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SUPPORTING INFORMATION

Rh-Catalyzed Tunable Defluorinative Borylation

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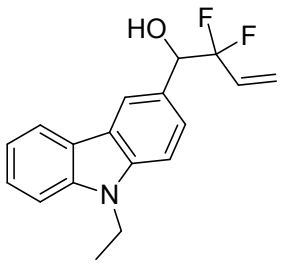
1. General Information

Reagents and solvents were obtained commercially and used without further purification unless indicated otherwise. Molecular sieves (4Å, powder) were dried under vacuum at 220 °C and stored in a glove box before use. Tetramethylsilane or residual proton signals of the deuterated solvents were used as internal standard for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra. Data for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

2. Experimental Procedure for the Synthesis of Substrates

Substrates **1a** - **1o** were synthesized using the method reported by Masayuki Kirihara *et al*. (**Ref.** *Tetrahedron* 2000, **56**, 8275), and the corresponding characterization data were the same as provided in our previous paper (**Ref.** *Org. Biomol. Chem.* 2014, **12***,* 581-588). Substrate **1p** was synthesized using the method reported by Xingang Zhang *et al*. (**Ref.** *J. Am. Chem. Soc.* 2014**, 136**, 1230-1233) and the corresponding characterization data were the same as provided in their paper.

1o is a new compound. The characterization data are shown as follows.



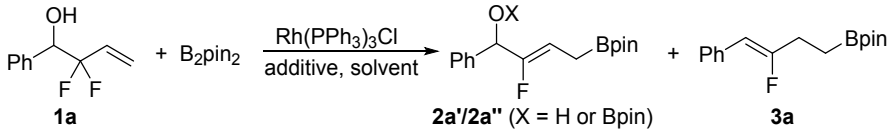
1-(9-Ethyl-9*H*-carbazol-3-yl)-2,2-difluorobut-3-en-1-ol (1o). 67% yield; Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 – 7.87 (m, 2H), 7.51 – 7.37 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.10 (m, 2H), 5.98 – 5.76 (m, 1H), 5.57 (d, *J* = 17.4 Hz, 1H), 5.39 (d, *J* = 11.1 Hz, 1H), 4.99 (t, *J* = 9.9 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.82 (brs, 1H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 (s), 139.9 (s), 129.7 (t, *J* = 25.7 Hz), 126.4 (s), 125.7 (s), 125.1 (s), 122.6 (s), 122.5 (s), 121.3 (t, *J* = 9.1 Hz), 120.4 (s), 119.8 (t, *J* = 244.3 Hz), 119.7 (s), 118.9 (s), 108.5 (s), 108.0 (s), 76.2 (t, *J* = 29.5 Hz), 37.4 (s), 13.6 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ -107.26 – -109.41 (m, 2F); IR (neat) ν = 3413, 2988, 1599, 1492, 1472, 1332, 1233, 1066 cm^{-1}; HRMS(EI) for $C_{18}H_{17}F_2NO$ $[M]^+$: calcd. 301.1273, found 301.1281.

3. The Optimization of Reaction Conditions

In our previous Rh-catalyzed defluorination of allylic *gem*-difluorides, 1,4-dioxane and DMF were used as cosolvents (**Ref.** *Org. Biomol. Chem.* 2014, **12***,* 581-588). We then first examined the defluorinative borylation of substrate **1a** in 1,4-dioxane and DMF, respectively (Table S1, entries 1-2). Two completely different borylation reactions were observed. In 1,4-dioxane, a dehydroxylative/defluorinative borylation occurred to provide homoallylborylated monofluoroalkene **3a** (entry 1). However, in DMF, the hydroxyl group remained intact and allylborylated monofluoroalkenes **2a'** and **2a''** were produced as major products (entry 2). Other reaction solvents cannot increase the yields of **2a'**/**2a''** or **3a** (entries 3-7), and some additives were then investigated (entries 8-14). The addition of a ligand, BINAP (entry 9) or 2,2'-bipyridine (entry 10), was not effective either. To our delight, the use of PPh_3 (0.2 equiv) as an additive significantly increased the yield of **3a** (entry 11). It seemed that 2 equiv of $B_2(pin)_2$ has to be used for the

formation of **3a**, as evidenced by the dramatically lower yield with decreasing its loading (entry 12). We originally thought that 4Å MS would dry the reaction system and thus its presence might lead to an increase in the yield of **3a**. However, **3a** was completely suppressed and the reaction afforded **2a'/2a''** as products instead (entry 13). Without using PPh_3, the yields of **2a'/2a''** were not decreased (entry 14). As can be seen from the results in entries 11, 13 and 14, two different paths were observed in the same reaction solvent, 1,4-dioxane. Apparently, it was 4Å MS that resulted in the **2a'/2a''** path. Since DMF was also found to favor the **2a'/2a''** path (entry 2), 4Å MS was used as an additive for the reaction in DMF. Indeed, the yields of **2a'/2a''** were further increased (entry 15). The reaction efficiency was not affected by shortening the reaction time to 70 min (entry 16).

Table S1 The optimization of the reaction conditions[a]

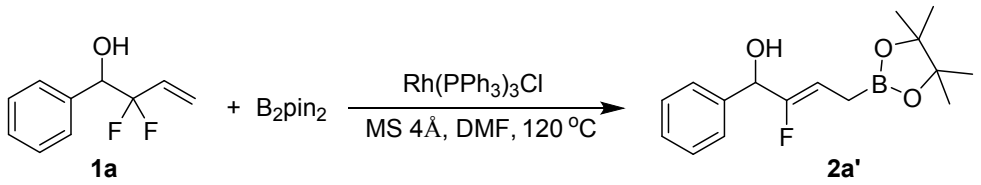


1a **2a'/2a''** (X = H or Bpin) **3a**

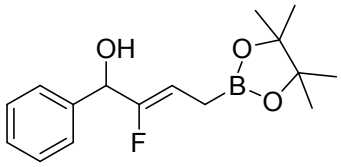
entry	additive (equiv)	solvent	yield (%)[b]	
			2a'/2a''	**3a**
1	-	dioxane	trace	52
2	-	DMF	72	ND
3	-	THF	5	44
4	-	DCE	ND	14
5	-	CH_3CN	ND	ND
6	-	DMAC	trace	ND
7	-	toluene	trace	36
8	H_2O (1)	DMF	31	ND
9	BINAP (0.05)	THF	ND	12
10[c]	2,2'-bipy (0.05)	THF	10	14
11	PPh_3 (0.2)	dioxane	4	73
12[d]	PPh_3 (0.2)	dioxane	2	36
13[e]	4Å MS + PPh_3	dioxane	80	ND
14[f,g]	4Å MS	dioxane	80	ND
15[f,h]	4Å MS	DMF	86	ND
16[d,f,h]	4Å MS	DMF	87	ND

[a]Reaction conditions: **1a** (0.5 mmol), B_2pin_2 (1.0 mmol), $Rh(PPh_3)_3Cl$ (5 mol %) in solvent (2 mL) at 80 °C under a N_2 atmosphere for around 18 h; [b]The yields were determined by ^{19}F NMR spectroscopy; ND = Not Detected; [c]2,2'-bipy = 2,2' -bipyridine; [d]1.5 equiv of $B_2(pin)_2$ was used; [e]4Å MS (100 mg) and PPh_3 (0.1 mmol) were used as additives; [f]100 mg of 4Å MS was used and the reaction temperature was 120 °C; [g]The reaction time was 0.5 h; [h]The reaction time was 70 min.

4. Experimental Procedure for Rh(I)-catalyzed Defluorinative Borylation to Allylborylated Monofluoroalkene

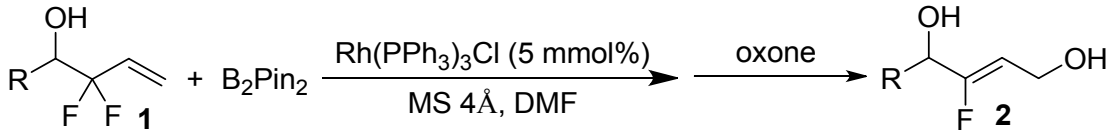


In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (191 mg, 0.75 mmol), and 4Å MS (100 mg) were added into a sealable tube. DMF (2 mL) and compound **1** (0.5 mmol) were then added to the mixture. The tube was sealed and the mixture was stirred at 120 °C for 70 min. The stereoselectivity was determined by ^{19}F NMR before the reaction was quenched with water (30 mL). The mixture was extracted with 50 mL Et_2O. The Et_2O solution was washed with brine (20 mL × 3), and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography using PE/EtOAc as eluent.



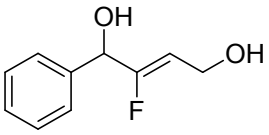
(*Z*)-2-Fluoro-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-ol (2a'). 40% yield; Colorless oil; ^1H NMR (400 MHz, DMF-d_7) δ 7.49 (d, J = 7.2 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 5.91 (d, J = 4.9 Hz, 1H), 5.27 – 5.06 (m, 2H), 1.62 (d, J = 7.9 Hz, 2H), 1.24 (s, 12H); ^{13}C NMR (101 MHz, DMF-d_7) δ 159.8 (d, J = 254.9 Hz), 141.9 (s), 128.1 (s), 127.4 (s), 126.9 (s), 101.5 (d, J = 13.9 Hz), 83.3 (s), 71.6 (d, J = 31.5 Hz), 24.4 (s); ^{19}F NMR (376 MHz, DMF-d_7) δ -124.05 (dd, J = 37.4, 14.2 Hz, 1F); IR (neat) ν = 3448, 2979, 1702, 1372, 1274, 1144, 967, 701 cm^{-1}; HRMS(ESI) for $C_{16}H_{21}{}^{11}BFO_2$ $[M\text{-}H_2O+H]^+$: calcd. 275.1613, found 275.1614.

5. Experimental Procedure for Rh(I)-catalyzed Defluorinative Borylation/Oxidation to 1,4-Dihydroxy Monofluoroalkenes

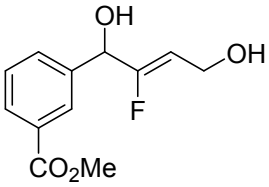


In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (191 mg, 0.75 mmol), and 4Å MS (100 mg) were added to a sealable tube. DMF (2 mL) and starting material **1** (0.5 mmol) were then added and the tube was sealed. The mixture was stirred at 120 °C for 70 min and then cooled to room temperature. Water (2 mL) and acetone (0.5 mL) were added, followed by Na_2CO_3 (0.8 g, 7.5 mmol) and oxone (308 mg, 0.5 mmol). The mixture was stirred for another 15 min. Saturated aqueous $NaHSO_3$ solution (0.5 mL) was added and stirring was continued for another 30 min. The excellent stereoselectivity was observed by ^{19}F NMR (Z/E > 98 / 2). Water (30 mL) was added and the resulting mixture was then extracted with Et_2O (30 mL ×3). The organic solutions were combined and dried over anhydrous Na_2SO_4.

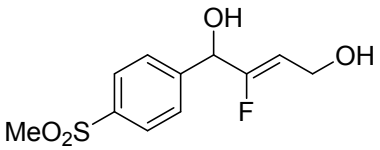
After filtration, the solvent was removed under reduced pressure. The pure product **2** was obtained by flash column chromatography using PE/Acetone as eluent.



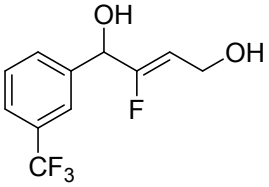
(*Z*)-2-Fluoro-1-phenylbut-2-ene-1,4-diol (2a). 87% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.41 – 7.25 (m, 3H), 5.37 – 5.16 (m, 2H), 5.04 (d, *J* = 4.8 Hz, 1H), 4.20 – 4.14 (m, 2H), 3.89 (t, *J* = 5.5 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 160.1 (d, *J* = 259.2 Hz), 140.8 (s), 128.1 (s), 127.7 (s), 126.8 (s), 106.6 (d, *J* = 11.3 Hz), 71.5 (d, *J* = 31.9 Hz), 54.3 (d, *J* = 7.0 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -120.63 (dd, *J* = 37.2, 12.1 Hz, 1F); IR (neat) ν = 3229, 2881, 1708, 1455, 1333, 1060, 1011, 771 cm^{-1}; HRMS(EI) for $C_{10}H_{11}FO_2$ $[M]^+$: calcd. 182.0743, found 182.0739.



(*Z*)-Methyl 3-(2-fluoro-1,4-dihydroxybut-2-en-1-yl)benzoate (2b). 85% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.14 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 5.46 – 5.19 (m, 3H), 4.22 – 4.14 (m, 2H), 3.93 (t, *J* = 5.6 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, acetone-d_6) δ 166.3 (s), 159.6 (d, *J* = 259.3 Hz), 141.5 (s), 131.4 (s), 130.2 (s), 128.7 (s), 128.5 (s), 127.6 (s), 107.1 (d, *J* = 11.2 Hz), 71.0 (d, *J* = 31.6 Hz), 54.2 (d, *J* = 7.0 Hz), 51.5 (s); ^{19}F NMR (376 MHz, acetone-d_6) δ -121.36 (dd, *J* = 37.0, 13.0 Hz, 1F); IR (neat) ν = 3397, 2954, 1716, 1435, 1293, 1201, 1008, 758 cm^{-1}; HRMS(EI) for $C_{12}H_{13}FO_4$ $[M]^+$: calcd. 240.0798, found 240.0795.

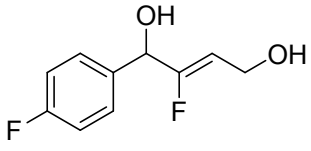


(*Z*)-2-Fluoro-1-(4-(methylsulfonyl)phenyl)but-2-ene-1,4-diol (2c). 73% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 5.47 – 5.24 (m, 3H), 4.17 (d, *J* = 5.9 Hz, 2H), 3.93 (brs, 1H), 3.13 (s, 3H); ^{13}C NMR (101 MHz, acetone-d_6) δ 159.1 (d, *J* = 259.6 Hz), 146.6 (s), 140.7 (s), 127.5 (s), 127.2 (s), 107.6 (d, *J* = 11.0 Hz), 70.8 (d, *J* = 31.3 Hz), 54.2 (d, *J* = 6.9 Hz), 43.4 (s); ^{19}F NMR (376 MHz, acetone-d_6) δ -121.81 (dd, *J* = 37.1, 13.7 Hz, 1F); IR (neat) ν = 3457, 2928, 1706, 1406, 1300, 1149, 1089, 771 cm^{-1}; HRMS(ESI) for $C_{11}H_{12}FO_4S$ $[M-H]^-$: calcd. 259.04458, found 259.04480.

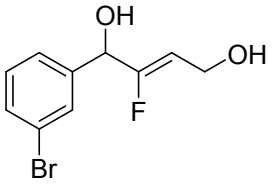


(*Z*)-2-Fluoro-1-(3-(trifluoromethyl)phenyl)but-2-ene-1,4-diol (2d). 57% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.82 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.69 – 7.57 (m,

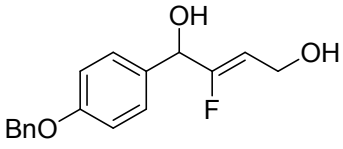
2H), 5.46 – 5.22 (m, 3H), 4.24 – 4.12 (m, 2H), 3.87 (t, J = 5.7 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 159.4 (d, J = 259.4 Hz), 142.3 (s), 1307 (s), 130.0 (q, J = 31.8 Hz), 129.1 (s), 124.5 (q, J = 271.5 Hz), 124.5 (q, J = 3.8 Hz), 123.3 (q, J = 3.8 Hz), 107.5 (d, J = 11.1 Hz), 70.9 (d, J = 31.5 Hz), 54.3 (d, J = 6.9 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -63.05 (s, 3F), -122.03 (dd, J = 37.1, 13.5 Hz, 1F); IR (neat) ν = 3348, 2893, 1706, 1330, 1166, 1126, 1074 cm^{-1}; LRMS(EI) $C_{11}H_{10}F_4O_2$ $[M]^+$: calcd. for 250.1, found 250.0; Anal. for $C_{11}H_{10}F_4O_2$: calcd. C 52.81, H 4.03, found C 52.85, H, 3.93.



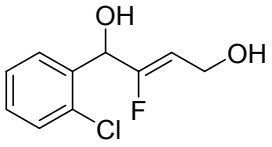
(*Z*)-2-Fluoro-1-(4-fluorophenyl)but-2-ene-1,4-diol (2e). 84% yield; Colorless solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.58 – 7.34 (m, 2H), 7.21 – 7.01 (m, 2H), 5.35 – 5.18 (m, 2H), 5.14 (d, J = 4.8 Hz, 1H), 4.21 – 4.12 (m, 2H), 3.92 (t, J = 5.5 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 162.3 (d, J = 243.8 Hz), 159.9 (d, J = 259.2 Hz), 137.0 (d, J = 3.1 Hz), 128.7 (d, J = 8.3 Hz), 114.8 (d, J = 21.5 Hz), 106.8 (d, J = 11.2 Hz), 70.8 (d, J = 31.9 Hz), 54.3 (d, J = 7.1 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -116.31 – 1116.43 (m, 1F), -121.03 (dd, J = 37.2, 12.1 Hz, 1F); IR (neat) ν = 3335, 1712, 1604, 1509, 1228, 1158, 840 cm^{-1}; LRMS(EI) for $C_{10}H_{10}F_2O_2$ $[M]^+$: calcd. 200.1, found 200.1; Anal. for $C_{10}H_{10}F_2O_2$: calcd. C 60.00, H 5.04, found C 59.90, H 5.05.



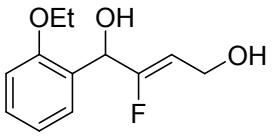
(*Z*)-1-(3-Bromophenyl)-2-fluorobut-2-ene-1,4-diol (2g). 64% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.65 (s, 1H), 7.52 – 7.42 (m, 2H), 7.32 (t, J = 7.8 Hz, 1H), 5.39 – 5.15 (m, 3H), 4.20 – 4.13 (m, 2H), 3.84 (t, J = 5.7 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 159.4 (d, J = 259.2 Hz), 143.6 (s), 130.7 (s), 130.2 (s), 129.6 (s), 125.8 (s), 121.8 (s), 107.4 (d, J = 11.2 Hz), 70.8 (d, J = 31.7 Hz), 54.2 (d, J = 6.9 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -121.77 (dd, J = 37.1, 13.1 Hz,1F); IR (neat) ν = 3349, 2887, 1705, 1571, 1474, 1189, 999, 784 cm^{-1}; HRMS(EI) for $C_{10}H_{10}FO_2Br$ $[M]^+$: calcd. 259.9848, found 259.9844.



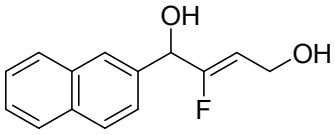
(*Z*)-1-(4-(Benzyloxy)phenyl)-2-fluorobut-2-ene-1,4-diol (2h). 72% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.48 (d, J = 7.3 Hz, 2H), 7.44 – 7.28 (m, 5H), 7.00 (d, J = 8.7 Hz, 2H), 5.33 – 5.08 (m, 4H), 4.90 (d, J = 4.8 Hz, 1H), 4.20 – 4.13 (m, 2H), 3.81 (t, J = 5.7 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 160.3 (d, J = 258.7 Hz), 158.6 (s), 137.5 (s), 133.2 (s), 128.4 (s), 128.1 (s), 127.7 (s), 127.5 (s), 114.4 (s), 106.3 (d, J = 11.4 Hz), 71.1 (d, J = 32.2 Hz), 69.5 (s), 54.3 (d, J = 7.1 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -120.43 (dd, J = 37.2, 11.3 Hz, 1F); IR (neat) ν = 3336, 2882, 1701, 1508, 1245, 1170, 1013, 744 cm^{-1}; HRMS(ESI) for $C_{17}H_{16}FO_3$ $[M\text{-}H]^-$: calcd. 287.1089, found 287.1089.



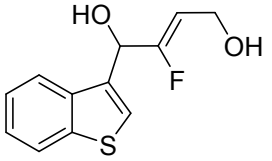
(*Z*)-1-(2-Chlorophenyl)-2-fluorobut-2-ene-1,4-diol (2j). 79% yield; White solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.74 – 7.67 (m, 1H), 7.47 – 7.19 (m, 3H), 5.64 (dd, *J* = 11.2, 4.9 Hz, 1H), 5.28 (d, *J* = 4.9 Hz, 1H), 5.14 (dt, *J* = 37.0, 6.8 Hz, 1H), 4.21 – 4.13 (m, 2H), 3.91 (t, *J* = 5.5 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 158.7 (d, *J* = 259.4 Hz), 138.0 (s), 132.5 (s), 129.4 (s), 129.2 (s), 128.7 (s), 127.1 (s), 107.8 (d, *J* = 11.5 Hz), 68.0 (d, *J* = 32.0 Hz), 54.3 (d, *J* = 7.0 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -120.66 (dd, *J* = 37.0, 11.2 Hz, 1F); IR (neat) ν = 3346, 2889, 1706, 1473, 1443, 1237, 1007 cm^{-1}; LRMS(EI) for $C_{10}H_{10}ClFO_2$ [M]$^+$: calcd. 216.0, found 216.0; Anal. for $C_{10}H_{10}ClFO_2$: calcd. C 55.44, H 4.65, found C 55.56, H 4.68.



(*Z*)-1-(2-Ethoxyphenyl)-2-fluorobut-2-ene-1,4-diol (2k). 52% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.51 (d, *J* = 7.2 Hz, 1H), 7.29-7.22 (m, 1H), 6.95 (t, *J* = 7.3 Hz, 2H), 5.60 (dd, *J* = 11.8, 5.3 Hz, 1H), 5.09 (dt, *J* = 37.1, 7.0 Hz, 1H), 4.73 (d, *J* = 5.3 Hz, 1H), 4.19 – 4.11 (m, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 3.71 (t, *J* = 5.7 Hz, 1H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, acetone-d_6) δ 159.9 (d, *J* = 259.4 Hz), 156.1 (s), 128.9 (d, *J* = 1.1 Hz), 128.8 (s), 127.5 (d, *J* = 0.7 Hz), 120.2 (s), 111.5 (s), 106.7 (d, *J* = 11.9 Hz), 65.7 (d, *J* = 31.9 Hz), 63.6 (s), 54.4 (d, *J* = 7.1 Hz), 14.2 (s); ^{19}F NMR (376 MHz, acetone-d_6) δ -120.62 (dd, *J* = 37.0, 11.8 Hz, 1F); IR (neat) ν = 3305, 2980, 1707, 1493, 1456, 1246, 1046, 757 cm^{-1}; LRMS(EI) for $C_{12}H_{15}FO_3$ [M]$^+$: calcd. 226.1, found 226.1; Anal. for $C_{12}H_{15}FO_3$: calcd. C 63.70, H 6.68, found C 63.63, H 6.61.

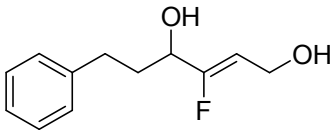


(*Z*)-2-Fluoro-1-(naphthalen-2-yl)but-2-ene-1,4-diol (2l). 67% yield; White solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.99 (s, 1H), 7.93 – 7.83 (m, 3H), 7.63-7.58 (m, 1H), 7.56 – 7.44 (m, 2H), 5.47 – 5.26 (m, 2H), 5.21 (d, *J* = 4.8 Hz, 1H), 4.25 – 4.17 (m, 2H), 3.90 (t, *J* = 5.4 Hz, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 160.0 (d, *J* = 259.2 Hz), 138.4 (s), 133.3 (s), 133.2 (s), 127.9 (s), 127.8 (s), 127.6 (s), 126.1 (s), 126.0 (s), 125.7 (s), 124.9 (s), 107.0 (d, *J* = 11.3 Hz), 71.6 (d, *J* = 31.9 Hz), 54.3 (d, *J* = 7.0 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -120.44 (dd, *J* = 37.1, 12.2 Hz, 1F); IR (neat) ν = 3337, 3057, 1704, 1507, 1271, 1158, 1080, 817 cm^{-1}; LRMS(EI) for $C_{14}H_{13}FO_2$ [M]$^+$: calcd. 232.1, found 232.1; Anal. for $C_{14}H_{13}FO_2$: calcd. C 72.40, H 5.64, found C 72.37, H 5.73.

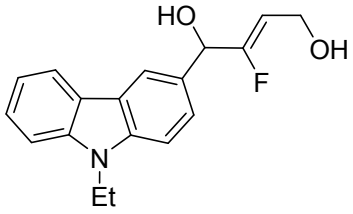


(*Z*)-1-(Benzo[*b*]thiophen-3-yl)-2-fluorobut-2-ene-1,4-diol (2m). 54% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.05 – 7.99 (m, 1H), 7.98 – 7.90 (m, 1H), 7.67 (s, 1H), 7.42 – 7.34 (m, 2H), 5.67 (dd, *J* = 12.0, 4.6 Hz, 1H), 5.38 (dt, *J* = 37.0, 6.9 Hz, 1H), 5.22 (d, *J* = 5.1 Hz, 1H), 4.22 (br, 2H), 3.89 (br, 1H); ^{13}C NMR (101 MHz, acetone-d_6) δ 159.1 (d, *J* = 259.7 Hz), 140.6 (s),

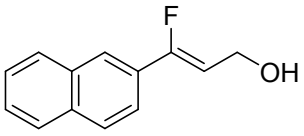
137.6 (s), 135.6 (s), 124.4 (s), 124.0 (s), 122.9 (s), 122.7 (s), 107.5 (d, J = 11.4 Hz), 67.5 (d, J = 32.5 Hz), 54.4 (d, J = 6.9 Hz); ^{19}F NMR (376 MHz, acetone-d_6) δ -119.81 (dd, J = 37.0, 12.1 Hz, 1F); IR (neat) ν = 3346, 1705, 1460, 1428, 1245, 1155, 1079, 761 cm^{-1}; HRMS(EI) for $C_{12}H_{11}FO_2S$ $[M]^+$: calcd. 288.0464, found 288.0463.



(*Z*)-3-Fluoro-6-phenylhex-2-ene-1,4-diol (2n). 60% yield; Colorless oil; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.31 – 7.13 (m, 5H), 5.13 (dt, J = 37.9, 6.9 Hz, 1H), 4.44 (d, J = 5.5 Hz, 1H), 4.20 – 4.03 (m, 3H), 3.73 (t, J = 5.7 Hz, 1H), 2.83 – 2.60 (m, 2H), 2.01 – 1.77 (m, 2H); ^{13}C NMR (101 MHz, acetone-d_6) δ 161.0 (d, J = 259.9 Hz), 142.0 (s), 128.4 (s), 128.3 (s), 125.8 (s), 106.1 (d, J = 11.6 Hz), 68.6 (d, J = 30.9 Hz), 54.3 (d, J = 7.5 Hz), 36.0 (s), 31.3 (s); ^{19}F NMR (376 MHz, acetone-d_6) δ -123.10 (dd, J = 37.9, 13.5 Hz, 1F); IR (neat) ν = 3358, 2950, 1705, 1454, 1297, 1088, 1009, 748 cm^{-1}; HRMS(EI) for $C_{12}H_{15}FO_2$ $[M]^+$: calcd. 210.1056, found 210.1053.



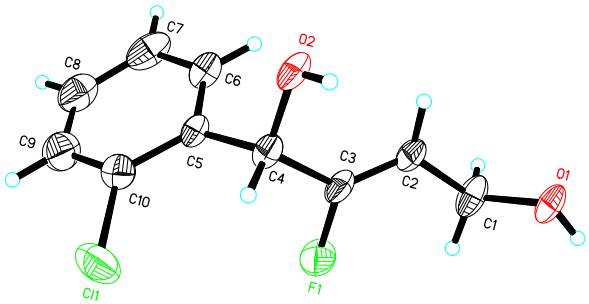
(*Z*)-1-(9-Ethyl-9*H*-carbazol-3-yl)-2-fluorobut-2-ene-1,4-diol (2o). 50% yield; Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.39 – 8.13 (m, 2H), 7.68 – 7.38 (m, 4H), 7.20 (t, J = 7.4 Hz, 1H), 6.01 (d, J = 4.7 Hz, 1H), 5.41 – 5.07 (m, 2H), 4.78 (t, J = 5.5 Hz, 1H), 4.42 (q, J = 6.8 Hz, 2H), 4.12 – 4.03 (m, 2H), 1.30 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.3 (d, J = 258.6 Hz), 139.9 (s), 139.2 (s), 131.6 (s), 125.7 (s), 124.8 (s), 122.1 (s), 121.8 (s), 120.3 (s), 118.8(s), 118.7 (s), 109.1 (s), 108.7 (s), 106.4 (d, J = 11.5 Hz), 71.1 (d, J = 31.2 Hz), 53.7 (d, J = 6.7 Hz), 37.0 (s), 13.7 (s); ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.84 (dd, J = 38.2, 11.7 Hz, 1F); IR (neat) ν = 3363, 1704, 1601, 1491, 1471, 1331, 1233, 748 cm^{-1}; HRMS(ESI) for $C_{18}H_{17}FO_2N$ $[M-H]^-$: calcd. 298.12488, found 298.12497.

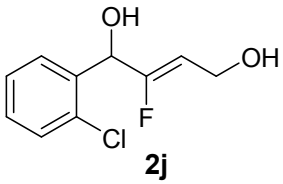


(*Z*)-3-fluoro-3-(naphthalen-2-yl)prop-2-en-1-ol (2p). 73% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.89 – 7.70 (m, 3H), 7.62 – 7.39 (m, 3H), 5.79 (dt, J = 36.7, 6.9 Hz, 1H), 4.51 (d, J = 6.8 Hz, 2H), 1.63 (brs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (d, J = 250.8 Hz), 133.7 (s), 133.1 (s), 129.0 (d, J = 28.1 Hz), 128.7 (s), 128.5 (d, J = 2.3 Hz), 127.8 (s), 127.0 (s), 126.8 (s), 124.0 (d, J = 7.4 Hz), 121.9 (d, J = 6.8 Hz), 105.5 (d, J = 15.3 Hz), 56.3 (d, J = 7.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.49 (d, J = 36.6 Hz, 1F); **GCMS** (EI) for $C_{13}H_{11}FO^+$ $[M]^+$ calcd.: 202.1, found: 202.1.

6. X-ray Structure of 2f

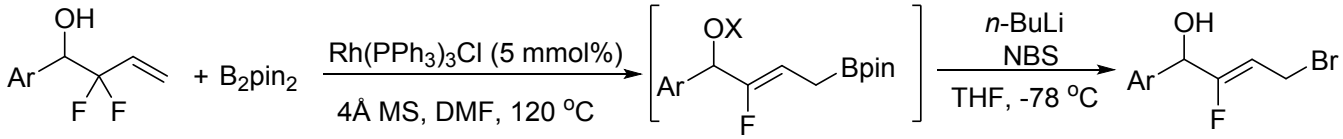
CCDC 929444





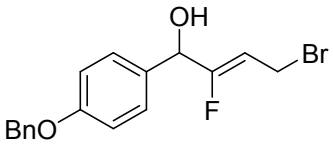
2j

7. Experimental Procedure for Transformation of 2h'/2h" to 2h"'



1h (Ar = 4'-BnOC$_6$H$_4$) **2h'/2h"** (X = H or Bpin) **2h"'**

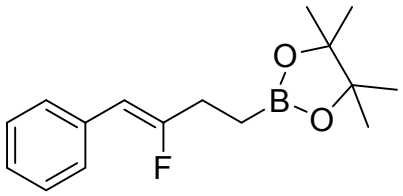
In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (191 mg, 0.75 mmol) and 4Å MS (100 mg) were added into a sealable tube. DMF (2 mL) and compound **1h** (0.5 mmol) were then added and the tube was sealed. The mixture was stirred at 120 °C for 70 min and then cooled to room temperature. Water (30 mL) was added and the resulting mixture was extracted with Et_2O (30 mL ×3). The organic solutions were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and **2h'/2h"** mixture was obtained. The transformation of Bpin moiety to Br group was performed following the procedure reported by Feng-Ling Qing *et al*. (**Ref.** *ACS Catal.* 2019, **9**, 5726−5731). Under N_2, *n*-BuLi (0.25 mL, 2.4 M in hexanes, 0.60 mmol) was added dropwise to a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (175.8 mg, 0.6 mmol) in THF (2.0 mL) at -78 °C. The mixture was stirred at -78 °C for 1 h, and then a solution of **2h'/2h"** mixture in THF (1.0 mL) was added. The mixture was stirred at -78 °C for 30 min. Next, *N*-bromosuccinimide (106.8 mg, 0.6 mmol) was added at –78 °C. The reaction mixture was stirred at –78 °C for 5 min, and then it was warmed to room temperature and stirred for 1 h. Na_2SO_3 (aq, 10.0 mL) was added, and the reaction mixture was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and concentrated. The pure product **2h"'** was obtained by flash column chromatography using hexane/EtOAc as eluent.



(*Z*)-1-(4-(benzyloxy)phenyl)-4-bromo-2-fluorobut-2-en-1-ol (5h). 42% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 7H), 6.99 (d, *J* = 8.7 Hz, 2H), 5.42 (dt, *J* = 33.1, 8.6 Hz, 1H), 5.19 (d, *J* = 8.6 Hz, 1H), 5.08 (s, 2H), 4.05 (d, *J* = 8.9 Hz, 2H), 1.31 (d, *J* = 19.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 265.6 Hz), 159.3 (s), 136.9 (s), 131.3 (s), 128.8 (s), 128.4 (s), 128.2 (s), 127.6 (s), 115.3 (s), 104.1 (d, *J* = 10.8 Hz), 71.9 (d, *J* = 32.6 Hz), 70.2 (s), 22.9 (d, *J* = 8.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.87 (dd, *J* = 32.9, 8.5 Hz, 1F); HRMS(DART) for $C_{17}H_{20}BrFNO_2$ $[M+NH_4]^+$: calcd. 368.0661, found 368.0656.

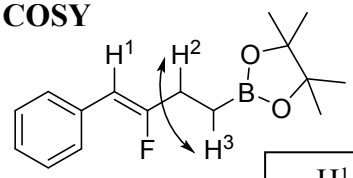
8. Experimental Procedure for Rh(I)-Catalyzed Dehydroxylative/Defluorinative Borylation to Homoallylborylated Monofluoroalkenes and the 2D NMR Spectrum of 3a

In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (254 mg, 1.0 mmol) and PPh_3 (26.2 mg, 0.1 mmol) were added to a sealable tube. Dioxane (2 mL) and compound **1** (78 μL, 0.5 mmol) were then added and the tube was sealed. The mixture was stirred at 80 °C for 18 h and then cooled to room temperature. Water (30 mL) was added and the resulting mixture was extracted with Et_2O (30 mL ×3). The organic solutions were combined and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The product **3** was obtained by flash column chromatography using Et_2O/hexane as eluent.



(*Z*)-2-(3-Fluoro-4-phenylbut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(3a). 67% yield; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 5.37 (d, *J* = 39.6 Hz, 1H), 2.36 (dt, *J* = 15.6, 7.8 Hz, 2H), 1.14 (s, 12H), 0.99 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 266.6 Hz), 133.9 (d, *J* = 2.4 Hz), 128.2 (s), 128.1 (s), 126.4 (d, *J* = 2.0 Hz), 104.6 (d, *J* = 8.8 Hz), 83.2 (s), 27.3 (d, *J* = 27.4 Hz), 24.7 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ -100.97 (dt, *J* = 39.6, 15.6 Hz, 1F); IR (neat) ν = 2978, 2926, 1691, 1379, 1325, 1144, 968, 694 cm^{-1}; HRMS(EI) for $C_{16}H_{22}FO_2{}^{11}B$ $[M]^+$: calcd. 276.1697, found 276.1696.

COSY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H2
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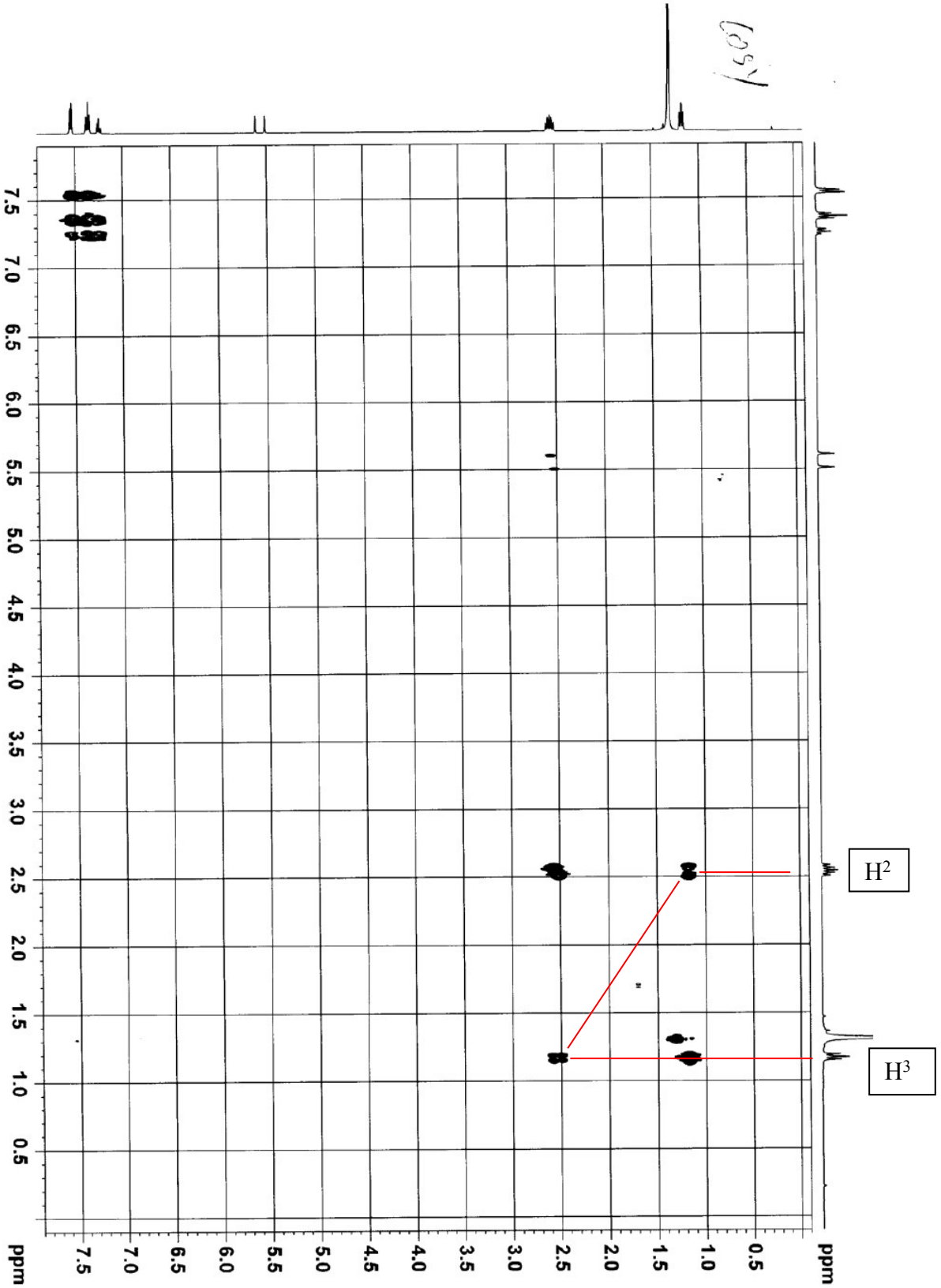
B
O
F
H3

H^1	H^2	H^3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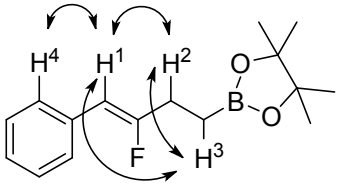
H2
H3

NOESY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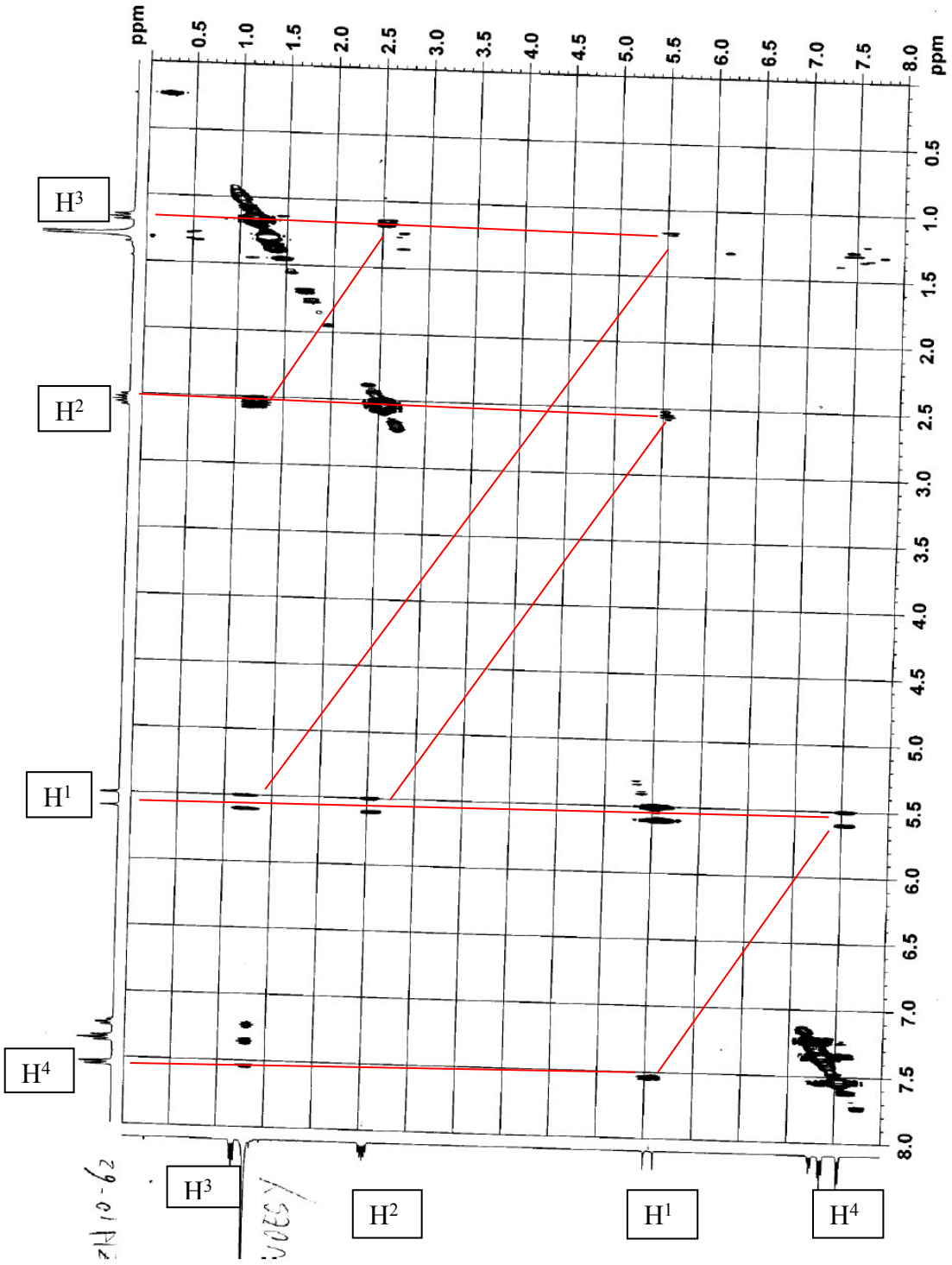
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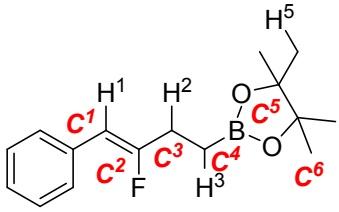
H1
H4
H3
H2
H1
H4

HMQC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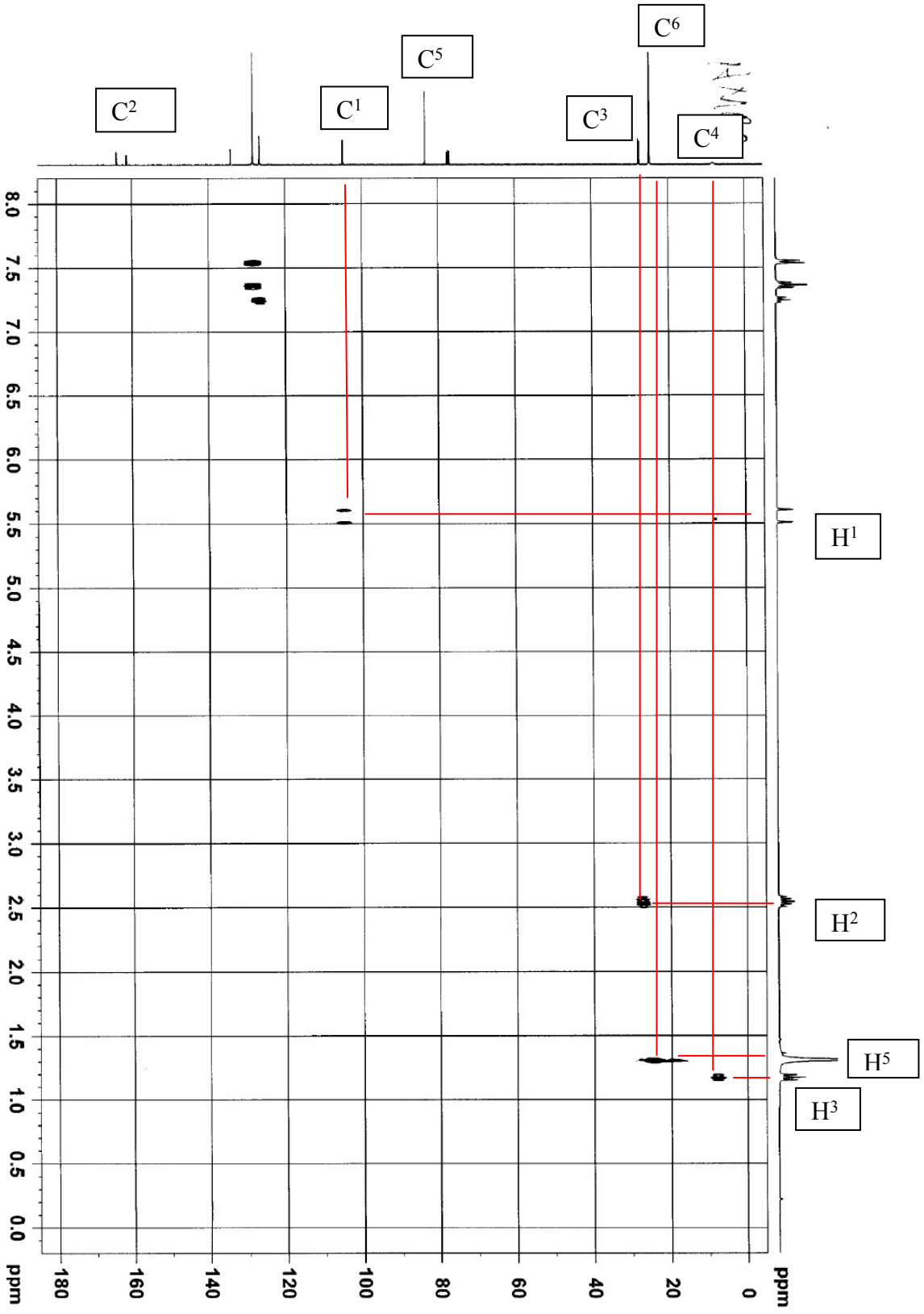
B
C2
C3
C4
O
C6
F
H3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C4
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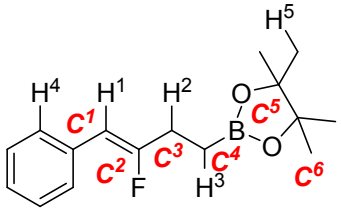
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C2
C3
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O
C6
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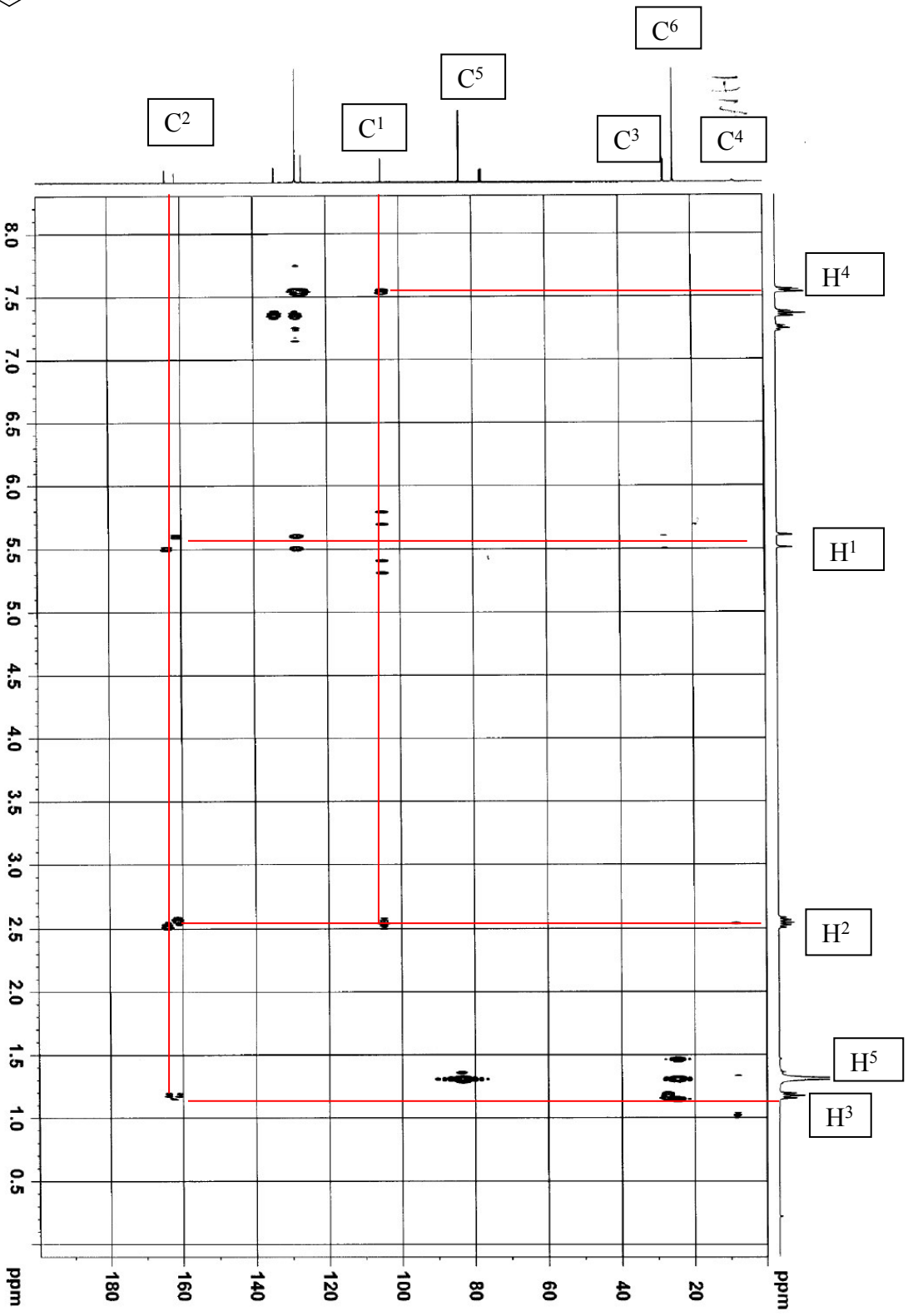
H3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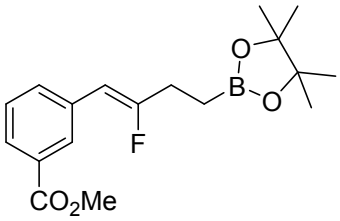
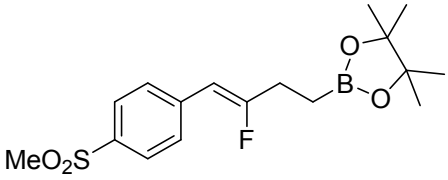
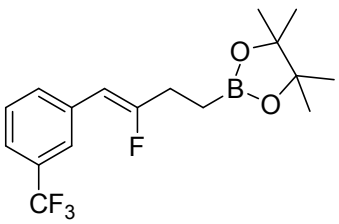


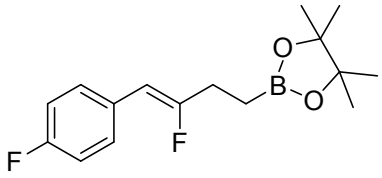
(*Z*)-Methyl 3-(2-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)benzoate(3b). 73% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 5.52 (d, *J* = 38.9 Hz, 1H), 3.91 (s, 3H), 2.46 (dt, *J* = 15.8, 7.8 Hz, 2H), 1.25 (s, 12H), 1.09 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (s), 163.4 (d, *J* = 268.1 Hz), 134.2 (d, *J* = 2.3 Hz), 132.5 (d, *J* = 8.3 Hz), 130.2 (s), 129.3 (d, *J* = 6.6 Hz), 128.4 (s), 127.5 (d, *J* = 2.0 Hz), 104.0 (d, *J* = 8.6 Hz), 83.3 (s), 52.1 (s), 27.4 (d, *J* = 27.2 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.13 (dt, *J* = 38.9, 15.8 Hz, 1F); IR (neat) ν = 2978, 2928, 1687, 1407,1380, 1308, 1150, 966 cm^{-1}; HRMS(EI) for $C_{18}H_{24}FO_4{}^{10}B$ [M]$^+$: calcd. 333.1788, found 333.1786.



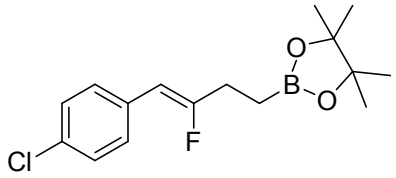
(*Z*)-2-(3-Fluoro-4-(4-(methylsulfonyl)phenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c). 66% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 5.53 (d, *J* = 38.3 Hz, 1H), 3.00 (s, 3H), 2.46 (dt, *J* = 15.8, 7.7 Hz, 2H), 1.21 (s, 12H), 1.06 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (d, *J* = 272.1 Hz), 139.6 (d, *J* = 2.4 Hz), 137.8 (d, *J* = 2.6 Hz), 128.8 (d, *J* = 7.9 Hz), 127.4 (s), 103.6 (d, *J* = 8.2 Hz), 83.4 (s), 44.5 (s), 27.5 (d, *J* = 26.7 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.79 (dt, *J* = 38.3, 15.8 Hz, 1F); IR (neat) ν = 2978, 2928, 1687, 1407,1308, 1150, 965, 767 cm^{-1}; HRMS(EI) calcd. for $C_{17}H_{24}FO_4S^{10}B$ [M]$^+$ 353.1509, found 353.1507.



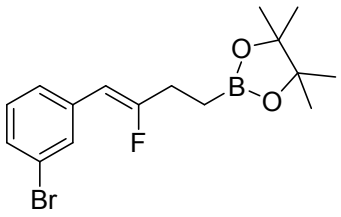
(*Z*)-2-(3-Fluoro-4-(3-(trifluoromethyl)phenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d). 52% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.31 (m, 2H), 5.52 (d, *J* = 38.5 Hz, 1H), 2.48 (dt, *J* = 15.8, 7.8 Hz, 2H), 1.25 (s, 12H), 1.09 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (d, *J* = 268.9 Hz), 134.6 (d, *J* = 2.3 Hz), 131.3 (d, *J* = 7.6 Hz), 130.7 (q, *J* = 32.1 Hz), 128.7 (s), 124.8 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 272.3 Hz), 123.0 (q, *J* = 2.2 Hz), 103.7 (d, *J* = 8.5 Hz), 83.4 (s), 27.4 (d, *J* = 27.1 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.78 (s, 3F), -98.21 (dt, *J* = 38.5, 15.8 Hz, 1F); IR (neat) ν = 2980, 1690, 1380, 1329,1211, 1166, 1128, 846 cm^{-1}; HRMS(EI) for $C_{17}H_{21}F_4O_2{}^{10}B$ [M]$^+$: calcd. 343.1607, found 343.1604.



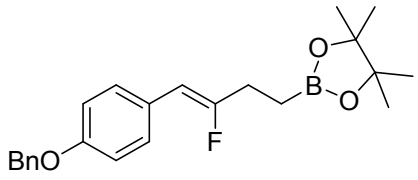
(*Z*)-2-(3-Fluoro-4-(4-fluorophenyl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e). 63% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.0, 5.7 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 2H), 5.43 (d, *J* = 39.1 Hz, 1H), 2.44 (dt, *J* = 15.7, 7.8 Hz, 2H), 1.24 (s, 12H), 1.07 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (dd, *J* = 266.0, 2.3 Hz), 161.3 (dd, *J* = 246.0, 3.3 Hz), 130.0 (dd, *J* = 3.4, 2.4 Hz), 129.7 (t, *J* = 7.7 Hz), 115.2 (d, *J* = 21.3 Hz), 103.6 (d, *J* = 9.1 Hz), 83.3 (s), 27.4 (d, *J* = 27.4 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.95 (dt, *J* = 39.1, 15.7 Hz, 1F), -112.71 – -119.22 (m, 1F); IR (neat) ν = 2979, 2930, 1692, 1606, 1509, 1380, 1327, 848 cm^{-1}; HRMS(EI) for $C_{16}H_{21}F_2O_2{}^{10}B$ $[M]^+$: calcd. 293.1639, found 293.1645.



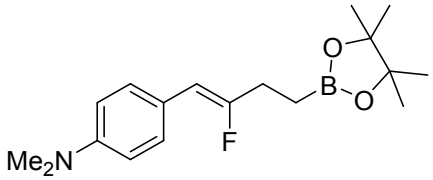
(*Z*)-2-(4-(4-Chlorophenyl)-3-fluorobut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f). 62% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 5.43 (d, *J* = 39.0 Hz, 1H), 2.44 (dt, *J* = 16.0, 7.6 Hz, 2H), 1.24 (s, 12H), 1.07 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 267.5 Hz), 132.4 (d, *J* = 2.4 Hz), 131.9 (d, *J* = 3.4 Hz), 129.4 (d, *J* = 7.7 Hz), 128.4 (s), 103.7 (d, *J* = 8.8 Hz), 83.3 (s), 27.4 (d, *J* = 27.2 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.65 (dt, *J* = 39.0, 16.0 Hz, 1F); IR (neat) ν = 2979, 2927, 1690, 1491, 1406, 1372, 1144, 905 cm^{-1}; LRMS(EI) for $C_{16}H_{21}FO_2C^{11}B$ $[M]^+$: calcd. 310.1, found 310.1; Anal. for $C_{16}H_{21}FO_2ClB$: calcd. C 61.87, H 6.81, found C 62.00, H 6.93.



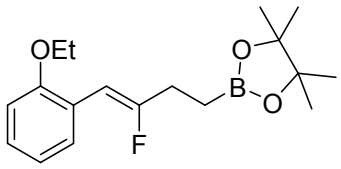
(*Z*)-2-(4-(3-Bromophenyl)-3-fluorobut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g). 46% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.41 (d, *J* = 39.0 Hz, 1H), 2.45 (dt, *J* = 15.7, 7.9 Hz, 2H), 1.24 (s, 12H), 1.07 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (d, *J* = 268.7 Hz), 136.0 (d, *J* = 2.4 Hz), 131.0 (d, *J* = 8.2 Hz), 129.8 (s), 129.4 (s), 126.73 (d, *J* = 7.3 Hz), 122.4 (s), 103.6 (d, *J* = 8.6 Hz), 83.3 (s), 27.4 (d, *J* = 27.1 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.81 (dt, *J* = 39.0, 15.7 Hz, 1F); IR (neat) ν = 2979, 2928, 1688, 1593, 1472, 1328, 1074, 847 cm^{-1}; HRMS(EI) for $C_{16}H_{21}FO_2Br^{10}B$ $[M]^+$: calcd. 353.0838, found 353.0833.



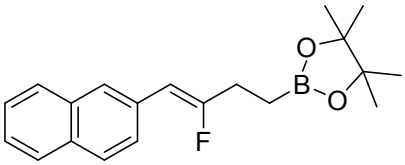
(*Z*)-2-(4-(4-(Benzyloxy)phenyl)-3-fluorobut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h). 64% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.21 (m, 7H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.41 (d, *J* = 39.8 Hz, 1H), 5.05 (s, 2H), 2.43 (dt, *J* = 15.7, 7.9 Hz, 2H), 1.24 (s, 12H), 1.07 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 264.2 Hz), 157.4 (d, *J* = 2.8 Hz), 137.1 (s), 129.6 (d, *J* = 7.4 Hz), 128.7 (s), 128.0 (s), 127.6 (s), 127.1 (d, *J* = 2.2 Hz), 114.8 (s), 104.2 (d, *J* = 9.2 Hz), 83.4 (s), 70.1 (s), 27.5 (d, *J* = 27.5 Hz), 24.9 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.40 (dt, *J* = 39.8, 15.7 Hz, 1F); IR (neat) ν = 2978, 2927, 1691, 1608, 1437, 1380, 1323, 848 cm^{-1}; LRMS(EI) $C_{23}H_{28}FO_3{}^{11}B$ $[M]^+$: calcd. for 382, found 382; Anal. for $C_{23}H_{28}FO_3B$: calcd. C 72.26, H 7.38, found C 72.75, H 7.60.



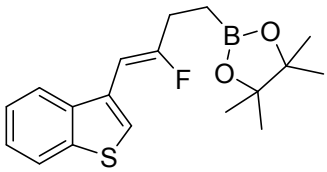
(*Z*)-4-(2-Fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-N,N-dimethylaniline (3i). 72% yield; Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.37 (d, *J* = 40.5 Hz, 1H), 2.94 (s, 6H), 2.42 (dt, *J* = 15.6, 7.8 Hz, 2H), 1.24 (s, 12H), 1.06 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (d, *J* = 262.2 Hz), 148.9 (s), 129.1 (d, *J* = 7.2 Hz), 123.0 (s), 112.6 (s), 104.3 (d, *J* = 9.5 Hz), 83.2 (s), 40.7 (s), 27.4 (d, *J* = 27.8 Hz), 24.8 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.19 (dt, *J* = 40.5, 15.6 Hz, 1F); IR (neat) ν = 2978, 2926, 2853, 1690, 1612, 1272, 1144, 847 cm^{-1}; HRMS(EI) for $C_{18}H_{27}NFO_2{}^{10}B$ $[M]^+$: calcd. 318.2155, found 318.2158.



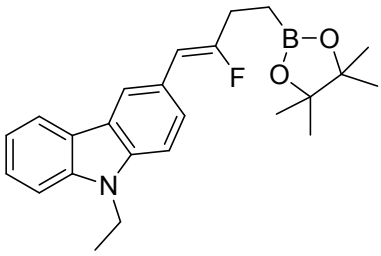
(*Z*)-2-(4-(2-Ethoxyphenyl)-3-fluorobut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k). 50% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 40.8 Hz, 1H), 4.01 (q, *J* = 6.8 Hz, 2H), 2.47 (dt, *J* = 16.1, 7.8 Hz, 2H), 1.42 (t, *J* = 6.9 Hz, 3H), 1.25 (s, 12H), 1.10 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 266.0 Hz), 155.2 (s), 129.6 (d, *J* = 12.9 Hz), 127.5 (d, *J* = 1.6 Hz), 122.9 (d, *J* = 2.9 Hz), 120.4 (s), 111.5 (s), 98.1 (d, *J* = 7.0 Hz), 83.2 (s), 63.8 (s), 27.8 (d, *J* = 28.0 Hz), 24.8 (s), 14.9 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.71 (dt, *J* = 40.8, 16.1 Hz, 1F); IR (neat) ν = 2979, 2931, 1687, 1489,1454, 1379, 1324, 1144 cm^{-1}; HRMS(EI) for $C_{18}H_{26}FO_3{}^{10}B$ $[M]^+$: calcd. 319.1995, found 319.1994.



(*Z*)-2-(3-Fluoro-4-(naphthalen-2-yl)but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l). 67% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.83-7.74 (m, 3H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.48-7.38 (m, 2H), 5.63 (d, *J* = 39.5 Hz, 1H), 2.51 (dt, *J* = 15.4, 7.7 Hz, 2H), 1.24 (s, 12H), 1.12 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 267.2 Hz), 133.5 (s), 132.1 (d, *J* = 1.6 Hz), 131.5 (d, *J* = 2.5 Hz), 127.9 (s), 127.8 (s), 127.5 (s), 126.9 (d, *J* = 7.4 Hz), 126.6 (d, *J* = 7.6 Hz), 125.9 (s), 125.5 (s), 104.8 (d, *J* = 8.6 Hz), 83.3 (s), 27.6 (d, *J* = 27.4 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.00 (dt, *J* = 39.5, 15.4 Hz, 1F); IR (neat) ν = 2978, 2928, 1687, 1379, 1326, 1214, 1144, 745 cm^{-1}; LRMS(EI) for $C_{20}H_{24}FO_2{}^{11}B$ $[M]^+$: calcd. 382, found 382; Anal. for $C_{20}H_{24}FO_2B$: calcd. C 73.64, H 7.42, found C 73.43, H 7.51.

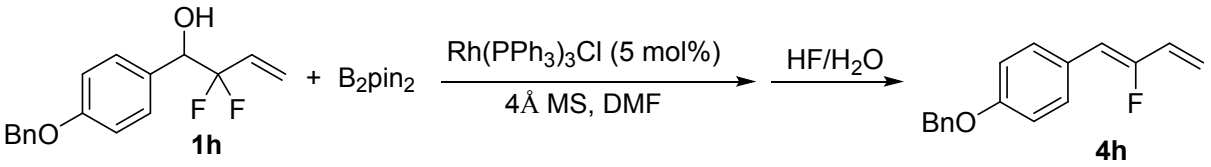


(*Z*)-2-(4-(Benzo[*b*]thiophen-3-yl)-3-fluorobut-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m). 53% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.71 (s, 1H), 7.49 – 7.28 (m, 2H), 5.87 (d, *J* = 38.8 Hz, 1H), 2.56 (dt, *J* = 15.3, 7.7 Hz, 2H), 1.24 (s, 14H), 1.15 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (d, *J* = 266.8 Hz), 139.3 (s), 138.1 (s), 127.7 (s), 124.2 (s), 123.9 (t, *J* = 6.8 Hz), 122.6 (s), 121.2 (s), 96.6 (d, *J* = 11.4 Hz), 83.3 (s), 27.3 (d, *J* = 26.9 Hz), 24.8 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.48 (dt, *J* = 38.8, 15.3 Hz, 1F); IR (neat) ν = 2978, 2928, 1688, 1379, 1325, 1143, 967, 758 cm^{-1}; HRMS(EI) or $C_{18}H_{22}F_2O_2S^{10}B$ $[M]^+$: calcd. 331.1454, found 331.1449.

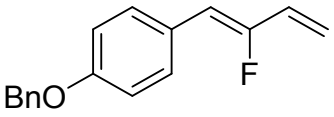


(*Z*)-9-Ethyl-3-(2-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-9*H*-carbazole (3o). 69% yield; Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 5.64 (d, *J* = 40.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.51 (dt, *J* = 15.6, 7.8 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.24 (s, 12H), 1.14 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, *J* = 262.9 Hz), 140.1 (s), 138.6 (d, *J* = 2.1 Hz), 126.3 (d, *J* = 6.9 Hz), 125.5 (s), 124.9 (d, *J* = 2.3 Hz), 122.9 (s), 120.4 (s), 120.1 (s), 120.0 (s), 118.7 (s), 108.4 (s), 108.1 (s), 105.2 (d, *J* = 9.0 Hz), 83.2 (s), 37.4 (s), 27.5 (d, *J* = 27.7 Hz), 24.7 (s), 13.7 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.23 (dt, *J* = 40.0, 15.6 Hz, 1F); IR (neat) ν = 2977, 2933, 1689, 1599, 1491, 1379, 1331, 1144 cm^{-1}; HRMS(ESI) for $C_{16}H_{21}F_2O_2{}^{11}B$ $[M+H]^+$: calcd. 394.2348, found 394.2369.

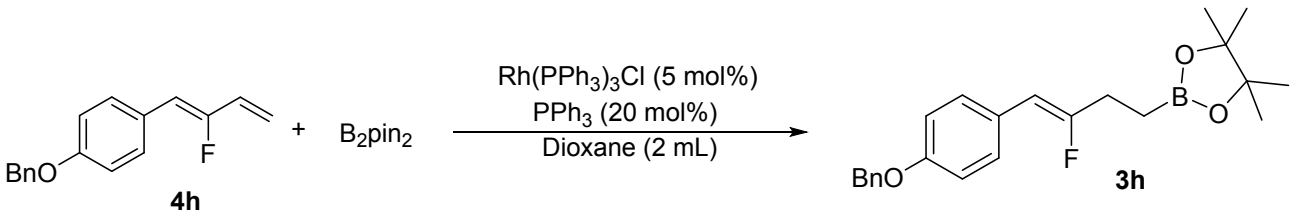
9. Evidence for the Proposed Mechanism



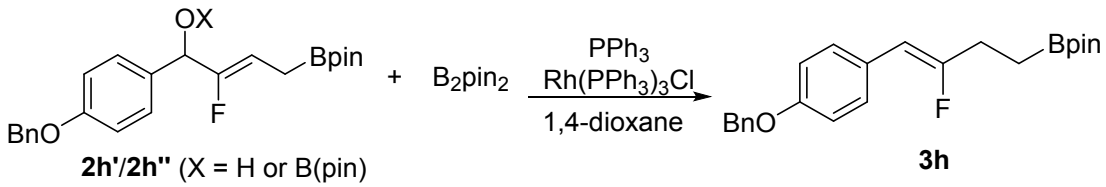
In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (191 mg, 0.75 mmol), 4Å MS (100 mg), **1h** (0.5 mmol) and DMF (2 mL) were added into a sealable tube and the tube was sealed. The mixture was stirred at 120 °C for 70 min and then cooled to room temperature. HF (35% in water) (5 drops) was added using a plastic dropper. The mixture was stirred for another 5 min. No isomers of **4h** were detected by ^{19}F NMR. Water (30 mL) was added and the resulting mixture was extracted with Et_2O (30 mL ×3). The organic solutions were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The pure product **4h** was obtained by flash column chromatography.



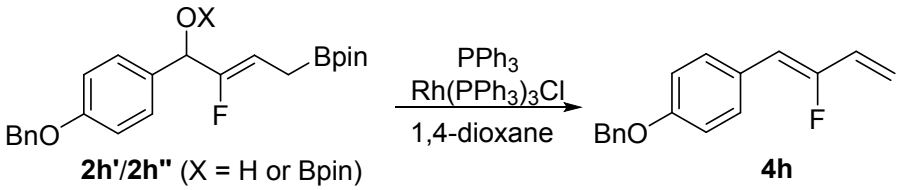
(*Z*)-1-(Benzyloxy)-4-(2-fluorobuta-1,3-dien-1-yl)benzene (4h). 65% yield; White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.45-7.29 (m, 5H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.33 – 6.09 (m, 1H), 5.68 – 5.16 (m, 3H), 5.06 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (d, *J* = 3.0 Hz), 155.6 (d, *J* = 258.4 Hz), 136.8 (s), 130.3 (d, *J* = 7.8 Hz), 129.6 (d, *J* = 25.3 Hz), 128.6 (s), 128.0 (s), 127.4 (s), 126.5 (d, *J* = 3.2 Hz), 114.9 (s), 114.2 (d, *J* = 4.7 Hz), 109.8 (d, *J* = 9.8 Hz), 69.9 (s); ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.14 (dd, *J* = 38.4, 26.4 Hz, 1F); IR (neat) ν = 2901, 1597, 1509, 1350, 1173, 1025, 980, 734 cm^{-1}; HRMS(EI) for $C_{17}H_{15}OF$ $[M]^+$: calcd. 254.1107, found 254.1106.



In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (254 mg, 1.0 mmol), PPh_3 (26.2 mg, 0.1 mmol), diene **4h** (0.5 mmol) and dioxane (2 mL) were added to a sealable tube and the tube was sealed. The mixture was stirred at 80 °C for 12 h and cooled to room temperature. Water (30 mL) was added and the resulting mixture was extracted with Et_2O (30 mL ×3). The organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The product **3h** was detected by ^{19}F NMR in 25% yield.

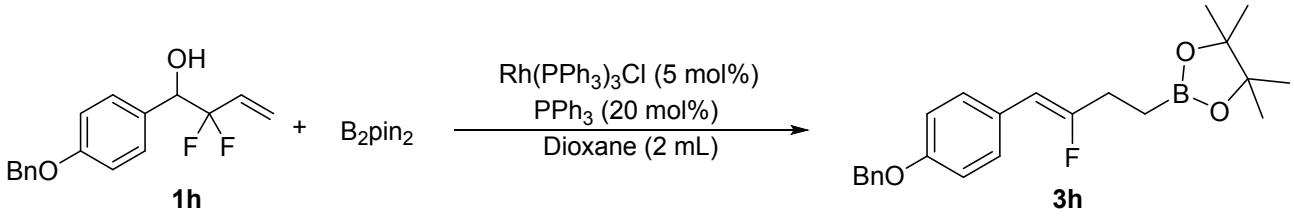


In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), B_2pin_2 (254 mg, 1.0 mmol), PPh_3 (26.2 mg, 0.1 mmol), the mixture of **2h'/2h''** (0.5 mmol), obtained by the procedure mentioned in Supporting Information Section **6**, and dioxane (2 mL) were added to a sealable tube and the tube was sealed. The mixture was stirred at 80 °C for 12 h and cooled to room temperature. Water (30 mL) was added and the resulting mixture was extracted with Et_2O (30 mL ×3). The organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The product **3h** detected by ^{19}F NMR in 19% yield.



2h'/2h'' (X = H or Bpin) **4h**

In a glove box, $Rh(PPh_3)_3Cl$ (23.1 mg, 0.025 mmol), PPh_3 (131.0 mg, 0.5 mmol), the mixture of **2h'/2h''** (0.5 mmol), obtained by the procedure mentioned in Supporting Information Section **6**, and dioxane (2 mL) were added to a sealable tube and the tube was sealed. The mixture was stirred at 80 °C for 12 h and cooled to room temperature. Water (30 mL) was added and the resulting mixture was extracted with Et_2O (30 mL ×3). The organic layers were combined and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The product **4h** was detected by ^{19}F NMR in 82% yield.



1h **3h**

General Kinetics Experimental Procedure: In a glove box, substrate **1h** (0.5 mmol, 1.0 equiv), B_2pin_2 (1.0 mmol, 2.0 equiv), $Rh(PPh_3)_3Cl$ (23.1 mg, 5 mol%), PPh_3 (26.2 mg, 0.2 equiv) were added in a 10 mL tube, followed by addition of internal standard 1-fluoronaphthalene (14.6 mg, 0.1 mmol) and dioxane (2.0 mL). The tube was sealed using an open top cap with PTFE cap liner, and moved outside the glovebox, the tube was then heated to 80 °C. The reaction progress was monitored by removing aliquots (~50 μL) from the reaction mixture via syringe under N_2. Each aliquot was disssolved in C_6D_6 and analyzed by ^{19}F NMR.

Kinetic Plots for "Different Excess" Experiment

"Different excess" studies were performed using general kinetics experimental procedure and the data was analyzed using the method reported by Donna G. Blackmond *et al* (**Ref.** *Angew. Chem. Int. Ed.* 2005, **44**, 4302–4320; *J. Org. Chem.* 2006, **71**, 4711−4722).

"Different excess" experiments reveal that this reaction is zero order to substrate and B_2pin_2.

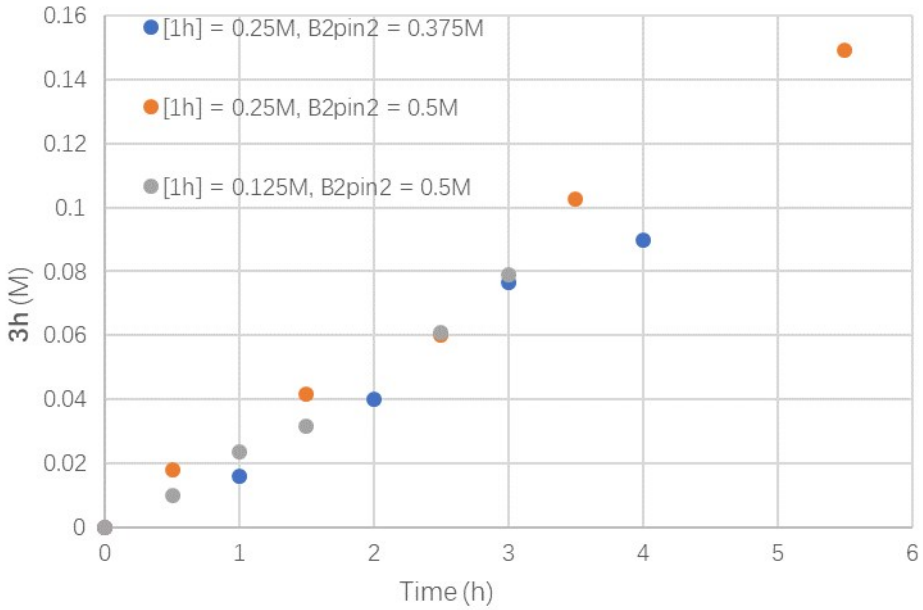
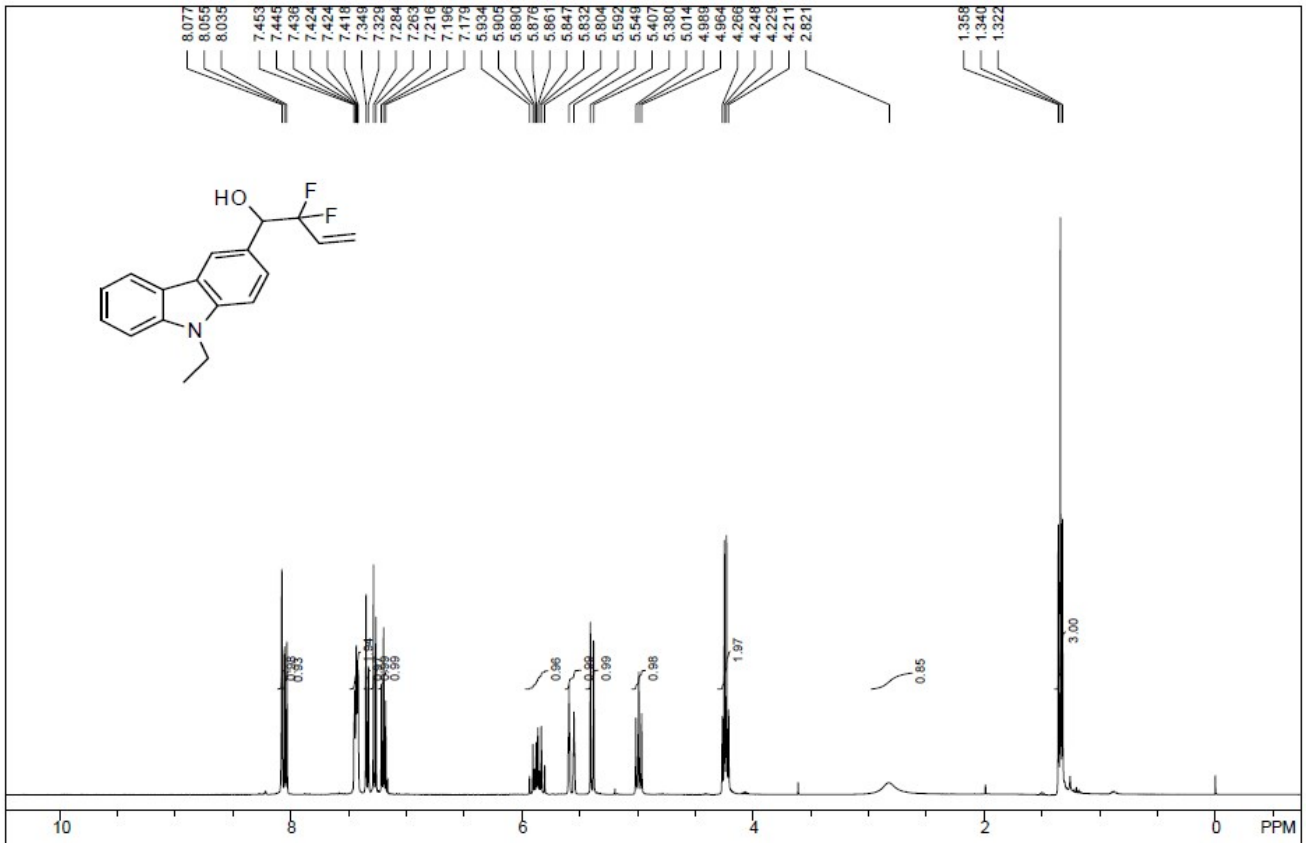


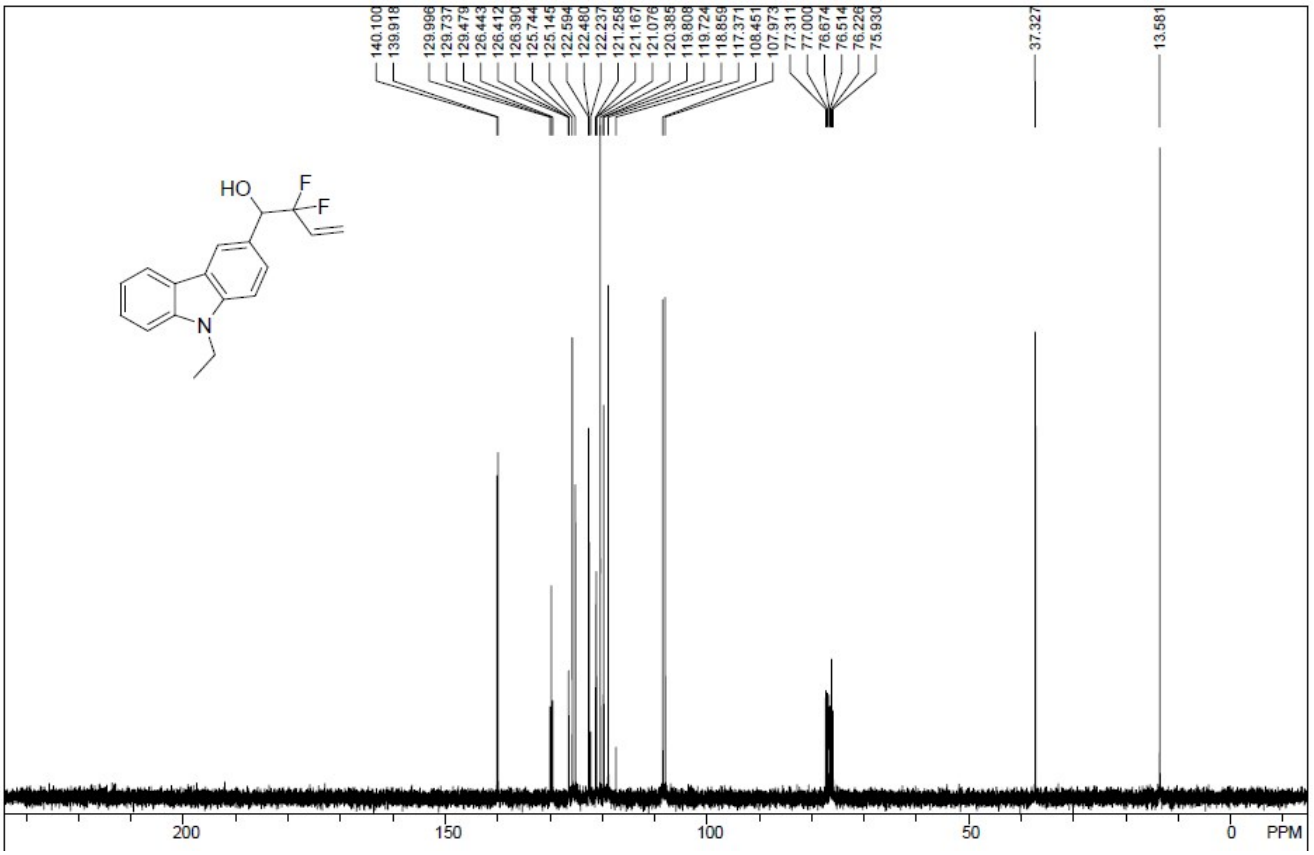
Figure S1 Time-course for the dehydroxylative/defluorinative borylation reaction.

10. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra

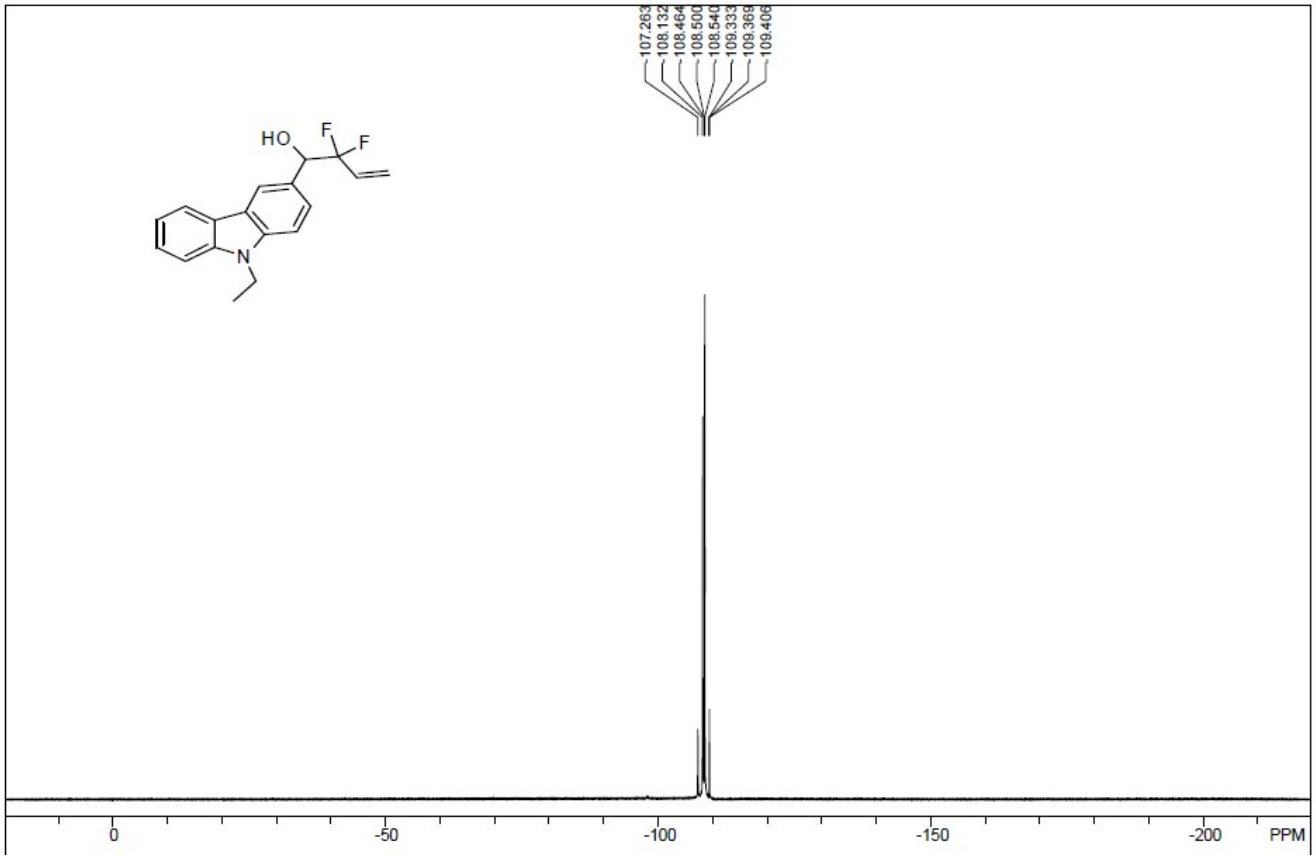
^{1}H NMR spectrum of compound **1o**



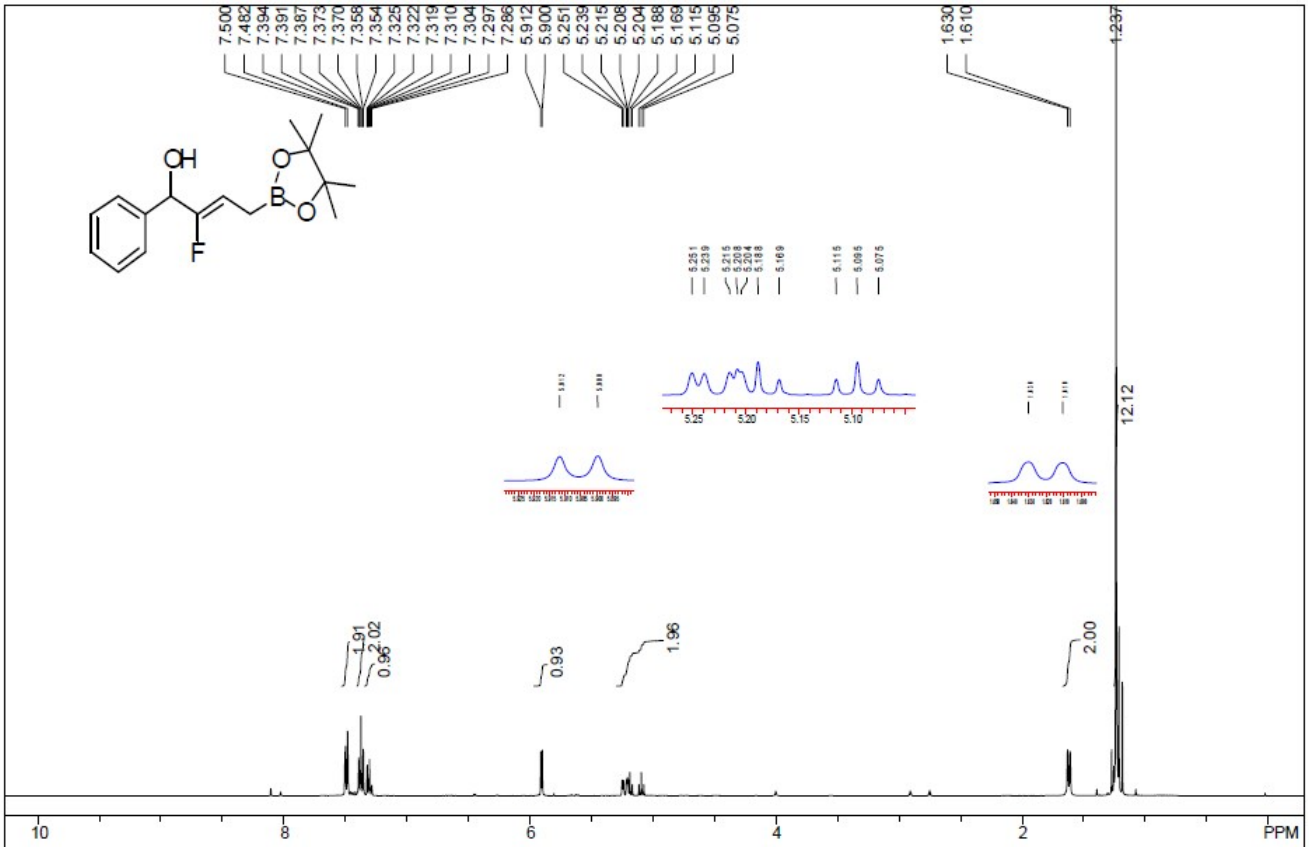
^{13}C NMR spectrum of compound **1o**



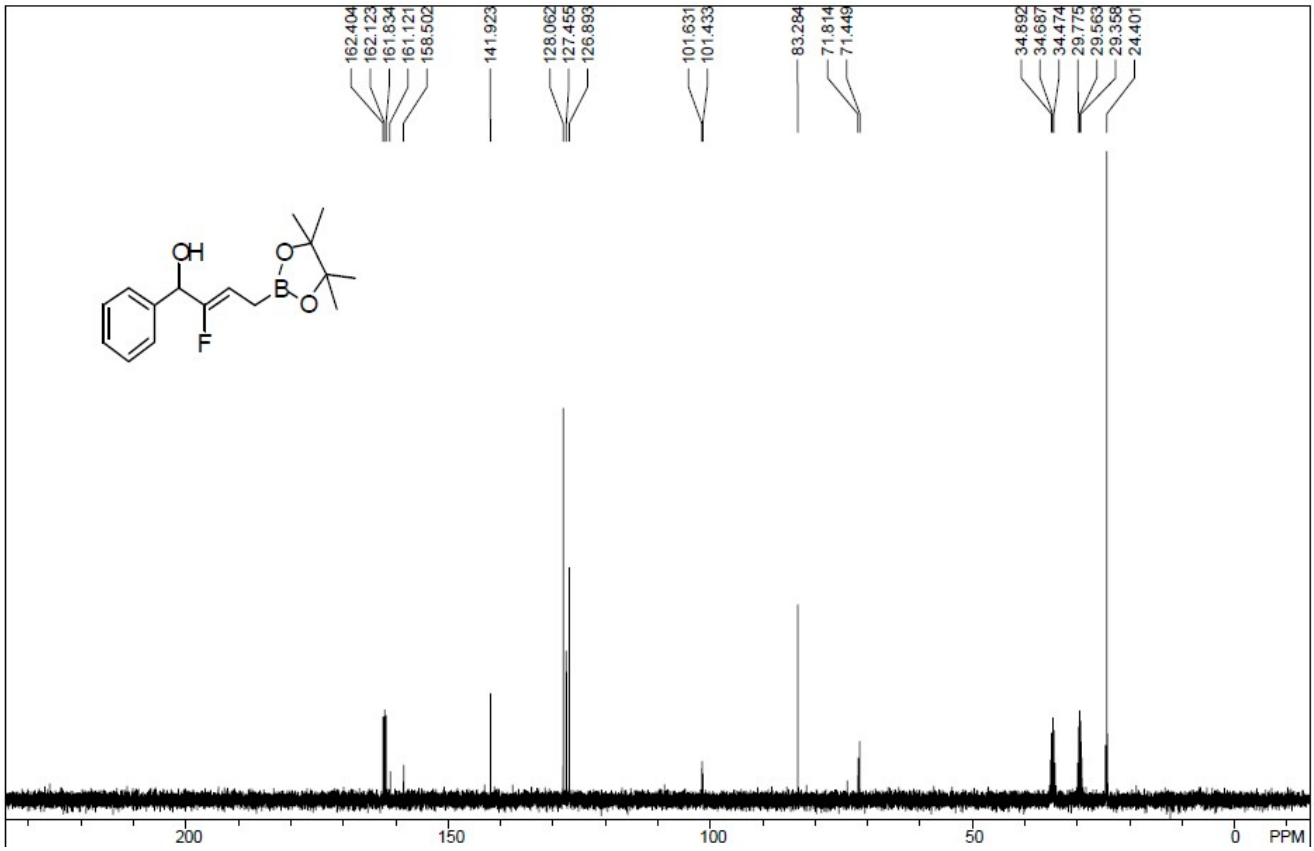
^{19}F NMR spectrum of compound **1o**



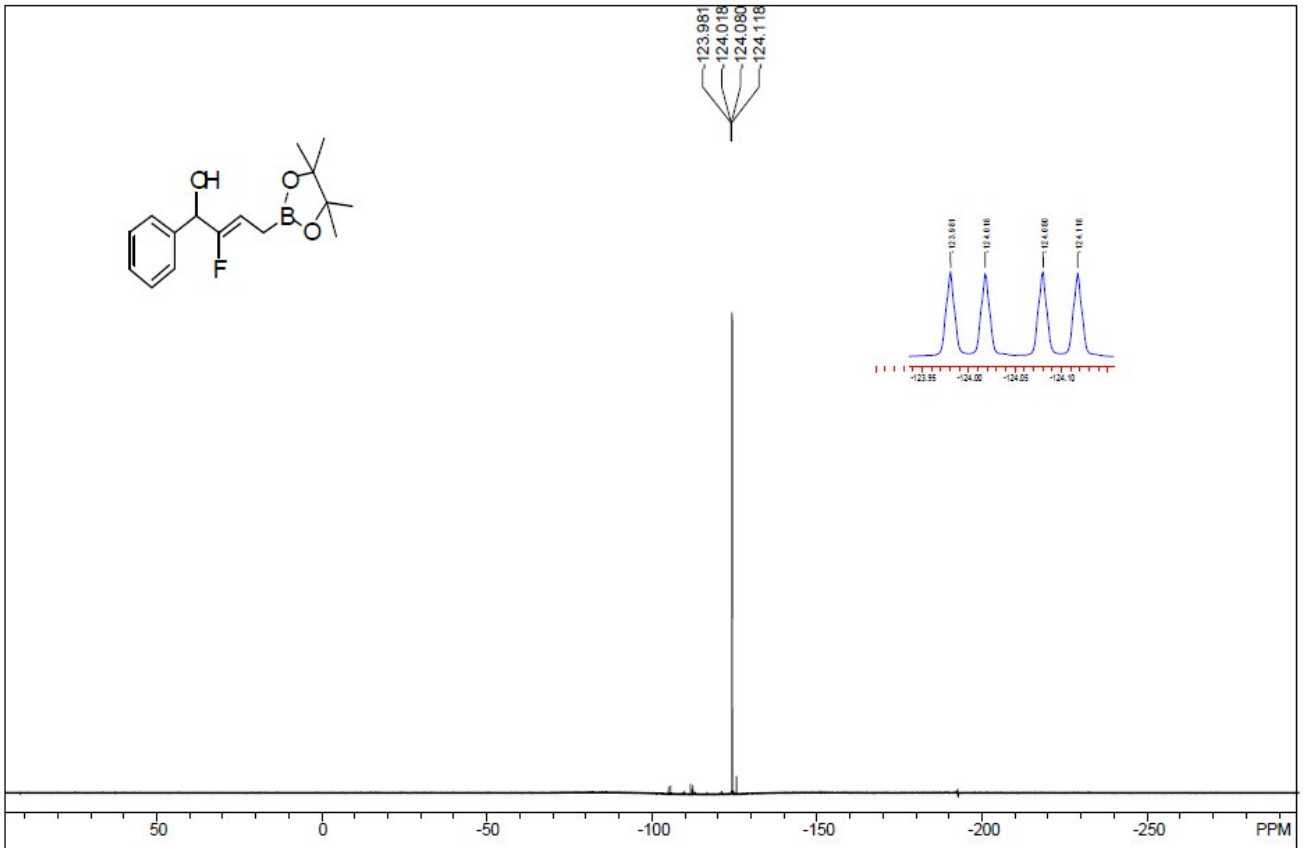
^{1}H NMR spectrum of compound **2a'**



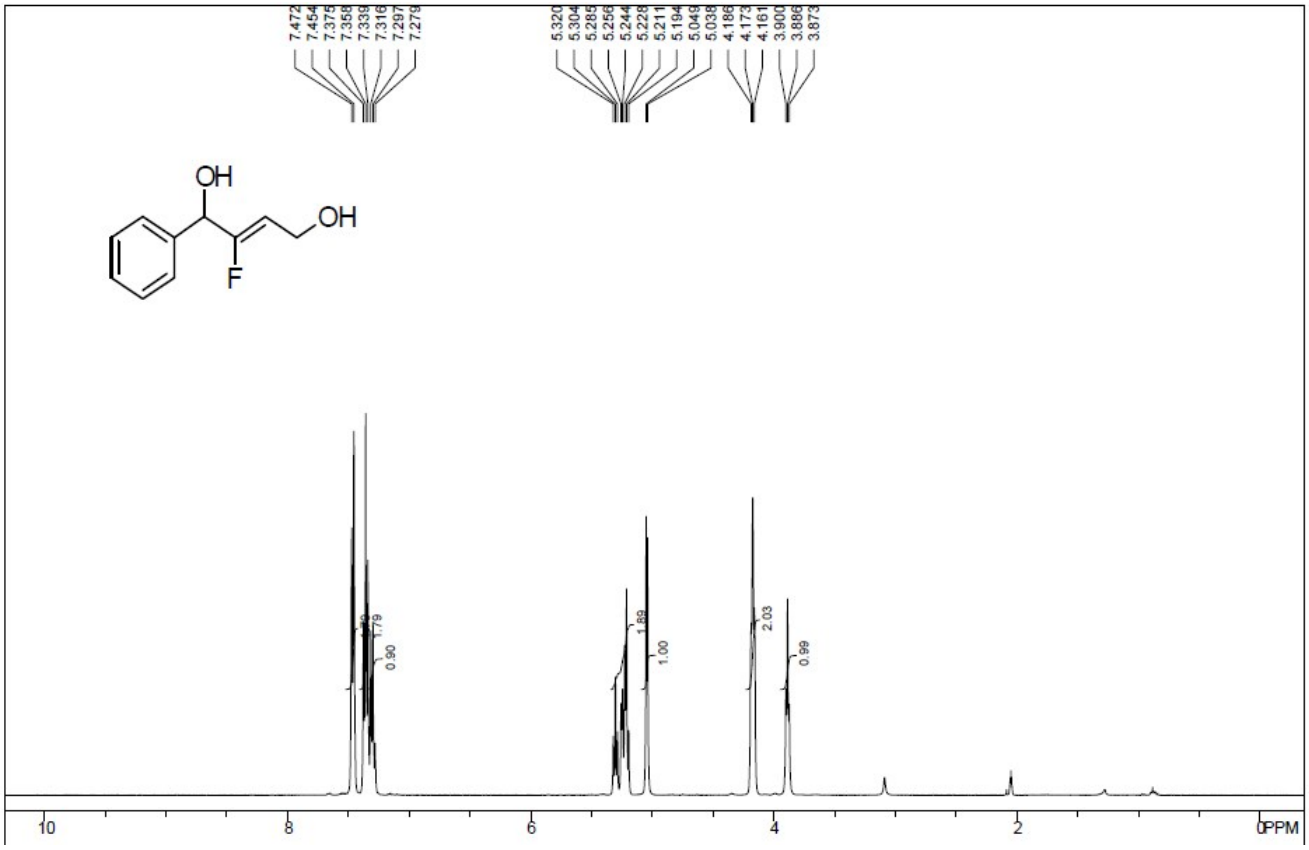
^{13}C NMR spectrum of compound **2a'**



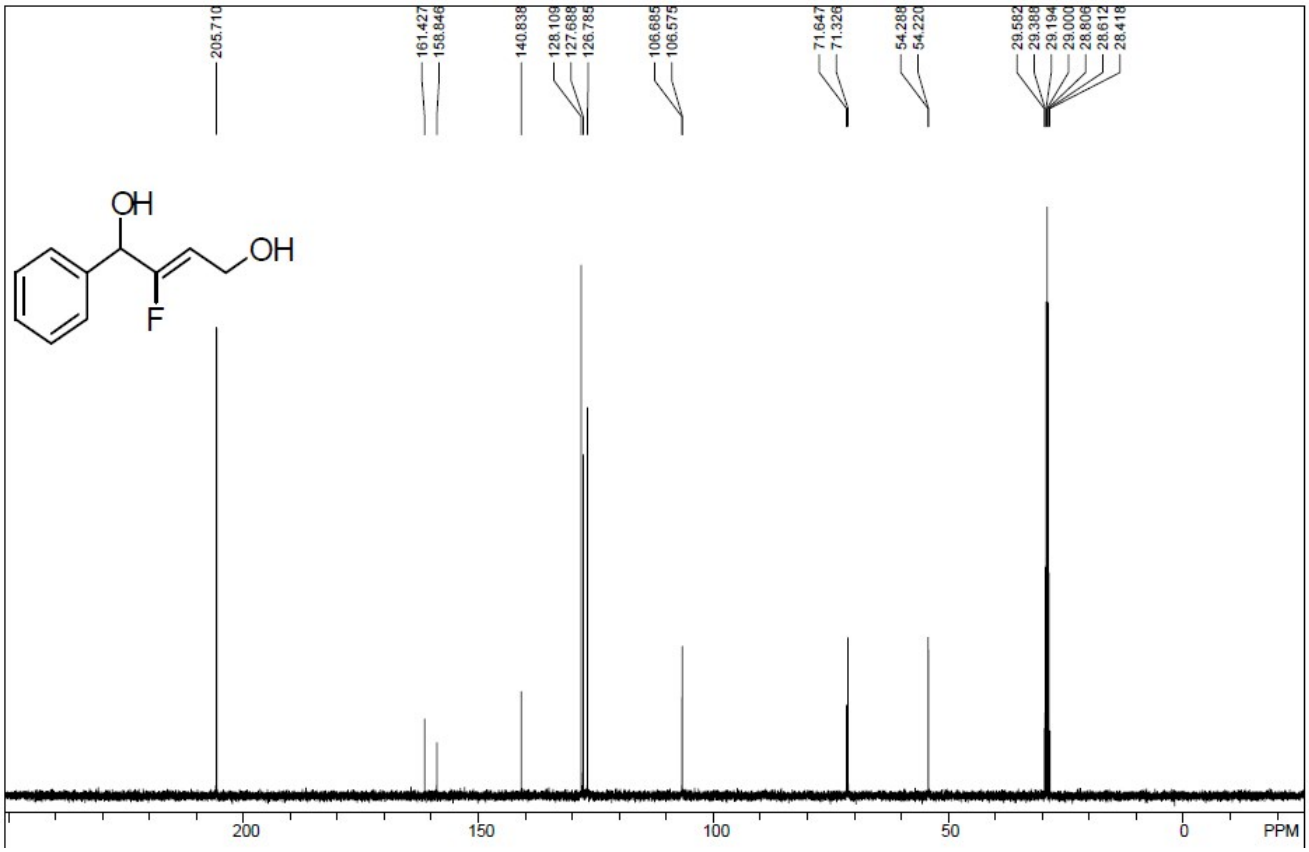
^{19}F NMR spectrum of compound **2a'**



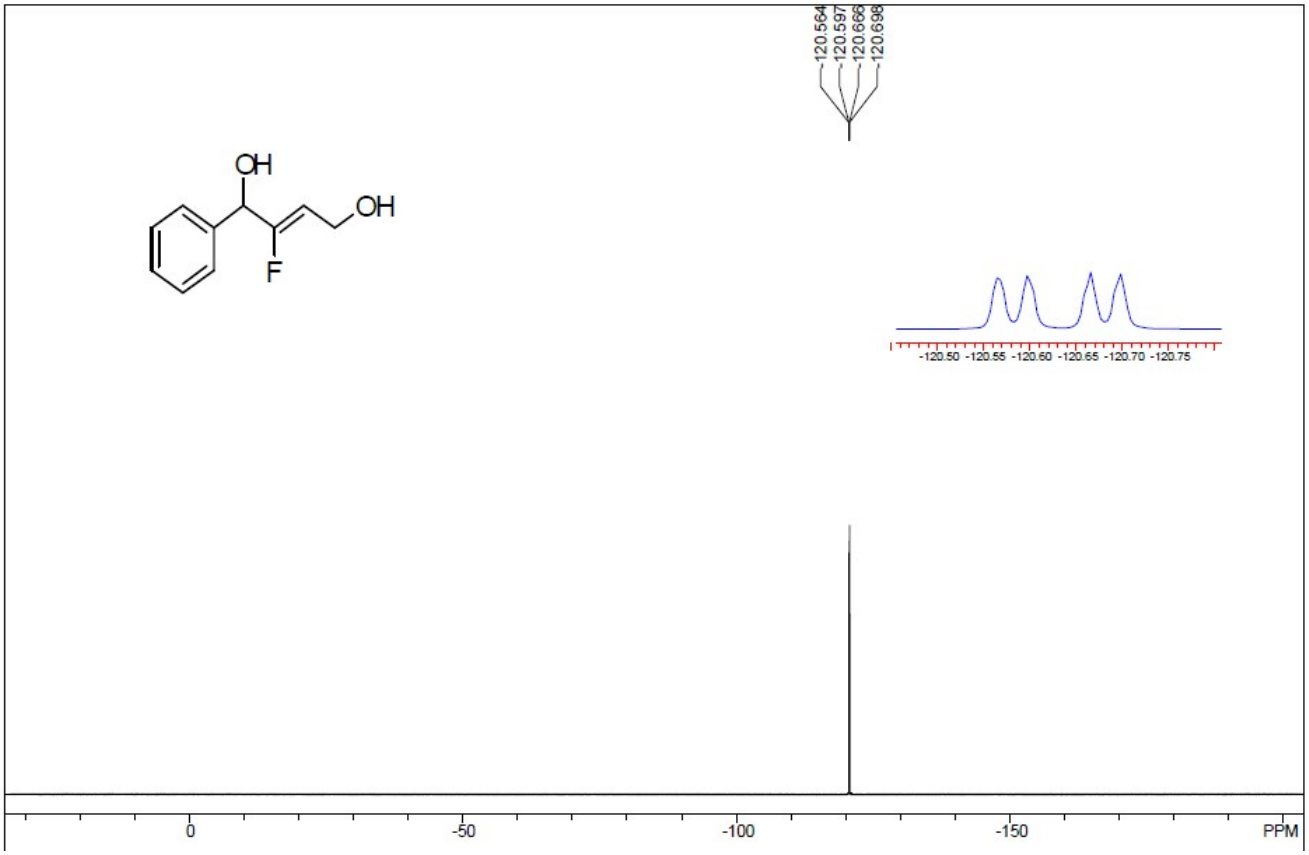
^{1}H NMR spectrum of compound **2a**



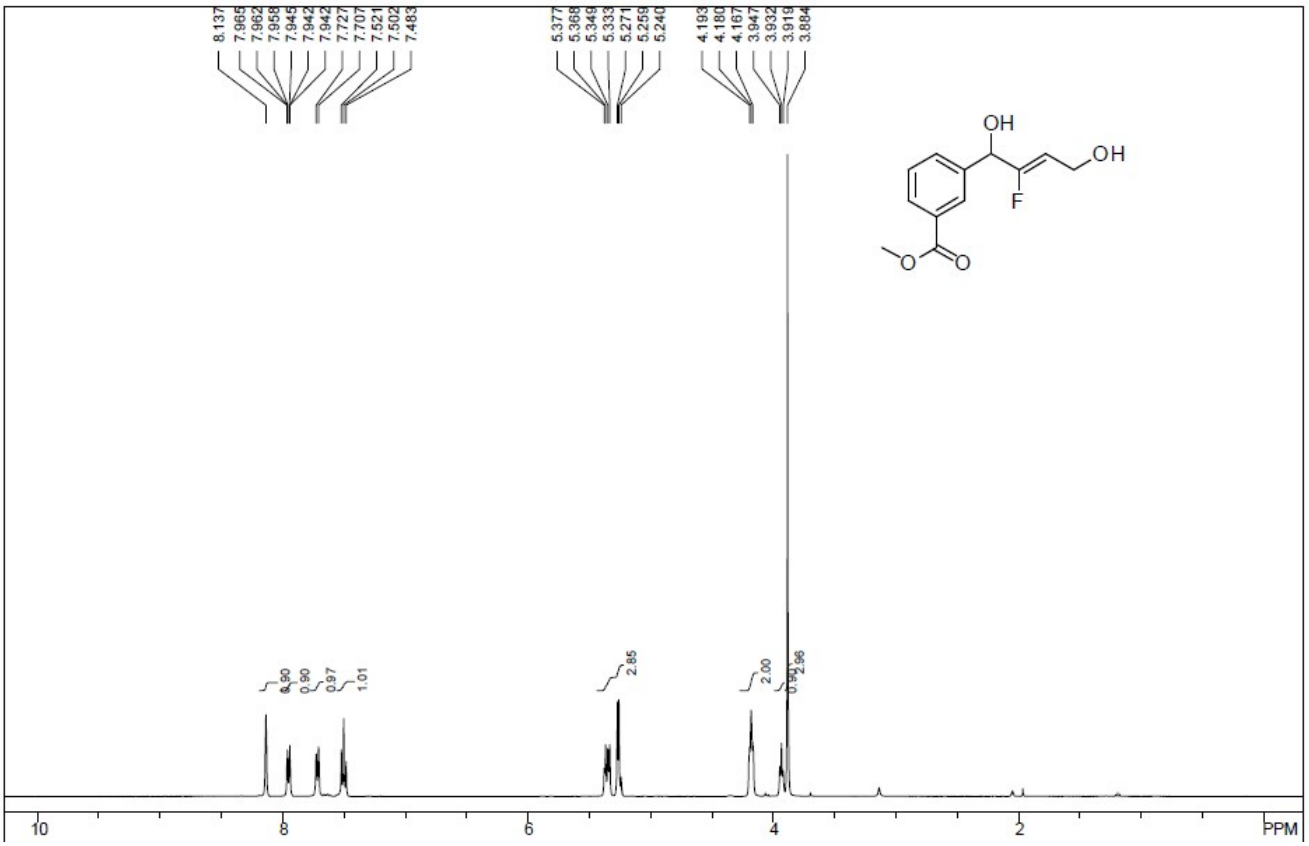
^{13}C NMR spectrum of compound **2a**



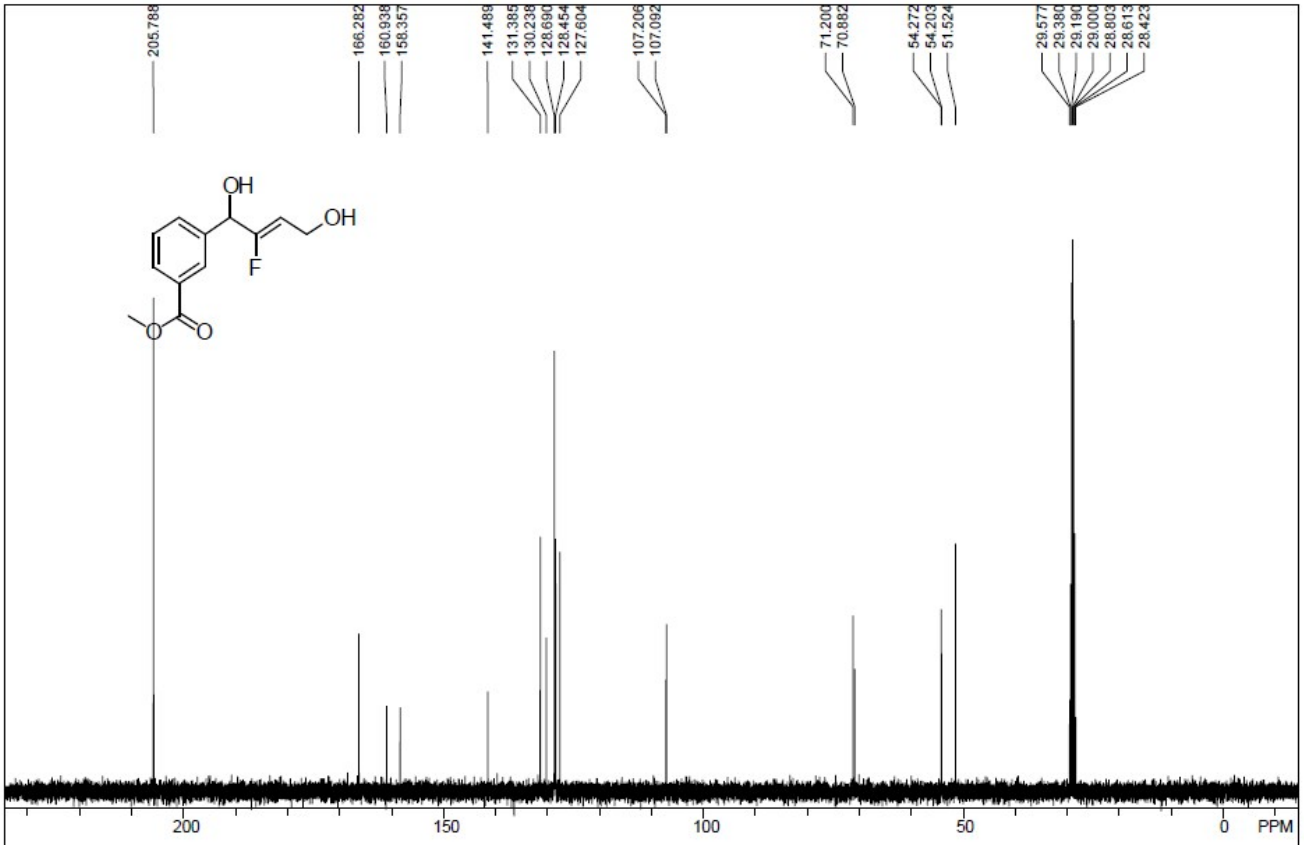
^{19}F NMR spectrum of compound **2a**



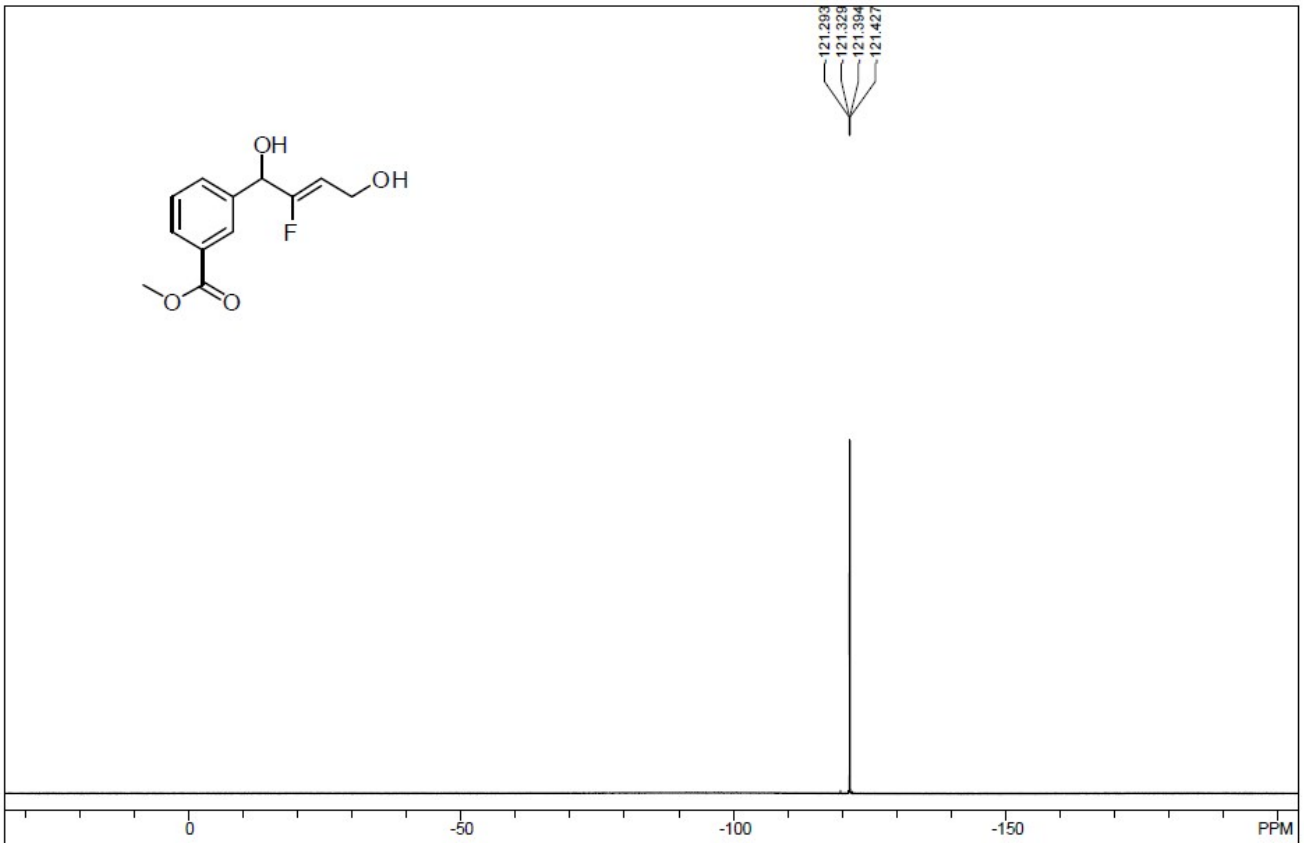
^{1}H NMR spectrum of compound **2b**



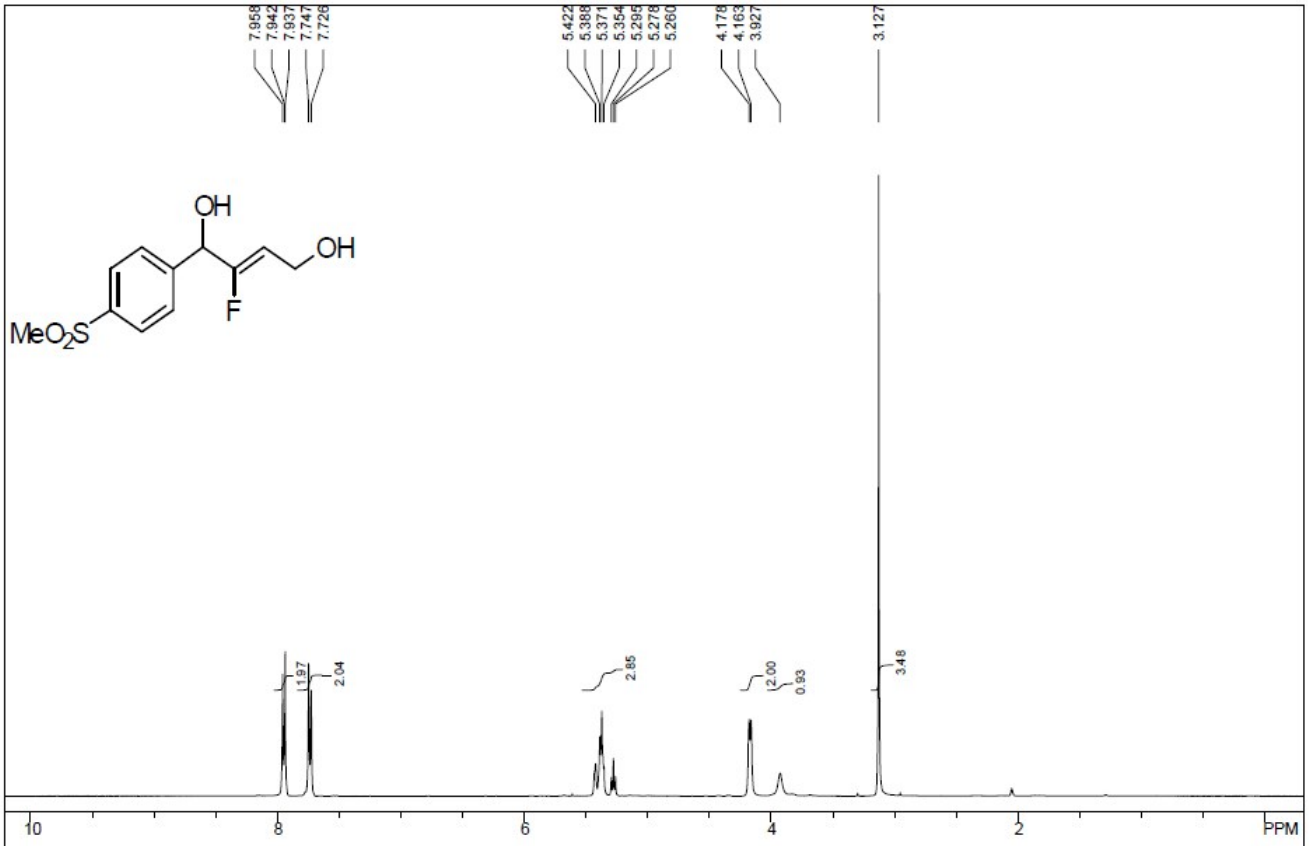
^{13}C NMR spectrum of compound **2b**



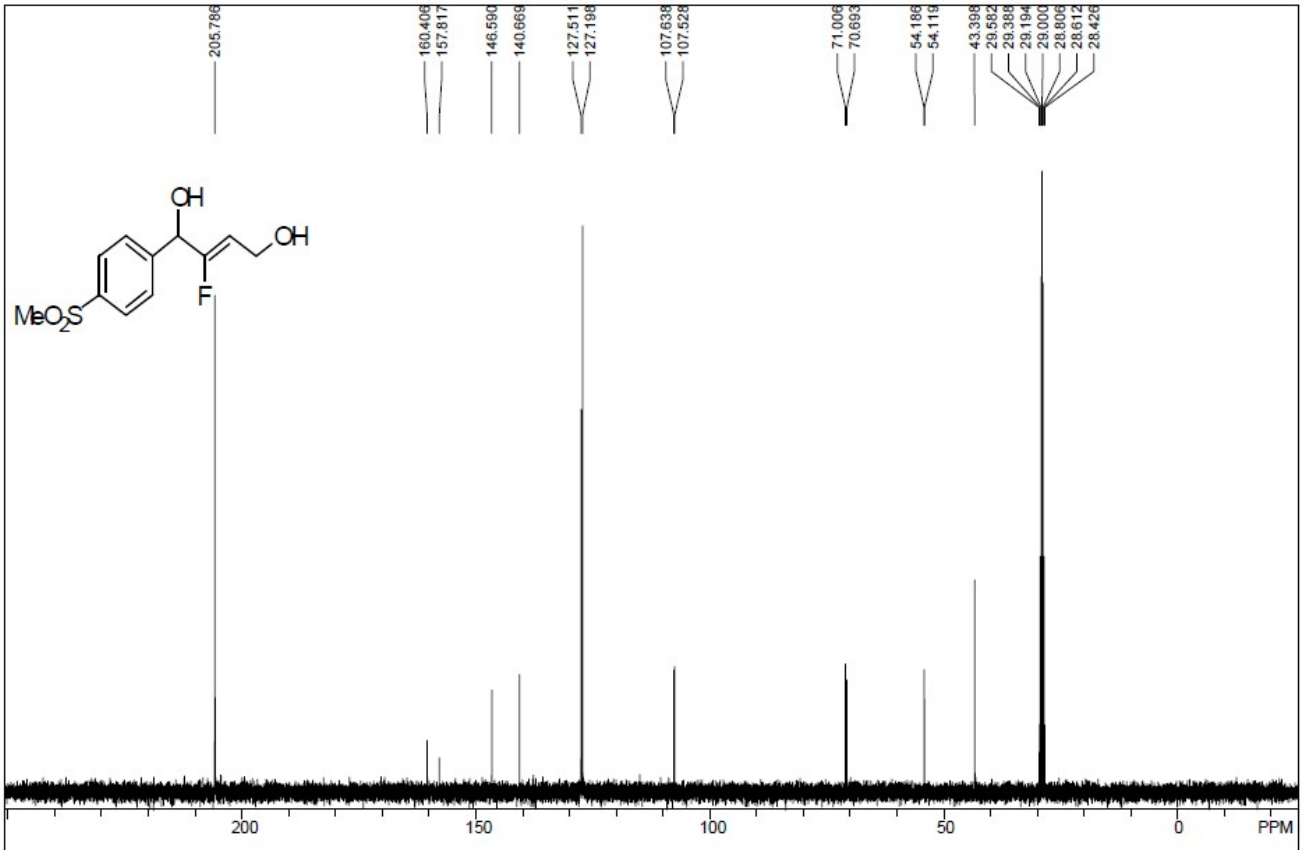
^{19}F NMR spectrum of compound **2b**



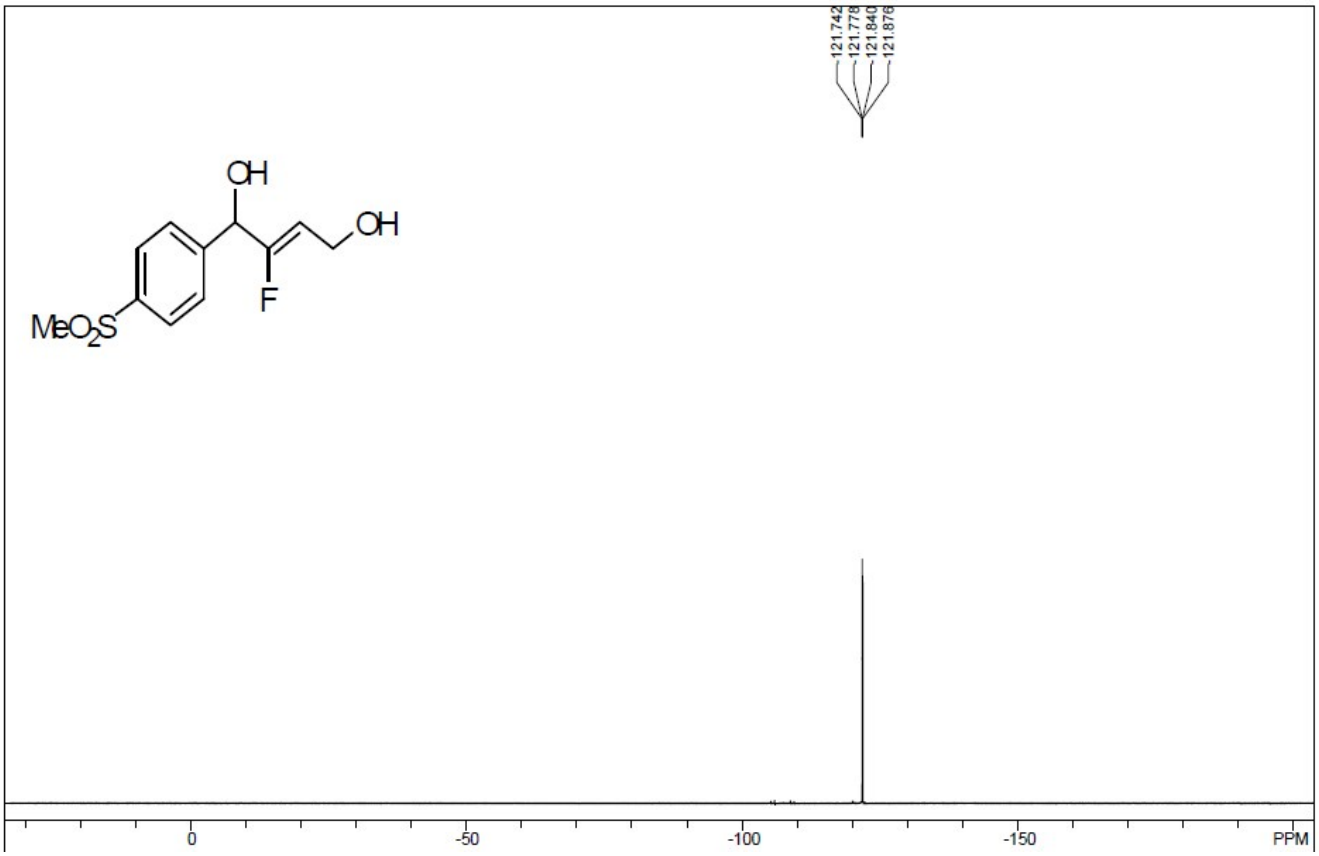
^{1}H NMR spectrum of compound **2c**



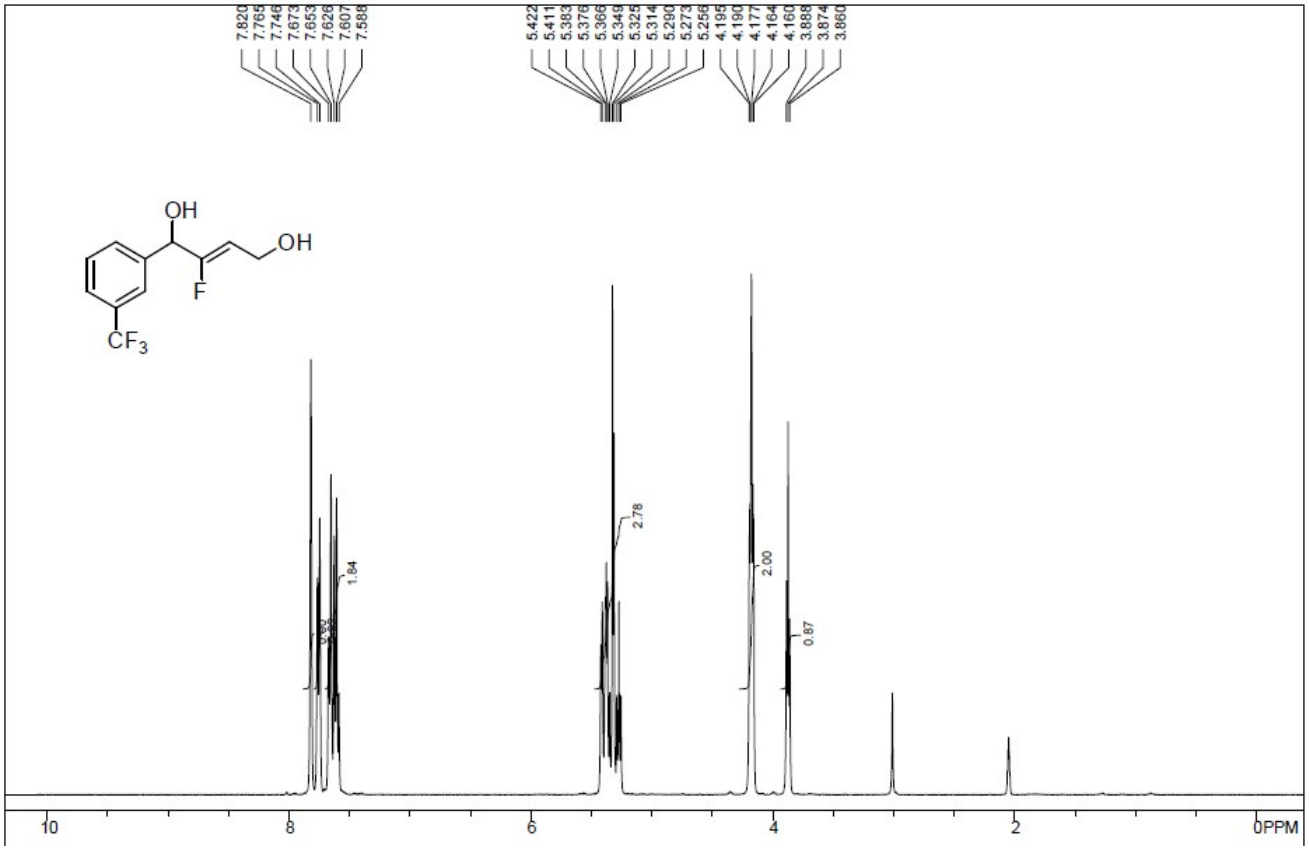
^{13}C NMR spectrum of compound **2c**



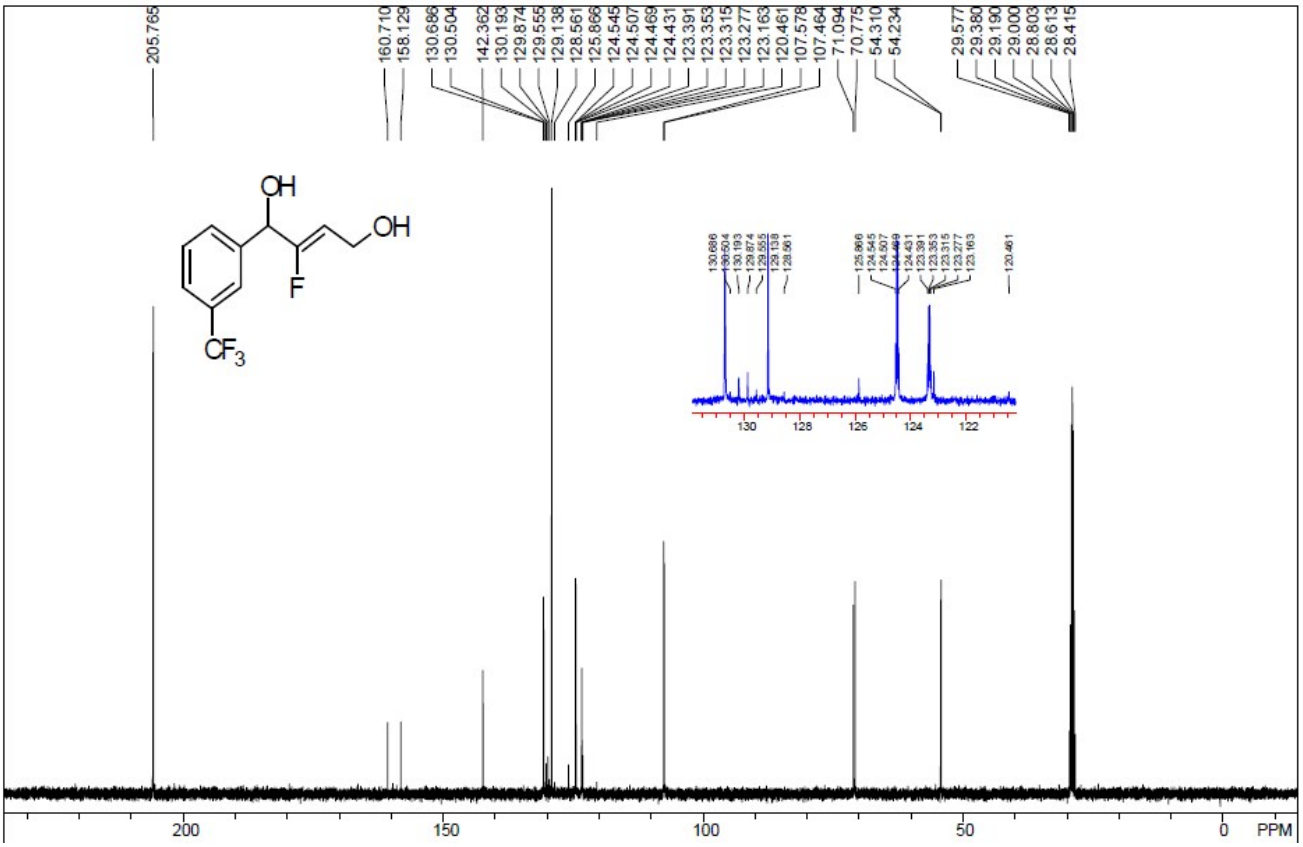
^{19}F NMR spectrum of compound **2c**



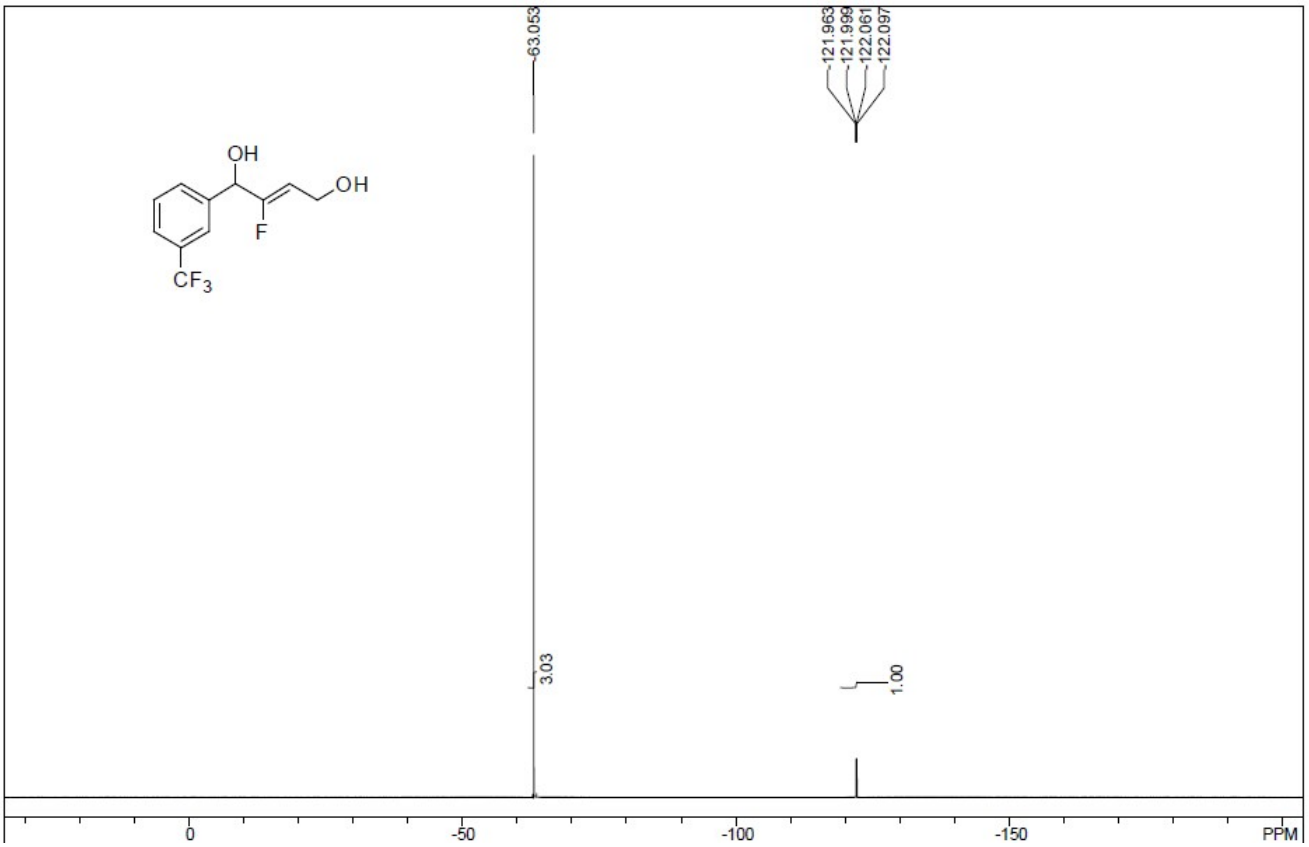
^{1}H NMR spectrum of compound **2d**



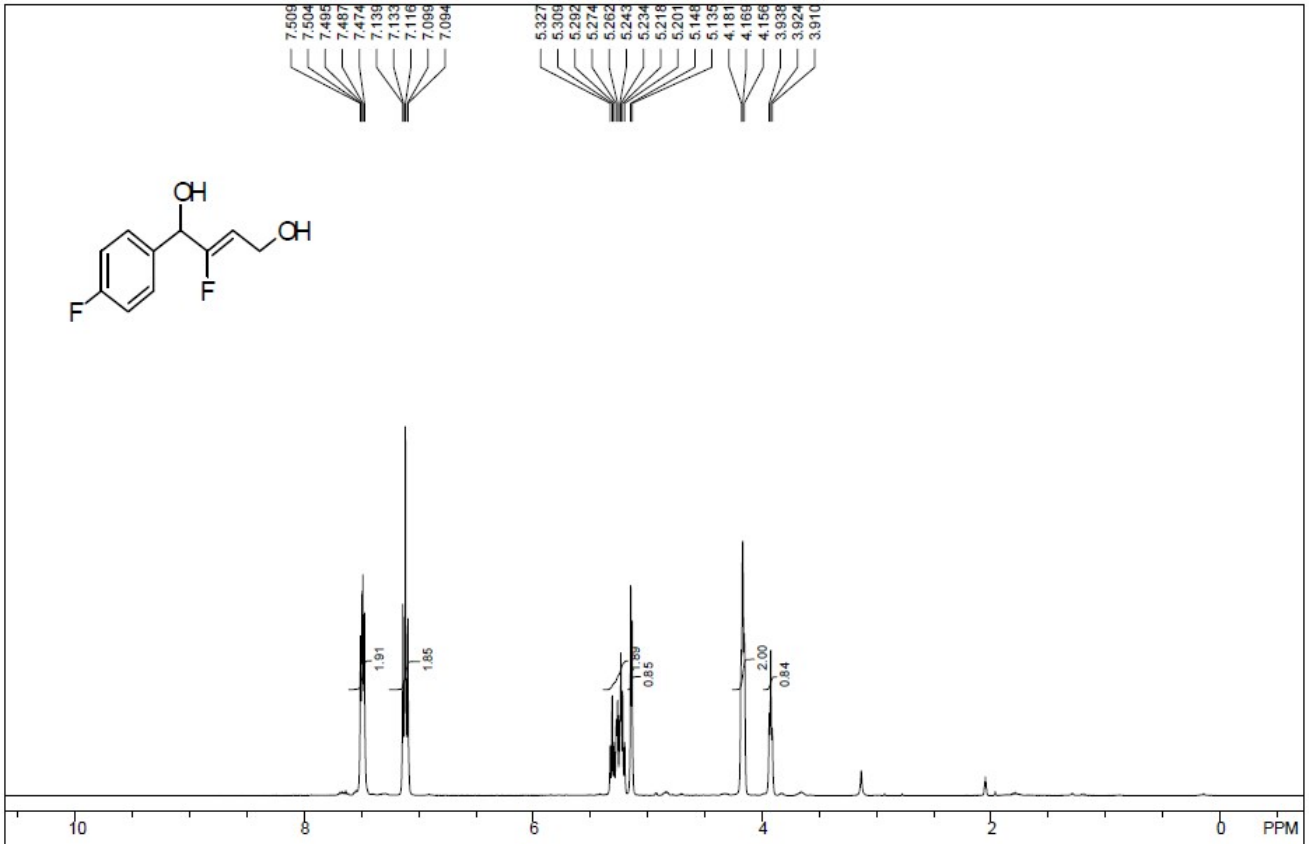
^{13}C NMR spectrum of compound **2d**



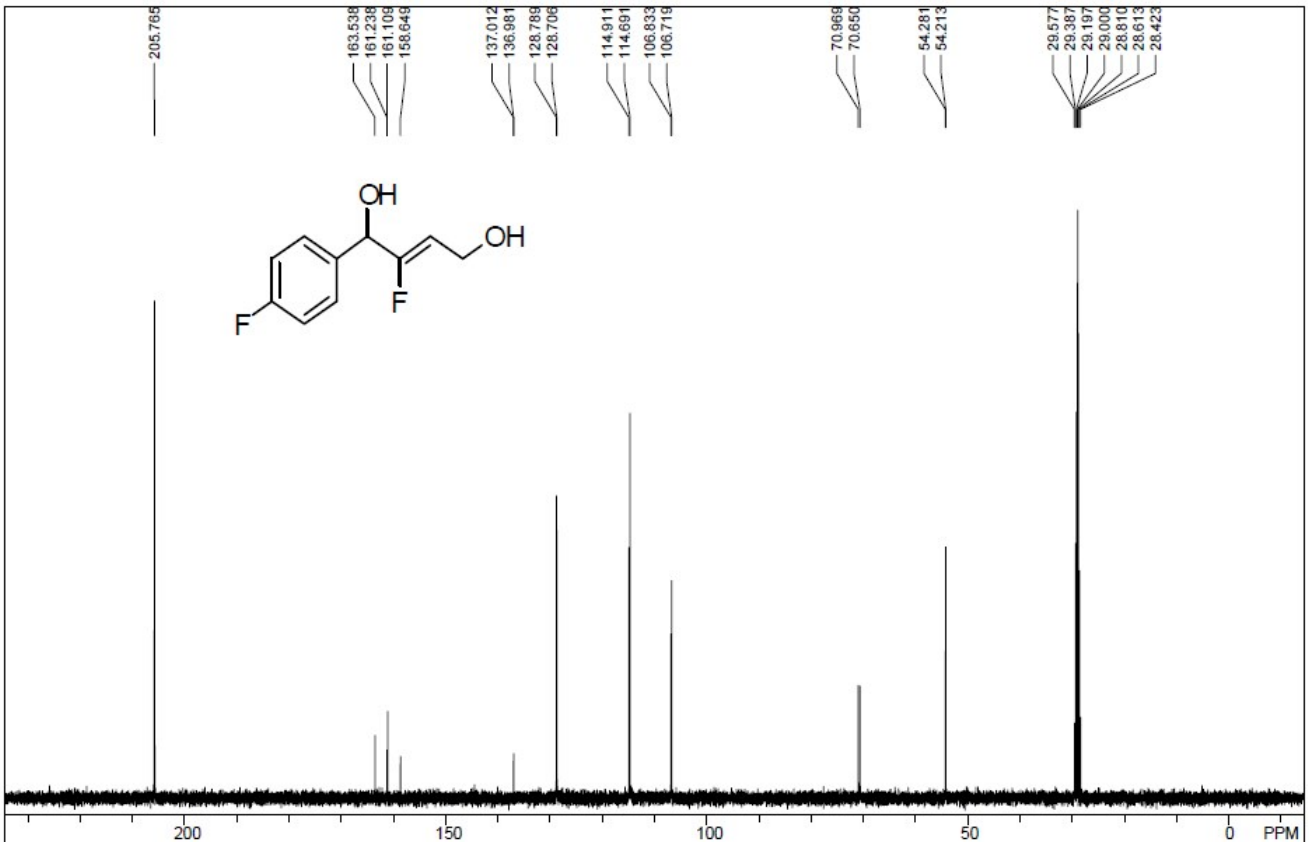
^{19}F NMR spectrum of compound **2d**



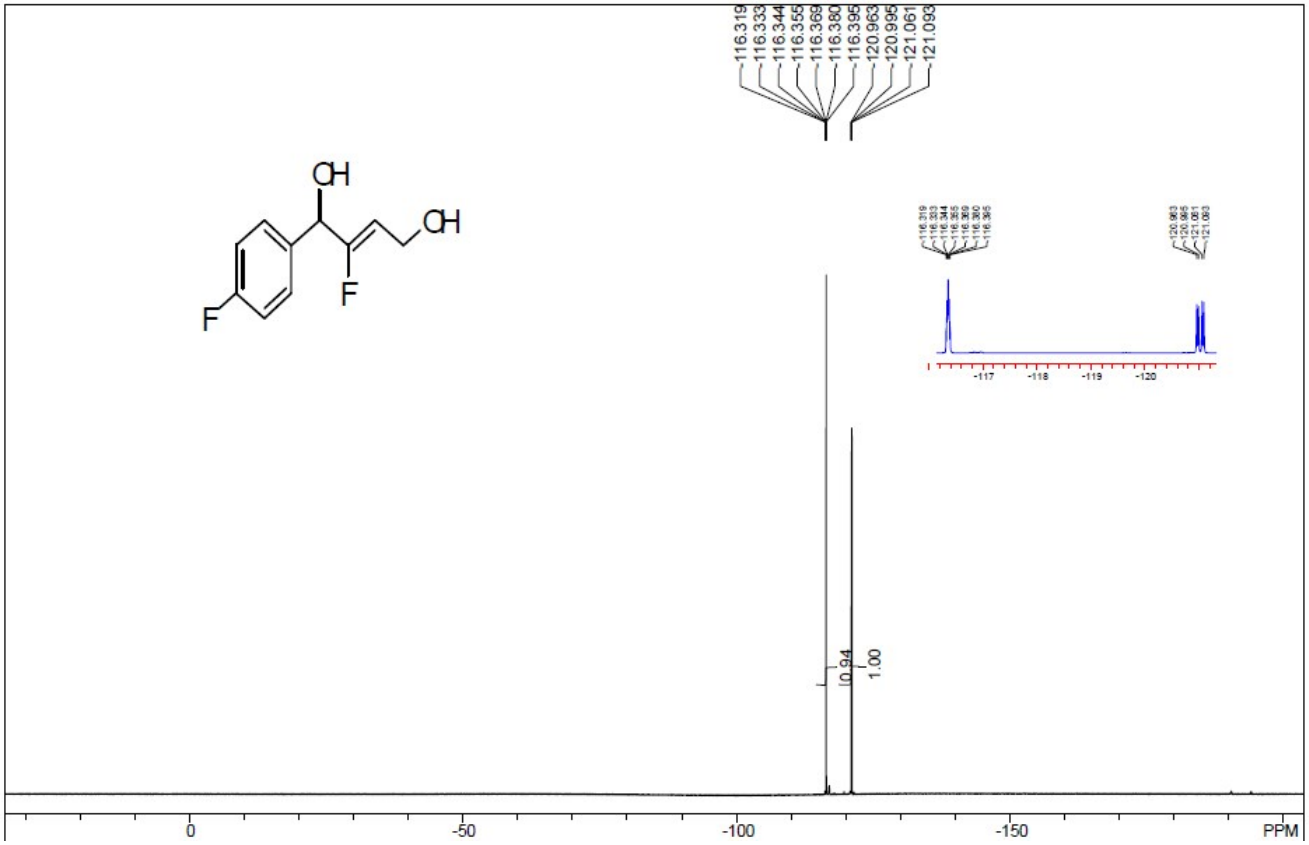
^{1}H NMR spectrum of compound **2e**



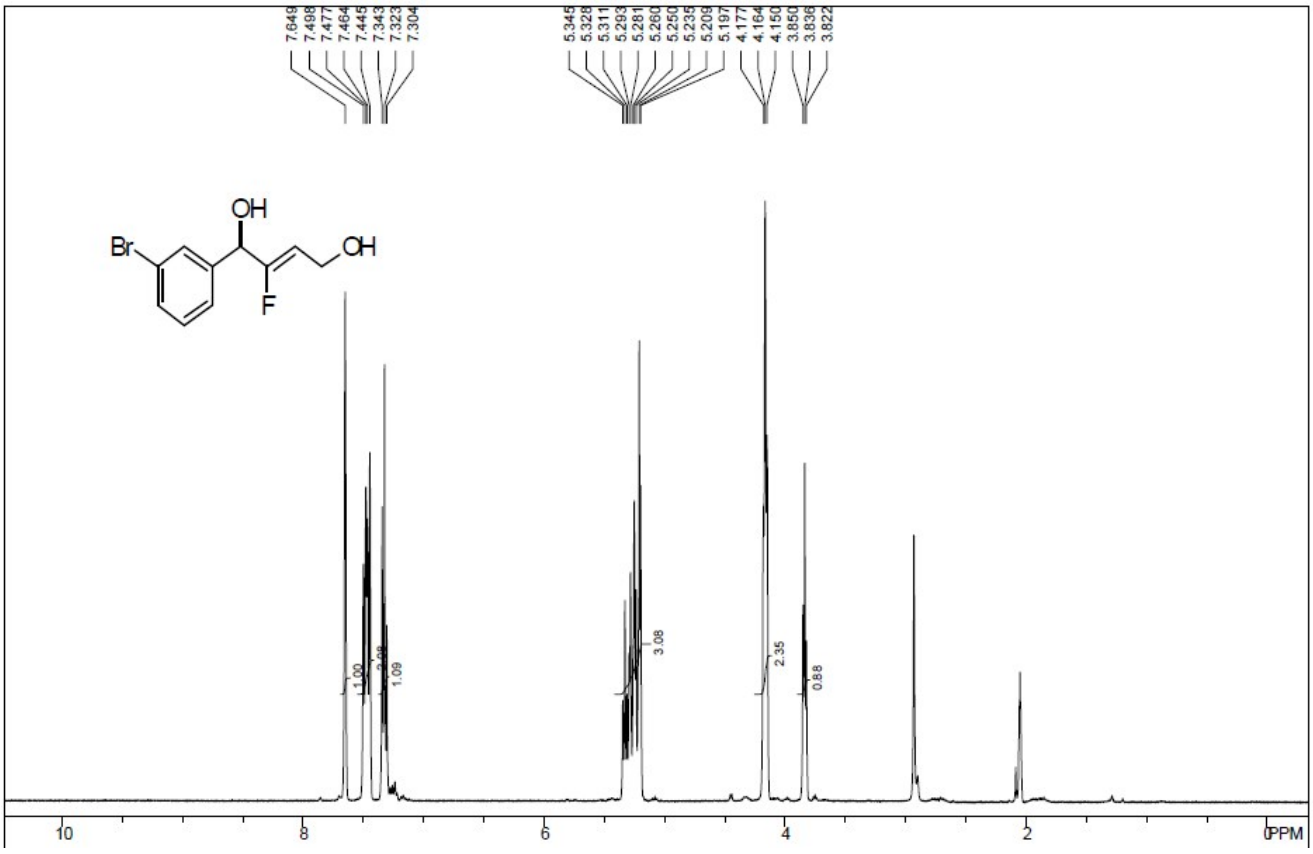
^{13}C NMR spectrum of compound **2e**



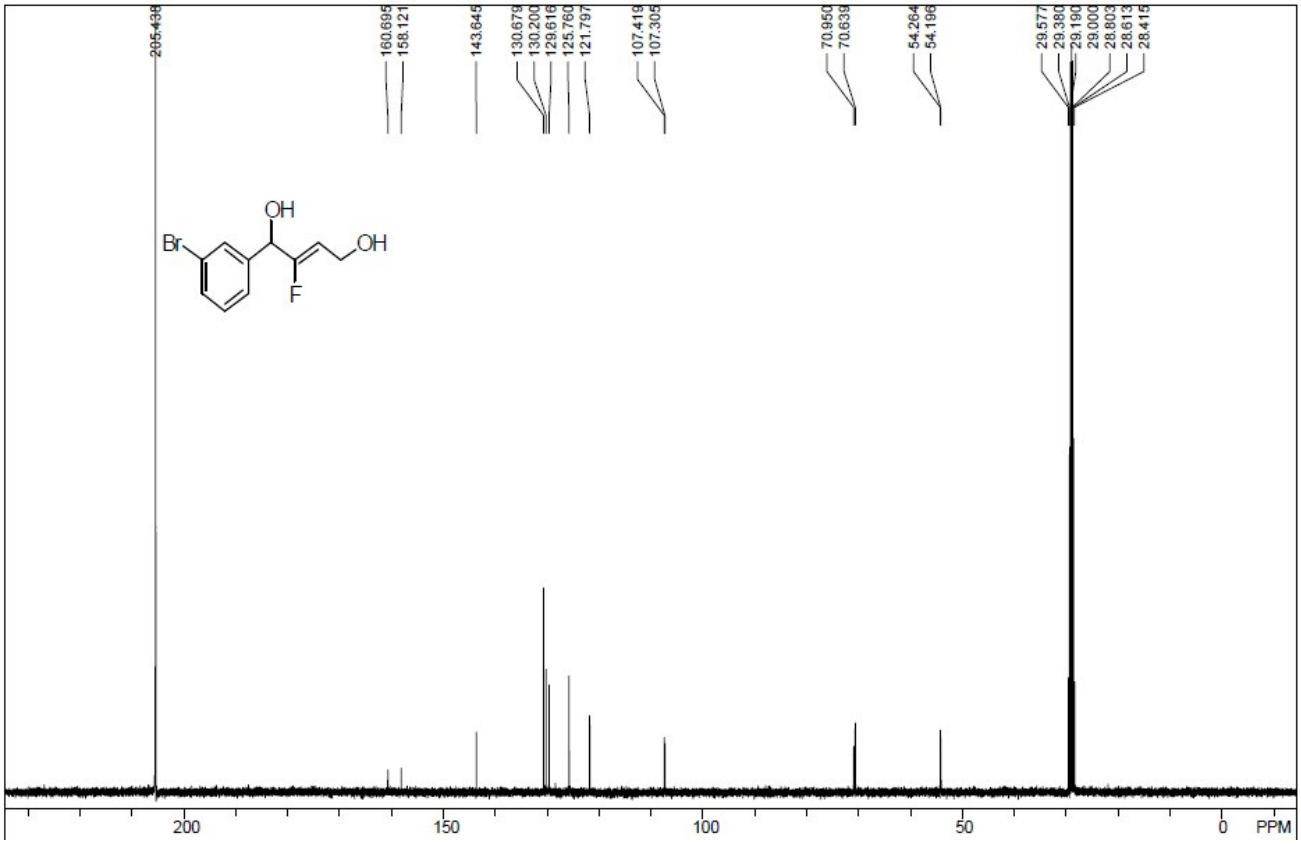
^{19}F NMR spectrum of compound **2e**



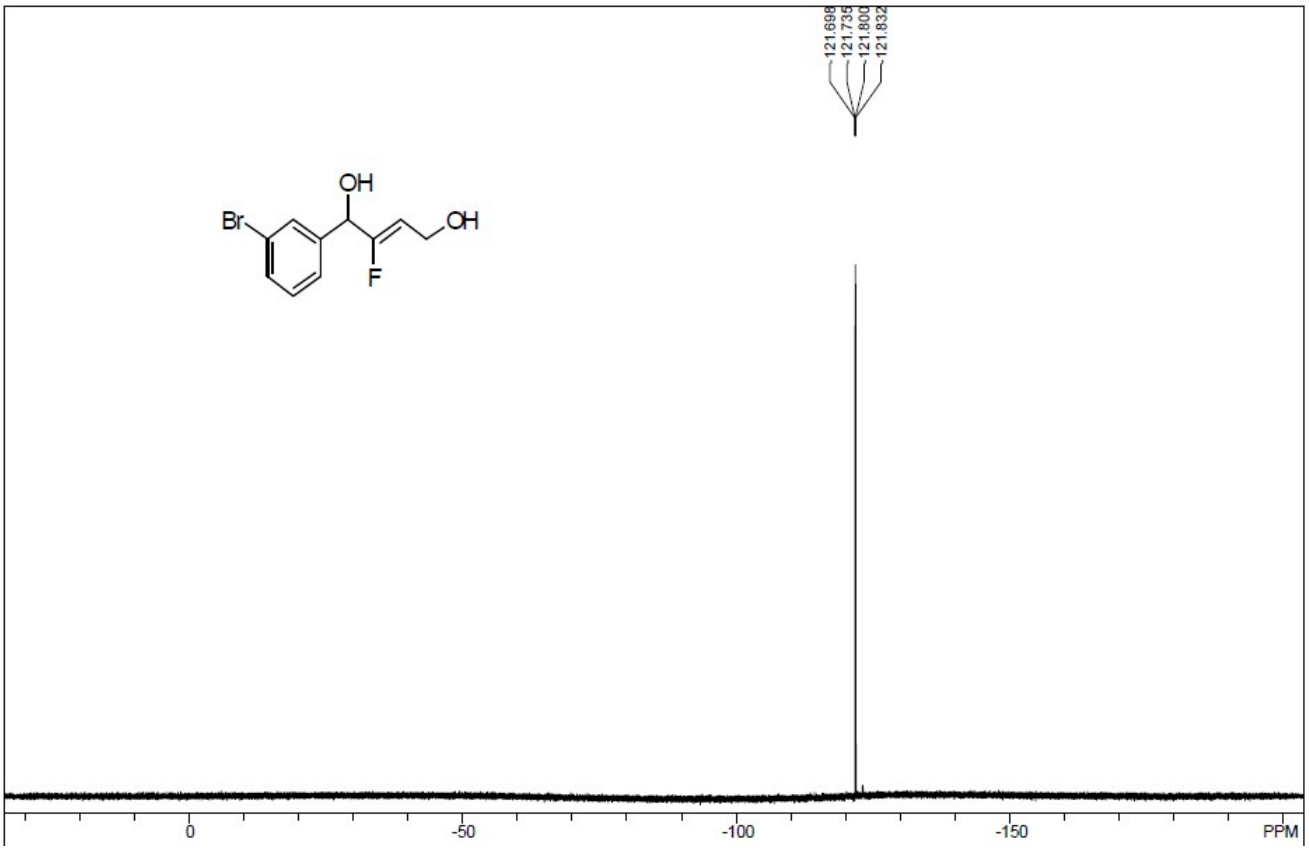
^{1}H NMR spectrum of compound **2g**



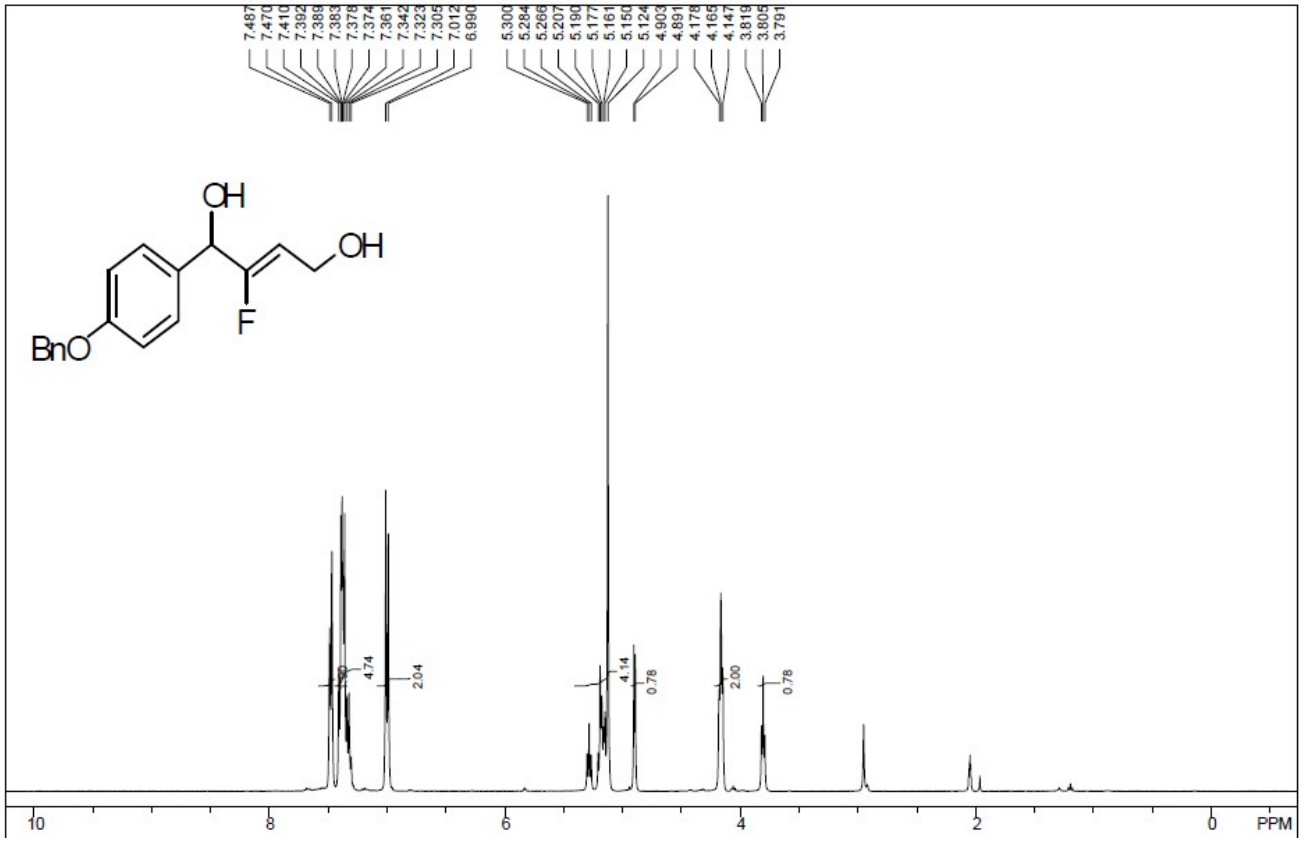
^{13}C NMR spectrum of compound **2g**



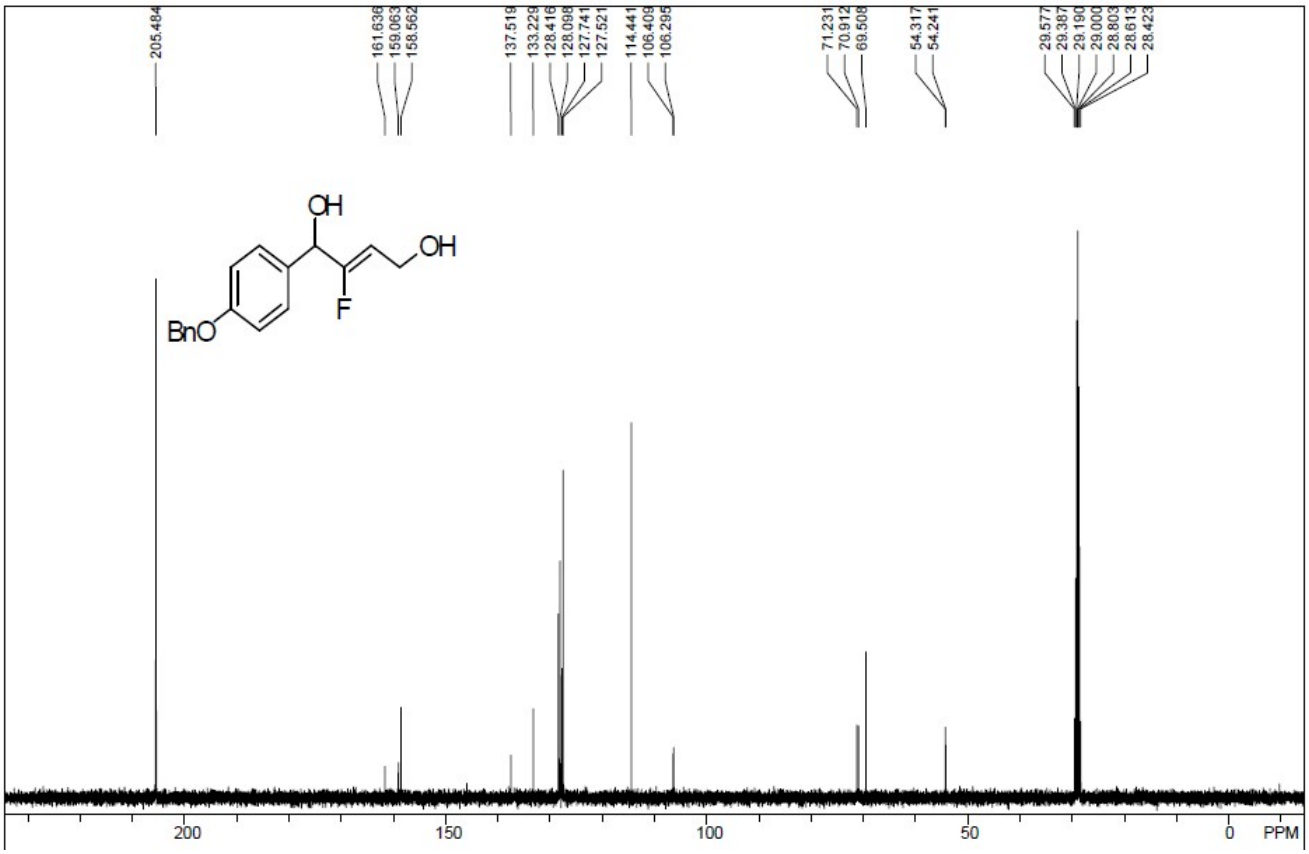
^{19}F NMR spectrum of compound **2g**



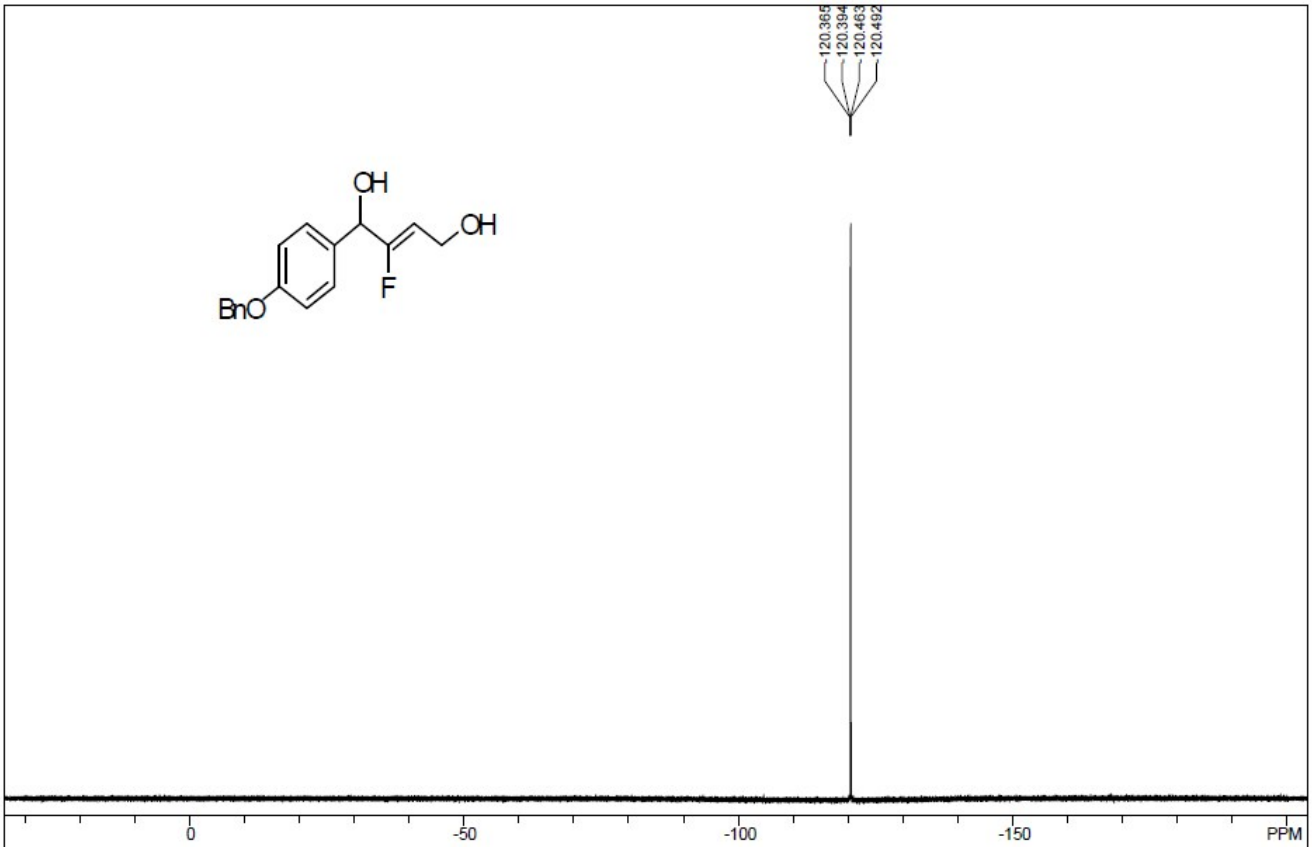
^{1}H NMR spectrum of compound **2h**



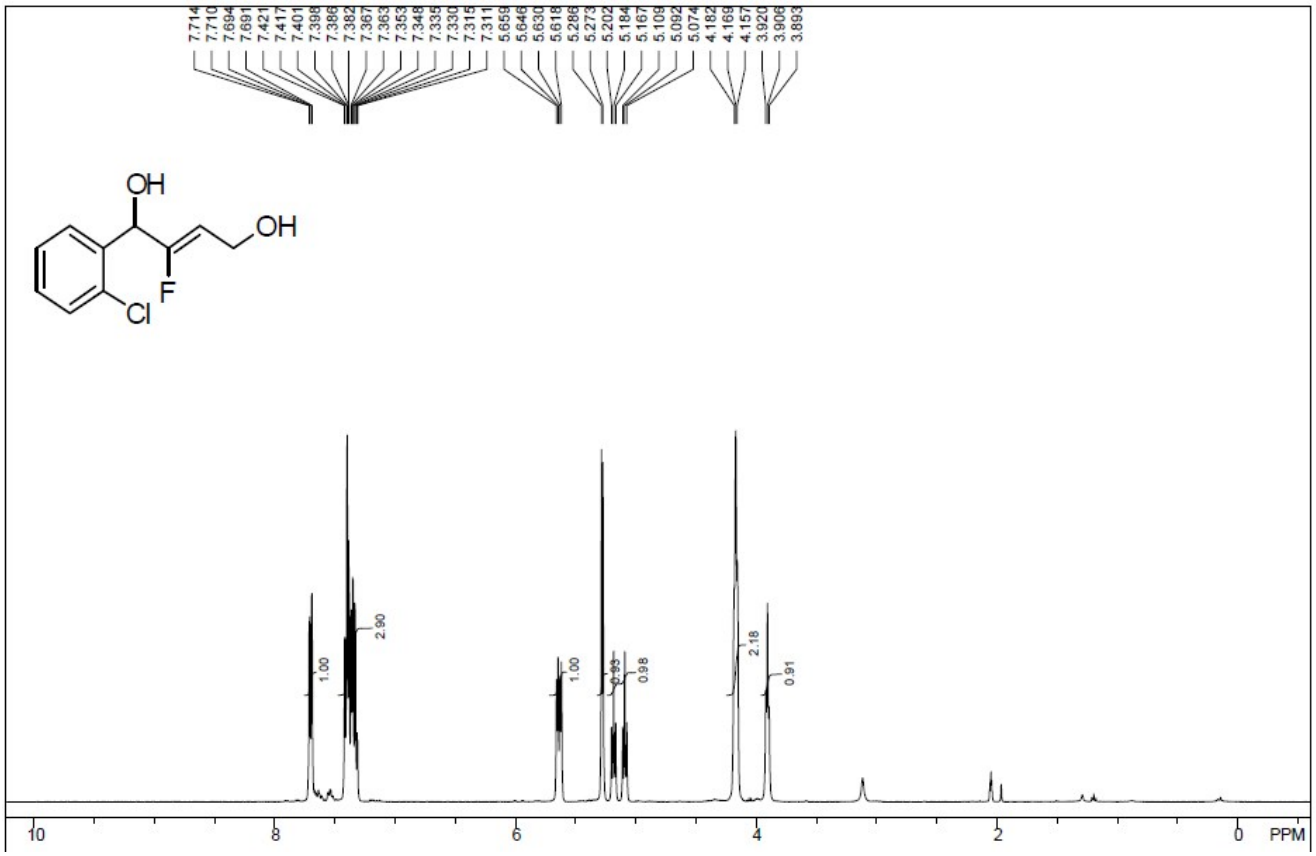
^{13}C NMR spectrum of compound **2h**



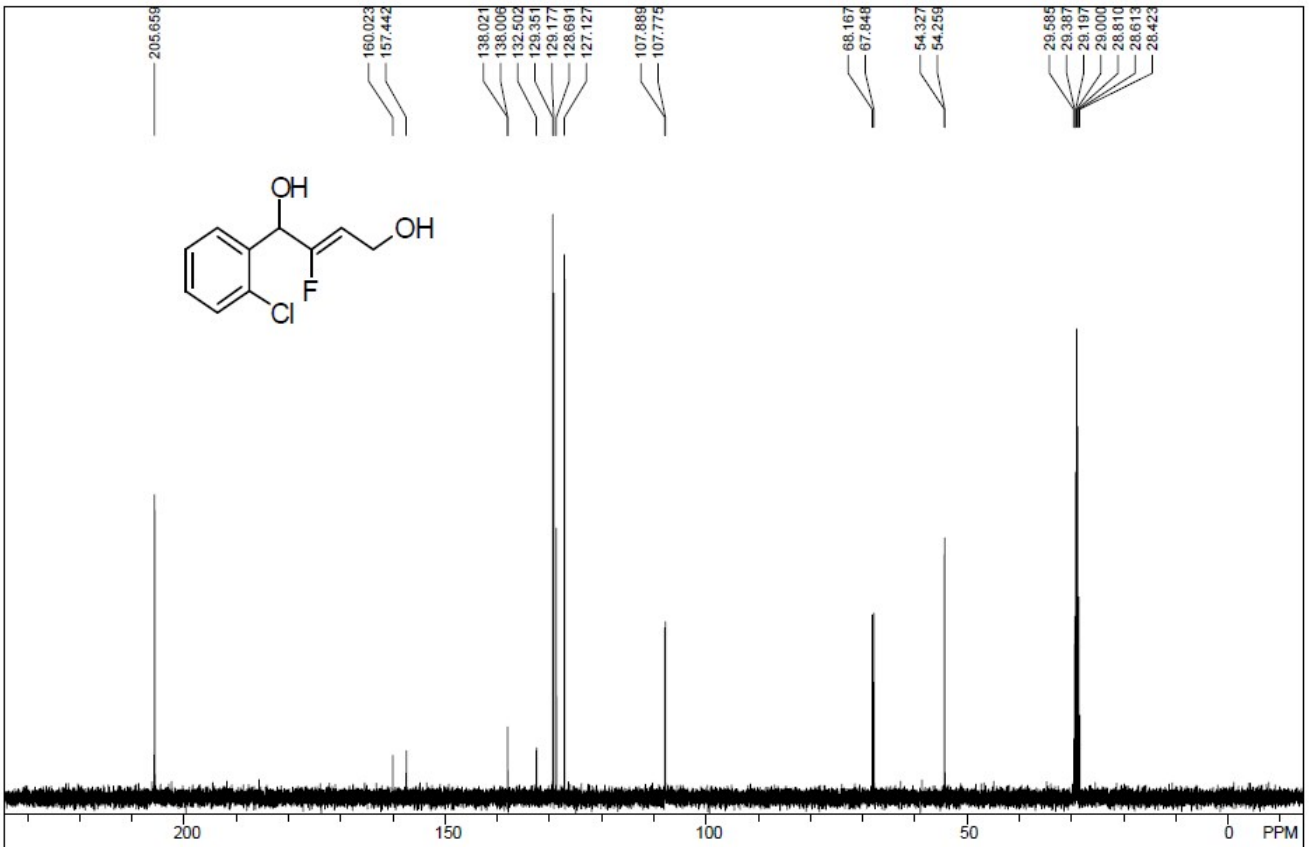
^{19}F NMR spectrum of compound **2h**



^{1}H NMR spectrum of compound **2j**

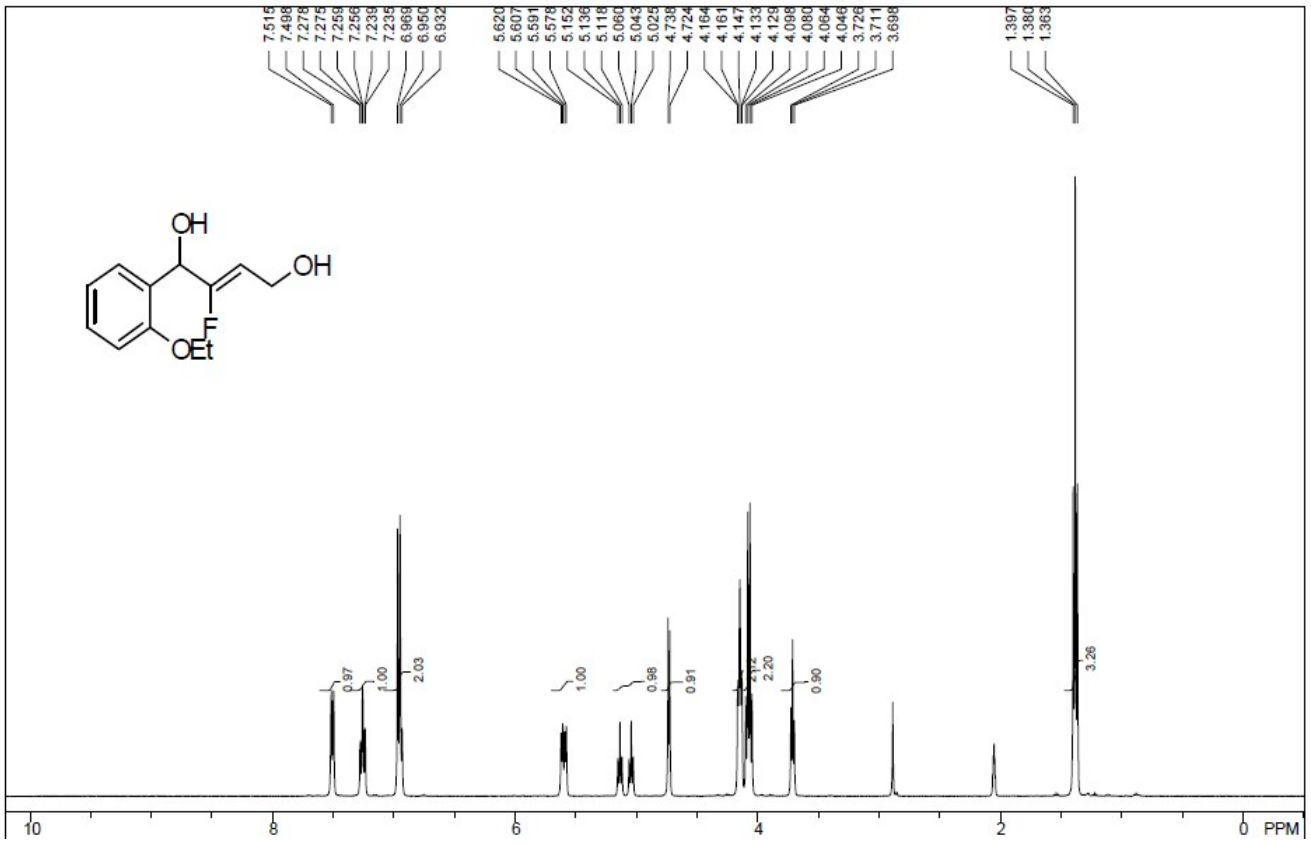


^{13}C NMR spectrum of compound **2j**

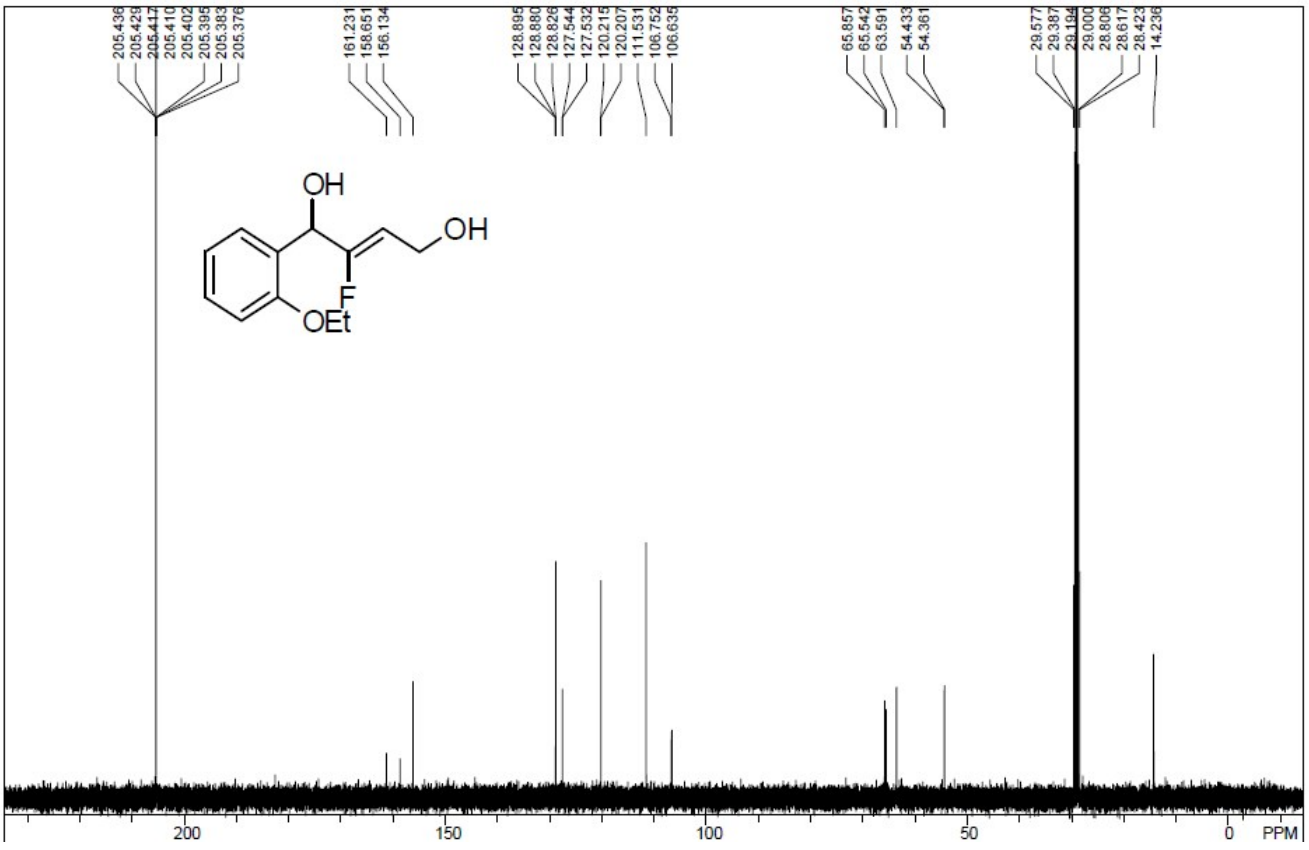


^{19}F NMR spectrum of compound **2j**

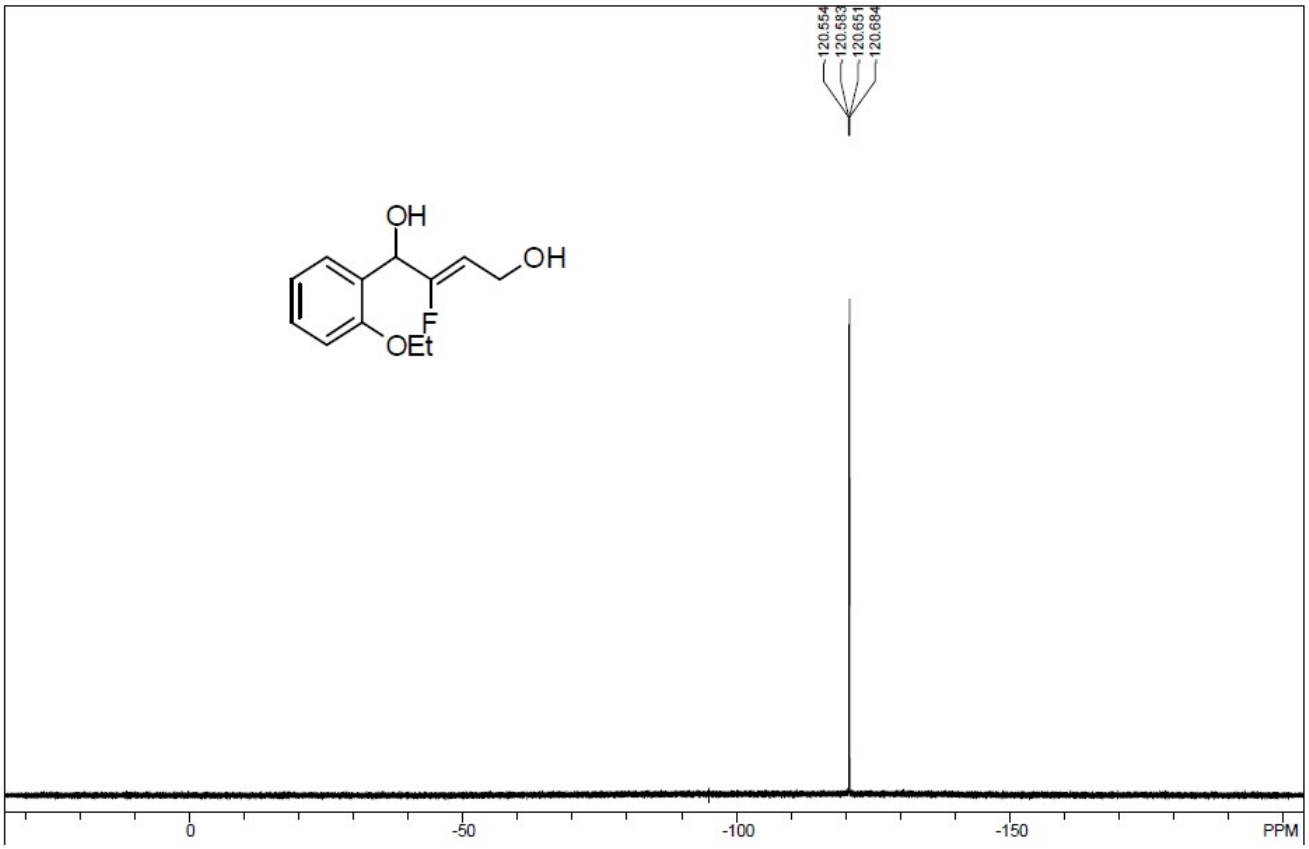
^{1}H NMR spectrum of compound **2k**



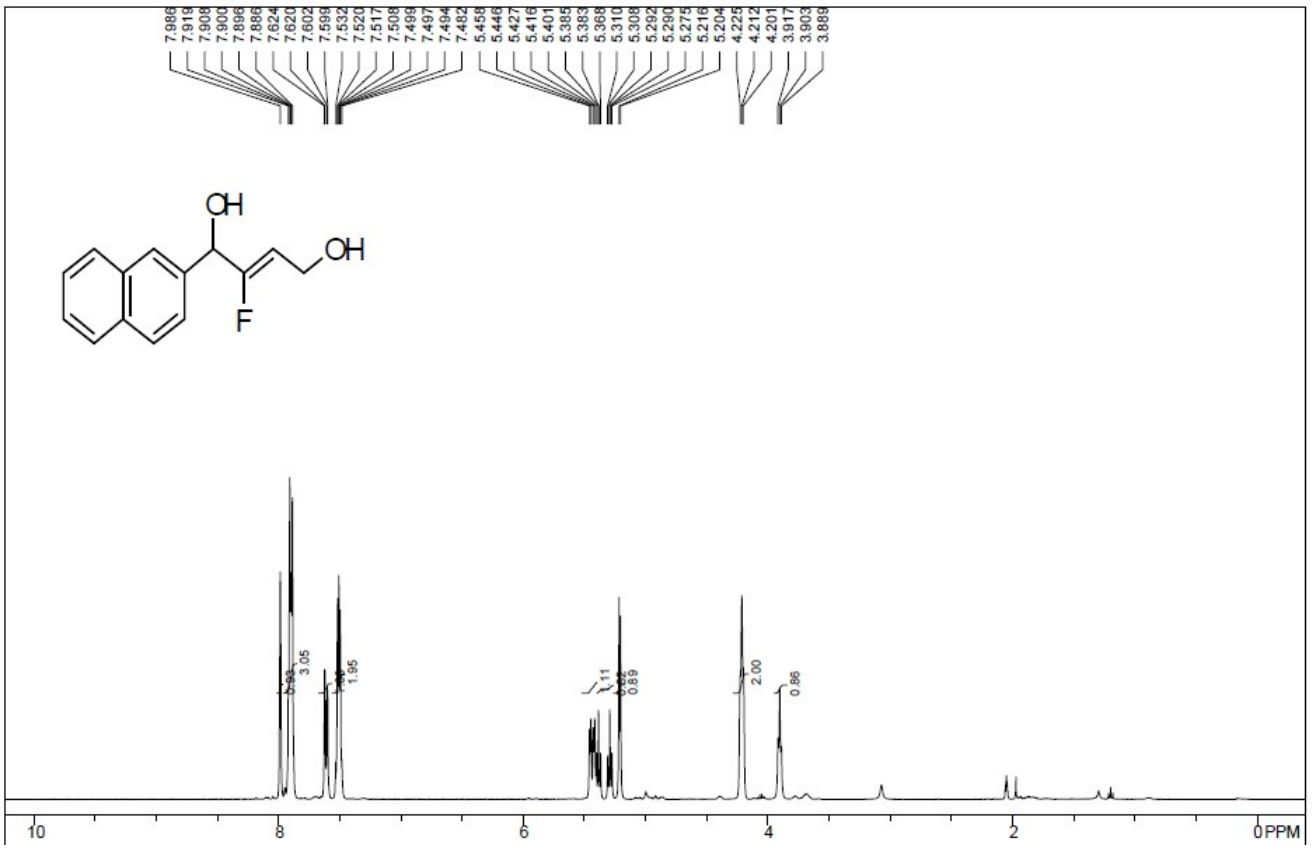
^{13}C NMR spectrum of compound **2k**



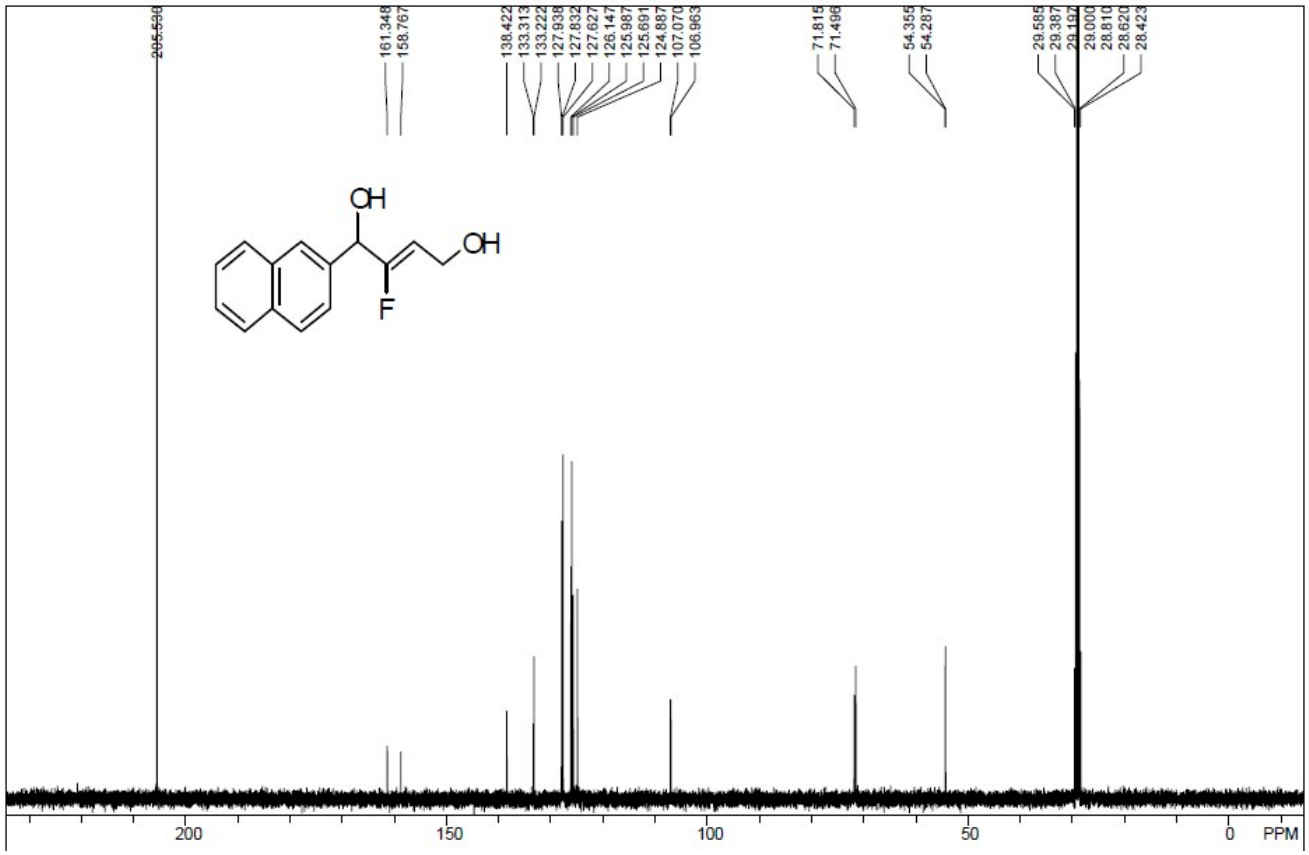
^{19}F NMR spectrum of compound **2k**



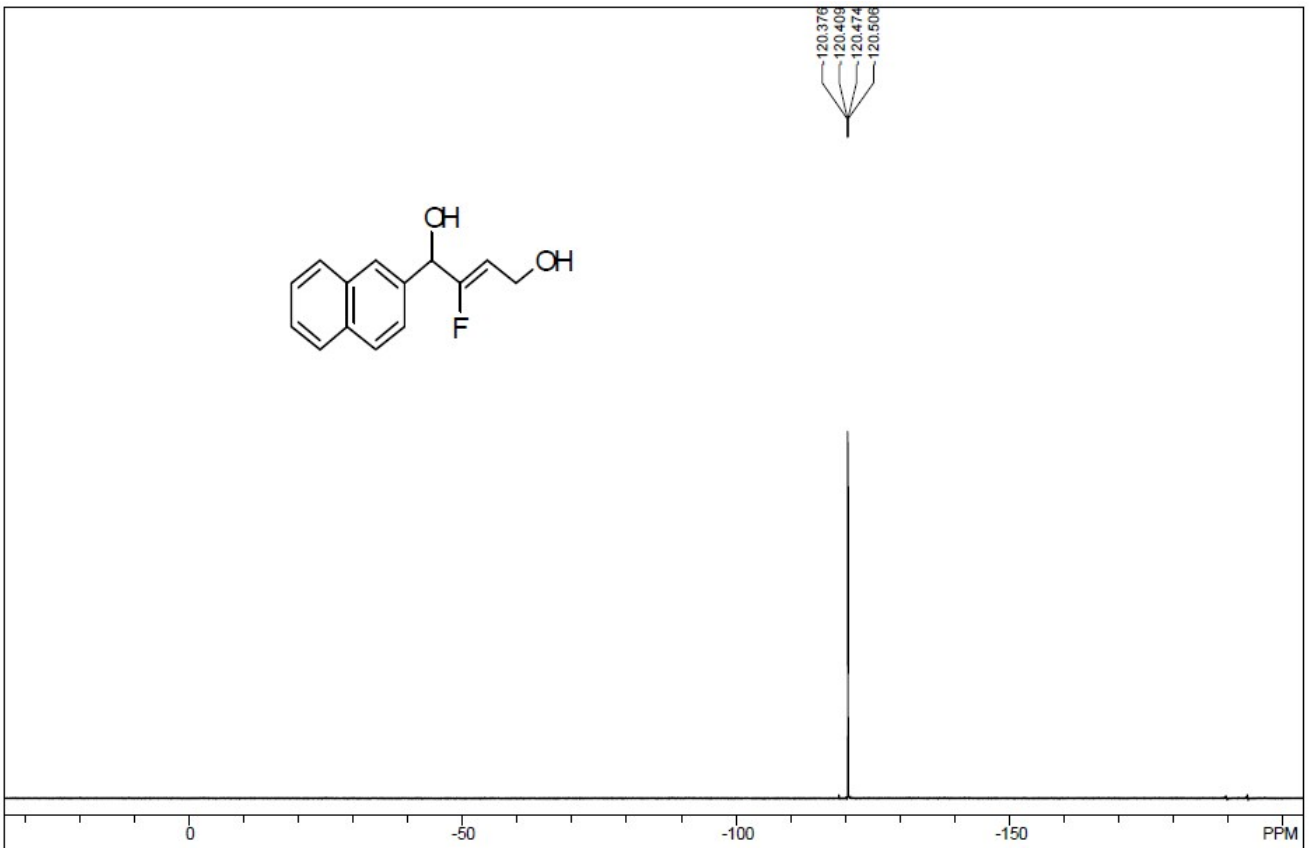
^{1}H NMR spectrum of compound **2l**



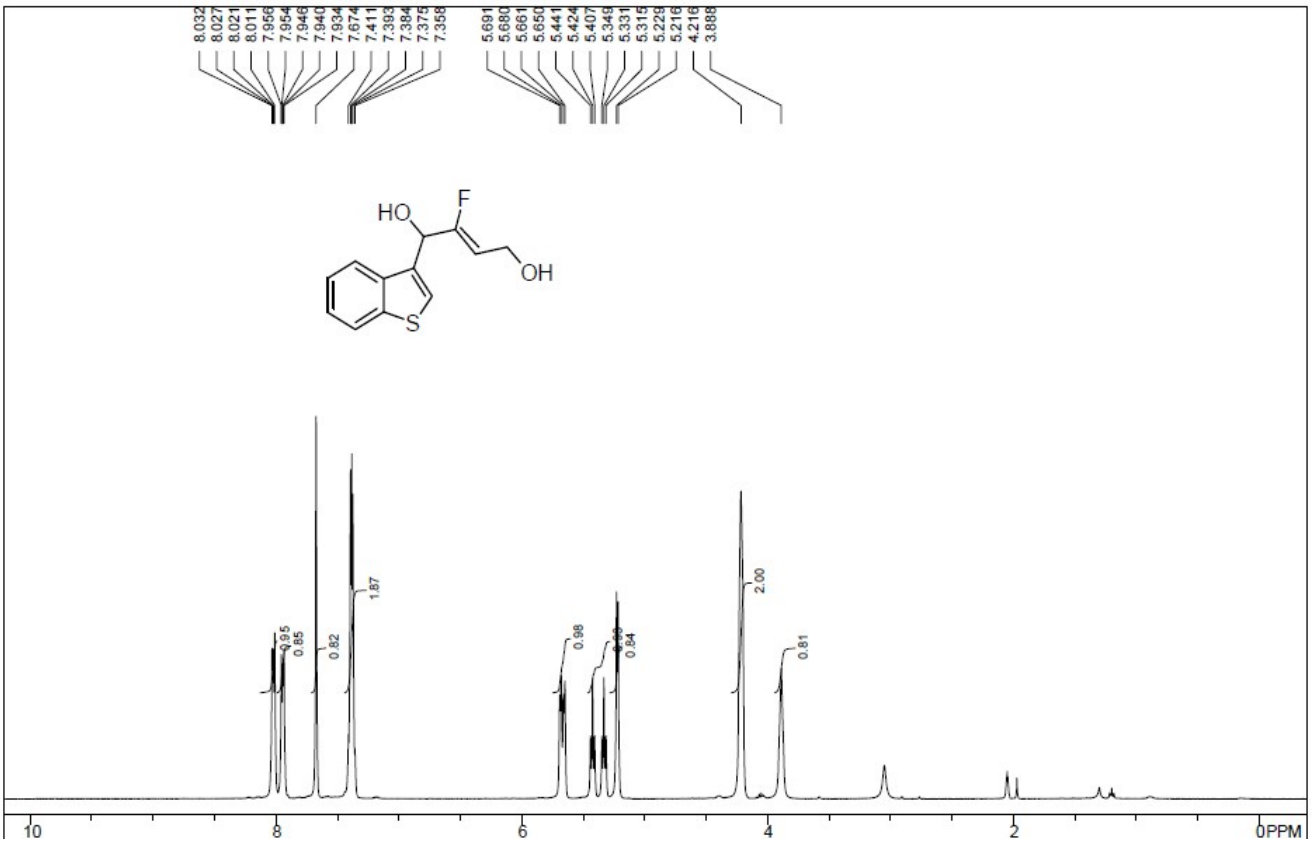
^{13}C NMR spectrum of compound **2l**



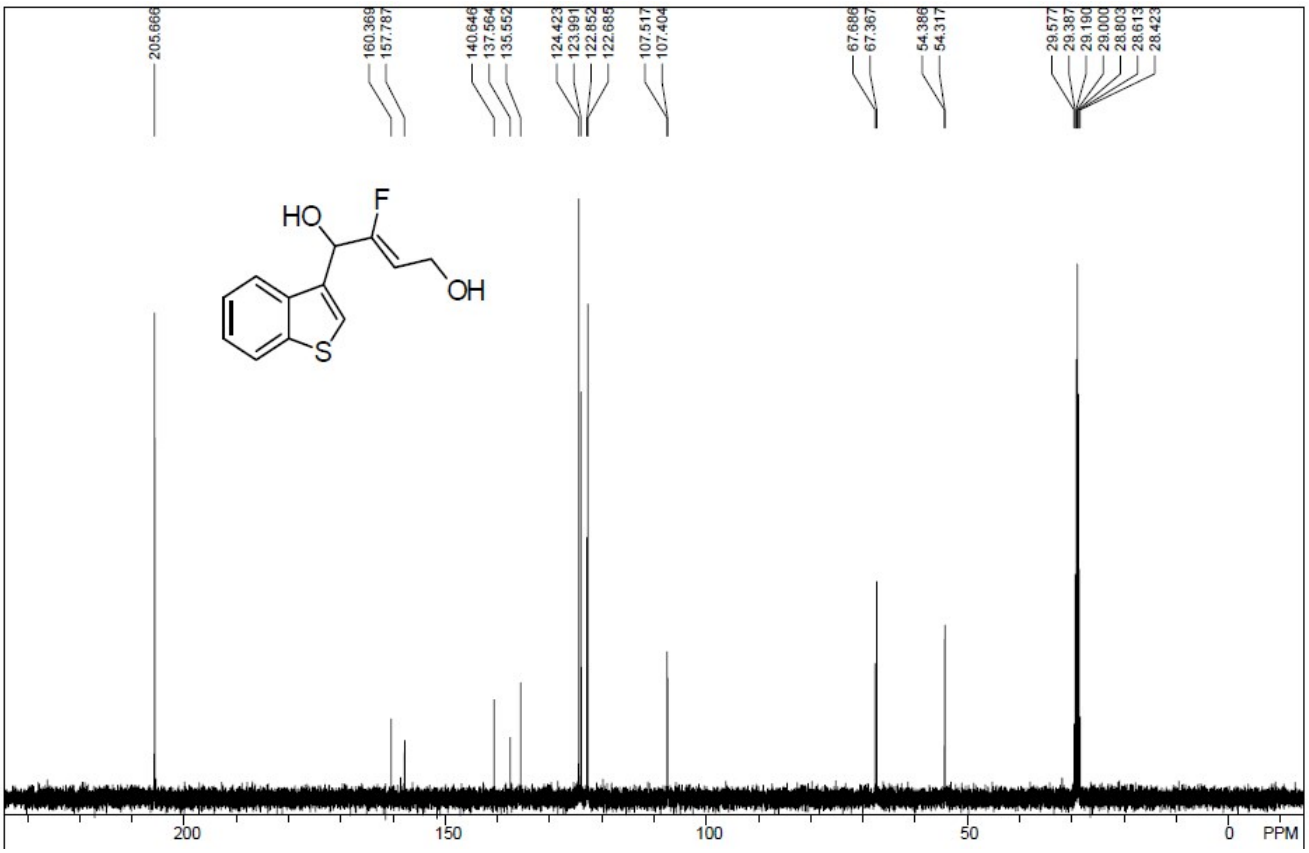
^{19}F NMR spectrum of compound **2l**



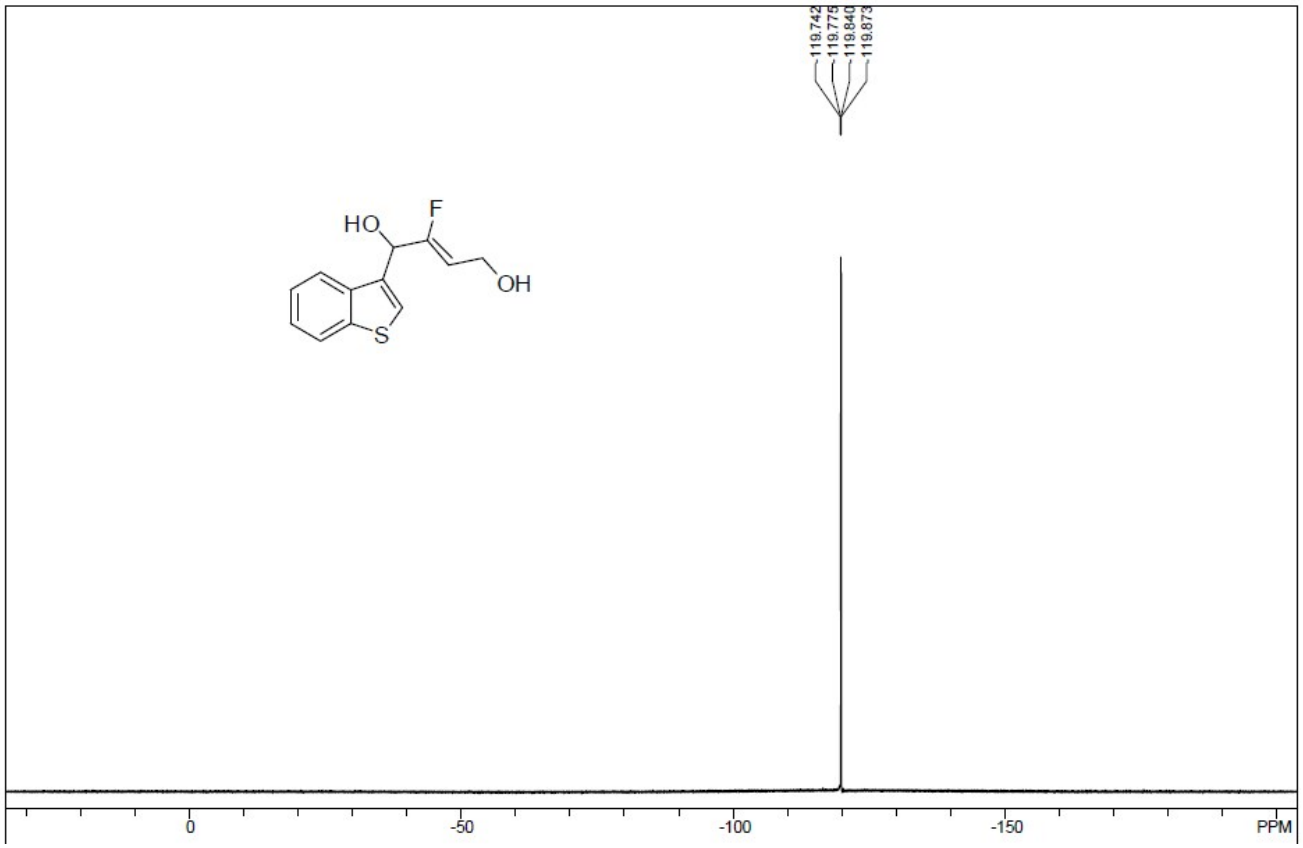
^{1}H NMR spectrum of compound **2m**



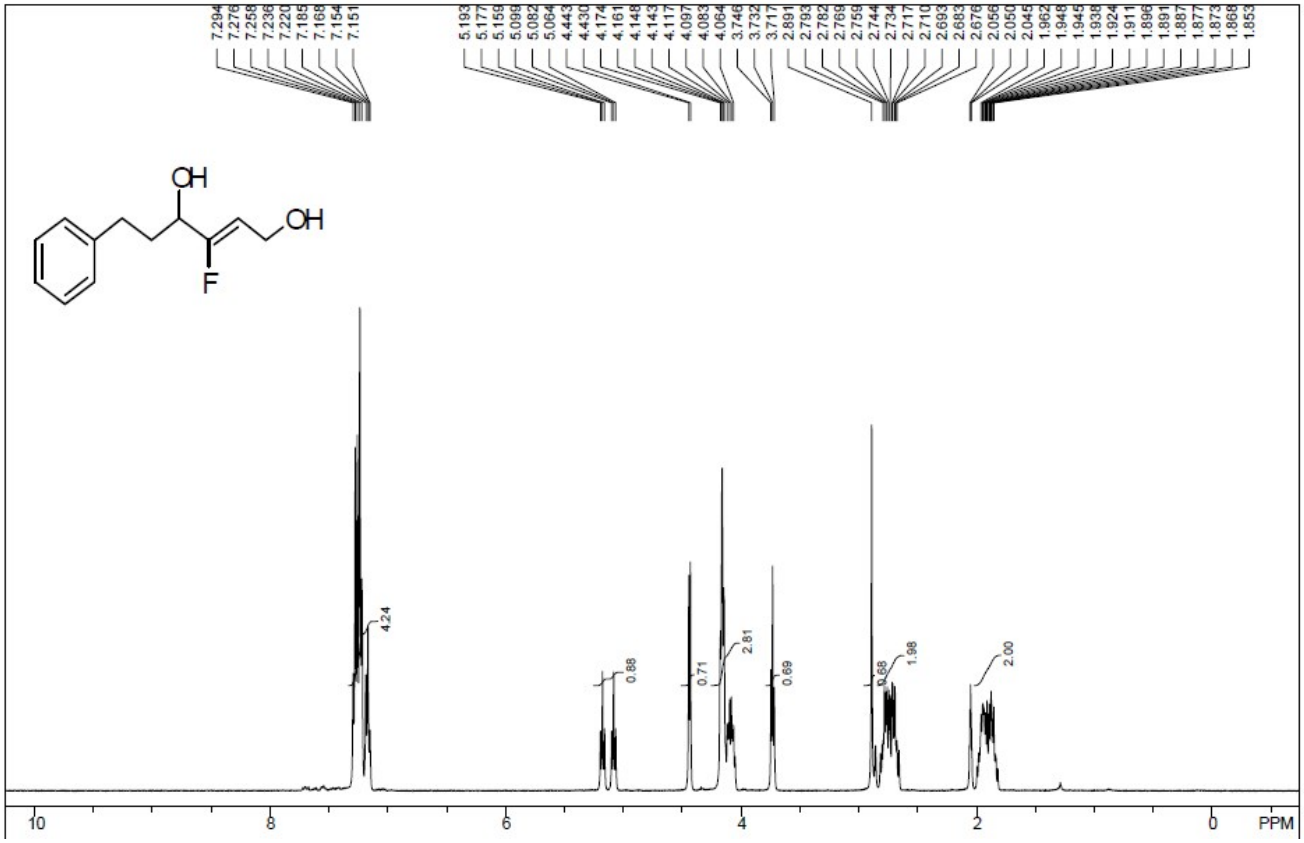
^{13}C NMR spectrum of compound **2m**



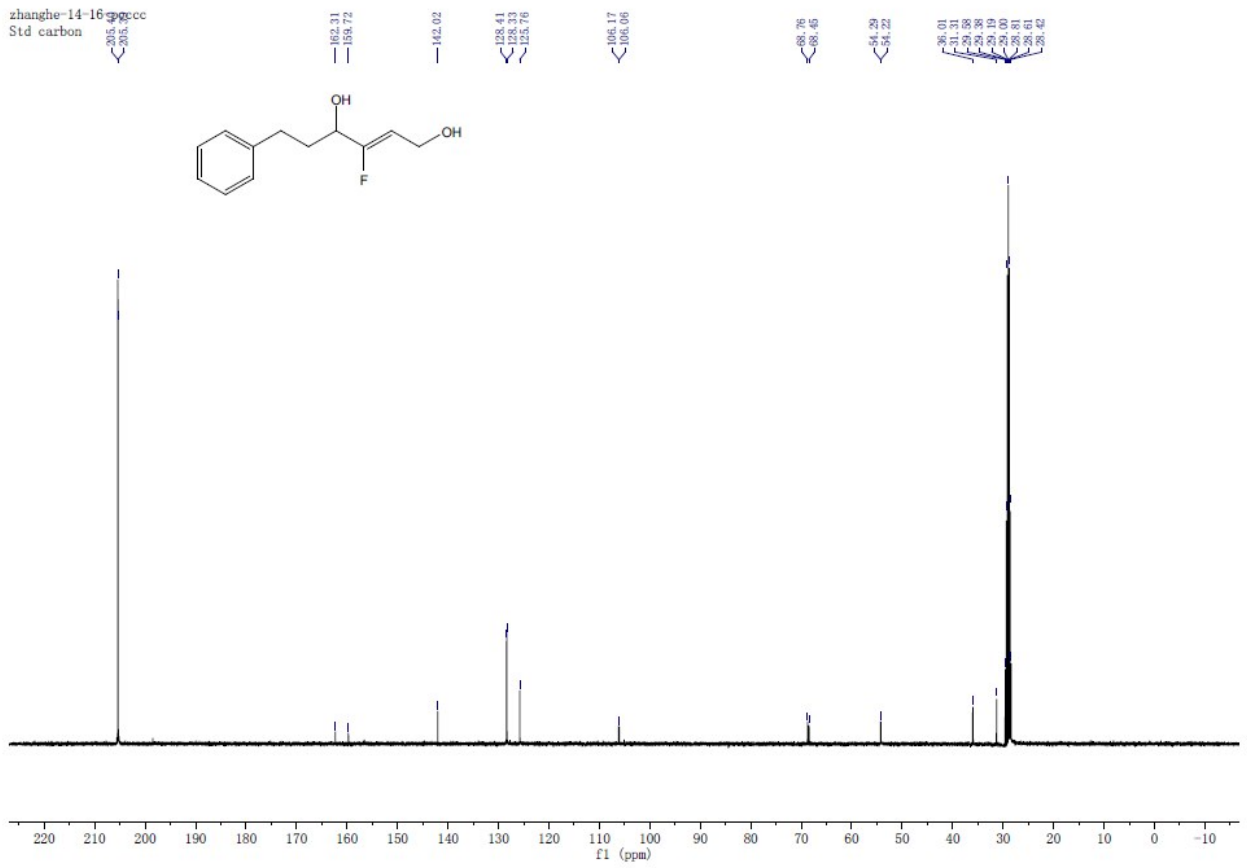
^{19}F NMR spectrum of compound **2m**



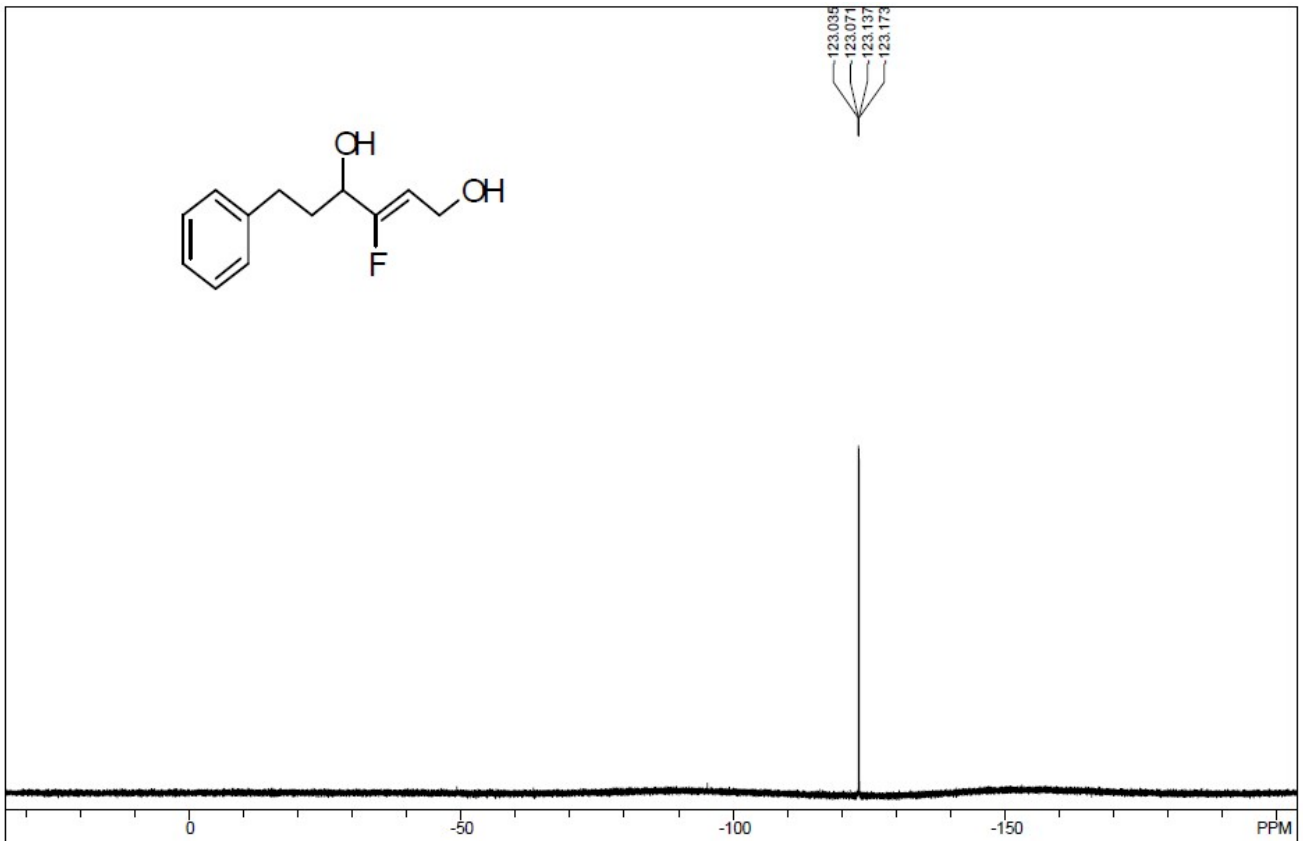
^{1}H NMR spectrum of compound **2n**



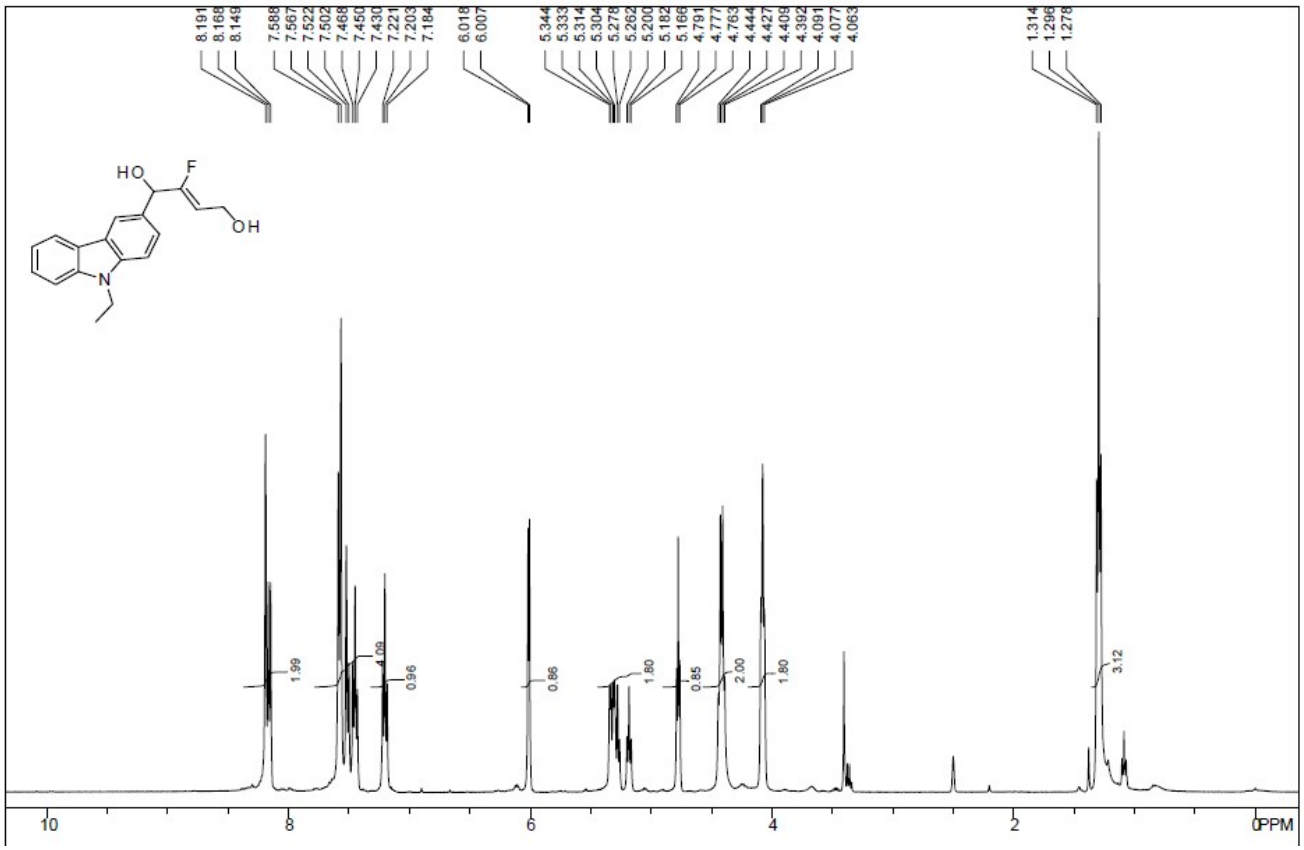
^{13}C NMR spectrum of compound **2n**



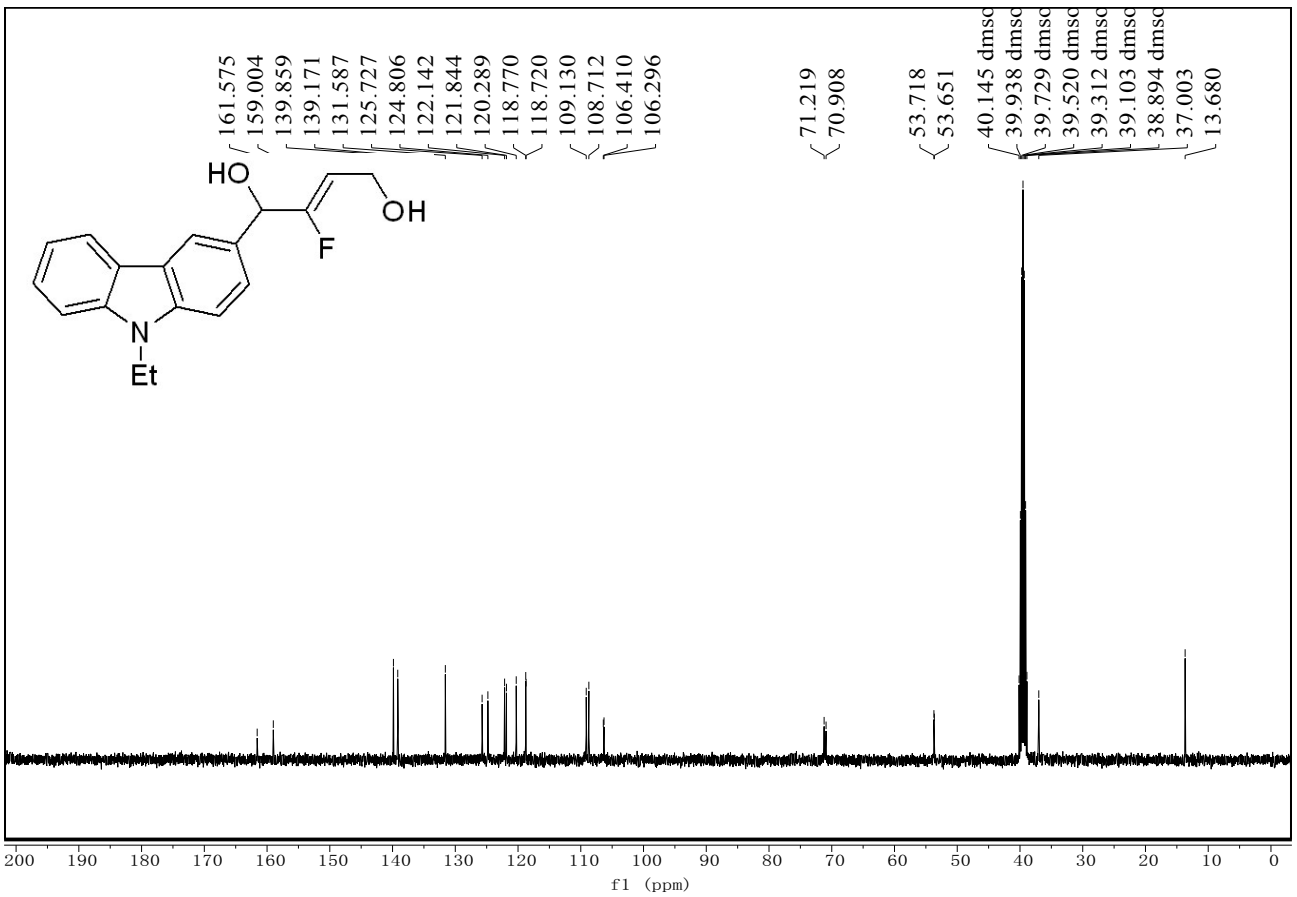
^{19}F NMR spectrum of compound **2n**



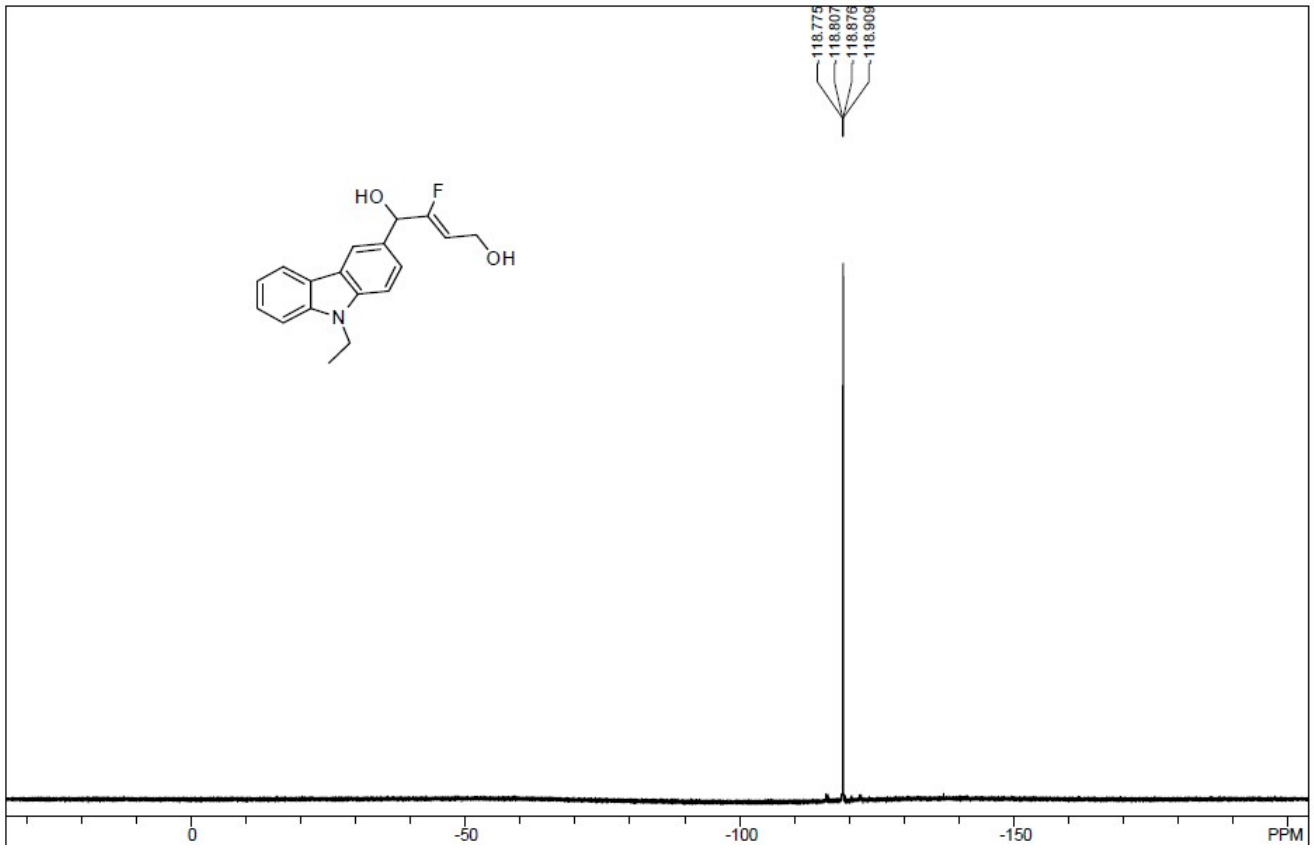
^{1}H NMR spectrum of compound **2o**



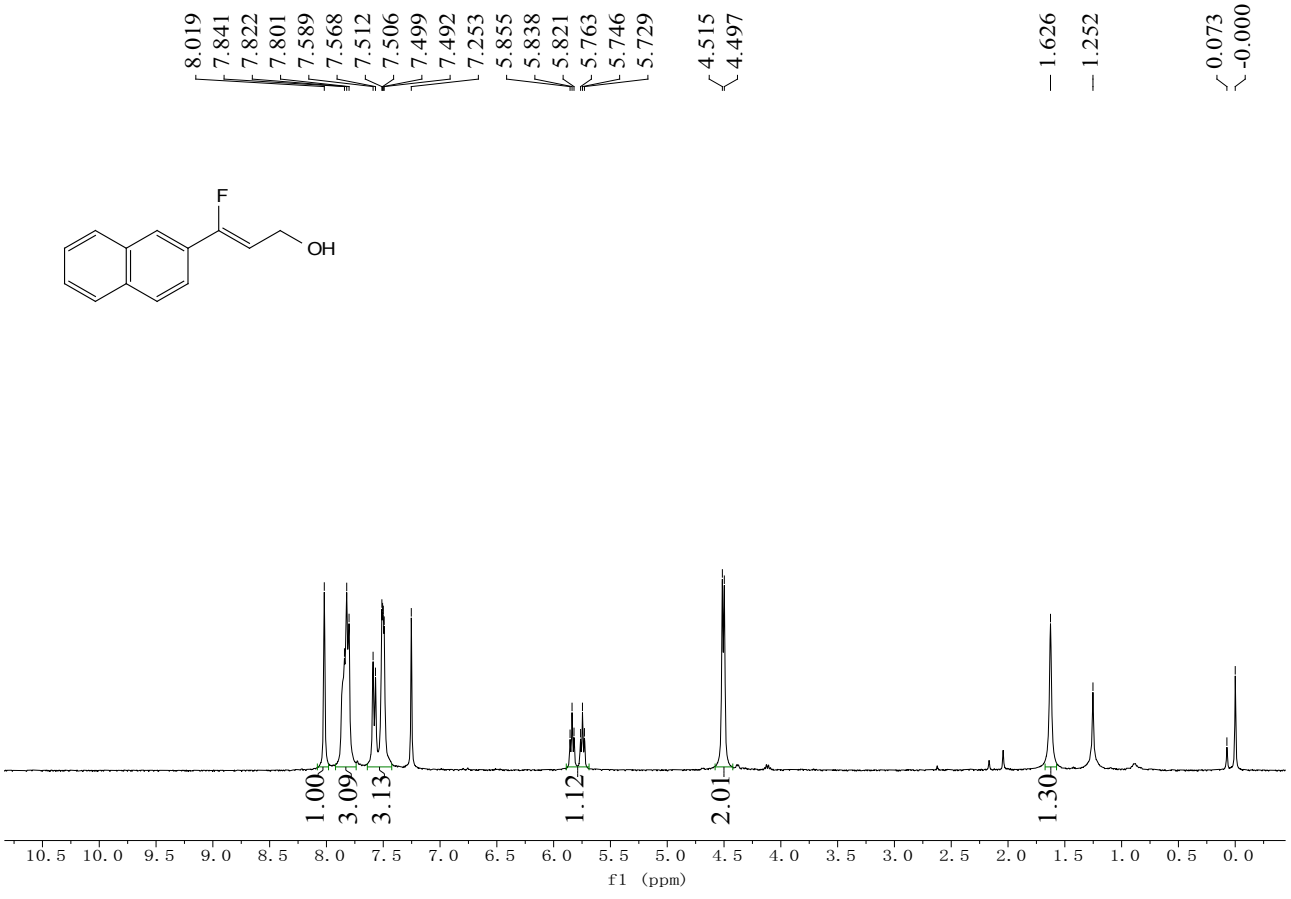
^{13}C NMR spectrum of compound **2o**



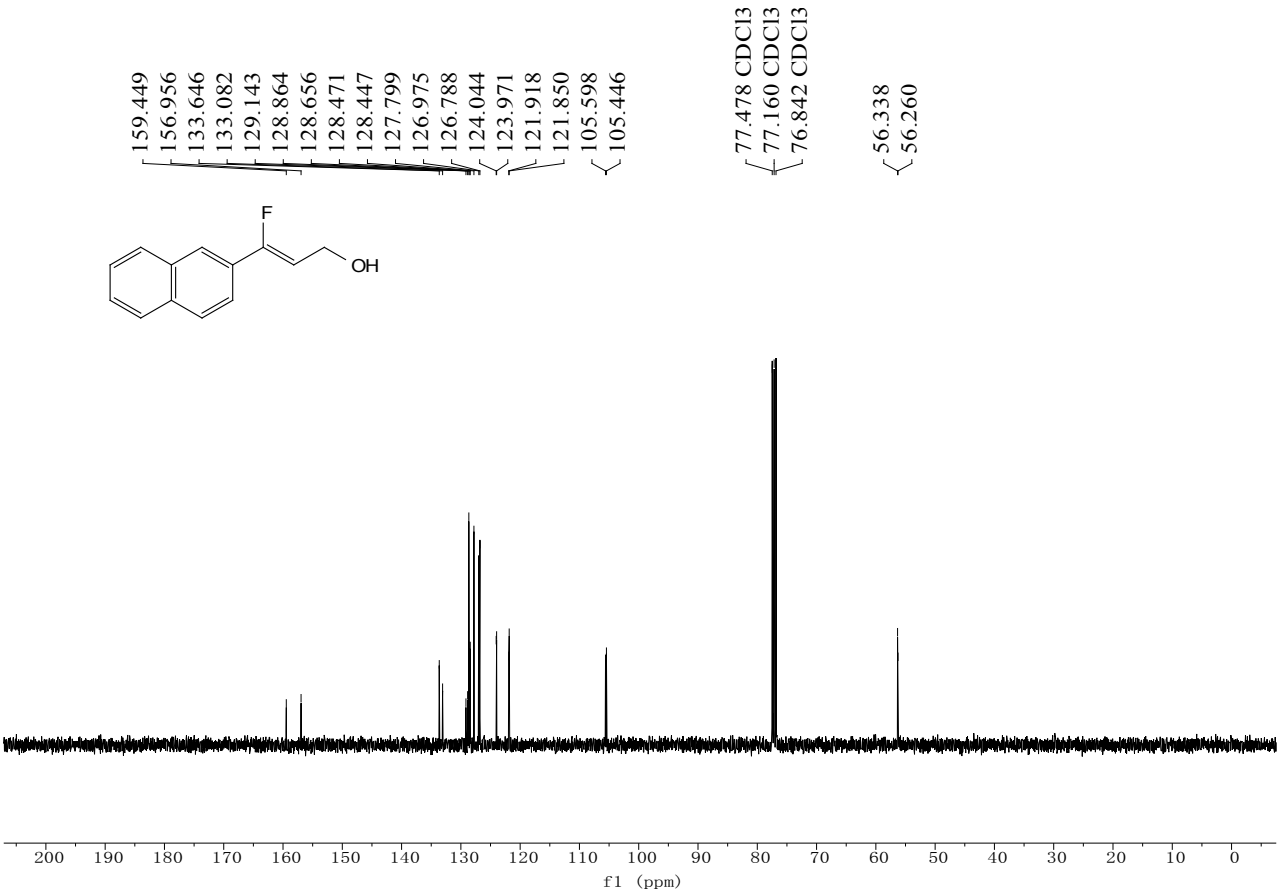
^{19}F NMR spectrum of compound **2o**



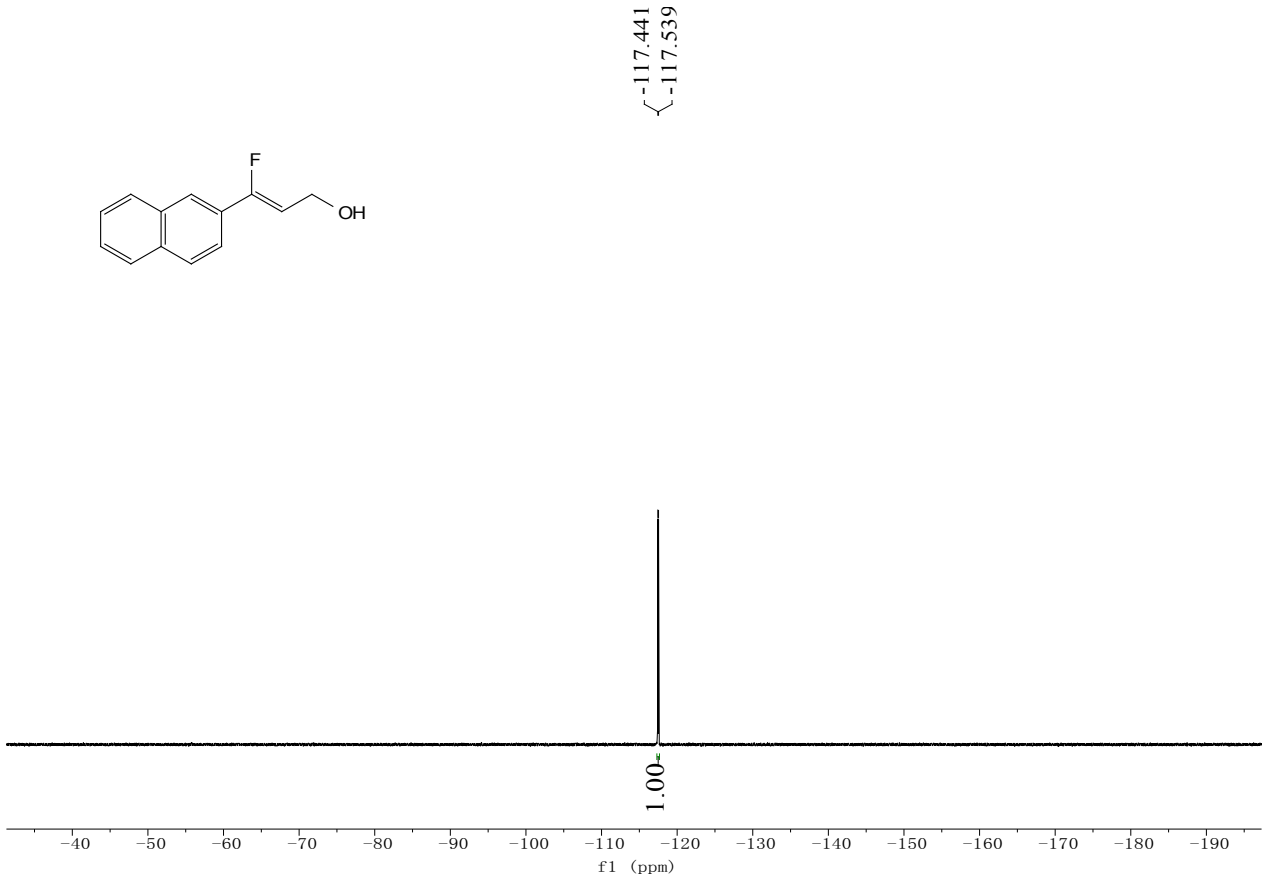
^{1}H NMR spectrum of compound **2p**



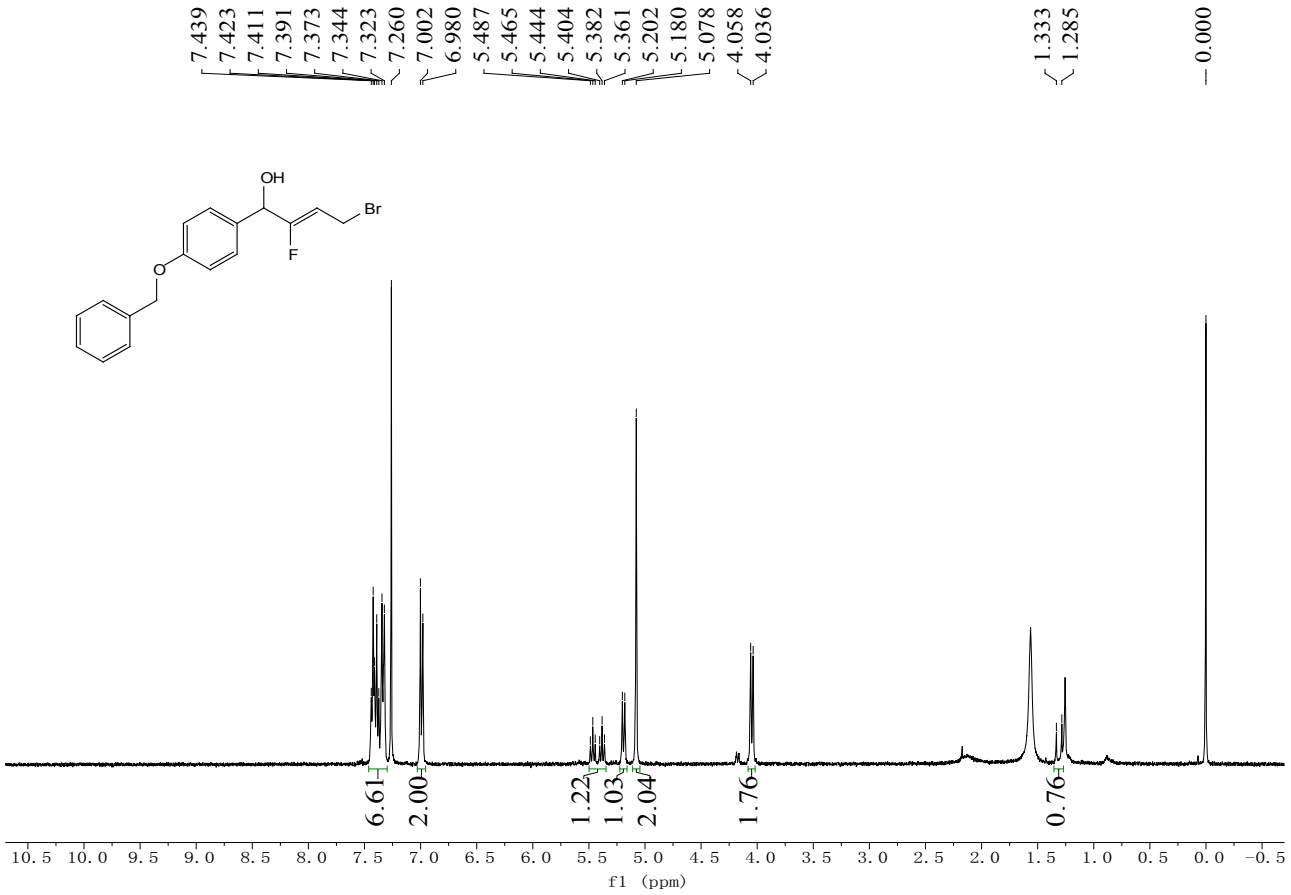
^{13}C NMR spectrum of compound **2p**



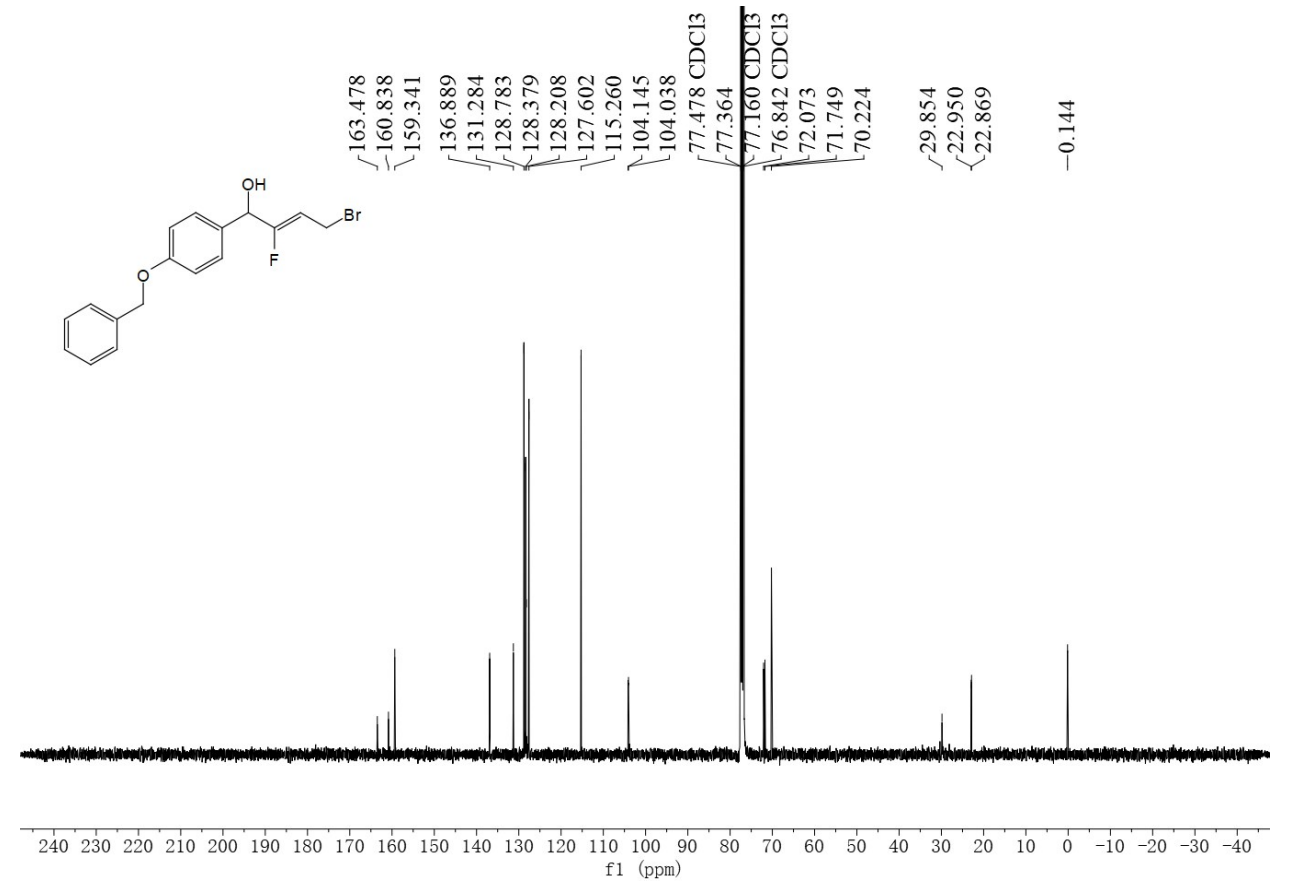
^{19}F NMR spectrum of compound **2p**



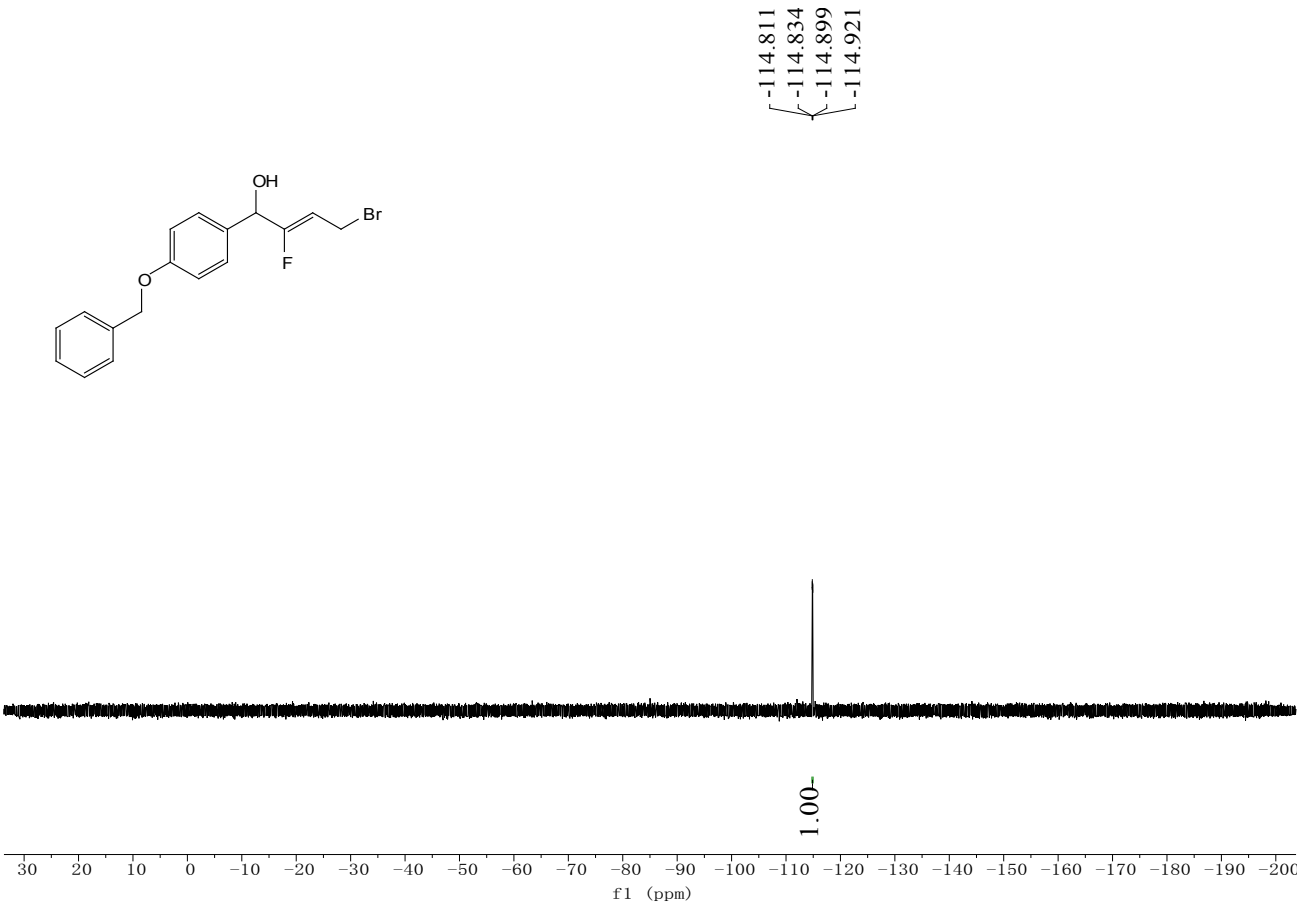
^{1}H NMR spectrum of compound **2h'''**



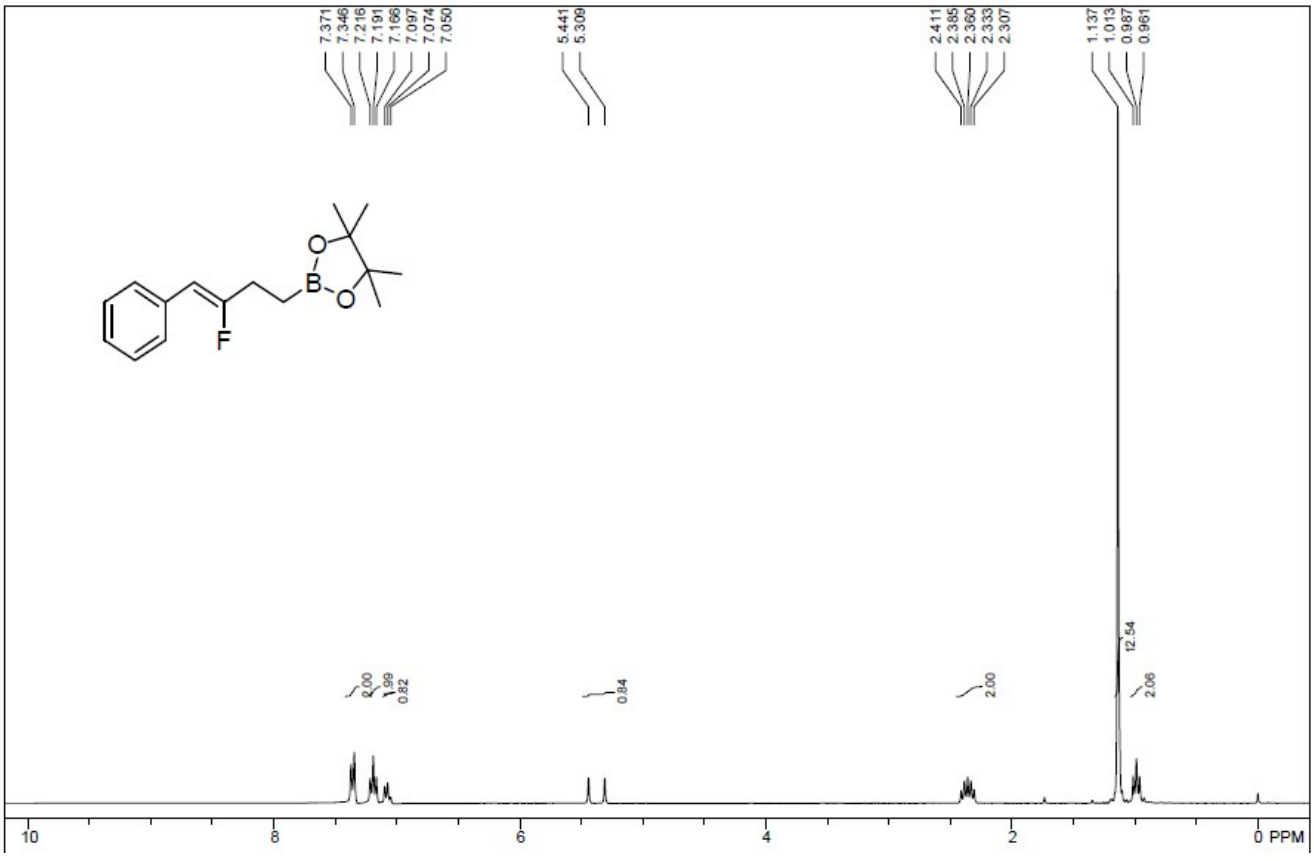
^{13}C NMR spectrum of compound **2h'''**



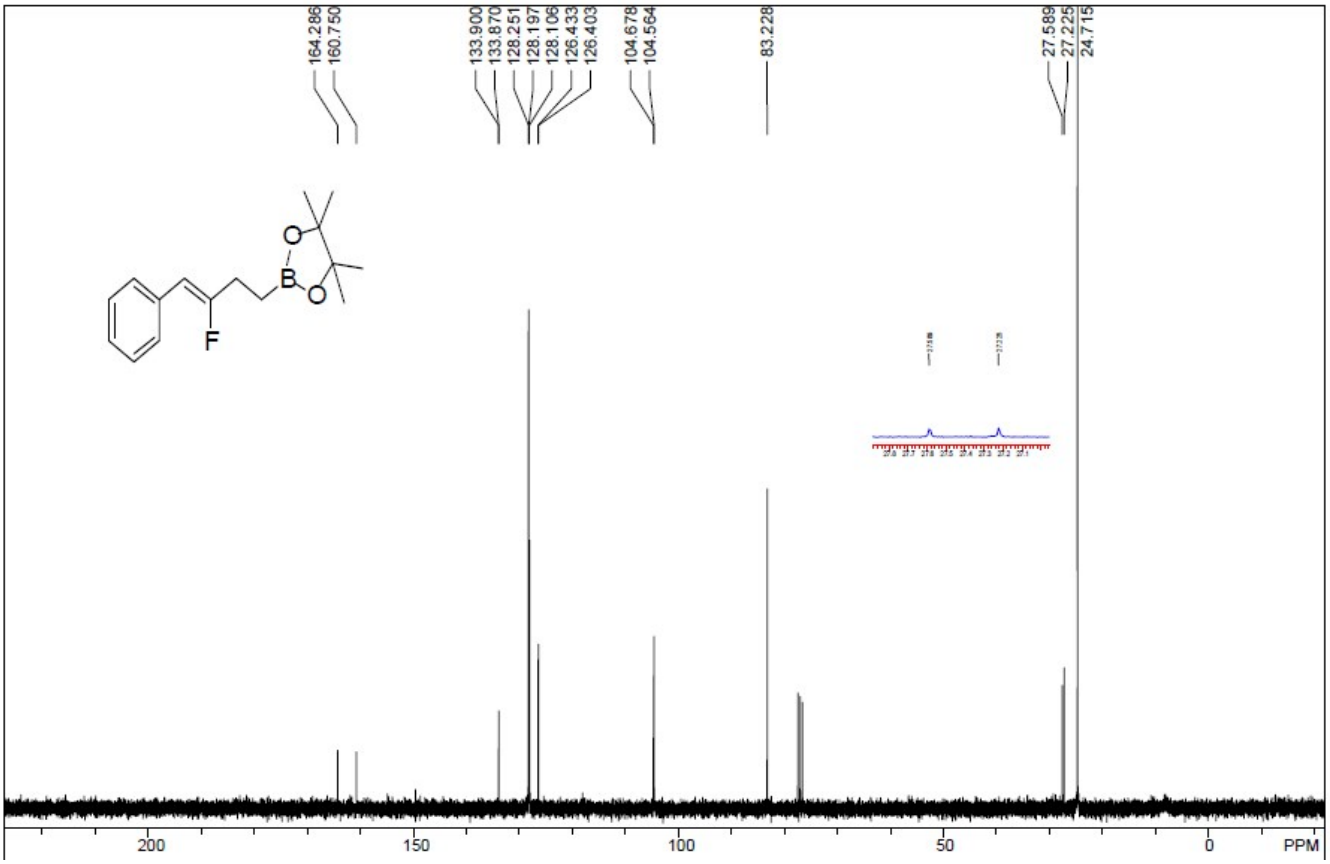
^{19}F NMR spectrum of compound **2h'''**



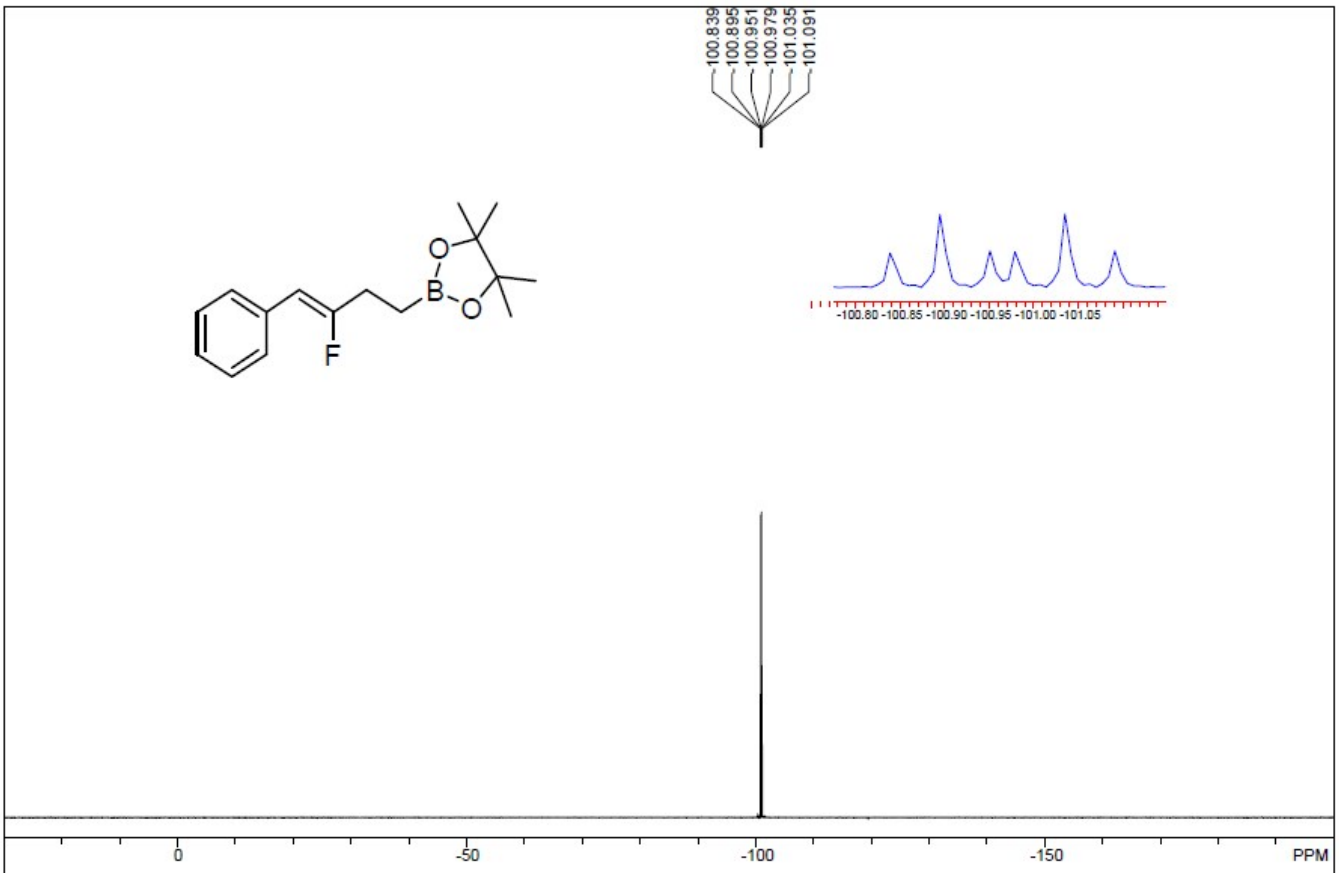
^{1}H NMR spectrum of compound **3a**



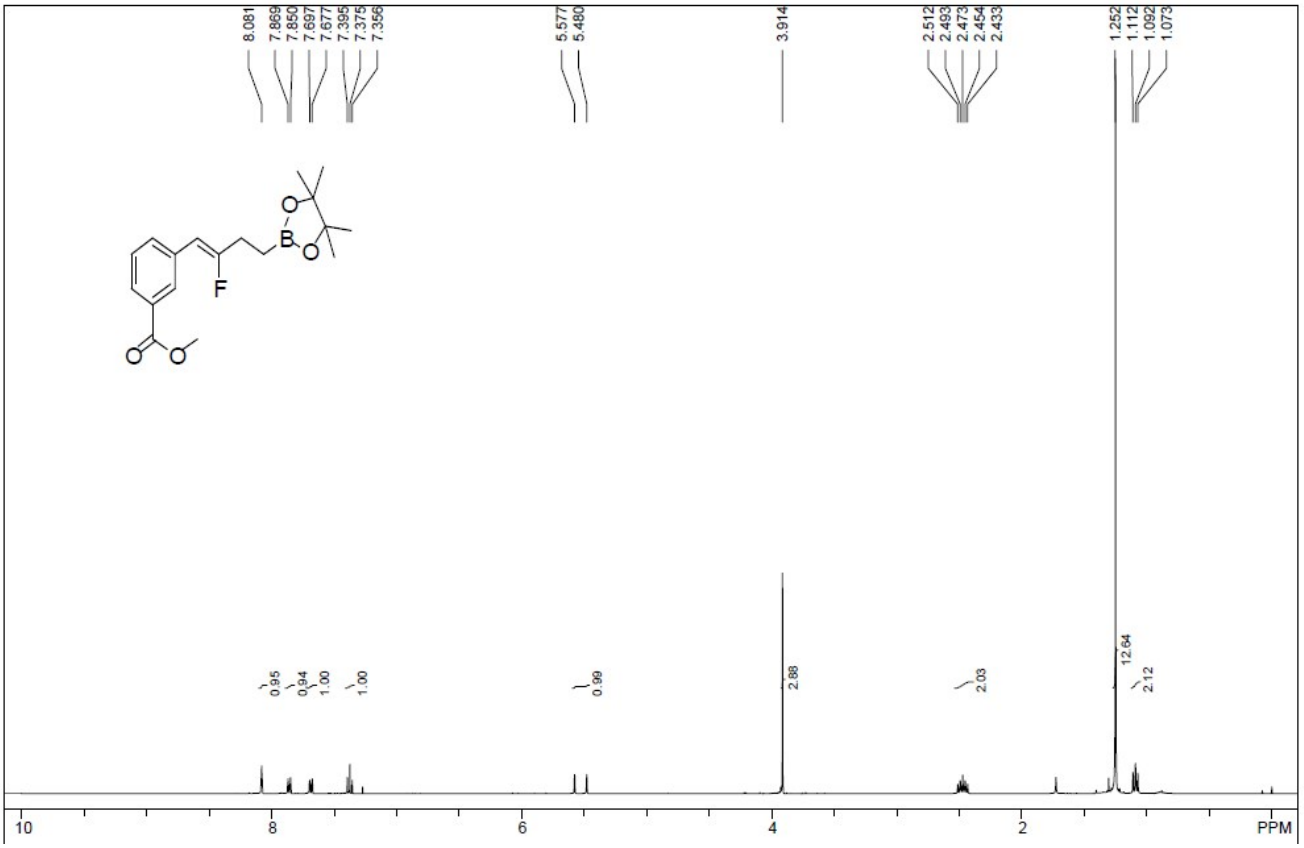
^{13}C NMR spectrum of compound **3a**



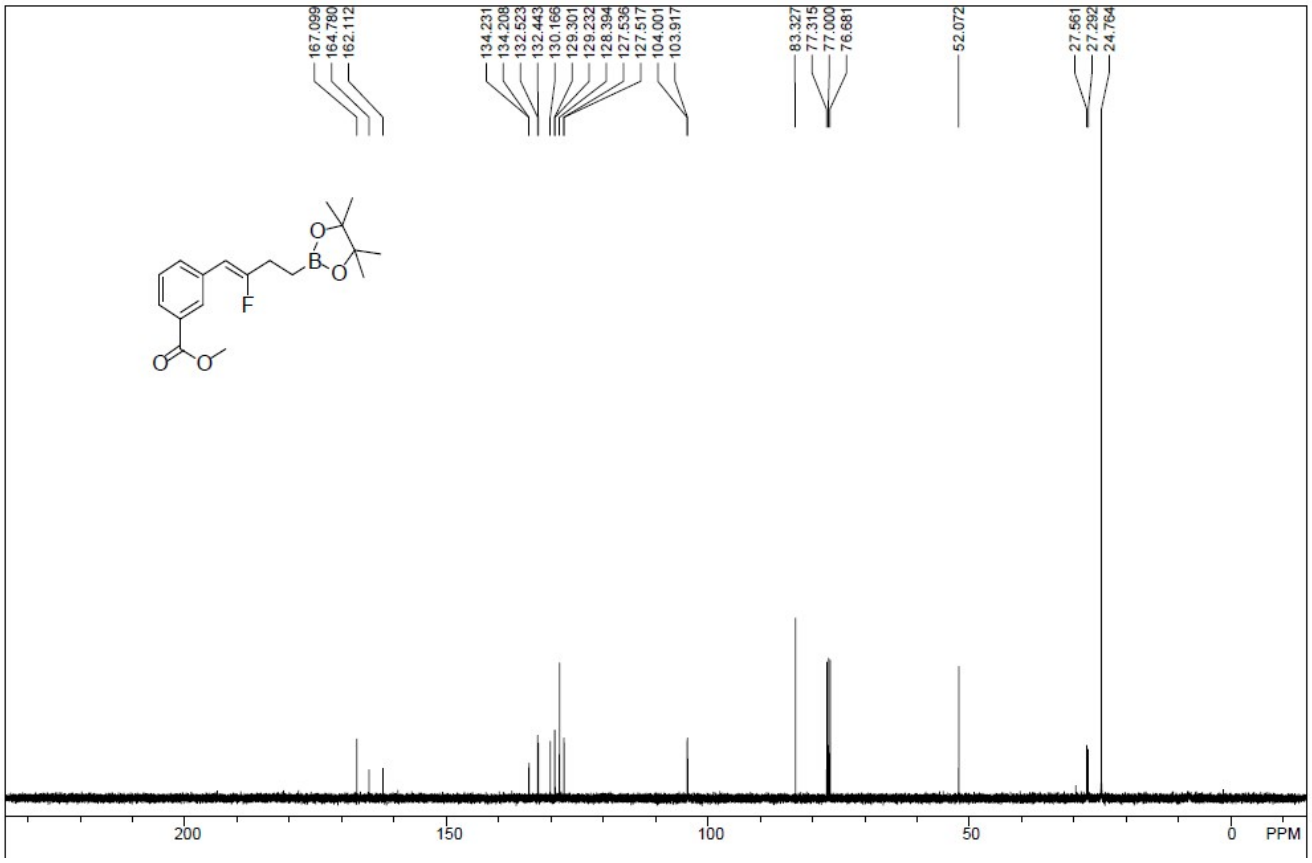
^{19}F NMR spectrum of compound **3a**



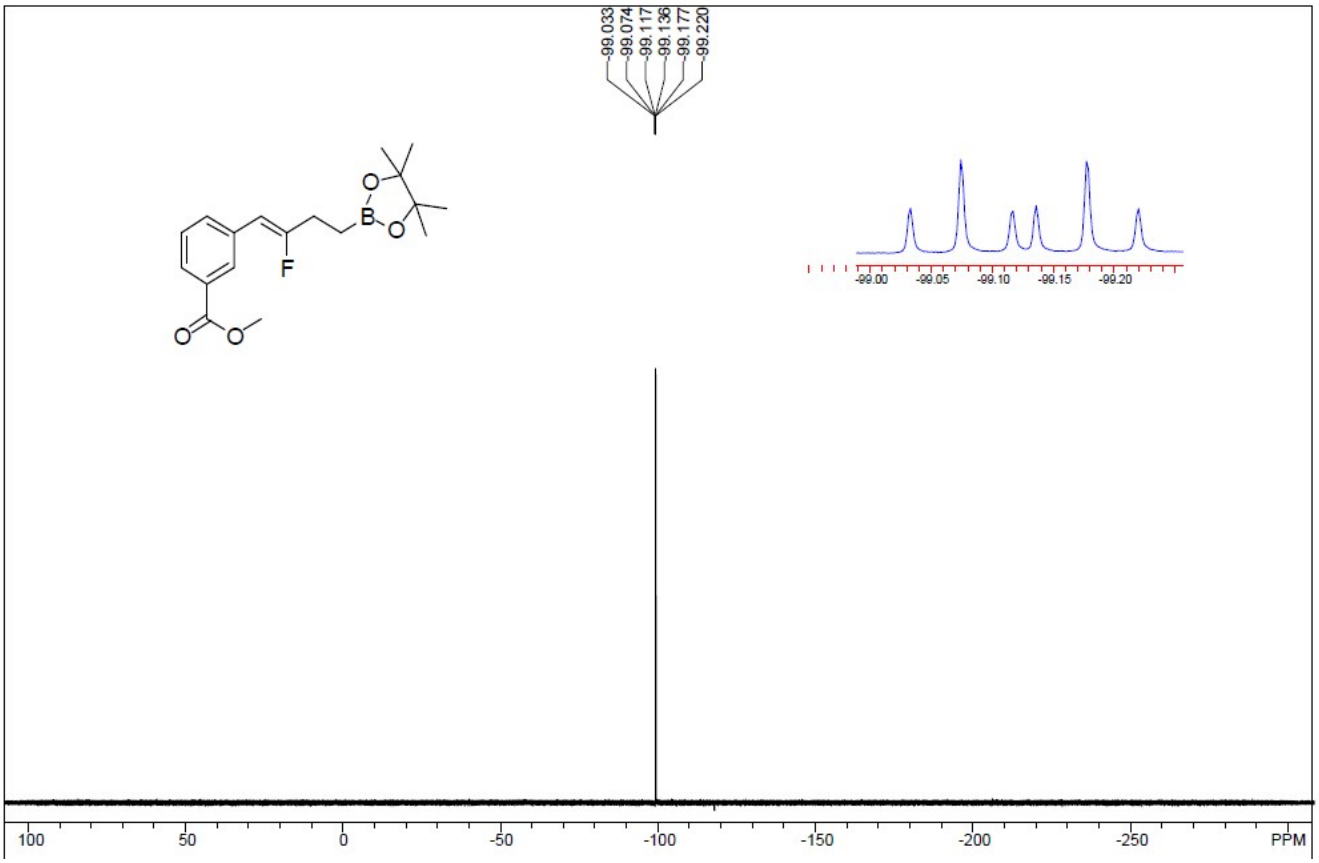
^{1}H NMR spectrum of compound **3b**



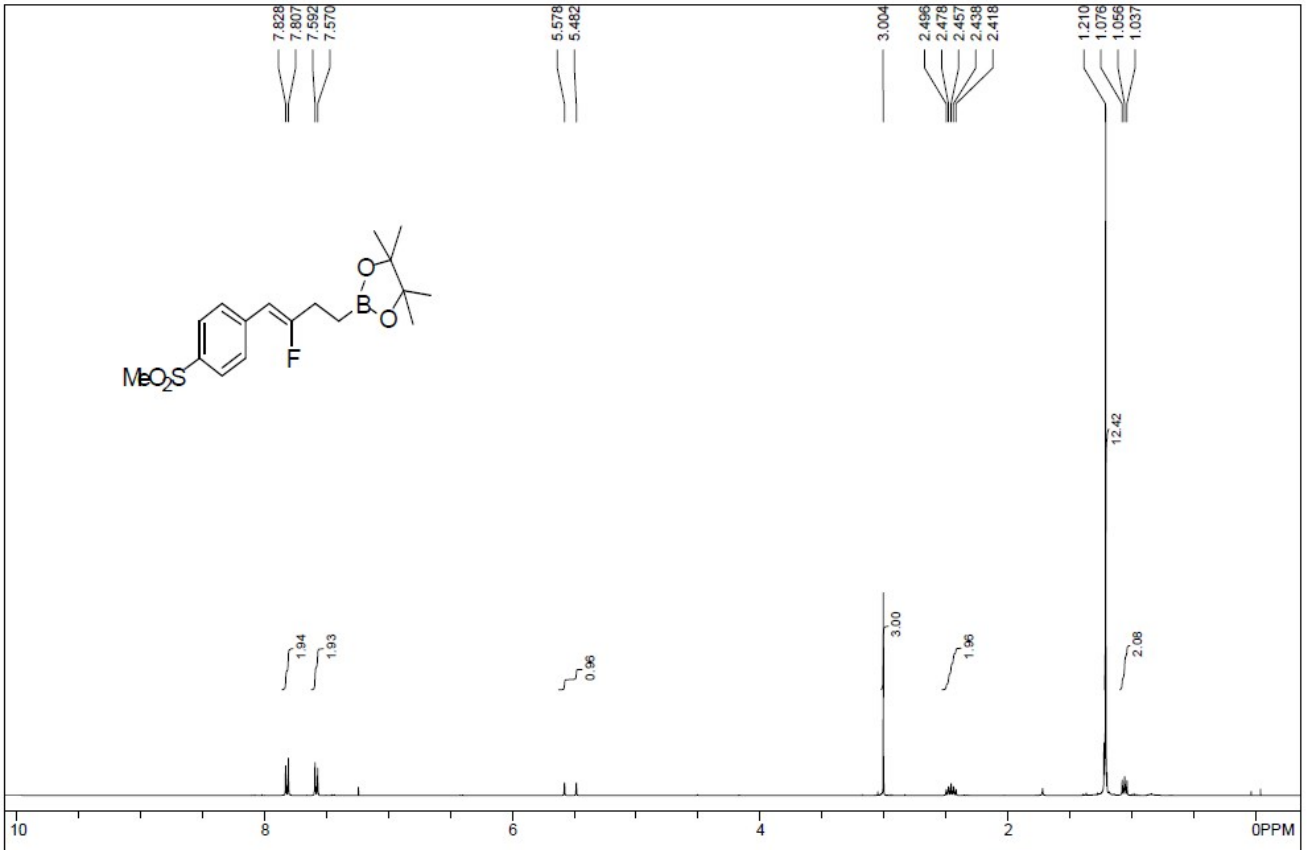
^{13}C NMR spectrum of compound **3b**



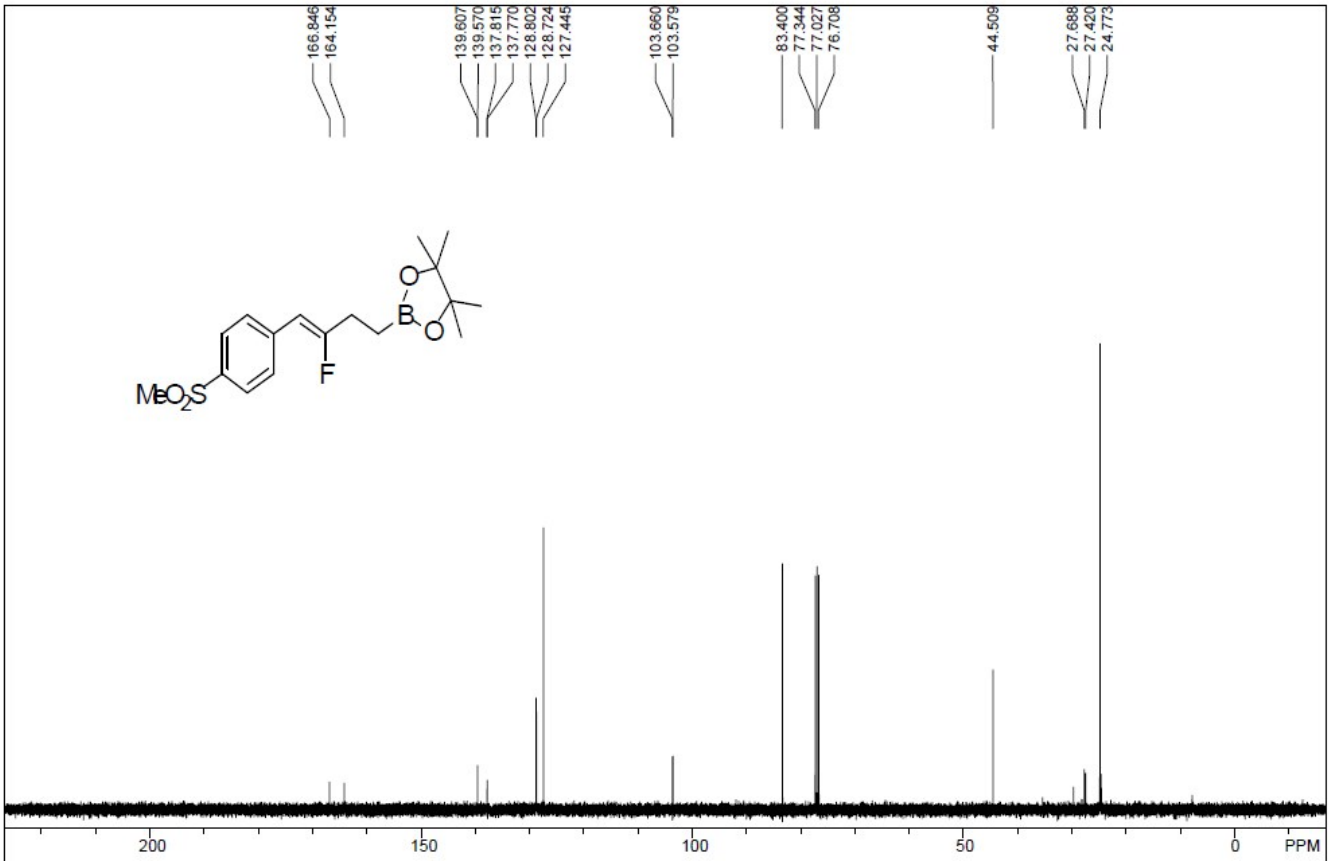
^{19}F NMR spectrum of compound **3b**



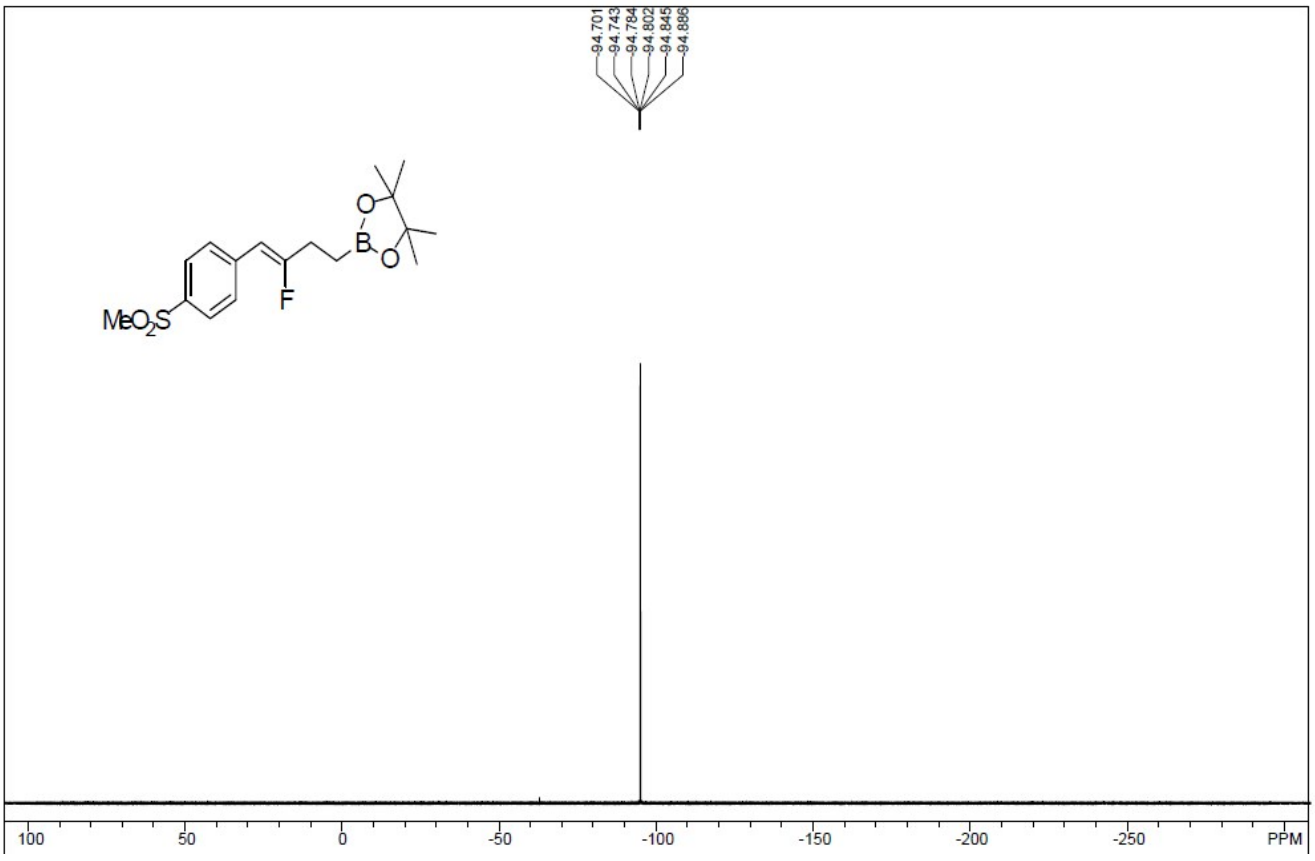
^{1}H NMR spectrum of compound **3c**



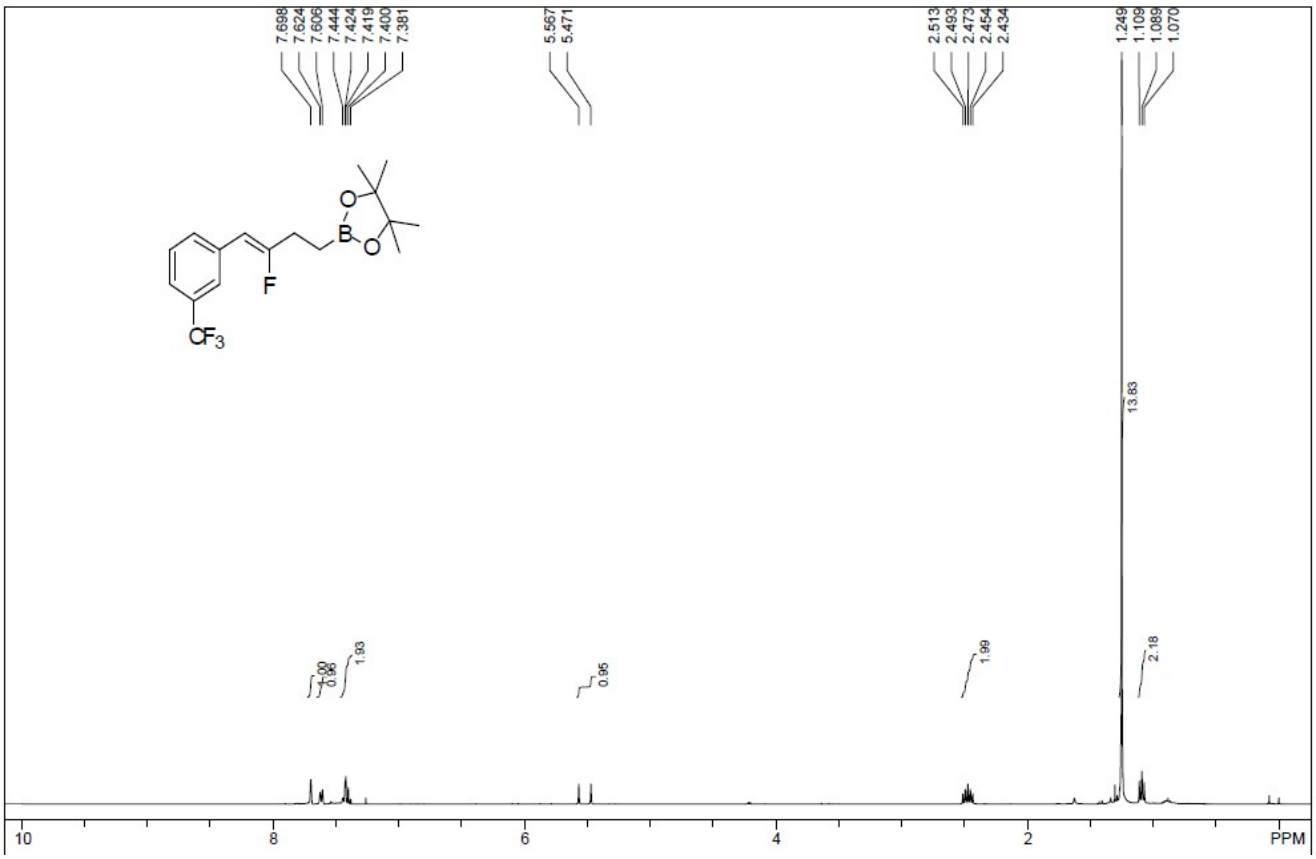
^{13}C NMR spectrum of compound **3c**



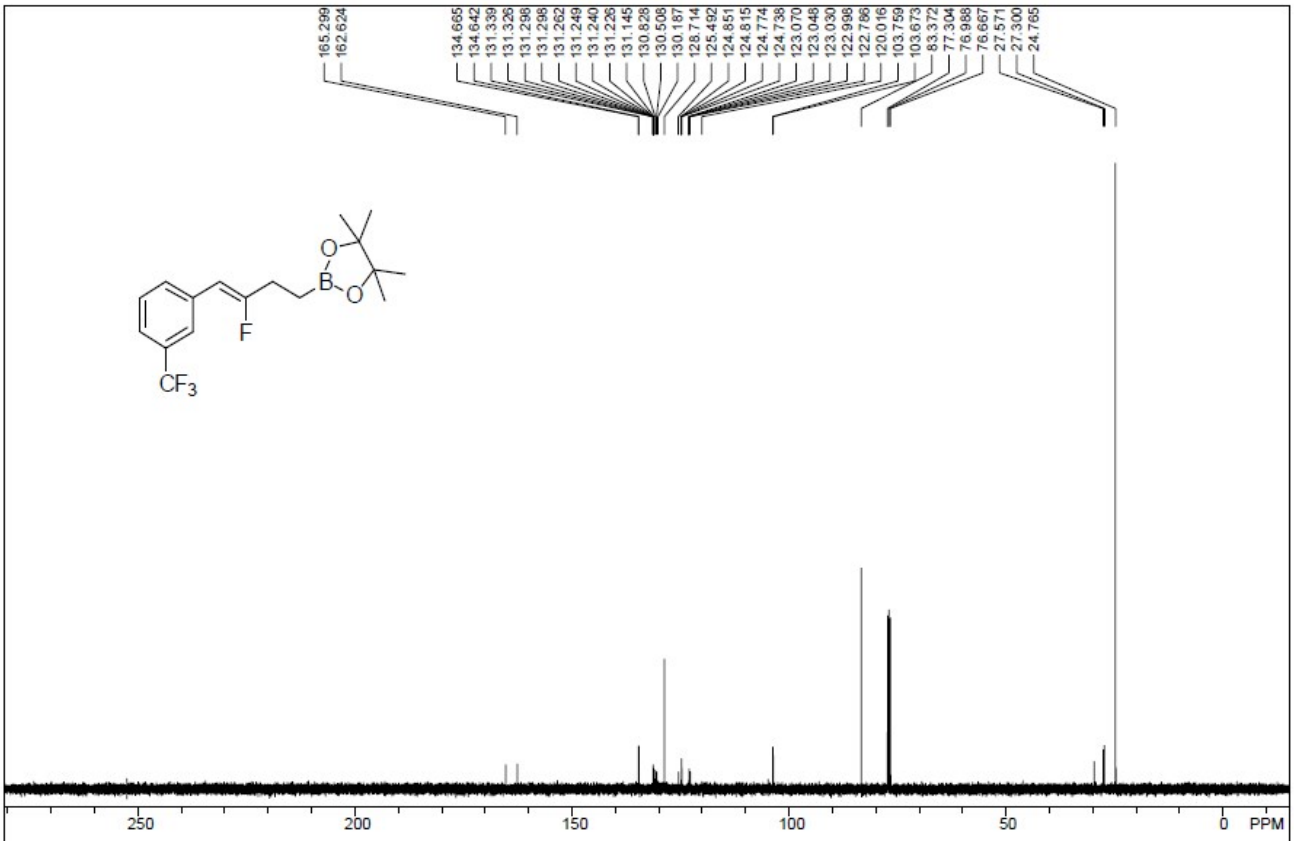
^{19}F NMR spectrum of compound **3c**



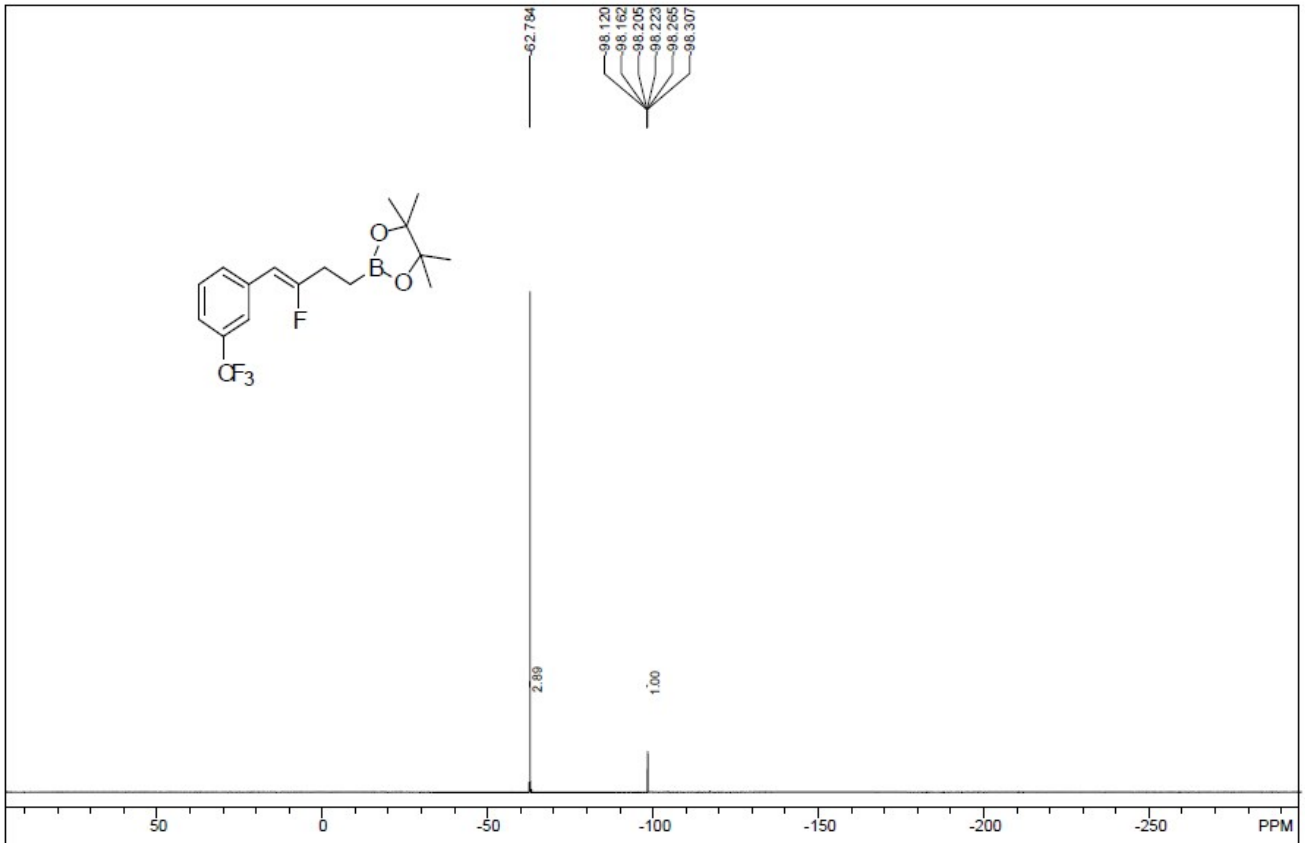
^{1}H NMR spectrum of compound **3d**



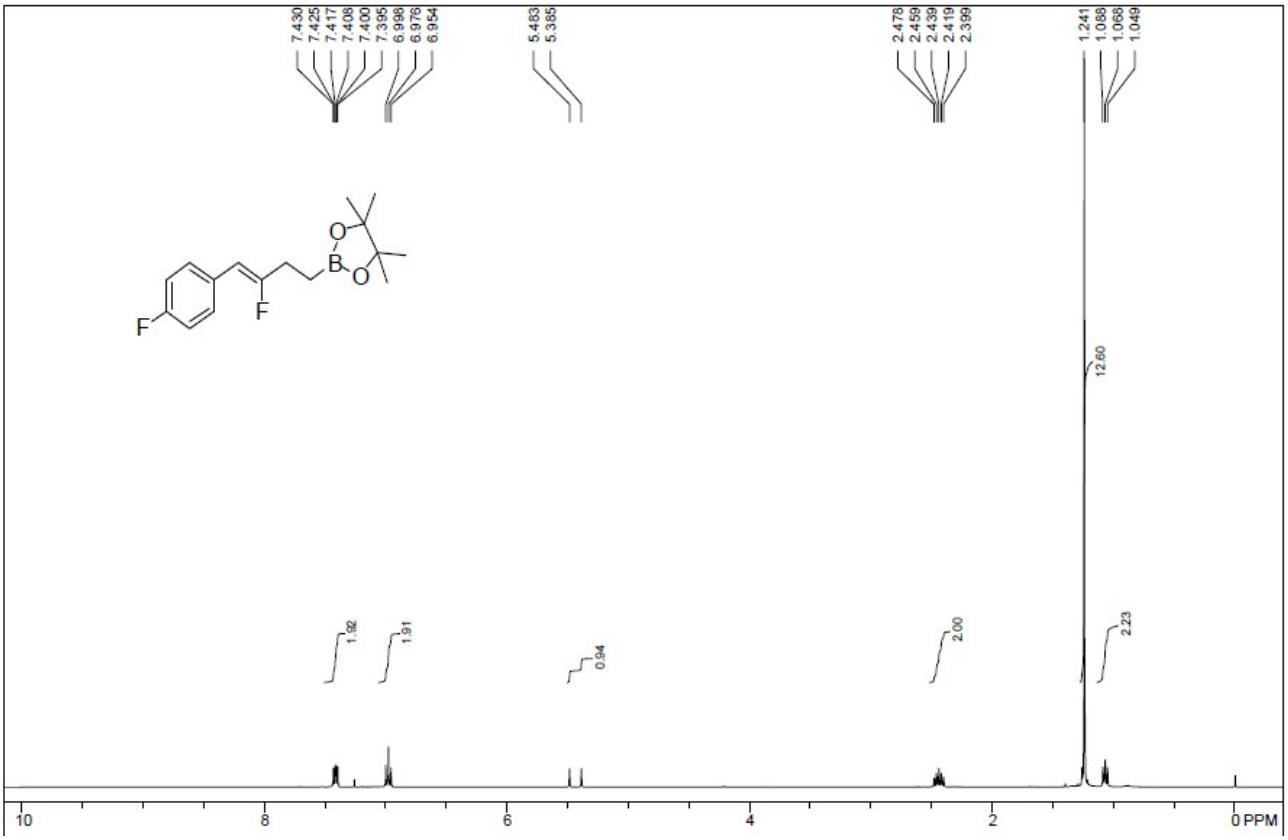
^{13}C NMR spectrum of compound **3d**



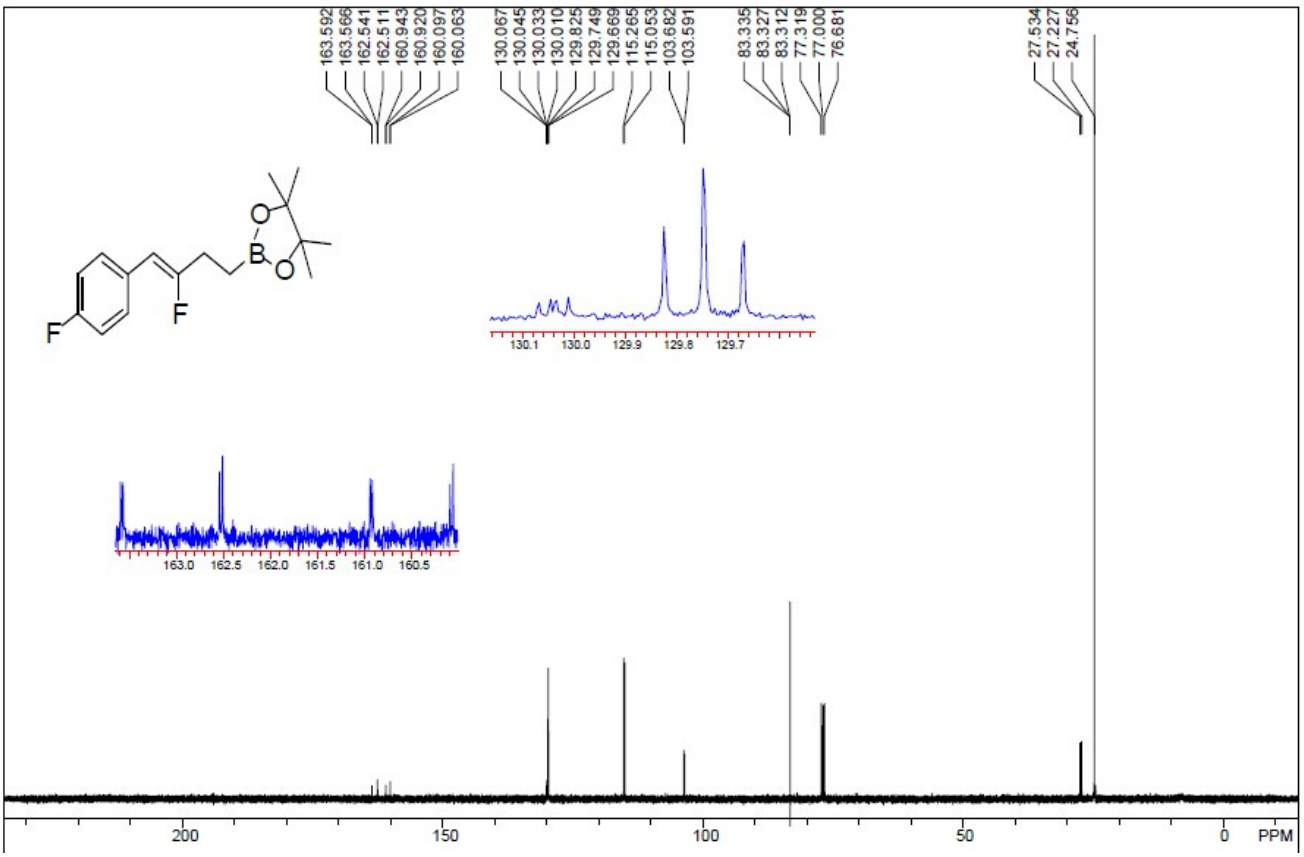
^{19}F NMR spectrum of compound **3d**



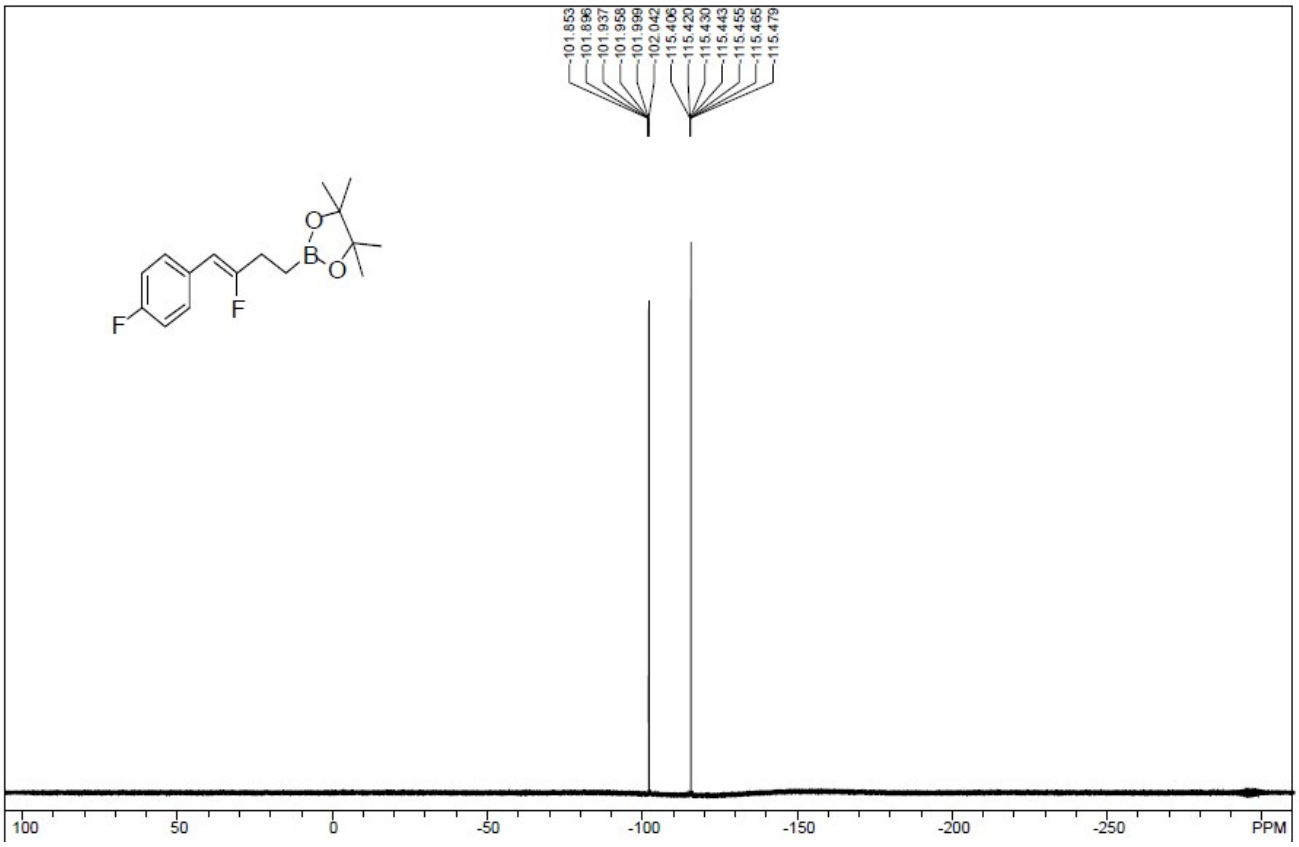
^{1}H NMR spectrum of compound **3e**



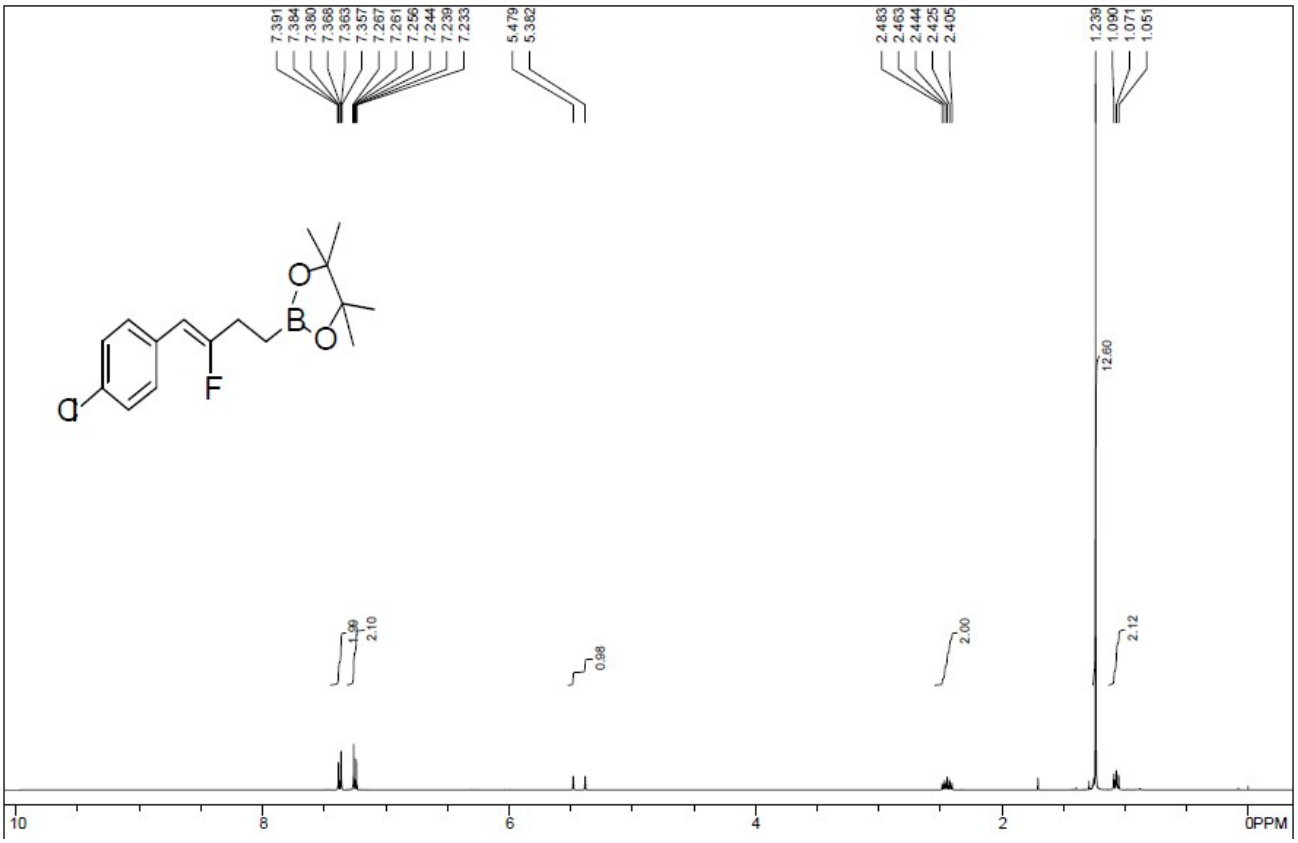
^{13}C NMR spectrum of compound **3e**



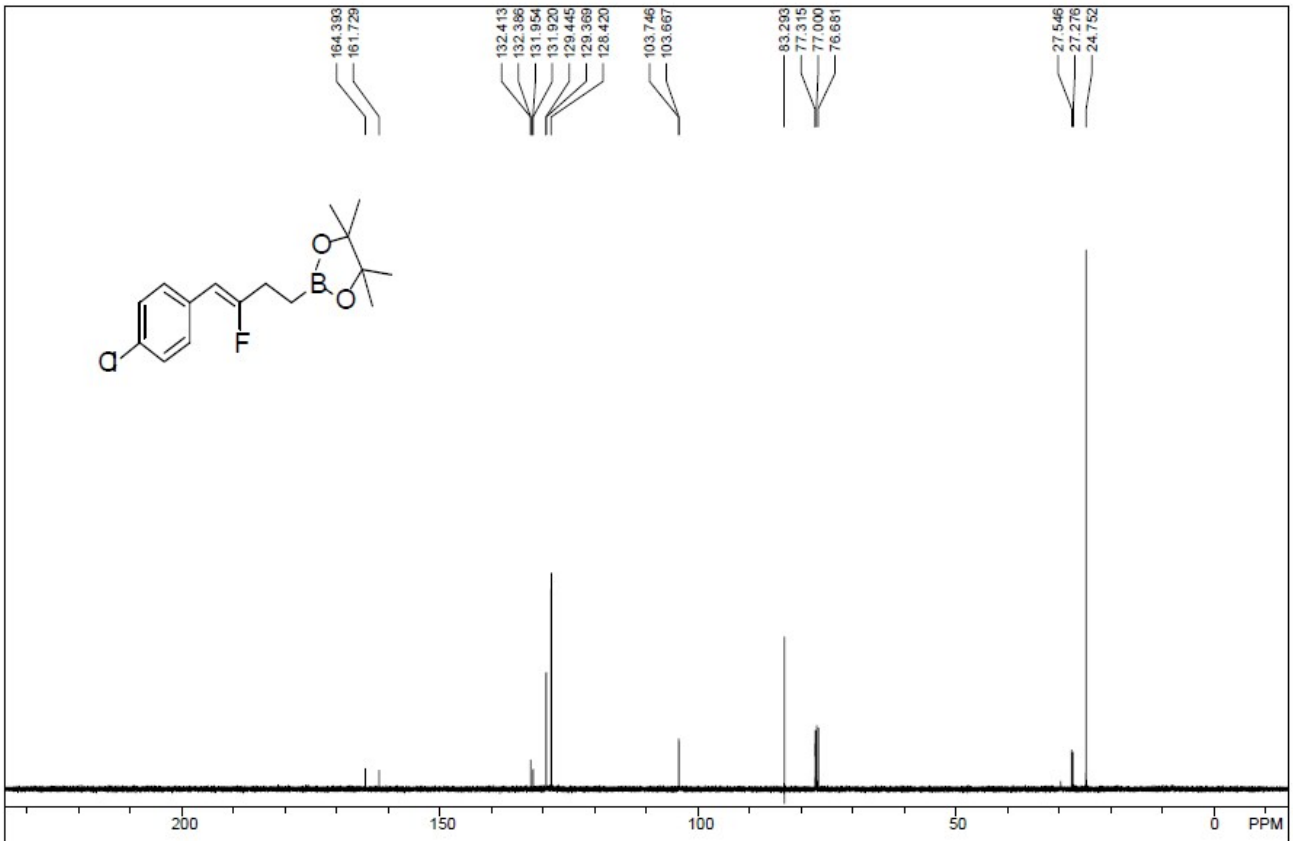
^{19}F NMR spectrum of compound **3e**



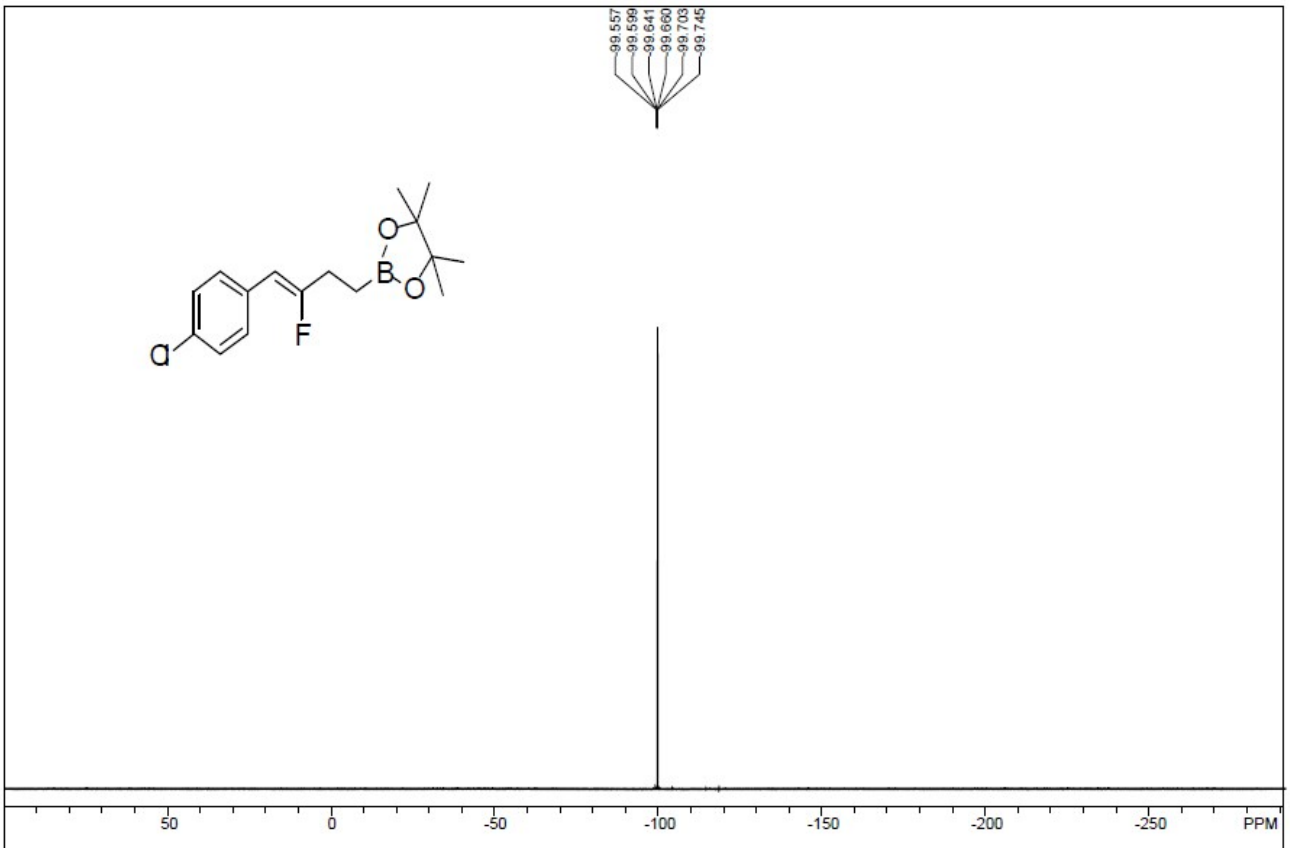
^{1}H NMR spectrum of compound **3f**



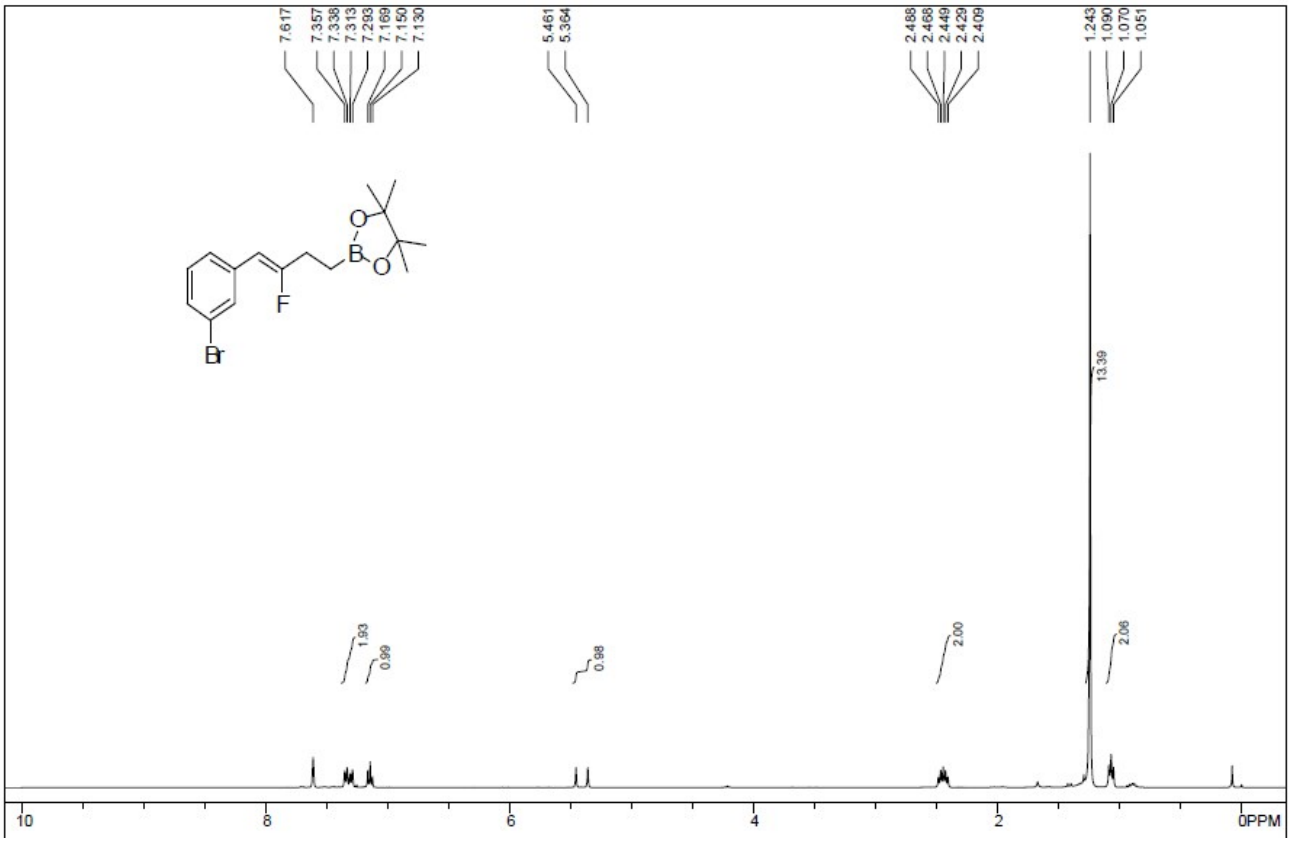
^{13}C NMR spectrum of compound **3f**



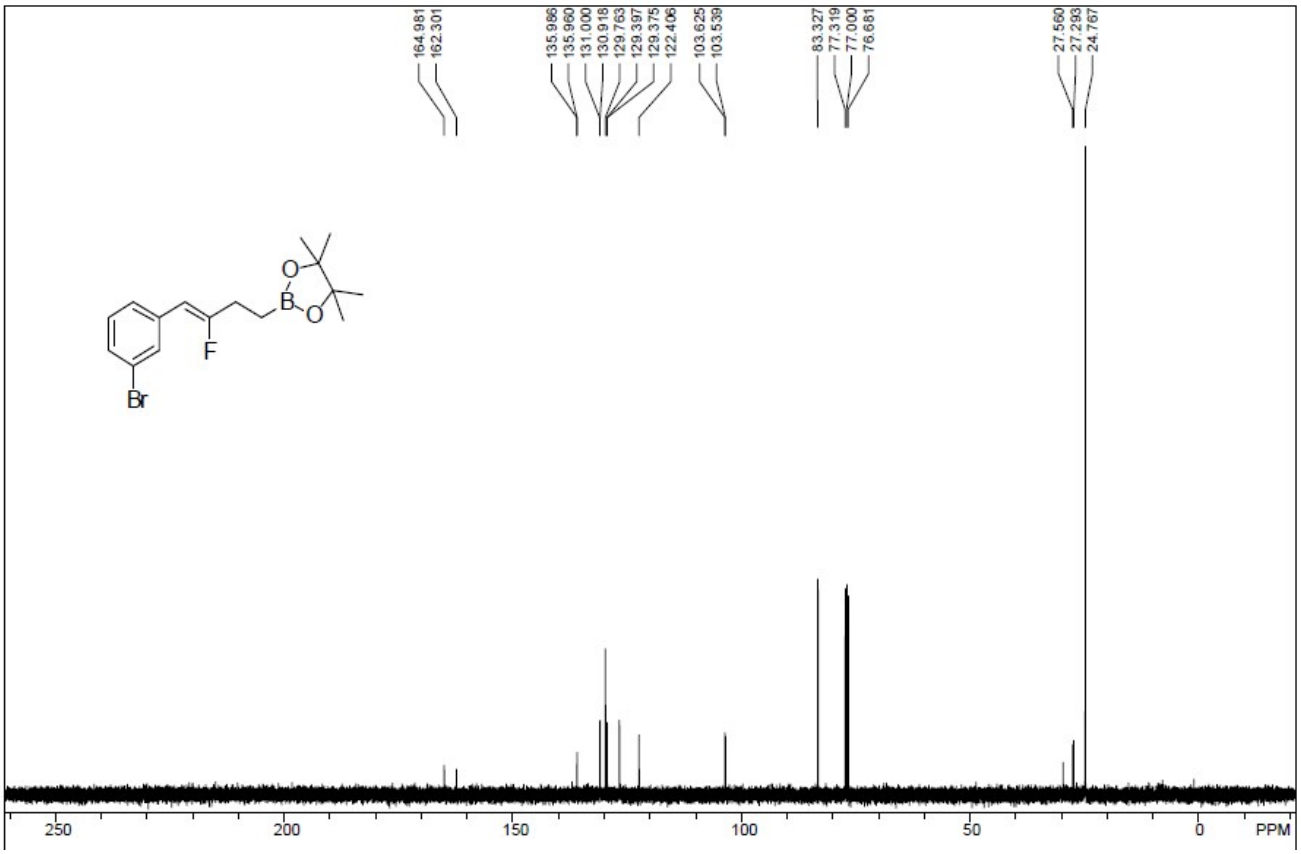
^{19}F NMR spectrum of compound **3f**



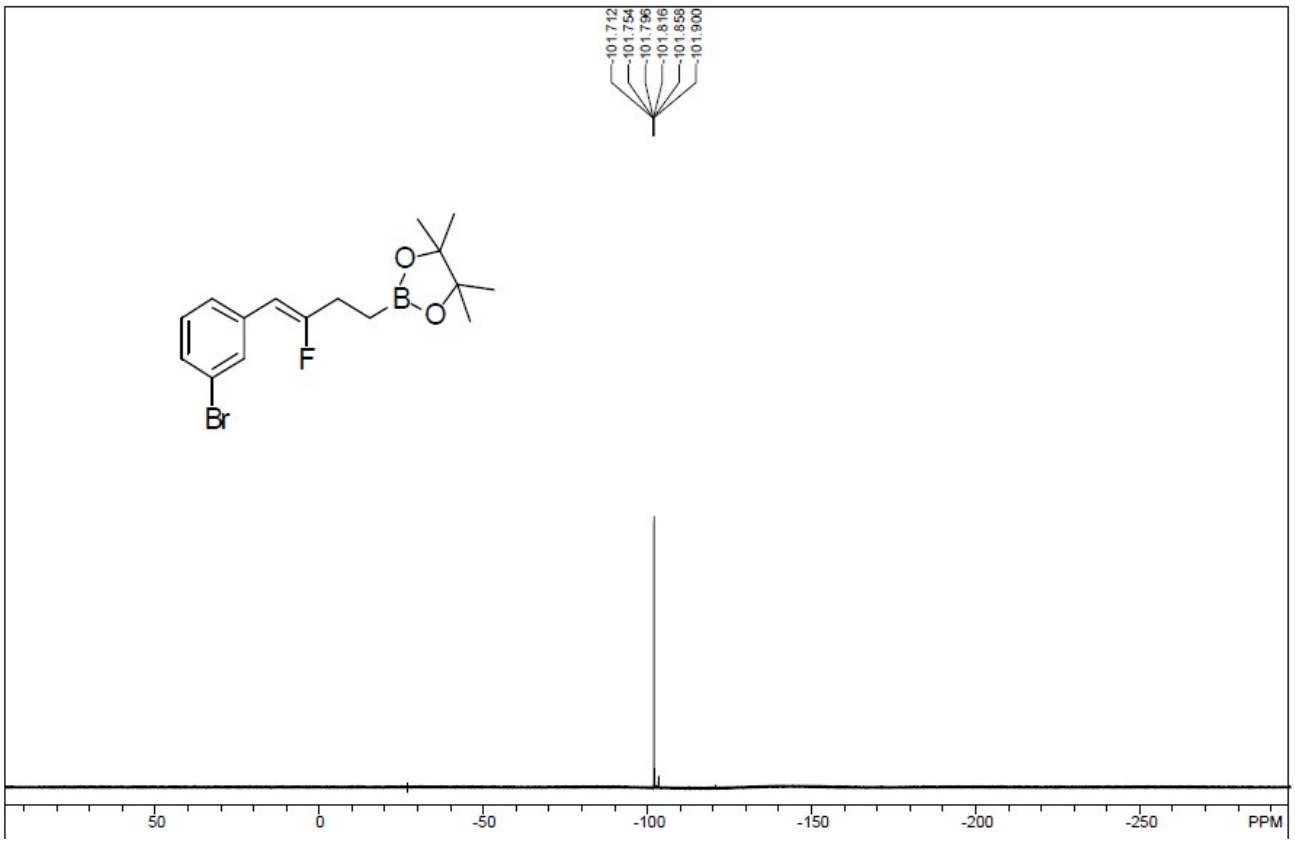
^{1}H NMR spectrum of compound **3g**



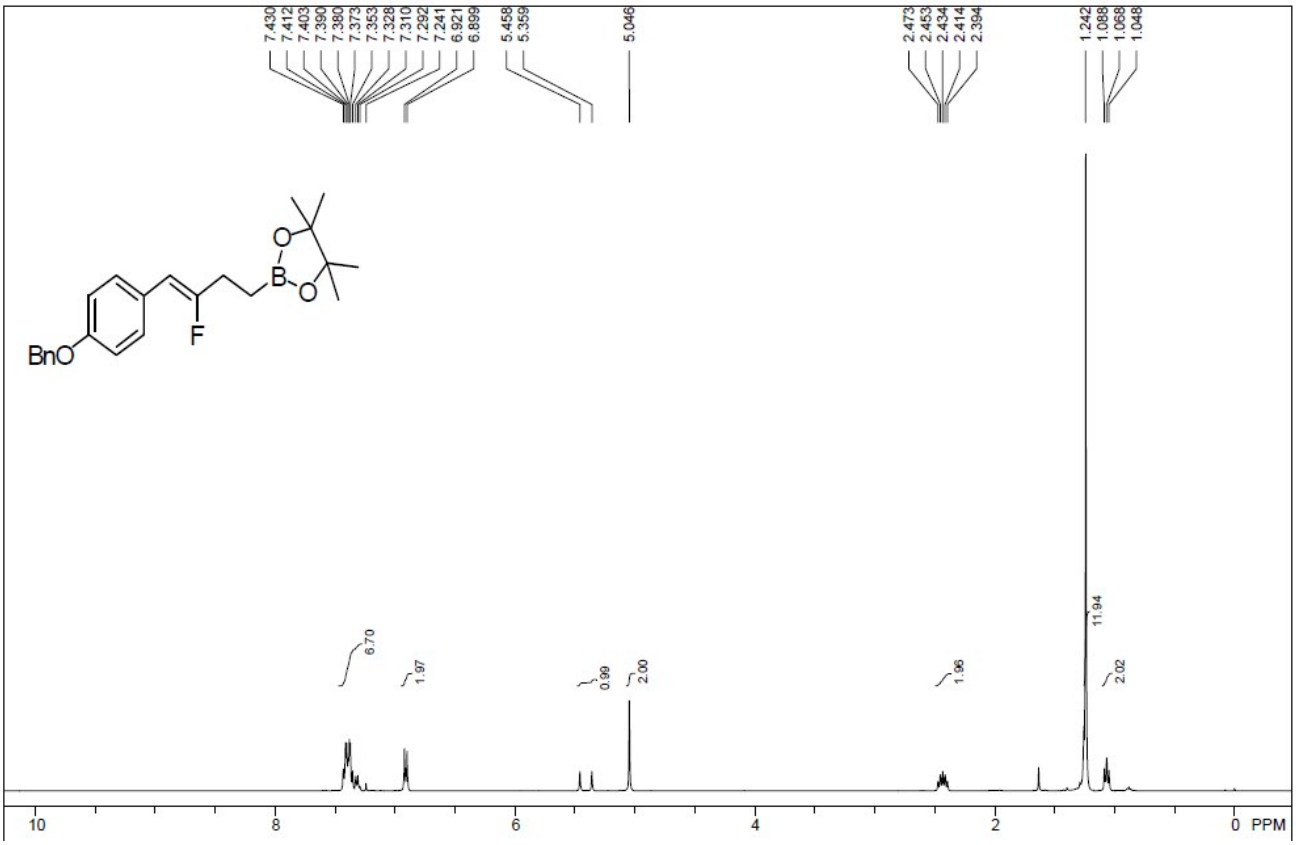
^{13}C NMR spectrum of compound **3g**



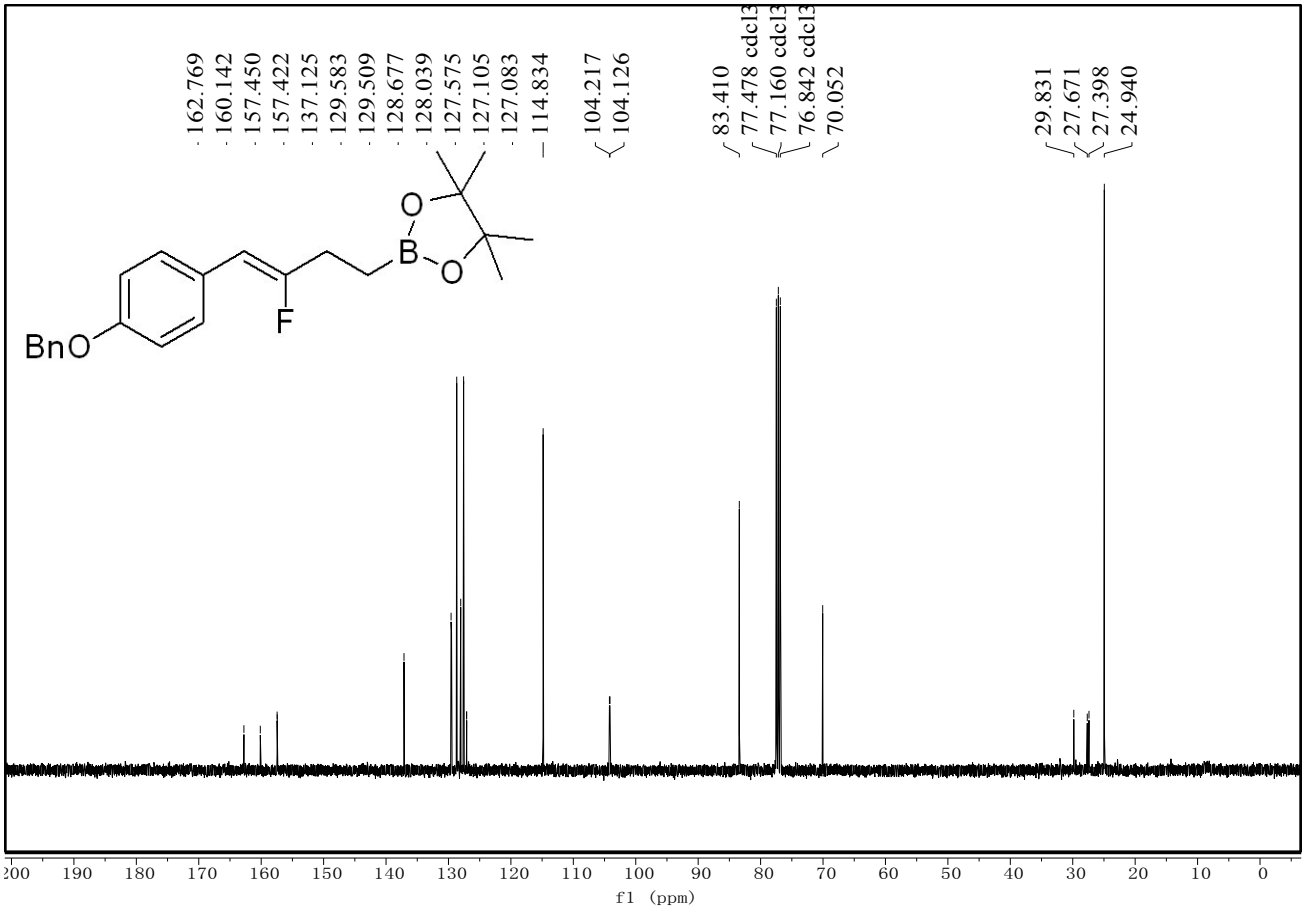
^{19}F NMR spectrum of compound **3g**



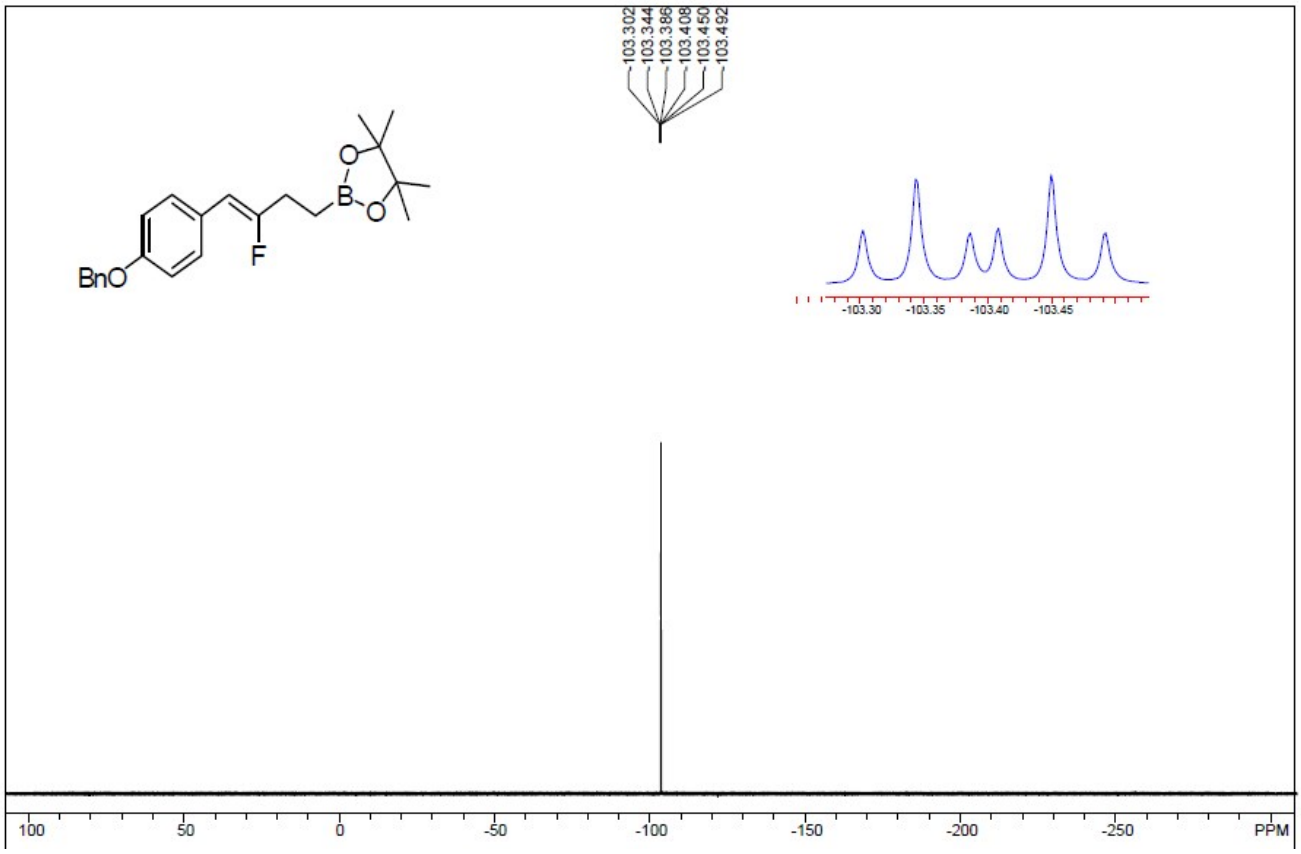
^{1}H NMR spectrum of compound **3h**



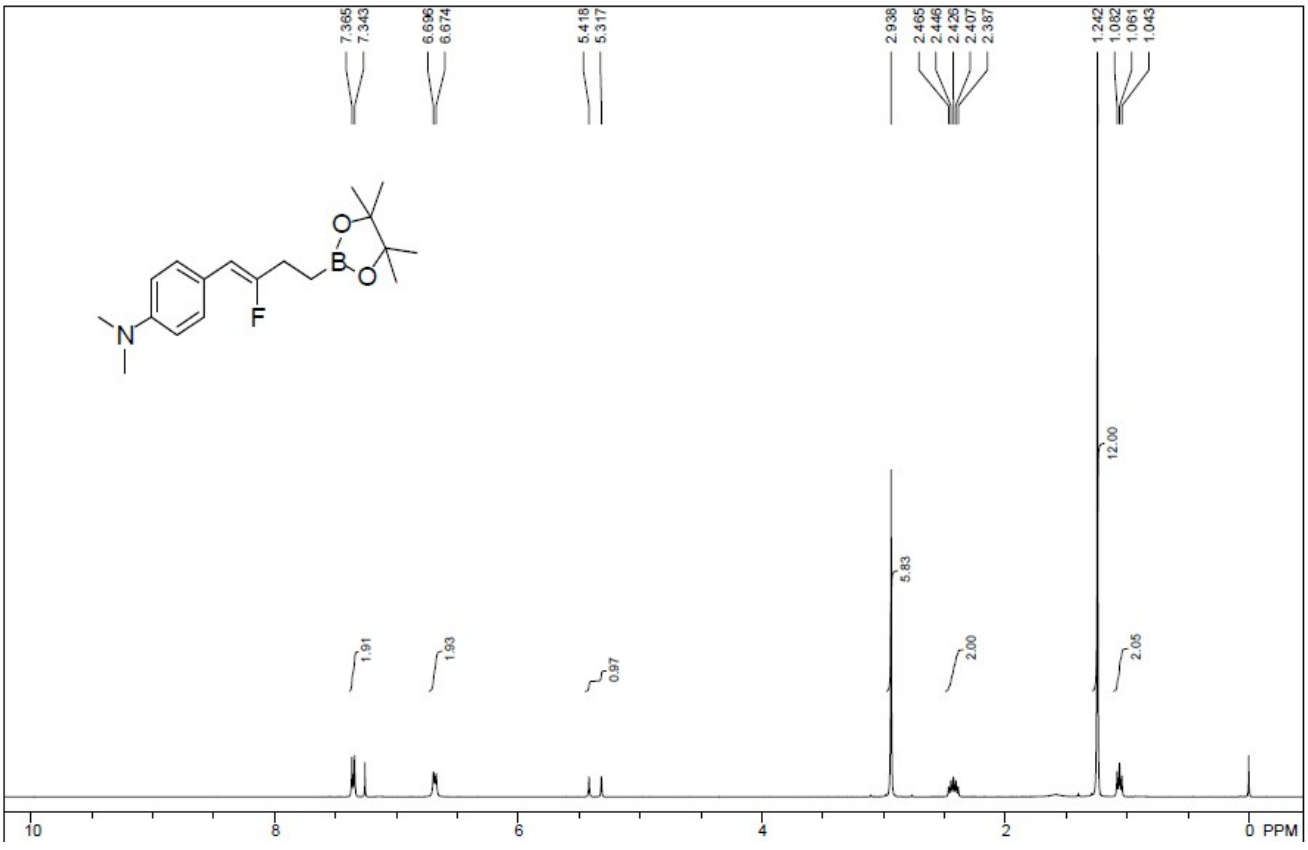
^{13}C NMR spectrum of compound **3h**



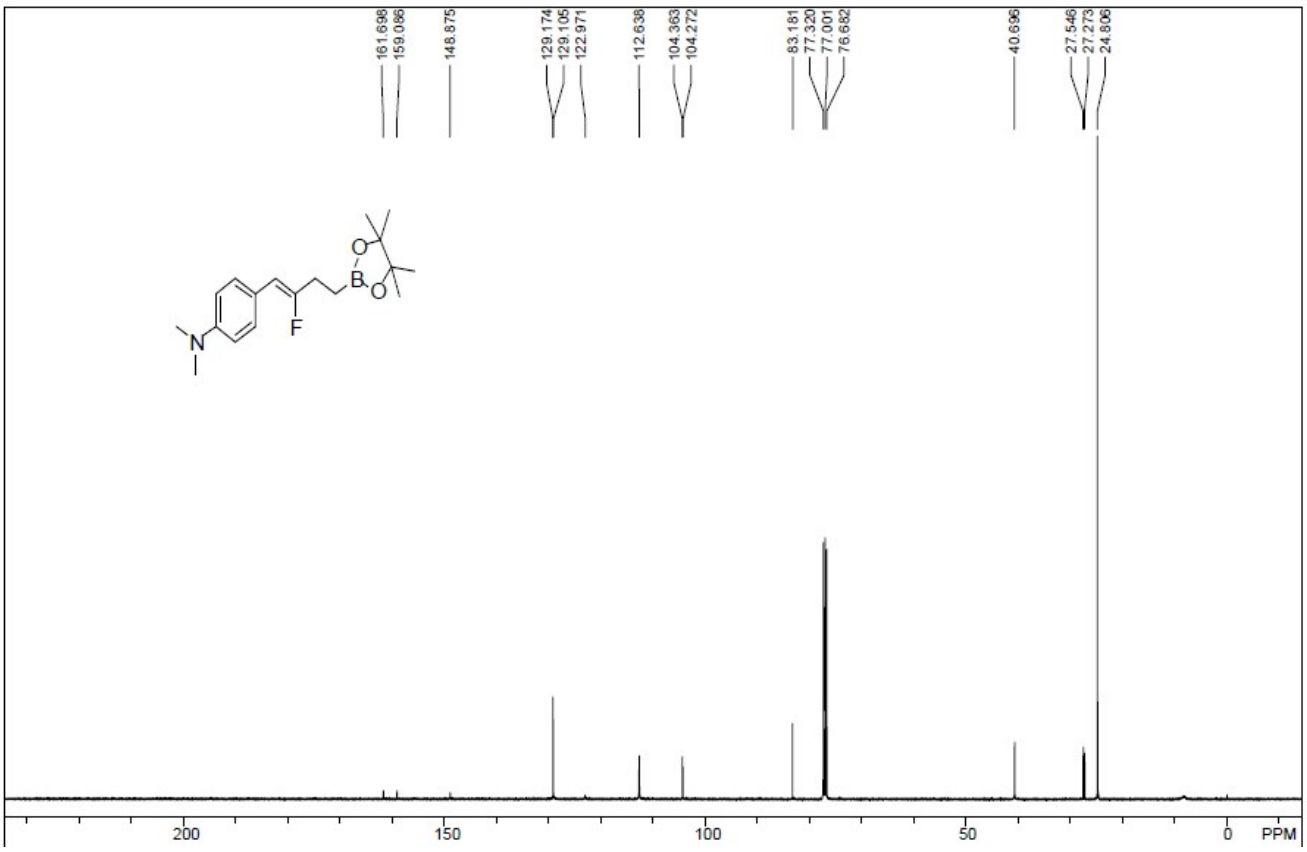
^{19}F NMR spectrum of compound **3h**



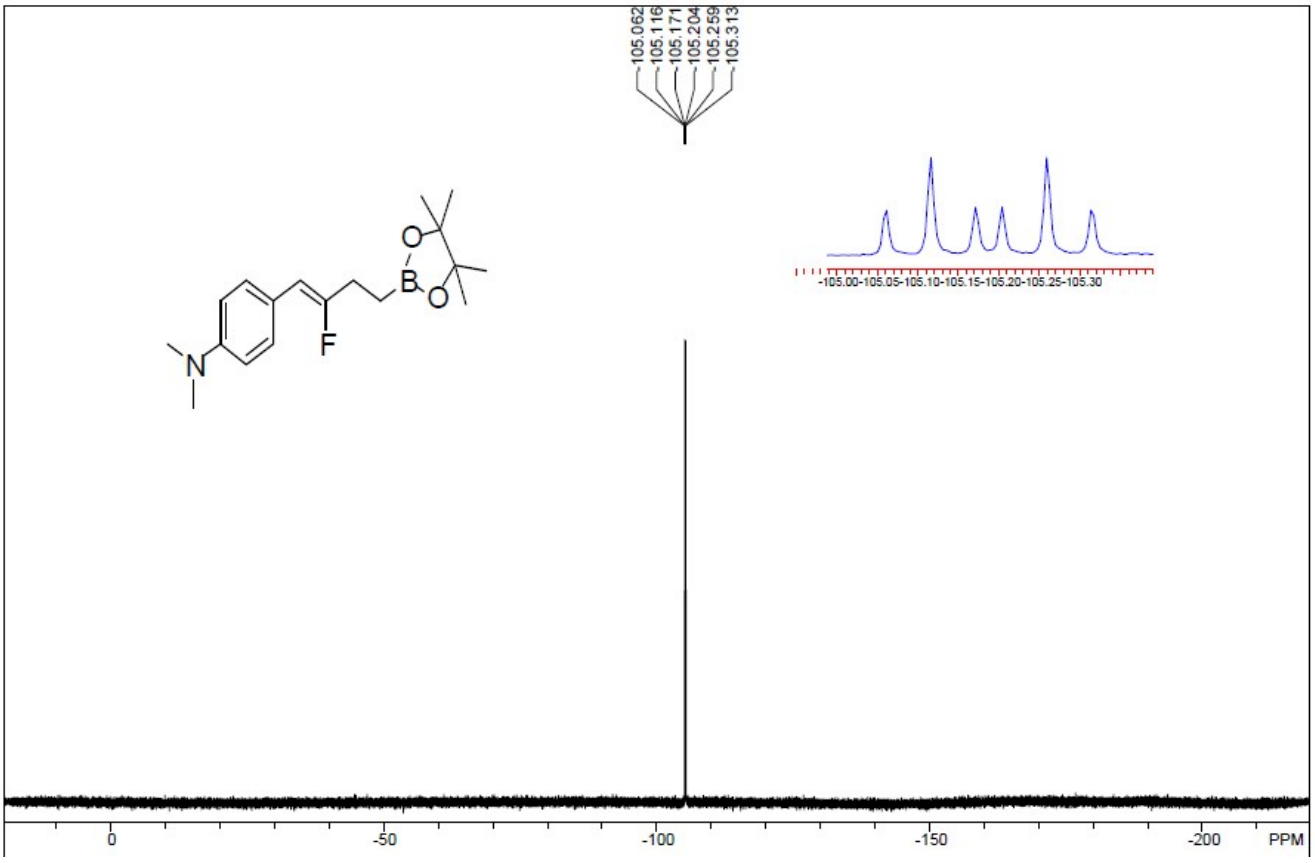
^{1}H NMR spectrum of compound **3i**



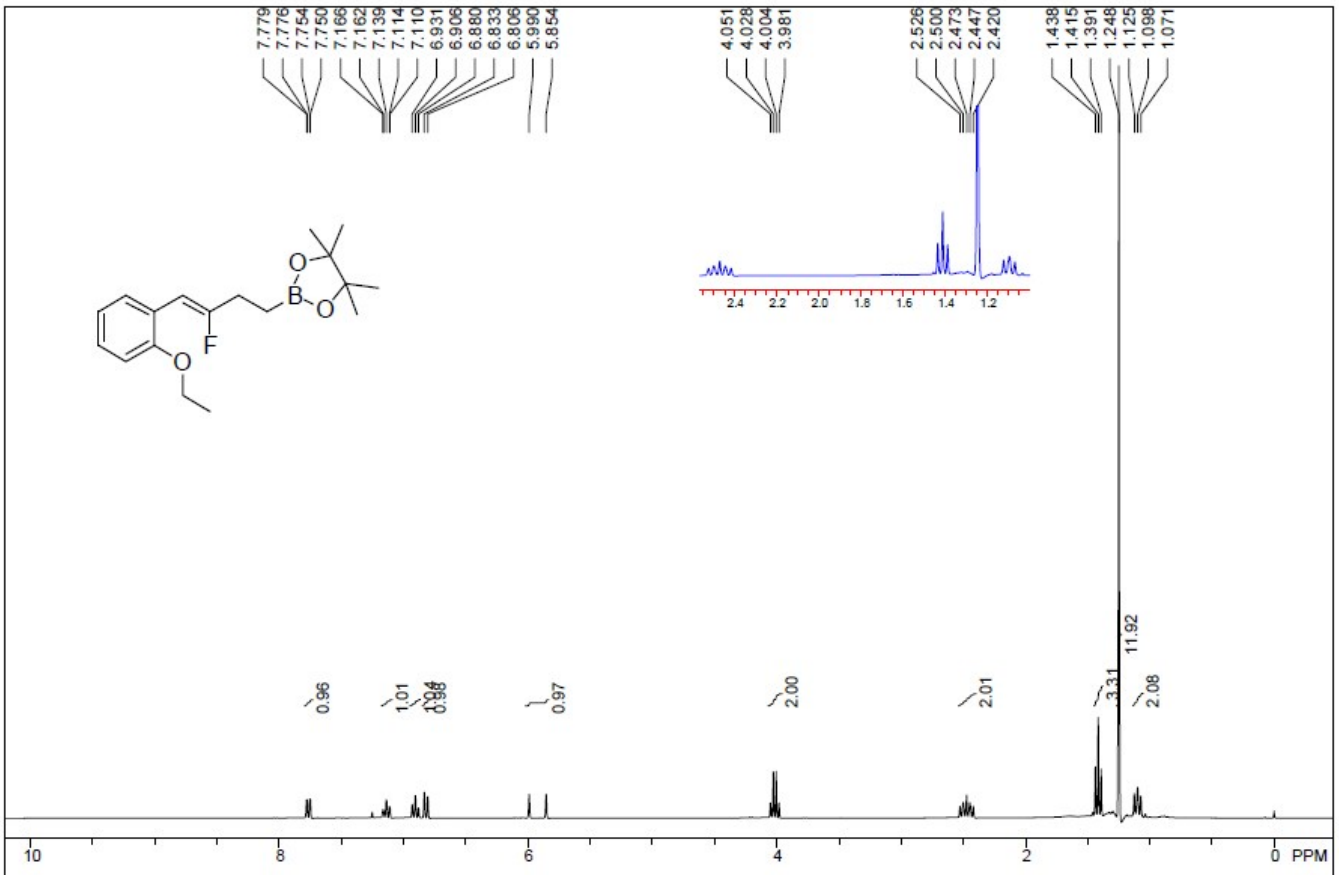
^{13}C NMR spectrum of compound **3i**



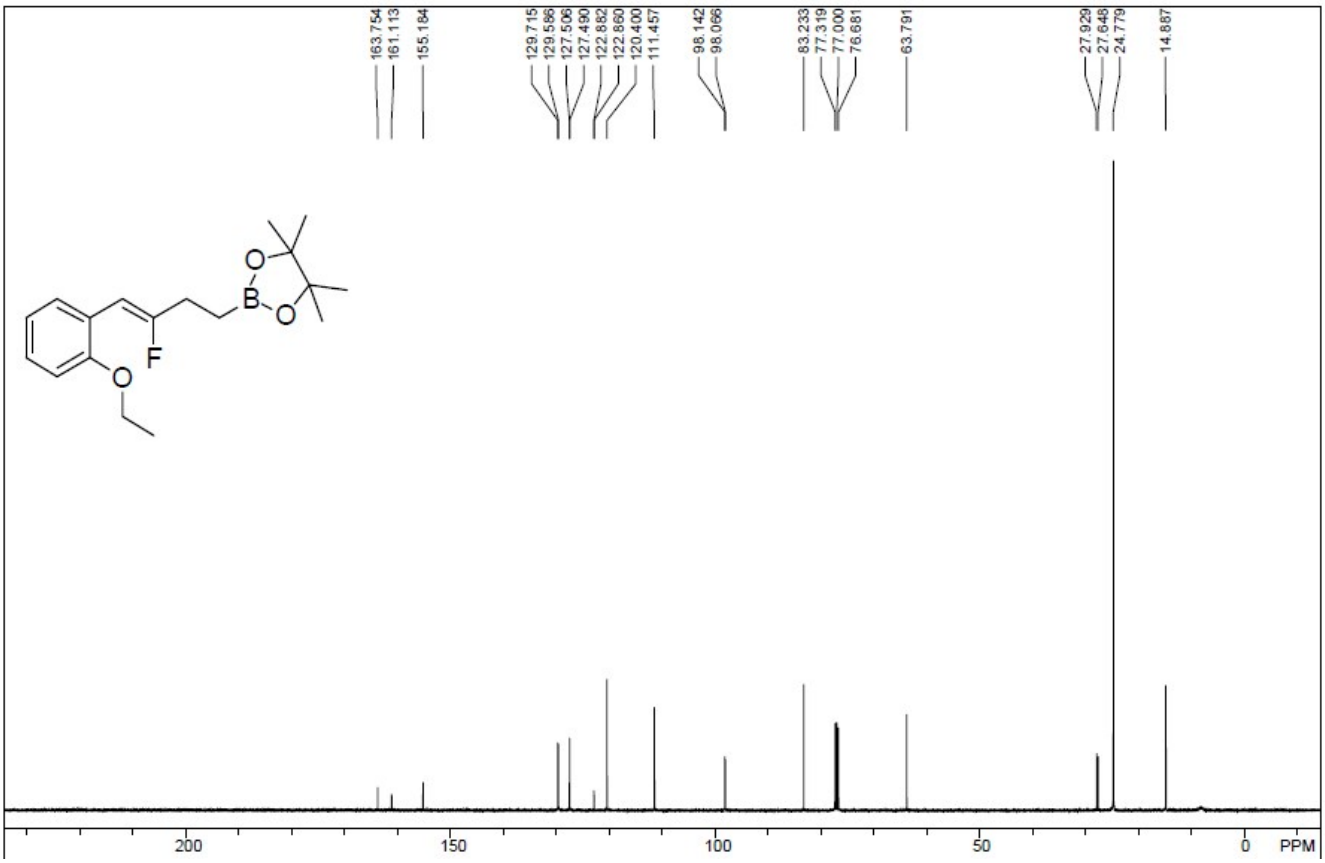
^{19}F NMR spectrum of compound **3i**



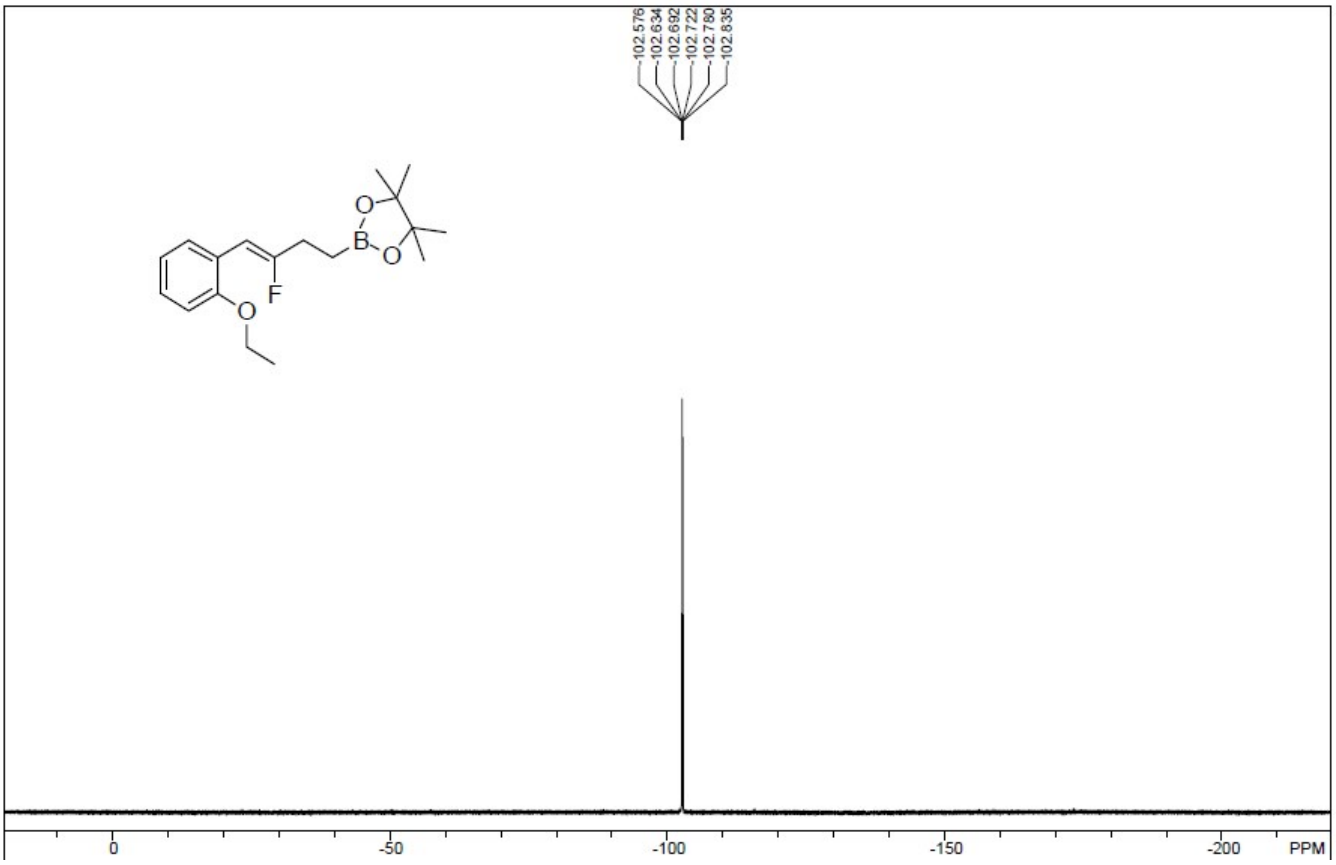
^{1}H NMR spectrum of compound **3k**



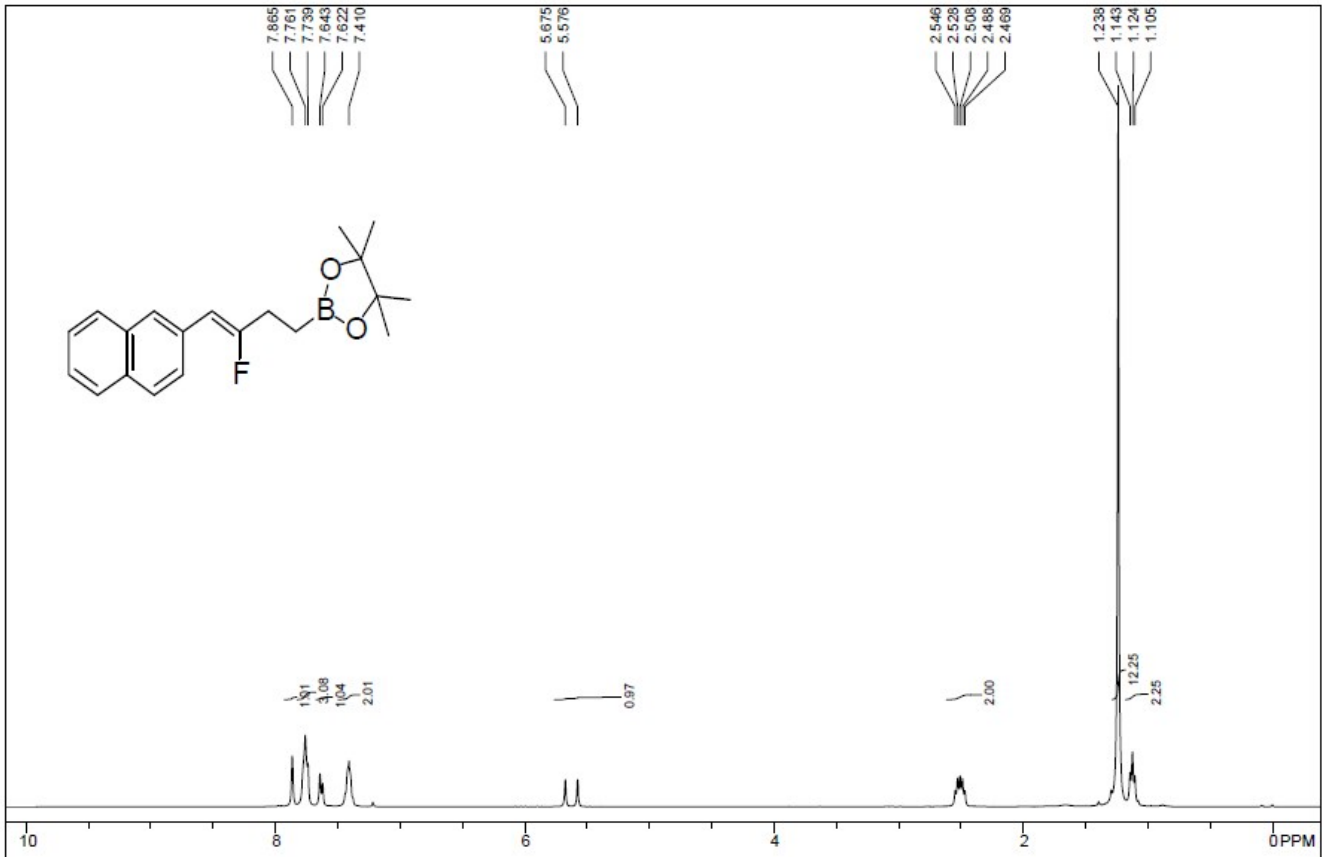
^{13}C NMR spectrum of compound **3k**



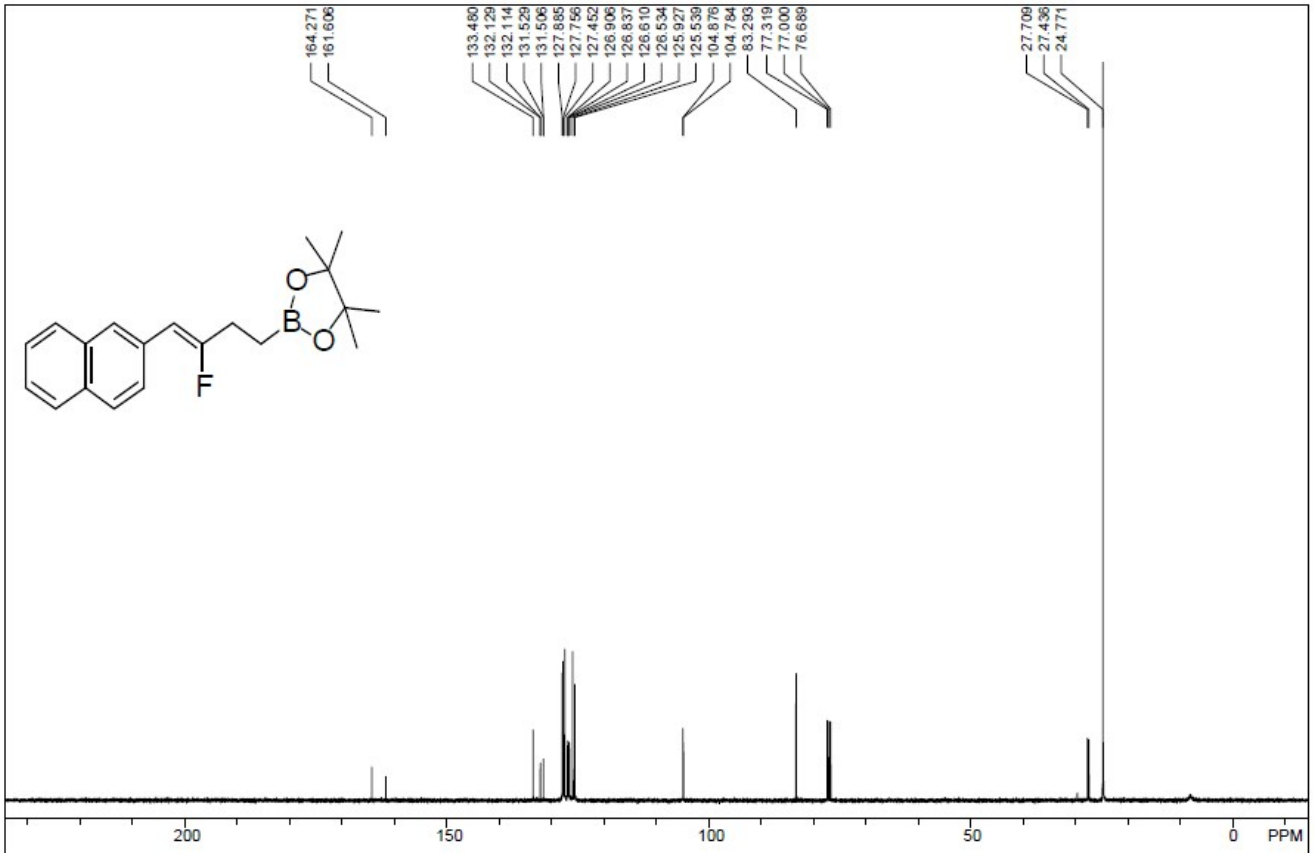
^{19}F NMR spectrum of compound **3k**



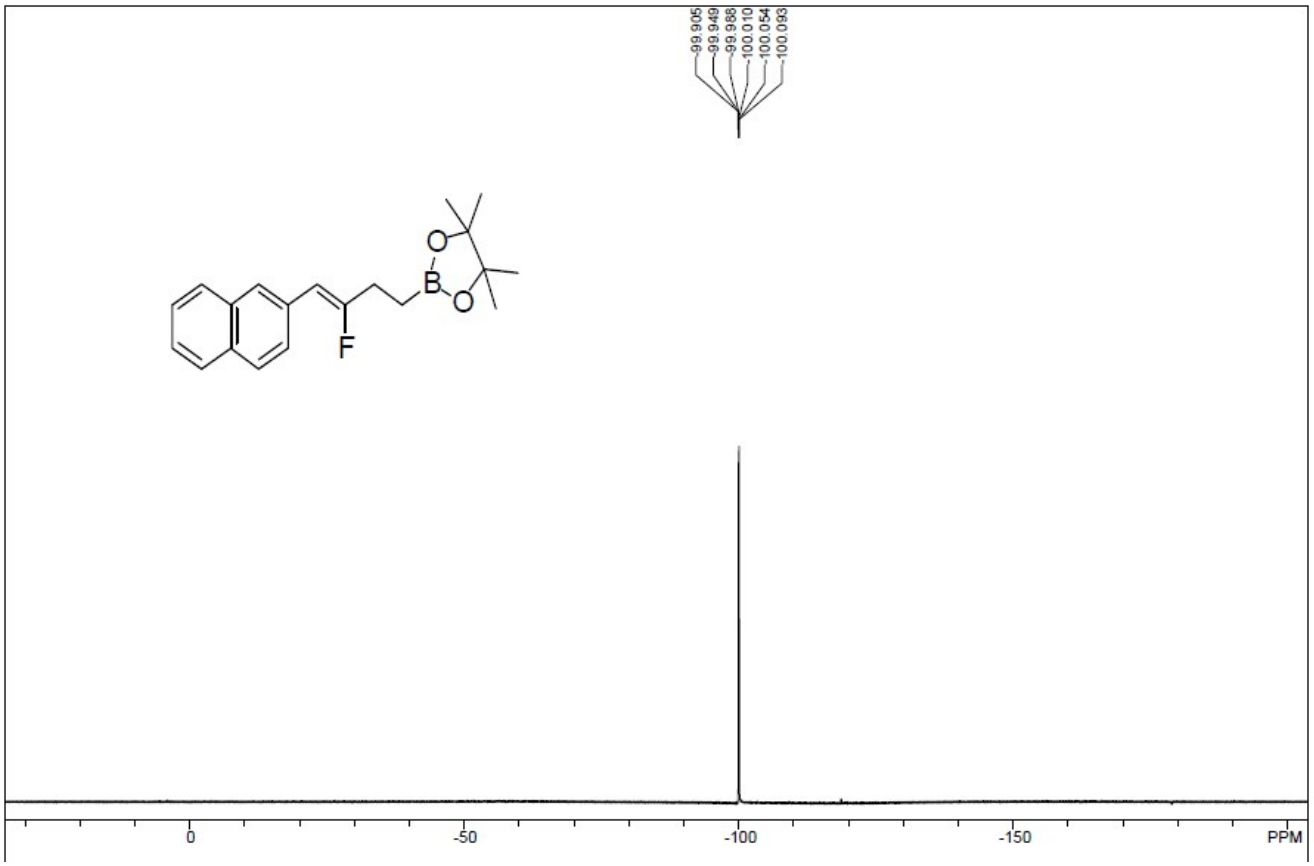
^{1}H NMR spectrum of compound **3l**



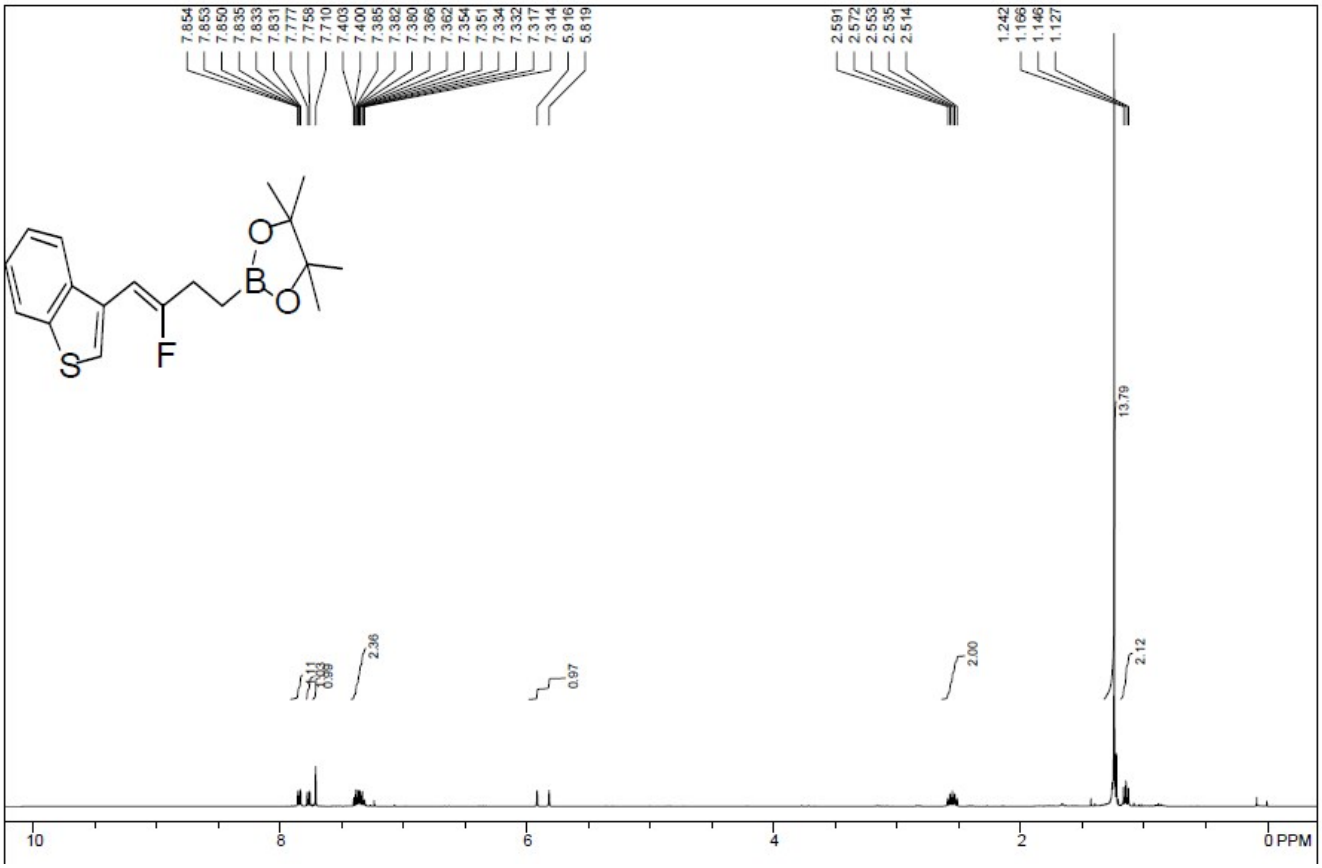
^{13}C NMR spectrum of compound **3l**



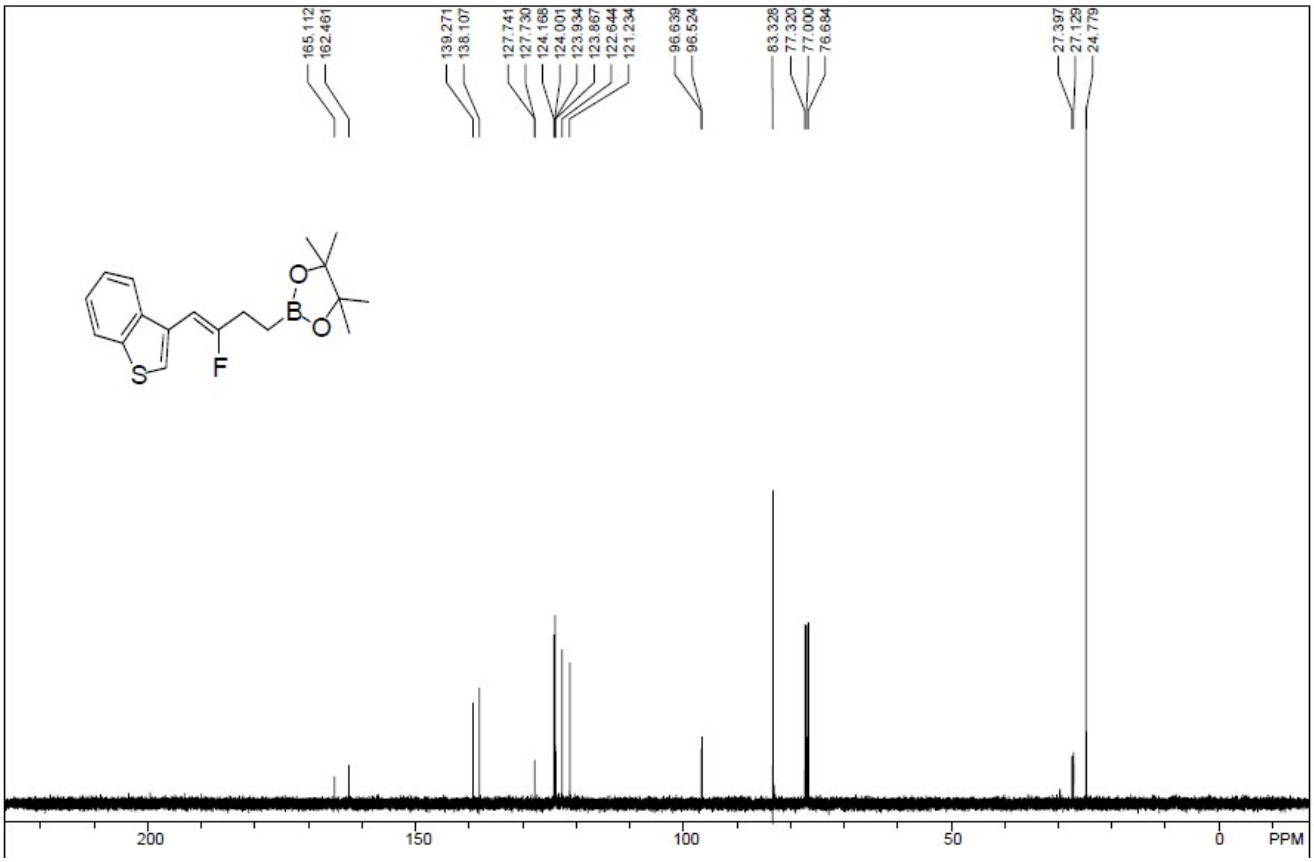
^{19}F NMR spectrum of compound **3l**



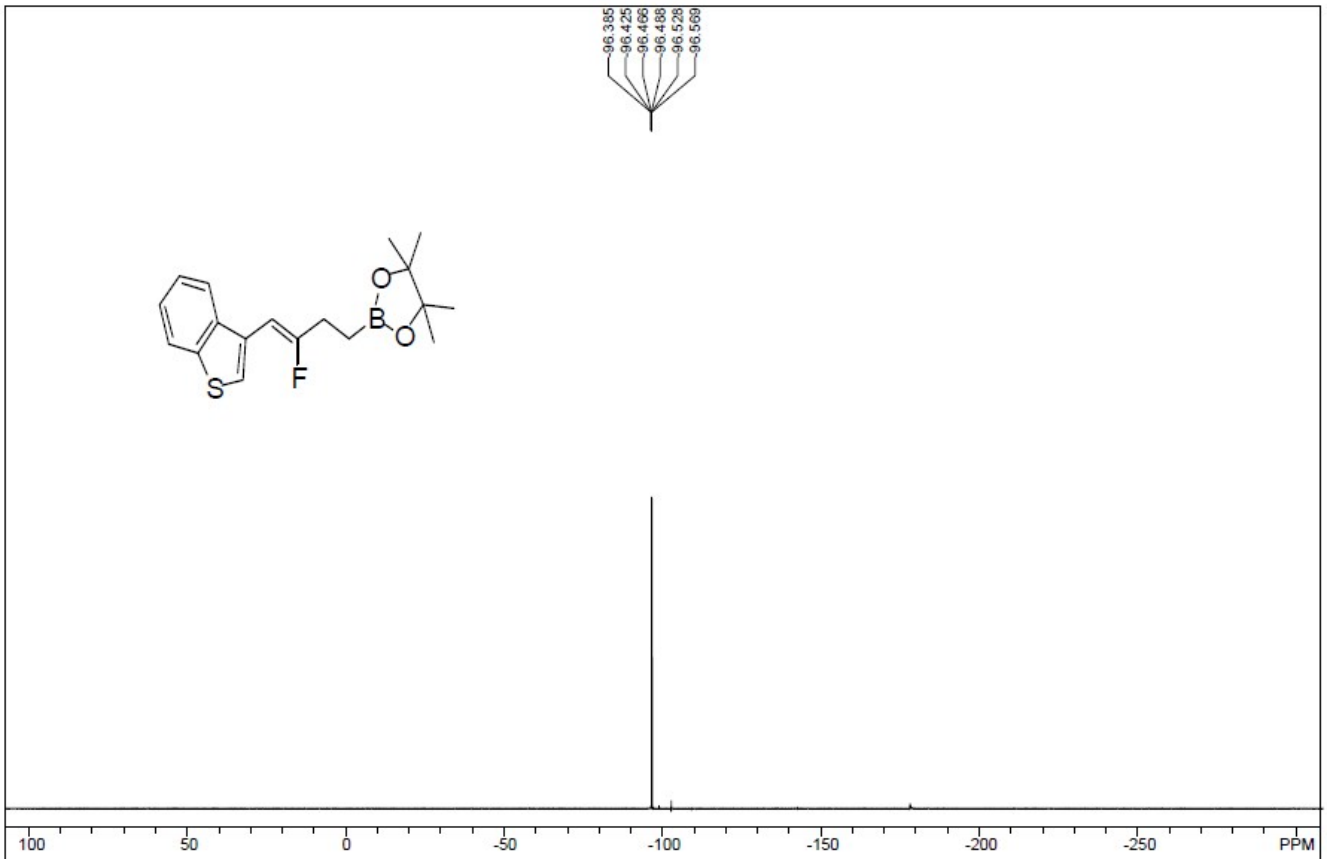
^{1}H NMR spectrum of compound **3m**



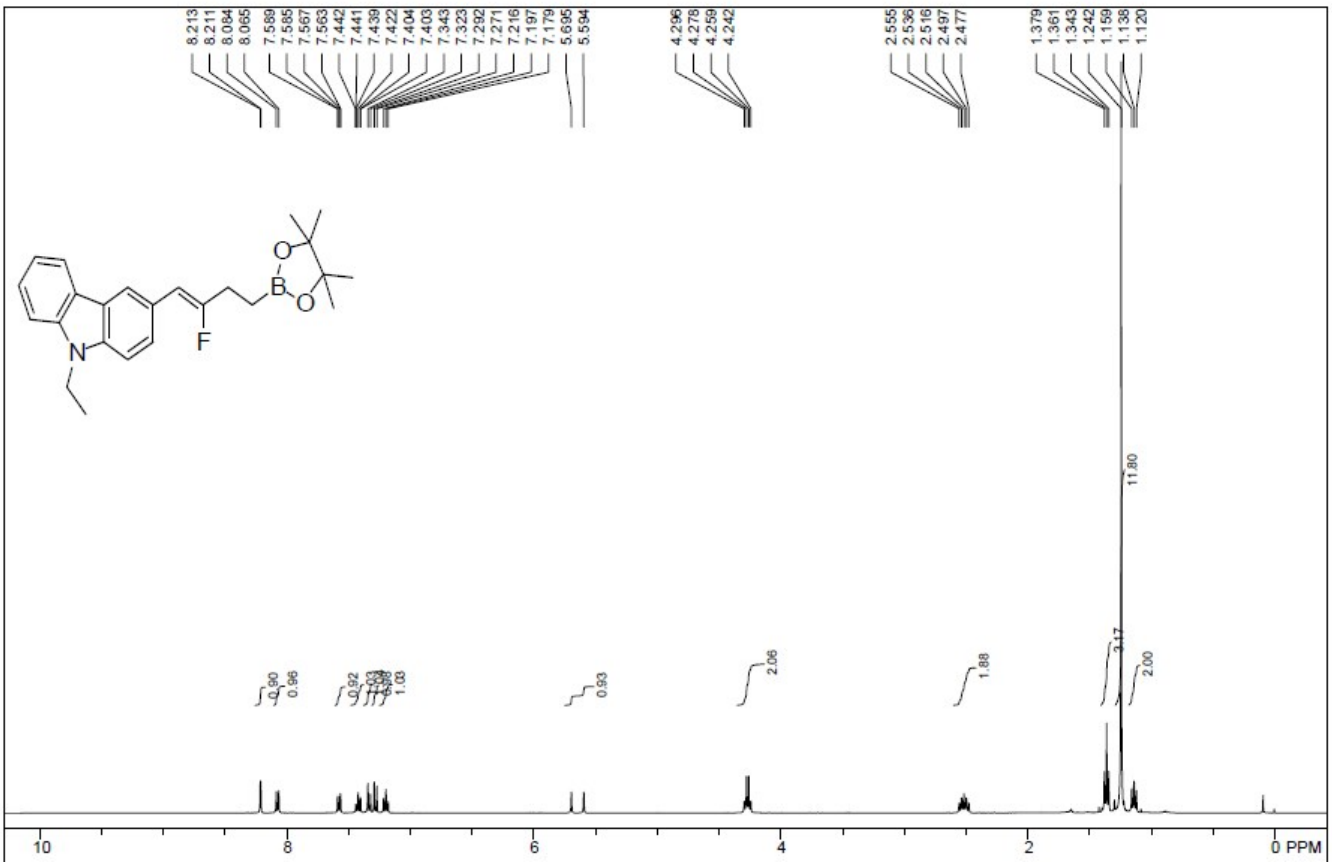
^{13}C NMR spectrum of compound **3m**



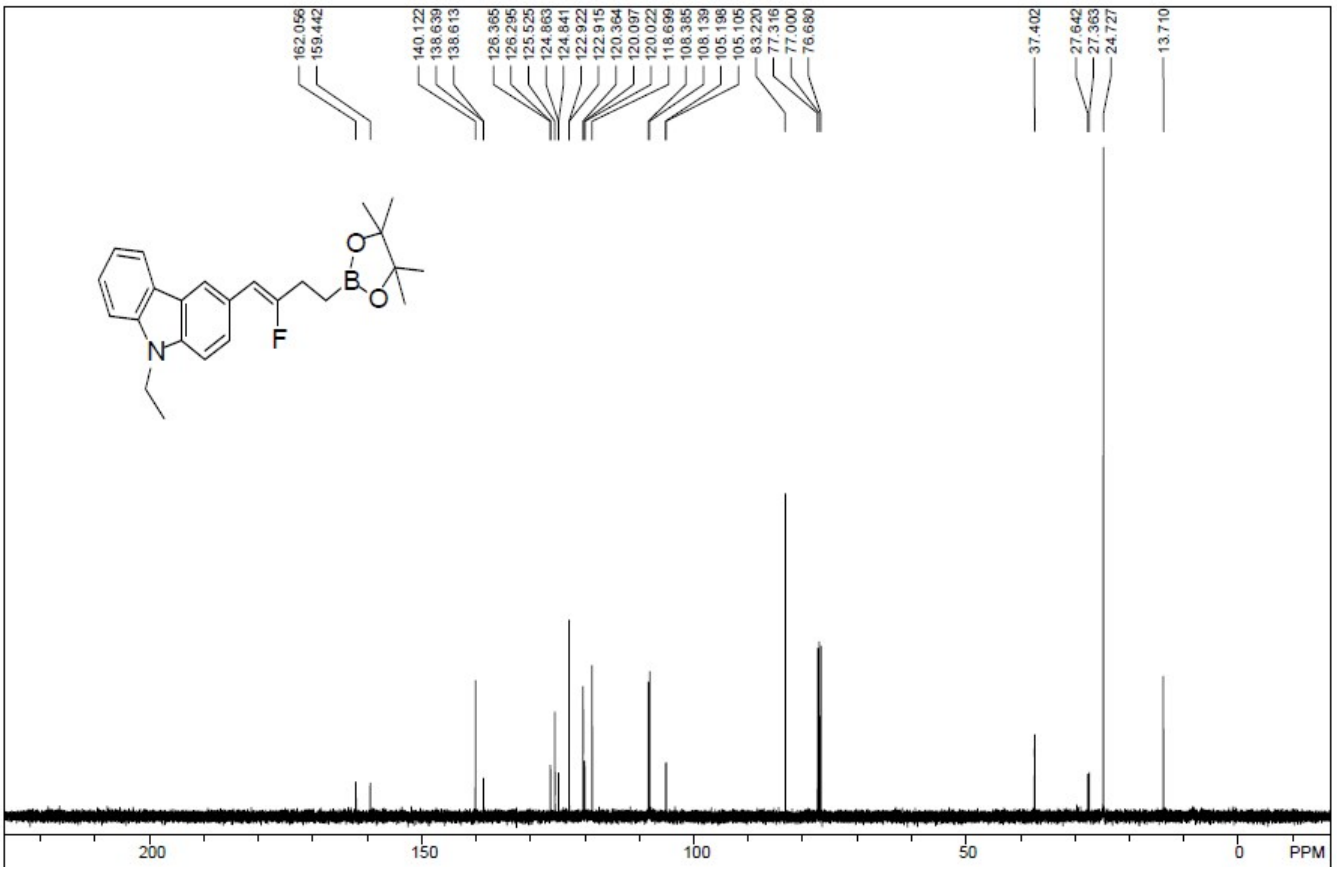
^{19}F NMR spectrum of compound **3m**



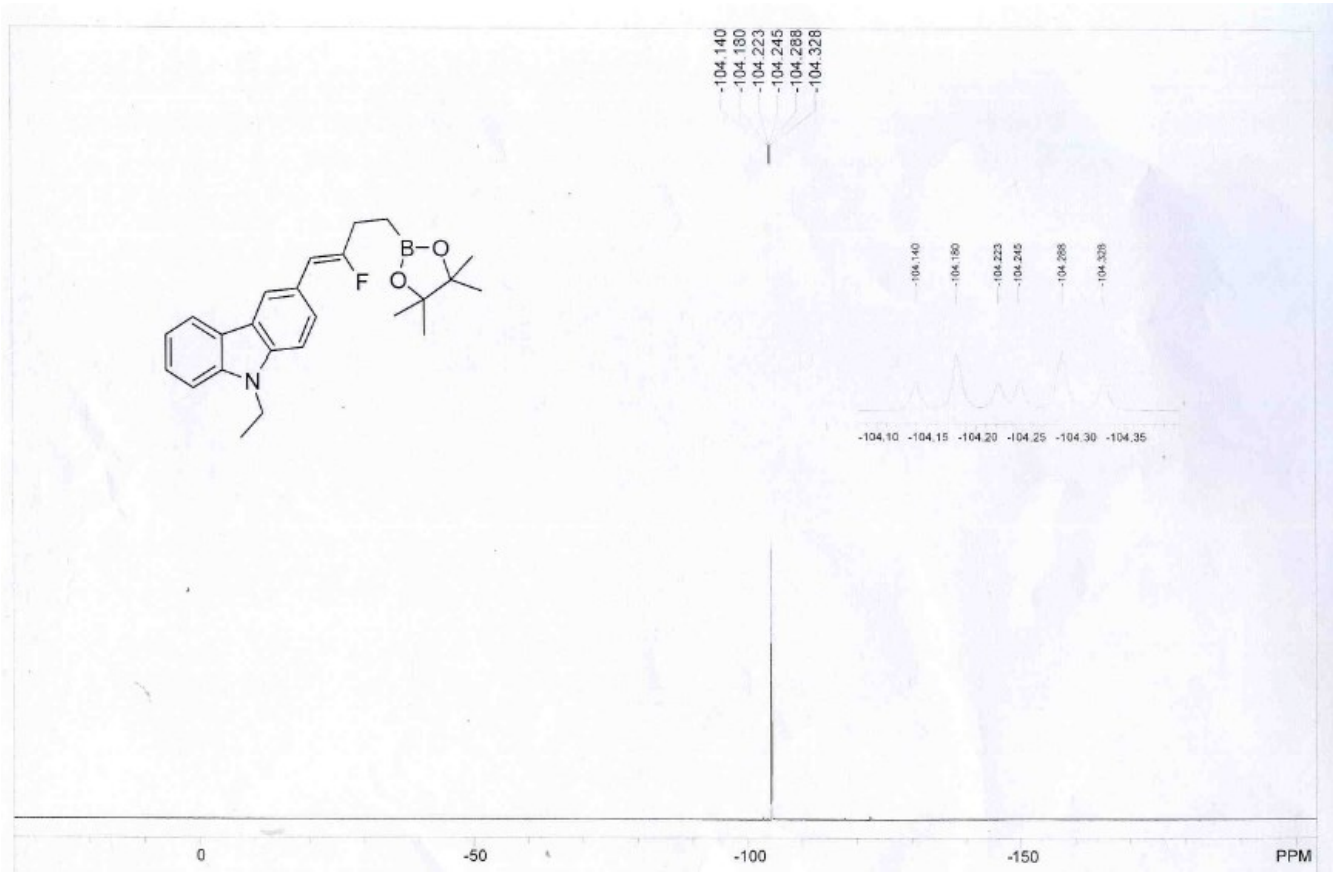
^{1}H NMR spectrum of compound **3o**



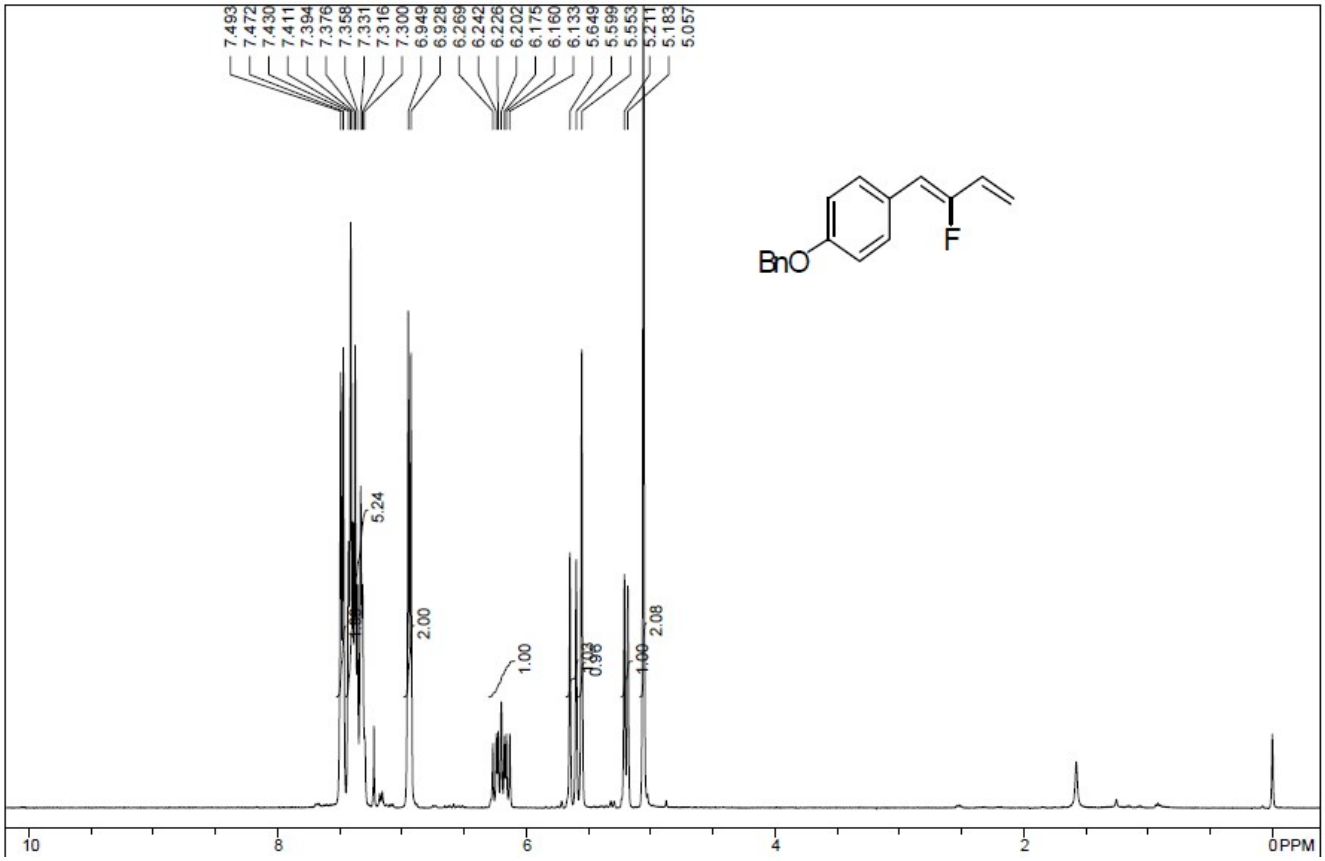
^{13}C NMR spectrum of compound **3o**



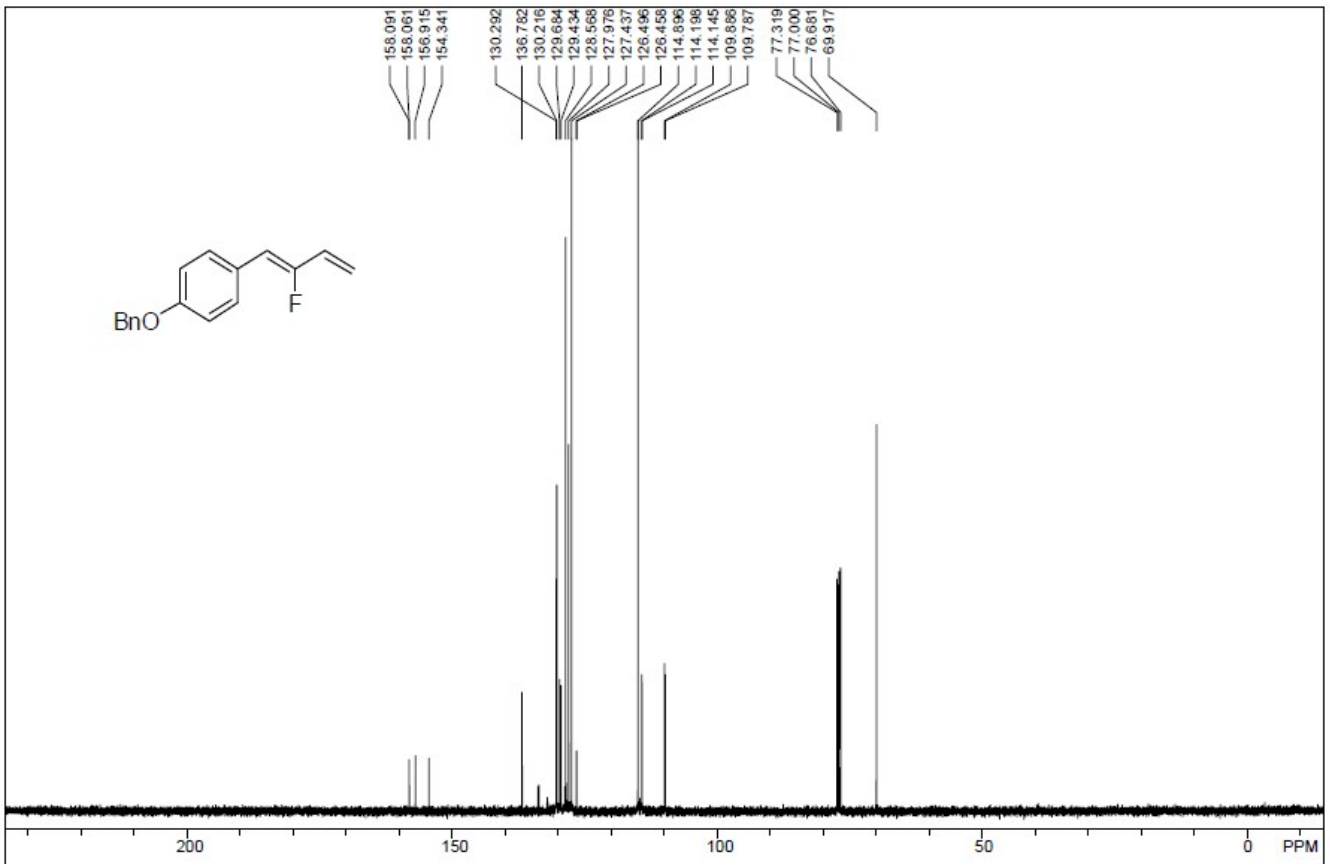
^{19}F NMR spectrum of compound **3o**



^{1}H NMR spectrum of compound **4h**



^{13}C NMR spectrum of compound **4h**



^{19}F NMR spectrum of compound **4h**