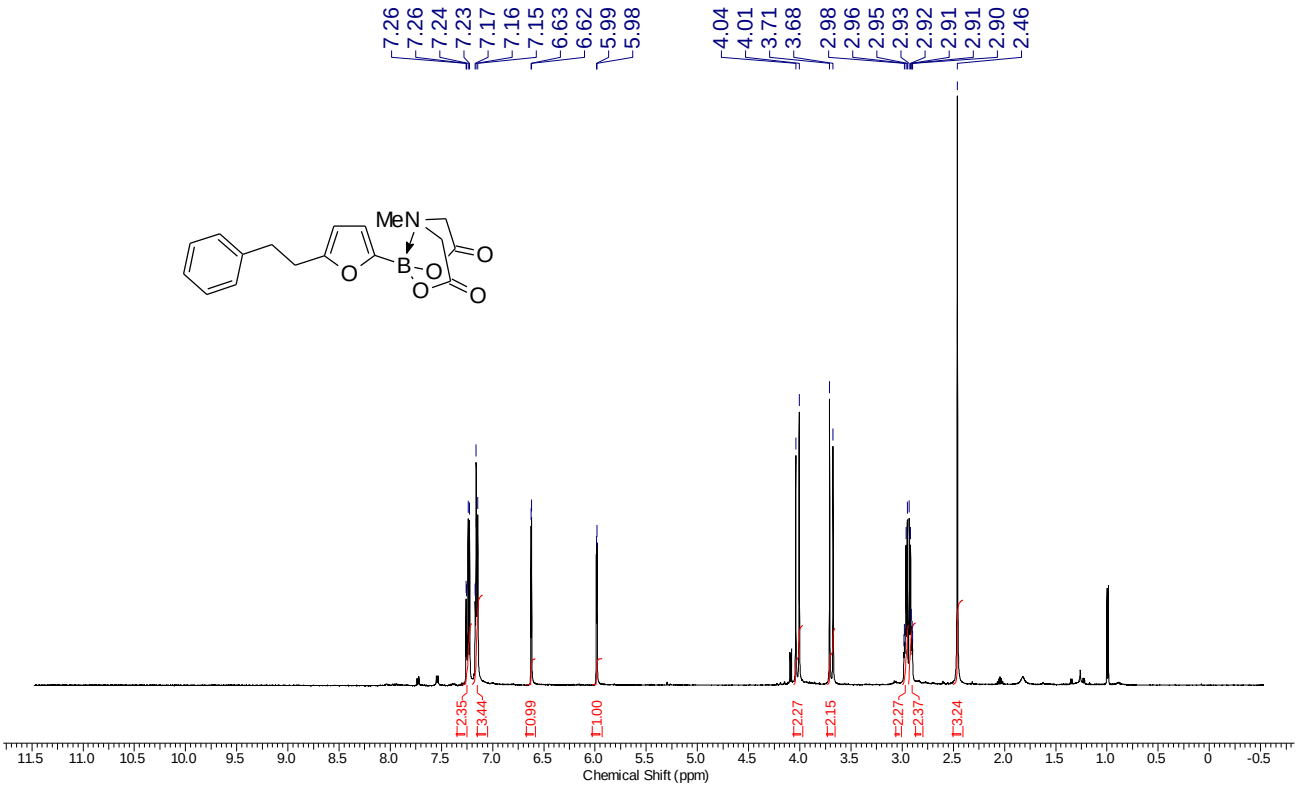
^{1}H Spectrum of **6f** in $CDCl_3$



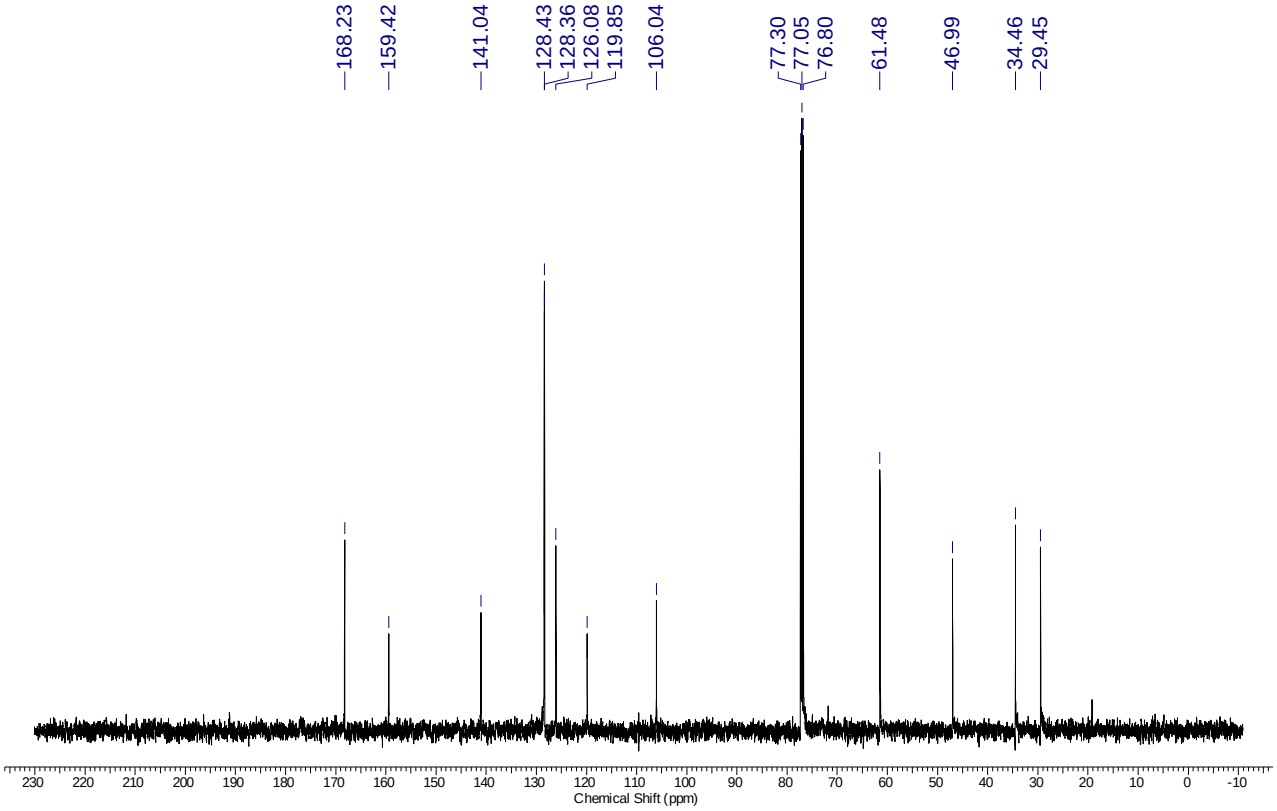
^{13}C Spectrum of **6f** in $CDCl_3$



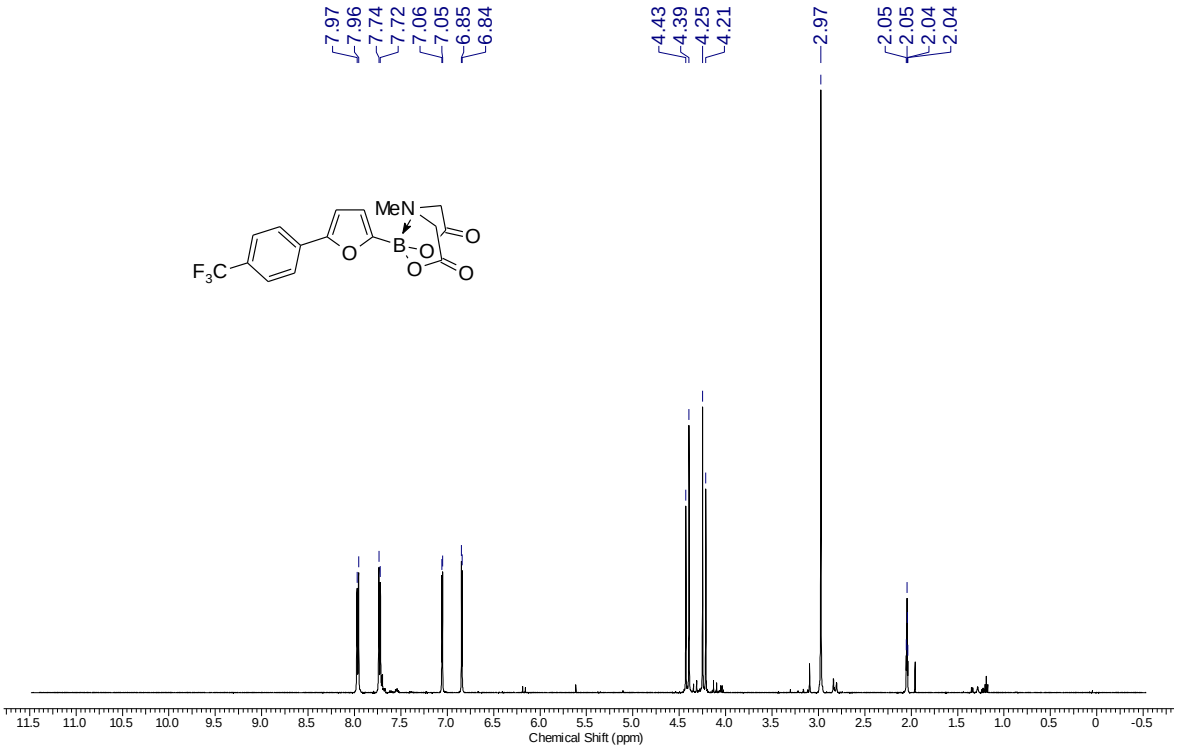
^{1}H Spectrum of **6g** in $CDCl_3$



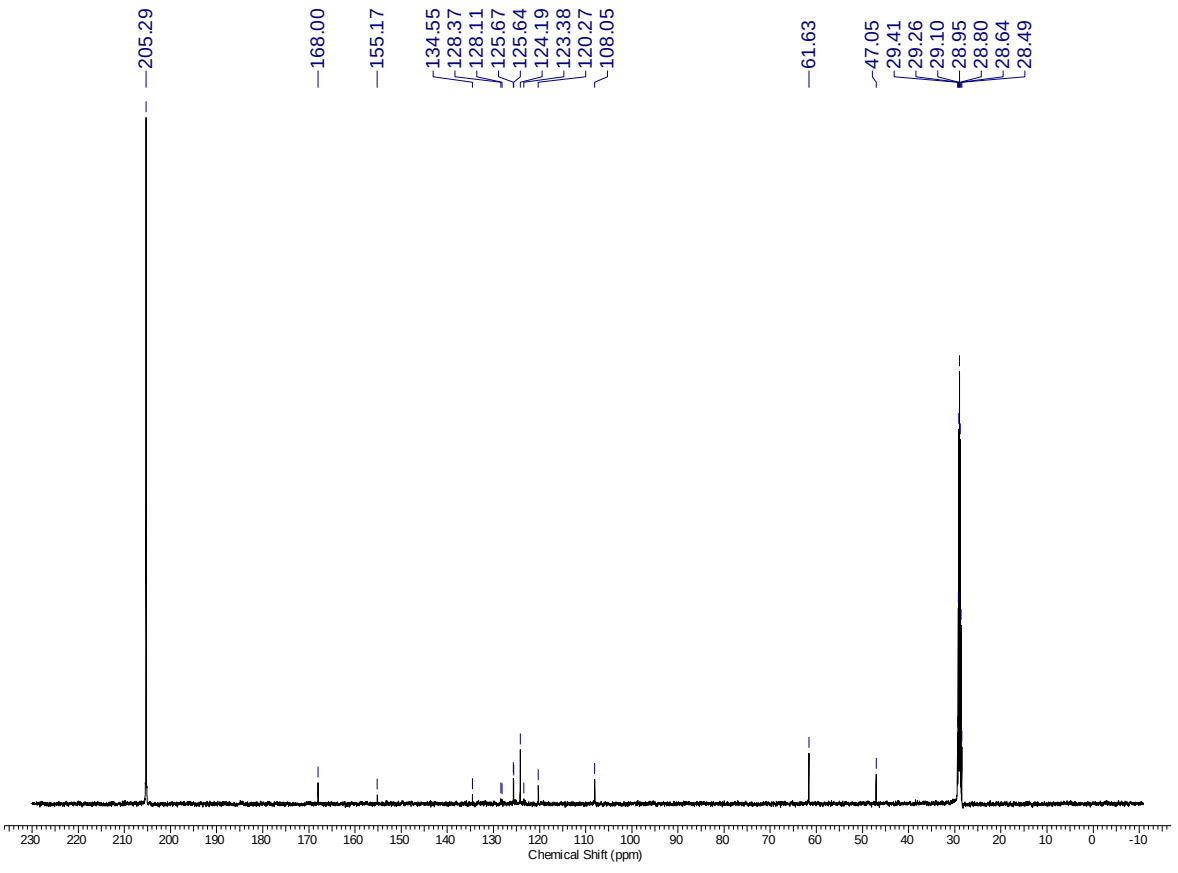
^{13}C Spectrum of **6g** in $CDCl_3$



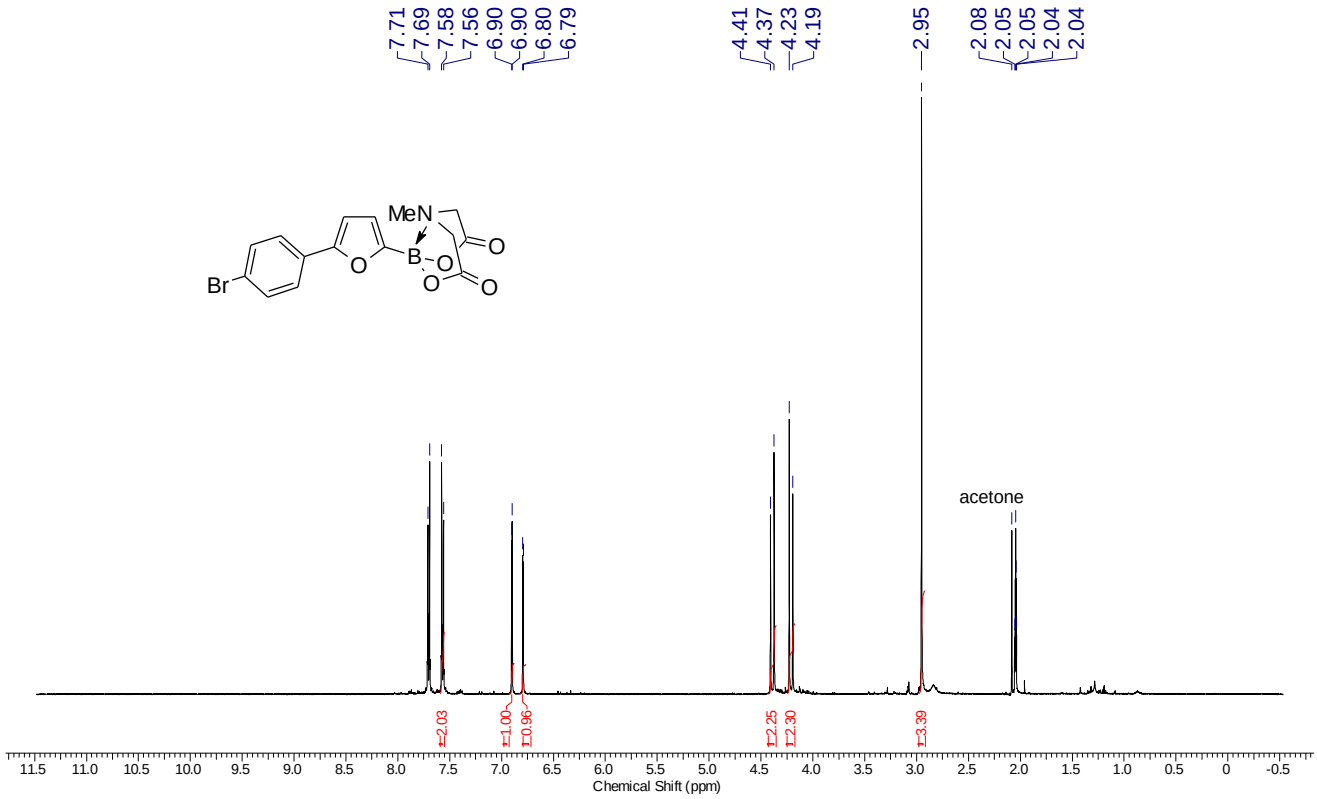
^{1}H Spectrum of **6h** in $(CD_3)_2CO$



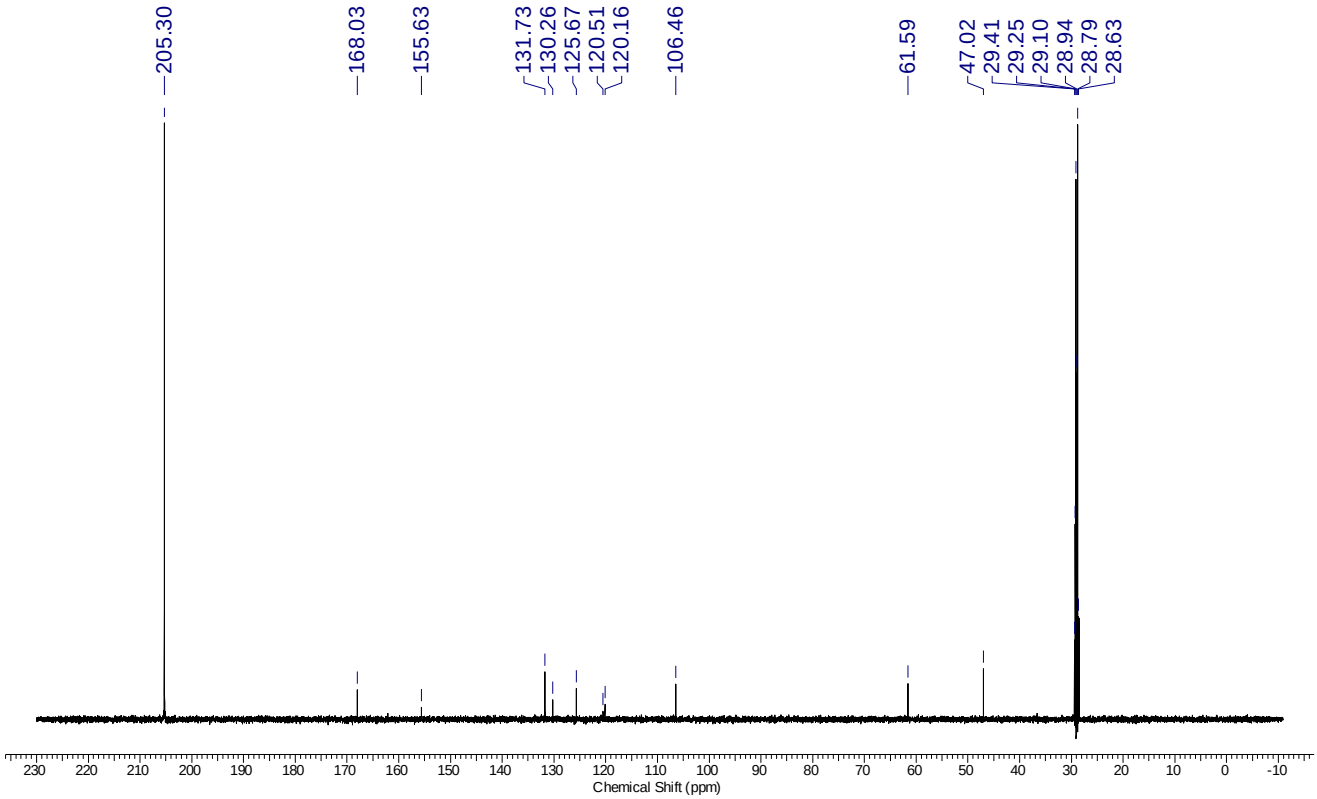
^{13}C Spectrum of **2g** $(CD_3)_2CO$



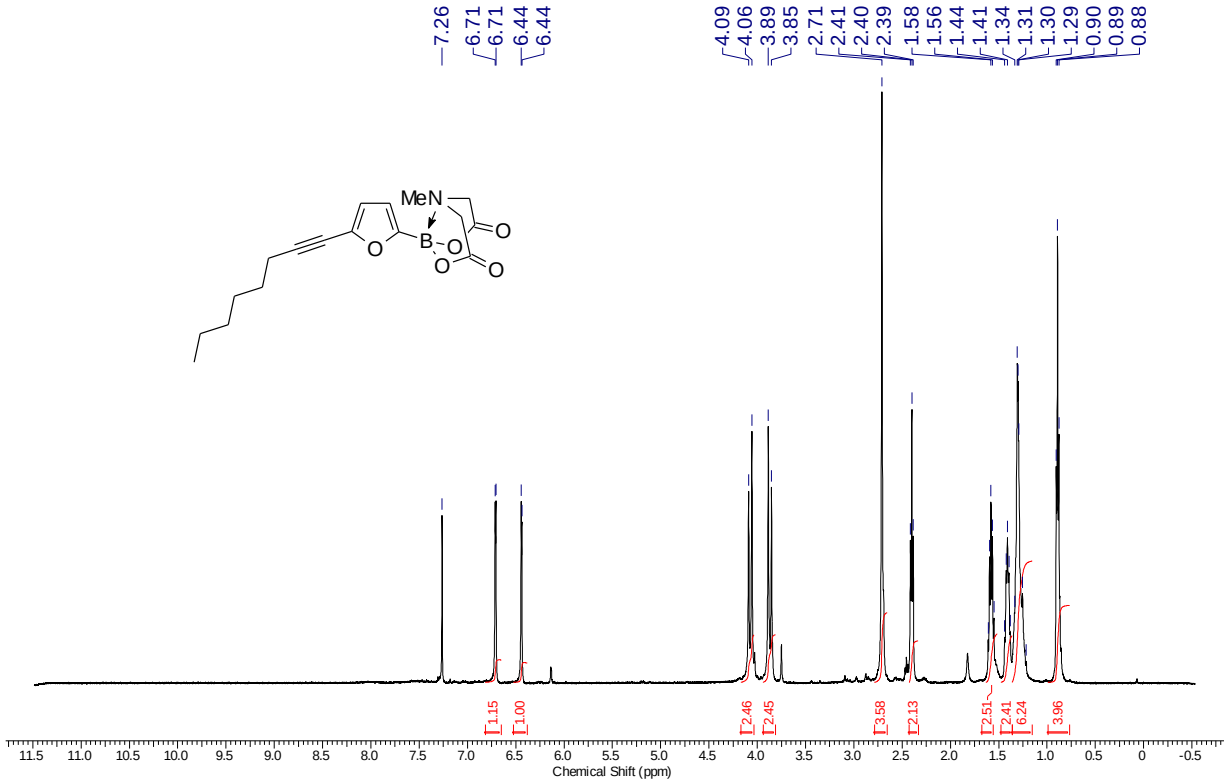
^{1}H Spectrum of **6i** in $(CD_3)_2CO$



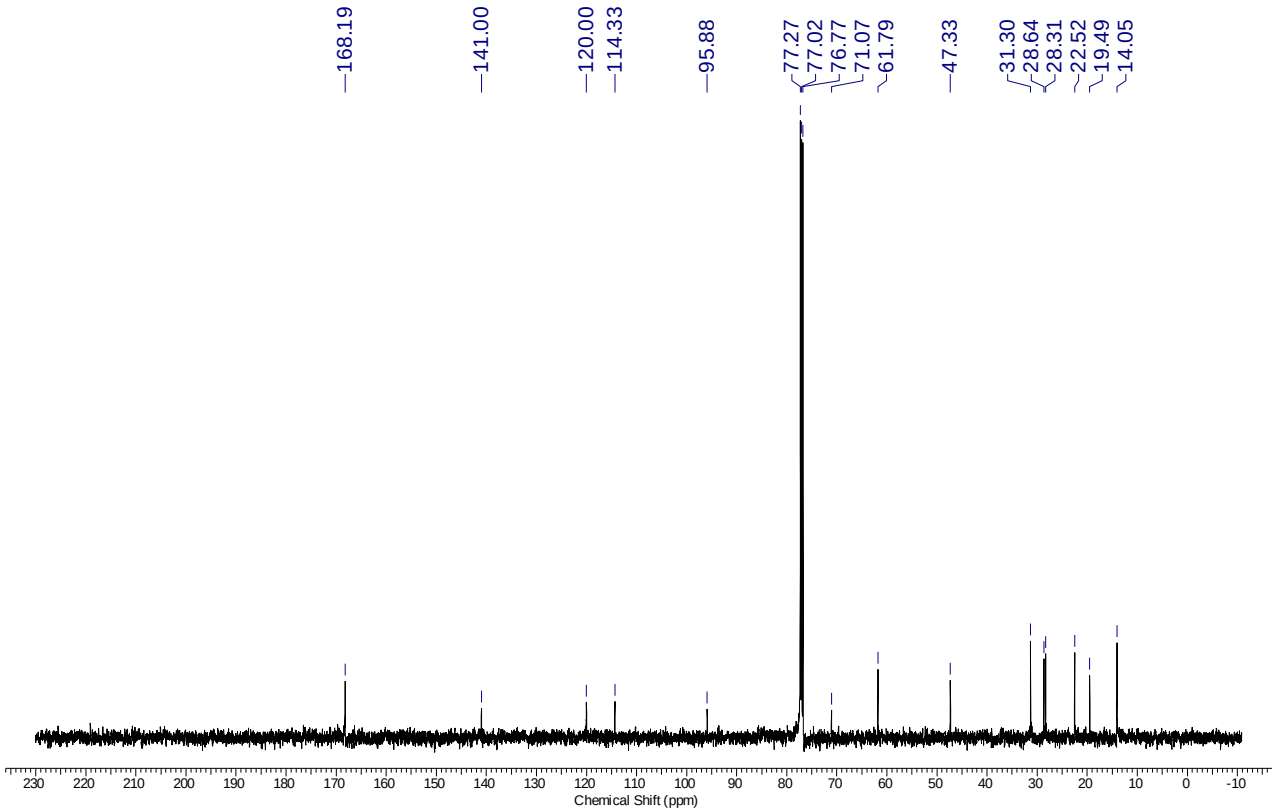
^{13}C Spectrum of **6i** in $(CD_3)_2CO$



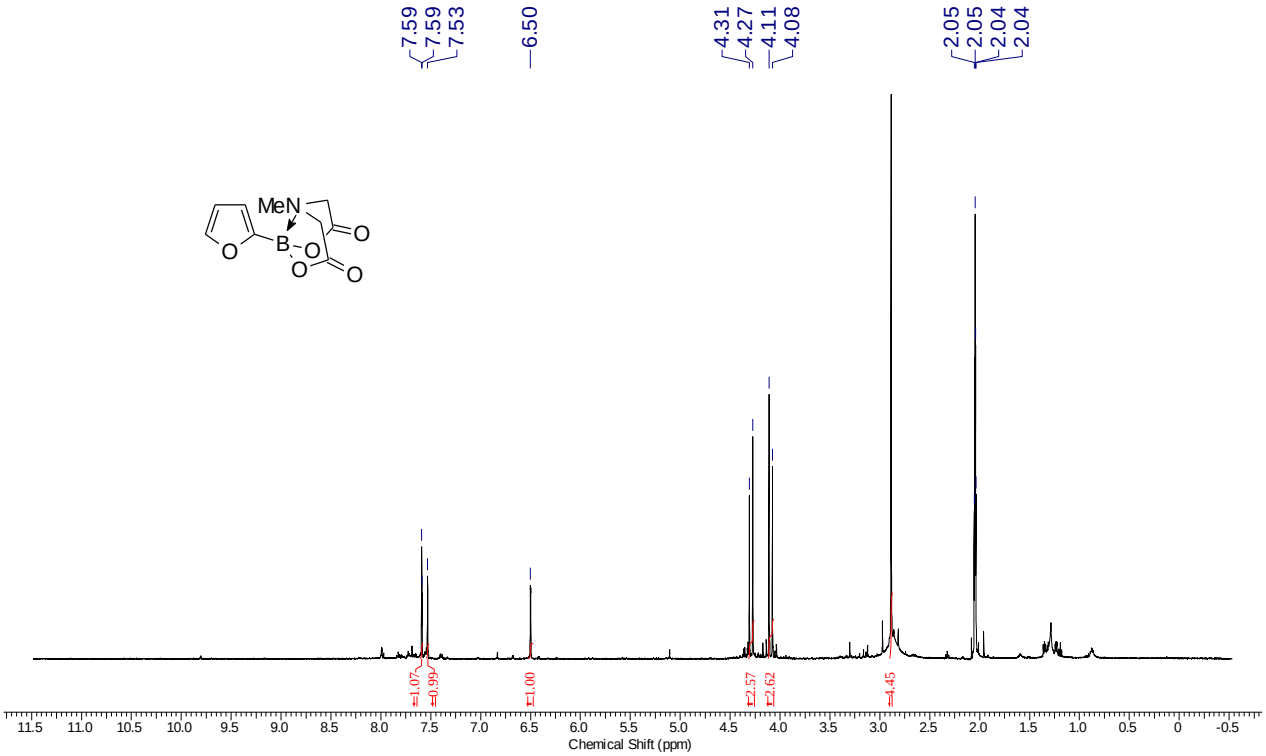
^{1}H Spectrum of **6j** in $CDCl_3$



^{13}C Spectrum of **6j** in $CDCl_3$



^{1}H Spectrum of **6l** in $(CD_3)_2CO$



^{13}C Spectrum of **6l** in $(CD_3)_2CO$