Supporting Information

Photoredox catalyzed stereo- and regioselective vicinal fluorosulfonyl-borylation of unsaturated hydrocarbons

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Supplementary Methods

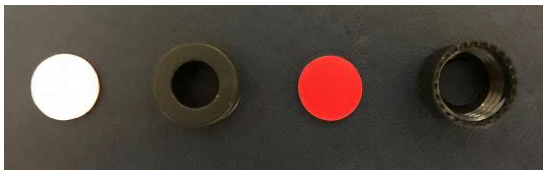
I. General Methods

All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica Gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was done using silica Gel (silica gel 60 F254). TLC plates were analyzed by an exposure to ultraviolet (UV) light and/or submersion in phosphomolybdic acid solution or submersion in $KMnO_4$ solution or in I_2. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out in chloroform-*d* ($CDCl_3$) or acetonitrile-d_3 (CD_3CN). ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers, respectively.^{19}F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as δ values relative to internal TMS (δ 0.00 for ^1H NMR), chloroform (δ 7.26 for ^1H NMR), acetonitrile (δ 1.94 for ^1H NMR), chloroform (δ 77.00 for ^{13}C NMR), and acetonitrile (δ 1.32 or 118.26 for ^{13}C NMR) in parts per million (ppm). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd: doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; Coupling constants (*J*) are reported in Hertz (Hz). Melting points were uncorrected. Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker miccOTOF-Q111. GC-MS spectra were performed on Agilent 5977B.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.10 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C)

Supplementary Figure 1. Fisher 13 x 100 mm tubes

Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)



Supplementary Figure 2. Cap with Septa

II. Synthesis of Starting Materials

Substrates **1a-1e**, **1m-1x, 5a, 5f-5m** were purchased from commercial sources (Alfa, TCI, Energy, Bide and Macklin) and used as received.

Substrates **1f-1l, 5n** were prepared according to the literature.[1]

Substrates **5b-5e** were prepared according to the literature.[2]

III. Synthesis of Sulfonyl fluoride imidazolium salt (2a-2d)[3]

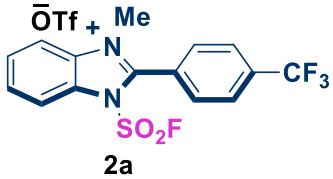
Int-A **2a-2d**

General Procedure:

1) Sodium hydride (60% dispersion in mineral oil.) (36 mmol, 1.2 equiv.) was added to corresponding imidazole (30 mmol, 1 equiv.) in N,N-Dimethylformamide (100 mL). The mixture was stirred at room temperature for 1 hour; A balloon volume of sulfuryl fluoride gas was then added to the reaction system. After the reaction was completed by TLC monitoring, the reaction mixture was evaporated in *vacuo*. Then, the reaction mixture was quenched with water and extracted with ethyl acetate (60 mL x 3). The organic layer was dried over Na_2SO_4, and evaporated in vacuo. The product was purified by flash column chromatography on silica gel with n-pentane/ethyl acetate as eluent to give the corresponding intermediate A.

2) To a solution of the corresponding intermediate A in DCM (50 mL) was added dropwise MeOTf (45 mmol) at 0 ºC. Then, the mixture was stirred at room temperature for 12 hours, while monitoring by TLC. After that time, the mixture was concentrated under rotary evaporation to give a white solid (or a viscous liquid) crude product, to which *tert*-butyl methyl ether (30 mL) was added. With vigorous stirring, a solid precipitate was formed. The precipitate was washed with *tert*-butyl methyl ether (30 mL × 3) and dried in *vacuo* to yield the title compound (**2a-2d**) as a white solid.

1-(fluorosulfonyl)-3-methyl-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazol-3-ium trifluoromethanesulfonate (2a)

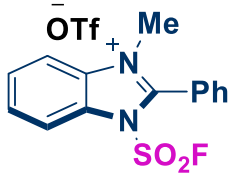


2a

69%; white solid: m.p. 165-166 ºC; ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.24 – 8.20 (m, 1H), 8.17 – 8.11 (m, 1H), 8.09 (d, J = 0.9 Hz, 4H), 8.03 – 7.95 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 152.5, 136.1 (q, J = 33.1 Hz), 132.8, 132.6, 132.0, 130.7, 130.6, 127.6

(q, *J* = 3.8 Hz), 125.9, 124.8, 123.1, 122.0 (q, *J* = 320.8 Hz), 116.0, 115.9, 35.6. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ 64.62, -63.88, -79.31.; HRMS(ESI): caled for $C_{15}H_{11}F_4N_2O_2S^+$ $[M]^+$ 359.0472; found 359.0471.

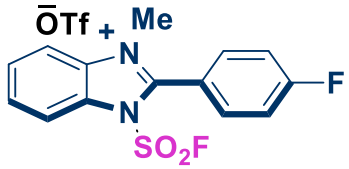
1-(fluorosulfonyl)-3-methyl-2-phenyl-1H-benzo[d]imidazol-3-ium trifluoromethanesulfonate (2b)



2b

73%, white solid: m.p. 169-170 ºC; ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.24 – 8.17 (m, 1H), 8.15 – 8.06 (m, 1H), 8.03 – 7.91 (m, 2H), 7.91 – 7.85 (m, 3H), 7.83 – 7.72 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 154.2, 135.4, 132.7, 131.6, 131.4, 130.6, 130.4, 122.0 (q, *J* = 320.8 Hz), 120.79, 115.92, 115.90, 35.45. 120.8, 115.9, 115.9, 35.5. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ 64.76, -79.23. HRMS(ESI): caled for $C_{14}H_{12}FN_2O_2S^+$ $[M]^+$ 291.0598; found 291.0596.

2-(4-fluorophenyl)-1-(fluorosulfonyl)-3-methyl-1H-benzo[d]imidazol-3-iumtrifluoromethanesulfonate (2c)



2c

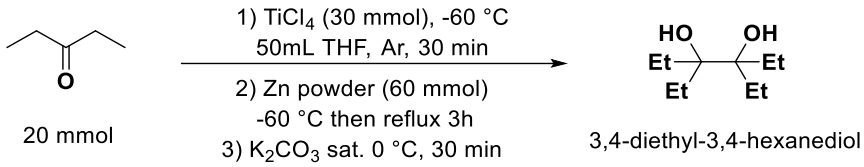
60%; white solid: m.p. 148-149 ºC; ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.24 – 8.16 (m, 1H), 8.14 – 8.04 (m, 1H), 8.01 – 7.95 (m, 2H), 7.94 – 7.89 (m, 2H), 7.59 – 7.48 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.4, 165.8, 153.4, 134.6 (d, *J* = 9.8 Hz), 132.7, 131.8, 130.6, 122.0 (q, *J* = 320.7 Hz), 118.1, 116.9 (d, *J* = 3.4 Hz), 116.0, 115.9, 35.49. ^{19}F NMR (376 MHz, $CDCl_3$) δ 64.65, -79.30, -104.18– -104.25 (m). HRMS(ESI): caled for $C_{14}H_{11}F_2N_2O_2S^+$ $[M]^+$ 309.0504; found 309.0505.

1-(fluorosulfonyl)-2-(4-methoxyphenyl)-3-methyl-1H-benzo[d]imidazol-3-iumtrifluoromethanesulfonate (2d)

2d

43%; white solid: m.p. 162-163 ºC; ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.23 – 8.13 (m, 1H), 8.12 – 8.00 (m, 1H), 7.99 – 7.89 (m, 2H), 7.85 – 7.74 (m, 2H), 7.33 – 7.25 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 165.4, 154.7, 133.7, 132.7, 131.4, 130.6, 130.3, 122.1 (q, *J* = 320.9 Hz), 116.1, 116.0, 115.7, 111.9, 56.8, 35.4. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ 64.72, -79.28. HRMS(ESI): caled for $C_{15}H_{14}FN_2O_3S^+$ $[M]^+$ 321.0704; found 321.0704.

Synthesis of 3,4-Diethyl-3,4-hexanediol[4]

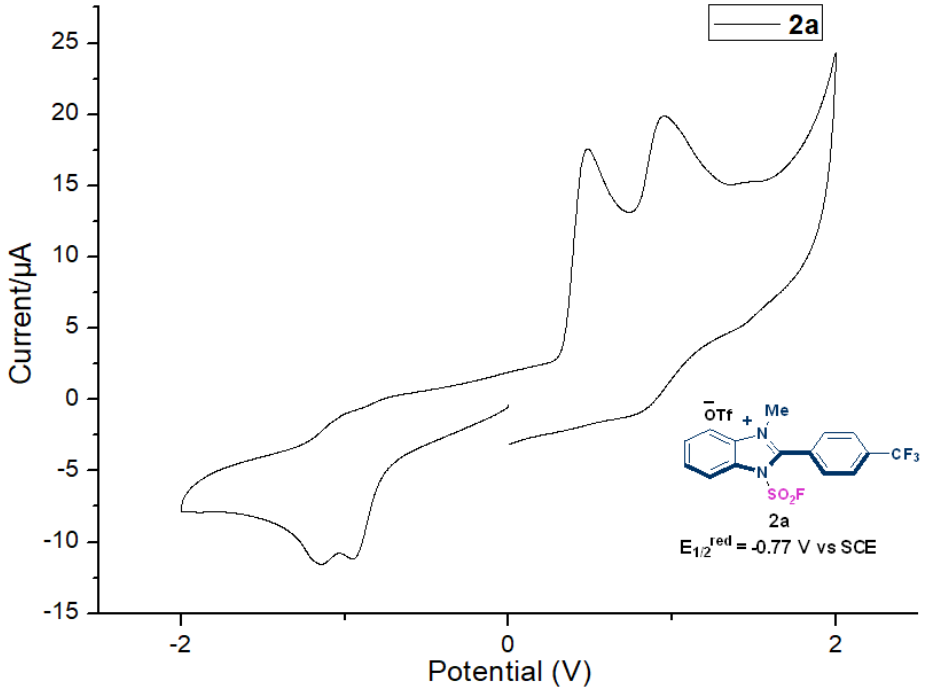


According to the method previously reported by Roberto Sanz et al[4], in an oven dried Schlenck flask (100 mL), the corresponding ketone (20 mmol) and anhydrous THF (50 mL) were added under an inert nitrogen atmosphere. The resulting solution was cooled to -60 ºC and $TiCl_4$ (3.3 mL, 30 mmol) was added slowly via a syringe. The mixture was stirred for 30 min and Zn dust (3.93 g, 60 mmol) was added. Then, the obtained suspension was stirred and refluxed (70 ºC) for 3 h. The reaction mixture was cooled to 0 ºC, saturated aqueous K_2CO_3 (25 mL) was added slowly and stirred for 30 min. The resulting mixture was filtered through a pad of Celite and washed with EtOAc. The filtrate was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/EtOAc = 20:1), 3,4-diethyl-3,4-hexanediol which was obtained pure without further purification.

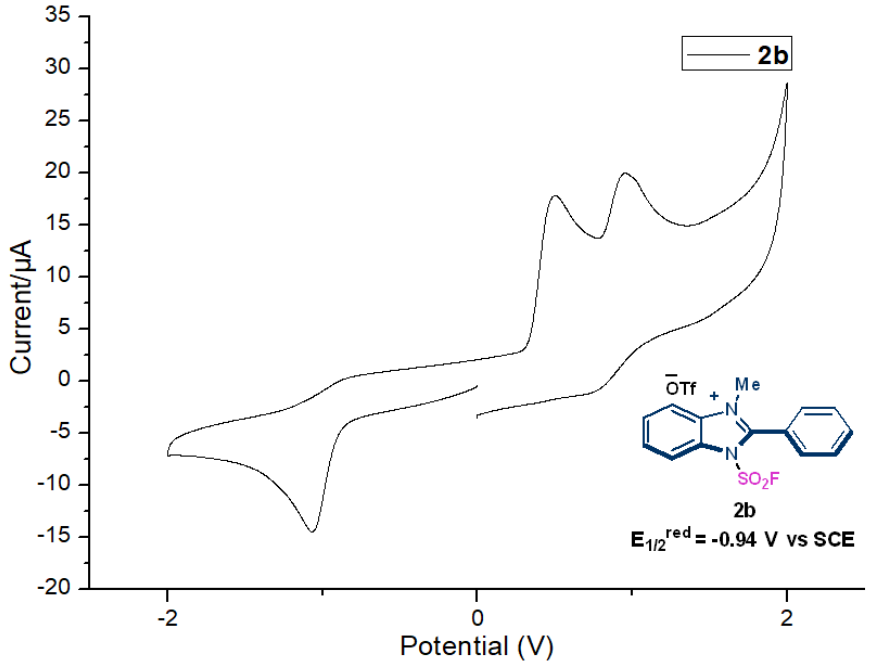
All data matched that reported in the literature.[4]

IV. Cyclic Voltammetry Studies for 2a-2d

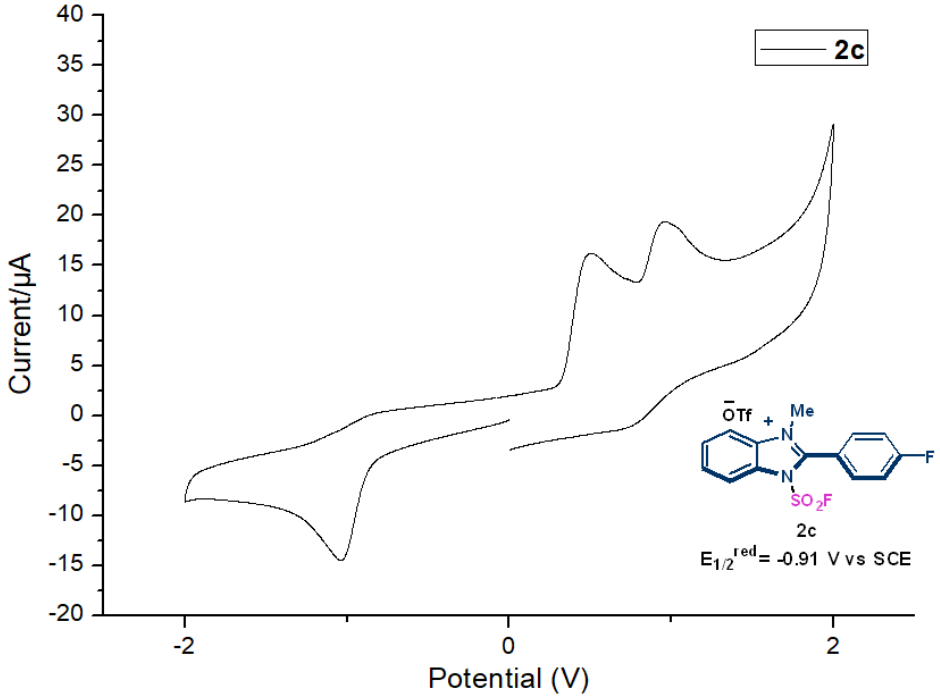
Unless otherwise noted, the cyclic voltammetry measurements were conducted on a MPI-A multi-functional electrochemical and chemiluminescent system (Shanghai CH Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-$AgNO_3$ (0.1 M) in CH_3CN as the reference electrode, tetrabutylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte, using Fc+/Fc as the internal standard, the scan rate was 0.2 V/s.



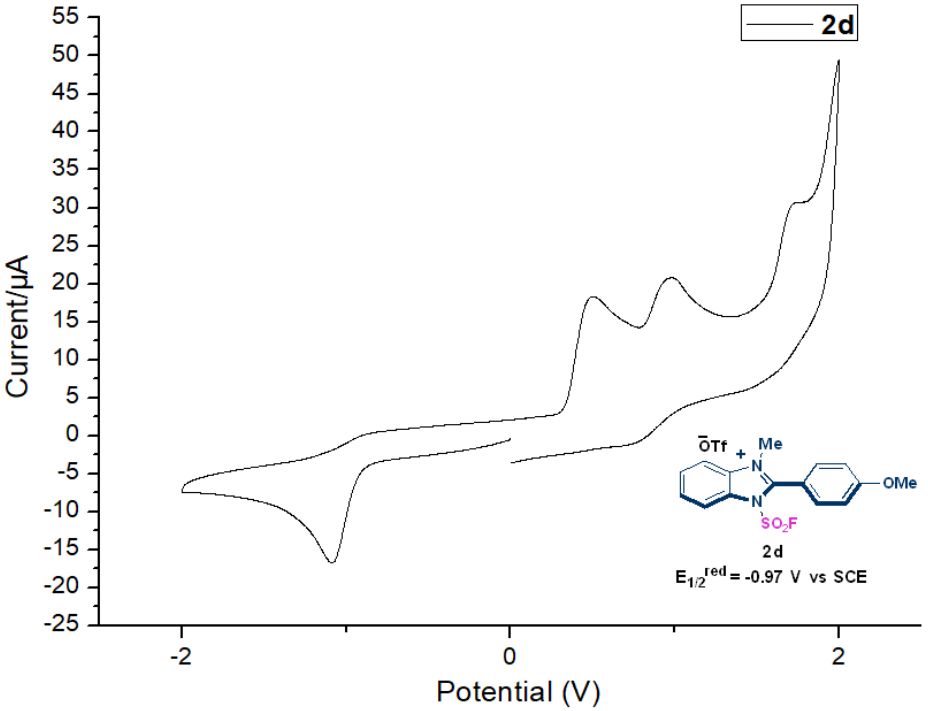
Supplementary Figure 3. Cyclic voltammograms of **2a**



Supplementary Figure 4. Cyclic voltammograms of **2b**



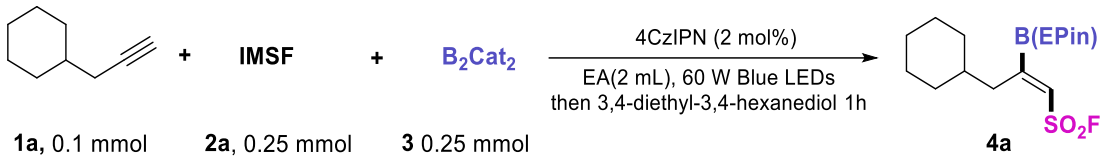
Supplementary Figure 5. Cyclic voltammograms of **2c**



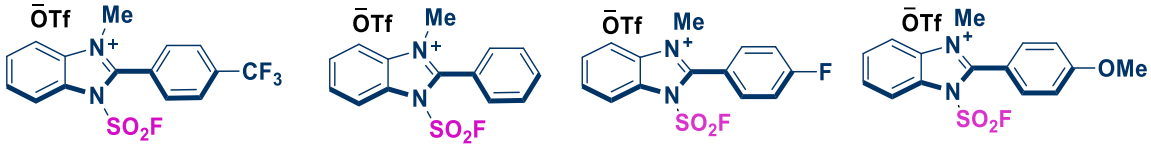
Supplementary Figure 6. Cyclic voltammograms of **2d**

V. Optimizations of the Reaction Conditions

Supplementary Table 1: Optimization of IMSF-reagents[a]



1a, 0.1 mmol **2a**, 0.25 mmol **3** 0.25 mmol **4a**

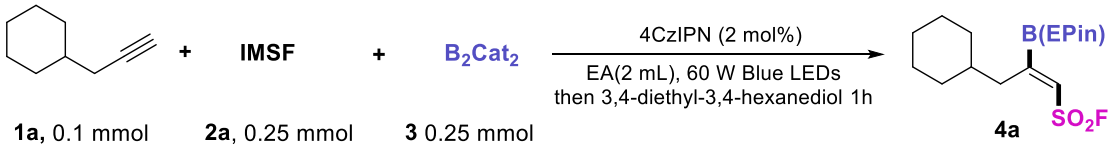


2a **2b** **2c** **2d**

Entry	Change of conditions	Yield of **4a**[b]	*Z/E* ratio[c]
1	None	**23%**	> 20:1
2	**2b** instead of **2a**	8%	> 20:1
3	**2c** instead of **2a**	9%	> 20:1
4	**2d** instead of **2a**	5%	5.6:1

[a] All reactions were carried out with **1a** (12.2 mg, 0.10 mmol), **2** (0.25 mmol, 2.5 equiv.), **3** (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in EA (2.0 mL) under Ar and 60 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The *Z/E* ratio was determined by ^{1}H NMR and ^{19}F NMR.

Supplementary Table 2: Optimization of photocatalysts[a]



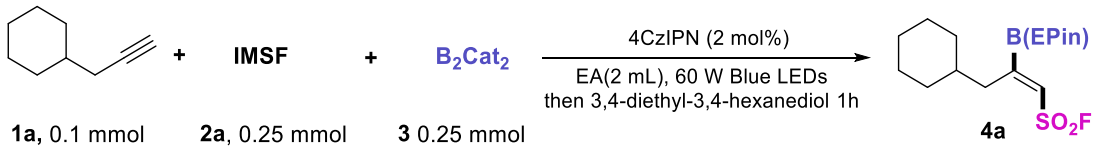
1a, 0.1 mmol **2a**, 0.25 mmol **3** 0.25 mmol **4a**

Entry	Change of conditions	Yield of **4a**[b]	*Z/E* ratio[c]
1	**None**	**23%**	**> 20:1**
2	*fac*-Ir(ppy)$_3$	11%	> 20:1
3	*fac*-Ir[*d*-F-(*p*-*t*-Bu)ppy]$_3$	9%	5.6:1
4	Ir{[dF(CF$_3$)ppy]$_2$(dtbbpy) }PF$_6$	8%	6:1

5	$Ir(mppy)_3$	11%	1.3:1
6	4-DPA-iPN	7%	> 20:1
7	$Ir[(bpy)_2dtbbpy]PF_6$	7%	> 20:1
8	2-Isopropylthioxanthone	11%	4.9:1

[a] All reactions were carried out with **1a** (12.2 mg, 0.10 mmol), **2a** (0.25 mmol, 2.5 equiv.), **3** (0.25 mmol, 2.5 equiv.), photocatalysts (2 mol%) in EA (2.0 mL) under Ar and 60 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The *Z/E* ratio was determined by ^1H NMR and ^{19}F NMR.

Supplementary Table 3: Optimization of solutions[a]

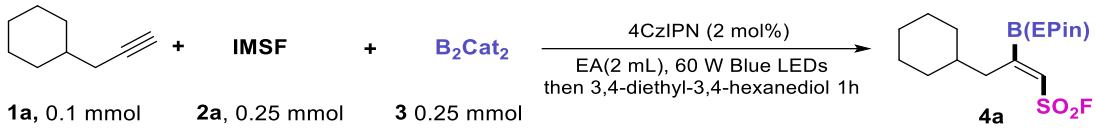


1a, 0.1 mmol **2a**, 0.25 mmol **3** 0.25 mmol **4a**

Entry	Change of additives	Yield of **4a**[b]	*Z/E* ratio[c]
1	**None**	**23%**	**> 20:1**
2	Methyl acetate	7%	> 20:1
3	1,4-dioxane	0	-
4	CH_3CN	6%	> 20:1
5	Mesitylene	trace	-
6	Acetone	0	-
7	CH_3CH_2OH	0	-

[a] All reactions were carried out with **1a** (12.2 mg, 0.10 mmol), **2a** (0.25 mmol, 2.5 equiv.), **3** (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solution (2.0 mL) under Ar and 60 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The *Z/E* ratio was determined by ^1H NMR and ^{19}F NMR.

Supplementary Table 4: Optimization of conditions[a]

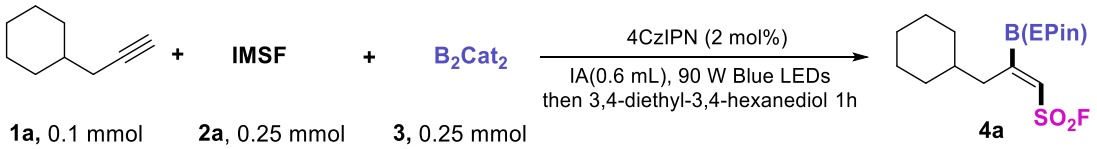


1a, 0.1 mmol **2a**, 0.25 mmol **3** 0.25 mmol **4a**

Entry	Change of conditions	Yield of **4a**[b]	*Z/E* ratio[c]
1	None	23%	> 20:1
2	30W Blue LEDs	32%	> 20:1
3	90W Blue LEDs	46%	> 20:1
4	EA (1 mL)	36%	> 20:1
5	EA (1.5 mL)	33%	> 20:1
6	EA (2.5 mL)	25%	> 20:1
7	Isopropyl acetate (1 mL), 90W Blue LEDs	60%	> 20:1
8	**Isopropyl acetate (0.6 mL), 90W Blue LEDs**	**95% (70%)[d]**	**> 20:1**
9	Isopropyl acetate (0.8 mL), 90W Blue LEDs	49%	> 20:1
10	Isopropyl acetate (1.2 mL), 90W Blue LEDs	31%	> 20:1
11	In darkness	0	-
12	w/o 4CzIPN	0	-

[a] All reactions were carried out with **1a** (12.2 mg, 0.10 mmol), **2a** (0.25 mmol, 2.5 equiv.), **3** (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solution (X mL) under Ar and light irradiation, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The *Z/E*ratio was determined by ^{1}H NMR and ^{19}F NMR. [d] Isolated yield.

Supplementary Table 5: Optimization of solvents under the optimal condition[a]

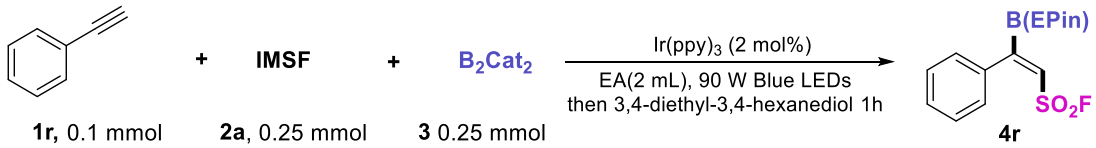


1a, 0.1 mmol **2a**, 0.25 mmol **3,** 0.25 mmol **4a**

Entry	Change of additives	Yield of **4a**[b]	Surplus of **1a**[b]
1	**None**	**95% (70%)**[c]	**5%**
2	EtOH	0%	100%
3	CH_3CN	27%	73%
4	EA	84%	16%
5	THF	35%	65%
6	DCM	44%	56%
7	Toluene	17%	83%
8	DMF	0%	100%
9	Methyl acetate (MA)	82%	18%
10	DME	38%	62%

[a] All reactions were carried out with **1a** (12.2 mg, 0.10 mmol), **2a** (0.25 mmol, 2.5 equiv.), **3** (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solvents (0.6 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated yield.

Supplementary Table 6: Optimization of conditions for aryl alkynes[a]



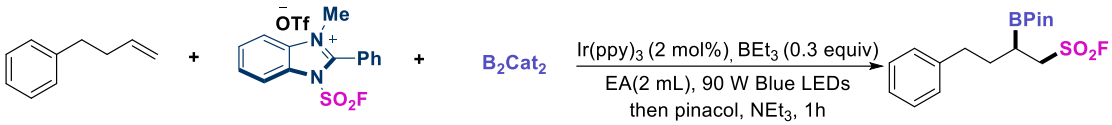
1r, 0.1 mmol **2a**, 0.25 mmol **3** 0.25 mmol **4r**

Entry	Change of conditions	Yield of **4r**[b]	*Z/E* ratio[c]
1	None	41	> 20:1
2	30W, 24h	41	> 20:1
3	60W, 24h	38	> 20:1
4	**2b**, 90W, 24h	34	> 20:1

5	**2b**, 60W, 24h	32	> 20:1
6	**2b**, 30W, 24h	30	> 20:1
7	4CzIPN 30W, 12h	31	> 20:1
8	4CzIPN 90W, 12h	7	> 20:1
9	**2a**, 4CzIPN 30W, 12h	24	> 20:1
10	**2a**, 4CzIPN 90W, 12h	42	> 20:1
11	**2a**, 4CzIPN 90W, 24h	36	> 20:1
12	**2a**, 4CzIPN 30W, 24h	50	> 20:1
13	**2a**, 4CzIPN 60W, 24h	55	> 20:1
14	**2a** (3.0 equiv), 4CzIPN 30W, 24h	40	> 20:1
15	**2a**, 4CzIPN 60W, 12h	54	> 20:1
16	**2a**, 4CzIPN 60W, 6h	49	> 20:1
17	**2a:3**=3:3, 60W, 12h	52	> 20:1
18	**2a:3**=3:3, 60W, 24h	44	> 20:1
19	Isopropyl acetate instead EA	26	> 20:1
20	Methyl acetate instead EA	48	> 20:1
21	**2a, Isopropyl acetate (0.6 mL), 4CzIPN 90W, 13h**	**69(50)[d]**	**> 20:1**

[a] All reactions were carried out with **1r** (10.2 mg, 0.10 mmol), **2a** (0.25 mmol, 2.5 equiv.), **3** (0.25 mmol, 2.5 equiv.), 4CzIPN (2 mol%) in solution (X mL) under Ar and light irradiation, the reaction was completed as monitored by TLC analysis, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 hour. [b] Yields determined by GC using dodecane as an internal standard. [c] The *E/Z* ratio was determined by ^{1}H NMR and ^{19}F NMR. [d] Isolated yield.

Supplementary Table 7: Optimization of solvents for fluorosulfonyl-borylation of olefins[a]

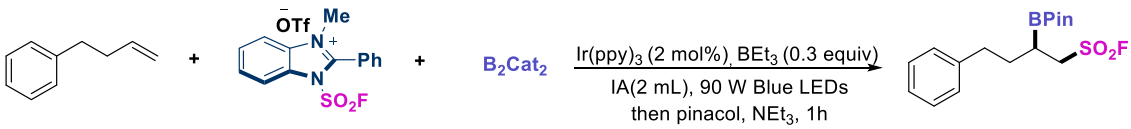


5a, 0.1 mmol | **2b**, 0.25 mmol | **3** 0.30 mmol | **6a**

Entry	Change of reagents	Yield of **6a**[b]
1	None	54
2	Methyl acetate	49
3	**Isopropyl acetate(IA)**	**68**
4	DCM	nd
5	THF	nd
6	CH_3CN	13
7	DME	7
8	Acetone	11
9	DCE	3

[a] All reactions were carried out with **5a** (13.2 mg, 0.10 mmol), **2b** (0.25 mmol, 2.5 equiv.), **3** (0.3 mmol, 3.0 equiv.), BEt_3 (0.03 mmol, 0.3 equiv.), *fac*-Ir(ppy)$_3$ (2 mol%), in Solvents (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 8: Optimization of photocatalysts for fluorosulfonyl-borylation of olefins[a]



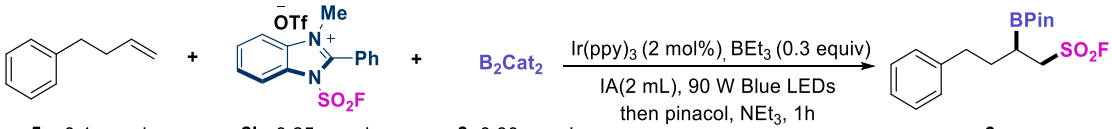
5a, 0.1 mmol | **2b**, 0.25 mmol | **3** 0.30 mmol | **6a**

Entry	Change of Photocatalysts	Yield of **6a**[b]
1	**None**	**68**
2	*fac*-Ir[*d*-F-(*p*-*t*-Bu)ppy]$_3$	46
3	Ir[{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6	38

4	4CzIPN	52
5	$Ir(mppy)_3$	61
6	4-DPA-iPN	29
7	$Ir[dF(CF_3)ppy]_3$	41
8	$Ir[dFppy]_3$	48

[a] All reactions were carried out with **5a** (13.2 mg, 0.10 mmol), **2b** (0.25 mmol, 2.5 equiv.), **3** (0.3 mmol, 3.0 equiv.), BEt_3 (0.03 mmol, 0.3 equiv.), photocatalysts (2 mol%), in IA (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 9: Optimization of material ratio for fluorosulfonyl-borylation of olefins[a]



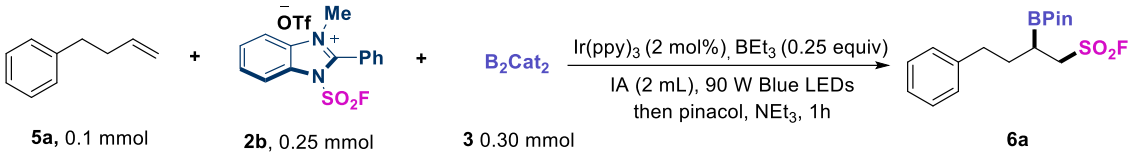
5a, 0.1 mmol **2b**, 0.25 mmol **3,** 0.30 mmol **6a**

Entry	Change of material ratio(**5a**:**2a**:**3**:BEt_3)	Yield of **6a**[b]
1	None	68
2	1:1.5:2:0.2	28
3	1:2:2:0.2	19
4	1:2.5:2:0.2	28
5	1:2.5:1.5:0.2	10
6	1:2.5:2.5:0.2	23
7	1:2.5:3:0.2	64
8	1:2.5:3:0.15	47
9	**1:2.5:3:0.25**	**69**
10	1:2.5:3:0.35	66
11	1:2:2:0.15	49
12	1:2:3:0.3	19
13	1:2:2:0.3	49
14	1:2:3:0.2	49
15	1:1.5:3:0.3	17

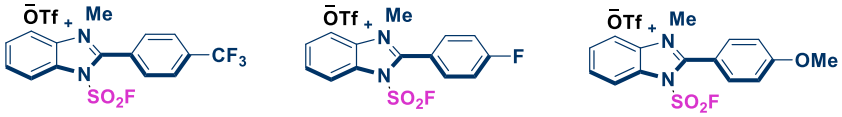
[a] All reactions were carried out with **5a** (13.2 mg, 0.10 mmol), **2b** (x mmol, x equiv.), **3** (y mmol, y equiv.), BEt_3 (z mmol, z equiv.), *fac*-$Ir(ppy)_3$ (2 mol%), in IA (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and

triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 10: Optimization of IMSF reagents and control experiments for fluorosulfonyl-borylation of olefins[a]



5a, 0.1 mmol **2b**, 0.25 mmol **3** 0.30 mmol **6a**

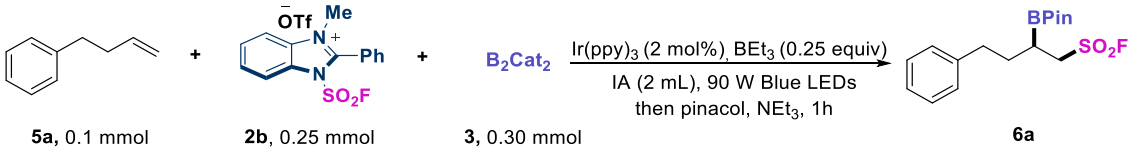


2a **2c** **2d**

Entry	PC	Yield of **6a**[b]
1	**None**	**69**
2	**2a** instead of **2b**	68
3	**2c** instead of **2b**	59
4	**2d** instead of **2b**	8
5	w/o $Ir(ppy)_3$	nd
6	In the drakness	nd

[a] All reactions were carried out with **5a** (13.2 mg, 0.10 mmol), **2** (0.25 mmol, 2.5 equiv.), **3** (0.3 mmol, 3 equiv.), BEt_3 (0.025 mmol, 0.25 equiv.), *fac*-$Ir(ppy)_3$ (2 mol%), in IA (2.0 mL) under Ar and 90 W blue LEDs, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard.

Supplementary Table 11: Optimization of IMSF reagents and other conditons for fluorosulfonyl-borylation of olefins[a]



5a, 0.1 mmol **2b**, 0.25 mmol **3,** 0.30 mmol **6a**

2a

Entry	Change of conditions	Yield of **6a**[b]
1	None	69
2	30W, 12h	67

3	60W, 12h	62
4	90W, 24h	25
5	**2a**, 90W, 24h	80
6	3 equiv of **2b**, 12h	54
7	3.5 equiv of **2b**, 12h	62
8	3.0 equiv of **2b**, 12h, 30W	21
10	**3.0 equiv of 2a, 12h, 30W**	**86(73)[c]**
11	3.0 equiv of **2b**, 12h, 60W	50

[a] All reactions were carried out with **5a** (13.2 mg, 0.10 mmol), **2** (x mmol, x equiv.), **3** (0.3 mmol, 3 equiv.), BEt_3 (0.025 mmol, 0.25 equiv.), *fac*-$Ir(ppy)_3$ (2 mol%), in IA (2.0 mL) under Ar and Light irradiation, the reaction was completed as monitored by TLC analysis, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. [b] Yields determined by GC using dodecane as an internal standard. [c] Isolated Yields.

VI. General Procedure for the Synthesis of the Products 4, 6-9, 11, 13-15, 17-18, 20-21.

General Procedure for the synthesis of products 4a, 4c-4e. Condition A: Under argon, to a solution of 4CzIPN (2 mol%), 2,2'-Bis-1,3,2-benzodioxaborole **3** (0.25 mmol, 2.5 equiv.) and IMSF reagent **2a** (0.2 mmol, 2 equiv.) in dried isopropyl acetate (0.6 mL) was added corresponding alkynes **1a, 1c-1e** (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min-12h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of products 4b, 4f-4l. Condition B: Under argon, to a solution of 4CzIPN (2 mol%), 2,2'-Bis-1,3,2-benzodioxaborole **3** (0.25 mmol, 2.5 equiv.) and IMSF reagent **2a** (0.2 mmol, 2 equiv.) in dried isopropyl acetate : ethyl acetate= 2:1 (0.8 mL) was added corresponding alkynes **1b**, **1f-1l** (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min-12h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of products 4m-4x. Condition C: Under argon, to a solution of 4CzIPN (2 mol%), 2,2'-Bis-1,3,2-benzodioxaborole **3** (0.25 mmol, 2.5 equiv.) and IMSF reagent **2a** (0.2 mmol, 2 equiv.) in dried isopropyl acetate (0.6 mL) was added corresponding alkynes **1m-1x** (0.1 mmol) at room temperature. After that, the tube was

exposed to a 90 W blue LEDs about 13 h, after which 3,4-diethyl-3,4-hexanediol was added to the reaction system and stirred for 1 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of product 6. Condition D: Under argon, to a solution of *fac*-Ir(ppy)$_3$ (2 mol%), BEt$_3$ (0.025 mmol, 0.25 equiv.), 2,2'-Bis-1,3,2-benzodioxaborole **3** (0.3 mmol, 3.0 equiv.) and IMSF reagent **2a** (0.3 mmol, 3.0 equiv.) in dried isopropyl acetate (2 mL) was added corresponding olefins **5** (0.1 mmol) at room temperature. After that, the tube was exposed to a 30 W blue LEDs about 12 h, after which pinacol and triethylamine was added to the reaction system and stirred for 1-2 h. The reaction was completed as monitored by TLC analysis and the reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of product 7 and 8[5]**. Condition E:** Under argon, to a solution of **4m** (0.05 mmol) in dried MeOH (1 mL) was added CuX_2 (1.0 equiv.) at room temperature. After that, the tube was heated to 80 ºC about 12 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of product 9[6]**. Condition F:** Under argon, to a solution of **4m** (0.05 mmol), Pd(OAc)$_2$ (5 mol%), P(o-Tol)$_3$ (10 mol%), in dried toluene (0.5 mL) was added H_2O (2.5 equiv.) at room temperature. After that, the tube was heated to 80 ºC about 12

h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of product 11, 13, 17, 20[7]**. Condition G:** Under argon, to a solution of **4m** (0.05 mmol), $Pd(OAc)_2$ (15 mol%), SPhos (35 mol%), K_3PO_4 (1.5 equiv.) in dried toluene (0.5 mL) was added corresponding aryl bromides **12**, **16**, **19** (0.06 mmol) or 3,6-dihydro-2H-pyran-4-yl trifluoromethanesulfonate **10** (0.06 mmol) at room temperature. After that, the tube was heated to 80 ºC about 12 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of product 14[8]**. Condition H:** To a solution of sesamol (1.0 equiv.), HMDS (1.0 equiv.), and BTMG (20 mol%) in dried MeCN (0.5 mL) was added corresponding alkenes **13** at room temperature. After that, the tube was heated to a 60 ºC about 1 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

General Procedure for the synthesis of product 15, 21[9]**. Condition I:** To a solution of amines (2.0 equiv.), $Ca(NTf)_2$ (1.0 equiv.) in t-amylOH (0.5 mL) was added corresponding alkenes **13** or **20** at room temperature. After that, the tube was heated to a 60 ºC about 24 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was

evaporated in *vacuo*. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

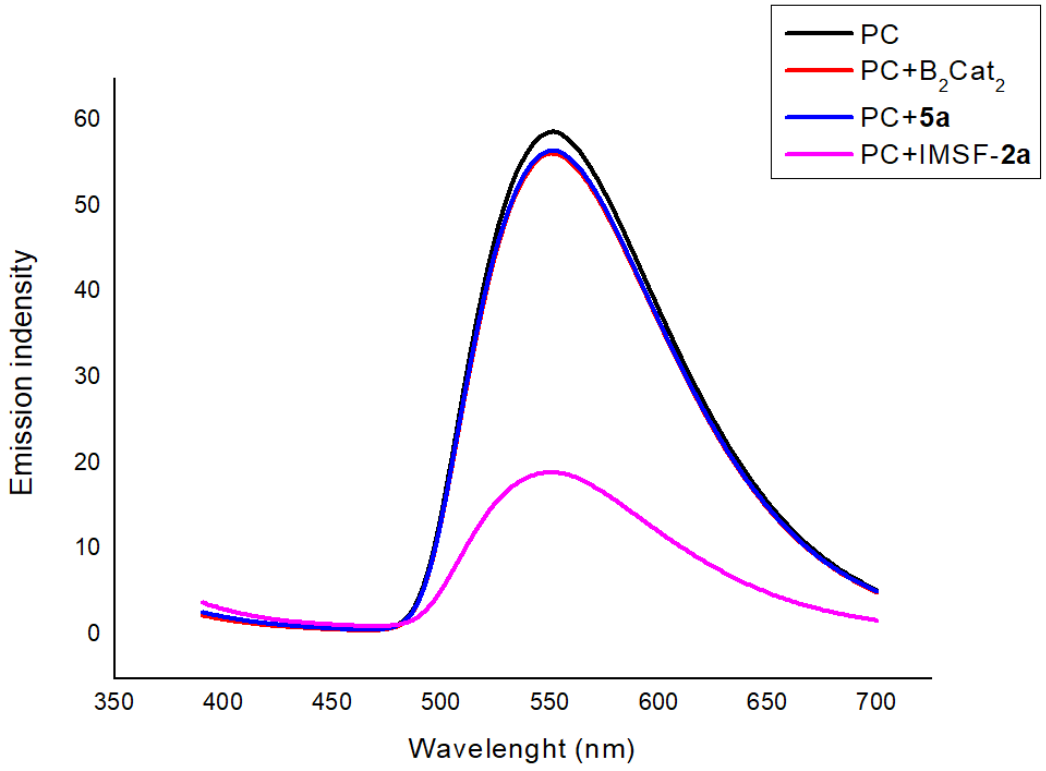
General Procedure for the synthesis of product 18[3]**. Condition J:** To a solution of estrone (2.0 equiv.), KOH (2.0 equiv.) in MeCN (0.5 mL) was added corresponding alkene **17** at room temperature. After that, the tube was heated to a 50 ºC about 12 h, then until the reaction was completed as monitored by TLC analysis. The reaction mixture was evaporated in vacuo. The crude products were directly purified by flash chromatography on silica gel to give the desired products.

VII. Mechanistic experiments

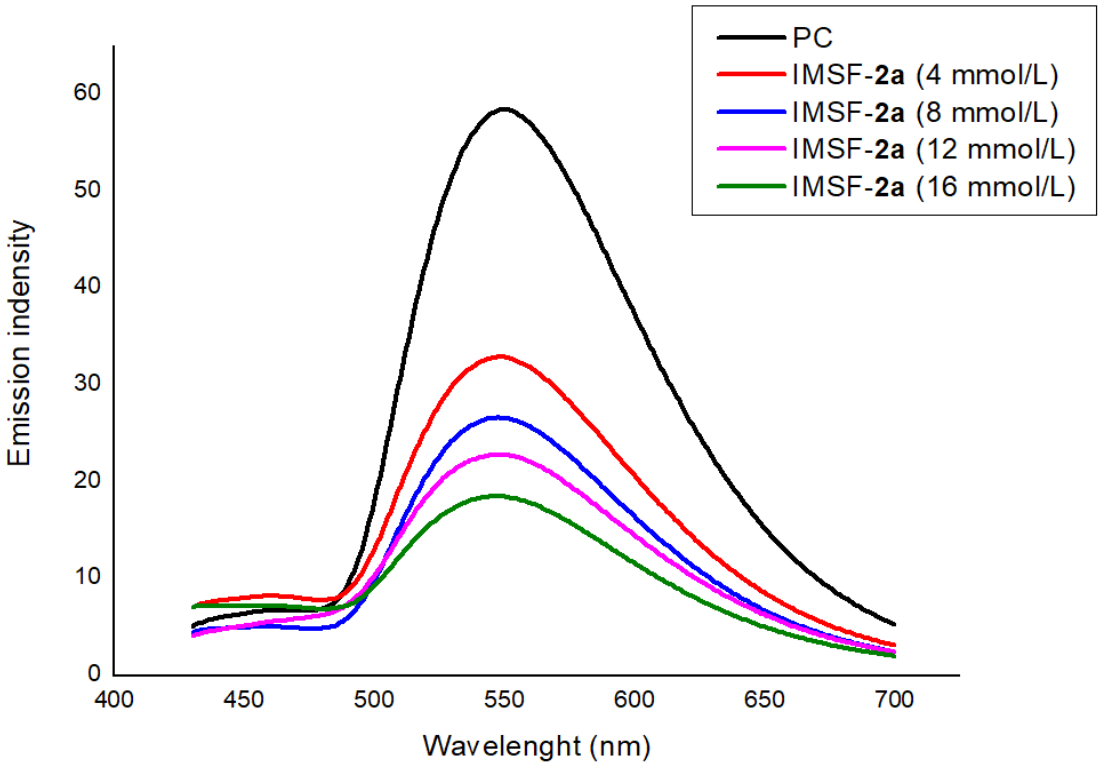
A. Luminescence quenching experiment

The luminescence quenching experiment was taken using a F-4600 FL Spectrophotometer (Hitachi, Japan). The experiments were carried out in 5 x 10^{-4} mol/L of $Ir(ppy)_3$ in CH_3CN at 25 ^oC with an excitation wavelength of 380 nm and an excitation and emission bandwidth of 5 nm, The scanspeed was set at 1200 nm/min and the PMT voltage was set to 500 V. The concentrations of quencher (**5a**, IMSF-**2a**, B_2Cat_2) in CH_3CN were 0.01 mmol/mL. The concentrations of quencher IMSF-**2a** in CH_3CN was 4 mmol/L, 8 mmol/L, 12 mmol/L, 16 mmol/L. (see supplementary figure **7** and supplementary figure **8-9**)

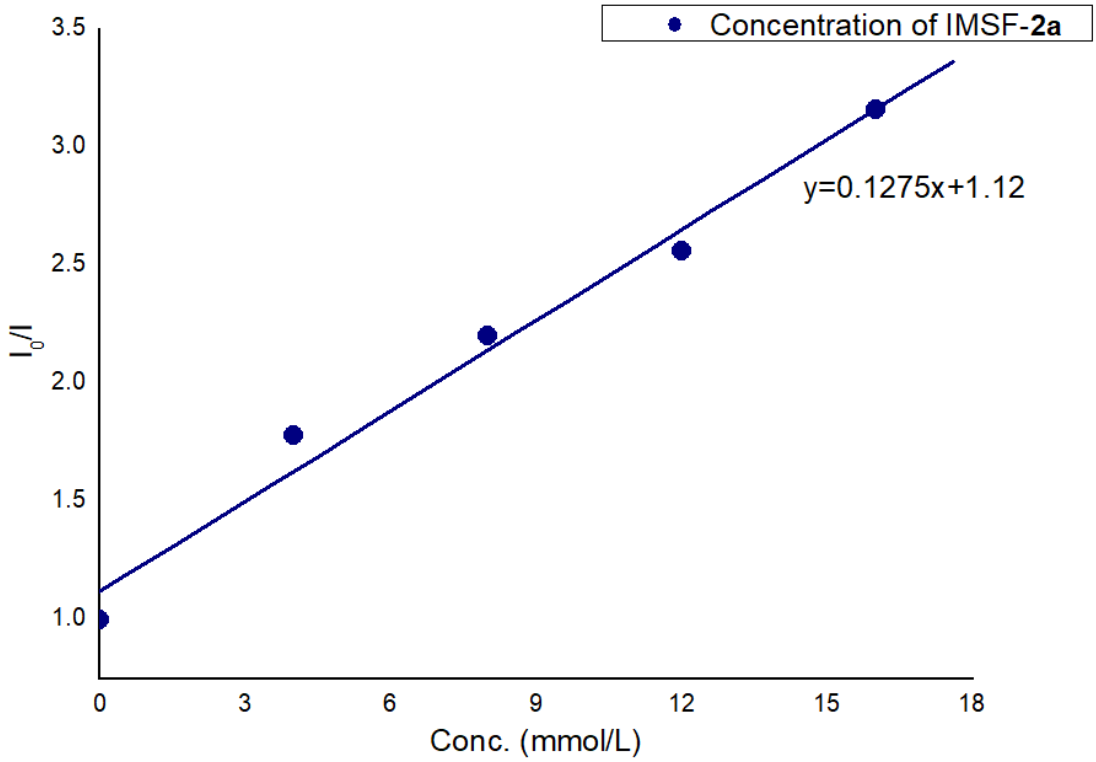
To determine whether a reductive or oxidative quenching cycle is operative in the reaction, fluorescence quenching studies were conducted. Based on the above data, photoexcited $Ir(ppy)_3$* can be quenched by IMSF-**2a**, which involving a oxidative quenching cycle.



Supplementary Figure 7. The data of fluorescence quenching of $Ir(ppy)_3$, B_2Cat_2, **5a**, IMSF-**2a**



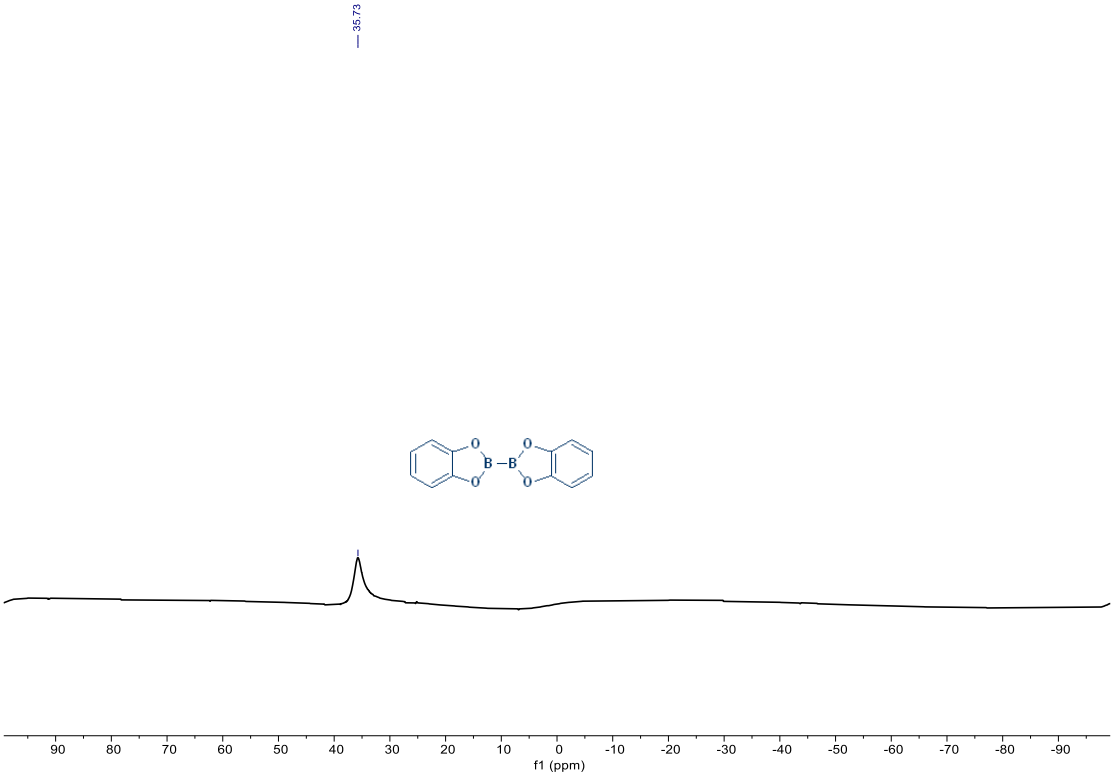
Supplementary Figure 8. The data of fluorescence quenching of $Ir(ppy)_3$ by different concentrations of IMSF-**2a**



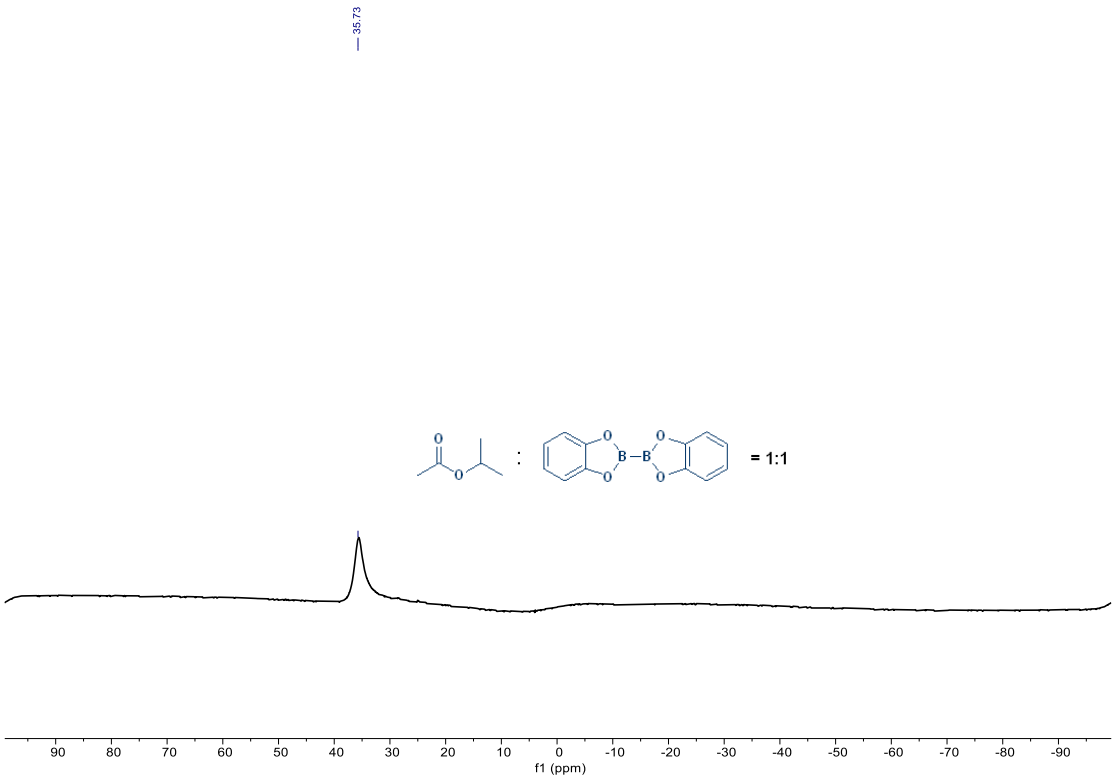
Supplementary Figure 9. Stern-Volmer plot of $Ir(ppy)_3$ at different concentrations of IMSF-**2a**

B. ^{11}B NMR experiments

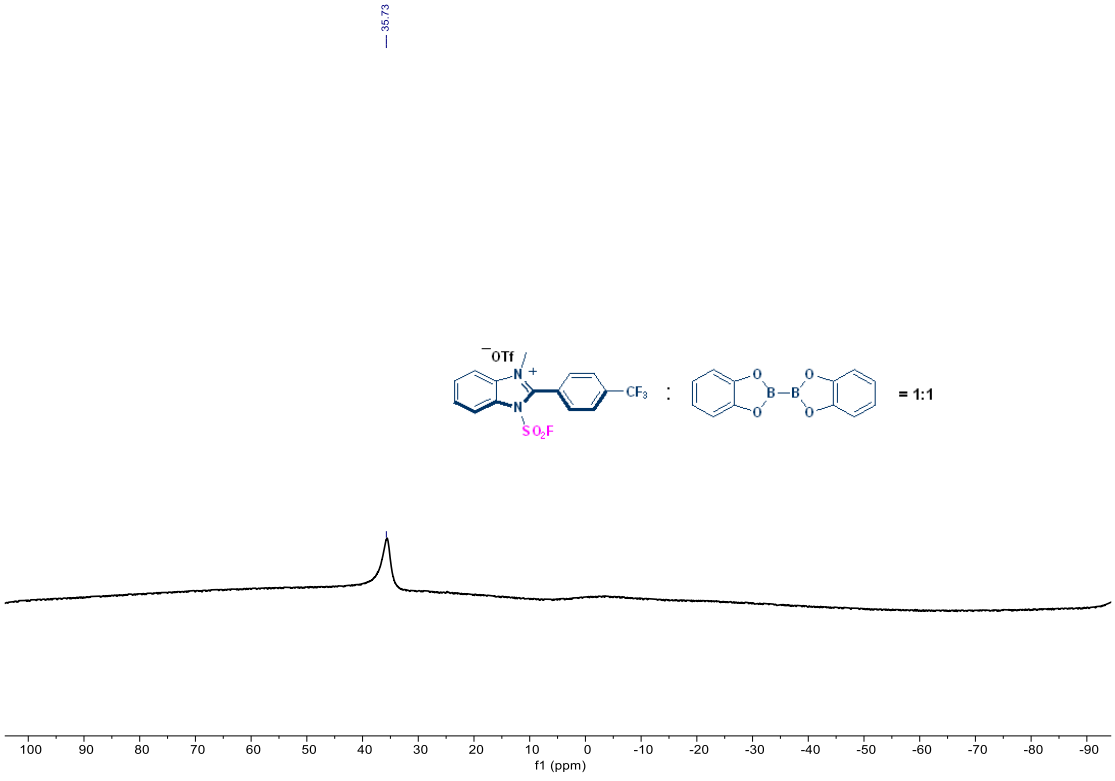
All ^{11}B NMR data was recorded at 25 ^{o}C. See supplementary figure **10-13** for details of reagents and solvents; supplementary figure **10** shows B_2Cat_2 in CD_3CN; supplementary figure **11** shows B_2Cat_2 : Isopropyl acetate (IA) = 1:1 in CD_3CN; supplementary figure **12** shows B_2Cat_2 : IMSF-**2a** = 1:1 in CD_3CN; supplementary Figure **13** shows B_2Cat_2 : 1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole = 1:1 in CD_3CN.



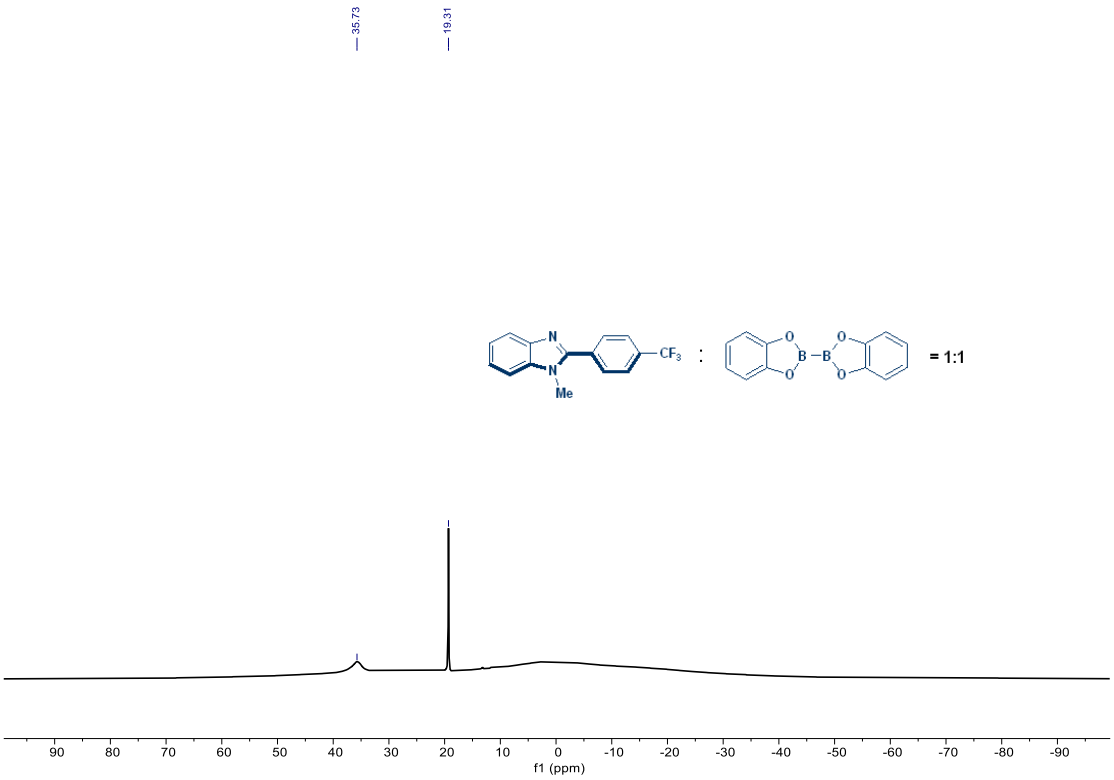
Supplementary Figure 10. B_2Cat_2 in CD_3CN



Supplementary Figure 11. B_2Cat_2 : Isopropyl acetate =1:1 in CD_3CN



Supplementary Figure 12. B_2Cat_2 : IMSF-**2a** =1:1 in CD_3CN

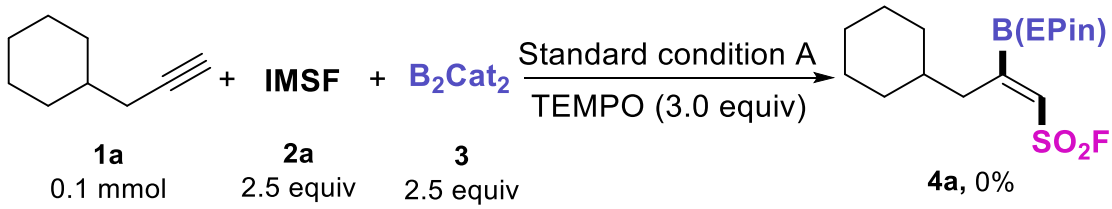


Supplementary Figure 13. B_2Cat_2 : 1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole =1:1 in CD_3CN

^{11}B NMR experiments reveal that there is just a single signal whether only B_2Cat_2 in CD_3CN, mix isopropyl acetate with B_2Cat_2 in CD_3CN or mix IMSF-**2a** with B_2Cat_2 in CD_3CN (supplementary figure 10-12); when mix imidazole residue with B_2Cat_2 in CD_3CN, the latter shows one upfield signal (supplementary figure 13). The upfield shifting supports the ligation of imidazole residue with diboron species.

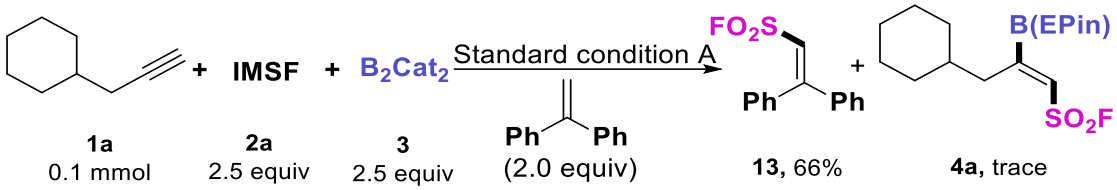
C. Control Experiment

(a)



Under argon, to a solution of 4CzIPN (2 mol%), B_2Cat_2 (2.5 equiv.), TEMPO (3.0 equiv.) and **IMSF-2a** (0.25 mmol, 2.5 equiv.) in dried IA (0.6 mL) was added corresponding alkyne **1a** (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC. GC showed that no major product **4a** was formed after addition of 0.3 mmol of TEMPO.

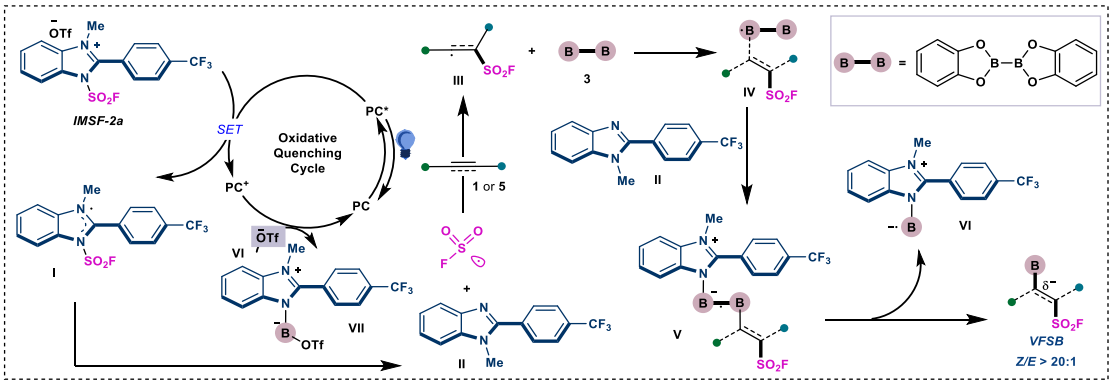
(b)



Under argon, to a solution of 4CzIPN (2 mol%), B_2Cat_2 (2.5 equiv), 1,1-diphenylethylene (0.2 mmol, 2.0 equiv.) and **IMSF**- **2a** (0.25 mmol, 2.5 equiv.) in dried IA (0.6 mL) was added corresponding alkyne **1a** (0.1 mmol) at room temperature. After that, the tube was exposed to a 90 W blue LEDs about 40min until the reaction was completed as monitored by TLC analysis. Subsequently, the reaction mixture was analyzed by GC. GC showed that trace product **4a** was formed after addition of 0.2 mmol of 1,1-diphenylethylene. In addition, product **13** can be obtained with a 66% separation yield.

D. Proposed mechanism

From the above mechanistic experiments, we speculate on the possible mechanism of the reaction: First, under the irradiation, the cationic reagent **2a** can be reduced by excited state photocatalyst (PC*) to generate radical intermediate **I** and releases SO_2F radical and imidazole residue **II**. Then the addition of·SO_2F radical to the alkynes regioselectively furnishes vinylic radical intermediate **III**. Subsequent addition of vinyl radical **III** to B_2cat_2 afforded a *Z*-vinyl diboron radical species **IV**. The control of stereoselectivity is governed by steric repulsion between the fluorosulfonyl group and the boronates. Then, the activation of diboron reagent by in situ generated imidazole residues **II** forms a highly reactive B–N heteroleptic intermediate **V**, which leads to the desired bifunctional products **4** or **6** and imidazole stabilized boryl radical species **VI**. Finally, photo-oxidation of **VI** followed by coupling with ⁻OTf affords boryl imidazolium salt **VII** and regenerates PC. (**supplementary figure 14**).



Supplementary Figure 14. Proposed mechanism

VIII. References

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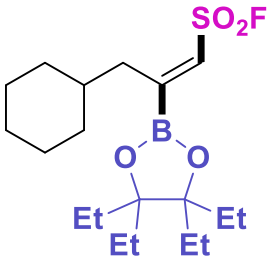
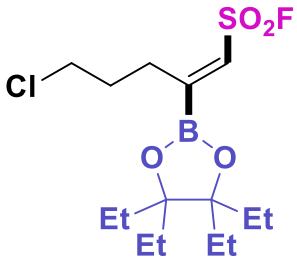
IX. Characteristic Data

(Z)-3-cyclohexyl-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)prop-1-ene-1-sulfonyl fluoride (4a)



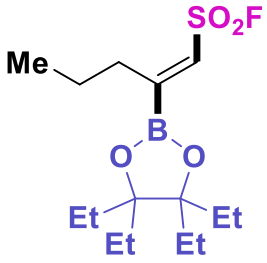
70% (27.2 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (s, 1H), 2.59 (d, *J* = 6.8 Hz, 2H), 1.79 – 1.60 (m, 13H), 1.34 – 1.11 (m, 6H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 129.8 (d, *J* = 23.2 Hz), 90.3, 38.1, 37.9, 33.2, 32.8, 26.3, 26.2, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 65.06. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.09. HRMS(ESI): caled for $C_{19}H_{35}BFO_4S^+$ [M + H]$^+$ 389.2328; found 389.2326.

(Z)-5-chloro-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene-1-sulfonyl fluoride (4b)



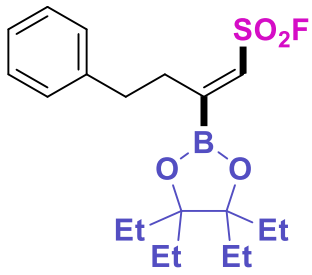
57% (20.9 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.91 (s, 1H), 3.56 (t, *J* = 6.7 Hz, 2H), 2.80 (ddt, *J* = 9.2, 5.9, 1.3 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.71 (qd, *J* = 7.3, 4.5 Hz, 8H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 130.8 (d, *J* = 23.6 Hz), 90.6, 44.3, 31.6, 28.5, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.99. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.87. HRMS(ESI): caled for $C_{15}H_{28}BClFO_4S^+$ [M + H]$^+$ 369.1469; found 369.1466.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene-1-sulfonyl fluoride (4c)



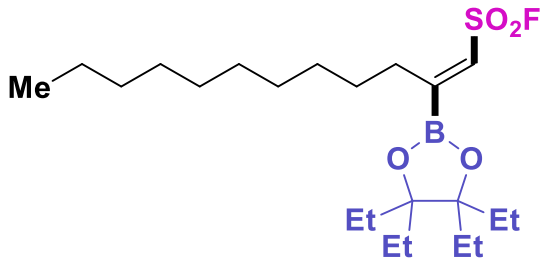
54% (18.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (s, 1H), 2.69 – 2.61 (m, 2H), 1.70 (qd, *J* = 7.3, 4.3 Hz, 8H), 1.59 – 1.49 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 129.7 (d, *J* = 23.2 Hz), 90.3, 32.6, 26.3, 22.3, 14.1, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.92. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.94. HRMS(ESI): caled for $C_{15}H_{29}BFO_4S^+$ [M + H]$^+$ 335.1858; found 335.1856.

(Z)-4-phenyl-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)but-1-ene-1-sulfonyl fluoride (4d)



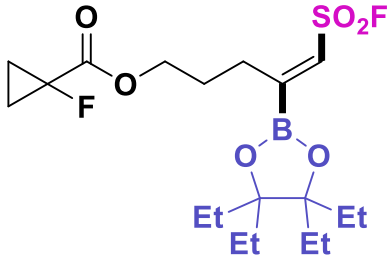
40% (15.8 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 8.0, 6.9 Hz, 2H), 7.24 (dd, *J* = 5.8, 2.7 Hz, 3H), 6.92 (s, 1H), 3.03 – 2.96 (m, 2H), 2.85 – 2.79 (m, 2H), 1.72 (qd, *J* = 7.3, 4.3 Hz, 8H), 0.96 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.7, 130.3 (d, *J* = 23.3 Hz), 128.5, 128.5, 126.3, 125.3, 90.5, 35.1, 32.9, 26.3, 8.7, The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 64.98. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.27. HRMS(ESI): caled for $C_{20}H_{31}BFO_4S^+$ $[M + H]^+$ 397.2015; found 397.2016.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)dodec-1-ene-1-sulfonyl fluoride (4e)



51% (22.0 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.83 (s, 1H), 2.68 – 2.60 (m, 2H), 1.76 – 1.63 (m, 8H), 1.48 (ddd, *J* = 11.4, 8.6, 6.2 Hz, 2H), 1.37 – 1.22 (m, 14H), 0.92 (t, *J* = 7.5 Hz, 12H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 129.4 (d, *J* = 22.9 Hz), 90.3, 31.9, 30.8, 29.6, 29.6, 29.4, 29.3, 29.2, 28.8, 26.3, 22.7, 14.1, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 64.94. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.41. HRMS(ESI): caled for $C_{22}H_{43}BFO_4S^+$ $[M + H]^+$ 433.2954; found 433.2952.

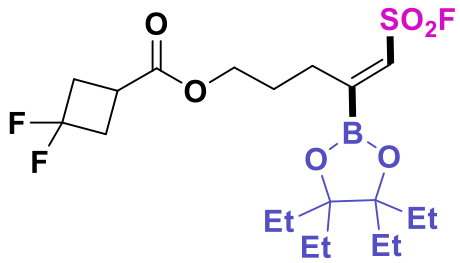
(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 1-fluorocyclopropane-1-carboxylate (4f)



50% (21.8 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-d) δ 6.91 (s, 1H), 4.23 (t, J = 6.2 Hz, 2H), 2.77 – 2.71 (m, 2H), 1.89 (ddt, J = 9.3, 7.8, 6.2 Hz, 2H), 1.70 (m, 8H), 1.39 (s, 2H), 1.37 – 1.35 (m, 2H), 0.92 (t, J = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.5 (d, *J* = 24.2 Hz), 130.8 (d, *J* = 23.6 Hz), 90.6, 73.8, 64.8, 27.8, 27.3, 26.3, 14.6, 14.5, 8.7. The signal

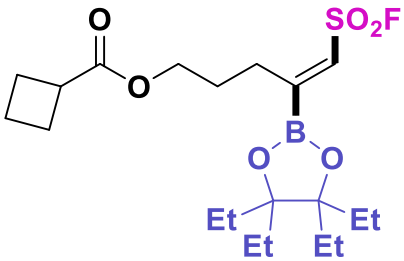
of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 64.96, -197.85. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 28.99. HRMS(ESI): caled for $C_{19}H_{32}BF_2O_6S^+$ [M + H]$^+$ 437.1975; found 437.1977.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 3,3-difluorocyclobutane-1-carboxylate (4g)



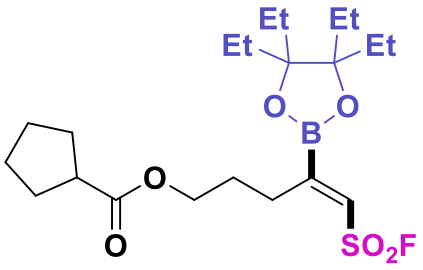
45% (21.1 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.91 (s, 1H), 4.16 (t, *J* = 6.1 Hz, 2H), 3.01 – 2.91 (m, 1H), 2.90 – 2.71 (m, 6H), 1.93 – 1.82 (m, 2H), 1.79 – 1.58 (m, 8H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 130.8 (d, *J* = 23.8 Hz), 90.6, 64.4, 38.7 (t, *J* = 24.5 Hz), 27.8, 27.3, 26.5 (dd, *J* = 14.5, 5.0 Hz), 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.93, -82.69-83.26 (m), -96.99-97.67 (m). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.01. HRMS(ESI): caled for $C_{20}H_{33}BF_3O_6S^+$ [M + H]$^+$ 469.2038; found 469.2036.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl cyclobutanecarboxylate (4h)



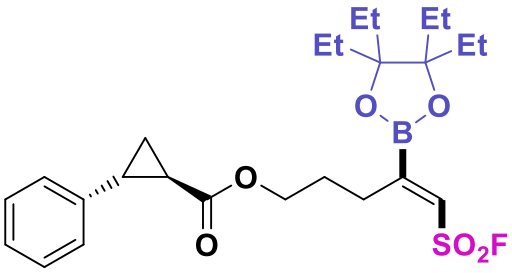
54% (23.3 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.89 (s, 1H), 4.11 (t, *J* = 6.2 Hz, 2H), 3.13 (pd, *J* = 8.5, 1.1 Hz, 1H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.36 – 2.23 (m, 2H), 2.24 – 2.13 (m, 2H), 2.03 – 1.92 (m, 1H), 1.92 – 1.82 (m, 3H), 1.77 – 1.62 (m, 8H), 0.92 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 175.4, 130.5 (d, *J* = 23.3 Hz), 90.5, 63.6, 38.1, 28.0, 27.5, 26.3, 25.3, 18.4, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 64.97. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 29.37. HRMS(ESI): caled for $C_{20}H_{35}BFO_6S^+$ [M + H]$^+$ 433.2226; found 433.2224.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl cyclopentanecarboxylate (4i)



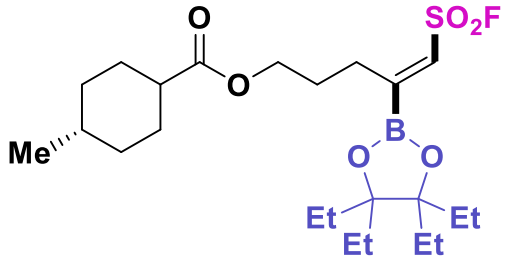
51% (22.8 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 (s, 1H), 4.11 (t, *J* = 6.2 Hz, 2H), 2.80 – 2.68 (m, 3H), 1.93 – 1.76 (m, 6H), 1.70 (qd, *J* = 7.3, 3.7 Hz, 9H), 1.58 (tdt, *J* = 6.3, 4.7, 2.2 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.7, 130.5 (d, *J* = 23.4 Hz), 90.5, 63.6, 43.9, 30.0, 28.0, 27.6, 26.3, 25.8, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.98. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.98. HRMS(ESI): caled for $C_{21}H_{37}BFO_6S^+$ [M + H]$^+$ 447.2383; found 447.2380.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl (1R,2R)-2-phenylcyclopropane-1-carboxylate (4j)



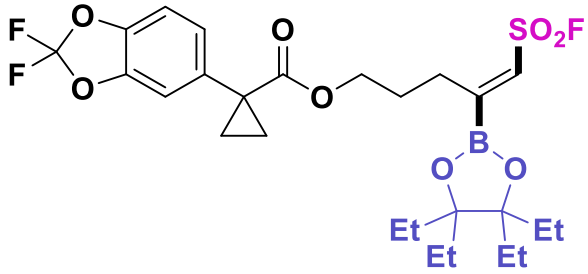
41% (20.3 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 2H), 7.24 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 6.89 (s, 1H). 4.15 (t, *J* = 6.2 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.53 (ddd, *J* = 9.3, 6.5, 4.1 Hz, 1H), 1.95 – 1.82 (m, 3H), 1.77 – 1.62 (m, 8H), 1.60 (ddd, *J* = 9.6, 5.3, 4.5 Hz, 1H), 1.32 (ddd, *J* = 8.4, 6.5, 4.5 Hz, 1H), 0.90 (td, *J* = 7.5, 2.4 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 140.1, 130.5 (d, *J* = 23.6 Hz), 128.4, 126.5, 126.2, 90.5, 27.9, 27.5, 26.3, 26.2, 24.1, 17.0, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 65.03. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.06. HRMS(ESI): caled for $C_{25}H_{37}BFO_6S^+$ [M + H]$^+$ 495.2383; found 495.2386.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 4-methylcyclohexane-1-carboxylate (4k)



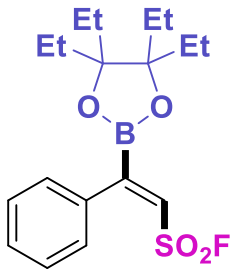
50% (23.7 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 (s, 1H), 4.10 (t, *J* = 6.1 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.20 (tt, *J* = 12.3, 3.6 Hz, 1H), 1.95 (dq, *J* = 12.4, 3.5, 3.0 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.80 – 1.63 (m, 11H), 1.50 – 1.28 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 12H), 0.89 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.2, 130.5 (d, *J* = 23.5 Hz), 90.5, 63.4, 43.2, 34.3, 32.0, 29.0, 28.0, 27.6, 26.3, 22.5, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.98. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.88. HRMS(ESI): caled for $C_{23}H_{41}BFO_6S^+$ $[M + H]^+$ 475.2696; found 475.2699.

(Z)-5-(fluorosulfonyl)-4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl 1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopropane-1-carboxylate (4l)



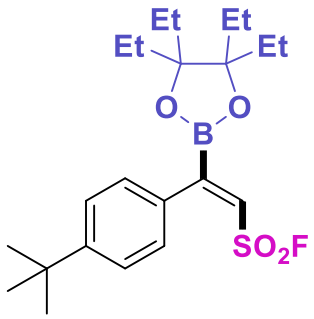
32% (18.4 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 – 7.03 (m, 2H), 6.97 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.88 (s, 1H), 4.08 (t, *J* = 6.0 Hz, 2H), 2.66 – 2.58 (m, 2H), 1.78 – 1.62 (m, 12H), 1.17 (q, *J* = 4.0 Hz, 2H), 0.91 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 135.8, 131.7, 130.8 (d, *J* = 23.6 Hz), 125.8, 112.0, 108.9, 90.6, 64.5, 29.7, 29.0, 27.9, 27.5, 26.3, 16.9, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.87, -49.90. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.30; HRMS(ESI): caled for $C_{26}H_{35}BF_3O_8S^+$ $[M + H]^+$ 575.2093; found 575.2091.

(Z)-2-phenyl-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4m)



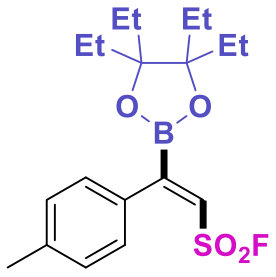
50% (18.4 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.37 – 7.30 (m, 2H), 7.08 (s, 1H), 1.71 (hept, *J* = 7.0 Hz, 8H), 0.91 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.8, 130.4 (d, *J* = 25.8 Hz), 129.2, 128.1, 127.8 (d, *J* = 1.3 Hz), 90.8, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.47. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.98. HRMS(ESI): caled for $C_{18}H_{27}BFO_4S^+$ $[M + H]^+$ 369.1702; found 369.1705.

(Z)-2-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4n)



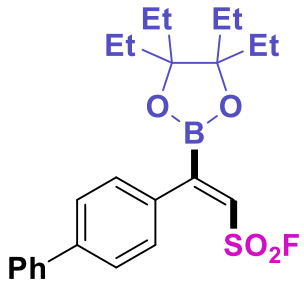
52% (22.0 mg); white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.29 (m, 4H), 7.03 (s, 1H), 1.72 (hept, *J* = 7.4 Hz, 8H), 1.33 (s, 9H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.5, 131.6, 129.4 (d, *J* = 25.9 Hz), 128.1, 125.1, 90.7, 34.8, 31.2, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.17. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.87. HRMS(ESI): caled for $C_{22}H_{35}BFO_4S^+$ $[M + H]^+$ 425.2328; found 425.2325.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)ethene-1-sulfonyl fluoride (4o)



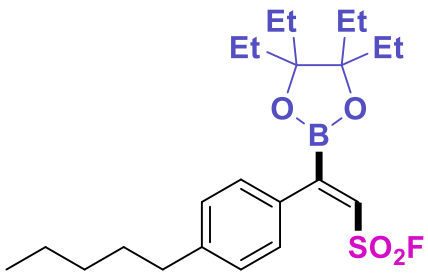
62% (23.6 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 2.42 (s, 3H), 1.83 – 1.69 (m, 8H), 0.96 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.4, 131.8, 129.7 (d, *J* = 25.8 Hz), 128.9, 128.1, 90.7, 26.3, 21.4, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.38. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.18. HRMS(ESI): caled for $C_{19}H_{29}BFO_4S^+$ $[M + H]^+$ 383.1858; found 383.1859.

(Z)-2-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4p)



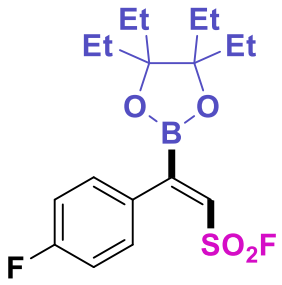
51% (22.6 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 7.8, 1.6 Hz, 4H), 7.48 – 7.40 (m, 4H), 7.40 – 7.31 (m, 1H), 7.10 (s, 1H), 1.72 (dq, *J* = 14.6, 7.3 Hz, 8H), 0.93 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.0, 140.3, 133.6, 130.1 (d, *J* = 25.9 Hz), 128.8, 128.6 (d, *J* = 1.3 Hz), 127.7, 127.1, 126.8, 90.9, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.40. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.23. HRMS(ESI): caled for $C_{24}H_{31}BFO_4S^+$ $[M + H]^+$ 445.2015; found 445.2018.

(Z)-2-(4-pentylphenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4q)



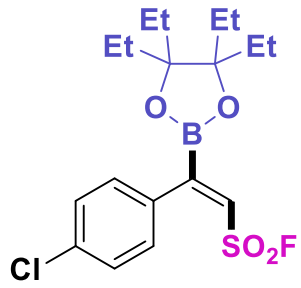
44% (19.3 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.21 – 7.18 (m, 2H), 7.03 (s, 1H), 2.69 – 2.55 (m, 2H), 1.78 – 1.66 (m, 8H), 1.66 – 1.59 (m, 2H), 1.37 – 1.30 (m, 4H), 0.98 – 0.87 (m, 15H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.4, 131.9, 129.48 (d, J = 25.7 Hz), 128.1, 128.1, 90.7, 35.8, 31.6, 30.7, 26.3, 22.5, 14.0, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.27. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.42. HRMS(ESI): caled for $C_{23}H_{37}BFO_4S^+$ $[M + H]^+$ 439.2484; found 439.2483.

(Z)-2-(4-fluorophenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4r)



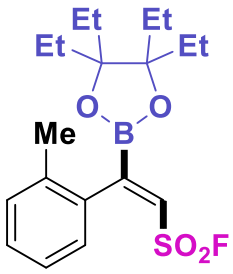
52% (20.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.31 (m, 2H), 7.14 – 7.05 (m, 3H), 2.00 – 1.62 (m, 8H), 0.91 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.5, 162.0, 130.6 (d, *J* = 26.1 Hz), 130.1 (d, *J* = 9.6 Hz), 115.3 (d, *J* = 21.8 Hz), 90.9, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.37, -111.54 – -111.66 (m). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.33. HRMS(ESI): caled for $C_{18}H_{26}BF_2O_4S^+$ $[M + H]^+$ 387.1608; found 387.1610.

(Z)-2-(4-chlorophenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4s)



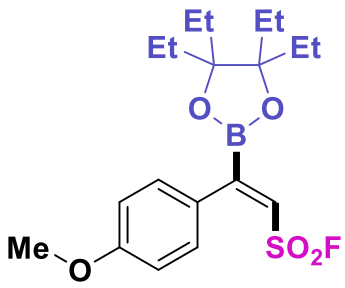
50% (20.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 7.09 (s, 1H), 1.79 – 1.63 (m, 8H), 0.91 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.4, 133.1, 130.9 (d, *J* = 26.0 Hz), 129.3 (d, *J* = 1.4 Hz), 128.5, 91.0, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.50. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.19. HRMS(ESI): caled for $C_{18}H_{26}BClFO_4S^+$ $[M + H]^+$ 403.1312; found 403.1314.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-(o-tolyl)ethene-1-sulfonyl fluoride (4t)



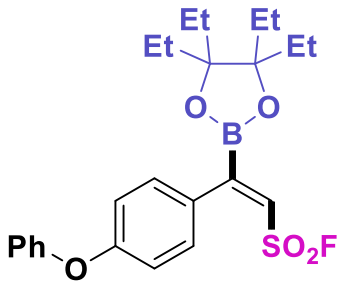
56% (21.4 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.13 (m, 4H), 7.03 – 6.97 (m, 1H), 2.19 (s, 3H), 1.78 – 1.61 (m, 8H), 0.88 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.0, 134.0, 131.8 (d, *J* = 24.5 Hz), 129.8, 128.3, 126.4, 125.5, 90.6, 26.3, 19.9, 8.6. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.22. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.76. HRMS(ESI): caled for $C_{19}H_{29}BFO_4S^+$ $[M + H]^+$ 383.1858; found 383.1860.

(Z)-2-(4-methoxyphenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4u)



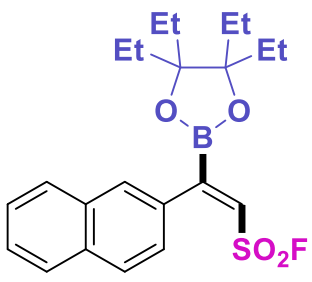
52% (18.8 mg); yellow solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 6.99 (s, 1H), 6.95 – 6.88 (m, 2H), 3.83 (s, 3H), 1.81 – 1.64 (m, *J* = 7.4 Hz, 8H), 0.92 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7, 130.2 (d, *J* = 1.7 Hz), 128.6 (d, *J* = 25.7 Hz), 126.9, 113.6, 90.7, 55.2, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.19. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.66. HRMS(ESI): caled for $C_{19}H_{29}BFO_5S^+$ [M + H]$^+$ 399.1808; found 399.1805.

(Z)-2-(4-phenoxyphenyl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4v)



44% (20.2 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 4H), 7.20 – 7.11 (m, 1H), 7.07 (dt, *J* = 7.7, 1.1 Hz, 2H), 7.03 (s, 1H), 7.02 – 6.94 (m, 2H), 1.83 – 1.62 (m, *J* = 7.4 Hz, 8H), 0.92 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.8, 156.1, 130.1 (d, *J* = 1.5 Hz), 129.9, 129.4 (d, *J* = 25.9 Hz), 129.0, 124.0, 119.9, 117.5, 90.8, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.31. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.21. HRMS(ESI): caled for $C_{24}H_{31}BFO_5S^+$ [M + H]$^+$ 461.1964; found 461.1967.

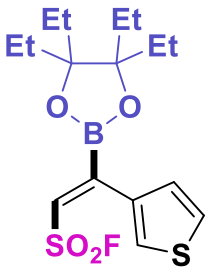
(Z)-2-(naphthalen-2-yl)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)ethene-1-sulfonyl fluoride (4w)



51% (21.3 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.80 (m, 4H), 7.53 – 7.38 (m, 3H), 7.15 (s, 1H), 1.82 – 1.62 (m, 8H), 0.92 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.4, 132.8, 132.4, 130.5 (d, *J* = 25.9 Hz), 128.6, 127.8 (d, *J* = 1.7 Hz), 127.7, 126.9, 126.4, 125.4, 125.3, 90.9, 26.3, 8.7. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.46. ^{11}B

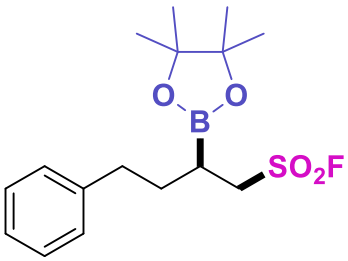
NMR (128 MHz, Chloroform-*d*) δ 29.26. HRMS(ESI): caled for $C_{22}H_{29}BFO_4S^+$ [M + H]$^+$ 419.1858; found 419.1859.

(Z)-2-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-3-yl)ethene-1-sulfonyl fluoride (4x)



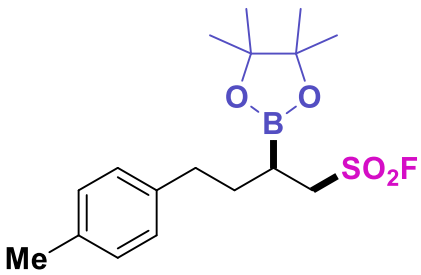
43% (16.0 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.38 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.33 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.99 (s, 1H), 1.80 – 1.67 (m, 8H), 0.94 (t, *J* = 7.5 Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.5, 129.0, 128.5, 128.0 (d, *J* = 26.1 Hz), 125.4, 90.8, 26.3, 8.8. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 62.81. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.09. HRMS(ESI): caled for $C_{16}H_{25}BFO_4S_2^+$ [M + H]$^+$ 375.1266; found 375.1264.

4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6a)



73% (25.0 mg); white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.12 (m, 3H), 3.63 (ddd, *J* = 14.4, 8.1, 6.0 Hz, 1H), 3.48 – 3.34 (m, 1H), 2.78 – 2.59 (m, 2H), 2.03 – 1.80 (m, 2H), 1.76 (ddd, *J* = 14.0, 8.1, 5.9 Hz, 1H), 1.30 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.2, 128.5, 128.3, 126.1, 84.3, 52.3 (d, *J* = 14.6 Hz), 34.4, 31.5, 24.8 (d, *J* = 13.0 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 56.00. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.53. HRMS(ESI): caled for $C_{16}H_{24}BFO_4SNa^+$ [M + Na]$^+$ 365.1364; found 365.1362.

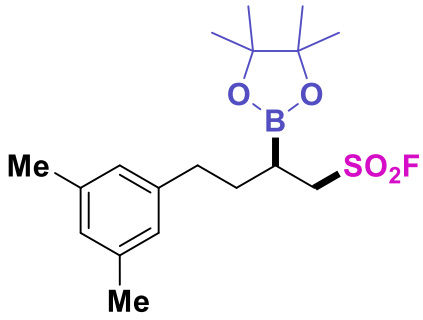
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(p-tolyl)butane-1-sulfonyl fluoride (6b)



50% (17.8 mg); white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 6.98 (m, 4H), 3.62 (ddd, *J* = 14.4, 8.2, 6.1 Hz, 1H), 3.42 (ddd, *J* = 14.6, 5.8, 2.9 Hz, 1H), 2.75 – 2.50 (m, 2H), 2.32 (s, 3H), 1.98 – 1.79 (m, 2H), 1.75 (ddd, *J* = 14.0, 8.1, 5.8 Hz, 1H), 1.29 (s, 12H). ^{13}C

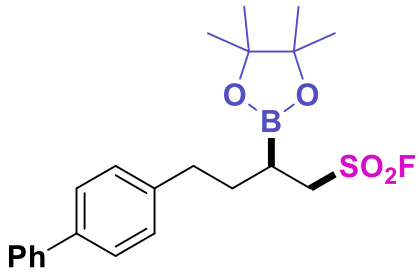
NMR (101 MHz, Chloroform-*d*) δ 138.1, 135.6, 129.2, 128.2, 84.3, 52.4 (d, *J* = 14.9 Hz), 33.9, 31.7, 24.8 (d, *J* = 13.3 Hz), 21.0. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 55.88 (d, *J* = 8.4 Hz). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.37. HRMS(ESI): caled for $C_{17}H_{27}BFO_4S^+$ [M + H]$^+$ 357.1702; found 357.1704.

4-(3,5-dimethylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6c)



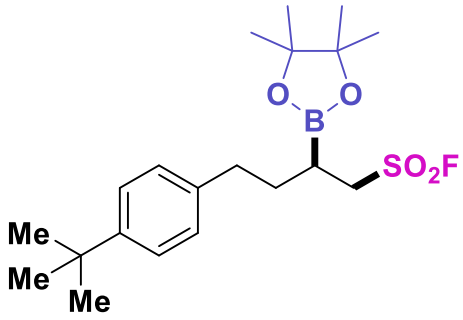
54% (20.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.99 – 6.71 (m, 3H), 3.62 (ddd, *J* = 14.5, 8.2, 6.1 Hz, 1H), 3.47 – 3.33 (m, 1H), 2.59 (qdd, *J* = 13.5, 10.0, 6.3 Hz, 2H), 2.29 (s, 6H), 2.00 – 1.81 (m, 2H), 1.75 (tt, *J* = 8.1, 5.8 Hz, 1H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.1, 138.0, 127.8, 126.2, 84.3, 52.4 (d, *J* = 14.8 Hz), 34.2, 31.6, 24.8 (d, *J* = 13.0 Hz), 21.2. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 55.88 (d, *J* = 8.9 Hz). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.79. HRMS(ESI): caled for $C_{18}H_{29}BFO_4S^+$ [M + H]$^+$ 371.1858; found 371.1856.

4-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6d)



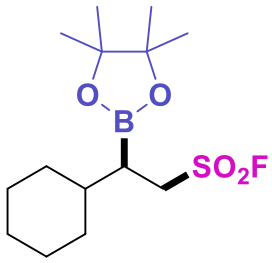
36% (15.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.49 (m, 4H), 7.46 – 7.39 (m, 2H), 7.35 – 7.30 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 3.64 (ddd, *J* = 14.2, 8.0, 5.9 Hz, 1H), 3.44 (ddd, *J* = 14.7, 6.0, 2.9 Hz, 1H), 2.81 – 2.62 (m, 2H), 1.95 (dddd, *J* = 23.6, 17.3, 13.6, 7.8 Hz, 2H), 1.78 (tt, *J* = 8.1, 5.9 Hz, 1H), 1.29 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.0, 140.3, 139.2, 128.8, 128.7, 127.3, 127.1, 127.0, 84.4, 52.4 (d, *J* = 14.8 Hz), 34.0, 31.5, 24.8 (d, *J* = 12.7 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 56.07 (d, *J* = 6.3 Hz). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.74. HRMS(ESI): caled for $C_{22}H_{29}BFO_4S^+$ [M + H]$^+$ 419.1858; found 419.1859.

4-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6e)



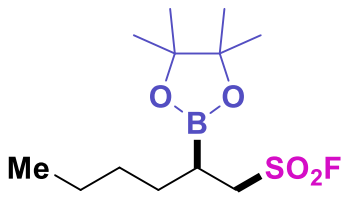
40% (15.9 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.30 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 3.63 (ddd, *J* = 14.5, 8.3, 6.1 Hz, 1H), 3.43 (ddd, *J* = 14.7, 5.8, 2.8 Hz, 1H), 2.74 – 2.56 (m, 2H), 1.98 – 1.82 (m, 2H), 1.76 (tt, *J* = 8.2, 5.8 Hz, 1H), 1.31 (s, 9H), 1.28 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0, 138.1, 128.0, 125.4, 84.3, 52.4 (d, *J* = 14.9 Hz), 34.4, 33.8, 31.5, 31.4, 24.8 (d, *J* = 12.9 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 55.84. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.68. HRMS(ESI): caled for $C_{20}H_{32}BFO_4SNa^+$ [M + Na]$^+$ 421.1990; found 421.1989.

2-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane-1-sulfonyl fluoride (6f)



30% (9.6 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.65 (ddd, *J* = 14.6, 10.0, 7.2 Hz, 1H), 3.40 (ddd, *J* = 14.5, 3.9, 2.2 Hz, 1H), 1.82 – 1.61 (m, 5H), 1.29 (d, *J* = 2.1 Hz, 12H), 1.17 – 1.05 (m, 3H), 0.97 – 0.85 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 84.2, 51.2 (d, *J* = 15.0 Hz), 39.3, 32.2, 31.3, 26.5, 26.3 (d, *J* = 13.3 Hz), 24.9 (d, *J* = 25.5 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 53.86. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 32.62. HRMS(ESI): caled for $C_{14}H_{27}BFO_4S^+$ [M + H]$^+$ 321.1702; found 321.1701.

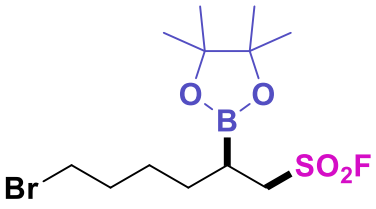
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane-1-sulfonyl fluoride (6g)



70% (20.6 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.58 (ddd, *J* = 14.7, 8.3, 6.4 Hz, 1H), 3.37 (ddd, *J* = 14.7, 5.8, 2.7 Hz, 1H), 1.75 – 1.62 (m, 1H), 1.61 – 1.52 (m, 2H), 1.38 – 1.29 (m, 4H), 1.25 (s, 12H). 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 84.2, 52.4 (d, *J* = 14.6 Hz), 30.2, 29.3, 24.7 (d, *J* = 15.5 Hz), 22.6,

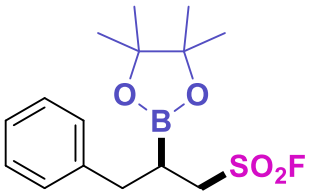
13.9. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 55.35 (d, *J* = 6.1 Hz). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.33. HRMS(ESI): caled for $C_{12}H_{25}BFO_4S^+$ $[M + H]^+$ 295.1545; found 295.1543.

6-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexane-1-sulfonyl fluoride (6h)



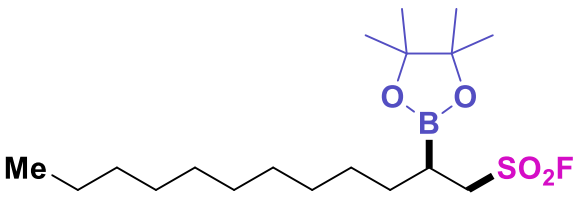
60% (22.3 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.60 (ddd, *J* = 14.7, 7.6, 5.8 Hz, 1H), 3.45 – 3.34 (m, 3H), 1.88 (ddt, *J* = 9.7, 8.0, 6.5 Hz, 2H), 1.75 – 1.67 (m, 1H), 1.66 – 1.50 (m, 4H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 84.4, 52.3 (d, *J* = 14.8 Hz), 33.4, 32.4, 28.7, 26.5, 24.8 (d, *J* = 14.0 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 55.89. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.28. HRMS(ESI): caled for $C_{12}H_{23}BBrFO_4SNa^+$ $[M + Na]^+$ 395.0470; found 395.0471.

3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propane-1-sulfonyl fluoride (6i)



63% (20.8 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (tt, *J* = 7.0, 1.1 Hz, 2H), 7.25 – 7.19 (m, 3H), 3.52 (ddd, *J* = 14.5, 8.4, 6.0 Hz, 1H), 3.36 – 3.28 (m, 1H), 2.97 (dd, *J* = 14.0, 6.6 Hz, 1H), 2.86 – 2.75 (m, 1H), 2.11 – 1.99 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 129.0, 128.7, 126.8, 84.4, 51.3 (d, *J* = 15.2 Hz), 34.8, 24.8 (d, *J* = 8.0 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 55.73. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.25. HRMS(ESI): caled for $C_{15}H_{23}BFO_4S^+$ $[M + H]^+$ 329.1389; found 329.1390.

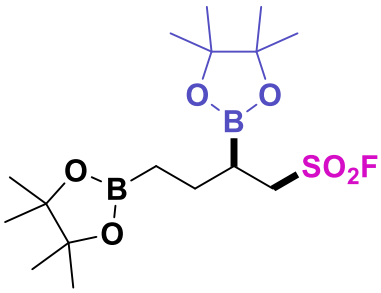
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecane-1-sulfonyl fluoride (6j)



79% (30.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.58 (ddd, *J* = 14.8, 8.4, 6.4 Hz, 1H), 3.37 (ddd, *J* = 14.7, 5.8, 2.6 Hz, 1H), 1.75 – 1.64 (m, 1H), 1.26 (s, 29H), 0.88 (t, *J* = 6.8 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 84.2, 52.4 (d, *J* = 14.7 Hz),

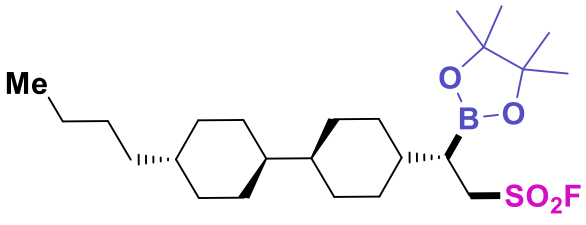
31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 28.0, 24.8 (d, *J* = 15.6 Hz), 22.7, 14.1. The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 55.33 (d, *J* = 9.6 Hz). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.50. HRMS(ESI): caled for $C_{18}H_{37}BFO_4S^+$ $[M + H]^+$ 379.2484; found 379.2487.

2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butane-1-sulfonyl fluoride (6k)



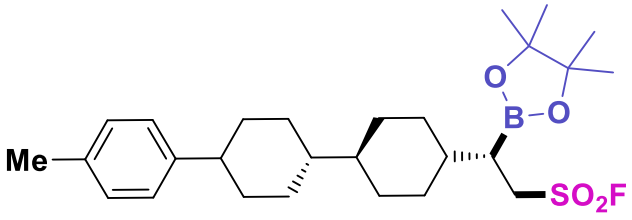
38% (15.0 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.57 (ddd, *J* = 14.9, 8.4, 6.6 Hz, 1H), 3.40 (dq, *J* = 14.2, 2.5 Hz, 1H), 1.68 (dt, *J* = 7.4, 3.5 Hz, 3H), 1.25 (s, 12H), 1.24 (s, 12H), 0.88 – 0.79 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 84.2, 83.2, 52.3 (d, *J* = 14.7 Hz), 24.8 (d, *J* = 18.0 Hz), 24.8, 24.2. The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 54.97. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.02. HRMS(ESI): caled for $C_{16}H_{32}B_2FO_6S^+$ $[M + H]^+$ 393.2084; found 393.2085.

(S)-2-((1R,1's,4S,4'R)-4'-butyl-[1,1'-bi(cyclohexan)]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane-1-sulfonyl fluoride (6l)



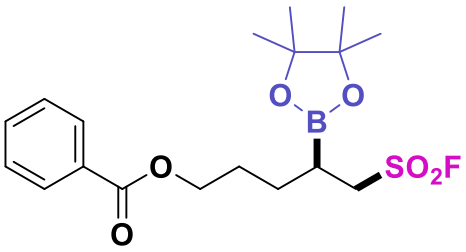
33% (15.1 mg); white soild; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.64 (ddd, *J* = 14.5, 10.2, 7.2 Hz, 1H), 3.39 (ddd, *J* = 14.6, 4.1, 2.1 Hz, 1H), 1.77 (d, *J* = 13.5 Hz, 4H), 1.73 – 1.68 (m, 2H), 1.63 (dt, *J* = 9.8, 4.6 Hz, 1H), 1.29 (d, *J* = 2.1 Hz, 12H), 1.22 – 1.11 (m, 3H), 1.03 – 0.94 (m, 6H), 0.95 – 0.83 (m, 14H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 84.2, 51.3 (d, *J* = 15.0 Hz), 43.3, 43.1, 39.5, 37.9, 37.2, 33.6, 32.4, 31.4, 30.1, 30.0, 29.8, 29.3, 24.9 (d, *J* = 24.8 Hz), 23.0, 14.2. The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 53.88. ^{11}B NMR (160 MHz, Chloroform-*d*) δ 32.83. HRMS(ESI): caled for $C_{24}H_{45}BFO_4S^+$ $[M + H]^+$ 459.3110; found 459.3113.

(2S)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-((1R,4s)-4'-(p-tolyl)-[1,1'-bi(cyclohexan)]-4-yl)ethane-1-sulfonyl fluoride (6m)



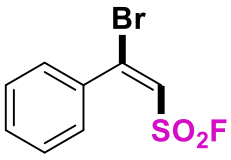
32% (15.6 mg); white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 1.6 Hz, 4H), 3.63 (ddd, *J* = 14.5, 10.0, 7.1 Hz, 1H), 3.38 (ddd, *J* = 14.6, 4.2, 2.2 Hz, 1H), 2.39 (tq, *J* = 7.1, 3.5 Hz, 1H), 2.31 (s, 3H), 1.96 – 1.72 (m, 10H), 1.27 (s, 12H), 1.19 – 0.99 (m, 10H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.8, 135.2, 129.0, 126.6, 84.2, 51.2 (d, *J* = 15.0 Hz), 44.2, 43.0, 42.7, 39.4, 34.6, 32.4, 31.3, 30.3, 30.0, 29.8, 24.9 (d, *J* = 19.6 Hz), 21.0. The signal of the α-B-carbon was not observed. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 53.93. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.20. HRMS(ESI): caled for $C_{27}H_{43}BFO_4S^+$ [M + H]$^+$ 493.2954; found 493.2957.

5-(fluorosulfonyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl benzoate (6n)



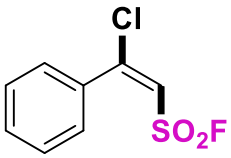
35% (14.0 mg); colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.00 (m, 2H), 7.61 – 7.52 (m, 1H), 7.44 (dd, *J* = 8.3, 7.1 Hz, 2H), 4.33 (t, *J* = 4.9 Hz, 2H), 3.73 – 3.57 (m, 1H), 3.47 – 3.37 (m, 1H), 1.94 – 1.71 (m, 5H), 1.25 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.5, 132.9, 130.3, 129.6, 128.4, 84.4, 64.4, 52.3 (d, *J* = 15.0 Hz), 27.4, 26.2, 24.8 (d, *J* = 14.8 Hz). The signal of the α-B-carbon was not observed. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 56.11. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.37. HRMS(ESI): caled for $C_{18}H_{27}BFO_6S^+$ [M + H]$^+$ 401.1600; found 401.1603.

(E)-2-bromo-2-phenylethene-1-sulfonyl fluoride (7)



76% (10.0 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 5H), 7.11 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.0, 135.3, 131.7, 128.5, 128.2, 123.6 (d, *J* = 29.6 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ 66.19. HRMS(ESI): caled for $C_8H_6BrFO_2SNa^+$ [M + Na]$^+$ 286.9148; found 286.9145.

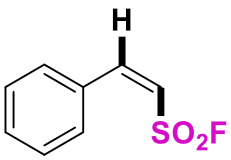
(E)-2-chloro-2-phenylethene-1-sulfonyl fluoride (8)



73% (8.0 mg); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (dq, *J* = 6.4, 1.4 Hz, 3H), 7.51 – 7.44 (m, 2H), 6.90 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.4, 133.5, 132.0, 128.6, 128.4, 120.4 (d, *J* = 31.1 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ 67.08.

All data matched that reported in the literature.[10]

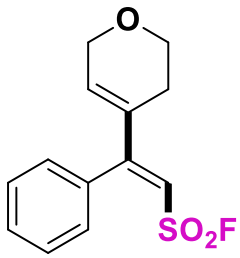
(Z)-2-phenylethene-1-sulfonyl fluoride (9)



54% (5.0 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.38 (dd, *J* = 11.9, 5.8 Hz, 1H), 6.51 (dd, *J* = 11.9, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.7, 131.3, 130.1 (d, *J* = 1.8 Hz), 128.7, 120.3 (d, *J* = 28.5 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 64.00.

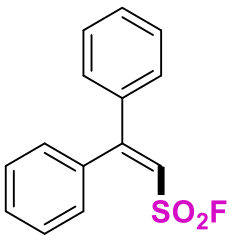
All data matched that reported in the literature.[3]

(Z)-2-(3,6-dihydro-2H-pyran-4-yl)-2-phenylethene-1-sulfonyl fluoride (11)



60% (8.1 mg); light yellow solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 3H), 7.24 – 7.17 (m, 2H), 6.46 (s, 1H), 5.84 (s, 1H), 4.24 (d, *J* = 2.7 Hz, 2H), 3.90 (t, *J* = 5.5 Hz, 2H), 2.39 (dddd, *J* = 6.7, 4.0, 2.5, 1.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 139.4, 133.9, 133.2, 129.3, 128.7, 128.1, 116.7 (d, *J* = 27.5 Hz), 66.1, 63.7, 25.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 68.89. HRMS(ESI): caled for $C_{13}H_{13}FO_3SNa^+$ [M + Na]$^+$ 291.0461; found 291.0465.

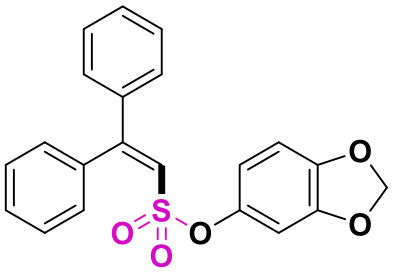
2,2-diphenylethene-1-sulfonyl fluoride (13)



61% (8.0 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.44 (m, 4H), 7.40 (dd, *J* = 8.6, 6.9 Hz, 2H), 7.32 (ddd, *J* = 8.7, 6.9, 1.5 Hz, 4H), 6.84 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3 (d, *J* = 3.9 Hz), 138.1 (d, *J* = 2.2 Hz), 135.2, 131.5, 130.2, 129.3, 128.9, 128.8, 128.4, 117.7 (d, *J* = 28.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ 68.08.

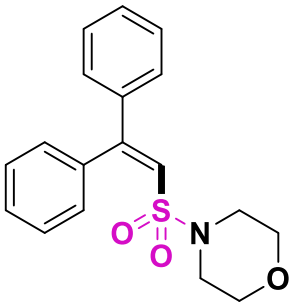
All data matched that reported in the literature.[3]

benzo[d][1,3]dioxol-5-yl 2,2-diphenylethene-1-sulfonate (14)



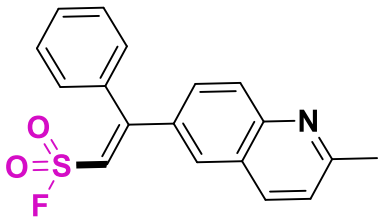
89% (17.0 mg); Light yellow solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.33 (m, 6H), 7.28 – 7.21 (m, 4H), 6.81 (s, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.71 – 6.61 (m, 2H), 5.98 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 148.2, 146.5, 143.4, 139.0, 135.7, 130.8, 129.5, 129.5, 128.8, 128.6, 128.0, 120.4, 115.2, 108.0, 104.6, 102.0. HRMS(ESI): caled for $C_{21}H_{16}O_5SNa^+$ $[M + Na]^+$ 403.0610; found 403.0608.

4-((2,2-diphenylvinyl)sulfonyl)morpholine (15)



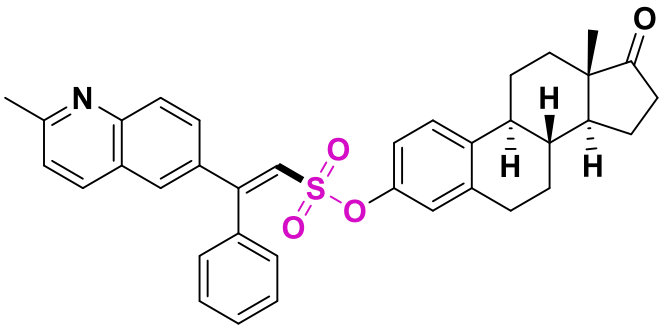
94% (15.6 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 5H), 7.35 – 7.31 (m, 3H), 7.27 – 7.22 (m, 2H), 6.63 (s, 1H), 3.89 – 3.50 (m, 4H), 3.35 – 2.84 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 139.8, 136.4, 130.2, 129.8, 129.1, 128.6, 128.3, 127.9, 121.9, 66.4, 45.5. HRMS(ESI): caled for $C_{18}H_{20}NO_3S^+$ $[M + H]^+$ 330.1159; found 330.1160.

(E)-2-(2-methylquinolin-6-yl)-2-phenylethene-1-sulfonyl fluoride (17)



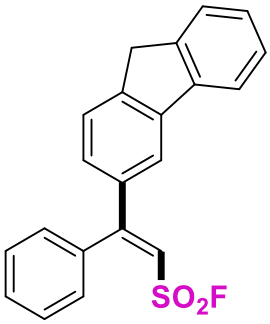
50% (8.2 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (t, *J* = 8.1 Hz, 2H), 7.72 – 7.61 (m, 2H), 7.57 – 7.47 (m, 3H), 7.41 – 7.32 (m, 3H), 6.97 (s, 1H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.5, 137.0, 135.1, 135.0, 130.3, 129.6, 129.5, 129.3, 128.5, 128.4, 126.0, 123.2, 120.8, 118.3 (d, *J* = 28.3 Hz), 115.2, 25.5. ^{19}F NMR (471 MHz, Chloroform-*d*) δ 68.18. HRMS(ESI): caled for $C_{18}H_{15}FNO_2S^+$ $[M + H]^+$ 328.0802; found 328.0803.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (E)-2-(2-methylquinolin-6-yl)-2-phenylethene-1-sulfonate (18)



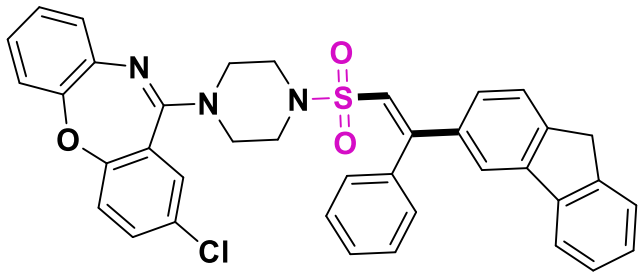
51% (7.4 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (t, *J* = 8.4 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.50 – 7.27 (m, 7H), 7.00 – 6.92 (m, 3H), 2.89 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.77 (s, 3H), 2.51 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.39 (d, *J* = 11.9 Hz, 1H), 2.28 (t, *J* = 10.0 Hz, 1H), 2.21 – 2.08 (m, 1H), 2.08 – 1.94 (m, 3H), 1.54 (dddd, *J* = 34.4, 27.9, 22.3, 11.5 Hz, 7H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.5, 161.0, 147.2, 138.8, 138.6, 136.9, 135.5, 129.6, 129.6, 129.3, 129.0, 128.9, 128.7, 128.5, 128.1, 126.7, 126.2, 123.0, 122.4, 121.6, 119.3, 50.4, 47.9, 44.2, 38.0, 35.8, 31.5, 29.7, 29.4, 26.2, 25.8, 25.5, 21.6, 13.8. HRMS(ESI): caled for $C_{36}H_{36}NO_4S^+$ [M + H]$^+$ 578.2360; found 578.2364.

(E)-2-(9H-fluoren-3-yl)-2-phenylethene-1-sulfonyl fluoride (20)



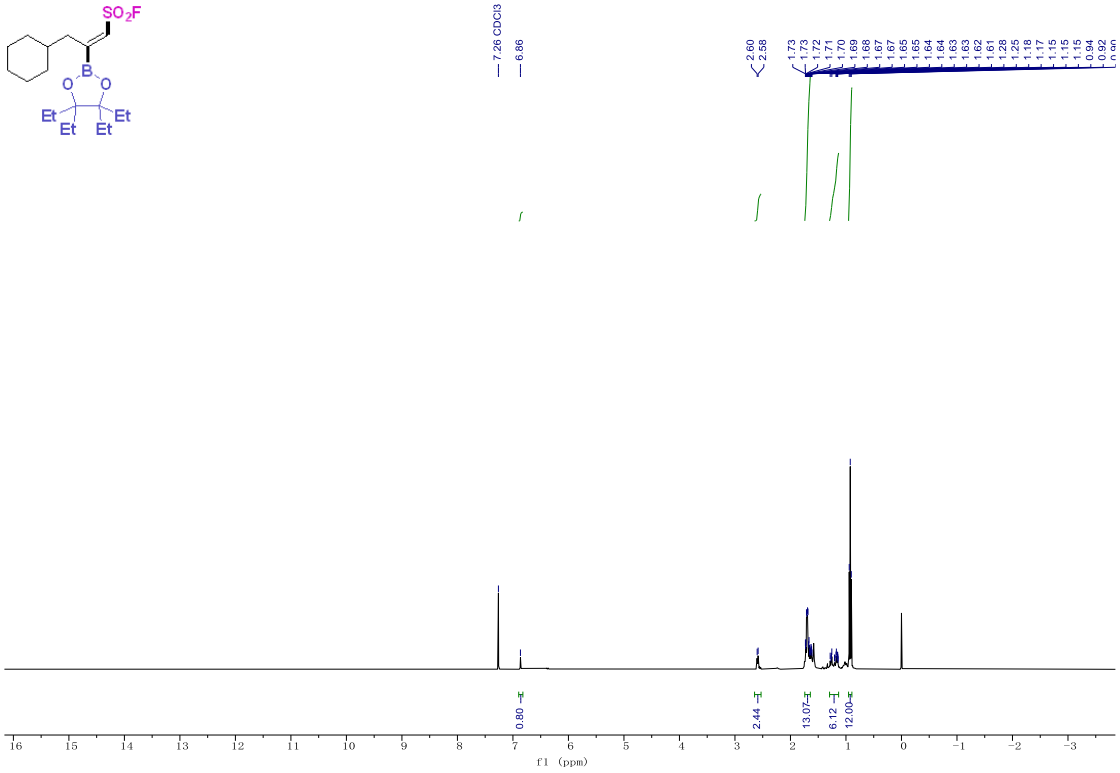
54% (9.5 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.75 (m, 2H), 7.61 – 7.46 (m, 5H), 7.45 – 7.31 (m, 5H), 6.89 (s, 1H), 3.90 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 145.2, 144.0, 143.7, 140.3, 136.3, 135.5, 130.1, 129.4, 128.4, 128.1, 128.0, 127.1, 125.5, 125.2, 120.7, 120.0, 116.7 (d, *J* = 27.8 Hz), 36.9. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 68.69. HRMS(ESI): caled for $C_{21}H_{15}FO_2SNa^+$ [M + Na]$^+$ 373.0669; found 373.0666.

(E)-11-(4-((2-(9H-fluoren-3-yl)-2-phenylvinyl)sulfonyl)piperazin-1-yl)-2-chlorodibenzo[b,f][1,4]oxazepine (21)

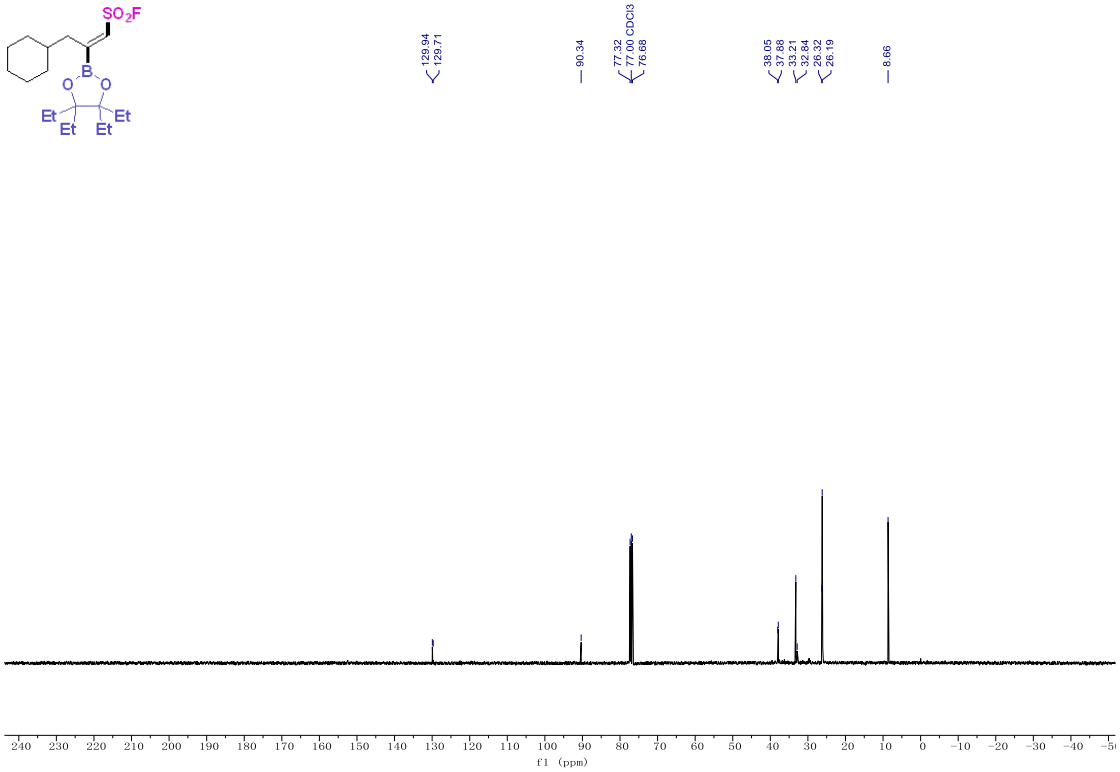


63% (10.0 mg); white solids; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.48 – 7.29 (m, 9H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.25 (d, *J* = 2.6 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.14 – 7.06 (m, 3H), 7.01 (td, *J* = 7.4, 2.0 Hz, 1H), 6.74 (s, 1H), 3.86 (s, 2H), 3.50 (s, 4H), 3.19 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.4, 158.4, 155.7, 151.7, 144.0, 143.9, 143.6, 140.6, 138.0, 136.8, 132.9, 130.5, 129.9, 129.2, 128.8, 128.1, 127.6, 127.5, 127.1, 127.1, 125.9, 125.2, 125.0, 124.7, 122.9, 121.7, 120.5, 120.2, 119.9, 47.2, 45.0, 36.9. HRMS(ESI): caled for $C_{38}H_{31}ClN_3O_3S^+$ $[M + H]^+$ 644.1769; found 644.1767.

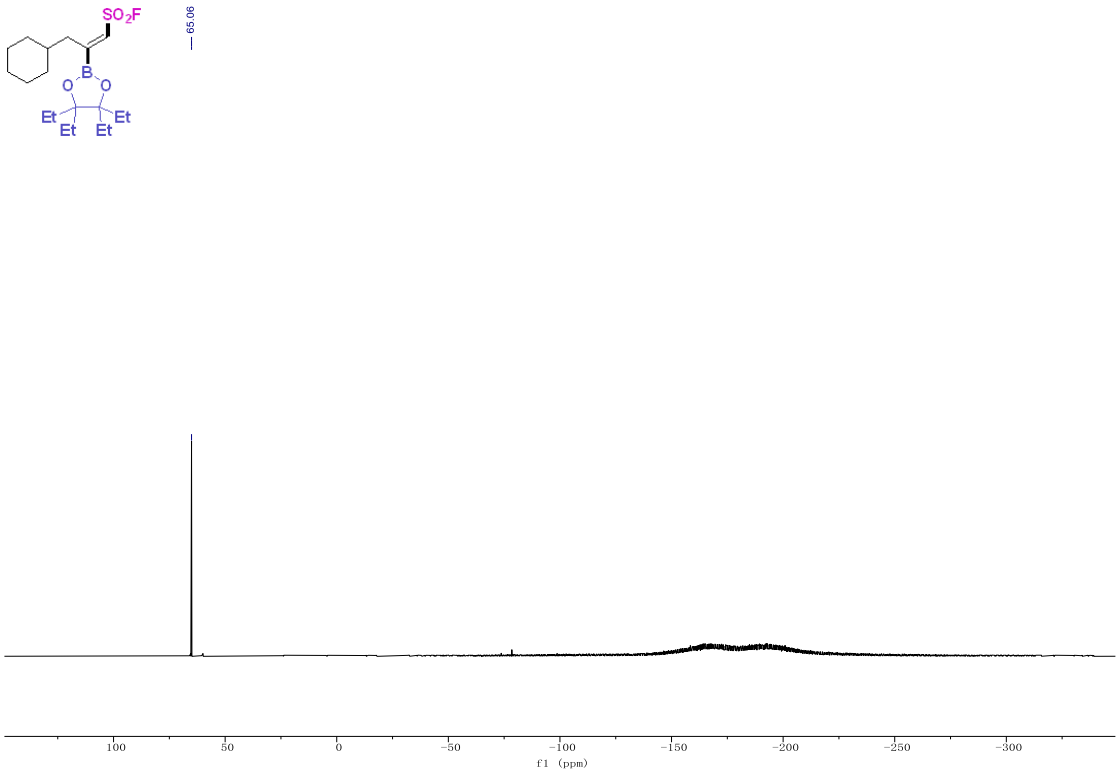
X. NMR Spectra of, 4, 6-9, 11, 13-15, 17-18, 20-21.



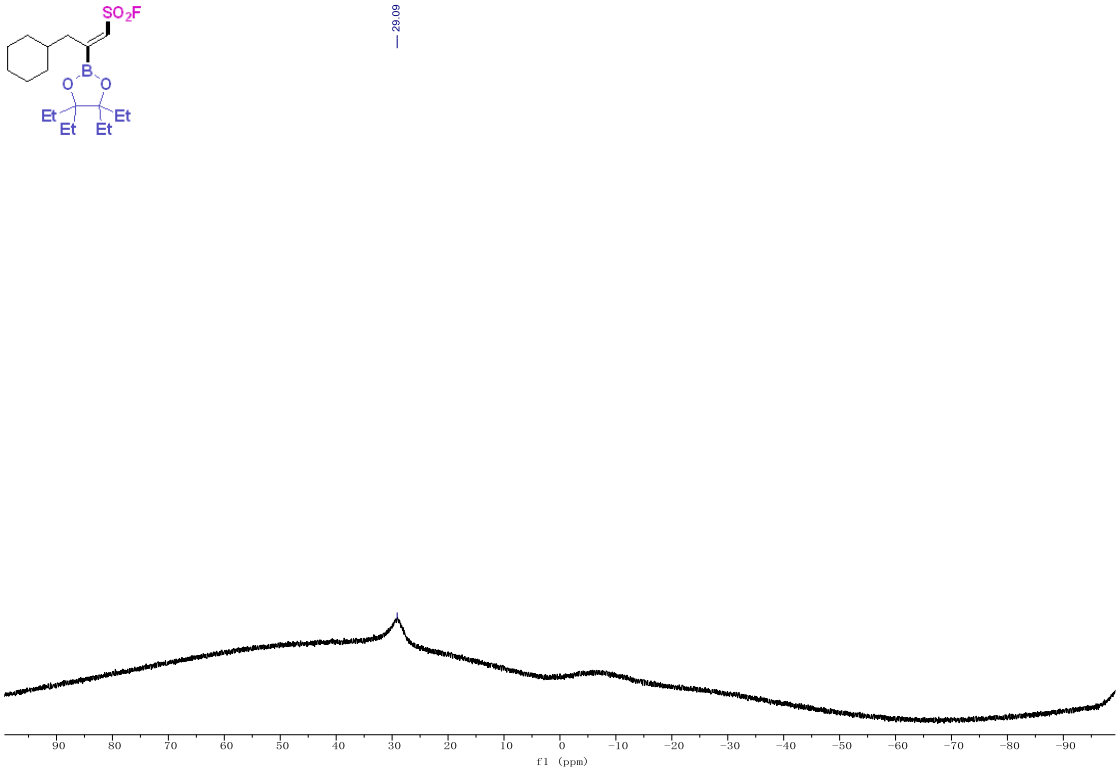
Supplementary Figure 15. ^{1}H NMR spectra of product **4a**



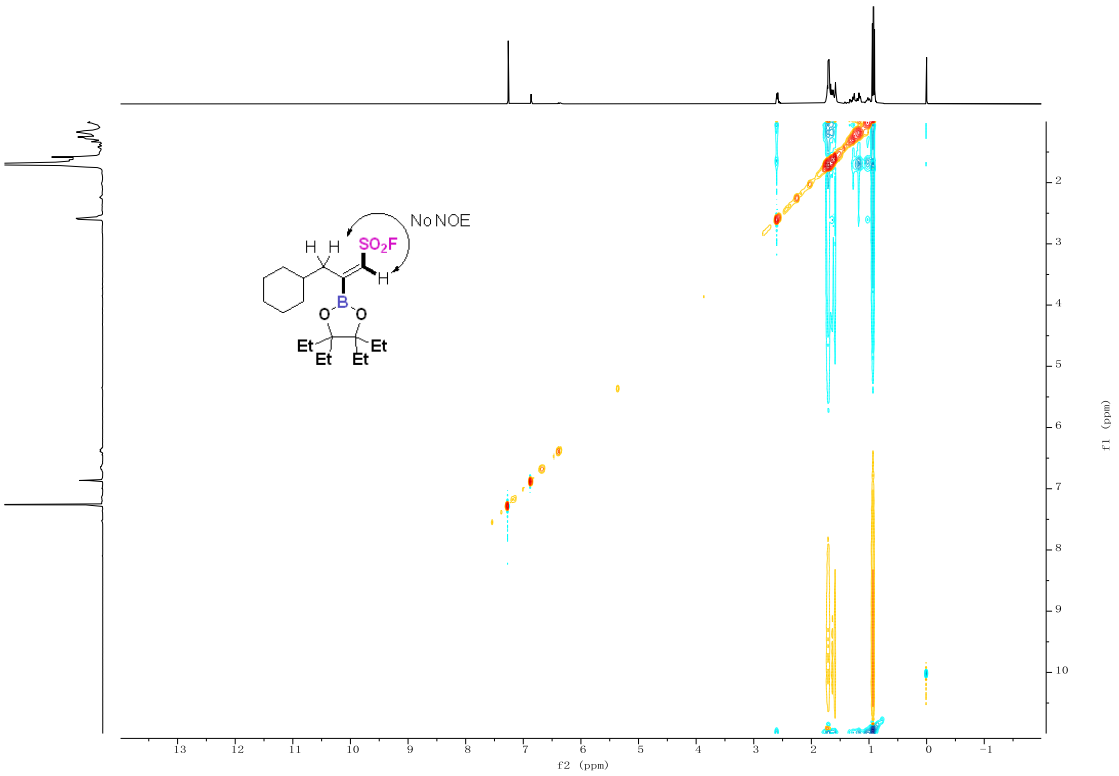
Supplementary Figure 16. ^{13}C NMR spectra of product **4a**



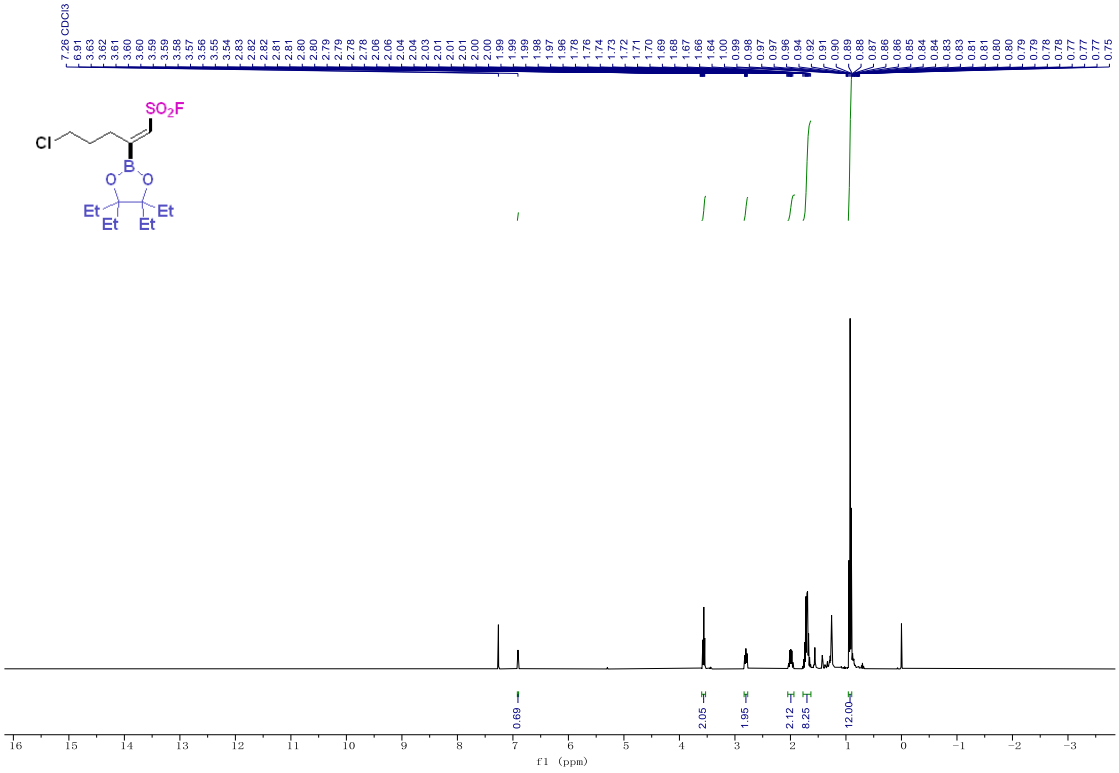
Supplementary Figure 17. ^{19}F NMR spectra of product **4a**



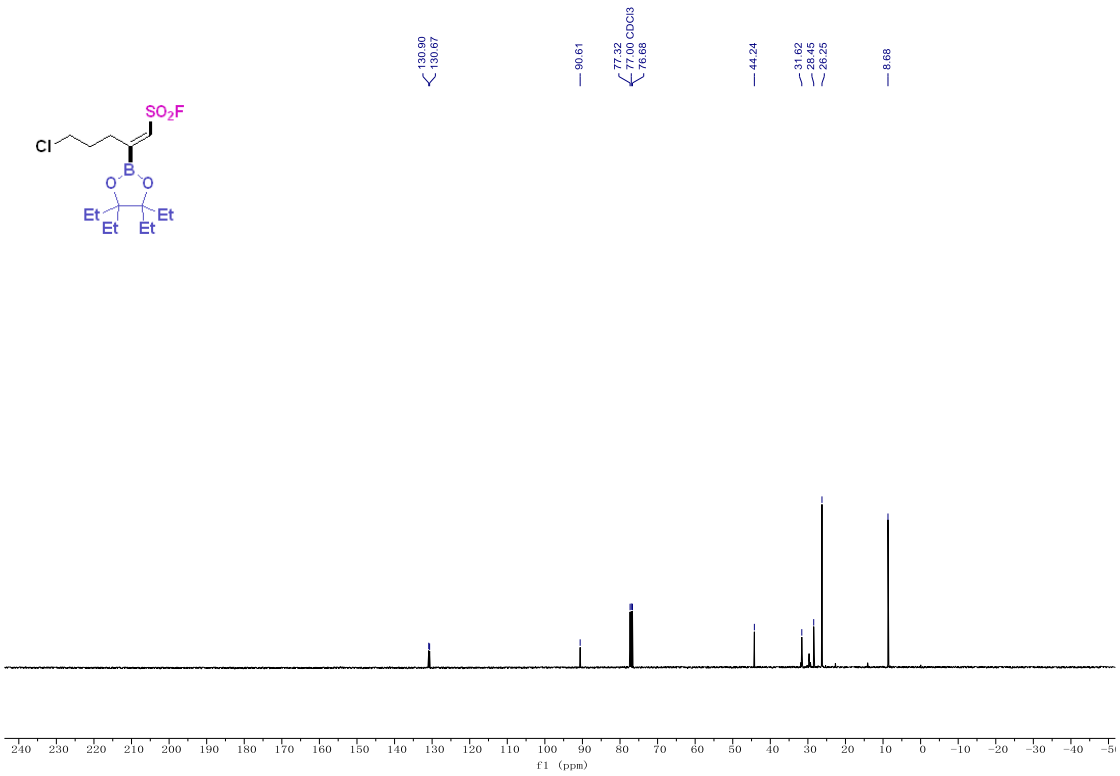
Supplementary Figure 18. ^{11}B NMR spectra of product **4a**



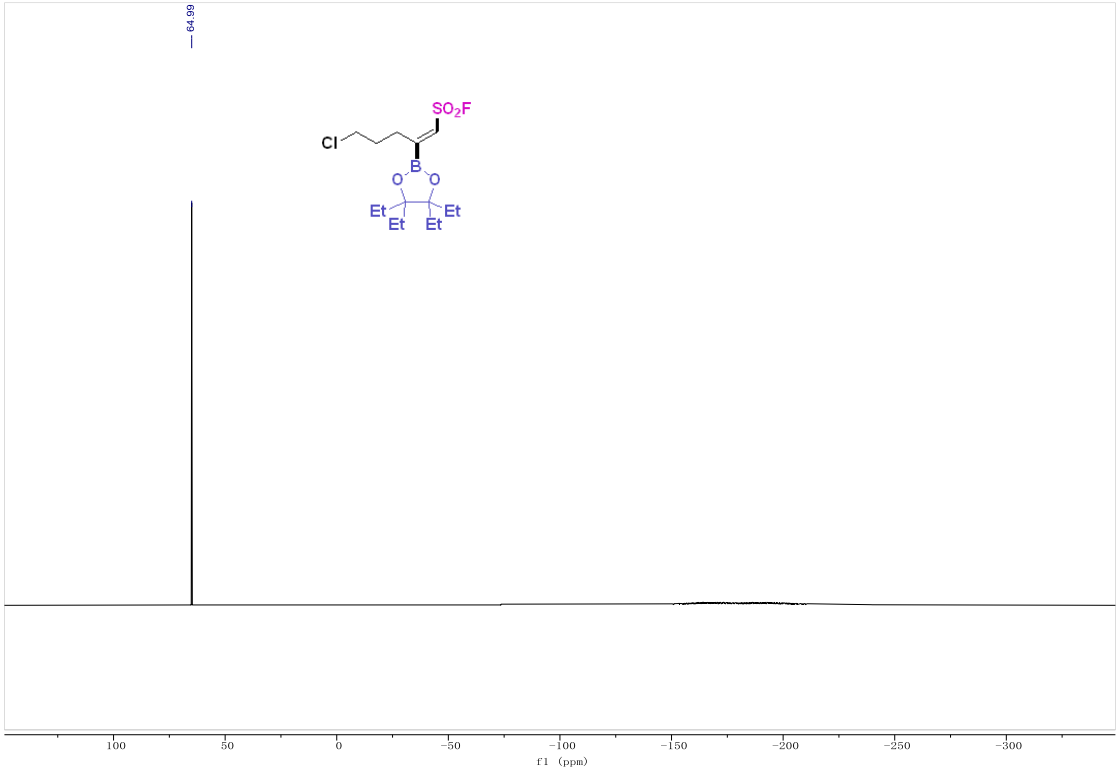
Supplementary Figure 19. NOESY spectra of product **4a**



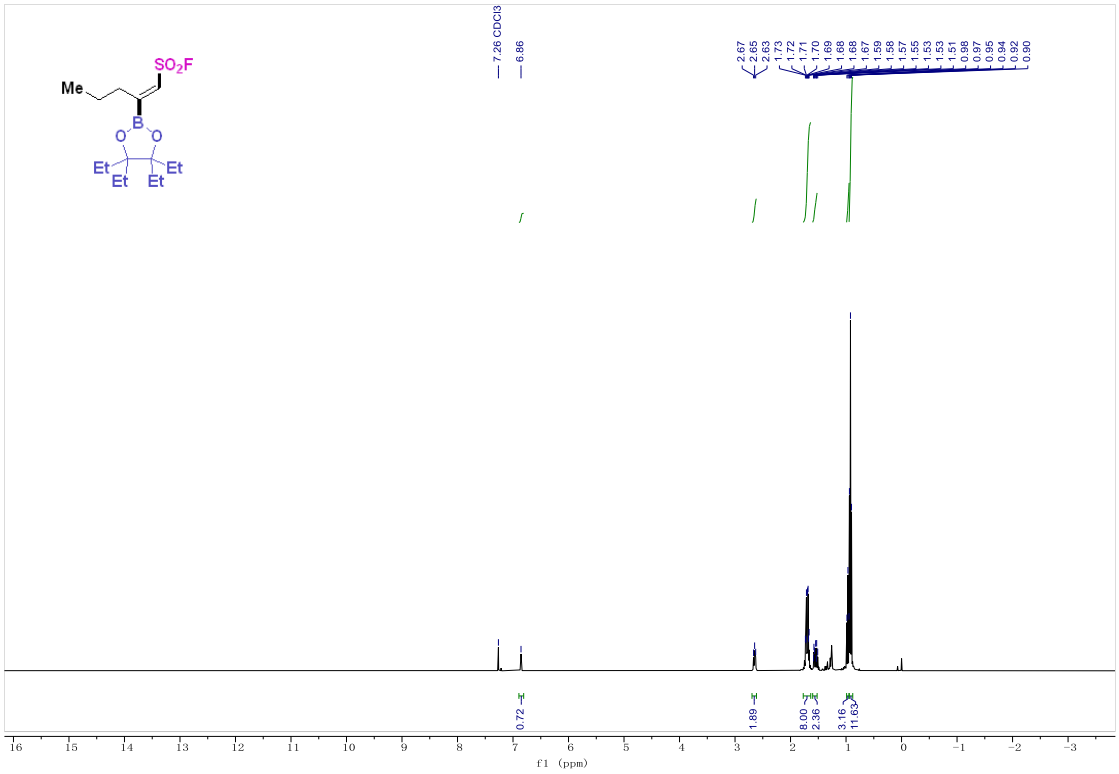
Supplementary Figure 20. ^{1}H NMR spectra of product **4b**



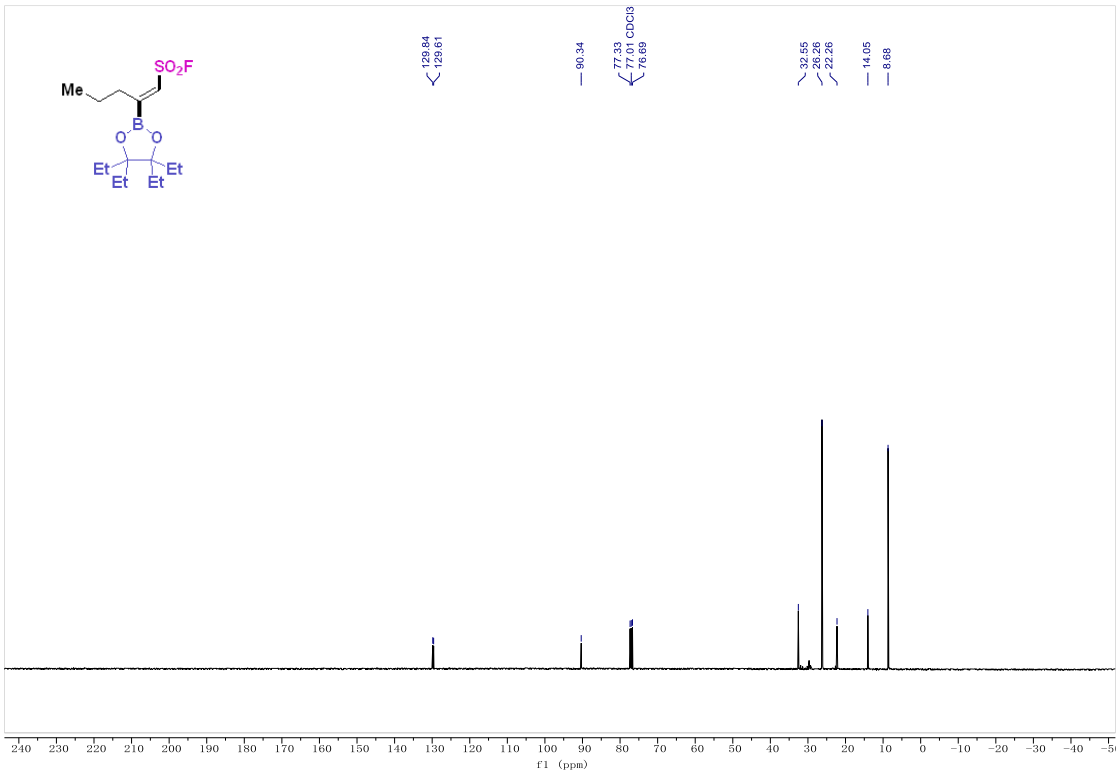
Supplementary Figure 21. ^{13}C NMR spectra of product **4b**



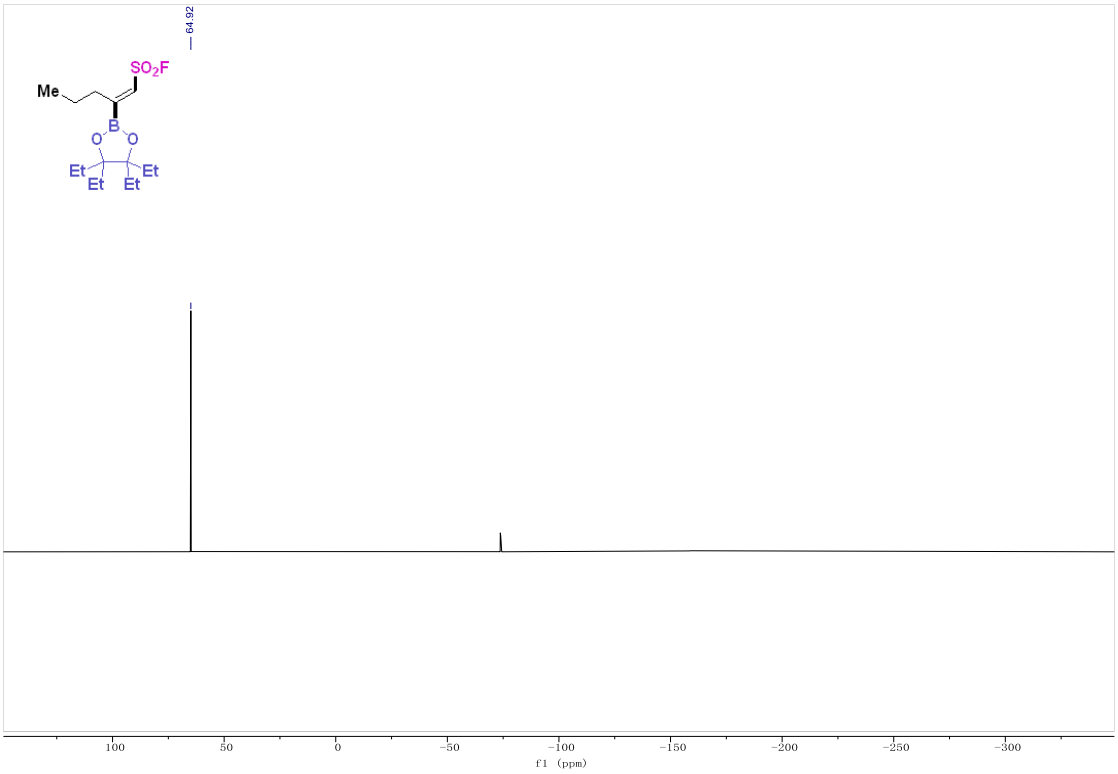
Supplementary Figure 22. ^{19}F NMR spectra of product **4b**



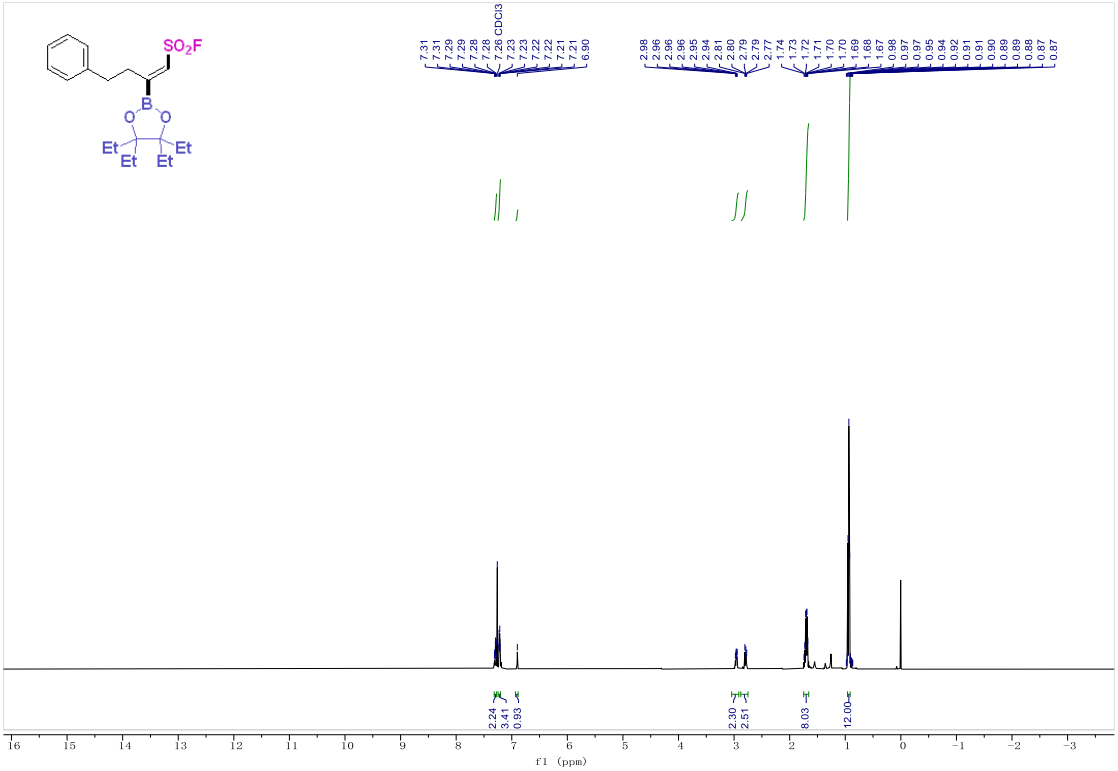
Supplementary Figure 23. ^{1}H NMR spectra of product **4c**



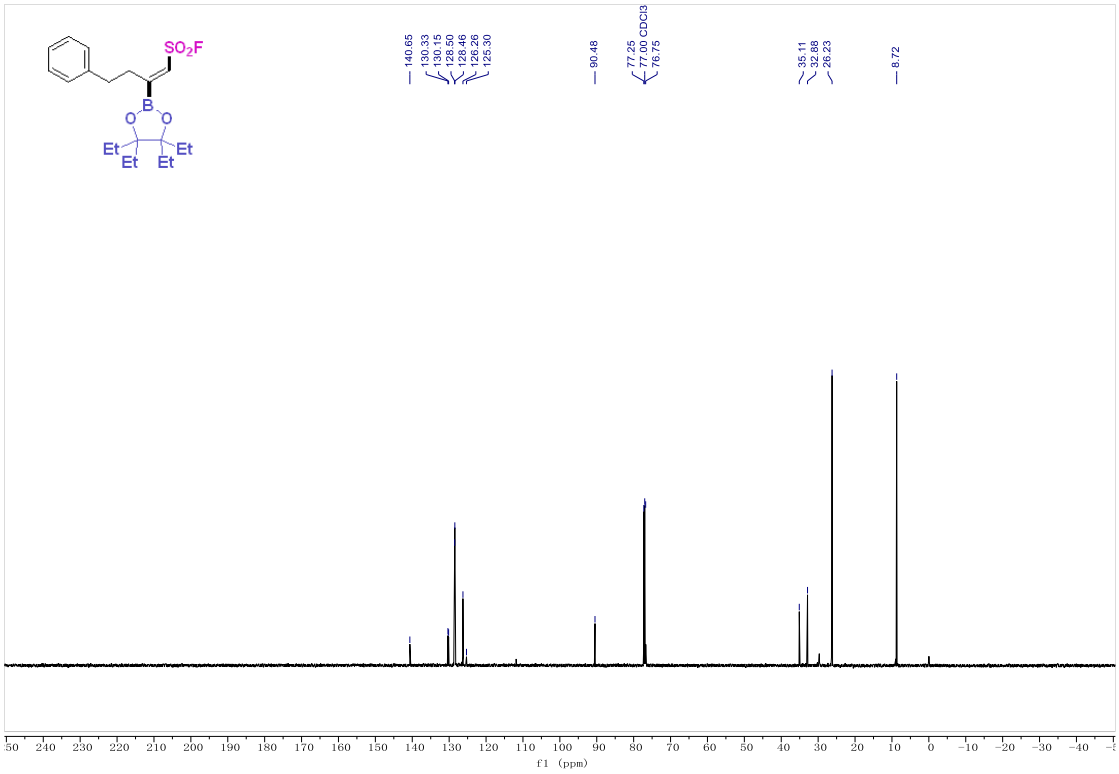
Supplementary Figure 24. ^{13}C NMR spectra of product **4c**



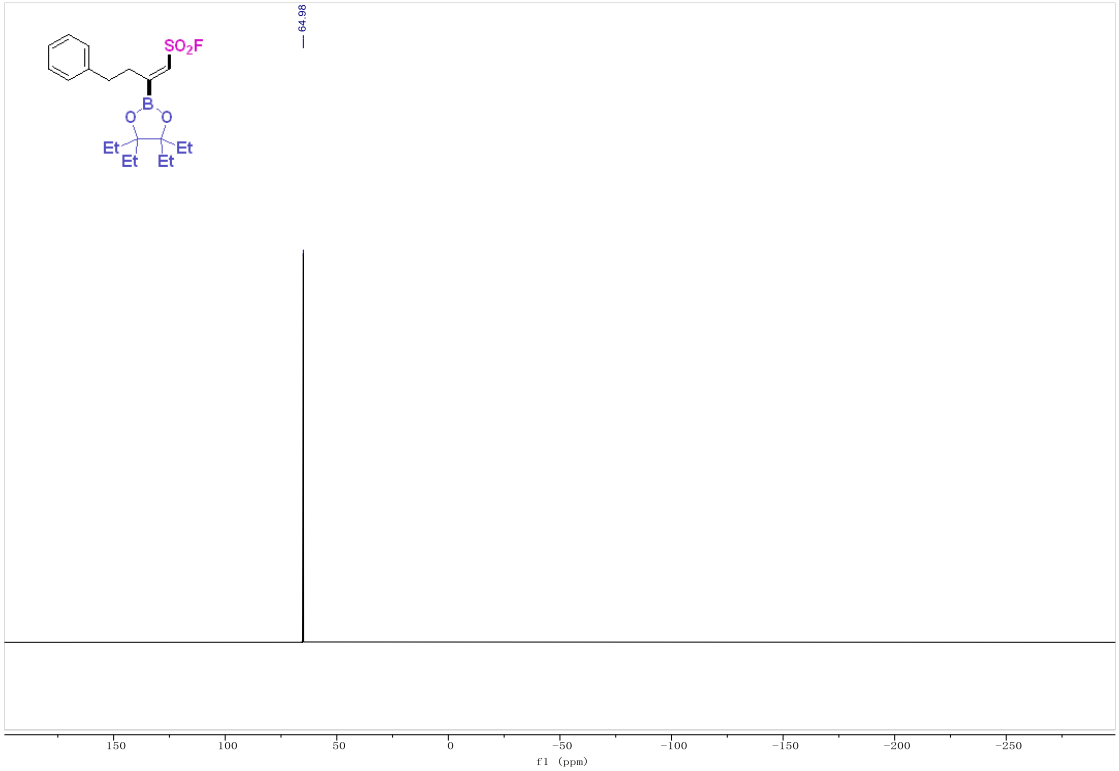
Supplementary Figure 25. ^{19}F NMR spectra of product **4c**



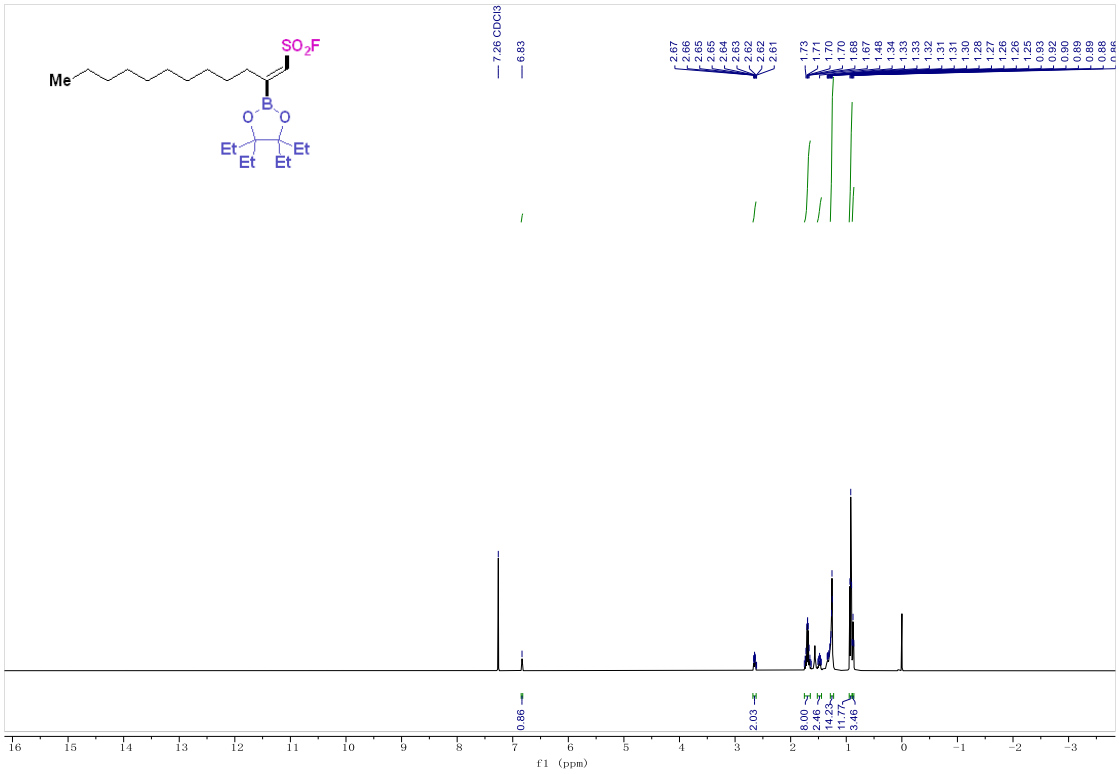
Supplementary Figure 26. ^{1}H NMR spectra of product **4d**



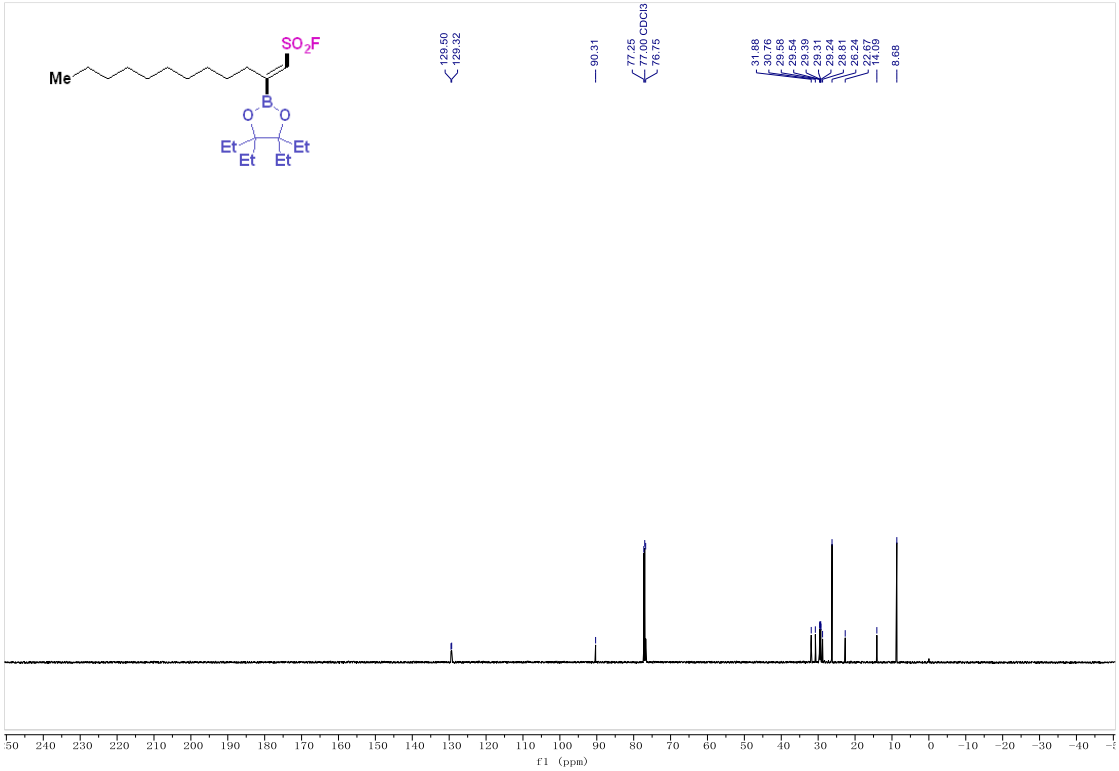
Supplementary Figure 27. ^{13}C NMR spectra of product **4d**



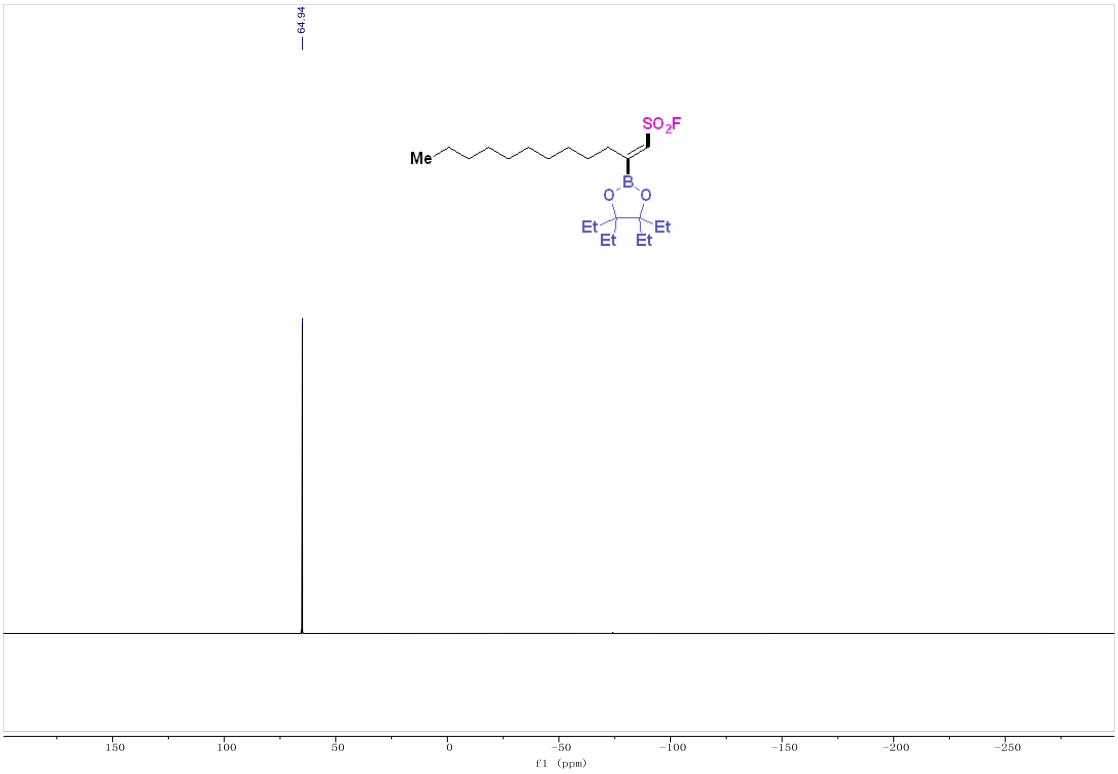
Supplementary Figure 28. ^{19}F NMR spectra of product **4d**



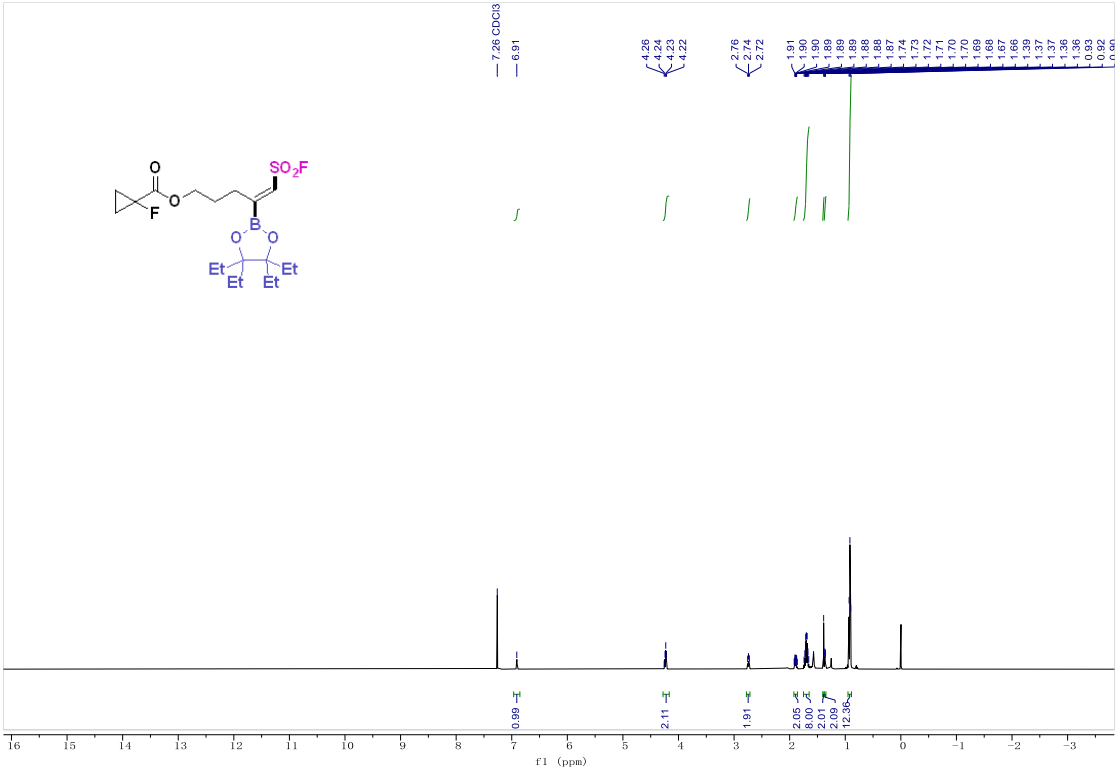
Supplementary Figure 29. ^{1}H NMR spectra of product **4e**



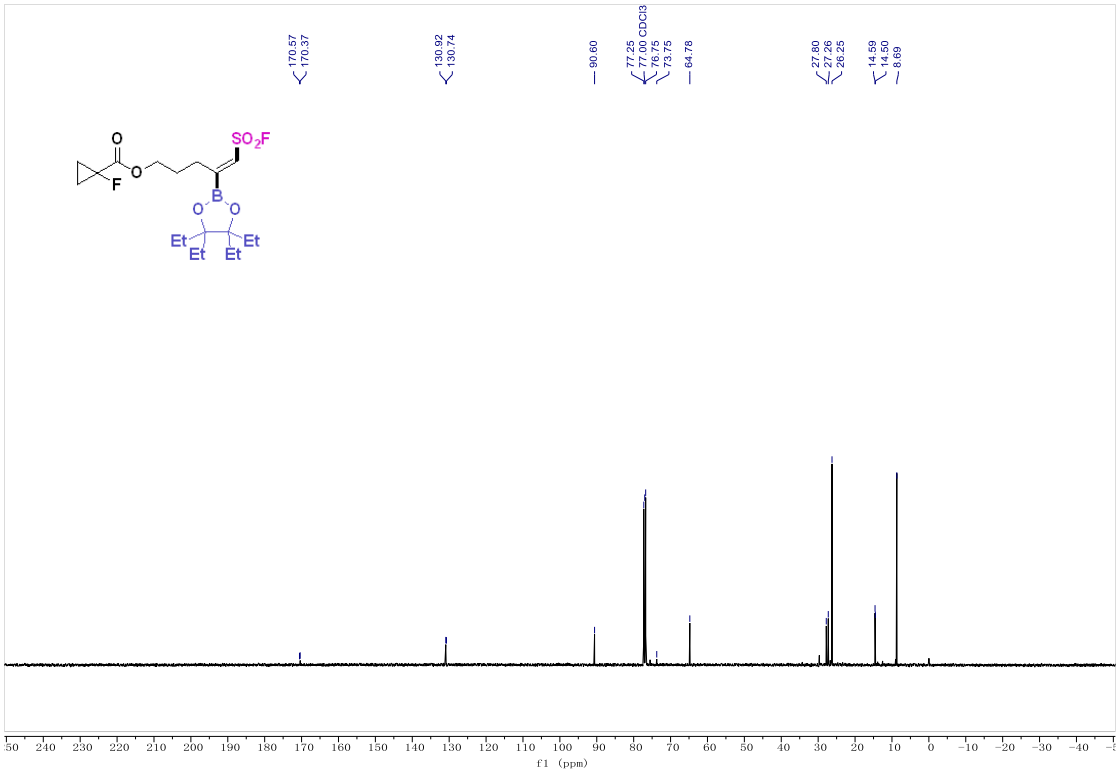
Supplementary Figure 30. ^{13}C NMR spectra of product **4e**



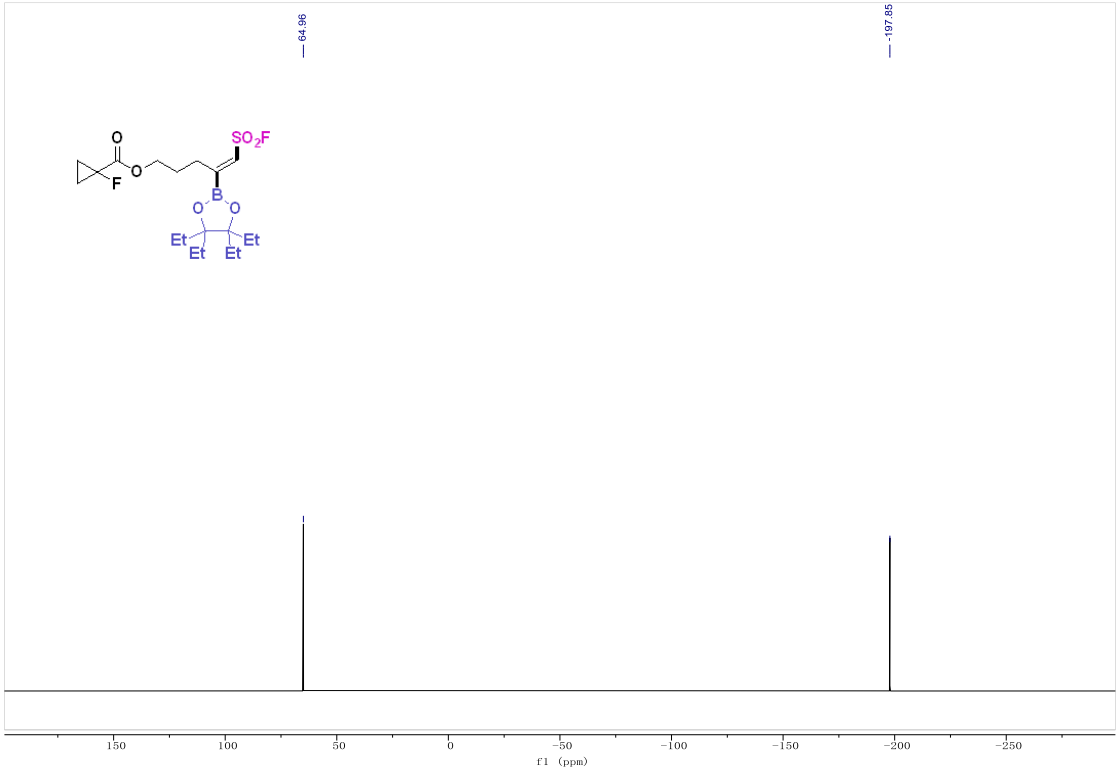
Supplementary Figure 31. ^{19}F NMR spectra of product **4e**



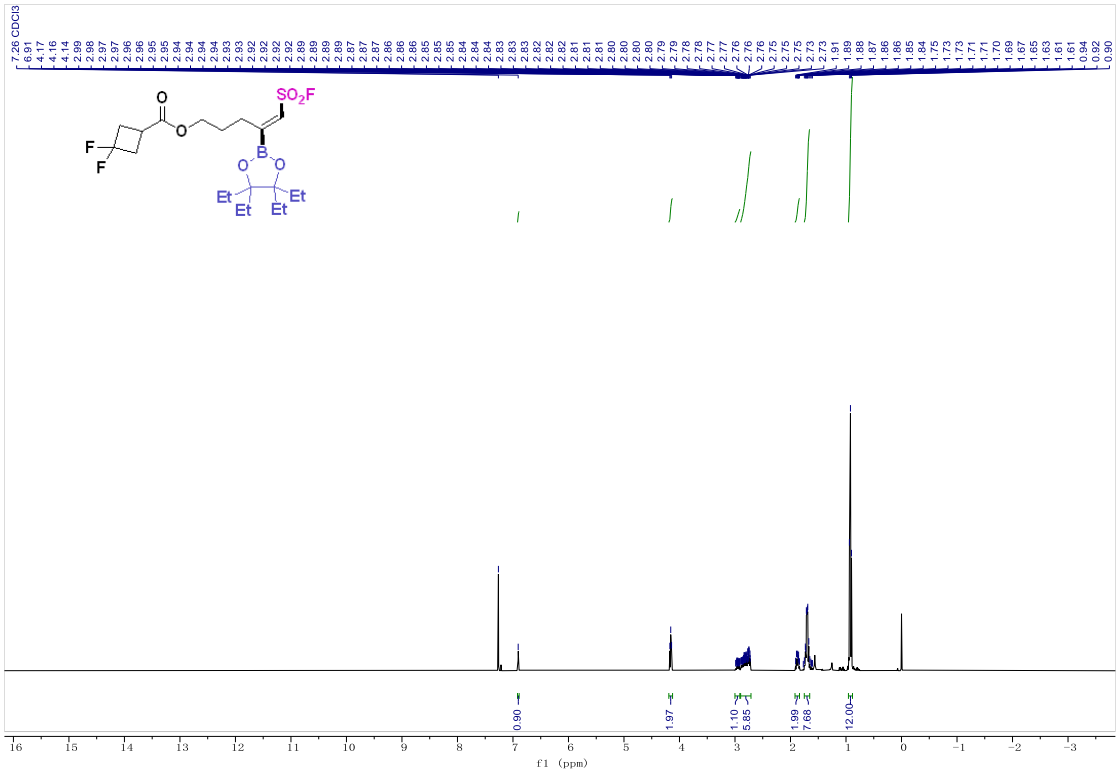
Supplementary Figure 32. ^{1}H NMR spectra of product **4f**



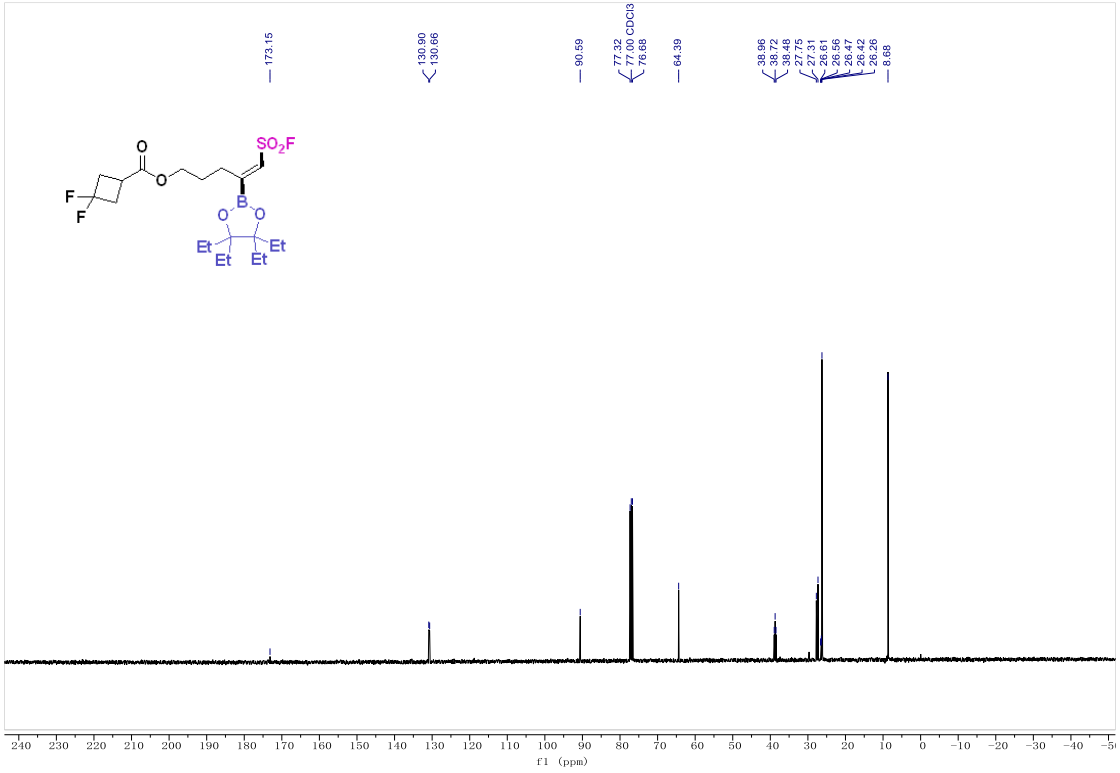
Supplementary Figure 33. ^{13}C NMR spectra of product **4f**



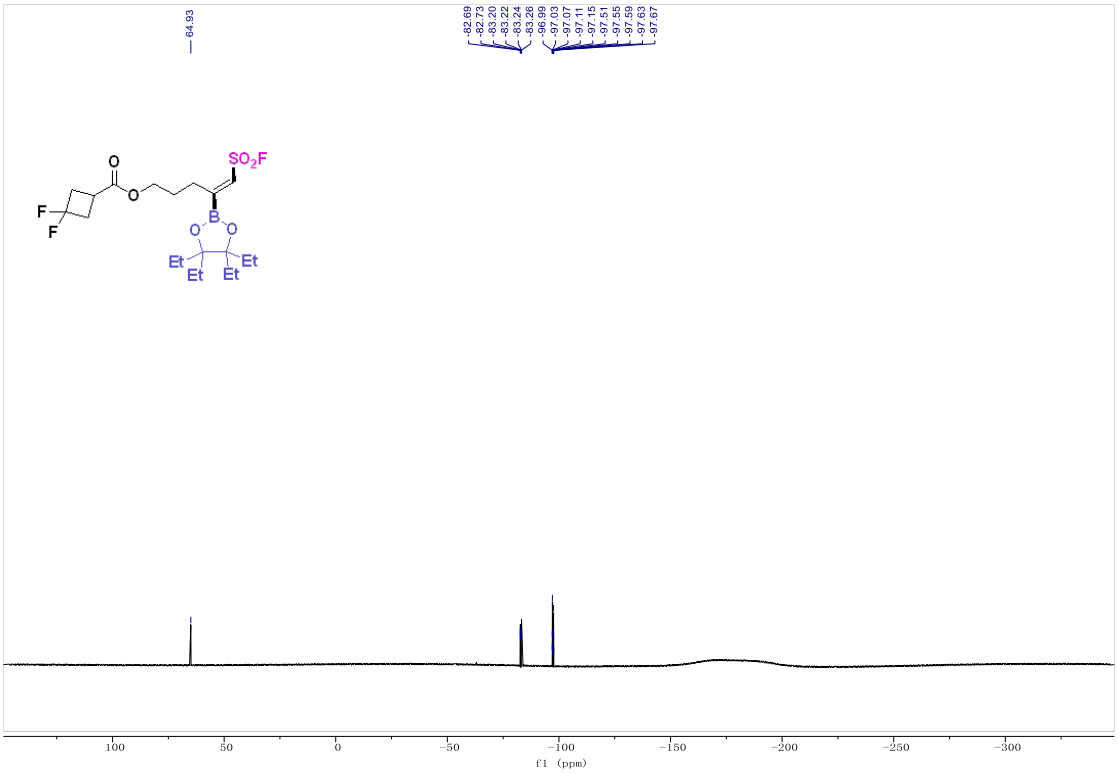
Supplementary Figure 34. ^{19}F NMR spectra of product **4f**



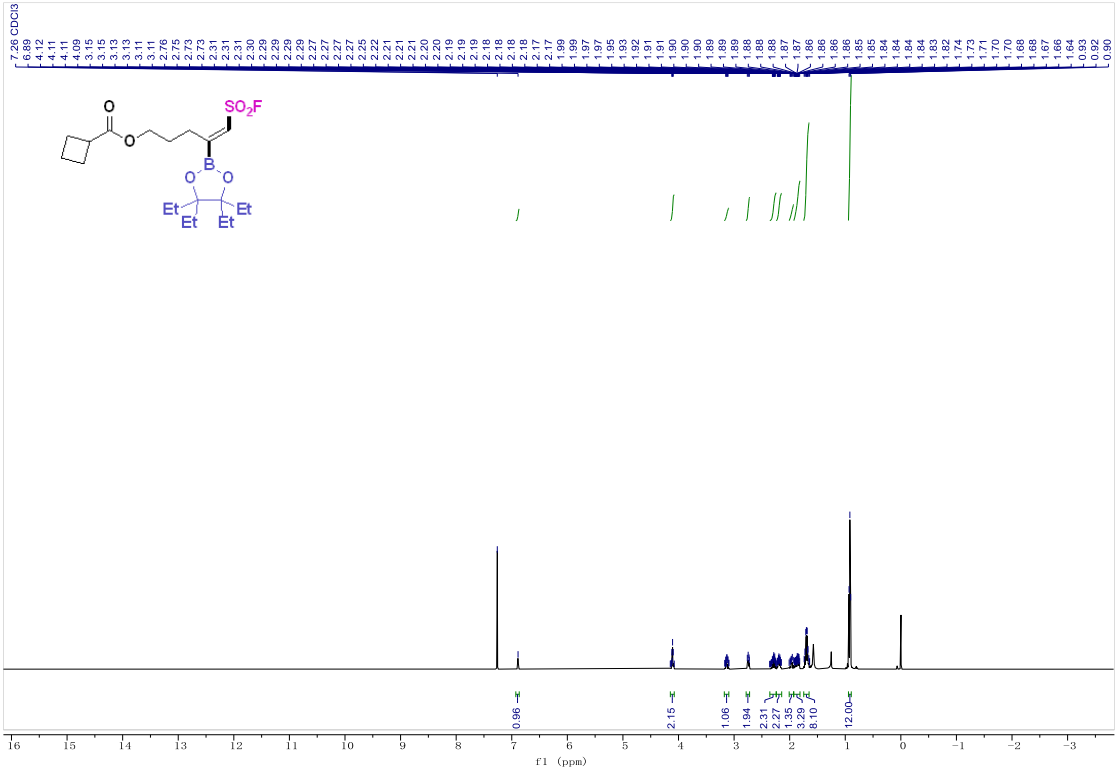
Supplementary Figure 35. ^{1}H NMR spectra of product **4g**



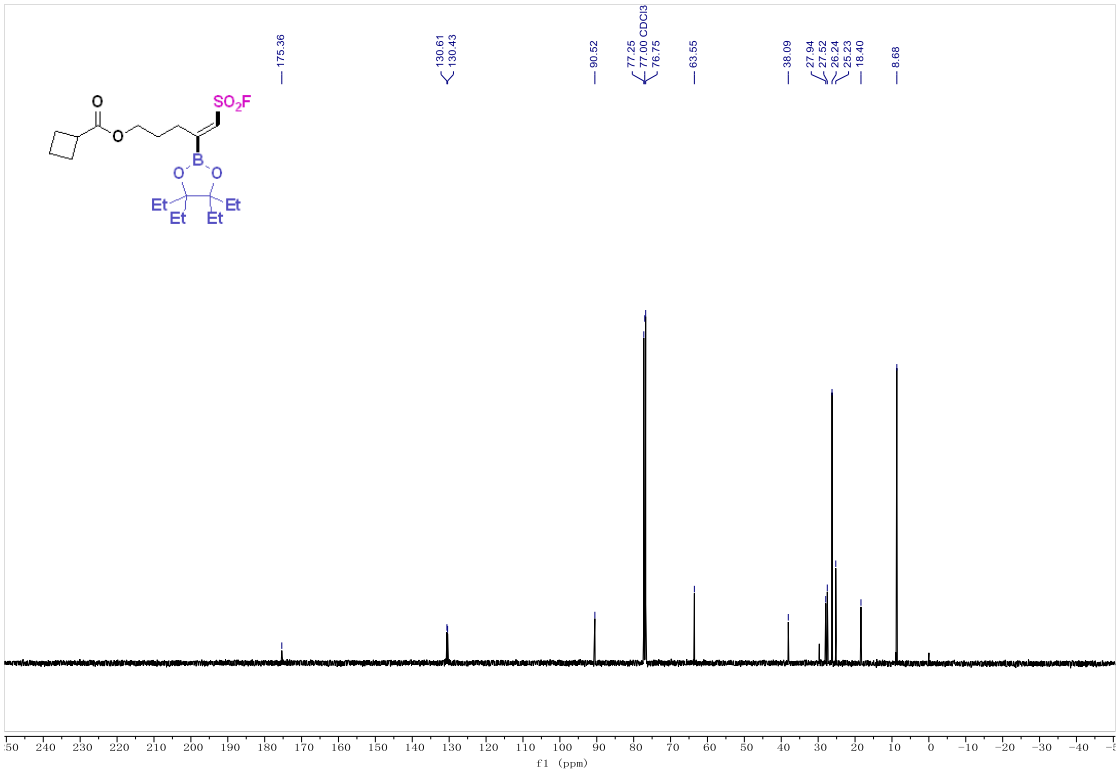
Supplementary Figure 36. ^{13}C NMR spectra of product **4g**



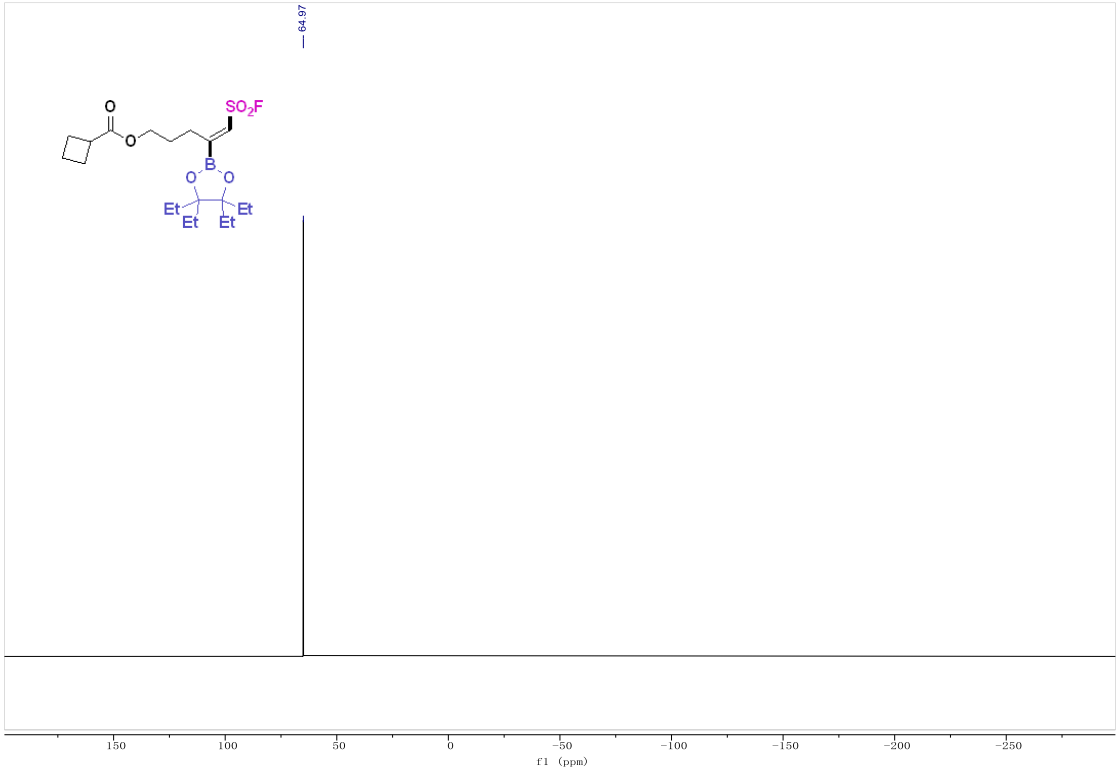
Supplementary Figure 37. ^{19}F NMR spectra of product **4g**



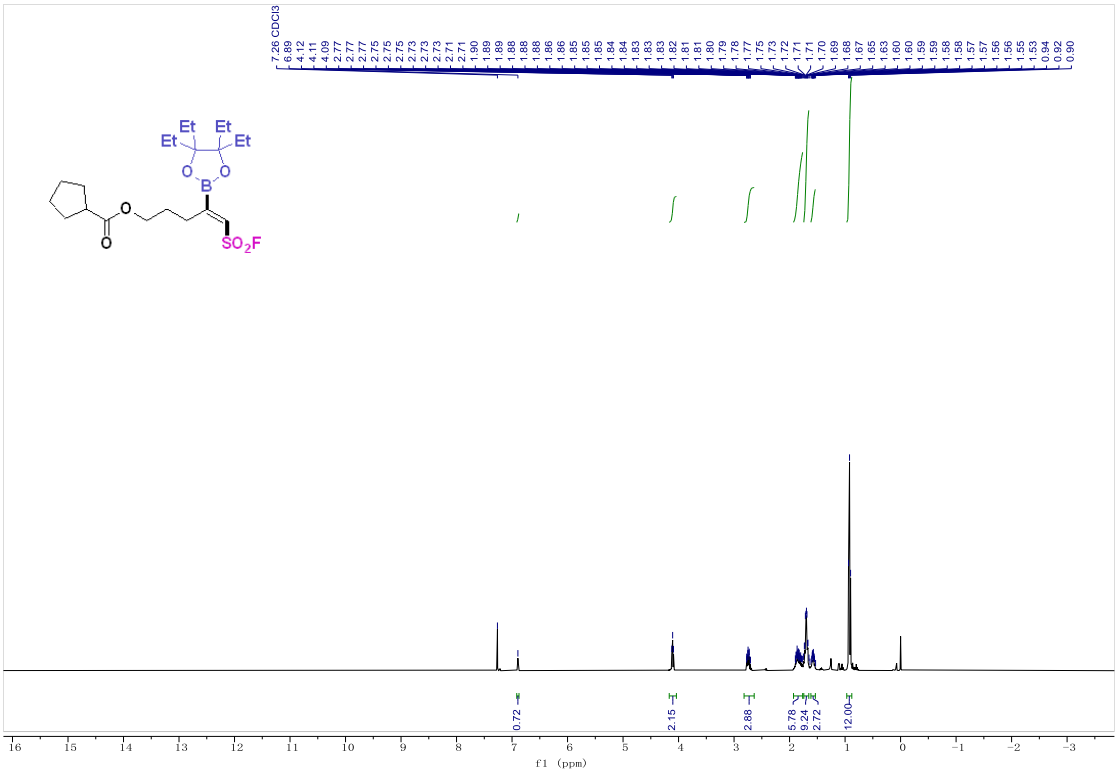
Supplementary Figure 38. ^{1}H NMR spectra of product **4h**



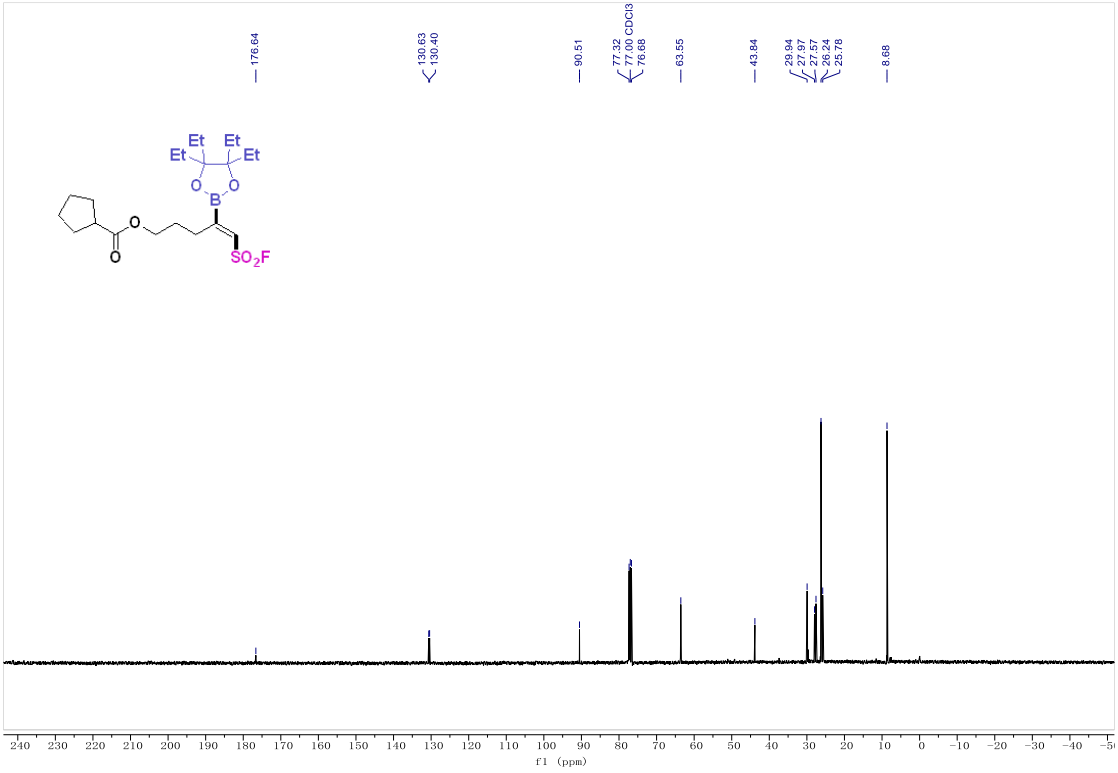
Supplementary Figure 39. ^{13}C NMR spectra of product **4h**



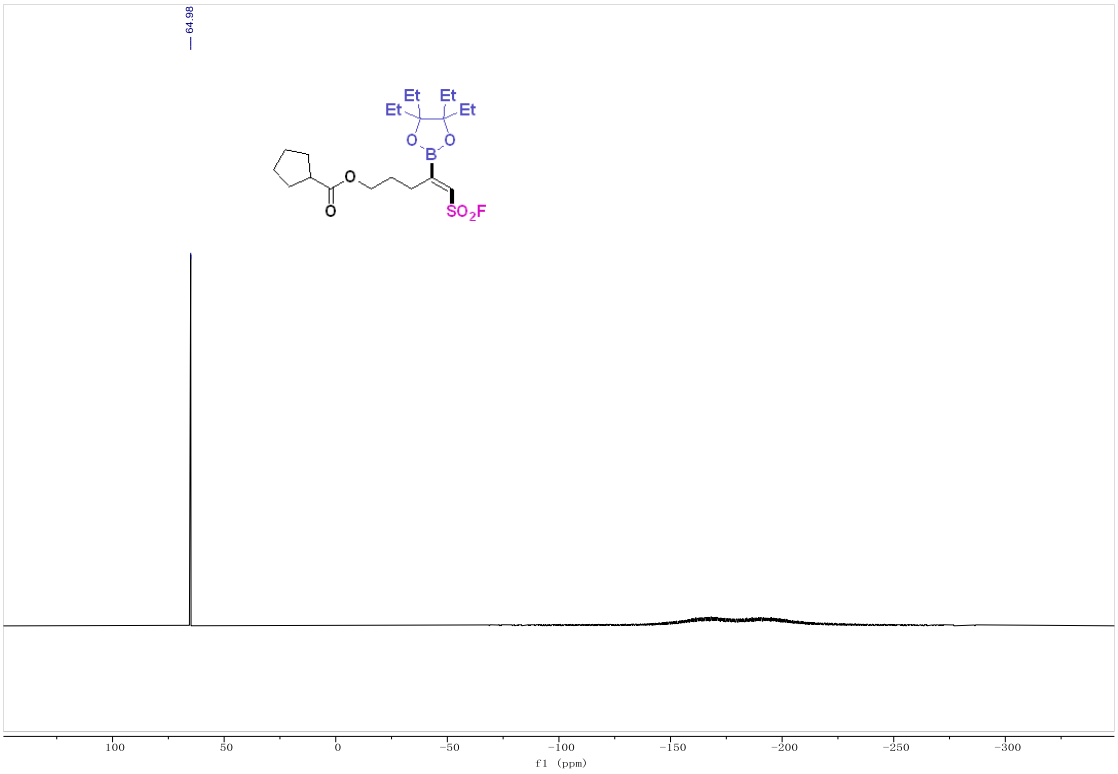
Supplementary Figure 40. ^{19}F NMR spectra of product **4h**



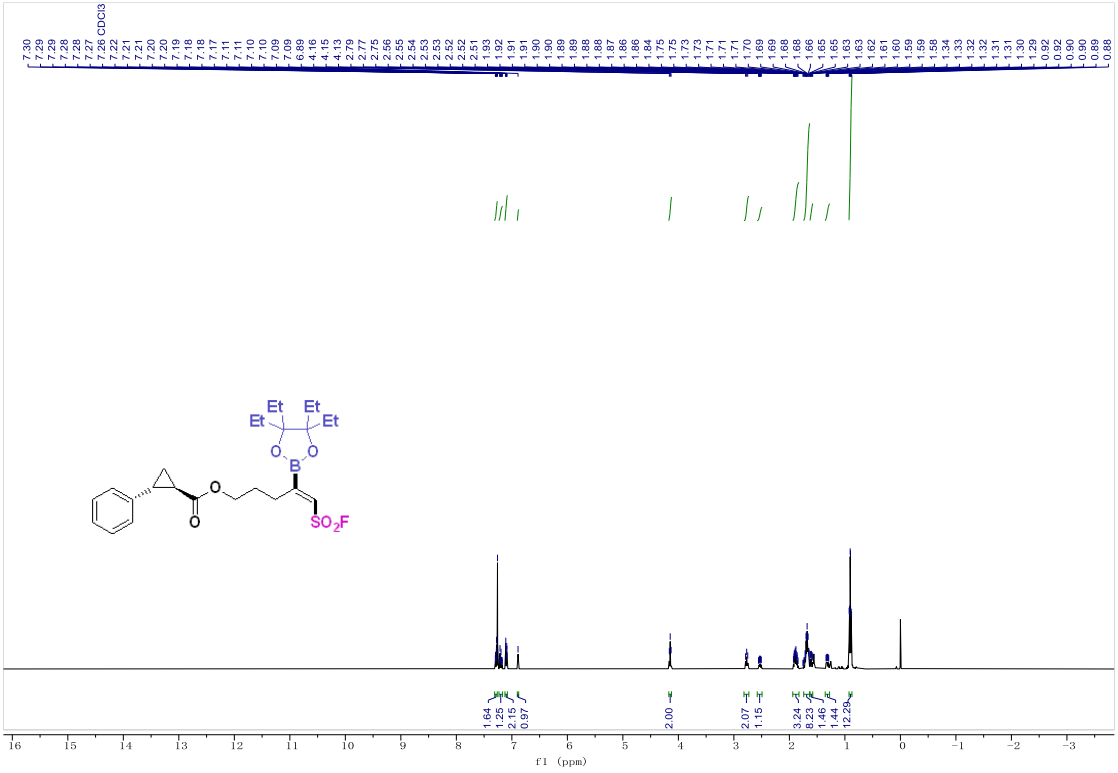
Supplementary Figure 41. ^{1}H NMR spectra of product **4i**



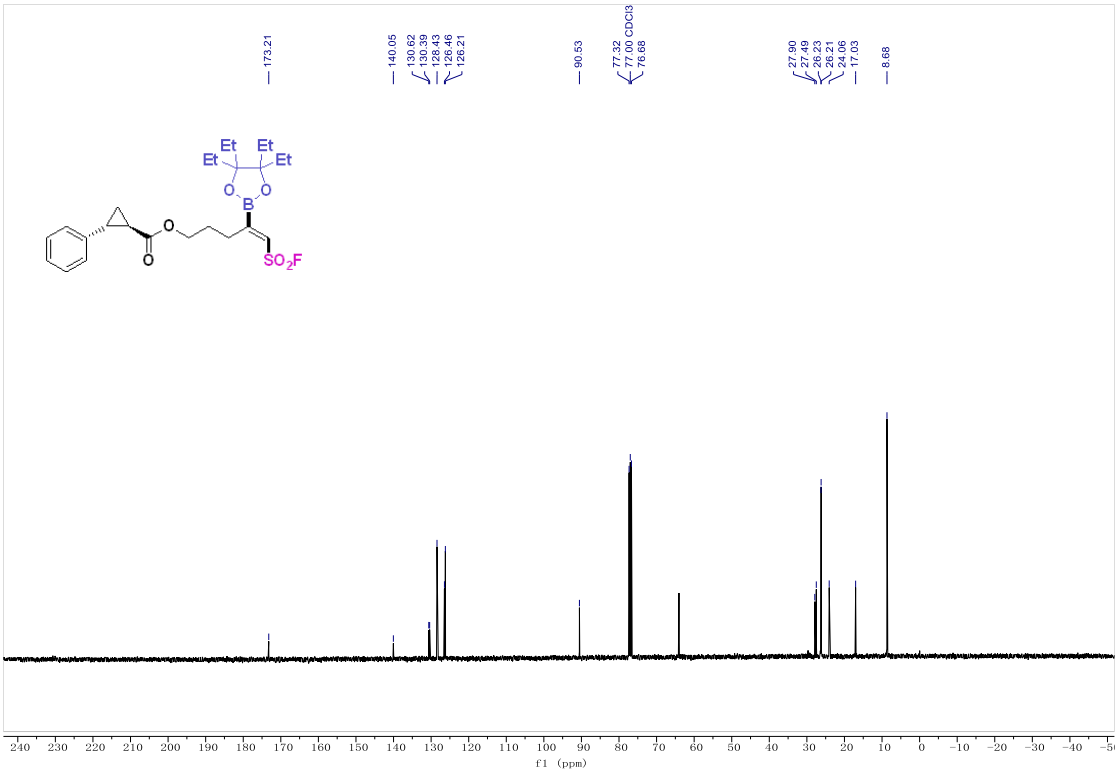
Supplementary Figure 42. ^{13}C NMR spectra of product **4i**



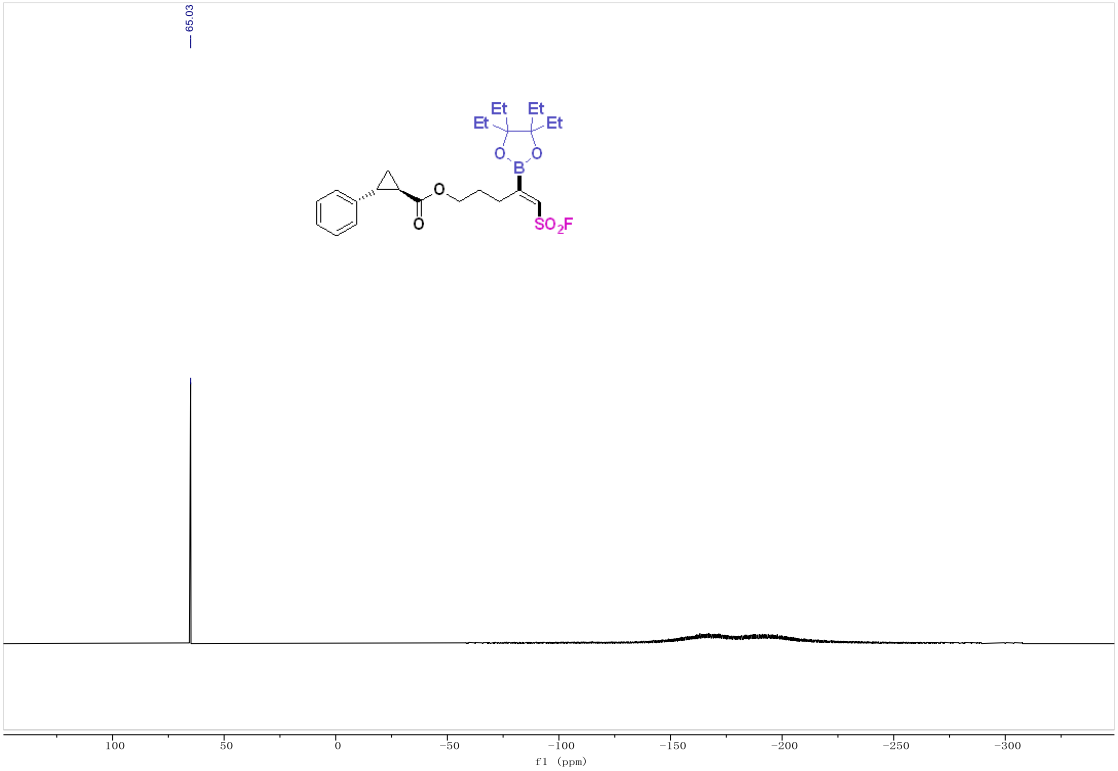
Supplementary Figure 43. ^{19}F NMR spectra of product **4i**



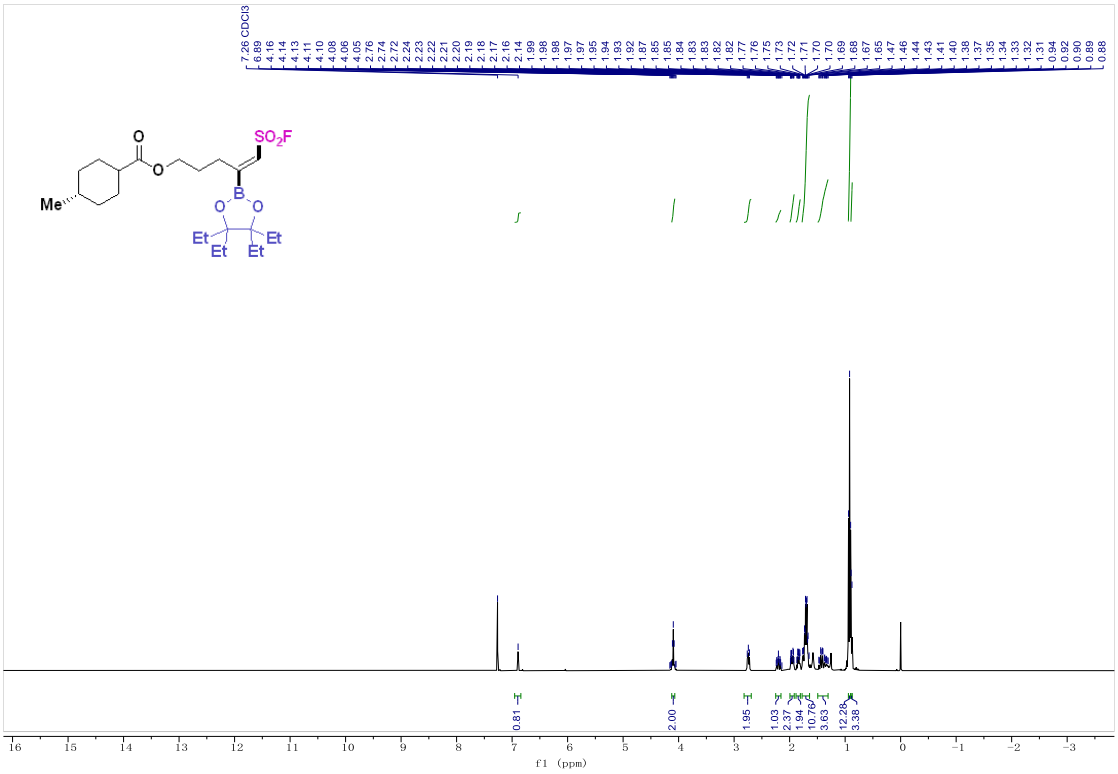
Supplementary Figure 44. ^{1}H NMR spectra of product **4j**



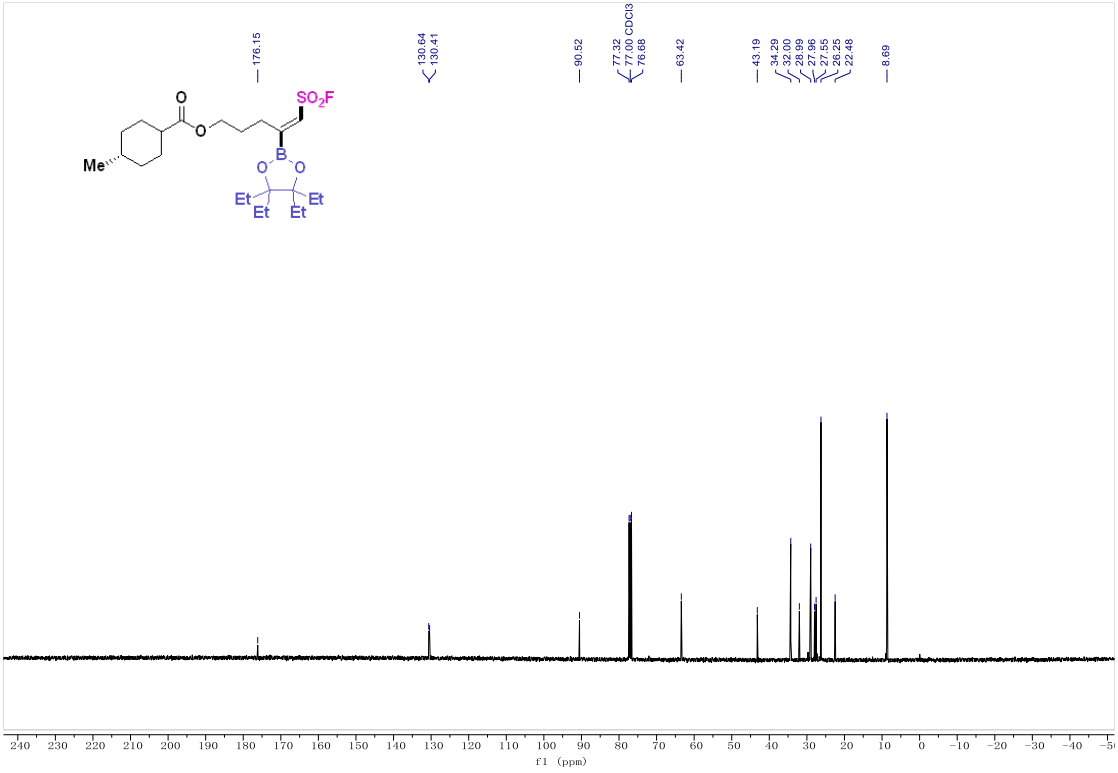
Supplementary Figure 45. ^{13}C NMR spectra of product **4j**



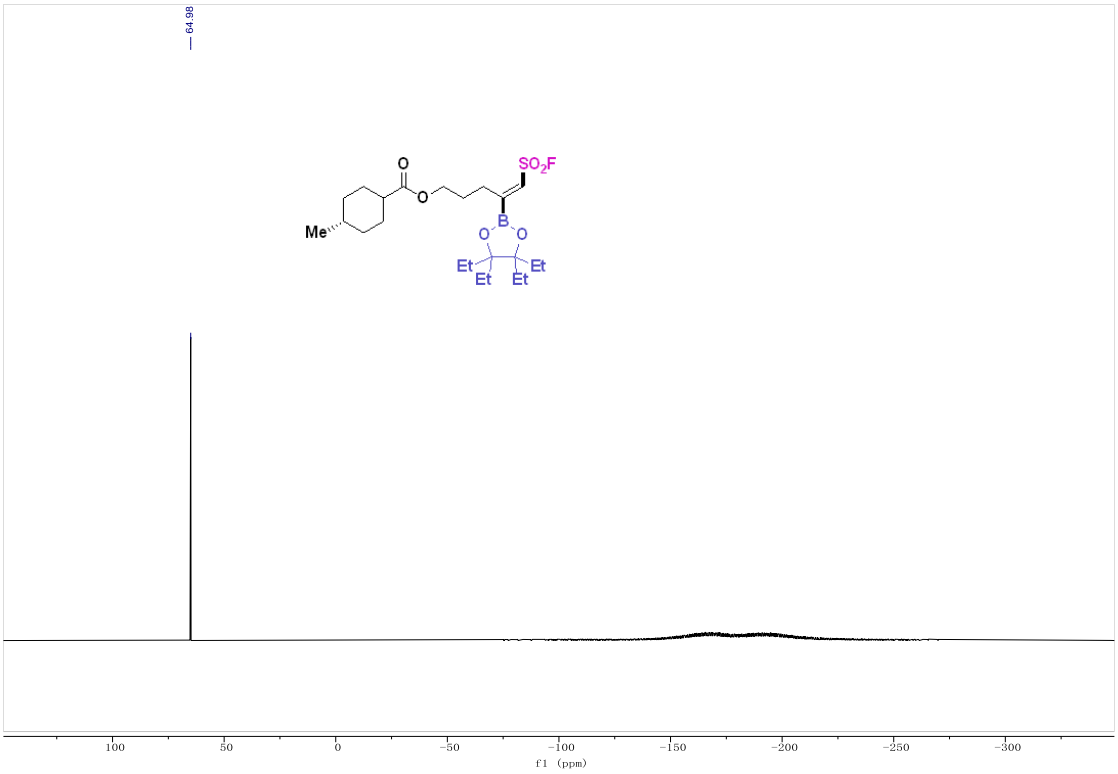
Supplementary Figure 46. ^{19}F NMR spectra of product **4j**



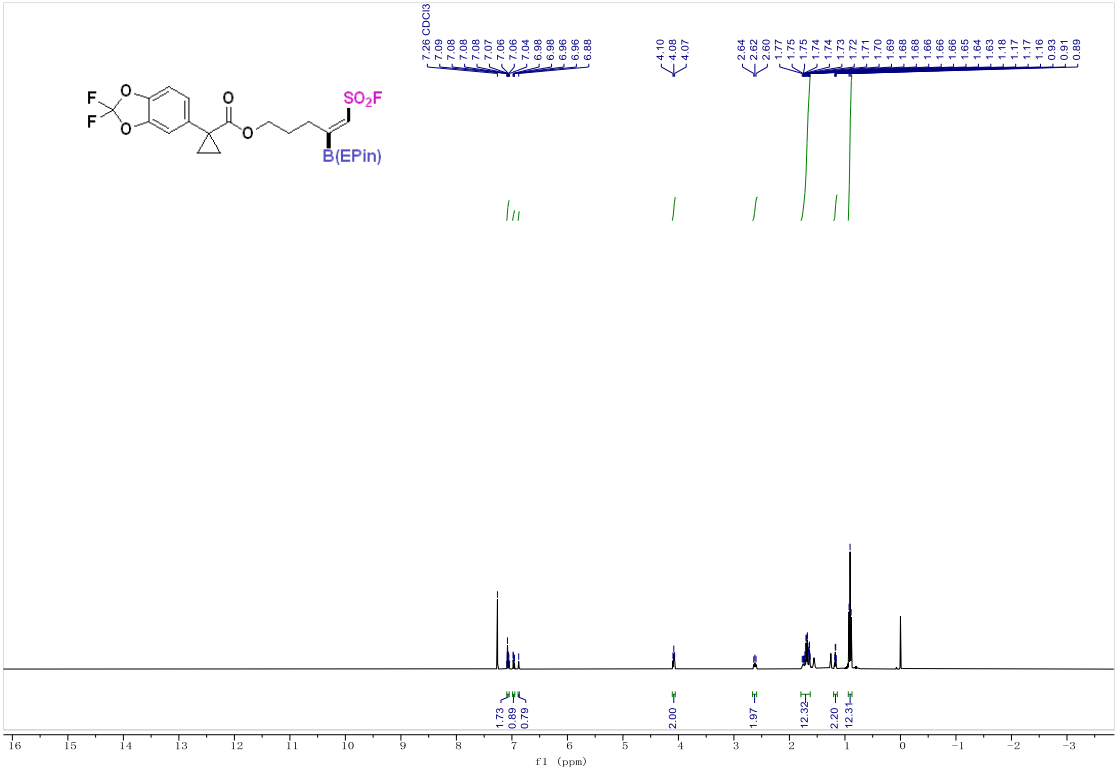
Supplementary Figure 47. ^{1}H NMR spectra of product **4k**



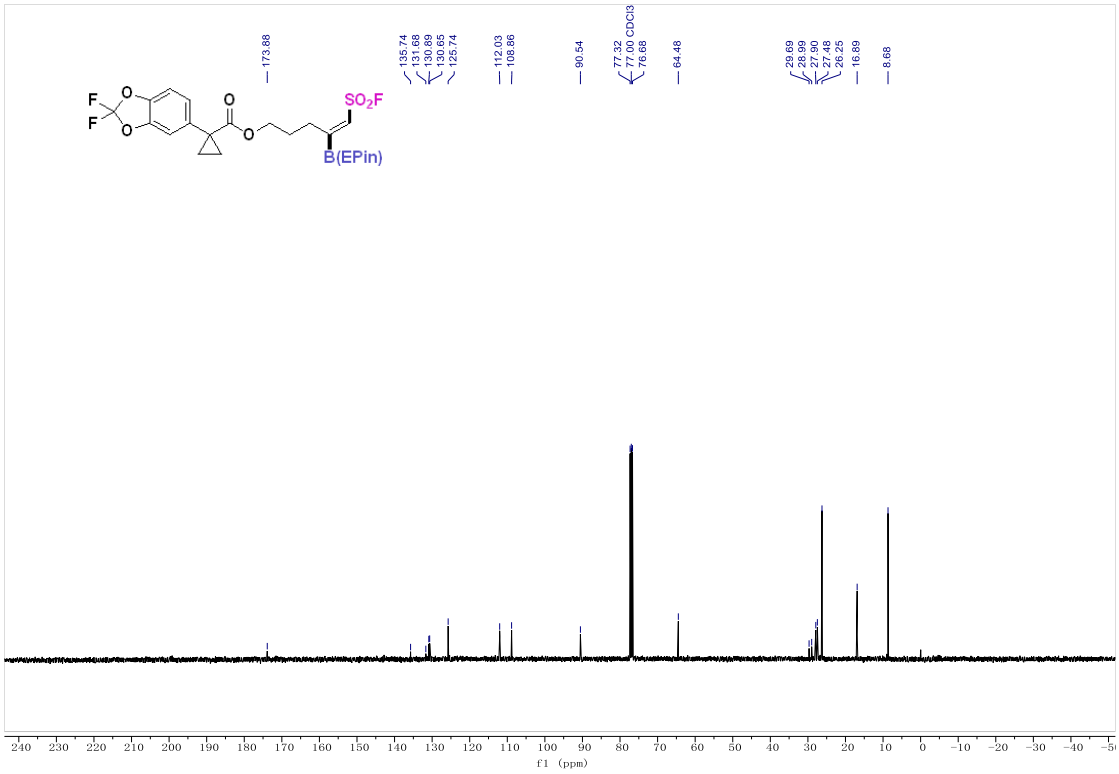
Supplementary Figure 48. ^{13}C NMR spectra of product **4k**



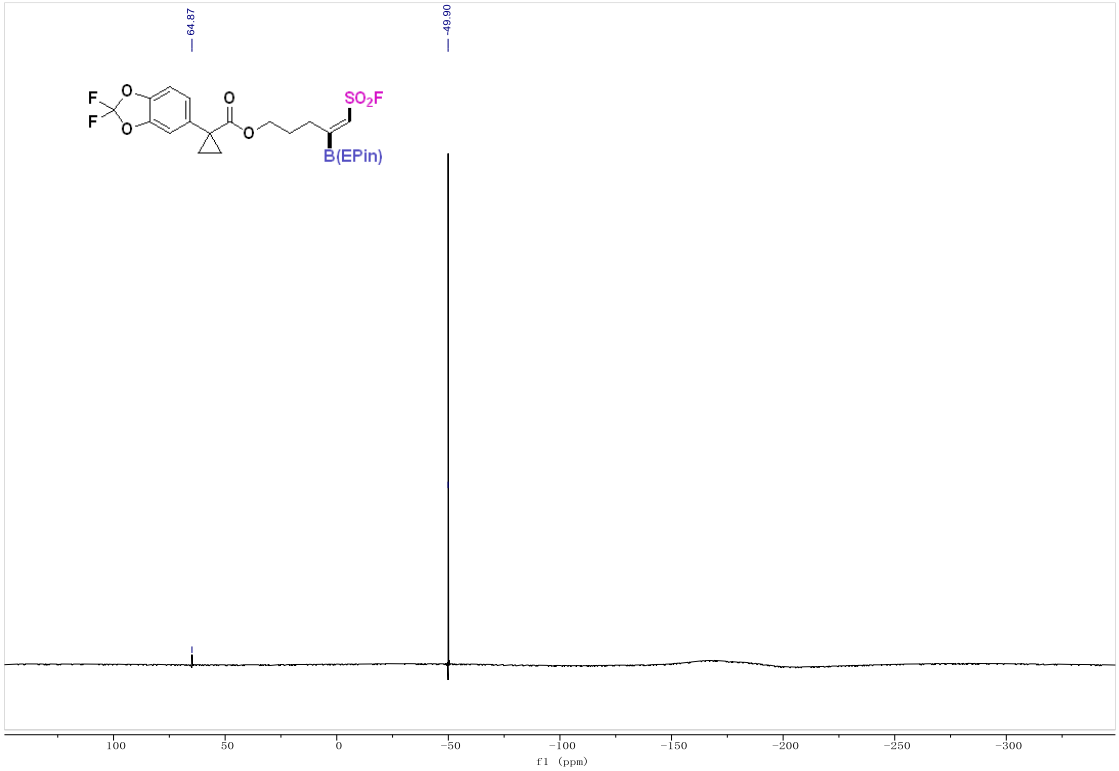
Supplementary Figure 49. ^{19}F NMR spectra of product **4k**



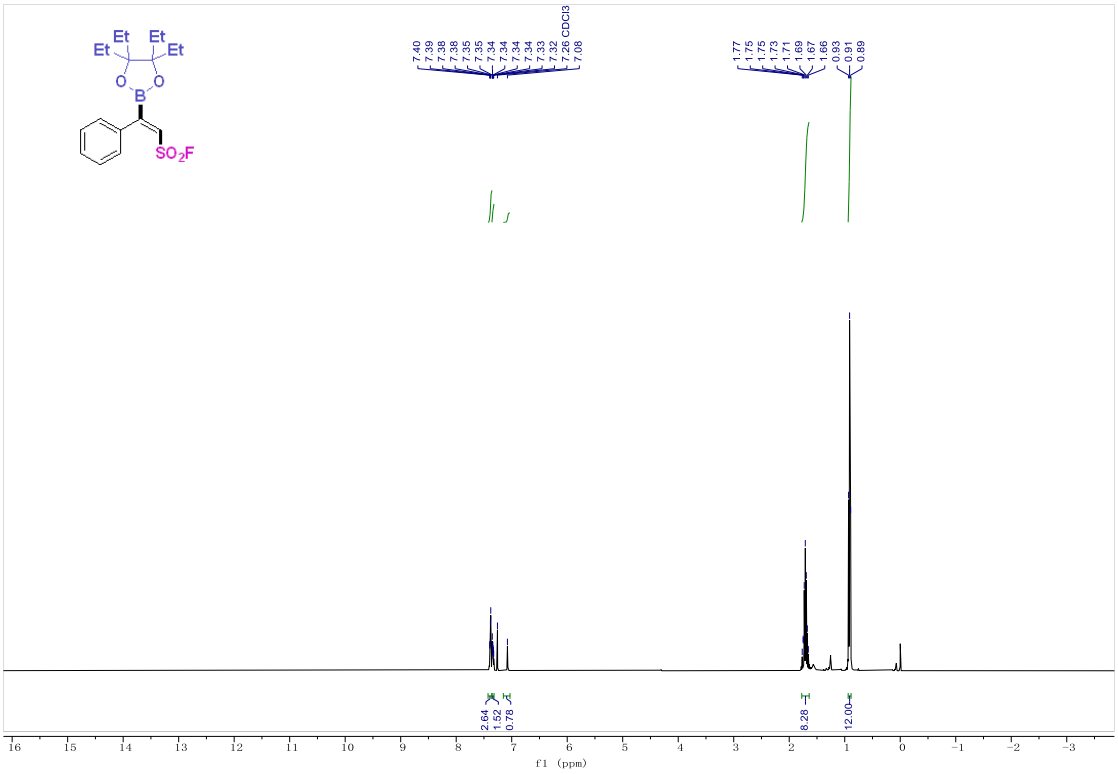
Supplementary Figure 50. ^{1}H NMR spectra of product **4l**



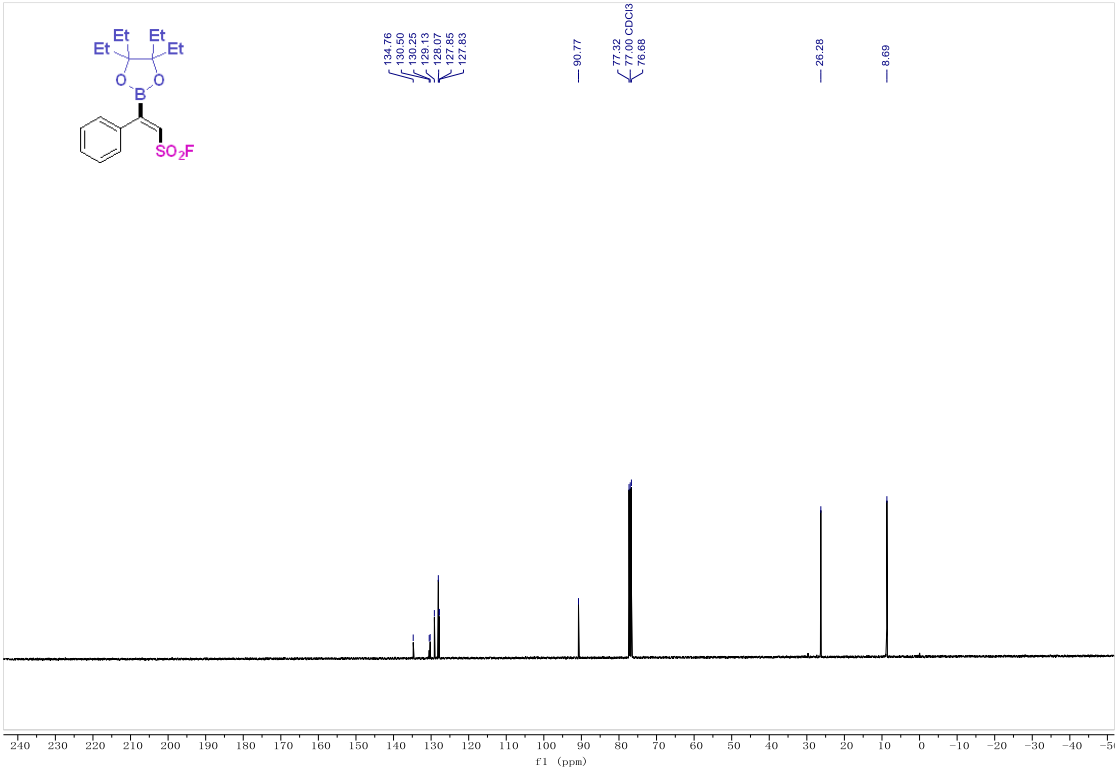
Supplementary Figure 51. ^{13}C NMR spectra of product **4l**



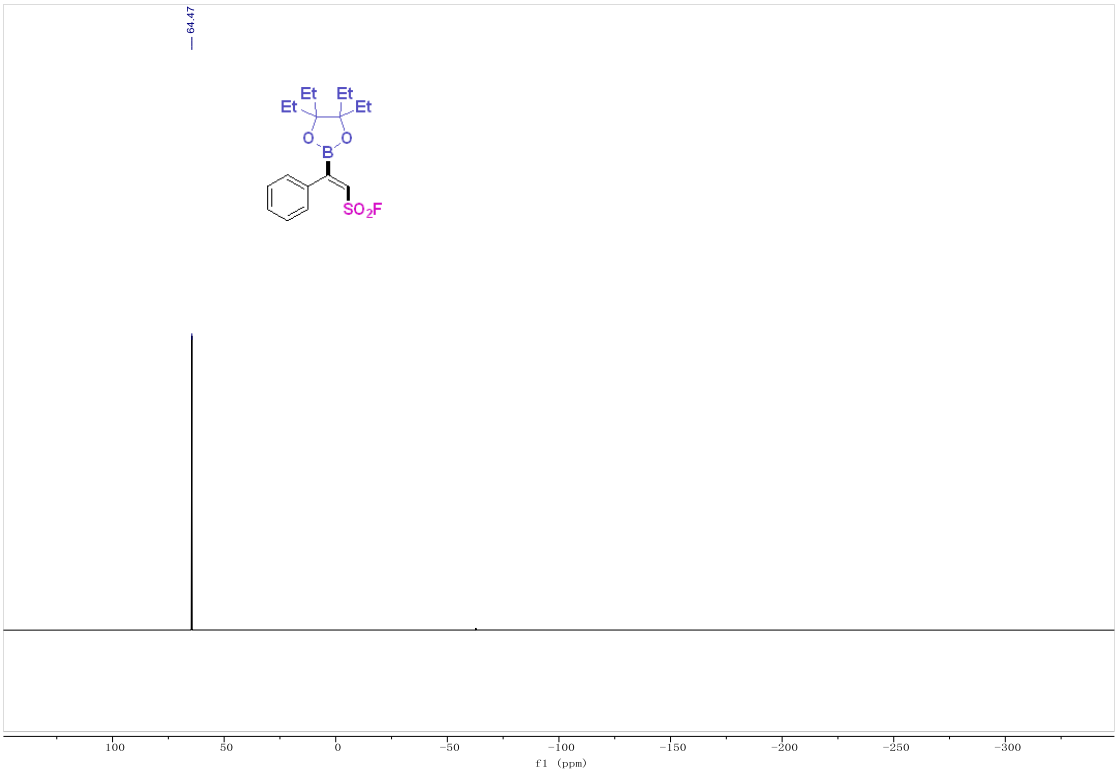
Supplementary Figure 52. ^{19}F NMR spectra of product **4l**



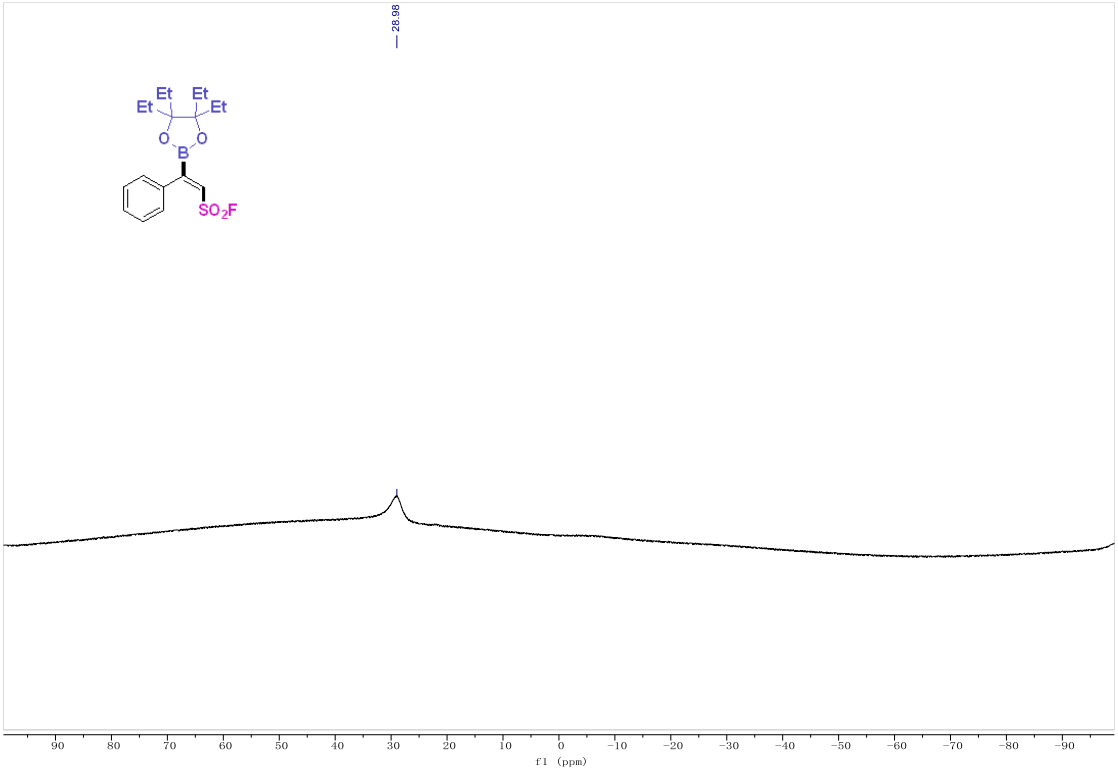
Supplementary Figure 53. ^{1}H NMR spectra of product **4m**



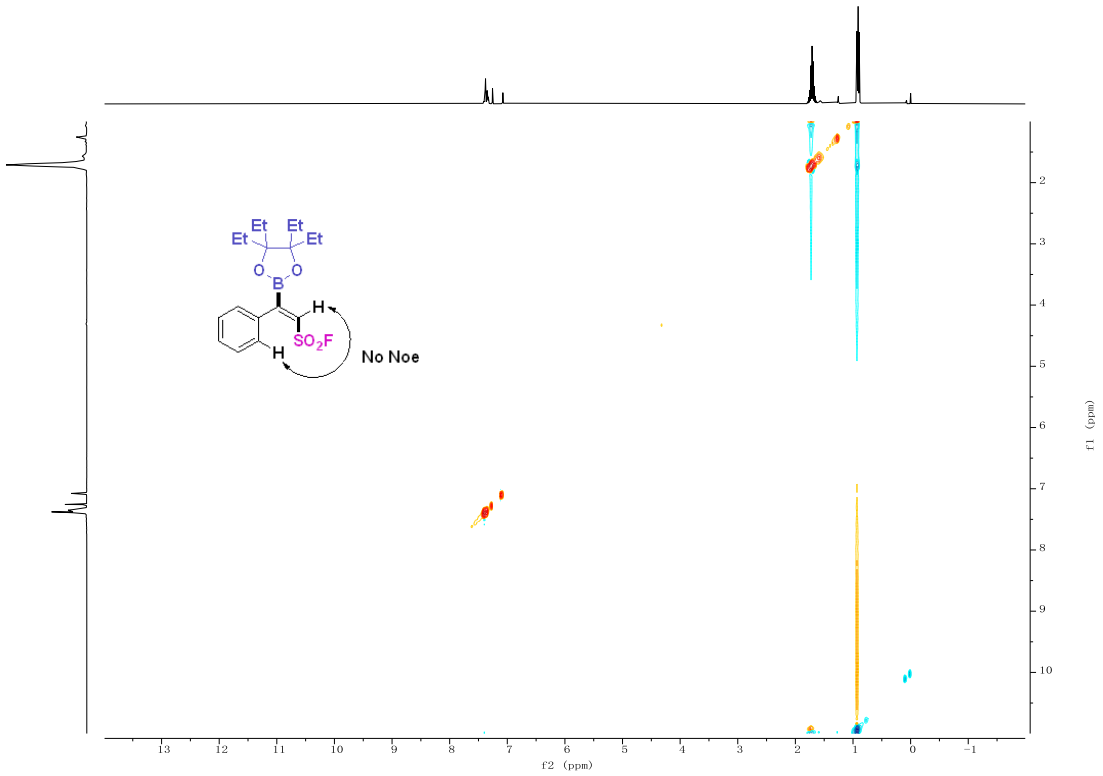
Supplementary Figure 54. ^{13}C NMR spectra of product **4m**



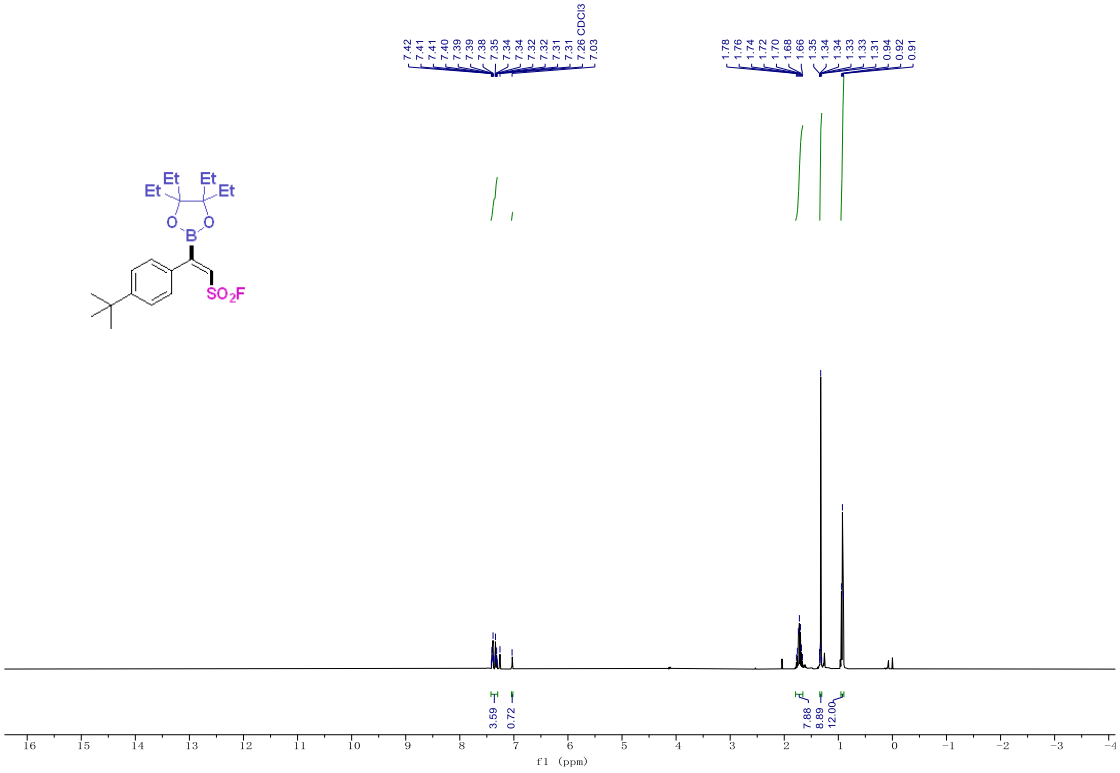
Supplementary Figure 55. ^{19}F NMR spectra of product **4m**



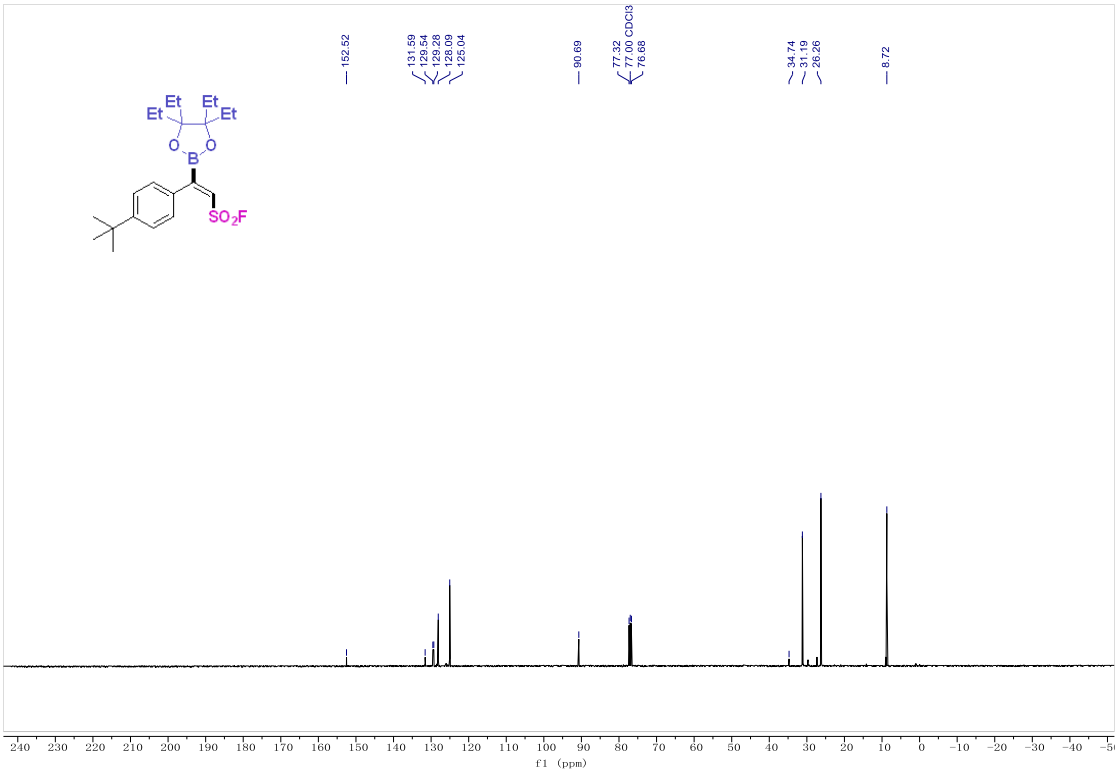
Supplementary Figure 56. ^{11}B NMR spectra of product **4m**



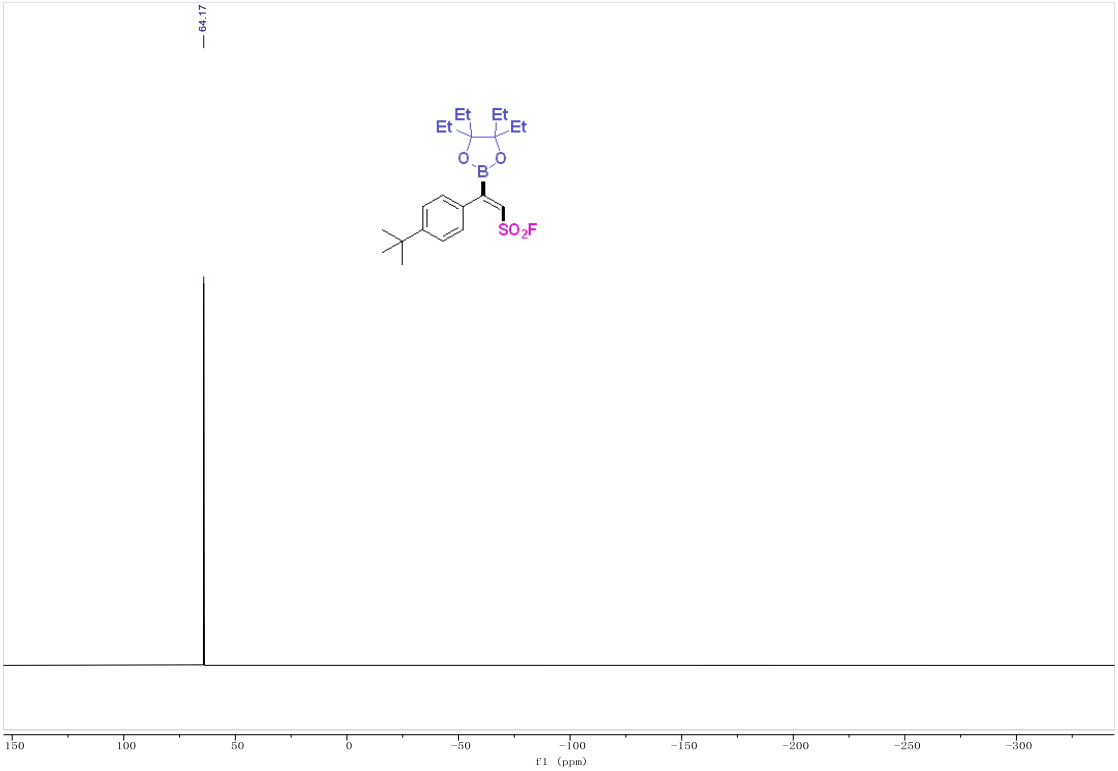
Supplementary Figure 57. NOESY spectra of product **4m**



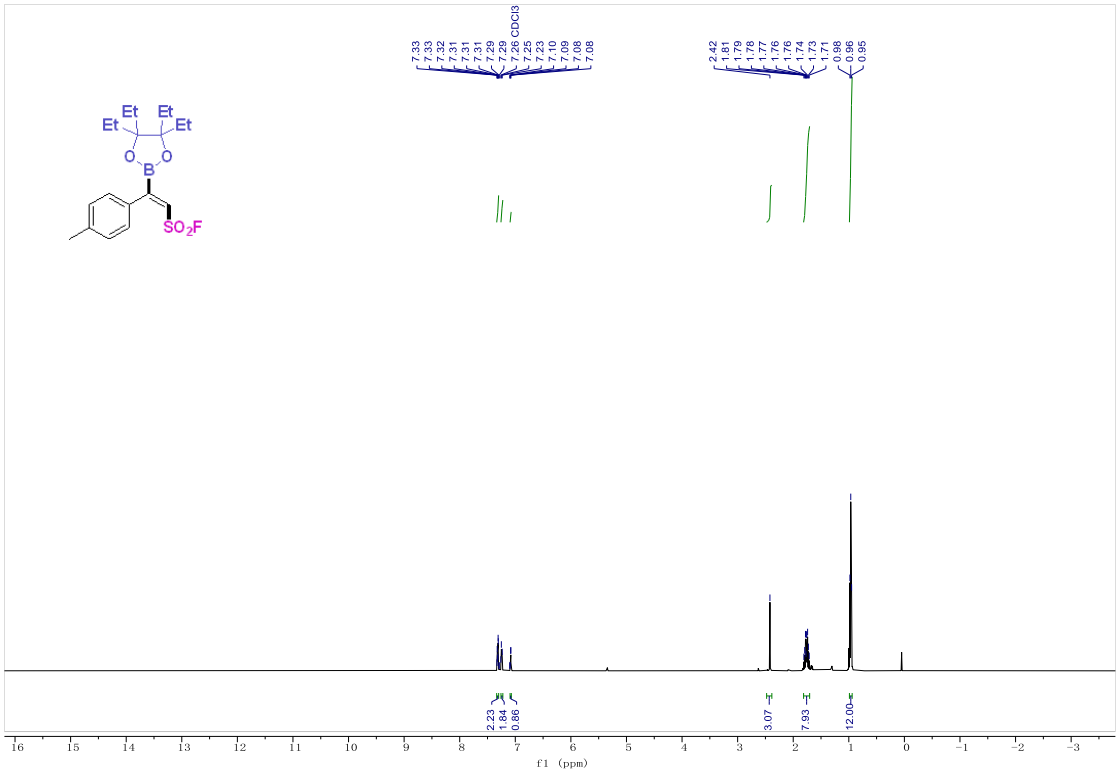
Supplementary Figure 58. ^{1}H NMR spectra of product **4n**



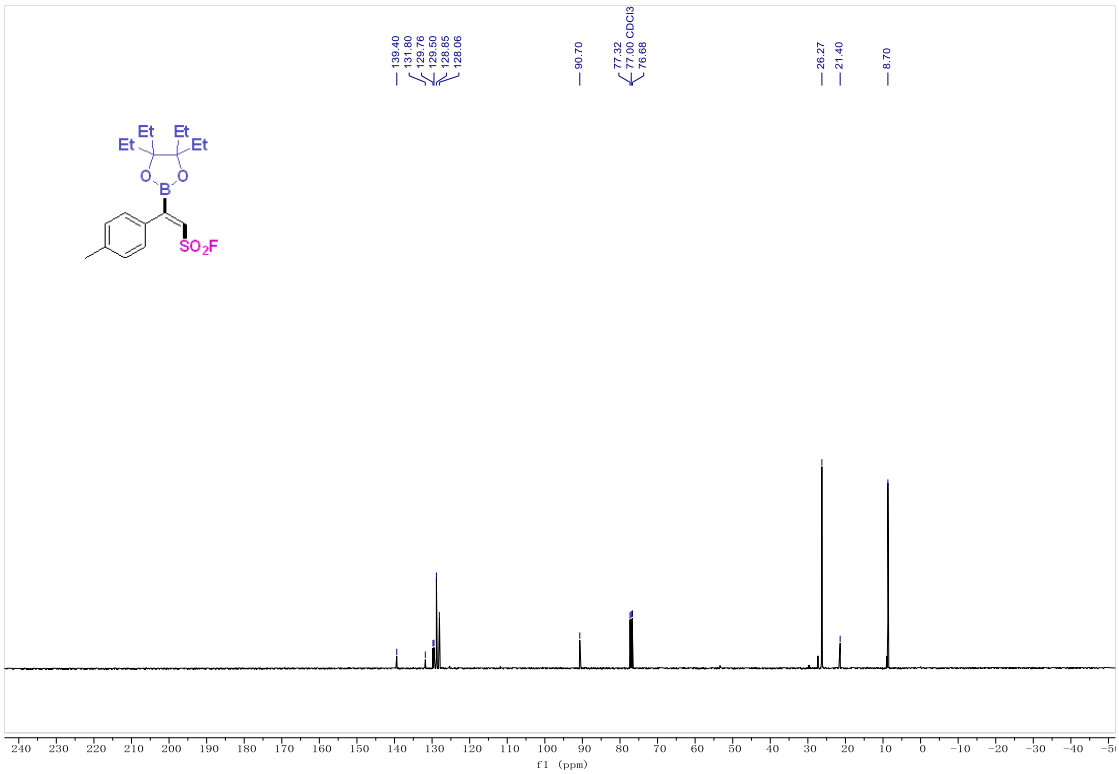
Supplementary Figure 59. ^{13}C NMR spectra of product **4n**



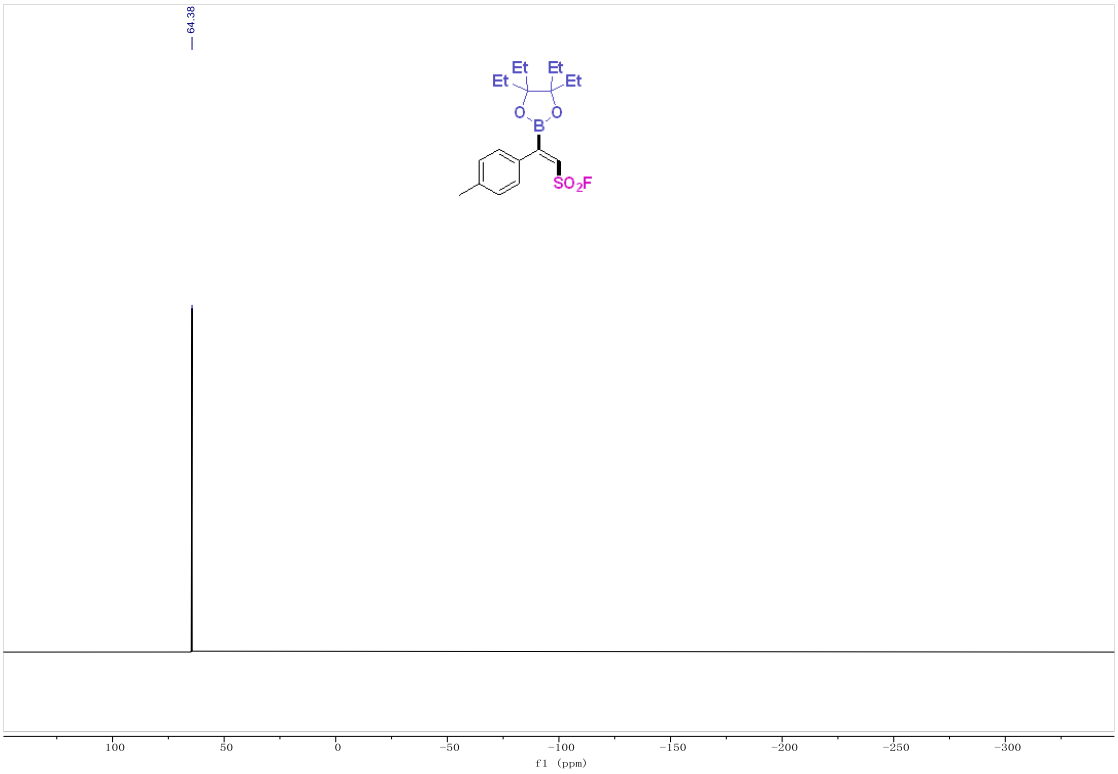
Supplementary Figure 60. ^{19}F NMR spectra of product **4n**



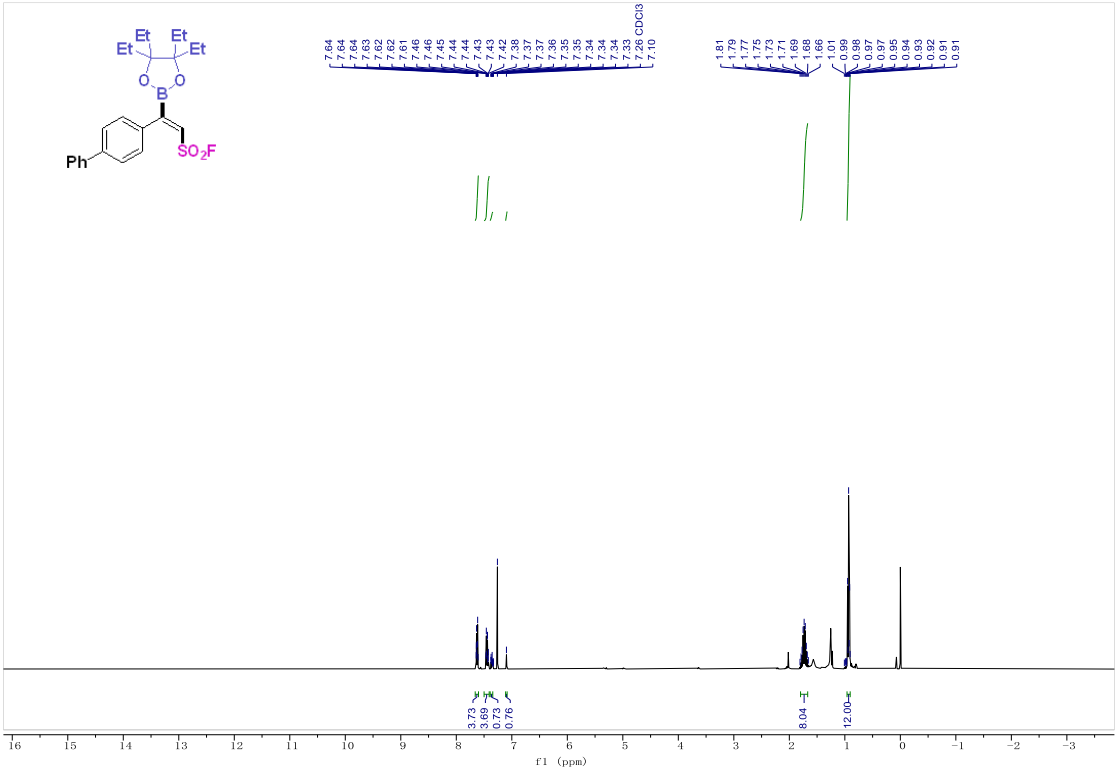
Supplementary Figure 61. ^{1}H NMR spectra of product **4o**



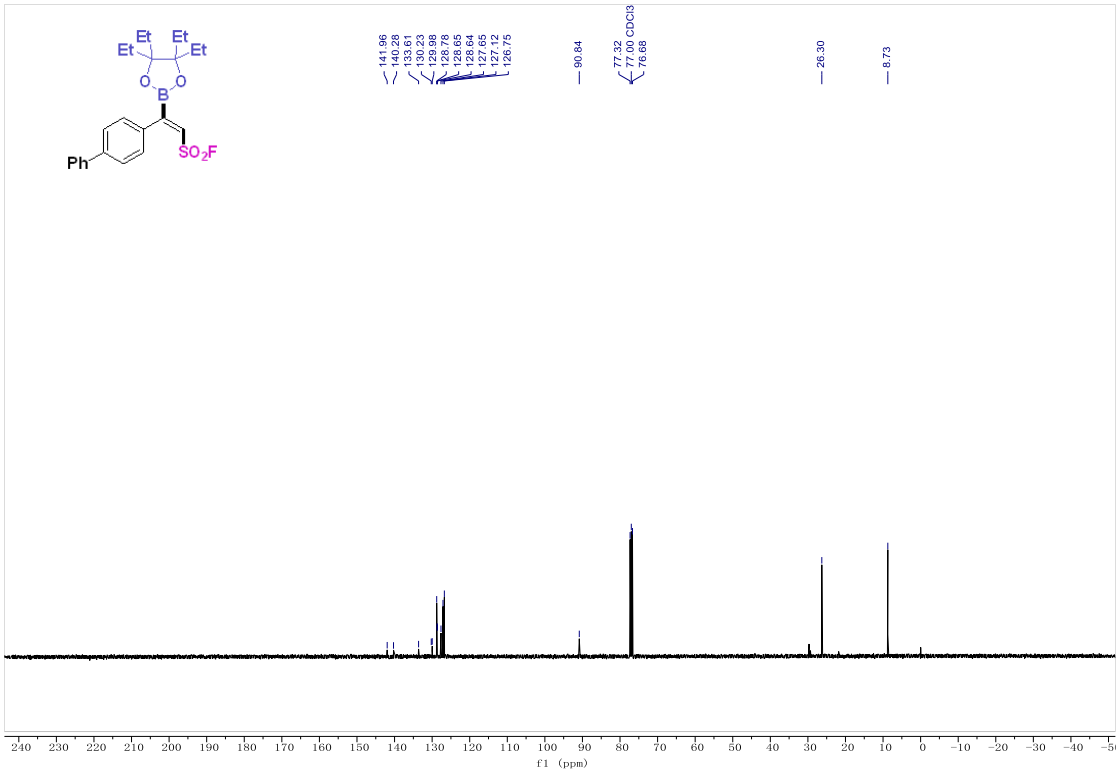
Supplementary Figure 62. ^{13}C NMR spectra of product **4o**



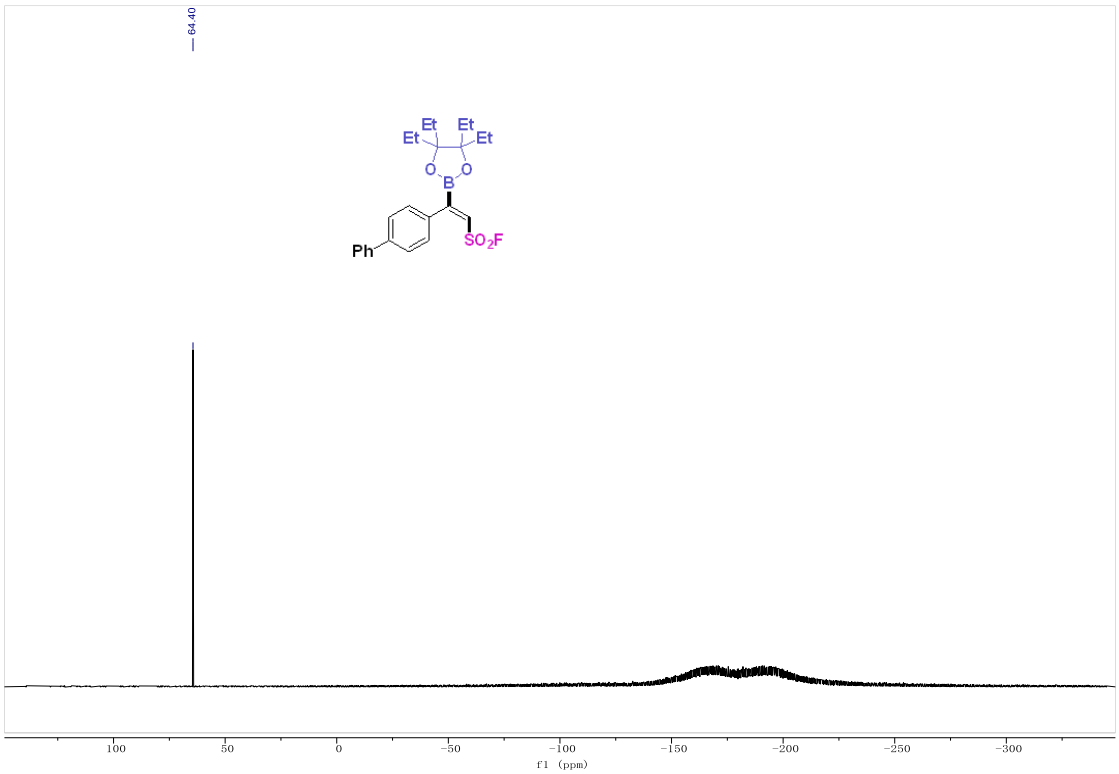
Supplementary Figure 63. ^{19}F NMR spectra of product **4o**



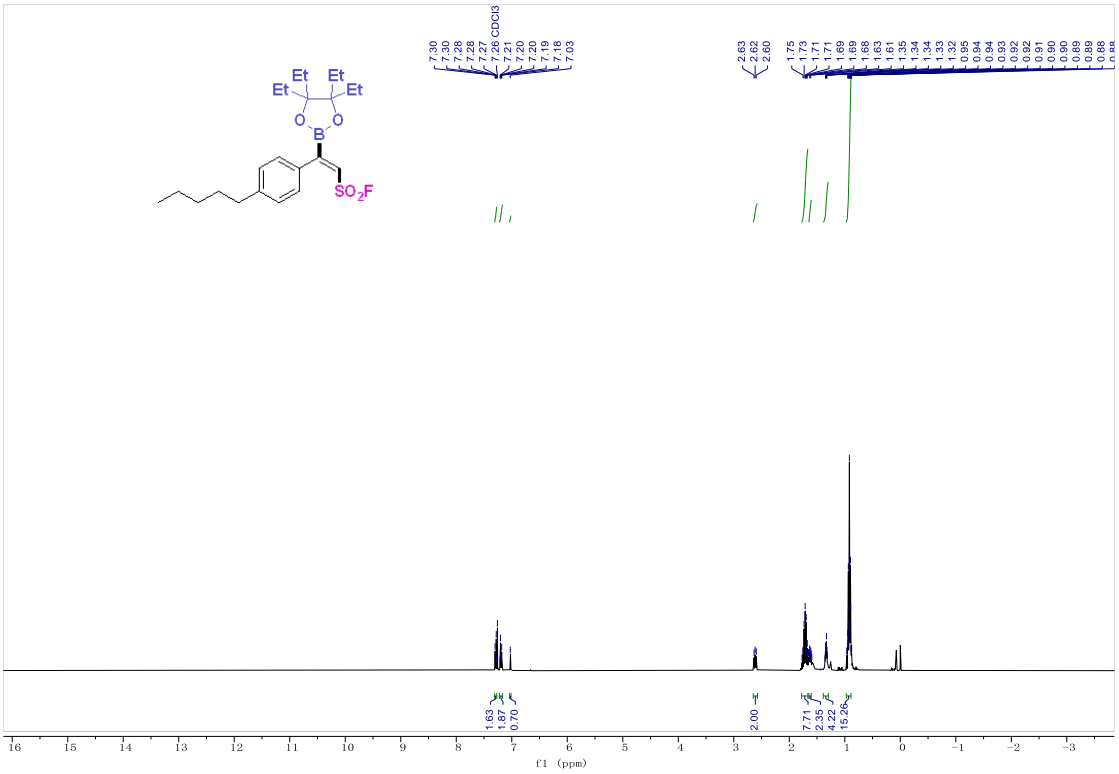
Supplementary Figure 64. ^{1}H NMR spectra of product **4p**



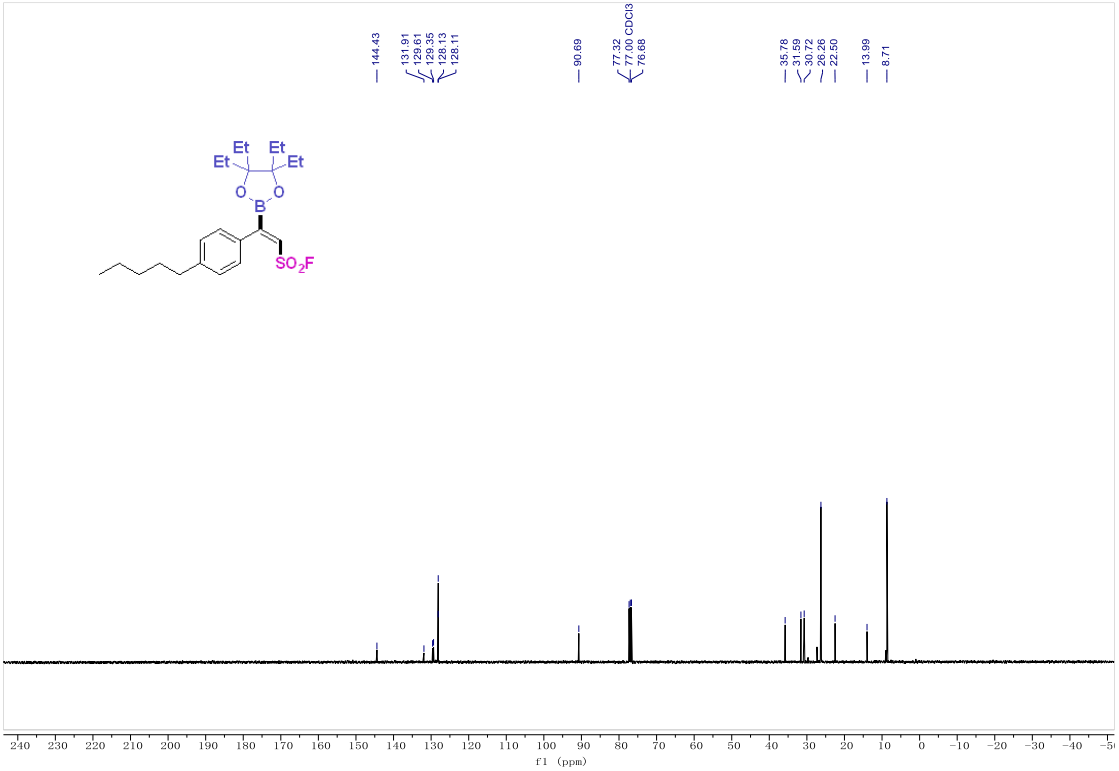
Supplementary Figure 65. ^{13}C NMR spectra of product **4p**



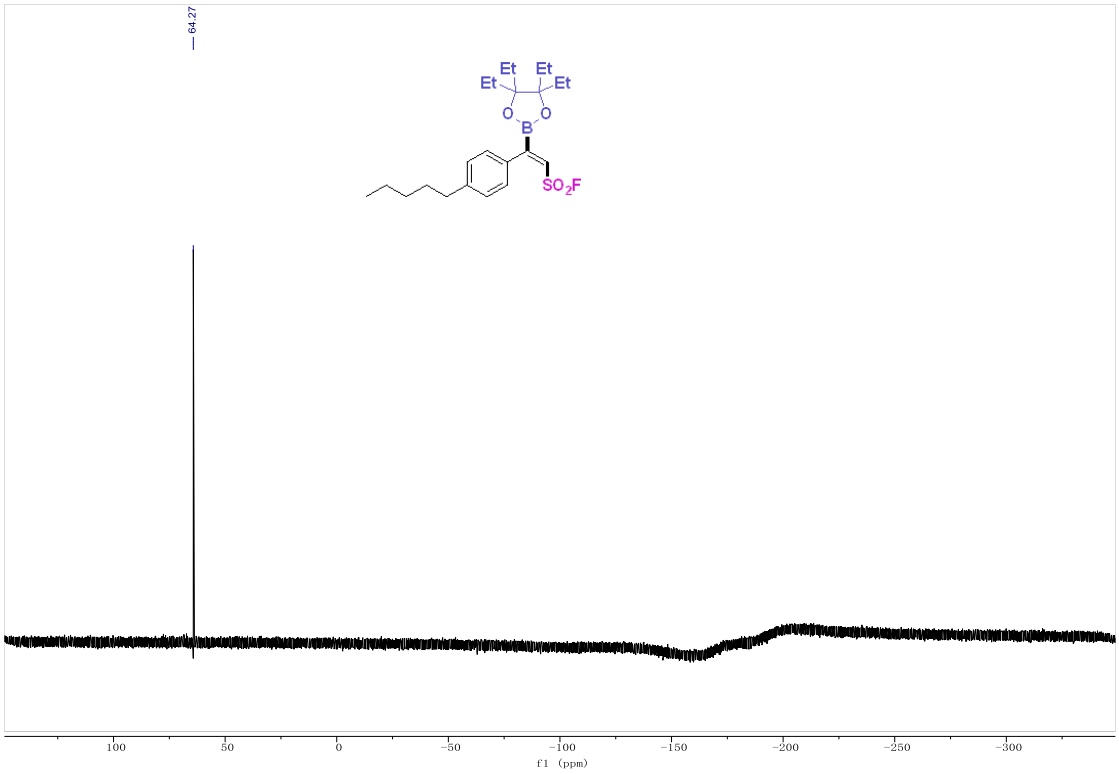
Supplementary Figure 66. ^{19}F NMR spectra of product **4p**



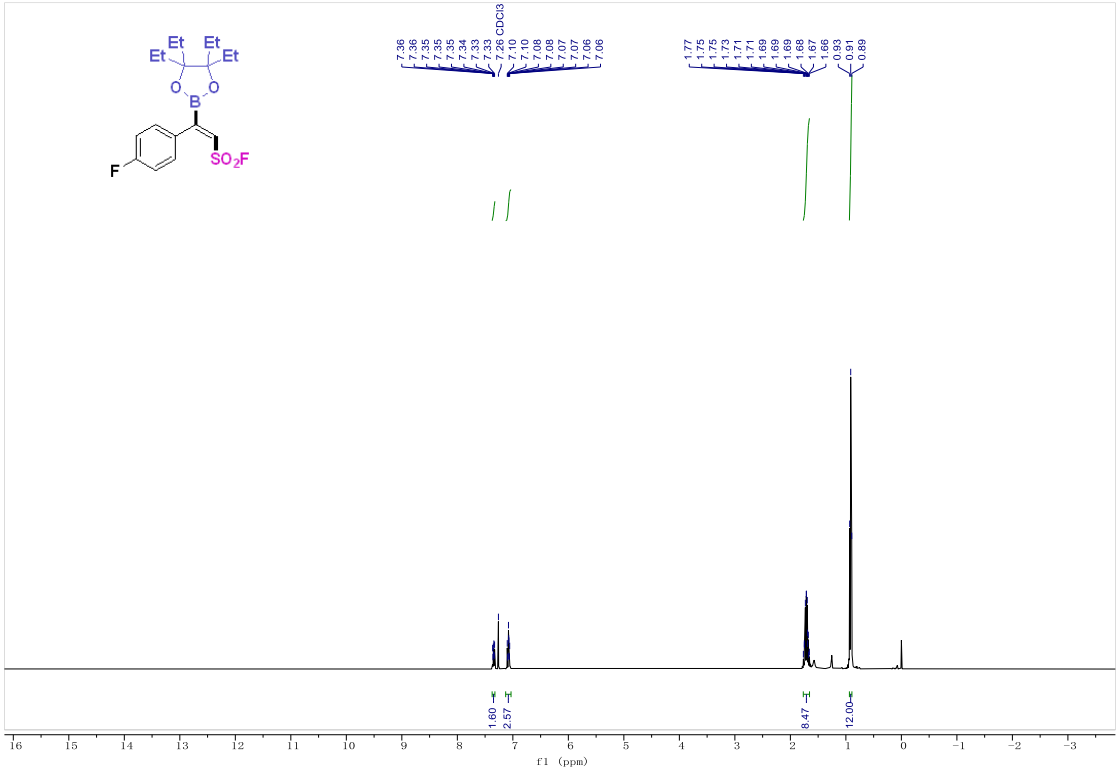
Supplementary Figure 67. ^{1}H NMR spectra of product **4q**



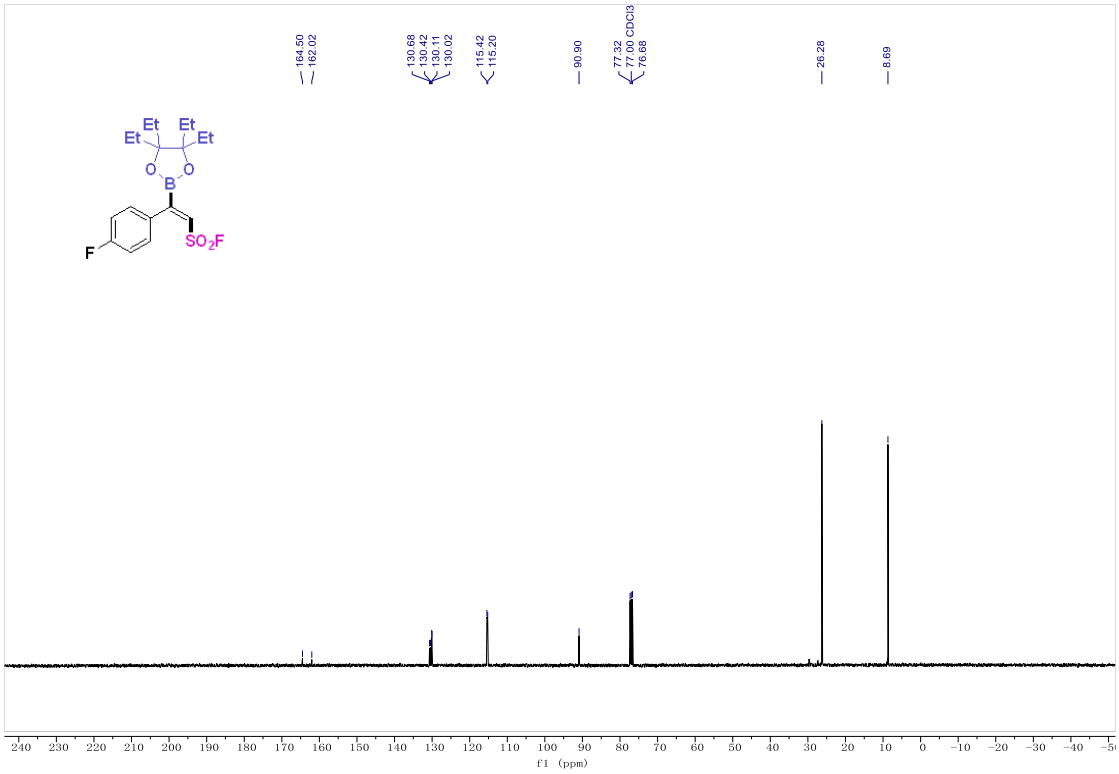
Supplementary Figure 68. ^{13}C NMR spectra of product **4q**



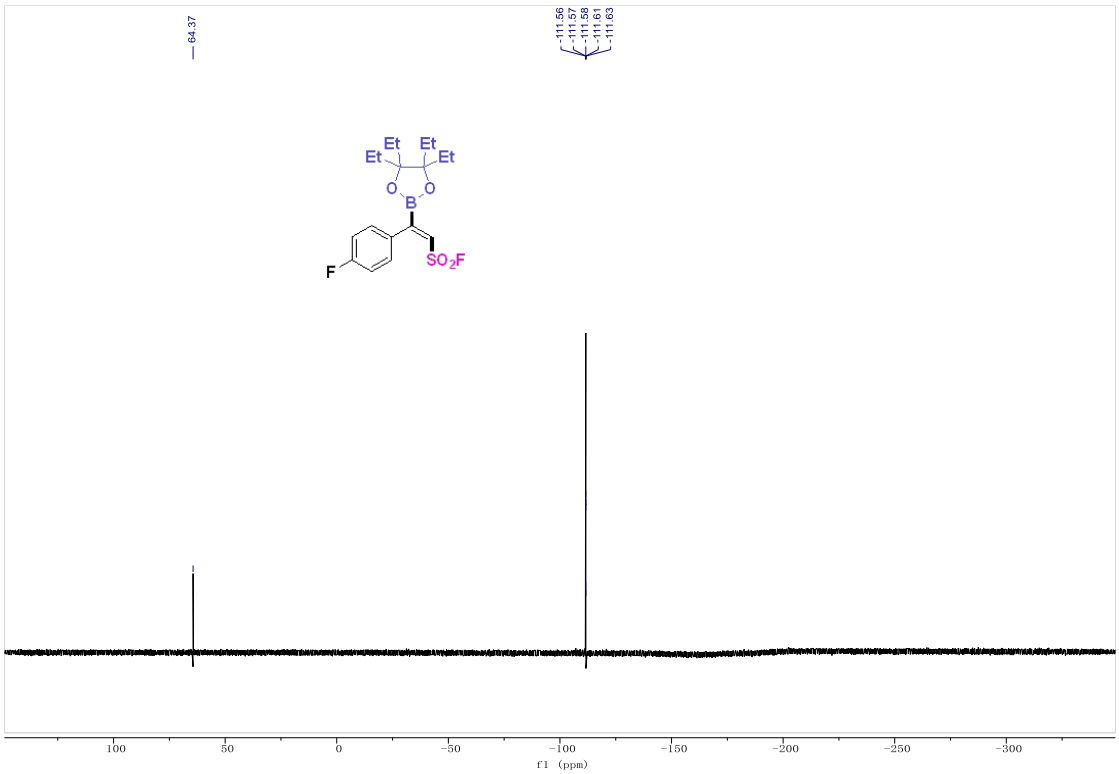
Supplementary Figure 69. ^{19}F NMR spectra of product **4q**



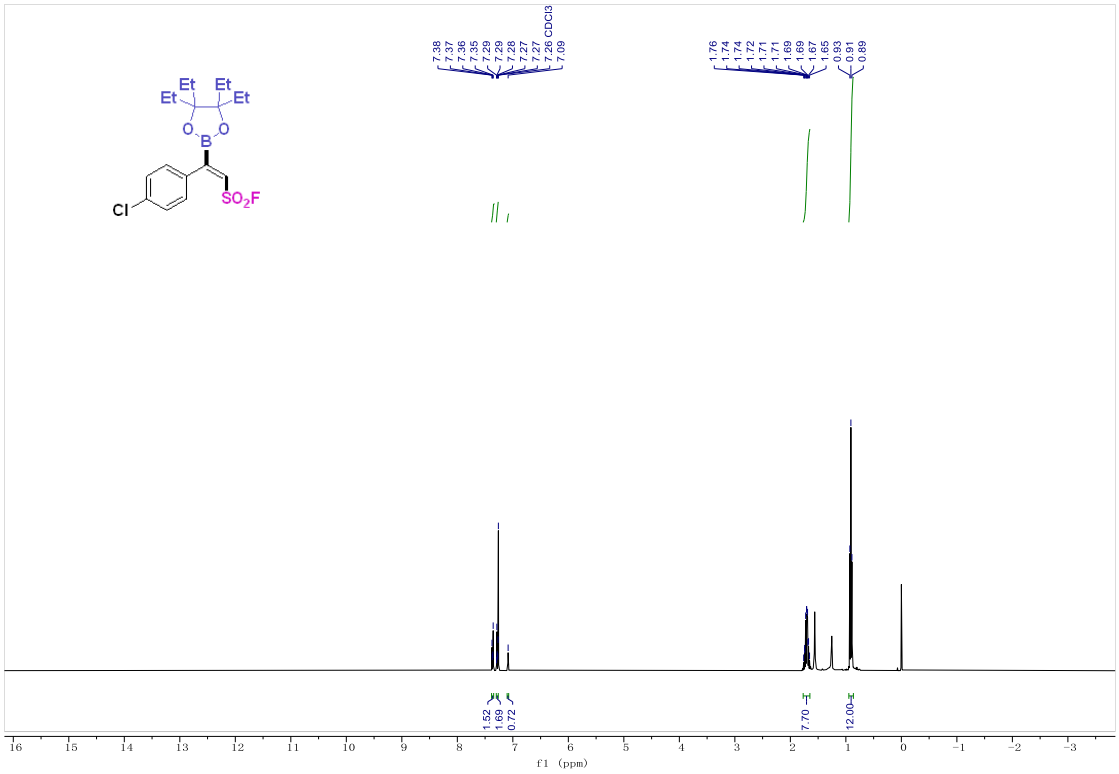
Supplementary Figure 70. ^{1}H NMR spectra of product **4r**



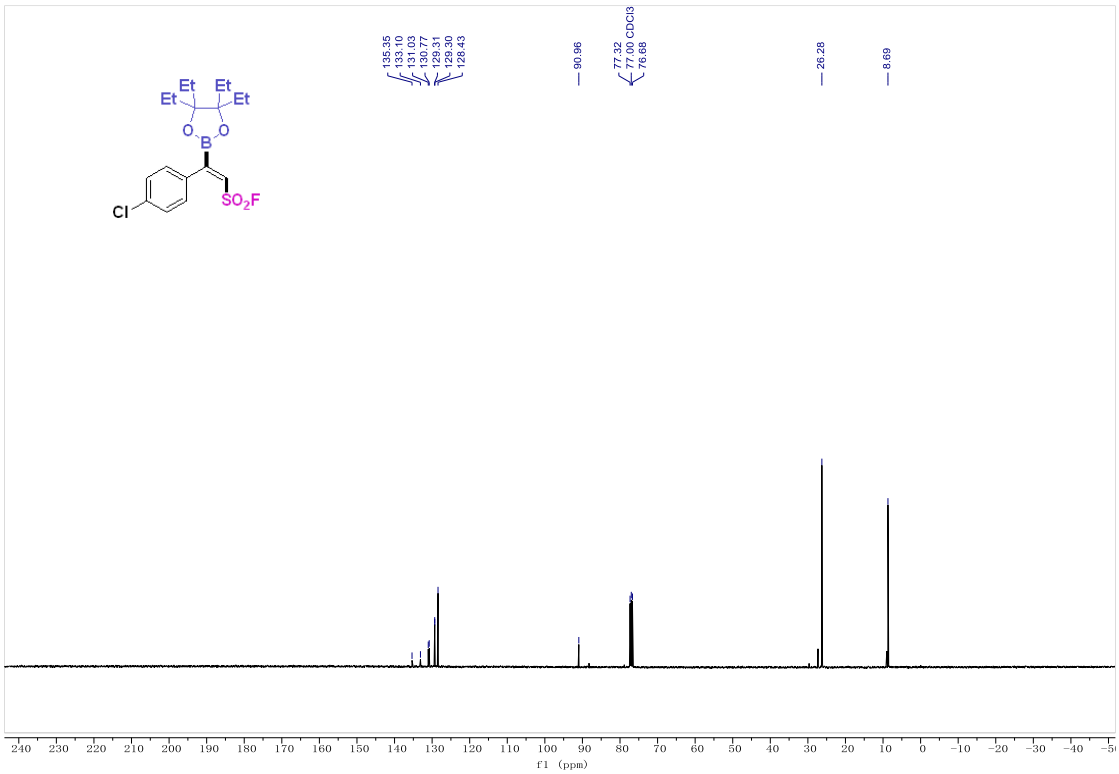
Supplementary Figure 71. ^{13}C NMR spectra of product **4r**



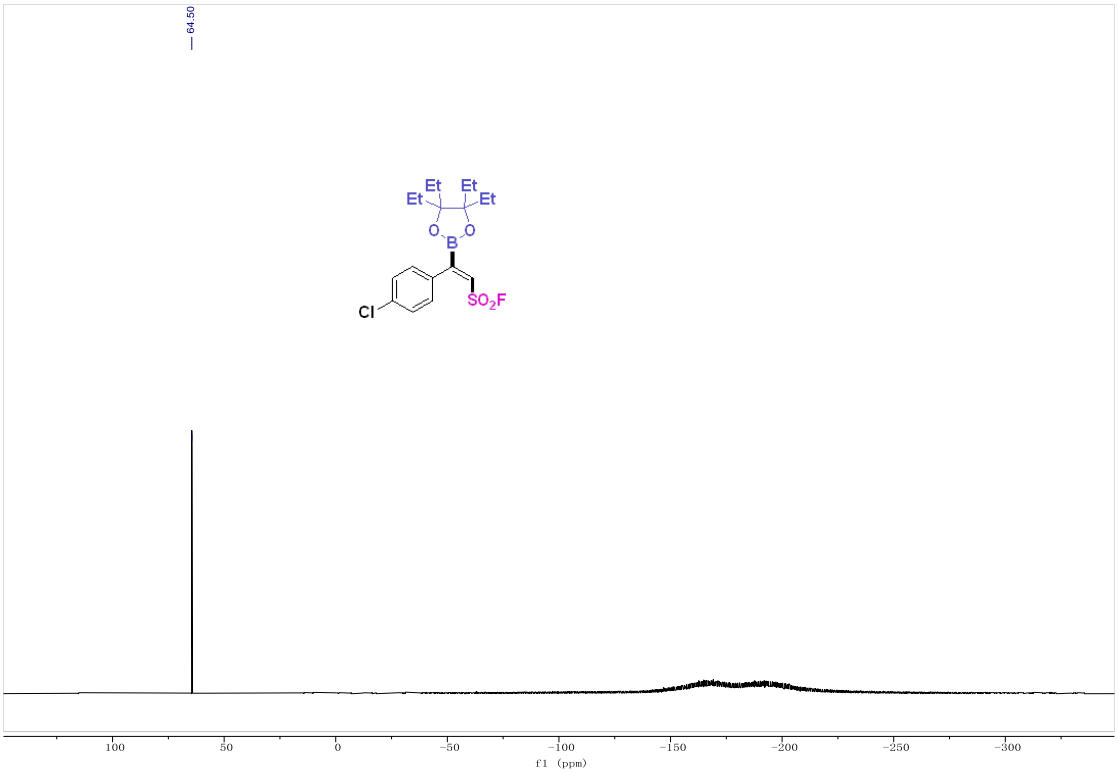
Supplementary Figure 72. ^{19}F NMR spectra of product **4r**



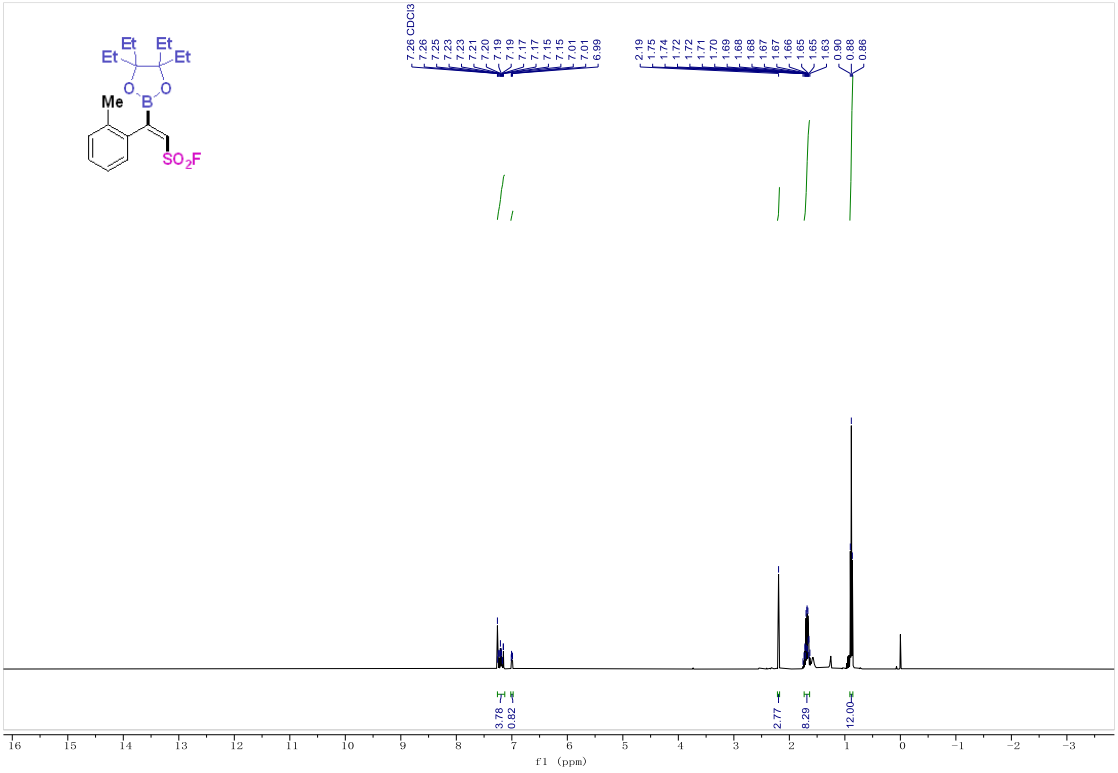
Supplementary Figure 73. ^{1}H NMR spectra of product **4s**



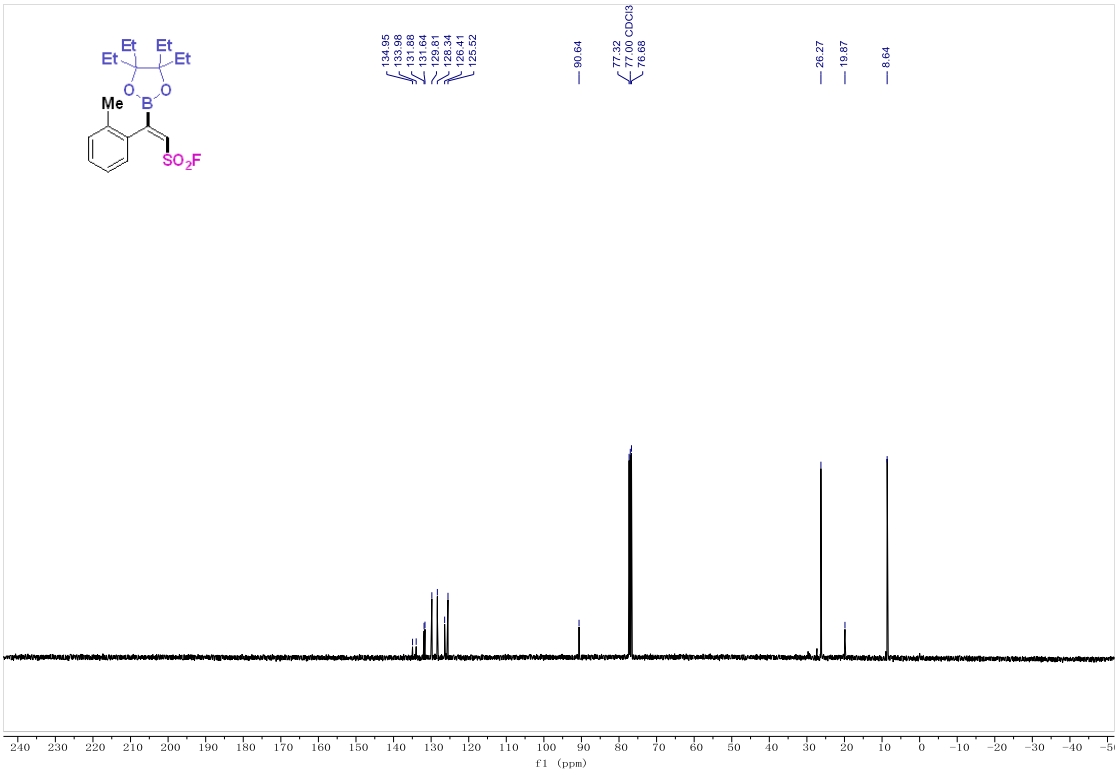
Supplementary Figure 74. ^{13}C NMR spectra of product **4s**



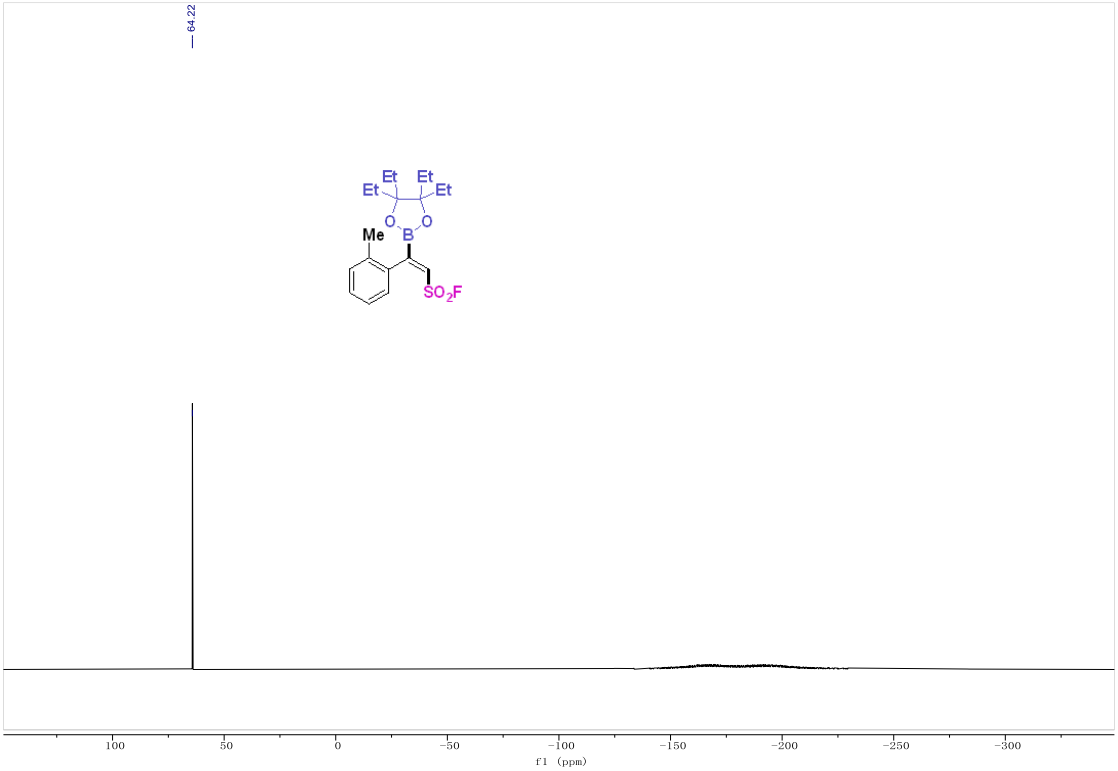
Supplementary Figure 75. ^{19}F NMR spectra of product **4s**



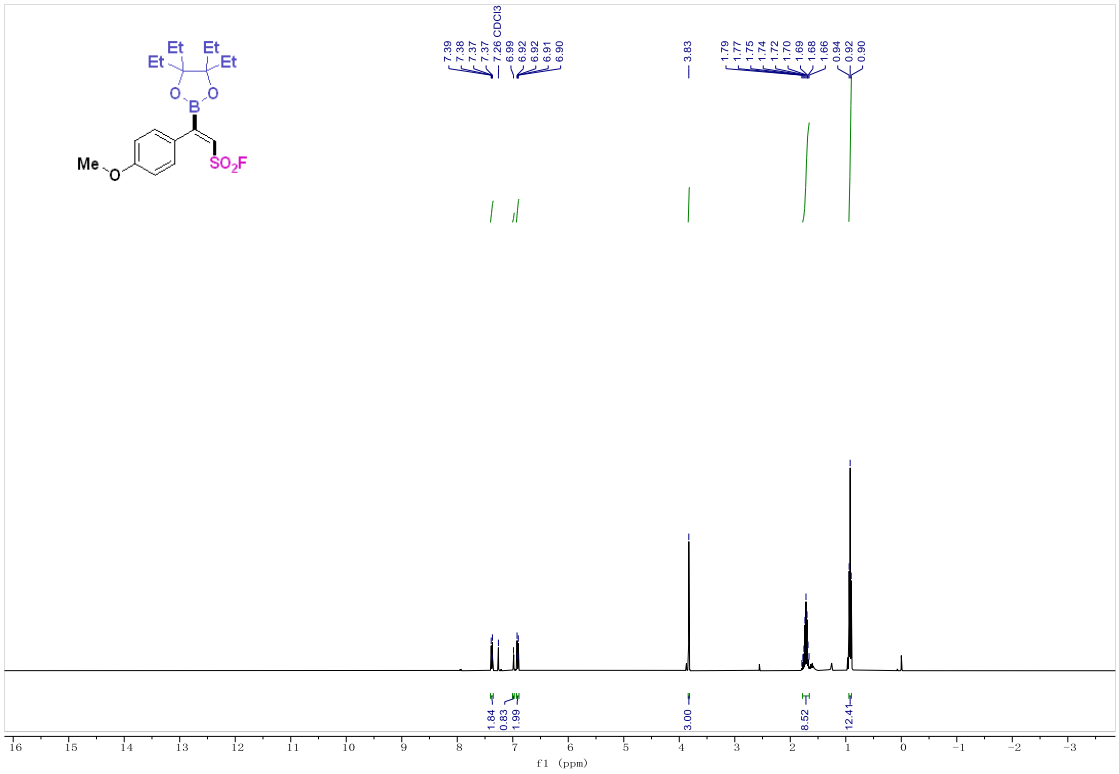
Supplementary Figure 76. ^{1}H NMR spectra of product **4t**



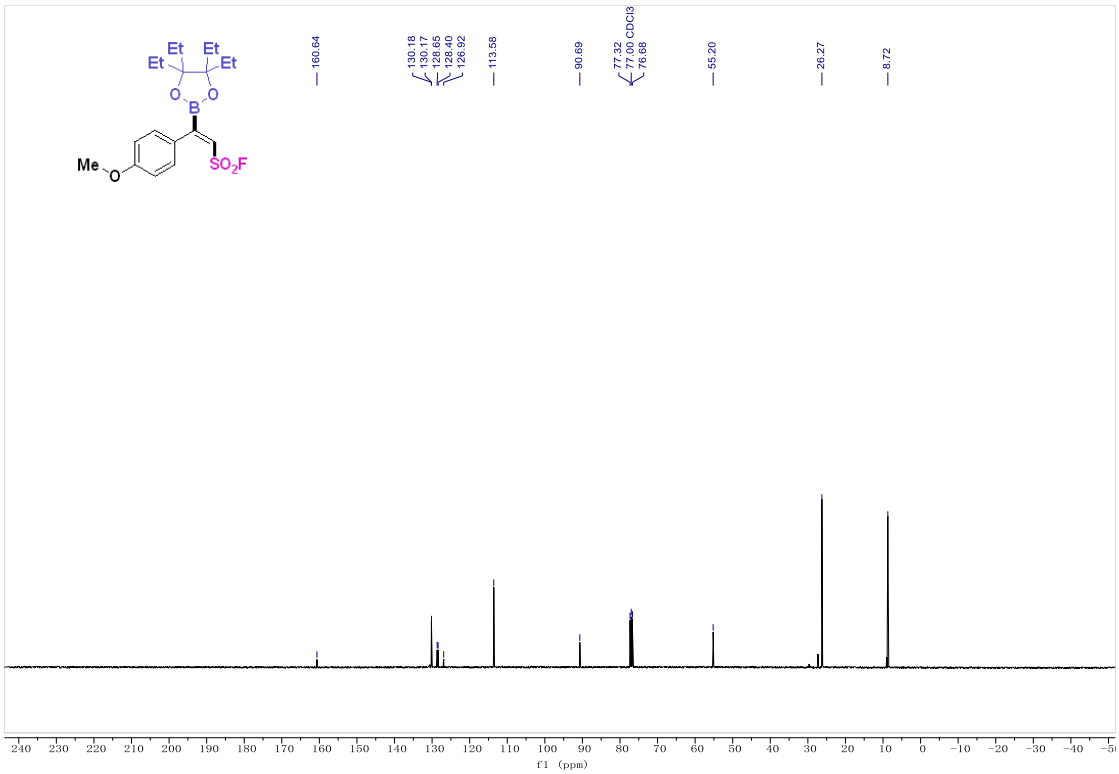
Supplementary Figure 77. ^{13}C NMR spectra of product **4t**



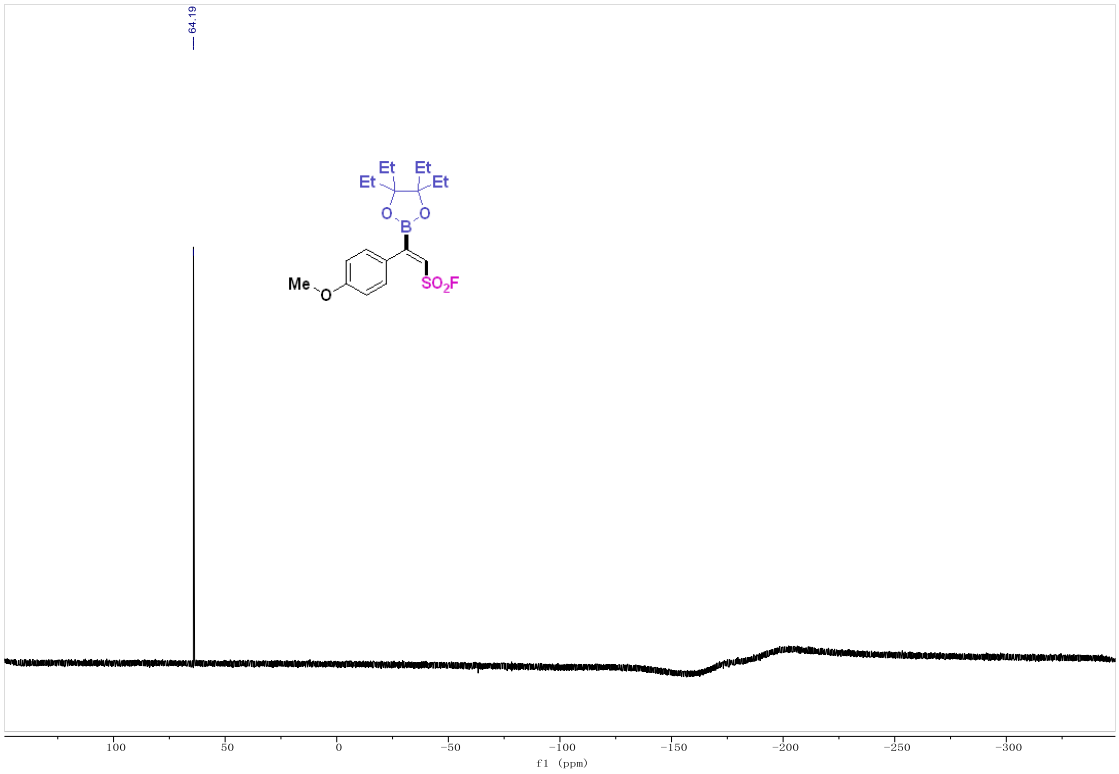
Supplementary Figure 78. ^{19}F NMR spectra of product **4t**



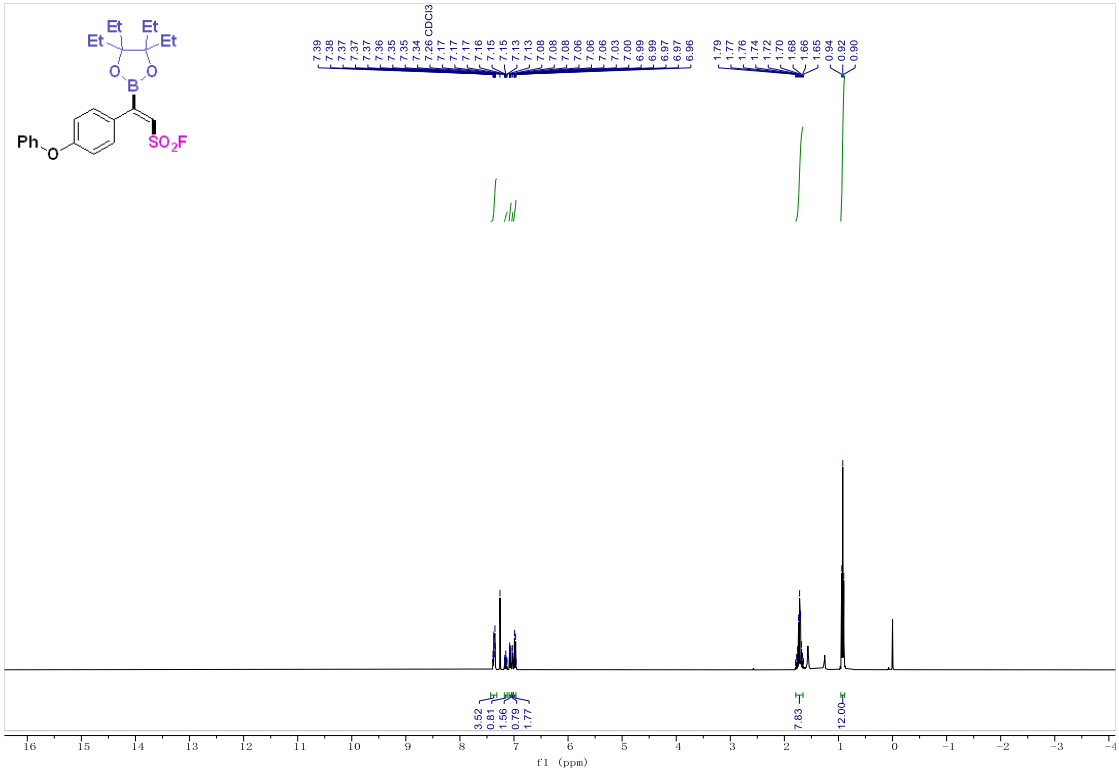
Supplementary Figure 79. ^{1}H NMR spectra of product **4u**



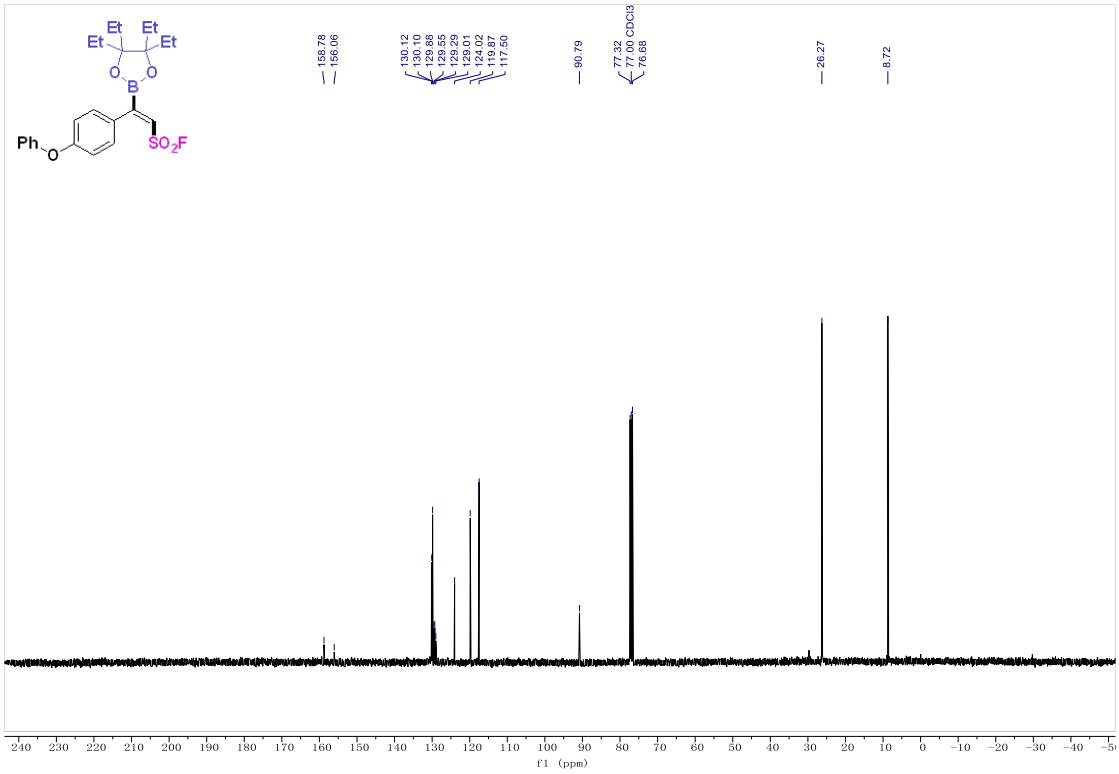
Supplementary Figure 80. ^{13}C NMR spectra of product **4u**



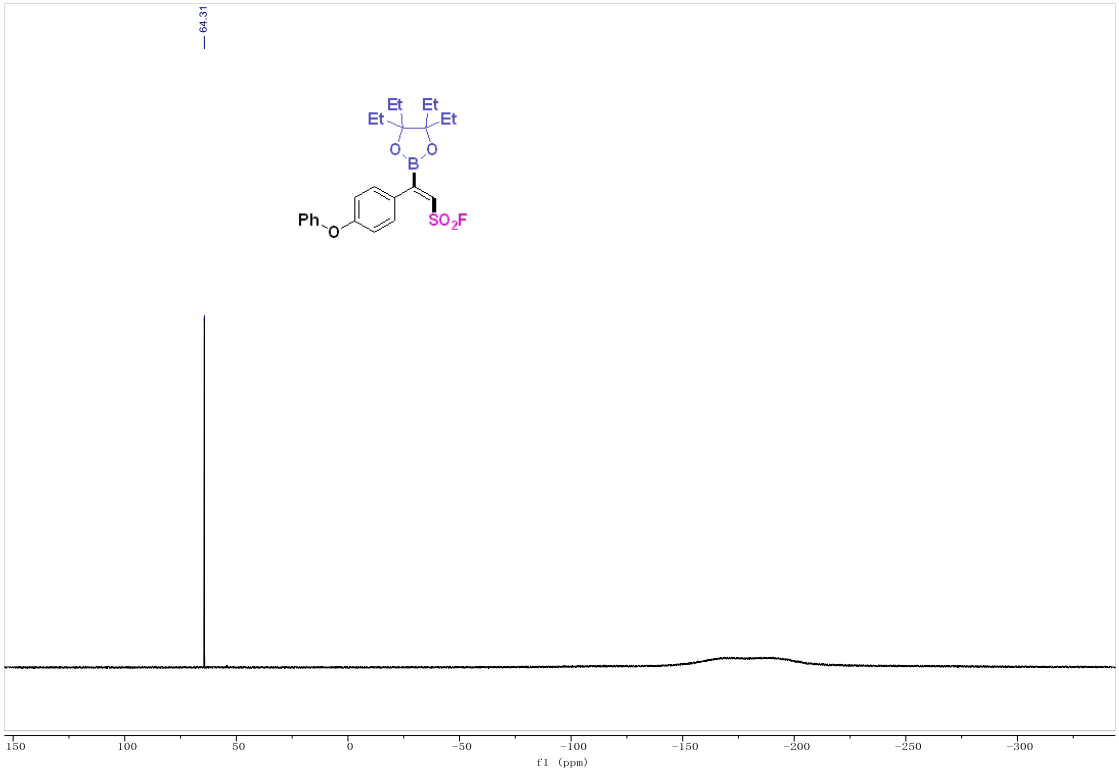
Supplementary Figure 81. ^{19}F NMR spectra of product **4u**



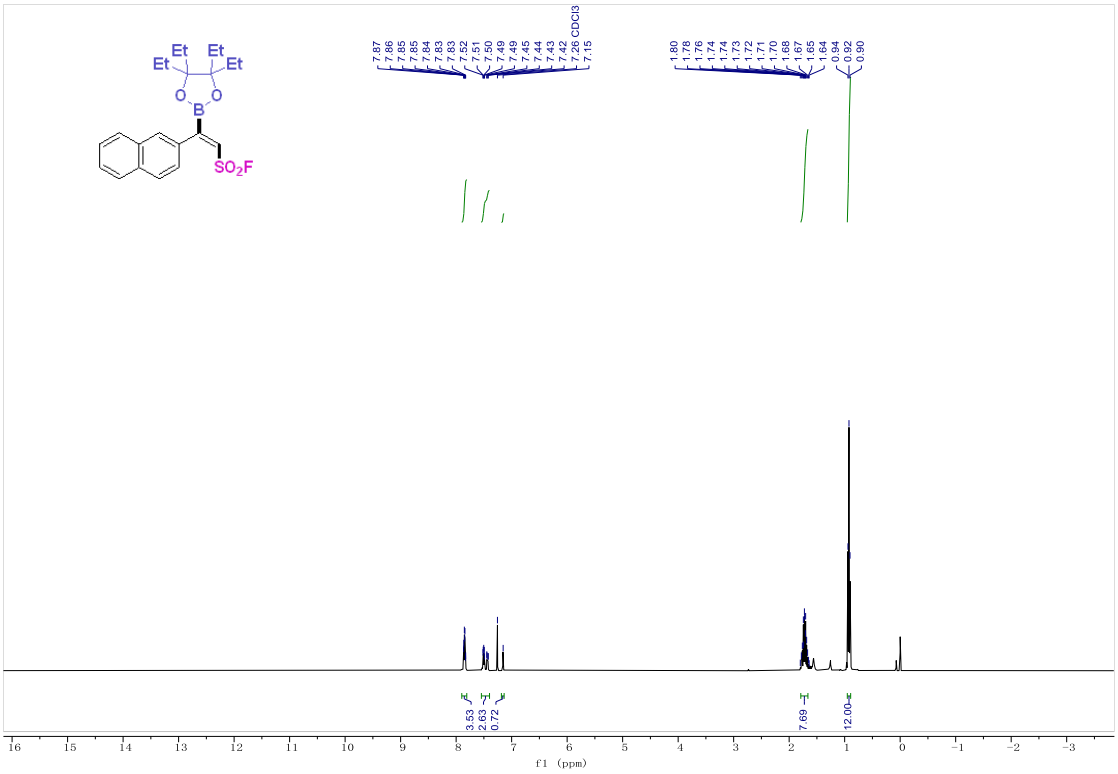
Supplementary Figure 82. ^{1}H NMR spectra of product **4v**



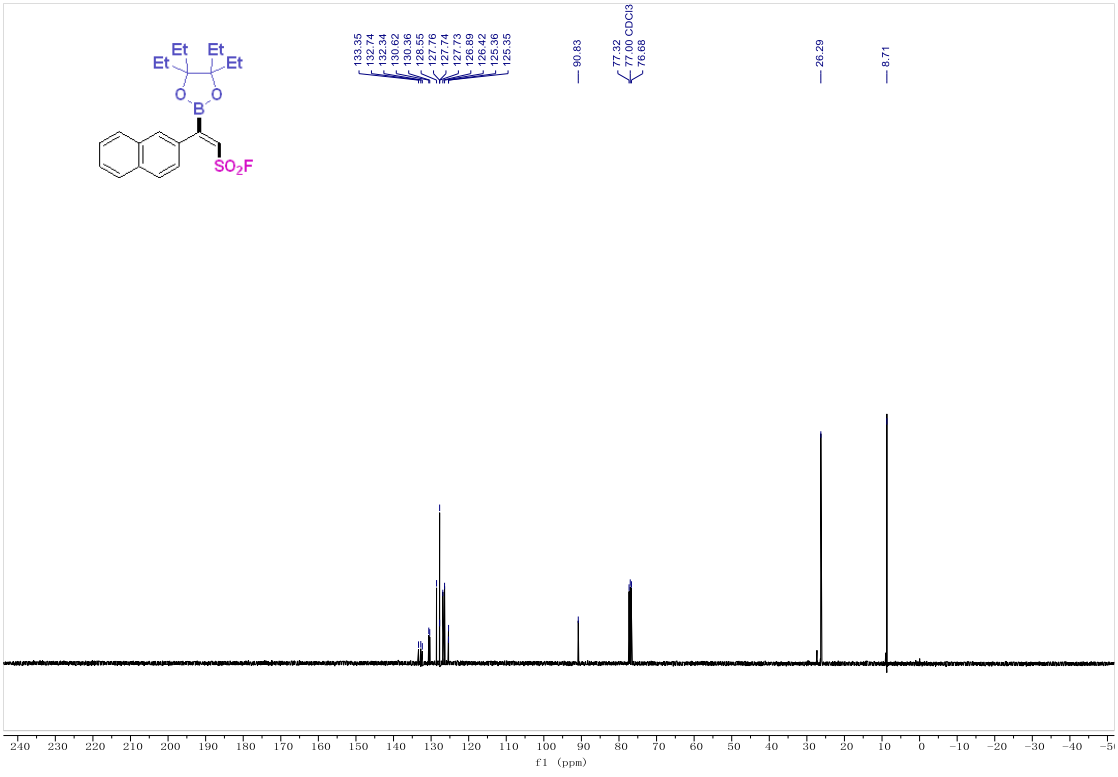
Supplementary Figure 83. ^{13}C NMR spectra of product **4v**



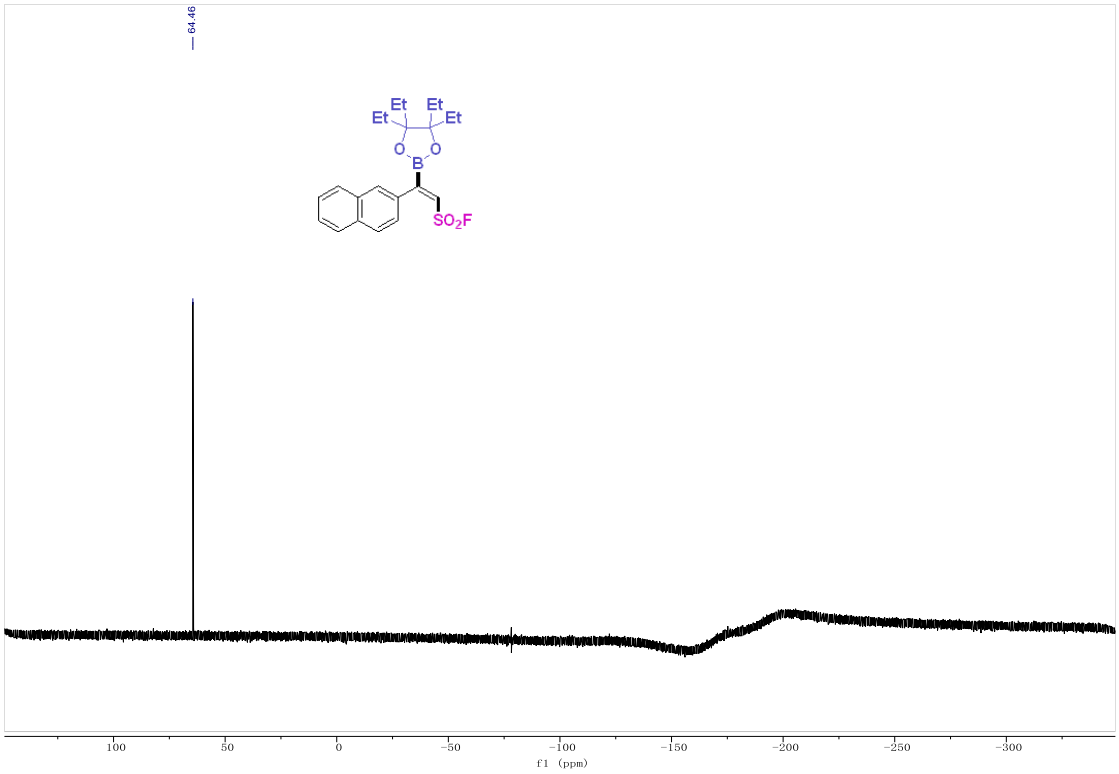
Supplementary Figure 84. ^{19}F NMR spectra of product **4v**



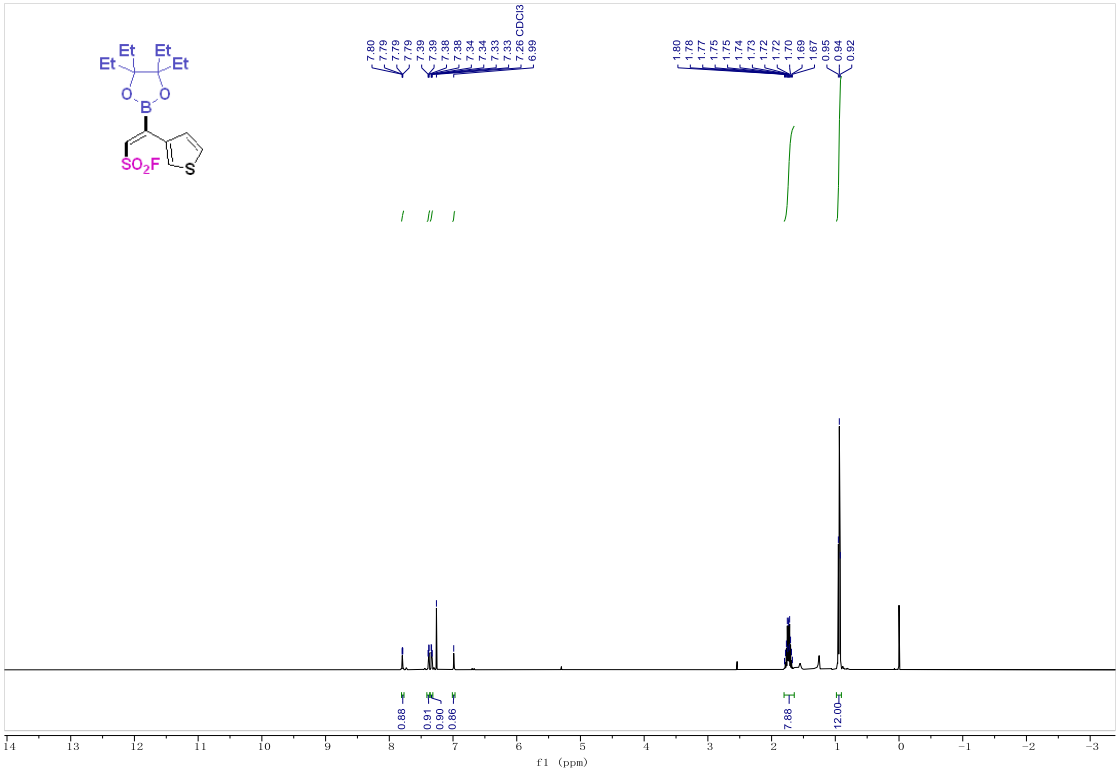
Supplementary Figure 85. ^{1}H NMR spectra of product **4w**



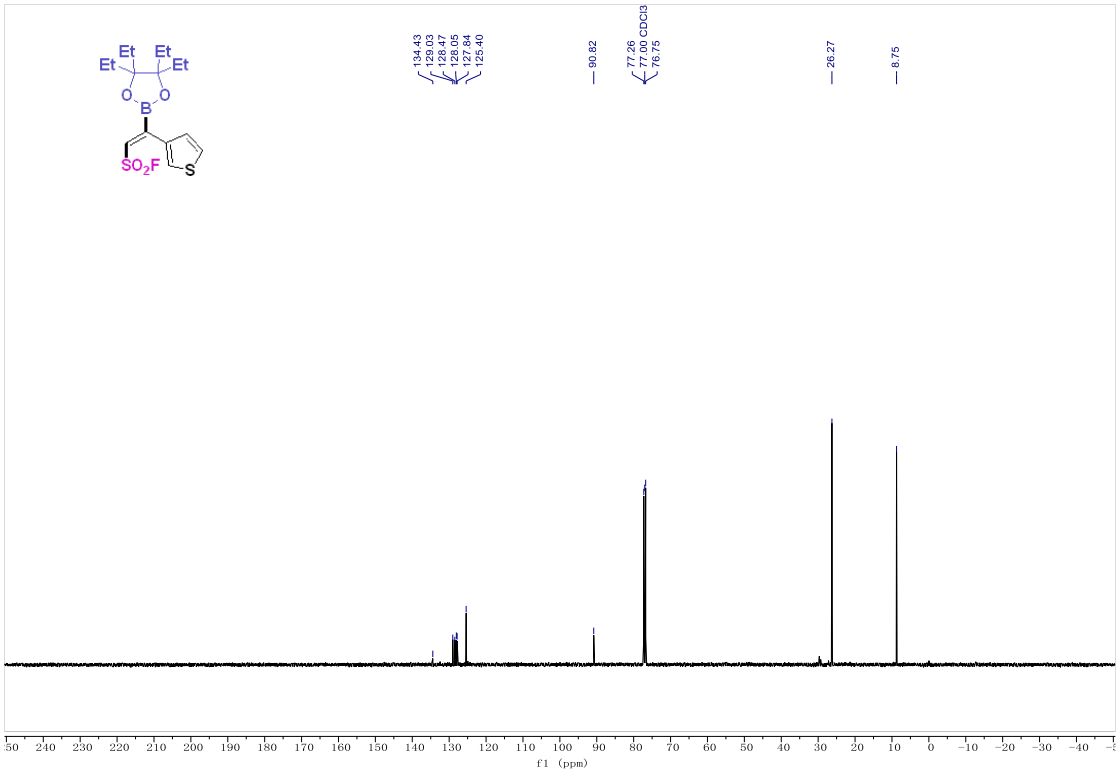
Supplementary Figure 86. ^{13}C NMR spectra of product **4w**



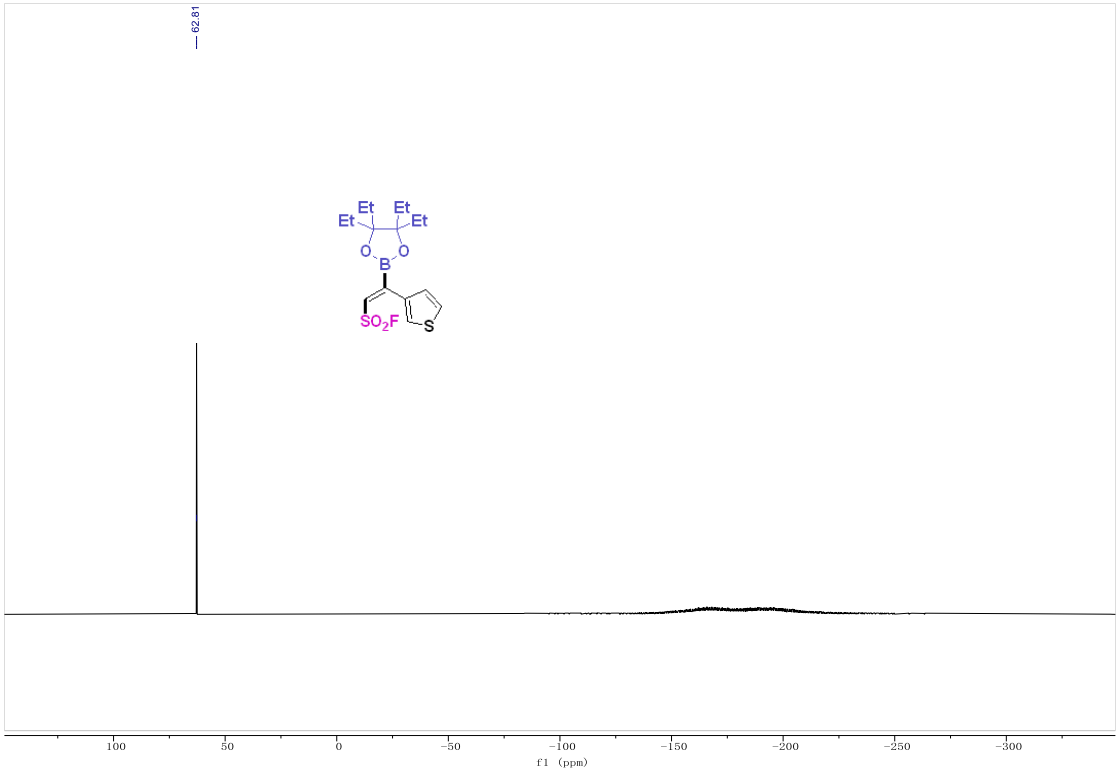
Supplementary Figure 87. ^{19}F NMR spectra of product **4w**



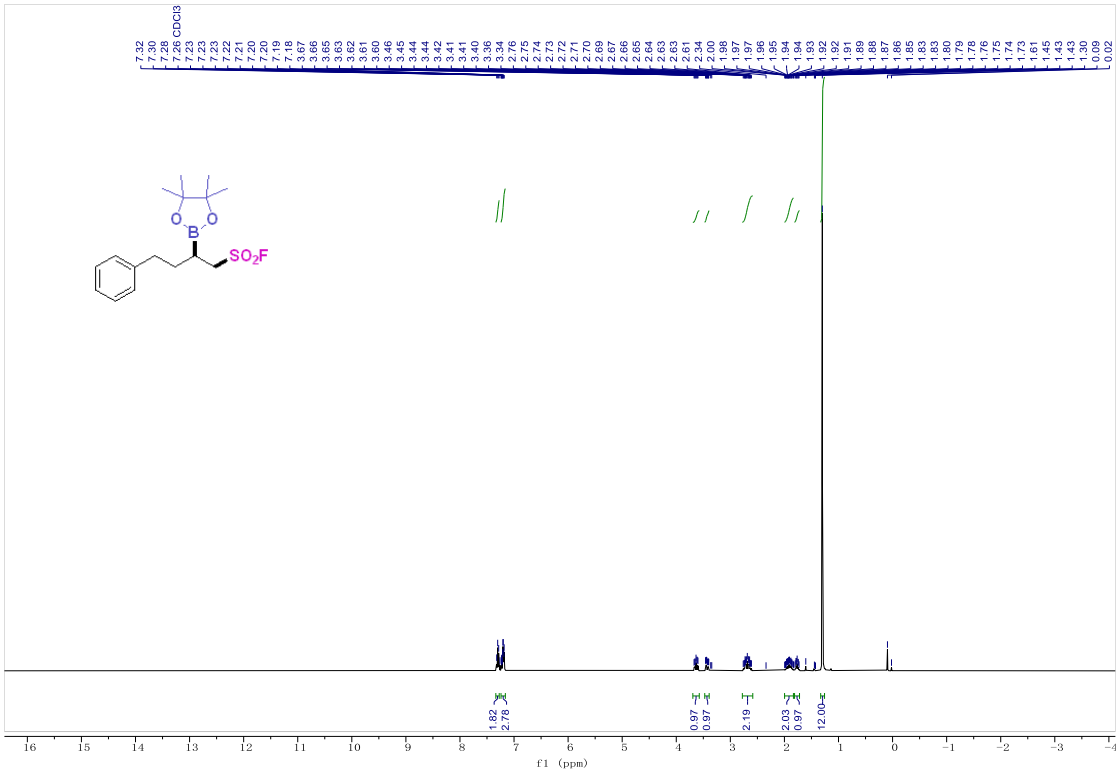
Supplementary Figure 88. ^{1}H NMR spectra of product **4x**



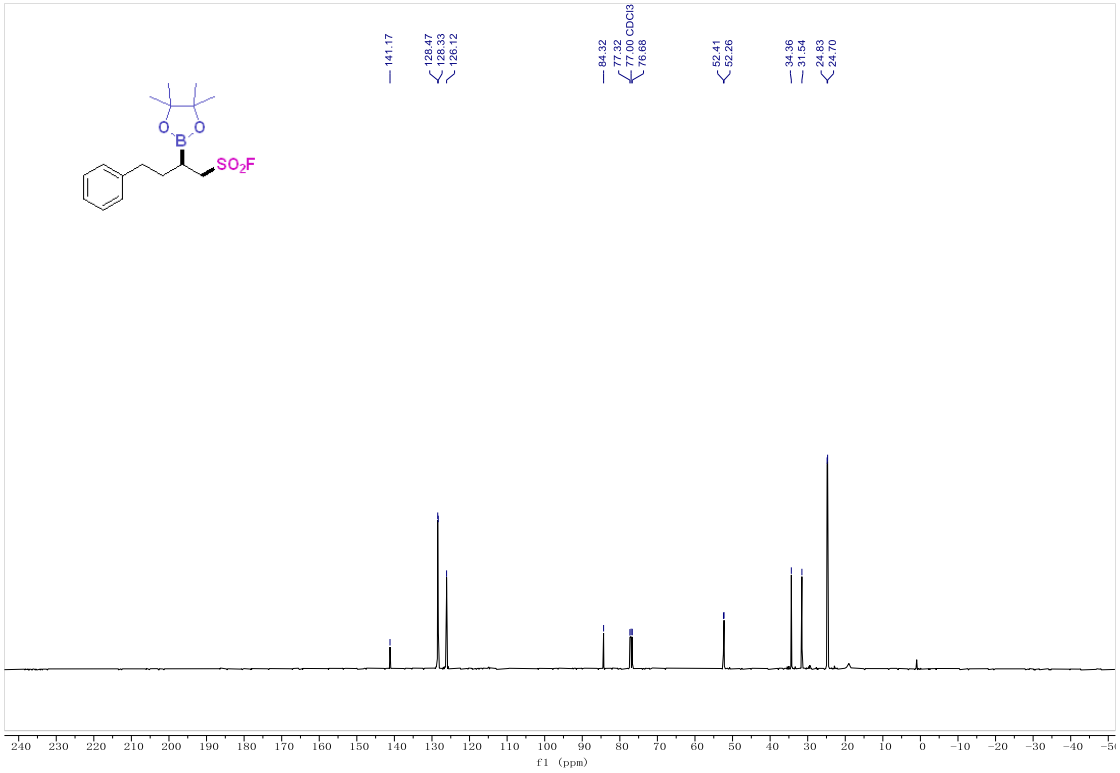
Supplementary Figure 89. ^{13}C NMR spectra of product **4x**



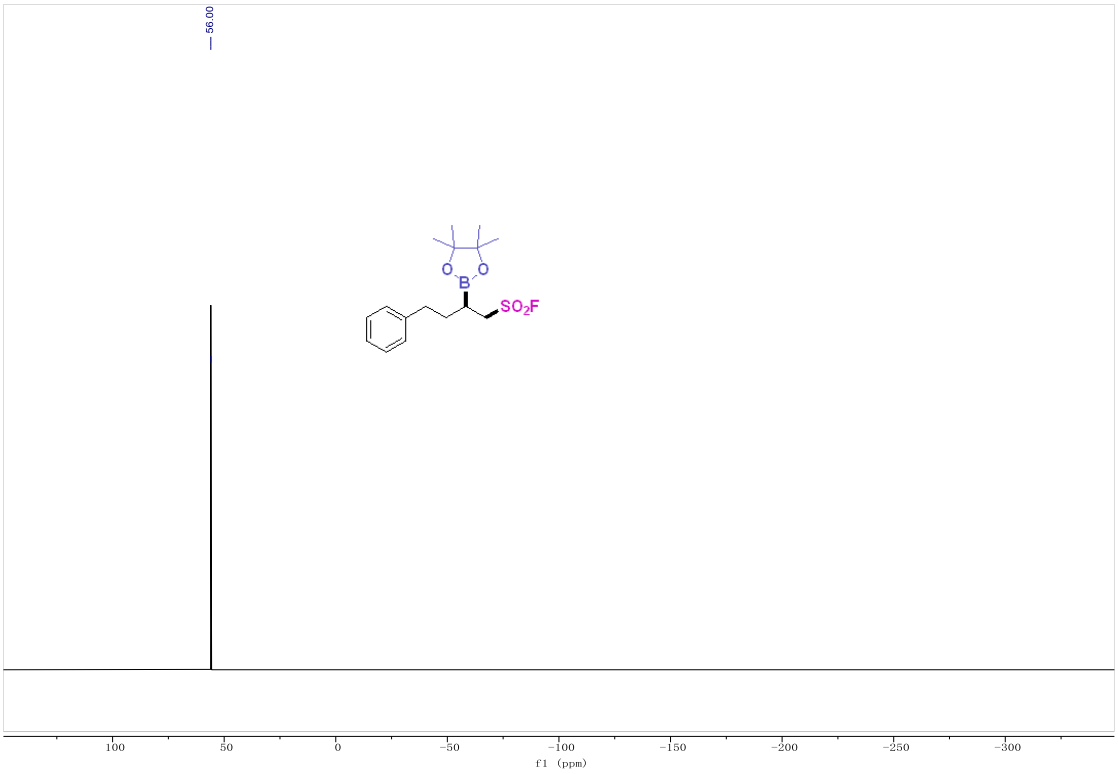
Supplementary Figure 90. ^{19}F NMR spectra of product **4x**



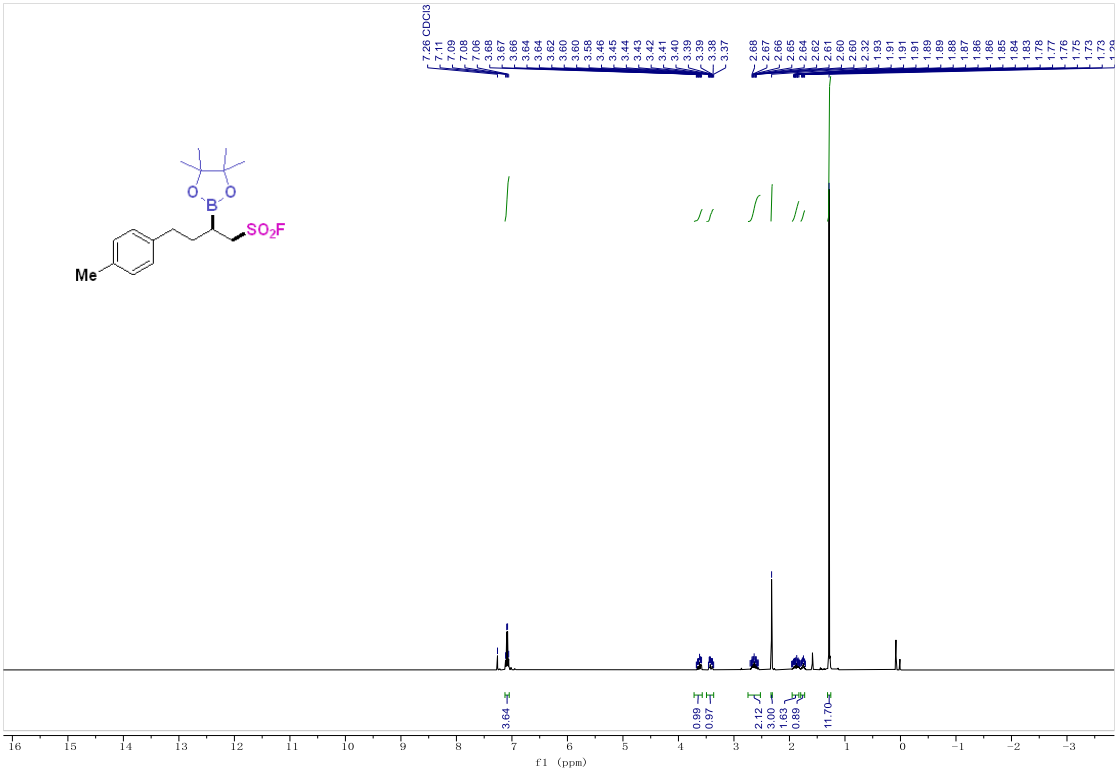
Supplementary Figure 91. ^{1}H NMR spectra of product **6a**



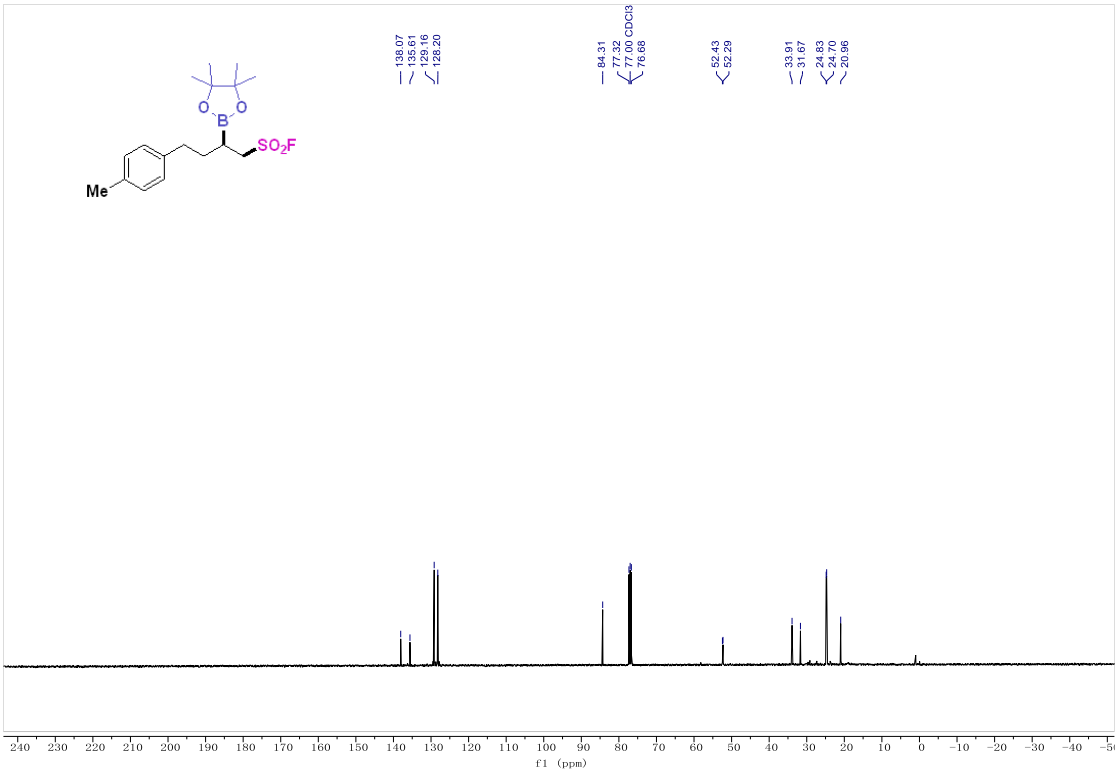
Supplementary Figure 92. ^{13}C NMR spectra of product **6a**



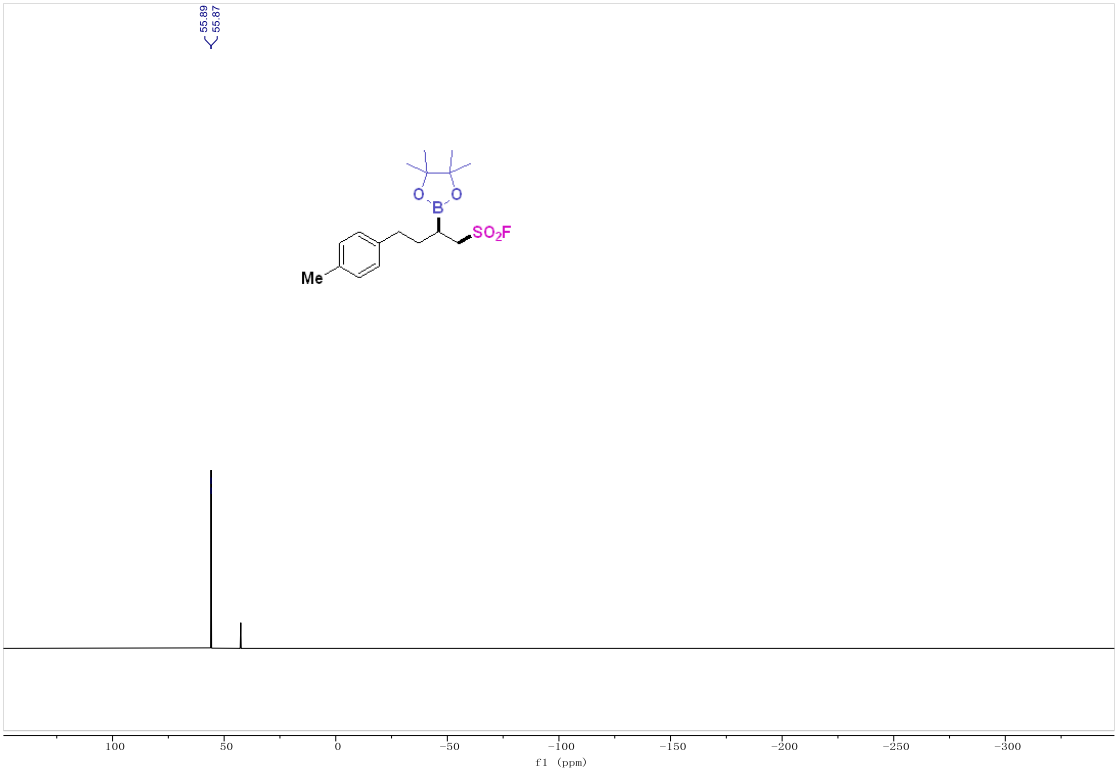
Supplementary Figure 93. ^{19}F NMR spectra of product **6a**



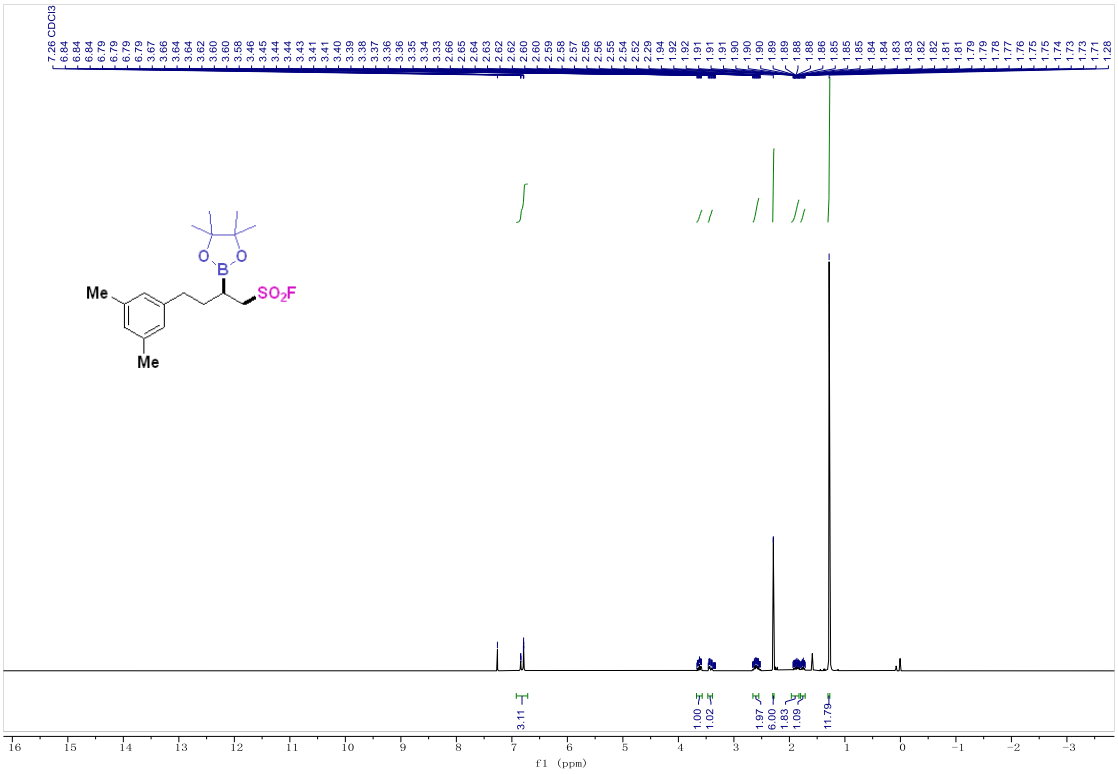
Supplementary Figure 94. ^{1}H NMR spectra of product **6b**



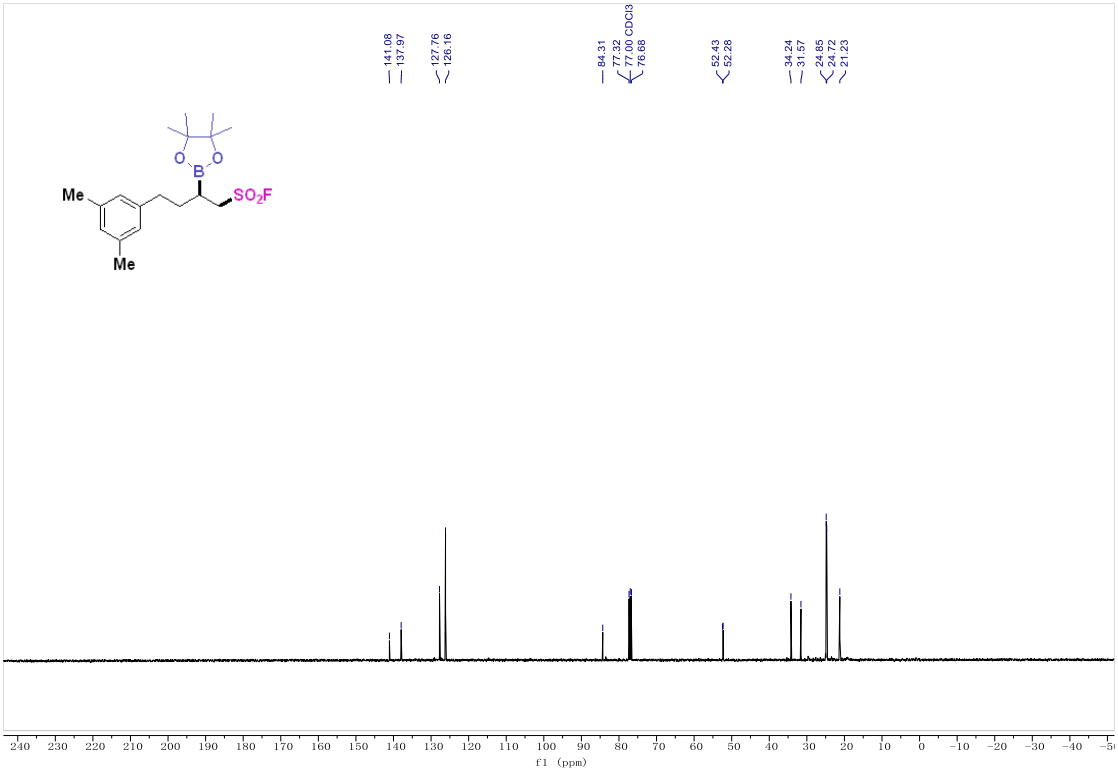
Supplementary Figure 95. ^{13}C NMR spectra of product **6b**



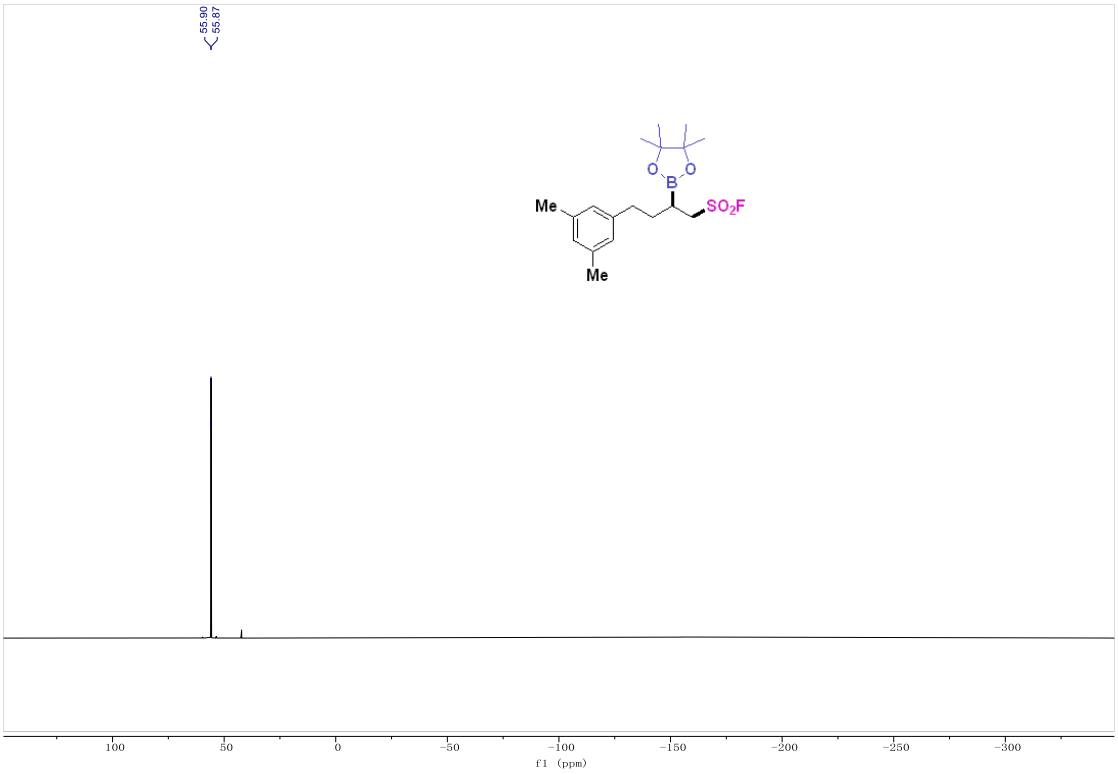
Supplementary Figure 96. ^{19}F NMR spectra of product **6b**



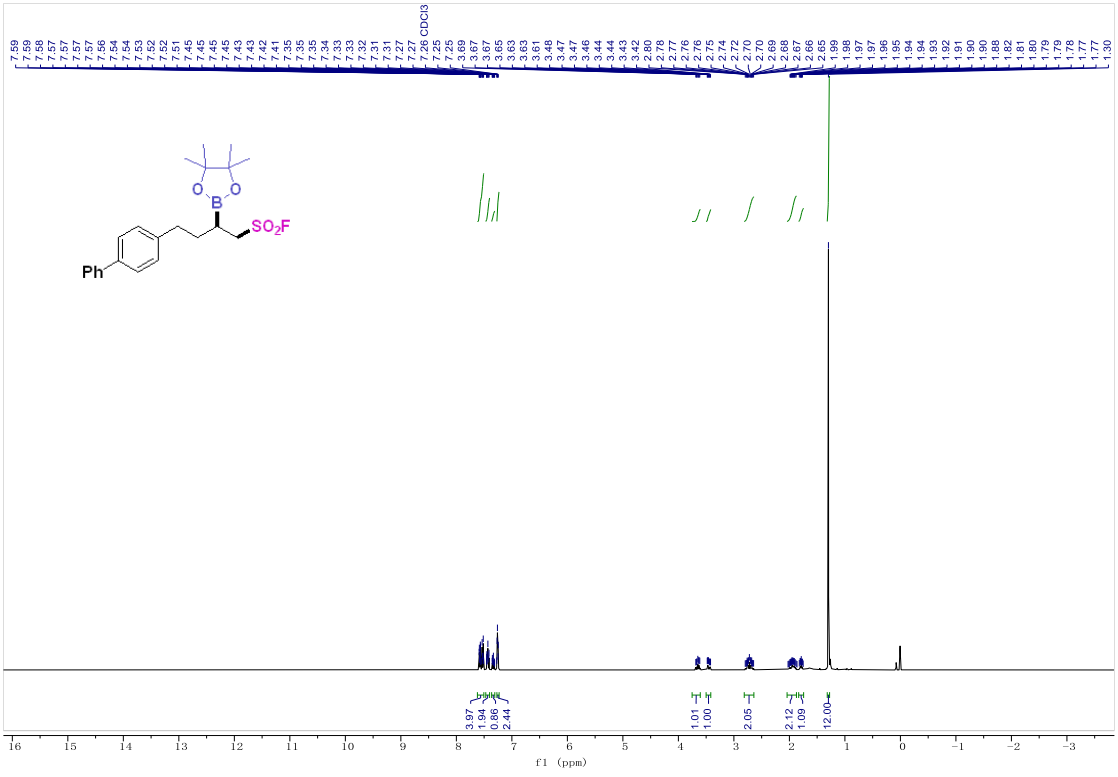
Supplementary Figure 97. ^{1}H NMR spectra of product **6c**



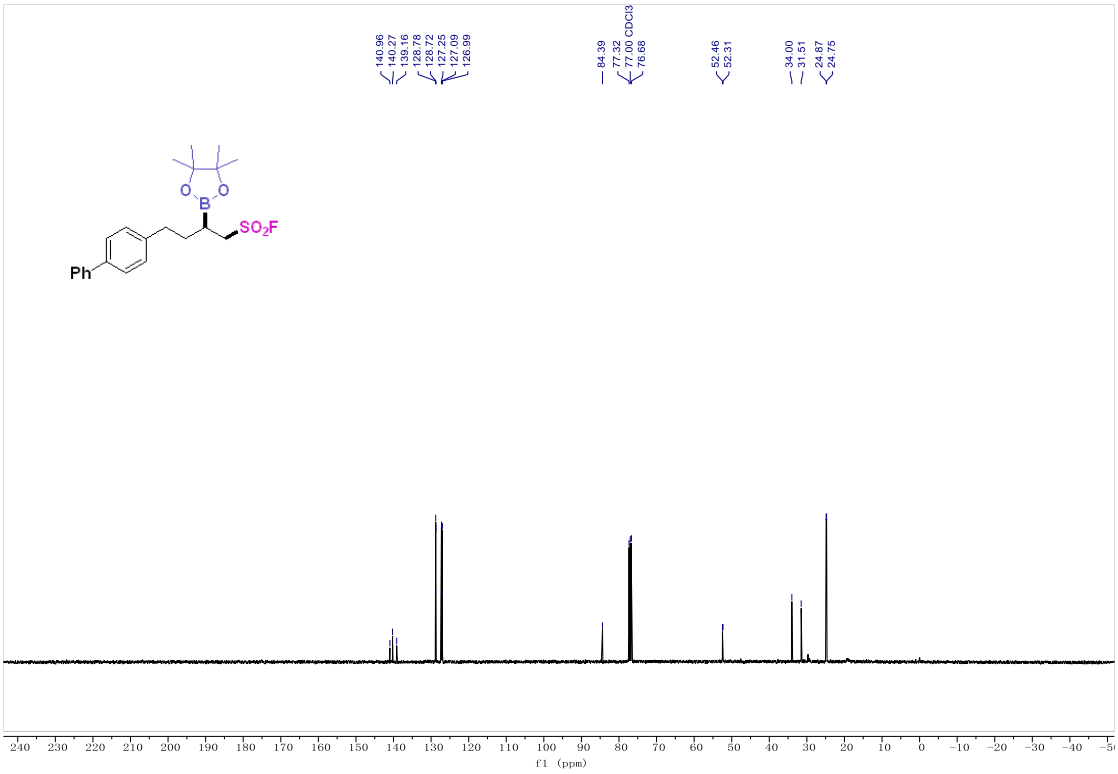
Supplementary Figure 98. ^{13}C NMR spectra of product **6c**



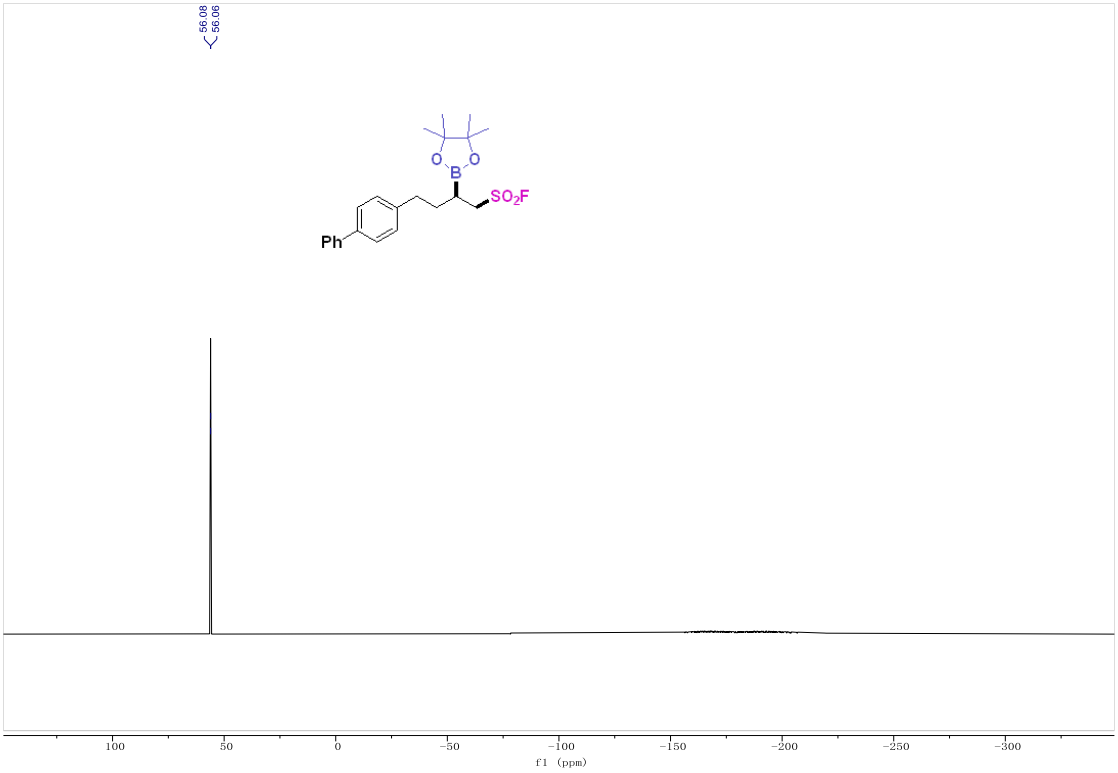
Supplementary Figure 99. ^{19}F NMR spectra of product **6c**



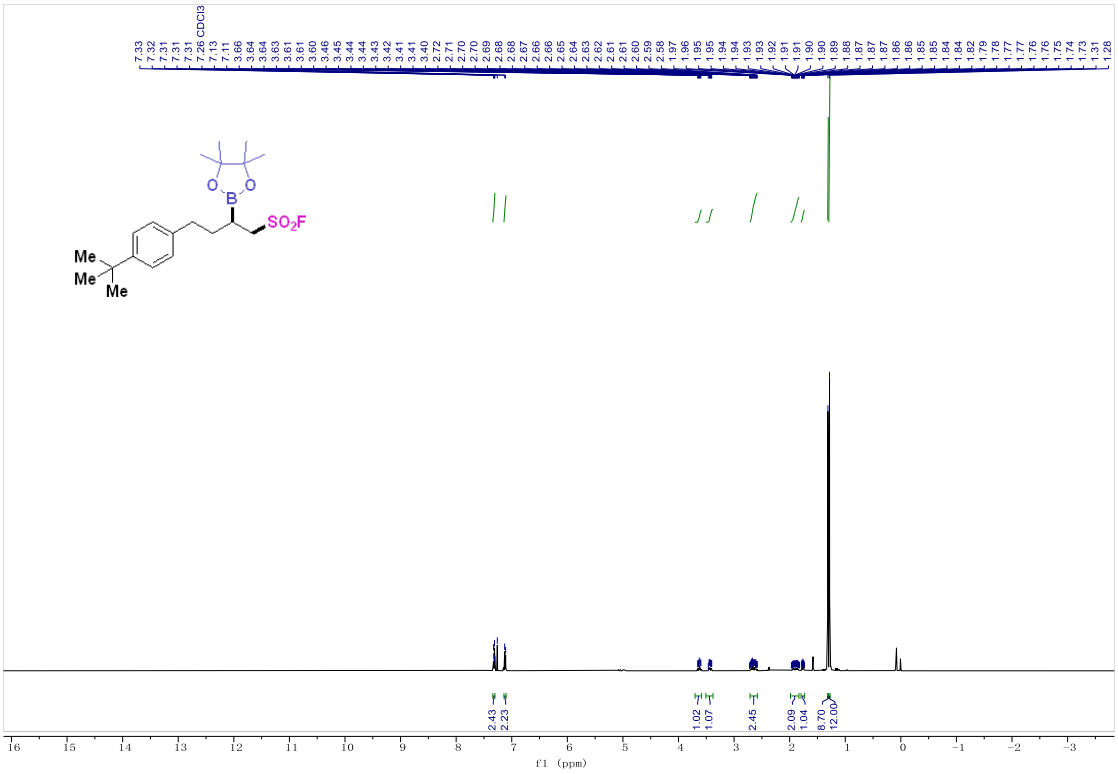
Supplementary Figure 100. ^{1}H NMR spectra of product **6d**



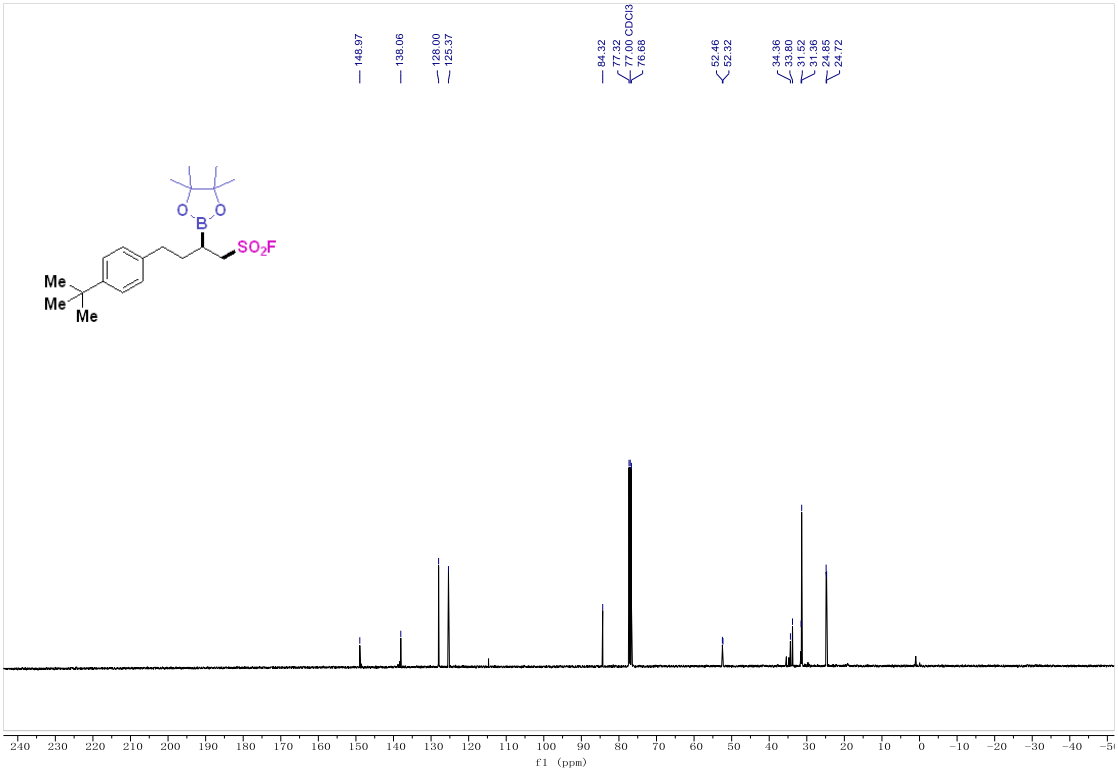
Supplementary Figure 101. ^{13}C NMR spectra of product **6d**



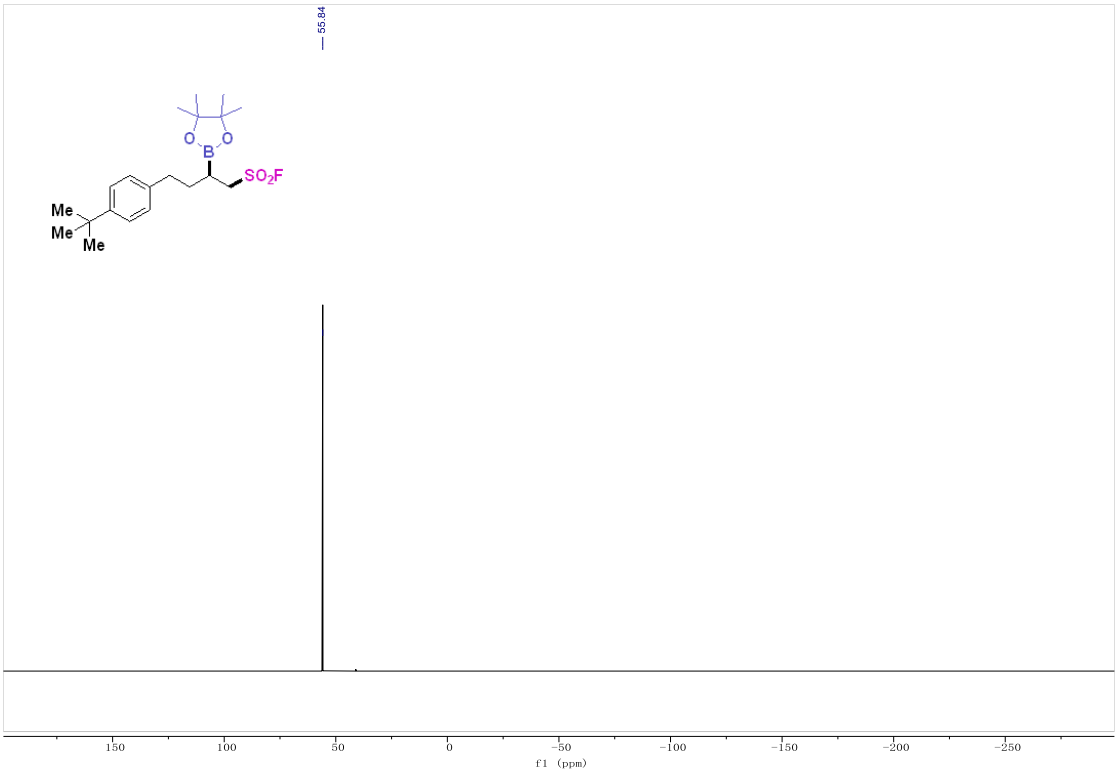
Supplementary Figure 102. ^{19}F NMR spectra of product **6d**



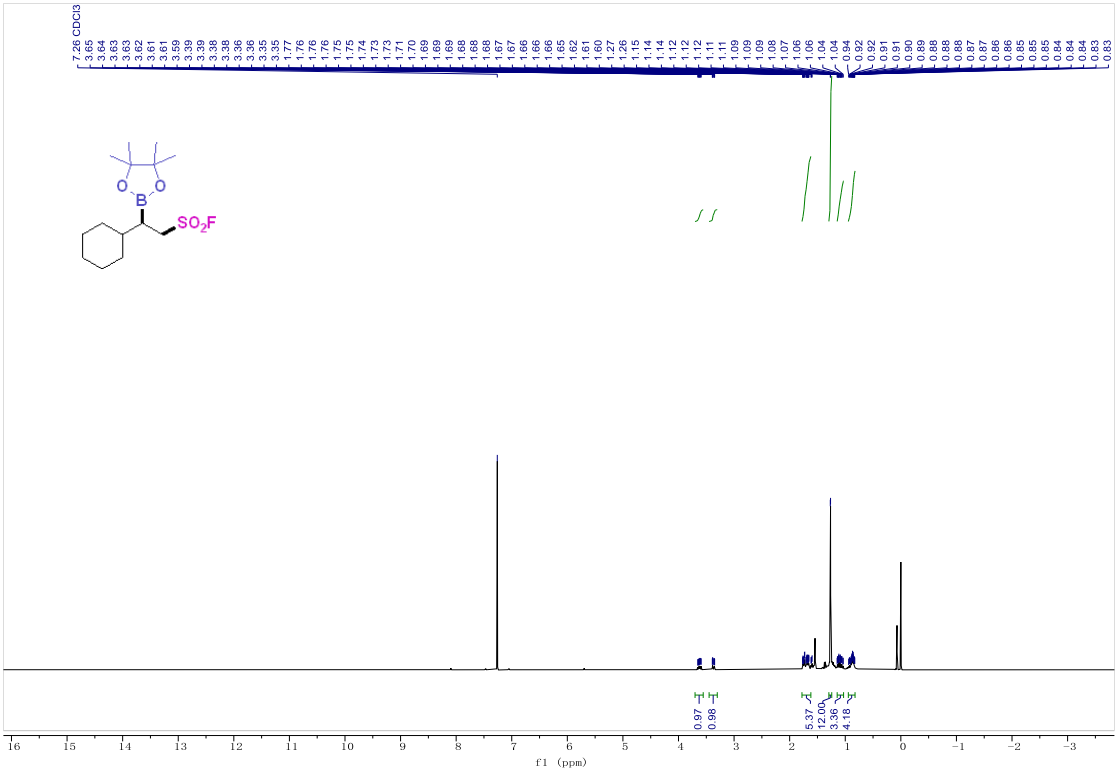
Supplementary Figure 103. ^{1}H NMR spectra of product **6e**



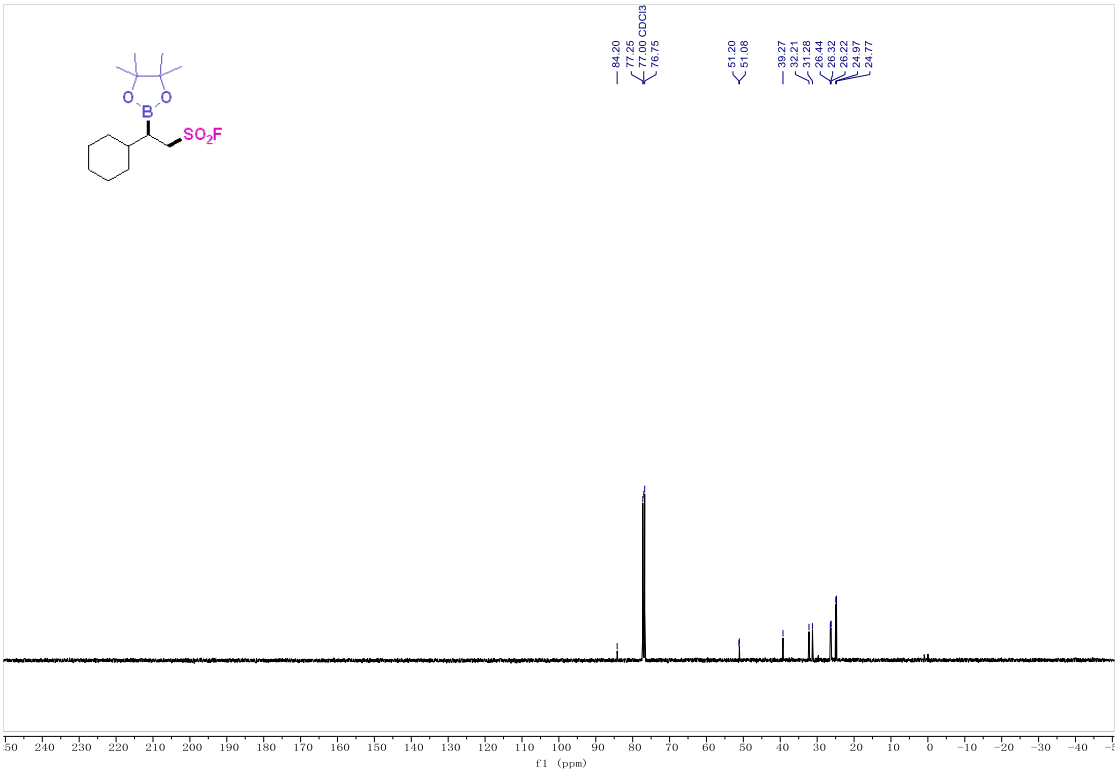
Supplementary Figure 104. ^{13}C NMR spectra of product **6e**



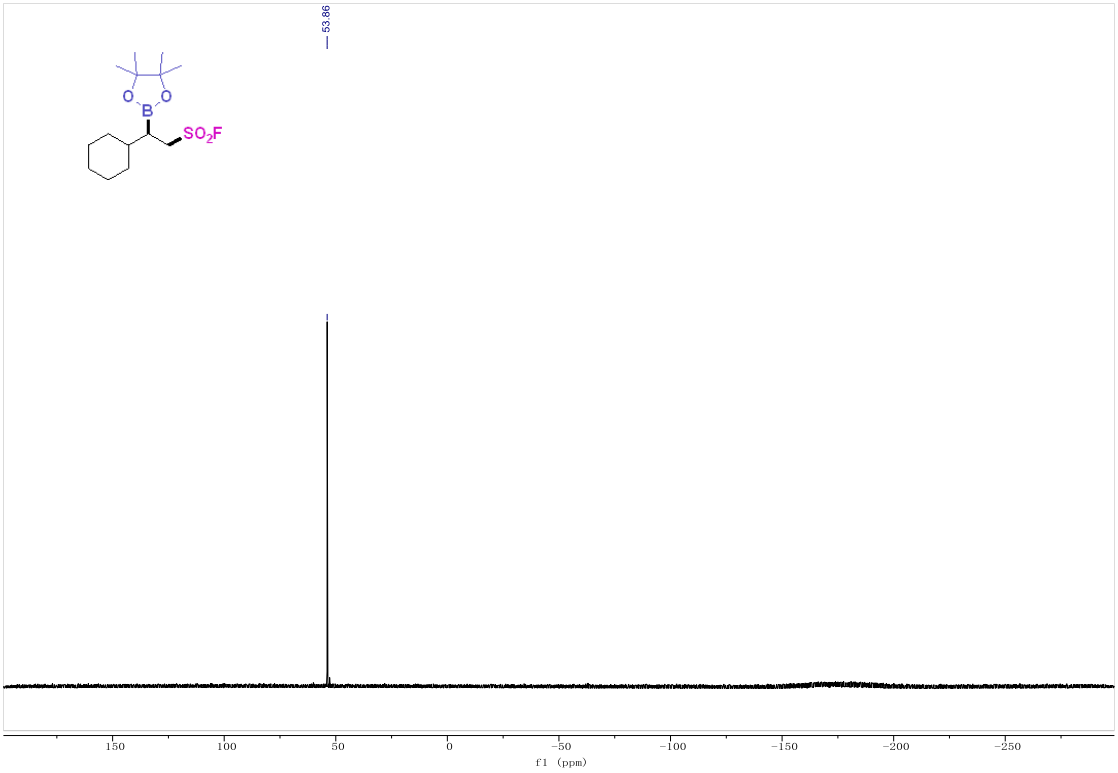
Supplementary Figure 105. ^{19}F NMR spectra of product **6e**



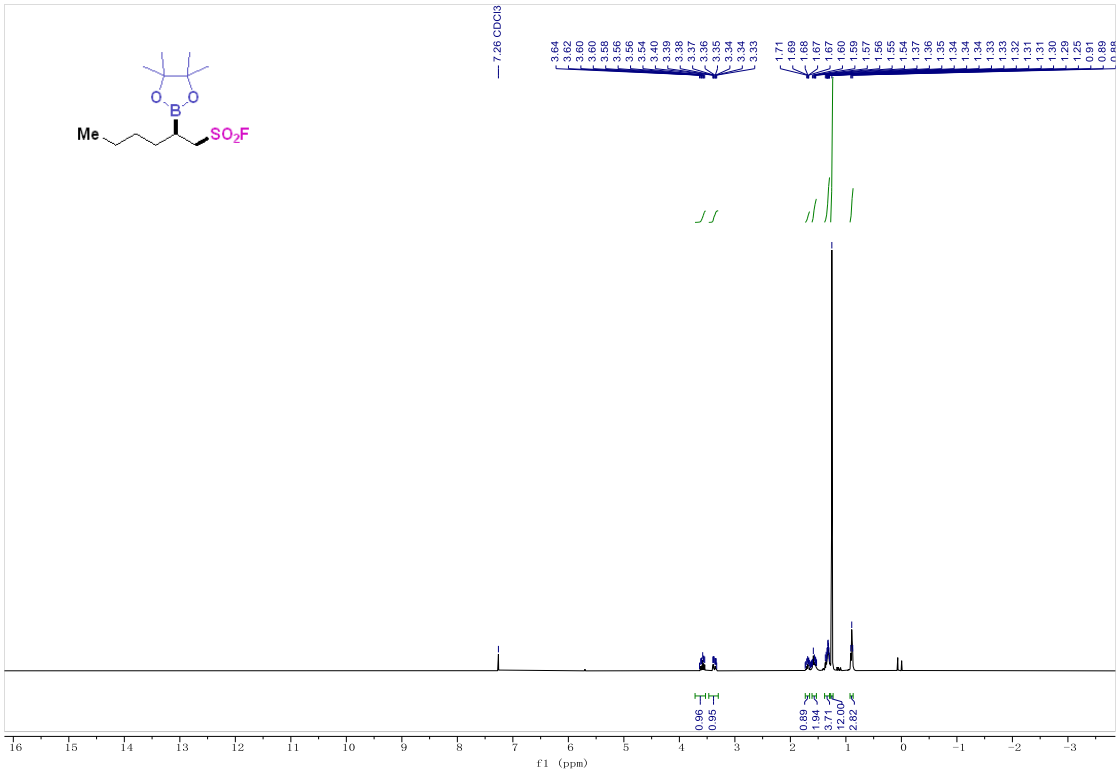
Supplementary Figure 106. ^{1}H NMR spectra of product **6f**



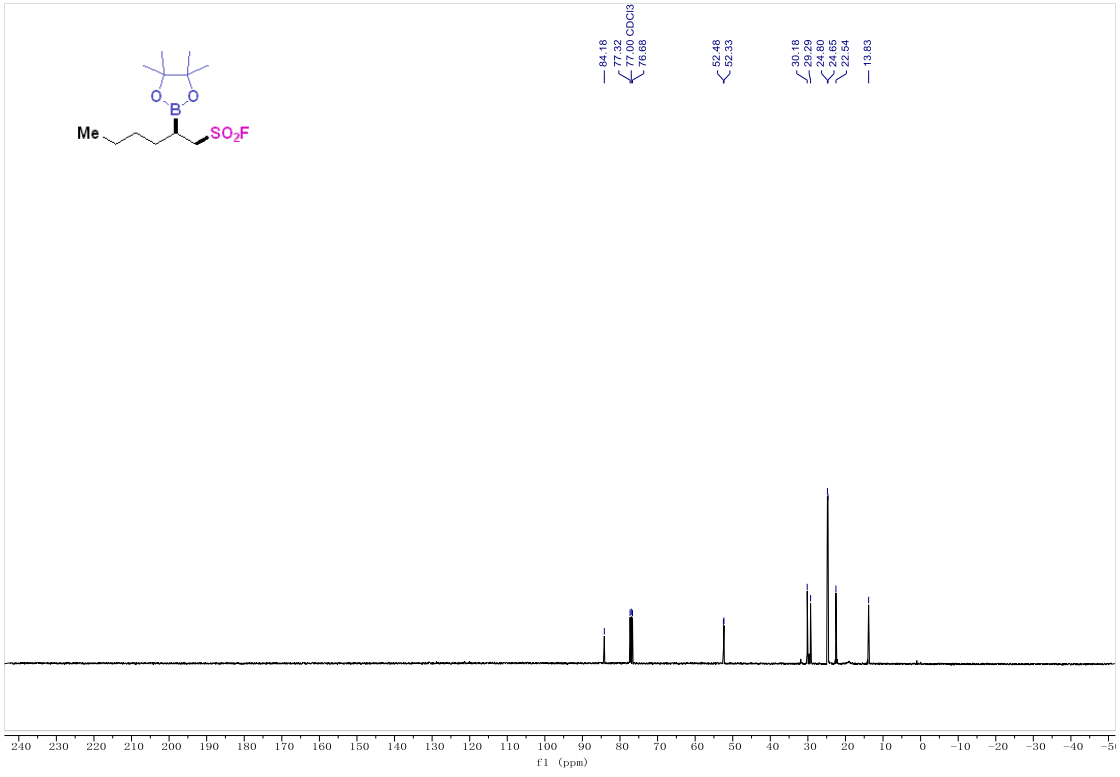
Supplementary Figure 107. ^{13}C NMR spectra of product **6f**



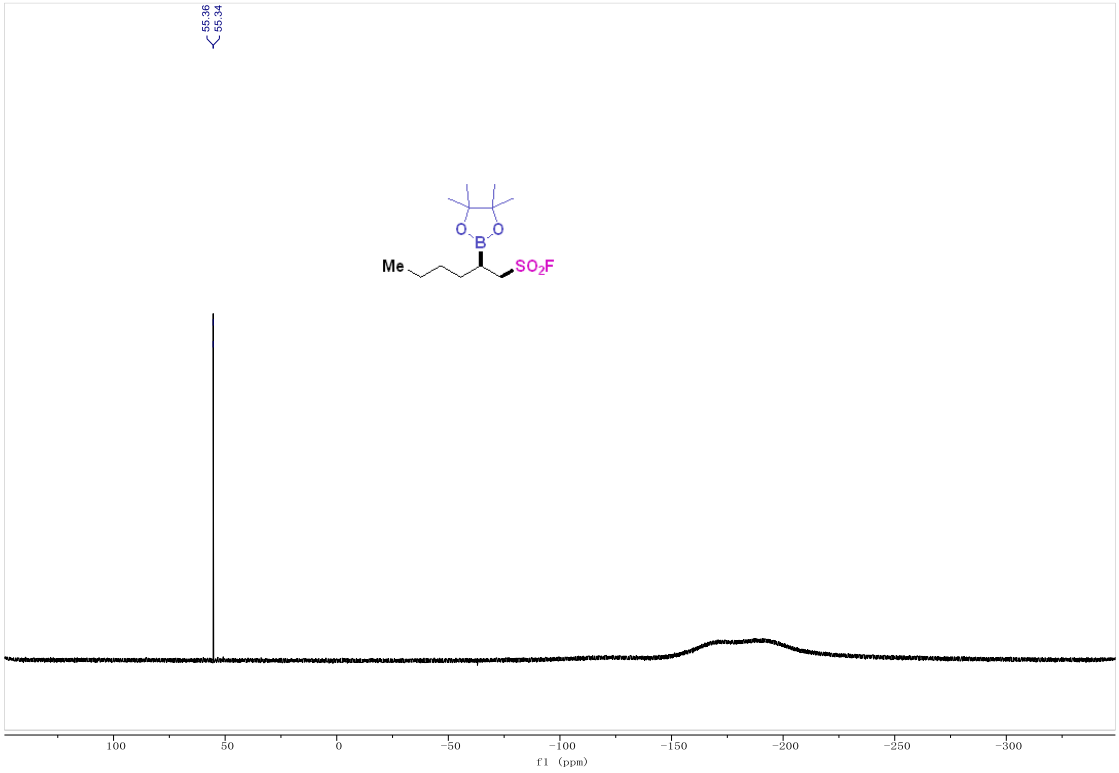
Supplementary Figure 108. ^{19}F NMR spectra of product **6f**



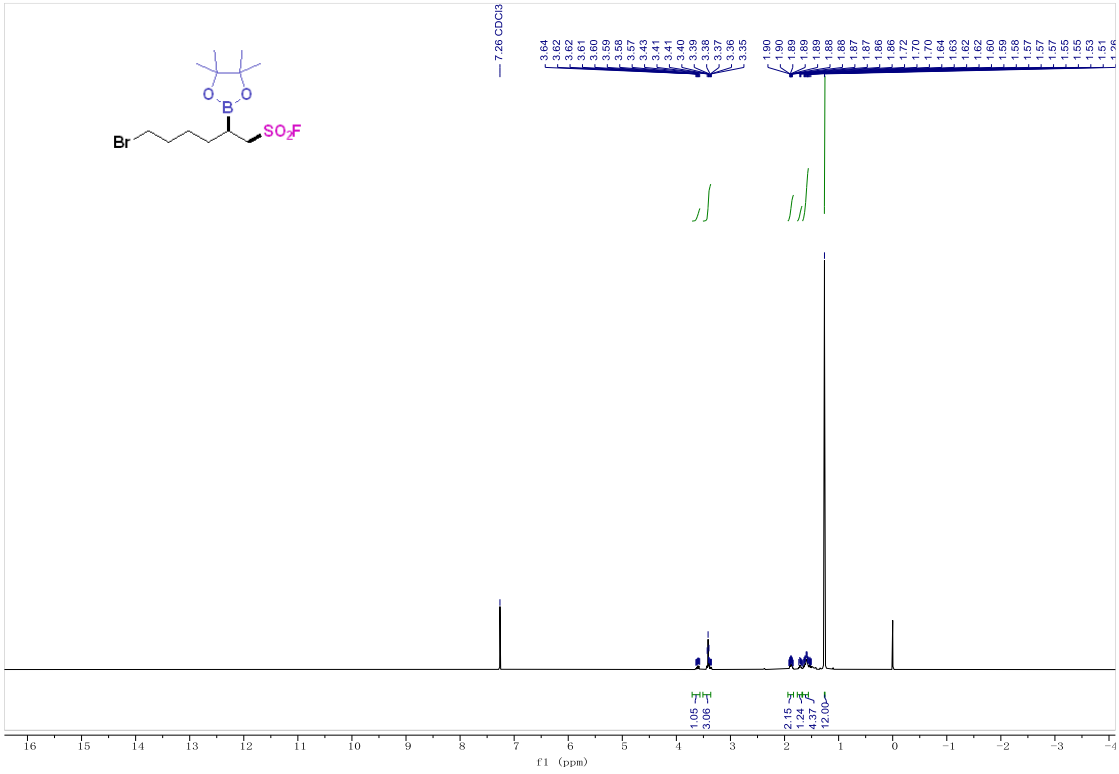
Supplementary Figure 109. ^{1}H NMR spectra of product **6g**



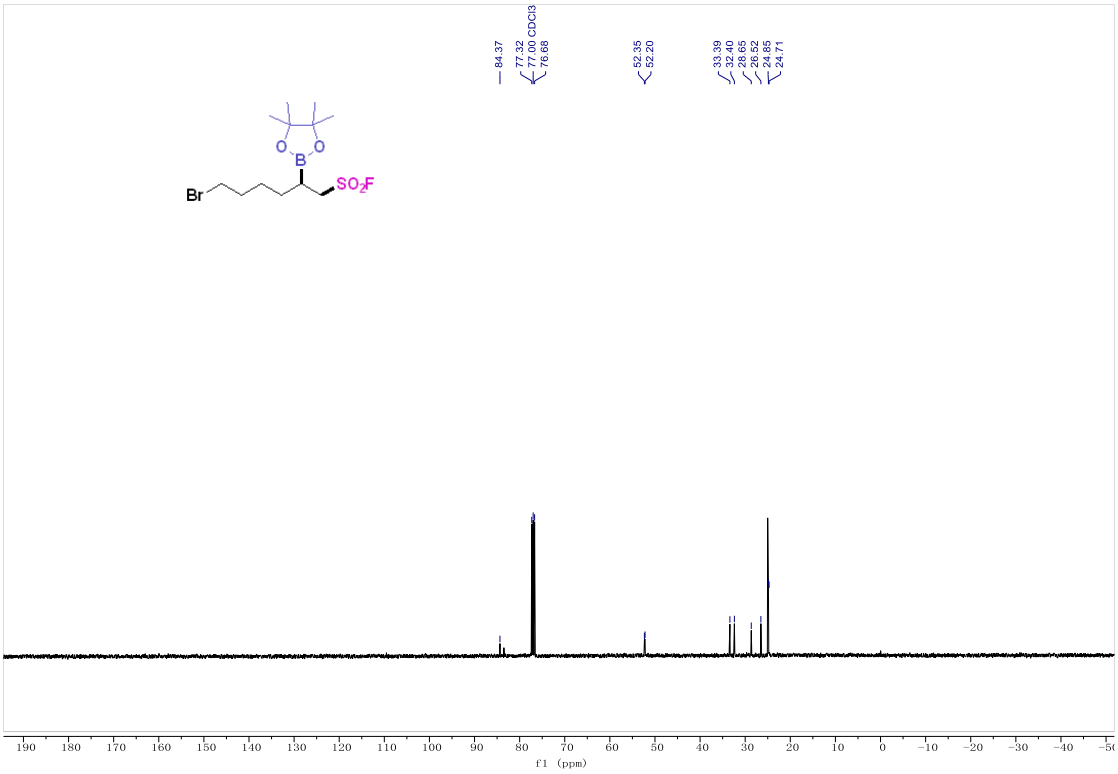
Supplementary Figure 110. ^{13}C NMR spectra of product **6g**



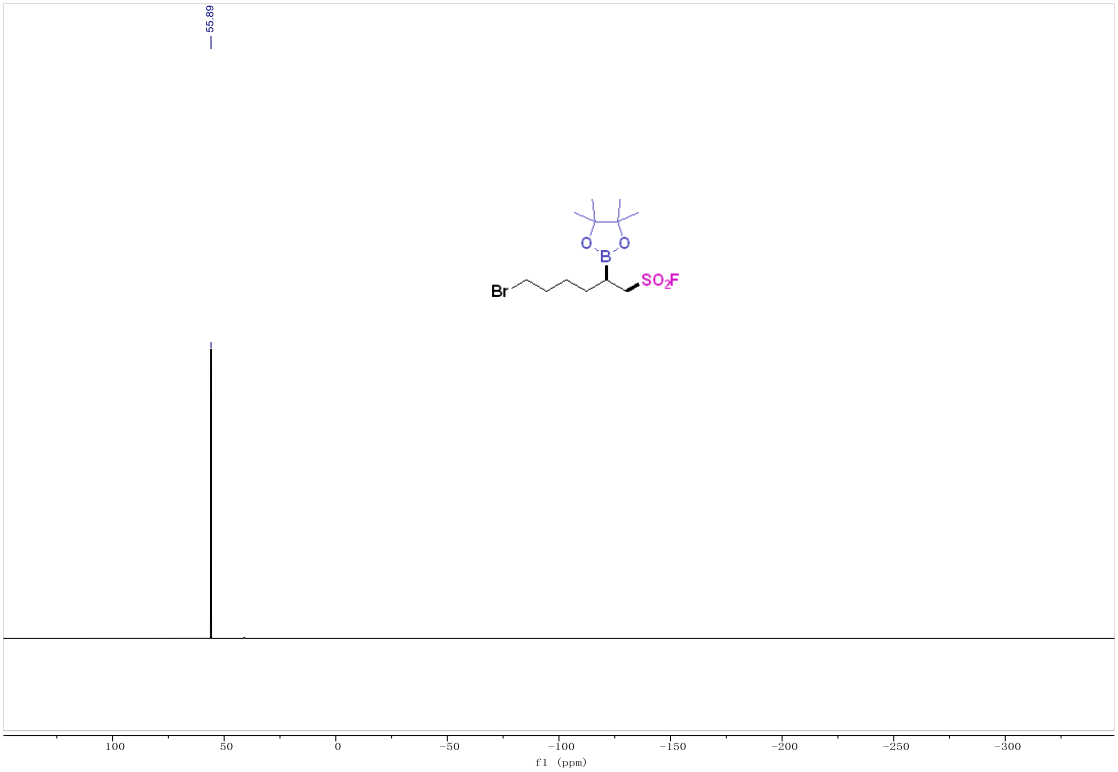
Supplementary Figure 111. ^{19}F NMR spectra of product **6g**



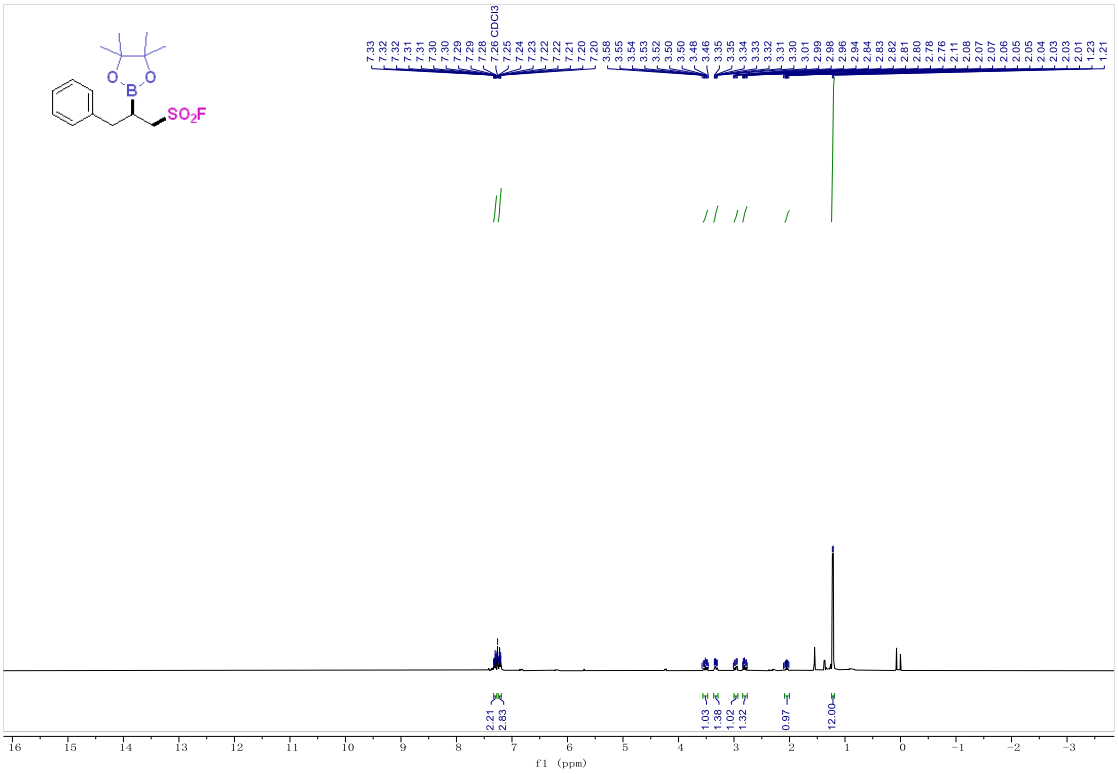
Supplementary Figure 112. ^{1}H NMR spectra of product **6h**



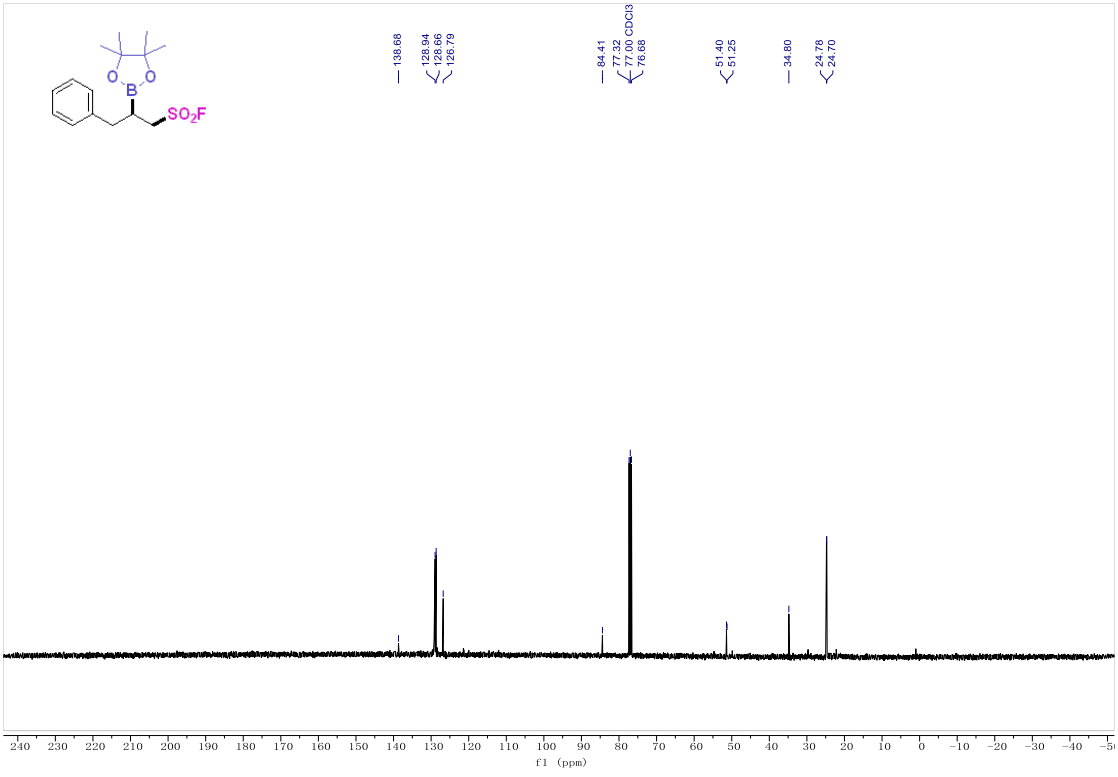
Supplementary Figure 113. ^{13}C NMR spectra of product **6h**



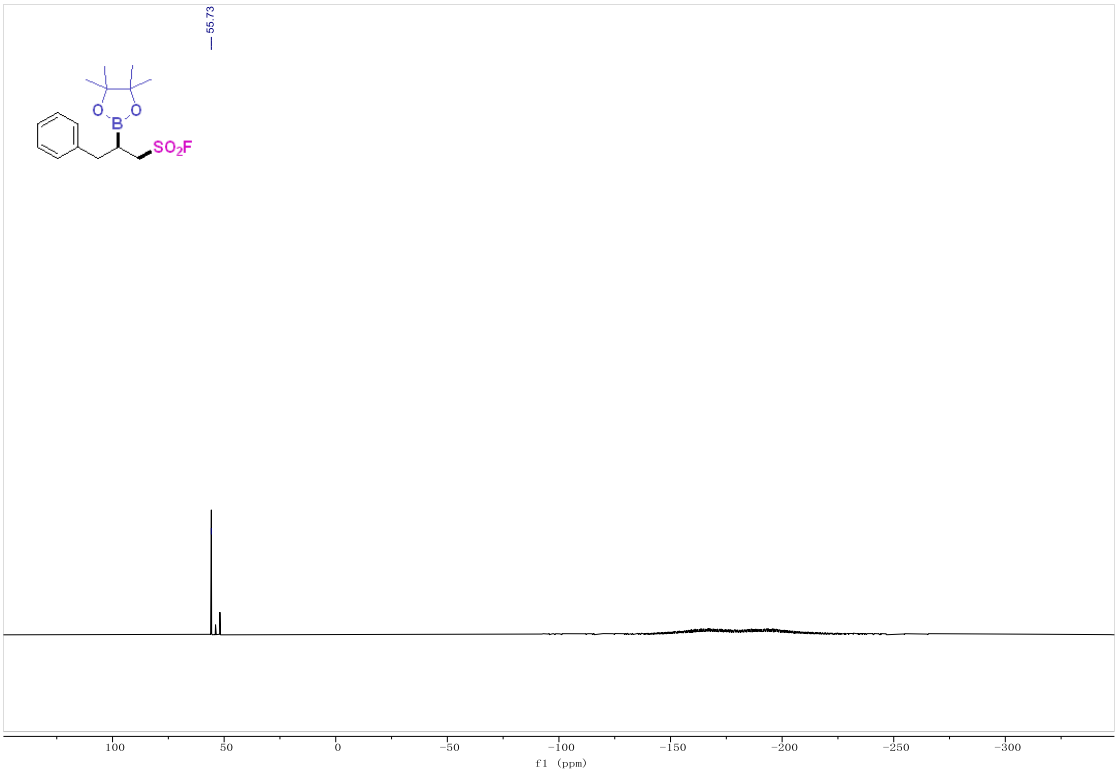
Supplementary Figure 114. ^{19}F NMR spectra of product **6h**



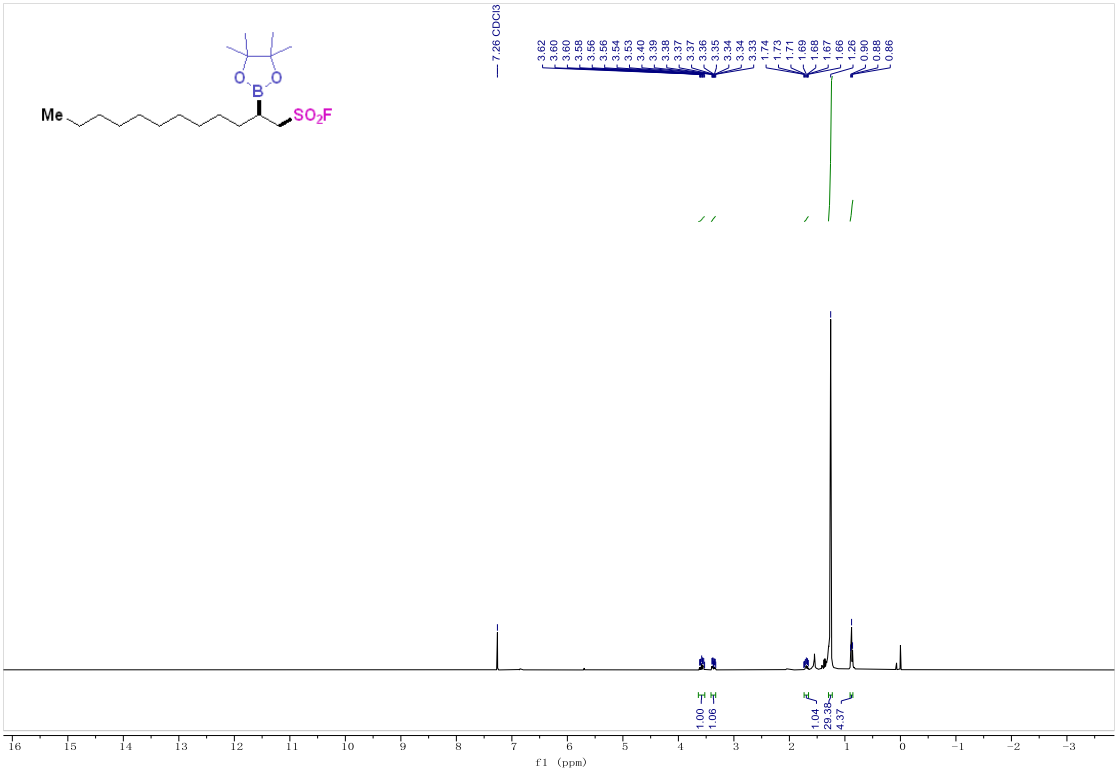
Supplementary Figure 115. ^{1}H NMR spectra of product **6i**



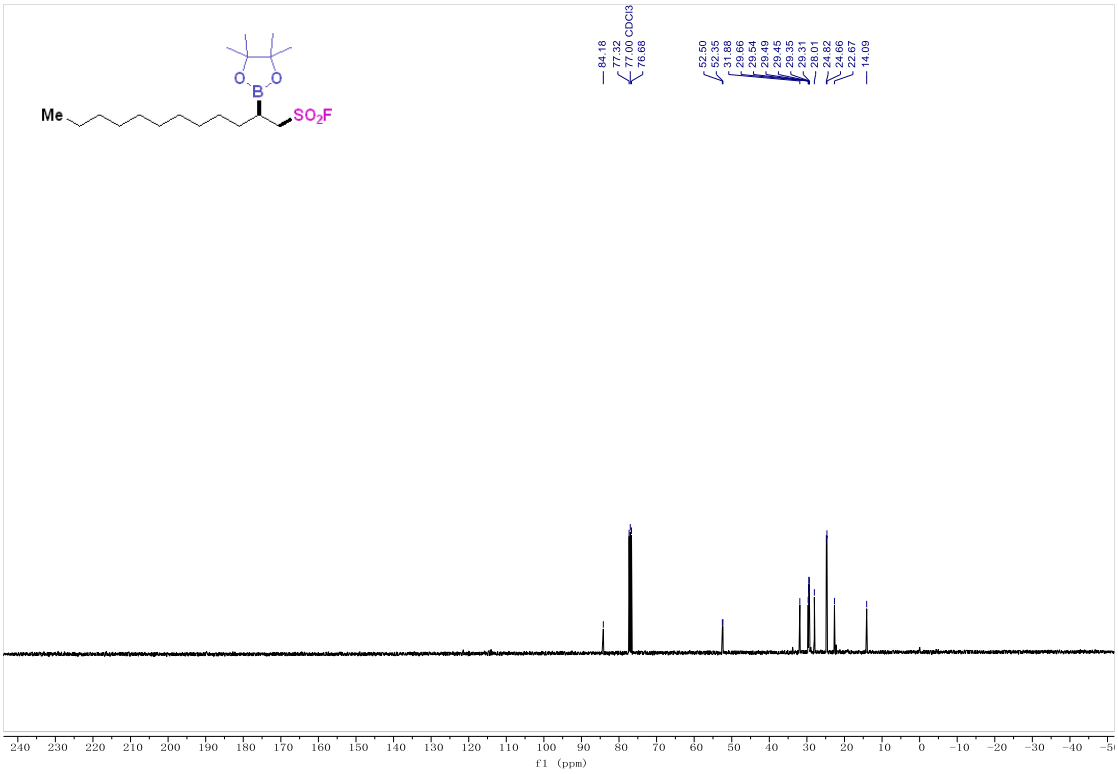
Supplementary Figure 116. ^{13}C NMR spectra of product **6i**



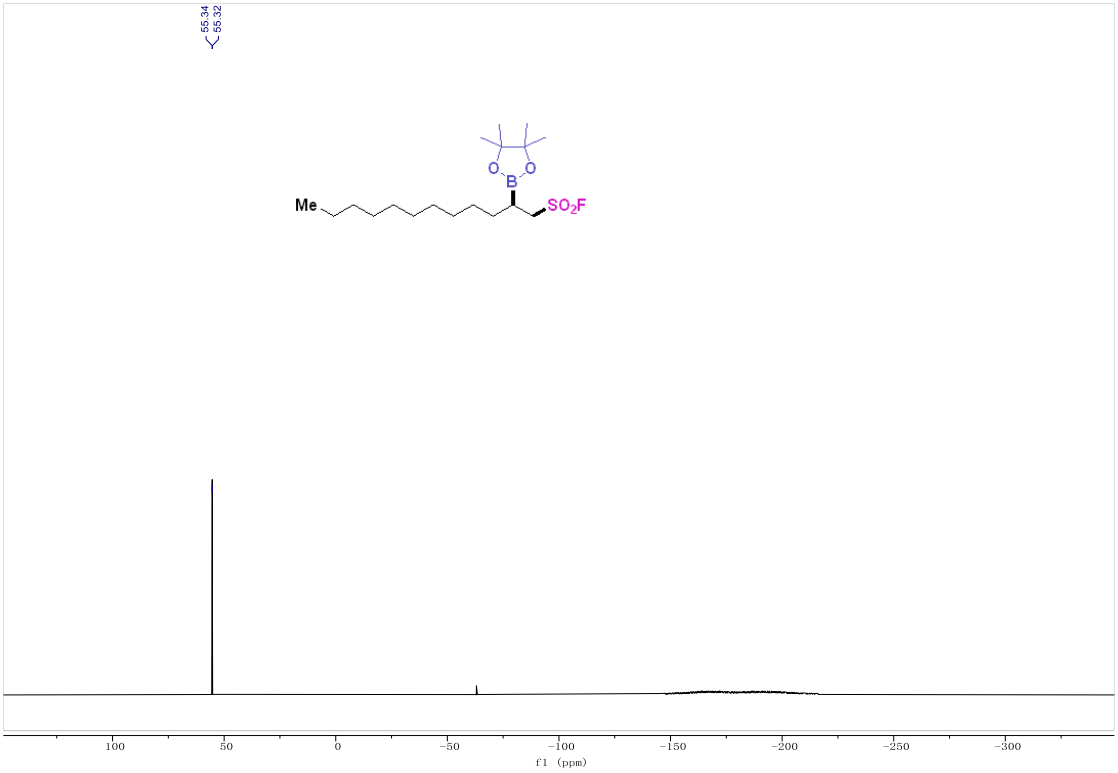
Supplementary Figure 117. ^{19}F NMR spectra of product **6i**



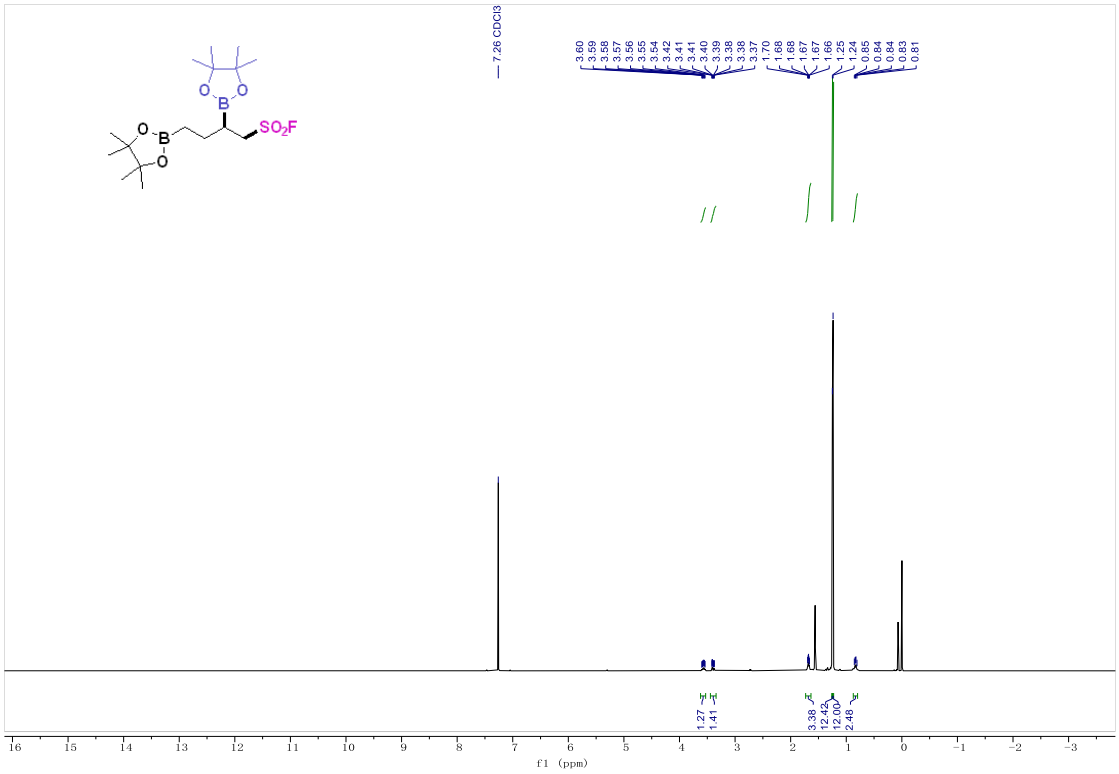
Supplementary Figure 118. ^{1}H NMR spectra of product **6j**



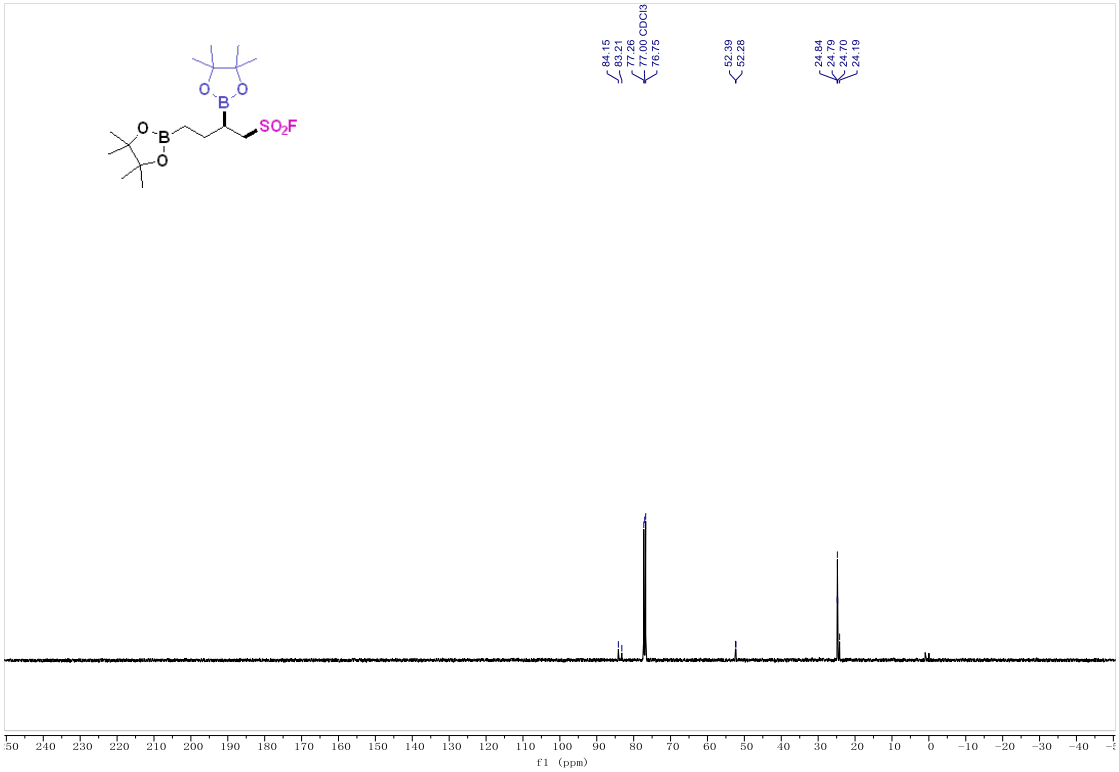
Supplementary Figure 119. ^{13}C NMR spectra of product **6j**



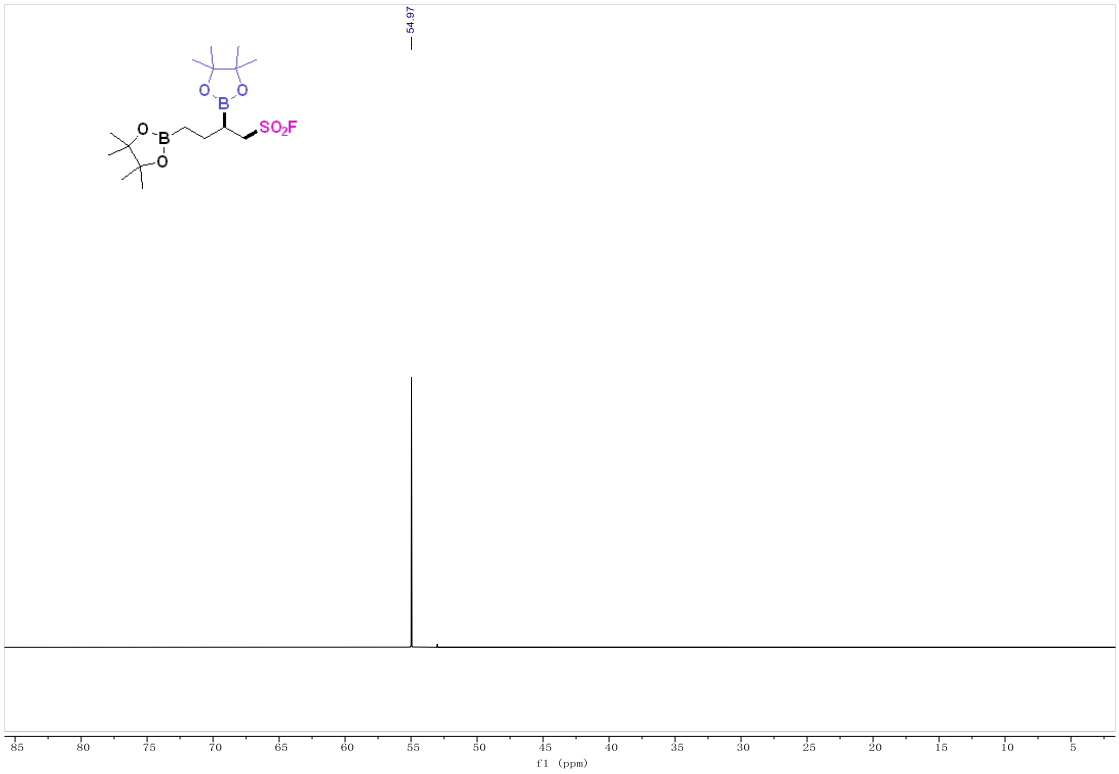
Supplementary Figure 120. ^{19}F NMR spectra of product **6j**



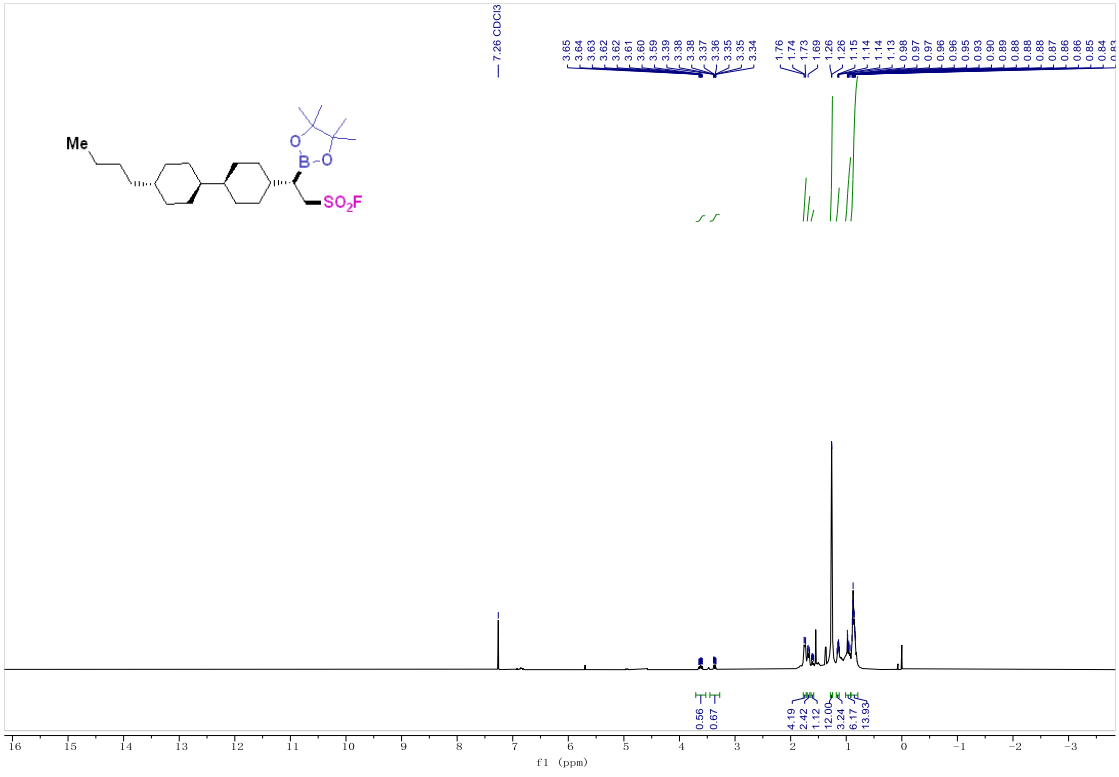
Supplementary Figure 121. ^{1}H NMR spectra of product **6k**



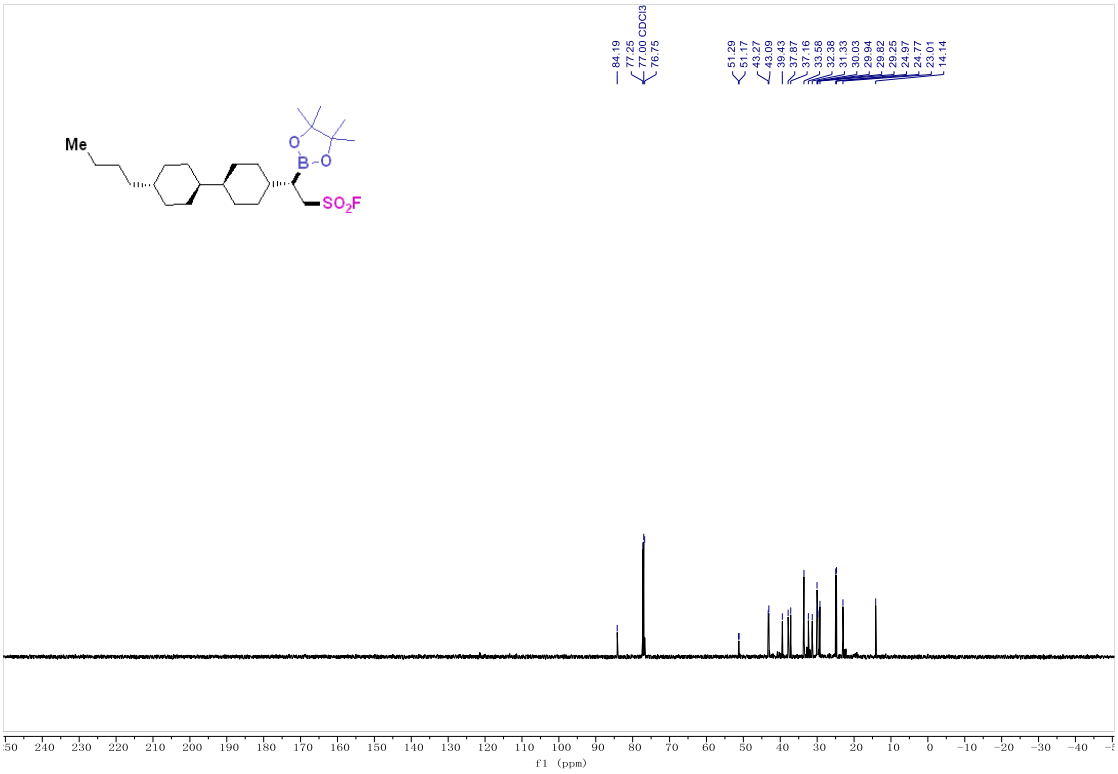
Supplementary Figure 122. ^{13}C NMR spectra of product **6k**



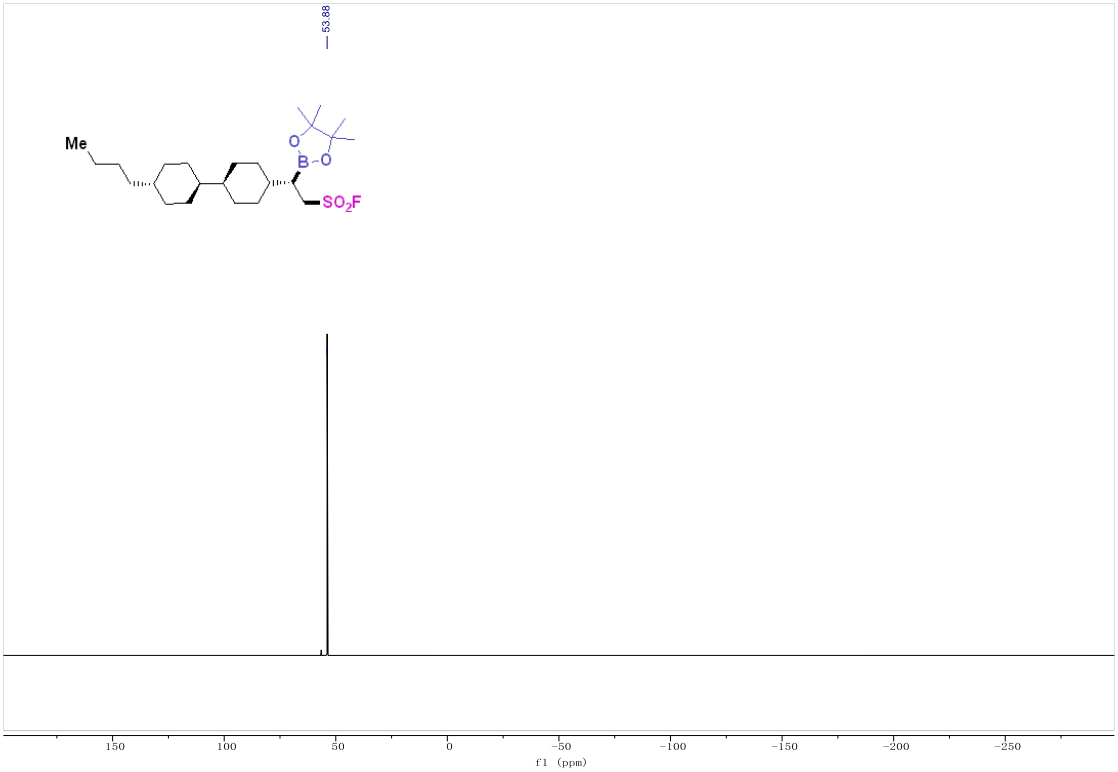
Supplementary Figure 123. ^{19}F NMR spectra of product **6k**



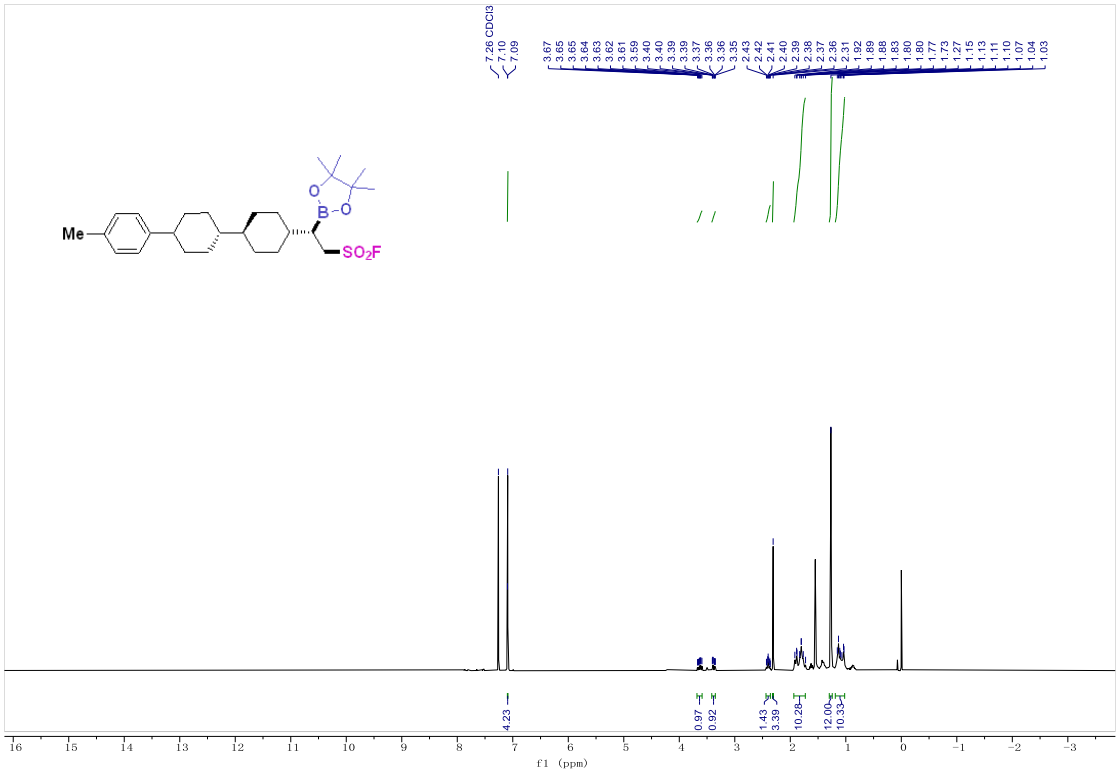
Supplementary Figure 124. ^{1}H NMR spectra of product **6l**



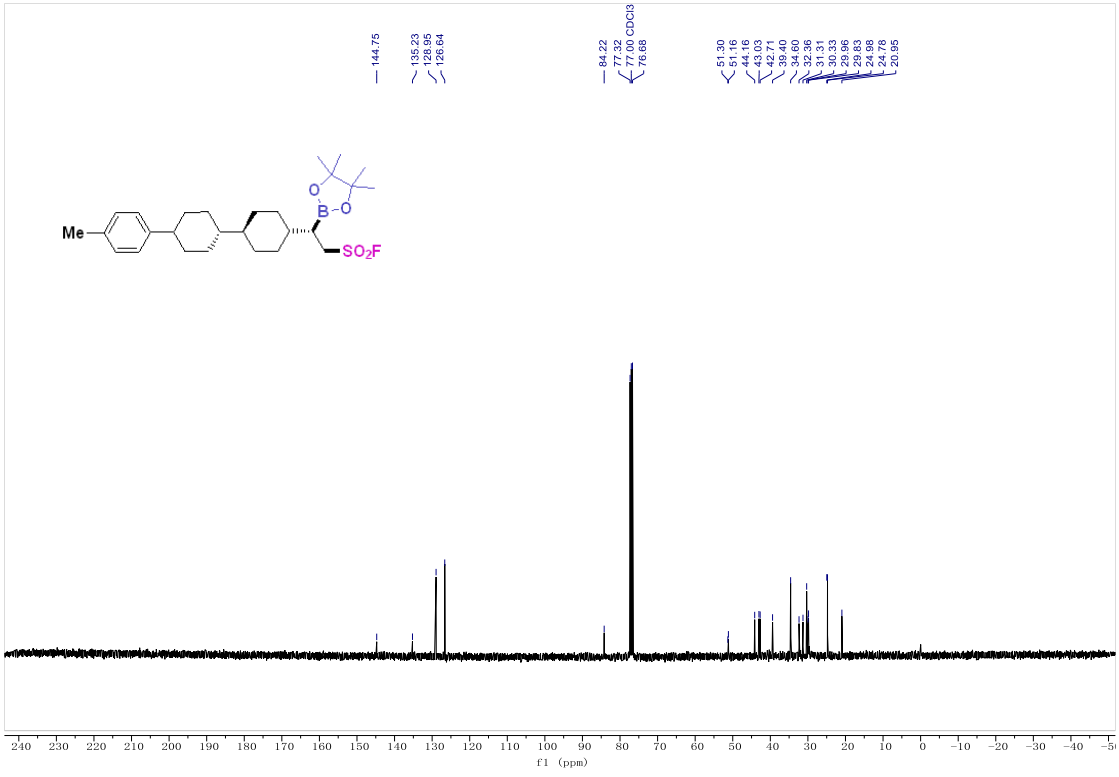
Supplementary Figure 125. ^{13}C NMR spectra of product **6l**



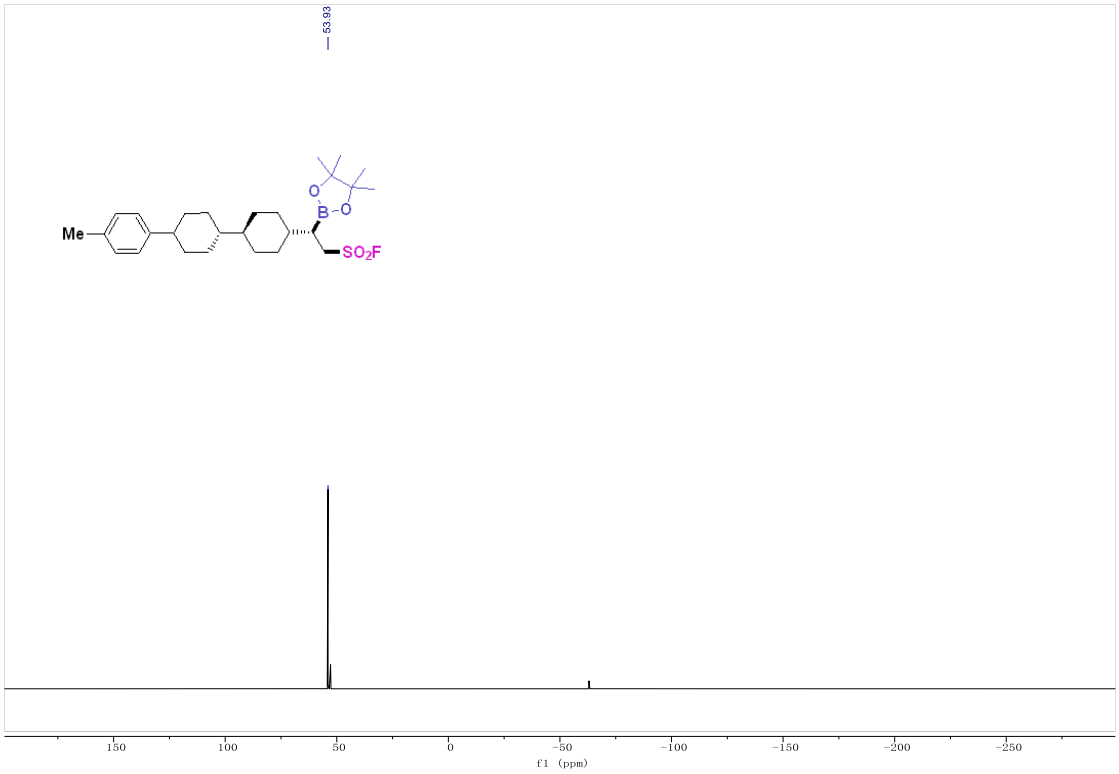
Supplementary Figure 126. ^{19}F NMR spectra of product **6l**



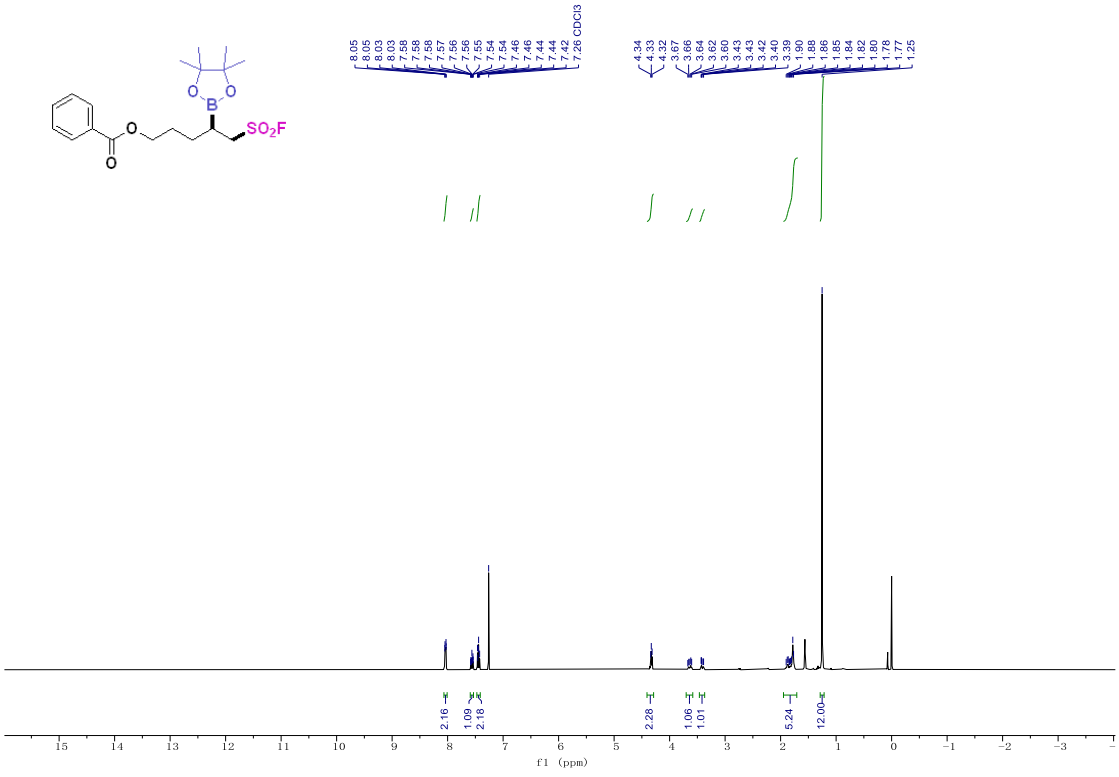
Supplementary Figure 127. ^{1}H NMR spectra of product **6m**



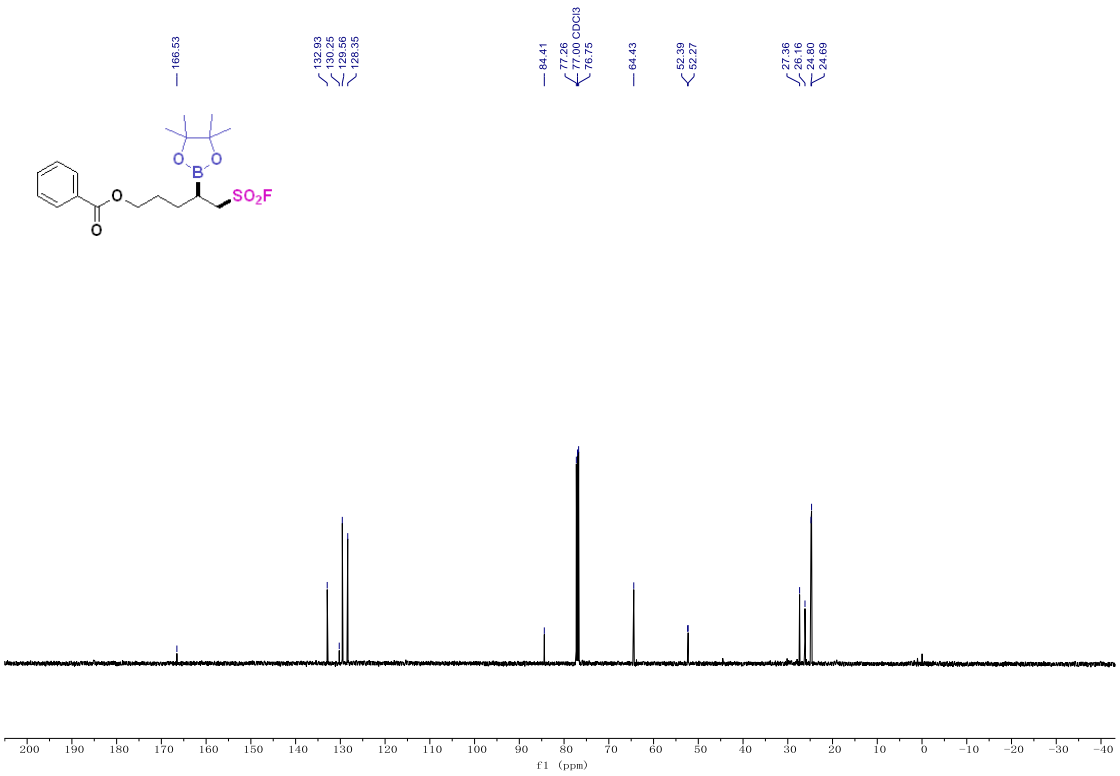
Supplementary Figure 128. ^{13}C NMR spectra of product **6m**



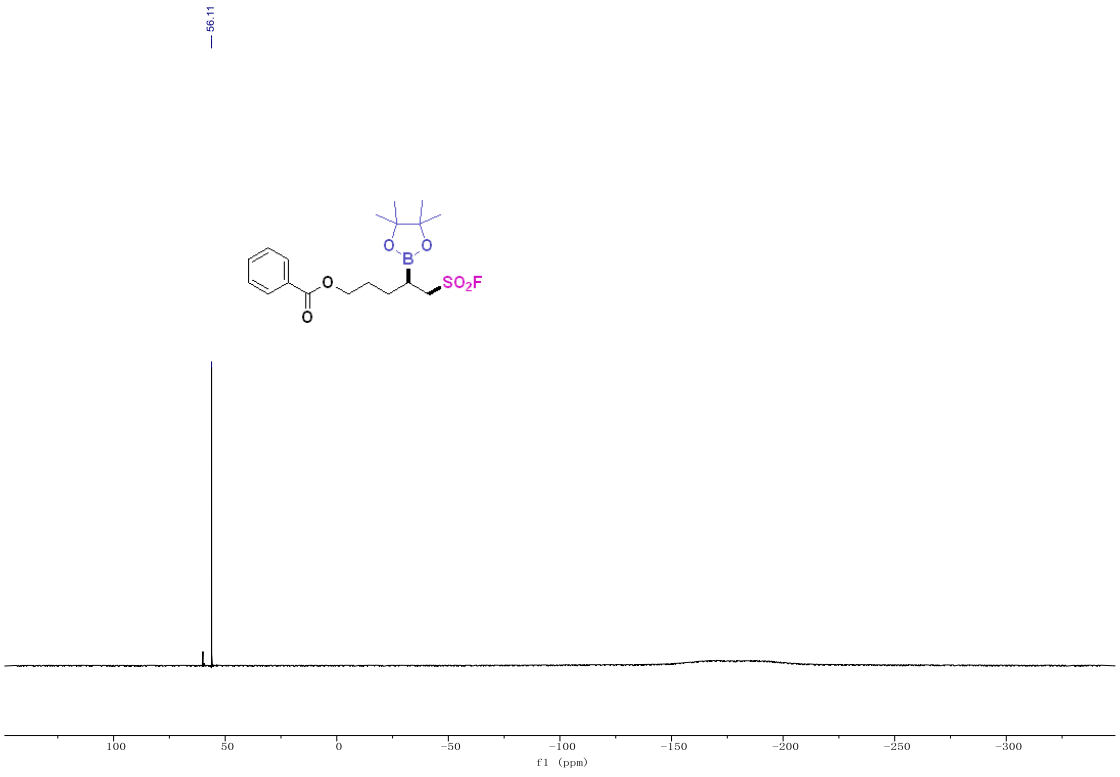
Supplementary Figure 129. ^{19}F NMR spectra of product **6m**



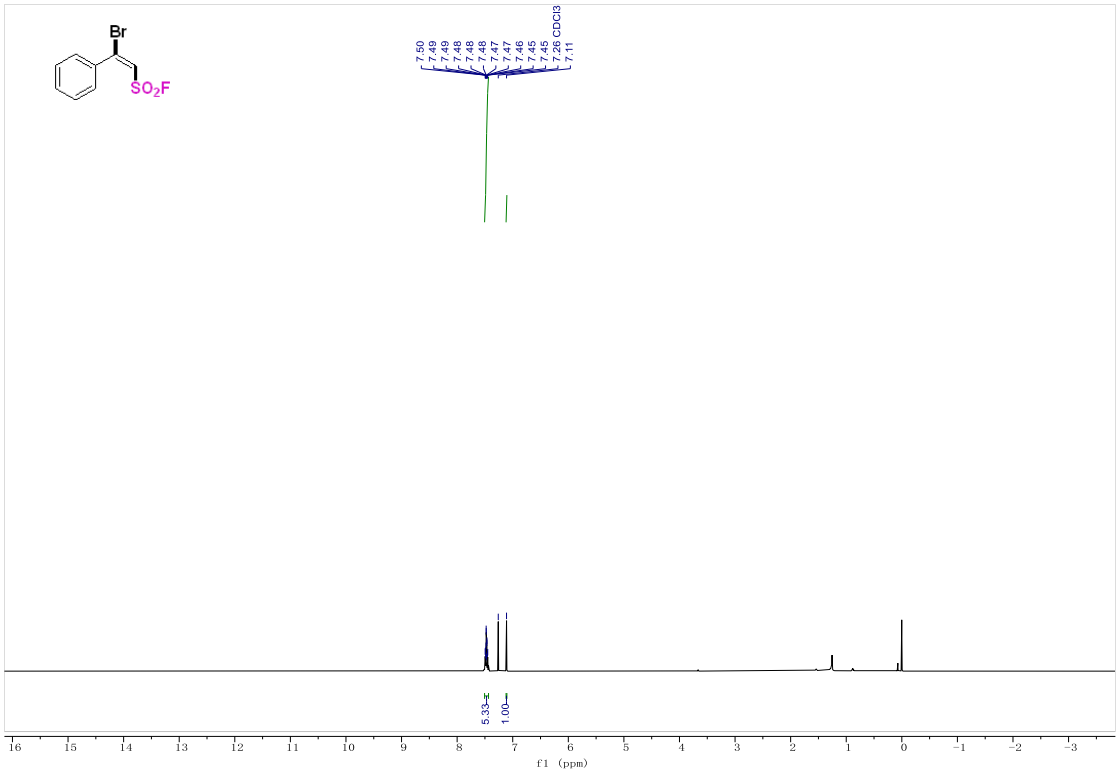
Supplementary Figure 130. ^{1}H NMR spectra of product **6n**



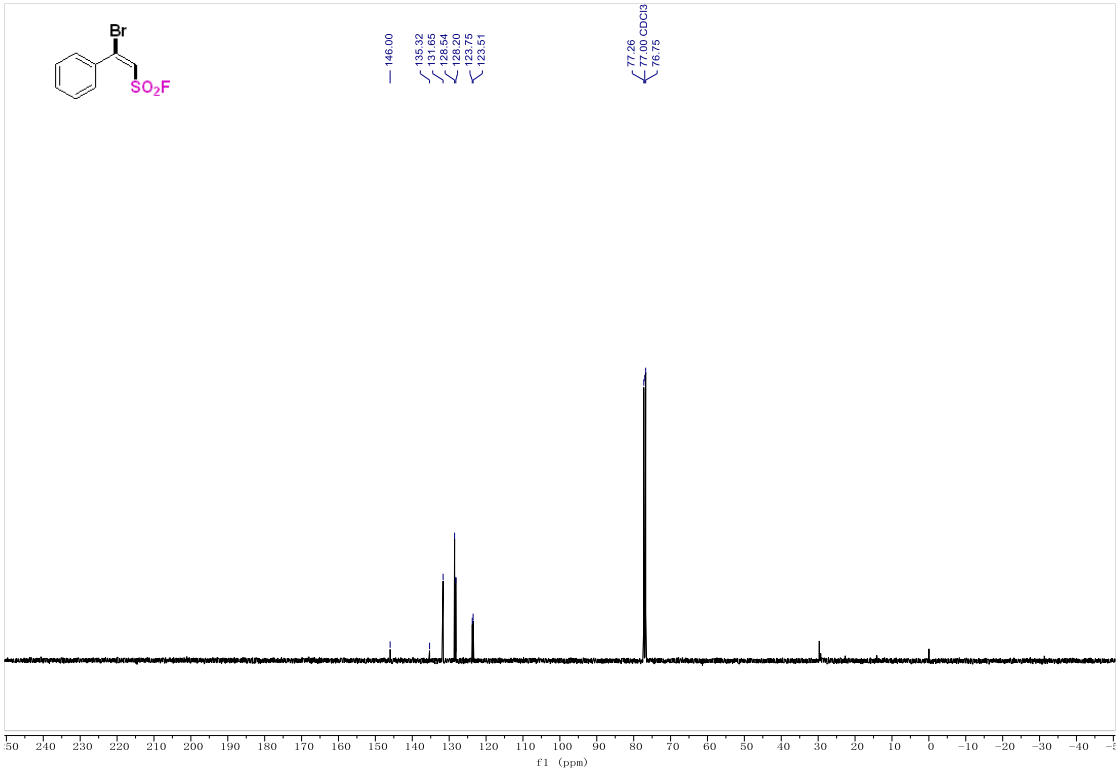
Supplementary Figure 131. ^{13}C NMR spectra of product **6n**



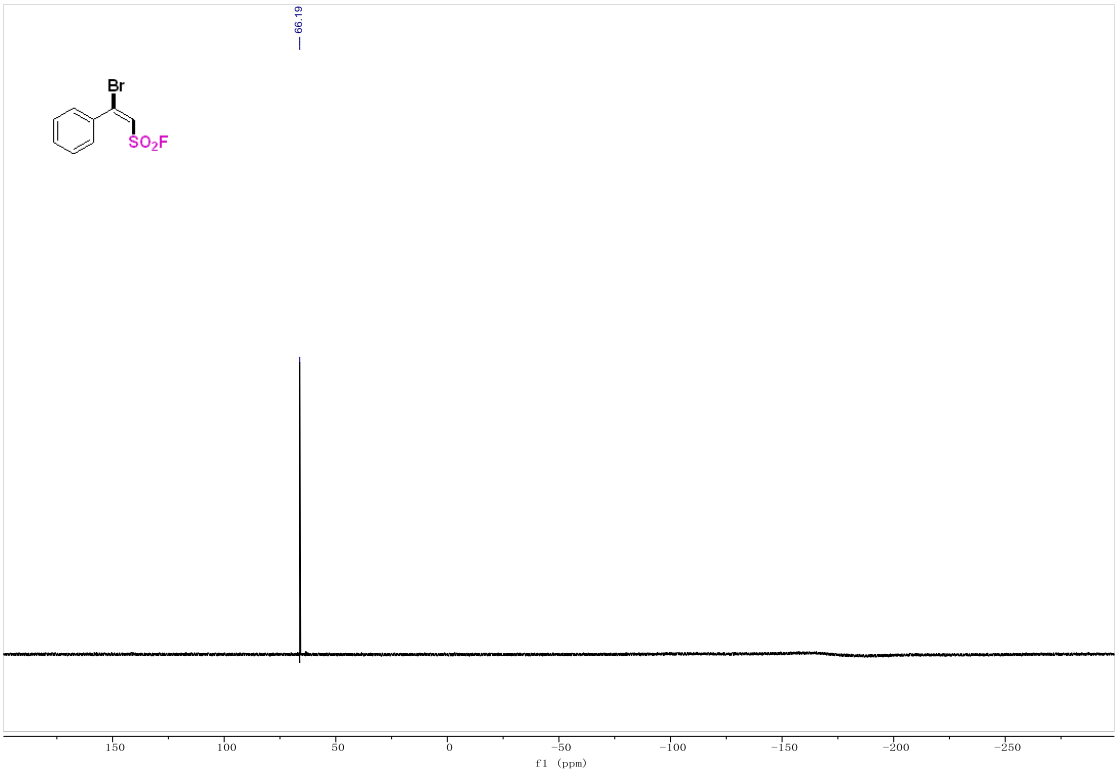
Supplementary Figure 132. ^{19}F NMR spectra of product **6n**



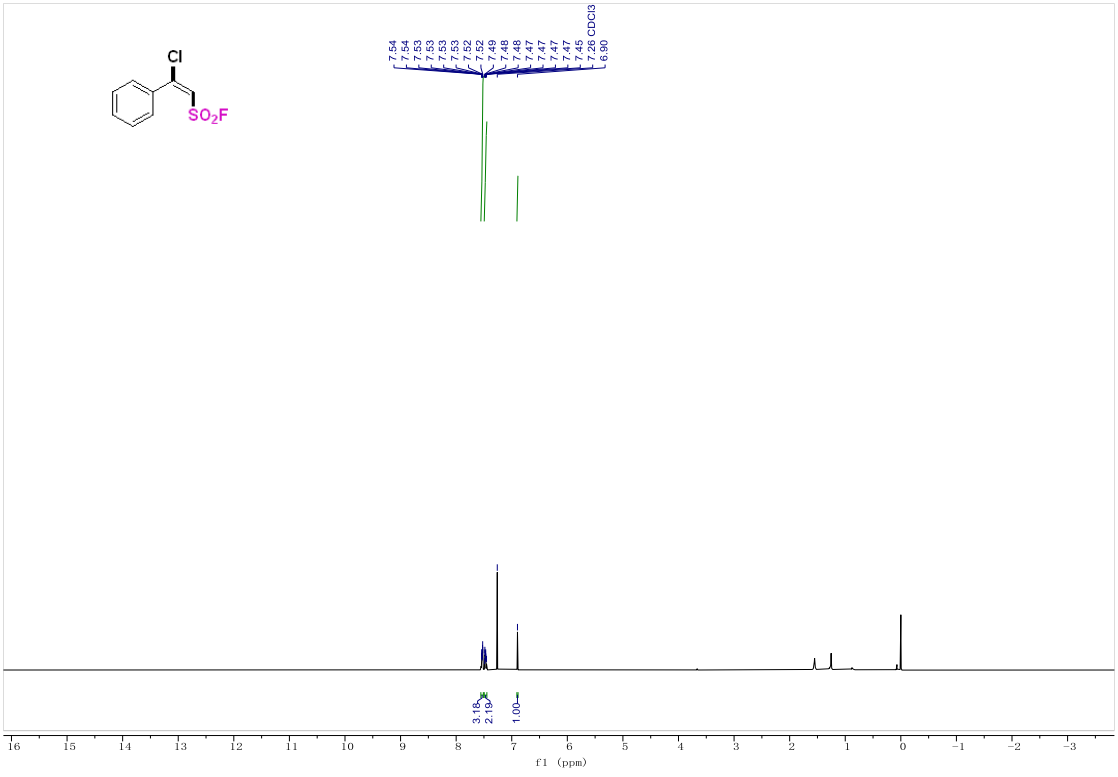
Supplementary Figure 133. ^{1}H NMR spectra of product **7**



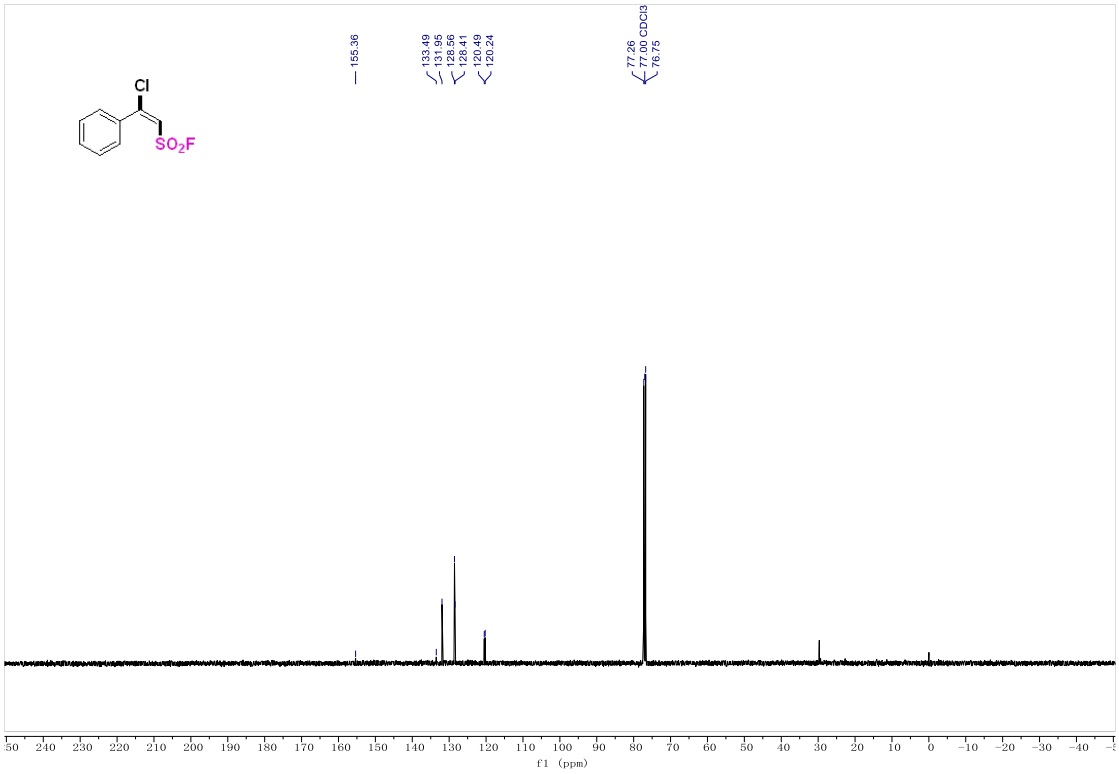
Supplementary Figure 134. ^{13}C NMR spectra of product **7**



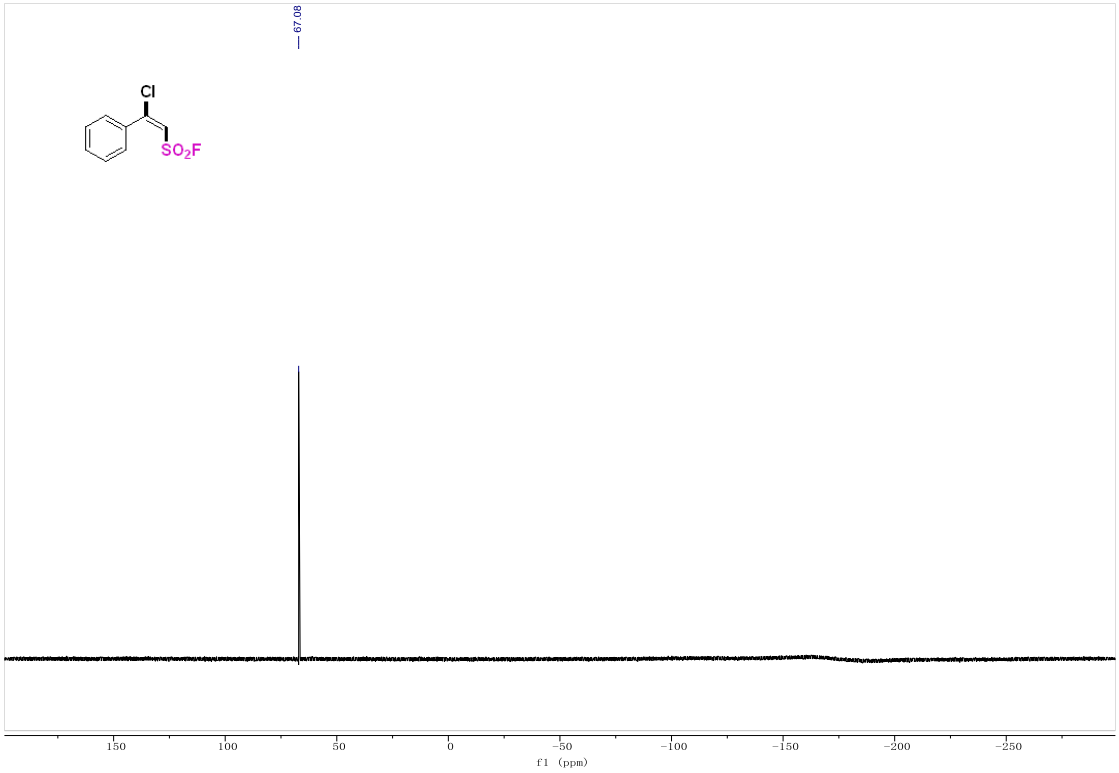
Supplementary Figure 135. ^{19}F NMR spectra of product **7**



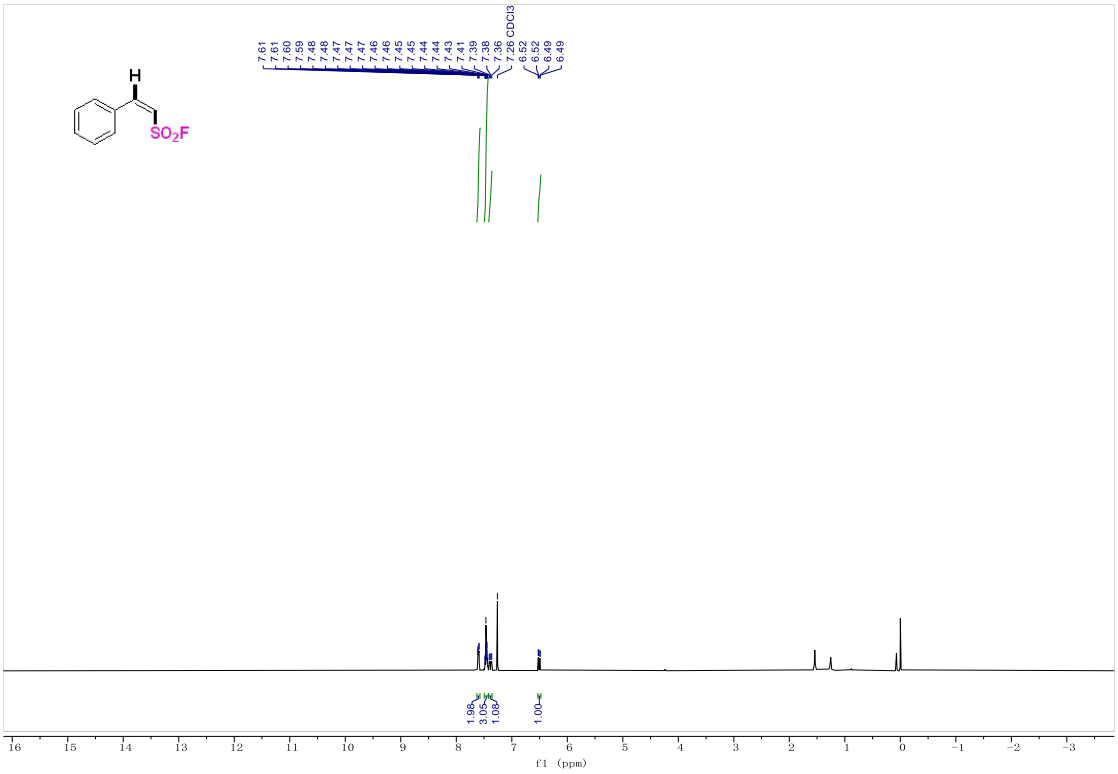
Supplementary Figure 136. ^{1}H NMR spectra of product **8**



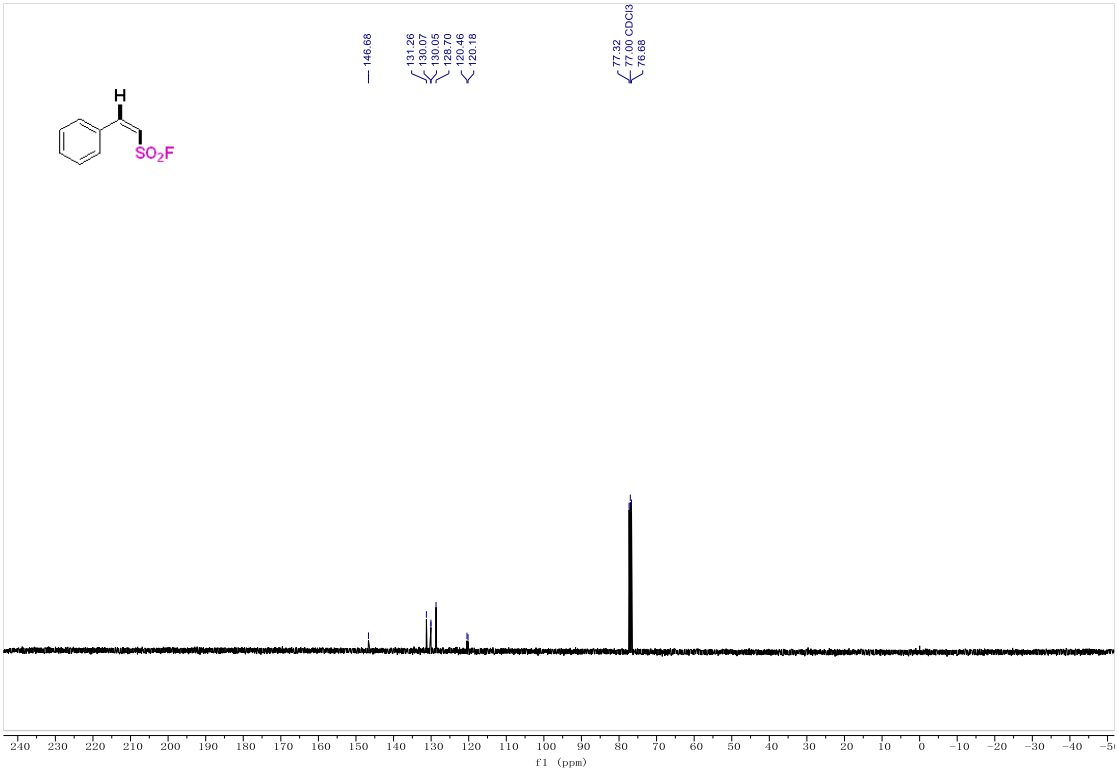
Supplementary Figure 137. ^{13}C NMR spectra of product **8**



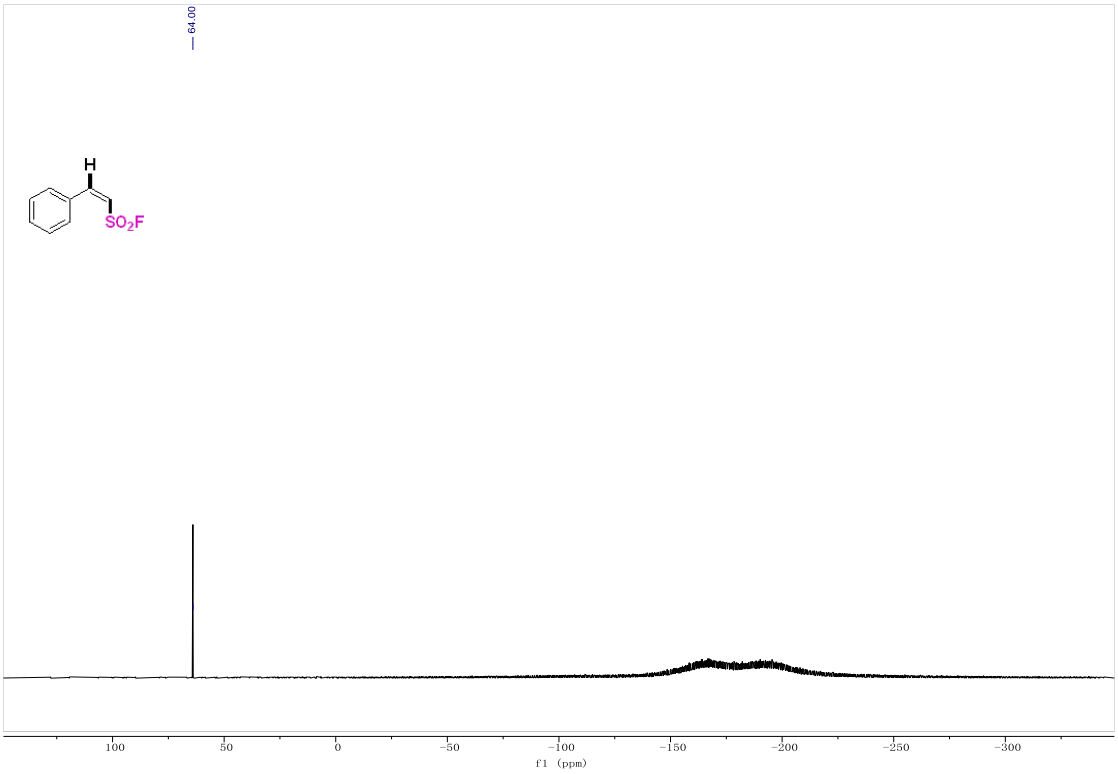
Supplementary Figure 138. ^{19}F NMR spectra of product **8**



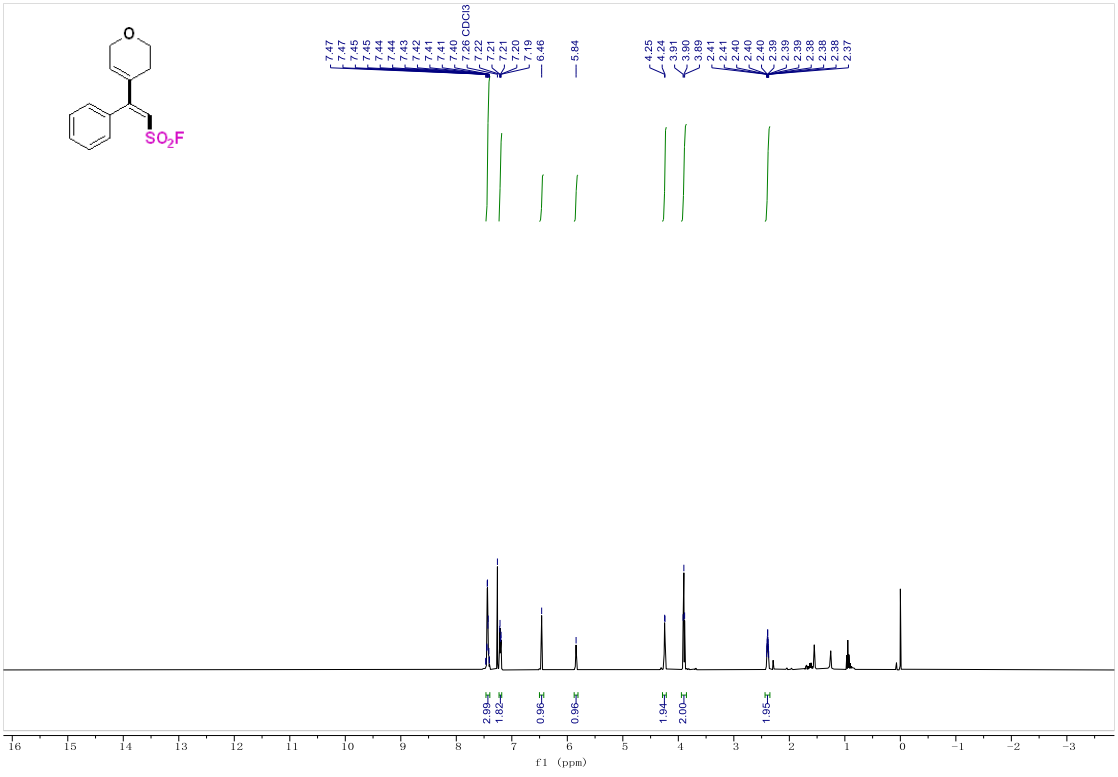
Supplementary Figure 139. ^{1}H NMR spectra of product **9**



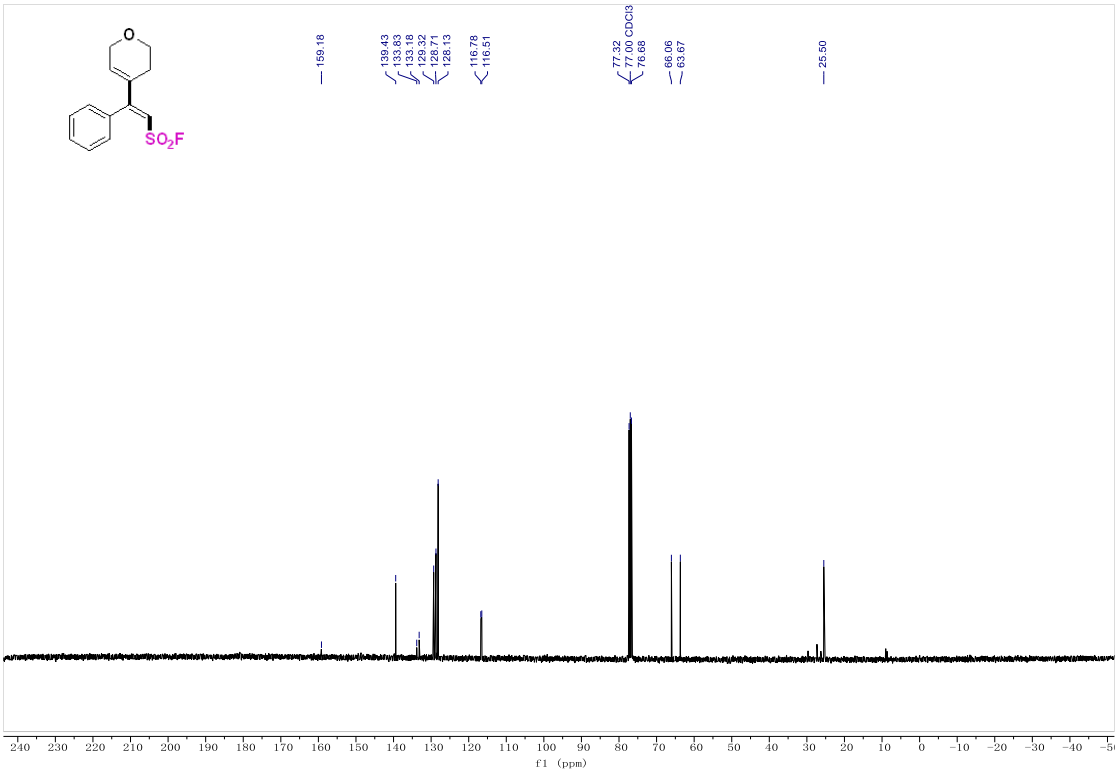
Supplementary Figure 140. ^{13}C NMR spectra of product **9**



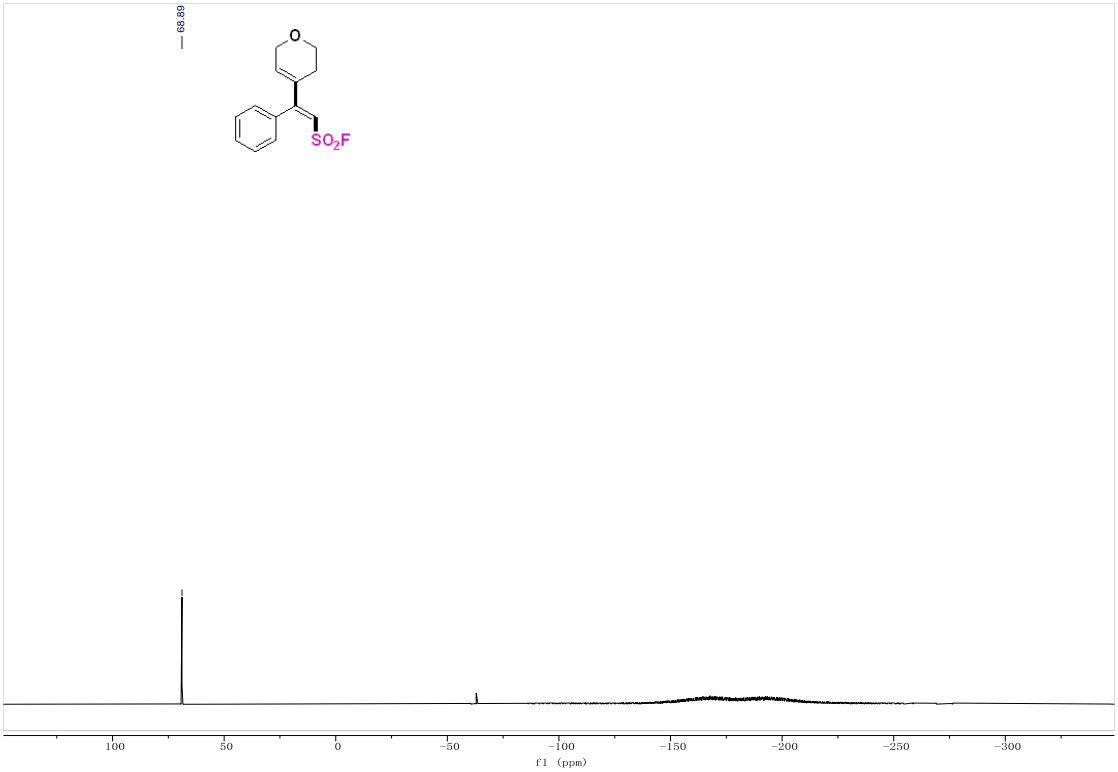
Supplementary Figure 141. ^{19}F NMR spectra of product **9**



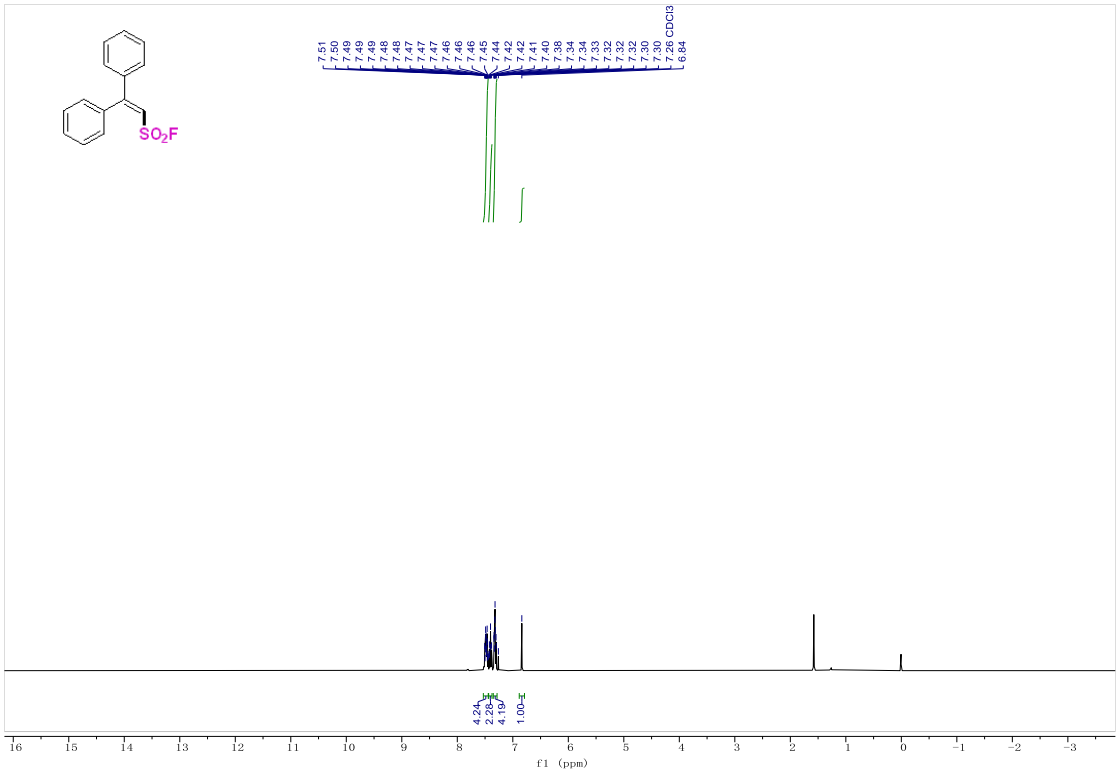
Supplementary Figure 142. ^{1}H NMR spectra of product **11**



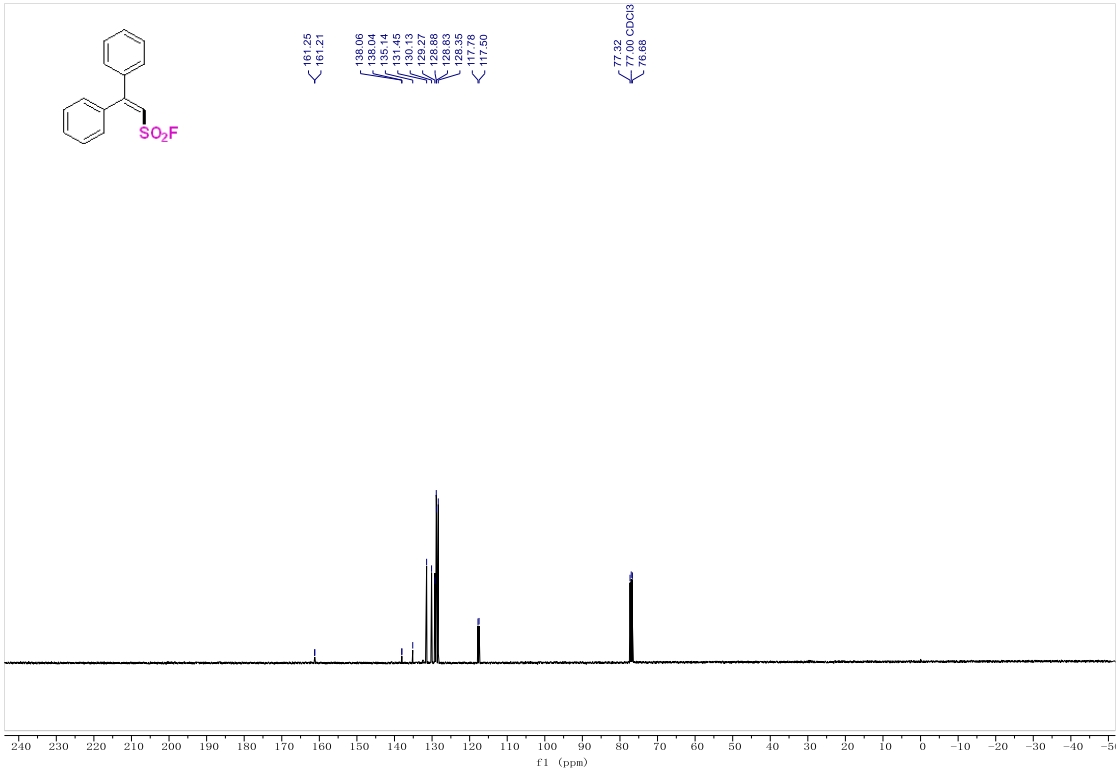
Supplementary Figure 143. ^{13}C NMR spectra of product **11**



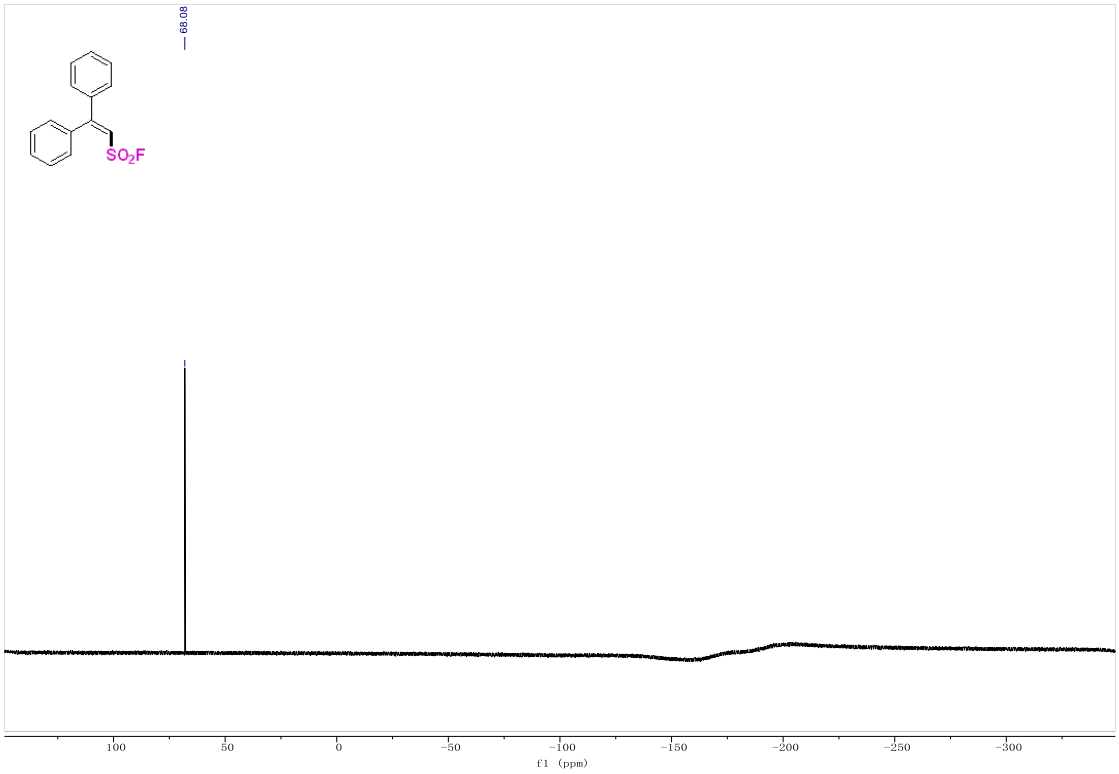
Supplementary Figure 144. ^{19}F NMR spectra of product **11**



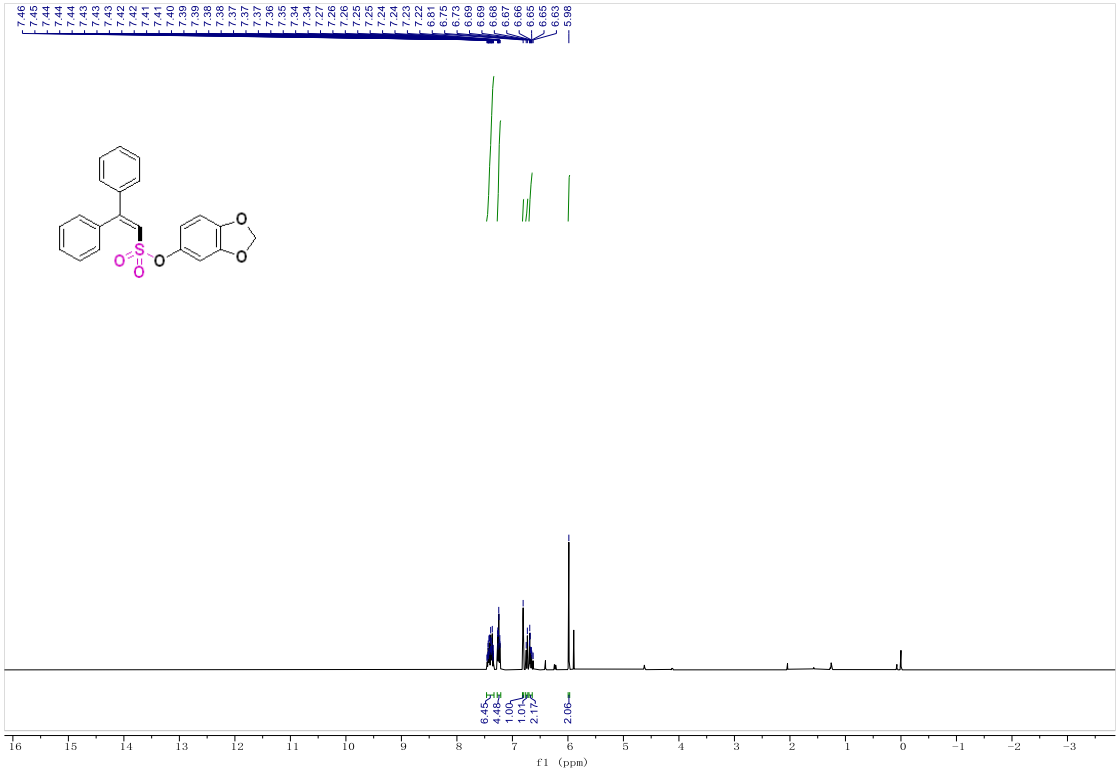
Supplementary Figure 145. ^{1}H NMR spectra of product **13**



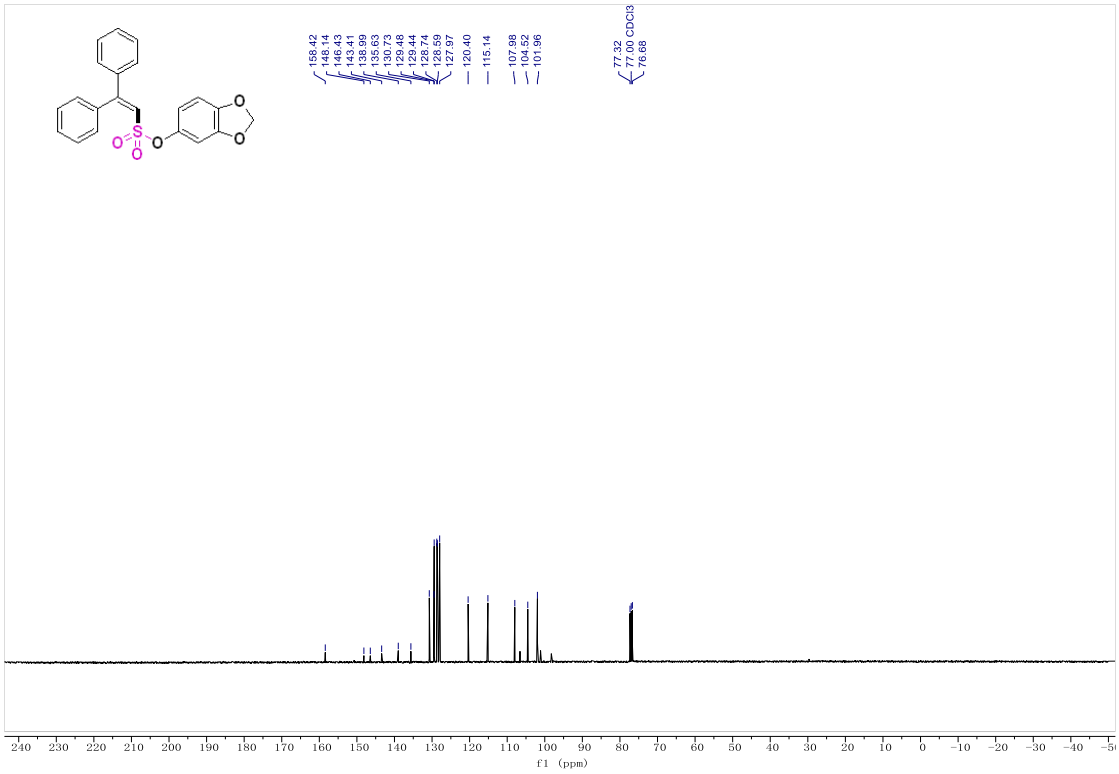
Supplementary Figure 146. ^{13}C NMR spectra of product **13**



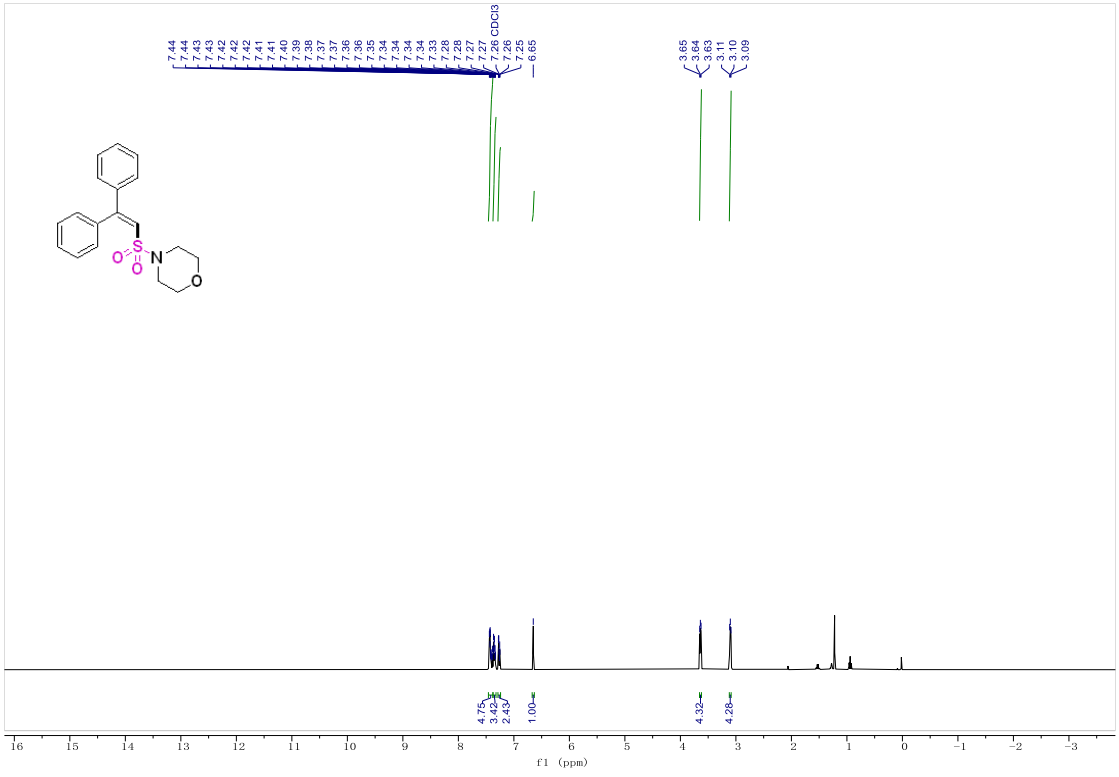
Supplementary Figure 147. ^{19}F NMR spectra of product **13**



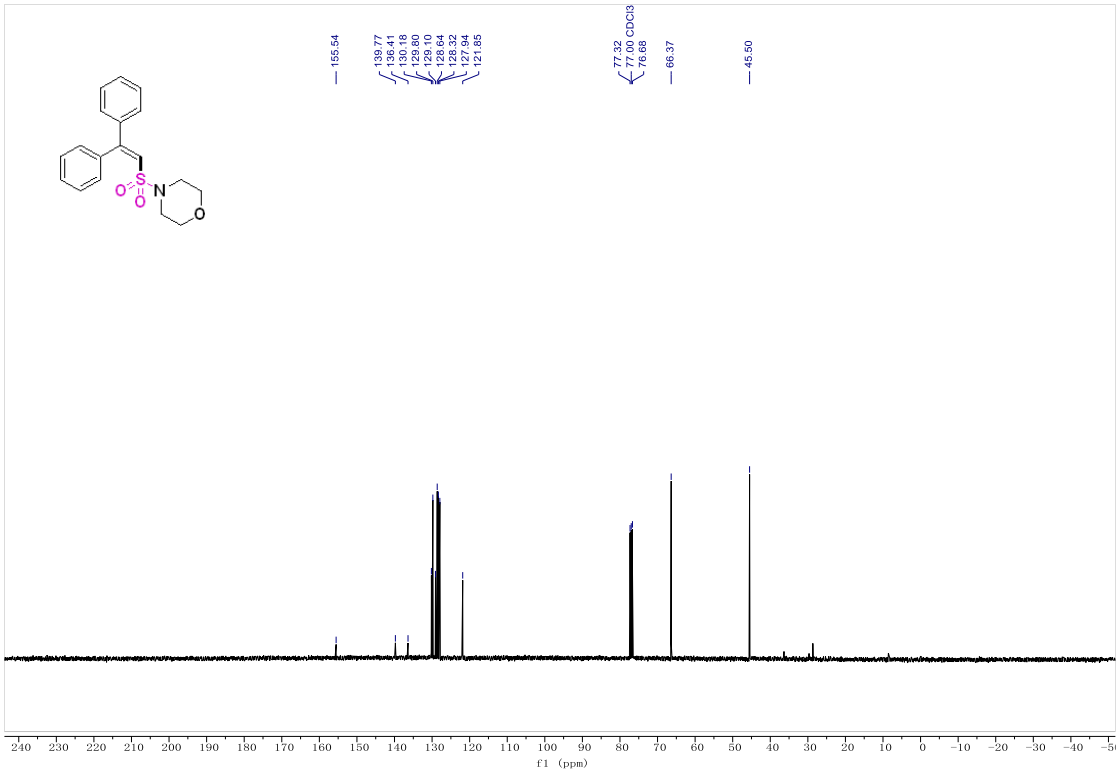
Supplementary Figure 148. ^{1}H NMR spectra of product **14**



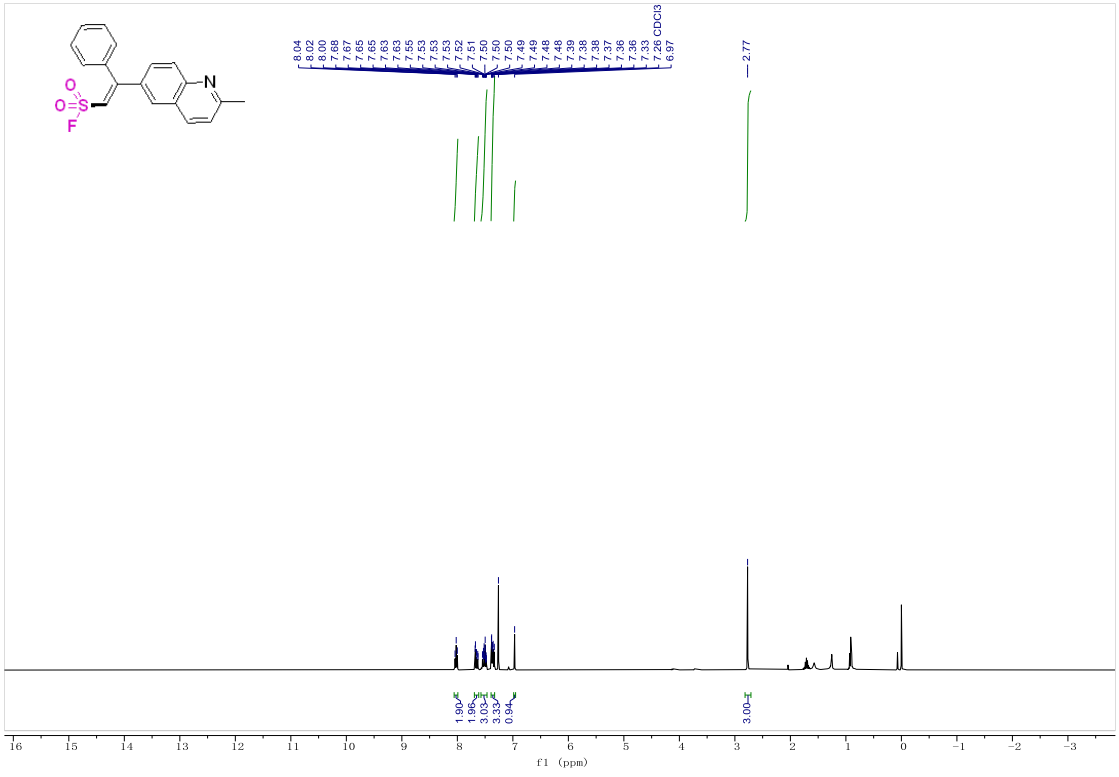
Supplementary Figure 149. ^{13}C NMR spectra of product **14**



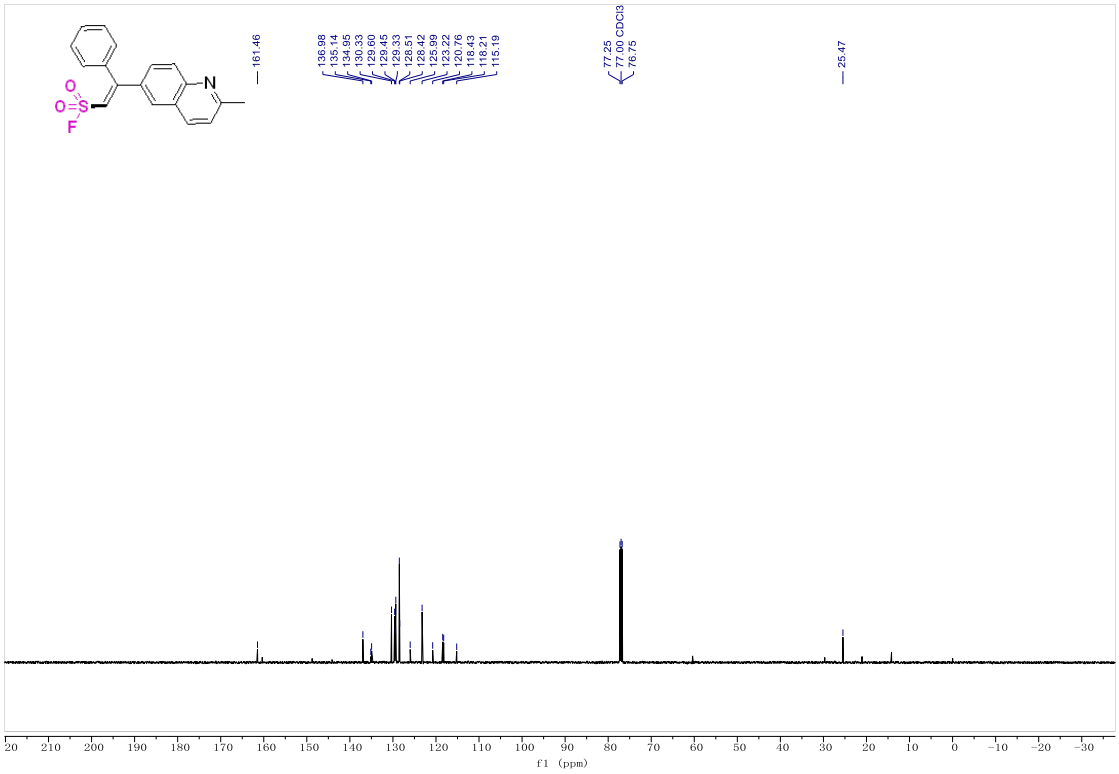
Supplementary Figure 150. ^{1}H NMR spectra of product **15**



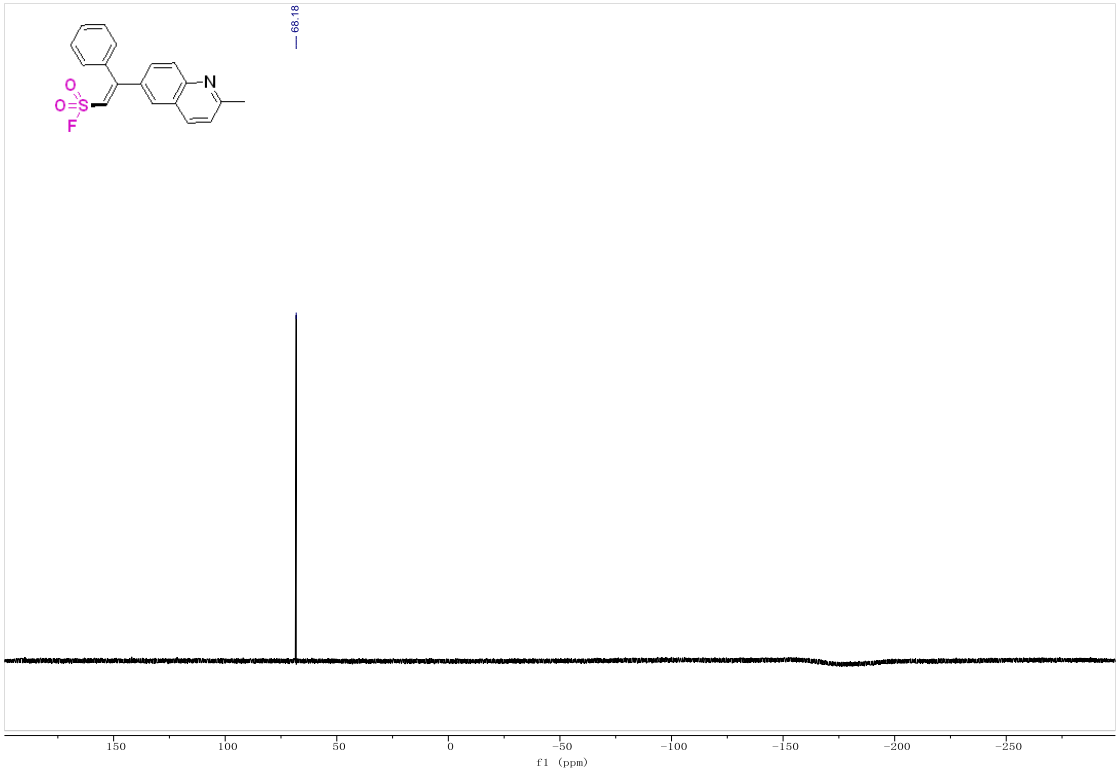
Supplementary Figure 151. ^{13}C NMR spectra of product **15**



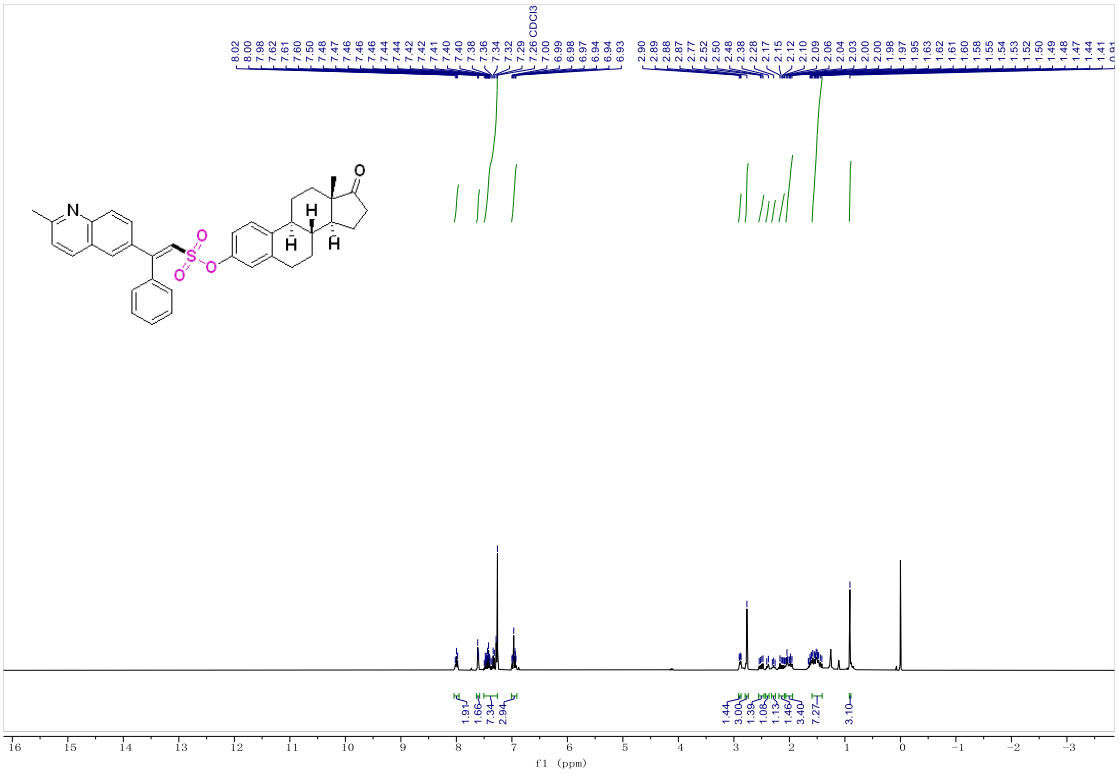
Supplementary Figure 152. ^{1}H NMR spectra of product **17**



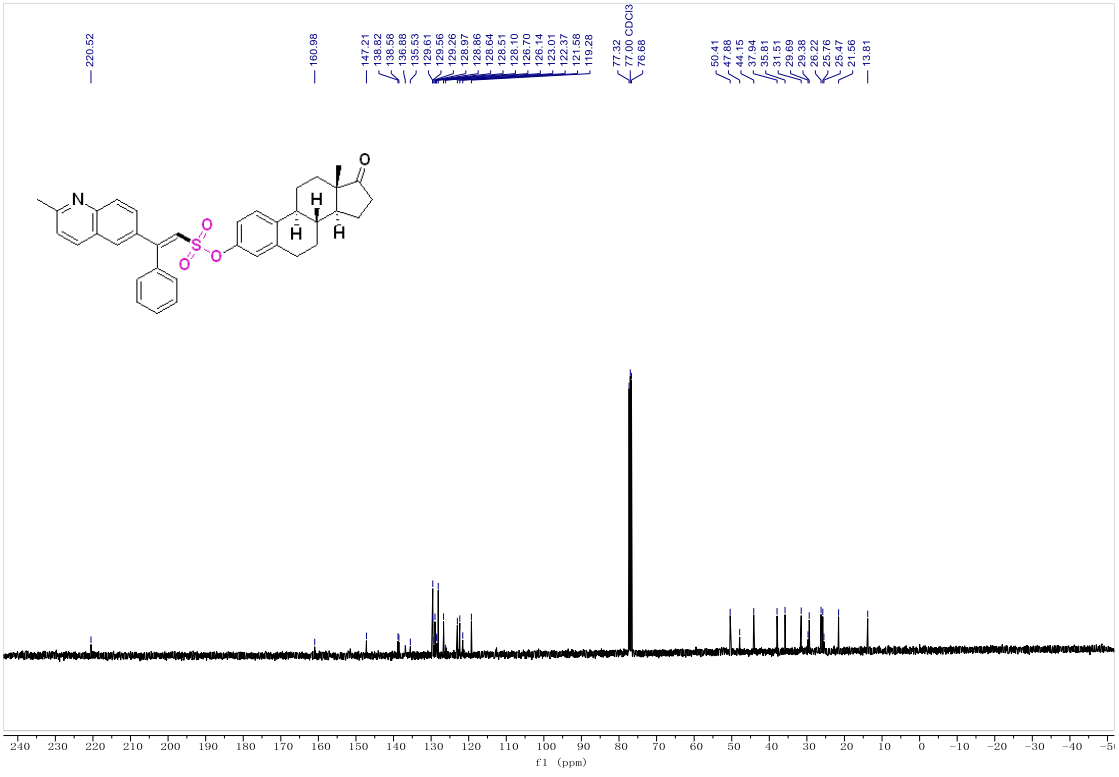
Supplementary Figure 153. ^{13}C NMR spectra of product **17**



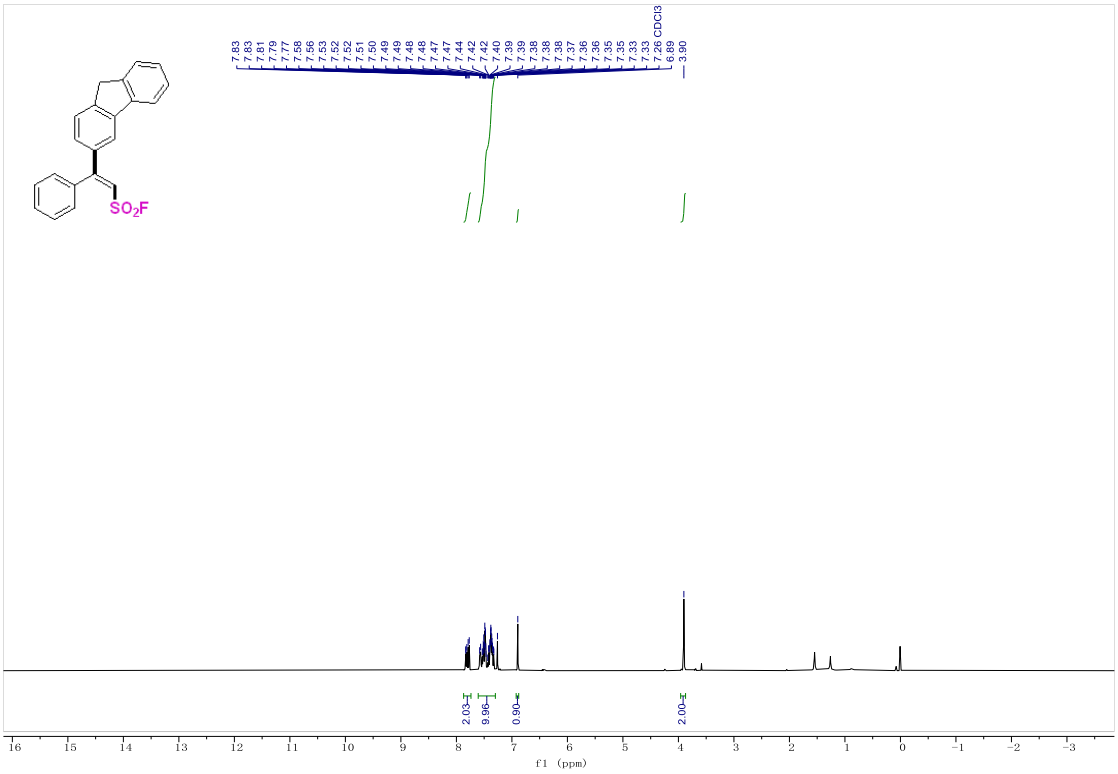
Supplementary Figure 154. ^{19}F NMR spectra of product **17**



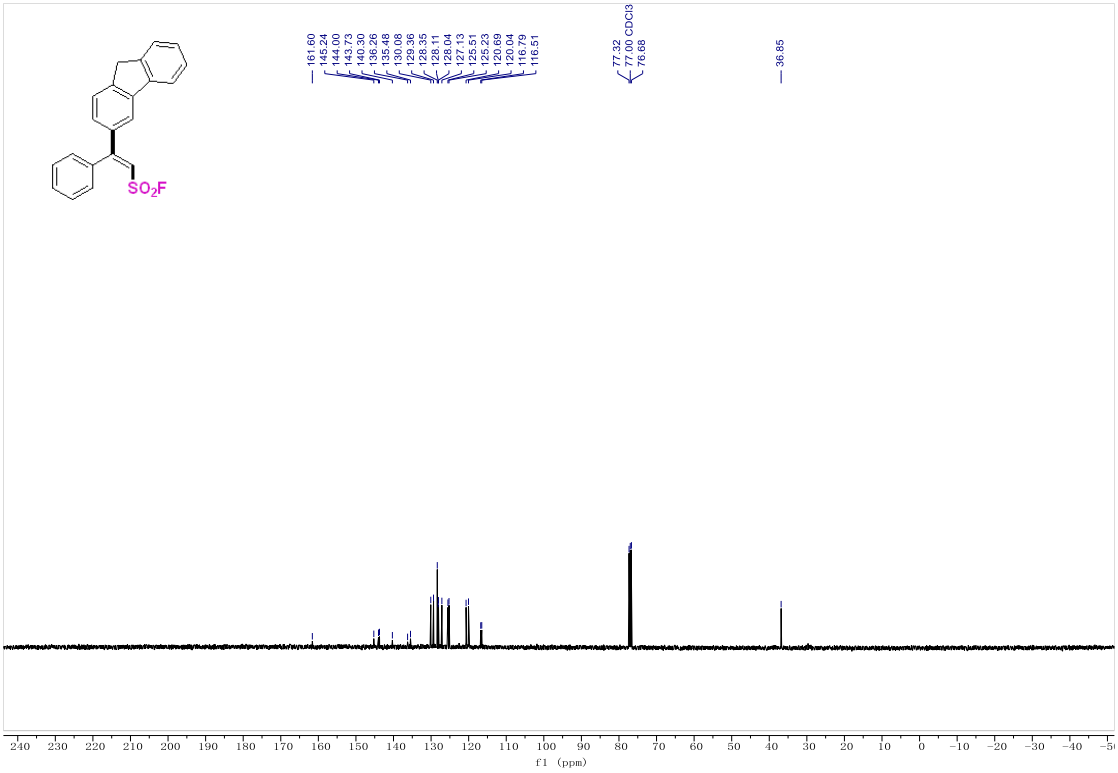
Supplementary Figure 155. ^{1}H NMR spectra of product **18**



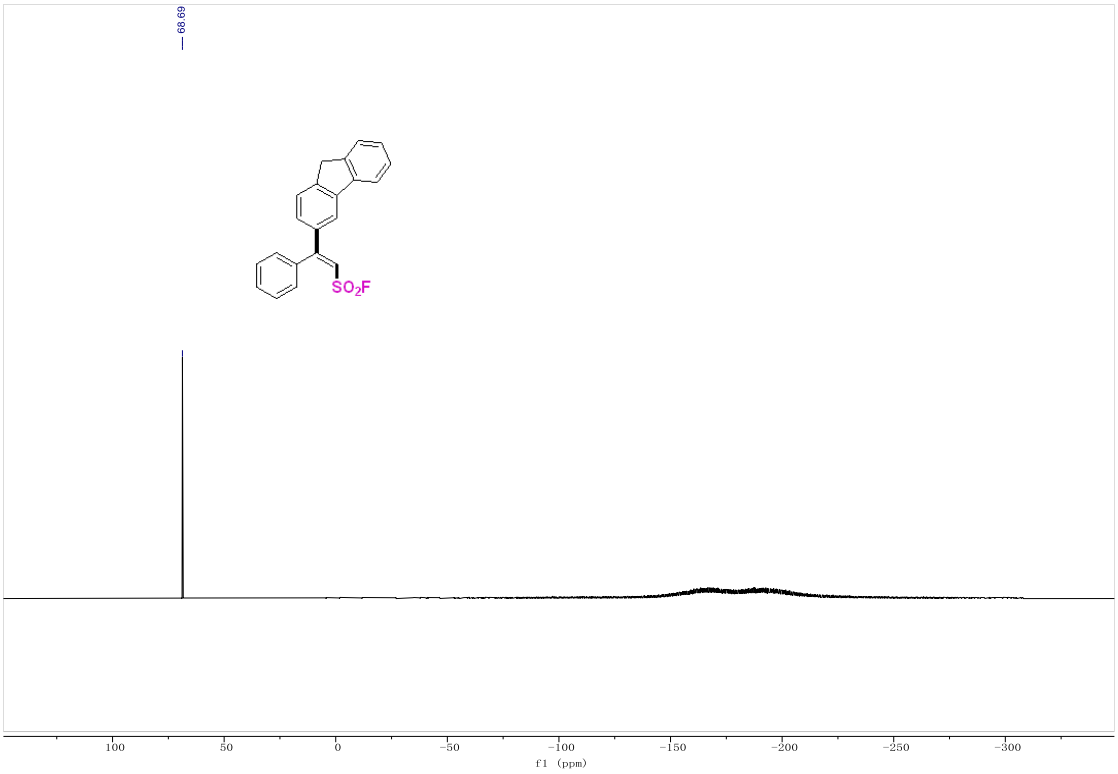
Supplementary Figure 156. ^{13}C NMR spectra of product **18**



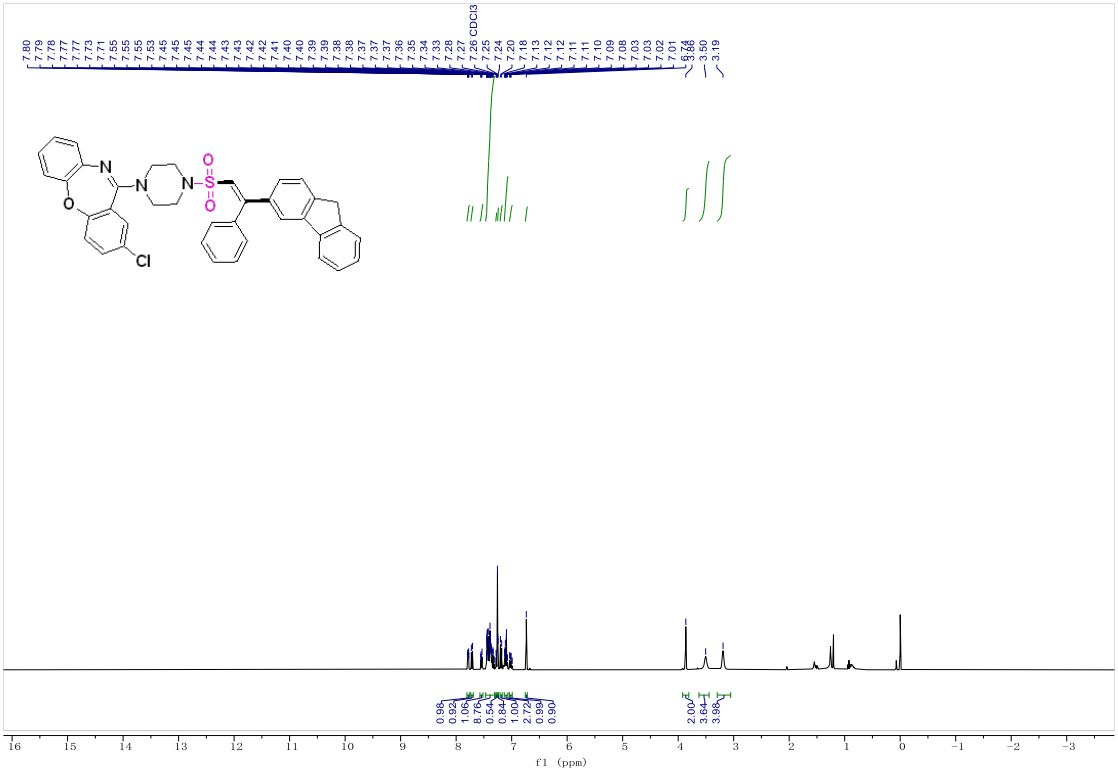
Supplementary Figure 157. ^{1}H NMR spectra of product **20**



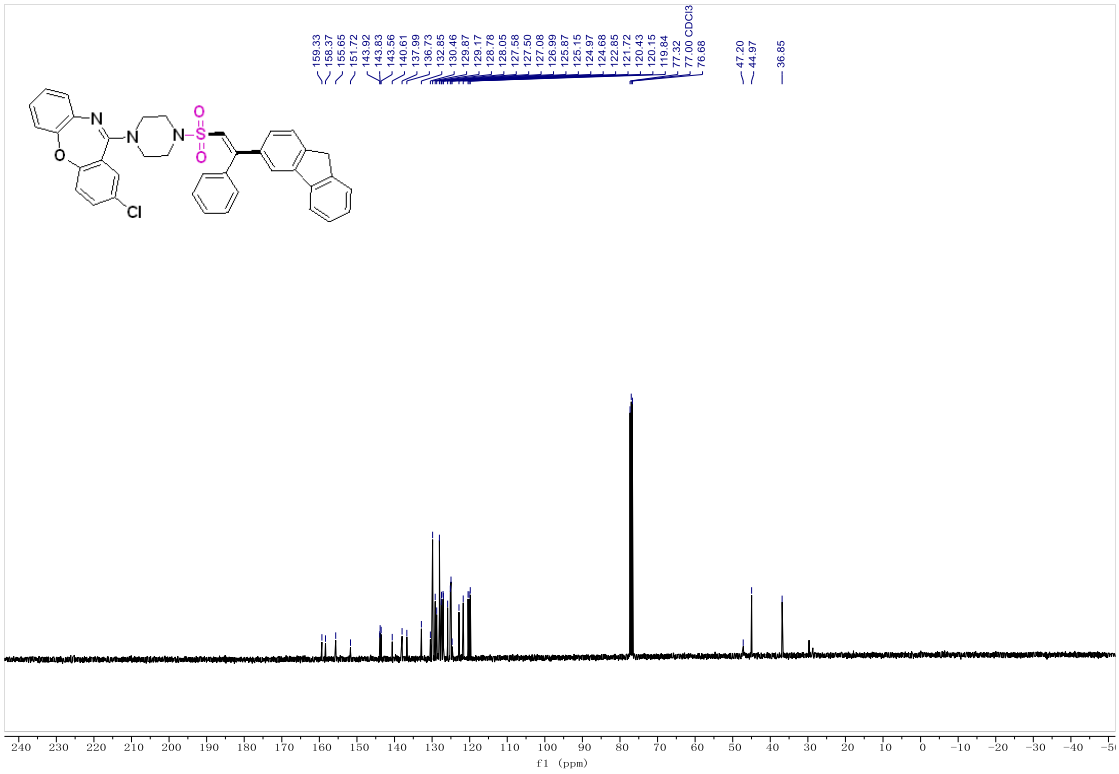
Supplementary Figure 158. ^{13}C NMR spectra of product **20**



Supplementary Figure 159. ^{19}F NMR spectra of product **20**



Supplementary Figure 160. ^{1}H NMR spectra of product **21**



Supplementary Figure 161. ^{13}C NMR spectra of product **21**