

Supporting Information

Enantioselective [1,2]-Stevens Rearrangement of Thiosulfonates to Construct Dithio-Substituted Quaternary Carbon Centers

Linfeng Hu, Jinzhao Li, Yongyan Zhang, Xiaoming Feng and Xiaohua Liu*
Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of
Chemistry, Sichuan University, Chengdu 610064, China
E-mail: liuxh@scu.edu.cn

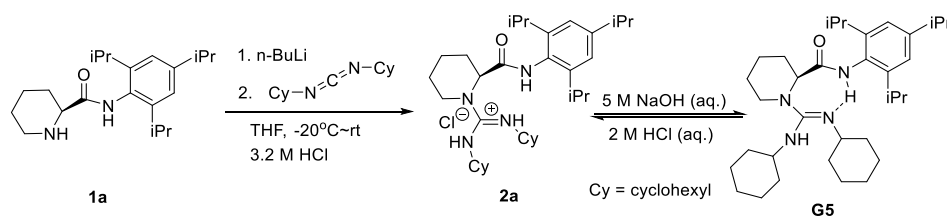
content

1. General information	3
2. General procedure for the synthesis of chiral guanidines.....	3
3. Typical procedure for the synthesis of the benzenesulfonothioate and α -diazoesters ..	4
4. Typical procedure for the catalytic asymmetric reactions.....	4
5. General procedure for the preparation of the racemic products	5
6. Optimization of reaction conditions.....	5
7. The analytical and spectral characterization data of the products.....	9
8. Copies of NMR spectra of products.....	44
9. Unsuccessful substrate scopes.....	93
10. X-ray crystal structure of product D1	93
11. References	94

1. General information

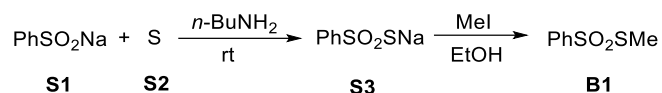
^1H NMR spectra were recorded on Bruker ASCENDTM 400M (400MHz) and ASCENDTM 600M (600MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 , $\delta = 7.26$). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. $^{13}\text{C}\{^1\text{H}\}$ NMR data were collected on ASCENDTM 400M (101 MHz) and ASCENDTM 600M (153 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta = 77.0$). ^{19}F NMR spectra were collected on Bruker ASCENDTM 400M (376 MHz) with complete proton decoupling. HRMS was recorded on a Q-Exactive hybrid quadrupole-Orbitrap mass spectrometer (ESI). IR spectra was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiral IA, ODH, and IB at 23 °C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were tested with a path length of 1 dm (using the sodium D line, 589 nm) and reported as follows: $[\alpha]_D^{25}$ (c, g/100 mL). Silica gel for thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. All the solvents were purified by usual methods before use or directly use the super dried solvents.

2. General procedure for the synthesis of chiral guanidines.

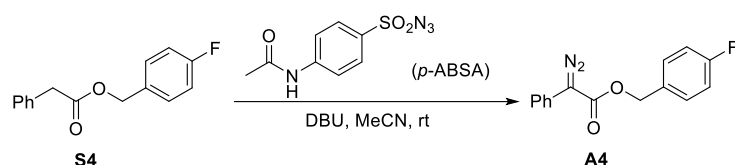


Solution of *n*-BuLi in *n*-hexane (2.4 M, 2.2 equiv, 3.7 mL, 8.8 mmol) was injected into a solution of *L*-pipecolic acid-derived amide **1a** (4.0 mmol) in THF (40 mL) dropwise over 5 minutes under nitrogen atmosphere at -20 °C with well stirring. After additional 10 minutes, a solution of *N,N'*-dicyclohexylcarbodiimide (1.2 equiv, 4.8 mmol) in 10 mL of THF was added dropwise within 5 minutes. The reaction was allowed to warm to room temperature and detected by TLC. After 12 h, the mixture was evaporated under reduced pressure to get rid of THF, and the pH value of the mixture was brought into the range of 0–1 by the addition of 2 M HCl. The aqueous phase was extracted with CH_2Cl_2 (3 \times 30 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 , evaporated in vacuum, and purified through flash chromatograph on silica gel (EtOAc:MeOH = 40:1) to produce **2a**. The white foam **2a** can be recrystallized in CH_2Cl_2 and petroleum ether to get white crystal. Then, **2a** in CH_2Cl_2 (10 mL) was added 4 M NaOH (15 mL) and stirred until the basification was finished (10 minutes). The pH value of the mixture was kept in the range of 11–12. The aqueous phase was extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic phase was washed with 4 M NaOH, dried over anhydrous Na_2SO_4 and evaporated in vacuum. Finally a white solid was obtained. Then it was dissolved in CH_2Cl_2 and filtration through celite to remove the silicone gel, concentrate to get a kind of white foam **G5** (41% yield). For other guanidine catalyts, this synthesis method could be applied.¹

3. Typical procedure for the synthesis of the benzenesulfonothioate and α -diazoesters

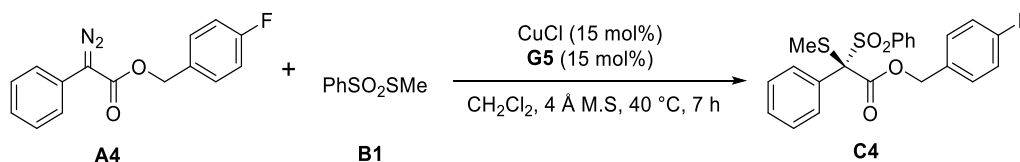


A mixture of **S1** (6.56 g, 40 mmol) and **S2** (1.28 g, 40 mmol) in *n*-BuNH₂ (40 mL) was stirred at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the residue was washed by Et₂O to obtain a white solid **S3**. Then **S3** was dissolved in EtOH (40 mL), then CH₃I (11.36 g, 80 mmol) was added to the solution. The reaction mixture was stirred at 40–45 °C for 24 h. After removal of the solvent under reduced pressure, the reaction mixture was poured on a solution of Na₂S₂O₃ and CH₂Cl₂ (30 mL). The precipitate was filtered and dried by anhydrous Na₂SO₄, the residue was purified through column chromatography (petroleum ether: EtOAc = 20:1) to afford the desired reactant **B1** (3.1 g, 40% yield) as a yellow oil. The other substrates were obtained by the similar method.²



To a solution of **S4** (2.44 g, 10 mmol) and *p*-ABSA (3.12 g, 13 mmol) in dry CH₃CN (20 mL) was added DBU (1.94 mL, 13 mmol) dropwise at 0 °C. Then the mixture was stirred overnight at room temperature. The reaction was then quenched with 10 w% NH₄Cl, followed by extraction with Et₂O (2 × 20 mL). The combined organic extracts were anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The yellow crude product was purified by silica gel column chromatography (petroleum ether:Et₂O = 30:1) to give the product **A4** as a yellow solid (2.3 g, 84% yield). The other α -aryl α -diazoesters were prepared by the similar procedure.³

4. Typical procedure for the catalytic asymmetric reactions



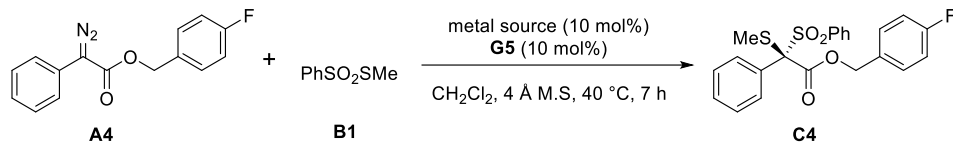
Typical Procedure: To an oven-dried reaction tube under nitrogen atmosphere was added CuCl (1.5 mg, 15 mol%), **G5** (8.1 mg, 15 mol%), 4 Å MS (60 mg), and CH₂Cl₂ (0.5 mL). The reaction mixture was stirred at 40 °C for 10 min. Subsequently, **B1** (15.0 μ L, 0.1 mmol) was added, then 4-fluorobenzyl 2-diazo-2-phenylacetate **A4** (53.0 mg, 0.2 mmol) dissolving in CH₂Cl₂ (0.5 mL) was added dropwise and the reaction mixture was stirred at 40 °C for 7 h, then directly purified by flash column chromatography (petroleum ether:EtOAc = 5:1) to afford the desired product **C4**.

5. General procedure for the preparation of the racemic products

The corresponding racemic products were obtained through the use of racemic guanidine under the same reaction conditions

6. Optimization of reaction conditions

Table S1. Screening of metal salts^a

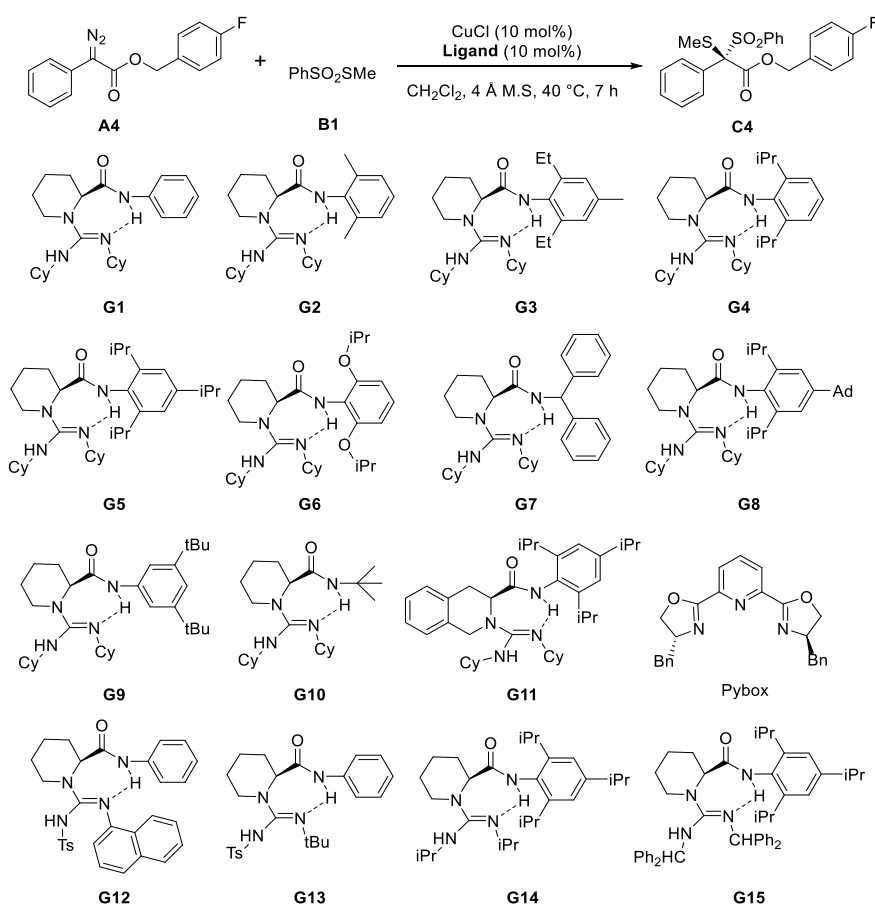


entry	metal source	yield ^b %	er ^c
1	CuCl	75	91.5:8.5
2	CuI	n. r.	\
3	CuBr	trace	\
4	CuTc	trace	\
5	Cu(CH ₃ CN) ₄ PF ₆	58	81:19
6	Cu(CH ₃ CN) ₄ BF ₄	77	83.5:16.5
7	CuOTf	58	70.5:29.5
8	CuCl ₂	72	86:14
9	Cu(OTf) ₂	63	77.5:22.5
10	Rh ₂ (OAc) ₄	32	racemic
11	Pd ₂ (dba) ₃	27	racemic
12	AgOTf	30	racemic
13	Fe(acac) ₃	n. r.	\
14	AuPPh ₃ Cl	trace	\

^aUnless otherwise noted, all reactions were carried out with metal source (10 mol%), 4 Å MS (60 mg), **G5** (10 mol%), **A4** (0.20 mmol), and **B1** (0.10 mmol) in CH₂Cl₂ (1.0 mL) at 40 °C for 7 h.

^bIsolated yield. ^cDetermined by chiral HPLC analysis. n. r. = No reaction.

Table S2. Screening of chiral guanidines^a



entry	Ligand	yield ^b %	er ^c .
1	G1	32	50:50
2	G2	76	76.5:23.5
3	G3	81	87:13
4	G4	52	86:14
5	G5	75	91.5:8.5
6	G6	70	73:27
7	G7	57	60:40
8	G8	74	87.5:12.5
9	G9	30	52:48
10	G10	trace	\
11	G11	78	75:25
12	Pybox	62	50:50
13	G12	33	50:50
14	G13	43	50:50
15	G14	63	90:10
16	G15	70	80:20

^aUnless otherwise noted, all reactions were carried out with **CuCl** (10 mol%), 4 Å MS (60 mg), **Ligand** (10 mol%), **A4** (0.20 mmol), and **B1** (0.10 mmol) in CH_2Cl_2 (1.0 mL) at 40 °C for 7 h.

^bIsolated yield. ^cDetermined by chiral HPLC analysis. n. r. = No reaction.

Table S3. Screening of the solvents^a

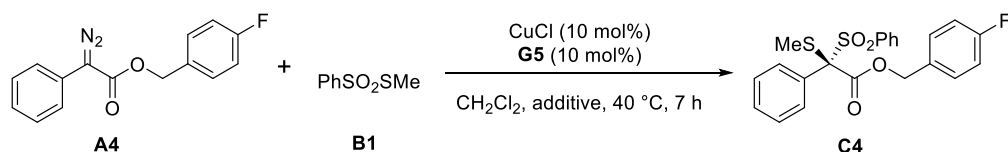
entry	solvent	yield ^b %	er ^c .
1	THF	n. r.	\
2	PhMe	35	61.5:38.5
3	MTBE	n. r.	\
4	CH ₃ CN	n. r.	\
5	EtOAc	n. r.	\
6	MeOH	trace	\
7	CCl ₄	51	racemic
8	CH ₂ ClCH ₂ Cl	62	80.5:19.5
9	CHCl ₂ CHCl	70	86:14
10	CHCl ₂ CHCl ₂	61	73.5:26.5
11	CHCl ₃	28	56.5:43.5
12	CH ₂ Cl ₂	75	91.5:8.5
13 ^d	CH ₂ Cl ₂	88	90.5:9.5
14 ^e	CH ₂ Cl ₂	86	90:10

^aUnless otherwise noted, all reactions were carried out with CuCl (10 mol%), 4 Å MS (60 mg), **G5** (10 mol%), **A4** (0.20 mmol), and **B1** (0.10 mmol) in CH₂Cl₂ (1.0 mL) at 40 °C for 7 h. ^bIsolated yield. ^cDetermined by chiral HPLC analysis. n. r. = No reaction. ^d4 Å MS (30 mg) was added. ^e4 Å MS (90 mg) was added.

Table S4. Screening of reaction temperature^a

entry	Temp (°C)/time	yield ^b %	er ^c .
1 ^d	10 / 12 h	trace	\
2 ^e	25 / 10 h	54	77.5:22.5
3	35 / 7 h	82	91:9
4	40 / 7h	75	91.5:8.5

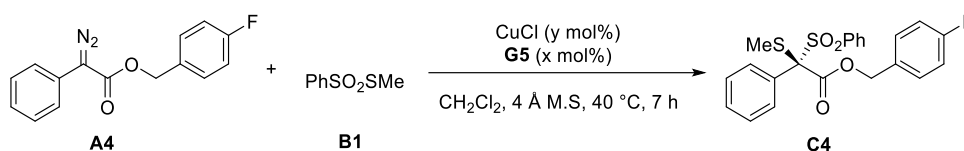
^aUnless otherwise noted, all reactions were carried out with CuCl (10 mol%), 4 Å MS (60 mg), **G5** (10 mol%), **A4** (0.20 mmol), and **B1** (0.10 mmol) in CH₂Cl₂ (1.0 mL) at x °C for 7 h. ^bIsolated yield. ^cDetermined by chiral HPLC analysis. n. r. = No reaction.

Table S5. Screening of the additives

entry	additive	yield ^b %	er ^c .
1	–	18	67.5:32.5
2	3 Å MS (60 mg)	47	90:10
3	4 Å MS (60 mg)	75	91.5:8.5
4	5 Å MS (60 mg)	73	89:11
5	H ₂ O	67	87.5:12.5
6	MeOH	38	75.5:24.5
7	PhCOOH	68	89:11
8	LiCl	71	90:10
9	LiBr	73	76.5:23.5
10	NaBAr ^F ₄	43	racemic
11	Et ₃ N	47	racemic

^aUnless otherwise noted, all reactions were carried out with CuCl (10 mol%), additive (10 mol%), **G5** (10 mol%), **A4** (0.20 mmol), and **B1** (0.10 mmol) in CH₂Cl₂ (1.0 mL) at 40 °C for 7 h. ^bIsolated yield. ^cDetermined by chiral HPLC analysis. n. r. = No reaction.

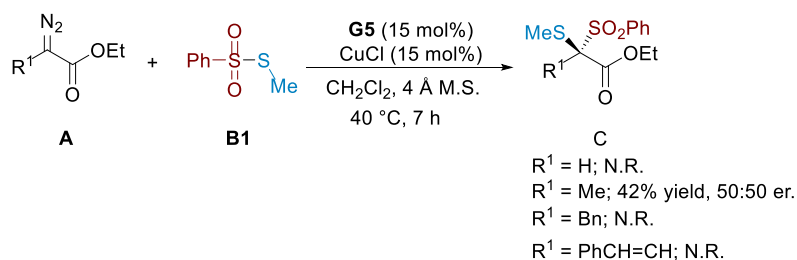
Table S6. Screening of the ratio between guanidine and copper salt



entry	x:y	yield ^b %	er ^c .
1	15:10	77	89:11
2	12:10	78	89.5:10.5
3	10:10	75	91.5:8.5
4	10:15	65	81.5:18.5
5	10:20	66	75:25
6 ^d	15:15	78	92:8
7 ^e	20:20	82	92:8
8 ^f	30:30	96	92.5:7.5

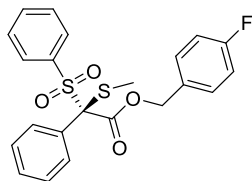
^aUnless otherwise noted, all reactions were carried out with CuCl (y mol%), 4 Å MS (60 mg), **G5** (x mol%), **A4** (0.20 mmol), and **B1** (0.10 mmol) in CH₂Cl₂ (1.0 mL) at 40 °C for 7 h. ^bIsolated yield. ^cDetermined by chiral HPLC analysis. n. r. = No reaction. ^dCuCl (15 mol%), **G5** (15 mol%). ^eCuCl (20 mol%), **G5** (20 mol%). ^fCuCl (30 mol%), **G5** (30 mol%).

S7. Other types of α -diazoesters



7. The analytical and spectral characterization data of the products

4-fluorobenzyl (S)-2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C4)



Yellow liquid . 78% yield, 92:8 er. $[\alpha]^{21.3}_D = +33.7$ ($c = 0.64$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 17.17$ min, $t_R(\text{minor}) = 21.22$ min.

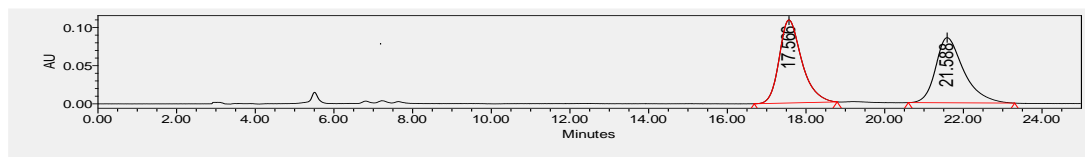
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.54 - 7.45$ (m, 1H), 7.42 - 7.33 (m, 4H), 7.33 - 7.29 (m, 1H), 7.28 - 7.23 (m, 2H), 7.23 - 7.14 (m, 2H), 7.16 - 7.11 (m, 2H), 7.03 (t, $J = 8.8$ Hz, 2H), 5.37 - 5.23 (m, 2H), 2.29 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.7, 162.9$ (d, 249.0 Hz), 135.4, 133.7, 131.4, 131.3, 130.9 (d, 8.4 Hz), 130.4 (d, 3.3 Hz), 129.6, 129.4, 127.9, 127.6, 115.5 (d, 21.7 Hz), 82.8, 67.6, 15.2.

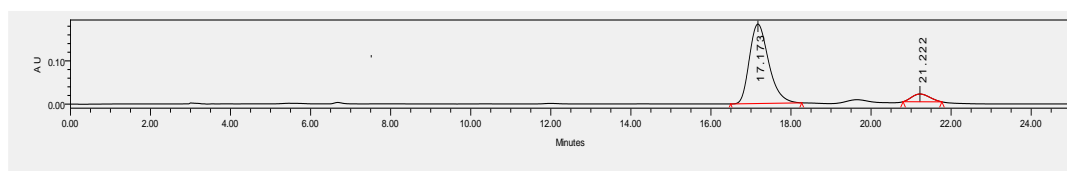
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -112.58$.

IR (neat): 2926, 1733, 1604, 1510, 1446, 1372, 1311, 1214, 1144, 1079, 1008, 967 cm^{-1} .

HRMS (ESI) calcd for m/z : ($[\text{M}]+\text{K}^+$) $\text{C}_{22}\text{H}_{19}\text{FO}_4\text{S}_2\text{K}^+ = 469.0340$, Found 469.0334.

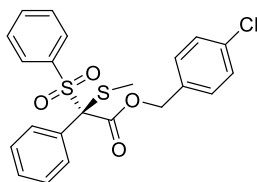


	Retention Time	Area	% Area
1	17.566	4331351	50.54
2	21.588	4239486	49.46



	Retention Time	Area	% Area
1	17.173	6169177	92.00
2	21.222	536770	8.00

4-chlorobenzyl (S)-2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C5)



Yellow liquid. 71% yield, 90:10 er. $[\alpha]_{D}^{27.8} = +36.9$ ($c = 0.56$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH/n-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 18.99$ min, $t_R(\text{minor}) = 23.90$ min.

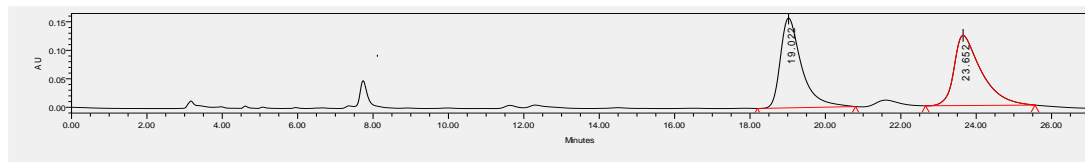
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.54 - 7.45$ (m, 1H), 7.43 - 7.38 (m, 2H), 7.31 (m, 5H), 7.28 - 7.23 (m, 2H), 7.22 - 7.16 (m, 2H), 7.16 - 7.11 (m, 2H), 5.36 - 5.24 (m, 2H), 2.31 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.7, 135.4, 134.6, 133.7, 133.0, 131.4, 131.3, 130.1, 129.6, 129.4, 128.8, 127.9, 127.6, 82.8, 67.4, 15.3$.

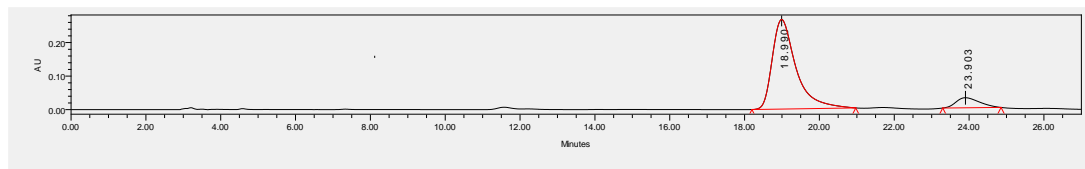
IR (neat): 2927, 1735, 1591, 1492, 1447, 1371, 1314, 1214, 1145, 1084, 1010, 811, 756, 693 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{19}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 485.0045$, Found 485.0045,

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{19}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 487.0015$, Found 487.0015.

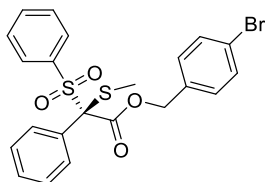


	Retention Time	Area	% Area
1	19.022	6151041	49.85
2	23.652	6187640	50.15



	Retention Time	Area	% Area
1	18.990	11775286	90.00
2	23.903	1309025	10.00

4-bromobenzyl (S)-2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C6)



Yellow liquid. 83% yield, 90.5: 9.5 er. $[\alpha]^{27.1}_D = +19.2$ ($c = 0.30$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 19.78$ min, $t_R(\text{minor}) = 24.69$ min.

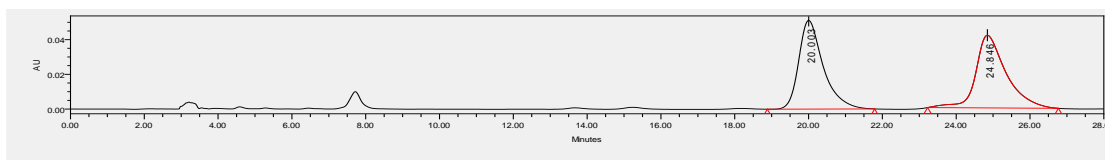
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.54 - 7.44$ (m, 3H), 7.42 - 7.39 (m, 2H), 7.36 - 7.30 (m, 1H), 7.28 - 7.23 (m, 4H), 7.21 - 7.16 (m, 2H), 7.16 - 7.11 (m, 2H), 5.36 - 5.21 (m, 2H), 2.31 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.7, 135.4, 133.7, 133.5, 131.8, 131.4, 131.3, 130.4, 129.6, 129.4, 127.9, 127.6, 122.8, 82.8, 67.4, 15.3$.

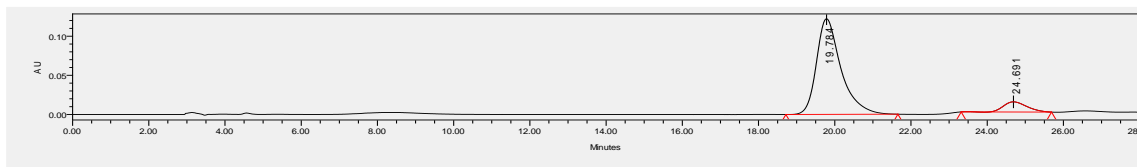
IR (neat): 3063, 1734, 1589, 1488, 1446, 1370, 1311, 1212, 1144, 1076, 1008 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{19}^{79}\text{BrO}_4\text{S}_2\text{K}^+ = 528.9539$, Found 528.9534.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{19}^{81}\text{BrO}_4\text{S}_2\text{K}^+ = 530.9519$, Found 530.9515.

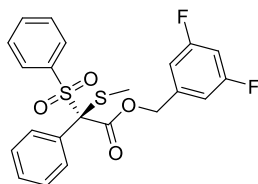


	Retention Time	Area	% Area
1	20.003	2354760	49.63
2	24.846	2389769	50.37



	Retention Time	Area	% Area
1	19.784	5455293	90.65
2	24.691	562613	9.35

3,5-difluorobenzyl (S)-2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C7)



Colorless liquid. 90% yield, 91.5:8.5 er. $[\alpha]_{D}^{27.5} = +39.7$ ($c = 0.59$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/ n -hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 18.30$ min, $t_R(\text{minor}) = 26.89$ min.

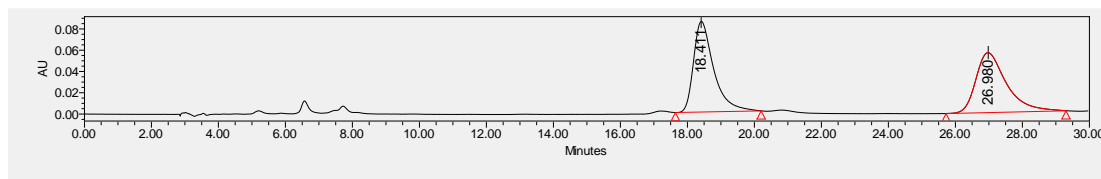
^1H NMR (400 MHz, Chloroform- d) $\delta = 7.54 - 7.49$ (m, 1H), 7.44 - 7.40 (m, 2H), 7.37 - 7.32 (m, 1H), 7.32 - 7.23 (m, 2H), 7.26 - 7.14 (m, 4H), 6.94 - 6.84 (m, 2H), 6.77 (tt, $J = 8.9, 2.4$ Hz, 1H), 5.37 - 5.21 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 165.6, 163.0$ (d, 250.6 Hz), 162.9 (d, 250.6 Hz), 138.2 (t, 9.3 Hz), 135.2, 133.8, 131.3, 131.2, 129.7, 129.5, 127.9, 127.7, 110.9 (d, 26.2 Hz), 110.9 (d, 11.7 Hz), 104.0 (t, 25.3 Hz), 82.70, 66.58, 15.30.

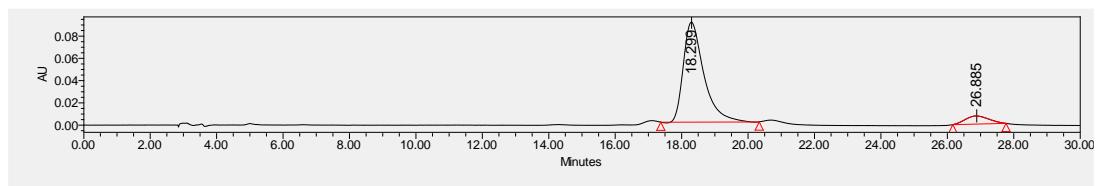
^{19}F NMR (376 MHz, Chloroform- d) $\delta = -108.76$.

IR (neat): 3067, 1738, 1628, 1597, 1450, 1375, 1317, 1216, 1145, 960 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{O}_4\text{S}_2\text{K}^+ = 487.0246$, Found 487.0243.

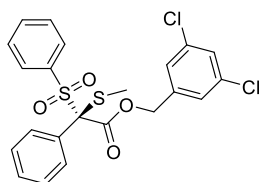


	Retention Time	Area	% Area
1	18.411	3565251	49.99
2	26.980	3566378	50.01



	Retention Time	Area	% Area
1	18.299	3870932	91.56
2	26.885	357020	8.44

3,5-dichlorobenzyl (S)-2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C8)



Colorless liquid. 90% yield, 92.5:7.5 er. $[\alpha]^{28.2}_D = +29.7$ ($c = 0.33$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 18.41$ min, $t_R(\text{minor}) = 29.05$ min.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.54 - 7.49$ (m, 1H), 7.44 - 7.40 (m, 2H), 7.38 - 7.31 (m, 2H), 7.32 - 7.21 (m, 3H), 7.24 - 7.20 (m, 3H), 7.19 - 7.14 (m, 2H), 5.26 (s, 2H), 2.36 (s, 3H).

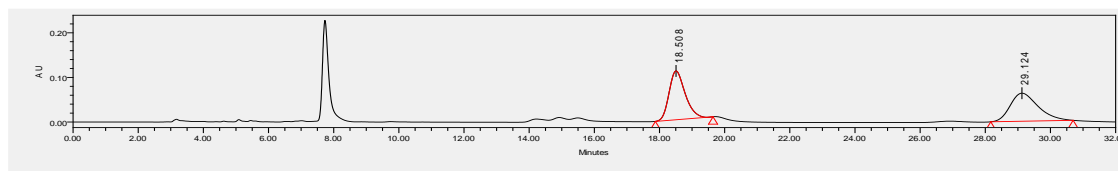
$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.5, 137.8, 135.2, 133.8, 131.3, 131.1, 129.7, 129.5, 128.7, 128.0, 127.7, 126.5, 82.6, 66.4, 15.3$.

IR (neat): 2921, 1738, 1571, 1442, 1370, 1315, 1212, 1145, 1079, 855, 797, 755 cm^{-1} .

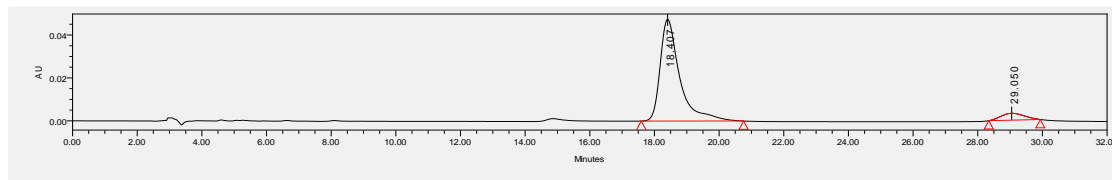
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 518.9655$, Found 518.9655.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 520.9626$, Found 520.9626.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 522.9596$, Found 522.9596.

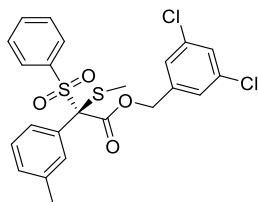


	Retention Time	Area	% Area
1	18.508	3752023	50.09
2	29.124	3737863	49.91



	Retention Time	Area	% Area
1	18.407	1991215	92.58
2	29.050	159705	7.42

3,5-dichlorobenzyl (S)-2-(methylthio)-2-(phenylsulfonyl)-2-(m-tolyl)acetate (C9)



Yellow liquid. 78% yield, 90:10 er. $[\alpha]_{D}^{27.1} = +30.3$ ($c = 0.45$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IB column, *i*-PrOH/n-hexane = 20/80, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 10.59$, $t_R(\text{minor}) = 18.12$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.57 - 7.47$ (m, 1H), 7.45 - 7.41 (m, 2H), 7.34 - 7.25 (m, 3H), 7.22 (d, $J = 2.0$ Hz, 2H), 7.19 - 7.06 (m, 2H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.88 (s, 1H), 5.26 (q, $J = 12.4$ Hz, 2H), 2.36 (s, 3H), 2.20 (s, 3H).

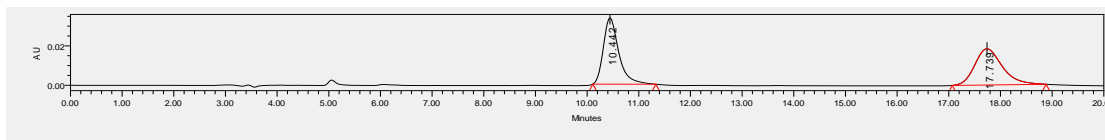
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 165.6, 137.8, 137.7, 135.2, 133.7, 131.4, 130.9, 130.4, 120.0, 128.7, 127.8, 127.6, 126.6, 126.5, 82.7, 66.3, 21.2, 15.3$.

IR (neat): 3071, 1738, 1571, 1439, 1313, 1207, 1146, 1079, 996, 856, 797 cm^{-1} .

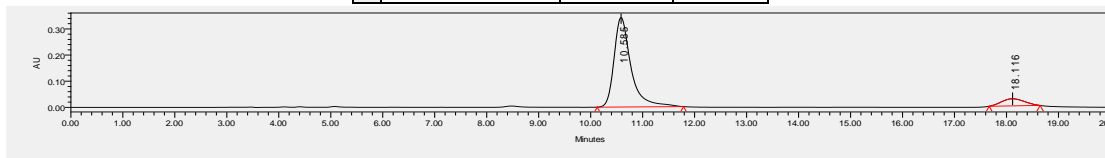
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{20}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 532.9812$, Found 532.9808.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{20}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 534.9782$, Found 534.9778.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{20}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 536.9753$, Found 536.9752.

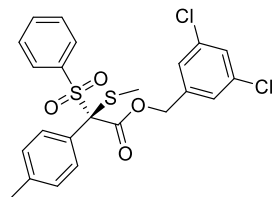


	Retention Time	Area	% Area
1	10.442	695492	50.49
2	17.739	681908	49.51



	Retention Time	Area	% Area
1	10.585	7740124	90.23
2	18.116	837720	9.77

3,5-dichlorobenzyl (S)-2-(methylthio)-2-(phenylsulfonyl)-2-(p-tolyl)acetate (C10)



Colorless liquid. 78% yield, 89:11 er. $[\alpha]_{D}^{27.7} = +34.8$ ($c = 0.62$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, *i*-PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 20.34$, $t_R(\text{minor}) = 29.86$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.56 - 7.47$ (m, 1H), 7.47 - 7.43 (m, 2H), 7.34 - 7.25 (m, 3H), 7.21 (d, $J = 2.0$ Hz, 2H), 7.09 - 6.99 (m, 4H), 5.25 (s, 2H), 2.34 (s, 3H), 2.33 (s, 3H).

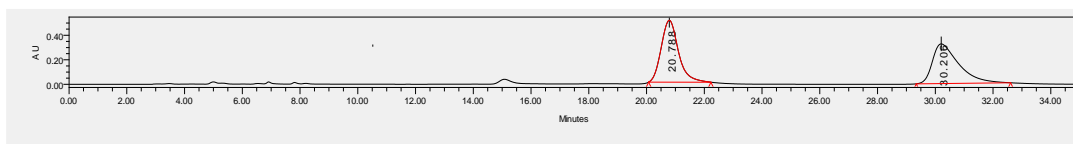
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 165.6, 139.9, 137.9, 135.3, 135.2, 133.7, 131.3, 129.3, 128.7, 128.0, 127.6, 126.5, 82.5, 66.3, 21.2, 15.3$.

IR (neat): 3071, 1739, 1571, 1510, 1439, 1367, 1313, 1211, 1107, 851, 798, 714, 685 cm^{-1} .

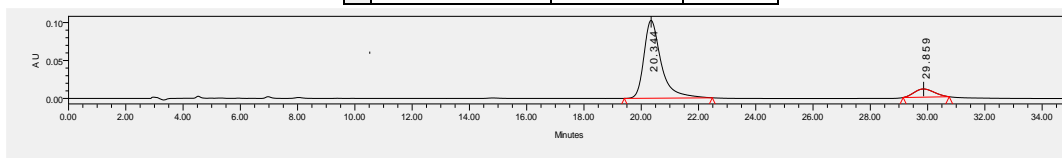
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{20}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 532.9812$, Found 532.9810.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{20}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 534.9782$, Found 534.9782.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{20}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 536.9753$, Found 536.9753.

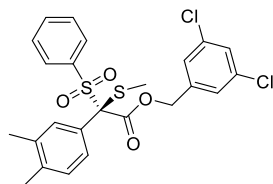


	Retention Time	Area	% Area
1	20.788	20909397	50.65
2	30.206	20374069	49.35



	Retention Time	Area	% Area
1	20.344	4272699	89.08
2	29.859	523687	10.92

3,5-dichlorobenzyl (S)-2-(3,4-dimethylphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C11)



Colorless liquid. 75% yield, 80:20 er. $[\alpha]_{D}^{27.0} = +25.7$ ($c = 0.77$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral ODH column, i -PrOH/ n -hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 30.05$, $t_R(\text{minor}) = 18.85$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.55 - 7.49$ (m, 1H), 7.48 - 7.44 (m, 2H), 7.32 - 7.28 (m, 3H), 7.21 (d, $J = 1.6$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.90 - 6.80 (m, 2H), 5.25 (q, $J = 12.8$ Hz, 2H), 2.34 (s, 3H), 2.24 (s, 3H), 2.11 (s, 3H).

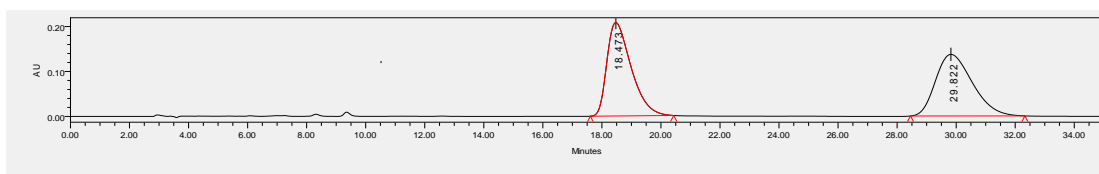
$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.7, 138.6, 137.9, 136.3, 135.4, 135.2, 133.7, 131.4, 130.4, 129.1, 128.7, 128.3, 127.5, 126.8, 126.6, 82.6, 66.2, 19.7, 19.5, 15.4$.

IR (neat): 2921, 1739, 1570, 1443, 1372, 1317, 1204, 1145, 1079, 1028, 854, 798, 755, 714 cm^{-1} .

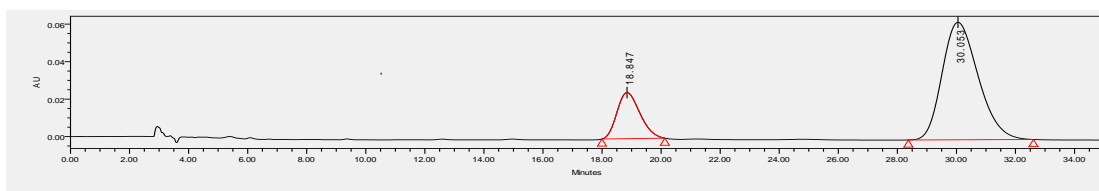
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{24}\text{H}_{22}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 546.9968$, Found 546.9968.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{24}\text{H}_{22}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 548.9939$, Found 548.9939.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{24}\text{H}_{22}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 550.9909$, Found 550.9909.

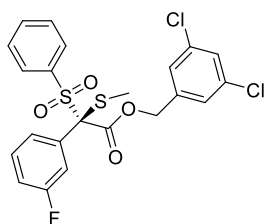


	Retention Time	Area	% Area
1	18.473	11835347	50.01
2	29.822	11831834	49.99



	Retention Time	Area	% Area
1	18.847	1330177	20.00
2	30.053	5322111	80.00

3,5-dichlorobenzyl (S)-2-(3-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C12)



Colorless liquid. 83% yield, 90:10 er. $[\alpha]_D^{25.9} = +34.8$ ($c = 0.54$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 20/80, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 11.71$, $t_R(\text{minor}) = 21.37$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.55$ (t, $J = 7.4$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.36 – 7.29 (m, 3H), 7.25 – 7.17 (m, 3H), 7.06 (t, $J = 8.4$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.93 (d, $J = 10.0$ Hz, 1H), 5.27 (s, 2H), 2.32 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.1$, 161.9 (d, 248.5 Hz), 137.6, 135.2, 134.9, 134.1, 133.3 (d, 7.7 Hz), 131.2, 129.4 (d, 8.1 Hz), 128.8, 127.8, 126.5, 125.4 (d, 3.1 Hz), 117.0, 116.9 (d, 24.4 Hz), 116.7 (d, 21.0 Hz), 82.0, 66.6, 15.3.

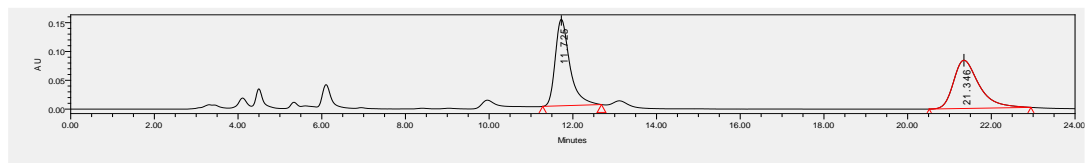
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -111.67$.

IR (neat): 3074, 1739, 1579, 1485, 1438, 1367, 1319, 1208, 1146, 1080, 856, 796, 686 cm^{-1} .

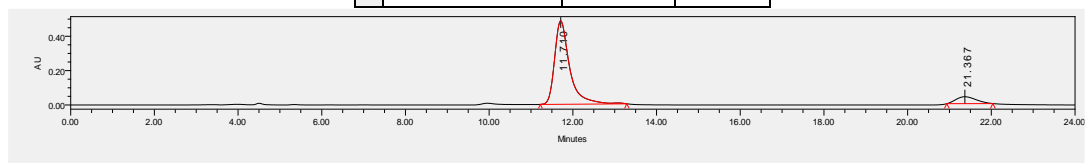
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{35}\text{ClFO}_4\text{S}_2\text{K}^+ = 536.9561$, Found 536.9559.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{37}\text{ClFO}_4\text{S}_2\text{K}^+ = 538.9531$, Found 538.9529.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{37}\text{Cl}^{37}\text{ClFO}_4\text{S}_2\text{K}^+ = 540.9502$, Found 540.9501.

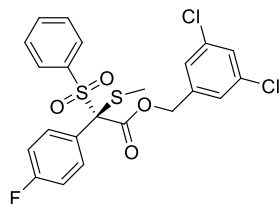


	Retention Time	Area	% Area
1	11.725	3628026	50.52
2	21.346	3553672	49.48



	Retention Time	Area	% Area
1	11.710	12132784	90.05
2	21.367	1340897	9.95

3,5-dichlorobenzyl (S)-2-(4-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C13)



Colorless liquid. 81% yield, 90.5:9.5 er. $[\alpha]^{26.9}_D = +20.7$ ($c = 0.23$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH/n-hexane} = 5/95$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 32.23$, $t_R(\text{minor}) = 34.63$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.54$ (t, $J = 7.4$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.36 – 7.27 (m, 3H), 7.24 (s, 2H), 7.20 – 7.15 (m, 2H), 6.93 (t, $J = 8.4$ Hz, 2H), 5.27 (s, 2H), 2.32 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.4$, 163.2 (d, 252.6 Hz), 137.7, 135.2, 135.0, 134.0, 131.6 (d, 8.6 Hz), 131.2, 128.8, 127.8, 127.0 (d, 3.6 Hz), 126.5, 115.1 (d, 22.0 Hz), 81.8, 66.5, 15.3.

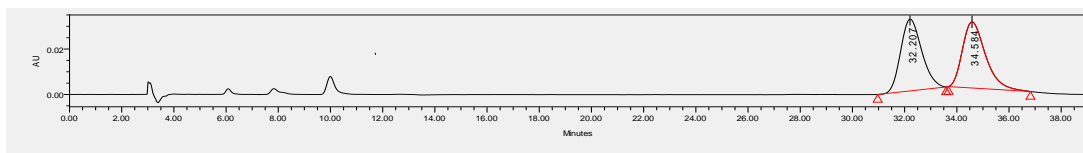
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -110.27$.

IR (neat): 3074, 1738, 1571, 1507, 1437, 1367, 1315, 1216, 1145, 1014, 850, 799, 684 cm^{-1} .

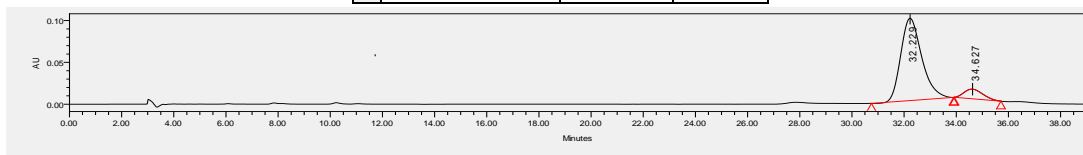
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{35}\text{ClFO}_4\text{S}_2\text{K}^+$ = 536.9561, Found 536.9561.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{37}\text{ClFO}_4\text{S}_2\text{K}^+$ = 538.9531, Found 538.9531.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{37}\text{Cl}^{37}\text{ClFO}_4\text{S}_2\text{K}^+$ = 540.9502, Found 540.9503.

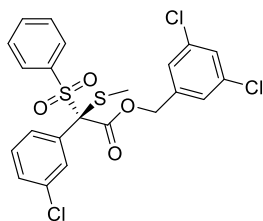


	Retention Time	Area	% Area
1	32.207	1775708	49.87
2	34.584	1784882	50.13



	Retention Time	Area	% Area
1	32.229	5508635	90.53
2	34.627	576343	9.47

3,5-dichlorobenzyl (S)-2-(3-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C14)



Colorless liquid. 71% yield, 90:10 er. $[\alpha]_{D}^{26.9} = +31.9$ ($c = 0.60$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 20/80, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 11.10$, $t_R(\text{minor}) = 17.19$.

^1H NMR (400 MHz, Chloroform- d) $\delta = 7.59 - 7.53$ (m, 1H), 7.49 – 7.45 (m, 2H), 7.37 – 7.30 (m, 4H), 7.24 (d, $J = 2.0$ Hz, 2H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.15 – 7.10 (m, 1H), 7.08 (t, $J = 2.0$ Hz, 1H), 5.32 – 5.22 (m, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 165.1, 137.6, 135.3, 134.8, 134.2, 134.0, 133.0, 131.3, 129.8, 129.7, 129.1, 128.8, 127.9, 127.8, 126.6, 82.0, 66.6, 15.3$.

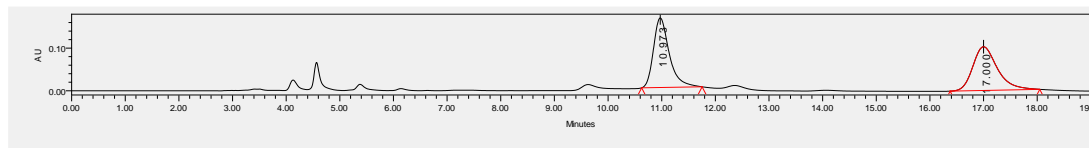
IR (neat): 2926, 1739, 1570, 1437, 1368, 1324, 1211, 1145, 1080, 855, 797, 686 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 552.9265$, Found 552.9266.

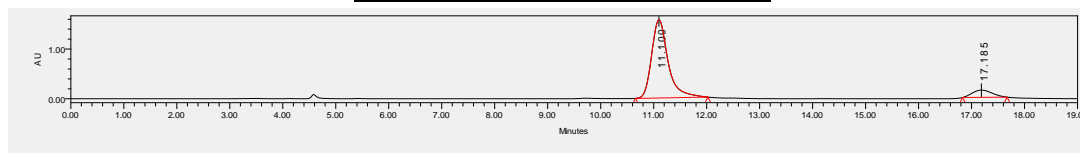
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 554.9236$, Found 554.9236.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 556.9206$, Found 556.9204.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{37}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 558.9177$, Found 558.9177.

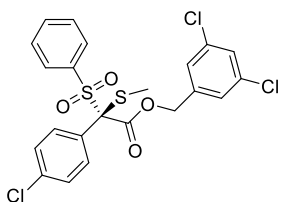


	Retention Time	Area	% Area
1	10.973	3319407	50.45
2	17.000	3259917	49.55



	Retention Time	Area	% Area
1	11.100	34003544	90.04
2	17.185	3762262	9.96

3,5-dichlorobenzyl (S)-2-(4-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C15)



Colorless liquid. 83% yield, 91.5:8.5 er. $[\alpha]_{D}^{27.8} = +37.3$ ($c = 0.62$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/ n -hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 20.03$, $t_R(\text{minor}) = 22.35$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.58 - 7.51$ (m, 1H), 7.50 - 7.46 (m, 2H), 7.35 - 7.30 (m, 3H), 7.24 - 7.18 (m, 4H), 7.16 - 7.11 (m, 2H), 5.26 (s, 2H), 2.30 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.2$, 137.7, 136.0, 135.2, 134.9, 134.0, 131.2, 130.9, 129.6, 128.7, 128.2, 127.9, 126.5, 81.9, 66.5, 15.3.

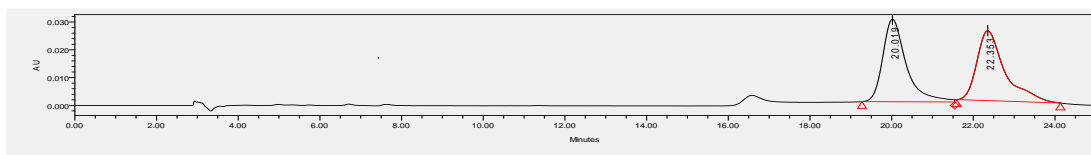
IR (neat): 3073, 1739, 1571, 1489, 1439, 1319, 1213, 1145, 1090, 1013, 851, 799, 715, 684 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 552.9265$, Found 552.9258.

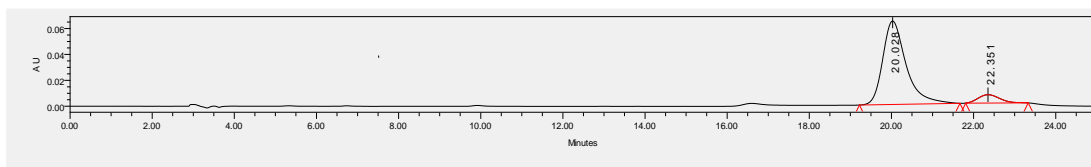
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 554.9236$, Found 554.9229.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{35}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 556.9206$, Found 556.9201.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{37}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 558.9177$, Found 558.9179.

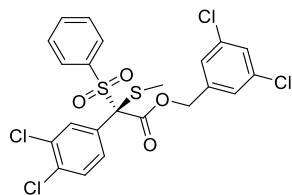


	Retention Time	Area	% Area
1	20.019	1184731	49.85
2	22.353	1191748	50.15



	Retention Time	Area	% Area
1	20.028	2546820	91.58
2	22.351	234252	8.42

3,5-dichlorobenzyl (S)-2-(3,4-dichlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C16)



Yellow liquid. 68% yield, 88:12 er. $[\alpha]^{28.0}_D = +27.9$ ($c = 0.41$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 19.99$, $t_R(\text{minor}) = 30.07$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.59$ (t, $J = 7.4$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.41 – 7.30 (m, 4H), 7.25 – 7.20 (m, 3H), 7.11 (dd, $J = 8.4, 2.8$ Hz, 1H), 5.27 (s, 2H), 2.28 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.8, 137.5, 135.3, 134.7, 134.4, 134.3, 132.4, 131.6, 131.3, 131.1, 129.8, 129.0, 128.9, 128.0, 126.6, 81.4, 66.7, 15.3$.

IR (neat): 2925, 1739, 1570, 1468, 1322, 1213, 1145, 1079, 1030, 854, 799, 684 cm^{-1} .

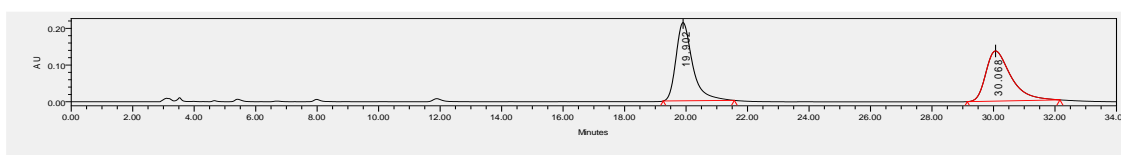
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{16}^{35}\text{Cl}^{35}\text{Cl}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 586.8876$, Found 586.8876,

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{16}^{35}\text{Cl}^{35}\text{Cl}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 588.8846$, Found 588.8846.

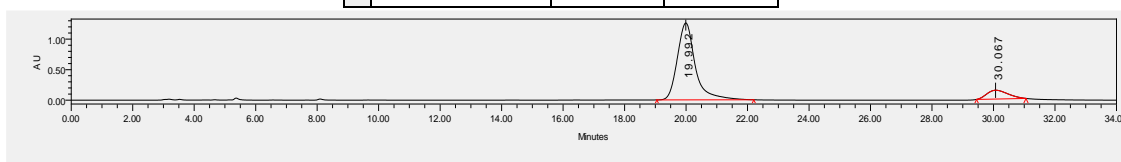
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{16}^{35}\text{Cl}^{35}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 590.8817$, Found 590.8816.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{16}^{35}\text{Cl}^{37}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 592.8787$, Found 592.8788.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{16}^{37}\text{Cl}^{37}\text{Cl}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 594.8745$, Found 594.8752.

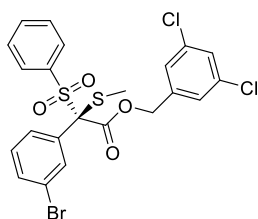


	Retention Time	Area	% Area
1	19.902	7989082	50.84
2	30.068	7726136	49.16



	Retention Time	Area	% Area
1	19.992	51010646	88.15
2	30.067	6854812	11.85

3,5-dichlorobenzyl (S)-2-(3-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C17)



Colorless liquid. 72% yield, 90:10 er. $[\alpha]_{D}^{27.8} = +23.2$ ($c = 0.49$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, *i*-PrOH/n-hexane = 20/80, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 11.59$, $t_R(\text{minor}) = 16.49$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.62 - 7.52$ (m, 1H), 7.50 - 7.46 (m, 3H), 7.37 - 7.30 (m, 3H), 7.24 (d, $J = 2.0$ Hz, 2H), 7.23 - 7.15 (m, 2H), 7.17 - 7.08 (m, 1H), 5.32 - 5.21 (m, 2H), 2.32 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 165.1, 137.6, 135.3, 134.8, 134.2, 133.3, 132.8, 132.5, 131.3, 129.4, 128.9, 128.4, 127.9, 126.7, 121.9, 81.9, 66.6, 15.3$.

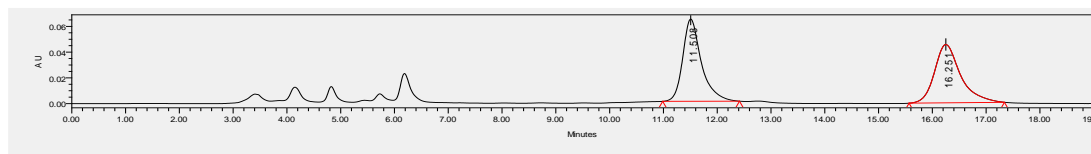
IR (neat): 2924, 1738, 1568, 1438, 1367, 1319, 1210, 1145, 1078, 994, 855, 796, 712 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{79}\text{Br}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 596.8760$, Found 596.8757.

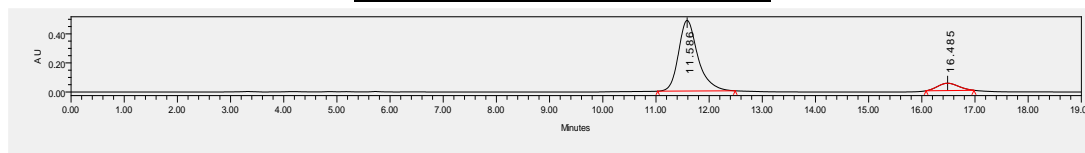
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{79}\text{Br}^{37}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 598.8740$, Found 598.8734.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{81}\text{Br}^{37}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 600.8710$, Found 600.8706.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{81}\text{Br}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 602.8681$, Found 602.8682.

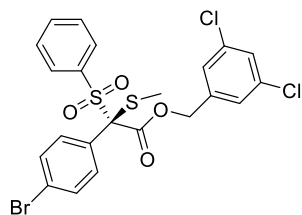


	Retention Time	Area	% Area
1	11.508	1536779	50.29
2	16.251	1519193	49.71



	Retention Time	Area	% Area
1	11.586	12309269	90.09
2	16.485	1354608	9.91

3,5-dichlorobenzyl (S)-2-(4-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C18)



Colorless liquid. 89% yield, 90:10 er. $[\alpha]^{24.0}_D = +41.0$ ($c = 0.83$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH/n-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 21.13$, $t_R(\text{minor}) = 24.83$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.59 - 7.53$ (m, 1H), 7.52 – 7.46 (m, 2H), 7.41 – 7.31 (m, 5H), 7.23 (d, $J = 2.0$ Hz, 2H), 7.09 – 7.05 (m, 2H), 5.26 (s, 2H), 2.30 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.19$, 137.66, 135.29, 134.97, 134.10, 131.30, 131.18, 130.17, 128.85, 127.91, 126.55, 124.34, 82.03, 66.52, 15.28.

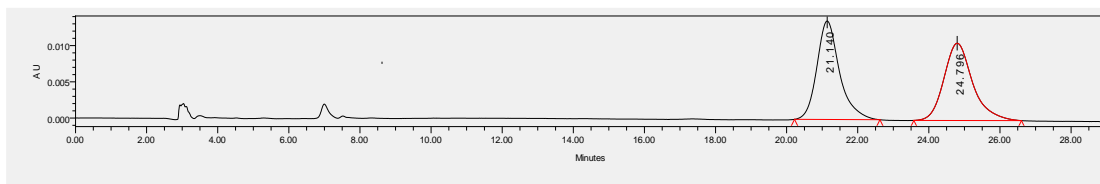
IR (neat): 3073, 1740, 1572, 1486, 1439, 1322, 1275, 1146, 1078, 1009, 851, 799, 756 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{79}\text{Br}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+$ = 596.8760, Found 596.8761.

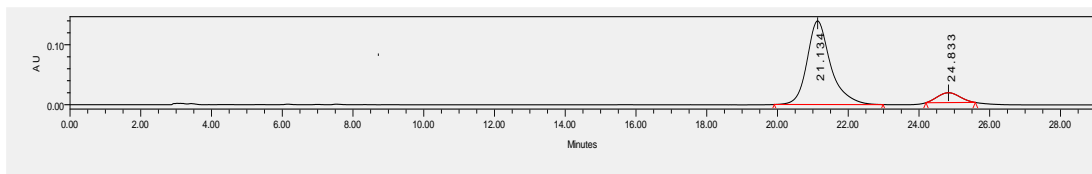
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{79}\text{Br}^{37}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+$ = 598.8740, Found 598.8740.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{81}\text{Br}^{37}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+$ = 600.8710, Found 600.8711.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{17}^{81}\text{Br}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+$ = 602.8681, Found 602.8683.

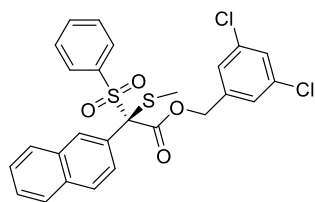


	Retention Time	Area	% Area
1	21.140	601532	50.18
2	24.796	597144	49.82



	Retention Time	Area	% Area
1	21.134	6457406	90.01
2	24.833	716607	9.99

3,5-dichlorobenzyl (S)-2-(methylthio)-2-(naphthalen-2-yl)-2-(phenylsulfonyl)acetate (C19)



Yellow liquid. 78% yield, 80:20 er. $[\alpha]_{D}^{27.4} = +27.9$ ($c = 0.54$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IB column, *i*-PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 24.42$, $t_R(\text{minor}) = 19.31$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.74$ (d, $J = 8.0$ Hz, 1H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.50 – 7.43 (m, 2H), 7.44 – 7.34 (m, 2H), 7.33 (d, $J = 7.2$ Hz, 2H), 7.26 – 7.21 (m, 2H), 7.15 (d, $J = 2.0$ Hz, 2H), 7.11 (t, $J = 8.0$ Hz, 2H), 5.26 – 5.16 (m, 2H), 2.31 (s, 3H).

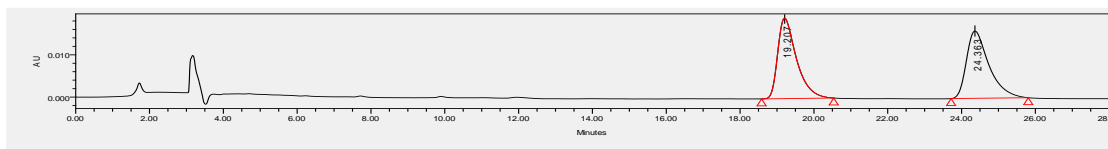
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 165.6$, 137.8, 135.2, 135.0, 133.8, 133.2, 132.1, 131.3, 129.8, 128.8, 128.5, 128.4, 127.6, 127.6, 127.5, 127.4, 126.6, 126.1, 82.8, 66.4, 15.4.

IR (neat): 3061, 1737, 1570, 1436, 1365, 1313, 1206, 1143, 1078, 855, 798, 733 cm^{-1} .

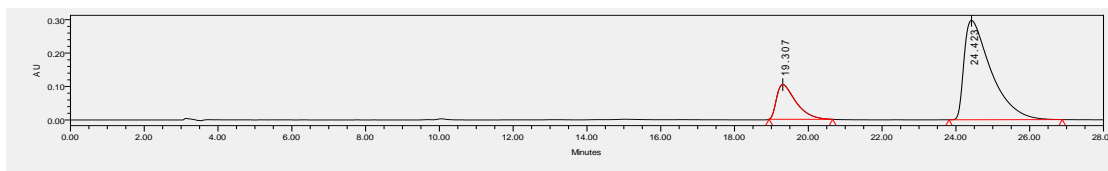
HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{26}\text{H}_{20}^{35}\text{Cl}^{35}\text{ClO}_4\text{S}_2\text{K}^+ = 568.9812$, Found 568.9808.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{26}\text{H}_{20}^{35}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 570.9782$, Found 570.9781.

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{26}\text{H}_{20}^{37}\text{Cl}^{37}\text{ClO}_4\text{S}_2\text{K}^+ = 572.9753$, Found 572.9753.

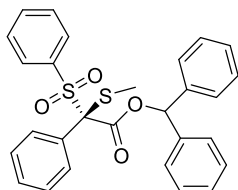


	Retention Time	Area	% Area
1	19.207	668456	49.91
2	24.363	670890	50.09



	Retention Time	Area	% Area
1	19.307	3766840	20.00
2	24.423	15067412	80.00

benzhydryl (S)-2-(methylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C20)



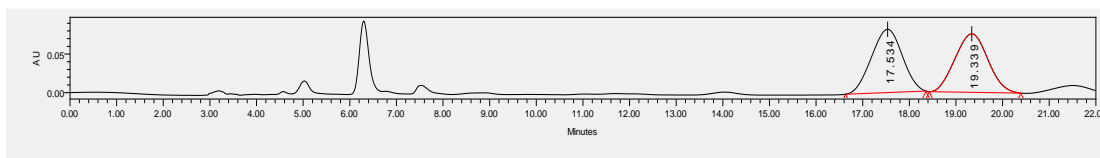
Colorless liquid. 81% yield, 95.5:4.5 er. $[\alpha]^{19.7}_D = +39.0$ ($c = 1.36$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 17.29$ min, $t_R(\text{minor}) = 19.17$ min.

$^1\text{H NMR}$ (600 MHz, Chloroform- d) $\delta = 7.49 - 7.44$ (m, 1H), 7.41 - 7.38 (m, 4H), 7.34 - 7.28 (m, 4H), 7.27 - 7.21 (m, 7H), 7.16 - 7.09 (m, 5H), 2.17 (s, 3H).

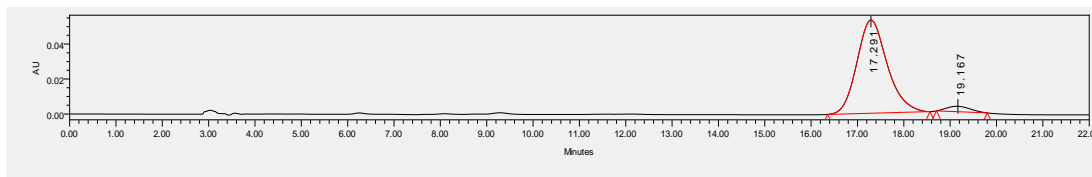
$^{13}\text{C NMR}$ (151 MHz, Chloroform- d) $\delta = 164.9, 139.1, 138.8, 135.3, 133.6, 131.5, 131.3, 129.6, 129.4, 128.5, 128.4, 128.3, 128.1, 127.7, 127.6, 127.3, 127.2, 82.7, 79.3, 14.9$.

IR (neat): 3062, 1732, 1586, 1494, 1447, 1312, 1219, 1144, 1078, 951, 693 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_4\text{S}_2\text{K}^+ = 527.0748$, Found 527.0749.

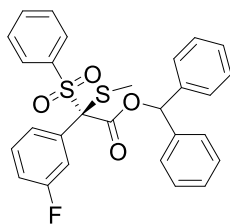


	Retention Time	Area	% Area
1	17.534	3774435	50.39
2	19.339	3715414	49.61



	Retention Time	Area	% Area
1	17.291	2419866	95.65
2	19.167	110179	4.35

benzhydryl (S)-2-(3-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C21)



Colorless liquid. 80% yield, 95.5:4.5 er. $[\alpha]_D^{23.4} = +37.3$ ($c = 0.54$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 15.29$ min, $t_R(\text{minor}) = 17.71$ min.

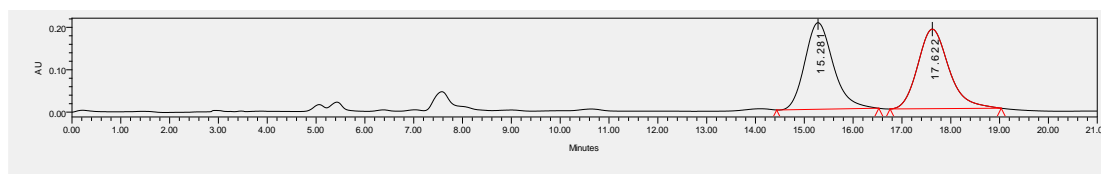
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.51$ (t, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 6.8$ Hz, 2H), 7.38 – 7.28 (m, 3H), 7.32 – 7.22 (m, 7H), 7.17 – 7.06 (m, 2H), 7.02 (td, $J = 8.0, 2.0$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.86 (d, $J = 10.0$ Hz, 1H), 2.16 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.4, 161.7$ (d, $J = 248.1$ Hz), 138.9, 138.6, 135.1, 133.9, 133.7 (d, $J = 7.7$ Hz), 131.3, 129.2 (d, $J = 8.1$ Hz), 128.6, 128.4, 128.3, 128.2, 127.7, 127.2, 125.5 (d, $J = 3.1$ Hz), 117.0 (d, $J = 24.4$ Hz), 116.5 (d, $J = 21.0$ Hz), 82.1, 79.6, 15.0.

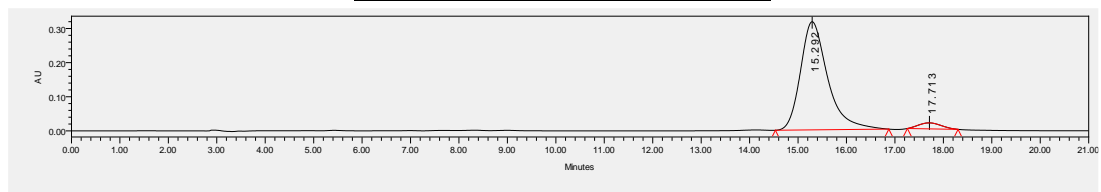
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -112.09$.

IR (neat): 3065, 1735, 1587, 1489, 1446, 1319, 1222, 1147, 1080, 952, 695 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}] + \text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}\text{FO}_4\text{S}_2\text{Na}^+ = 529.0914$, Found 529.0914.

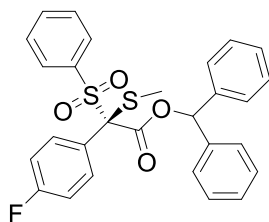


	Retention Time	Area	% Area
1	15.281	8259858	49.86
2	17.622	8305014	50.14



	Retention Time	Area	% Area
1	15.292	12369727	95.57
2	17.713	573945	4.43

benzhydryl (S)-2-(4-fluorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C22)



Colorless liquid. 70% yield, 94:6 er. $[\alpha]^{24.6}_D = +31.5$ ($c = 0.27$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 13.54$ min, $t_R(\text{minor}) = 15.16$ min.

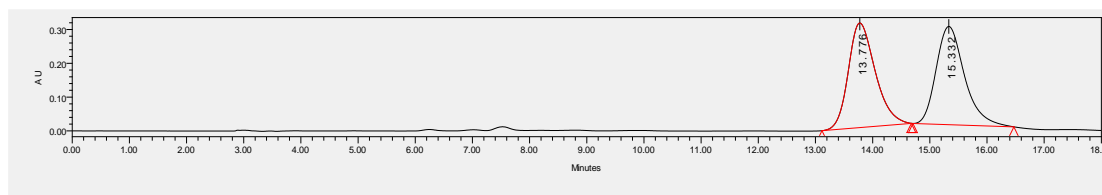
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.50$ (t, $J = 7.4$ Hz, 1H), 7.46 – 7.37 (m, 4H), 7.36 – 7.30 (m, 3H), 7.30 – 7.24 (m, 7H), 7.14 – 7.06 (m, 3H), 6.84 (t, $J = 8.4$ Hz, 2H), 2.16 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.72$, 163.1 (d, $J = 252.0$ Hz), 138.9, 138.7, 135.2, 133.8, 131.7 (d, $J = 8.6$ Hz), 131.3, 128.6, 128.4, 128.3, 128.2, 127.7, 127.4 (d, $J = 3.5$ Hz), 127.2, 114.8 (d, $J = 21.9$ Hz), 81.9, 79.4, 15.1.

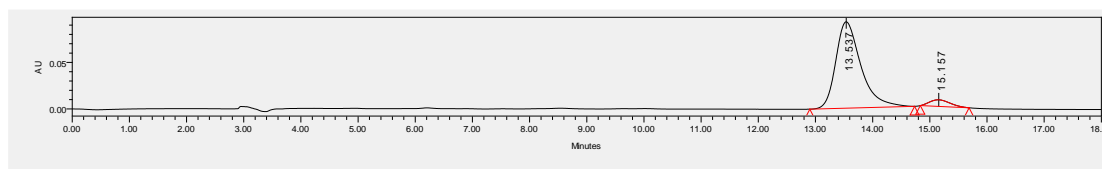
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -110.72$.

IR (neat): 2924, 1735, 1601, 1505, 1451, 1316, 1228, 1185, 1146, 1079, 644 cm^{-1} .

HRMS (ESI) m/z : $([\text{M}] + \text{Na}^+)$ calcd for $\text{C}_{28}\text{H}_{23}\text{FO}_4\text{S}_2\text{Na}^+ = 529.0914$, Found 529.0914.

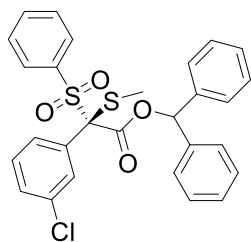


	Retention Time	Area	% Area
1	13.776	10105443	50.24
2	15.332	10007048	49.76



	Retention Time	Area	% Area
1	13.537	2825105	94.10
2	15.157	177273	5.90

benzhydryl (S)-2-(3-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C23)



Colorless liquid. 74% yield, 95.5:4.5 er. $[\alpha]^{24.5}_D = +33.7$ ($c = 0.50$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/ n -hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 13.84$ min, $t_R(\text{minor}) = 17.08$ min.

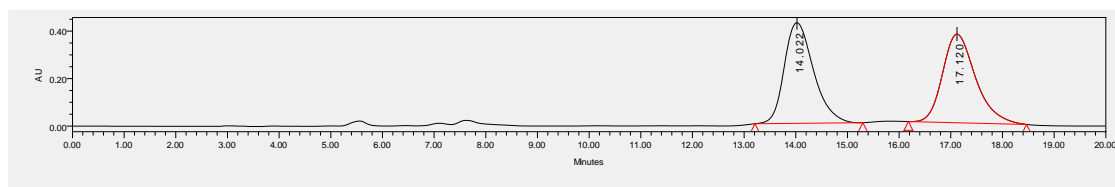
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.52$ (t, $J = 7.4$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 7.6$ Hz, 2H), 7.36 – 7.30 (m, 4H), 7.30 – 7.24 (m, 7H), 7.15 – 7.01 (m, 4H), 2.15 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.4, 138.9, 138.6, 134.9, 133.9, 133.7, 133.4, 131.3, 129.8, 129.6, 128.9, 128.6, 128.5, 128.3, 128.3, 127.9, 127.7, 127.2, 127.2, 82.0, 79.6, 15.0$.

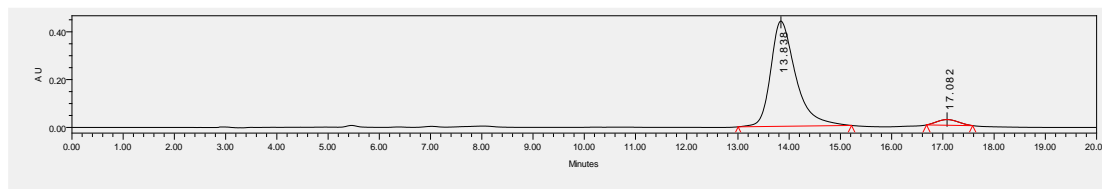
IR (neat): 2924, 1735, 1577, 1450, 1321, 1223, 1185, 1147, 1080, 752, 695 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}^{35}\text{ClO}_4\text{S}_2\text{Na}^+$ = 545.0618, Found 545.0618.

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}^{37}\text{ClO}_4\text{S}_2\text{Na}^+$ = 547.0589, Found 547.0590.

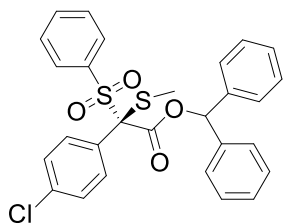


	Retention Time	Area	% Area
1	14.022	16675619	50.14
2	17.120	16585782	49.86



	Retention Time	Area	% Area
1	13.838	14868387	95.59
2	17.082	685372	4.41

benzhydryl (S)-2-(4-chlorophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C24)



Colorless liquid. 74% yield, 94:6 er. $[\alpha]^{25.5}_D = +40.2$ ($c = 0.64$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH/n-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 14.02$ min, $t_R(\text{minor}) = 16.34$ min.

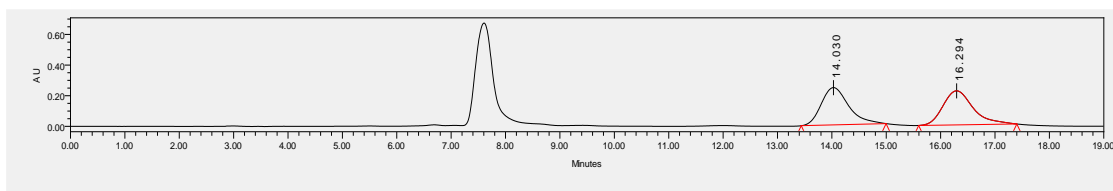
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.51$ (t, $J = 7.6$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 7.2$ Hz, 2H), 7.36 – 7.24 (m, 10H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.10 – 7.02 (m, 3H), 2.15 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.6, 138.9, 138.6, 135.7, 135.1, 133.9, 131.3, 131.0, 130.1, 128.6, 128.5, 128.3, 128.3, 127.9, 127.8, 127.3, 127.2, 82.0, 79.5, 15.0$.

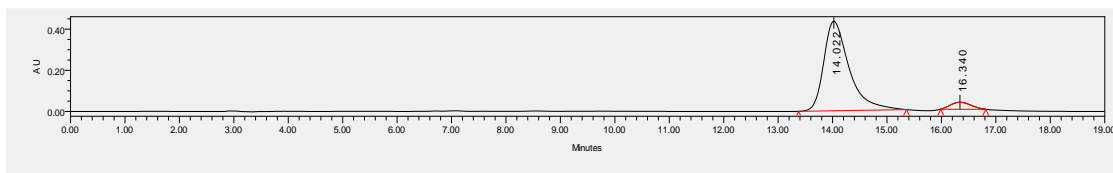
IR (neat): 2923, 1735, 1589, 1491, 1451, 1319, 1223, 1184, 1146, 1086, 697 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}^{35}\text{ClO}_4\text{S}_2\text{Na}^+$ = 545.0618, Found 545.0618.

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}^{37}\text{ClO}_4\text{S}_2\text{Na}^+$ = 547.0589, Found 547.0589.

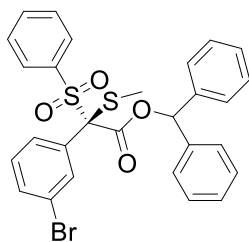


	Retention Time	Area	% Area
1	14.030	8543348	49.94
2	16.294	8562419	50.06



	Retention Time	Area	% Area
1	14.022	14099889	94.06
2	16.340	889871	5.94

benzhydryl (S)-2-(3-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C25)



Colorless liquid. 90% yield, 95.5:4.5 er. $[\alpha]^{24.6}_D = +26.9$ ($c = 0.69$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 14.44$ min, $t_R(\text{minor}) = 17.78$ min.

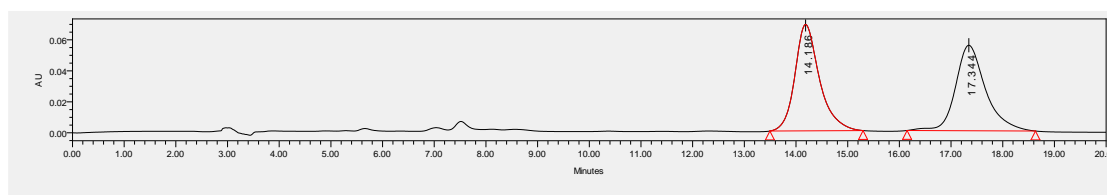
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.52$ (t, $J = 7.4$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 3H), 7.42 – 7.34 (m, 2H), 7.38 – 7.25 (m, 8H), 7.26 – 7.23 (m, 2H), 7.18 (s, 1H), 7.15 – 7.08 (m, 2H), 7.04 (t, $J = 7.8$ Hz, 1H), 2.15 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.3, 138.9, 138.6, 134.8, 133.9, 133.6, 132.5, 131.3, 129.8, 129.2, 128.6, 128.5, 128.4, 128.3, 128.2, 127.7, 127.2, 127.2, 121.6, 81.9, 79.5, 15.0$.

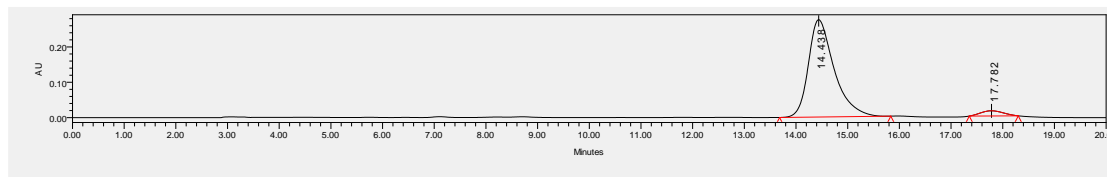
IR (neat): 2924, 1735, 1566, 1450, 1323, 1222, 1183, 1147, 1079, 951, 694 cm^{-1} .

HRMS (ESI) m/z : $([\text{M}]+\text{Na}^+)$ calcd for $\text{C}_{28}\text{H}_{23}^{79}\text{BrO}_4\text{S}_2\text{Na}^+ = 589.0113$, Found 589.0114.

HRMS (ESI) m/z : $([\text{M}]+\text{Na}^+)$ calcd for $\text{C}_{28}\text{H}_{23}^{81}\text{BrO}_4\text{S}_2\text{Na}^+ = 591.0093$, Found 591.0093.

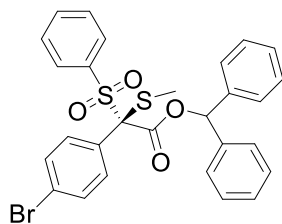


	Retention Time	Area	% Area
1	14.186	2261449	50.45
2	17.344	2221546	49.55



	Retention Time	Area	% Area
1	14.438	9521520	95.54
2	17.782	444658	4.46

benzhydryl (S)-2-(4-bromophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C26)



Colorless liquid. 75% yield, 94:6 er. $[\alpha]^{23.6}_D = +54.3$ ($c = 0.23$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 14.61$ min, $t_R(\text{minor}) = 17.07$ min.

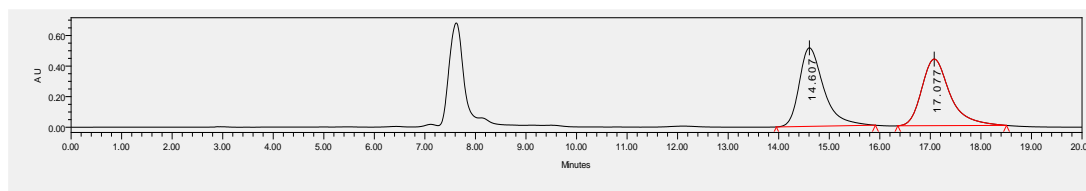
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.51$ (t, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 6.8$ Hz, 2H), 7.38 – 7.22 (m, 12H), 7.07 (s, 1H), 6.99 (d, $J = 8.4$ Hz, 2H), 2.14 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 164.5, 138.9, 138.6, 135.1, 133.9, 131.3, 131.3, 130.9, 130.6, 128.6, 128.5, 128.3, 128.3, 127.8, 127.3, 127.2, 124.0, 82.1, 79.5, 15.0$.

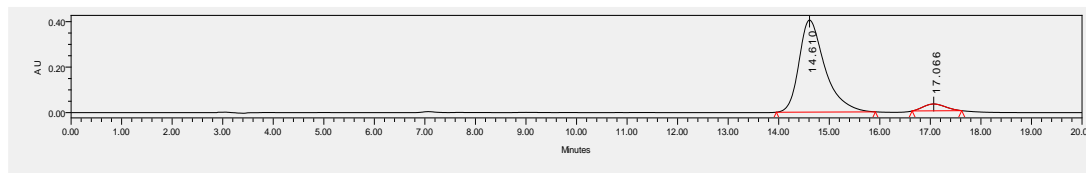
IR (neat): 2926, 1735, 1585, 1489, 1448, 1319, 1224, 1184, 1146, 1078, 697 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}^{79}\text{BrO}_4\text{S}_2\text{Na}^+ = 589.0113$, Found 589.0113.

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}^{81}\text{BrO}_4\text{S}_2\text{Na}^+ = 591.0093$, Found 591.0093.

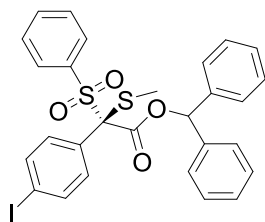


	Retention Time	Area	% Area
1	14.607	17236677	50.48
2	17.077	16911239	49.52



	Retention Time	Area	% Area
1	14.610	14386376	94.03
2	17.066	913457	5.97

benzhydryl (S)-2-(4-iodophenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C27)



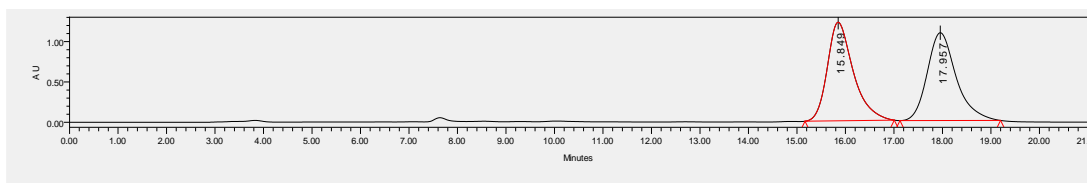
Colorless liquid. 83% yield, 91:9 er. $[\alpha]^{22.5}_D = +52.5$ ($c = 0.55$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 15.74$ min, $t_R(\text{minor}) = 17.87$ min.

$^1\text{H NMR}$ (600 MHz, Chloroform- d) $\delta = 7.53 - 7.47$ (m, 3H), 7.45 (d, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 6.6$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.32 - 7.23 (m, 8H), 7.07 (s, 1H), 6.85 (d, $J = 8.4$ Hz, 2H), 2.13 (s, 3H).

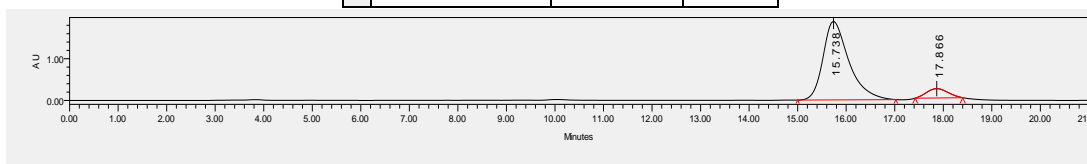
$^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta = 164.5, 138.9, 138.6, 136.8, 135.0, 133.9, 131.3, 128.6, 128.4, 128.3, 128.3, 127.8, 127.2, 127.2, 95.9, 82.3, 79.5, 14.9$.

IR (neat): 3062, 1734, 1583, 1487, 1448, 1319, 1223, 1146, 1077, 1004, 697 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}] + \text{Na}^+$) calcd for $\text{C}_{28}\text{H}_{23}\text{IO}_4\text{S}_2\text{Na}^+$ = 636.9975, Found 636.9974.

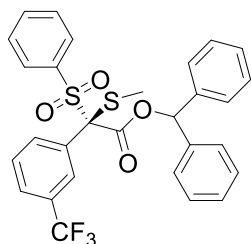


	Retention Time	Area	% Area
1	15.849	45310665	50.18
2	17.957	44979041	49.82



	Retention Time	Area	% Area
1	15.738	69627494	91.04
2	17.866	6855687	8.96

benzhydryl (S)-2-(methylthio)-2-(phenylsulfonyl)-2-(3-(trifluoromethyl)phenyl)acetate (C28)



Colorless liquid. 65% yield, 96:4 er. $[\alpha]^{22}_D = +30.0$ ($c = 0.57$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 10.78$ min, $t_R(\text{minor}) = 12.42$ min.

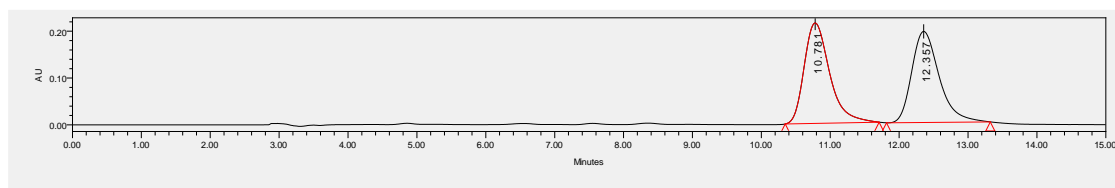
$^1\text{H NMR}$ (600 MHz, Chloroform- d) $\delta = 7.50$ (d, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 7.7$ Hz, 4H), 7.27 (t, $J = 7.6$ Hz, 3H), 7.26 – 7.16 (m, 8H), 7.14 (s, 1H), 7.03 (s, 1H), 2.07 (s, 3H).

$^{13}\text{C NMR}$ (151 MHz, Chloroform- d) $\delta = 164.4, 138.9, 138.6, 134.7, 134.1, 133.5, 132.8, 131.2, 130.2$ (d, $J = 32.7$ Hz), 128.6, 128.5, 128.4 (d, $J = 2.1$ Hz), 128.3, 127.9, 127.3, 127.2, 126.5 (q, $J = 3.9$ Hz), 126.2 (q, $J = 3.5$ Hz), 82.0, 79.8, 14.9.

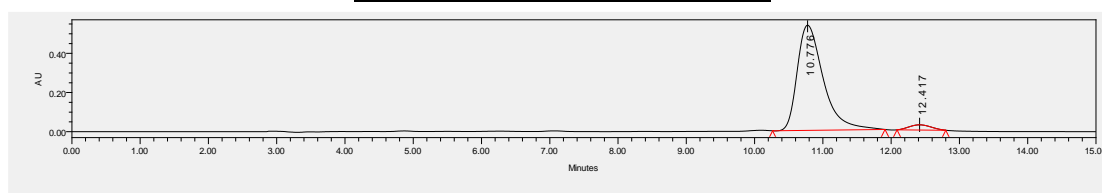
$^{19}\text{F NMR}$ (565 MHz, CDCl_3) $\delta = -62.77$.

IR (neat): 2925, 1736, 1495, 1447, 1328, 1222, 1169, 1147, 1079, 1012, 697 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}] + \text{Na}^+$) calcd for $\text{C}_{29}\text{H}_{23}\text{F}_3\text{O}_4\text{S}_2\text{Na}^+$ = 579.0882, Found 579.0883.

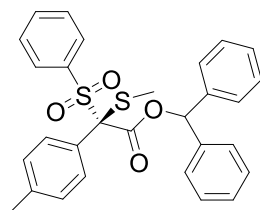


	Retention Time	Area	% Area
1	10.781	5509265	50.63
2	12.357	5371085	49.37



	Retention Time	Area	% Area
1	10.776	14217467	96.00
2	12.417	591849	4.00

benzhydryl (S)-2-(methylthio)-2-(phenylsulfonyl)-2-(p-tolyl)acetate (C29)



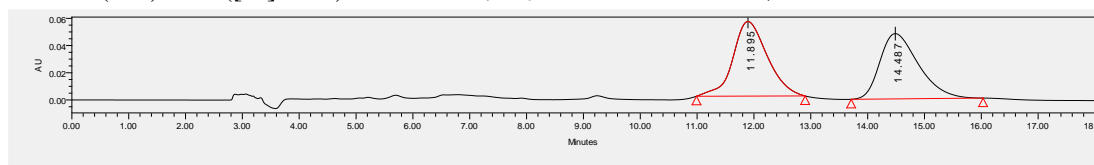
Colorless liquid. 86% yield, 83.5:16.5 er. $[\alpha]^{24.3}_D = +37.2$ ($c = 0.59$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral ODH column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 11.84$ min, $t_R(\text{minor}) = 14.57$ min.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.39$ (d, $J = 7.4$ Hz, 1H), 7.38 – 7.28 (m, 4H), 7.26 – 7.21 (m, 3H), 7.21 – 7.13 (m, 7H), 7.01 (s, 1H), 6.90 (q, $J = 8.4$ Hz, 4H), 2.24 (s, 3H), 2.08 (s, 3H).

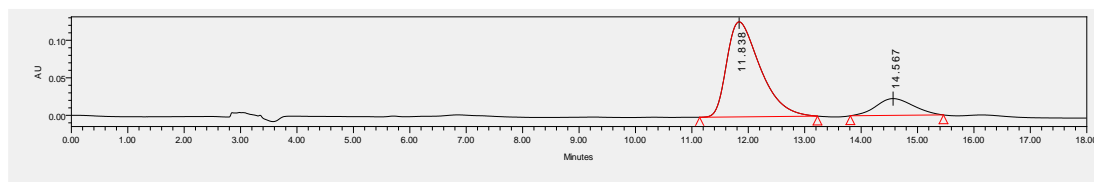
$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.0, 139.6, 139.1, 138.8, 135.5, 133.5, 131.3, 129.4, 128.5, 128.4, 128.3, 128.2, 128.1, 127.5, 127.3, 127.2, 82.7, 79.2, 21.1, 15.0$.

IR (neat): 3062, 1733, 1586, 1502, 1448, 1311, 1220, 1144, 1079, 951, 694 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{29}\text{H}_{26}\text{O}_4\text{S}_2\text{Na}^+ = 525.1165$, Found 525.1165.

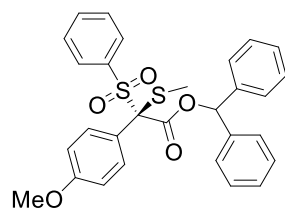


	Retention Time	Area	% Area
1	11.895	2307577	50.49
2	14.487	2263140	49.51



	Retention Time	Area	% Area
1	11.838	5215224	83.53
2	14.567	1028649	16.47

benzhydryl (S)-2-(4-methoxyphenyl)-2-(methylthio)-2-(phenylsulfonyl)acetate (C30)



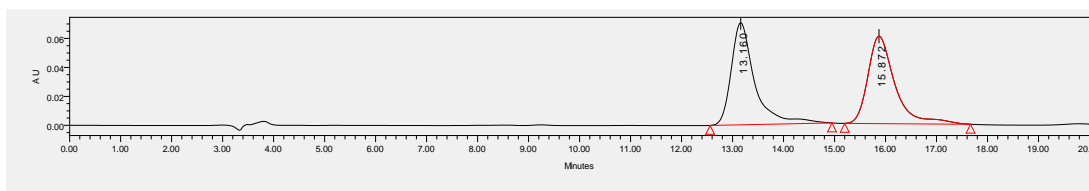
White solid. Melting point: 53.5-58.7 °C. 84% yield, 58.5:41.5 er. $[\alpha]_{D}^{23.7} = +9.1$ ($c = 0.59$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 20/80$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 13.13$ min, $t_R(\text{minor}) = 15.88$ min.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.51 - 7.45$ (m, 1H), 7.46 - 7.36 (m, 4H), 7.33 - 7.29 (m, 3H), 7.28 - 7.22 (m, 7H), 7.09 (s, 1H), 7.02 (d, $J = 8.8$ Hz, 2H), 6.66 (d, $J = 9.2$ Hz, 2H), 3.78 (s, 3H), 2.16 (s, 3H).

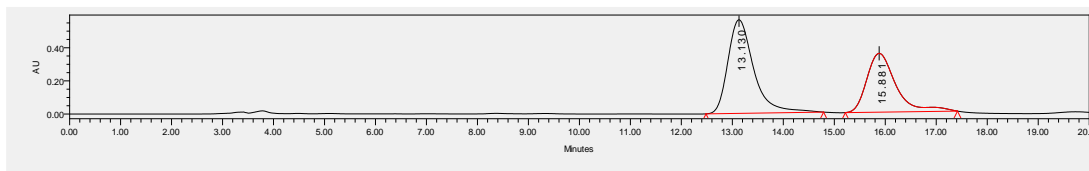
$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.1, 160.3, 139.2, 138.8, 135.5, 133.5, 131.3, 131.0, 128.5, 128.4, 128.2, 128.1, 127.6, 127.3, 127.2, 123.3, 113.1, 82.3, 79.2, 55.3, 15.1$.

IR (neat): 2925, 1734, 1606, 1509, 1450, 1305, 1257, 1223, 1181, 1029, 697 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{Na}^+$) calcd for $\text{C}_{29}\text{H}_{26}\text{O}_5\text{S}_2\text{Na}^+ = 541.1114$, Found 541.1114.

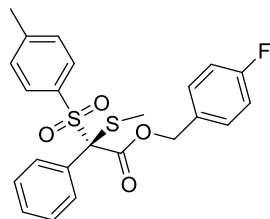


	Retention Time	Area	% Area
1	13.160	2255700	50.43
2	15.872	2216899	49.57



	Retention Time	Area	% Area
1	13.130	19837393	58.57
2	15.881	14032899	41.43

4-fluorobenzyl (S)-2-(methylthio)-2-phenyl-2-tosylacetate (C31)



Yellow liquid. 78% yield, 89:11 er. $[\alpha]^{22.3}_D = +39.5$ ($c = 0.58$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 23.06$, $t_R(\text{minor}) = 33.11$.

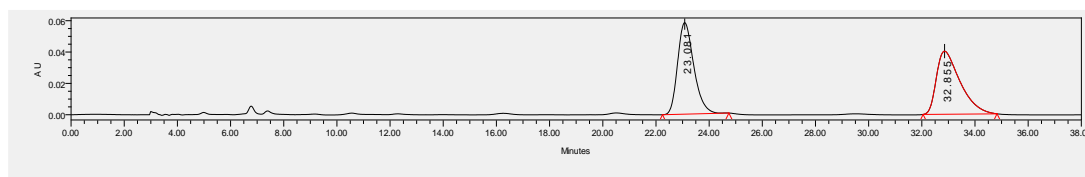
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.39 - 7.30$ (m, 3H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.22 - 7.13 (m, 4H), 7.08 - 6.98 (m, 4H), 5.57 - 5.00 (m, 2H), 2.35 (s, 3H), 2.28 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.8$, 162.8 (d, 248.6 Hz), 144.7, 132.4, 131.5, 131.3, 130.8 (d, 8.4 Hz), 130.4 (d, 3.2 Hz), 129.4, 129.4, 128.3, 127.8, 115.5 (d, 21.7 Hz), 82.7, 67.5, 21.6, 15.2.

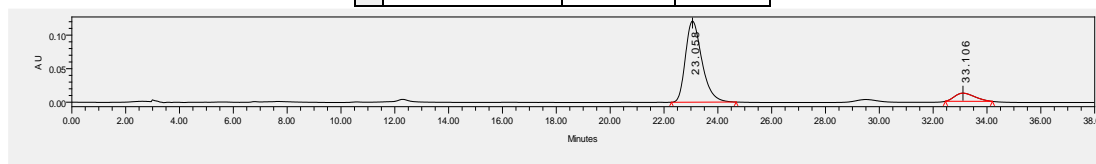
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -112.66$.

IR (neat): 2922, 1733, 1599, 1510, 1450, 1373, 1318, 1216, 1143, 1081, 1011, 968 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{23}\text{H}_{21}\text{FO}_4\text{S}_2\text{K}^+ = 483.0497$, Found 484.0500.

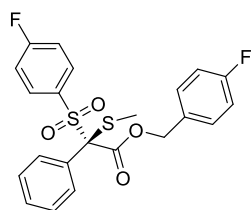


	Retention Time	Area	% Area
1	23.081	2469190	49.85
2	32.855	2484383	50.15



	Retention Time	Area	% Area
1	23.058	5125712	89.08
2	33.106	628149	10.92

4-fluorobenzyl (S)-2-((4-fluorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate (C32)



Yellow liquid. 72% yield, 90.5:9.5 er. $[\alpha]_D^{28.2} = +30.9$ ($c = 0.69$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, i -PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 14.01$, $t_R(\text{minor}) = 16.62$.

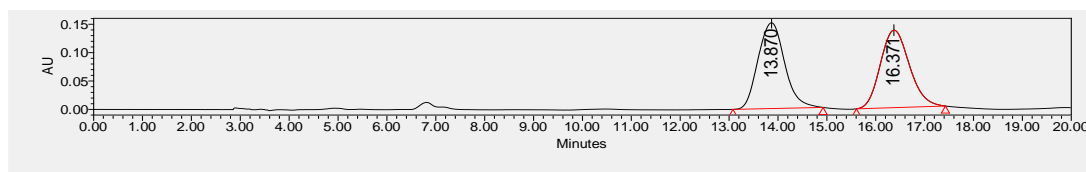
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.43 - 7.31$ (m, 5H), 7.21 (t, $J = 7.9$ Hz, 2H), 7.17 - 7.09 (m, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 6.92 (t, $J = 8.4$ Hz, 2H), 5.36 - 5.23 (m, 2H), 2.30 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.83$ (d, 257.9 Hz), 165.63, 162.9 (d, 249.0 Hz), 134.1 (d, 9.8 Hz), 131.4, 131.2 (d, 3.0 Hz), 130.9 (d, 8.4 Hz), 130.3 (d, 3.3 Hz), 129.7, 129.3, 127.9, 115.5 (d, 21.7 Hz), 114.9 (d, 22.6 Hz), 82.9, 67.6, 15.2.

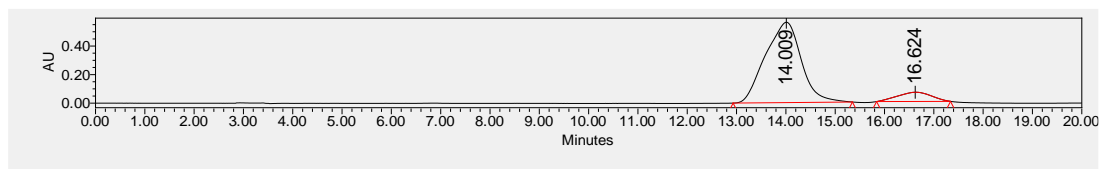
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -103.18, -112.42$.

IR (neat): 2926, 1735, 1591, 1504, 1449, 1325, 1220, 1146, 1082, 968, 828 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{O}_4\text{S}_2\text{K}^+ = 487.0246$, Found 487.0246.

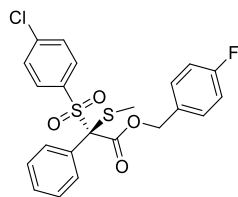


	Retention Time	Area	% Area
1	13.870	5705783	50.33
2	16.371	5631159	49.67



	Retention Time	Area	% Area
1	14.009	28203751	90.60
2	16.624	2927123	9.40

4-fluorobenzyl (S)-2-((4-chlorophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate (C33)



Yellow liquid. 90% yield, 90:10 er. $[\alpha]^{28.1}_D = +26.6$ ($c = 0.35$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 15.94$, $t_R(\text{minor}) = 19.93$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.40 - 7.27$ (m, 5H), 7.25 – 7.17 (m, 4H), 7.18 – 7.10 (m, 2H), 7.03 (t, $J = 8.8$ Hz, 2H), 5.37 – 5.22 (m, 2H), 2.30 (s, 3H).

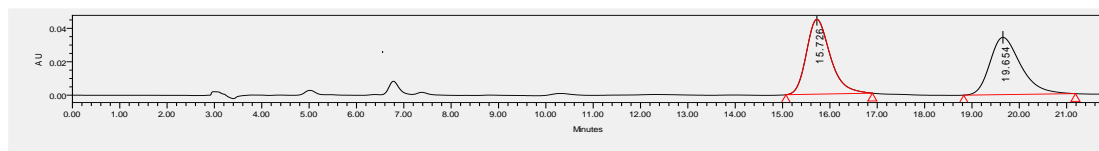
$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.6$, 162.9 (d, 249.0 Hz), 140.5, 133.9, 132.7, 131.2, 130.9 (d, 8.4 Hz), 130.2 (d, 3.3 Hz), 129.8, 129.3, 128.0, 127.9, 115.6 (d, 21.7 Hz), 83.1, 67.6, 15.3.

$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -112.35$.

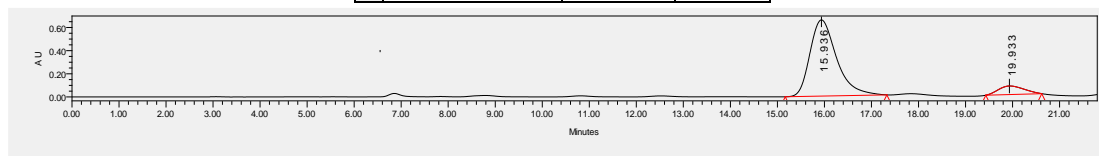
IR (neat): 2923, 1735, 1511, 1454, 1324, 1219, 1148, 1088, 1012, 823 cm^{-1} .

HRMS(ESI) m/z: ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}^{35}\text{ClFO}_4\text{S}_2\text{K}^+ = 502.9951$, Found 502.9951.

HRMS(ESI) m/z: ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{22}\text{H}_{18}^{37}\text{ClFO}_4\text{S}_2\text{K}^+ = 504.9921$, Found 504.9921.

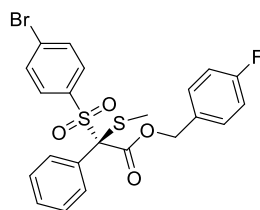


	Retention Time	Area	% Area
1	15.726	1566706	50.21
2	19.654	1553643	49.79



	Retention Time	Area	% Area
1	15.936	25847747	90.25
2	19.933	2791669	9.75

4-fluorobenzyl (S)-2-((4-bromophenyl)sulfonyl)-2-(methylthio)-2-phenylacetate (C34)



Yellow liquid. 81% yield, 88:12 er. $[\alpha]_{D}^{27.8} = +29.5$ ($c = 0.81$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH}/n\text{-hexane} = 10/90$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 17.66$, $t_R(\text{minor}) = 22.37$.

$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.42 - 7.32$ (m, 5H), 7.26 - 7.17 (m, 4H), 7.17 - 7.12 (m, 2H), 7.08 - 7.00 (m, 2H), 5.43 - 5.16 (m, 2H), 2.30 (s, 3H).

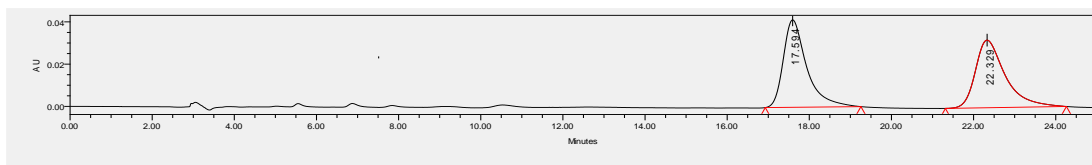
$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.6$, 162.9 (d, 249.0 Hz), 134.5, 132.7, 131.2, 131.0, 130.9, 130.2 (d, 3.3 Hz), 129.8, 129.3 (d, 8.1 Hz), 128.0, 115.6 (d, 21.7 Hz), 83.1, 67.6, 15.3.

$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -112.33$.

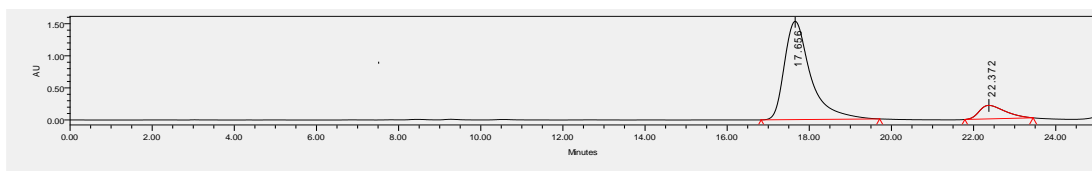
IR (neat): 2927, 1734, 1605, 1571, 1511, 1451, 1384, 1324, 1219, 1147, 1072 cm^{-1} .

HRMS (ESI) m/z : $([\text{M}]+\text{K}^+)$ calcd for $\text{C}_{22}\text{H}_{18}^{79}\text{BrFO}_4\text{S}_2\text{K}^+ = 546.9445$, Found 546.9439.

HRMS (ESI) m/z : $([\text{M}]+\text{K}^+)$ calcd for $\text{C}_{22}\text{H}_{18}^{81}\text{BrFO}_4\text{S}_2\text{K}^+ = 548.9425$, Found 548.9418.

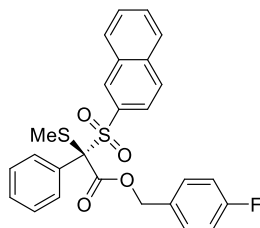


	Retention Time	Area	% Area
1	17.594	1638146	50.36
2	22.329	1614406	49.64



	Retention Time	Area	% Area
1	17.666	67720648	88.01
2	22.372	9221717	11.99

4-fluorobenzyl (S)-2-(methylthio)-2-(naphthalen-2-ylsulfonyl)-2-phenylacetate (C35)



Yellow liquid. 89% yield, 89:11 er. $[\alpha]_{D}^{27.2} = +27.4$ ($c = 1.0$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, $i\text{-PrOH/n-hexane} = 20/80$, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 15.84$, $t_R(\text{minor}) = 21.15$.

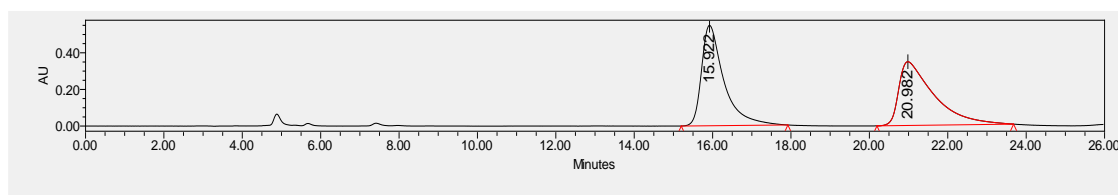
$^1\text{H NMR}$ (400 MHz, Chloroform- d) $\delta = 7.91$ (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.75 – 7.57 (m, 3H), 7.58 – 7.48 (m, 1H), 7.40 – 7.28 (m, 4H), 7.21 – 7.10 (m, 4H), 7.00 (t, $J = 8.8$ Hz, 2H), 5.38 – 5.20 (m, 2H), 2.34 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) $\delta = 165.8$, 162.8 (d, 248.7 Hz), 135.2, 133.6, 132.4, 131.6, 131.3, 130.8 (d, 8.4 Hz), 130.4 (d, 3.2 Hz) 129.6, 129.5, 129.3, 127.8, 127.6, 127.2, 127.1, 125.7, 115.5 (d, 21.7 Hz), 83.1, 67.6, 15.3.

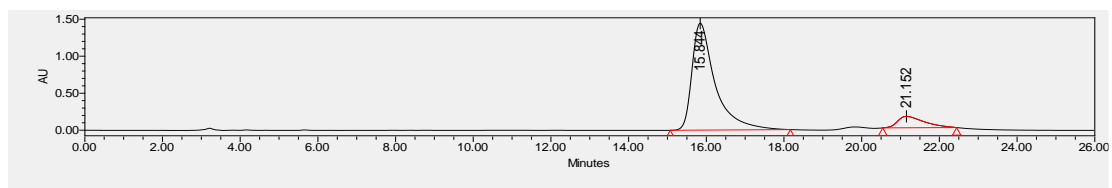
$^{19}\text{F NMR}$ (376 MHz, Chloroform- d) $\delta = -112.56$.

IR (neat): 2921, 1734, 1604, 1509, 1452, 1374, 1316, 1216, 1143, 1070, 818 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{26}\text{H}_{21}\text{FO}_4\text{S}_2\text{K}^+$ = 519.0497, Found 519.0497.

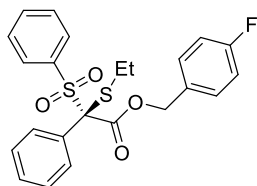


	Retention Time	Area	% Area
1	15.922	21695704	50.14
2	20.982	21576510	49.86



	Retention Time	Area	% Area
1	15.844	59949790	89.03
2	21.152	7383796	10.97

4-fluorobenzyl (S)-2-(ethylthio)-2-phenyl-2-(phenylsulfonyl)acetate (C36)



Yellow liquid. 81% yield, 73:27 er. $[\alpha]_{D}^{27.8} = +18.5$ ($c = 1.5$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral IA column, *i*-PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 15.57$, $t_R(\text{minor}) = 18.73$.

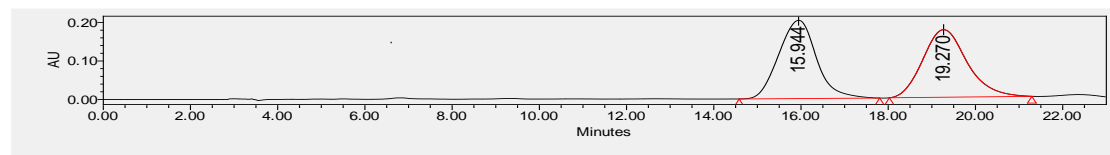
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.49$ (t, $J = 7.4$ Hz, 1H), 7.44 – 7.29 (m, 5H), 7.31 – 7.23 (m, 3H), 7.21 – 7.11 (m, 4H), 7.03 (t, $J = 8.6$ Hz, 2H), 5.39 – 5.21 (m, 2H), 3.23 – 2.99 (m, 1H), 2.61 – 2.44 (m, 1H), 1.17 (t, $J = 7.6$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 166.0$, 162.8 (d, 248.7 Hz), 135.4, 133.6, 131.6, 131.3, 130.9 (d, 8.4 Hz), 130.3 (d, 3.3 Hz), 129.5, 129.4, 127.8, 127.6, 115.5 (d, 21.7 Hz), 83.2, 67.5, 26.4, 13.1.

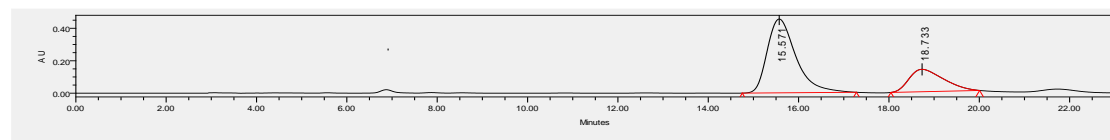
$^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) $\delta = -112.62$.

IR (neat): 2925, 1734, 1605, 1510, 1488, 1374, 1316, 1217, 1146, 1079, 823, 756 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}] + \text{K}^+$) calcd for $\text{C}_{23}\text{H}_{21}\text{FO}_4\text{S}_2\text{K}^+ = 483.0497$, Found 484.0500.

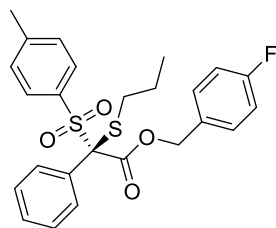


	Retention Time	Area	% Area
1	15.944	12212235	49.72
2	19.270	12349786	50.28



	Retention Time	Area	% Area
1	15.571	20037611	73.27
2	18.733	7311070	26.73

4-fluorobenzyl (S)-2-phenyl-2-(propylthio)-2-tosylacetate (C37)



Yellow liquid. 47% yield, 62:38 er. $[\alpha]^{20.9}_D = +7.1$ ($c = 0.64$ in CH_2Cl_2). Dissolved in hexane for HPLC; HPLC (Chiral ODH column, *i*-PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 18.62$, $t_R(\text{minor}) = 14.06$.

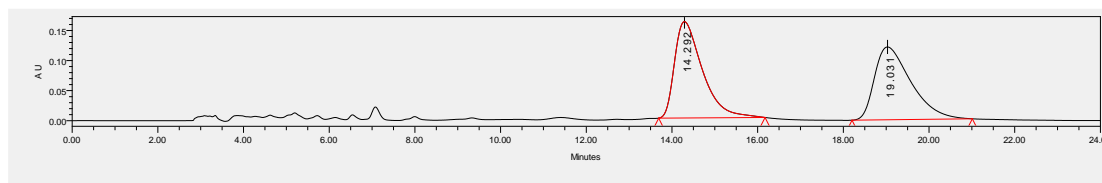
^1H NMR (400 MHz, Chloroform- d) $\delta = 7.42 - 7.35$ (m, 2H), 7.32 (d, $J = 7.2$ Hz, 1H), 7.30 - 7.23 (m, 2H), 7.22 - 7.12 (m, 4H), 7.10 - 6.99 (m, 4H), 5.34 (d, $J = 12.0$ Hz, 1H), 5.22 (d, $J = 12.0$ Hz, 1H), 3.10 - 2.98 (m, 1H), 2.48 - 2.39 (m, 1H), 2.36 (s, 3H), 1.58 - 1.44 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) $\delta = 166.2$, 162.8 (d, 248.7 Hz), 144.7, 132.4, 131.8, 131.4, 131.1 (d, 8.4 Hz), 130.4 (d, 3.2 Hz), 129.5, 129.4, 128.3, 127.8, 115.5 (d, 21.6 Hz), 82.8, 67.4, 34.0, 21.8, 21.6, 13.5.

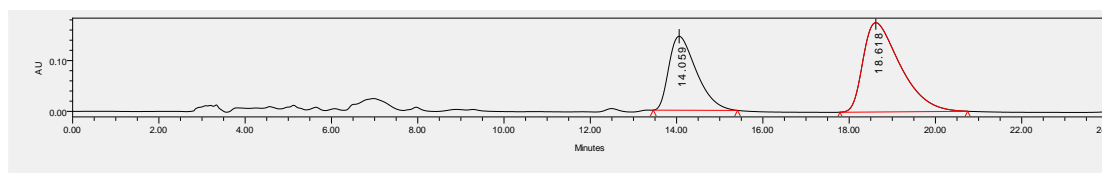
^{19}F NMR (377 MHz, CDCl_3) $\delta = -112.68$.

IR (neat): 2963, 1734, 1601, 1510, 1451, 1375, 1319, 1217, 1146, 1082, 818, 698 cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}] + \text{Na}^+$) calcd for $\text{C}_{25}\text{H}_{25}\text{FO}_4\text{S}_2\text{Na}^+$ = 495.1071, Found 495.1071.

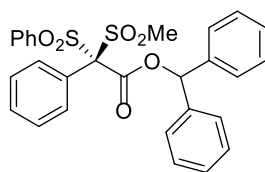


	Retention Time	Area	% Area
1	14.292	7240762	50.35
2	19.031	7140362	49.65



	Retention Time	Area	% Area
1	14.059	6442365	37.97
2	18.618	10522762	62.03

benzhydryl (S)-2-(methylsulfonyl)-2-phenyl-2-(phenylsulfonyl)acetate (D1)



White solid. Melting point: 70.1-74.7 °C. 70% yield, 94:6 er. $[\alpha]_{21.6}^{25} = +18.8$ ($c = 0.63$ in CH_2Cl_2).

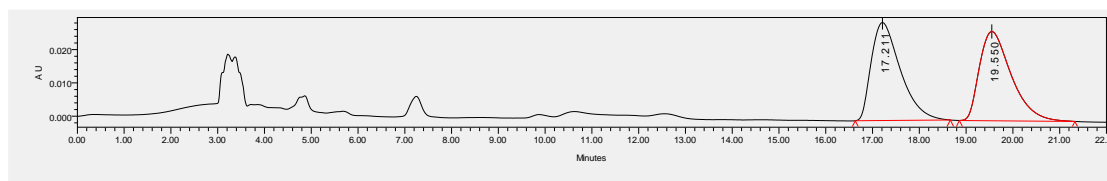
Dissolved in hexane for HPLC; HPLC (Chiral IB column, *i*-PrOH/n-hexane = 10/90, flow rate: 1.0 mL/min, 254 nm), $t_R(\text{major}) = 17.06$, $t_R(\text{minor}) = 19.97$.

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) $\delta = 7.54$ (d, $J = 7.2$ Hz, 2H), 7.52 – 7.41 (m, 3H), 7.44 – 7.35 (m, 3H), 7.37 – 7.29 (m, 7H), 7.29 – 7.17 (m, 5H), 7.10 (s, 1H), 3.05 (s, 3H).

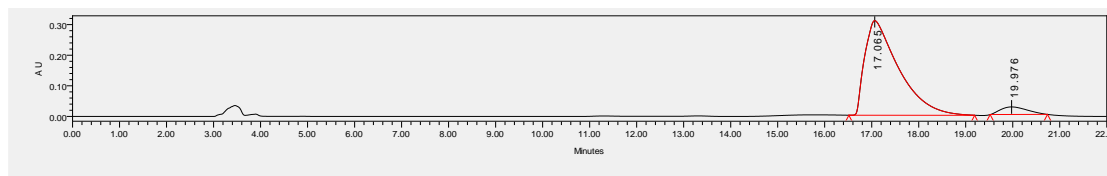
$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) $\delta = 162.6, 138.0, 137.9, 136.3, 134.5, 131.9, 131.3, 130.4, 128.6, 128.5, 128.5, 128.2, 127.8, 127.6, 127.5, 127.2, 96.7, 81.2, 42.2$.

IR (neat): 3063, 1736, 1585, 1495, 1450, 1334, 1227, 1146, 1077, 996, 956, 847, 751, 695. cm^{-1} .

HRMS (ESI) m/z : ($[\text{M}]+\text{K}^+$) calcd for $\text{C}_{28}\text{H}_{24}\text{O}_6\text{S}_2\text{K}^+ = 559.0646$, Found 559.0646.



	Retention Time	Area	% Area
1	17.211	1272631	50.13
2	19.550	1265920	49.87



	Retention Time	Area	% Area
1	17.065	15473695	94.01
2	19.976	985169	5.99

8. Copies of NMR spectra of products

Figure S1. ^1H NMR of C4

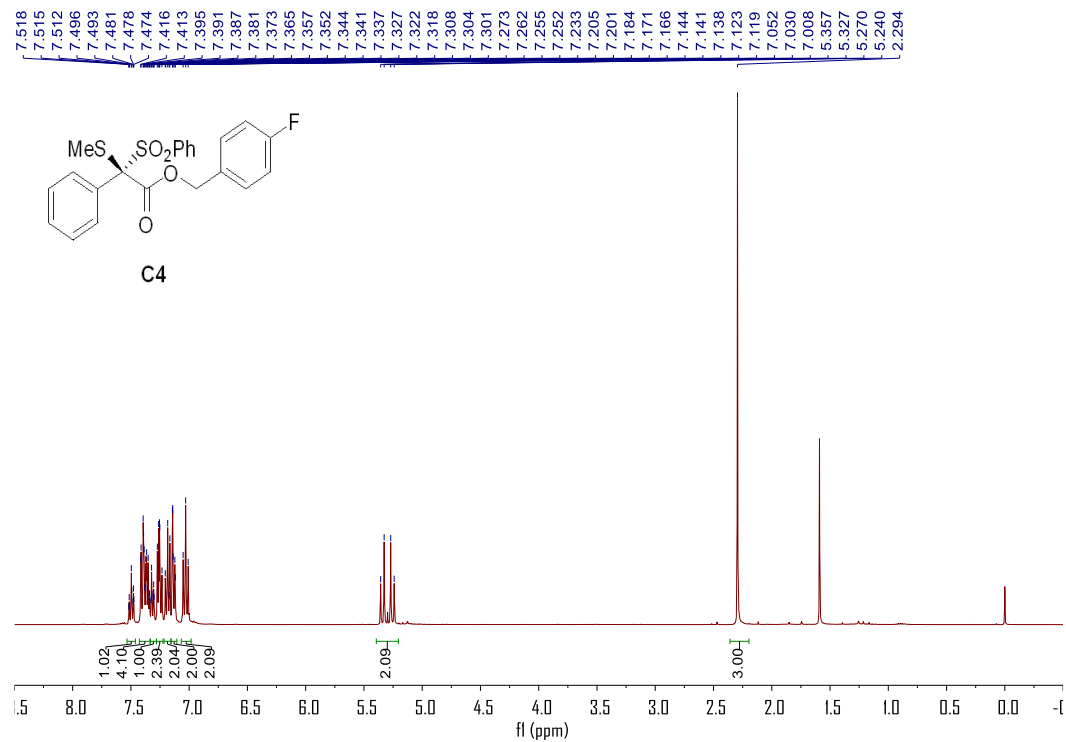


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR of C4

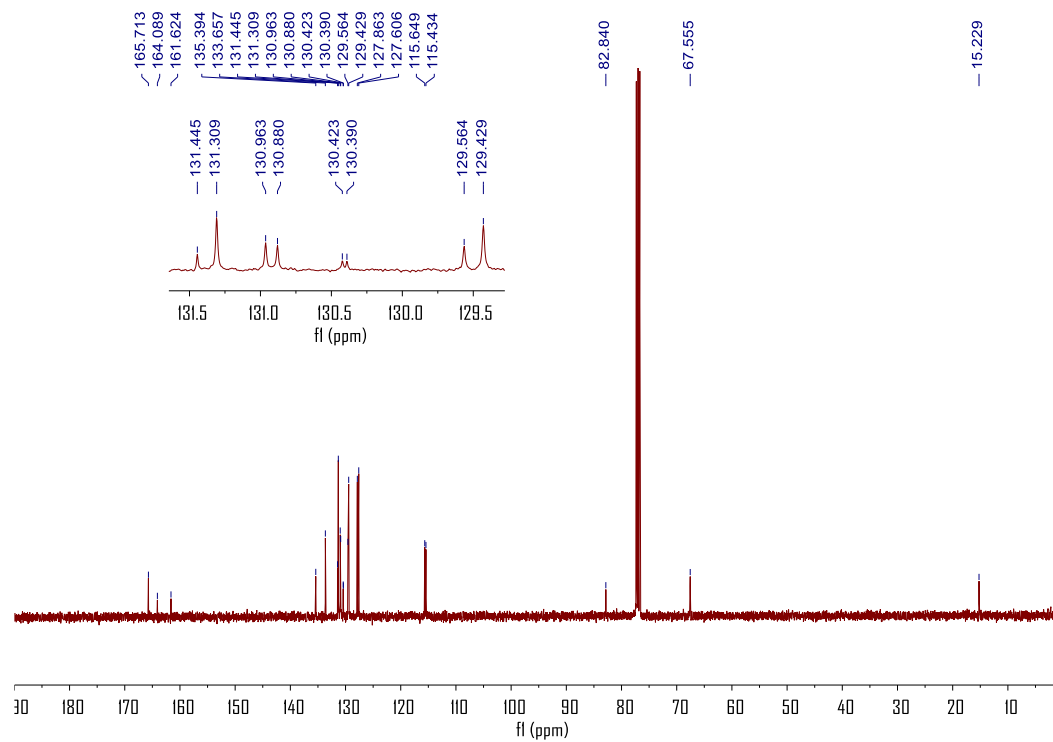


Figure S3. ^{19}F NMR of C4

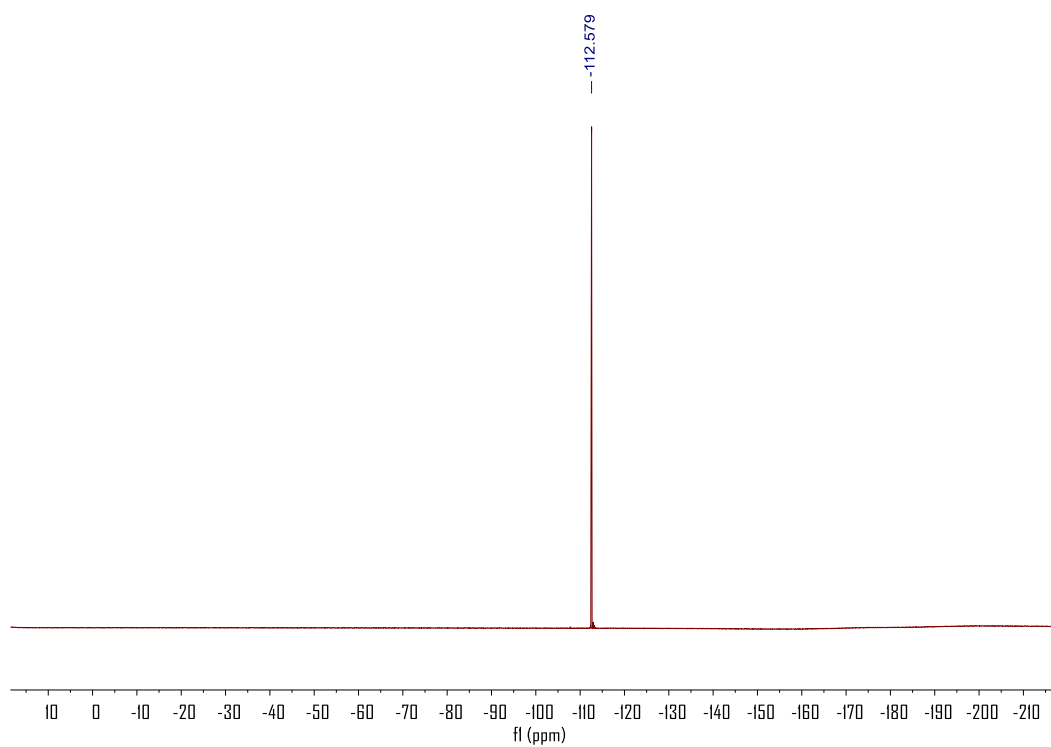


Figure S4. ^1H NMR of C5

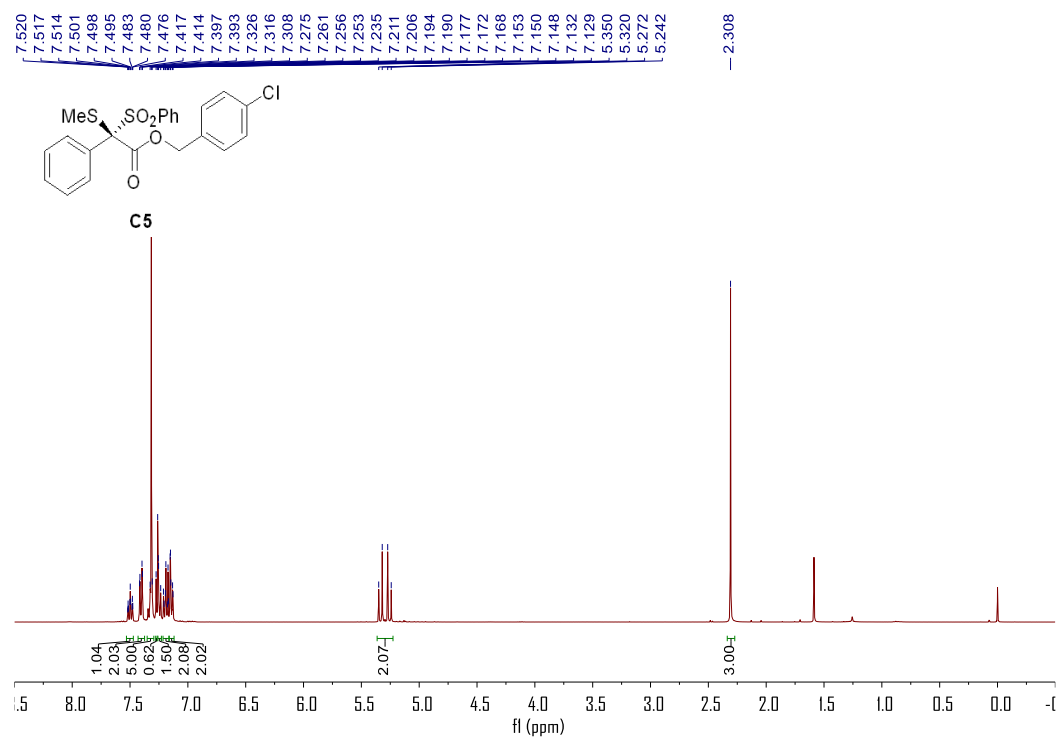


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR of C5

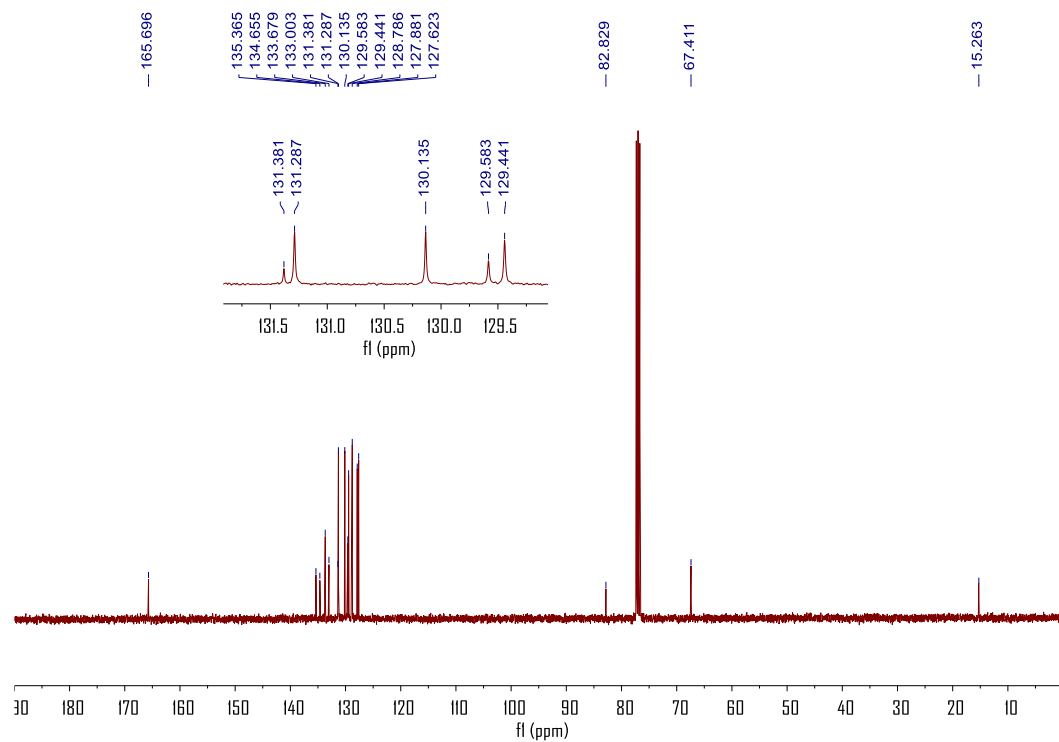


Figure S6. ^1H NMR of C6

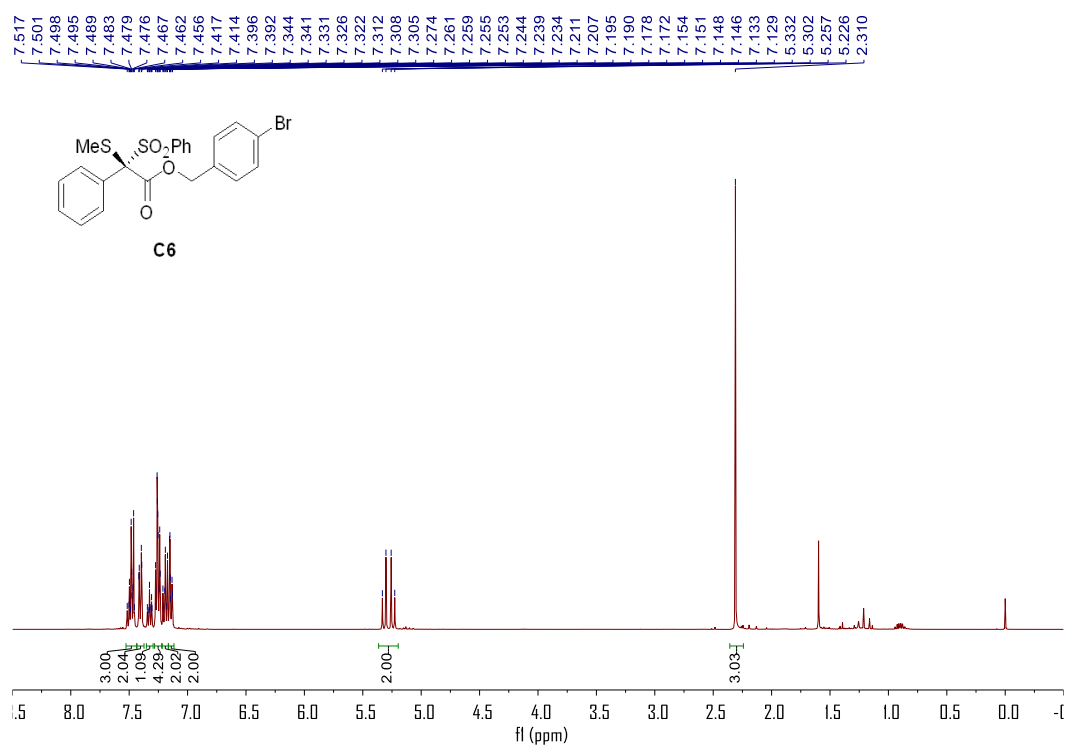


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR of C6

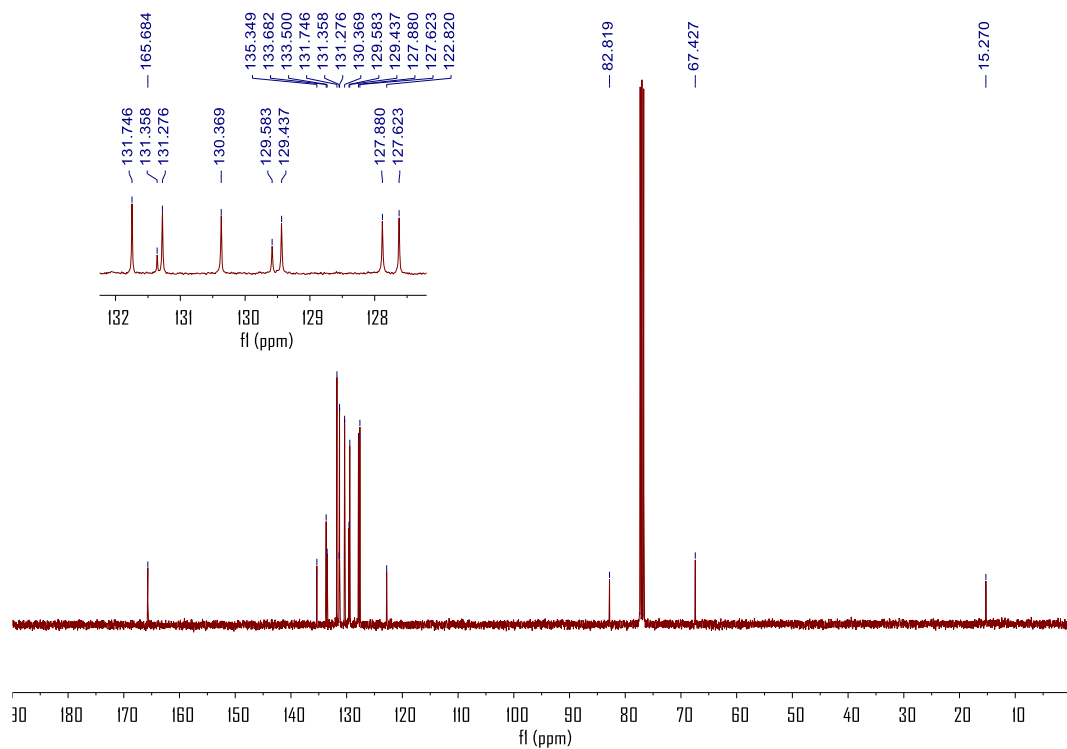


Figure S8. ^1H NMR of C7

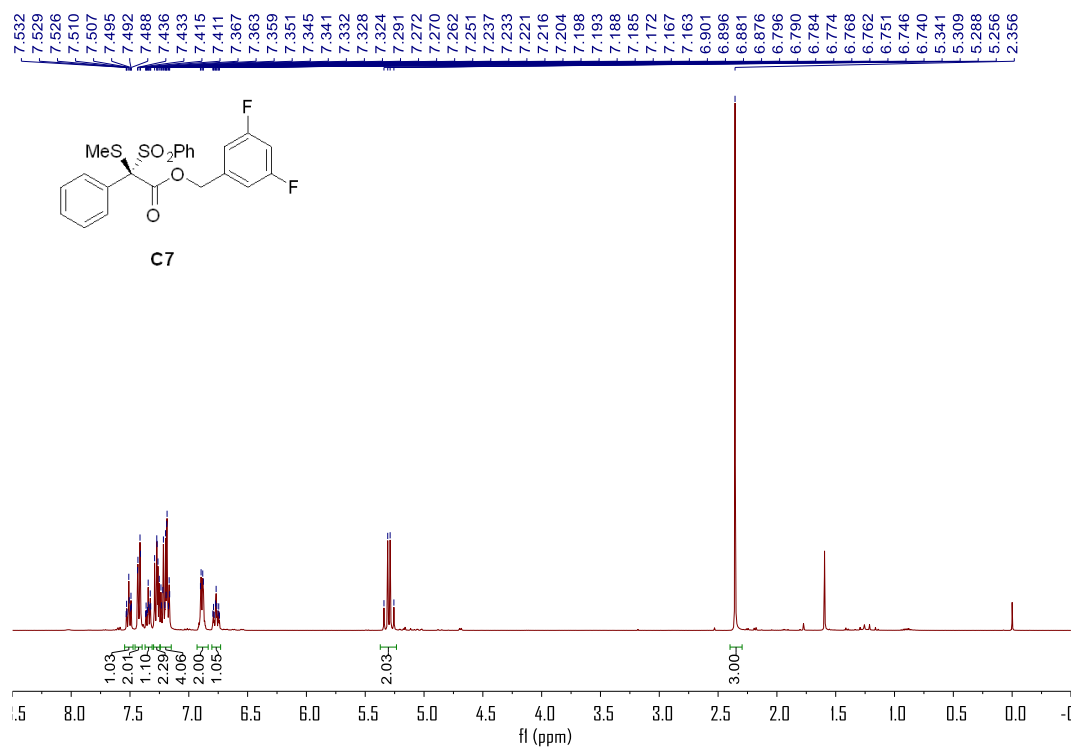


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR of C7

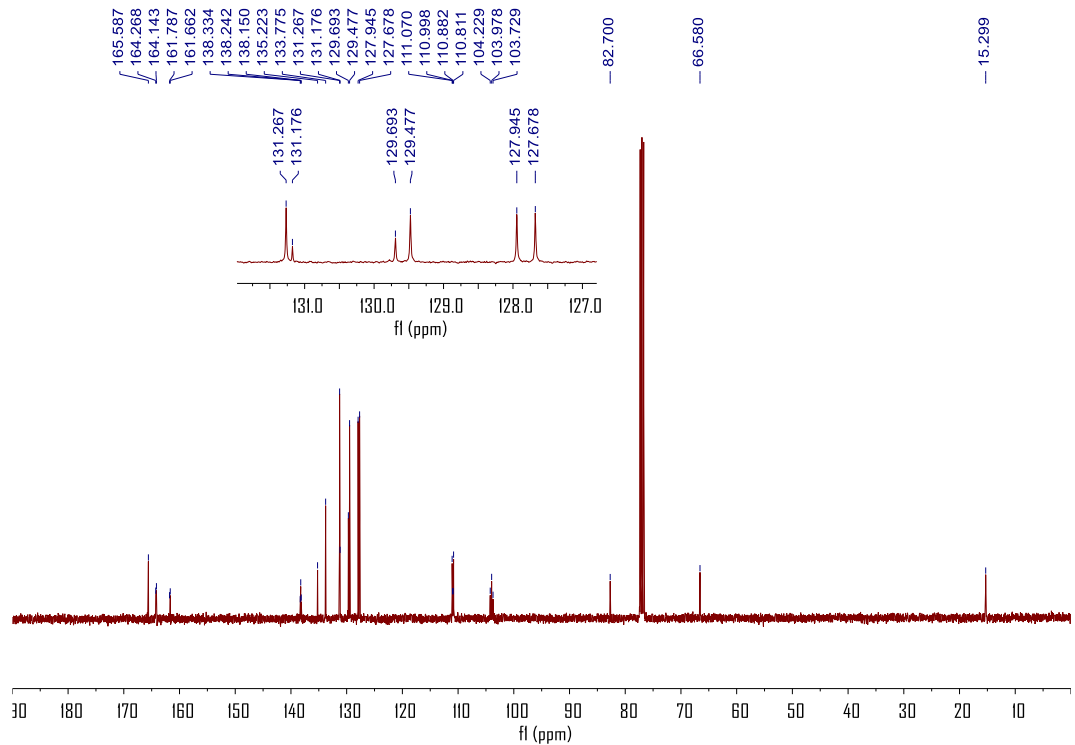


Figure S10. ^{19}F NMR of C7

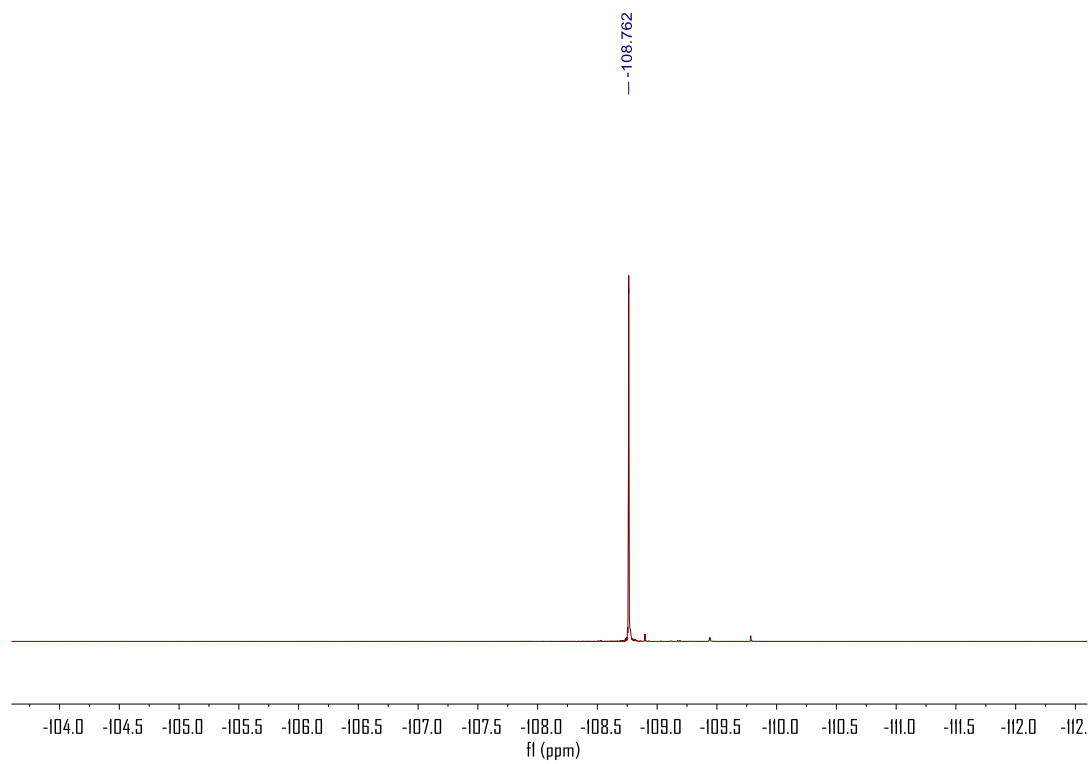


Figure S11. ¹H NMR of C8

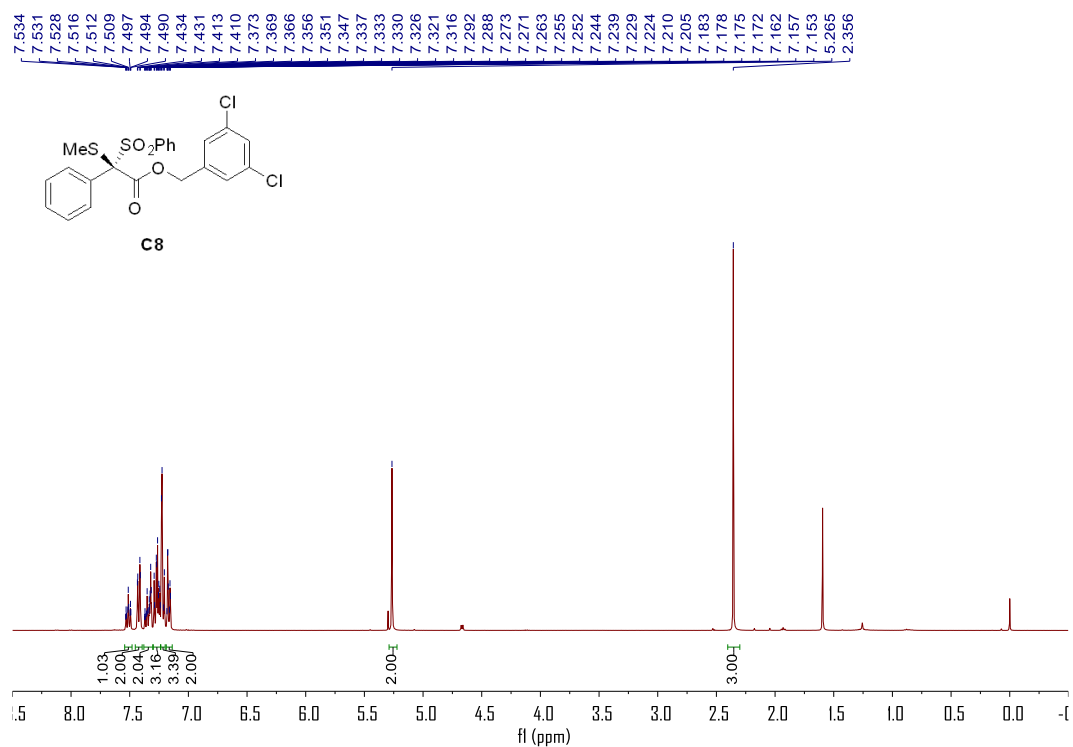


Figure S12. ¹³C{¹H} NMR of C8

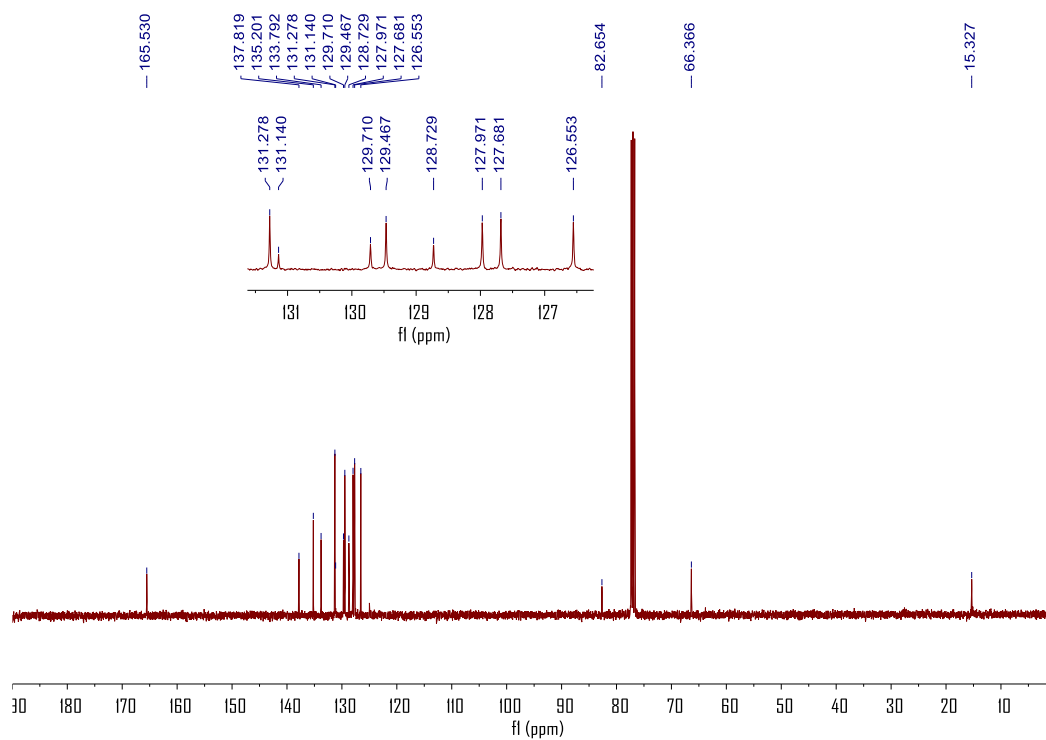


Figure S13. ^1H NMR of C9

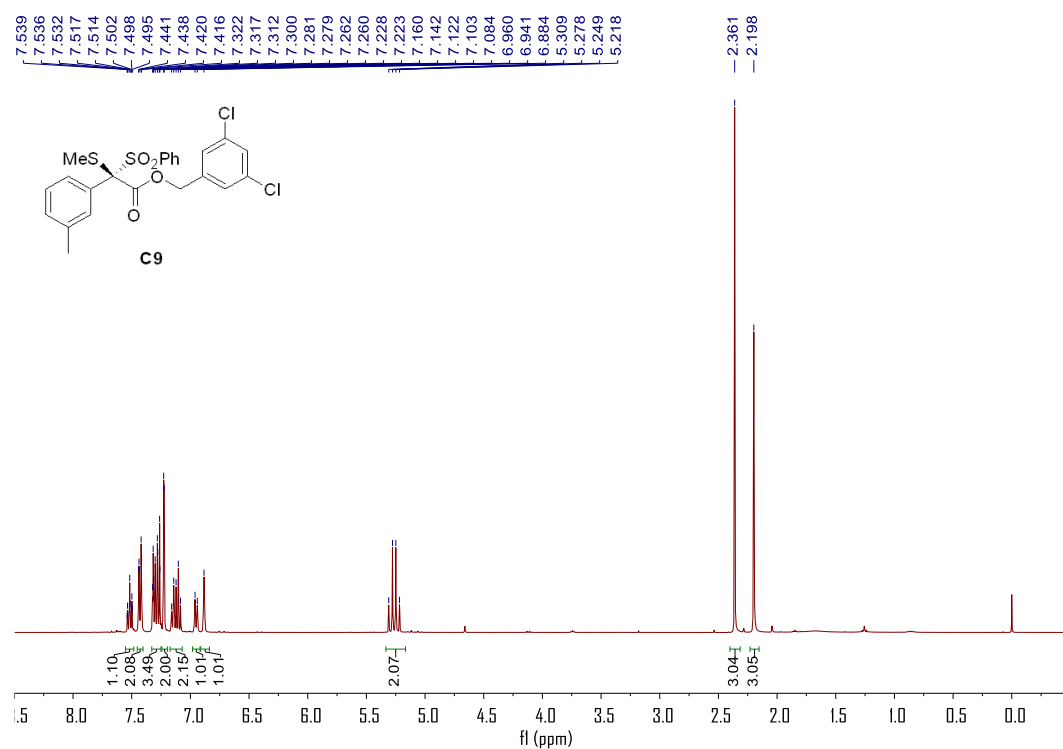


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR of C9

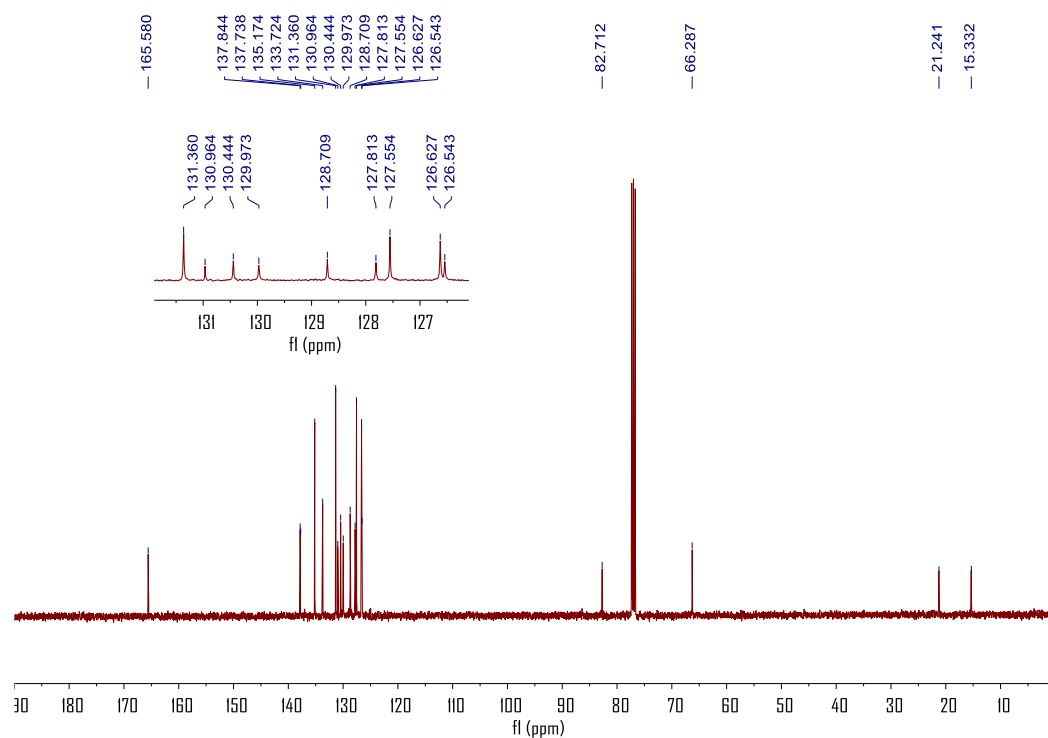


Figure S15. ^1H NMR of C10

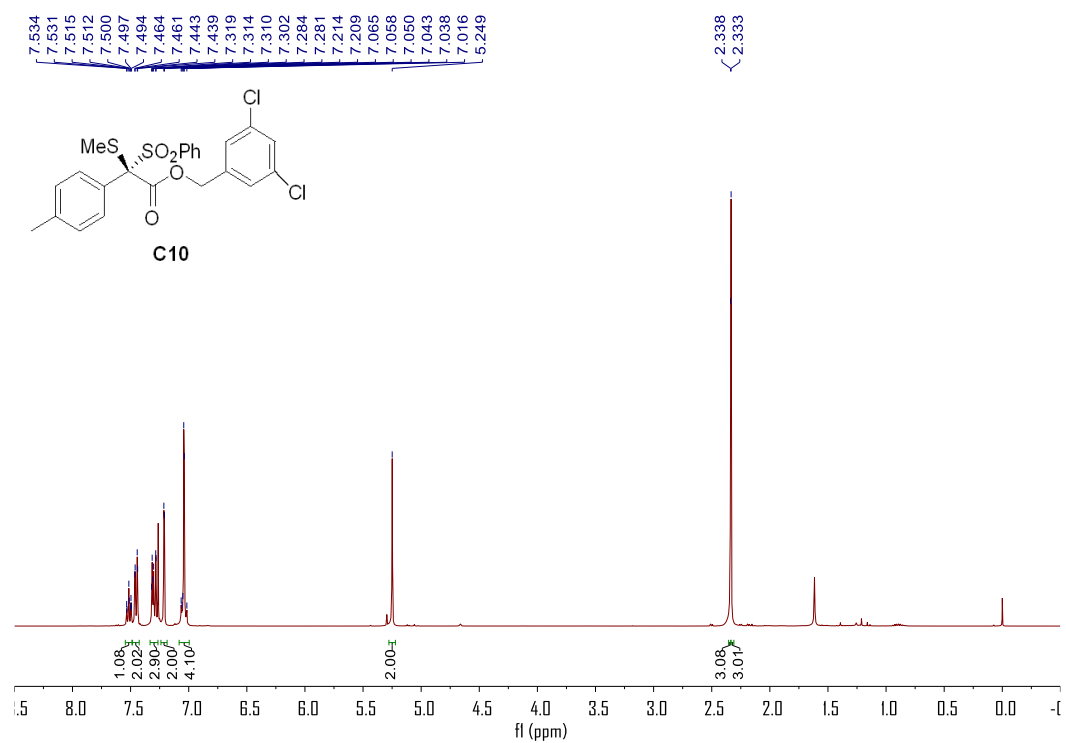


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR of C10

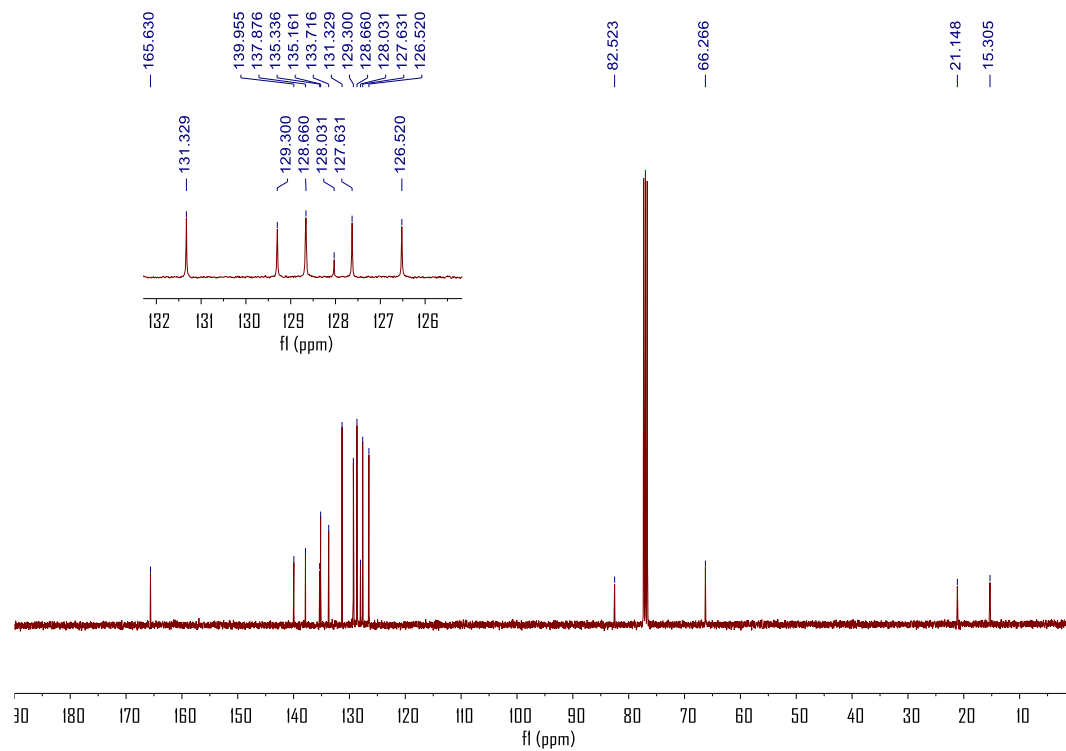


Figure S17. ¹H NMR of C11

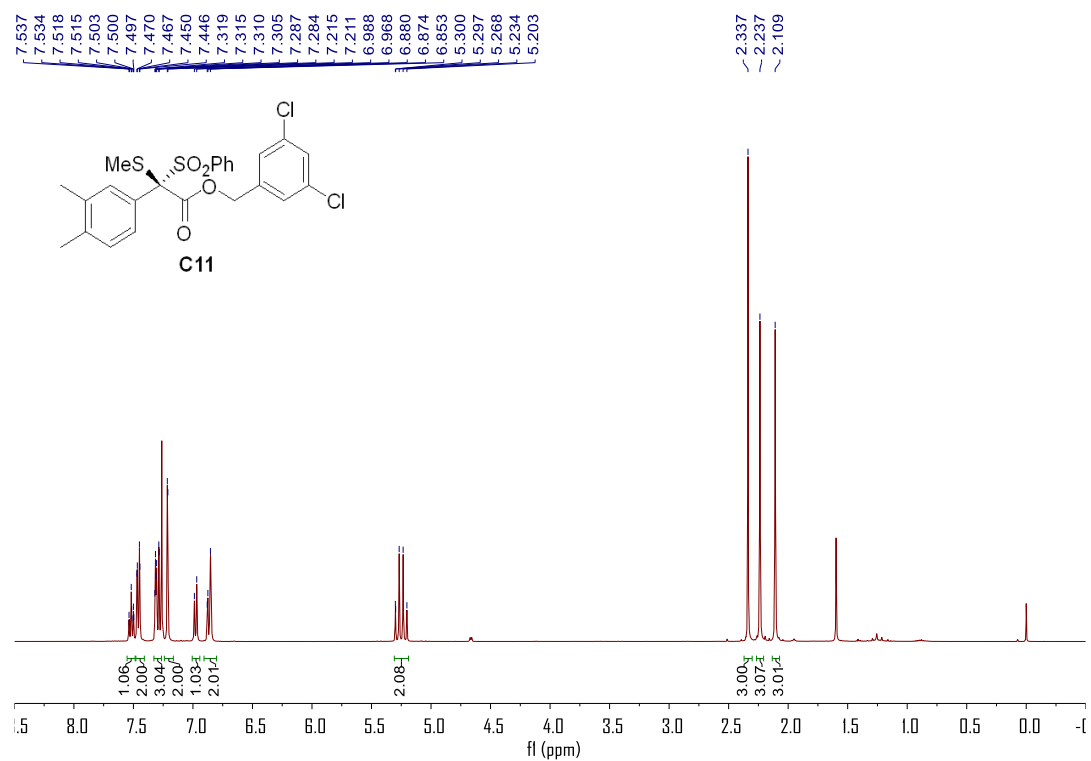


Figure S18. ¹³C{¹H} NMR of C11

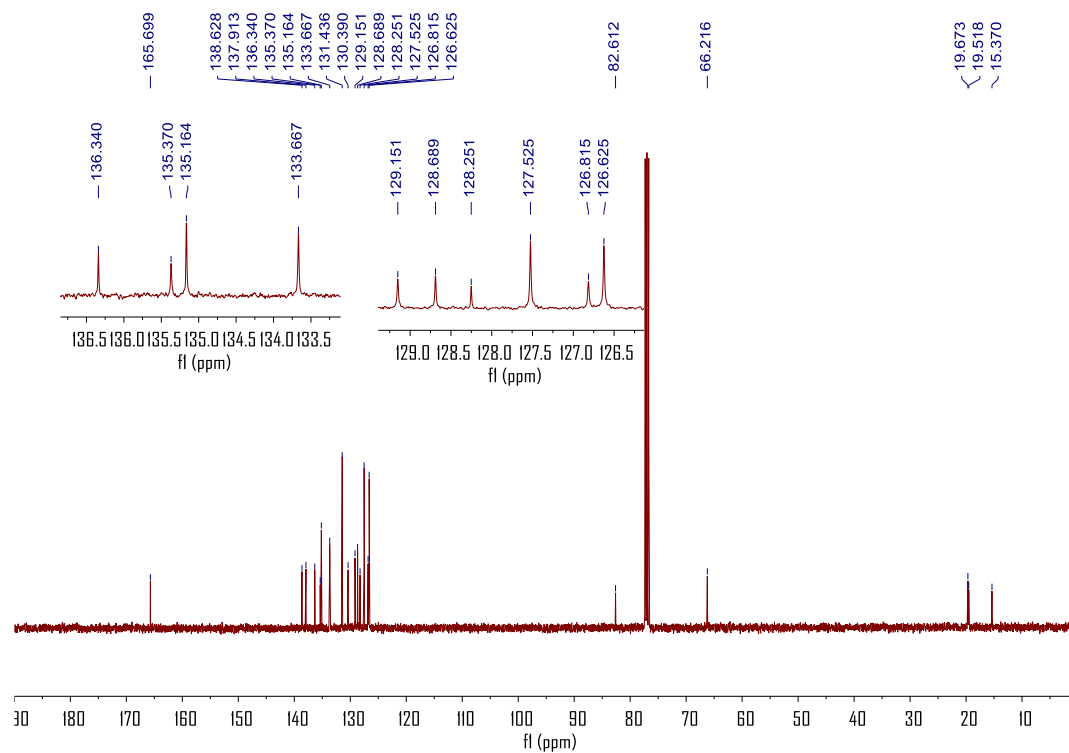


Figure S19. ^1H NMR of C12

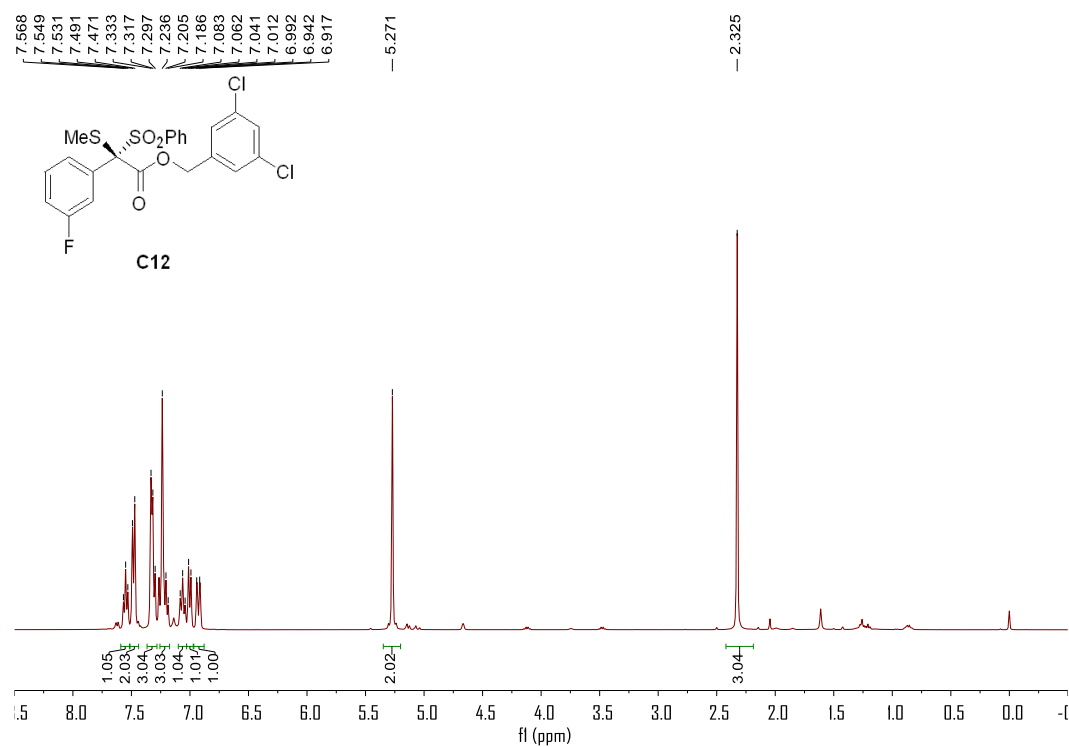


Figure S20. $^{13}\text{C}\{^1\text{H}\}$ NMR of C12

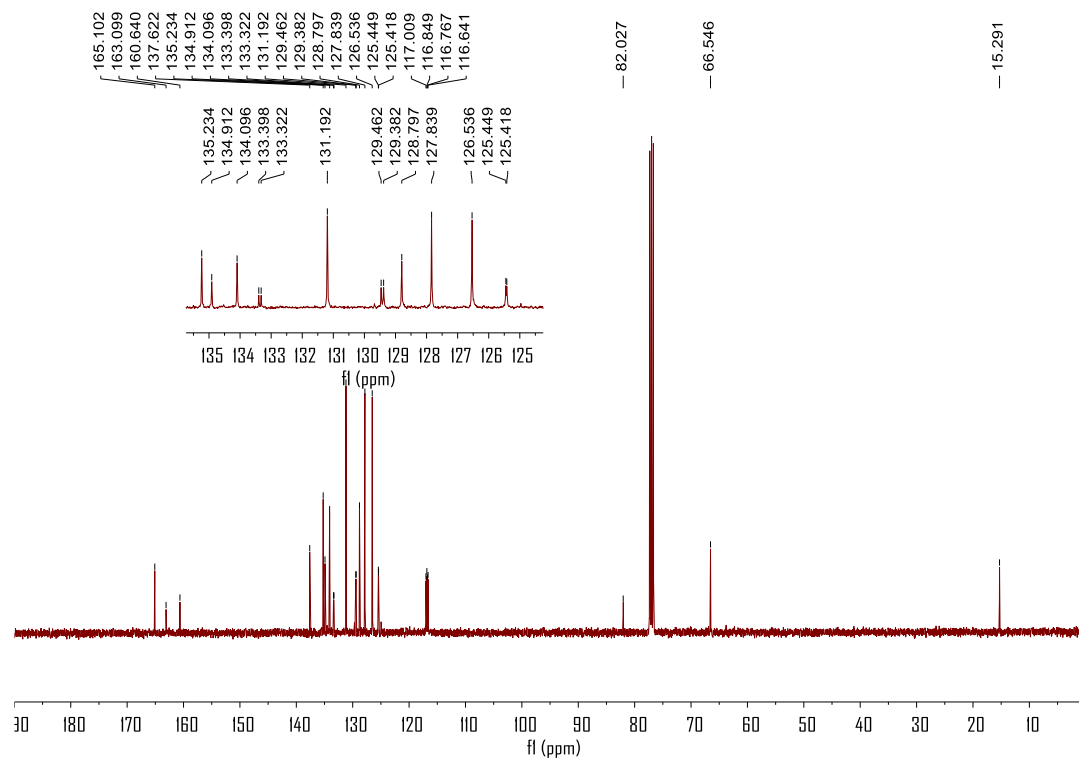


Figure S21. ^{19}F NMR of C12

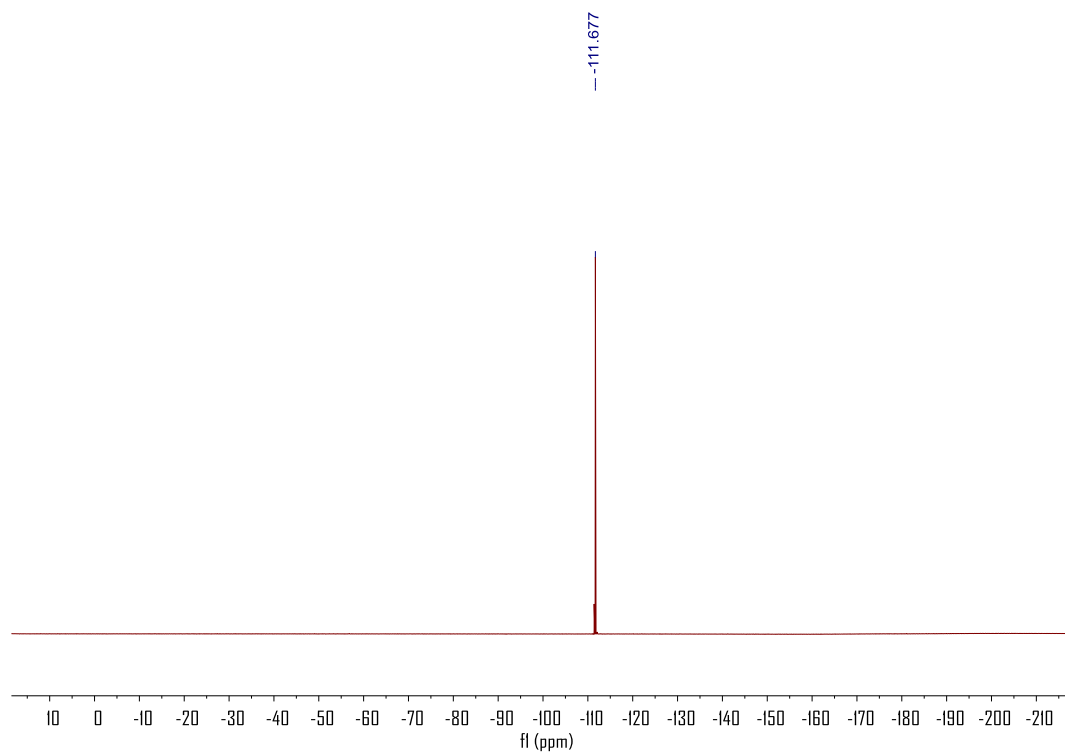


Figure S22. ^1H NMR of C13

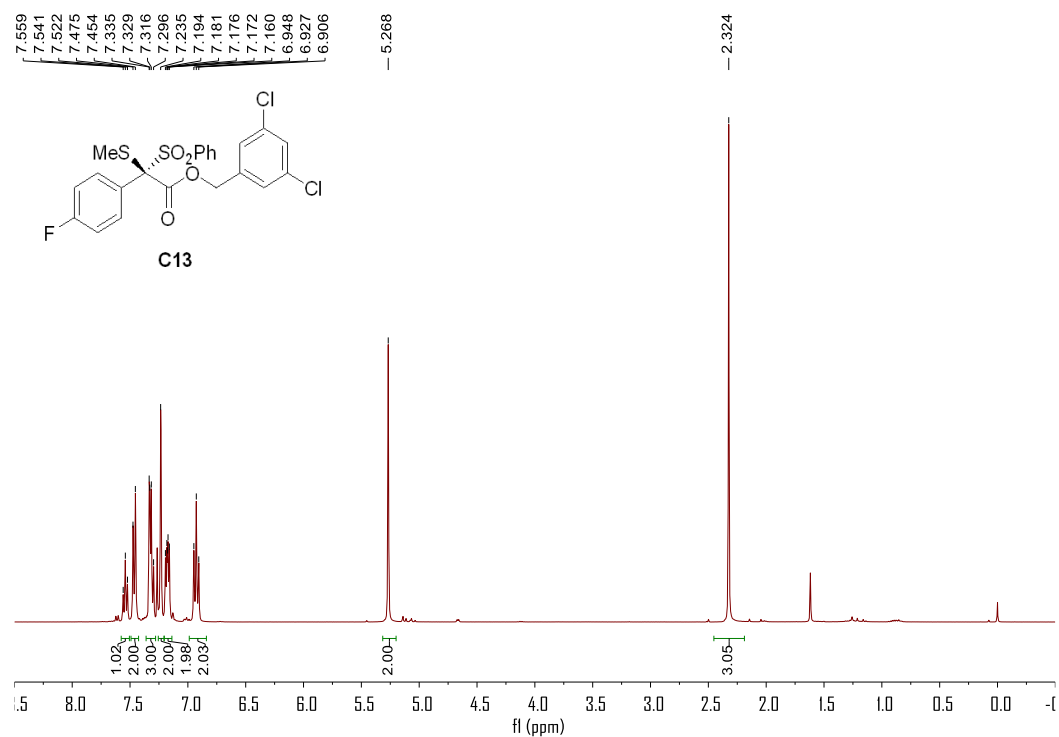


Figure S23. $^{13}\text{C}\{^1\text{H}\}$ NMR of C13

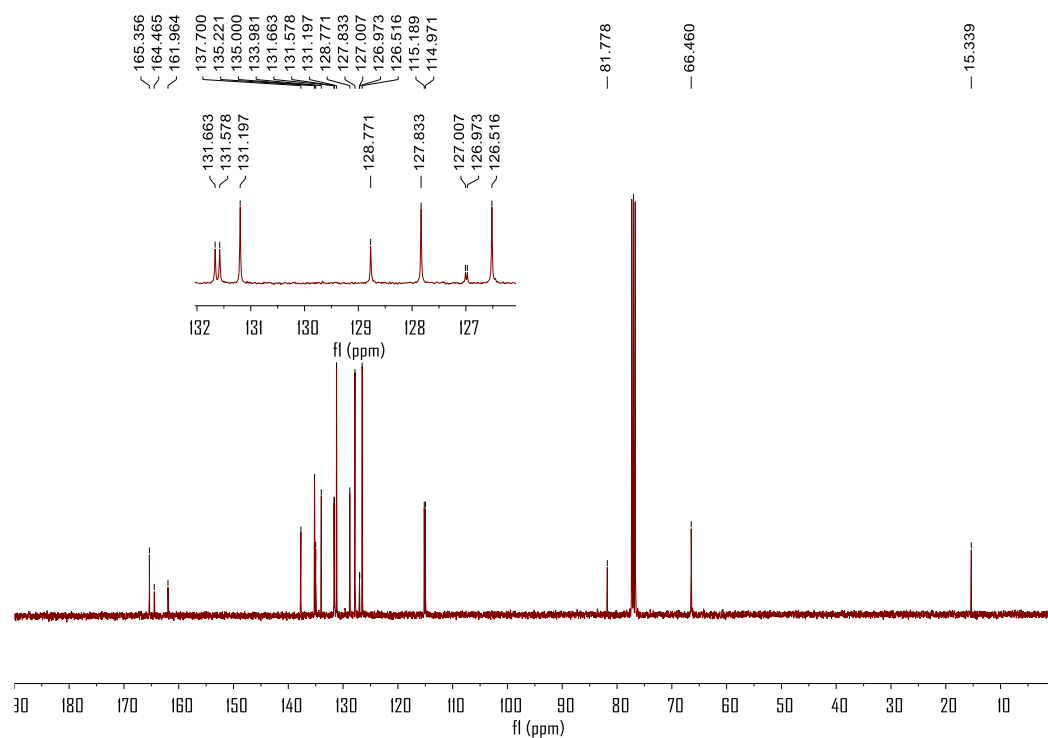


Figure S24. ^{19}F NMR of C13

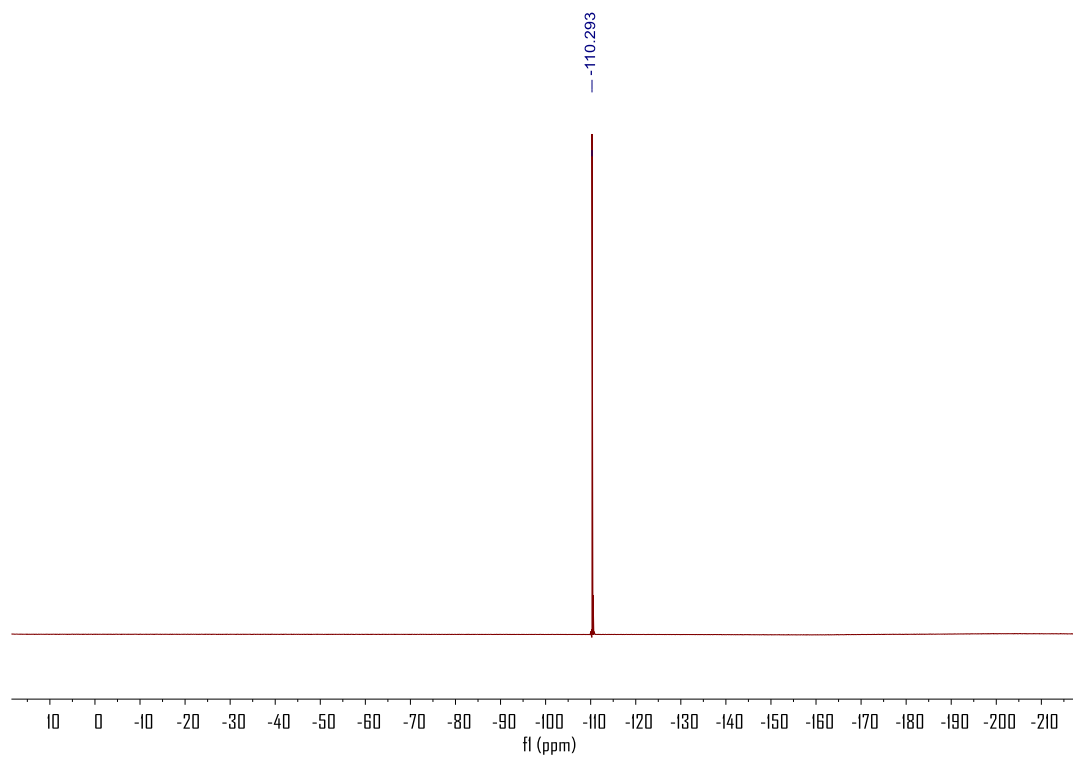


Figure S25. ^1H NMR of C14

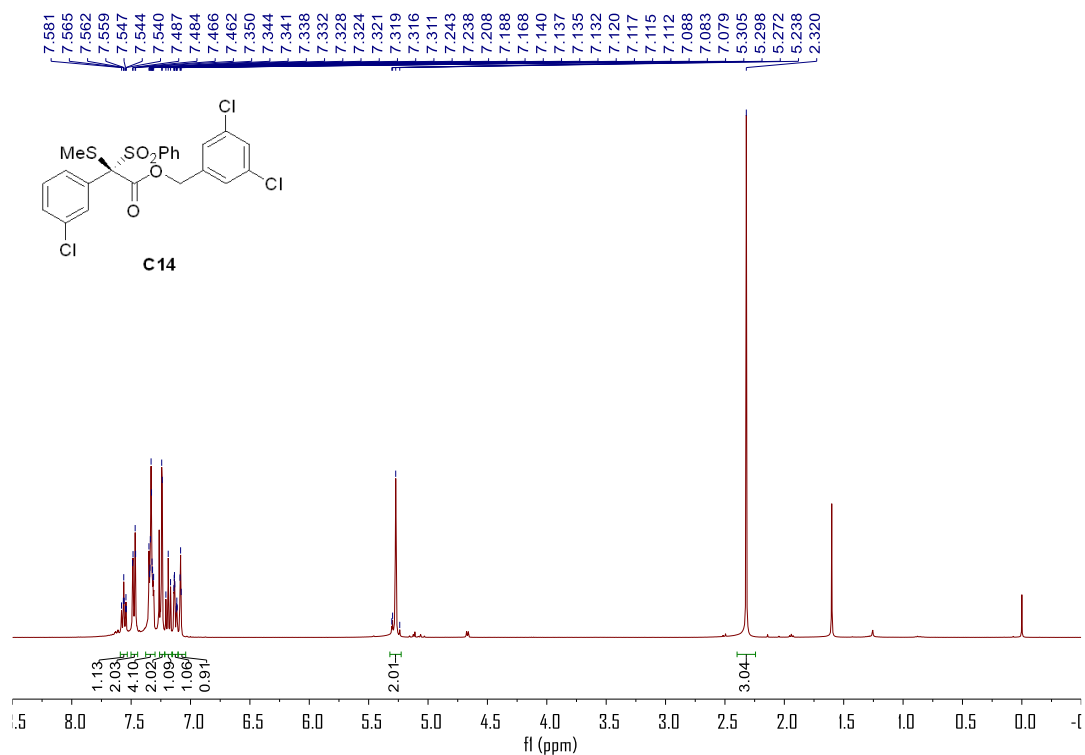


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ NMR of C14

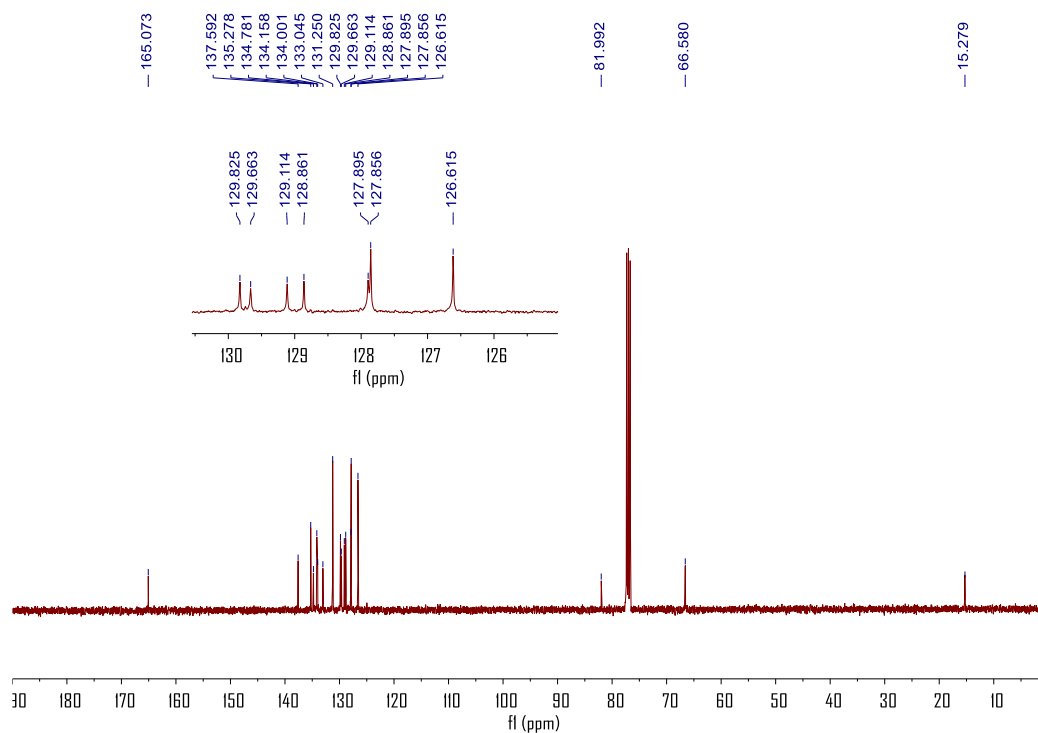


Figure S27. ^1H NMR of C15

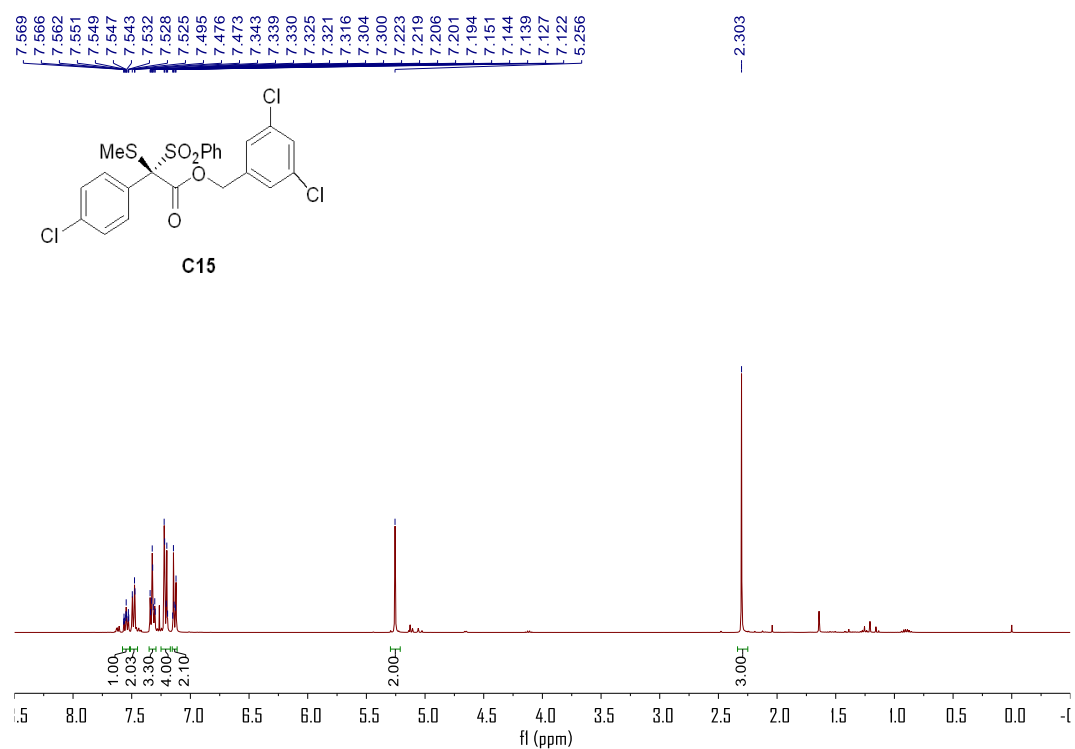


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR of C15

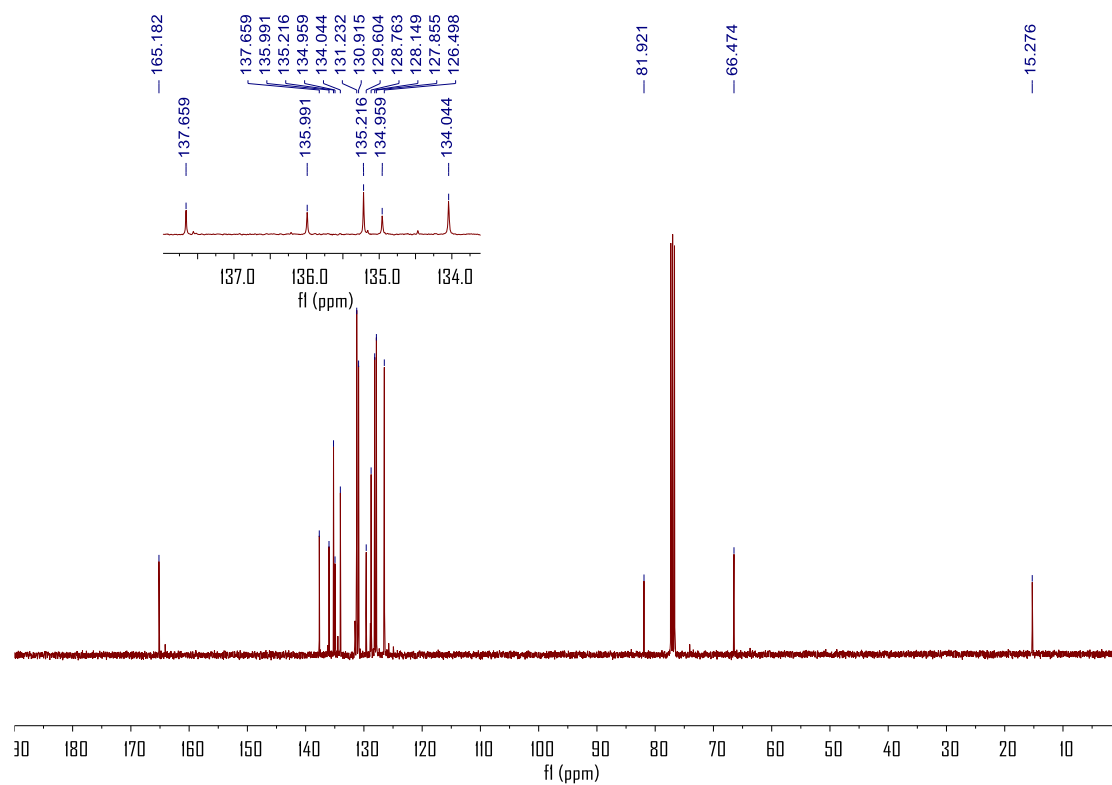


Figure S29. ¹H NMR of C16

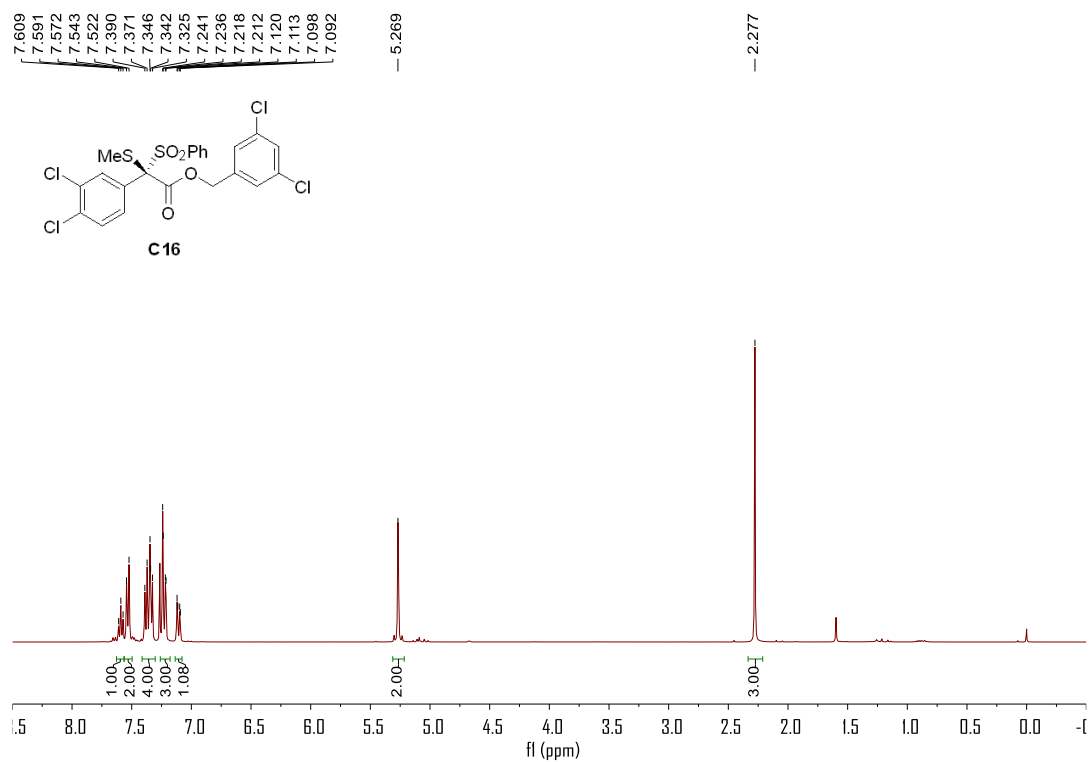


Figure S30. ¹³C{¹H} NMR of C16

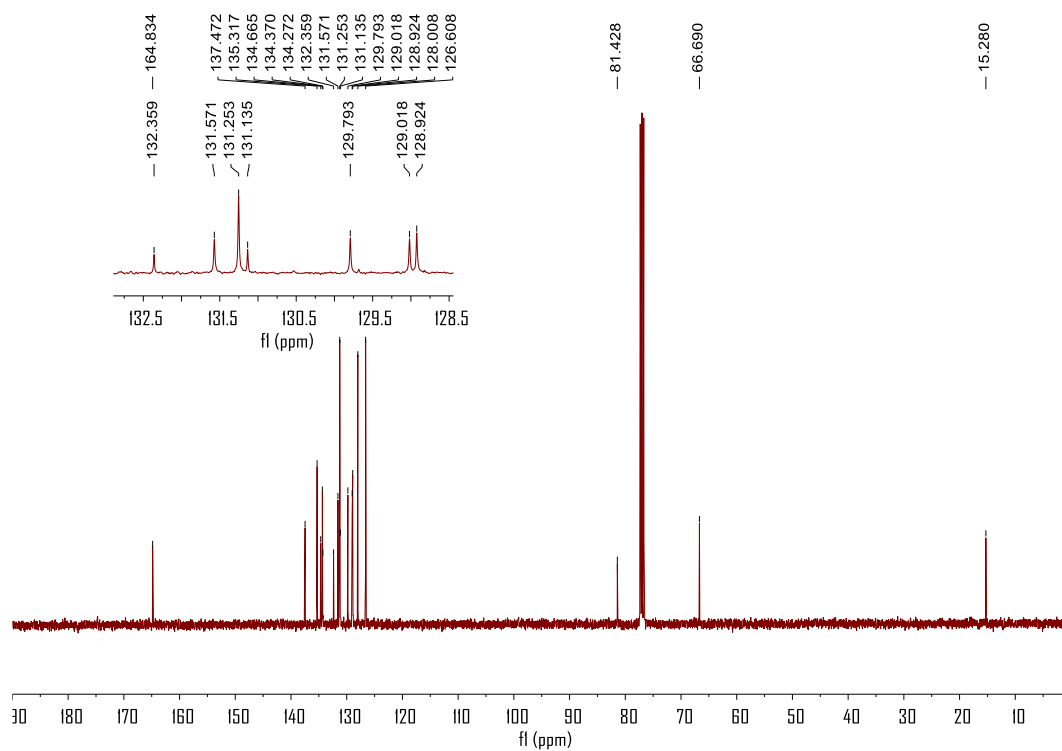


Figure S31. ^1H NMR of C17

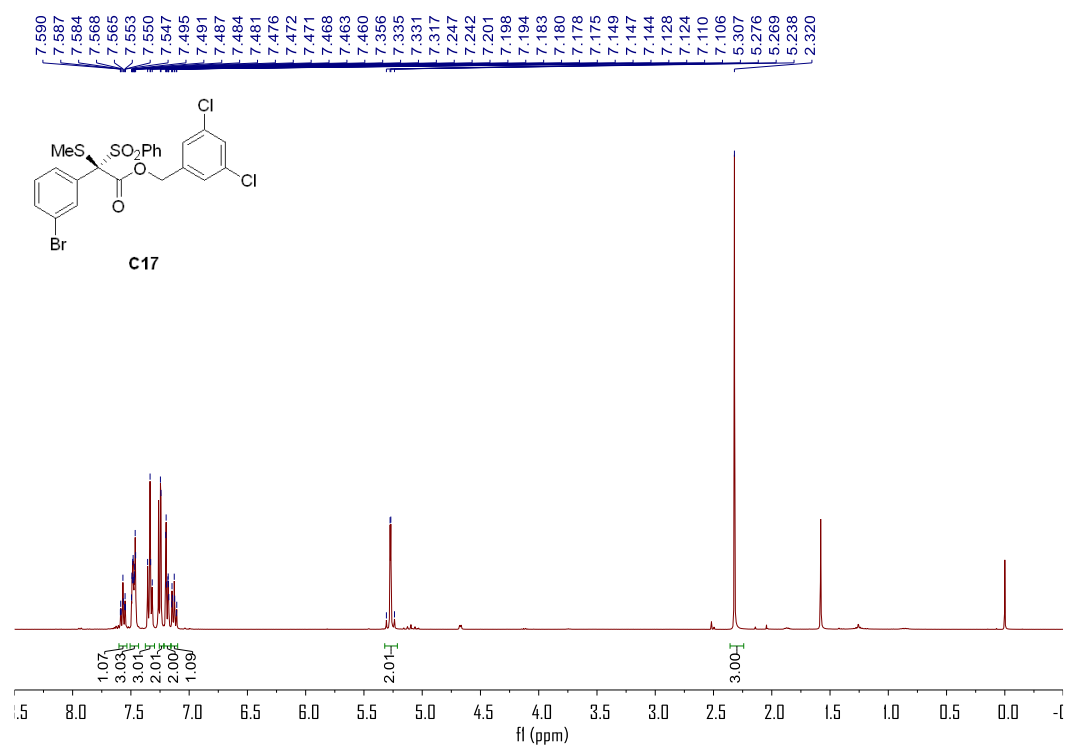


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR of C17

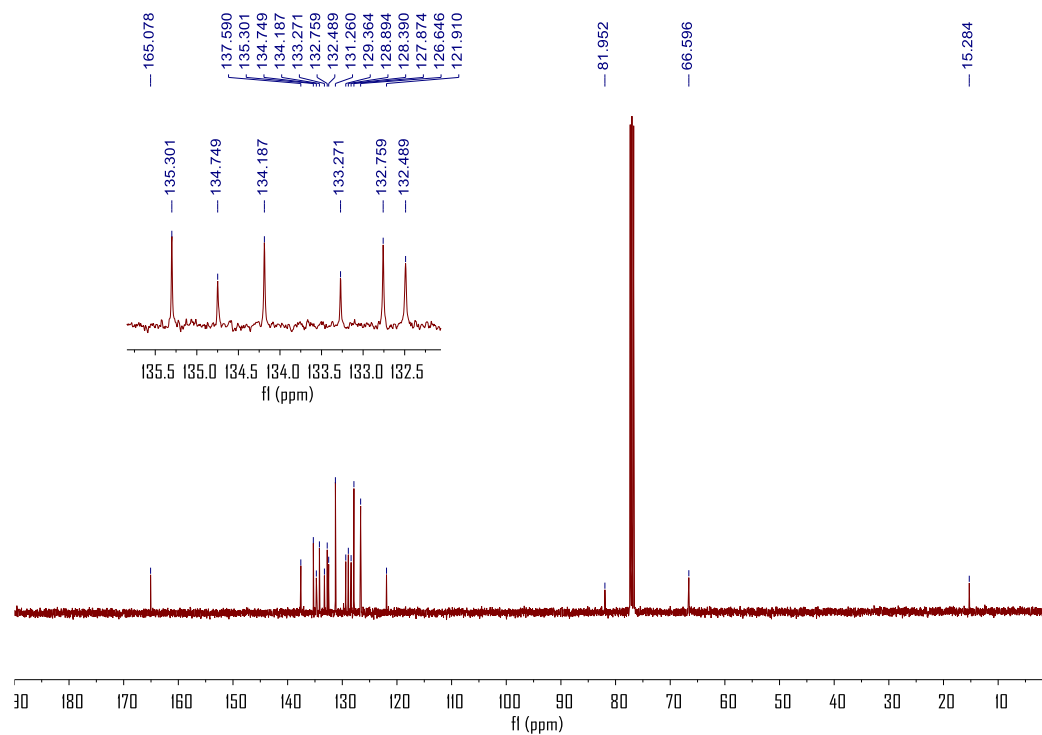


Figure S33. ^1H NMR of C18

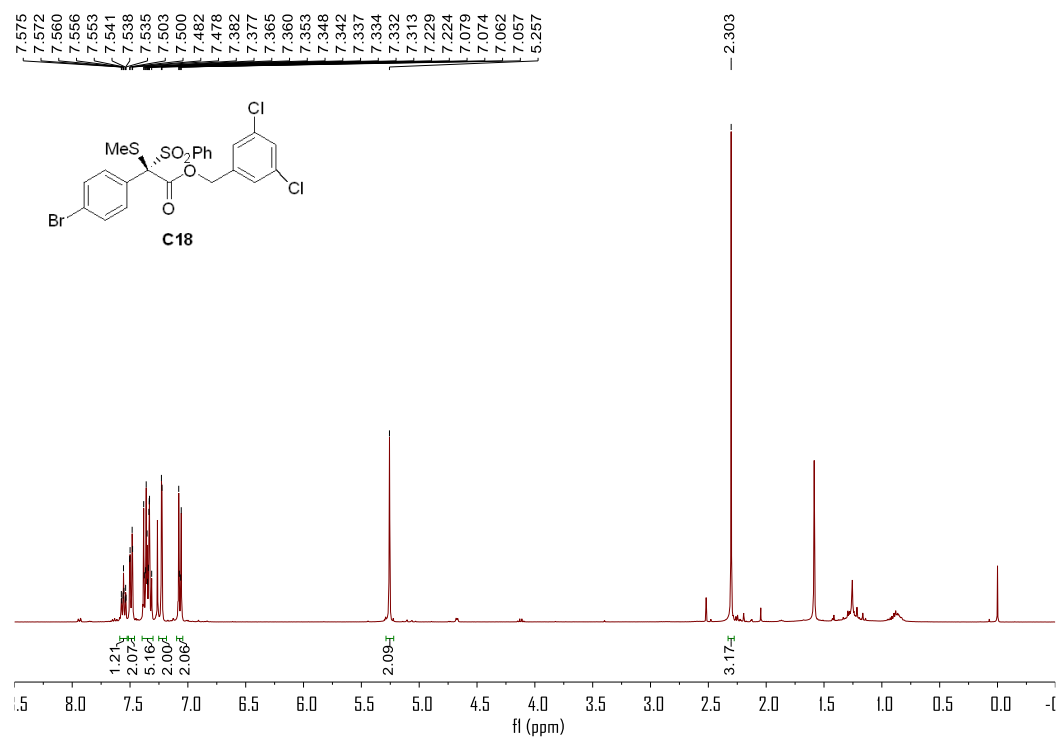


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR of C18

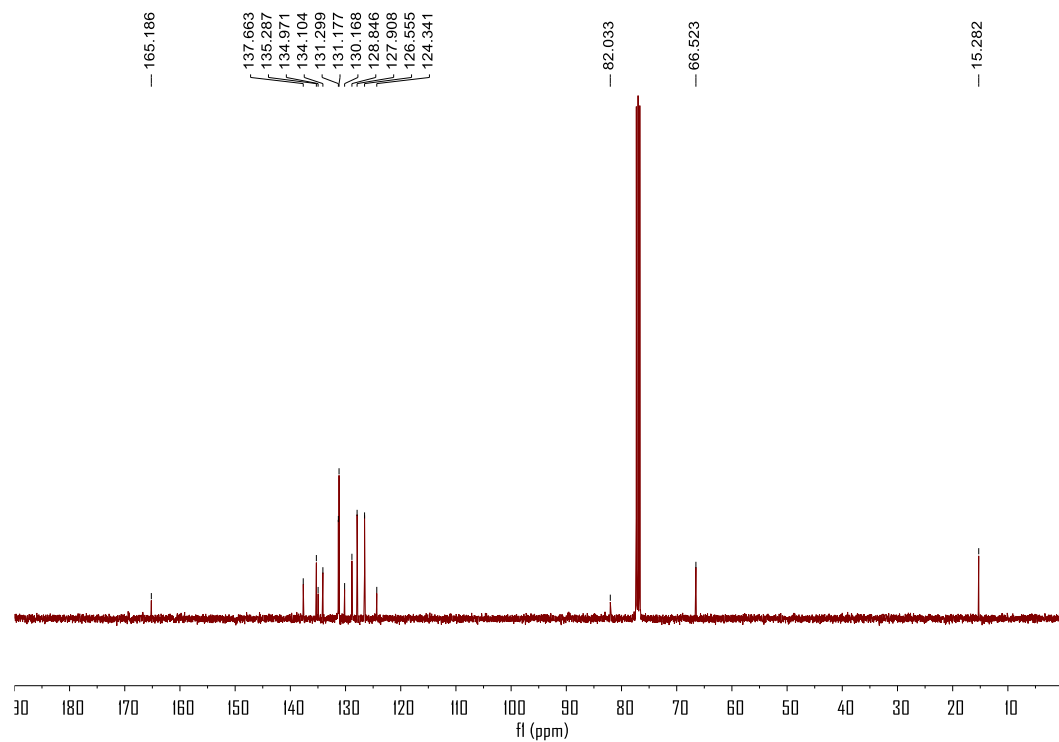


Figure S35. ^1H NMR of C19

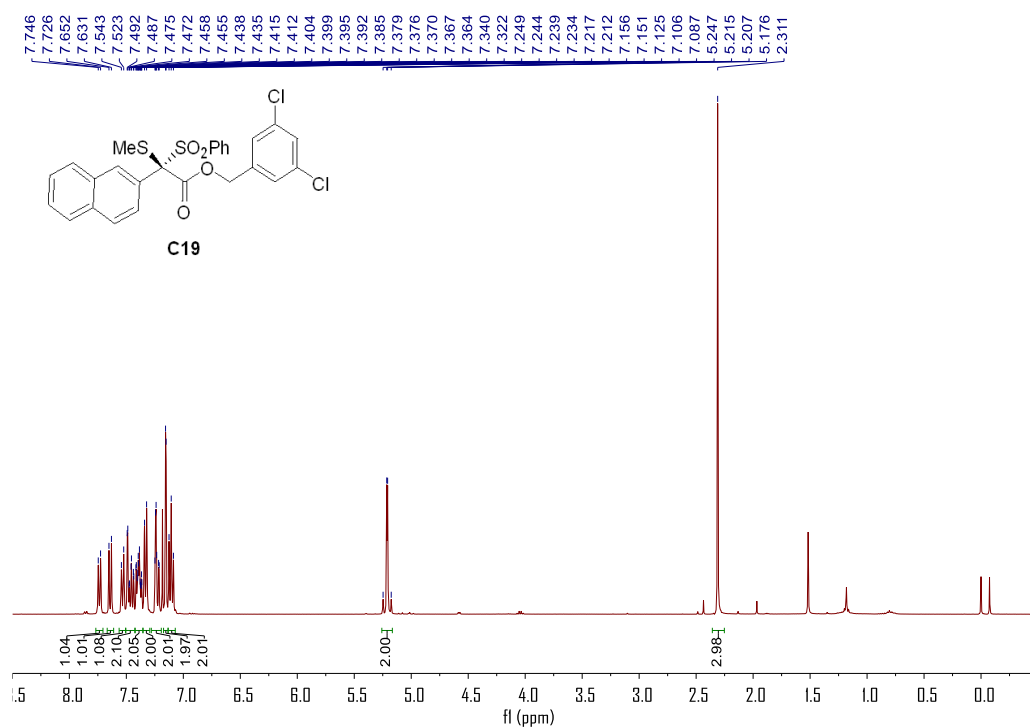


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR of C19

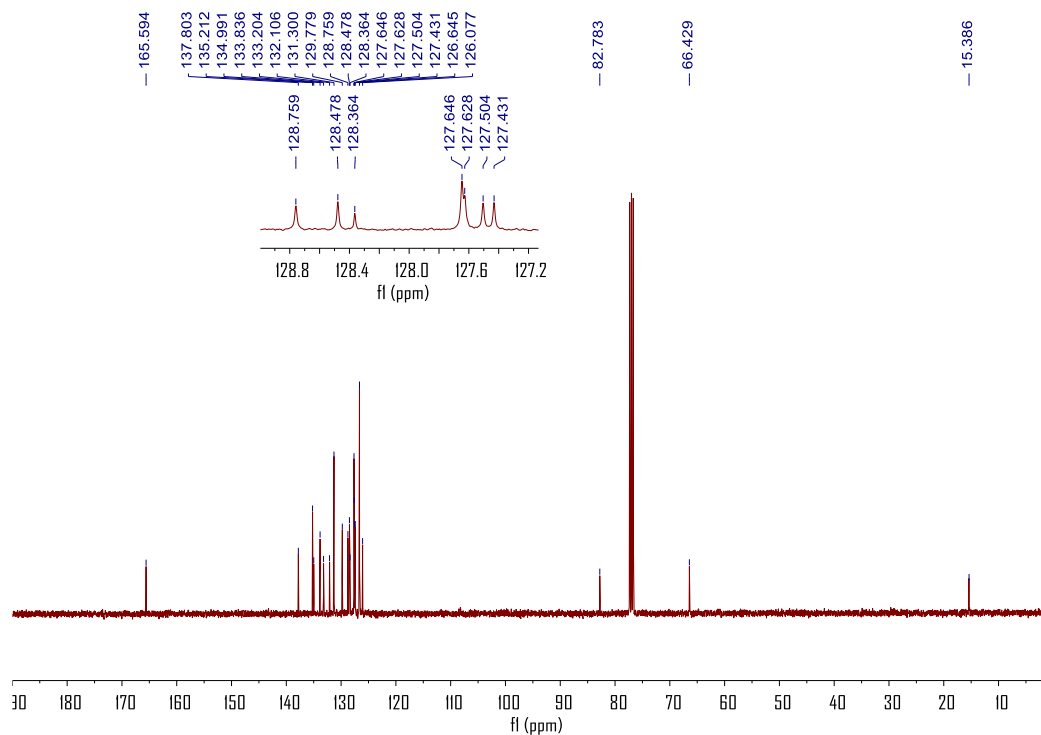


Figure S37. ^1H NMR of C20

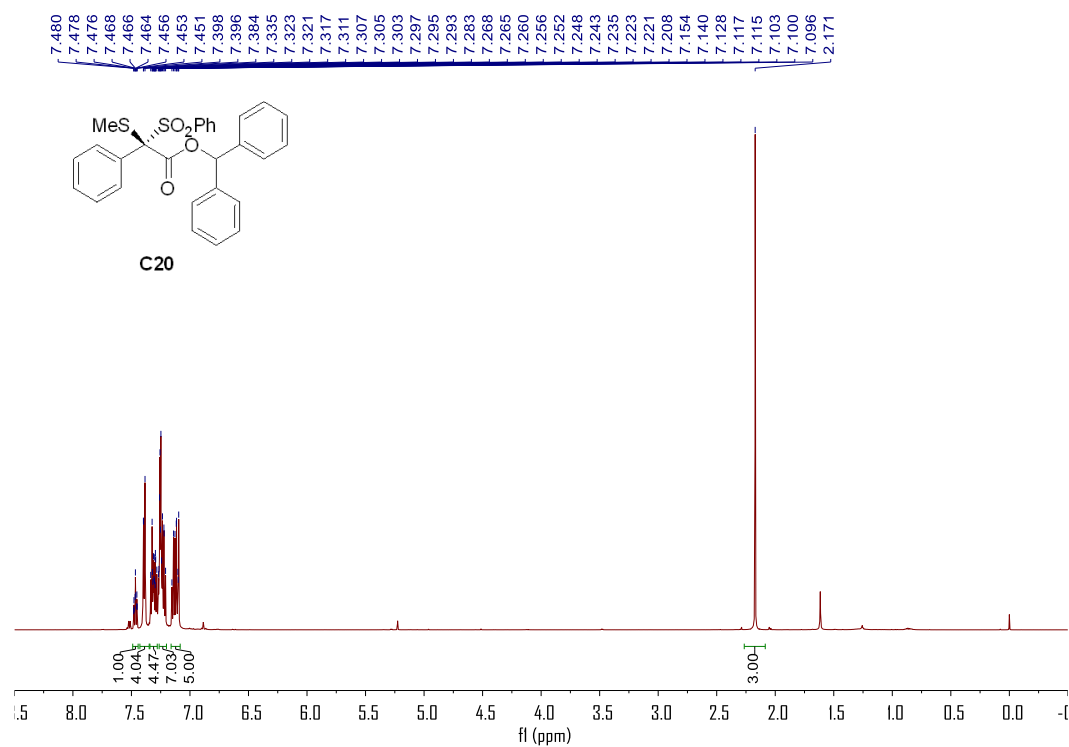


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR of C20

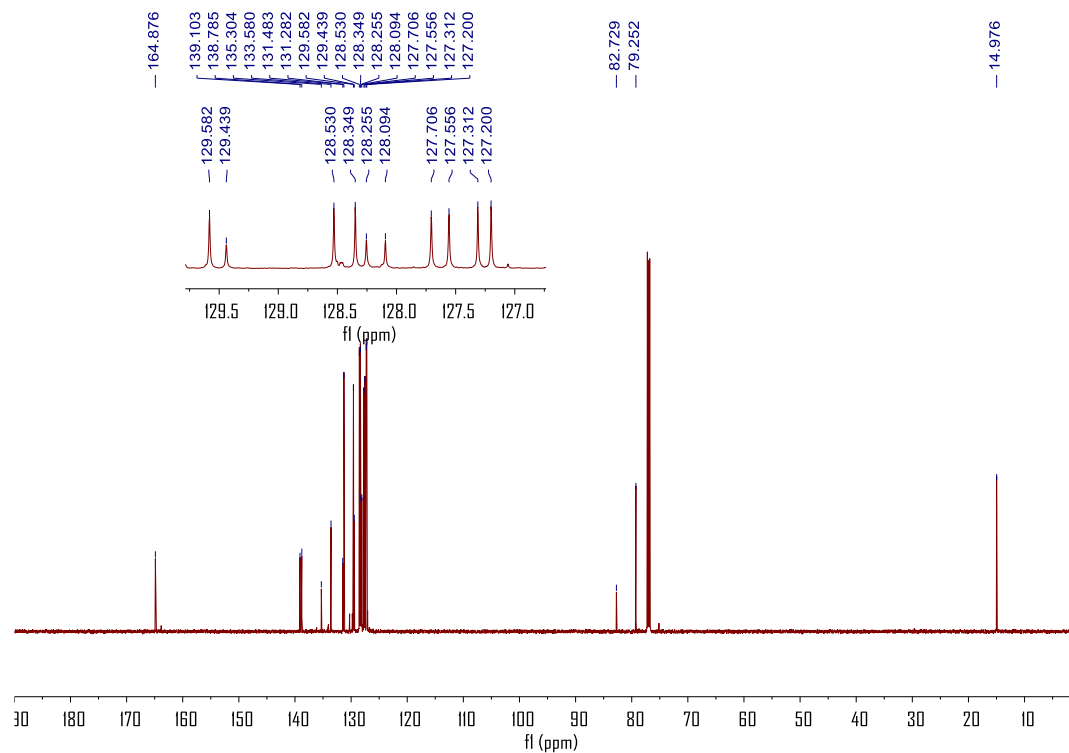


Figure S39. ¹H NMR of C21

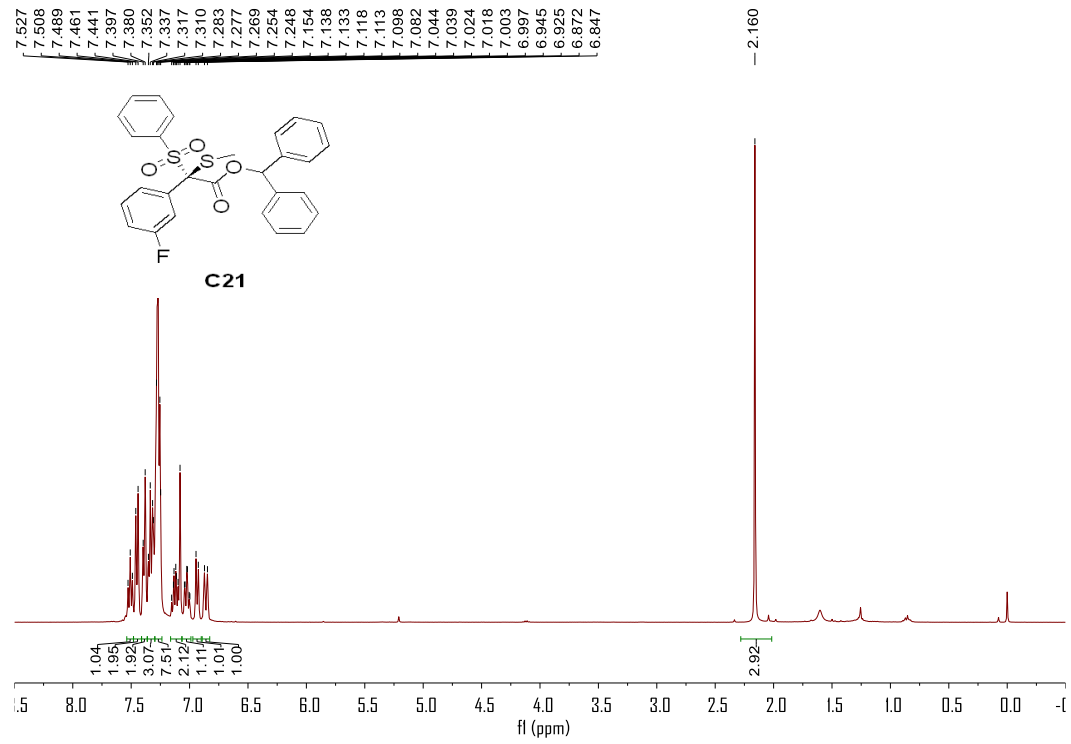


Figure S40. ¹³C{¹H} NMR of C21

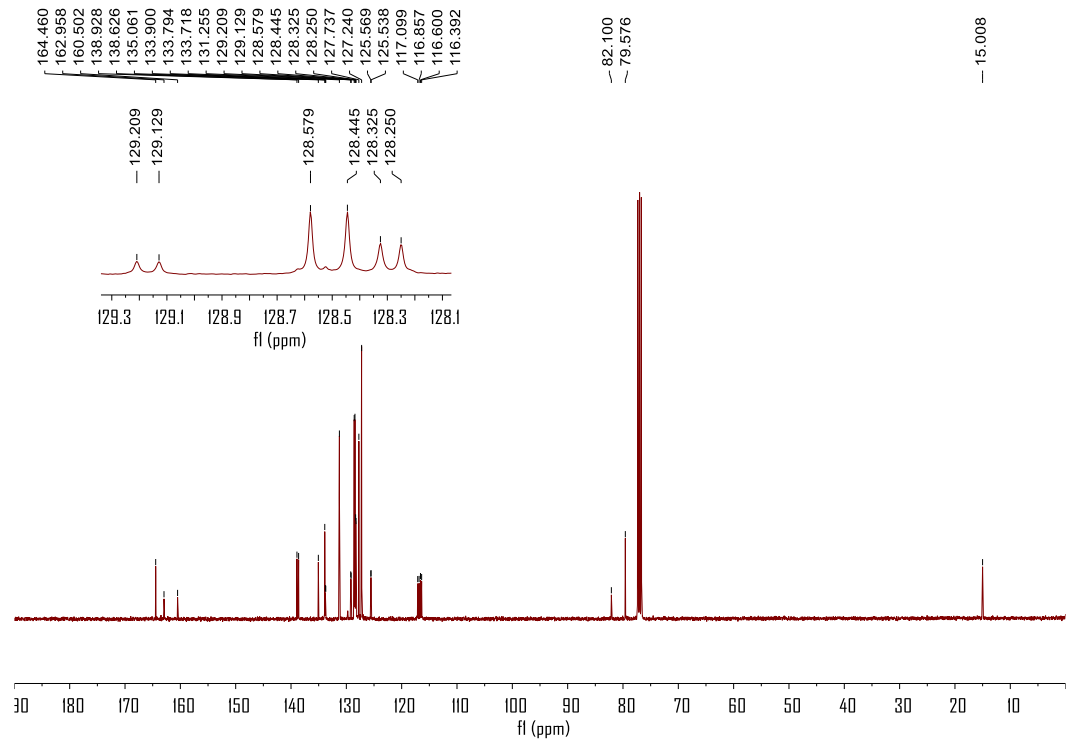


Figure S41. ^{19}F NMR of C21

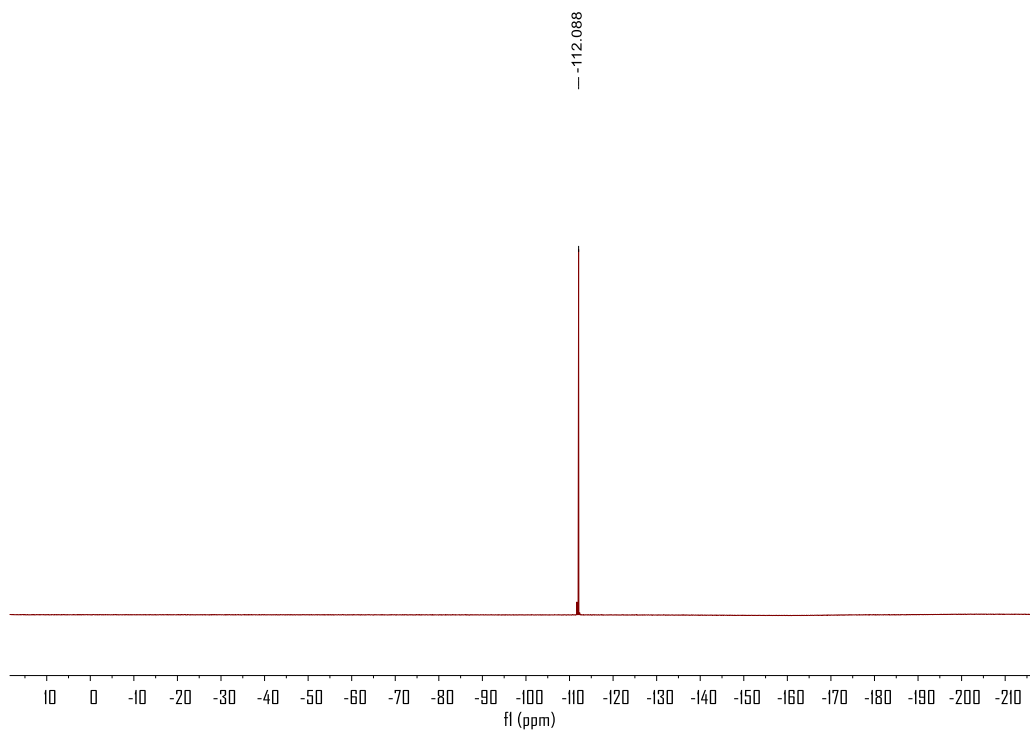


Figure S42. ^1H NMR of C22

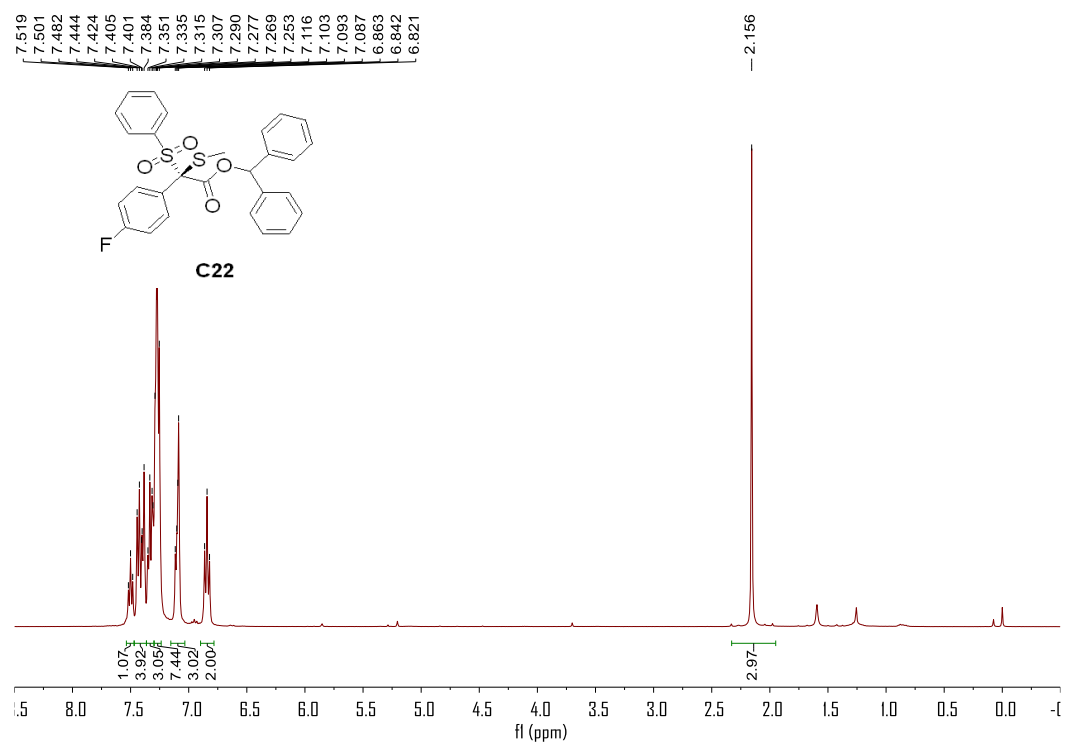


Figure S43. $^{13}\text{C}\{^1\text{H}\}$ NMR of C22

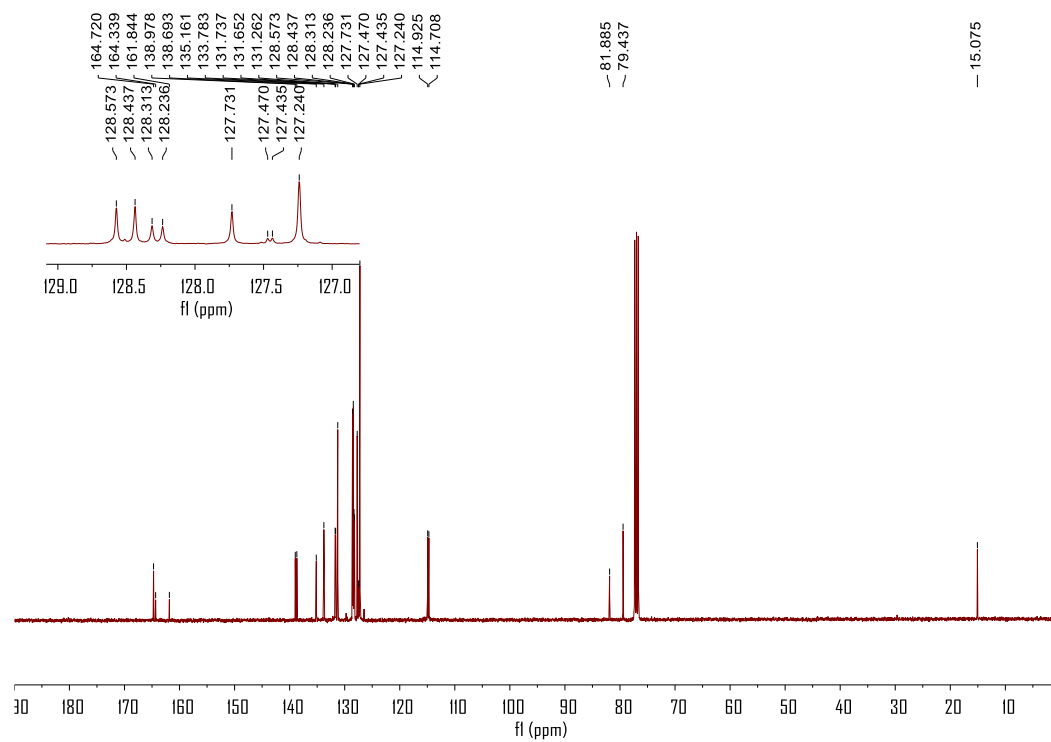


Figure S44. ^{19}F NMR of C22

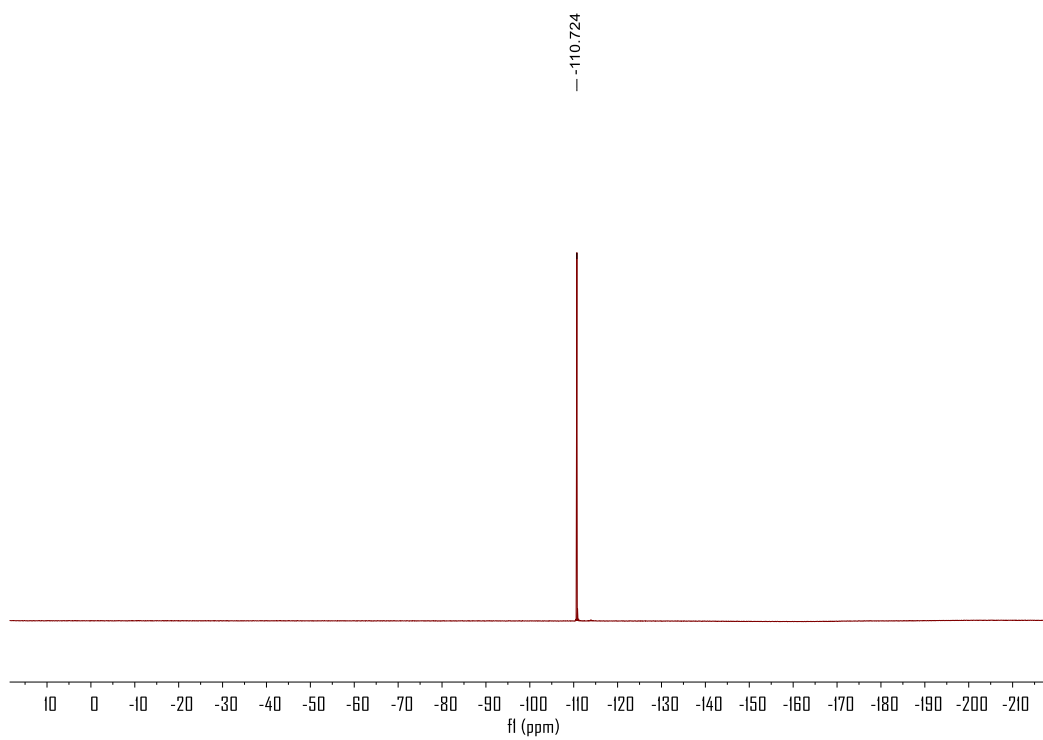


Figure S45. ^1H NMR of C23

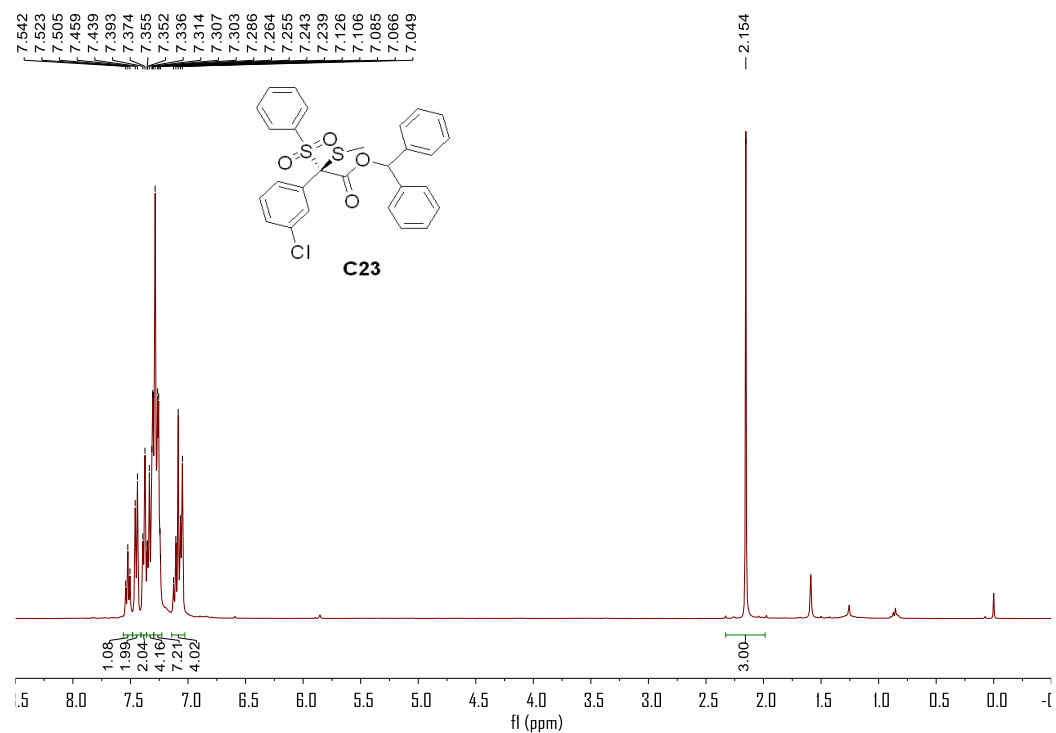


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR of C23

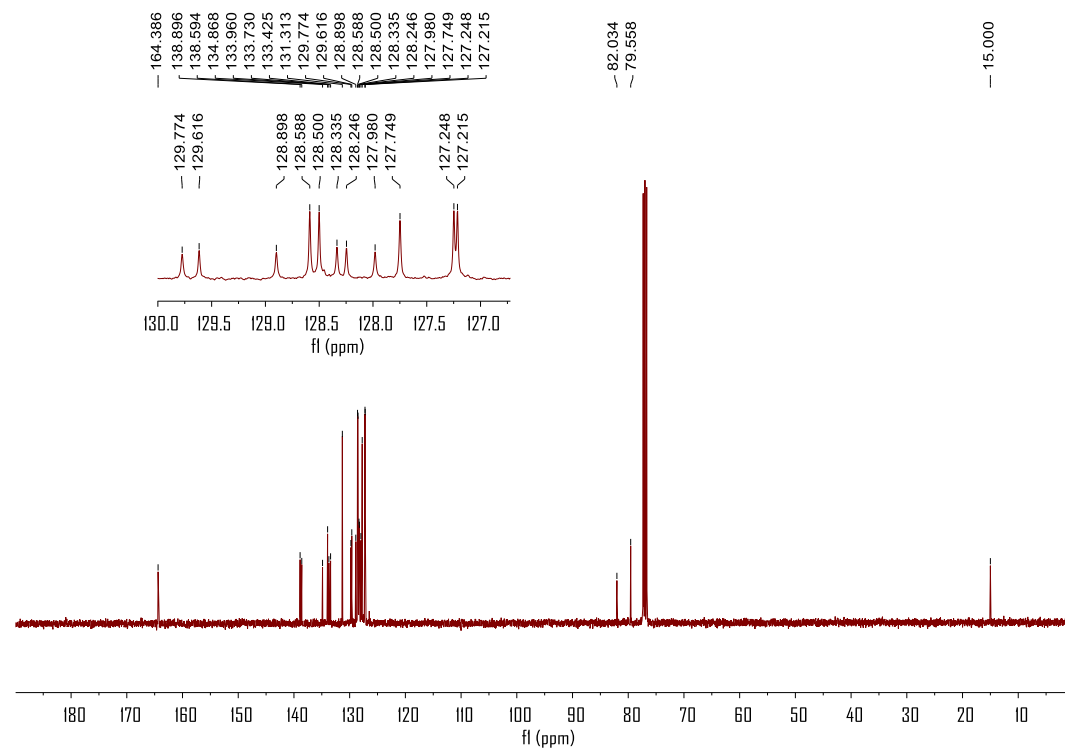


Figure S47. ^1H NMR of C24

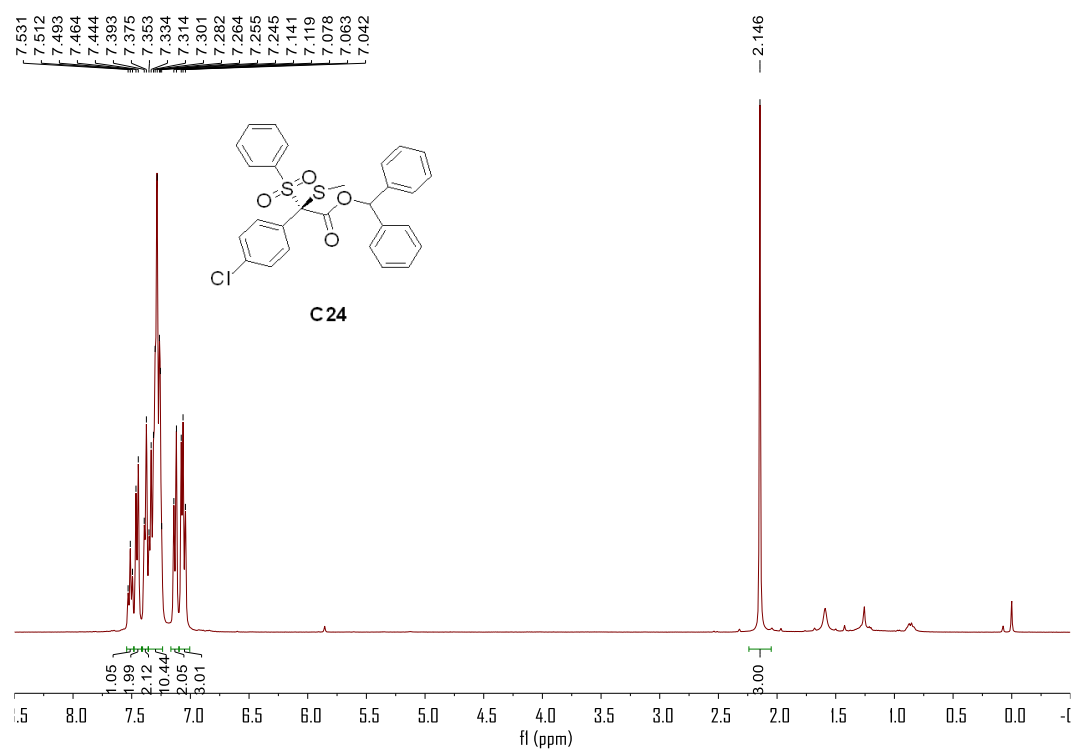


Figure S48. $^{13}\text{C}\{^1\text{H}\}$ NMR of C24

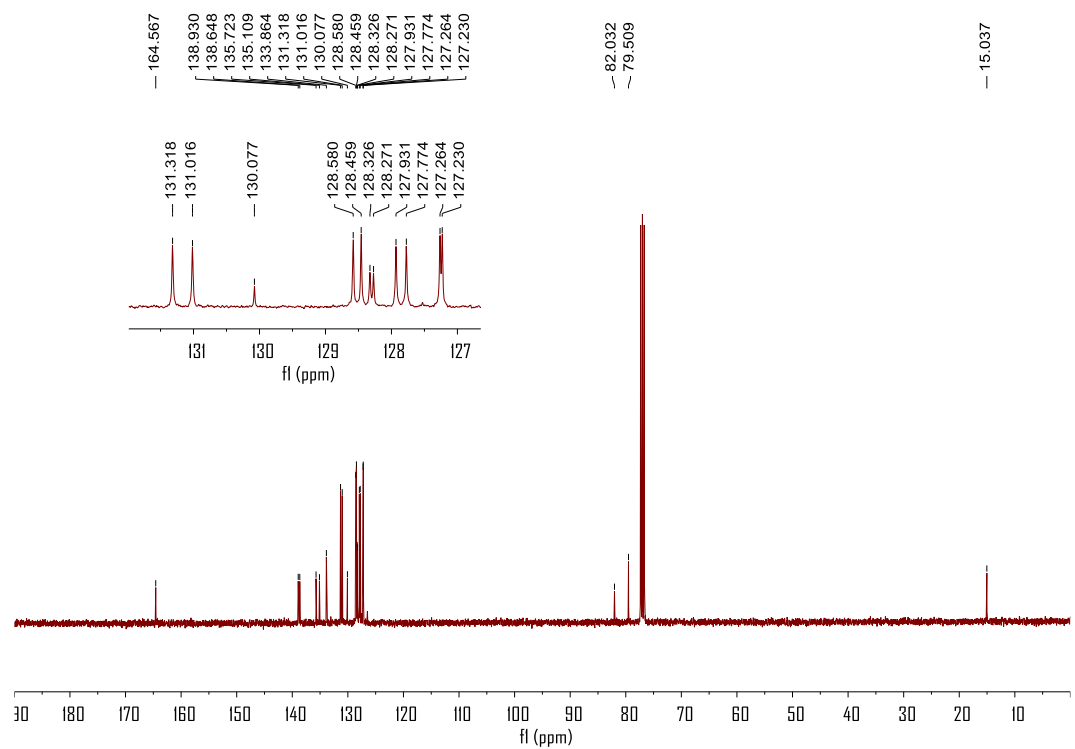


Figure S49. ^1H NMR of C25

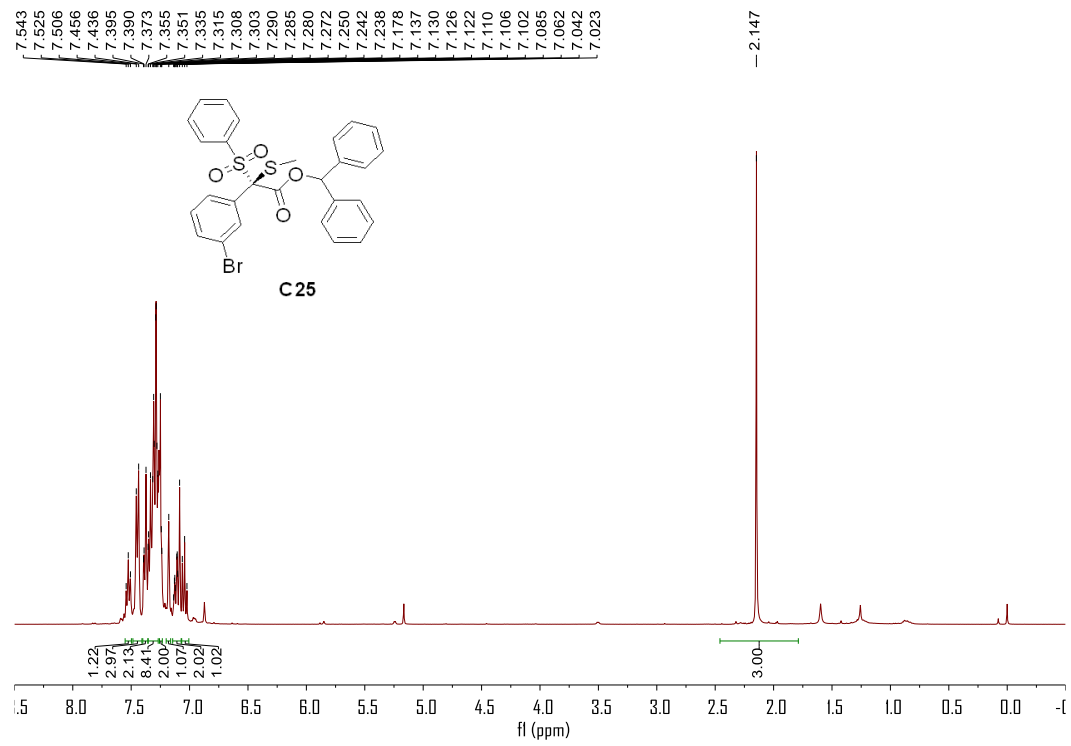


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR of C25

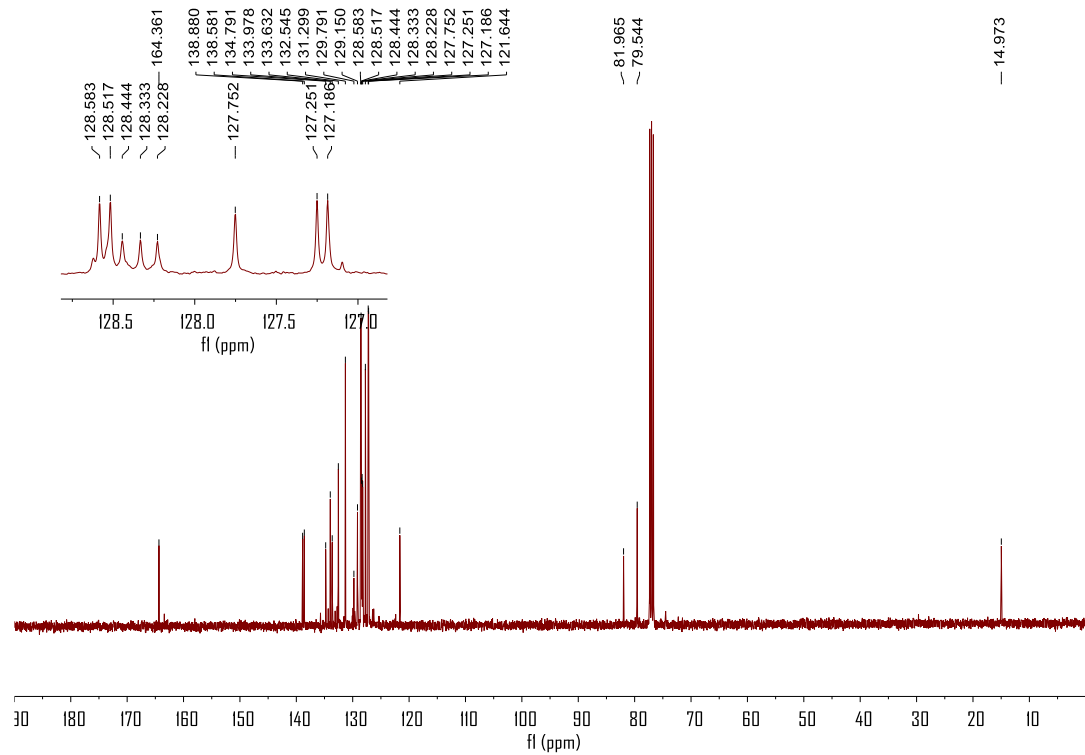


Figure S51. ^1H NMR of C26

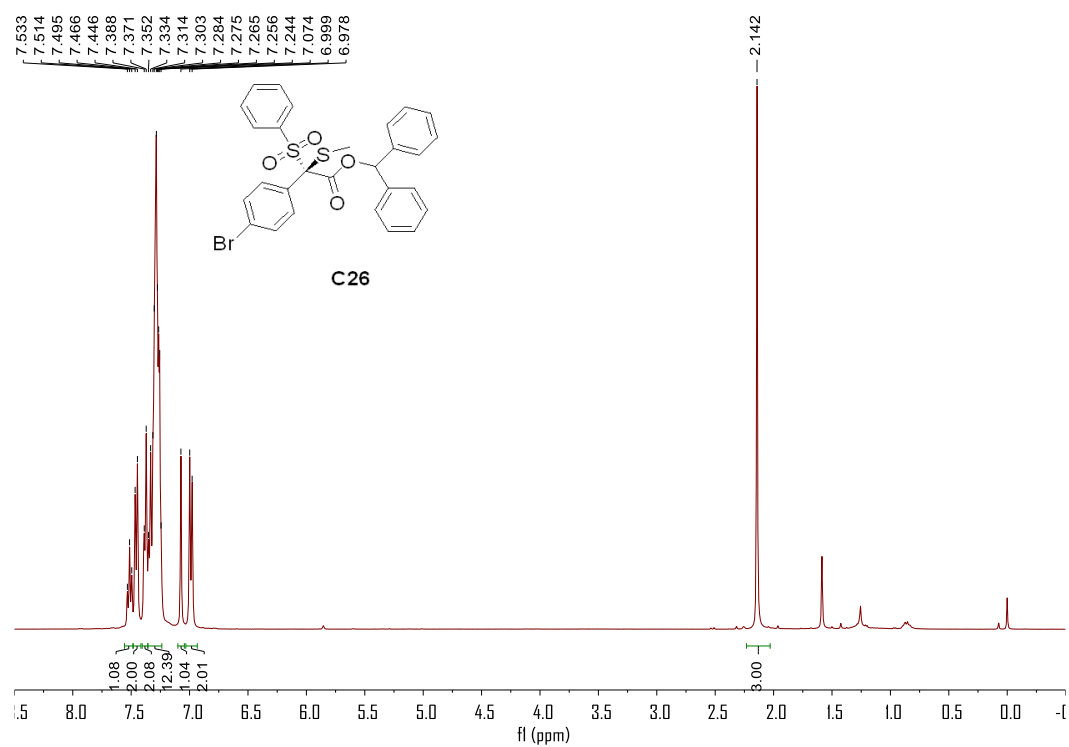


Figure S52. $^{13}\text{C}\{^1\text{H}\}$ NMR of C26

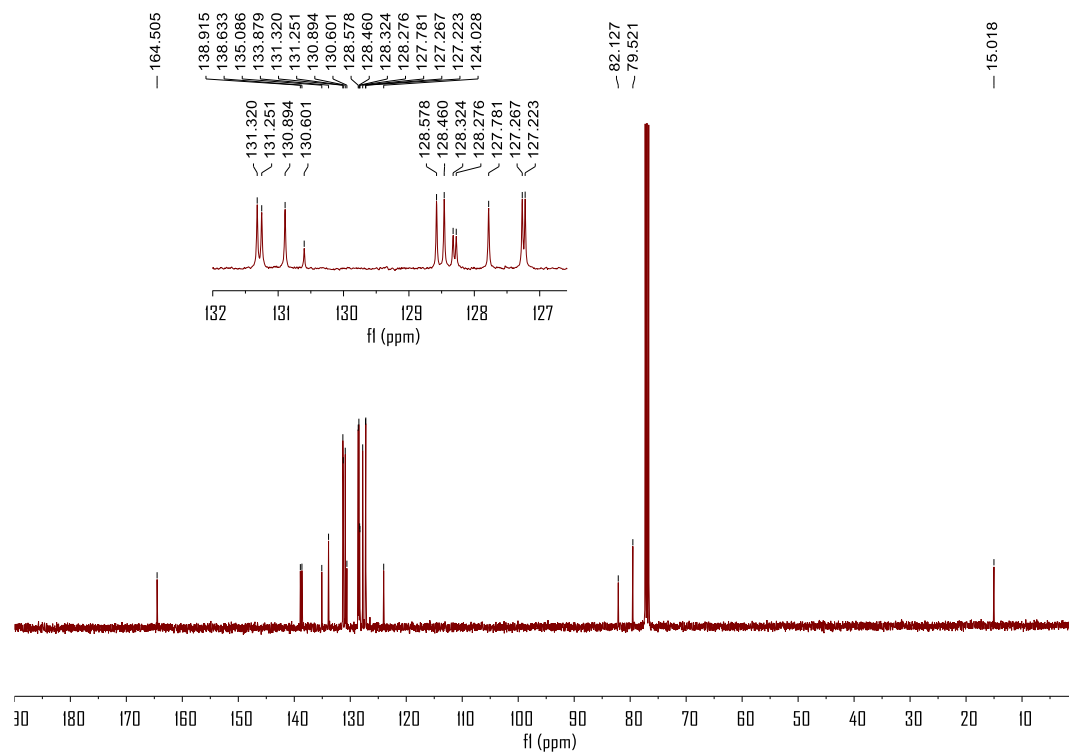


Figure S53. ^1H NMR of C27

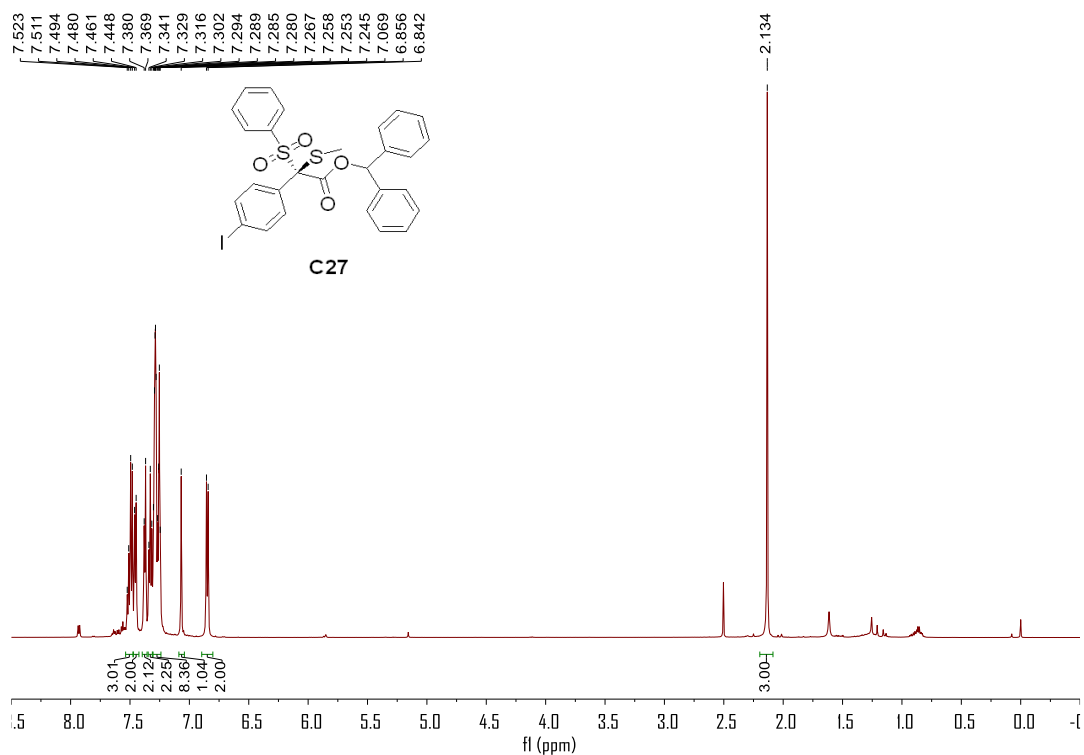


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR of C27

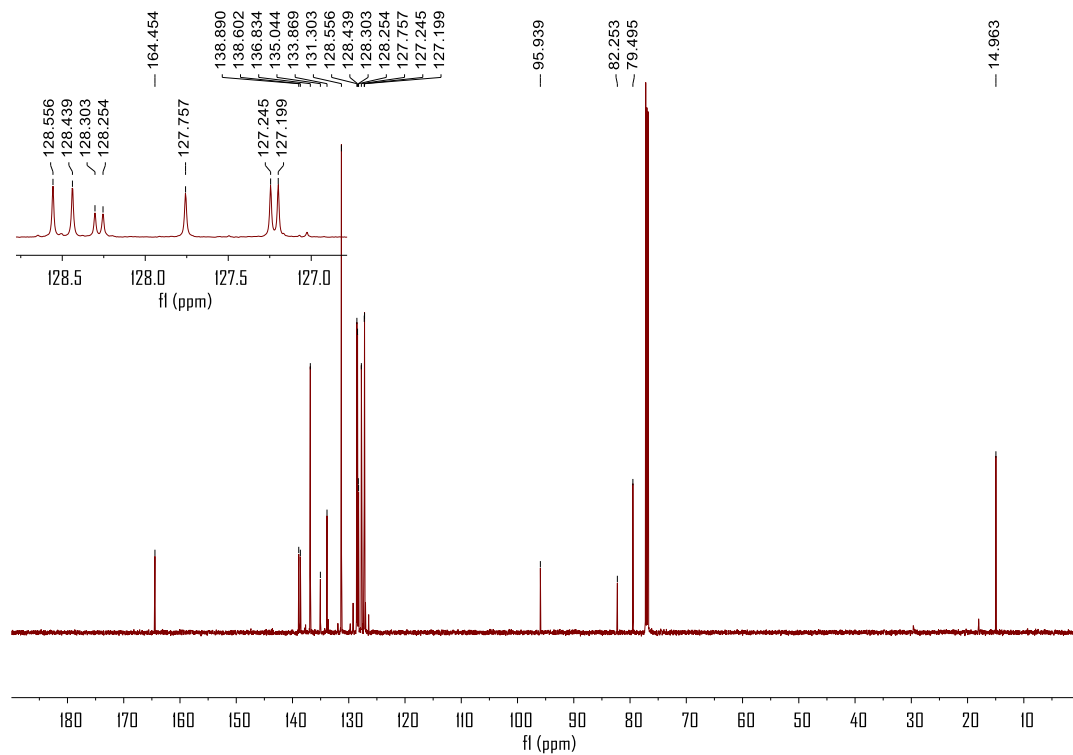


Figure S55. ¹H NMR of C28

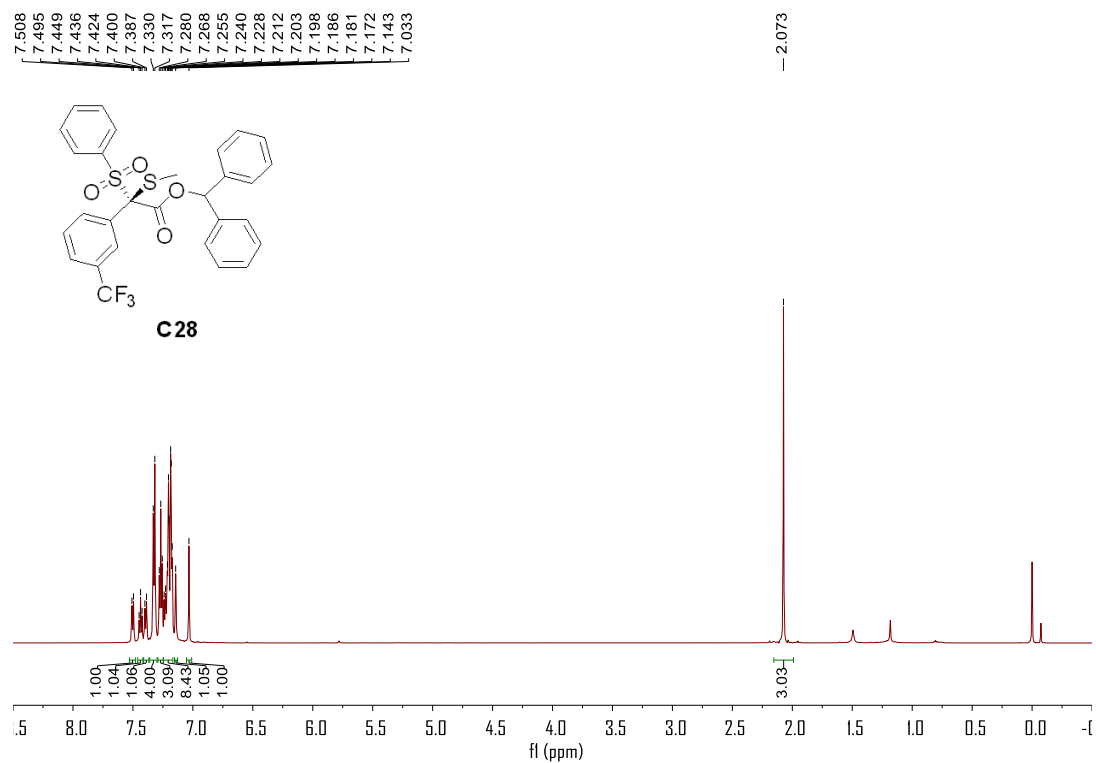


Figure S56. ¹³C{¹H} NMR of C28

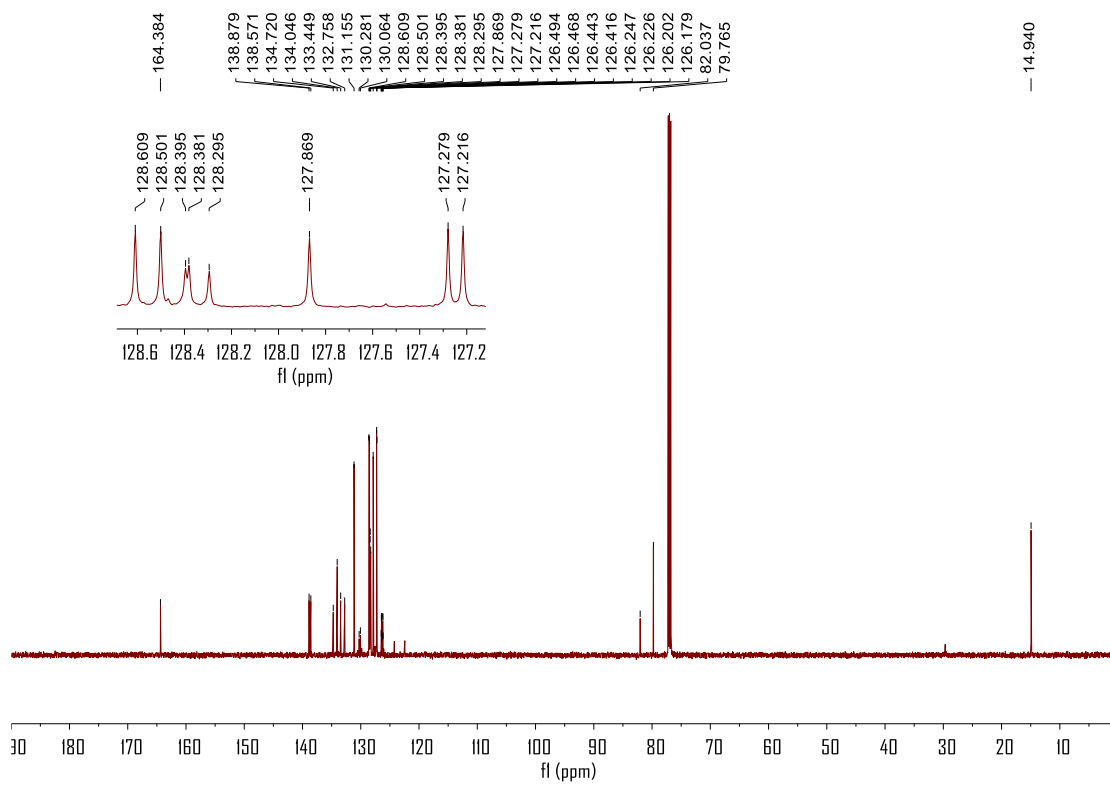


Figure S57. ^{19}F NMR of C28

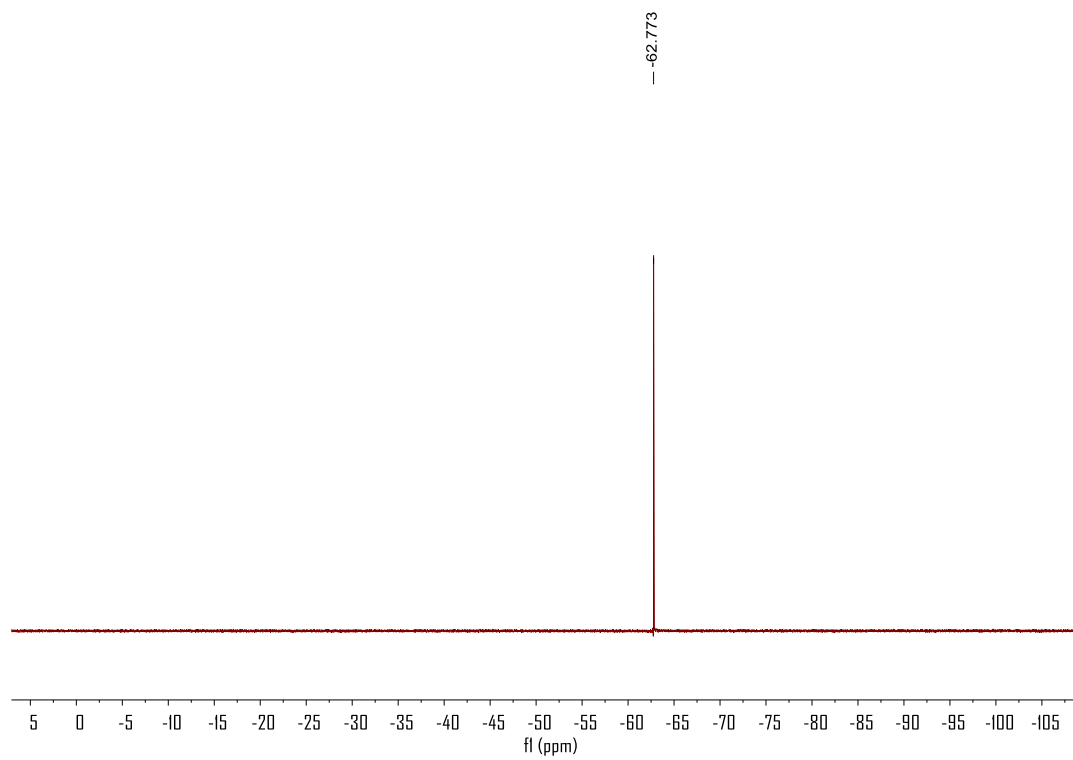


Figure S58. ^1H NMR of C29

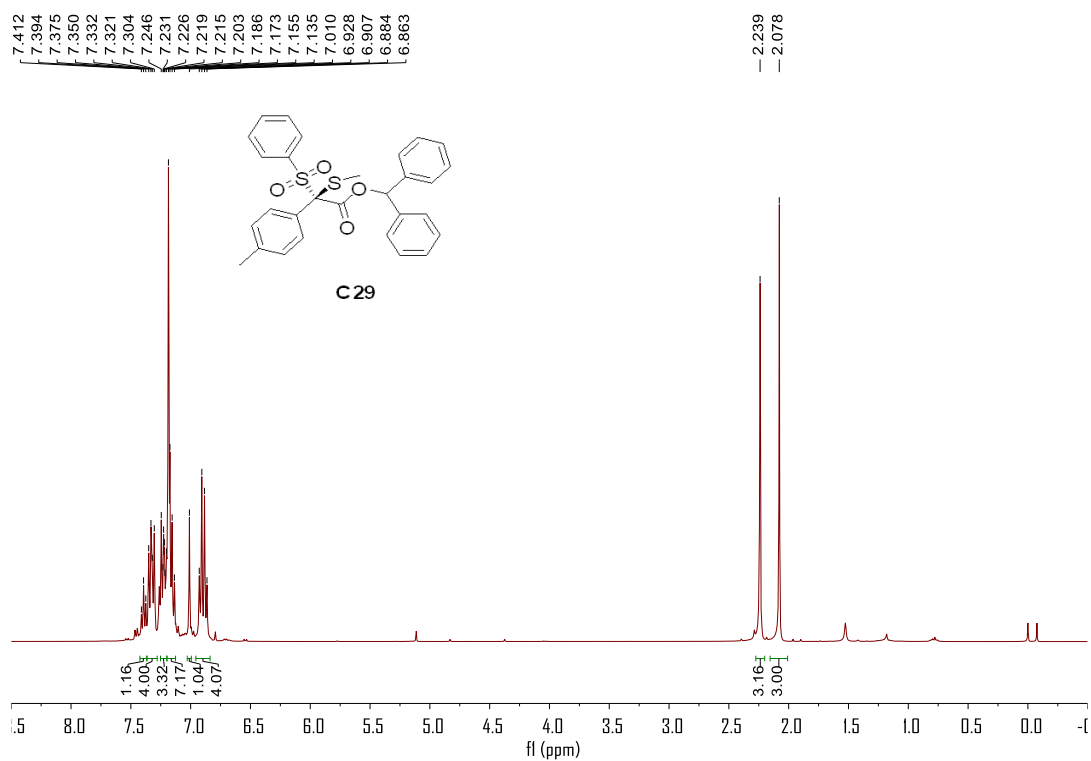


Figure S59. $^{13}\text{C}\{^1\text{H}\}$ NMR of C29

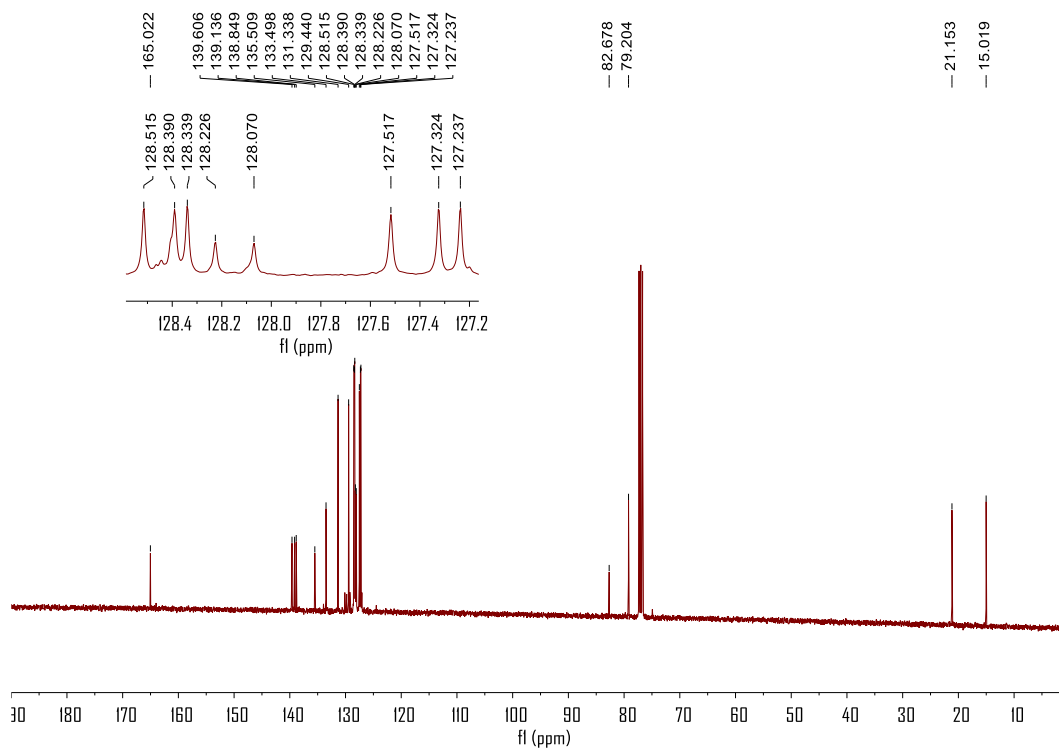


Figure S60. ^1H NMR of C30

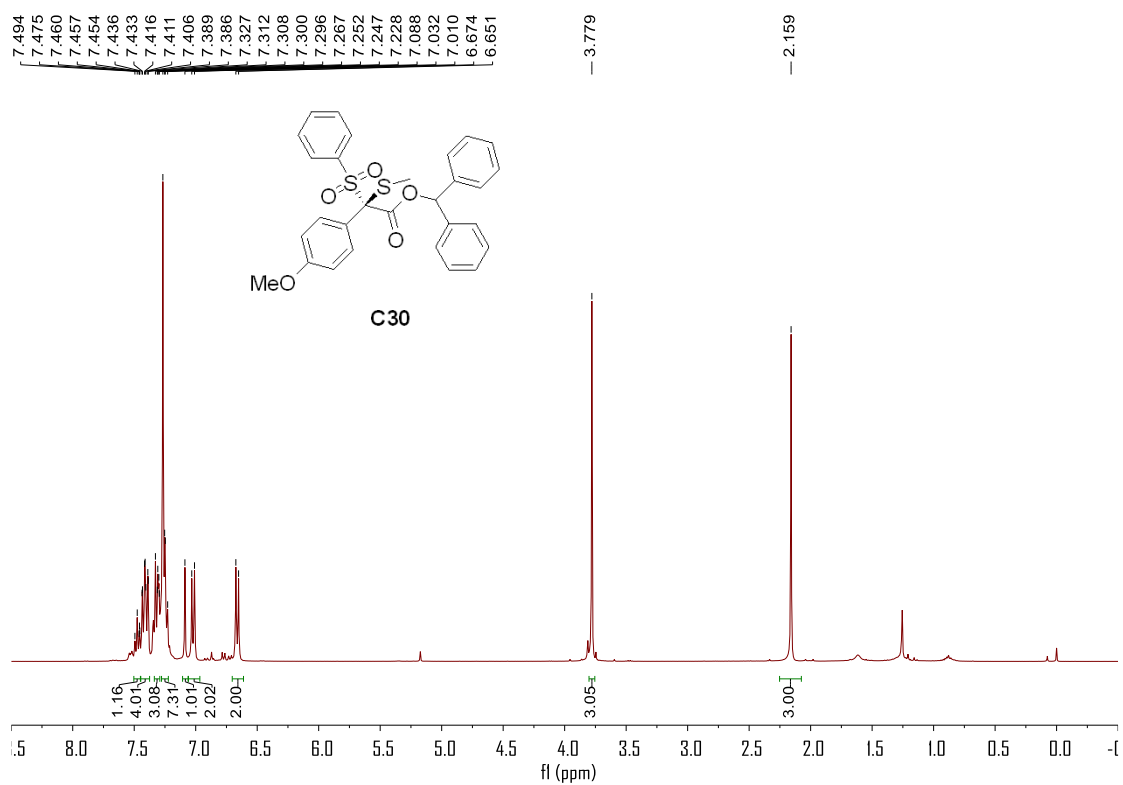


Figure S61. $^{13}\text{C}\{^1\text{H}\}$ NMR of C30

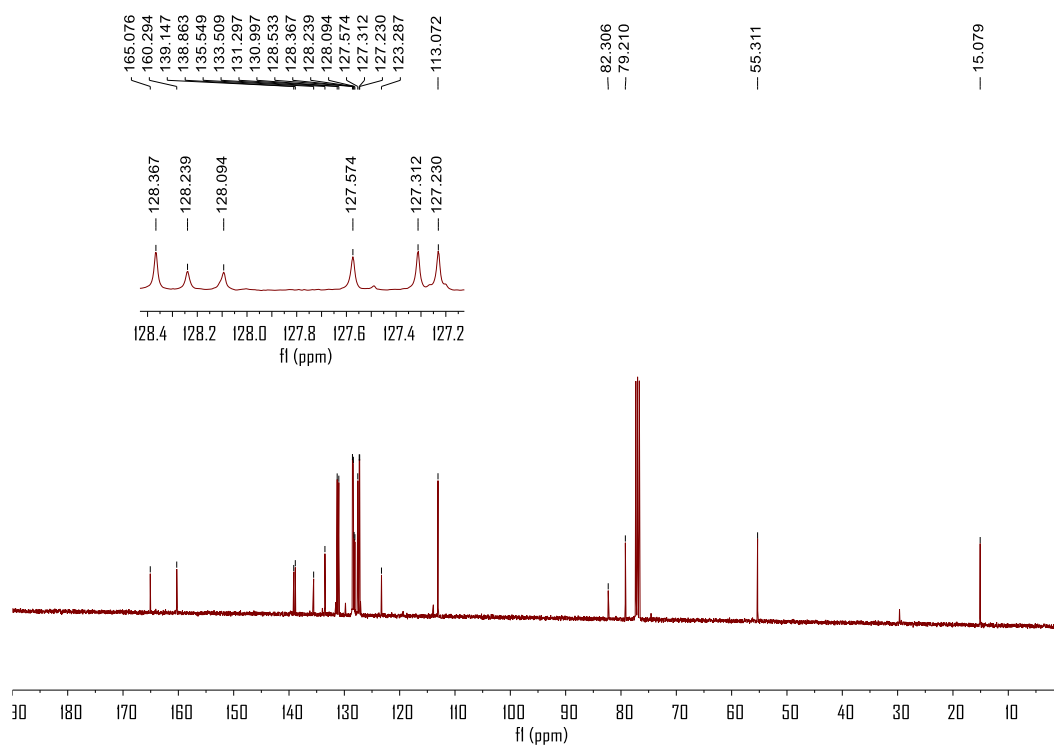


Figure S62. ^1H NMR of C31

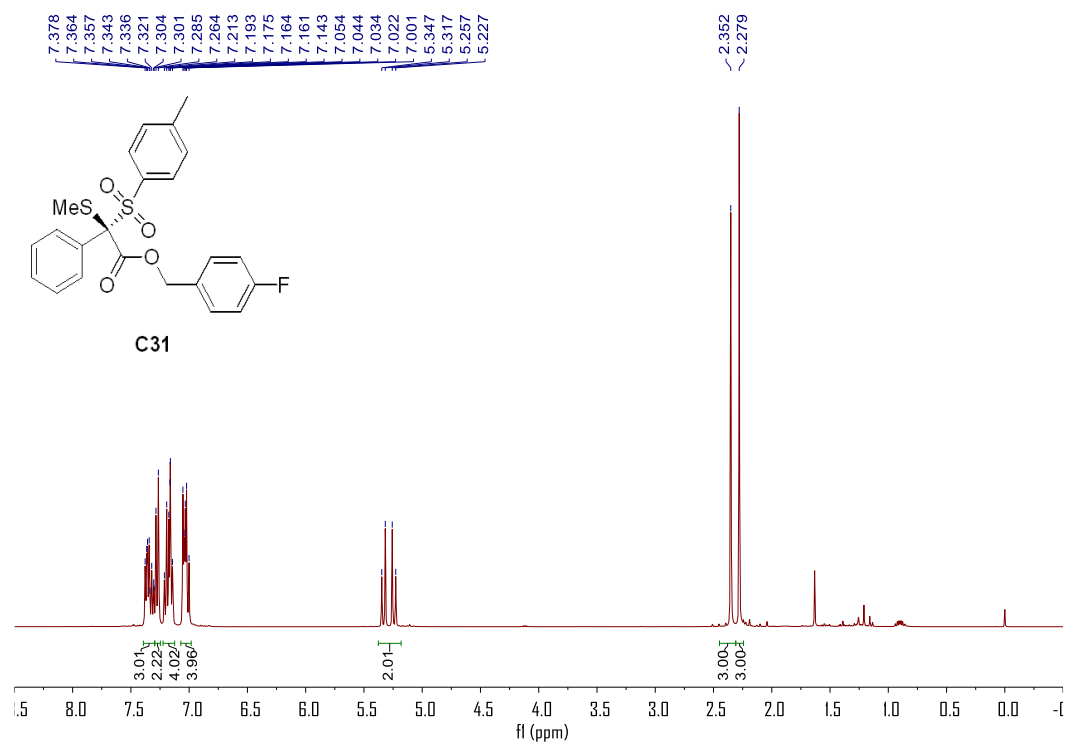


Figure S63. $^{13}\text{C}\{^1\text{H}\}$ NMR of C31

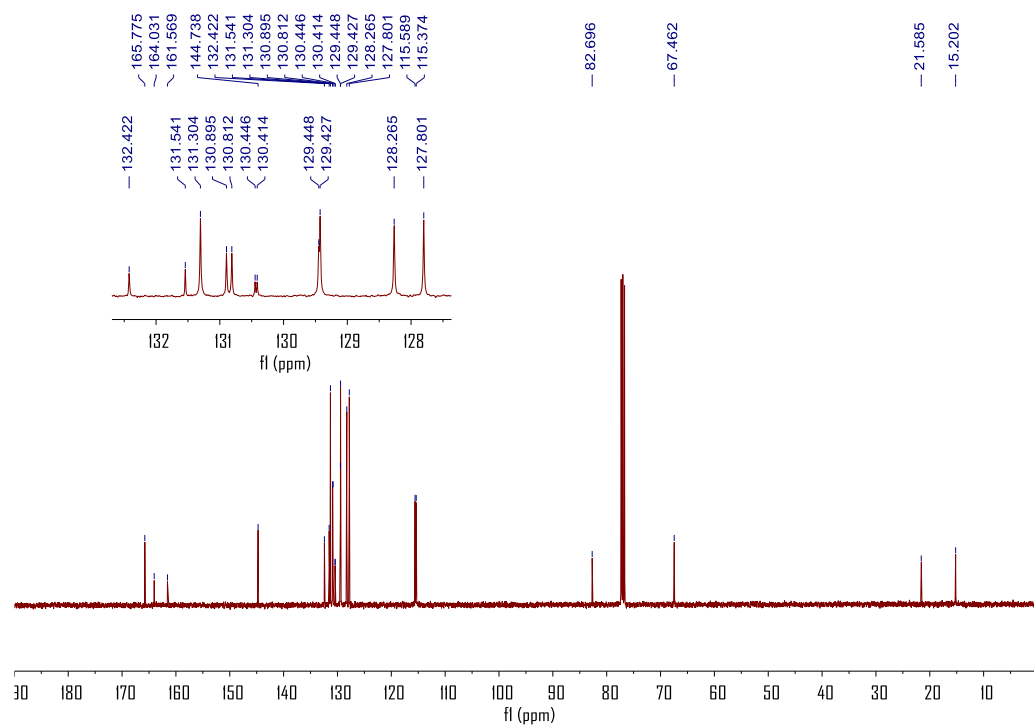


Figure S64. ^{19}F NMR of C31

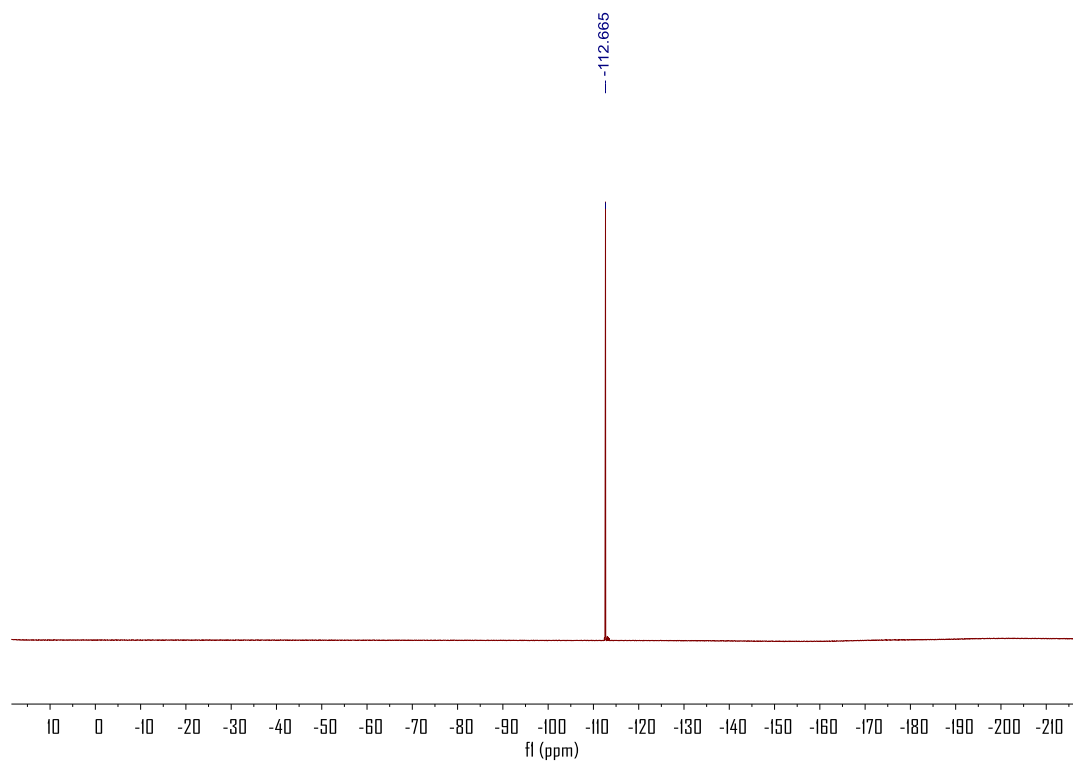


Figure S65. ^1H NMR of C32

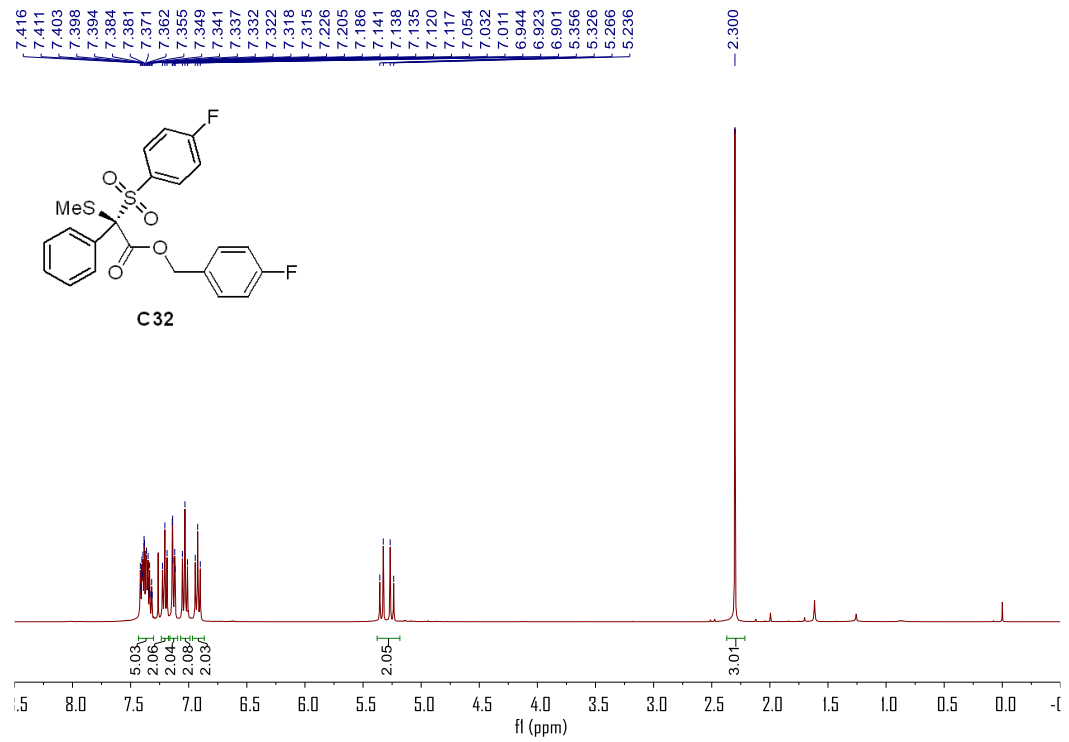


Figure S66. $^{13}\text{C}\{^1\text{H}\}$ NMR of C32

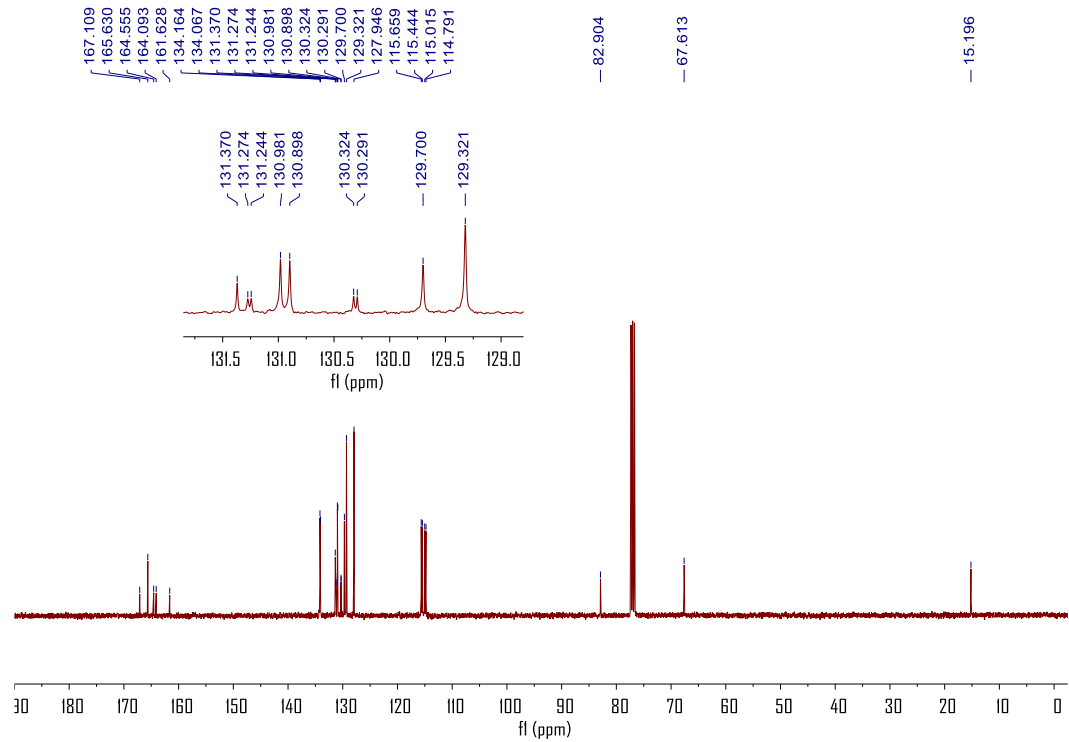


Figure S67. ^{19}F NMR of C32

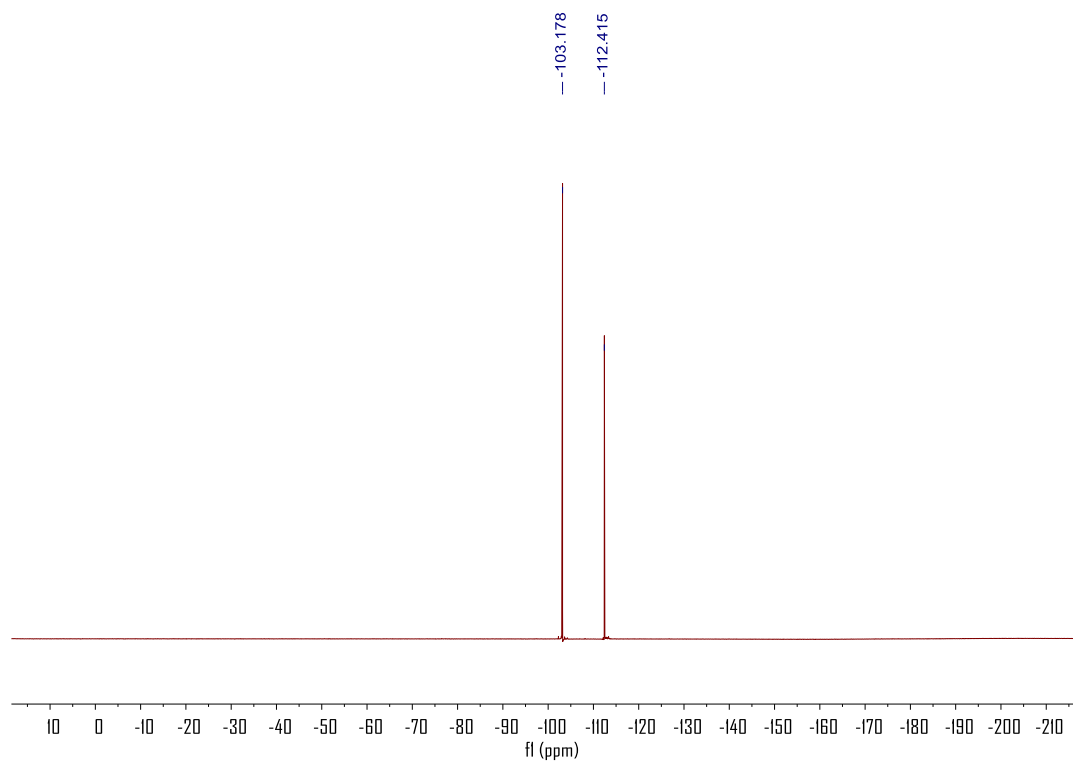


Figure S68. ^1H NMR of C33

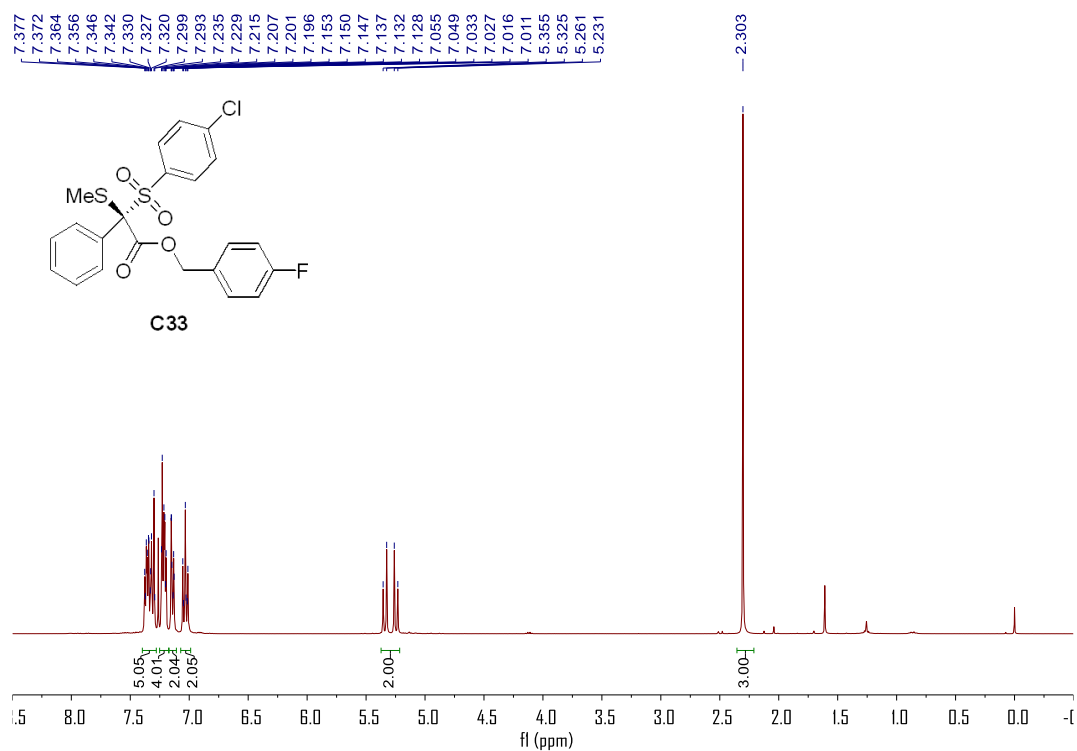


Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR of C33

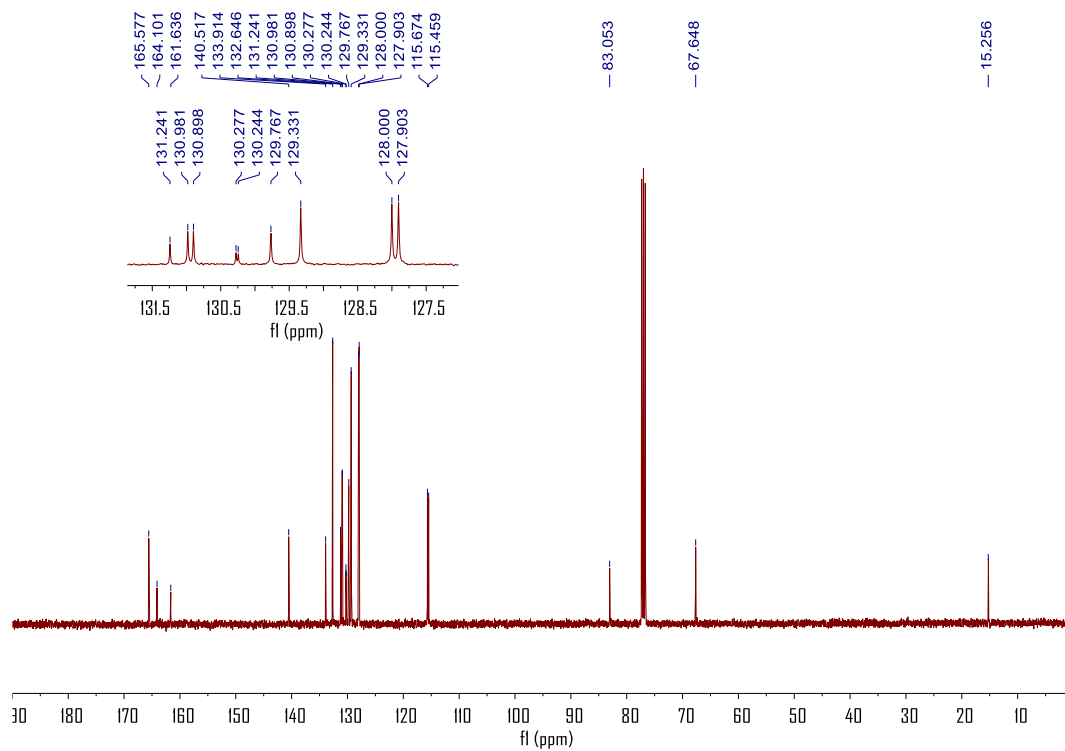


Figure S70. ^{19}F NMR of C33

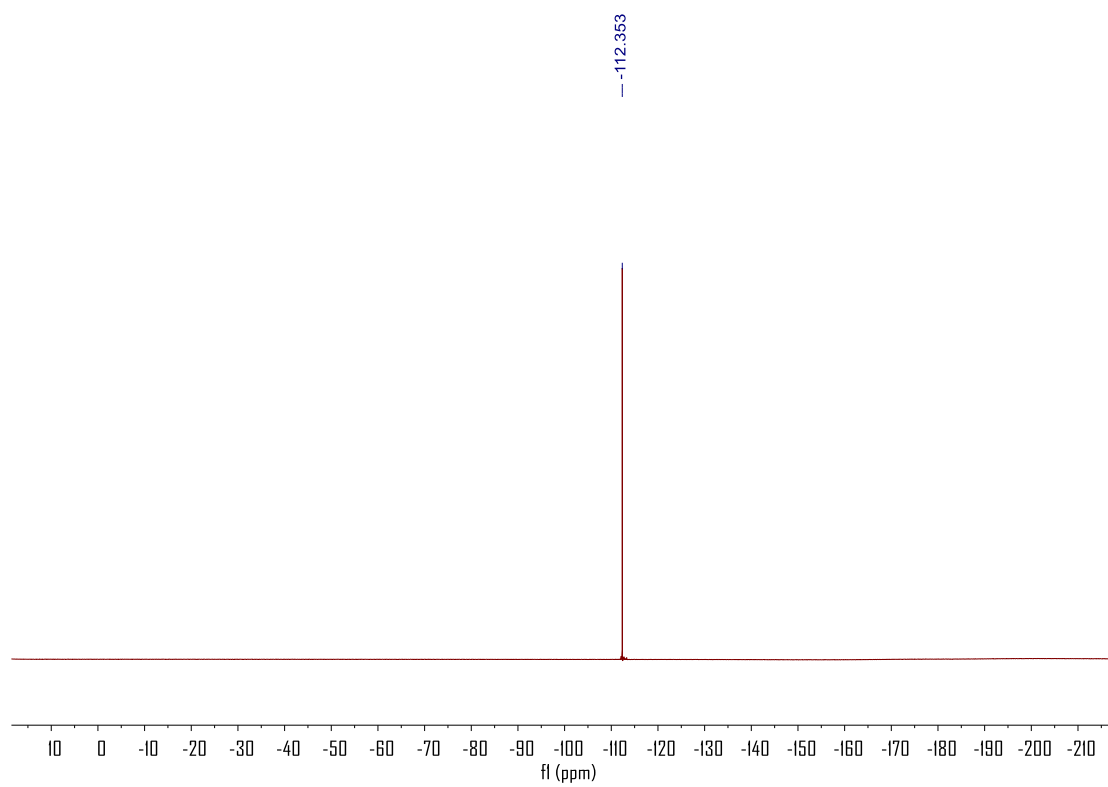


Figure S71. ^1H NMR of C34

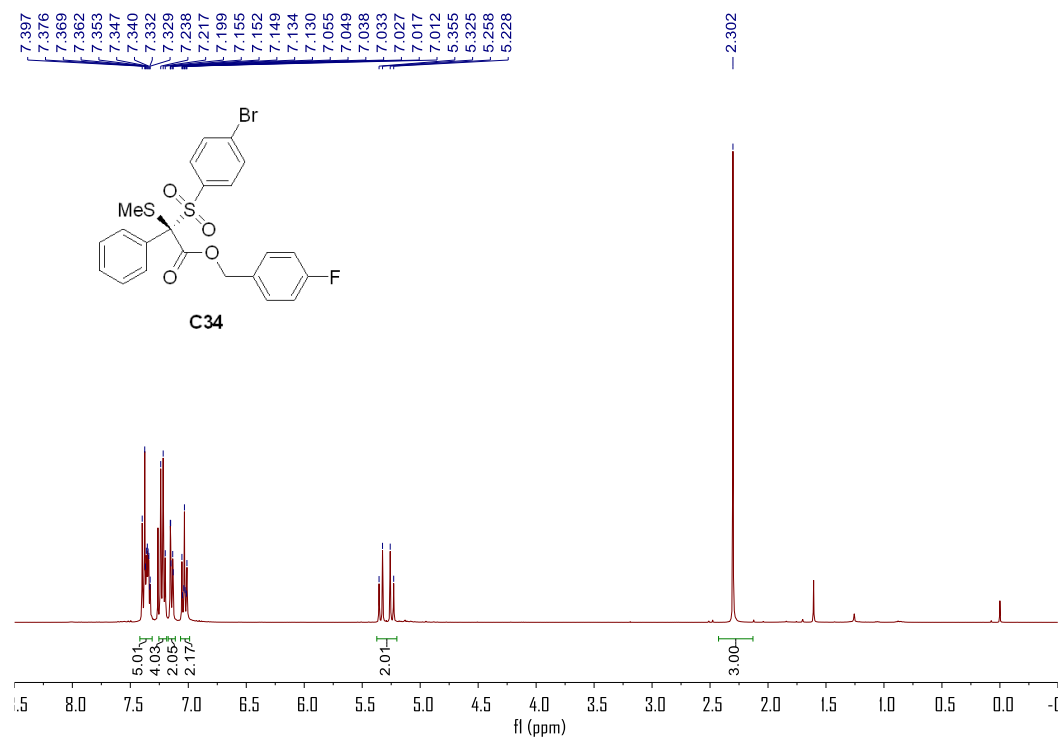


Figure S72. $^{13}\text{C}\{^1\text{H}\}$ NMR of C34

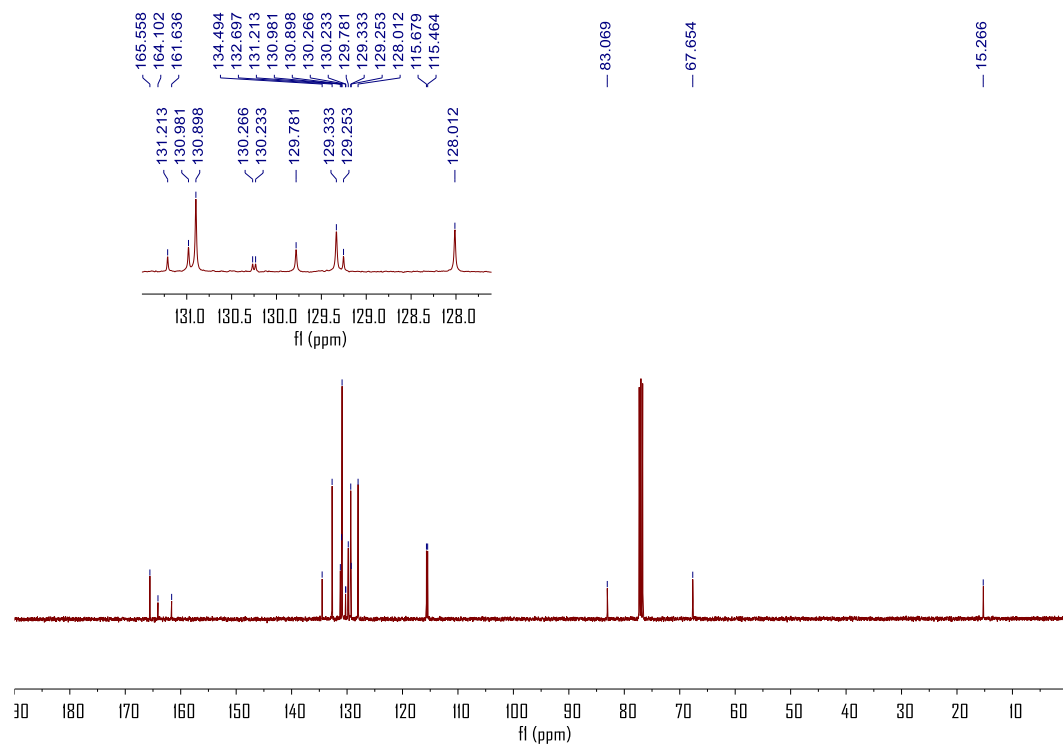


Figure S73. ^{19}F NMR of C34

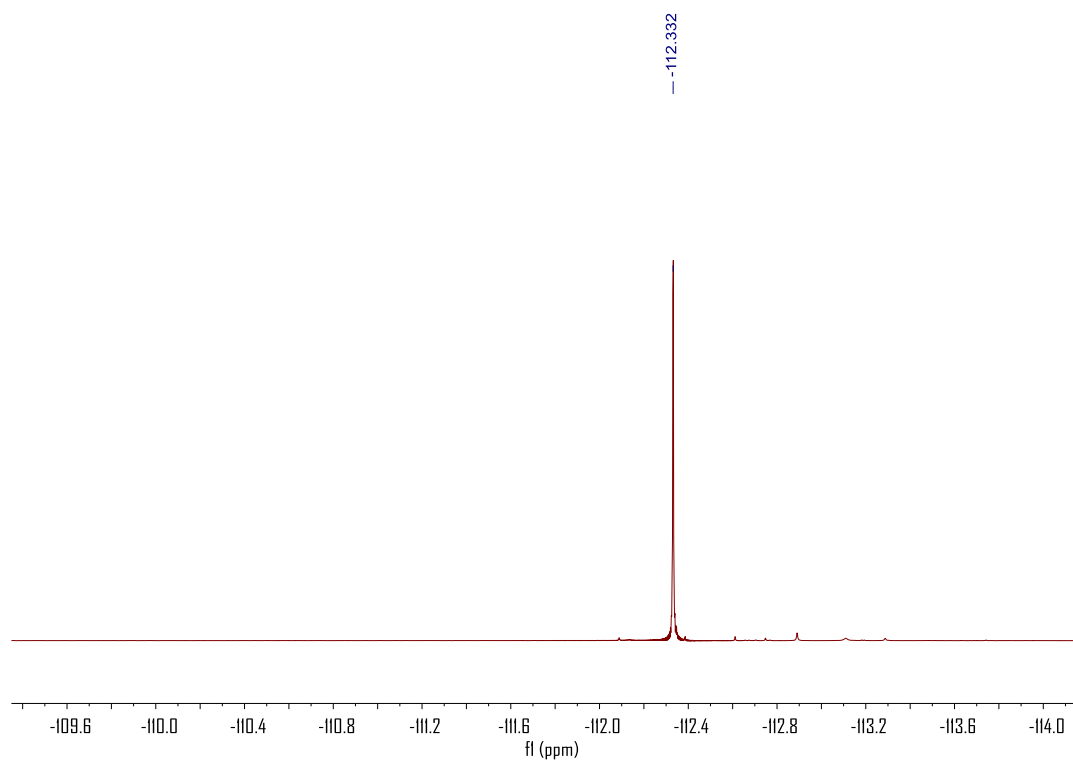


Figure S74. ^1H NMR of C35

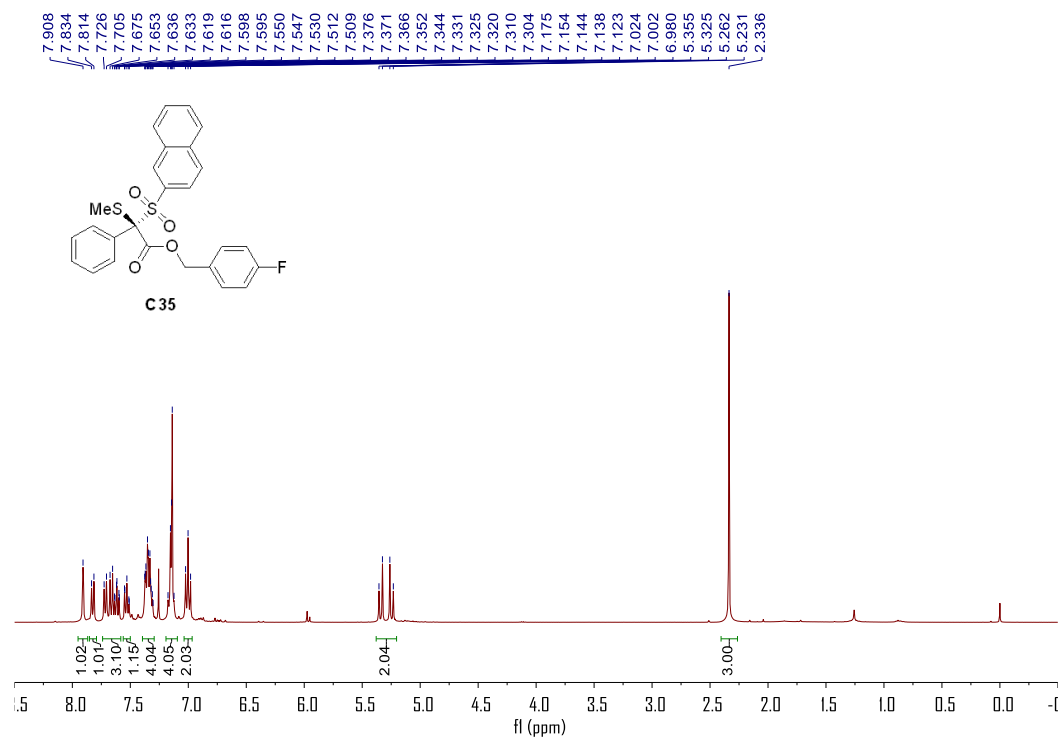


Figure S75. $^{13}\text{C}\{^1\text{H}\}$ NMR of C35

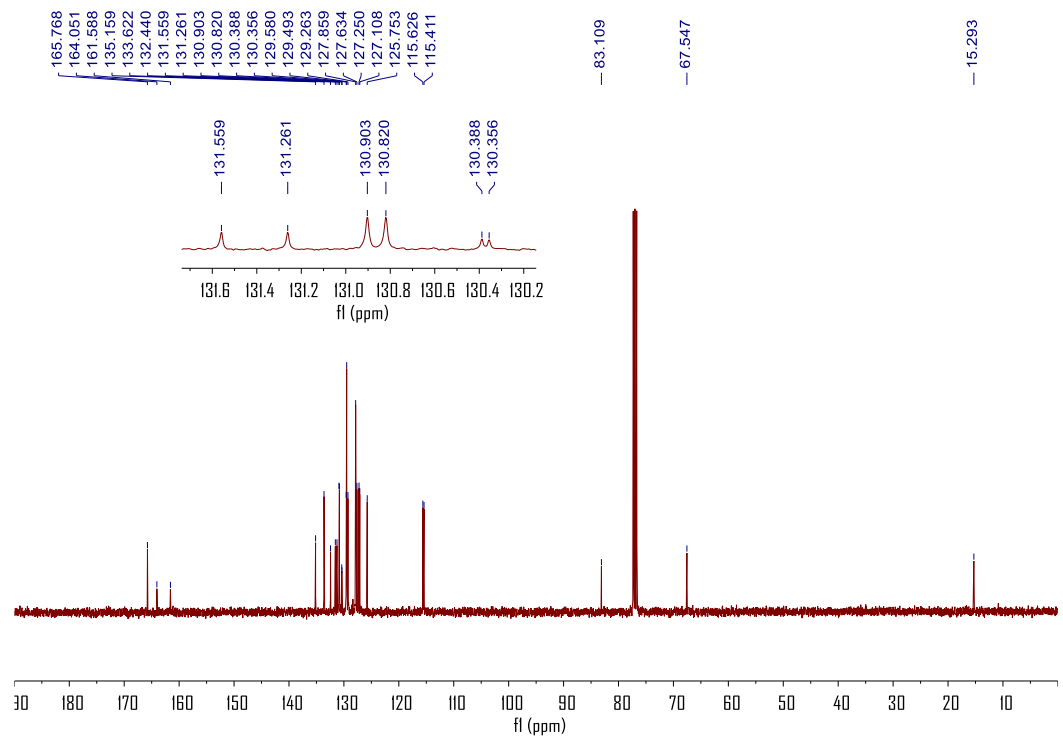


Figure S76. ^{19}F NMR of C35

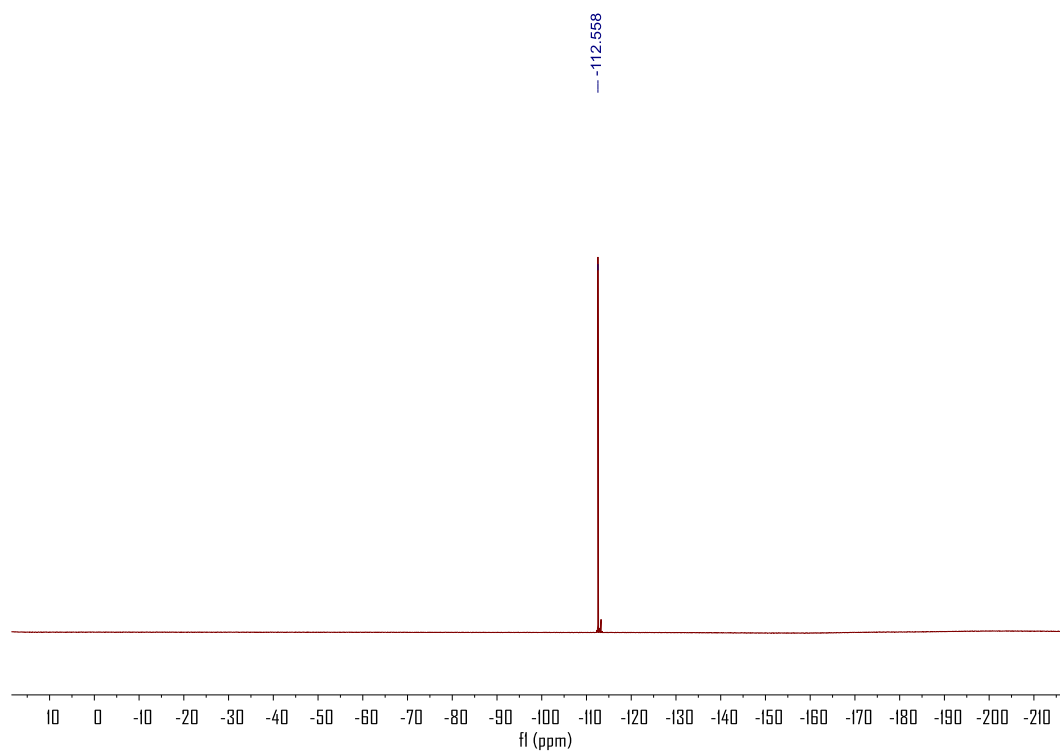


Figure S77. ^1H NMR of C36

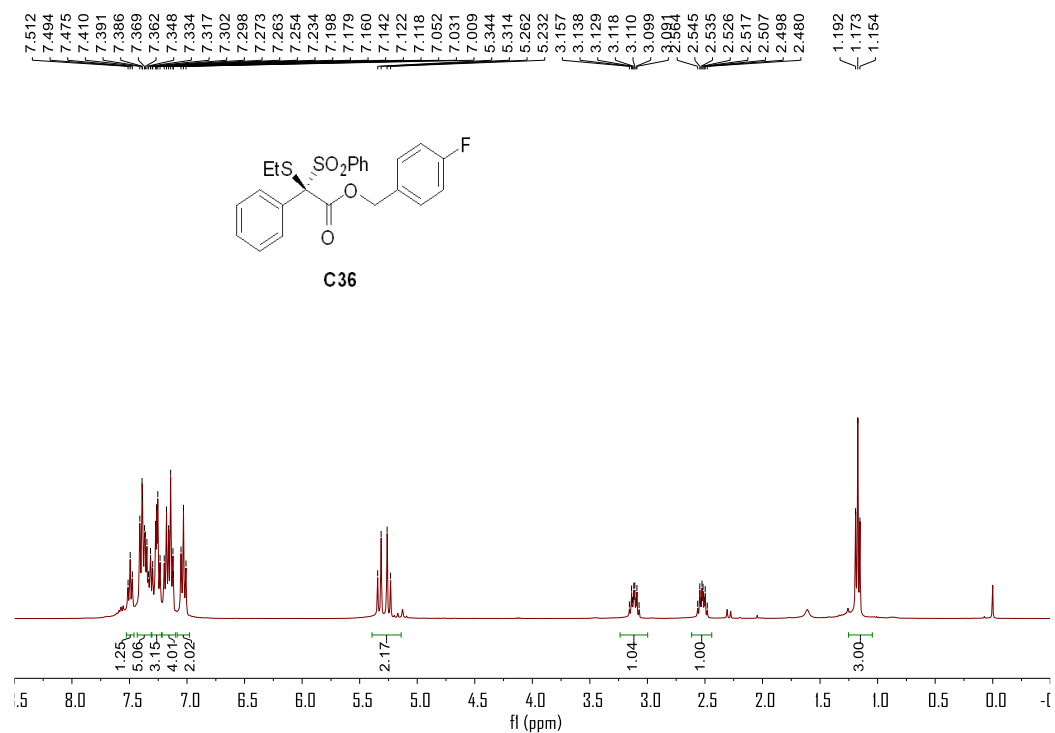


Figure S78. $^{13}\text{C}\{^1\text{H}\}$ NMR of C36

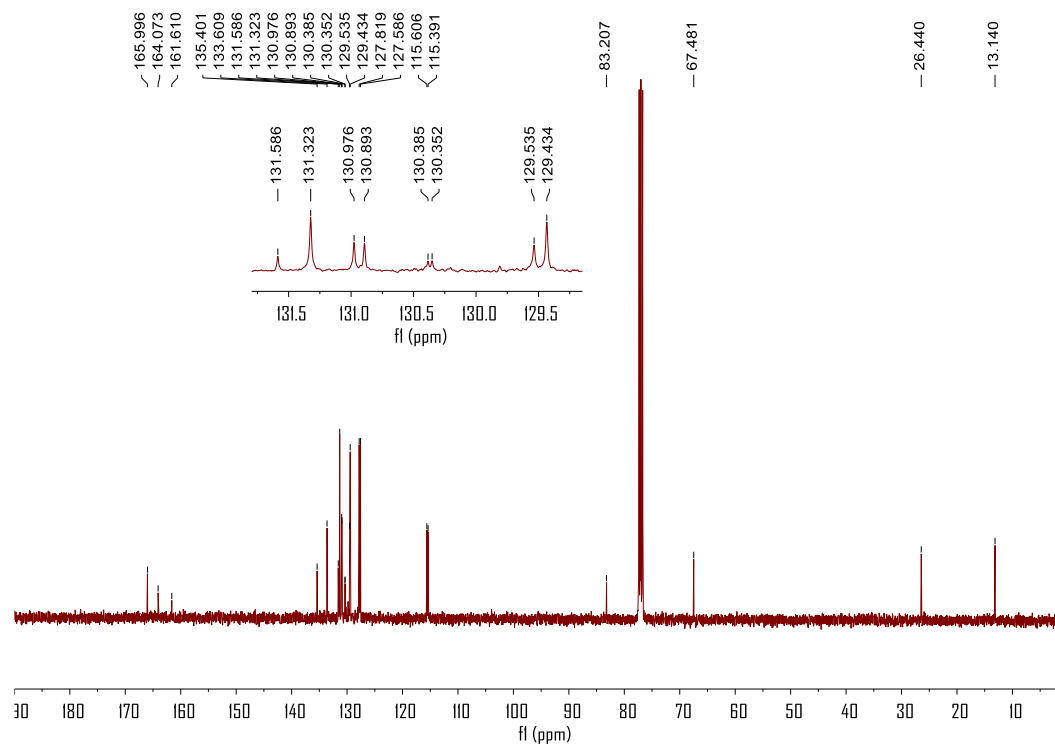


Figure S79. ^{19}F NMR of C36

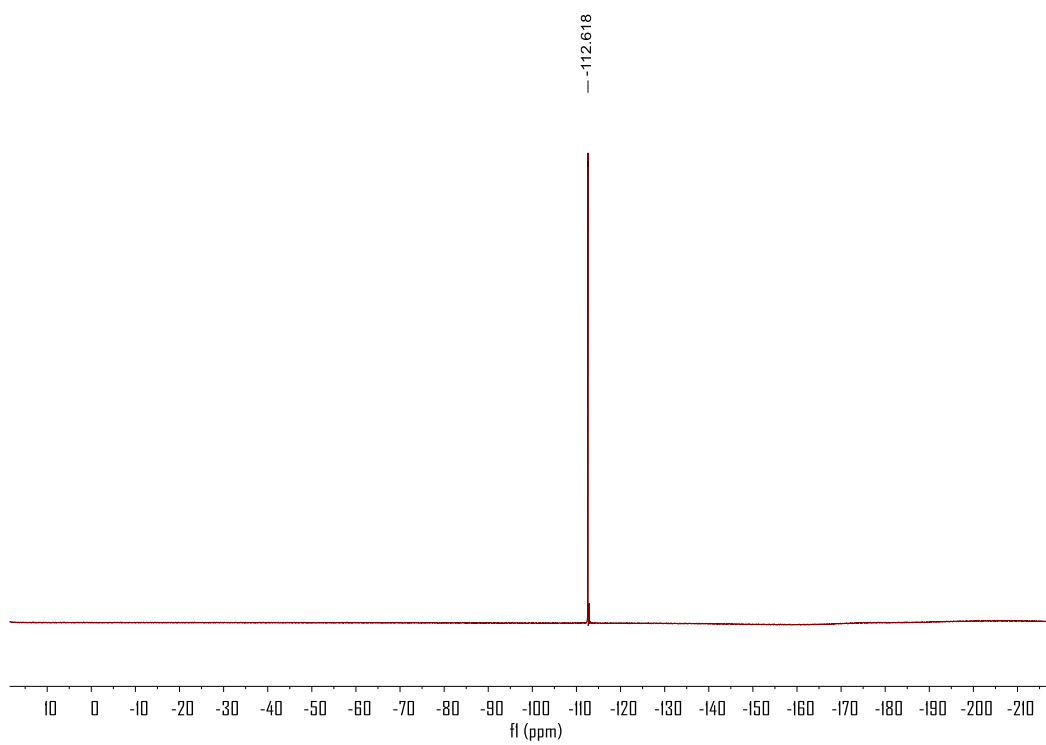


Figure S80. ^1H NMR of C37

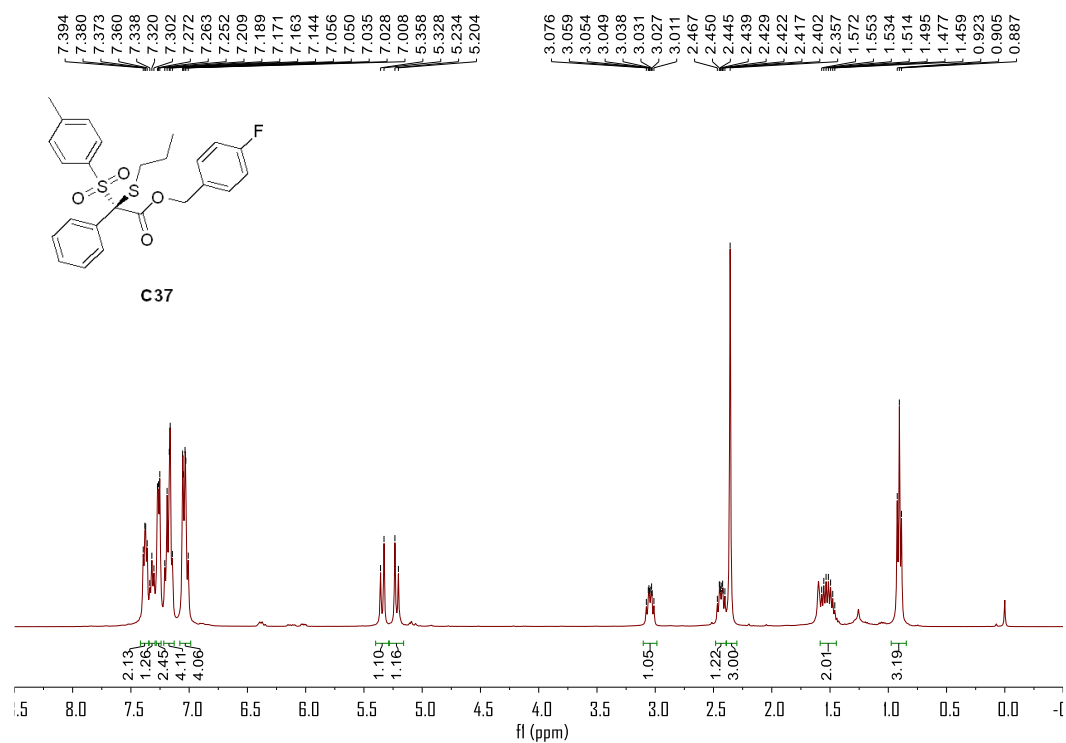


Figure S81. $^{13}\text{C}\{^1\text{H}\}$ NMR of C37

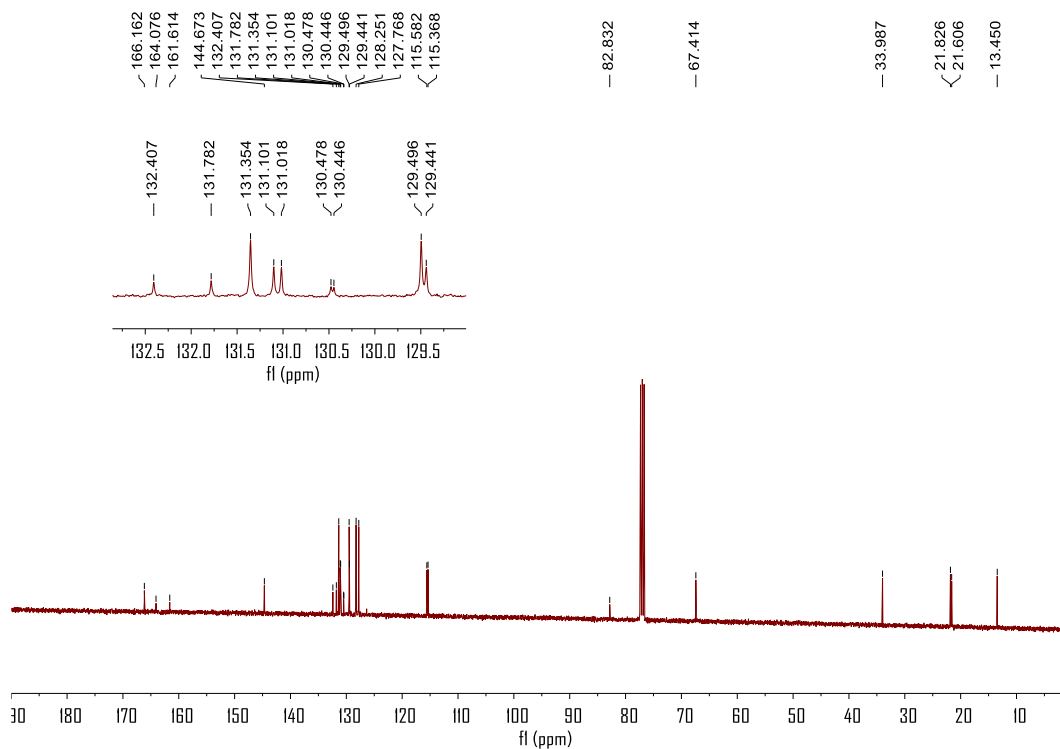


Figure S82. ^{19}F NMR of C37

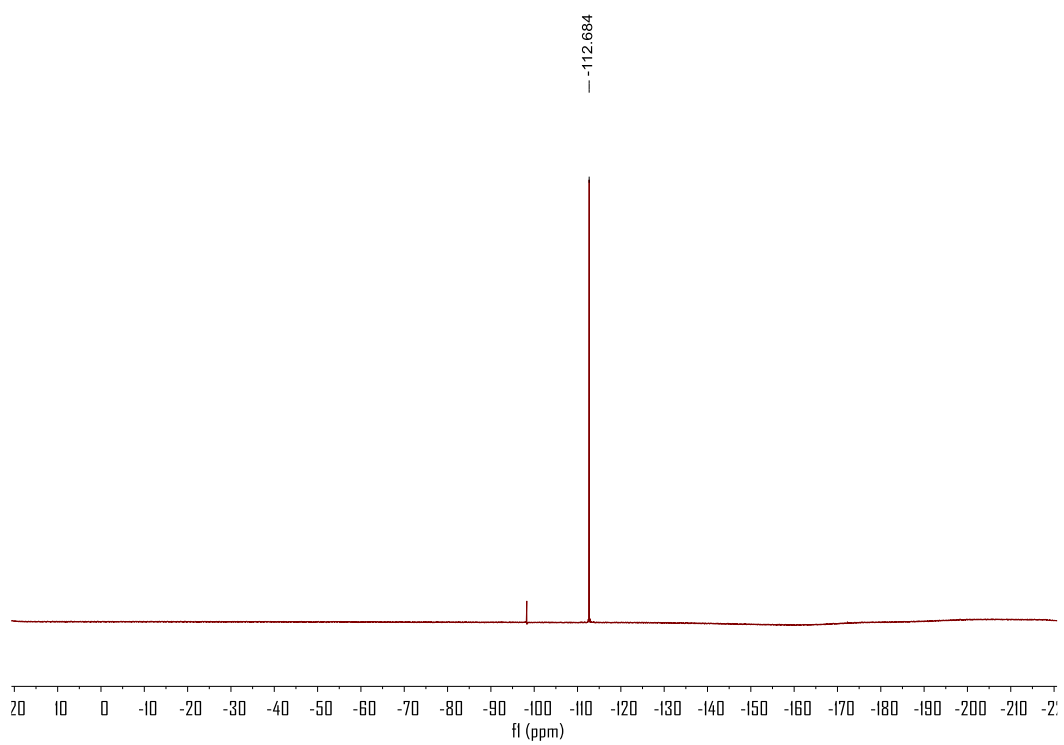


Figure S83. ^1H NMR of D1

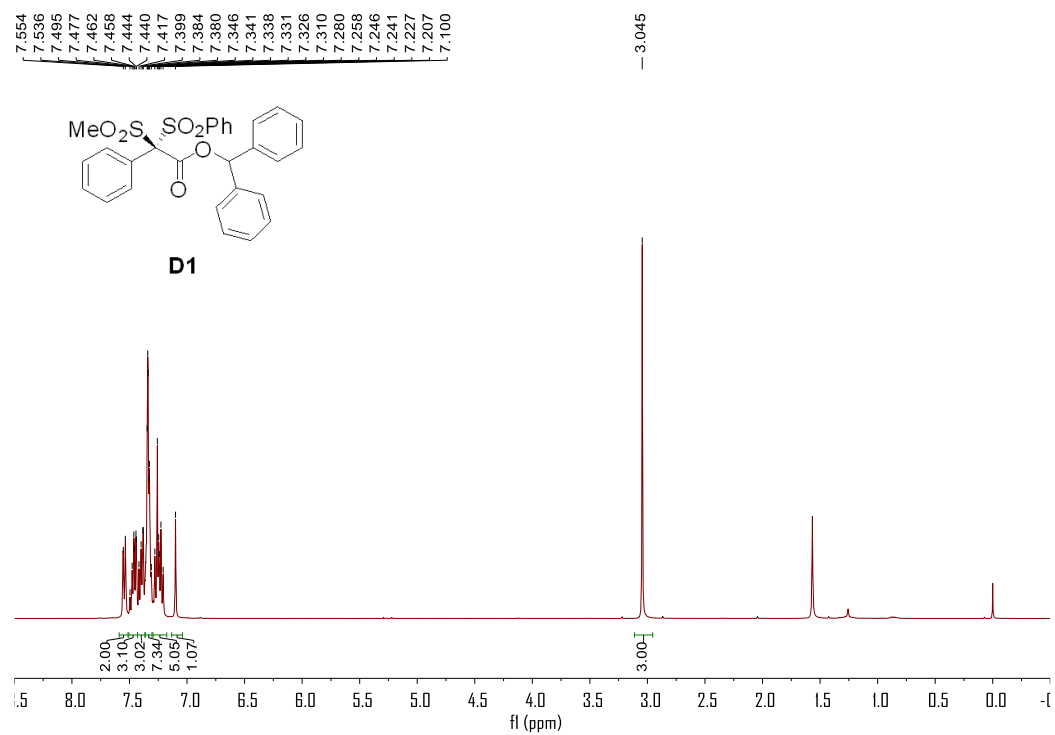
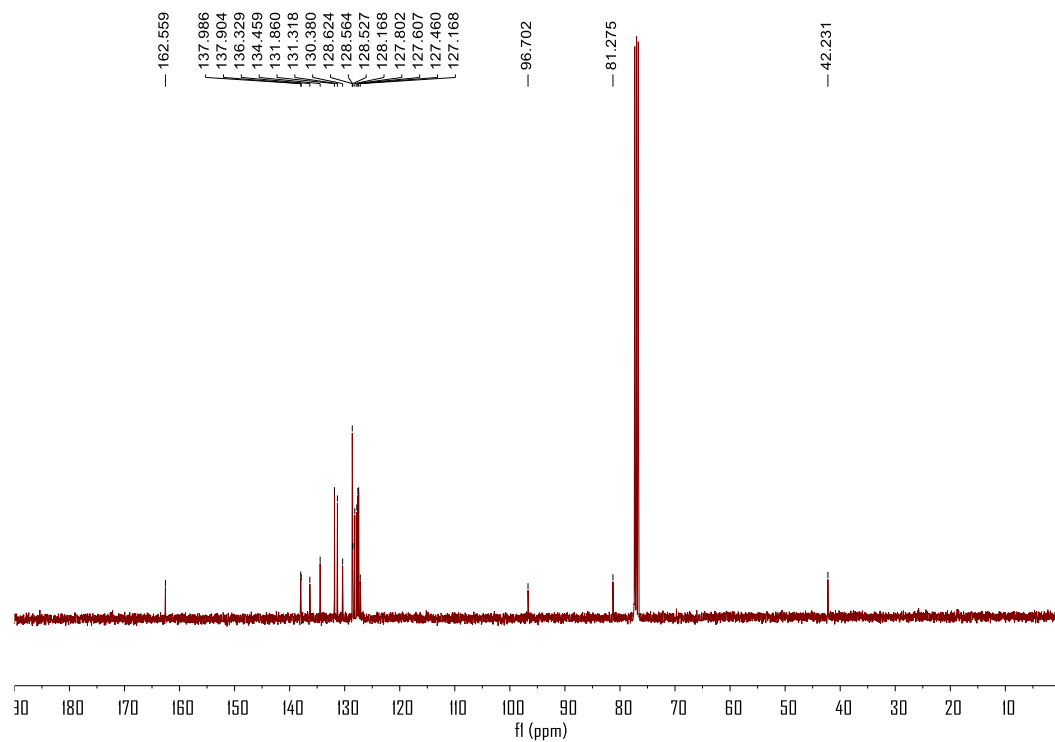
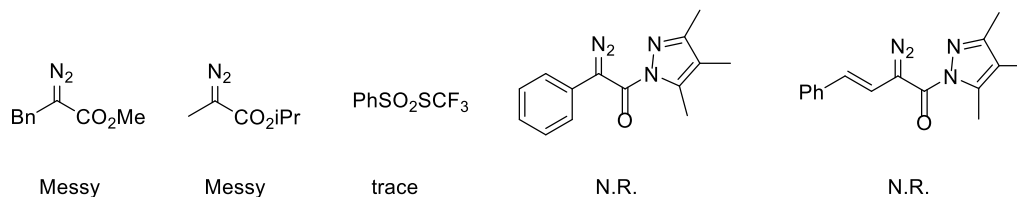


Figure S84. $^{13}\text{C}\{^1\text{H}\}$ NMR of D1



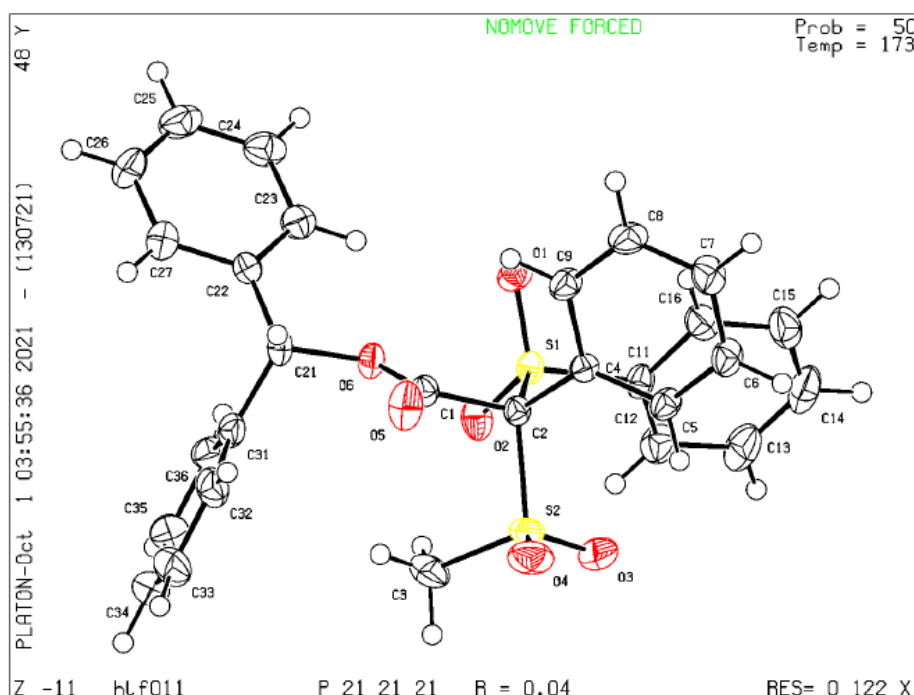
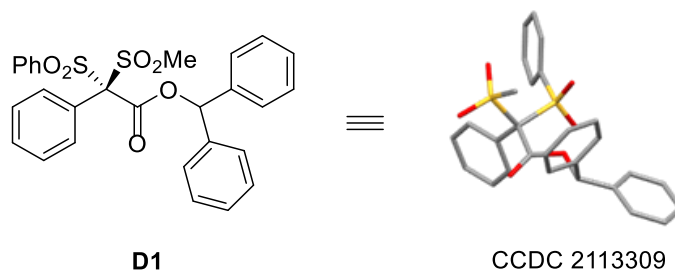
9. Unsuccessful substrate scopes.



10. X-ray crystal structure of product D1

Single crystal of (C₂₈H₂₄O₆S₂) **D1** was recrystallized from mixed solvents of DCM and PE. The absolute configuration of the product **D1** was determined to be (*S*) according to X-ray crystal structural analysis. CCDC 2113309 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center.

The colourless crystal in flake-shape, with approximate dimensions of 0.274 × 0.345 × 0.564 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^{a, b, c, d}. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^e.



Formula	C ₂₈ H ₂₄ O ₆ S ₂
Formula mass (amu)	520.59
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	9.2608 (3)
<i>b</i> (Å)	14.3014 (5)
<i>c</i> (Å)	18.9339 (6)
<i>α</i> (deg)	90
<i>β</i> (deg)	90
<i>γ</i> (deg)	90
<i>V</i> (Å ³)	2507.65 (14)
<i>Z</i>	4
<i>λ</i> (Å)	1.54178
<i>T</i> (K)	173 K
<i>ρ</i> _{calcd} (g cm ⁻³)	1.379
<i>μ</i> (mm ⁻¹)	2.281
Transmission factors	0.375,0.742
<i>θ</i> _{max} (deg)	68.531
No. of unique data, including <i>F</i> _o ² < 0	4414
No. of unique data, with <i>F</i> _o ² > 2 σ (<i>F</i> _o ²)	4222
No. of variables	327
<i>R</i> (<i>F</i>) for <i>F</i> _o ² > 2 σ (<i>F</i> _o ²) ^a	0.0373
<i>R</i> _w (<i>F</i> _o ²) ^b	0.0973
Goodness of fit	1.090

11. References

- (1) Z. P. Yu, X. H. Liu, L. Zhou, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, **2009**, *48*, 5195.
- (2) a) W. G. Wang, X. L. Peng, F. Wei, C. H. Tung, Z. H. Xu, *Angew. Chem. Int. Ed.*, **2016**, *55*, 649; b) H. Li, C. Shan, C. Tung and Z. Xu, *Chem. Sci.*, **2017**, *8*, 2610; c) C. Q. Rao, S. Y. Mai and Q. L. Song, *Chem. Commun.*, **2018**, *54*, 5964.
- (3) a) M. Y. Hu, J. Rong, W. J. Miao, C. F. Ni, Y. X. Han and J. B. Hu, *Org. Lett.*, **2014**, *16*, 2030; b) J. X. Guo, T. Zhou, B. Xu., S. F. Zhu and Q. L. Zhou, *Chem. Sci.*, **2016**, *7*, 1104.

^aG. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.

^bG. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3.

^cG. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3.

^dO. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

^eA. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7.