Supporting Information

For Radical 1,3-boron Shift of Allylboronic Esters

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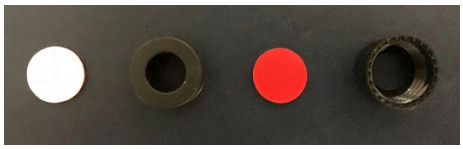
General Experimental

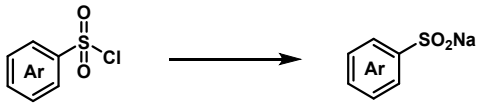
All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unlessotherwise noted. Silica gel column chromatography 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. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out indeuterochloroform ($CDCl_3$) ^{1}H 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 valuesrelative to chloroform (δ 7.26 for ^{1}H NMR), chloroform (δ 77.16 for ^{13}C NMR). 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). Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker microTOF-Q111. GC-MS spectra were performed on Shimadzu QP2010 (EI Source). In a general experiment, 10 W blue LEDs were used as a blue light source. A borosilicate glass tube was used as a reaction tube. The reaction mixture was irradiated with two Kessil LEDs (Saltwater Aquarium Light A360WE Series Tuna Blue; Rating:19VDC 90W Max http://www.kessil.com/products/saltwater_A360.php) from 5 cm away. We have not used any filters. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were underargon.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C), Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)



Substrate Variation

General procedure for the preparation of sodium sulfinates[1]



Sulfonyl chlorides (5.00 mmol) were added to a solution of sodium sulfites (10.0 mmol) and sodium bicarbonate (840 mg, 10.0 mmol) in water (5 mL, 1 M) and heated at 80 °C for 3 h, after cooling to room temperaturethe volatiles were removed in vacuo. The resultant solids were repeatedly washed with ethanol. The combined ethanol washes were evaporated under reduced pressure to yield the titled sulfinates as an amorphous solid.

Various sodium sulfinate and other radical precursors.

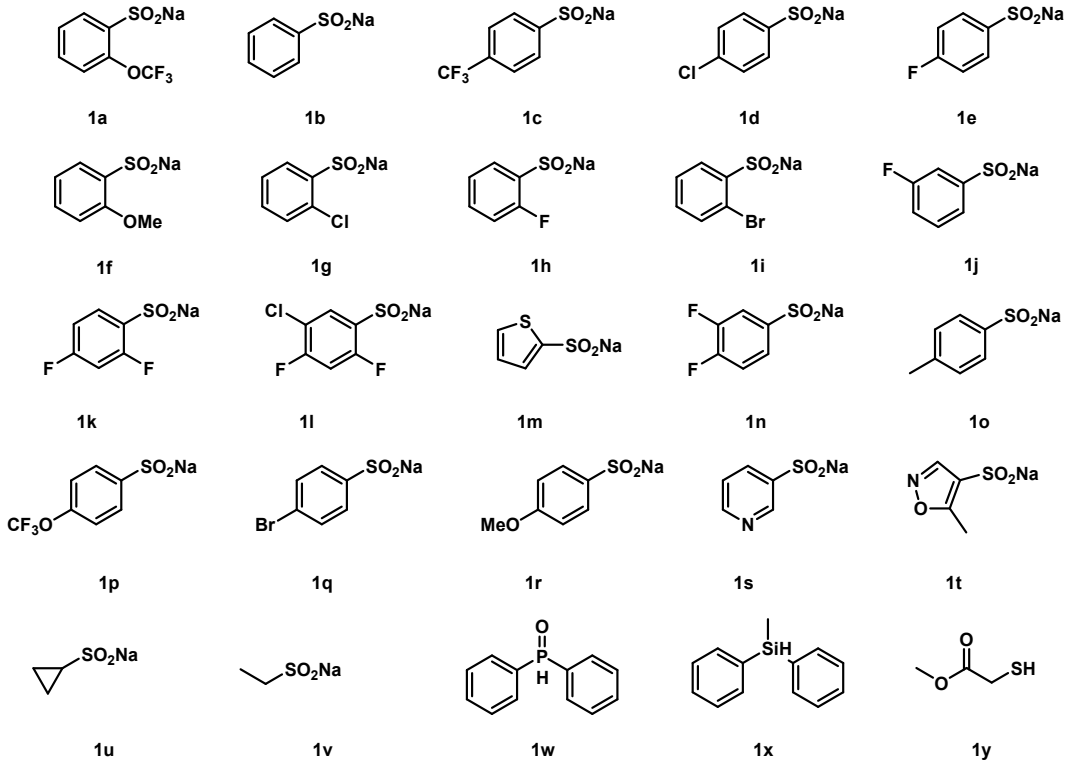


Table S1: Various sodium sulfinates and other heteroatom radical precursors used in this study

Various allylboronic esters.

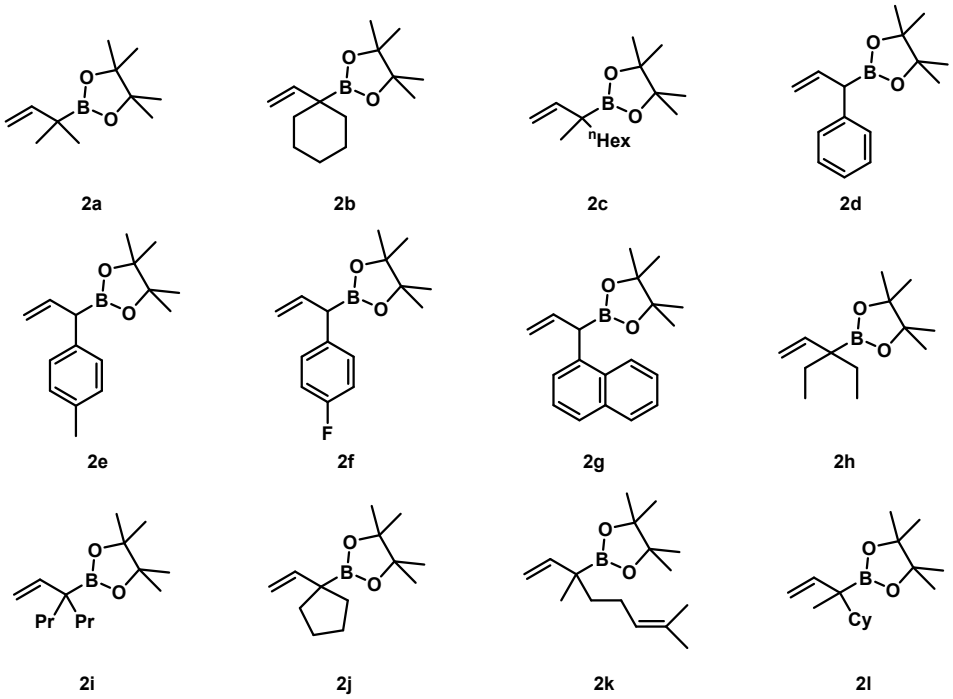


Table S2: Various allylboronic esters used

2a-2c, **2h-2i** were prepared according to the literature procedure[2]; **2d-2g** were prepared according to the literature procedure[3]

Optimizations of the Reaction Conditions

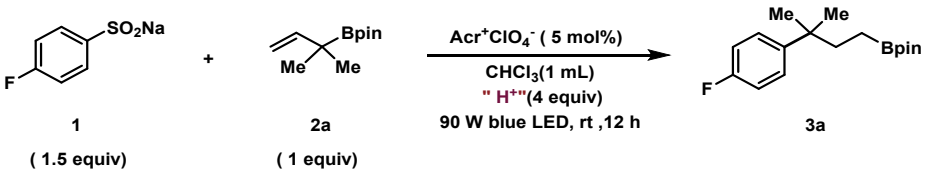
All reactions were conducted at 0.1 mmol sacle.

Table S3. Optimization of solvent

Entry	Solvent	Yield [a]
1	**$CHCl_3$**	**40%**
2	DCM	33%
3	EA	trace
4	DCE	6%
5	DMF	n.r.
6	DMA	n.r.
7	DMSO	n.r.
8	MeOH	trace
9	acetone	n.r.
10	MeCN	n.r.
11	CCl_4	n.r.
12	PhCl	n.r.

[a] Yields were determined by ^{19}F NMR with 1,4-difluorobenzene as the internal standard.

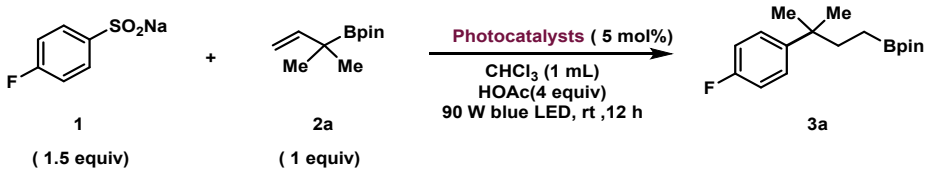
Table S4. Optimization of acids



Entry	Additive	Yield [a]
1	^{t}BuCOOH	38%
2	$MeSO_3H$	n.r.
3	$PhSO_3H$	n.r.
4	HNO_3	n.r.
5	H_2SO_4	n.r.
6	HCOOH	25%
7	HCl	n.r.
8	**HOAc**	**40%**

[a] Yields were determined by ^{19}F NMR with 1,4-difluorobenzene as the internal standard.

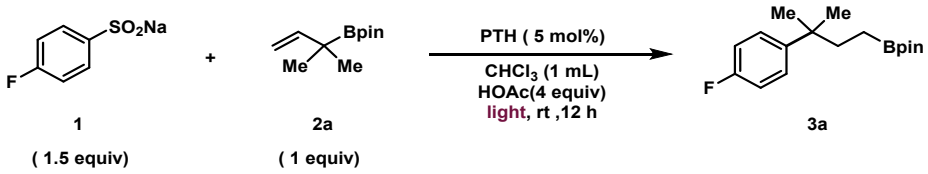
Table S5. Optimization of photocatalysts



Entry	PC	Yield [a]
1	$Ir(ppy)_3$	10%
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	28%
3	$Ir[dF(CF_3)ppy]_3$	22%
4	$Ir[\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$	33%
5	$(Ir[dF(CF_3)ppy]_2(d(CF_3)bpy))PF_6$	n.d.
6	$Ru(bpy)_3Cl_2$	6%
7	Eosin B	26%
8	Eosin Y	16%
9	4CzIPN	18%
10	Rose Bengal	14%
11	PDI	24%
12	Na_2Eosin Y	Trace
13	DDQ	Trace
14	Mes-Acr•ClO_4	40%
15	**PTH**	**43%**

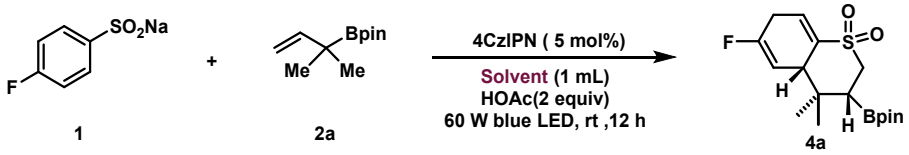
[a] Yields were determined by ^{19}F NMR with 1,4-difluorobenzene as the internal standard.

Table S6. Screening of the light source.



Entry	Light source	Yield [b]
1	10 W UV(395 nm)	10%
2	10 W UV(365 nm)	7%
3	10 W blue LED	42%
4	**60 W blue LED**	**45%**
5	90 W blue LED	43%

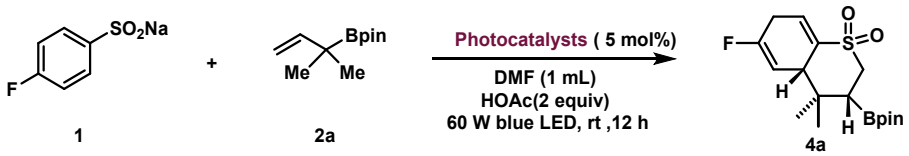
Table S7. Screening of the solvents.



Entry	Solvent	Yield [b]
1	$CHCl_3$	16%
2	**DMF**	**95%**
3	DMA	89%
4	DMSO	93%
5	MeCN	n.r.
6	MeOH	n.r.

[a] Yields were determined by ^{19}F NMR with 1,4-difluorobenzene as the internal standard.

Table S8. Screening of the photocatalysts



Entry	PC	Yield [a]
1	$Ir(ppy)_3$	76%
2	$[Ir(dtbbpy)(ppy)_2]PF_6$	77%
3	Mes-Acr•ClO_4	n.d.
4	$Ru(bpy)_3Cl_2$	85%
5	**4CzIPN**	**95%(82%)**
6	Rose Bengal	70%
7	**Eosin Y**	**96%**

[a] Yields were determined by ^{19}F NMR with 1,4-difluorobenzene as the internal standard.

Experimental procedure

General Procedure A for the synthesis of the product 3

Under argon, PTH (4.4 mg, 8 mol%) and sodium benzenesulfinate **1** (0.3 mmol, 1.5 equiv), corresponding allylboronic acid pinacol ester (0.2 mmol, 1.0 equiv) and HOAc (48 uL, 0.8 mmol, 4.0 equiv), were placed in a tube with a stirring bar, then $CHCl_3$ (2 mL) was added at room temperature. After that, the tube was exposed to a 60 W blue LEDs at room temperature about 12 h. The mixture was concentrated in vacuo. Then it was passed through a short pad of silica gel. The organic layer was concentrated under vacuo and the yellow oily residue was diluted with THF (1 mL) and water (1 mL) followed by addition of $NaBO_3 \cdot 4H_2O$ (61.5 mg, 0.4 mmol). The mixture was allowed to stir for 3h at rt. The reaction mixture was washed with EtOAc (5 mL x 3) and the combined organic layers was dried over $MgSO_4$. It was then concentrated and purified by silica gel chromatography to afford the desired product.

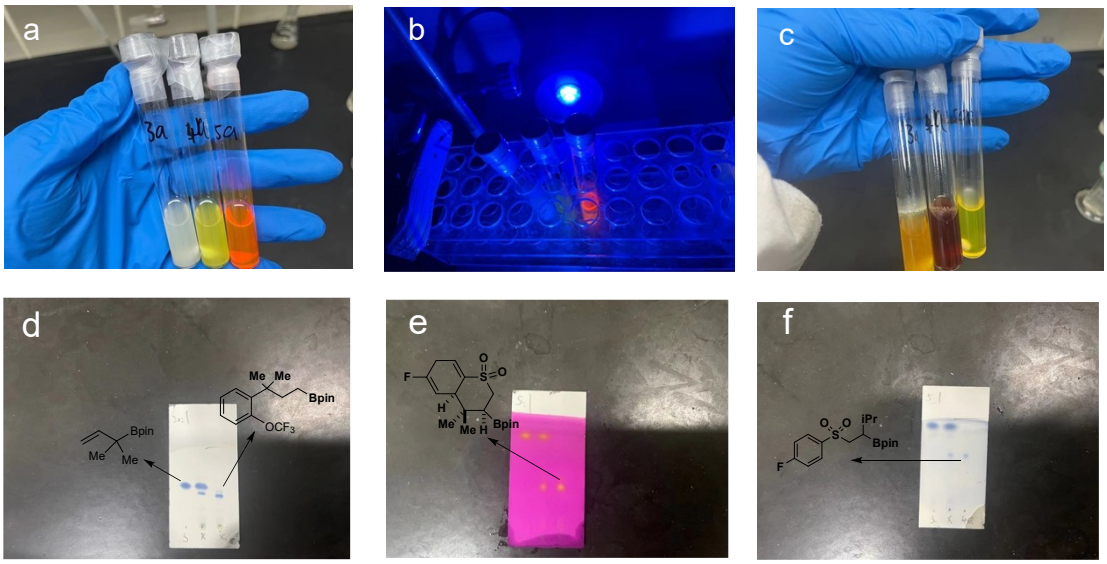
General Procedure B for the synthesis of the product 4

Under argon, Eosin Y (3.9 mg, 3 mol%) and sodium benzenesulfinate **1** (0.3 mmol, 1.5 equiv), corresponding allylboronic acid pinacol ester (0.2 mmol, 1.0 equiv) and HOAc (24 uL, 0.4 mmol, 2.0 equiv) were placed in a tube with a stirring bar, then DMF (2 mL) was added at room temperature. After that, the tube was exposed to a 60 W blue LEDs at room temperature about 12-24 h. Upon completion, the solution was passed through a pad of silica gel and washed with ethyl acetate. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel using 10:1-5:1 hexane: EtOAc as eluent to give the corresponding pure product **4**.

General Procedure C for the synthesis of the product 5

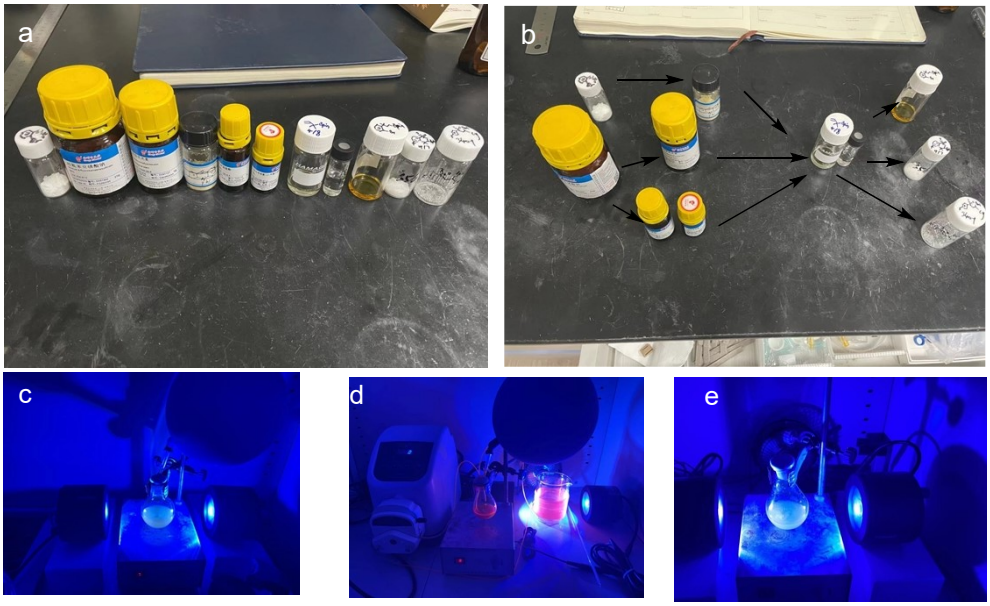
Underargon, $Acr^+ClO_4^-$ (4.1 mg, 5 mol%) and sodium benzenesulfinate **1** (0.3 mmol, 1.5 equiv), corresponding allylboronic acid pinacol ester (0.2 mmol, 1.0 equiv), p-toluenethiol (5 mg, 0.04 mmol, 0.2 equiv) and HOAc (24 uL, 0.4 mmol, 2.0 equiv) were placed in a tube with a stirring bar, then $CHCl_3$ (2 mL) was added at room temperature. After that, the tube was exposed to a 60 W blue LEDs at room temperature about 12 h. The mixture was concentrated and purified by silica gel chromatography to afford the desired product **5**.

Graphical Support Information for the Synthesis of Products under Different Conditions



a) Before reaction; **b)** During reaction; **c)** After reaction; **d)** TLC plate showed the formation of product **3a** (hexanes/ethyl acetate = 20/1); **e)** TLC plate showed the formation of product **4a** (hexanes/ethyl acetate = 5/1); **f)** TLC plate showed the formation of product **5a** (hexanes/ethyl acetate = 5/1).

Graphical Support Information for the Gram-scale Synthesis of Products



a)&**b)** Reagents and products in reactions; **c)** Gram-scale synthesis of **3l**; **d)** Gram-scale synthesis of **4a** (continuous-flow); **e)** Gram-scale synthesis of **5a**.

Reagents and products in reactions (From left to right, Picture **a**).
sodium 2-bromobenzenesulfinate (stored under air before used),
sodium 4-fluorobenzenesulfinate (stored under air before used),
Eosin Y (under air before used),
PTH (under air before used),
4-methylbenzenethiol (stored under air before used),
$Acr^{+}ClO_4^{-}$ (stored in the refrigerator, under air before used),
Olefin (stored in the refrigerator, under air before used),
acetic acid (stored under air before used).
Product **3i** (stored under air).
Product **4a** (stored under air).
Product **5a** (stored under air).

Method for 3i (**picture c)**: To a 50 mL round bottom flask equipped with a magnetic stir bar was charged with PTH (69 mg, 5 mol%) and sodium 2-bromobenzenesulfinate (1.7 g, 7 mmol). The flask was then evacuated and backfilled with Ar 3 times. Afterwards, $CHCl_3$ (25 mL), **2a** (980 mg, 5 mmol) and HOAc (1.2 g, 20 mmol) were added sequentially by syringe. The flask was exposed to a 60 W blue LEDs at room temperature about 30 h. The mixture was concentrated in vacuo. Then it was passed through a short pad of silica gel to afford the crude **3i** as yellow oil (0.93 g, 53%).

Method for 4a (picture d): In the glove box, a 50 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with eosin Y (61 mg, 3 mol%), sodium 4-fluorobenzenesulfinate (0.83 g, 4.5 mmol), **2a** (588 mg, 3 mmol), HOAc (360 mg, 6 mmol)

and DMF (20 mL). The resulting mixture was sealed and taken out from the glove box. The flow apparatus was purged with argon. The tubing (HPFA, O.D. 1/16", I.D. 0.6", 18.6 m, volume = 9.0 mL) was attached to the flask and equipped with Peristaltic pump. Then, the tubing was equipped with 60 W blue LEDs. The flow apparatus itself was set up with flow rate = 2 mL/min. After 2 h of continuous irradiation, the mixture was diluted with EtOAc and washed with brine. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product, which was purified by flash chromatography on silica gel to give **4a** (0.88 g, 83%).

Method for 5a (picture e): To a 50 mL round bottom flask equipped with a magnetic stir bar was charged with $Acr^+ClO_4^-$ (108 mg, 5 mol%), 4-methylbenzenethiol (124 mg, 1 mmol) and sodium 4-fluorobenzenesulfinate (1.3 g, 7 mmol). The flask was then evacuated and backfilled with Ar 3 times. Afterwards, $CHCl_3$ (25 mL), **2a** (980 mg, 5 mmol) and HOAc (0.6 g, 10 mmol) were added sequentially by syringe. After that, the flask was exposed to a 60 W blue LEDs at room tempe88%rature about 36 h. The mixture was concentrated and purified by silica gel chromatography to afford the product **5a** (1.56 g, 88%).

Stern-Volmer quenching experiments

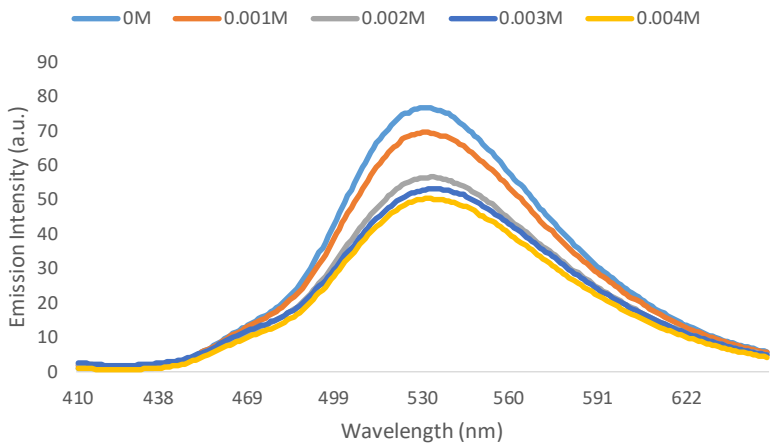


Figure S1 Emission spectra of PHT at different concentrations of sodium 4-fluorobenzenesulfinate

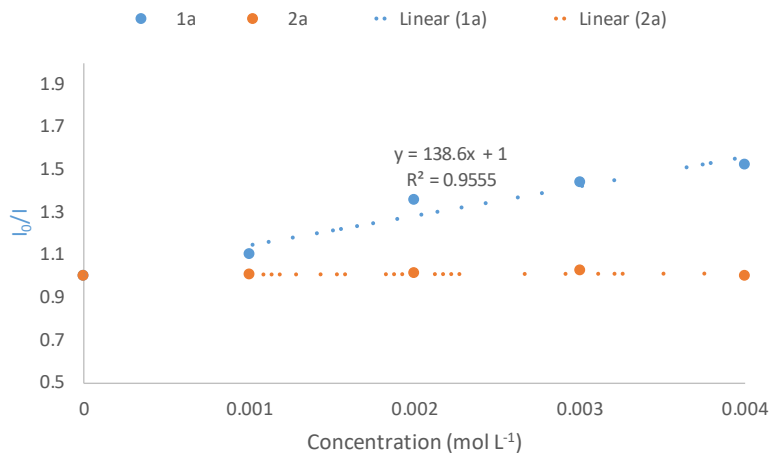
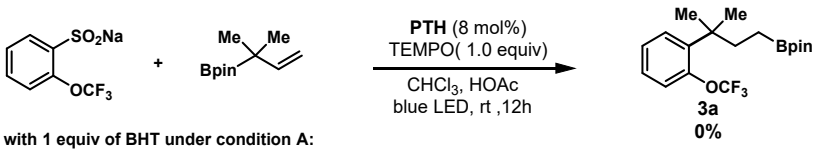


Figure S2 Stern-Volmer plot of PHT at different concentrations of sodium 4-fluorobenzenesulfinate

Mechanistic Investigation

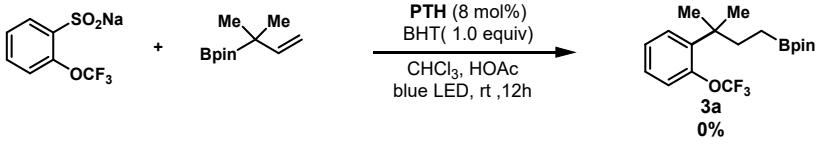
Reaction with 1 equiv of TEMPO under condition A:



3a
0%

(eq -1)

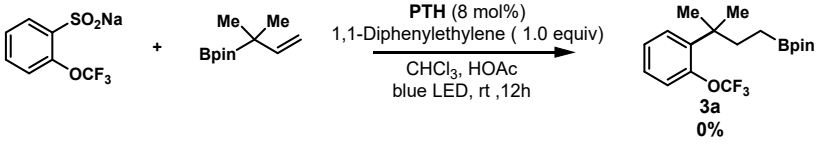
Reaction with 1 equiv of BHT under condition A:



3a
0%

(eq -2)

Reaction with 1 equiv of 1,1-Diphenylethylene under condition A:



3a
0%

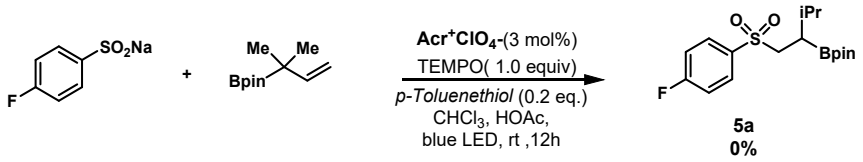
(eq -3)

Reaction with 1 equiv of TEMPO under condition B:

4a
trace

(eq -4)

Reaction with 1 equiv of TEMPO under condition C:

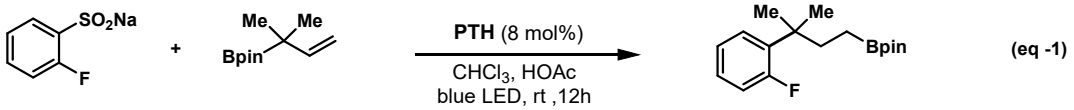


5a
0%

(eq -5)

Fig. S3 | Radical suppression experiment

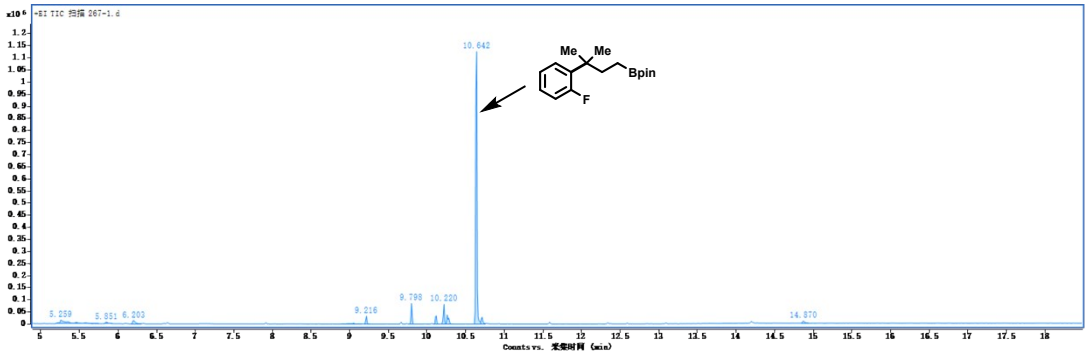
Deuteration exprtiments

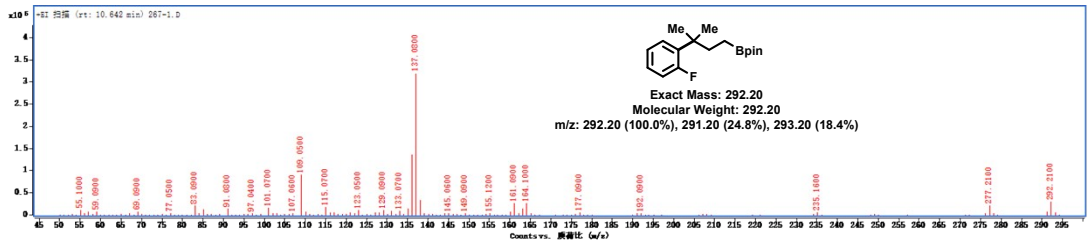


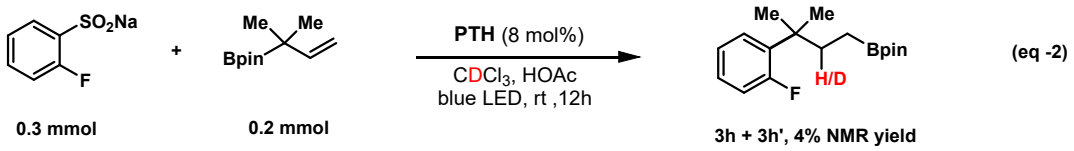
0.3 mmol **0.2 mmol** **3h, 92% NMR yield**

(eq -1)

The TIC of reaction in $CHCl_3$ (eq-1).

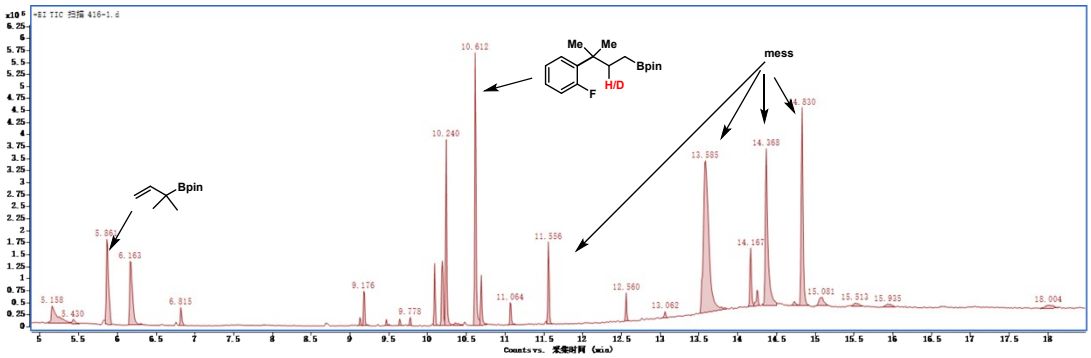


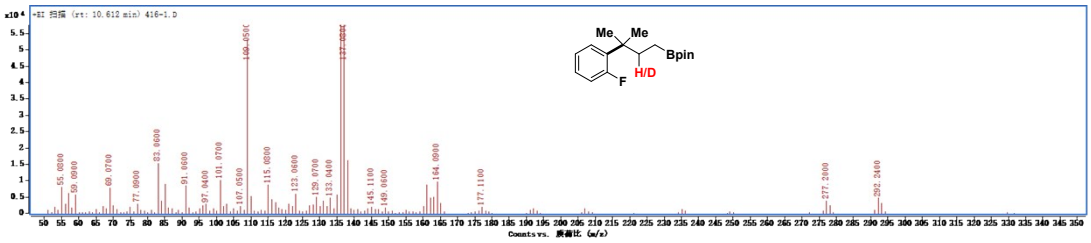


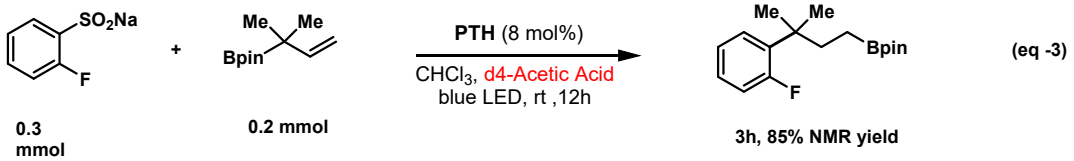


0.3 mmol **0.2 mmol** **3h + 3h', 4% NMR yield**

The TIC of reaction in $CDCl_3$ (eq-2).

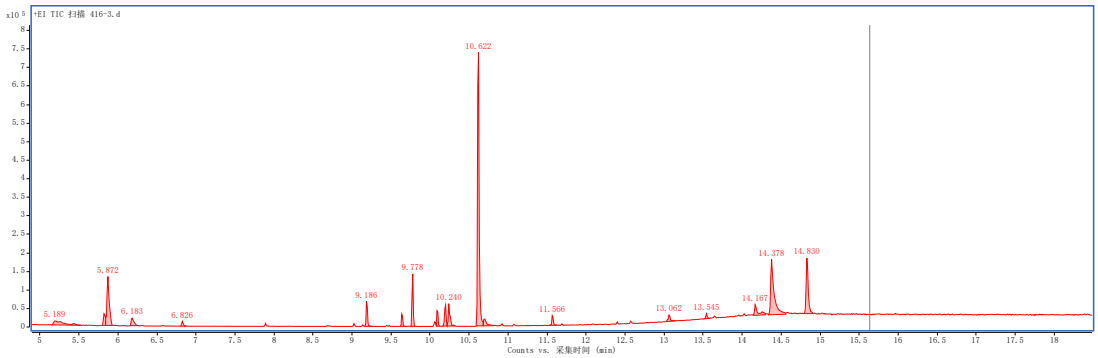


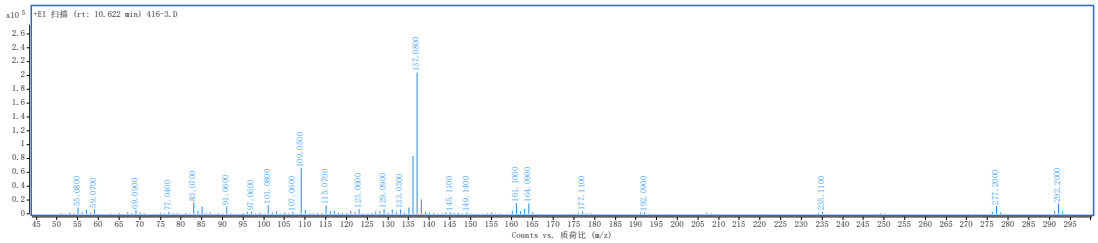




0.3 mmol **0.2 mmol** **3h, 85% NMR yield**

The TIC of reaction (eq-3).



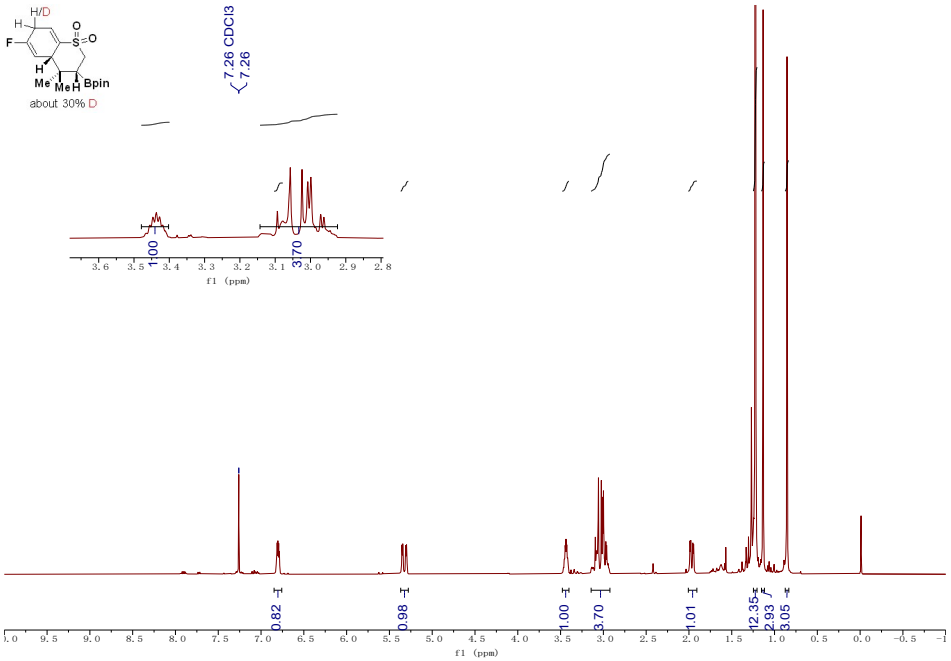


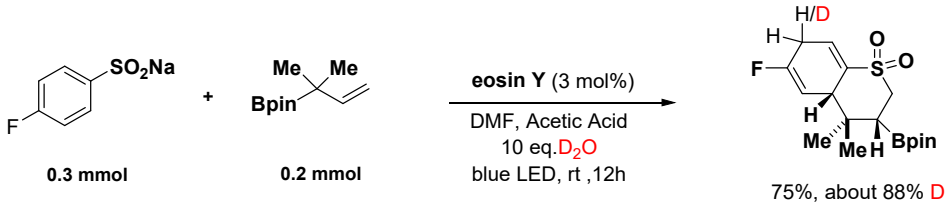
0.3 mmol 0.2 mmol

76%, about 30% D

(eq -4)

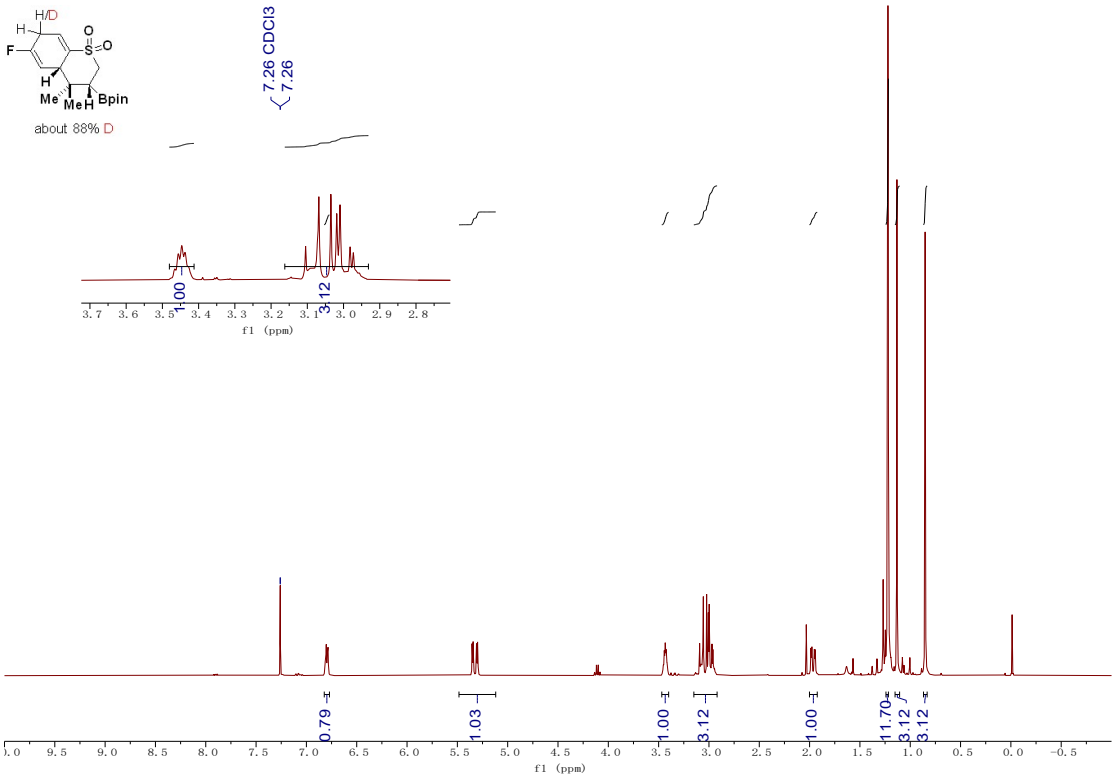
The ^{1}H-NMR of product (eq-4).





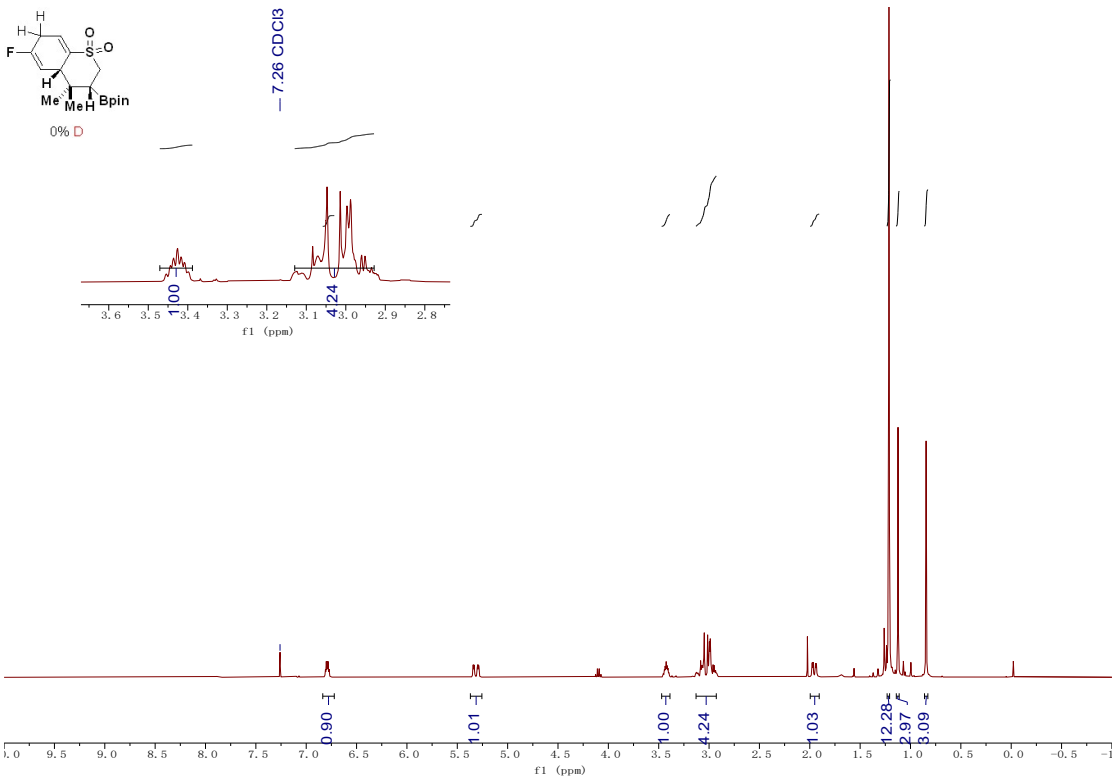
(eq -5)

The ^{1}H-NMR of product (eq-5).



(eq -6)

The ^{1}H-NMR of product (eq-6).


H
H
F
O
S
O
H
Me
Me
H
Bpin
0% D
7.26 CDCl3
1.00
4.24
f1 (ppm)
0.90
1.01
1.00
4.24
1.03
12.28
2.97
3.09
f1 (ppm)

X-ray crystallography

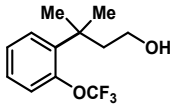
Single crystal of the product **4a** was obtained by recrystallization from CH_2Cl_2/n-hexane. X-ray diffractional data and the refinement were shown in Table S9.

Table S9 Crystal data and structure refinement for 4a.

Identification code	**4a**
Empirical formula	$C_{17}H_{26}BFO_4S$
Formula weight	356.25
Temperature/K	193
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1868(10)
b/Å	10.5562(9)
c/Å	15.7691(15)
α/°	90
β/°	106.700(3)
γ/°	90
Volume/Å^3	1783.6(3)
Z	4
ρ_{calc}g/cm^3	1.327
μ/mm^{-1}	0.209
F(000)	760.0
Crystal size/mm^3	0.17 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.708 to 56.592
Index ranges	$-14 \le h \le 13$, $-14 \le k \le 14$, $-21 \le l \le 21$
Reflections collected	15928
Independent reflections	4404 [R_{int} = 0.0771, R_{sigma} = 0.0753]
Data/restraints/parameters	4404/0/223
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0613, wR_2 = 0.1690
Final R indexes [all data]	R_1 = 0.0763, wR_2 = 0.1860
Largest diff. peak/hole / e Å^{-3}	0.65/-0.34

Characteristic Data

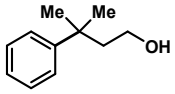
3-methyl-3-(2-(trifluoromethoxy)phenyl)butan-1-ol (3a)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 40.6 mg (82%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 3.48 – 3.39 (m, 2H), 2.10 (t, *J* = 7.5 Hz, 2H), 1.42 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 148.76, 138.42, 128.73, 127.85, 126.07, 120.77 (q, *J* = 259.6 Hz),118.94 (q, *J* = 2.3 Hz), 60.48, 44.14, 37.15, 29.27. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -54.49. HRMS(EI) m/z: [M] Caled for $C_{12}H_{15}F_3O_2$ 248.1024; found 248.1021.

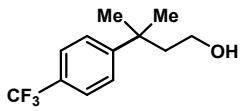
3-methyl-3-phenylbutan-1-ol (3b)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 14.3 mg (44%). Physical State: colorless oil. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.31 (dd, *J* = 8.8, 6.9 Hz, 2H), 7.22 – 7.15 (m, 1H), 3.50 (t, *J* = 7.4 Hz, 2H), 1.96 (t, *J* = 7.4 Hz, 2H), 1.35 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 148.83, 128.43, 125.92, 125.78, 60.33, 47.06, 36.79, 29.44. HRMS(EI) m/z: [M] Caled for $C_{11}H_{15}O$ 164.1201; found 164.1200.

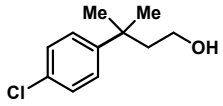
3-methyl-3-(4-(trifluoromethyl)phenyl)butan-1-ol (3c)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 25.4 mg (55%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 3.48 (dd, *J* = 8.0, 7.0 Hz, 2H), 1.97 (dd, *J* = 8.0, 7.0 Hz, 2H), 1.37 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 152.99, 128.08 (q, *J* = 32.2 Hz), 126.05, 125.18 (q, *J* = 3.6 Hz), 124.29 (q, *J* = 271.6 Hz), 59.89, 46.58, 36.99, 29.16. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.38. HRMS (Dart Postive) m/z: $[M + H]^+$Caled for $C_{12}H_{16}OF_3$ 233.1148; found 233.1147.

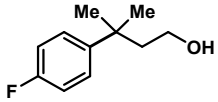
3-(4-chlorophenyl)-3-methylbutan-1-ol (3d)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 24.4 mg (62%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 5.9 Hz, 4H), 3.53 – 3.41 (m, 2H), 1.96 – 1.87 (m, 2H), 1.33 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 147.43, 131.64, 128.44, 127.28, 60.12, 46.83, 36.61, 29.40. HRMS(EI) m/z: [M] Caled for $C_{11}H_{15}ClO$ 198.0811; found 198.0803.

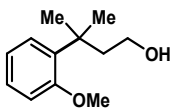
3-(4-fluorophenyl)-3-methylbutan-1-ol (3e)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 9.8 mg (28%). Physical State: colorless oil. Rf= 0.2 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, *J* = 8.9, 5.3 Hz, 2H), 6.99 (t, *J* = 8.8 Hz, 2H), 3.52 – 3.44 (m, 2H), 2.00 – 1.87 (m, 2H), 1.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 160.99 (d, *J* = 244.3 Hz), 127.16 (d, *J* = 7.7 Hz), 116.61, 114.88 (d, *J* = 20.9 Hz), 60.06, 46.92, 36.34, 29.45. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -118.01. HRMS(EI) m/z: [M] Caled for $C_{11}H_{15}FO$ 182.1107; found 182.1103.

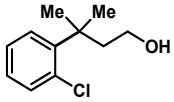
3-(2-methoxyphenyl)-3-methylbutan-1-ol (3f)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 17.1 mg (44%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.17 (m, 2H), 6.92 – 6.85 (m, 2H), 3.84 (s, 3H), 3.43 (dd, *J* = 7.8, 7.0 Hz, 2H), 2.18 – 2.12 (m, 2H), 1.39 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 158.49, 135.83, 127.59, 127.46, 120.59, 111.57, 61.03, 55.15, 43.35, 37.04, 28.94. HRMS (Dart Postive) m/z: $[M + H]^+$ Caled for $C_{12}H_{19}O$ 195.1380; found 195.1379.

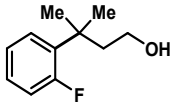
3-(2-chlorophenyl)-3-methylbutan-1-ol (3g)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 26.0 mg (66%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (ddd, *J* = 11.0, 7.8, 1.7 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.14 (td, *J* = 7.6, 1.8 Hz, 1H), 3.44 (dd, *J* = 7.9, 7.1 Hz, 2H), 2.30 (dd, *J* = 7.9, 7.0 Hz, 2H), 1.49 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.33, 133.73, 132.10, 128.70, 127.66, 126.92, 60.58, 42.65, 38.36, 29.11. HRMS(EI) m/z: $[M]^+$Caled for $C_{11}H_{15}ClO$ 198.0811; found 198.0803.

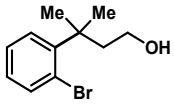
3-(2-fluorophenyl)-3-methylbutan-1-ol (3h)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 29.1 mg (81%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 1H), 7.21 – 7.16 (m, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 6.99 (ddd, *J* = 13.0, 8.1, 1.4 Hz, 1H), 3.48 (td, *J* = 7.5, 0.9 Hz, 2H), 2.08 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 2H), 1.40 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 161.89 (d, *J* = 247.5 Hz), 134.95 (d, *J* = 11.4 Hz), 128.02 (d, *J* = 15.0 Hz), 128.00, 124.04 (d, *J* = 3.2 Hz), 116.46 (d, *J* = 24.1 Hz), 60.56, 44.32 (d, *J* = 4.5 Hz), 36.55 (d, *J* = 2.7 Hz), 28.78 (d, *J* = 2.7 Hz). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -109.16. HRMS(ESI) m/z: $[M + Na]^+$Caled for $C_{11}H_{15}FNaO$ 205.0999; found 205.0916.

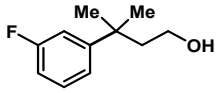
3-(2-bromophenyl)-3-methylbutan-1-ol (3i)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 35.5 mg (73%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.39 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.04 (ddd, *J* = 7.9, 7.2, 1.7 Hz, 1H), 3.44 (dd, *J* = 7.9, 7.0 Hz, 2H), 2.36 (dd, *J* = 8.0, 7.0 Hz, 2H), 1.52 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 145.67, 135.96, 129.05, 127.90, 127.49, 122.73, 60.60, 42.45, 38.89, 29.28. HRMS(EI) m/z: [M] Caled for $C_{12}H_{19}O$ 242.0306; found 242.0302.

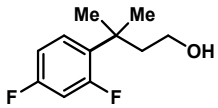
3-(3-fluorophenyl)-3-methylbutan-1-ol (3j)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 26.1 mg (73%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 1H), 7.12 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.04 (dt, *J* = 11.1, 2.1 Hz, 1H), 6.88 (tdd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 3.48 (dd, *J* = 7.9, 7.0 Hz, 2H), 1.93 (dd, *J* = 7.9, 7.0 Hz, 2H), 1.33 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 163.08 (d, *J* = 244.5 Hz), 151.84 (d, *J* = 6.4 Hz), 129.74 (d, *J* = 8.1 Hz), 121.42 (d, *J* = 2.9 Hz), 113.01 (d, *J* = 22.0 Hz), 112.70 (d, *J* = 20.8 Hz), 60.10, 46.83, 36.93 (d, *J* = 1.7 Hz), 29.33. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -113.23. HRMS(ESI) m/z: $[M + Na]^+$Caled for $C_{11}H_{15}FNaO$ 205.0999; found 205.0990.

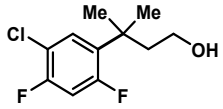
3-(2,4-difluorophenyl)-3-methylbutan-1-ol (3k)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 32.4 mg (81%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (td, *J* = 9.0, 6.4 Hz, 1H), 6.84 – 6.71 (m, 2H), 3.48 (t, *J* = 7.4 Hz, 2H), 2.05 (td, *J* = 7.5, 1.5 Hz, 2H), 1.38 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 162.94 (dd, *J* = 12.0, 7.5 Hz), 160.47 (dd, *J* = 8.1, 4.5 Hz), 130.97 (d, *J* = 11.8 Hz), 110.70 (dd, *J* = 20.2, 3.4 Hz), 104.70 (dd, *J* = 28.4, 24.8 Hz), 60.44, 44.19 (d, *J* = 4.1 Hz), 36.31 (d, *J* = 3.2 Hz), 28.85 (d, *J* = 2.7 Hz). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -105.04 (d, *J* = 8.2 Hz), -114.17 (d, *J* = 10.9 Hz). HRMS(EI) m/z: [M] Caled for $C_{11}H_{14}F_2O$ 200.1013; found 200.1011.

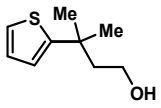
3-(5-chloro-2,4-difluorophenyl)-3-methylbutan-1-ol (3l)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 40.7 mg (87%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 1H), 6.86 (dd, *J* = 11.7, 8.8 Hz, 1H), 3.49 (t, *J* = 7.3 Hz, 2H), 2.04 (td, *J* = 7.3, 1.5 Hz, 2H), 1.38 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 162.93 (dd, *J* = 12.0, 7.5 Hz), 160.44 (dd, *J* = 12.7 Hz, 4.5 Hz), 130.97 (d, *J* = 11.8 Hz), 128.64 (dd, *J* = 9.5, 7.3 Hz), 110.70 (dd, *J* = 20.2, 3.4 Hz), 104.70 (dd, *J* = 28.4, 24.8 Hz), 60.44, 44.19 (d, *J* = 4.1 Hz), 36.31 (d, *J* = 3.2 Hz), 28.84 (d, *J* = 2.7 Hz).**^{19}F NMR (376 MHz, $CDCl_3$):** δ -106.69 (d, *J* = 8.2 Hz), -114.90 (d, *J* = 10.9 Hz). HRMS(EI) m/z: [M] Caled for $C_{11}H_{13}ClF_2NO$ 234.0623; found 234.0617.

3-methyl-3-(thiophen-2-yl)butan-1-ol (3m)

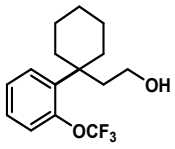


Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 8.5 mg (25%). Physical State: colorless oil. Rf= 0.3 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (dd, J = 5.0, 1.2 Hz, 1H), 6.92 (dd, J = 5.0, 3.5 Hz, 1H), 6.83 (dd, J = 3.5, 1.2 Hz, 1H), 3.69 – 3.54 (m, 2H), 1.95 (t, J = 7.2 Hz, 2H), 1.41 (s, 6H). **^{13}C NMR**

(126 MHz, $CDCl_3$): δ 155.32, 126.65, 123.07, 122.32, 60.23, 48.04, 36.54, 30.68. HRMS(ESI) m/z: [Dart Postive]$^+$ Caled for $C_9H_{15}OS$ 171.0838; found 171.0838.

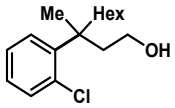
2-(1-(2-(trifluoromethoxy)phenyl)cyclohexyl)ethan-1-ol (3n)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 21.8 mg (38%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.22 – 7.18 (m, 1H), 3.34 (t, *J* = 7.6 Hz, 2H), 2.25 – 2.16 (m, 2H), 2.05 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.64 – 1.58 (m, 2H), 1.48 – 1.41 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 146.92, 135.89, 131.47, 131.16, 127.00, 120.32 (q, *J* = 262.0 Hz), 120.25 (q, *J* = 2.0 Hz), 70.01, 59.80, 43.25, 28.55, 27.72, 26.34, 26.08, 25.98. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -54.31. HRMS(EI) m/z: [M] Caled for $C_{11}H_{19}F_3O_2$ 288.1337; found 288.1327

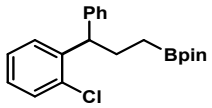
3-(2-chlorophenyl)-3-methylnonan-1-ol (3o)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 25.0 mg (44%). Physical State: colorless oil. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 2H), 7.19 (td, *J* = 7.6, 1.7 Hz, 1H), 7.13 (td, *J* = 7.5, 1.8 Hz, 1H), 3.50 (ddd, *J* = 10.5, 9.3, 5.9 Hz, 1H), 3.38 (ddd, *J* = 10.5, 9.2, 5.9 Hz, 1H), 2.69 (ddd, *J* = 13.7, 9.3, 5.9 Hz, 1H), 2.36 (ddd, *J* = 13.7, 11.8, 4.5 Hz, 1H), 1.85 (ddd, *J* = 13.7, 9.2, 5.9 Hz, 1H), 1.53 (ddd, *J* = 13.6, 12.3, 4.2 Hz, 1H), 1.46 (s, 3H), 1.27 – 1.09 (m, 7H), 0.91 – 0.85 (m, 1H), 0.84 – 0.80 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.95, 133.66, 131.99, 129.89, 127.60, 126.75, 60.33, 42.56, 41.86, 40.16, 32.56, 26.48, 24.06, 22.63, 14.19. HRMS(EI) m/z: [M] Caled for $C_{16}H_{23}ClO$ 282.1387; found 282.1385.

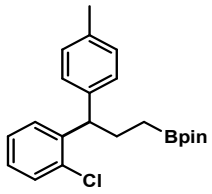
2-(3-(2-chlorophenyl)-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=20:1) afforded 31.0 mg (44%). Physical State: colorless oil. Rf= 0.5 (Hexane: ethyl acetate=20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 3H), 7.26 (d, *J* = 1.0 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.18 – 7.13 (m, 1H), 7.12 – 7.07 (m, 1H), 4.43 (t, *J* = 7.7 Hz, 1H), 2.17 – 2.09 (m, 2H), 1.24 (s, 12H), 0.82 – 0.73 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 143.86, 142.42, 134.61, 129.72, 128.69, 128.45, 128.38, 127.28, 126.96, 126.22, 83.15, 49.03, 29.88, 25.00. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{21}H_{27}BClO_2$ 357.1793; found 357.1794.

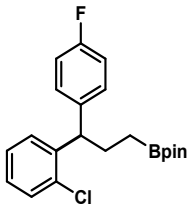
2-(3-(2-chlorophenyl)-3-(p-tolyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3q)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=20:1) afforded 23.7 mg (32%). Physical State: colorless oil. Rf= 0.5 (Hexane: ethyl acetate=20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.30 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.20 (td, *J* = 7.6, 1.5 Hz, 1H), 7.15 – 7.13 (m, 2H), 7.09 – 7.05 (m, 2.7 Hz, 3H), 4.38 (t, *J* = 7.7 Hz, 1H), 2.29 (s, 3H), 2.15 – 2.07 (m, 2H), 1.23 (s, 12H), 0.82 – 0.74 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.67, 140.84, 135.66, 134.56, 129.70, 129.09, 128.64, 128.30, 127.19, 126.94, 83.12, 48.64, 29.92, 25.00, 24.98, 24.94, 21.13. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{22}H_{29}BClO_2$ 371.1949; found 371.1950.

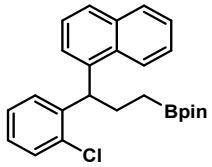
2-(3-(2-chlorophenyl)-3-(4-fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=20:1) afforded 30.5 mg (41%). Physical State: colorless oil. Rf= 0.5 (Hexane: ethyl acetate=20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 2H), 7.26 – 7.17 (m, 3H), 7.11 (td, J = 7.6, 1.8 Hz, 1H), 6.98 – 6.91 (m, 2H), 4.40 (t, J = 7.8 Hz, 1H), 2.11 (q, J = 7.9 Hz, 2H), 1.24 (s, 12H), 0.77 (td, J = 7.8, 3.1 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 161.43 (d, J = 243.9 Hz), 142.23, 139.53 (d, J = 3.5 Hz), 134.56, 129.83 (d, J = 4.0 Hz), 128.48, 127.44, 127.04, 115.21, 115.05, 83.20, 48.32, 29.96, 24.99 (d, J = 2.3 Hz). **^{19}F NMR (471 MHz, $CDCl_3$):** δ -117.25. HRMS(EI) m/z: [M] Caled for $C_{21}H_{25}{}^{10}BCl_2O_2$ 389.1361; found 389.1360.

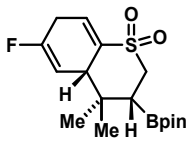
2-(3-(2-chlorophenyl)-3-(naphthalen-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)



Following Procedure A on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=20:1) afforded 20.3 mg (25%). Physical State: colorless oil. Rf= 0.5 (Hexane: ethyl acetate=20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (ddd, *J* = 7.6, 5.7, 2.2 Hz, 2H), 7.74 – 7.70 (m, 2H), 7.44 – 7.40 (m, 2H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.24 – 7.19 (m, 1H), 7.10 (td, *J* = 7.6, 1.7 Hz, 1H), 4.59 (t, *J* = 7.7 Hz, 1H), 2.28 – 2.15 (m, 2H), 1.23 (s, 12H), 0.85 – 0.81 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.36, 141.36, 133.60, 129.76, 128.90, 127.96, 127.91, 127.66, 127.39, 127.34, 127.01, 126.57, 125.94, 125.46, 83.18, 49.12, 29.75, 24.99. HRMS(Dart Postive) m/z: $[M + NH_4]^+$ Caled for $C_{25}H_{32}{}^{10}BO_2NCl$ 423.2245; found 423.2244.

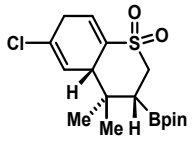
6-fluoro-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4a)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 58.4 mg (82%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (ddd, *J* = 7.0, 4.0, 0.8 Hz, 1H), 5.34 (ddd, *J* = 17.8, 4.2, 1.5 Hz, 1H), 3.50 – 3.40 (m, 1H), 3.12 – 3.04 (m, 2H), 3.03 – 2.94 (m, 2H), 1.98 (dd, *J* = 13.2, 3.6 Hz, 1H), 1.24 (s, 12H), 1.15 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 157.31 (d, *J* = 255.4 Hz), 137.40, 131.19 (d, *J* = 11.3 Hz), 100.65 (d, *J* = 16.8 Hz), 84.07, 50.50, 48.92 (d, *J* = 6.9 Hz), 38.23, 27.32, 27.02, 26.84, 24.84, 24.76, 17.16. **^{19}F NMR (376 MHz, $CDCl_3$):**δ -103.94. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{27}BFO_4S$ 357.1702; found 357.1702.

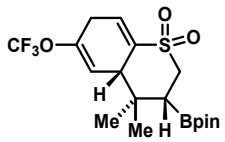
6-chloro-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4b)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 35.0 mg (47%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 – 6.77 (m, 1H), 5.90 – 5.87 (m, 1H), 3.43 – 3.35 (m, 1H), 3.23 – 3.08 (m, 2H), 3.05 – 2.95 (m, 2H), 1.96 (dd, *J* = 13.2, 3.0 Hz, 1H), 1.22 (s, 12H), 1.17 (s, 3H), 0.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.57, 132.00, 130.10, 122.05, 84.10, 50.47, 50.20, 38.45, 33.54, 26.84, 24.85, 24.77, 17.46. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{27}BClO_4S$ 373.1406; found 373.1408.

4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethoxy)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4c)

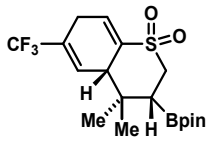


Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 72.6 mg (86%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (dd, *J* = 4.0, 3.2 Hz, 1H), 5.64 (dd, *J* = 2.2, 0.7 Hz, 1H), 3.46 (td, *J* = 7.2, 4.6 Hz, 1H), 3.11 – 3.02 (m, 2H), 3.01 – 2.94 (m, 2H), 1.98 (dd, *J* = 13.1, 3.5 Hz, 1H), 1.22 (s, 12H), 1.17 (s, 3H), 0.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.81, 136.77, 131.25, 120.47 (q, *J* = 257.9 Hz), 111.86, 84.15, 50.55, 48.99, 38.49, 28.50, 26.84, 24.85,

24.78, 17.26. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -57.42. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{18}H_{27}BF_3O_5S$ 423.1619; found 423.1619

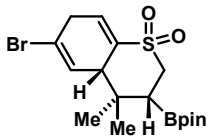
4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4d)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 48.7 mg (60%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (t, *J* = 3.3 Hz, 1H), 6.39 – 6.36 (m, 1H), 3.42 (dd, *J* = 10.9, 7.5 Hz, 1H), 3.12 – 3.03 (m, 2H), 3.02 – 2.97 (m, 2H), 2.01 (dd, *J* = 13.2, 3.5 Hz, 1H), 1.23 (s, 3H), 1.22 (s, 12H), 0.84 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.39, 131.33, 127.63 (q, *J* = 5.6 Hz), 126.93 (q, *J* = 30.9 Hz), 84.19, 50.46, 47.84, 38.43, 26.79, 24.85, 24.78, 24.02. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -69.74. HRMS(ESI) m/z: $[M + H]^+$Caled for $C_{18}H_{27}BF_3O_4S$ 407.1670; found 407.1670

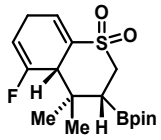
6-bromo-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4e)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 45.6 mg (55%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (t, *J* = 3.2 Hz, 1H), 6.15 – 6.11 (m, 1H), 3.39 – 3.32 (m, 1H), 3.27 – 3.14 (m, 2H), 3.10 – 2.95 (m, 2H), 1.96 (dd, *J* = 13.3, 3.4 Hz, 1H), 1.22 (s, 12H), 1.18 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.42, 132.37, 126.27, 119.65, 84.12, 50.95, 50.47, 38.38, 35.70, 26.85, 24.87, 24.79, 17.53. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{27}BBrO_4S$ 417.0901; found 417.0900.

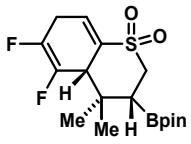
5-fluoro-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4f)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded37.7 mg (53%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, *J* = 1.4 Hz, 1H), 5.40 (dddd, *J* = 17.4, 4.6, 2.5, 1.2 Hz, 1H), 3.53 (q, *J* = 6.0 Hz, 1H), 3.12 – 2.99 (m, 2H), 2.93 (dt, *J* = 13.8, 4.8 Hz, 2H), 1.99 (dd, *J* = 13.7, 3.1 Hz, 1H), 1.25 (d, *J* = 4.0 Hz, 3H), 1.23 (s, 12H), 0.97 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 157.29 (d, *J* = 258.9 Hz), 136.46 (d, *J* = 10.0 Hz), 133.92 (d, *J* = 2.2 Hz), 102.14 (d, *J* = 19.7 Hz), 84.10, 50.78, 49.63 (d, *J* = 25.5 Hz), 38.97 (d, *J* = 4.2 Hz), 28.60 (d, *J* = 7.6 Hz), 26.01 (d, *J* = 7.5 Hz), 24.83, 24.83, 17.07. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -99.69. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{27}BFO_4S$ 357.1702; found 357.1702.

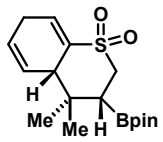
5,6-difluoro-4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4g)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 49.4 mg (66%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

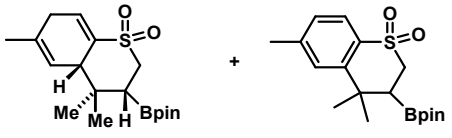
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.73 – 3.63 (m, 1H), 3.34 – 3.20 (m, 1H), 3.15 (td, *J* = 11.1, 5.5 Hz, 1H), 3.10 – 2.96 (m, 2H), 1.99 (dd, *J* = 13.1, 3.6 Hz, 1H), 1.26 (d, *J* = 3.8 Hz, 3H), 1.23 (s, 12H), 0.97 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.42 (dd, *J* = 117.0, 11.9 Hz), 139.88 (dd, *J* = 119.7, 11.7 Hz), 136.51 (dd, *J* = 9.1, 1.8 Hz), 130.96 (d, *J* = 10.1 Hz), 84.21, 50.70, 50.55 (d, *J* = 21.3 Hz), 39.27 (dd, *J* = 4.3, 2.1 Hz), 28.31 (d, *J* = 7.4 Hz), 27.61 (d, *J* = 25.1 Hz), 24.84, 24.81, 17.01. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -136.37 (d, *J* = 10.7 Hz), -138.49 (d, *J* = 10.7 Hz). HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{26}BF_2O_4S$ 375.1607; found 375.1607.

4,4-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4h)



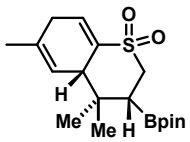
Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 35.0 mg (52%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (ddt, *J* = 4.4, 3.0, 1.3 Hz, 1H), 5.84 – 5.78 (m, 1H), 5.75 (q, *J* = 1.6 Hz, 1H), 3.27 (d, *J* = 3.6 Hz, 1H), 3.10 – 2.94 (m, 2H), 2.85 (t, *J* = 4.3 Hz, 2H), 1.96 (dd, *J* = 13.7, 3.2 Hz, 1H), 1.21 (s, 12H), 1.16 (s, 3H), 0.85 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.93, 133.37, 124.87, 124.51, 83.95, 50.55, 47.61, 38.04, 26.73, 26.65, 24.86, 24.78, 17.22. HRMS(ESI) m/z: $[M + H]^+$Caled for $C_{17}H_{28}BO_4S$ 339.1796; found339.1797.



(10 : 1)

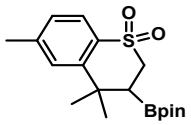
4,4,6-trimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4i)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 40.8 mg (58%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

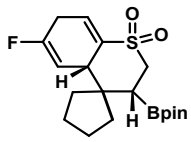
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (ddd, *J* = 4.1, 2.9, 1.1 Hz, 1H), 5.44 (dp, *J* = 4.0, 1.4 Hz, 1H), 3.20 (tdd, *J* = 7.0, 3.4, 1.4 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.92 (dd, *J* = 14.4, 3.3 Hz, 1H), 2.84 – 2.74 (m, 1H), 2.67 (ddd, *J* = 23.5, 7.0, 4.0 Hz, 1H), 1.93 (dd, *J* = 13.8, 3.1 Hz, 1H), 1.71(s, 3H), 1.20 (s, 12H), 1.13 (s, 3H), 0.77 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 136.83,

133.41, 132.22, 118.81, 83.87, 50.53, 48.56, 38.21, 31.21, 26.80, 24.80, 24.72, 23.07, 17.07. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{18}H_{30}BO_4S$ 353.1952; found 353.1953.



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.14 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 3.26 (dd, *J* = 14.5, 2.1 Hz, 1H), 2.35 (s, 3H), 2.32 – 2.25 (m, 1H), 1.54 (s, 3H), 1.30 (s, 3H), 1.25 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 146.74, 142.90, 129.80, 128.01, 127.97, 123.48, 84.26, 48.02, 36.10, 30.40, 28.31, 25.03, 21.85. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{18}H_{28}BO_4S$ 351.1796; found 351.1748.

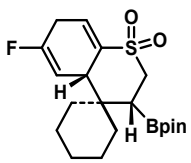
6'-fluoro-3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2',3',4a',7'-tetrahydrospiro[cyclopentane-1,4'-thiochromene] 1',1'-dioxide (4j)



Following Procedure B on 0.10 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 16.5 mg (45%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.79 (dddd, *J* = 7.3, 4.3, 3.2, 1.2 Hz, 1H), 5.30 (ddd, *J* = 17.9, 4.2, 1.3 Hz, 1H), 3.62 (tq, *J* = 7.3, 4.1, 3.7 Hz, 1H), 3.22 – 3.08 (m, 1H), 3.06 – 2.93 (m, 3H), 2.19 (dd, *J* = 10.6, 5.9 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.73 – 1.57 (m, 6H), 1.51 – 1.42 (m, 2H), 1.28 (dd, *J* = 6.7, 1.8 Hz, 2H), 1.23 (d, *J* = 2.7 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)**: δ 138.22, 131.19, 131.10, 101.89, 101.75, 84.06, 52.17, 48.99, 48.94, 37.50, 29.42, 27.71, 27.45, 27.21, 26.92, 25.07, 24.89. **^{19}F NMR (471 MHz, $CDCl_3$)**: δ -103.99. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{20}H_{31}BFO_4S$ 382.1785; found 3382.1786.

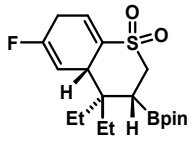
6'-fluoro-3'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2',3',4a',7'-tetrahydrospiro[cyclohexane-1,4'-thiochromene] 1',1'-dioxide (4k)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 32.5 mg 41%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (ddd, *J* = 7.2, 4.1, 1.0 Hz, 1H), 5.42 (ddd, *J* = 18.2, 4.3, 1.5 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.32 (dd, *J* = 14.1, 2.9 Hz, 1H), 3.14 – 2.89 (m, 4H) , 2.22 – 2.14 (m, 2H), 1.66 (d, *J* = 13.4 Hz, 1H), 1.57 – 1.48 (m, 3H), 1.39 – 1.30 (m, 2H), 1.28 (s, 12H), 1.24 – 1.09 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 157.05 (d, *J* = 254.3 Hz), 137.59 (d, *J* = 2.8 Hz), 131.06 (d, *J* = 11.3 Hz), 100.27 (d, *J* = 16.7 Hz), 84.12, 50.68, 44.54 (d, *J* = 7.0 Hz), 40.22, 32.26, 27.11 (d, *J* = 29.6 Hz), 26.81, 25.91, 25.23, 24.72, 21.14, 20.78. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.82. HRMS(ESI) m/z: $[M + H]^+$Caled for $C_{20}H_{31}BFO_4S$ 397.2015; found 397.2016.

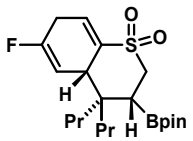
4,4-diethyl-6-fluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4l)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 45.3 mg (59%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.90 – 6.76 (m, 1H), 5.28 – 5.18 (m, 1H), 3.67 (dq, J = 8.1, 4.0 Hz, 1H), 3.17 (dd, J = 14.8, 2.7 Hz, 1H), 3.14 – 2.88 (m, 4H), 2.06 (dd, J = 13.6, 2.7 Hz, 1H), 1.32 (ddt, J = 10.7, 7.0, 3.3 Hz, 4H), 1.27 (d, J = 2.9 Hz, 3H), 1.20 (d, J = 3.4 Hz, 12H), 0.92 (d, J = 7.0 Hz, 3H), 0.87 – 0.84 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.15 (d, J = 254.9 Hz), 137.97 (d, J = 2.9 Hz), 131.24 (d, J = 11.6 Hz), 100.53 (d, J = 16.8 Hz), 83.89, 50.50, 45.50 (d, J = 6.4 Hz), 44.12, 36.78, 34.93, 27.16 (d, J = 29.5 Hz), 24.87 (d, J = 19.7 Hz), 17.49, 16.02, 15.15, 14.62. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -103.94. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{20}H_{31}BFO_4S$ 384.1942; found 384.1940.

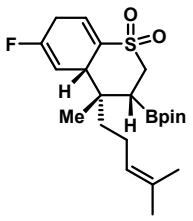
6-fluoro-4,4-dipropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4m)



Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 28.4 mg (38%). Physical State: white solid. Rf= 0.45 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.83 (dq, *J* = 8.4, 4.4, 3.9 Hz, 1H), 5.28 – 5.18 (m, 1H), 3.67 (dq, *J* = 8.1, 4.0 Hz, 1H), 3.17 (dd, *J* = 14.8, 2.7 Hz, 1H), 3.14 – 2.88 (m, 4H), 2.06 (dd, *J* = 13.6, 2.7 Hz, 1H), 1.34 – 1.28 (m, 4H), 1.27 (d, *J* = 2.9 Hz, 3H), 1.20 (d, *J* = 3.4 Hz, 12H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.87 – 0.84 (m, 4H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ157.15 (d, *J* = 254.9 Hz), 137.97 (d, *J* = 2.9 Hz), 131.24 (d, *J* = 11.6 Hz), 100.53 (d, *J* = 16.8 Hz), 83.89, 50.50, 45.52, 45.47, 44.12, 36.78, 34.93, 27.27, 27.04, 24.95, 24.79, 17.49, 16.02, 15.15, 14.62. **^{19}F NMR (471 MHz, $CDCl_3$):** δ -103.94. HRMS(ESI) m/z: $[M + H]^+$Caled for $C_{21}H_{35}BFO_4S$ 413.2333; found 413.2331.

6-fluoro-4-methyl-4-(4-methylpent-3-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,4a,7-tetrahydro-2H-thiochromene 1,1-dioxide (4n)

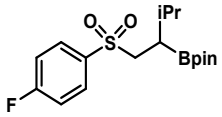


Following Procedure B on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 22.7 mg (27%) as single diastereoisomer (dr >19:1). Physical State: white solid. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (dddd, *J* = 7.2, 4.2, 3.0, 1.1 Hz, 1H), 5.23 (ddd, *J* = 17.6, 4.2, 1.7 Hz, 1H), 5.04 (ddt, *J* = 7.3, 5.8, 1.5 Hz, 1H), 3.71 (tt, *J* = 7.7, 4.2 Hz, 1H), 3.23 – 3.06 (m, 2H), 2.98 (dd, *J* = 14.6, 3.1 Hz, 2H), 2.20 (ddd, *J* = 25.7, 13.3, 4.7 Hz, 2H), 1.96 – 1.84 (m, 1H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.50 – 1.35 (m, 2H), 1.21 (d, *J* = 3.4 Hz, 12H), 0.85 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 157.54 (d, *J* = 255.6 Hz), 137.75 (d, *J* = 2.6 Hz), 132.05, 131.30 (d, *J* = 11.1 Hz), 100.10 (d, *J* = 16.7 Hz), 84.01, 50.36, 44.24 (d, *J* = 6.7 Hz), 40.77 (d, *J* = 1.7 Hz), 38.85, 27.30, 27.07,25.91, 24.84 (d, *J* = 8.7 Hz), 21.56, 18.51, 17.89.

^{19}F NMR (471 MHz, $CDCl_3$): δ -103.58. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{22}H_{35}BFO_4S$ 425.2328; found 425.2327.

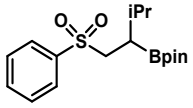
2-(1-((4-fluorophenyl)sulfonyl)-3-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 62.0 mg (87%). Physical State: white solid. Rf= 0.7 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.89 (m, 2H), 7.24 – 7.19 (m, 2H), 3.39 (dd, *J* = 13.9, 10.9 Hz, 1H), 3.03 (dd, *J* = 13.9, 3.3 Hz, 1H), 1.80 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.34 – 1.29 (m, 1H), 1.26 (d, *J* = 1.0 Hz, 12H), 0.87 (dd, *J* = 6.8, 4.7 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.09, 164.55, 135.79, 135.75, 131.21, 131.12, 116.67, 116.44, 83.99, 56.86, 29.61, 25.13, 25.11, 21.88, 20.95. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -104.22. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{27}BFO_4S$ 357.1702; found 357.1703.

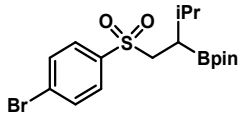
4,4,5,5-tetramethyl-2-(3-methyl-1-(phenylsulfonyl)butan-2-yl)-1,3,2-dioxaborolane (5b)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 50.7 mg (75%). Physical State: white solid. Rf= 0.7 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.88 (m, 2H), 7.65 – 7.58 (m, 1H), 7.54 (dd, *J* = 8.1, 6.9 Hz, 2H), 3.39 (dd, *J* = 13.9, 10.8 Hz, 1H), 3.04 (dd, *J* = 13.9, 3.4 Hz, 1H), 1.80 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.34 (ddd, *J* = 10.7, 5.4, 3.4 Hz, 1H), 1.26 (d, *J* = 0.9 Hz, 12H), 0.87 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 139.70, 133.50, 129.25, 128.26, 83.92, 56.65, 29.60, 25.10, 21.88, 20.92. HRMS(ESI) m/z: $[M + H]^+$Caled for $C_{17}H_{27}BO_4S$ 339.1796; found 339.1799.

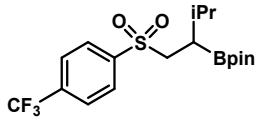
2-(1-((4-bromophenyl)sulfonyl)-3-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 68.4 mg (72%). Physical State: white solid. Rf= 0.7 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 3.38 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.02 (dd, *J* = 14.0, 3.3 Hz, 1H), 1.80 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.30 (ddd, *J* = 10.8, 5.4, 3.4 Hz, 1H), 1.25 (s, 12H), 0.87 (dd, *J* = 6.8, 4.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 138.68, 132.57, 129.89, 128.81, 83.98, 56.73, 29.62, 25.09, 21.86, 20.91. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{17}H_{27}BBrO_4S$ 417.0901; found 417.0901.

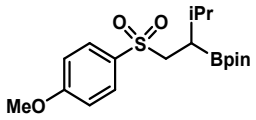
4,4,5,5-tetramethyl-2-(3-methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)-1,3,2-dioxaborolane (5d)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 69.1 mg (85%). Physical State: white solid. Rf= 0.7 (Hexane: ethyl acetate=5:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 3.42 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.06 (dd, *J* = 14.0, 3.3 Hz, 1H), 1.82 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.33 (ddd, *J* = 10.7, 5.3, 3.4 Hz, 1H), 1.25 (d, *J* = 2.5 Hz, 12H), 0.88 (dd, *J* = 6.8, 5.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 143.08, 135.13 (q, *J* = 33.0 Hz), 128.81, 126.27 (q, *J* = 3.7 Hz), 123.15 (q, *J* = 273.1 Hz), 83.90, 56.46, 29.52, 24.91, 21.68, 20.74. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -63.20. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{18}H_{27}BF_3O_4S$ 407.1670; found 407.1666.

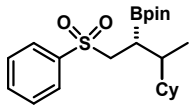
2-(1-((4-methoxyphenyl)sulfonyl)-3-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5e)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 32.4 mg (44%). Physical State: white solid. Rf= 0.4 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.37 (dd, *J* = 13.9, 10.8 Hz, 1H), 3.00 (dd, *J* = 13.9, 3.3 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.33 – 1.29 (m, 1H), 1.26 (s, 12H), 0.86 (dd, *J* = 6.8, 4.6 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 163.61, 131.28, 130.43, 114.42, 83.88, 56.97, 55.76, 29.59, 25.12, 21.92, 20.97. HRMS(ESI) m/z: $[M + H]^+$Caled for $C_{18}H_{30}BO_5S$ 369.1902; found 369.1902.

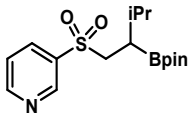
2-(3-cyclohexyl-1-(phenylsulfonyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 52.7 mg (65%). Physical State: white solid. Rf= 0.7 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.86 (m, 2H), 7.67 – 7.57 (m, 1H), 7.59 – 7.50 (m, 2H), 3.42 (dd, *J* = 14.0, 10.5 Hz, 1H), 3.04 (dd, *J* = 14.1, 3.4 Hz, 1H), 1.69 – 1.49 (m, 8H), 1.42 – 1.32 (m, 2H), 1.27 (d, *J* = 2.1 Hz, 12H), 1.09 – 0.94 (m, 4H), 0.80 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 139.64, 133.48, 129.24, 128.31, 83.84, 57.54, 55.09, 41.11, 40.01, 31.60, 28.39, 26.65, 25.13, 15.03. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{22}H_{36}BO_4S$ 407.2422; found 407.2426.

3-((3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)sulfonyl)pyridine (5g)

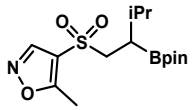


Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 44.1 mg (61%). Physical State: white solid. Rf= 0.4 (Hexane: ethyl acetate=2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (d, *J* = 2.7 Hz, 1H), 8.86 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.19 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.50 (ddd, *J* = 8.1, 4.9, 1.0 Hz, 1H), 3.44 (dd, *J* = 14.1, 10.8 Hz, 1H), 3.08 (dd, *J* = 14.0, 3.4 Hz, 1H), 1.83 (pd, *J* = 6.8, 5.3 Hz, 1H), 1.38 – 1.33 (m, 1H), 1.26 (d, *J* = 2.1

Hz, 12H), 0.89 (dd, *J* = 6.8, 4.6 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 154.13, 149.40, 136.24, 136.15, 123.83, 84.07, 57.08, 29.65, 25.11, 21.84, 20.91. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{16}H_{27}BNO_4S$ 340.1748; found 340.1746.

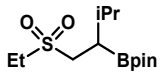
5-methyl-4-((3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)sulfonyl)isoxazole (5h)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 50.2 mg (74%). Physical State: white solid. Rf= 0.3 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 3.42 (dd, *J* = 14.1, 10.9 Hz, 1H), 3.05 (dd, *J* = 14.1, 3.0 Hz, 1H), 2.70 (s, 3H), 1.86 (pd, *J* = 6.8, 5.3 Hz, 1H), 1.31 (ddd, *J* = 10.9, 5.3, 2.9 Hz, 1H), 1.24 (s, 12H), 0.92 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.58, 149.29, 117.09, 84.12, 57.66, 29.79, 25.18, 25.04, 21.76, 20.99, 12.05. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{15}H_{27}BNO_5S$ 344.1698; found 344.1699.

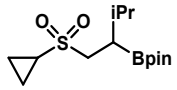
2-(1-(ethylsulfonyl)-3-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5i)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 44.1 mg (76%). Physical State: Colorless oil. Rf= 0.6 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (dd, *J* = 13.8, 10.9 Hz, 1H), 3.01 – 2.91 (m, 3H), 1.91 (pd, *J* = 6.8, 5.2 Hz, 1H), 1.50 (ddd, *J* = 10.9, 5.4, 3.6 Hz, 1H), 1.39 (t, *J* = 7.5 Hz, 3H), 1.27 (s, 12H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$):** δ 83.98, 52.25, 47.36, 29.79, 25.12, 25.06, 21.98, 21.09, 6.83. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{13}H_{28}BO_4S$ 291.1796; found 291.1797.

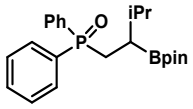
2-(1-(cyclopropylsulfonyl)-3-methylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5j)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 26.7 mg (46%). Physical State: Colorless oil. Rf= 0.7 (Hexane: ethyl acetate=5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.31 (dd, *J* = 13.8, 10.9 Hz, 1H), 3.04 (dd, *J* = 13.7, 3.7 Hz, 1H), 2.39 (tt, *J* = 7.9, 4.9 Hz, 1H), 1.91 (pd, *J* = 6.8, 5.4 Hz, 1H), 1.56 (ddd, *J* = 11.0, 5.5, 3.7 Hz, 1H), 1.27 (s, 12H), 1.26 – 1.24 (m, 1H), 1.21 – 1.15 (m, 1H), 1.06 – 1.01 (m, 1H), 0.98 (m, *J* = 8.7, 6.7 Hz, 7H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 83.89, 54.32, 29.70, 29.55, 25.11, 25.07, 22.00, 21.04, 4.96, 4.48. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{14}H_{28}BO_4S$ 303.1796; found 303.1795.

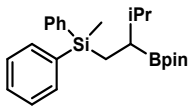
(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)diphenylphosphine oxide (5k)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 47.8 mg (60%). Physical State: white solid. Rf= 0.7 (Hexane: ethyl acetate=5:1).

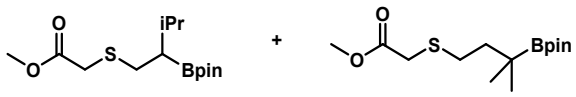
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.66 (m, 4H), 7.52 – 7.36 (m, 6H), 2.56 (ddd, *J* = 14.9, 12.1, 10.0 Hz, 1H), 2.16 (ddd, *J* = 14.9, 11.1, 3.7 Hz, 1H), 1.82 (pd, *J* = 6.8, 4.8 Hz, 1H), 1.32 (dddd, *J* = 14.9, 10.0, 5.0, 3.5 Hz, 1H), 1.20 (d, *J* = 2.7 Hz, 12H), 0.90 (dd, *J* = 6.8, 4.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 134.08 (dd, *J* = 96.7, 49.5 Hz), 131.42 (d, *J* = 3.2 Hz), 131.05 (dd, *J* = 9.1, 2.7 Hz), 128.51 (dd, *J* = 11.4, 4.1 Hz), 83.49, 31.08 (d, *J* = 11.4 Hz), 28.66 (d, *J* = 71.8 Hz), 25.06 (d, *J* = 11.8 Hz), 24.97, 21.87, 20.80. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 33.06. HRMS(ESI) m/z: $[M + H]^+$ Caled for $C_{23}H_{32}BO_3P$ 399.2255; found 399.2254.

methyl(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)diphenylsilane (5l)



Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 64.6 mg (82%). Physical State: Colorless oil. Rf= 0.7 (Hexane: ethyl acetate=5:1).

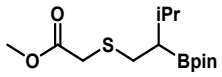
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.51 (m, 4H), 7.40 – 7.30 (m, 6H), 1.77 (pd, *J* = 6.8, 4.5 Hz, 1H), 1.37 (dd, *J* = 14.5, 10.2 Hz, 1H), 1.16 (d, *J* = 3.1 Hz, 12H), 1.16 – 1.10 (m, 1H), 1.13 – 1.03 (m, 1H), 0.92 (d, *J* = 6.8 Hz, 6H), 0.59 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 138.19, 137.84, 134.78, 134.73, 129.05, 129.03, 127.80, 127.78, 127.76, 32.58, 25.20, 25.02, 21.58, 20.92, 18.76, 11.71, -3.91. HRMS(Dart Postive) m/z: $[M + NH_4]^+$ Caled for $C_{24}H_{35}{}^{10}BO_2NSi$ 411.2874; found 411.2874.



(1 : 1.5)

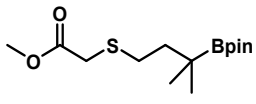
Following Procedure C on 0.20 mmol scale. Purification by column chromatography (Hexane: ethyl acetate=5:1) afforded 52.5 mg (82%). Physical State: Colorless oil. Rf= 0.7 (Hexane: ethyl acetate=5:1).

Methyl-2-((3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)thio)acetate (5m)



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.24 (d, *J* = 14.4 Hz, 1H), 3.18 (d, *J* = 14.4 Hz, 1H), 2.77 (dd, *J* = 12.3, 6.2 Hz, 1H), 2.66 (dd, *J* = 12.3, 10.1 Hz, 1H), 1.79 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.24(s, 12H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.22, 83.43, 52.35, 33.70, 32.89, 29.81, 29.46, 24.71, 22.40, 21.33. HRMS(Dart Postive) m/z: $[M]^+$ Caled for $C_{14}H_{28}{}^{10}BO_4S$ 302.1832; found 302.1832.

Methyl-2-((3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)thio)acetate (5m')



Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.23 (s, 2H), 2.61 – 2.54 (m, 2H), 1.59 – 1.53 (m, 2H), 1.21 (s, 12H), 0.92 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.20, 83.20, 52.37, 40.34,

33.44, 29.75, 25.10, 24.93, 24.79. HRMS(Dart Postive) m/z: $[M]^+$ Caled for $C_{14}H_{28}{}^{10}BO_4S$ 302.1832; found 302.1832.

Spectral data

Figure S4. ^{1}H-NMR of **3a**

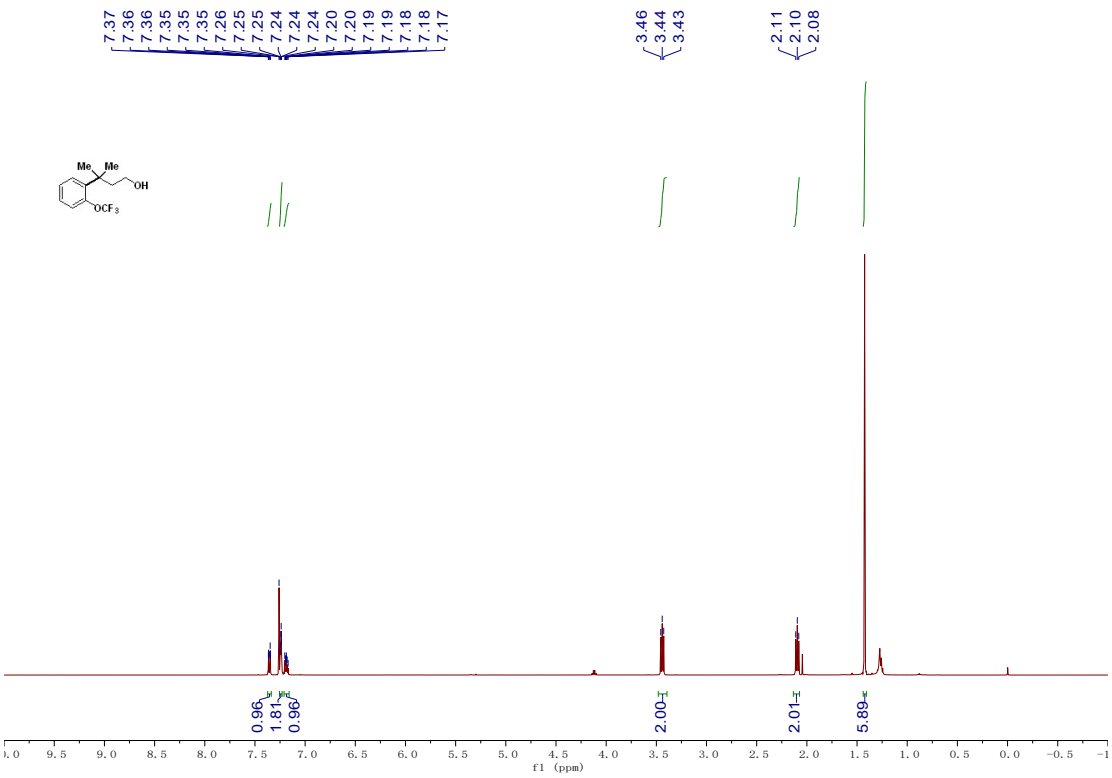


Figure S5. ^{13}C-NMR of **3a**

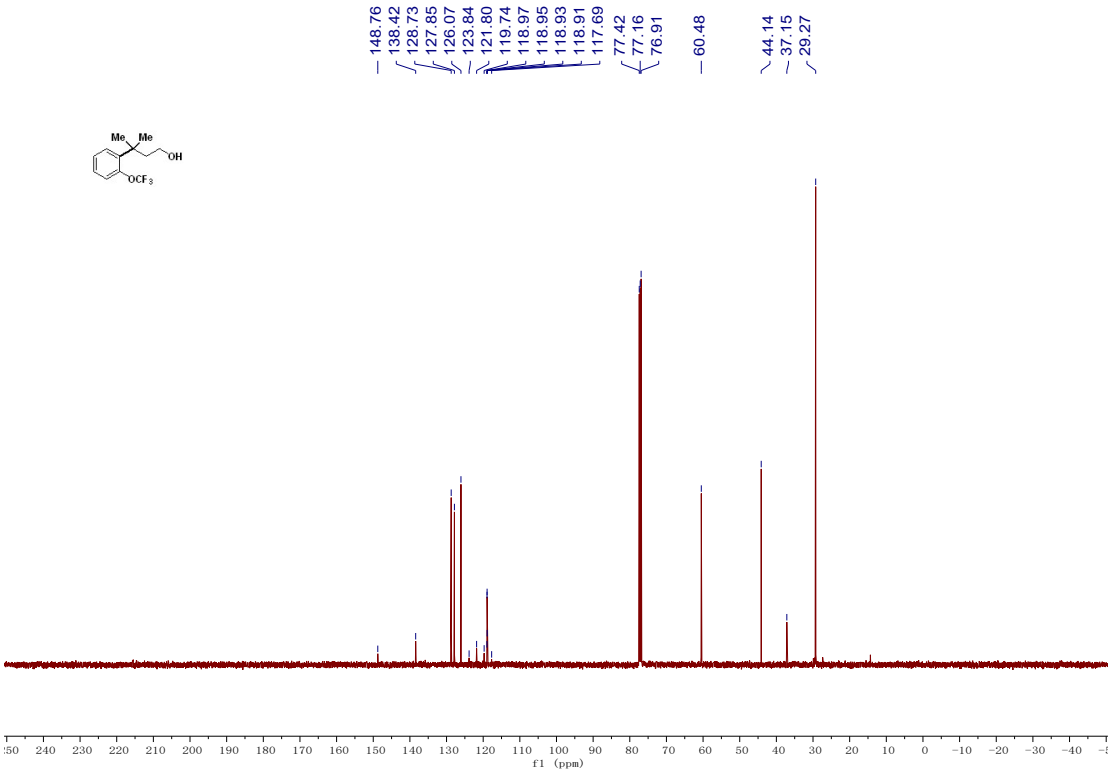


Figure S6. ^{19}F-NMR of **3a**

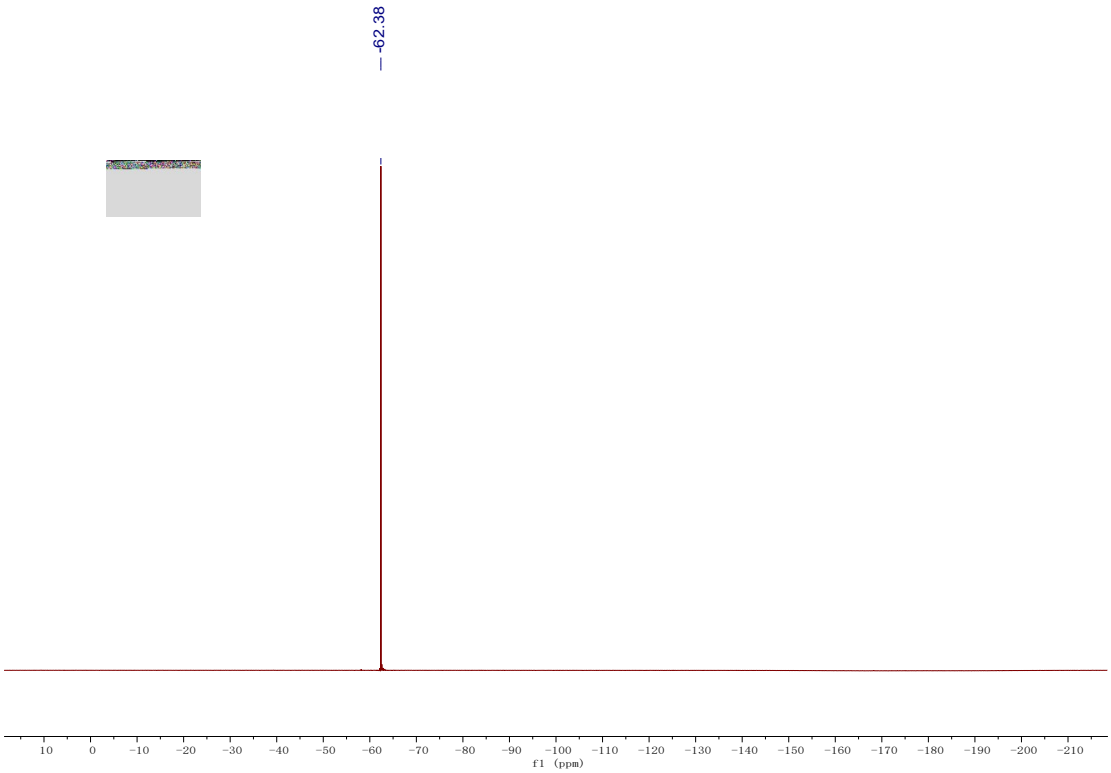


Figure S7. ^{1}H-NMR of **3b**

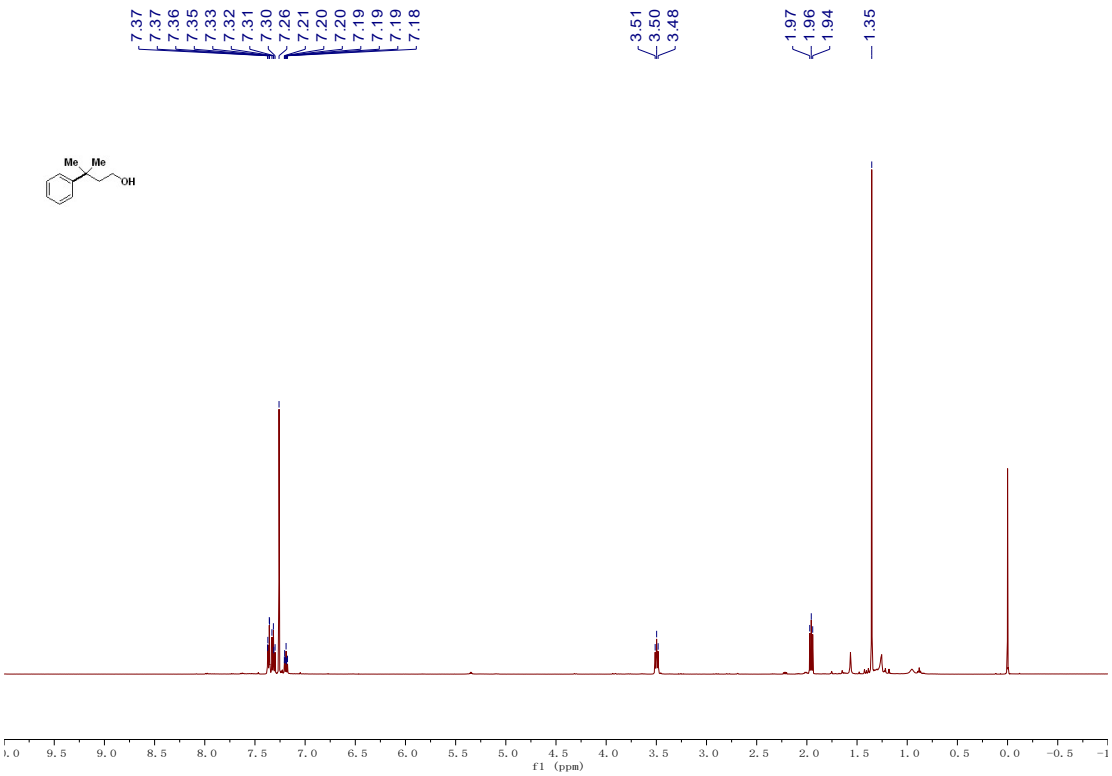


Figure S8. ^{13}C-NMR of **3b**

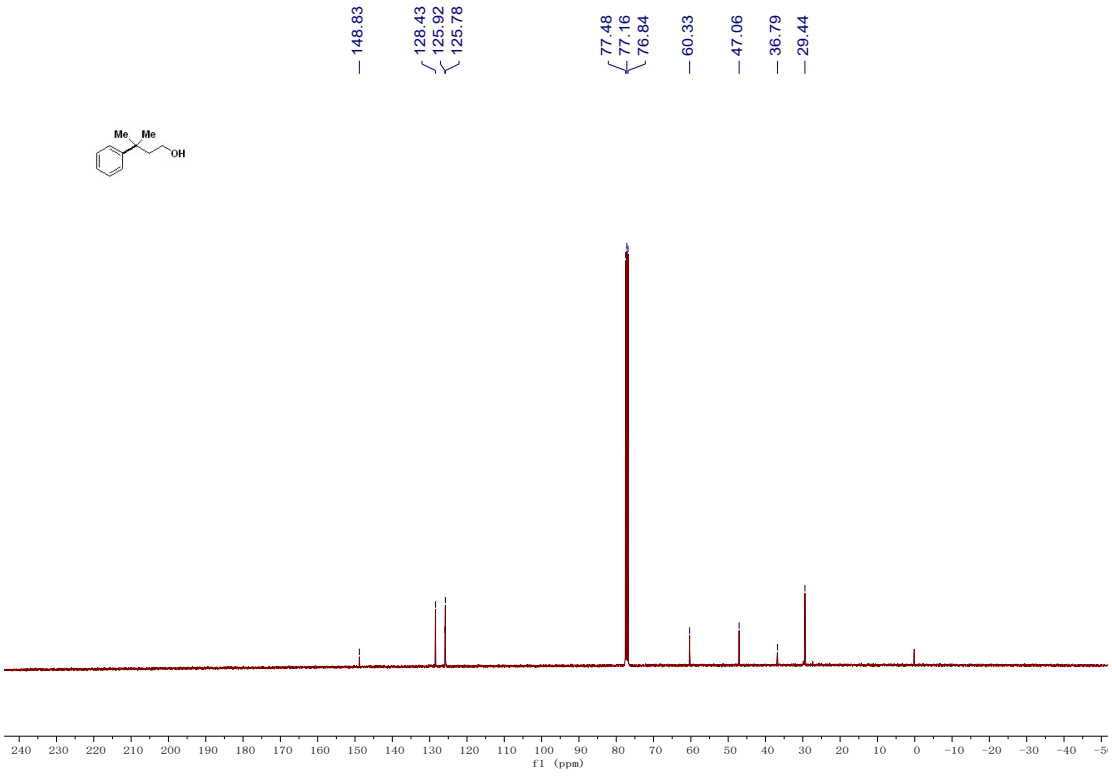


Figure S9. ^{1}H-NMR of **3c**

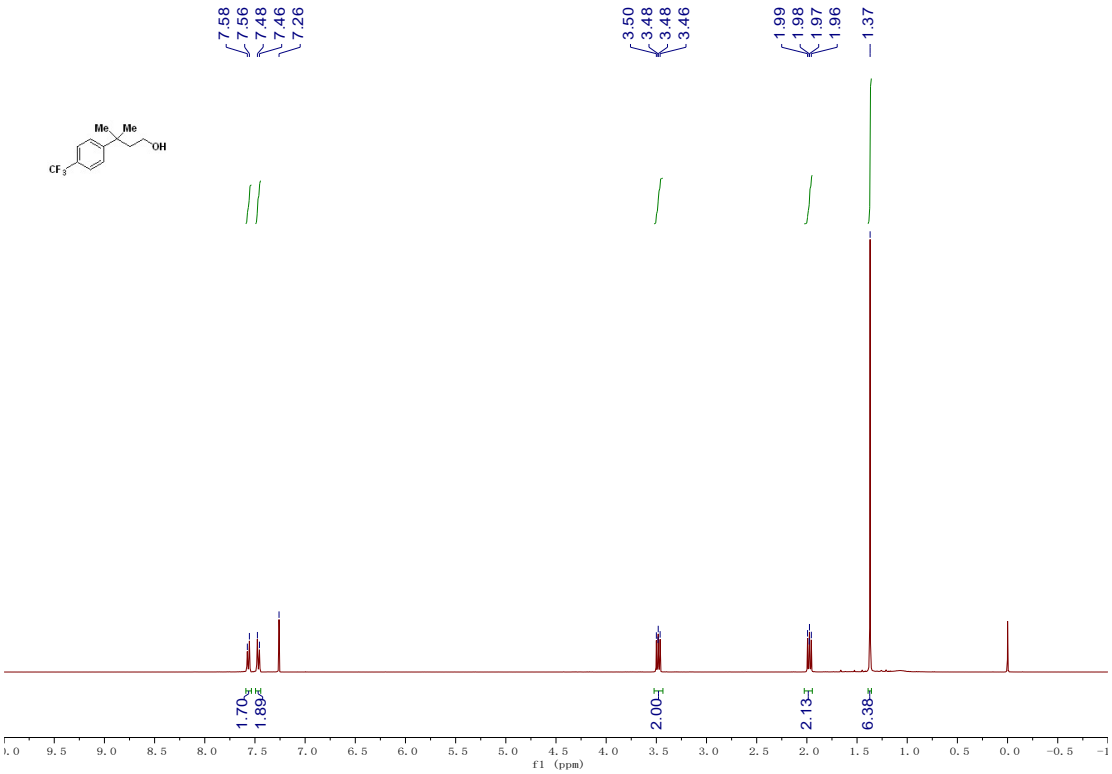


Figure S10. ^{13}C-NMR of **3c**

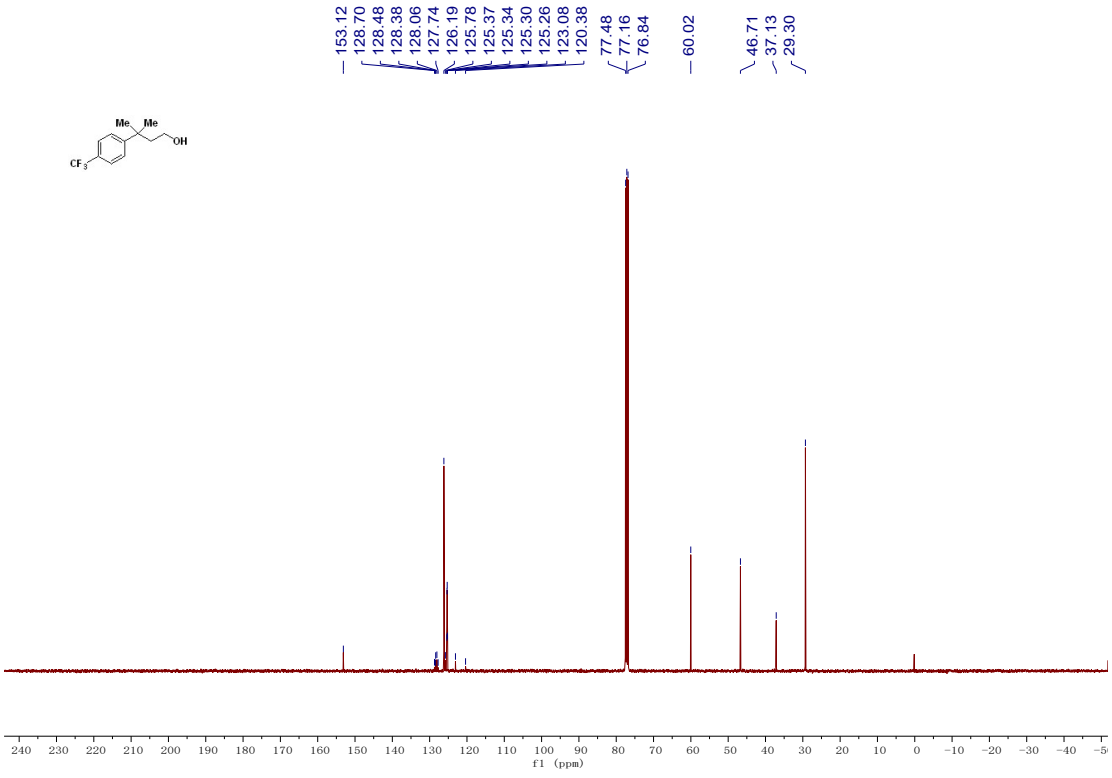


Figure S11. ^{19}F-NMR of **3c**

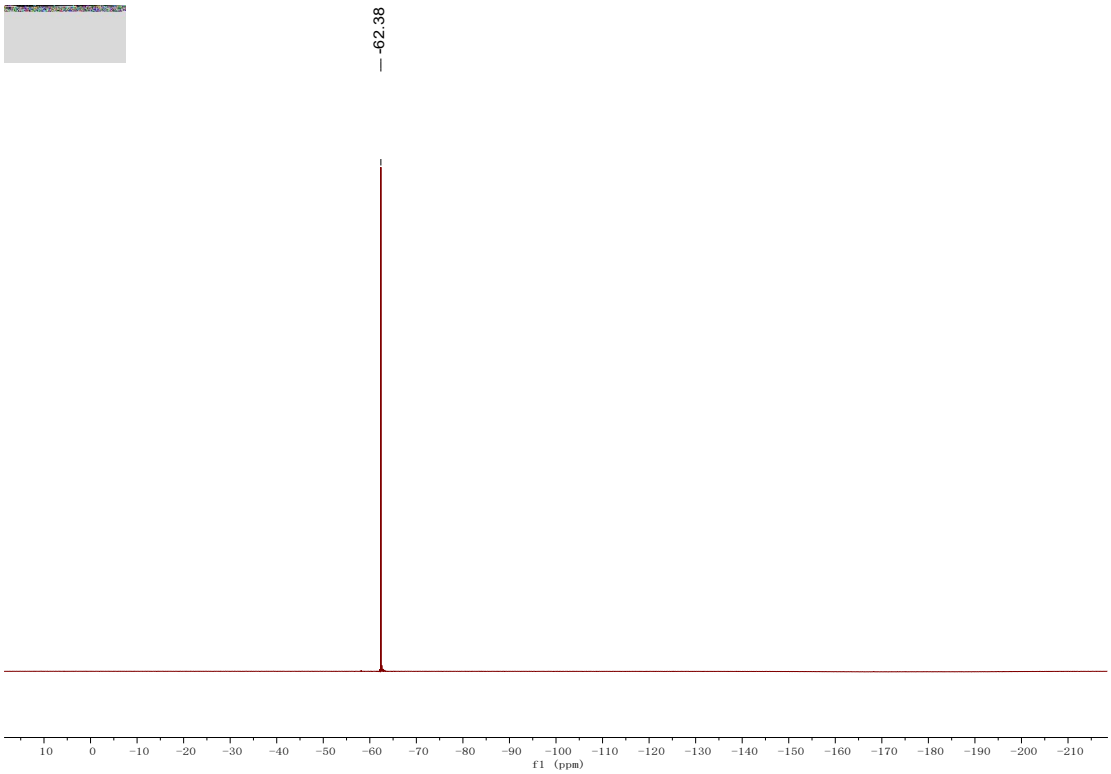


Figure S12. ^{1}H-NMR of **3d**

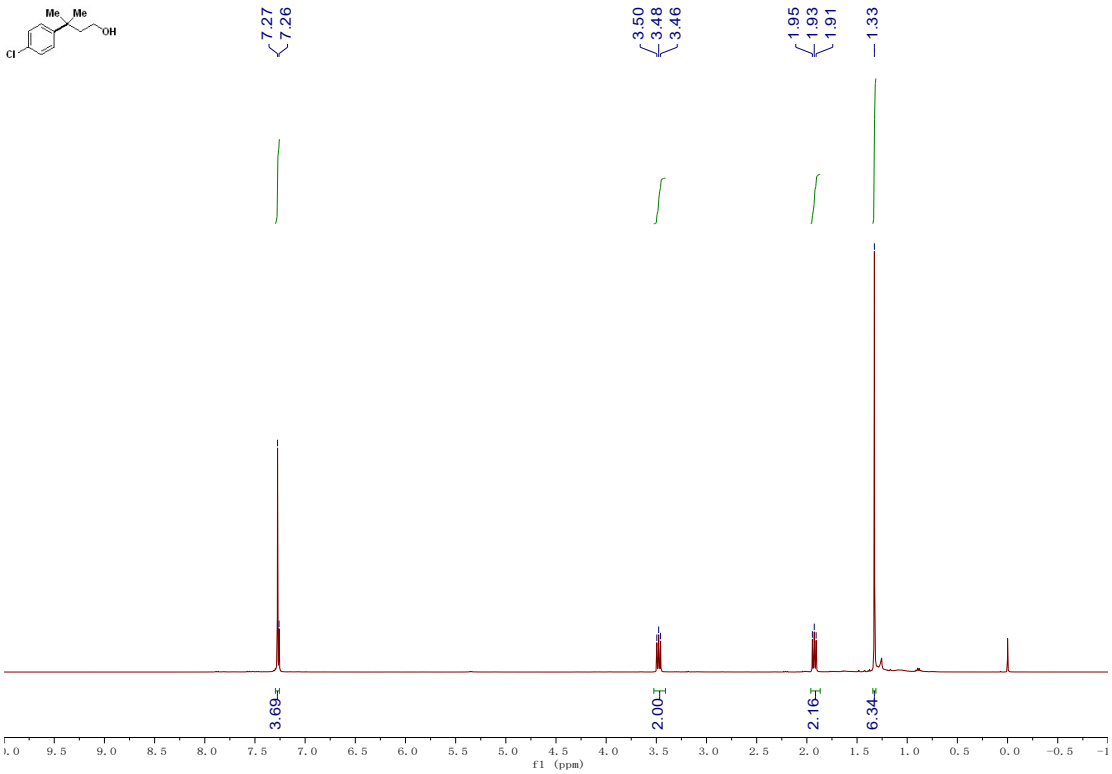


Figure S13. ^{13}C-NMR of **3d**

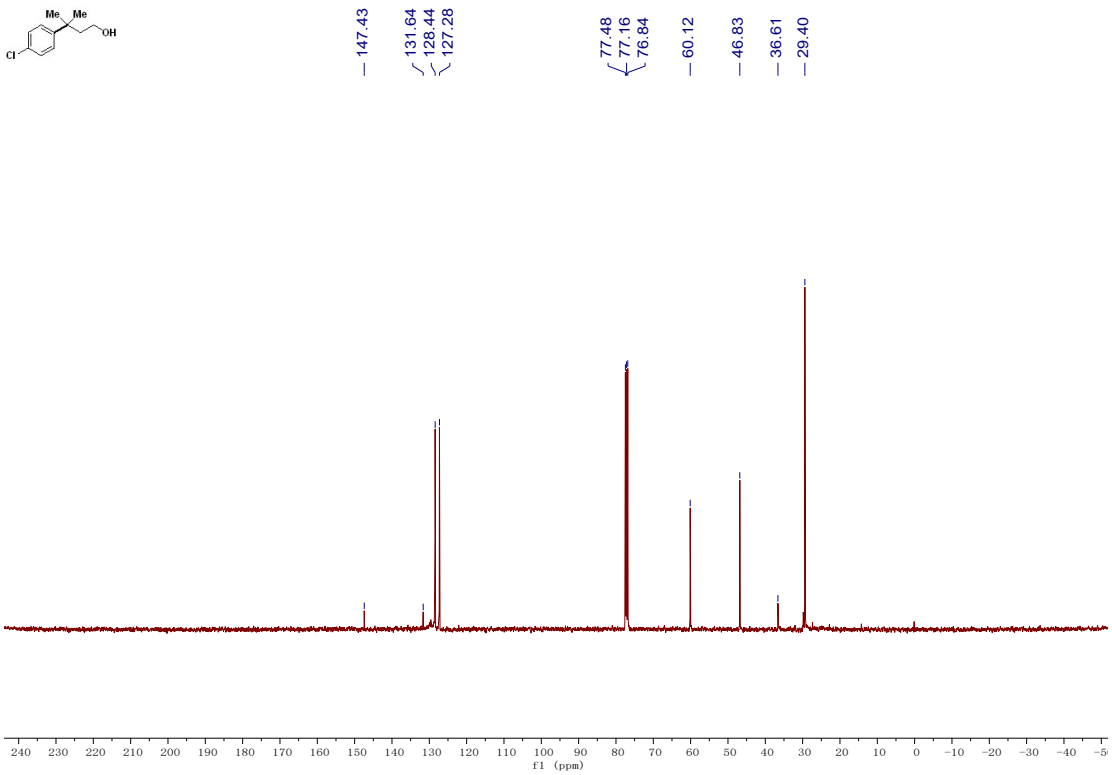


Figure S14. ^{1}H-NMR of **3e**

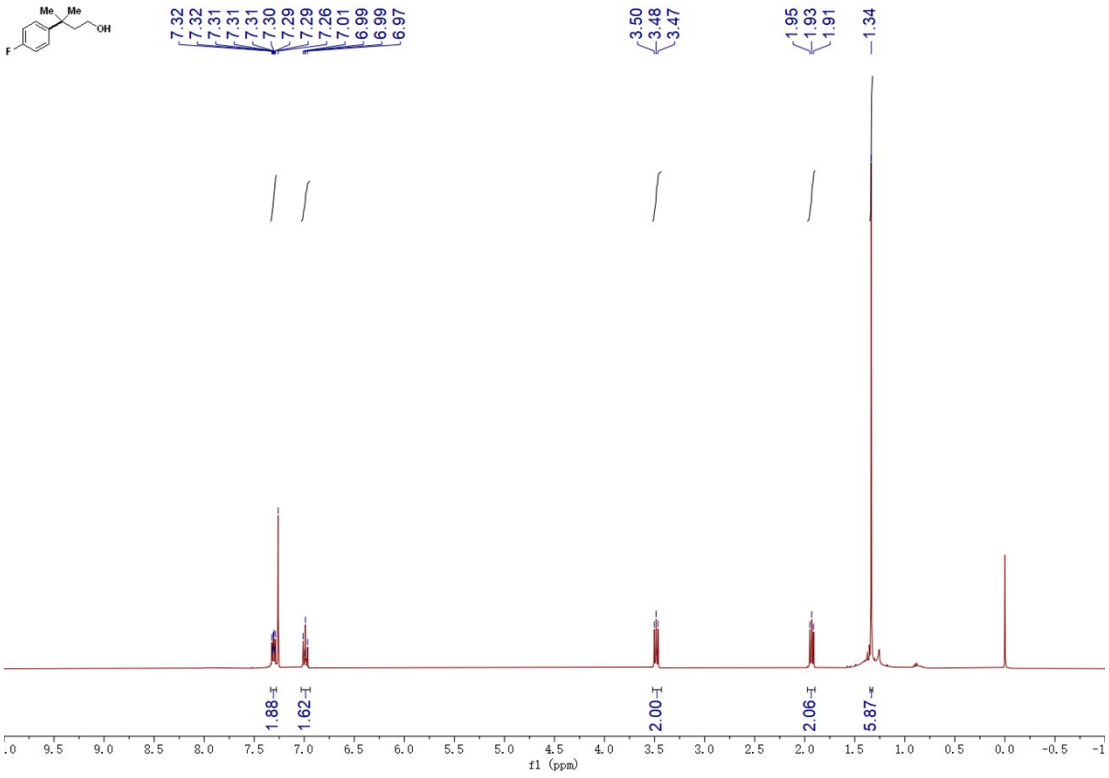


Figure S15. ^{13}C-NMR of **3e**

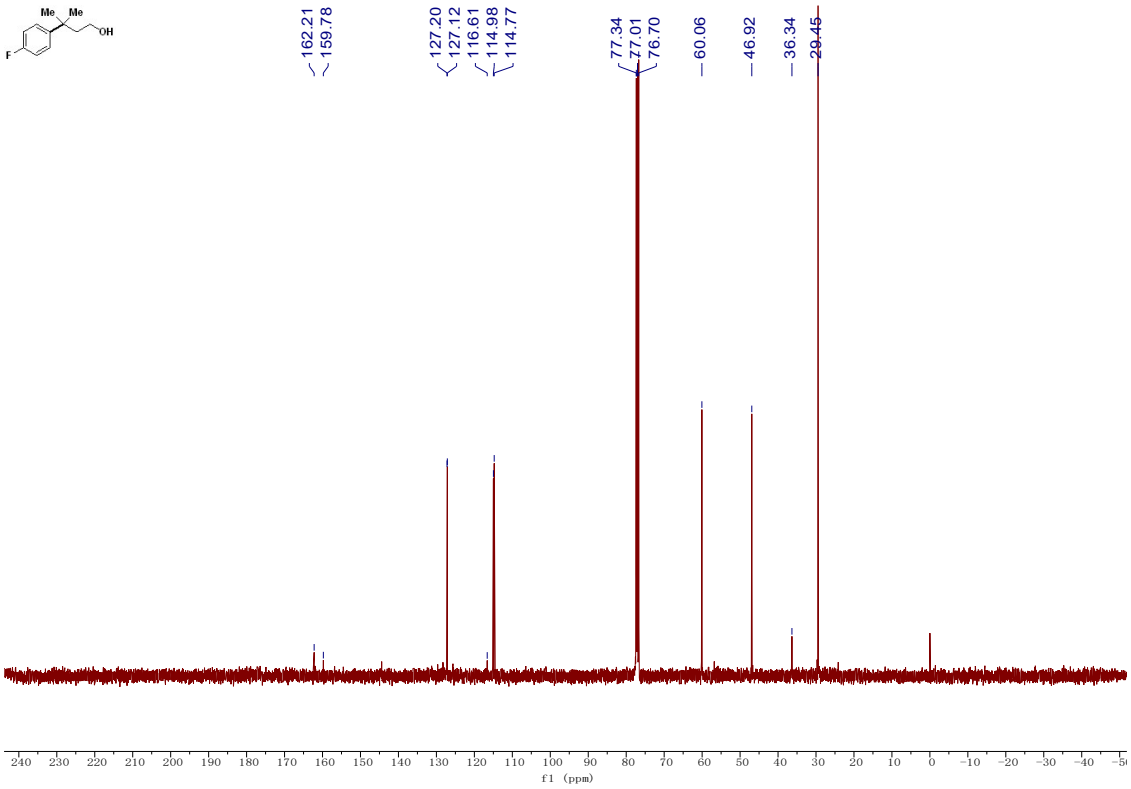


Figure S16. ^{19}F-NMR of **3e**

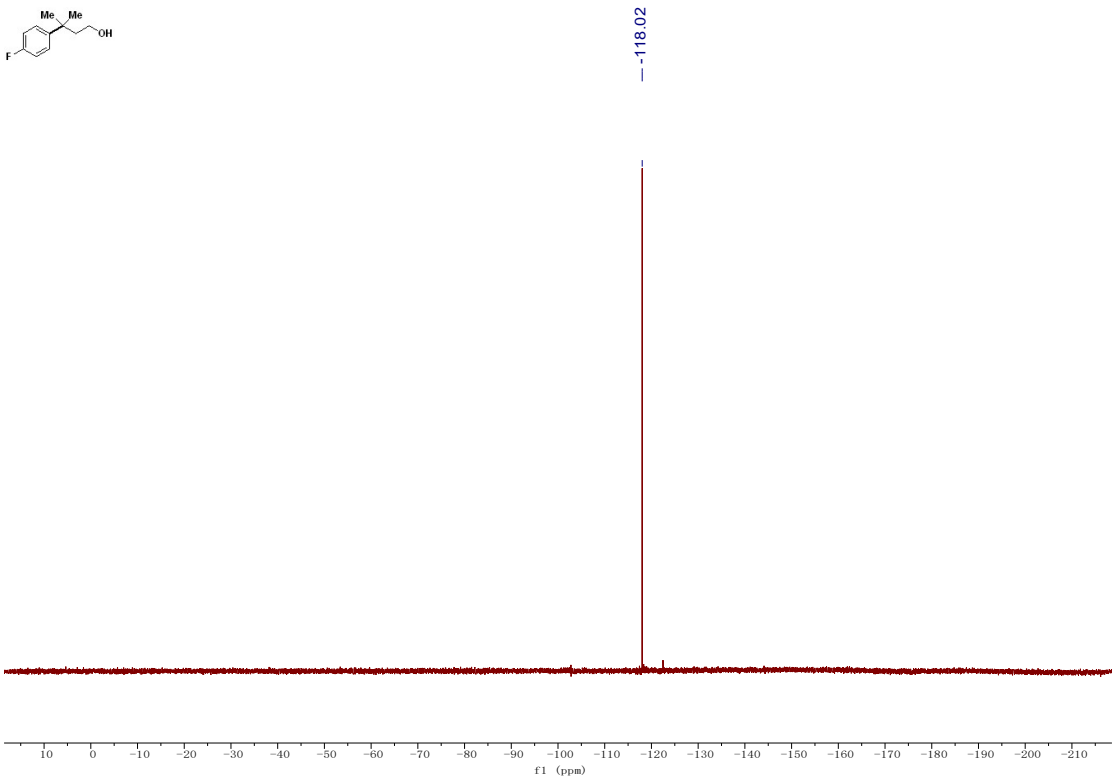


Figure S17. ^{1}H-NMR of **3f**

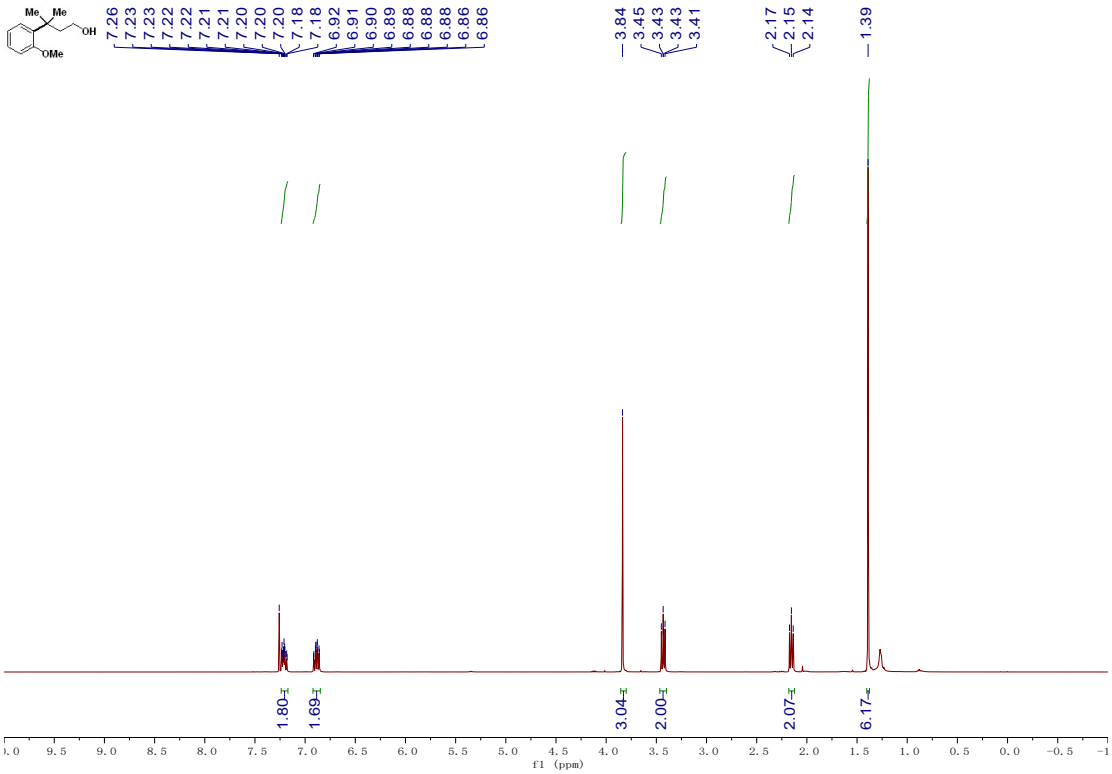


Figure S18. ^{13}C-NMR of **3f**

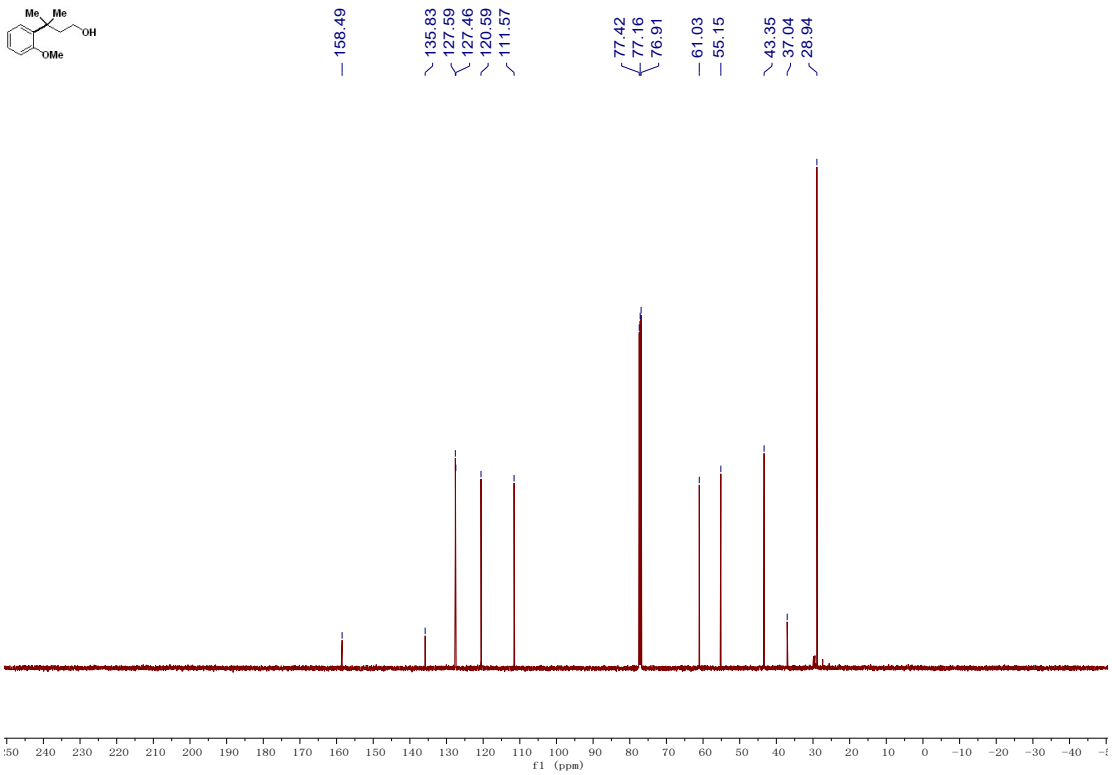


Figure S19. ^{1}H-NMR of **3g**

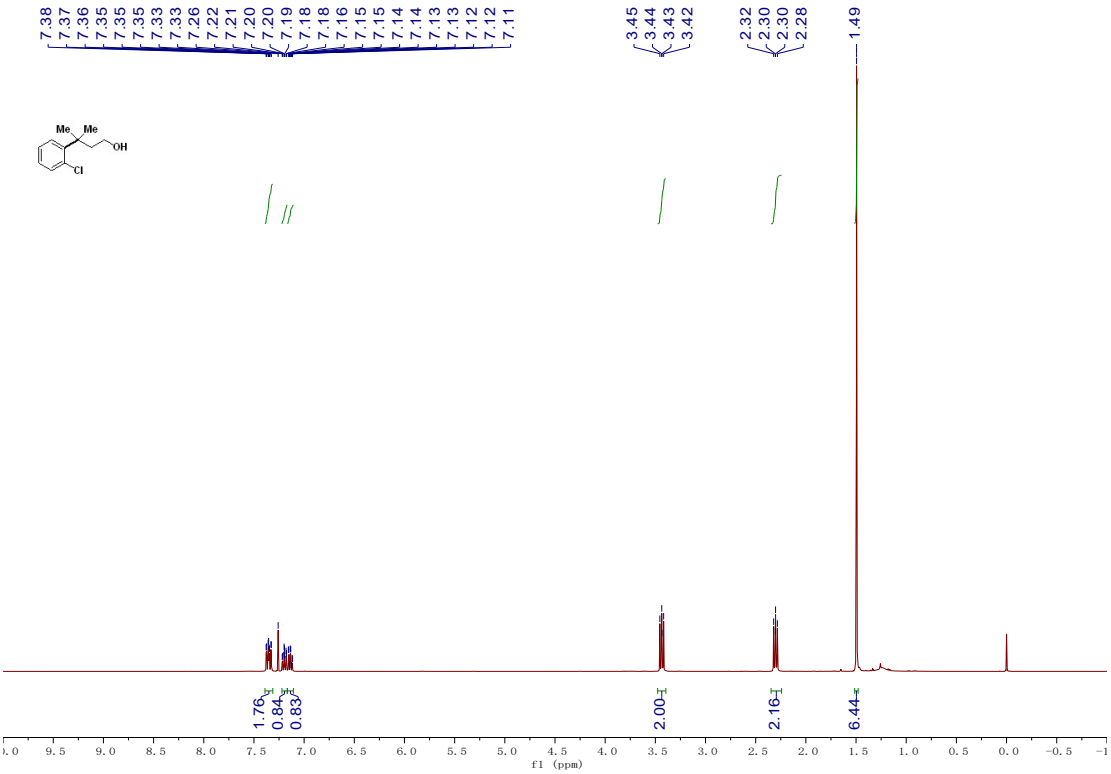


Figure S20. ^{13}C-NMR of **3g**

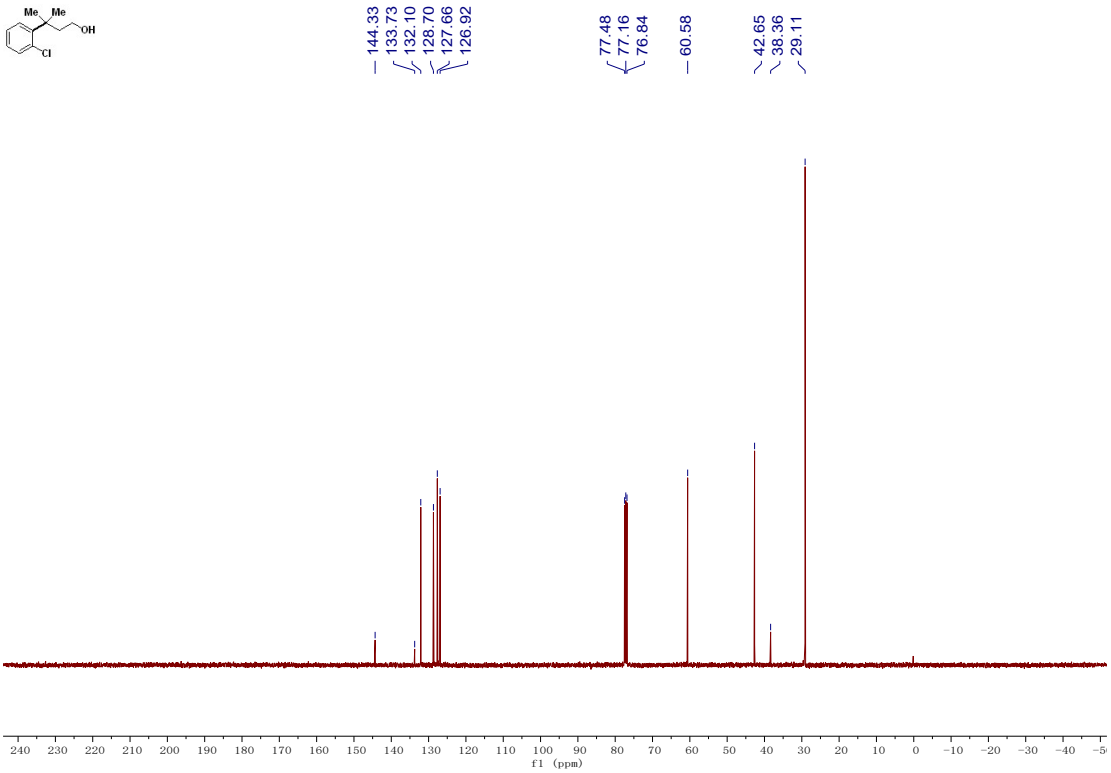


Figure S21. ^{1}H-NMR of **3h**

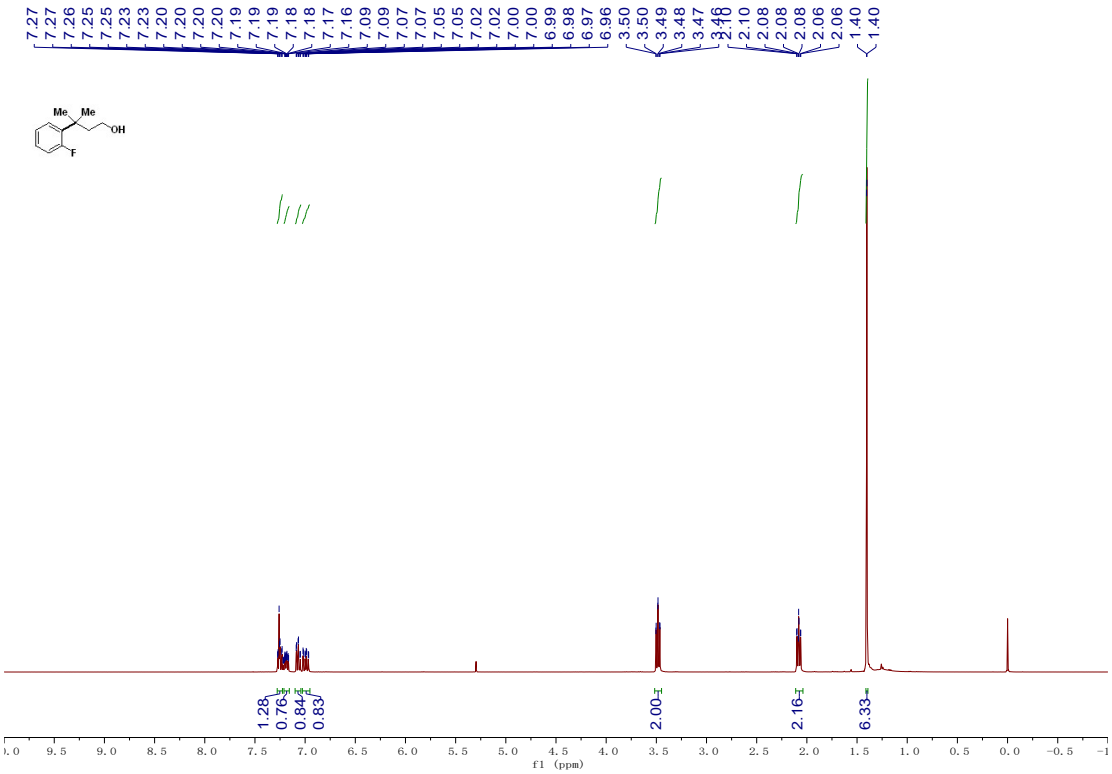


Figure S22. ^{13}C-NMR of **3h**

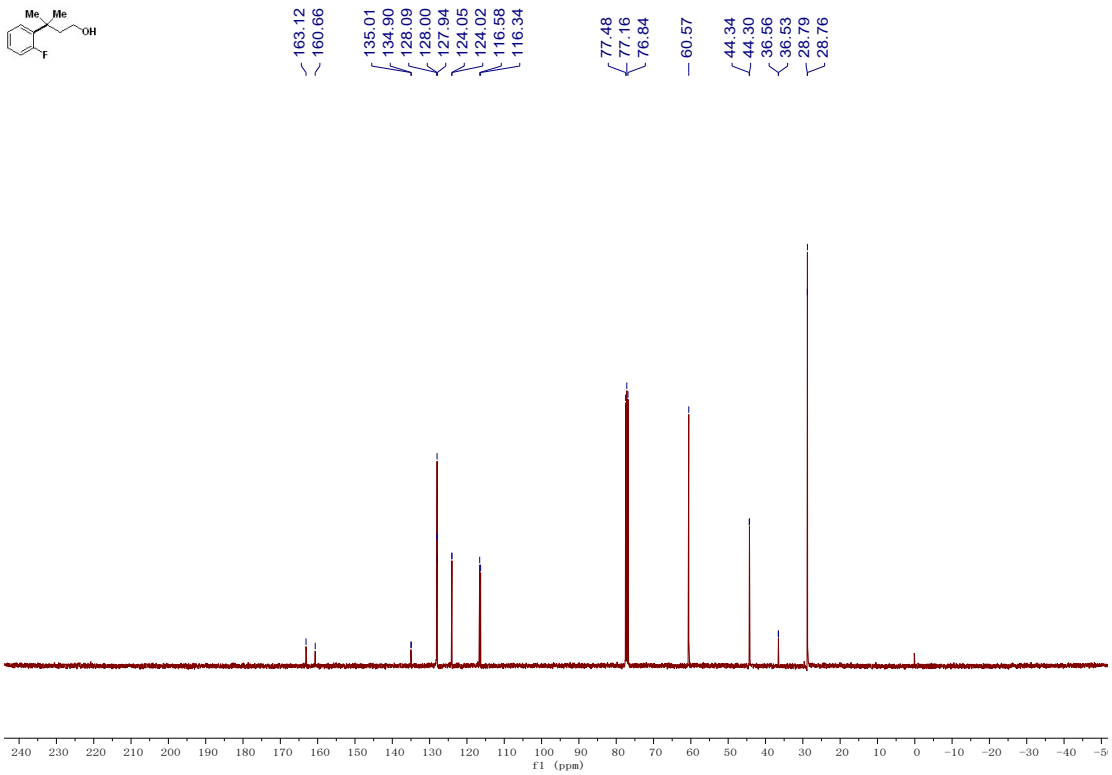


Figure S23. ^{19}F-NMR of **3h**

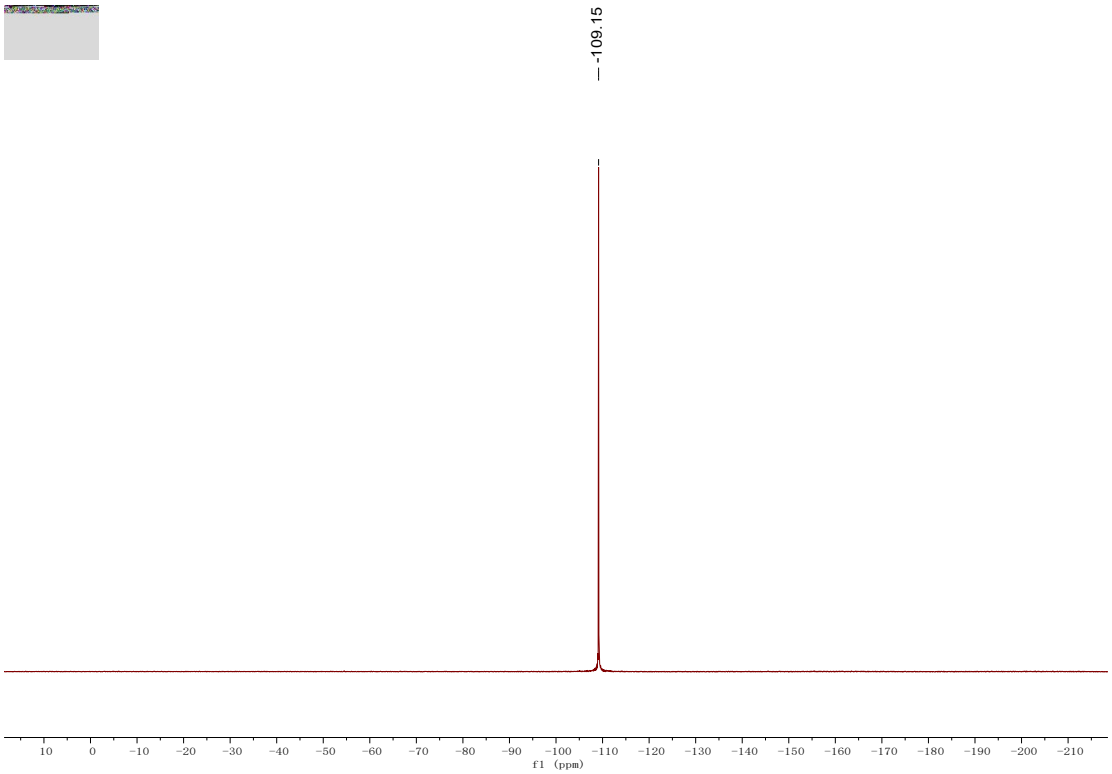


Figure S24. ^{1}H-NMR of **3i**

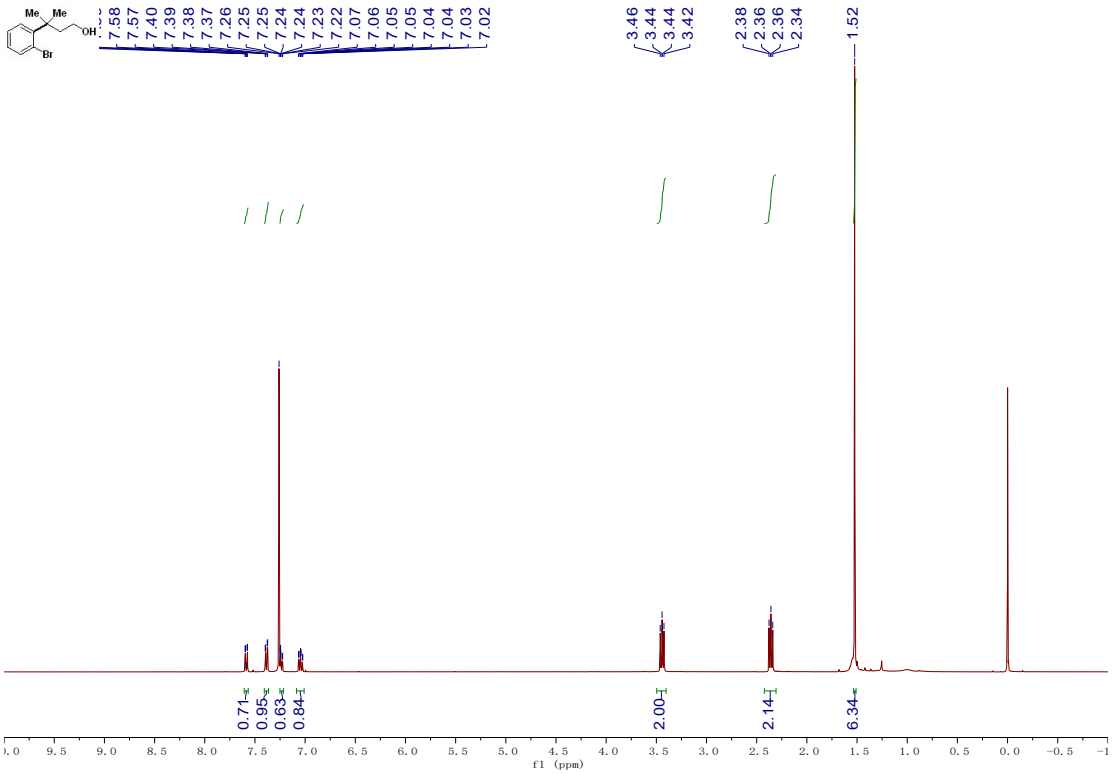


Figure S25. ^{13}C-NMR of **3i**

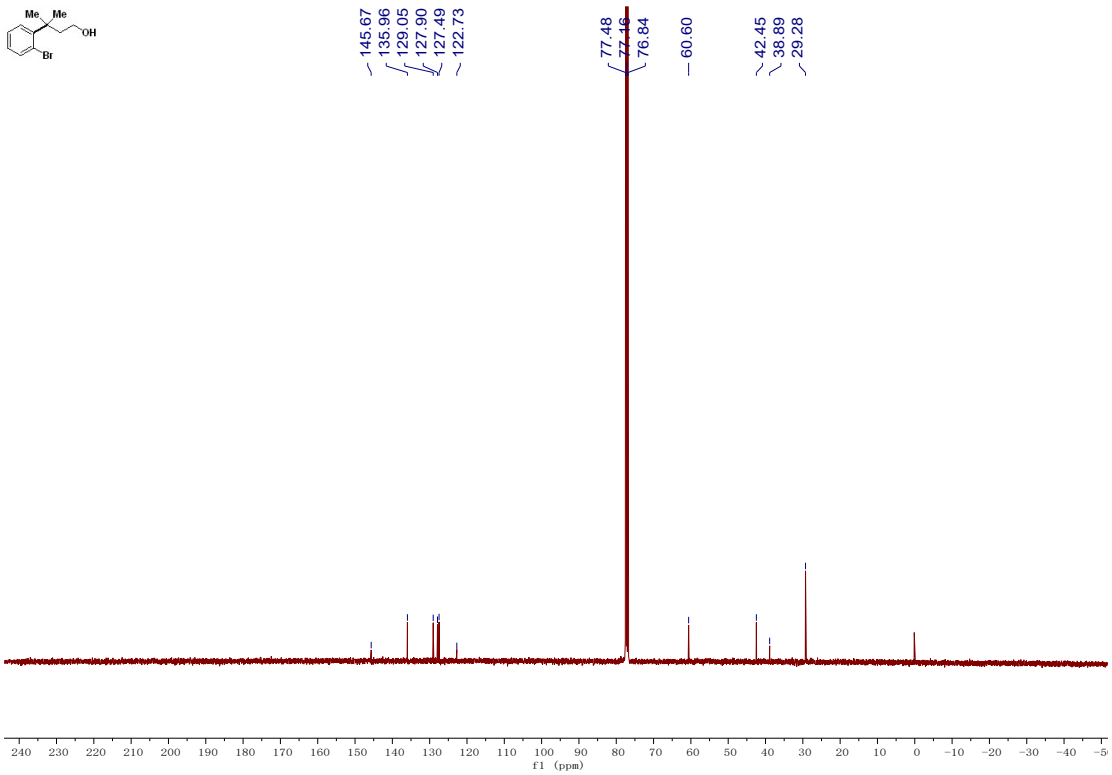


Figure S26. ^{1}H-NMR of **3j**

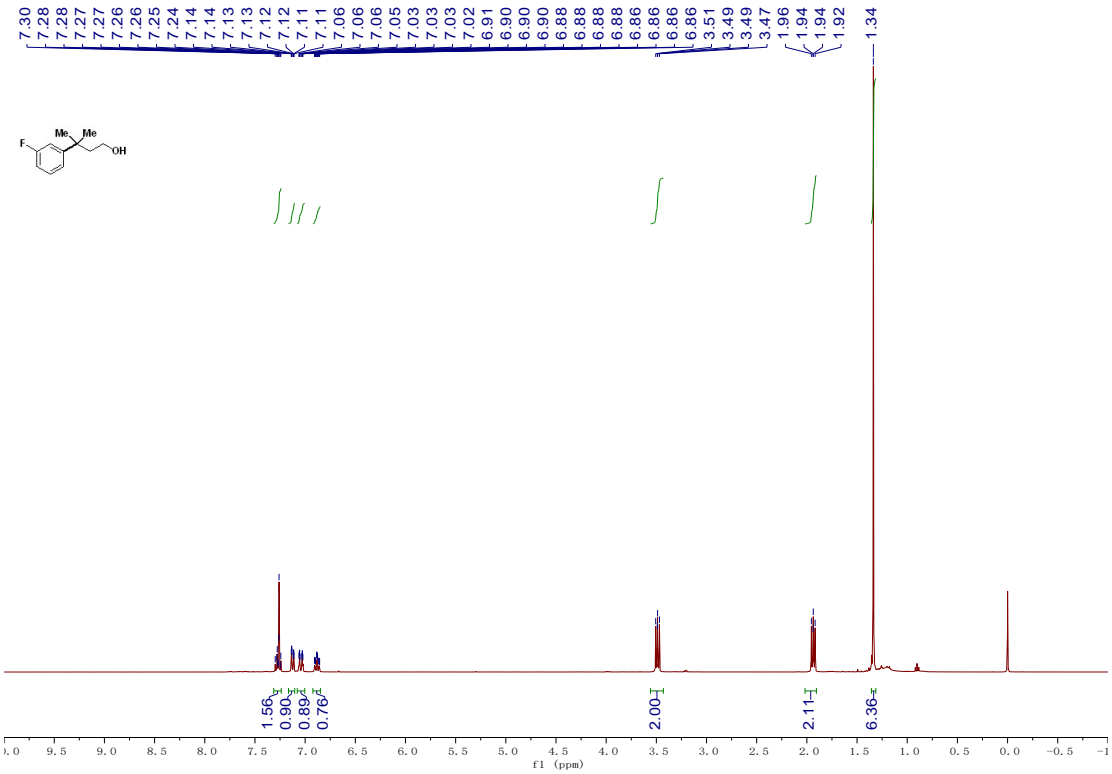


Figure S27. ^{13}C-NMR of **3j**

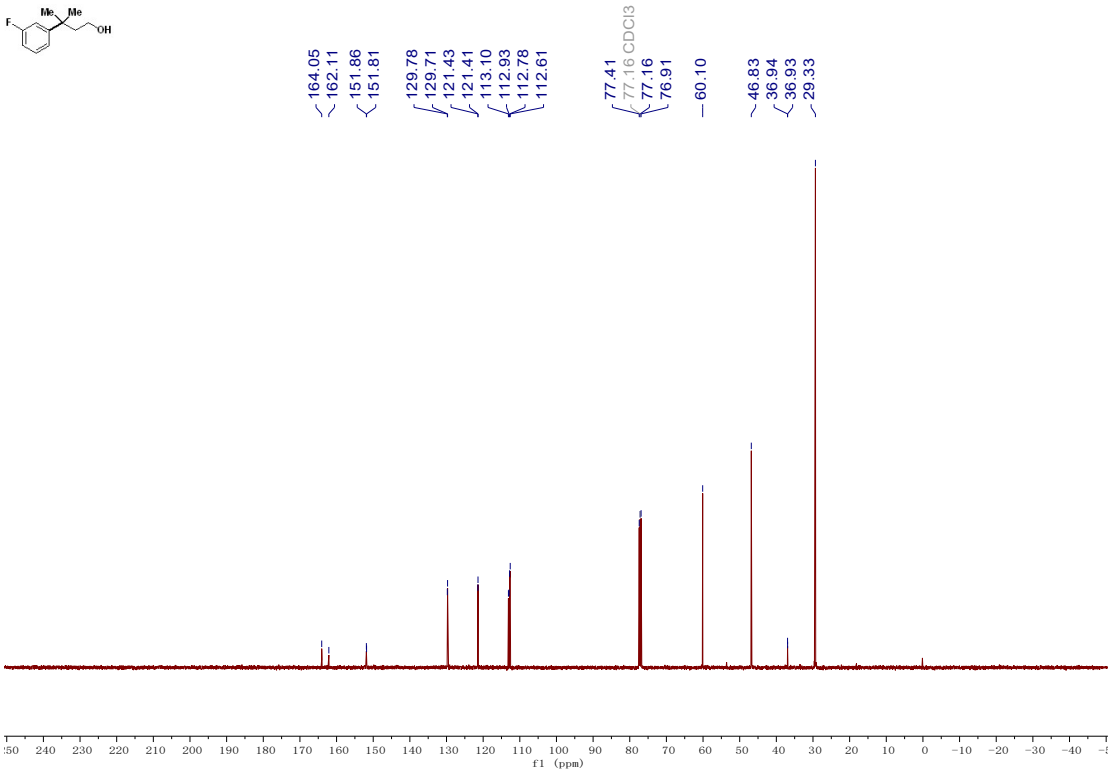


Figure S28. ^{19}F-NMR of **3j**

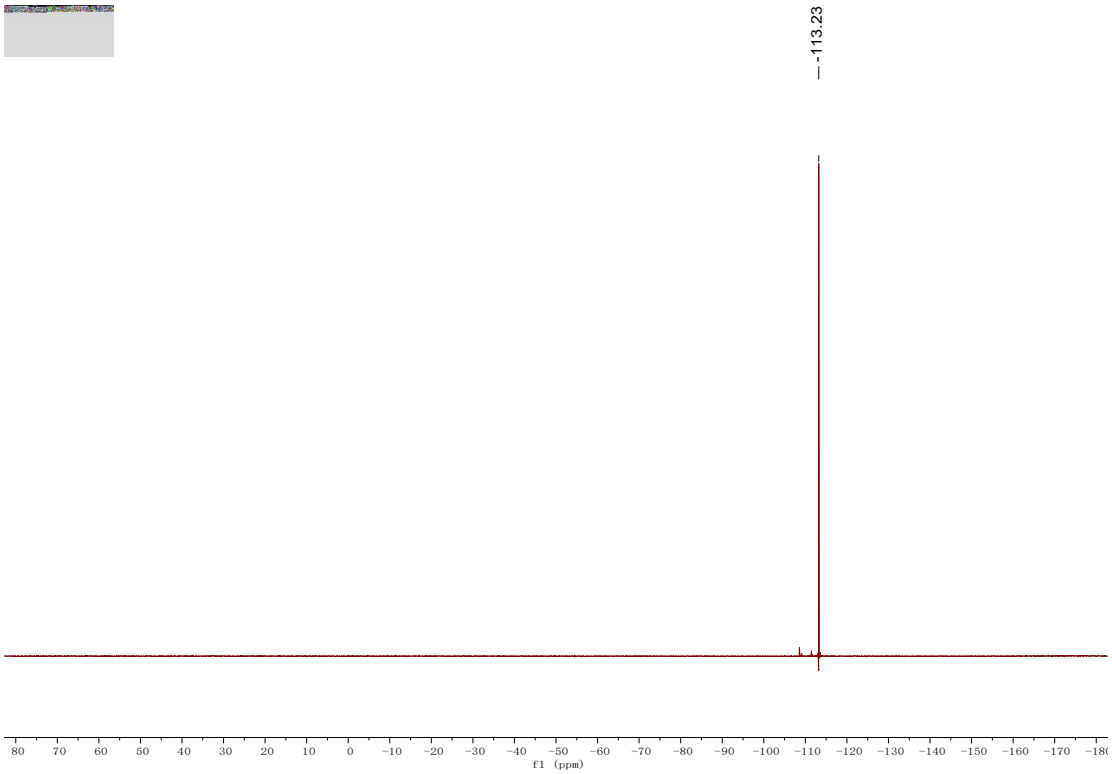


Figure S29. ^{1}H-NMR of **3k**

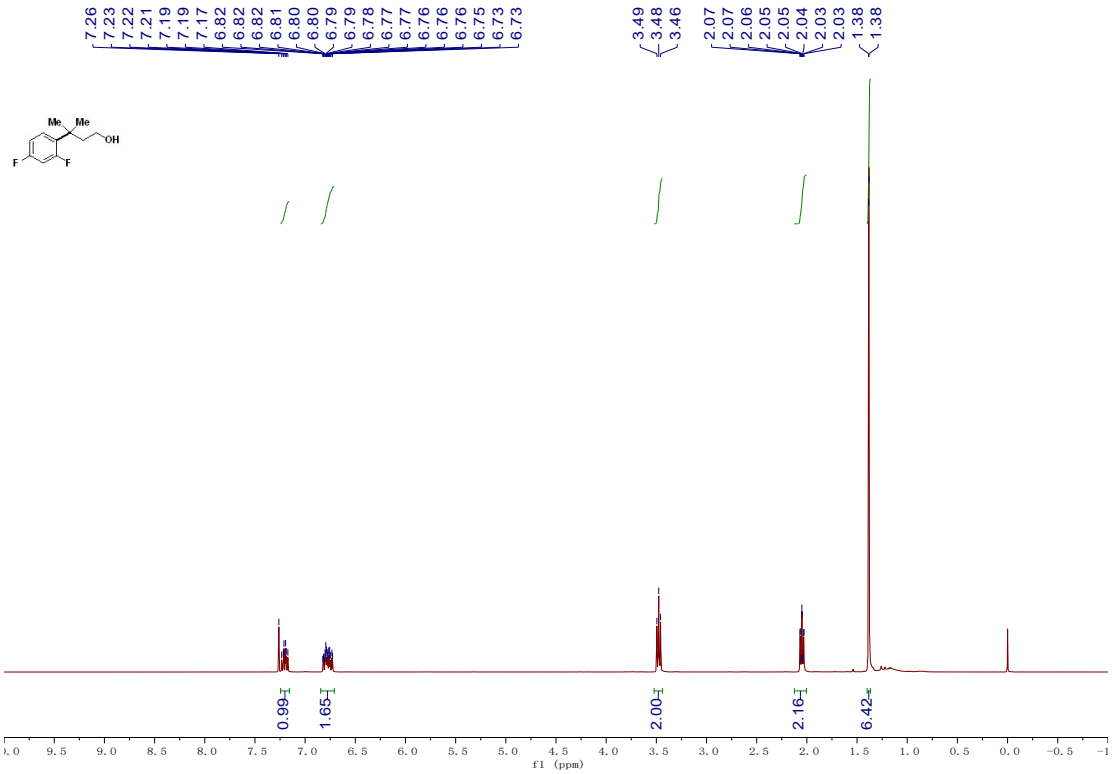


Figure S30. ^{13}C-NMR of **3k**

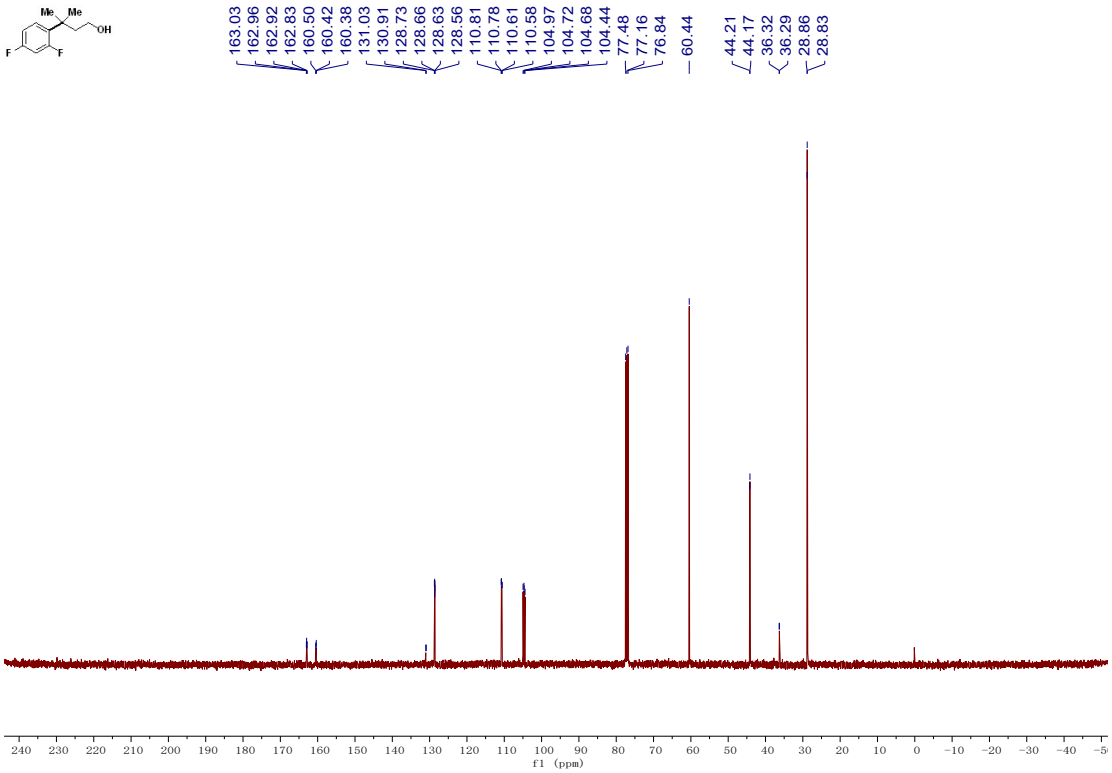


Figure S31. ^{19}F-NMR of **3k**

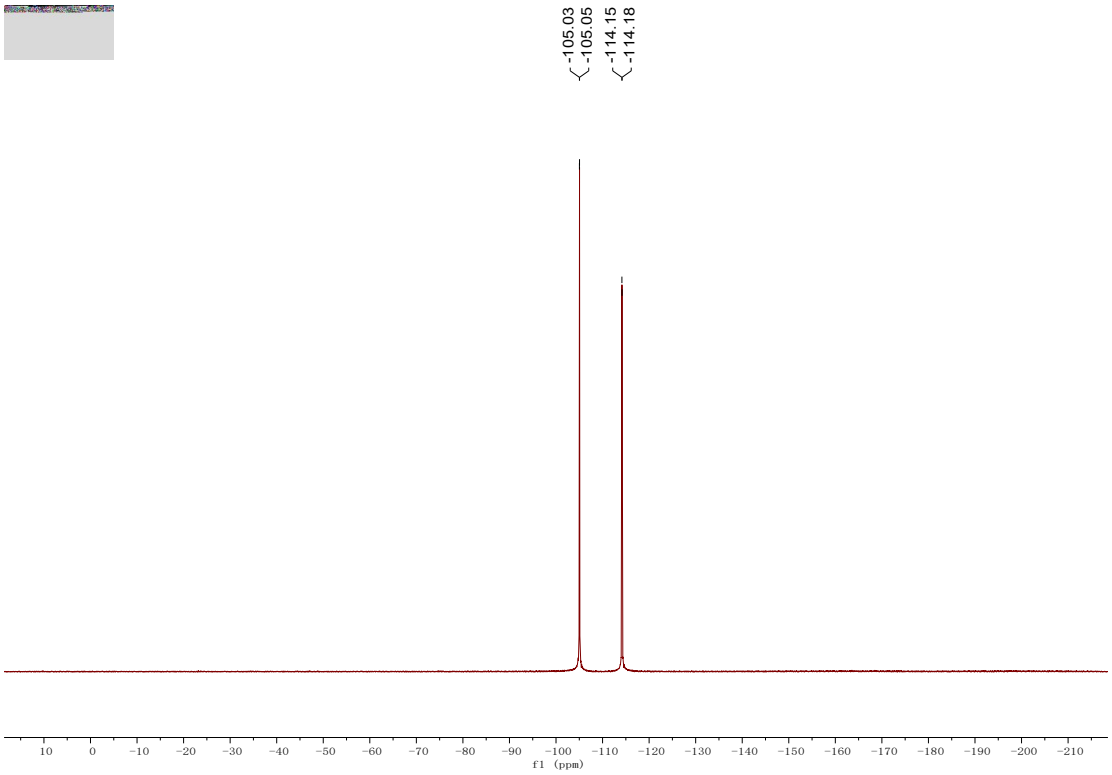


Figure S32. ^{1}H-NMR of **3l**

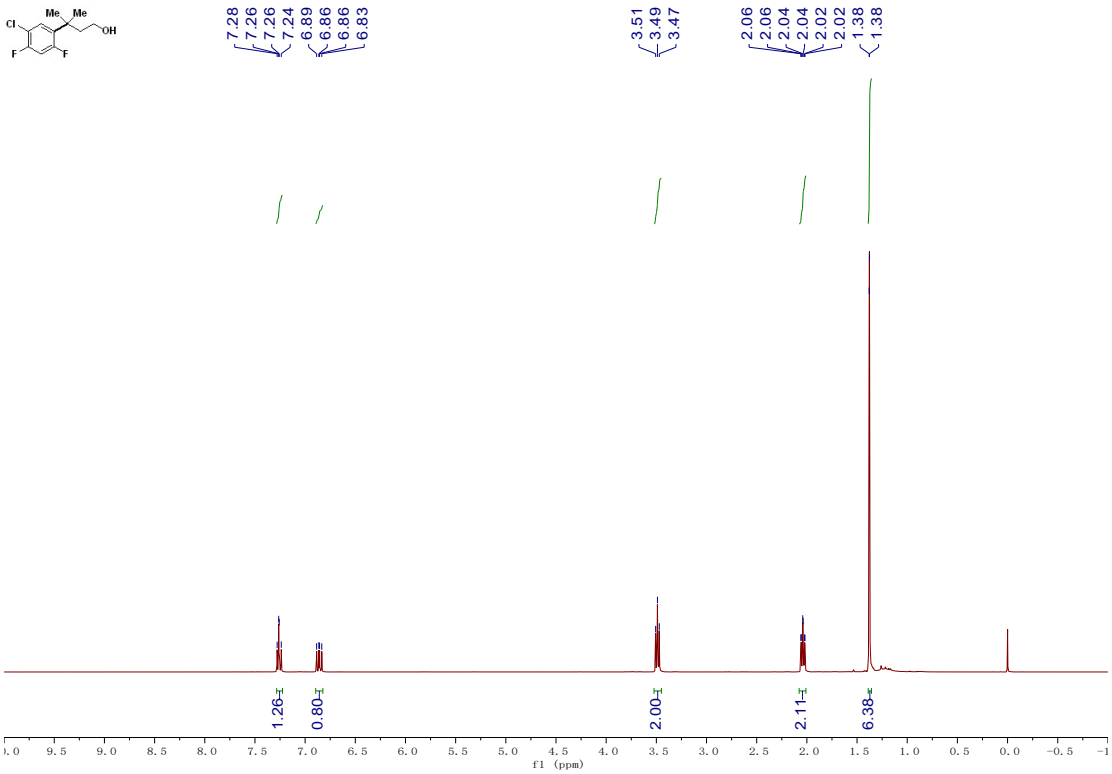


Figure S33. ^{13}C-NMR of **3l**

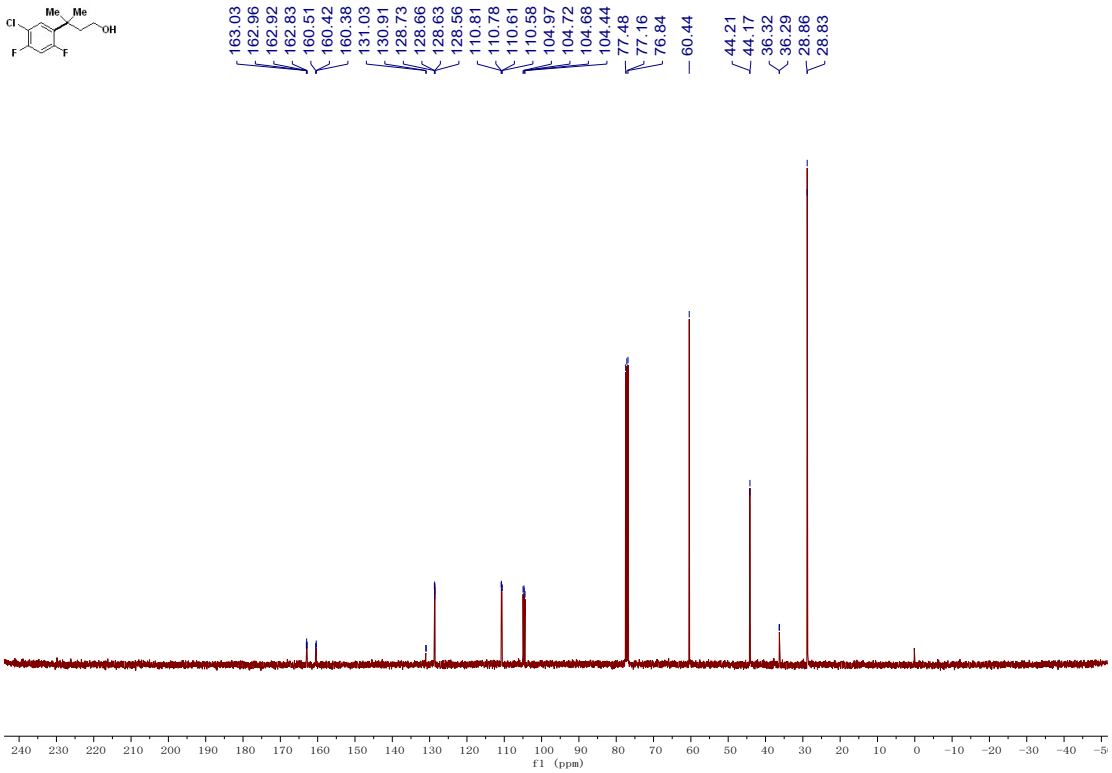


Figure S34. ^{19}F-NMR of **3l**

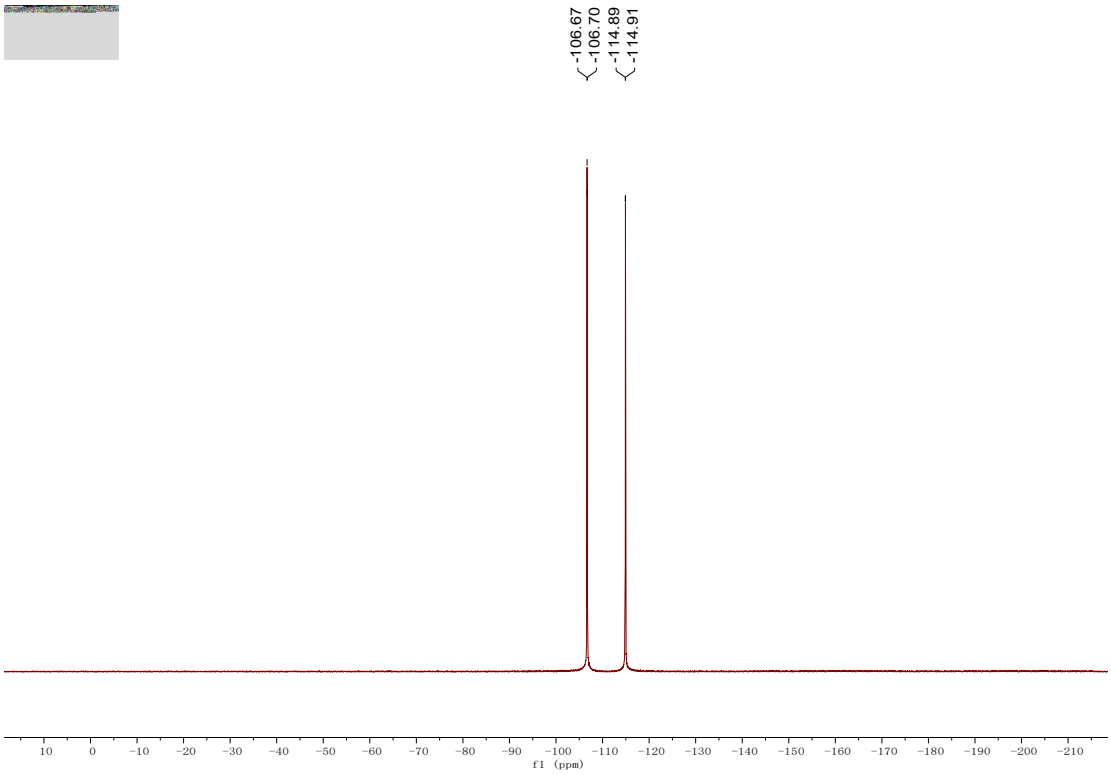


Figure S35. ^{1}H-NMR of **3m**

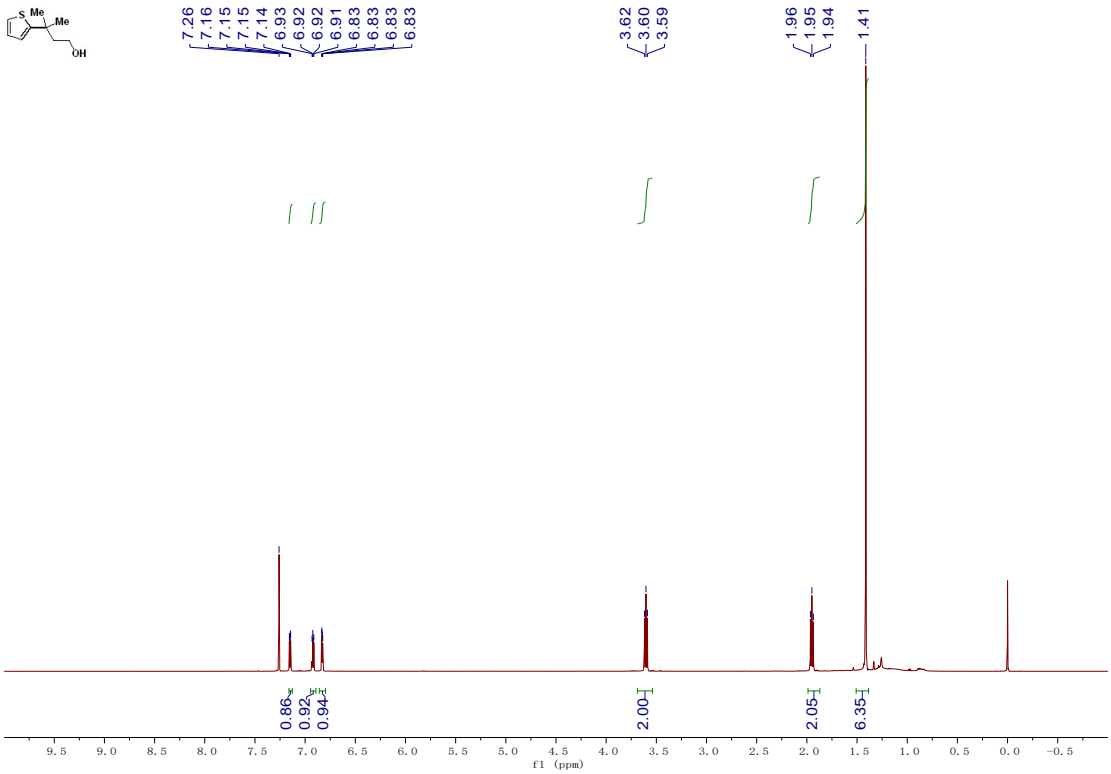


Figure S36. ^{13}C-NMR of **3m**

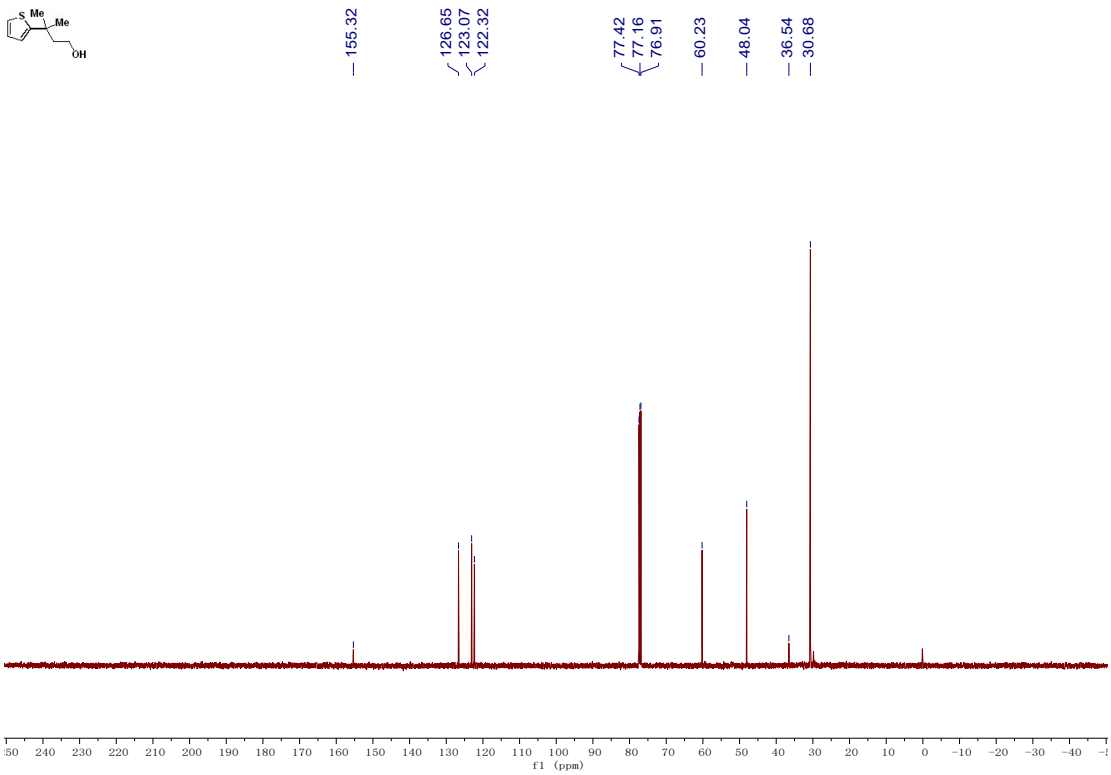


Figure S37. ^{1}H-NMR of **3n**

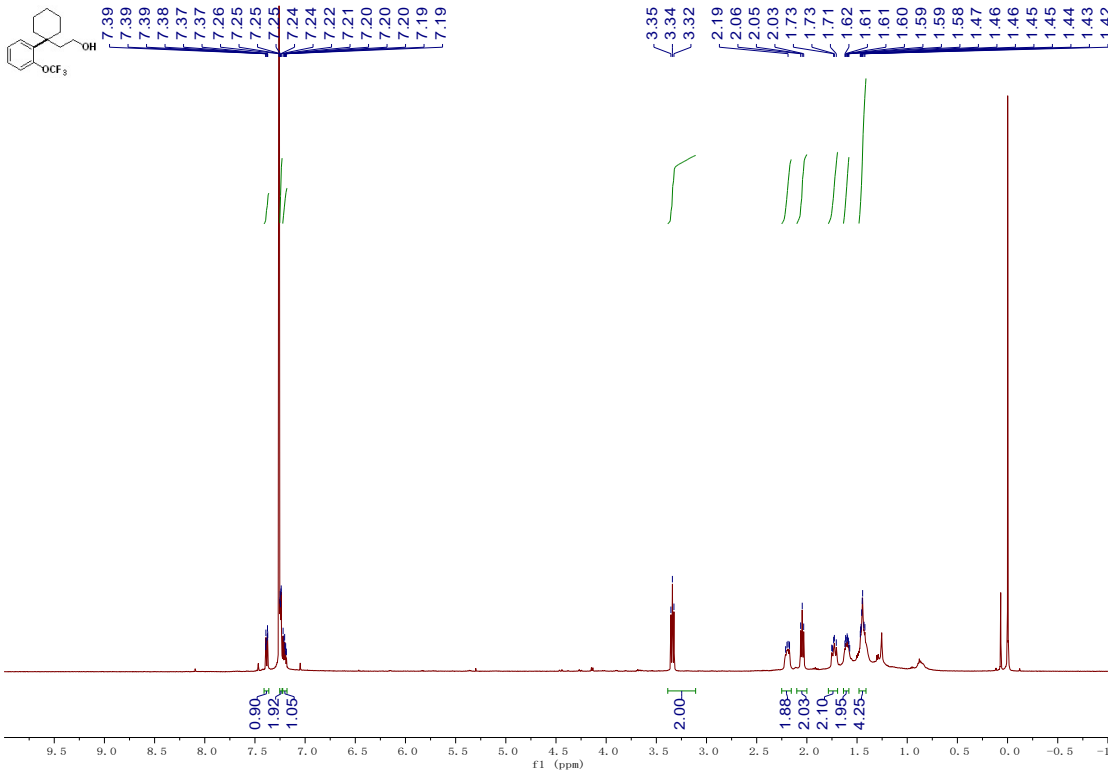


Figure S38. ^{13}C-NMR of **3n**

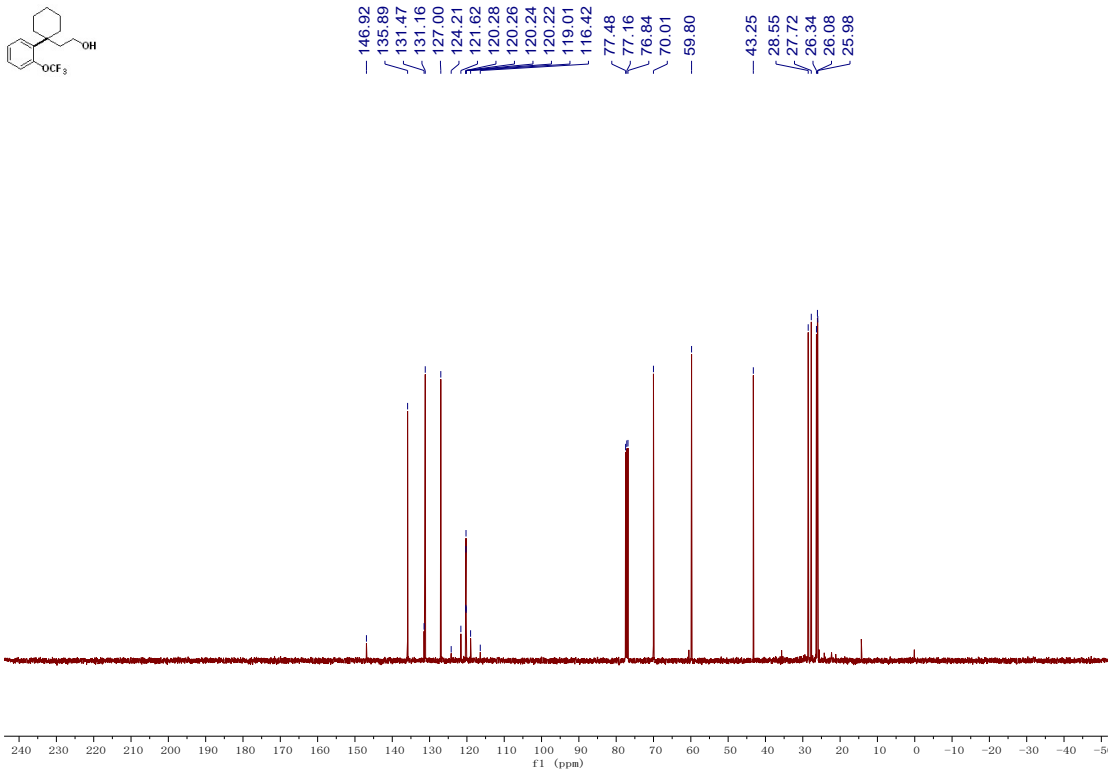


Figure S39. ^{19}F-NMR of **3n**

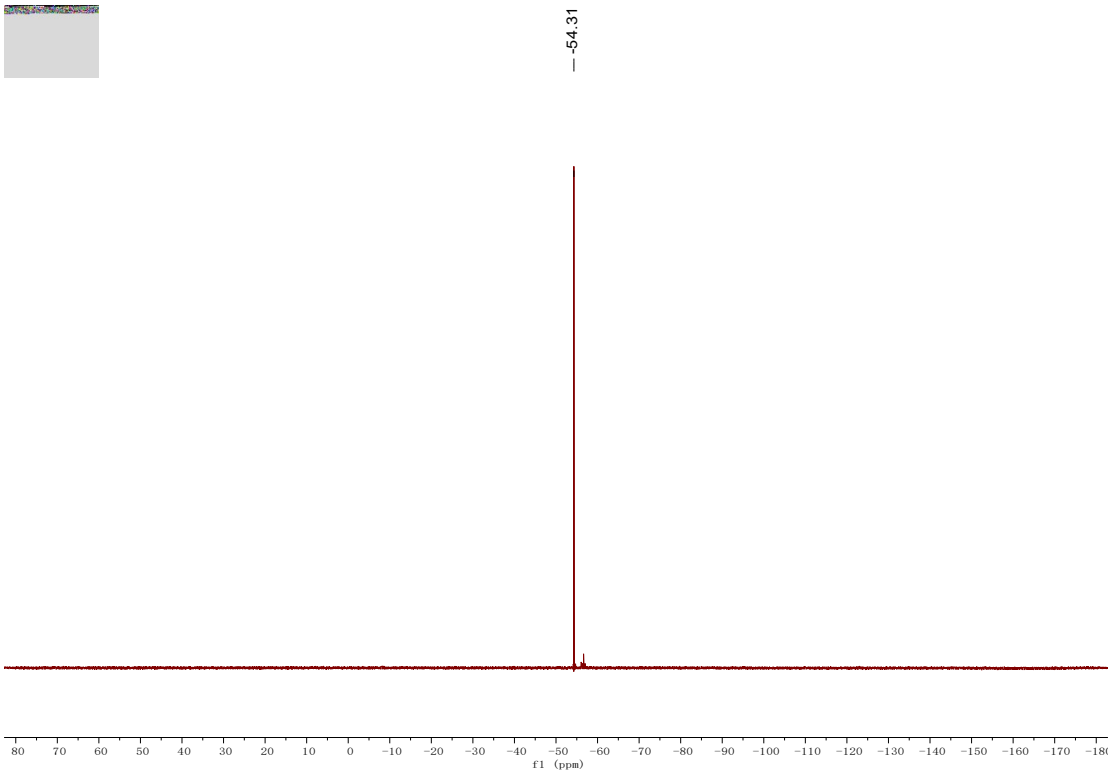


Figure S40. ^{1}H-NMR of **3o**

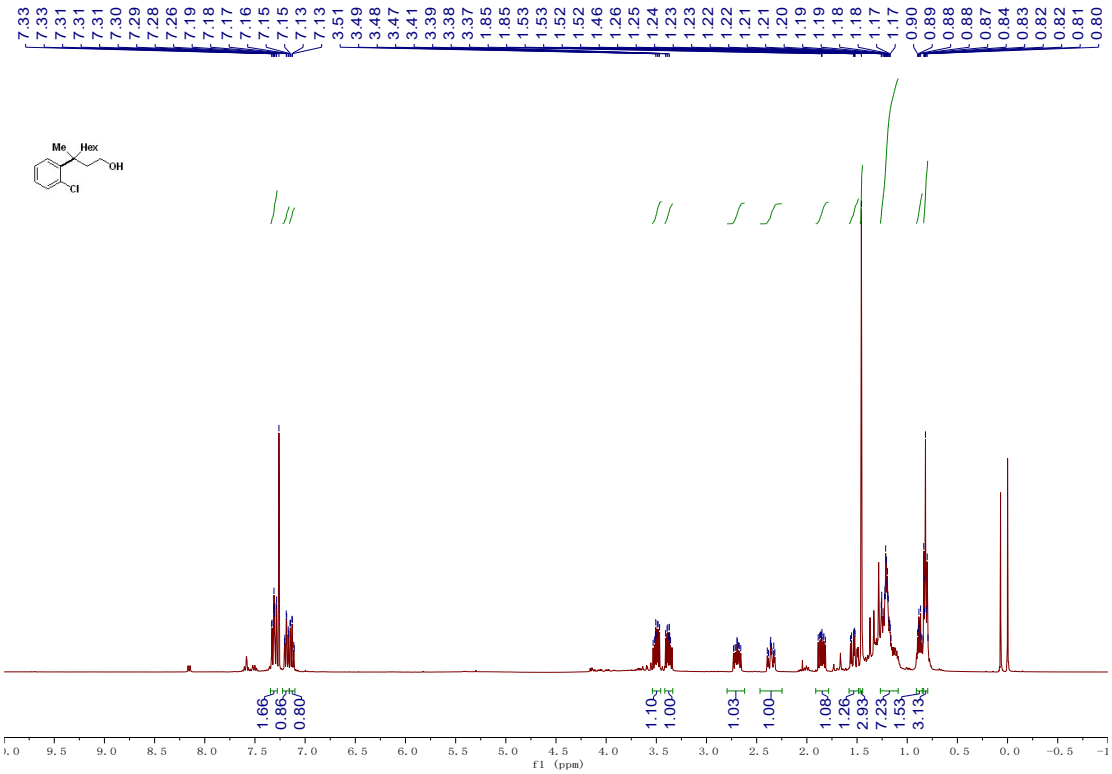


Figure S41. ^{13}C-NMR of **3o**

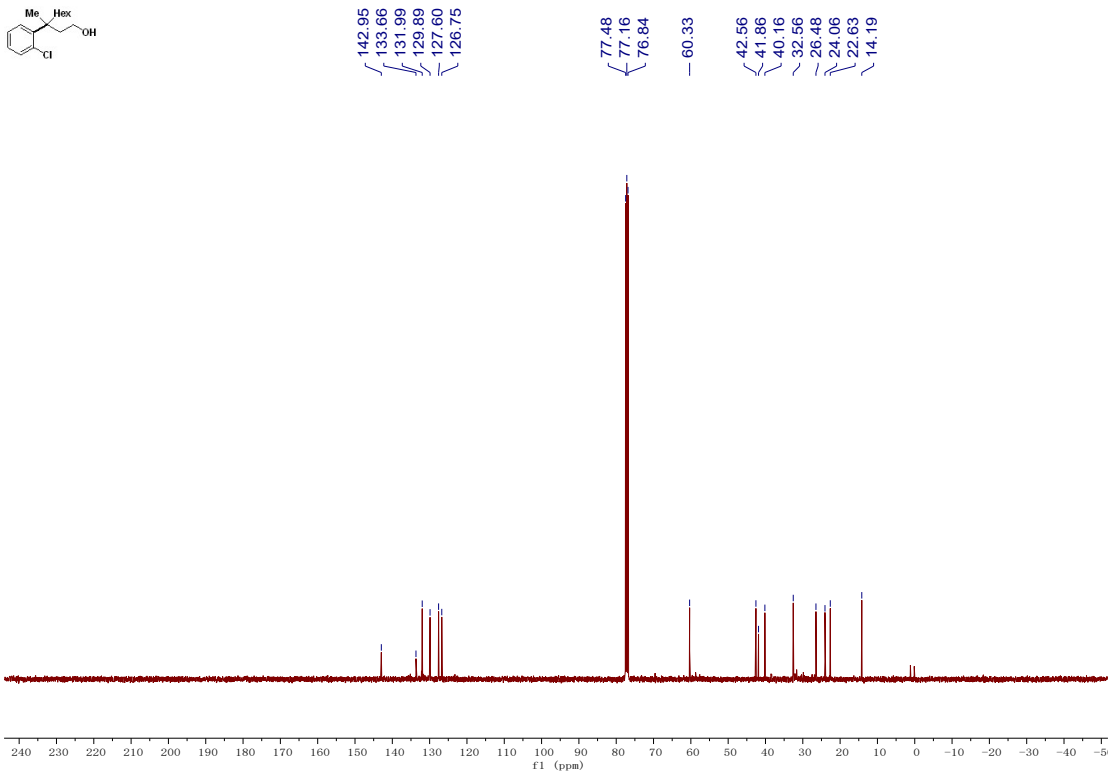


Figure S42. ^{1}H-NMR of **3p**

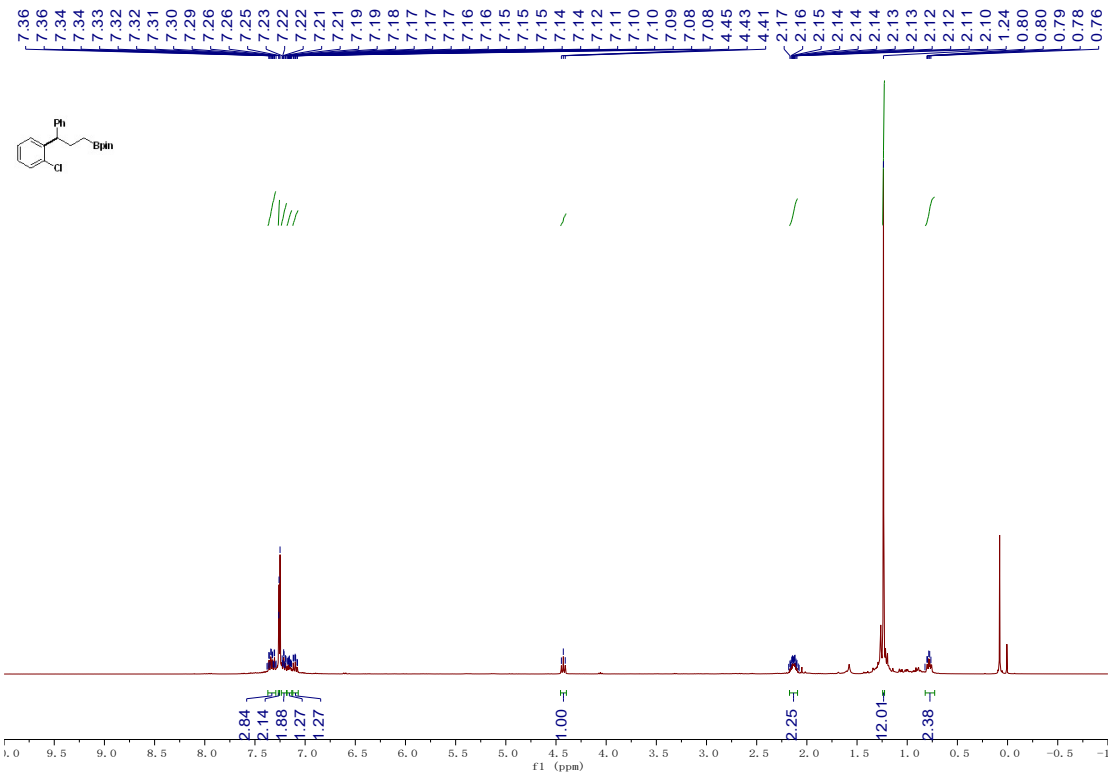


Figure S43. ^{13}C-NMR of **3p**

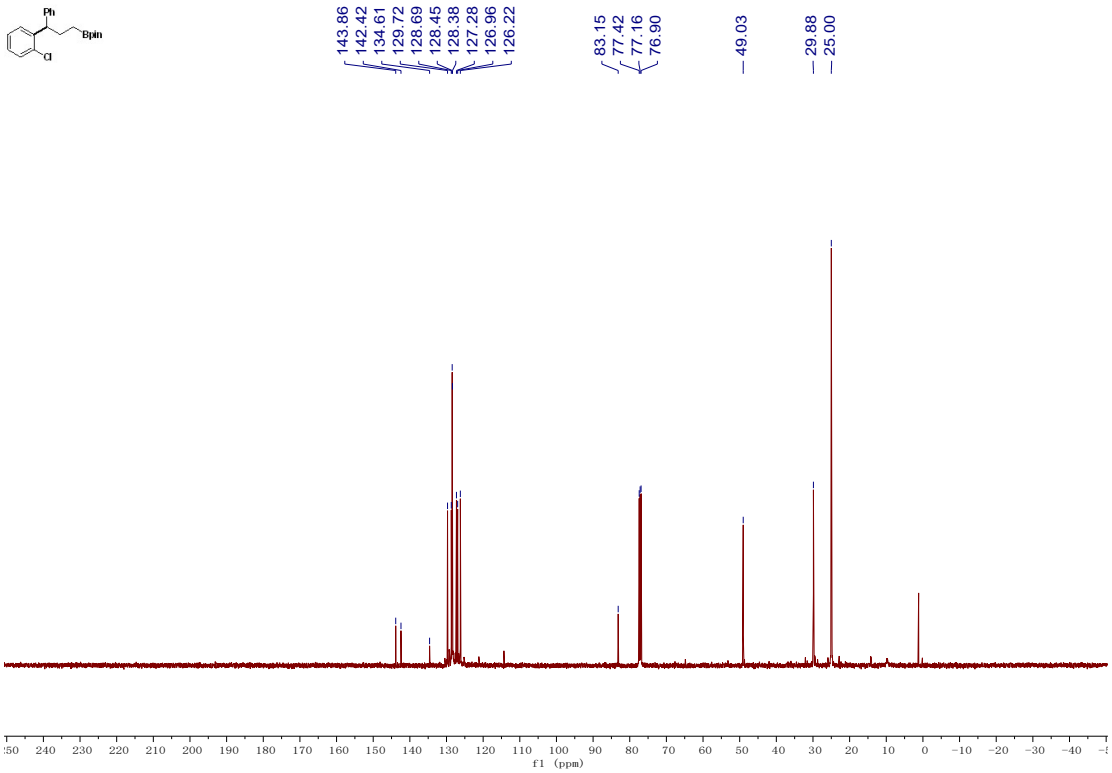


Figure S44. ^{1}H-NMR of **3q**

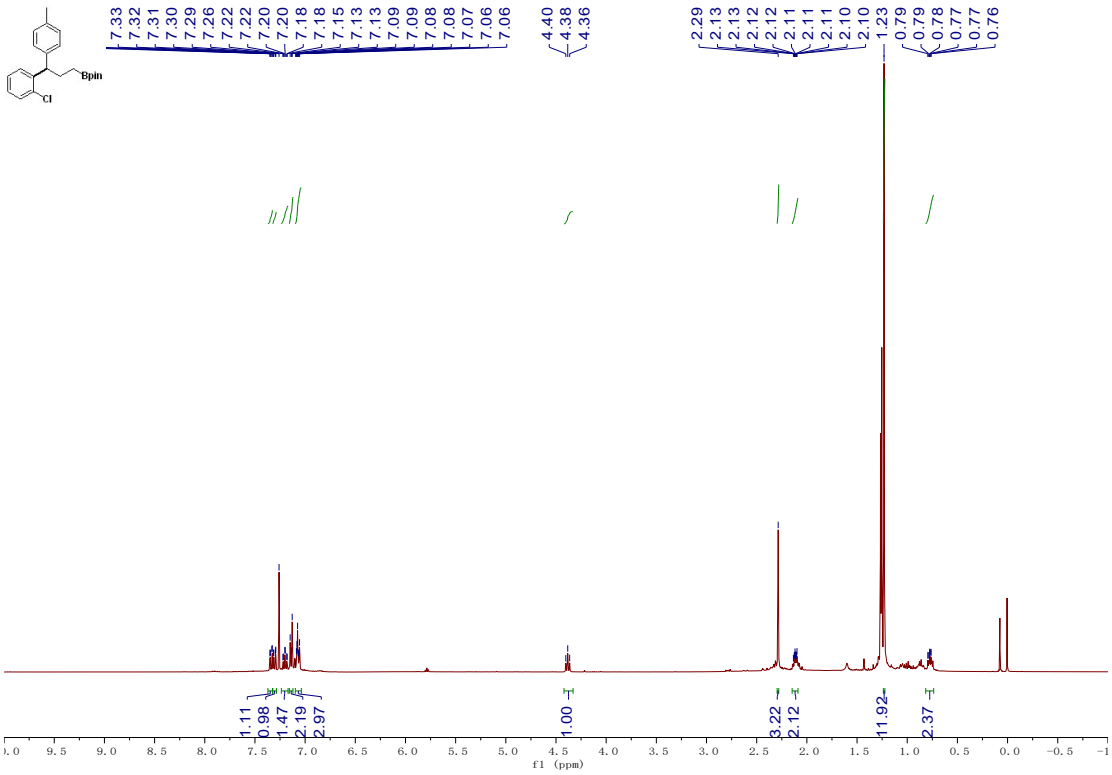


Figure S45. ^{13}C-NMR of **3q**

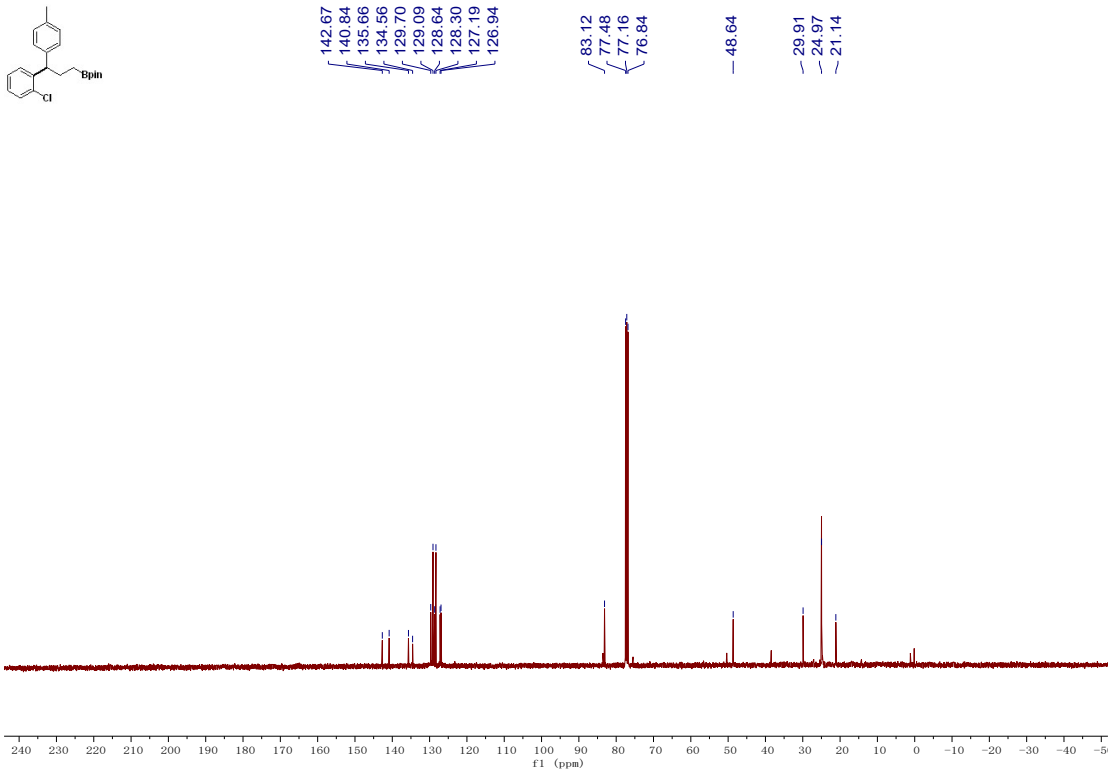


Figure S46. ^{1}H-NMR of **3r**

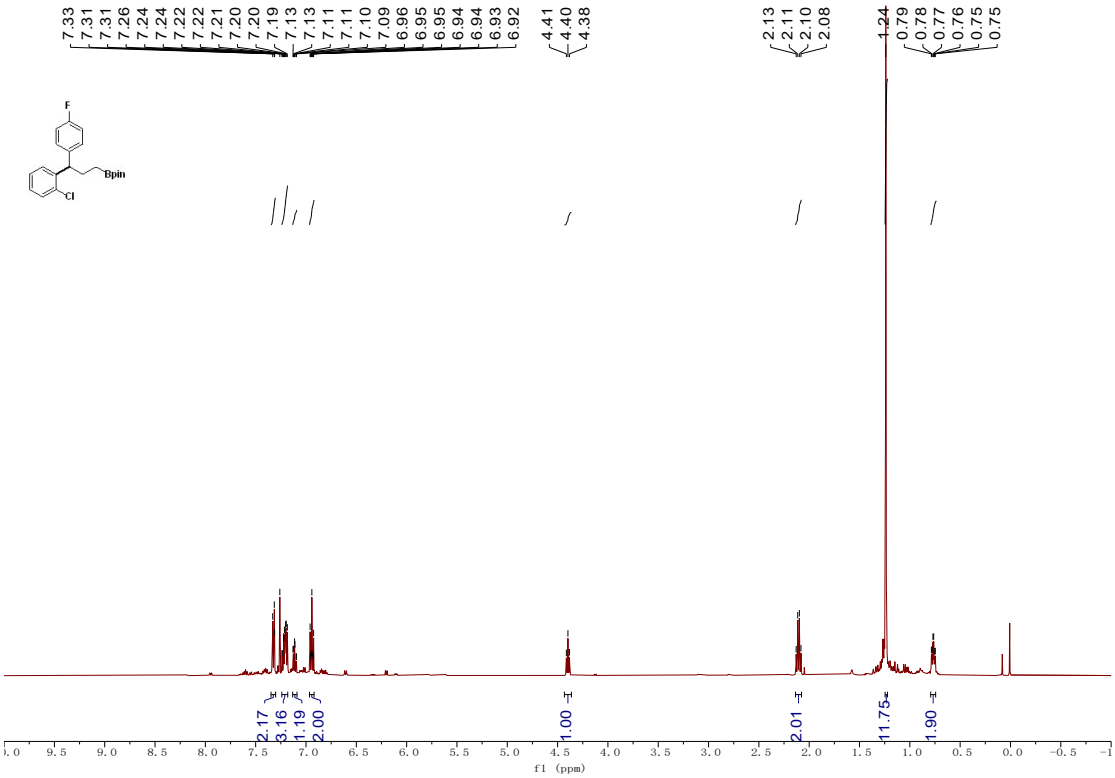


Figure S47. ^{13}C-NMR of **3r**

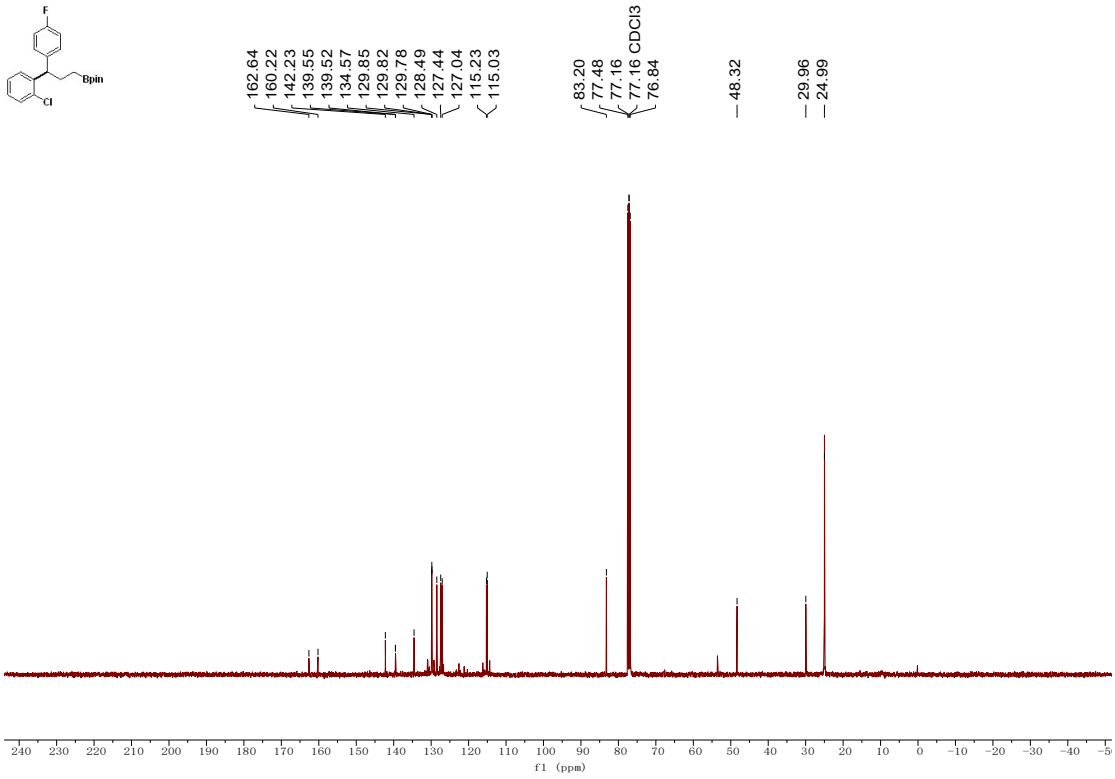


Figure S48. ^{19}F-NMR of **3r**

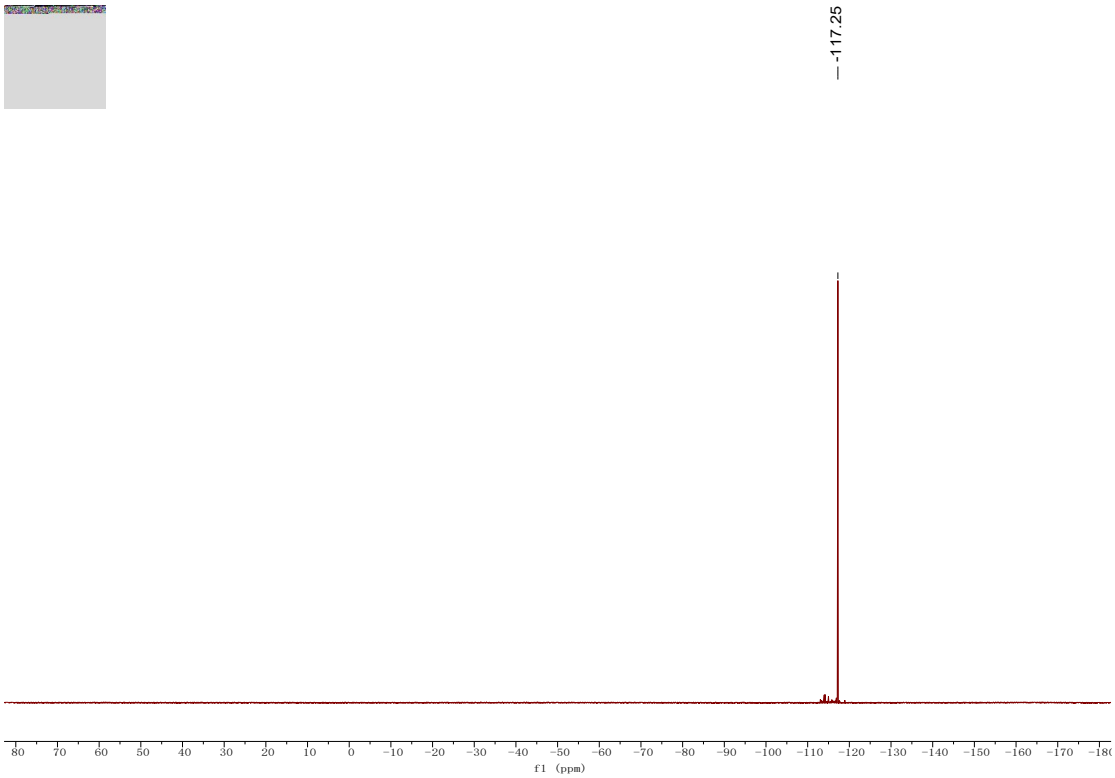


Figure S49. ^{1}H-NMR of **3s**

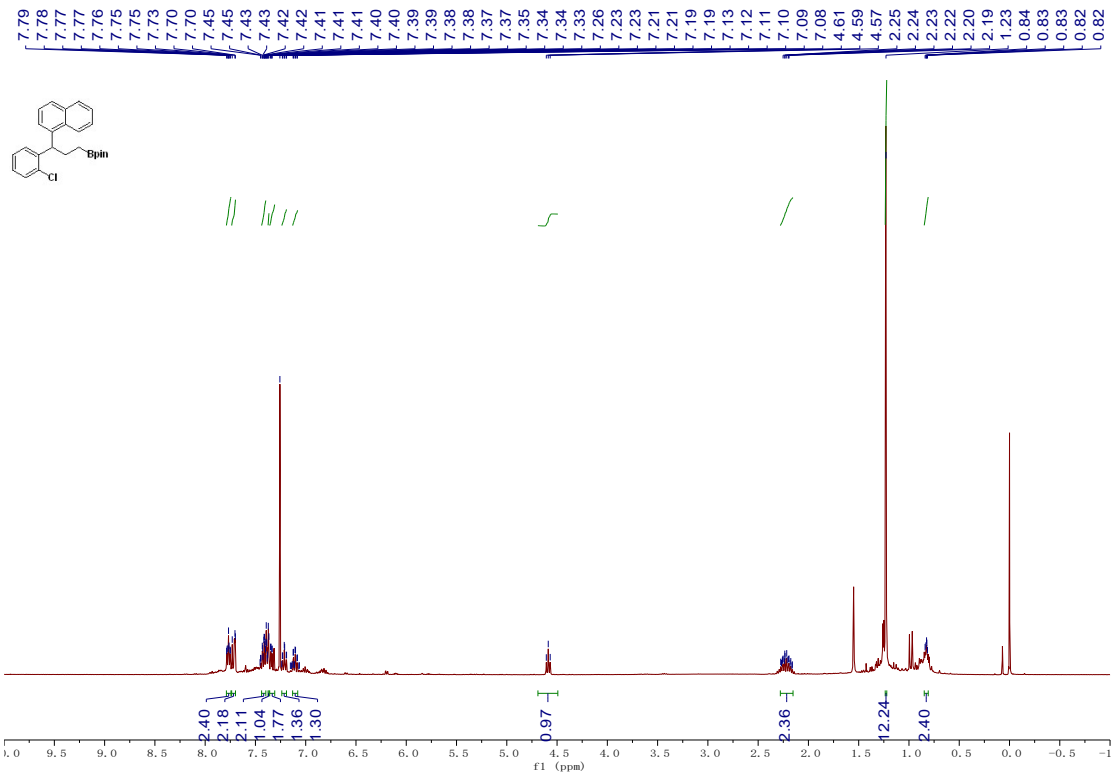


Figure S50. ^{13}C-NMR of **3s**

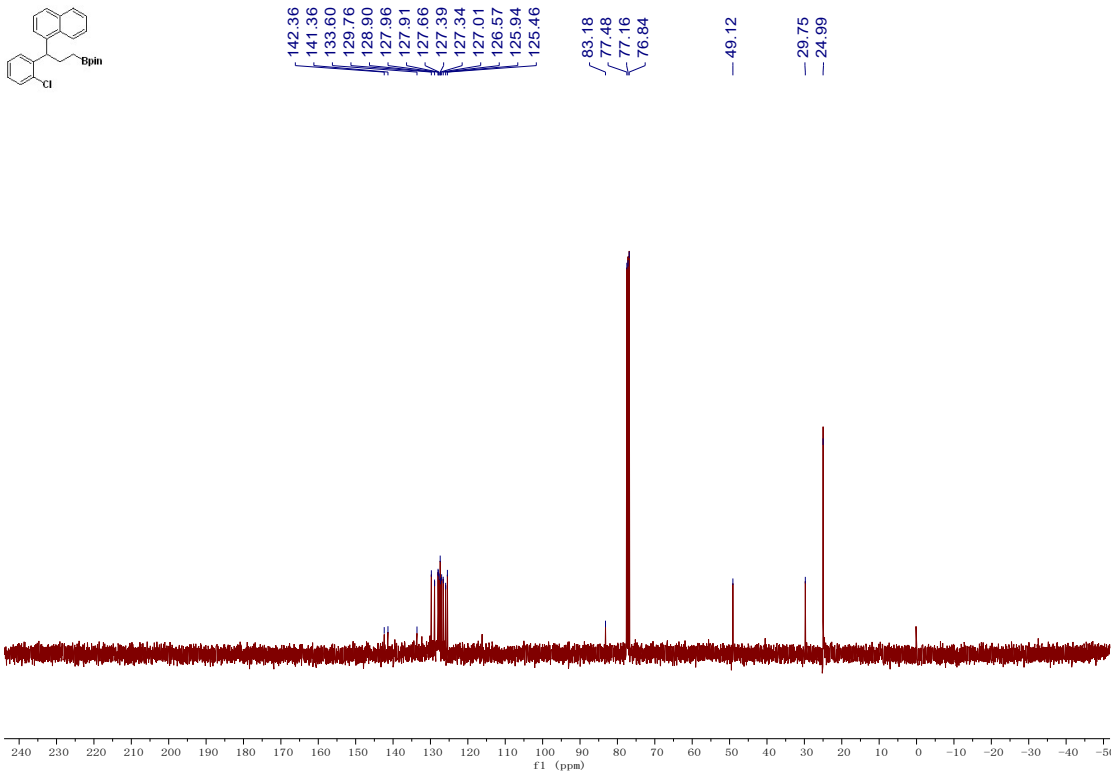


Figure S51. ^{1}H-NMR of **4a**

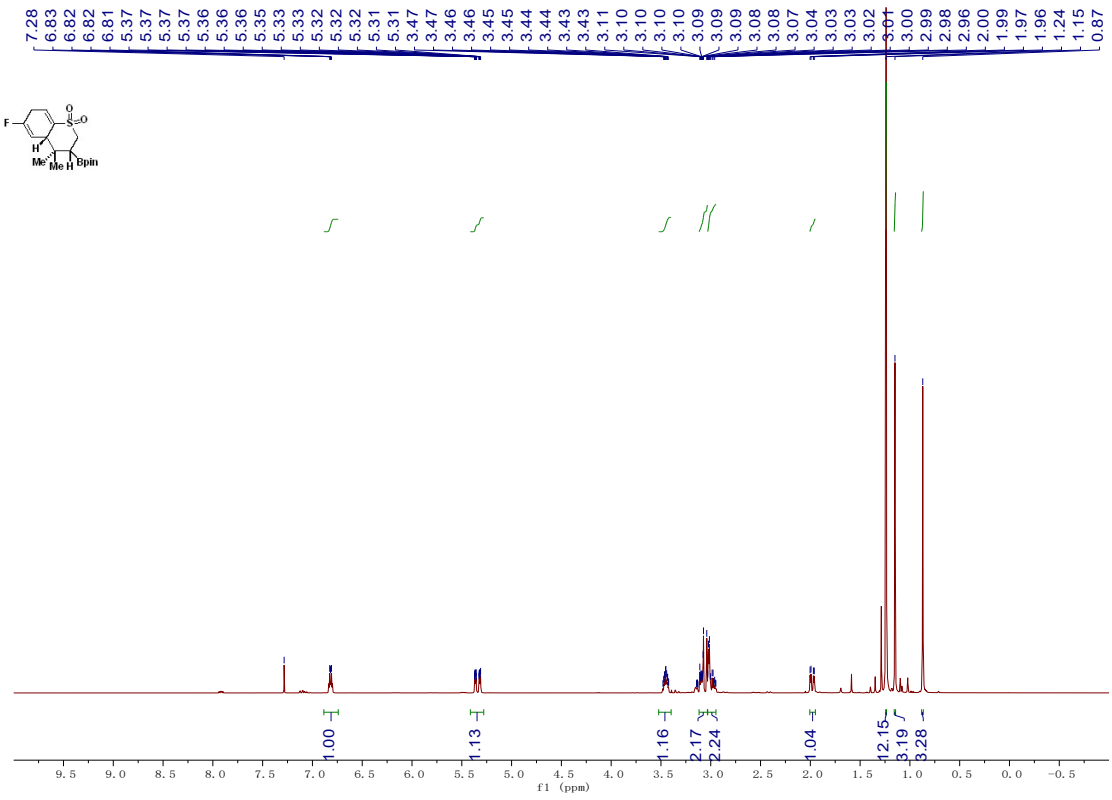


Figure S52. ^{13}C-NMR of **4a**

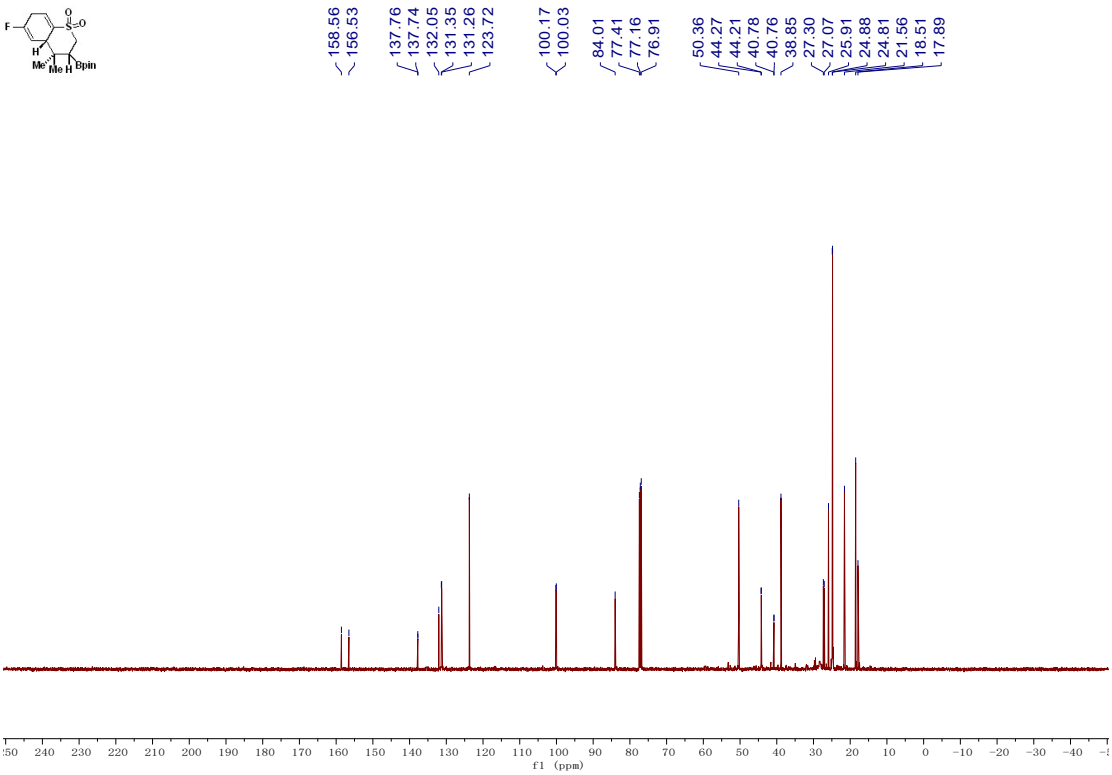


Figure S53. ^{19}F-NMR of **4a**

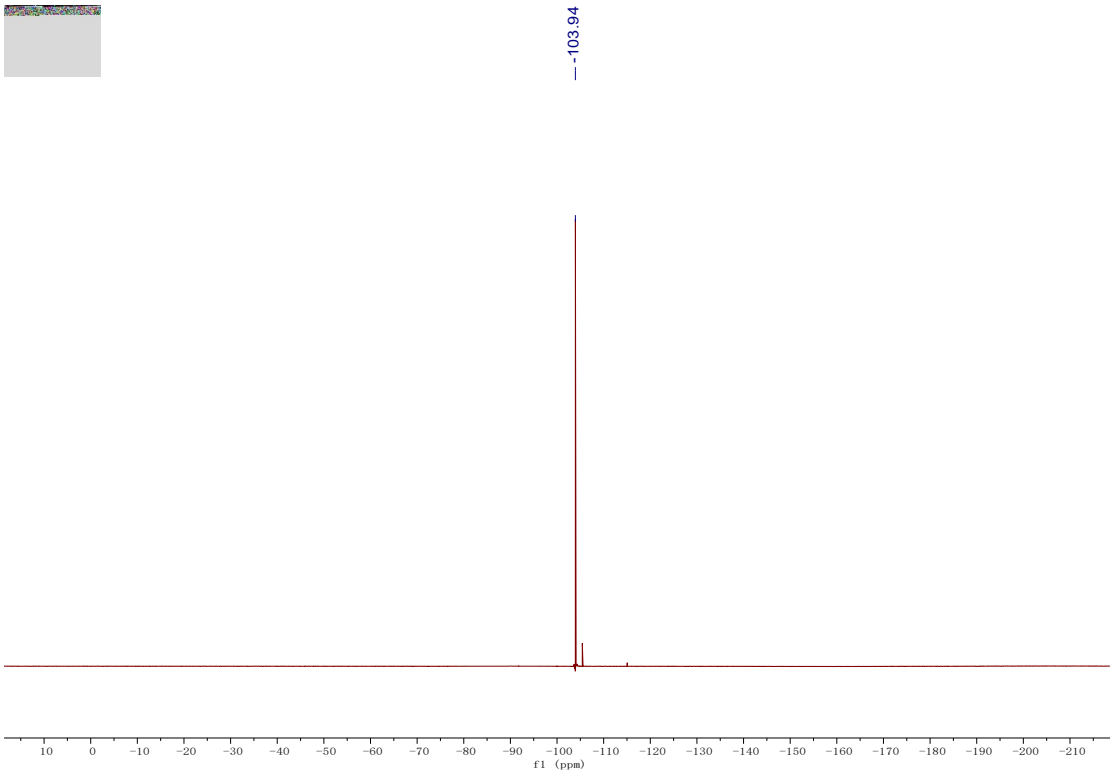


Figure S54. ^{1}H-NMR of **4b**

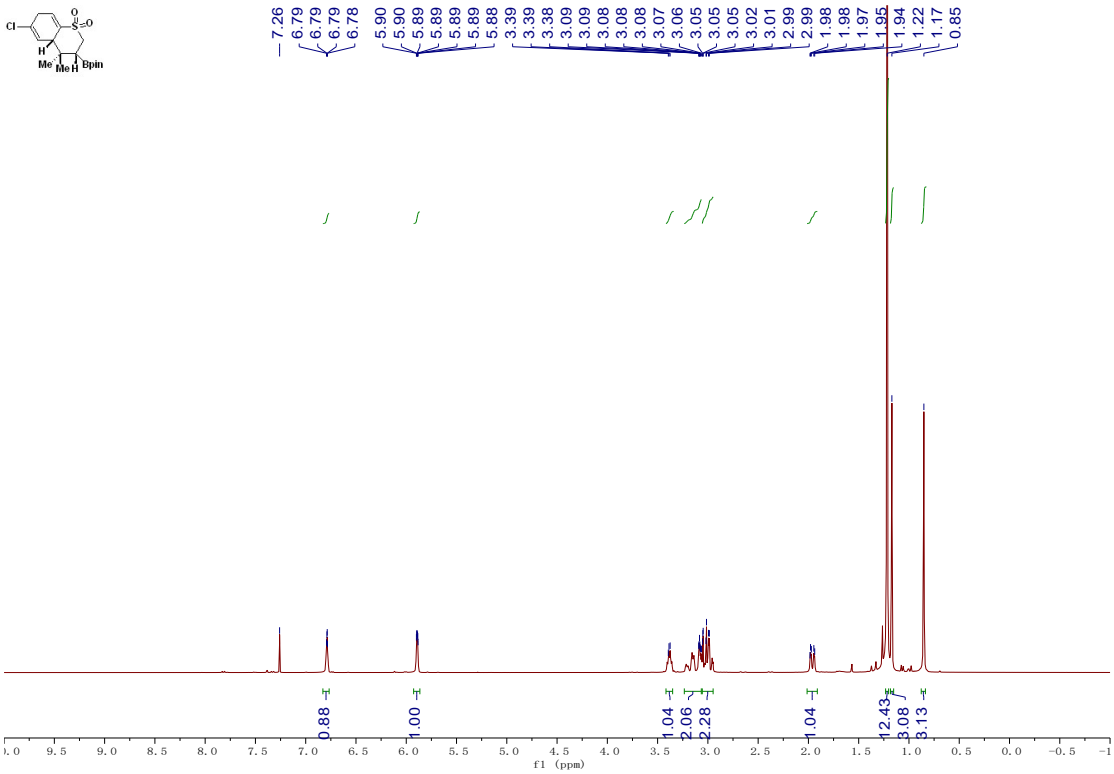


Figure S55. ^{13}C-NMR of **4b**

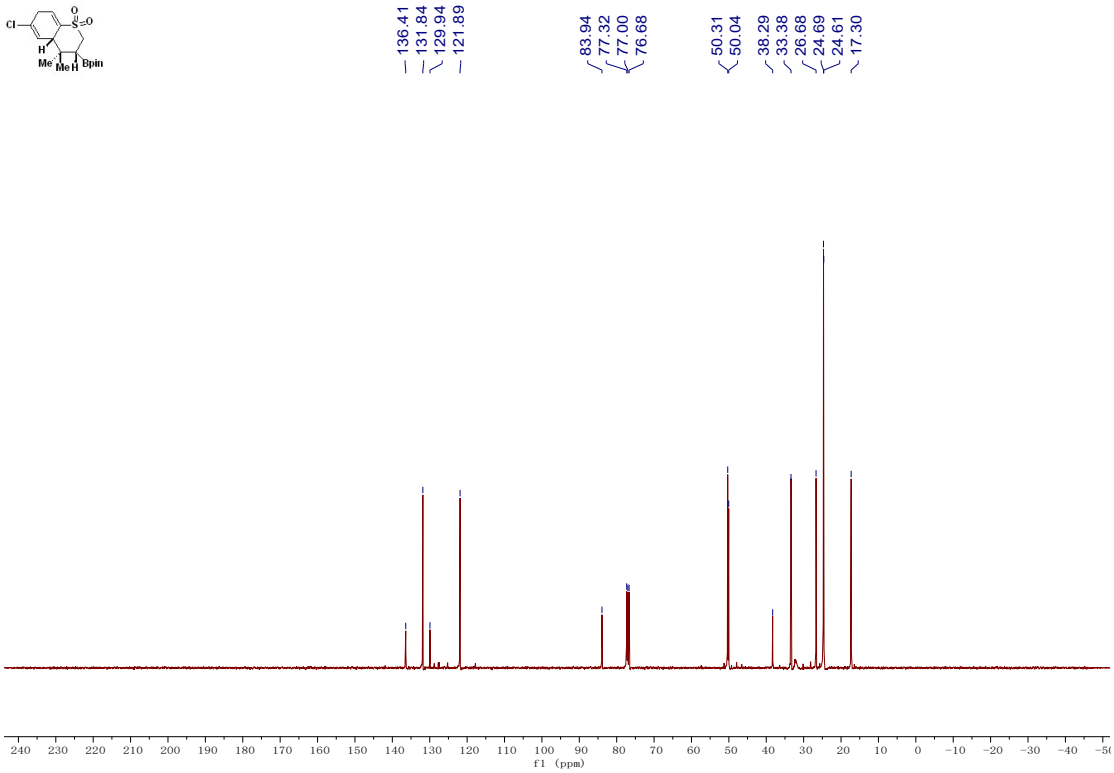


Figure S56. ^{1}H-NMR of **4c**

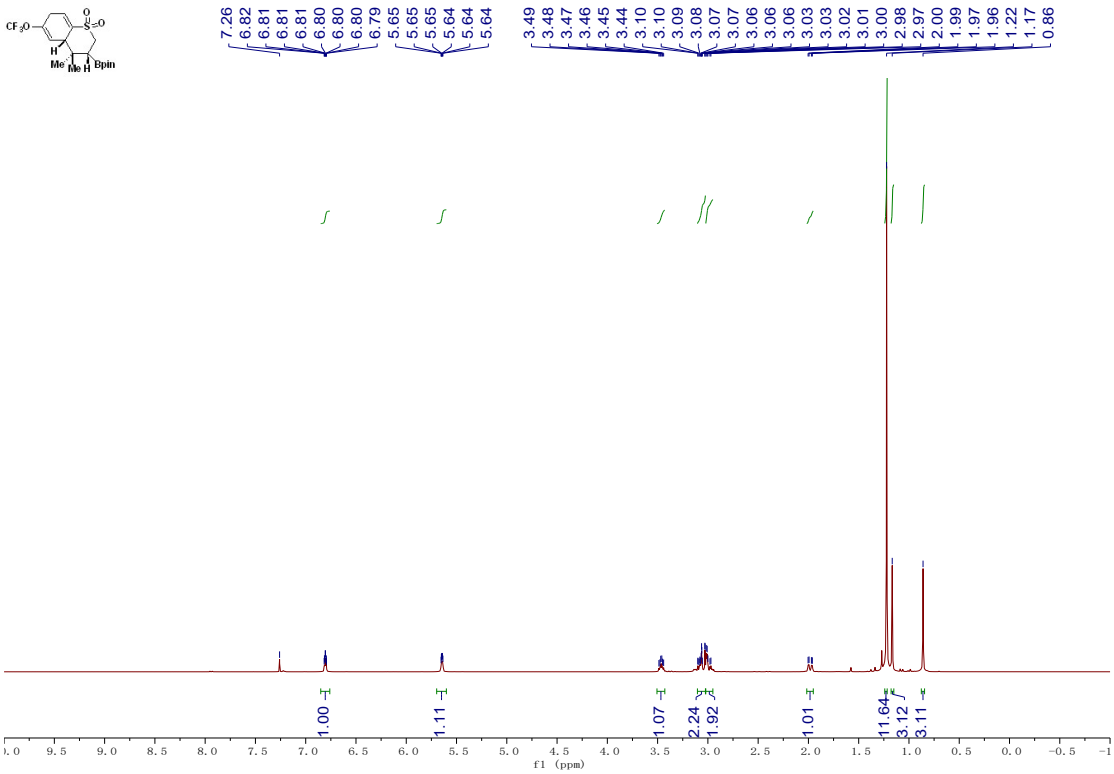


Figure S57. ^{13}C-NMR of **4c**

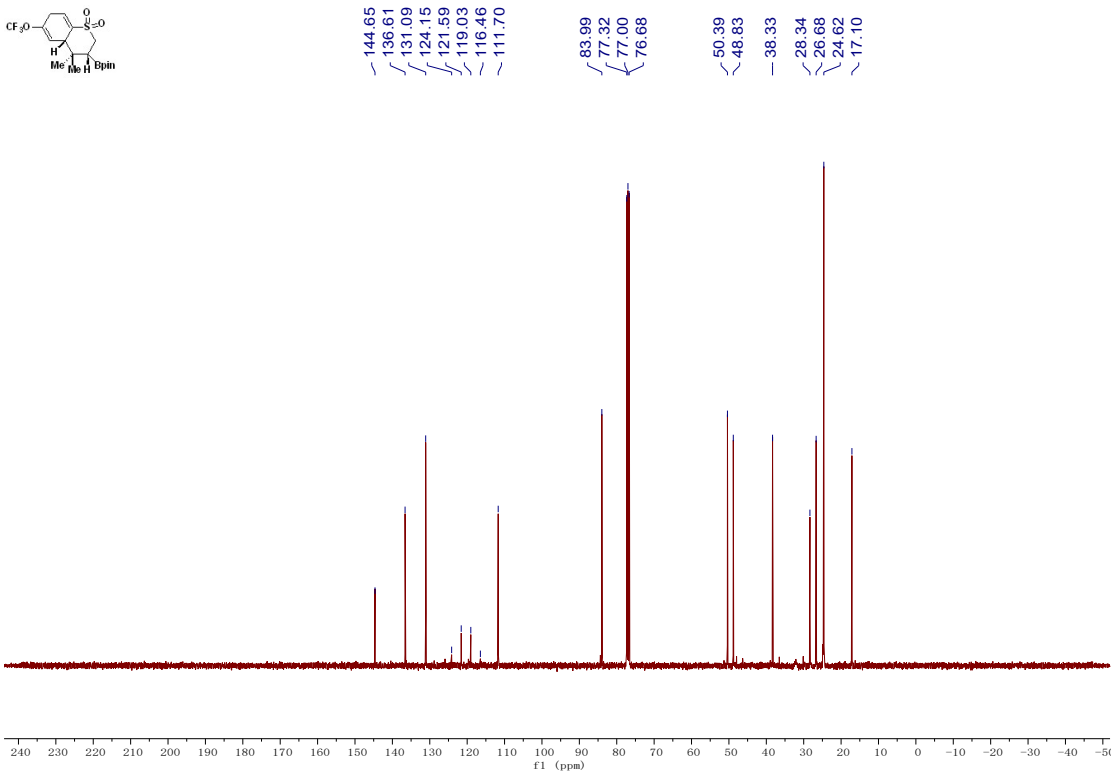


Figure S58. ^{19}F-NMR of **4c**

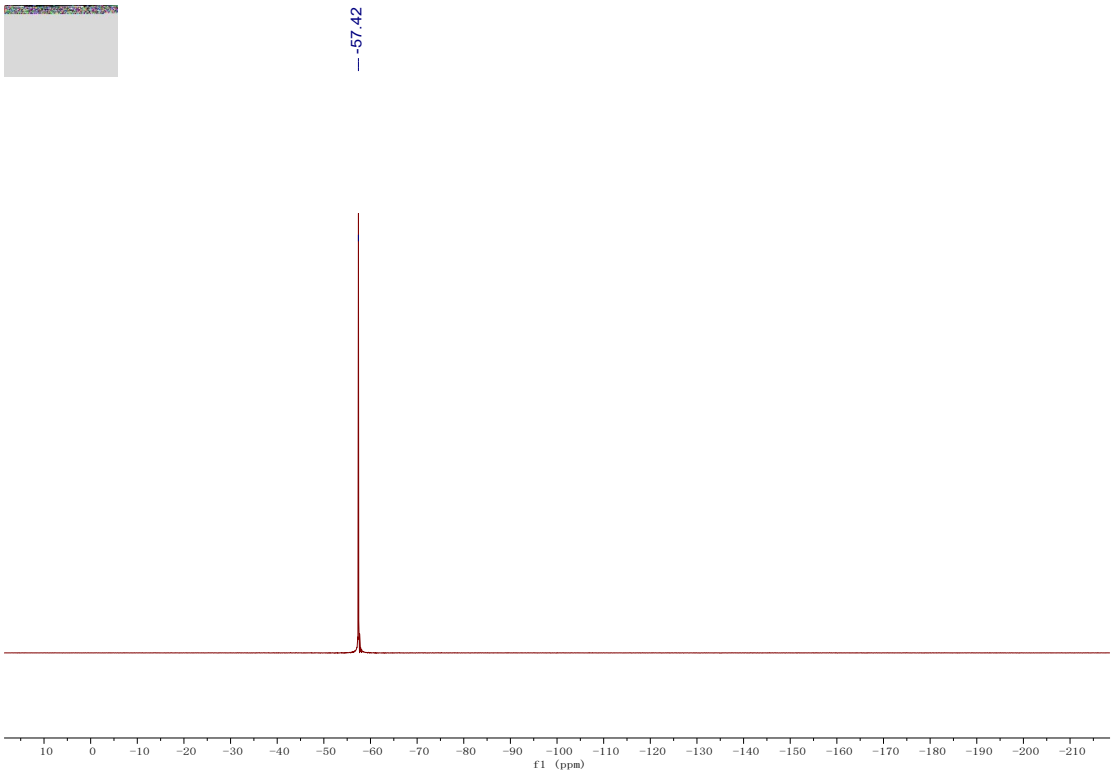


Figure S59. ^{1}H-NMR of **4d**

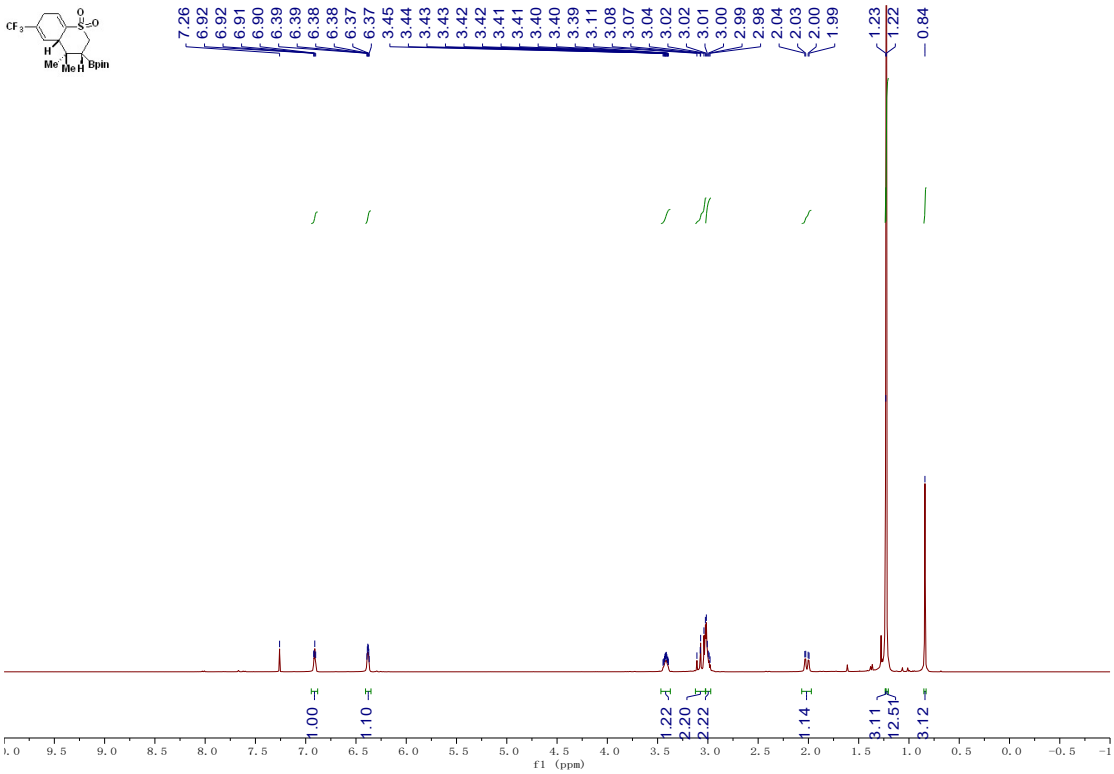


Figure S60. ^{13}C-NMR of **4d**

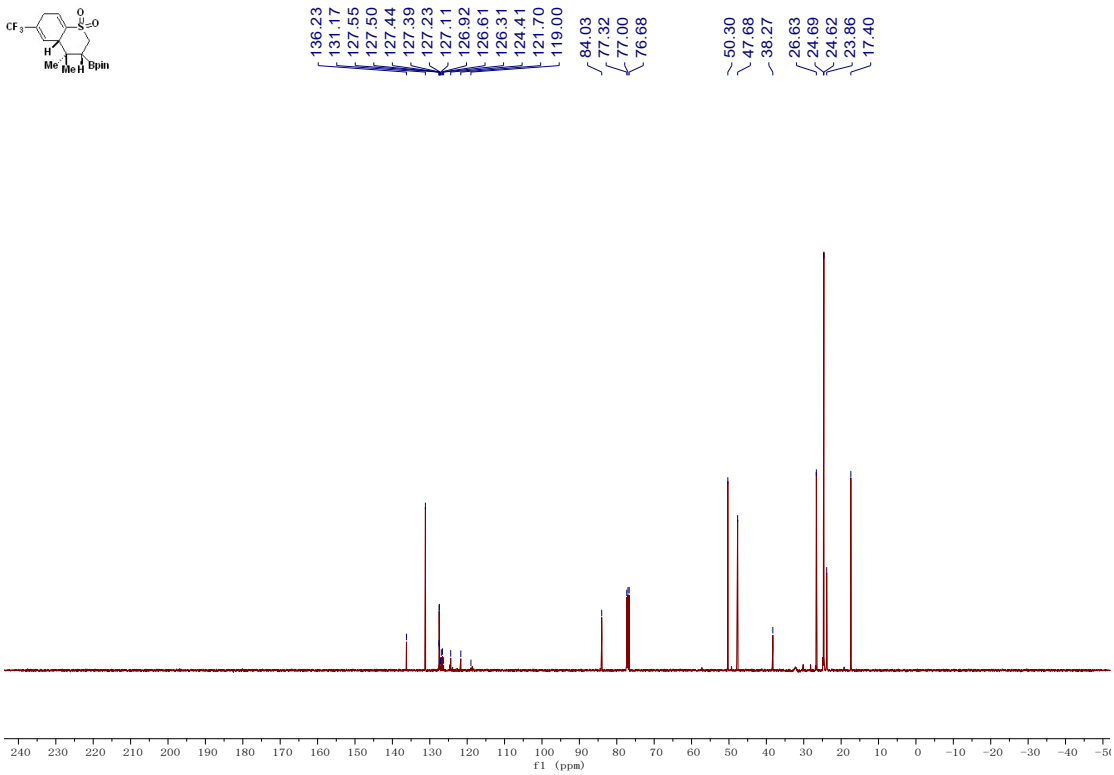


Figure S61. ^{19}F-NMR of **4d**

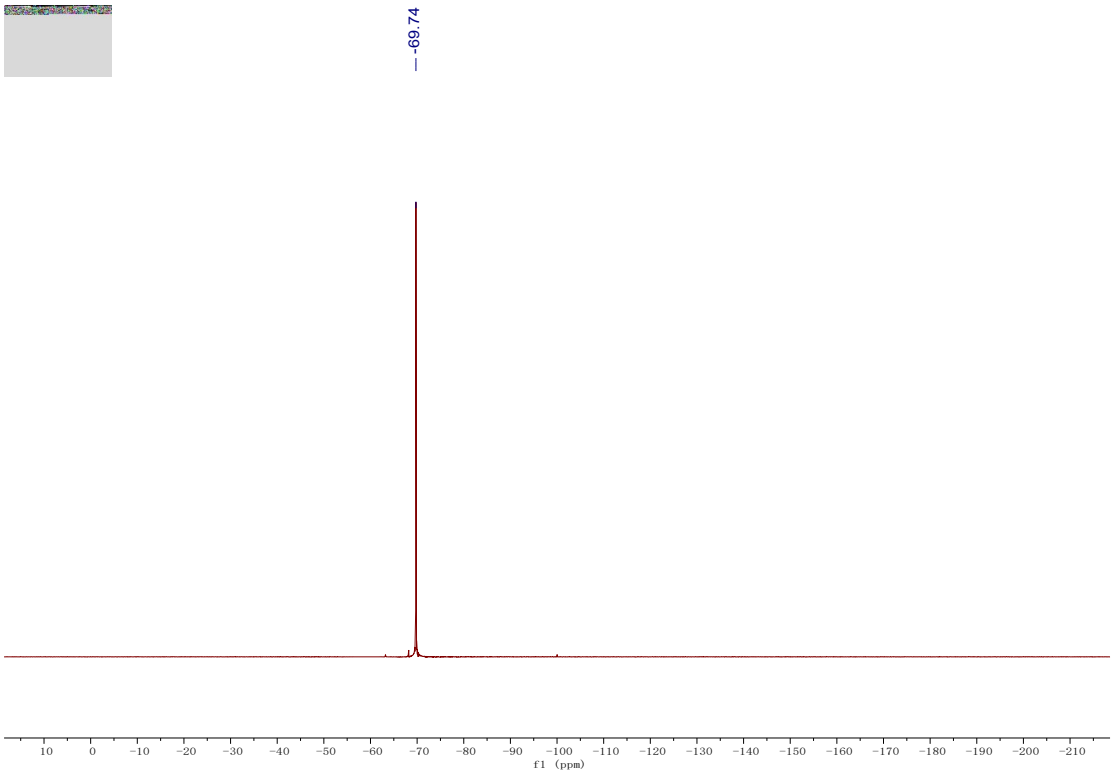


Figure S62. ^{1}H-NMR of **4e**

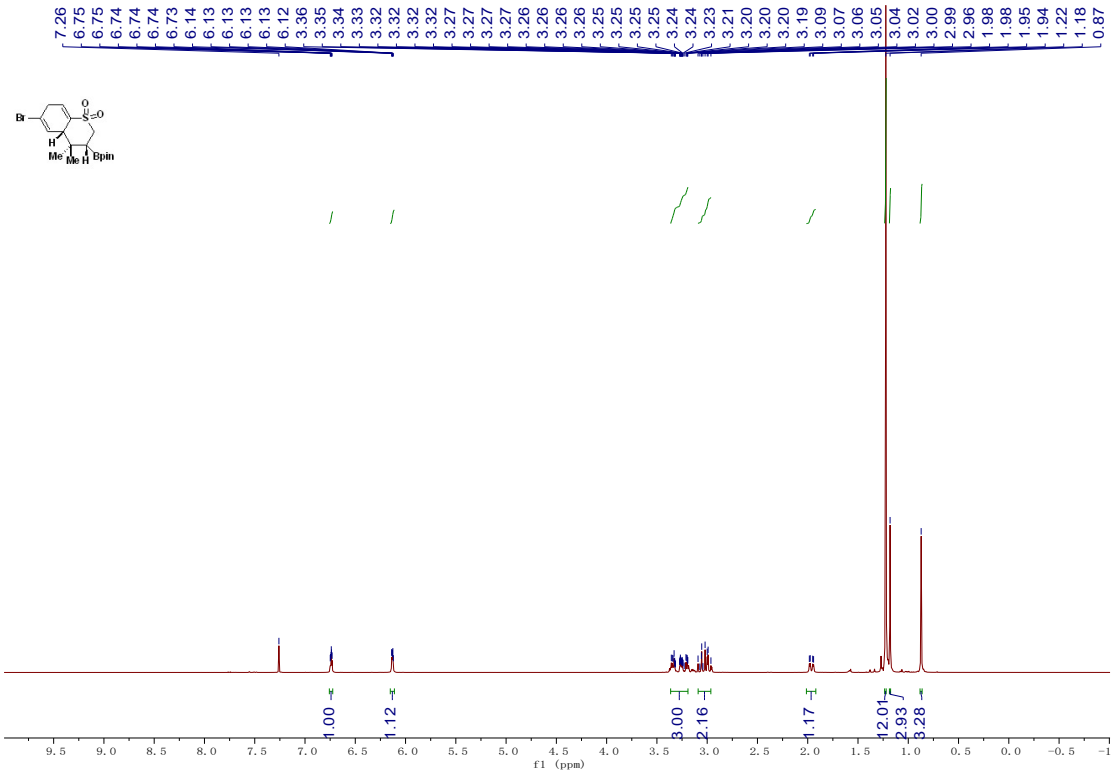


Figure S63. ^{13}C-NMR of **4e**

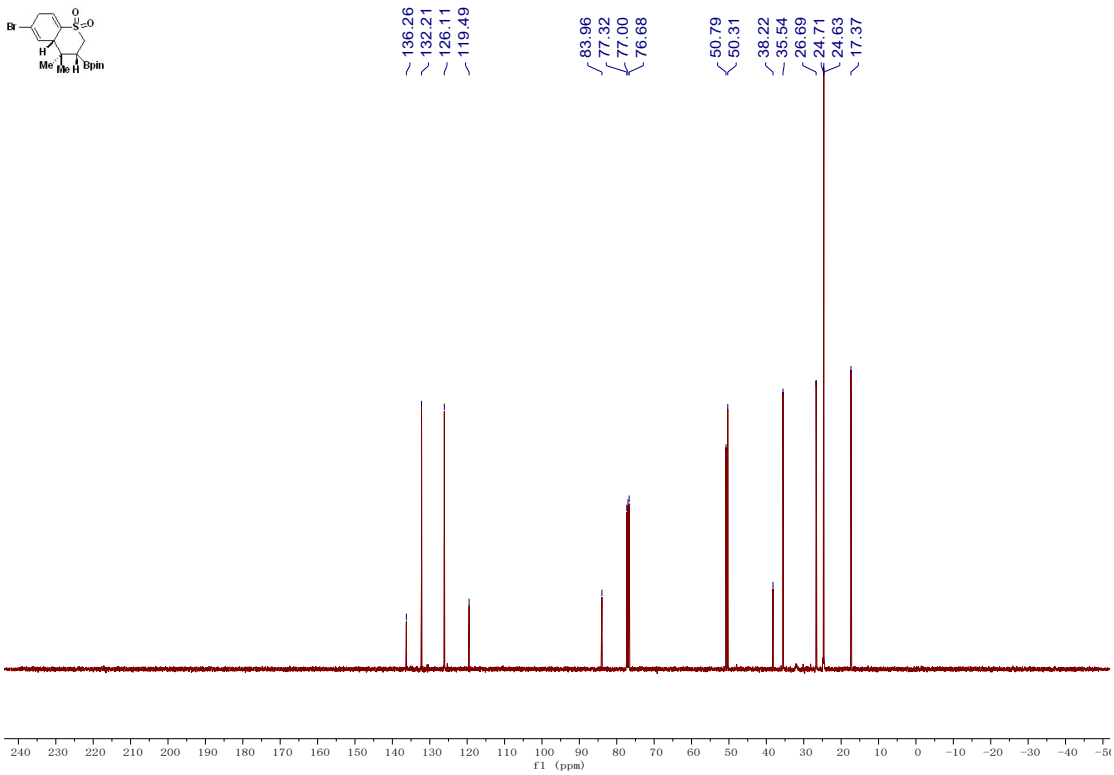


Figure S64. ^{1}H-NMR of **4f**

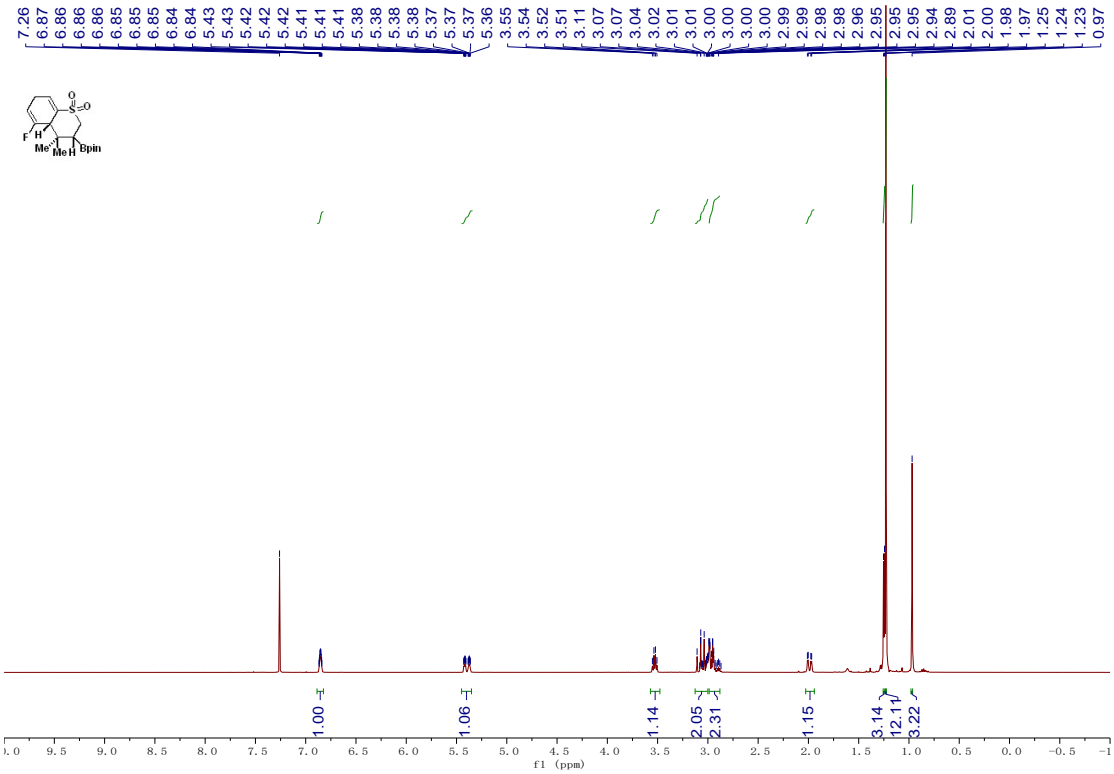


Figure S65. ^{13}C-NMR of **4f**

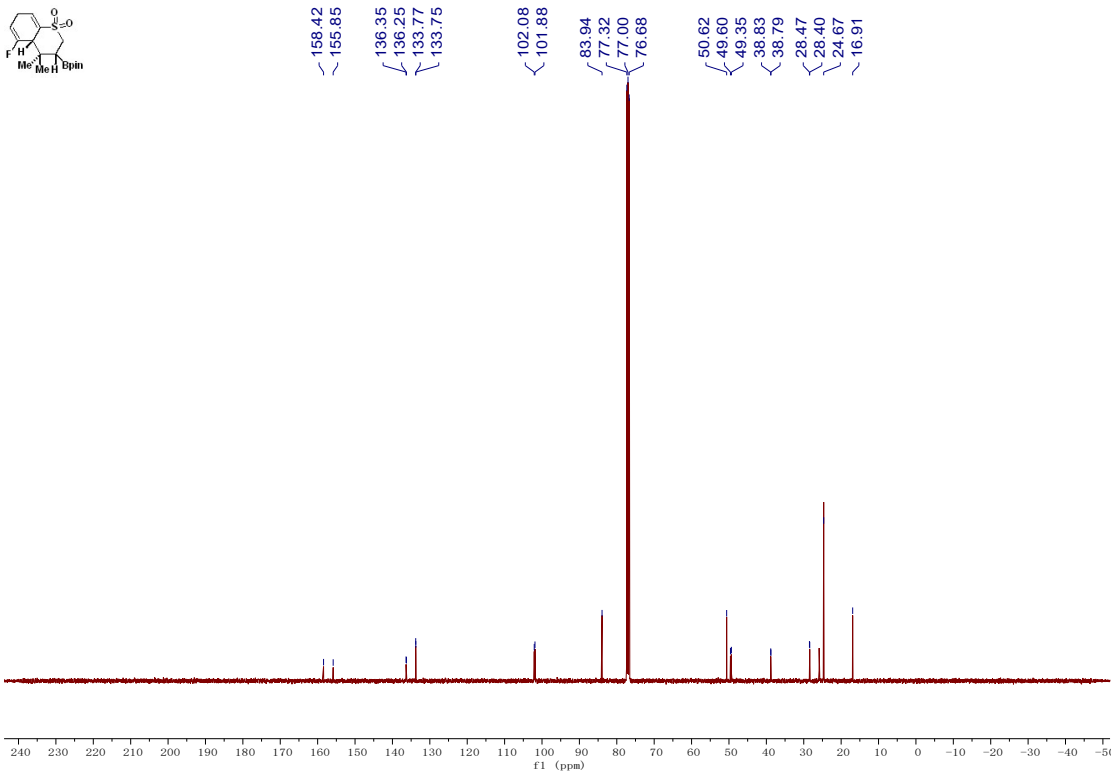


Figure S66. ^{19}F-NMR of **4f**

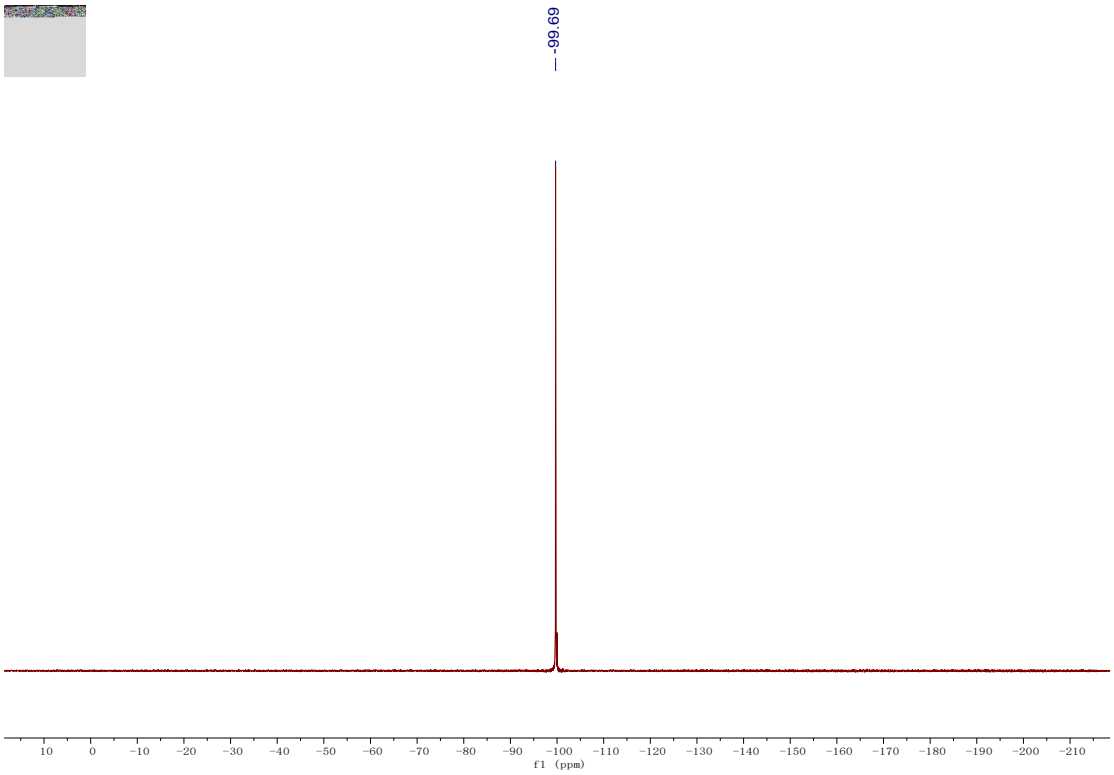


Figure S67. ^{1}H-NMR of **4g**

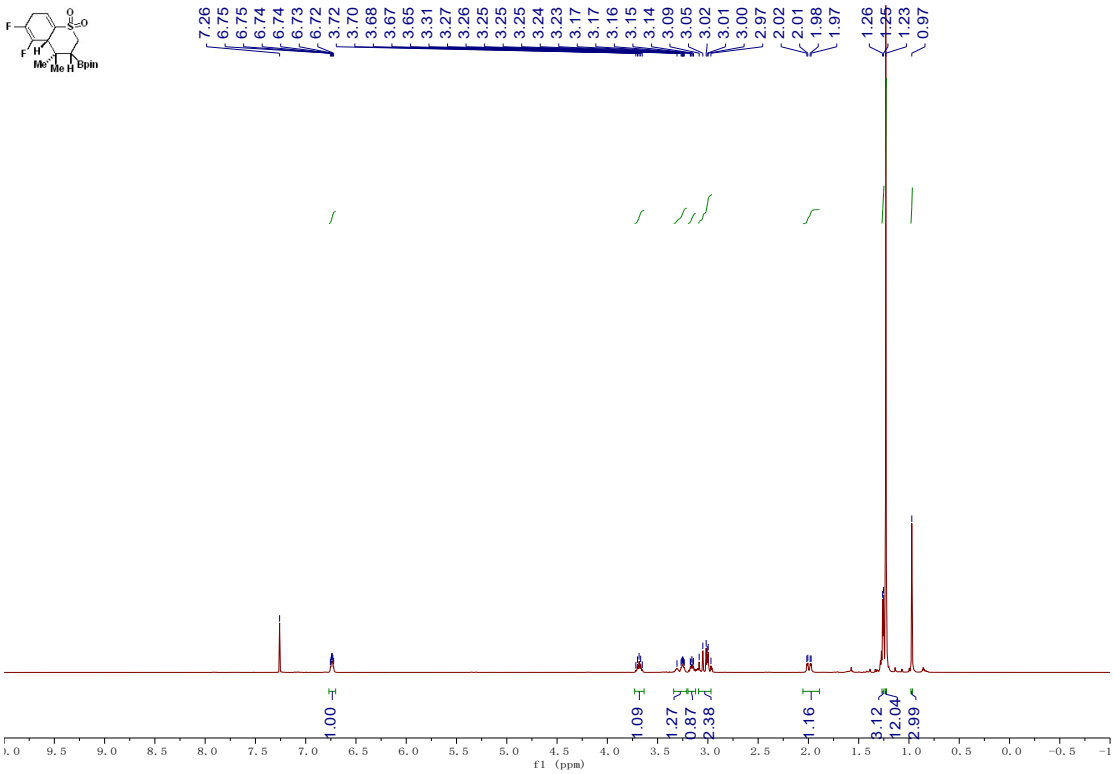


Figure S68. ^{13}C-NMR of **4g**

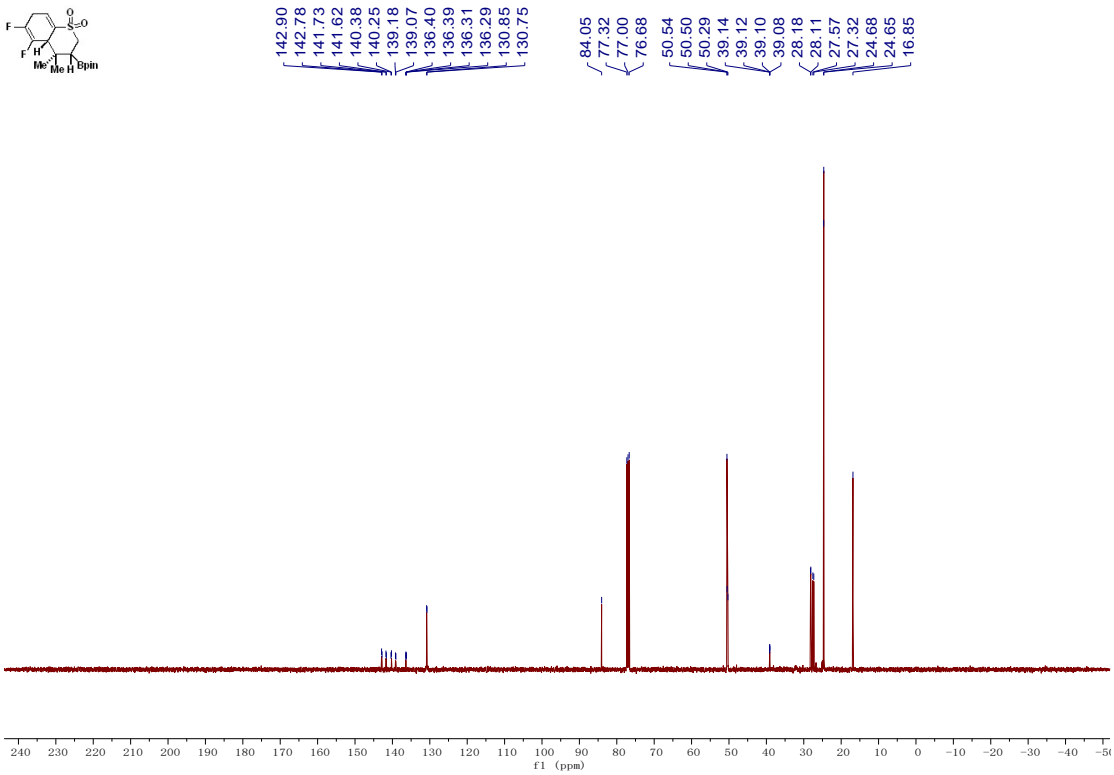


Figure S69. ^{19}F-NMR of **4g**

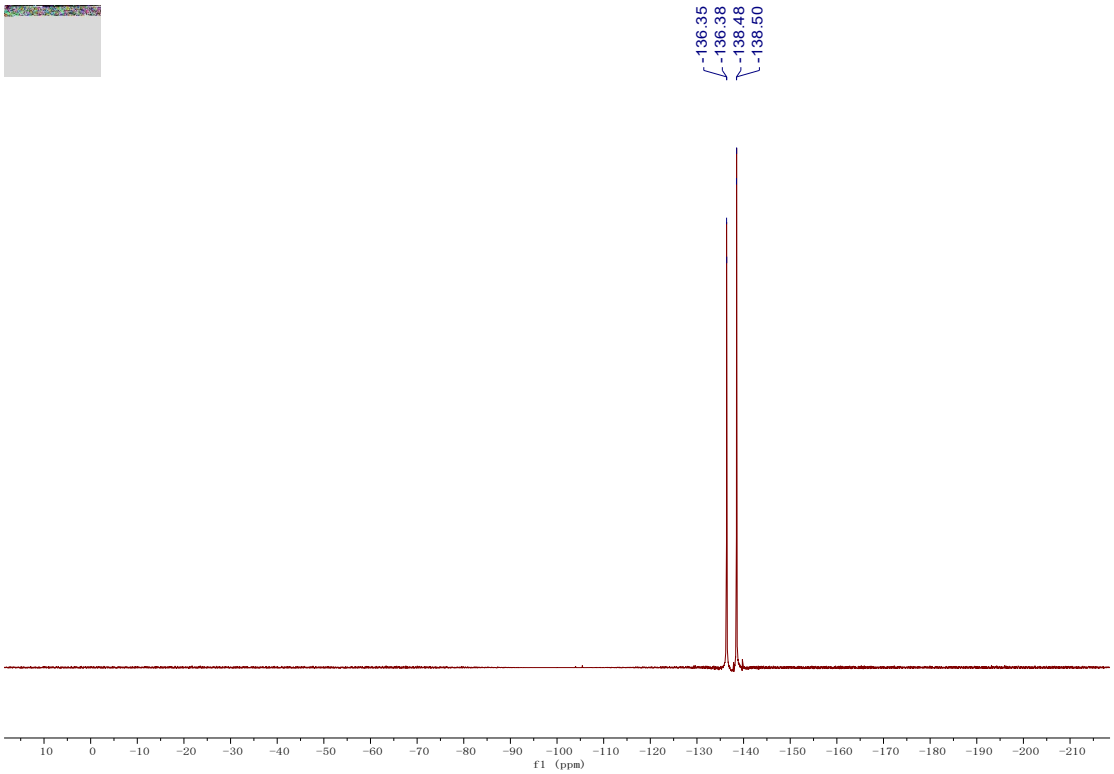


Figure S70. ^{1}H-NMR of **4h**

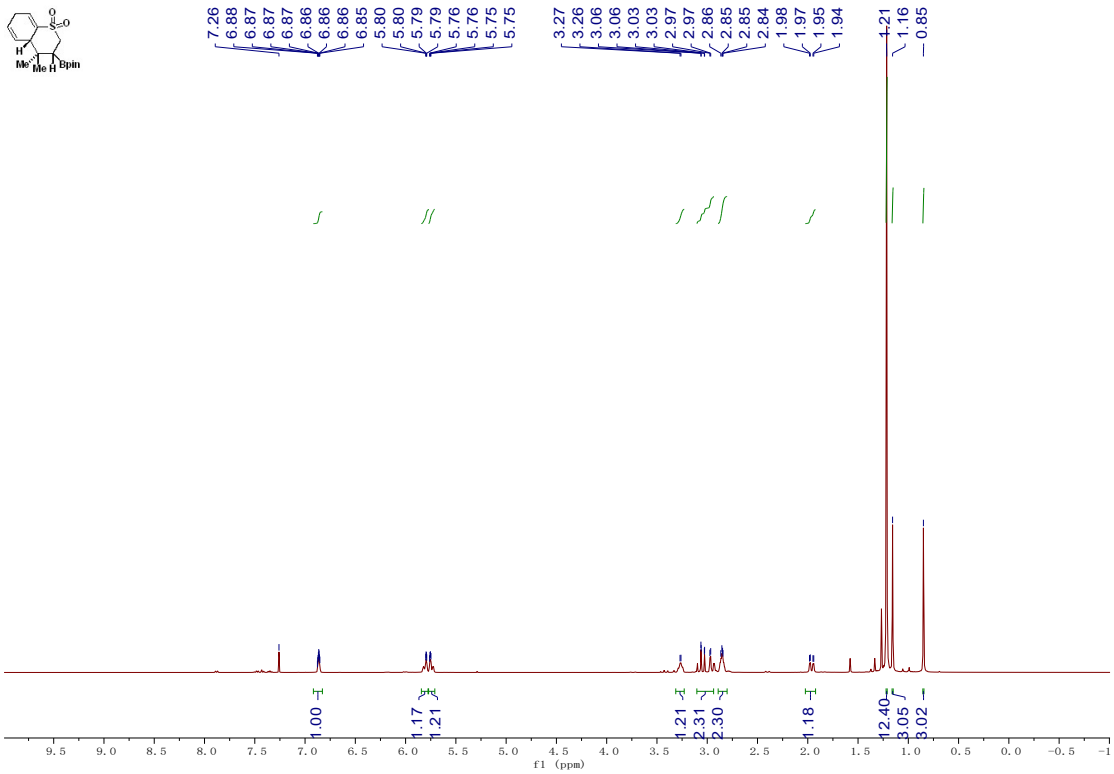


Figure S71. ^{13}C-NMR of **4h**

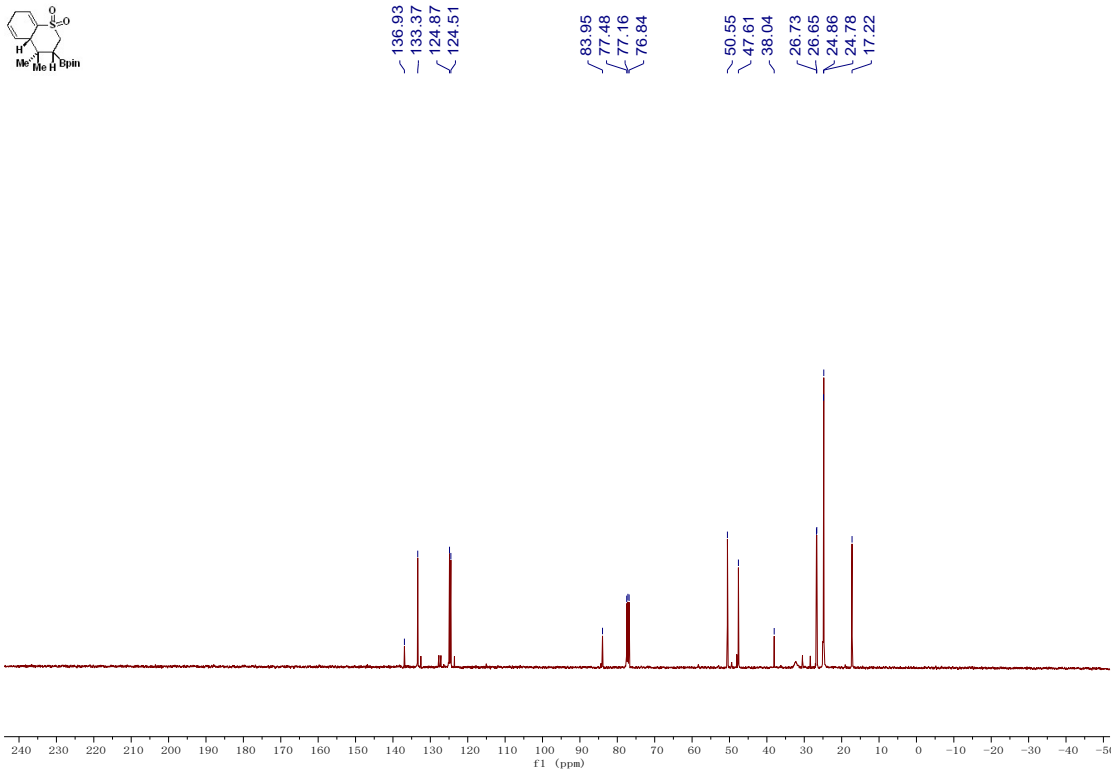


Figure S72. ^{1}H-NMR of **4i**

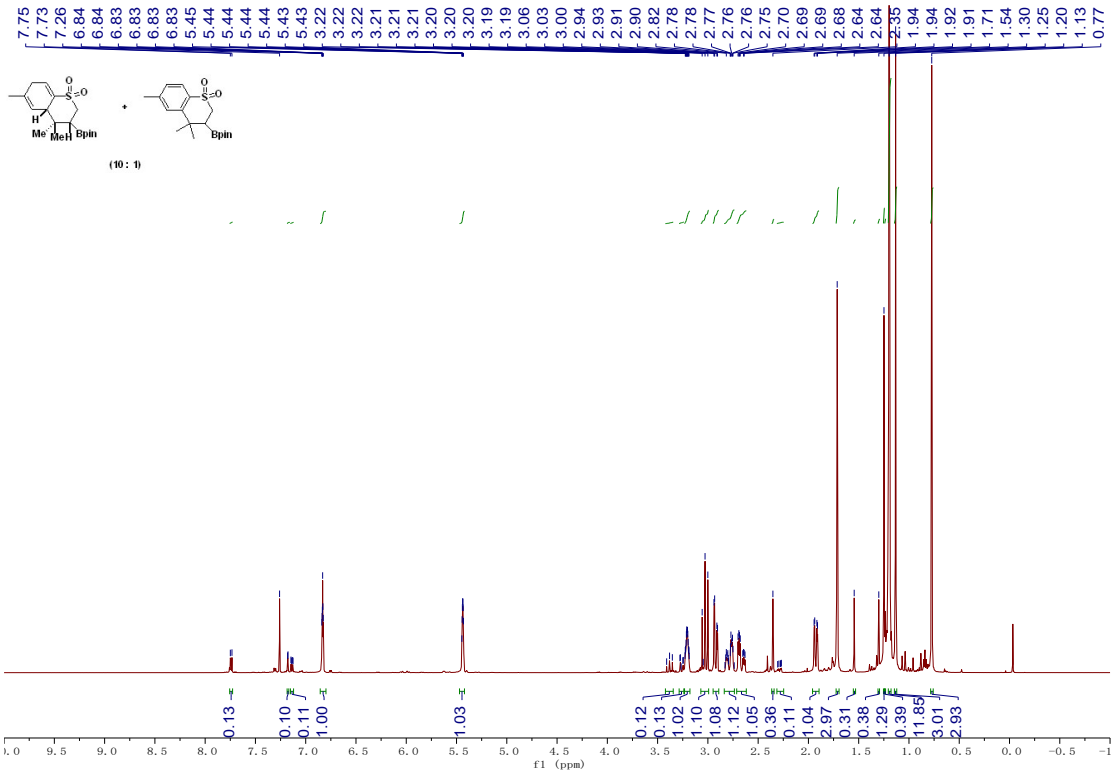


Figure S73. ^{13}C-NMR of **4i**

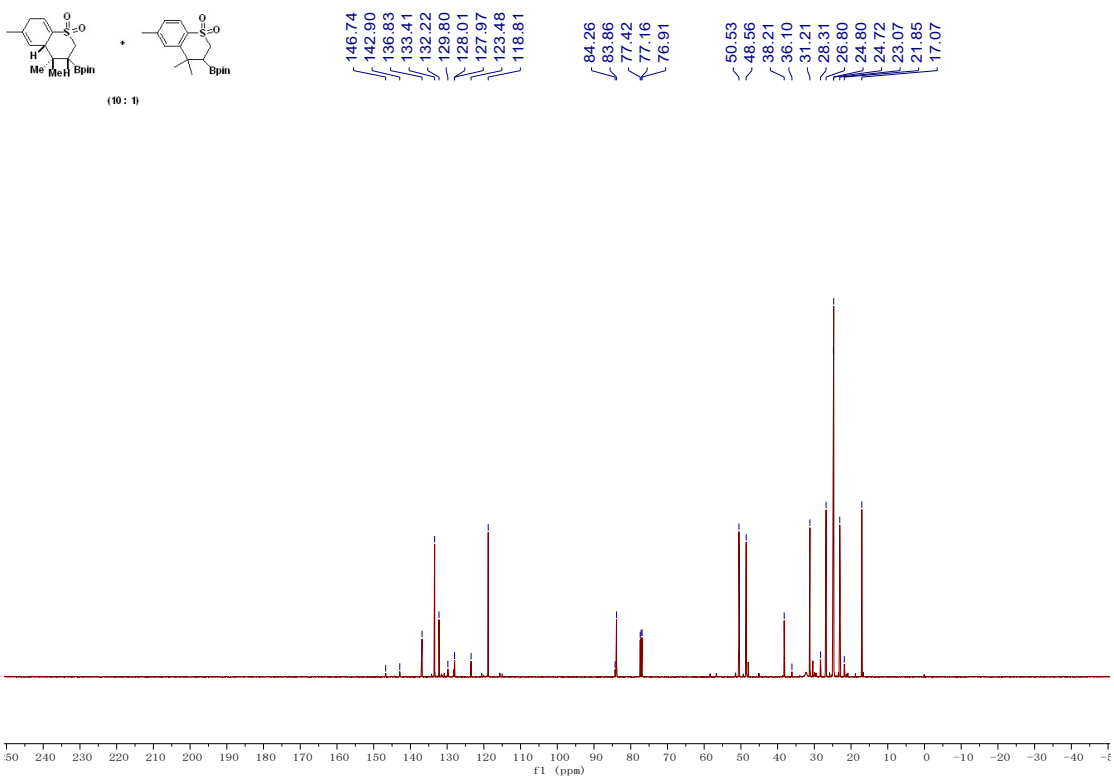


Figure S74. ^{1}H-NMR of **4j**

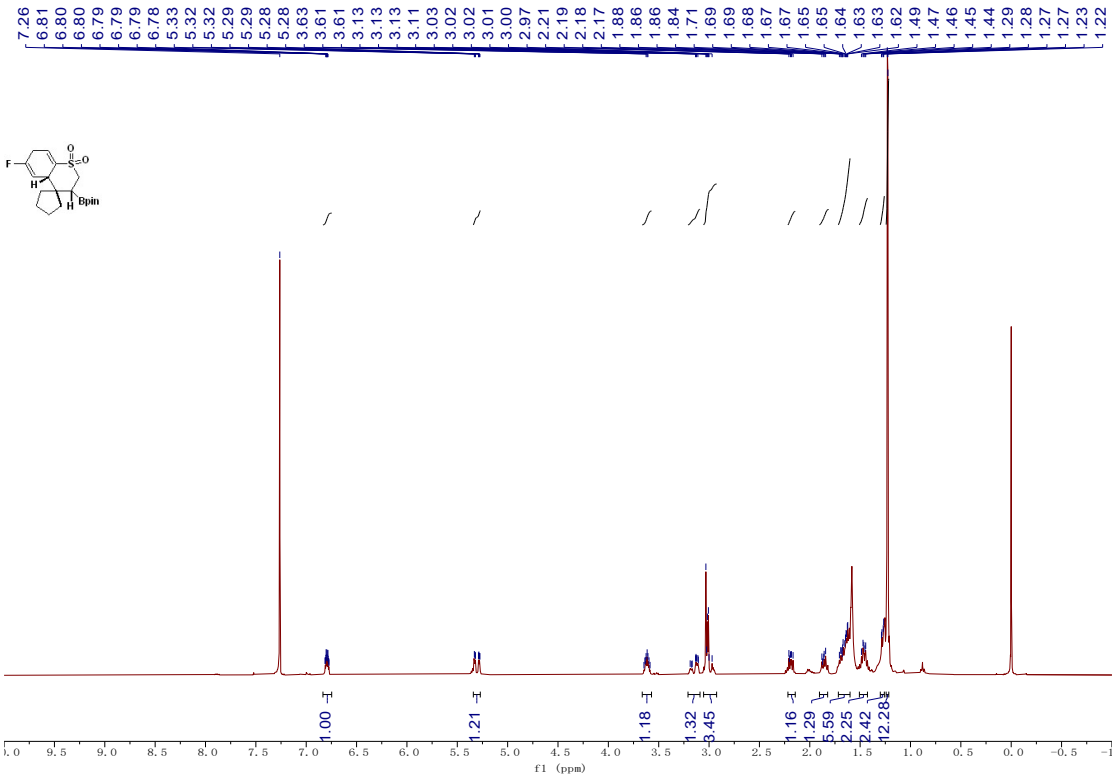


Figure S75. ^{13}C-NMR of **4j**

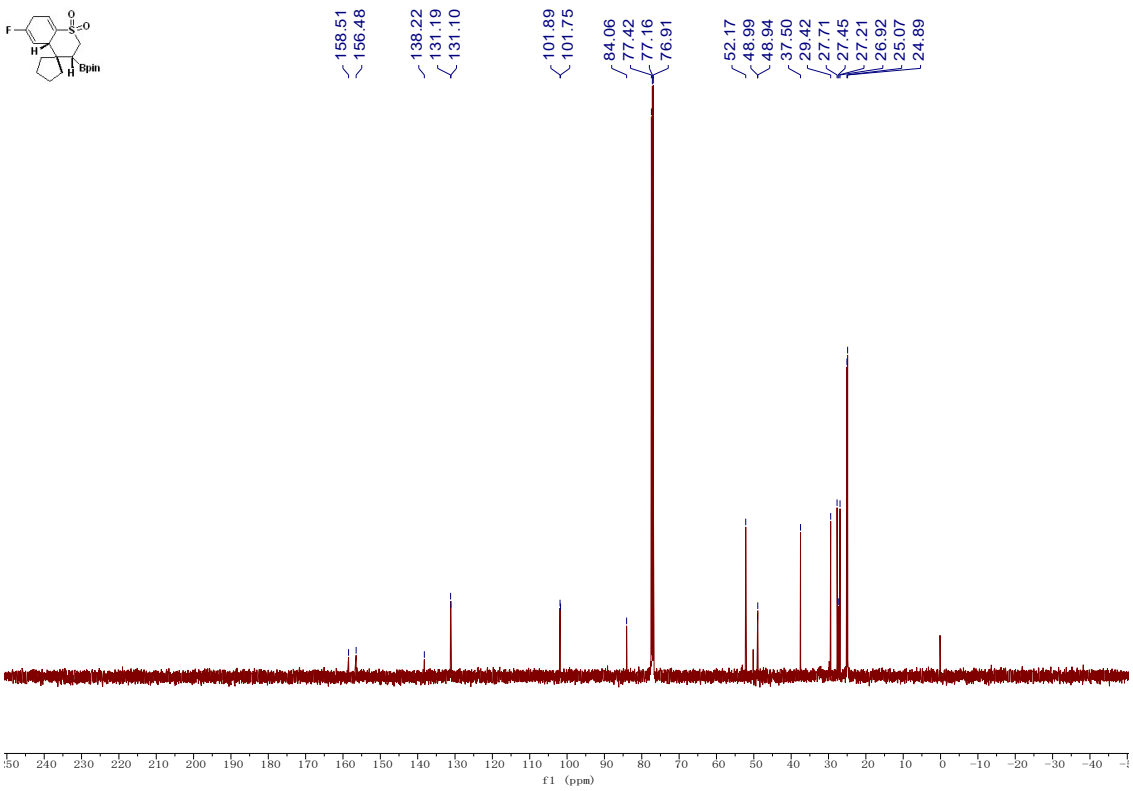


Figure S76. ^{19}F-NMR of **4j**

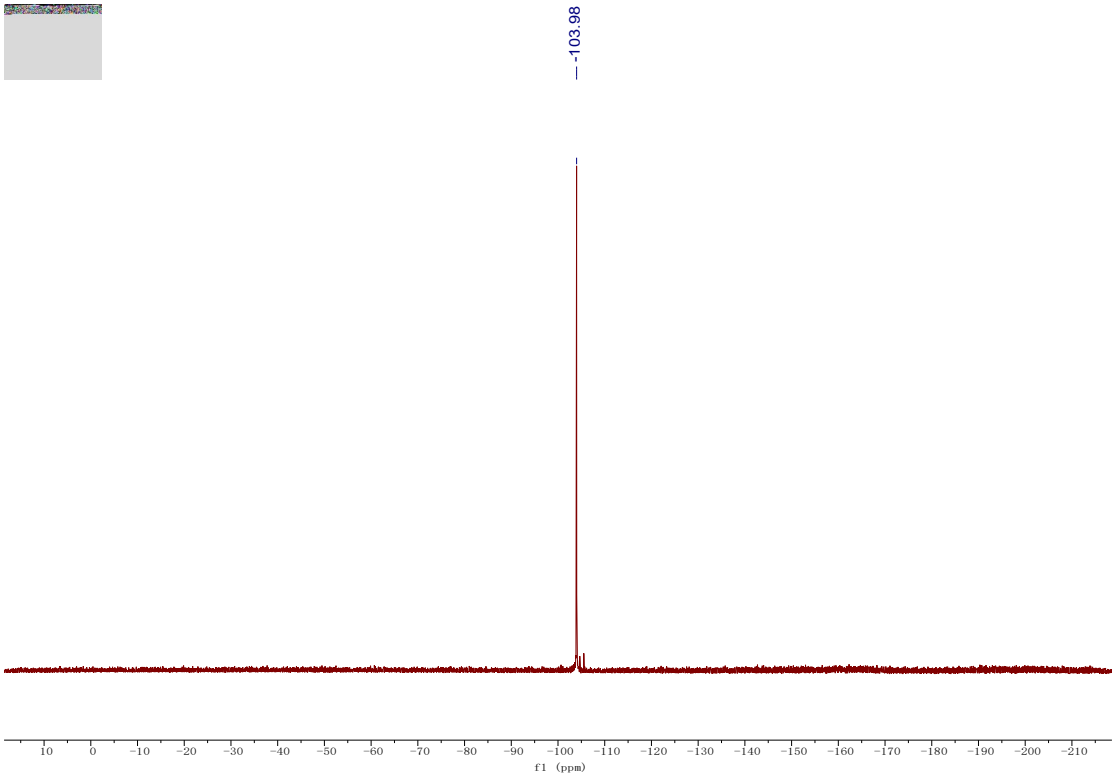


Figure S77. ^{1}H-NMR of **4k**

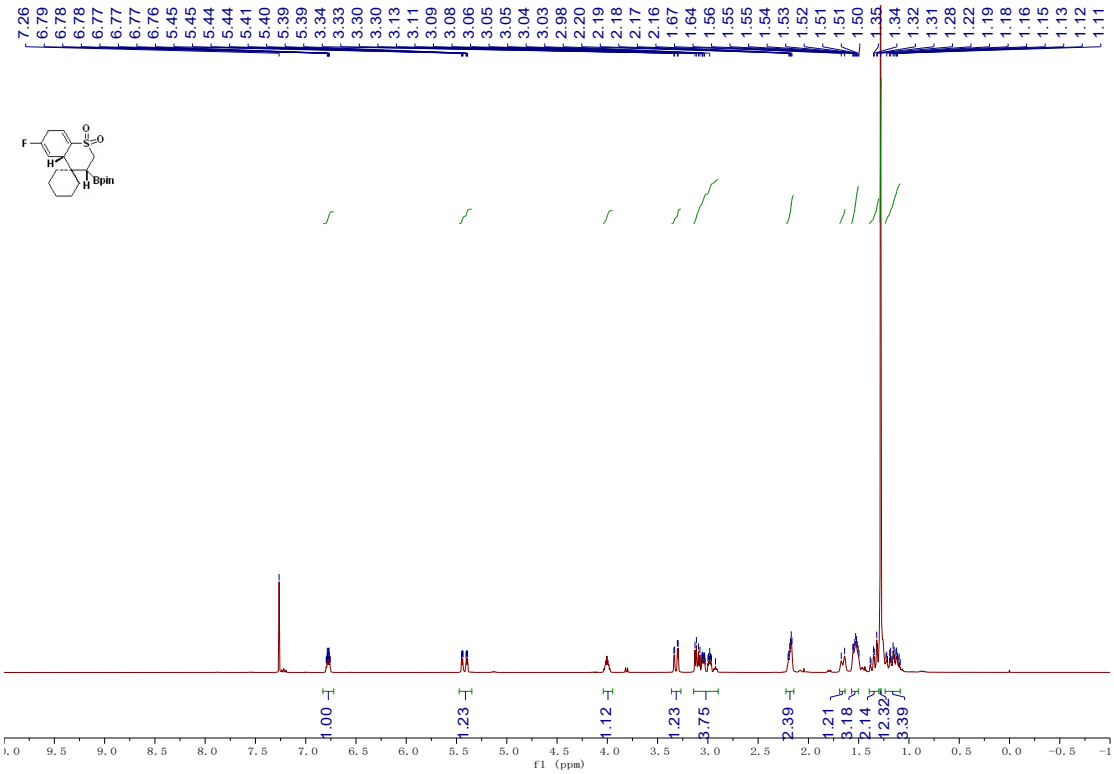


Figure S78. ^{13}C-NMR of **4k**

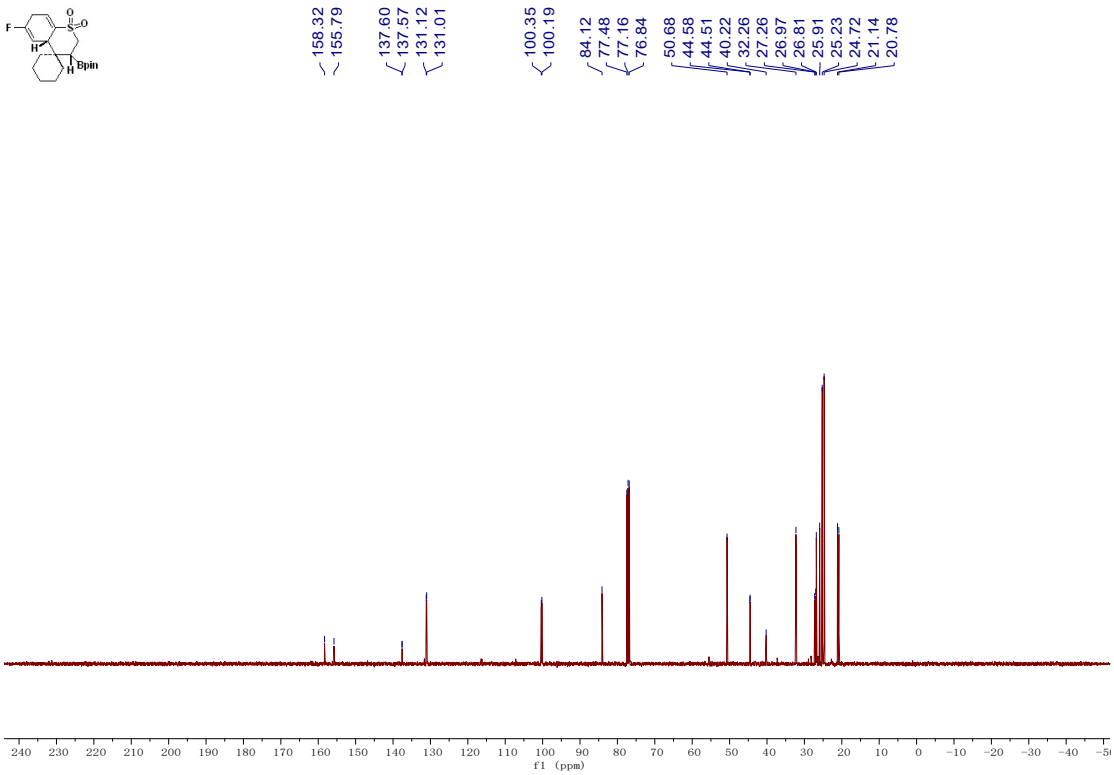


Figure S79. ^{19}F-NMR of **4k**

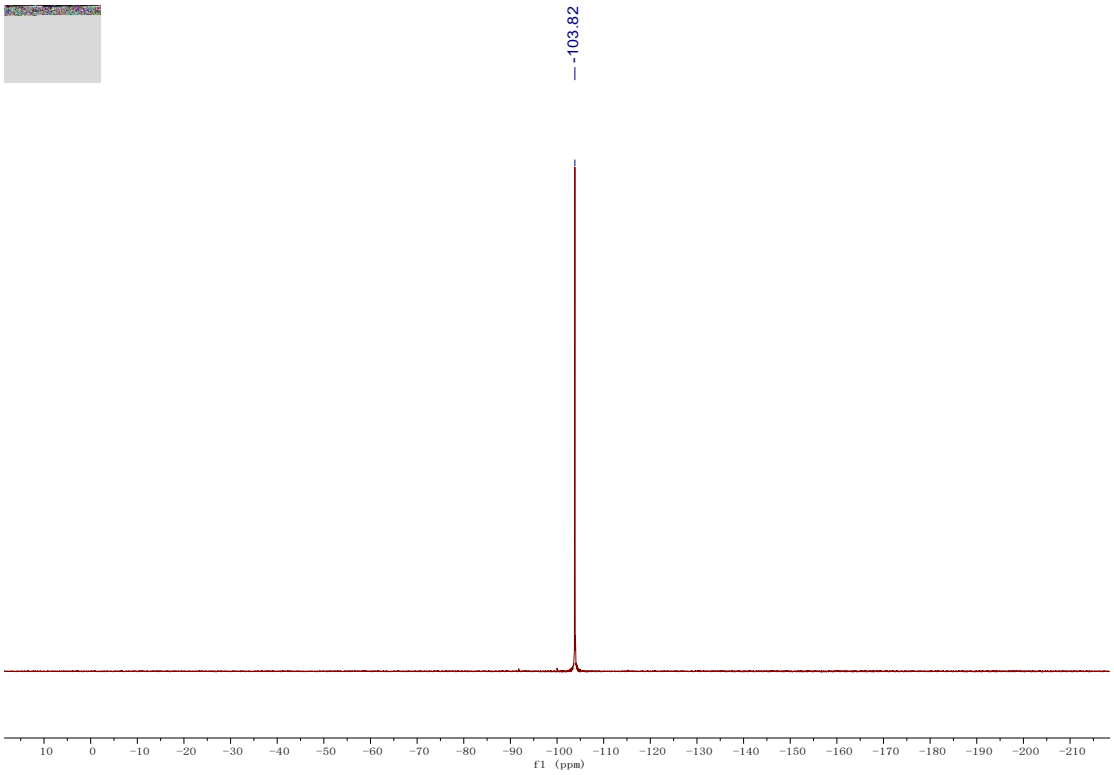


Figure S80. ^{1}H-NMR of **4l**

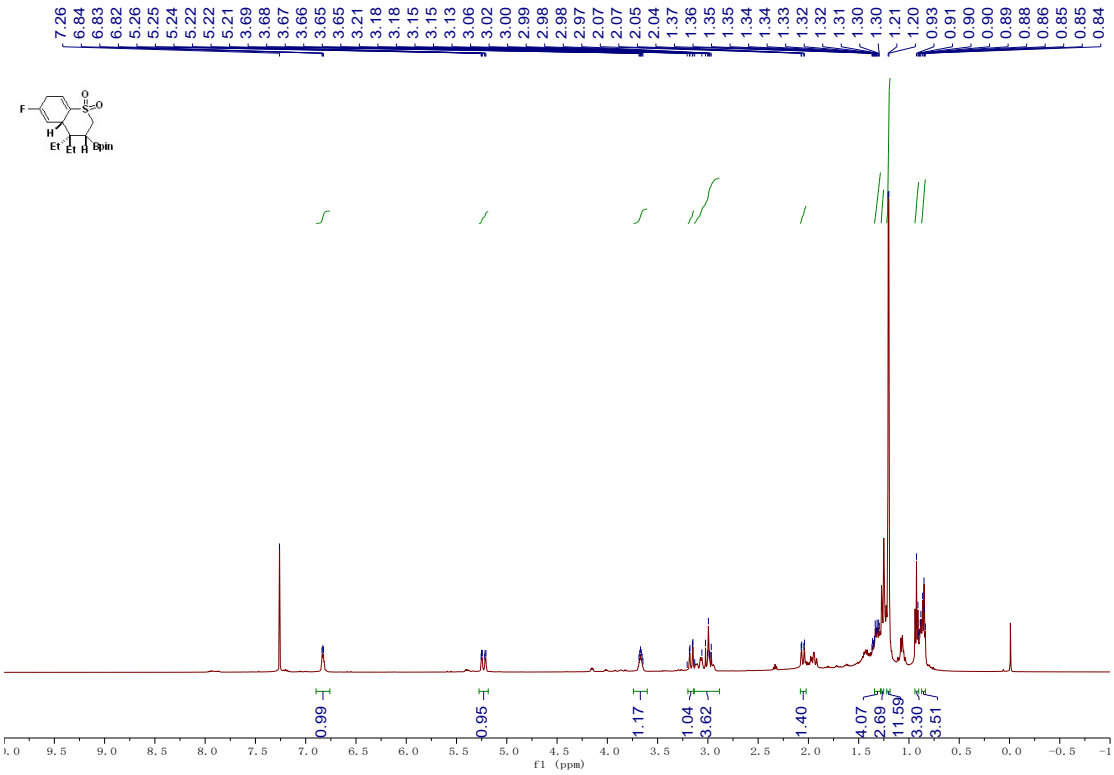


Figure S81. ^{13}C-NMR of **4l**

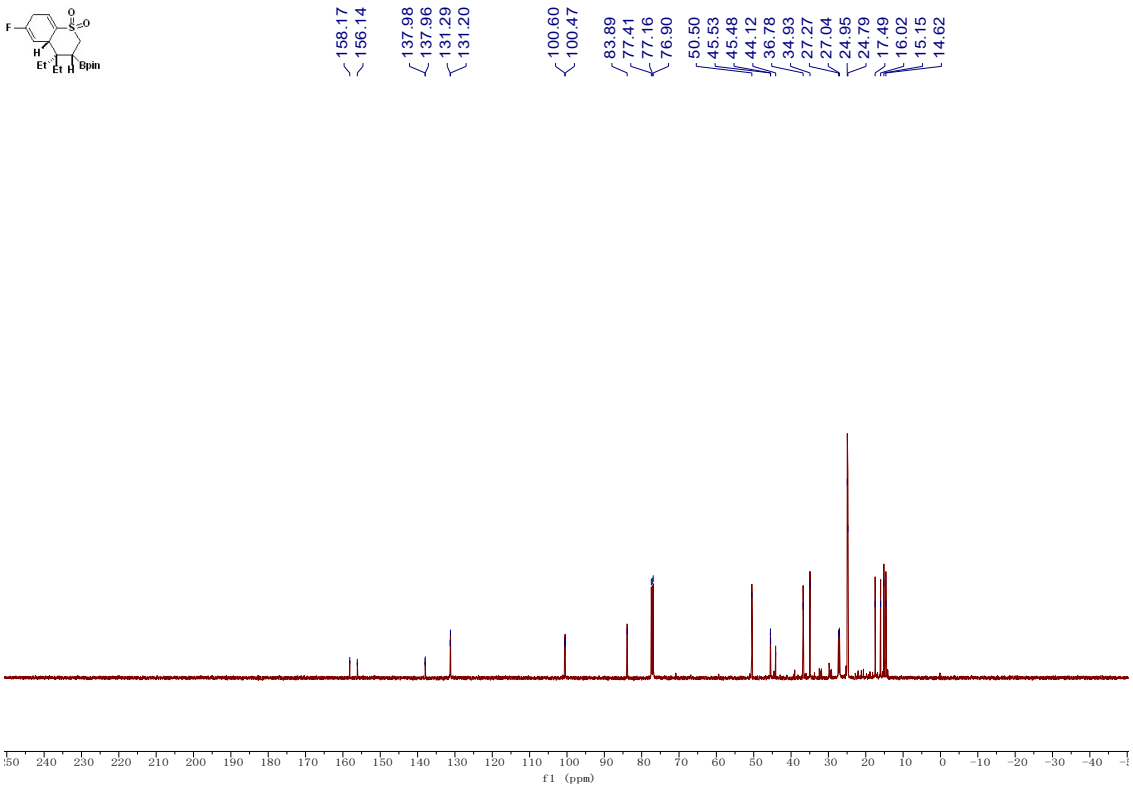


Figure S82. ^{19}F-NMR of **4l**

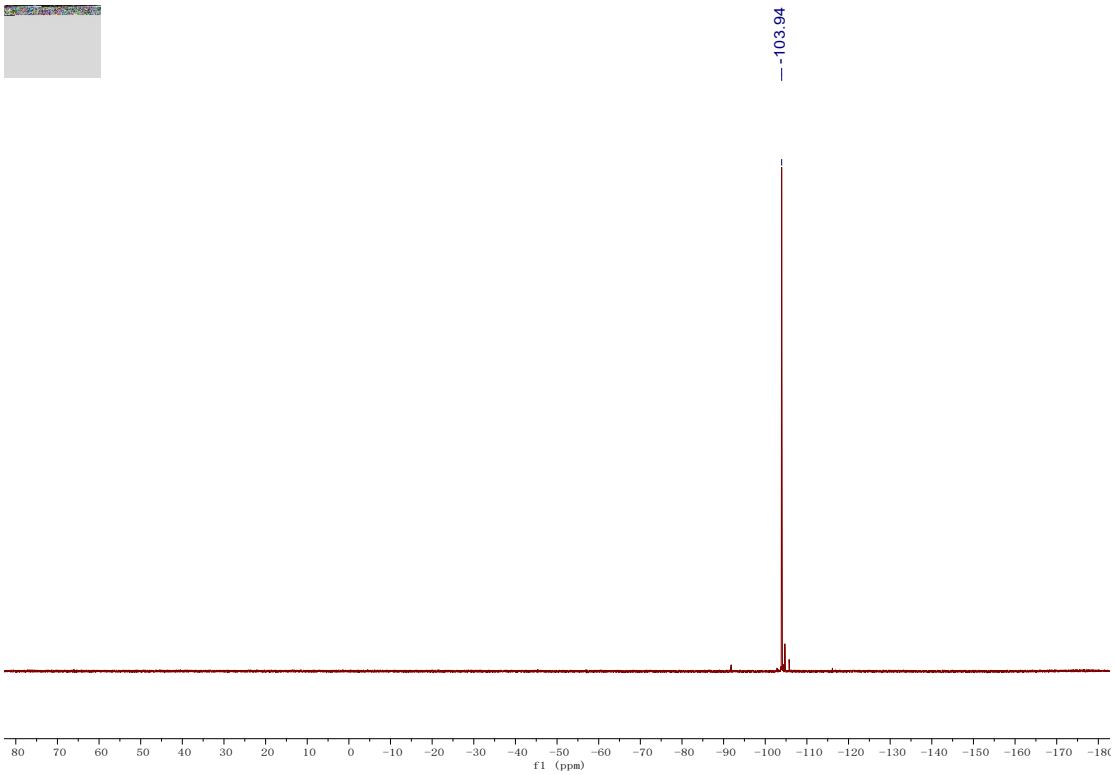


Figure S83. ^{1}H-NMR of **4m**

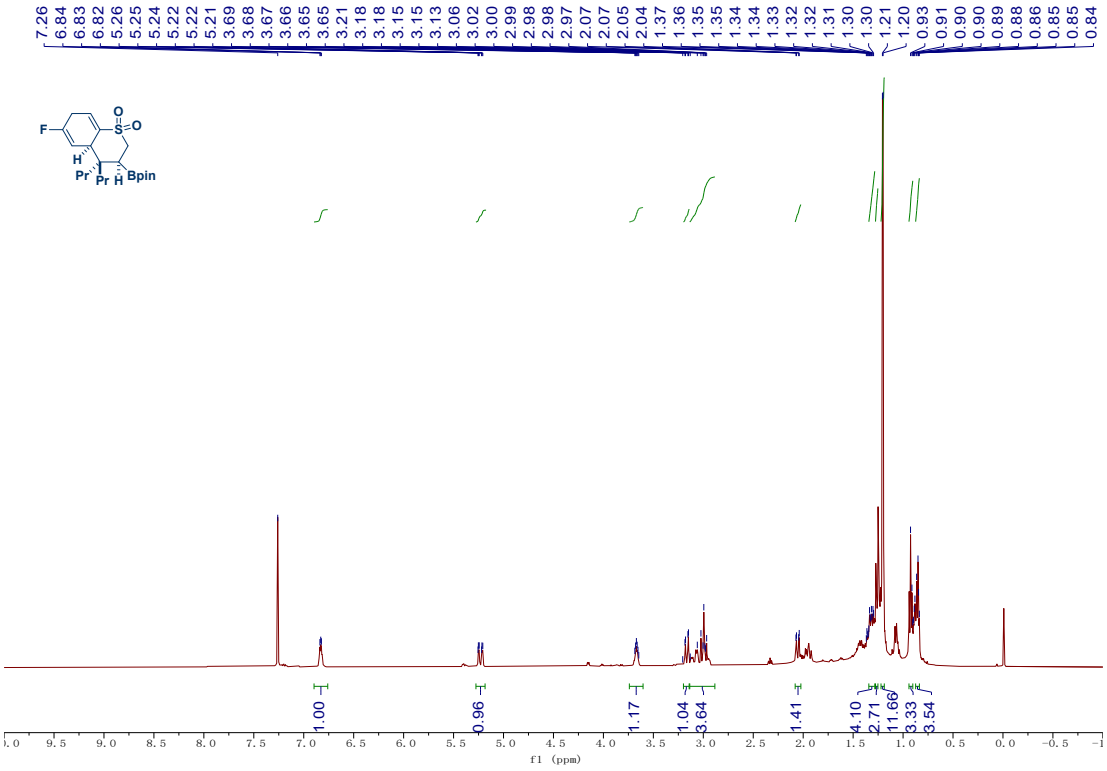


Figure S84. ^{13}C-NMR of **4m**

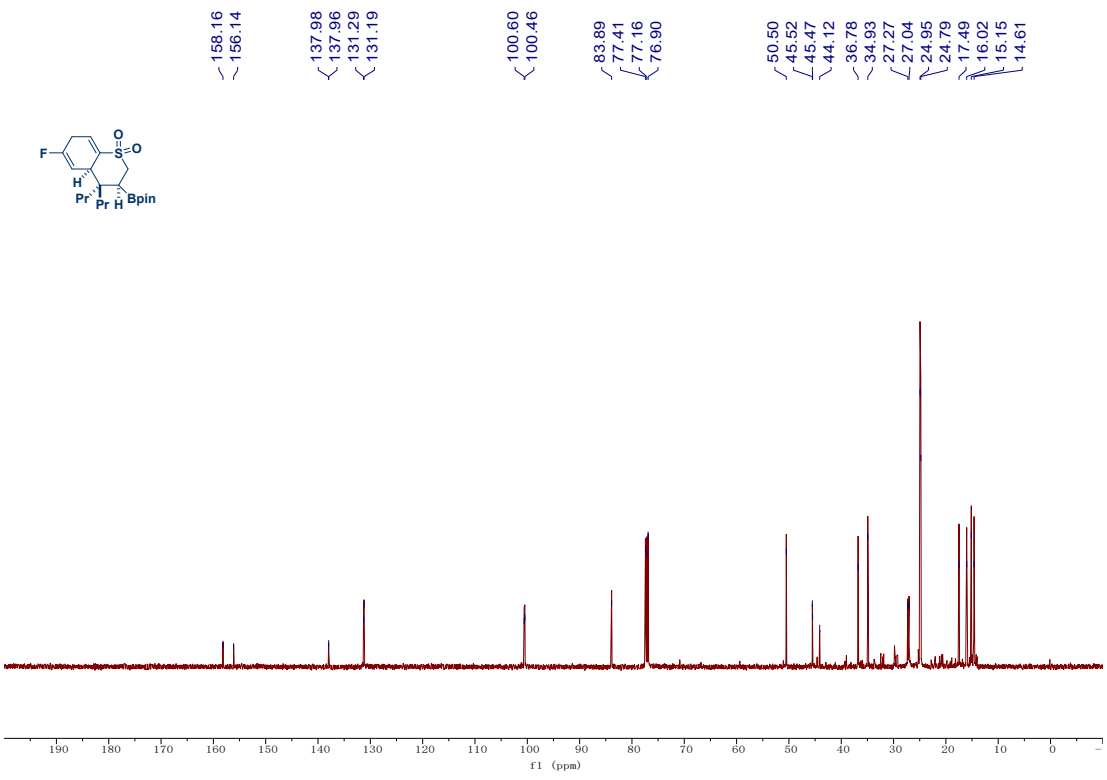


Figure S85. ^{19}F-NMR of **4m**

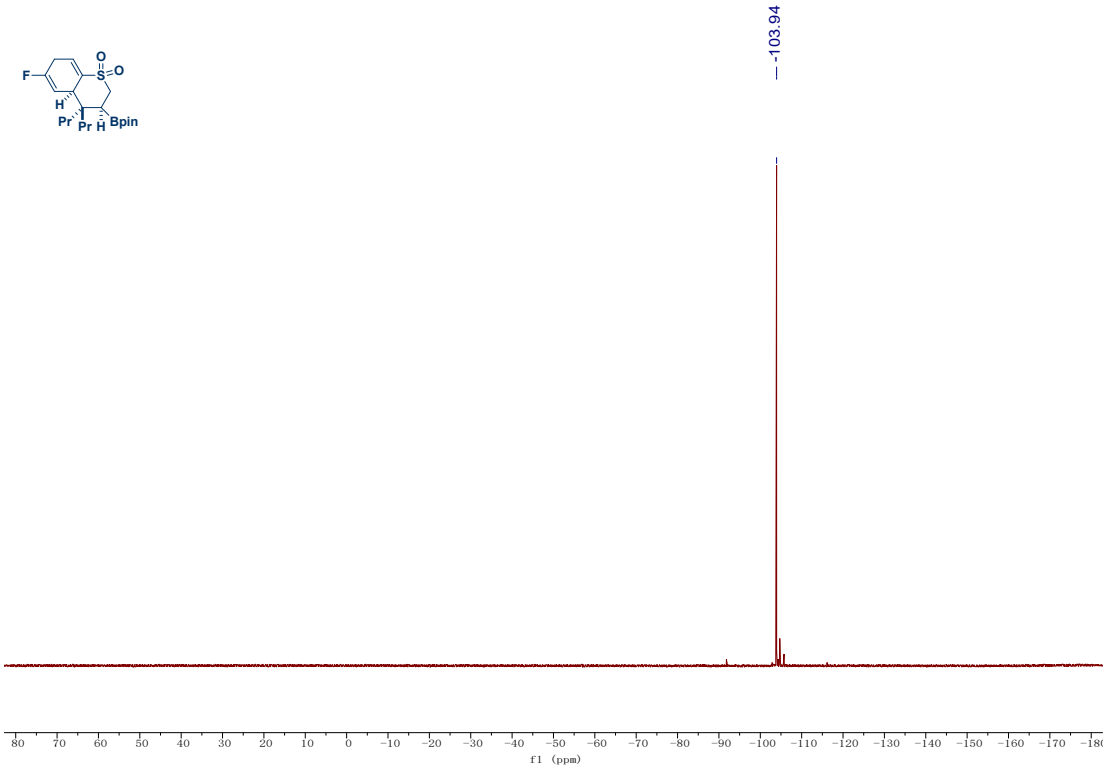


Figure S86. ^{1}H-NMR of **4n**

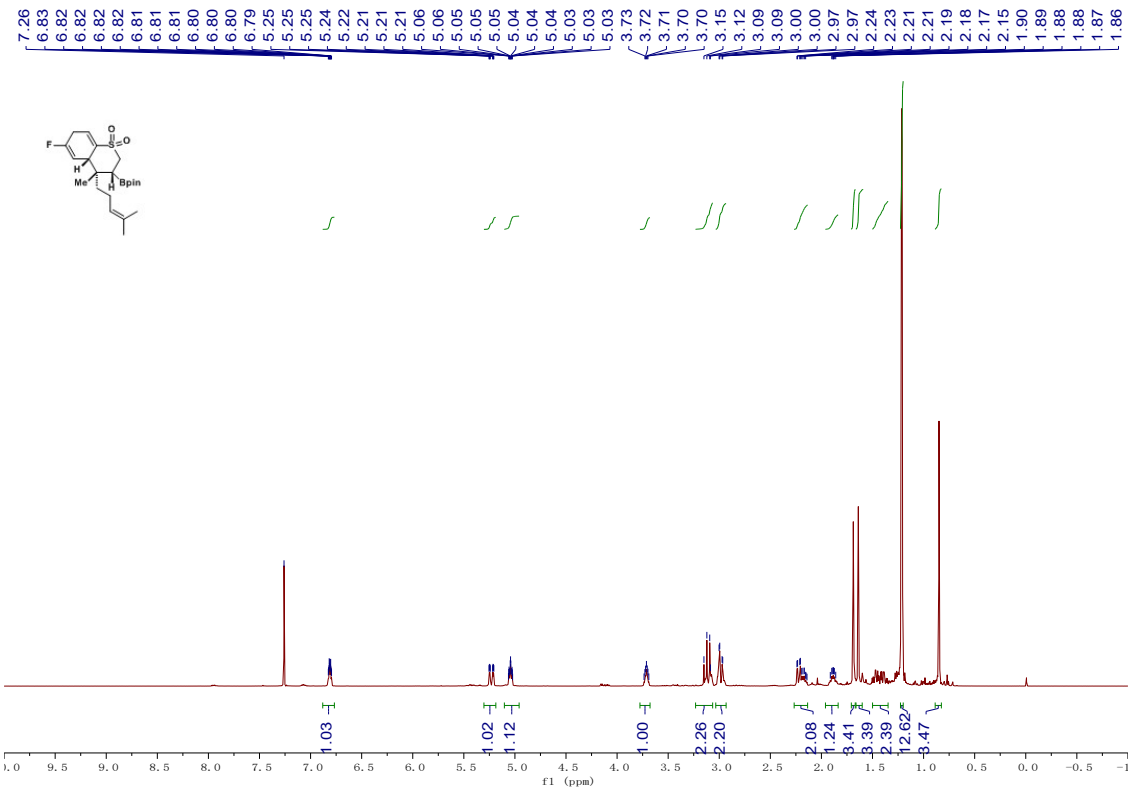


Figure S87. ^{13}C-NMR of **4n**

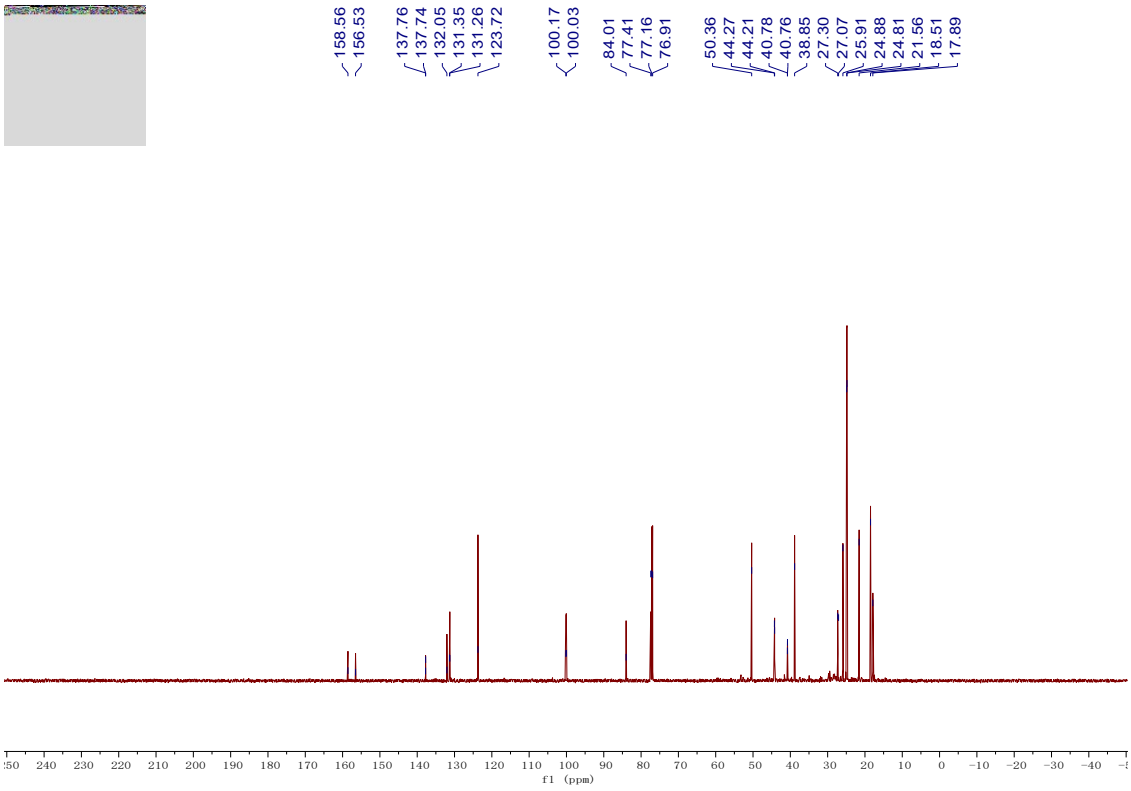


Figure S88. ^{19}F-NMR of **4n**

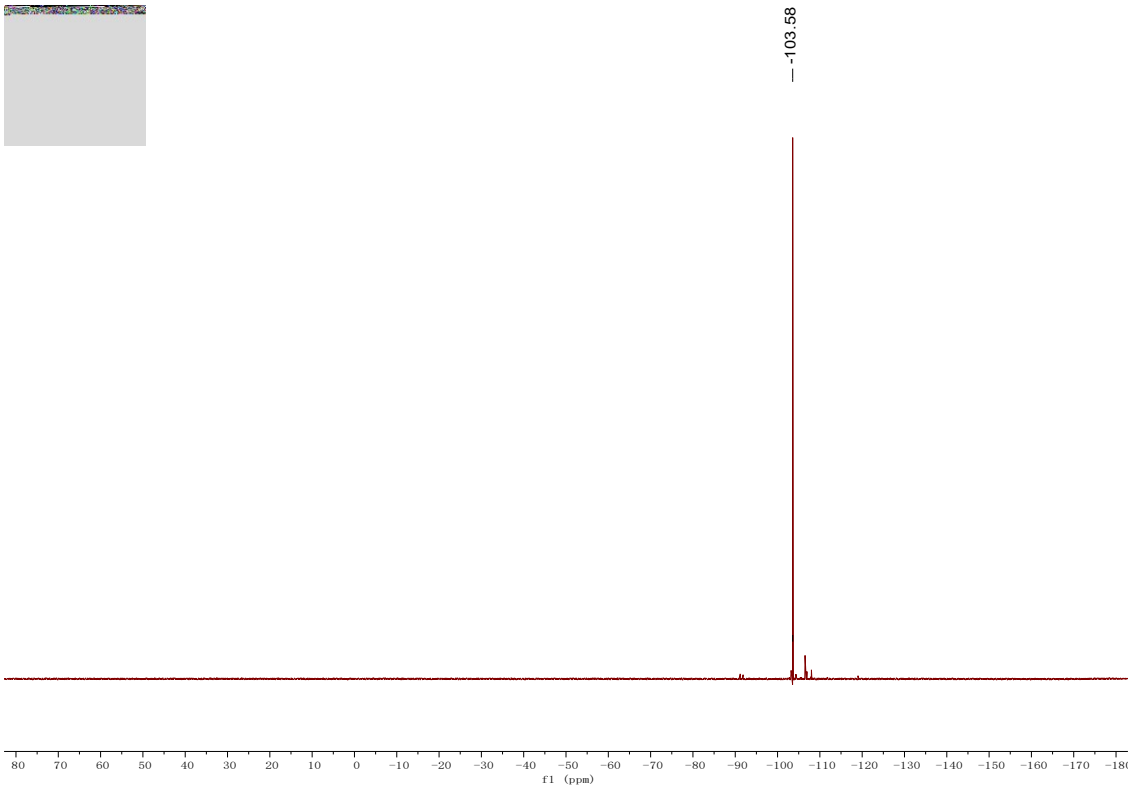

-103.58
80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180
f1 (ppm)

Figure S89. ^{1}H-NMR of **5a**

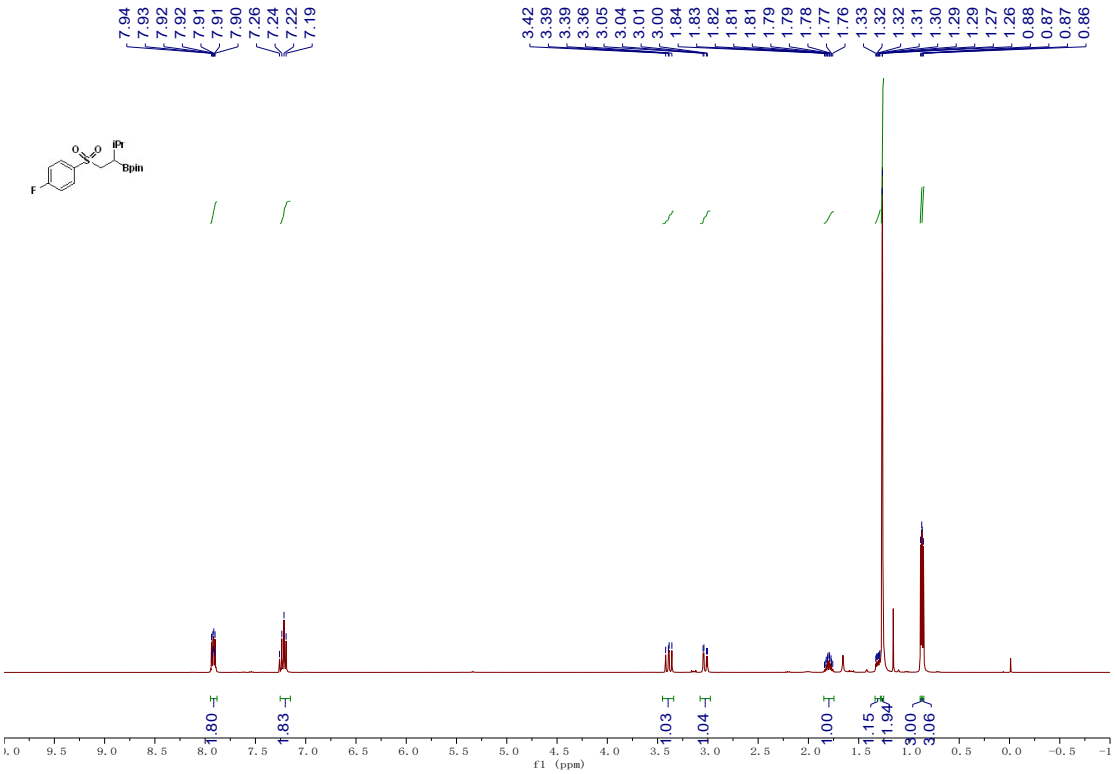


Figure S90. ^{13}C-NMR of **5a**

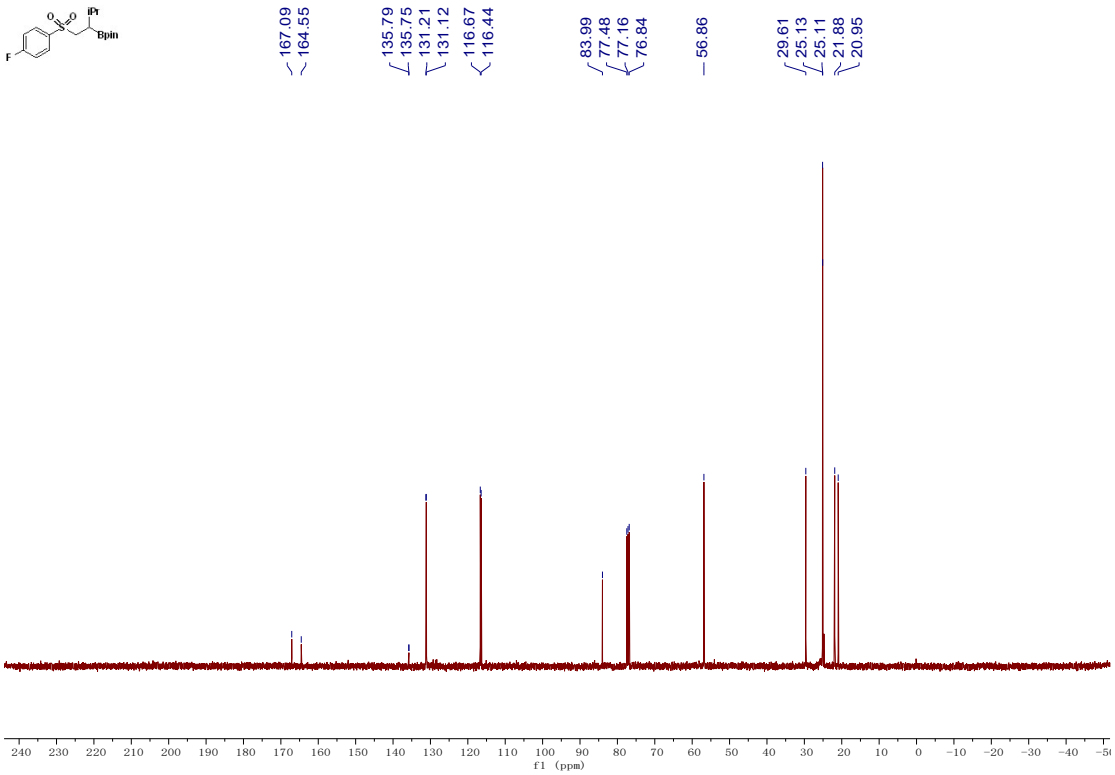


Figure S91. ^{19}F-NMR of **5a**

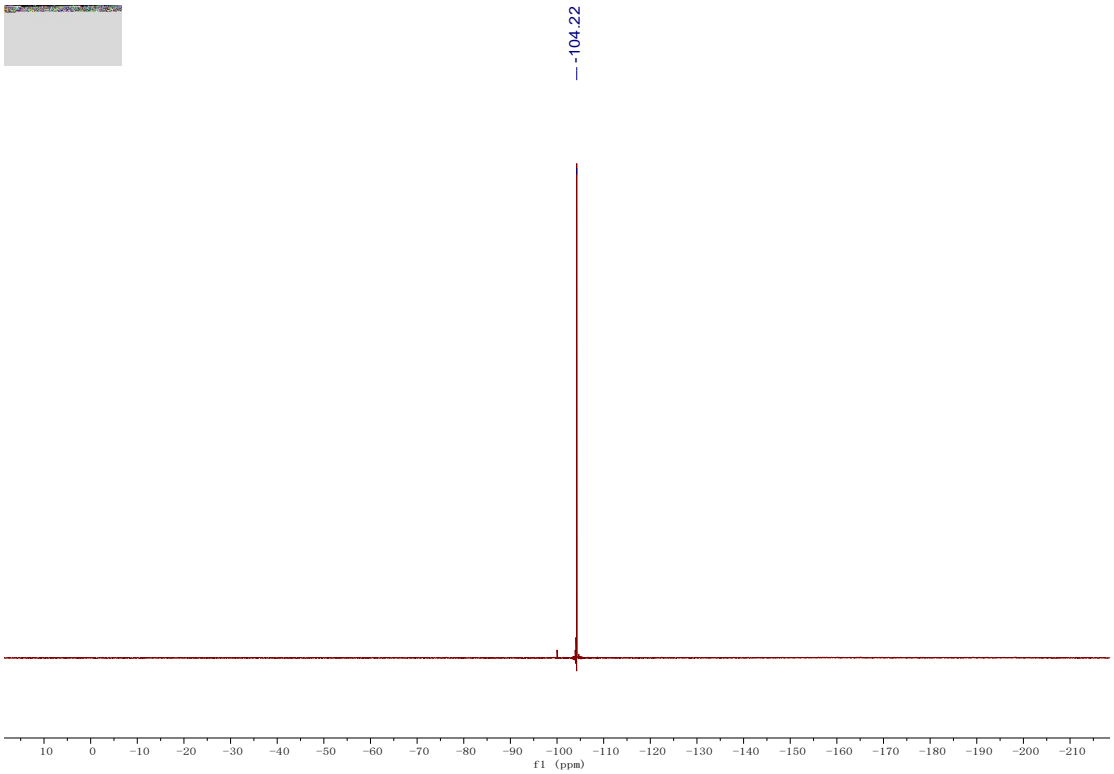


Figure S92. ^{1}H-NMR of **5b**

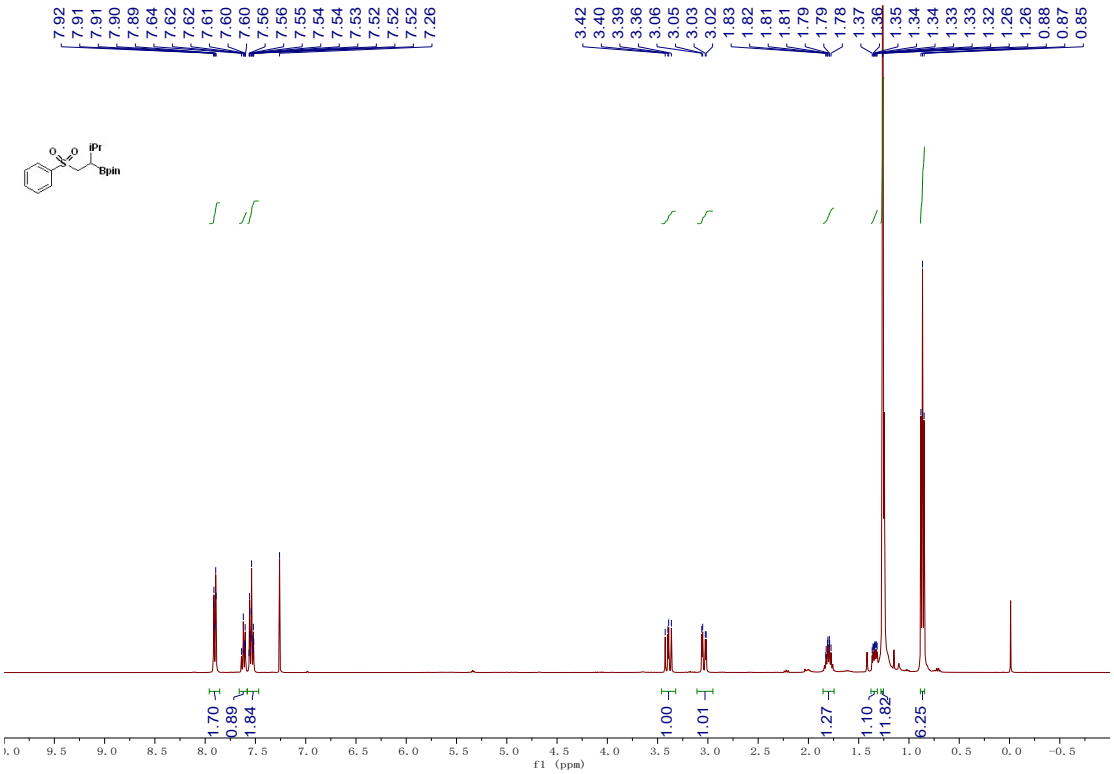


Figure S93. ^{13}C-NMR of **5b**

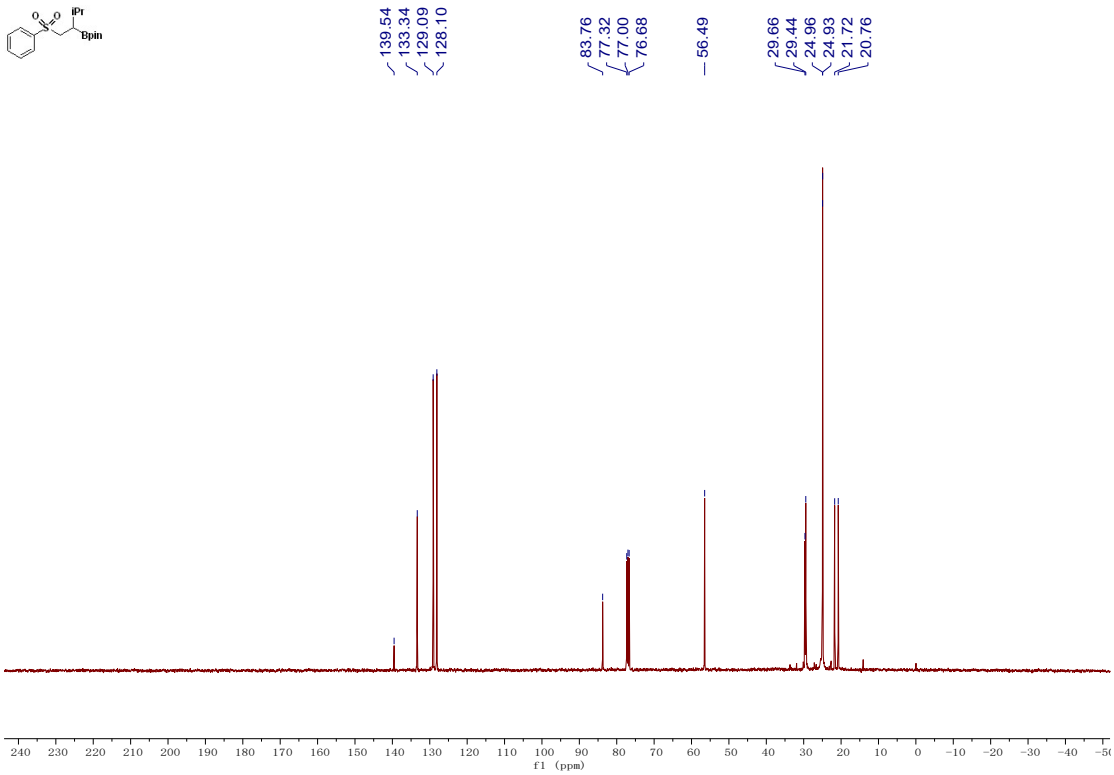


Figure S94. ^{1}H-NMR of **5c**

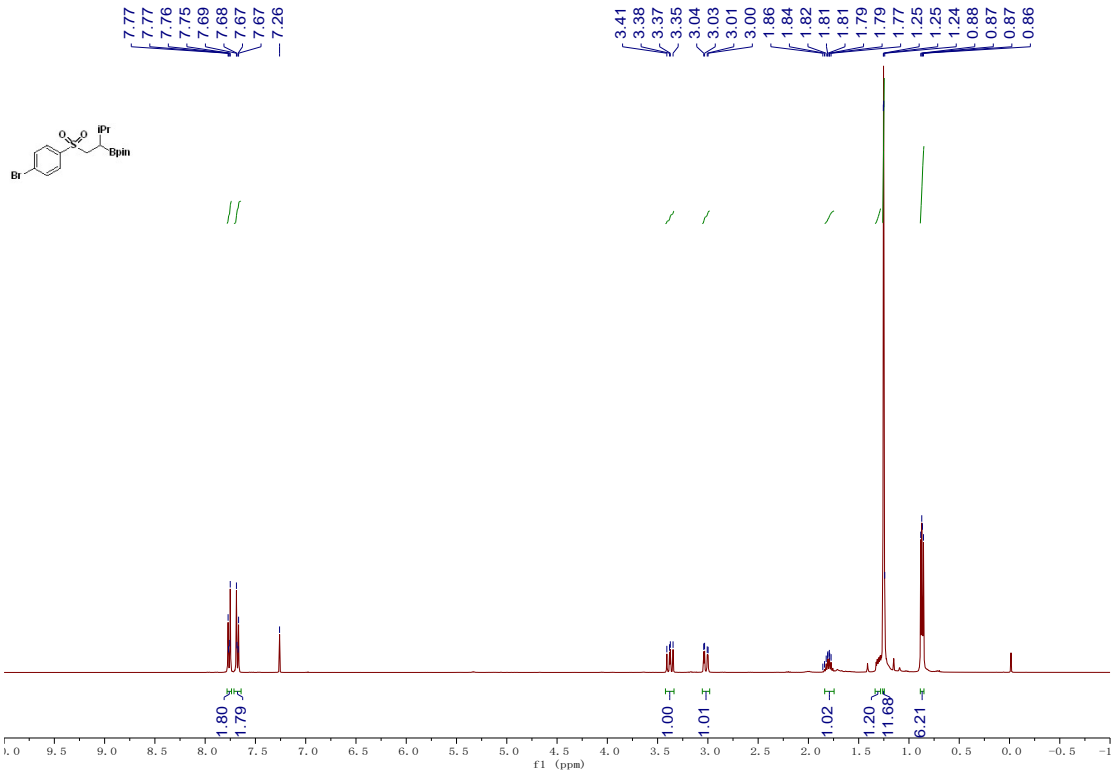


Figure S95. ^{13}C-NMR of **5c**

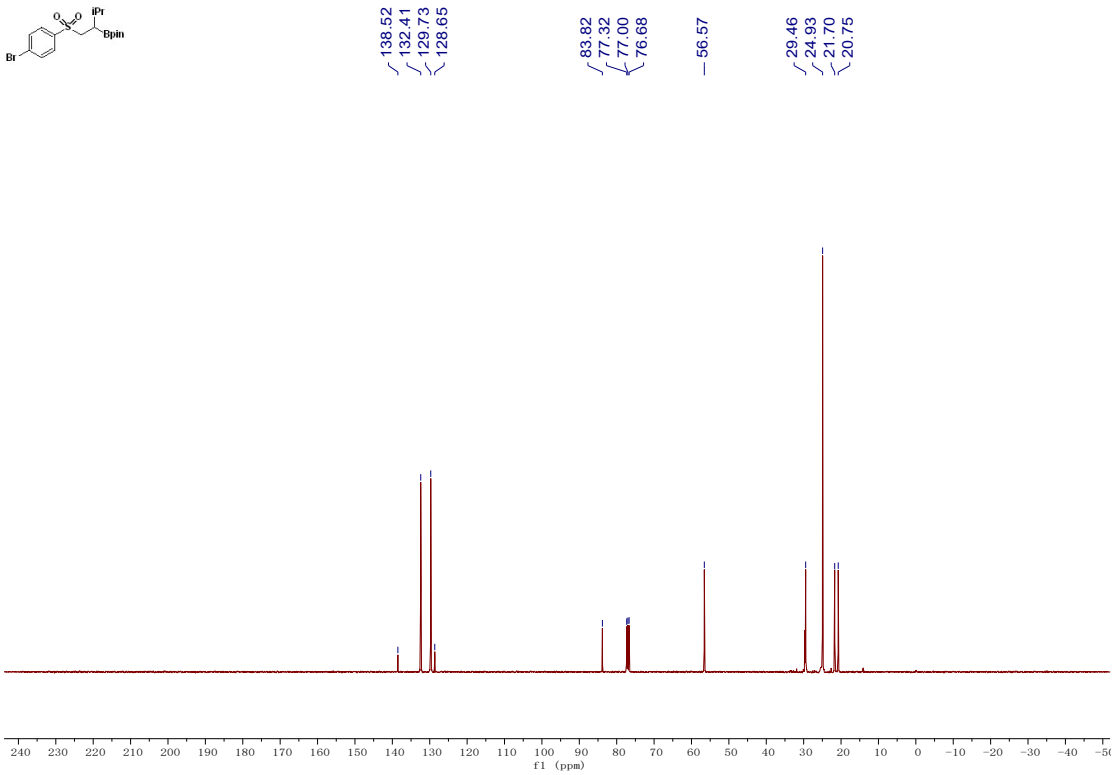


Figure S96. ^{1}H-NMR of **5d**

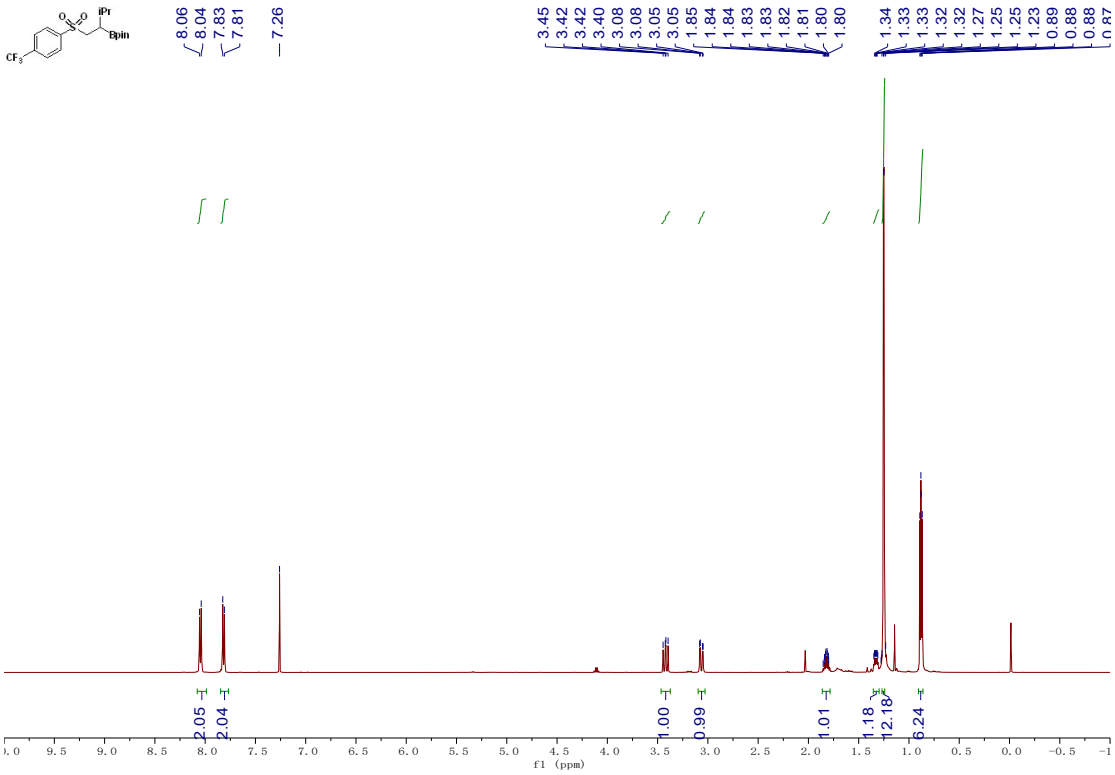


Figure S97. ^{13}C-NMR of **5d**

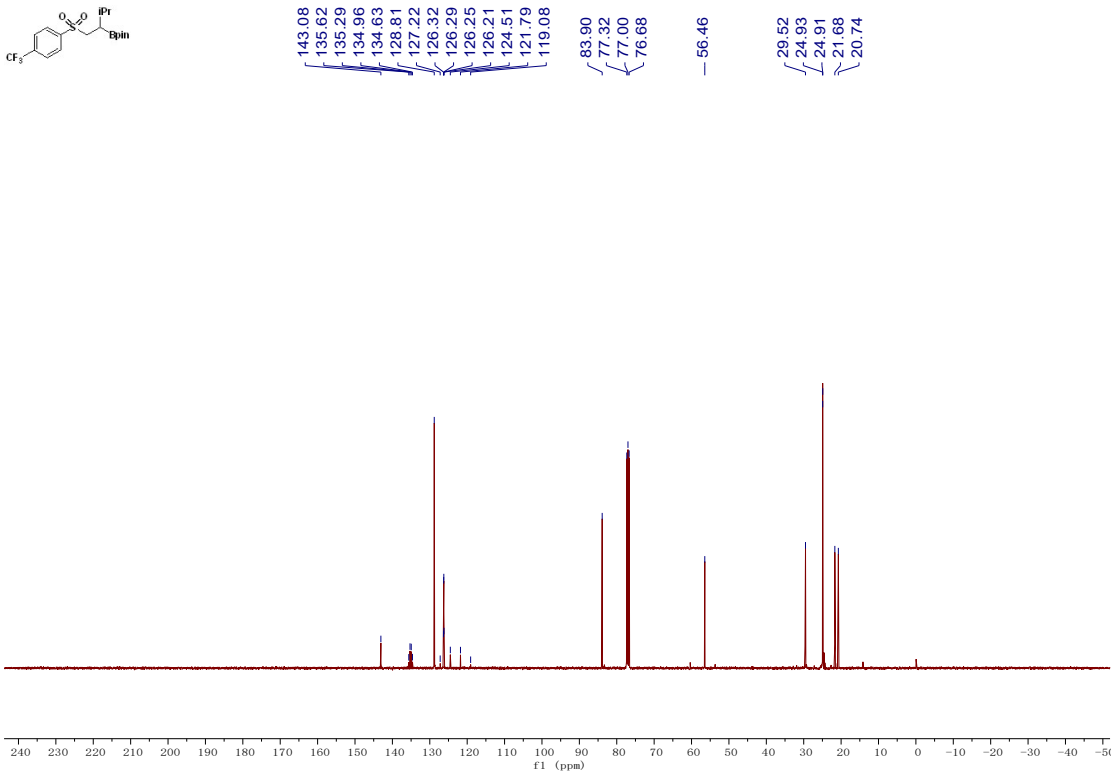


Figure S98. ^{19}F-NMR of **5d**

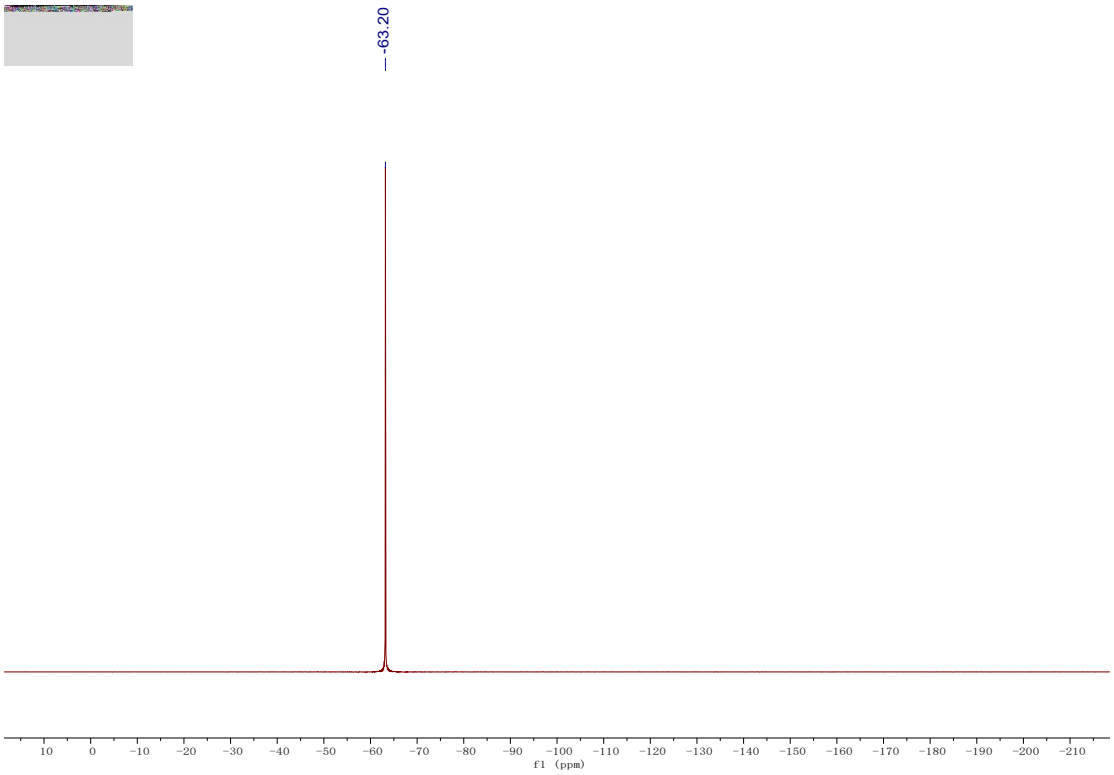


Figure S99. ^{1}H-NMR of **5e**

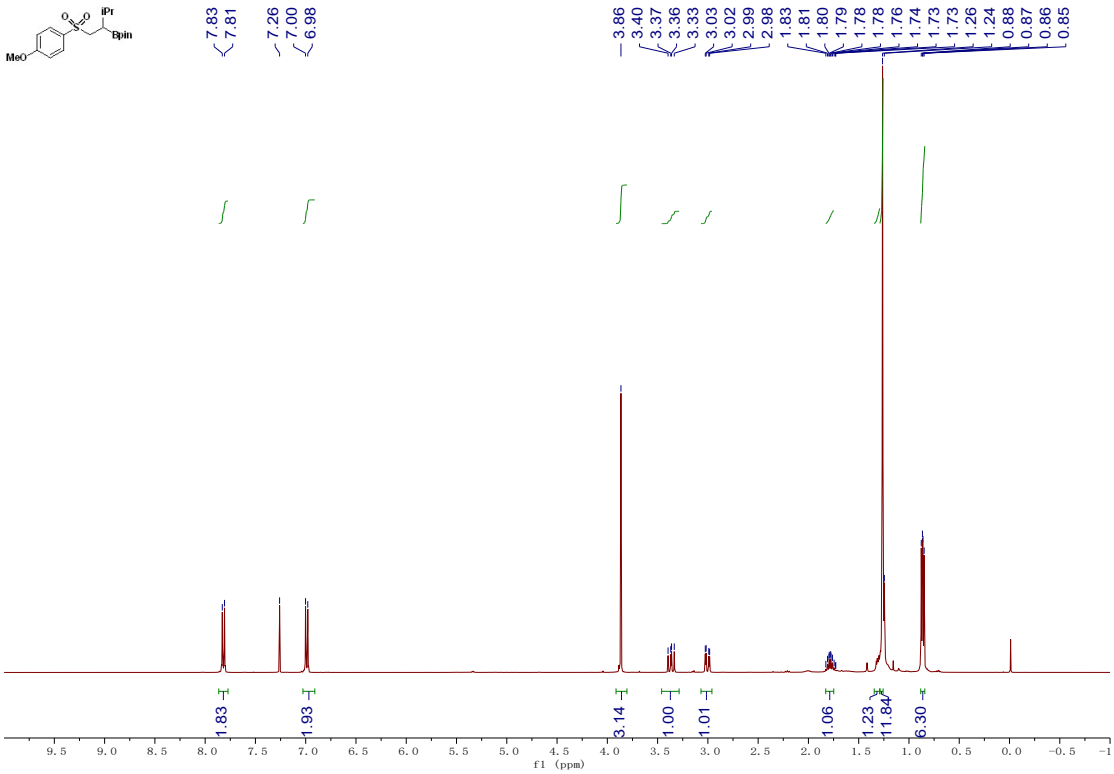


Figure S100. ^{13}C-NMR of **5e**

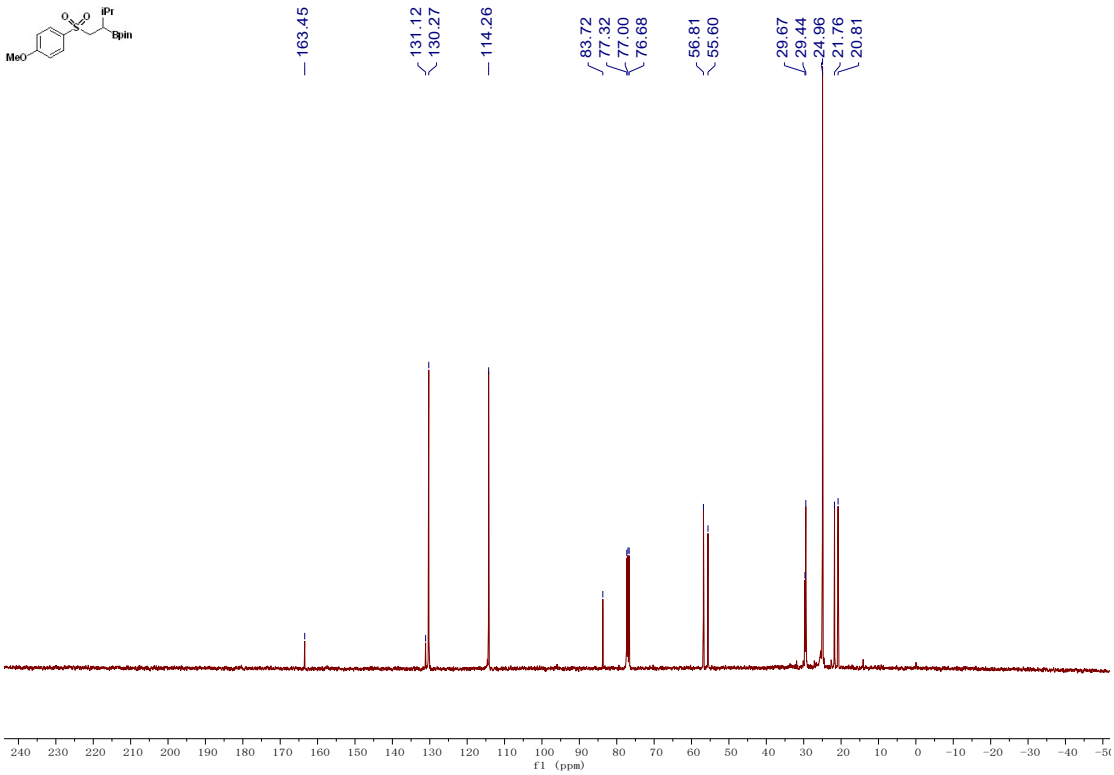


Figure S101. ^{1}H-NMR of **5f**

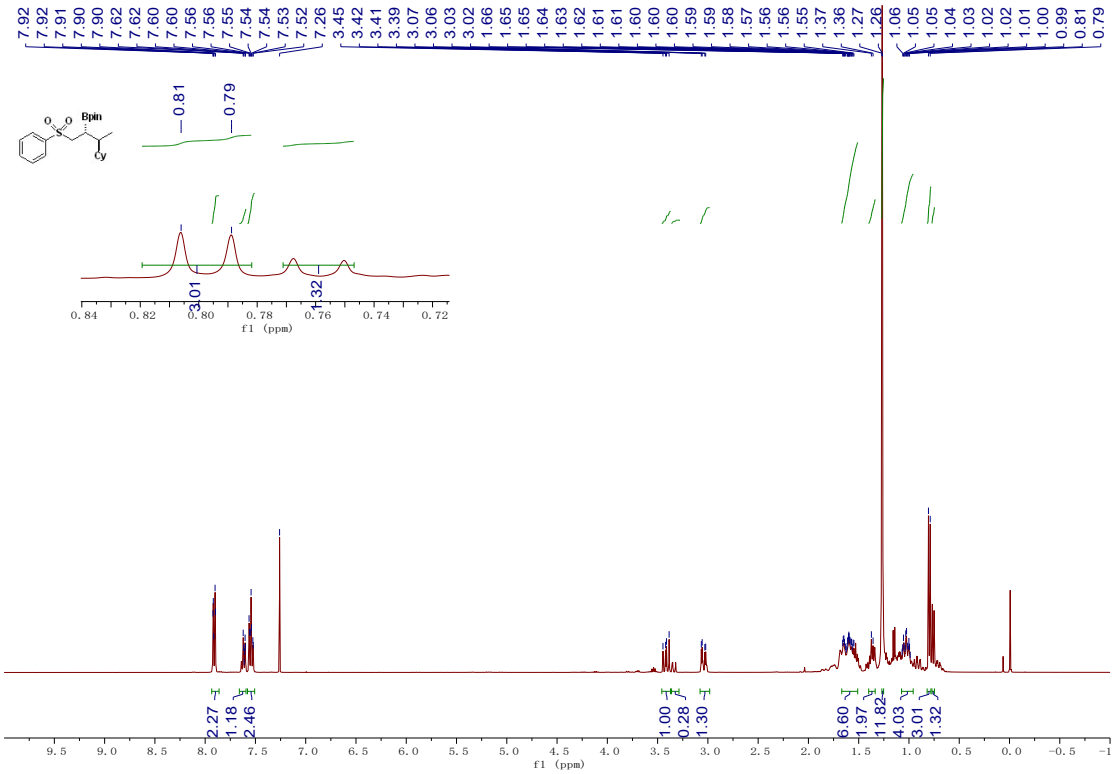


Figure S102. ^{13}C-NMR of **5f**

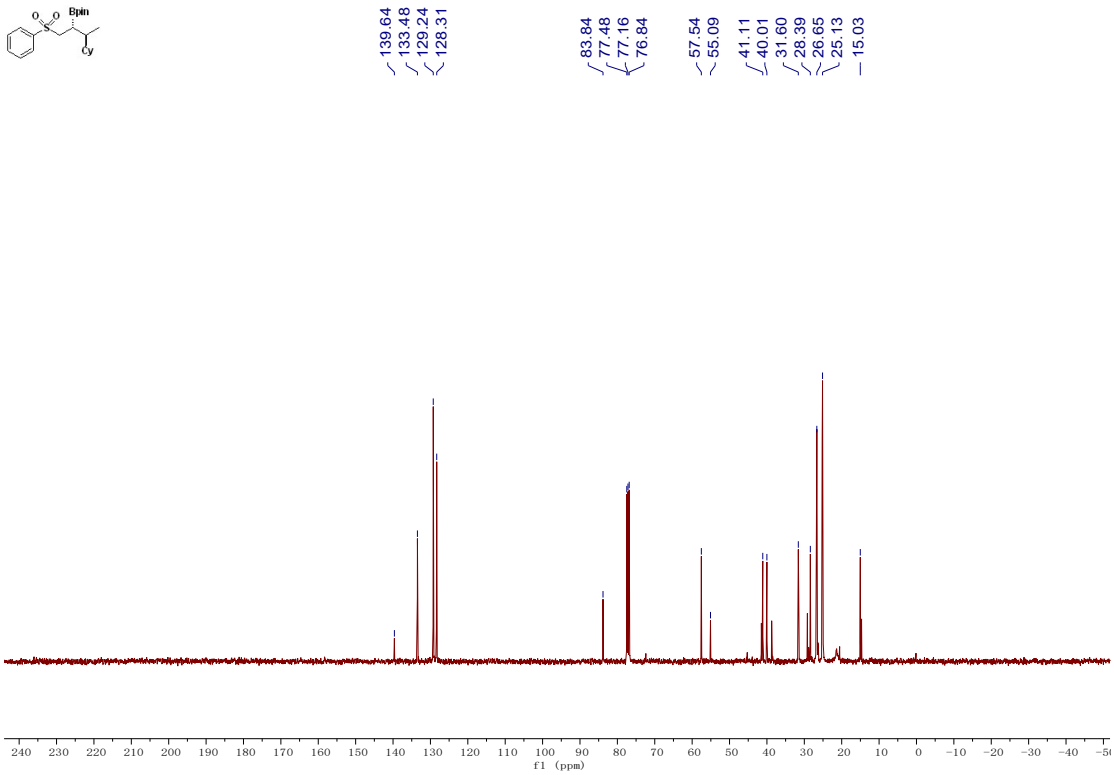


Figure S103. ^{1}H-NMR of **5g**

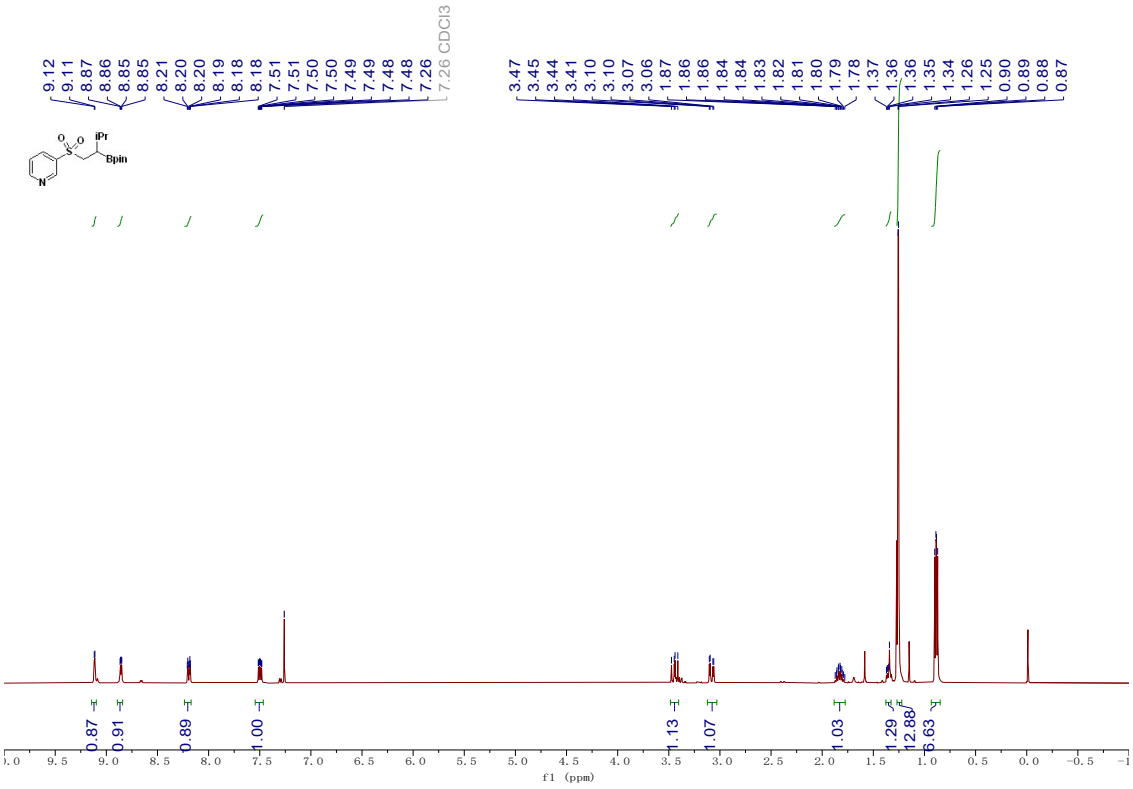


Figure S104. ^{13}C-NMR of **5g**

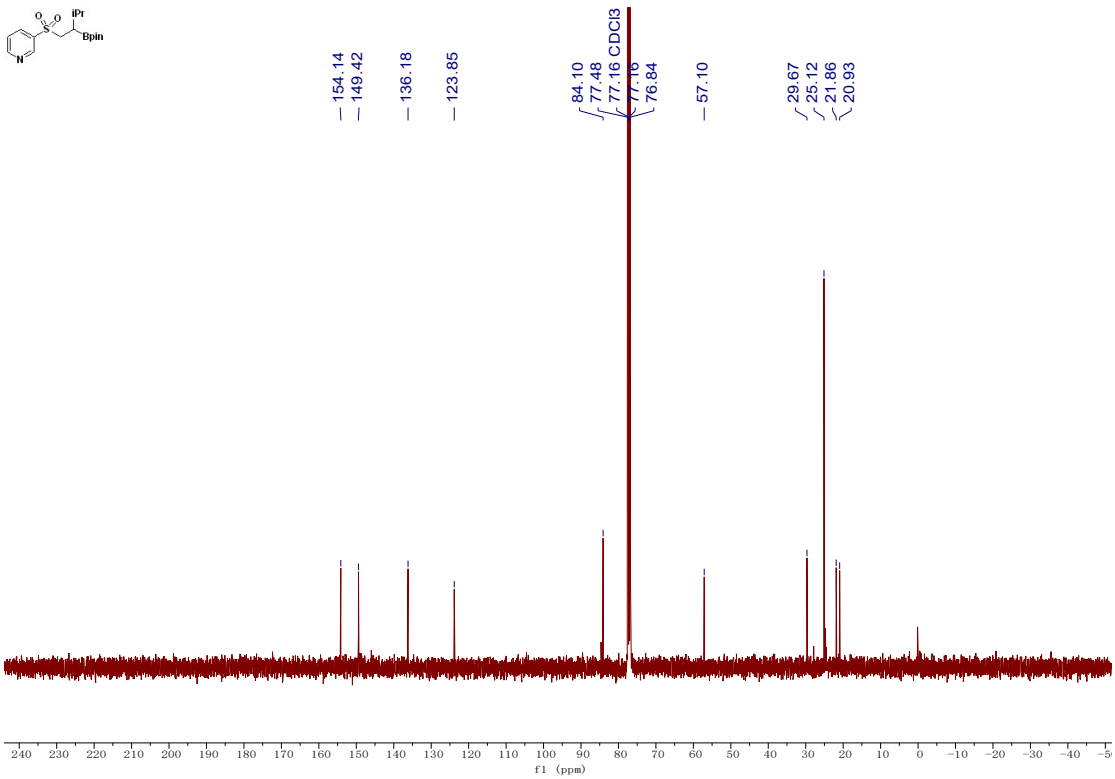


Figure S105. ^{1}H-NMR of **5h**

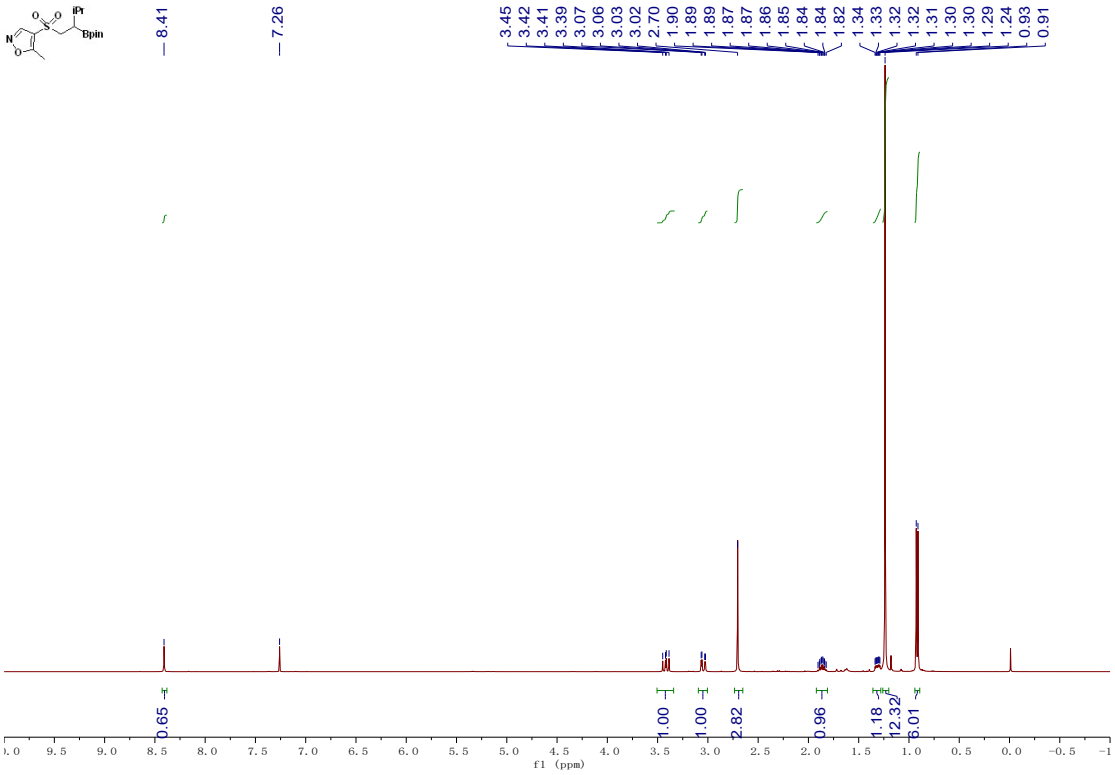


Figure S106. ^{13}C-NMR of **5h**

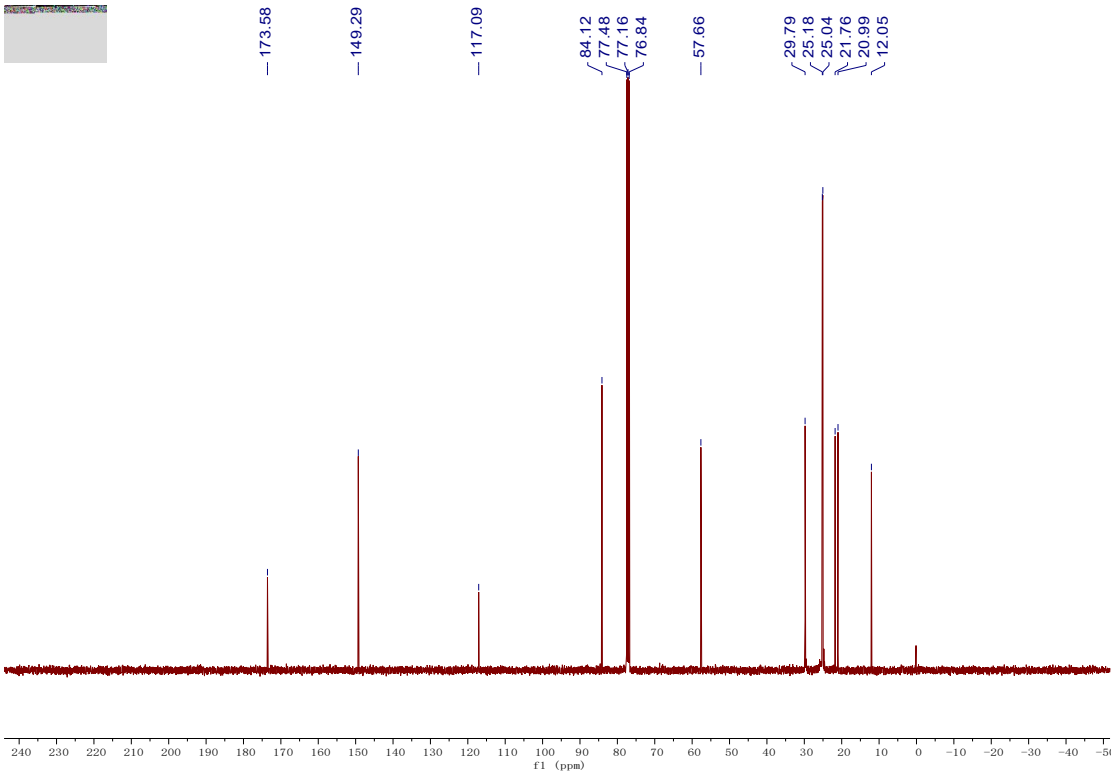


Figure S107. [1]H-NMR of **5i**

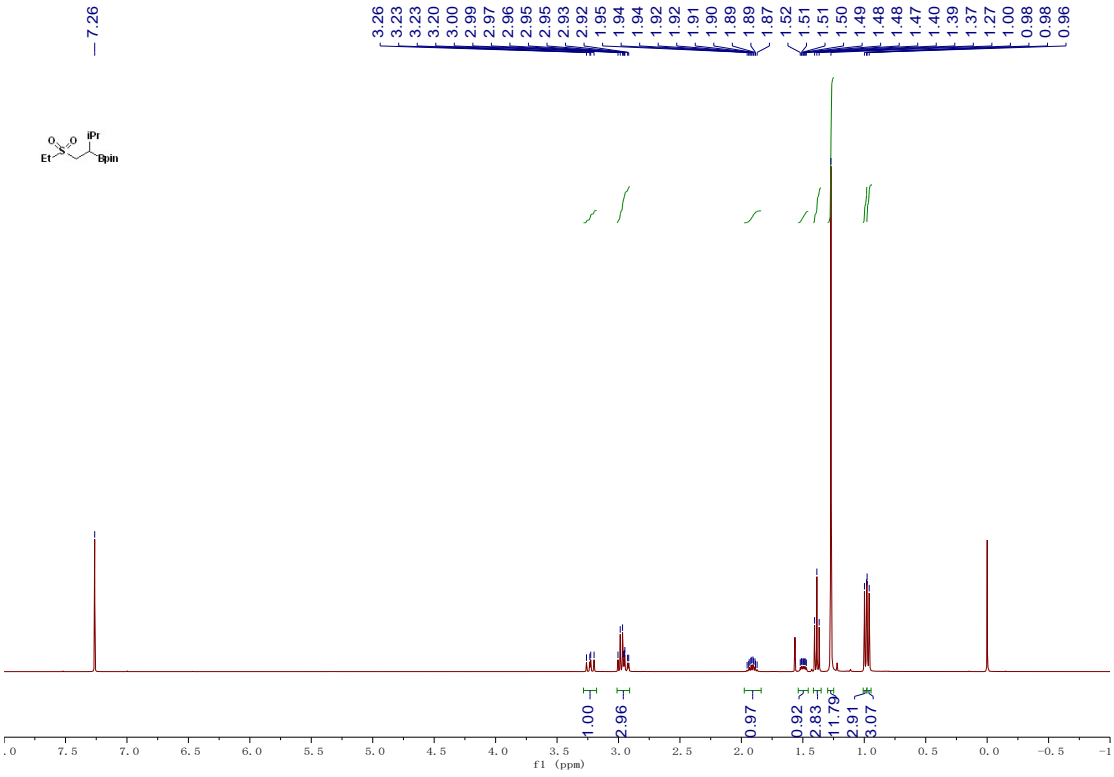


Figure S108. [13]C-NMR of **5i**

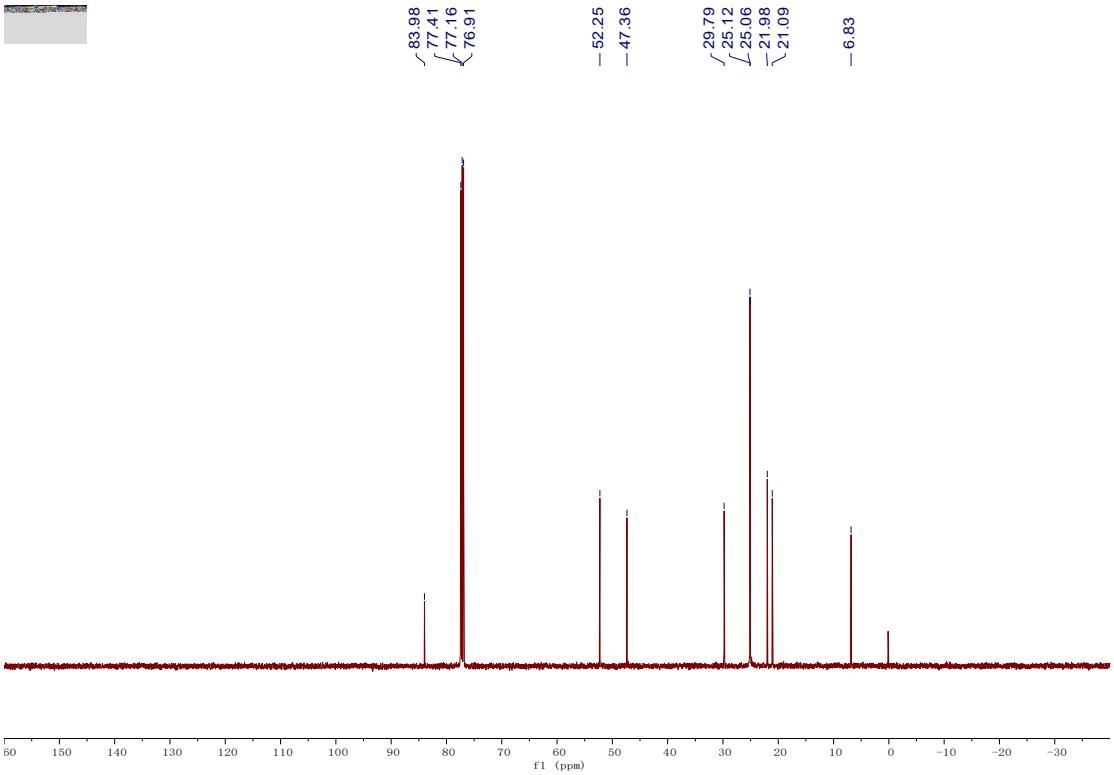


Figure S109. [1]H-NMR of **5j**

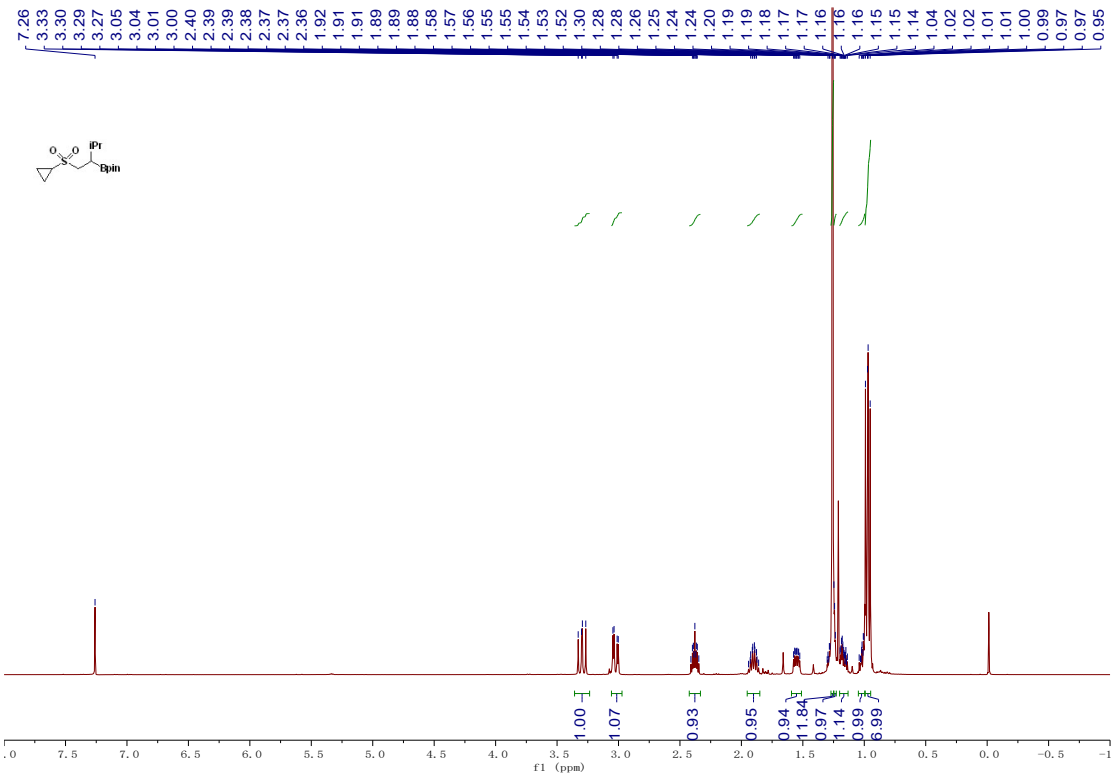


Figure S110. [13]C-NMR of **5j**

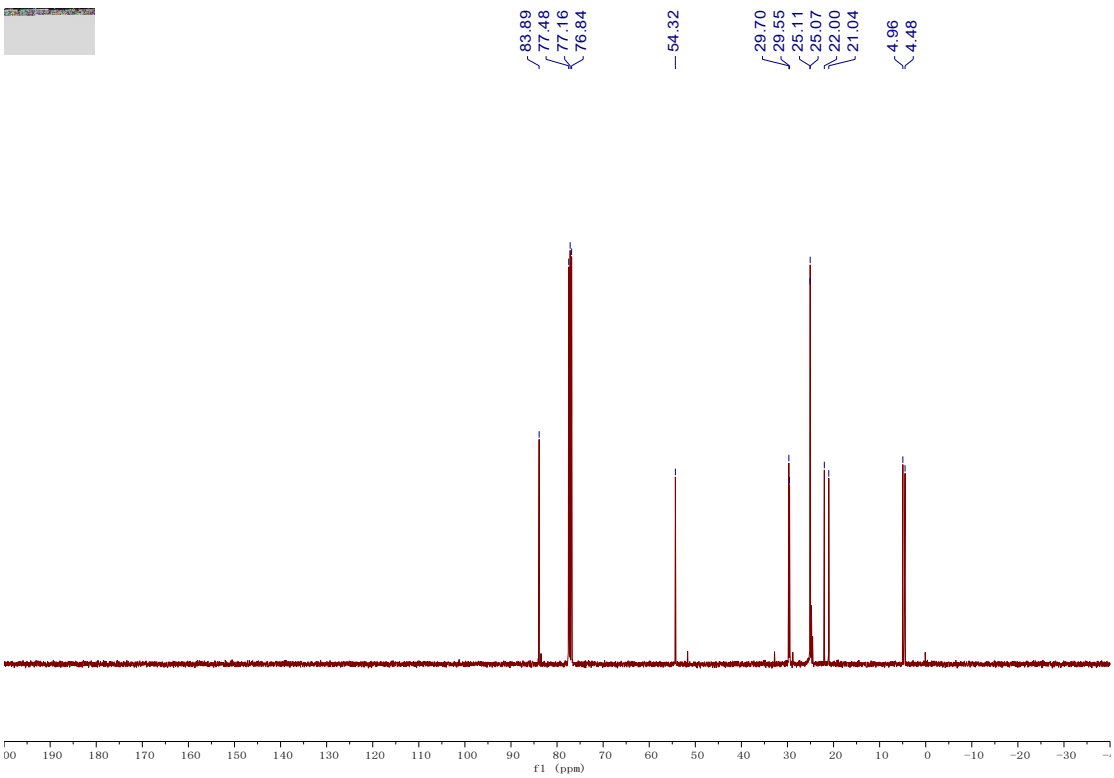


Figure S111. ^{1}H-NMR of **5k**

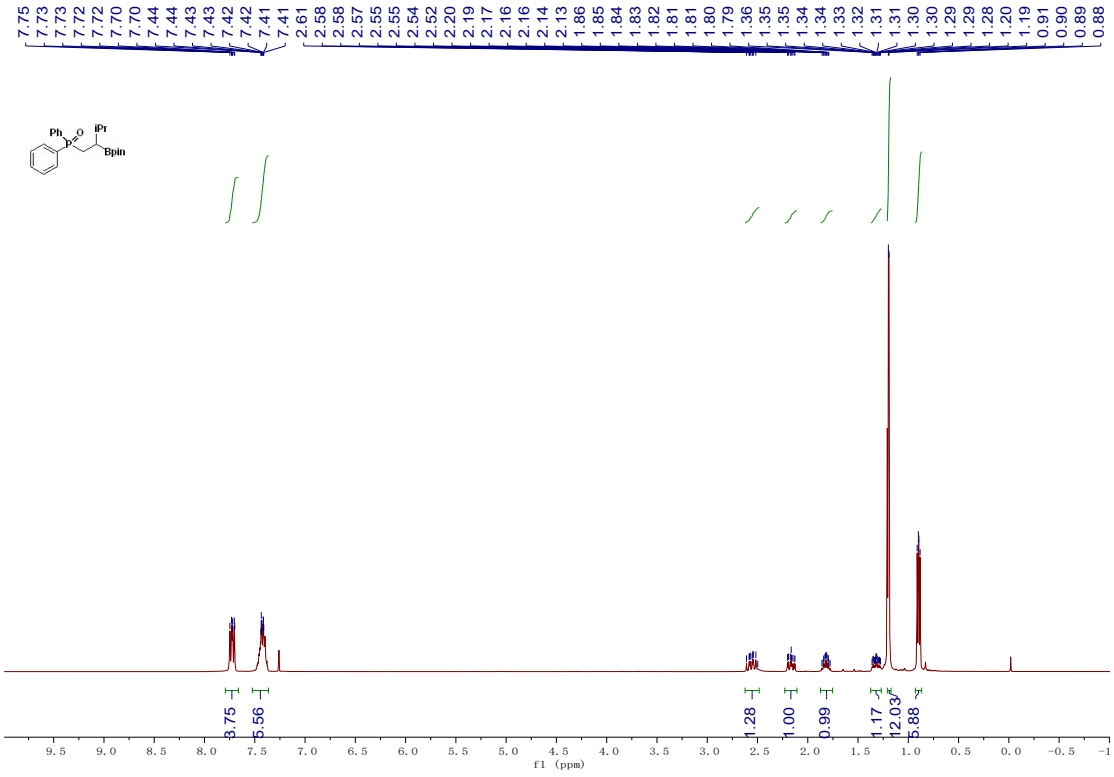


Figure S112. ^{13}C-NMR of **5k**

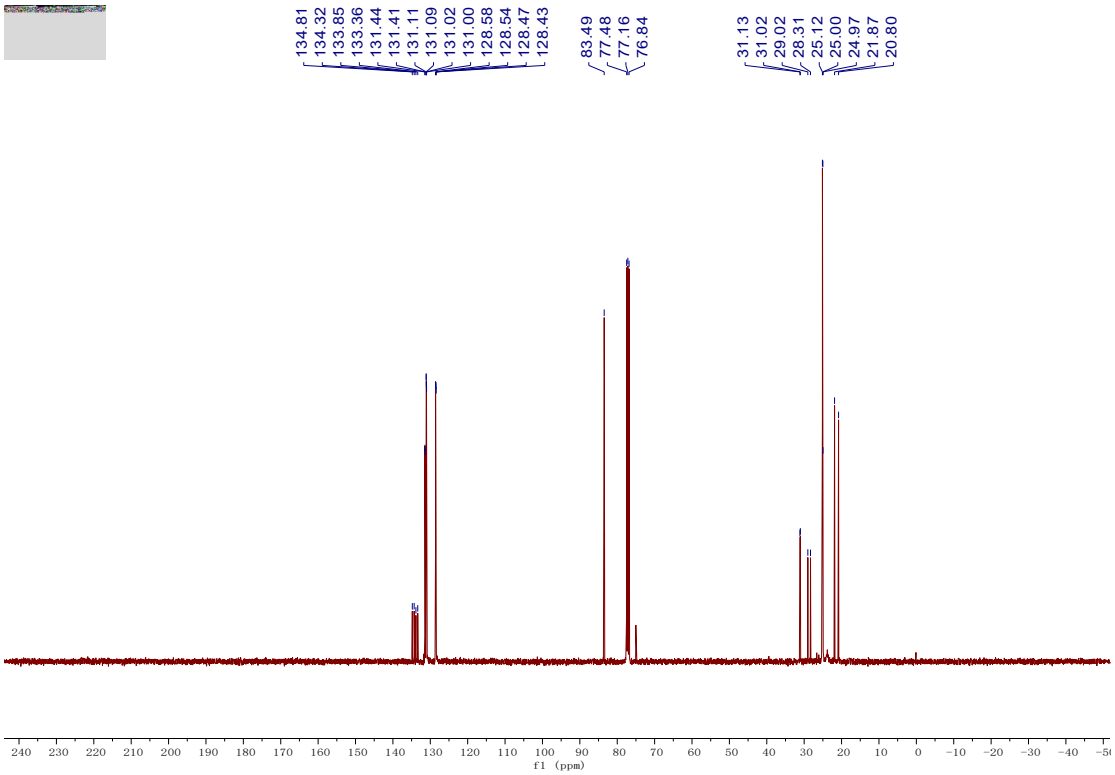


Figure S113. ^{19}F-NMR of **5k**

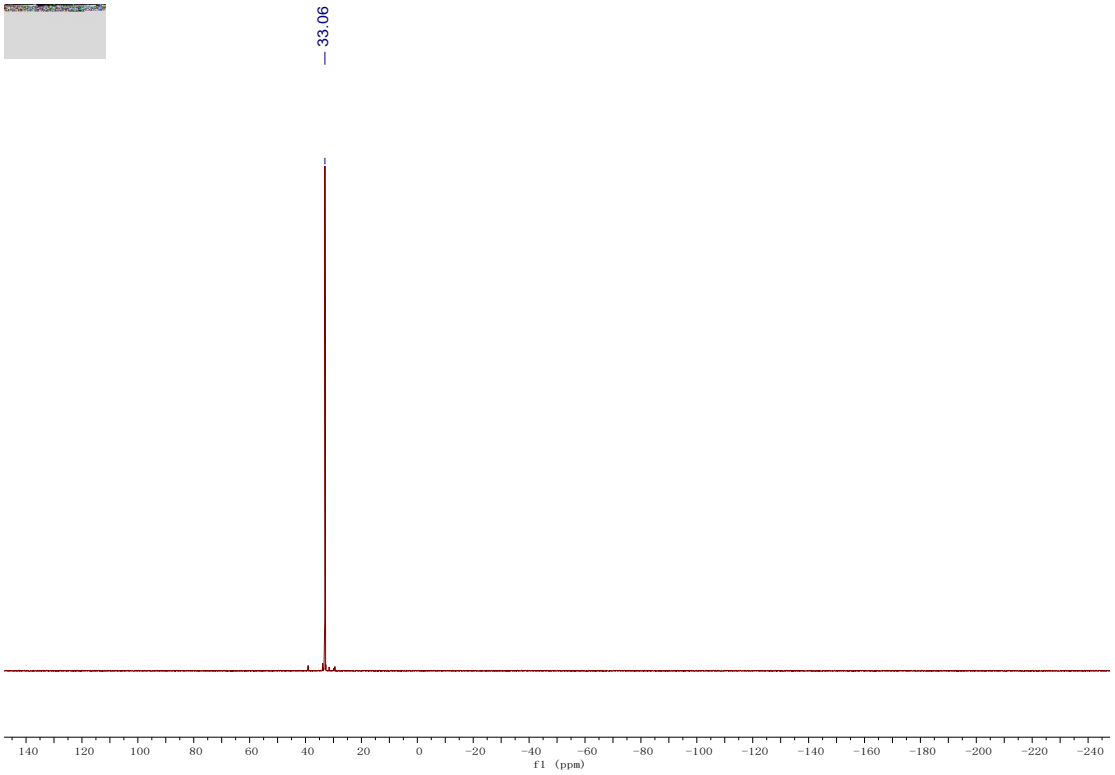


Figure S114. ^{1}H-NMR of **5l**

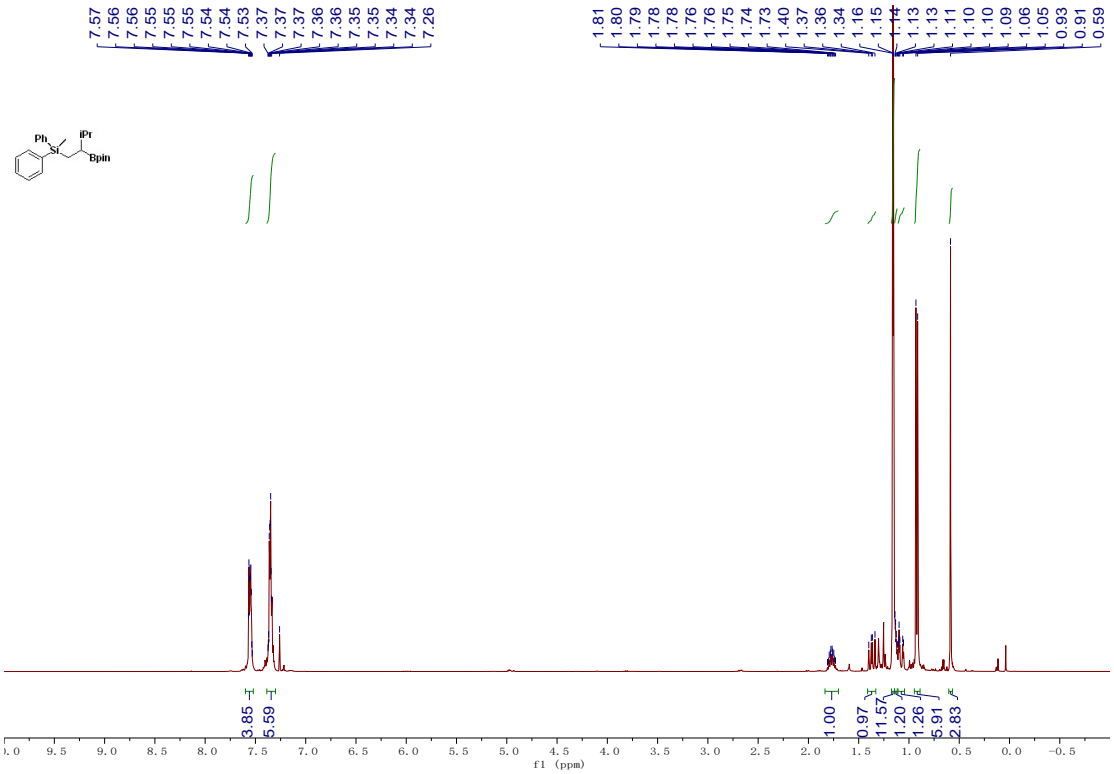


Figure S115. ^{13}C-NMR of **5l**

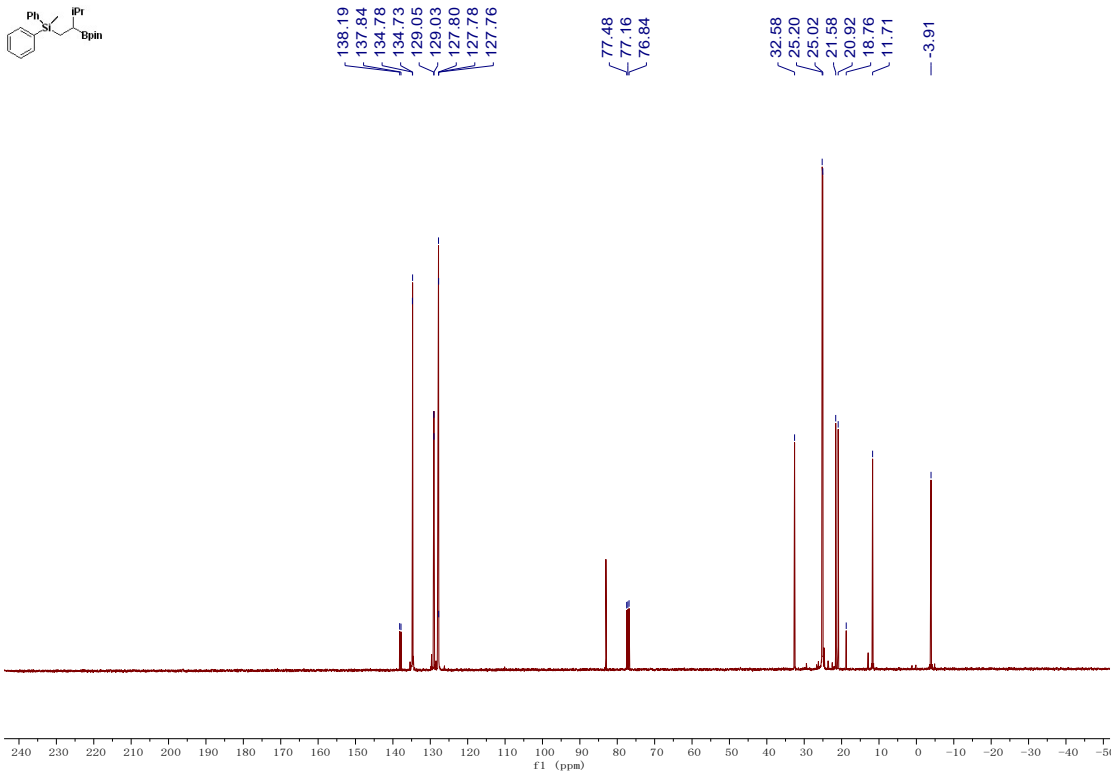


Figure S116. ^{1}H-NMR of **5m**

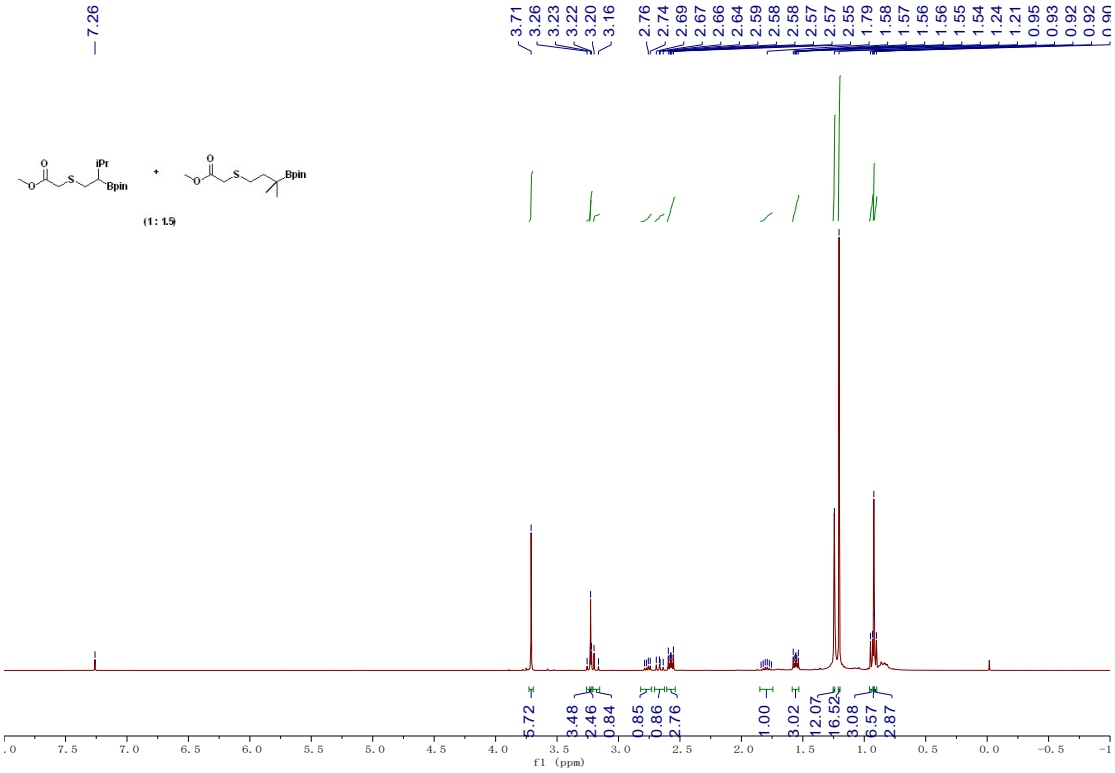
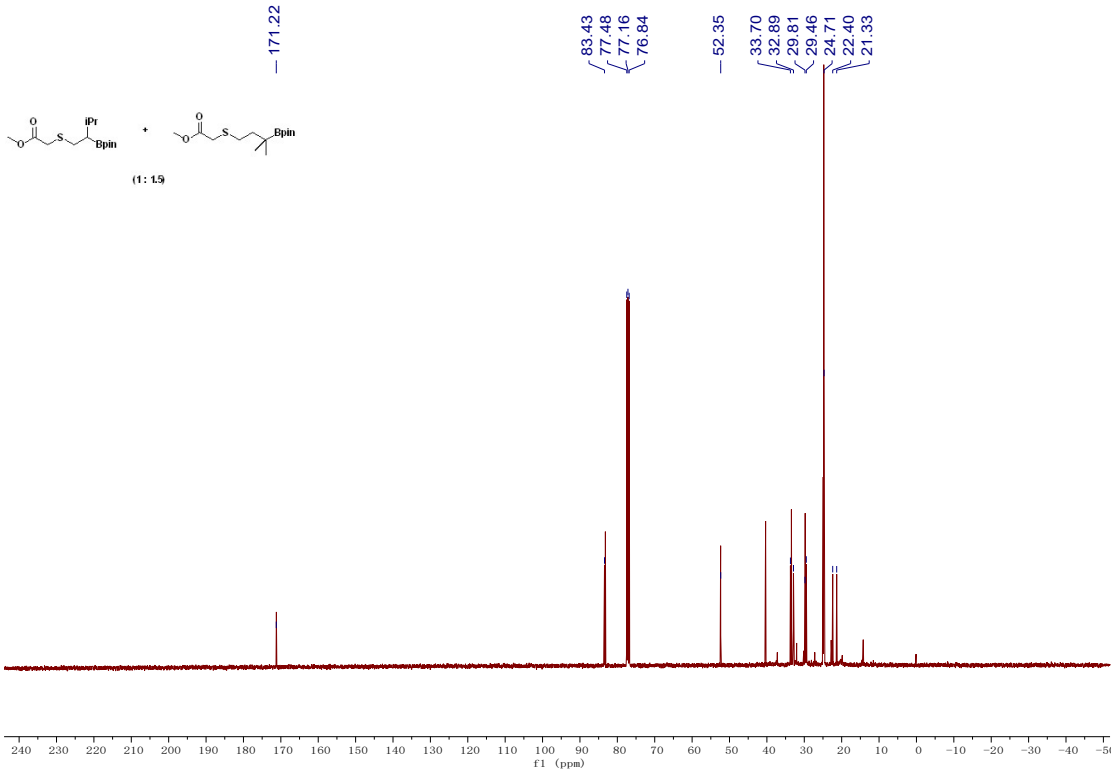


Figure S117. ^{13}C-NMR of **5m**



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2. M. J. Ardolino, M. S. Eno, J. P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 7092-7096.
3. F.M. Dennis, C.C. Robertson, B.M. Partridge, *Synthesis* **2020**, *52*, 1903-1906.