

Supporting Information

Silyloxymethanesulfinate as a sulfoxylate equivalent for the modular synthesis of sulfones and sulfonyl derivatives

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Table of Contents

General Information	S3
Supplementary Experiments	S4
Optimization studies on the <i>S</i> -arylation of TBSOMS-Na with iodonium salts	S4
Optimization studies on the <i>S</i> -arylation of TBSOMS-Na with aryl halides	S5
Preliminary investigations on the direct <i>S</i> -arylation of TBSOCH ₂ sulfones	S6
Optimization studies on the <i>S</i> -arylation of alkyl TBSOCH ₂ sulfones with aryl halides	S7
Optimization studies on the <i>S</i> -arylation of aryl TBSOCH ₂ sulfones with aryl halides	S8
Effects of additives on the copper catalysis system	S9
Experimental Details	S10
Synthesis of TBSOMS-Na from Rongalite™	S10
Synthesis of TBSOM sulfones	S11
Modular synthesis of sulfones	S21
Streamlined synthesis of unsymmetrical sulfones	S37
Synthesis of sulfonyl derivatives	S39
Utilization of TBSOM sulfone intermediates	S46
Synthetic sequence orthogonal to radical processes	S49
Synthesis of bicalutamide	S50
Spectra of Compounds	S52

I. General Information

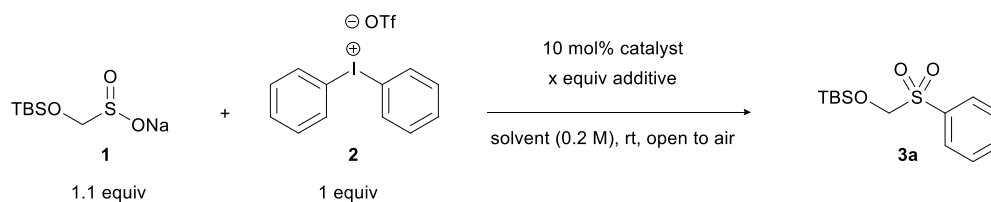
All solvents were obtained by passing through activated alumina columns of solvent purification systems from Glass Contour. Commercially available reagents were obtained from Sigma-Aldrich, Alfa Aesar, Strem, Acros or TCI and used without further purification.

NMR spectra were obtained on an Agilent 400-MR DD2 Magnetic Resonance System (400 MHz) and a Varian/Oxford As-500 (500 MHz) spectrophotometer. Chemical shift values in ^1H NMR spectra were recorded as parts per million (ppm) relative to tetramethylsilane (0.00 ppm), chloroform (7.26 ppm), dimethyl sulfoxide (2.50 ppm) or methanol (3.31 ppm) as an internal standard, and coupling constants in hertz. Chemical shift values in ^{13}C NMR spectra were recorded as parts per million (ppm) relative to chloroform (77.16 ppm), dimethyl sulfoxide (39.52 ppm) or methanol (49.00 ppm) as an internal standard, and coupling constants in hertz. Chemical shift values in ^{19}F NMR spectra were recorded as parts per million (ppm) relative to trifluoroacetic acid (-75.39 ppm) or hexafluorobenzene (-161.64 ppm) as an internal standard. The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were measured on a Thermo Scientific Nicolet 6700 spectrometer. High resolution mass spectra were recorded from the Organic Chemistry Research Center at Sogang University (Seoul) on a Bruker Compact or ThermoFisher Scientific using electrospray ionization (ESI) method.

The progress of reaction was checked on thin layer chromatography (TLC) plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm UV and/or charring after dipping the TLC plate into a vanillin solution (15.0 g of vanillin and 2.5 mL of concentrated sulfuric acid in 250 mL of ethanol), a KMnO_4 solution (3.0 g of potassium permanganate, 20.0 g of potassium carbonate, and 5.0 mL of 5% sodium hydroxide solution in 300 mL of water), or a ceric ammonium sulfate (CAM) solution (5 g of cerium sulfate, 25 g of ammonium molybdate tetrahydrate, 50 mL of concentrated sulfuric acid in 450 mL of water). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60) using an appropriate eluent system.

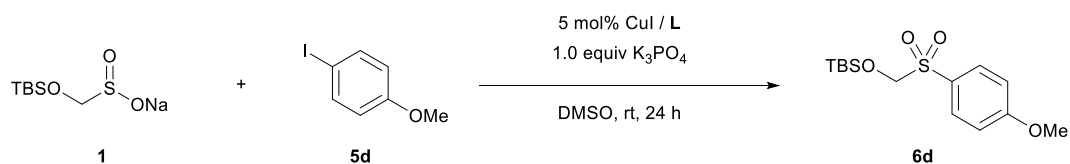
II. Supplementary Experiments

Table S1 Optimization studies on the S-arylation of TBSOMS-Na with iodonium salts^a



Entry	Solvent	Catalyst	Additive (equiv)	Note	Time	Isolated Yield
1	H ₂ O	Cu(OAc) ₂	30% aq. NH ₃ (2)	1 equiv Cu(OAc) ₂	1 h	54%
2	H ₂ O	Cu(OAc) ₂	30% aq. NH ₃ (2)	under N ₂ atmosphere	20 h	20% ^b
3	H ₂ O	Cu(OAc) ₂	30% aq. NH ₃ (2)	2 equiv 1	21 h	59%
4	MeOH	Cu(OAc) ₂	30% aq. NH ₃ (2)	2 equiv 1	3 h	8% ^b
5	MeOH	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	3 h	3% ^b
6	THF	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	3 h	74% ^b
7	DMF	Cu(OAc) ₂	30% aq. NH ₃ (2)	2 equiv 1	0.5 h	50% ^b
8	DMF	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	1 h	76% ^b
9	DMF	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	1 h	79%
10	DMA	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	1 h	54%
11	DMSO	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	1 h	75%
12	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	2 equiv 1	1 h	90%
13	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	1.5 equiv 1	1 h	80%
14	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (2)	-	1 h	86%
15	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (1)	-	1 h	83%
16	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (0.4)	-	1 h	87%
17	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (0.2)	-	1 h	82%
18	DME	Cu(OAc) ₂	no additive	-	1 h	57%
19	DME	Cu powder	7 N NH ₃ in MeOH (0.4)	-	1 h	trace
20	DME	CuI	7 N NH ₃ in MeOH (0.4)	-	1 h	37%
21	DME	CuI	7 N NH ₃ in MeOH (0.4)	-	3 h	75%
22	DME	CuOAc	7 N NH ₃ in MeOH (0.4)	-	1 h	58%
23	DME	Cu(OAc) ₂	proline-Na salt (0.2)	-	2 h	73%
24	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (0.4)	OTs ⁻ instead of OTf ⁻	1 h	86%
25	DME	Cu(OAc) ₂	7 N NH ₃ in MeOH (0.4)	BF ₄ ⁻ instead of OTf ⁻	0.5 h	80%

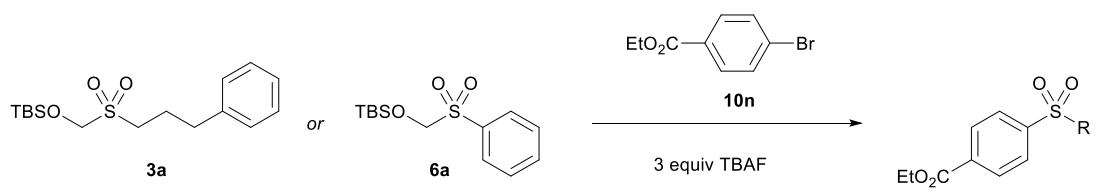
^a 0.22 mmol of 1 and 0.2 mmol of 2. ^b NMR yield with respect to 1,3,5-trimethoxybenzene.

Table S2 Optimization studies on the S-arylation of TBSOMS-Na with aryl halides^a

Ratio (1 : 5d)	Solvent	Concentration	Note	Yield ^b
1.3 : 1	DMSO	1.25 M (0.4 mL)	0.5 mol% CuI / L	irreproducible
1.3 : 1	DMSO	1.25 M (0.4 mL)	-	18%
1.3 : 1	2-methoxyethanol	1.25 M (0.4 mL)	-	N.D.
1.3 : 1	<i>tert</i> -butanol	1.25 M (0.4 mL)	-	N.D.
1.3 : 1	DMSO	0.625 M (0.8 mL)	-	18%
1.3 : 1	DMSO	0.3125 M (1.6 mL)	-	33%
1.3 : 1	DMSO	0.3125 M (1.6 mL)	10 mol% CuI / L	32%
1.3 : 1	DMSO	ca. 0.21 M (2.4 mL)	-	44%
1.3 : 1	DMSO	ca. 0.16 M (3.2 mL)	-	55%
1.3 : 1	DMSO	ca. 0.16 M (3.2 mL)	10 mol% CuI / L	44%
1.3 : 1	DMSO	0.125 M (4.0 mL)	-	50%
1.3 : 1	DMSO	ca. 0.10 M (4.8 mL)	-	47%
1 : 1.3	DMSO	ca. 0.16 M (3.2 mL)	-	72%
1 : 1.3	DMSO	ca. 0.16 M (3.2 mL)	35 °C for reproducibility	63%
1 : 1.3	DMSO	ca. 0.16 M (3.2 mL)	35 °C, 10 mol% CuI / L	76%
1 : 1.5	DMSO	ca. 0.16 M (3.2 mL)	35 °C	65%
1 : 2.0	DMSO	ca. 0.16 M (3.2 mL)	35 °C	72%
1 : 2.0	DMSO	ca. 0.16 M (3.2 mL)	35 °C, 10 mol% CuI / L	85%

^a 0.5 mmol scale.^b NMR yield with respect to 1,3,5-trimethoxybenzene.

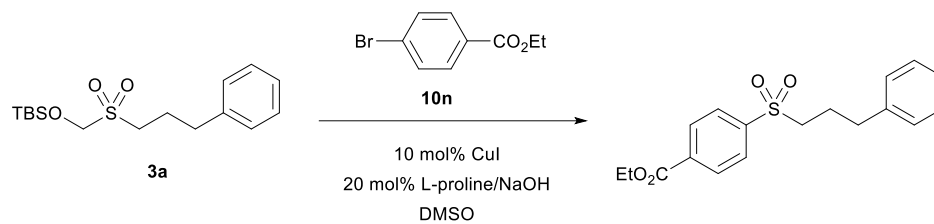
Table S3 Preliminary investigations on the direct S-arylation of TBSOCH₂ sulfones^a



Substrate	Ratio (3a or 6a : 10n)	Conditions	Isolated Yield
3a	1.2 : 1	2.5 mol% Pd ₂ (dba) ₃	N.D.
6a		5.0 mol% XantPhos 1.5 equiv Cs ₂ CO ₃ toluene (0.1 M), 120 °C, 24 h	N.D.
3a	1.2 : 1	10 mol% CuI	40%
6a		20 mol% L-proline 20 mol% NaOH DMSO (0.4 M), 80 °C, 24 h	37%
3a	1.3 : 1	2 mol% CuI	N.D.
6a		2 mol% L 1.0 equiv K ₃ PO ₄ DMSO (0.4 M), 90 °C, 24 h	N.D.

^a 0.24 mmol or 0.26 mmol of masked sulfinate and 0.2 mmol of aryl halide.

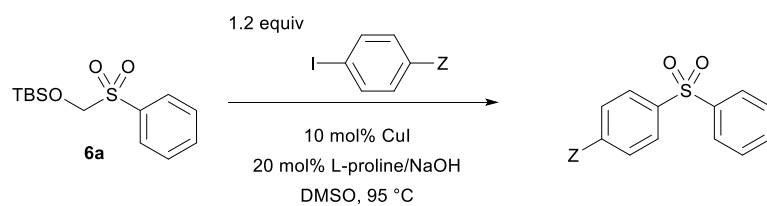
Table S4 Optimization studies on the S-arylation of alkyl TBSOCH₂ sulfones with aryl halides^a



Ratio (3a: 10n)	Unmasking-arylation conditions	Yield ^b
1.2 : 1	3 equiv TBAF, rt, 1 h, then, 80 °C, 24 h (stepwise)	60%
1.2 : 1	3 equiv TBAF, 80 °C, 24 h (one-pot)	59%
1.2 : 1	1.5 equiv TBAF, 80 °C, 24 h	54%
1.2 : 1	1.5 equiv CsF, 80 °C, 24 h	47%
1.2 : 1	1.5 equiv KF, 80 °C, 24 h	47%
1.2 : 1	1.5 equiv NH ₄ F, 80 °C, 24 h	32%
1.2 : 1	1.5 equiv HF•pyridine, 80 °C, 24 h	9%
1.2 : 1	1.5 equiv 3HF•TEA, 80 °C, 24 h	10%
1.2 : 1	1.5 equiv CuF ₂ , 80 °C, 24 h	49%
1.2 : 1	1.5 equiv AgF, 80 °C, 24 h	N.D.
1.2 : 1	1.5 equiv TBAF, 95 °C	58% (24 h) 72% (36 h) 77% (48 h)
1.2 : 1	1.5 equiv CsF, 95 °C	56% (24 h) 69% (36 h)
1.2 : 1	1.5 equiv KF, 95 °C	60% (24 h) 60% (36 h)
1 : 1.2	1.5 equiv TBAF, 95 °C	70% (24 h) 70% (36 h)
1 : 1.2	1.5 equiv CsF, 95 °C	70% (24 h) 68% (36 h)

^a 0.2 mmol scale.

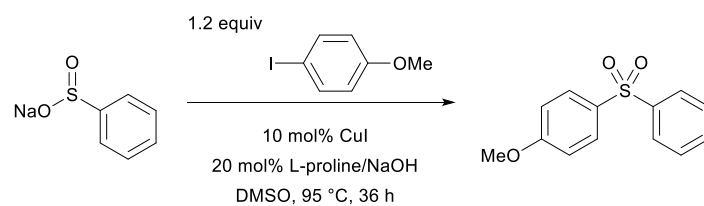
^b NMR yield with respect to 1,3,5-trimethoxybenzene.

Table S5 Optimization studies on the S-arylation of aryl TBSOCH₂ sulfones with aryl halides^a

Z	Unmasking-arylation conditions	Yield ^b
CO ₂ Et	1.5 equiv CsF, 95 °C, 24 h	59%
CO ₂ Et	1.5 equiv CsF, 95 °C, 36 h	61%
OMe	1.5 equiv CsF, 95 °C, 24 h	49%
OMe	1.5 equiv CsF, 95 °C, 36 h	59%
CO ₂ Et	1.5 equiv TBAF, 95 °C, 24 h	71%
CO ₂ Et	1.5 equiv TBAF, 95 °C, 36 h	64%
OMe	1.5 equiv TBAF, 95 °C, 24 h	62%
OMe	1.5 equiv TBAF, 95 °C, 36 h	66%
Me	1.5 equiv TBAF, 95 °C, 24 h	53%
CF ₃	1.5 equiv TBAF, 95 °C, 24 h	63%
OMe	1.5 equiv CsF, 2.0 equiv H ₂ NCH ₂ CH ₂ OH, 95 °C, 36 h	3%
OMe	1.5 equiv CsF, 2.0 equiv (CH ₂ OH) ₂ , 95 °C, 36 h	36%
OMe	1.5 equiv CsF, 2.0 equiv L-proline, 95 °C, 36 h	94%
OMe	1.5 equiv CsF, 1.5 equiv L-proline, 95 °C, 36 h	99%
OMe	1.5 equiv CsF, 1.0 equiv L-proline, 95 °C, 36 h	99%

^a 0.2 mmol scale.^b NMR yield with respect to 1,3,5-trimethoxybenzene.

Table S6 Effects of additives on the copper catalysis system^a



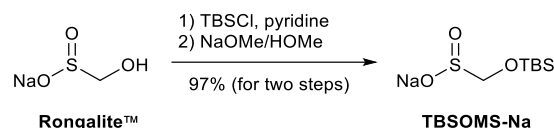
Additive	Yield ^b
none	90%
1.5 equiv CsF	91%
1.0 equiv (HCHO) _n	36%

^a 0.2 mmol scale.

^b NMR yield with respect to 1,3,5-trimethoxybenzene.

III. Experimental Details

A. Synthesis of TBSOMS-Na from Rongalite™



To an argon-purged and flame-dried flask were added 80 mmol of TBSCl (4.0 equiv) and 20 mmol of Rongalite™ (1.0 equiv). The solid mixture was cooled to 0 °C with an ice-water bath while being gently stirred. 20 mL of pyridine (1 M with respect to Rongalite™) was slowly added to the flask over a few minutes. The resulting mixture was stirred overnight at room temperature under inert atmosphere. Volatiles including pyridine were evaporated under reduced pressure at 50 °C for 5 min. The residue was filtered through a Celite® 545 pad with hexanes and the filtrate was concentrated under reduced pressure. After several cycles of evacuation-backfill processes, 60 mL of CH₂Cl₂ was added to prepare a DCM solution under inert atmosphere. To the cooled solution with an ice-water bath was dropwise added 19 mmol of sodium methoxide (5.4 M in MeOH; 0.95 equiv) over 10 minutes while being vigorously stirred. The reaction mixture was stirred for 1 h at room temperature. As the solution turned into a heterogeneous white solution, volatiles were removed under reduced pressure. The waxy precipitate was collected through washing and trituration with hexanes, and dried for a day under vacuum (or under a stream of nitrogen) to afford TBSOMS-Na as a white solid (4.2886 g, 97% yield). ¹H NMR (400 MHz, CD₃OD) δ 3.86 (s, 2H), 0.92 (s, 9H), 0.13 (s, 6H); ¹³C NMR (101 MHz, CD₃OD) δ 88.1, 26.4, 19.3, -4.9. Analytical data are consistent with the previous report.¹

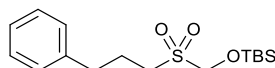
B. Synthesis of TBSOM sulfones

i) S-Alkylation of TBSOMS-Na



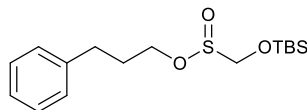
General Procedure A

A solution of alkyl halide (0.4 mmol, 1 equiv) and TBSOMS-Na (139.4 mg, 0.6 mmol, 1.5 equiv) in 1.6 mL of anhydrous DMSO was stirred under N₂ atmosphere at room temperature for the indicated period. The reaction mixture was diluted in diethyl ether and washed twice with H₂O. The organic layer was dried with MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 50:1 to 20:1) to afford the desired alkyl sulfone product.



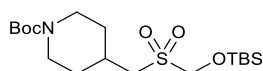
tert-butyl dimethyl((3-phenylpropyl)sulfonyl)methoxy)silane (3a)

The general procedure A with 1-bromo-3-phenylpropane (61 μ L, 0.4 mmol) was adopted to afford the desired product as a clear liquid (16 h, 94.1 mg, 72% yield); R_f 0.28 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.25 (ddd, *J* = 24.5, 15.9, 7.2 Hz, 5H), 4.50 (s, 2H), 2.97 (dd, *J* = 9.3, 6.7 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.16 (dt, *J* = 20.2, 7.5 Hz, 2H), 0.89 (s, 9H), 0.15 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 140.0, 128.8, 128.6, 126.6, 77.9, 48.3, 34.5, 25.7, 23.3, 18.3, -5.3; IR (neat, ν_{max}) 3086, 3063, 3028, 2952, 2930, 2898, 2857, 1326, 1305, 1256, 1153, 1113 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₆H₂₈NaO₃SSi [M+Na]⁺ 351.1421, found 351.1420.



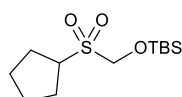
3-phenylpropyl ((tert-butyl dimethylsilyl)oxy)methanesulfinate (3a')

The general procedure A with 1-bromo-3-phenylpropane (61 μ L, 0.4 mmol) was adopted to afford the desired product as a clear liquid (16 h, 9.6 mg, 7% yield); R_f 0.30 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 3H), 4.42 (q, *J* = 9.9 Hz, 2H), 4.10 (qt, *J* = 10.2, 6.4 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.05 (dq, *J* = 13.0, 6.6 Hz, 2H), 0.92 (s, 9H), 0.15 (d, *J* = 1.5 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 141.0, 128.6, 128.6, 126.2, 83.5, 68.5, 31.9, 25.8, 25.8, 18.4, -5.0; IR (neat, ν_{max}) 3063, 2952, 2929, 2886, 2857, 1604, 1471, 1257, 1151, 1116, 1006 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₆H₂₈NaO₃SSi [M+Na]⁺ 351.1426, found 351.1423.



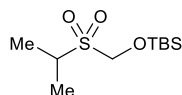
tert-butyl 4-((((tert-butyl dimethylsilyl)oxy)methyl)sulfonyl)methyl)piperidine-1-carboxylate (3b)

The general procedure A with *tert*-butyl 4-(bromomethyl)piperidine-1-carboxylate (111.3 mg, 0.4 mmol) was adopted to afford the desired product as a white solid (24 h, 75.9 mg, 47% yield); R_f 0.19 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 4.52 (s, 2H), 4.17 – 4.04 (m, J = 7.1 Hz, 2H), 2.93 (d, J = 6.2 Hz, 2H), 2.77 (t, J = 12.4 Hz, 2H), 2.23 (ttd, J = 10.5, 6.8, 3.4 Hz, 1H), 1.93 (d, J = 12.9 Hz, 2H), 1.45 (s, 9H), 1.37 – 1.28 (m, 2H), 0.93 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.1, 171.0, 154.6, 79.5, 78.8, 60.3, 54.3, 32.0, 30.2, 28.3, 25.5, 18.1, 16.4, 14.1, -5.4; IR (neat, ν_{max}) 2954, 2929, 2857, 1689, 1421, 1365, 1302, 1249, 1155, 1114 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{37}\text{NNaO}_5\text{SSi}$ $[\text{M}+\text{Na}]^+$ 430.2054, found 430.2055.



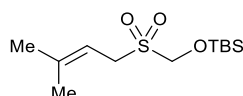
tert-butyl((cyclopentylsulfonyl)methoxy)dimethylsilane (3c)

The general procedure A with bromocyclopentane (41 μL , 0.4 mmol) was adopted to afford the desired product as a clear liquid (24 h, 40.1 mg, 36% yield); R_f 0.35 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 4.55 (s, 2H), 3.64 – 3.50 (m, 1H), 2.15 – 1.95 (m, 4H), 1.91 – 1.74 (m, 2H), 1.74 – 1.55 (m, 2H), 0.92 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 77.1, 57.5, 26.3, 25.9, 25.5, 18.2, -5.4; IR (neat, ν_{max}) 2954, 2931, 2873, 2858, 1471, 1463, 1450, 1288, 1254, 1113, 1082 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{26}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 301.1270; found 301.1267.



tert-butyl((isopropylsulfonyl)methoxy)dimethylsilane (3d)

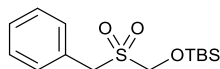
The general procedure A with 2-iodopropane (40 μL , 0.4 mmol) was adopted to afford the desired product as a clear liquid (24 h, 55.3 mg, 55% yield); R_f 0.30 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 4.59 (s, 2H), 3.37 – 3.28 (m, 1H), 1.39 (d, J = 6.9 Hz, 3H), 0.92 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 75.7, 49.4, 25.5, 17.9, 14.6, -5.4; IR (neat, ν_{max}) 2953, 2931, 2889, 2858, 1468, 1324, 1303, 1255, 1151, 1112, 1052 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 275.1113, found 275.1112.



tert-butyl dimethyl(((3-methylbut-2-en-1-yl)sulfonyl)methoxy)silane (3e)

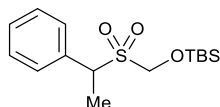
The general procedure A with 1-bromo-3-methyl-2-butene (51 μL , 0.4 mmol) was adopted to afford the desired product as a clear liquid (1 h, 104.0 mg, 93% yield); R_f 0.48 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 5.27 (t, J = 7.9 Hz, 1H), 4.47 (s, 2H), 3.73 (d, J = 7.9 Hz, 2H), 1.83 (s, 3H), 1.75 (s, 3H), 0.93

(s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.0, 110.1, 76.1, 49.1, 26.2, 25.7, 18.5, 18.4, -5.2; IR (neat, ν_{max}) 2954, 2931, 2858, 1472, 1326, 1306, 1257, 1117 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{26}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 301.1264, found 301.1262.



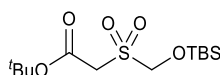
((benzylsulfonyl)methoxy)(*tert*-butyl)dimethylsilane (3f)

The general procedure A with benzyl bromide (48 μL , 0.4 mmol) was adopted to afford the desired product as a clear liquid (1 h, 110.7 mg, 92% yield); R_f 0.49 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.35 (m, 5H), 4.36 (s, 2H), 4.25 (s, 2H), 0.96 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 130.8, 129.1, 129.0, 128.0, 75.5, 55.4, 25.7, 18.4, -5.2; IR (neat, ν_{max}) 3065, 3035, 2953, 2930, 2893, 2857, 1329, 1307, 1255, 1118 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 323.1108, found 323.1110.



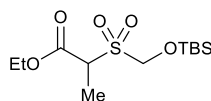
***tert*-butyldimethyl(((1-phenylethyl)sulfonyl)methoxy)silane (3g)**

The general procedure A with (1-bromoethyl)benzene (55 μL , 0.4 mmol) was adopted to afford the desired product as a white solid (2 h, 72.6 mg, 58% yield); R_f 0.44 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.35 (m, 5H), 4.45 (q, J = 7.3 Hz, 1H), 4.30 (s, 2H), 1.77 (d, J = 7.3 Hz, 3H), 0.94 (s, 9H), 0.19 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 134.2, 129.4, 129.1, 128.9, 75.3, 59.2, 25.7, 18.4, 13.0, -5.1, -5.4; IR (neat, ν_{max}) 3065, 3034, 2952, 2930, 2892, 2857, 1455, 1323, 1295, 1256, 1150, 1116, 1085 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{26}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 337.1264, found 337.1263.



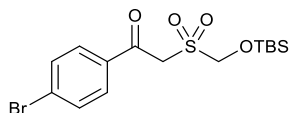
***tert*-butyl 2-(((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)acetate (3h)**

The general procedure A with *tert*-butyl bromoacetate (59 μL , 0.4 mmol) was adopted to afford the desired product as a white solid (2 h, 113.0 mg, 87% yield); R_f 0.46 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 4.74 (s, 2H), 3.92 (s, 2H), 1.51 (s, 9H), 0.93 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.0, 84.1, 77.8, 54.1, 28.0, 25.7, 18.4, -5.2; IR (neat, ν_{max}) 2978, 2954, 2932, 2894, 2859, 1731, 1472, 1370, 1337, 1315, 1257, 1119 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{28}\text{NaO}_5\text{SSi}$ $[\text{M}+\text{Na}]^+$ 347.1319, found 347.1322.



ethyl 2-(((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)propanoate (3i)

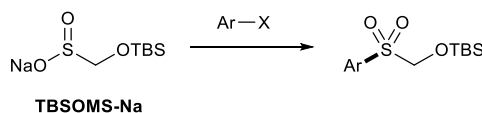
The general procedure A with ethyl 2-bromopropionate (52 μ L, 0.4 mmol) was adopted to afford the desired product as a clear liquid (5 h, 98.3 mg, 79% yield); R_f 0.39 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 4.89 (d, J = 11.3 Hz, 1H), 4.67 (d, J = 11.3 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.4 Hz, 1H), 1.63 (d, J = 7.4 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H), 0.92 (d, J = 5.2 Hz, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 77.9, 62.6, 58.7, 25.7, 18.4, 14.1, 9.8, -5.2, -5.3; IR (neat, ν_{max}) 2953, 2932, 2893, 2859, 1742, 1333, 1310, 1257, 1185, 1153, 1120 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{26}\text{NaO}_5\text{SSi}$ $[\text{M}+\text{Na}]^+$ 333.1162, found 333.1164.



1-(4-bromophenyl)-2-((((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)ethan-1-one (3j)

The general procedure A with 2,4'-dibromoacetophenone (111.2 mg, 0.4 mmol) was adopted to afford the desired product as a white solid (10 min, 139.0 mg, 85% yield); R_f 0.31 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 4.75 (s, 2H), 4.58 (s, 2H), 0.92 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 187.9, 134.7, 132.5, 130.7, 130.2, 78.5, 55.6, 25.6, 18.4, -5.2; IR (neat, ν_{max}) 3008, 2955, 2929, 2889, 2857, 1680, 1584, 1309, 1283, 1259, 1156, 1131, 1114, 1069 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{23}\text{BrNaO}_4\text{SSi}$ $[\text{M}+\text{Na}]^+$ 429.0167, found 429.0165.

ii) S-Arylation of TBSOMS-Na



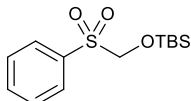
General Procedure B1

A mixture of copper(II) acetate hydrate (4.0 mg, 0.1 equiv) and NH_3 (11 μ L, 0.4 equiv, 7 N in MeOH) in 0.5 mL of dimethoxyethane was stirred under atmospheric conditions for 30 min at room temperature. To this blue solution were added TBSOMS-Na (51.1 mg, 1.1 equiv) and the corresponding iodonium salt (1.0 equiv) with 0.5 mL of dimethoxyethane as a solvent. The reaction mixture was stirred under atmospheric conditions for 1 h at room temperature. The turbid reaction mixture became clear after 5 to 10 minutes. After full conversion of the iodonium salt was confirmed by TLC analysis, 15 mL of water was then added. Organic fractions were extracted with ethyl acetate (10 mL x 3), washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 30:1 to 10:1) to afford the desired aryl sulfone product.

General Procedure B2

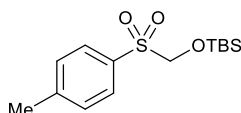
A mixture of TBSOMS-Na (116.2 mg, 0.5 mmol, 1.0 equiv), aryl iodide (1.0 mmol, 2.0 equiv), copper(I) iodide (9.6 mg, 0.05 mmol, 0.1 equiv), (2*S*,4*R*)-*N*-(2,6-dimethylphenyl)-4-hydroxypyrrolidine-2-carboxamide² (DMPHPC, 11.7 mg, 0.05 mmol, 0.1 equiv) and potassium phosphate tribasic (108.3 mg, 0.5 mmol, 1.0 equiv) in 3.2 mL of anhydrous DMSO was prepared under Ar atmosphere. The reaction mixture was stirred at 35 $^\circ\text{C}$ for 24 h. 15 mL of water was added to the mixture and organic fractions

were gathered with ethyl acetate (15 mL x 3). Combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 30:1 to 10:1) to afford the desired aryl sulfone product.



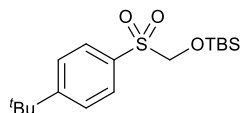
tert-butyl((phenylsulfonyl)methoxy)silane (6a)

The general procedure B1 with diphenyliodonium triflate (86.0 mg, 0.2 mmol) was adopted to afford the desired product as a colorless oil (49.8 mg, 87% yield); The general procedure B2 with iodobenzene (112 μ L, 1.0 mmol) was adopted to afford the desired product as a colorless oil (114.9 mg, 80% yield); R_f 0.29 (Hex:EA 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 7.2 Hz, 6H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 4.64 (s, 2H), 0.82 (s, 9H), 0.03 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 134.1, 129.3, 129.1, 80.3, 25.6, 18.3, -5.4; IR (neat, ν_{max}) 2953, 2930, 2892, 2858, 1586, 1472, 1464, 1447, 1329, 1303, 1256, 1155, 1129, 1082 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₃H₂₂NaO₃SSi [M+Na]⁺ 309.0957, found 309.0955.



tert-butyl((4-methylphenylsulfonyl)methoxy)silane (6b)

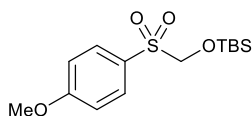
The general procedure B1 with bis(4-methylphenyl)iodonium triflate (91.6 mg, 0.2 mmol) was adopted to afford the desired product as a white solid (57.6 mg, 96% yield); The general procedure B2 with 4-iodotoluene (218.0 mg, 1.0 mmol) was adopted to afford the desired product as a white solid (115.7 mg, 77% yield); R_f 0.35 (Hex:EA 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 2H), 2.45 (s, 3H), 0.83 (s, 9H), 0.04 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.0, 134.1, 129.7, 129.3, 80.3, 25.6, 21.8, 18.3, -5.5; IR (neat, ν_{max}) 2954, 2930, 2894, 2858, 1597, 1472, 1330, 1310, 1257, 1155, 1133, 1084 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₄H₂₄NaO₃SSi [M+Na]⁺ 323.1113, found 323.1100.



tert-butyl(((4-(tert-butyl)phenyl)sulfonyl)methoxy)dimethylsilane (6c)

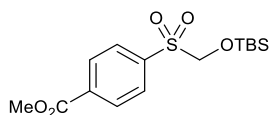
The general procedure B1 with bis(4-*tert*-butylphenyl)iodonium triflate (108.5 mg, 0.2 mmol) was adopted to afford the desired product as a clear liquid (58.6 mg, 86% yield); The general procedure B2 with 4-*tert*-butyliodobenzene (177 μ L, 1.0 mmol) was adopted to afford the desired product as a clear liquid (106.1 mg, 62% yield); R_f 0.37 (Hex:EA 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 4.62 (s, 2H), 1.35 (s, 9H), 0.81 (s, 9H), 0.02 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 158.0, 134.0, 129.2, 126.1, 80.4, 35.4, 31.2, 25.6, 18.3, -5.5; IR (neat, ν_{max}) 2958, 2931, 2899, 2858, 1595, 1329, 1306, 1157, 1135, 1183, 1106 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₇H₃₀NaO₃SSi [M+Na]⁺

[M+Na]⁺ 365.1583, found 365.1579.



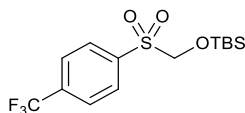
tert-butyl(((4-methoxyphenyl)sulfonyl)methoxy)dimethylsilane (6d)

The general procedure B1 with bis(4-methoxyphenyl)iodonium tetrafluoroborate (94.6 mg, 0.2 mmol) was adopted to afford the desired product as a white solid (52.7 mg, 83% yield); The general procedure B2 with 4-iodoanisole (234 mg, 1.0 mmol) was adopted to afford the desired product as a white solid (137.2 mg, 87% yield); R_f 0.58 (Hex:EA 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.58 (s, 2H), 3.86 (s, 3H), 0.82 (s, 9H), 0.02 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 164.1, 131.4, 128.5, 114.3, 80.3, 55.8, 25.6, 18.3, -5.5; IR (neat, ν_{max}) 2953, 2931, 2898, 2858, 1595, 1497, 1297, 1259, 1151, 1085, 1133, 1025 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₄H₂₄NaO₄SSi [M+Na]⁺ 339.1062, found 339.1060.



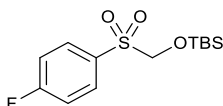
methyl 4-(((tert-butyldimethylsilyl)oxy)methyl)sulfonylbenzoate (6e)

The general procedure B1 with bis(4-methoxycarbonylphenyl)iodonium triflate (109.3 mg, 0.2 mmol) was adopted to afford the desired product as an orange solid (53.0 mg, 77% yield); The general procedure B2 with methyl 4-iodobenzoate (262.0 mg, 1.0 mmol) was adopted to afford the desired product as an orange solid (110.8 mg, 62% yield); R_f 0.24 (Hex:EA 10:1); ¹H NMR (499 MHz, CDCl₃) δ 8.23 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.3 Hz, 2H), 4.67 (s, 2H), 3.98 (s, 3H), 0.83 (s, 9H), 0.06 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 165.7, 141.1, 135.1, 130.2, 129.4, 80.3, 52.8, 25.6, 18.3, -5.4; IR (neat, ν_{max}) 3097, 3049, 2956, 2928, 2885, 2857, 1726, 1436, 1274, 1252, 1156, 1116, 1079 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₅H₂₄NaO₅SSi [M+Na]⁺ 367.1011, found 367.1010.



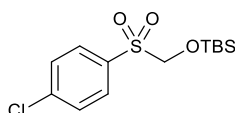
tert-butyldimethyl(((4-(trifluoromethyl)phenyl)sulfonyl)methoxy)silane (6f)

The general procedure B1 with bis(4-trifluoromethylphenyl)iodonium tetrafluoroborate (100.8 mg, 0.2 mmol) was adopted to afford the desired product as a white solid (55.7 mg, 79% yield); The general procedure B2 with 4-iodobenzotrifluoride (272.0 mg, 1.0 mmol) was adopted to afford the desired product as a white solid (90.8 mg, 51% yield); R_f 0.38 (Hex:EA 10:1); ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 4.66 (s, 2H), 0.82 (s, 9H), 0.07 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 136.0, 135.6, 129.9, 126.3, 126.2, 93.5, 80.3, 25.6, 18.3, -5.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.94; IR (neat, ν_{max}) 2955, 2932, 2893, 2860, 1403, 1320, 1130, 1086, 1060, 1017 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₄H₂₁F₃NaO₃SSi [M+Na]⁺ 377.0831, found 377.0830.



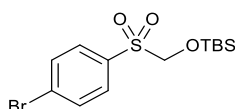
tert-butyl(((4-fluorophenyl)sulfonyl)methoxy)dimethylsilane (6g)

The general procedure B1 with bis(4-fluorophenyl)iodonium triflate (186.4 mg, 0.4 mmol, 2.0 equiv) was adopted to afford the desired product as a white solid (50.1 mg, 82% yield); The general procedure B2 with 4-fluoroiodobenzene (115 μ L, 1.0 mmol) was adopted to afford the desired product as a white solid (126.3 mg, 83% yield); R_f 0.31 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.85 (m, 2H), 7.24 – 7.16 (m, 2H), 4.58 (s, 2H), 0.79 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.5, 165.0, 133.1, 133.1, 132.2, 132.1, 116.6, 116.3, 80.3, 25.6, 18.3, -5.4; ^{19}F NMR (376 MHz, CDCl_3) δ -102.52; IR (neat, ν_{max}) 2954, 2931, 2894, 2859, 1591, 1492, 1333, 1311, 1290, 1256, 1235, 1152, 1134, 1084 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{FNaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 327.0862, found 327.0865.



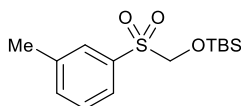
tert-butyl(((4-chlorophenyl)sulfonyl)methoxy)dimethylsilane (6h)

The general procedure B1 with bis(4-chlorophenyl)iodonium triflate (100.0 mg, 0.2 mmol) was adopted to afford the desired product as a white solid (64.0 mg, 99% yield); R_f 0.38 (Hex:EA 10:1); The general procedure B2 with 4-chloroiodobenzene (238.5 mg, 1.0 mmol) was adopted to afford the desired product as a white solid (91.7 mg, 57% yield); R_f 0.38 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 4.61 (s, 2H), 0.82 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 135.5, 130.7, 129.4, 80.3, 25.5, 18.3, -5.4; IR (neat, ν_{max}) 2954, 2931, 2892, 2858, 1583, 1474, 1332, 1310, 1257, 1157, 1133, 1085, 1014 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{ClNaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 343.0567, found 343.0568.



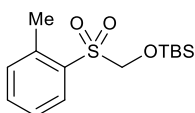
(((4-bromophenyl)sulfonyl)methoxy)(tert-butyl)dimethylsilane (6i)

The general procedure B1 with bis(4-bromophenyl)iodonium triflate (117.6 mg, 0.2 mmol) was adopted to afford the desired product as a white solid (63.9 mg, 88% yield); The general procedure B2 with 4-bromoiodobenzene (282.9 mg, 1.0 mmol) was adopted to afford the desired product as a white solid (128.3 mg, 70% yield); R_f 0.33 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 4.61 (s, 2H), 0.82 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.2, 132.5, 130.8, 130.0, 80.3, 25.6, 18.3, -5.4; IR (neat, ν_{max}) 3090, 3071, 2952, 2928, 2884, 2857, 1573, 1472, 1330, 1307, 1258, 1161, 1136, 1083, 1064 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{21}\text{BrNaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 387.0056, found 387.0061.



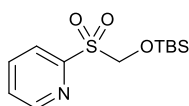
tert-butyl dimethyl((*m*-tolylsulfonyl)methoxy)silane (6j)

The general procedure B1 with bis(3-methylphenyl)iodonium tetrafluoroborate (79.2 mg, 0.2 mmol) was adopted to afford the desired product as a clear liquid (56.6 mg, 94% yield); The general procedure B2 with 3-iodotoluene (128 μ L, 1.0 mmol) was adopted to afford the desired product as a clear liquid (128.6 mg, 86% yield); R_f 0.36 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.71 (s, 1H), 7.49 – 7.40 (m, 2H), 4.62 (s, 2H), 2.44 (s, 3H), 0.83 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.3, 136.8, 134.8, 129.7, 129.0, 126.3, 80.3, 25.6, 21.3, 18.3, -5.5; IR (neat, ν_{max}) 2954, 2930, 2893, 2858, 1472, 1464, 1330, 1301, 1257, 1156, 1128, 1083 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 323.1113, found 323.1111.



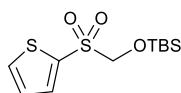
tert-butyl dimethyl((*o*-tolylsulfonyl)methoxy)silane (6k)

The general procedure B1 with bis(2-methylphenyl)iodonium tetrafluoroborate (79.2 mg, 0.2 mmol) was adopted to afford the desired product as a clear liquid (31.7 mg, 53% yield); The general procedure B2 with 2-iodotoluene (127 μ L, 1.0 mmol) was adopted to afford the desired product as a clear liquid (5.6 mg, 4% yield); R_f 0.22 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.40 – 7.30 (m, 2H), 4.68 (s, 2H), 2.70 (s, 3H), 0.79 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.3, 134.0, 132.6, 131.7, 127.6, 126.5, 80.2, 25.6, 20.9, 18.3, -5.5; IR (neat, ν_{max}) 2954, 2931, 2892, 2858, 1595, 1472, 1327, 1306, 1256, 1158, 1143, 1120, 1061 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 323.1113, found 323.1110.



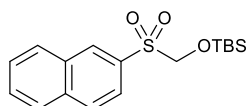
2-((((tert-butyl dimethylsilyl)oxy)methyl)sulfonyl)pyridine (6l)

The general procedure B2 with 2-iodopyridine (215.8 mg, 1.0 mmol) was adopted to afford the desired product as a white solid (123.9 mg, 86% yield); R_f 0.17 (Hex:EA 5:1); ^1H NMR (500 MHz, CDCl_3) δ 8.75 (d, J = 4.3 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.94 (t, J = 7.3 Hz, 1H), 7.54 (dd, J = 7.1, 5.0 Hz, 1H), 4.94 (s, 2H), 0.72 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.5, 150.4, 137.9, 127.5, 124.3, 76.9, 25.4, 18.1, -5.5; IR (neat, ν_{max}) 2954, 2930, 2858, 1579, 1428, 1329, 1305, 1254, 1166, 1140, 1106, 1081 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{21}\text{NO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 310.0909, found 310.0907.



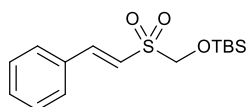
tert-butyl dimethyl((thiophen-2-ylsulfonyl)methoxy)silane (6m)

The general procedure B1 with bis(2-thiophenyl)iodonium tosylate (168.9 mg, 0.2 mmol, 55% purity) was adopted to afford the desired product as a brown liquid (30.7 mg, 53% yield); The general procedure B2 with 2-iodothiophene (102 μ L, 1.0 mmol) was adopted to afford the desired product as a brown liquid (116.2 mg, 79% yield); R_f 0.19 (Hex:EA 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, J = 4.9 Hz, 1H), 7.70 (dd, J = 3.6, 0.7 Hz, 1H), 7.19 – 7.15 (m, 1H), 4.68 (s, 2H), 0.86 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 135.3, 134.8, 127.8, 81.1, 25.7, 18.4, -5.4; IR (neat, ν_{max}) 3101, 2953, 2930, 2858, 1464, 1402, 1331, 1307, 1256, 1155, 1124, 1089, 1015 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{20}\text{NaO}_3\text{S}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 315.0521, found 315.0519.



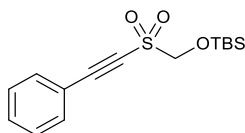
***tert*-butyldimethyl((naphthalen-2-ylsulfonyl)methoxy)silane (6n)**

The general procedure B1 with bis(2-naphthalenyl)iodonium tetrafluoroborate (93.6 mg, 0.2 mmol) was adopted to afford the desired product as a yellow oil (62.2 mg, 92% yield); The general procedure B2 with 2-iodonaphthalene (254 mg, 1.0 mmol) was adopted to afford the desired product as a yellow oil (151.5 mg, 90% yield); R_f 0.33 (Hex:EA 10:1); ^1H NMR (499 MHz, CDCl_3) δ 8.50 (s, 1H), 7.99 (t, J = 7.4 Hz, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.89 (dd, J = 8.6, 1.4 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 4.71 (s, 2H), 0.81 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 135.6, 134.1, 132.2, 131.3, 129.5, 129.4, 129.2, 128.1, 127.7, 123.8, 80.4, 25.6, 18.3, -5.4; IR (neat, ν_{max}) 3058, 2953, 2929, 2892, 2857, 1626, 1591, 1472, 1327, 1304, 1256, 1147, 1137, 1071, 1118, 1071 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{17}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 359.1113, found 359.1110.



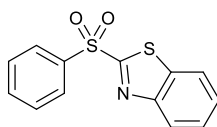
***(E)*-tert-butyl dimethyl((styrylsulfonyl)methoxy)silane (6o)**

A mixture of copper(II) acetate hydrate (8.0 mg, 0.04 mmol, 0.1 equiv) and NH_3 (22 μ L, 0.16 mmol, 0.4 equiv, 7 N in MeOH) in 0.5 mL of dimethoxyethane was stirred under atmospheric conditions for 30 min at room temperature. This blue solution was transferred to a vial charged with TBSOMS-Na (92.9 mg, 0.4 mmol, 1.0 equiv) and (*E*)-phenyl(styryl)iodonium tetrafluoroborate (173.4 mg, 0.44 mmol, 1.1 equiv). The reaction mixture was stirred under atmospheric conditions for 1 h at room temperature. The turbid reaction mixture became clear after 5 to 10 minutes. After 1 h of stirring, 15 mL of water was then added. Organic fractions were extracted with ethyl acetate (10 mL x 3), washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 30:1 to 10:1) to afford the desired alkenyl sulfone product as a yellow solid (105.0 mg, 84% yield); The general procedure B2 with (*E*)-(2-iodovinyl)benzene (230.0 mg, 1.0 mmol) was adopted to afford the desired product as a brown liquid (139.4 mg, 89% yield); R_f 0.28 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 15.6 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.46 – 7.39 (m, 2H), 6.83 (d, J = 15.6 Hz, 1H), 4.63 (s, 2H), 0.89 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.5, 132.5, 131.5, 129.2, 128.7, 122.7, 79.7, 25.6, 18.3, -5.2; IR (neat, ν_{max}) 3060, 2953, 2930, 2893, 2857, 1618, 1471, 1449, 1327, 1300, 1255, 1152, 1118 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 335.1113, found 335.1111.



tert-butyl dimethyl((phenylethynyl)sulfonyl)methoxy silane (6p)

A solution of TBSOMS-Na (51.1 mg, 0.22 mmol, 1.1 equiv) and (2-methoxyphenyl)(phenylethynyl)iodonium trifluoroacetate (89.6 mg, 0.2 mmol, 1 equiv) in 1.0 mL of dimethoxyethane was stirred under atmospheric conditions for 2 h at room temperature. After 2 h of stirring, 15 mL of water was then added. Organic fractions were extracted with ethyl acetate (10 mL x 3), washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 30:1 to 10:1) to afford the desired alkynyl sulfone product as a white solid (58.5 mg, 94% yield); *R*_f 0.14 (Hex:EA 20:1); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.36 (m, 5H), 4.86 (s, 2H), 0.92 (s, 9H), -0.09 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 131.7, 129.8, 128.6, 128.4, 123.7, 79.2, 26.7, 17.2, -6.2; IR (neat, *v*_{max}) 3054, 2949, 2930, 2899, 2885, 2859, 1614, 1471, 1303, 1290, 1250, 1137, 1110 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₅H₂₂NaO₃SSi [M+Na]⁺ 333.0957, found 333.0955.

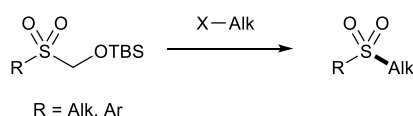


2-(phenylsulfonyl)benzo[d]thiazole

The general procedure B1 with sodium benzo[d]thiazole-2-sulfinate (48.7 mg, 0.22 mmol) and diphenyliodonium triflate (86.0 mg, 0.2 mmol) was adopted to afford the desired product as a white solid (19.2 mg, 35% yield); *R*_f 0.28 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.19 – 8.10 (m, 3H), 7.98 – 7.91 (m, 1H), 7.65 (dd, *J* = 8.5, 6.3 Hz, 1H), 7.60 – 7.46 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 152.9, 138.5, 137.0, 134.5, 129.5, 128.9, 127.9, 127.5, 125.5, 122.2. Analytical data are consistent with the previous report.³

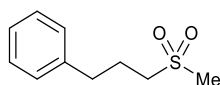
C. Modular synthesis of sulfones

i) S-Alkylation of TBSOM sulfones with alkyl halides



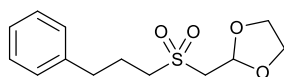
General Procedure C

A mixture of TBSOM sulfone (131.4 mg or 114.6 mg, 0.4 mmol, 1.0 equiv), alkyl halide (0.6 mmol, 1.5 equiv) and tetrabutylammonium fluoride (0.6 mL, 0.6 mmol, 1.5 equiv, 1.0 M in THF) in 1.6 mL of anhydrous DMSO was prepared under Ar atmosphere. The reaction mixture was stirred at 80 °C for 24 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 2:1) to afford the desired alkyl sulfone product.



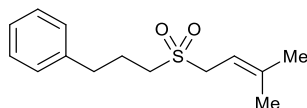
(3-(methylsulfonyl)propyl)benzene (8a)

The general procedure C with iodomethane (38 μ L, 0.60 mmol) was adopted to afford the desired product as a yellow liquid (78.0 mg, 98% yield); *R*_f 0.17 (Hex:EA 2:1); ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.20 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 3.04 – 2.92 (m, 2H), 2.86 (s, 3H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.27 – 2.11 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 139.9, 128.8, 128.5, 126.7, 54.0, 40.7, 34.3, 24.0; IR (neat, ν_{max}) 3085, 3061, 3025, 2929, 2866, 1603, 1496, 1454, 1291, 1138, 1119 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₀H₁₄O₂S [M+Na]⁺ 221.0607, found 221.0609.



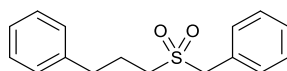
2-(((3-phenylpropyl)sulfonyl)methyl)-1,3-dioxolane (8b)

The general procedure C with 2-bromomethyl-1,3-dioxolane (63 μ L, 0.60 mmol) was adopted to afford the desired product as a yellow liquid (94.1 mg, 87% yield); *R*_f 0.27 (Hex:EA 2:1); ¹H NMR (400 MHz, CDCl₃) δ 7.30 (td, *J* = 7.3, 1.5 Hz, 2H), 7.25 – 7.14 (m, 3H), 5.26 (td, *J* = 4.9, 2.1 Hz, 1H), 4.04 – 3.82 (m, 4H), 3.25 (dd, *J* = 4.9, 1.7 Hz, 2H), 3.12 (dd, *J* = 9.0, 6.9 Hz, 2H), 2.77 (td, *J* = 7.5, 2.9 Hz, 2H), 2.26 – 2.09 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 128.7, 128.6, 126.5, 99.2, 65.3, 56.5, 53.5, 34.4, 23.5; IR (neat, ν_{max}) 3061, 3026, 2984, 2932, 2894, 1496, 1454, 1400, 1305, 1250, 1112 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₃H₁₈O₄S [M+Na]⁺ 293.0818, found 293.0820.



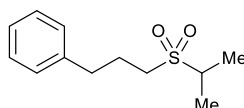
(3-((3-methylbut-2-en-1-yl)sulfonyl)propyl)benzene (8c)

The general procedure C with 3,3-dimethylallyl bromide (74 μL , 0.60 mmol) was adopted to afford the desired product as a yellow liquid (99.8 mg, 99% yield); R_f 0.53 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.25 (m, 2H), 7.22 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.4 Hz, 2H), 5.23 (td, J = 7.8, 1.3 Hz, 1H), 3.64 (d, J = 7.8 Hz, 2H), 2.96 – 2.82 (m, 2H), 2.76 (t, J = 7.3 Hz, 2H), 2.23 – 2.06 (m, 2H), 1.78 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.6, 140.0, 128.6, 128.5, 126.5, 110.4, 110.4, 53.1, 50.5, 34.3, 26.0, 23.4, 18.4; IR (neat, ν_{max}) 3085, 3061, 3027, 2973, 2922, 1496, 1452, 1300, 1246, 1115 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 275.1076, found 275.1079.



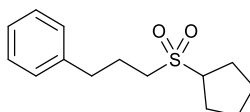
(3-(benzylsulfonyl)propyl)benzene (8d)

The general procedure C with benzyl bromide (72 μL , 0.60 mmol) was adopted to afford the desired product as a white solid (108.4 mg, 99% yield); R_f 0.50 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.17 (m, 8H), 7.12 (d, J = 7.0 Hz, 2H), 4.17 (s, 2H), 2.84 – 2.75 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H), 2.17 – 2.06 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.0, 130.6, 129.2, 129.1, 128.8, 128.6, 128.2, 126.6, 59.6, 50.2, 34.3, 23.7; IR (neat, ν_{max}) 3058, 3036, 3022, 2985, 2968, 2953, 2932, 1493, 1453, 1448, 1410, 1295, 1250, 1152, 1117, 1024 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 297.0920, found 297.0920.



(3-(isopropylsulfonyl)propyl)benzene (8e)

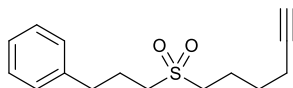
The general procedure C with isopropyl bromide (56 μL , 0.60 mmol) was adopted to afford the desired product as a yellow liquid (59.0 mg, 65% yield); R_f 0.12 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.31 (dd, J = 10.1, 4.5 Hz, 2H), 7.25 – 7.15 (m, 3H), 3.07 (hept, J = 6.9 Hz, 1H), 2.97 – 2.84 (m, 2H), 2.79 (t, J = 7.4 Hz, 2H), 2.25 – 2.13 (m, 2H), 1.36 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 128.8, 128.6, 126.6, 53.0, 48.4, 34.5, 23.1, 15.4; IR (neat, ν_{max}) 3085, 3027, 2978, 2938, 1496, 1454, 1300, 1256, 1116, 1052 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 249.0920, found 249.0921.



(3-(cyclopentylsulfonyl)propyl)benzene (8f)

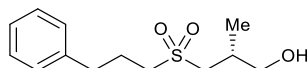
The general procedure C with bromocyclopentane (66 μL , 0.60 mmol) was adopted to afford the desired product as a yellow liquid (73.2 mg, 73% yield); R_f 0.43 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.35

– 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 3.40 – 3.28 (m, 1H), 2.97 – 2.86 (m, 2H), 2.78 (t, J = 7.4 Hz, 2H), 2.26 – 2.13 (m, 2H), 2.05 (ddd, J = 15.3, 10.5, 6.1 Hz, 2H), 1.94 (tdt, J = 9.0, 4.4, 1.6 Hz, 2H), 1.87 – 1.73 (m, 2H), 1.71 – 1.56 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.1, 128.8, 128.6, 126.6, 61.1, 50.8, 34.5, 26.8, 26.1, 23.3; IR (neat, ν_{max}) 3026, 2952, 2871, 1603, 1496, 1452, 1299, 1284, 1116 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 275.1076, found 275.1080.



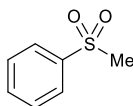
(3-(hex-5-yn-1-ylsulfonyl)propyl)benzene (8g)

The general procedure C with 6-iodo-1-hexyne (81 μL , 0.60 mmol) was adopted to afford the desired product as a white solid (104.7 mg, 99% yield); R_f 0.40 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, J = 7.4 Hz, 2H), 7.28 – 7.15 (m, 3H), 3.02 – 2.88 (m, 4H), 2.79 (t, J = 7.4 Hz, 2H), 2.24 (td, J = 6.9, 2.6 Hz, 2H), 2.18 (ddd, J = 12.8, 8.0, 5.3 Hz, 2H), 2.00 – 1.87 (m, 3H), 1.66 (dt, J = 14.4, 7.0 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 128.8, 128.6, 126.7, 83.1, 69.5, 52.4, 52.0, 34.4, 27.1, 23.6, 21.2, 18.1; IR (neat, ν_{max}) 3281, 3087, 3062, 3028, 2944, 2931, 1603, 1498, 1461, 1412, 1325, 1273, 1244, 1229, 1119 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 287.1076, found 287.1078.



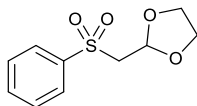
(*R*)-2-methyl-3-((3-phenylpropyl)sulfonyl)propan-1-ol (8h)

The general procedure C with (*R*)-3-bromo-2-methylpropan-1-ol (65 μL , 0.60 mmol) was adopted to afford the desired product as a colorless liquid (92.9 mg, 91% yield); R_f 0.34 (Hex:EA 1:2); ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, J = 7.4 Hz, 2H), 7.25 – 7.14 (m, 3H), 3.73 (d, J = 10.8 Hz, 1H), 3.52 – 3.40 (m, 1H), 3.20 (dd, J = 13.9, 6.0 Hz, 1H), 3.03 – 2.90 (m, 2H), 2.85 – 2.72 (m, 3H), 2.36 (qd, J = 11.5, 6.7 Hz, 1H), 2.25 – 2.07 (m, 3H), 1.12 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 128.8, 128.6, 126.7, 66.3, 55.7, 53.3, 34.4, 31.1, 23.7, 17.4; IR (neat, ν_{max}) 3475 (broad), 3062, 3027, 2927, 2876, 1496, 1454, 1287, 1117, 1066, 1037 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 279.1025, found 279.1026.



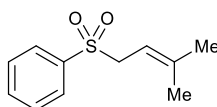
(methylsulfonyl)benzene (9a)

The general procedure C with iodomethane (38 μL , 0.60 mmol) was adopted to afford the desired product as a yellow solid (59.8 mg, 96% yield); R_f 0.29 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.95 (dd, J = 5.3, 3.3 Hz, 2H), 7.72 – 7.62 (m, 1H), 7.62 – 7.54 (m, 2H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 133.8, 129.5, 127.5, 44.6; IR (neat, ν_{max}) 3064, 3018, 2928, 1447, 1301, 1148, 1088 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_7\text{H}_8\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 179.0137, found 179.0139.



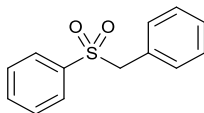
2-((phenylsulfonyl)methyl)-1,3-dioxolane (9b)

The general procedure C with 2-bromomethyl-1,3-dioxolane (63 μ L, 0.60 mmol) was adopted to afford the desired product as a colorless liquid (65.2 mg, 71% yield); R_f 0.23 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 7.9 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 5.31 (t, J = 4.7 Hz, 1H), 3.98 – 3.77 (m, 4H), 3.45 (d, J = 4.7 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.8, 134.0, 129.2, 128.3, 98.8, 98.8, 65.1, 59.9; IR (neat, ν_{max}) 3064, 2985, 2931, 2894, 1447, 1398, 1307, 1149, 1125, 1083 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}$ $[\text{M}+\text{Na}]^+$ 251.0349, found 251.0350.



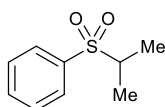
((3-methylbut-2-en-1-yl)sulfonyl)benzene (9c)

The general procedure C with 3,3-dimethylallyl bromide (74 μ L, 0.60 mmol) was adopted to afford the desired product as a yellow liquid (83.9 mg, 99% yield); R_f 0.26 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 5.19 (t, J = 8.0 Hz, 1H), 3.79 (d, J = 8.0 Hz, 2H), 1.71 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.0, 138.7, 133.6, 129.0, 128.5, 110.5, 56.2, 25.9, 17.8; IR (neat, ν_{max}) 3063, 2975, 2916, 2806, 1446, 1304, 1148, 1130, 1084 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 233.0607, found 233.0608.



(benzylsulfonyl)benzene (9d)

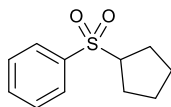
The general procedure C with benzyl bromide (72 μ L, 0.60 mmol) was adopted to afford the desired product as a white solid (58.4 mg, 63% yield); R_f 0.18 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.55 (m, 3H), 7.44 (dd, J = 11.7, 4.1 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.29 – 7.22 (m, 2H), 7.08 (d, J = 7.3 Hz, 2H), 4.31 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 138.0, 133.8, 130.9, 129.0, 128.9, 128.8, 128.7, 128.2, 63.0; IR (neat, ν_{max}) 3061, 3031, 2994, 2944, 2921, 1492, 1446, 1308, 1293, 1282, 1150, 1086 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 255.0450, found 255.0453.



(isopropylsulfonyl)benzene (9e)

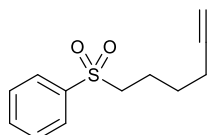
The general procedure C with isopropyl bromide (56 μ L, 0.60 mmol) was adopted to afford the desired product as a yellow liquid (49.0 mg, 66% yield); R_f 0.50 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.89

(dd, $J = 5.1, 3.9$ Hz, 2H), 7.66 (dd, $J = 8.4, 6.5$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 2H), 3.20 (hept, $J = 6.9$ Hz, 1H), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 137.1, 133.7, 129.2, 55.7, 15.8; IR (neat, ν_{max}) 3065, 1982, 2938, 2876, 1468, 1446, 1303, 1290, 1262, 1141, 1086, 1051 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_{12}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 207.0450, found 207.0451



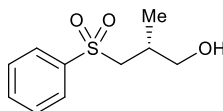
(cyclopentylsulfonyl)benzene (9f)

The general procedure C with bromocyclopentane (66 μL , 0.60 mmol) was adopted to afford the desired product as a yellow liquid (62.2 mg, 74% yield); R_f 0.53 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.90 (dd, $J = 5.1, 4.4$ Hz, 2H), 7.70 – 7.61 (m, 1H), 7.56 (t, $J = 7.8$ Hz, 2H), 3.61 – 3.39 (m, 1H), 2.07 (td, $J = 14.4, 7.2$ Hz, 2H), 1.95 – 1.71 (m, 4H), 1.62 (ddd, $J = 10.8, 8.4, 3.7$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.2, 133.6, 129.3, 128.6, 64.3, 27.4, 26.0; IR (neat, ν_{max}) 3064, 2959, 2871, 1446, 1302, 1287, 1145, 1086, 1071 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 233.0607, found 233.0609.



(hex-5-yn-1-ylsulfonyl)benzene (9g)

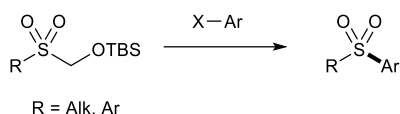
The general procedure C with 6-iodo-1-hexyne (81 μL , 0.60 mmol) was adopted to afford the desired product as a yellow liquid (89.2 mg, 99% yield); R_f 0.47 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.7$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.58 (t, $J = 7.7$ Hz, 2H), 3.17 – 3.07 (m, 2H), 2.20 (td, $J = 6.9, 2.6$ Hz, 2H), 1.93 (t, $J = 2.6$ Hz, 1H), 1.86 (tt, $J = 8.0, 6.6$ Hz, 2H), 1.68 – 1.56 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.2, 133.8, 129.4, 128.2, 83.1, 69.4, 55.9, 27.0, 22.0, 18.1; IR (neat, ν_{max}) 3283, 3064, 2940, 2872, 1447, 1304, 1291, 1148, 1086 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 245.0607, found 245.0608.



(R)-2-methyl-3-(phenylsulfonyl)propan-1-ol (9h)

The general procedure C with (*R*)-3-bromo-2-methylpropan-1-ol (65 μL , 0.60 mmol) was adopted to afford the desired product as a yellow liquid (73.8 mg, 86% yield); R_f 0.41 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.6$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.57 (t, $J = 7.7$ Hz, 2H), 3.67 (dd, $J = 10.9, 4.6$ Hz, 1H), 3.45 (dd, $J = 10.6, 6.5$ Hz, 1H), 3.38 (dd, $J = 14.1, 5.5$ Hz, 1H), 2.95 (dd, $J = 14.1, 7.1$ Hz, 1H), 2.61 (s, 1H), 2.29 (td, $J = 12.2, 6.6$ Hz, 1H), 1.07 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 133.8, 129.4, 127.8, 66.2, 59.3, 31.5, 17.1; IR (neat, ν_{max}) 3479 (broad), 3065, 2964, 2928, 2879, 1447, 1299, 1288, 1141, 1084, 1071, 1038 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 237.0556, found 237.0557.

ii) S-Arylation of TBSOM sulfones with aryl halides

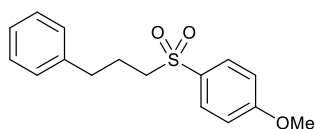


General Procedure D1

A mixture of TBSOM sulfone (131.4 mg, 0.4 mmol, 1.0 equiv), aryl halide (0.48 mmol, 1.2 equiv), copper(I) iodide (7.7 mg, 0.04 mmol, 0.1 equiv), L-proline (9.3 mg, 0.08 mmol, 0.2 equiv), sodium hydroxide (3.3 mg, 0.08 mmol, 0.2 equiv) and cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) in 0.4 mL of anhydrous DMSO was prepared under Ar atmosphere. The reaction mixture was stirred at 95 °C for 24 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 1:1) to afford the desired aryl sulfone product.

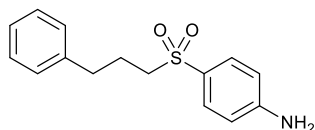
General Procedure D2

A mixture of TBSOM sulfone (131.4 mg or 114.6 mg, 0.4 mmol, 1.0 equiv), aryl halide (0.48 mmol, 1.2 equiv), copper(I) iodide (7.7 mg, 0.04 mmol, 0.1 equiv), L-proline (55.8 mg, 0.48 mmol, 1.2 equiv), sodium hydroxide (3.3 mg, 0.08 mmol, 0.2 equiv) and cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) in 0.4 mL of anhydrous DMSO was prepared under Ar atmosphere. The reaction mixture was stirred at 95 °C for 36 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 1:1) to afford the desired aryl sulfone product.



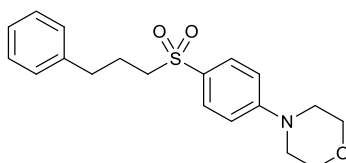
1-methoxy-4-((3-phenylpropyl)sulfonyl)benzene (11a)

The general procedure D1 with 4-iodoanisole (114.6 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (103.0 mg, 89% yield), or the general procedure D1 with 4-bromoanisole (90.7 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (91.2 mg, 78% yield); *R*_f 0.083 (Hex:EA 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.77 (m, 2H), 7.27 (dd, *J* = 8.8, 5.7 Hz, 2H), 7.20 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.14 – 7.07 (m, 2H), 7.04 – 6.96 (m, 2H), 3.88 (s, 3H), 3.10 – 3.00 (m, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.09 – 1.97 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 163.8, 140.1, 130.8, 130.4, 128.7, 128.5, 126.5, 114.6, 55.9, 55.8, 34.3, 24.5; IR (neat, *v*_{max}) 3062, 3026, 2943, 2841, 1594, 1578, 1455, 1316, 1293, 1257, 1139, 1088, 1023 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₆H₁₈O₃S [M+Na]⁺ 313.0869, found 313.0871.



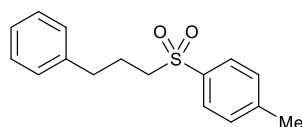
4-((3-phenylpropyl)sulfonyl)aniline (11b)

The general procedure D1 with 4-iodoaniline (107.3 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (96.9 mg, 88% yield); R_f 0.44 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.60 (m, 2H), 7.31 – 7.23 (m, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.0 Hz, 2H), 6.73 – 6.66 (m, 2H), 4.18 (s, 2H), 3.10 – 2.95 (m, 2H), 2.68 (t, J = 7.5 Hz, 2H), 2.10 – 1.95 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.5, 150.7, 140.2, 130.2, 130.2, 128.7, 128.7, 128.5, 126.5, 126.5, 114.2, 112.7, 56.0, 34.3, 24.6; IR (neat, ν_{max}) 3473, 3374, 3251, 3084, 3060, 3028, 3003, 2924, 2856, 1632, 1593, 1503, 1453, 1286, 1273, 1137, 1129, 1086 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 298.0872, found 298.0875.



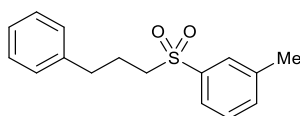
4-((3-phenylpropyl)sulfonyl)phenyl)morpholine (11c)

The general procedure D1 with 4-(4-iodophenyl)morpholine (143.1 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (124.8 mg, 90% yield); R_f 0.029 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.76 – 7.69 (m, 2H), 7.26 (dd, J = 8.0, 6.5 Hz, 2H), 7.23 – 7.16 (m, 1H), 7.14 – 7.07 (m, 2H), 6.95 – 6.88 (m, 2H), 3.91 – 3.81 (m, 4H), 3.36 – 3.26 (m, 4H), 3.09 – 2.98 (m, 2H), 2.68 (t, J = 7.5 Hz, 2H), 2.08 – 1.97 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.5, 140.2, 129.9, 128.7, 128.5, 127.8, 126.5, 113.9, 66.6, 56.0, 47.5, 34.3, 24.6; IR (neat, ν_{max}) 3061, 3026, 2962, 2917, 2855, 1592, 1506, 1451, 1293, 1268, 1245, 1142, 1123, 1091 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 368.1291, found 368.1294.



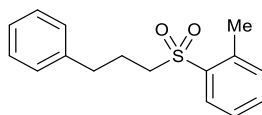
1-methyl-4-((3-phenylpropyl)sulfonyl)benzene (11d)

The general procedure D1 with 4-iodotoluene (105.7 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (97.5 mg, 89% yield); R_f 0.12 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.26 (dd, J = 8.6, 5.9 Hz, 2H), 7.19 (dd, J = 8.5, 6.1 Hz, 1H), 7.10 (d, J = 6.9 Hz, 2H), 3.10 – 3.00 (m, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.44 (s, 3H), 2.09 – 1.96 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.8, 140.0, 136.3, 130.0, 128.7, 128.5, 128.2, 126.5, 55.7, 34.2, 24.4, 21.8; IR (neat, ν_{max}) 3062, 3027, 2924, 2868, 1597, 1454, 1496, 1314, 1301, 1288, 1146, 1087 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 297.0920, found 297.0921.



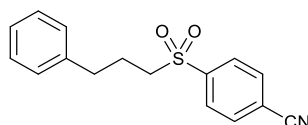
1-methyl-3-((3-phenylpropyl)sulfonyl)benzene (11e)

The general procedure D1 with 3-iodotoluene (105.7 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (96.3 mg, 88% yield); R_f 0.11 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.72 – 7.64 (m, 2H), 7.50 – 7.41 (m, 2H), 7.26 (dd, J = 9.4, 5.1 Hz, 2H), 7.19 (dd, J = 8.5, 6.1 Hz, 1H), 7.10 (d, J = 7.1 Hz, 2H), 3.11 – 3.02 (m, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.43 (s, 3H), 2.11 – 1.98 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.0, 139.7, 139.1, 134.6, 129.3, 128.7, 128.5, 128.4, 126.5, 125.3, 55.5, 34.2, 24.3, 21.5; IR (neat, ν_{max}) 3061, 3026, 2923, 2865, 1602, 1454, 1316, 1296, 1222, 1140, 1126, 1093, 1083 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 297.09120, found 297.0921.



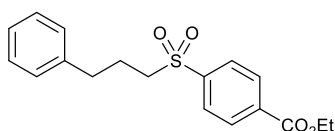
1-methyl-2-((3-phenylpropyl)sulfonyl)benzene (11f)

The general procedure D1 with 2-iodotoluene (106.8 mg, 0.48 mmol) was adopted to afford the desired product as a white liquid (96.3 mg, 69% yield), or the general procedure D1 with 2-iodotoluene (75.9 mg, 0.48 mmol) was adopted for 36 h to afford the desired product as a white liquid (84.9 mg, 77% yield); R_f 0.14 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.19 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.3 Hz, 2H), 3.15 – 3.03 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.59 (s, 3H), 2.10 – 1.98 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.0, 138.0, 137.2, 133.7, 132.8, 130.3, 128.7, 128.5, 126.7, 126.5, 54.4, 34.1, 24.0, 20.4; IR (neat, ν_{max}) 3061, 3026, 2931, 2865, 1496, 1453, 1305, 1287, 1147, 1212, 1060 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 297.0920, found 297.0922.



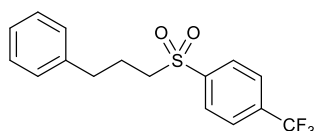
4-((3-phenylpropyl)sulfonyl)benzonitrile (11g)

The general procedure D1 with 4-iodobenzonitrile (113.3 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (86.0 mg, 75% yield); R_f 0.15 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.04 – 7.96 (m, 2H), 7.90 – 7.82 (m, 2H), 7.33 – 7.25 (m, 2H), 7.25 – 7.18 (m, 1H), 7.09 (d, J = 6.9 Hz, 2H), 3.16 – 3.04 (m, 2H), 2.72 (t, J = 7.4 Hz, 2H), 2.05 (dq, J = 12.7, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.3, 139.5, 133.2, 128.9, 128.8, 128.5, 126.8, 117.7, 117.2, 55.3, 34.1, 24.2; IR (neat, ν_{max}) 3087, 3063, 3039, 3026, 2984, 2944, 2923, 2868, 2241, 1494, 1454, 1402, 1320, 1308, 1277, 1148, 1085, 1023 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 308.0716, found 308.0721.



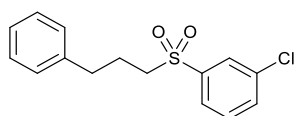
ethyl 4-((3-phenylpropyl)sulfonyl)benzoate (11h)

The general procedure D1 with ethyl 4-iodobenzoate (135.2 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (102.4 mg, 77% yield), or the general procedure D1 with ethyl 4-bromobenzoate (112.2 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (102.2 mg, 77% yield); R_f 0.11 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.2 Hz, 2H), 7.27 (dd, J = 9.1, 5.4 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 3.15 – 3.03 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.11 – 1.98 (m, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 142.9, 139.8, 135.4, 130.5, 128.8, 128.5, 128.3, 126.7, 62.0, 55.5, 34.2, 24.3, 14.4; IR (neat, ν_{max}) 3103, 3085, 3061, 3030, 3024, 3000, 2989, 2962, 2942, 2924, 2908, 2868, 2856, 1715, 1403, 1316, 1295, 1273, 1151, 1117, 1084, 1020 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_4\text{S}$ $[\text{M}+\text{Na}]^+$ 355.0975, found 355.0977.



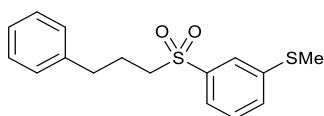
1-((3-phenylpropyl)sulfonyl)-4-(trifluoromethyl)benzene (11i)

The general procedure D1 with 1-iodo-4-(trifluoromethyl)benzene (134.6 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (112.7 mg, 86% yield); R_f 0.31 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H), 7.20 (dd, J = 8.6, 6.0 Hz, 1H), 7.09 (d, J = 7.1 Hz, 2H), 3.16 – 3.05 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H), 2.06 (dq, J = 12.7, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 142.7, 139.7, 135.7, 135.4, 128.8, 128.8, 128.5, 126.7, 126.6, 126.6, 126.6, 126.5, 124.6, 121.9, 55.4, 34.1, 24.2; ^{19}F NMR (376 MHz, CDCl_3) δ -63.12; IR (neat, ν_{max}) 3087, 3032, 2934, 2896, 1497, 1455, 1402, 1326, 1292, 1282, 1157, 1144, 1125, 1087, 1064, 1015 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 351.0637, found 351.0638.



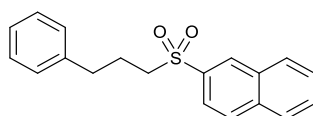
1-chloro-3-((3-phenylpropyl)sulfonyl)benzene (11j)

The general procedure D1 with 1-chloro-3-iodobenzene (118.0 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (103.9 mg, 88% yield); R_f 0.11 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.87 (t, J = 1.8 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.62 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.21 (dd, J = 8.6, 6.0 Hz, 1H), 7.15 – 7.06 (m, 2H), 3.13 – 3.03 (m, 2H), 2.71 (t, J = 7.4 Hz, 2H), 2.12 – 1.99 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.0, 139.8, 135.7, 134.0, 130.7, 128.8, 128.5, 128.3, 126.7, 126.3, 55.5, 34.2, 24.2; IR (neat, ν_{max}) 3088, 3063, 3024, 2981, 2875, 1578, 1496, 1460, 1408, 1320, 1284, 1254, 1149, 1108, 1077, 1030 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{ClO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 317.0374, found 317.0376.



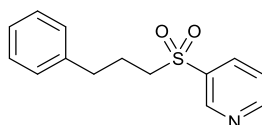
methyl(3-((3-phenylpropyl)sulfonyl)phenyl)sulfane (11l)

The general procedure D1 with 3-bromothioanisole (99.5 mg, 0.48 mmol) was adopted to afford the desired product as a yellow liquid (114.5 mg, 94% yield); R_f 0.091 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.60 (d, J = 7.3 Hz, 1H), 7.52 – 7.40 (m, 2H), 7.27 (dd, J = 10.3, 4.1 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 2H), 3.12 – 3.01 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.52 (s, 3H), 2.06 (dq, J = 15.4, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 141.5, 139.9, 139.9, 131.2, 129.6, 128.7, 128.5, 126.6, 124.8, 124.2, 55.5, 34.2, 24.2, 15.5; IR (neat, ν_{max}) 3061, 3026, 2922, 2865, 1579, 1439, 1454, 1313, 1295, 1149, 1110, 1082 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2$ $[\text{M}+\text{Na}]^+$ 329.0640, found 329.0643.



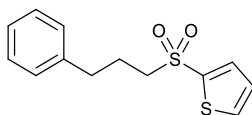
2-((3-phenylpropyl)sulfonyl)naphthalene (11m)

The general procedure D1 with 2-bromonaphthalene (102.5 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (107.2 mg, 86% yield); R_f 0.24 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.46 (s, 1H), 8.06 – 7.95 (m, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.83 (dd, J = 8.6, 1.7 Hz, 1H), 7.72 – 7.58 (m, 2H), 7.24 (dd, J = 9.6, 4.7 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.1 Hz, 2H), 3.21 – 3.11 (m, 2H), 2.69 (t, J = 7.5 Hz, 2H), 2.08 (dq, J = 12.8, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 136.1, 135.4, 132.3, 130.0, 129.7, 129.5, 129.4, 128.7, 128.5, 128.1, 127.8, 126.5, 122.8, 55.6, 34.2, 24.4; IR (neat, ν_{max}) 3058, 3026, 2944, 2928, 2868, 1495, 1317, 1282, 1147, 1127, 1074, 1027 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 333.0920, found 333.0921.



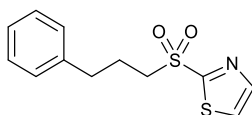
3-((3-phenylpropyl)sulfonyl)pyridine (11o)

The general procedure D1 with 3-bromopyridine (77.4 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (81.9 mg, 78% yield); R_f 0.059 (Hex:EA 3:1); ^1H NMR (400 MHz, CDCl_3) δ 9.10 (d, J = 2.1 Hz, 1H), 8.88 (dd, J = 4.8, 1.3 Hz, 1H), 8.16 (dt, J = 8.0, 1.8 Hz, 1H), 7.51 (dd, J = 8.0, 4.9 Hz, 1H), 7.27 (dd, J = 10.4, 4.1 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.2 Hz, 2H), 3.16 – 3.07 (m, 2H), 2.73 (t, J = 7.4 Hz, 2H), 2.08 (dq, J = 12.7, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.4, 149.3, 139.6, 136.0, 135.7, 128.8, 128.5, 126.7, 124.0, 55.9, 34.1, 24.2; IR (neat, ν_{max}) 3083, 3062, 3026, 2987, 2944, 2923, 2868, 1573, 1496, 1454, 1415, 1310, 1195, 1152, 1119, 1101, 1020 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 284.0716, found 284.0717.



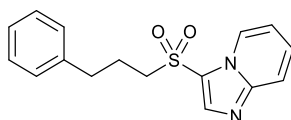
2-((3-phenylpropyl)sulfonyl)thiophene (11p)

The general procedure D2 with 2-bromothiophene (50 μ L, 0.48 mmol) was adopted to afford the desired product as a yellow liquid (92.7 mg, 87% yield); R_f 0.20 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, J = 5.0, 1.3 Hz, 1H), 7.66 (dd, J = 3.8, 1.3 Hz, 1H), 7.28 (t, J = 7.3 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.17 – 7.08 (m, 3H), 3.24 – 3.13 (m, 2H), 2.72 (t, J = 7.5 Hz, 2H), 2.17 – 2.05 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.2, 139.9, 134.2, 134.1, 128.7, 128.5, 128.0, 126.6, 57.0, 34.1, 24.7; IR (neat, ν_{max}) 3091, 3062, 3027, 2944, 2923, 2867, 1602, 1506, 1496, 1454, 1402, 1312, 1225, 1141, 1126, 1090, 1017 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}_2$ $[\text{M}+\text{Na}]^+$ 289.0327, found 289.0331.



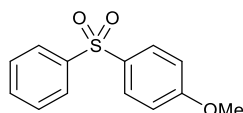
2-((3-phenylpropyl)sulfonyl)thiazole (11q)

The general procedure D2 with 2-bromothiazole (81.2 mg, 0.48 mmol) was adopted to afford the desired product as a colorless liquid (75.8 mg, 71% yield); R_f 0.12 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.04 (d, J = 3.0 Hz, 1H), 7.73 (d, J = 3.0 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.21 (dd, J = 10.4, 4.2 Hz, 1H), 7.14 (d, J = 7.1 Hz, 2H), 3.45 – 3.36 (m, 2H), 2.76 (t, J = 7.5 Hz, 2H), 2.23 – 2.09 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 145.3, 139.7, 128.8, 128.5, 126.7, 126.2, 54.2, 34.1, 24.0; IR (neat, ν_{max}) 3111, 3088, 3062, 3027, 2930, 2865, 1602, 1496, 1473, 1454, 1363, 1322, 1313, 1168, 1137, 1060 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{S}_2$ $[\text{M}+\text{Na}]^+$ 290.0280, found 290.0282.



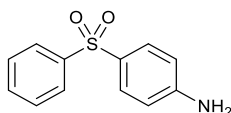
3-((3-phenylpropyl)sulfonyl)imidazo[1,2-a]pyridine (11r)

The general procedure D2 with 3-bromoimidazo[1,2-a]pyridine (97.5 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (92.4 mg, 77% yield); R_f 0.21 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, J = 6.9 Hz, 1H), 8.19 (s, 1H), 7.77 (d, J = 9.1 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.24 (dd, J = 14.8, 7.9 Hz, 3H), 7.16 (dd, J = 8.6, 5.9 Hz, 3H), 7.05 (t, J = 6.3 Hz, 3H), 3.23 – 3.12 (m, 2H), 2.70 (t, J = 7.4 Hz, 2H), 2.16 – 2.02 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 141.6, 141.6, 140.0, 128.7, 128.4, 128.3, 126.6, 125.9, 119.7, 118.8, 115.1, 55.9, 33.9, 24.3; IR (neat, ν_{max}) 3112, 3061, 3027, 2933, 2866, 1635, 1497, 1452, 1320, 1302, 1271, 1151, 1139, 1121, 1029 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 323.0825, found 323.0825.



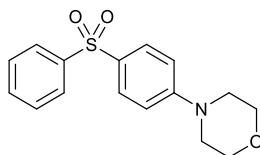
1-methoxy-4-(phenylsulfonyl)benzene (12a)

The general procedure D2 with 4-iodoanisole (114.6 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (82.9 mg, 83% yield); The general procedure D2 with 4-bromoanisole (89.8 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (21.2 mg, 21% yield); R_f 0.17 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.79 (m, 4H), 7.62 – 7.41 (m, 3H), 7.05 – 6.87 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.5, 142.5, 133.3, 133.0, 130.0, 129.3, 127.5, 114.6, 55.8; IR (neat, ν_{max}) 3097, 3064, 3007, 2966, 2944, 1841, 1592, 1577, 1496, 1445, 1317, 1298, 1258, 1147, 1104, 1071, 1021 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 271.0399, found 271.0401.



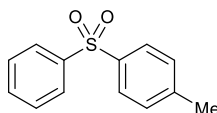
4-(phenylsulfonyl)aniline (12b)

The general procedure D2 with 4-iodoaniline (107.3 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (56.9 mg, 61% yield); R_f 0.43 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.83 (m, 2H), 7.70 (t, J = 5.7 Hz, 2H), 7.60 – 7.40 (m, 3H), 6.65 (d, J = 8.7 Hz, 2H), 4.16 (s, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.1, 143.1, 132.6, 130.0, 129.6, 129.2, 127.2, 114.3; IR (neat, ν_{max}) 3463, 3377, 3256, 3061, 1640, 1594, 1502, 1445, 1323, 1293, 1286, 1147, 1107, 1071 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 256.0403, found 256.0404.



4-(4-(phenylsulfonyl)phenyl)morpholine (12c)

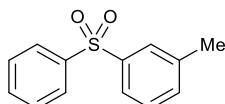
The general procedure D2 with 4-(4-iodophenyl)morpholine (143.1 mg, 0.48 mmol) was adopted to afford the desired product as a yellow solid (100.2 mg, 83% yield); R_f 0.44 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.87 (m, 2H), 7.80 (d, J = 9.0 Hz, 2H), 7.60 – 7.41 (m, 3H), 6.88 (d, J = 9.0 Hz, 2H), 3.91 – 3.74 (m, 4H), 3.36 – 3.19 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.2, 142.9, 132.7, 130.2, 129.6, 129.2, 127.3, 113.9, 66.6, 47.5; IR (neat, ν_{max}) 3062, 2964, 2893, 2851, 1588, 1504, 1445, 1382, 1297, 1267, 1244, 1148, 1121, 1102, 1071, 1051, 1025 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 326.0821, found 326.0823.



1-methyl-4-(phenylsulfonyl)benzene (12d)

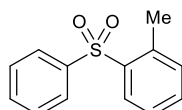
The general procedure D2 with 4-iodotoluene (105.7 mg, 0.48 mmol) was adopted to afford the desired product as a yellow solid (72.7 mg, 78% yield); R_f 0.15 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.02 – 7.89 (m, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.63 – 7.40 (m, 3H), 7.40 – 7.21 (m, 2H), 2.39 (s, 3H); ^{13}C

NMR (101 MHz, CDCl₃) δ 144.3, 142.1, 138.8, 133.1, 130.0, 129.3, 127.9, 127.6, 21.7; IR (neat, ν_{\max}) 3064, 2926, 1593, 1447, 1318, 1307, 1294, 1153, 1106, 1070 cm⁻¹; HRMS (ESI) m/z calcd. for C₁₃H₁₂O₂S [M+Na]⁺ 255.0450 found 255.0450.



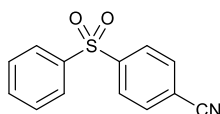
1-methyl-3-(phenylsulfonyl)benzene (12e)

The general procedure D2 with 3-iodotoluene (104.7 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (65.9 mg, 71% yield); R_f 0.27 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.3 Hz, 2H), 7.74 (d, J = 6.3 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.41 – 7.32 (m, 2H), 2.38 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 141.8, 141.5, 139.6, 134.1, 133.2, 129.3, 129.2, 128.0, 127.7, 124.9, 21.4. Analytical data are consistent with the previous report.³



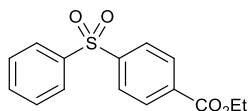
1-methyl-2-(phenylsulfonyl)benzene (12f)

The general procedure D2 with 2-iodotoluene (104.7 mg, 0.48 mmol) was adopted to afford the desired product as an orange oil (37.3 mg, 40% yield); R_f 0.31 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.39 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 141.4, 138.9, 138.1, 133.7, 133.1, 132.8, 129.5, 129.1, 127.7, 126.6, 20.3. Analytical data are consistent with the previous report.³



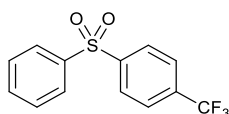
4-(phenylsulfonyl)benzonitrile (12g)

The general procedure D2 with 4-iodobenzonitrile (113.3 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (57.3 mg, 59% yield); R_f 0.17 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.5 Hz, 2H), 7.99 – 7.92 (m, 2H), 7.84 – 7.77 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 146.0, 140.3, 134.2, 133.2, 129.8, 128.4, 128.1, 117.3, 117.1; IR (neat, ν_{\max}) 3093, 3067, 3043, 2234, 1446, 1323, 1309, 1286, 1182, 1155, 1102, 1070 cm⁻¹; HRMS (ESI) m/z calcd. for C₁₃H₉NO₂S [M+Na]⁺ 266.0246, found 266.0247.



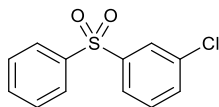
ethyl 4-(phenylsulfonyl)benzoate (12h)

The general procedure D2 with ethyl 4-iodobenzoate (135.2 mg, 0.48 mmol) was adopted to afford the desired product as a yellow liquid (77.1 mg, 66% yield); The general procedure D2 with ethyl 4-bromobenzoate (110.0 mg, 0.48 mmol) was adopted to afford the desired product as a yellow oil (69.9 mg, 60% yield); R_f 0.25 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.3 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.59 (dd, J = 10.6, 4.1 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.1, 145.5, 141.0, 134.8, 133.7, 130.5, 129.6, 128.0, 127.8, 61.9, 14.4; IR (neat, ν_{max}) 3094, 3066, 2983, 2938, 1717, 1446, 1398, 1323, 1271, 1156, 1096, 1070, 1016 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_4\text{S}$ $[\text{M}+\text{Na}]^+$ 313.0505 found 313.0507.



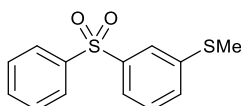
1-(phenylsulfonyl)-4-(trifluoromethyl)benzene (12i)

The general procedure D2 with 1-iodo-4-(trifluoromethyl)benzene (134.6 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (61.4 mg, 54% yield); R_f 0.18 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.2 Hz, 2H), 8.00 – 7.93 (m, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.4, 140.7, 135.1, 134.8, 133.9, 129.7, 128.3, 128.0, 126.6, 126.6, 126.6, 126.5, 124.6, 121.9; ^{19}F NMR (376 MHz, CDCl_3) δ -63.14; IR (neat, ν_{max}) 3101, 3067, 1447, 1403, 1319, 1296, 1156, 1128, 1105, 1060, 1016 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_9\text{F}_3\text{O}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 309.0168, found 309.0170.



1-chloro-3-(phenylsulfonyl)benzene (12j)

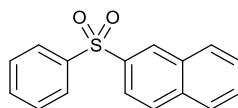
The general procedure D2 with 1-chloro-3-iodobenzene (118.0 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (66.9 mg, 66% yield); R_f 0.15 (Hex:EA 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.90 (m, 3H), 7.86 – 7.80 (m, 1H), 7.60 (dd, J = 8.5, 6.2 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.45 (t, J = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.5, 141.0, 135.6, 133.7, 133.5, 130.7, 129.6, 128.0, 127.9, 125.9; IR (neat, ν_{max}) 3068, 1581, 1460, 1445, 1411, 1317, 1306, 1289, 1153, 1120, 1089, 1069, 1023 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_9\text{ClO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 274.9904, found 274.9905.



methyl(3-(phenylsulfonyl)phenyl)sulfane (12l)

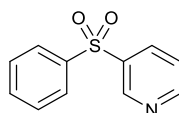
The general procedure D2 with 3-bromothioanisole (97.5 mg, 0.48 mmol) was adopted to afford the desired product as a pale yellow oil (66.8 mg, 63% yield); R_f 0.15 (Hex:EA 5:1); ^1H NMR (400 MHz,

CDCl₃) δ 7.94 (d, J = 7.4 Hz, 2H), 7.78 (s, 1H), 7.68 – 7.63 (m, 1H), 7.56 (t, J = 7.3 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.40 – 7.36 (m, 2H), 2.49 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 142.3, 141.4, 141.3, 133.4, 130.6, 129.6, 129.4, 127.7, 124.5, 123.9, 15.5. IR (neat, ν_{max}) 3063, 2922, 1578, 1446, 1317, 1306, 1157, 1122, 1093, 1072 cm⁻¹; HRMS (ESI) m/z calcd. for C₁₃H₁₂O₂S₂ [M+Na]⁺ 287.0176, found 287.0175.



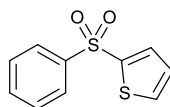
2-(phenylsulfonyl)naphthalene (12m)

The general procedure D2 with 2-bromonaphthalene (99.4 mg, 0.48 mmol) was adopted to afford the desired product as an orange solid (89.5 mg, 83% yield); R_f 0.23 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 8.01 (d, J = 7.1 Hz, 2H), 7.95 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.59 (dq, J = 14.4, 7.0 Hz, 2H), 7.54 – 7.44 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 138.5, 135.0, 133.3, 132.3, 129.7, 129.4, 129.4, 129.2, 129.1, 128.0, 127.8, 127.7, 122.7. Analytical data are consistent with the previous report.⁴



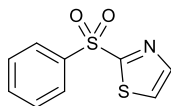
3-(phenylsulfonyl)pyridine (12o)

The general procedure D2 with 3-bromopyridine (48 μ L, 0.48 mmol) was adopted to afford the desired product as a white solid (63.3 mg, 72% yield); R_f 0.086 (Hex:EA 3:1); ¹H NMR (400 MHz, CDCl₃) δ 9.15 (d, J = 1.9 Hz, 1H), 8.79 (dd, J = 4.8, 1.3 Hz, 1H), 8.27 – 8.18 (m, 1H), 8.04 – 7.93 (m, 2H), 7.62 (dd, J = 8.5, 6.2 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H), 7.45 (dd, J = 8.0, 4.8 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 153.8, 148.9, 140.9, 138.5, 135.4, 134.0, 129.7, 127.9, 124.0; IR (neat, ν_{max}) 3062, 2924, 1572, 1467, 1446, 1415, 1311, 1295, 1197, 1159, 1123, 1110, 1078, 1018 cm⁻¹; HRMS (ESI) m/z calcd. for C₁₁H₉NO₂S [M+Na]⁺ 242.0246, found 242.0247.



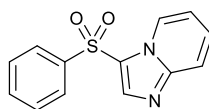
2-(phenylsulfonyl)thiophene (12p)

The general procedure D2 with 2-bromothiophene (50 μ L, 0.48 mmol) was adopted to afford the desired product as a white solid (78.5 mg, 87% yield); R_f 0.23 (Hex:EA 5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.96 (m, 2H), 7.70 (dd, J = 3.8, 1.2 Hz, 1H), 7.65 (dd, J = 4.9, 1.0 Hz, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.09 (dd, J = 4.8, 4.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 142.2, 134.0, 133.5, 133.4, 129.4, 128.0, 127.4; IR (neat, ν_{max}) 3118, 3085, 3072, 1582, 1505, 1447, 1398, 1319, 1309, 1229, 1149, 1102, 1079, 1013 cm⁻¹; HRMS (ESI) m/z calcd. for C₁₀H₈O₂S₂ [M+Na]⁺ 246.9858, found 246.9859.



2-(phenylsulfonyl)thiazole (12q)

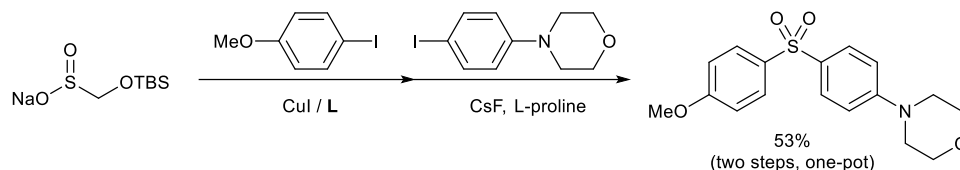
The general procedure D2 with 2-bromothiazole (44 μ L, 0.48 mmol) was adopted to afford the desired product as a white solid (64.9 mg, 72% yield); R_f 0.26 (Hex:EA 3:1); ^1H NMR (400 MHz, CDCl_3) δ 8.16 – 8.08 (m, 2H), 7.97 (d, J = 3.0 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.58 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.3, 145.5, 139.0, 134.5, 129.6, 128.8, 126.0; IR (neat, ν_{max}) 3117, 3093, 3068, 2582, 1472, 1447, 1363, 1328, 1311, 1168, 1148, 1093, 1051 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_7\text{NO}_2\text{S}_2$ $[\text{M}+\text{Na}]^+$ 247.9810, found 247.9812.



3-(phenylsulfonyl)imidazo[1,2-a]pyridine (12r)

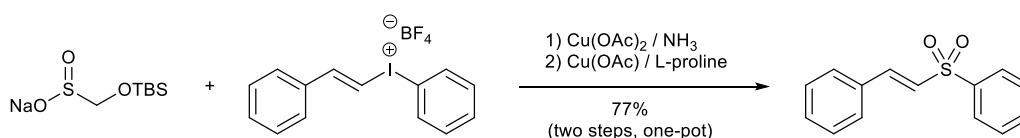
The general procedure D2 with 3-bromoimidazo[1,2-a]pyridine (97.5 mg, 0.48 mmol) was adopted to afford the desired product as a white solid (90.1 mg, 87% yield); R_f 0.21 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, J = 6.9 Hz, 1H), 8.33 (s, 1H), 8.00 (d, J = 7.4 Hz, 2H), 7.73 (d, J = 9.1 Hz, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.48 – 7.39 (m, 1H), 7.04 (t, J = 6.9 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 141.2, 141.0, 133.8, 129.6, 128.2, 127.1, 125.6, 121.8, 118.7, 115.0; IR (neat, ν_{max}) 3112, 1635, 1496, 1464, 1446, 1319, 1304, 1272, 1149, 1129, 1085 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 259.0536, found 259.0538.

D. Streamlined synthesis of unsymmetrical sulfones



4-(4-((4-methoxyphenyl)sulfonyl)phenyl)morpholine (13)

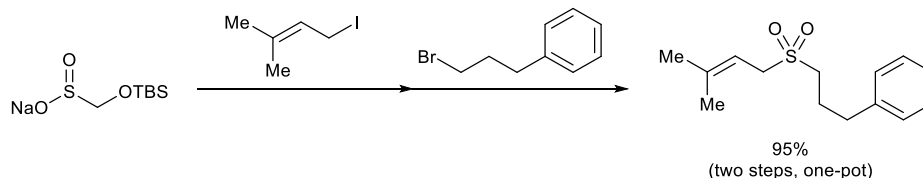
A mixture of TBSOMS-Na (116.2 mg, 0.5 mmol, 1.0 equiv), iodoanisole (155.2 mg, 0.65 mmol, 1.3 equiv), copper(I) iodide (9.6 mg, 0.05 mmol, 0.1 equiv), (2*S*,4*R*)-*N*-(2,6-dimethylphenyl)-4-hydroxypyrrolidine-2-carboxamide² (DMPHPC, 11.7 mg, 0.05 mmol, 0.1 equiv) and potassium phosphate tribasic (108.3 mg, 0.5 mmol, 1.0 equiv) in 3.2 mL of anhydrous DMSO was prepared under Ar atmosphere. The reaction mixture was stirred at 35 °C for 24 h. To the mixture were then added 4-(4-iodophenyl)morpholine (178.8 mg, 0.6 mmol, 1.2 equiv), L-proline (69.8 mg, 0.6 mmol, 1.2 equiv), sodium hydroxide (4.1 mg, 0.1 mmol, 0.2 equiv) and cesium fluoride (114.0 mg, 0.75 mmol, 1.5 equiv). The reaction mixture was stirred at 95 °C for 36 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 5:1 to 1:1) to afford the desired unsymmetrical diaryl sulfone product as a white solid (88.7 mg, 53% yield); *R*_f 0.29 (Hex:EA=1:1); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.90 – 3.72 (m, 7H), 3.32 – 3.18 (m, 4H); ¹³C NMR (101 MHz, cdcl₃) δ 163.0, 154.0, 134.6, 131.1, 129.4, 129.2, 114.4, 114.0, 66.6, 55.7, 47.6; IR (neat, *v*_{max}) 3097, 3074, 2964, 2896, 2839, 1589, 1497, 1448, 1382, 1292, 1258, 1243, 1177, 1144, 1101, 1075 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₇H₁₉NO₄S [M+Na]⁺ 356.0927, found 356.0928.



(*E*)-2-(phenylsulfonyl)vinylbenzene (14)

A mixture of copper(II) acetate hydrate (4.0 mg, 0.02 mmol, 0.1 equiv) and NH₃ (11 μL, 0.08 mmol, 0.4 equiv, 7 N in MeOH) in 0.4 mL of dimethoxyethane was stirred under atmospheric conditions for 30 min at room temperature. This blue solution was transferred to a vial charged with TBSOMS-Na (46.5 mg, 0.2 mmol, 1.0 equiv) and (*E*)-phenyl(styryl)iodonium tetrafluoroborate (86.7 mg, 0.22 mmol, 1.1 equiv). The reaction mixture was stirred under atmospheric conditions for 1 h at room temperature. After 1 h of stirring, solvent was removed under a flow of nitrogen gas. To the same vial were added copper(I) acetate (2.5 mg, 0.02 mmol, 0.1 equiv), L-proline (23.0 mg, 0.2 mmol, 1.0 equiv), tetrabutylammonium fluoride (0.3 mL, 0.3 mmol, 1.5 equiv, 1 M in THF) and 0.4 mL of anhydrous DMSO as solvent. The reaction mixture was stirred at 95 °C for 36 h under Ar atmosphere. After the reaction mixture was cooled to room temperature, 15 mL of water was added. Organic fractions were extracted with ethyl acetate (10 mL x 3), washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (Hex:EA = 30:1 to 10:1) to afford the desired unsymmetrical sulfone product as a brown liquid (37.6 mg, 77% yield); *R*_f 0.15 (Hex:EA = 10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.92 (m, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.62 (ddd, *J* = 7.4, 4.2, 1.3 Hz,

¹H), 7.57 – 7.53 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.34 (m, 3H), 6.87 (d, *J* = 15.4 Hz, 1H); ¹³C NMR (101 MHz, cdcl₃) δ 142.4, 140.6, 133.3, 132.3, 131.2, 129.3, 129.0, 128.5, 127.6, 127.2. Analytical data are consistent with the previous report.⁵

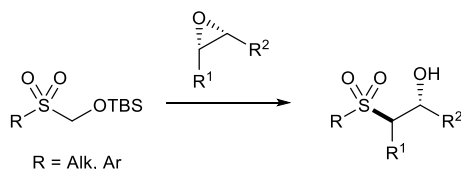


(3-((3-methylbut-2-en-1-yl)sulfonyl)propyl)benzene (8c)

A mixture of TBSOMS-Na (3.4852 g, 15 mmol, 1.5 equiv) and 1-bromo-3-methyl-2-butene (1.64 g, 10 mmol, 1 equiv) in 40 mL of anhydrous DMSO was stirred at room temperature for 1 h under N₂ atmosphere. To the mixture were then added tetrabutylammonium fluoride (15 mL, 15 mmol, 1.5 equiv, 1.0 M in THF) and 3-bromo-1-phenylpropane (2.28 mL, 15 mmol, 1.5 equiv). The reaction mixture was stirred at 80 °C for 24 h. After the reaction mixture was cooled to room temperature, 100 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (50 mL x 3), washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 10:1 to 5:1) to afford the desired unsymmetrical dialkyl sulfone product as a clear oil (2.4004 g, 95% yield); *R*_f 0.53 (Hex:EA 2:1); ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.25 (m, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 2H), 5.23 (td, *J* = 7.8, 1.3 Hz, 1H), 3.64 (d, *J* = 7.8 Hz, 2H), 2.96 – 2.82 (m, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.23 – 2.06 (m, 2H), 1.78 (s, 3H), 1.67 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 142.6, 140.0, 128.6, 128.5, 126.5, 110.4, 110.4, 53.1, 50.5, 34.3, 26.0, 23.4, 18.4; IR (neat, *v*_{max}) 3085, 3061, 3027, 2973, 2922, 1496, 1452, 1300, 1246, 1115 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₄H₂₀O₂S [M+Na]⁺ 275.1076, found 275.1079.

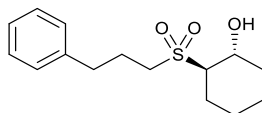
E. Synthesis of sulfonyl derivatives

i) S-Alkylation of TBSOM sulfones with epoxides



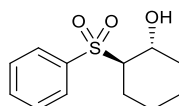
General Procedure E

A mixture of TBSOM sulfone (131.4 mg or 114.6 mg, 0.4 mmol, 1.0 equiv), cyclohexene oxide (81 μL , 0.6 mmol, 1.5 equiv) and cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) in 0.8 mL of H_2O was prepared under Ar atmosphere. The reaction mixture was stirred at 90 $^\circ\text{C}$ for 24 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 1:1) to afford the desired alkyl sulfone product.



(1*RS*,2*RS*)-2-((3-phenylpropyl)sulfonyl)cyclohexan-1-ol (15)

The general procedure E with TBSOM sulfone (131.4 mg, 0.4 mmol) was adopted to afford the desired product as a white solid (85.7 mg, 76% yield); R_f 0.17 (Hex:EA 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.29 (t, $J = 7.5$ Hz, 2H), 7.21 (d, $J = 7.3$ Hz, 1H), 7.18 (d, $J = 7.5$ Hz, 2H), 3.94 (td, $J = 10.2, 4.7$ Hz, 1H), 3.39 (s, 1H), 3.14 – 3.08 (m, 2H), 2.86 – 2.79 (m, 1H), 2.76 (t, $J = 7.5$ Hz, 2H), 2.23 – 2.15 (m, 1H), 2.14 – 2.02 (m, 2H), 1.82 (d, $J = 13.2$ Hz, 2H), 1.75 (dd, $J = 12.2, 2.2$ Hz, 2H), 1.47 (qd, $J = 13.0, 3.8$ Hz, 1H), 1.39 – 1.15 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 140.1, 128.7, 128.5, 126.5, 69.0, 66.4, 52.9, 35.0, 34.4, 24.7, 24.1, 23.9, 23.1; IR (neat, ν_{max}) 3469 (broad), 3085, 3061, 3026, 2934, 2860, 1603, 1496, 1452, 1293, 1273, 1117, 1064 cm^{-1} ; HRMS (ESI) m/z calcd. for $[\text{M}+\text{Na}]^+$ 263.0718, found 263.0711.

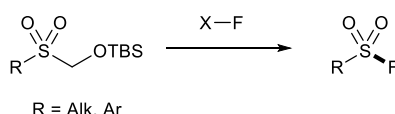


(1*RS*,2*RS*)-2-(phenylsulfonyl)cyclohexan-1-ol (16)

The general procedure E with TBSOM sulfone (114.6 mg, 0.4 mmol) was adopted to afford the desired product as a white solid (71.3 mg, 74% yield); R_f 0.23 (Hex:EA 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.91

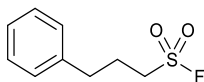
(d, $J = 7.5$ Hz, 2H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 2H), 4.29 (s, 1H), 3.92 (td, $J = 10.2$, 4.9 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.13 (dd, $J = 9.5$, 4.0 Hz, 1H), 1.93 – 1.89 (m, 1H), 1.72 (dd, $J = 7.9$, 1.8 Hz, 2H), 1.40 – 1.24 (m, 2H), 1.18 (ddd, $J = 12.2$, 9.3, 2.4 Hz, 2H). ; ^{13}C NMR (126 MHz, CDCl_3) δ 137.1, 134.1, 129.3, 129.1, 69.1, 68.4, 34.3, 25.8, 24.6, 23.7; IR (neat, ν_{max}) 3506 (broad), 3064, 2937, 2862, 1584, 1447, 1301, 1280, 1139, 1086, 1066 cm^{-1} ; HRMS (ESI) m/z calcd. for $[\text{M}+\text{Na}]^+$ 305.1187, found 305.1183.

ii) S-Fluorination of TBSOM sulfones with fluorinating reagents



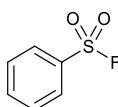
General Procedure F

A mixture of TBSOM sulfone (131.4 mg or 114.6 mg, 0.4 mmol, 1.0 equiv), fluoride (0.6 mmol, 1.5 equiv.) and a fluorinating reagent (0.8 mmol, 2.0 equiv) in 1.0 mL of anhydrous solvent was prepared under Ar atmosphere. The reaction mixture was stirred at room temperature for 24 h. 15 mL of water was then added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 5:1) to afford the desired sulfonyl fluoride.



3-phenylpropane-1-sulfonyl fluoride (17)

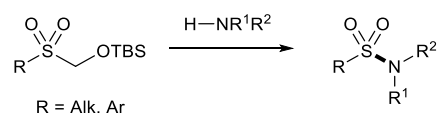
The general procedure F with cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor, 289.2 mg, 0.8 mmol) in ACN was adopted to afford the desired product as a yellow liquid (79.4 mg, 98% yield) or the general procedure F with tetrabutylammonium fluoride (0.6 mL, 0.6 mmol, 1.5 equiv, 1.0 M in THF) and *N*-fluorobenzenesulfonimide (NFSI, 260.1 mg, 0.8 mmol) in THF was adopted to afford the desired product as a yellow liquid (75.6 mg, 93% yield); R_f 0.50 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.29 (m, 2H), 7.29 – 7.22 (m, 1H), 7.22 – 7.14 (m, 2H), 3.38 – 3.26 (m, 2H), 2.82 (t, $J = 7.3$ Hz, 2H), 2.36 – 2.22 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 139.0, 129.0, 128.5, 127.0, 50.2, 50.0, 33.7, 25.0; ^{19}F NMR (376 MHz, CDCl_3) δ 53.96; IR (neat, ν_{max}) 3087, 3065, 3029, 2932, 2866, 1604, 1497, 1454, 1399, 1203, 1194 cm^{-1} ; HRMS (ESI) data were not available.



benzenesulfonyl fluoride (18)

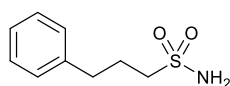
The general procedure F with cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor, 289.2 mg, 0.8 mmol) in ACN was adopted to afford the desired product as a yellow liquid (62.6 mg, 98% yield) or the general procedure F with tetrabutylammonium fluoride (0.6 mL, 0.6 mmol, 1.5 equiv, 1.0 M in THF) and *N*-fluorobenzenesulfonimide (NFSI, 260.1 mg, 0.8 mmol) in THF was adopted to afford the desired product as a yellow liquid (63.4 mg, 99% yield); R_f 0.47 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.11 – 7.96 (m, 2H), 7.79 (t, J = 7.5 Hz, 1H), 7.65 (dd, J = 11.6, 4.1 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 135.7, 133.4, 133.2, 129.8, 128.6; ^{19}F NMR (376 MHz, CDCl_3) δ 65.99; IR (neat, ν_{max}) 3072, 2956, 2923, 2852, 1451, 1406, 1210, 1179, 1096 cm^{-1} ; HRMS (ESI) data were not available.

iii) S-Amination of TBSOM sulfones with amines



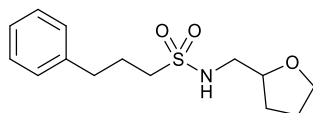
General Procedure G

A mixture of TBSOM sulfone (131.4 mg or 114.6 mg, 0.4 mmol, 1.0 equiv), amine (0.8 mmol, 2.0 equiv), cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) and *N*-chlorosuccinimide (81.7 mg, 0.6 mmol, 1.5 equiv) in 4.0 mL of anhydrous THF was prepared under Ar atmosphere. The reaction mixture was stirred at room temperature for 24 h. 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 1:1) to afford the desired sulfonamide product.



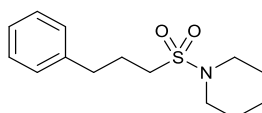
3-phenylpropane-1-sulfonamide (19a)

A mixture of TBSOM sulfone (131.4 mg, 0.4 mmol, 1.0 equiv), hydroxylamine *O*-sulfonic acid (93.3 mg, 0.8 mmol, 2.0 equiv), cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) and sodium acetate (66.3 mg, 0.8 mmol, 2.0 equiv) in 4.0 mL of anhydrous dimethyl sulfoxide was prepared under Ar atmosphere. The reaction mixture was stirred at room temperature for 24 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 5:1 to 1:1) to afford the desired primary sulfonamide product as a yellow oil (58.5 mg, 73%); R_f 0.43 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, J = 7.3 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.18 (d, J = 7.0 Hz, 2H), 4.77 (s, 2H), 3.14 – 3.03 (m, 2H), 2.76 (t, J = 7.5 Hz, 2H), 2.23 – 2.12 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.2, 128.8, 128.6, 126.6, 54.6, 34.1, 25.6; IR (neat, ν_{max}) 3363 (broad), 3266 (broad), 3086, 3063, 3027, 3016, 2866, 1603, 1553, 1496, 1454, 1323, 1149, 1129, 1077, 1029, 904 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_9\text{H}_{13}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 222.0559, found 222.0557.



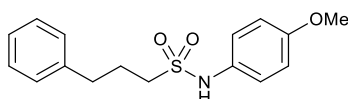
3-phenyl-*N*-((tetrahydrofuran-2-yl)methyl)propane-1-sulfonamide (19b)

The general procedure G with tetrahydrofurfurylamine (83 μ L, 0.8 mmol) was adopted to afford the desired product as a yellow liquid (103.6 mg, 91% yield); R_f 0.18 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, J = 7.3 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.18 (d, J = 7.1 Hz, 2H), 4.60 (t, J = 5.7 Hz, 1H), 3.95 (qd, J = 6.9, 3.4 Hz, 1H), 3.83 (dt, J = 13.0, 6.6 Hz, 1H), 3.78 – 3.67 (m, 1H), 3.24 (ddd, J = 13.0, 6.7, 3.4 Hz, 1H), 3.07 – 2.95 (m, 3H), 2.76 (t, J = 7.4 Hz, 2H), 2.22 – 2.08 (m, 2H), 2.02 – 1.82 (m, 3H), 1.61 (ddd, J = 11.1, 9.4, 5.4 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 128.7, 128.6, 126.5, 77.7, 68.4, 52.1, 47.0, 34.3, 28.5, 26.0, 25.4; IR (neat, ν_{max}) 3282 (broad), 3026, 2946, 2871, 1496, 1412, 1453, 1320, 1145, 1128, 1074 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 306.1134, found 306.1131.



1-((3-phenylpropyl)sulfonyl)piperidine (19c)

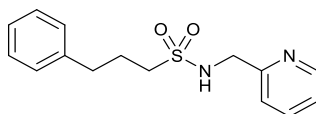
The general procedure G with piperidine (48 μ L, 0.8 mmol) was adopted to afford the desired product as a white solid (106.5 mg, 99% yield); R_f 0.23 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.30 (t, J = 7.4 Hz, 2H), 7.20 (dd, J = 16.4, 7.3 Hz, 3H), 3.27 – 3.10 (m, 4H), 2.93 – 2.82 (m, 2H), 2.75 (t, J = 7.5 Hz, 2H), 2.23 – 2.05 (m, 2H), 1.70 – 1.58 (m, 4H), 1.58 – 1.48 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.4, 128.7, 128.6, 126.5, 48.5, 46.8, 34.5, 25.8, 24.8, 24.0; IR (neat, ν_{max}) 3064, 3028, 2946, 2928, 2850, 1495, 1466, 1454, 1336, 1321, 1264, 1157, 1144, 1051, 932 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 290.1185, found 290.1187.



N-(4-methoxyphenyl)-3-phenylpropane-1-sulfonamide (19d)

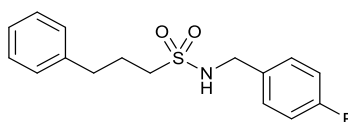
A mixture of TBSOM sulfone (32.8 mg, 0.1 mmol, 1.0 equiv) and cesium fluoride (22.8 mg, 0.15 mmol, 1.5 equiv) in 0.5 mL of THF was prepared under N_2 atmosphere. The reaction mixture was stirred at 50 $^\circ\text{C}$ for 2 h. The reaction mixture was cooled to room temperature and azeotroped three times with methanol until solidified. Then, a mixture of residue with 4-methoxyaniline (61.6 mg, 0.5 mmol, 5.0 equiv) in 3.0 mL of THF was prepared and cooled to 0 $^\circ\text{C}$, to which was added *N*-chlorosuccinimide (26.7 mg, 0.2 mmol, 2 equiv). The reaction mixture was warmed to room temperature and stirred for 6 h. After the reaction mixture was cooled to room temperature, 20 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL \times 3), dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 5:1 to 3:1) to afford the product as a brown oil (24.6 mg, 81%); R_f 0.36 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.23 (m, 2H), 7.22 – 7.15 (m, 1H), 7.11 – 7.07 (m, 4H), 6.84 – 6.79 (m, 2H), 6.42 (s, 1H), 3.78 (s, 3H), 3.03 – 2.96 (m, 2H), 2.69 (t, J = 7.4 Hz, 2H), 2.17 – 2.07 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.0, 140.1, 129.1, 128.7, 128.5, 126.5, 124.7, 114.9, 55.6, 50.4, 34.1, 25.2. Analytical data are

consistent with the previous report.⁶



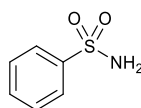
3-phenyl-*N*-(pyridin-2-ylmethyl)propane-1-sulfonamide (S19e)

The general procedure G with 2-picolylamine (83 μ L, 0.8 mmol) was adopted to afford the desired product as a yellow liquid (108.2 mg, 93% yield); R_f 0.15 (Hex:EA 1:1); ^1H NMR (400 MHz, CDCl_3) δ 8.52 (d, J = 4.3 Hz, 1H), 7.65 (td, J = 7.7, 1.7 Hz, 1H), 7.30 – 7.23 (m, 3H), 7.19 (dt, J = 9.4, 6.6 Hz, 2H), 7.09 (d, J = 7.0 Hz, 2H), 6.07 (t, J = 5.4 Hz, 1H), 4.36 (d, J = 5.5 Hz, 2H), 2.98 – 2.86 (m, 2H), 2.65 (t, J = 7.5 Hz, 2H), 2.15 – 2.00 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 155.8, 149.3, 140.2, 137.1, 128.6, 128.5, 126.4, 122.9, 122.1, 52.2, 47.7, 34.2, 25.2; IR (neat, ν_{max}) 3270 (broad), 3062, 3026, 2942, 2760 (broad), 1775, 1705, 1594, 1453, 1436, 1321, 1181, 1142, 1076 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 291.1162, found 291.1165.



N-(4-fluorobenzyl)-3-phenylpropane-1-sulfonamide (S19f)

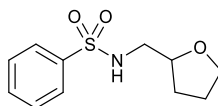
The general procedure G with 4-fluorobenzylamine (93 μ L, 0.8 mmol) was adopted to afford the desired product as a white solid (114.1 mg, 93% yield); R_f 0.11 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.17 (m, 5H), 7.10 (d, J = 7.1 Hz, 2H), 6.99 (t, J = 8.6 Hz, 2H), 4.90 (t, J = 6.0 Hz, 1H), 4.17 (d, J = 6.1 Hz, 2H), 2.93 – 2.78 (m, 2H), 2.65 (t, J = 7.4 Hz, 2H), 2.04 (dq, J = 12.8, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.7, 161.3, 140.1, 132.9, 132.9, 129.8, 129.7, 128.7, 128.5, 126.5, 115.9, 115.7, 52.7, 46.4, 34.1, 25.2; ^{19}F NMR (376 MHz, CDCl_3) δ -113.83; IR (neat, ν_{max}) 3275 (broad), 3087, 3065, 3033, 2871, 1602, 1510, 1496, 1455, 1427, 1316, 1286, 1228, 1140 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{FNO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 330.0935, found 330.0933.



Benzenesulfonamide (20a)

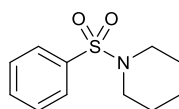
A mixture of TBSOM sulfone (114.6 mg, 0.4 mmol, 1.0 equiv), hydroxylamine *O*-sulfonic acid (93.3 mg, 0.8 mmol, 2.0 equiv), cesium fluoride (91.2 mg, 0.6 mmol, 1.5 equiv) and sodium acetate (66.3 mg, 0.8 mmol, 2.0 equiv) in 4.0 mL of anhydrous dimethyl sulfoxide was prepared under Ar atmosphere. The reaction mixture was stirred at room temperature for 24 h. After the reaction mixture was cooled to room temperature, 15 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), washed with water and brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 5:1 to 1:1) to afford the desired primary sulfonamide product as a white solid (42.5 mg, 68%); R_f 0.47 (Hex:EA 1:1); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.83 (dd, J = 7.9, 1.6 Hz, 2H), 7.64 – 7.52 (m, 3H), 7.35 (s, 2H); ^{13}C NMR (101

MHz, DMSO- d_6) δ 144.1, 131.8, 128.9, 125.6; IR (neat, ν_{\max}) 3348, 3254, 2923, 1553, 1447, 1334, 1311, 1153, 1091 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_6\text{H}_7\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 180.0090, found 180.0084.



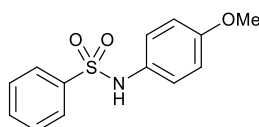
***N*-((tetrahydrofuran-2-yl)methyl)benzenesulfonamide (20b)**

The general procedure G with tetrahydrofurfurylamine (83 μL , 0.8 mmol) was adopted to afford the desired product as a colorless liquid (93.4 mg, 97% yield); R_f 0.20 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.82 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 (dd, J = 10.1, 4.6 Hz, 2H), 4.85 (s, 1H), 3.93 (qd, J = 6.8, 3.6 Hz, 1H), 3.78 (dt, J = 13.0, 6.6 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.14 (ddd, J = 12.5, 6.8, 3.6 Hz, 1H), 2.97 – 2.85 (m, 1H), 2.00 – 1.80 (m, 3H), 1.62 (ddd, J = 11.1, 9.6, 5.6 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.0, 132.7, 129.2, 127.1, 77.1, 68.4, 46.9, 28.5, 26.0; IR (neat, ν_{\max}) 3274 (broad), 3066, 2975, 2873, 1446, 1326, 1158, 1094, 1073 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 264.0665, found 264.0666.



1-(phenylsulfonyl)piperidine (20c)

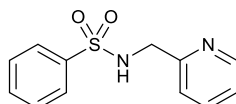
The general procedure G with piperidine (48 μL , 0.8 mmol) was adopted to afford the desired product as a white solid (82.7 mg, 92% yield); R_f 0.36 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.72 (m, 2H), 7.62 – 7.56 (m, 1H), 7.53 (t, J = 7.4 Hz, 2H), 3.08 – 2.92 (m, 4H), 1.64 (dt, J = 11.4, 5.8 Hz, 4H), 1.50 – 1.36 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.5, 132.7, 129.0, 127.8, 47.1, 25.3, 23.6; IR (neat, ν_{\max}) 3058, 2999, 2983, 2962, 2927, 2946, 2840, 1444, 1335, 1325, 1310, 1164, 1093, 1050, 1021, 930 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 248.0716, found 248.0717.



***N*-(4-methoxyphenyl)benzenesulfonamide (20d)**

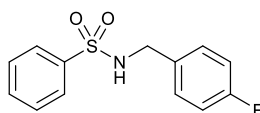
A mixture of TBSOM sulfone (28.6 mg, 0.1 mmol, 1.0 equiv) and cesium fluoride (22.8 mg, 0.15 mmol, 1.5 equiv) in 0.5 mL of THF was prepared under N_2 atmosphere. The reaction mixture was stirred at 50 $^\circ\text{C}$ for 2 h. The reaction mixture was cooled to room temperature and azeotroped three times with methanol until solidified. Then, a mixture of residue with 4-methoxyaniline (61.6 mg, 0.5 mmol, 5.0 equiv) in 3.0 mL of THF was prepared and cooled to 0 $^\circ\text{C}$, to which was added *N*-chlorosuccinimide (26.7 mg, 0.2 mmol, 2 equiv). The reaction mixture was warmed to room temperature and stirred for 6 h. After the reaction mixture was cooled to room temperature, 20 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (15 mL x 3), dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 5:1 to 3:1) to afford the product as a brown solid (21.0 mg, 80%); R_f 0.36 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ

7.73 – 7.69 (m, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.00 – 6.94 (m, 2H), 6.79 – 6.73 (m, 2H), 6.55 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 138.9, 132.8, 128.9, 128.6, 127.3, 125.6, 114.4, 55.4. Analytical data are consistent with the previous report.⁷



***N*-(pyridin-2-ylmethyl)benzenesulfonamide (S20e)**

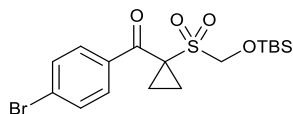
The general procedure G with 2-picolylamine (83 μL , 0.8 mmol) was adopted to afford the desired product as a yellow liquid (99.6 mg, 99% yield); R_f 0.057 (Hex:EA 2:1); ^1H NMR (400 MHz, CDCl_3) δ 8.44 (d, $J = 4.6$ Hz, 1H), 7.89 – 7.79 (m, 2H), 7.59 (td, $J = 7.7$, 1.6 Hz, 1H), 7.51 (dd, $J = 8.5$, 6.2 Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.21 – 7.10 (m, 2H), 6.29 (s, 1H), 4.26 (d, $J = 5.4$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.9, 149.1, 139.8, 136.9, 132.6, 129.1, 127.2, 122.8, 122.1, 47.6; IR (neat, ν_{max}) 3261 (broad), 3066 (broad), 2862, 2760, 1775, 1708, 1595, 1572, 1479, 1446, 1327, 1158, 1093, 1072 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 249.0692, found 249.0694.



***N*-(4-fluorobenzyl)benzenesulfonamide (S20f)**

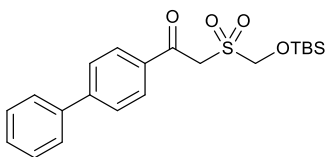
The general procedure G with 4-fluorobenzylamine (93 μL , 0.8 mmol) was adopted to afford the desired product as a white solid (88.2 mg, 83% yield); R_f 0.12 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.85 (dd, $J = 5.2$, 3.3 Hz, 2H), 7.63 – 7.55 (m, 1H), 7.55 – 7.45 (m, 2H), 7.19 – 7.10 (m, 2H), 6.99 – 6.88 (m, 2H), 4.95 (t, $J = 5.9$ Hz, 1H), 4.11 (d, $J = 6.2$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.7, 161.3, 140.0, 132.9, 132.2, 132.1, 129.8, 129.7, 129.3, 127.2, 115.8, 115.6, 46.7; ^{19}F NMR (376 MHz, CDCl_3) δ -114.11; IR (neat, ν_{max}) 3263, 3061, 1601, 1508, 1445, 1423, 1322, 1220, 1155, 1092, 1041 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{12}\text{FNO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 288.0465, found 288.0466.

F. Utilization of TBSOM sulfone intermediates



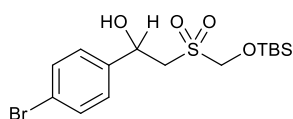
(4-bromophenyl)(1-(((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)cyclopropylmethanone (21a)

To a vial were added sulfone **3j** (40.7 mg, 0.1 mmol, 1.0 equiv), dibromoethane (12 μ L, 0.14 mmol, 1.4 equiv) and potassium carbonate (27.8 mg, 0.2 mmol, 2.0 equiv) with 0.1 mL of anhydrous DMF as a solvent. The reaction mixture was stirred at 60 °C for 6 h under Ar atmosphere. After the mixture was cooled to ambient temperature, 3 mL of water was added and organic fractions were gathered with ethyl acetate (5 mL x 3). Combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 10:1) to afford the desired product (41.9 mg, 98% yield); *R*_f 0.56 (Hex:EA=5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.89 (m, 2H), 7.66 – 7.56 (m, 2H), 4.70 (s, 2H), 1.89 (q, *J* = 5.3 Hz, 2H), 1.45 (q, *J* = 5.5 Hz, 2H), 0.88 (s, 9H), 0.11 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.1, 134.1, 131.9, 131.8, 129.5, 78.8, 78.8, 78.8, 44.7, 25.6, 18.4, 11.6, -5.4; IR (neat, ν_{max}) 3111, 2954, 2931, 2897, 2859, 1663, 1585, 1395, 1331, 1310, 1263, 1254, 1160, 1116 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₇H₂₅BrO₄SSi [M+Na]⁺ 455.0318, found 455.0319.



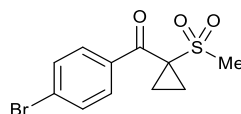
1-([1,1'-biphenyl]-4-yl)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)sulfonyl)ethan-1-one (21b)

To a vial were added sulfone **3j** (40.7 mg, 0.1 mmol, 1.0 equiv), phenylboronic acid (24.9 mg, 0.2 mmol, 2.0 equiv), palladium(II)bis(triphenylphosphine) dichloride (PdCl₂(PPh₃)₂, 7.2 mg, 0.01 mmol, 0.1 equiv) and potassium carbonate (27.8 mg, 0.2 mmol, 2.0 equiv) with 0.5 mL of toluene and 0.05 mL of H₂O as a solvent system. The reaction mixture was stirred at 100 °C for 24 h under Ar atmosphere. After cooled to ambient temperature, the mixture went through a pad of silica with diethyl ether. Filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (Hex:EA = 50:1 to 5:1) to afford the desired product as a yellow solid (40.5 mg, 99% yield); *R*_f 0.31 (Hex:EA=5:1); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.43 (dd, *J* = 8.4, 6.1 Hz, 1H), 4.79 (s, 2H), 4.64 (s, 2H), 0.93 (s, 9H), 0.20 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 188.3, 147.4, 139.6, 134.7, 129.9, 129.2, 128.8, 127.7, 127.5, 78.5, 55.7, 25.7, 18.4, -5.2; IR (neat, ν_{max}) 3064, 3037, 3007, 2958, 2929, 2892, 2857, 1673, 1603, 1309, 1260, 1154, 1137, 1110, 1002 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₂₁H₂₈O₄SSi [M+Na]⁺ 427.1370, found 427.1372.



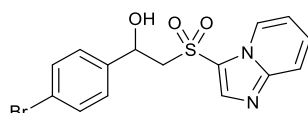
1-(4-bromophenyl)-2-((((tert-butyldimethylsilyl)oxy)methyl)sulfonyl)ethan-1-ol (21c)

A solution of sulfone **3j** (40.7 mg, 0.1 mmol, 1.0 equiv) in anhydrous THF (1.0 mL) was prepared under atmospheric conditions. To a cooled (0 °C) solution was added sodium borohydride (7.7 mg, 0.2 mmol, 2.0 equiv). The reaction mixture was warmed to room temperature and stirred for 4 h. After full conversion, aqueous ammonium chloride solution was added. Organic fractions were gathered with ethyl acetate (5 mL x 3), washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 5:1) to afford the desired product as a white solid (37.2 mg, 91% yield); A solution of sulfone **3j** (40.7 mg, 0.1 mmol, 1.0 equiv) in anhydrous THF (0.5 mL) was prepared under Ar conditions. To a cooled (-78 °C) solution was added diisobutylaluminum hydride (0.2 mL, 0.2 mmol, 2.0 equiv, 1.0 M in hexanes). The reaction mixture stirred at -78 °C for 9 h. After full conversion, aqueous ammonium chloride solution and aqueous sodium tartrate (Rochelle salt) solution were added. Organic fractions were gathered with ethyl acetate (5 mL x 3), washed with brine, dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 5:1) to afford the desired product as a white solid (35.2 mg, 86% yield); R_f 0.15 (Hex:EA=5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 9.2 Hz, 2H), 5.32 (d, *J* = 10.3 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 3.53 – 3.36 (m, 2H), 3.17 (dd, *J* = 14.7, 1.4 Hz, 1H), 0.94 (s, 9H), 0.21 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 140.0, 132.2, 127.5, 122.5, 79.3, 68.2, 57.9, 25.7, 18.4, -5.2; IR (neat, ν_{max}) 3481, 2953, 2930, 2891, 2858, 1592, 1488, 1472, 1464, 1302, 1257, 1148, 1116, 1011 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₅H₂₅BrO₄SSi [M+Na]⁺ 431.0318, found 431.0319.



(4-bromophenyl)(1-(methylsulfonyl)cyclopropyl)methanone (22)

To a vial were added sulfone **21a** (43.3 mg, 0.1 mmol, 1.0 equiv), iodomethane (9.4 μL, 0.15 mmol, 1.5 equiv) and tetrabutylammonium fluoride (0.15 mL, 0.15 mmol, 1.5 equiv, 1.0 M in THF) with 0.4 mL of anhydrous DMSO as a solvent. The reaction mixture was stirred at room temperature for 24 h under Ar atmosphere. After full conversion, 3 mL of water was added and organic fractions were gathered with ethyl acetate (5 mL x 3). Combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 20:1 to 5:1) to afford the desired product as a red solid (29.4 mg, 97% yield); R_f 0.088 (Hex:EA=10:1); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 3.03 (s, 3H), 1.85 (q, *J* = 5.6 Hz, 2H), 1.43 (q, *J* = 5.7 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 192.2, 133.8, 132.0, 132.0, 130.0, 47.4, 40.3, 12.3; IR (neat, ν_{max}) 3095, 3016, 2929, 2854, 1666, 1582, 1566, 1397, 1310, 1189, 1175, 1131, 1070 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₁H₁₁BrO₃S [M+H]⁺ 324.9505, found 324.9503.

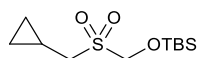


1-(4-bromophenyl)-2-(imidazo[1,2-a]pyridin-3-ylsulfonyl)ethan-1-ol (23)

To a vial were added sulfone **21c** (40.9 mg, 0.1 mmol, 1.0 equiv), 3-bromoimidazo[1,2-a]pyridine (24.4 mg, 0.12 mmol, 1.2 equiv), copper(I) iodide (1.9 mg, 0.01 mmol, 0.1 equiv), L-proline (14.0 mg, 0.12 mmol, 1.2 equiv), sodium hydroxide (0.8 mg, 0.02 mmol, 0.2 equiv) and cesium fluoride (22.8 mg, 0.15

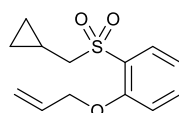
mmol, 1.5 equiv) with 0.1 mL of anhydrous DMSO as a solvent. The reaction mixture was stirred at 95 °C for 24 h under Ar atmosphere. After the reaction mixture was cooled to room temperature, 5 mL of water was added to the mixture. Organic fractions were extracted with ethyl acetate (5 mL x 3), washed with water and brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 5:1 to 1:2) to afford the desired aryl sulfone product as a yellow liquid (31.8 mg, 83% yield); R_f 0.15 (Hex:EA=1:2); ¹H NMR (400 MHz, CDCl₃) δ 8.77 (d, *J* = 6.5 Hz, 1H), 8.20 (s, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 6.9 Hz, 1H), 5.32 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 1H), 3.61 (dd, *J* = 14.5, 9.8 Hz, 1H), 3.44 (dd, *J* = 14.5, 2.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.9, 139.8, 132.1, 128.7, 127.5, 126.2, 122.6, 118.6, 115.2, 68.5, 64.7; IR (neat, ν_{max}) 3110, 2920, 1635, 1497, 1449, 1303, 1273, 1151, 1136, 1122, 1070, 1029, 1008 cm⁻¹; HRMS (ESI) *m/z* calcd. for C₁₅H₁₃BrN₂O₃S [M+H]⁺ 380.9903, found 380.9905.

G. Synthetic sequence orthogonal to radical processes



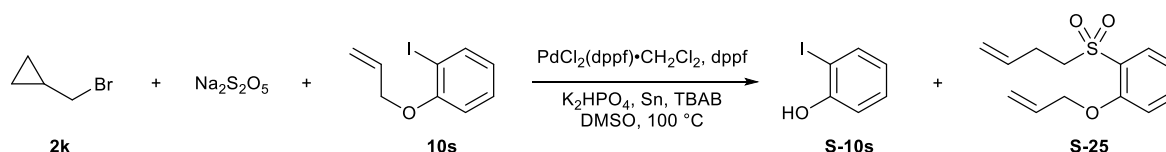
tert-butyl(((cyclopropylmethyl)sulfonyl)methoxy)dimethylsilane (**24**)

The general procedure A with (bromomethyl)cyclopropane (39 μ L, 0.4 mmol) was adopted to afford the desired product as a yellow liquid (83.0 mg, 79% yield); R_f 0.43 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 4.58 (s, 2H), 2.92 (d, J = 7.2 Hz, 2H), 1.21 – 1.10 (m, 1H), 0.91 (s, 9H), 0.77 – 0.66 (m, 2H), 0.46 – 0.37 (m, 2H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 54.3, 25.7, 18.3, 4.6, 4.4, -5.2; IR (neat, ν_{max}) 2954, 2930, 2887, 2858, 1326, 1307, 1255, 1153, 1119 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{24}\text{NaO}_3\text{SSi}$ $[\text{M}+\text{Na}]^+$ 287.1108, found 287.1111.



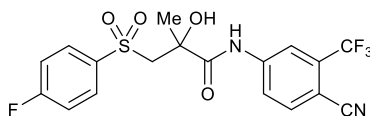
1-(allyloxy)-2-((cyclopropylmethyl)sulfonyl)benzene (**25**)

The general procedure D1 with 1-(allyloxy)-2-iodobenzene (31.2 mg, 0.12 mmol) was adopted to afford the desired product as a yellow liquid (14.6 mg, 58% yield); R_f 0.12 (Hex:EA 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.00 (dd, J = 7.8, 1.6 Hz, 1H), 7.61 – 7.49 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.07 (ddt, J = 20.9, 10.4, 5.1 Hz, 1H), 5.51 (dd, J = 17.2, 1.3 Hz, 1H), 5.34 (d, J = 10.6 Hz, 1H), 4.77 – 4.63 (m, 2H), 3.31 (d, J = 7.3 Hz, 2H), 1.07 – 0.89 (m, 1H), 0.51 (d, J = 8.0 Hz, 2H), 0.19 (d, J = 5.2 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 156.5, 135.4, 132.0, 131.0, 127.8, 121.1, 118.7, 113.6, 70.0, 59.4, 4.7, 4.2; IR (neat, ν_{max}) 3084, 3009, 2920, 1590, 1476, 1448, 1308, 1281, 1146, 1132 cm^{-1} ; HRMS (ESI) m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 275.0712, found 275.0709.



A mixture of alkyl bromide **2k** (0.03 mL, 0.3 mmol, 3.0 equiv), $\text{Na}_2\text{S}_2\text{O}_5$ (0.0392 g, 0.2 mmol, 2.0 equiv), aryl iodide **10s** (0.0260g, 0.1 mmol, 1.0 equiv), $\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$ (0.0082 g, 0.01 mmol, 0.1 equiv), dppf (0.0114 g, 0.02 mmol, 0.2 equiv), K_2HPO_4 (0.0355 g, 0.2 mmol, 2.0 equiv), Sn (0.0356 g, 0.3 mmol, 3.0 equiv) and TBAB (0.0493 g, 0.15 mmol, 1.5 equiv) in anhydrous DMSO (1.0 mL) was prepared under N_2 atmosphere using the Schlenk technique. The reaction mixture was stirred at 100 $^\circ\text{C}$ for 10 h. 2 mL of water was added to the mixture and organic fractions were extracted with ethyl acetate. Combined organic layers were collected, dried over Na_2SO_4 and concentrated in vacuo. Residue was purified by flash column chromatography to afford 2-iodophenol **S-10s** as the major product derived from deallylation in a yield of 55% (71% for 14 h). NMR Analysis on the reaction mixture revealed that unreacted aryl iodide **10s** and deallylated 2-iodophenol **S-10s** constituted the majority of the reaction mixture without any trace of **25**. Furthermore, MS data implied the formation of **S-25** in a trace amount, an isomer of **25** in which the cyclopropane moiety was opened under conditions generating alkyl radicals.

H. Synthesis of bicalutamide

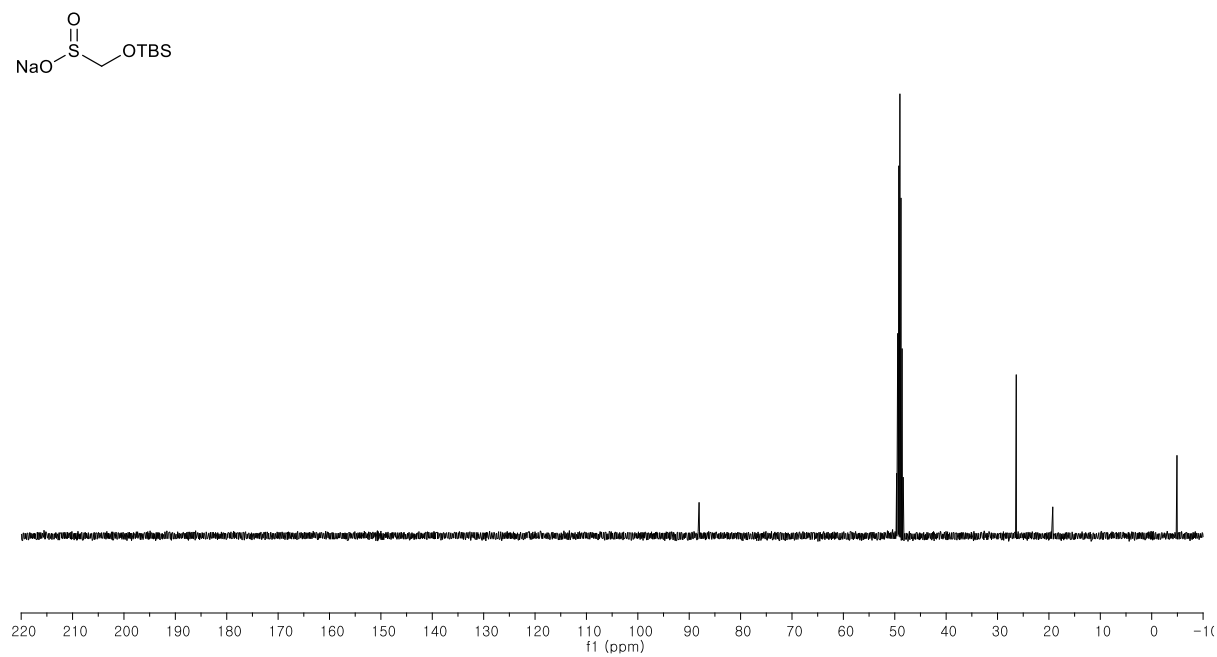
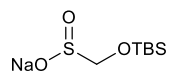
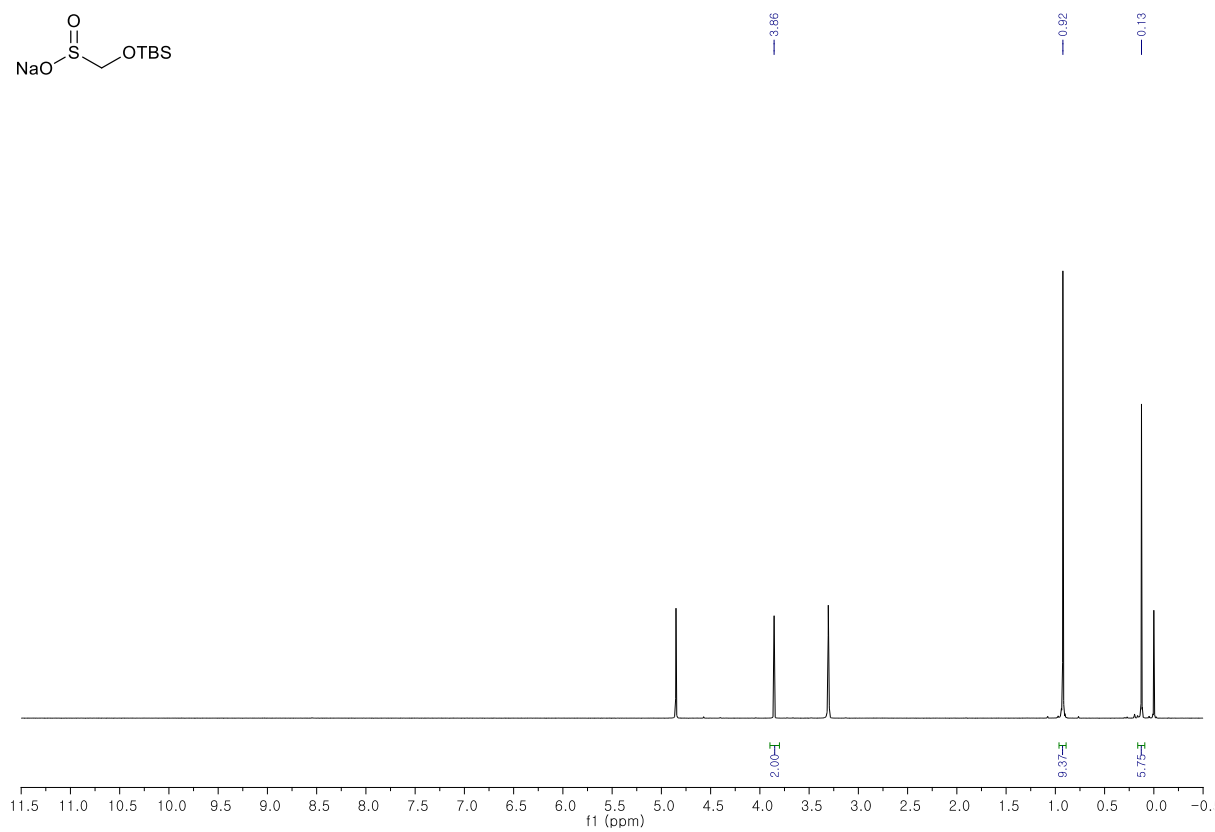
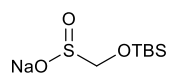


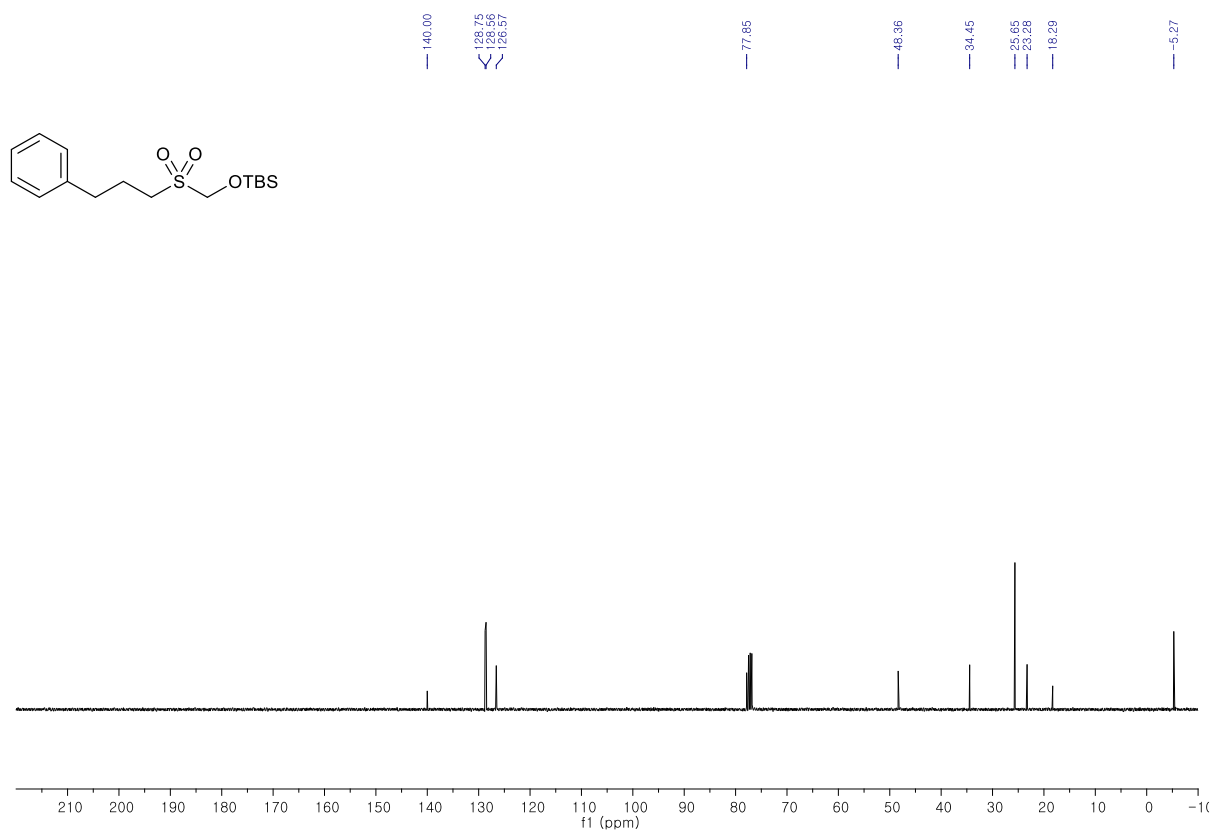
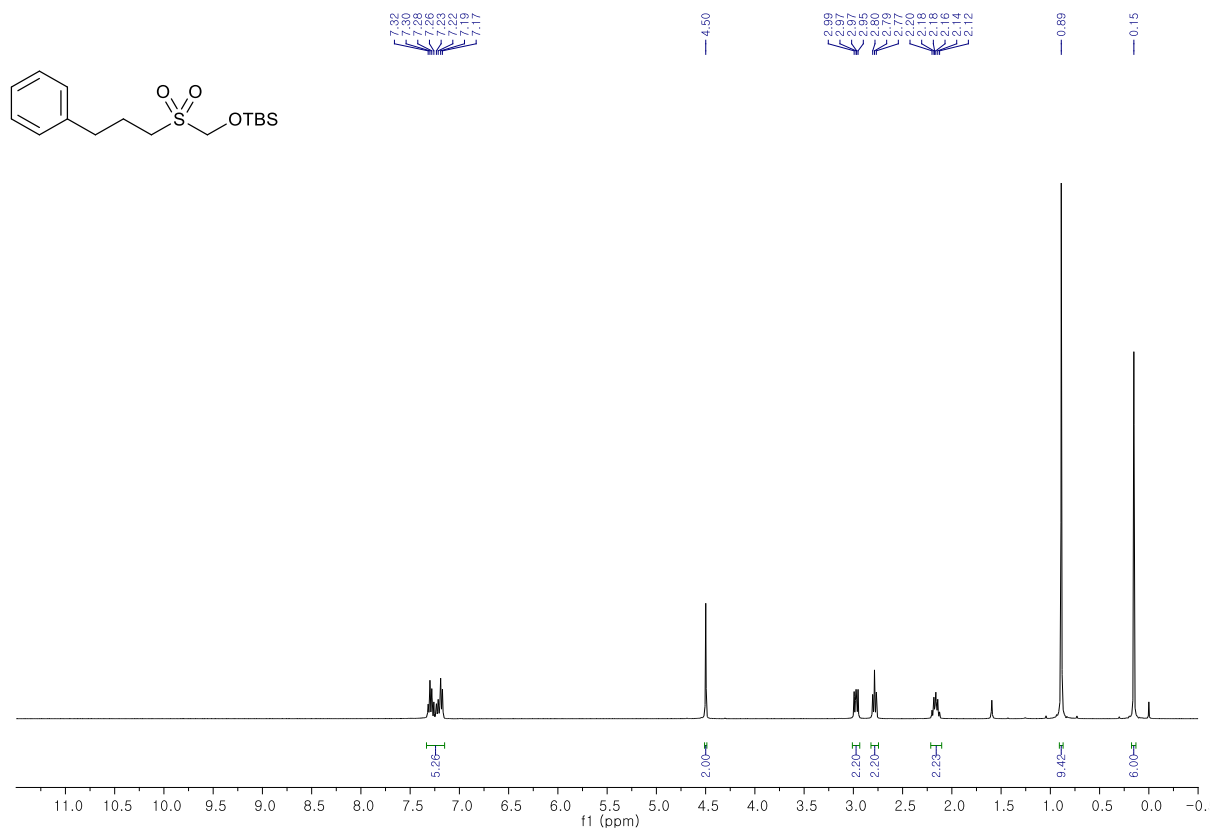
***N*-(4-cyano-3-(trifluoromethyl)phenyl)-3-((4-fluorophenyl)sulfonyl)-2-hydroxy-2-methylpropanamide (27)**

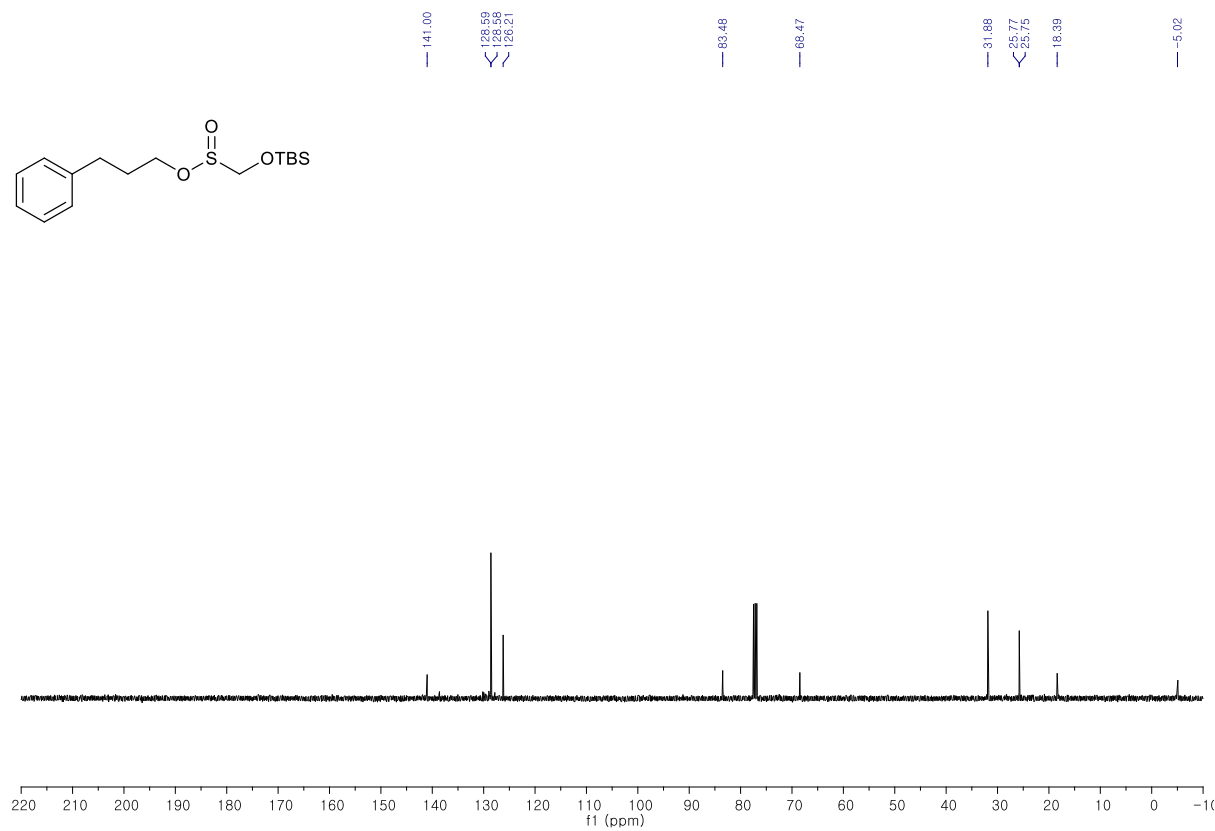
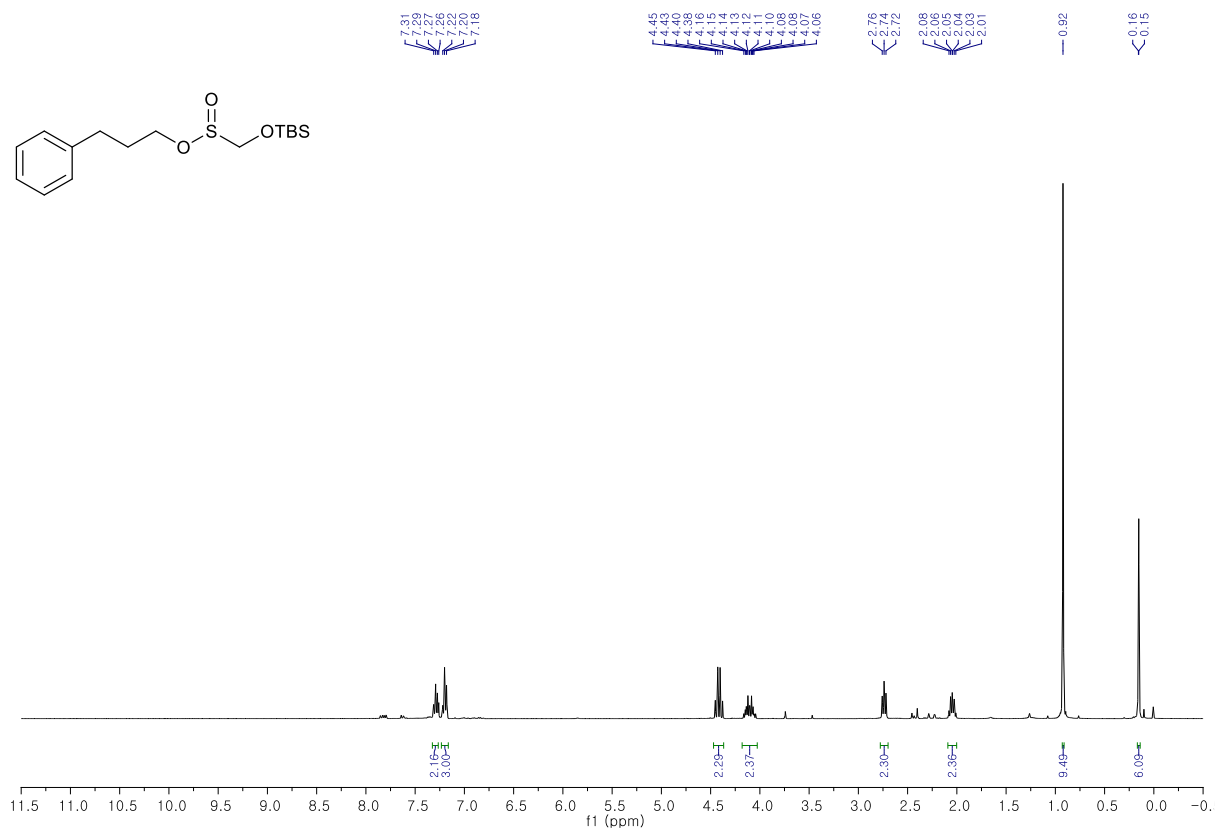
In a vial filled with (((*tert*-butyldimethylsilyl)oxy)methyl)(4-fluorophenyl) sulfone (30.5 mg, 0.1 mmol, 1 equiv), *N*-(4-cyano-3-(trifluoromethyl)phenyl)-2-methyloxirane-2-carboxamide⁸ (**26**, 54 mg, 0.2 mmol, 2 equiv) and cesium fluoride (22.8 mg, 0.15 mmol, 1.5 equiv) was added 0.2 mL of H₂O. The reaction mixture was stirred at 90 °C for 15 h under Ar atmosphere. After cooled to room temperature, the reaction mixture was diluted with additional water. Organic fractions were extracted with ethyl acetate (20 mL x 3), washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EA = 3:1 to 1:1) to afford the desired compound as a white solid (39.8 mg, 93% yield); R_f 0.47 (Hex:EA=1:1); ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.38 (s, 1H), 8.43 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.93 (dd, *J* = 8.3, 5.3 Hz, 2H), 7.37 (t, *J* = 8.7 Hz, 2H), 6.41 (s, 1H), 3.95 (d, *J* = 14.8 Hz, 1H), 3.72 (d, *J* = 14.8 Hz, 1H), 1.41 (s, 3H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 164.8 (d, *J* = 252.4 Hz), 137.2 (d, *J* = 2.9 Hz), 131.4 (q, *J* = 31.7 Hz), 131.3 (d, *J* = 9.9 Hz), 122.5 (q, *J* = 274.1 Hz), 116.0 (d, *J* = 22.8 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -61.38, -105.79. Analytical data are consistent with the previous report.⁸

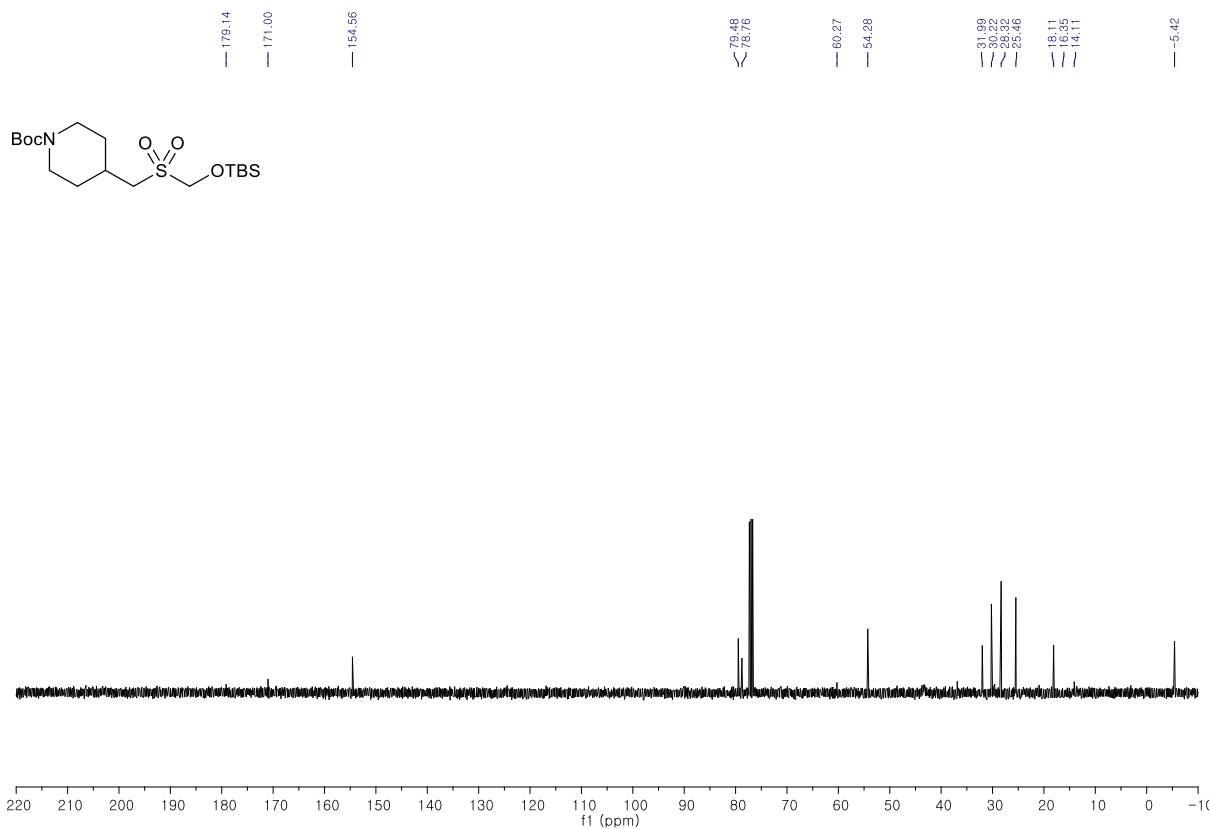
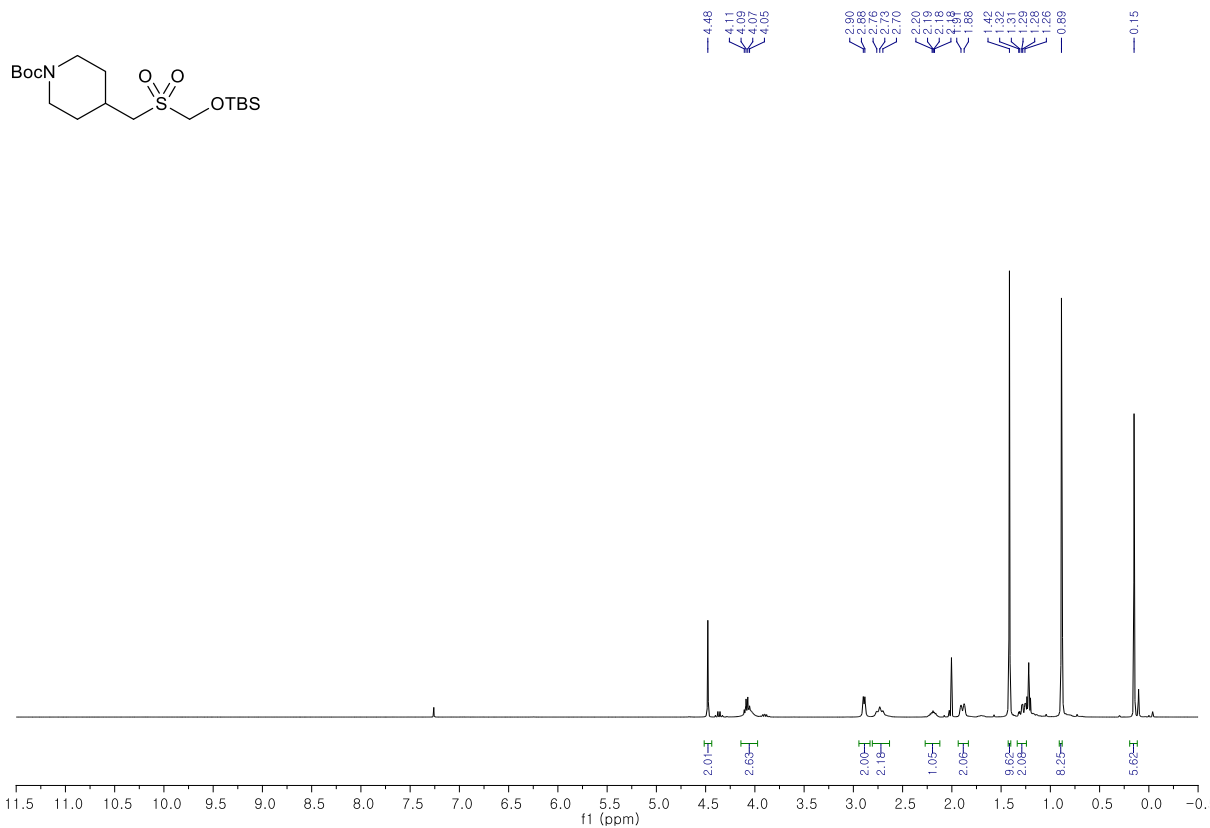
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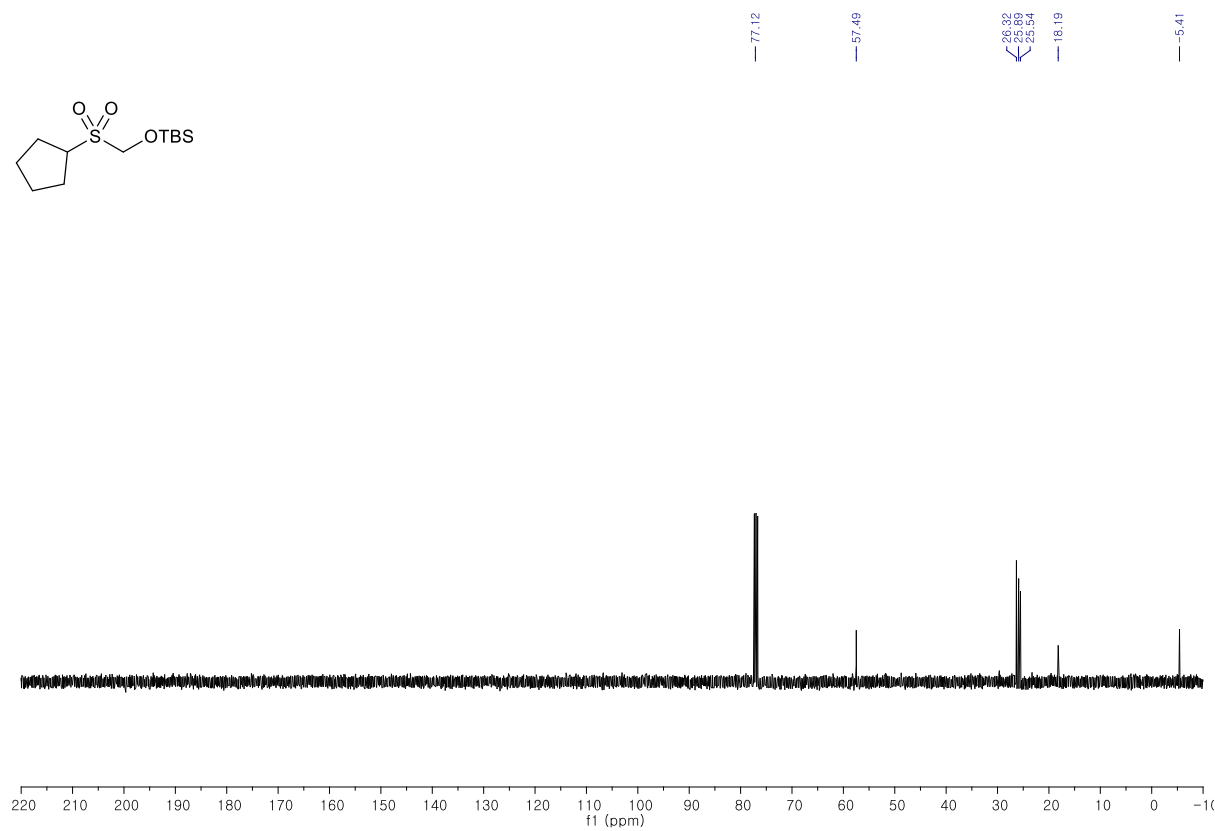
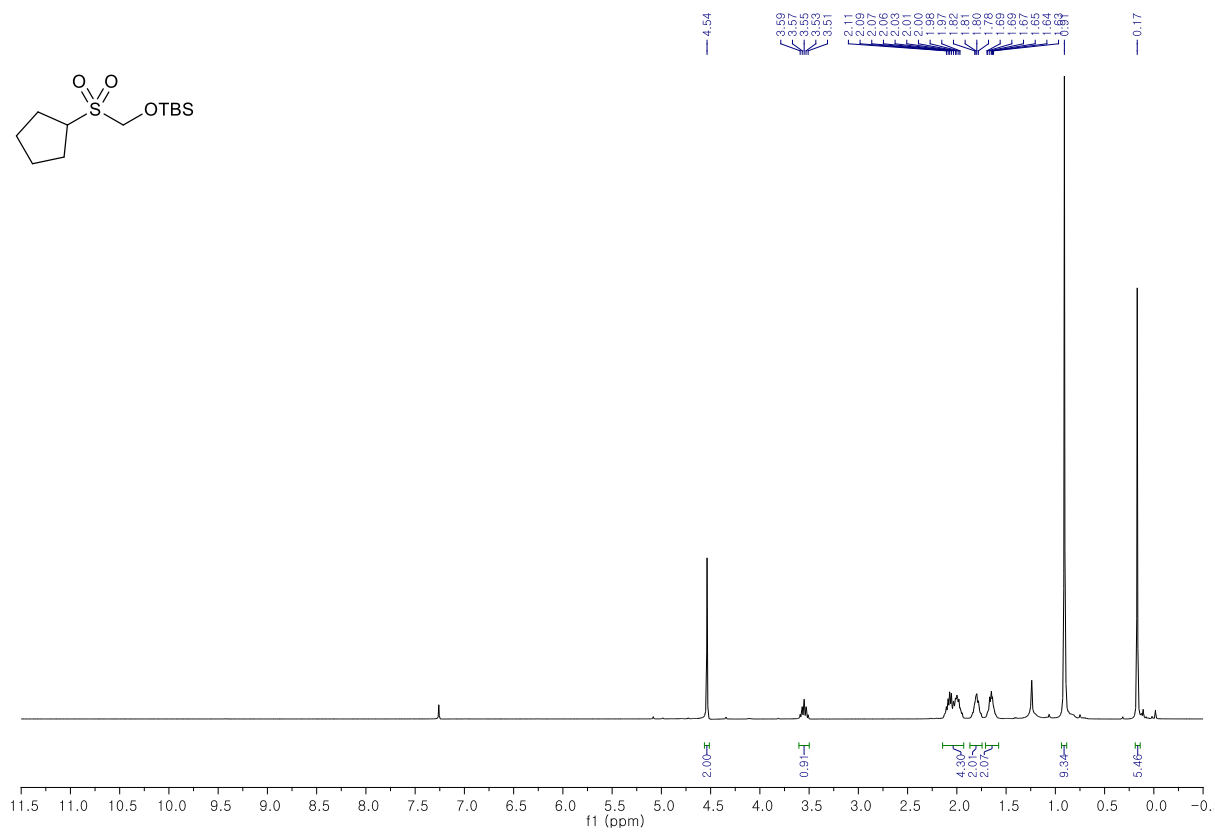
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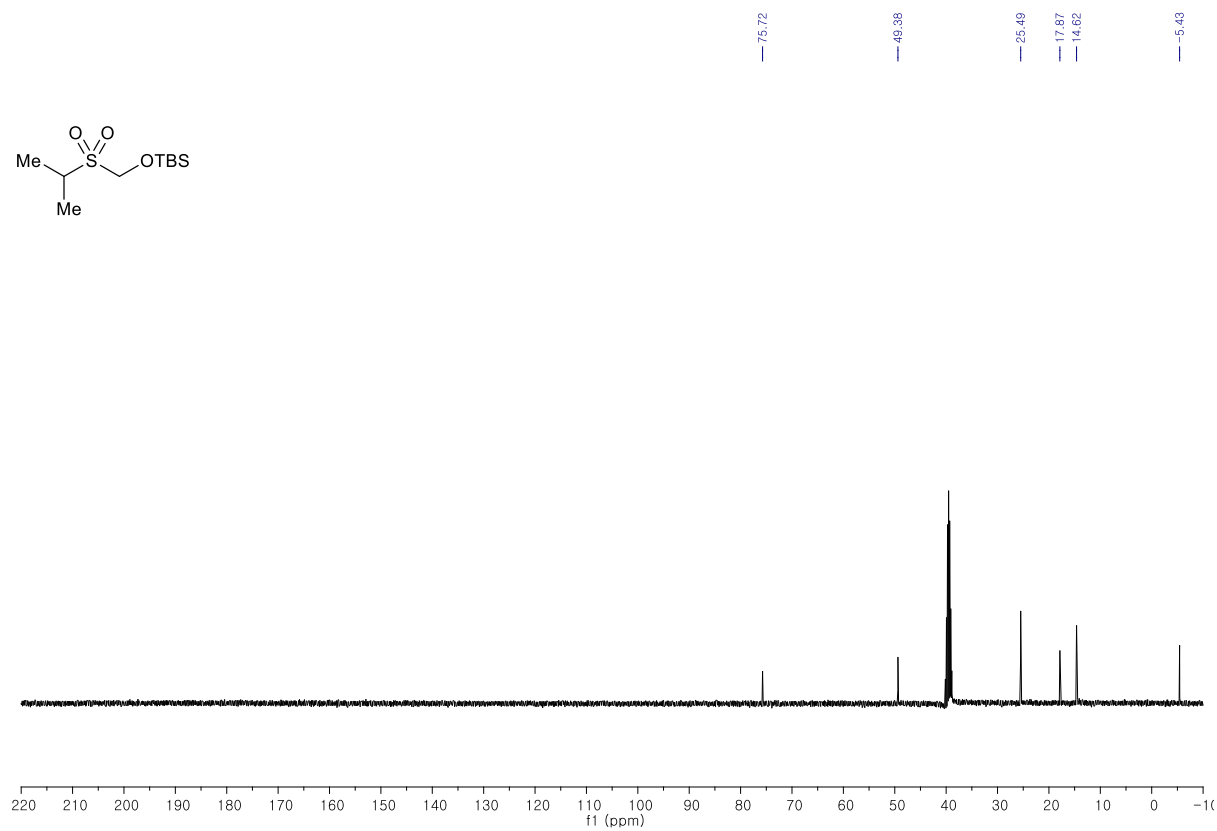
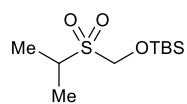
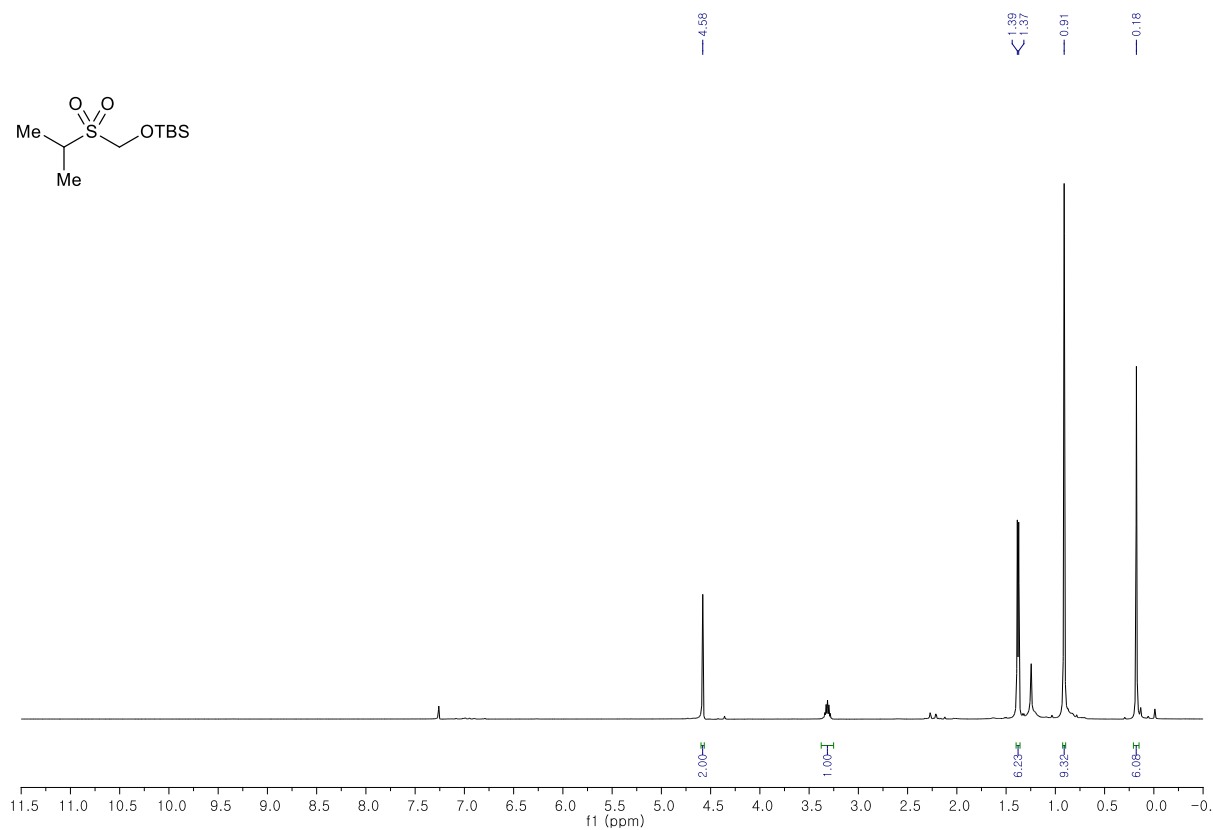
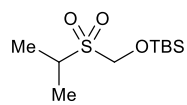


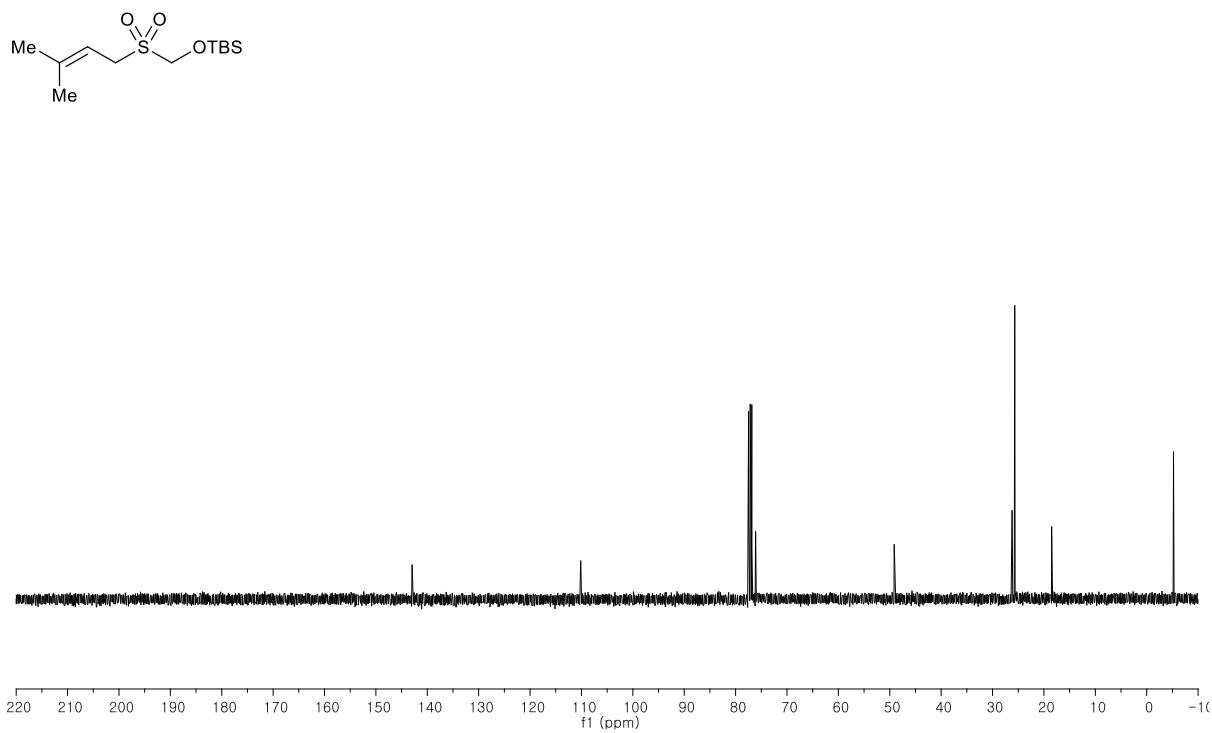
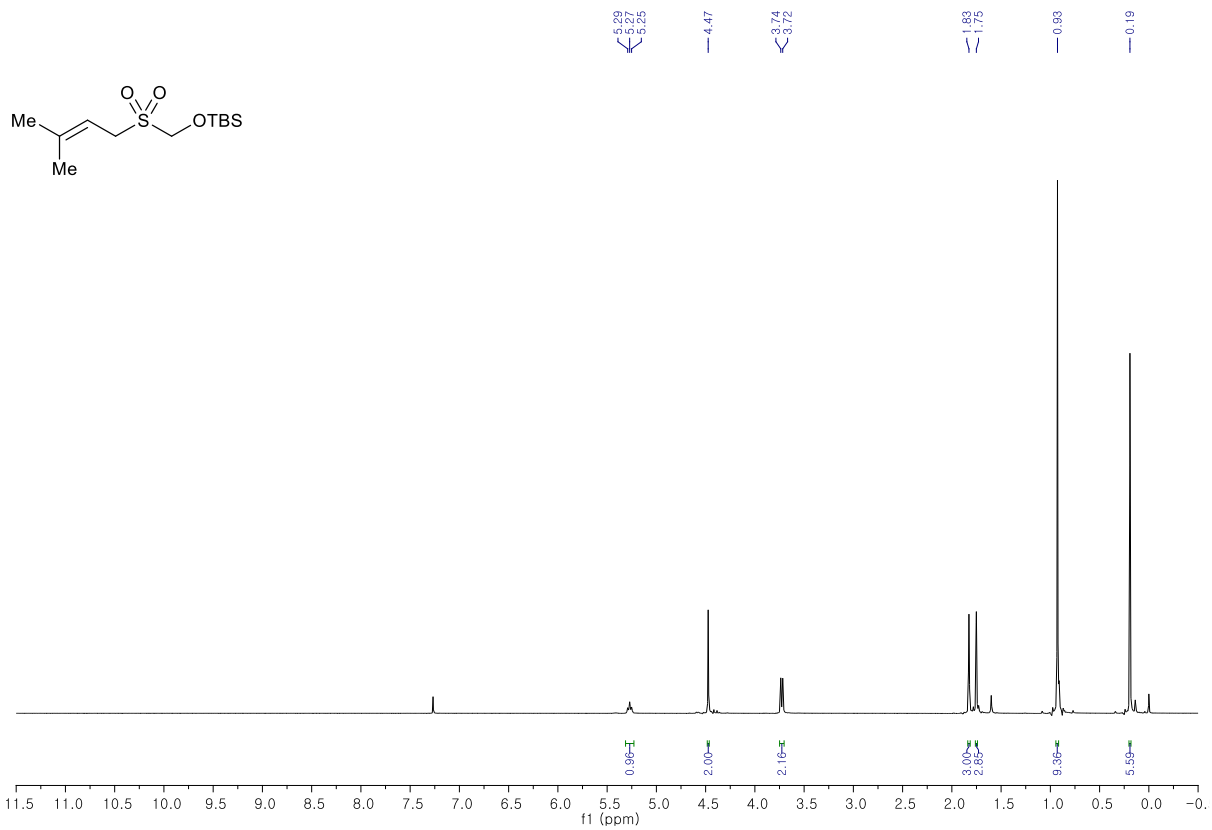


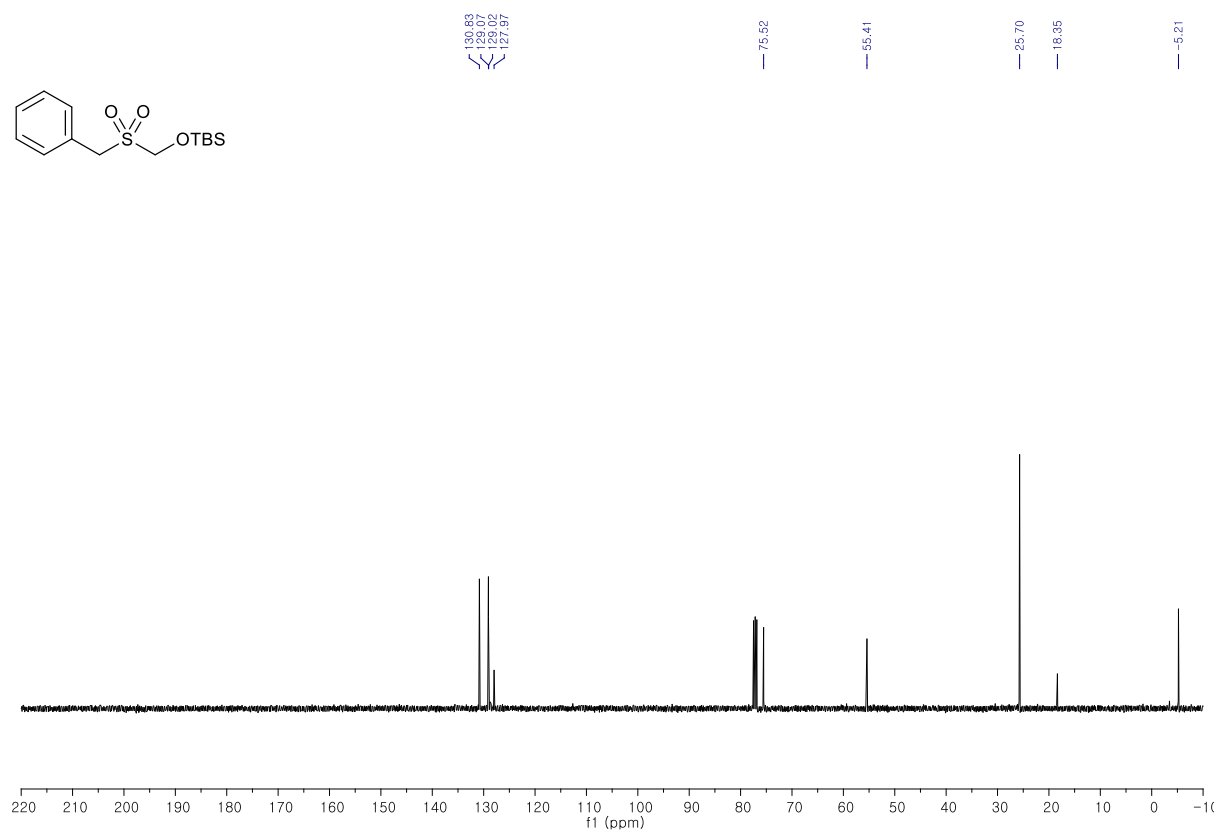
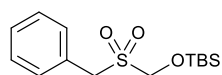
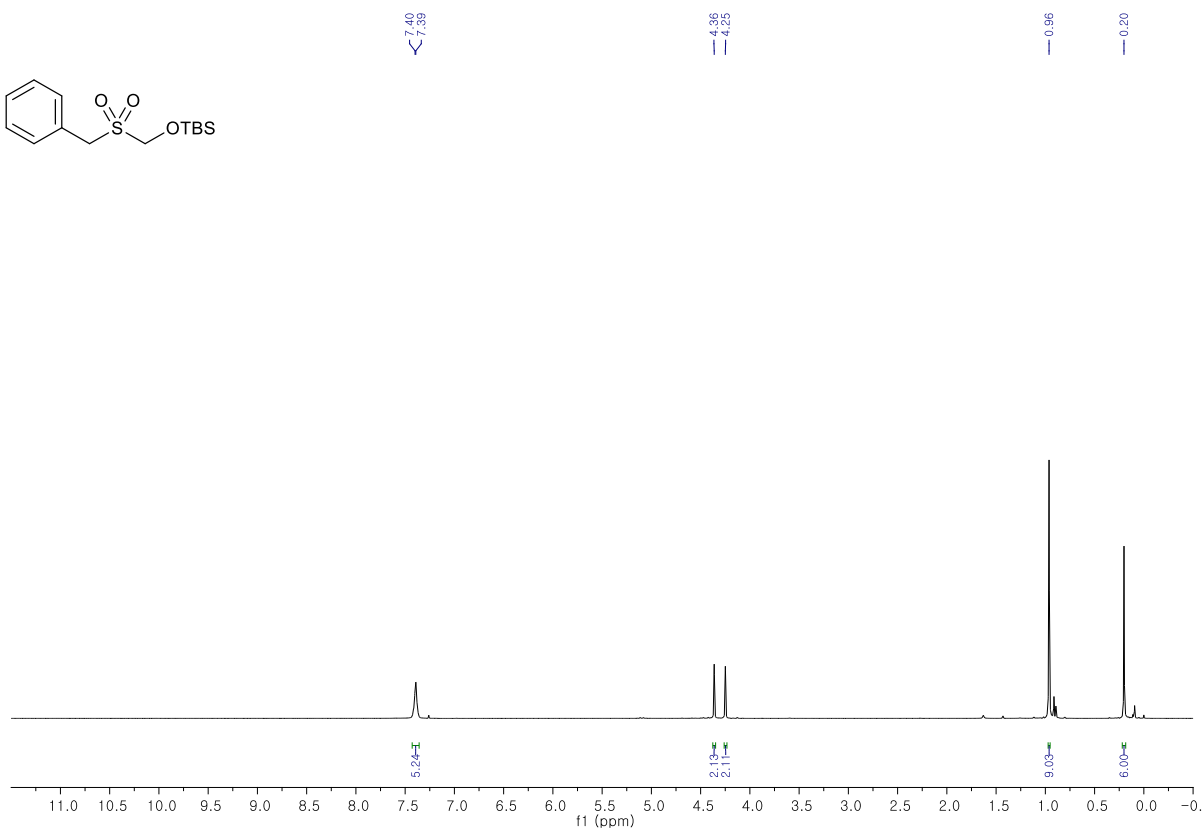
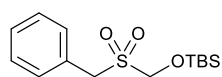


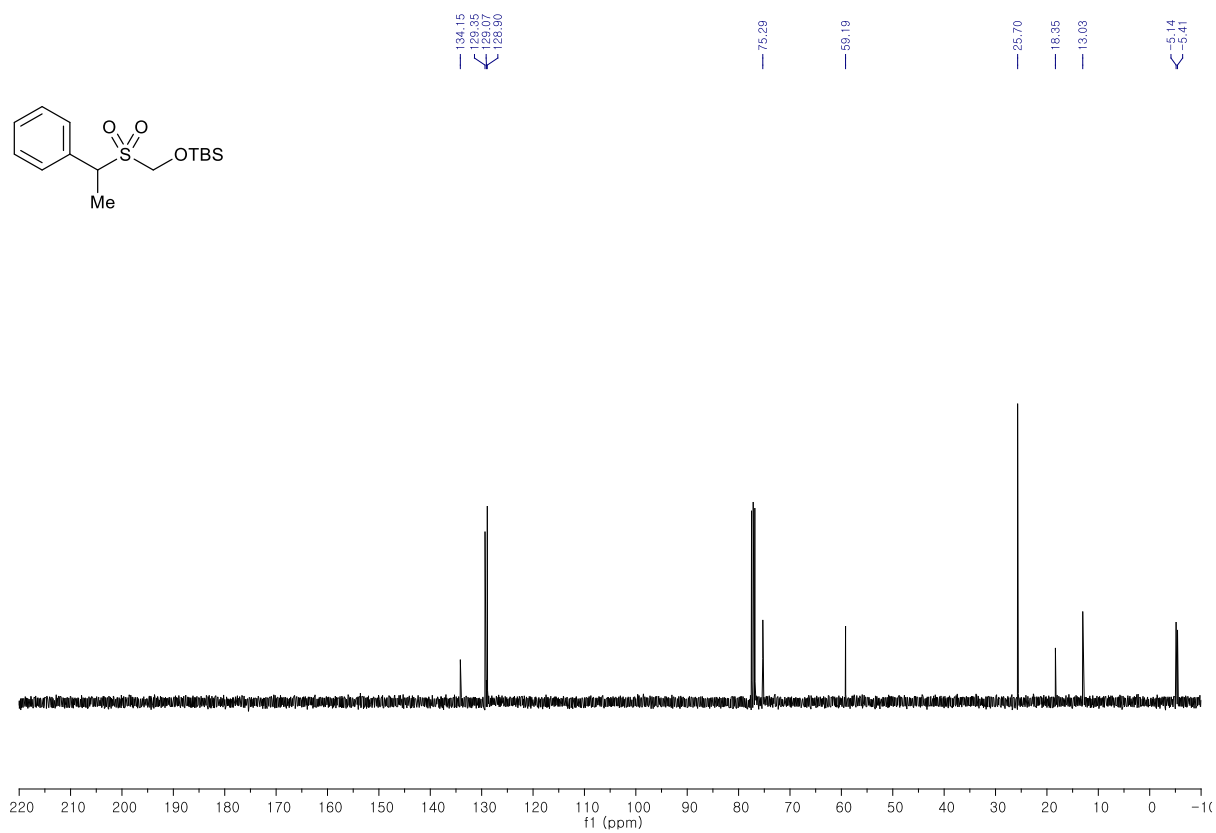
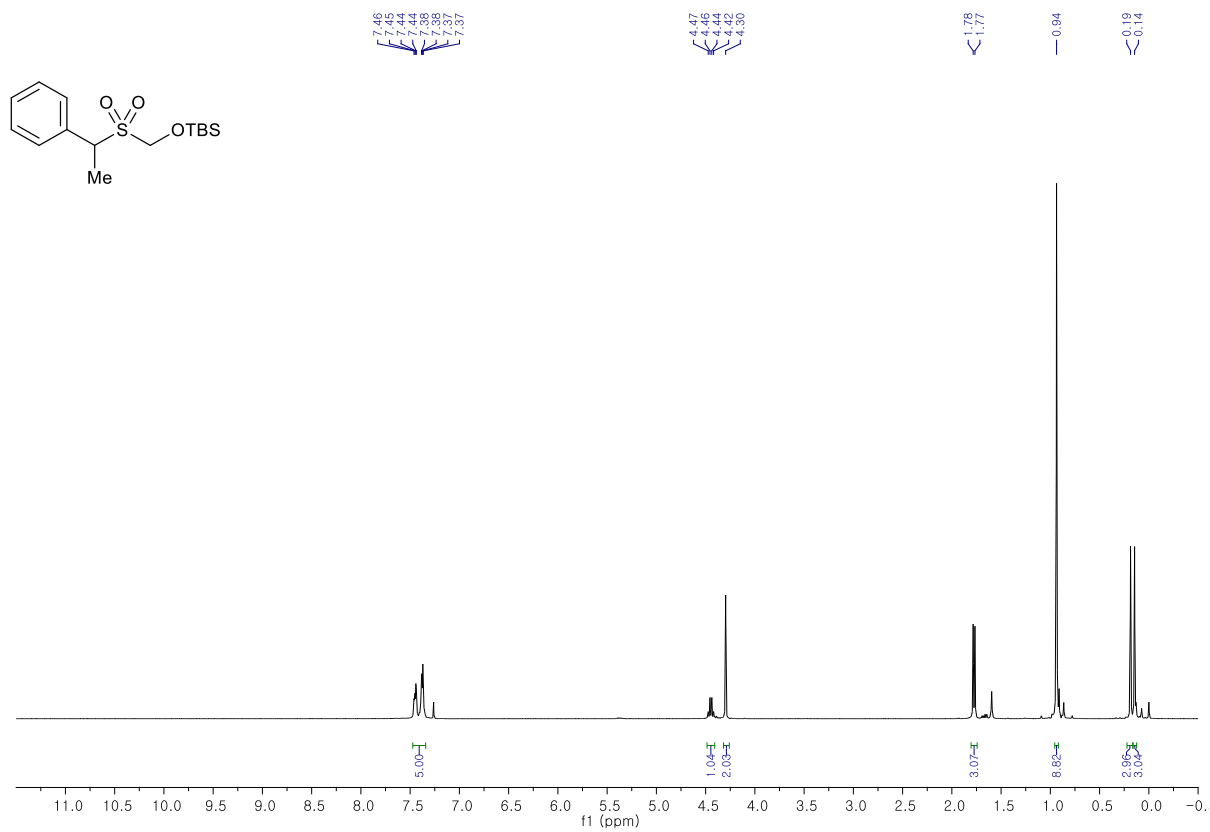


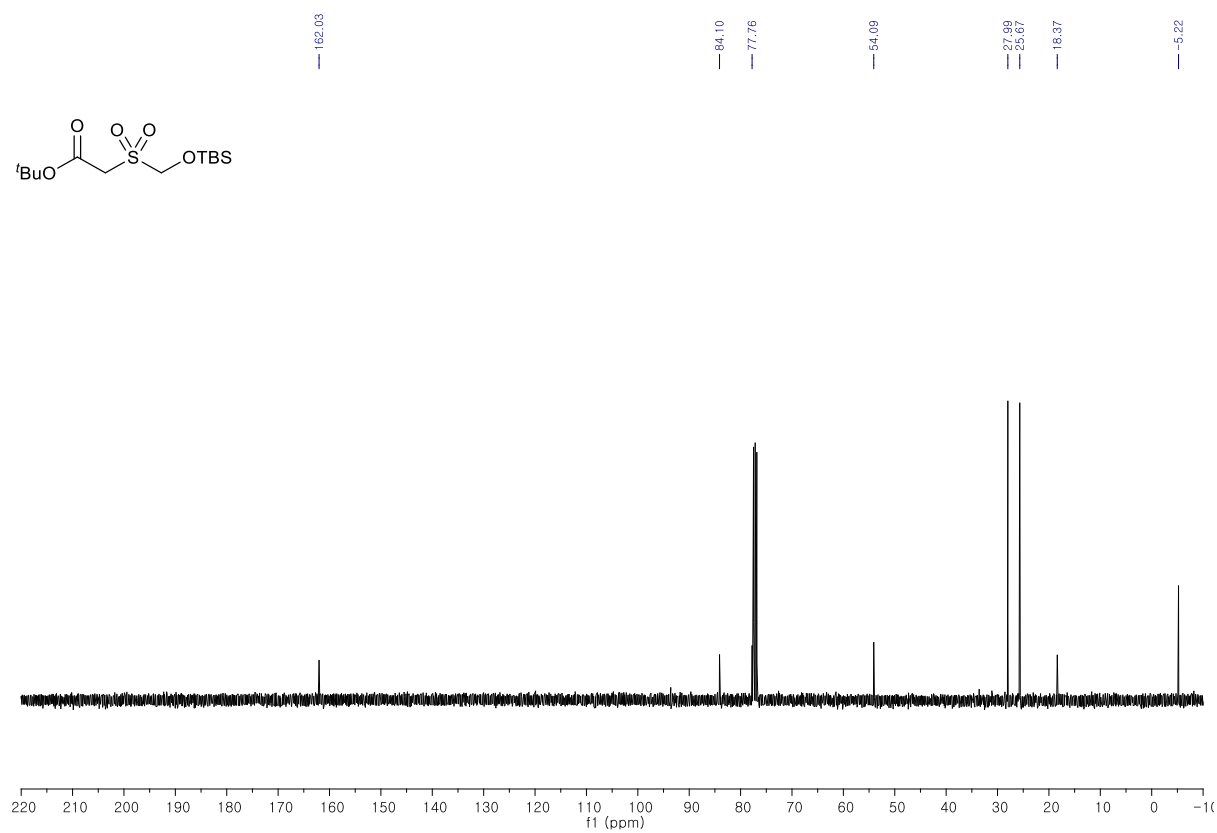
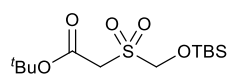
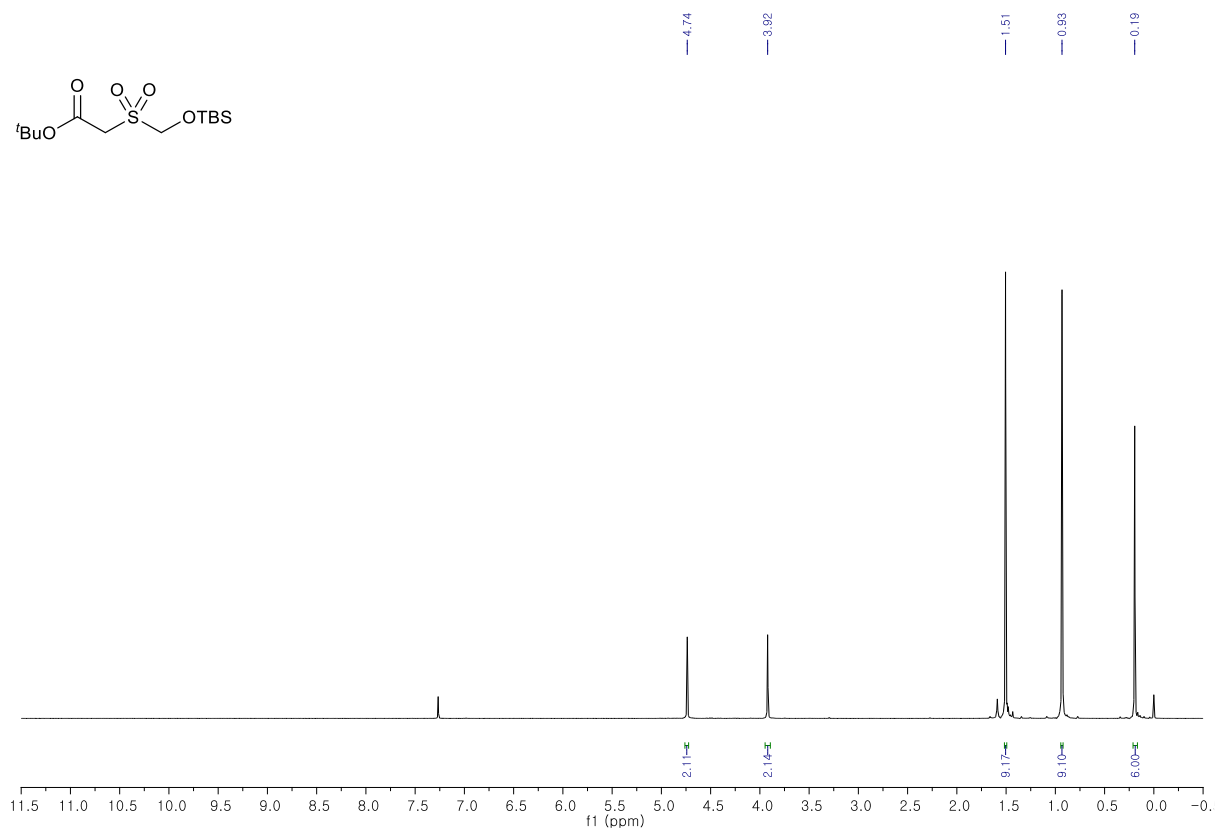
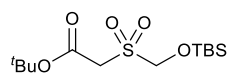


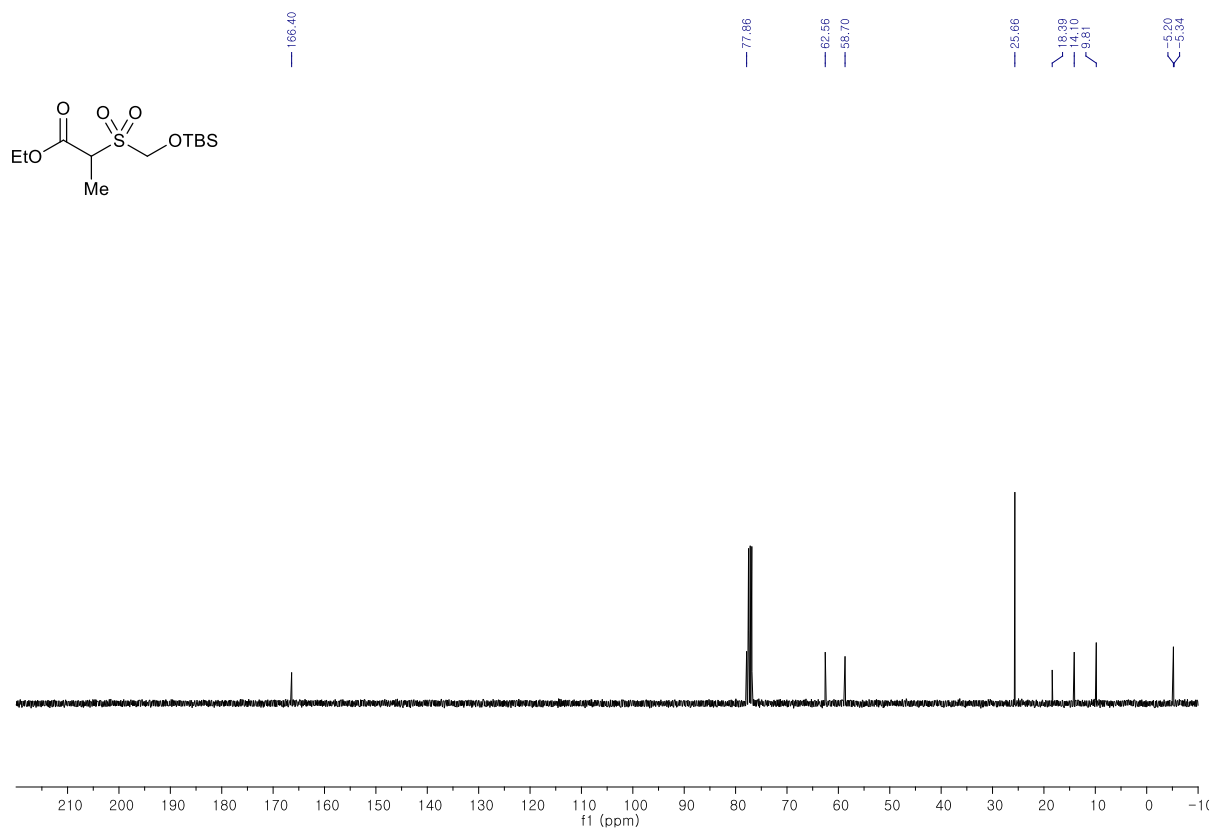
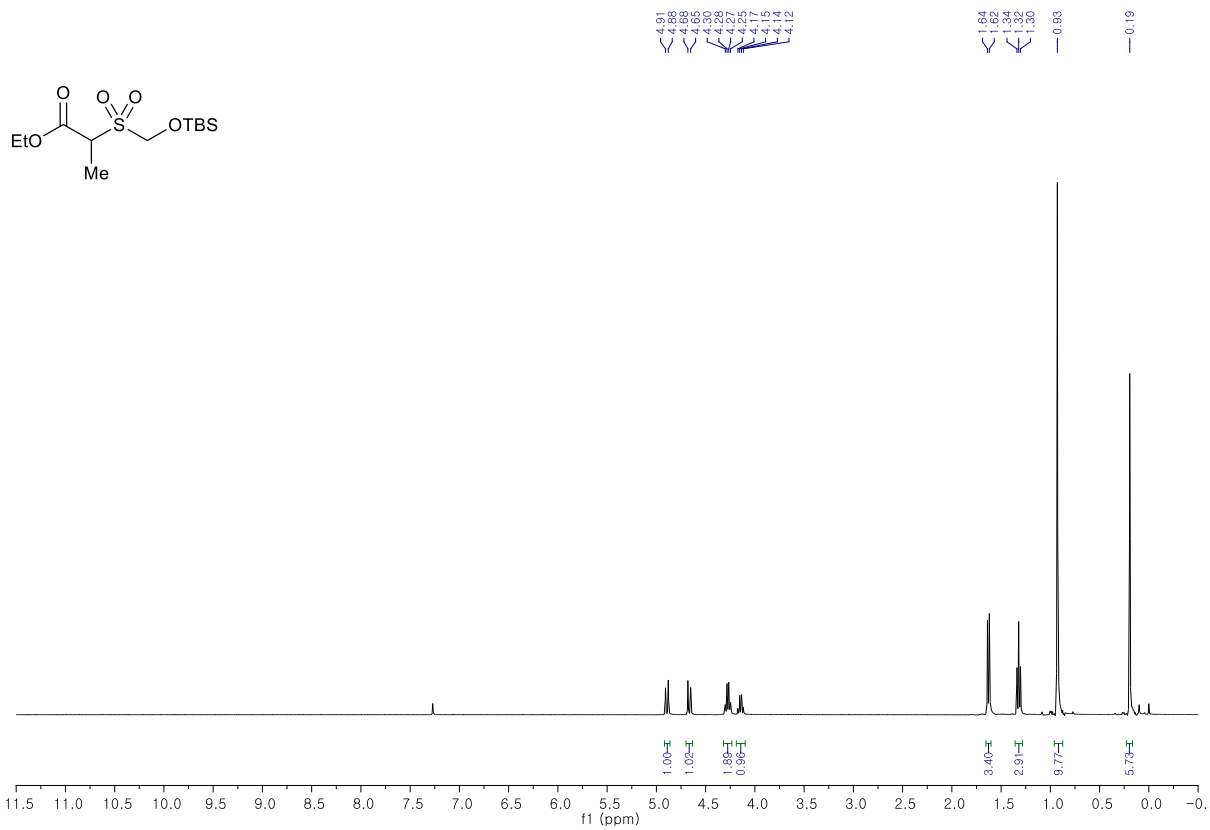


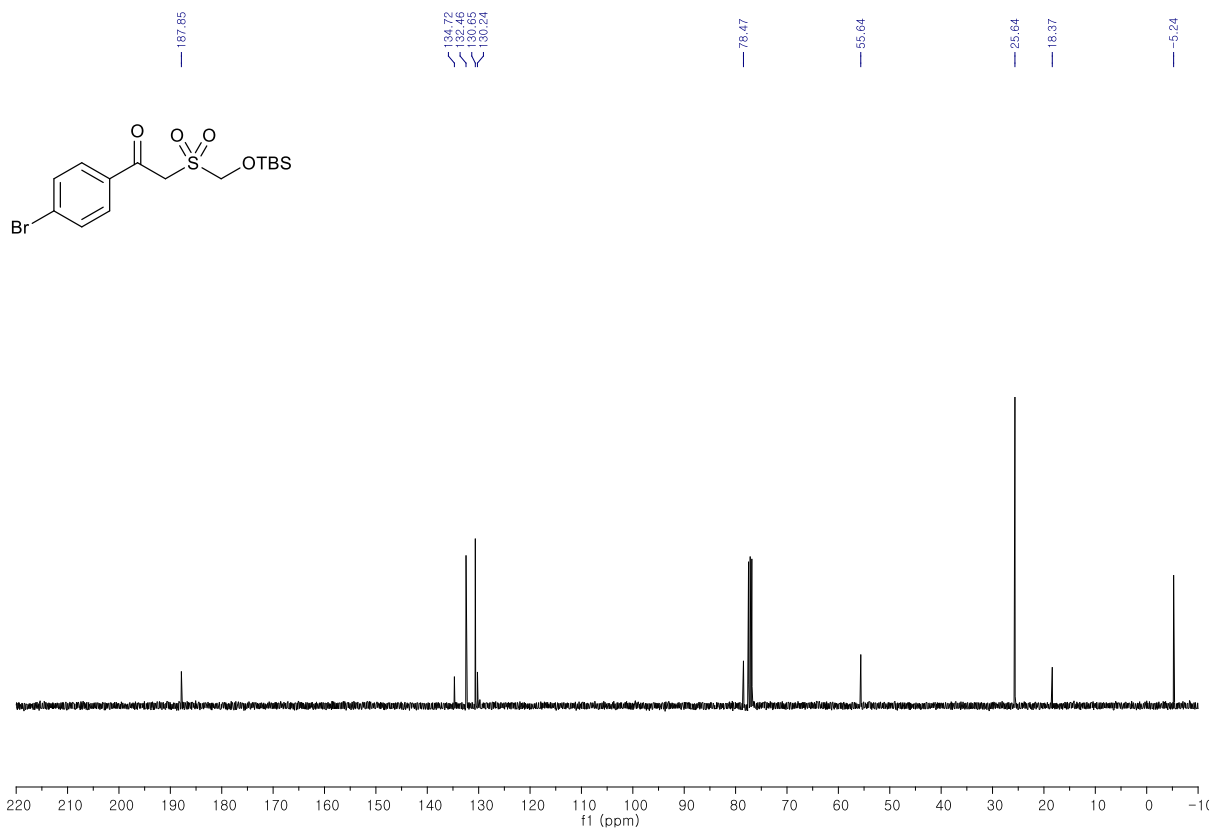
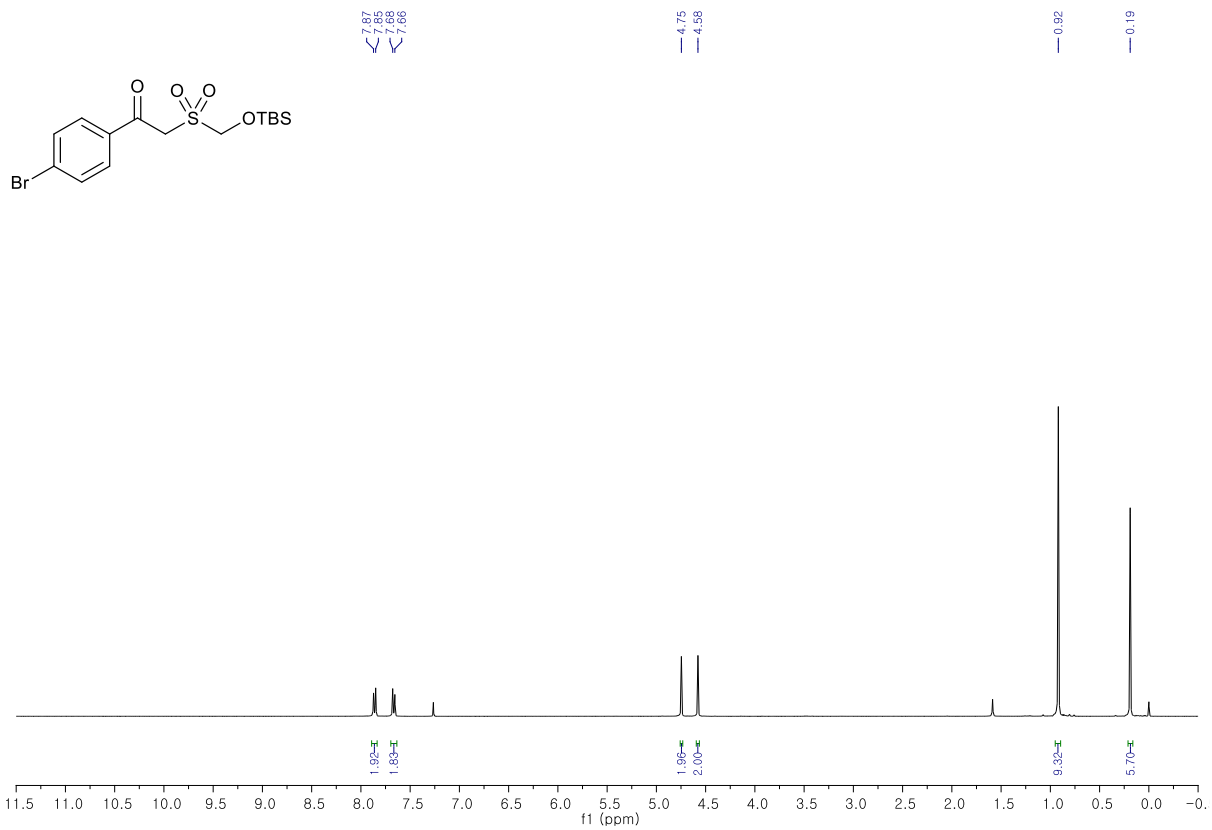


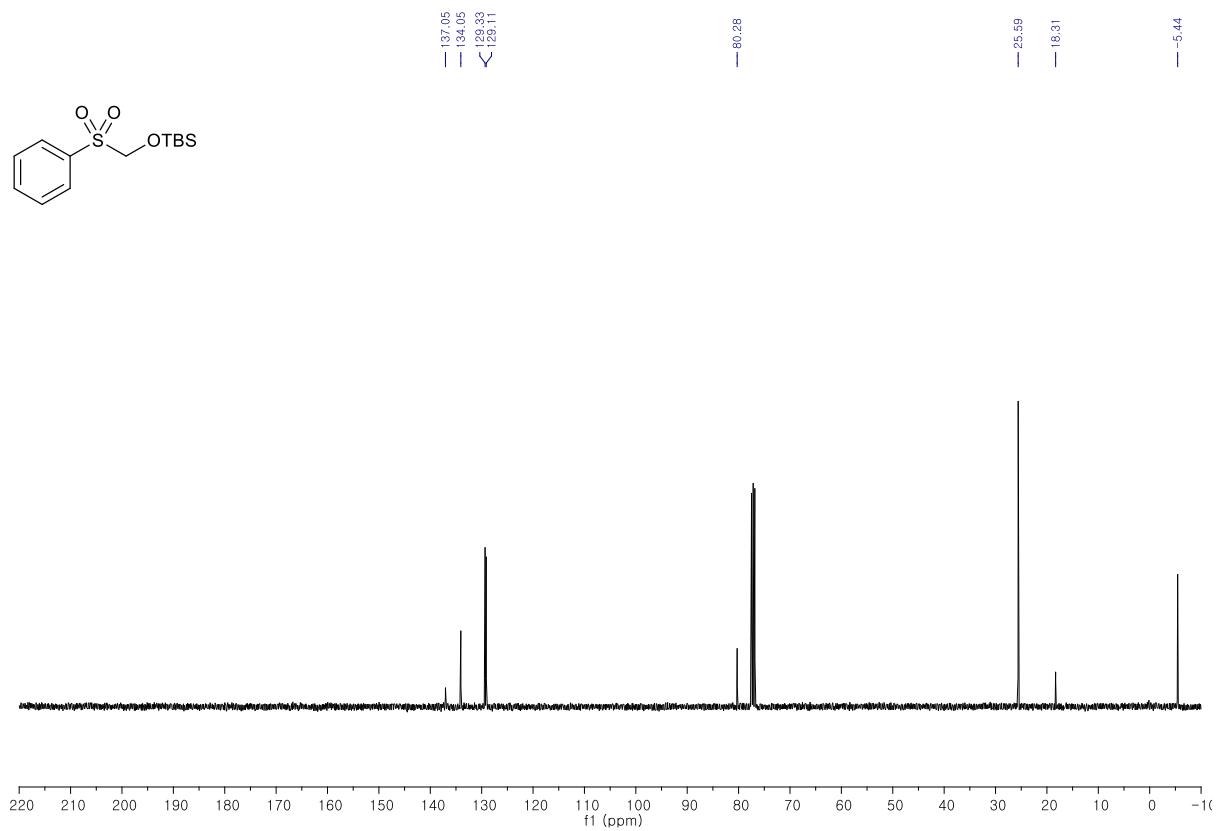
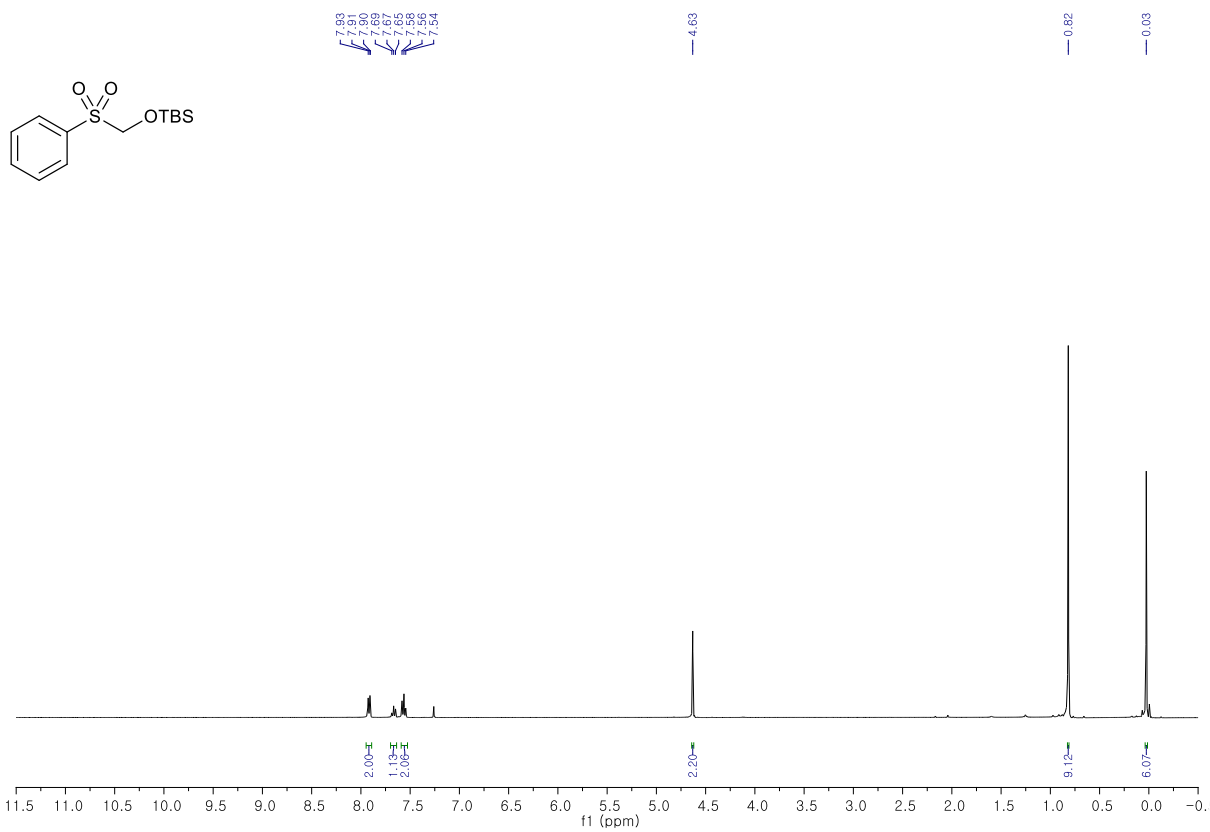


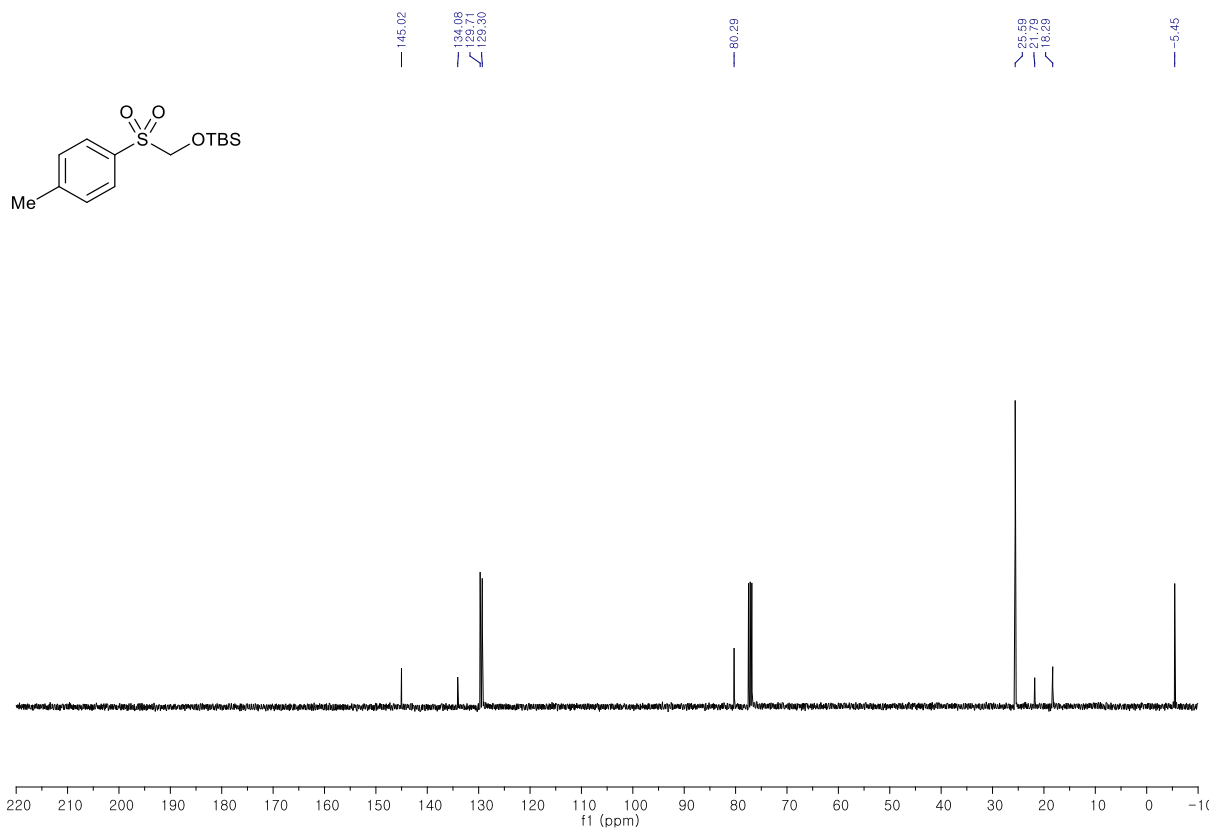
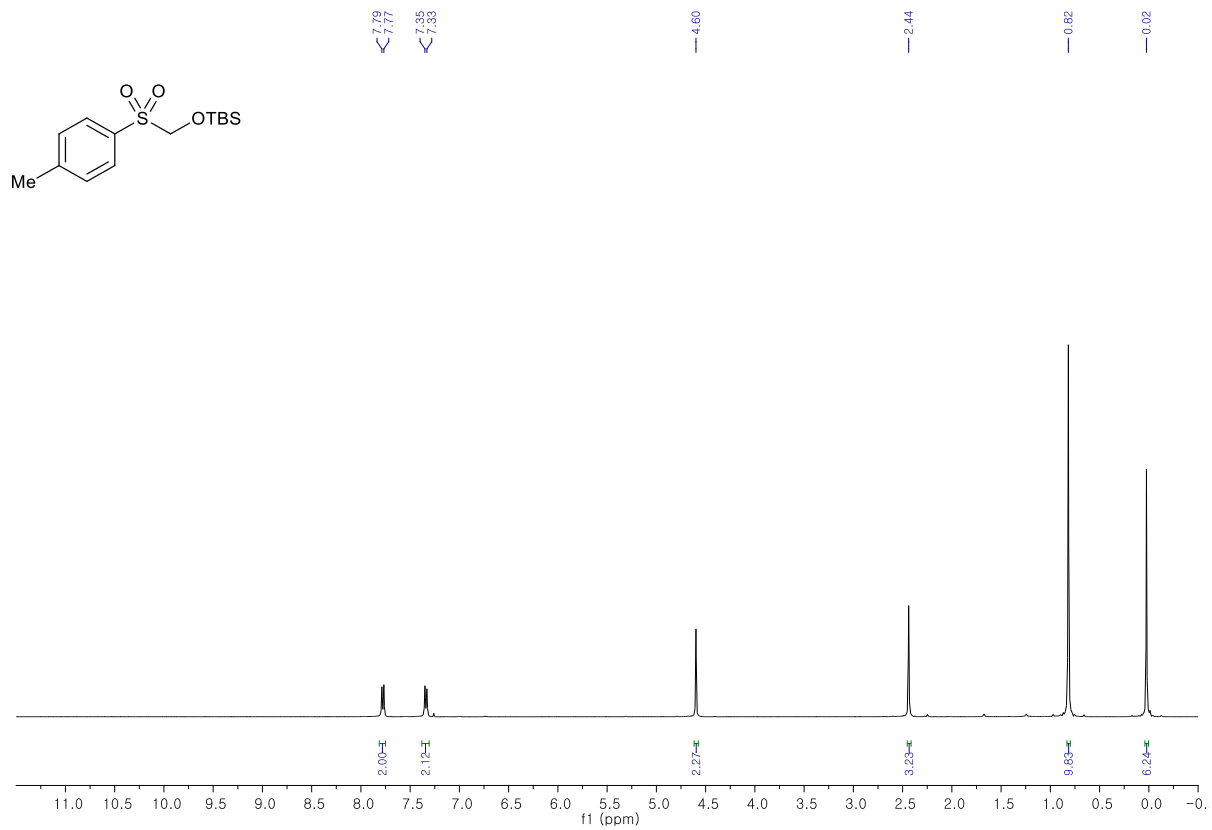


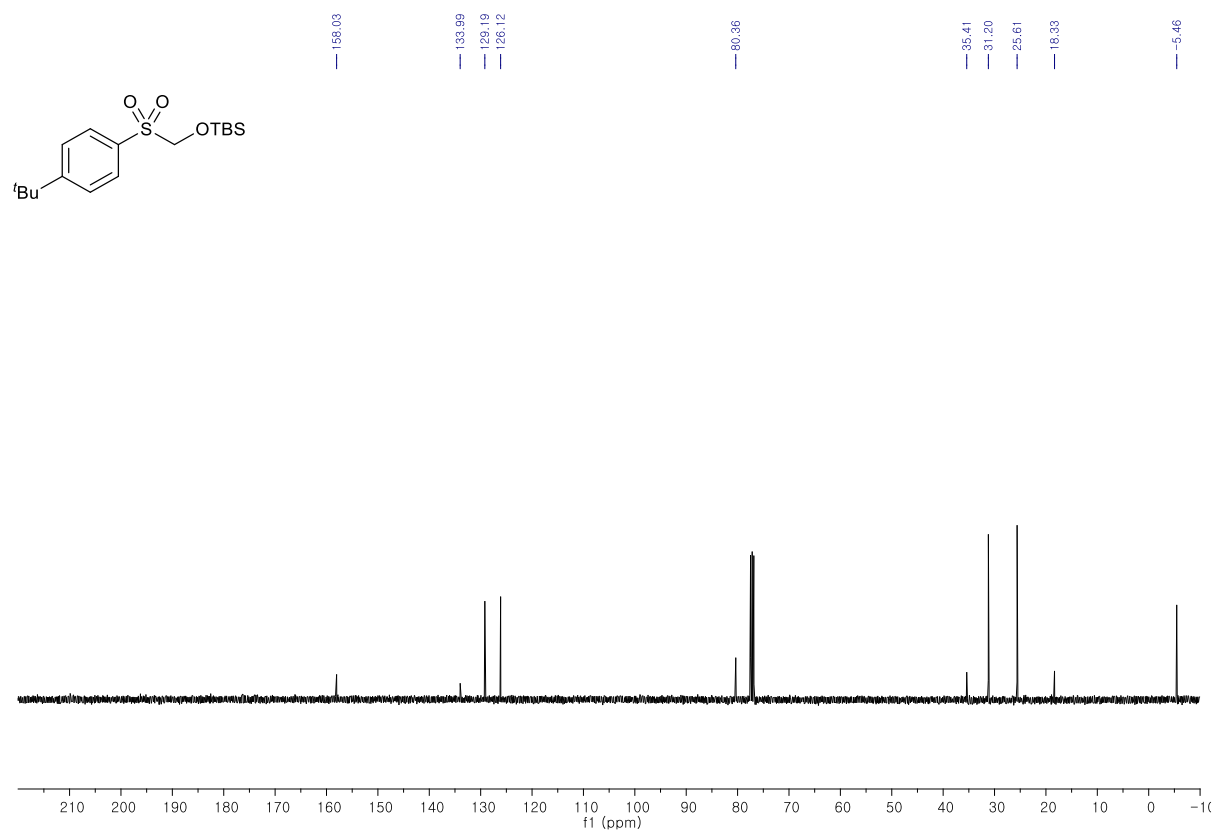
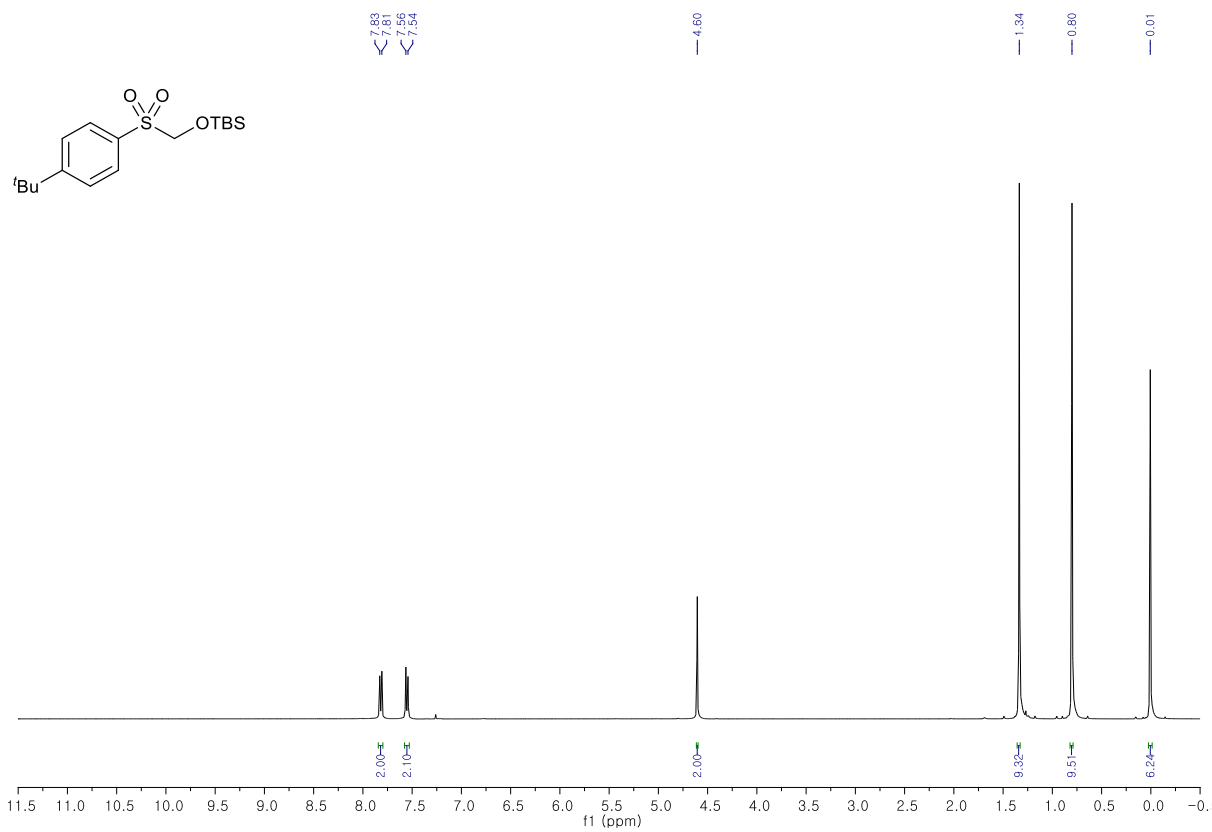


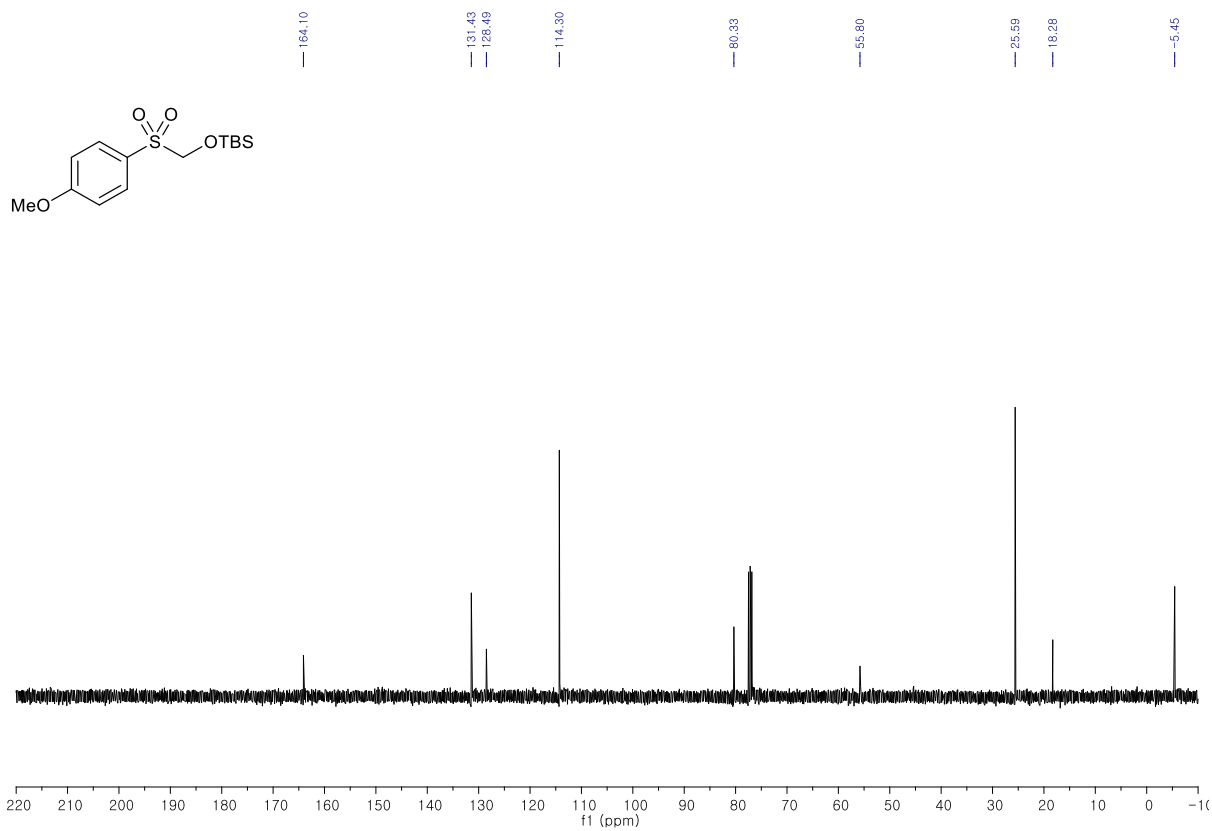
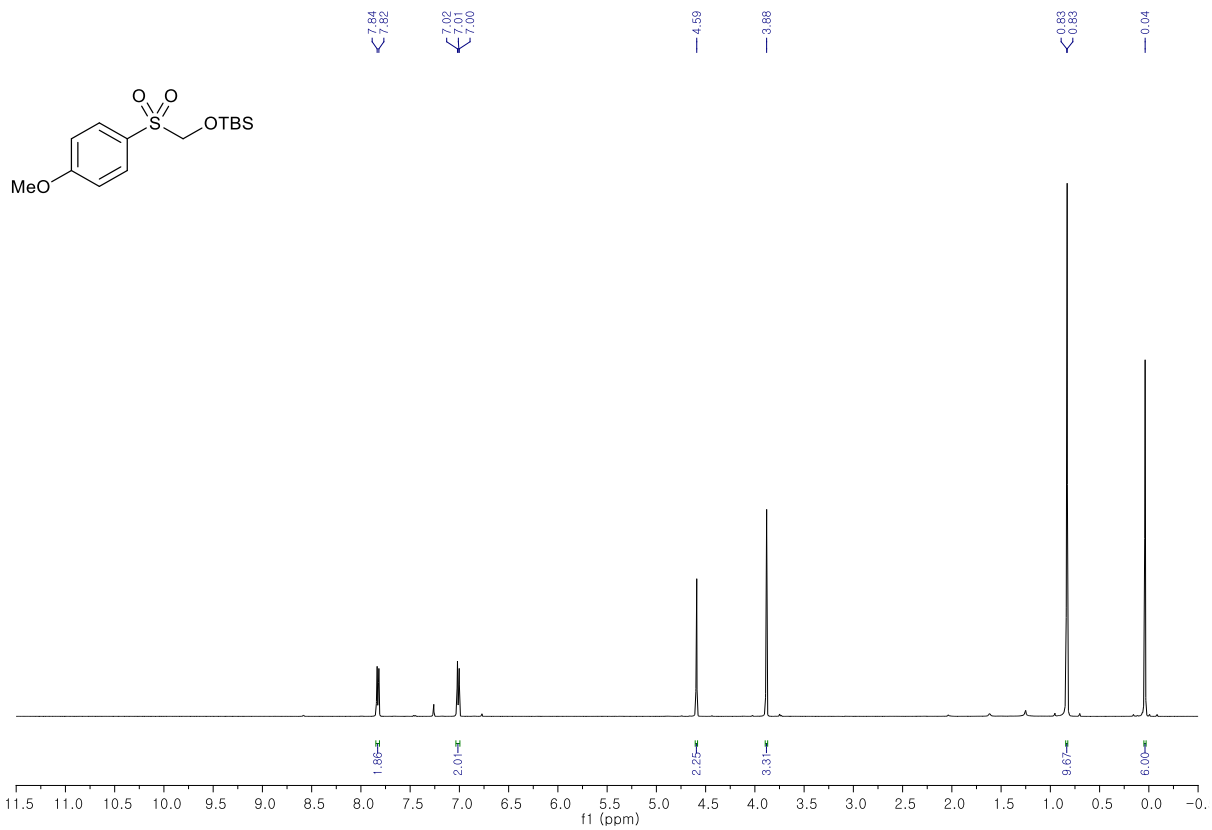


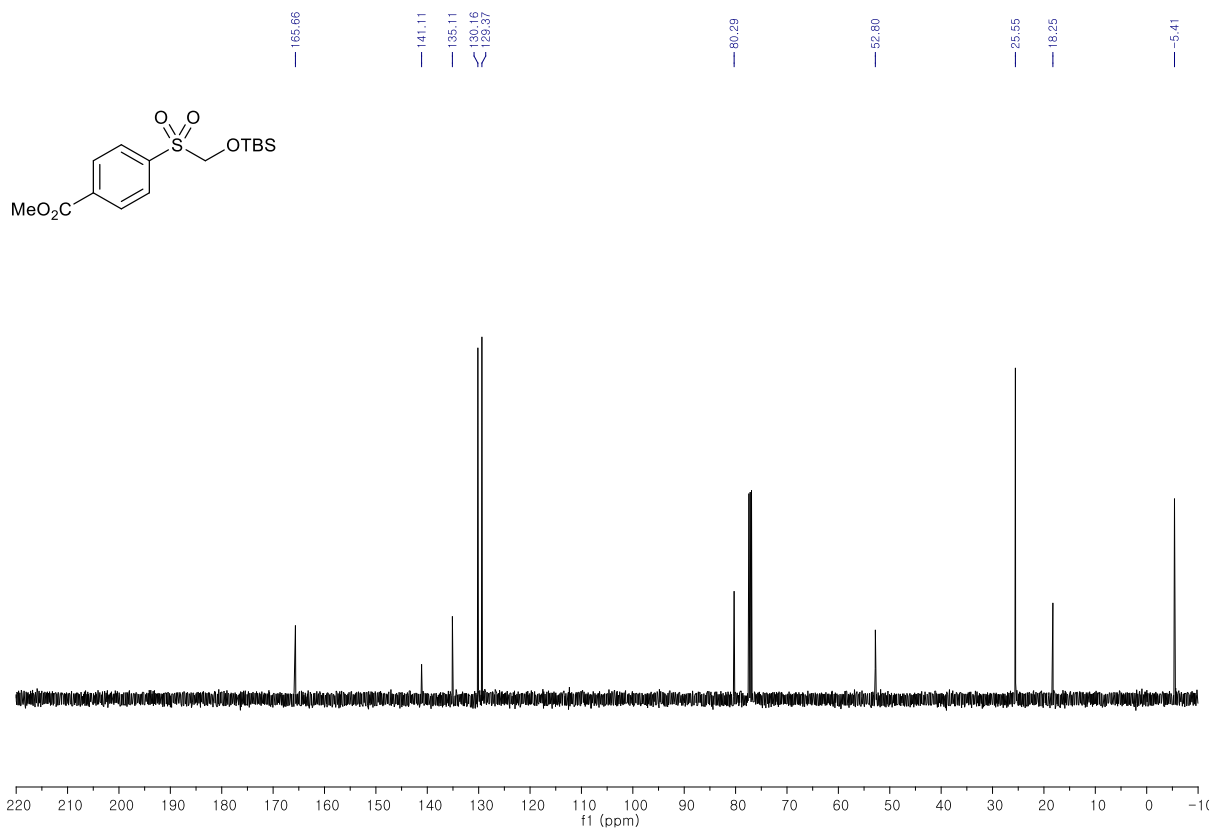
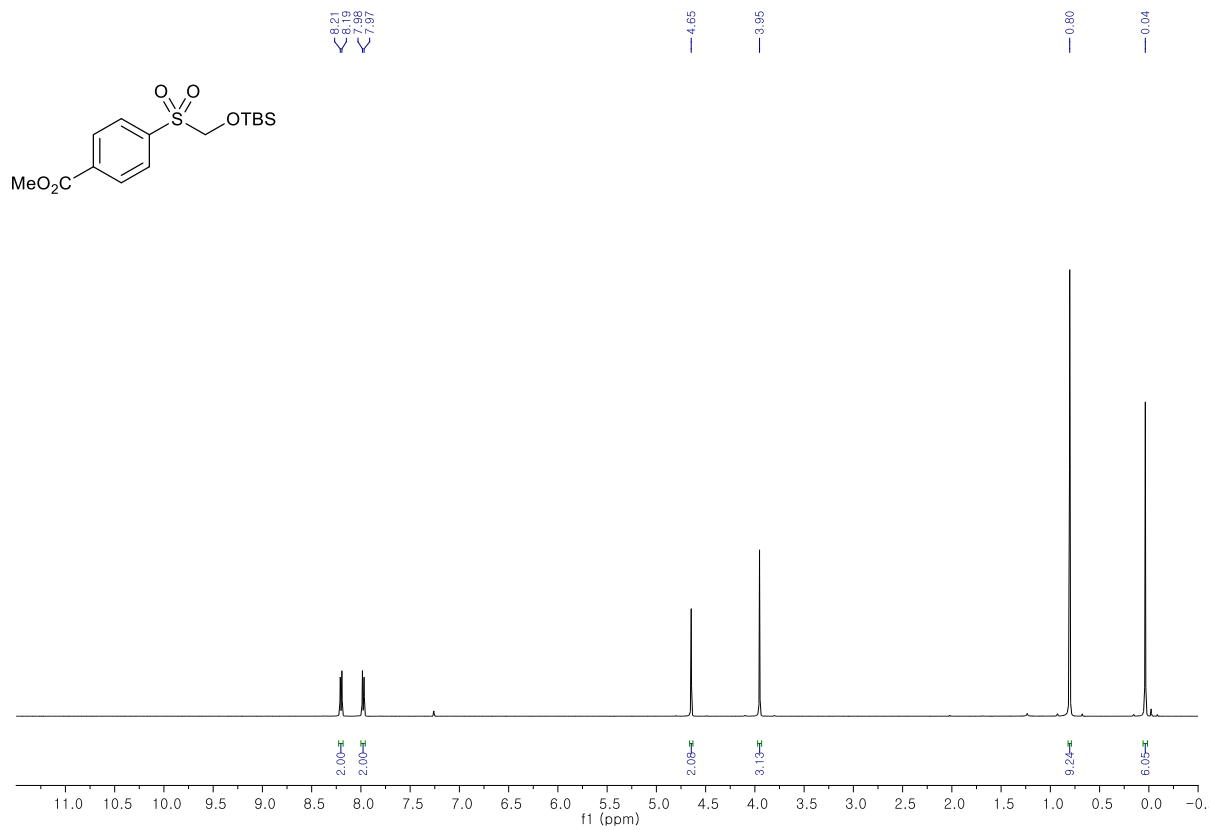


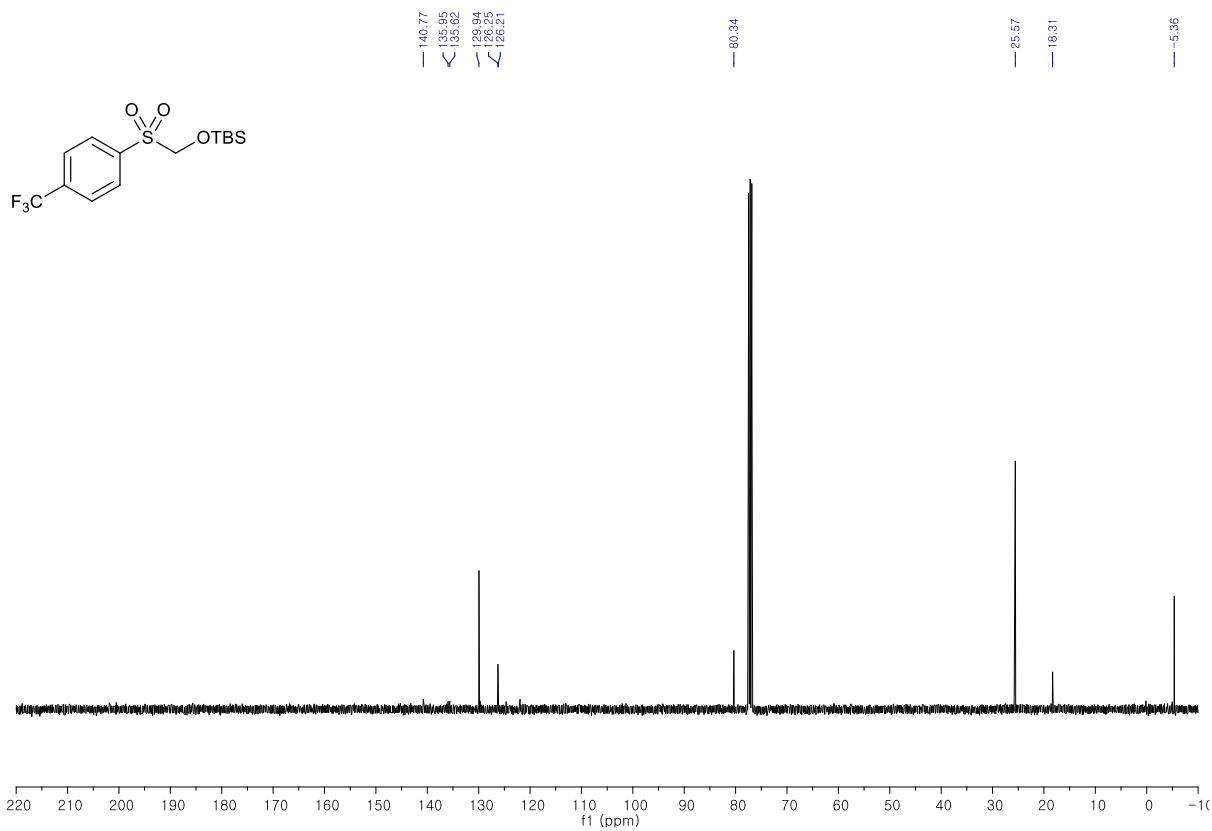
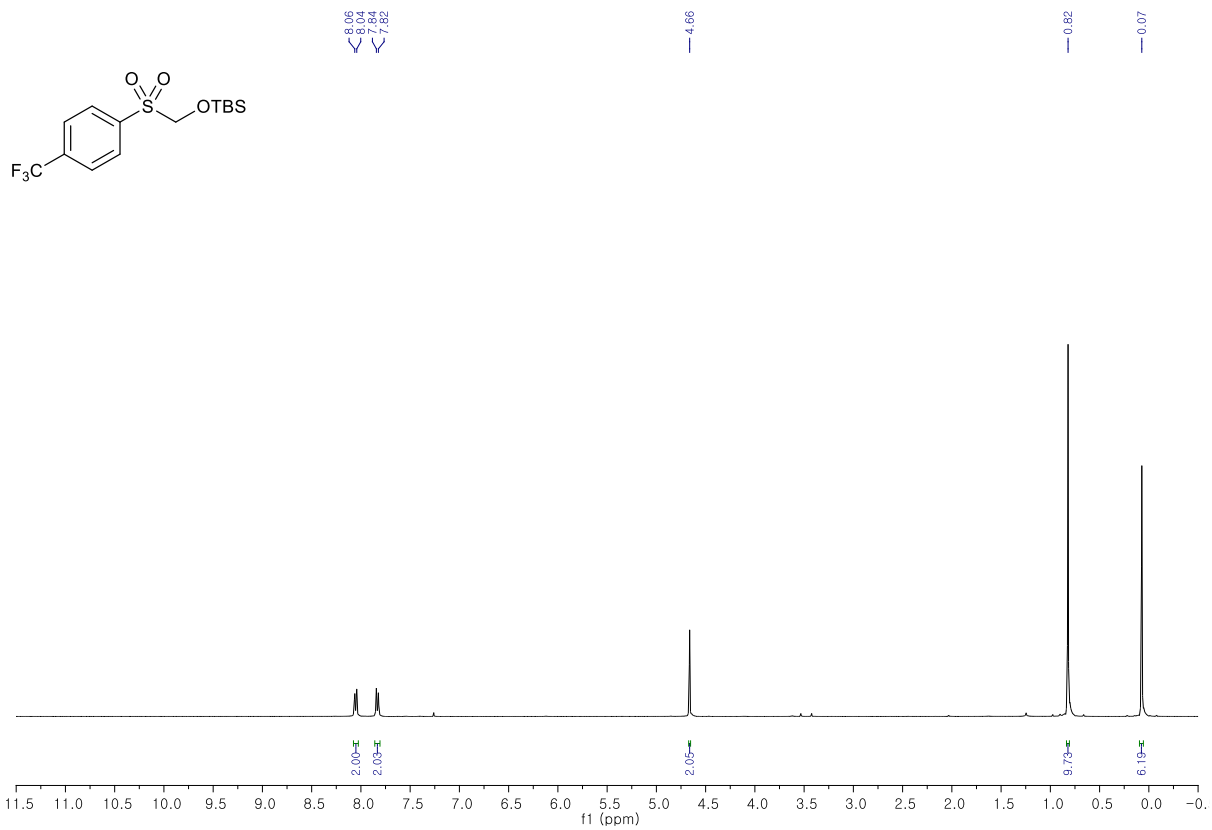


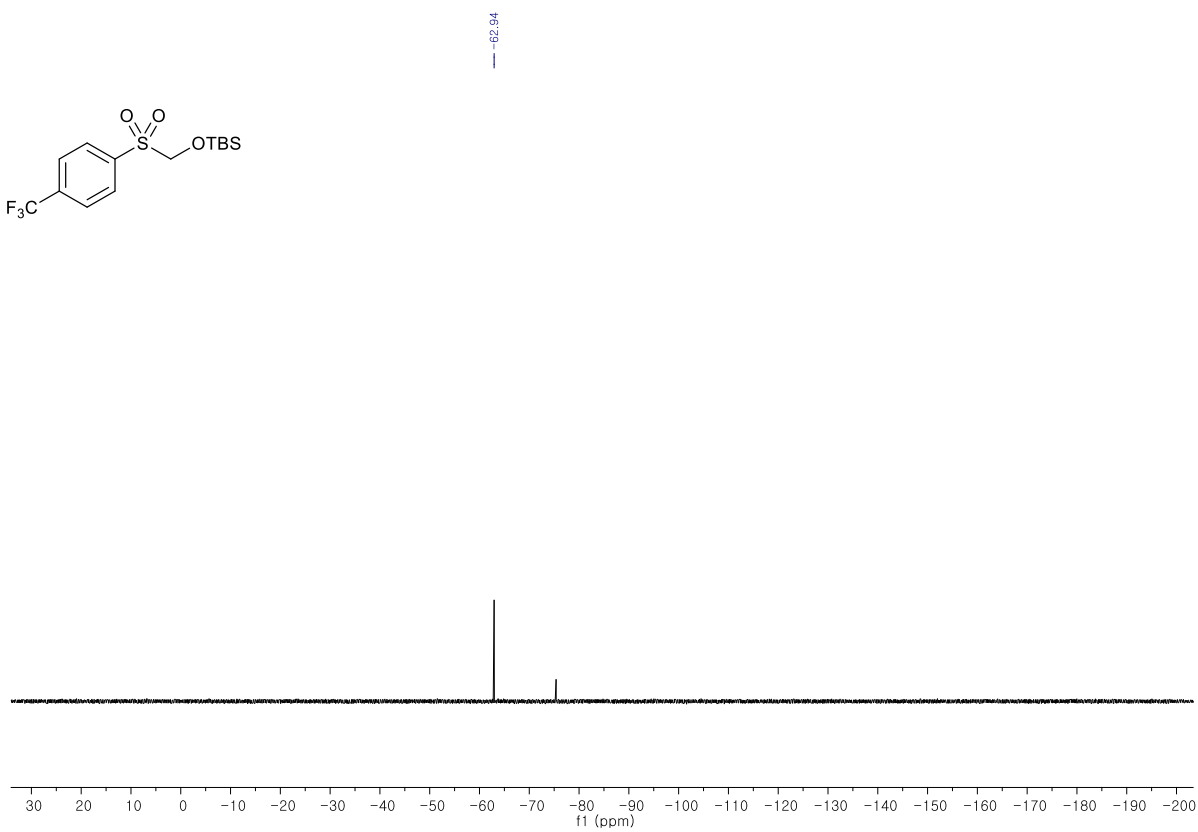
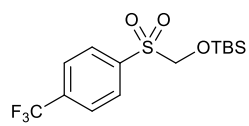


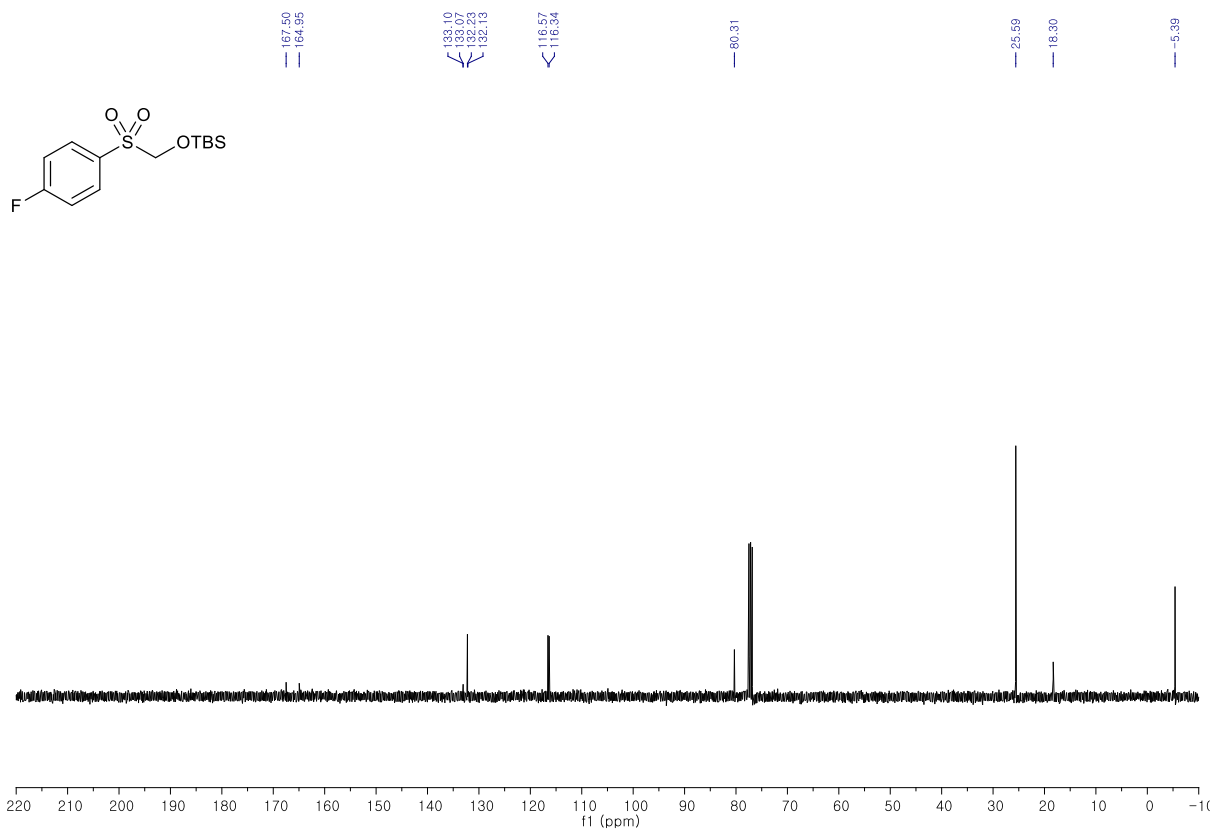
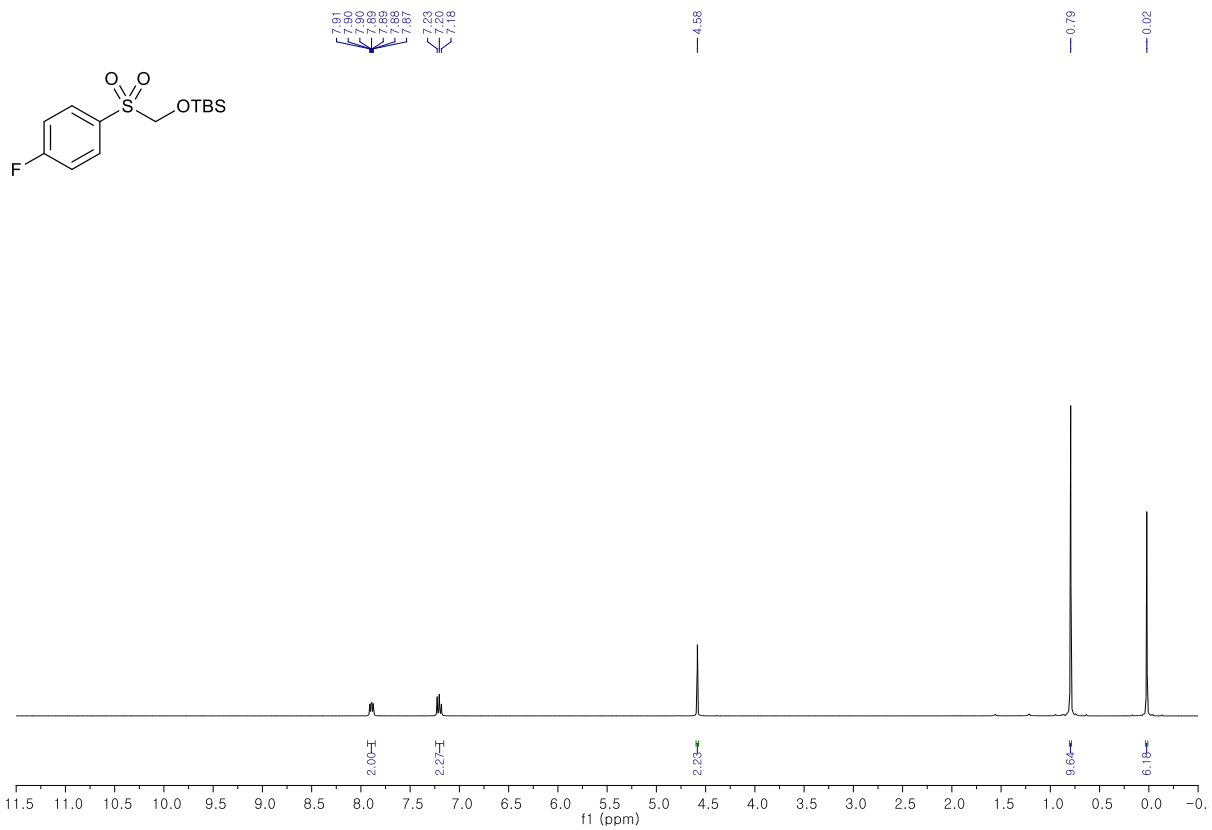


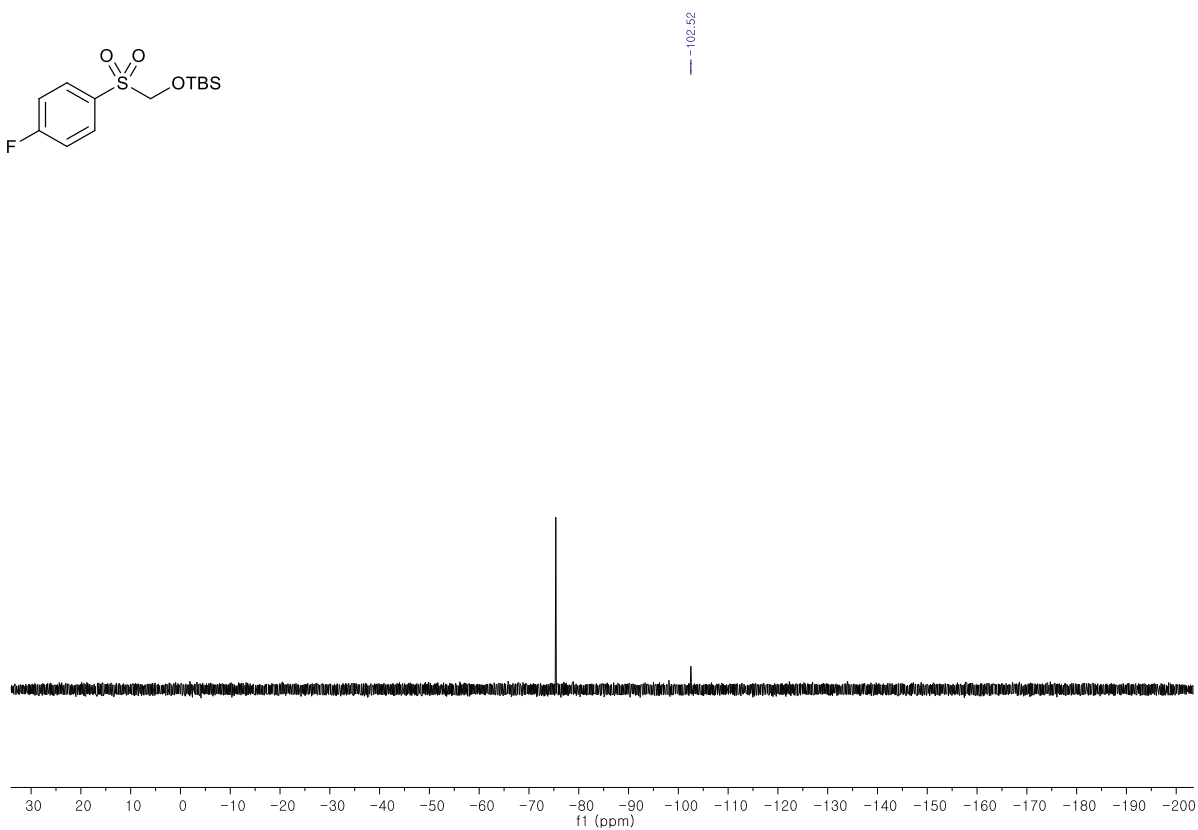
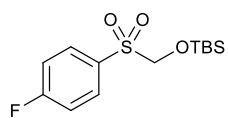


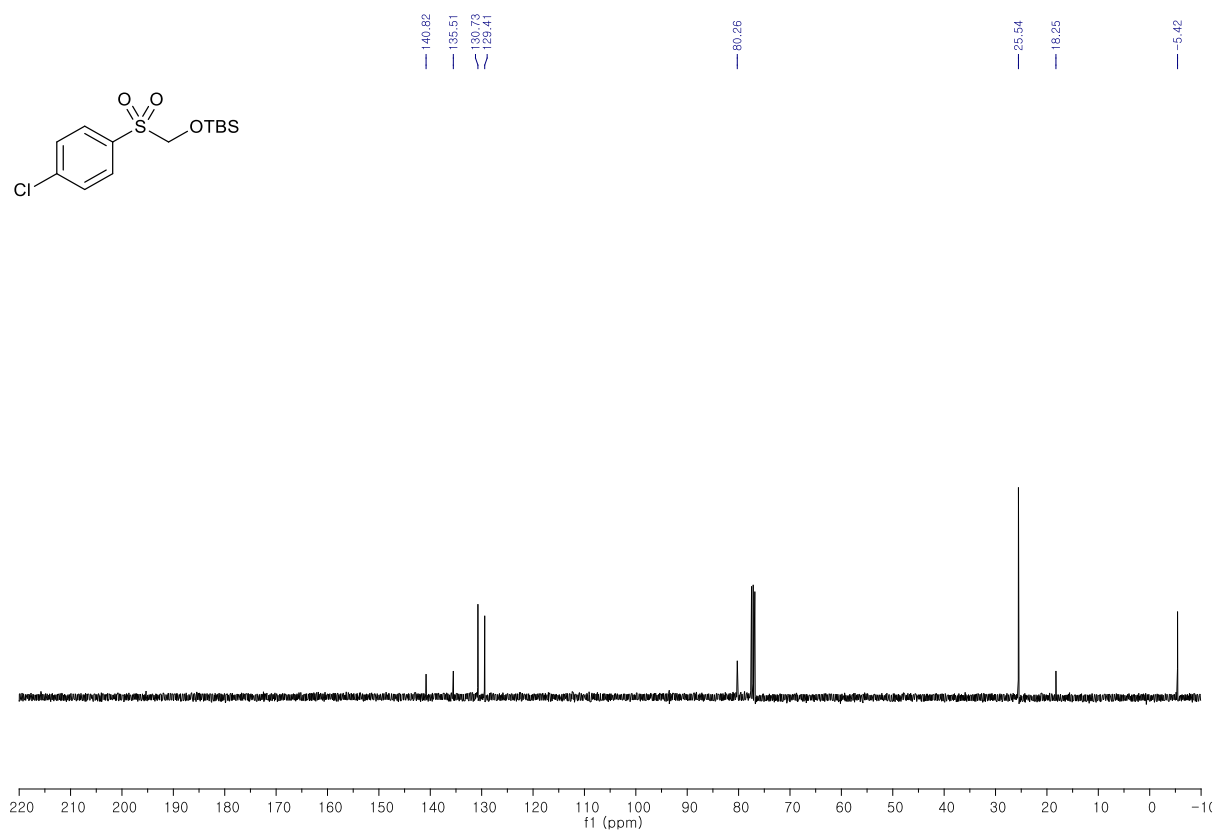
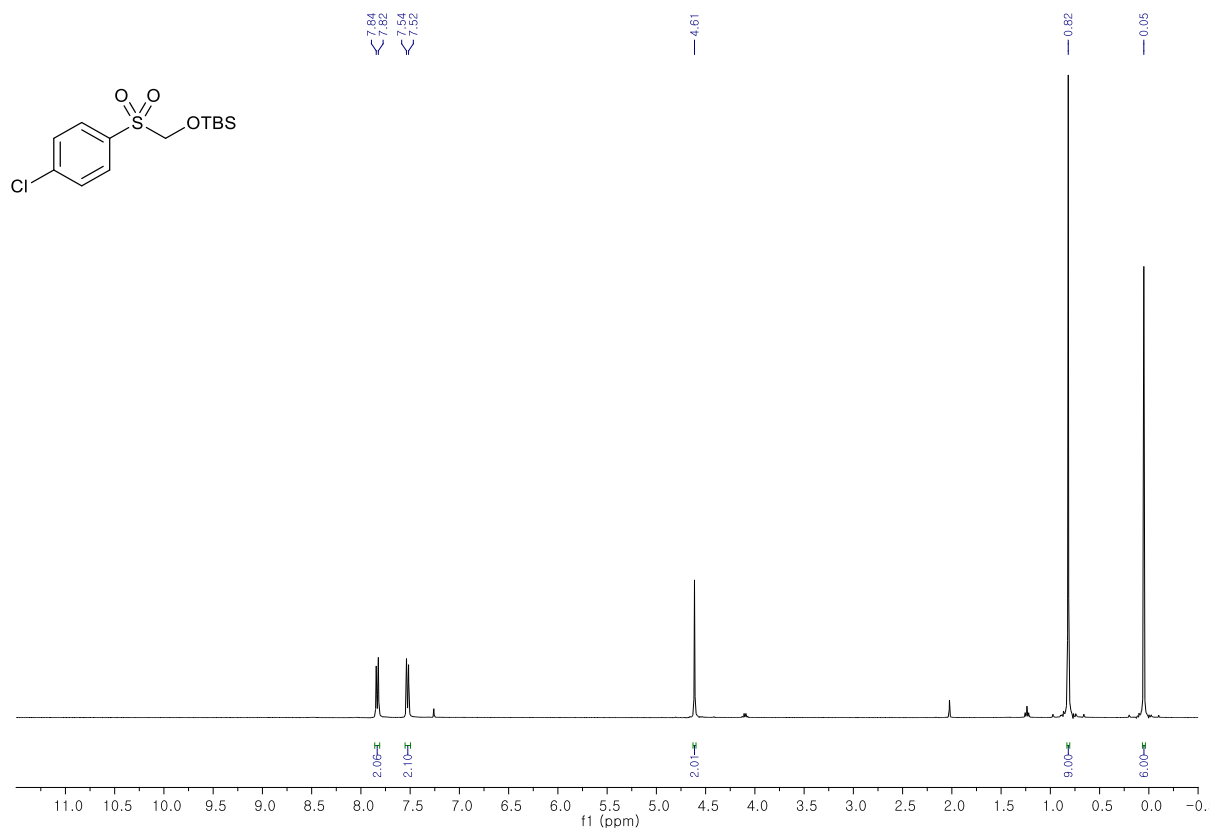


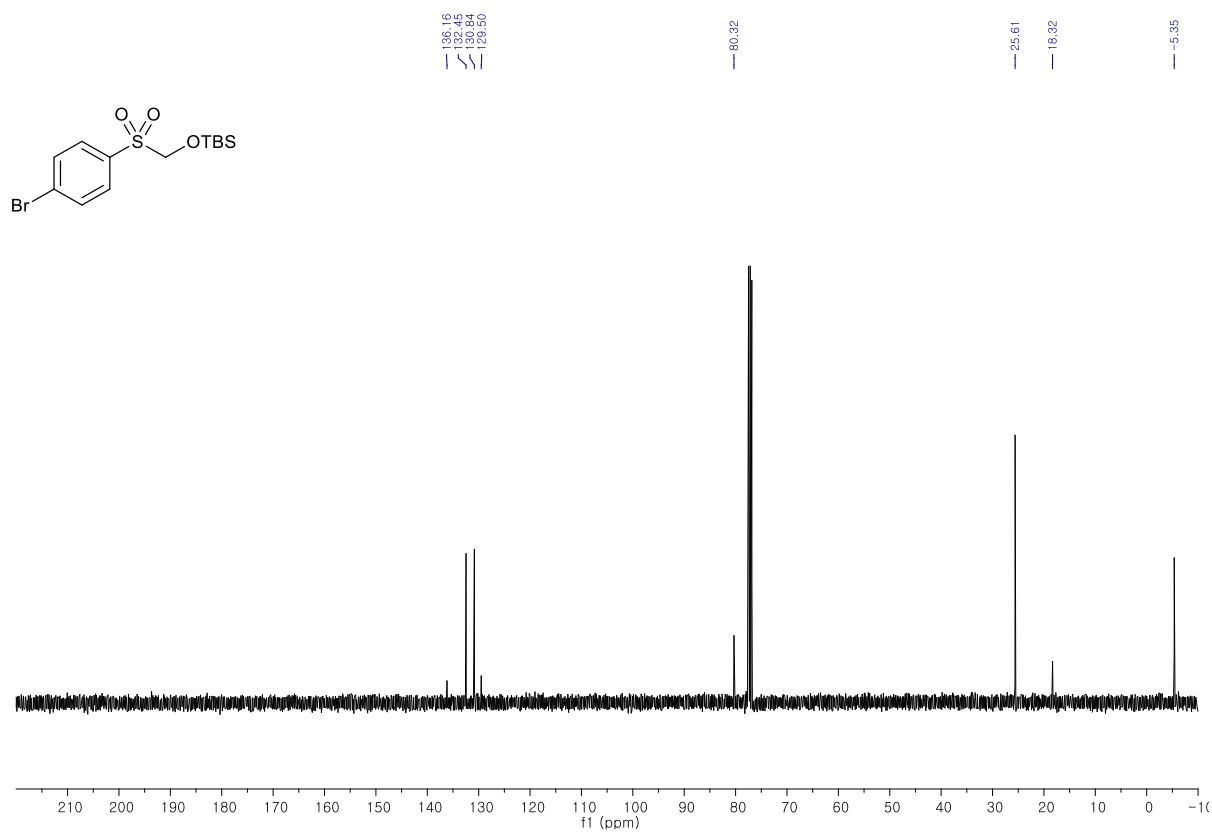
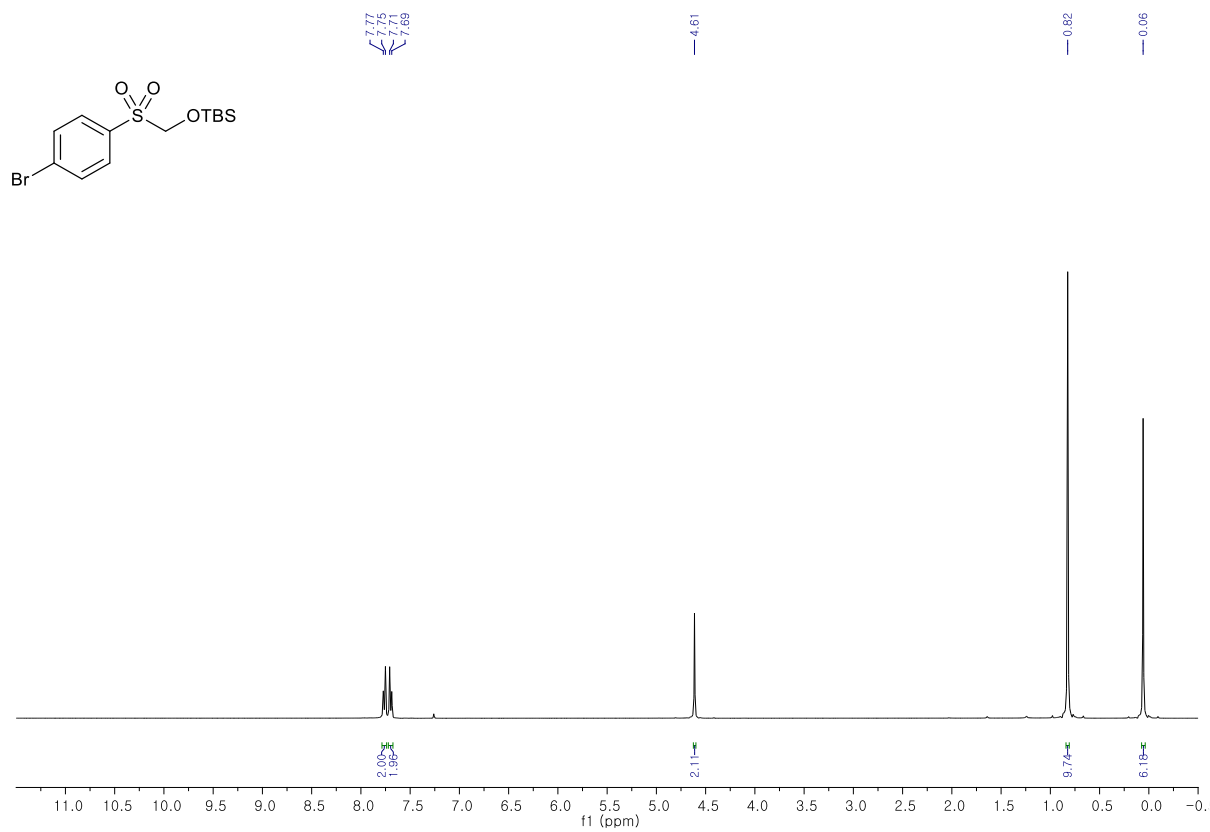


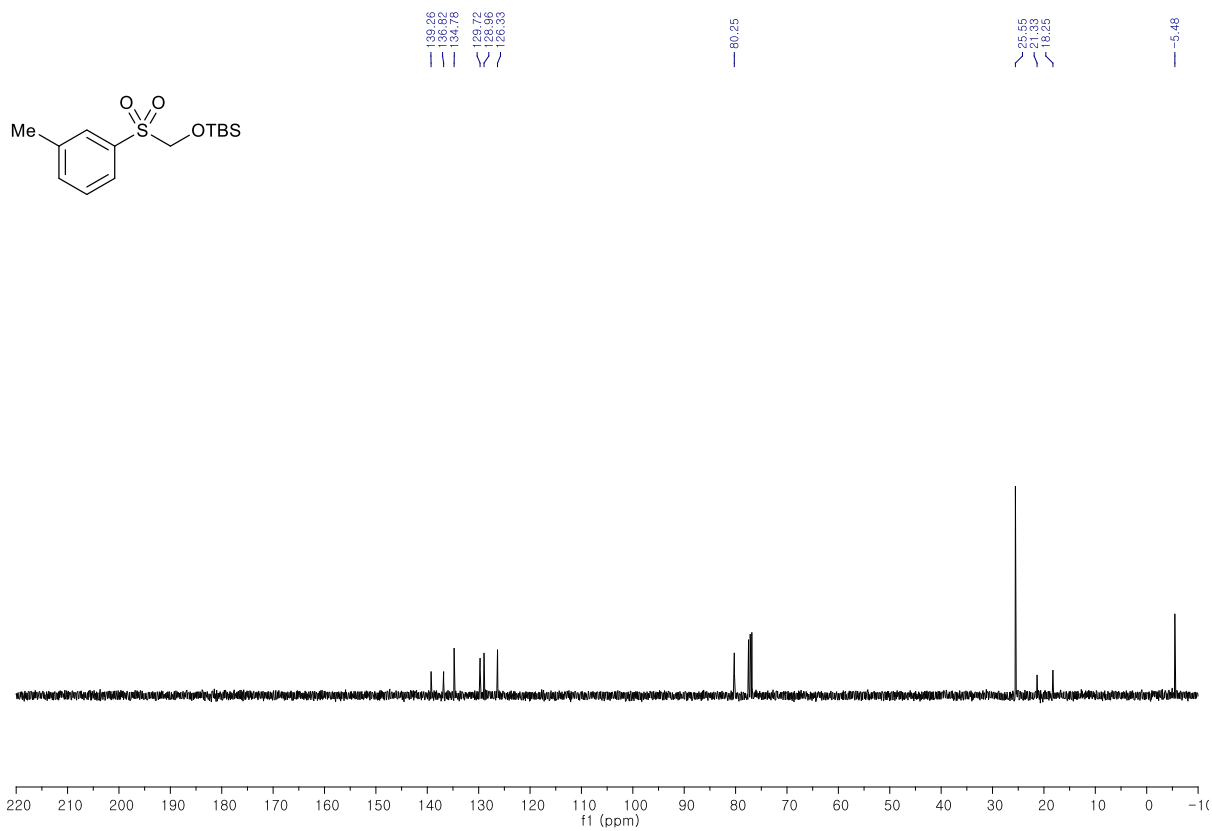
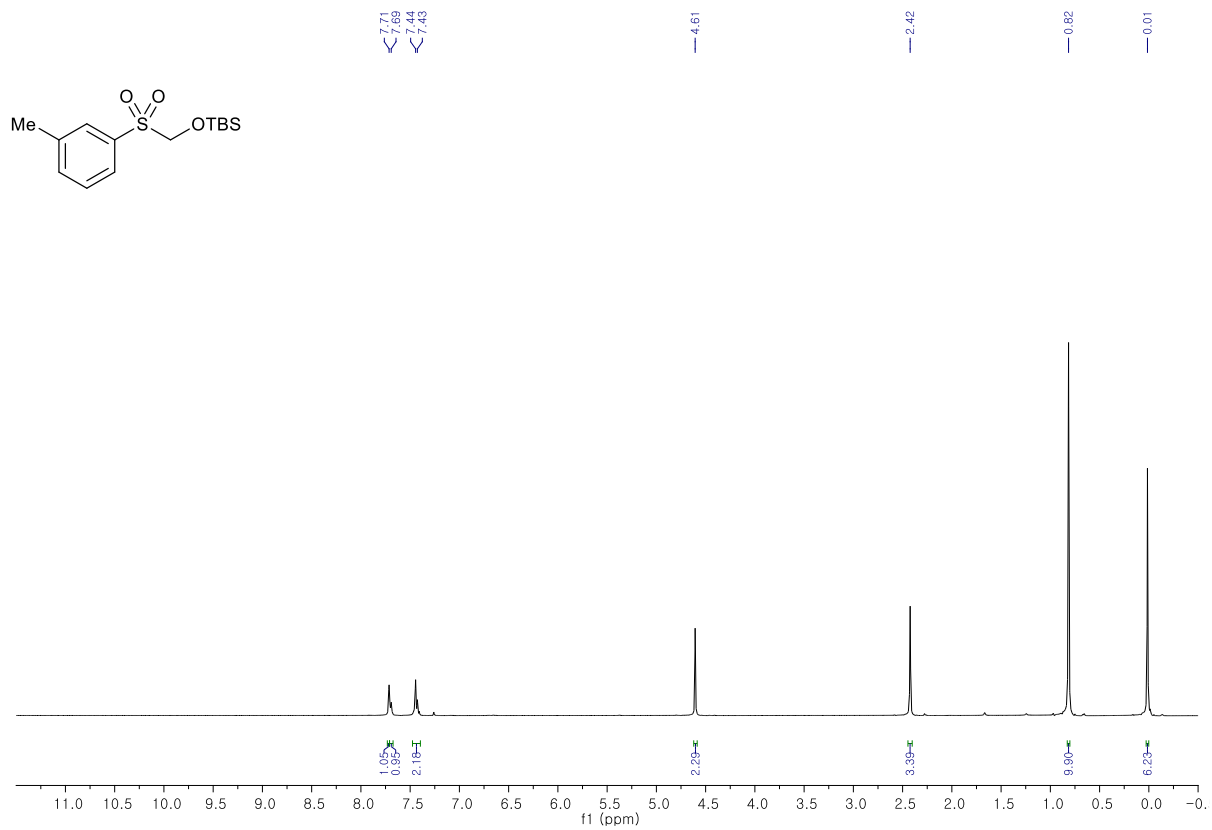


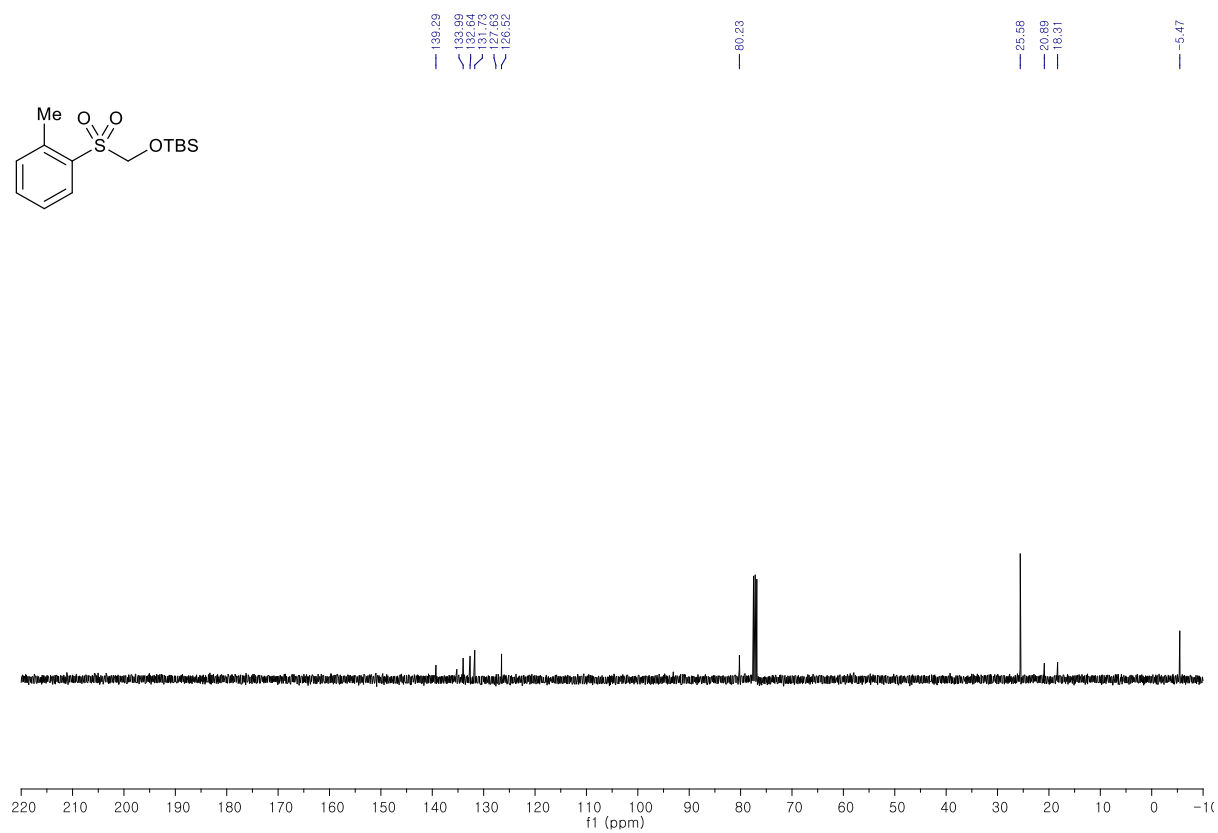
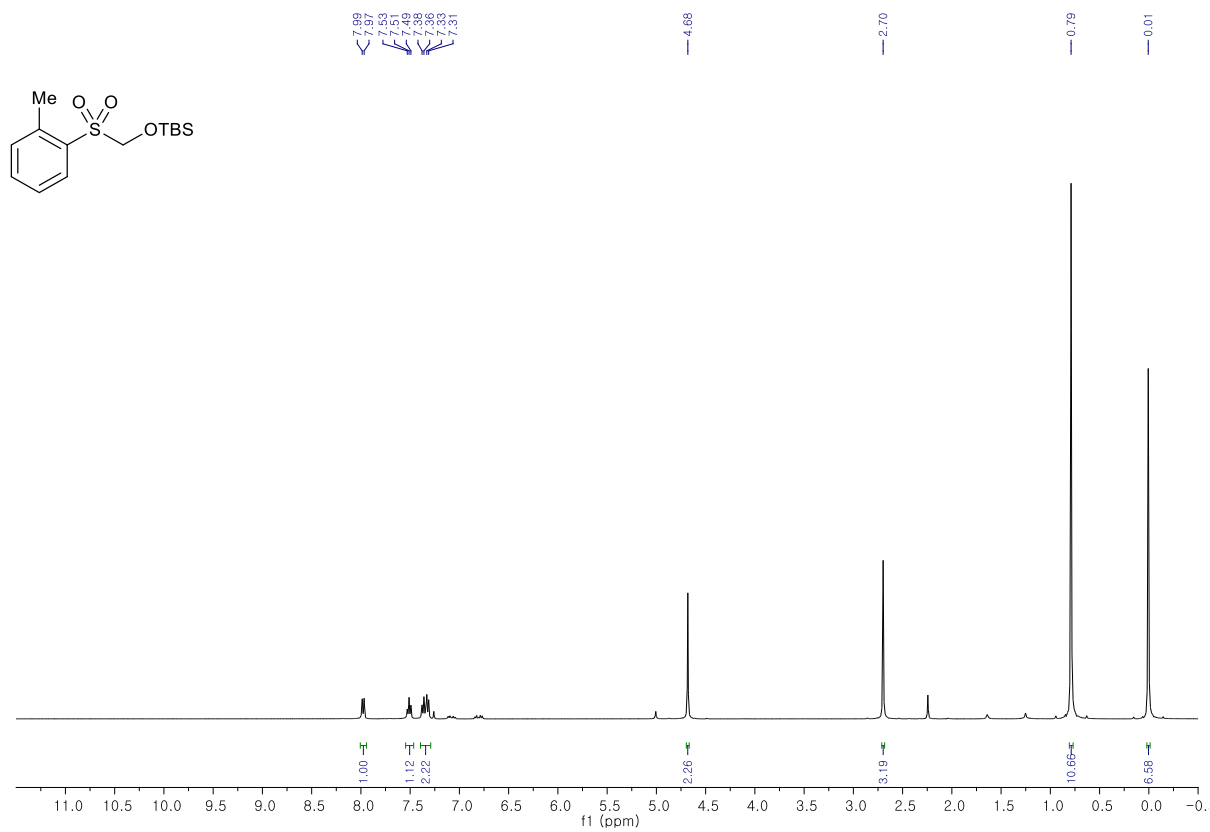


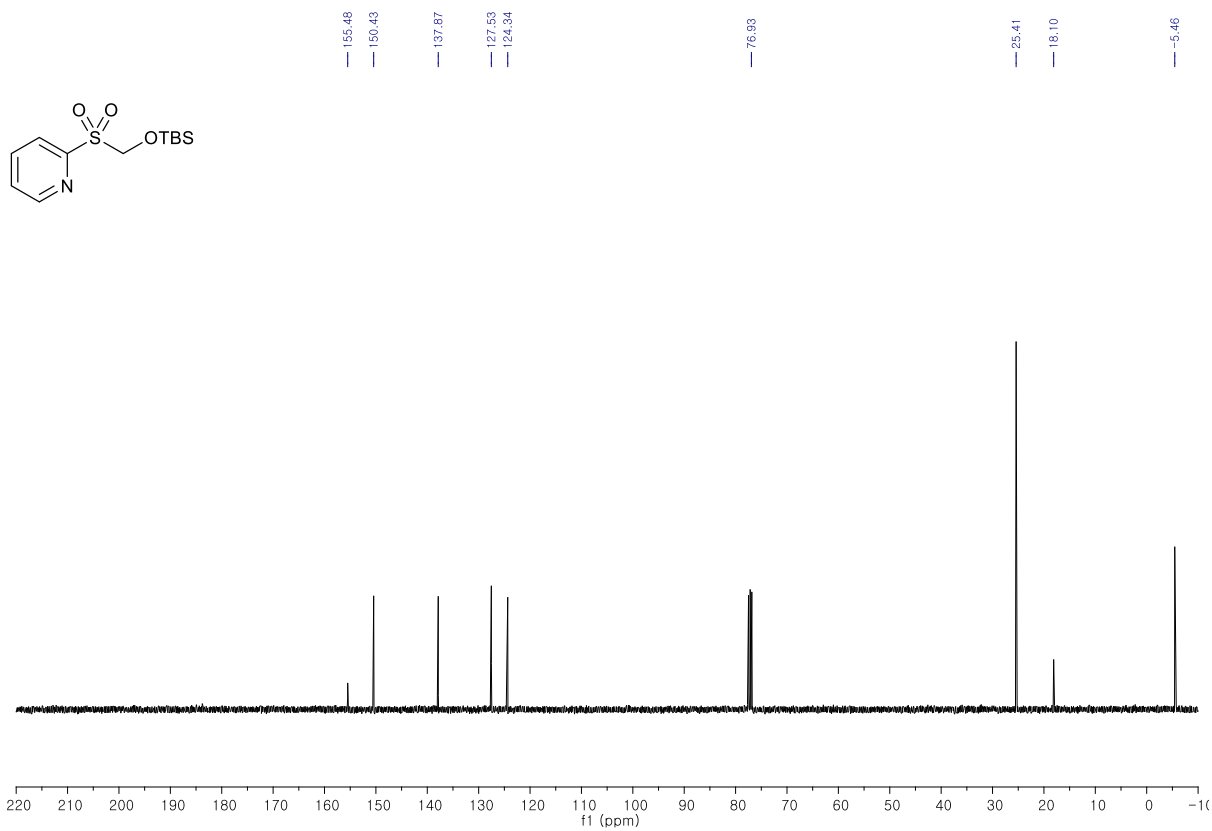
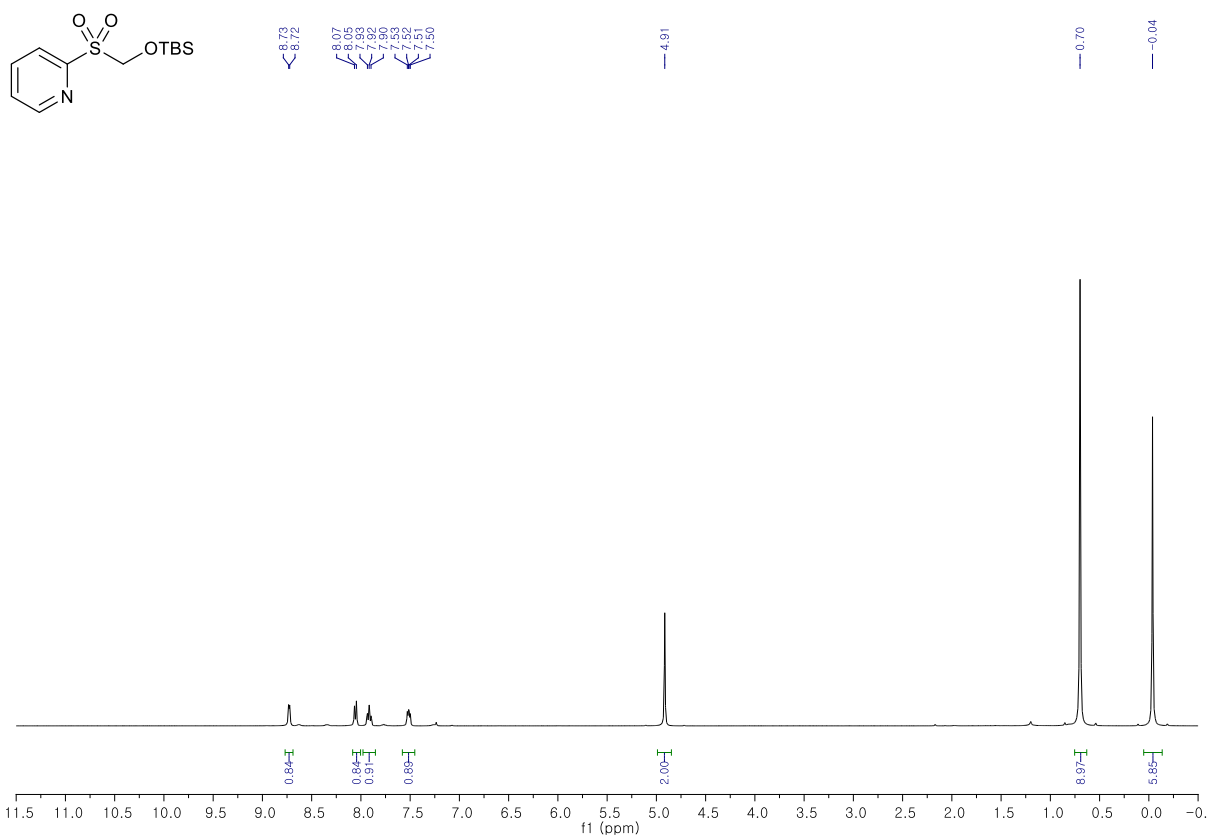


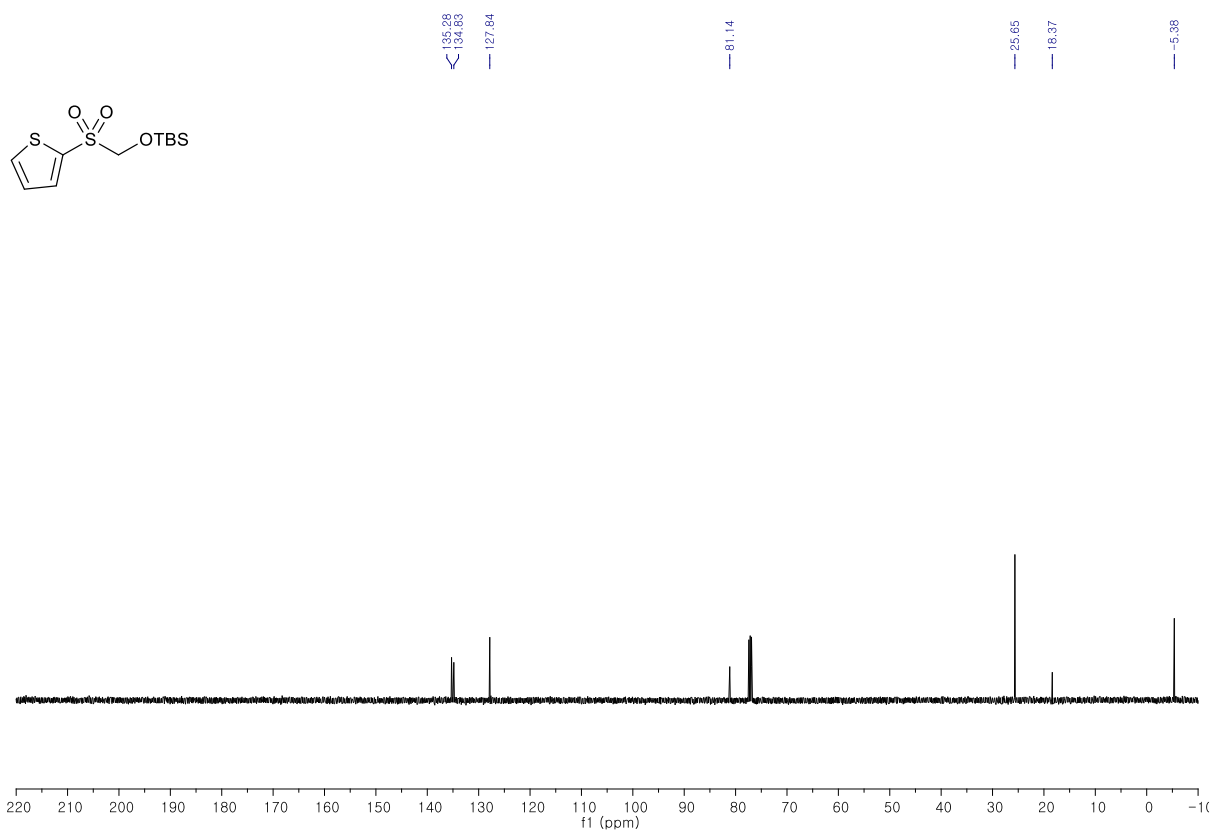
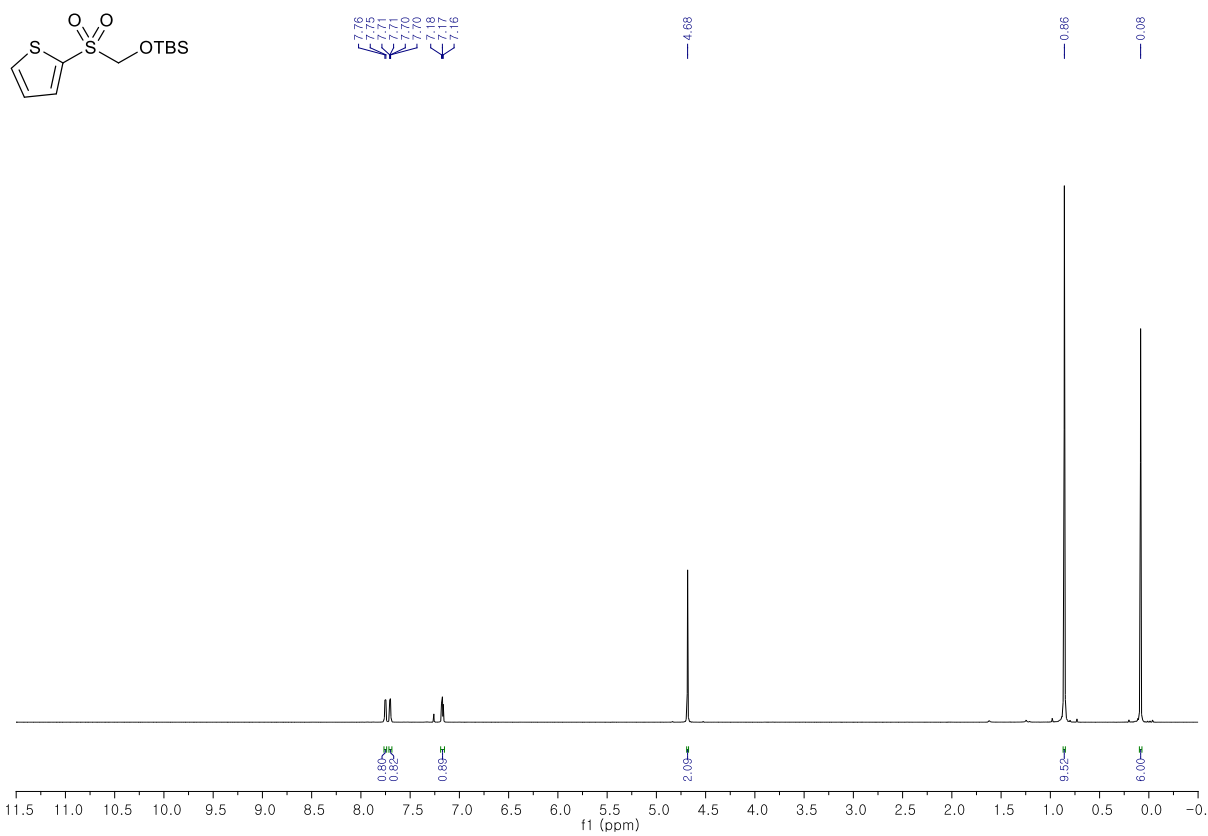


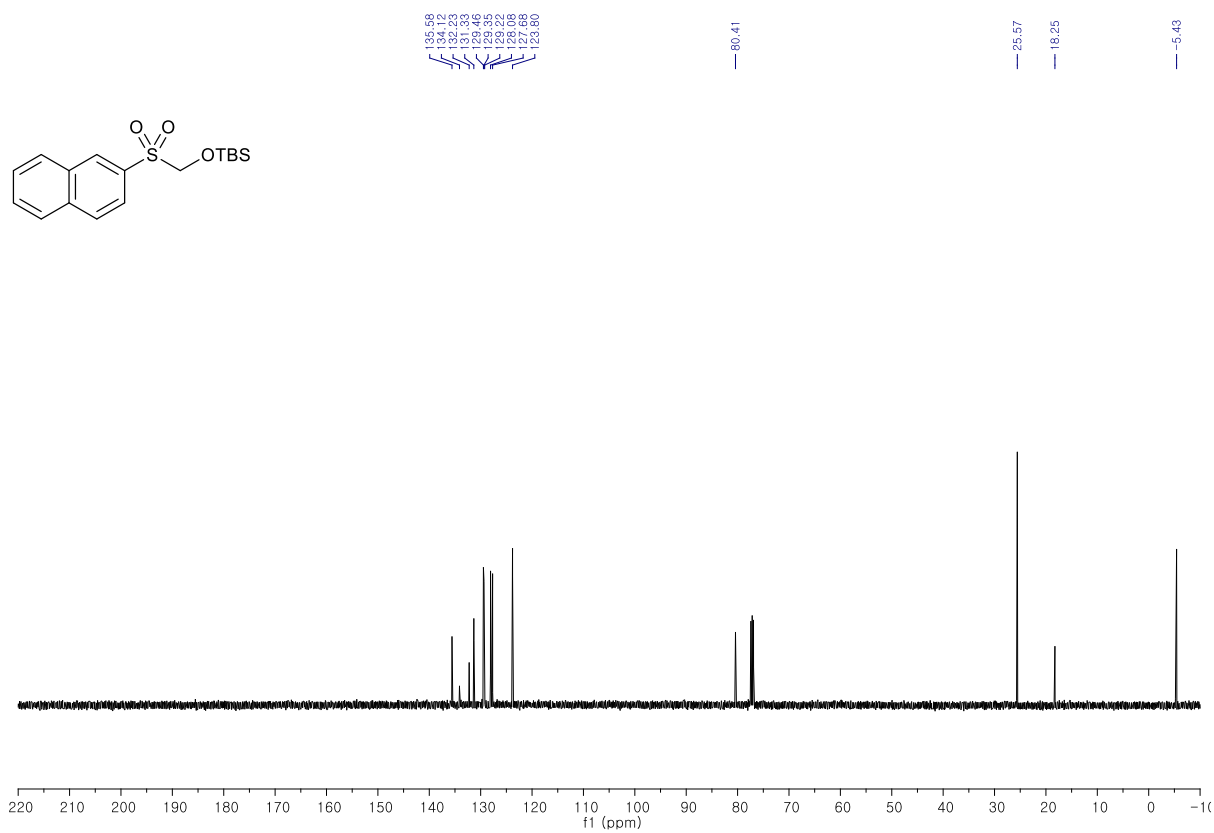
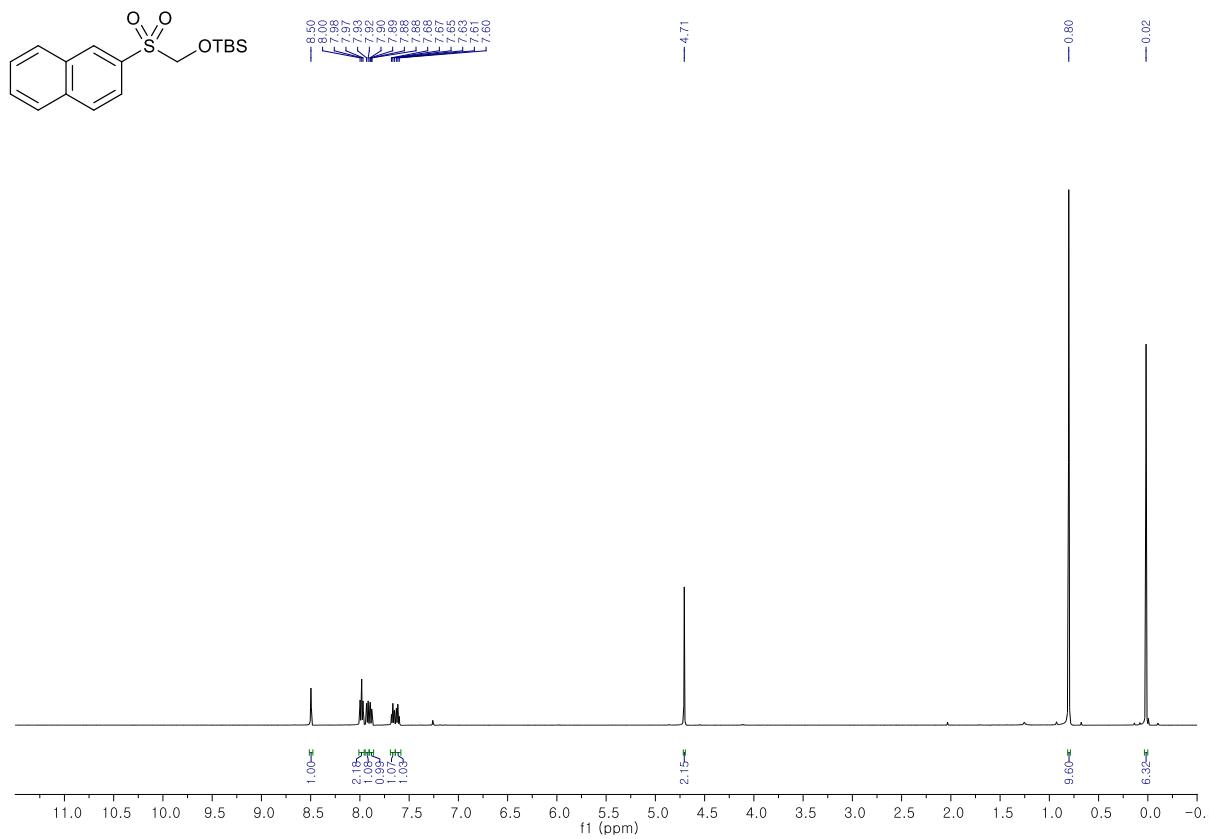


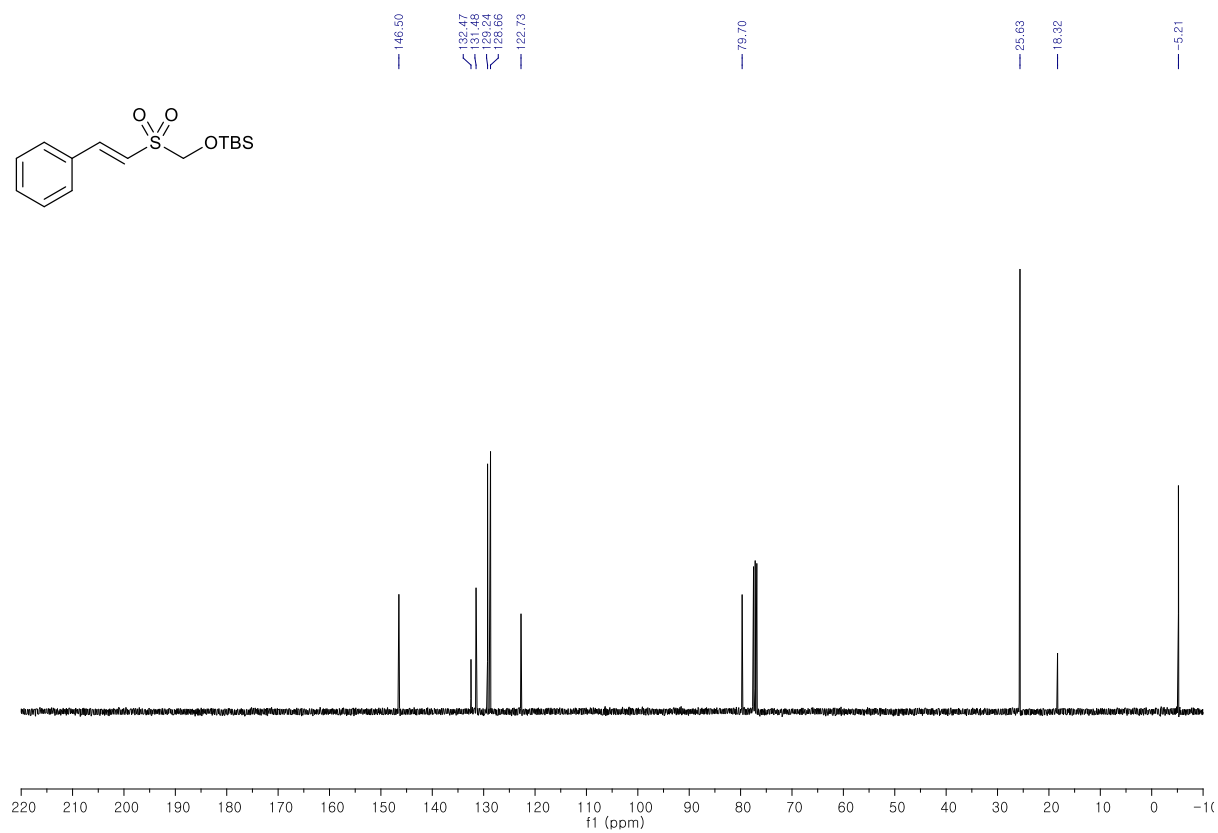
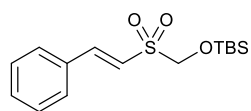
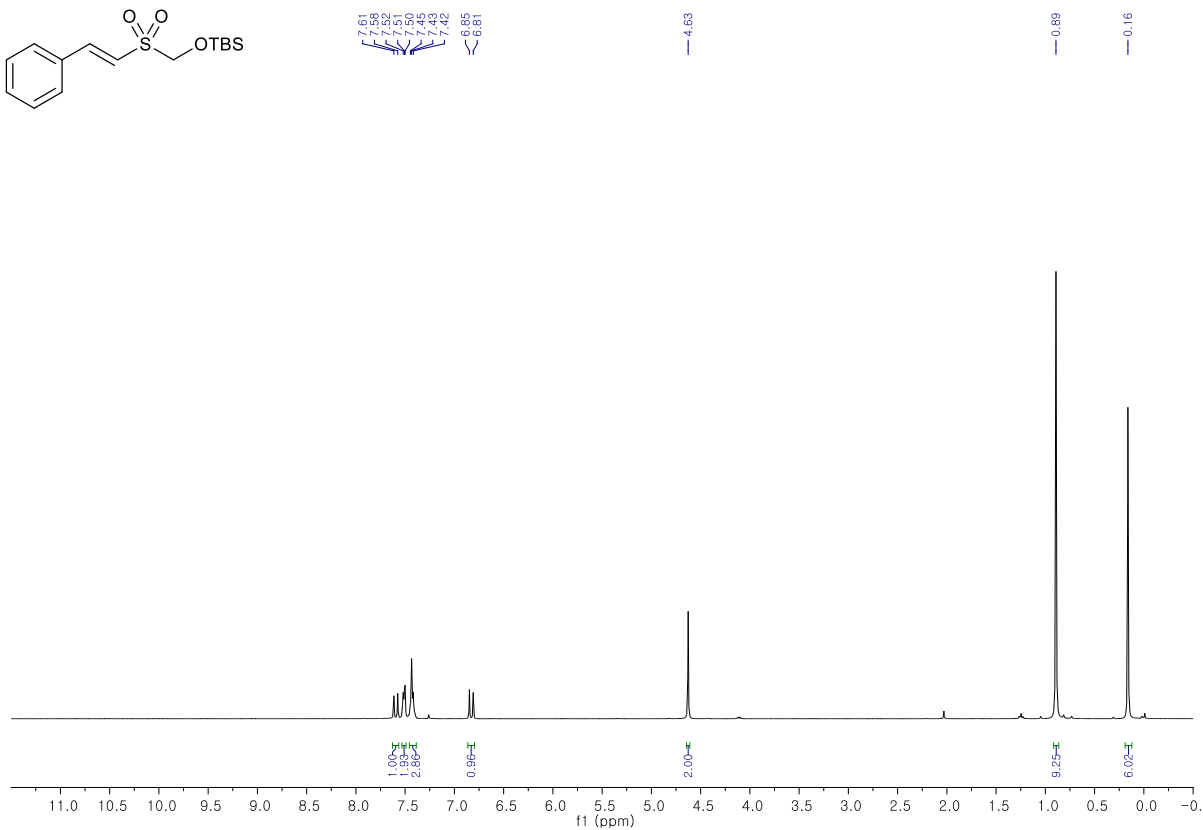
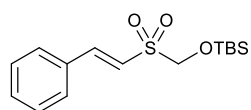


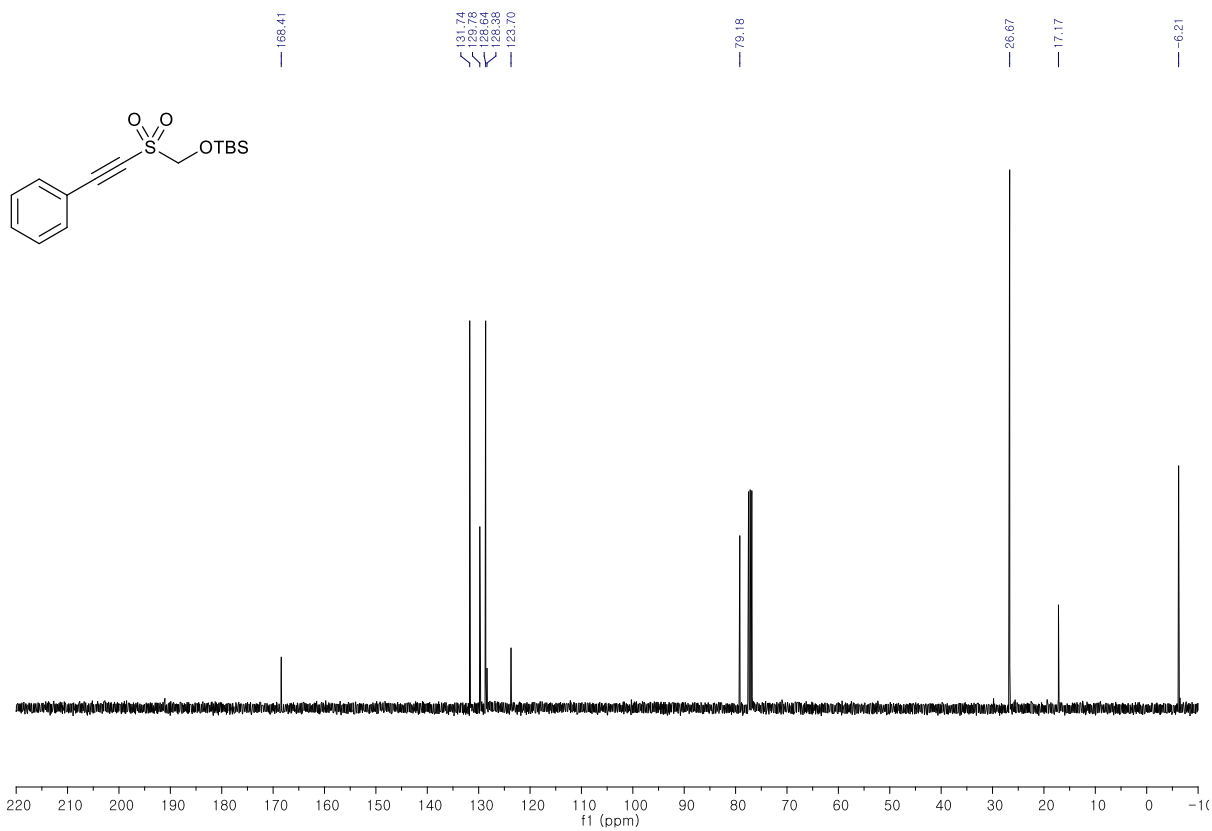
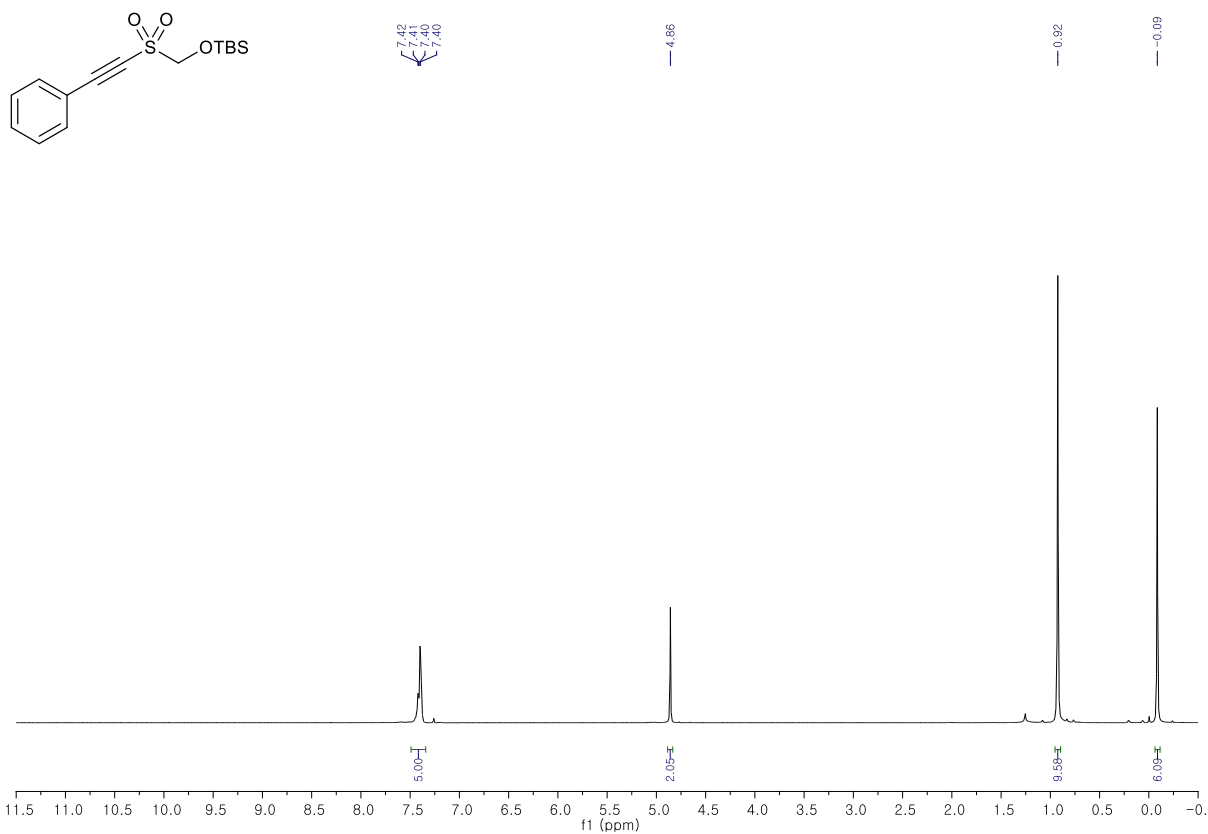


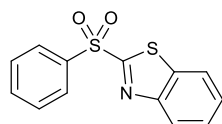




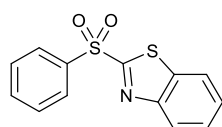
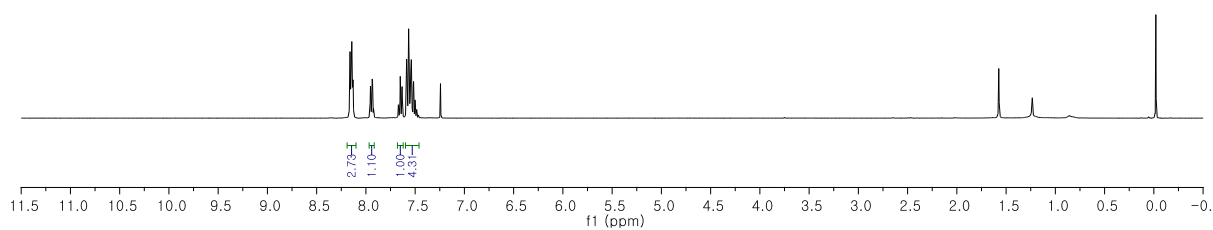








8.16
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152.88
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134.53
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122.16

