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Cu-catalysed enantioselective radical heteroatomic S–O cross-coupling

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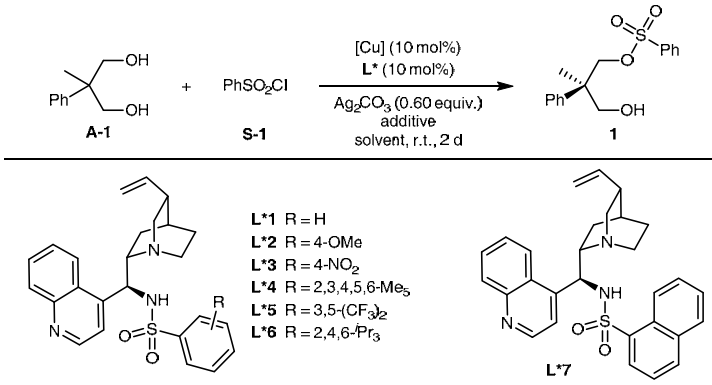
Contents

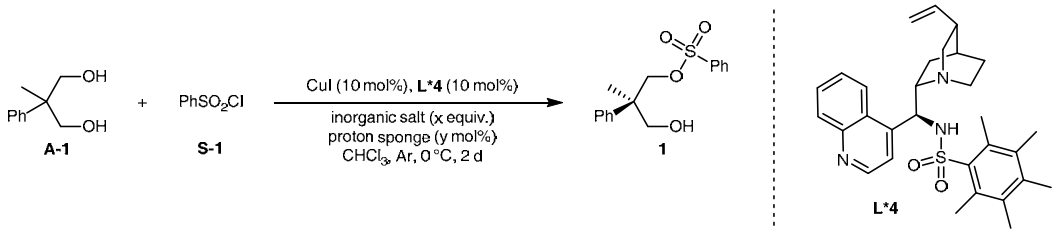
Supplementary Table 1 | Optimization of reaction conditions



Entry	[Cu]	L*	Solvent	Additive	Yield	E.e.
1	$Cu(BH_4)(PPh_3)_2$	**L*1**	CH_2Cl_2	-	49%	47%
2	$Cu(BH_4)(PPh_3)_2$	**L*2**	CH_2Cl_2	-	34%	45%
3	$Cu(BH_4)(PPh_3)_2$	**L*3**	CH_2Cl_2	-	29%	31%
4	$Cu(BH_4)(PPh_3)_2$	**L*4**	CH_2Cl_2	-	83%	83%
5	$Cu(BH_4)(PPh_3)_2$	**L*5**	CH_2Cl_2	-	54%	26%
6	$Cu(BH_4)(PPh_3)_2$	**L*6**	CH_2Cl_2	-	84%	79%
7	$Cu(BH_4)(PPh_3)_2$	**L*7**	CH_2Cl_2	-	48%	43%
8	$Cu(BH_4)(PPh_3)_2$	**L*4**	Toluene	-	10%	51%
9	$Cu(BH_4)(PPh_3)_2$	**L*4**	THF	-	7%	22%
10	$Cu(BH_4)(PPh_3)_2$	**L*4**	1,4-Dioxane	-	trace	-
11	$Cu(BH_4)(PPh_3)_2$	**L*4**	DCE	-	58%	78%
12	$Cu(BH_4)(PPh_3)_2$	**L*4**	$CHCl_3$	-	84%	89%
13	CuCl	**L*4**	$CHCl_3$	-	96%	89%
14	CuI	**L*4**	$CHCl_3$	-	98%	89%
15	CuOAc	**L*4**	$CHCl_3$	-	90%	88%
16	CuCN	**L*4**	$CHCl_3$	-	95%	88%
17	Cu_2O	**L*4**	$CHCl_3$	-	36%	34%
18	$Cu(MeCN)_4PF_6$	**L*4**	$CHCl_3$	-	45%	80%
19	CuI	**L*4**	$CHCl_3$	$MgSO_4$ (20 mg)	98%	89%
20	CuI	**L*4**	$CHCl_3$	Proton sponge (20 mol%)	98%	90%
21[a]	CuI	**L*4**	$CHCl_3$	Proton sponge (20 mol%)	92%	93%

Reaction conditions: **A-1** (0.050 mmol), **S-1** (1.2 equiv.), [Cu] (10 mol%), L* (10 mol%), and Ag_2CO_3 (0.60 equiv.) in solvent (0.10 M) at r.t. for 2 d; Yield was based on ^1H NMR analysis of the crude products using CH_2Br_2 as an internal standard; E.e. values were based on chiral HPLC analysis. [a]The reaction was performed at 0 °C.

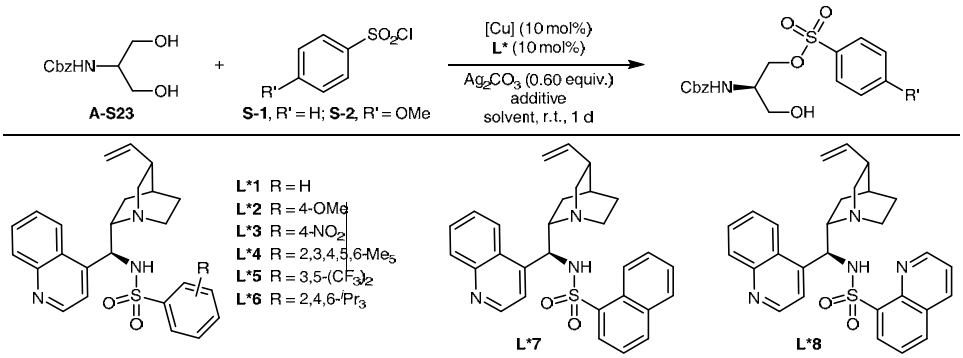
Supplementary Table 2 | The effect of silver carbonate and proton sponge



Entry	Inorganic salt (x/equiv.)	Y/mol%	Yield	E.e.
1	Ag_2CO_3 (0.60)	20	95%	93%
2	Li_2CO_3 (0.60)	20	25%	84%
3	Na_2CO_3 (0.60)	20	78%	93%
4	K_2CO_3 (0.60)	20	88%	93%
5	Cs_2CO_3 (0.60)	20	91%	82%
6	$AgNO_3$ (1.2)	20	5%	24%
7	Ag_2O (0.60)	20	85%	92%
8	AgOTf (1.2)	20	33%	1%
9	Ag_2CO_3 (0.60)	0	72%	88%
10	Ag_2CO_3 (1.0)	0	92%	88%
11	Ag_2CO_3 (2.0)	0	91%	87%

Reaction conditions: **A-1** (0.050 mmol), **S-1** (1.2 equiv.), CuI (10 mol%), **L*4** (10 mol%), inorganic salt (x equiv.), and proton sponge (y equiv.) in $CHCl_3$ (0.50 mL) under Ar at 0 °C for 2 d; Yield was based on ^1H NMR analysis of the crude products using CH_2Br_2 as an internal standard; E.e. values were based on chiral HPLC analysis.

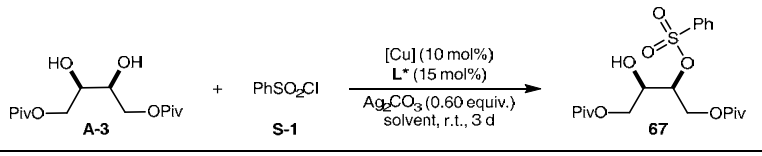
Supplementary Table 3 | Optimization of reaction conditions for the serinol substrate

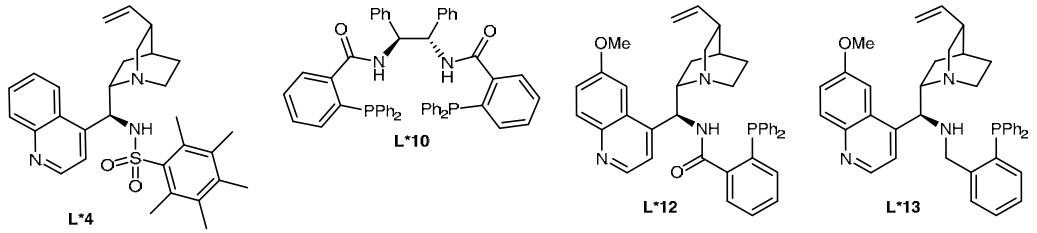


Entry	[Cu]	L*	Solvent	R'	Additive	Yield	E.e.
1	CuI	**L*1**	$CHCl_3$	H	-	29%	49%
2	CuI	**L*2**	$CHCl_3$	H	-	60%	50%
3	CuI	**L*3**	$CHCl_3$	H	-	39%	71%
4	CuI	**L*4**	$CHCl_3$	H	-	17%	37%
5	CuI	**L*5**	$CHCl_3$	H	-	22%	59%
6	CuI	**L*6**	$CHCl_3$	H	-	9%	-
7	CuI	**L*7**	$CHCl_3$	H	-	26%	50%
8	CuI	**L*8**	$CHCl_3$	H	-	55%	82%
9	CuI	**L*8**	THF	H	-	11%	37%
10	CuI	**L*8**	EtOAc	H	-	6%	42%
11	CuI	**L*8**	DCE	H	-	32%	63%
12	CuI	**L*8**	CH_2Cl_2	H	-	43%	70%
13	CuCl	**L*8**	$CHCl_3$	H	-	50%	86%
14	Cu_2O	**L*8**	$CHCl_3$	H	-	11%	20%
15	CuOAc	**L*8**	$CHCl_3$	H	-	32%	79%
16	CuCN	**L*8**	$CHCl_3$	H	-	43%	85%
17	$Cu(BH_4)(PPh_3)_2$	**L*8**	$CHCl_3$	H	-	24%	65%
18	$Cu(MeCN)_4PF_6$	**L*8**	$CHCl_3$	H	-	8%	64%
19	CuCl	**L*8**	$CHCl_3$	H	Proton sponge (20 mol%)	46%	90%
20	CuCl	**L*8**	$CHCl_3$	H	Proton sponge (5.0 mol%)	52%	92%
21	CuCl	**L*8**	$CHCl_3$	OMe	Proton sponge (5.0 mol%)	72%	89%

Reaction conditions: **A-S23** (0.050 mmol), **S-1** or **S-2** (1.2 equiv.), [Cu] (10 mol%), L* (10 mol%), and Ag_2CO_3 (0.60 equiv.) in solvent (0.10 M) at r.t. for 1 d; Yield was based on ^1H NMR analysis of the crude products using CH_2Br_2 as an internal standard; E.e. values were based on chiral HPLC analysis.

Supplementary Table 4 | Optimization of reaction conditions for the protected erythritol

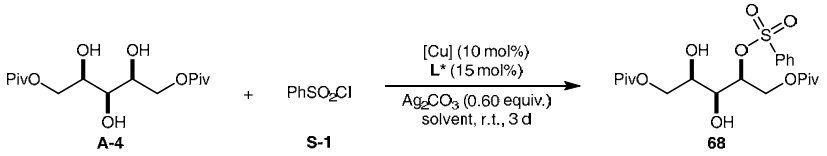


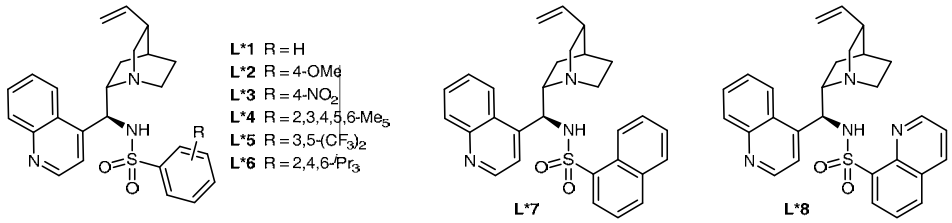


Entry	[Cu]	L*	Solvent	Yield	E.e.
1	$Cu(BH_4)(PPh_3)_2$	**L*4**	CH_2Cl_2	10%	65%
2	$Cu(BH_4)(PPh_3)_2$	**L*12**	CH_2Cl_2	8%	9%
3	$Cu(BH_4)(PPh_3)_2$	**L*13**	CH_2Cl_2	5%	42%
4	$Cu(BH_4)(PPh_3)_2$	**L*10**	CH_2Cl_2	44%	95%
5	$Cu(BH_4)(PPh_3)_2$	**L*10**	Toluene	26%	53%
6	$Cu(BH_4)(PPh_3)_2$	**L*10**	THF	24%	48%
7	$Cu(BH_4)(PPh_3)_2$	**L*10**	1,4-dioxane	10%	64%
8	$Cu(BH_4)(PPh_3)_2$	**L*10**	DCE	38%	94%
9	$Cu(BH_4)(PPh_3)_2$	**L*10**	$CHCl_3$	53%	97%
10	$Cu(BH_4)(PPh_3)_2$	**L*10**	MeOH	trace	-
11	CuBr	**L*10**	$CHCl_3$	52%	96%
12	$CuBr(PPh_3)_2$	**L*10**	$CHCl_3$	36%	96%
13	$CuBr•SMe_2$	**L*10**	$CHCl_3$	84%	96%
14	CuI	**L*10**	$CHCl_3$	64%	97%
15	CuOAc	**L*10**	$CHCl_3$	52%	96%
16	CuCN	**L*10**	$CHCl_3$	64%	96%
17	Cu_2O	**L*10**	$CHCl_3$	66%	97%
18	$CuPF_6(MeCN)_4$	**L*10**	$CHCl_3$	30%	96%

Reaction conditions: **A-3** (0.050 mmol), **S-1** (1.2 equiv.), [Cu] (10 mol%), L* (15 mol%), and Ag_2CO_3 (0.60 equiv.) in solvent (0.10 M) at r.t. for 3 d; Yield was based on ^1H NMR analysis of the crude products using CH_2Br_2 as an internal standard; E.e. values were based on chiral HPLC analysis.

Supplementary Table 5 | Optimization of reaction conditions for the protected xylitol

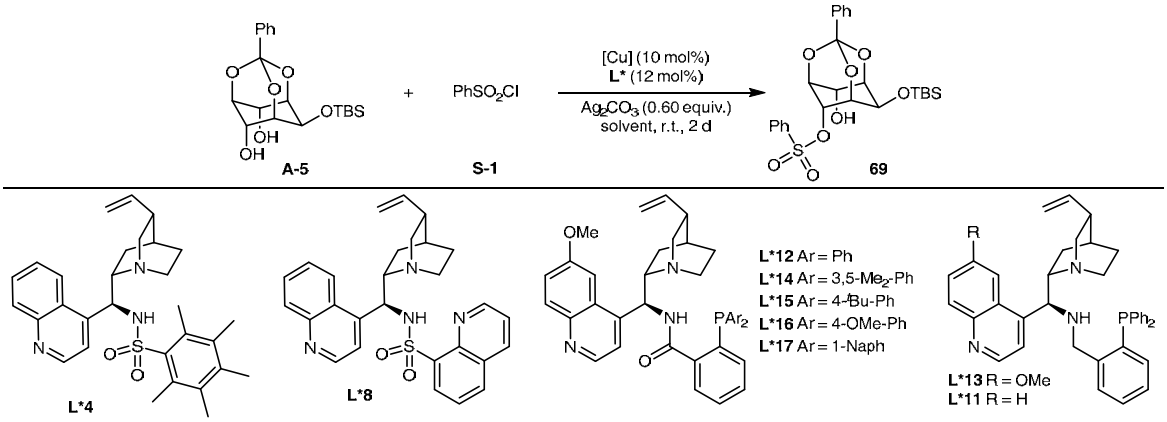




Entry	[Cu]	L*	Solvent	Yield	E.e.
1	$Cu(BH_4)(PPh_3)_2$	**L*1**	CH_2Cl_2	80%	51%
2	$Cu(BH_4)(PPh_3)_2$	**L*2**	CH_2Cl_2	94%	51%
3	$Cu(BH_4)(PPh_3)_2$	**L*3**	CH_2Cl_2	72%	36%
4	$Cu(BH_4)(PPh_3)_2$	**L*4**	CH_2Cl_2	88%	96%
5	$Cu(BH_4)(PPh_3)_2$	**L*5**	CH_2Cl_2	76%	54%
6	$Cu(BH_4)(PPh_3)_2$	**L*6**	CH_2Cl_2	85%	96%
7	$Cu(BH_4)(PPh_3)_2$	**L*7**	CH_2Cl_2	80%	44%
8	$Cu(BH_4)(PPh_3)_2$	**L*8**	CH_2Cl_2	78%	67%
9	$Cu(BH_4)(PPh_3)_2$	**L*4**	Toluene	62%	85%
10	$Cu(BH_4)(PPh_3)_2$	**L*4**	EtOAc	48%	68%
11	$Cu(BH_4)(PPh_3)_2$	**L*4**	1,4-dioxane	9%	20%
12	$Cu(BH_4)(PPh_3)_2$	**L*4**	DCE	83%	92%

Reaction conditions: **A-4** (0.050 mmol), **S-1** (1.2 equiv.), [Cu] (10 mol%), L* (15 mol%), and Ag_2CO_3 (0.60 equiv.) in solvent (0.10 M) at r.t. for 3 d; Yield was based on ^1H NMR analysis of the crude products using CH_2Br_2 as an internal standard; E.e. values were based on chiral HPLC analysis.

Supplementary Table 6 | Optimization of reaction conditions for the protected *myo*-inositol



Entry	[Cu]	L*	Solvent	Additive	Yield	E.e.
1	CuI	**L*4**	CH_2Cl_2	-	9%	0%
2	CuI	**L*8**	CH_2Cl_2	-	5%	0%
3	CuI	**L*12**	CH_2Cl_2	-	43%	11%
4	CuI	**L*14**	CH_2Cl_2	-	40%	18%
5	CuI	**L*15**	CH_2Cl_2	-	33%	8%
6	CuI	**L*16**	CH_2Cl_2	-	12%	5%
7	CuI	**L*17**	CH_2Cl_2	-	48%	11%
8	CuI	**L*13**	CH_2Cl_2	-	92%	76%
9	CuI	**L*11**	CH_2Cl_2	-	88%	78%
10	CuCl	**L*11**	CH_2Cl_2	-	85%	68%
11	CuCN	**L*11**	CH_2Cl_2	-	90%	50%
12	$Cu(MeCN)_4PF_6$	**L*11**	CH_2Cl_2	-	83%	79%
13	$Cu(BH_4)(PPh_3)_2$	**L*11**	CH_2Cl_2	-	70%	87%
14	$Cu(BH_4)(PPh_3)_2$	**L*11**	THF	-	31%	85%
15	$Cu(BH_4)(PPh_3)_2$	**L*11**	EtOAc	-	trace	-
16	$Cu(BH_4)(PPh_3)_2$	**L*11**	DCE	-	70%	88%
17	$Cu(BH_4)(PPh_3)_2$	**L*11**	$CHCl_3$	-	79%	93%
18	$Cu(BH_4)(PPh_3)_2$	**L*11**	$CHCl_3$	4Å MS (20 mg)	94%	93%

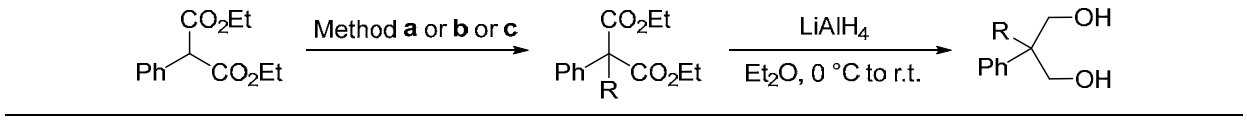
Reaction conditions: **A-5** (0.050 mmol), **S-1** (1.2 equiv.), [Cu] (10 mol%), L* (12 mol%), and Ag_2CO_3 (0.60 equiv.) in solvent (0.10 M) at r.t. for 2 d; Yield was based on ^1H NMR analysis of the crude products using CH_2Br_2 as an internal standard; E.e. values were based on chiral HPLC analysis.

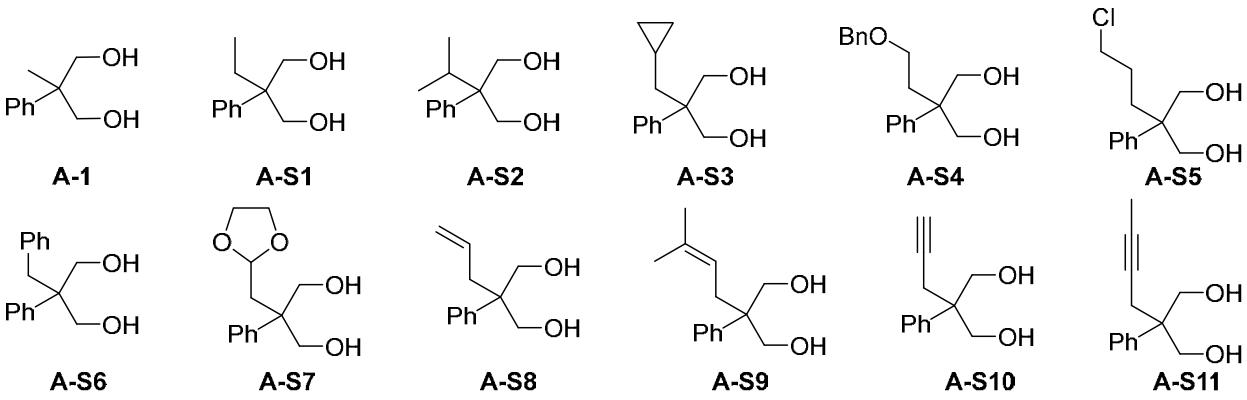
General information

All reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. Extra dry solvents were purchased from J&K®. Chloroform ($CHCl_3$) was distilled from anhydrous calcium hydride (CaH_2) and stored under argon. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). ^{1}H, ^{13}C, ^{19}F, and ^{31}P-NMR spectra were recorded on Bruker Avance-400 or -500 spectrometers. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (e.e.) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hitachi detector or SHIMADZU LC-20AD with an SPD-20AV detector; column conditions are reported in the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. X-ray diffraction was measured on a “Bruker APEX-II CCD” diffractometer with Cu–Kα radiation.

Synthesis of substrates

The synthesis of 2,2-disubstituted diol substrates A-1 and A-S1–A-S22





General procedure 1:

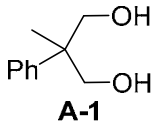
Method a: To a suspension of NaH (60% dispensed in mineral oil, 240.0 mg, 6.0 mmol, 1.2 equiv.) in dry THF (15 mL) at 0 °C was slowly added diethyl 2-phenylmalonate (196.0 mg, 5.0 mmol, 1.0 equiv.). After stirring for 30 min, the corresponding alkyl halide (1.2 equiv.) was added dropwise. The reaction mixture was warmed to r.t. and stirred overnight. Then the reaction was quenched with saturated NH_4Cl (aq.) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was briefly purified by silica gel column chromatography to give the crude diester product.

Method b: To a suspension of NaH (60% dispensed in mineral oil, 400.0 mg, 10.0 mmol, 2.0 equiv.) in dry DMF (15 mL) at 0 °C was slowly added diethyl 2-phenylmalonate (196.0 mg, 5.0 mmol, 1.0 equiv.). After stirring for 30 min, the corresponding alkyl halide (4.0 equiv.) was added dropwise. The reaction mixture was heated to 80 °C for 1 d. After completion of the reaction, the mixture was cooled to r.t., quenched with saturated NH_4Cl (aq.), and extracted with EtOAc (3x). The combined organic layers were washed with H_2O (4x), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was briefly purified by silica gel column chromatography to give the crude diester product.

Method c: Under argon atmosphere, Na (1.2 g, 50 mmol, 10 equiv.) was added to dry ^{i}PrOH (10 mL) at r.t. After stirring for 12 h, diethyl 2-phenylmalonate (196.0 mg, 5.0 mmol, 1.0 equiv.) was added dropwise. After stirring for an additional 6 h, the corresponding alkyl halide (5.0 equiv.) was added dropwise and the reaction mixture was stirred at r.t. overnight. Then the reaction mixture was quenched with saturated NH_4Cl (aq.) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was directly used in the next step without further purification.

To a suspension of $LiAlH_4$ (760.0 mg, 20 mmol, 4.0 equiv.) in Et_2O (15 mL) at 0 °C was slowly added a solution of the diester in Et_2O (5 mL). Then the reaction mixture was warmed to r.t. and stirred for 2 h. Next, it was quenched by slow, portionwise addition of wet Na_2SO_4 (4.0 mL water in 32.0 g Na_2SO_4) at 0 °C. Upon completion, the mixture was warmed to r.t., stirred for an additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography to give the corresponding diol products.

2-Methyl-2-phenylpropane-1,3-diol (A-1)



A-1

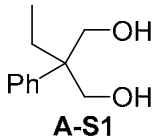
According to **General procedure 1** with methyl iodide (0.85 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-1** as a white solid (590.7 mg, 71% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.21 (m, 1H), 3.97 (dd, *J* = 11.1, 4.8 Hz, 2H), 3.84 (dd, *J* = 11.1, 4.8 Hz, 2H), 2.19 – 2.06 (m, 2H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.7, 126.7, 126.6, 70.1, 44.6, 20.7.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NaO_2$ $[M + Na]^+$ 189.0886, found 189.0884.

2-Ethyl-2-phenylpropane-1,3-diol (A-S1)



A-S1

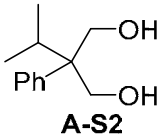
According to **General procedure 1** with ethyl iodide (0.94 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S1** as a white solid (594.4 mg, 66% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.24 (t, *J* = 7.5 Hz, 1H), 4.07 (d, *J* = 11.0 Hz, 2H), 3.89 (d, *J* = 11.0 Hz, 2H), 2.65 (br s, 2H), 1.66 (q, *J* = 7.5 Hz, 2H), 0.66 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.6, 127.0, 126.4, 68.2, 47.3, 26.7, 7.8.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NaO_2$ $[M + Na]^+$ 203.1043, found 203.1040.

2-Isopropyl-2-phenylpropane-1,3-diol (A-S2)



A-S2

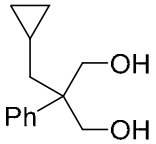
According to **General procedure 1** with isopropyl bromide (3.10 g, 25.0 mmol, 5.0 equiv.) and ***Method c***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **A-S2** as a white solid (165.2 mg, 17% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.26 – 7.19 (m, 1H), 4.16 (d, *J* = 10.8 Hz, 2H), 4.05 (d, *J* = 10.8 Hz, 2H), 3.13 (br s, 2H), 1.88 (hept, *J* = 7.0 Hz, 1H), 0.73 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.1, 127.9, 126.1, 66.8, 49.3, 33.0, 17.6.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NaO_2$ $[M + Na]^+$ 217.1199, found 217.1195.

2-(Cyclopropylmethyl)-2-phenylpropane-1,3-diol (A-S3)



A-S3

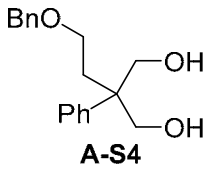
According to **General procedure 1** with cyclopropylmethyl chloride (1.81 g, 20.0 mmol, 4.0 equiv.), KI (830 mg, 5.0 mmol, 1.0 equiv.) and ***Method b***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S3** as a white solid (577.1 mg, 56% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.27 – 7.21 (m, 1H), 4.16 (d, *J* = 10.6 Hz, 2H), 4.00 (d, *J* = 10.7 Hz, 2H), 2.60 (br s, 2H), 1.55 (d, *J* = 6.1 Hz, 2H), 0.42 – 0.28 (m, 3H), –0.01 – –0.06 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 128.6, 127.1, 126.5, 68.6, 48.3, 39.9, 5.8, 4.6.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}NaO_2$ $[M + Na]^+$ 229.1199, found 229.1195.

2-(2-(Benzyloxy)ethyl)-2-phenylpropane-1,3-diol (A-S4)



A-S4

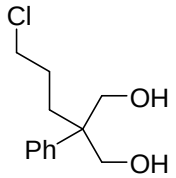
According to **General procedure 1** with ((2-bromoethoxy)methyl)benzene (1.30 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S4** as a white solid (100.4 mg, 7% yield over two steps). (Note: in ***Method a,*** the reaction mixture was refluxed for 2 d before workup).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.14 (m, 10H), 4.43 (s, 2H), 4.02 – 3.87 (m, 4H), 3.49 (t, *J* = 5.6 Hz, 2H), 2.91 (t, *J* = 6.3 Hz, 2H), 2.17 (t, *J* = 5.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 137.4, 128.7, 128.5, 127.9, 127.8, 126.8, 126.7, 73.4, 68.5, 66.8, 47.3, 33.0.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NaO_3$ $[M + Na]^+$ 309.1461, found 309.1456.

2-(3-Chloropropyl)-2-phenylpropane-1,3-diol (A-S5)



A-S5

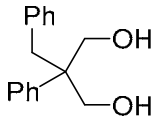
According to **General procedure 1** with 1-bromo-3-chloropropane (3.14 g, 20.0 mmol, 4.0 equiv.) and ***Method b***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S5** as a white solid (240.1 mg, 21% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 4.00 (d, *J* = 12.5 Hz, 2H), 3.83 (d, *J* = 12.1 Hz, 2H), 3.41 (t, *J* = 6.5 Hz, 2H), 3.05 – 2.94 (m, 2H), 1.84 – 1.72 (m, 2H), 1.53 – 1.46 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 128.7, 126.7, 67.6, 46.6, 45.5, 30.9, 26.7.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{17}ClNaO_2$ $[M + Na]^+$ 251.0809, found 251.0806.

2-Benzyl-2-phenylpropane-1,3-diol (A-S6)



A-S6

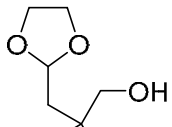
According to **General procedure 1** with benzyl bromide (1.81 g, 20.0 mmol, 4.0 equiv.) and ***Method b***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S6** as a white solid (532.4 mg, 44% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 2H), 7.30 – 7.23 (m, 3H), 7.17 – 7.06 (m, 3H), 6.81 – 6.78 (m, 2H), 4.03 (d, *J* = 11.0 Hz, 2H), 3.96 (d, *J* = 11.0 Hz, 2H), 2.94 (s, 2H), 2.27 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.7, 130.2, 128.6, 127.7, 127.2, 126.8, 126.2, 67.3, 48.3, 40.9.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NaO_2$ $[M + Na]^+$ 265.1199, found 265.1194.

2-((1,3-Dioxolan-2-yl)methyl)-2-phenylpropane-1,3-diol (A-S7)



A-S7

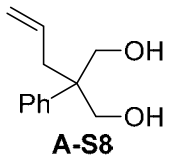
According to **General procedure 1** with 2-(bromomethyl)-1,3-dioxolane (3.34 g, 20.0 mmol, 4.0 equiv.) and ***Method b***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S7** as a white solid (238.4 mg, 20% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.27 – 7.20 (m, 1H), 4.74 – 4.72 (m, 1H), 4.01 – 3.89 (m, 6H), 3.81 – 3.74 (m, 2H), 2.89 – 2.78 (m, 2H), 2.25 (dd, *J* = 4.7, 1.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 128.7, 126.8, 126.6, 102.2, 68.1, 64.8, 46.0, 37.1.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}NaO_4$ $[M + Na]^+$ 261.1097, found 261.1093.

2-Allyl-2-phenylpropane-1,3-diol (A-S8)



A-S8

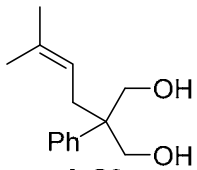
According to **General procedure 1** with allyl bromide (0.73 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S8** as a white solid (547.8 mg, 57% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.27 – 7.22 (m, 1H), 5.59 – 5.40 (m, 1H), 5.04 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.00 – 4.93 (m, 1H), 4.00 (dd, *J* = 11.2, 3.9 Hz, 2H), 3.88 (dd, *J* = 11.2, 2.4 Hz, 2H), 2.68 (br s, 2H), 2.43 (d, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 133.6, 128.6, 126.9, 126.6, 117.9, 67.8, 47.0, 38.8.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}O$ $[M + H – H_2O]^+$ 175.1117, found 175.1114.

2-(3-Methylbut-2-en-1-yl)-2-phenylpropane-1,3-diol (A-S9)



A-S9

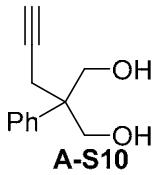
According to **General procedure 1** with 3,3-dimethylallyl bromide (0.89 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S9** as a white solid (600.0 mg, 55% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.28 – 7.21 (m, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.06 (dd, *J* = 11.0, 3.3 Hz, 2H), 3.91 (dd, *J* = 11.0, 3.4 Hz, 2H), 2.36 (d, *J* = 7.3 Hz, 2H), 2.32 – 2.11 (m, 2H), 1.61 (s, 3H), 1.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 134.5, 128.6, 127.1, 126.5, 118.8, 68.5, 47.8, 32.9, 25.9, 17.9.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{19}O$ $[M + H – H_2O]^+$ 203.1430, found 203.1427.

2-Phenyl-2-(prop-2-yn-1-yl)propane-1,3-diol (A-S10)



A-S10

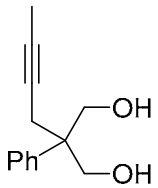
According to **General procedure 1** with 2-propynyl bromide (0.71 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S10** as a white solid (408.0 mg, 43% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 4H), 7.32 – 7.25 (m, 1H), 4.10 (dd, *J* = 11.1, 5.7 Hz, 2H), 4.00 (dd, *J* = 11.1, 6.0 Hz, 2H), 2.76 (d, *J* = 2.6 Hz, 2H), 2.17 (t, *J* = 6.0 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 128.8, 127.2, 126.7, 80.9, 71.3, 67.8, 47.4, 23.2.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1067, found 191.1064.

2-(But-2-yn-1-yl)-2-phenylpropane-1,3-diol (A-S11)



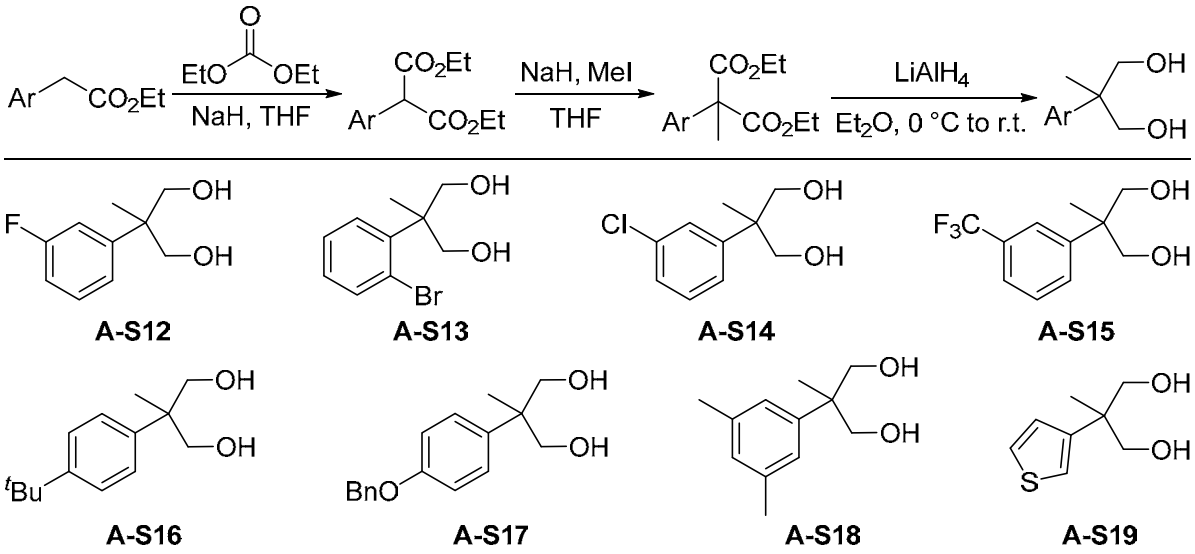
A-S11

According to **General procedure 1** with 1-bromo-2-butyne (0.80 g, 6.0 mmol, 1.2 equiv.) and ***Method a***, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S11** as a white solid (458.8 mg, 45% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 3.96 (d, *J* = 11.0 Hz, 2H), 3.87 (d, *J* = 11.0 Hz, 2H), 3.09 (br s, 2H), 2.59 (d, *J* = 2.3 Hz, 2H), 1.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 128.3, 126.7, 126.6, 78.4, 75.2, 67.3, 47.2, 23.5, 3.4.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{16}NaO_2$ $[M + Na]^+$ 227.1043, found 227.1042.



A-S12 A-S13 A-S14 A-S15

A-S16 A-S17 A-S18 A-S19

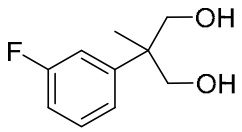
General procedure 2:

To a suspension of NaH (60% dispensed in mineral oil, 480.0 mg, 12.0 mmol, 2.4 equiv.) in dry THF (15 mL) at 0 °C was slowly added the corresponding ester (5.0 mmol, 1.0 equiv.). After stirring for 30 min, ethyl carbonate (1.7 g, 15 mmol, 3.0 equiv.) was added dropwise. The mixture was warmed to r.t. and then heated to reflux under inert atmosphere for 24 h. After cooling to r.t., saturated NH_4Cl (aq.) was carefully added to the above reaction solution to quench the reaction and the mixture was extracted with EtOAc (3x). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The crude malonate diester product was used directly in the next step without further purification.

The crude malonate diester was dissolved in dry THF (15 mL) and the solution was cooled to 0 °C. Then NaH (60% dispensed in mineral oil, 240.0 mg, 6.0 mmol, 1.2 equiv.) was added in four portions under inert atmosphere. After stirring for 30 min, methyl iodide (852.0 mg, 6.0 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was warmed to r.t. and stirred overnight. Then the reaction was quenched with saturated NH_4Cl (aq.) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give the α,α-disubstituted malonate diester product.

To a suspension of $LiAlH_4$ (4.0 equiv.) in Et_2O (15 mL) at 0 °C was slowly added a solution of the α,α-disubstituted malonate diester in Et_2O (5 mL). Then the reaction mixture was warmed to r.t. and stirred for 2 h. Next, it was quenched by slow, portionwise addition of wet Na_2SO_4 (4.0 mL water in 32.0 g Na_2SO_4) at 0 °C. Upon completion, the mixture was warmed to r.t., stirred for an additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography to give the corresponding diol products.

2-(3-Fluorophenyl)-2-methylpropane-1,3-diol (A-S12)



A-S12

According to **General procedure 2** with ethyl 2-(3-fluorophenyl)acetate (0.91 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S12** as a white solid (331.2 mg, 36% yield over three steps).

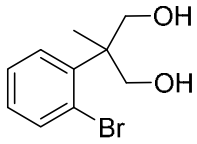
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.13 (dt, *J* = 11.1, 2.1 Hz, 1H), 6.94 (td, *J* = 8.3, 2.2 Hz, 1H), 3.90 (d, *J* = 11.0 Hz, 2H), 3.77 (d, *J* = 10.9 Hz, 2H), 2.66 (br s, 2H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 245.2 Hz), 146.0 (d, *J* = 6.7 Hz), 129.9 (d, *J* = 8.3 Hz), 122.2 (d, *J* = 2.8 Hz), 114.0 (d, *J* = 21.9 Hz), 113.5 (d, *J* = 20.9 Hz). 69.6, 44.5 (d, *J* = 1.5 Hz), 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ −112.5 (ddd, *J* = 11.3, 8.5, 6.0 Hz).

HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}FNaO_2$ $[M + Na]^+$ 207.0792, found 207.0789.

2-(2-Bromophenyl)-2-methylpropane-1,3-diol (A-S13)



A-S13

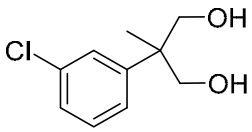
According to **General procedure 2** with ethyl 2-(2-bromophenyl)acetate (1.22 g, 5.0 mmol, 1.0 equiv.), except that DIBAL-H (4.0 equiv.) was used instead of $LiAlH_4$, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S13** as a white solid (269.8 mg, 22% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (ddd, *J* = 15.0, 8.0, 1.5 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.10 (td, *J* = 7.8, 1.7 Hz, 1H), 4.43 (dd, *J* = 11.0, 5.4 Hz, 2H), 4.01 (dd, *J* = 11.2, 4.5 Hz, 2H), 2.39 (t, *J* = 5.1 Hz, 2H), 1.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 135.9, 131.3, 128.5, 127.6, 122.3, 69.2, 46.5, 19.5.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}BrNaO_2$ $[M + Na]^+$ 266.9991, found 266.9987.

2-(3-Chlorophenyl)-2-methylpropane-1,3-diol (A-S14)



A-S14

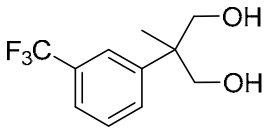
According to **General procedure 2** with ethyl 2-(3-chlorophenyl)acetate (0.99 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S14** as a white solid (350.5 mg, 35% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 1H), 7.35 – 7.27 (m, 2H), 7.24 (dt, *J* = 7.1, 1.9 Hz, 1H), 3.95 (d, *J* = 10.9 Hz, 2H), 3.83 (d, *J* = 11.0 Hz, 2H), 2.18 (br s, 2H), 1.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 134.6, 129.8, 127.1, 126.9, 124.9, 69.9, 44.6, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{13}ClNaO_2$ $[M + Na]^+$ 223.0496, found 223.0493.

2-Methyl-2-(3-(trifluoromethyl)phenyl)propane-1,3-diol (A-S15)



A-S15

According to **General procedure 2** with ethyl 2-(3-(trifluoromethyl)phenyl)acetate (1.16 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S15** as a white solid (468.4 mg, 40% yield over three steps).

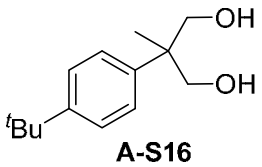
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 3.91 (d, *J* = 11.0 Hz, 2H), 3.77 (d, *J* = 11.0 Hz, 2H), 2.97 (br s, 2H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 130.7 (q, *J* = 31.7 Hz), 130.22, 130.21, 128.9, 124.2 (q, *J* = 270.7 Hz), 123.4 (q, *J* = 3.9 Hz), 69.4, 44.4, 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{13}F_3NaO_2$ $[M + Na]^+$ 257.0760, found 257.0756.

2-(4-(*tert*-Butyl)phenyl)-2-methylpropane-1,3-diol (A-S16)



A-S16

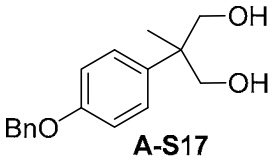
According to **General procedure 2** with ethyl 2-(4-(*tert*-butyl)phenyl)acetate (1.10 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S16** as a white solid (488.2 mg, 44% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 3.97 (dd, *J* = 11.0, 6.0 Hz, 2H), 3.84 (dd, *J* = 11.0, 5.9 Hz, 2H), 1.96 (t, *J* = 6.0 Hz, 2H), 1.32 (s, 9H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 152.4, 145.0, 130.1, 128.6, 71.7, 48.0, 37.6, 34.3, 23.1.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}NaO_2$ $[M + Na]^+$ 245.1512, found 245.1508.

2-(4-(Benzyloxy)phenyl)-2-methylpropane-1,3-diol (A-S17)



A-S17

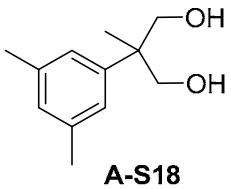
According to **General procedure 2** with ethyl 2-(4-(benzyloxy)phenyl)acetate (1.35 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S17** as a white solid (340.0 mg, 25% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 7H), 7.01 – 6.94 (m, 2H), 5.05 (s, 2H), 3.91 (dd, *J* = 10.9, 5.7 Hz, 2H), 3.79 (dd, *J* = 11.0, 5.6 Hz, 2H), 2.14 (t, *J* = 5.8 Hz, 2H), 1.27 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 157.4, 136.9, 135.0, 128.6, 128.0, 127.8, 127.4, 114.9, 70.2, 44.0, 20.8.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}NaO_3$ $[M + Na]^+$ 295.1305, found 295.1300.

2-(3,5-Dimethylphenyl)-2-methylpropane-1,3-diol (A-S18)



A-S18

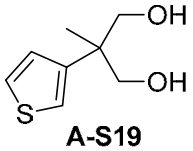
According to **General procedure 2** with ethyl 2-(3,5-dimethylphenyl)acetate (0.96 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S18** as a white solid (475.8 mg, 49% yield over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.85 (s, 1H), 3.83 (d, *J* = 10.9 Hz, 2H), 3.67 (d, *J* = 11.0 Hz, 2H), 3.21 (br s, 2H), 2.29 (s, 6H), 1.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 137.7, 128.1, 124.2, 69.3, 44.0, 21.4, 20.5.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NaO_2$ $[M + Na]^+$ 217.1199, found 217.1200.

2-Methyl-2-(thiophen-3-yl)propane-1,3-diol (A-S19)



A-S19

According to **General procedure 2** with ethyl 2-(thiophen-3-yl)acetate (0.85 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **A-S19** as a white solid (154.6 mg, 18% yield over three steps).

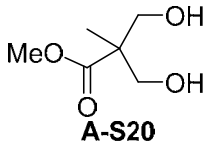
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.21 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.13 (dd, *J* = 5.0, 1.4 Hz, 1H), 3.89 (dd, *J* = 10.9, 5.9 Hz, 2H), 3.80 (dd, *J* = 10.9, 6.0 Hz, 2H), 2.02 – 1.94 (m, 2H), 1.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 126.1, 126.0, 121.0, 69.9, 43.5, 20.6.

HRMS (ESI) *m/z* calcd. for $C_8H_{12}NaO_2S$ $[M + Na]^+$ 195.0450, found 195.0449.

A-S20 was synthesized according to the reported literature[1].

Methyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (A-S20)



A-S20

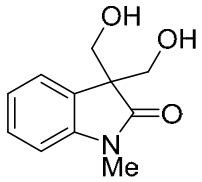
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (d, *J* = 11.3 Hz, 2H), 3.80 – 3.64 (m, 5H), 3.08 (br s, 2H), 1.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 67.9, 52.2, 49.1, 17.1.

HRMS (ESI) *m/z* calcd. for $C_6H_{13}O_4$ $[M + H]^+$ 149.0808, found 149.0809.

A-S21 was synthesized according to the reported literature[2].

3,3-Bis(hydroxymethyl)-1-methylindolin-2-one (A-S21)



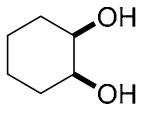
A-S21

^{1}H NMR (400 MHz, CD_3OD) δ 7.45 (d, *J* = 7.3 Hz, 1H), 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.17 – 7.09 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 3.93 (d, *J* = 10.8 Hz, 2H), 3.83 (d, *J* = 10.8 Hz, 2H), 3.23 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 178.2, 144.6, 129.5, 128.0, 123.6, 122.3, 107.9, 63.3, 57.8, 25.1.

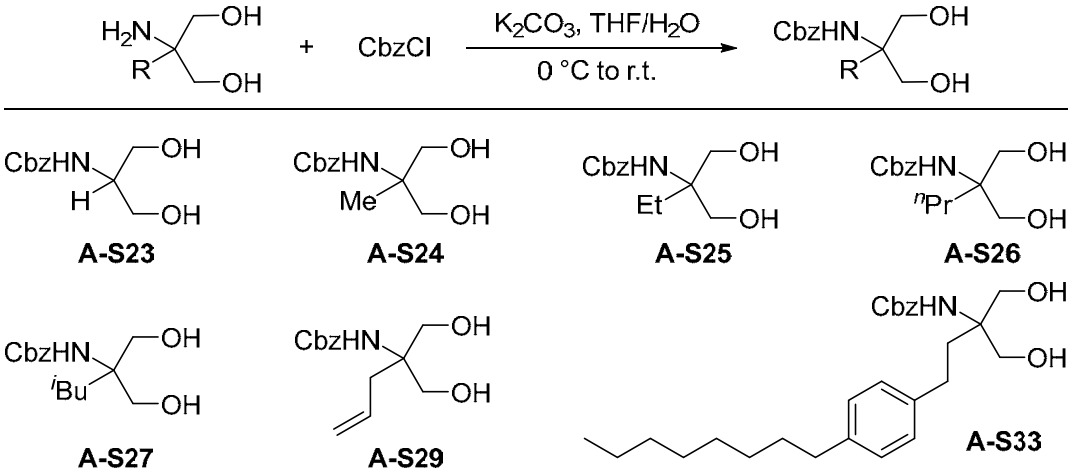
HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}NO_3$ $[M + H]^+$ 208.0968, found 208.0967.

A-S22 (*meso* cyclohexane-1,2-diol) was bought from commercial sources and employed directly.



A-S22

The synthesis of 2-amino-1,3-diol substrates A-S23–A-S33

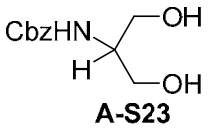


General procedure 3:

To a solution of unprotected 2-amino propanediol (3.0 mmol) in THF/H_2O (v/v = 1/1) (5.0 mL) were successively added K_2CO_3 (0.83 g, 6.0 mmol, 2.0 equiv.) and benzyl chloroformate (0.50 mL, 3.6 mmol, 1.2 equiv.) at 0 °C. The resulting reaction mixture was stirred at r.t. for 3 h. Upon completion, aqueous 3N HCl was added dropwise until the pH reached ~3 and the reaction mixture was extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with water (1 × 10 mL) and brine (1 × 10 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1 ~ 20/1) to afford the corresponding product.

Note: The corresponding unprotected 2-amino propanediols for the synthesis of substrates **A-S23**, **A-S24**, and **A-S33** were commercially available, and the corresponding unprotected 2-amino propanediols for the synthesis of substrates **A-S25**, **A-S26**, **A-S27**, and **A-S29** were synthesized according to reported literature[3].

Benzyl (1,3-dihydroxypropan-2-yl)carbamate (A-S23)



A-S23

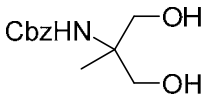
According to **General procedure 3**, product **A-S23** was obtained as a white solid (423.1 mg, 62%).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.41 – 7.27 (m, 5H), 6.09 (s, 1H), 5.06 (s, 2H), 3.94 (t, J = 5.2 Hz, 2H), 3.66 (m, 5H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 156.3, 137.5, 128.3, 127.8, 127.7, 65.7, 61.4, 54.7.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NO_4$ $[M + H]^+$ 226.1074, found 226.1068.

Benzyl (1,3-dihydroxy-2-methylpropan-2-yl)carbamate (A-S24)



A-S24

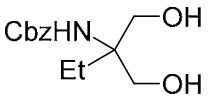
According to **General procedure 3**, product **A-S24** was obtained as a white solid (650.6 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 5.38 (s, 1H), 5.06 (s, 2H), 3.77 – 3.73 (m, 2H), 3.65 – 3.61 (m, 2H), 3.56 (s, 2H), 1.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 136.1, 128.6, 128.3, 128.1, 67.7, 66.9, 57.2, 20.0.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NO_4$ $[M + H]^+$ 240.1230, found 240.1225.

Benzyl (1-hydroxy-2-(hydroxymethyl)butan-2-yl)carbamate (A-S25)



A-S25

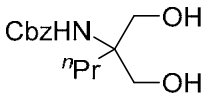
According to **General procedure 3**, product **A-S25** was obtained as a colorless oil (709.2 mg, 93% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.46 (s, 1H), 5.07 (s, 2H), 3.88 (s, 2H), 3.80 (d, *J* = 11.4 Hz, 2H), 3.60 (d, *J* = 11.5 Hz, 2H), 1.63 (q, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 136.2, 128.6, 128.2, 128.1, 66.8, 65.7, 59.6, 25.2, 7.6.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{20}NO_4$ $[M + H]^+$ 254.1387, found 254.1381.

Benzyl (1-hydroxy-2-(hydroxymethyl)pentan-2-yl)carbamate (A-S26)



A-S26

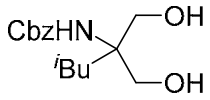
According to **General procedure 3**, product **A-S26** was obtained as a colorless oil (662.9 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 5H), 5.49 (s, 1H), 5.04 (s, 2H), 4.01 (s, 2H), 3.76 (d, *J* = 11.5 Hz, 2H), 3.57 (d, *J* = 11.4 Hz, 2H), 1.60 – 1.43 (m, 2H), 1.24 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 136.2, 128.6, 128.2, 128.1, 66.8, 65.9, 59.5, 34.9, 16.3, 14.5.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}NO_4$ $[M + H]^+$ 268.1543, found 268.1537.

Benzyl (1-hydroxy-2-(hydroxymethyl)-4-methylpentan-2-yl)carbamate (A-S27)



A-S27

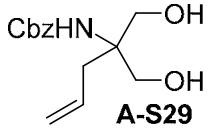
According to **General procedure 3**, product **A-S27** was obtained as a white solid (512.2 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 5H), 5.24 (s, 1H), 5.07 (s, 2H), 3.90 (d, *J* = 11.5 Hz, 2H), 3.61 (d, *J* = 11.5 Hz, 2H), 1.71 (m, 1H), 1.48 (d, *J* = 6.1 Hz, 2H), 0.92 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 136.2, 128.6, 128.3, 128.1, 66.9, 59.9, 41.8, 24.7 (2C), 23.4.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{24}NO_4$ $[M + H]^+$ 282.1700, found 282.1694.

Benzyl (1-hydroxy-2-(hydroxymethyl)pent-4-en-2-yl)carbamate (A-S29)



A-S29

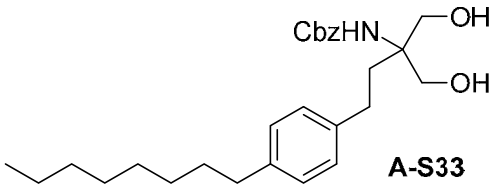
According to **General procedure 3**, product **A-S29** was obtained as a yellow oil (769.4 mg, 97% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 5H), 5.74 (ddt, *J* = 15.7, 10.6, 7.5 Hz, 1H), 5.46 (s, 1H), 5.12 (s, 1H), 5.10 – 5.08 (m, 1H), 5.04 (s, 2H), 3.84 (s, 2H), 3.76 (d, *J* = 11.6 Hz, 2H), 3.58 (d, *J* = 11.6 Hz, 2H), 2.35 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 136.1, 132.3, 128.6, 128.3, 128.1, 119.7, 66.9, 65.4, 59.1, 37.0.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{20}NO_4$ $[M + H]^+$ 266.1387, found 266.1380.

Benzyl (1-hydroxy-2-(hydroxymethyl)-4-(4-octylphenyl)butan-2-yl)carbamate (A-S33)



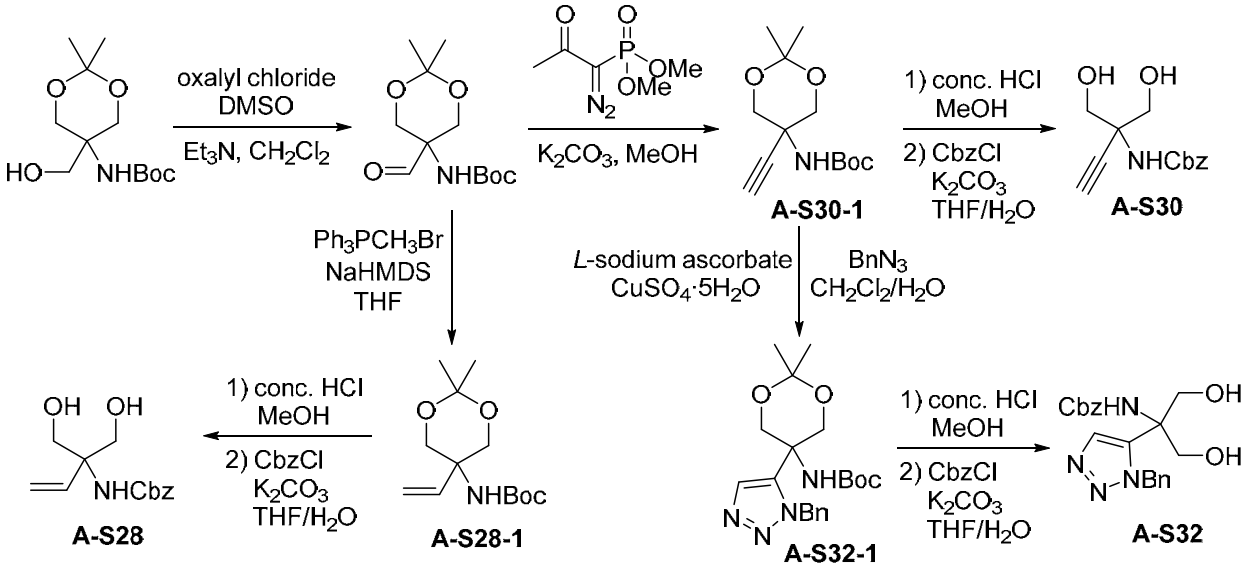
A-S33

According to **General procedure 3**, product **A-S33** was obtained as a white solid (1.018 g, 77%).

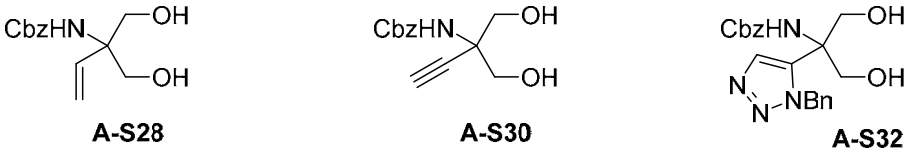
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 5H), 7.09 – 7.04 (m, 5H), 5.32 (s, 1H), 5.08 (s, 2H), 3.90 (dd, *J* = 11.5, 4.0 Hz, 2H), 3.66 (dd, *J* = 11.7, 4.5 Hz, 2H), 3.31 (s, 2H), 2.59 – 2.53 (m, 4H), 1.91 – 1.85 (m, 2H), 1.61 – 1.53 (m, 2H), 1.30 – 1.25 (m, 10 H), 0.91 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 140.7, 138.6, 136.2, 128.6, 128.5, 128.3, 128.2 – 128.0 (m, 2C), 67.0, 66.5, 59.6, 35.6, 35.1, 31.9, 31.6, 29.5, 29.4, 29.3, 29.1, 22.7, 14.2.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{40}NO_4$ $[M + H]^+$ 442.2952, found 442.2943.



A-S30-1 **A-S30** **A-S28** **A-S28-1** **A-S32-1** **A-S32**



A-S28 **A-S30** **A-S32**

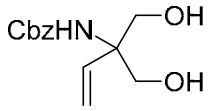
To a solution of oxalyl chloride (1.05 mL, 12.4 mmol, 1.24 equiv.) in CH_2Cl_2 (25 mL) was added DMSO (1.85 mL, 25.8 mmol, 2.58 equiv.) at −78 °C. After the mixture was stirred for 30 min at −78 °C, a solution of *N*-Boc protected acetonide alcohol (2.613 g, 10 mmol) in CH_2Cl_2 (25 mL) was added, and stirring was continued at −78 °C for 30 min. The reaction mixture was treated with triethylamine (3.65 mL, 26.3 mmol, 2.63 equiv.), allowed to warm to r.t., and stirred for 30 min. The reaction mixture was diluted with 1M HCl (5 mL), washed with saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1 ~ 3/1) to give the *N*-Boc protected acetonide aldehyde (1.591 g, 62% yield) as a white solid.

Synthesis of A-S28:

To a solution of Ph_3PCH_3Br (3.215 g, 9.0 mmol, 3.0 equiv.) in THF (18 ml) was added NaHMDS (2.0 M in THF, 4.5 ml, 9.0 mmol, 3.0 equiv.) at 0 °C. The mixture was stirred for 1 h and then treated with a solution of the aldehyde (777.9 mg, 3.0 mmol) in THF (15 ml). The reaction mixture was stirred at r.t. for 30 min and then quenched with a saturated aqueous NH_4Cl solution. The aqueous phase was extracted with EtOAc (2 × 20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (petroleum ether/EtOAc = 24/1 ~ 11/1) afforded **A-S28-1** (701.3 mg, 91%) as a white solid.

A-S28-1 (701.3 mg, 2.7 mmol) was demasked using concentrated HCl (3 mL) in MeOH (9 mL) at r.t. overnight. After evaporation of all the volatile materials *in vacuo*, the residue was dissolved in a mixture of THF/H_2O (1/1 (v/v), 6 mL). Then, K_2CO_3 (753.4 mg, 5.5 mmol, 2.0 equiv.) and benzyl chloroformate (0.46 mL, 3.3 mmol, 1.2 equiv.) were added at 0 °C under stirring. The reaction mixture was stirred at r.t. for 3 h. Aqueous 3N HCl was added dropwise until the pH reached ~3. The reaction mixture was extracted with EtOAc (2 × 10 mL). The organic layers were combined, washed with water (1 × 10 mL) and brine (1 × 10 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting crude compound was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1 ~ 20/1) to afford product **A-S28** as a colorless oil (514.6 mg, 73% over two steps).

Benzyl (1-hydroxy-2-(hydroxymethyl)but-3-en-2-yl) carbamate (A-S28)



A-S28

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 5H), 5.82 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.68 (s, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 17.5 Hz, 1H), 5.07 (s, 2H), 3.83 (s, 2H), 3.70 (q, *J* = 11.5 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 136.5, 136.1, 128.6, 128.3, 128.1, 116.3, 67.1, 65.9, 62.1.

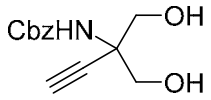
HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}NO_4$ $[M + H]^+$ 252.1230, found 252.1224.

Synthesis of A-S30:

To a solution of the aldehyde (777.9 mg, 3.0 mmol) in MeOH (24 mL) were sequentially added (1-diazo-2-oxo-propyl)-phosphonic acid dimethyl ester (0.68 mL, 4.5 mmol, 1.5 equiv.) and K_2CO_3 (828.5 mg, 6.0 mmol, 2.0 equiv.) at 0 °C. The mixture was reacted at 0 °C for 1 h and then at r.t. for another 1 h. After the removal of MeOH *in vacuo*, H_2O (25 mL) was added and the reaction mixture was extracted with EtOAc (3 × 25 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (petroleum ether/EtOAc = 24/1 ~ 5/1) produced **A-S30-1** (697.9 mg, 92% yield).

A-S30-1 (1.5 mmol) was demasked using concentrated HCl (2 mL) in MeOH (5 mL) at r.t. overnight. After evaporation of all the volatile materials *in vacuo*, the residue was dissolved in a mixture of THF/H_2O (1/1 (v/v), 3.0 mL). Then, K_2CO_3 (0.415 g, 3.0 mmol, 2.0 equiv.) and benzyl chloroformate (0.25 mL, 1.8 mmol, 1.2 equiv.) were successively added at 0 °C under stirring. The reaction mixture was stirred at r.t. for 3 h. Aqueous 3N HCl was added dropwise until the pH reached ~3. The reaction mixture was extracted with EtOAc (2 × 5 mL). The combined organic layers were washed with water (1 × 5 mL) and brine (1 × 5 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1 ~ 20/1) to afford product **A-S30** as a white solid (340.3 mg, 91% over two steps).

Benzyl (1-hydroxy-2-(hydroxymethyl)but-3-yn-2-yl) carbamate (A-S30)



A-S30

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 5.62 (s, 1H), 5.14 (s, 2H), 3.96 (dd, *J* = 11.5, 6.4 Hz, 2H), 3.87 (dd, *J* = 11.5, 6.9 Hz, 2H), 3.01 (s, 2H), 2.50 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 135.8, 128.6, 128.3, 128.2, 90.0, 74.1, 67.2, 65.8, 56.6.

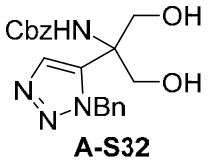
HRMS (ESI) *m/z* calcd. for $C_{13}H_{16}NO_4$ $[M + H]^+$ 250.1074, found 250.1068.

Synthesis of A-S32:

To a solution of BnN_3 (777.9 mg, 3.0 mmol) in CH_2Cl_2/H_2O (1/1 (v/v), 5 mL) were sequentially added **A-S30-1** (254.3 mg, 1.0 mmol), *L*-sodium ascorbate (89.0 mg, 0.45 mmol, 0.45 equiv.), and $CuSO_4 \cdot 5H_2O$ (37.5 mg, 0.15 mmol, 0.15 equiv.) at r.t. and the mixture was reacted at r.t. for 1 d. Upon completion, the reaction mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography (petroleum ether/EtOAc = 10/1 ~ 1/1) produced **A-S32-1** (369.0 mg, 95% yield).

A-S32-1 (0.75 mmol) was demasked using concentrated HCl (1 mL) in MeOH (2.5 mL) at r.t. overnight. After evaporation of all the volatile materials *in vacuo*, the residue was dissolved in a mixture of THF/H_2O (1/1 (v/v), 2 mL). Then, K_2CO_3 (0.208 g, 1.5 mmol, 2.0 equiv.) and benzyl chloroformate (0.13 mL, 0.9 mmol, 1.2 equiv.) were successively added at 0 °C under stirring. The reaction mixture was stirred at r.t. for 3 h. Aqueous 3N HCl was added dropwise until the pH reached ~3. The reaction mixture was extracted with EtOAc (2 × 2.5 mL). The combined organic layers were washed with water (1 × 2.5 mL) and brine (1 × 2.5 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 100/1 ~ 20/1) to afford product **A-S32** as a white solid (200.8 mg, 70% over two steps).

Benzyl (2-(1-benzyl-1H-1,2,3-triazol-5-yl)-1,3-dihydroxypropan-2-yl)carbamate (A-S32)

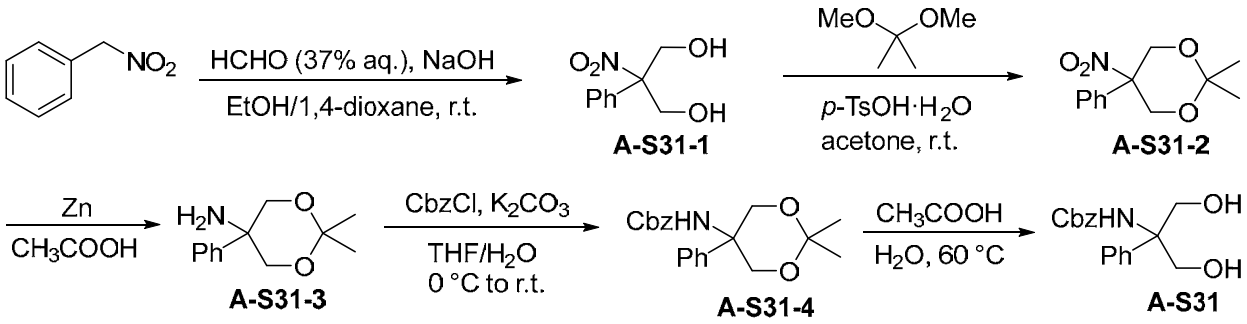


A-S32

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.34 – 7.25 (m, 10H), 6.26 (s, 1H), 5.46 (s, 2H), 5.02 (s, 2H), 4.12 – 4.01 (m, 4H), 3.87 (d, *J* = 11.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 148.0, 136.0, 134.3, 129.2, 128.8, 128.6, 128.2, 128.1, 128.0, 122.6, 67.0, 66.0, 58.6, 54.3.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{23}N_4O_4$ $[M + H]^+$ 383.1714, found 383.1704.



Synthesis of A-S31:

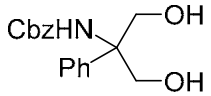
To a solution of phenylnitromethane (4.658 g, 34.0 mmol) in EtOH (46 mL) and 1,4-dioxane (19 mL) were added aqueous NaOH (1.0 M, 0.19 mL, 0.6 mol%) and formalin (37%, 5.6 mL, 68.0 mmol, 2.0 equiv.) at r.t. and the mixture was stirred at r.t. for 5 h. After evaporation of all the volatile materials *in vacuo*, H_2O (45 mL) was added. The resulting mixture was extracted with EtOAc (3 × 45 mL), dried, and concentrated. The residue was purified by flash chromatography (petroleum ether/EtOAc = 10/1 ~ 2/1) to afford **A-S31-1** (4.738 g, 71% yield).

To a solution of **A-S31-1** (3.434 g, 17.4 mmol) in acetone (40 mL) were added *p*-TsOH·H_2O (330.9 mg, 1.74 mmol, 0.1 equiv.) and 2,2-dimethoxypropane (2.4 mL, 19 mmol, 1.1 equiv.) at r.t. and the reaction mixture was stirred at r.t. for 2 h. Upon completion, the reaction was quenched with Et_3N (0.34 mL, 2.38 mmol, 0.14 equiv.) at r.t. and the stirring was continued for an additional 30 min. The resulting mixture was concentrated *in vacuo* and the residue was purified by column chromatography (petroleum ether/EtOAc = 12/1 ~ 5/1) to provide the acetonide **A-S31-2** (3.709 g, 90% yield).

To a solution of the acetonide **A-S31-2** (1.427 g, 6.0 mmol) in CH_3COOH (36 mL) were added zinc powders (1.56 g, 72.0 mmol, 12.0 equiv.) portionwise in 15-min intervals at r.t. and upon completion, the reaction mixture was stirred for additional 3 h. After filtration, the filtrate was concentrated *in vacuo*. The residue was diluted with CH_2Cl_2 (30 mL), washed with saturated $NaHCO_3$ (30 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to provide the crude amine **A-S31-3** (1.192 g, 96% yield).

To a solution of **A-S31-3** (1.192 g, 5.75 mmol) in THF/H_2O (1/1 (v/v), 10 mL) were successively added K_2CO_3 (1.589 g, 11.5 mmol, 2.0 equiv.) and benzyl chloroformate (0.96 mL, 6.9 mmol, 1.2 equiv.) at 0 °C under stirring. The reaction mixture was stirred at r.t. for 3 h. Aqueous 3N HCl was added dropwise until the pH reached ~3. The reaction mixture was extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with water (1 × 15 mL) and brine (1 × 15 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50/1 ~ 4/1) to afford the benzyl carbamate acetonide **A-S31-4**. The acetonide **A-S31-4** was demasked by stirring in acetic acid and H_2O (4/1 (v/v), 35 mL) at 60 °C for 1 h. Upon completion, all the volatile materials were removed *in vacuo* and the residue was purified by column chromatography (petroleum ether/EtOAc = 50/1 ~ 1/3) to offer product **A-S31** as a white solid (1.482 g, 86% over two steps).

Benzyl (1,3-dihydroxy-2-phenylpropan-2-yl) carbamate (A-S31)



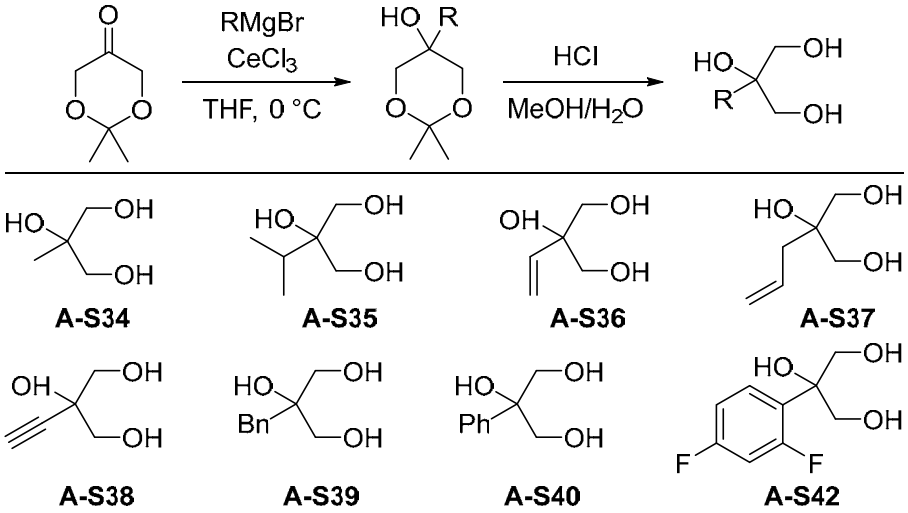
A-S31

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 10H), 5.91 (s, 1H), 5.11 (s, 2H), 4.00 (dd, *J* = 11.8, 5.0 Hz, 2H), 3.92 (dd, *J* = 11.8, 5.4 Hz, 2H), 3.31 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 139.5, 136.1, 128.8, 128.6, 128.3, 128.2, 127.8, 126.0, 67.8, 67.2, 63.9.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}NO_4$ $[M + H]^+$ 302.1387, found 302.1380.

The synthesis of 1,2,3-triol substrates A-S34–A-S42

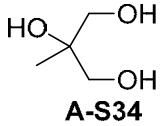


General procedure 4:

To a suspension of cerium(III) chloride (1.85 g, 7.5 mmol, 1.5 equiv.) in anhydrous THF (10 mL) was added the corresponding Grignard reagent (7.5 mmol, 1.5 equiv.). After stirring for 1.5 h at 0 ℃, a solution of 2,2-dimethyl-1,3-dioxan-5-one (0.6 mL, 5 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise at 0 ℃ by cannula. The resulting mixture was stirred at 0 ℃ for 1.5 h. After being neutralized with saturated NH_4Cl (aq.), the mixture was vigorously stirred for 15 min. The resulting gummy residue was removed by decantation and filtration through celite. The filtrate was concentrated under reduced pressure, and the residual solids were washed and extracted with CH_2Cl_2 (3x). The combined organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to provide the tertiary alcohol.

To a solution of the tertiary alcohol obtained above in a 2/1 mixture of MeOH (6 mL) and H_2O (3 mL) was added two drops of conc. HCl at r.t. and the mixture was stirred at r.t. for 6 h. Evaporation of the volatile materials *in vacuo* followed by chromatographic purification ($MeOH/CH_2Cl_2$ = 1/20) of the residue gave the corresponding product.

2-Methylpropane-1,2,3-triol (A-S34)



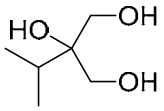
According to **General procedure 4** with methyl magnesium bromide (7.5 mL, 1.0 M in THF, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S34** as a colorless oil (181 mg, 34% yield over two steps).

^{1}H NMR (400 MHz, CD_3OD) δ 3.36 (d, *J* = 1.9 Hz, 4H), 1.03 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ 72.6, 66.3, 20.0.

HRMS (ESI) *m/z* calcd. for $C_4H_{10}NaO_3$ $[M + Na]^+$ 129.0522, found 129.0522.

2-Isopropylpropane-1,2,3-triol (A-S35)



A-S35

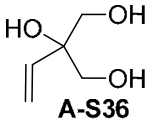
According to **General procedure 4** with isopropyl magnesium bromide (7.5 mL, 1.0 M in THF, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S35** as a colorless oil (308 mg, 46% yield over two steps).

^{1}H NMR (400 MHz, CD_3OD) δ 3.73 (d, *J* = 11.2 Hz, 2H), 3.64 (d, *J* = 11.3 Hz, 2H), 3.43 (s, 3H), 1.93 – 1.74 (m, 1H), 0.92 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, CD_3OD) δ 75.3, 65.7, 32.3, 16.8.

HRMS (ESI) *m/z* calcd. for $C_6H_{14}NaO_3$ $[M + Na]^+$ 157.0835, found 157.0835.

2-Vinylpropane-1,2,3-triol (A-S36)



A-S36

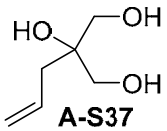
According to **General procedure 4** with vinyl magnesium bromide (7.5 mL, 1.0 M in THF, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S36** as a colorless oil (266 mg, 45% yield over two steps).

^{1}H NMR (400 MHz, Acetone-d_6) δ 5.99 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.39 (dd, *J* = 17.4, 1.9 Hz, 1H), 5.13 (dd, *J* = 10.9, 2.0 Hz, 1H), 3.87 (d, *J* = 36.9 Hz, 3H), 3.55 (q, *J* = 10.8 Hz, 4H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 205.9, 140.0, 114.0, 75.4, 65.9.

HRMS (ESI) *m/z* calcd. for $C_5H_{10}NaO_3$ $[M + Na]^+$ 141.0522, found 141.0521.

2-Allylpropane-1,2,3-triol (A-S37)



A-S37

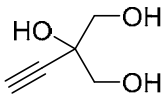
According to **General procedure 4** with allyl magnesium bromide (7.5 mL, 1.0 M in THF, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S37** as a colorless oil (397 mg, 60% yield over two steps).

^{1}H NMR (400 MHz, CD_3OD) δ 5.89 (m, 1H), 5.16 – 4.99 (m, 2H), 4.85 (s, 4H), 2.26 (d, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, CD_3OD) δ 133.4, 116.9, 73.9, 64.5, 38.2.

HRMS (ESI) *m/z* calcd. for $C_6H_{12}NaO_3$ $[M + Na]^+$ 155.0679, found 155.0677.

2-Ethynylpropane-1,2,3-triol (A-S38)



A-S38

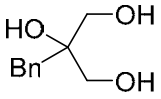
According to **General procedure 4** with ethynyl magnesium bromide (15 mL, 0.50 M in THF, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S38** as a white solid (400 mg, 69% yield over two steps).

^{1}H NMR (400 MHz, CD_3OD) δ 3.61 (d, *J* = 2.4 Hz, 4H), 2.81 (s, 1H).

^{13}C NMR (100 MHz, CD_3OD) δ 83.8, 73.4, 71.0, 65.2.

HRMS (ESI) *m/z* calcd. for $C_5H_8NaO_3$ $[M + Na]^+$ 139.0366, found 139.0365.

2-Benzylpropane-1,2,3-triol (A-S39)



A-S39

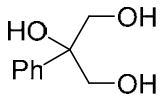
According to **General procedure 4** with benzyl magnesium bromide (7.5 mL, 1.0 M in THF, 1.5 equiv.). The reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S39** as a white solid (292 mg, 32% yield over two steps).

^{1}H NMR (400 MHz, CD_3OD) δ 7.35 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 3.42 (s, 4H), 2.80 (s, 2H).

^{13}C NMR (100 MHz, CD_3OD) δ 137.0, 130.3, 127.4, 125.8, 74.4, 64.2, 39.4.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NaO_3$ $[M + Na]^+$ 205.0835, found 205.0834.

2-Phenylpropane-1,2,3-triol (A-S40)



A-S40

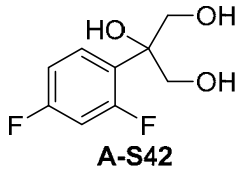
According to **General procedure 4** with phenyl magnesium bromide (7.5 mL, 1.0 M in THF, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S40** as a white solid (463 mg, 55% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 4.54 (s, 1H), 4.03 (s, 2H), 3.73 (d, *J* = 11.7 Hz, 2H), 3.57 (d, *J* = 11.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.3, 127.4, 125.3, 76.7, 67.7.

HRMS (ESI) *m/z* calcd. for $C_9H_{12}NaO_3$ $[M + Na]^+$ 191.0679, found 191.0676.

2-(2,4-Difluorophenyl)propane-1,2,3-triol (A-S42)



A-S42

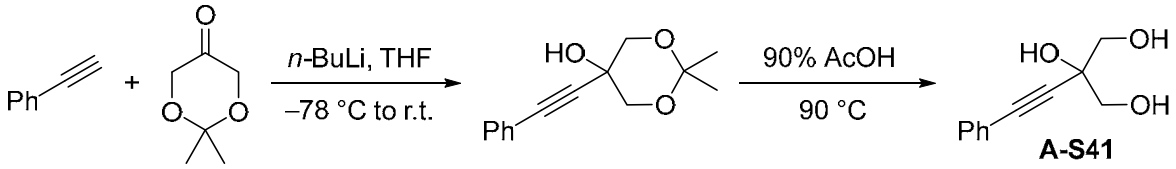
According to **General procedure 4** with 2,4-difluorophenyl magnesium bromide (1.5 equiv.) prepared using 1-bromo-2,4-difluorobenzene and Mg, the reaction mixture was purified by column chromatography on silica gel ($MeOH/CH_2Cl_2$ = 1/20) to yield product **A-S42** as a white solid (530 mg, 52% yield over two steps).

^{1}H NMR (400 MHz, CD_3OD) δ 7.74 (td, *J* = 8.9, 6.8 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.92 – 6.86 (m, 1H), 3.95 – 3.79 (m, 4H).

^{13}C NMR (100 MHz, CD_3OD) δ 162.4 (dd, *J* = 244.8, 12.4 Hz), 159.7 (dd, *J* = 245.6, 11.8 Hz), 130.7 (dd, *J* = 9.5, 6.6 Hz), 125.3 (dd, *J* = 13.4, 3.7 Hz), 110.4 (dd, *J* = 20.7, 3.4 Hz), 103.3 (dd, *J* = 28.6, 25.7 Hz), 76.7 (d, *J* = 5.6 Hz), 65.4 (d, *J* = 5.3 Hz).

^{19}F NMR (376 MHz, CD_3OD) δ −110.1 (m), −114.8 (m).

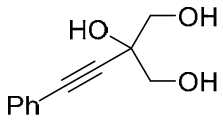
HRMS (ESI) *m/z* calcd. for $C_9H_{10}F_2NaO_3$ $[M + Na]^+$ 227.0490, found 227.0488.



Synthesis of A-S41:

To a solution of phenylacetylene (2.2 mL, 20 mmol) in THF (20 mL) was dropwise added *n*-BuLi (2.4 M in THF, 8.3 mL, 20 mmol) at −78 ℃. After stirring for 1 h, the ketone (2.4 mL, 20 mmol, 1.0 equiv.) in THF (20 mL) was slowly added via syringe and the mixture was stirred at −78 ℃ for 2 h. The reaction mixture was quenched with saturated NH_4Cl (aq.) and extracted with EtOAc (3x). The combined organic layers were washed with H_2O (1x), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was dissolved in acetic acid (90%, 30 mL) and the solution was stirred at 90 ℃ for 15 min. The reaction mixture was concentrated *in vacuo* and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **A-S41** as a white solid (2.5 g, 65% yield over two steps).

2-(Phenylethynyl)propane-1,2,3-triol (A-S41)



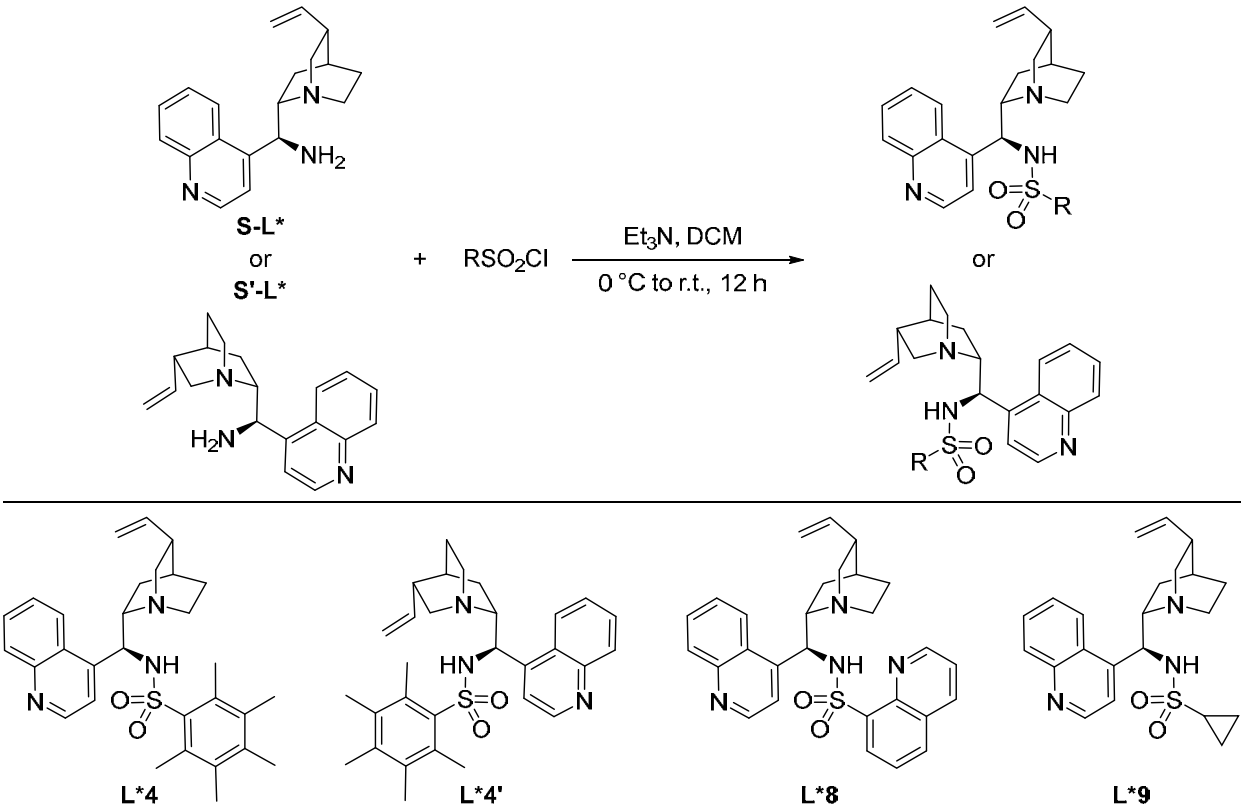
A-S41

^{1}H NMR (400 MHz, CD_3OD) δ 7.51 – 7.41 (m, 2H), 7.36 – 7.26 (m, 3H), 3.79 – 3.64 (m, 4H).

^{13}C NMR (100 MHz, CD_3OD) δ 131.4, 128.04, 127.97, 122.8, 89.1, 84.7, 71.6, 65.3.

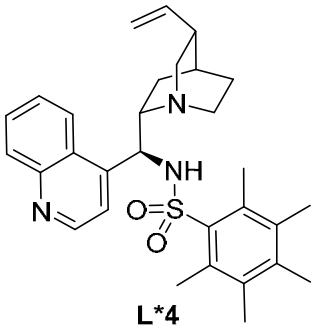
HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}NaO_3$ $[M + Na]^+$ 215.0679, found 215.0678.

Synthesis of ligands



General procedures 5:

To a solution of amine **S-L*** or **S'-L*** (1.47 g, 5.0 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (10 mL) were successively added the corresponding sulfonyl chloride (6.0 mmol, 1.2 equiv.) and Et_3N (1.67 mL, 12.0 mmol, 2.0 equiv.) under argon at 0 °C. The reaction mixture was stirred for 12 h at r.t. and quenched by H_2O. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel flash column chromatography (eluent: CH_2Cl_2/MeOH = 20/1 ~ 10/1) to afford the product.



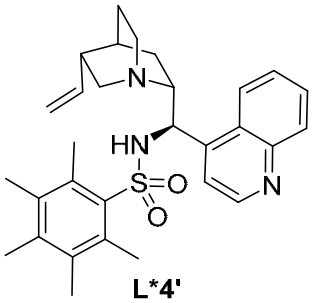
According to **General procedure 5** with amine **S-L*** (1.47 g, 5.0 mmol, 1.0 equiv.) and pentamethylbenzenesulfonyl chloride (1.48 g, 6.0 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 20/1 ~ 10/1) to yield product **L*4** as a white solid (1.81 g, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.3 Hz, 1H × 0.4), 8.55 (d, *J* = 4.6 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H × 0.4), 8.08 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H × 0.4), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 – 7.51 (m, 1H + 1H × 0.4), 7.39 (t, *J* = 7.5 Hz, 1H × 0.4), 7.18 – 7.16 (m, 1H + 1H × 0.4), 5.72 – 5.63 (m, 1H), 5.61 – 5.54 (m, 1H × 0.4), 5.08 (d, *J* = 10.6 Hz, 1H), 5.01 – 4.89 (m, 2H + 1H × 0.4), 4.84 (d, *J* = 10.3 Hz, 1H × 0.4), 4.44 (d, *J* = 10.9 Hz, 1H × 0.4), 3.37 (q, *J* = 9.6 Hz, 1H × 0.4), 3.28 – 3.22 (m, 1H + 1H × 0.4), 3.20 – 3.10 (m, 1H), 3.10 – 3.00 (m, 1H × 0.4), 2.86 (q, *J* = 9.8 Hz, 1H), 2.77 – 2.71 (m, 2H + 2H × 0.4), 2.35 (s, 6H × 0.4), 2.27 (s, 6H), 1.98 (s, 3H), 1.86 (s, 3H × 0.4), 1.81 (s, 6H), 1.77 (s, 6H × 0.4), 1.67 – 1.65 (m, 2H × 0.4), 1.60 – 1.50 (m, 4H), 1.27 – 1.21 (m, 1H + 2H × 0.4), 0.87 (dd, *J* = 13.0, 7.5 Hz, 1H × 0.4), 0.72 (dd, *J* = 13.5, 7.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.6, 148.3, 147.6, 144.2, 141.4, 141.2, 141.1, 139.2, 139.0, 134.6, 134.4, 134.1, 133.9, 133.7, 129.8, 128.8, 128.3, 127.3, 126.2, 125.6, 125.0, 124.7, 123.2, 122.5, 119.1, 114.5, 62.9, 60.6, 56.5, 55.8, 55.6, 52.6, 40.1, 39.7, 39.6, 39.4, 27.6, 27.4, 27.3, 26.1, 25.1, 18.5, 18.4, 17.3, 16.5, 16.4.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{38}N_3O_2S$ $[M + H]^+$ 504.2679, found 504.2680.

The structure of **L*4** was further confirmed by X-ray diffraction analysis (Supplementary Fig. 18).



L*4'

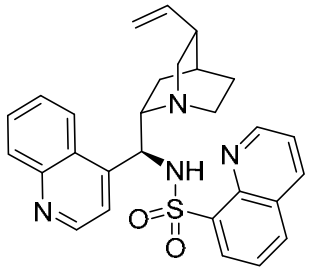
According to **General procedure 5** with amine **S'-L*** (1.47 g, 5.0 mmol, 1.0 equiv.) and pentamethylbenzenesulfonyl chloride (1.48 g, 6.0 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 20/1 ~ 10/1) to yield product **L*4'** as a white solid (1.50 g, 60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.3 Hz, 1H × 0.4), 8.58 (d, *J* = 4.6 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H × 0.4), 7.99 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H × 0.4), 7.65 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H × 0.4), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H × 0.4), 7.24 (d, *J* = 4.6 Hz, 1H), 7.11 (d, *J* = 4.3 Hz, 1H × 0.4), 5.85 – 5.78 (m, 1H + 1H × 0.4), 5.15 – 5.10 (m, 1H + 1H × 0.4), 5.04 – 5.00 (m, 1H + 1H × 0.4), 4.97 (d, *J* = 10.4 Hz, 1H), 4.38 (d, *J* = 10.8 Hz, 1H × 0.4), 3.29 (q, *J* = 9.4 Hz, 1H × 0.4), 2.96 – 2.87 (m, 3H + 3H ×

0.4), 2.82 – 2.75 (m, 2H), 2.73 – 2.68 (m, 1H × 0.4), 2.37 (s, 6H × 0.4), 2.28 (s, 6H), 2.05 (s, 3H), 1.91 (s, 3H × 0.4), 1.89 (s, 6H), 1.83 (s, 6H × 0.4), 1.64 (s, 1H × 0.4), 1.58 – 1.42 (m, 3H + 2H × 0.4), 1.19 – 1.14 (m, 1H × 0.4), 1.09 – 1.04 (m, 1H), 0.82 – 0.76 (m, 1H + 1H × 0.4).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 148.8, 148.4, 147.7, 144.7, 141.9, 140.2, 139.9, 139.3, 139.1, 134.7, 134.5, 134.2, 134.1, 133.9, 129.8, 128.8, 128.4, 127.4, 126.2, 125.1, 124.9, 123.0, 122.4, 119.3, 114.8, 114.5, 62.3, 60.8, 56.6, 52.0, 49.13, 49.06, 45.9, 45.7, 39.0, 38.8, 27.4, 27.3, 26.5, 26.4, 25.3, 24.2, 18.48, 18.46, 17.4, 16.7, 16.6.

HRMS (ESI) *m/z* calcd. for $C_{30}H_{38}N_3O_2S$ $[M + H]^+$ 504.2679, found 504.2680.



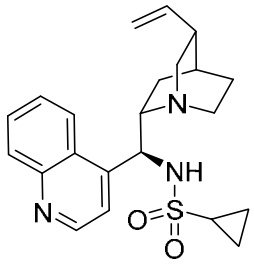
L*8

According to **General procedure 5** with amine **S-L*** (1.47 g, 5.0 mmol, 1.0 equiv.) and quinoline-8-sulfonyl chloride (1.37 g, 6.0 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 20/1 ~ 10/1) to yield product **L*8** as a white solid (1.70 g, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 4.0 Hz, 1H), 8.75 (d, *J* = 4.5 Hz, 1H), 8.58 (s, 2H × 0.1), 8.23 – 8.22 (m, 1H + 1H × 0.1), 8.11 – 8.05 (m, 2H + 2H × 0.1), 7.94 (dd, *J* = 20.0, 7.3 Hz, 2H), 7.67 – 7.63 (m, 1H + 1H × 0.1), 7.56 – 7.53 (m, 3H), 7.46 – 7.42 (m, 1H + 2H × 0.1), 7.31 (s, 2H × 0.1), 7.09 (s, 2H × 0.1), 5.62 – 5.58 (m, 1H + 1H × 0.1), 4.90 – 4.86 (m, 3H), 4.09 (s, 3H × 0.1), 3.35 (s, 2H × 0.1), 3.10 – 2.77 (m, 2H), 2.65 – 2.62 (m, 1H + 1H × 0.1), 2.10 (s, 1H + 1H × 0.1), 1.91 (s, 1H + 1H × 0.1), 1.76 – 1.69 (m, 1H + 1H × 0.1), 1.45 (s, 1H + 1H × 0.1), 1.26 – 1.20 (m, 2H + 2H × 0.1), 1.10 – 1.06 (m, 1H + 1H × 0.1), 0.81 – 0.51 (m, 1H + 1H × 0.1).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8, 149.8, 149.1, 148.0, 146.1, 143.2, 142.9, 141.1, 136.5, 135.7, 133.2, 131.0, 130.2, 128.8, 128.4, 127.2, 126.5, 125.7, 125.1, 122.8, 122.1, 122.0, 119.6, 114.4, 63.0, 61.2, 57.0, 55.4, 52.8, 39.5, 39.3, 39.0, 27.4, 27.0, 25.9, 24.9.

HRMS (ESI) *m/z* calcd. for $C_{28}H_{29}N_4O_2S$ $[M + H]^+$ 485.2006, found 485.2007.



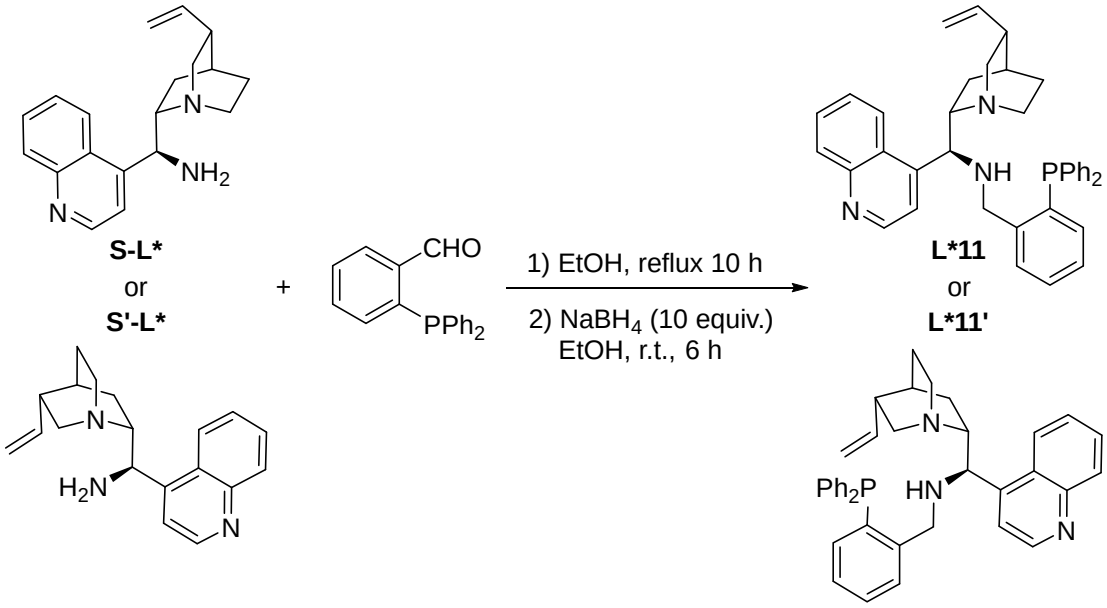
L*9

According to **General procedure 5** with amine **S-L*** (1.47 g, 5.0 mmol, 1.0 equiv.) and cyclopropanesulfonyl chloride (0.61 mL, 6.0 mmol, 1.2 equiv.). The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH = 50/1 ~ 30/1) to yield product **L*9** as a yellow solid (1.57 g, 79% yield).

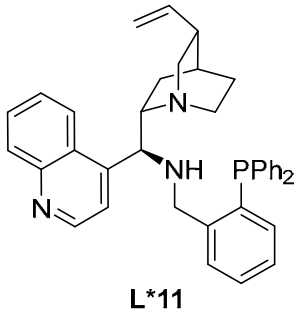
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 4.5 Hz, 1H), 8.86 (d, *J* = 4.1 Hz, 1H × 0.55), 8.71 (d, *J* = 8.5 Hz, 1H × 0.55), 8.31 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H + 1H × 0.55), 7.81 – 7.70 (m, 2H + 1H × 0.55), 7.66 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H × 0.55), 7.38 (d, *J* = 4.1 Hz, 1H × 0.55), 5.75 – 5.56 (m, 1H + 1H × 0.55), 5.29 (d, *J* = 10.5 Hz, 1H), 4.95 – 4.92 (m, 2H + 1H × 0.55), 4.87 (d, *J* = 10.3 Hz, 1H × 0.55), 4.52 (d, *J* = 10.8 Hz, 1H × 0.55), 3.38 (q, *J* = 9.6 Hz, 1H × 0.55), 3.29 – 3.16 (m, 2H + 1H × 0.55), 3.11 – 3.03 (m, 1H × 0.55), 2.98 – 2.66 (m, 3H + 2H × 0.55), 2.30 (s, 1H + 1H × 0.55), 1.95 – 1.88 (m, 1H), 1.71 – 1.61 (m, 3H + 4H × 0.55), 1.39 – 1.22 (m, 1H + 1H × 0.55), 1.08 – 0.80 (m, 2H + 2H × 0.55), 0.72 – 0.65 (m, 1H), 0.51 – 0.27 (m, 1H + 2H × 0.55), 0.18 – 0.10 (m, 1H), –0.04 – –0.25 (m, 1H × 0.55).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.5, 149.0, 148.2, 146.4, 142.7, 141.1, 141.0, 130.5, 130.2, 129.3, 129.1, 127.5, 127.1, 126.2, 126.2, 124.9, 123.5, 122.4, 120.0, 114.5, 62.5, 61.3, 56.6, 55.6, 55.4, 52.5, 40.2, 39.8, 39.5, 39.3, 30.9, 30.8, 27.6, 27.4, 27.2, 26.2, 25.0, 5.6, 5.5, 4.9, 4.8.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{28}N_3O_2S$ $[M + H]^+$ 398.1897, found 398.1895.



A solution of amine **S-L*** or **S'-L*** (1.47 g, 5.0 mmol, 1.0 equiv.) and 2-(diphenylphosphanyl)benzaldehyde (1.45 g, 5.0 mmol, 1.0 equiv.) in anhydrous ethanol (150 mL) was heated under reflux for 10 h. The reaction was then cooled to r.t. Sodium borohydride (1.90 g, 50 mmol, 10 equiv.) was added at r.t. After stirring for 6 h, the reaction was quenched by adding acetone (50 mL) and the solvents were removed under reduced pressure. The residue was dissolved in a mixture of saturated ammonium hydrochloride solution (100 mL) and dichloromethane (100 mL) with vigorous stirring. The aqueous phase was extracted with dichloromethane (3x). The combined organic phase was washed with brine, dried (Na_2SO_4), concentrated, and purified by silica gel flash column chromatography (eluent: petroleum ether/EtOAc = 1/1, then EtOAc) to afford the product.



L*11 was obtained as a white solid (1.79 g, 63% yield).

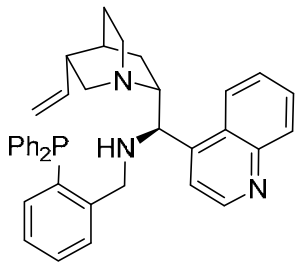
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H × 0.3), 9.00 – 8.84 (m, 1H), 8.76 (s, 1H × 0.3), 8.17 – 8.15 (m, 2H + 1H × 0.3), 7.91 – 7.78 (m, 1H), 7.73 – 7.69 (m, 1H + 1H × 0.3), 7.58 – 7.49 (m, 1H + 1H × 0.3), 7.35 – 7.05 (m, 13H + 14H × 0.3), 6.89 – 6.80 (m, 1H + 1H × 0.3), 5.77 – 5.54 (m, 1H + 1H × 0.3), 4.98 – 4.76 (m, 2H + 2H × 0.3), 4.60 (d, *J* = 9.5 Hz, 1H), 3.98 – 3.84 (m, 2H × 0.3), 3.79 (d, *J* = 12.8 Hz, 1H), 3.51 (d, *J* = 13.1 Hz, 1H + 1H × 0.3), 3.40 (s, 1H × 0.3), 3.23 –

3.04 (m, 1H + 2H × 0.3), 3.04 – 2.76 (m, 4H), 2.76 – 2.41 (m, 3H), 2.19 (s, 1H + 1H × 0.3), 1.51 (s, 4H + 2H × 0.3), 1.20 – 1.02 (m, 1H + 2H × 0.3), 0.91 – 0.63 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.6, 148.2, 144.7, 144.4, 141.8, 136.9, 136.8, 136.6, 135.7, 135.5, 133.8, 133.7, 133.6, 133.5, 130.4, 129.44, 129.38, 129.0, 128.8, 128.7, 128.5, 128.44, 128.41, 128.34, 128.28, 127.2, 126.2, 122.7, 120.1, 114.1, 69.2, 62.4, 58.3, 57.0, 56.0, 50.0, 49.8, 40.9, 39.9, 29.2, 28.1, 27.5, 26.8, 25.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –16.3.

HRMS (ESI) *m/z* calcd. for $C_{38}H_{39}N_3P$ $[M + H]^+$ 568.2876, found 568.2873.



L*11'

L*11' was obtained as a yellow solid (1.48 g, 52% yield).

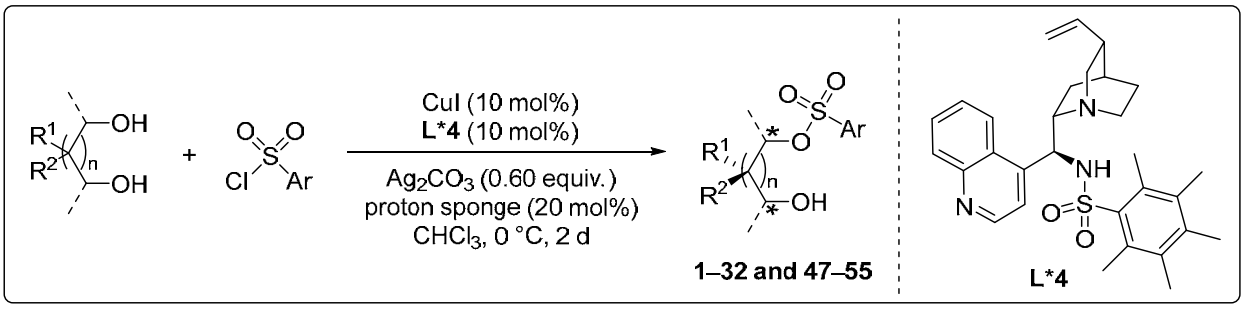
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H × 0.3), 8.92 – 8.91 (m, 1H), 8.76 (s, 1H × 0.3), 8.17 – 8.11 (m, 2H + 1H × 0.3), 7.87 – 7.80 (m, 1H), 7.73 – 7.69 (m, 1H + 1H × 0.3), 7.57 – 7.50 (m, 1H + 1H × 0.3), 7.33 – 7.10 (m, 13H + 14H × 0.3), 6.88 – 6.83 (m, 1H + 1H × 0.3), 5.87 – 5.78 (m, 1H + 1H × 0.3), 5.08 (d, *J* = 10.5 Hz, 1H + 1H × 0.3), 4.99 (d, *J* = 17.3 Hz, 1H + 1H × 0.3), 4.61 (d, *J* = 9.5 Hz, 1H), 3.96 – 3.83 (m, 2H × 0.3), 3.76 (d, *J* = 13.3 Hz, 1H), 3.53 (d, *J* = 13.3 Hz, 1H + 1H × 0.3), 3.32 (s, 1H × 0.3), 2.97 – 2.70 (m, 5H + 5H × 0.3), 2.21 – 2.15 (m, 1H + 2H × 0.3), 1.51 – 1.43 (m, 3H + 3H × 0.3), 1.15 – 1.09 (m, 1H + 1H × 0.3), 0.73 – 0.68 (m, 1H + 1H × 0.3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.8, 148.2, 144.8, 144.5, 140.8, 136.9, 136.8, 136.7, 135.8, 135.7, 133.9, 133.8, 133.7, 133.6, 130.4, 129.42, 129.38, 129.1, 128.8, 128.6, 128.5, 128.42, 128.35, 127.3, 126.1, 122.9, 120.1, 114.3, 62.5, 56.3, 50.1, 49.9, 49.3, 47.3, 39.6, 27.7, 26.7, 24.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ –16.3.

HRMS (ESI) *m/z* calcd. for $C_{38}H_{39}N_3P$ $[M + H]^+$ 568.2876, found 568.2871.

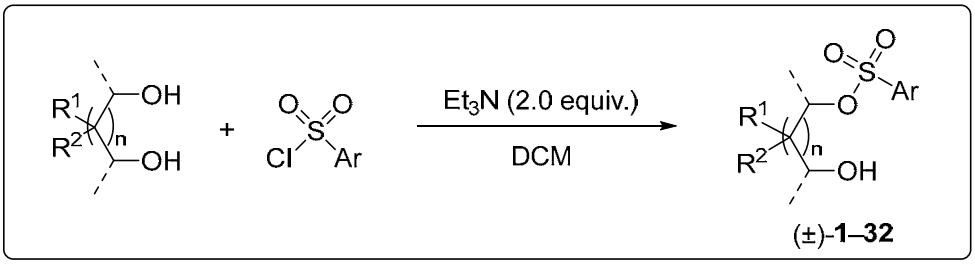
Cu-catalyzed enantioselective radical S–O cross-coupling of 2,2-disubstituted 1,3-diols, *meso* 1,2-diol, and 1,2,3-triols



General procedure A:

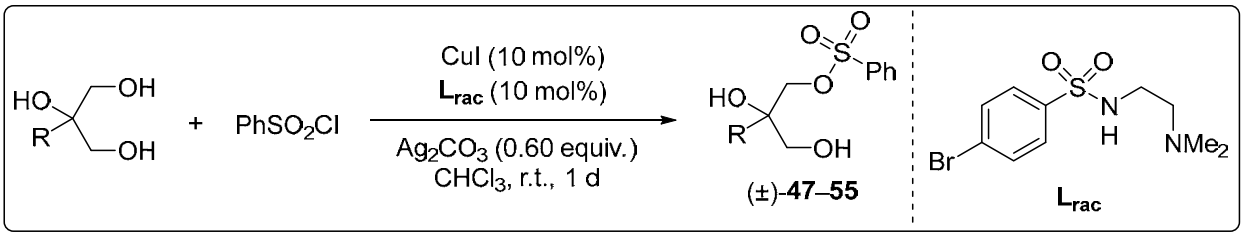
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (5.7 mg, 0.030 mmol, 10 mol%), **L*4** (15.1 mg, 0.030 mmol, 10 mol%), Ag_2CO_3 (49.6 mg, 0.18 mmol, 0.60 equiv.), proton sponge (12.8 mg, 0.060 mmol, 0.20 equiv.), alcohol (0.30 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (3.0 mL). Then the corresponding sulfonyl chloride (0.36 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at 0 °C. Upon completion (monitored by TLC), the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic products (±)-**1**–**32**:



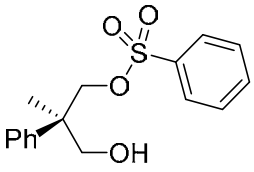
To a solution of diol (0.10 mmol, 1.0 equiv.) and Et_3N (27.7 µL, 0.20 mmol, 2.0 equiv.) in dry DCM (1.0 mL) was added the corresponding sulfonyl chloride (0.11 mmol, 1.1 equiv.). After stirring for 24 h, saturated NH_4Cl (aq.) was added to the above reaction solution to quench the reaction. Then, the mixture was extracted with DCM (3x) and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by silica gel column chromatography to afford the desired racemate.

The preparation of racemic products (±)-**47**–**55**:



The racemates of products (±)-**47**–**55** were prepared by following **General procedure A** described above using $\mathbf{L_{rac}}$ (10 mol%) as ligand. After stirring at r.t. for 24 h, the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford the desired racemates.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl benzenesulfonate (1)



1

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **1** as a colorless oil (79.0 mg, 86% yield, 94% e.e.).

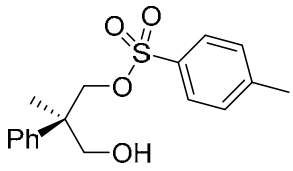
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 26.64 min, t_R (minor) = 29.12 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.77 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.24 (m, 5H), 4.27 (d, *J* = 9.6 Hz, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 3.80 (d, *J* = 11.3 Hz, 1H), 3.76 (d, *J* = 11.3 Hz, 1H), 1.63 (br s, 1H), 1.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 135.6, 133.8, 129.2, 128.7, 127.9, 127.1, 126.3, 74.2, 67.4, 43.8, 20.1.

HRMS (ESI) calcd for $C_{16}H_{18}NaO_4S$ $[M + Na]^+$ 329.0818, found: 329.0814.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-methylbenzenesulfonate (2)



2

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 4-methylbenzenesulfonyl chloride (68.4 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **2** as a white solid (82.5 mg, 86% yield, 93% e.e.).

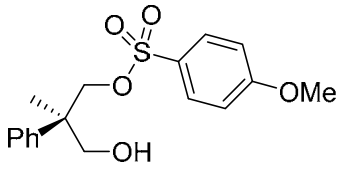
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 23.40 min, t_R (minor) = 25.24 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.20 (m, 7H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.19 (d, *J* = 9.6 Hz, 1H), 3.77 (d, *J* = 11.4 Hz, 1H), 3.73 (d, *J* = 11.4 Hz, 1H), 2.44 (s, 3H), 1.84 (br s, 1H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.3, 132.5, 129.8, 128.6, 127.8, 127.0, 126.3, 74.0, 67.3, 43.7, 21.6, 20.1.

HRMS (ESI) calcd for $C_{17}H_{20}NaO_4S$ $[M + Na]^+$ 343.0975, found: 343.0975.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-methoxybenzenesulfonate (3)



3

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 4-methoxybenzenesulfonyl chloride (74.4 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **3** as a colorless oil (57.5 mg, 57% yield, 92% e.e.).

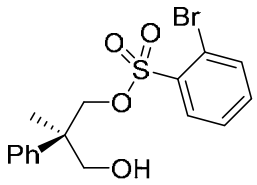
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 19.66 min, t_R (minor) = 22.23 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 2H), 7.37 – 7.21 (m, 5H), 7.02 – 6.95 (m, 2H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 3.88 (s, 3H), 3.79 (d, *J* = 11.4 Hz, 1H), 3.75 (d, *J* = 11.4 Hz, 1H), 1.74 (br s, 1H), 1.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 141.4, 130.1, 128.6, 127.1, 126.9, 126.4, 114.4, 73.8, 67.4, 55.7, 43.8, 20.2.

HRMS (ESI) calcd for $C_{17}H_{20}NaO_5S$ $[M + Na]^+$ 359.0924, found: 359.0918.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-bromobenzenesulfonate (4)



4

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 2-bromobenzenesulfonyl chloride (92.0 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **4** as a slightly yellow solid (77.1 mg, 67% yield, 93% e.e.).

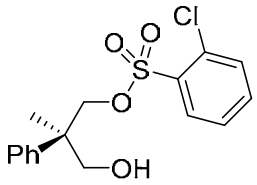
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 40.56 min, t_R (minor) = 44.23 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 1H), 7.80 – 7.72 (m, 1H), 7.53 – 7.43 (m, 2H), 7.36 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 4.33 (d, *J* = 9.6 Hz, 1H), 4.27 (d, *J* = 9.6 Hz, 1H), 3.84 (d, *J* = 11.6 Hz, 1H), 3.81 (d, *J* = 11.6 Hz, 1H), 1.82 (br s, 1H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 135.6, 135.4, 134.7, 132.1, 128.7, 127.6, 127.2, 126.4, 120.8, 74.9, 67.4, 43.8, 20.3.

HRMS (ESI) calcd for $C_{16}H_{17}BrNaO_4S$ $[M + Na]^+$ 406.9923, found: 406.9918.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-chlorobenzenesulfonate (5)



5

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 2-chlorobenzenesulfonyl chloride (76.0 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **5** as a colorless oil (56.9 mg, 56% yield, 91% e.e.).

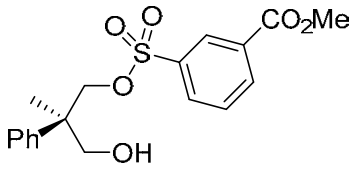
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.4 mL/min, λ = 214 nm), t_R (major) = 29.06 min, t_R (minor) = 31.01 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 1H), 7.59 – 7.53 (m, 2H), 7.45 – 7.41 (m, 1H), 7.32 – 7.31 (m, 4H), 7.26 – 7.23 (m, 1H), 4.35 (d, *J* = 9.6 Hz, 1H), 4.29 (d, *J* = 9.6 Hz, 1H), 3.84 (d, *J* = 11.2 Hz, 1H), 3.81 (d, *J* = 11.2 Hz, 1H), 1.70 (br s, 1H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 134.8, 133.7, 132.9, 132.1, 131.9, 128.7, 127.2, 127.1, 126.3, 74.9, 67.4, 43.8, 20.3.

HRMS (ESI) calcd for $C_{16}H_{17}ClNaO_4S$ $[M + Na]^+$ 363.0428, found: 363.0423.

Methyl (*R*)-3-((3-hydroxy-2-methyl-2-phenylpropoxy)sulfonyl)benzoate (6)



6

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and methyl 3-(chlorosulfonyl)benzoate (59.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **6** as a white solid (95.1 mg, 87% yield, 91% e.e.).

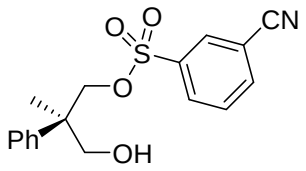
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.6 mL/min, λ = 214 nm), t_R (major) = 16.41 min, t_R (minor) = 19.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (t, *J* = 1.6 Hz, 1H), 8.30 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.99 (dt, *J* = 7.9, 1.4 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.32 – 7.19 (m, 5H), 4.28 (s, 2H), 3.96 (s, 3H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.75 (d, *J* = 11.2 Hz, 1H), 1.81 (br s, 1H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 141.1, 136.3, 134.6, 131.7, 131.4, 129.5, 128.9, 128.6, 127.1, 126.2, 74.6, 67.2, 52.7, 43.8, 20.1.

HRMS (ESI) calcd for $C_{18}H_{20}NaO_6S$ $[M + Na]^+$ 387.0873, found: 387.0867.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 3-cyanobenzenesulfonate (7)



7

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 3-cyanobenzenesulfonyl chloride (72.6 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **7** as a white solid (97.1 mg, 98% yield, 95% e.e.).

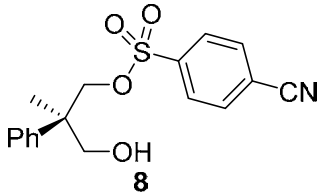
HPLC analysis: Chiralcel AZ3 (*n*-Hexane/*i*-PrOH = 70/30, flow rate 0.7 mL/min, λ = 214 nm), t_R (major) = 21.05 min, t_R (minor) = 24.77 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.89 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.68 – 7.59 (m, 1H), 7.32 – 7.20 (m, 5H), 4.33 (d, *J* = 9.5 Hz, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 3.79 (d, *J* = 11.1 Hz, 1H), 3.73 (d, *J* = 11.1 Hz, 1H), 1.93 (br s, 1H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 137.3, 136.7, 131.6, 131.2, 130.2, 128.6, 127.2, 126.1, 116.7, 113.8, 75.2, 67.0, 43.7, 19.9.

HRMS (ESI) calcd for $C_{17}H_{17}NNaO_4S$ $[M + Na]^+$ 354.0770, found: 354.0765.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-cyanobenzenesulfonate (8)



8

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 4-cyanobenzenesulfonyl chloride (72.6 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **8** as a white solid (96.2 mg, 97% yield, 94% e.e.).

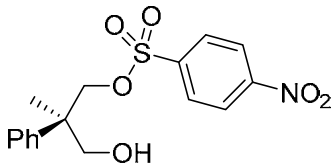
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 28.18 min, t_R (minor) = 33.00 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.81 – 7.75 (m, 2H), 7.34 – 7.20 (m, 5H), 4.32 (d, *J* = 9.5 Hz, 1H), 4.29 (d, *J* = 9.5 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 3.73 (d, *J* = 11.2 Hz, 1H), 1.89 (br s, 1H), 1.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 139.8, 132.9, 128.7, 128.4, 127.2, 126.2, 117.4, 116.9, 75.1, 67.1, 43.7, 20.0.

HRMS (ESI) calcd for $C_{17}H_{18}NO_4S$ $[M + Na]^+$ 332.0951, found: 332.0943.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-nitrobenzenesulfonate (9)



9

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride (79.8 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **9** as a slightly yellow solid (85.2 mg, 81% yield, 94% e.e.).

HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 18.52 min, t_R (minor) = 22.55 min.

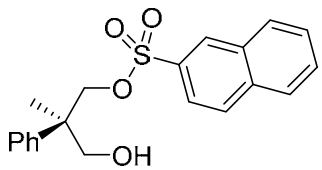
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.20 (m, 5H), 4.35 (d, *J* = 9.5 Hz, 1H), 4.32 (d, *J* = 9.5 Hz, 1H), 3.80 (d, *J* = 11.2 Hz, 1H), 3.75 (d, *J* = 11.1 Hz, 1H), 1.73 (br s, 1H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 141.3, 140.9, 129.1, 128.7, 127.3, 126.2, 124.3, 75.3, 67.1, 43.8, 20.0.

HRMS (ESI) calcd for $C_{10}H_{13}O$ $[M\text{-}p NO_2PhSO_3]^+$ 149.0961, found: 149.0963.

Note: The product was unstable in neat state at r.t. after purification and should be stored in refrigerator at −20 °C.

(*R*)-3-Hydroxy-2-methyl-2-phenylpropyl naphthalene-2-sulfonate (10)



10

According to **General procedure A** with **A-1** (49.9 mg, 0.30 mmol, 1.0 equiv.) and naphthalene-2-sulfonyl chloride (81.6 mg, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column

chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **10** as a white solid (77.2 mg, 72% yield, 91% e.e.).

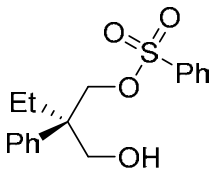
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 17.95 min, t_R (minor) = 20.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.36 (m, 1H), 7.96 – 7.91 (m, 3H), 7.76 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.72 – 7.60 (m, 2H), 7.33 – 7.13 (m, 5H), 4.29 (d, *J* = 9.6 Hz, 1H), 4.25 (d, *J* = 9.6 Hz, 1H), 3.78 (d, *J* = 11.3 Hz, 1H), 3.74 (d, *J* = 11.3 Hz, 1H), 1.79 (br s, 1H), 1.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 135.2, 132.3, 131.8, 129.8, 129.6, 129.4, 129.3, 128.6, 127.9, 127.8, 127.0, 126.3, 122.4, 74.3, 67.3, 43.8, 20.1.

HRMS (ESI) calcd for $C_{20}H_{20}NaO_4S$ $[M + Na]^+$ 379.0975, found: 379.0970.

(*R*)-2-(Hydroxymethyl)-2-phenylbutyl benzenesulfonate (11)



11

According to **General procedure A** with **A-S1** (54.1 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **11** as a colorless oil (88.2 mg, 92% yield, 93% e.e.).

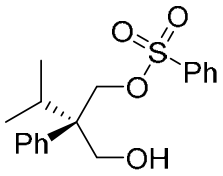
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 88/12, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 19.67 min, t_R (minor) = 21.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.18 – 7.12 (m, 2H), 4.38 (d, *J* = 9.5 Hz, 1H), 4.33 (d, *J* = 9.5 Hz, 1H), 3.88 (d, *J* = 11.3 Hz, 1H), 3.82 (d, *J* = 11.3 Hz, 1H), 1.77 – 1.66 (m, *J* = 7.2 Hz, 3H), 0.61 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 135.5, 133.8, 129.2, 128.6, 127.8, 126.8, 126.4, 71.6, 64.8, 47.0, 25.7, 7.4.

HRMS (ESI) calcd for $C_{17}H_{20}NaO_4S$ $[M + Na]^+$ 343.0975, found: 343.0971.

(*R*)-2-(Hydroxymethyl)-3-methyl-2-phenylbutyl benzenesulfonate (12)



12

According to **General procedure A** with **A-S2** (58.3 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **12** as a colorless oil (88.5 mg, 88% yield, 94% e.e.).

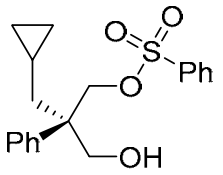
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 22.85 min, t_R (minor) = 25.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.83 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.15 – 7.13 (m, 2H), 4.57 (d, *J* = 9.6 Hz, 1H), 4.48 (d, *J* = 9.6 Hz, 1H), 4.06 (d, *J* = 11.5 Hz, 1H), 3.99 (d, *J* = 11.5 Hz, 1H), 2.07 – 2.00 (m, 2H), 0.76 (d, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.5, 133.8, 129.2, 128.2, 127.9, 127.1, 126.7, 70.7, 63.1, 49.4, 31.4, 17.8, 17.6.

HRMS (ESI) calcd for $C_{18}H_{22}NaO_4S$ $[M + Na]^+$ 357.1131, found: 357.1123.

(*R*)-3-Cyclopropyl-2-(hydroxymethyl)-2-phenylpropyl benzenesulfonate (13)



13

According to **General procedure A** with **A-S3** (61.9 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **13** as a white solid (92.5 mg, 89% yield, 96% e.e.).

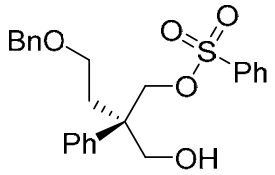
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 21.19 min, t_R (minor) = 23.90 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 4.47 (s, 2H), 4.03 – 3.84 (m, 2H), 1.72 – 1.55 (m, 3H), 0.39 – 0.23 (m, 3H), –0.01 – –0.10 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 135.6, 133.8, 129.3, 128.6, 127.9, 126.9, 126.5, 71.8, 65.1, 47.9, 38.6, 5.4, 4.6, 4.4.

HRMS (ESI) calcd for $C_{19}H_{22}NaO_4S$ $[M + Na]^+$ 369.1131, found: 369.1127.

(*R*)-4-(Benzyloxy)-2-(hydroxymethyl)-2-phenylbutyl benzenesulfonate (14)



14

According to **General procedure A** with **A-S4** (85.9 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **14** as a white solid (102.5 mg, 80% yield, 93% e.e.).

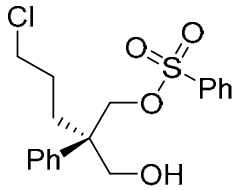
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 44.97 min, t_R (minor) = 40.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 2H), 7.61 (tt, *J* = 7.1, 1.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.19 (m, 8H), 7.16 – 7.14 (m, 2H), 4.40 – 4.33 (m, 2H), 4.32 (d, *J* = 9.6 Hz, 1H), 4.28 (d, *J* = 9.6 Hz, 1H), 3.91 (d, *J* = 11.8 Hz, 1H), 3.84 (d, *J* = 11.8 Hz, 1H), 3.47 – 3.39 (m, 1H), 3.39 – 3.31 (m, 1H), 2.51 (br s, 1H), 2.18 – 2.09 (m, 1H), 2.08 – 2.01 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 137.4, 135.5, 133.7, 129.1, 128.6, 128.4, 127.8, 127.8, 127.7, 126.9, 126.5, 73.5, 73.2, 66.2, 64.9, 46.4, 33.4.

HRMS (ESI) calcd for $C_{24}H_{26}NaO_5S$ $[M + Na]^+$ 449.1393, found: 449.1386.

(*R*)-5-Chloro-2-(hydroxymethyl)-2-phenylpentyl benzenesulfonate (15)



15

According to **General procedure A** with **A-S5** (68.6 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by

column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **15** as a colorless oil (74.2 mg, 67% yield, 89% e.e.).

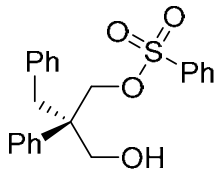
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 20.23 min, t_R (minor) = 25.96 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 4.38 (d, *J* = 9.6 Hz, 1H), 4.31 (d, *J* = 9.6 Hz, 1H), 3.91 (d, *J* = 11.3 Hz, 1H), 3.83 (d, *J* = 11.3 Hz, 1H), 3.39 (t, *J* = 6.4 Hz, 2H), 1.93 – 1.76 (m, 2H), 1.71 (br s, 1H), 1.52 – 1.39 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 135.5, 133.9, 129.3, 128.9, 127.9, 127.2, 126.3, 71.7, 64.9, 46.5, 45.1, 30.5, 26.4.

HRMS (ESI) calcd for $C_{18}H_{21}ClNaO_4S$ $[M + Na]^+$ 391.0741, found: 391.0736.

(*R*)-2-Benzyl-3-hydroxy-2-phenylpropyl benzenesulfonate (16)



16

According to **General procedure A** with **A-S6** (72.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **16** as a white solid (111.2 mg, 97% yield, 98% e.e.).

HPLC analysis: Chiralcel IA (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 17.96 min, t_R (minor) = 22.41 min.

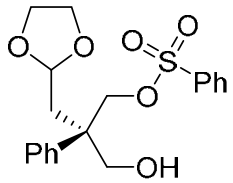
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.13 – 7.04 (m, 5H), 6.71 (d, *J* = 7.0 Hz, 2H), 4.35 (d, *J* = 9.5 Hz, 1H), 4.30 (d, *J* = 9.5 Hz, 1H), 3.88 (s, 2H), 2.96 (s, 2H), 1.71 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 135.6, 135.5, 133.9, 130.2, 129.3, 128.5, 127.9, 127.8, 127.0, 126.6, 126.5, 70.8, 63.9, 47.8, 39.9.

HRMS (ESI) calcd for $C_{22}H_{22}NaO_4S$ $[M + Na]^+$ 405.1131, found: 405.1126.

The structure of **16** was further confirmed by X-ray diffraction analysis (Supplementary Fig. 19).

(*R*)-2-((1,3-Dioxolan-2-yl)methyl)-3-hydroxy-2-phenylpropyl benzenesulfonate (17)



17

According to **General procedure A** with **A-S7** (71.5 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **17** as a white solid (93.2 mg, 82% yield, 93% e.e.).

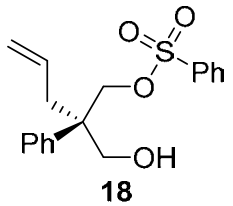
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 60/40, flow rate 1.0 mL/min, λ = 210 nm), t_R (major) = 12.90 min, t_R (minor) = 15.76 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.65 – 7.58 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.18 (m, 5H), 4.65 – 4.58 (m, 1H), 4.31 (s, 2H), 4.01 – 3.86 (m, 4H), 3.78 – 3.65 (m, 2H), 2.73 (t, *J* = 7.0 Hz, 1H), 2.25 (dd, *J* = 14.8, 3.7 Hz, 1H), 2.05 (dd, *J* = 14.8, 5.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 135.5, 133.6, 129.1, 128.6, 127.8, 127.0, 126.4, 101.7, 73.4, 64.8, 64.6, 64.5, 45.2, 37.4.

HRMS (ESI) calcd for $C_{19}H_{22}NaO_6S$ $[M + Na]^+$ 401.1029, found: 401.1024.

(*R*)-2-(Hydroxymethyl)-2-phenylpent-4-en-1-yl benzenesulfonate (18)



18

According to **General procedure A** with **A-S8** (57.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **18** as a colorless oil (87.6 mg, 88% yield, 95% e.e.).

HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), t_R (major) = 16.21 min, t_R (minor) = 13.84 min.

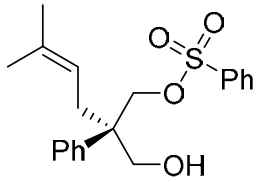
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.69 – 7.61 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.16 (m, 3H), 5.45 – 5.34 (m, 1H), 5.00 (dd, *J* = 17.1, 1.9 Hz, 1H),

4.96 – 4.87 (m, 1H), 4.37 (d, *J* = 9.5 Hz, 1H), 4.32 (d, *J* = 9.5 Hz, 1H), 3.88 (d, *J* = 11.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 2.48 (d, *J* = 7.5 Hz, 2H), 1.70 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.5, 133.8, 132.3, 129.2, 128.7, 127.9, 127.0, 126.5, 118.8, 71.7, 65.0, 46.6, 37.9.

HRMS (ESI) calcd for $C_{18}H_{20}NaO_4S$ $[M + Na]^+$ 355.0975, found: 355.0970.

(*R*)-2-(Hydroxymethyl)-5-methyl-2-phenylhex-4-en-1-yl benzenesulfonate (19)



19

According to **General procedure A** with **A-S9** (66.1 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **19** as a white solid (87.4 mg, 81% yield, 97% e.e.).

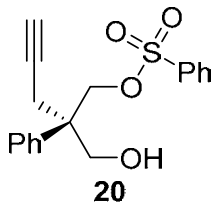
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 31.62 min, t_R (minor) = 29.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.21 – 7.17 (m, 2H), 4.73 (t, *J* = 7.3 Hz, 1H), 4.36 (d, *J* = 9.4 Hz, 1H), 4.31 (d, *J* = 9.4 Hz, 1H), 3.88 – 3.80 (m, 2H), 2.41 (d, *J* = 7.3 Hz, 2H), 1.62 (br s, 1H), 1.56 (s, 3H), 1.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 135.6, 135.3, 133.8, 129.2, 128.6, 127.9, 126.9, 126.6, 117.7, 71.9, 65.3, 47.2, 31.9, 25.9, 17.9.

HRMS (ESI) calcd for $C_{20}H_{24}NaO_4S$ $[M + Na]^+$ 383.1288, found: 383.1281.

(*R*)-2-(Hydroxymethyl)-2-phenylpent-4-yn-1-yl benzenesulfonate (20)



20

According to **General procedure A** with **A-S10** (57.1 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **20** as a colorless oil (93.4 mg, 94% yield, 95% e.e.).

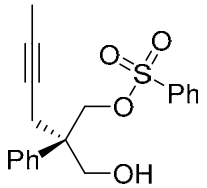
HPLC analysis: Chiralcel AZ3 (*n*-Hexane/*i*-PrOH = 70/30, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 21.55 min, t_R (minor) = 23.42 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 2H), 7.68 – 7.62 (m, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.25 (m, 5H), 4.44 (d, *J* = 9.6 Hz, 1H), 4.38 (d, *J* = 9.6 Hz, 1H), 3.89 (s, 2H), 2.70 (t, *J* = 2.3 Hz, 2H), 1.84 (t, *J* = 2.7 Hz, 1H), 1.79 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 135.3, 133.8, 129.2, 128.7, 128.0, 127.5, 126.5, 79.4, 71.8, 71.7, 65.6, 46.6, 23.2.

HRMS (ESI) calcd for $C_{18}H_{18}NaO_4S$ $[M + Na]^+$ 353.0818, found: 353.0813.

(*R*)-2-(Hydroxymethyl)-2-phenylhex-4-yn-1-yl benzenesulfonate (21)



21

According to **General procedure A** with **A-S11** (61.3 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **21** as a white solid (89.9 mg, 87% yield, 95% e.e.).

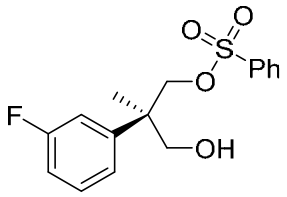
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 210 nm), t_R (major) = 32.38 min, t_R (minor) = 36.35 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.67 – 7.60 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.20 (m, 5H), 4.41 (d, *J* = 9.5 Hz, 1H), 4.37 (d, *J* = 9.5 Hz, 1H), 3.87 (d, *J* = 11.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H), 2.63 – 2.60 (m, 2H), 1.89 (br s, 1H), 1.60 (t, *J* = 2.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 135.4, 133.7, 129.1, 128.5, 127.9, 127.2, 126.6, 79.1, 74.0, 72.2, 65.8, 46.7, 23.5, 3.4.

HRMS (ESI) calcd for $C_{19}H_{21}O_4S$ $[M + H]^+$ 345.1155, found: 345.1153.

(*R*)-2-(3-Fluorophenyl)-3-hydroxy-2-methylpropyl benzenesulfonate (22)



22

According to **General procedure A** with **A-S12** (55.3 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **22** as a colorless oil (75.6 mg, 78% yield, 84% e.e.).

HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 21.12 min, t_R (minor) = 18.00 min.

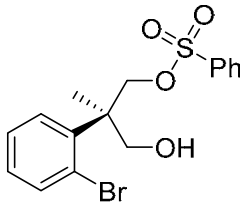
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.69 – 7.63 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.98 – 6.90 (m, 2H), 4.22 (d, *J* = 9.6 Hz, 1H), 4.21 (d, *J* = 10.0 Hz, 1H), 3.79 – 3.72 (m, 2H), 1.77 (br s, 1H), 1.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 244.2 Hz), 144.1 (d, *J* = 6.7 Hz), 135.5, 133.9, 130.0 (d, *J* = 8.3 Hz), 129.3, 127.8, 122.0 (d, *J* = 2.9 Hz), 114.0 (d, *J* = 20.8 Hz), 113.7 (d, *J* = 22.3 Hz), 73.8, 67.1, 43.9 (d, *J* = 1.7 Hz), 20.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –112.2.

HRMS (ESI) calcd for $C_{16}H_{17}FNaO_4S$ $[M + Na]^+$ 347.0724, found: 347.0720.

(*R*)-2-(2-Bromophenyl)-3-hydroxy-2-methylpropyl benzenesulfonate (23)



23

According to **General procedure A** with **A-S13** (73.5 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **23** as a colorless oil (86.6 mg, 75% yield, 88% e.e.).

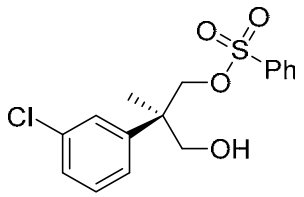
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 17.15 min, t_R (minor) = 13.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.46 (m, 3H), 7.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.08 (td, *J* = 7.8, 1.7 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 1H), 4.54 (d, *J* = 9.7 Hz, 1H), 4.09 (d, *J* = 11.4 Hz, 1H), 4.05 (d, *J* = 11.4 Hz, 1H), 1.84 (br s, 1H), 1.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 136.0, 135.6, 133.8, 130.4, 129.2, 128.8, 127.9, 127.7, 122.0, 72.1, 65.3, 45.7, 19.3.

HRMS (ESI) calcd for $C_{16}H_{17}BrNaO_4S$ $[M + Na]^+$ 406.9923, found: 406.9919.

(*R*)-2-(3-Chlorophenyl)-3-hydroxy-2-methylpropyl benzenesulfonate (24)



24

According to **General procedure A** with **A-S14** (60.2 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **24** as a white solid (81.6 mg, 80% yield, 85% e.e.).

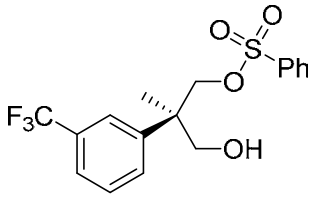
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 20.61 min, t_R (minor) = 16.36 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.69 – 7.63 (m, 1H), 7.564 – 7.52 (m, 2H), 7.25 – 7.19 (m, 3H), 7.18 – 7.15 (m, 1H), 4.22 (d, *J* = 9.6 Hz, 1H), 4.20 (d, *J* = 9.6 Hz, 1H), 3.80 – 3.72 (m, 2H), 1.78 (br s, 1H), 1.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 135.5, 134.5, 133.9, 129.8, 129.3, 127.8, 127.3, 126.8, 124.6, 73.8, 67.1, 43.9, 20.1.

HRMS (ESI) calcd for $C_{16}H_{17}ClNaO_4S$ $[M + Na]^+$ 363.0428, found: 363.0424.

(*R*)-3-Hydroxy-2-methyl-2-(3-(trifluoromethyl)phenyl)propyl benzenesulfonate (25)



25

According to **General procedure A** with **A-S15** (70.3 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **25** as a white solid (61.7 mg, 55% yield, 84% e.e.).

HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 37.21 min, t_R (minor) = 40.29 min.

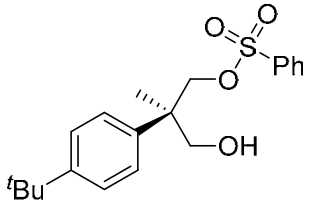
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.45 (m, 5H), 7.41 (t, *J* = 7.9 Hz, 1H), 4.26 (d, *J* = 9.6 Hz, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 3.80 (d, *J* = 11.3 Hz, 1H), 3.76 (d, *J* = 11.3 Hz, 1H), 2.07 (br s, 1H), 1.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 135.3, 133.9, 130.8 (q, *J* = 31.9 Hz), 130.0 (q, *J* = 1.0 Hz), 129.3, 129.0, 127.7, 124.0 (q, *J* = 270.7 Hz), 123.9 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 3.8 Hz), 73.7, 66.9, 43.9, 20.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.5.

HRMS (ESI) calcd for $C_{17}H_{17}F_3NaO_4S$ $[M + Na]^+$ 397.0692, found: 397.0688.

(*R*)-2-(4-(*tert*-Butyl)phenyl)-3-hydroxy-2-methylpropyl benzenesulfonate (26)



26

According to **General procedure A** with **A-S16** (66.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **26** as a white solid (80.2 mg, 74% yield, 94% e.e.).

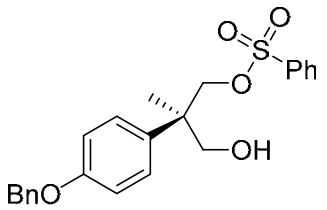
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.3 mL/min, λ = 214 nm), t_R (major) = 41.91 min, t_R (minor) = 29.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 4.26 (d, *J* = 9.6 Hz, 1H), 4.20 (d, *J* = 9.6 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 3.74 (d, *J* = 11.2 Hz, 1H), 1.65 (br s, 2H), 1.32 (s, 3H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 138.0, 135.6, 133.8, 129.2, 127.9, 126.0, 125.6, 74.3, 67.4, 43.4, 34.3, 31.2, 20.1.

HRMS (ESI) calcd for $C_{20}H_{26}NaO_4S$ $[M + Na]^+$ 385.1444, found: 385.1440.

(*R*)-2-(4-(Benzyloxy)phenyl)-3-hydroxy-2-methylpropyl benzenesulfonate (27)



27

According to **General procedure A** with **A-S17** (81.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **27** as a white solid (95.2 mg, 77% yield, 92% e.e.).

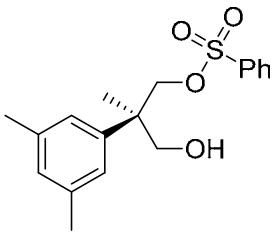
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 60.00 min, t_R (minor) = 46.09 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.42 – 7.30 (m, 5H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.03 (s, 2H), 4.21 (d, *J* = 9.6 Hz, 1H), 4.16 (d, *J* = 9.6 Hz, 1H), 3.73 (d, *J* = 11.2 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 1.98 (br s, 1H), 1.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 136.8, 135.6, 133.8, 133.3, 129.2, 128.6, 128.0, 127.8, 127.5, 127.4, 114.8, 74.4, 69.9, 67.4, 43.2, 20.1.

HRMS (ESI) calcd for $C_{23}H_{24}NaO_5S$ $[M + Na]^+$ 435.1237, found: 435.1232.

(*R*)-2-(3,5-Dimethylphenyl)-3-hydroxy-2-methylpropyl benzenesulfonate (28)



28

According to **General procedure A** with **A-S18** (58.3 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **28** as a colorless oil (86.5 mg, 86% yield, 94% e.e.).

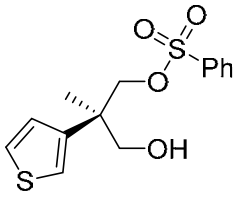
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.4 mL/min, λ = 214 nm), t_R (major) = 23.05 min, t_R (minor) = 24.65 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.67 – 7.60 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 6.86 (s, 1H), 6.83 (s, 2H), 4.26 (d, *J* = 9.5 Hz, 1H), 4.19 (d, *J* = 9.5 Hz, 1H), 3.74 (d, *J* = 11.2 Hz, 1H), 3.71 (d, *J* = 11.2 Hz, 1H), 2.26 (s, 6H), 1.83 (br s, 1H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.0, 135.6, 133.7, 129.1, 128.7, 127.8, 124.0, 74.4, 67.4, 43.6, 21.4, 20.1.

HRMS (ESI) calcd for $C_{18}H_{22}NaO_4S$ $[M + Na]^+$ 357.1131, found: 357.1129.

(*R*)-3-Hydroxy-2-methyl-2-(thiophen-3-yl)propyl benzenesulfonate (29)



29

According to **General procedure A** with **A-S19** (51.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **29** as a colorless oil (67.5 mg, 72% yield, 91% e.e.).

HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 29.07 min, t_R (minor) = 22.64 min.

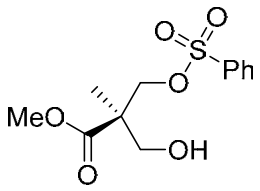
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.69 – 7.62 (m, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.28 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.08 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.01 (dd, *J* = 5.1, 1.4 Hz, 1H), 4.21

(d, *J* = 9.6 Hz, 1H), 4.14 (d, *J* = 9.6 Hz, 1H), 3.73 (d, *J* = 11.2 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 1.86 (br s, 1H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 135.6, 133.8, 129.3, 127.8, 126.0, 125.9, 121.3, 73.9, 67.1, 42.6, 20.2.

HRMS (ESI) calcd for $C_{14}H_{16}NaO_4S_2$ $[M + Na]^+$ 335.0382, found: 335.0378.

Methyl (*R*)-3-hydroxy-2-methyl-2-(((phenylsulfonyl)oxy)methyl)propanoate (30)



30

According to **General procedure A** with **A-S20** (44.4 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **30** as a colorless oil (36.5 mg, 42% yield, 79% e.e.).

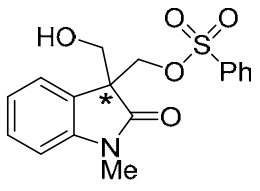
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 216 nm), t_R (major) = 17.95 min, t_R (minor) = 20.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 4.29 (d, *J* = 9.8 Hz, 1H), 4.13 (d, *J* = 9.8 Hz, 1H), 3.71 (s, 2H), 3.67 (s, 3H), 2.24 (br s, 1H), 1.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 135.5, 134.0, 129.3, 127.9, 70.9, 64.3, 52.4, 48.3, 17.2.

HRMS (ESI) calcd for $C_{12}H_{17}O_6S$ $[M + H]^+$ 289.0740, found: 289.0741.

(*S*)-(3-(Hydroxymethyl)-1-methyl-2-oxoindolin-3-yl)methyl benzenesulfonate (31)



31

According to **General procedure A** with **A-S21** (62.2 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by

column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **31** as a colorless oil (88.5 mg, 85% yield, 85% e.e.).

$[\alpha]_D^{20}$ = +43.8 (*c* 0.5, $CHCl_3$).

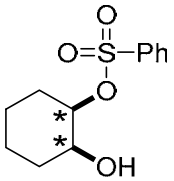
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 60/40, flow rate 0.5 mL/min, λ = 210 nm), t_R (major) = 24.49 min, t_R (minor) = 28.34 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.64 (tt, *J* = 7.0, 1.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.34 (td, *J* = 7.8, 1.2 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.05 (td, *J* = 7.6, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.51 (d, *J* = 9.6 Hz, 1H), 4.33 (d, *J* = 9.6 Hz, 1H), 3.88 – 3.83 (m, 1H), 3.73 (d, *J* = 11.3 Hz, 1H), 3.18 (s, 3H), 2.67 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 143.8, 135.2, 133.9, 129.2, 129.2, 127.9, 126.4, 124.0, 123.1, 108.6, 69.8, 63.8, 53.3, 26.3.

HRMS (ESI) calcd for $C_{17}H_{18}NO_5S$ $[M + H]^+$ 348.0900, found: 348.0898.

(1*R*,2*S*)-2-Hydroxycyclohexyl benzenesulfonate (32)



32

According to **General procedure A** with **A-S22** (34.8 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **32** as a colorless oil (74.5 mg, 97% yield, 95% e.e.).

$[\alpha]_D^{20}$ = +13.5 (*c* 1.0, $CHCl_3$).

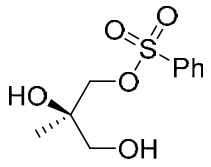
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), t_R (major) = 34.66 min, t_R (minor) = 20.08 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.87 (m, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 2H), 4.68 – 4.65 (m, 1H), 3.85 – 3.82 (m, 1H), 2.06 (br s, 1H), 1.96 – 1.88 (m, 1H), 1.82 – 1.70 (m, 1H), 1.68 – 1.46 (m, 4H), 1.36 – 1.24 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 133.7, 129.2, 127.6, 83.4, 68.9, 30.2, 27.7, 21.7, 20.7.

HRMS (ESI) calcd for $C_{12}H_{16}NO_4S$ $[M + Na]^+$ 279.0662, found: 279.0662.

(*R*)-2,3-Dihydroxy-2-methylpropyl benzenesulfonate (47)



47

According to **General procedure A** with **A-S34** (31.8 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 24 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **47** as light yellow oil (51 mg, 69% yield, 97% e.e.).

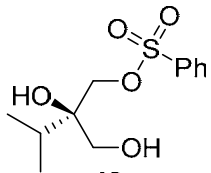
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 216 nm), t_R (major) = 43.63 min, t_R (minor) = 48.05 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 4.00 (d, *J* = 9.9 Hz, 1H), 3.93 (d, *J* = 9.9 Hz, 1H), 3.58 (d, *J* = 11.4 Hz, 1H), 3.46 (d, *J* = 11.4 Hz, 1H), 1.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.1, 129.4, 127.9, 73.2, 71.6, 66.3, 20.9.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NaO_5S$ $[M + Na]^+$ 247.0635, found 247.0632.

(*R*)-2-Hydroxy-2-(hydroxymethyl)-3-methylbutyl benzenesulfonate (48)



48

According to **General procedure A** with **A-S35** (40.3 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 10 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **48** as a colorless oil (54.3 mg, 66% yield, 91% e.e.).

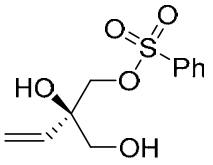
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 45.13 min, t_R (major) = 55.98 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.73 – 7.66 (m, 1H), 7.63 – 7.50 (m, 2H), 4.20 – 3.96 (m, 2H), 3.68 – 3.54 (m, 2H), 1.96 – 1.82 (m, 1H), 0.90 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.1, 129.4, 127.9, 74.7, 70.8, 63.3, 31.4, 16.55, 16.48.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NaO_5S$ $[M + Na]^+$ 297.0767, found 297.0765.

(*R*)-2-Hydroxy-2-(hydroxymethyl)but-3-en-1-yl benzenesulfonate (49)



49

According to **General procedure A** with **A-S36** (35.4 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 14 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **49** as a white solid (51.1 mg, 66% yield, 97% e.e.).

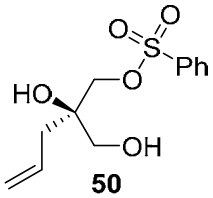
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 19.70 min, t_R (major) = 26.14 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 5.80 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 4.06 (s, 2H), 3.71 – 3.59 (m, 1H), 3.53 (d, *J* = 11.4 Hz, 1H), 2.79 (s, 1H), 2.25 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.4, 134.1, 129.4, 128.0, 117.7, 74.3, 72.2, 65.6.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}NaO_5S$ $[M + Na]^+$ 281.0454, found 281.0451.

(*R*)-2-Hydroxy-2-(hydroxymethyl)pent-4-en-1-yl benzenesulfonate (50)



50

According to **General procedure A** with **A-S37** (39.6 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 14 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **50** as a yellow oil (60.5 mg, 74% yield, 94% e.e.).

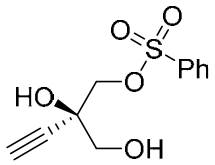
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 16.90 min, t_R (major) = 23.02 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 5.88 – 5.62 (m, 1H), 5.21 – 4.97 (m, 2H), 4.12 – 3.83 (m, 2H), 3.58 (d, *J* = 11.5 Hz, 1H), 3.49 (d, *J* = 11.5 Hz, 1H), 2.98 – 2.34 (m, 2H), 2.27 (d, *J* = 7.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.1, 131.4, 129.4, 128.0, 120.0, 72.9, 71.3, 64.9, 38.4.

HRMS (ESI) *m/z* calcd. for $C_{12}H_{16}NaO_5S$ $[M + Na]^+$ 295.0611, found 295.0607.

(*R*)-2-Hydroxy-2-(hydroxymethyl)but-3-yn-1-yl benzenesulfonate (51)



51

According to **General procedure A** with **A-S38** (34.8 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 14 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **51** as a white solid (55.4 mg, 72% yield, 99% e.e.).

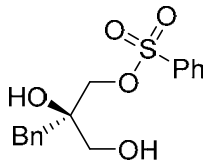
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 71.90 min, t_R (major) = 74.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.84 (m, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 4.22 – 4.05 (m, 2H), 3.71 (d, *J* = 5.5 Hz, 2H), 3.21 (s, 1H), 2.51 (s, 1H), 2.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.2, 129.4, 128.1, 80.8, 75.5, 71.7, 69.6, 65.9.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}NaO_5$ $[M + Na]^+$ 279.0298, found 279.0294.

(*R*)-2-benzyl-2,3-dihydroxypropyl benzenesulfonate (52)



52

According to **General procedure A** with **A-S39** (54.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 7 h, the reaction mixture was

purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **52** as a light yellow solid (66.7 mg, 69% yield, 95% e.e.).

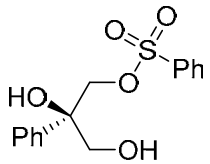
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 39.84 min, t_R (major) = 41.20 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.07 (m, 5H), 3.94 (d, *J* = 9.8 Hz, 1H), 3.83 (d, *J* = 9.8 Hz, 1H), 3.56 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.46 (dd, *J* = 11.6, 4.3 Hz, 1H), 2.80 (s, 2H), 2.63 (s, 1H), 2.44 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 135.0, 134.2, 130.5, 129.4, 128.5, 128.0, 127.0, 73.4, 70.6, 64.6, 39.7.

HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NaO_5S$ $[M + Na]^+$ 345.0767, found 345.0765.

(*R*)-2,3-Dihydroxy-2-phenylpropyl benzenesulfonate (53)



53

According to **General procedure A** with **A-S40** (50.5 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 8 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **53** as a light yellow solid (50 mg, 54% yield, 94% e.e.) along with an epoxide side product.

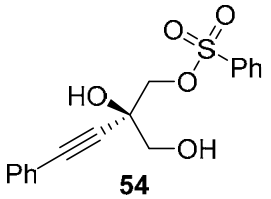
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 33.31 min, t_R (major) = 49.66 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.24 (m, 6H), 4.36 – 4.25 (m, 2H), 3.91 – 3.80 (m, 1H), 3.73 (d, *J* = 11.7 Hz, 1H), 3.35 (s, 1H), 2.48 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.3, 134.1, 129.4, 128.6, 128.1, 127.9, 125.5, 75.4, 73.4, 66.8.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}NaO_5S$ $[M + Na]^+$ 331.0611, found 331.0604.

(*R*)-2-Hydroxy-2-(hydroxymethyl)-4-phenylbut-3-yn-1-yl benzenesulfonate (54)



54

According to **General procedure A** with **A-S41** (57.7 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 7 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **54** as a white solid (79.8 mg, 80% yield, 99% e.e.).

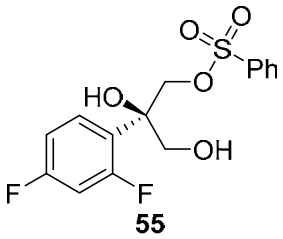
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 25.12 min, t_R (major) = 33.78 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.69 – 7.60 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.43 – 7.28 (m, 5H), 4.24 (d, *J* = 2.2 Hz, 2H), 3.90 – 3.70 (m, 2H), 3.04 (s, 1H), 2.33 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.1, 132.0, 129.4, 129.1, 128.4, 128.0, 121.4, 87.3, 85.5, 72.0, 70.2, 66.1.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}NaO_5S$ $[M + Na]^+$ 355.0611, found 355.0611.

(*R*)-2-(2,4-Difluorophenyl)-2,3-dihydroxypropyl benzenesulfonate (55)



55

According to **General procedure A** with **A-S42** (61.2 mg, 0.30 mmol, 1.0 equiv.) and benzenesulfonyl chloride (46.1 μL, 0.36 mmol, 1.2 equiv.) for 24 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **55** as a white solid (65.0 mg, 63% yield, 95% e.e.) along with an epoxide side product.

HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 214 nm), t_R (minor) = 17.95 min, t_R (major) = 16.09 min.

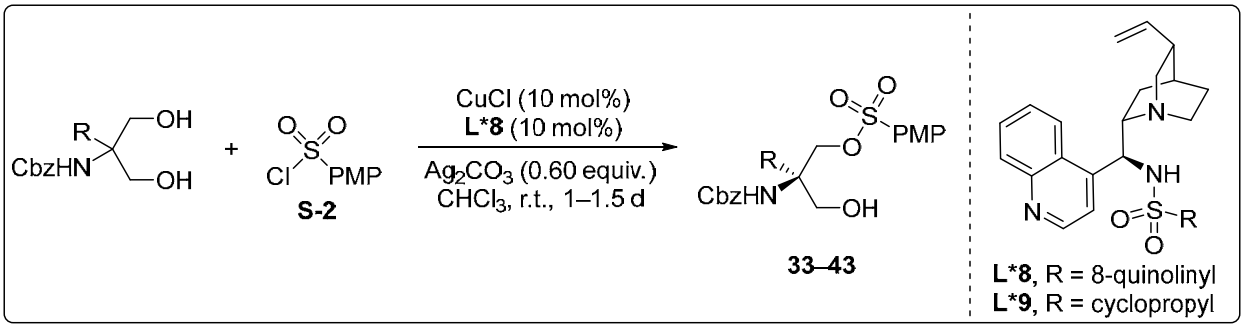
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.68 – 7.57 (m, 2H), 7.54 – 7.50 (m, 2H), 6.91 – 6.86 (m, 1H), 6.71 – 6.65 (m, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 10.9 Hz, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 3.74 – 3.72 (m, 2H), 2.53 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (dd, *J* = 249.9, 12.3 Hz), 159.1 (dd, *J* = 247.7, 11.8 Hz), 130.1 (dd, *J* = 9.5, 5.9 Hz), 122.2 (dd, *J* = 13.0, 3.9 Hz), 111.6 (dd, *J* = 20.7, 3.4 Hz), 104.2 (dd, *J* = 27.6, 25.4 Hz), 75.0 (d, *J* = 5.0 Hz), 73.0 (d, *J* = 5.7 Hz), 65.6 (d, *J* = 5.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ −109.3 (d, *J* = 8.1 Hz), −110.3 (d, *J* = 8.1 Hz).

HRMS (ESI) *m/z* calcd. for $C_{15}H_{14}ClF_2O_5S$ $[M + Cl]^-$ 379.0224, found 379.0218.

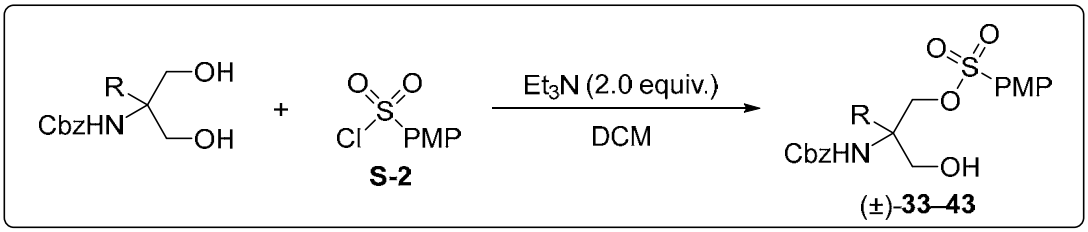
Cu-catalyzed enantioselective radical S–O cross-coupling of 2-amino 1,3-diols



General procedure B:

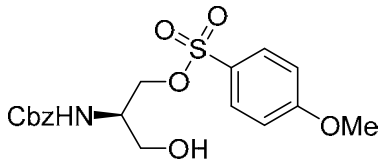
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuCl (2.0 mg, 0.020 mmol, 10 mol%), **L*8** (9.7 mg, 0.020 mmol, 10 mol%), Ag_2CO_3 (33.0 mg, 0.12 mmol, 0.60 equiv.), diol (0.20 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then 4-methoxybenzenesulfonyl chloride (49.5 mg, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at r.t. Upon completion (monitored by TLC), the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on basic aluminum oxide to afford the desired product.

Note: Most of the products were unstable in neat state at r.t. after purification and should be stored in refrigerator at −20 °C.



To a solution of diol (0.10 mmol, 1.0 equiv.) and Et_3N (27.7 µL, 0.20 mmol, 2.0 equiv.) in dry DCM (1.0 mL) was added 4-methoxybenzenesulfonyl chloride (22.7 mg, 0.11 mmol, 1.1 equiv.). After stirring for 24 h at r.t., saturated NH_4Cl (aq.) was added to the above reaction solution to quench the reaction. Then, the mixture was extracted with DCM (3x) and the combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography on basic aluminum oxide to afford the desired racemate.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxypropyl 4-methoxybenzene-sulfonate (33)



33

According to **General procedure B** with **A-S23** (67.6 mg, 0.30 mmol, 1.0 equiv.) and additional proton sponge (5 mol%), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 80/1) to yield product **33** as a colorless oil (41.0 mg, 67% yield, 87% e.e.).

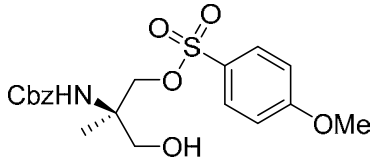
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 43.69 min, t_R (major) = 49.07 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.29 (m, 5H), 6.99 (d, *J* = 8.6 Hz, 2H), 5.30 (s, 1H), 5.05 (s, 2H), 4.16 – 4.08 (m, 2H), 3.94 – 3.87 (m, 1H), 3.86 (s, 3H), 3.79 – 3.75 (m, 1H), 3.64 (dd, *J* = 11.5, 5.3 Hz, 1H), 2.24 – 2.20 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 136.1, 130.2, 128.6, 128.3, 128.1, 126.6, 114.6, 67.9, 67.1, 60.9, 55.8, 51.3.

HRMS (ESI) *m/z* calcd. for $C_{18}H_{22}NO_7S$ $[M + H]^+$ 396.1111, found 396.1103.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxy-2-methylpropyl 4-methoxy-benzenesulfonate (34)



34

According to **General procedure B** with **A-S24** (71.8 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to yield product **34** as a colorless oil (66.0 mg, 81% yield, 95% e.e.).

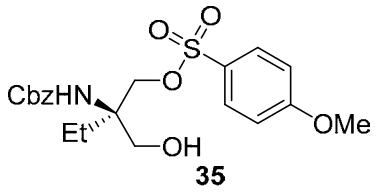
HPLC analysis: Chiralcel IB (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 32.56 min, t_R (major) = 35.70 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.30 (m, 5H), 6.99 (d, *J* = 8.9 Hz, 2H), 5.16 (s, 1H), 5.04 – 4.97 (m, 2H), 4.23 (d, *J* = 10.0 Hz, 1H), 4.08 (d, *J* = 10.0 Hz, 1H), 3.87 (s, 3H), 3.69 – 3.61 (m, 2H), 2.74 (s, 1H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.7, 136.0, 130.2, 128.6, 128.3, 128.0, 126.8, 114.6, 71.0, 66.8, 66.6, 56.3, 55.7, 19.8.

HRMS (ESI) *m/z* calcd. for $C_{19}H_{24}NO_7S$ $[M + H]^+$ 410.1268, found 410.1257.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)butyl 4-methoxybenzene-sulfonate (35)



35

According to **General procedure B** with **A-S25** (76.0 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to yield product **35** as a colorless oil (50.5 mg, 60% yield, 94% e.e.).

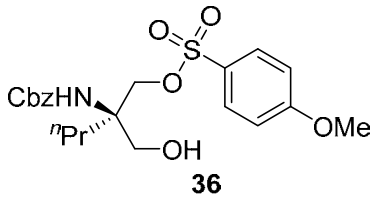
HPLC analysis: Chiralcel IB (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 31.03 min, t_R (major) = 35.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.31 (m, 5H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.05 – 4.98 (m, 3H), 4.20 (d, *J* = 10.1 Hz, 1H), 4.12 (d, *J* = 10.1 Hz, 1H), 3.87 (s, 3H), 3.74 – 3.64 (m, 2H), 3.45 (s, 1H), 1.78 (dq, *J* = 15.0, 7.6 Hz, 1H), 1.56 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.83 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 155.9, 136.0, 130.2, 128.6, 128.3, 128.0, 126.7, 114.6, 70.1, 66.9, 64.6, 58.9, 55.7, 25.6, 7.3.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}NO_7S$ $[M + H]^+$ 424.1424, found 424.1415.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)pentyl 4-methoxy-benzenesulfonate (36)



36

According to **General procedure B** with **A-S26** (80.2 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 120/1) to yield product **36** as a colorless oil (70.1 mg, 80% yield, 95% e.e.).

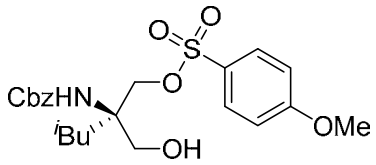
HPLC analysis: Chiralcel IB (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 27.82 min, t_R (major) = 30.50 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.9 Hz, 2H), 7.39 – 7.32 (m, 5H), 6.99 (d, *J* = 8.9 Hz, 2H), 5.04 – 4.98 (m, 3H), 4.20 (d, *J* = 10.1 Hz, 1H), 4.10 (d, *J* = 10.1 Hz, 1H), 3.87 (s, 3H), 3.74 (dd, *J* = 11.8, 4.6 Hz, 1H), 3.66 (dd, *J* = 12.2, 6.8 Hz, 1H), 3.49 (s, 1H), 1.72 – 1.64 (m, 1H), 1.48 (ddd, *J* = 13.9, 11.5, 5.4 Hz, 1H), 1.27 – 1.19 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.9, 136.0, 130.2, 128.6, 128.3, 128.0, 126.7, 114.6, 70.4, 66.9, 64.9, 58.8, 55.7, 35.2, 16.2, 14.3.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{28}NO_7S$ $[M + H]^+$ 438.1581, found 438.1574.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)-4-methylpentyl 4-methoxybenzenesulfonate (37)



37

According to **General procedure B** with **A-S27** (84.4 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 160/1) to yield product **37** as a colorless oil (48.8 mg, 54% yield, 97% e.e.).

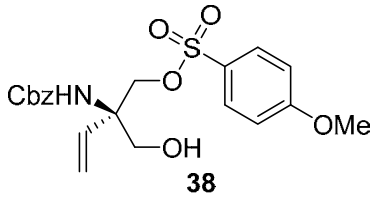
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 45.54 min, t_R (major) = 48.93 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.39 – 7.30 (m, 5H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.03 (s, 1H), 5.01 (s, 2H), 4.19 (d, *J* = 9.9 Hz, 1H), 4.12 (d, *J* = 9.9 Hz, 1H), 3.87 (s, 3H), 3.80 (dd, *J* = 12.5, 4.9 Hz, 1H), 3.67 (dd, *J* = 12.0, 6.8 Hz, 1H), 3.43 (s, 1H), 1.72 – 1.64 (m, 3H), 0.90 (dd, *J* = 6.3, 3.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.7, 136.1, 130.2, 128.6, 128.2, 128.0, 126.7, 114.6, 70.8, 66.85, 64.7, 59.1, 55.7, 40.9, 24.8, 24.2, 23.3.

HRMS (ESI) *m/z* calcd. for $C_{22}H_{30}NO_7S$ $[M + H]^+$ 452.1737, found 452.1728.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)but-3-en-1-yl 4-methoxybenzenesulfonate (38)



38

According to **General procedure B** with **A-S29** (75.4 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 120/1) to yield product **38** as a colorless oil (43.8 mg, 52% yield, 95% e.e.).

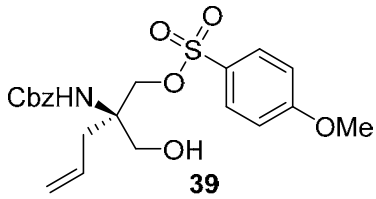
HPLC analysis: Chiralcel IB (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 35.74 min, t_R (major) = 37.84 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.39 – 7.31 (m, 5H), 6.98 (d, *J* = 9.0 Hz, 2H), 5.78 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.35 (s, 1H), 5.30 – 5.22 (m, 2H), 5.02 (s, 2H), 4.30 (d, *J* = 10.1 Hz, 1H), 4.20 (d, *J* = 10.0 Hz, 1H), 3.87 (s, 3H), 3.75 – 3.67 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.7, 135.9, 135.2, 130.2, 128.6, 128.3, 128.0, 126.6, 117.4, 114.6, 70.2, 67.0, 65.4, 60.5, 55.7.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}NO_7S$ $[M + H]^+$ 422.1268, found 422.1259.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)pent-4-en-1-yl 4-methoxybenzenesulfonate (39)



39

According to **General procedure B** with **A-S29** (79.6 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 120/1) to yield product **39** as a colorless oil (56.6 mg, 65% yield, 95% e.e.).

HPLC analysis: Chiralcel IB (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (minor) = 29.85 min, t_R (major) = 32.45 min.

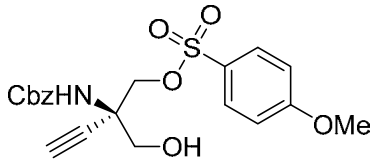
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.32 (m, 5H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.69 (ddt, *J* = 17.3, 10.3, 7.5 Hz, 1H), 5.15 – 5.08 (m, 3H), 5.01 (s, 2H), 4.16 (q, *J* = 10.1 Hz,

2H), 3.88 (s, 3H), 3.70 (d, *J* = 6.1 Hz, 2H), 3.43 (s, 1H), 2.54 (dd, *J* = 14.1, 6.9 Hz, 1H), 2.27 (dd, *J* = 14.1, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.8, 135.9, 131.2, 130.2, 128.6, 128.3, 128.0, 126.7, 120.6, 114.6, 69.7, 67.0, 64.9, 58.2, 55.7, 37.1.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{26}NO_7S$ $[M + H]^+$ 436.1424, found 436.1414.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)but-3-yn-1-yl 4-methoxybenzenesulfonate (40)



40

According to **General procedure B** with **A-S30** (74.8 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 120/1) to yield product **40** as a colorless oil (39.4 mg, 47% yield, 95% e.e.).

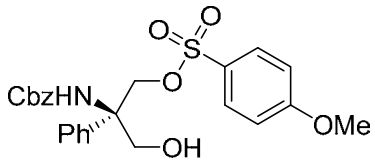
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 39.44 min, t_R (major) = 43.33 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.38 – 7.30 (m, 5H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.46 (s, 1H), 5.04 (s, 2H), 4.32 (d, *J* = 1.8 Hz, 2H), 3.92 – 3.87 (m, 1H), 3.86 (s, 3H), 3.82 (dd, *J* = 11.7, 6.8 Hz, 1H), 2.94 (s, 1H), 2.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 154.9, 135.8, 130.3, 128.6, 128.3, 128.1, 126.5, 114.6, 79.2, 74.6, 69.0, 67.1, 65.2, 55.7, 55.0.

HRMS (ESI) *m/z* calcd. for $C_{20}H_{22}NO_7S$ $[M + H]^+$ 420.1111, found 420.1103.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxy-2-phenylpropyl 4-methoxybenzenesulfonate (41)



41

According to **General procedure B** with **A-S31** (90.4 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to yield product **41** as a colorless oil (80.8 mg, 86% yield, 95% e.e.).

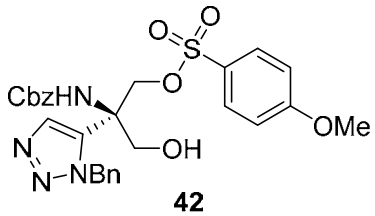
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 230 nm), t_R (minor) = 48.63 min, t_R (major) = 51.86 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H), 7.41 – 7.33 (m, 5H), 7.30 – 7.28 (m, 2H), 7.26 – 7.24 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.69 (s, 1H), 5.03 (s, 2H), 4.59 (d, *J* = 10.2 Hz, 1H), 4.50 (d, *J* = 10.3 Hz, 1H), 3.97 (d, *J* = 12.4 Hz, 1H), 3.87 – 3.84 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.8, 138.3, 136.0, 130.3, 128.8, 128.6, 128.3, 128.1, 128.0, 126.4, 125.8, 114.6, 70.7, 67.3, 67.0, 62.4, 55.7.

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}NO_7S$ $[M + H]^+$ 472.1424, found 472.1417.

(*R*)-2-(1-Benzyl-1H-1,2,3-triazol-5-yl)-2-(((benzyloxy)carbonyl)amino)-3-hydroxy-propyl 4-methoxybenzenesulfonate (42)



42

According to **General procedure B** with **A-S32** (114.7 mg, 0.30 mmol, 1.0 equiv.) and **L*9** (10 mol%) instead of **L*8** (10 mol%), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to yield product **42** as a colorless oil (79.8 mg, 72% yield, 86% e.e.).

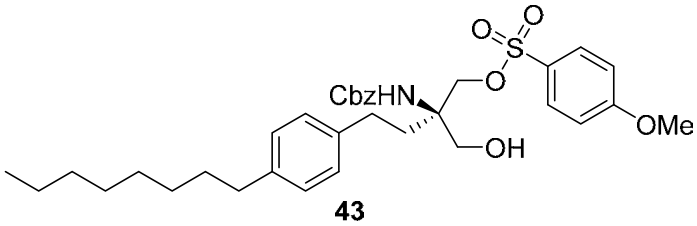
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 214 nm), t_R (minor) = 24.07 min, t_R (major) = 28.90 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.0 Hz, 2H), 7.54 (s, 1H), 7.39 – 7.35 (m, 3H), 7.34 – 7.31 (m, 3H), 7.29 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.94 (s, 1H), 5.51 – 5.42 (m, 2H), 5.00 – 4.93 (m, 2H), 4.53 (d, *J* = 10.0 Hz, 1H), 4.47 (d, *J* = 10.0 Hz, 1H), 4.10 – 4.07 (m, 1H), 3.99 (dd, *J* = 11.7, 7.6 Hz, 1H), 3.85 (s, 3H), 3.72 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 155.3, 146.4, 135.9, 134.2, 130.2, 129.2, 128.9, 128.6, 128.2, 128.0, 127.9, 126.6, 122.7, 114.5, 69.3, 66.9, 65.7, 57.2, 55.7, 54.3.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{29}N_4O_7S$ $[M + H]^+$ 553.1751, found 553.1739.

(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)-4-(4-octylphenyl)butyl 4-methoxybenzenesulfonate (43)



43

According to **General procedure B** with **A-S33** (132.5 mg, 0.30 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to yield product **43** as a colorless oil (70.9 mg, 58% yield, 95% e.e.).

HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 230 nm), t_R (major) = 48.42 min, t_R (minor) = 54.09 min.

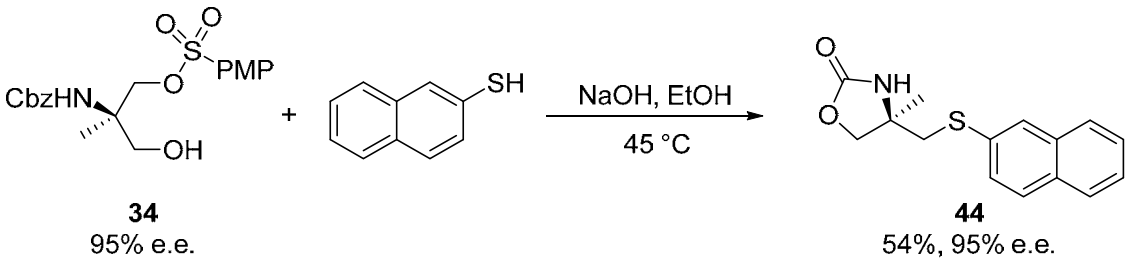
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.31 (m, 5H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.99 (dd, *J* = 10.5, 7.7 Hz, 4H), 5.08 (s, 1H), 5.02 (s, 2H), 4.22 – 4.15 (m, 2H), 3.87 (s, 3H), 3.76 (q, *J* = 12.0 Hz, 2H), 2.56 – 2.46 (m, 4H), 2.07 – 2.02 (m, 1H), 1.81 (ddd, *J* = 14.1, 11.5, 5.7 Hz, 1H), 1.57 (t, *J* = 7.5 Hz, 2H), 1.30 – 1.25 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.7, 140.8, 138.1, 136.0, 130.2, 128.6, 128.5, 128.3, 128.1, 128.0, 126.6, 114.6, 70.2, 66.9, 64.5, 58.7, 55.7, 35.5, 34.5, 31.9, 31.6, 29.5, 29.4, 29.3, 28.8, 22.7, 14.1.

HRMS (ESI) *m/z* calcd. for $C_{34}H_{46}NO_7S$ $[M + H]^+$ 612.2989, found 612.2976.

Synthetic transformations

a) Diversification of 1,2-aminoalcohols

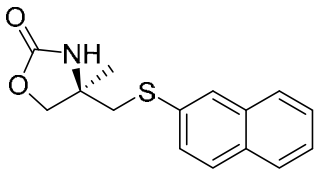


34
95% e.e.

44
54%, 95% e.e.

A 10 mL resealable Schlenk tube equipped with a magnetic stir bar was charged with naphthalene-2-thiol (64.0 mg, 0.40 mmol, 2.0 equiv.), NaOH (16.0 mg, 0.40 mmol, 2.0 equiv.), and EtOH **(**4.0 mL). The Schlenk tube was sealed and heated to 45 °C for 0.5 h under stirring before **34** (81.9 mg, 0.20 mmol, 1.0 equiv.) was added into the mixture. The reaction was stirred at the same temperature for another 16 h. The tube was allowed to cool to r.t. The solvent was then removed *in vacuo* and the residue was purified with flash column chromatography (CH_2Cl_2/MeOH = 120/1 ~ 50/1) to give product **44** as a white solid (29.5 mg, 54% yield, 95% e.e.).

(*R*)-4-Methyl-4-((naphthalen-2-ylthio)methyl)oxazolidin-2-one (44)



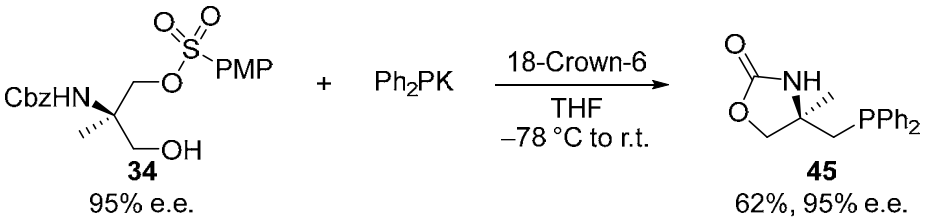
44

HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 27.54 min, t_R (minor) = 30.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.8 Hz, 1H), 7.79 – 7.73 (m, 3H), 7.50 – 7.43 (m, 3H), 6.17 (s, 1H), 4.28 (d, *J* = 8.7 Hz, 1H), 4.04 (d, *J* = 8.7 Hz, 1H), 3.25 – 3.17 (m, 2H), 1.39 (s, 3H).

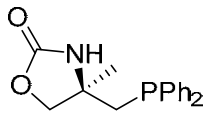
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 133.7, 132.8, 132.1, 129.0, 128.6, 127.8, 127.7, 127.3, 126.8, 126.2, 74.8, 58.8, 44.7, 25.4.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}NO_2S$ $[M + H]^+$ 274.0896, found 274.0890.



To a solution of Ph_2PK (0.5 M in THF, 0.48 mL, 0.24 mmol, 1.2 equiv.) was slowly added a solution of **34** (81.9 mg, 0.20 mmol, 1.0 equiv.) and 18-crown-6 (64.0 mg, 0.24 mmol, 1.2 equiv.) in THF (2.0 mL) at –78 °C under argon. Then, the reaction was allowed to warm to r.t. slowly and was further stirred overnight. Upon completion, the solvent was removed *in vacuo* and the residue was purified with flash column chromatography (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to give product **45** as a white solid (37.0 mg, 62% yield, 95% e.e.).

(*R*)-4-((Diphenylphosphanyl)methyl)-4-methyloxazolidin-2-one (45)



45

HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 254 nm), t_R (major) = 32.60 min, t_R (minor) = 37.19 min.

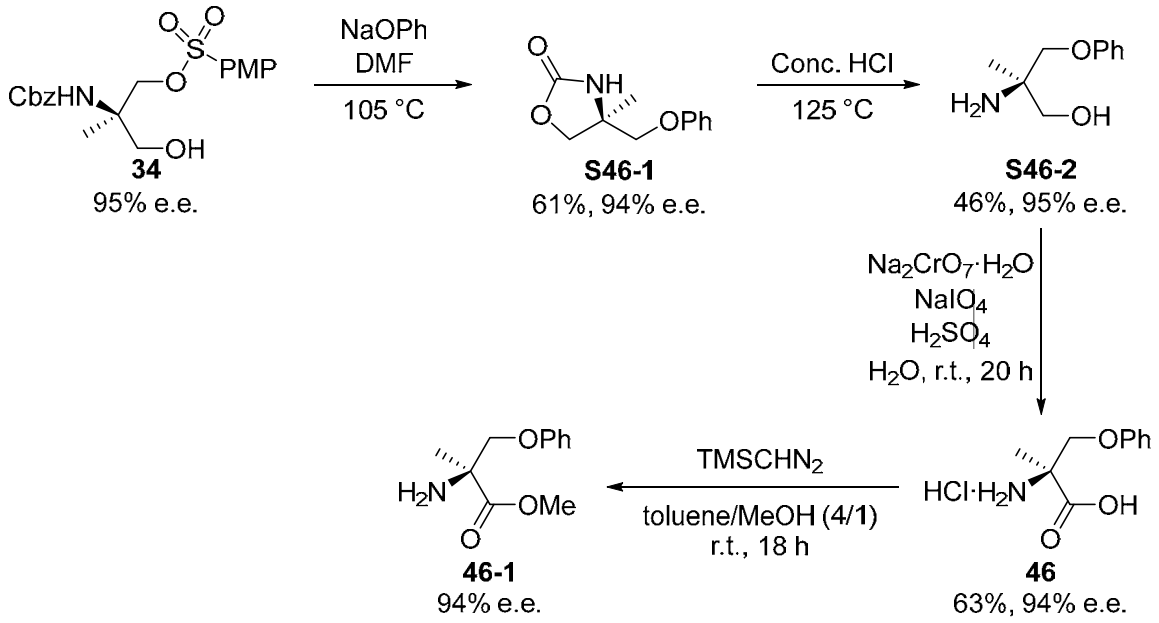
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 4H), 7.36 – 7.33 (m, 6H), 5.63 (s, 1H), 4.23 (d, *J* = 8.5 Hz, 1H), 4.05 (dd, *J* = 8.5, 1.5 Hz, 1H), 2.49 (t, *J* = 2.6 Hz, 2H), 1.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 137.6 (dd, *J* = 10.4, 7.9 Hz), 132.8 (dd, *J* = 19.7, 11.9 Hz), 129.1 (d, *J* = 6.6 Hz), 128.8 (dd, *J* = 7.3, 2.0 Hz), 76.5 (d, *J* = 8.8 Hz), 57.9 (d, *J* = 16.5 Hz), 41.1 (d, *J* = 17.7 Hz), 27.4 (d, *J* = 8.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –26.2.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}NO_2P$ $[M + H]^+$ 300.1148, found 300.1142.

The structure of **45** was further confirmed by X-ray diffraction analysis (Supplementary Fig. 20).



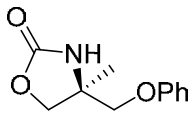
Step1: A 10 mL resealable Schlenk tube equipped with a magnetic stir bar was charged with **34** (81.9 mg, 0.20 mmol, 1.0 equiv.), NaOPh (66.4 mg, 0.40 mmol, 2.0 equiv.), and DMF **(**2.0 mL). The Schlenk tube was sealed and heated to 105 °C for 13 h. Upon completion, the tube was allowed to cool to r.t. Brine (10.0 mL) was added and the reaction mixture was extracted with Et_2O (2 × 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo* and the residue was purified with flash column chromatography (CH_2Cl_2/MeOH = 200/1 ~ 100/1) to give product **S46-1** as a white solid (25.2 mg, 61% yield, 94% e.e.).

Step2: A solution of **S46-1** (25.2 mg, 0.12 mmol) in 12 M HCl (1 mL) was heated in a pressure vessel at 125 °C for 16 h. The solution was then concentrated *in vacuo* and the residue was further purified with flash column chromatography (CH_2Cl_2/MeOH = 100/1 ~ 10/1) to give product **S46-2** as a white solid (10.0 mg, 46% yield, 95% e.e.).

Step3: Sodium dichromate (6.0 mg, 0.020 mmol, 10 mol%), sodium periodate (231.0 mg, 1.08 mmol, 5.4 equiv.), and sulfuric acid (75 μL, 0.40 mmol, 2.0 equiv.) were dissolved in water (2.0 mL) and **S46-2** (36.2 mg, 0.20 mmol) was added at r.t. After stirring for 20 h at r.t., Dowex 50WX8 in water was added to the reaction mixture and the suspension was stirred for an additional 60 min at r.t. Thereafter, the ion exchange resin was washed with water and the product was eluted using aqueous ammonia (3 M) as an eluent. The solution was then concentrated *in vacuo* and the residue was acidified by HCl (4 M in 1,4-dioxane). After evaporation, product **46** (29.0 mg, 0.125 mmol, 63%, 94% e.e.) was obtained as a light-yellow powder. (The enantiomeric excess was determined after conversion to the corresponding methyl ester).

Step4: To a suspension of **46** (11.6 mg, 0.050 mmol, 1.0 equiv.) in anhydrous benzene/MeOH (1.00 mL, 0.05 M, 4/1) was added (diazomethyl)trimethylsilane (0.10 mL, 0.20 mmol, 2.0 M in hexanes, 4.0 equiv.). The reaction mixture was stirred at r.t. for 18 h. The reaction was quenched with acetic acid (0.1 mL) and the resulting mixture was concentrated *in vacuo*, yielding a white powder containing the methyl ester **46-1** (94% e.e.).

(*S*)-4-Methyl-4-(phenoxymethyl)oxazolidin-2-one (S46-1)



S46-1

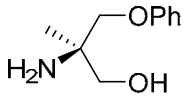
HPLC analysis: Chiralcel IB (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 220 nm), t_R (minor) = 11.01 min, t_R (major) = 13.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.01 – 6.97 (m, 1H), 6.91 – 6.87 (m, 2H), 6.16 (s, 1H), 4.38 (d, *J* = 8.7 Hz, 1H), 4.11 (d, *J* = 8.7 Hz, 1H), 3.91 – 3.85 (m, 2H), 1.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 158.2, 129.6, 121.6, 114.6, 73.2, 72.6, 57.6, 23.1.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}NO_3$ $[M + H]^+$ 208.0968, found 208.0965.

(*R*)-2-Amino-2-methyl-3-phenoxypropan-1-ol (S46-2)



S46-2

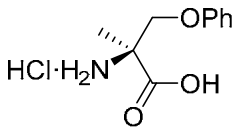
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 9.68 min, t_R (minor) = 12.68 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 8.6, 7.3 Hz, 1H)., 6.95 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 2H), 3.87 (d, *J* = 9.0 Hz, 1H), 3.78 (d, *J* = 9.0 Hz, 1H), 3.60 (d, *J* = 11.0 Hz, 1H), 3.48 (d, *J* = 11.0 Hz, 1H), 3.43 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 129.5, 121.1, 114.6, 73.0, 67.3, 54.1, 21.8.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}NO_2$ $[M + H]^+$ 182.1176, found 182.1175.

(*S*)-2-Amino-2-methyl-3-phenoxypropanoic acid hydrochloride (46)



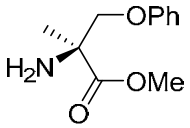
46

^{1}H NMR (400 MHz, D_2O) δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 4.49 (d, *J* = 10.3 Hz, 1H), 4.22 (d, *J* = 10.3 Hz, 1H), 1.66 (s, 3H).

^{13}C NMR (100 MHz, D_2O) δ 172.5, 157.3, 129.9, 122.2, 114.8, 70.1, 60.0, 18.3.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}NO_2$ $[M + H]^+$ 196.0968, found 196.0968.

Methyl (*S*)-2-amino-2-methyl-3-phenoxypropanoate (46-1)



46-1

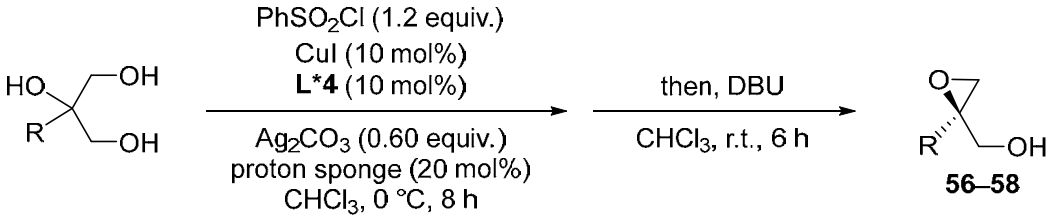
HPLC analysis: Chiralcel OJH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, λ = 220 nm), t_R (minor) = 18.50 min, t_R (major) = 20.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.8 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.22 (d, *J* = 8.5 Hz, 1H), 3.88 (d, *J* = 8.5 Hz, 1H), 3.73 (s, 3H), 1.97 (s, 2H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 158.5, 129.4, 121.2, 114.7, 74.4, 58.2, 52.5, 23.2.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{15}NO_3$ $[M + H]^+$ 210.1125, found 210.1120.

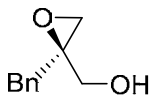
b) One-pot synthesis of quaternary epoxides



56–58

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (5.7 mg, 0.030 mmol, 10 mol%), **L*4** (15.1 mg, 0.030 mmol, 10 mol%), Ag_2CO_3 (49.6 mg, 0.18 mmol, 0.60 equiv.), proton sponge (12.8 mg, 0.060 mmol, 0.20 equiv.), the corresponding triol (0.30 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (3.0 mL). Then, benzenesulfonyl chloride (4to, 0.36 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at 0 °C. After 8 h, the reaction mixture was filtered through a plug of celite (rinsed with 2.0 mL $CHCl_3$). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (53.6 μL, 0.36 mmol, 1.2 equiv.) was added to the filtrate and the reaction mixture was stirred at r.t. for 6 h. Solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to give the product.

(*R*)-(2-Benzyloxiran-2-yl)methanol (56)



56

Product **56** was obtained as a yellow oil (36.0 mg, 73% yield, 95% e.e.).

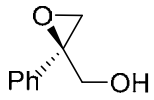
HPLC analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), t_R (minor) = 6.83 min, t_R (major) = 7.74 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.13 (m, 5H), 3.74 (dd, *J* = 12.3, 4.4 Hz, 1H), 3.59 (dd, *J* = 12.3, 7.9 Hz, 1H), 3.08 (d, *J* = 14.3 Hz, 1H), 2.92 – 2.82 (m, 2H), 2.66 (d, *J* = 4.7 Hz, 1H), 1.96 – 1.82 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 129.6, 128.5, 126.9, 62.8, 60.0, 49.7, 38.3.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{12}NaO_2$ $[M + Na]^+$ 187.0730 found 187.0728.

(*R*)-(2-Phenyloxiran-2-yl)methanol (57)



57

Product **57** was obtained as a colorless oil (27.2 mg, 60% yield, 94% e.e.).

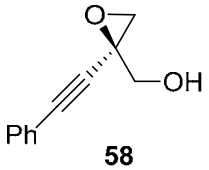
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 14.22 min, t_R (major) = 17.58 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 5H), 4.11 (dd, *J* = 12.6, 2.5 Hz, 1H), 4.02 (dd, *J* = 12.9, 7.7 Hz, 1H), 3.28 (d, *J* = 5.3 Hz, 1H), 2.83 (d, *J* = 5.3 Hz, 1H), 1.95 – 1.77 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 128.6, 128.2, 126.0, 63.1, 60.4, 52.5.

HRMS (ESI) *m/z* calcd. for $C_9H_{10}NaO_2$ $[M + Na]^+$ 173.0573, found 173.0574.

(*R*)-(2-(Phenylethynyl)oxiran-2-yl)methanol (58)



58

Product **58** was obtained as a yellow solid (45.0 mg, 86% yield, 96% e.e.).

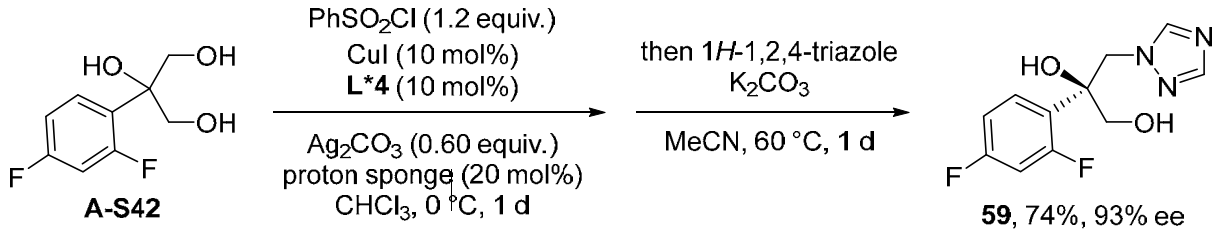
HPLC analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.6 mL/min, λ = 214 nm), t_R (minor) = 9.56 min, t_R (major) = 14.18 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.36 – 7.28 (m, 3H), 4.09 – 3.97 (m, 1H), 3.96 – 3.81 (m, 1H), 3.20 (d, *J* = 5.6 Hz, 1H), 3.14 (d, *J* = 5.5 Hz, 1H), 1.97 – 1.86 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 129.0, 128.4, 121.6, 84.9, 84.8, 63.0, 51.6, 51.4.

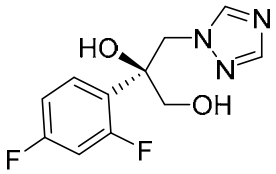
HRMS (ESI) *m/z* calcd. for $C_{11}H_{11}O_2$ $[M + H]^+$ 175.0754, found 175.0754.

c) Synthesis of a key intermediate for antifungal agents



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (5.7 mg, 0.030 mmol, 10 mol%), **L*4** (15.1 mg, 0.030 mmol, 10 mol%), Ag_2CO_3 (49.6 mg, 0.18 mmol, 0.60 equiv.), proton sponge (12.8 mg, 0.060 mmol, 0.20 equiv.), **A-S42** (61.3 mg, 0.30 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (3.0 mL). Then, benzenesulfonyl chloride (46 to0.36 mmol, 1.2 equiv.) was added into the mixture and the reaction mixture was stirred at 0 ℃. After stirring for 1 d, the reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was dissolved in MeCN (3.0 mL), then K_2CO_3 (82.8 mg, 0.60 mmol, 2.0 equiv.) and 1,2,4-triazole (41.4 mg, 0.60 mmol, 2.0 equiv.) were added. The reaction mixture was heated to 60 °C for 1 d while stirring. After cooled to r.t., the reaction mixture was diluted with EtOAc (80 mL), washed with H_2O and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was briefly purified by silica gel column chromatography (petroleum ether/EtOAc = 1/1 ~ 1/3) to give product **59** as a white solid (56.5 mg, 74% yield).

(*S*)-2-(2,4-Difluorophenyl)-3-(1*H*-1,2,4-triazol-1-yl)propane-1,2-diol (59)



59

$[\alpha]_D^{27}$ = 57 (*c* 1.0, MeOH).

HPLC analysis: Chiralcel OZ3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.4 mL/min, λ = 214 nm), t_R (major) = 42.35 min, t_R (minor) = 35.05 min, 93% e.e.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.84 (s, 1H), 7.51 (td, *J* = 8.9, 6.6 Hz, 1H), 6.94 – 6.66 (m, 2H), 4.78 (d, *J* = 14.3 Hz, 1H), 4.71 (d, *J* = 14.3 Hz, 1H), 3.98 (dd, *J* = 11.7, 1.6 Hz, 1H), 3.77 (d, *J* = 11.7 Hz, 1H), 2.17 (br s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8 (dd, *J* = 250.9, 12.8 Hz), 158.7 (dd, *J* = 246.4, 12.0 Hz), 151.9, 144.4, 130.0 (dd, *J* = 9.6, 6.0 Hz), 122.9 (dd, *J* = 13.3, 3.9 Hz), 111.8 (dd, *J* = 20.7, 3.4 Hz), 104.2 (dd, *J* = 27.6, 25.6 Hz), 76.2 (d, *J* = 5.2 Hz), 66.6 (d, *J* = 4.3 Hz), 54.3 (d, *J* = 6.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –109.8 (d, *J* = 8.1 Hz), –109.9 (d, *J* = 7.9 Hz).

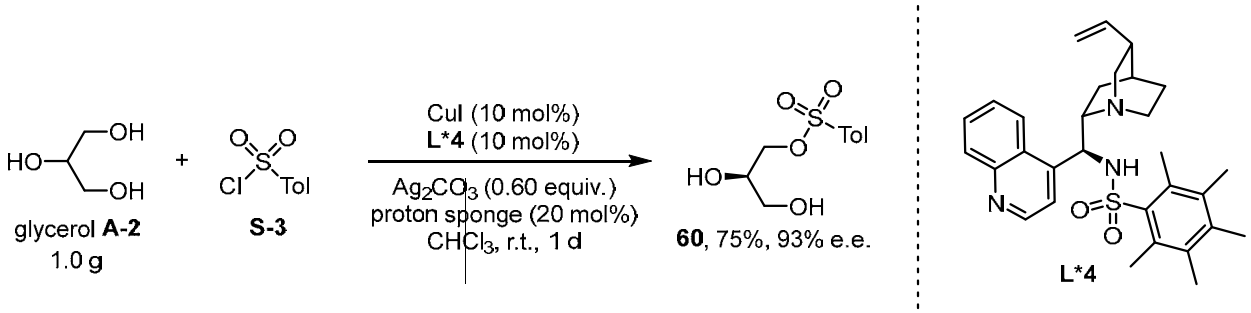
HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}F_2N_3O_2$ $[M + H]^+$ 256.0892, found 256.0889.

Note: The absolute configuration of **59** was determined by X-ray diffraction analysis (Supplementary Fig. 21).

Desymmetrization of polyols from natural resources

(A) Desymmetrization of glycerol and subsequent transformations

Gram-scale desymmetrization of glycerol for the synthesis of 60



According to **General procedure A** with glycerol **A-2** (1.0 g, 11 mmol, 1.0 equiv.) and tosyl chloride **S-3** (2.5 g, 13 mmol, 1.2 equiv.) at r.t. for 1 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **60** as a white solid (2.0 g, 75% yield, 93% e.e.).

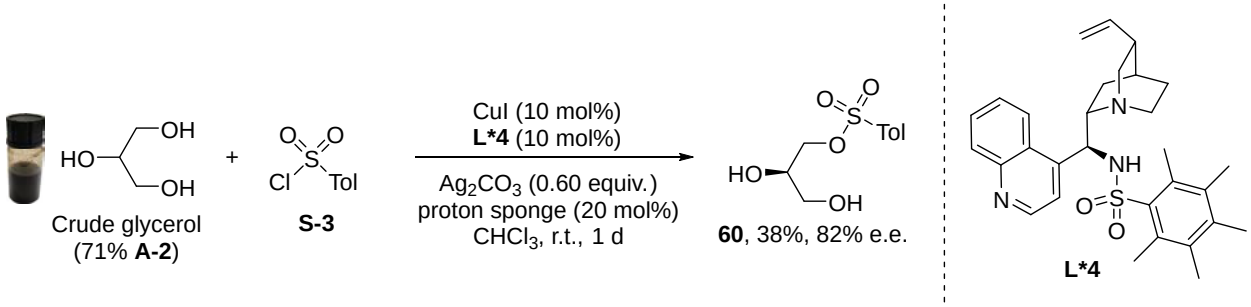
HPLC analysis: Chiralcel ADH (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 17.73 min, t_R (minor) = 18.99 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.15 – 4.02 (m, 2H), 4.01 – 3.91 (m, 1H), 3.75 – 3.52 (m, 2H), 3.21 (s, 1H), 2.65 (s, 1H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 132.4, 130.0, 128.0, 70.7, 69.7, 62.7, 21.7.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{14}NaO_5S$ $[M + Na]^+$ 269.0454, found 269.0453.

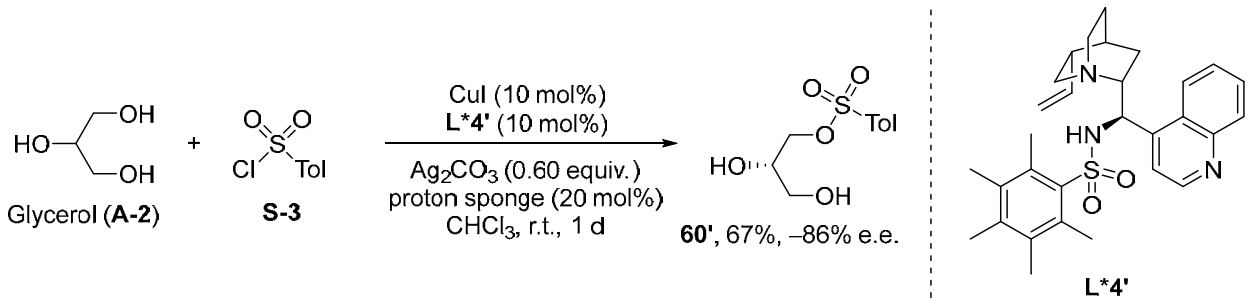
Desymmetrization of crude glycerol (71%) for the synthesis of 60



According to **General procedure A** with crude glycerol **A-2** (129.6 mg, 1.0 mmol, 1.0 equiv.) and tosyl chloride **S-3** (228.7 mg, 1.2 mmol, 1.2 equiv.) at r.t. for 1 d, the reaction mixture was purified

by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **60** as a white solid (93.5 mg, 38% yield, 82% e.e.).

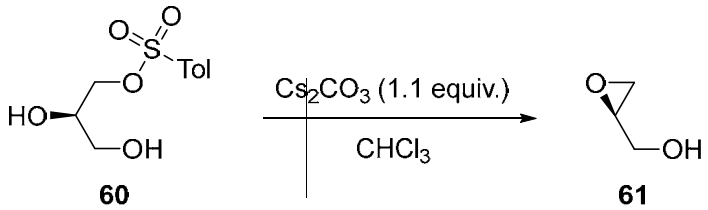
Desymmetrization of glycerol for the synthesis of 60'



According to **General procedure A** with glycerol **A-2** (92.0 mg, 1.0 mmol, 1.0 equiv.) and tosyl chloride **S-3** (228.7 mg, 1.2 mmol, 1.2 equiv.) at r.t. for 1 d (**L*4'** (50.4 mg, 0.10 mmol, 0.10 equiv.) was used instead of **L*4**), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **60'** as a white solid (165.0 mg, 67% yield, –86% e.e.)

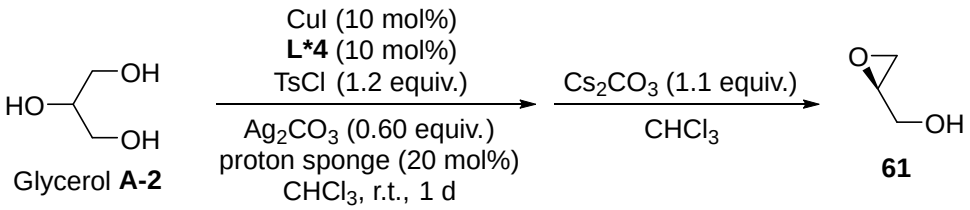
HPLC analysis: Chiralcel ADH (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (minor) = 17.65 min, t_R (major) = 18.89 min.

The synthesis of 61



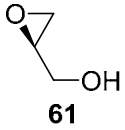
To a solution of compound **60** (1.58 g, 6.42 mmol, 1.0 equiv.) in $CHCl_3$ (60.0 mL) was added cesium carbonate (2.30 g, 7.07 mmol, 1.1 equiv.). The reaction mixture was stirred at r.t. for 4 h and then filtered over a short plug of celite. The filtrate was concentrated *in vacuo* at 25 °C and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **61** as a colorless oil (425 mg, 89% yield).

One-pot procedure for the synthesis of **61**.



Step 1 was performed in a 1.0-mmol scale according to **General procedure A** with glycerol **A-2** (92.0 mg, 1.0 mmol, 1.0 equiv.) and tosyl chloride **S-3** (228.7 mg, 1.2 mmol, 1.2 equiv.) at r.t. for 1 d. Then the reaction mixture was filtered over a plug of celite and the filter-cake was washed with chloroform (2 × 1.0 mL). Cesium carbonate (0.36 g, 1.1 mmol, 1.1 equiv.) was added to the filtrate and the mixture was stirred at r.t. Upon completion, the reaction mixture was filtered over a short plug of celite and the solvent was evaporated *in vacuo* at 25 ℃. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **61** (49.5 mg, 67% yield in two steps) as a colorless oil.

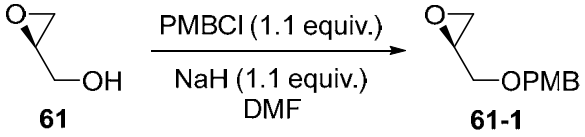
(*R*)-Oxiran-2-ylmethanol (61)



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (d, *J* = 12.3 Hz, 1H), 3.62 – 3.54 (m, 1H), 3.20 – 3.15 (m, 1H), 2.82 (t, *J* = 4.4 Hz, 1H), 2.78 – 2.74 (m, 1H), 2.71 (br s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 61.9, 52.3, 44.2.

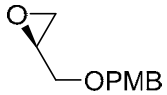
Determination of the e.e. and absolute configuration of **61**



To a suspension of NaH (60% dispensed in mineral oil, 44 mg, 1.1 mmol, 1.1 equiv.) in DMF (2.0 mL) was added 4-methoxybenzyl chloride (150.0 μL, 1.1 mmol, 1.1 equiv.) at 0 ℃ under argon. After stirring for 20 min, **61** (65.0 μL, 1.0 mmol, 1.0 equiv.) was added dropwise and the reaction mixture was allowed to warm to r.t. After 1 d, the reaction mixture was diluted with EtOAc (80 mL) and washed with saturated NH_4Cl (aq.) (20 mL) and H_2O (3 × 20 mL). The organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 1/1) to yield product **61-1** (174.5 mg, 90% yield, 90% e.e.) as a colorless oil.

Note: The absolute configuration of **61-1** was determined by comparing its HPLC traces with those in literature[4].

(*S*)-2-(((4-Methoxybenzyl)oxy)methyl)oxirane (61-1)



61-1

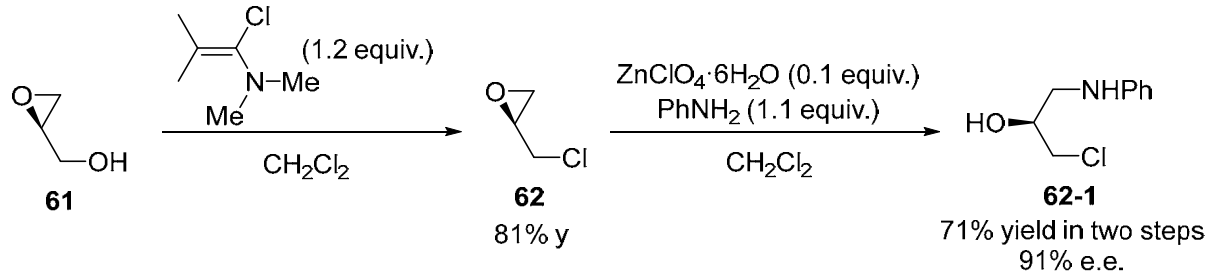
HPLC analysis: Chiralcel IA (*n*-Hexane/*i*-PrOH = 98/2, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 11.57 min, t_R (minor) = 12.33 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 3H), 6.91 – 6.86 (m, 2H), 4.52 (q, *J* = 11.5 Hz, 2H), 3.80 (s, 3H), 3.73 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.41 (dd, *J* = 11.4, 5.8 Hz, 1H), 3.23 – 3.12 (m, 1H), 2.80 (t, *J* = 4.6 Hz, 1H), 2.66 – 2.58 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 130.0, 129.5, 113.8, 73.0, 70.5, 55.3, 50.9, 44.4.

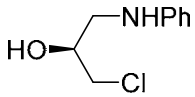
HRMS (ESI) *m/z* calcd. for $C_{11}H_{14}NaO_3$ $[M + Na]^+$ 217.0835, found 217.0836.

The synthesis of 62



To a solution of **61** (65.0 μL, 1.0 mmol, 1.0 equiv.) in CH_2Cl_2 (2.0 mL) was added 1-chloro-*N*,*N*,2-trimethylprop-1-en-1-amine (160.0 μL, 1.2 mmol, 1.2 equiv.) at 0 ℃ under argon. After stirring for 4 h at 0 ℃, the internal standard CH_2Br_2 (70.0 μL, 1.0 mmol, 1.0 equiv.) was added into the reaction mixture and 20 μL of the solution was transferred into the NMR tube followed by the addition of $CDCl_3$. The subsequent ^{1}H NMR analysis indicated 81% yield for **62**.

Then, to the reaction mixture were added aniline (81 μL, 0.89 mmol, 1.1 equiv.) and $Zn(ClO_4)_2·6H_2O$ (29.8 mg, 0.080 mmol, 0.10 equiv.). The mixture was warmed to r.t. and stirred for 3 d. After removing the solvent, the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 4/1) to give **62-1** (132.0 mg, 71% yield in two steps, 91% e.e.) as a colorless oil.



62-1

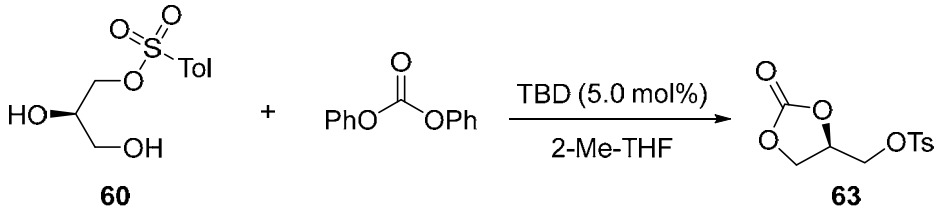
HPLC analysis: Chiralcel OD3 (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 17.62 min, t_R (minor) = 18.75 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.69 – 6.64 (m, 2H), 4.08 – 4.03 (m, 1H), 3.68 – 3.59 (m, 2H), 3.36 (dd, *J* = 13.3, 4.4 Hz, 1H), 3.21 (dd, *J* = 13.3, 7.2 Hz, 1H), 3.04 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 129.3, 118.2, 113.3, 69.8, 47.6, 47.1.

HRMS (ESI) *m/z* calcd. for $C_9H_{13}ClNO$ $[M + H]^+$ 186.0680, found 186.0680.

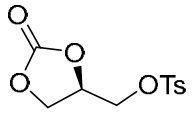
The synthesis of 63



60 **63**

To a solution of compound **60** (49.3 mg, 0.20 mmol, 1.0 equiv.) and diphenyl carbonate (47.2 mg, 0.22 mmol, 1.1 equiv.) in 2-Me-THF (2.0 mL) was added 1,5,7-triazabicylo[4.4.0]dec-5-ene (1.4 mg, 0.010 mmol, 5.0 mol%). The reaction mixture was stirred at r.t. Upon completion, solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **63** as a light yellow solid (40.0 mg, 74% yield, 93% e.e.).

(*R*)-(2-Oxo-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate (63)



63

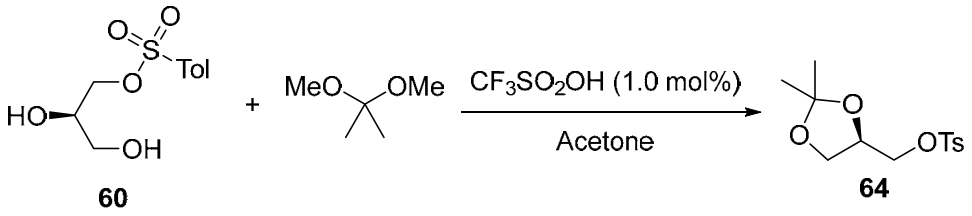
HPLC analysis: Chiralcel ADH (*n*-Hexane/*i*-PrOH = 85/15, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 27.76 min, t_R (minor) = 28.79 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.97 – 4.82 (m, 1H), 4.54 (t, *J* = 8.7 Hz, 1H), 4.36 (dd, *J* = 8.9, 5.9 Hz, 1H), 4.29 – 4.17 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 145.9, 131.8, 130.2, 128.0, 72.9, 67.2, 65.5, 21.7.

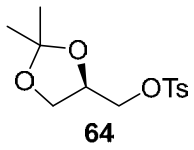
HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}NaO_6S$ $[M + Na]^+$ 295.0247, found 295.0248.

The synthesis of 64



To a solution of **60** (49.3 mg, 0.20 mmol, 1.0 equiv.) in acetone (3.0 mL)were added 2,2-dimethoxypropane (31.2 mg, 0.30 mmol, 1.5 equiv.) and trifluoromethanesulfonic acid (0.21 mg, 0.0020 mmol, 1.0 mol%) at r.t. After stirring at r.t. for 1 h, triethylamine was added and the reaction mixture was concentrated to a minimum volume. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **64** as a light yellow solid (42 mg, 77% yield, 92% e.e.).

(*R*)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate (64)



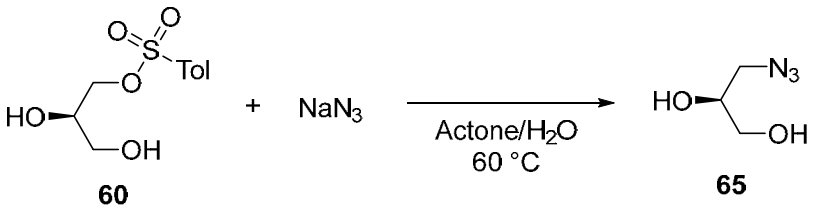
HPLC analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 17.20 min, t_R (minor) = 20.64 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.32 – 4.23 (m, 1H), 4.10 – 3.94 (m, 3H), 3.77 (dd, *J* = 8.8, 5.1 Hz, 1H), 2.45 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 132.7, 129.9, 128.0, 110.1, 72.9, 69.5, 66.2, 26.6, 25.2, 21.7.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{19}O_5S$ $[M + H]^+$ 287.0948, found 287.0947.

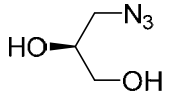
The synthesis of 65



To a solution of **60** (49.3 mg, 0.20 mmol, 1.0 equiv.) in acetone (1.8 mL) and H_2O (0.6 mL) was added NaN_3 (65 mg, 1.0 mmol, 5.0 equiv.). The mixture was stirred at 60 ℃ overnight before

removing the solvent *in vacuo*. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 10/1) to yield product **65** as a colorless oil (22.8 mg, 97% yield, 92% e.e.).

(*S*)-3-Azidopropane-1,2-diol (65)



65

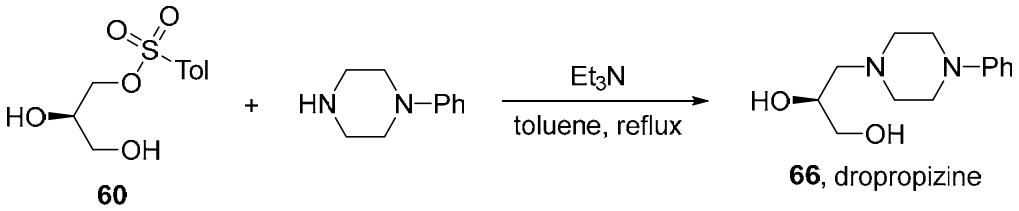
HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 97/3, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 57.01 min, t_R (minor) = 61.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 – 3.85 (m, 1H), 3.71 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.60 (dd, *J* = 11.4, 6.3 Hz, 1H), 3.46 – 3.35 (m, 2H), 3.06 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 70.9, 64.0, 53.5.

HRMS (ESI) *m/z* calcd. for $C_3H_7N_3NaO_2$ $[M + Na]^+$ 140.0430, found 140.0431.

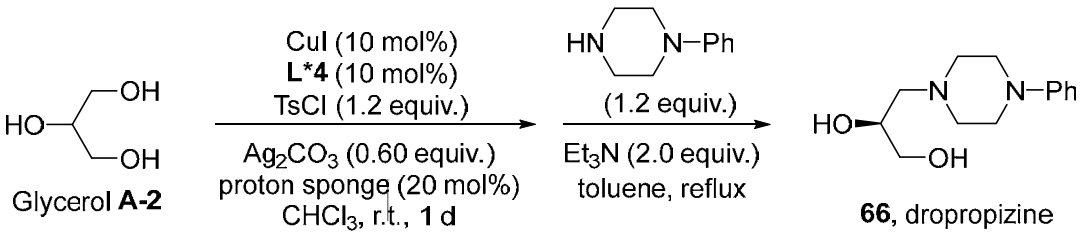
The synthesis of 66



60 **66**, dropropizine

To a solution of compound **60** (49.3 mg, 0.20 mmol, 1.0 equiv.) and 1-phenylpiperazine (38.9 mg, 0.24 mmol, 1.2 equiv.) in toluene (2.0 mL) was added triethylamine (40.5 mg, 0.40 mmol, 2.0 equiv.). The mixture was heated to reflux while stirring. Upon completion, the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 20/1) to yield product **66** as a white solid (35.0 mg, 72% yield, 93% e.e.).

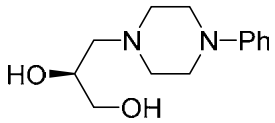
One-pot procedure for the synthesis of **66**.



Glycerol **A-2** **66**, dropropizine

Step 1 was performed in a 0.2-mmol scale according to **General procedure A**. Upon completion, the reaction mixture was filtered over a plug of celite and the filter-cake was washed with chloroform several times. The filtrate was concentrated *in vacuo* and the residue was redissolved in toluene (2.0 mL). Then, 1-phenylpiperazine (38.9 mg, 0.24 mmol, 1.2 equiv.) was added and the mixture was heated to reflux. Upon completion, the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 20/1) to yield product **66** as a white solid (22.0 mg, 47% yield in two steps, 93% e.e.).

(*S*)-3-(4-Phenylpiperazin-1-yl)propane-1,2-diol (66)



66

HPLC analysis: Chiralcel OJH (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 254 nm), t_R (major) = 15.85 min, t_R (minor) = 19.41 min.

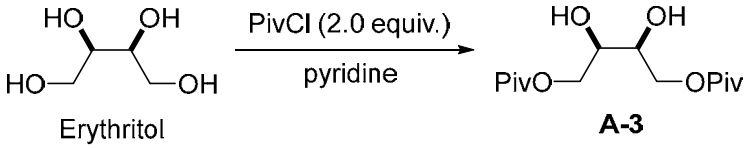
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 6.97 – 6.90 (m, 2H), 6.90 – 6.83 (m, 1H), 3.94 – 3.84 (m, 1H), 3.77 (dd, *J* = 11.4, 3.7 Hz, 1H), 3.53 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.28 – 3.14 (m, 4H), 2.90 – 2.79 (m, 2H), 2.71 – 2.57 (m, 3H), 2.43 (dd, *J* = 12.5, 3.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 129.2, 120.0, 116.2, 66.9, 64.8, 60.3, 53.4, 49.2.

HRMS (ESI) *m/z* calcd. for $C_{13}H_{21}N_2O_2$ $[M + H]^+$ 237.1598, found 237.1596.

(B) Desymmetrization of protected erythritol and xylitol

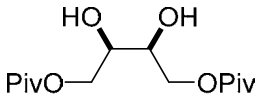
The synthesis of 67



Erythritol **A-3**

To a solution of erythritol (5.0 g, 41 mmol, 1.0 equiv.) in pyridine (100 mL) at 0 °C was slowly added pivaloyl chloride (10.1 mL, 82 mmol, 2.0 equiv.). The reaction mixture was stirred at r.t. overnight. Then the resulting mixture was diluted with EtOAc (200 mL) and washed with 1N HCl (5 × 50 mL) to remove pyridine. The organic layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was dissolved in a minimum amount of CH_2Cl_2 (10 mL). Then pentane (300 mL) was added (in the beginning it should be added slowly) while swirling by hand, during which time the product started precipitating out. The resulting solution was swirled by hand for a few min. This was then filtered with a Büchner funnel to give product **A-3** as a white solid (6.78 g, 57% yield).

2,3-Dihydroxybutane-1,4-diyl bis(2,2-dimethylpropanoate) (A-3)

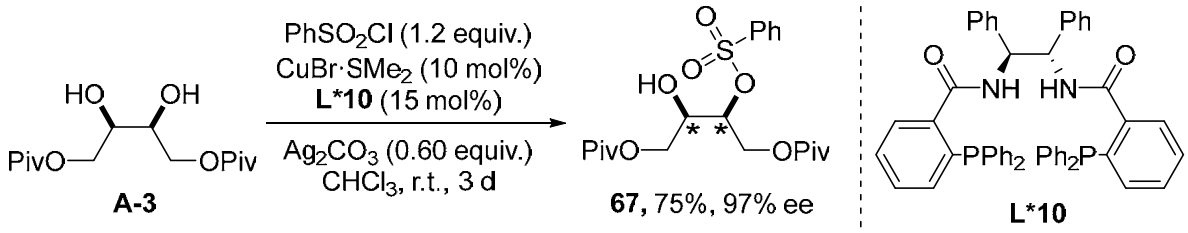


A-3

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.4 – 4.2 (m, 4H), 3.9 – 3.7 (m, 2H), 2.8 (br s, 2H), 1.2 (s, 18H).

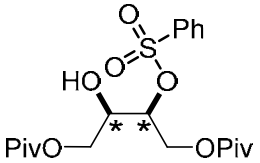
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 70.7, 65.6, 38.9, 27.2.

HRMS (ESI) *m/z* calcd. for $C_{14}H_{27}O_6$ $[M + H]^+$ 291.1802, found 291.1801.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBr{\cdot}SMe_2$ (4.1 mg, 0.020 mmol, 10 mol%), **L*10** (23.7 mg, 0.030 mmol, 15 mol%), Ag_2CO_3 (33.1 mg, 0.12 mmol, 0.60 equiv.), **A-3** (58.0 mg, 0.20 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then benzenesulfonyl chloride (30.8 μL, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at r.t. for 3 d. Upon completion, the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the desired product **67** as a white solid (64.2 mg, 75% yield, 97% e.e.).

2-Hydroxy-3-((phenylsulfonyl)oxy)butane-1,4-diyl bis(2,2-dimethylpropanoate) (67)



67

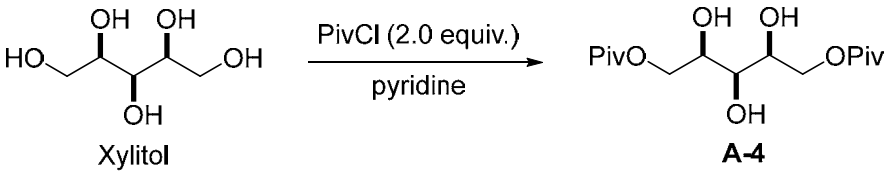
HPLC analysis: Chiralcel OD (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.3 mL/min, λ = 210 nm), t_R (major) = 29.16 min, t_R (minor) = 24.61 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.71 – 7.64 (m, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 4.88 – 4.81 (m, 1H), 4.40 – 4.28 (m, 2H), 4.24 (dd, *J* = 11.9, 3.8 Hz, 1H), 4.08 (dd, *J* = 11.9, 5.4 Hz, 1H), 4.03 – 3.96 (m, 1H), 2.61 (br s, 1H), 1.22 (s, 9H), 1.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 178.3, 136.6, 134.0, 129.3, 127.6, 78.9, 68.6, 64.2, 61.8, 38.85, 38.79, 27.1, 27.0.

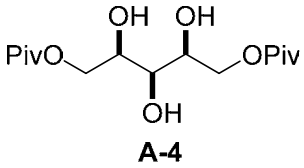
HRMS (ESI) *m/z* calcd. for $C_{20}H_{31}O_8S$ $[M + H]^+$ 431.1734, found 431.1733.

The synthesis of 68



To a solution of xylitol (3.0 g, 20 mmol, 1.0 equiv.) in pyridine (50 mL) at 0 °C was slowly added pivaloyl chloride (5.0 mL, 40 mmol, 2.0 equiv.). The reaction mixture was stirred at r.t. overnight. Then the resulting mixture was diluted with EtOAc (150 mL) and washed with 1N HCl (5 × 40 mL) to remove pyridine. The organic layer was dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was dissolved in a minimum amount of CH_2Cl_2 (8 mL). Then pentane (300 mL) was added (in the beginning it should be added slowly) while swirling by hand, during which time the product started precipitating out. The resulting solution was swirled by hand for a few min. This was then filtered with a Büchner funnel to give product **A-4** as a white solid (3.50 g, 55% yield).

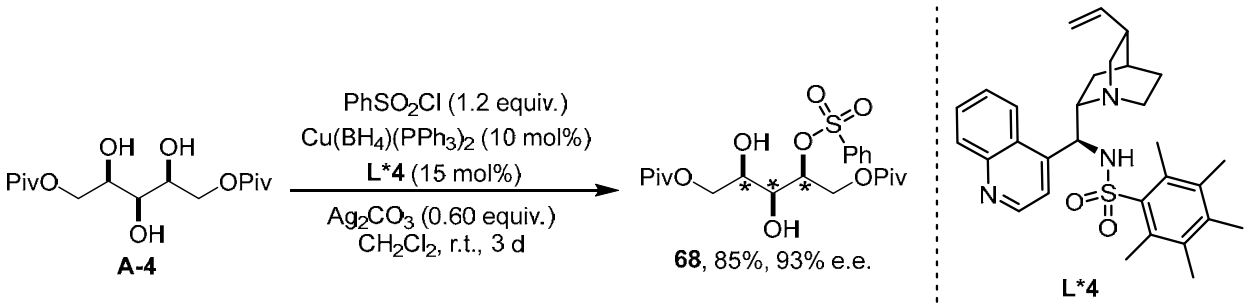
2,3,4-Trihydroxypentane-1,5-diyl bis(2,2-dimethylpropanoate) (A-4)



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (d, *J* = 6.1 Hz, 4H), 4.00 (s, 2H), 3.61 – 3.52 (m, 1H), 3.28 (br s, 2H), 3.11 (br s, 1H), 1.21 (s, 18H).

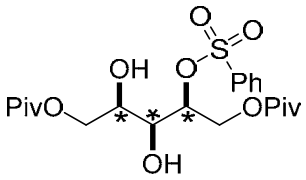
^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 71.6, 69.9, 65.4, 38.8, 27.1.

HRMS (ESI) *m/z* calcd. for $C_{15}H_{28}NaO_7$ $[M + Na]^+$ 343.1727, found 343.1725.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (12.0 mg, 0.020 mmol, 10 mol%), **L*4** (15.1 mg, 0.030 mmol, 15 mol%), Ag_2CO_3 (33.1 mg, 0.12 mmol, 0.60 equiv.), **A-4** (64.0 mg, 0.20 mmol, 1.0 equiv.), and anhydrous CH_2Cl_2 (2.0 mL). Then benzenesulfonyl chloride (30.8 μL, 0.24 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at r.t. for 3 d. Upon completion, the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to afford the desired product **68** as a white solid (78.3 mg, 85% yield, 93% e.e.).

2,3-Dihydroxy-4-((phenylsulfonyl)oxy)pentane-1,5-diyl bis(2,2-dimethylpropanoate) (68)



68

HPLC analysis: Chiralcel IG (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 21.73 min, t_R (minor) = 25.88 min.

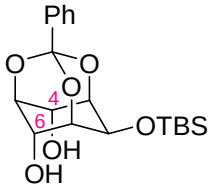
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.90 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 5.01 – 4.92 (m, 1H), 4.40 (dd, *J* = 12.6, 3.8 Hz, 1H), 4.23 – 4.11 (m, 3H), 3.95 (td, *J* = 6.0, 2.3 Hz, 1H), 3.83 (dd, *J* = 5.6, 2.3 Hz, 1H), 2.74 (br s, 2H), 1.20 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 178.0, 136.5, 134.1, 129.3, 127.7, 80.6, 69.5, 68.6, 65.1, 62.2, 38.8, 38.7, 27.1, 27.0.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{33}O_9S$ $[M + H]^+$ 461.1840, found 461.1838.

(C) 4,6-Desymmetrization of protected inositol and subsequent transformations to D-*myo*-inositol-4-phosphate

A-5 was synthesized according to the reported literature[5].



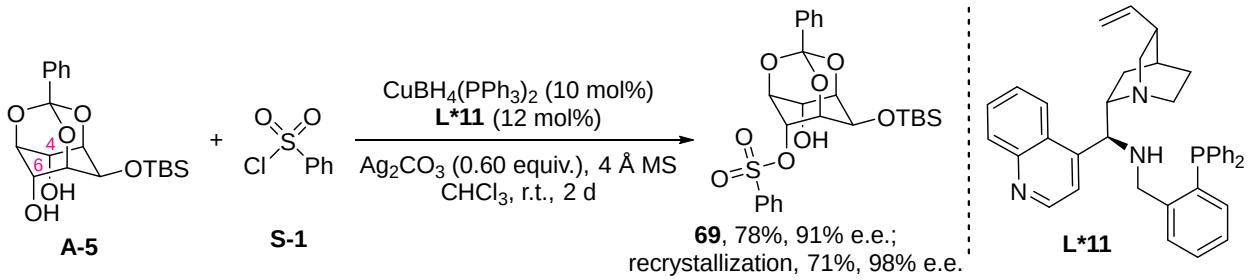
A-5

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.41 – 7.30 (m, 3H), 4.55 (s, 2H), 4.30 – 4.16 (m, 4H), 3.79 – 3.51 (m, 2H), 0.96 (s, 9H), 0.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 129.5, 128.1, 125.3, 107.0, 76.0, 69.4, 68.3, 59.6, 25.8, 18.3, –4.6.

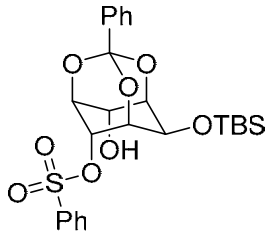
HRMS (ESI) *m/z* calcd. for $C_{19}H_{29}O_6Si$ $[M + H]^+$ 381.1728, found 381.1724.

The synthesis of 69



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (157.8 mg, 0.26 mmol, 10 mol%), **L*11** (179.3 mg, 0.32 mmol, 12 mol%), Ag_2CO_3 (435.5 mg, 1.6 mmol, 0.60 equiv.), **A-5** (1.0 g, 2.6 mmol, 1.0 equiv.), 4 Å MS (0.40 g), and anhydrous $CHCl_3$ (50.0 mL). Then benzenesulfonyl chloride (0.40 mL, 3.2 mmol, 1.2 equiv.) was added and the reaction mixture was stirred at r.t. for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the desired product **69** as a white solid (1.07 g, 78% yield, 91% e.e.). Recrystallization from *n*-Hexane/i-PrOH (20/1) produced **69** in 71% yield with 98% e.e.

(1*R*,3*S*,5*S*,6*R*,7*R*,8*R*,9*R*)-8-((*tert*-Butyldimethylsilyl)oxy)-9-hydroxy-3-phenyl-2,4,10-trioxaadamantan-6-yl benzenesulfonate (69)



69

HPLC analysis: Chiralcel OD (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 20.81 min, t_R (minor) = 14.33 min.

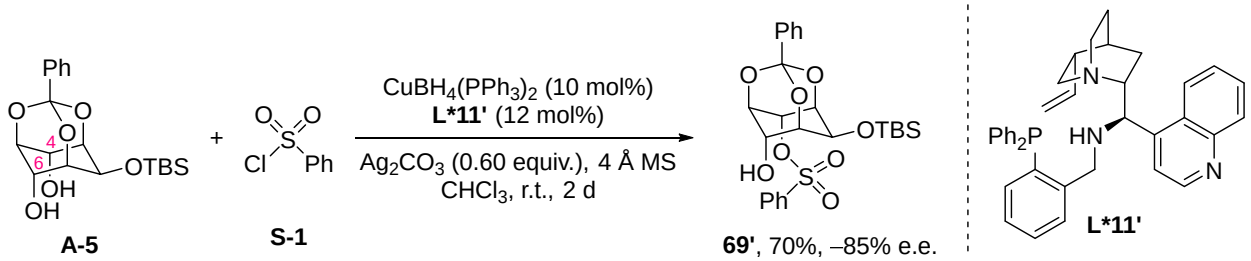
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.77 – 7.69 (m, 1H), 7.66 – 7.56 (m, 4H), 7.37 – 7.30 (m, 3H), 5.25 (td, *J* = 4.0, 1.7 Hz, 1H), 4.68 – 4.64 (m, 1H), 4.44 – 4.39 (m, 1H), 4.30 – 4.27 (m, 1H), 4.25 (t, *J* = 1.8 Hz, 1H), 4.19 – 4.16 (m, 1H), 2.43 (d, *J* = 6.6 Hz, 1H), 0.92 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 135.3, 134.7, 129.7, 129.6, 128.03, 127.95, 125.3, 107.4, 75.4, 74.6, 73.4, 69.5, 67.5, 59.3, 25.8, 18.2, –4.65, –4.71.

HRMS (ESI) *m/z* calcd. for $C_{25}H_{33}O_8SSi$ $[M + H]^+$ 521.1660, found 521.1660.

The structure of **69** was further confirmed by X-ray diffraction analysis (Supplementary Fig. 22).

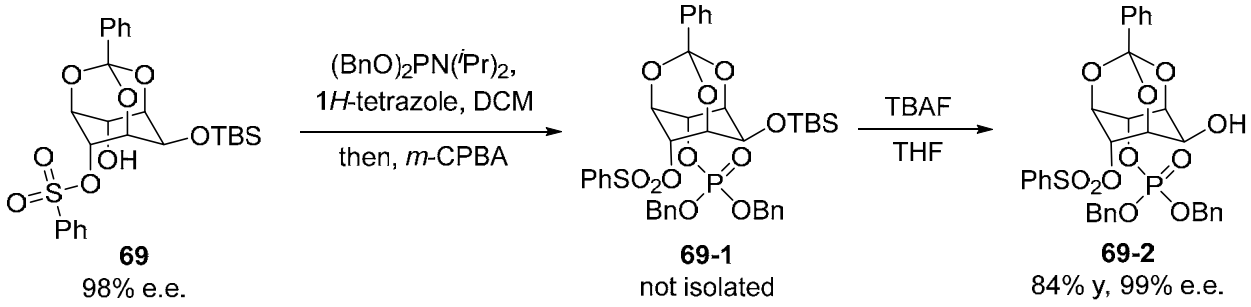
The synthesis of 69'



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol%), **L*11** (6.8 mg, 0.012 mmol, 12 mol%), Ag_2CO_3 (16.6 mg, 0.060 mmol, 0.60 equiv.), **A-5** (38.1 mg, 0.10 mmol, 1.0 equiv.), 4 Å MS (40 mg), and anhydrous $CHCl_3$ (2.0 mL). Then, benzenesulfonyl chloride (15.4 μL, to mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at r.t. for 2 d. Upon completion, the reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo.* The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the desired product **69'** as a white solid (36.3 mg, 70% yield, –85% e.e.).

HPLC analysis: Chiralcel OD (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, λ = 214 nm), t_R (major) = 14.23 min, t_R (minor) = 20.85 min.

The synthesis of 69-2



Step1: A mixture of **69** (230 mg, 0.44 mmol, 1.0 equiv.) and 1*H*-tetrazole (92.4 mg, 1.32 mmol, 3.0 equiv.) was dissolved in DCM (10.0 mL) and stirred for 10 min at r.t. Dibenzyl *N*,*N*-

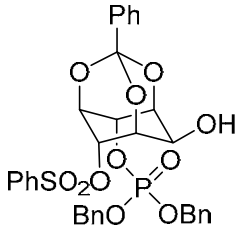
diisopropylphosphoramidite (0.22 mL, 0.66 mmol, 1.5 equiv.) was then added and the reaction mixture was stirred at r.t. for 1 h. The reaction flask was then cooled to −40 °C and *m*-CPBA (201mg (85% purity, 0.990 mmol, 2.25 equiv.) was added in one portion. The reaction mixture was gradually warmed to r.t. over a period of 2 h. DCM (40 mL) was then added to the mixture. The organic layer was washed with saturated $NaHCO_3$ (aq.), water, and brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was directly used in the next step without further purification.

Note: **69-1** has a very similar Rf value with that of **69** during TLC analysis.

Step2: To a solution of the thus-obtained residue in THF (5.0 mL) was dropwise added TBAF (0.44 mL, 1.0 M in THF) at 0 °C with stirring under argon. After stirring at 0 °C for 1 h and at r.t. for an additional 24 h, the reaction mixture was then diluted with EtOAc (80 mL), washed with water (50 mL) and brine (50 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product **69-2** as a colorless oil (246.1 mg, 84% yield over two steps, 99% e.e.).

Note: If **69-1** was purified after *Step 1*, the corresponding *Step 2* went to completion in 1 h at 0 °C.

(1*S*,3*R*,5*R*,6*S*,7*S*,8*R*,9*R*)-8-((Bis(benzyloxy)phosphoryl)oxy)-9-hydroxy-3-phenyl-2,4,10-trioxaadamantan-6-yl benzenesulfonate (69-2)



69-2

HPLC analysis: Chiralcel IA (*n*-Hexane/*i*-PrOH = 60/40, flow rate 0.7 mL/min, λ = 214 nm), t_R (major) = 25.25 min, t_R (minor) = 31.59 min.

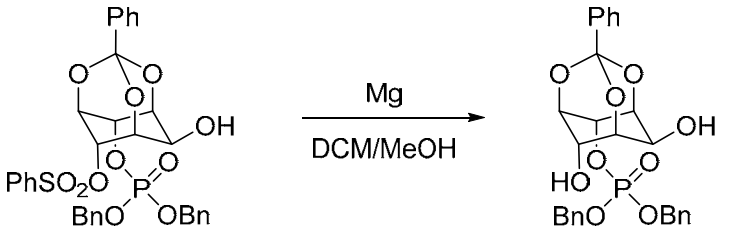
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 2H), 7.67 – 7.59 (m, 1H), 7.58 – 7.45 (m, 4H), 7.44 – 7.27 (m, 13H), 5.21 (t, *J* = 3.8 Hz, 1H), 5.18 – 5.04 (m, 5H), 4.43 – 4.41 (m, 1H), 4.33 – 4.31 (m, 2H), 4.01 (s, 1H), 3.20 (d, *J* = 8.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 135.34, 135.31, 135.27, 135.24, 134.4, 129.9, 129.5, 128.7 (d, *J* = 2.3 Hz), 128.6 (d, *J* = 1.2 Hz), 128.06, 128.03, 128.00, 127.9, 125.1, 107.6, 73.2 (d, *J* = 5.3 Hz), 72.9, 72.5, 70.03 (d, *J* = 2.7 Hz), 69.97 (d, *J* = 2.5 Hz), 69.84 (d, *J* = 5.2 Hz), 68.0 (d, *J* = 4.8 Hz), 58.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.03.

HRMS (ESI) *m/z* calcd. for $C_{33}H_{32}O_{11}PS$ $[M + H]^+$ 667.1397, found 667.1396.

The synthesis of 69-3

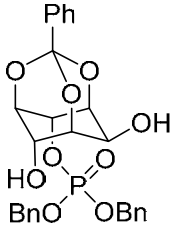


69-2
99% e.e.

69-3
68% y, 99% e.e.

To a solution of **69-2** (66.6 mg, 0.10 mmol, 1.0 equiv.) in DCM/MeOH (2.0 mL/1.0 mL) was added magnesium strips (24.0 mg, 1.0 mmol, 10.0 equiv.). After stirring for 4 h at r.t., the reaction mixture was diluted with EtOAc (40 mL) and quenched with saturated NH_4Cl (aq.) (20 mL). The organic layer was separated and washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo.* The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to afford the desired product **69-3** as a colorless oil (35.8 mg, 68% yield, 99% e.e.).

Dibenzyl ((1*S*,3*R*,5*R*,6*S*,7*S*,8*S*,9*S*)-8,9-dihydroxy-3-phenyl-2,4,10-trioxaadamantan-6-yl) phosphate (69-3)



69-3

HPLC analysis: Chiralcel ID (*n*-Hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 17.79 min, t_R (minor) = 21.08 min.

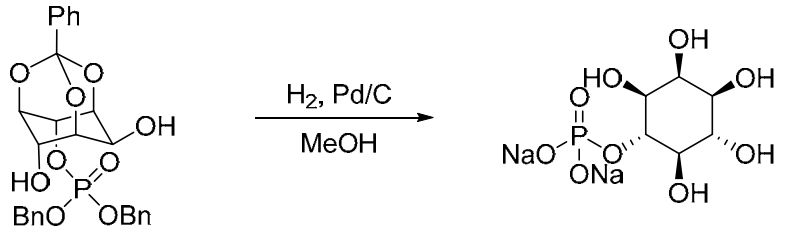
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.45 – 7.29 (m, 13H), 5.12 – 5.00 (m, 5H), 4.63 (s, 1H), 4.44 (s, 1H), 4.39 – 4.32 (m, 1H), 4.30 – 4.21 (m, 1H), 4.06 (s, 1H), 3.15 (br s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.0 (d, *J* = 2.7 Hz), 134.9 (d, *J* = 2.1 Hz), 129.7, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 125.2, 107.4, 75.3, 73.6 (d, *J* = 7.9 Hz), 71.7 (d, *J* = 5.7 Hz), 70.3 (d, *J* = 5.8 Hz), 70.2 (d, *J* = 5.8 Hz), 69.4 (d, *J* = 3.3 Hz), 66.9, 59.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.16.

HRMS (ESI) *m/z* calcd. for $C_{27}H_{28}O_9P$ $[M + H]^+$ 527.1465, found 527.1469.

The synthesis of 70

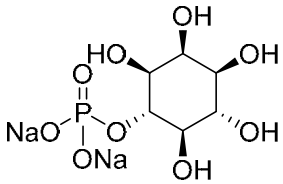


69-3
99% e.e.

70
99% y

To a solution of **69-3** (35.8 mg, 0.070 mmol) in MeOH (4.0 mL) was added Pd/C (10% wt, 100 mg, 0.094 mmol, 1.3 equiv.) under argon. The reaction flask was evacuated and refilled with hydrogen gas. The suspension was then allowed to stir under hydrogen atmosphere for 24 h. The reaction mixture was filtered through a plug of celite (rinsed with MeOH) and concentrated *in vacuo.* The residue was dissolved in deionized water and passed through Dowex 50WX8 ion-exchange resin (Na^+ form) using deionized water as the eluent. The fractions containing the product were concentrated *in vacuo* at 60 °C and further dried with an oil pump to afford **70** (20.9 mg, 99%) as a white fluffy solid.

Sodium (1*S*,2*R*,3*S*,4*S*,5*S*,6*S*)-2,3,4,5,6-pentahydroxycyclohexyl phosphate (70)



70

$[\alpha]_D^{27}$ = –0.6 (*c* 1.0, H_2O).

^{1}H NMR (400 MHz, D_2O) δ 4.07 (q, *J* = 9.1 Hz, 1H), 3.99 (t, *J* = 2.5 Hz, 1H), 3.65 – 3.56 (m, 2H), 3.47 (dd, *J* = 10.0, 2.7 Hz, 1H), 3.36 (t, *J* = 9.2 Hz, 1H).

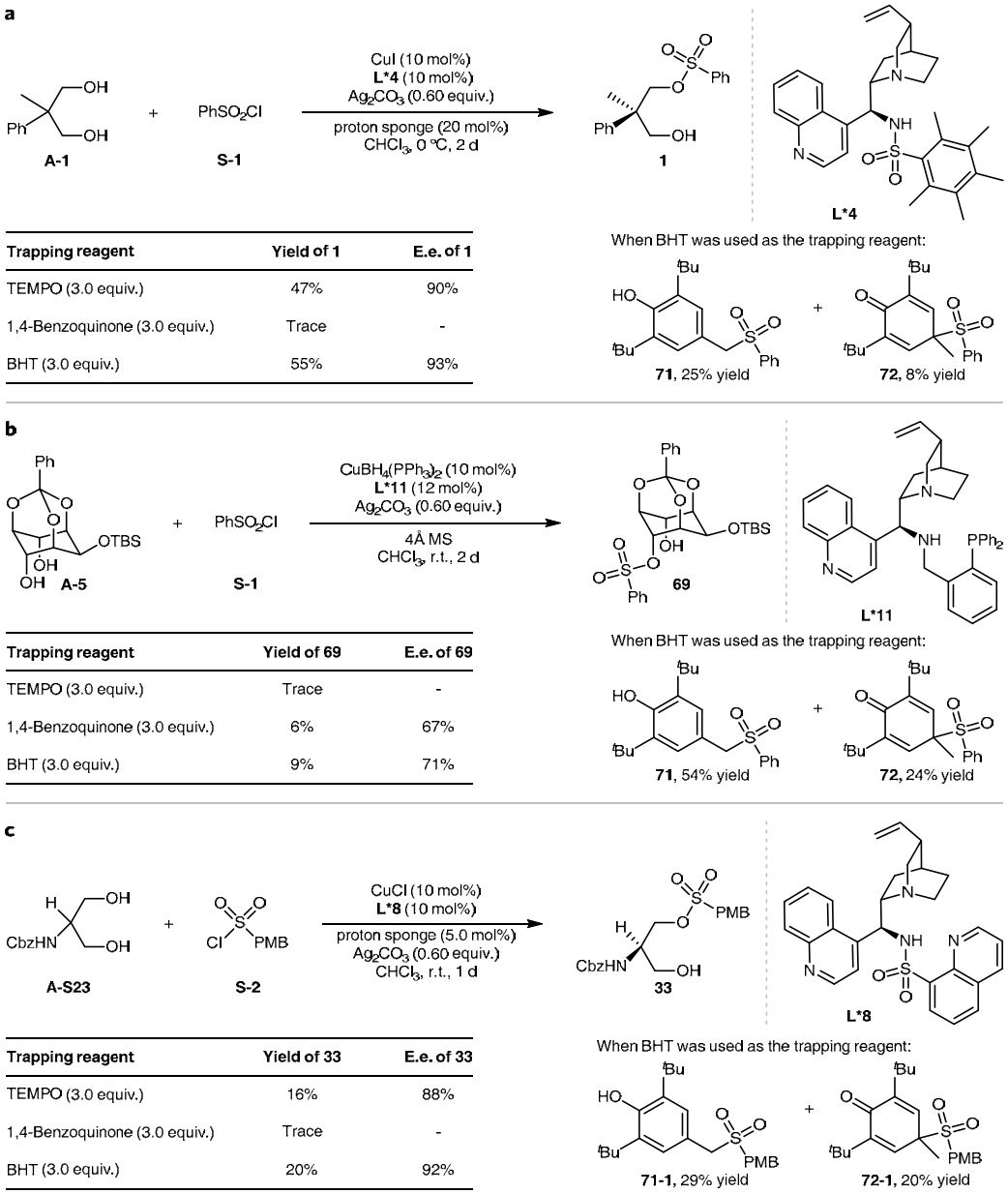
^{13}C NMR (100 MHz, D_2O) δ 77.9 (d, *J* = 6.0 Hz), 73.6 (d, *J* = 3.0 Hz), 72.1, 71.9, 70.9. 70.8 (d, *J* = 2.9 Hz).

^{31}P NMR (162 MHz, D_2O) δ 1.46.

HRMS (ESI) *m/z* calcd. for $C_6H_{12}O_9P$ $[M – 2Na + H]^-$ 259.0224, found 259.0224.

Mechanistic study

A. Radical inhibition experiments

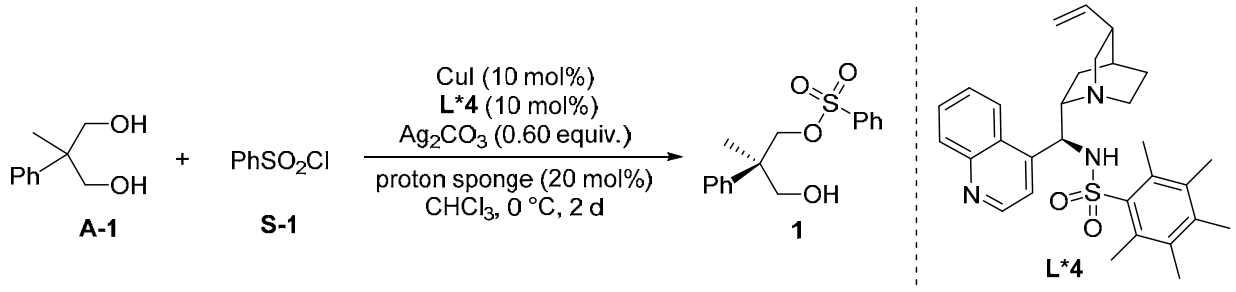


Trapping reagent	Yield of 1	E.e. of 1
TEMPO (3.0 equiv.)	47%	90%
1,4-Benzoquinone (3.0 equiv.)	Trace	-
BHT (3.0 equiv.)	55%	93%

Trapping reagent	Yield of 69	E.e. of 69
TEMPO (3.0 equiv.)	Trace	-
1,4-Benzoquinone (3.0 equiv.)	6%	67%
BHT (3.0 equiv.)	9%	71%

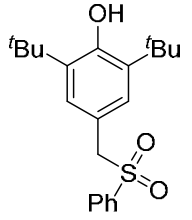
Trapping reagent	Yield of 33	E.e. of 33
TEMPO (3.0 equiv.)	16%	88%
1,4-Benzoquinone (3.0 equiv.)	Trace	-
BHT (3.0 equiv.)	20%	92%

Supplementary Fig. 1 | Radical inhibition experiments.

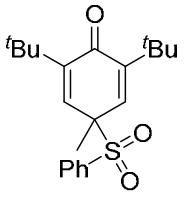


Trapping reagents	Yield of **1**	E.e. of **1**
TEMPO (3.0 equiv.)	47%	90%
1,4-Benzoquinone (3.0 equiv.)	trace	-
BHT (3.0 equiv.)	55%	93%

When BHT was used as the trapping reagent:



71, 25% yield

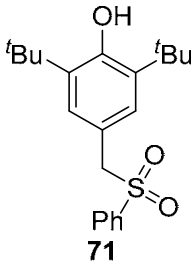


72, 8% yield

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (33.2 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L*4** (10.1 mg, 0.020 mmol, 10 mol%), Ag_2CO_3 (33.1 mg, 0.12 mmol, 0.60 equiv.), proton sponge (8.6 mg, 0.040 mmol, 0.20 equiv.), the corresponding trapping reagent (3.0 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then, benzenesulfonyl chloride **S-1** (30.7 μL, 0.24 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at 0 ℃ for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo.* The residue was purified with column chromatography (petroleum ether/EtOAc = 4/1) to give product **1**.

Note: When **BHT** was used as the trapping reagent, the residue was purified with column chromatography to afford **71** (21.5 mg, 25% yield) and **72** (7.0 mg, 8% yield) (both yields are based on benzenesulfonyl chloride).

2,6-Di-*tert*-butyl-4-((phenylsulfonyl)methyl)phenol (71)



71

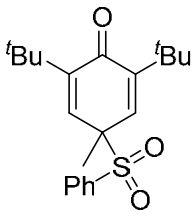
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.75 (s, 2H), 5.25 (s, 1H), 4.22 (s, 2H), 1.32 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 137.8, 136.0, 133.3, 128.8, 128.6, 127.6, 118.7, 63.1, 34.1, 30.0.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{28}NaO_3S$ $[M + Na]^+$ 383.1651, found 383.1651.

The NMR spectroscopic data match with those in literature[6].

2,6-Di-*tert*-butyl-4-methyl-4-(phenylsulfonyl)cyclohexa-2,5-dien-1-one (72)



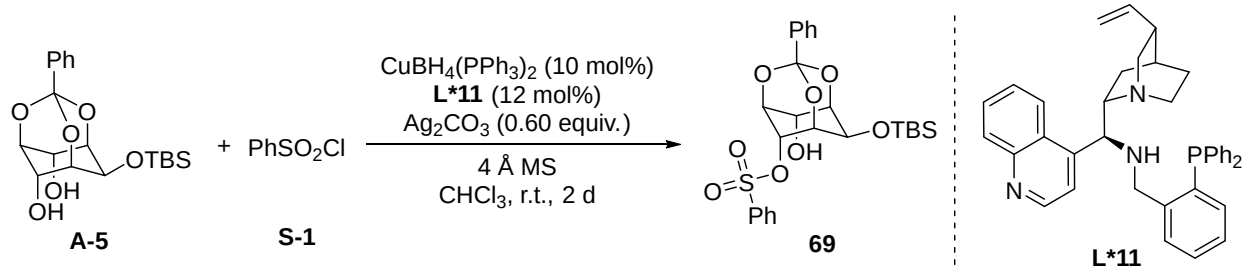
72

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.65 (s, 2H), 1.83 (s, 3H), 1.10 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 151.3, 135.5, 134.1, 133.4, 130.3, 128.2, 65.8, 35.2, 29.0, 18.4.

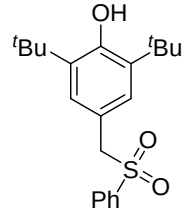
HRMS (ESI) *m/z* calcd. for $C_{21}H_{28}NaO_3S$ $[M + Na]^+$ 383.1651, found 383.1653.

The NMR spectroscopic data match with those in literature[7] and the structure was further confirmed by X-ray diffraction analysis (Supplementary Fig. 23).

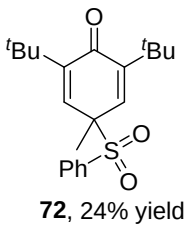


Trapping reagents	Yield of **69**	E.e. of **69**
TEMPO (3.0 equiv.)	trace	-
1,4-Benzoquinone (3.0 equiv.)	6%	67%
BHT (3.0 equiv.)	9%	71%

When BHT was used as the trapping reagent:



71, 54% yield

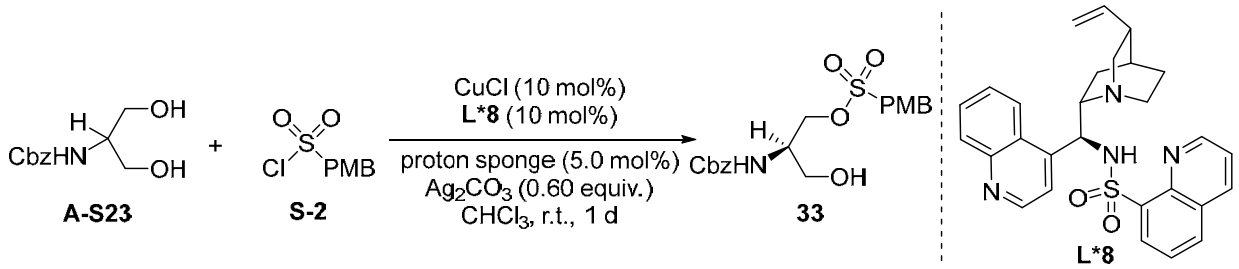


72, 24% yield

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-5** (114.2 mg, 0.30 mmol, 1.0 equiv.), $CuBH_4(PPh_3)_2$ (18.0 mg, 0.030

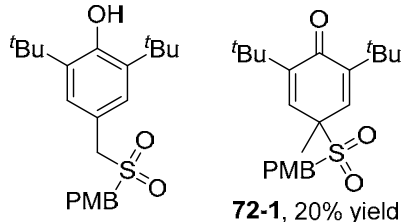
mmol, 10 mol%), **L*11** (20.4 mg, 0.036 mmol, 12 mol%), Ag_2CO_3 (49.6 mg, 0.18 mmol, 0.60 equiv.), 4 Å MS (60.0 mg), the corresponding trapping reagent (3.0 equiv.), and anhydrous $CHCl_3$ (3.0 mL). Then, benzenesulfonyl chloride **S-1** (46.1 μL, 0.36 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at r.t. for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo.* The residue was purified with column chromatography (petroleum ether/EtOAc = 4/1) to give product **69**.

Note: When **BHT** was used as the trapping reagent, the residue was purified with column chromatography to afford **71** (70.0 mg, 54% yield) and **72** (31.2 mg, 24% yield) (both yields are based on benzenesulfonyl chloride).



Trapping reagents	Yield of **33**	E.e. of **33**
TEMPO (3.0 equiv.)	16%	88%
1,4-Benzoquinone (3.0 equiv.)	trace	-
BHT (3.0 equiv.)	20%	92%

When BHT was used as the trapping reagent:



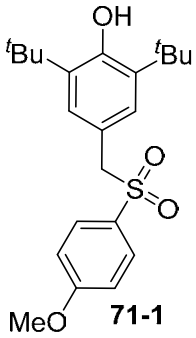
71-1, 29% yield

72-1, 20% yield

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-S23** (45.1 mg, 0.20 mmol, 1.0 equiv.), CuCl (2.0 mg, 0.020 mmol, 10 mol%), **L*8** (9.7 mg, 0.020 mmol, 10 mol%), Ag_2CO_3 (33.0 mg, 0.12 mmol, 0.60 equiv.), proton sponge (2.2 mg, 0.010 mmol, 5.0 mol%), the corresponding trapping reagent (3.0 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then, 4-methoxybenzenesulfonyl chloride **S-2** (49.5 mg, 0.24 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at r.t. for 1 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo.* The residue was purified by column chromatography on basic aluminum oxide (CH_2Cl_2/MeOH = 200/1 ~ 80/1) to give product **33**.

Note: When **BHT** was used as the trapping reagent, the residue was purified with column chromatography to afford **71-1** (27.2 mg, 29% yield) and **72-1** (18.5 mg, 20% yield) (both yields are based on 4-methoxybenzenesulfonyl chloride).

2,6-Di-*tert*-butyl-4-(((4-methoxyphenyl)sulfonyl)methyl)phenol (71-1)



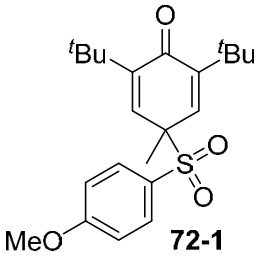
71-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.77 (s, 2H), 5.27 (s, 1H), 4.21 (s, 2H), 3.86 (s, 3H), 1.35 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 154.2, 136.0, 131.0, 129.4, 127.7, 119.1, 113.8, 63.4, 55.6, 34.1, 30.1.

HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}NO_2$ $[M - H]^+$ 389.1792, found 389.1787.

2,6-Di-*tert*-butyl-4-((4-methoxyphenyl)sulfonyl)-4-methylcyclohexa-2,5-dien-1-one (72-1)



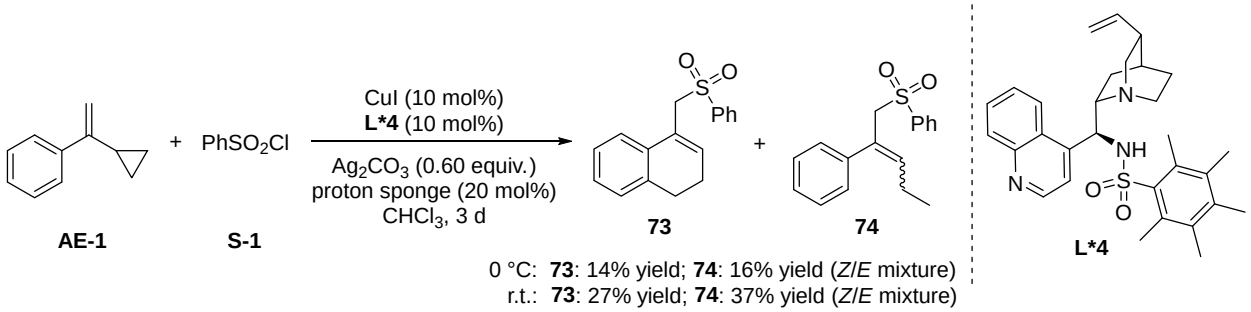
72-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 2H), 3.82 (s, 3H), 1.83 (s, 3H), 1.13 (s, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 164.1, 151.2, 135.8, 132.4, 124.9, 113.4, 65.9, 55.7, 35.2, 29.0, 18.6.

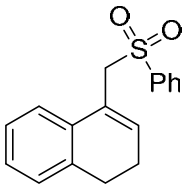
HRMS (ESI) *m/z* calcd. for $C_{10}H_{15}NO_2$ $[M + Na]^+$ 413.1757, found 413.1758.

B. Radical clock experiments



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene **AE-1** (68.4 mg, 0.60 mmol, 3.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L*4** (10.1 mg, 0.020 mmol, 10 mol%), Ag_2CO_3 (33.1 mg, 0.12 mmol, 0.60 equiv.), proton sponge (8.6 mg, 0.040 mmol, 0.20 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then, benzenesulfonyl chloride **S-1** (25.6 μL, 0.20 mmol, 1.0 equiv.) was added to the mixture and the reaction mixture was stirred at 0 ℃ or r.t. for 3 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 10/1) to give products **73** and **74**.

4-((Phenylsulfonyl)methyl)-1,2-dihydronaphthalene (73)



73

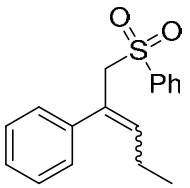
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.13 – 7.05 (m, 4H), 5.91 (t, *J* = 4.6 Hz, 1H), 4.22 (s, 2H), 2.71 – 2.65 (m, 2H), 2.27 – 2.17 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 135.8, 134.9, 133.6, 132.5, 128.7, 128.6, 127.6, 127.4, 126.3, 125.7, 123.1, 59.9, 27.6, 23.3.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}O_2S$ $[M + H]^+$ 285.0944, found 285.0943.

The NMR spectroscopic data match with those in literature[8].

((2-Phenylpent-2-en-1-yl)sulfonyl)benzene (74)



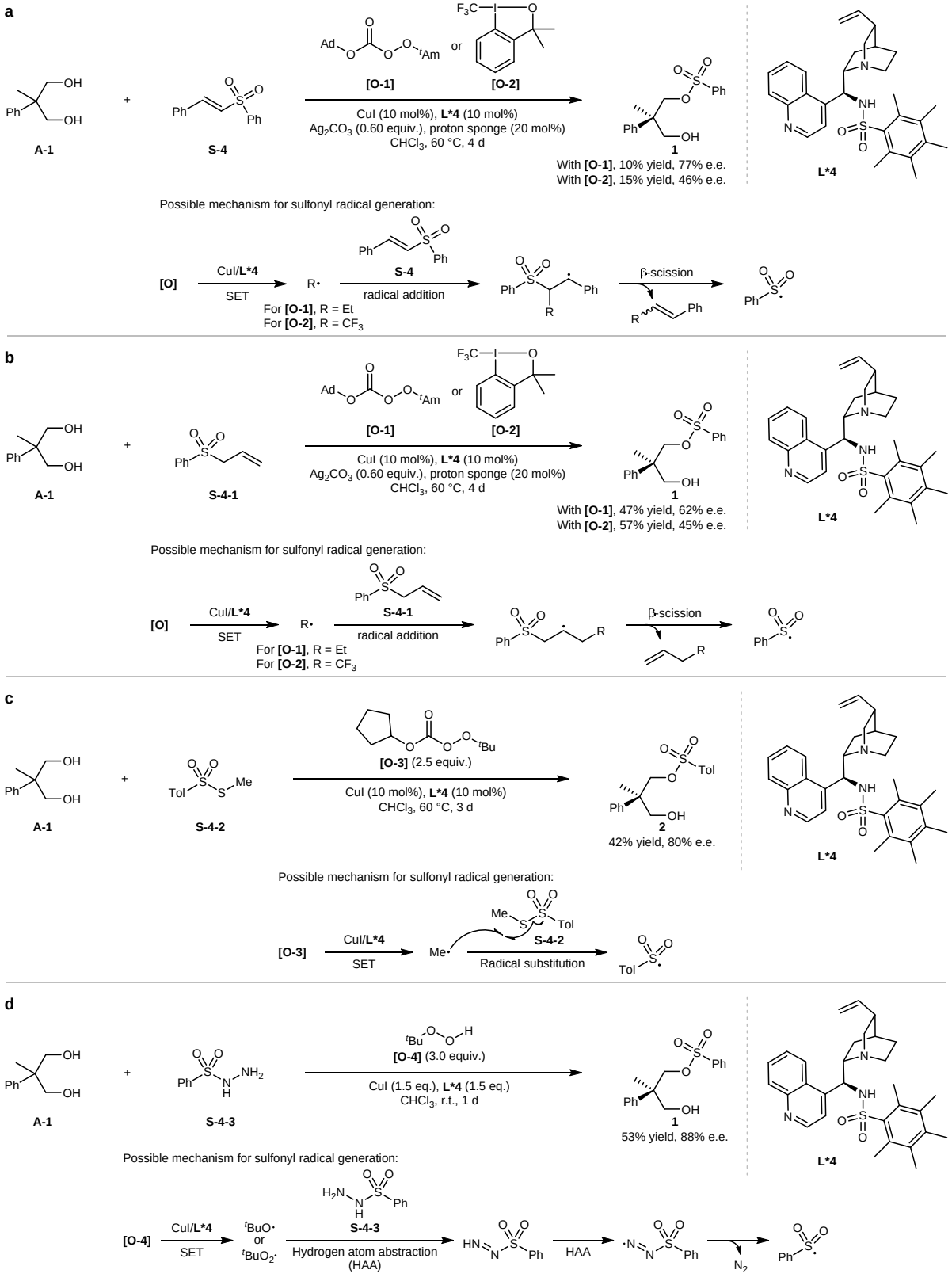
74

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H + 2H × 0.7), 7.56 (t, *J* = 7.6 Hz, 1 H × 0.7), 7.50 (t, *J* = 7.4 Hz, 2H × 0.7), 7.44 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.13 (m, 3H + 4H × 0.7), 7.04 (d, *J* = 6.6 Hz, 1H), 5.96 (t, *J* = 7.4 Hz, 1H), 5.60 (t, *J* = 7.5 Hz, 1H × 0.7), 4.36 (s, 2H), 4.12 (s, 2H × 0.7), 2.08 (p, *J* = 7.5 Hz, 2H), 1.99 (p, *J* = 7.5 Hz, 2H × 0.7), 0.96 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H × 0.7).

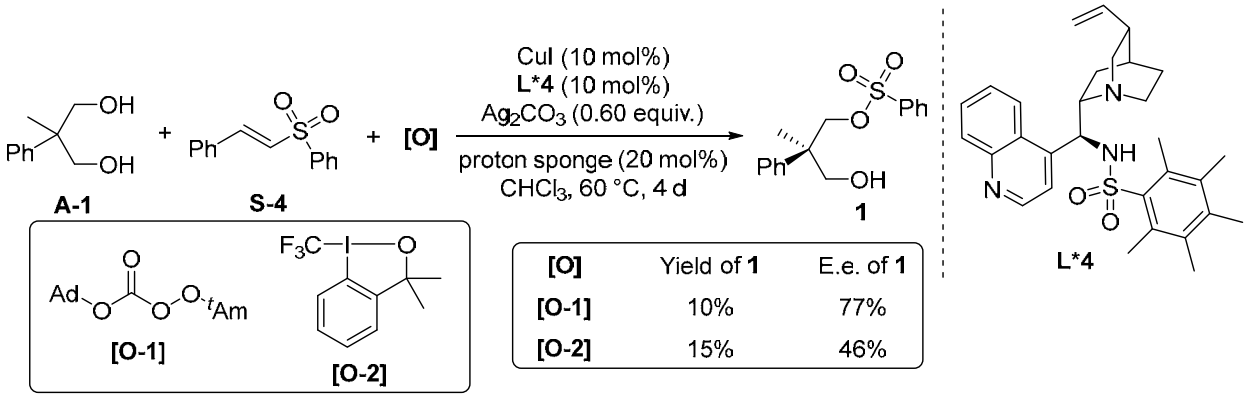
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.39, 140.38, 139.0, 138.8, 138.3, 133.5, 133.4, 128.9, 128.8, 128.53, 128.50, 128.49, 128.3, 128.1, 127.5, 127.23, 127.20, 127.1, 126.4, 65.0, 57.6, 22.8, 22.7, 13.9, 13.6.

HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}O_2S$ $[M + H]^+$ 287.1100, found 287.1099.

C. Copper catalyzed enantioselective S–O cross-coupling using an alternative method for generating sulfonyl radical

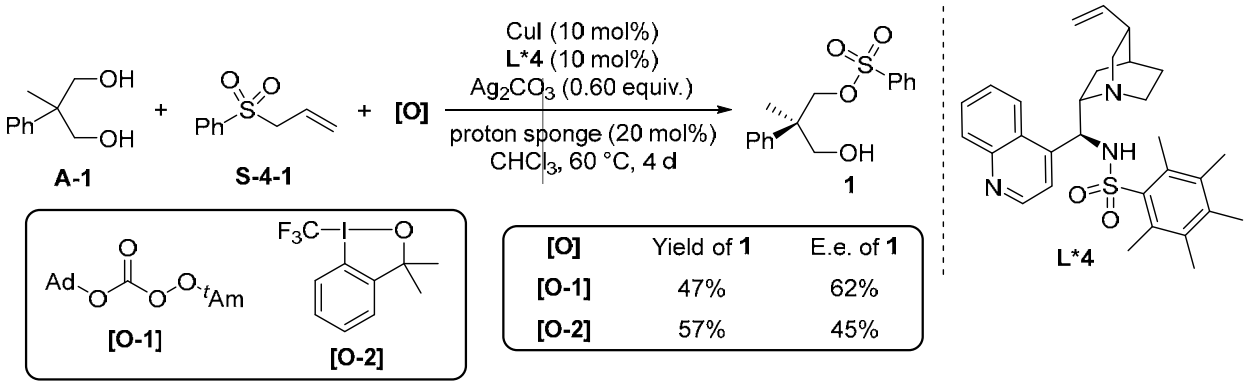


Supplementary Fig. 2 | Copper-catalyzed enantioselective S–O cross-coupling using alternative methods for generating sulfonyl radical. Possible reaction pathways are drawn by referring to literature (**a**[9–11]; **b**[9,12–14]; **c**[15];**d**[16]).



[O]	Yield of **1**	E.e. of **1**
[O-1]	10%	77%
[O-2]	15%	46%

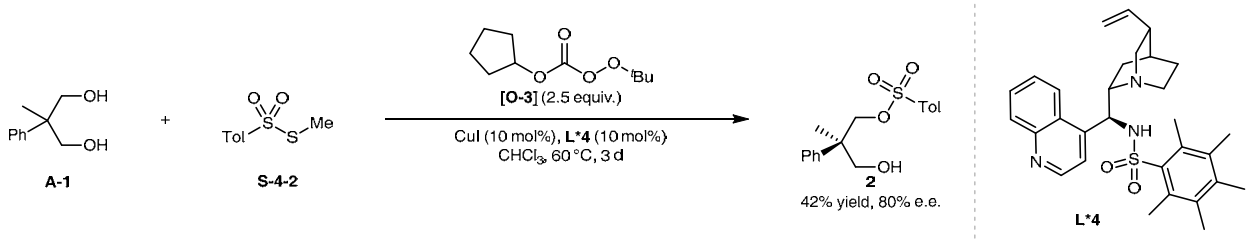
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (33.2 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L*4** (10.1 mg, 0.020 mmol, 10 mol%), Ag_2CO_3 (33.1 mg, 0.12 mmol, 0.60 equiv.), proton sponge (8.6 mg, 0.040 mmol, 0.20 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then, (*E*)-(2-(phenylsulfonyl)vinyl)benzene **S-4** (97.7 mg, 0.40 mmol, 2.0 equiv.) and the corresponding oxidant **[O]** (2.0 equiv.) were added into the mixture and the reaction mixture was stirred at 60 ℃ for 4 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo.* The residue was purified with column chromatography (petroleum ether/EtOAc = 4/1) to give product **1**.



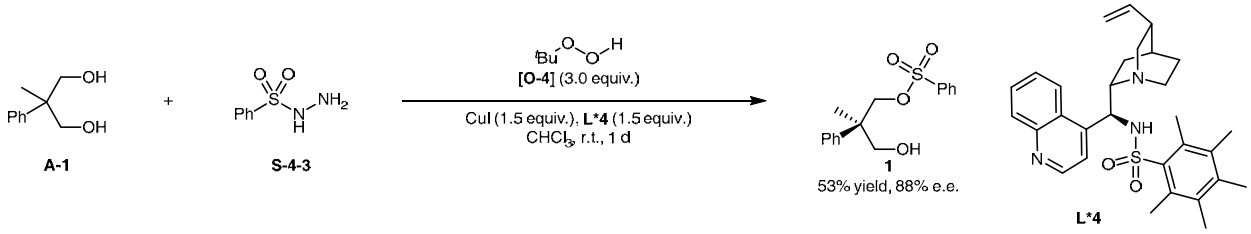
[O]	Yield of **1**	E.e. of **1**
[O-1]	47%	62%
[O-2]	57%	45%

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (33.2 mg, 0.20 mmol, 1.0 equiv.), CuI (3.8 mg, 0.020 mmol, 10 mol%), **L*4** (10.1 mg, 0.020 mmol, 10 mol%), Ag_2CO_3 (33.1 mg, 0.12 mmol, 0.60 equiv.), proton sponge (8.6 mg, 0.040 mmol, 0.20 equiv.), and anhydrous $CHCl_3$ (2.0 mL). Then, (allylsulfonyl)benzene **S-4-1** (62.0 µL, 0.40 mmol, 2.0 equiv.) and the corresponding oxidant **[O]** (2.0 equiv.) were added into the mixture and the reaction mixture was stirred at 60 ℃ for 4 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in*

vacuo. The residue was purified with column chromatography (petroleum ether/EtOAc = 4/1) to give product **1**.

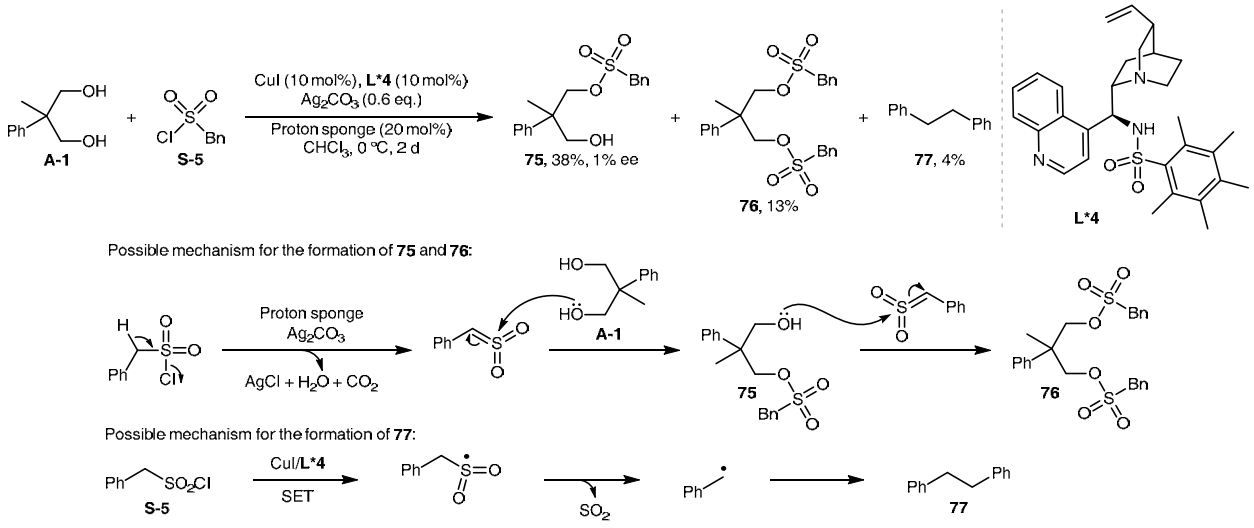


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (8.3 mg, 0.050 mmol, 1.0 equiv.), **S-4-2** (20.2 mg, 0.10 mmol, 2.0 equiv.), CuI (0.95 mg, 0.0050 mmol, 10 mol%), **L*4** (2.5 mg, 0.0050 mmol, 10 mol%), and anhydrous $CHCl_3$ (0.50 mL). Then, **O-3** (25.3 mg, 0.125 mmol, 2.5 equiv.) was added to the mixture and the reaction mixture was stirred at 60 °C for 3 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 2/1) to give product **2**.

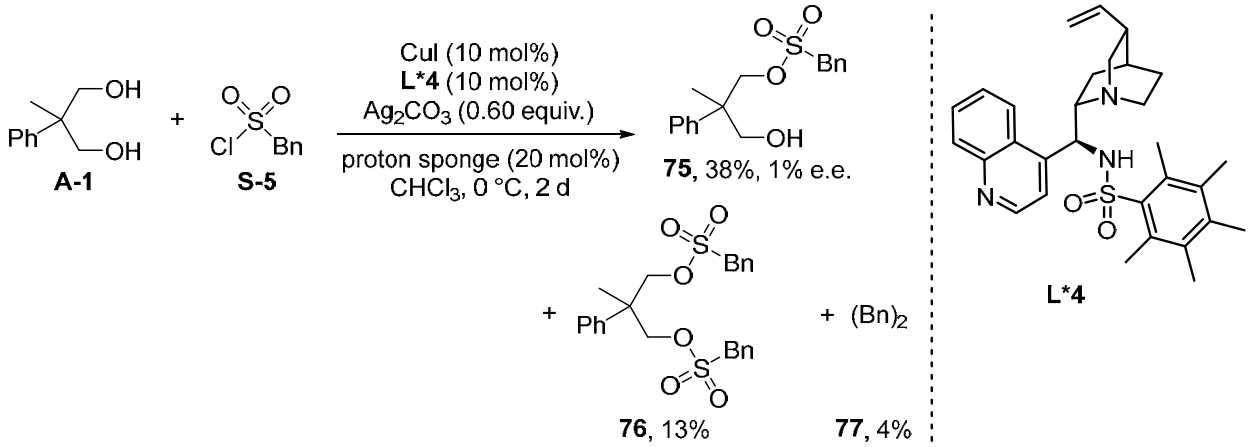


Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (8.3 mg, 0.050 mmol, 1.0 equiv.), **S-4-3** (8.6 mg, 0.050 mmol, 1.0 equiv.), CuI (14.2 mg, 0.075 mmol, 1.5 equiv.), **L*4** (37.8 mg, 0.075 mmol, 1.5 equiv.), and anhydrous $CHCl_3$ (1.0 mL). Then, **O-4** (30 µL, 5.0–6.0 mol/L in decane, 0.15 mmol, 3.0 equiv.) was added into the mixture and the reaction mixture was stirred at r.t. for 1 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1**.

D. Control experiment with unstable benzyl sulfonyl radical

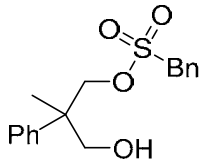


Supplementary Fig. 3 | Control experiment with unstable benzyl sulfonyl radical. Possible pathways for the formation of **75**/**76**[17] and **77**[18–20] were drawn by referring to literature.



Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (166.0 mg, 1.0 mmol, 1.0 equiv.), CuI (19.0 mg, 0.10 mmol, 10 mol%), **L*4** (50.4 mg, 0.10 mmol, 10 mol%), Ag_2CO_3 (165.6 mg, 0.60 mmol, 0.60 equiv.), proton sponge (42.8 mg, 0.20 mmol, 0.20 equiv.), and anhydrous $CHCl_3$ (10.0 mL). Then, phenylmethanesulfonyl chloride **S-5** (228.8 mg, 1.2 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at 0 °C for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography on silica gel to give **75** (121.9 mg, 38% yield, 1% e.e.), **76** (61.2 mg, 13% yield), and **77** (7.2 mg, 4% yield).

3-Hydroxy-2-methyl-2-phenylpropyl phenylmethanesulfonate (75)



75

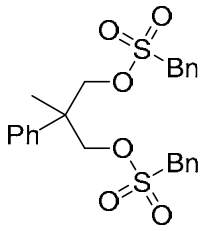
HPLC analysis: Chiralcel ASH (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), t_R (major) = 43.17 min, t_R (minor) = 51.04 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 10H), 4.31 – 4.29 (m, 4H), 3.73 – 3.66 (m, 2H), 1.79 (br s, 1H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 130.7, 129.1, 128.9, 128.7, 127.6, 127.1, 126.4, 73.7, 67.0, 56.6, 43.9, 20.2.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{28}NaO_3S$ $[M + Na]^+$ 343.0975, found 343.0976.

2-Methyl-2-phenylpropane-1,3-diyl bis(phenylmethanesulfonate) (76)



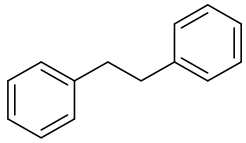
76

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 13H), 7.22 – 7.17 (m, 2H), 4.23 (s, 4H), 4.19 (s, 4H), 1.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 130.6, 129.0, 128.8, 128.7, 127.6, 127.4, 126.0, 72.6, 56.6, 42.4, 20.2.

HRMS (ESI) *m/z* calcd. for $C_{21}H_{28}NaO_3S$ $[M + Na]^+$ 497.1063, found 497.1060.

1,2-Diphenylethane (77)



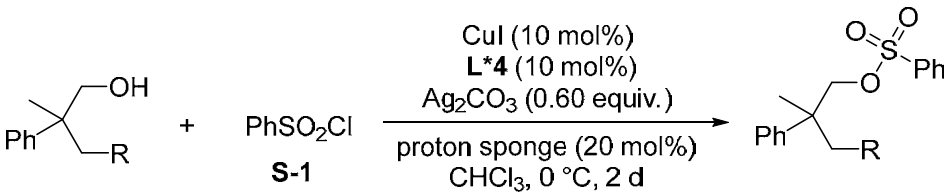
77

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 4H), 7.21 – 7.18 (m, 6H), 2.92 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 128.4, 128.3, 125.9, 37.9.

The NMR spectroscopic data match with those in the literature[21].

E. Control experiments with monoalcohols

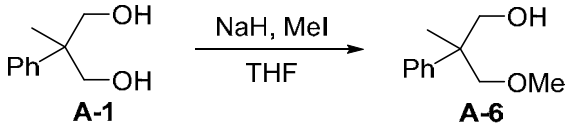


A-6, R = OMe
A-7, R = Me
A-8, R = OSO_2Ph

78, R= OMe, 0% y; recovery of **A-6**: 87% y
79, R= Me, 0% y; recovery of **A-7**: 84% y
80, R = OSO_2Ph, 0% y; recovery of **A-8**: 88% y, 0% e.e.

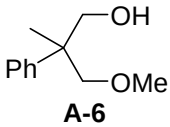
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (5.7 mg, 0.030 mmol, 10 mol%), **L*4** (15.1 mg, 0.030 mmol, 10 mol%), Ag_2CO_3 (49.6 mg, 0.18 mmol, 0.60 equiv.), proton sponge (12.8 mg, 0.060 mmol, 0.20 equiv.), the corresponding racemic monoalcohol (0.30 mmol, 1.0 equiv.), and anhydrous $CHCl_3$ (3.0 mL). Then, benzenesulfonyl chloride **S-1** (46.1 μL, 0.36 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at 0 ℃ for 2 d. Then, the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel.

The synthesis of A-6



To a solution of diol **A-1** (332.0 mg, 2.0 mmol) in dry THF (10.0 mL) was added NaH (60% dispensed in mineral oil, 88.0 mg, 2.2 mmol, 1.1 equiv.) in four portions at 0 °C under inert atmosphere. After stirring for 30 min, methyl iodide (312.0 mg, 2.2 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to r.t. and stirred overnight. Then the reaction was quenched with saturated NH_4Cl (aq.) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1 ~ 5/1) to give product **A-6** (241.5mg, 67% yield) as a colorless oil.

3-Methoxy-2-methyl-2-phenylpropan-1-ol (A-6)

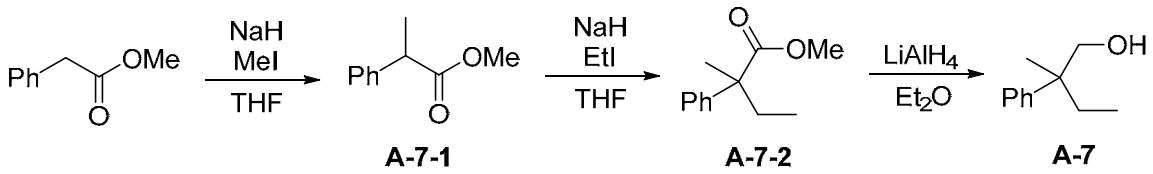


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.18 (m, 1H), 3.87 (d, *J* = 11.0 Hz, 1H), 3.77 – 3.69 (m, 2H), 3.55 (d, *J* = 9.1 Hz, 1H), 3.35 (s, 3H), 2.48 (br s, 1H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 128.3, 126.4, 126.3, 80.1, 70.2, 59.3, 43.7, 21.0.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NaO_2$ $[M + Na]^+$ 203.1043, found 203.1042.

The synthesis of A-7



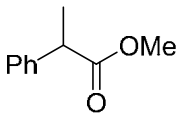
A-7-1 **A-7-2** **A-7**

Step 1: To a solution of methyl 2-phenylacetate (1.5 g, 10.0 mmol) in dry THF (50.0 mL) was added NaH (60% dispensed in mineral oil, 440.0 mg, 11.0 mmol, 1.1 equiv.) in four portions at 0 °C under inert atmosphere. After stirring for 30 min, methyl iodide (1.56 g, 11.0 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to r.t. and stirred overnight. Then the reaction was quenched with saturated NH_4Cl (aq.) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 80/1 ~ 40/1) to give product **A-7-1** (1.02 g, 62% yield) as a colorless oil.

Step 2: To a solution of methyl 2-phenylpropanoate **A-7-1** (1.02 g, 6.2 mmol) in dry THF (30.0 mL) was added NaH (60% dispensed in mineral oil, 273.3 mg, 6.8 mmol, 1.1 equiv.) in four portions at 0 °C under inert atmosphere. After stirring for 30 min, ethyl iodide (1.06 g, 6.8 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was warmed to r.t. and stirred overnight. Then the reaction was quenched with saturated NH_4Cl (aq.) and extracted with CH_2Cl_2 (3x). The combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 100/1) to give product **A-7-2** (0.75 g, 63% yield) as a colorless oil.

Step 3: To a suspension of $LiAlH_4$ (444.6 mg, 11.7 mmol, 3.0 equiv.) in Et_2O (15.0 mL) at 0 °C was slowly added a solution of **A-7-2** (0.75 g, 3.9 mmol) in Et_2O (5.0 mL). Then the reaction mixture was warmed to r.t. and stirred for 2 h. Next, the reaction was quenched by slow, portionwise addition of wet Na_2SO_4 (4.0 mL water in 32.0 g Na_2SO_4) at 0 °C. Upon completion, the mixture was warmed to r.t., stirred for an additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1 ~ 5/1) to give product **A-7** (0.47 g, 73% yield) as a colorless oil.

Methyl 2-phenylpropanoate (A-7-1)

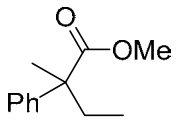


A-7-1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.26 – 7.20 (m, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 3.63 (s, 3H), 1.49 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 140.5, 128.5, 127.4, 127.0, 51.9, 45.3, 18.5.

Methyl 2-methyl-2-phenylbutanoate (A-7-2)

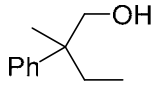


A-7-2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.23 – 7.20 (m, 1H), 3.63 (s, 3H), 2.10 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.95 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.52 (s, 3H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 143.8, 128.2, 126.5, 125.9, 51.9, 50.6, 31.8, 22.1, 9.0.

2-Methyl-2-phenylbutan-1-ol (A-7)



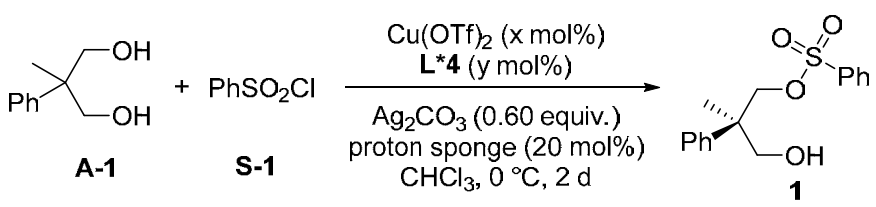
A-7

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 7.22 – 7.15 (m, 1H), 3.64 (d, *J* = 10.9 Hz, 1H), 3.47 (d, *J* = 10.9 Hz, 1H), 1.84 – 1.73 (m, 1H), 1.63 (s, 1H), 1.59 – 1.48 (m, 1H), 1.30 (s, 3H), 0.70 (t, *J* = 7.5 Hz, 3H).

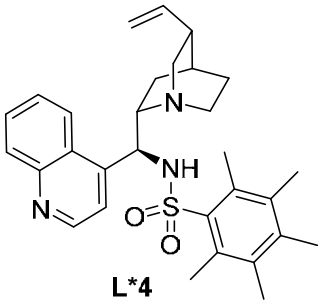
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 128.2, 126.7, 125.9, 72.2, 43.5, 30.7, 20.8, 8.1.

HRMS (ESI) *m/z* calcd. for $C_{11}H_{15}$ $[M + H - H_2O]^+$ 147.1168, found 147.1169.

F. Control experiments with catalytic/stoichiometric $Cu(OTf)_2$



X	Y	Yield of **1**	E.e. of **1**
10	10	92%	91%
100	100	6%	16%



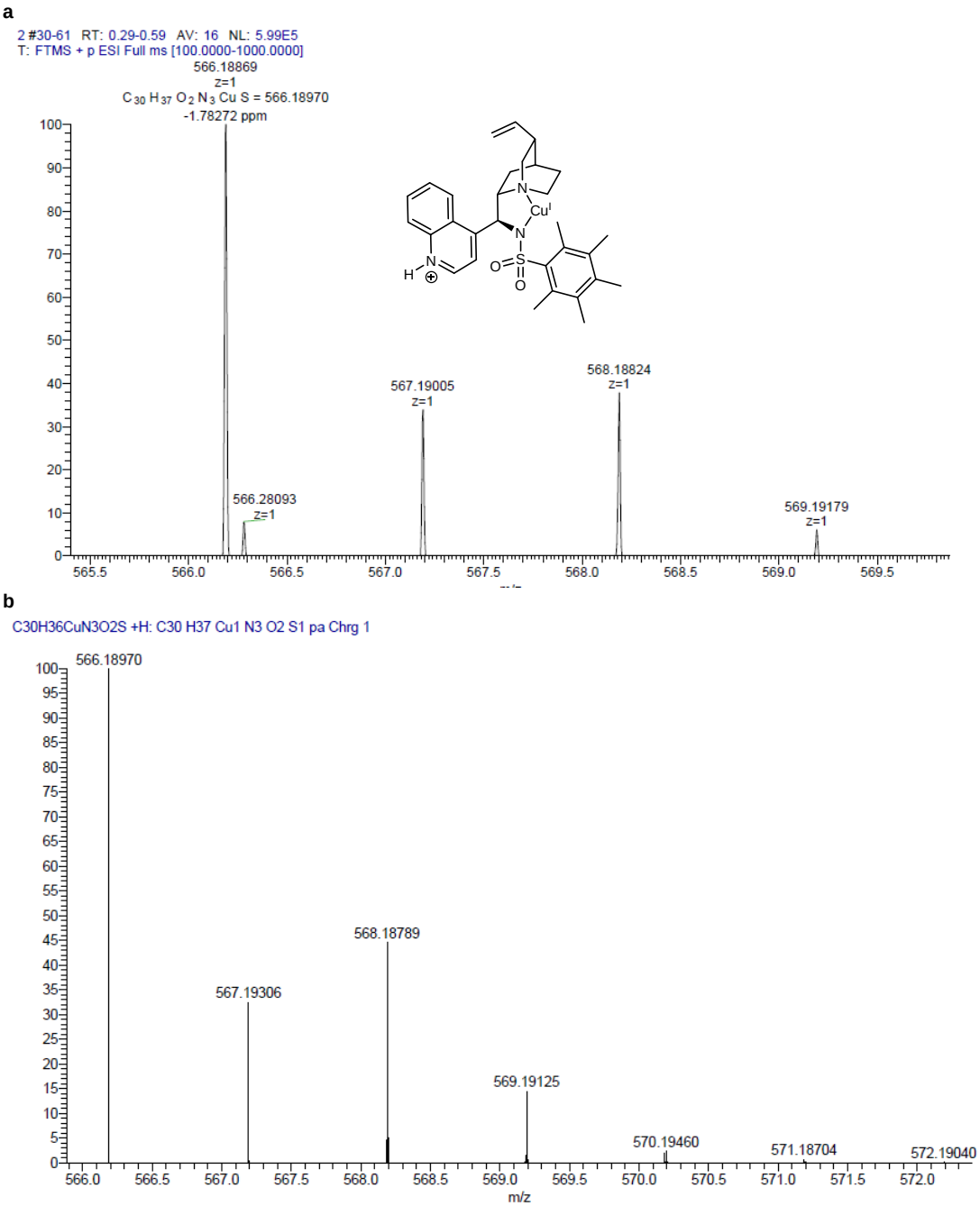
Control experiment with catalytic $Cu(OTf)_2$:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (16.6 mg, 0.10 mmol, 1.0 equiv.), $Cu(OTf)_2$ (3.6 mg, 0.010 mmol, 10 mol%), **L*4** (5.0 mg, 0.010 mmol, 10 mol%), Ag_2CO_3 (16.6 mg, 0.060 mmol, 0.60 equiv.), proton sponge (4.3 mg, 0.020 mmol, 0.20 equiv.), and anhydrous $CHCl_3$ (1.0 mL). Then, benzenesulfonyl chloride **S-1** (15.4 μL, 0.12 mmol, 1.2 equiv.) was added to the mixture and the reaction mixture was stirred at 0 ℃ for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 4/1) to give product **1** (28.1 mg, 92% yield, 91% e.e.).

Control experiment with stoichiometric $Cu(OTf)_2$:

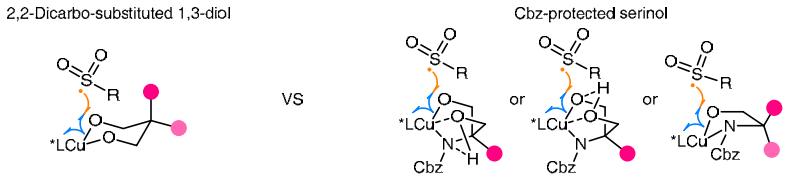
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with substrate **A-1** (16.6 mg, 0.10 mmol, 1.0 equiv.), $Cu(OTf)_2$ (36.2 mg, 0.10 mmol, 100 mol%), **L*4** (50.4 mg, 0.10 mmol, 100 mol%), Ag_2CO_3 (16.6 mg, 0.060 mmol, 0.60 equiv.), proton sponge (4.3 mg, 0.020 mmol, 0.20 equiv.), and anhydrous $CHCl_3$ (1.0 mL). The mixture was stirred at r.t. for 1 h before benzenesulfonyl chloride **S-1** (15.4 μL, 0.12 mmol, 1.2 equiv.) was added at 0 ℃ and the reaction mixture was stirred at 0 ℃ for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 4/1) to give product **1** (1.8 mg, 6% yield, 16% e.e.).

G. High-resolution mass spectroscopic characterization of the catalyst



Supplementary Fig. 4 | Electrospray ionization (ESI) mass spectroscopy (MS) analysis. A solution of $CuBH_4(PPh_3)_2$ (0.10 mmol), **L*4** (0.10 mmol), Ag_2CO_3 (0.60 equiv.), and proton sponge (20 mol%) in DCM (0.10 M) was stirred for 10 h at room temperature. Then the reaction mixture was analyzed by ESI MS, showing a peak at *m*/*z* 566.1887 ascribed to the Cu(I)-**L*4** complex. The observed isotopic distribution (**a**) well matches the calculated one (**b**).

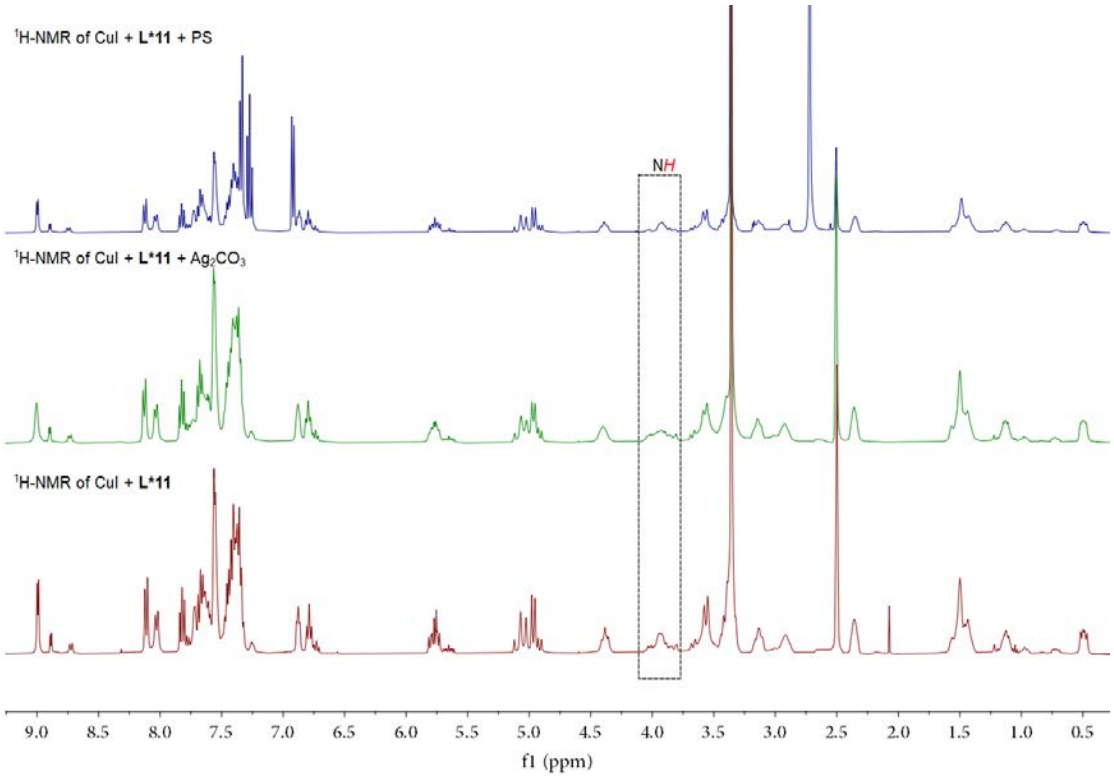
H. Possible changes in the coordination mode of substrates to the copper catalyst



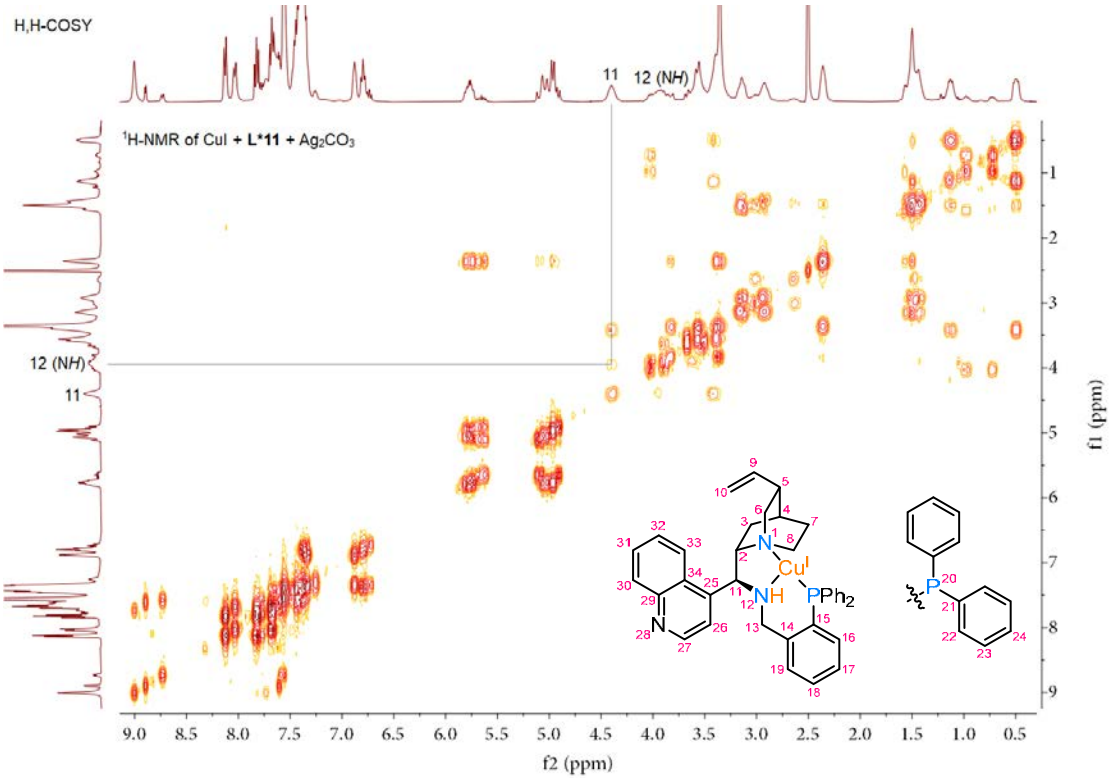
Supplementary Fig. 5 | Possible changes in the coordination mode of substrates to the copper catalyst.

I. NMR experiments with L*11

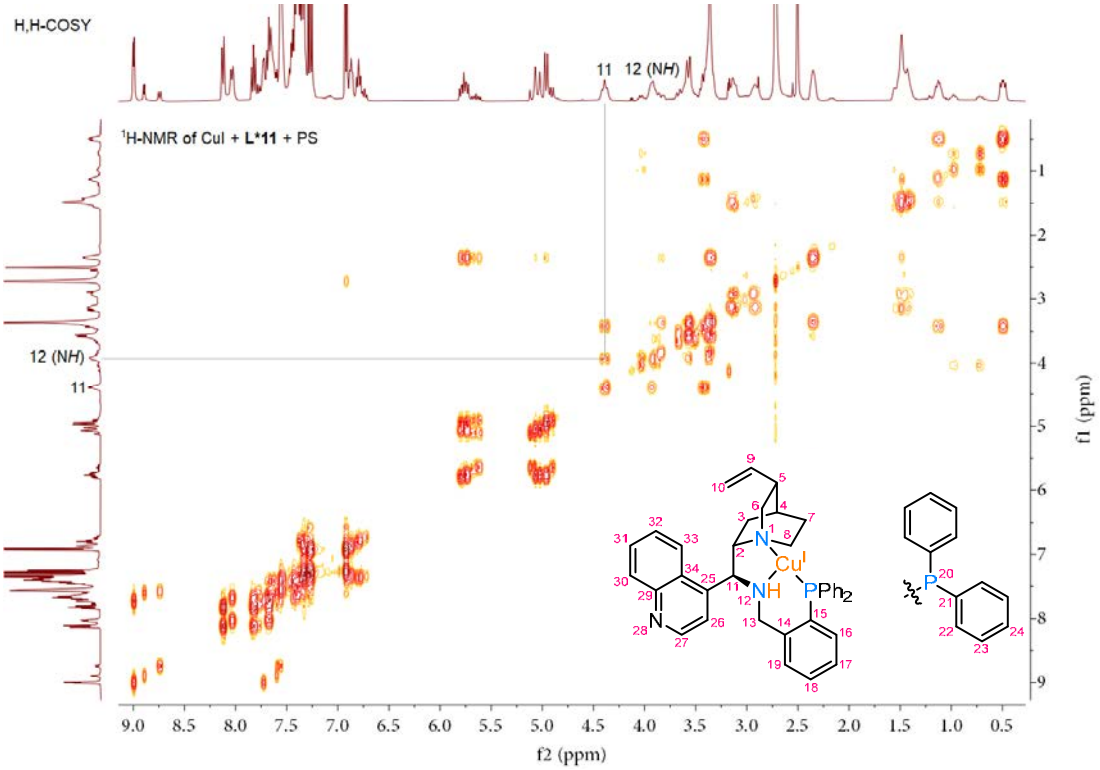
General procedure of the NMR experiments:
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with CuI (4.8 mg, 0.025 mmol, 1.0 equiv.), **L*11** (14.2 mg, 0.025 mmol, 1.0 equiv.), Ag_2CO_3 (6.9 or 0 mg, 0.025 or 0 mmol, 1.0 or 0 equiv.), proton sponge (5.4 or 0 mg, 0.025 or 0 mmol, 1.0 or 0 equiv.), and DMSO-d_6 (0.50 mL). The reaction mixture was stirred at r.t. for 0.5 h before being transferred to an NMR tube under argon for NMR experiments.



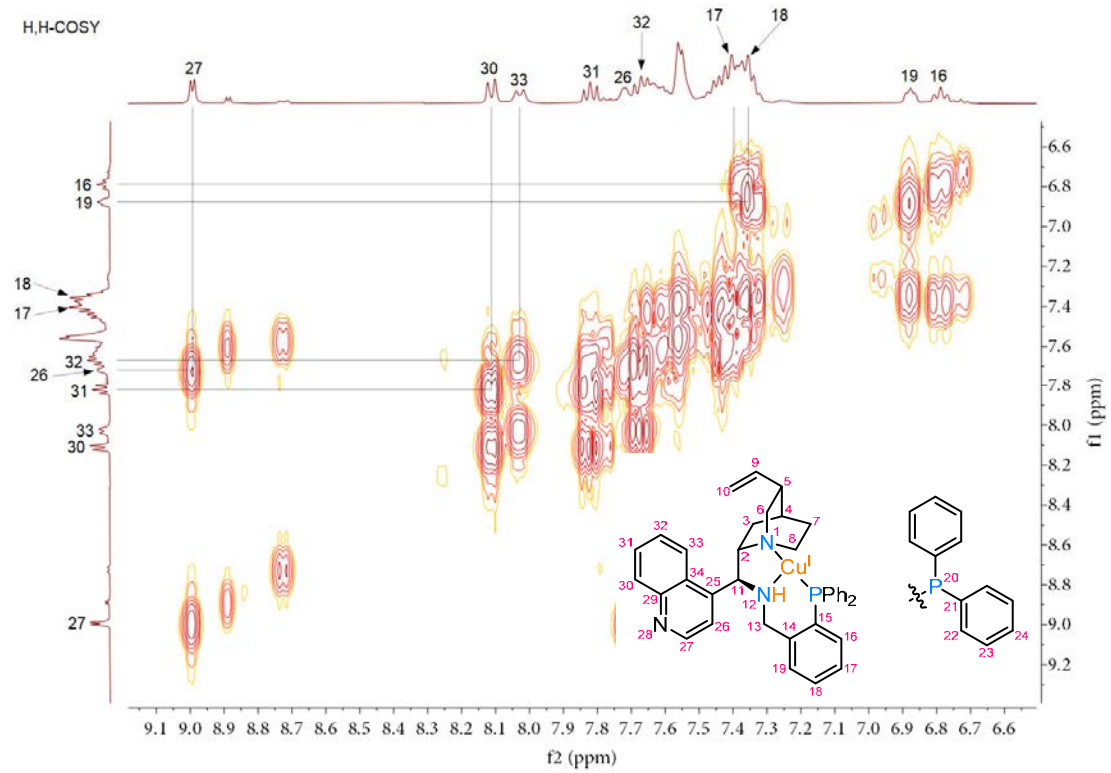
Supplementary Fig. 6 | ^{1}H-NMR spectra of the coordination complex from CuI and L*11 either in the absence (bottom) or in the presence of a base (middle and top) in DMSO-d_6.



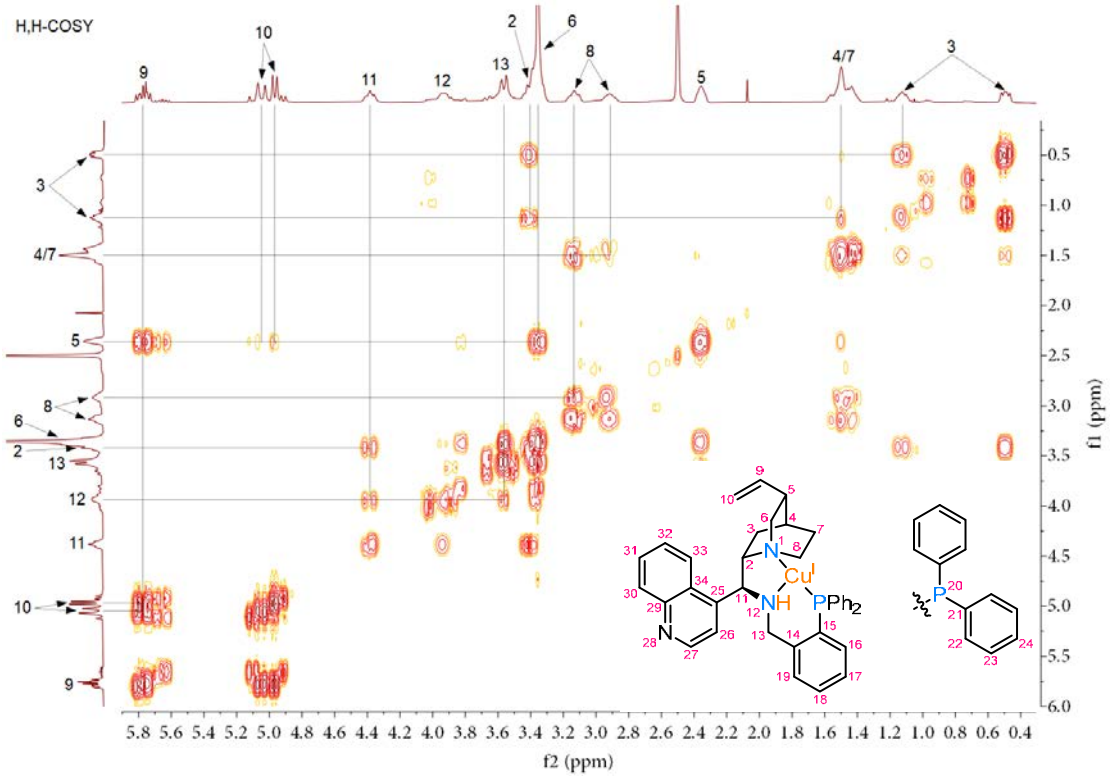
Supplementary Fig. 7 | ^{1}H,^{1}H-COSY 2D-NMR spectrum of the coordination complex from CuI and L*11 in the presence of Ag_2CO_3 in DMSO-d_6.



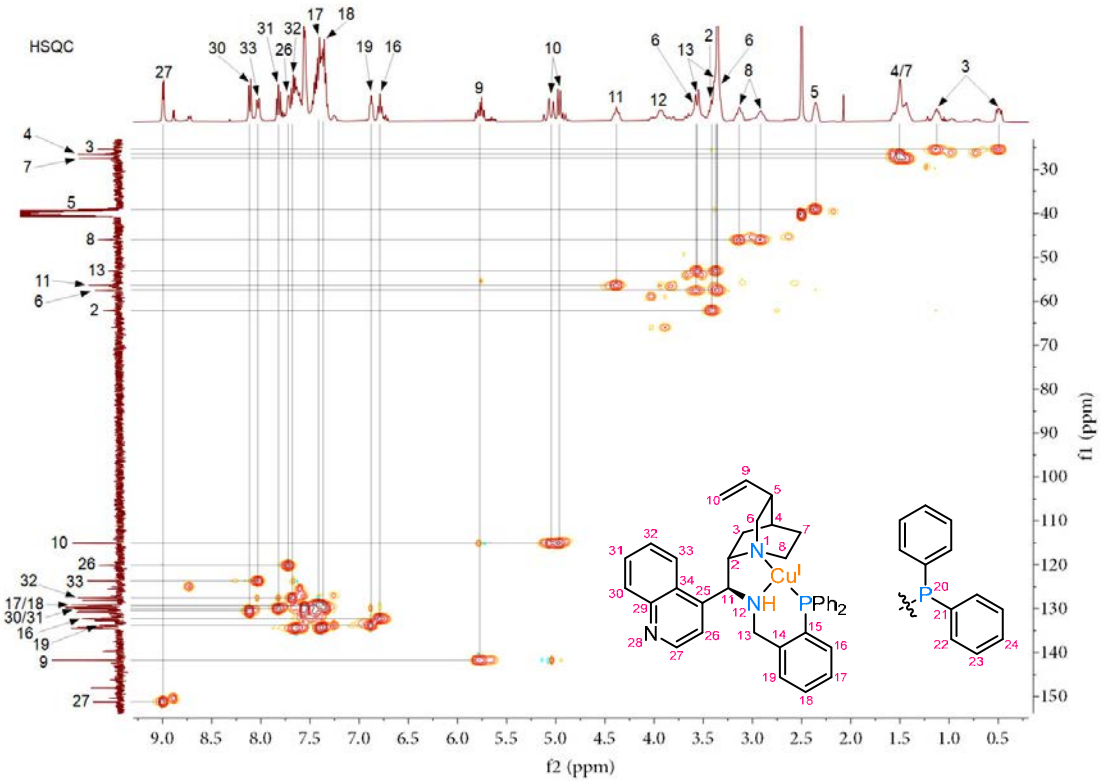
Supplementary Fig. 8 | ^{1}H,^{1}H-COSY 2D-NMR spectrum of the coordination complex from CuI and L*11 in the presence of proton sponge (PS) in DMSO-d_6.



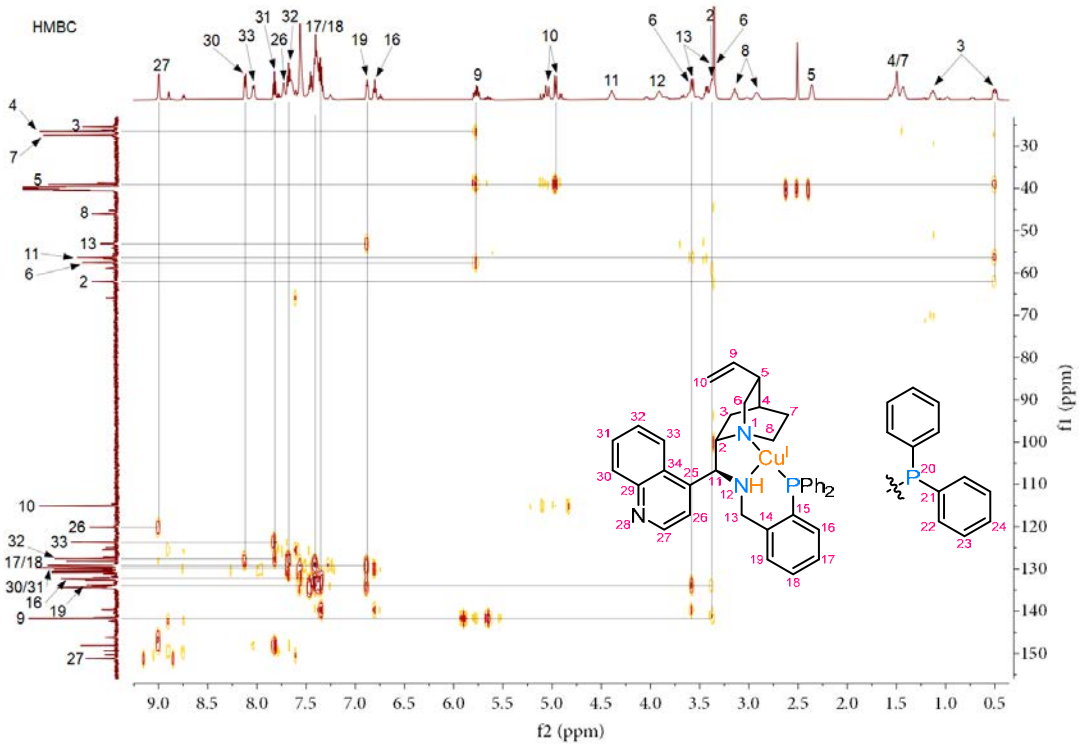
Supplementary Fig. 9 | ^{1}H,^{1}H-COSY 2D-NMR spectrum of the coordination complex from CuI and L*11 in DMSO-d_6 (Part I).



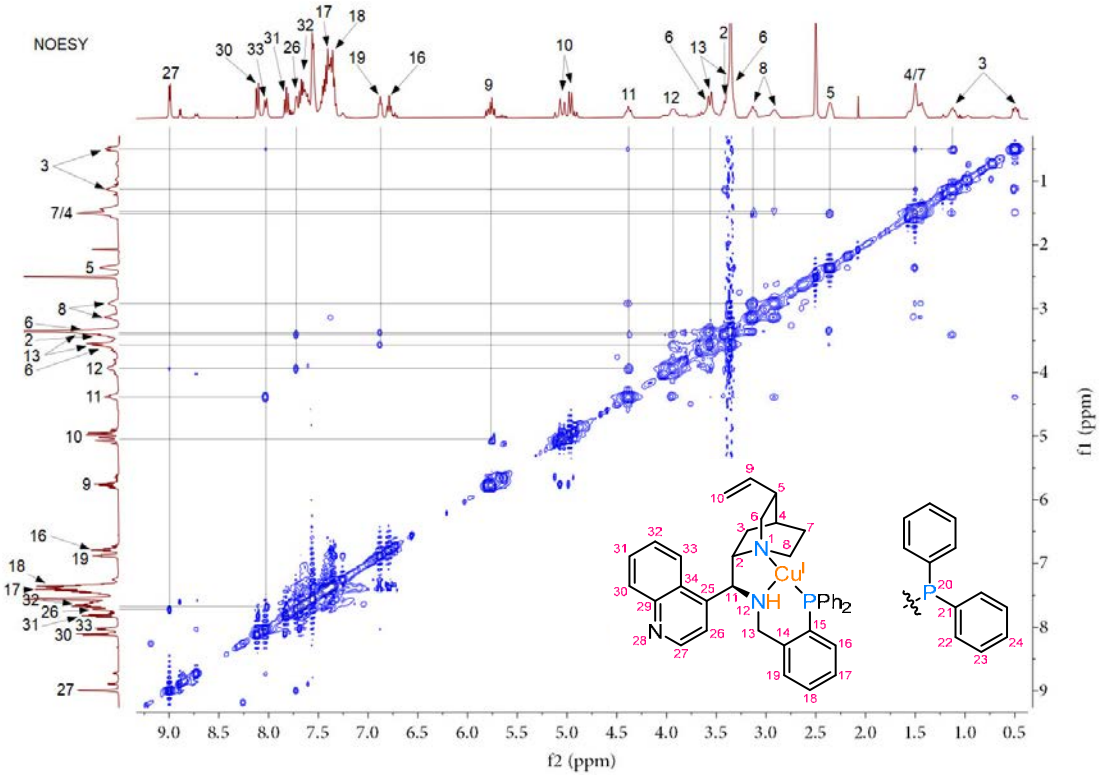
Supplementary Fig. 10 | ^{1}H,^{1}H-COSY 2D-NMR spectrum of the coordination complex from CuI and L*11 in DMSO-d_6 (Part II).



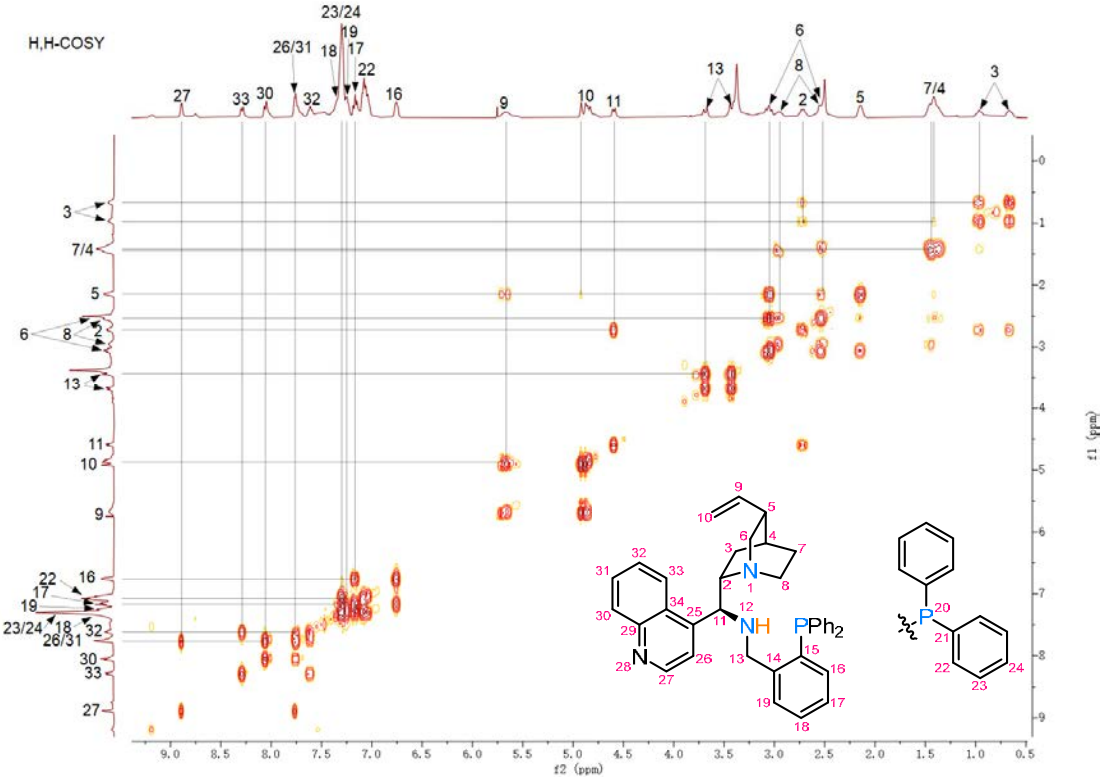
Supplementary Fig. 11 | HSQC 2D-NMR spectrum of the coordination complex from CuI and L*11 in DMSO-d_6.



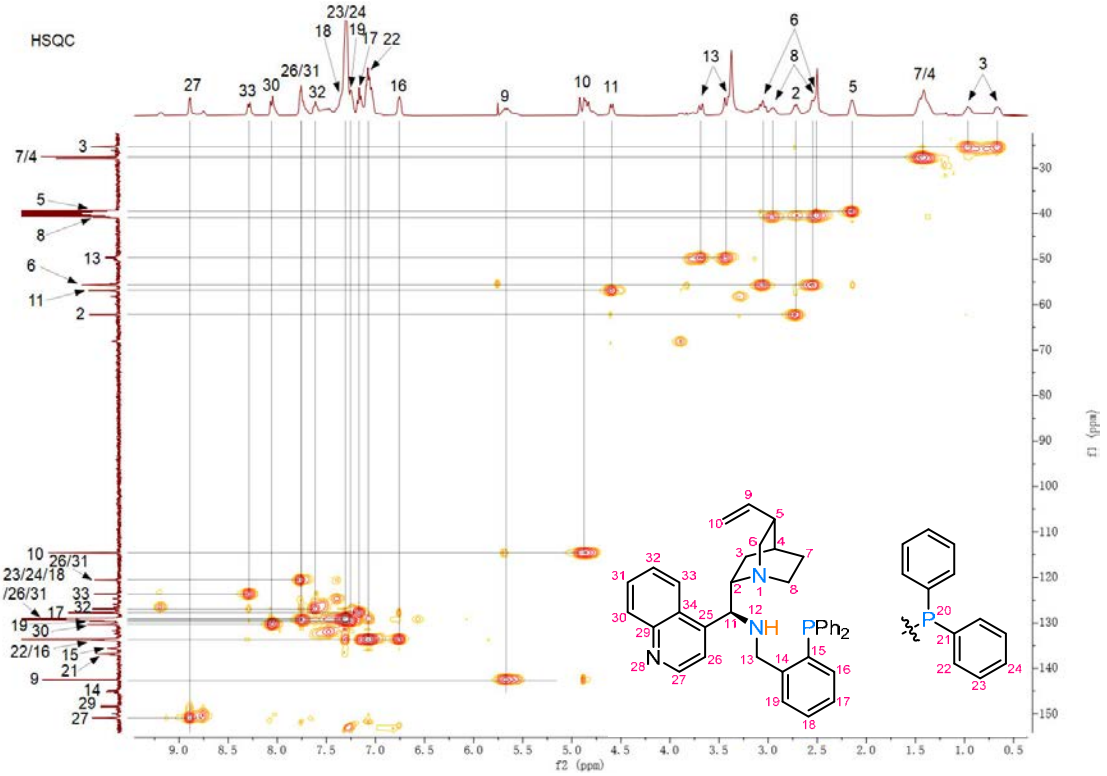
Supplementary Fig. 12 | HMBC 2D-NMR spectrum of the coordination complex from CuI and L*11 in DMSO-d_6.



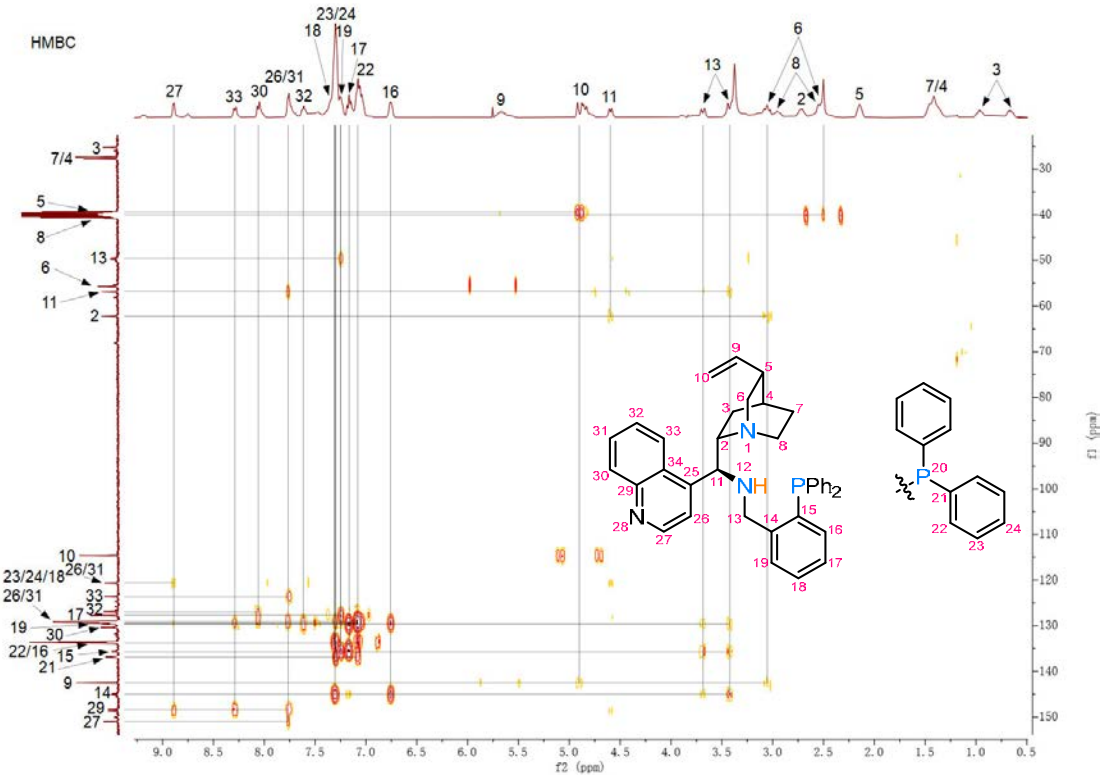
Supplementary Fig. 13 | NOESY 2D-NMR spectrum of the coordination complex from CuI and L*11 in DMSO-d_6.



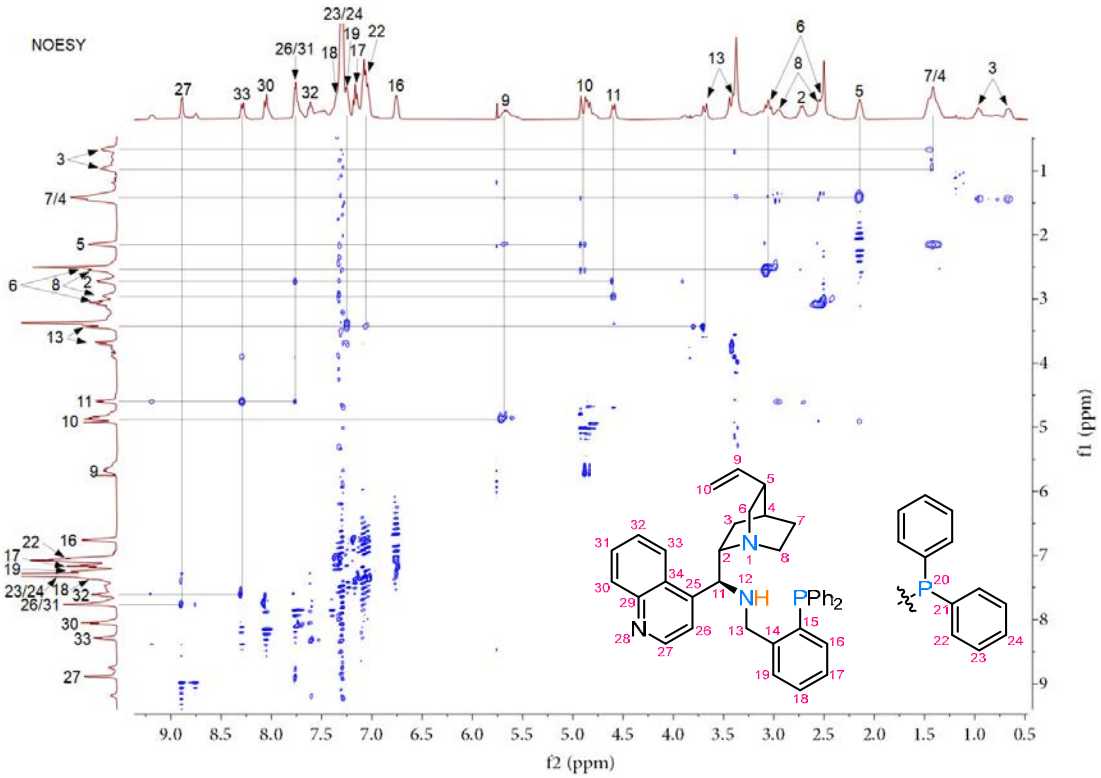
Supplementary Fig. 14 | ^{1}H,^{1}H-COSY 2D-NMR spectrum of L*11 in DMSO-d_6.



Supplementary Fig. 15 | HSQC 2D-NMR spectrum of L*11 in DMSO-d_6.

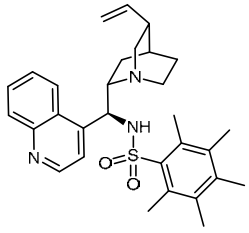


Supplementary Fig. 16 | HMBC 2D-NMR spectrum of L*11 in DMSO-d_6.

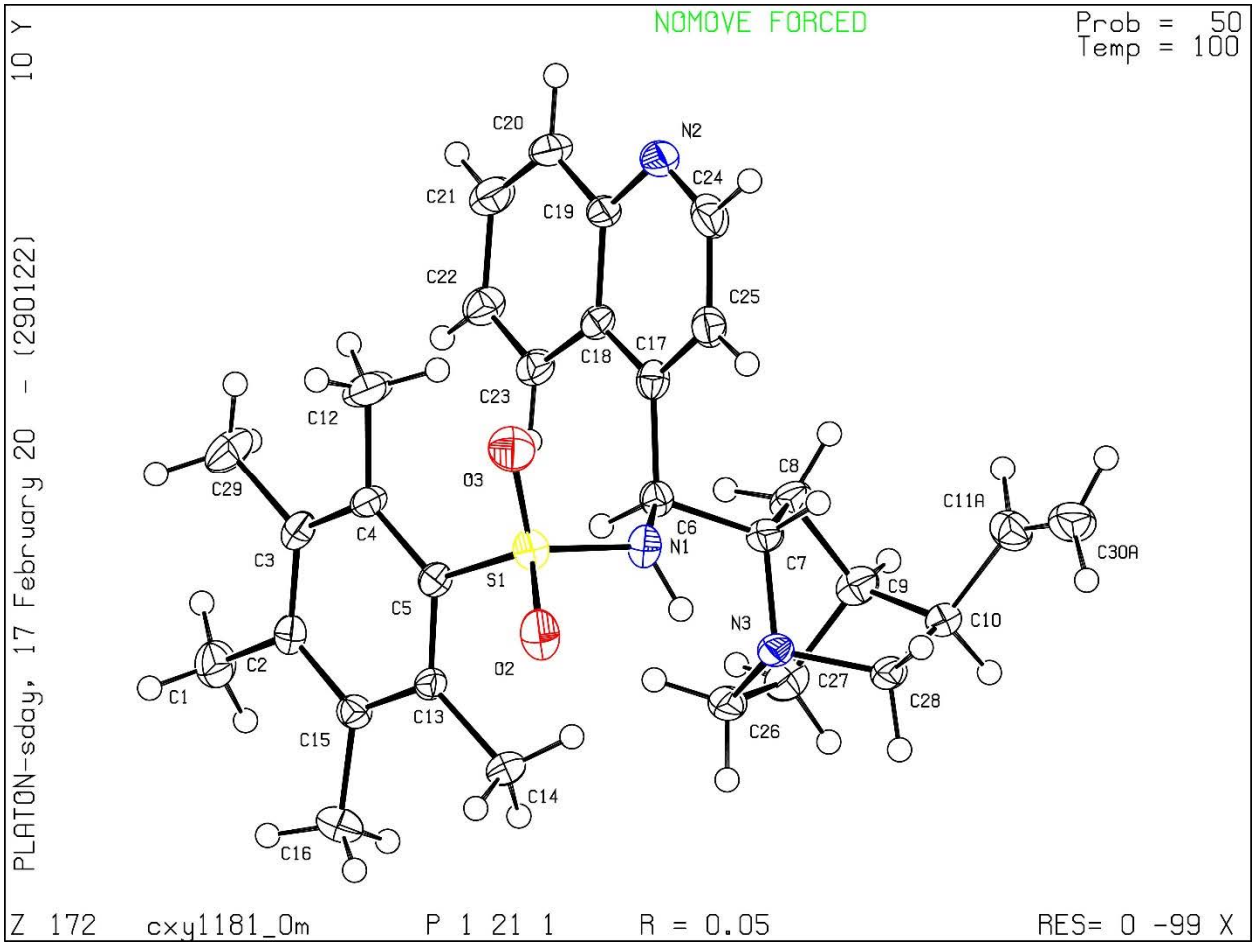


Supplementary Fig. 17 | NOESY 2D-NMR spectrum of L*11 in DMSO-d_6.

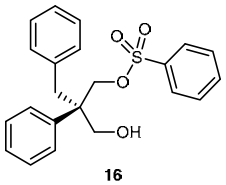
X-ray crystallography



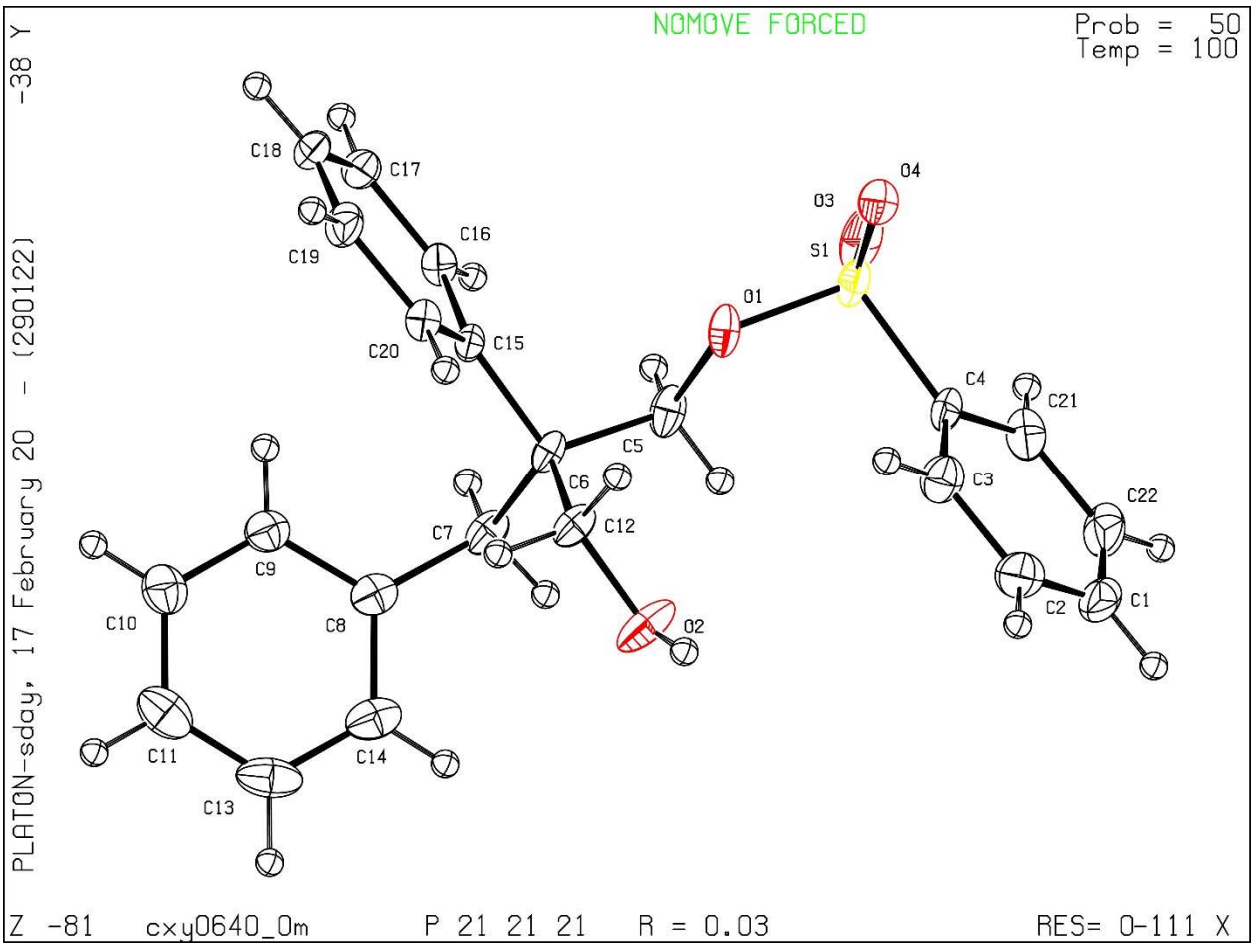
L*4



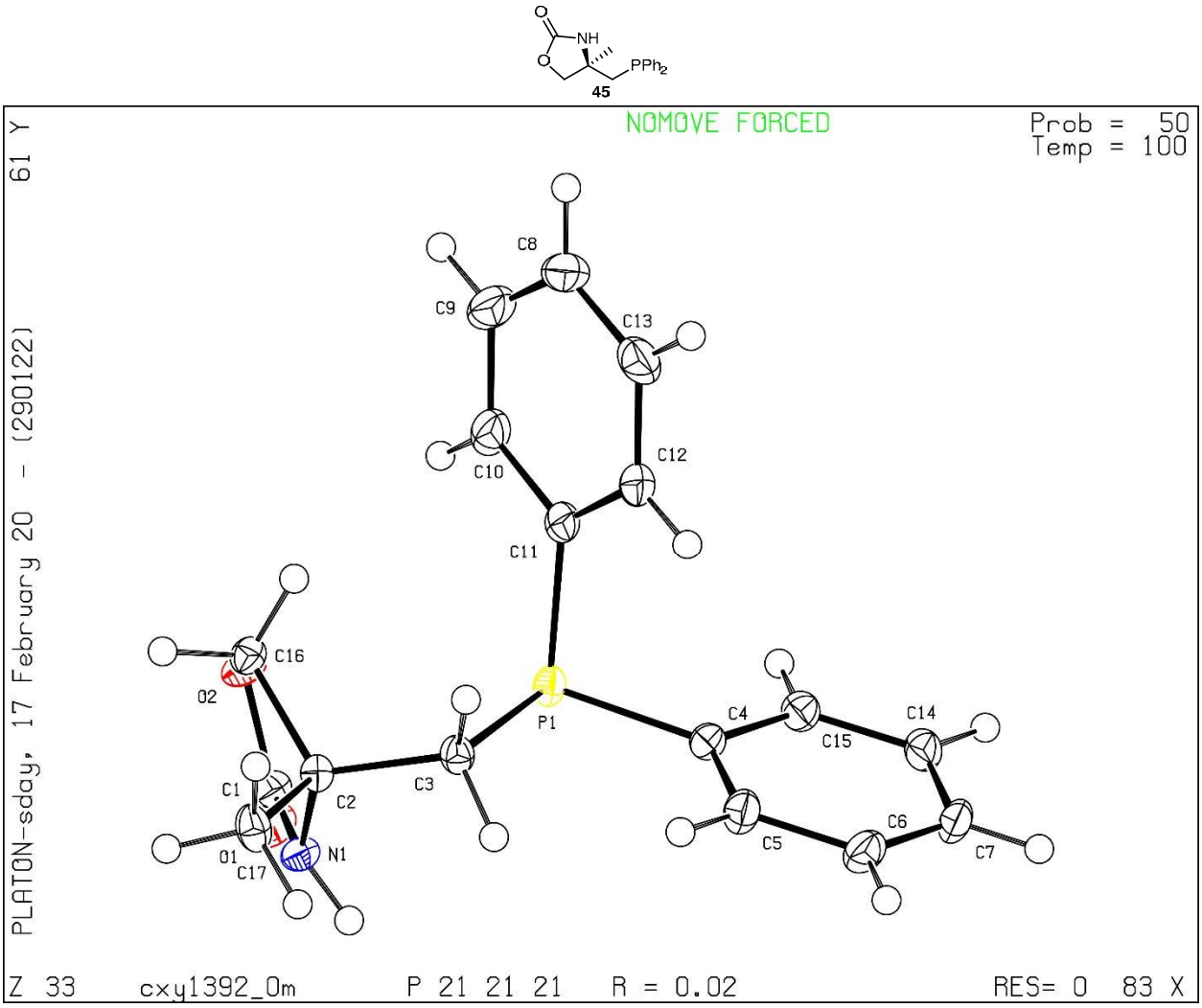
Supplementary Fig. 18 | X-ray structure of compound L*4 (CCDC 2102449, 50% probability ellipsoids).



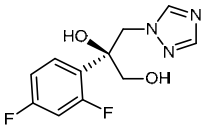
16



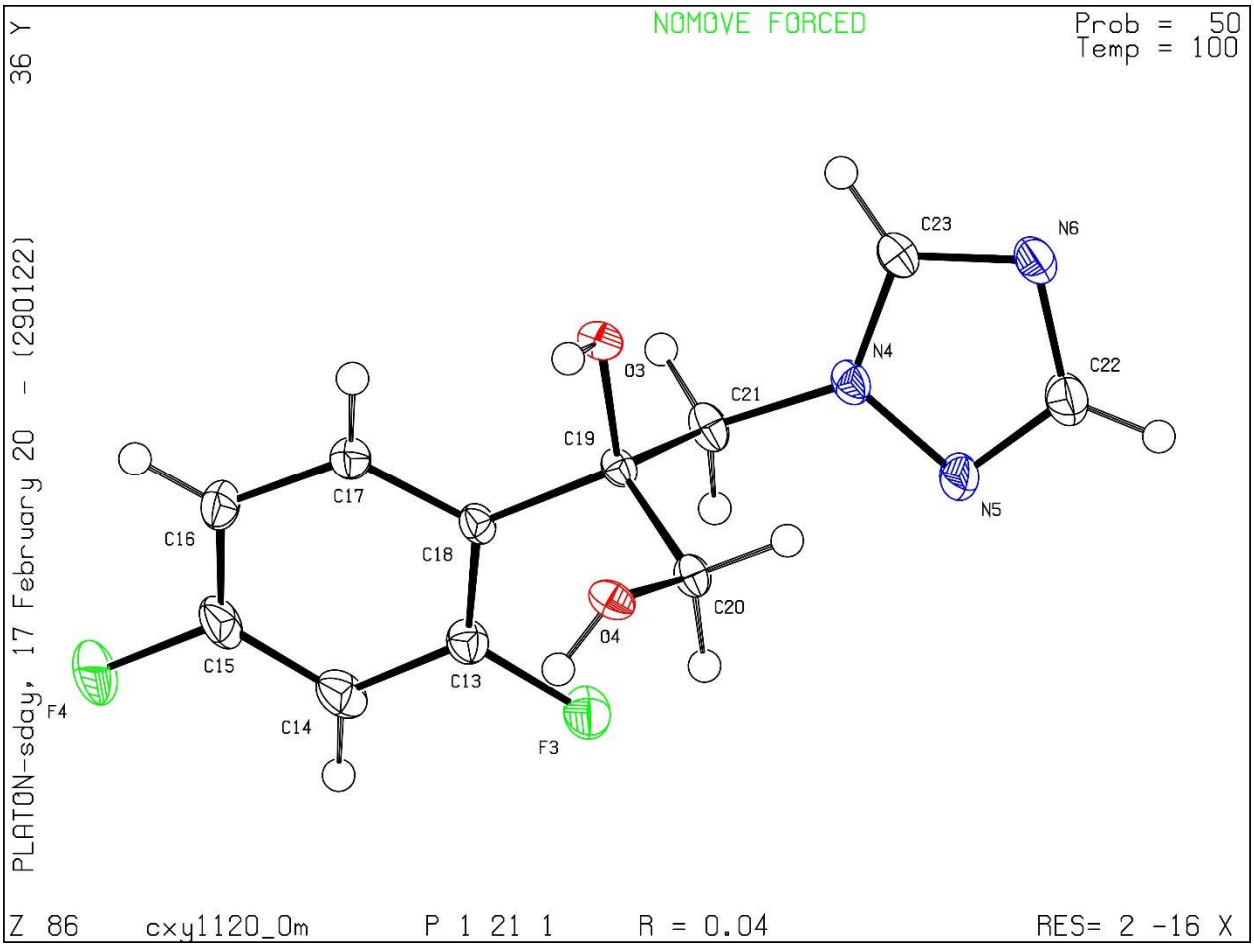
Supplementary Fig. 19 | X-ray structure of compound 16 (CCDC 2102446, 50% probability ellipsoids).



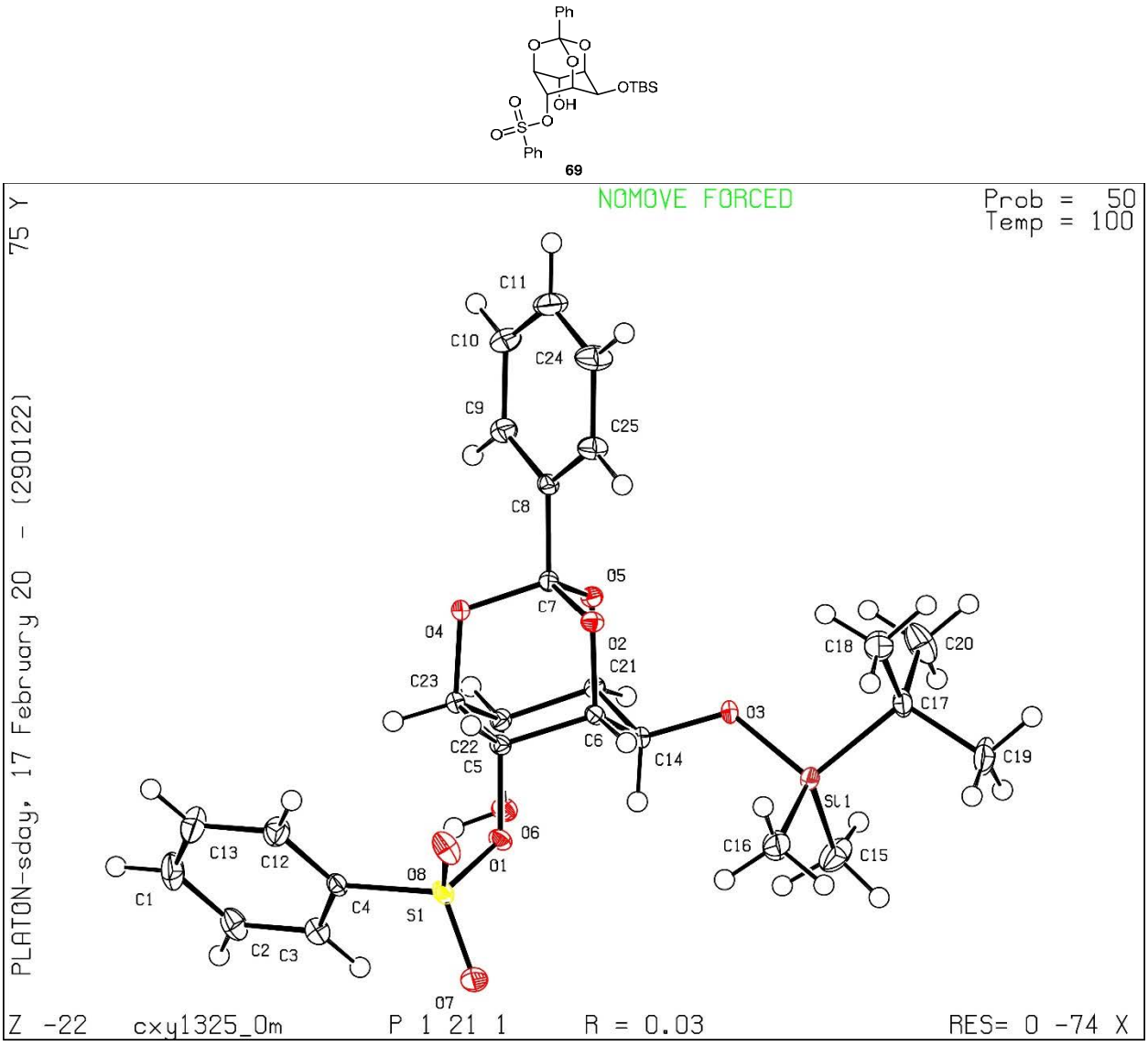
Supplementary Fig. 20 | X-ray structure of compound 45 (CCDC 2102451, 50% probability ellipsoids).



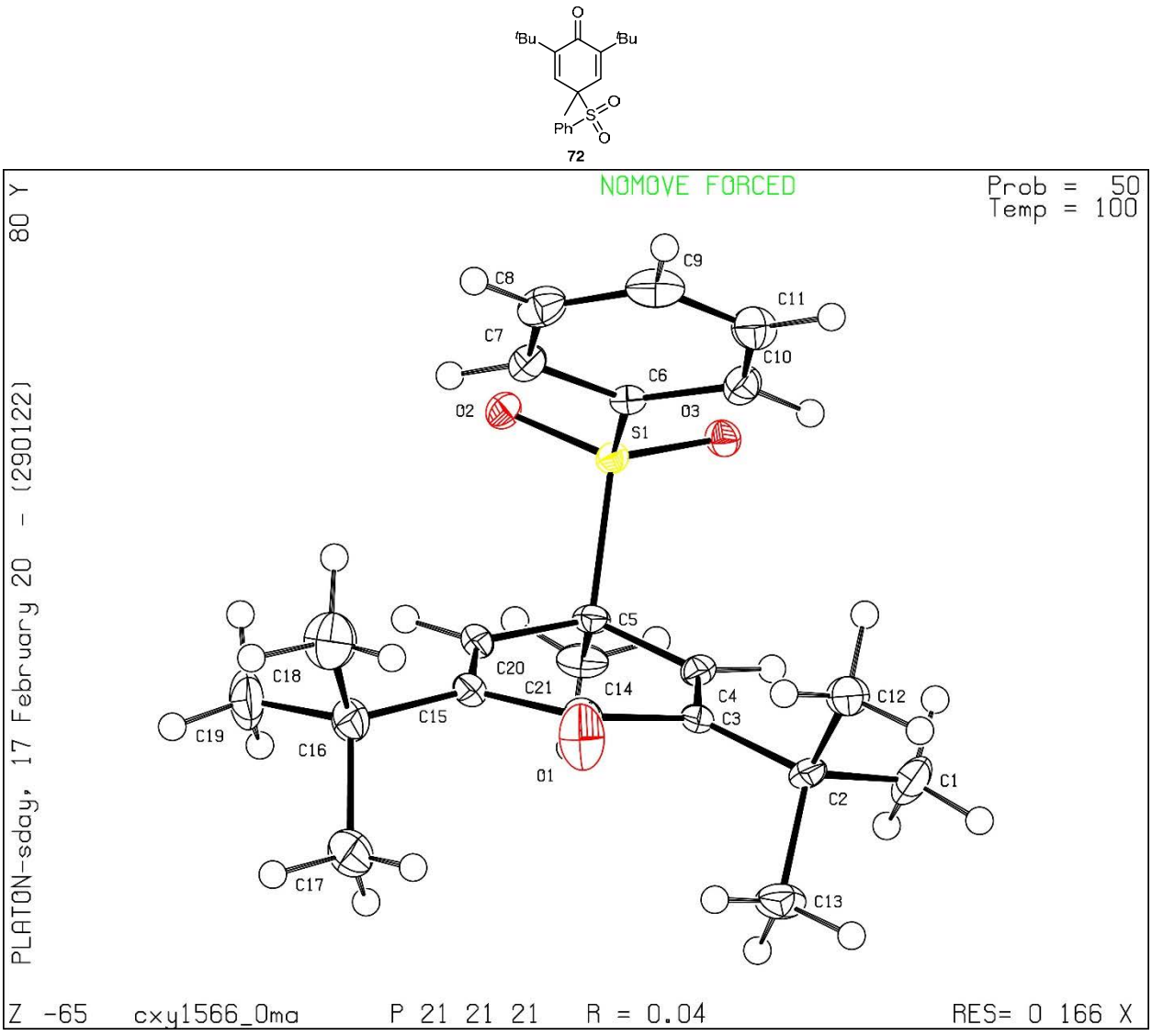
59



Supplementary Fig. 21 | X-ray structure of compound 59 (CCDC 2102448, 50% probability ellipsoids).



Supplementary Fig. 22 | X-ray structure of compound 69 (CCDC 2102450, 50% probability ellipsoids).



Supplementary Fig. 23 | X-ray structure of compound 72 (CCDC 2102452, 50% probability ellipsoids).

Computational study

1. Computational details

All density functional theory (DFT) calculations were performed using Gaussian 16 program[22]. Geometry optimizations were conducted with B3LYP functional[23,24], employing the D3 version of Grimme's dispersion corrections[25] with Becke-Johnson damping[26]. LANL2DZ basis set[27–29] was used for copper and 6-31G(d) basis set was used for all other atoms. Also, the (5d,7f) keyword in Gaussian 16 software was used. Single-point energies and solvent effects at chloroform were evaluated with M06-L functional[30]. SDD basis set[31–35] was used for copper the and 6-311+G(d,p) basis set was used for all other atoms. The solvation energies were calculated with a self-consistent reaction field (SCRF) using the SMD implicit solvent model[36] in chloroform or DMSO. For the specified structures containing the "-Sol" suffix, geometry optimizations were conducted using the SMD model in chloroform with the same functional, dispersion correction, and basis sets as gas-phase geometry optimization. Frequency analysis was also performed at the same level of theory as geometry optimization to confirm whether optimized stationary points were either local minimum or transition state, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K. Mulliken spin distribution was acquired at the same level of theory as geometry optimization.

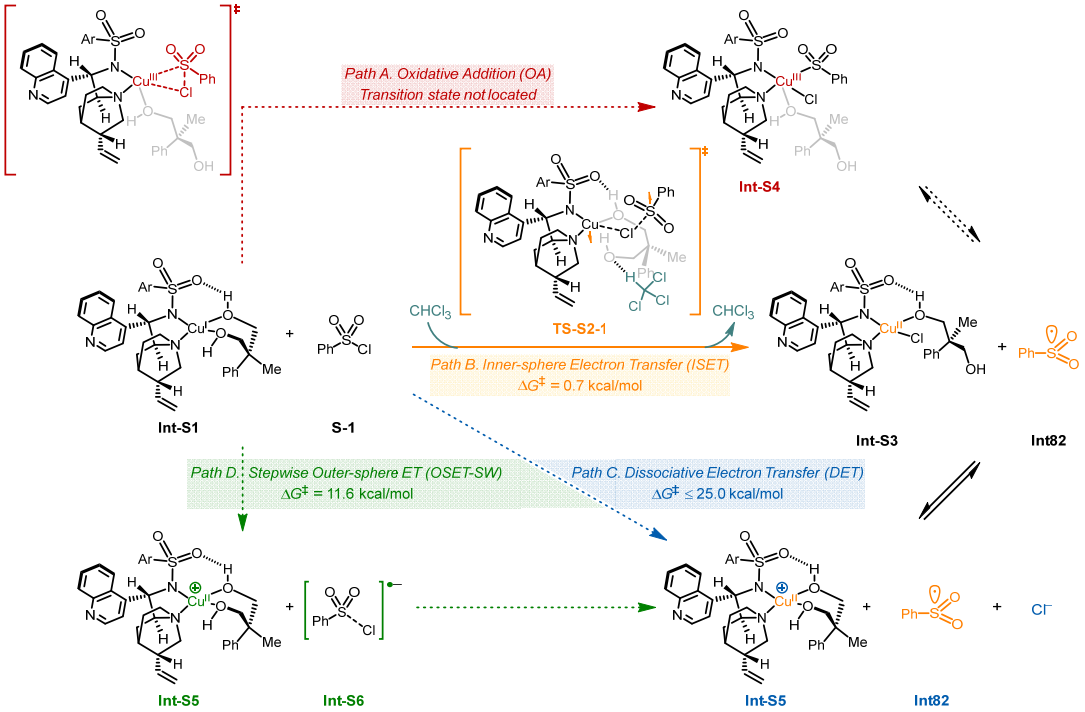
MECP (minimum energy crossing point)[37] was acquired using ORCA 5.0 software[38,39] at B3LYP/G-D3(BJ)/Def2-SVP[40] level of theory (optimization was conducted with Gaussian version of B3LYP functional with the D3 version of Grimme's dispersion corrections and Becke-Johnson damping; the Def2-SVP basis set was used for all atoms). After MECP was located, single-point energy at M06-L/6-311+G(d,p)-SDD was calculated to evaluate electronic energy with higher accuracy in Gaussian 16. The corresponding structures connecting to MECP were optimized at B3LYP-D3(BJ)/Def2-SVP level of theory in Gaussian 16, and single-point energies were calculated at M06-L/6-311+G(d,p)-SDD level of theory also in Gaussian 16.

In addition, geometry optimization, frequency analysis, and single point energy of open-shell local minimums were calculated with unrestricted DFT methods, while the same computations for close-shell transition states and local minimums were performed with restricted DFT methods. Wavefunction stability test at the same level of theory as geometry optimizations was employed to ensure that the SCF converged wavefunction was stable.

To correct the Gibbs free energies under 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_s/c_g)$ was added to the energies of all species. c_s stands for the standard molar concentration in solution (1 mol/L), c_g stands for the standard molar concentration in gas phase (about 0.040876 mol/L), and R is the gas constant. For calculated intermediates at the standard state of 1 mol/L at 298.15 K, the correction value equaling to 1.89 kcal/mol was used. For solvent chloroform with a density of 1480 g/L at 298.15 K and molecular weight of 119.38 g/mol, the correction value equaling to 3.38 kcal/mol was used.

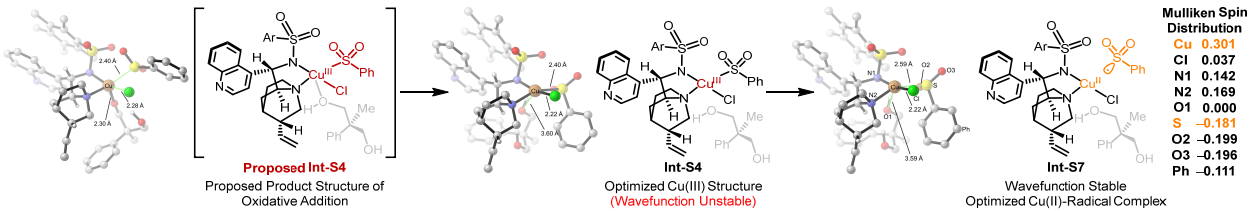
The 3D diagrams of optimized structures shown in the main text and below in the Supplementary Information for computations were generated with CYLview software[41].

2. Cu(I)-mediated generation of benzenesulfonyl radical Int82



Supplementary Fig. 24 | Calculated mechanisms for the generation of benzenesulfonyl radical Int82. Ar, 2,3,4,5,6-pentamethylphenyl.

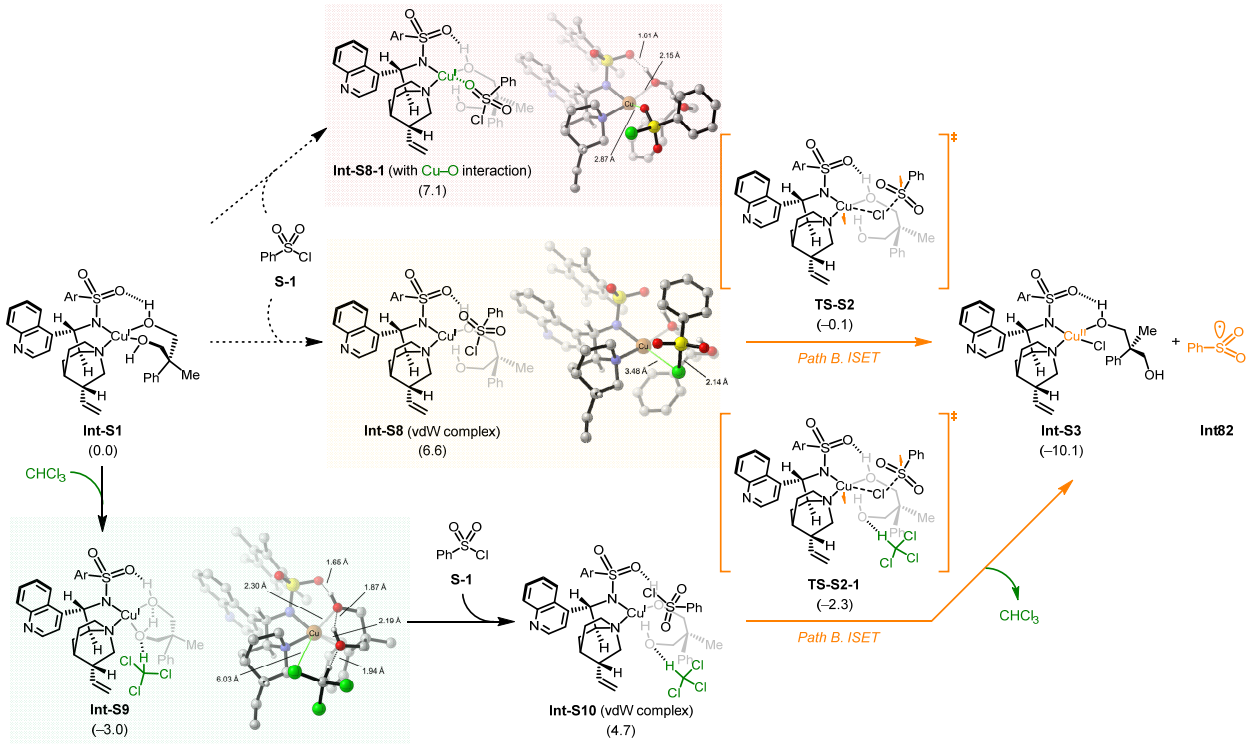
Based on previous mechanistic studies on the mechanism of Cu-mediated carbon–halide bond cleavage[42,43], four possible S–Cl bond cleavage pathways (oxidative addition, inner-sphere electron transfer, stepwise outer-sphere electron transfer, and dissociative electron transfer) were explored. The computational results are summarized in Supplementary Fig. 24. The inner-sphere electron transfer pathway is the most favorable, while the oxidative addition, dissociative electron transfer, and stepwise out-sphere electron transfer pathways are unlikely. Detailed explanations of each pathway are provided below.



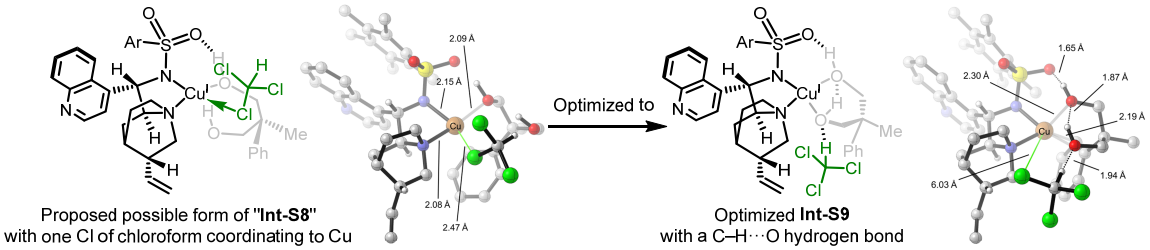
Supplementary Fig. 25 | Results of optimization of the post-oxidative addition Cu(III) intermediate. Ar, 2,3,4,5,6-pentamethylphenyl.

For the double electron oxidative addition (OA) pathway, the transition state cannot be located despite extensive efforts. The post-intermediate of this oxidative addition, the optimized **L*4**Cu(III)(benzenesulfonyl)Cl-diol species, is not a stable intermediate based on our computations. All the attempts to locate the proposed Cu(III) species were eventually optimized

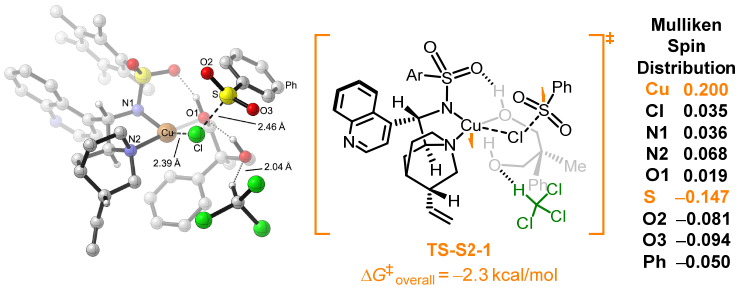
to the open-shell singlet vdW complex of **L*4**Cu(II)Cl and benzenesulfonyl radical **Int-S7** (Supplementary Fig. 25). This open-shell singlet complex **Int-S7** is actually the post-intermediate of radical-type S–Cl bond cleavage, and the open-shell singlet nature of **Int-S7** is confirmed by Mulliken spin distribution. Therefore, we believe that the double electron Cu(I)-Cu(III) oxidative addition pathway is unlikely for the S–Cl bond cleavage.



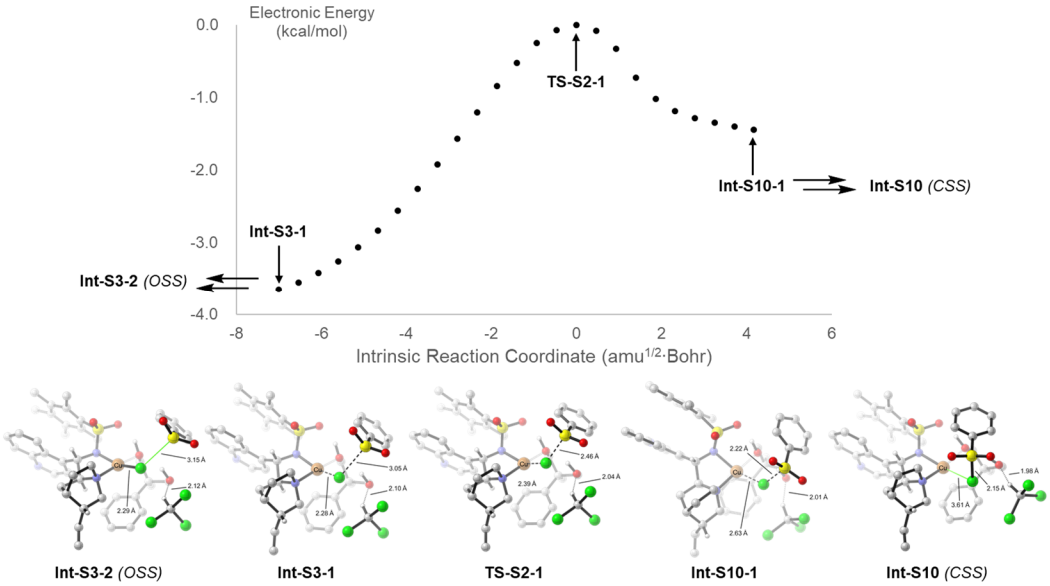
Supplementary Fig. 26 | Computed pathways for the ISET mechanism. Free energies in kcal/mol compared to **Int-S1**, **S-1**, and chloroform are shown in parentheses. Ar, 2,3,4,5,6-pentamethylphenyl.



Supplementary Fig. 27 | Geometry optimization results concerning a possible form of "Int-S8" with one Cl of chloroform coordinating to Cu. Ar, 2,3,4,5,6-pentamethylphenyl.

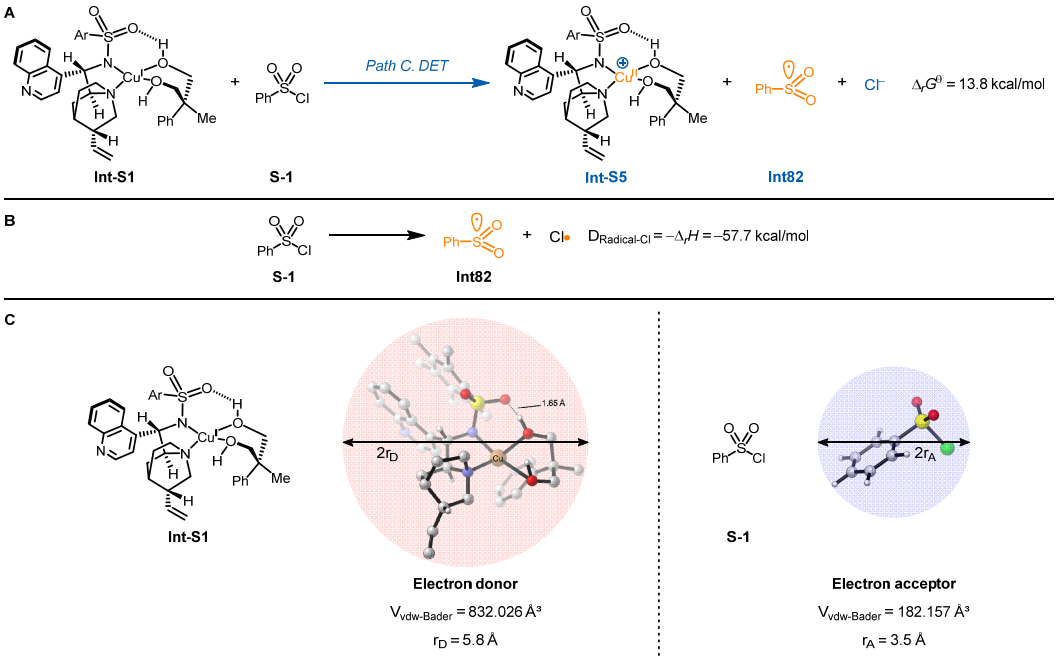


Supplementary Fig. 28 | Located favorable ISET transition state TS-S2-1. Ar, 2,3,4,5,6-pentamethylphenyl **.**



Supplementary Fig. 29 | IRC pathway of the favored ISET transition state TS-S2-1.

For the inner-sphere electron transfer (ISET) pathway, the transition state was successfully located as **TS-S2-1**. The **L*4**Cu(I)-diol complex **Int-S1** forms a complex **Int-S9** with chloroform, which is exergonic by 3.0 kcal/mol. The Cu ‒ Cl distance in **Int-S9** is 6.03Å, implying that the coordination of Cu and Cl in **Int-S9** is unfavorable (Supplementary Figs. 26 and 27). **Int-S9** then forms a complex **Int-S10** with sulfonyl chloride, which requires a free energy barrier of −7.0 kcal/mol to cleave the S−Cl bond via ISET transition state **TS-S2-1**. IRC calculation elucidates the direct connection between **TS-S2-1** and its pre-intermediate **Int-S10** (Supplementary Fig. 29). This negative free energy barrier is due to the subtle shift of saddle points mainly arising from a change of functionals and basis sets during geometry optimization (B3LYP-D3(BJ)/6-31G(d)-LANL2DZ) and single-point energy calculation (M06-L/6-311+G(d,p)-SDD-SMD(Chloroform)). The gas phase optimization results at the B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory indicate a positive barrier of 4.6 kcal/mol (**Int-S10** to **TS-S2-1**, Supplementary Table 13). Mulliken spin population of **TS-S2-1** confirms its open-shell singlet nature (Supplementary Fig. 28). Compared to the ISET pathway without explicit solvent, adding chloroform lowers the overall barrier by 2.2 kcal/mol (**TS-S2** vs. **TS-S2-1**, Supplementary Fig. 26). Thus, the favorable TS of ISET is **TS-S2-1**.



Supplementary Fig. 30 | (**A**) Reaction free energy of DET (dissociative electron transfer) mechanism for **Int-S1** and **S-1**. (**B**) C–Cl bond dissociation energy of radical precursor **S-1**. (**C**) Van der Waals radii for electron donor **Int-S1** and electron acceptor **S-1**. Ar, 2,3,4,5,6-pentamethylphenyl.

For the dissociative electron transfer (DET) and stepwise outer-sphere electron transfer (OSET-SW) pathways, modified Marcus theory[44] was used to estimate the free energy barriers following the studies by Coote, Matyjaszewski, and Liu[42,43].

The DET barrier is estimated by the following equations:

$$\Delta G_{DET}^{\ddagger} = \Delta G_0^{\ddagger}\left(1+\frac{\Delta_r G^{\Theta}-D_p}{4\Delta G_0^{\ddagger}}\right)^2 \quad (1)$$

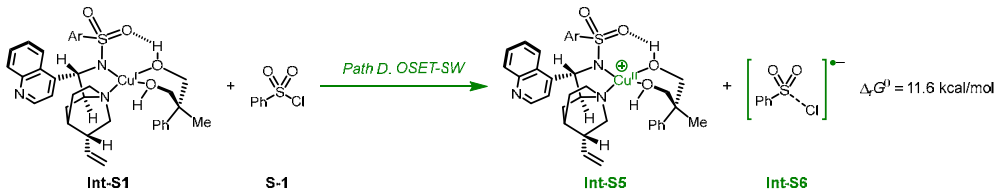
$$\Delta G_0^{\ddagger} = \frac{\left(\sqrt{D_{Radical-Cl}}-\sqrt{D_p}\right)^2+\lambda_0}{4} \quad (2)$$

$$\lambda_0 = A\times\left[(2r_D)^{-1}+(2r_A)^{-1}-(r_D+r_A)^{-1}\right] \approx 12.0\ kcal/mol \quad (3)$$

where $\Delta_r G^{\Theta}$ = 13.8 kcal/mol is the reaction energy of DET pathway (Supplementary Fig. 30A). $\Delta G_0^{\ddagger}$ is the intrinsic barrier, which is estimated using formula (2). λ_0 is the solvent reorganization energy that can be calculated with formula (3). D_p represents the interaction energy between the radical and Cl^- in the solvent cage. D_p = 0 gives the upper boundary of the estimated barrier. $D_{Radical\text{-}Cl}$ represents the S–Cl BDE of radical precursor **S-1** (Supplementary Fig. 30B). A equals to 99 kcal/mol as suggested in the previous studies by Coote, Matyjaszewski, and Liu[42,43]. r_D represents the van der Waals radius updated by Bader[45] for electron donor **Int-S1**. r_A represents the same van der Waals radius for electron acceptor **S-1** (Supplementary Fig. 30C). By including the above values into the formulas (1), (2), and (3), the upper boundary of the free energy barrier for DET is given as 25.0 kcal/mol.

$$\Delta G_0^{\ddagger} \approx \frac{(\sqrt{D_{Radical-Cl}} - \sqrt{D_p})^2 + \lambda_0}{4} = \frac{(\sqrt{57.7} - \sqrt{0})^2 + 12.0}{4} \approx 17.4\ kcal/mol\ (4)$$

$$\Delta G_{DET}^{\ddagger} \approx 17.4 \times \left(1 + \frac{13.8-0}{4\times 17.4}\right)^2 \approx 25.0\ kcal/mol\ (5)$$



Supplementary Fig. 31 | Free energy change for OSET-SW (stepwise outer-sphere electron-transfer) mechanism. Ar, 2,3,4,5,6-pentamethylphenyl.

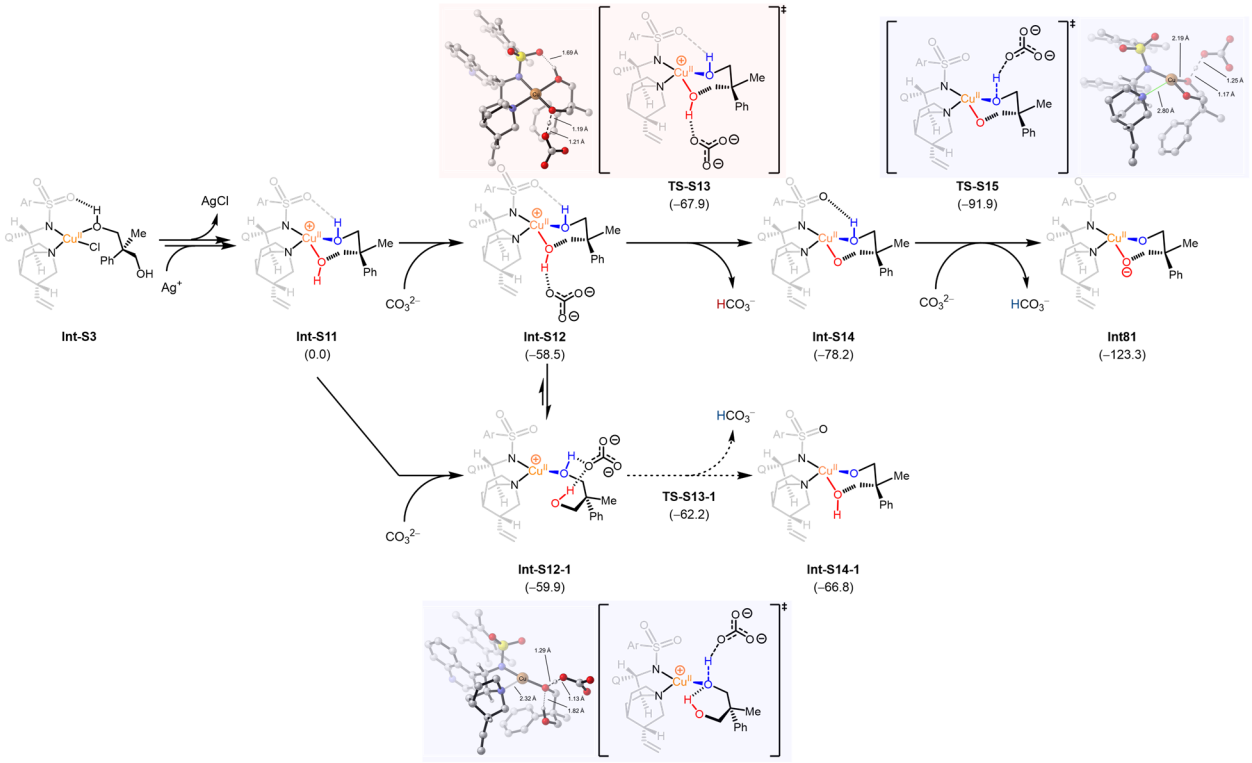
The barrier of OSET-SW is estimated using the following equation (6) (Supplementary Fig. 31), where λ_0 is calculated by the above equation (3). By including the above values into the equation (6), the free energy barrier for OSET-SW is estimated as 11.6 kcal/mol.

$$\Delta G_{OSET-SW}^{\ddagger} = \Delta G_0^{\ddagger}\left(1 + \frac{\Delta_r G^{\Theta}}{4\Delta G_0^{\ddagger}}\right)^2 = \frac{\lambda_0}{4}\left(1 + \frac{\Delta_r G^{\Theta}}{\lambda_0}\right)^2\ (6)$$

$$\Delta G_{OSET-SW}^{\ddagger} = 3.0 \times (1 + \frac{11.6}{4\times 3.0})^2 \approx 11.6\ kcal/mol\ (7)$$

Based on the above calculations and estimations, the inner-sphere electron transfer pathway via **TS-S2-1** is the most favorable pathway, which leads to the generation of benzenesulfonyl radical **Int82** and a **L*4**Cu(II)Cl species **Int-S3**.

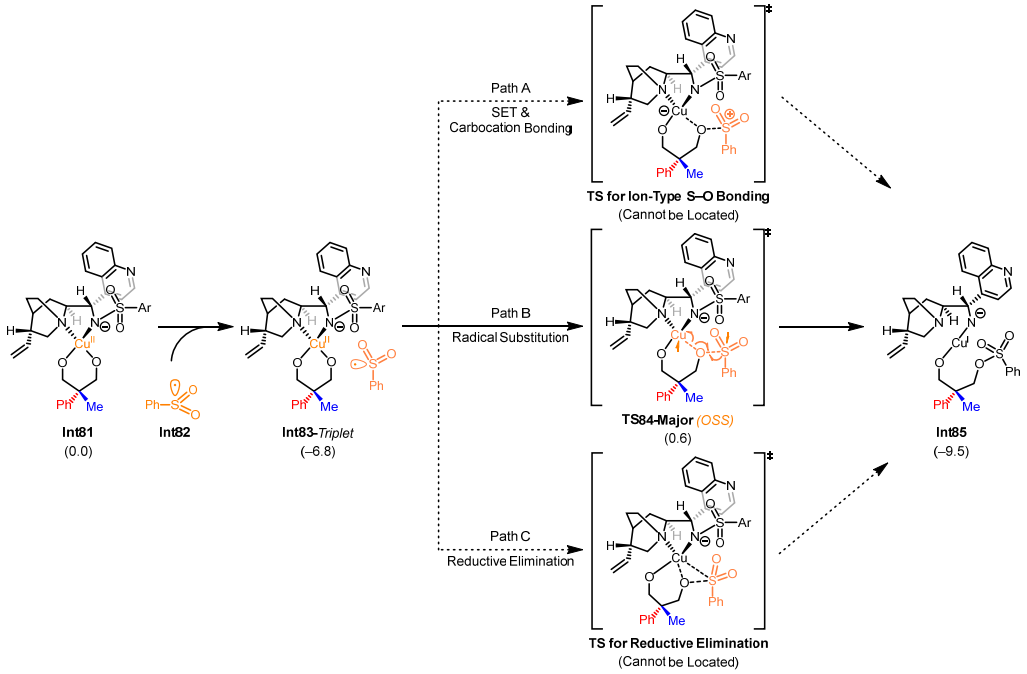
3. Mechanistic details of transformation from L*4Cu(II)Cl to L*4Cu(II)alkoxide



Supplementary Fig. 32 | DFT-Computed free energy changes of the generation of anionic LCu(II) alkoxide species Int81. Ar, 2,3,4,5,6-pentamethylphenyl; Q, quinolin-4-yl.

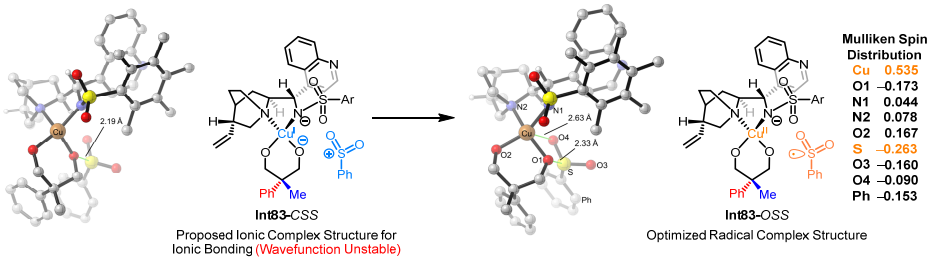
After the sulfonyl radical generation, the **L*4**Cu(II)Cl-diol **Int-S3** will be irreversibly dehalogenated by silver(I) salt (Supplementary Fig. 32), and the generated cationic **L*4**Cu(II) species will be complexed by the neutral diol substrate to form the intermediate **Int-S11**. From **Int-S11**, the hydroxyl group (labeled with red color) at the *trans*-position of sulfonamide is firstly deprotonated by carbonate anion via **TS-S13**, reversibly forming neutral copper(II) species **Int-S14**. In comparison, deprotonation of the hydroxyl group (labeled as blue color) at the *cis*-position of sulfonamide via **TS-S13-1** is 5.7 kcal/mol less favorable than **TS-S13** (Supplementary Fig. 32), suggesting that the alternative sequence of deprotonation is unlikely. **Int-S14** then undergoes another facile deprotonation via **TS-S15**, irreversibly generating the anionic **L*4**Cu(II)alkoxide species **Int81**.

4. Discussion on the S–O bonding mechanism



Supplementary Fig. 33 | DFT calculations on S–O bond formation pathways with Int81 and benzenesulfonyl radical Int82. Free energies in kcal/mol are shown in parentheses, which are compared to **Int81** and **Int82**. Ar, 2,3,4,5,6-pentamethylphenyl.

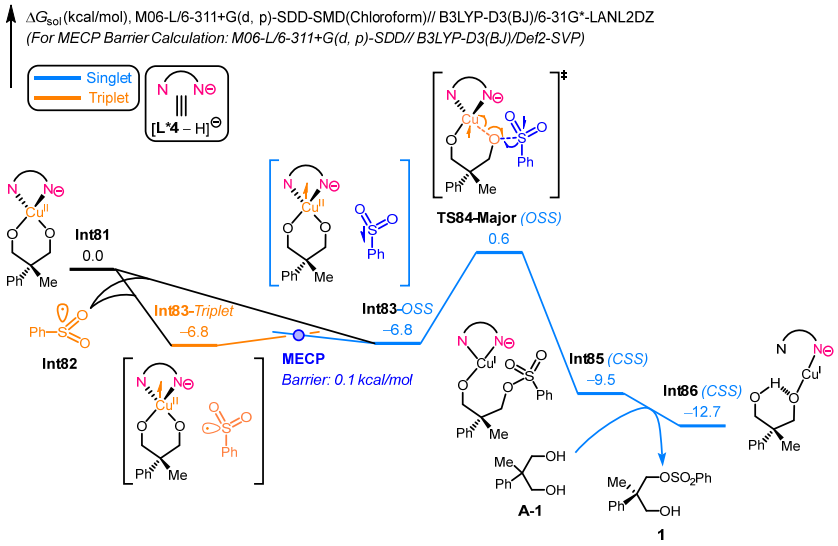
The S–O bond formation pathways between **L*4**Cu(II)alkoxide intermediate **Int81** and sulfonyl radical **Int82** include three major mechanistic possibilities: sequential SET and ion-type S–O bonding (path A in Supplementary Fig. 33), outer-sphere radical-substitution-type S–O bond formation via **TS84-Major** (path B in Supplementary Fig. 33), and reductive elimination (path C in Supplementary Fig. 33).



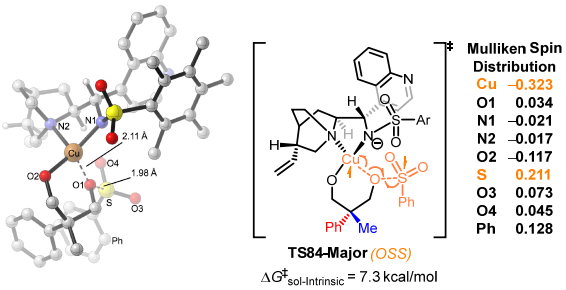
Supplementary Fig. 34 | The proposed closed-shell singlet pre-intermediate structure of the proposed TS for ion-type S–O bond formation pathway has an RHF to UHF 'wavefunction' instability. Further optimization on this proposed structure leads to the open-shell singlet intermediate **Int83-***OSS* with a stable 'wavefunction'. And the Mulliken spin distribution **Int83-***OSS* indicates its open-shell singlet nature. Ar, 2,3,4,5,6-pentamethylphenyl.

Regarding path A, the ion-type S–O bonding, the transition state cannot be located after extensive efforts. The structure of the pre-intermediate prior to the proposed ion-type S–O bonding

transition state, **Int83-***CSS*, has an RHF to UHF 'wavefunction' instability, indicating that such a closed-shell singlet intermediate does not exist at the computed potential energy surface. Further open-shell singlet optimization of the proposed **Int83-***CSS* led to the open-shell singlet intermediate **Int83-***OSS*, which is the pre-intermediate for the radical substitution S–O bond formation. Based on these results, the ion-type S–O bonding pathway is not operative (Supplementary Fig. 34).



Supplementary Fig. 35 | Detailed free energy diagram for radical-substitution-type S–O bond formation pathway. Ar, 2,3,4,5,6-pentamethylphenyl.

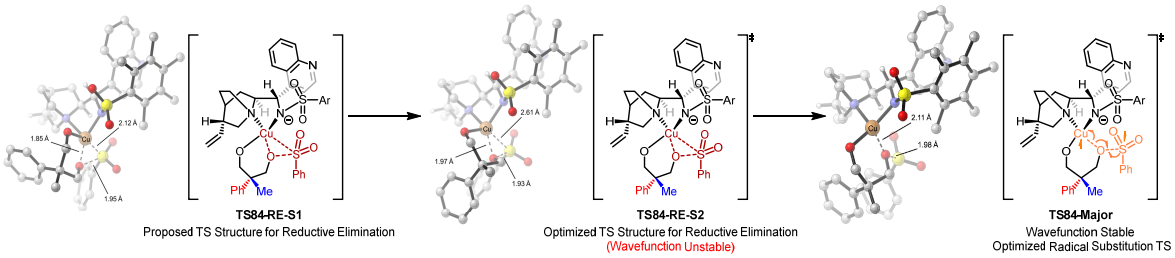


Supplementary Fig. 36 | Located structure and Mulliken spin distribution of located open-shell singlet S–O bond formation transition state TS84-Major. Ar, 2,3,4,5,6-pentamethylphenyl.

For path B, doublet radicals **Int81** and **Int82** can form both triplet diradical species **Int83-***Triplet* and open-shell singlet diradical species **Int83-***OSS*. **Int83-***Triplet* can transform into **Int83-***OSS* via a facile MECP with a 0.1 kcal/mol free energy barrier. **Int83-***OSS* undergoes S–O bond formation via open-shell singlet diradical transition state **TS84-Major**, leading to closed-shell singlet species **Int85** (Supplementary Fig. 35).

We should point out that MECP is acquired using ORCA 5.0 software at the B3LYP/G-D3(BJ)/Def2-SVP level of theory. And the change of basis set from 6-31G*-LANL2DZ to Def2-SVP gives a consistent free energy diagram of S–O bond formation (Supplementary Table 8).

As for the radical substitution transition state **TS84-Major**, it is an open-shell diradical singlet S–O bond formation transition state, whose nature of radical substitution is confirmed by the computed Mulliken spin distribution. Significant radical characters are identified on the carbons of the forming S–O bond, the coordinating nitrogen and oxygen atoms, and the copper centre (Supplementary Fig. 36)

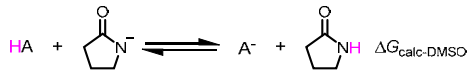


Supplementary Fig. 37 | The optimized TS structure for S–O bond reductive elimination has an RHF to UHF 'wavefunction' instability. Further geometry optimization on this structure leads to the open-shell singlet TS **TS84-Major** with a stable 'wavefunction'. Ar, 2,3,4,5,6-pentamethylphenyl.

Regarding path C, the reductive elimination, the located transition state **TS84-RE-S2** with RHF has an RHF to UHF 'wavefunction' instability, indicating that such a closed-shell singlet state is not the actual intrinsic electron state of the proposed reductive elimination transition state. Further open-shell singlet optimization of this **TS84-RE-S2** led to the open-shell singlet transition state **TS84-Major**. Based on these results, the reductive elimination pathway is not operative. (Supplementary Fig. 37)

Therefore, S–O bond formation undergoes an outer-sphere singlet radical-substitution-type S–O bond formation via **TS84-Major**.

5. Computations for relative dissociation constants of L*4 and L*11



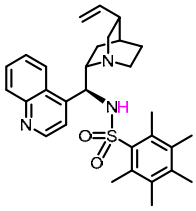
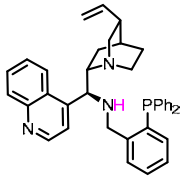
(a)

pyrrolidin-2-one, experimental reference pK_a = 24.2
(*J. Org. Chem.* **56,** 4218–4223 (1991))

$$pK_{a(HA)} = \Delta pK_a + pK_{a(pyrrolidin-2-one)} = \frac{\Delta G_{calc\text{-}DMSO}}{2.303RT} + 24.2 \qquad (b)$$

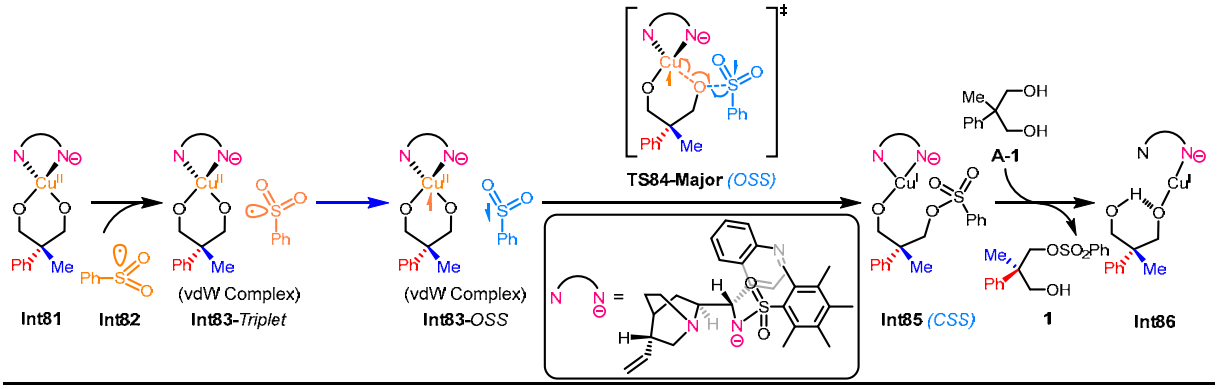
Free energy change ($\Delta G_{calc\text{-}DMSO}$) of acid-base reaction equation (a) in DMSO was calculated based on DFT calculations at M06-L/6-311+G(d,p)-SDD-SMD(DMSO)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory at 298.15K. The N–H pK_a values were then calculated with equation (b), using the experimentally measured N–H pK_a of pyrrolidin-2-one in DMSO as reference (N–H pK_a in DMSO = 24.2)[46]. Computed $\Delta G_{calc\text{-}DMSO}$ and N–H pK_a values of **L*4** and **L*11** are listed in Supplementary Table 7.

Supplementary Table 7 | Calculated free energy change of proton exchange reaction between L*4 or L*11 with the deprotonated anion of reference acid (N–H of pyrrolidin-2-one) and calculated ΔpK_a

HA	$\Delta G_{calc\text{-}DMSO}$ (kcal/mol)	Calculated pK_a
 L*4	–10.1	16.8
 L*11	22.6	40.8

6. Verification of computed S–O bond formation mechanism in various levels of theory for geometry optimization

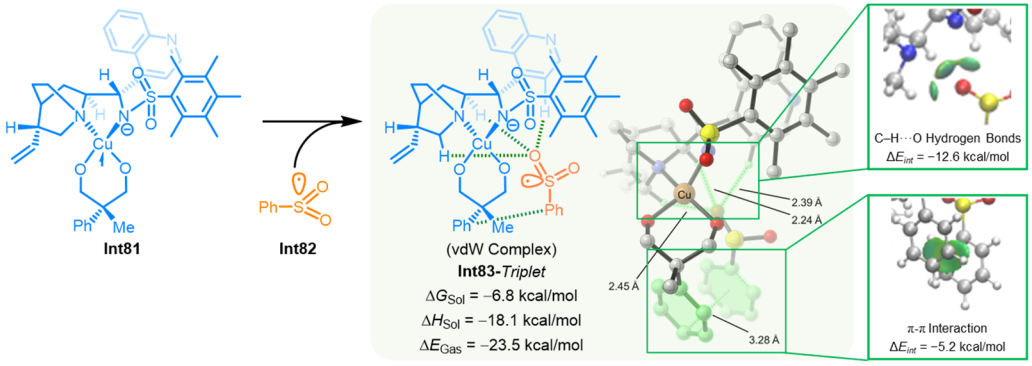
Supplementary Table 8 | Verification of computed S–O bond formation mechanism in various levels of theory for geometry optimization



Methods	Int81	Int83-*Triplet*	Int83-*OSS*	TS84-Major	Int85	Int86
A	0.0	−6.8	−6.8	0.6	−9.5	−12.7
B	0.0	−6.7	−6.3	0.8	−9.4	−13.6
C	0.0	−6.2	−5.6	1.7	−9.3	−12.2

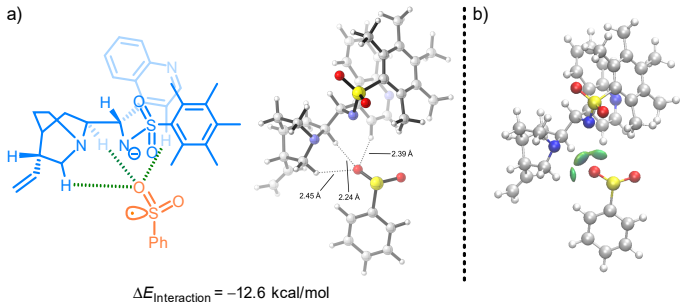
Method A: M06-L/6-311+G(d, p)-SDD-SMD(Chloroform)//B3LYP-D3(BJ)/6-31G(d)-LANL2-DZ
Method B: M06-L/6-311+G(d, p)-SDD-SMD(Chloroform)//B3LYP-D3(BJ)/6-31G(d)-LANL2-DZ-SMD(Chloroform)
Method C: M06-L/6-311+G(d, p)-SDD-SMD(Chloroform)//B3LYP-D3(BJ)/Def2-SVP[40]

7. Driving force for the formation of Int83-*Triplet*



Supplementary Fig. 38 | Overall analysis on the driving forces for generating Int83-*Triplet* with copper(II) species Int81 and sulfonyl radical Int82.

Doublet anionic copper(II) species **Int81** and sulfonyl radical **Int82** can form anionic species **Int83**-*Triplet*. The formation of several non-covalent interactions leads to an exergonic generation of **Int83**-*Triplet* by 6.8 kcal/mol. Further analysis using Multiwfn[47] with IGM[48] model and visualization with VMD software[49] support the existence of multiple hydrogen bonds between the ligand fragment and sulfonyl radical as well as the π-π stacking interaction between the phenyl fragment on the substrate and the phenylsulfonyl radical (green isosurfaces in Supplementary Figs. 38, 39b, and 40b).



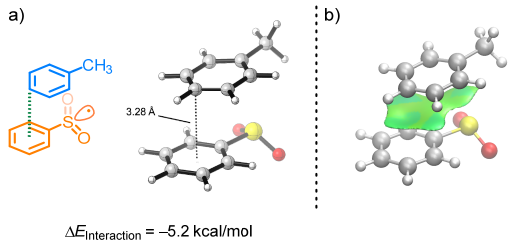
Supplementary Fig. 39 | a) Multiple hydrogen bonds of ligand fragment and sulfonyl radical. b) IGM visualization of these hydrogen bonds.

Calculations of interacting energy of multiple bonds between the ligand fragment and sulfonyl radical were performed at M06-L/6-311+G(d,p) level of theory in gas-phase. The interacting energy with BSSE correction of intermolecular hydrogen bonds ($\Delta E_{\text{H-Bonds}}$) was calculated using Gaussian 16 according to the following equation:

$$\Delta E_{\text{H-Bonds}} = E_{\text{complex-fragment}} - E_{\text{separate}} = E_{\text{complex-fragment}} - (E_{\text{fragment-1}} + E_{\text{fragment-2}})$$

where $E_{\text{complex-fragment}}$ refers to the gas-phase single point energy of the interacting ligand fragment and sulfonyl radical. The geometry of the interacting fragment (named as **Int83**-*Triplet*_**H-Bond-Frag-All**) is taken from the optimized geometry of **Int83**-*Triplet*. E_{separate} ($E_{\text{fragment-1}} + E_{\text{fragment-2}}$) refers to the gas-phase single point energies of ligand fragment (named as

Int83-*Triplet*_H-Bond-Frag-H-Donor) and sulfonyl radical (named as **Int83-*Triplet*_H-Bond-Frag-Sulf**) also taken from the optimized geometry of **Int83**-*Triplet*. The calculated interacting energy of these multiple bonds with BSSE correction is 12.6 kcal/mol (Supplementary Fig. 39).



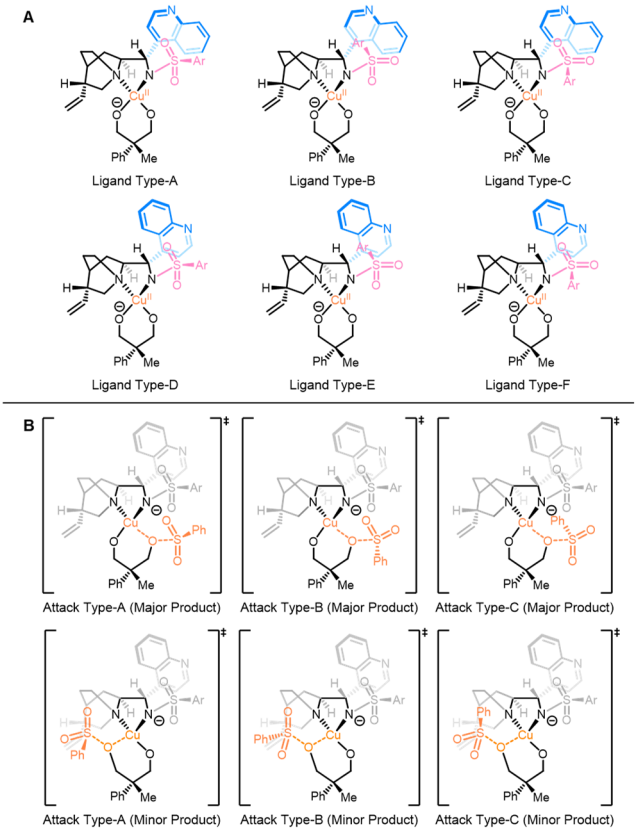
Supplementary Fig. 40 | a) π -π stacking between phenyl group of diol substrate fragment and sulfonyl radical. b) IGM visualization of π-π stacking.

Calculations of interacting energy of π-π stacking between the substrate fragment from **Int83-*Triplet*** and sulfonyl radical were performed at M06-L/6-311+G(d,p) level of theory in gas-phase. The interacting energy with BSSE correction of π-π stacking ($\Delta E_{\pi\text{-}\pi\ \text{stacking}}$) was calculated using Gaussian 16 according to the following equation:

$$\Delta E_{\pi\text{-}\pi\ \text{stacking}} = E_{\text{complex-fragment}} - E_{\text{separate}} = E_{\text{complex-fragment}} - (E_{\text{fragment-1}} + E_{\text{fragment-2}})$$

where $E_{\text{complex-fragment}}$ refers to the gas-phase single point energy of the interacting ligand fragment and sulfonyl radical. The geometry of the interacting fragment (named as **Int83-*Triplet*_pi-pi-Frag**) is taken from the optimized geometry of **Int83**-*Triplet* with appended C – H bonds (1.096 Å for C(sp^3)–H bond on toluene fragment). E_{separate} ($E_{\text{fragment-1}} + E_{\text{fragment-2}}$) refers to the gas-phase single point energies of ligand fragment (named as **Int83-*Triplet*_pi-pi-Frag-Tol**) and sulfonyl radical (named as **Int83-*Triplet*_pi-pi-Frag-Sulf**) also taken from the optimized geometry of **Int83**-*Triplet*. The calculated interacting energy of these multiple bonds with BSSE correction is 5.2 kcal/mol (Supplementary Fig. 40).

8. Conformational search of stereo-determining S–O bond formation transition state TS84



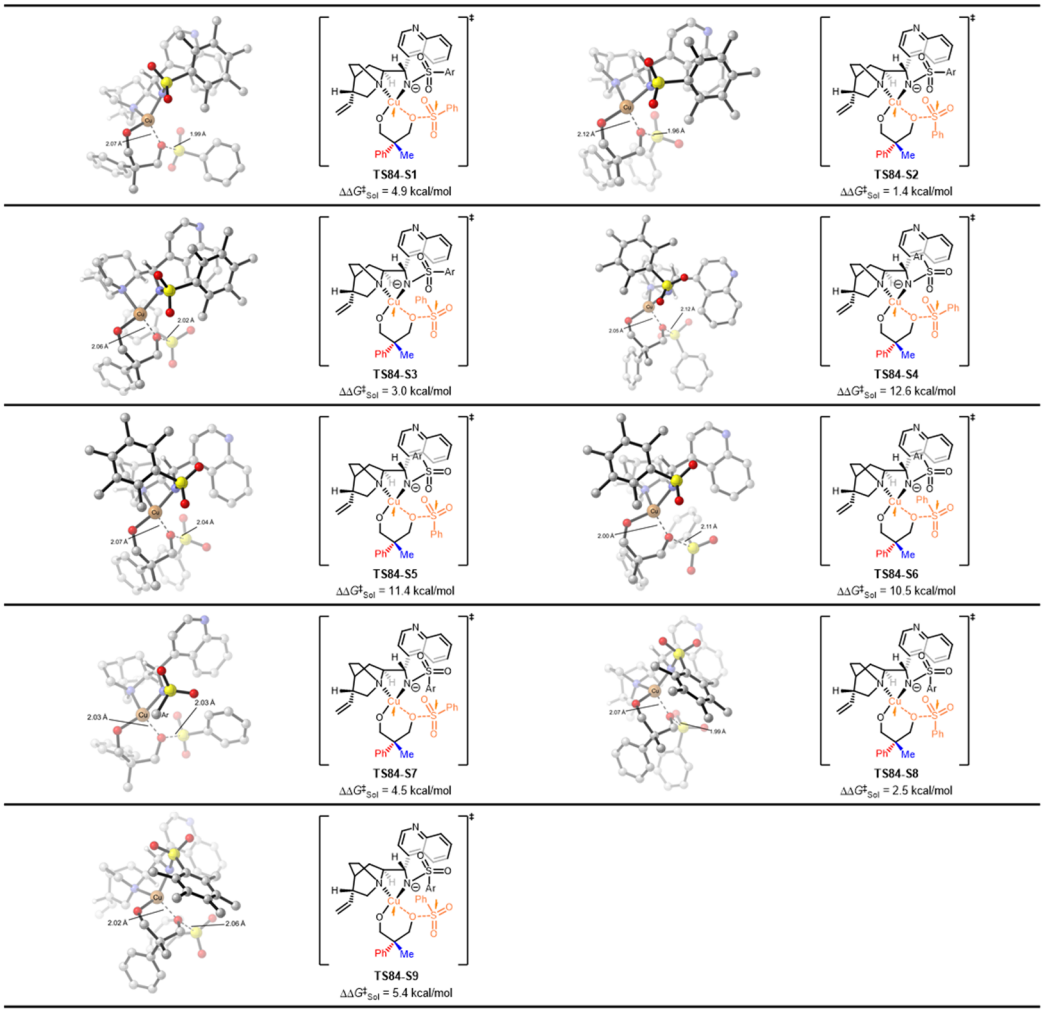
Supplementary Fig. 41 | (**A**) Considered conformational factors on the ligand in the conformational search of S–O bond formation transition state **TS84**. (**B**) Considered conformational factors on attack type of benzenesulfonyl radical **Int82** in the conformational search of S–O bond formation transition state **TS84**. Ar, 2,3,4,5,6-pentamethylphenyl.

Supplementary Table 9 | Conformational search of S–O bond formation transition state leading to major product. Free energies are compared to **TS84-Major**.

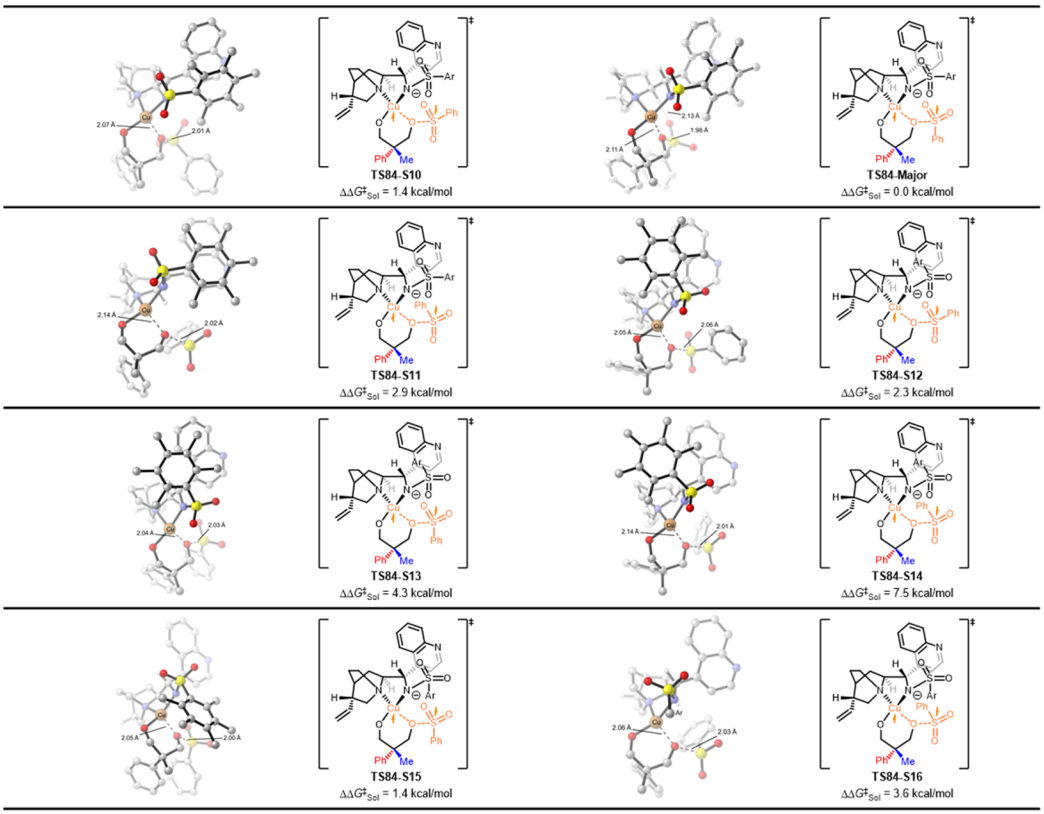
Configuration of Product	Catalyst Configuration	Attack-Type	No.	$\Delta\Delta G_{sol}^{\ddagger}$ (kcal/mol)
(R)	A	Major-A	**TS84-S1**	4.9
(R)	A	Major-B	**TS84-S2**	1.4
(R)	A	Major-C	**TS84-S3**	3.0
(R)	B	Major-A	**TS84-S4**	12.6
(R)	B	Major-B	**TS84-S5**	11.4
(R)	B	Major-C	**TS84-S6**	10.5
(R)	C	Major-A	**TS84-S7**	4.5
(R)	C	Major-B	**TS84-S8**	2.5
(R)	C	Major-C	**TS84-S9**	5.4
(R)	D	Major-A	**TS84-S10**	1.4
(R)	D	Major-B	**TS84-Major**	0.0
(R)	D	Major-C	**TS84-S11**	2.9
(R)	E	Major-A	**TS84-S12**	2.3
(R)	E	Major-B	**TS84-S13**	4.3
(R)	E	Major-C	**TS84-S14**	7.5
(R)	F	Major-A	/	Optimized to **TS84-S12**
(R)	F	Major-B	**TS84-S15**	1.4
(R)	F	Major-C	**TS84-S16**	3.6

Supplementary Table 10 | Conformational search of S–O bond formation transition state leading to the minor product. Free energies are compared to **TS84-Major**.

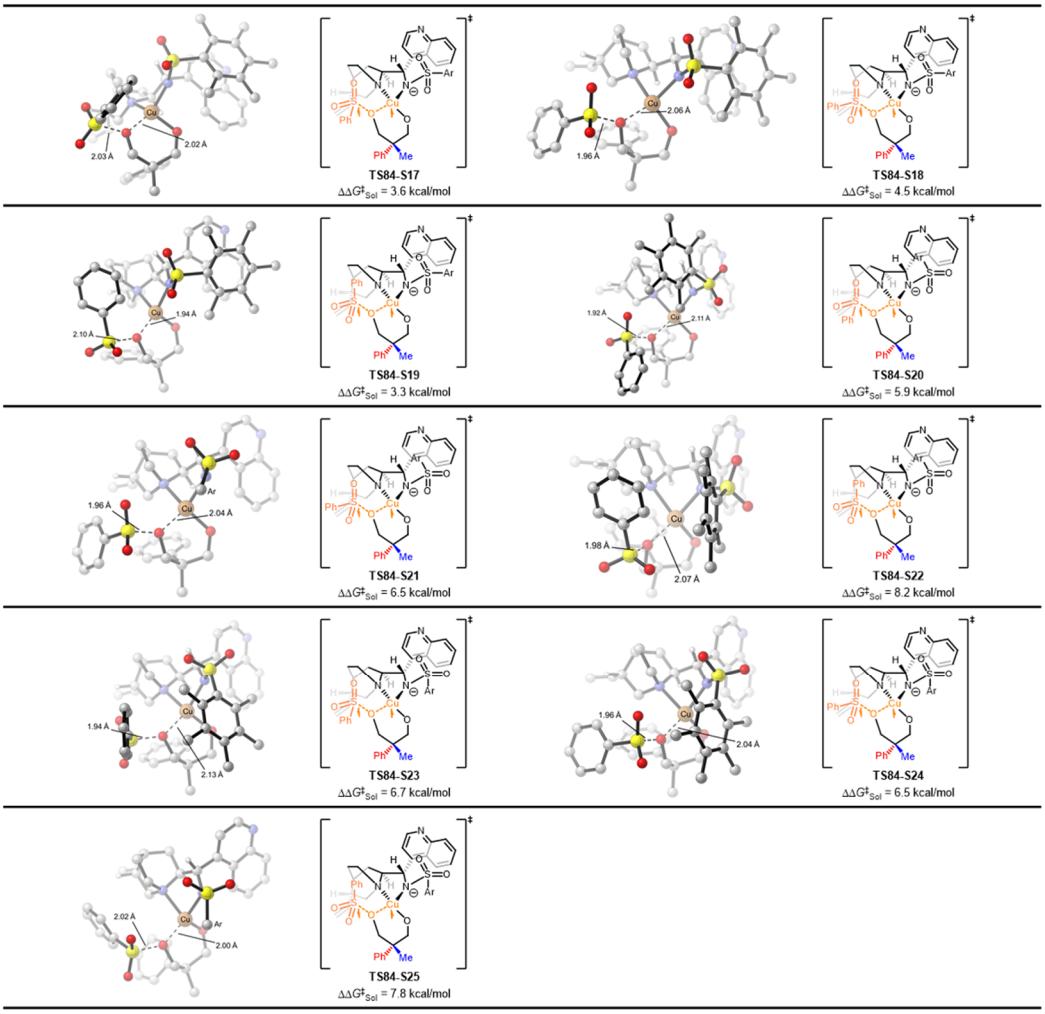
Configuration of Product	Catalyst Configuration	Attack-Type	No.	$\Delta\Delta G_{sol}^{\ddagger}$ (kcal/mol)
(S)	A	Minor-A	**TS84-S17**	3.6
(S)	A	Minor-B	**TS84-S18**	4.5
(S)	A	Minor-C	**TS84-S19**	3.3
(S)	B	Minor-A	**TS84-S20**	5.9
(S)	B	Minor-B	**TS84-S21**	6.5
(S)	B	Minor-C	**TS84-S22**	8.2
(S)	C	Minor-A	**TS84-S23**	6.7
(S)	C	Minor-B	**TS84-S24**	6.5
(S)	C	Minor-C	**TS84-S25**	7.8
(S)	D	Minor-A	**TS84-S26**	3.1
(S)	D	Minor-B	**TS84-S27**	4.2
(S)	D	Minor-C	**TS84-Minor**	2.7
(S)	E	Minor-A	**TS84-S28**	7.9
(S)	E	Minor-B	**TS84-S29**	7.4
(S)	E	Minor-C	**TS84-S30**	7.4
(S)	F	Minor-A	**TS84-S31**	7.6
(S)	F	Minor-B	**TS84-S32**	6.8
(S)	F	Minor-C	**TS84-S33**	7.8



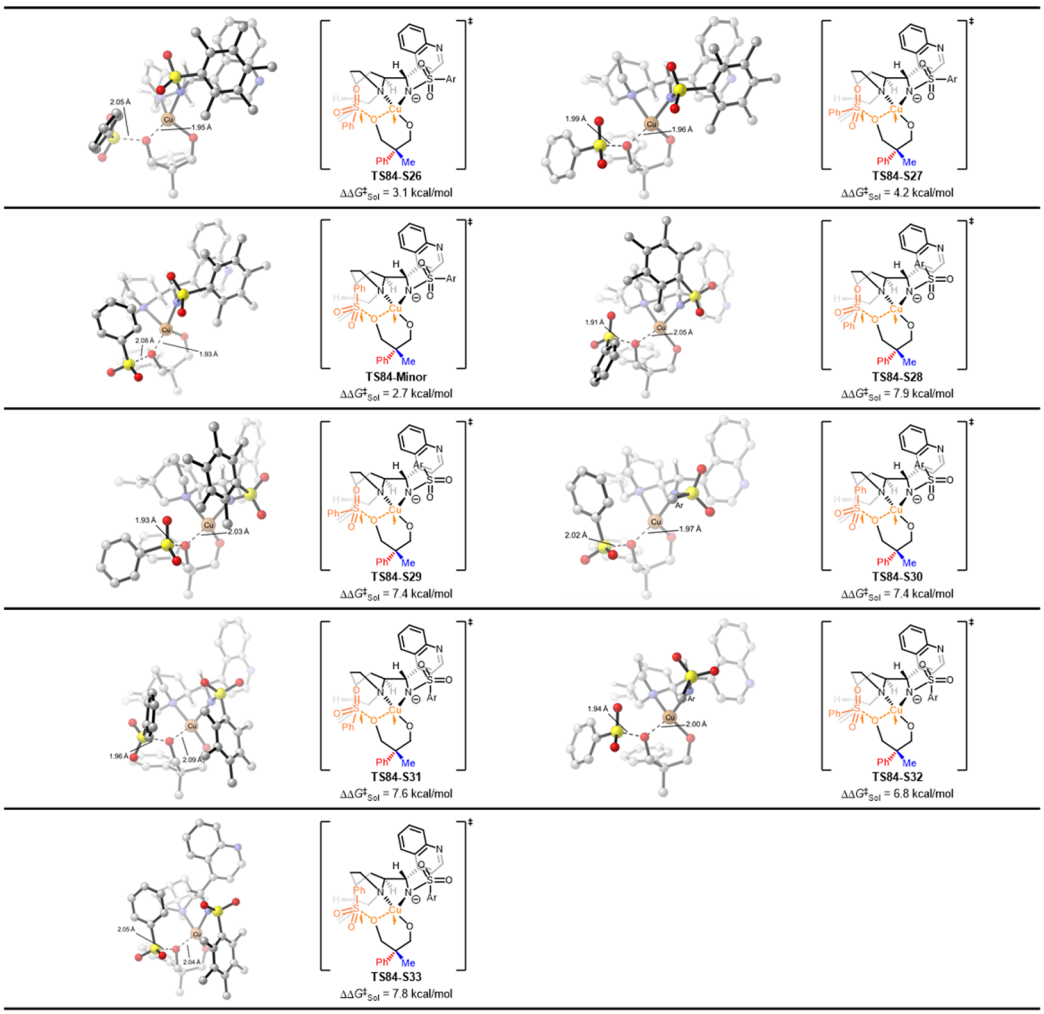
Supplementary Fig. 42 | Key conformers of S–O bond formation transition states leading to the major product with A, B, and C ligand conformation. Free energies are compared to **TS84-Major**. Trivial hydrogen atoms are omitted for clarity. Ar, 2,3,4,5,6-pentamethylphenyl.



Supplementary Fig. 43 | Key conformers of S–O bond formation transition states leading to the major product with D, E, and F ligand conformation. Free energies are compared to **TS84-Major**. Trivial hydrogen atoms are omitted for clarity. Ar, 2,3,4,5,6-pentamethylphenyl.



Supplementary Fig. 44 | Key conformers of S–O bond formation transition states leading to the minor product with A, B, and C ligand conformation. Free energies are compared to **TS84-Major**. Trivial hydrogen atoms are omitted for clarity. Ar, 2,3,4,5,6-pentamethylphenyl.



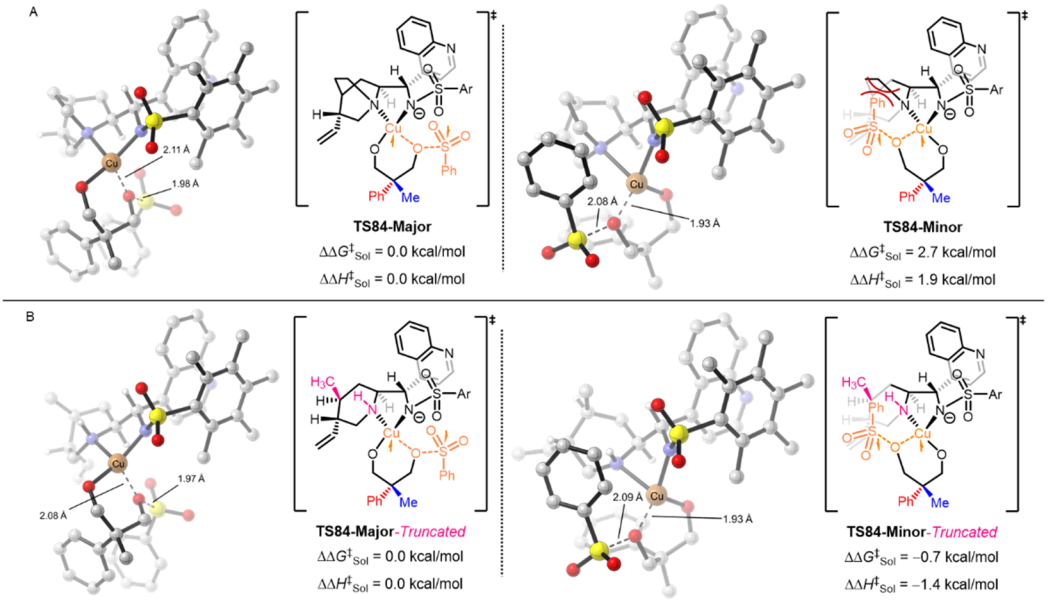
Supplementary Fig. 45 | Key conformers of S–O bond formation transition states leading to the minor product with D, E, and F ligand conformation. Free energies are compared to **TS84-Major**. Trivial hydrogen atoms are omitted for clarity. Ar, 2,3,4,5,6-pentamethylphenyl.

9. Verification of computed stereoselectivity by various levels of theory

Supplementary Table 11 | Verification of computed stereoselectivity by various levels of theory.

Computational Method for Single Point Energy Calculation	*$\Delta\Delta G^{\ddagger}$ (TS84-Minor) − $\Delta\Delta G^{\ddagger}$ (TS84-Major) /kcal/mol*
B3LYP-D3(BJ)/6-311+G(d, p)-SDD-SMD(Chloroform)	2.1
B3LYP-D3(BJ)/Def2-TZVP[40,50]-SMD(Chloroform)	2.4
M06-L/6-311+G(d, p)-SDD-SMD(Chloroform)	2.7
M06[51]/6-311+G(d, p)-SDD-SMD(Chloroform)	5.0
PBE0[52–54]-D3(BJ)/6-311+G(d, p)-SDD-SMD(Chloroform)	2.9
ωB97X-D[55]/6-311+G(d, p)-SDD-SMD(Chloroform)	1.2

10. Verification of the steric effects of quinuclidine moiety in enantioselectivity determination of S–O bond formation



Supplementary Fig. 46 | (**A**) Enantioisomeric S–O bond formation transition states with ligand **L*4**. (**B**) Enantioisomeric S–O bond formation transition states with the truncated ligand. Ar, 2,3,4,5,6-pentamethylphenyl.

To verify that the steric effects of quinuclidine moiety are the leading factor that controls the enantioselectivity of S–O bond formation, we also computed the enantioisomeric S–O bond formation transition states using the truncated ligand model. In the full ligand model (Ligand = **L*4**), **TS84-Minor** is 2.7 kcal/mol higher in free energy as compared to **TS84-Major**, which we believe is due to the steric repulsions between the attacking sulfonyl radical and the quinuclidine moiety in **TS84-Minor** (Supplementary Fig. 46A). By removing one of the carbon bridges of the quinuclidine moiety, such steric repulsions should be moved. We indeed found that the truncated model has a much lower and opposite enantioselectivity between the competing transition states (**TS84-Major-***Truncated* vs. **TS84-Minor-***Truncated*, Supplementary Fig. 46B), which verified our mechanistic rational of the enantioselectivity.

11. Table of energies

Supplementary Table 12 | Energies in Fig. 5, Supplementary Figs. 24–38 and 42–46, and Supplementary Tables 8–11

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
A-1	0.225009	0.237549	0.188009	−540.016082	−539.778533	−539.828073	
S-1	0.102043	0.111871	0.066658	−1240.507226	−1240.395355	−1240.440568	
1	0.316757	0.337158	0.266703	−1319.712180	−1319.375022	−1319.445477	
Int81	0.815423	0.862842	0.735681	−2614.278397	−2613.415555	−2613.542716	
Int82	0.098934	0.107484	0.065227	−780.274236	−780.166752	−780.209009	
Int83-*OSS*	0.915905	0.972632	0.824188	−3394.583715	−3393.611083	−3393.759527	
Int83-*Triplet*	0.916035	0.972659	0.824025	−3394.583528	−3393.610869	−3393.759503	
TS84-Major	0.915886	0.972038	0.826205	−3394.574038	−3393.602000	−3393.747833	277.0*i*
TS84-Minor	0.916422	0.972392	0.827898	−3394.571358	−3393.598966	−3393.743460	249.8*i*
Int85	0.918263	0.974585	0.827171	−3394.590997	−3393.616412	−3393.763826	
Int86	0.827070	0.875305	0.745943	−2614.897468	−2614.022163	−2614.151525	
Chloroform	0.019991	0.025395	-0.008185	−1419.312417	−1419.287022	−1419.320602	
Chlorine Radical	0.000000	0.002360	−0.015677	−460.138976	−460.136616	−460.154653	
Chlorine Anion	0.000000	0.002360	−0.015023	−460.359698	−460.357338	−460.374721	
Int-S1	0.841294	0.889743	0.761114	−2615.393446	−2614.503703	−2614.632332	
TS-S2	0.944260	1.003185	0.849387	−3855.919458	−3854.916273	−3855.070071	164.7*i*
TS-S2-1	0.965559	1.030912	0.860891	−5275.249721	−5274.218809	−5274.388830	168.1*i*
Int-S3	0.845033	0.894785	0.763117	−3075.643068	−3074.748283	−3074.879951	
Int-S3-2	0.965949	1.03194	0.860080	−5275.261833	−5274.229893	−5274.401753	
Int-S5	0.843392	0.891326	0.763926	−2615.234096	−2614.342770	−2614.470170	
Int-S6	0.099068	0.109905	0.059515	−1240.643806	−1240.533901	−1240.584291	
Int-S8	0.944965	1.004186	0.849362	−3855.908719	−3854.904533	−3855.059357	
Int-S8-1	0.944775	1.004125	0.848713	−3855.907353	−3854.903228	−3855.058640	
Int-S9	0.862533	0.917510	0.770320	−4034.722674	−4033.805164	−4033.952354	
Int-S10	0.966263	1.032133	0.859209	−5275.236748	−5274.204615	−5274.377539	
Bicarbonate Anion	0.026269	0.030730	0.000493	−264.584283	−264.553553	−264.583790	
Carbonate Anion	0.013999	0.018134	−0.011581	−264.010242	−263.992108	−264.021823	

Int-S11	0.843392	0.891326	0.763926	−2615.234096	−2614.342770	−2614.470170	
Int-S12	0.855042	0.908444	0.767822	−2879.350013	−2878.441569	−2878.582191	
Int-S12-1	0.855670	0.909260	0.765121	−2879.349635	−2878.440375	−2878.584514	
TS-S13	0.850960	0.903433	0.763813	−2879.360931	−2878.457498	−2878.597118	1193.4*i*
TS-S13-1	0.850827	0.903883	0.760885	−2879.348944	−2878.445061	−2878.588059	477.3*i*
Int-S14	0.830532	0.877779	0.751699	−2614.784577	−2613.906798	−2614.032878	
Int-S14-1	0.854825	0.908053	0.765152	−2879.360514	−2878.452461	−2878.595362	
TS-S15	0.835872	0.888506	0.747375	−2878.820832	−2877.932326	−2878.073457	1262.5*i*
TS84-S1	0.915759	0.972192	0.824791	−3394.564851	−3393.592659	−3393.740060	294.9*i*
TS84-S2	0.915862	0.972049	0.826597	−3394.572204	−3393.600155	−3393.745607	284.1*i*
TS84-S3	0.916216	0.972210	0.828326	−3394.571434	−3393.599224	−3393.743108	351.0*i*
TS84-S4	0.915690	0.971909	0.825185	−3394.552943	−3393.581034	−3393.727758	200.5*i*
TS84-S5	0.915662	0.971882	0.825360	−3394.554964	−3393.583082	−3393.729604	213.8*i*
TS84-S6	0.915847	0.972110	0.826523	−3394.557581	−3393.585471	−3393.731058	233.4*i*
TS84-S7	0.915790	0.972301	0.825141	−3394.565733	−3393.593432	−3393.740592	323.1*i*
TS84-S8	0.915667	0.972156	0.824532	−3394.568393	−3393.596237	−3393.743861	235.6*i*
TS84-S9	0.916632	0.972719	0.828463	−3394.567688	−3393.594969	−3393.739225	288.9*i*
TS84-S10	0.915129	0.971615	0.823191	−3394.568722	−3393.597107	−3393.745531	282.4*i*
TS84-S11	0.916251	0.972375	0.827232	−3394.570435	−3393.598060	−3393.743203	367.6*i*
TS84-S12	0.915419	0.972032	0.823745	−3394.567836	−3393.595804	−3393.744091	278.5*i*
TS84-S13	0.914762	0.971398	0.822372	−3394.563298	−3393.591900	−3393.740926	195.6*i*
TS84-S14	0.915119	0.971723	0.823253	−3394.559125	−3393.587402	−3393.735872	323.7*i*
TS84-S15	0.915389	0.972101	0.823016	−3394.568688	−3393.596587	−3393.745672	220.4*i*
TS84-S16	0.916106	0.972538	0.825695	−3394.567715	−3393.595177	−3393.742020	349.6*i*
TS84-S17	0.916362	0.972449	0.826675	−3394.568693	−3393.596244	−3393.742018	328.5*i*
TS84-S18	0.916442	0.972400	0.827365	−3394.567983	−3393.595583	−3393.740618	295.8*i*
TS84-S19	0.916175	0.972269	0.827604	−3394.570164	−3393.597895	−3393.742560	232.3*i*
TS84-S20	0.915683	0.972181	0.823936	−3394.562291	−3393.590110	−3393.738355	325.4*i*
TS84-S21	0.916777	0.972615	0.828974	−3394.566480	−3393.593865	−3393.737506	305.4*i*
TS84-S22	0.915839	0.972067	0.826999	−3394.561694	−3393.589627	−3393.734695	371.1*i*
TS84-S23	0.916295	0.972530	0.826623	−3394.563788	−3393.591258	−3393.737165	388.6*i*
TS84-S24	0.916774	0.972613	0.828963	−3394.566488	−3393.593875	−3393.737525	305.1*i*
TS84-S25	0.916050	0.972512	0.825776	−3394.561200	−3393.588688	−3393.735424	323.1*i*
TS84-S26	0.916180	0.972295	0.826346	−3394.569263	−3393.596968	−3393.742917	262.7*i*

TS84-S27	0.916120	0.972144	0.826671	−3394.567740	−3393.595596	−3393.741069	221.7*i*
TS84-S28	0.915307	0.972048	0.822098	−3394.557372	−3393.585324	−3393.735274	318.2*i*
TS84-S29	0.915403	0.971888	0.823661	−3394.559647	−3393.587759	−3393.735986	291.7*i*
TS84-S30	0.915090	0.971723	0.824042	−3394.560040	−3393.588317	−3393.735998	318.9*i*
TS84-S31	0.915794	0.972324	0.824560	−3394.560323	−3393.587999	−3393.735763	372.9*i*
TS84-S32	0.916209	0.972303	0.826888	−3394.563874	−3393.591571	−3393.736986	284.0*i*
TS84-S33	0.916217	0.972419	0.827709	−3394.563169	−3393.590750	−3393.735460	319.5*i*
TS84-Major-Truncated	0.907482	0.964310	0.817343	−3356.466391	−3355.502081	−3355.649048	260.6*i*
TS84-Minor-Truncated	0.908511	0.965012	0.819036	−3356.469264	−3355.504252	−3355.650228	227.9*i*

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at M06-L/6-311+G(d,p)-SDD-SMD(Chloroform)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Supplementary Table 13 | Energies for vdW complex Int-S10 and ISET transition state TS-S2-1

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
Int-S10	0.966253	1.032125	0.859243	−5273.832429	−5272.800304	−5272.973186	
TS-S2-1	0.965559	1.030912	0.860891	−5273.826775	−5272.795863	−5272.965884	168.1*i*

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

Supplementary Table 14 | Energies in Supplementary Table 7

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
Pyrrolidin-2-One	0.096644	0.102675	0.068168	−286.175174	−286.072499	−286.107006	
Pyrrolidin-2-One-Anion	0.111686	0.118022	0.082872	−286.687026	−286.569004	−286.604154	
L*11-Anion	0.658926	0.695247	0.588819	−1976.171867	−1975.476620	−1975.583048	
L*11	0.677210	0.713257	0.607901	−1976.724192	−1976.010935	−1976.116291	
L*4-Anion	0.610739	0.644804	0.547338	−1878.032365	−1877.387561	−1877.485027	
L*4	0.625782	0.659910	0.561983	−1878.528038	−1877.868128	−1877.966055	

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at M06-L/6-311+G(d,p)-SDD-(DMSO)//B3LYP-D3(BJ)/ 6-31G(d)-LANL2DZ level of theory.

Supplementary Table 15 | Energies in Supplementary Table 8

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
1-Sol	0.225153	0.237682	0.188141	−540.016098	−539.778416	−539.827957	
A-1-Sol	0.316901	0.337331	0.266563	−1319.712432	−1319.375101	−1319.445869	
Int81-Sol	0.815954	0.863398	0.735864	−2614.278545	−2613.415147	−2613.542681	
Int82-Sol	0.099005	0.107555	0.065296	−780.274265	−780.166710	−780.208969	
Int83-*OSS*-**Sol**	0.916684	0.97334	0.825439	−3394.584133	−3393.610793	−3393.758694	
Int83-*Triplet*-**Sol**	0.916699	0.973312	0.824521	−3394.583882	−3393.610570	−3393.759361	
TS84-Major-Sol	0.916675	0.972733	0.827632	−3394.574922	−3393.602189	−3393.747290	275.2*i*
Int85-Sol	0.919146	0.975403	0.828132	−3394.591692	−3393.616289	−3393.763560	
Int86-Sol	0.827530	0.875829	0.745563	−2614.897886	−2614.022057	−2614.152323	

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at M06-L/6-311+G(d,p)-SDD-SMD(Chloroform)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ-SMD(Chloroform) level of theory.

Supplementary Table 16 | Energies in Supplementary Table 8

Structure	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
1-S1	0.315396	0.335719	0.265586	−1319.711104	−1319.375385	−1319.445518	
A-1-S1	0.223965	0.236490	0.186892	−540.015547	−539.779057	−539.828655	
Int81-S1	0.809520	0.856932	0.729838	−2614.276498	−2613.419566	−2613.546660	
Int82-S1	0.098694	0.107218	0.065054	−780.273940	−780.166722	−780.208886	
Int83-*OSS*-**S1**	0.910062	0.966568	0.818299	−3394.580639	−3393.614071	−3393.762340	
Int83-*Triplet*-**S1**	0.910087	0.966619	0.819264	−3394.580794	−3393.614175	−3393.761530	
TS84-S34	0.910348	0.966255	0.821334	−3394.571105	−3393.604850	−3393.749771	305.1*i*
Int85-S1	0.912423	0.968578	0.821623	−3394.588981	−3393.620403	−3393.767358	
Int86-S1	0.821071	0.869273	0.739829	−2614.89494	−2614.025667	−2614.155111	

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at M06-L/6-311+G(d,p)-SDD-(Chloroform)//B3LYP-D3(BJ)/Def2-SVP level of theory.

Supplementary Table 17 | Energies in Supplementary Figs. 30 and 38–40

Structure	*E*
S-1	−1240.493976
Int82	−780.262100
Chlorine Radical	−460.136082
Int81	−2614.201946
Int83-*Triplet*	−3394.501427
Int83-*Triplet***_H-Bond-Frag-All**	−2658.220216
Int83-*Triplet***_H-Bond-Frag-H-Donor**	−1877.939996
Int83-*Triplet***_H-Bond-Frag-Sulf**	−780.256869
Int83-*Triplet***_pi-pi-Frag**	−1051.857699
Int83-*Triplet***_pi-pi-Frag-Sulf**	−780.256869
Int83-*Triplet***_pi-pi-Frag-Tol**	−271.590107

Energies (*E*) (in Hartree) of the structures calculated at M06-L/6-311+G(d,p)-SDD-(Gas Phase) level of theory.

Supplementary Table 18 | Energies for MECP and intermediates connecting to MECP

Structure	*E*
Int83-*OSS*-**S1**	−3394.499497
MECP	−3394.499174
Int83-*Triplet*-**S1**	−3394.499341

Energies (*E*) (in Hartree) of the structures calculated at M06-L/6-311+G(d,p)-SDD-(Gas Phase). MECP structure is optimized with ORCA 5.0 at B3LYP/G-D3(BJ)/Def2-SVP level of theory.

Supplementary Table 19 | Energies in Supplementary Table 11 for TS84-Major

Level of Theory	*E*
B3LYP-D3(BJ)/6-311+G(d, p)-SDD-SMD(Chloroform)	−3395.175851
B3LYP-D3(BJ)/Def2-TZVP-SMD(Chloroform)	−4838.735790
M06-L/6-311+G(d, p)-SDD-SMD(Chloroform)	−3394.574038
M06/6-311+G(d, p)-SDD-SMD(Chloroform)	−3393.134957
PBE0-D3(BJ)/6-311+G(d, p)-SDD-SMD(Chloroform)	−3391.854350
ωB97X-D/6-311+G(d, p)-SDD-SMD(Chloroform)	−3394.072393

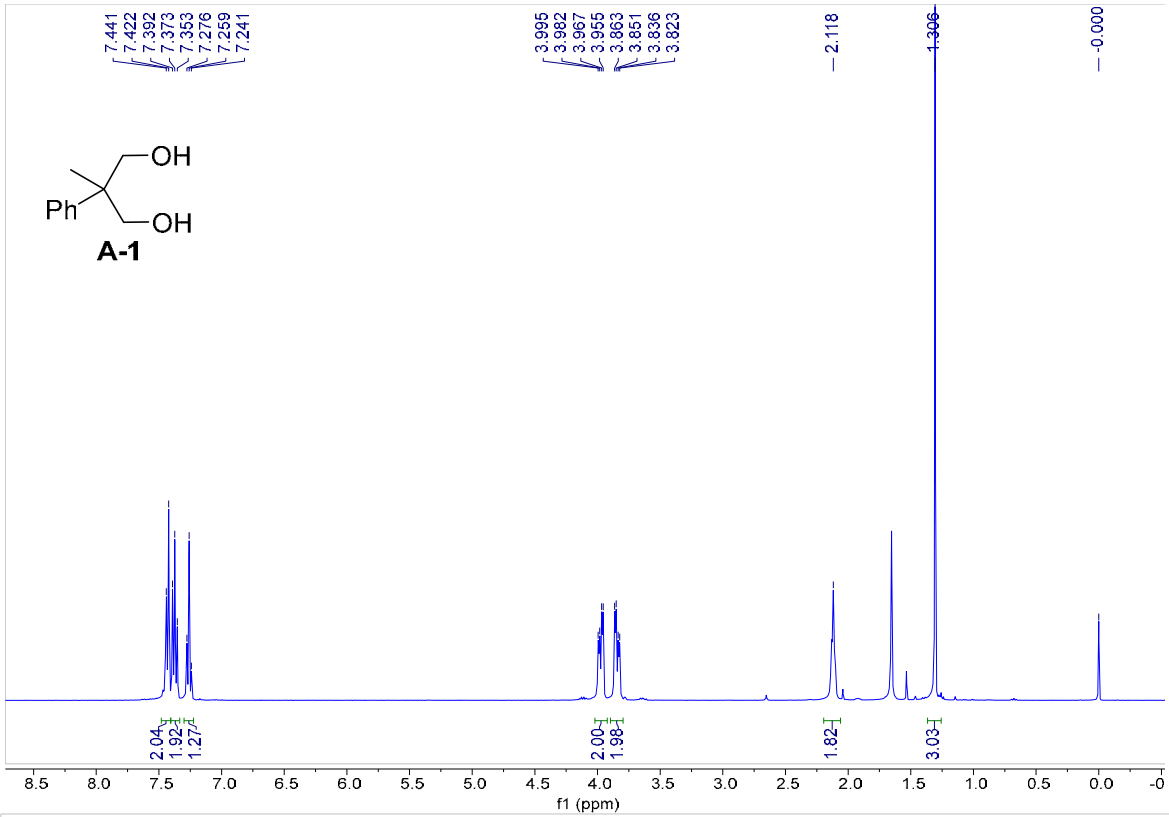
Energies (*E*) (in Hartree) of the structures. The level of theory for computation is labeled in this table.

Supplementary Table 20 | Energies in Supplementary Table 11 for TS84-Minor

Level of Theory	*E*
B3LYP-D3(BJ)/6-311+G(d, p)-SDD-SMD(Chloroform)	−3395.174246
B3LYP-D3(BJ)/Def2-TZVP-SMD(Chloroform)	−4838.733679
M06-L/6-311+G(d, p)-SDD-SMD(Chloroform)	−3394.571358
M06/6-311+G(d, p)-SDD-SMD(Chloroform)	−3393.128678
PBE0-D3(BJ)/6-311+G(d, p)-SDD-SMD(Chloroform)	−3391.851395
ωB97X-D/6-311+G(d, p)-SDD-SMD(Chloroform)	−3394.072122

Energies (*E*) (in Hartree) of the structures. The level of theory for computation is labelled in this table.

NMR spectra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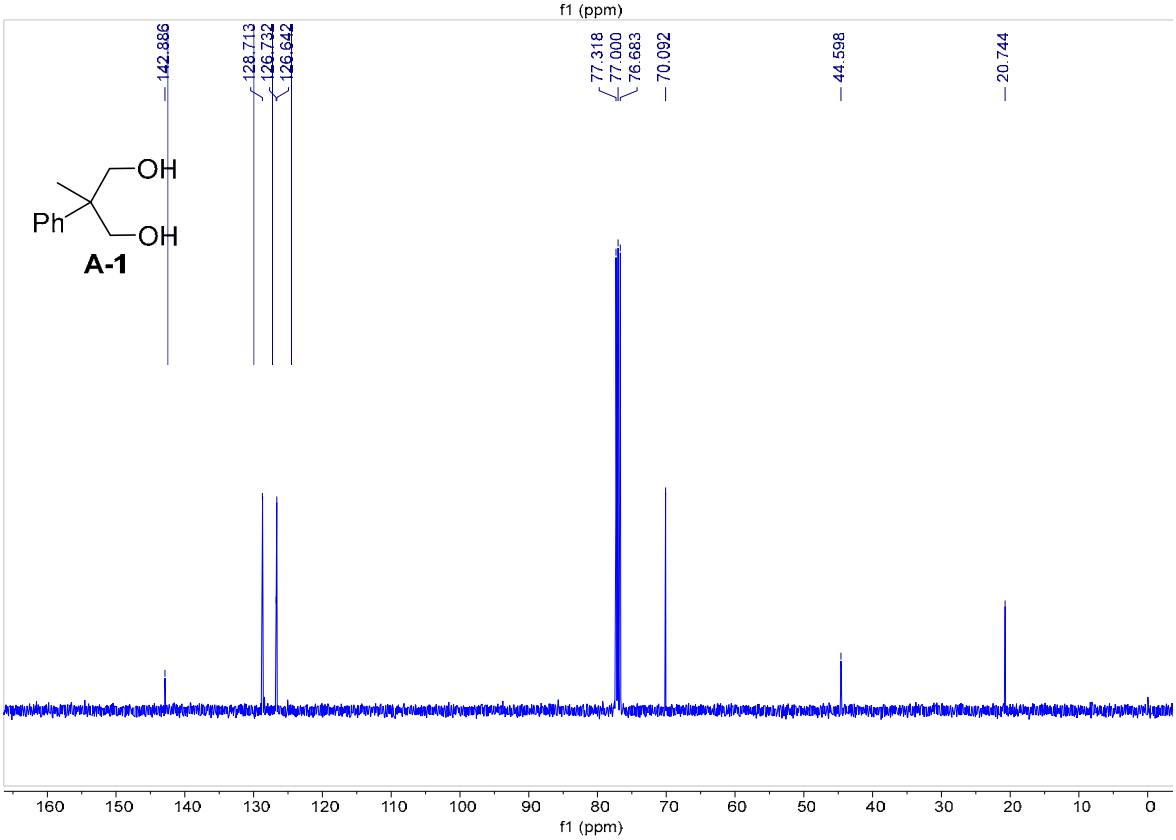
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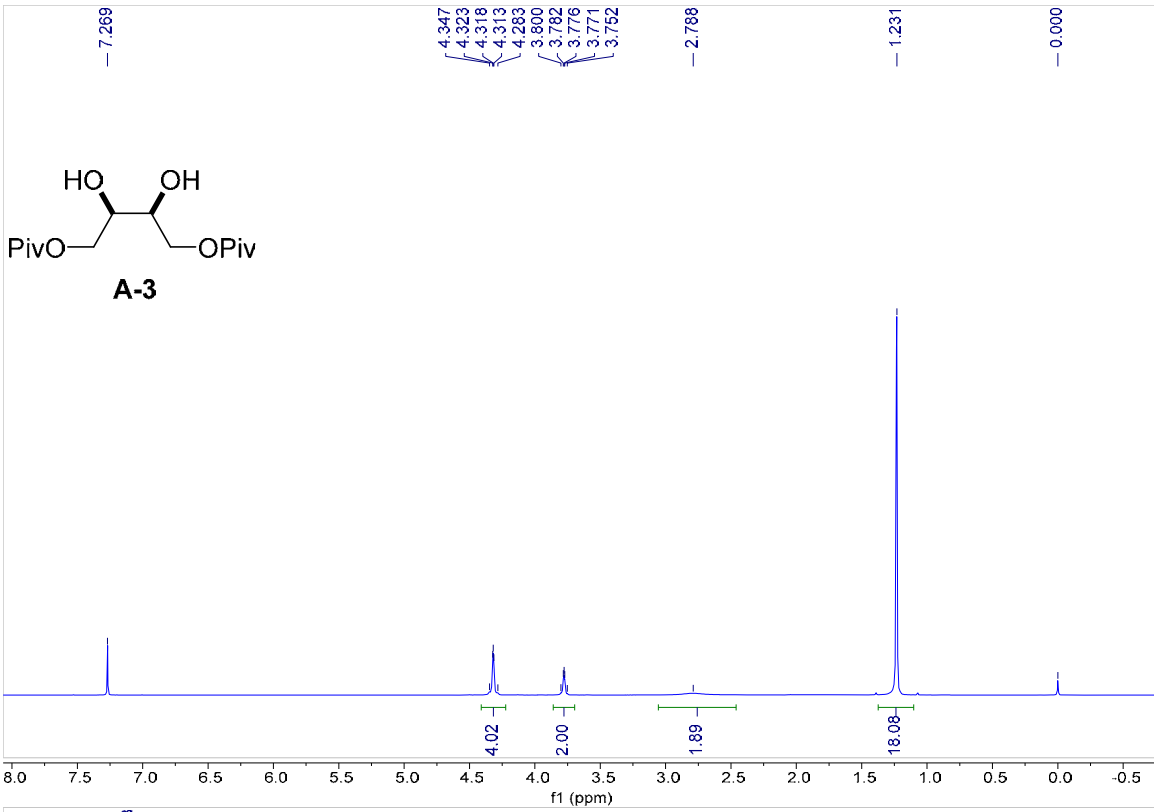
Ph
OH
A-1
f1 (ppm)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OH
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OPiv
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2.00
1.89
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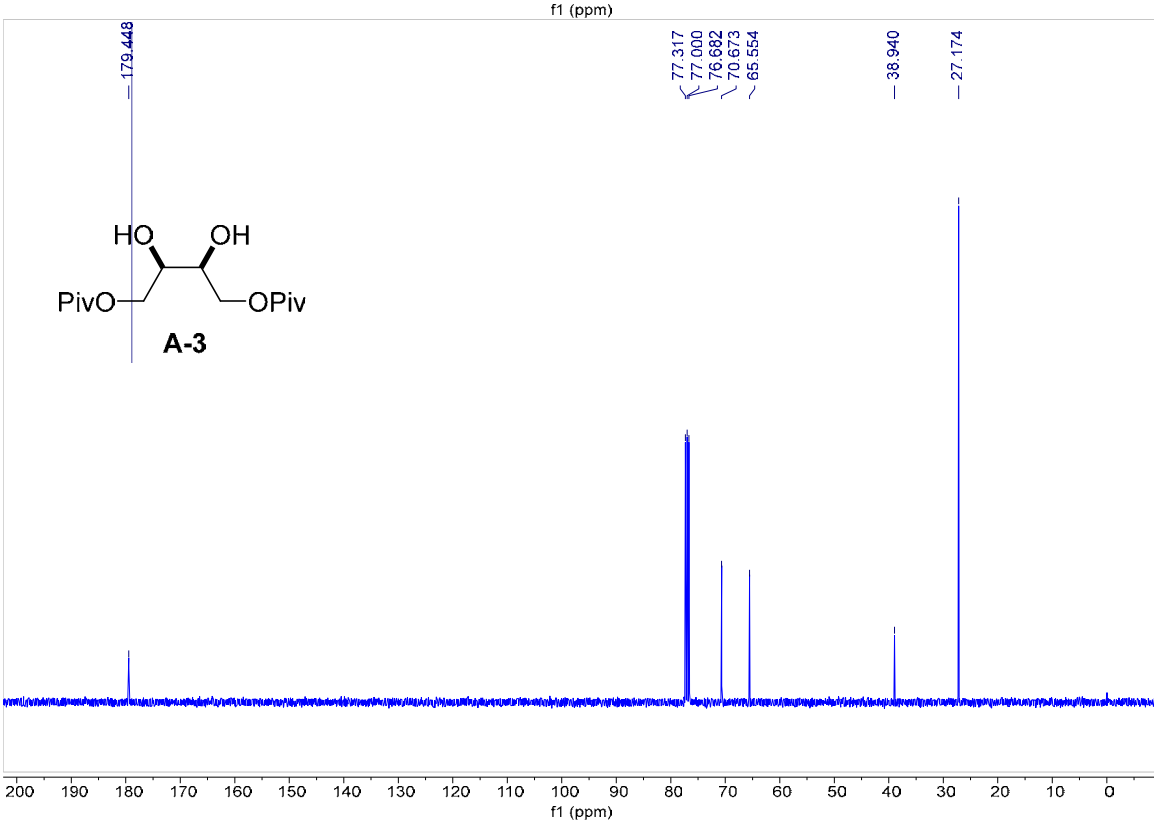
f1 (ppm)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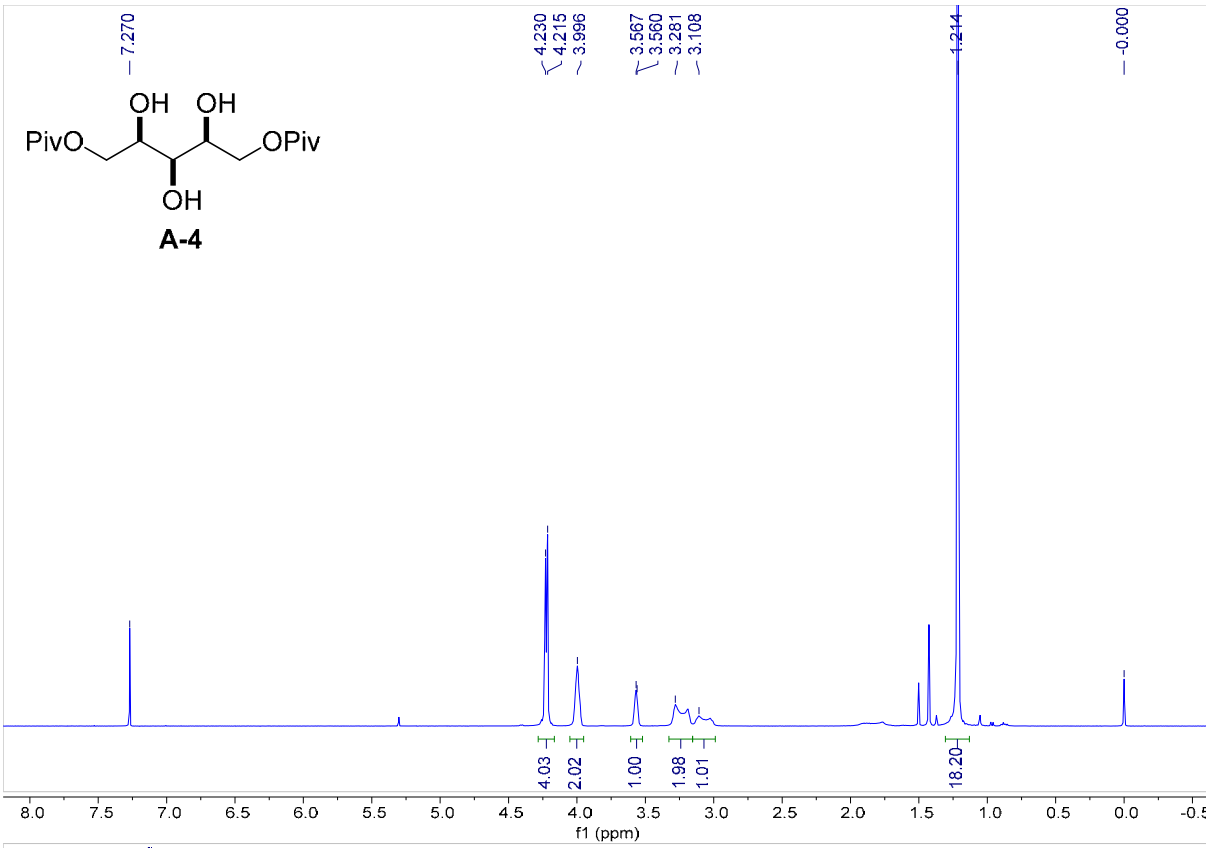
OH
PivO
OPiv
A-3
f1 (ppm)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OH
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OH
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2.02
1.00
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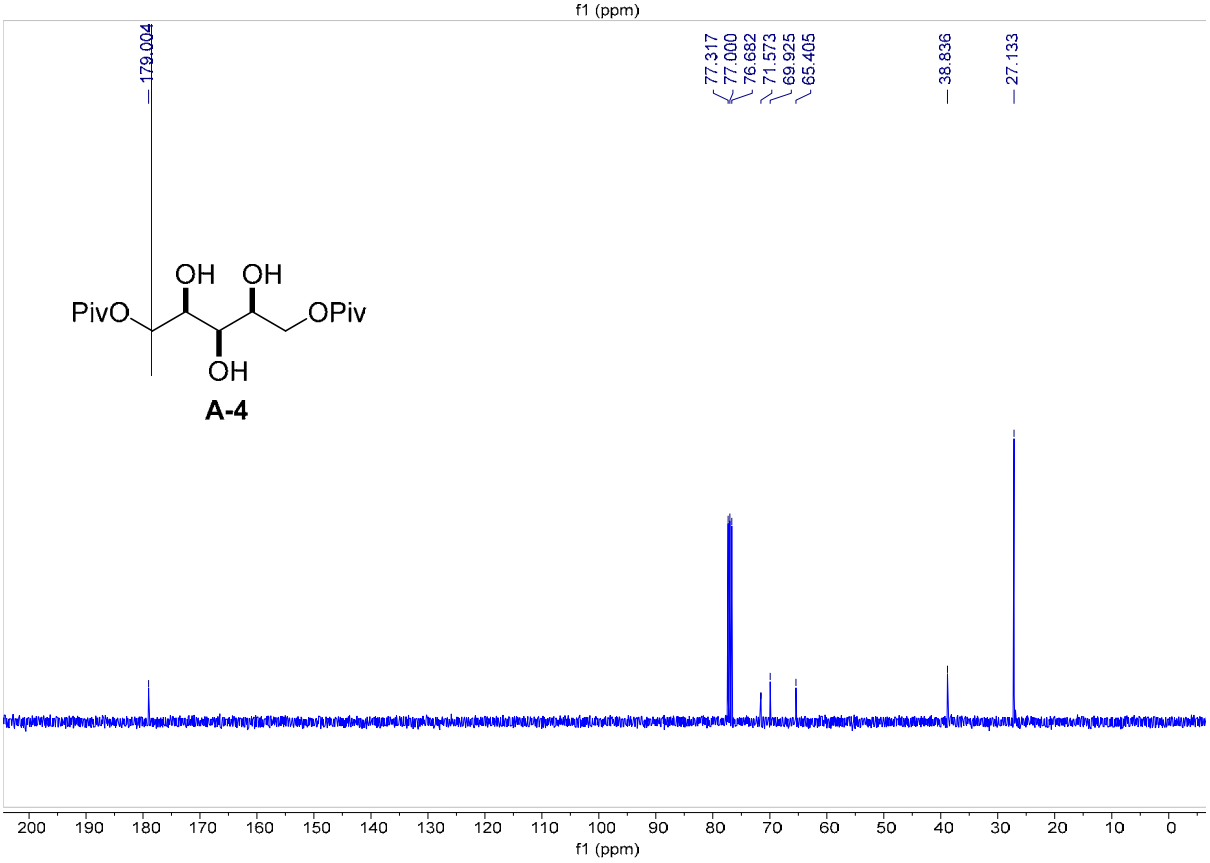
1.01
18.20
f1 (ppm)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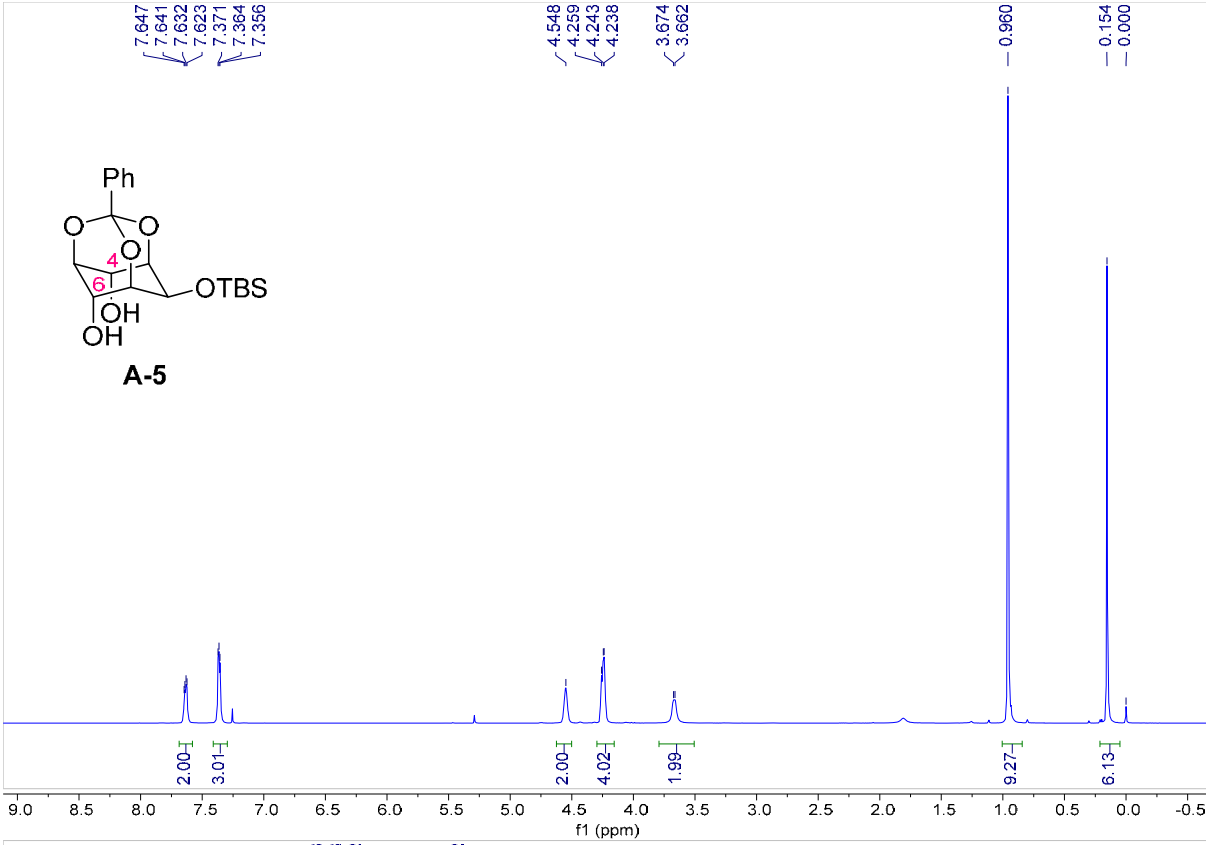
A-4
f1 (ppm)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0.000
Ph
O
O
O
4
6
OTBS
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OH
A-5
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2.00
4.02
1.99
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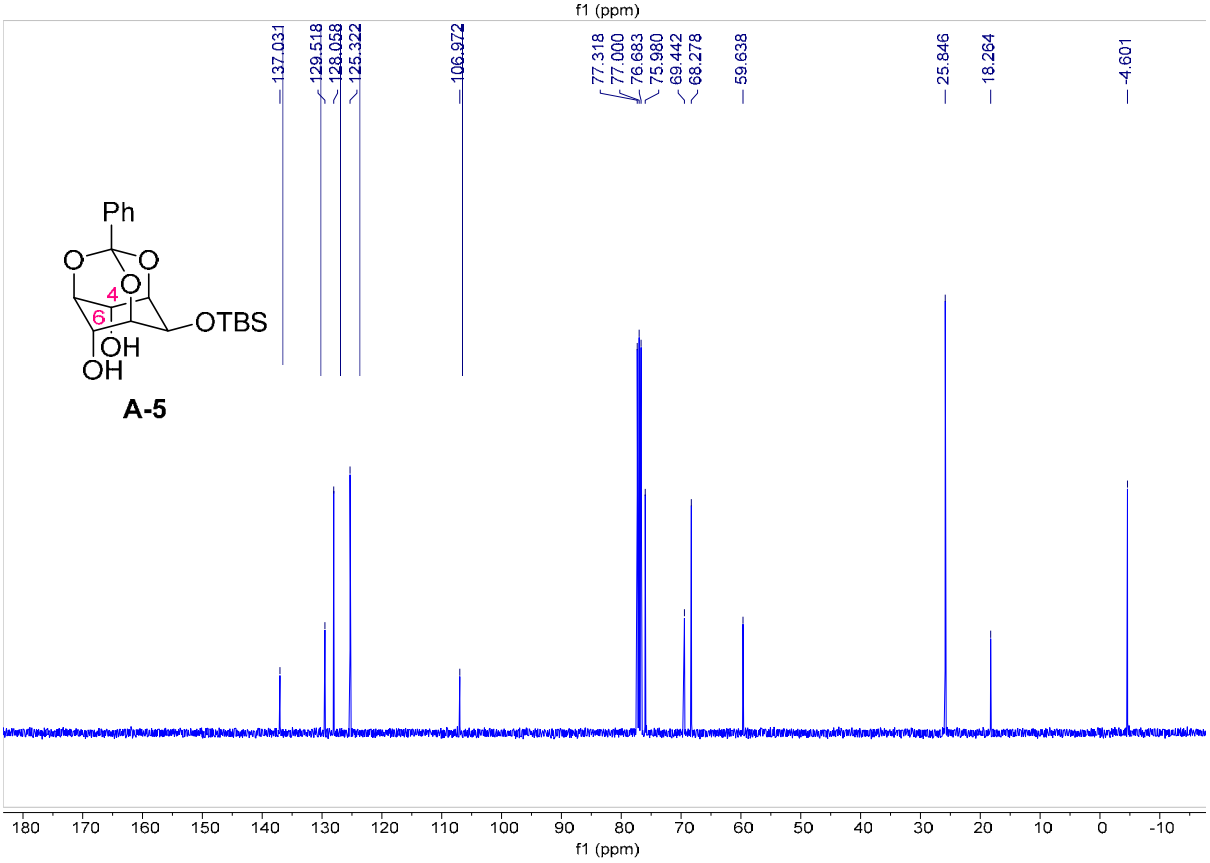
f1 (ppm)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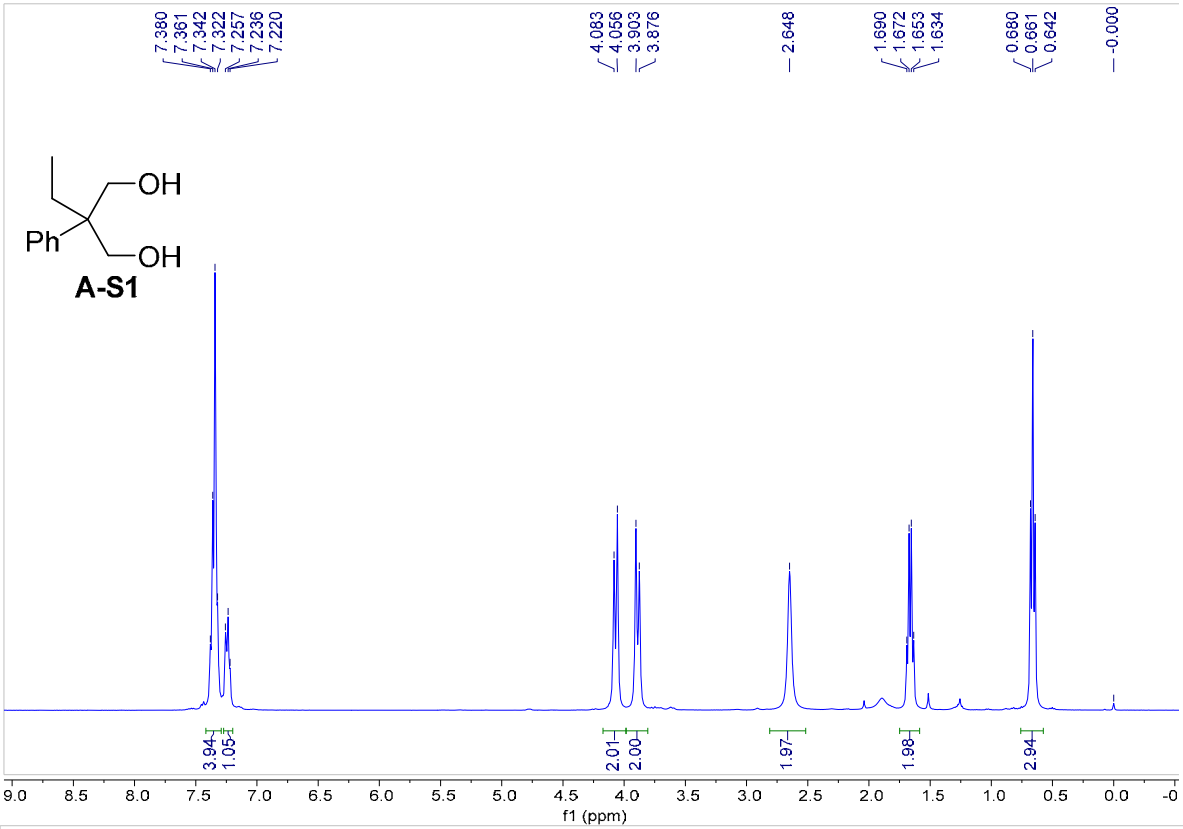
Ph
O
O
O
4
6
OTBS
OH
OH
A-5
f1 (ppm)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1.672
1.653
1.634
0.680
0.661
0.642
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OH
Ph
OH
A-S1
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1.05
2.01
2.00
1.97
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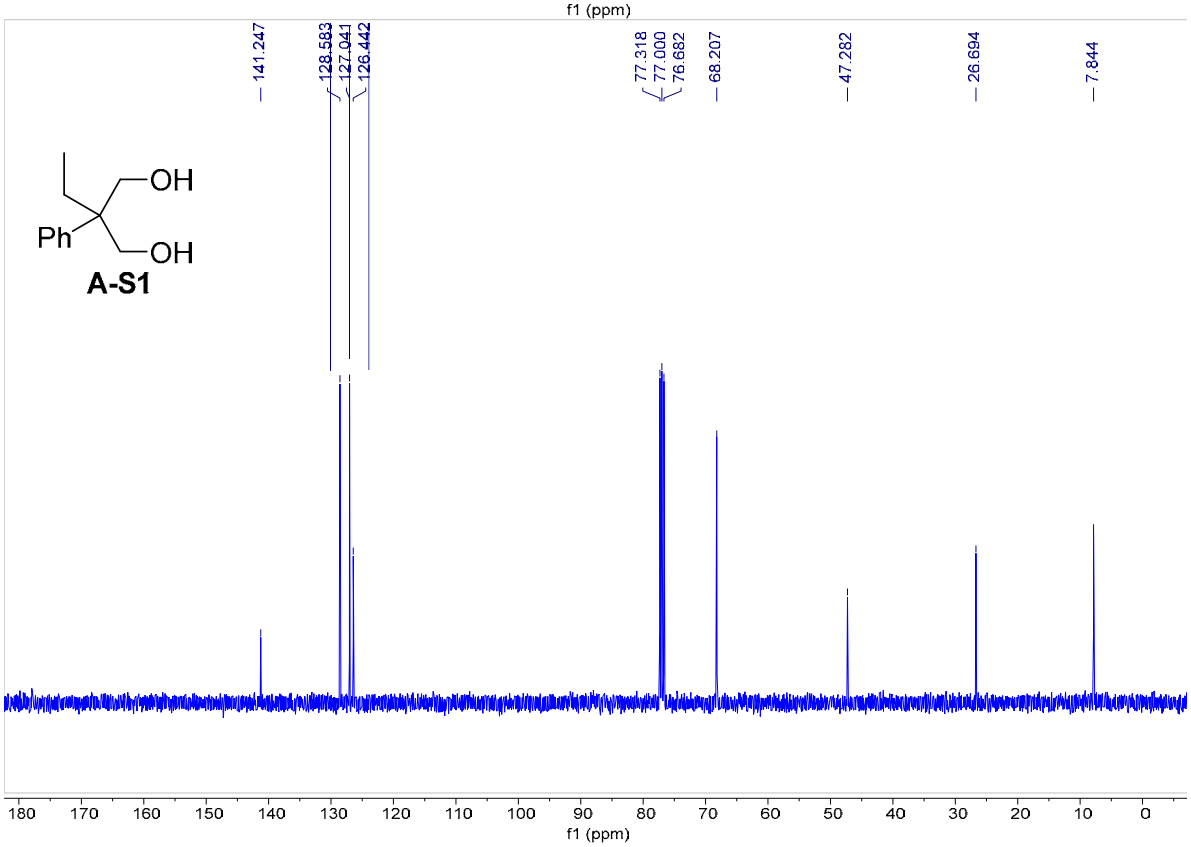
2.94
f1 (ppm)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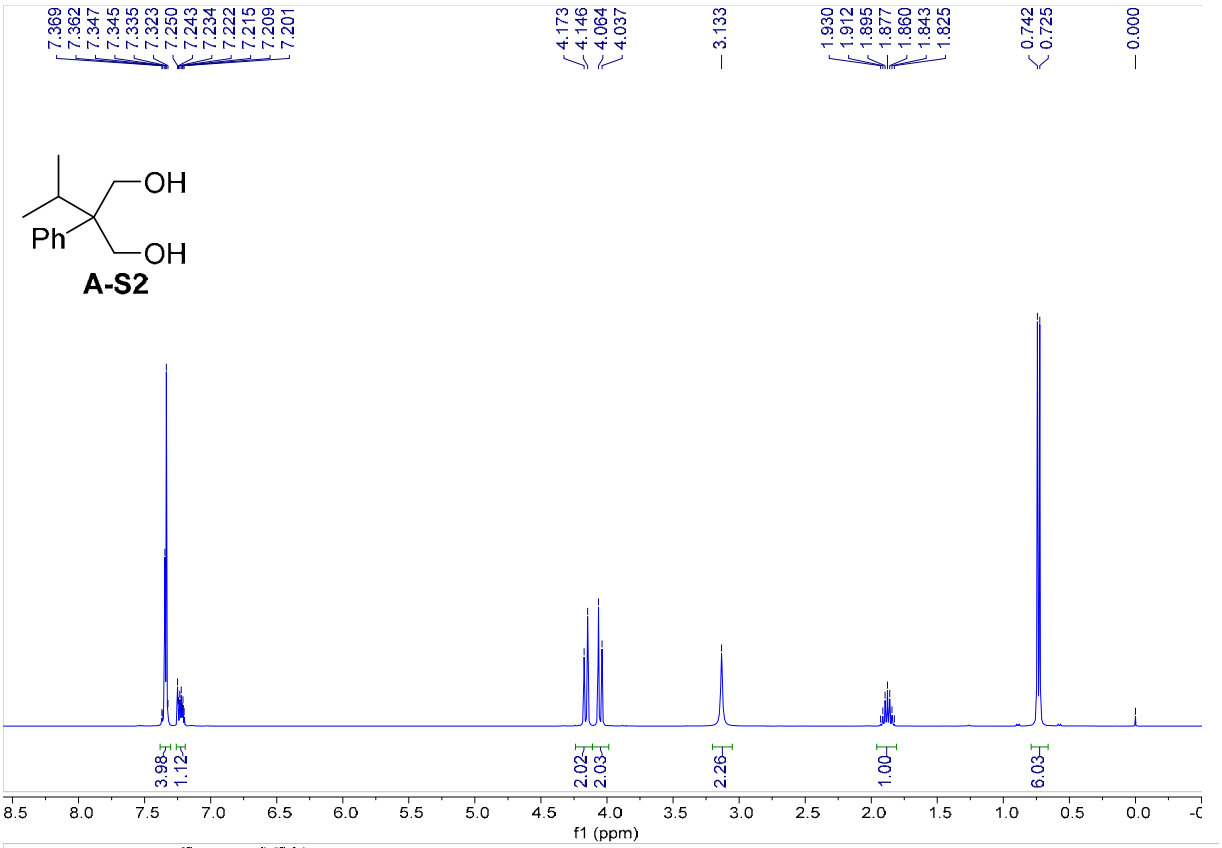
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1.912
1.895
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1.825
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0.725
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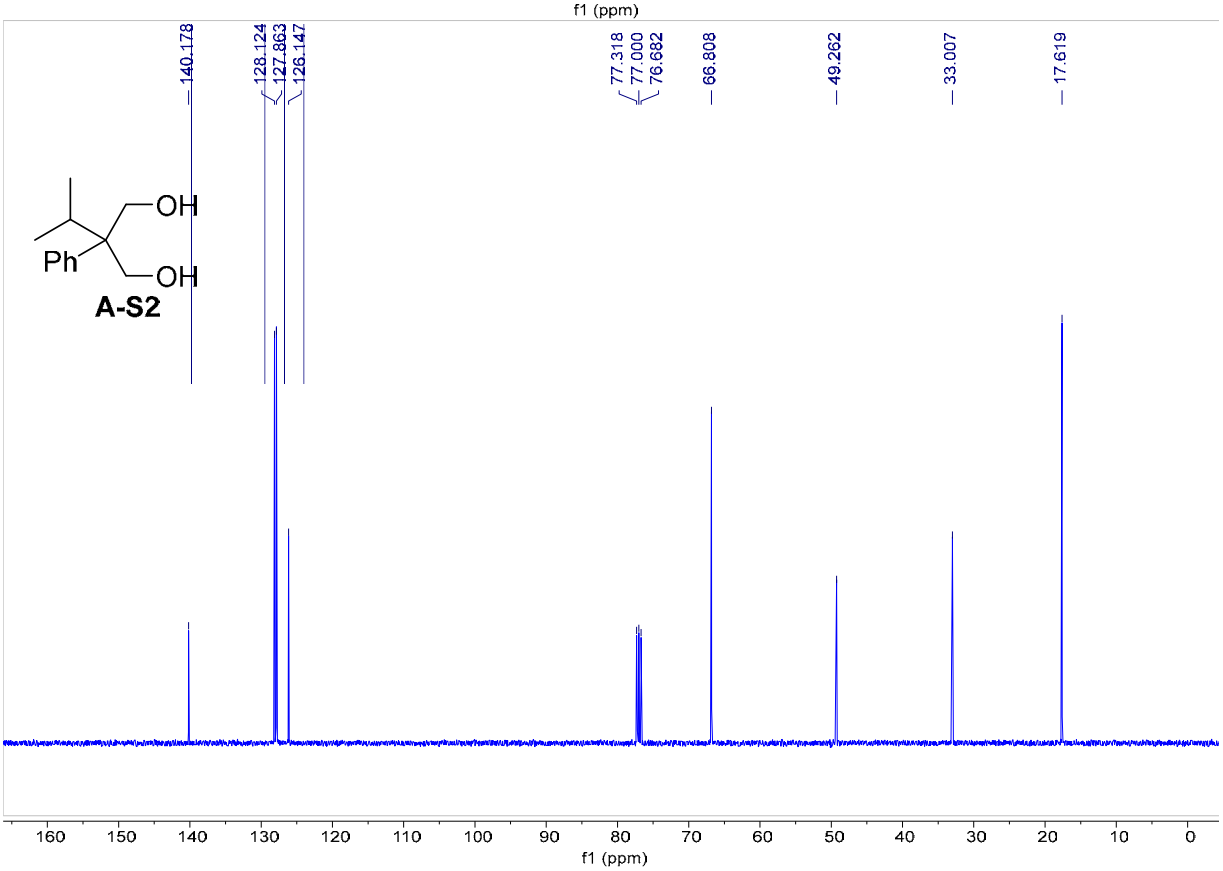
f1 (ppm)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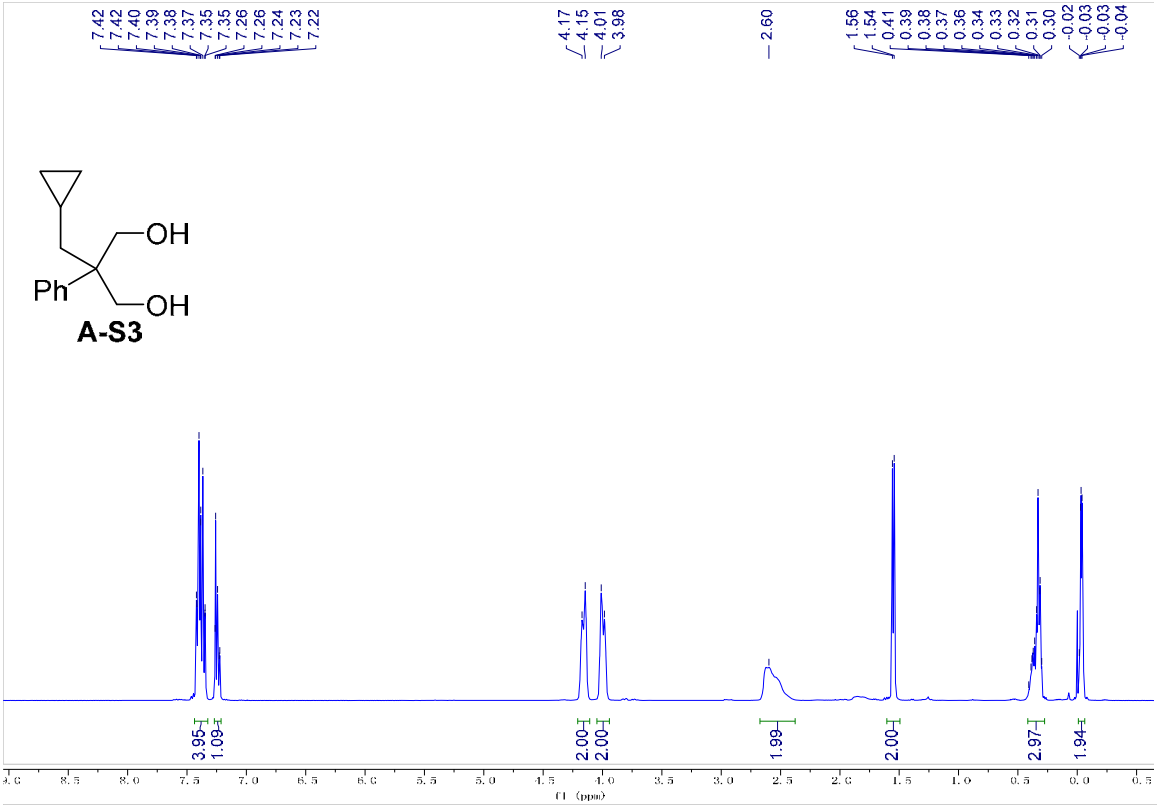
Ph
OH
A-S2
f1 (ppm)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4.15
4.01
3.98
2.60
1.56
1.54
0.41
0.39
0.38
0.37
0.36
0.34
0.33
0.32
0.31
0.30
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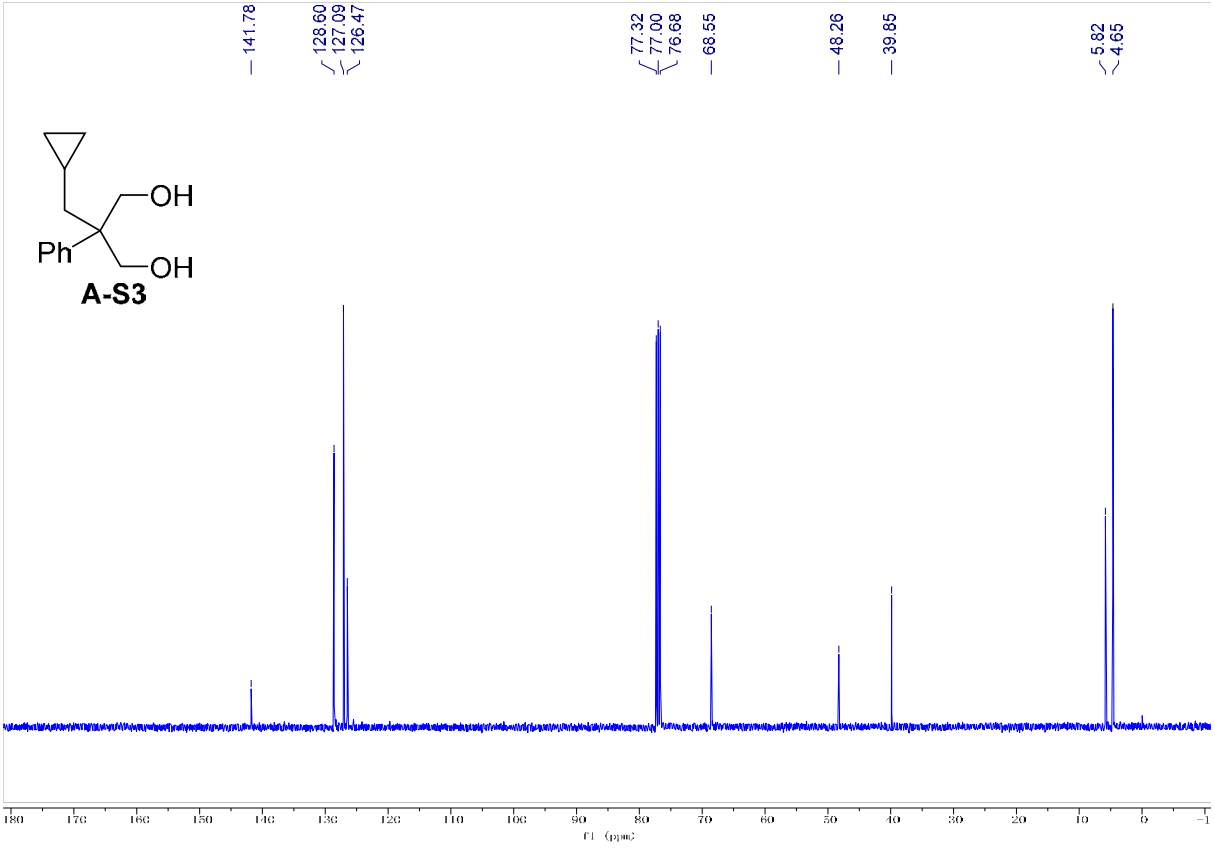
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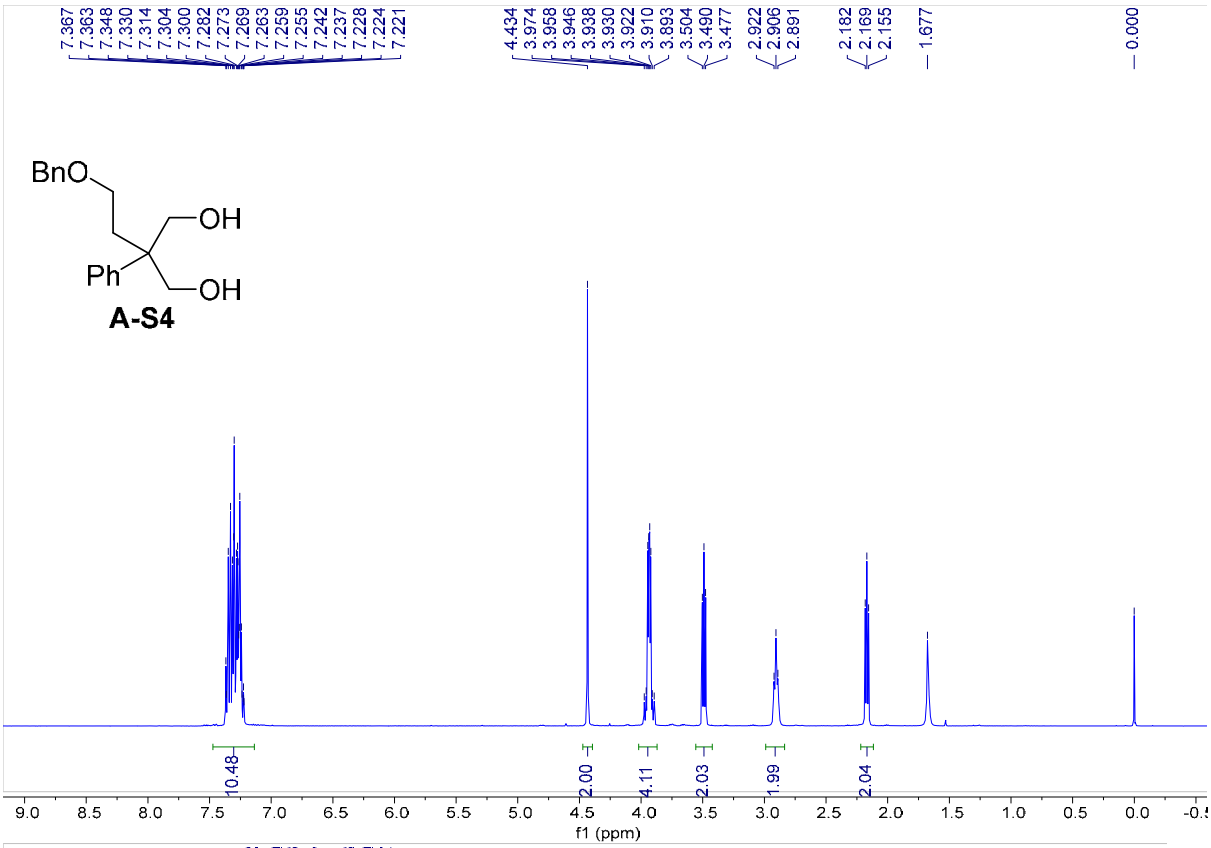
f1 (ppm)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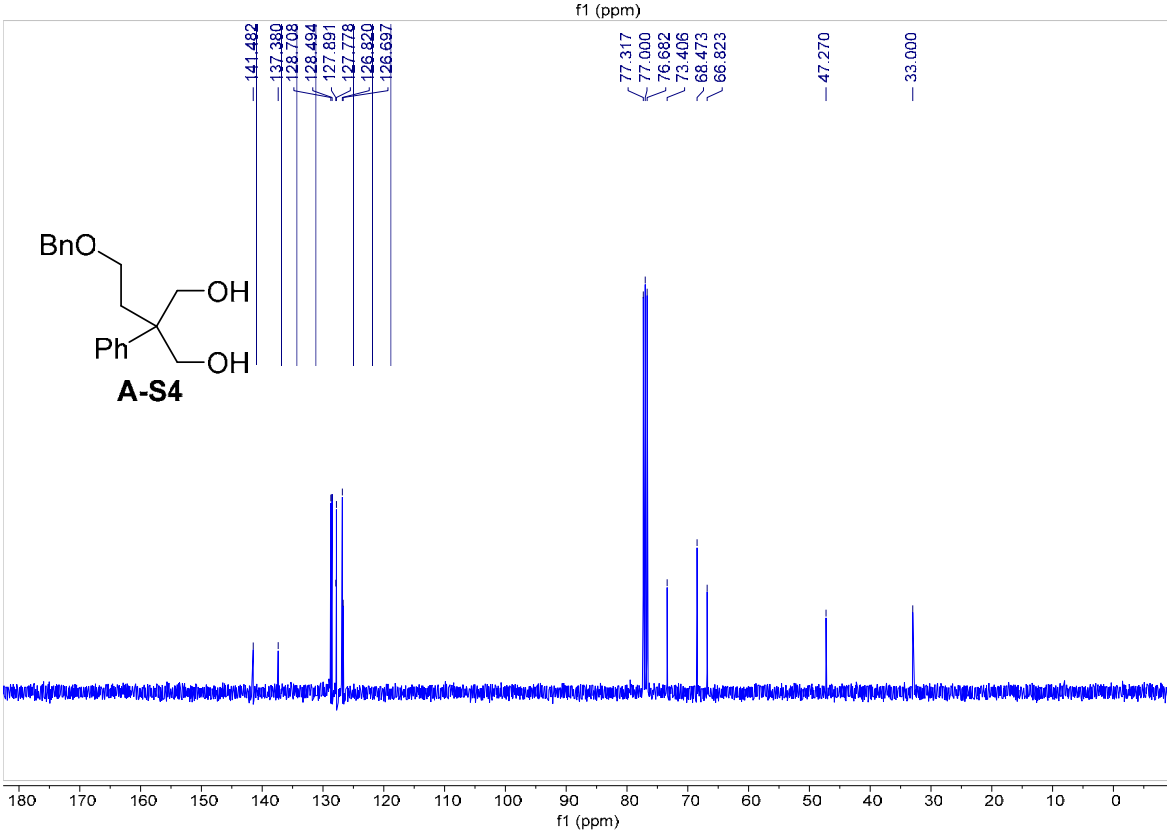
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BnO
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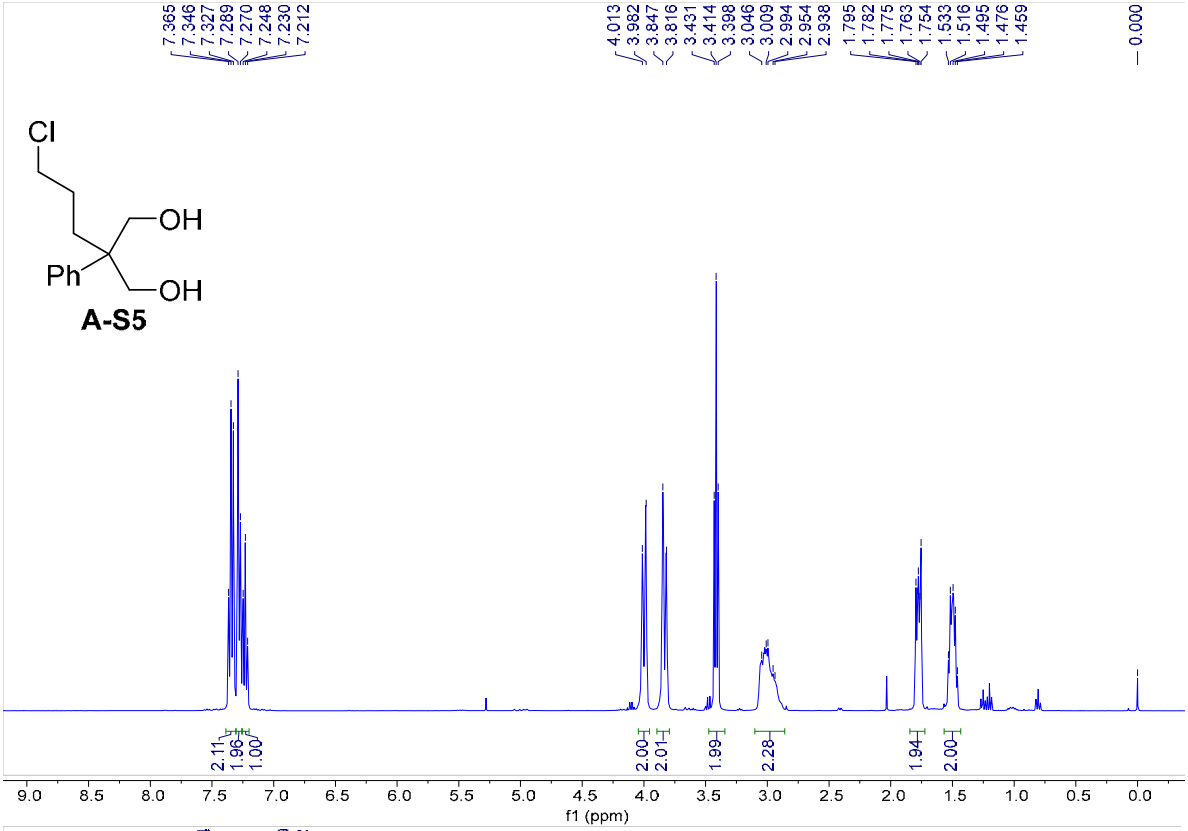
A-S4
f1 (ppm)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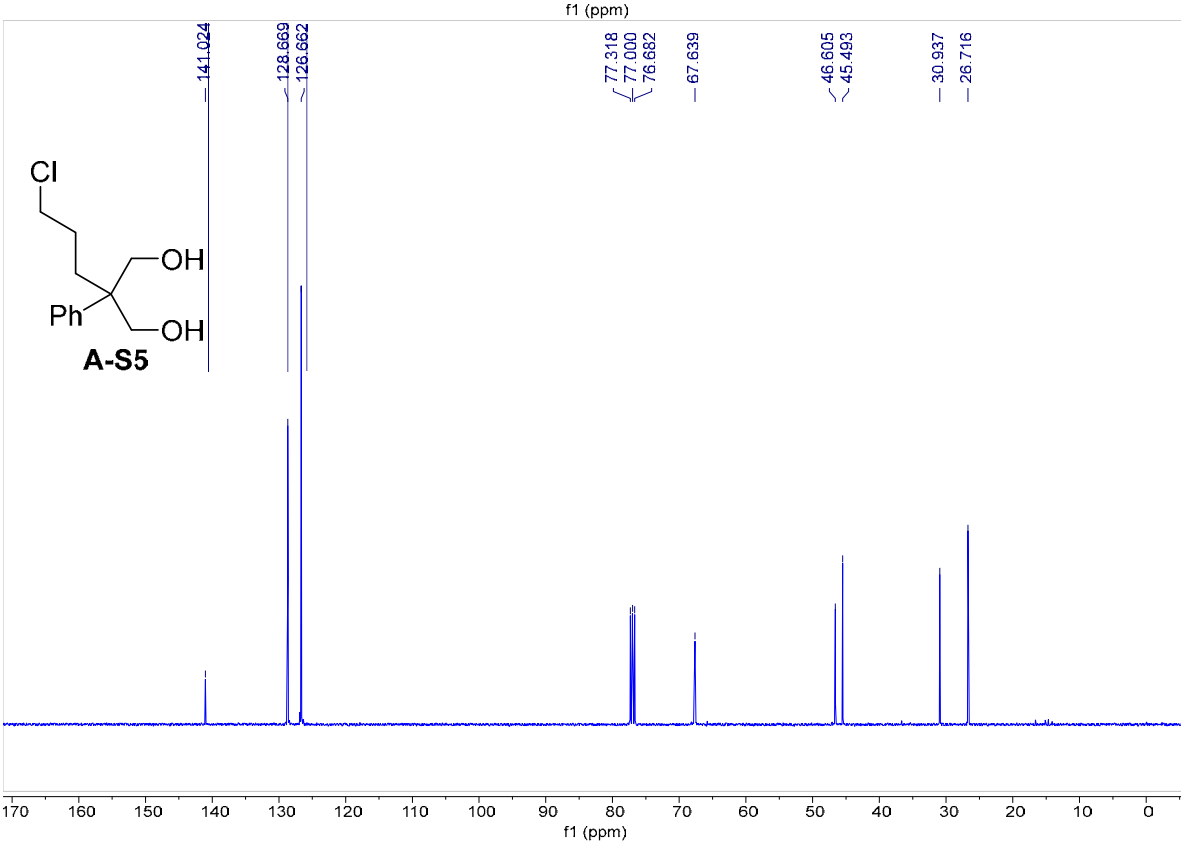
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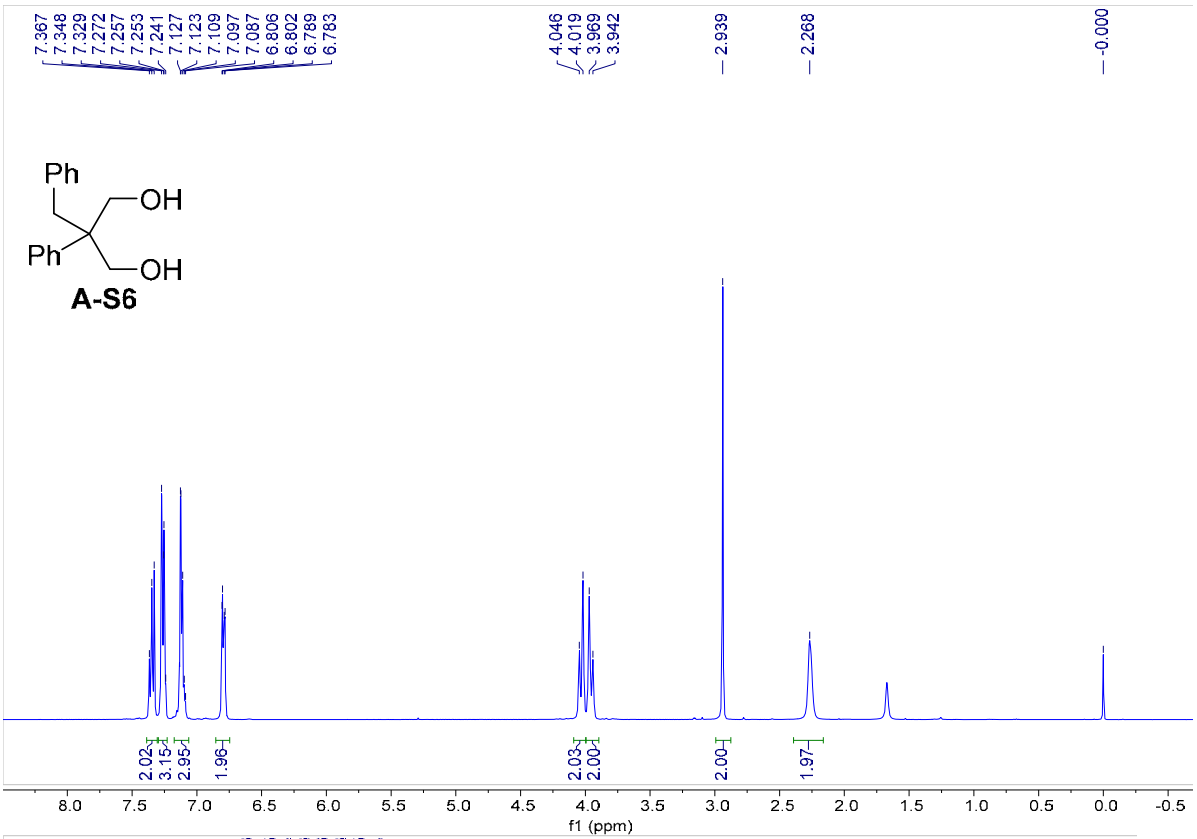
A-S5
f1 (ppm)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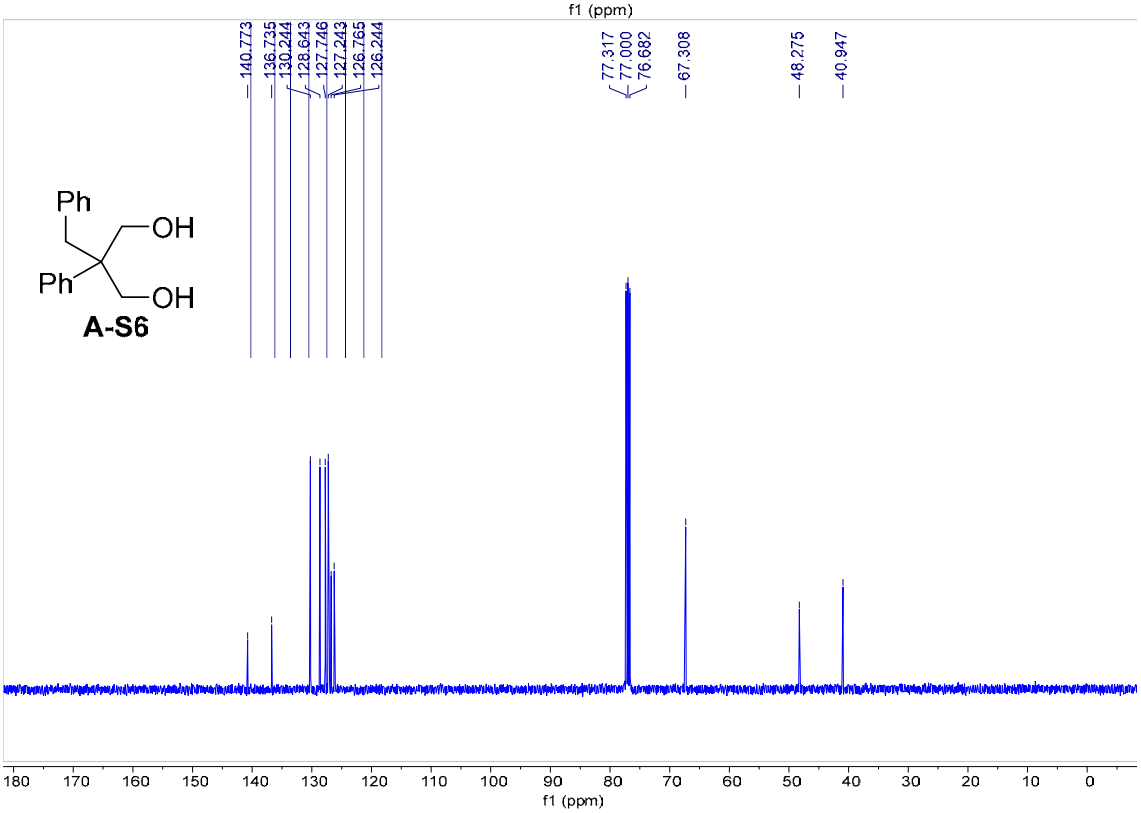
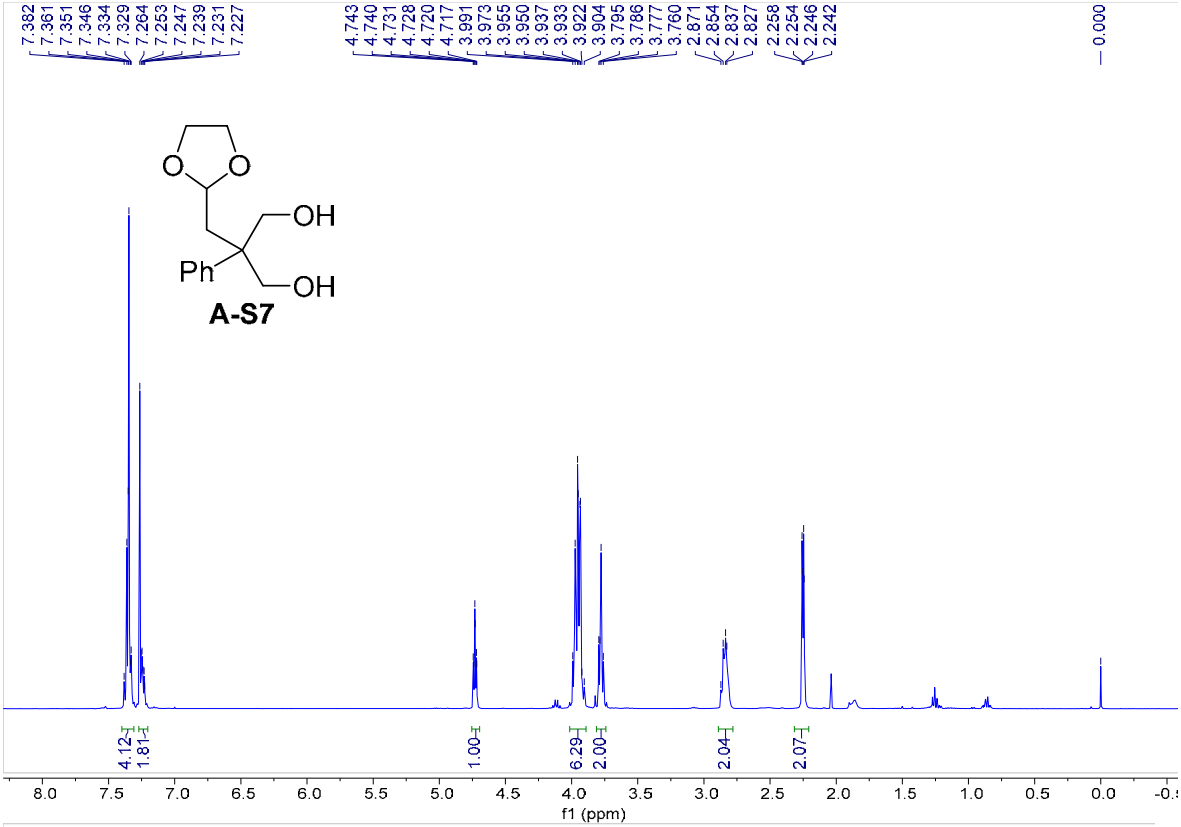
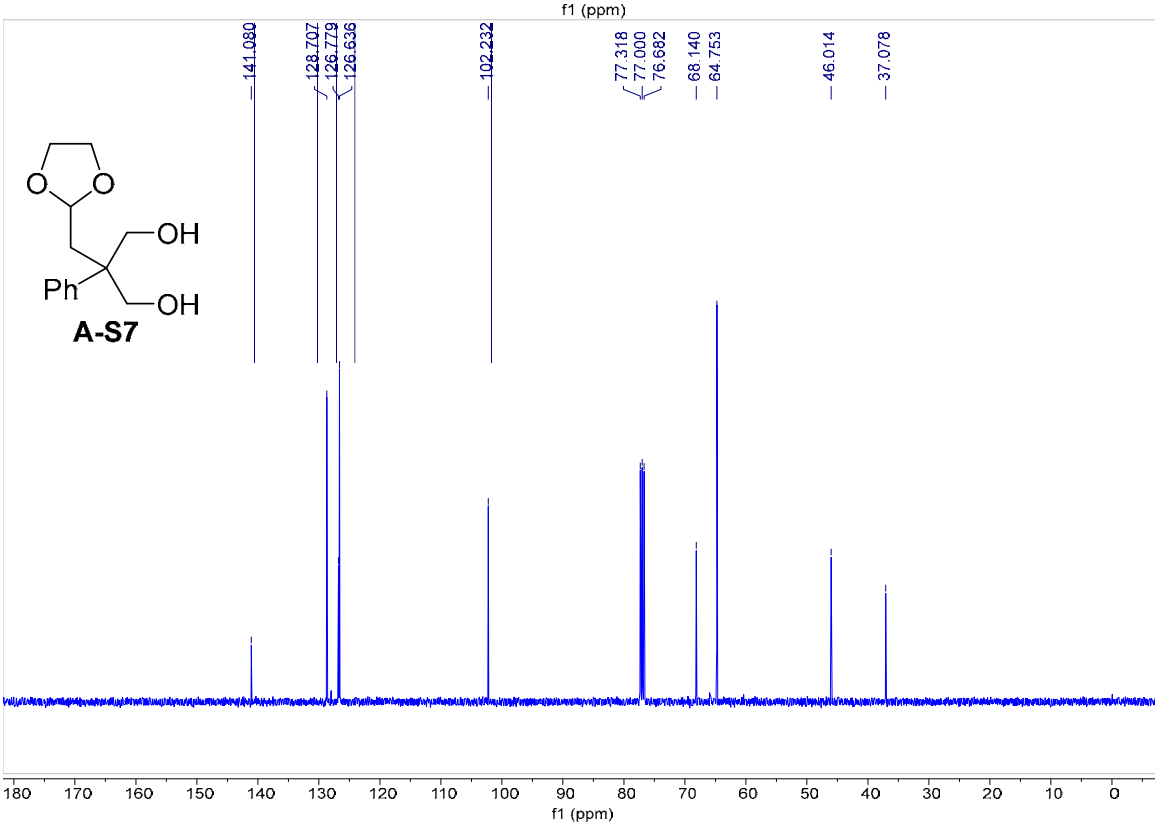
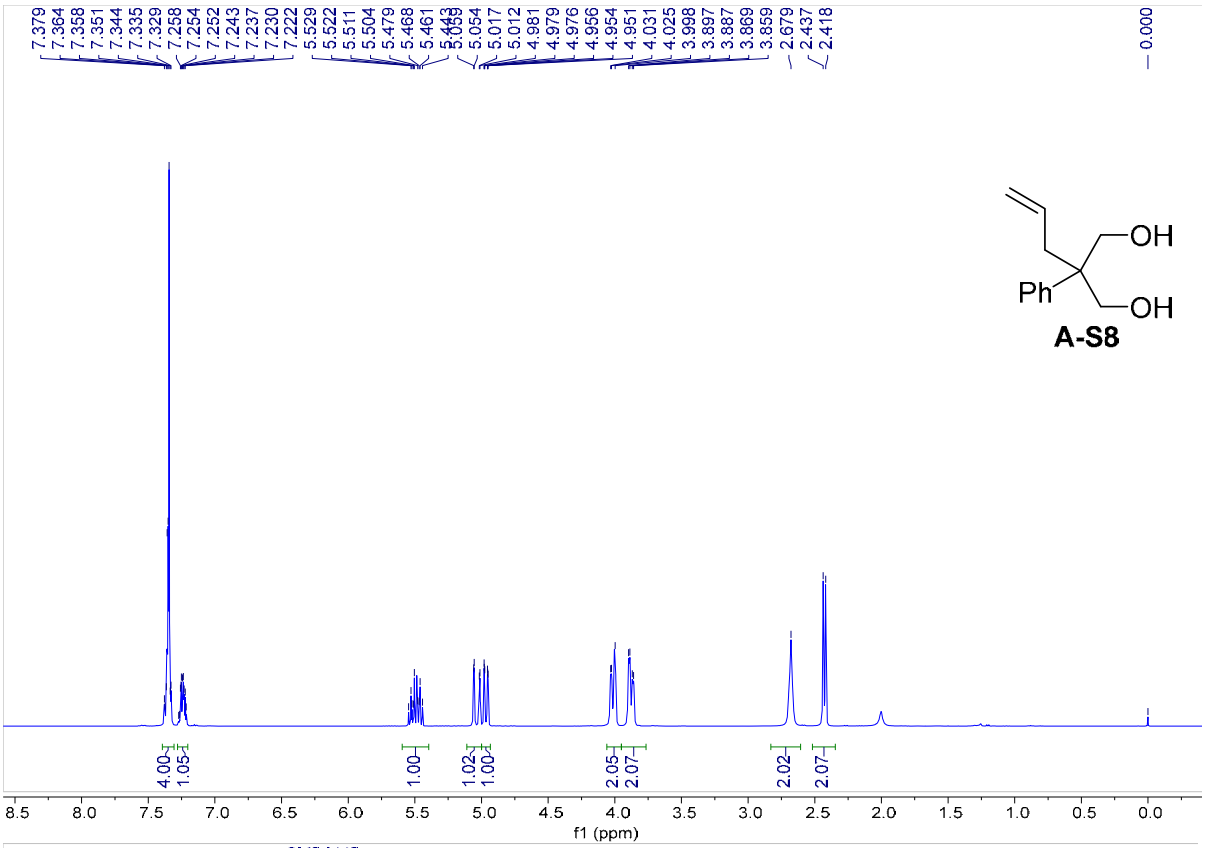
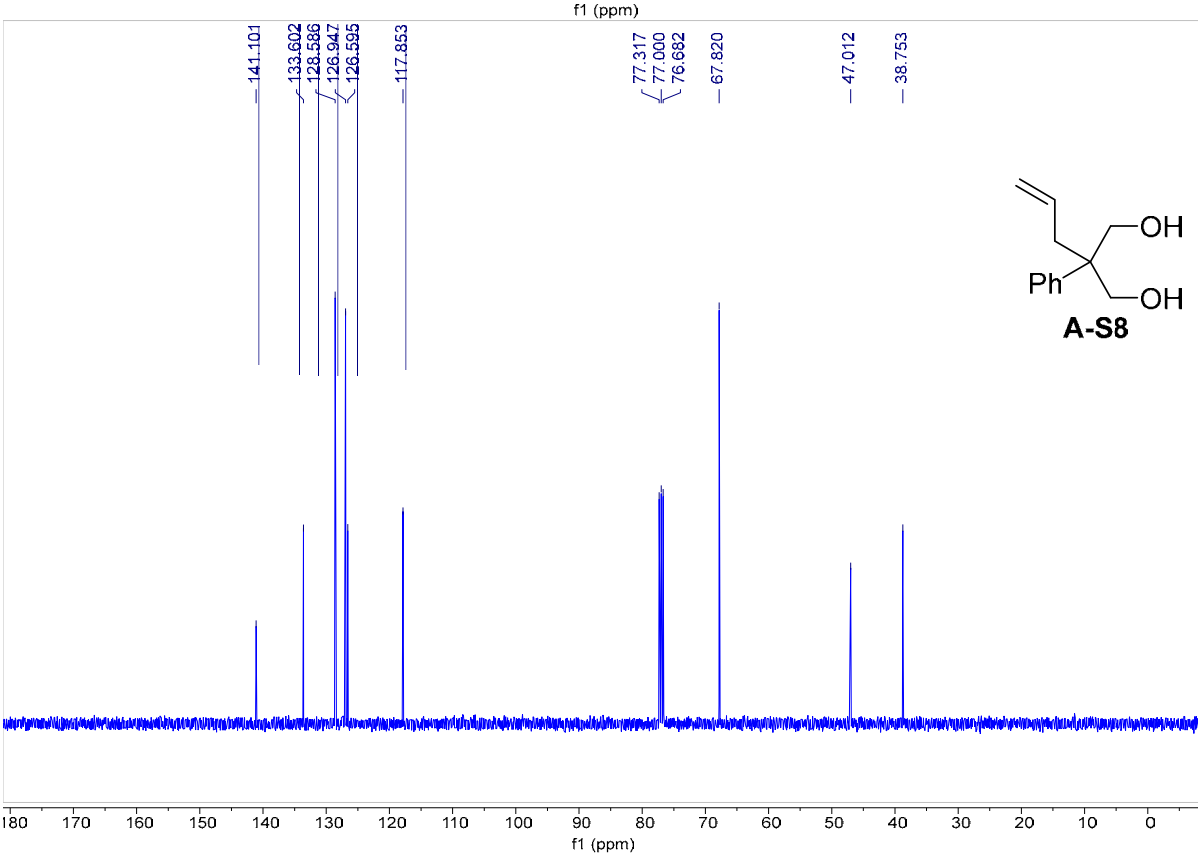
7.348
7.329
7.272
7.257
7.253
7.241
7.127
7.123
7.109
7.097
7.087
6.806
6.802
6.789
6.783
4.046
4.019
3.969
3.942
2.939
2.268
-0.000
Ph
OH
Ph
OH
A-S6
2.02
3.15
2.95
1.96
2.03
2.00
2.00
1.97
f1 (ppm)

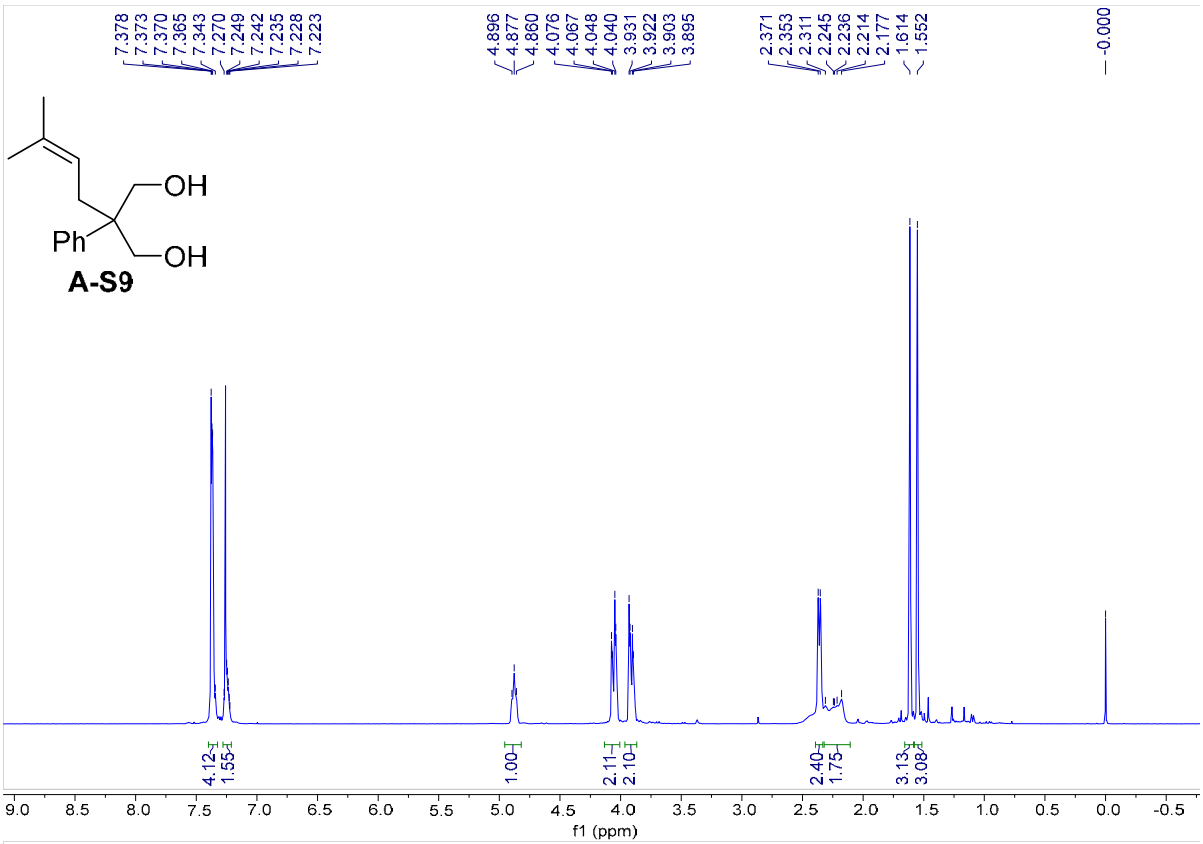

140.773
136.735
130.244
128.643
127.746
127.243
126.765
126.244
77.317
77.000
76.682
67.308
48.275
40.947
Ph
OH
Ph
OH
A-S6
f1 (ppm)

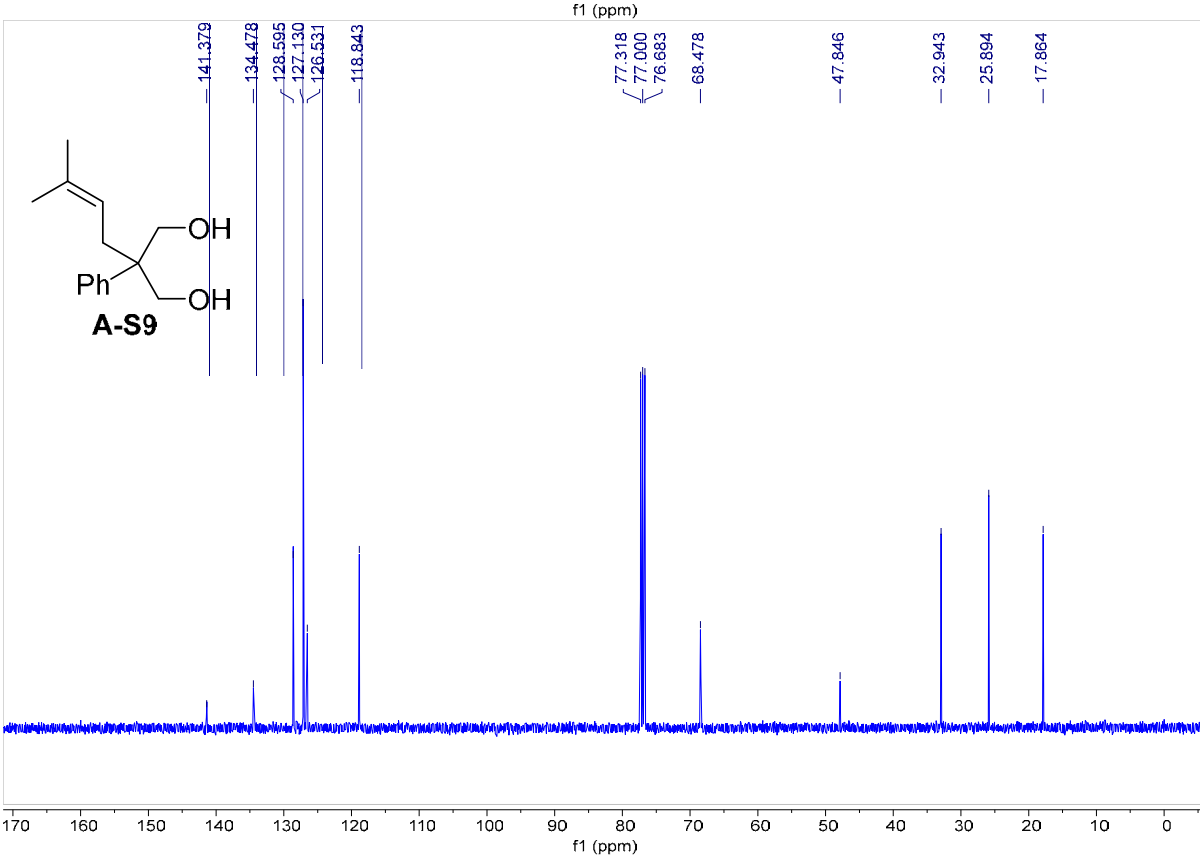

7.382
7.361
7.351
7.346
7.334
7.329
7.264
7.253
7.247
7.239
7.231
7.227
4.743
4.740
4.731
4.728
4.720
4.717
3.991
3.973
3.955
3.950
3.937
3.933
3.922
3.904
3.795
3.786
3.777
3.760
2.871
2.854
2.837
2.827
2.258
2.254
2.246
2.242
0.000
O
O
OH
Ph
OH
A-S7
4.12
1.81
1.00
6.29
2.00
2.04
2.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

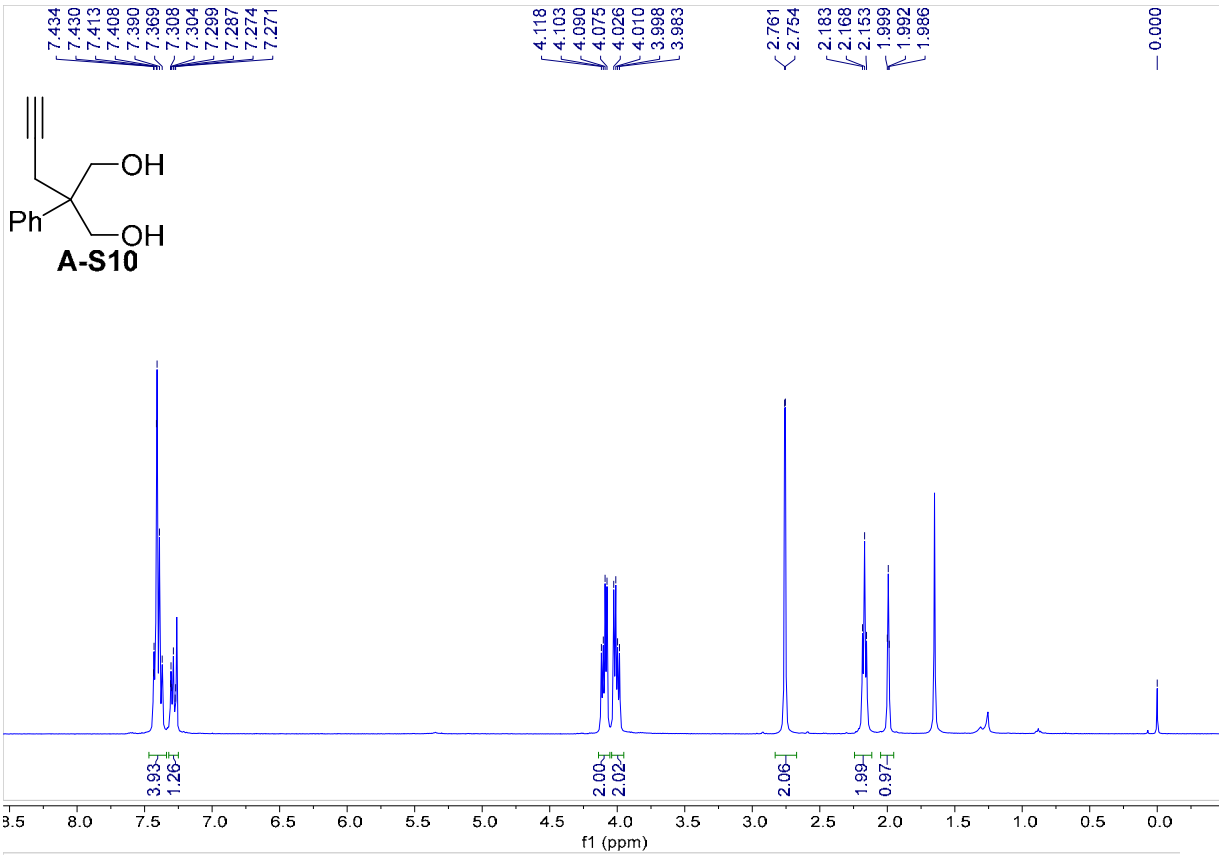

141.080
128.707
126.779
126.636
102.232
77.318
77.000
76.682
68.140
64.753
46.014
37.078
O
O
OH
Ph
OH
A-S7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

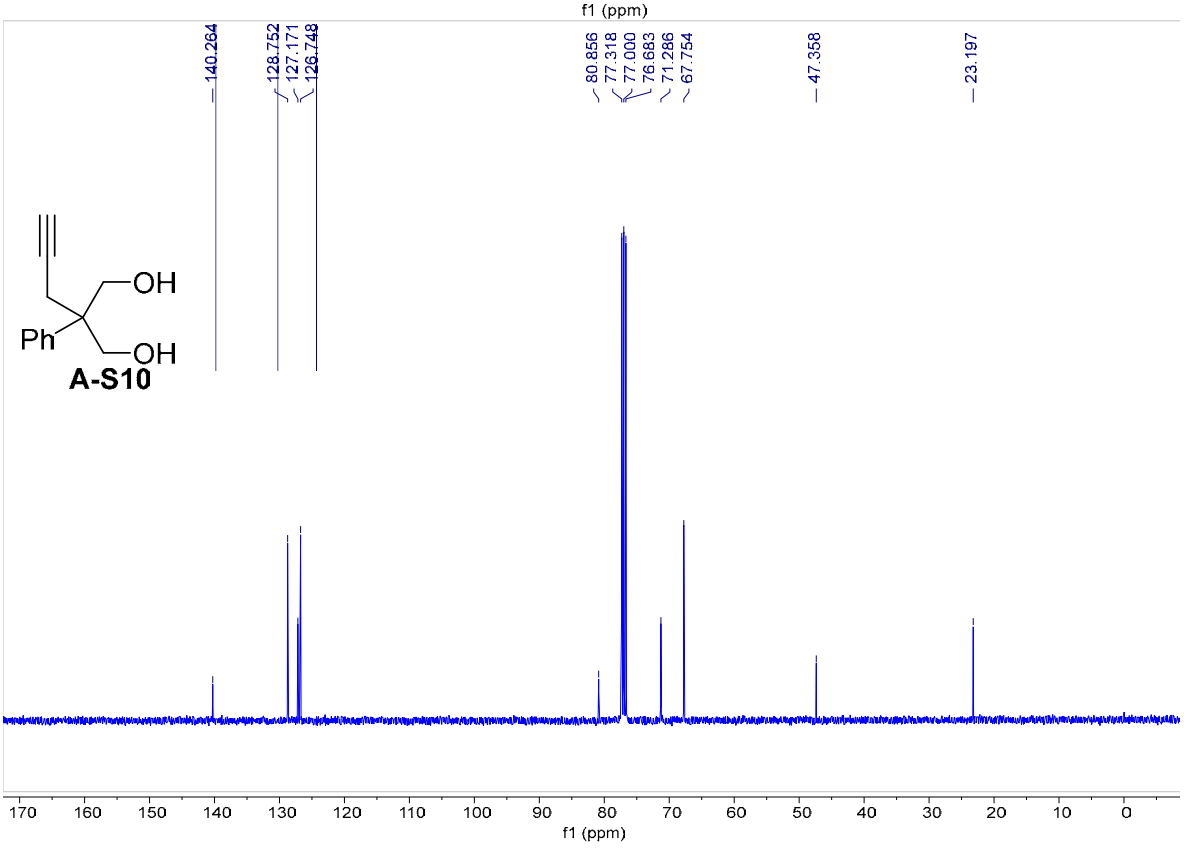

7.379
7.364
7.358
7.351
7.344
7.335
7.329
7.258
7.254
7.252
7.243
7.237
7.230
7.222
5.529
5.522
5.511
5.504
5.479
5.468
5.461
5.054
5.017
5.012
4.981
4.979
4.976
4.956
4.954
4.951
4.031
4.025
3.998
3.897
3.887
3.869
3.859
2.679
2.437
2.418
0.000
OH
Ph
OH
A-S8
4.00
1.05
1.00
1.02
1.00
2.05
2.07
2.02
2.07
f1 (ppm)

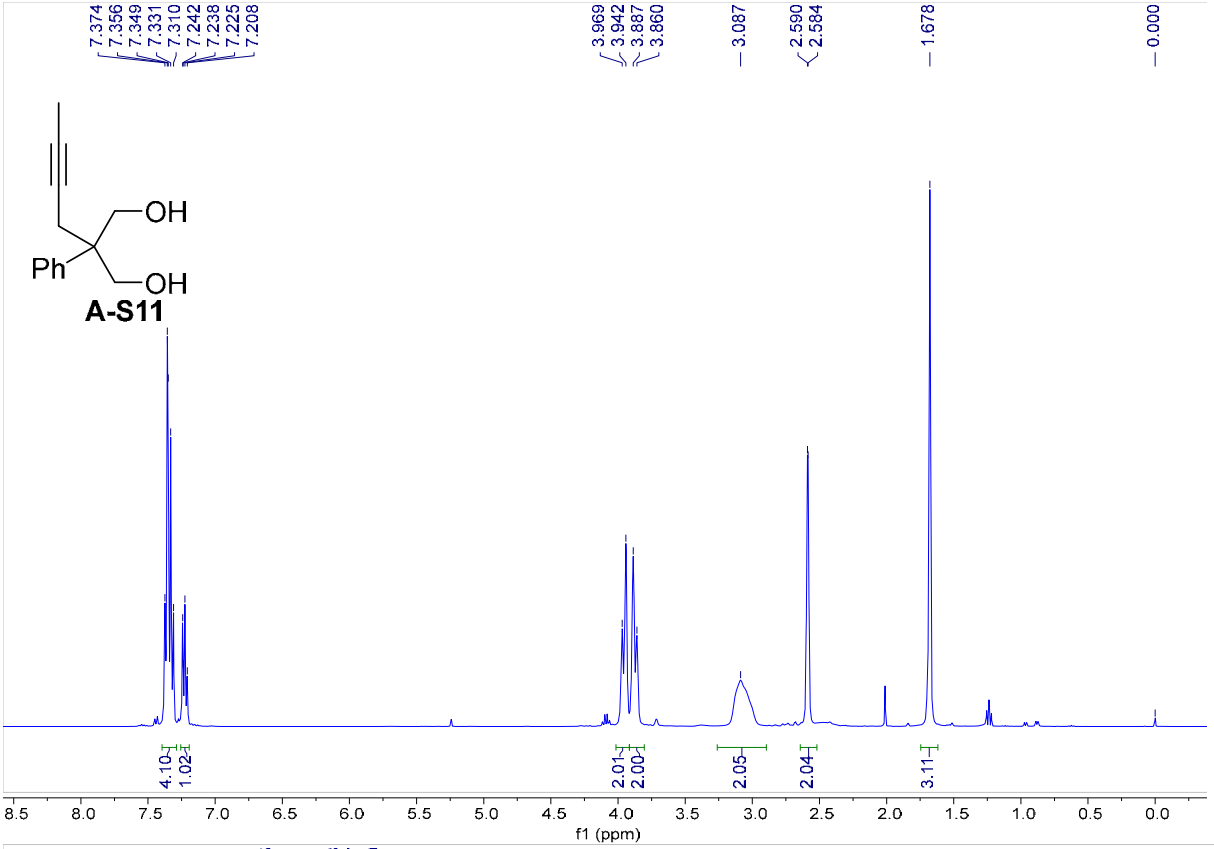

141.101
133.602
128.586
126.947
126.595
117.853
77.317
77.000
76.682
67.820
47.012
38.753
OH
Ph
OH
A-S8
f1 (ppm)

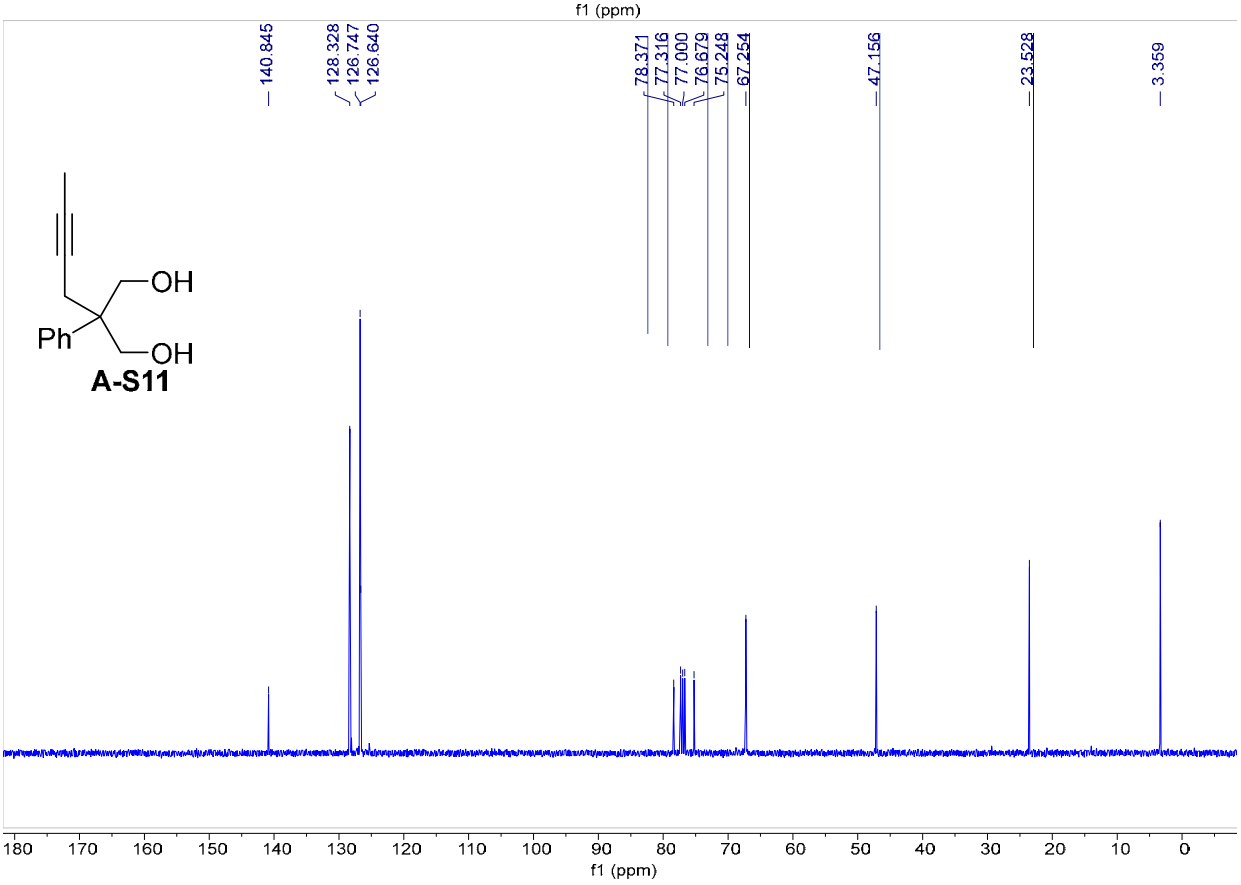

7.378
7.373
7.370
7.365
7.343
7.270
7.249
7.242
7.235
7.228
7.223
4.896
4.877
4.860
4.076
4.067
4.048
4.040
3.931
3.922
3.903
3.895
2.371
2.353
2.311
2.245
2.236
2.214
2.177
1.614
1.552
-0.000
OH
Ph
OH
A-S9
4.12
1.55
1.00
2.11
2.10
2.40
1.75
3.13
3.08
f1 (ppm)

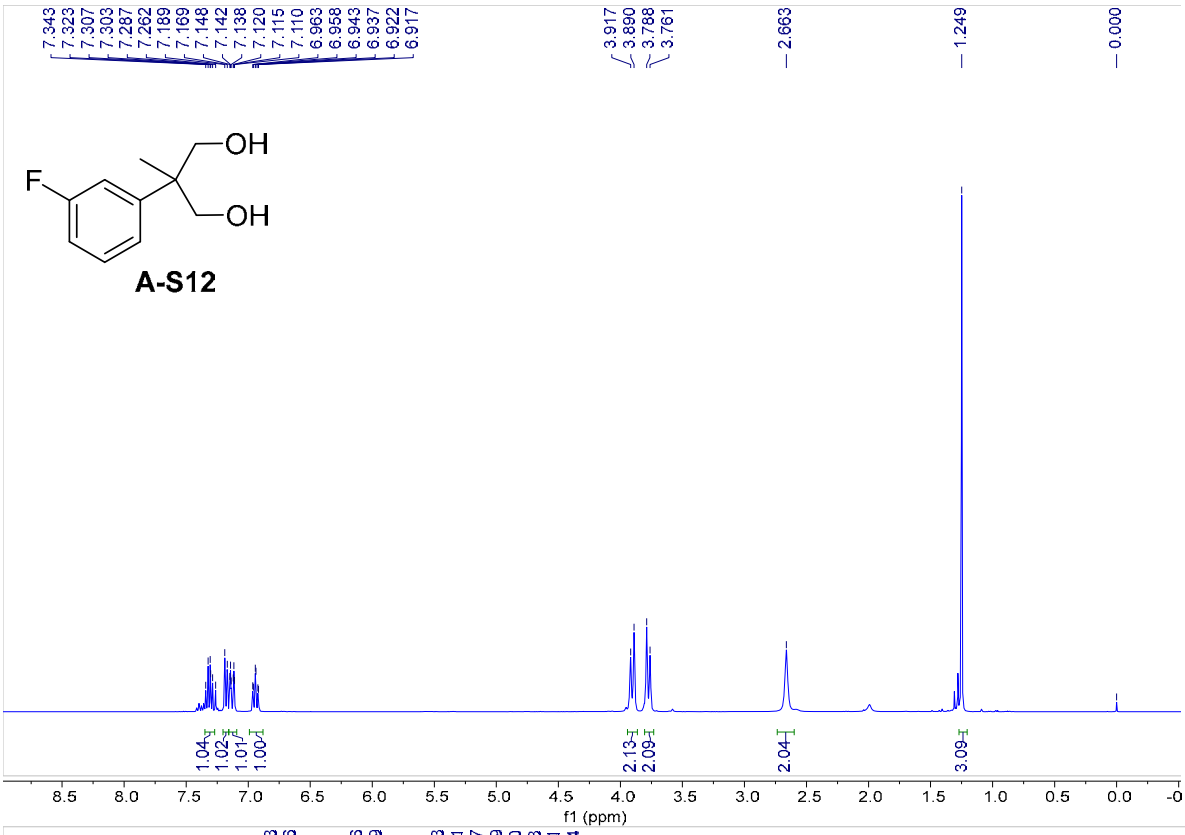

141.379
134.478
128.595
127.130
126.531
118.843
77.318
77.000
76.683
68.478
47.846
32.943
25.894
17.864
OH
Ph
OH
A-S9
f1 (ppm)

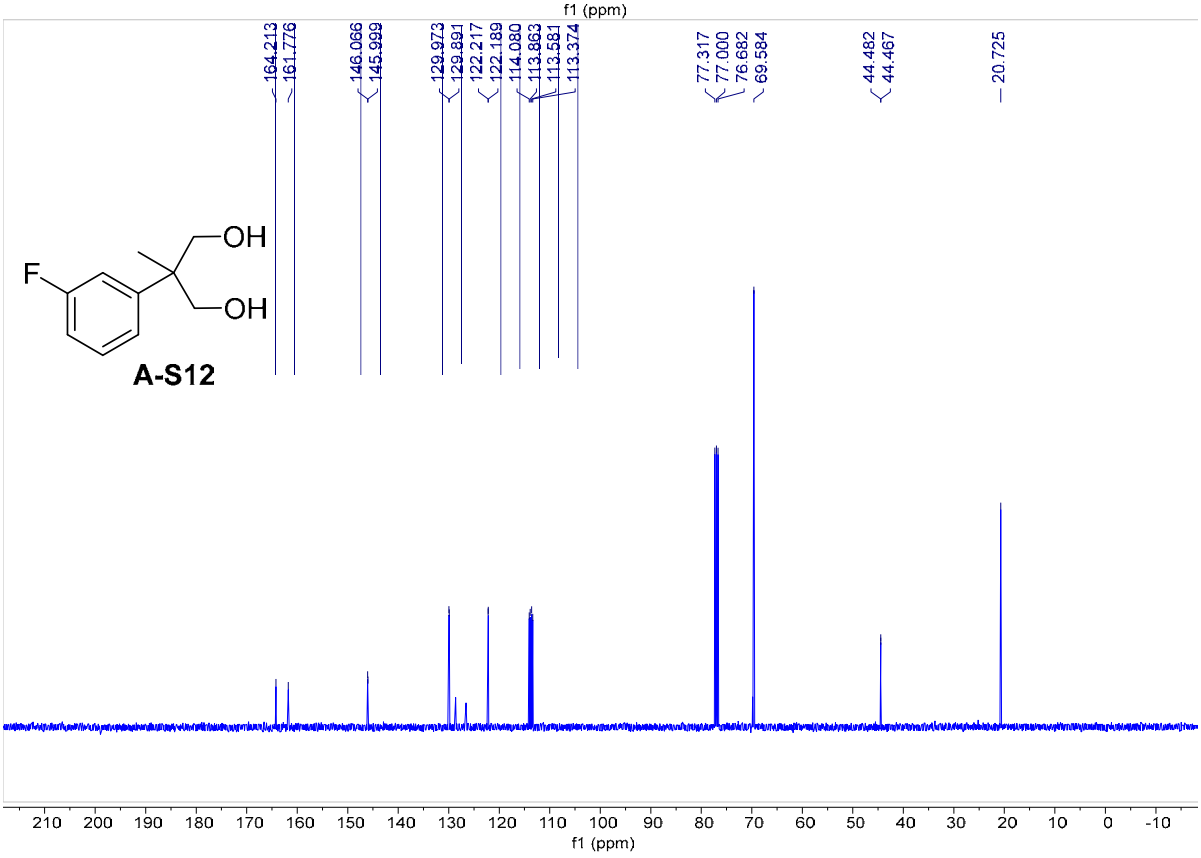

7.434
7.430
7.413
7.408
7.390
7.369
7.308
7.304
7.299
7.287
7.274
7.271
4.118
4.103
4.090
4.075
4.026
4.010
3.998
3.983
2.761
2.754
2.183
2.168
2.153
1.999
1.992
1.986
0.000
OH
Ph
OH
A-S10
3.93
1.26
2.00
2.02
2.06
1.99
0.97
f1 (ppm)

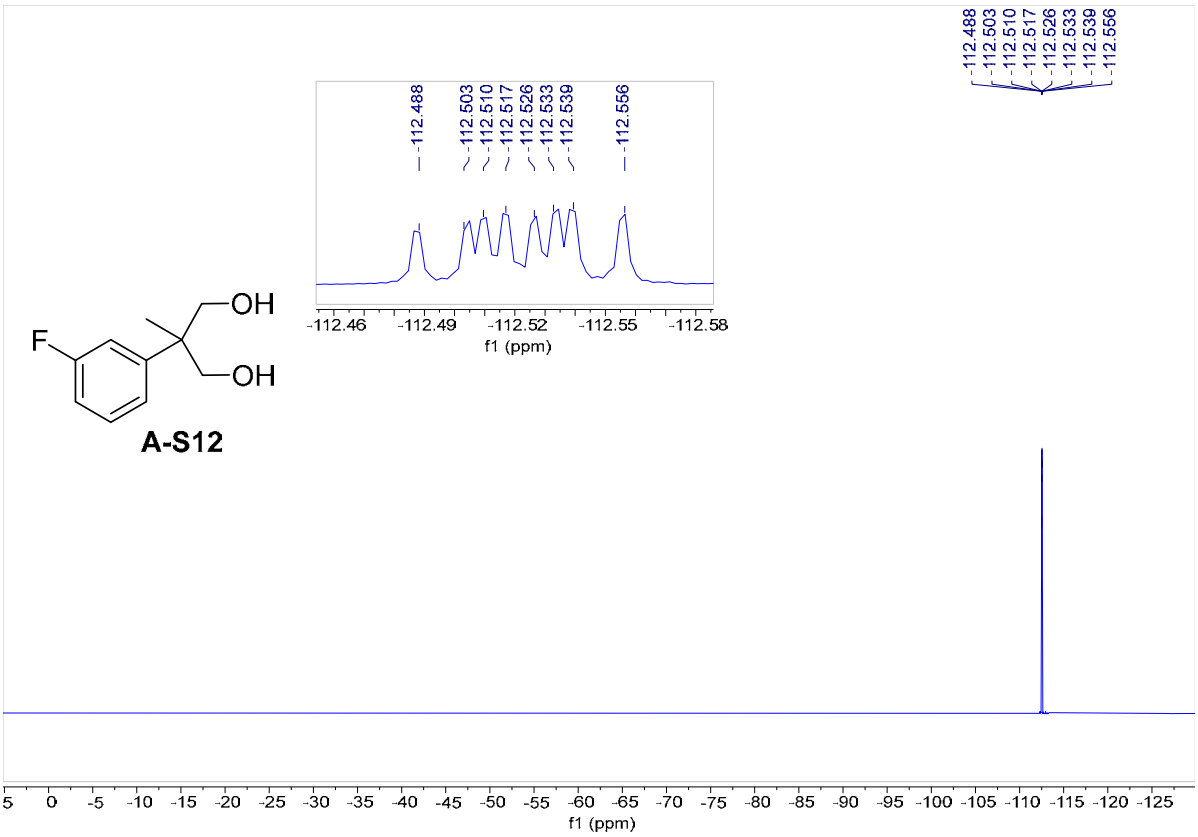

140.264
128.752
127.171
126.748
80.856
77.318
77.000
76.683
71.286
67.754
47.358
23.197
OH
Ph
OH
A-S10
f1 (ppm)

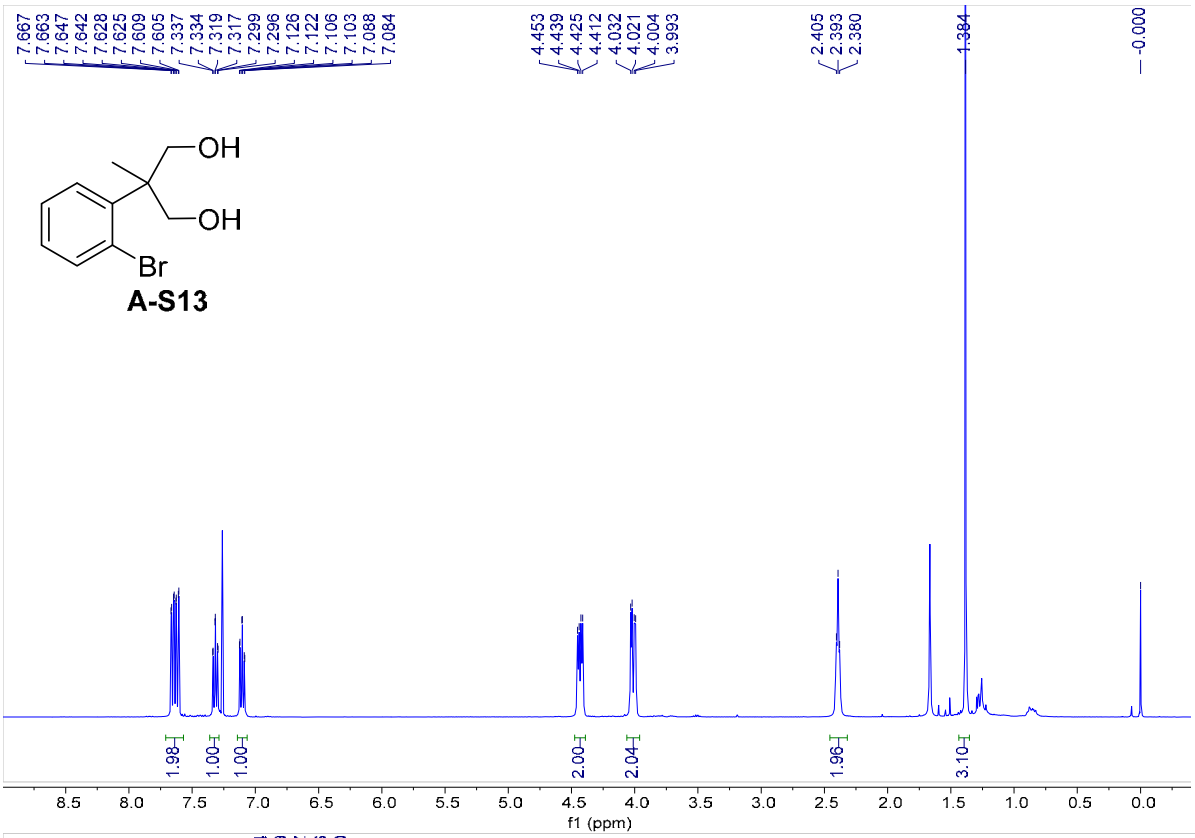

7.374
7.356
7.349
7.331
7.310
7.242
7.238
7.225
7.208
3.969
3.942
3.887
3.860
3.087
2.590
2.584
1.678
0.000
OH
Ph
OH
A-S11
4.10
1.02
2.01
2.00
2.05
2.04
3.11
f1 (ppm)

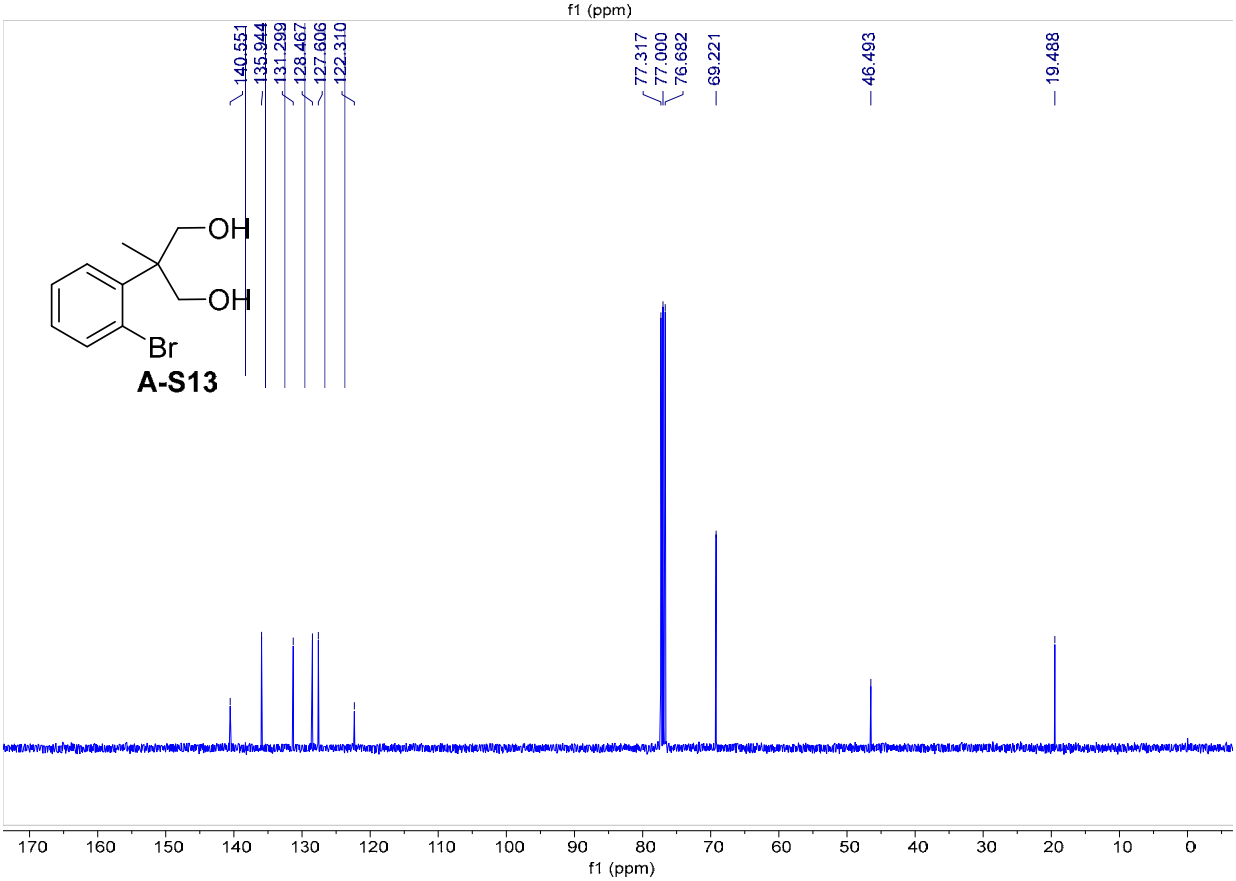

140.845
128.328
126.747
126.640
78.371
77.316
77.000
76.679
75.248
67.254
47.156
23.528
3.359
OH
Ph
OH
A-S11
f1 (ppm)

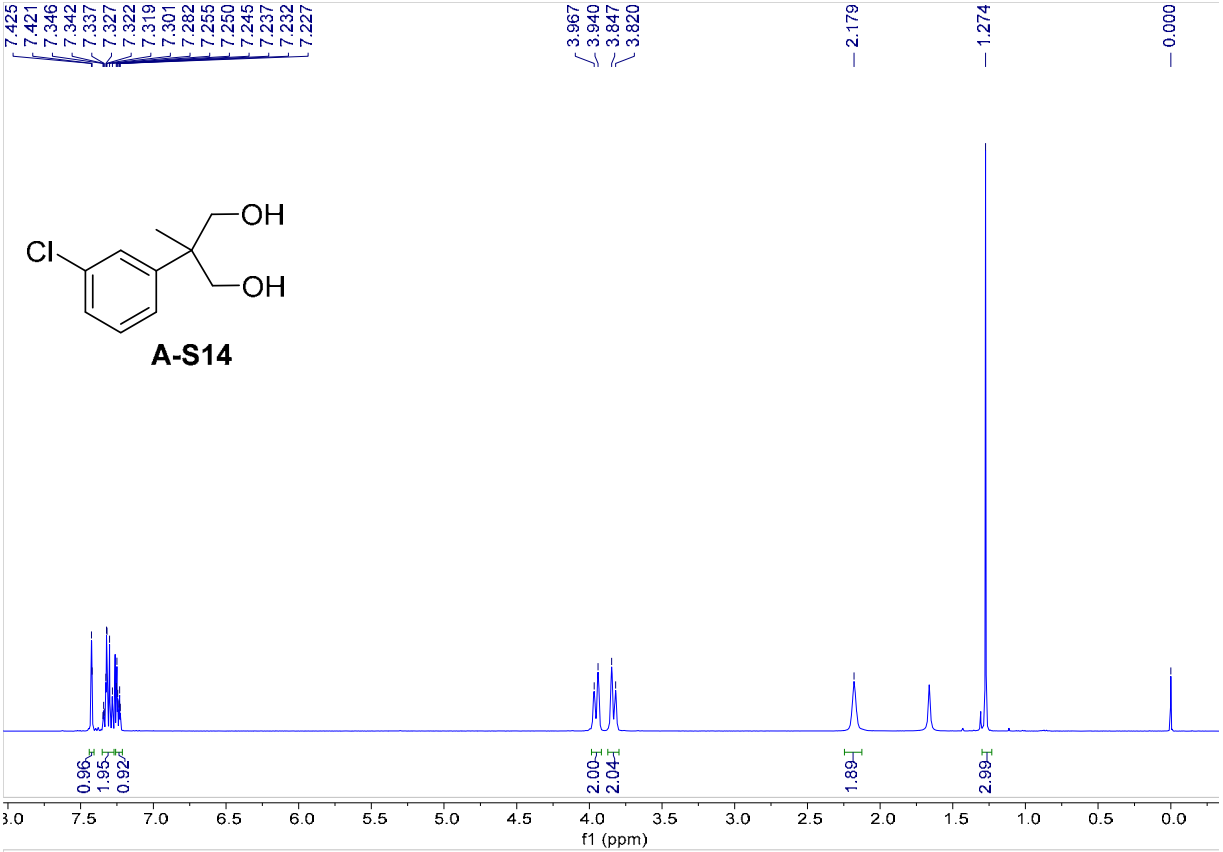

7.343
7.323
7.307
7.303
7.287
7.262
7.189
7.169
7.148
7.142
7.138
7.120
7.115
7.110
6.963
6.958
6.943
6.937
6.922
6.917
3.917
3.890
3.788
3.761
2.663
1.249
0.000
OH
F
OH
A-S12
1.04
1.02
1.01
1.00
2.13
2.09
2.04
3.09
f1 (ppm)

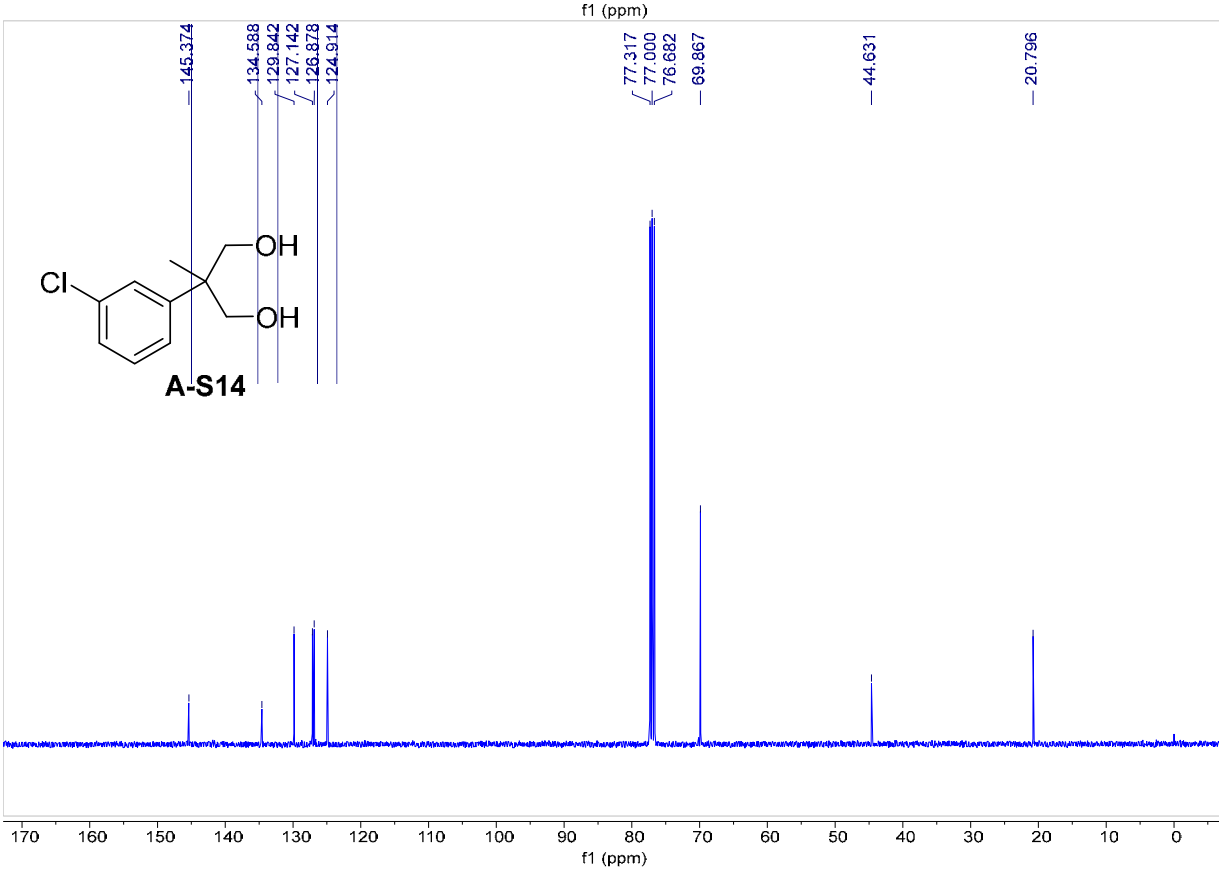

164.213
161.776
146.066
145.999
129.973
129.891
122.217
122.189
114.080
113.863
113.581
113.374
77.317
77.000
76.682
69.584
44.482
44.467
20.725
OH
F
OH
A-S12
f1 (ppm)

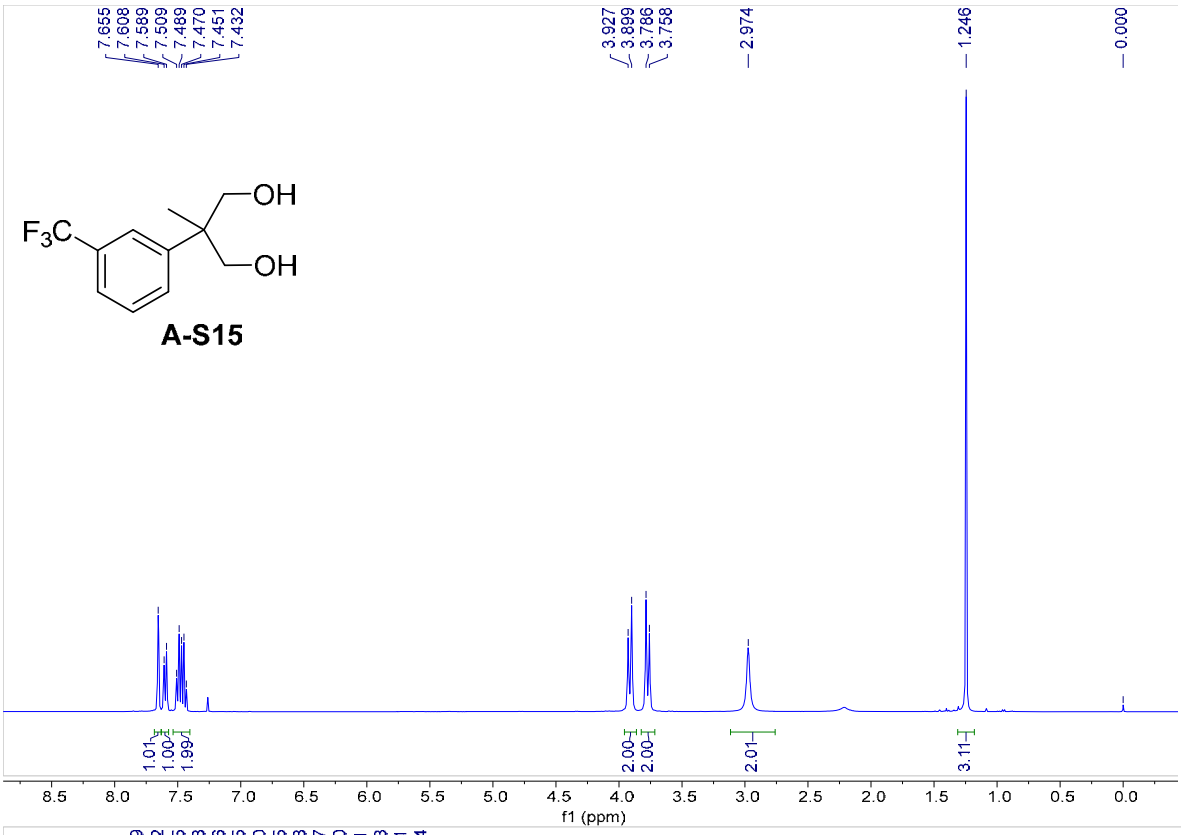

-112.488
-112.503
-112.510
-112.517
-112.526
-112.533
-112.539
-112.556
-112.46
-112.49
-112.52
-112.55
-112.58
f1 (ppm)
F
OH
OH
A-S12
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

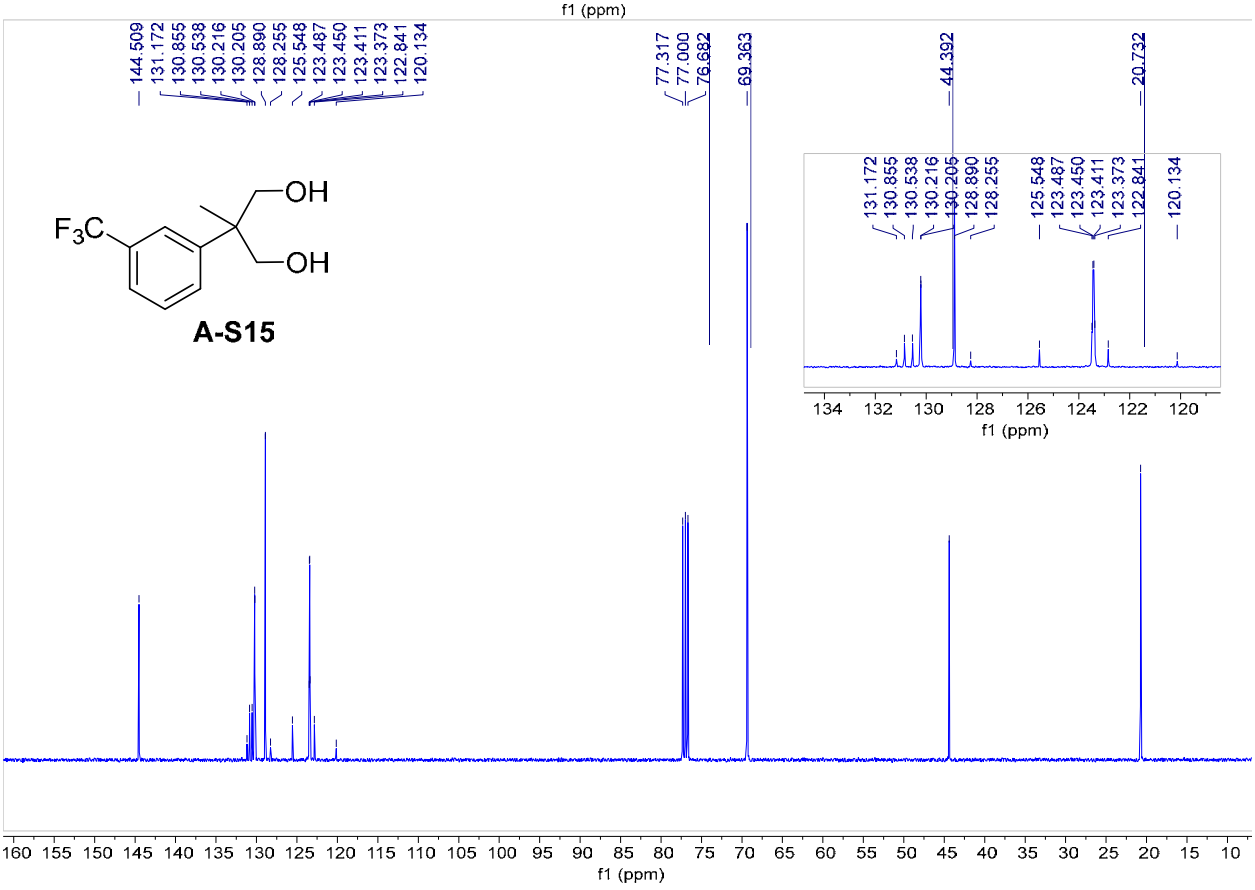

7.667
7.663
7.647
7.642
7.628
7.625
7.609
7.605
7.337
7.334
7.319
7.317
7.299
7.296
7.126
7.122
7.106
7.103
7.088
7.084
4.453
4.439
4.425
4.412
4.032
4.021
4.004
3.993
2.405
2.393
2.380
1.384
-0.000
OH
OH
Br
A-S13
1.98
1.00
1.00
2.00
2.04
1.96
3.10
f1 (ppm)

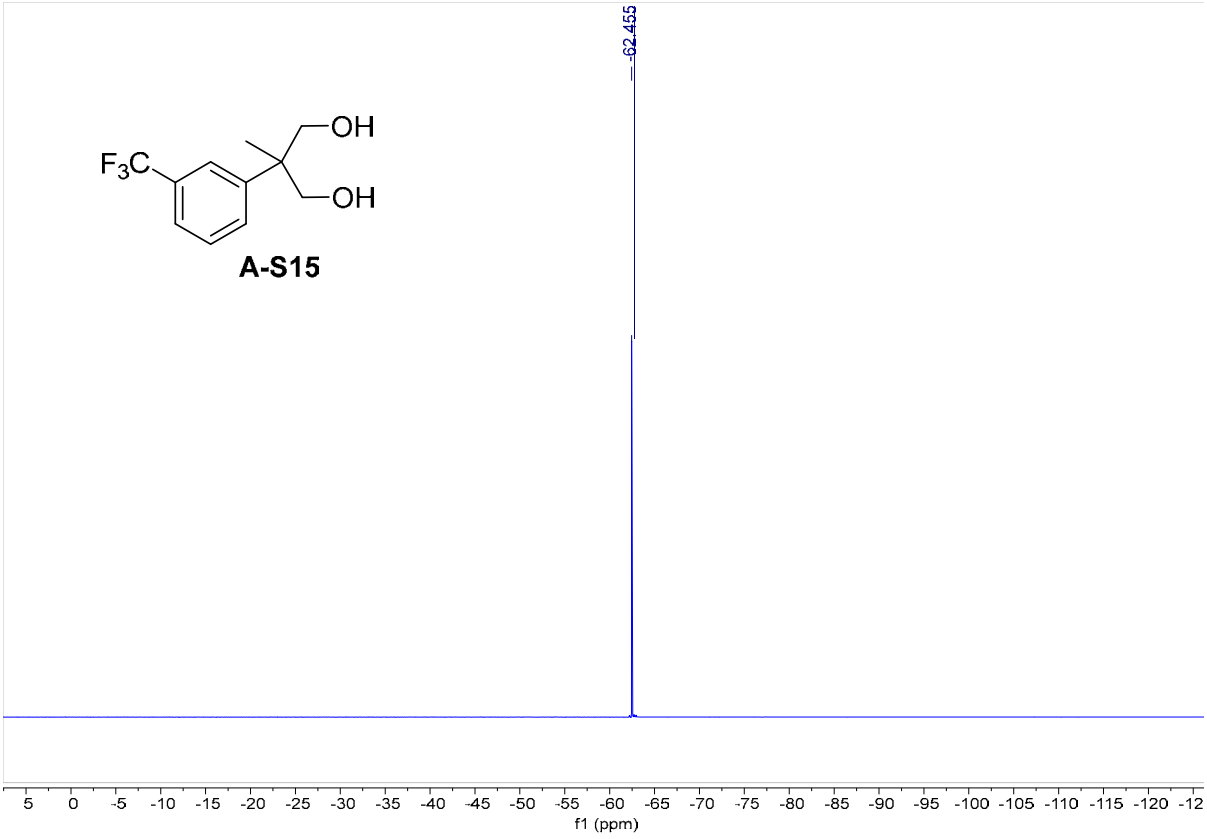

140.551
135.944
131.269
128.467
127.606
122.310
77.317
77.000
76.682
69.221
46.493
19.488
OH
OH
Br
A-S13
f1 (ppm)

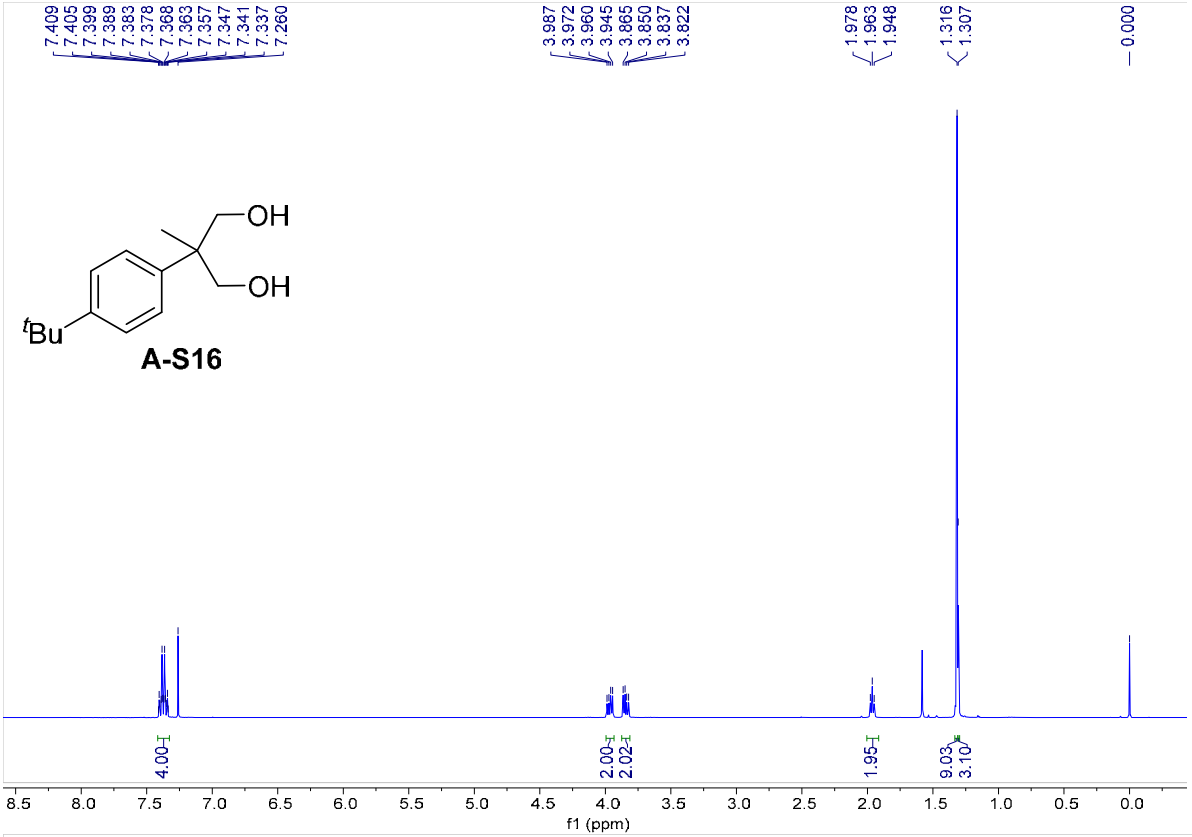

7.425
7.421
7.346
7.342
7.337
7.327
7.322
7.319
7.301
7.282
7.255
7.250
7.245
7.237
7.232
7.227
3.967
3.940
3.847
3.820
2.179
1.274
0.000
OH
Cl
OH
A-S14
0.96
1.95
0.92
2.00
2.04
1.89
2.99
f1 (ppm)

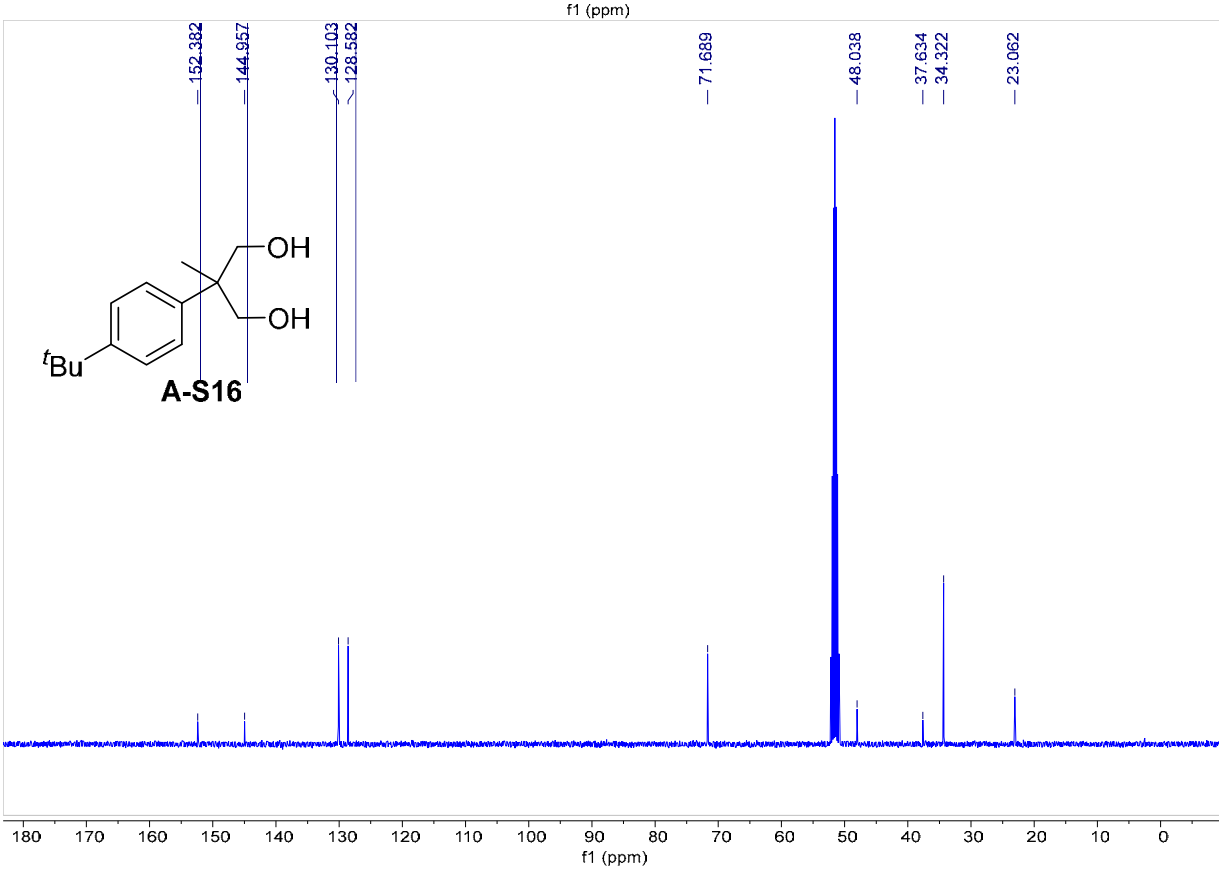

145.374
134.588
129.842
127.142
126.878
124.914
77.317
77.000
76.682
69.867
44.631
20.796
OH
Cl
OH
A-S14
f1 (ppm)

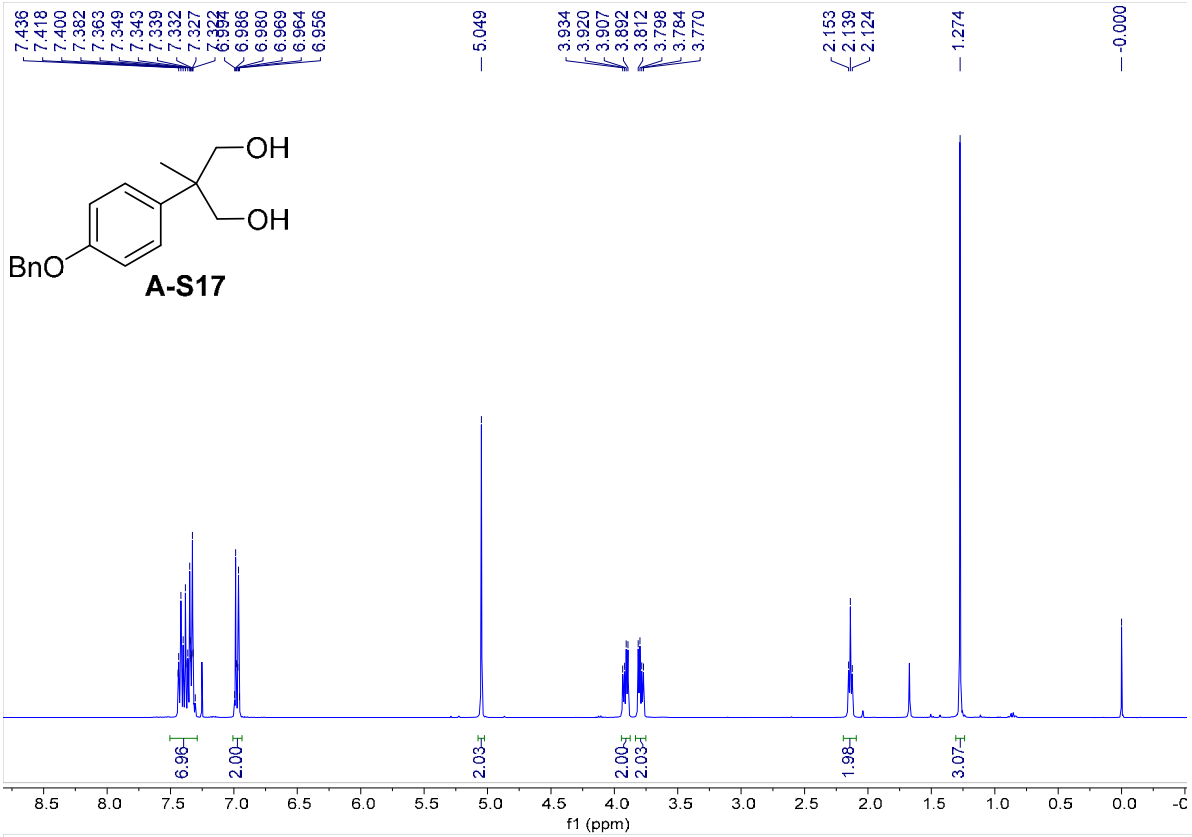

7.655
7.608
7.589
7.509
7.489
7.470
7.451
7.432
3.927
3.899
3.786
3.758
2.974
1.246
0.000
OH
OH
F3C
A-S15
1.01
1.00
1.99
2.00
2.00
2.01
3.11
f1 (ppm)


144.509
131.172
130.855
130.538
130.216
130.205
128.890
128.255
125.548
123.487
123.450
123.411
123.373
122.841
120.134
77.317
77.000
76.682
69.363
44.392
20.732
OH
OH
F3C
A-S15
f1 (ppm)


-62.455
OH
OH
F3C
A-S15
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -12
f1 (ppm)


7.409
7.405
7.399
7.389
7.383
7.378
7.368
7.363
7.357
7.347
7.341
7.337
7.260
3.987
3.972
3.960
3.945
3.865
3.850
3.837
3.822
1.978
1.963
1.948
1.316
1.307
0.000
OH
OH
tBu
A-S16
4.00
2.00
2.02
1.95
9.03
3.10
f1 (ppm)


152.382
144.957
130.103
128.582
71.689
48.038
37.634
34.322
23.062
OH
OH
tBu
A-S16
f1 (ppm)


7.436
7.418
7.400
7.382
7.363
7.349
7.343
7.339
7.332
7.327
6.986
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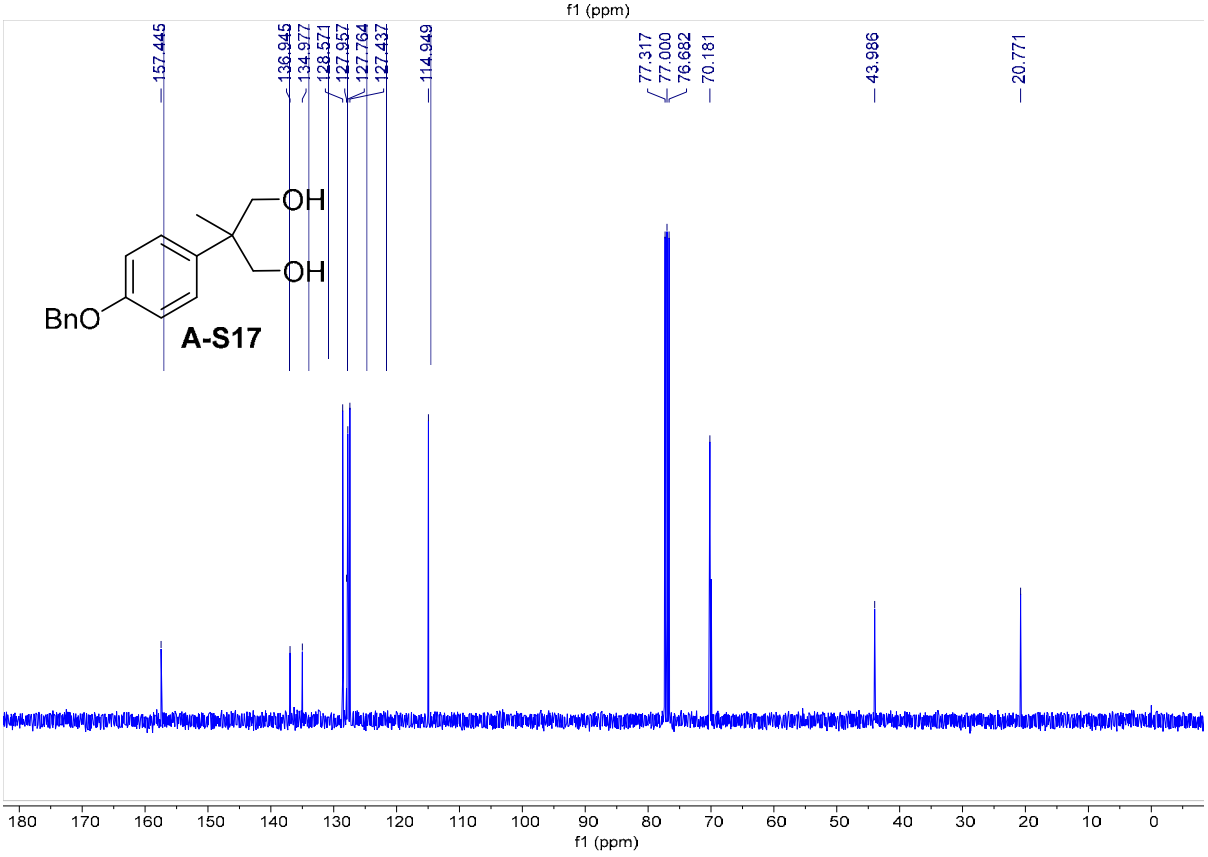
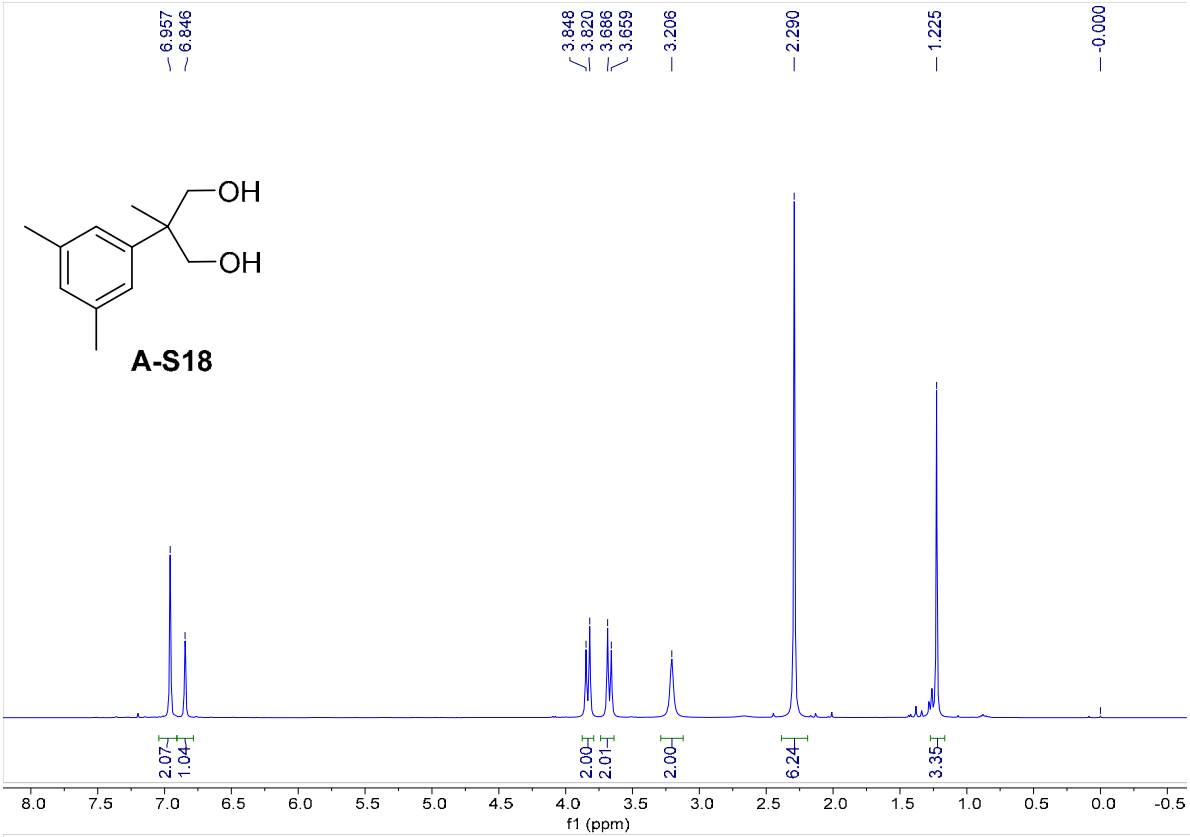
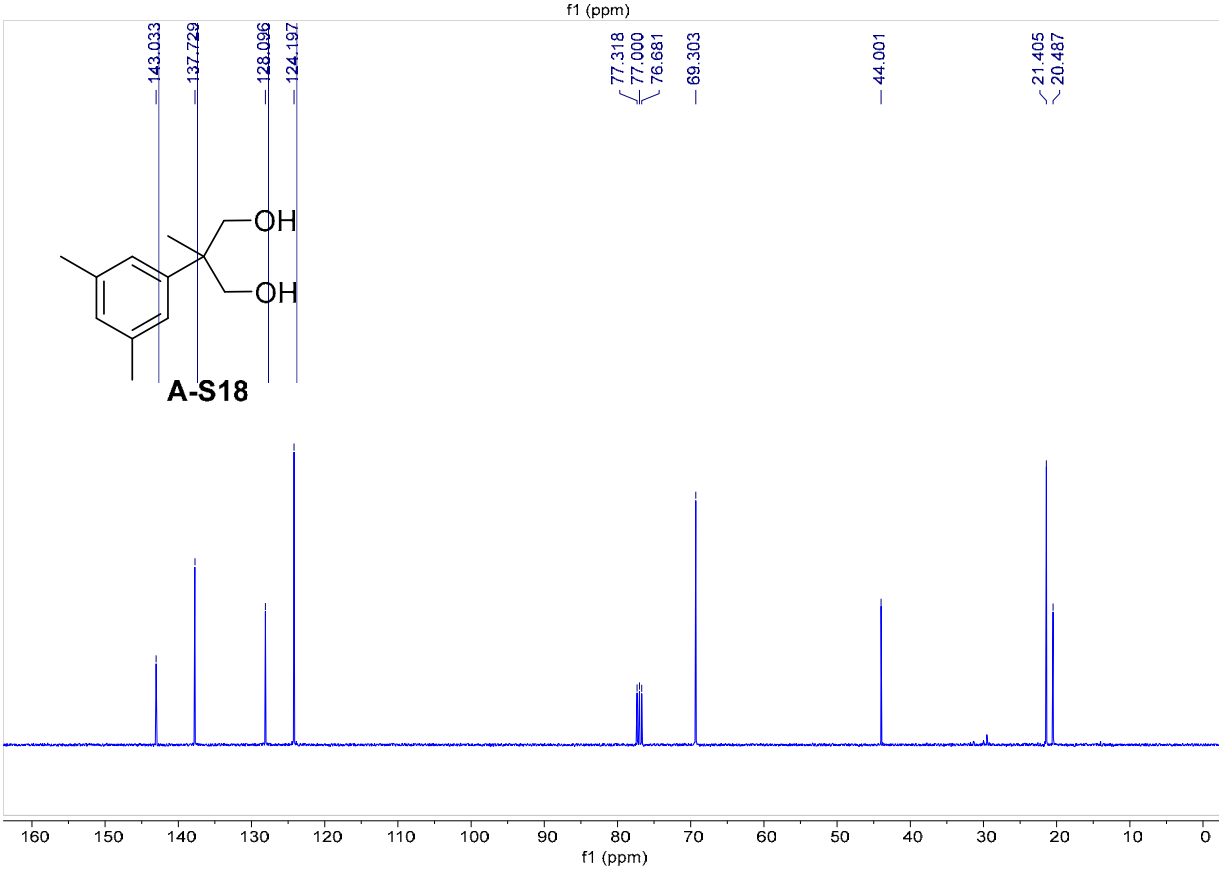
6.969
6.964
6.956
5.049
3.934
3.920
3.907
3.892
3.812
3.798
3.784
3.770
2.153
2.139
2.124
1.274
-0.000
OH
OH
BnO
A-S17
6.96
2.00
2.03
2.00
2.03
1.98
3.07
f1 (ppm)


157.445
136.945
134.977
128.571
127.957
127.764
127.437
114.949
77.317
77.000
76.682
70.181
43.986
20.771
OH
OH
BnO
A-S17
f1 (ppm)


6.957
6.846
3.848
3.820
3.686
3.659
3.206
2.290
1.225
-0.000
OH
OH
A-S18
2.07
1.04
2.00
2.01
2.00
6.24
3.35
f1 (ppm)


143.033
137.729
128.096
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77.318
77.000
76.681
69.303
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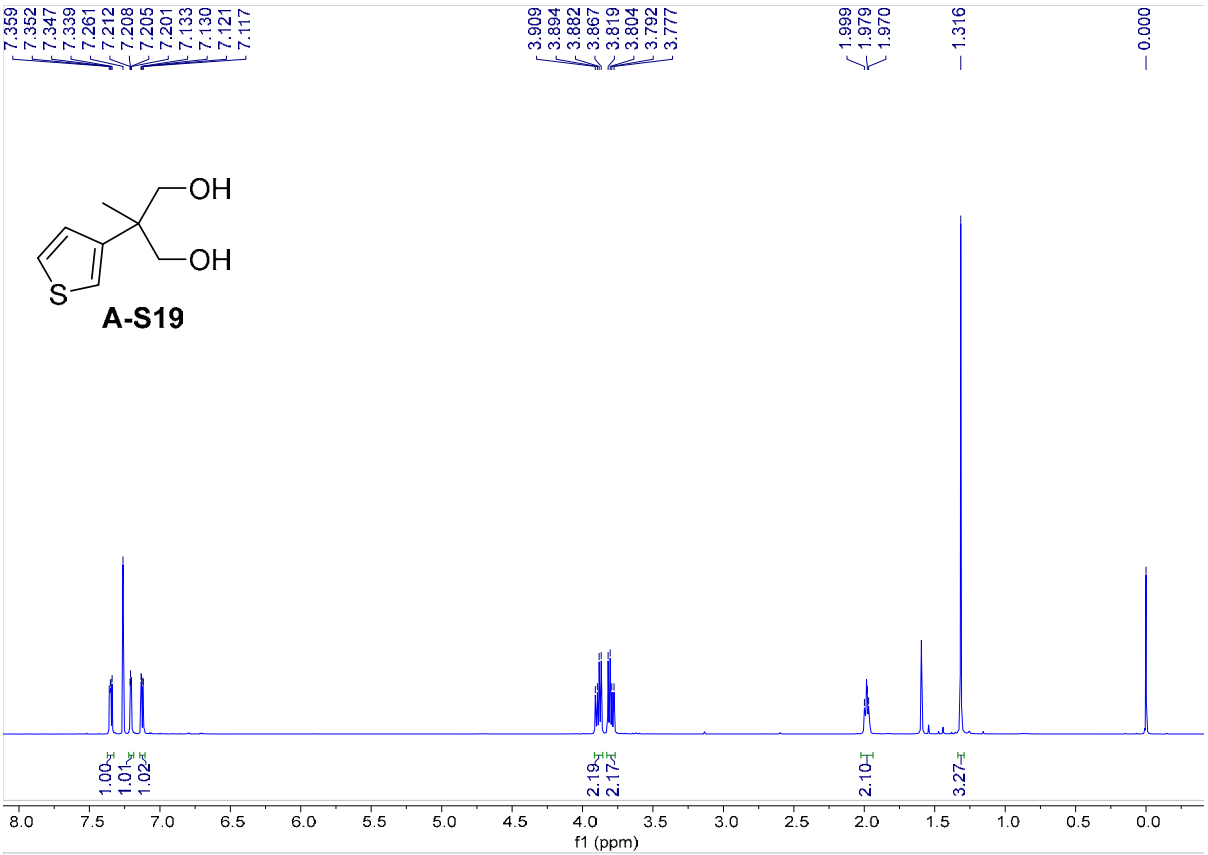
20.487
OH
OH
A-S18
f1 (ppm)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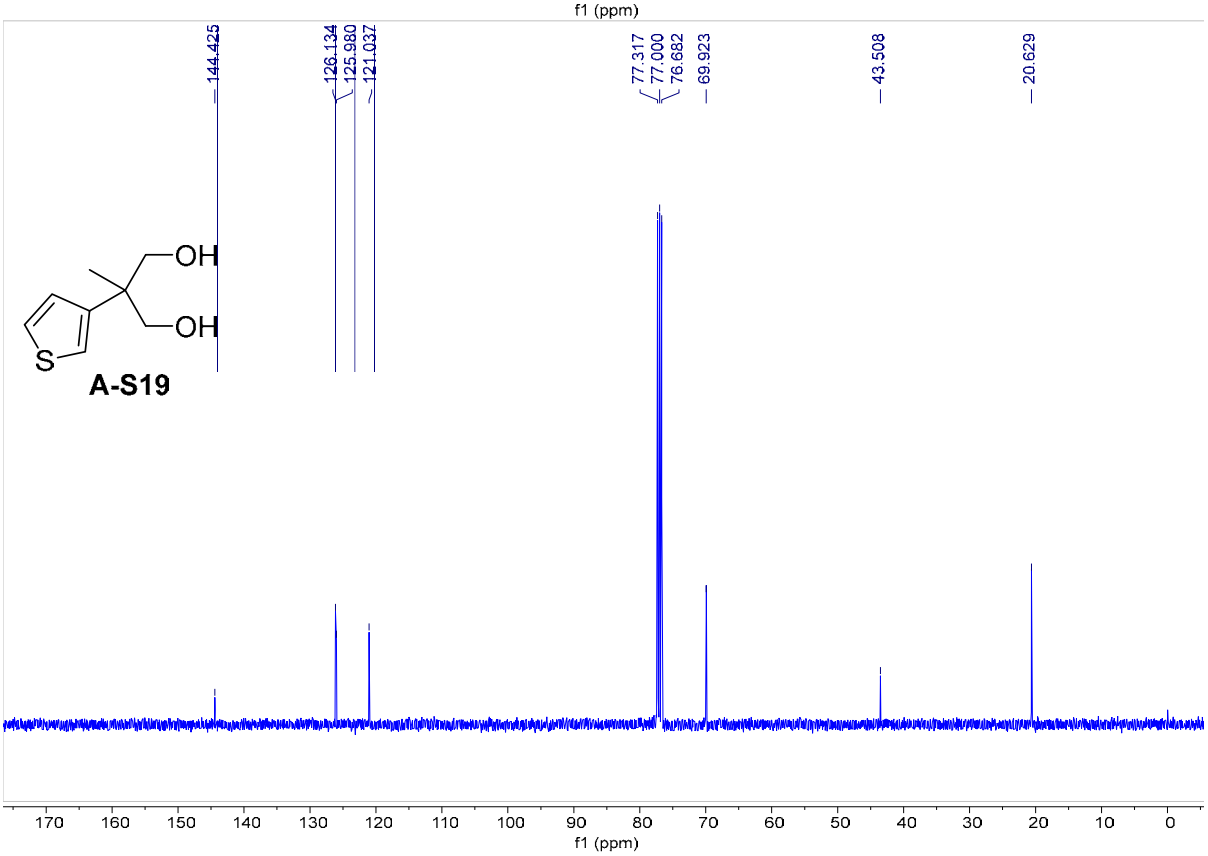
7.352
7.347
7.339
7.261
7.212
7.208
7.205
7.201
7.133
7.130
7.121
7.117
3.909
3.894
3.882
3.867
3.819
3.804
3.792
3.777
1.999
1.979
1.970
1.316
0.000
OH
OH
S
A-S19
1.00
1.01
1.02
2.19
2.17
2.10
3.27
f1 (ppm)


144.425
126.134
125.980
121.037
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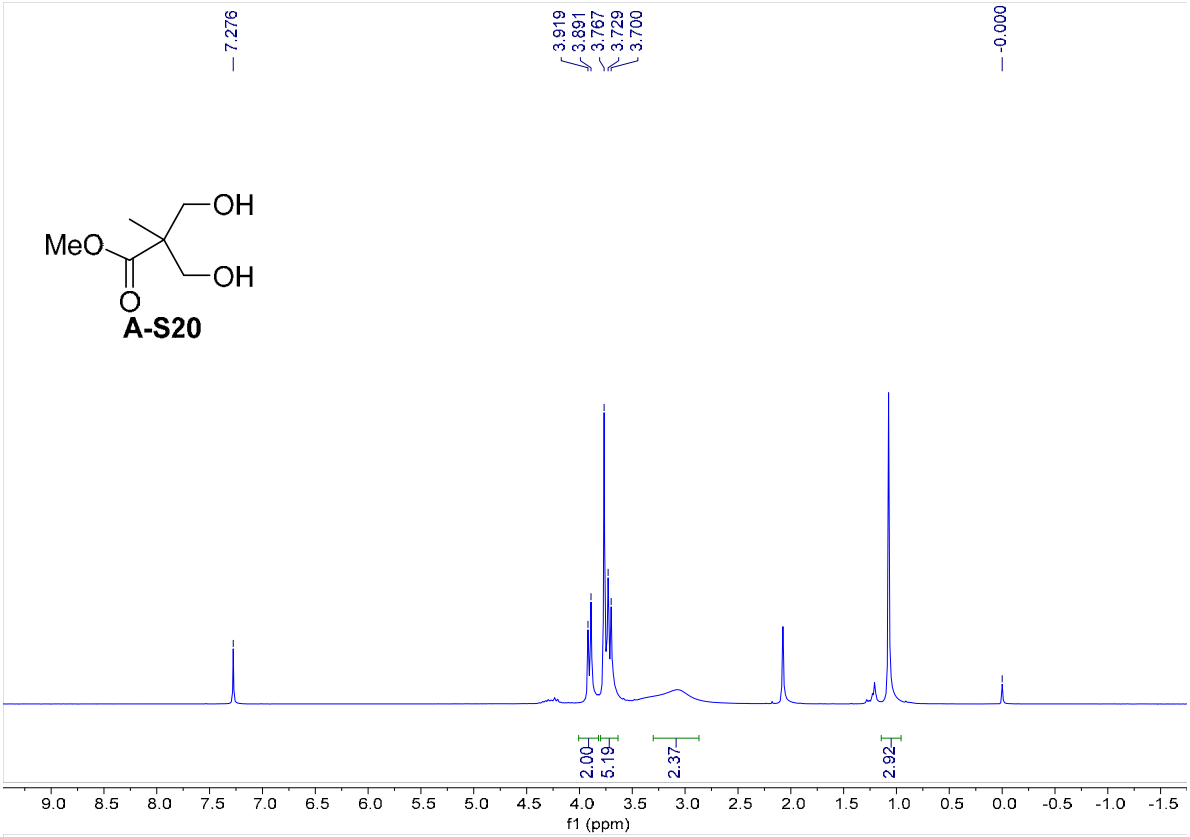
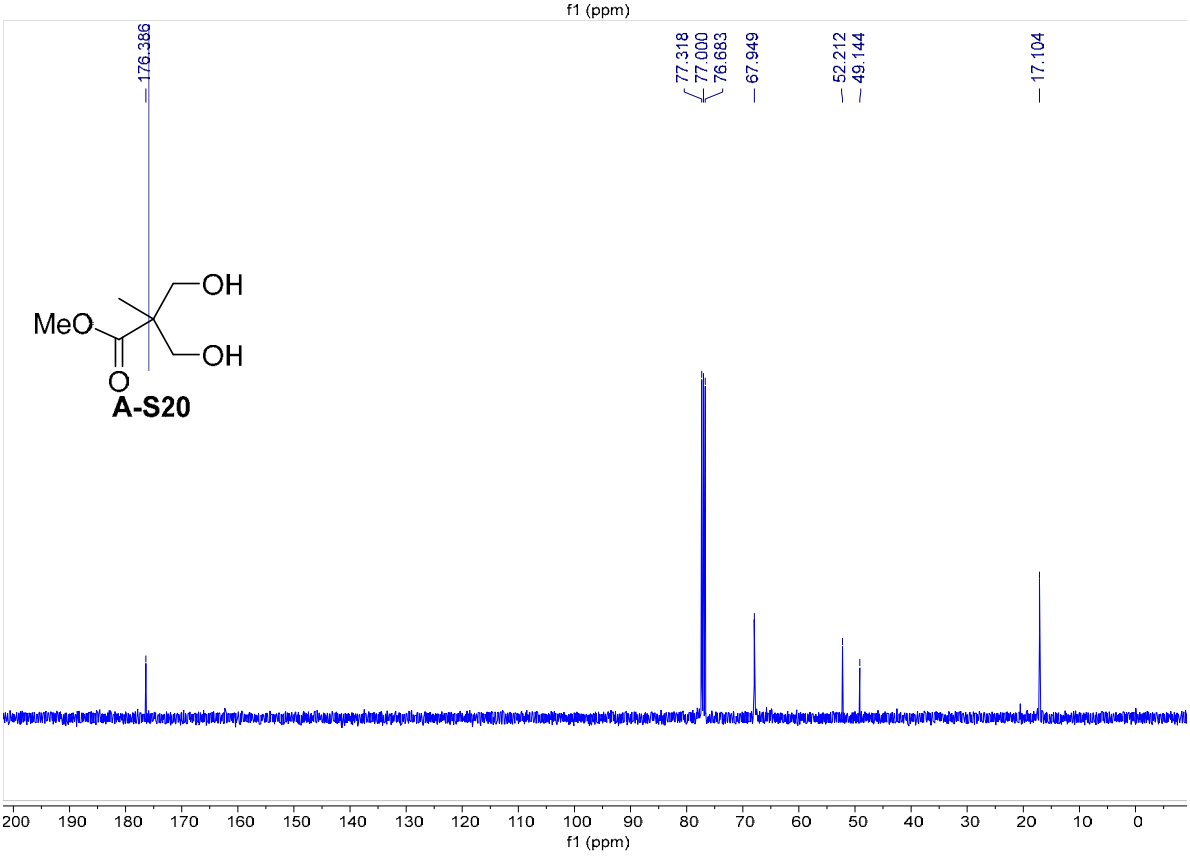
77.000
76.682
69.923
43.508
20.629
OH
OH
S
A-S19
f1 (ppm)


7.276
3.919
3.891
3.767
3.729
3.700
-0.000
OH
MeO
OH
O
A-S20
2.00
5.19
2.37
2.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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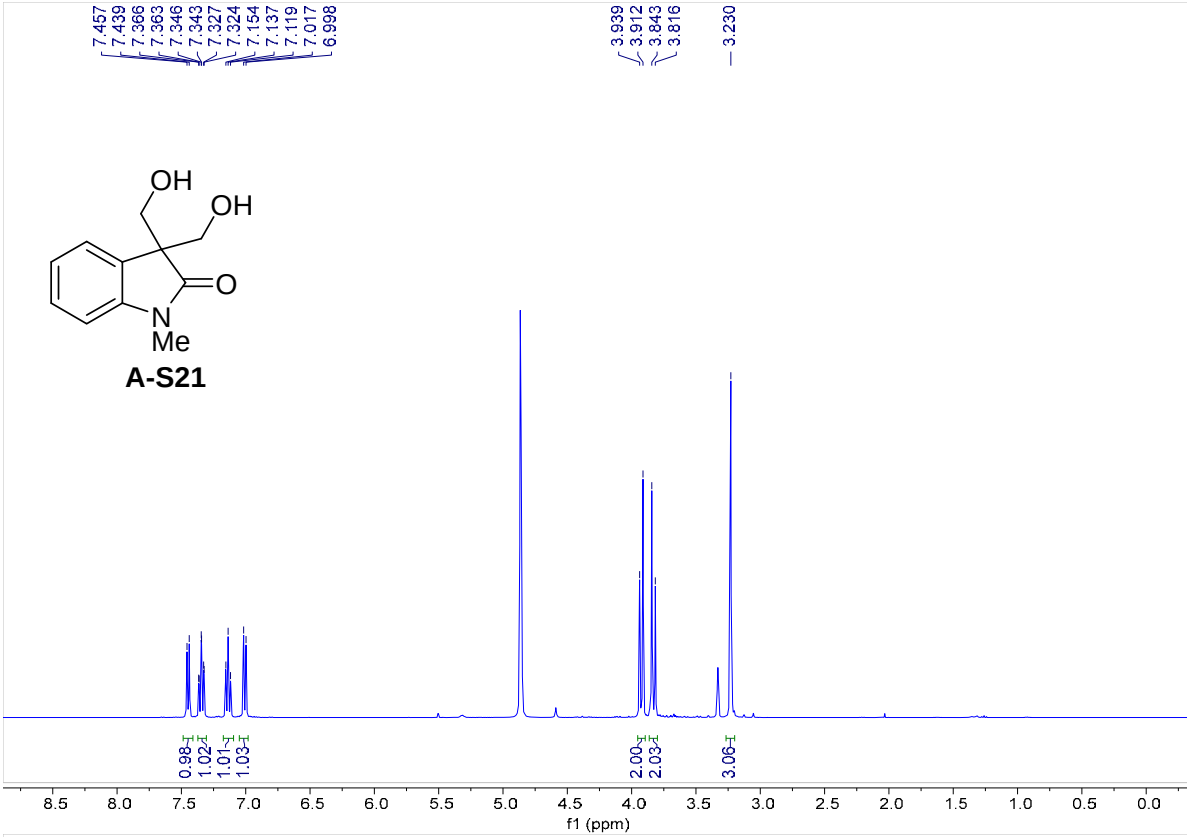
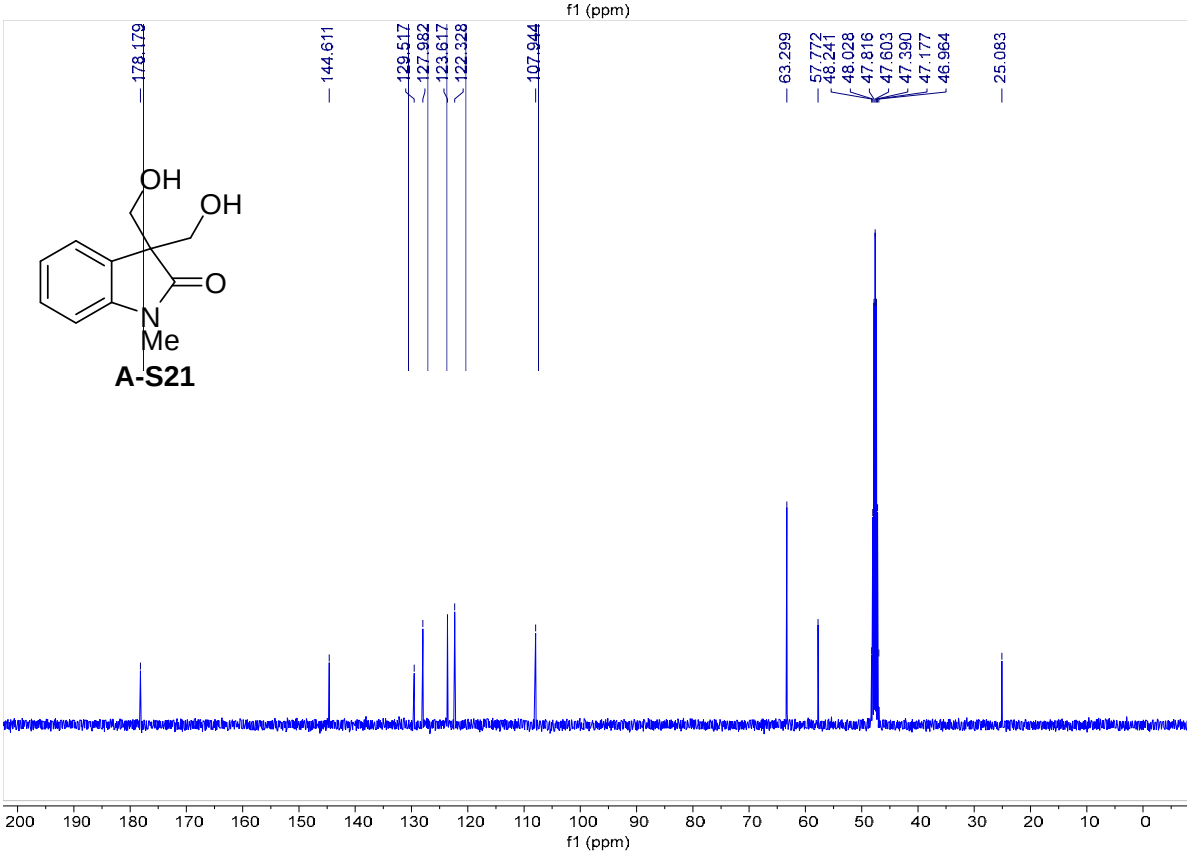
77.000
76.683
67.949
52.212
49.144
17.104
OH
MeO
OH
O
A-S20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.457
7.439
7.366
7.363
7.346
7.343
7.327
7.324
7.154
7.137
7.119
7.017
6.998
3.939
3.912
3.843
3.816
3.230
OH
OH
O
N
Me
A-S21
0.98
1.02
1.01
1.03
2.00
2.03
3.06
f1 (ppm)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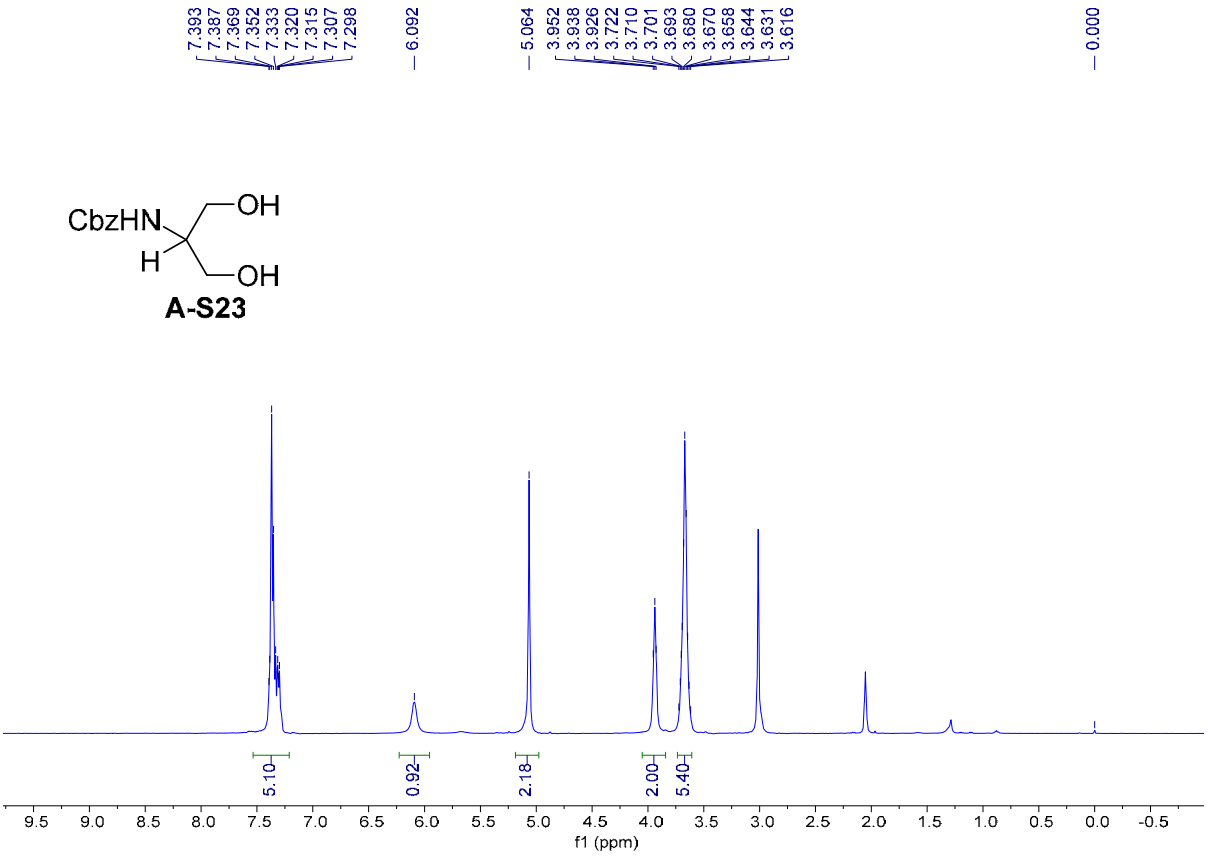
144.611
129.517
127.982
123.617
122.328
107.944
63.299
57.772
48.241
48.028
47.816
47.603
47.390
47.177
46.964
25.083
OH
OH
O
N
Me
A-S21
f1 (ppm)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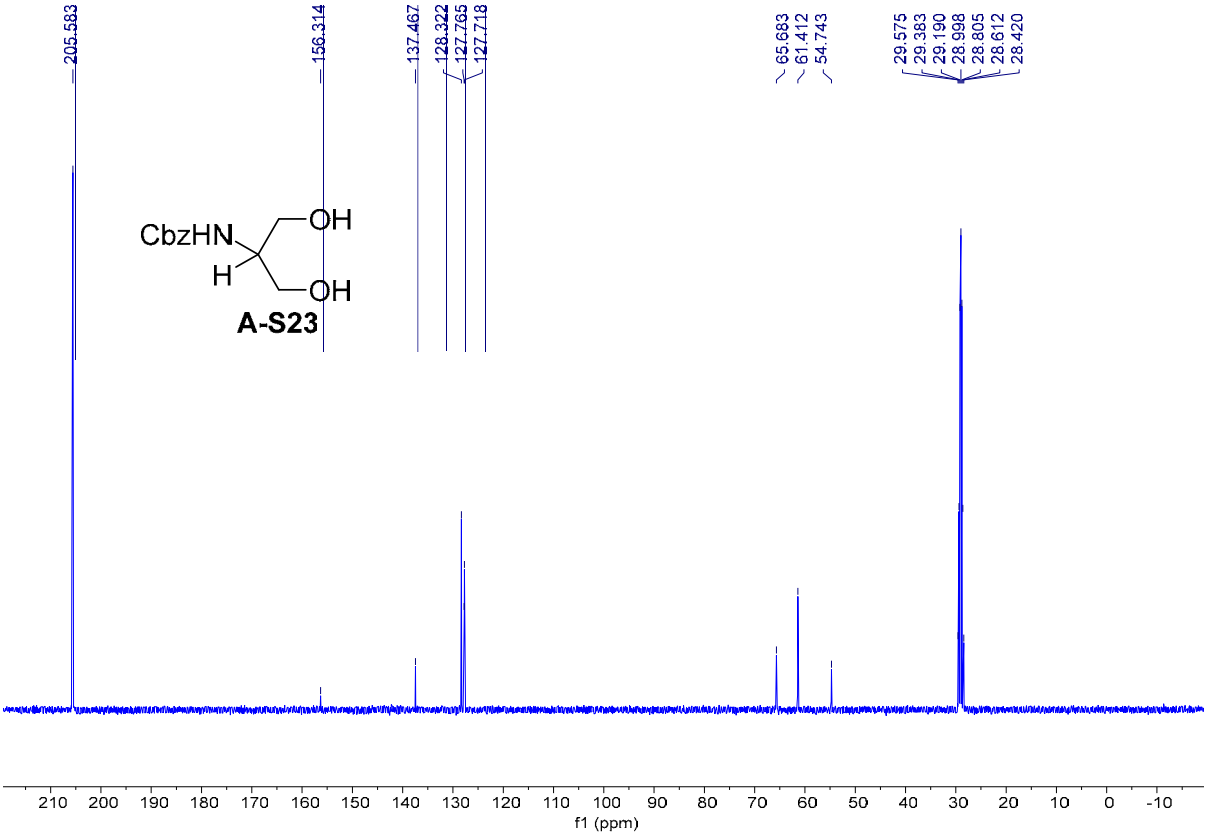
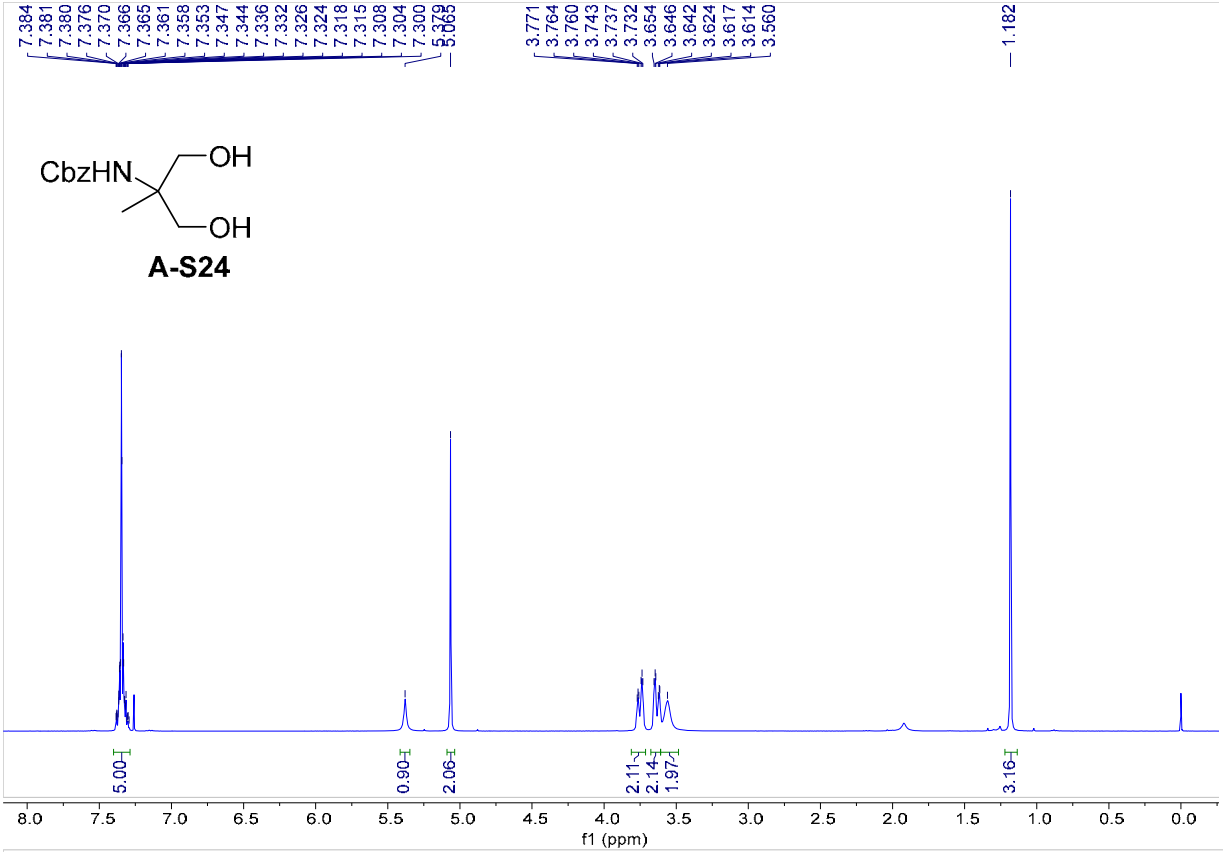
7.387
7.369
7.352
7.333
7.320
7.315
7.307
7.298
6.092
5.064
3.952
3.938
3.926
3.722
3.710
3.701
3.693
3.680
3.670
3.658
3.644
3.631
3.616
0.000
CbzHN
OH
H
OH
A-S23
5.10
0.92
2.18
2.00
5.40
f1 (ppm)


205.583
156.314
137.467
128.322
127.765
127.718
65.683
61.412
54.743
29.575
29.383
29.190
28.998
28.805
28.612
28.420
CbzHN
OH
H
OH
A-S23
f1 (ppm)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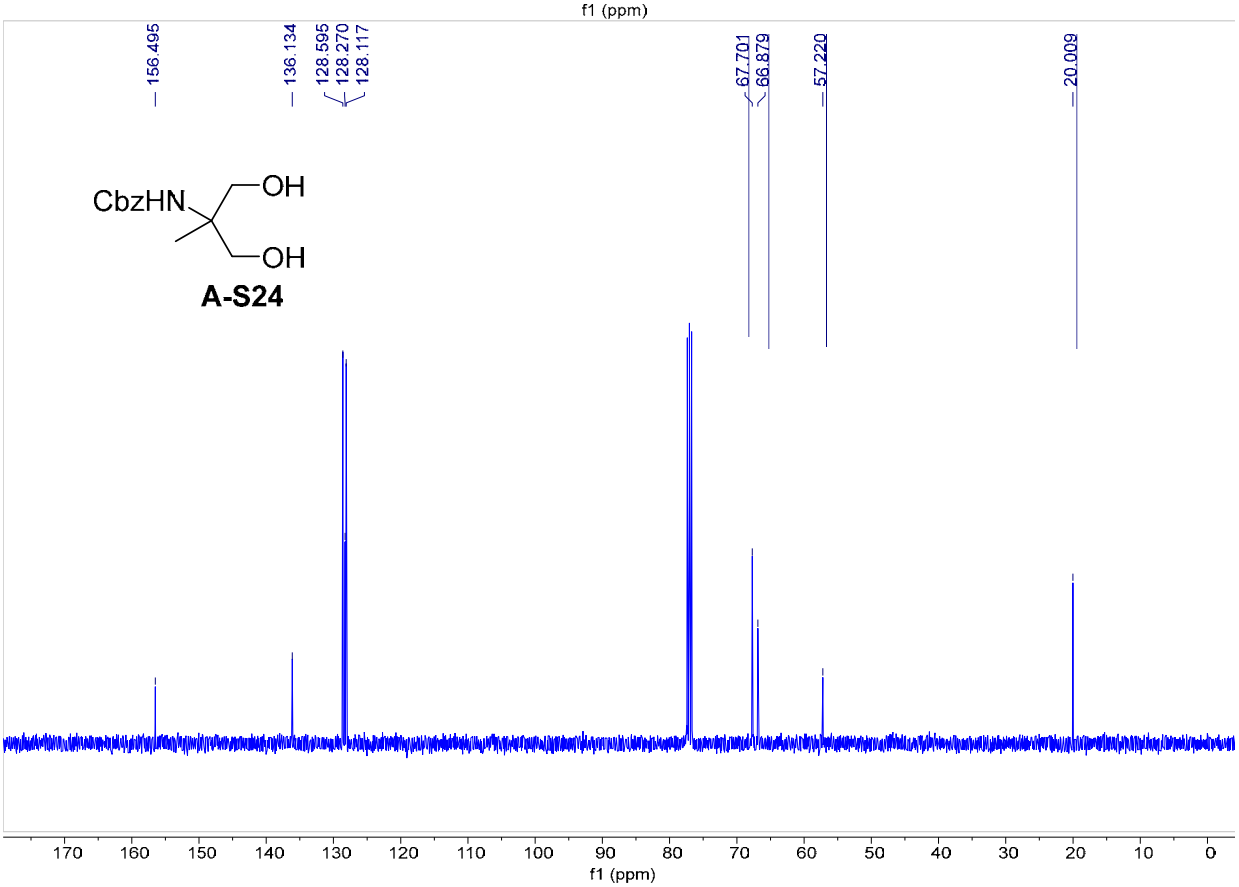
7.381
7.380
7.376
7.370
7.366
7.365
7.361
7.358
7.353
7.347
7.344
7.336
7.332
7.326
7.324
7.318
7.315
7.308
7.304
7.300
5.379
5.065
3.771
3.764
3.760
3.743
3.737
3.732
3.654
3.646
3.642
3.624
3.617
3.614
3.560
1.182
CbzHN
OH
OH
A-S24
5.00
0.90
2.06
2.11
2.14
1.97
3.16
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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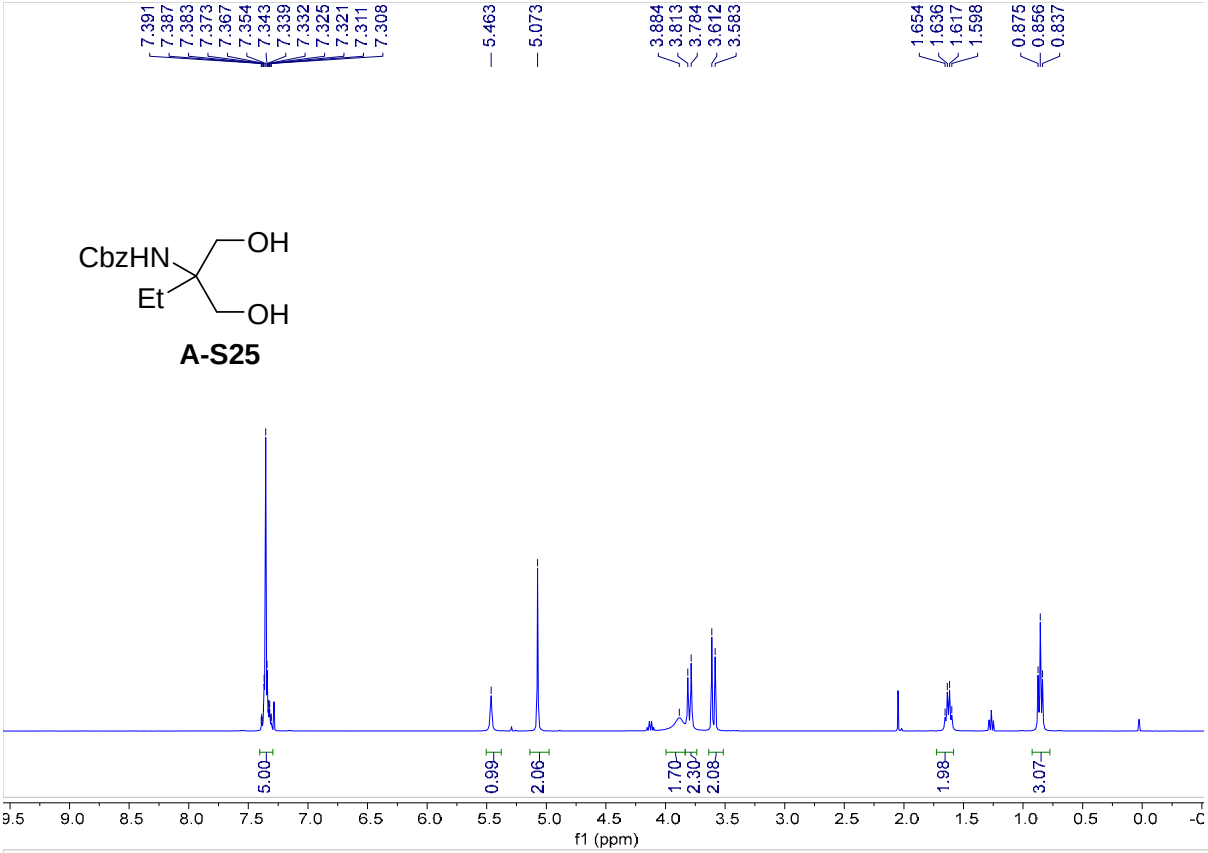
136.134
128.595
128.270
128.117
67.701
66.879
57.220
20.009
CbzHN
OH
OH
A-S24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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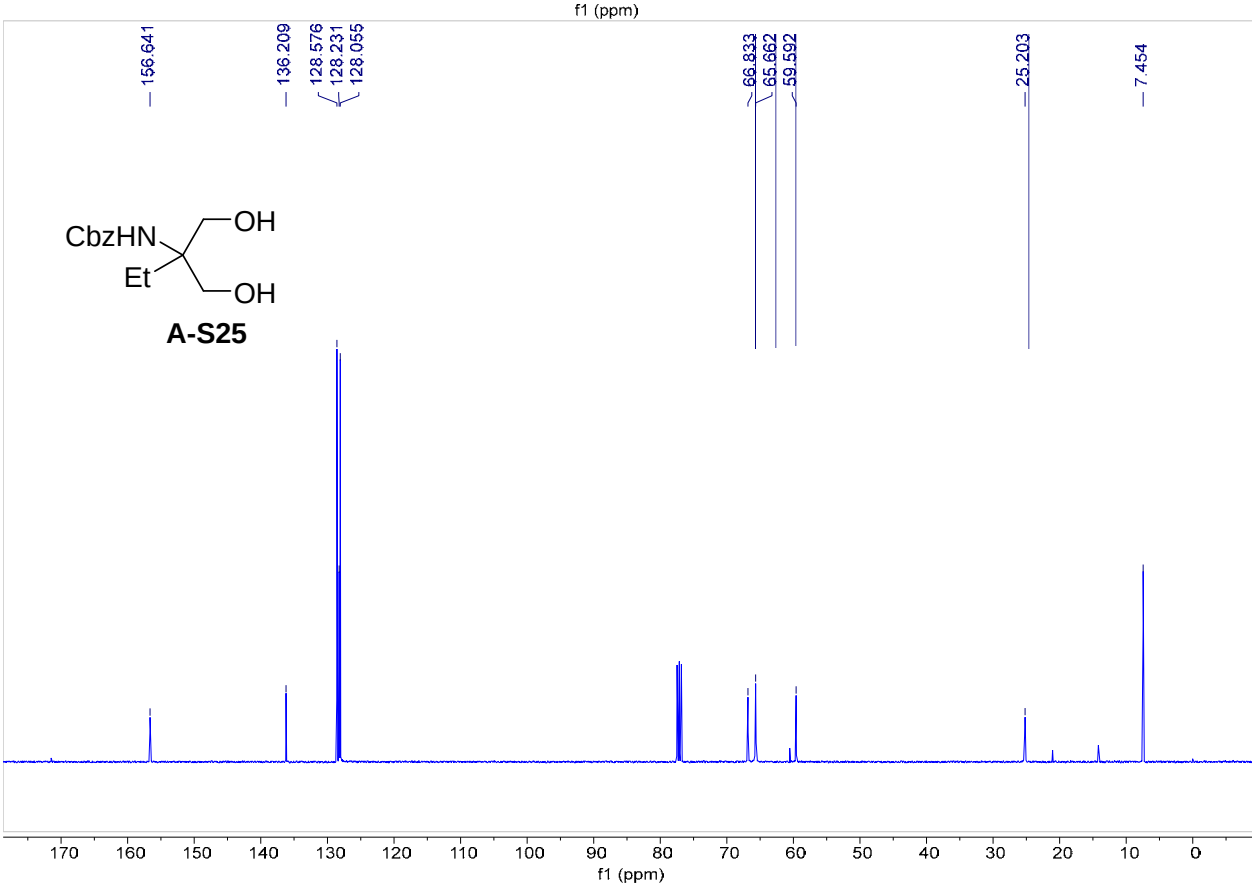
7.387
7.383
7.373
7.367
7.354
7.343
7.339
7.332
7.325
7.321
7.311
7.308
5.463
5.073
3.884
3.813
3.784
3.612
3.583
1.654
1.636
1.617
1.598
0.875
0.856
0.837
CbzHN
OH
Et
OH
A-S25
5.00
0.99
2.06
1.70
2.30
2.08
1.98
3.07
f1 (ppm)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128.576
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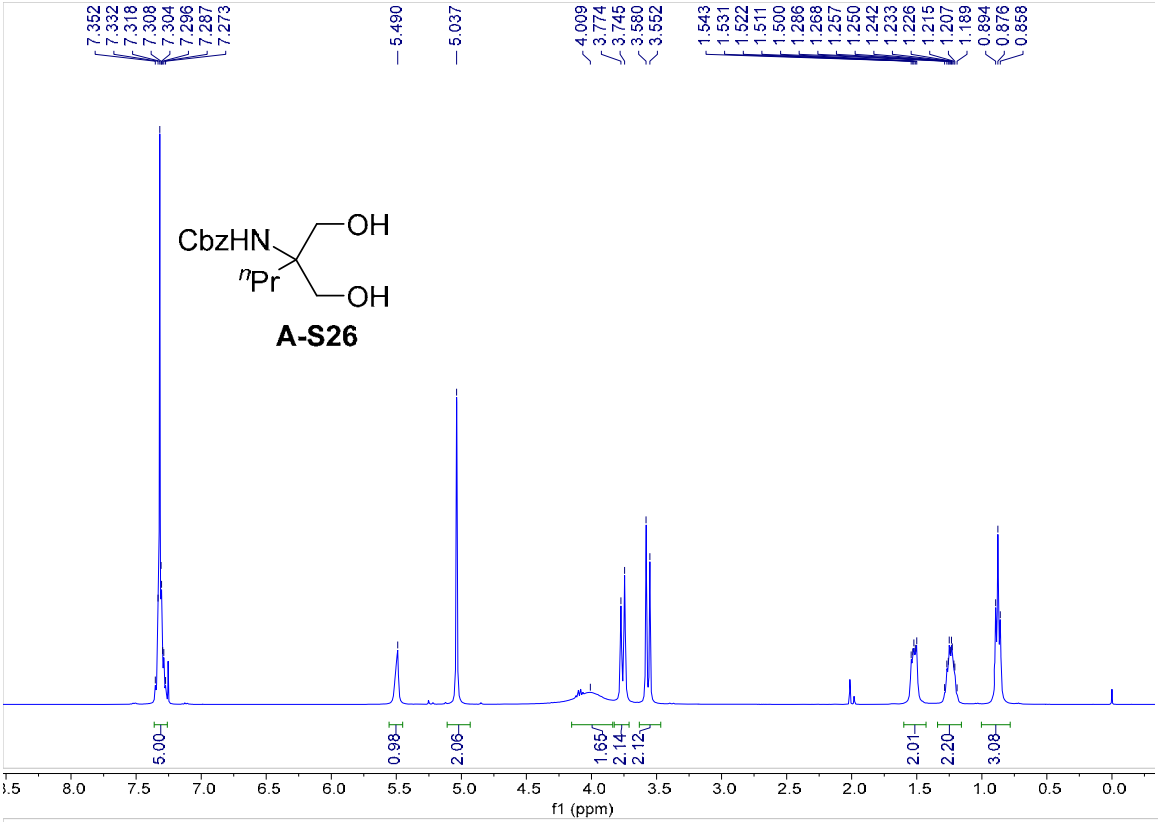
65.662
59.592
25.203
7.454
CbzHN
OH
Et
OH
A-S25
f1 (ppm)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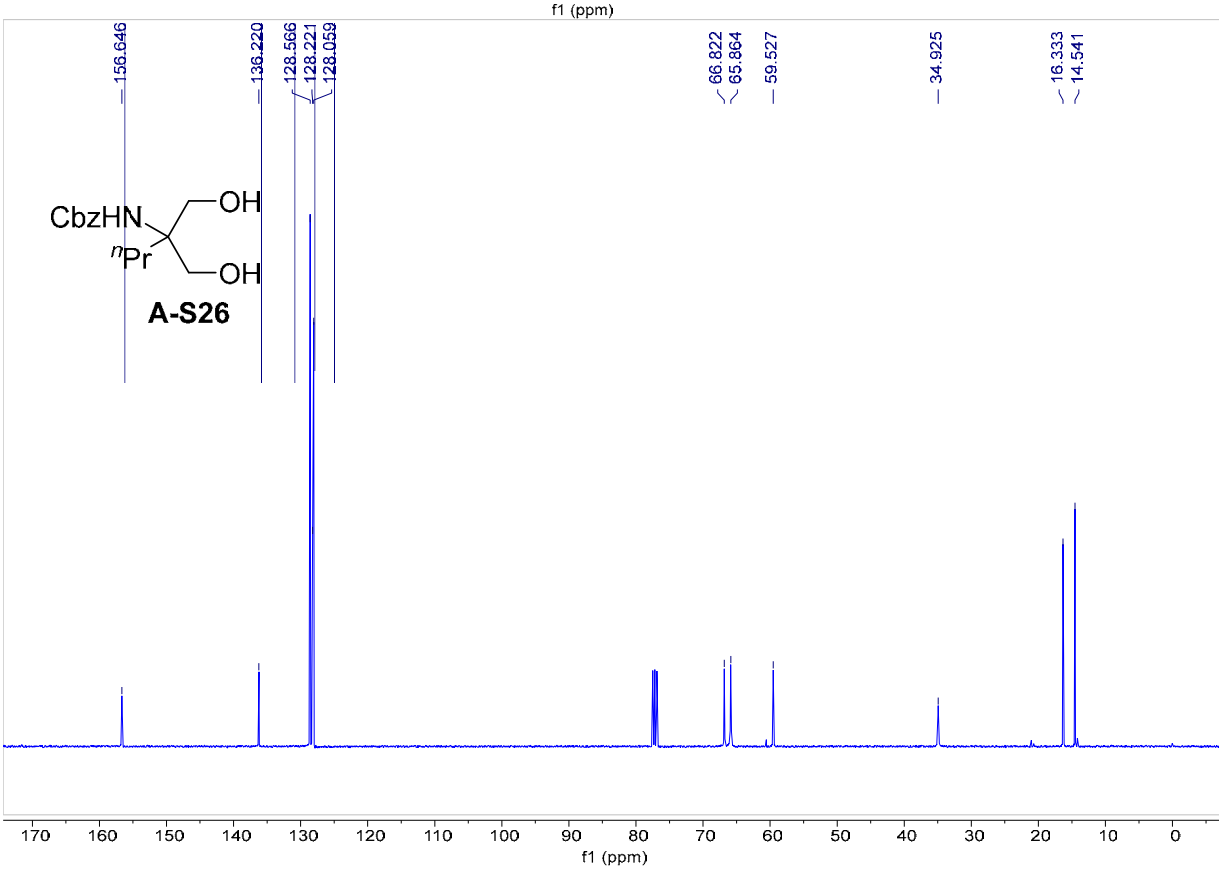
7.332
7.318
7.308
7.304
7.296
7.287
7.273
5.490
5.037
4.009
3.774
3.745
3.580
3.552
1.543
1.531
1.522
1.511
1.500
1.286
1.268
1.257
1.250
1.242
1.233
1.226
1.215
1.207
1.189
0.894
0.876
0.858
CbzHN
OH
nPr
OH
A-S26
5.00
0.98
2.06
1.65
2.14
2.12
2.01
2.20
3.08
f1 (ppm)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128.566
128.221
128.059
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59.527
34.925
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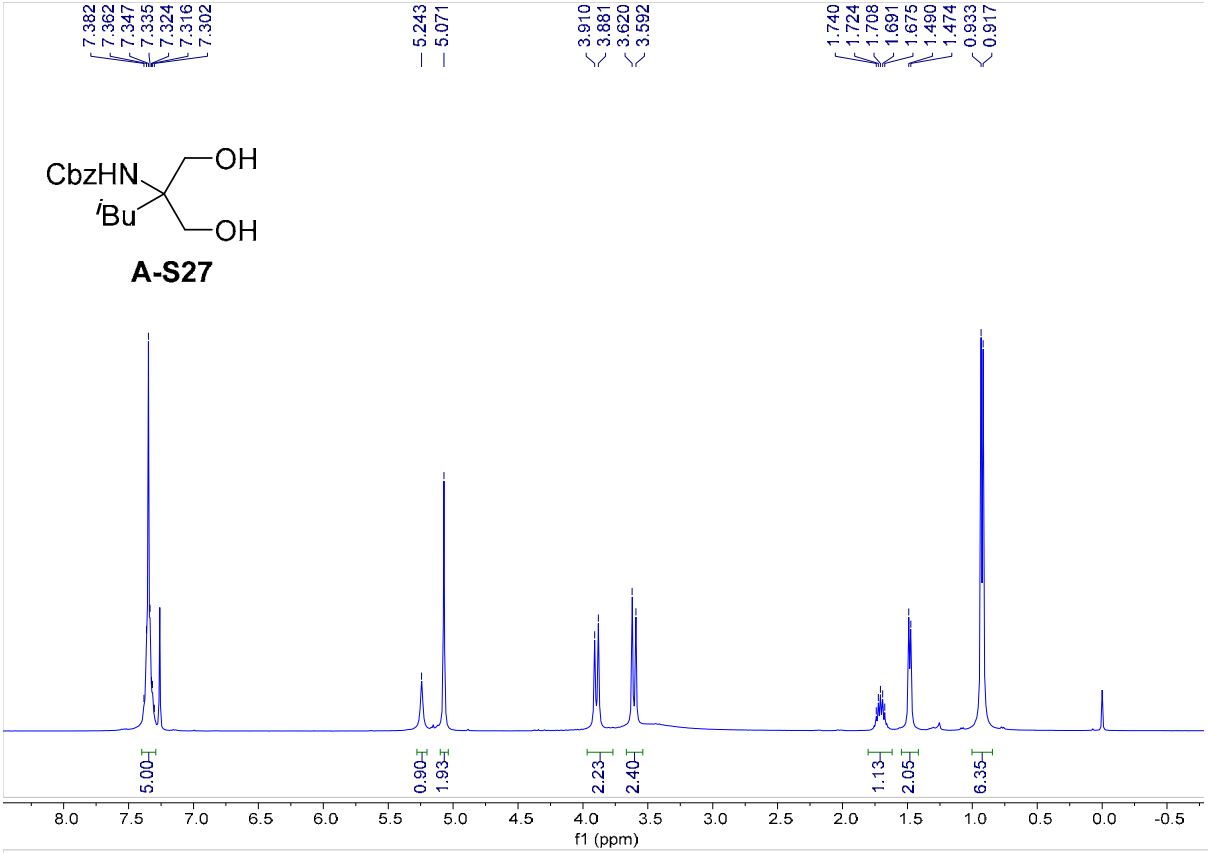
14.541
CbzHN
OH
nPr
OH
A-S26
f1 (ppm)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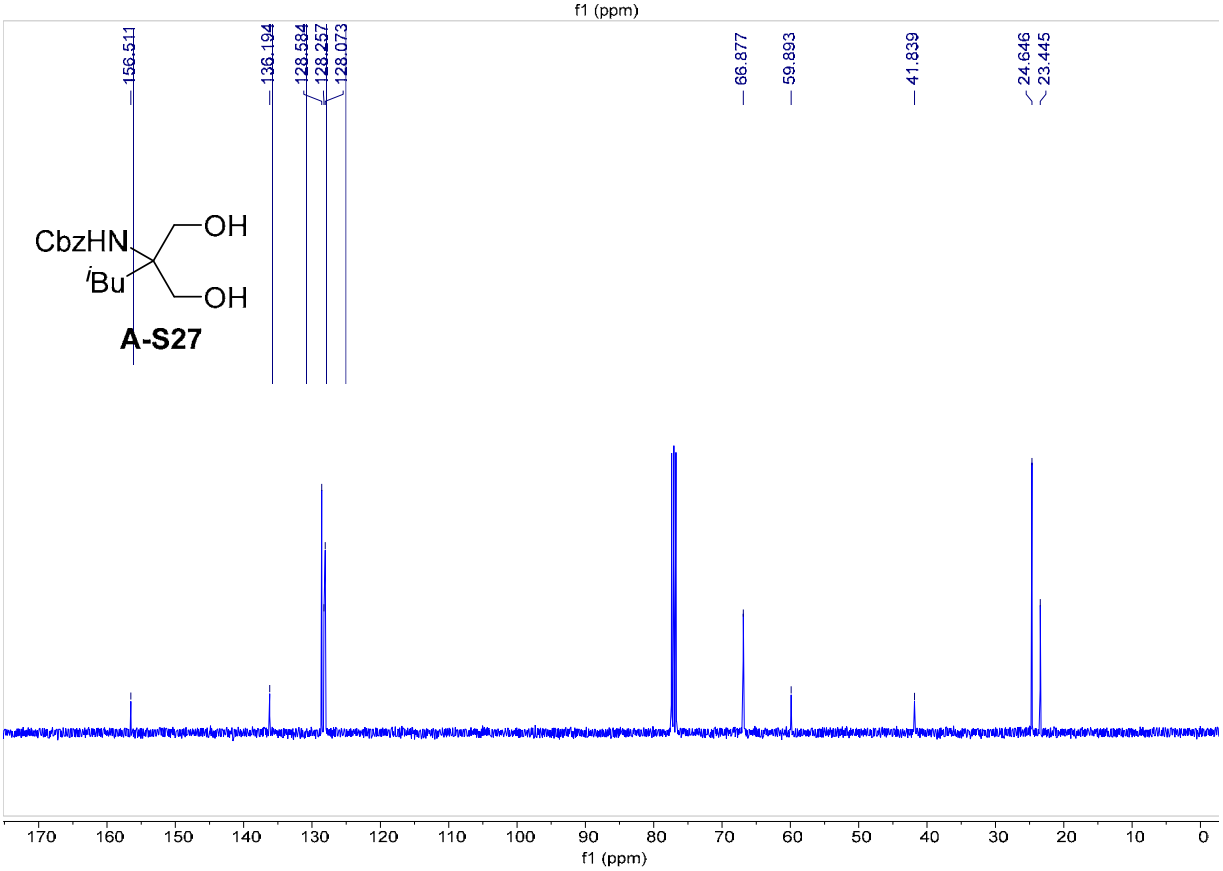
7.335
7.324
7.316
7.302
5.243
5.071
3.910
3.881
3.620
3.592
1.740
1.724
1.708
1.691
1.675
1.490
1.474
0.933
0.917
CbzHN
OH
iBu
OH
A-S27
5.00
0.90
1.93
2.23
2.40
1.13
2.05
6.35
f1 (ppm)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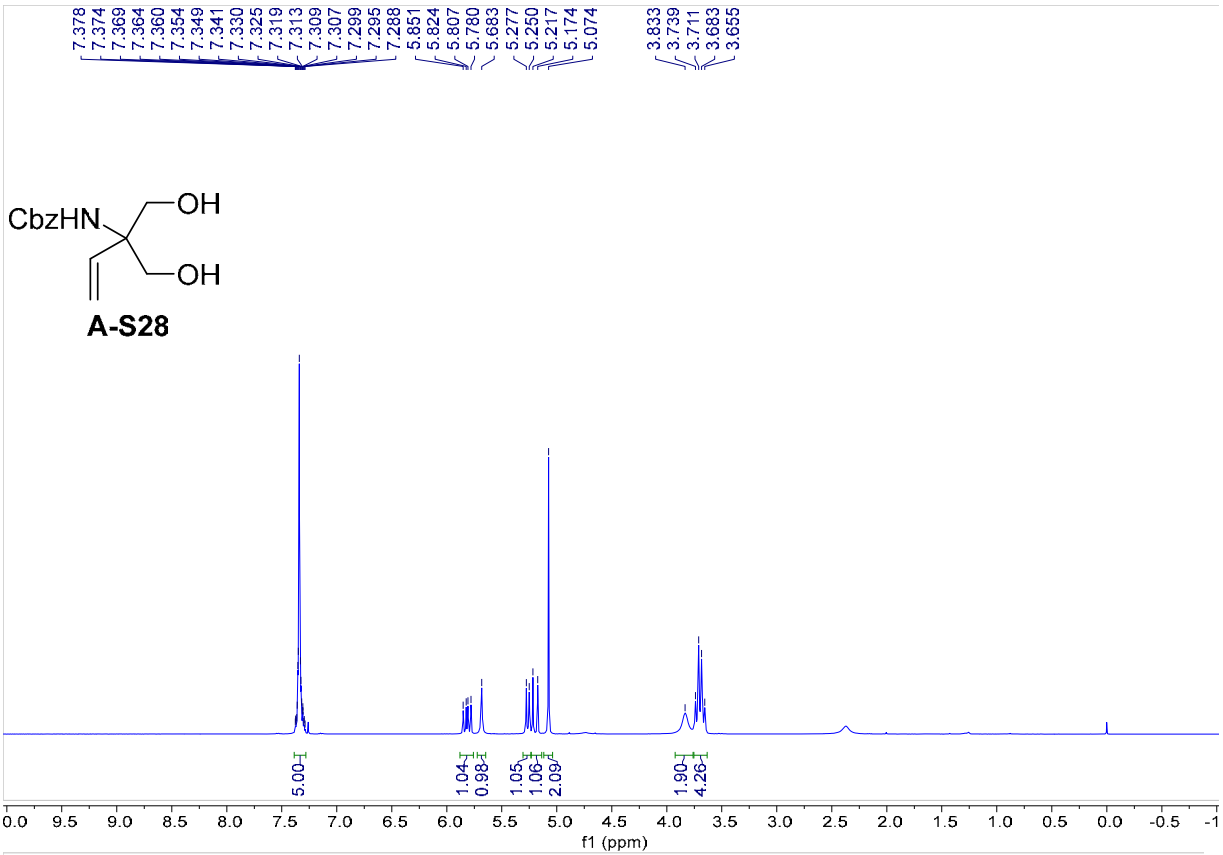
OH
iBu
OH
A-S27
f1 (ppm)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7.319
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7.309
7.307
7.299
7.295
7.288
5.851
5.824
5.807
5.780
5.683
5.277
5.250
5.217
5.174
5.074
3.833
3.739
3.711
3.683
3.655
CbzHN
OH
OH
A-S28
5.00
1.04
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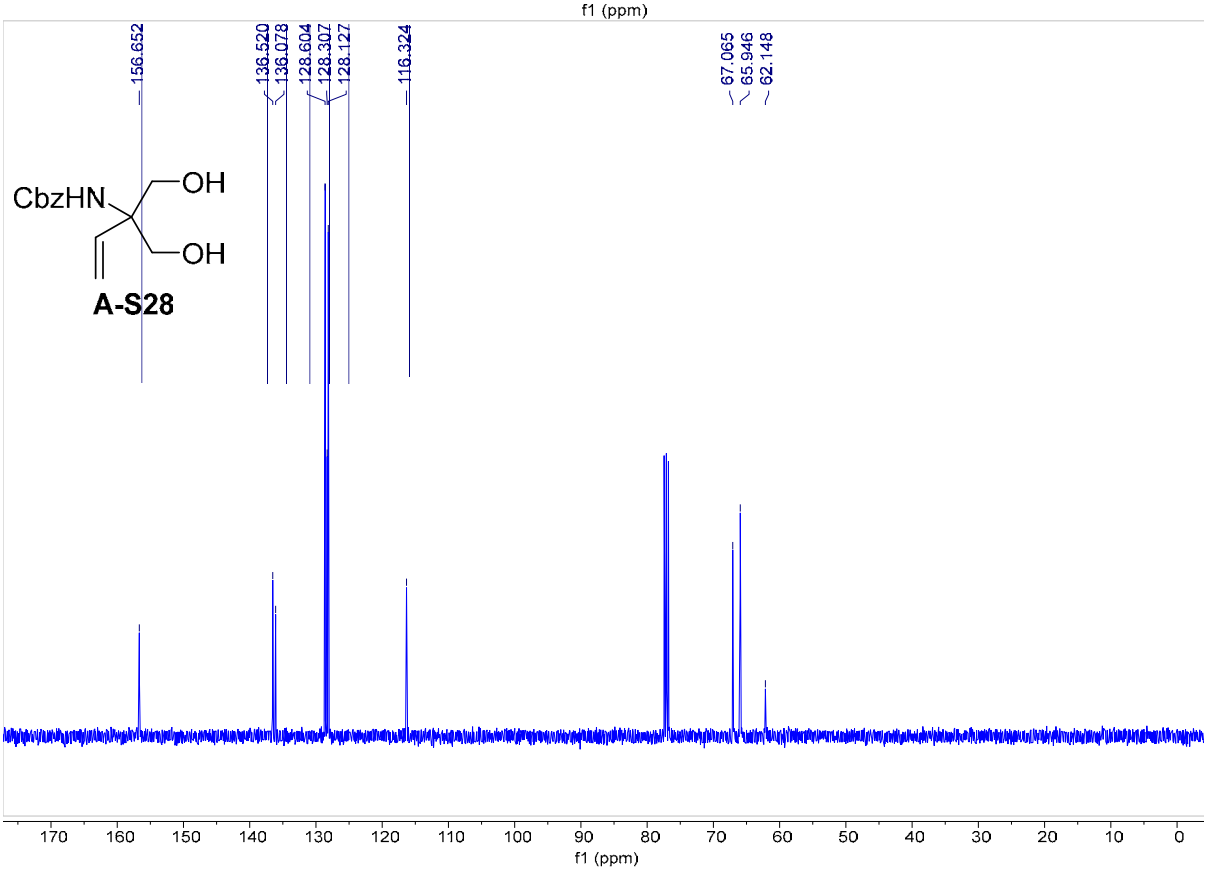
1.05
1.06
2.09
1.90
4.26
f1 (ppm)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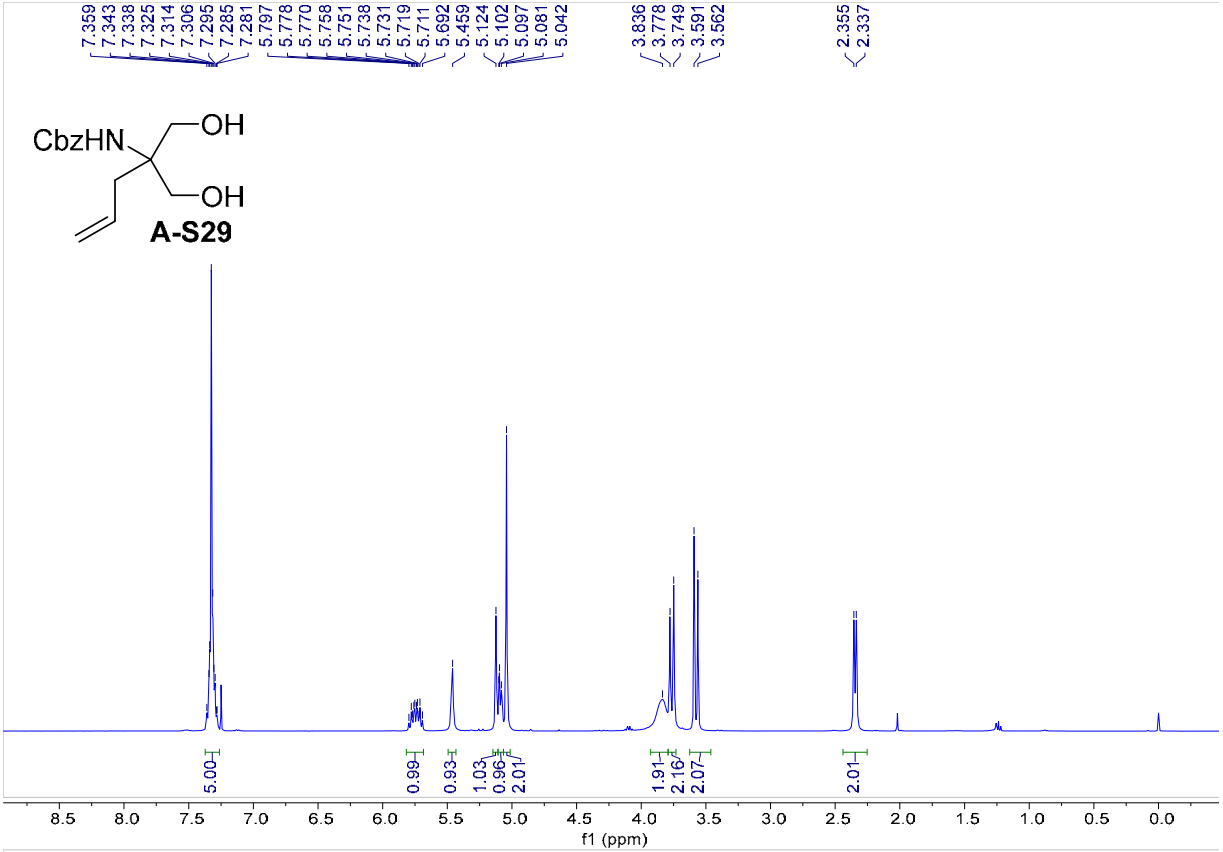
CbzHN
OH
OH
A-S28
f1 (ppm)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7.343
7.338
7.325
7.314
7.306
7.295
7.285
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5.778
5.770
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5.751
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5.731
5.719
5.711
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5.124
5.102
5.097
5.081
5.042
3.836
3.778
3.749
3.591
3.562
2.355
2.337
CbzHN
OH
OH
A-S29
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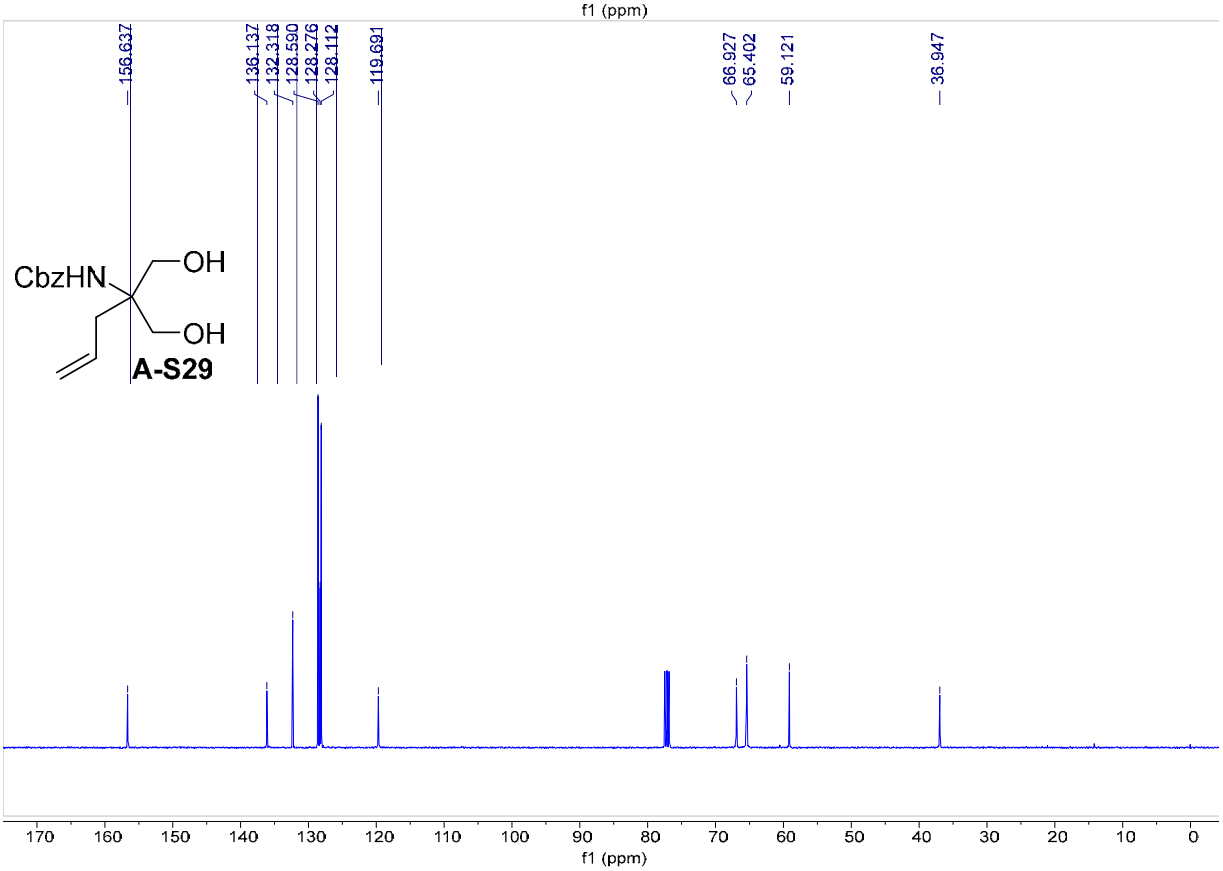
0.96
2.01
1.91
2.16
2.07
2.01
f1 (ppm)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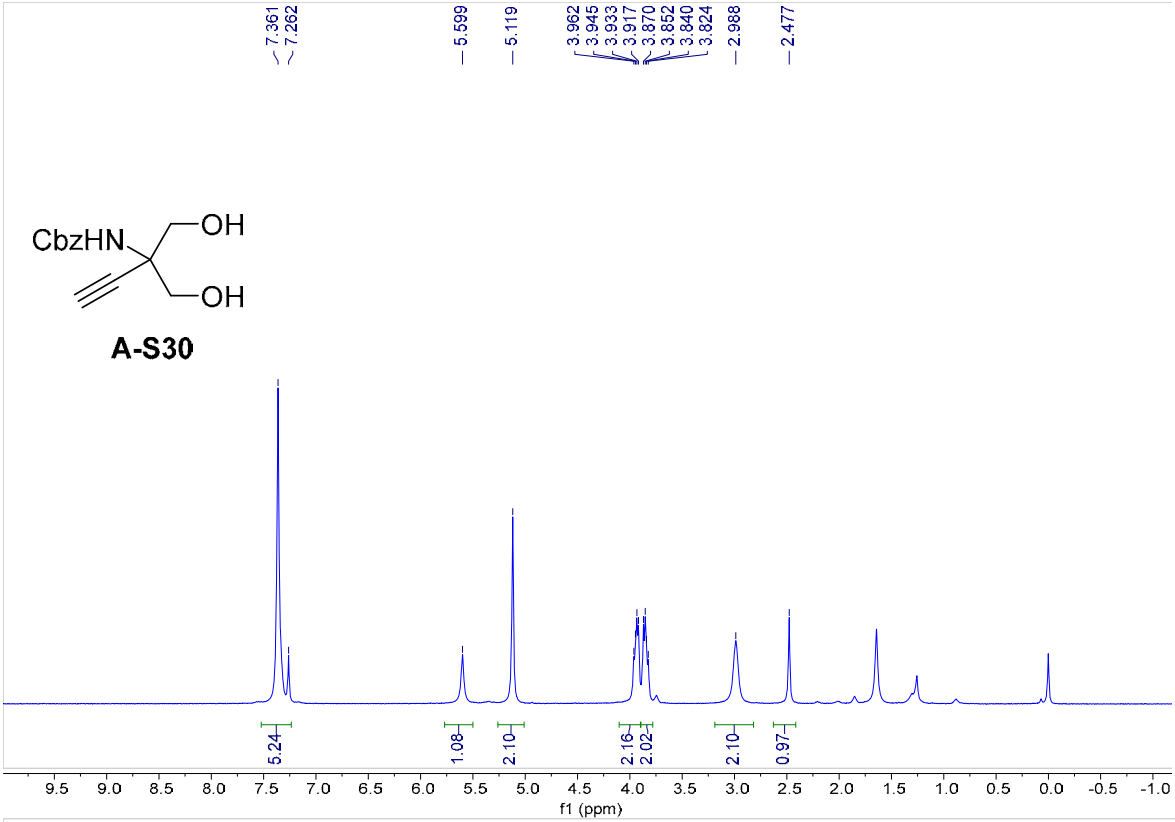
59.121
36.947
CbzHN
OH
OH
A-S29
f1 (ppm)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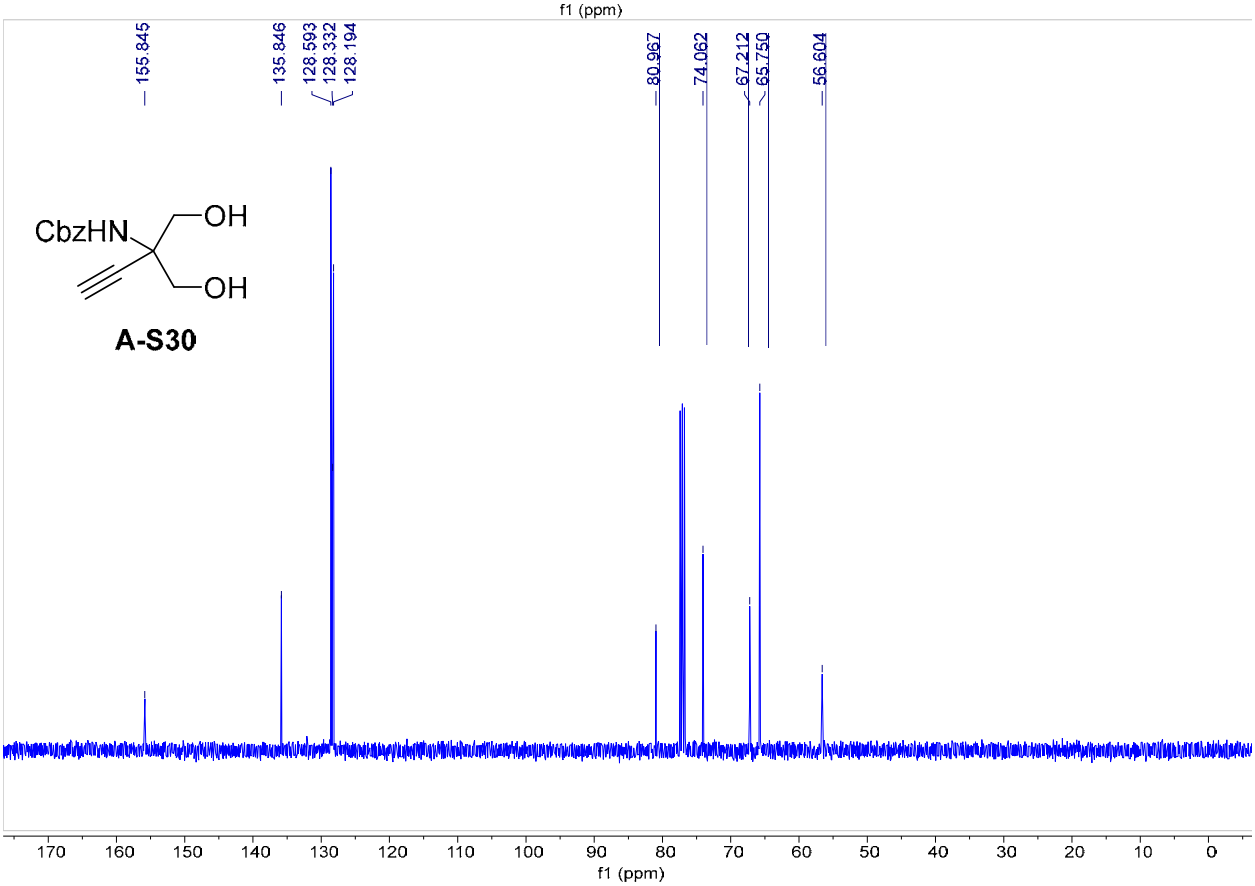
3.917
3.870
3.852
3.840
3.824
2.988
2.477
CbzHN
OH
OH
A-S30
5.24
1.08
2.10
2.16
2.02
2.10
0.97
f1 (ppm)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67.212
65.750
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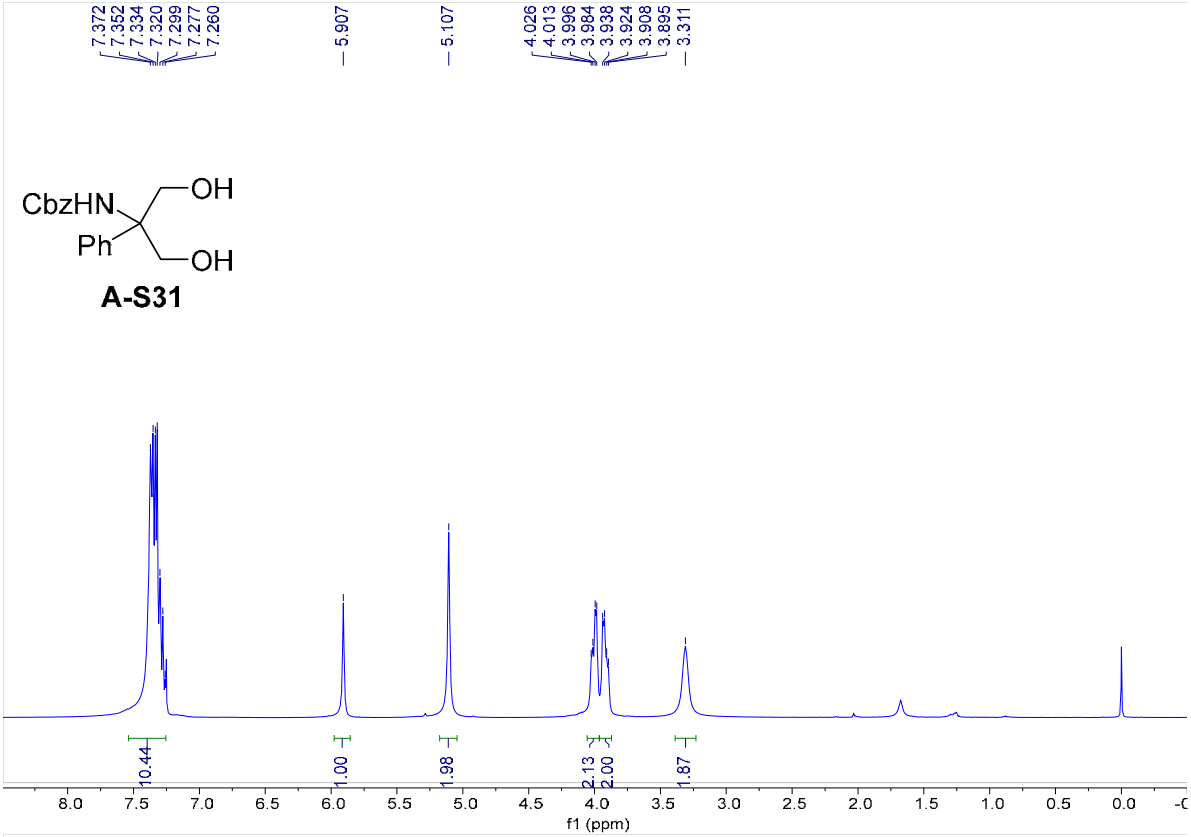
CbzHN
OH
OH
A-S30
f1 (ppm)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7.352
7.334
7.320
7.299
7.277
7.260
5.907
5.107
4.026
4.013
3.996
3.984
3.938
3.924
3.908
3.895
3.311
CbzHN
OH
Ph
OH
A-S31
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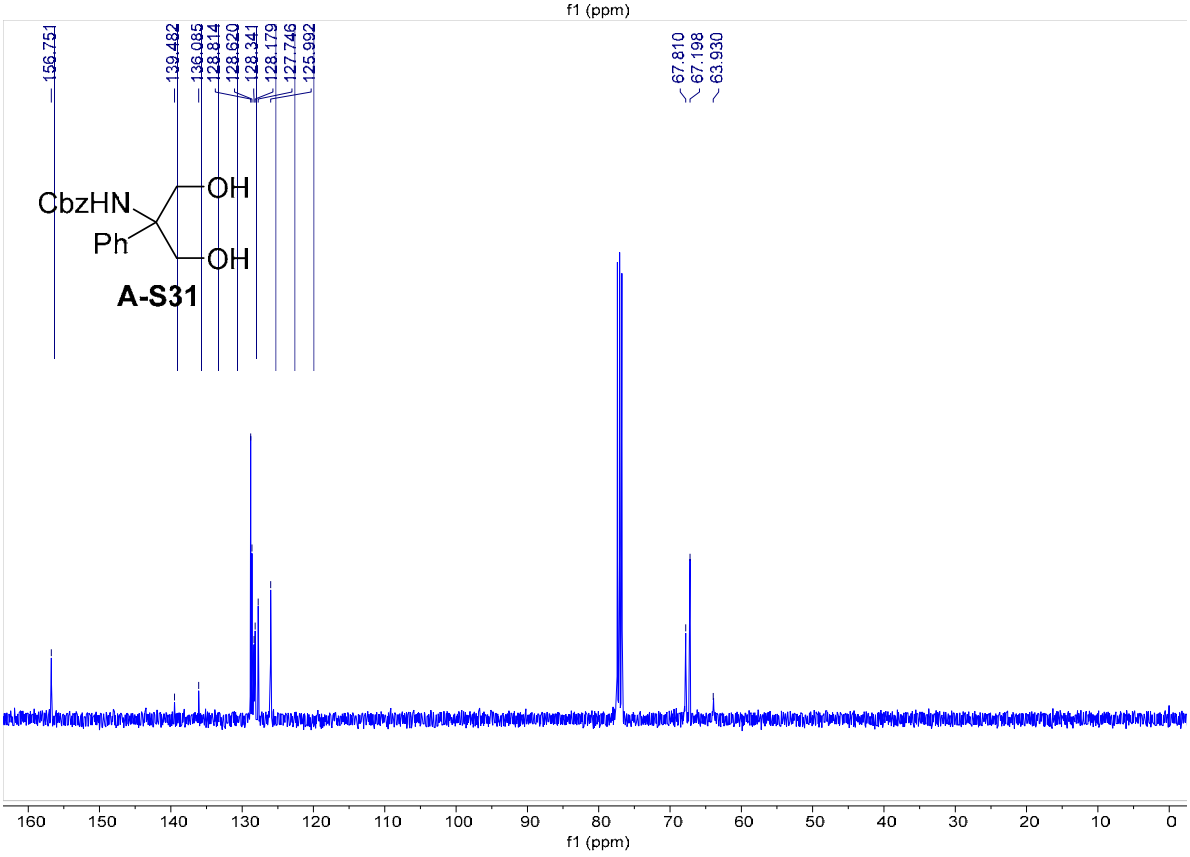
1.98
2.13
2.00
1.87
f1 (ppm)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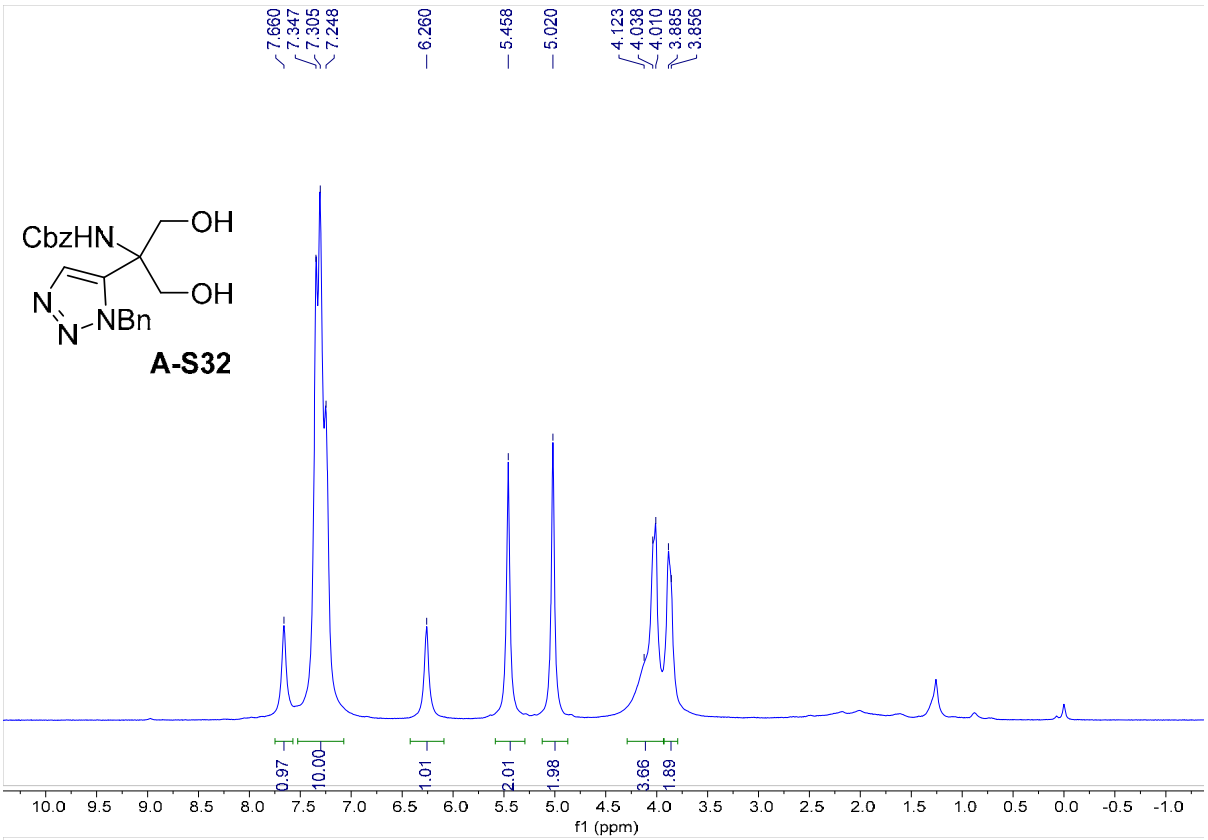
67.198
63.930
CbzHN
OH
Ph
OH
A-S31
f1 (ppm)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7.248
6.260
5.458
5.020
4.123
4.038
4.010
3.885
3.856
CbzHN
OH
OH
N
N
NBn
A-S32
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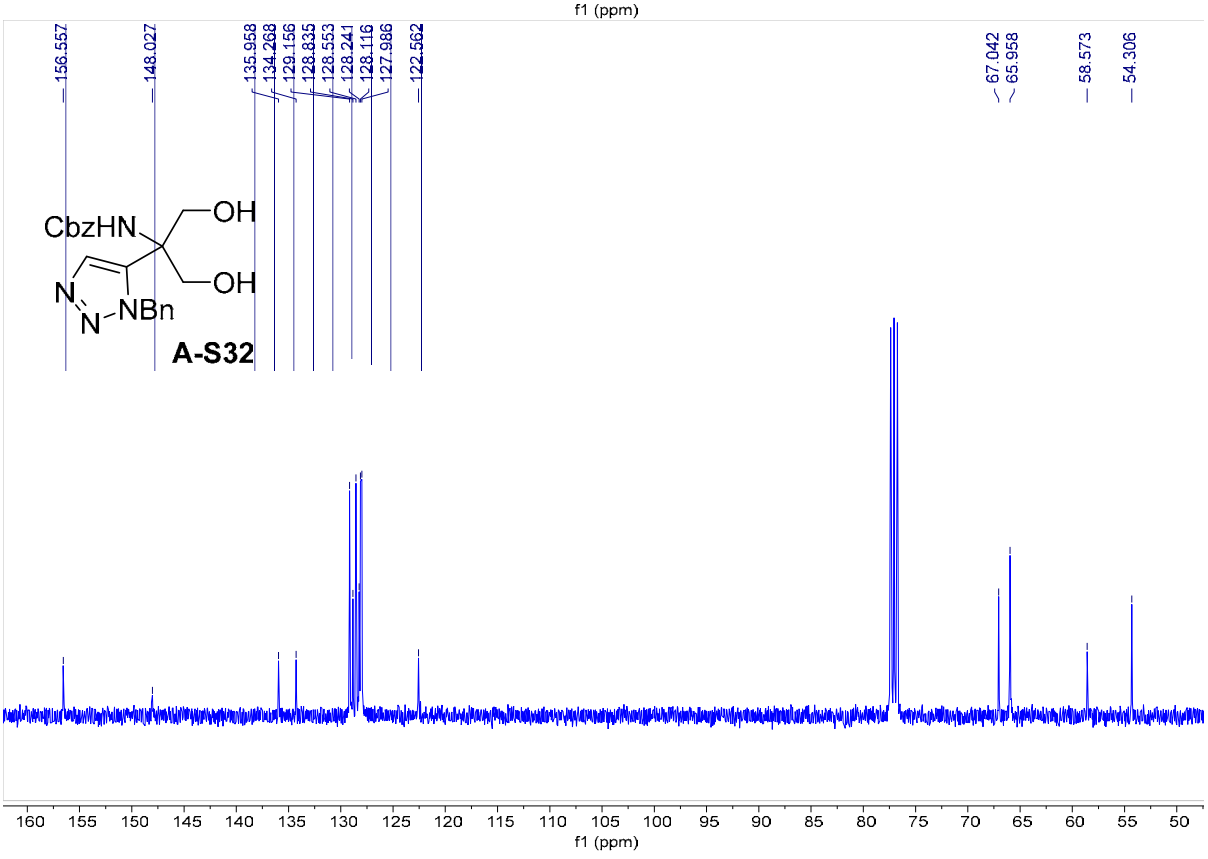
1.01
2.01
1.98
3.66
1.89
f1 (ppm)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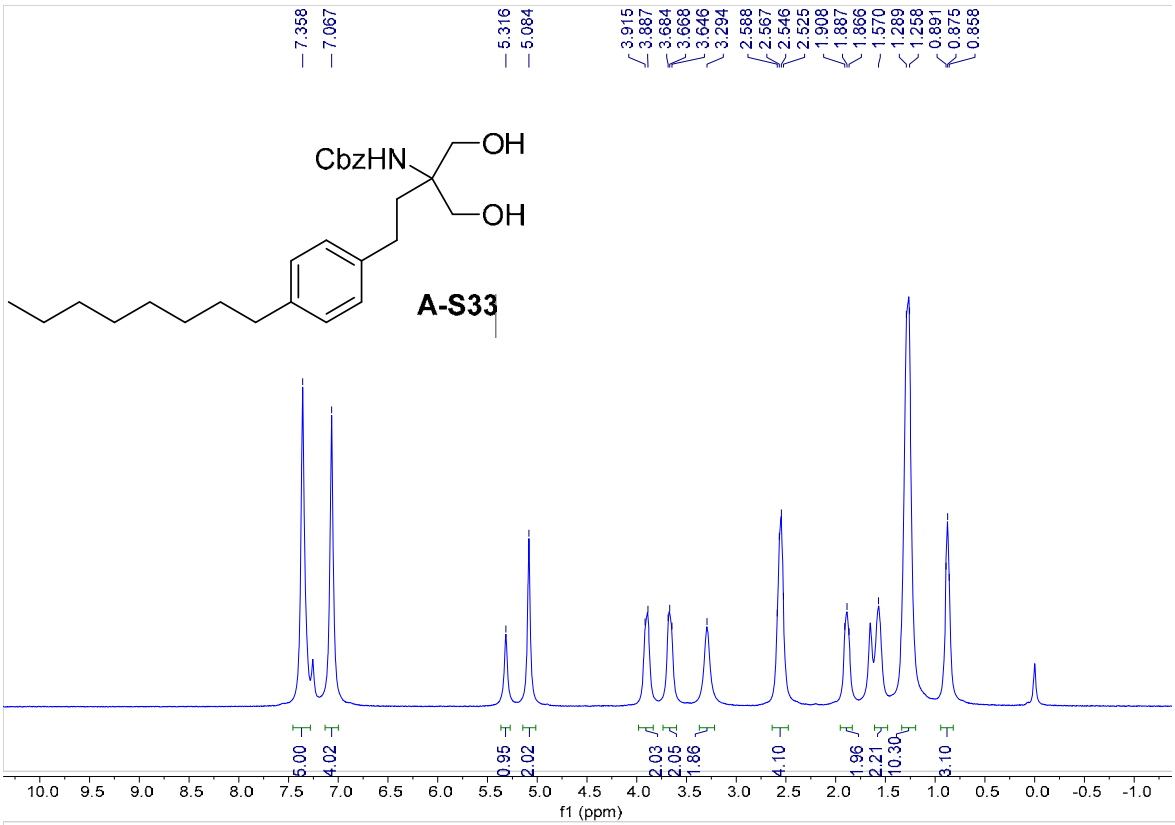
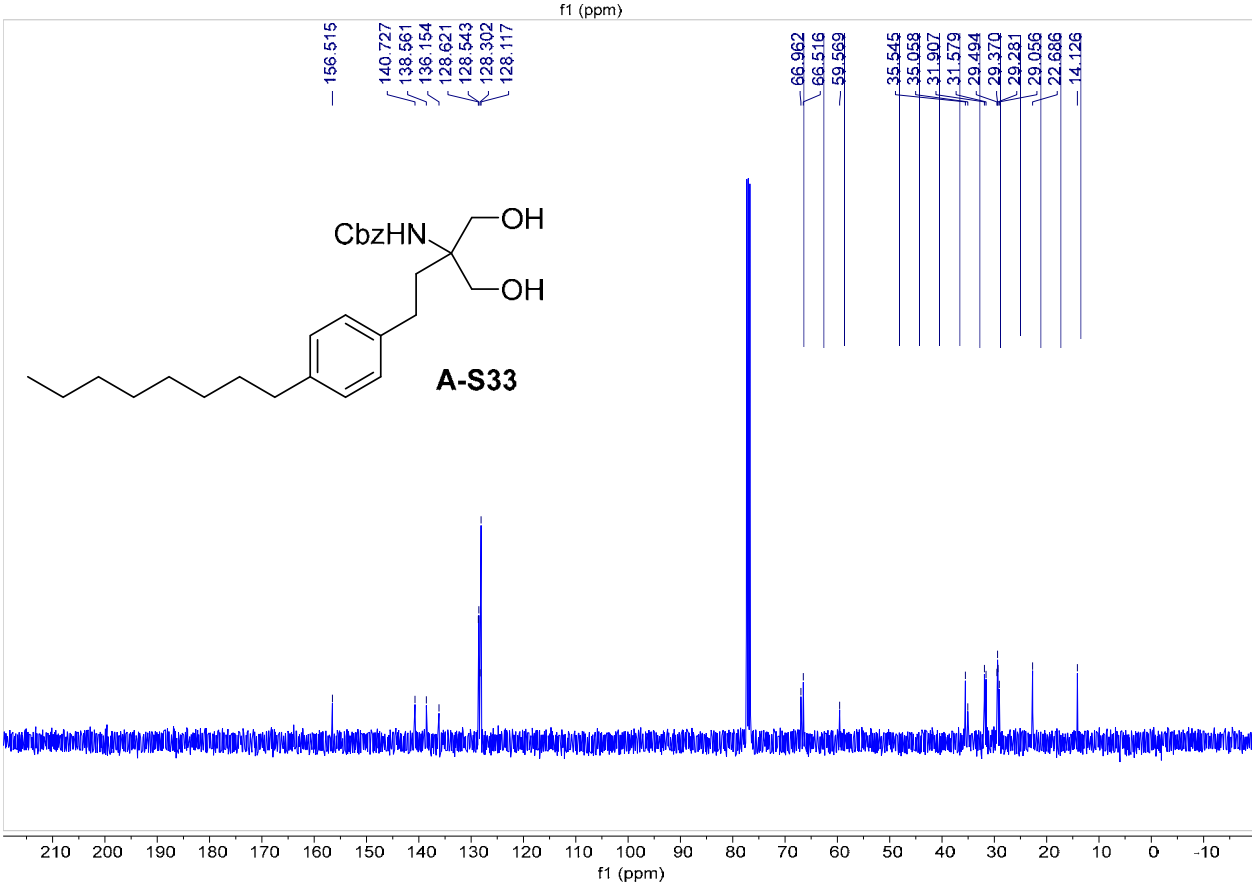
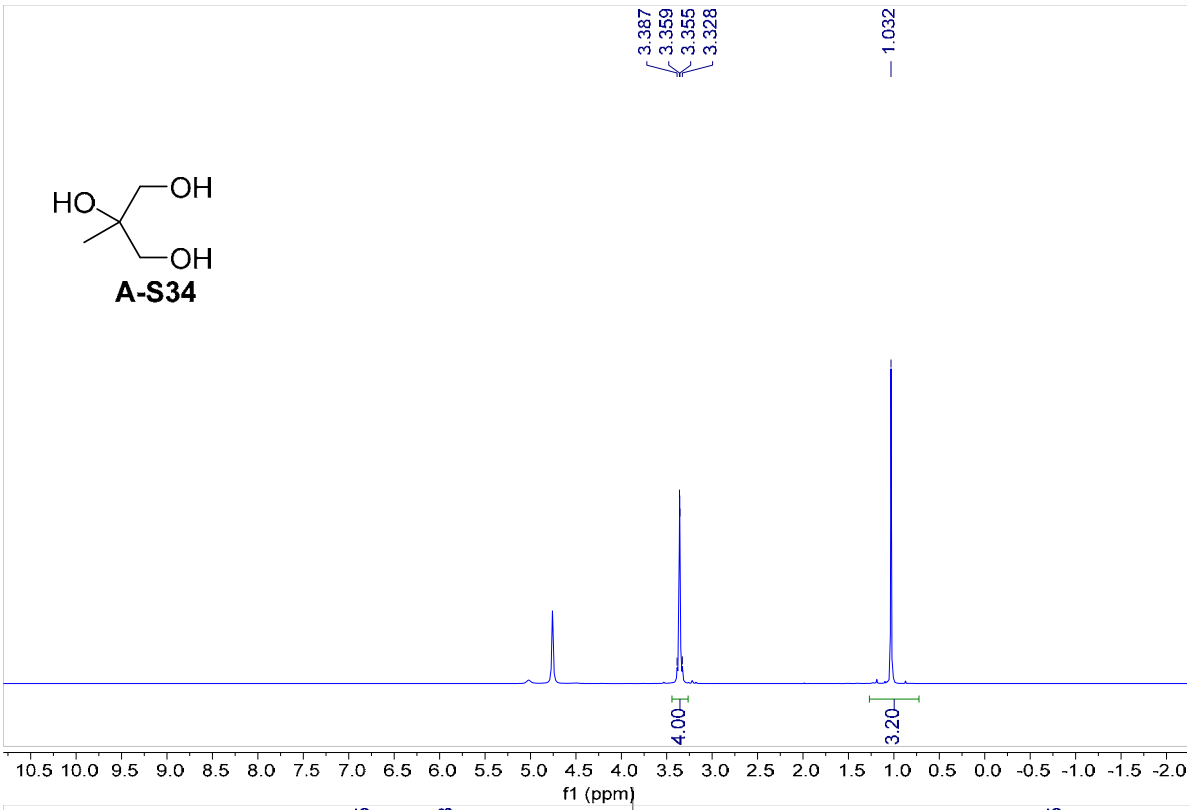
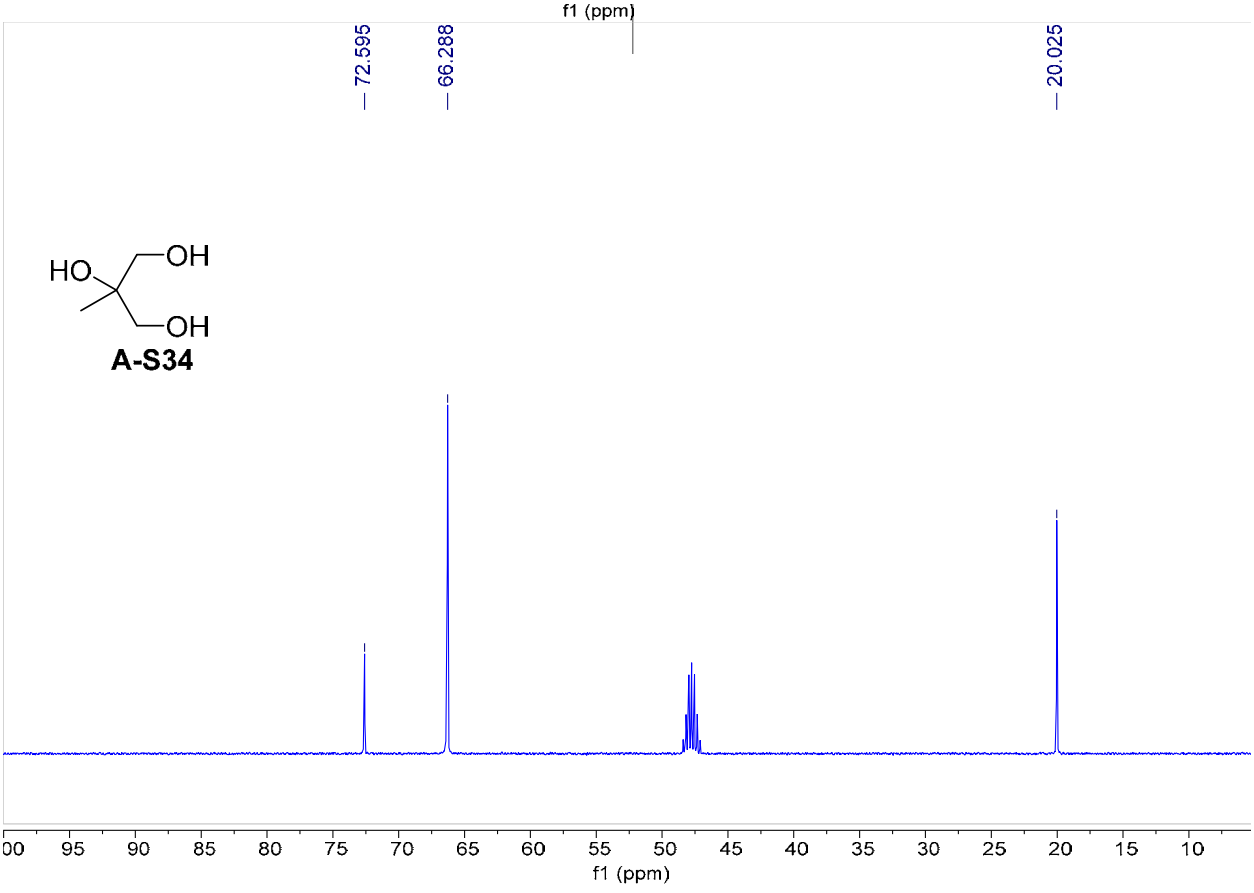
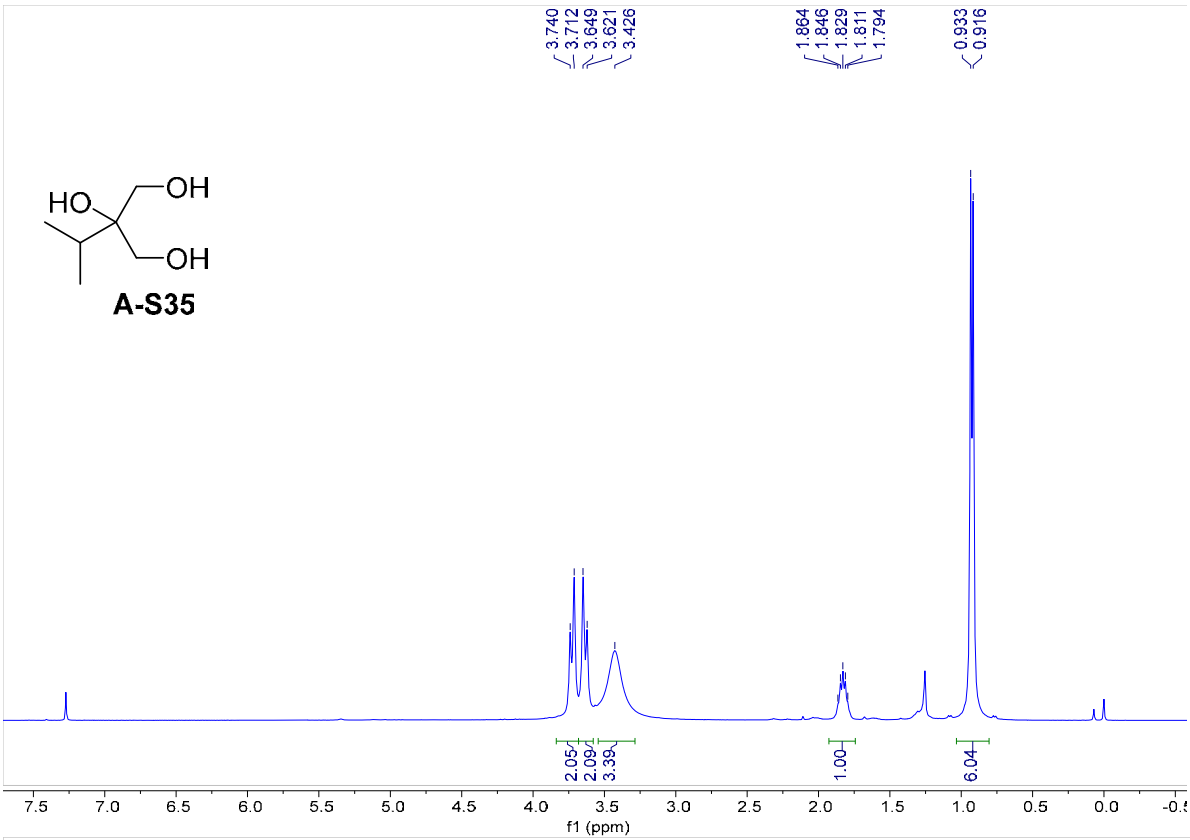
67.042
65.958
58.573
54.306
CbzHN
OH
OH
N
N
NBn
A-S32
f1 (ppm)

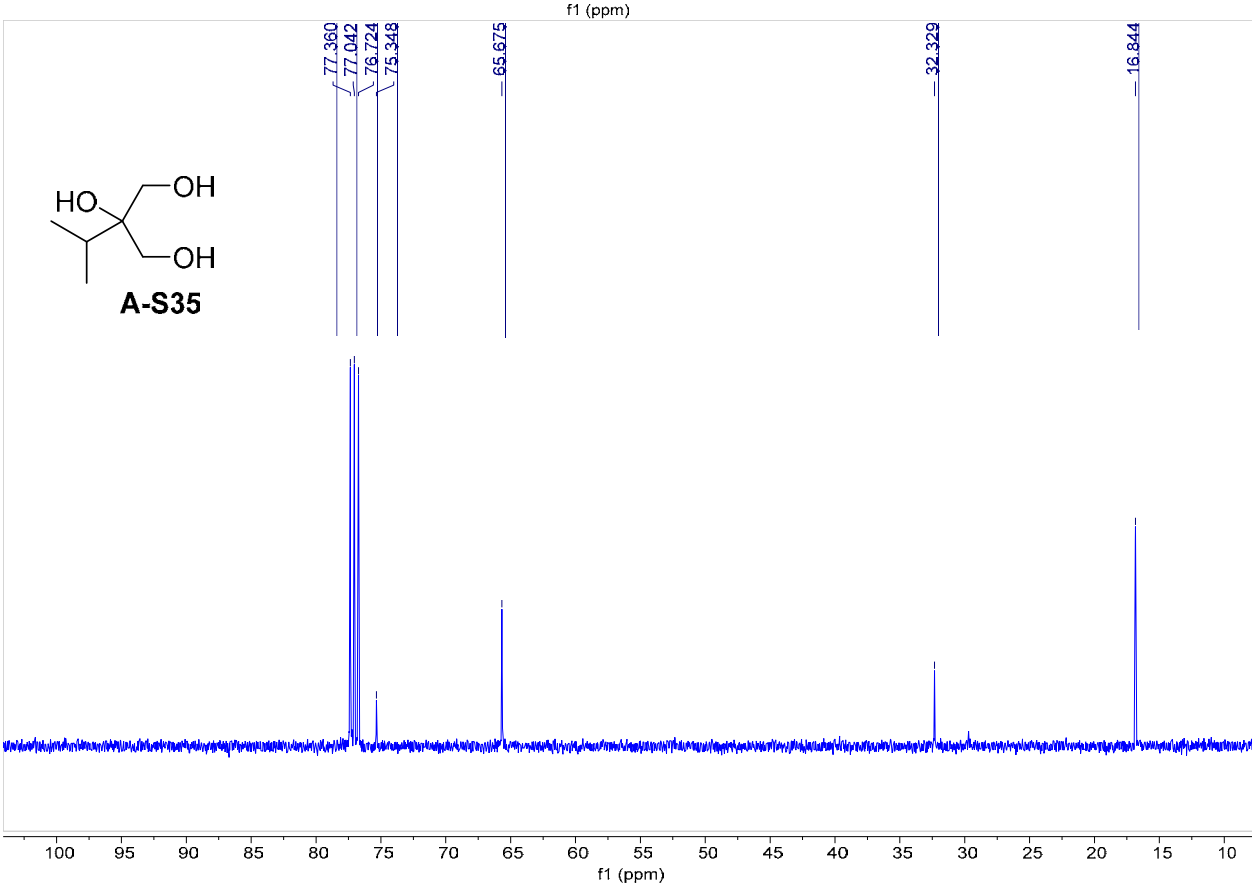

7.358
7.067
5.316
5.084
3.915
3.887
3.684
3.668
3.646
3.294
2.588
2.567
2.546
2.525
1.908
1.887
1.866
1.570
1.289
1.258
0.891
0.875
0.858
CbzHN
OH
OH
A-S33
5.00
4.02
0.95
2.02
2.03
2.05
1.86
4.10
1.96
2.21
10.30
3.10
f1 (ppm)

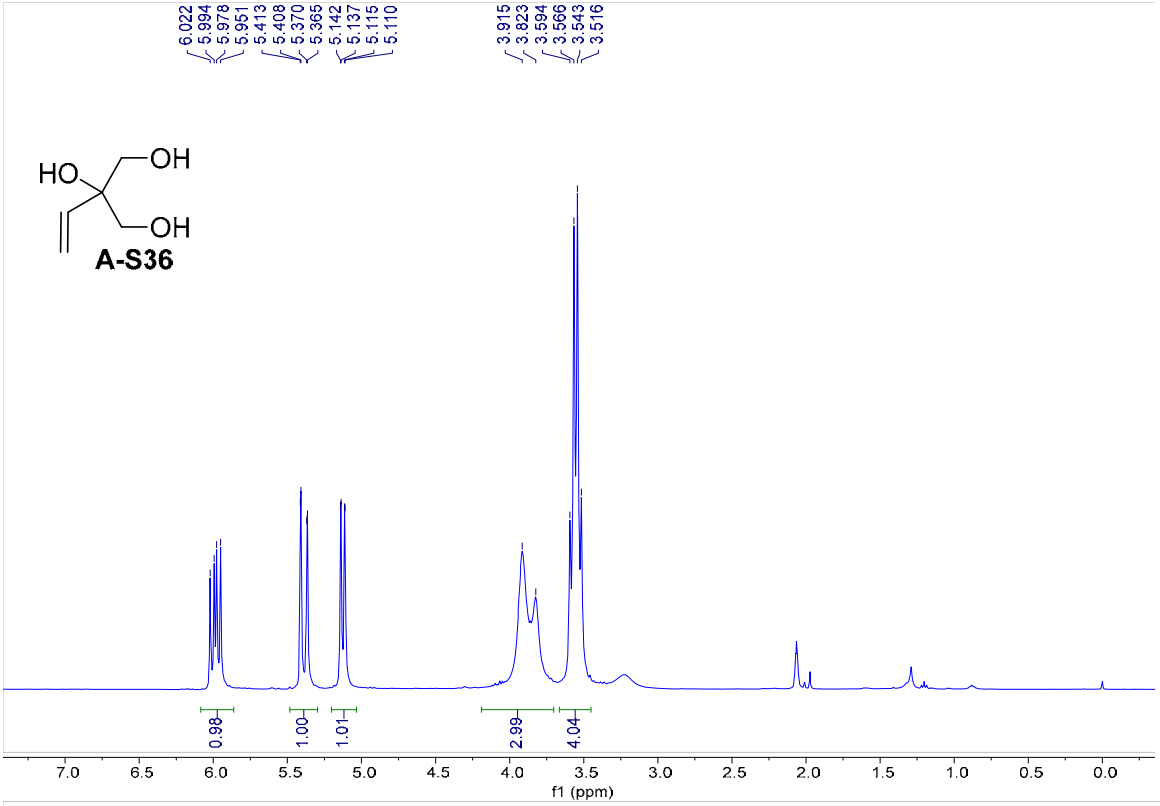

156.515
140.727
138.561
136.154
128.621
128.543
128.302
128.117
66.962
66.516
59.569
35.545
35.058
31.907
31.579
29.494
29.370
29.281
29.056
22.686
14.126
CbzHN
OH
OH
A-S33
f1 (ppm)

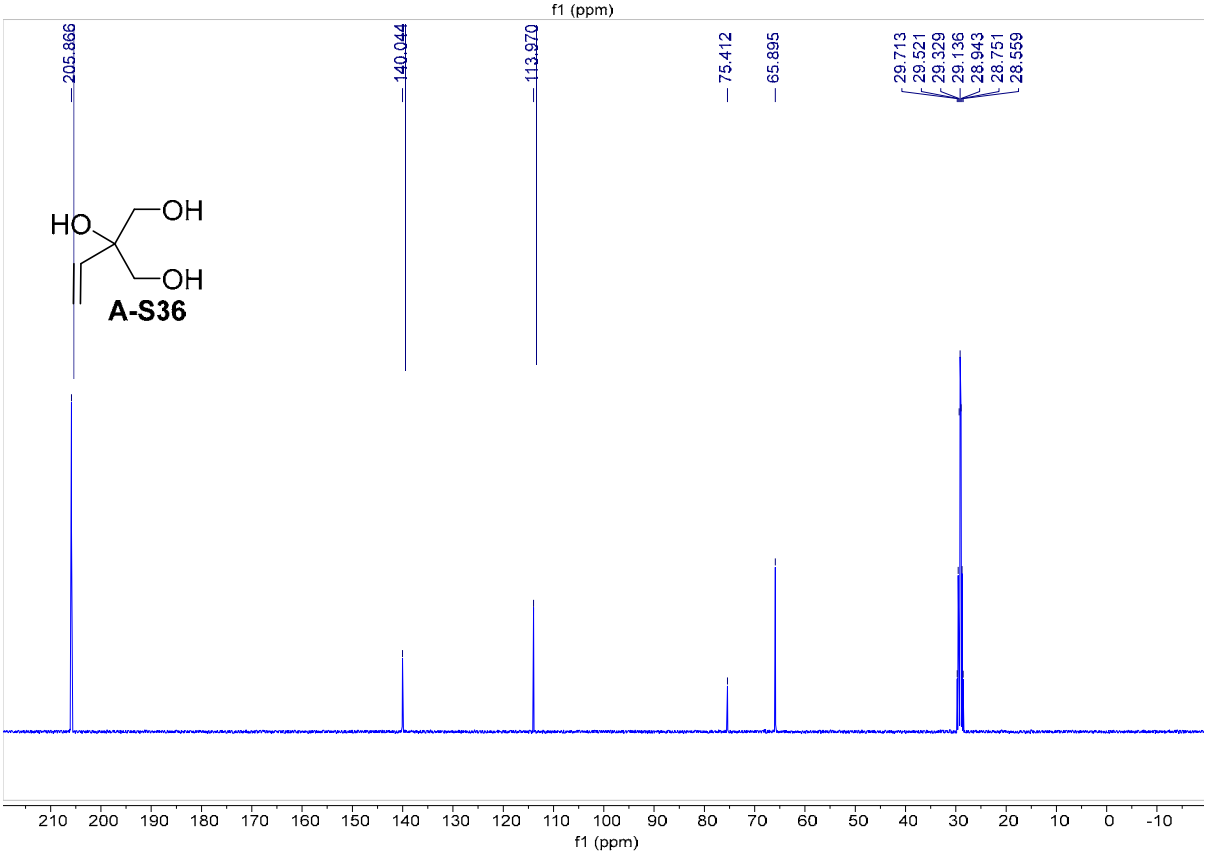

3.387
3.359
3.355
3.328
1.032
HO
OH
OH
A-S34
4.00
3.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

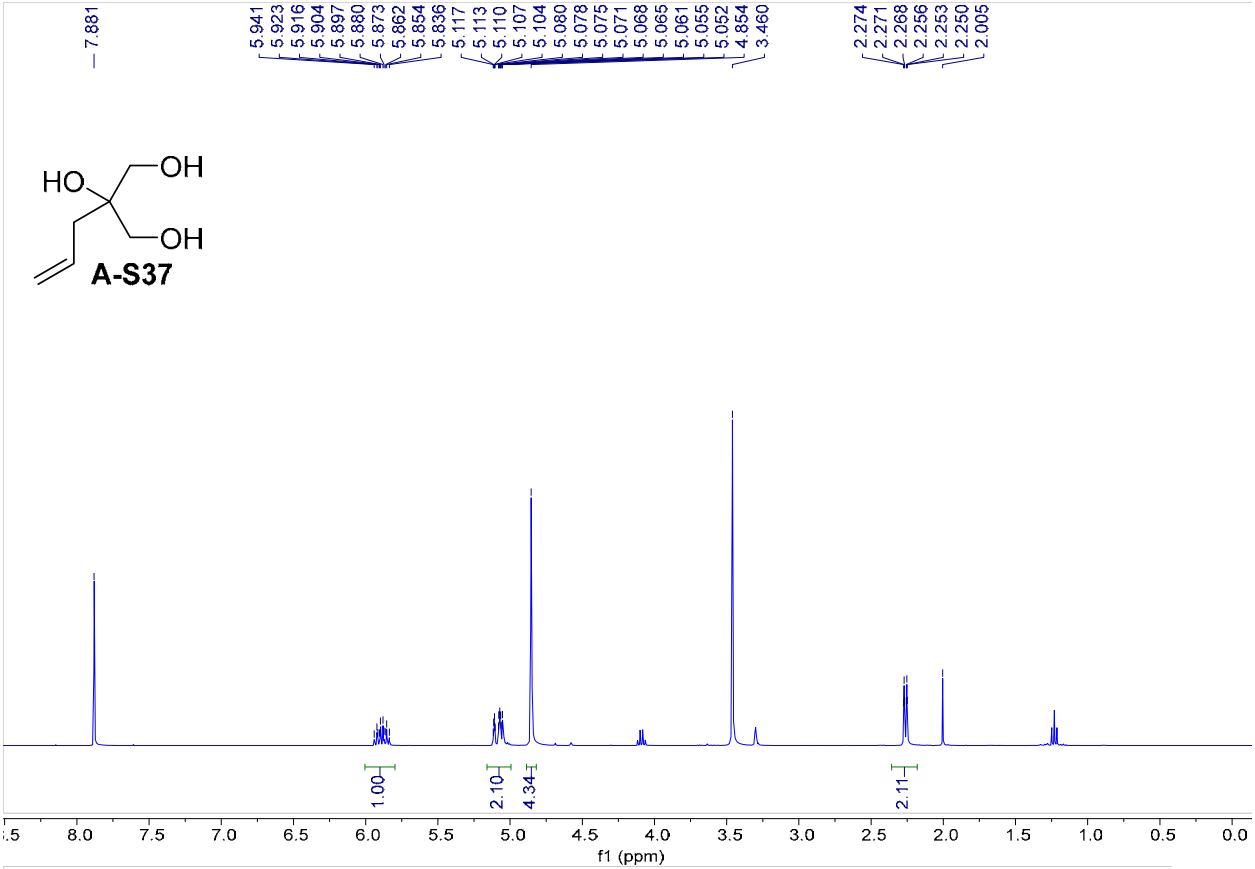

72.595
66.288
20.025
HO
OH
OH
A-S34
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

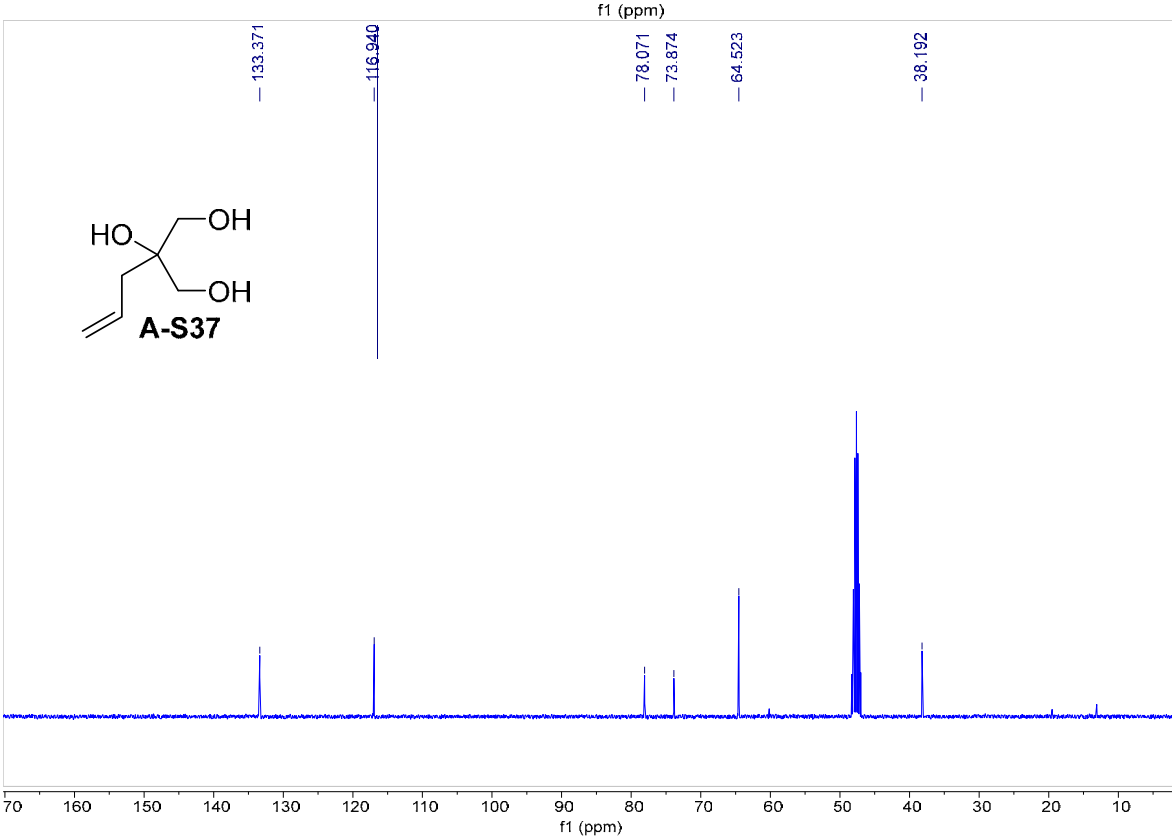

3.740
3.712
3.649
3.621
3.426
1.864
1.846
1.829
1.811
1.794
0.933
0.916
HO
OH
OH
A-S35
2.05
2.09
3.39
1.00
6.04
f1 (ppm)

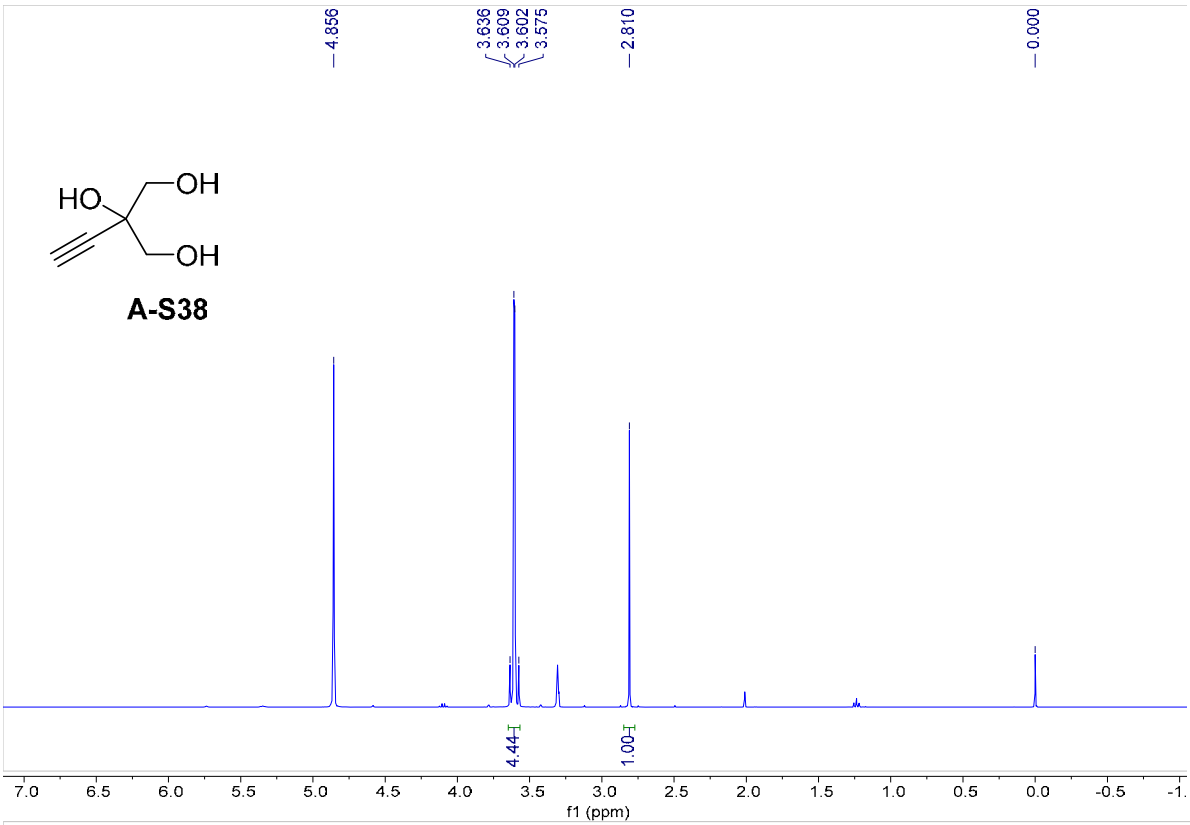

77.360
77.042
76.724
75.348
65.675
32.329
18.844
HO
OH
OH
A-S35
f1 (ppm)

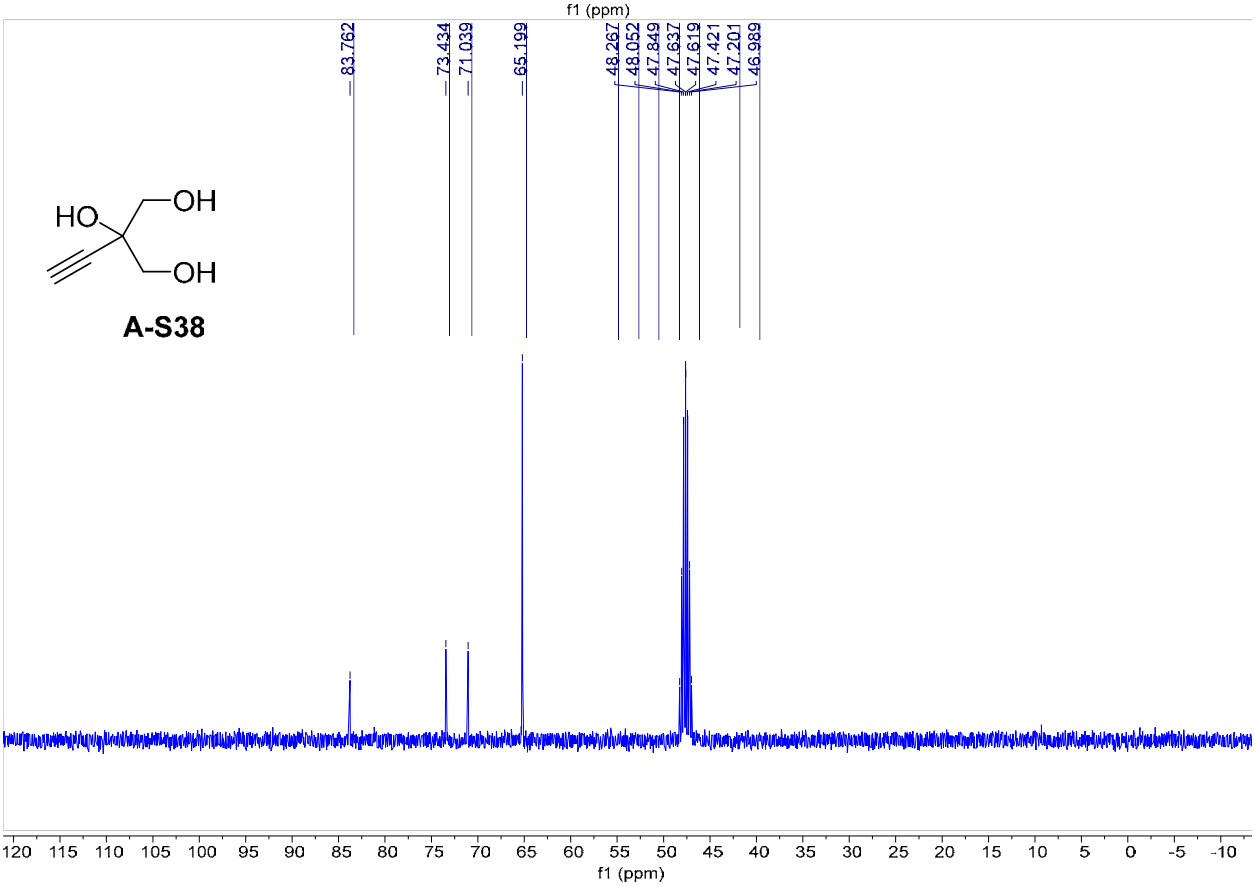

6.022
5.994
5.978
5.951
5.413
5.408
5.370
5.365
5.142
5.137
5.115
5.110
3.915
3.823
3.594
3.566
3.543
3.516
HO
OH
OH
A-S36
0.98
1.00
1.01
2.99
4.04
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

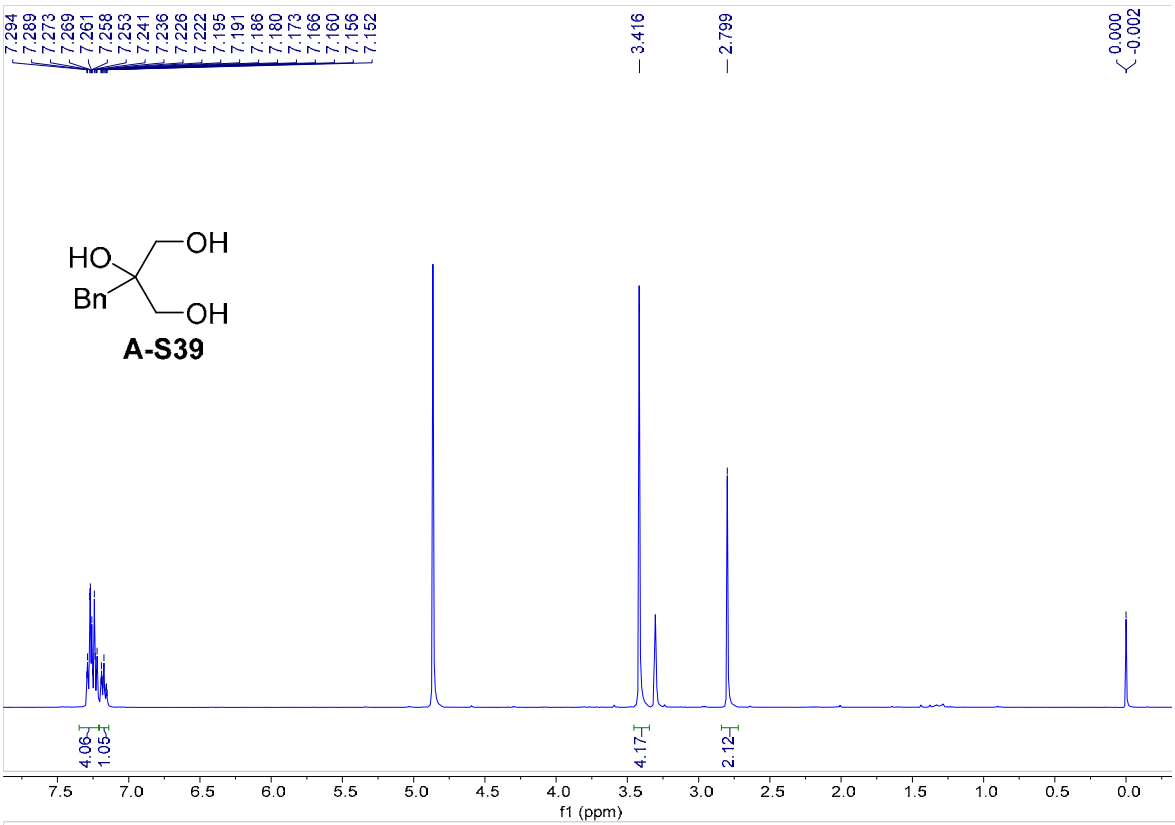

205.866
140.044
113.970
75.412
65.895
29.713
29.521
29.329
29.136
28.943
28.751
28.559
HO
OH
OH
A-S36
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

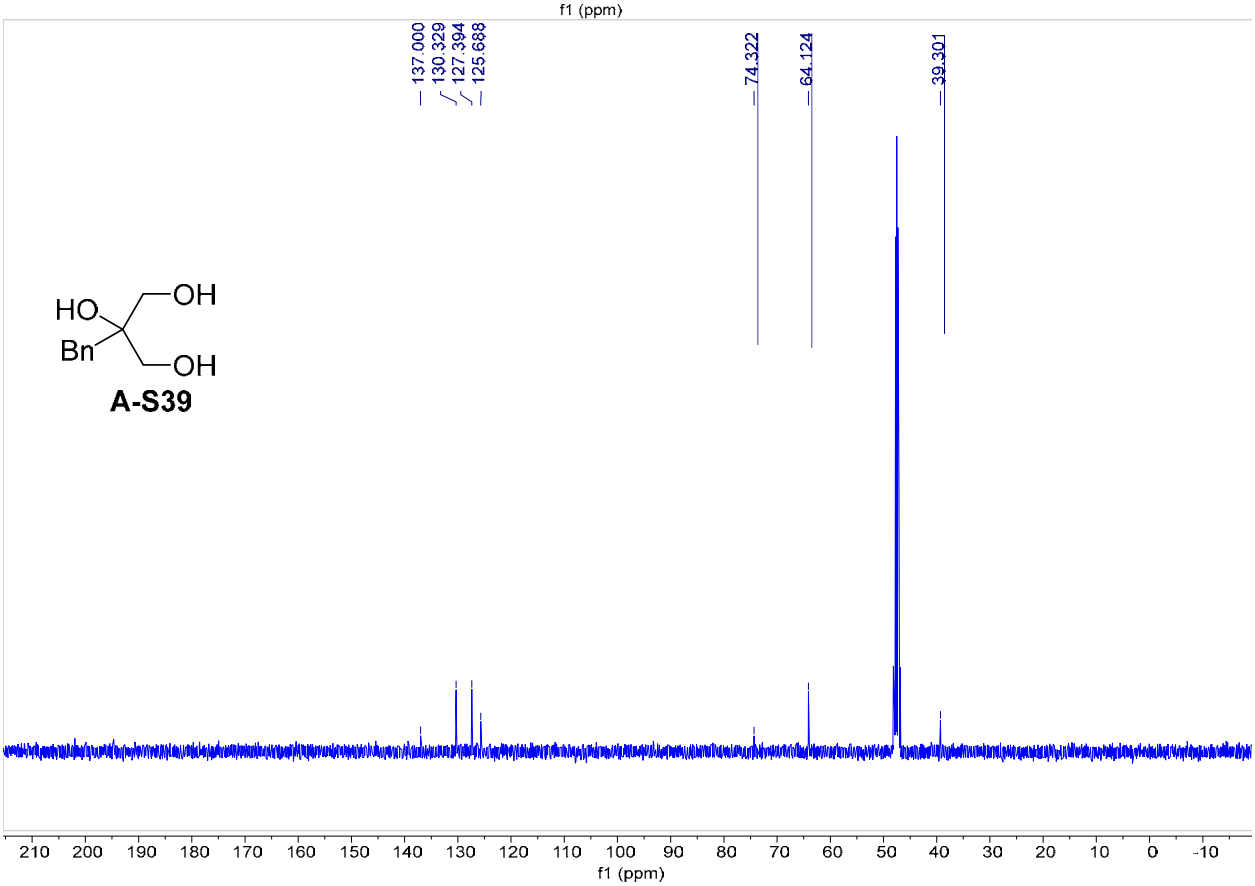

7.881
5.941
5.923
5.916
5.904
5.897
5.880
5.873
5.862
5.854
5.836
5.117
5.113
5.110
5.107
5.104
5.080
5.078
5.075
5.071
5.068
5.065
5.061
5.055
5.052
4.854
3.460
2.274
2.271
2.268
2.256
2.253
2.250
2.005
HO
OH
OH
A-S37
1.00
2.10
4.34
2.11
f1 (ppm)

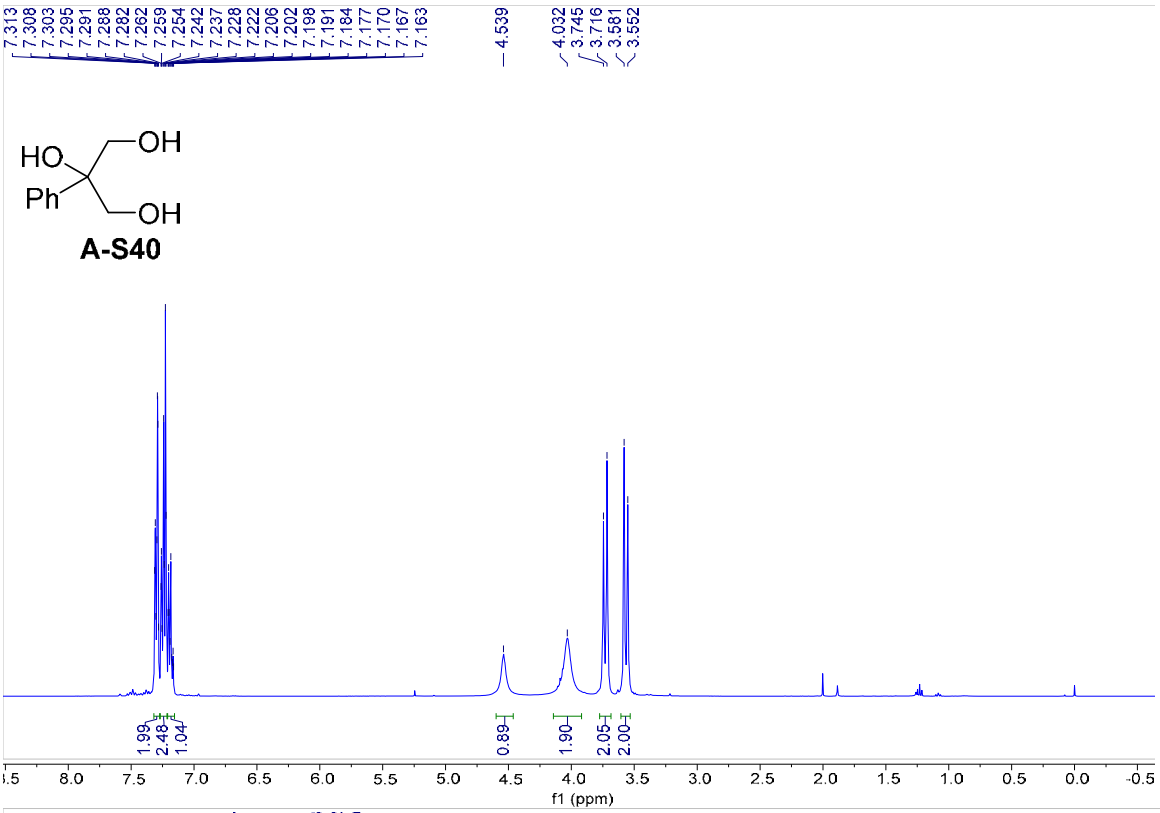

133.371
116.940
78.071
73.874
64.523
38.192
HO
OH
OH
A-S37
f1 (ppm)

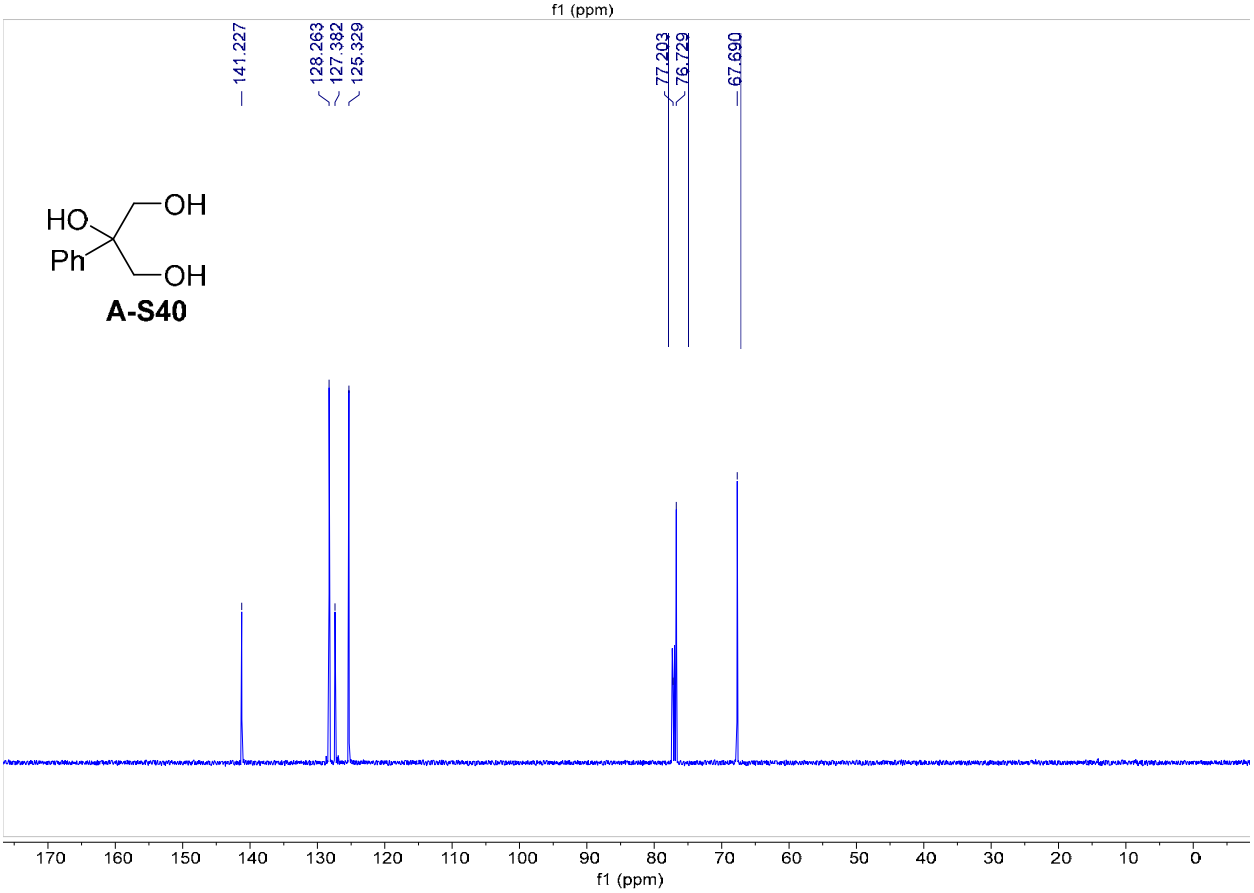

4.856
3.636
3.609
3.602
3.575
2.810
0.000
HO
OH
OH
A-S38
4.44
1.00
f1 (ppm)

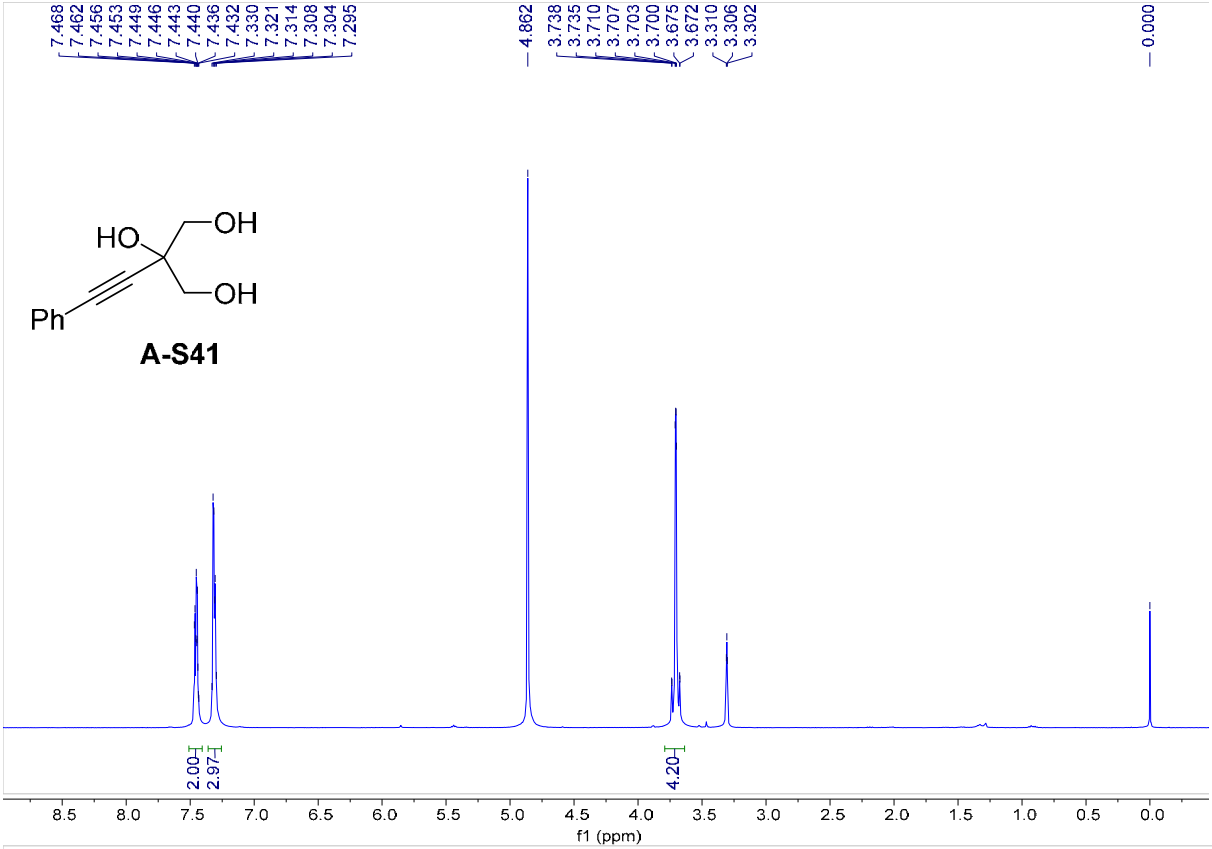

83.762
73.434
71.039
65.199
48.267
48.052
47.849
47.637
47.619
47.421
47.201
46.989
HO
OH
OH
A-S38
f1 (ppm)

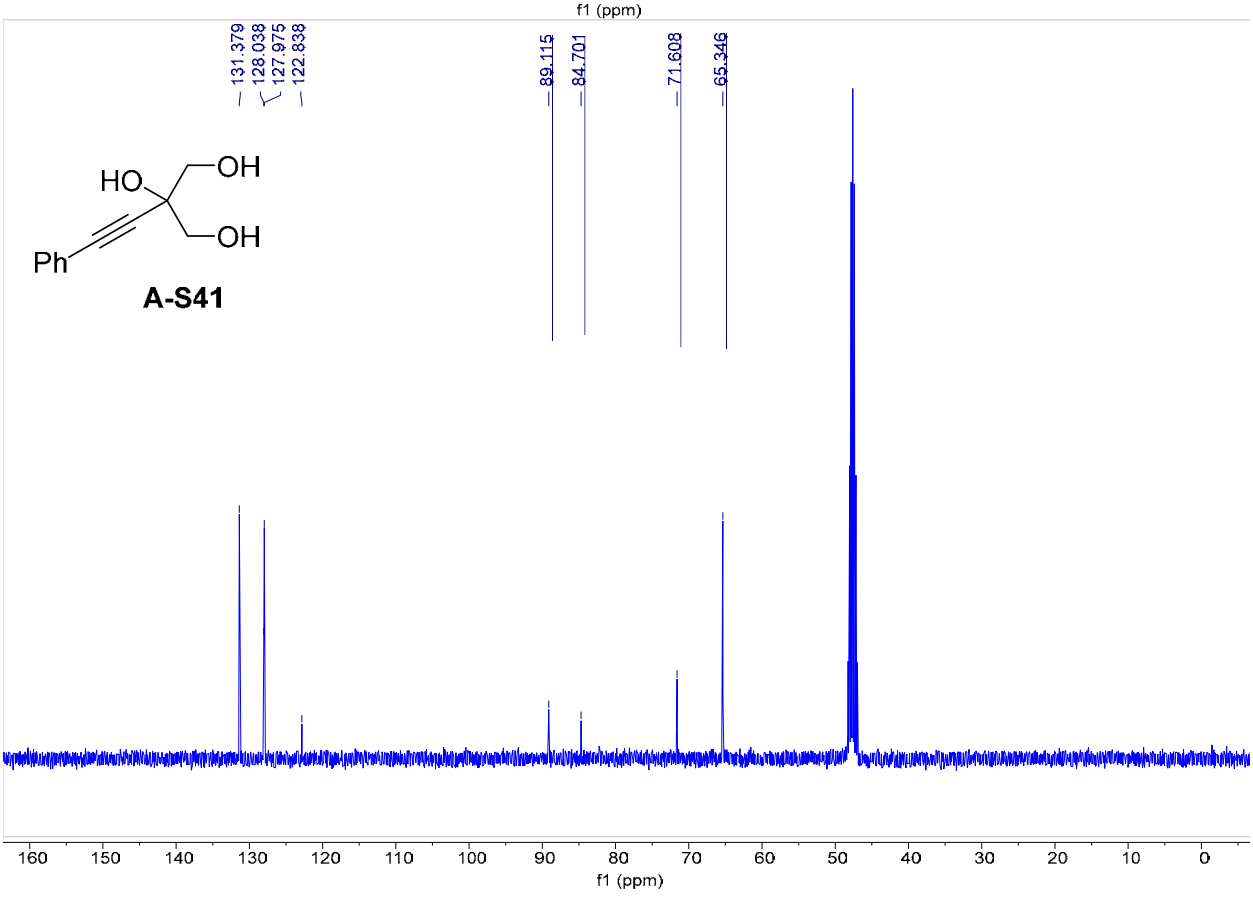

7.294
7.289
7.273
7.269
7.261
7.258
7.253
7.241
7.236
7.226
7.222
7.195
7.191
7.186
7.180
7.173
7.166
7.160
7.156
7.152
3.416
2.799
0.000
-0.002
HO
OH
Bn
OH
A-S39
4.06
1.05
4.17
2.12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

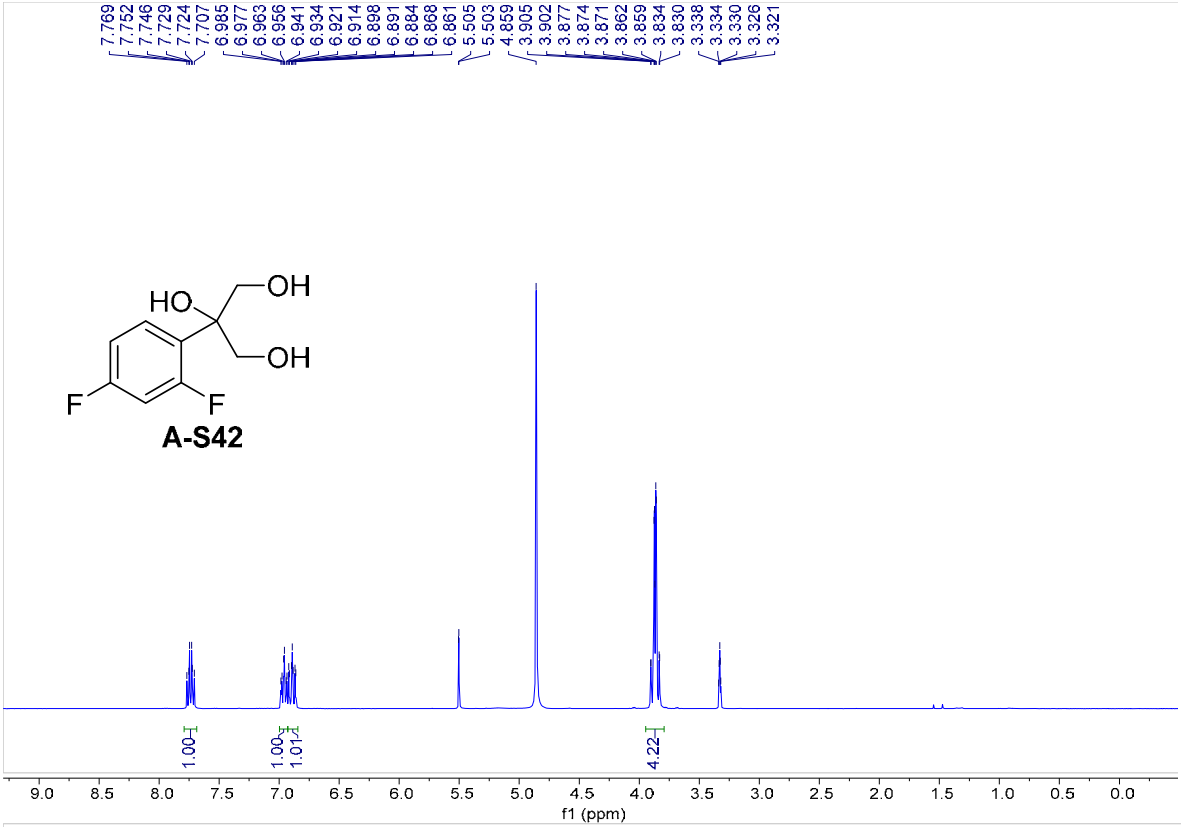

137.000
130.329
127.394
125.688
74.322
64.124
39.301
HO
OH
Bn
OH
A-S39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

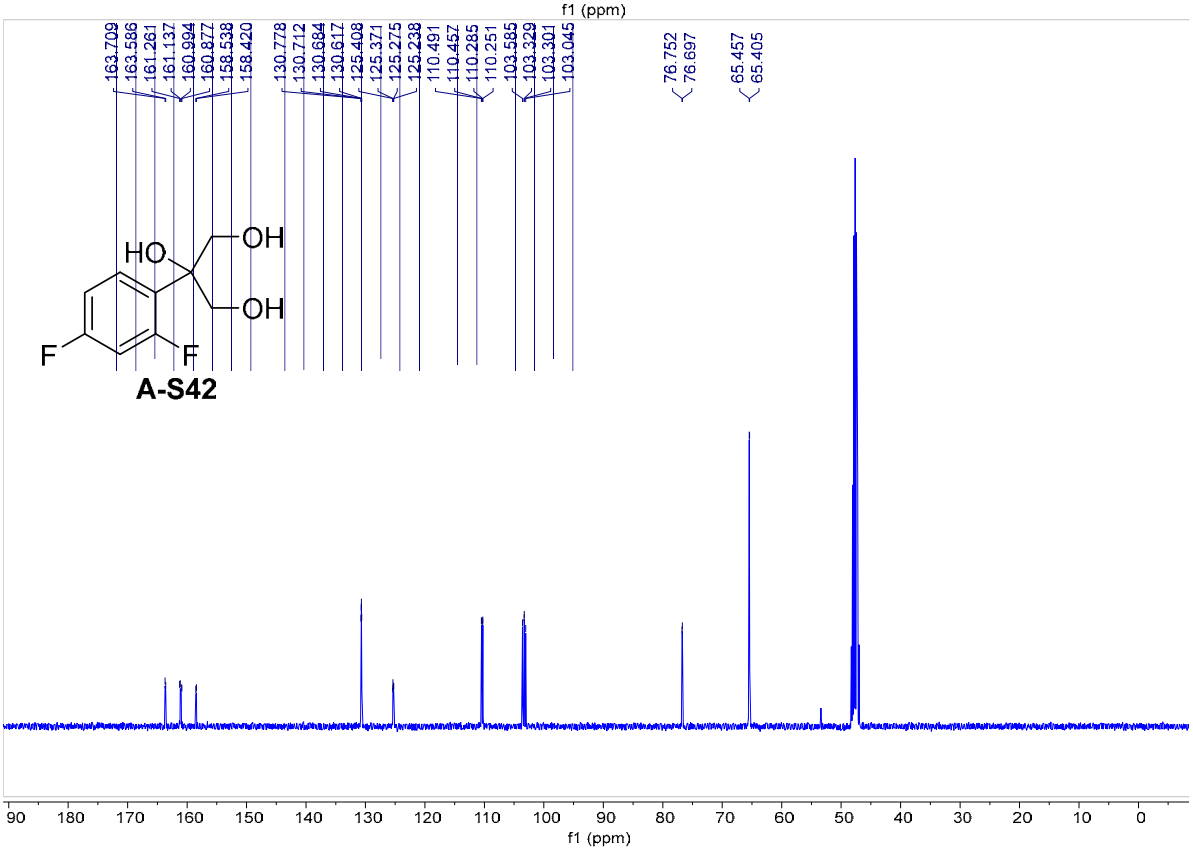

7.313
7.308
7.303
7.295
7.291
7.288
7.282
7.262
7.259
7.254
7.242
7.237
7.228
7.222
7.206
7.202
7.198
7.191
7.184
7.177
7.170
7.167
7.163
4.539
4.032
3.745
3.716
3.581
3.552
HO
OH
Ph
OH
A-S40
1.99
2.48
1.04
0.89
1.90
2.05
2.00
f1 (ppm)

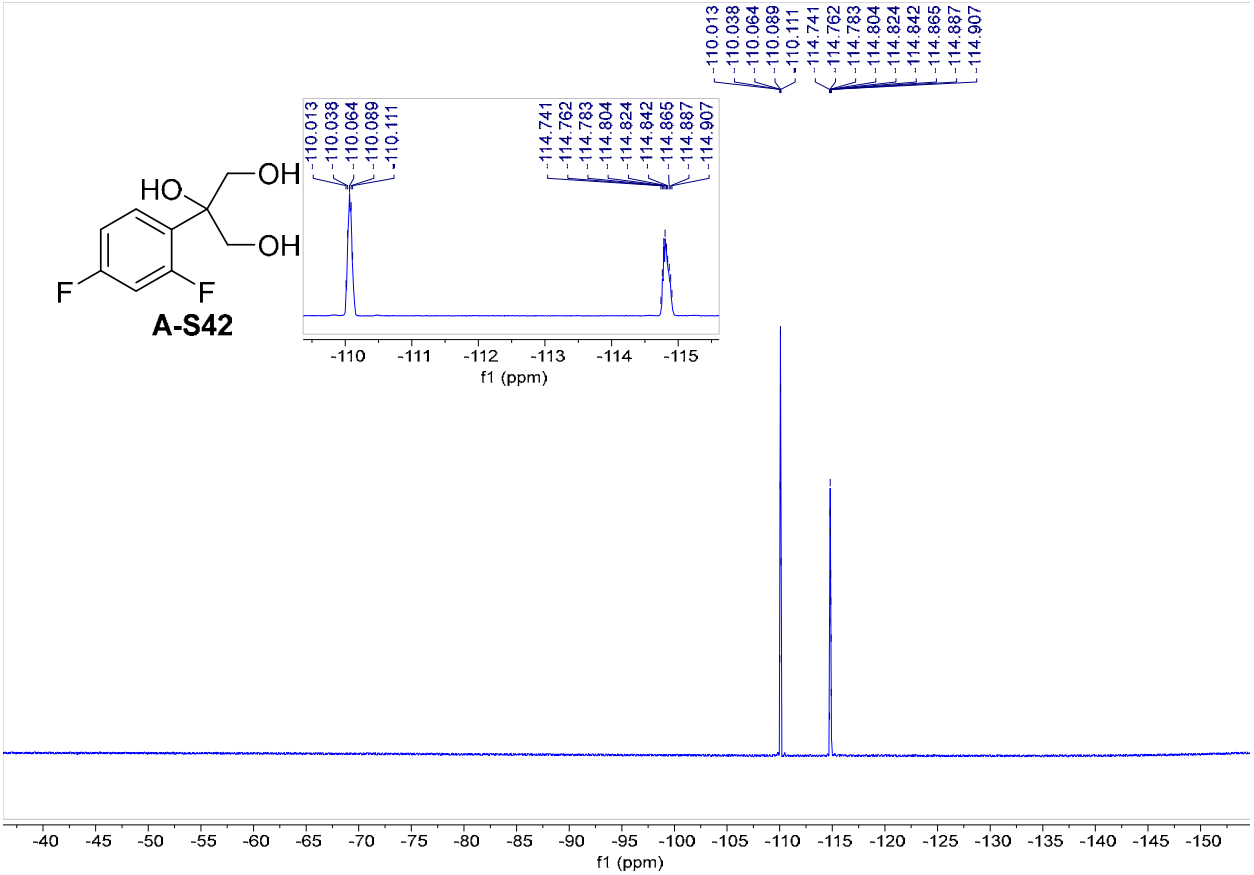

141.227
128.263
127.382
125.329
77.203
76.729
67.690
HO
OH
Ph
OH
A-S40
f1 (ppm)

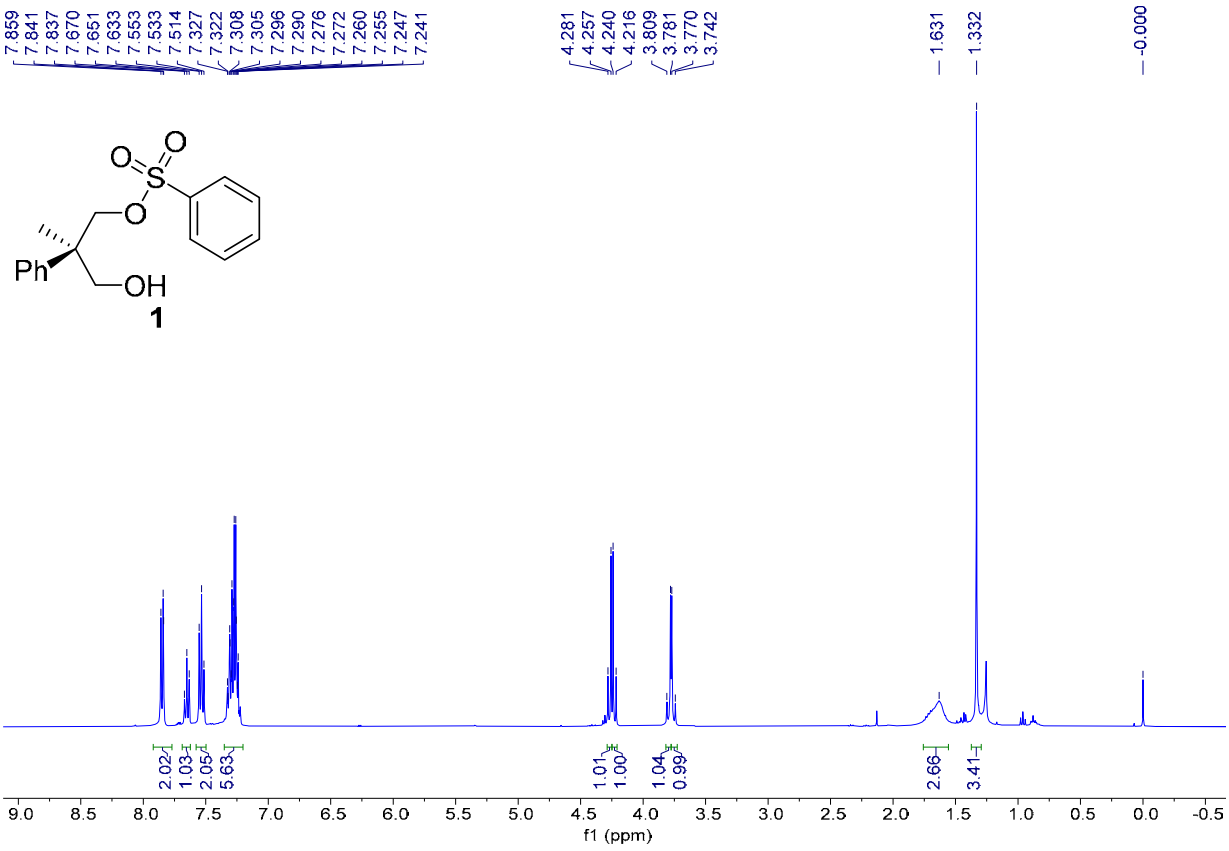

7.468
7.462
7.456
7.453
7.449
7.446
7.443
7.440
7.436
7.432
7.330
7.321
7.314
7.308
7.304
7.295
4.862
3.738
3.735
3.710
3.707
3.703
3.700
3.675
3.672
3.310
3.306
3.302
0.000
HO
OH
OH
Ph
A-S41
2.00
2.97
4.20
f1 (ppm)

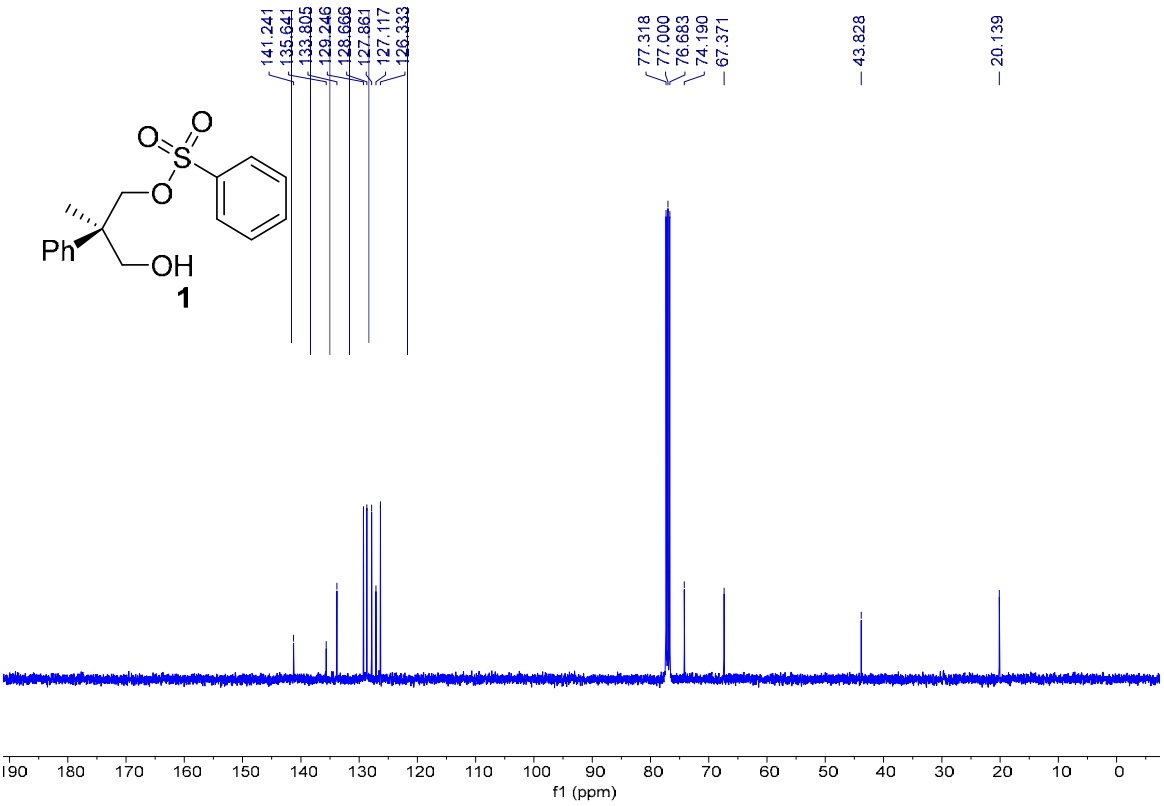

131.379
128.038
127.975
122.838
89.115
84.701
71.608
65.346
HO
OH
OH
Ph
A-S41
f1 (ppm)

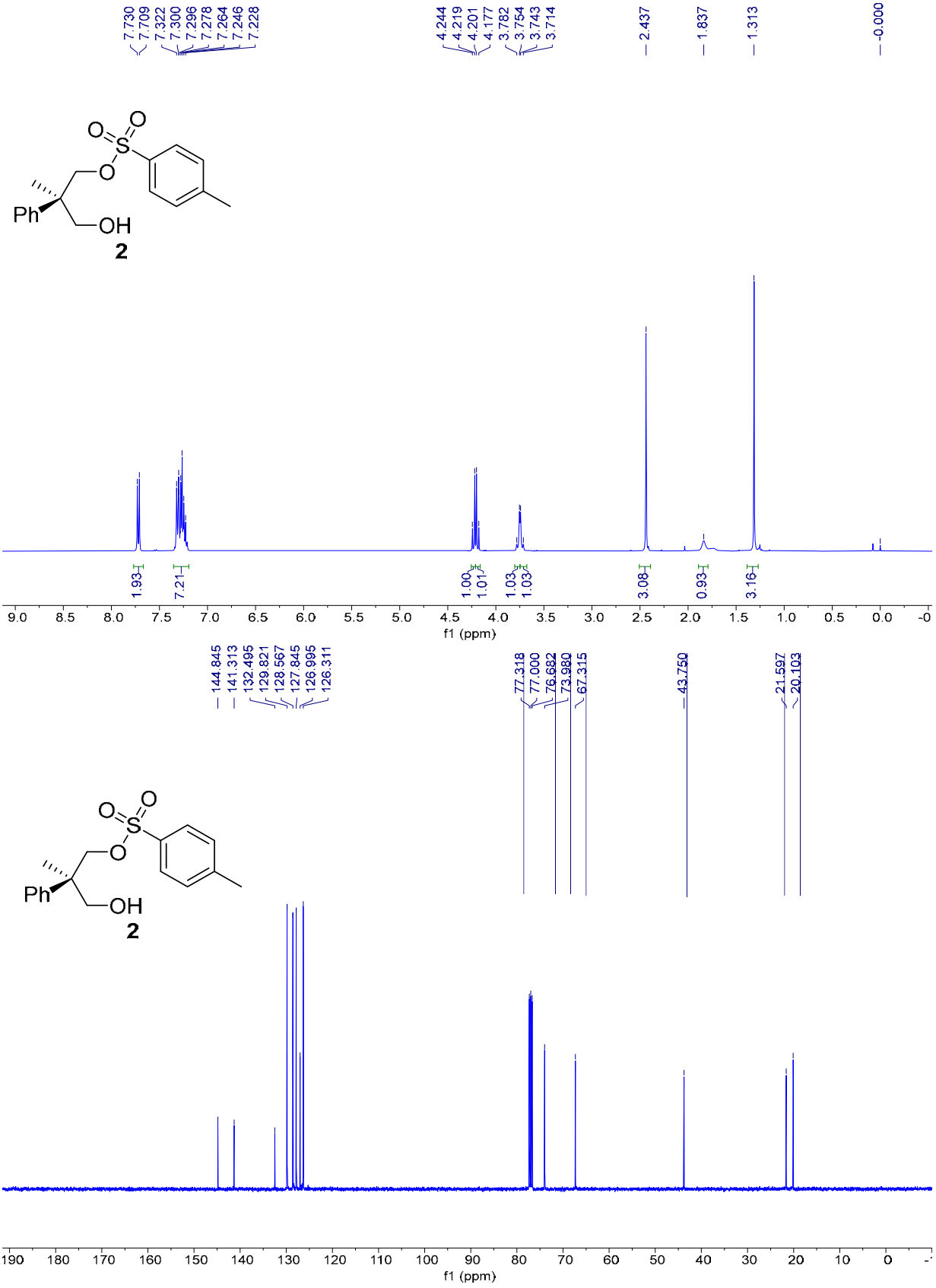

7.769
7.752
7.746
7.729
7.724
7.707
6.985
6.977
6.963
6.956
6.941
6.934
6.921
6.914
6.898
6.891
6.884
6.868
6.861
5.505
5.503
4.859
3.905
3.902
3.877
3.874
3.871
3.862
3.859
3.834
3.830
3.338
3.334
3.330
3.326
3.321
HO
OH
OH
F
F
A-S42
1.00
1.00
1.01
4.22
f1 (ppm)

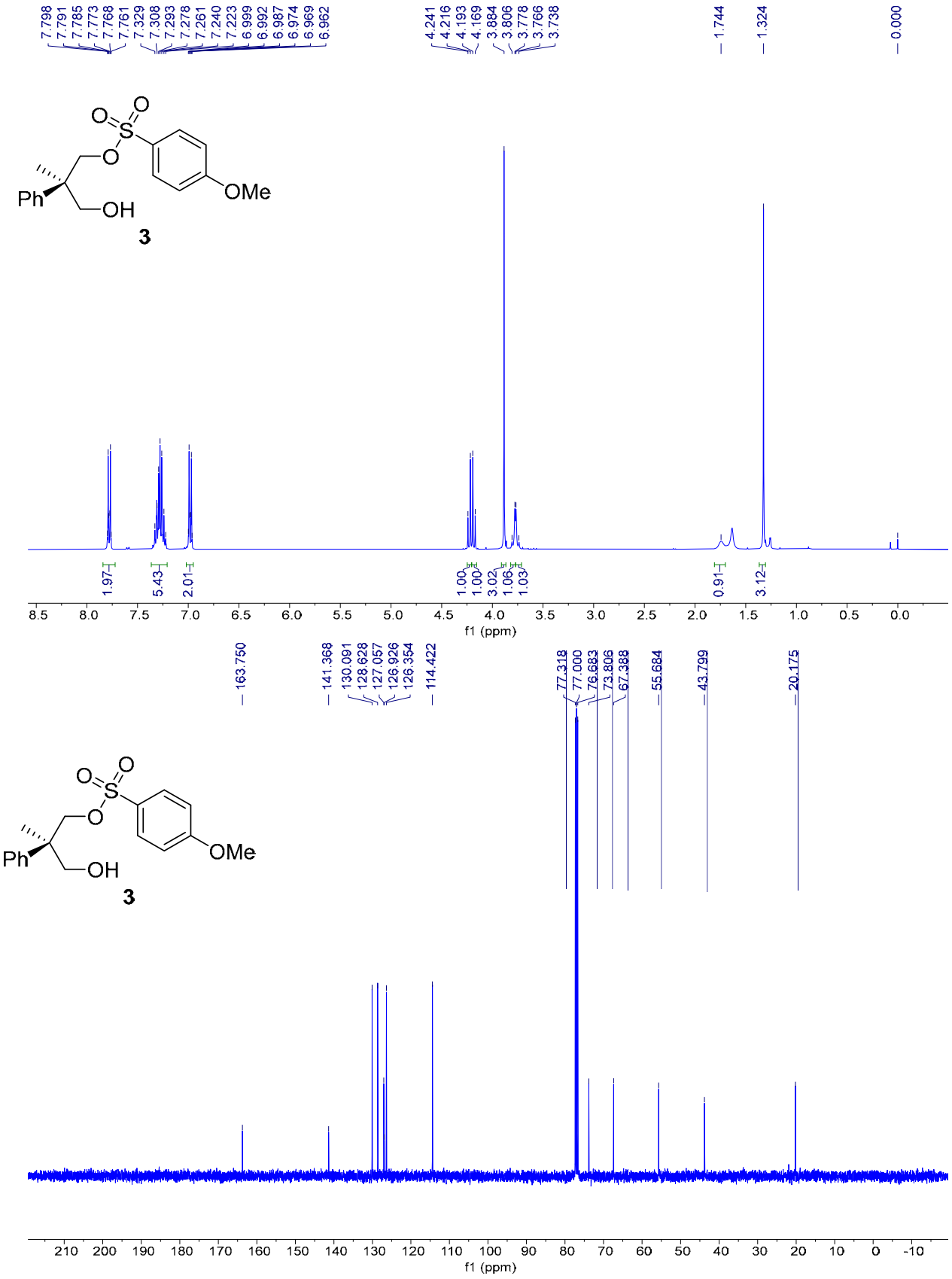

163.709
163.586
161.261
161.137
160.994
160.877
158.538
158.420
130.778
130.712
130.684
130.617
125.408
125.371
125.275
125.238
110.491
110.457
110.285
110.251
103.585
103.329
103.301
103.045
76.752
76.697
65.457
65.405
HO
OH
OH
F
F
A-S42
f1 (ppm)

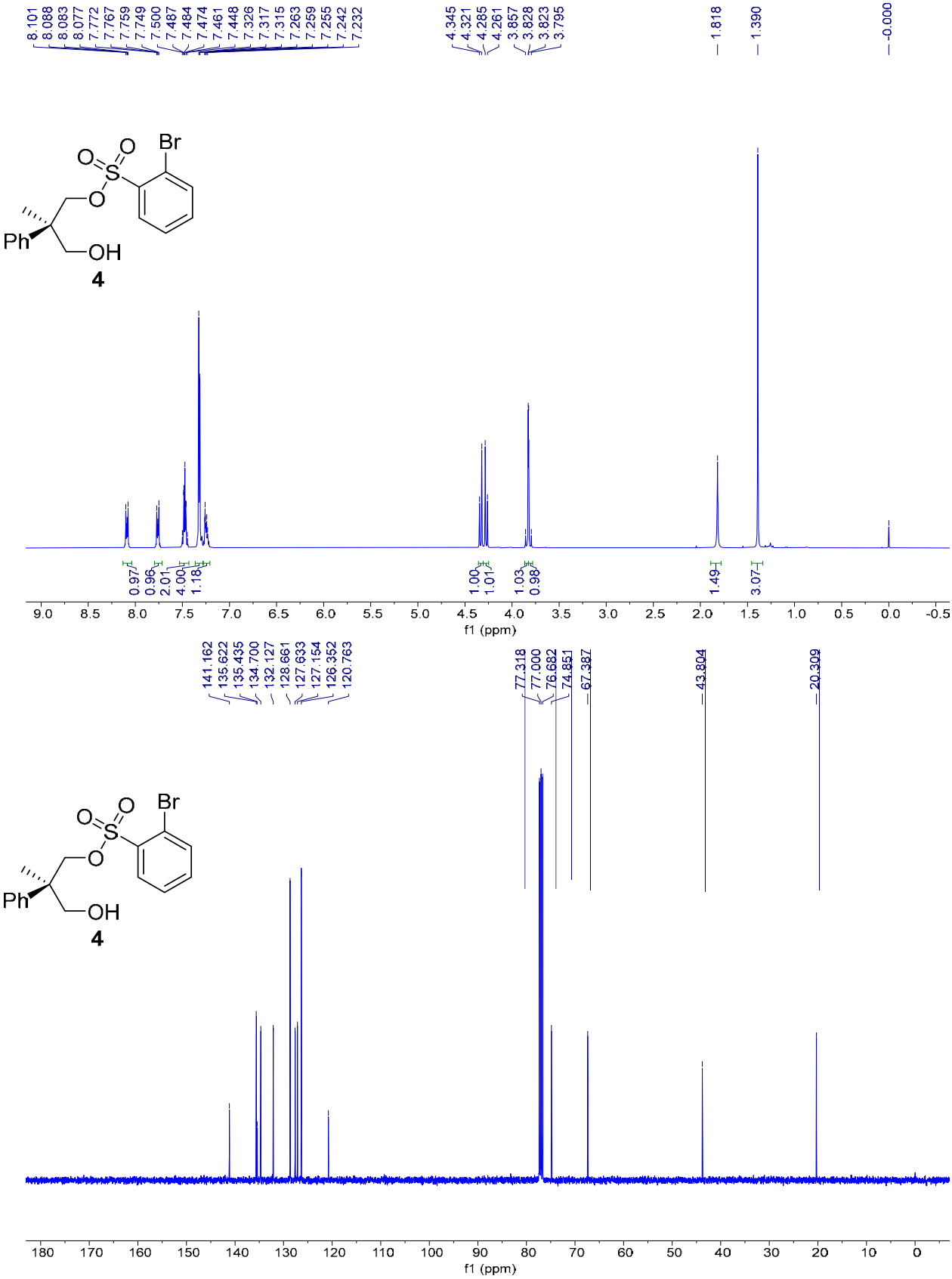

-110.013
-110.038
-110.064
-110.089
-110.111
-114.741
-114.762
-114.783
-114.804
-114.824
-114.842
-114.865
-114.887
-114.907
HO
OH
OH
F
F
A-S42
-110
-111
-112
-113
-114
-115
f1 (ppm)
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)

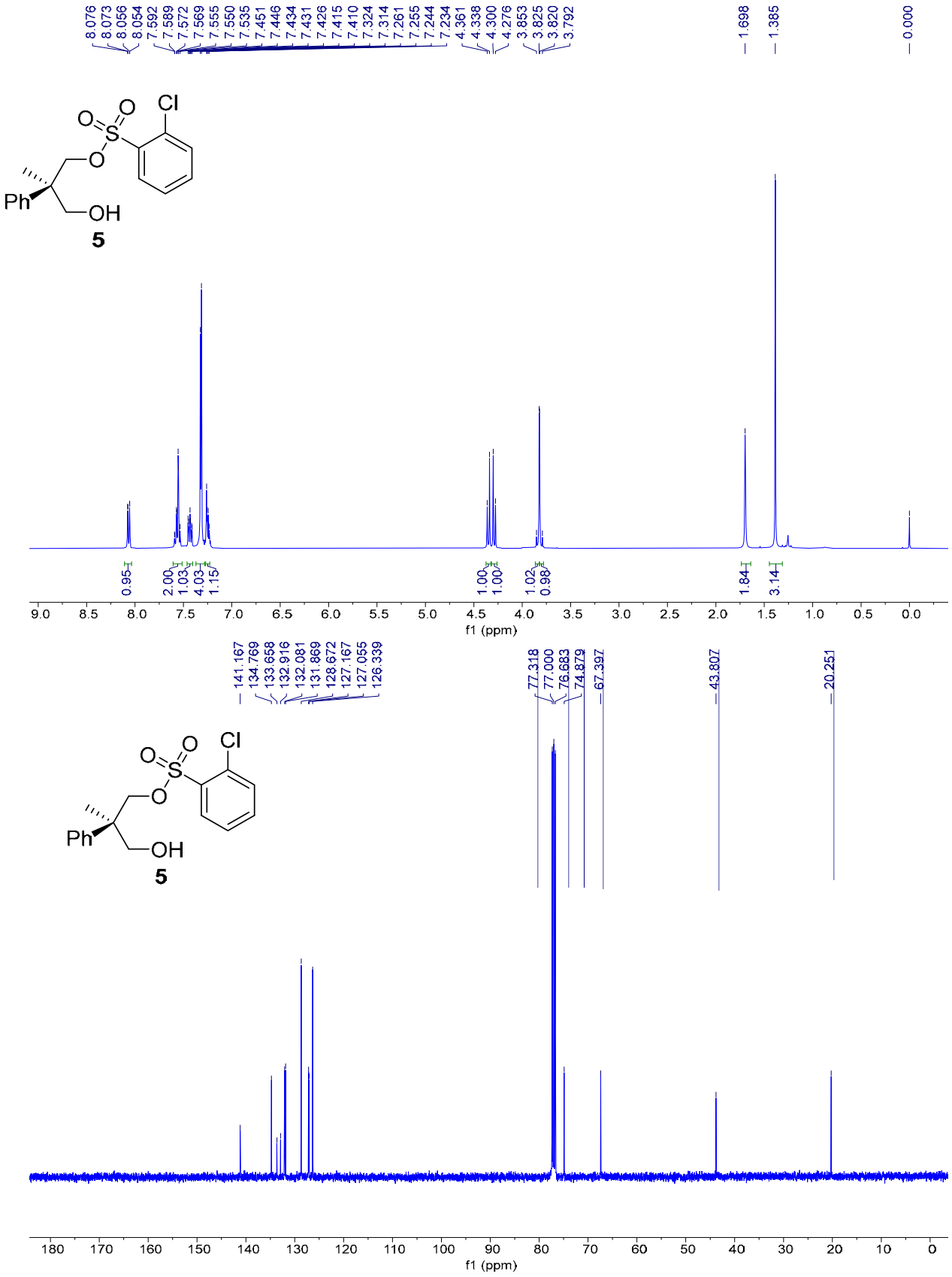

7.859
7.841
7.837
7.670
7.651
7.633
7.553
7.533
7.514
7.327
7.322
7.308
7.305
7.296
7.290
7.276
7.272
7.260
7.255
7.247
7.241
4.281
4.257
4.240
4.216
3.809
3.781
3.770
3.742
1.631
1.332
-0.000
Ph
OH
1
2.02
1.03
2.05
5.63
1.01
1.00
1.04
0.99
2.66
3.41
f1 (ppm)


141.241
135.641
133.805
129.246
128.666
127.861
127.117
126.333
77.318
77.000
76.683
74.190
67.371
43.828
20.139
Ph
OH
1
f1 (ppm)


7.730
7.709
7.322
7.300
7.296
7.278
7.264
7.246
7.228
4.244
4.219
4.201
4.177
3.782
3.754
3.743
3.714
2.437
1.837
1.313
-0.000
O
O
S
O
Ph
OH
2
1.93
7.21
1.00
1.01
1.03
1.03
3.08
0.93
3.16
f1 (ppm)
144.845
141.313
132.495
129.821
128.567
127.845
126.995
126.311
77.318
77.000
76.682
73.980
67.315
43.750
21.597
20.103
f1 (ppm)


7.798
7.791
7.785
7.773
7.768
7.761
7.329
7.308
7.293
7.278
7.261
7.240
7.223
6.999
6.992
6.987
6.974
6.969
6.962
4.241
4.216
4.193
4.169
3.884
3.806
3.778
3.766
3.738
1.744
1.324
0.000
O
O
S
O
Ph
OH
OMe
3
1.97
5.43
2.01
1.00
1.00
3.02
1.06
1.03
0.91
3.12
f1 (ppm)
163.750
141.368
130.091
128.628
127.057
126.926
126.354
114.422
77.318
77.000
76.683
73.806
67.388
55.684
43.799
20.175
f1 (ppm)


8.101
8.088
8.083
8.077
7.772
7.767
7.759
7.749
7.500
7.487
7.484
7.474
7.461
7.448
7.326
7.317
7.315
7.263
7.259
7.255
7.242
7.232
4.345
4.321
4.285
4.261
3.857
3.828
3.823
3.795
1.818
1.390
-0.000
Br
O
O
S
O
Ph
OH
4
0.97
0.96
2.01
4.00
1.18
1.00
1.01
1.03
0.98
1.49
3.07
f1 (ppm)
141.162
135.622
135.435
134.700
132.127
128.661
127.633
127.154
126.352
120.763
77.318
77.000
76.682
74.851
67.387
43.804
20.309
f1 (ppm)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8.073
8.056
8.054
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7.589
7.572
7.569
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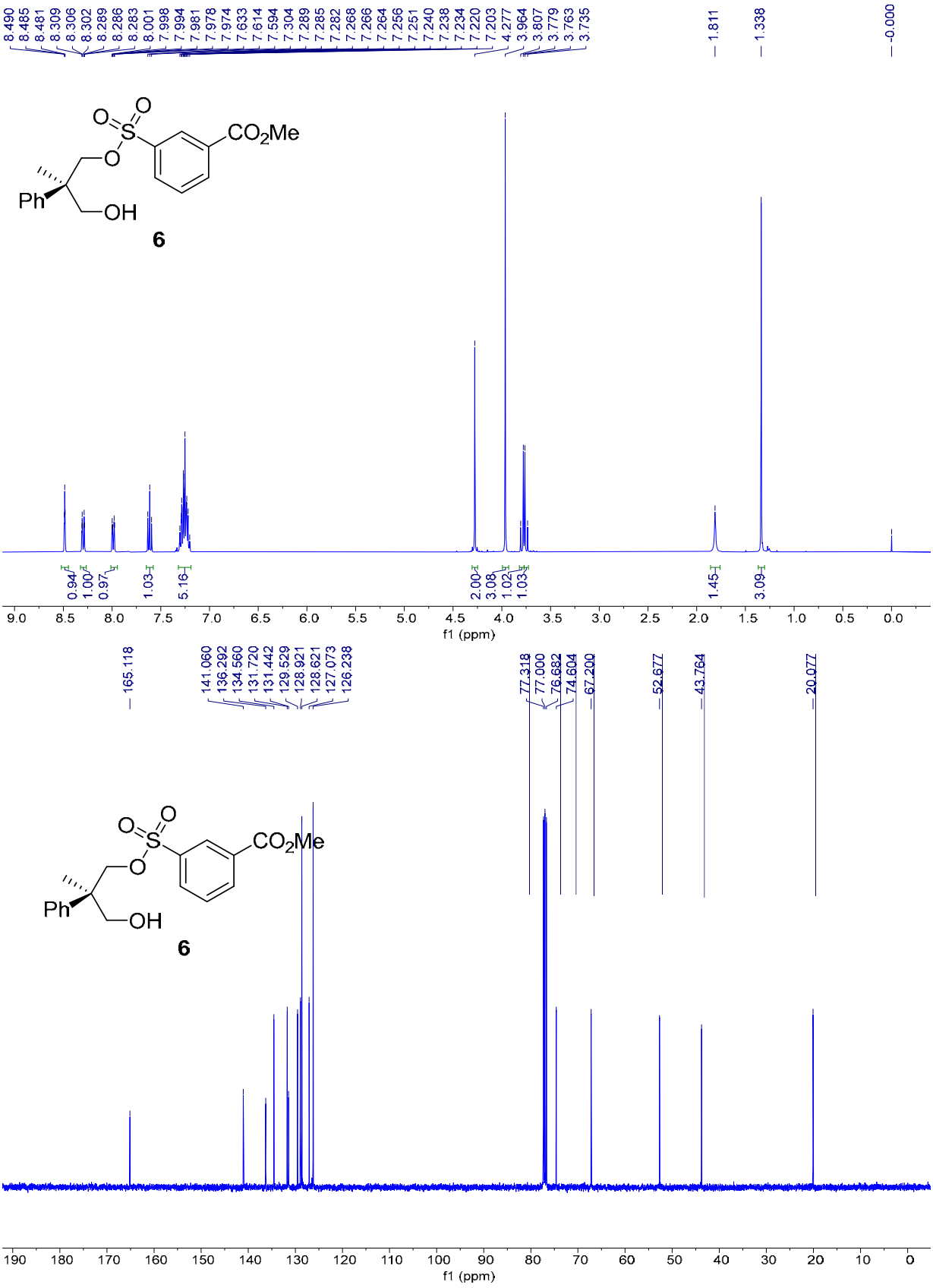
7.550
7.535
7.451
7.446
7.434
7.431
7.426
7.415
7.410
7.324
7.314
7.261
7.255
7.244
7.234
4.361
4.338
4.300
4.276
3.853
3.825
3.820
3.792
1.698
1.385
0.000
Cl
O
O
S
O
Ph
OH
5
0.95
2.00
1.03
4.03
1.15
1.00
1.00
1.02
0.98
1.84
3.14
f1 (ppm)
141.167
134.769
133.658
132.916
132.081
131.869
128.672
127.167
127.055
126.339
77.318
77.000
76.683
74.879
67.397
43.807
20.251
f1 (ppm)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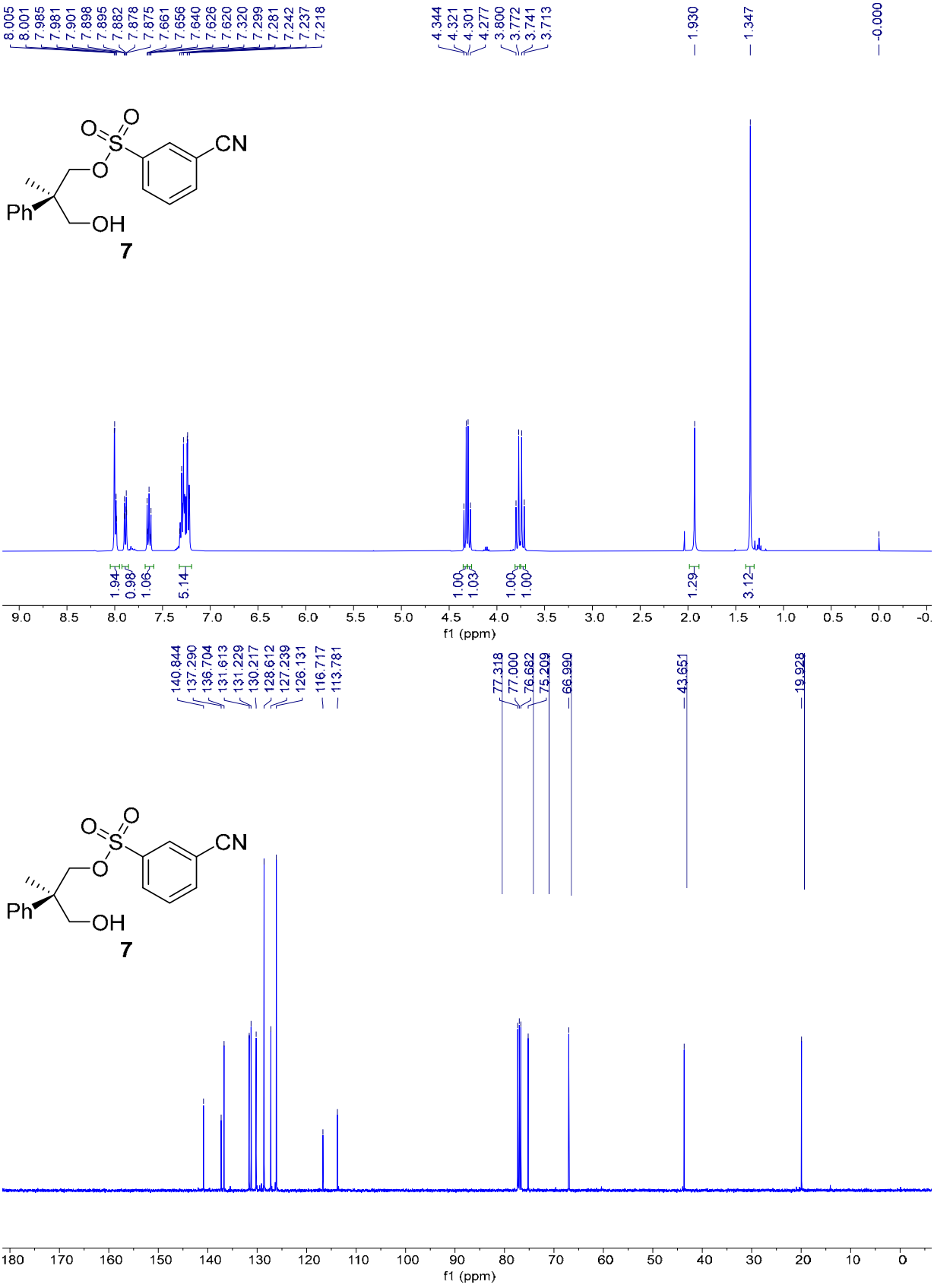
8.485
8.481
8.309
8.306
8.302
8.289
8.286
8.283
8.001
7.998
7.994
7.981
7.978
7.974
7.633
7.614
7.594
7.304
7.289
7.285
7.282
7.268
7.266
7.264
7.256
7.251
7.240
7.238
7.234
7.220
7.203
4.277
3.964
3.807
3.779
3.763
3.735
1.811
1.338
-0.000
O
O
S
O
CO2Me
Ph
OH
6
0.94
1.00
0.97
1.03
5.16
2.00
3.08
1.02
1.03
1.45
3.09
f1 (ppm)
165.118
141.060
136.292
134.560
131.720
131.442
129.529
128.921
128.621
127.073
126.238
77.318
77.000
76.682
74.604
67.200
52.677
43.764
20.077
O
O
S
O
CO2Me
Ph
OH
6
f1 (ppm)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7.985
7.981
7.901
7.898
7.895
7.882
7.878
7.875
7.661
7.656
7.640
7.626
7.620
7.320
7.299
7.281
7.242
7.237
7.218
4.344
4.321
4.301
4.277
3.800
3.772
3.741
3.713
1.930
1.347
-0.000
CN
O
S
O
O
Ph
OH
7
1.94
0.98
1.06
5.14
1.00
1.03
1.00
1.00
1.29
3.12
f1 (ppm)
140.844
137.290
136.704
131.613
131.229
130.217
128.612
127.239
126.131
116.717
113.781
77.318
77.000
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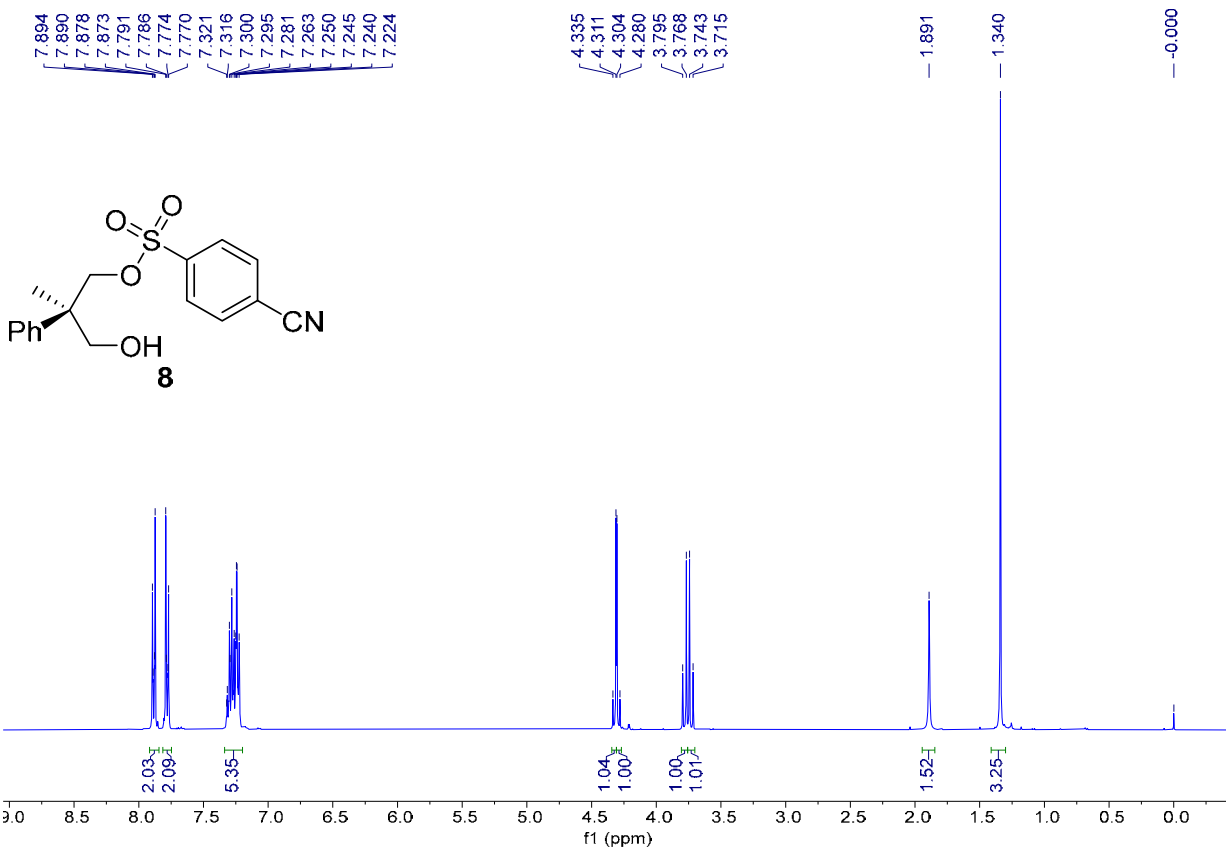
75.209
66.990
43.651
19.928
CN
O
S
O
O
Ph
OH
7
f1 (ppm)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7.890
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7.873
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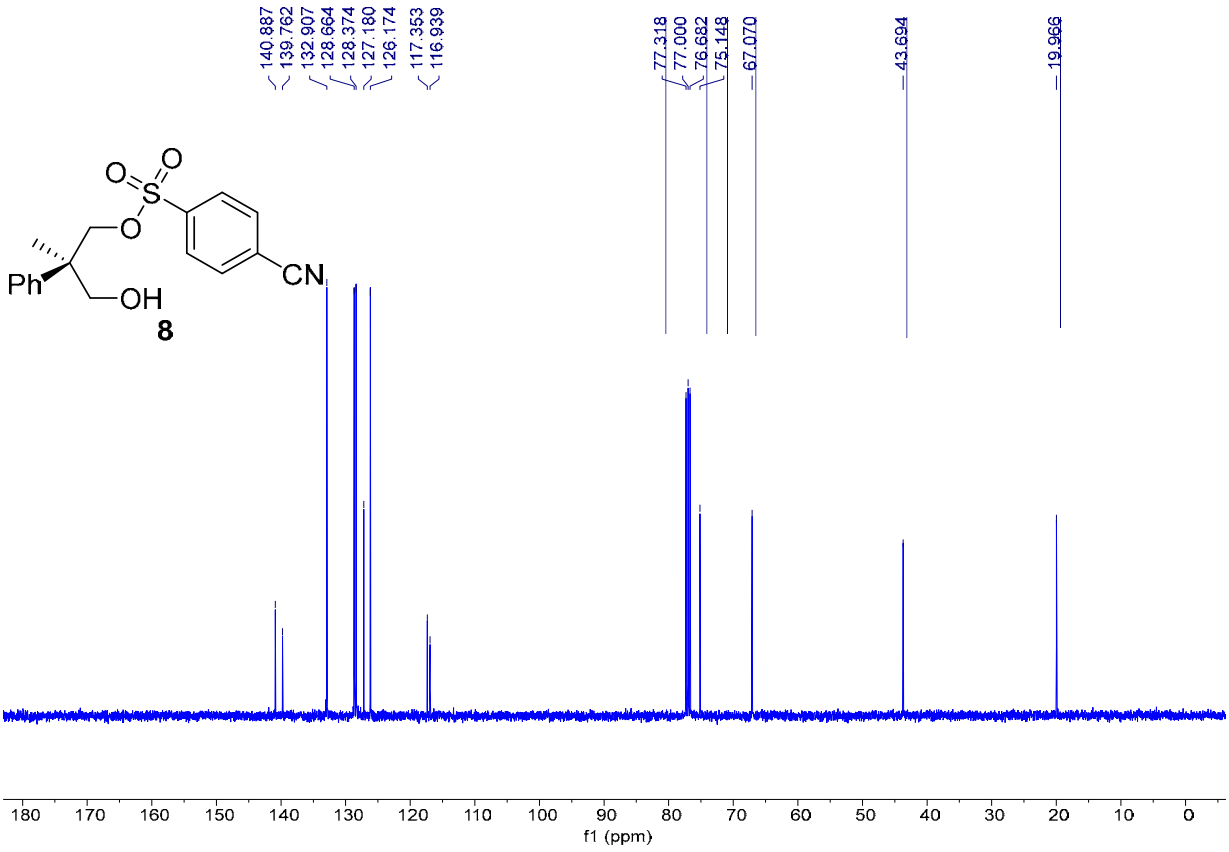
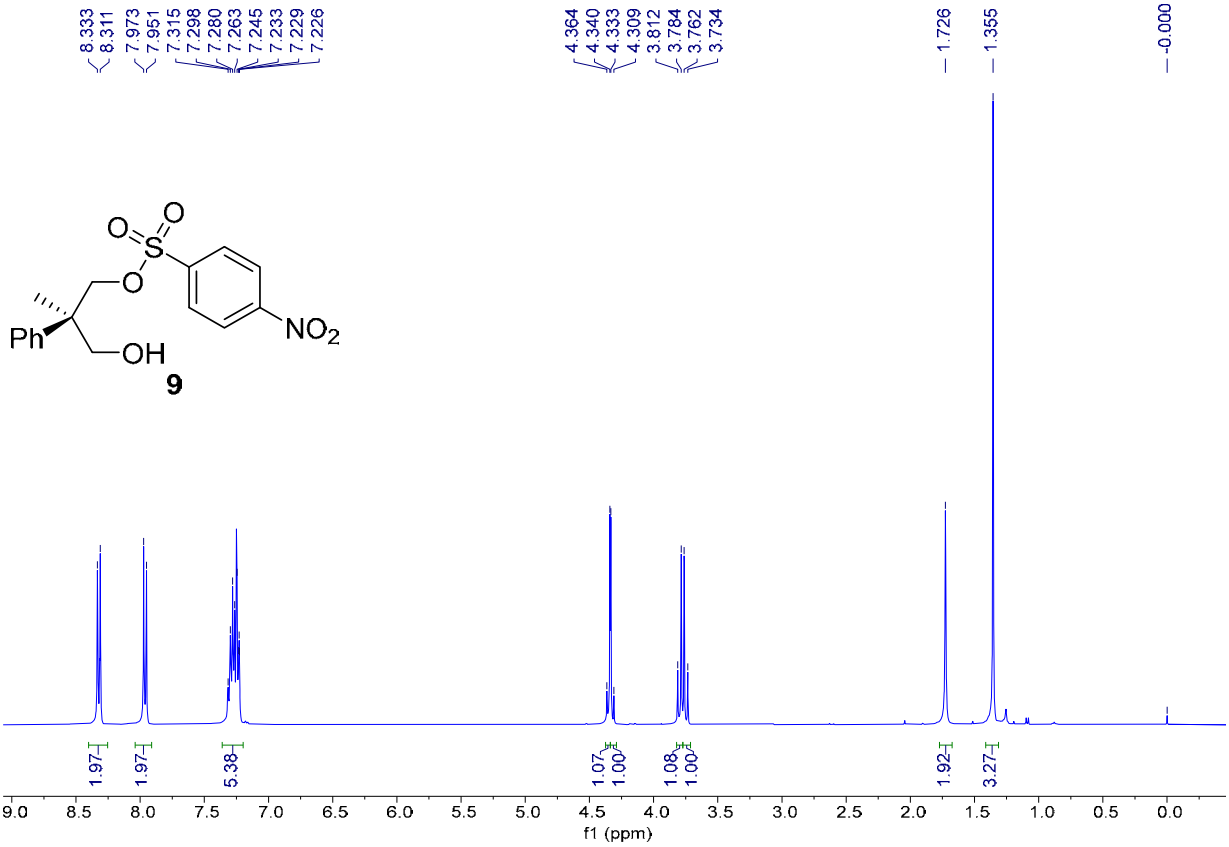
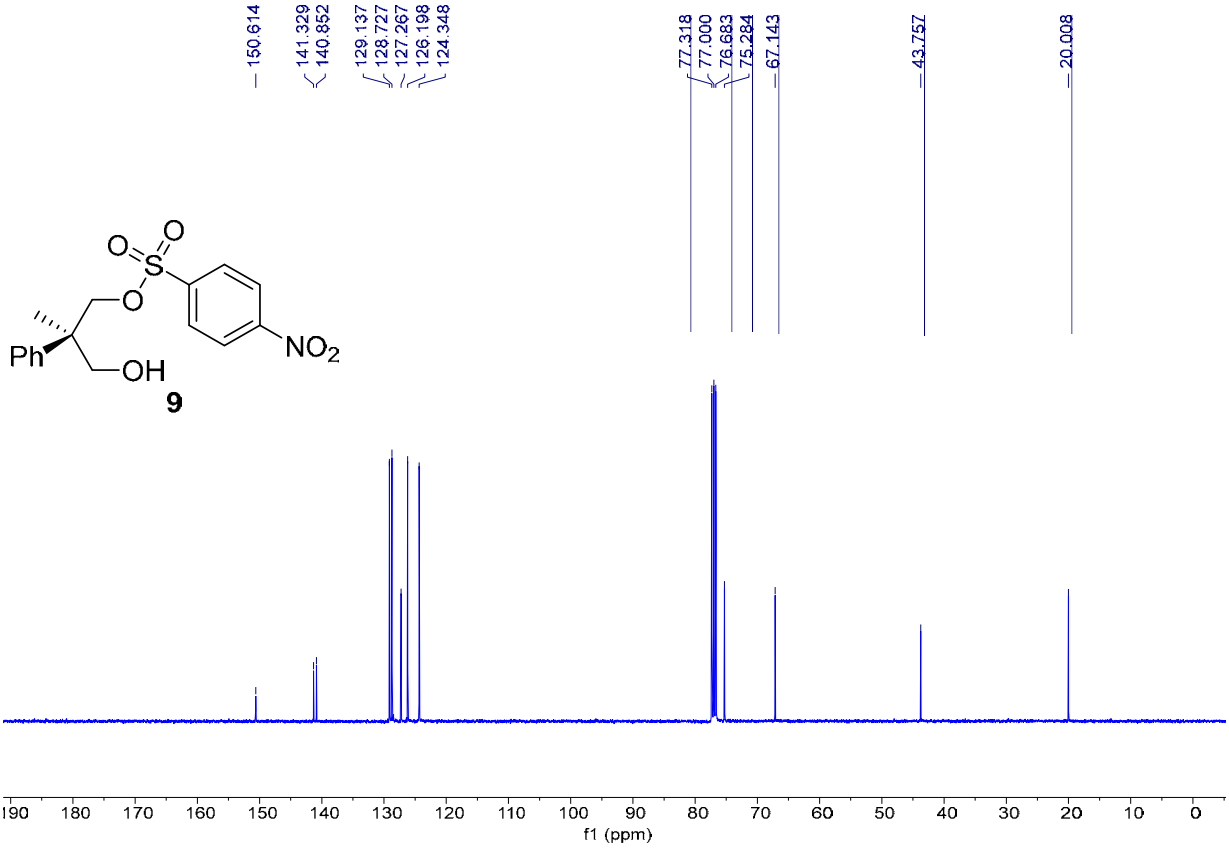
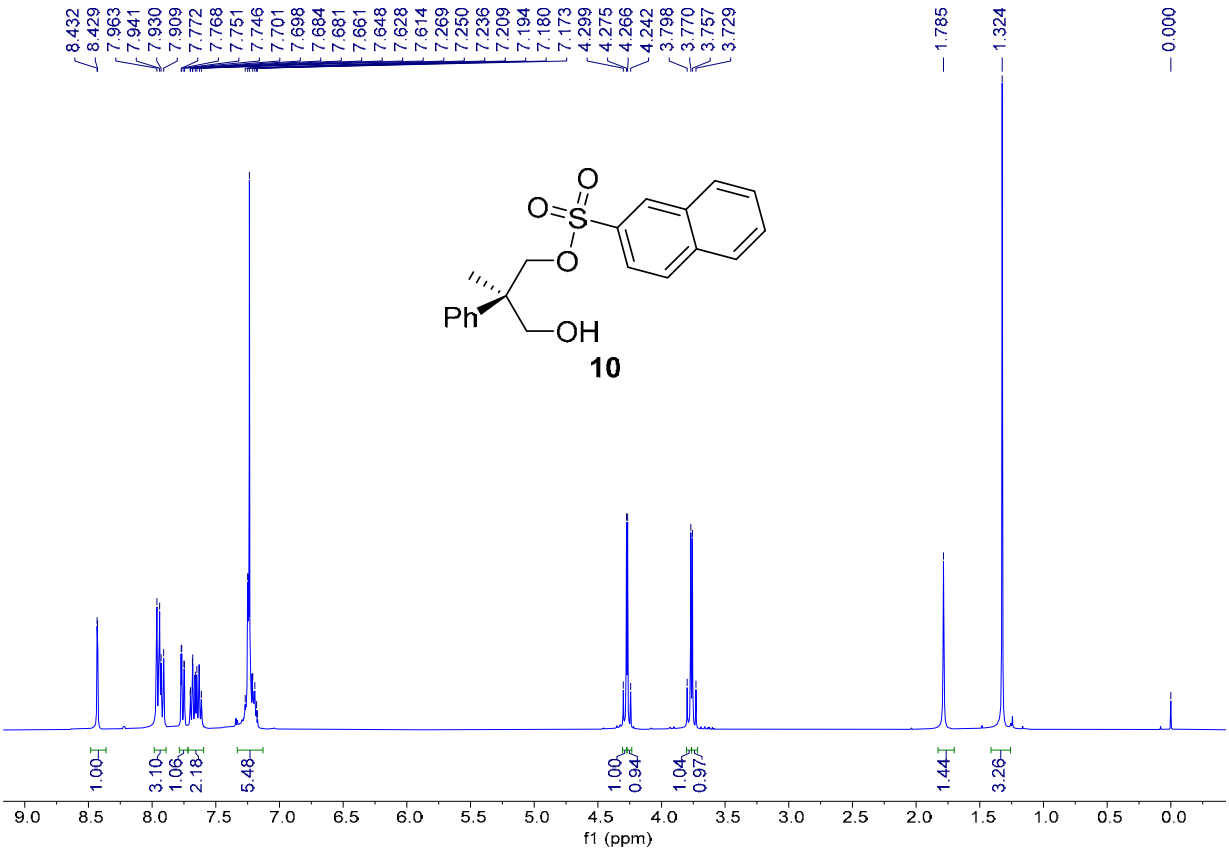
7.786
7.774
7.770
7.321
7.316
7.300
7.295
7.281
7.263
7.250
7.245
7.240
7.224
4.335
4.311
4.304
4.280
3.795
3.768
3.743
3.715
1.891
1.340
-0.000
O
O
S
O
Ph
OH
CN
8
2.03
2.09
5.35
1.04
1.00
1.00
1.01
1.52
3.25
f1 (ppm)


140.887
139.762
132.907
128.664
128.374
127.180
126.174
117.353
116.939
77.318
77.000
76.682
75.148
67.070
43.694
19.966
O
O
S
O
Ph
OH
CN
8
f1 (ppm)


8.333
8.311
7.973
7.951
7.315
7.298
7.280
7.263
7.245
7.233
7.229
7.226
4.364
4.340
4.333
4.309
3.812
3.784
3.762
3.734
1.726
1.355
-0.000
O
O
S
O
Ph
OH
NO2
9
1.97
1.97
5.38
1.07
1.00
1.08
1.00
1.92
3.27
f1 (ppm)


150.614
141.329
140.852
129.137
128.727
127.267
126.198
124.348
77.318
77.000
76.683
75.284
67.143
43.757
20.008
O
O
S
O
Ph
OH
NO2
9
f1 (ppm)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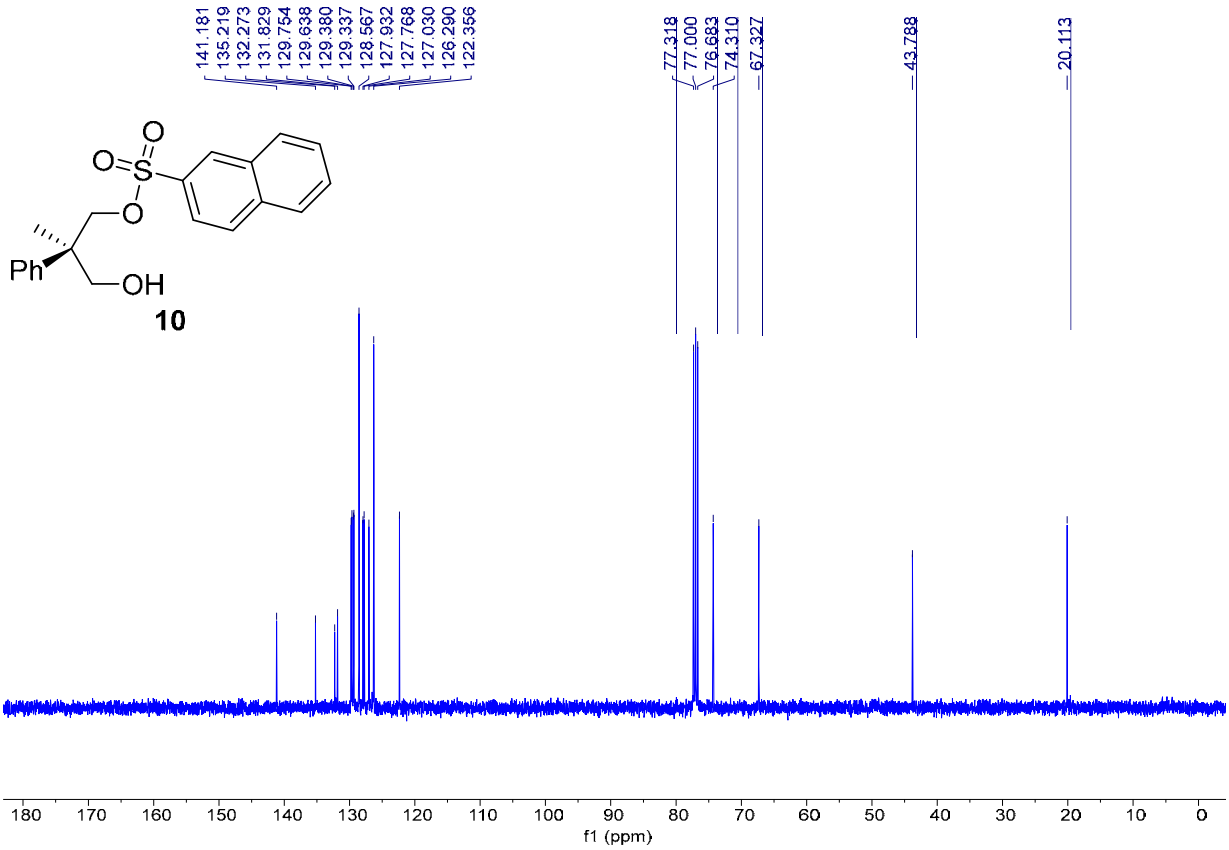
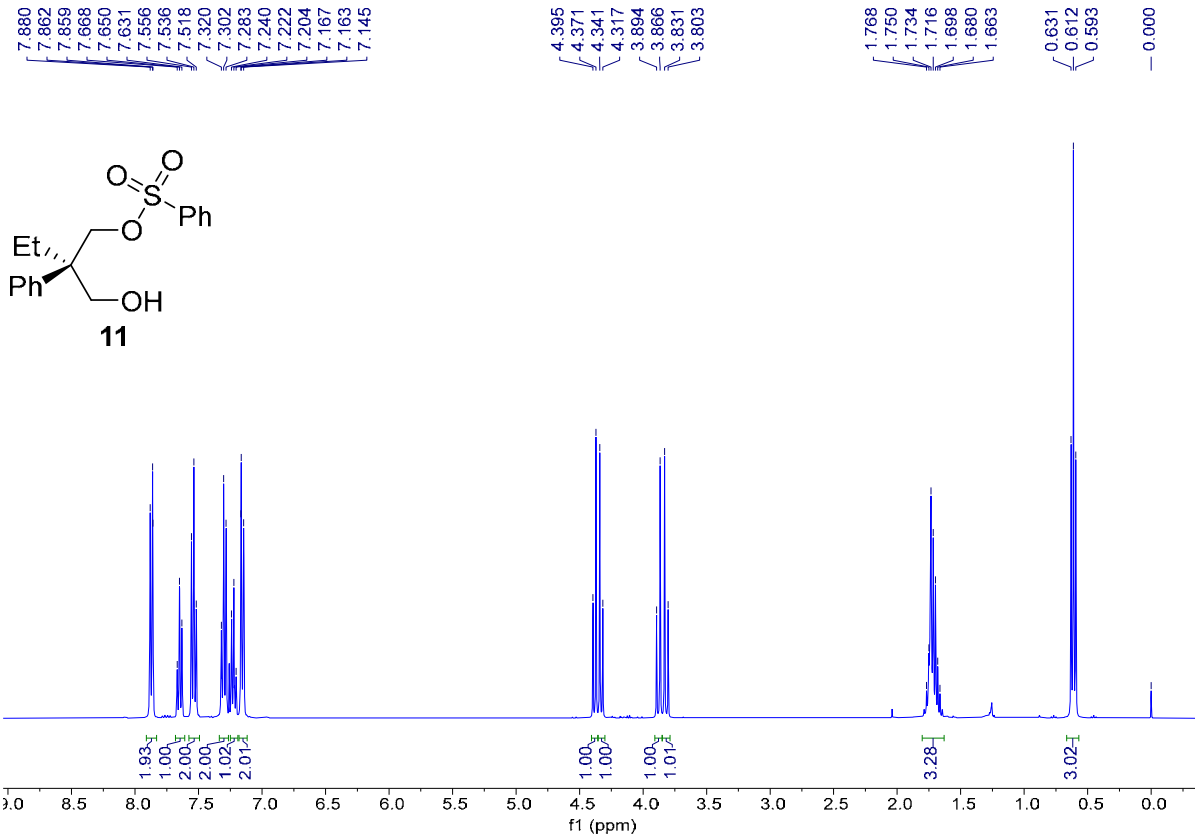
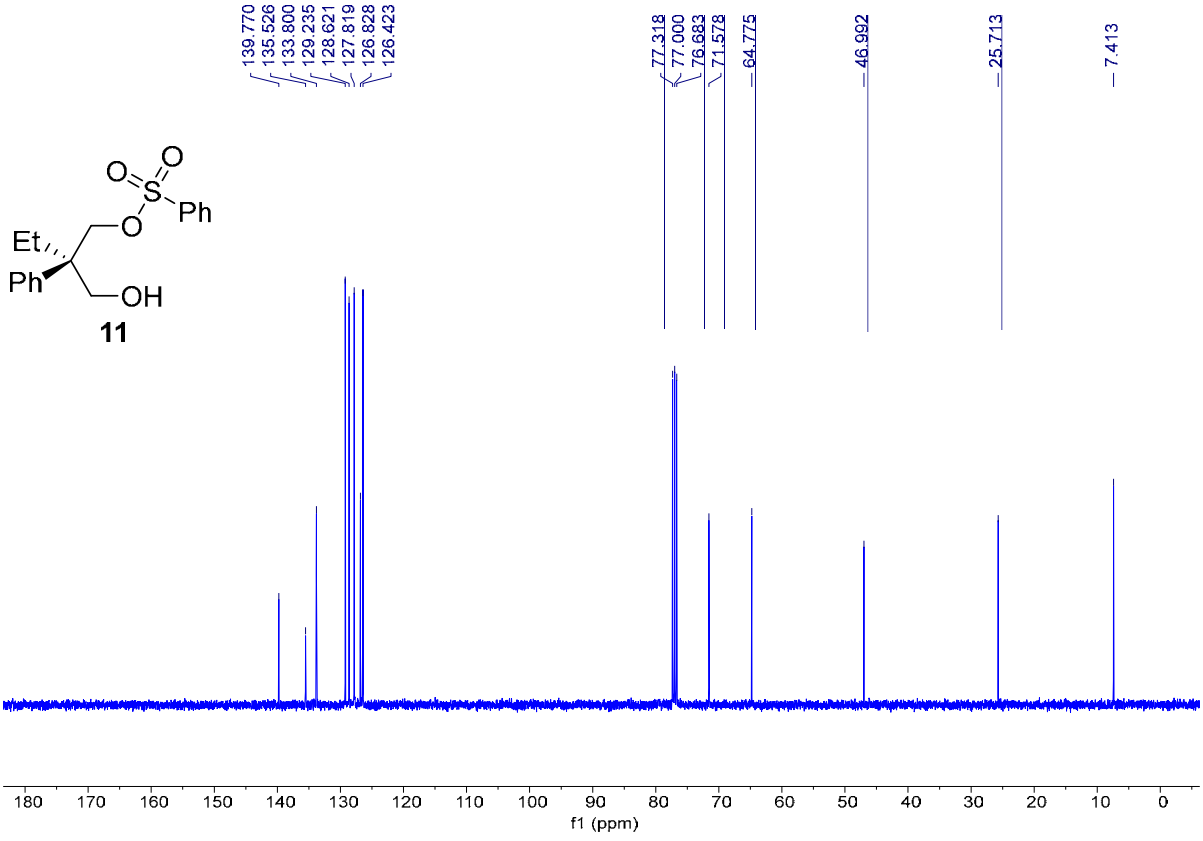
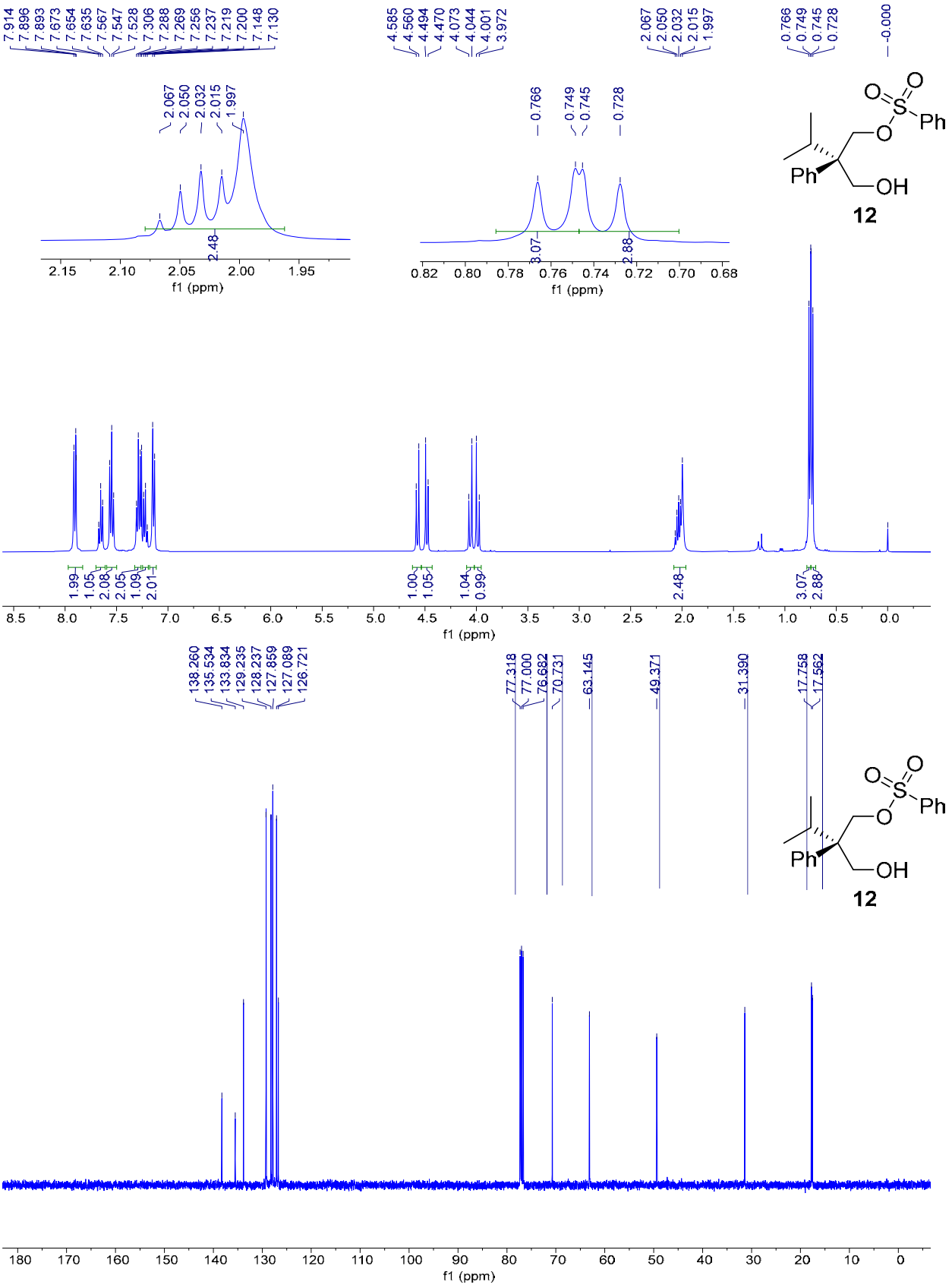
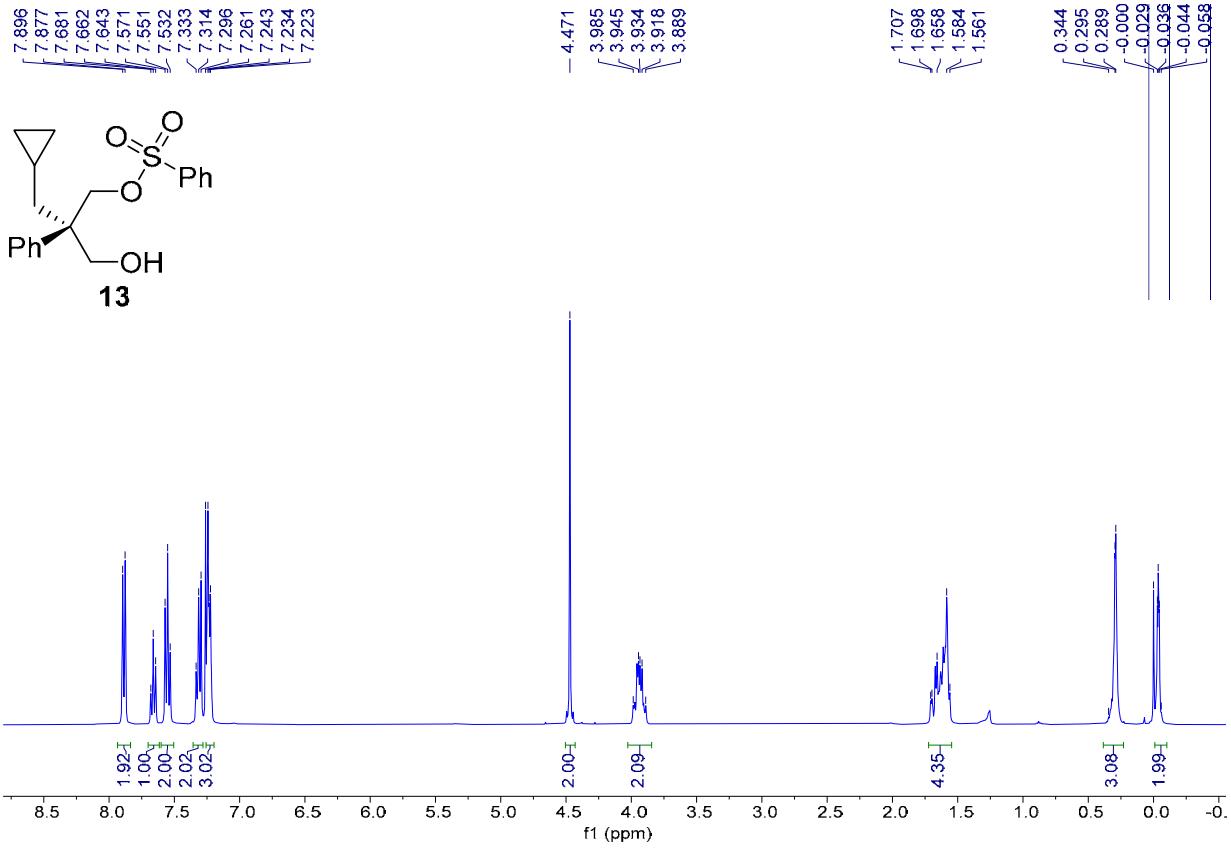
8.429
7.963
7.941
7.930
7.909
7.772
7.768
7.751
7.746
7.701
7.698
7.684
7.681
7.661
7.648
7.628
7.614
7.269
7.250
7.236
7.209
7.194
7.180
7.173
4.299
4.275
4.266
4.242
3.798
3.770
3.757
3.729
1.785
1.324
0.000
1.00
3.10
1.06
2.18
5.48
1.00
0.94
1.04
0.97
1.44
3.26
f1 (ppm)
10

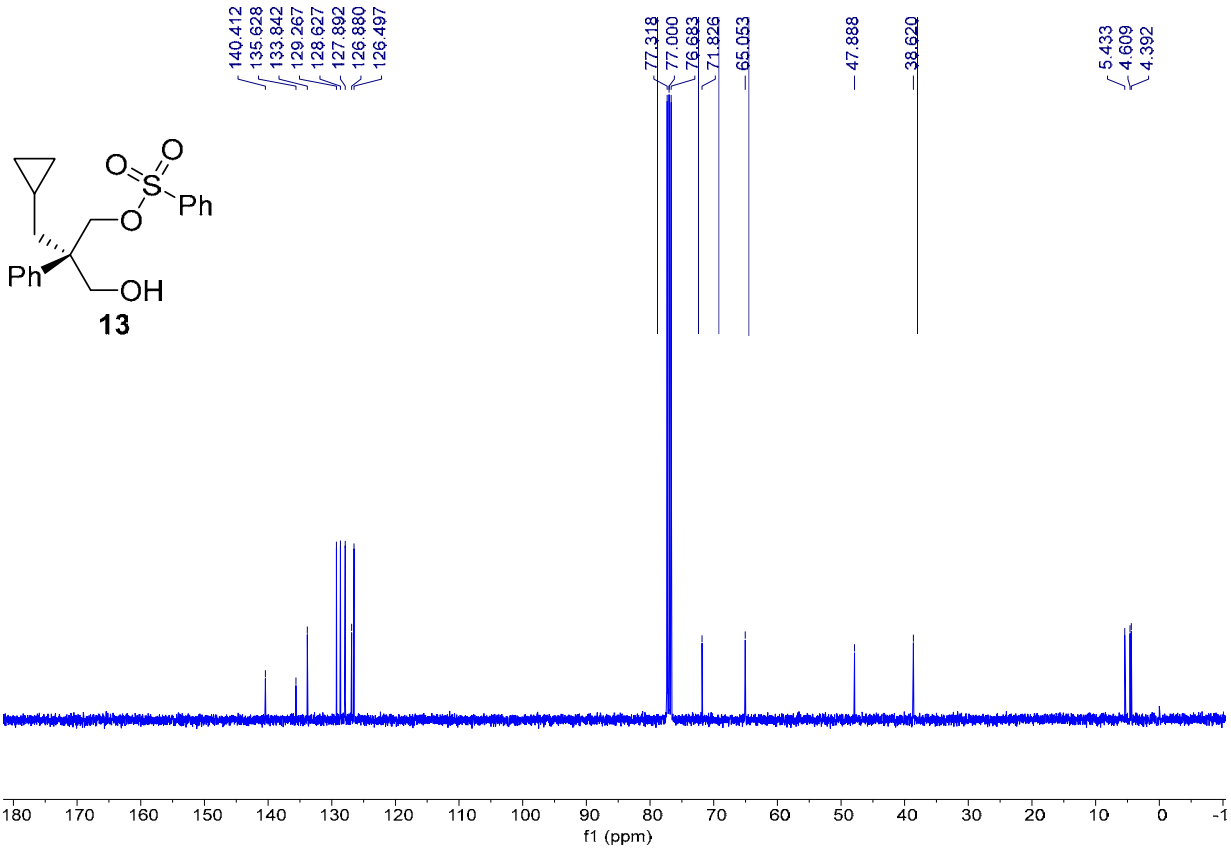

141.181
135.219
132.273
131.829
129.754
129.638
129.380
129.337
128.567
127.932
127.768
127.030
126.290
122.356
77.318
77.000
76.683
74.310
67.327
43.788
20.113
f1 (ppm)
10

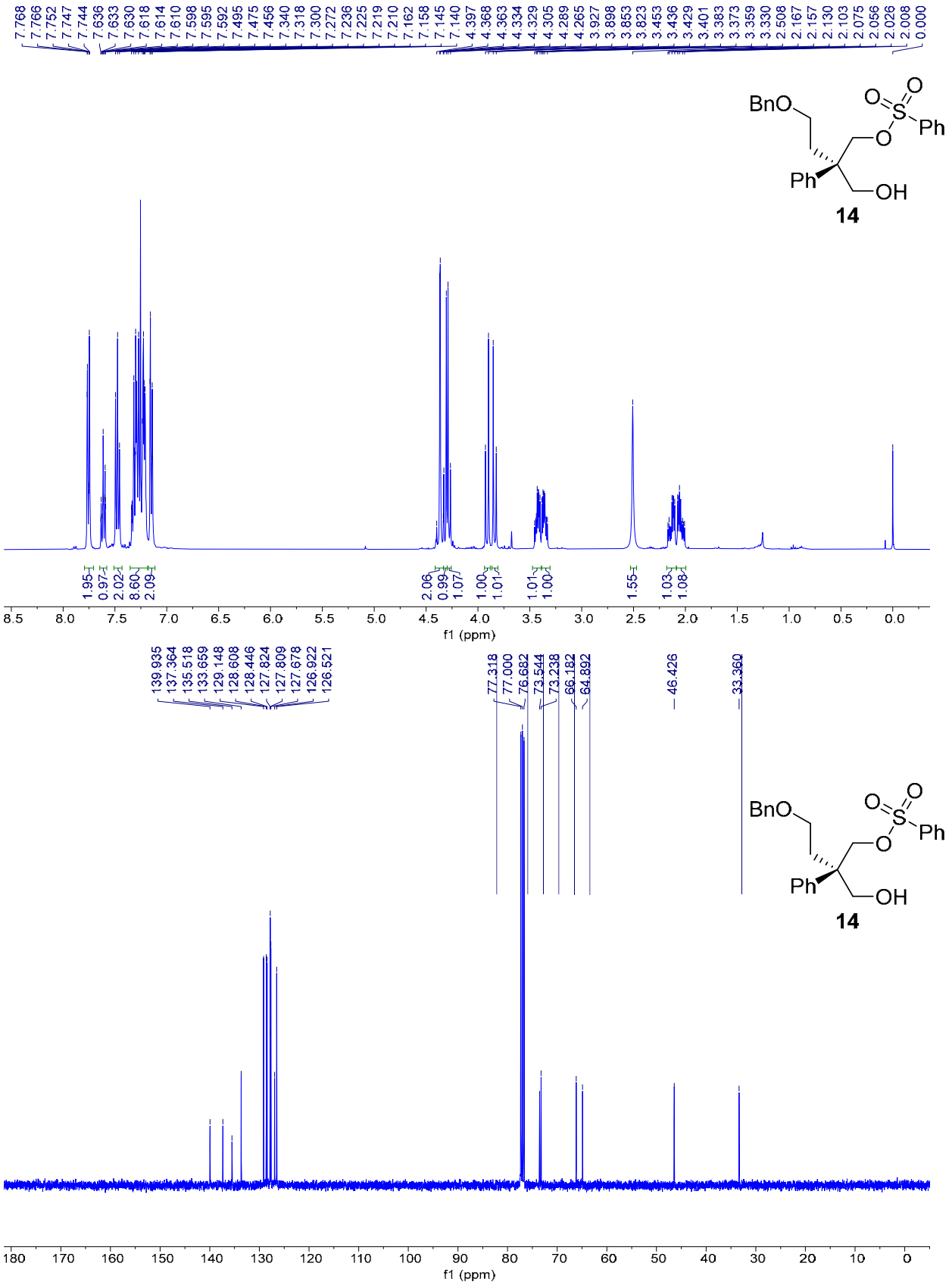

7.880
7.862
7.859
7.668
7.650
7.631
7.556
7.536
7.518
7.320
7.302
7.283
7.240
7.222
7.204
7.167
7.163
7.145
4.395
4.371
4.341
4.317
3.894
3.866
3.831
3.803
1.768
1.750
1.734
1.716
1.698
1.680
1.663
0.631
0.612
0.593
0.000
O
O
S
Ph
O
Et
Ph
OH
11
1.93
1.00
2.00
2.00
1.02
2.01
1.00
1.00
1.00
1.01
3.28
3.02
f1 (ppm)

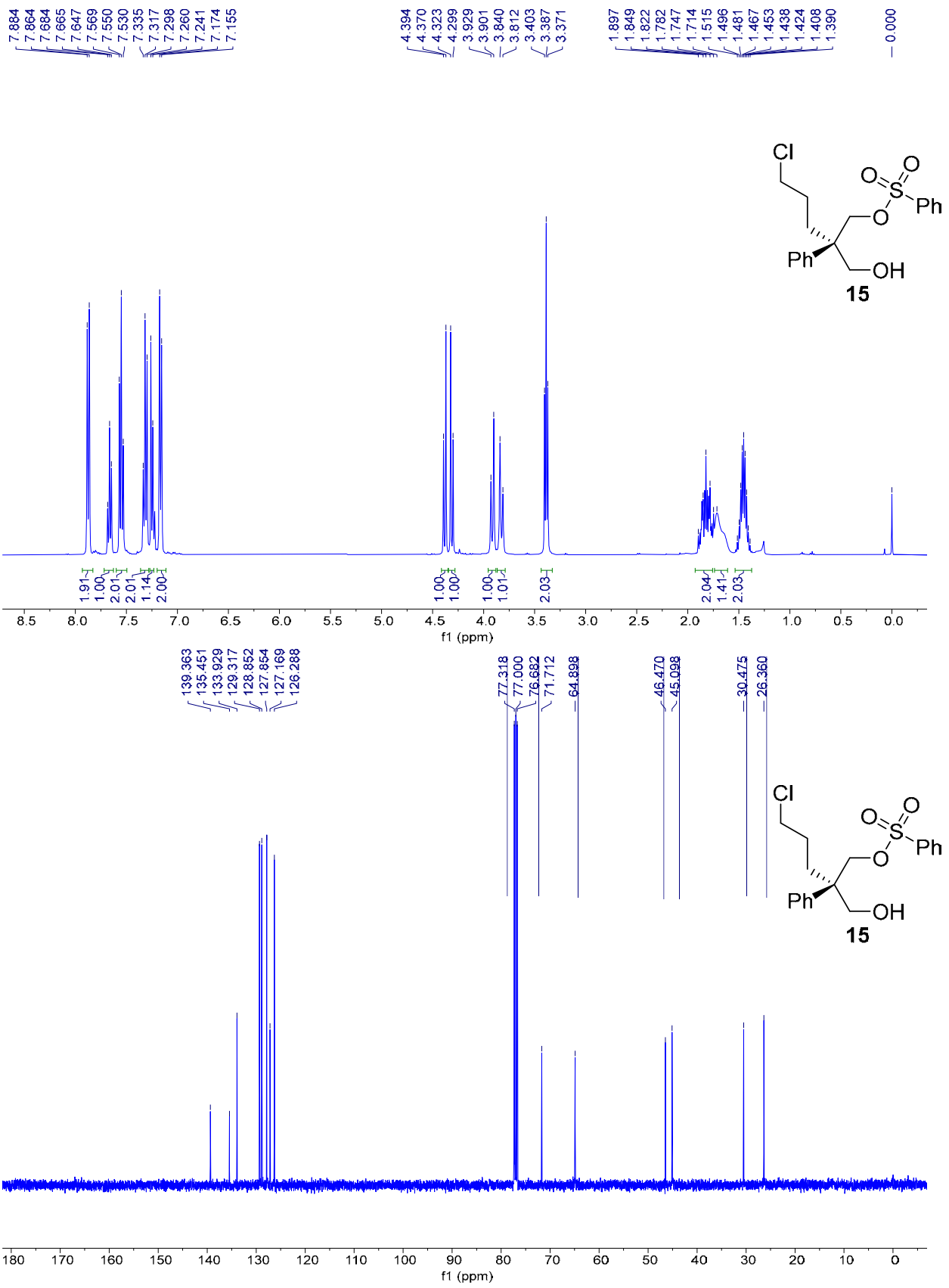

139.770
135.526
133.800
129.235
128.621
127.819
126.828
126.423
77.318
77.000
76.683
71.578
64.775
46.992
25.713
7.413
O
O
S
Ph
O
Et
Ph
OH
11
f1 (ppm)


7.914
7.896
7.893
7.673
7.654
7.635
7.567
7.547
7.528
7.306
7.288
7.269
7.256
7.237
7.219
7.200
7.148
7.130
4.585
4.560
4.494
4.470
4.073
4.044
4.001
3.972
2.067
2.050
2.032
2.015
1.997
0.766
0.749
0.745
0.728
-0.000
2.48
3.07
2.88
f1 (ppm)
1.99
1.05
2.08
2.05
1.09
2.01
1.00
1.05
1.04
0.99
2.48
3.07
2.88
138.260
135.534
133.834
129.235
128.237
127.859
127.089
126.721
77.318
77.000
76.682
70.731
63.145
49.371
31.390
17.758
17.562
O
S
Ph
O
Ph
OH
12


7.896
7.877
7.681
7.662
7.643
7.571
7.551
7.532
7.333
7.314
7.296
7.261
7.243
7.234
7.223
4.471
3.985
3.945
3.934
3.918
3.889
1.707
1.698
1.658
1.584
1.561
0.344
0.295
0.289
-0.000
-0.029
-0.036
-0.044
-0.058
O
O
S
Ph
O
Ph
OH
13
1.92
1.00
2.00
2.02
3.02
2.00
2.09
4.35
3.08
1.99
f1 (ppm)


140.412
135.628
133.842
129.267
128.627
127.892
126.880
126.497
77.318
77.000
76.683
71.826
65.053
47.888
38.620
5.433
4.609
4.392
O
O
S
Ph
O
Ph
OH
13
f1 (ppm)


7.768 7.766 7.752 7.747 7.744 7.636 7.633 7.630 7.618 7.614 7.610 7.598 7.595 7.592 7.495 7.475 7.456 7.340 7.318 7.300 7.272 7.236 7.225 7.219 7.210 7.162 7.158 7.145 7.140 4.397 4.368 4.363 4.334 4.329 4.305 4.289 4.265 3.927 3.898 3.853 3.823 3.453 3.436 3.429 3.401 3.383 3.373 3.359 3.330 2.508 2.167 2.157 2.130 2.103 2.075 2.056 2.026 2.008 0.000
BnO
O
S
O
O
Ph
Ph
OH
14
1.95 0.97 2.02 8.60 2.09 2.06 0.99 1.07 1.00 1.01 1.01 1.00 1.55 1.03 1.08
f1 (ppm)
139.935 137.364 135.518 133.659 129.148 128.608 128.446 127.824 127.809 127.678 126.922 126.521 77.318 77.000 76.682 73.544 73.238 66.182 64.892 46.426 33.360
BnO
O
S
O
O
Ph
Ph
OH
14
f1 (ppm)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7.530
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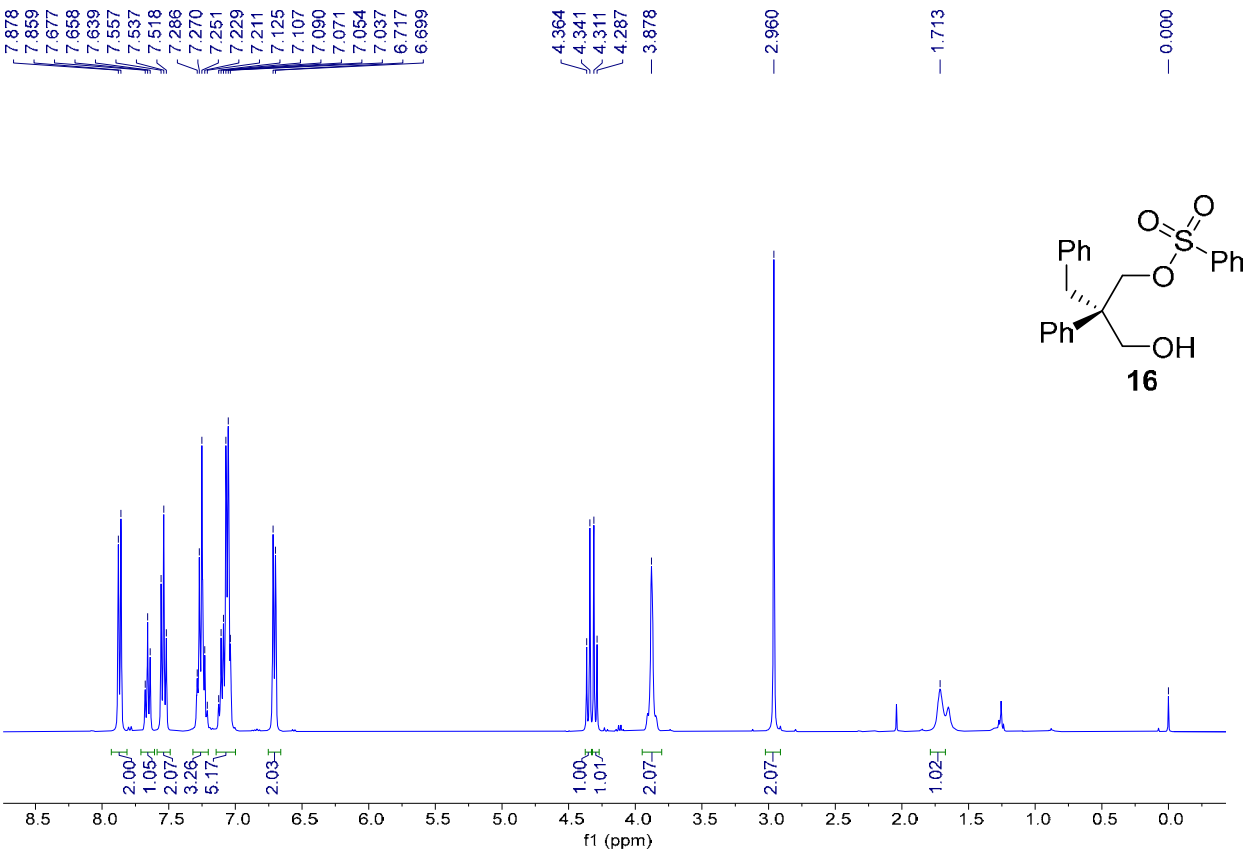
7.298
7.260
7.241
7.174
7.155
4.394
4.370
4.323
4.299
3.929
3.901
3.840
3.812
3.403
3.387
3.371
1.897
1.849
1.822
1.782
1.747
1.714
1.515
1.496
1.481
1.467
1.453
1.438
1.424
1.408
1.390
0.000
Cl
O
O
S
Ph
O
Ph
OH
15
1.91
1.00
2.01
2.01
1.14
2.00
1.00
1.00
1.00
1.01
2.03
2.04
1.41
2.03
f1 (ppm)
139.363
135.451
133.929
129.317
128.852
127.854
127.169
126.288
77.318
77.000
76.682
71.712
64.898
46.470
45.098
30.475
26.360
Cl
O
O
S
Ph
O
Ph
OH
15
f1 (ppm)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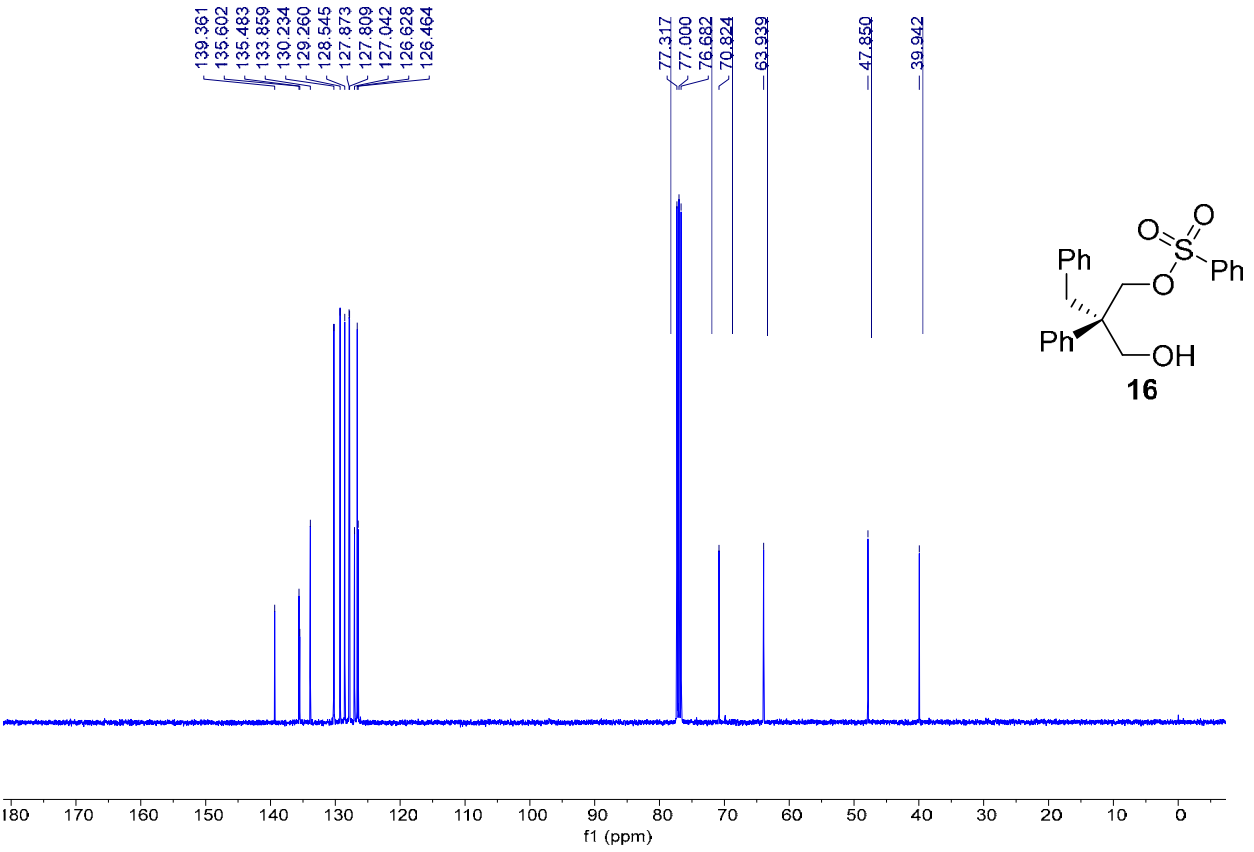
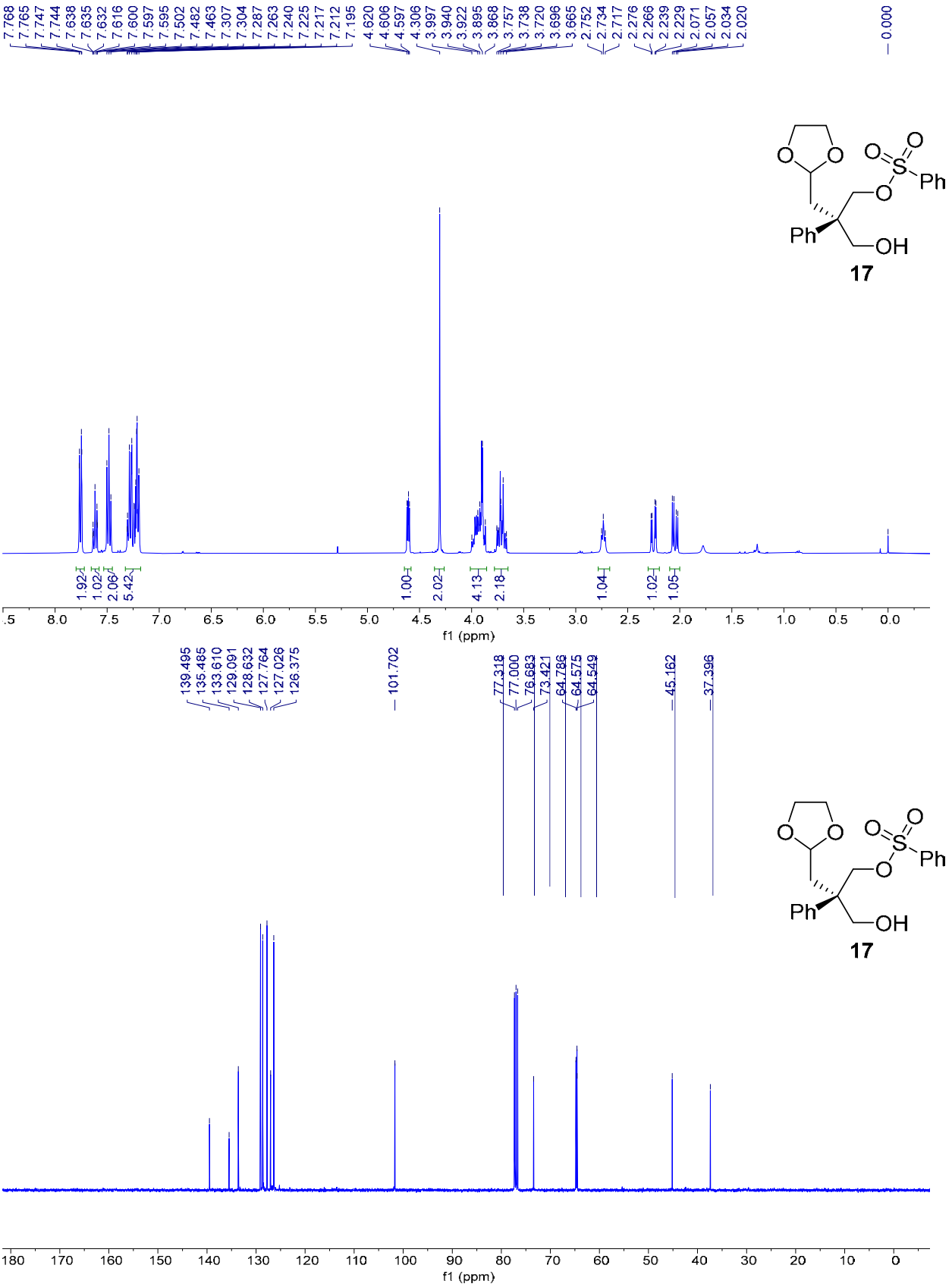
7.639
7.557
7.537
7.518
7.286
7.270
7.251
7.229
7.211
7.125
7.107
7.090
7.071
7.054
7.037
6.717
6.699
4.364
4.341
4.311
4.287
3.878
2.960
1.713
0.000
Ph
O
S
O
Ph
O
Ph
OH
16
2.00
1.05
2.07
3.26
5.17
2.03
1.00
1.01
2.07
2.07
1.02
f1 (ppm)


139.361
135.602
135.483
133.859
130.234
129.260
128.545
127.873
127.809
127.042
126.628
126.464
77.317
77.000
76.682
70.824
63.939
47.850
39.942
Ph
O
S
O
Ph
O
Ph
OH
16
f1 (ppm)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7.638
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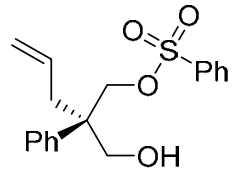
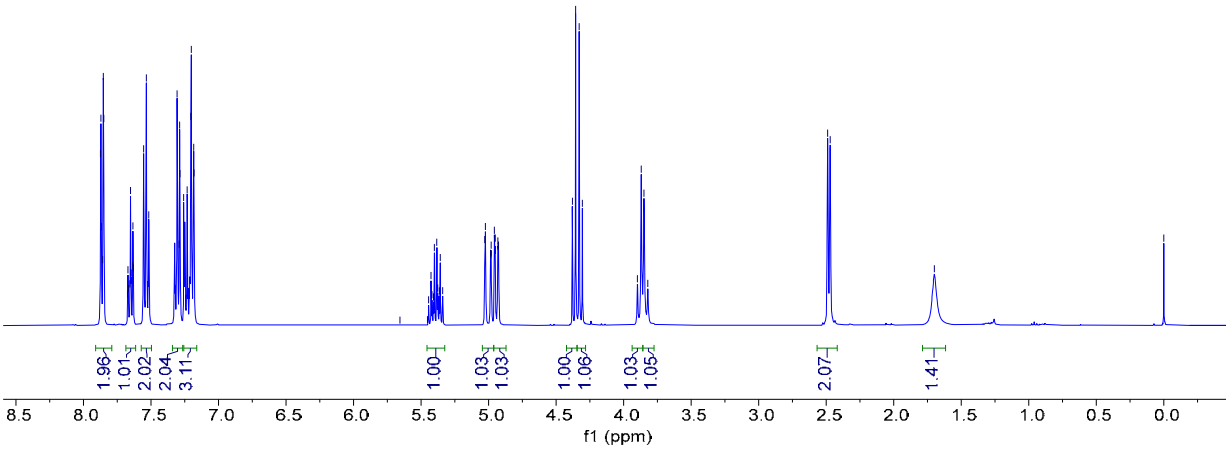
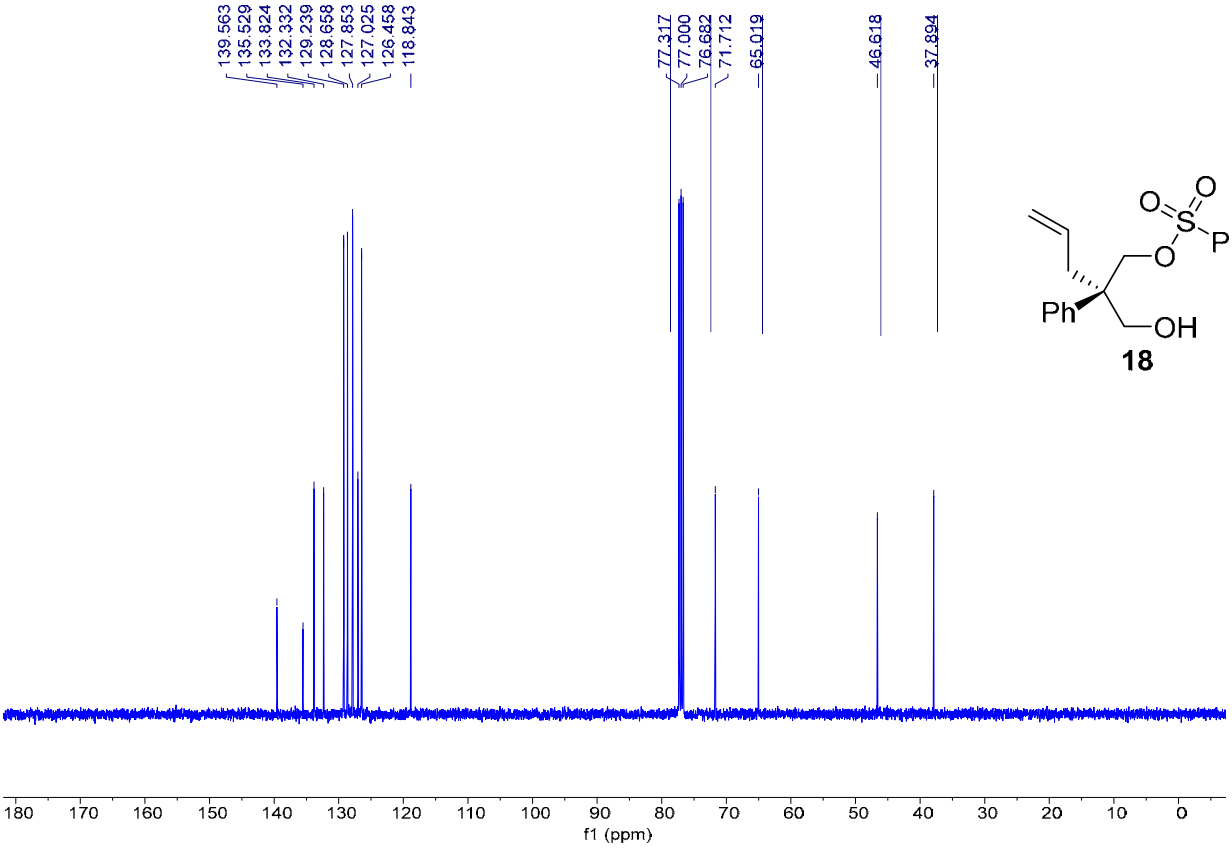
7.616
7.600
7.597
7.595
7.502
7.482
7.463
7.307
7.304
7.287
7.263
7.240
7.225
7.217
7.212
7.195
4.620
4.606
4.597
4.306
3.997
3.940
3.922
3.895
3.868
3.757
3.738
3.720
3.696
3.665
2.752
2.734
2.717
2.276
2.266
2.239
2.229
2.071
2.057
2.034
2.020
0.000
Ph
O
O
S
O
O
Ph
OH
17
1.92
1.02
2.06
5.42
1.00
2.02
4.13
2.18
1.04
1.02
1.05
f1 (ppm)
139.495
135.485
133.610
129.091
128.632
127.764
127.026
126.375
101.702
77.318
77.000
76.683
73.421
64.786
64.575
64.549
45.162
37.396
f1 (ppm)


7.874
7.871
7.867
7.858
7.854
7.850
7.674
7.671
7.668
7.657
7.652
7.648
7.637
7.634
7.630
7.555
7.535
7.516
7.307
7.292
7.288
7.286
7.258
7.232
7.206
7.202
7.184
7.181
5.426
5.419
5.408
5.401
5.384
5.377
5.366
5.358
5.340
5.028
5.024
4.986
4.981
4.957
4.955
4.952
4.932
4.929
4.927
4.380
4.356
4.330
4.306
3.898
3.870
3.849
3.821
2.489
2.471
1.699
0.000


O
O
S
Ph
O
Ph
OH

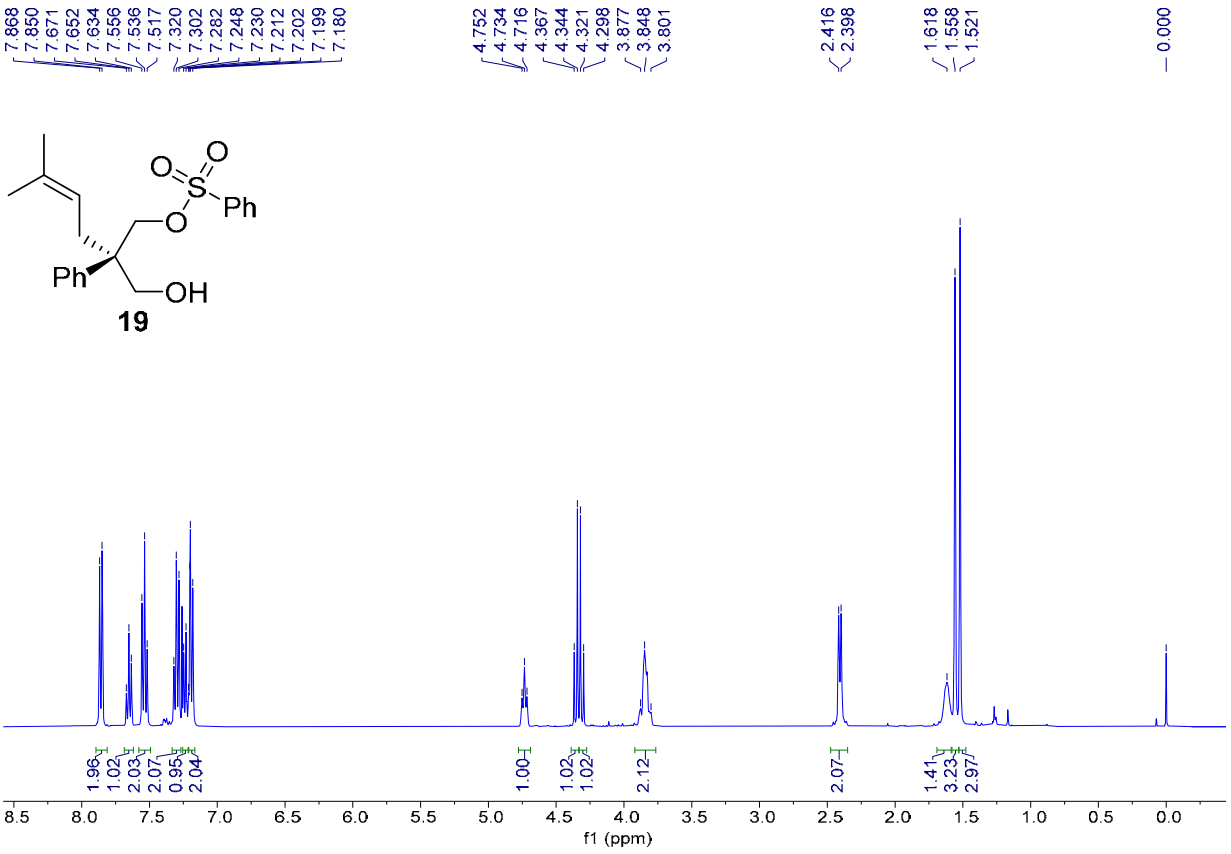
18

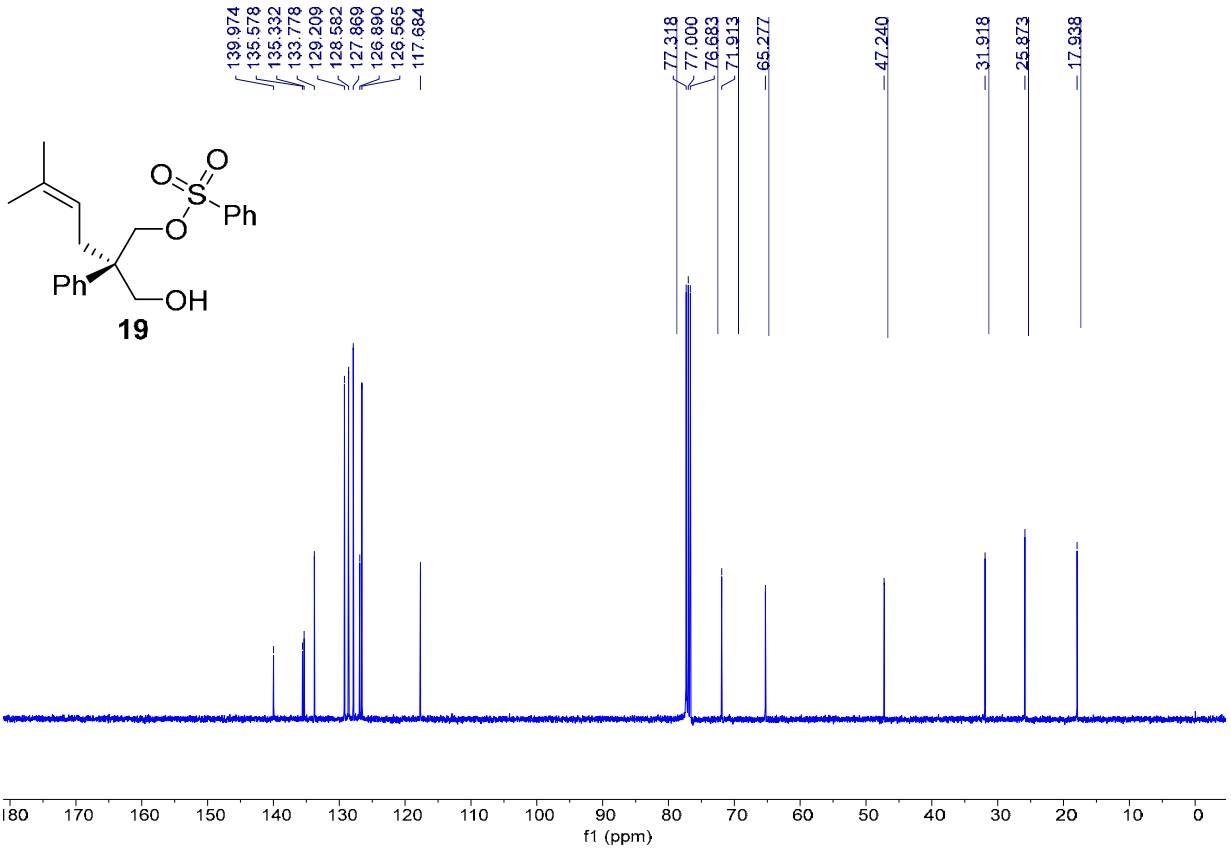

1.96
1.01
2.02
2.04
3.11
1.00
1.03
1.03
1.00
1.06
1.03
1.05
2.07
1.41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

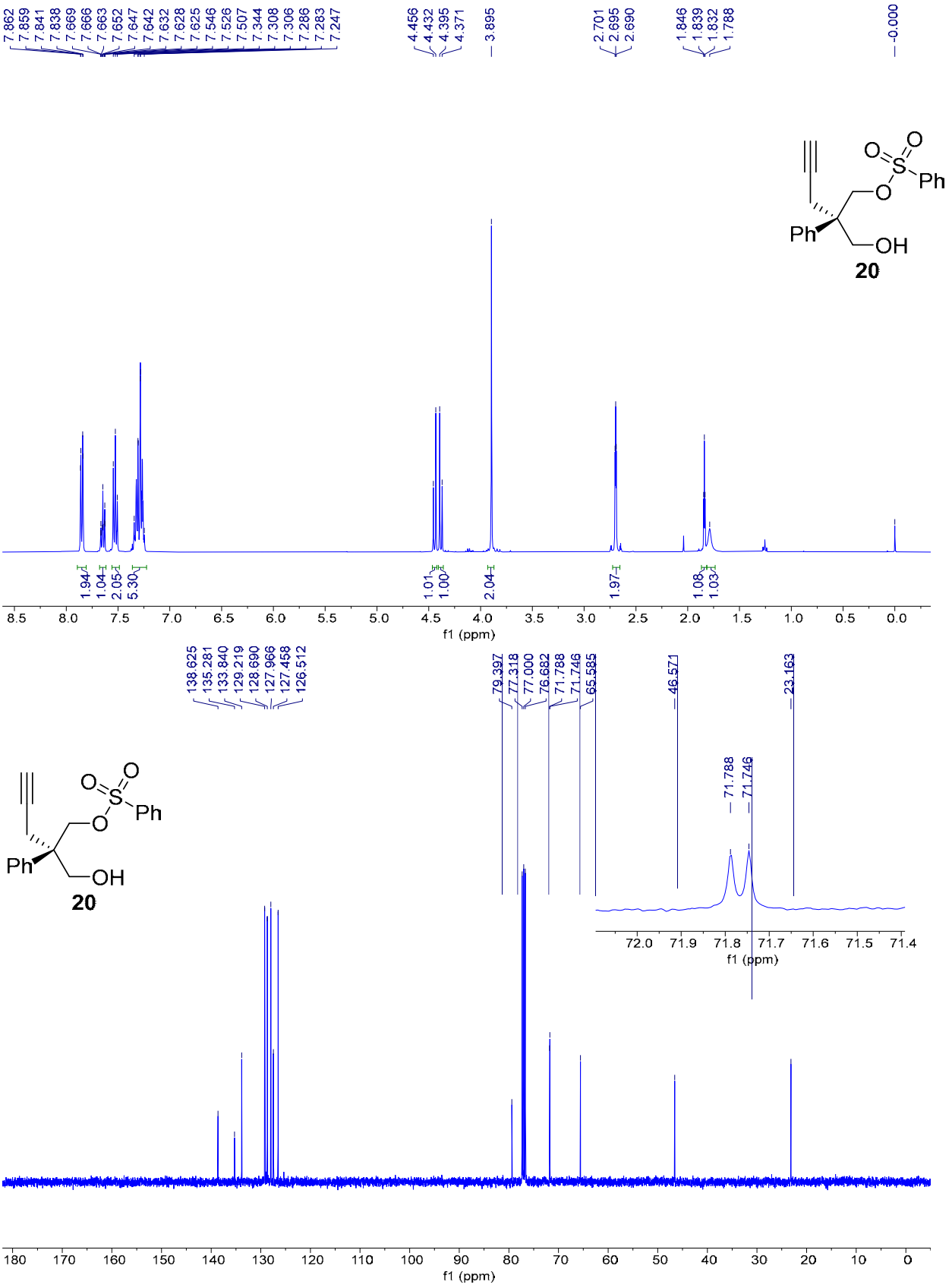

139.563
135.529
133.824
132.332
129.239
128.658
127.853
127.025
126.458
118.843
77.317
77.000
76.682
71.712
65.019
46.618
37.894
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

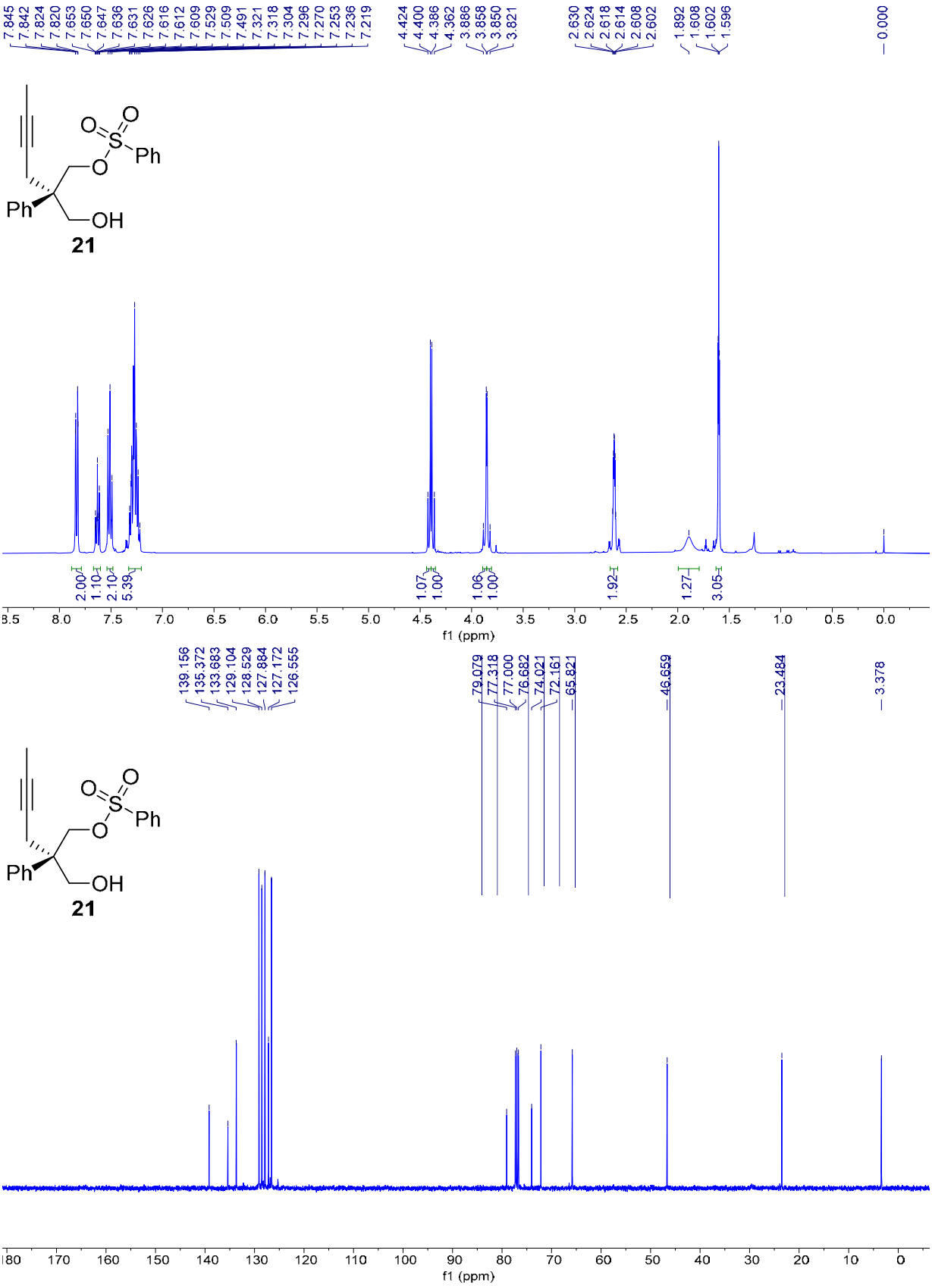
O
O
S
Ph
O
Ph
OH

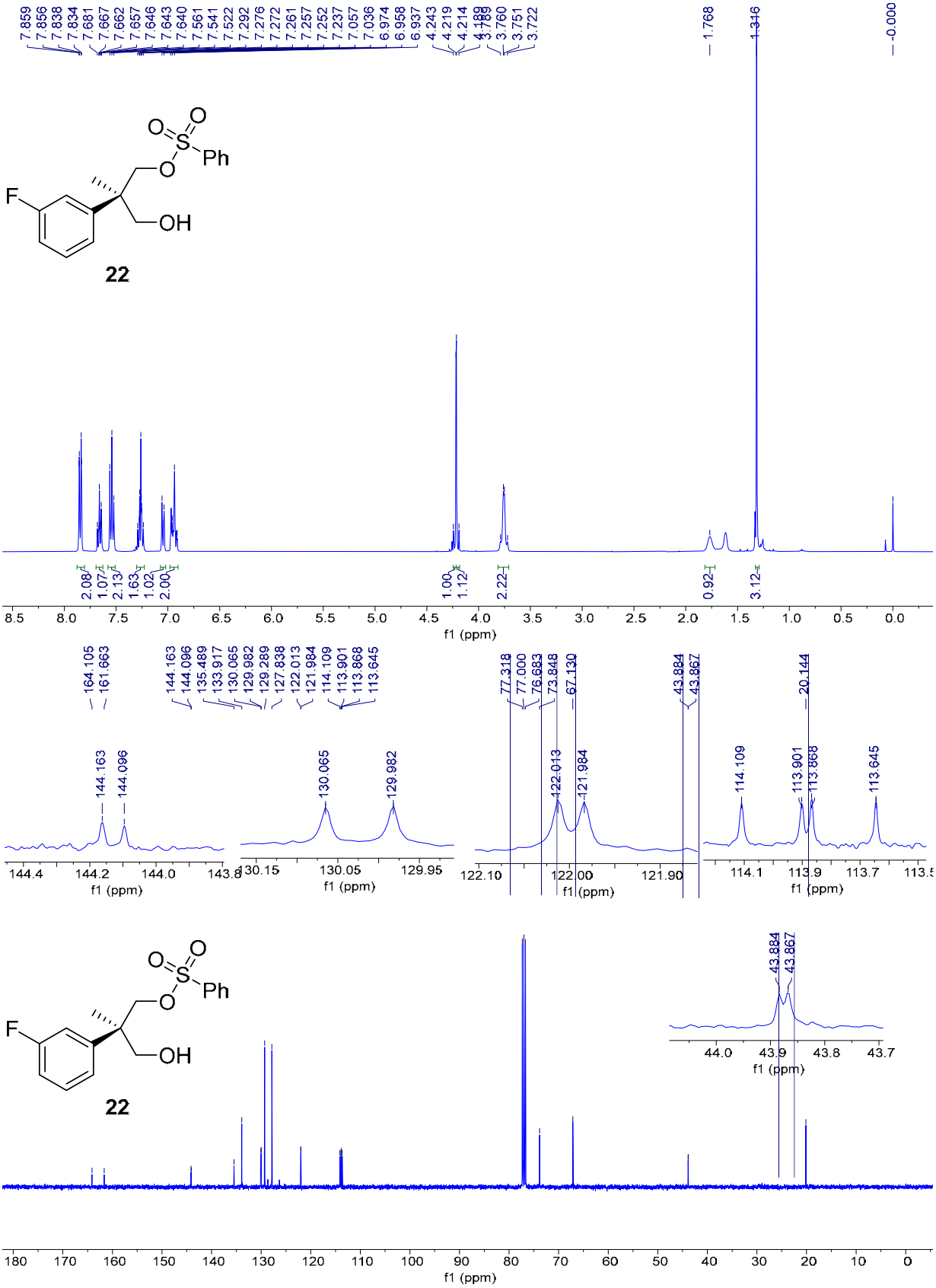
18

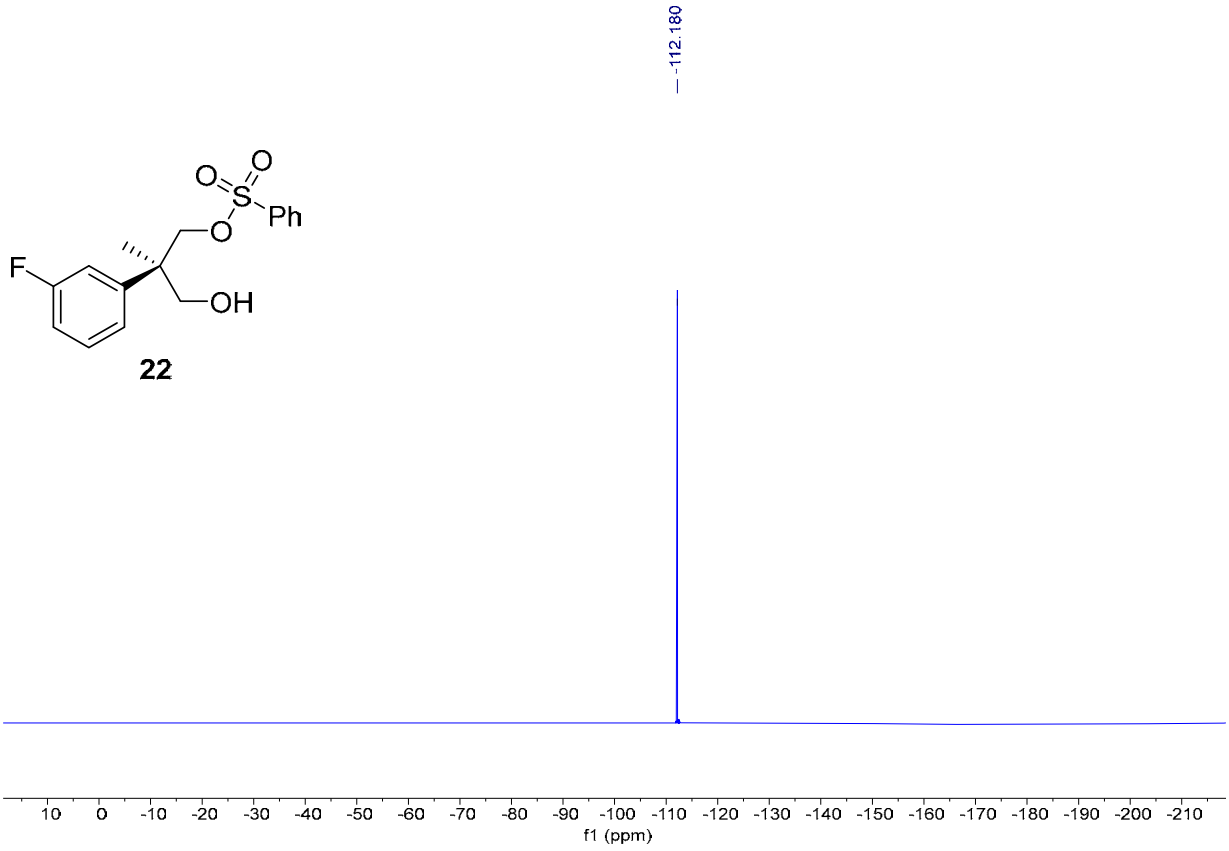

7.868
7.850
7.671
7.652
7.634
7.556
7.536
7.517
7.320
7.302
7.282
7.248
7.230
7.212
7.202
7.199
7.180
4.752
4.734
4.716
4.367
4.344
4.321
4.298
3.877
3.848
3.801
2.416
2.398
1.618
1.558
1.521
0.000
O
O
S
Ph
O
Ph
OH
19
1.96
1.02
2.03
2.07
0.95
2.04
1.00
1.02
1.02
2.12
2.07
1.41
3.23
2.97
f1 (ppm)

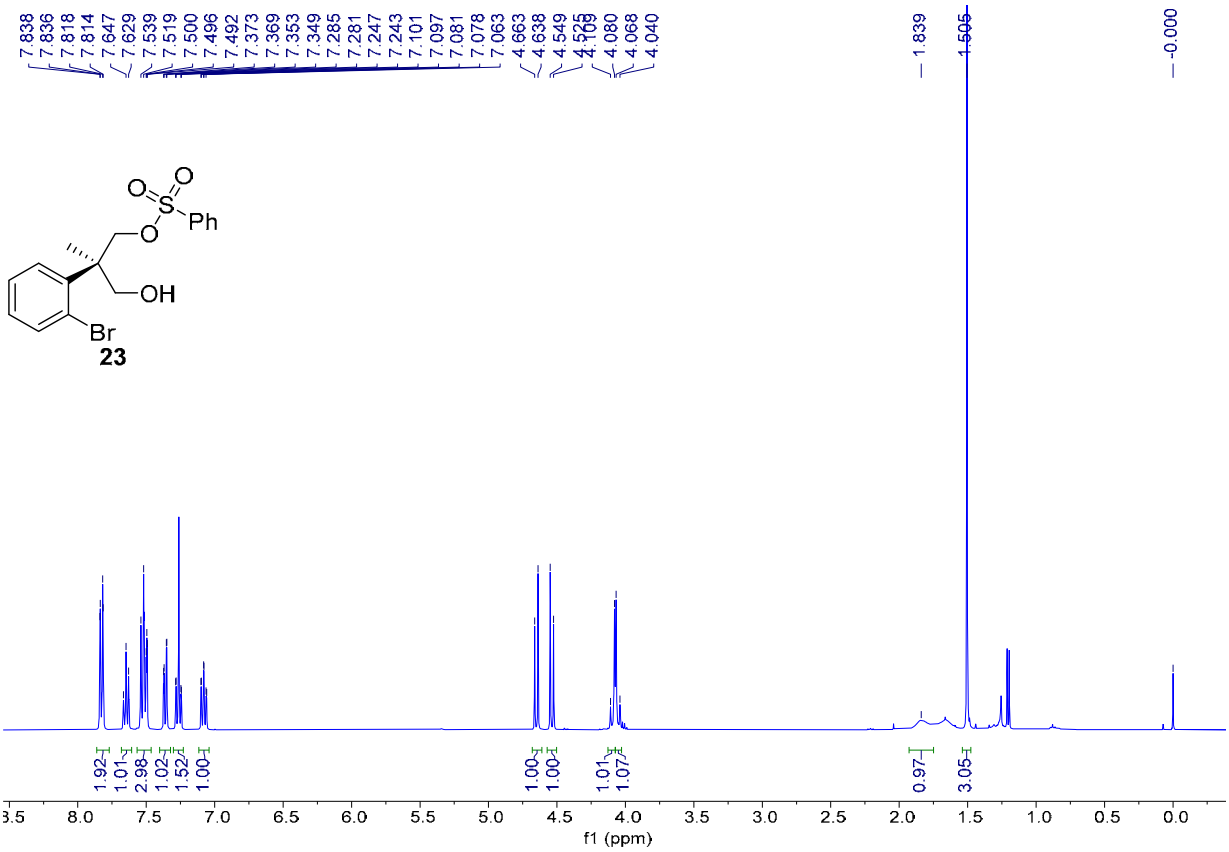

139.974
135.578
135.332
133.778
129.209
128.582
127.869
126.890
126.565
117.684
77.318
77.000
76.683
71.913
65.277
47.240
31.918
25.873
17.938
O
O
S
Ph
O
Ph
OH
19
f1 (ppm)

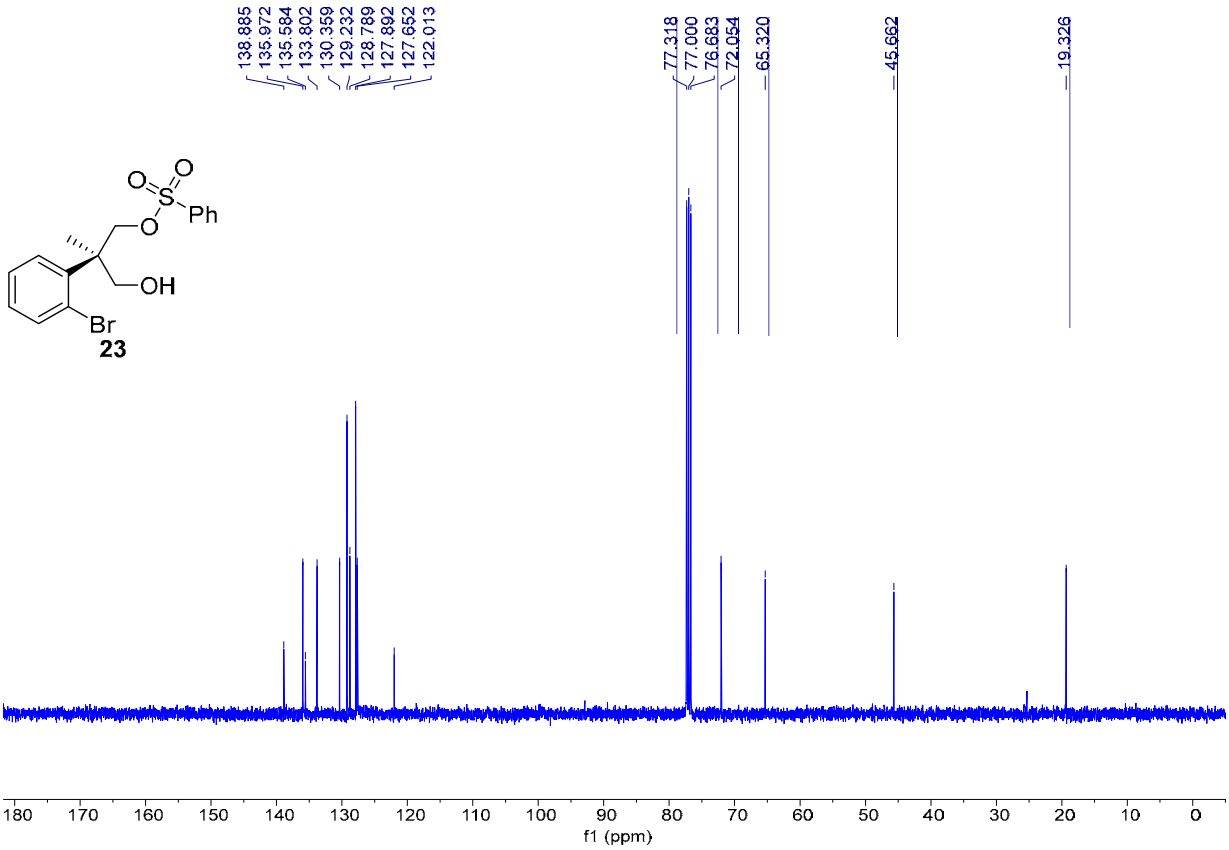

7.862
7.859
7.841
7.838
7.669
7.666
7.663
7.652
7.647
7.642
7.632
7.628
7.625
7.546
7.526
7.507
7.344
7.308
7.306
7.286
7.283
7.247
4.456
4.432
4.395
4.371
3.895
2.701
2.695
2.690
1.846
1.839
1.832
1.788
-0.000
Ph
O
S
O
O
Ph
OH
20
1.94
1.04
2.05
5.30
1.01
1.00
2.04
1.97
1.08
1.03
f1 (ppm)
138.625
135.281
133.840
129.219
128.690
127.966
127.458
126.512
79.397
77.318
77.000
76.682
71.788
71.746
65.585
46.571
23.163
71.788
71.746
72.0
71.9
71.8
71.7
71.6
71.5
71.4
f1 (ppm)
f1 (ppm)

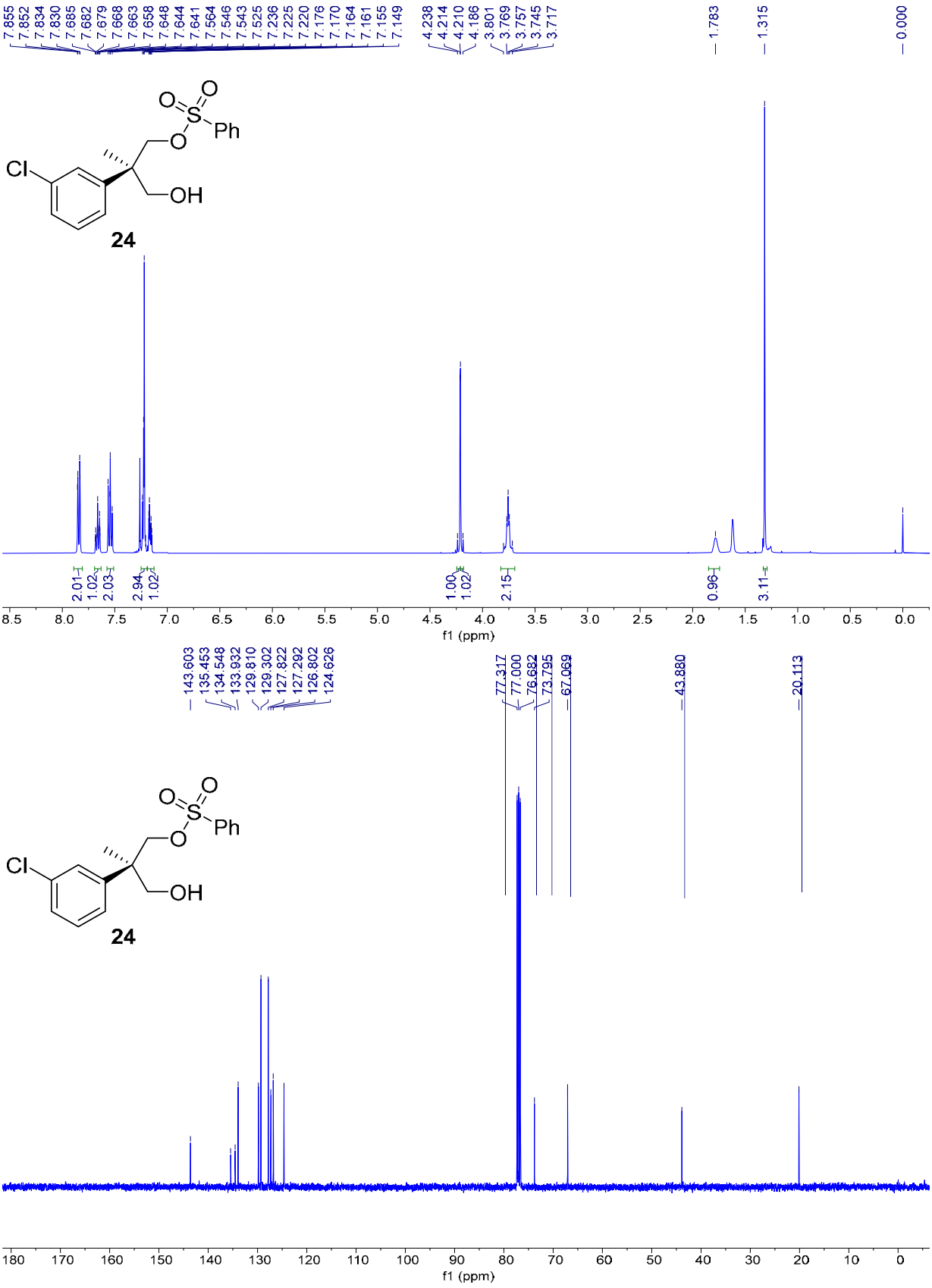

7.845
7.842
7.824
7.820
7.653
7.650
7.647
7.636
7.631
7.626
7.616
7.612
7.609
7.529
7.509
7.491
7.321
7.318
7.304
7.296
7.270
7.253
7.236
7.219
4.424
4.400
4.386
4.362
3.886
3.858
3.850
3.821
2.630
2.624
2.618
2.614
2.608
2.602
1.892
1.608
1.602
1.596
0.000
O
O
S
Ph
O
Ph
OH
21
2.00
1.10
2.10
5.39
1.07
1.00
1.06
1.00
1.92
1.27
3.05
f1 (ppm)
139.156
135.372
133.683
129.104
128.529
127.884
127.172
126.555
79.079
77.318
77.000
76.682
74.021
72.161
65.821
46.659
23.484
3.378
O
O
S
Ph
O
Ph
OH
21
f1 (ppm)

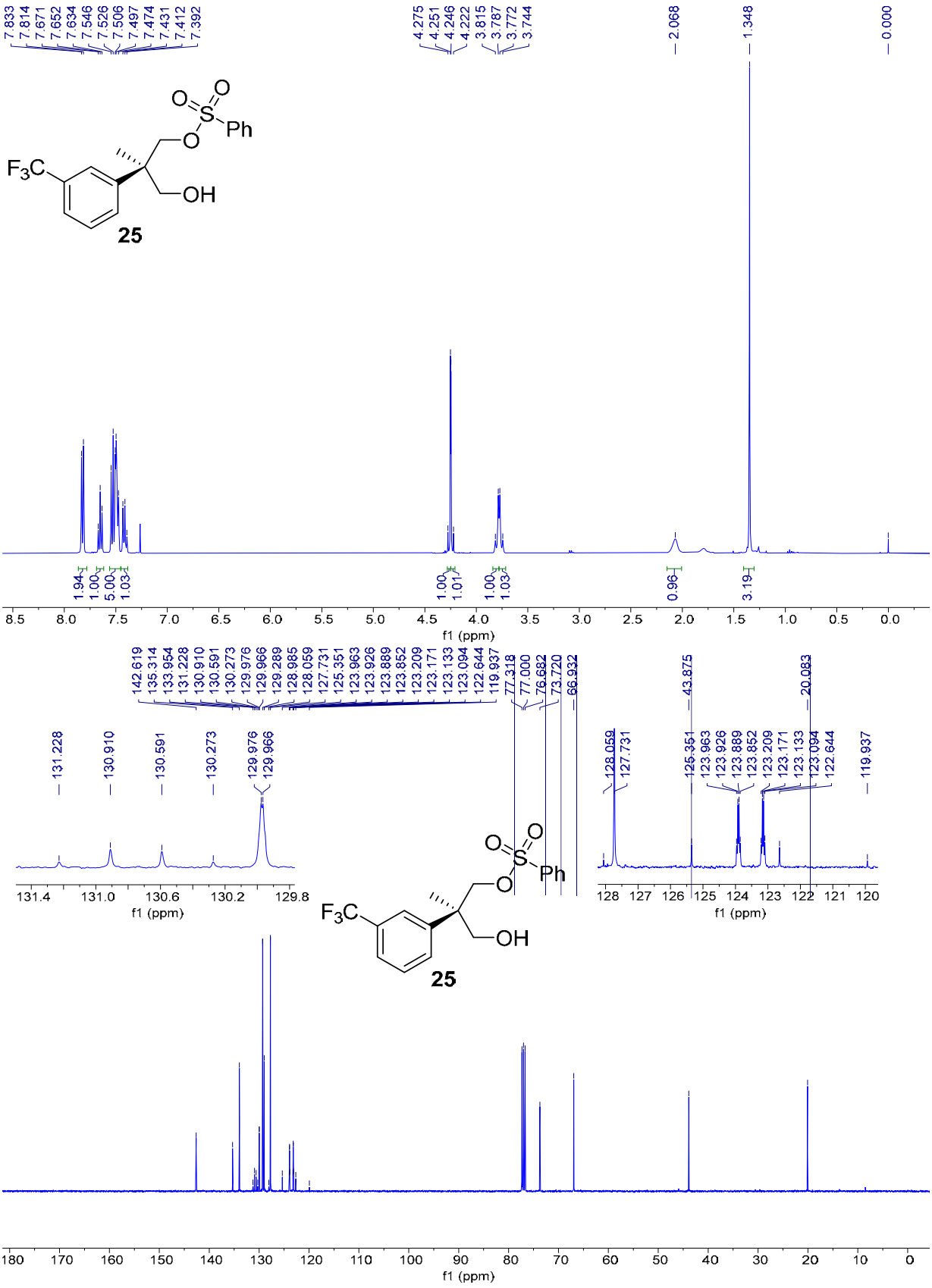

22
f1 (ppm)
22
f1 (ppm)

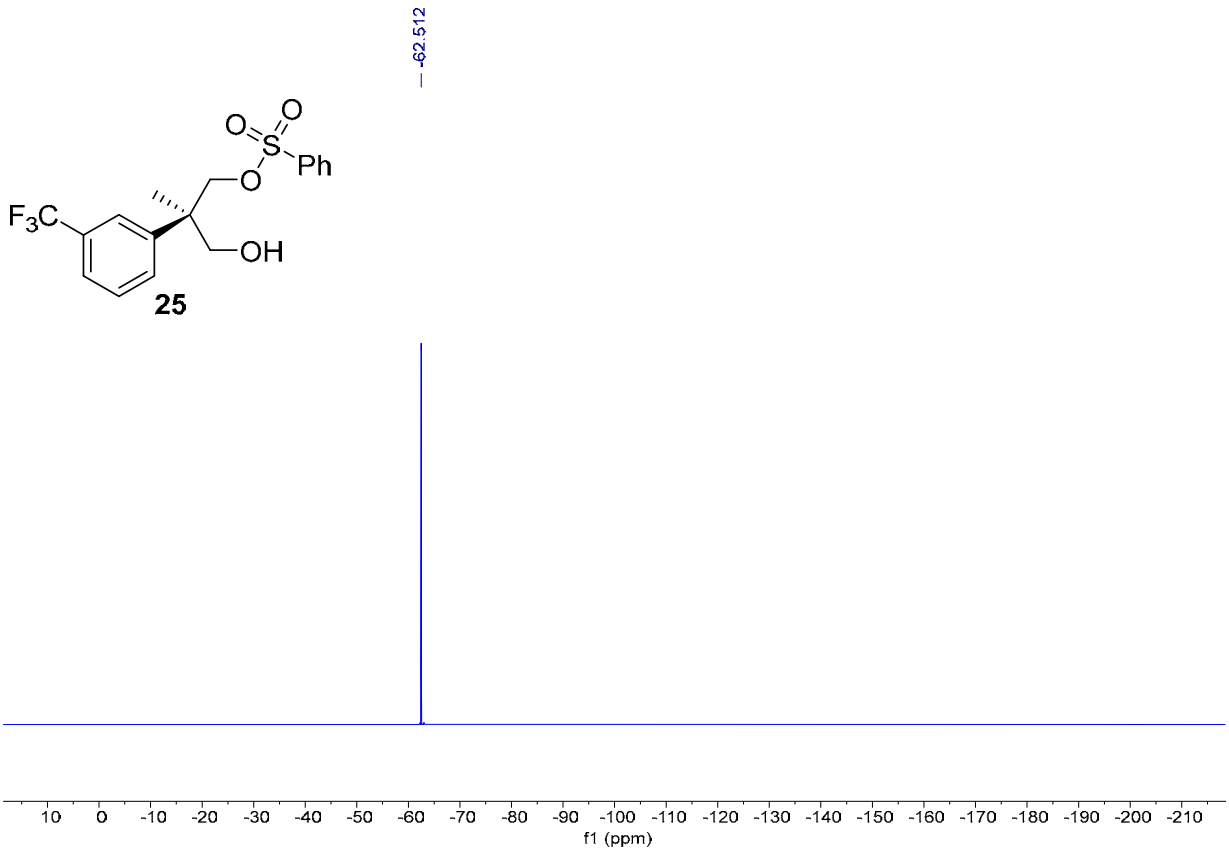

-112.180
O
O
S
Ph
O
F
OH
22
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

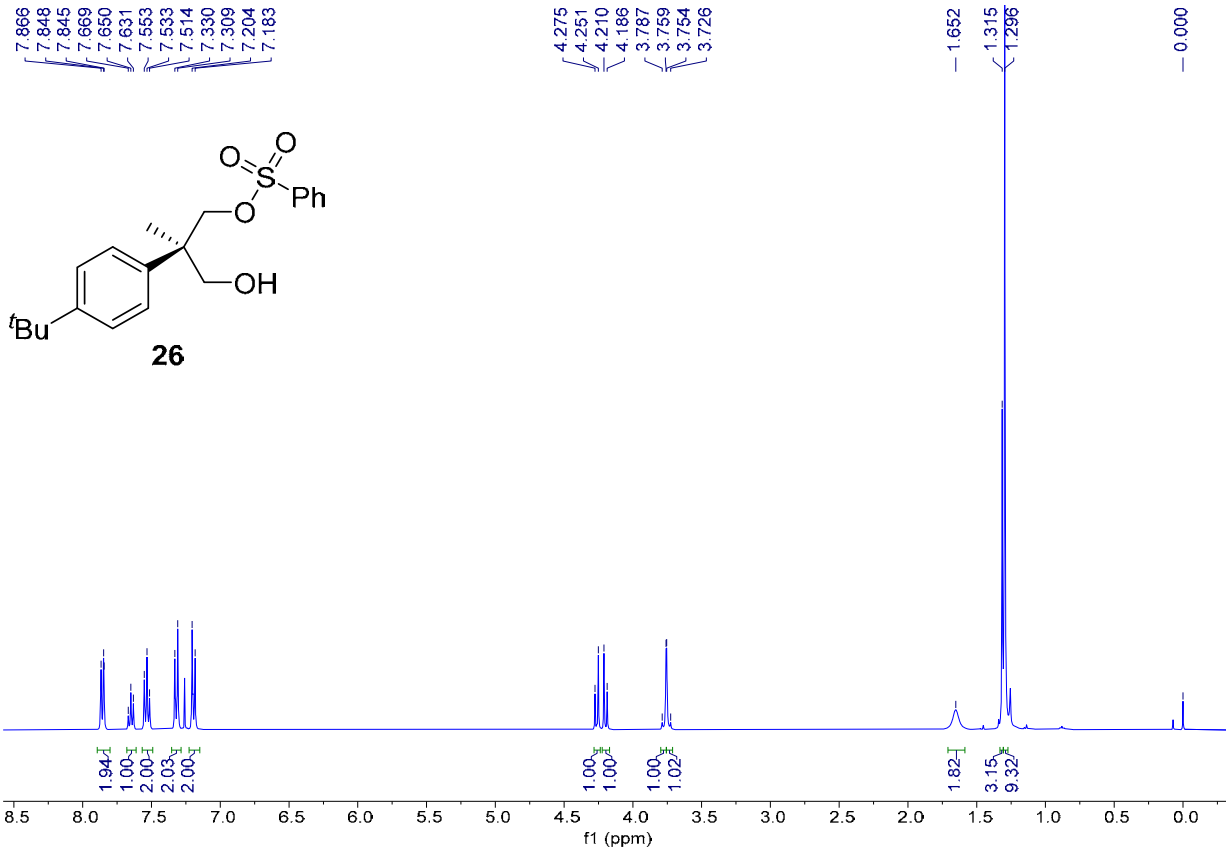

7.838
7.836
7.818
7.814
7.647
7.629
7.539
7.519
7.500
7.496
7.492
7.373
7.369
7.353
7.349
7.285
7.281
7.247
7.243
7.101
7.097
7.081
7.078
7.063
4.663
4.638
4.549
4.525
4.109
4.080
4.068
4.040
1.839
1.505
-0.000
O
O
S
Ph
O
OH
Br
23
1.92
1.01
2.98
1.02
1.52
1.00
1.00
1.00
1.01
1.07
0.97
3.05
f1 (ppm)

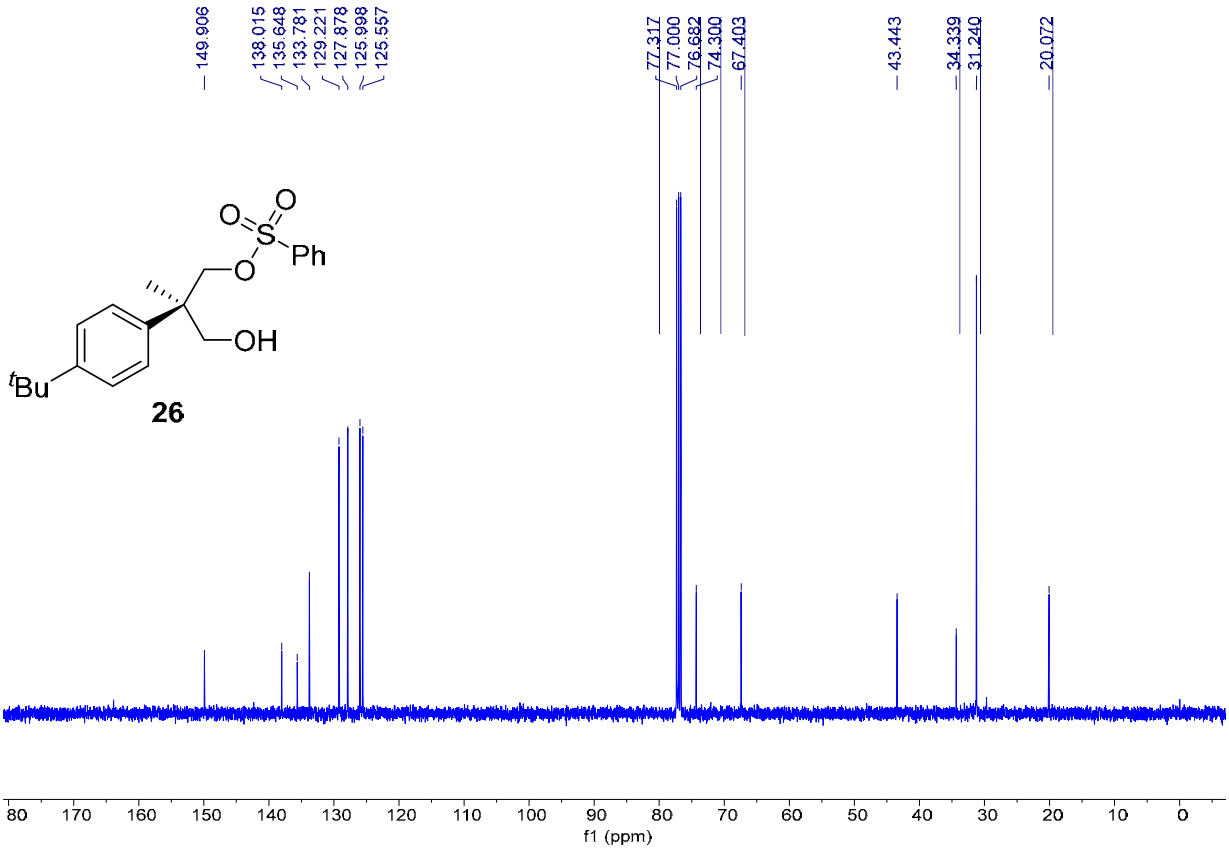

138.885
135.972
135.584
133.802
130.359
129.232
128.789
127.892
127.652
122.013
77.318
77.000
76.683
72.054
65.320
45.662
19.326
O
O
S
Ph
O
OH
Br
23
f1 (ppm)

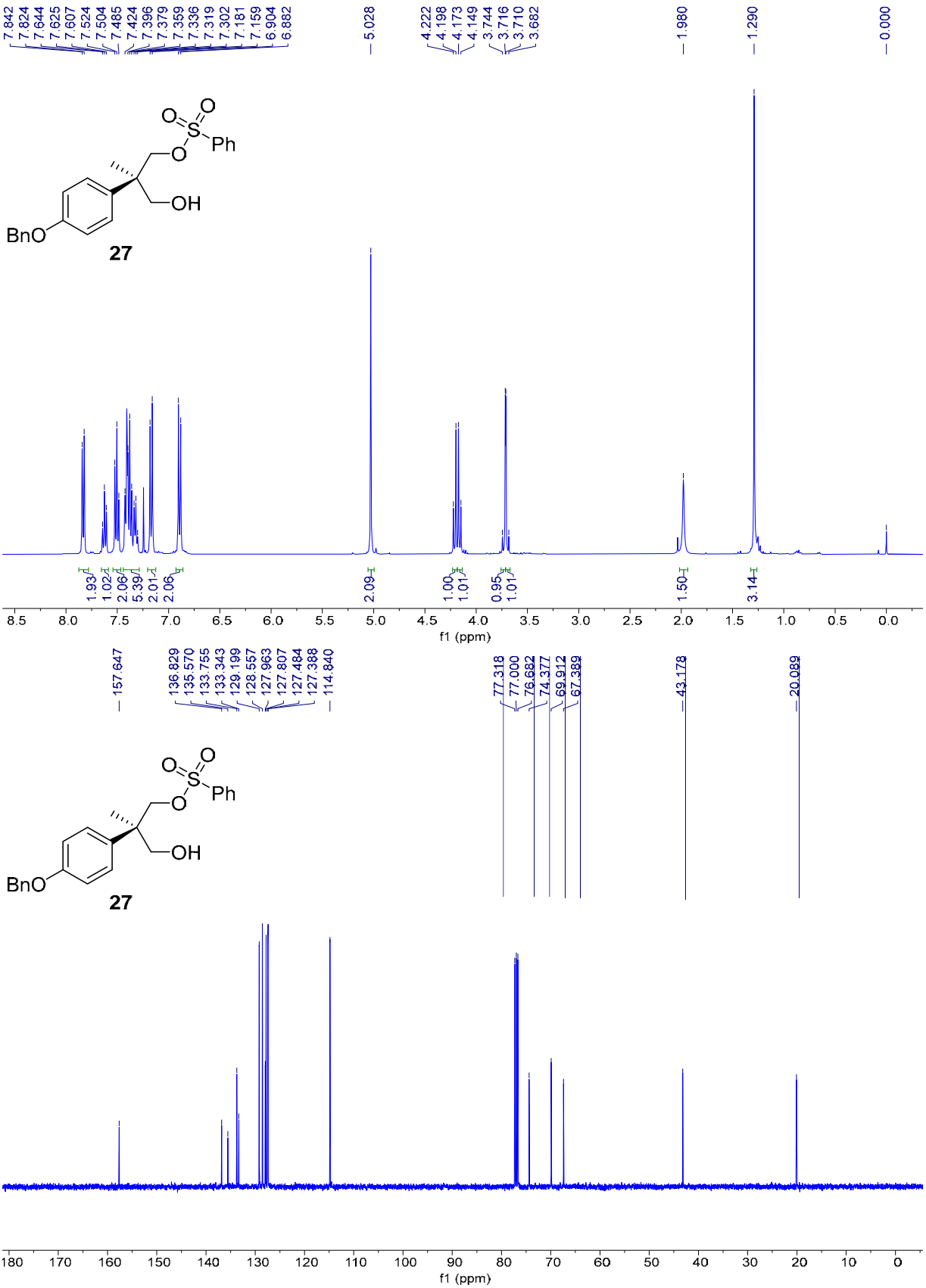

7.855
7.852
7.834
7.830
7.685
7.682
7.679
7.668
7.663
7.658
7.648
7.644
7.641
7.564
7.546
7.543
7.525
7.236
7.225
7.220
7.176
7.170
7.164
7.161
7.155
7.149
4.238
4.214
4.210
4.186
3.801
3.769
3.757
3.745
3.717
1.783
1.315
0.000
O
O
S
Ph
O
Cl
OH
24
2.01
1.02
2.03
2.94
1.02
1.00
1.02
2.15
0.96
3.11
f1 (ppm)
143.603
135.453
134.548
133.932
129.810
129.302
127.822
127.292
126.802
124.626
77.317
77.000
76.682
73.795
67.069
43.880
20.113
f1 (ppm)

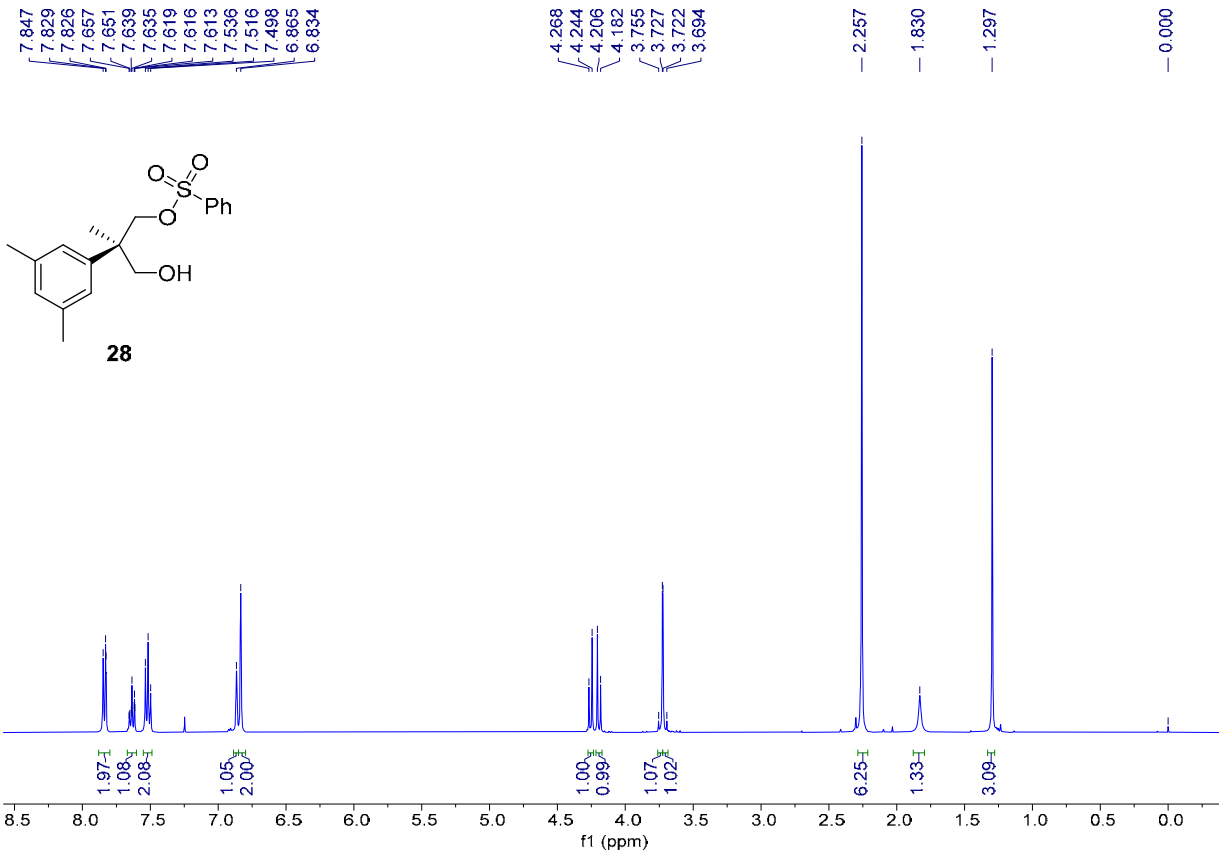

7.833
7.814
7.671
7.652
7.634
7.546
7.526
7.506
7.497
7.474
7.431
7.412
7.392
4.275
4.251
4.246
4.222
3.815
3.787
3.772
3.744
2.068
1.348
0.000
O
O
S
Ph
O
F3C
OH
25
1.94
1.00
5.00
1.03
1.00
1.01
1.00
1.03
0.96
3.19
f1 (ppm)
142.619
135.314
133.954
131.228
130.910
130.591
130.273
129.976
129.966
129.289
128.985
128.059
127.731
125.351
123.963
123.926
123.889
123.852
123.209
123.171
123.133
123.094
122.644
119.937
77.318
77.000
76.682
73.720
66.932
43.875
20.083
131.228
130.910
130.591
130.273
129.976
129.966
131.4
131.0
130.6
130.2
129.8
128.059
127.731
126.351
123.963
123.926
123.889
123.852
123.209
123.171
123.133
123.094
122.644
119.937
128
127
126
125
124
123
122
121
120
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

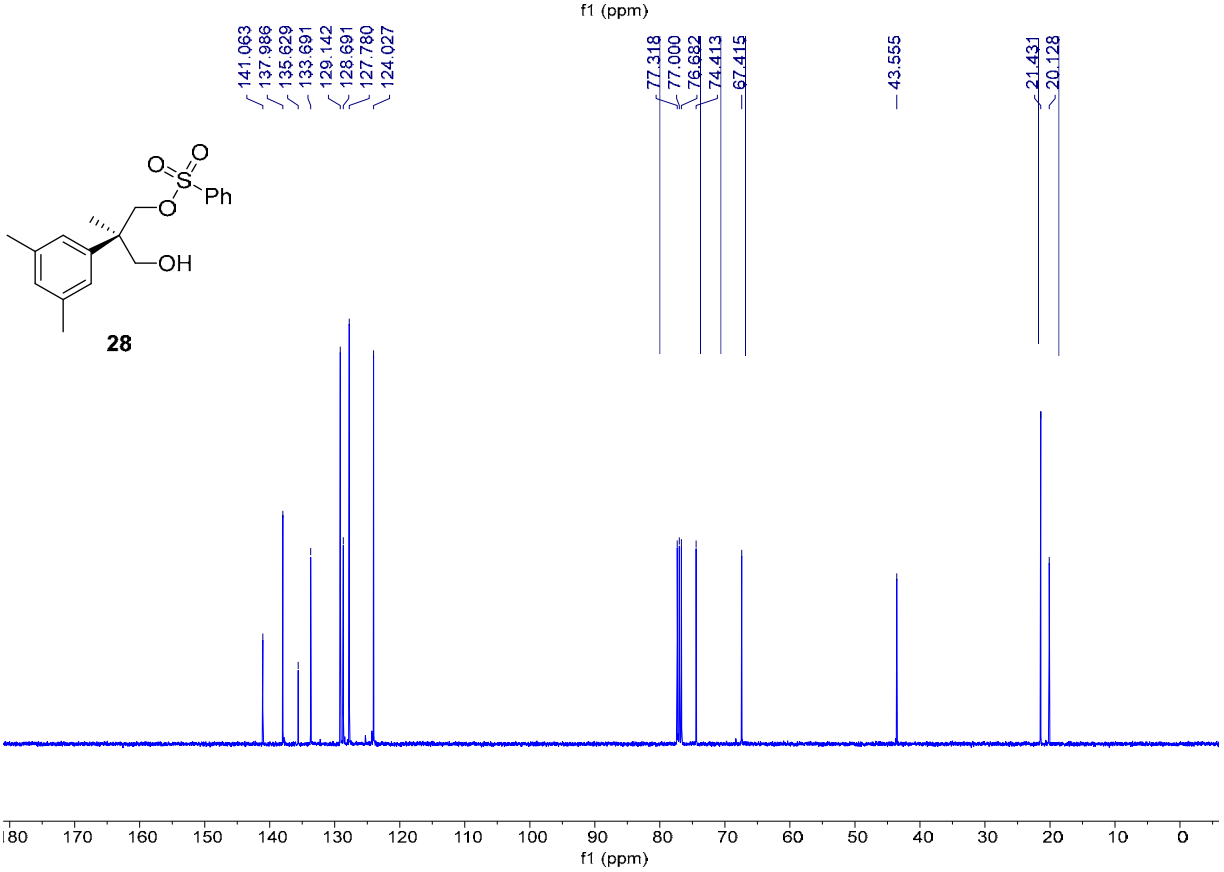

-62.512
O
O
S
Ph
O
F3C
OH
25
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

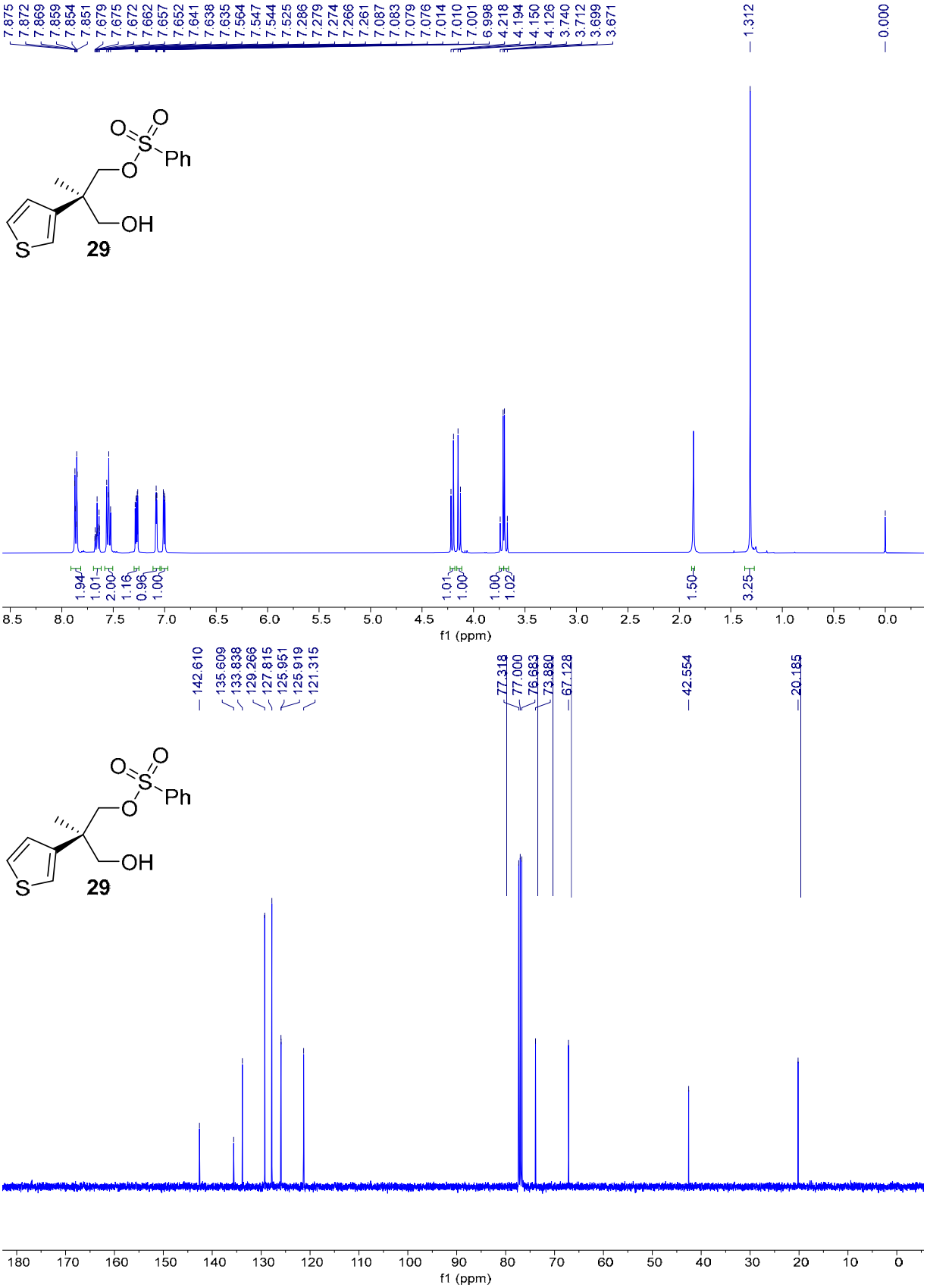

7.866
7.848
7.845
7.669
7.650
7.631
7.553
7.533
7.514
7.330
7.309
7.204
7.183
4.275
4.251
4.210
4.186
3.787
3.759
3.754
3.726
1.652
1.315
1.296
0.000
O
O
S
Ph
O
OH
tBu
26
1.94
1.00
2.00
2.03
2.00
1.00
1.00
1.02
1.82
3.15
9.32
f1 (ppm)

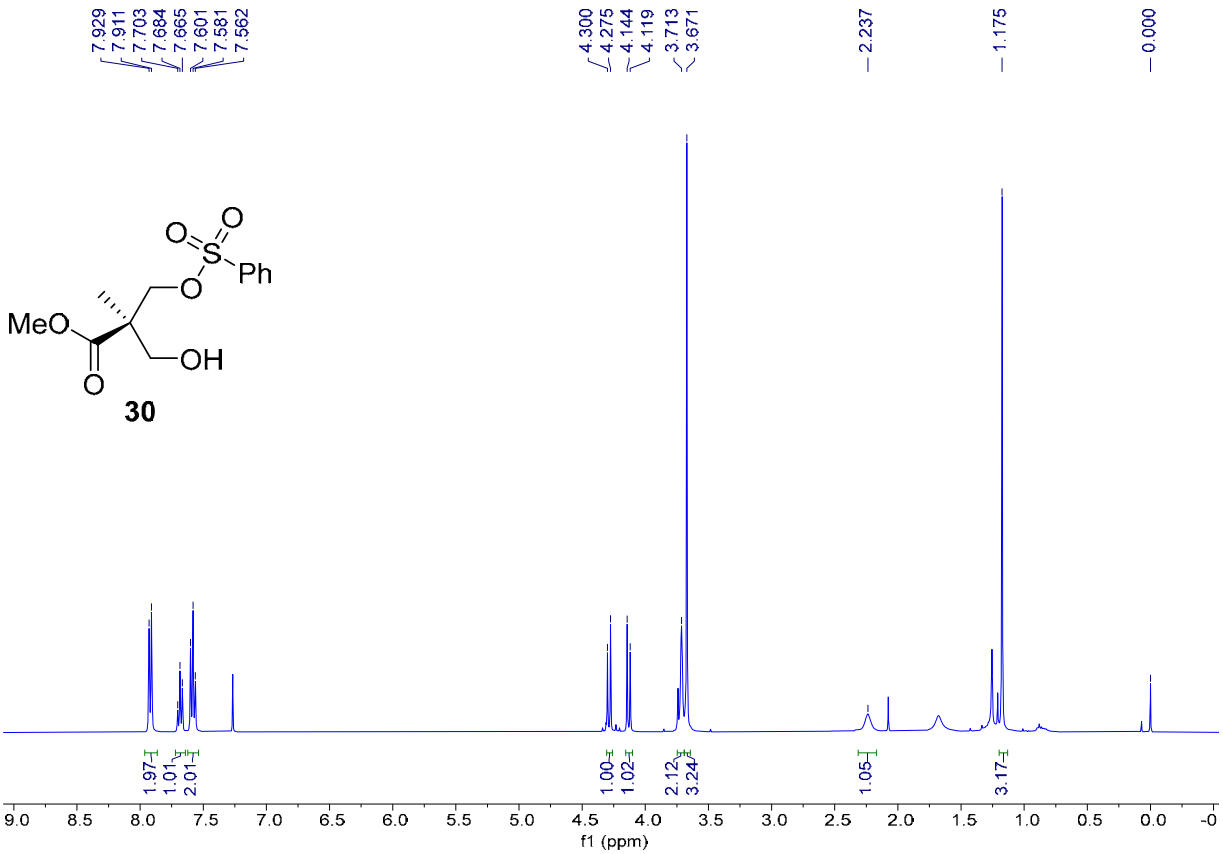

149.906
138.015
135.648
133.781
129.221
127.878
125.998
125.557
77.317
77.000
76.682
74.300
67.403
43.443
34.339
31.240
20.072
O
O
S
Ph
O
OH
tBu
26
f1 (ppm)

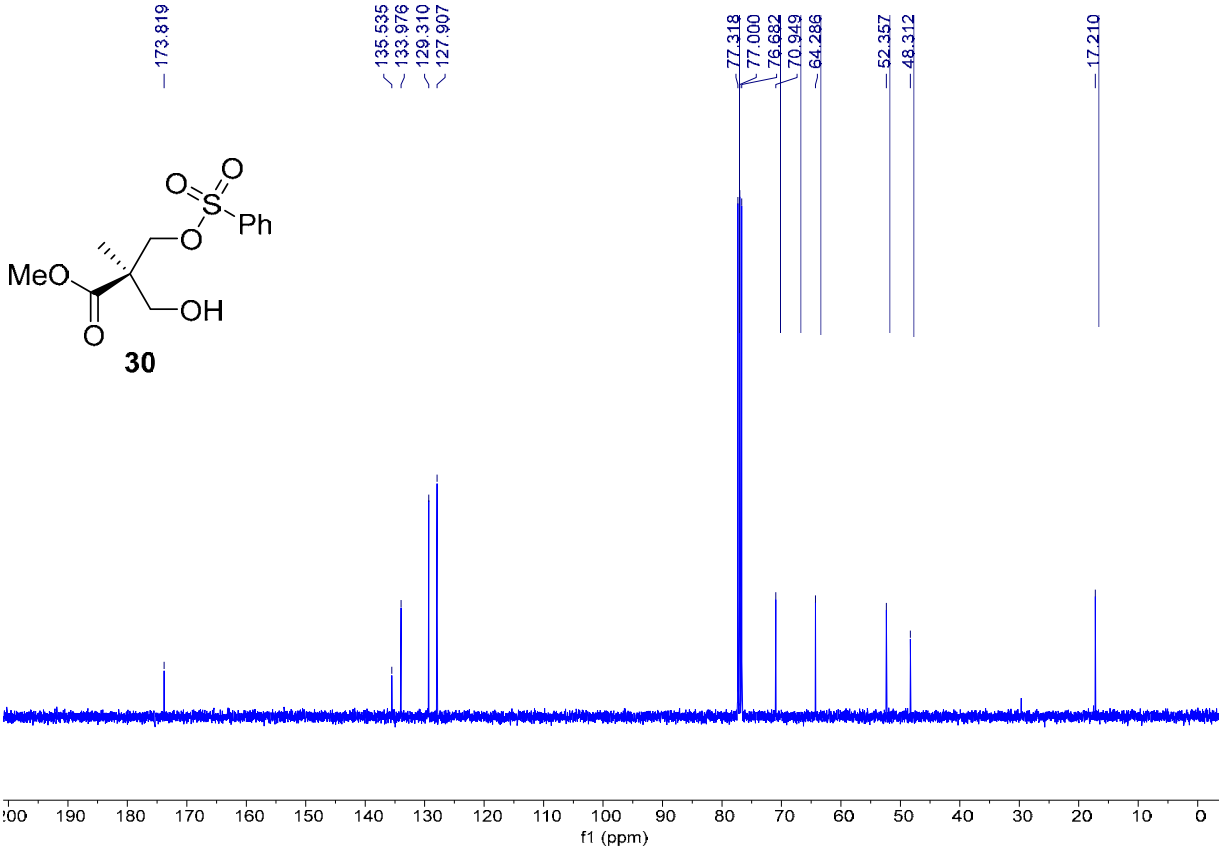

7.842
7.824
7.644
7.625
7.607
7.524
7.504
7.485
7.424
7.396
7.379
7.359
7.336
7.319
7.302
7.181
7.159
6.904
6.882
5.028
4.222
4.198
4.173
4.149
3.744
3.716
3.710
3.682
1.980
1.290
0.000
O
O
S
Ph
O
OH
BnO
27
1.93
1.02
2.06
5.39
2.01
2.06
2.09
1.00
1.01
0.95
1.01
1.50
3.14
f1 (ppm)
157.647
136.829
135.570
133.755
133.343
129.199
128.557
127.963
127.807
127.484
127.388
114.840
77.318
77.000
76.682
74.377
69.912
67.389
43.178
20.089
f1 (ppm)


7.847
7.829
7.826
7.657
7.651
7.639
7.635
7.619
7.616
7.613
7.536
7.516
7.498
6.865
6.834
4.268
4.244
4.206
4.182
3.755
3.727
3.722
3.694
2.257
1.830
1.297
0.000
O
O
S
Ph
O
OH
28
1.97
1.08
2.08
1.05
2.00
1.00
0.99
1.07
1.02
6.25
1.33
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.063
137.986
135.629
133.691
129.142
128.691
127.780
124.027
77.318
77.000
76.682
74.413
67.415
43.555
21.431
20.128
O
O
S
Ph
O
OH
28
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.875
7.872
7.869
7.859
7.854
7.851
7.679
7.675
7.672
7.662
7.657
7.652
7.641
7.638
7.635
7.564
7.547
7.544
7.525
7.286
7.279
7.274
7.266
7.261
7.087
7.083
7.079
7.076
7.014
7.010
7.001
6.998
4.218
4.194
4.150
4.126
3.740
3.712
3.699
3.671
1.312
0.000
O
O
S
Ph
O
OH
S
29
1.94
1.01
2.00
1.16
0.96
1.00
1.01
1.00
1.00
1.02
1.50
3.25
f1 (ppm)
142.610
135.609
133.838
129.266
127.815
125.951
125.919
121.315
77.318
77.000
76.683
73.880
67.128
42.554
20.185
f1 (ppm)


7.929
7.911
7.703
7.684
7.665
7.601
7.581
7.562
4.300
4.275
4.144
4.119
3.713
3.671
2.237
1.175
0.000
MeO
O
O
S
O
Ph
OH
O
30
1.97
1.01
2.01
1.00
1.02
2.12
3.24
1.05
3.17
f1 (ppm)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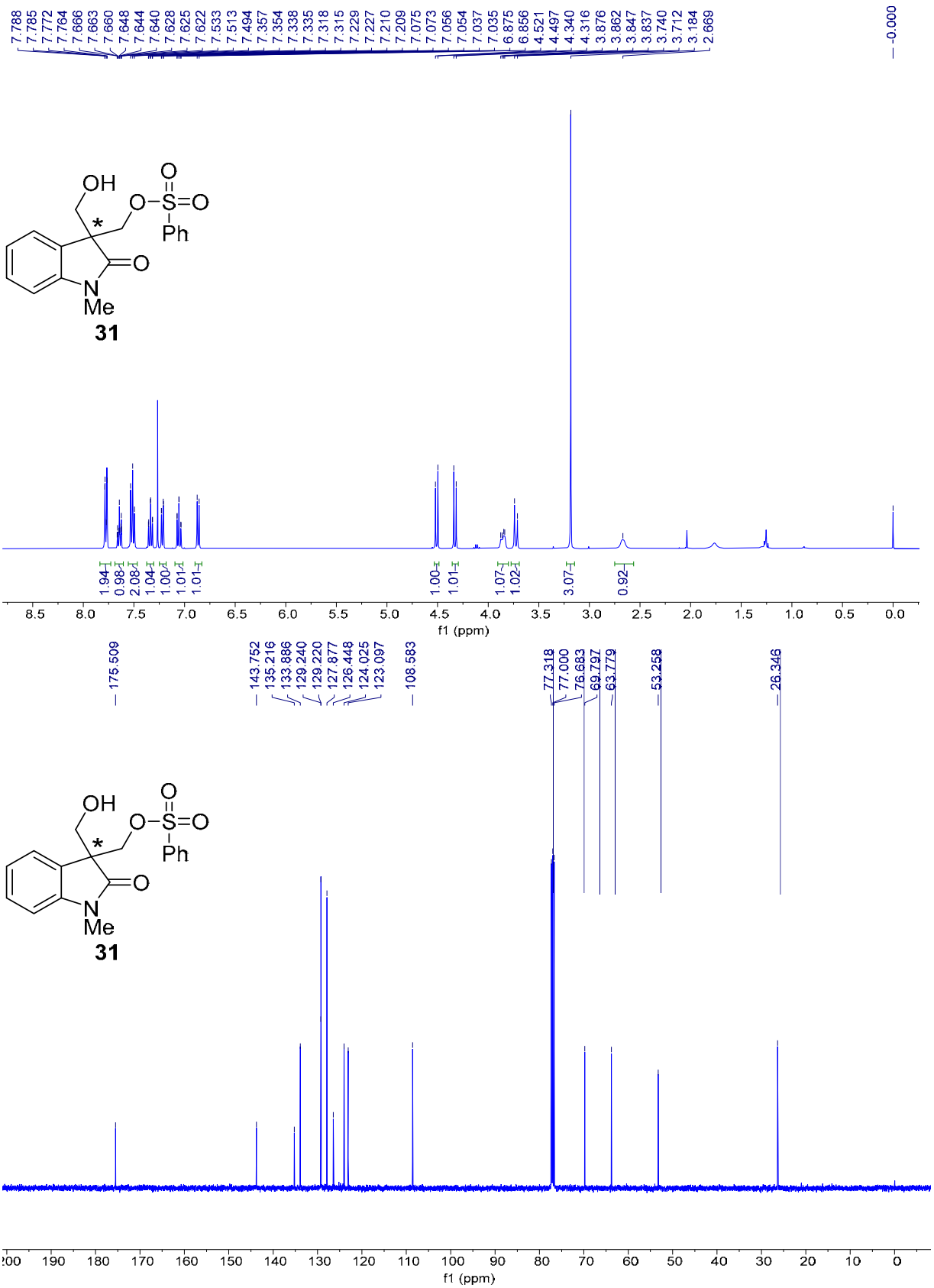
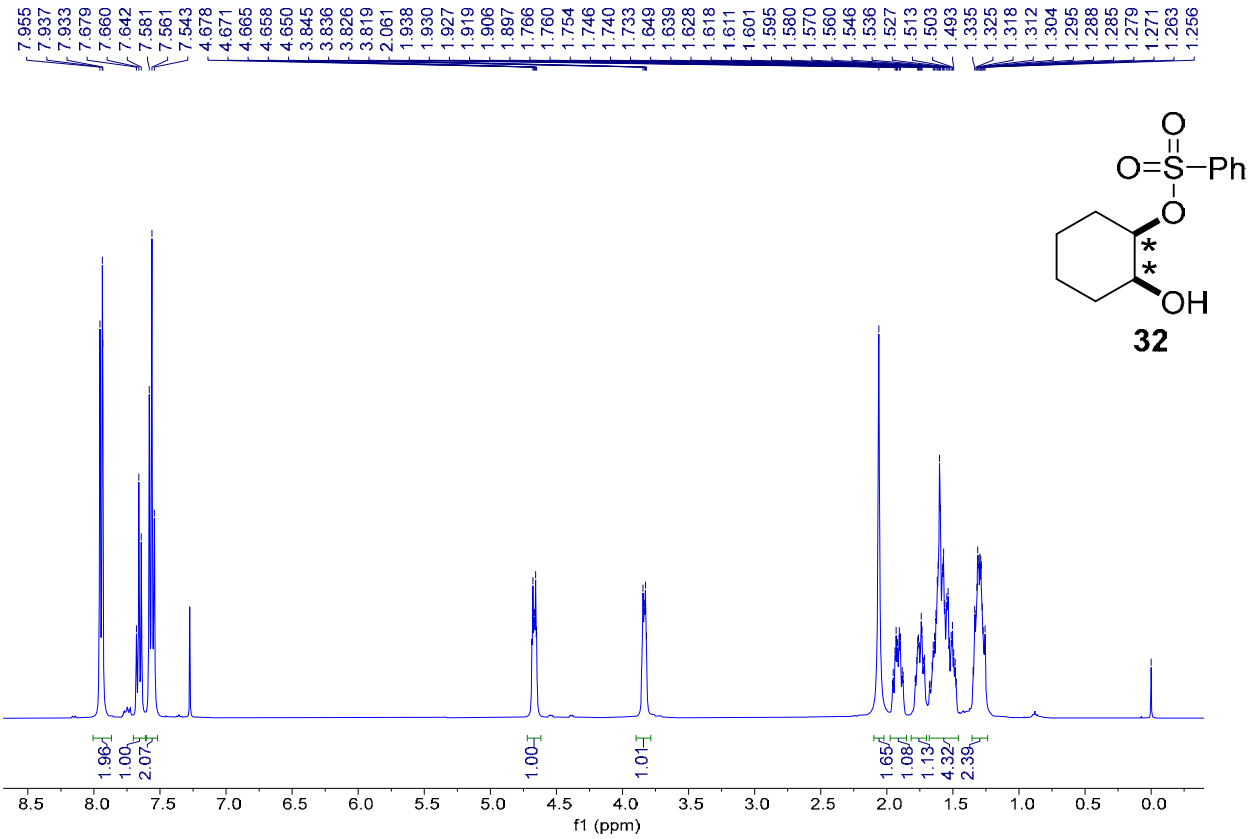
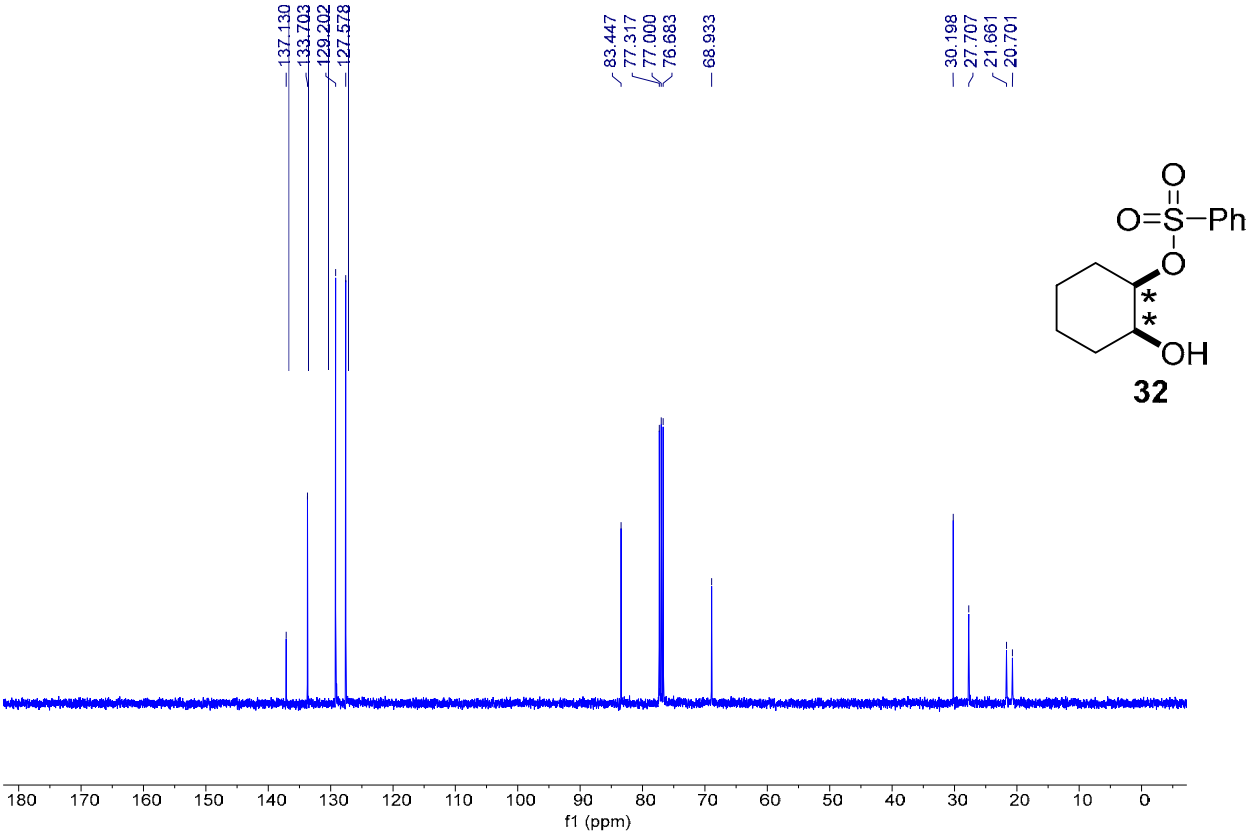
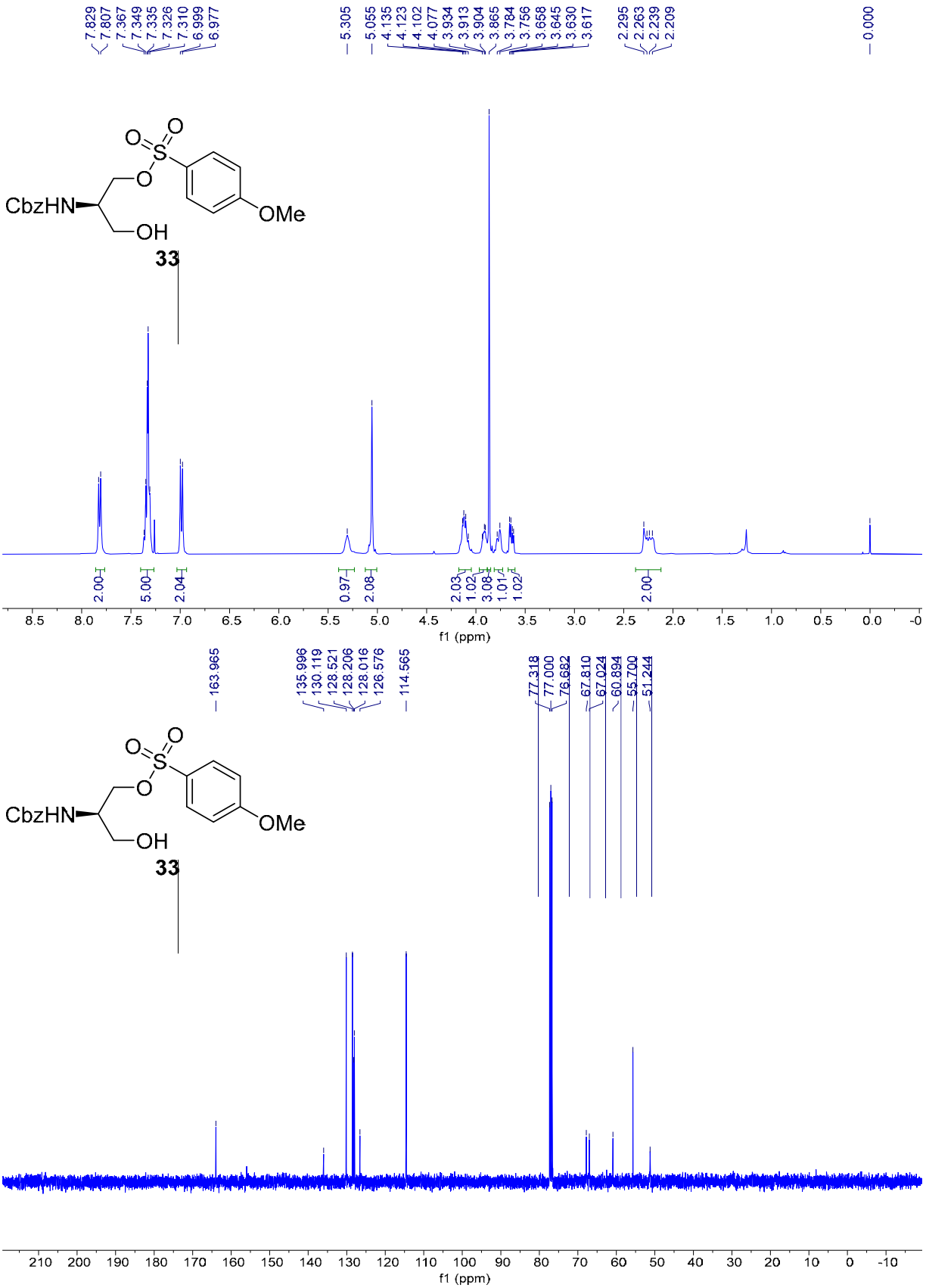
135.535
133.976
129.310
127.907
77.318
77.000
76.682
70.949
64.286
52.357
48.312
17.210
MeO
O
O
S
O
Ph
OH
O
30
f1 (ppm)


7.788
7.785
7.772
7.764
7.666
7.663
7.660
7.648
7.644
7.640
7.628
7.625
7.622
7.533
7.513
7.494
7.357
7.354
7.338
7.335
7.318
7.315
7.229
7.227
7.210
7.209
7.075
7.073
7.056
7.054
7.037
7.035
6.875
6.856
4.521
4.497
4.340
4.316
3.876
3.862
3.847
3.837
3.740
3.712
3.184
2.669
-0.000
OH
O
O–S=O
Ph
*
O
N
Me
31
1.94
0.98
2.08
1.04
1.00
1.01
1.01
1.00
1.01
1.07
1.02
3.07
0.92
f1 (ppm)
175.509
143.752
135.216
133.886
129.240
129.220
127.877
126.448
124.025
123.097
108.583
77.318
77.000
76.683
69.797
63.779
53.258
26.346
f1 (ppm)


7.955
7.937
7.933
7.679
7.660
7.642
7.581
7.561
7.543
4.678
4.671
4.665
4.658
4.650
3.845
3.836
3.826
3.819
2.061
1.938
1.930
1.927
1.919
1.906
1.897
1.766
1.760
1.754
1.746
1.740
1.733
1.649
1.639
1.628
1.618
1.611
1.601
1.595
1.580
1.570
1.560
1.546
1.536
1.527
1.513
1.503
1.493
1.335
1.325
1.318
1.312
1.304
1.295
1.288
1.285
1.279
1.271
1.263
1.256
O
O=S–Ph
O
*
*
OH
32
1.96
1.00
2.07
1.00
1.01
1.65
1.08
1.13
4.32
2.39
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.130
133.703
129.202
127.578
83.447
77.317
77.000
76.683
68.933
30.198
27.707
21.661
20.701
O
O=S–Ph
O
*
*
OH
32
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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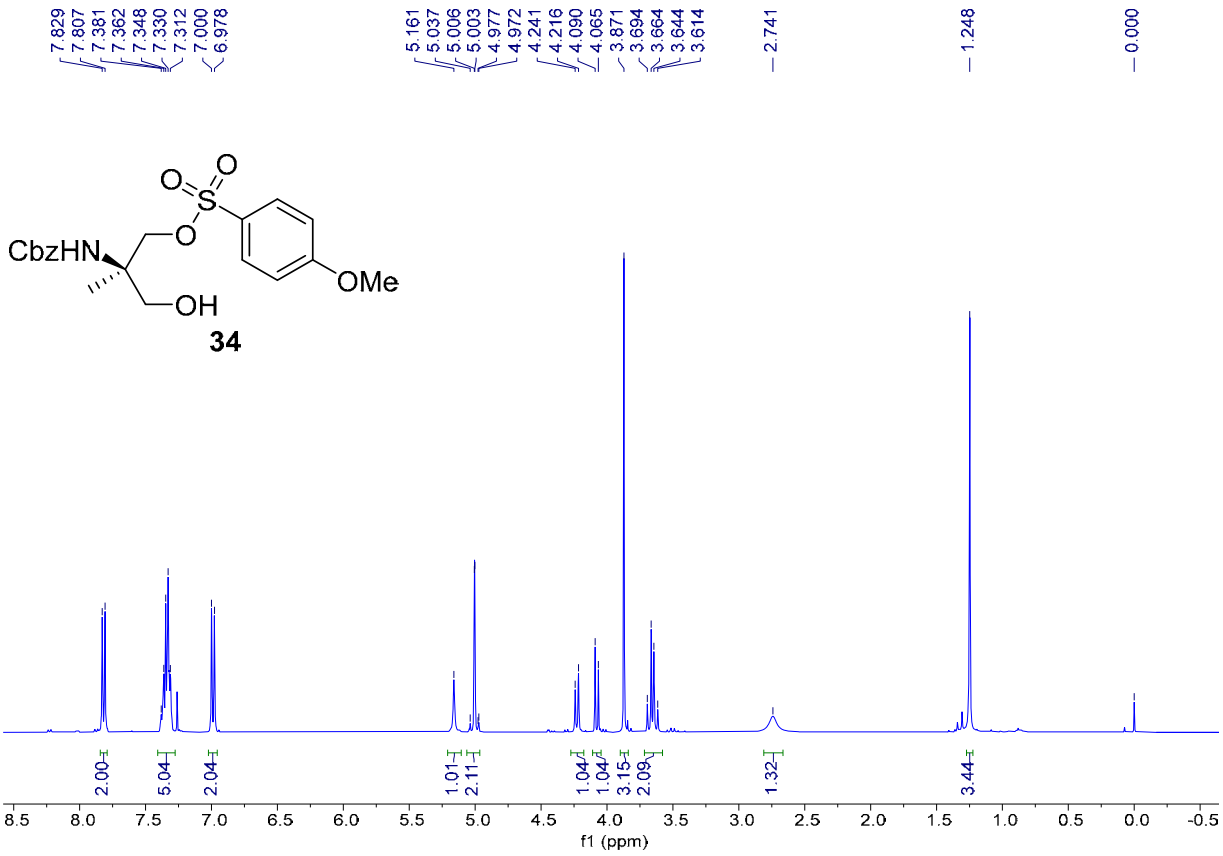
7.807
7.367
7.349
7.335
7.326
7.310
6.999
6.977
5.305
5.055
4.135
4.123
4.102
4.077
3.934
3.913
3.904
3.865
3.784
3.756
3.658
3.645
3.630
3.617
2.295
2.263
2.239
2.209
0.000
CbzHN
OH
OMe
33
2.00
5.00
2.04
0.97
2.08
2.03
1.02
3.08
1.01
1.02
2.00
f1 (ppm)
163.965
135.996
130.119
128.521
128.206
128.016
126.576
114.565
77.318
77.000
76.682
67.810
67.024
60.894
55.700
51.244
CbzHN
OH
OMe
33
f1 (ppm)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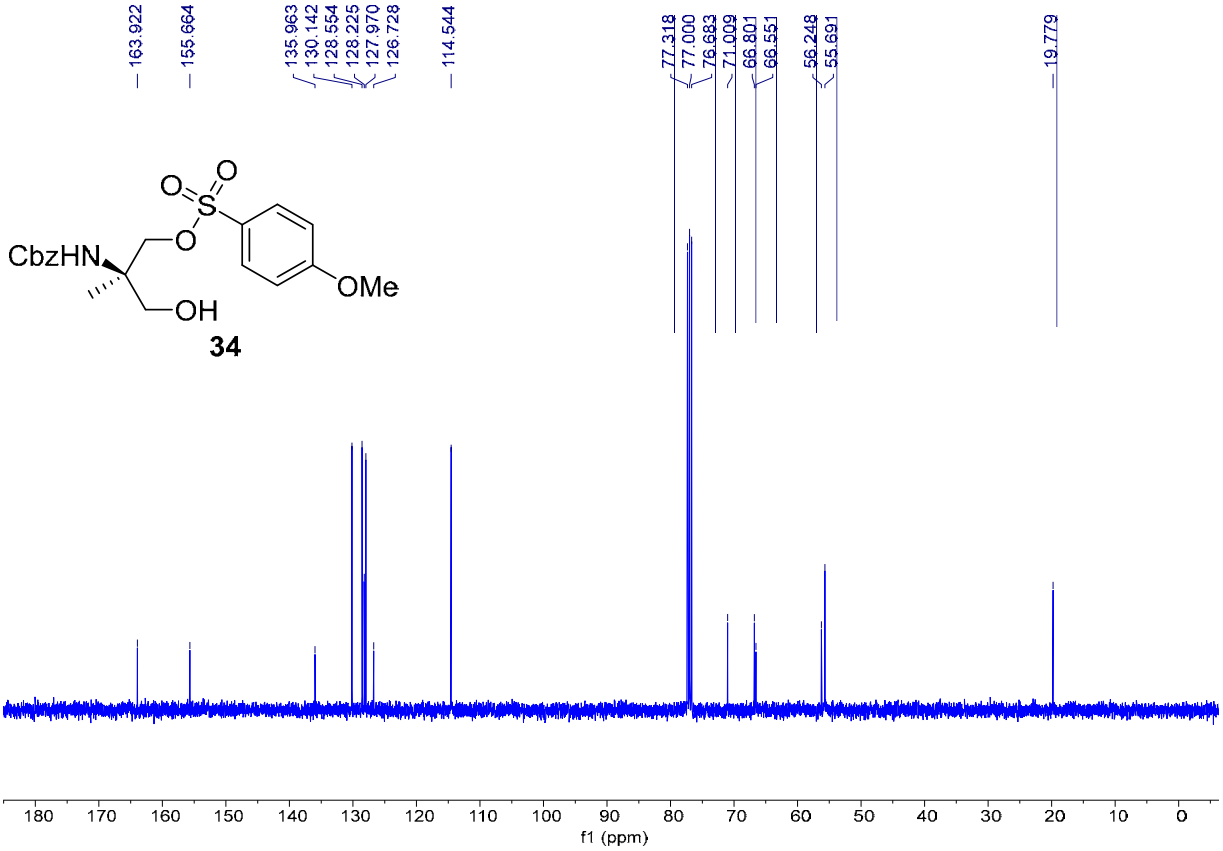
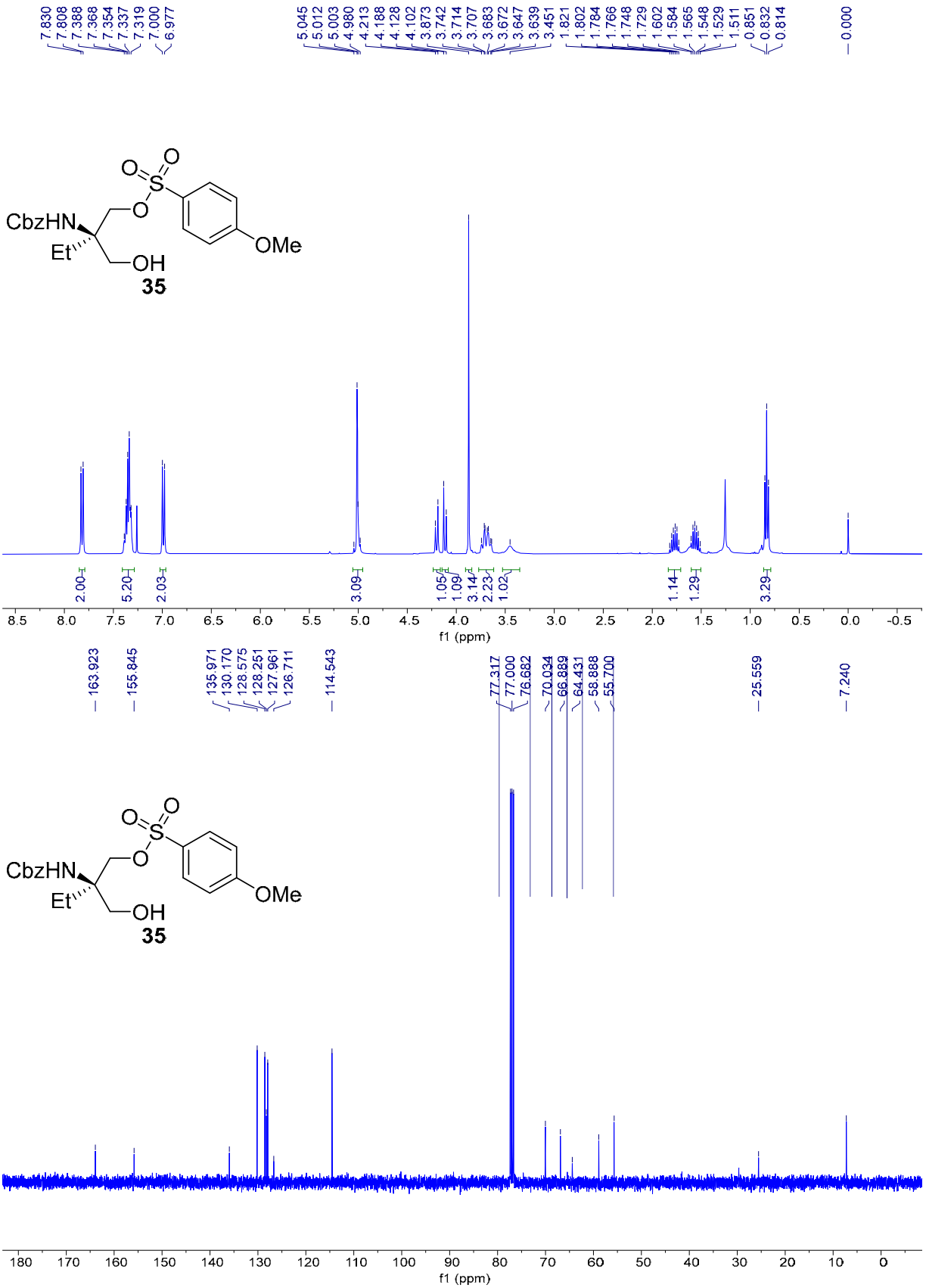
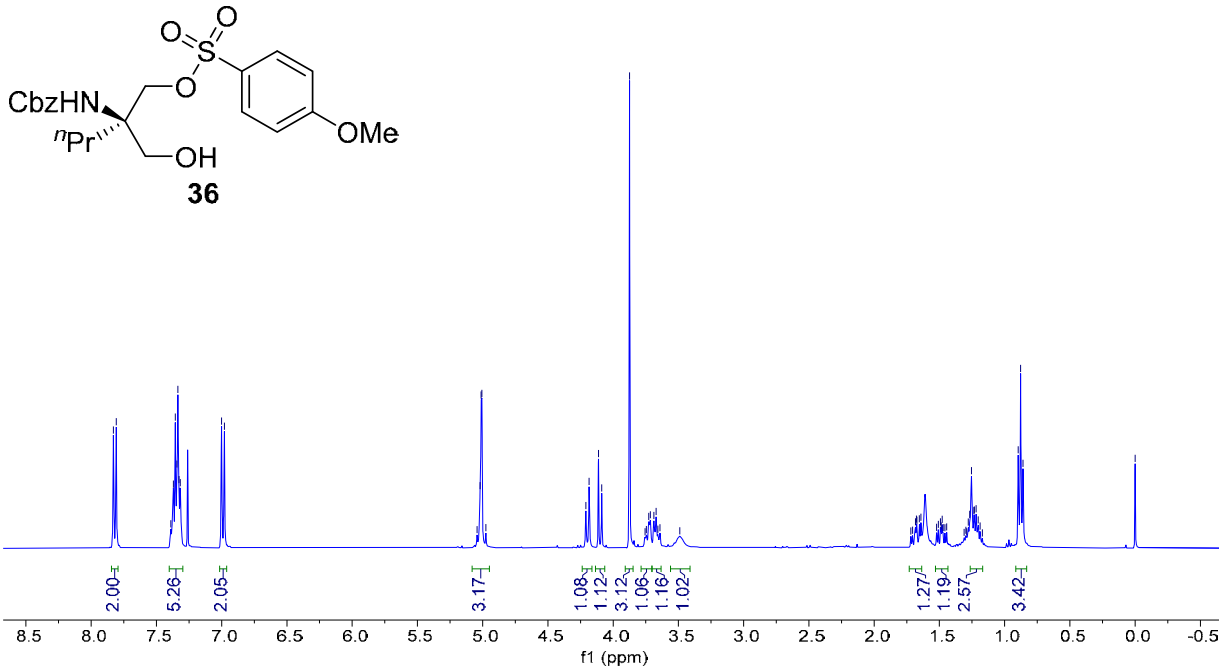
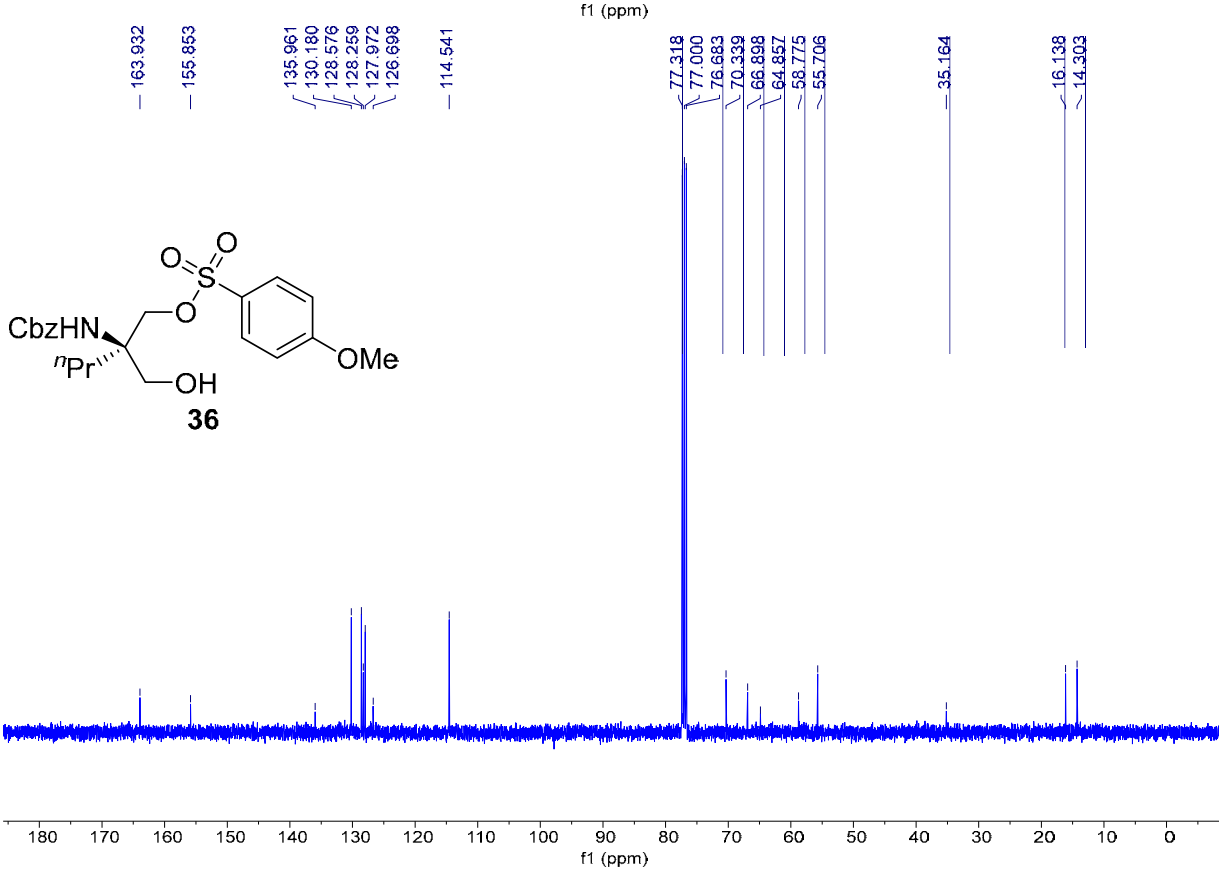
7.807
7.381
7.362
7.348
7.330
7.312
7.000
6.978
5.161
5.037
5.006
5.003
4.977
4.972
4.241
4.216
4.090
4.065
3.871
3.694
3.664
3.644
3.614
2.741
1.248
0.000
CbzHN
OH
OMe
34
2.00
5.04
2.04
1.01
2.11
1.04
1.04
3.15
2.09
1.32
3.44
f1 (ppm)


163.922
155.664
135.963
130.142
128.554
128.225
127.970
126.728
114.544
77.318
77.000
76.683
71.009
66.801
66.551
56.248
55.691
19.779
CbzHN
OH
OMe
34
f1 (ppm)

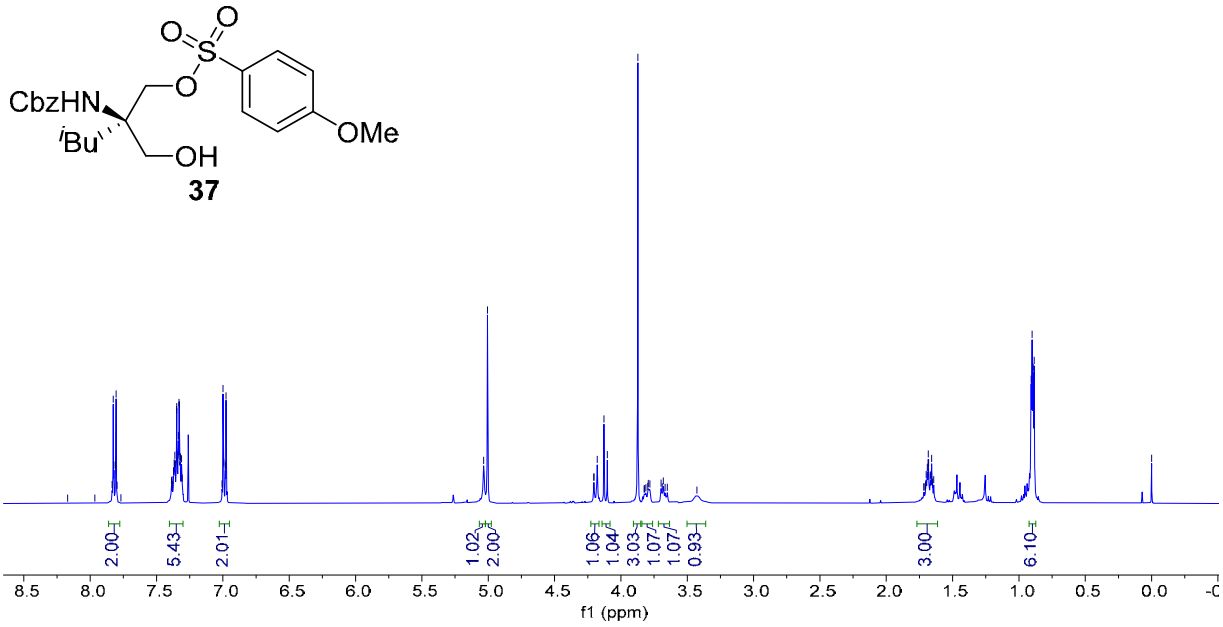

7.830
7.808
7.388
7.368
7.354
7.337
7.319
7.000
6.977
5.045
5.012
5.003
4.980
4.213
4.188
4.128
4.102
3.873
3.742
3.714
3.707
3.683
3.672
3.647
3.639
3.451
1.821
1.802
1.784
1.766
1.748
1.729
1.602
1.584
1.565
1.548
1.529
1.511
0.851
0.832
0.814
0.000
CbzHN
Et
OH
OMe
35
2.00
5.20
2.03
3.09
1.05
1.09
3.14
2.23
1.02
1.14
1.29
3.29
f1 (ppm)
163.923
155.845
135.971
130.170
128.575
128.251
127.961
126.711
114.543
77.317
77.000
76.682
70.034
66.889
64.431
58.888
55.700
25.559
7.240
CbzHN
Et
OH
OMe
35
f1 (ppm)

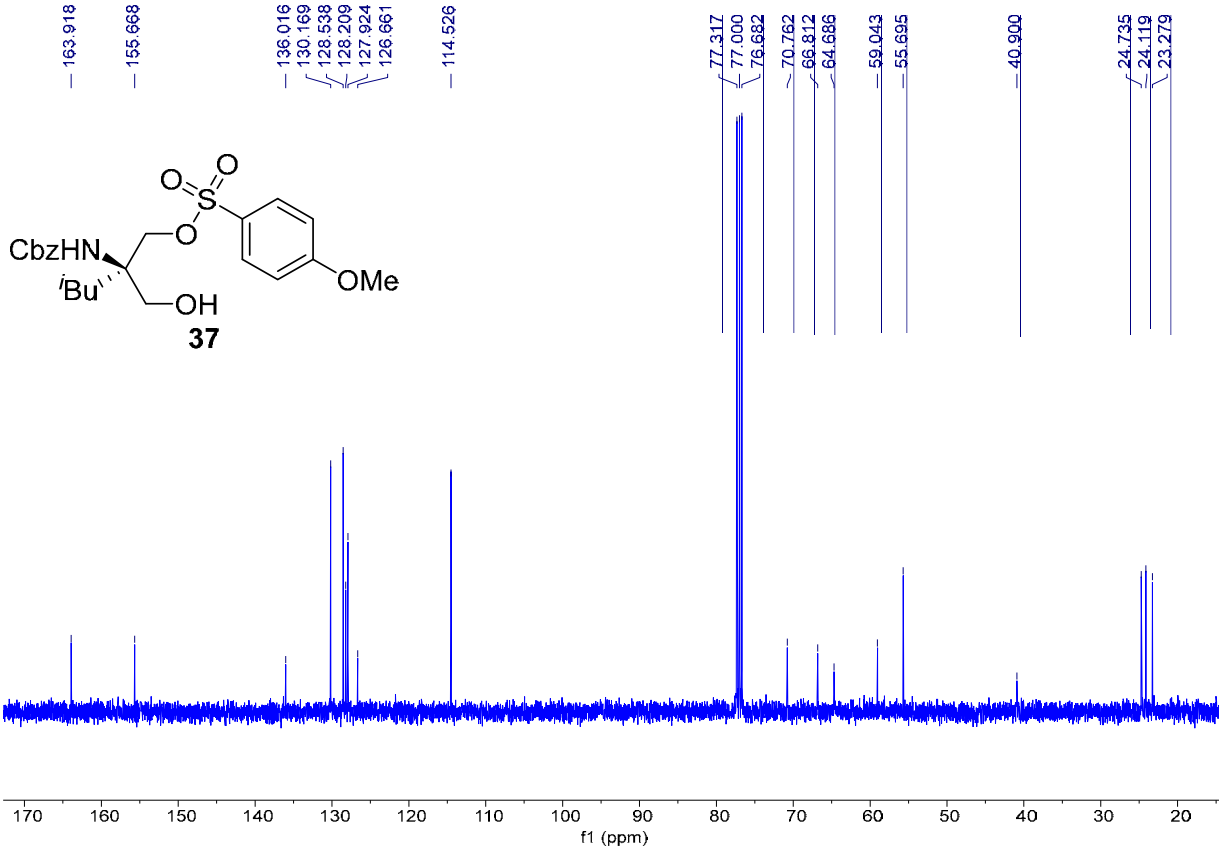

7.830
7.808
7.390
7.371
7.355
7.344
7.336
7.328
7.318
7.001
6.979
5.043
5.020
5.012
5.006
4.975
4.209
4.184
4.113
4.087
3.875
3.756
3.745
3.727
3.715
3.688
3.671
3.658
3.641
3.489
1.719
1.706
1.684
1.675
1.672
1.653
1.641
1.521
1.508
1.492
1.486
1.478
1.472
1.458
1.444
1.297
1.291
1.279
1.267
1.255
1.236
1.231
1.218
1.202
1.188
0.896
0.878
0.860
0.000

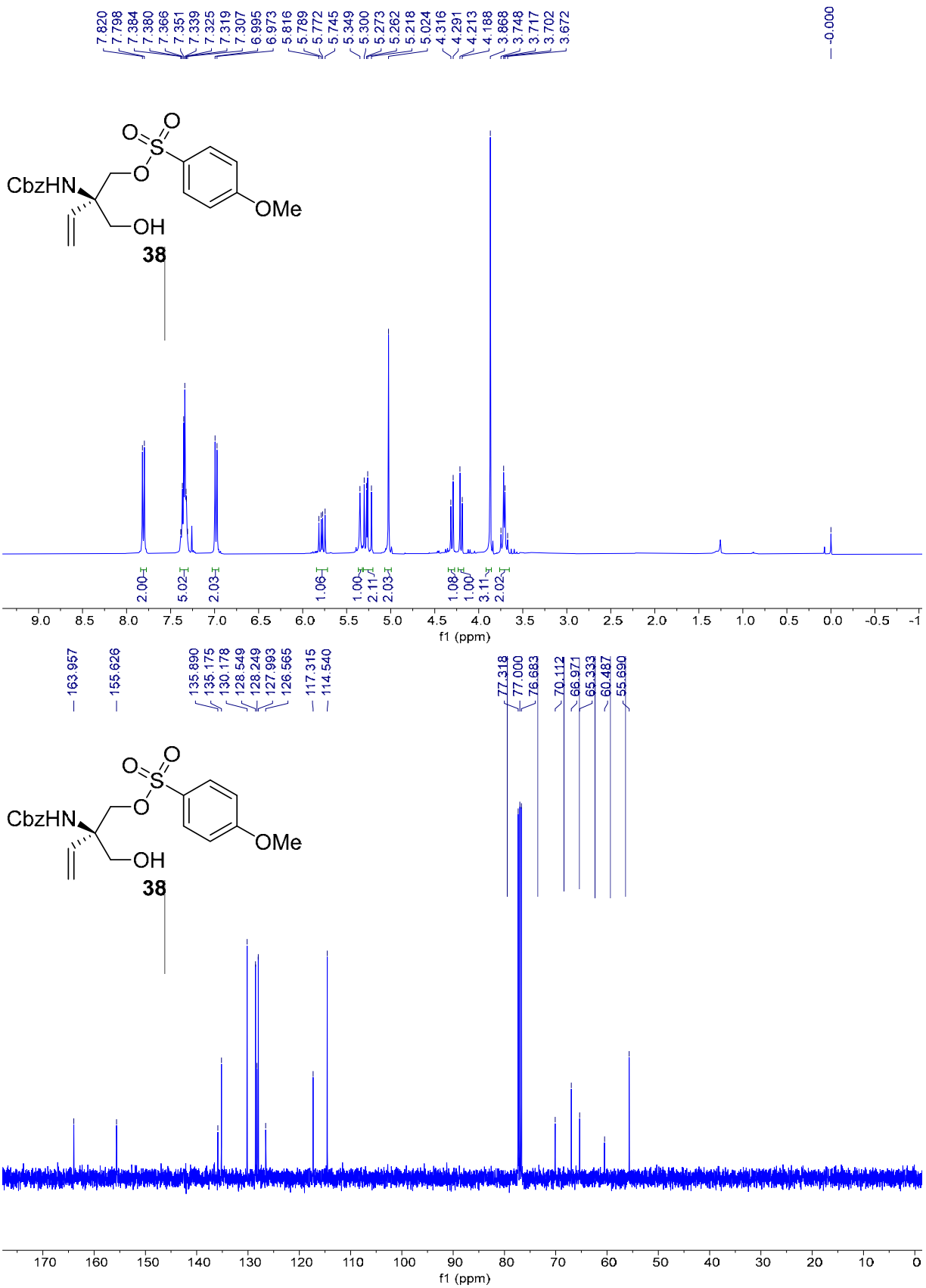

CbzHN
nPr
OH
OMe
36
2.00
5.26
2.05
3.17
1.08
1.12
3.12
1.06
1.16
1.02
1.27
1.19
2.57
3.42
f1 (ppm)

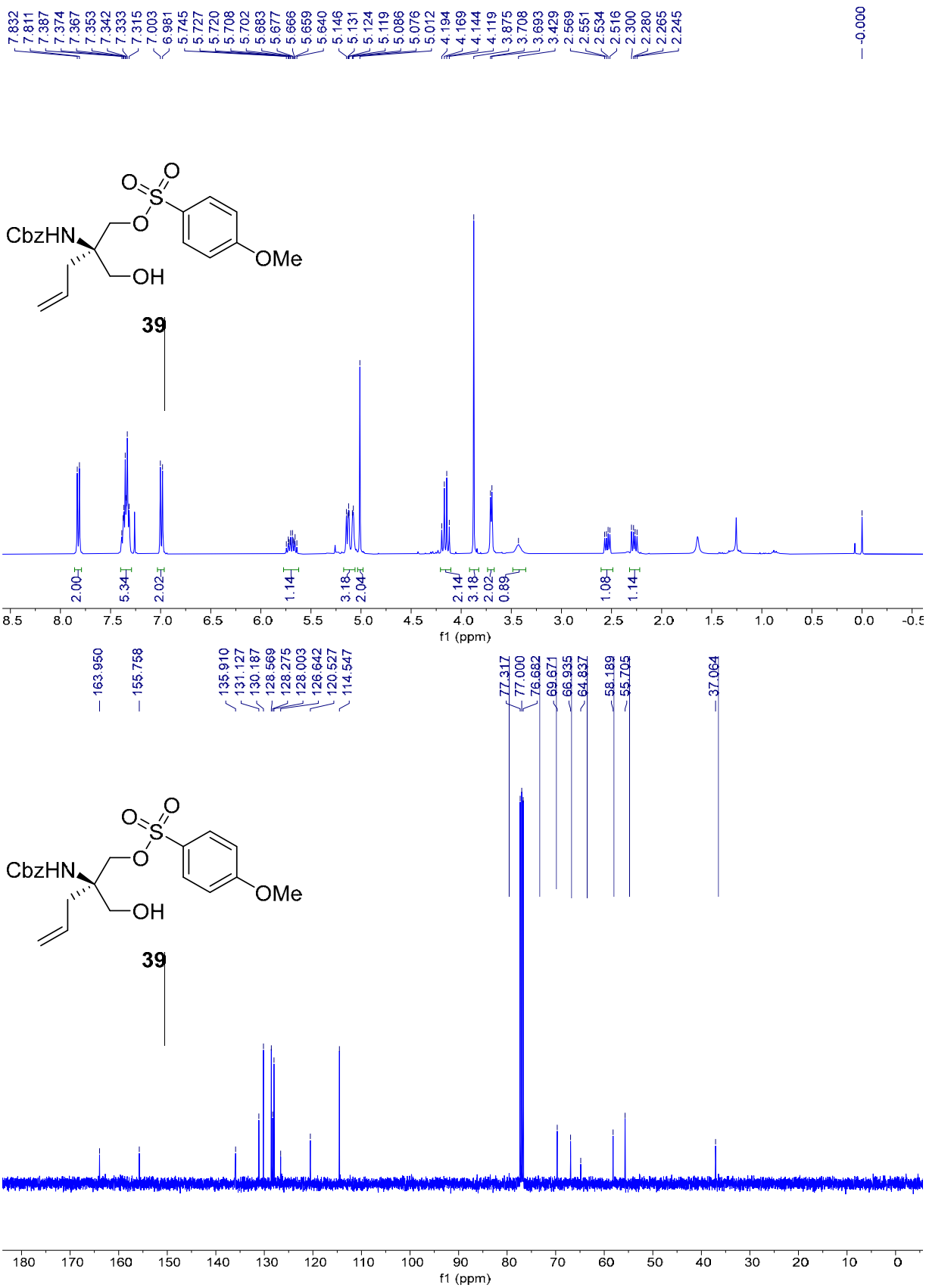

163.932
155.853
135.961
130.180
128.576
128.259
127.972
126.698
114.541
77.318
77.000
76.683
70.339
66.898
64.857
58.775
55.706
35.164
16.138
14.303
CbzHN
nPr
OH
OMe
36
f1 (ppm)


7.834
7.827
7.822
7.810
7.805
7.797
7.388
7.386
7.382
7.379
7.372
7.372
7.366
7.362
7.359
7.349
7.347
7.343
7.338
7.336
7.330
7.327
7.322
7.320
7.311
7.306
7.006
6.999
6.993
6.981
6.976
5.034
5.005
4.204
4.203
4.179
4.128
4.103
3.873
3.793
3.782
3.697
3.680
1.704
1.704
1.700
1.691
1.684
1.681
1.668
1.666
1.658
1.651
1.642
0.908
0.901
0.893
0.885
0.000


CbzHN
iBu
OH
OMe
O
S
37
2.00
5.43
2.01
1.02
2.00
1.06
1.04
3.03
1.07
1.07
0.93
3.00
6.10
f1 (ppm)


163.918
155.668
136.016
130.169
128.538
128.209
127.924
126.661
114.526
77.317
77.000
76.682
70.762
66.812
64.686
59.043
55.695
40.900
24.735
24.119
23.279
CbzHN
iBu
OH
OMe
O
S
37
f1 (ppm)


7.820
7.798
7.384
7.380
7.366
7.351
7.339
7.325
7.319
7.307
6.995
6.973
5.816
5.789
5.772
5.745
5.349
5.300
5.273
5.262
5.218
5.024
4.316
4.291
4.213
4.188
3.868
3.748
3.717
3.702
3.672
-0.000
CbzHN
OH
OMe
38
2.00
5.02
2.03
1.06
1.00
2.11
2.03
1.08
1.00
3.11
2.02
f1 (ppm)
163.957
155.626
135.890
135.175
130.178
128.549
128.249
127.993
126.565
117.315
114.540
77.318
77.000
76.683
70.112
66.971
65.333
60.487
55.690
CbzHN
OH
OMe
38
f1 (ppm)


7.832
7.811
7.387
7.374
7.367
7.353
7.342
7.333
7.315
7.003
6.981
5.745
5.727
5.720
5.708
5.702
5.683
5.677
5.666
5.659
5.640
5.146
5.131
5.124
5.119
5.086
5.076
5.012
4.194
4.169
4.144
4.119
3.875
3.708
3.693
3.429
2.569
2.551
2.534
2.516
2.300
2.280
2.265
2.245
-0.000
CbzHN
OH
OMe
39
2.00
5.34
2.02
1.14
3.18
2.04
2.14
3.18
2.02
0.89
1.08
1.14
f1 (ppm)
163.950
155.758
135.910
131.127
130.187
128.569
128.275
128.003
126.642
120.527
114.547
77.317
77.000
76.682
69.671
66.935
64.837
58.189
55.705
37.064
CbzHN
OH
OMe
39
f1 (ppm)


7.842
7.835
7.829
7.817
7.812
7.805
7.383
7.380
7.377
7.375
7.372
7.366
7.362
7.357
7.351
7.344
7.335
7.333
7.326
7.322
7.316
7.311
7.302
7.004
6.997
6.992
6.980
6.975
6.967
5.463
5.043
4.343
4.318
4.313
4.288
3.922
3.903
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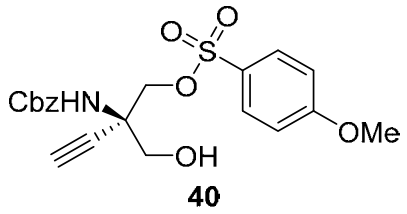
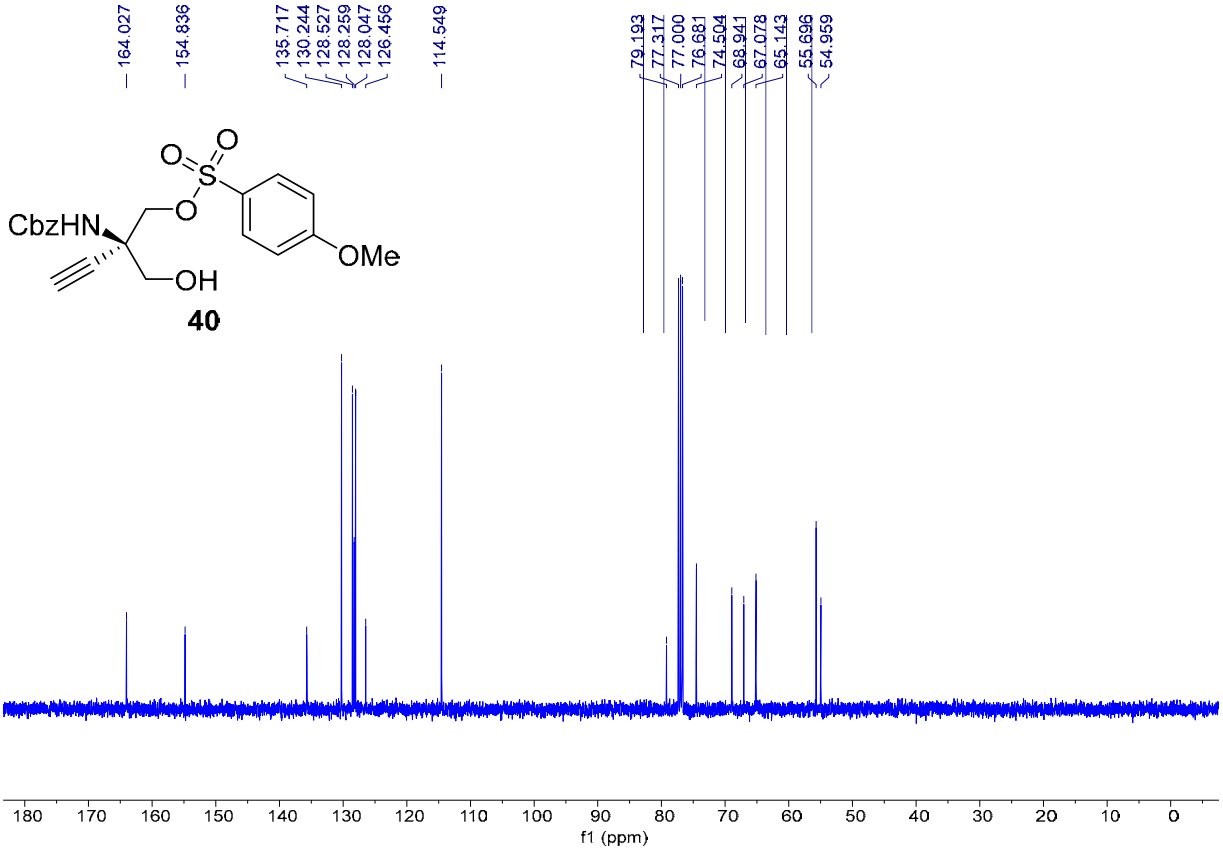
3.874
3.867
3.848
3.831
3.818
3.802
2.944
2.434
0.000


CbzHN
OH
OMe

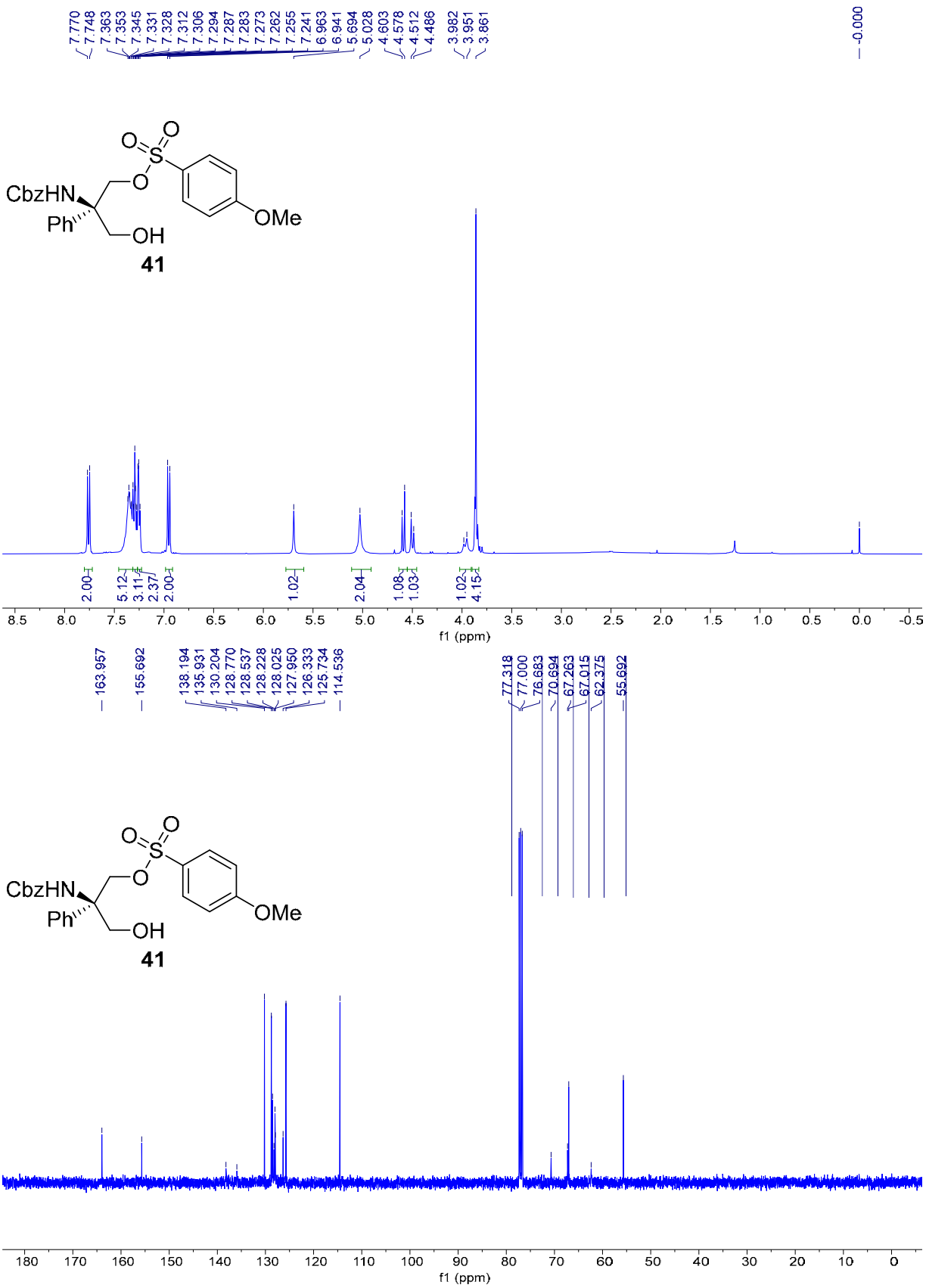
40

2.00
5.00
2.04
1.00
2.06
2.07
1.12
3.03
1.03
0.98
0.97
f1 (ppm)


164.027
154.836
135.717
130.244
128.527
128.259
128.047
126.456
114.549
79.193
77.317
77.000
76.681
74.504
68.941
67.078
65.143
55.696
54.959
f1 (ppm)

CbzHN
OH
OMe

40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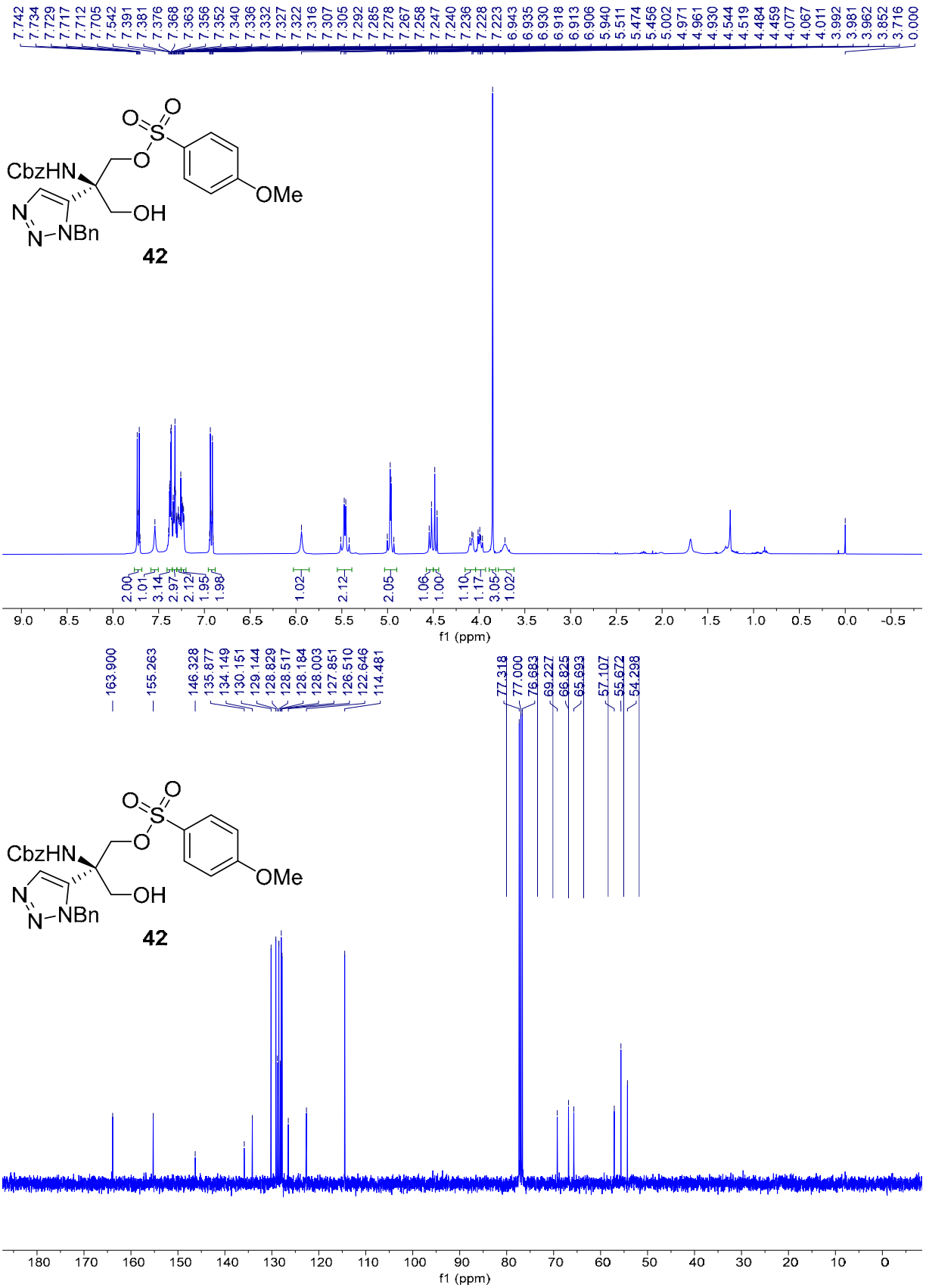
7.353
7.345
7.331
7.328
7.312
7.306
7.294
7.287
7.283
7.273
7.262
7.255
7.241
6.963
6.941
5.694
5.028
4.603
4.578
4.512
4.486
3.982
3.951
3.861
-0.000
CbzHN
Ph
OH
OMe
41
2.00
5.12
3.11
2.37
2.00
1.02
2.04
1.08
1.03
1.02
4.15
f1 (ppm)
163.957
155.692
138.194
135.931
130.204
128.770
128.537
128.228
128.025
127.950
126.333
125.734
114.536
77.318
77.000
76.683
70.694
67.263
67.015
62.375
55.692
CbzHN
Ph
OH
OMe
41
f1 (ppm)


7.742
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7.717
7.712
7.705
7.542
7.391
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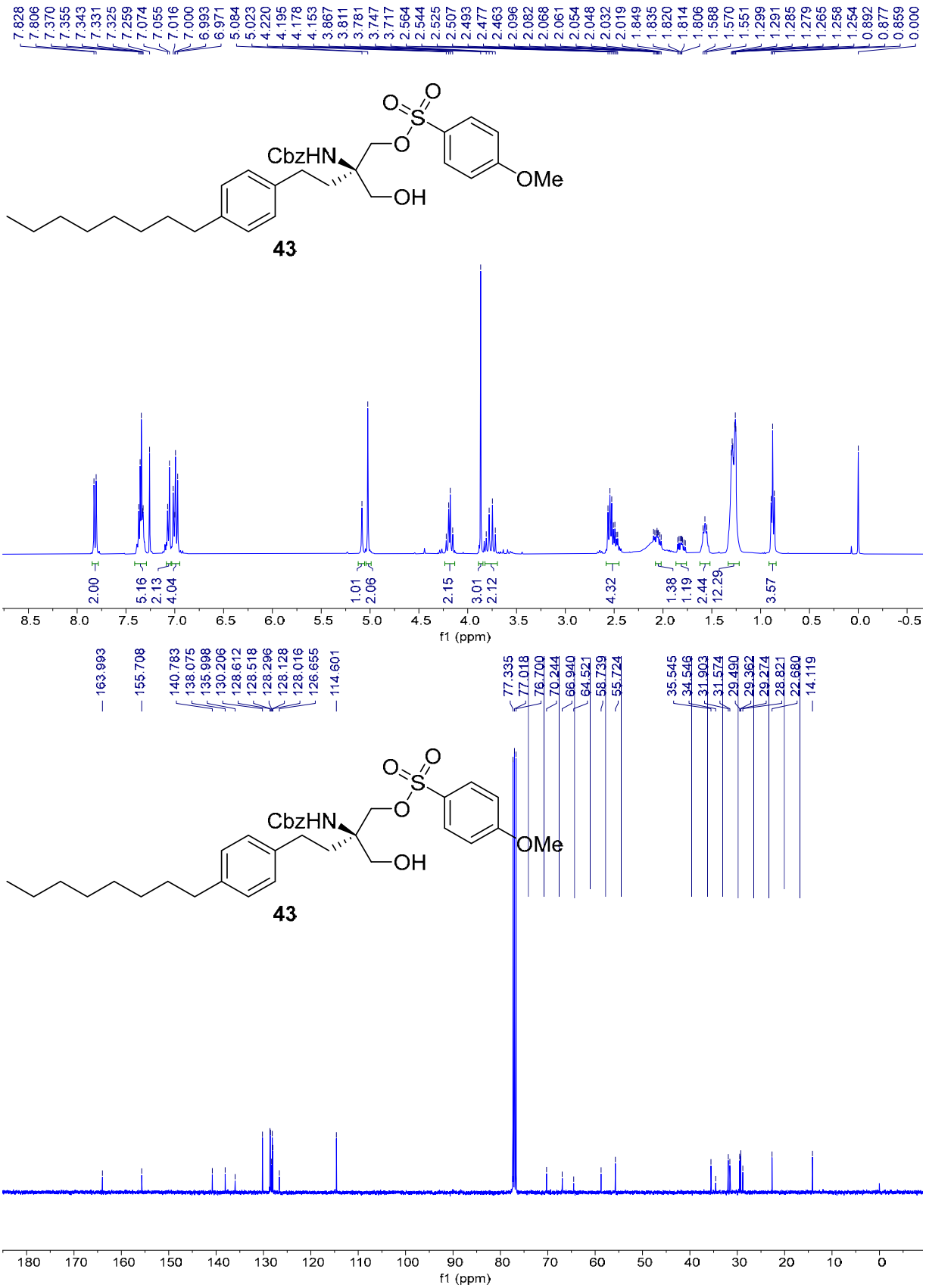
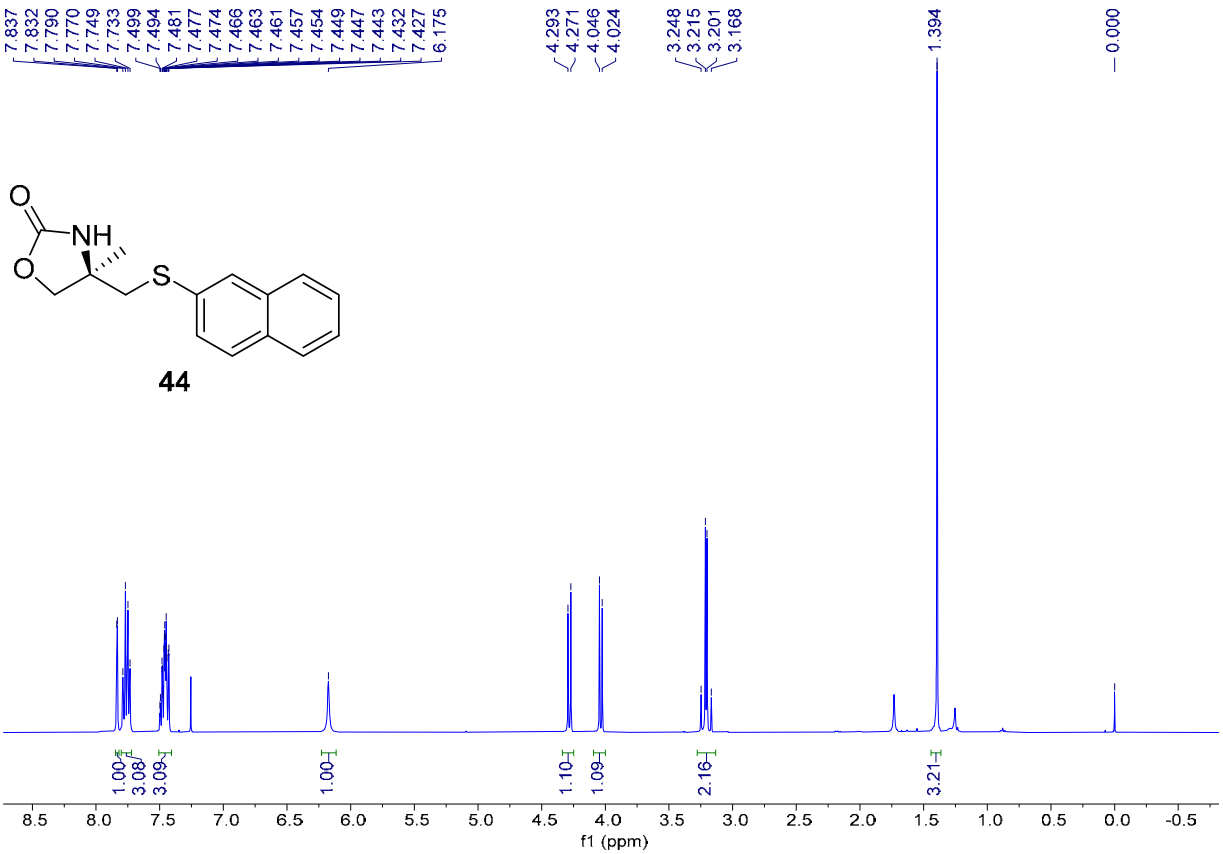
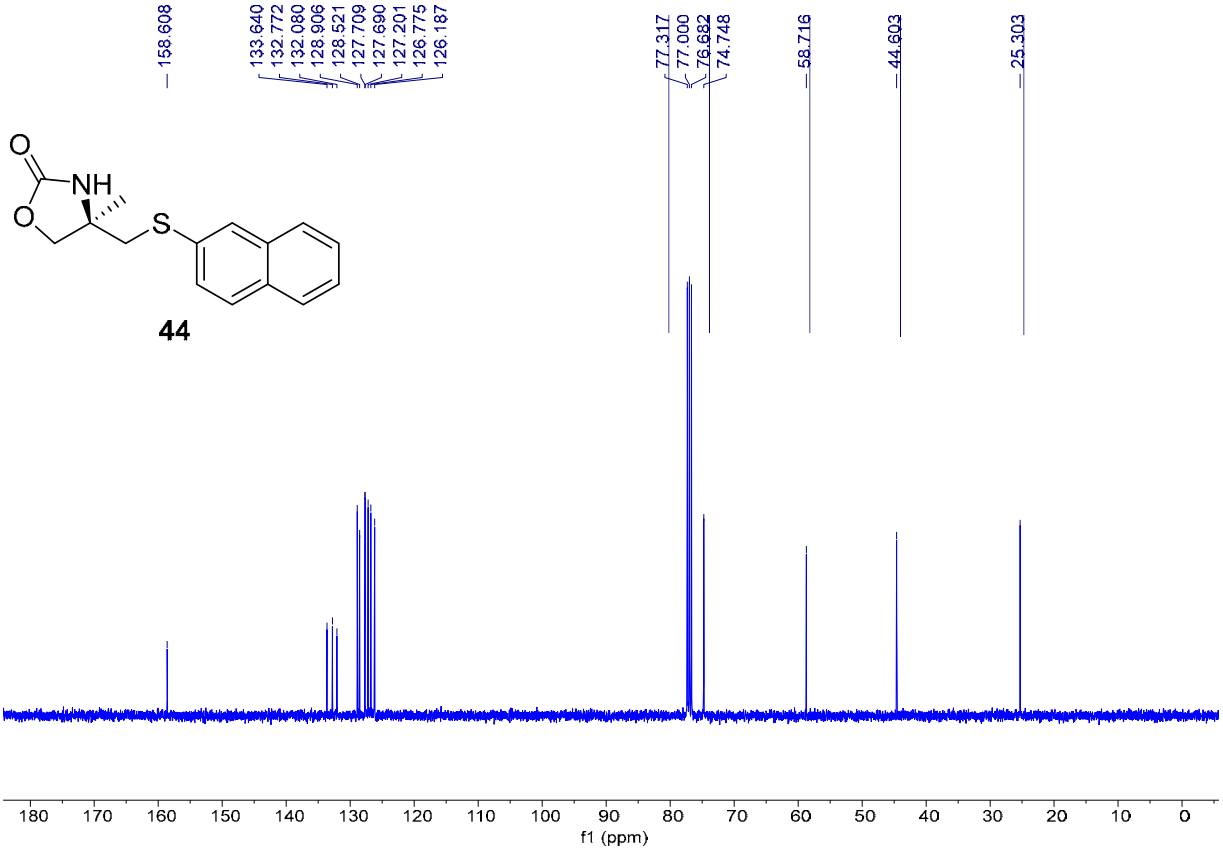
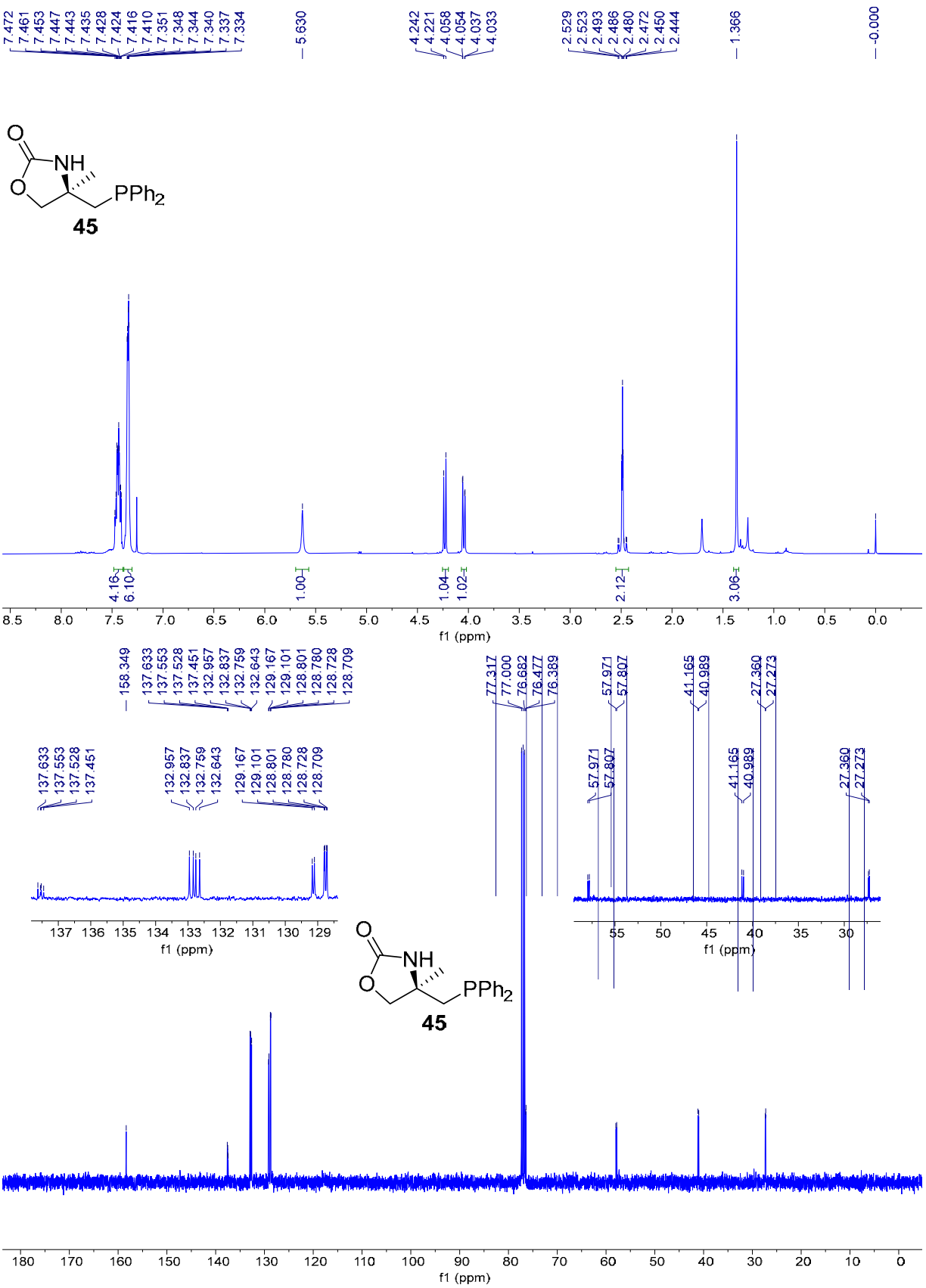
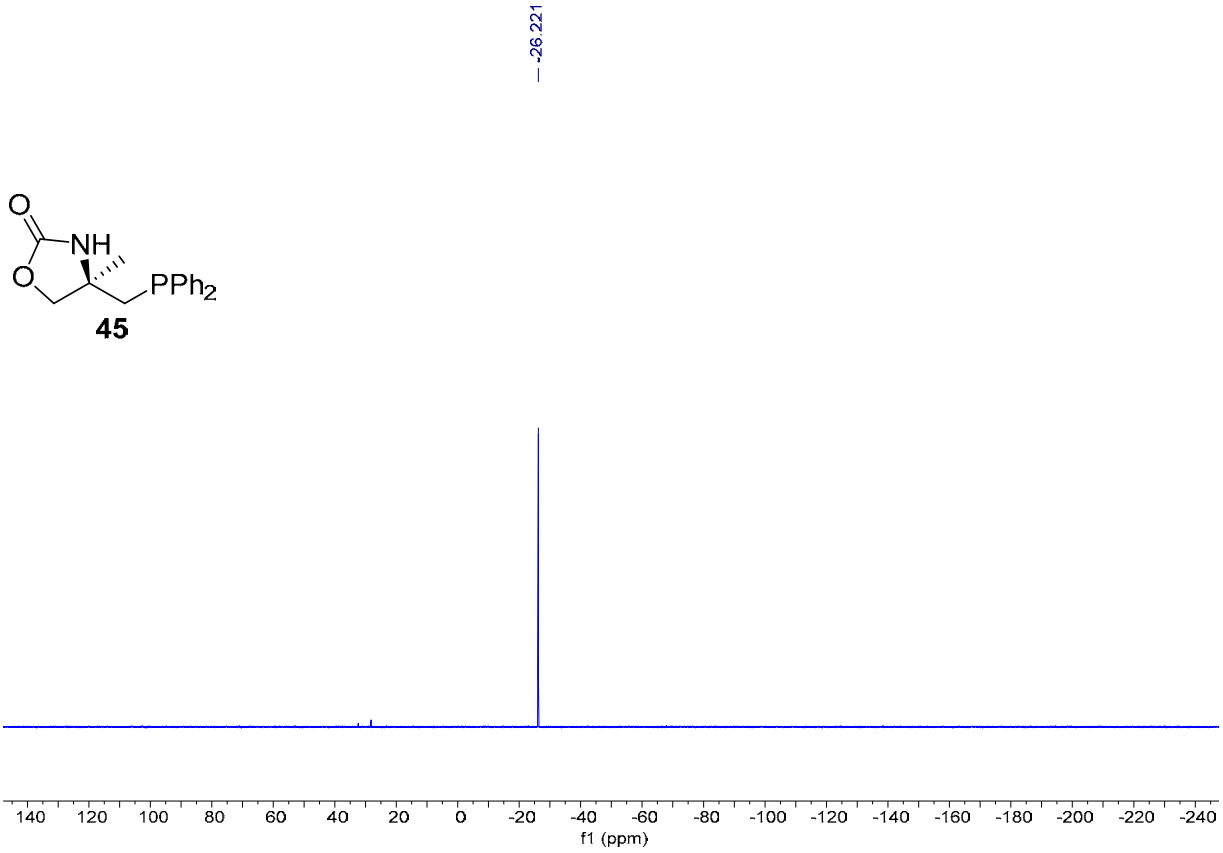
7.376
7.368
7.363
7.356
7.352
7.340
7.336
7.332
7.327
7.322
7.316
7.307
7.305
7.292
7.285
7.278
7.267
7.258
7.247
7.240
7.236
7.228
7.223
6.943
6.935
6.930
6.918
6.913
6.906
5.940
5.511
5.474
5.456
5.002
4.971
4.961
4.930
4.544
4.519
4.484
4.459
4.077
4.067
4.011
3.992
3.981
3.962
3.852
3.716
0.000
CbzHN
OH
OMe
NBn
42
2.00
1.01
3.14
2.97
2.12
1.95
1.98
1.02
2.12
2.05
1.06
1.00
1.10
1.17
3.05
1.02
f1 (ppm)
163.900
155.263
146.328
135.877
134.149
130.151
129.144
128.829
128.517
128.184
128.003
127.851
126.510
122.646
114.481
77.318
77.000
76.683
69.227
66.825
65.693
57.107
55.672
54.298
CbzHN
OH
OMe
NBn
42
f1 (ppm)

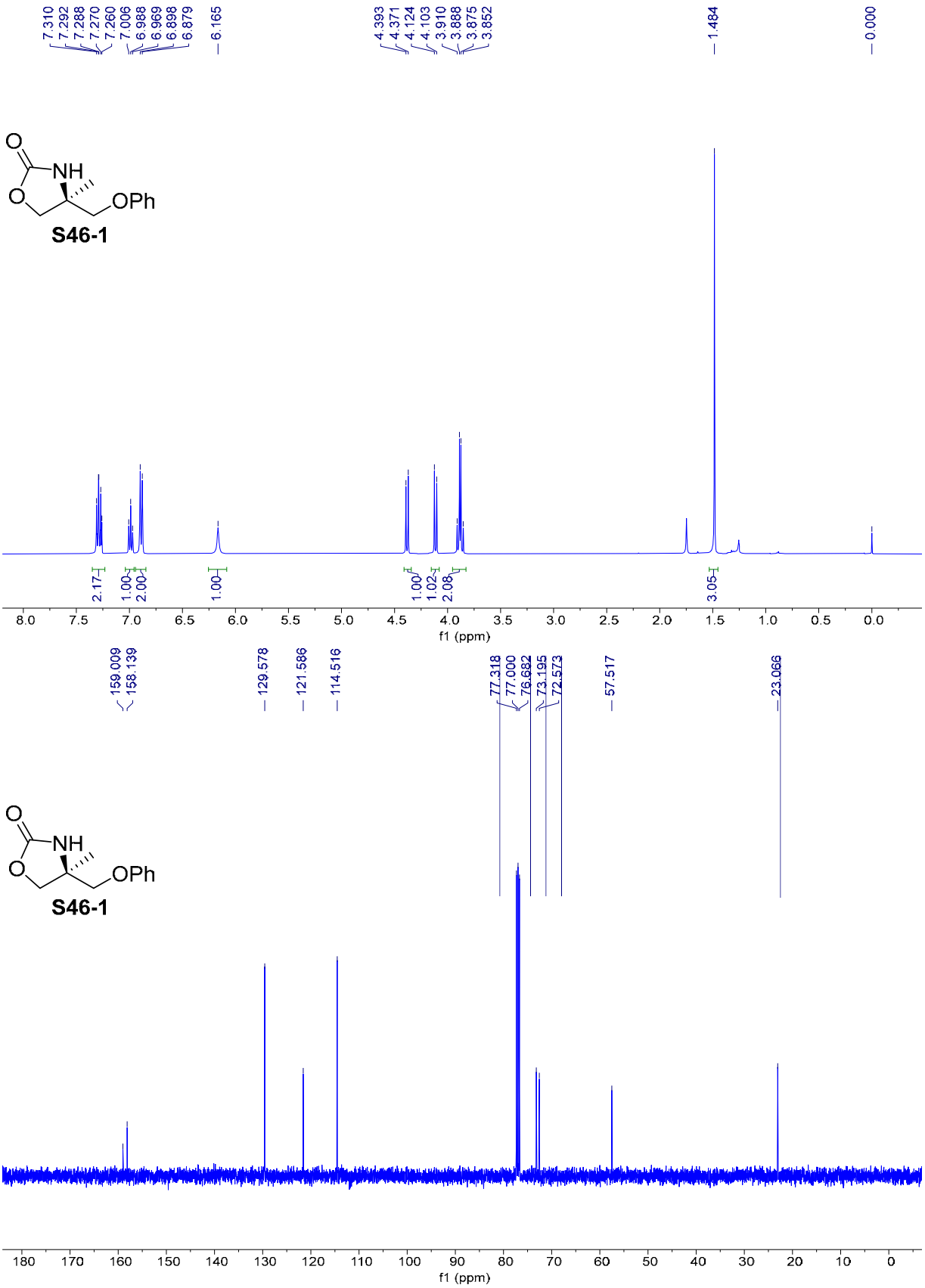

7.828
7.806
7.370
7.355
7.343
7.331
7.325
7.259
7.074
7.055
7.016
7.000
6.993
6.971
5.084
5.023
4.220
4.195
4.178
4.153
3.867
3.811
3.781
3.747
3.717
2.564
2.544
2.525
2.507
2.493
2.477
2.463
2.096
2.082
2.068
2.061
2.054
2.048
2.032
2.019
1.849
1.835
1.820
1.814
1.806
1.588
1.570
1.551
1.299
1.291
1.285
1.279
1.265
1.258
1.254
0.892
0.877
0.859
0.000
CbzHN
OH
OMe
43
2.00
5.16
2.13
4.04
1.01
2.06
2.15
3.01
2.12
4.32
1.38
1.19
2.44
12.29
3.57
f1 (ppm)
163.993
155.708
140.783
138.075
135.998
130.206
128.612
128.518
128.296
128.128
128.016
126.655
114.601
77.335
77.018
76.700
70.244
66.940
64.521
58.739
55.724
35.545
34.546
31.903
31.574
29.490
29.362
29.274
28.821
22.680
14.119
CbzHN
OH
OMe
43
f1 (ppm)

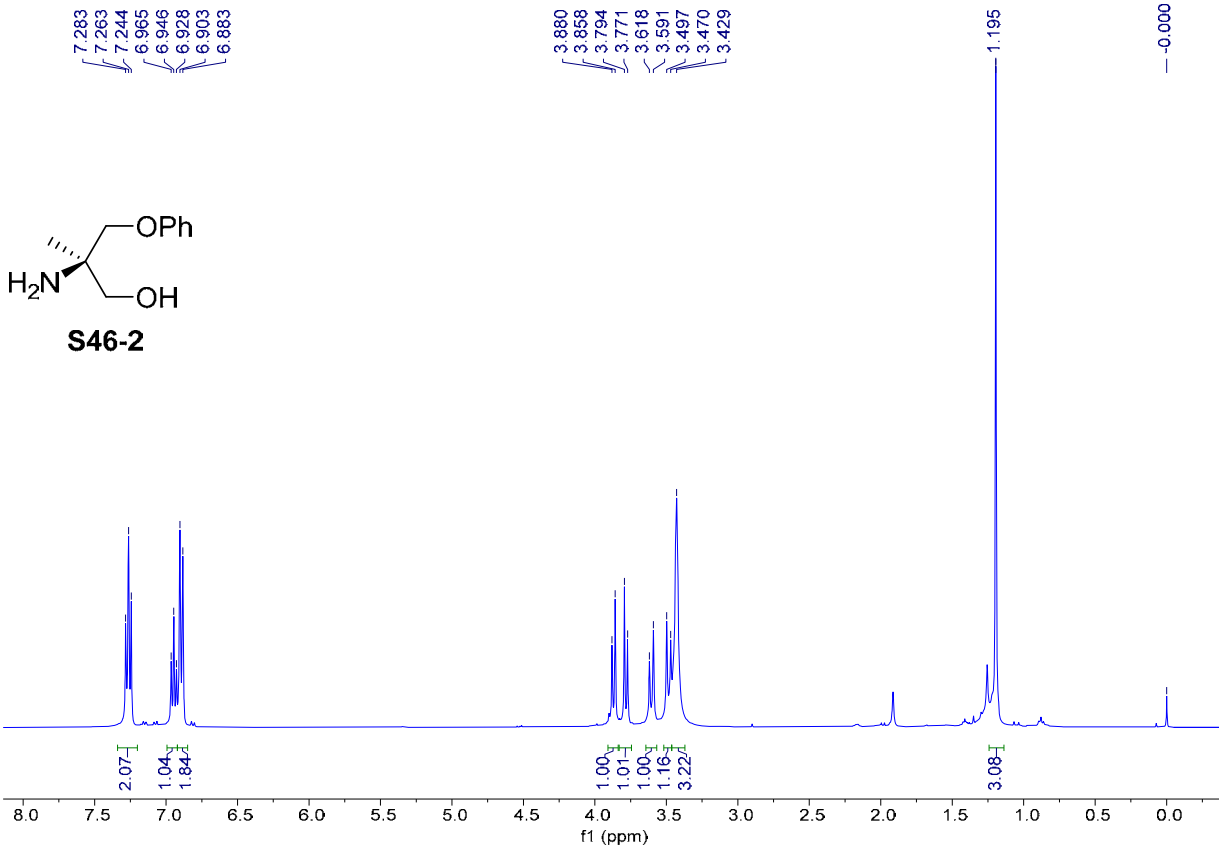

7.837
7.832
7.790
7.770
7.749
7.733
7.499
7.494
7.481
7.477
7.474
7.466
7.463
7.461
7.457
7.454
7.449
7.447
7.443
7.432
7.427
6.175
4.293
4.271
4.046
4.024
3.248
3.215
3.201
3.168
1.394
0.000
NH
O
O
S
44
1.00
3.08
3.09
1.00
1.10
1.09
2.16
3.21
f1 (ppm)

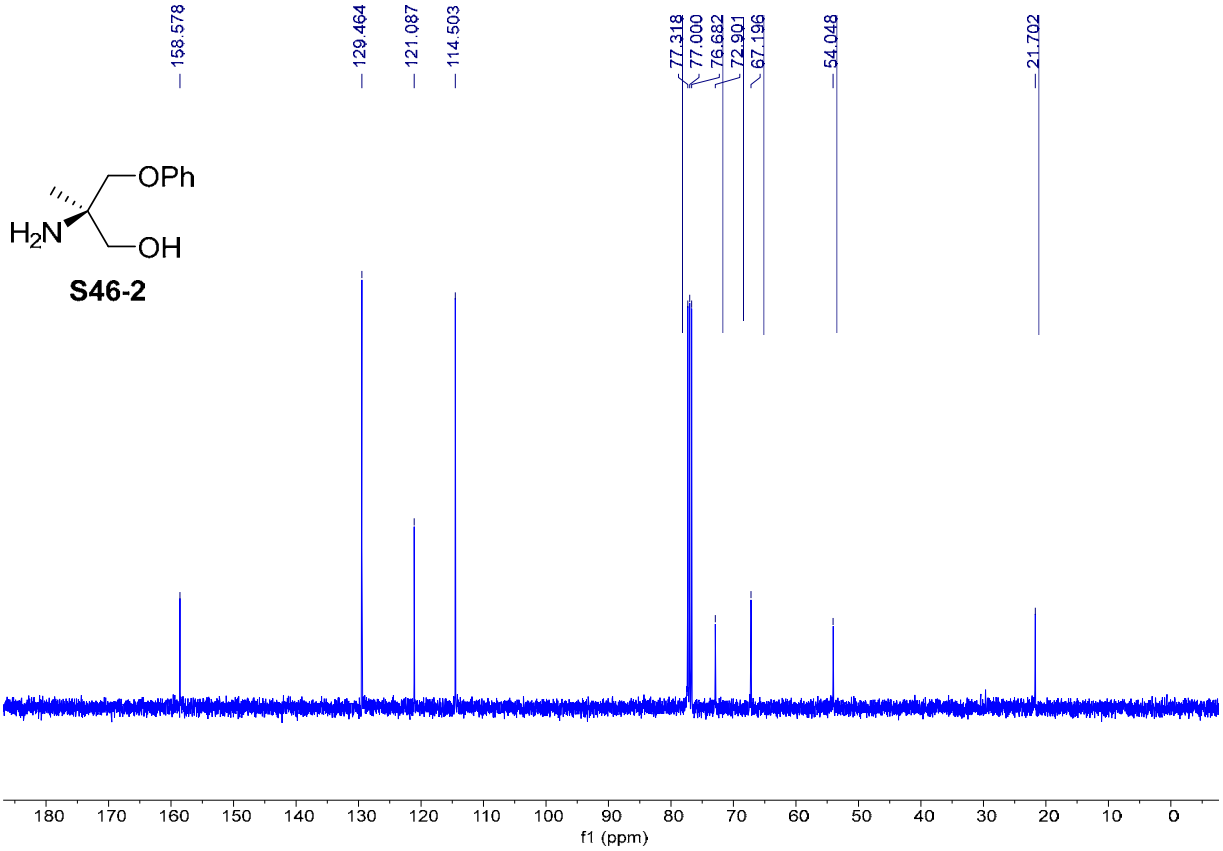

158.608
133.640
132.772
132.080
128.906
128.521
127.709
127.690
127.201
126.775
126.187
77.317
77.000
76.682
74.748
58.716
44.603
25.303
NH
O
O
S
44
f1 (ppm)

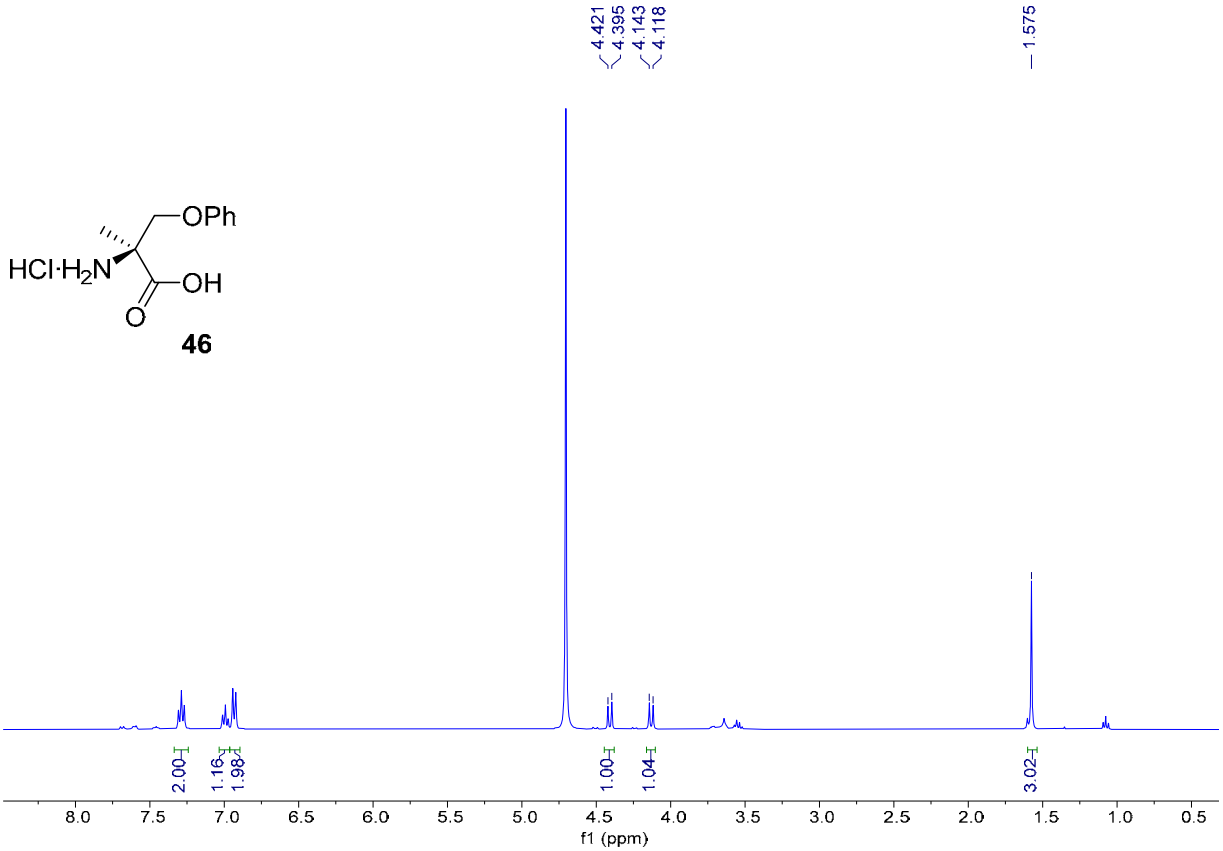

7.472
7.461
7.453
7.447
7.443
7.435
7.428
7.424
7.416
7.410
7.351
7.348
7.344
7.340
7.337
7.334
5.630
4.242
4.221
4.058
4.054
4.037
4.033
2.529
2.523
2.493
2.486
2.480
2.472
2.450
2.444
1.366
-0.000
NH
O
O
PPh2
45
4.16
6.10
1.00
1.04
1.02
2.12
3.06
f1 (ppm)
158.349
137.633
137.553
137.528
137.451
132.957
132.837
132.759
132.643
129.167
129.101
128.801
128.780
128.728
128.709
77.317
77.000
76.682
76.477
76.389
57.971
57.807
41.165
40.989
27.360
27.273
f1 (ppm)
f1 (ppm)

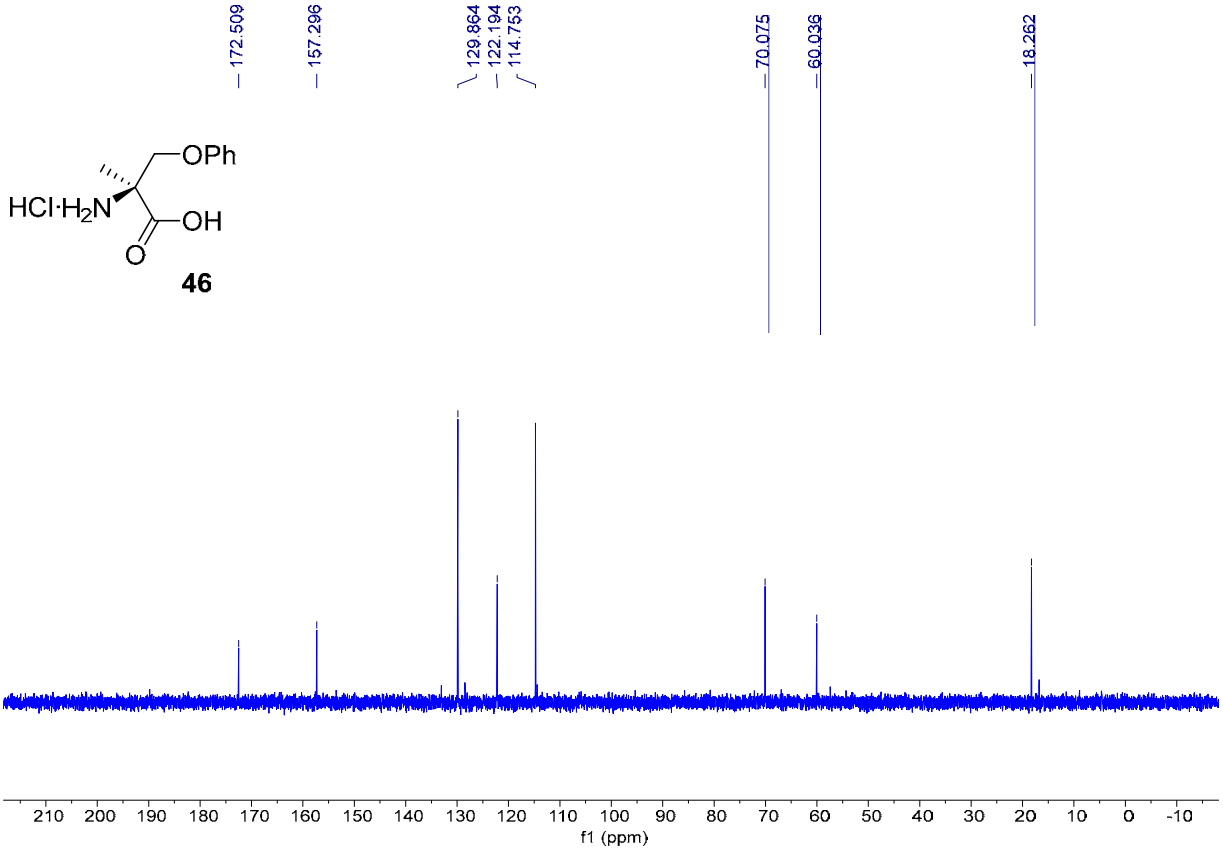

-26.221
O
NH
O
PPh2
45
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

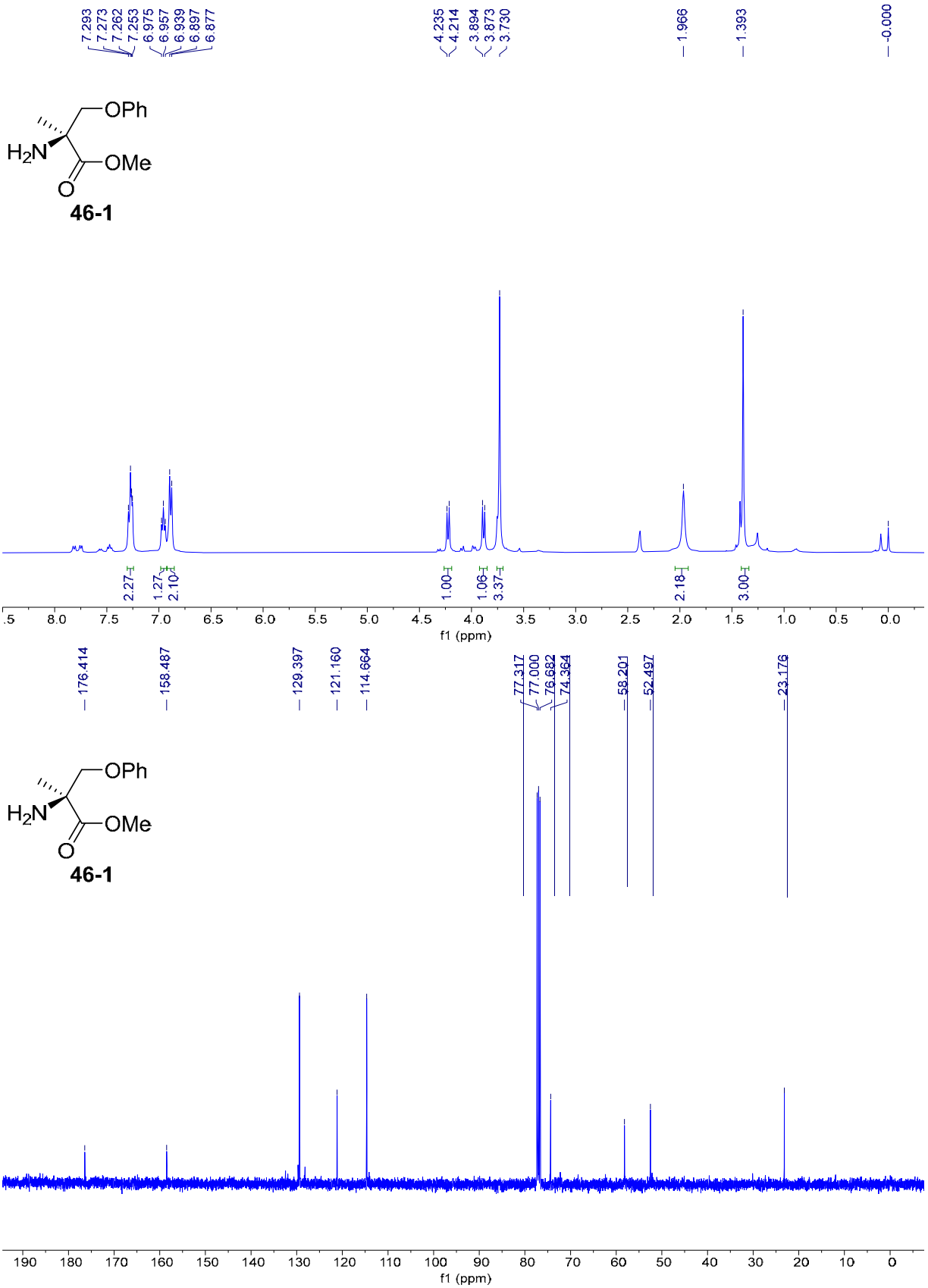

7.310
7.292
7.288
7.270
7.260
7.006
6.988
6.969
6.898
6.879
6.165
4.393
4.371
4.124
4.103
3.910
3.888
3.875
3.852
1.484
0.000
NH
O
O
OPh
S46-1
2.17
1.00
2.00
1.00
1.00
1.02
2.08
3.05
f1 (ppm)
159.009
158.139
129.578
121.586
114.516
77.318
77.000
76.682
73.195
72.573
57.517
23.066
NH
O
O
OPh
S46-1
f1 (ppm)

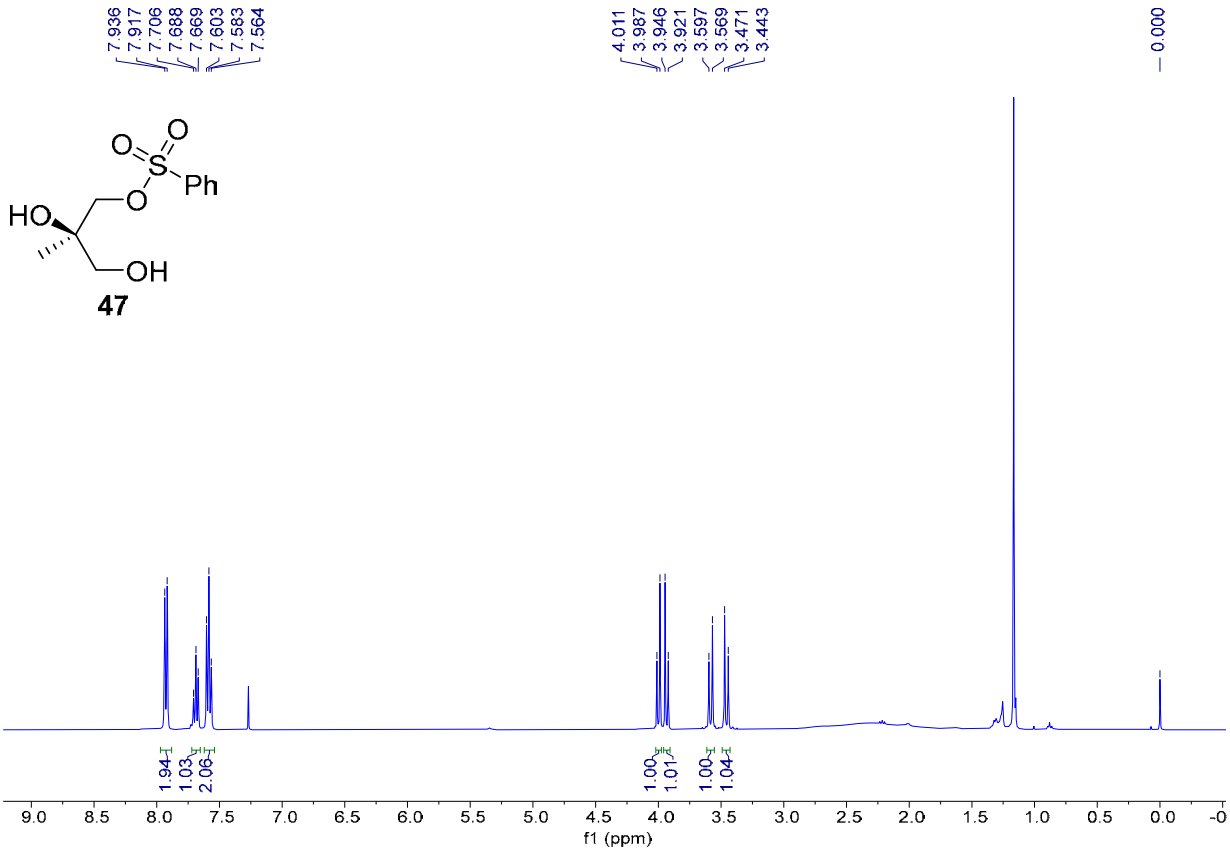

7.283
7.263
7.244
6.965
6.946
6.928
6.903
6.883
3.880
3.858
3.794
3.771
3.618
3.591
3.497
3.470
3.429
1.195
-0.000
OPh
H2N
OH
S46-2
2.07
1.04
1.84
1.00
1.01
1.00
1.16
3.22
3.08
f1 (ppm)

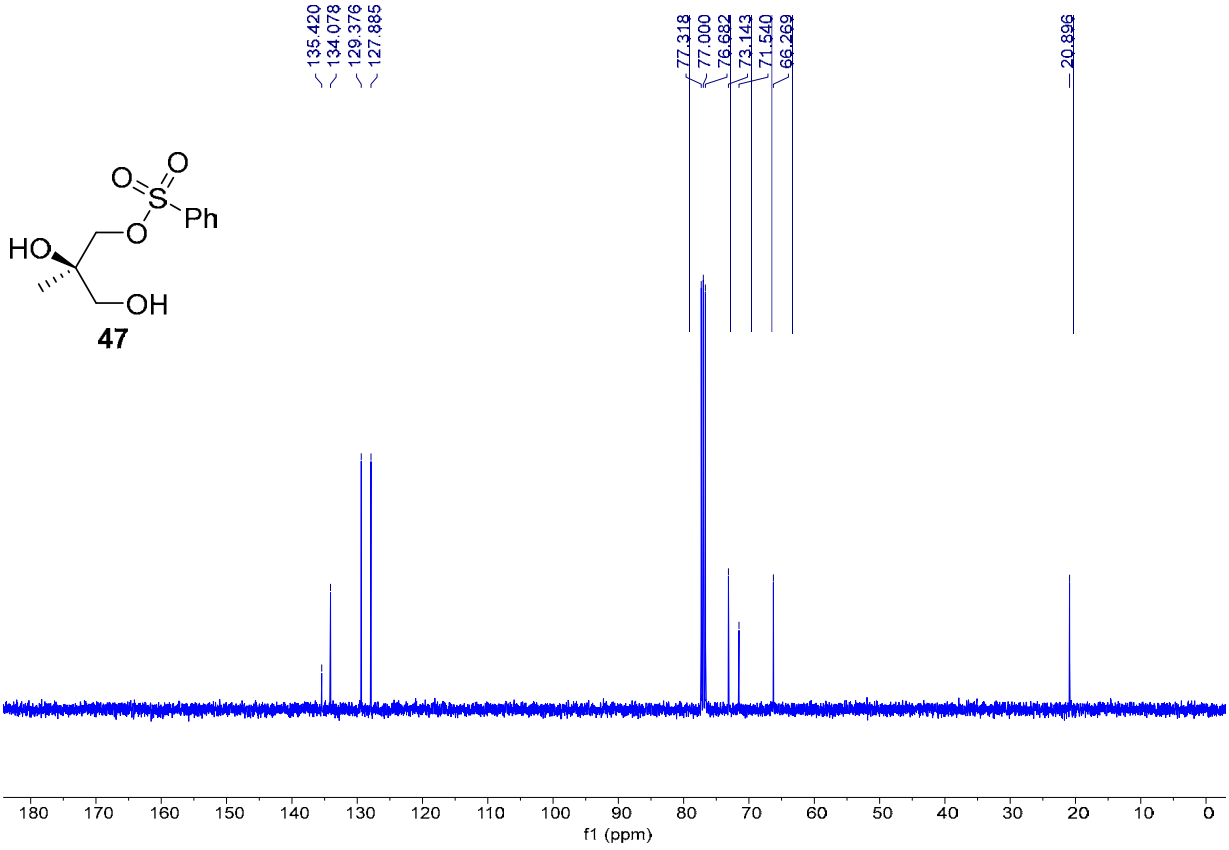

158.578
129.464
121.087
114.503
77.318
77.000
76.682
72.901
67.196
54.048
21.702
OPh
H2N
OH
S46-2
f1 (ppm)

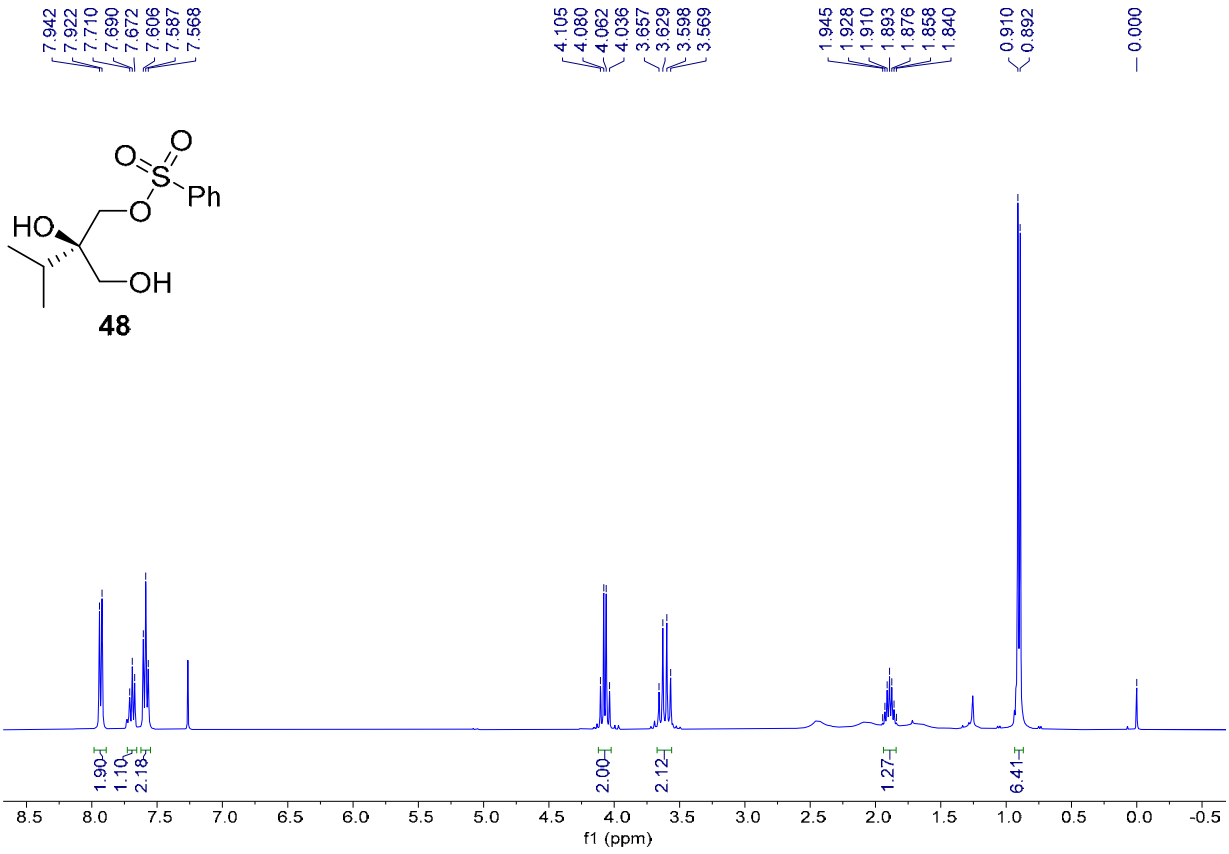

4.421
4.395
4.143
4.118
1.575
OPh
HCl·H2N
OH
O
46
2.00
1.16
1.98
1.00
1.04
3.02
f1 (ppm)

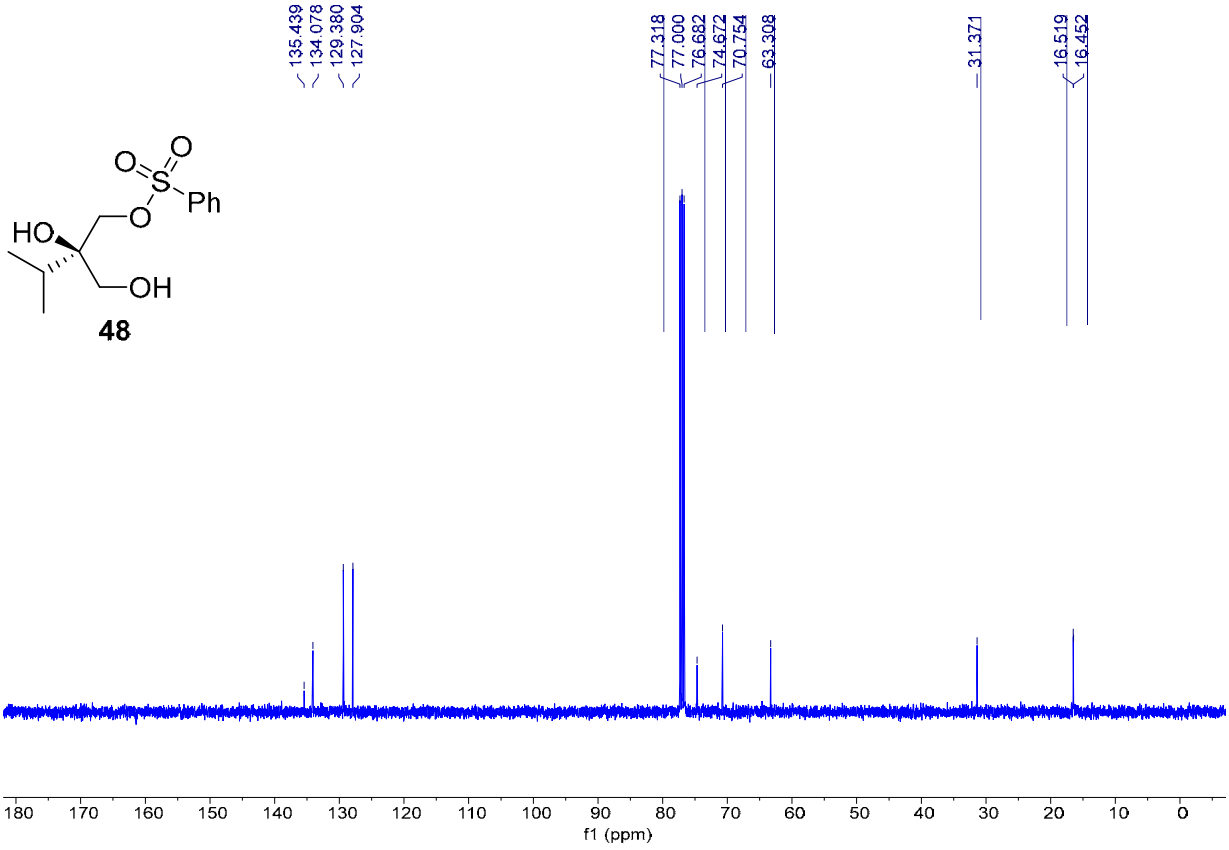

172.509
157.296
129.864
122.194
114.753
70.075
60.036
18.262
OPh
HCl·H2N
OH
O
46
f1 (ppm)

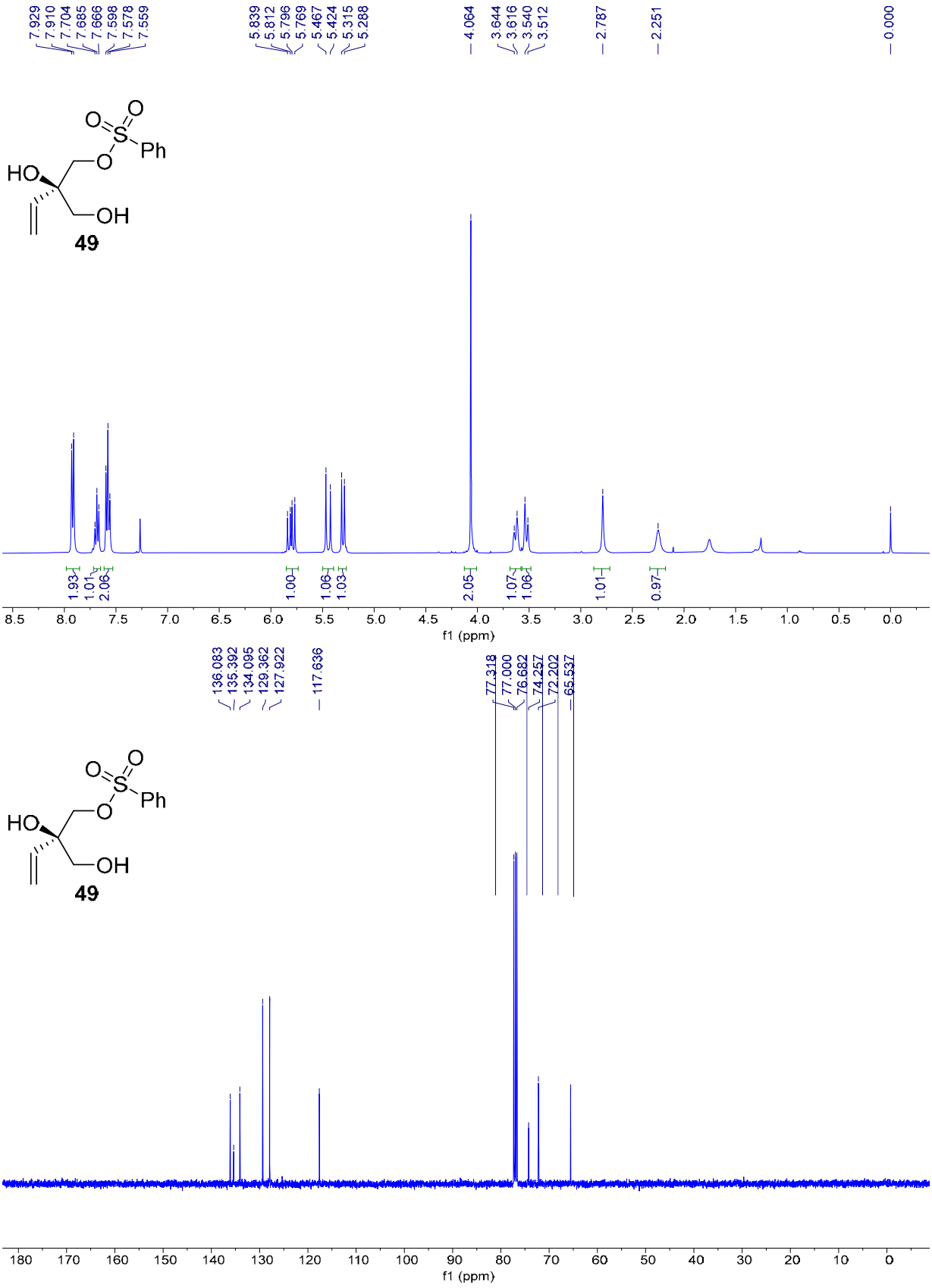

7.293
7.273
7.262
7.253
6.975
6.957
6.939
6.897
6.877
4.235
4.214
3.894
3.873
3.730
1.966
1.393
-0.000
OPh
H2N
OMe
O
46-1
2.27
1.27
2.10
1.00
1.06
3.37
2.18
3.00
f1 (ppm)
176.414
158.487
129.397
121.160
114.664
77.317
77.000
76.682
74.364
58.201
52.497
23.176
OPh
H2N
OMe
O
46-1
f1 (ppm)

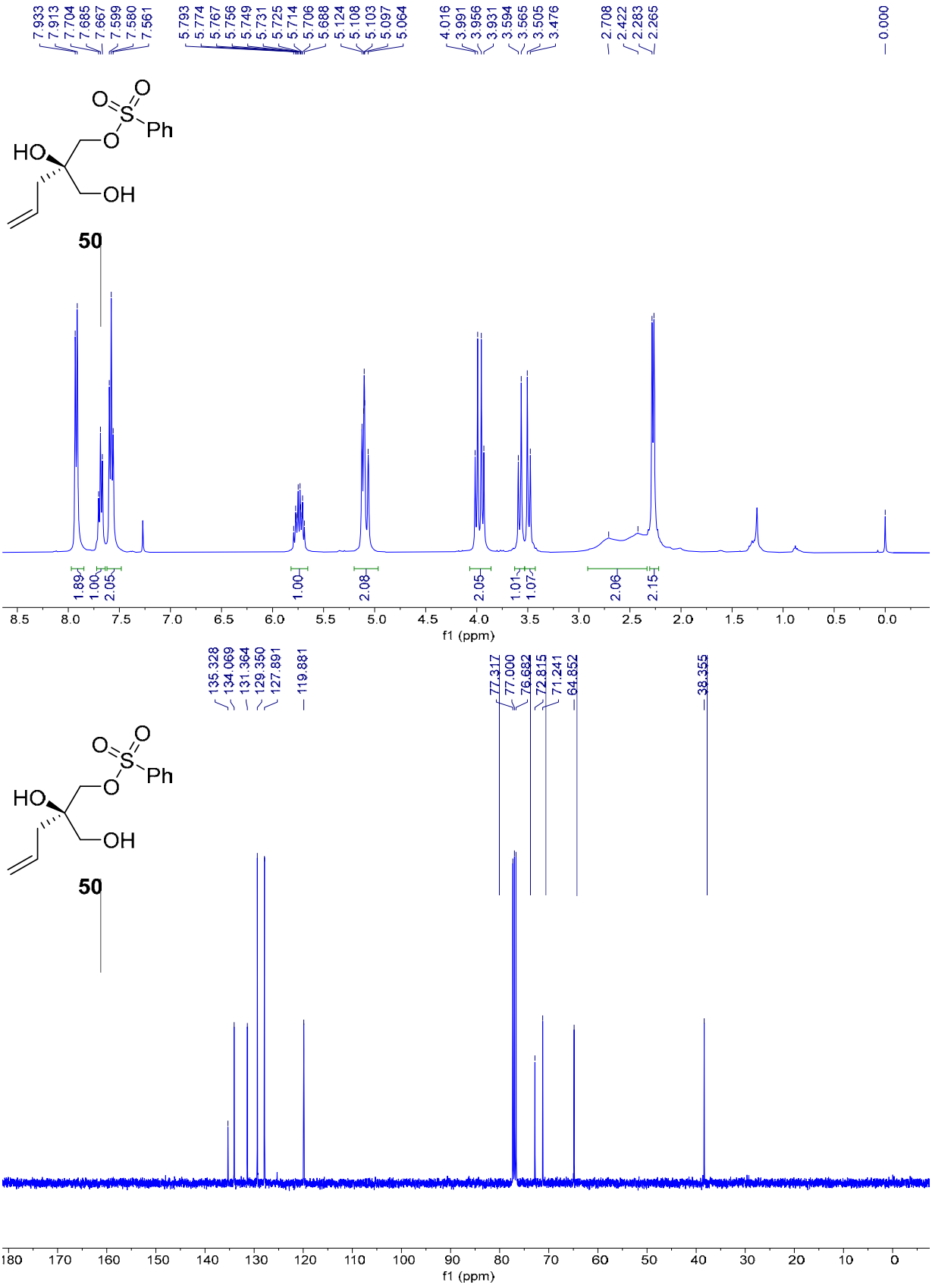

7.936
7.917
7.706
7.688
7.669
7.603
7.583
7.564
4.011
3.987
3.946
3.921
3.597
3.569
3.471
3.443
0.000
HO
O
S
O
O
Ph
OH
47
1.94
1.03
2.06
1.00
1.01
1.00
1.04
f1 (ppm)

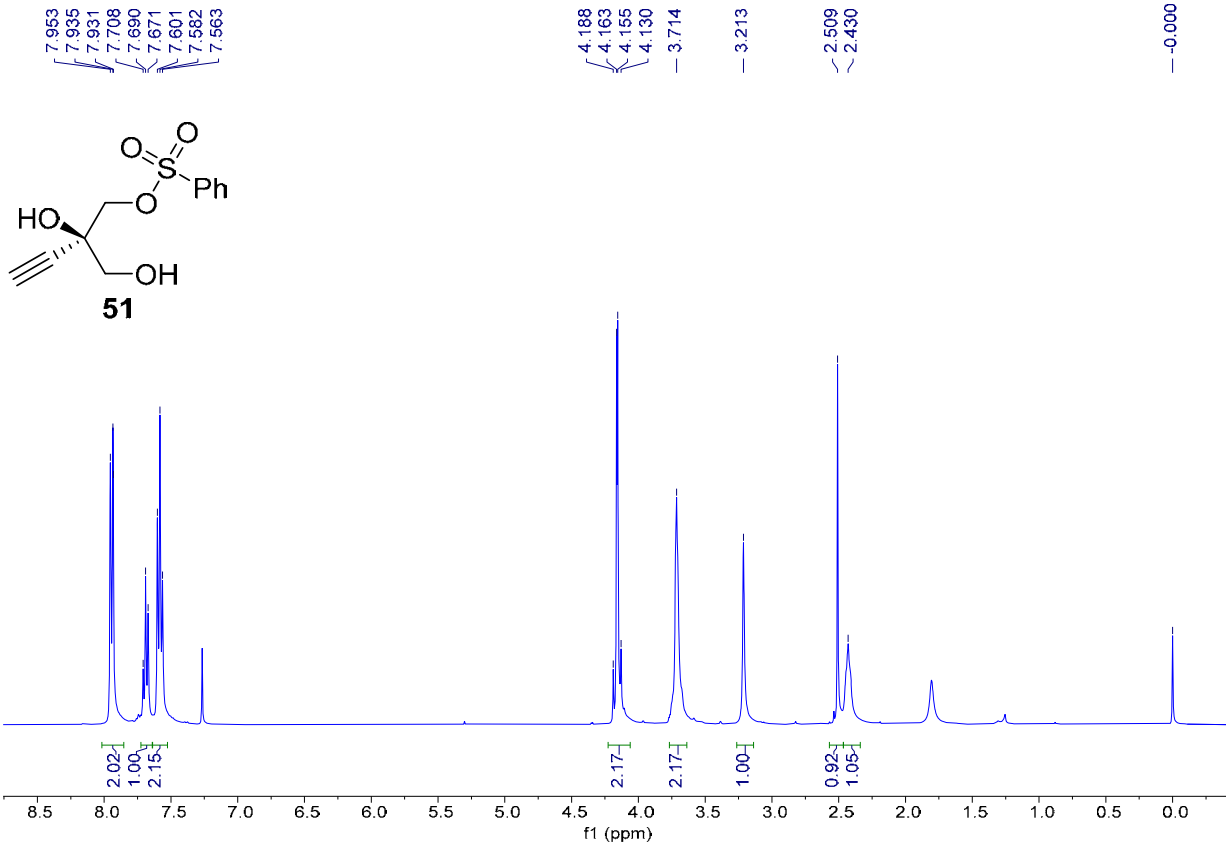

135.420
134.078
129.376
127.885
77.318
77.000
76.682
73.143
71.540
66.269
20.896
HO
O
S
O
O
Ph
OH
47
f1 (ppm)

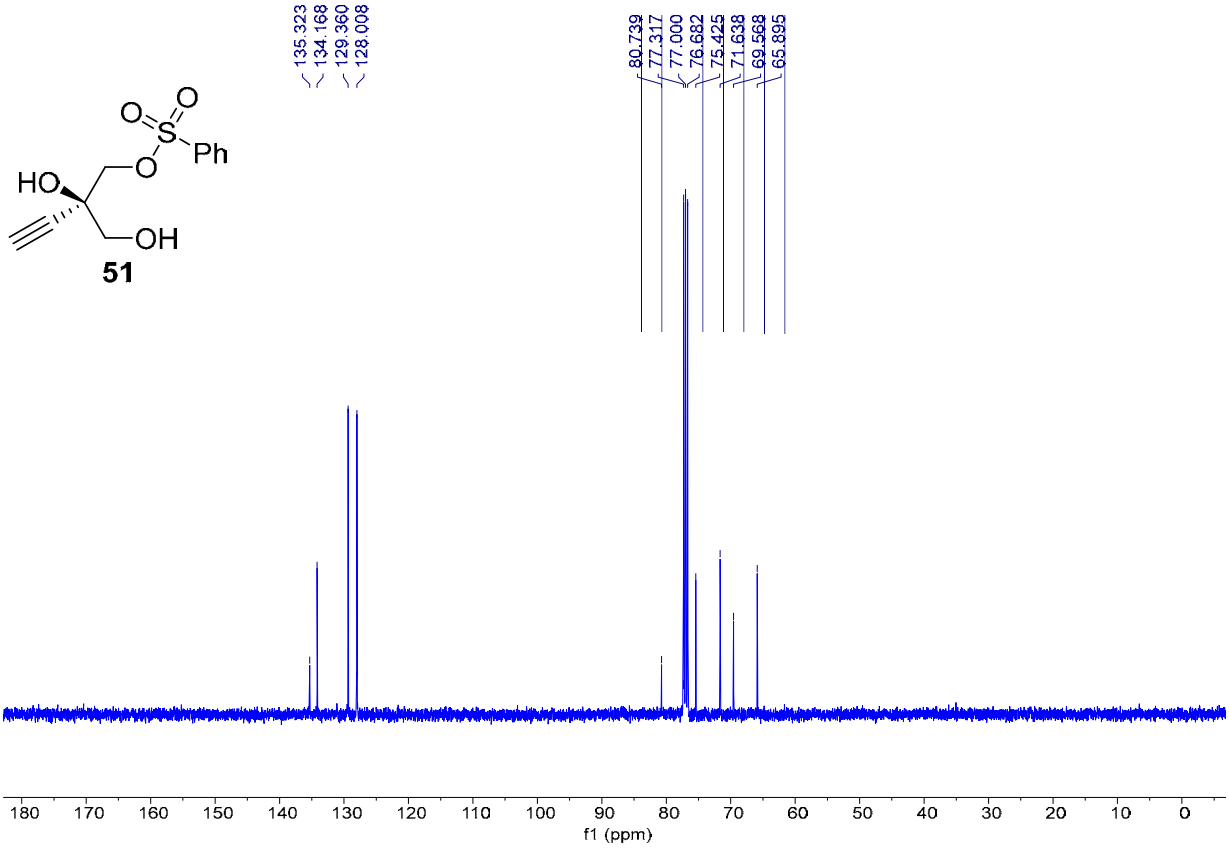

7.942
7.922
7.710
7.690
7.672
7.606
7.587
7.568
4.105
4.080
4.062
4.036
3.657
3.629
3.598
3.569
1.945
1.928
1.910
1.893
1.876
1.858
1.840
0.910
0.892
0.000
O
O
S
Ph
O
HO
OH
48
1.90
1.10
2.18
2.00
2.12
1.27
6.41
f1 (ppm)

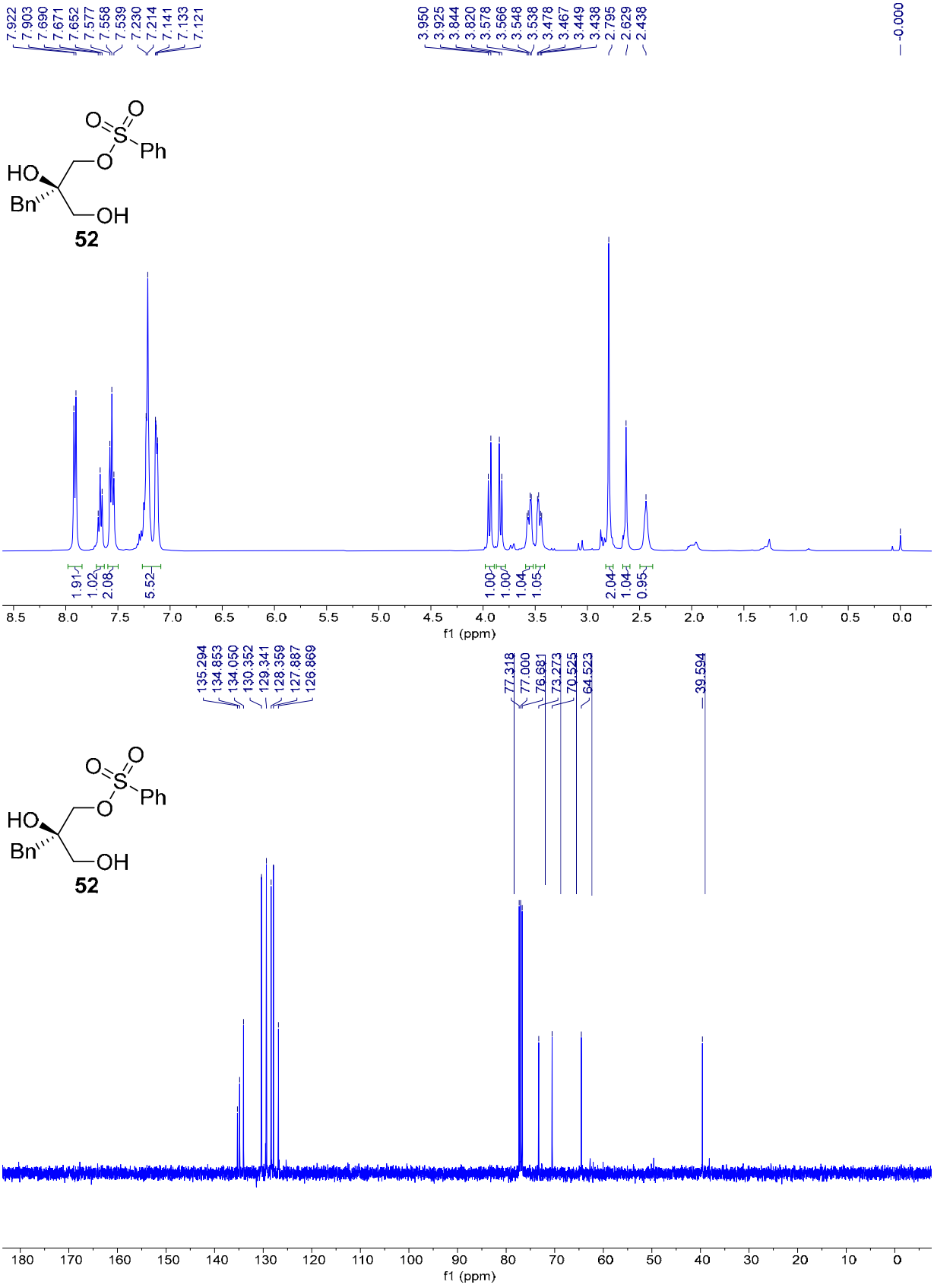

135.439
134.078
129.380
127.904
77.318
77.000
76.682
74.672
70.754
63.308
31.371
16.519
16.452
O
O
S
Ph
O
HO
OH
48
f1 (ppm)

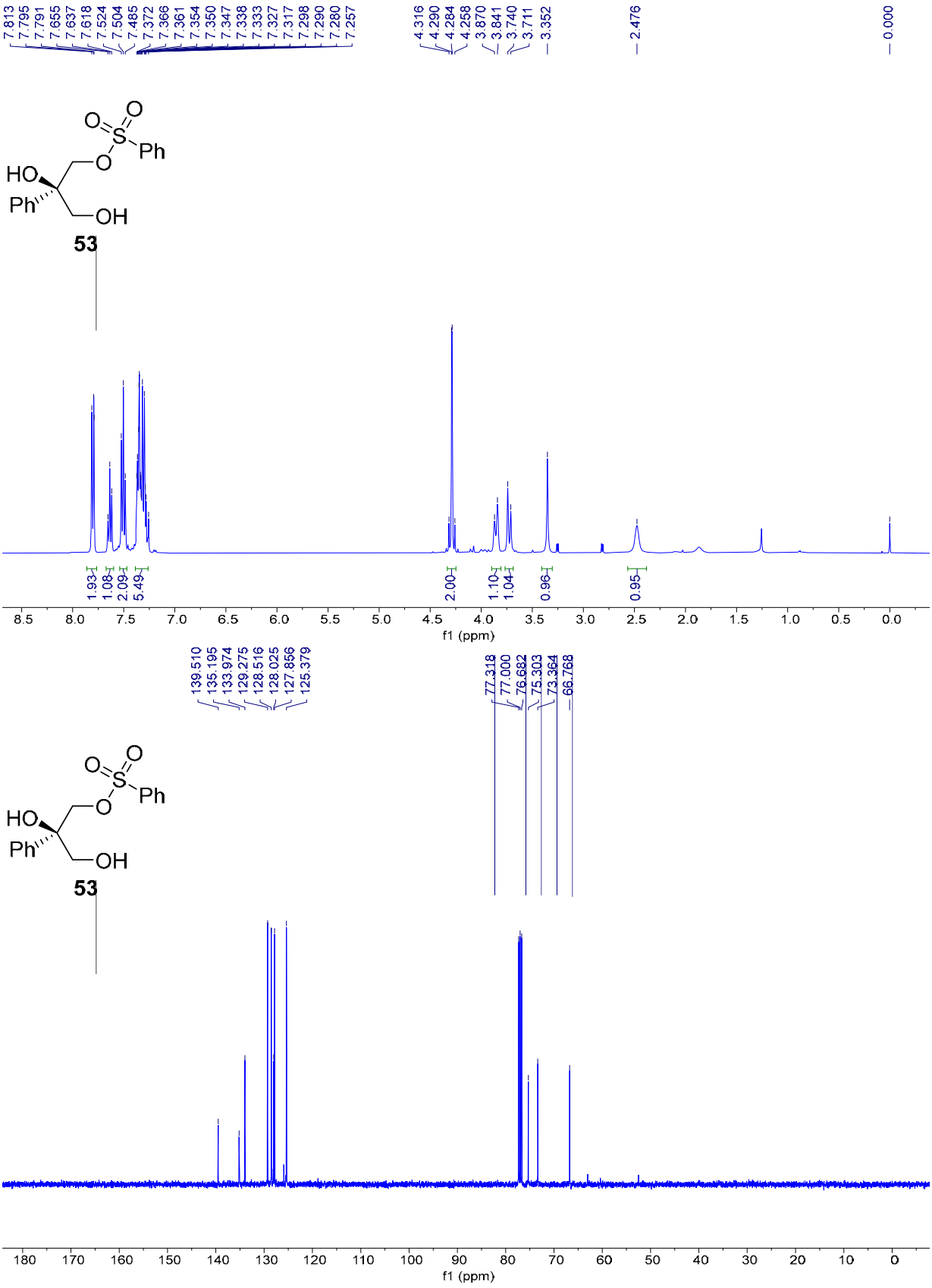

7.929
7.910
7.704
7.685
7.666
7.598
7.578
7.559
5.839
5.812
5.796
5.769
5.467
5.424
5.315
5.288
4.064
3.644
3.616
3.540
3.512
2.787
2.251
0.000
HO
OH
Ph
49
1.93
1.01
2.06
1.00
1.06
1.03
2.05
1.07
1.06
1.01
0.97
f1 (ppm)
136.083
135.392
134.095
129.362
127.922
117.636
77.318
77.000
76.682
74.257
72.202
65.537
HO
OH
Ph
49
f1 (ppm)

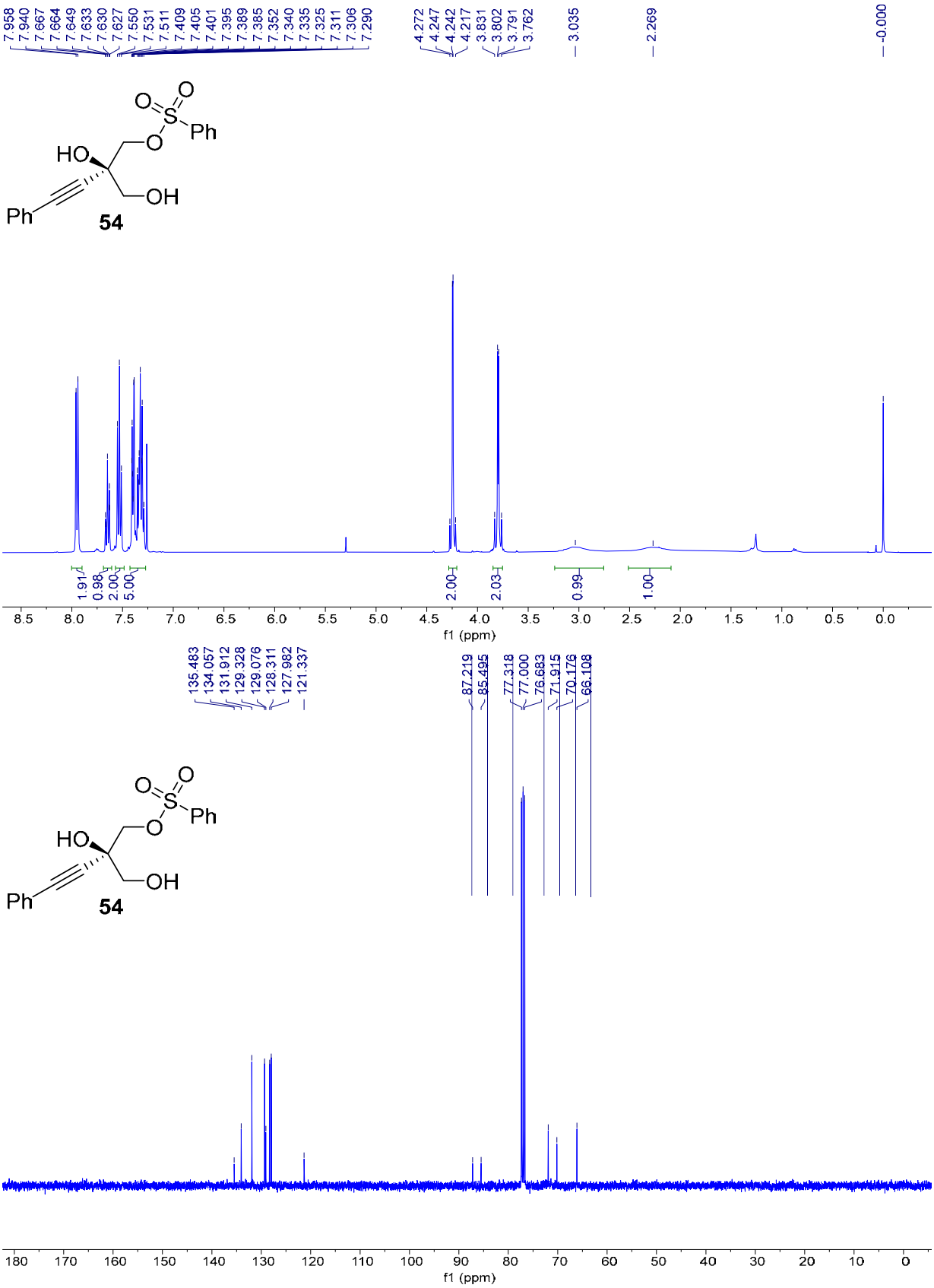

7.933
7.913
7.704
7.685
7.667
7.599
7.580
7.561
5.793
5.774
5.767
5.756
5.749
5.731
5.725
5.714
5.706
5.688
5.124
5.108
5.103
5.097
5.064
4.016
3.991
3.956
3.931
3.594
3.565
3.505
3.476
2.708
2.422
2.283
2.265
0.000
O
O
S
Ph
O
HO
OH
50
1.89
1.00
2.05
1.00
2.08
2.05
1.01
1.07
2.06
2.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
135.328
134.069
131.364
129.350
127.891
119.881
77.317
77.000
76.682
72.815
71.241
64.852
38.355
O
O
S
Ph
O
HO
OH
50
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

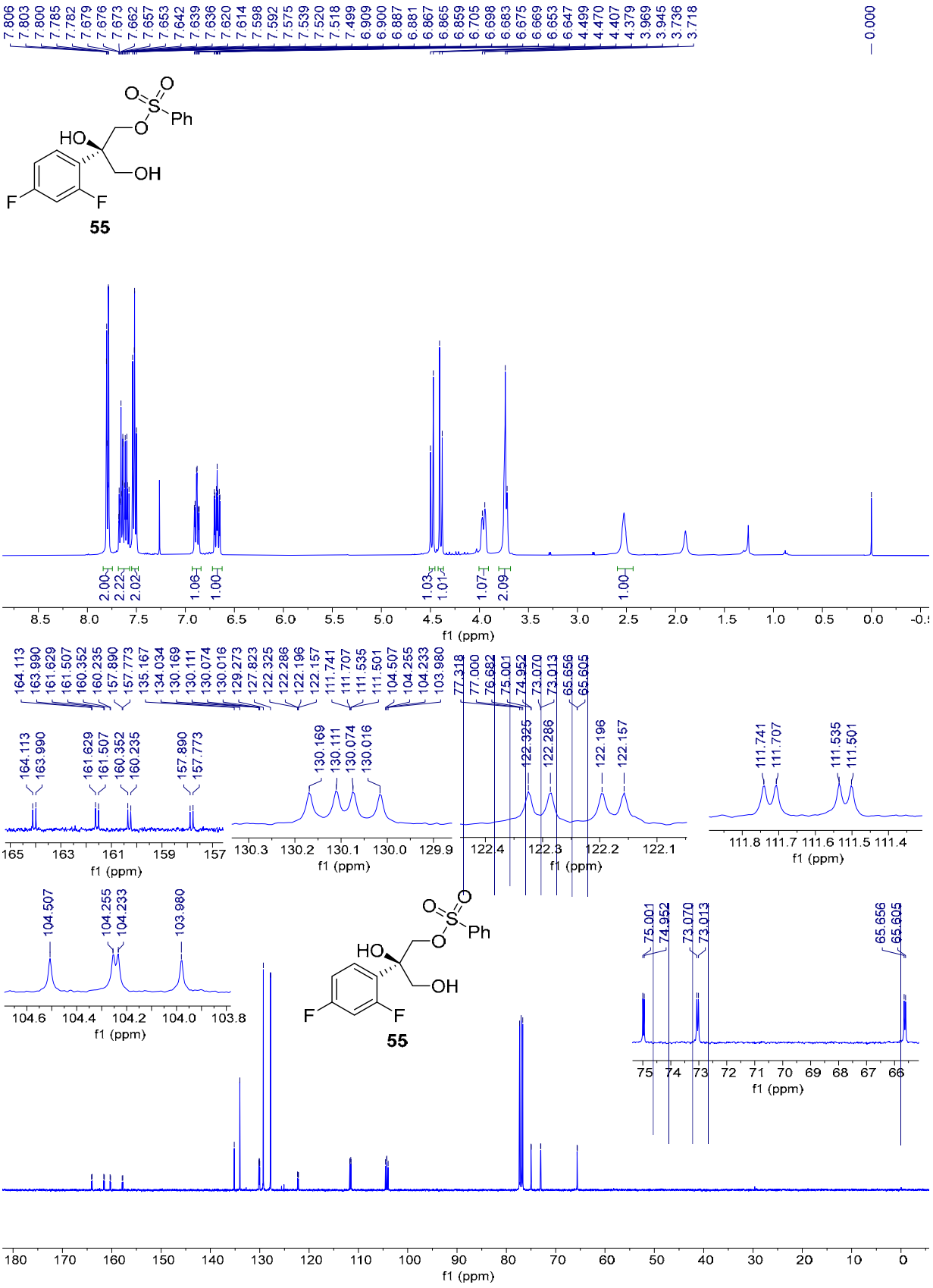

7.953
7.935
7.931
7.708
7.690
7.671
7.601
7.582
7.563
4.188
4.163
4.155
4.130
3.714
3.213
2.509
2.430
-0.000
O
O
S
Ph
O
HO
OH
51
2.02
1.00
2.15
2.17
2.17
1.00
0.92
1.05
f1 (ppm)

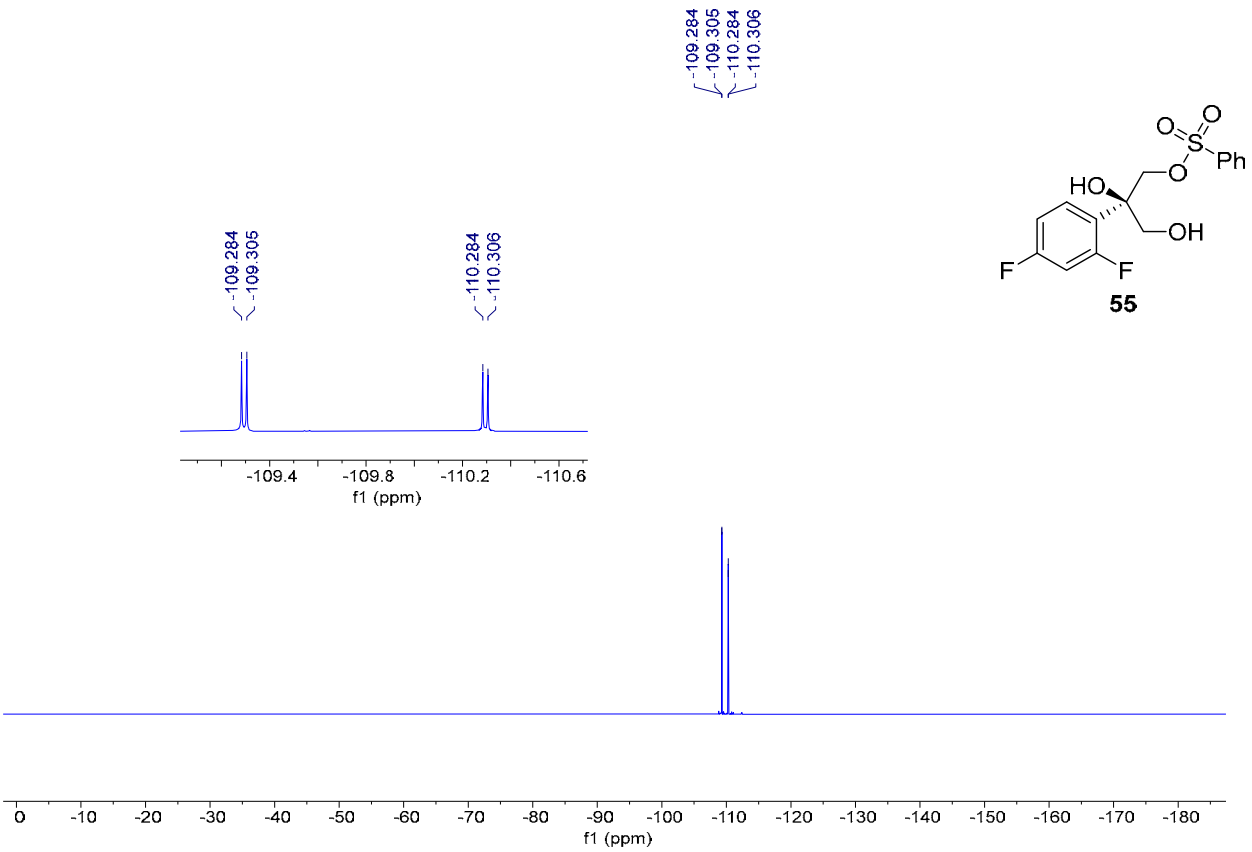

135.323
134.168
129.360
128.008
80.739
77.317
77.000
76.682
75.425
71.638
69.568
65.895
O
O
S
Ph
O
HO
OH
51
f1 (ppm)

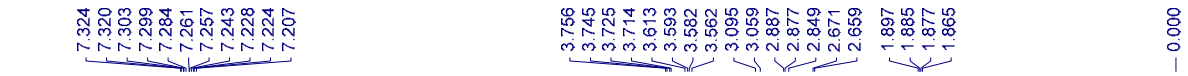

7.922
7.903
7.690
7.671
7.652
7.577
7.558
7.539
7.230
7.214
7.141
7.133
7.121
3.950
3.925
3.844
3.820
3.578
3.566
3.548
3.538
3.478
3.467
3.449
3.438
2.795
2.629
2.438
-0.000
HO
Bn
OH
O
S
Ph
52
1.91
1.02
2.08
5.52
1.00
1.00
1.04
1.05
2.04
1.04
0.95
f1 (ppm)
135.294
134.853
134.050
130.352
129.341
128.359
127.887
126.869
77.318
77.000
76.681
73.273
70.525
64.523
39.594
f1 (ppm)

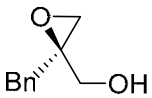

7.813
7.795
7.791
7.655
7.637
7.618
7.524
7.504
7.485
7.372
7.366
7.361
7.354
7.350
7.347
7.338
7.333
7.327
7.317
7.298
7.290
7.280
7.257
4.316
4.290
4.284
4.258
3.870
3.841
3.740
3.711
3.352
2.476
0.000
HO
Ph
OH
O
S
Ph
53
1.93
1.08
2.09
5.49
2.00
1.10
1.04
0.96
0.95
f1 (ppm)
139.510
135.195
133.974
129.275
128.516
128.025
127.856
125.379
77.318
77.000
76.682
75.303
73.364
66.768
f1 (ppm)


7.958
7.940
7.667
7.664
7.649
7.633
7.630
7.627
7.550
7.531
7.511
7.409
7.405
7.401
7.395
7.389
7.385
7.352
7.340
7.335
7.325
7.311
7.306
7.290
4.272
4.247
4.242
4.217
3.831
3.802
3.791
3.762
3.035
2.269
-0.000
HO
OH
Ph
O
S
Ph
54
1.91
0.98
2.00
5.00
2.00
2.03
0.99
1.00
f1 (ppm)
135.483
134.057
131.912
129.328
129.076
128.311
127.982
121.337
87.219
85.495
77.318
77.000
76.683
71.915
70.176
66.108
f1 (ppm)

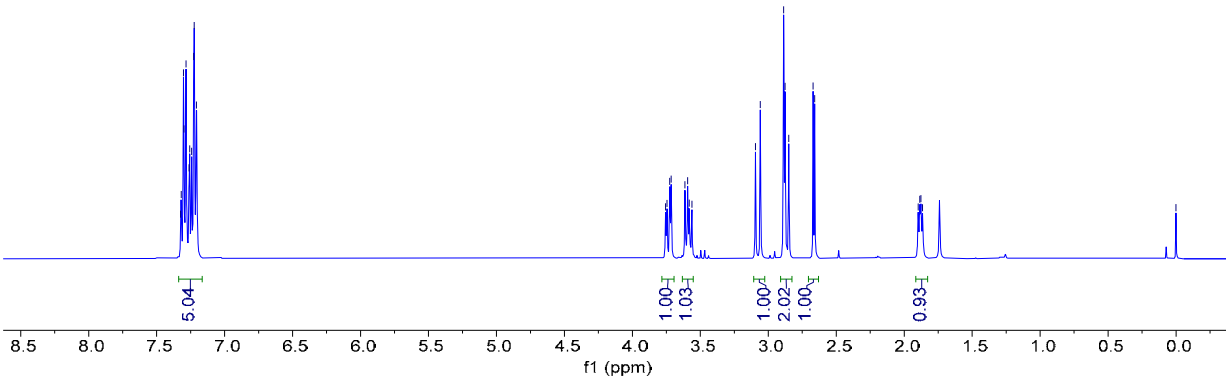

55
f1 (ppm)

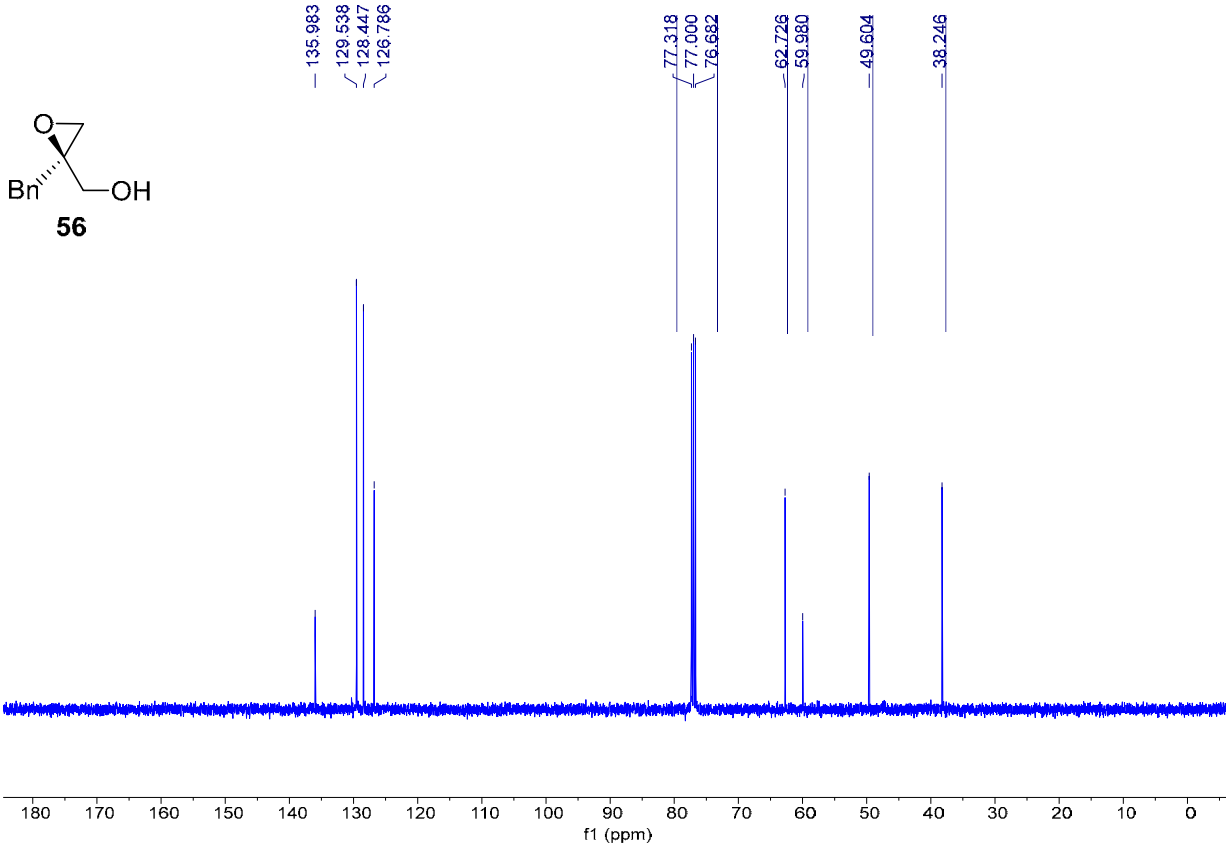

-109.284
-109.305
-110.284
-110.306
-109.284
-109.305
-110.284
-110.306
-109.4
-109.8
-110.2
-110.6
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)
O
O
S
Ph
O
HO
OH
F
F
55


7.324
7.320
7.303
7.299
7.284
7.261
7.257
7.243
7.228
7.224
7.207
3.756
3.745
3.725
3.714
3.613
3.593
3.582
3.562
3.095
3.059
2.887
2.877
2.849
2.671
2.659
1.897
1.885
1.877
1.865
0.000


O
Bn
OH

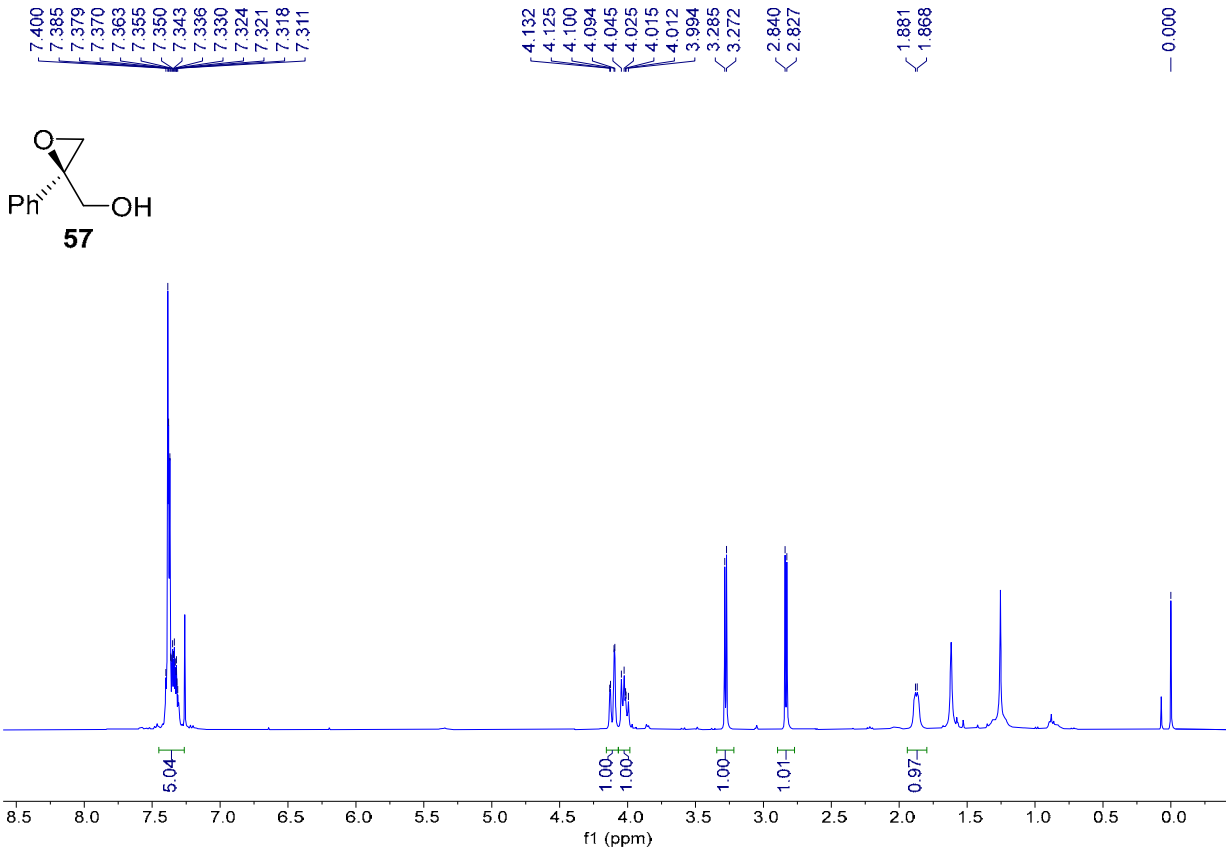
56

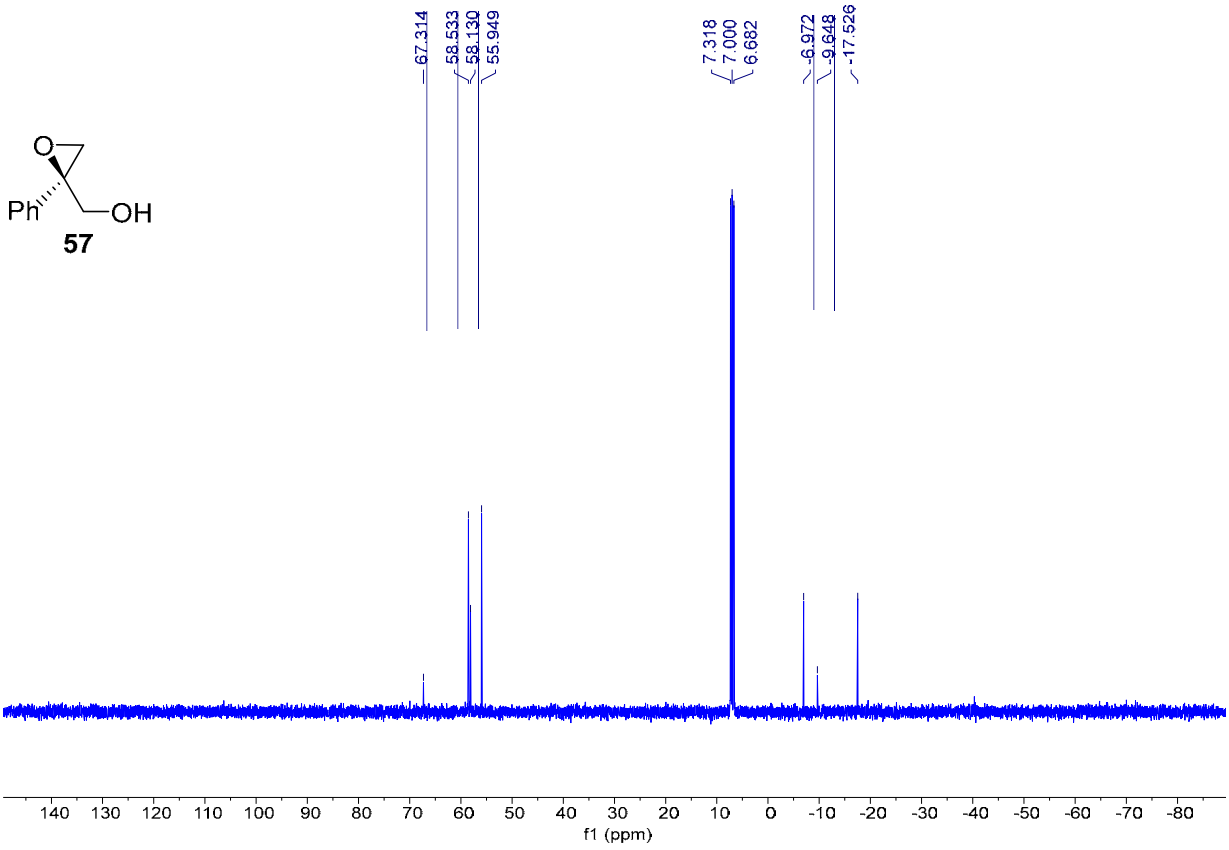

5.04
1.00
1.03
1.00
2.02
1.00
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

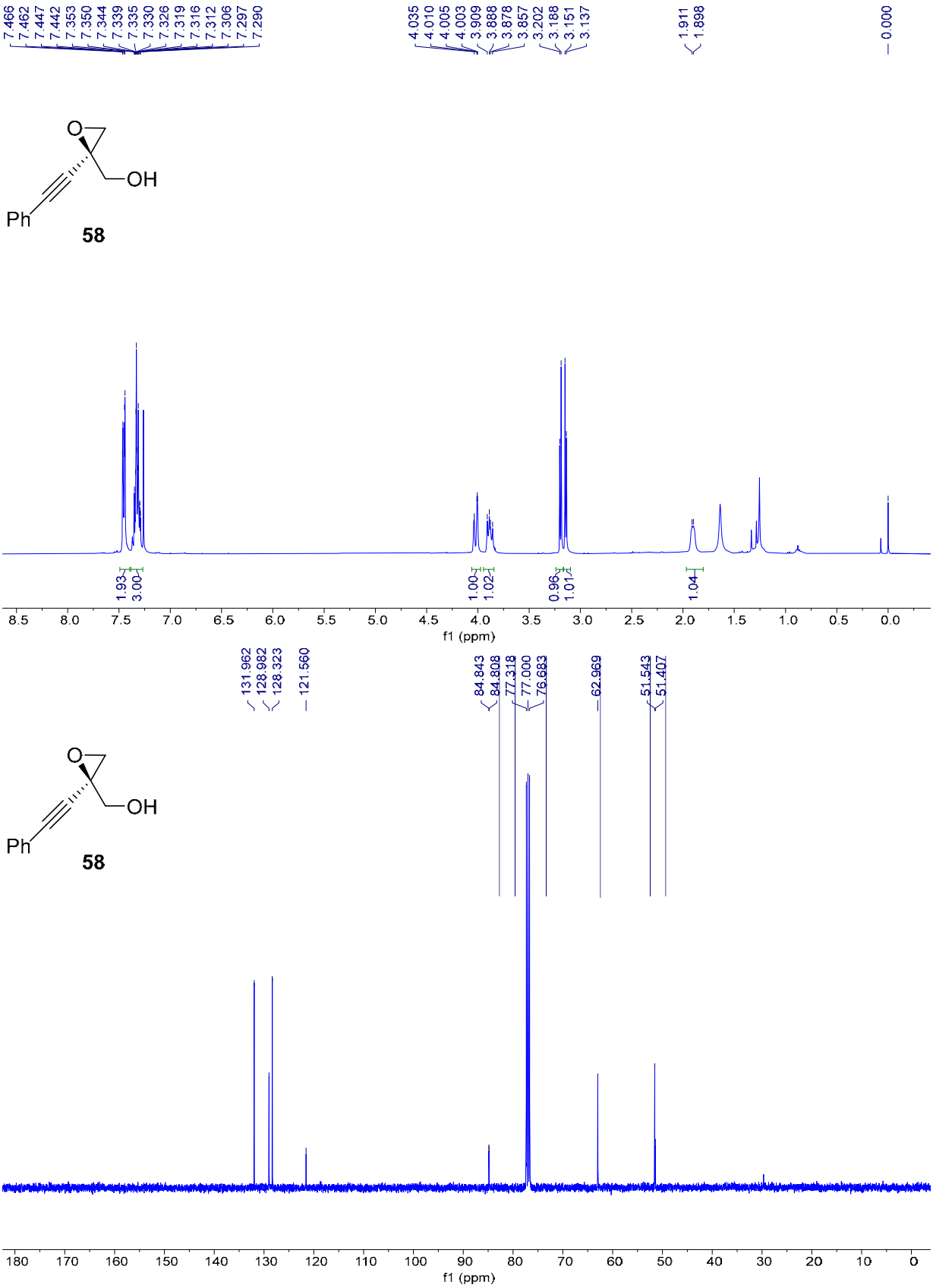

135.983
129.538
128.447
126.786
77.318
77.000
76.682
62.726
59.980
49.604
38.246
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

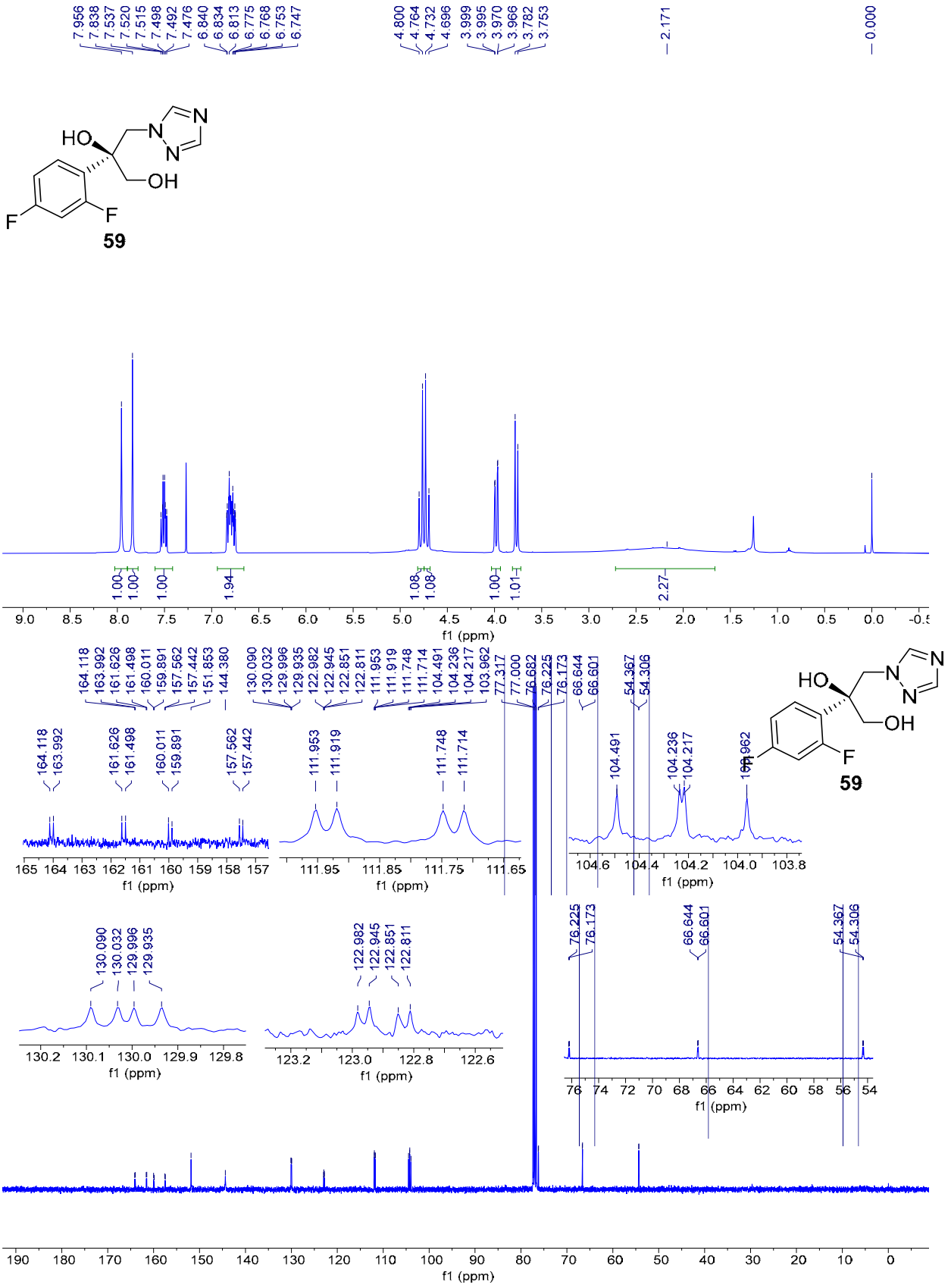
O
Bn
OH

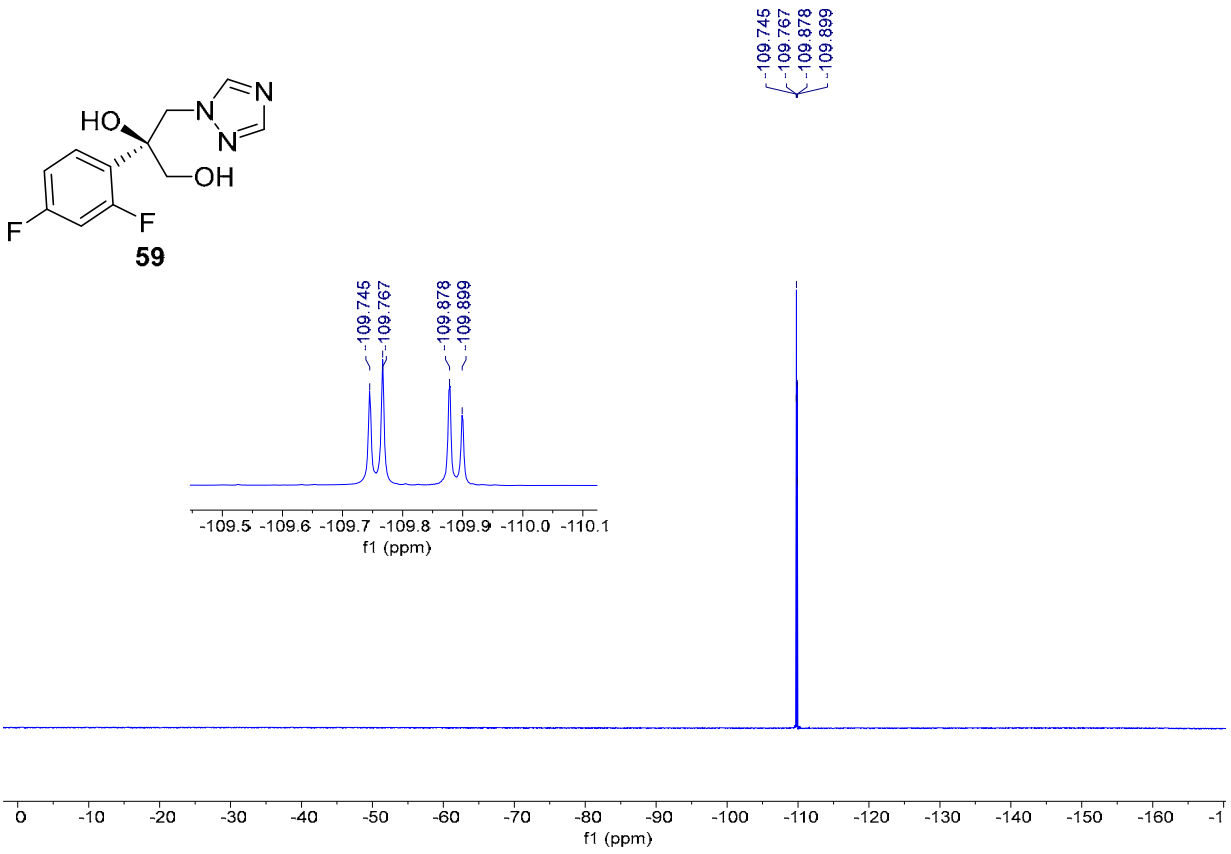
56

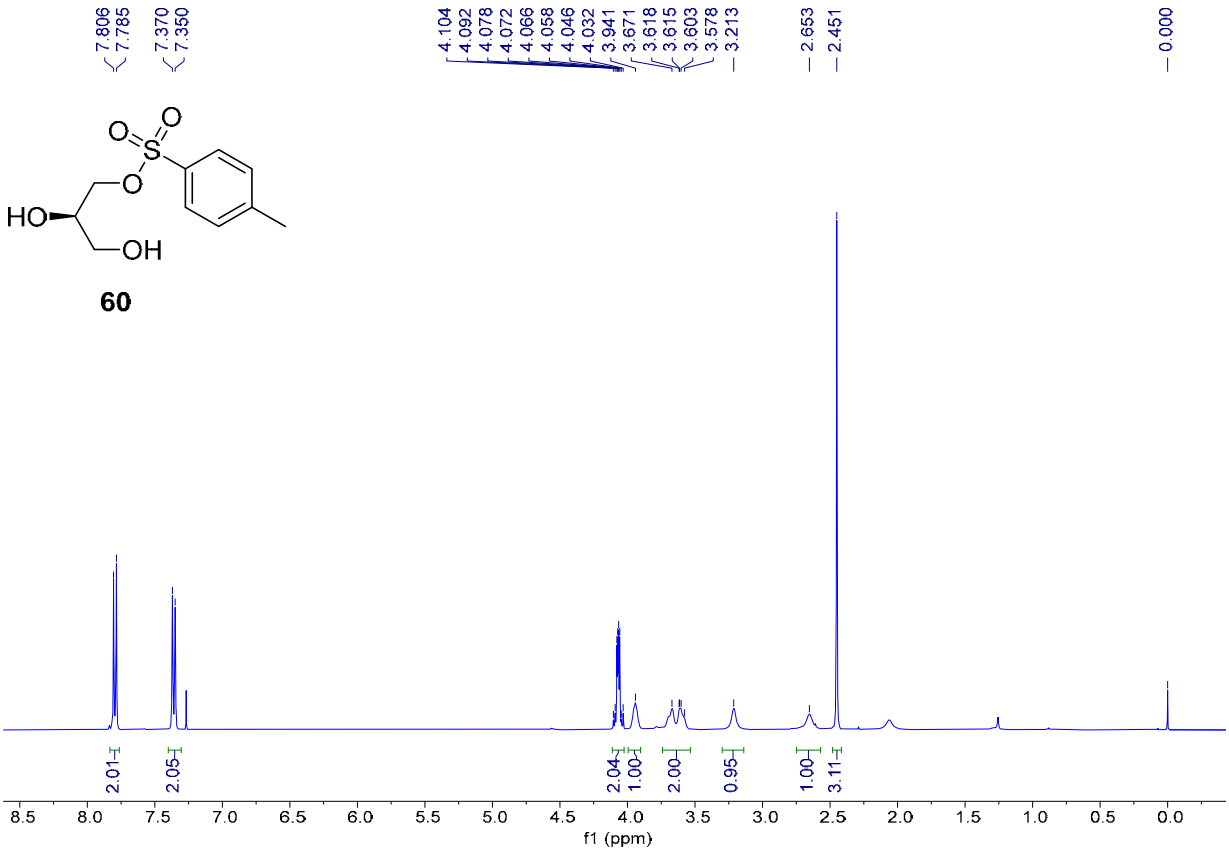

7.400
7.385
7.379
7.370
7.363
7.355
7.350
7.343
7.336
7.330
7.324
7.321
7.318
7.311
4.132
4.125
4.100
4.094
4.045
4.025
4.015
4.012
3.994
3.285
3.272
2.840
2.827
1.881
1.868
0.000
O
Ph
OH
57
5.04
1.00
1.00
1.00
1.01
0.97
f1 (ppm)

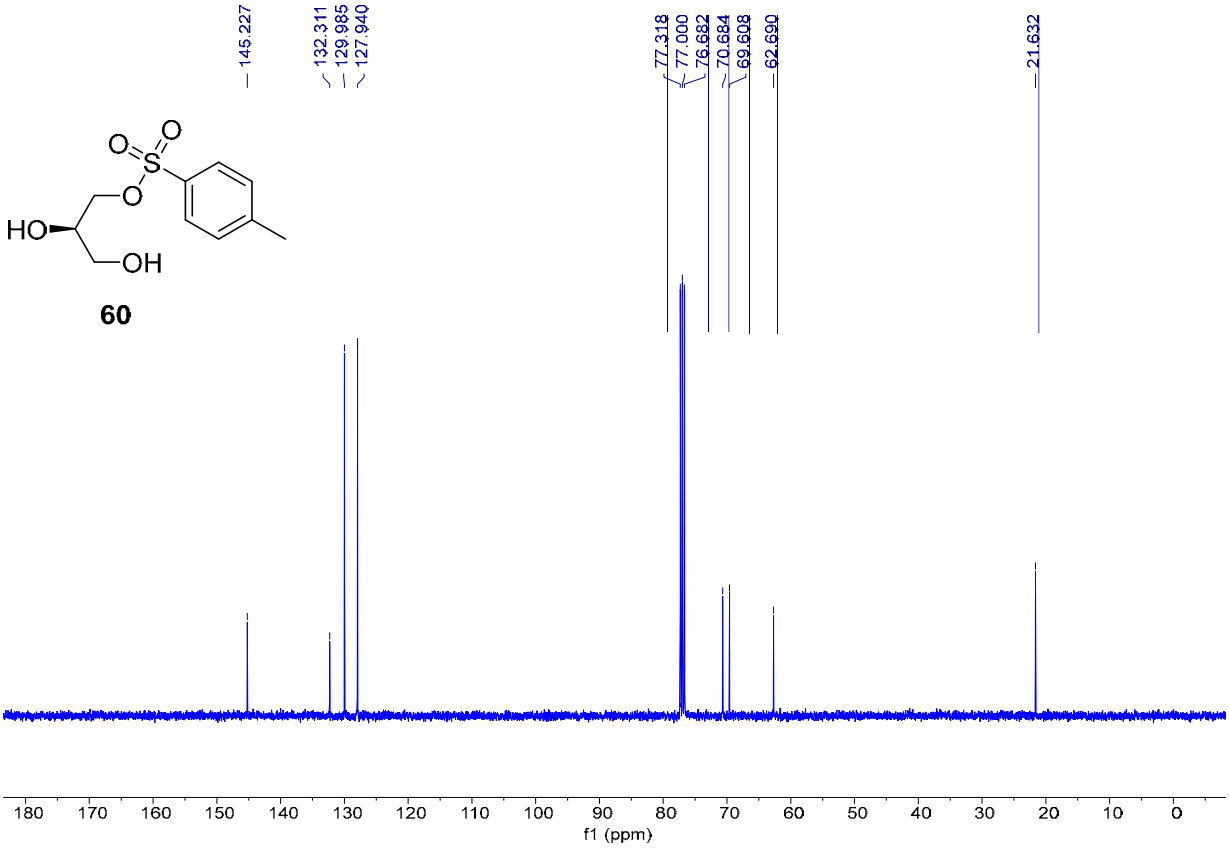

67.314
58.533
58.130
55.949
7.318
7.000
6.682
-6.972
-9.648
-17.526
O
Ph
OH
57
f1 (ppm)

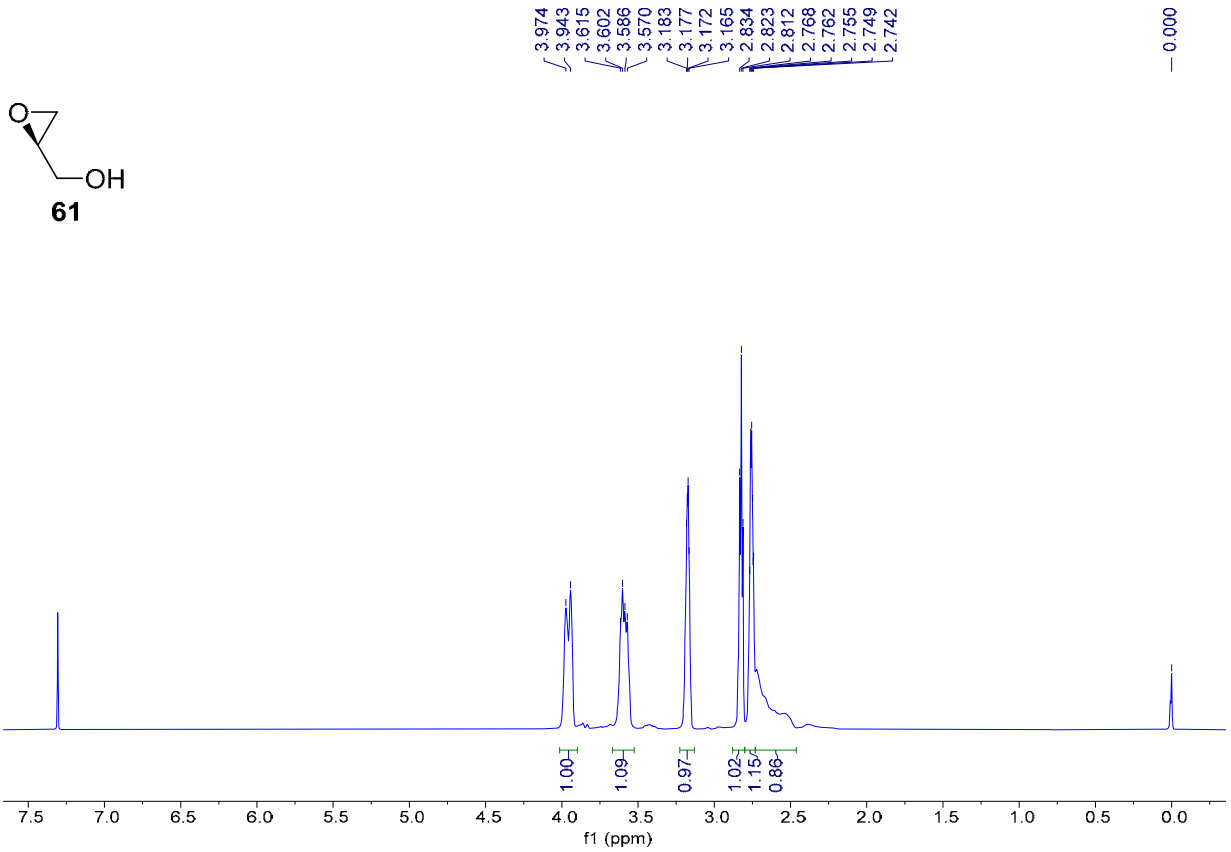

7.466
7.462
7.447
7.442
7.353
7.350
7.344
7.339
7.335
7.330
7.326
7.319
7.316
7.312
7.306
7.297
7.290
4.035
4.010
4.005
4.003
3.909
3.888
3.878
3.857
3.202
3.188
3.151
3.137
1.911
1.898
0.000
O
OH
Ph
58
1.93
3.00
1.00
1.02
0.96
1.01
1.04
f1 (ppm)
131.962
128.982
128.323
121.560
84.843
84.808
77.318
77.000
76.683
62.969
51.543
51.407
O
OH
Ph
58
f1 (ppm)

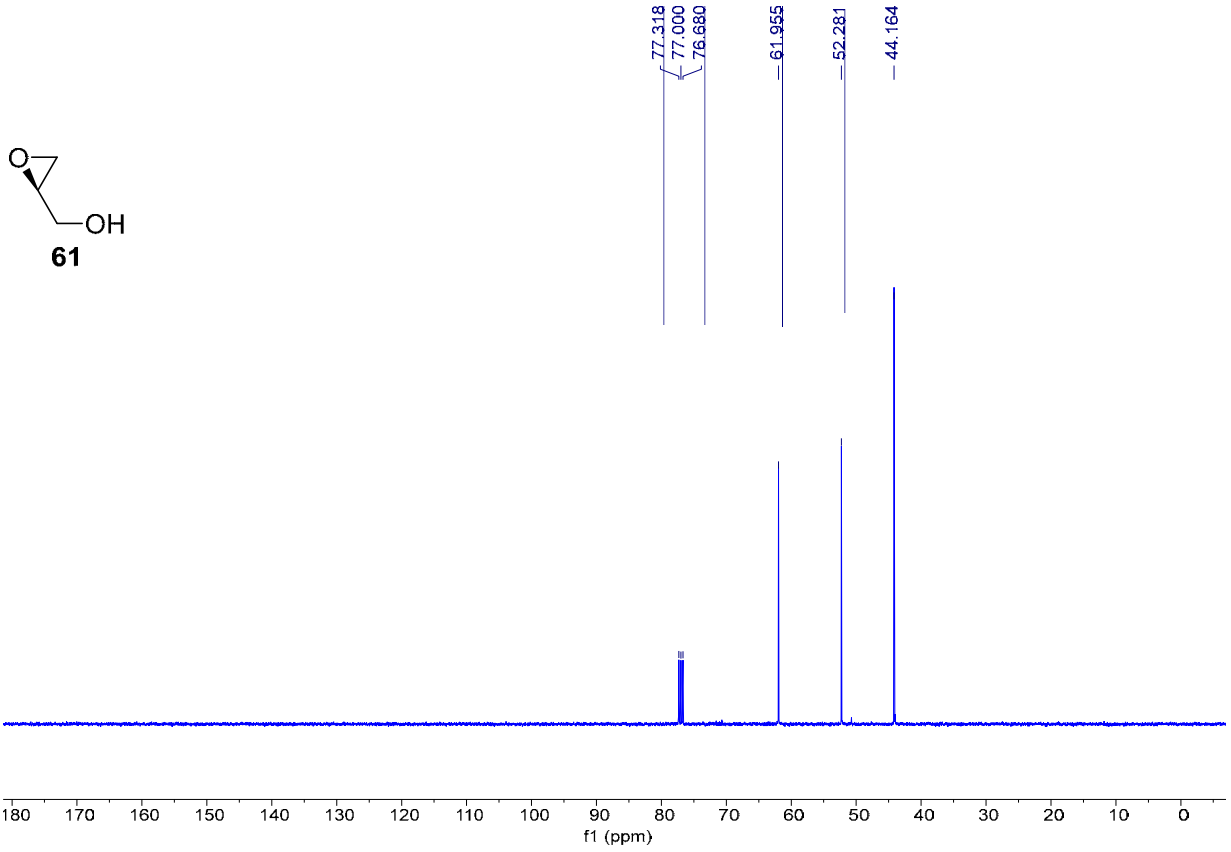

7.956
7.838
7.537
7.520
7.515
7.498
7.492
7.476
6.840
6.834
6.813
6.775
6.768
6.753
6.747
4.800
4.764
4.732
4.696
3.999
3.995
3.970
3.966
3.782
3.753
2.171
0.000
HO
N
N
N
OH
F
F
59
f1 (ppm)
164.118
163.992
161.626
161.498
160.011
159.891
157.562
157.442
151.853
144.380
130.090
130.032
129.996
129.935
122.982
122.945
122.851
122.811
111.953
111.919
111.748
111.714
104.491
104.236
104.217
103.962
77.317
77.000
76.682
76.225
76.173
66.644
66.601
54.367
54.306

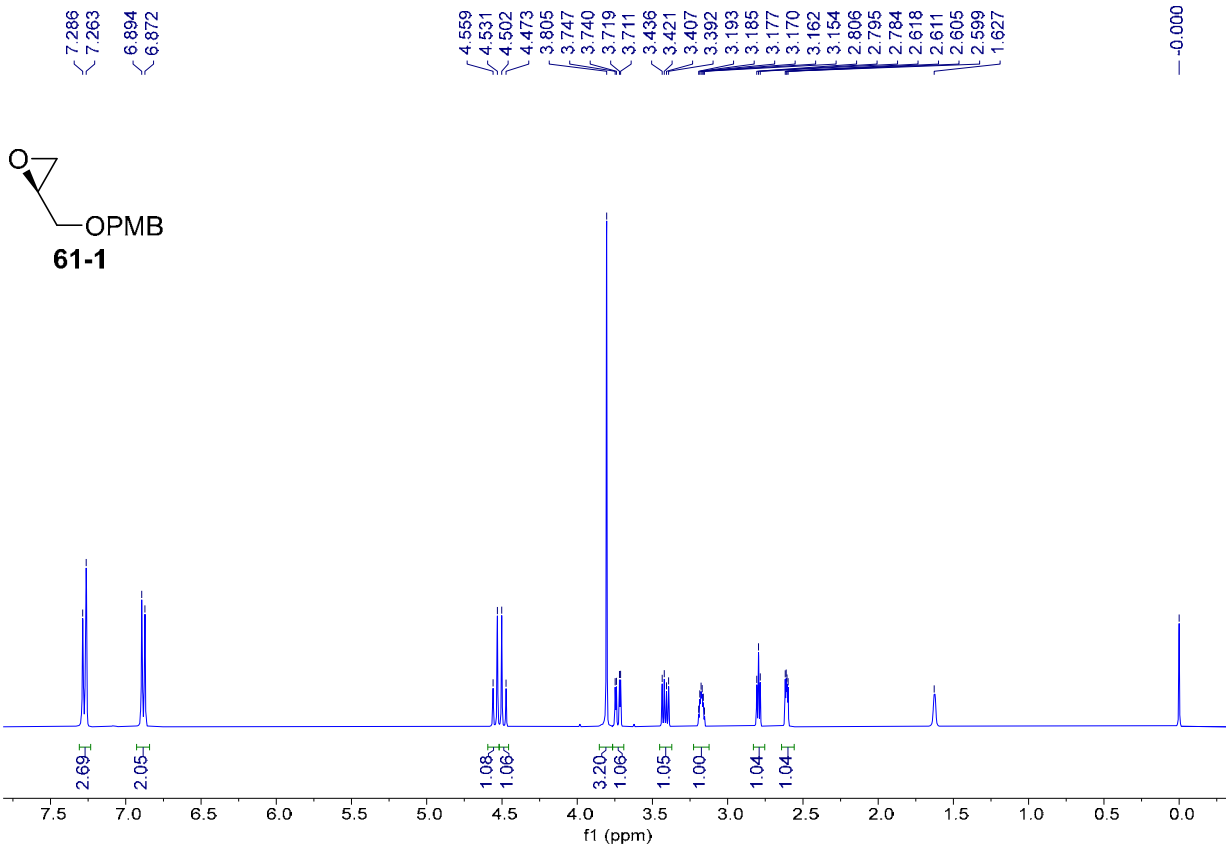

HO
N
N
N
OH
F
F
59
-109.745
-109.767
-109.878
-109.899
-109.5 -109.6 -109.7 -109.8 -109.9 -110.0 -110.1
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -1
f1 (ppm)

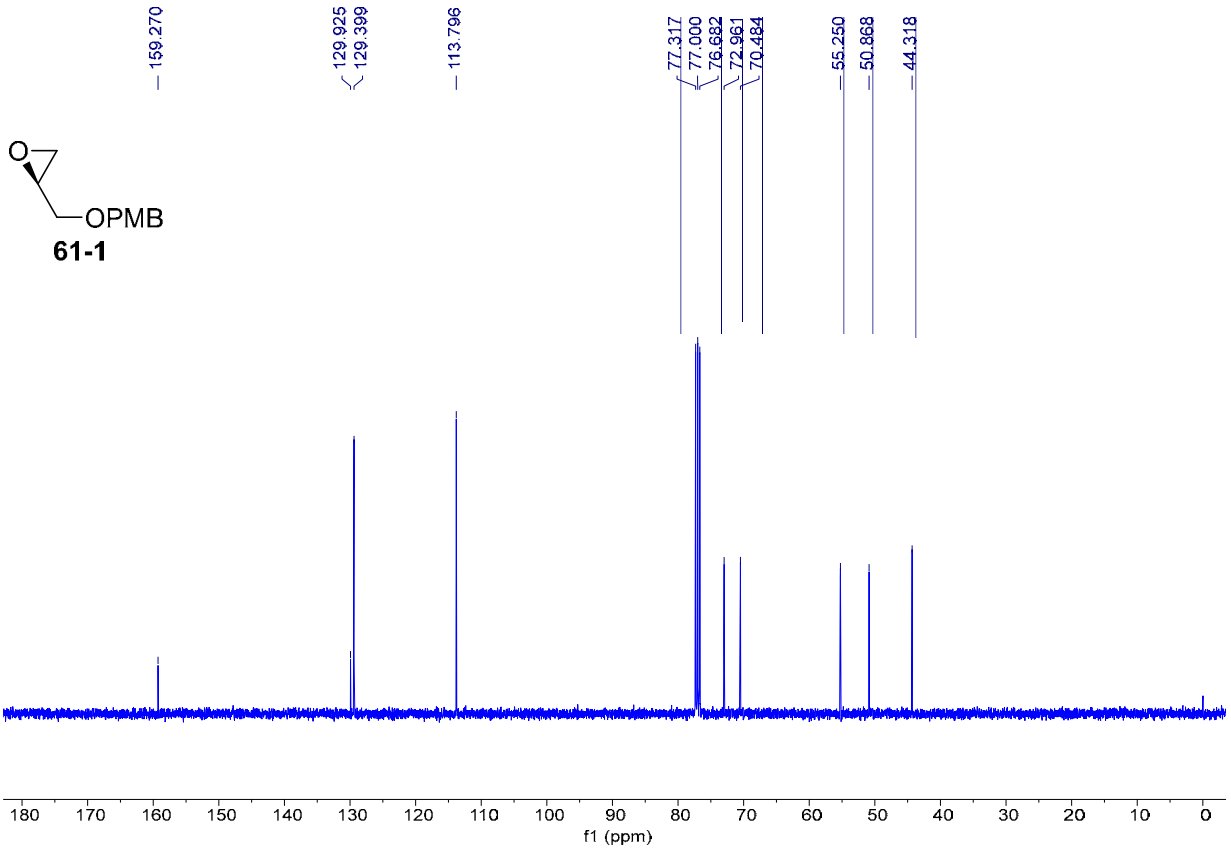

7.806
7.785
7.370
7.350
4.104
4.092
4.078
4.072
4.066
4.058
4.046
4.032
3.941
3.671
3.618
3.615
3.603
3.578
3.213
2.653
2.451
0.000
HO
OH
60
2.01
2.05
2.04
1.00
2.00
0.95
1.00
3.11
f1 (ppm)


145.227
132.311
129.985
127.940
77.318
77.000
76.682
70.684
69.608
62.690
21.632
HO
OH
60
f1 (ppm)

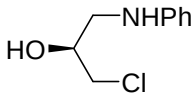

3.974
3.943
3.615
3.602
3.586
3.570
3.183
3.177
3.172
3.165
2.834
2.823
2.812
2.768
2.762
2.755
2.749
2.742
0.000
OH
61
1.00
1.09
0.97
1.02
1.15
0.86
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


77.318
77.000
76.680
61.955
52.281
44.164
OH
61
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

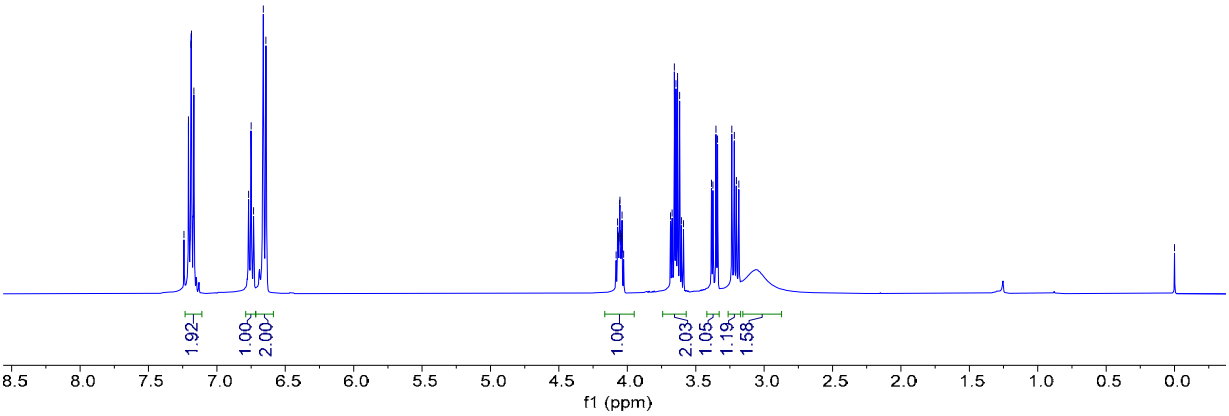

7.286
7.263
6.894
6.872
4.559
4.531
4.502
4.473
3.805
3.747
3.740
3.719
3.711
3.436
3.421
3.407
3.392
3.193
3.185
3.177
3.170
3.162
3.154
2.806
2.795
2.784
2.618
2.611
2.605
2.599
1.627
-0.000
O
OPMB
61-1
2.69
2.05
1.08
1.06
3.20
1.06
1.05
1.00
1.04
1.04
f1 (ppm)

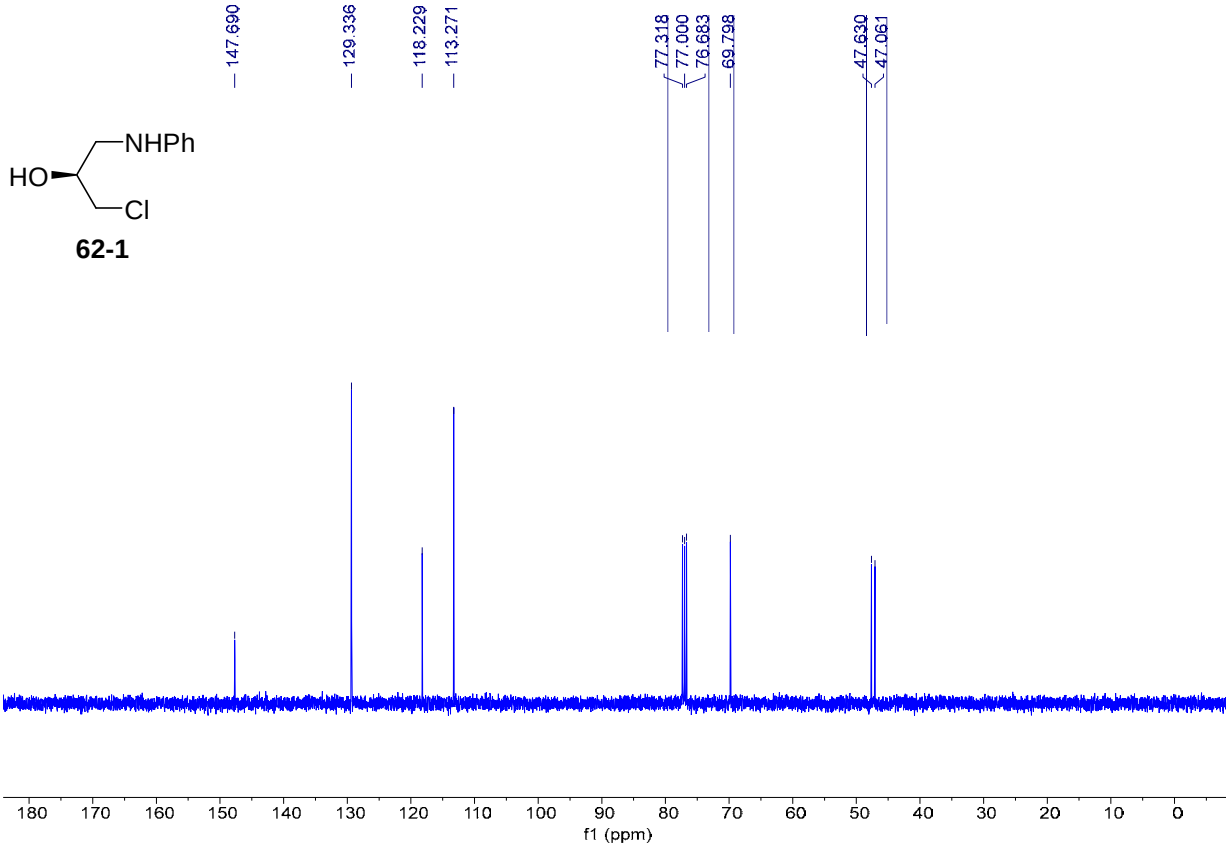

159.270
129.925
129.399
113.796
77.317
77.000
76.682
72.961
70.484
55.250
50.868
44.318
O
OPMB
61-1
f1 (ppm)


7.240
7.208
7.190
7.186
7.168
6.768
6.750
6.732
6.660
6.641
4.082
4.071
4.067
4.064
4.060
4.056
4.053
4.049
4.045
4.042
4.038
4.027
3.684
3.673
3.656
3.644
3.632
3.617
3.604
3.589
3.385
3.374
3.352
3.341
3.236
3.218
3.203
3.185
0.000


NHPh
HO
Cl

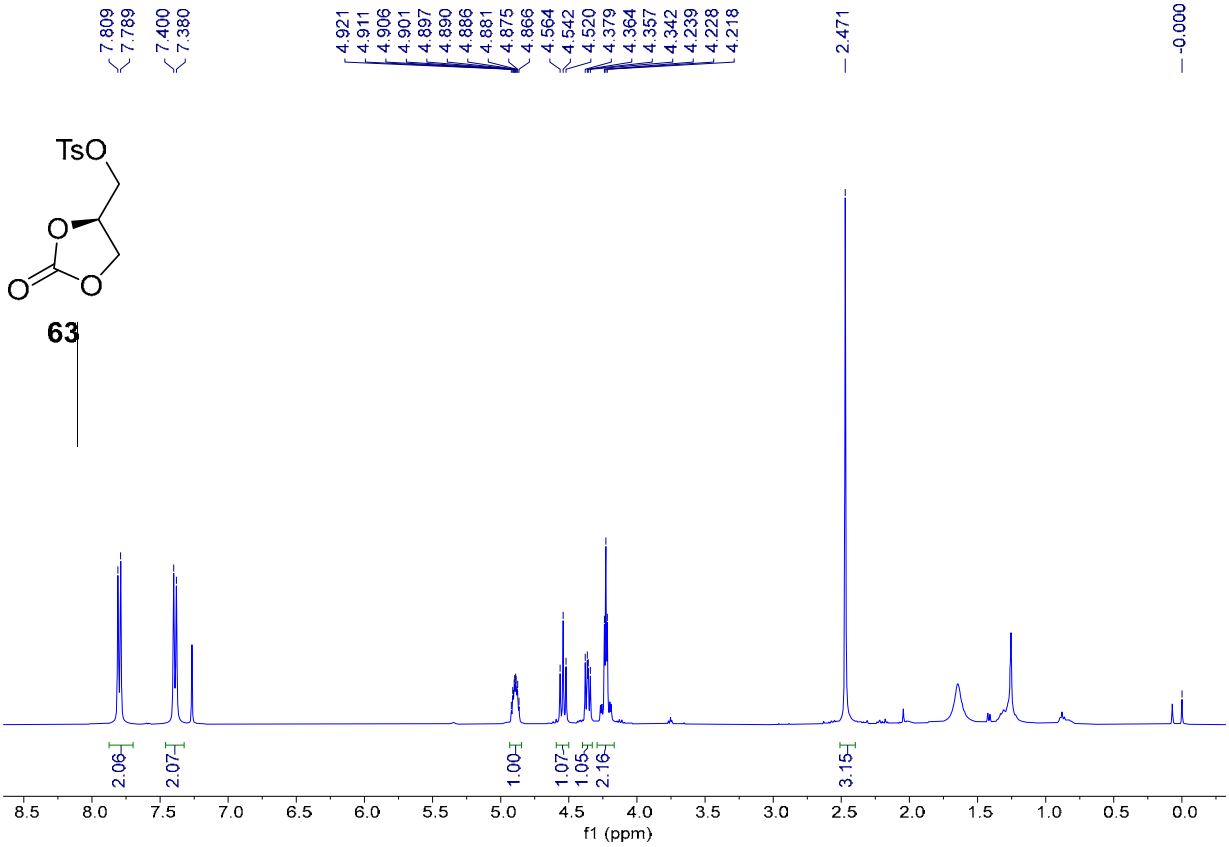
62-1

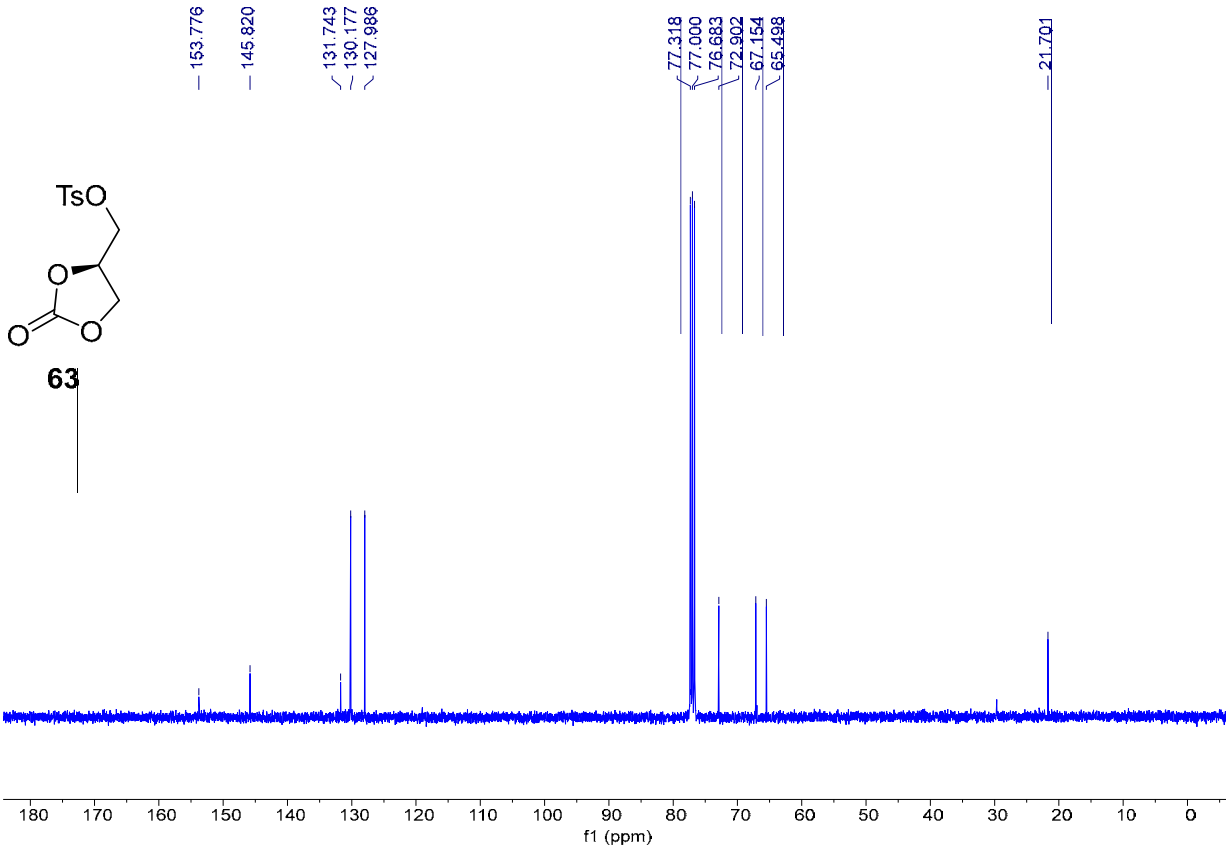

1.92
1.00
2.00
1.00
2.03
1.05
1.19
1.58
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

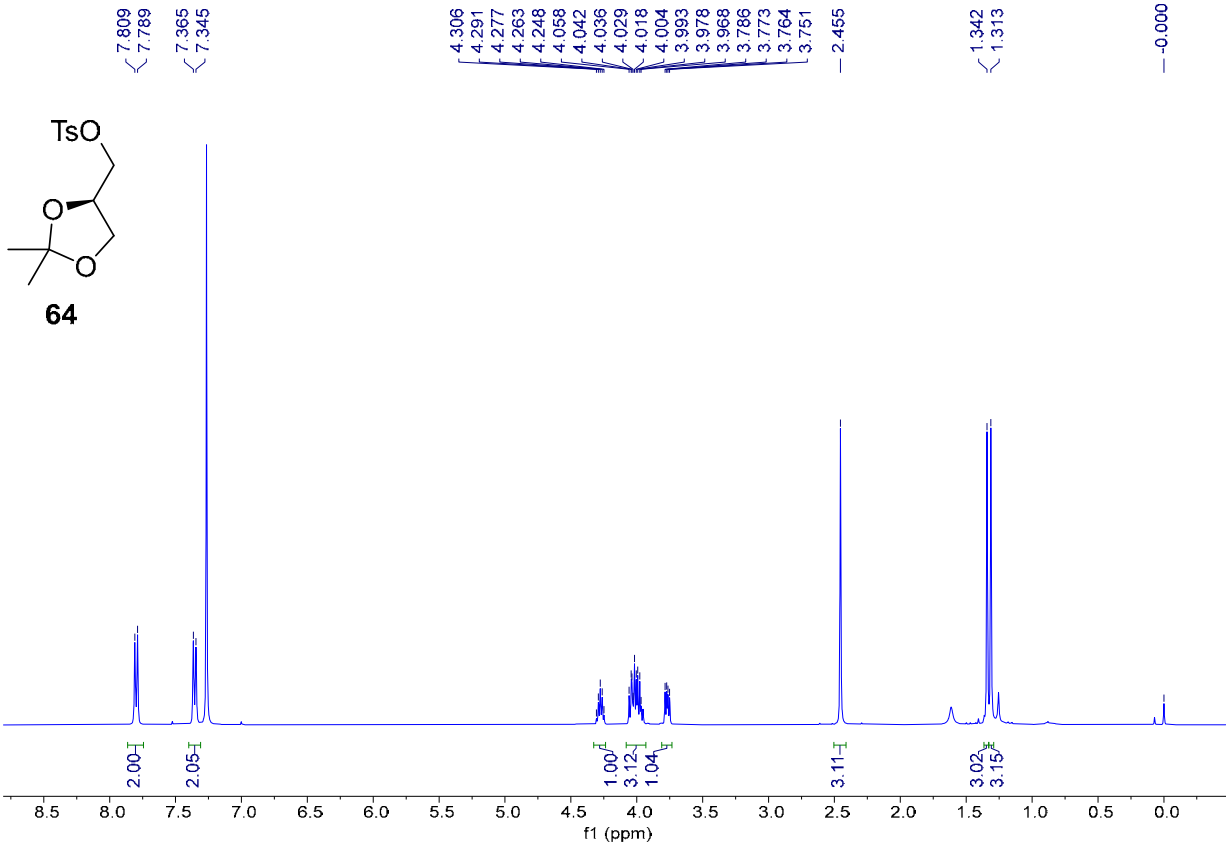

147.690
129.336
118.229
113.271
77.318
77.000
76.683
69.798
47.630
47.061
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

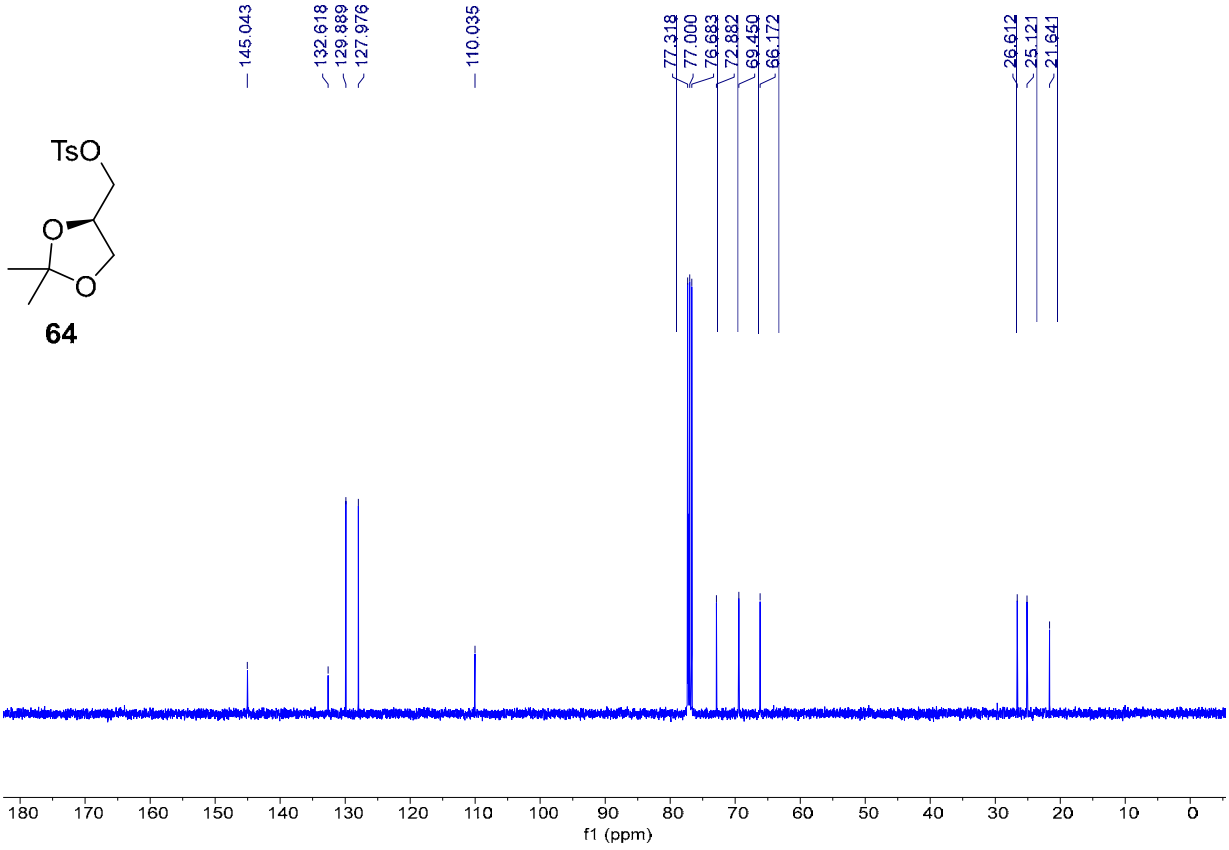
NHPh
HO
Cl

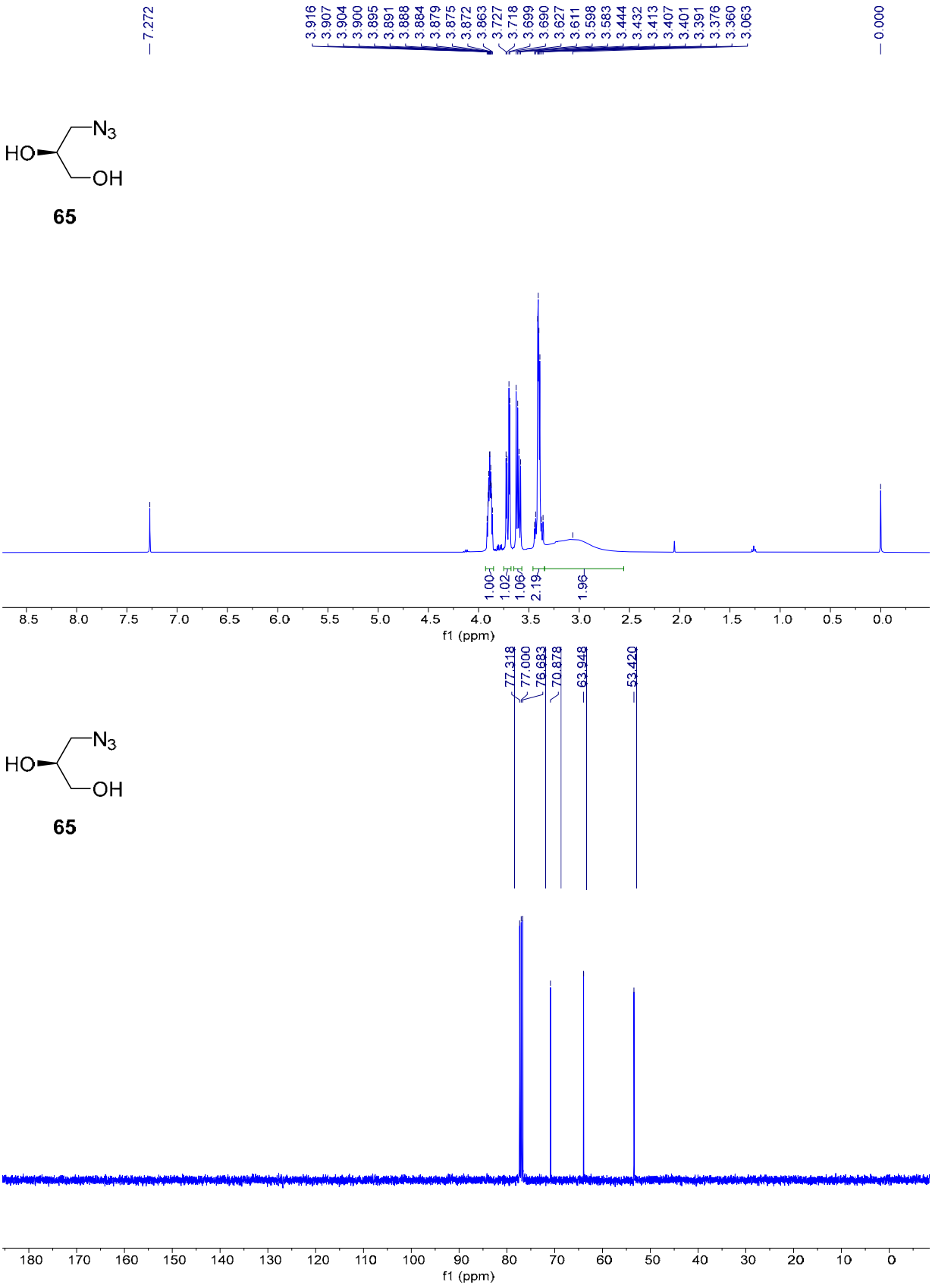
62-1


7.809
7.789
7.400
7.380
4.921
4.911
4.906
4.901
4.897
4.890
4.886
4.881
4.875
4.866
4.564
4.542
4.520
4.379
4.364
4.357
4.342
4.239
4.228
4.218
2.471
-0.000
TsO
O
O
O
63
2.06
2.07
1.00
1.07
1.05
2.16
3.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

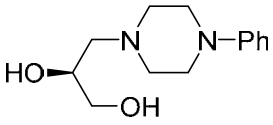

153.776
145.820
131.743
130.177
127.986
77.318
77.000
76.683
72.902
67.154
65.498
21.701
TsO
O
O
O
63
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.809
7.789
7.365
7.345
4.306
4.291
4.277
4.263
4.248
4.058
4.042
4.036
4.029
4.018
4.004
3.993
3.978
3.968
3.786
3.773
3.764
3.751
2.455
1.342
1.313
-0.000
TsO
O
O
64
2.00
2.05
1.00
3.12
1.04
3.11
3.02
3.15
f1 (ppm)

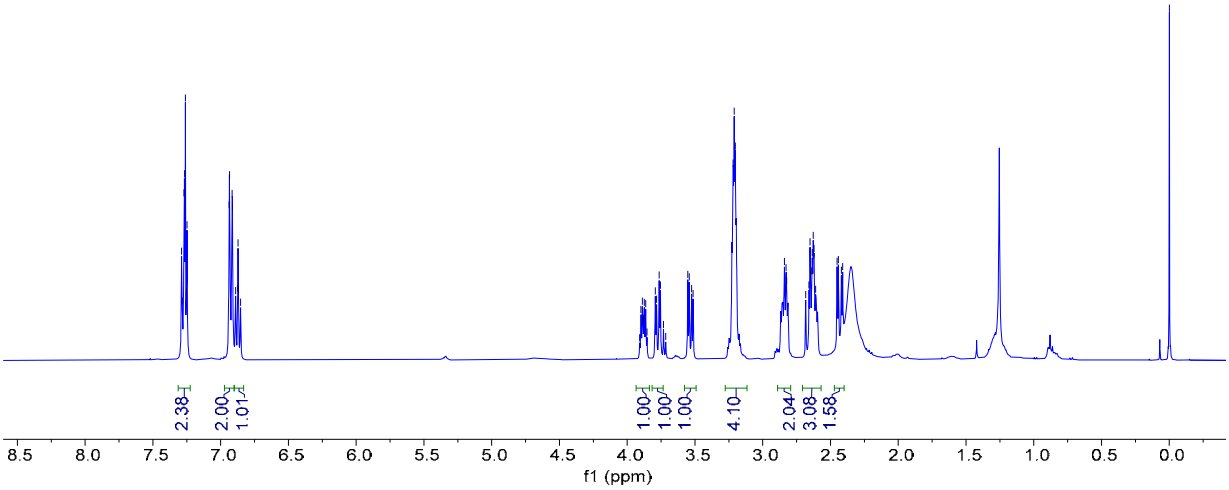

145.043
132.618
129.889
127.976
110.035
77.318
77.000
76.683
72.882
69.450
66.172
26.612
25.121
21.641
TsO
O
O
64
f1 (ppm)

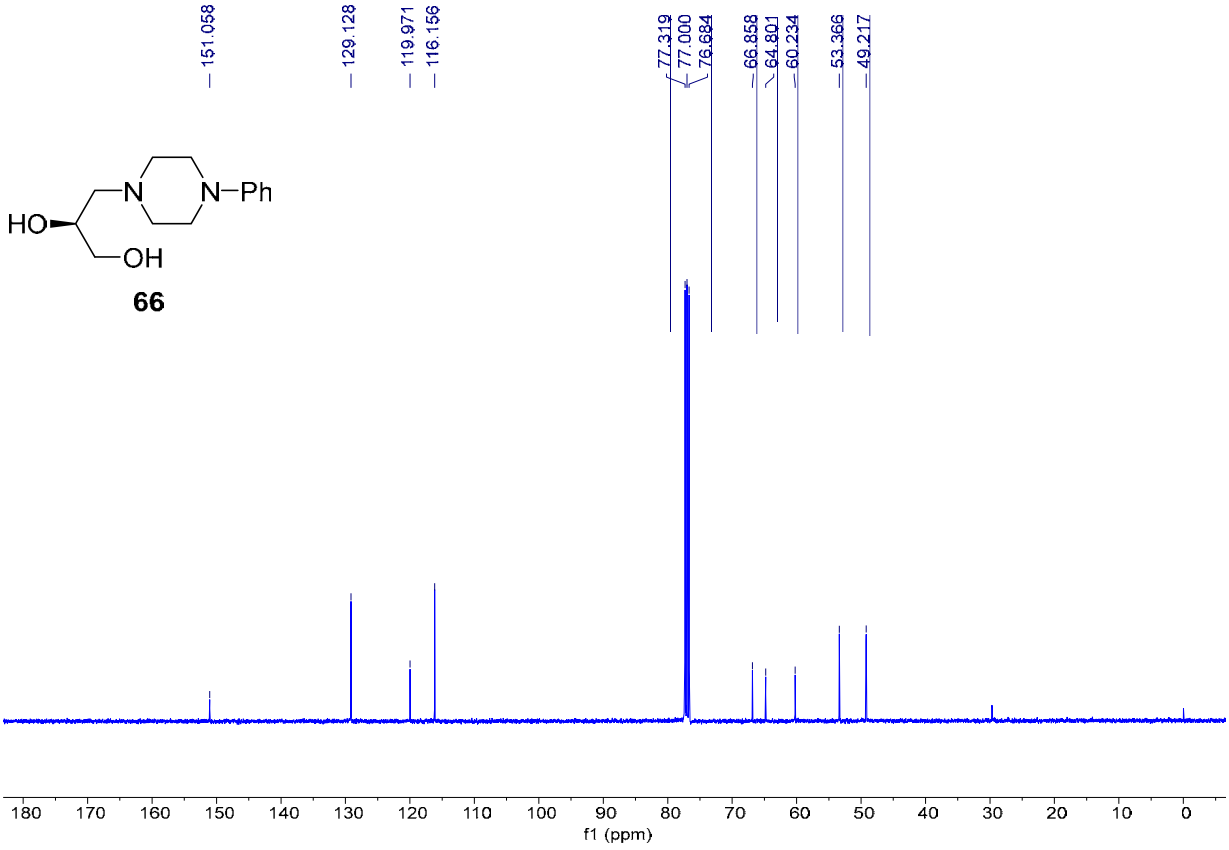

7.272
3.916
3.907
3.904
3.900
3.895
3.891
3.888
3.884
3.879
3.875
3.872
3.863
3.727
3.718
3.699
3.690
3.627
3.611
3.598
3.583
3.444
3.432
3.413
3.407
3.401
3.391
3.376
3.360
3.063
0.000
N3
HO
OH
65
1.00
1.02
1.06
2.19
1.96
f1 (ppm)
77.318
77.000
76.683
70.878
63.948
53.420
N3
HO
OH
65
f1 (ppm)


7.288
7.284
7.270
7.267
7.261
7.253
7.248
6.937
6.934
6.915
6.913
6.890
6.875
6.871
6.869
6.853
3.908
3.898
3.888
3.884
3.878
3.874
3.864
3.854
3.793
3.784
3.764
3.755
3.732
3.716
3.553
3.542
3.525
3.514
3.219
3.211
3.203
2.840
2.828
2.823
2.683
2.659
2.651
2.647
2.638
2.634
2.627
2.621
2.609
2.451
2.442
2.420
2.410
-0.000


HO
N
N–Ph
OH

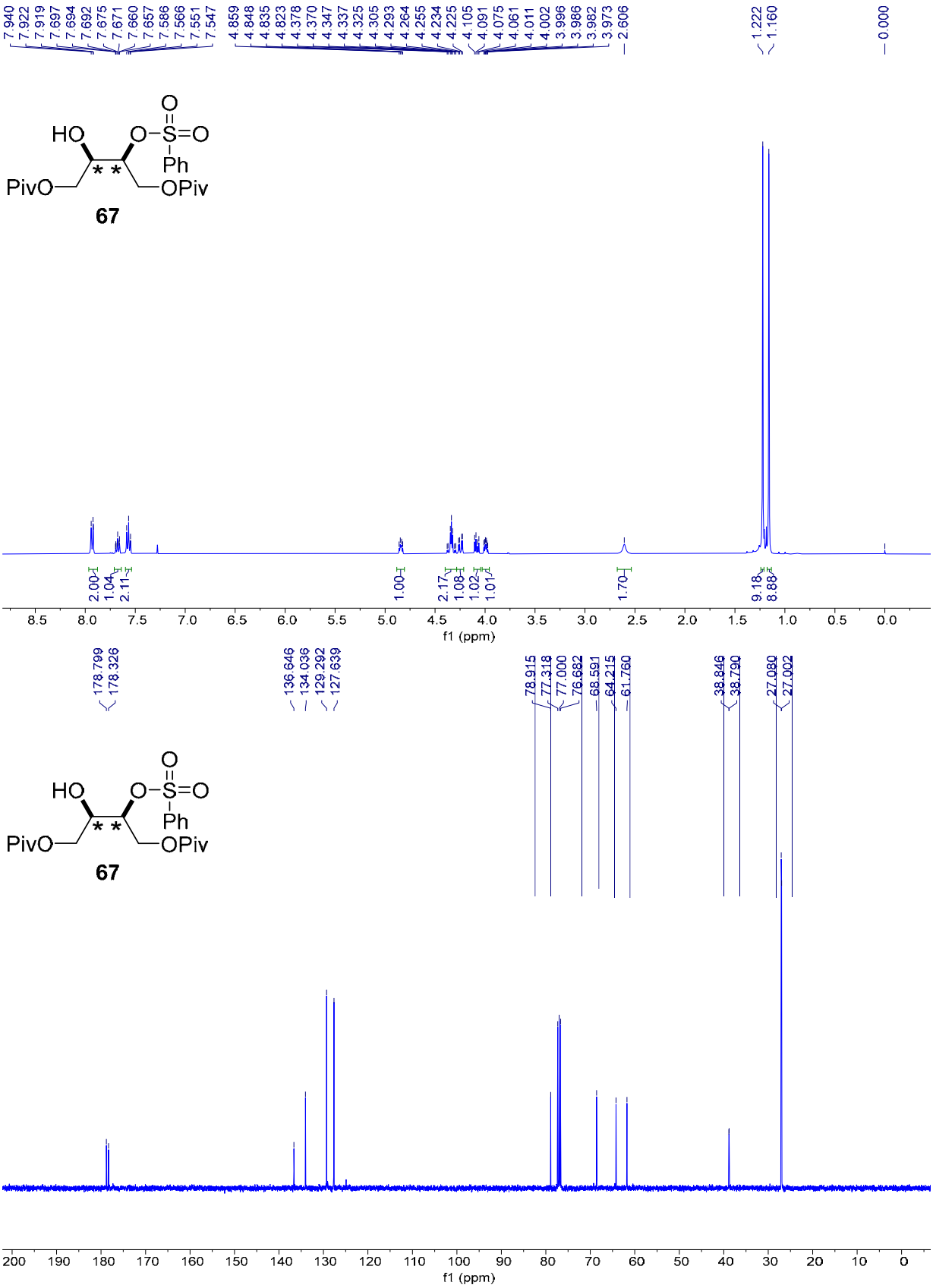
66

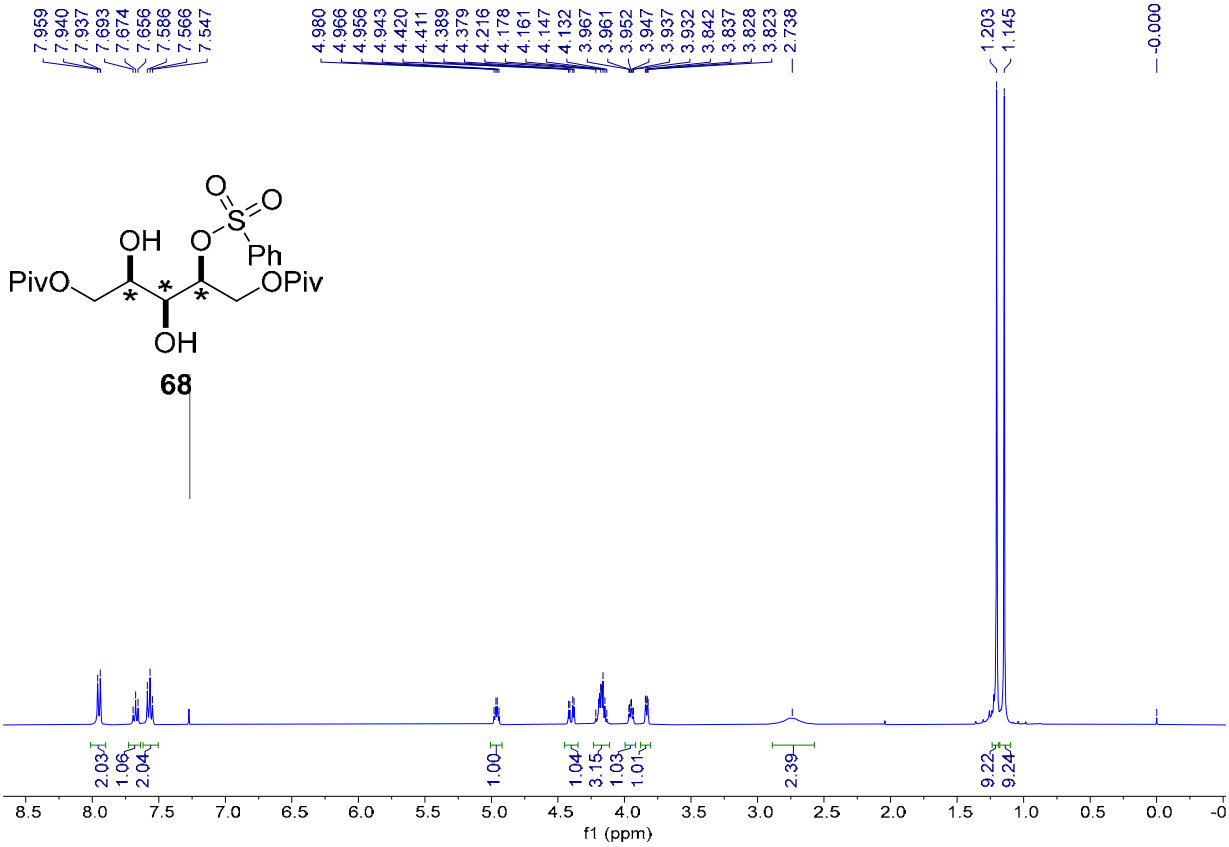

2.38
2.00
1.01
1.00
1.00
1.00
4.10
2.04
3.08
1.58
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

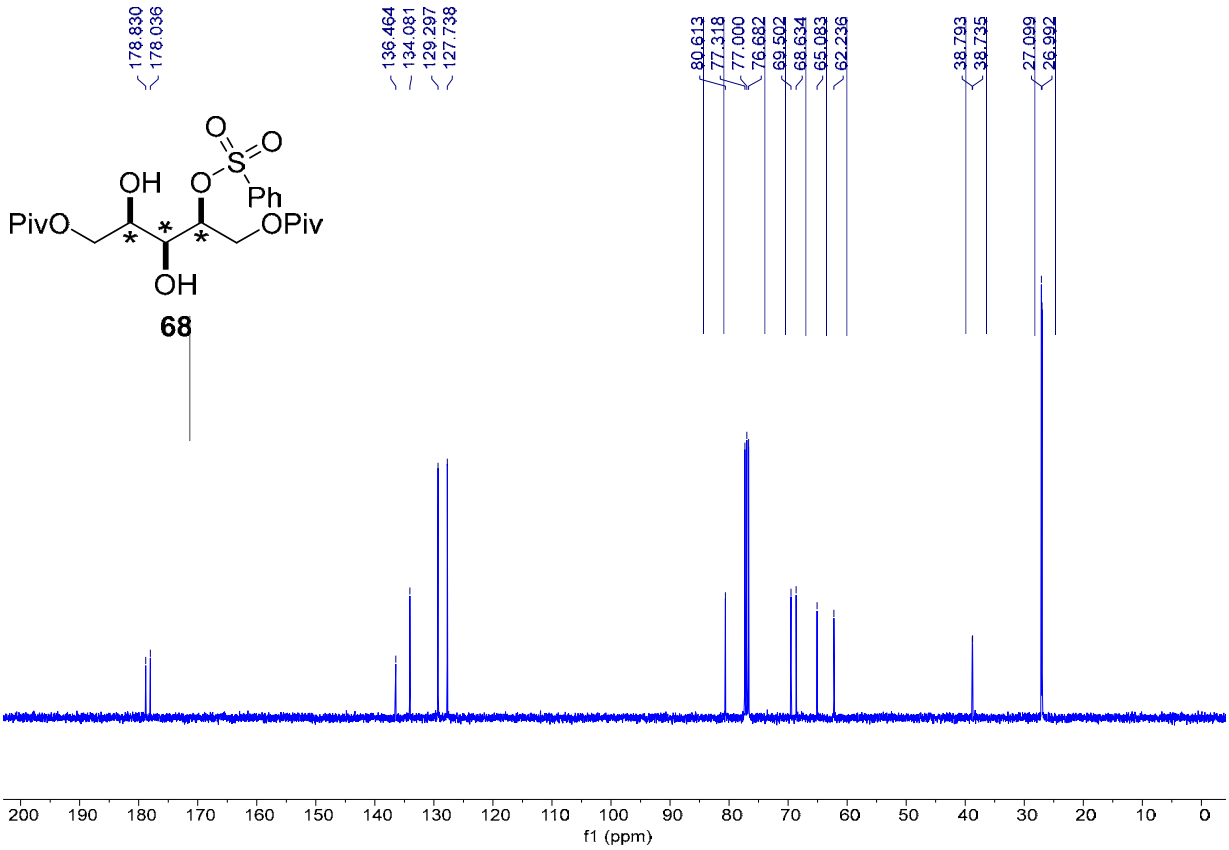

151.058
129.128
119.971
116.156
77.319
77.000
76.684
66.858
64.801
60.234
53.366
49.217
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

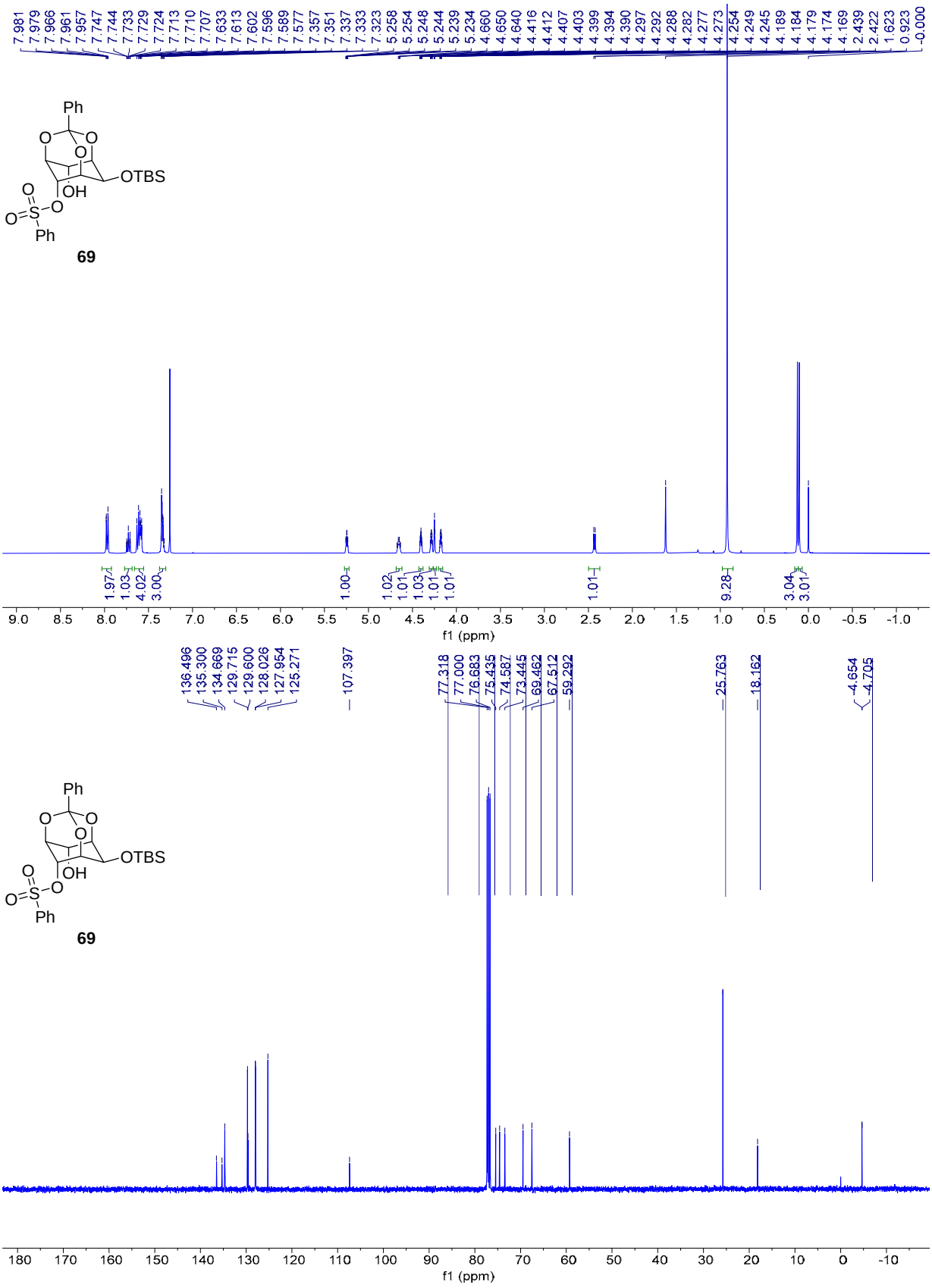
HO
N
N–Ph
OH

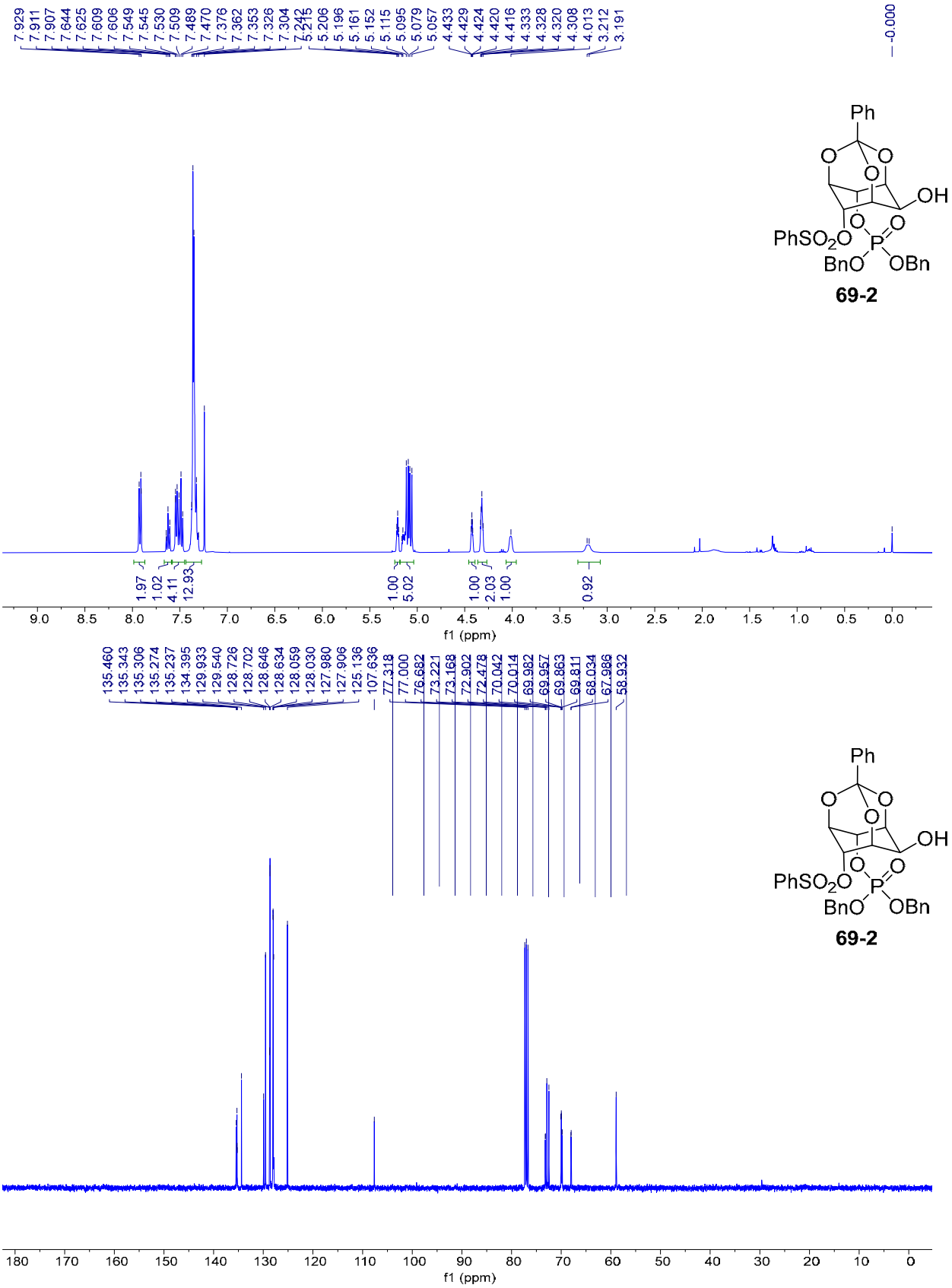
66

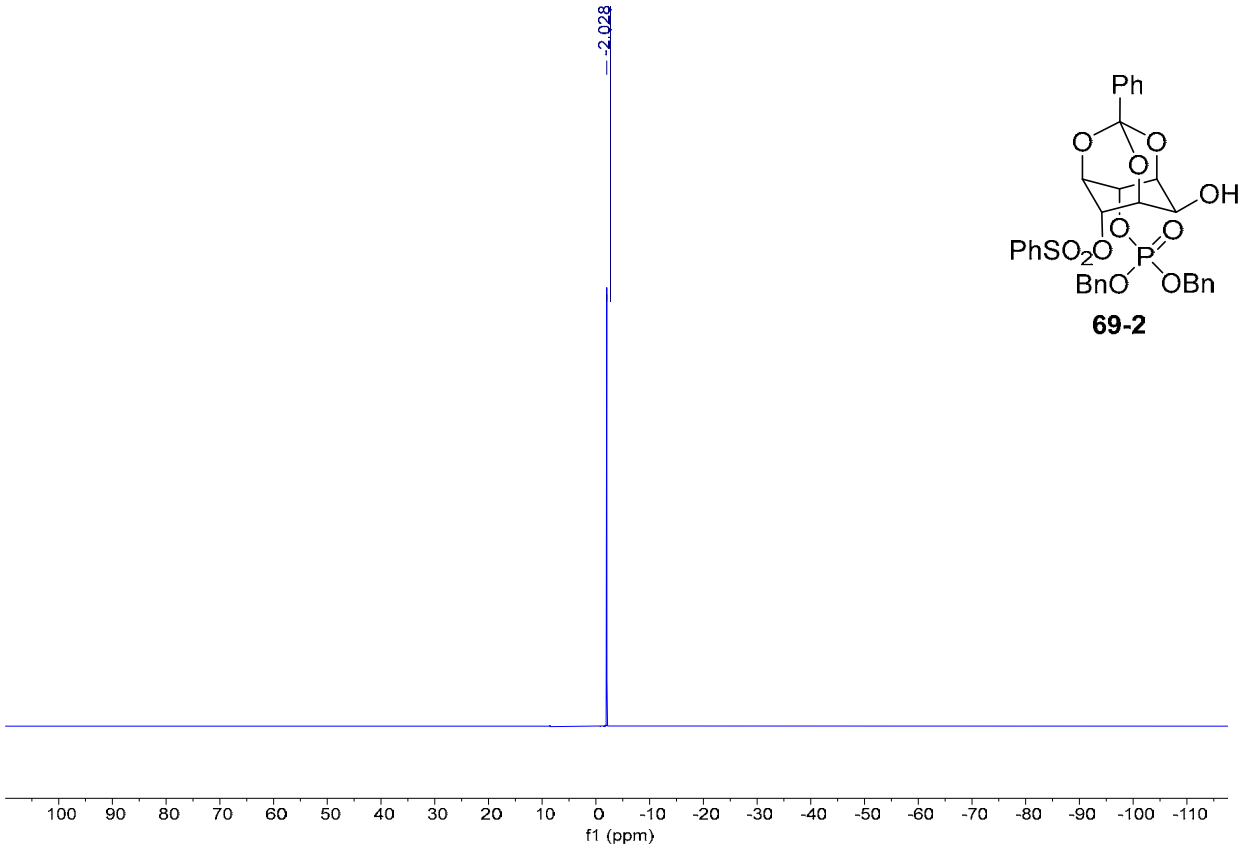

7.940
7.922
7.919
7.697
7.694
7.692
7.675
7.671
7.660
7.657
7.586
7.566
7.551
7.547
4.859
4.848
4.835
4.823
4.378
4.370
4.347
4.337
4.325
4.305
4.293
4.264
4.255
4.234
4.225
4.105
4.091
4.075
4.061
4.011
4.002
3.996
3.986
3.982
3.973
2.606
1.222
1.160
0.000
HO
O
O−S=O
Ph
PivO
OPiv
67
2.00
1.04
2.11
1.00
2.17
1.08
1.02
1.01
1.70
9.18
8.88
f1 (ppm)
178.799
178.326
136.646
134.036
129.292
127.639
78.915
77.318
77.000
76.682
68.591
64.215
61.760
38.846
38.790
27.080
27.002
HO
O
O−S=O
Ph
PivO
OPiv
67
f1 (ppm)


7.959
7.940
7.937
7.693
7.674
7.656
7.586
7.566
7.547
4.980
4.966
4.956
4.943
4.420
4.411
4.389
4.379
4.216
4.178
4.161
4.147
4.132
3.967
3.961
3.952
3.947
3.937
3.932
3.842
3.837
3.828
3.823
2.738
1.203
1.145
-0.000
OH
O
O
S
O
Ph
PivO
OPiv
OH
68
2.03
1.08
2.04
1.00
1.04
3.15
1.03
1.01
2.39
9.22
9.24
f1 (ppm)


178.830
178.036
136.464
134.081
129.297
127.738
80.613
77.318
77.000
76.682
69.502
68.634
65.083
62.236
38.793
38.735
27.099
26.992
OH
O
O
S
O
Ph
PivO
OPiv
OH
68
f1 (ppm)

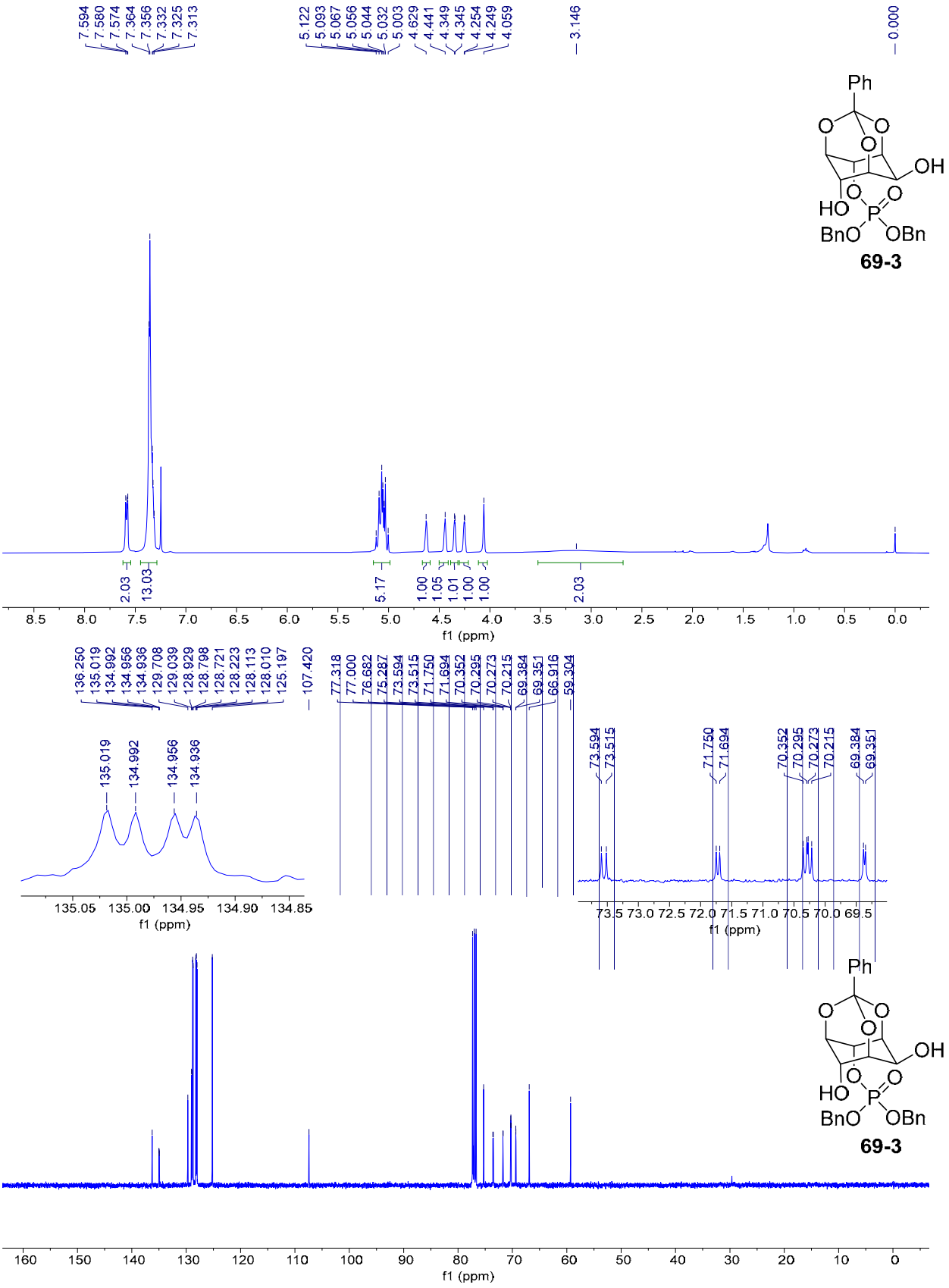

7.981
7.979
7.966
7.961
7.957
7.747
7.744
7.733
7.729
7.724
7.713
7.710
7.707
7.633
7.613
7.602
7.596
7.589
7.577
7.357
7.351
7.337
7.333
7.323
5.258
5.254
5.248
5.244
5.239
5.234
4.660
4.650
4.640
4.416
4.412
4.407
4.403
4.399
4.394
4.390
4.297
4.292
4.288
4.282
4.277
4.273
4.254
4.249
4.245
4.189
4.184
4.179
4.174
4.169
2.439
2.422
1.623
0.923
-0.000
Ph
O
O
O
OTBS
OH
O
O=S
O
Ph
69
1.97
1.03
4.02
3.00
1.00
1.02
1.01
1.03
1.01
1.01
1.01
9.28
3.04
3.01
f1 (ppm)
136.496
135.300
134.669
129.715
129.600
128.026
127.954
125.271
107.397
77.318
77.000
76.683
75.435
74.587
73.445
69.462
67.512
59.292
25.763
18.162
-4.654
-4.705
f1 (ppm)

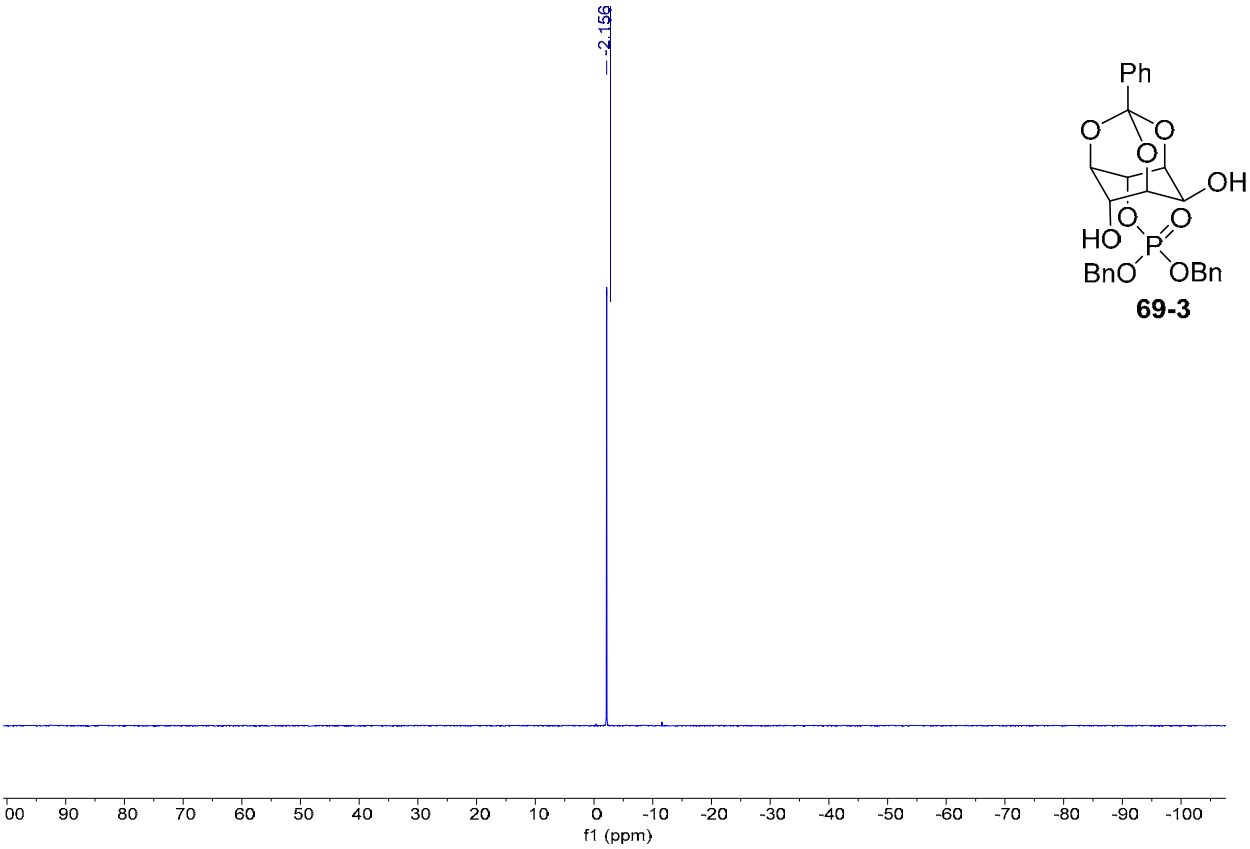

7.929
7.911
7.907
7.644
7.625
7.609
7.606
7.549
7.545
7.530
7.509
7.489
7.470
7.376
7.362
7.353
7.326
7.304
7.242
5.215
5.206
5.196
5.161
5.152
5.115
5.095
5.079
5.057
4.433
4.429
4.424
4.420
4.416
4.333
4.328
4.320
4.308
4.013
3.212
3.191
-0.000
1.97
1.02
4.11
12.93
1.00
5.02
1.00
2.03
1.00
0.92
f1 (ppm)
135.460
135.343
135.306
135.274
135.237
134.395
129.933
129.540
128.726
128.702
128.646
128.634
128.059
128.030
127.980
127.906
125.136
107.636
77.318
77.000
76.682
73.221
73.168
72.902
72.478
70.042
70.014
69.982
69.957
69.863
69.811
68.034
67.986
58.932
f1 (ppm)
Ph
O
O
O
O
OH
O
PhSO2O
P
O
BnO
OBn
69-2
Ph
O
O
O
O
OH
O
PhSO2O
P
O
BnO
OBn
69-2


-2.028
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

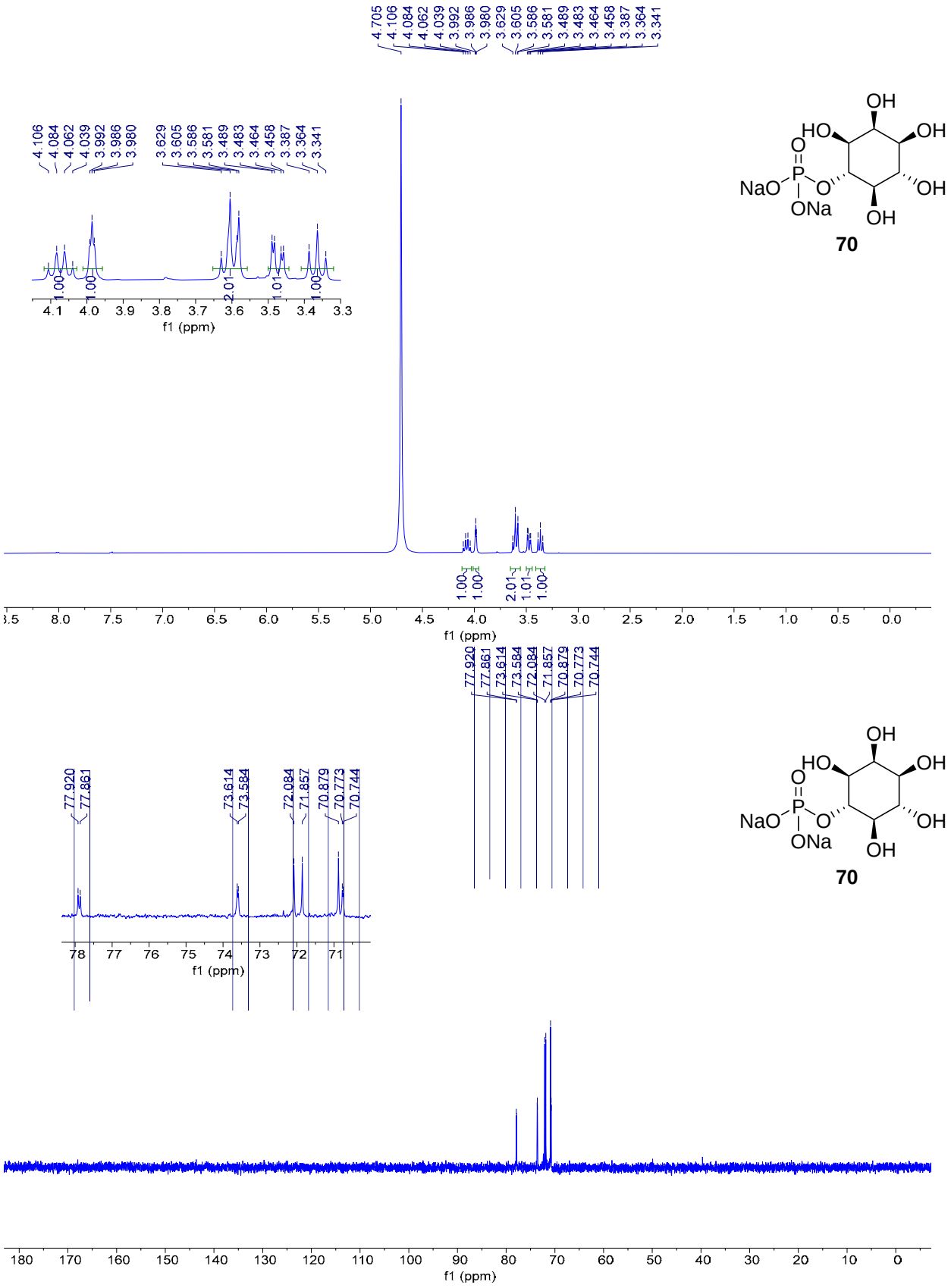
Ph
O
O
O
OH
O
O
PhSO2O
P
BnO
OBn

69-2


7.594
7.580
7.574
7.364
7.356
7.332
7.325
7.313
5.122
5.093
5.067
5.056
5.044
5.032
5.003
4.629
4.441
4.349
4.345
4.254
4.249
4.059
3.146
0.000
Ph
O
O
O
OH
HO
P
O
BnO
OBn
69-3
2.03
13.03
5.17
1.00
1.05
1.01
1.00
1.00
2.03
f1 (ppm)
136.250
135.019
134.992
134.956
134.936
129.708
129.039
128.929
128.798
128.721
128.223
128.113
128.010
125.197
107.420
77.318
77.000
76.682
75.287
73.594
73.515
71.750
71.694
70.352
70.295
70.273
70.215
69.384
69.351
66.916
59.304
135.019
134.992
134.956
134.936
135.05 135.00 134.95 134.90 134.85
f1 (ppm)
73.594
73.515
71.750
71.694
70.352
70.295
70.273
70.215
69.384
69.351
73.5 73.0 72.5 72.0 71.5 71.0 70.5 70.0 69.5
f1 (ppm)
Ph
O
O
O
OH
HO
P
O
BnO
OBn
69-3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

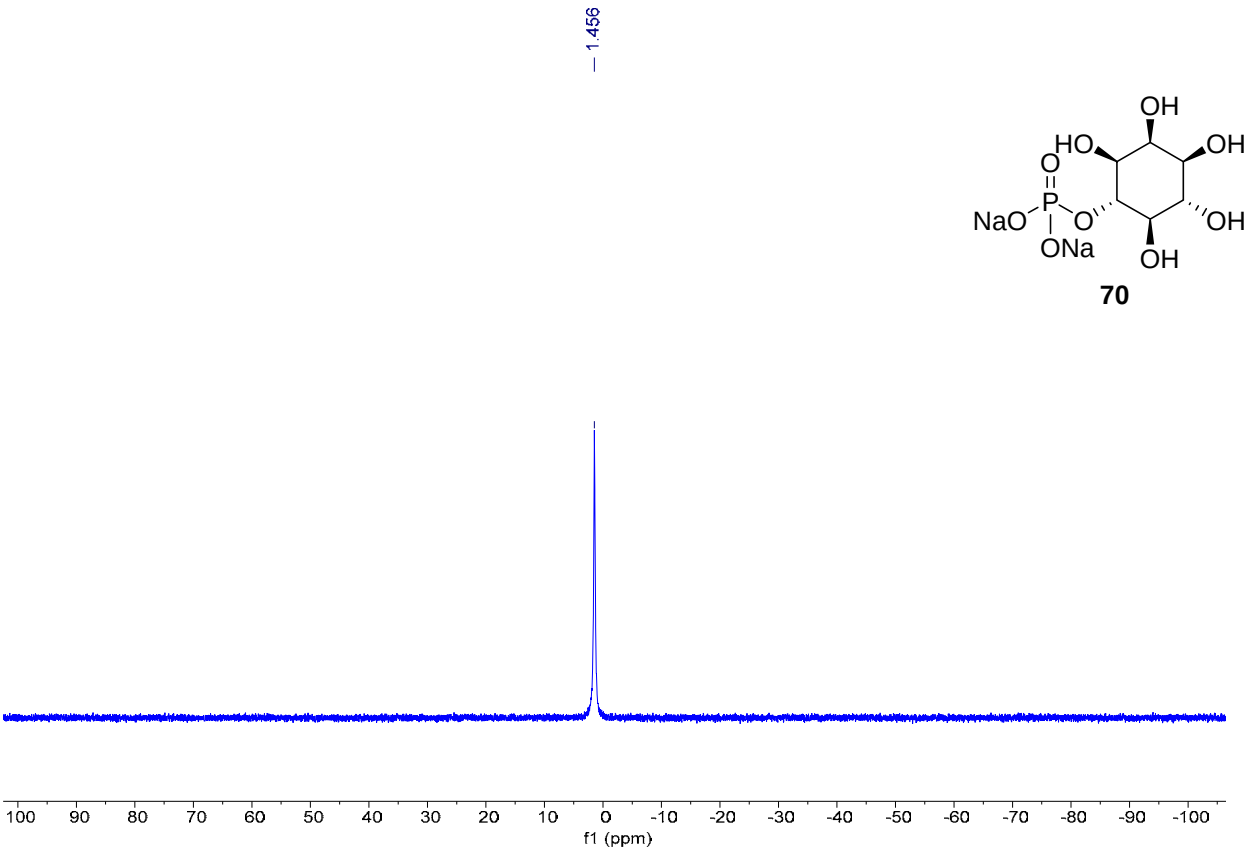

-2.156
Ph
O
O
O
OH
O
O
HO
P
BnO
OBn
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

69-3

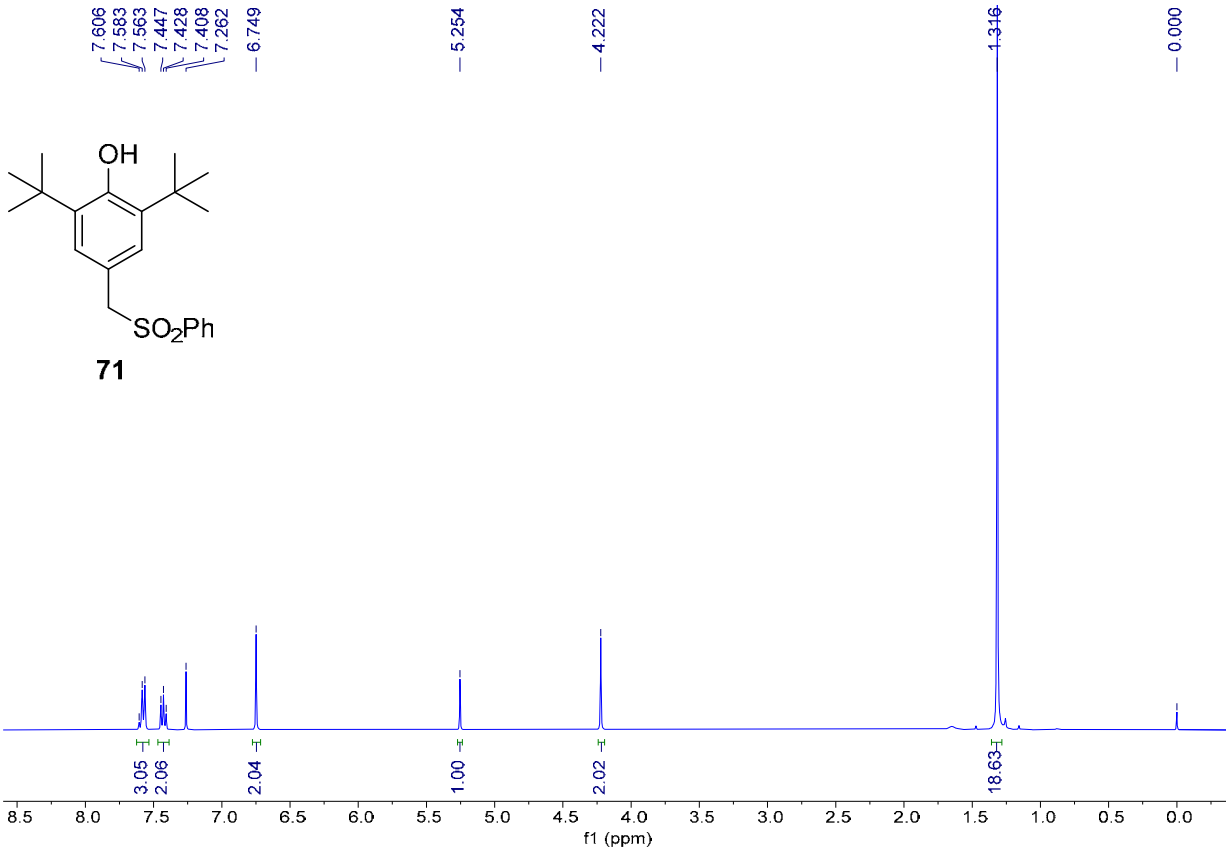

4.705
4.106
4.084
4.062
4.039
3.992
3.986
3.980
3.629
3.605
3.586
3.581
3.489
3.483
3.464
3.458
3.387
3.364
3.341
1.00
1.00
2.01
1.01
1.00
f1 (ppm)
OH
HO
OH
O
P
NaO
O
OH
ONa
OH
77.920
77.861
73.614
73.584
72.084
71.857
70.879
70.773
70.744
f1 (ppm)

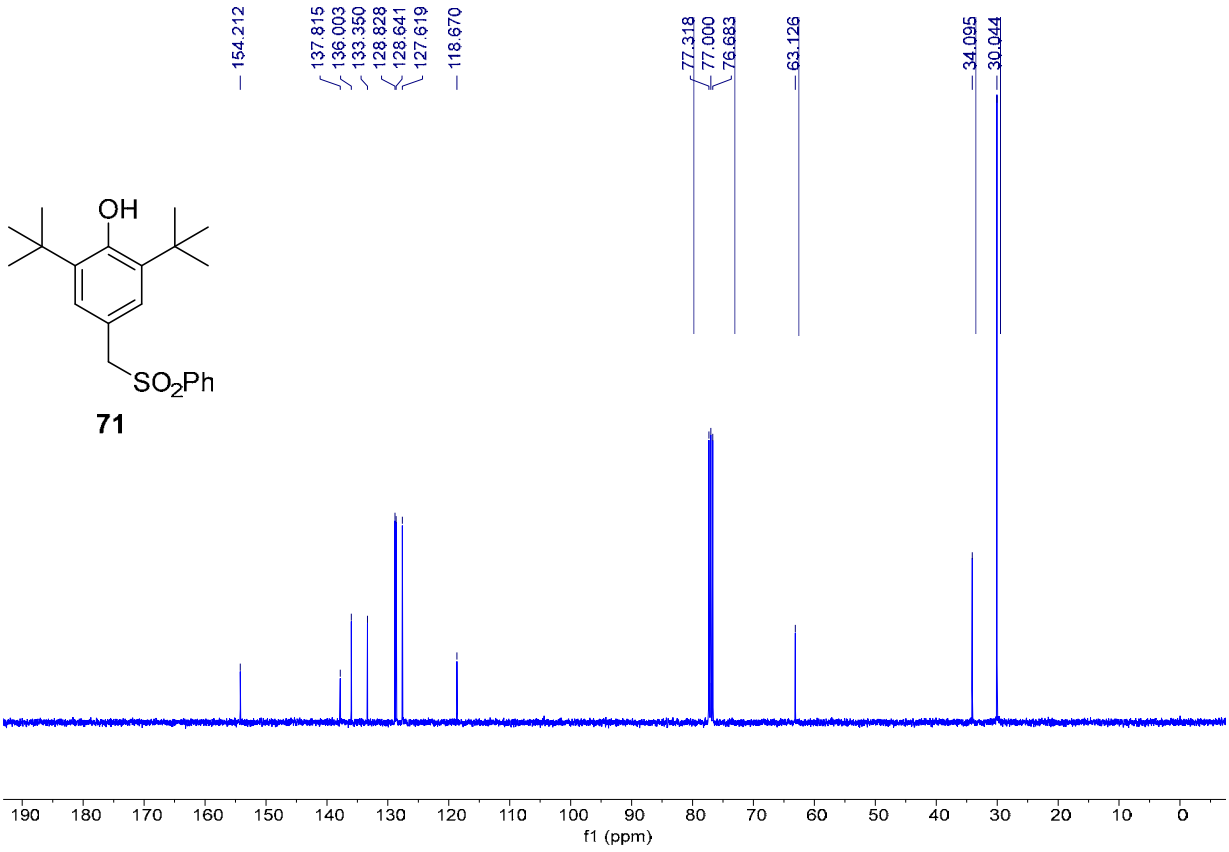
70

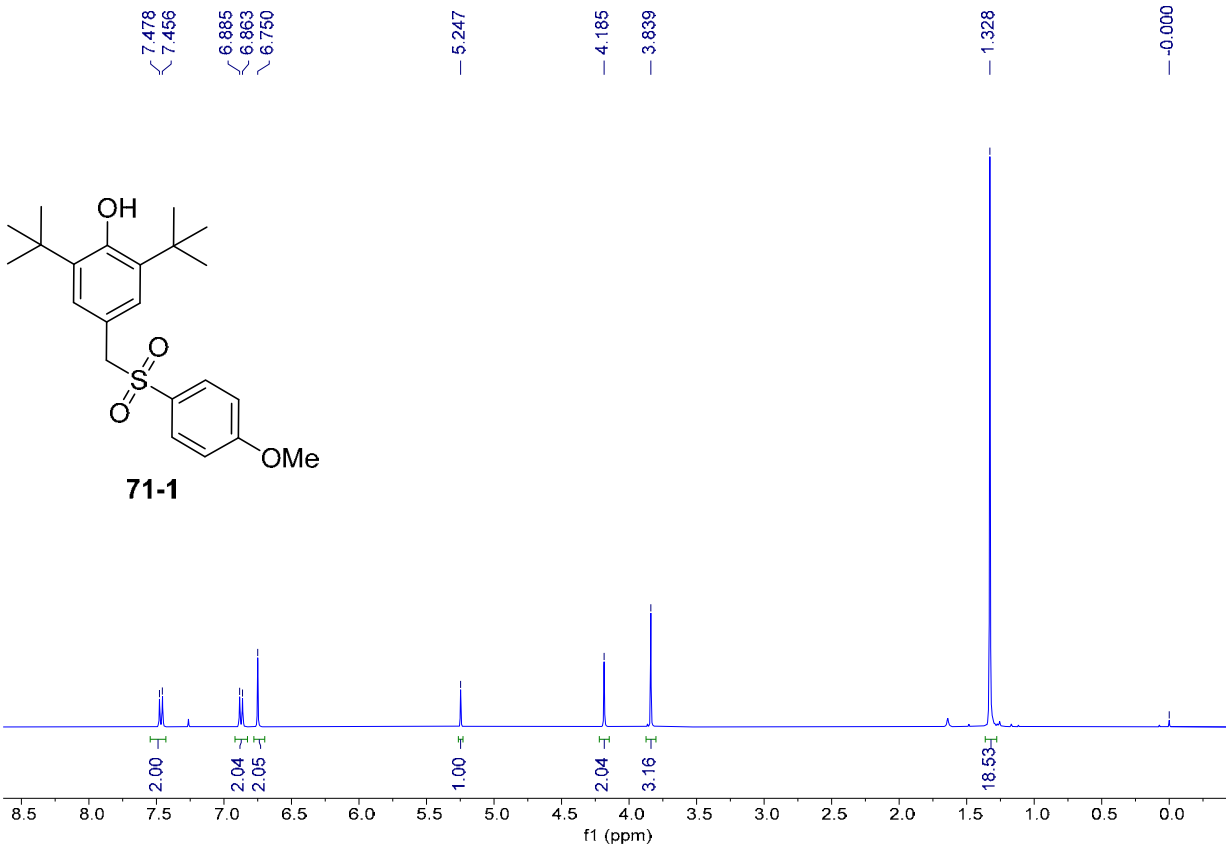
70

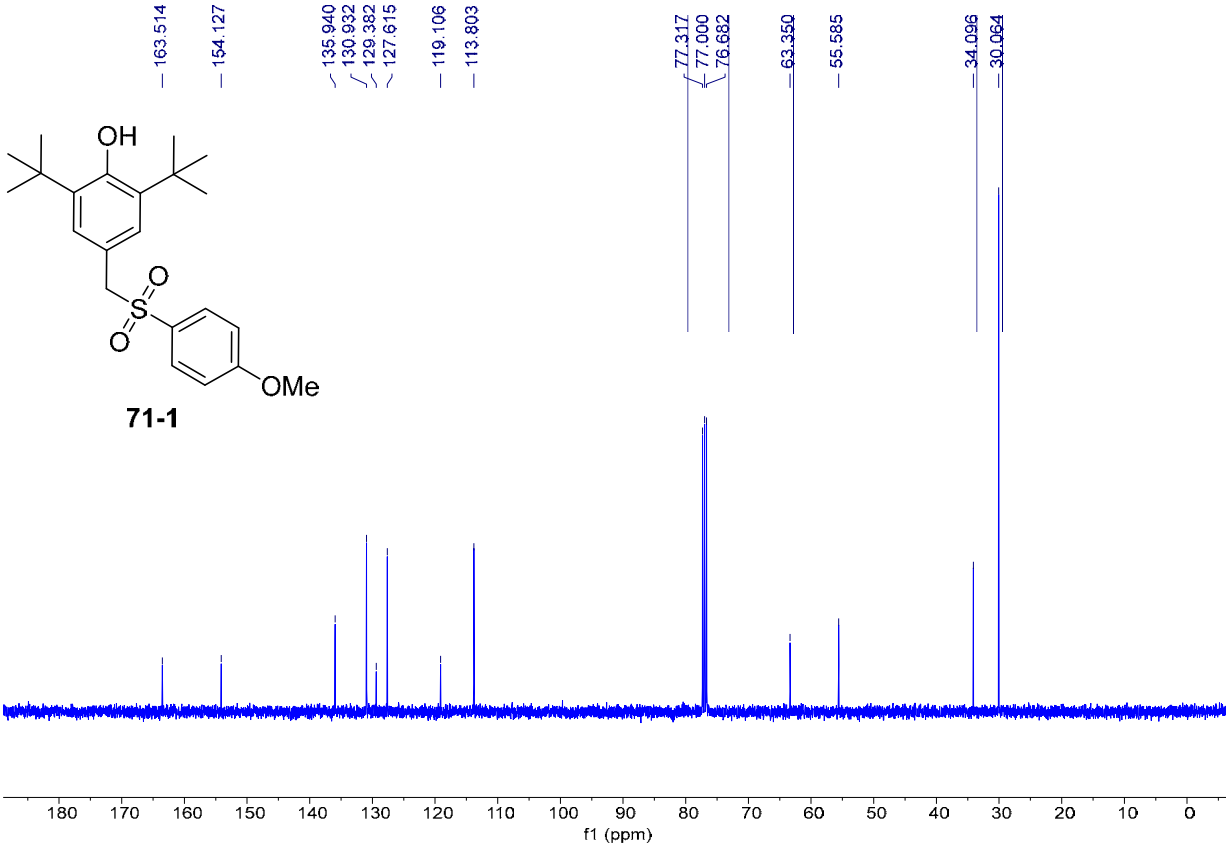

1.456
OH
HO
OH
O
NaO
P
O
OH
ONa
OH
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

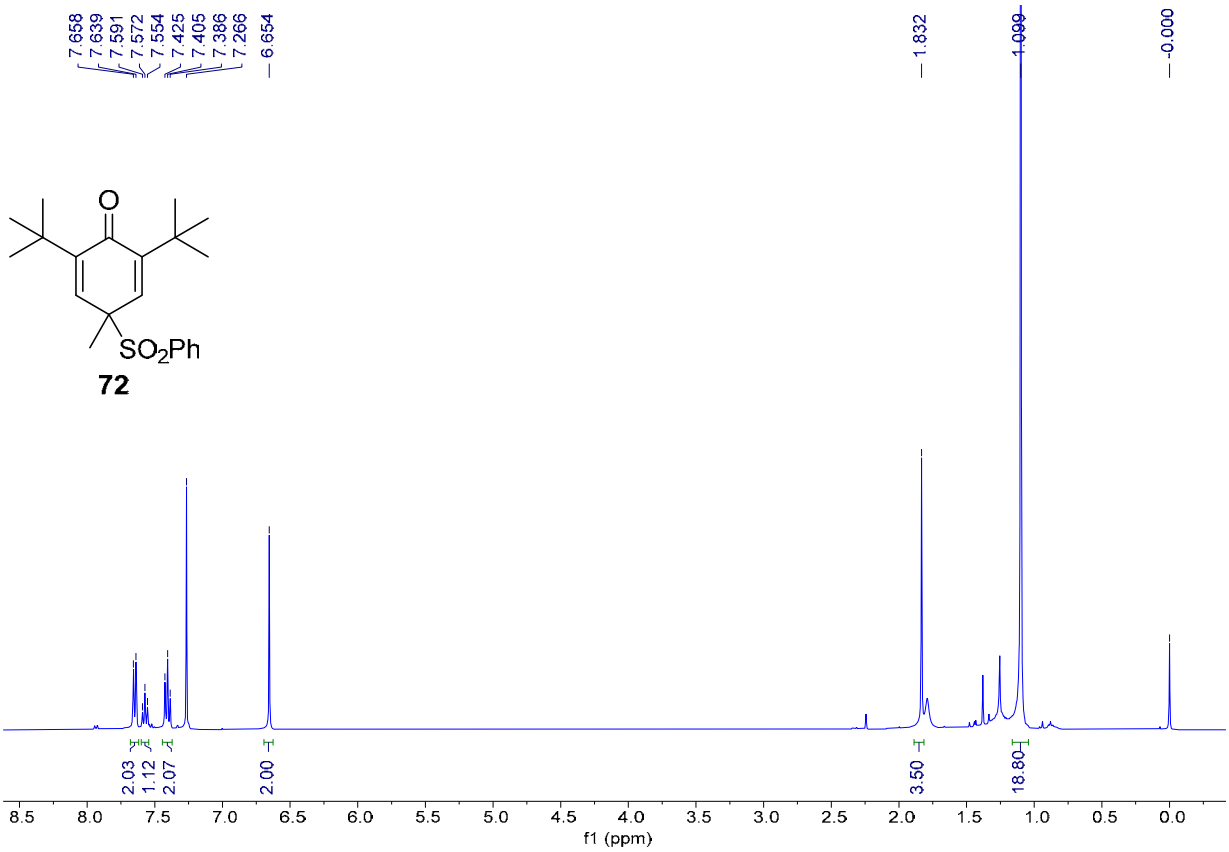
70

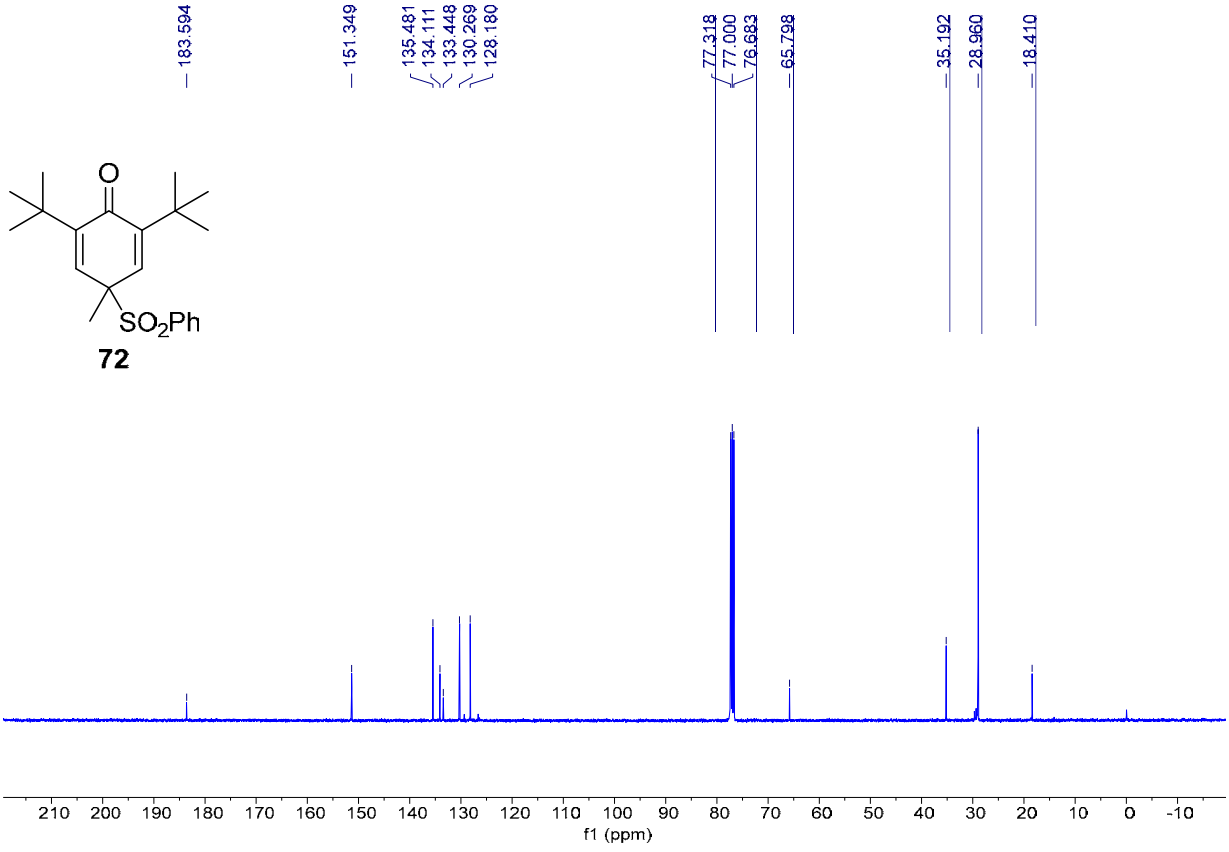

7.606
7.583
7.563
7.447
7.428
7.408
7.262
6.749
5.254
4.222
1.316
0.000
OH
SO2Ph
71
3.05
2.06
2.04
1.00
2.02
18.63
f1 (ppm)

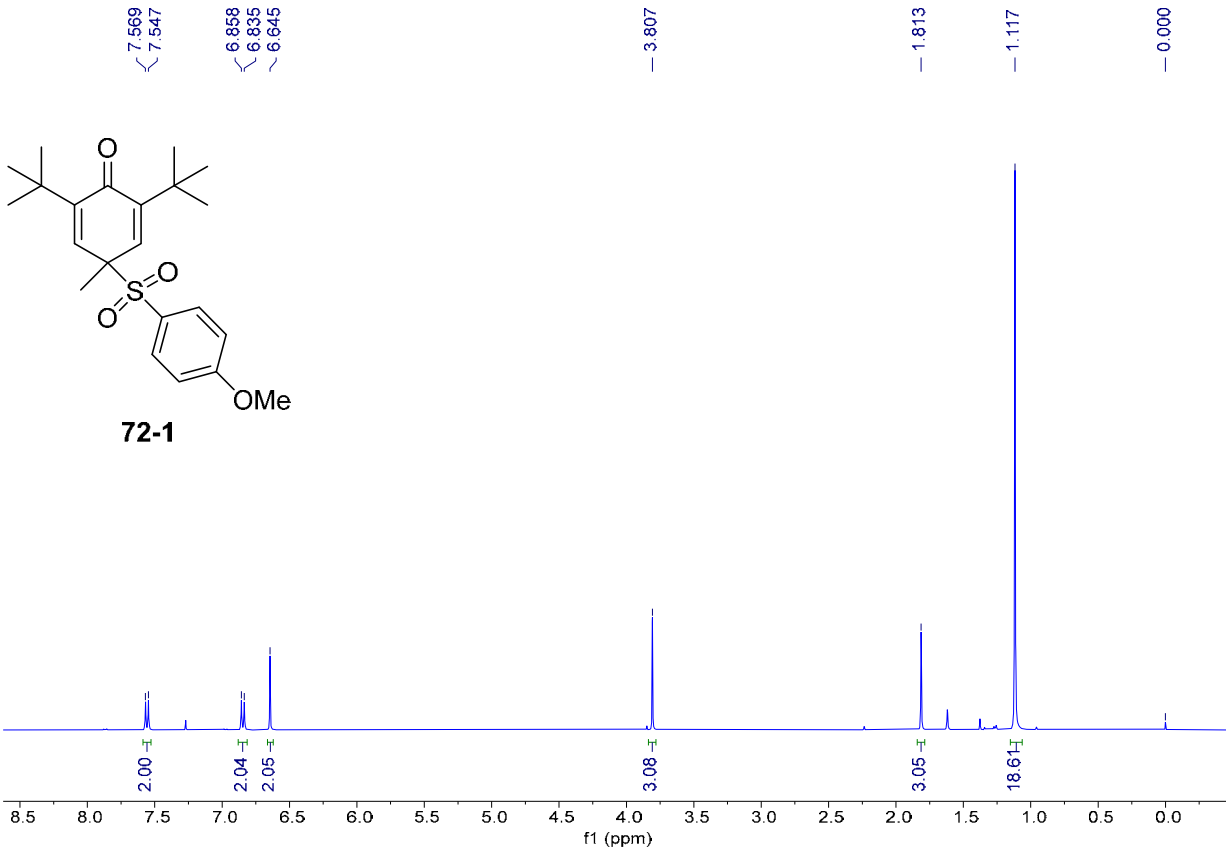

154.212
137.815
136.003
133.350
128.828
128.641
127.619
118.670
77.318
77.000
76.683
63.126
34.095
30.044
OH
SO2Ph
71
f1 (ppm)

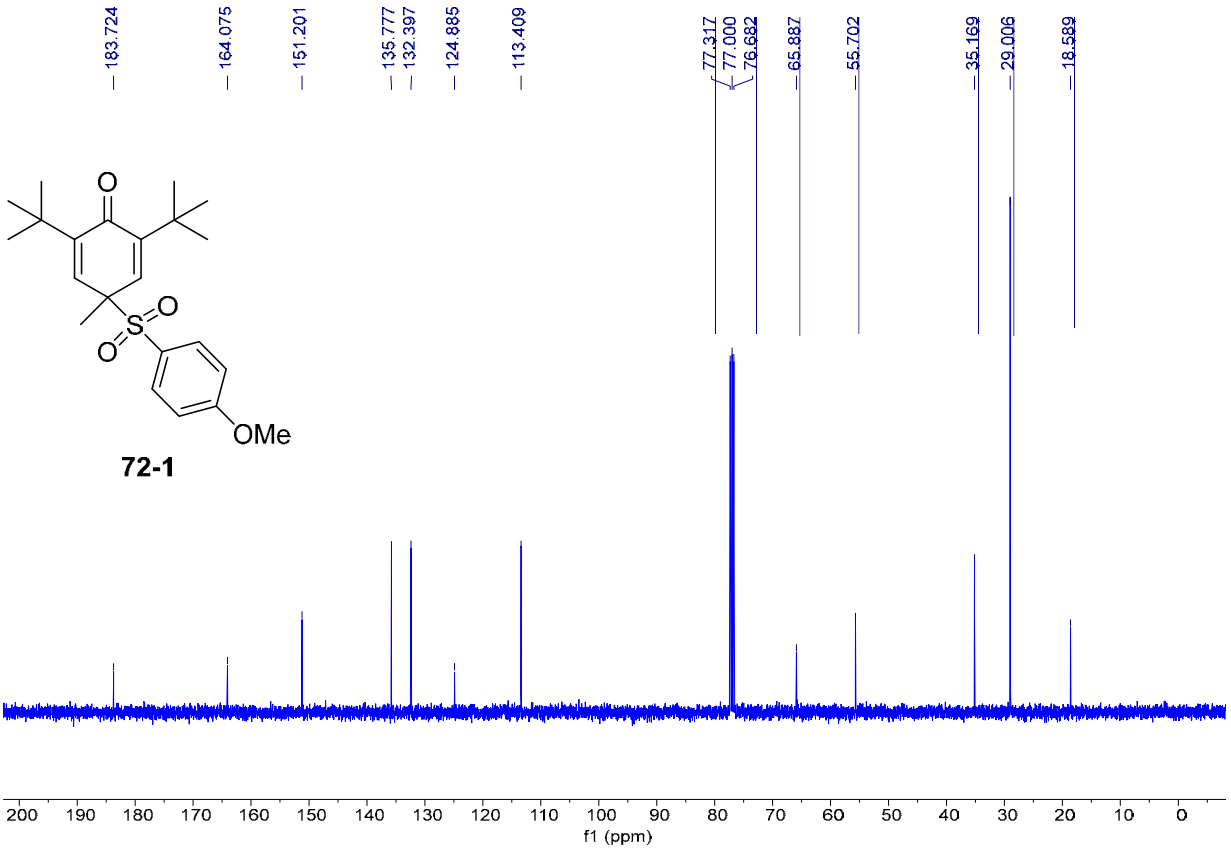

7.478
7.456
6.885
6.863
6.750
5.247
4.185
3.839
1.328
-0.000
OH
O
S
O
OMe
71-1
2.00
2.04
2.05
1.00
2.04
3.16
18.53
f1 (ppm)

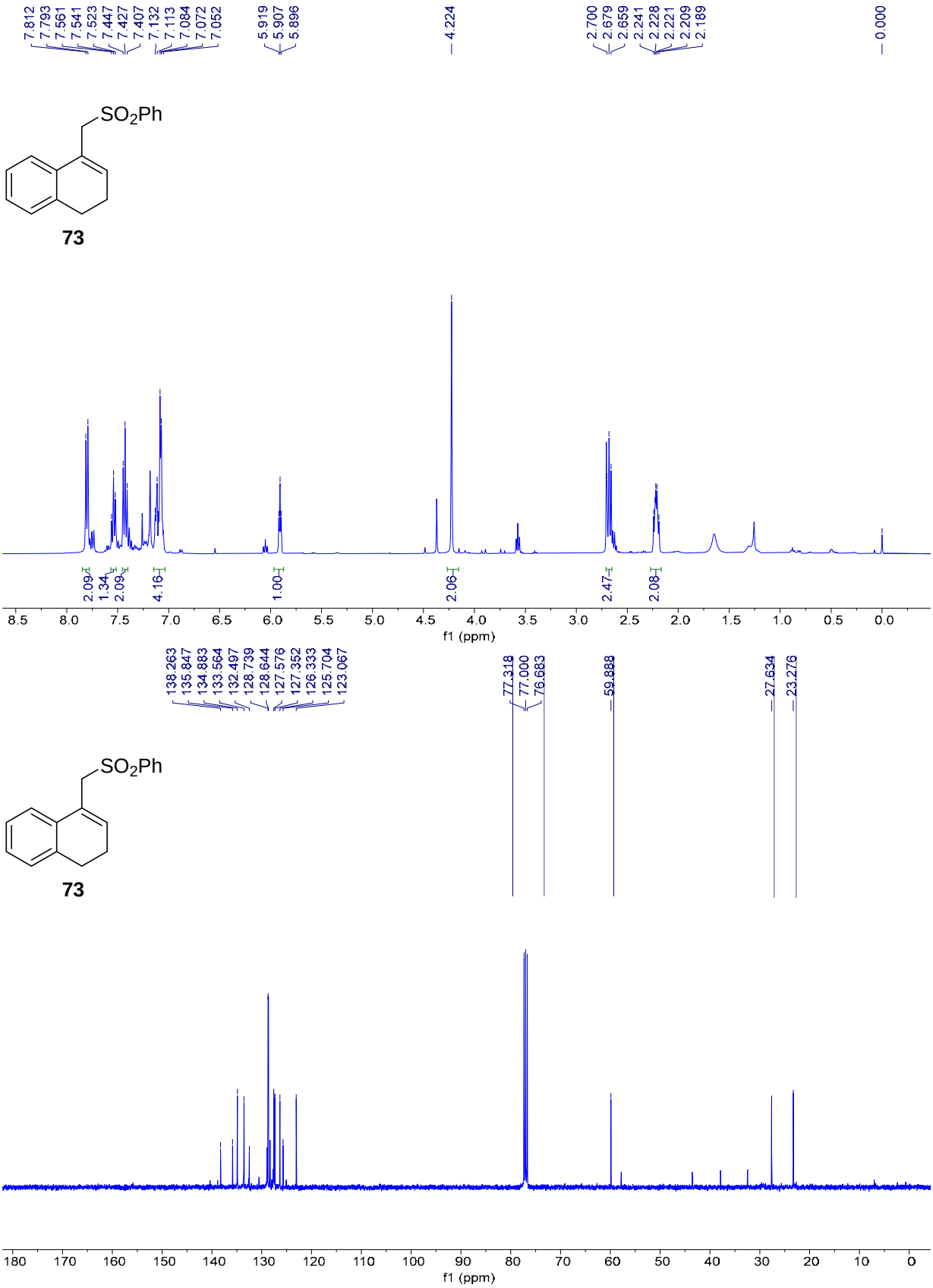

163.514
154.127
135.940
130.932
129.382
127.615
119.106
113.803
77.317
77.000
76.682
63.350
55.585
34.096
30.064
OH
O
S
O
OMe
71-1
f1 (ppm)


7.658
7.639
7.591
7.572
7.554
7.425
7.405
7.386
7.266
6.654
1.832
1.000
-0.000
O
SO2Ph
72
2.03
1.12
2.07
2.00
3.50
18.80
f1 (ppm)

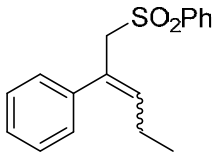

183.594
151.349
135.481
134.111
133.448
130.269
128.180
77.318
77.000
76.683
65.798
35.192
28.960
18.410
O
SO2Ph
72
f1 (ppm)


7.569
7.547
6.858
6.835
6.645
3.807
1.813
1.117
0.000
O
O
S
O
O
OMe
72-1
2.00
2.04
2.05
3.08
3.05
18.61
f1 (ppm)

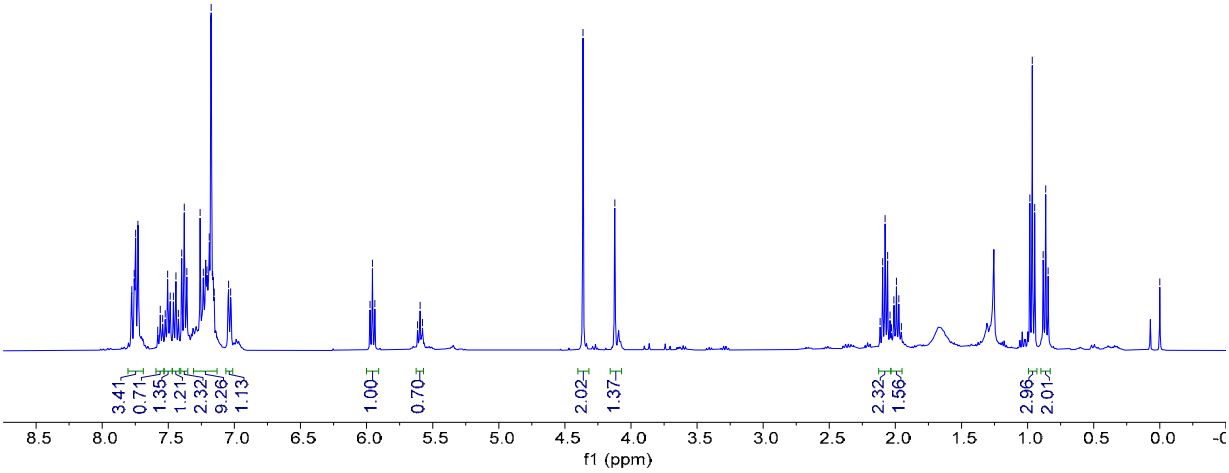

183.724
164.075
151.201
135.777
132.397
124.885
113.409
77.317
77.000
76.682
65.887
55.702
35.169
29.006
18.589
O
O
S
O
O
OMe
72-1
f1 (ppm)


7.812
7.793
7.561
7.541
7.523
7.447
7.427
7.407
7.132
7.113
7.084
7.072
7.052
5.919
5.907
5.896
4.224
2.700
2.679
2.659
2.241
2.228
2.221
2.209
2.189
0.000
SO2Ph
73
2.09
1.34
2.09
4.16
1.00
2.06
2.47
2.08
f1 (ppm)
138.263
135.847
134.883
133.564
132.497
128.739
128.644
127.576
127.352
126.333
125.704
123.067
77.318
77.000
76.683
59.888
27.634
23.276
SO2Ph
73
f1 (ppm)

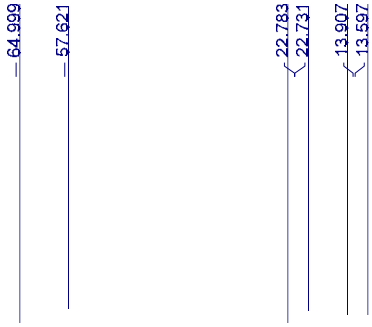

7.776
7.758
7.747
7.730
7.580
7.561
7.542
7.523
7.505
7.486
7.462
7.442
7.423
7.398
7.379
7.360
7.259
7.235
7.207
7.190
7.179
7.176
7.153
7.044
7.028
5.974
5.956
5.938
5.614
5.596
5.577
4.363
4.123
2.115
2.096
2.078
2.059
2.040
2.030
2.011
1.992
1.973
1.955
0.983
0.964
0.946
0.882
0.863
0.844
-0.000

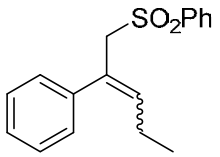

SO2Ph

74

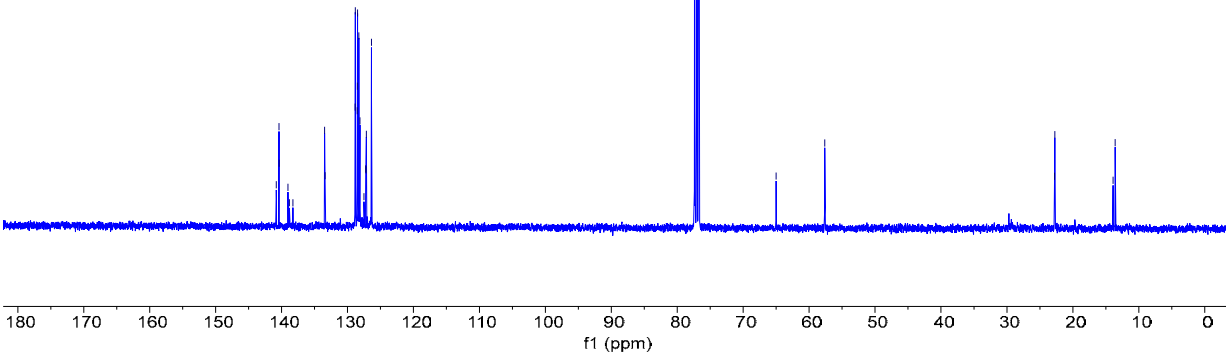

3.41
0.71
1.35
1.21
2.32
9.26
1.13
1.00
0.70
2.02
1.37
2.32
1.56
2.96
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

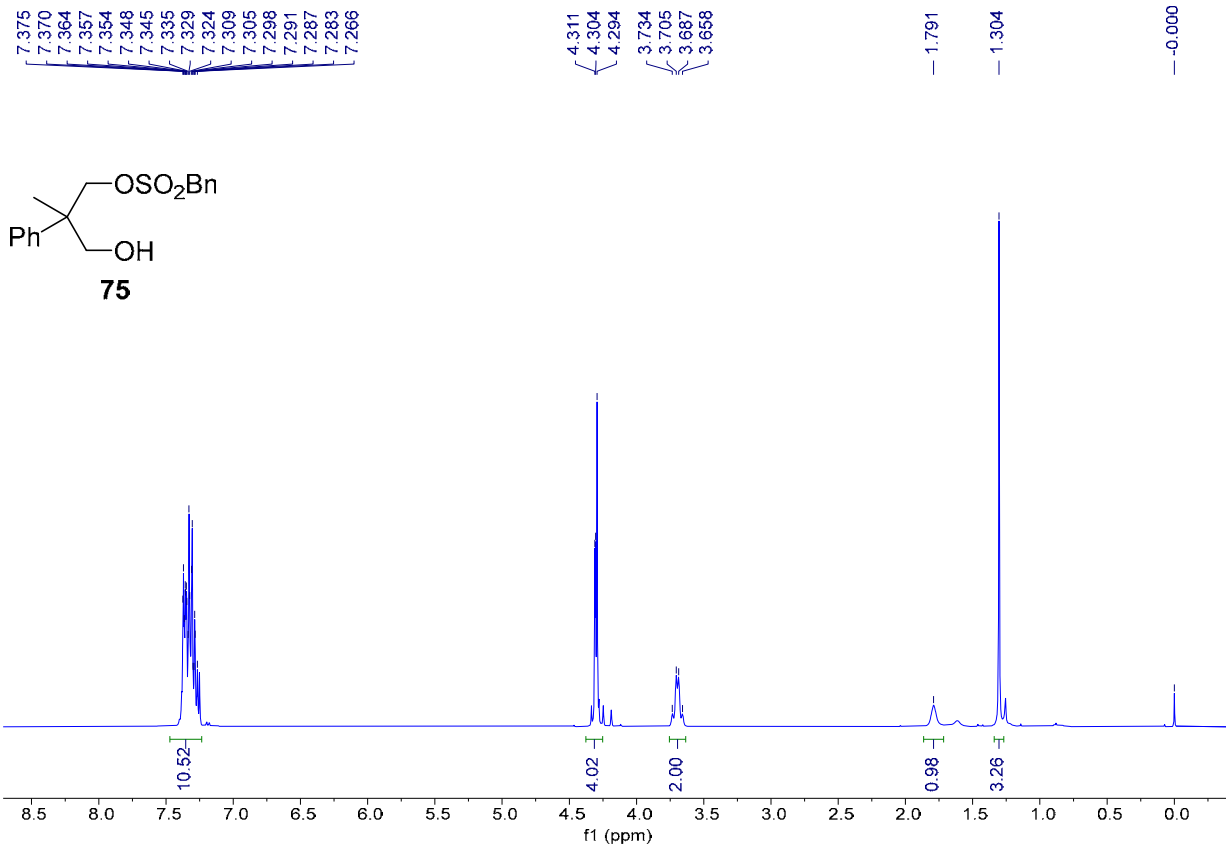

140.806
140.394
140.379
139.021
138.807
138.292
133.471
133.396
128.850
128.824
128.529
128.503
128.487
128.284
128.124
127.503
127.232
127.202
127.137
126.378

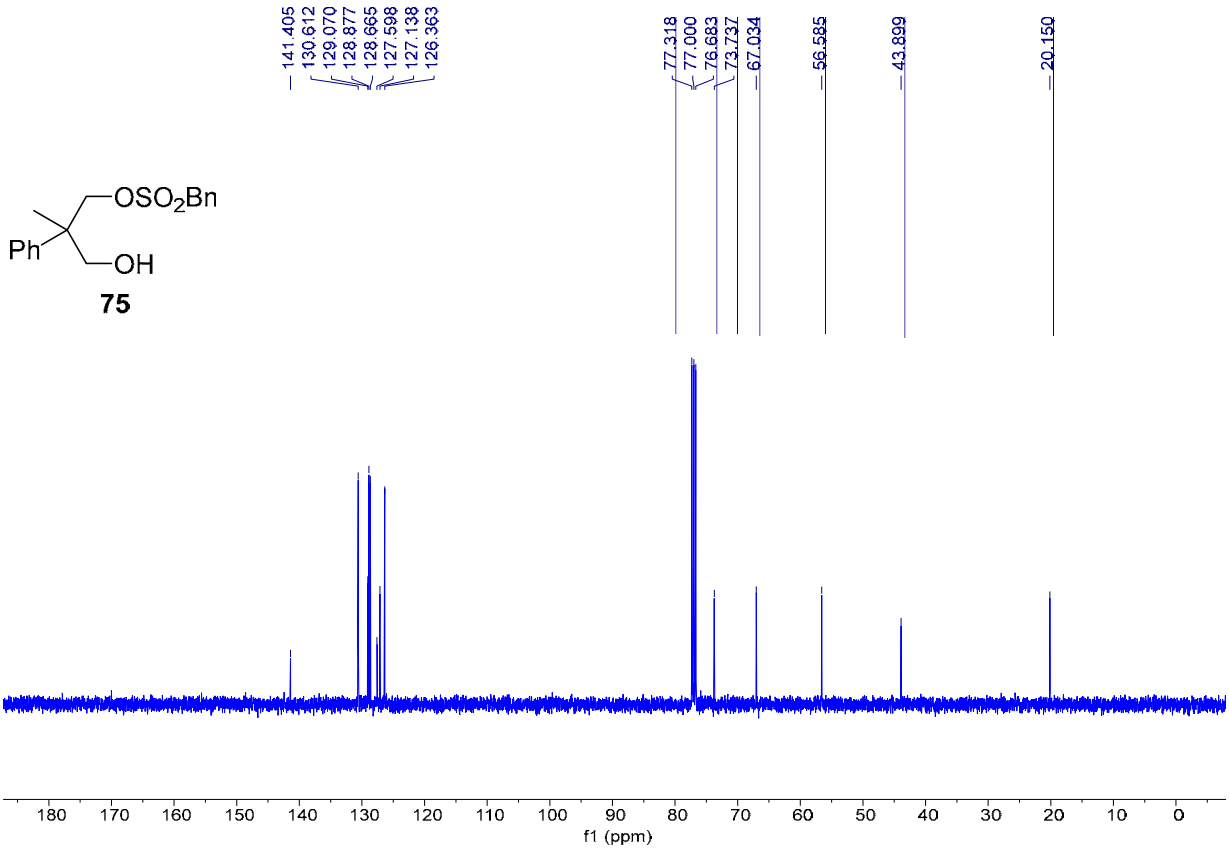

64.999
57.621
22.783
22.731
13.907
13.597

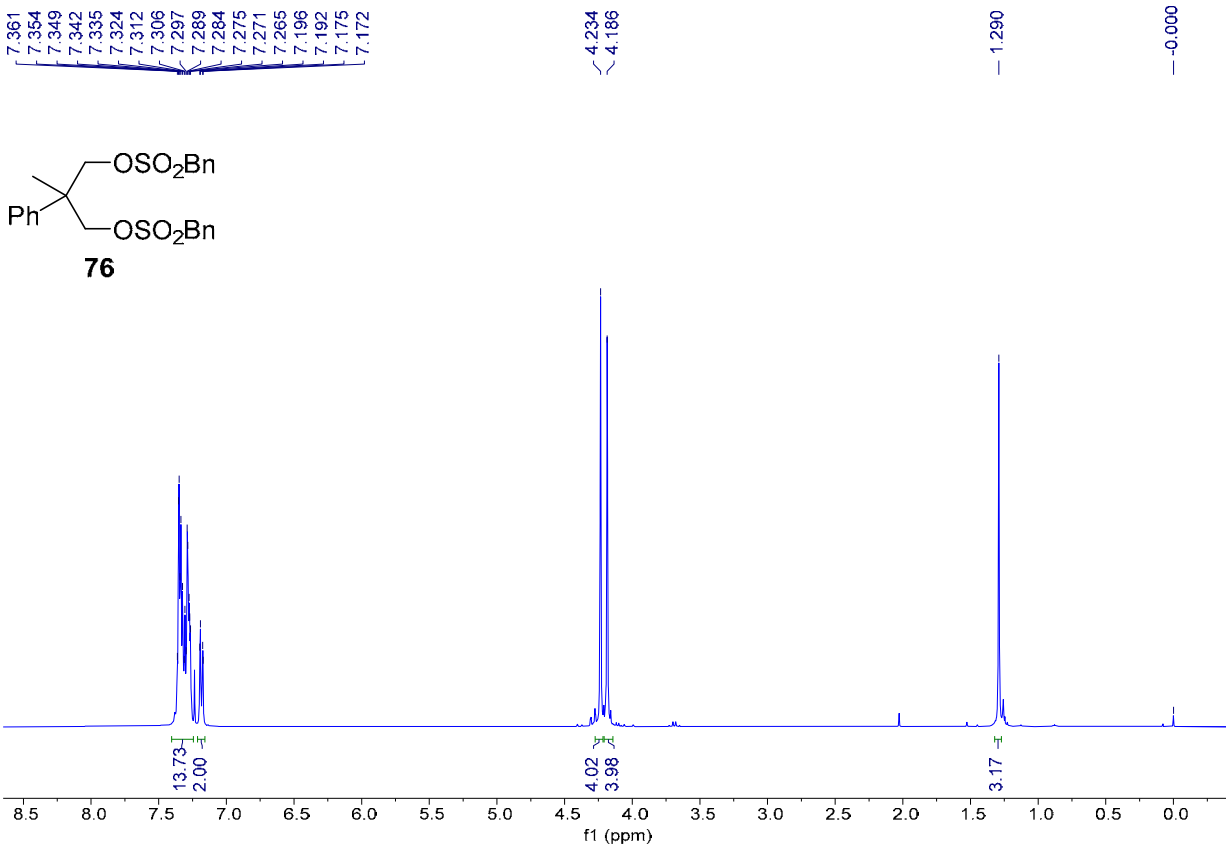

SO2Ph

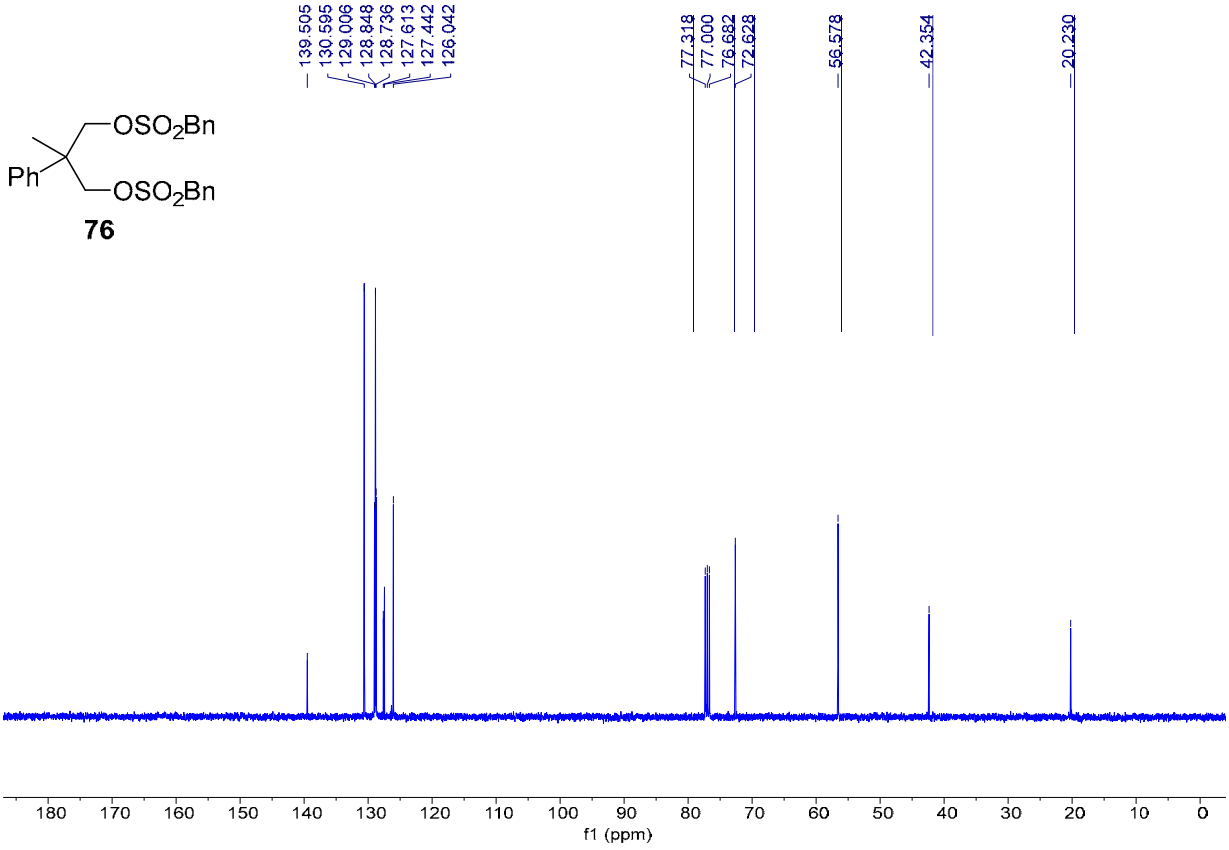
74

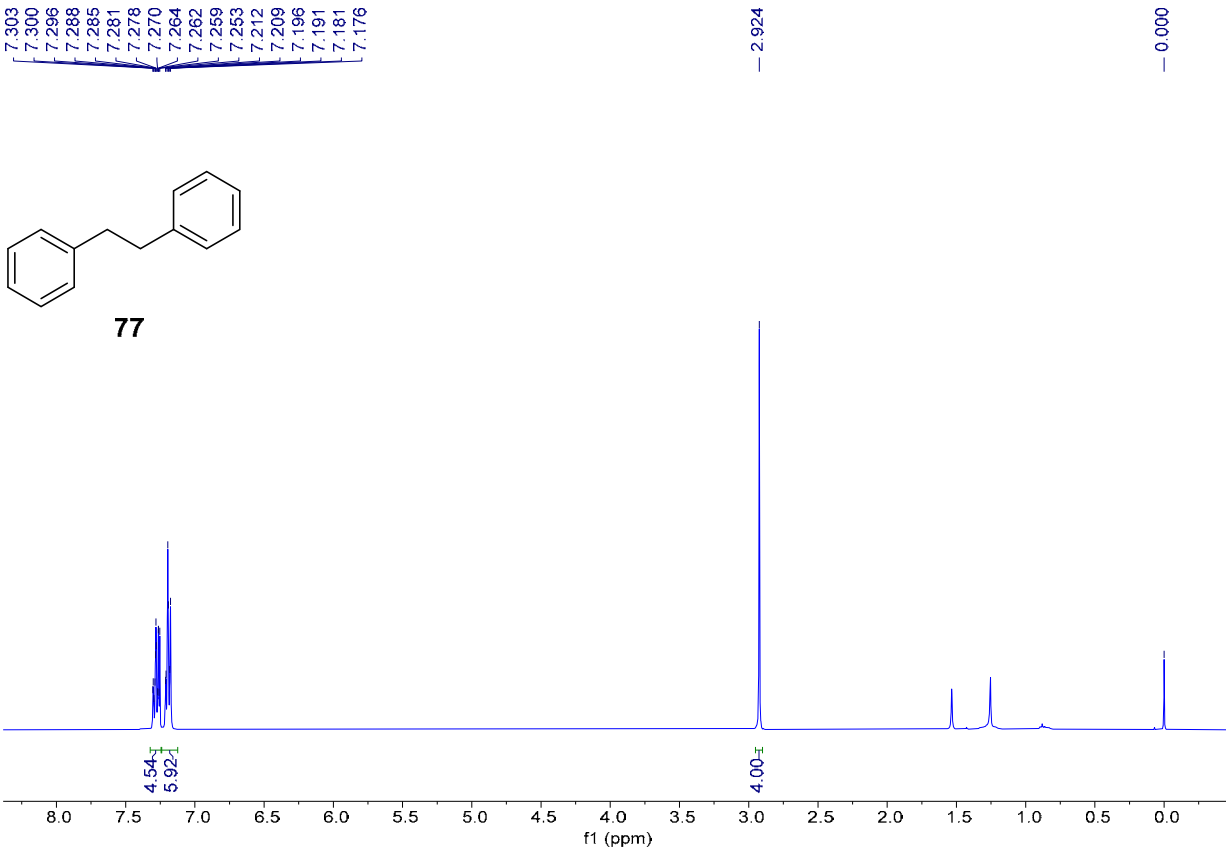

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.375
7.370
7.364
7.357
7.354
7.348
7.345
7.335
7.329
7.324
7.309
7.305
7.298
7.291
7.287
7.283
7.266
4.311
4.304
4.294
3.734
3.705
3.687
3.658
1.791
1.304
-0.000
OSO2Bn
Ph
OH
75
10.52
4.02
2.00
0.98
3.26
f1 (ppm)

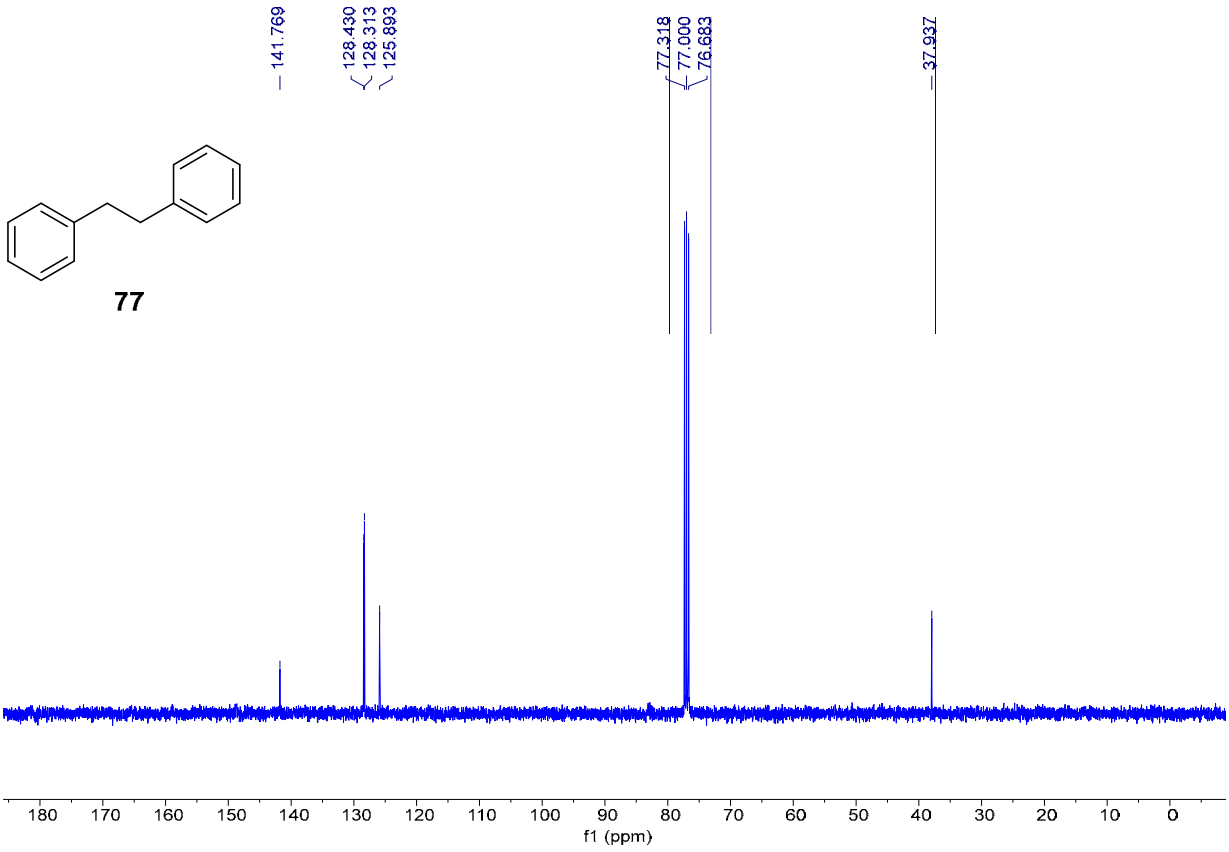

141.405
130.612
129.070
128.877
128.665
127.598
127.138
126.363
77.318
77.000
76.683
73.737
67.034
56.585
43.899
20.150
OSO2Bn
Ph
OH
75
f1 (ppm)


7.361
7.354
7.349
7.342
7.335
7.324
7.312
7.306
7.297
7.289
7.284
7.275
7.271
7.265
7.196
7.192
7.175
7.172
4.234
4.186
1.290
-0.000
OSO2Bn
Ph
OSO2Bn
76
13.73
2.00
4.02
3.98
3.17
f1 (ppm)

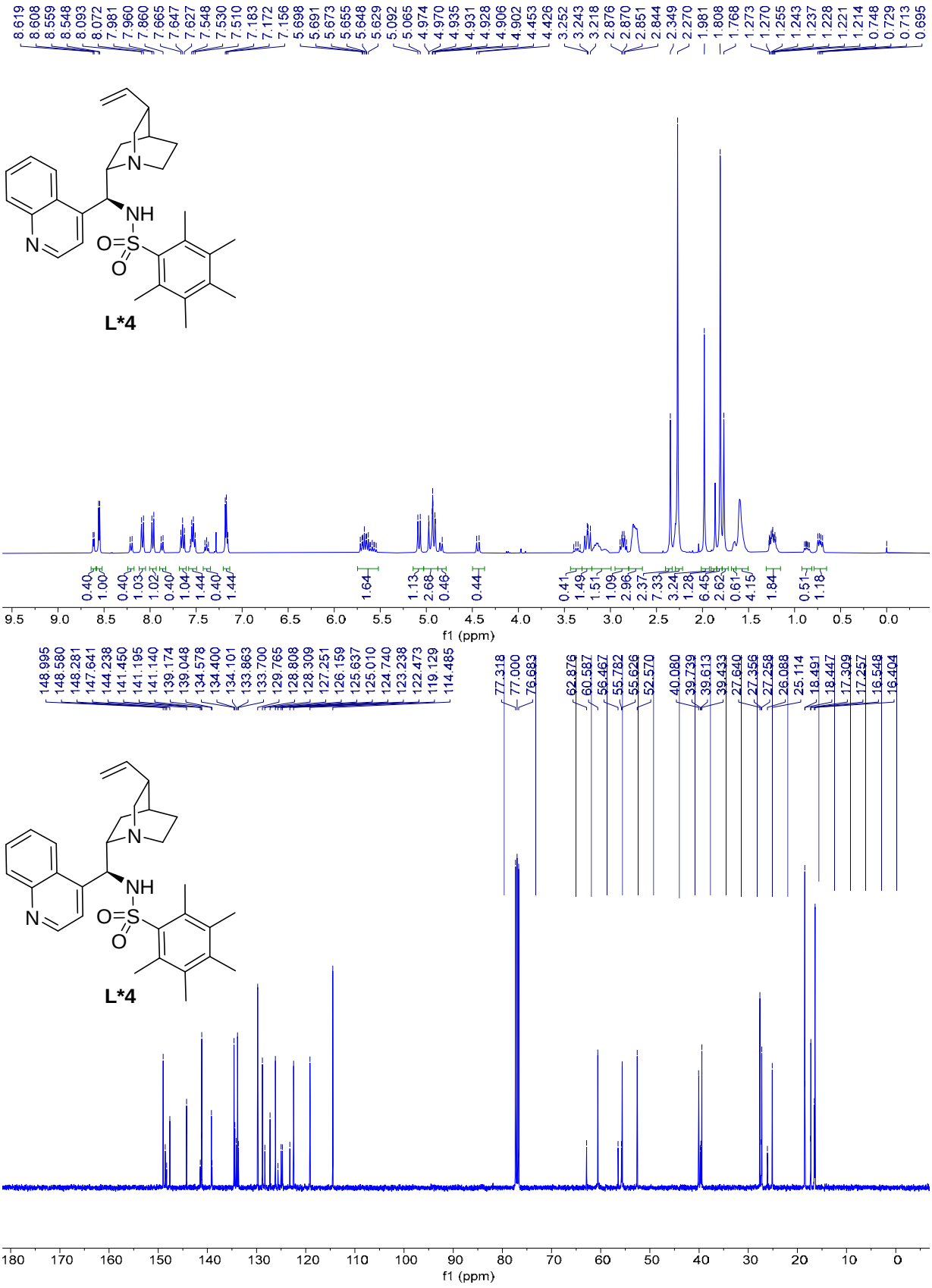

139.505
130.595
129.006
128.848
128.736
127.613
127.442
126.042
77.318
77.000
76.682
72.628
56.578
42.354
20.230
OSO2Bn
Ph
OSO2Bn
76
f1 (ppm)

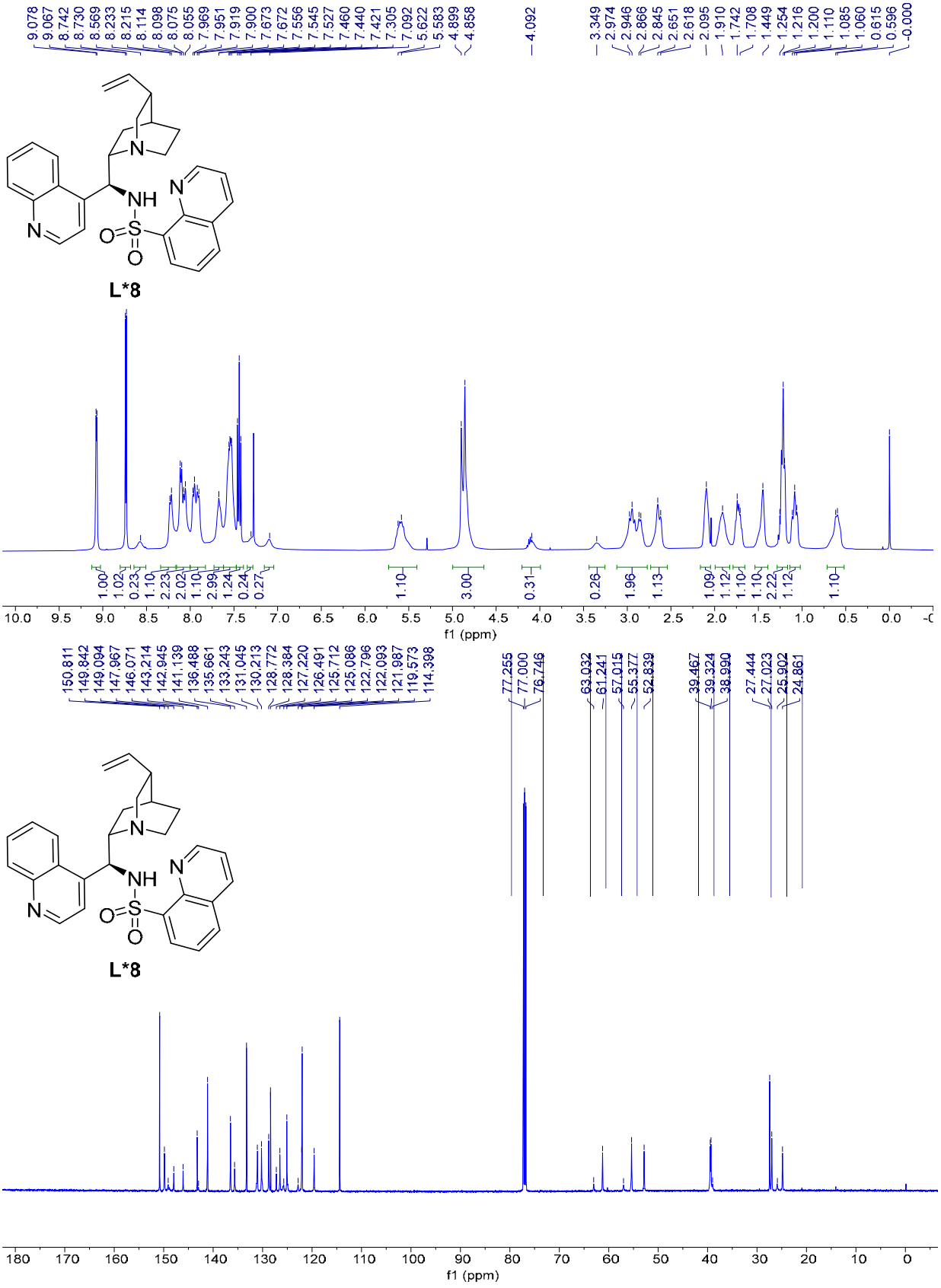

7.303
7.300
7.296
7.288
7.285
7.281
7.278
7.270
7.264
7.262
7.259
7.253
7.212
7.209
7.196
7.191
7.181
7.176
2.924
0.000
4.54
5.92
4.00
f1 (ppm)

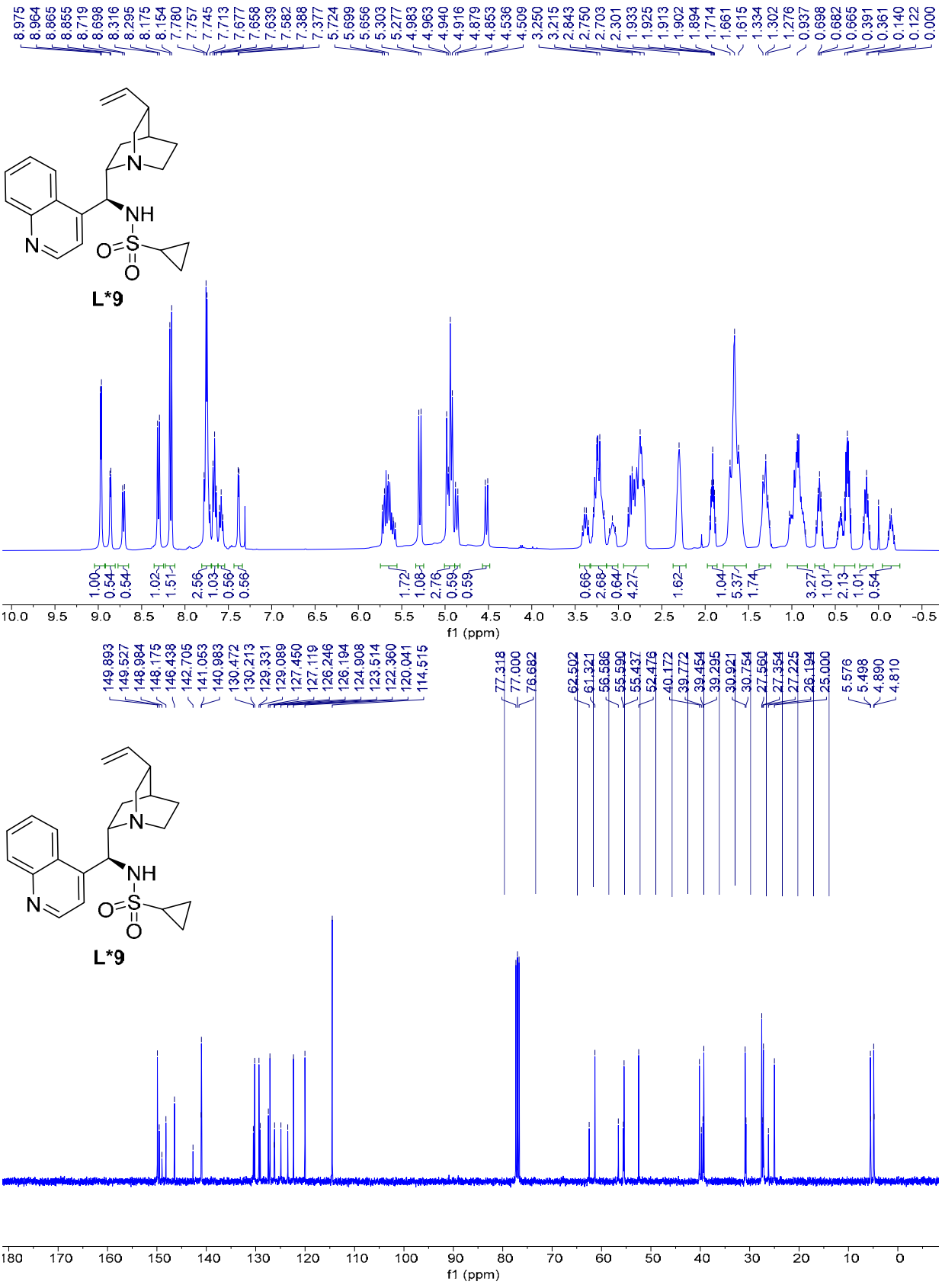
77

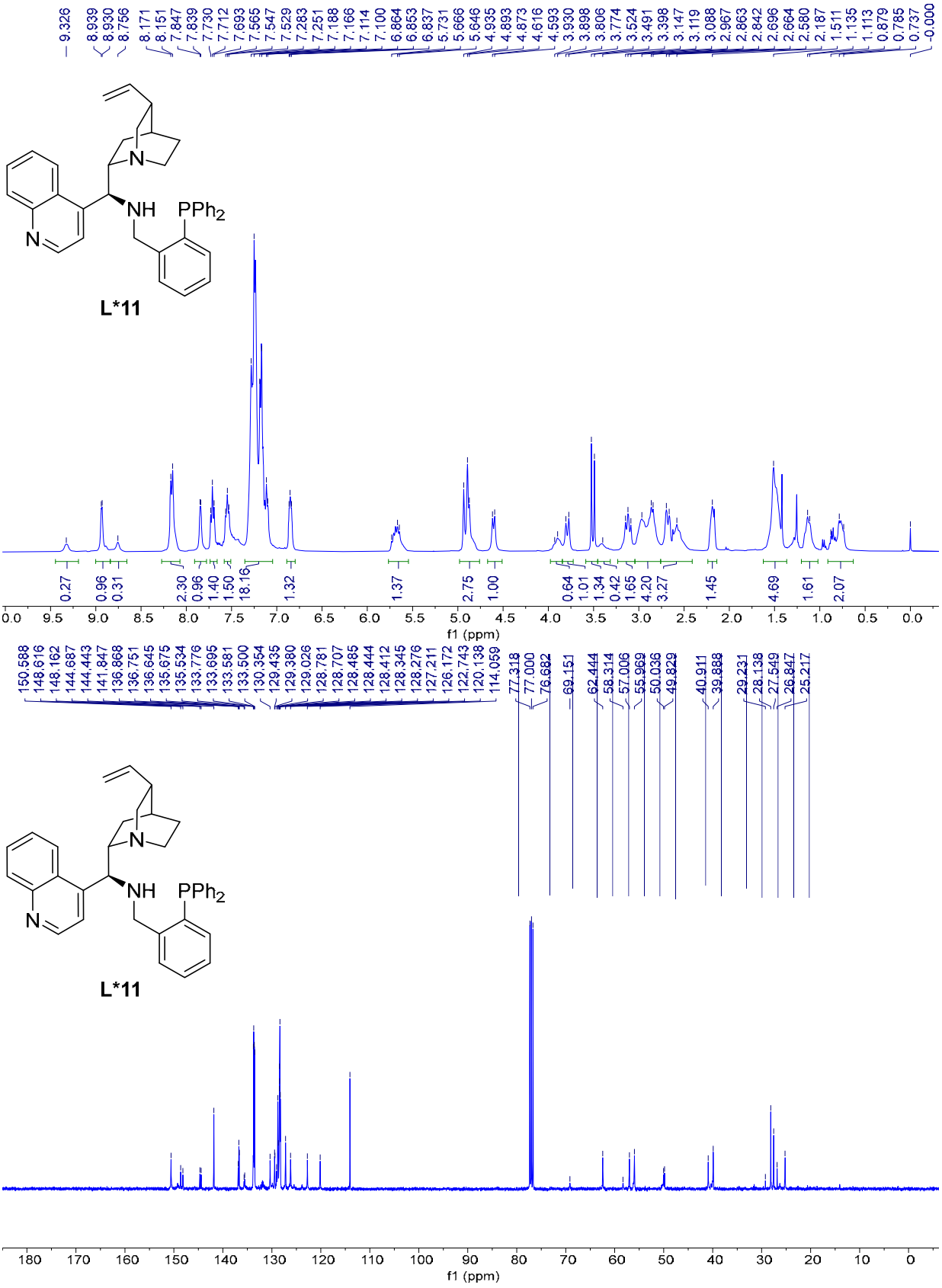

141.769
128.430
128.313
125.893
77.318
77.000
76.683
37.937
f1 (ppm)

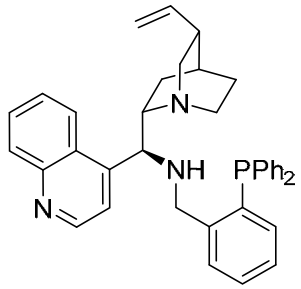
77


L*4
f1 (ppm)
L*4
f1 (ppm)


9.078
9.067
8.742
8.730
8.569
8.233
8.215
8.114
8.098
8.075
8.055
7.969
7.951
7.919
7.900
7.673
7.672
7.556
7.545
7.527
7.460
7.440
7.421
7.305
7.092
5.622
5.583
4.899
4.858
4.092
3.349
2.974
2.946
2.866
2.845
2.651
2.618
2.095
1.910
1.742
1.708
1.449
1.254
1.216
1.200
1.110
1.085
1.060
0.615
0.596
-0.000
L*8
1.00
1.02
0.23
1.10
2.23
2.02
1.10
2.99
1.24
0.24
0.27
1.10
3.00
0.31
0.26
1.96
1.13
1.09
1.12
1.10
2.22
1.12
1.10
f1 (ppm)
150.811
149.842
149.094
147.967
146.071
143.214
142.945
141.139
136.488
135.661
133.243
131.045
130.213
128.772
128.384
127.220
126.491
125.712
125.086
122.796
122.093
121.987
119.573
114.398
77.255
77.000
76.746
63.032
61.241
57.015
55.377
52.839
39.467
39.324
38.990
27.444
27.023
25.902
24.861
L*8
f1 (ppm)

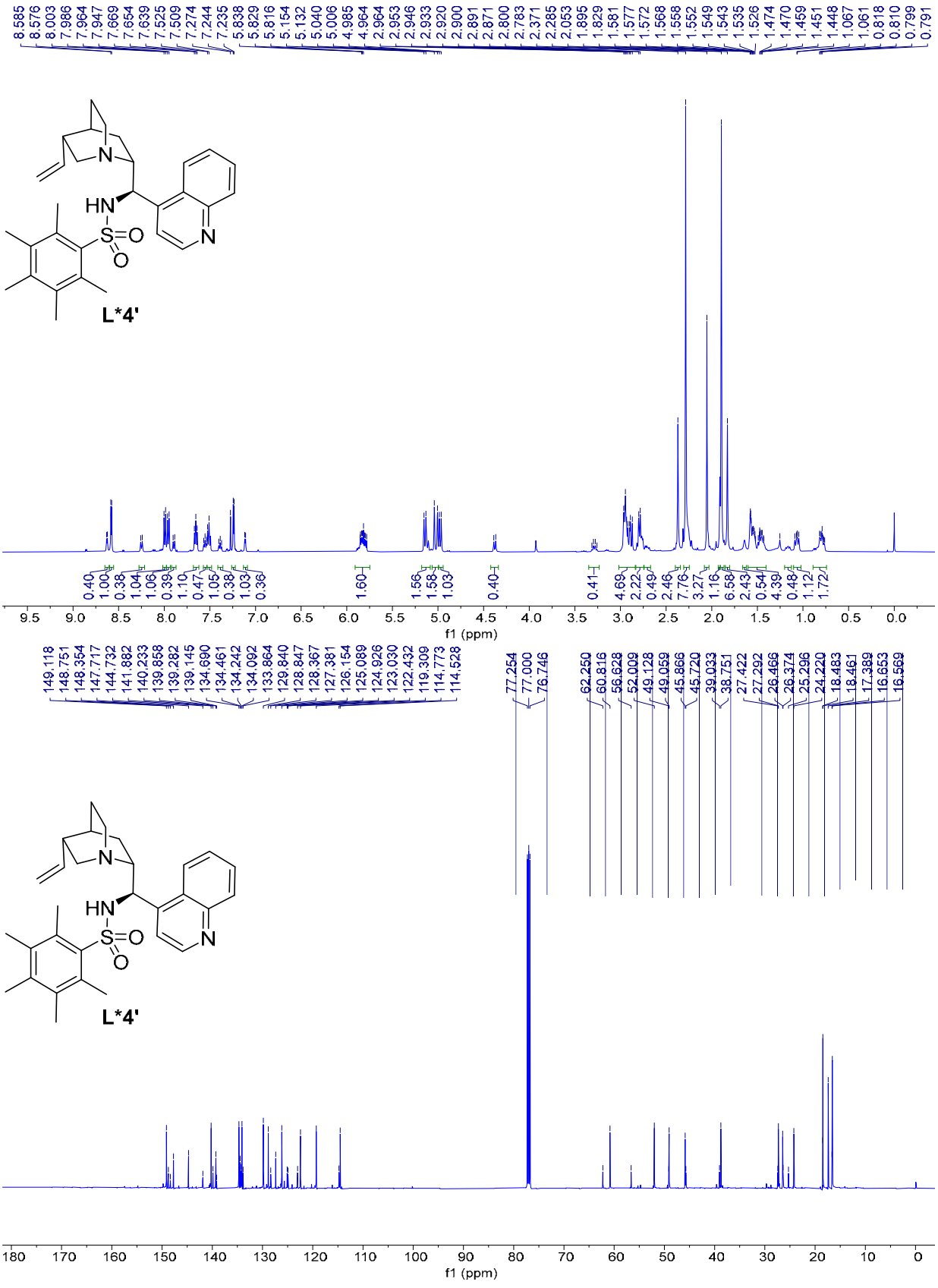

L*9
f1 (ppm)
L*9
f1 (ppm)

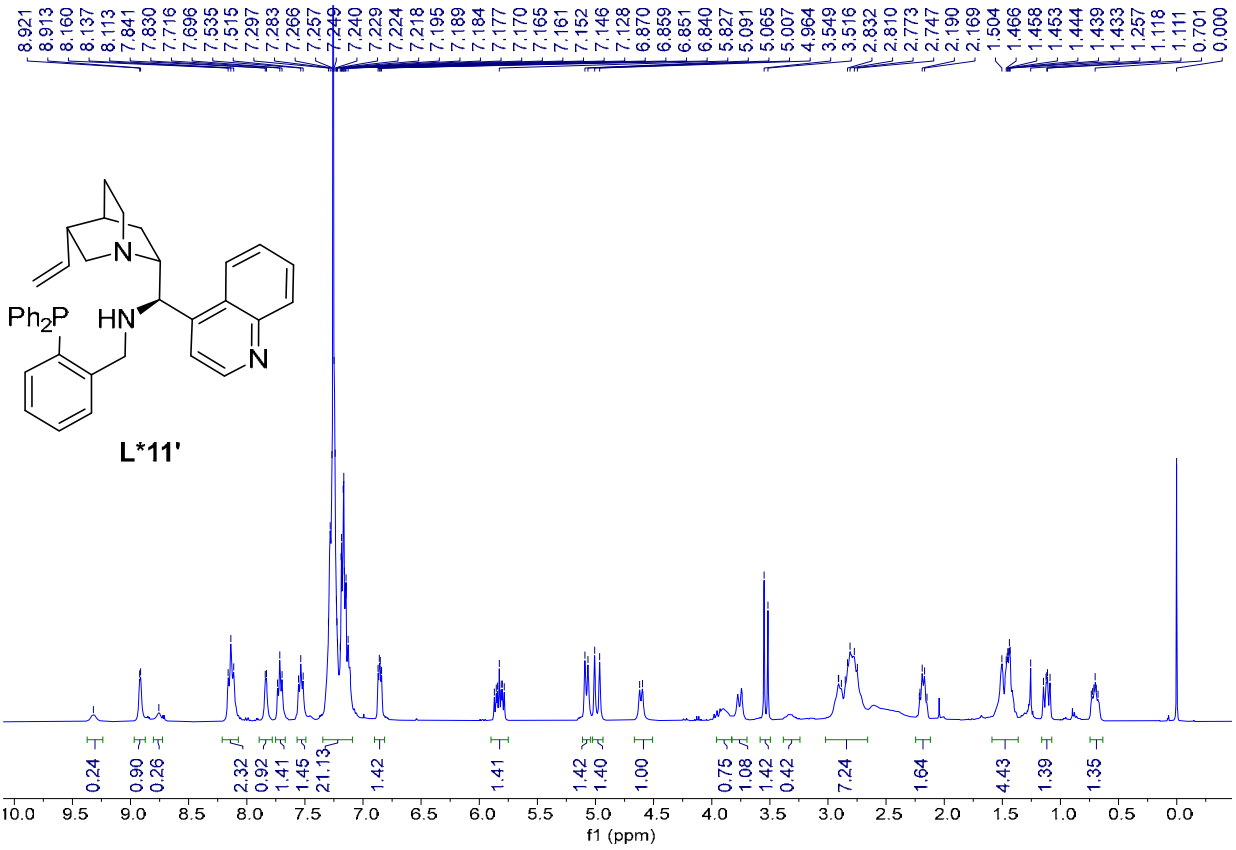

L*11
f1 (ppm)
L*11
f1 (ppm)

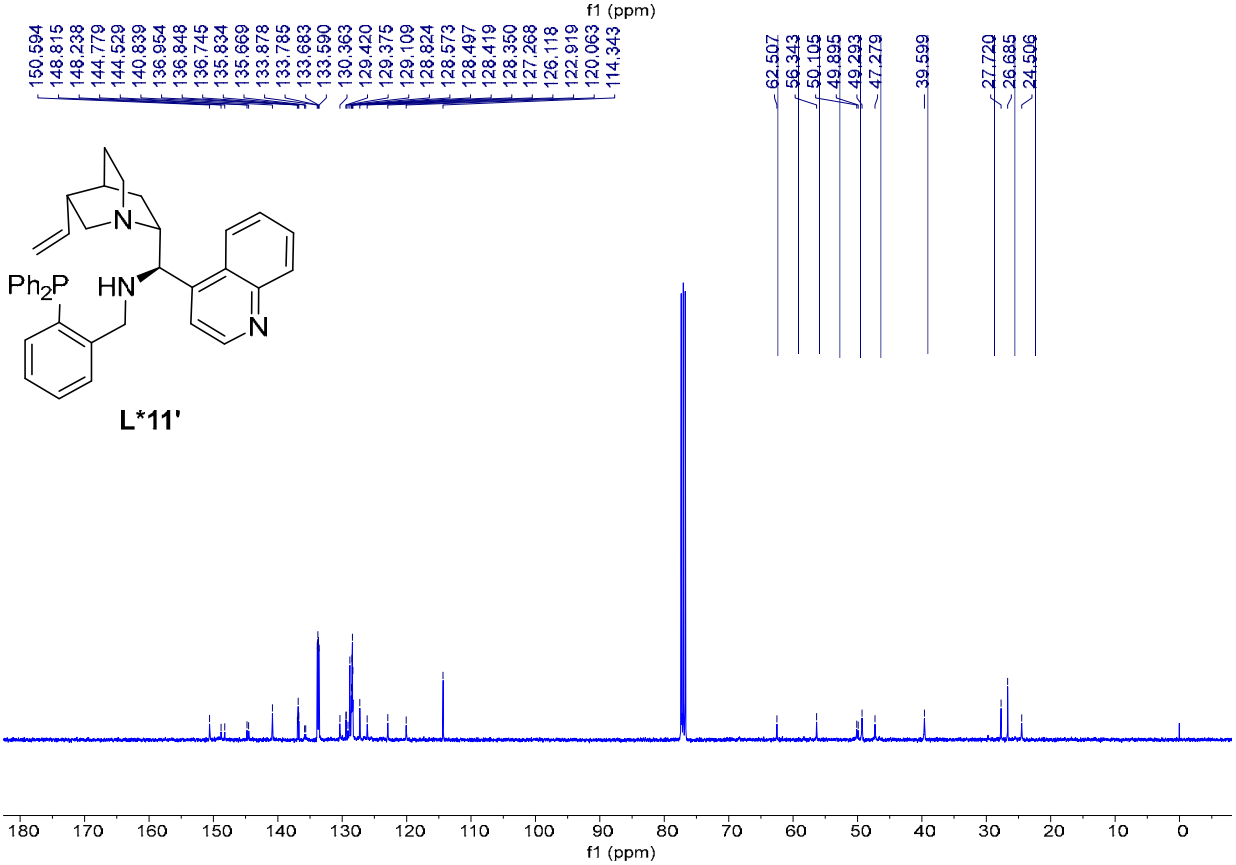

N
NH
PPh2
N

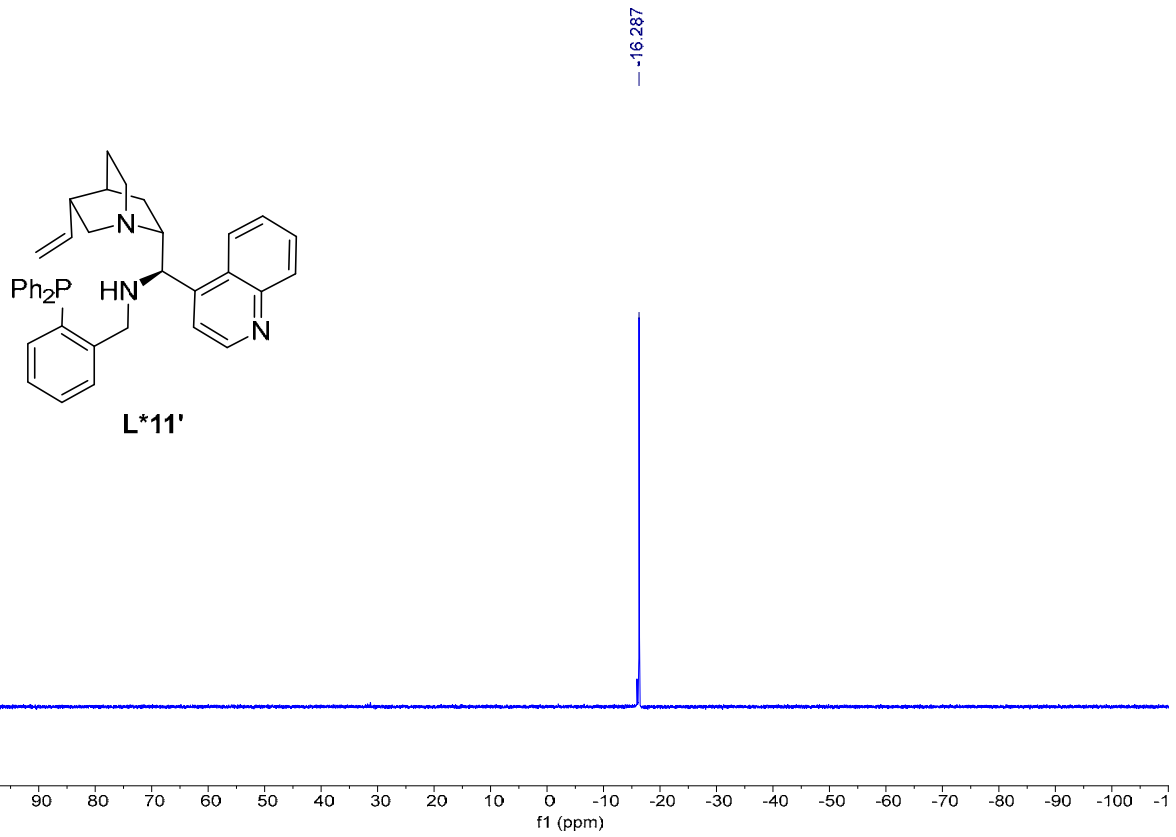
L*11

-16.314
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


L*4'
f1 (ppm)
L*4'
f1 (ppm)

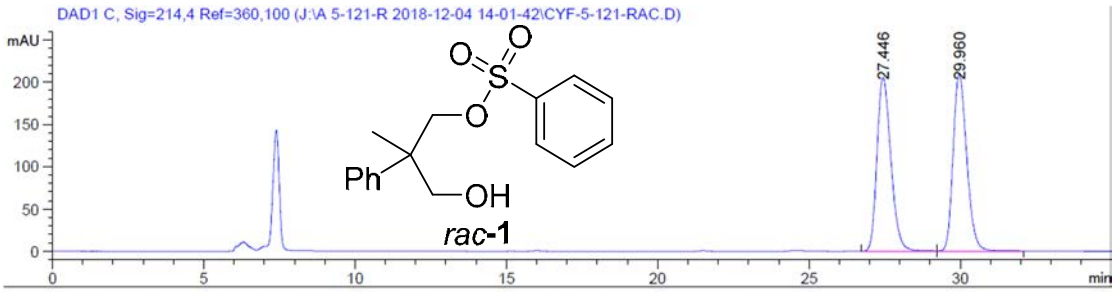

8.921
8.913
8.160
8.137
8.113
7.841
7.830
7.716
7.696
7.535
7.515
7.297
7.283
7.266
7.257
7.249
7.240
7.229
7.224
7.218
7.195
7.189
7.184
7.177
7.170
7.165
7.161
7.152
7.146
7.128
6.870
6.859
6.851
6.840
5.827
5.091
5.065
5.007
4.964
3.549
3.516
2.832
2.810
2.773
2.747
2.190
2.169
1.504
1.466
1.458
1.453
1.444
1.439
1.433
1.257
1.118
1.111
0.701
0.000
Ph2P
HN
N
N
L*11'
0.24
0.90
0.26
2.32
0.92
1.41
1.45
21.13
1.42
1.41
1.42
1.40
1.00
0.75
1.08
1.42
0.42
7.24
1.64
4.43
1.39
1.35
f1 (ppm)


150.594
148.815
148.238
144.779
144.529
140.839
136.954
136.848
136.745
135.834
135.669
133.878
133.785
133.683
133.590
130.363
129.420
129.375
129.109
128.824
128.573
128.497
128.419
128.350
127.268
126.118
122.919
120.063
114.343
62.507
56.343
50.105
49.895
49.293
47.279
39.599
27.720
26.685
24.506
Ph2P
HN
N
N
L*11'
f1 (ppm)


-16.287
N
Ph2P
HN
N
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

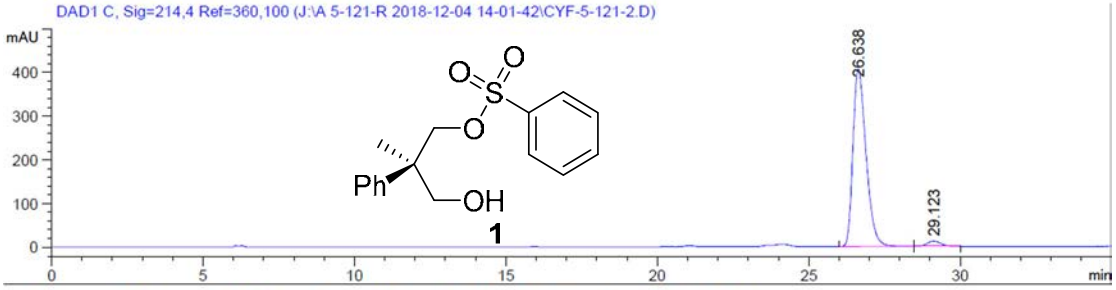
L*11'

HPLC spectra



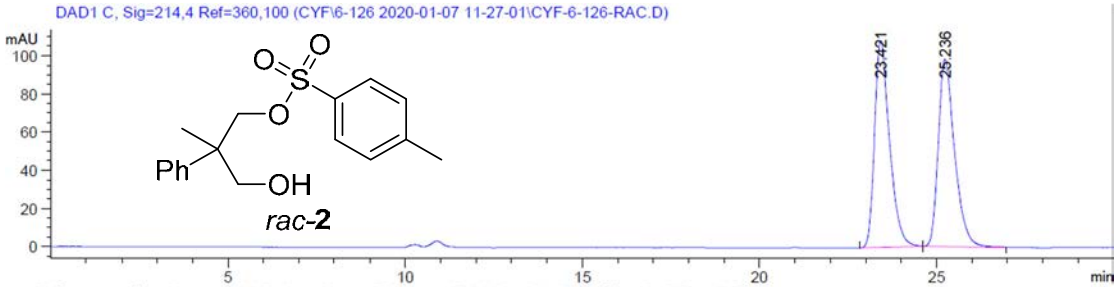
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.446	BB	0.4951	6546.12695	205.77153	50.0091
2	29.960	BB	0.4820	6543.74365	209.70865	49.9909
Totals :				1.30899e4	415.48018	



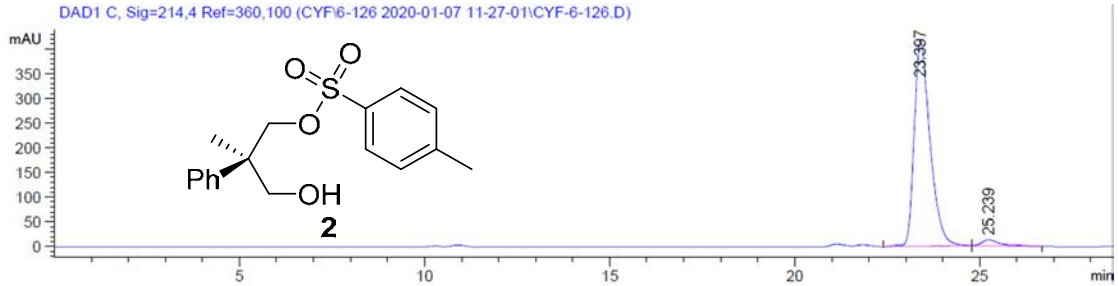
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.638	BB	0.4615	1.21728e4	406.30667	96.9703
2	29.123	BB	0.4776	380.32712	12.06976	3.0297
Totals :				1.25531e4	418.37643	



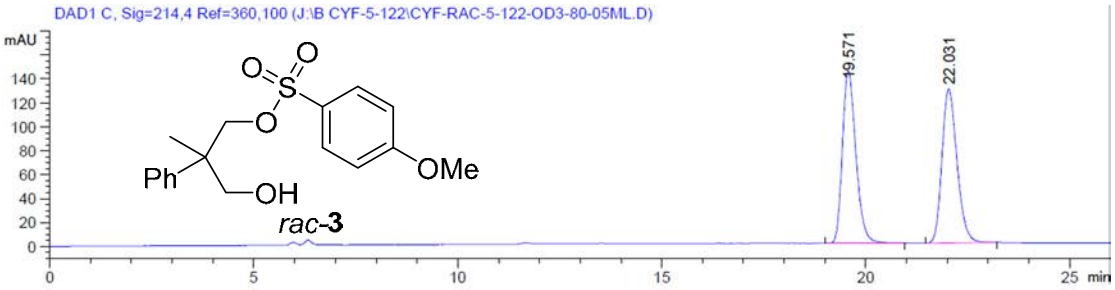
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.421	BB	0.4398	3175.39697	108.38940	50.3229
2	25.236	BB	0.4797	3134.64819	98.38332	49.6771
Totals :				6310.04517	206.77272	



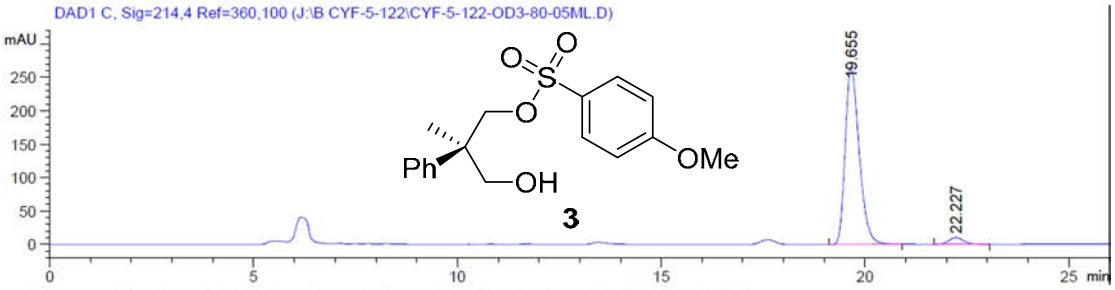
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.397	BB	0.4436	1.23510e4	416.88589	96.6532
2	25.239	BB	0.5131	427.68002	12.19695	3.3468
Totals :				1.27787e4	429.08284	



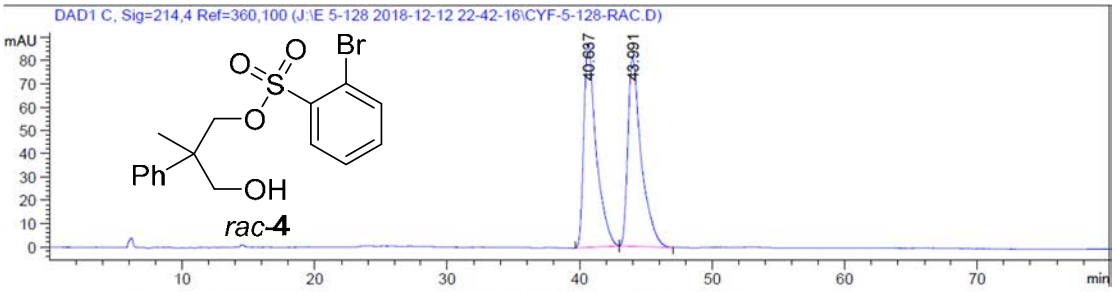
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.571	BB	0.3563	3312.99048	144.05716	50.1175
2	22.031	BB	0.3932	3297.45850	128.56339	49.8825
Totals :				6610.44897	272.62054	



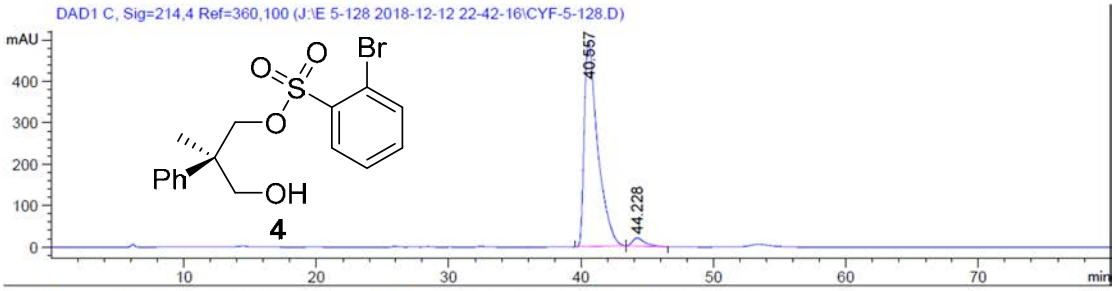
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.655	BB	0.3678	6316.80273	265.27060	96.0805
2	22.227	BB	0.3804	257.68695	9.94211	3.9195
Totals :				6574.48969	275.21271	



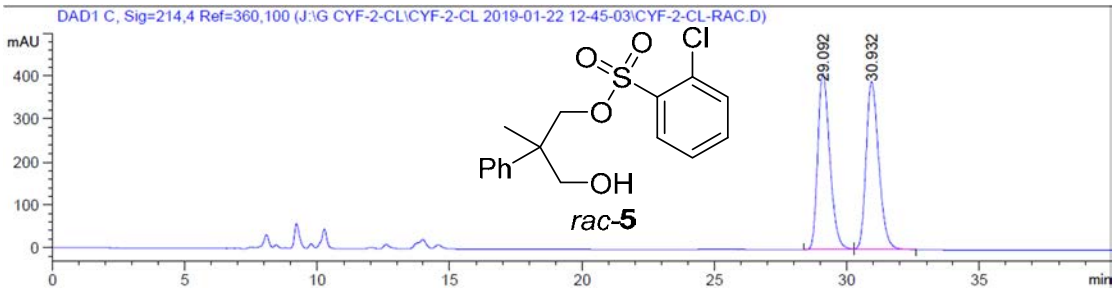
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.637	BB	0.9430	5680.95166	87.78540	49.9983
2	43.991	BB	1.0263	5681.33496	81.19753	50.0017
Totals :				1.13623e4	168.98293	



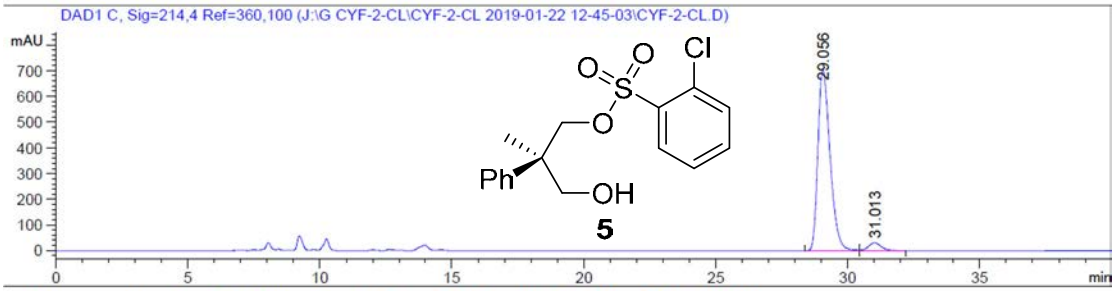
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.557	BB	1.0312	3.49591e4	496.64200	96.4715
2	44.228	BB	0.8974	1278.63330	19.80105	3.5285
Totals :				3.62377e4	516.44305	



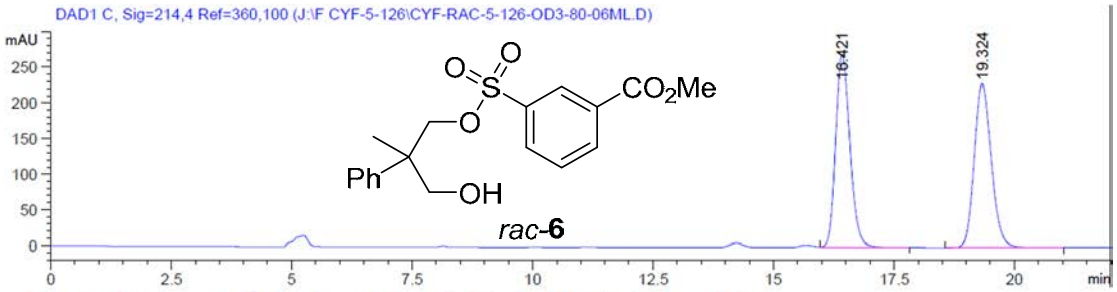
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.092	BV	0.4894	1.30439e4	411.93097	49.9016
2	30.932	VB	0.5126	1.30953e4	391.18246	50.0984
Totals :				2.61392e4	803.11343	



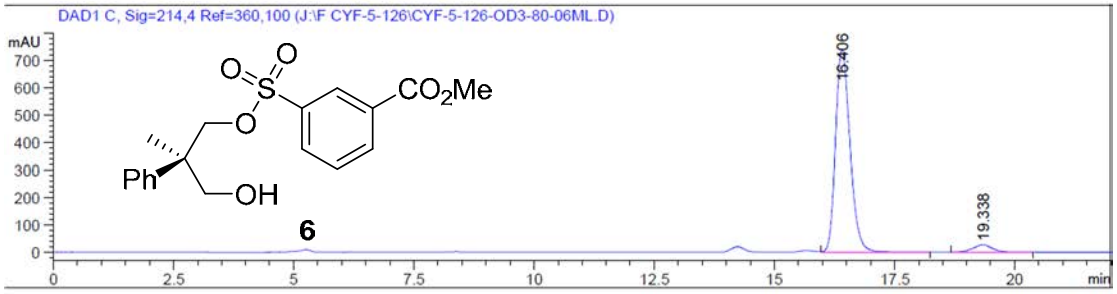
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.056	BV	0.4913	2.25506e4	704.79889	95.4932
2	31.013	VB	0.5132	1064.28271	31.25978	4.5068
Totals :				2.36149e4	736.05867	



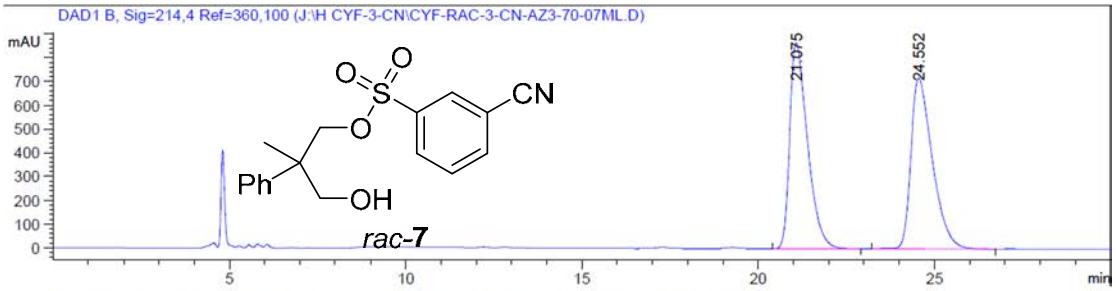
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.421	VB	0.3187	5588.94531	270.92761	49.6770
2	19.324	BB	0.3793	5661.63232	229.92053	50.3230
Totals :				1.12506e4	500.84814	



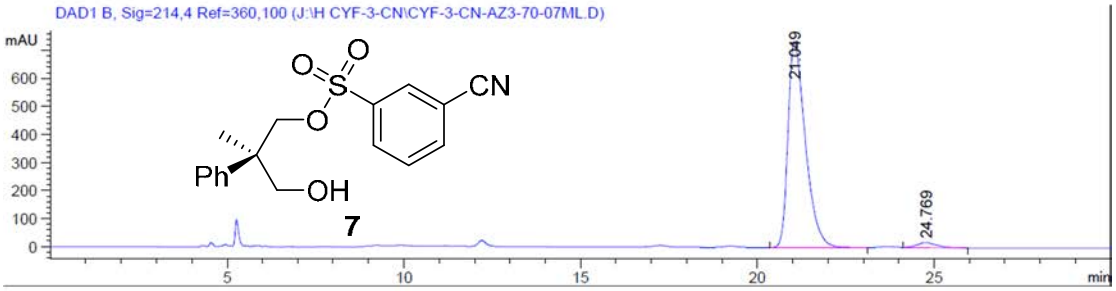
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.406	VB	0.3213	1.54474e4	740.68158	95.5041
2	19.338	BB	0.4242	727.19312	26.33344	4.4959
Totals :				1.61746e4	767.01502	



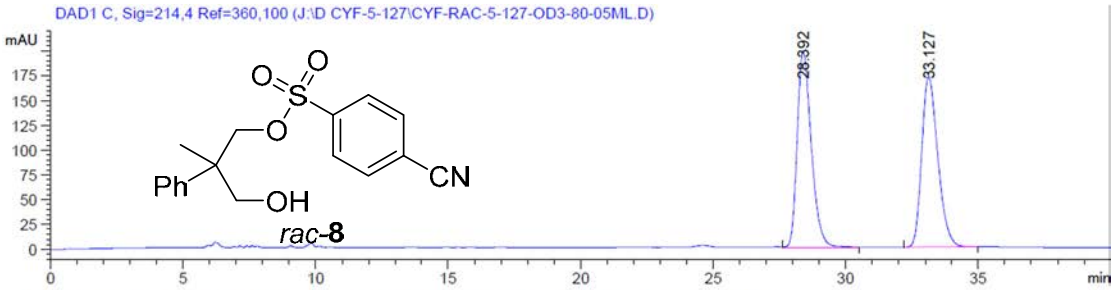
Signal 2: DAD1 B, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.075	BB	0.5304	3.03276e4	866.30450	50.0004
2	24.552	BB	0.6427	3.03271e4	718.09961	49.9996
Totals :				6.06547e4	1584.40411	



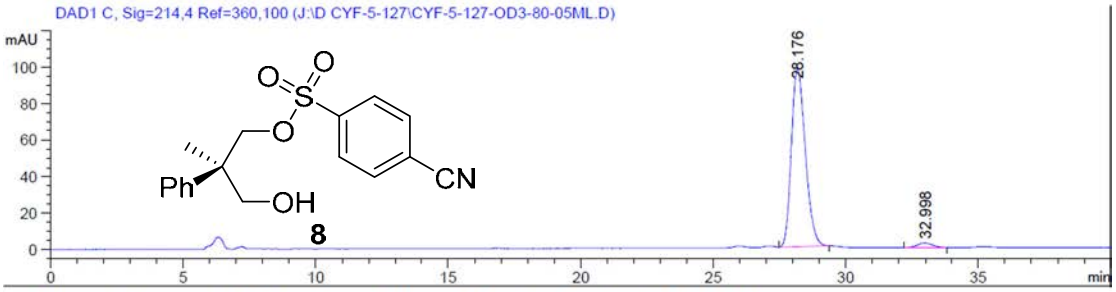
Signal 2: DAD1 B, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.049	BB	0.5159	2.50874e4	735.60181	97.4477
2	24.769	BB	0.5425	657.07574	17.48202	2.5523
Totals :				2.57445e4	753.08382	



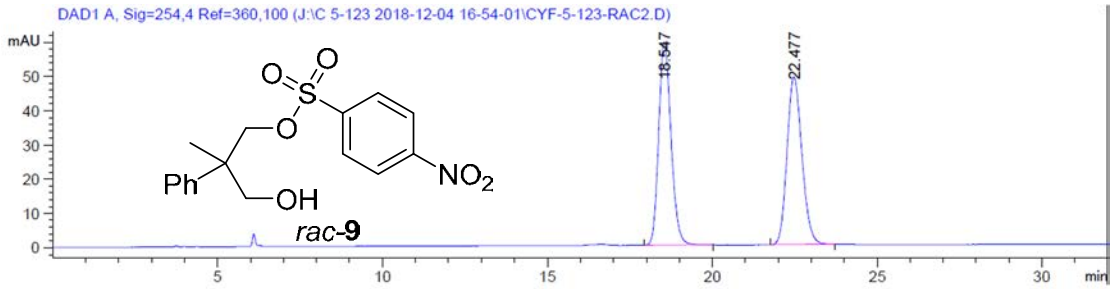
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.392	BB	0.5647	7239.03174	196.98079	50.0401
2	33.127	BB	0.6515	7227.41699	171.53909	49.9599
Totals :				1.44664e4	368.51988	



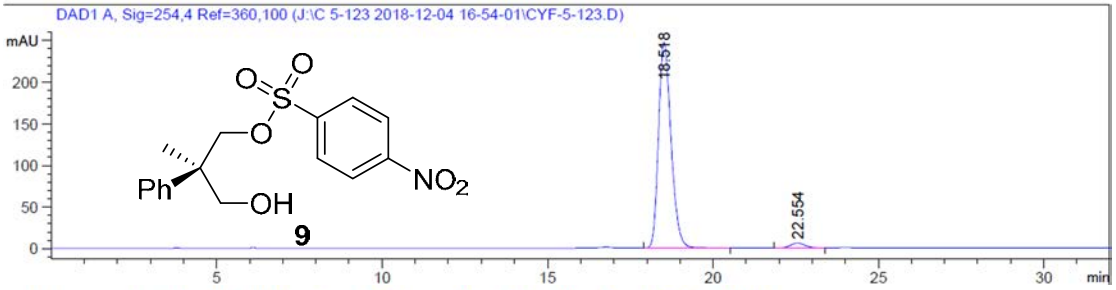
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.176	BB	0.5618	3568.46948	97.76511	97.1027
2	32.998	BB	0.4994	106.47512	2.55890	2.8973
Totals :				3674.94460	100.32402	



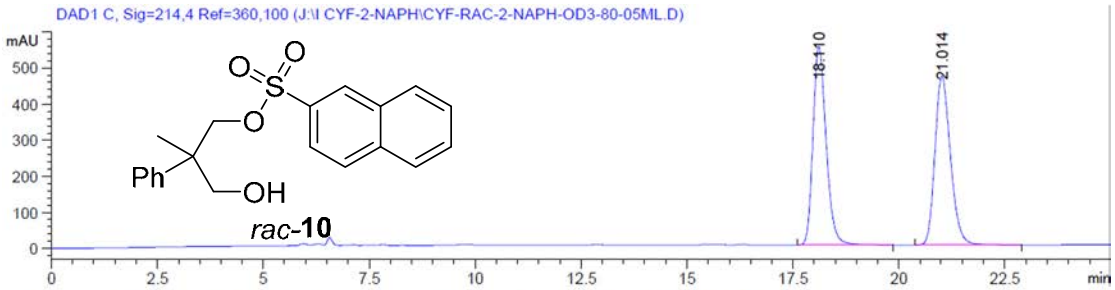
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.547	BB	0.4033	1540.53479	59.26131	50.0490
2	22.477	BB	0.4863	1537.52075	48.97441	49.9510
Totals :				3078.05554	108.23572	



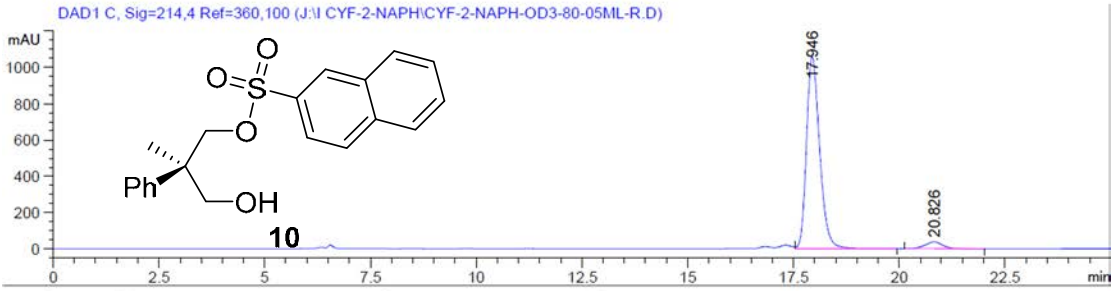
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.518	BB	0.4073	6512.91992	247.26157	97.1952
2	22.554	BB	0.4841	187.94423	5.95738	2.8048
Totals :				6700.86415	253.21895	



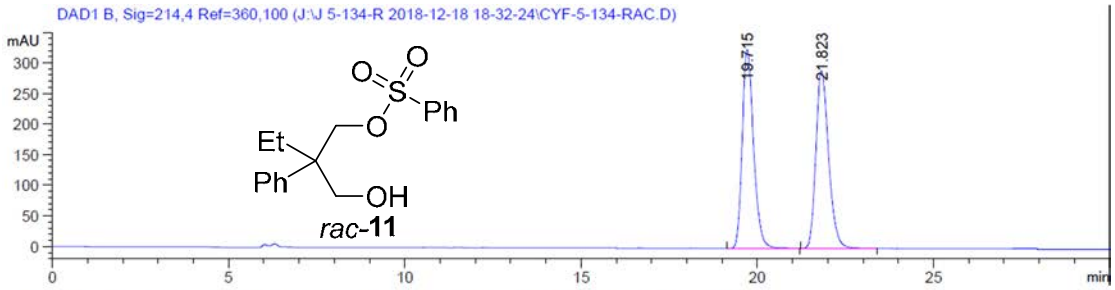
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.110	BB	0.3345	1.18807e4	549.04218	49.8904
2	21.014	BB	0.3941	1.19329e4	467.00278	50.1096
Totals :				2.38136e4	1016.04495	



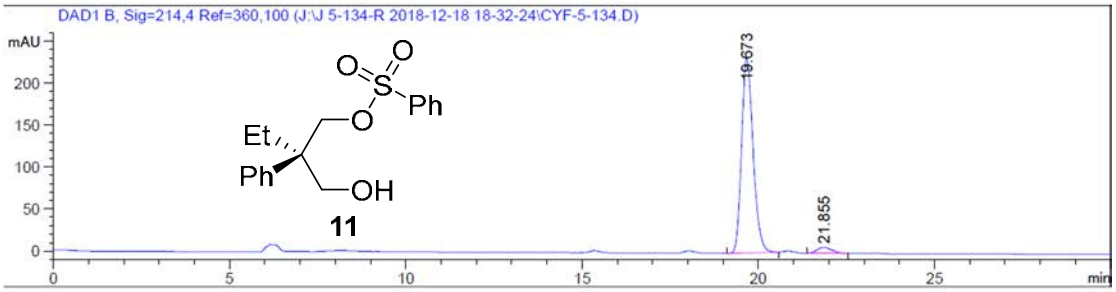
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.946	VB	0.3326	2.29115e4	1058.11353	95.5153
2	20.826	BB	0.4251	1075.75134	37.67390	4.4847
Totals :				2.39872e4	1095.78743	



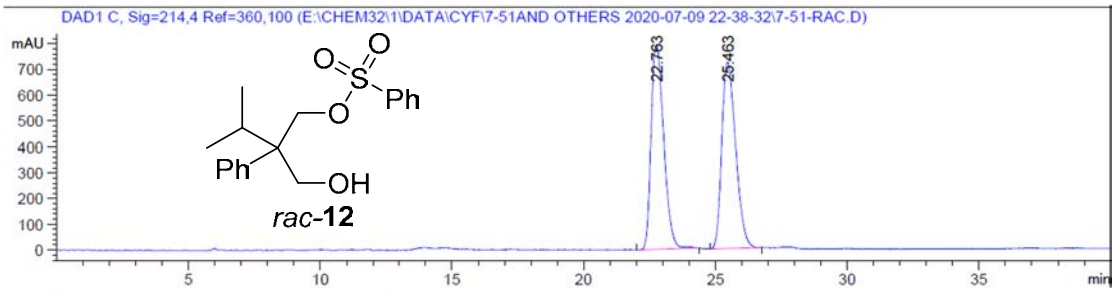
Signal 2: DAD1 B, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.715	BB	0.3459	7290.31738	324.71332	49.9950
2	21.823	BB	0.3852	7291.76904	290.15915	50.0050
Totals :				1.45821e4	614.87247	



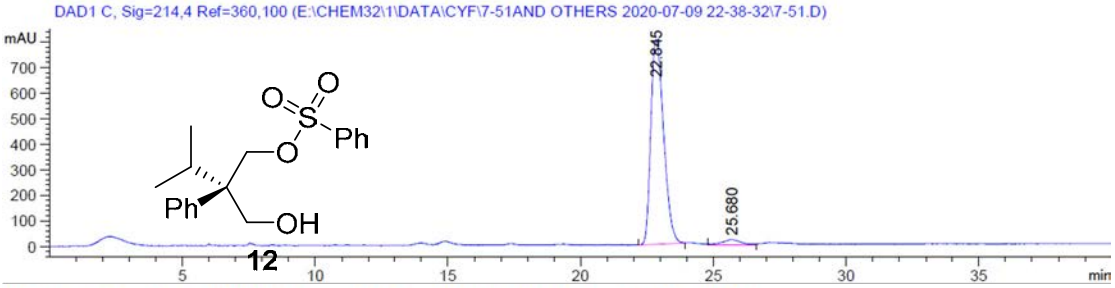
Signal 2: DAD1 B, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.673	BB	0.3518	5284.06445	231.88922	96.3103
2	21.855	BB	0.3739	202.43370	6.90801	3.6897
Totals :				5486.49815	238.79723	



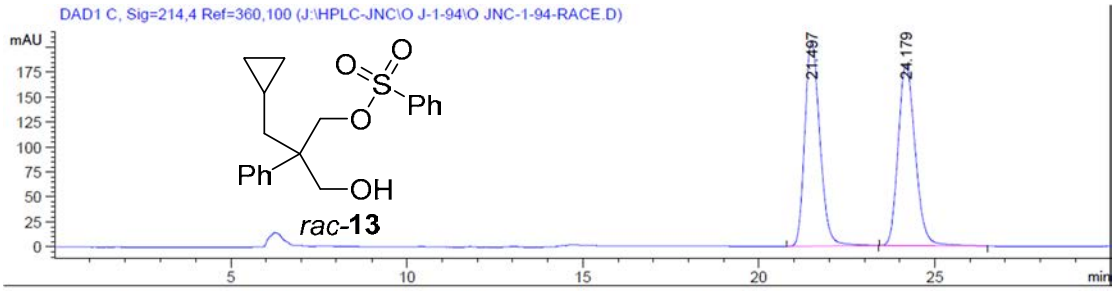
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.763	VV R	0.4712	2.64663e4	793.42444	49.9860
2	25.463	BV R	0.4760	2.64812e4	721.82117	50.0140
Totals :				5.29475e4	1515.24561	



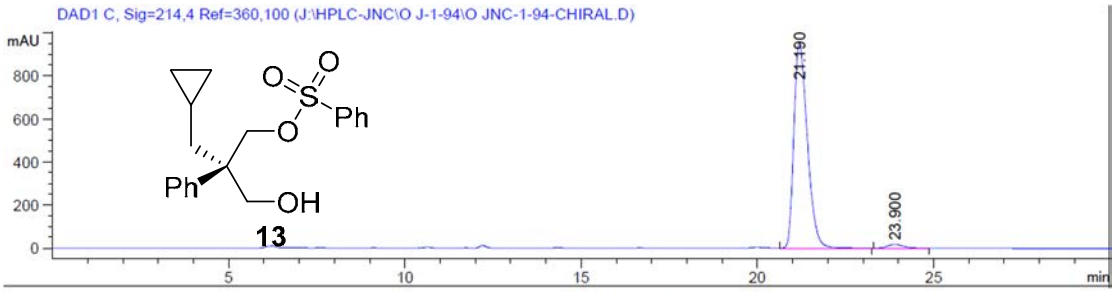
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.845	VB R	0.4042	2.68053e4	801.42841	96.8794
2	25.680	MM R	0.7481	863.42938	19.23664	3.1206
Totals :				2.76687e4	820.66504	



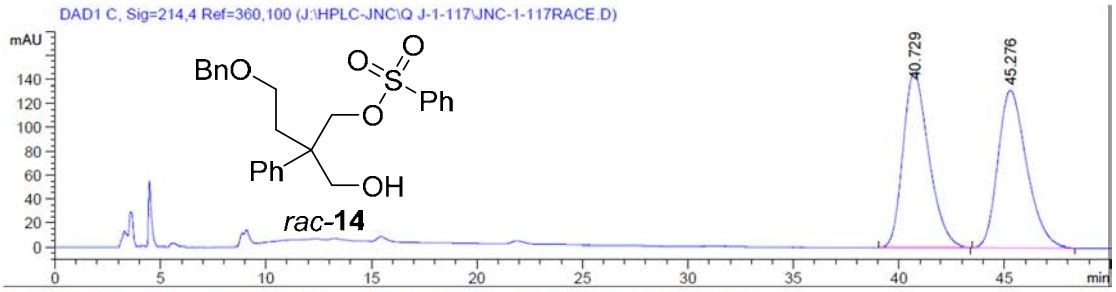
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.497	BB	0.4650	6125.73096	204.75266	49.9619
2	24.179	BB	0.5235	6135.07227	180.99455	50.0381
Totals :				1.22608e4	385.74721	



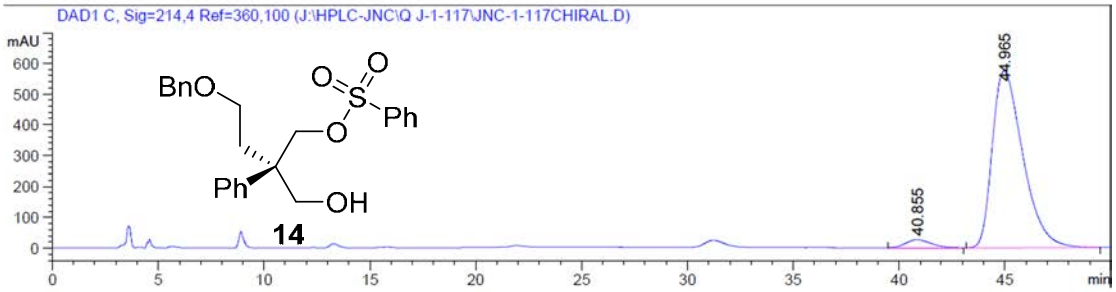
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.190	BB	0.4082	2.52645e4	956.27551	97.8889
2	23.900	BB	0.4575	544.86035	18.29020	2.1111
Totals :				2.58093e4	974.56571	



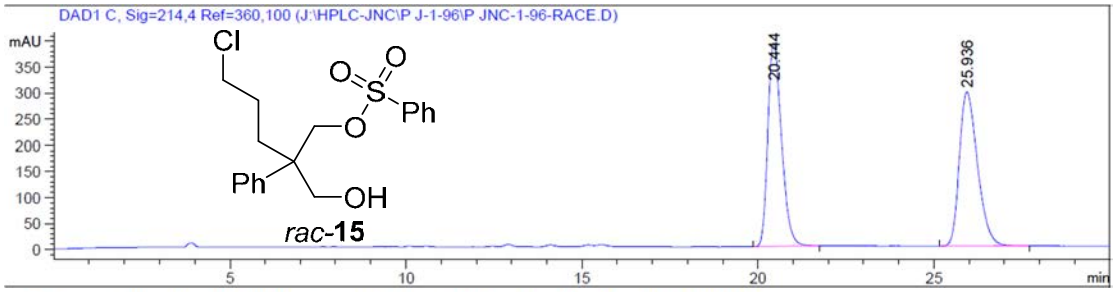
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.729	BB	1.1421	1.24472e4	146.08464	49.9344
2	45.276	BB	1.2531	1.24799e4	131.99074	50.0656
Totals :				2.49271e4	278.07538	



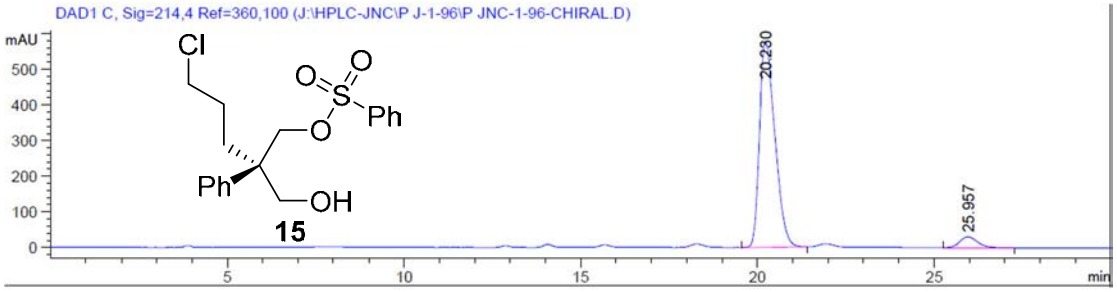
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.855	BB	0.9825	2172.73169	26.33521	3.6210
2	44.965	BB	1.4234	5.78305e4	575.96515	96.3790
Totals :				6.00033e4	602.30036	



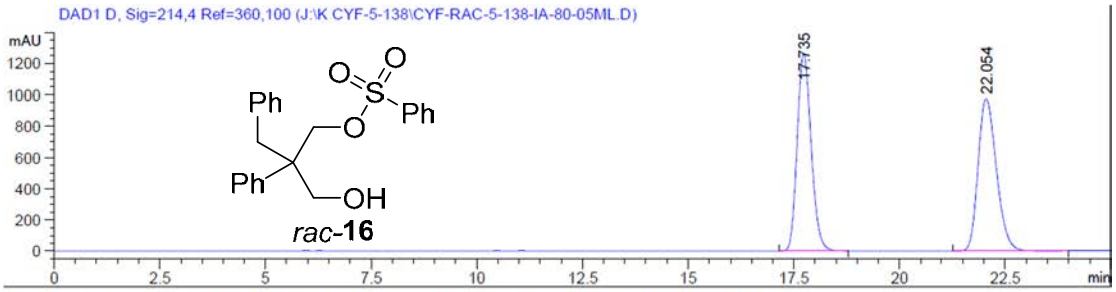
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.444	BB	0.4186	1.05288e4	390.50967	49.8595
2	25.936	BB	0.5536	1.05881e4	295.79929	50.1405
Totals :				2.11169e4	686.30896	



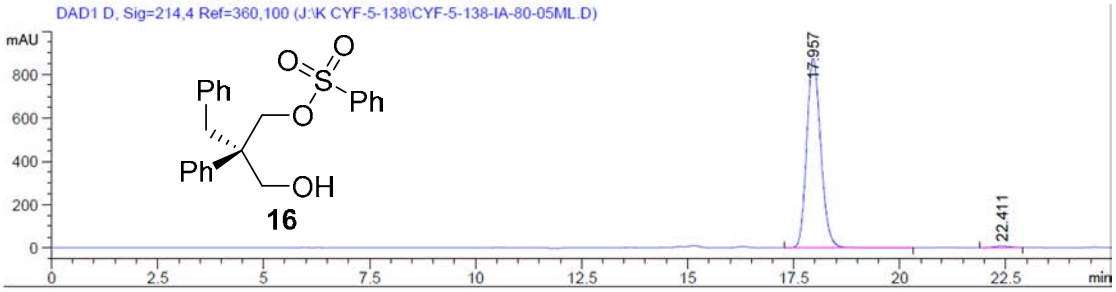
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.230	BB	0.4582	1.74597e4	578.41498	94.2752
2	25.957	BB	0.5397	1060.22070	30.48491	5.7248
Totals :				1.85199e4	608.89989	



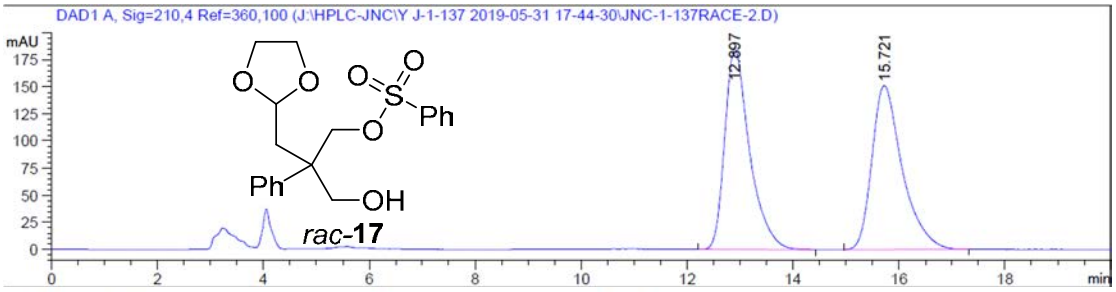
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.735	BB	0.3597	2.91049e4	1258.84668	49.7203
2	22.054	BB	0.4719	2.94324e4	975.66431	50.2797
Totals :				5.85373e4	2234.51099	



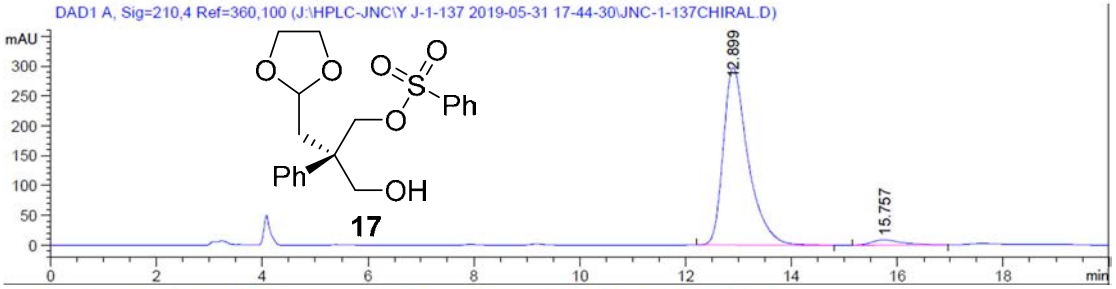
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.957	BB	0.3596	2.01939e4	873.74371	98.9850
2	22.411	BB	0.4158	207.06618	7.84785	1.0150
Totals :				2.04010e4	881.59157	



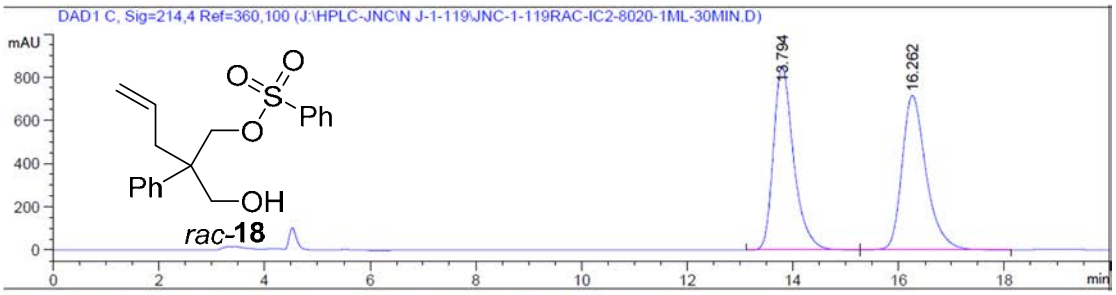
Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.897	BB	0.4878	6058.05176	185.09772	50.0626
2	15.721	BB	0.5898	6042.91260	151.36731	49.9374
Totals :				1.21010e4	336.46503	



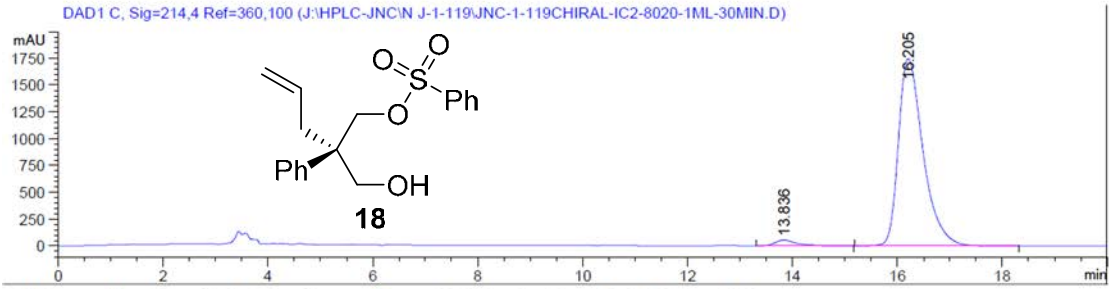
Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.899	BB	0.4847	9648.34375	297.27383	96.4599
2	15.757	BB	0.4924	354.09372	8.89554	3.5401
Totals :				1.00024e4	306.16937	



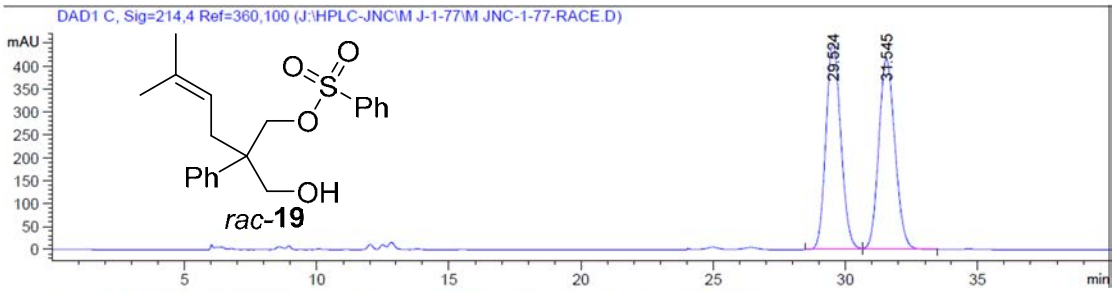
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.794	BB	0.4044	2.26347e4	850.85217	49.9647
2	16.262	BB	0.4816	2.26667e4	715.40497	50.0353
Totals :				4.53013e4	1566.25714	



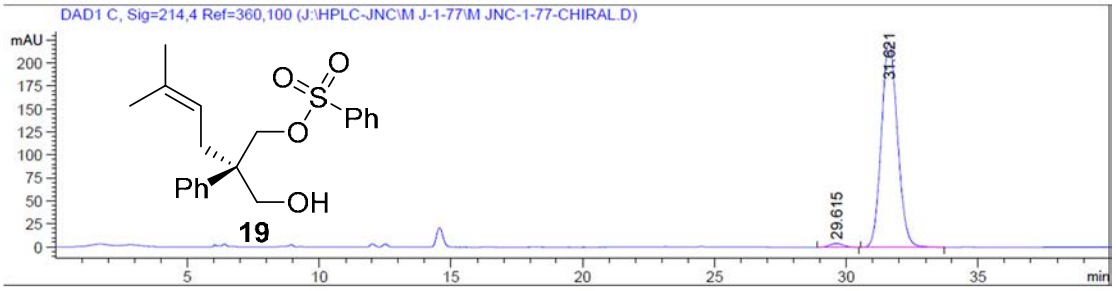
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.836	BB	0.4227	1519.28662	52.95740	2.5934
2	16.205	BB	0.4971	5.70629e4	1746.67407	97.4066
Totals :				5.85821e4	1799.63147	



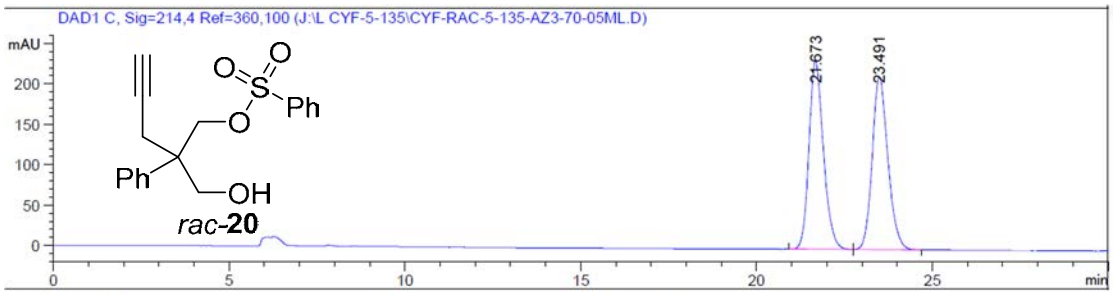
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.524	BV	0.6132	1.76897e4	449.40564	49.8741
2	31.545	VB	0.6574	1.77790e4	415.30038	50.1259
Totals :				3.54687e4	864.70602	



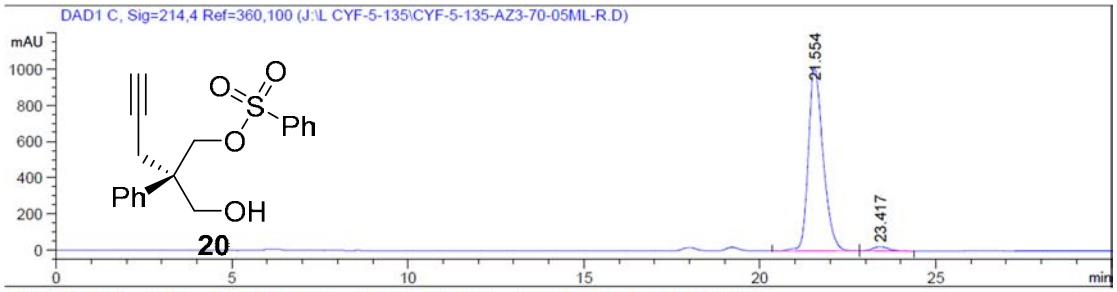
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.615	BB	0.4645	161.02058	4.20716	1.6608
2	31.621	BB	0.6682	9534.49609	223.29117	98.3392
Totals :				9695.51668	227.49833	



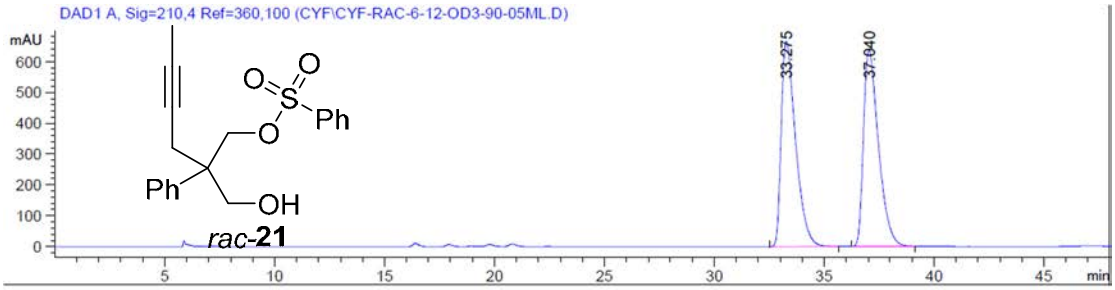
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.673	BB	0.4325	6663.60986	233.82124	50.1063
2	23.491	BB	0.4715	6635.34180	214.12151	49.8937
Totals :				1.32990e4	447.94275	



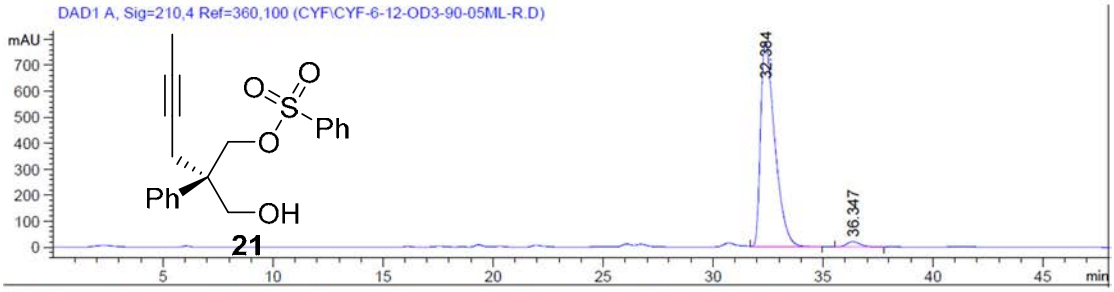
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.554	BB	0.4431	2.96180e4	1013.07269	97.6624
2	23.417	BB	0.4535	708.90771	23.66096	2.3376
Totals :				3.03269e4	1036.73365	



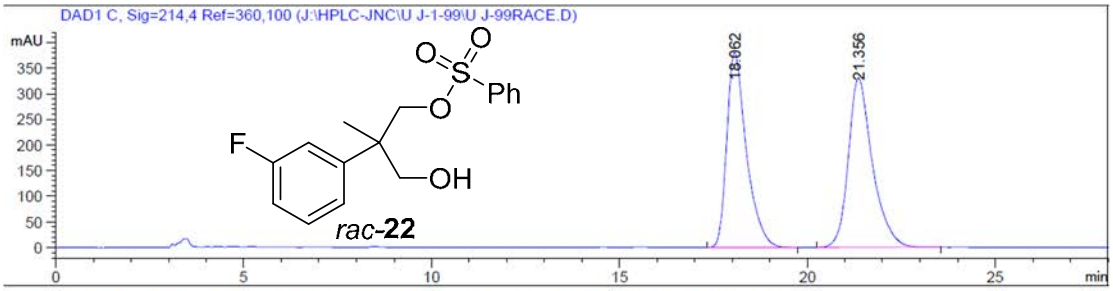
Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.275	BB	0.6829	3.01701e4	665.55096	50.0635
2	37.040	BB	0.7023	3.00936e4	635.71606	49.9365
Totals :				6.02636e4	1301.26703	



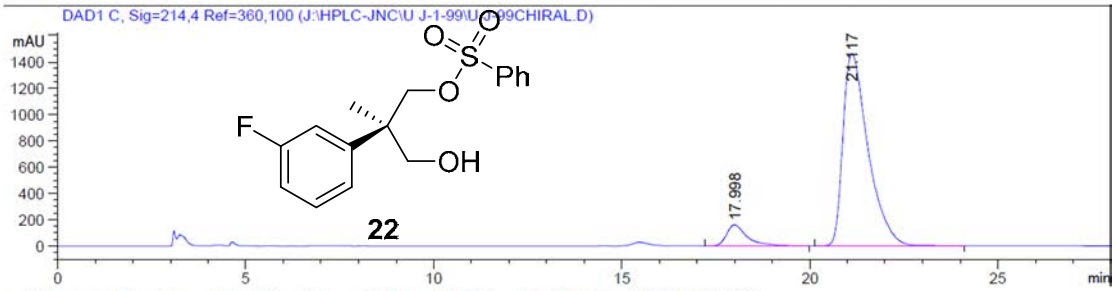
Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.384	VB	0.6700	3.55325e4	791.15167	97.5661
2	36.347	BB	0.5735	886.38678	20.45714	2.4339
Totals :				3.64188e4	811.60882	



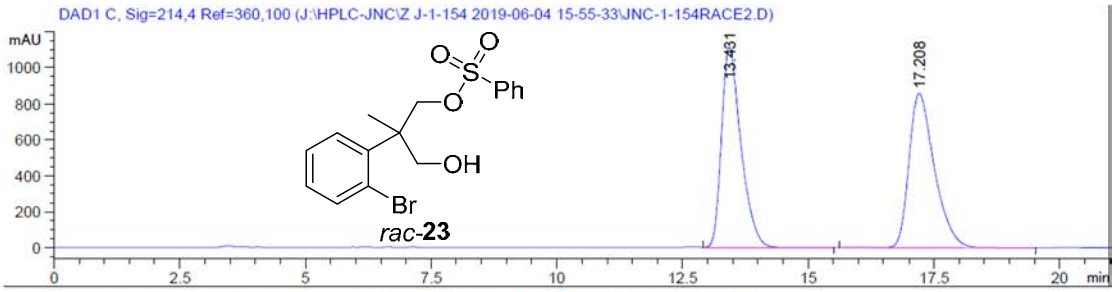
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.062	BB	0.5412	1.37816e4	379.94040	48.4019
2	21.356	BB	0.6594	1.46916e4	330.02811	51.5981
Totals :				2.84732e4	709.96851	



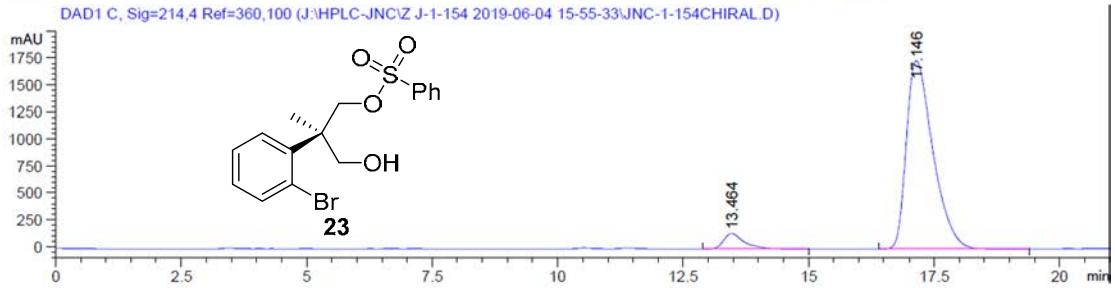
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.998	BB	0.5591	6059.41992	160.27577	8.2080
2	21.117	BB	0.6865	6.77639e4	1462.68982	91.7920
Totals :				7.38233e4	1622.96559	



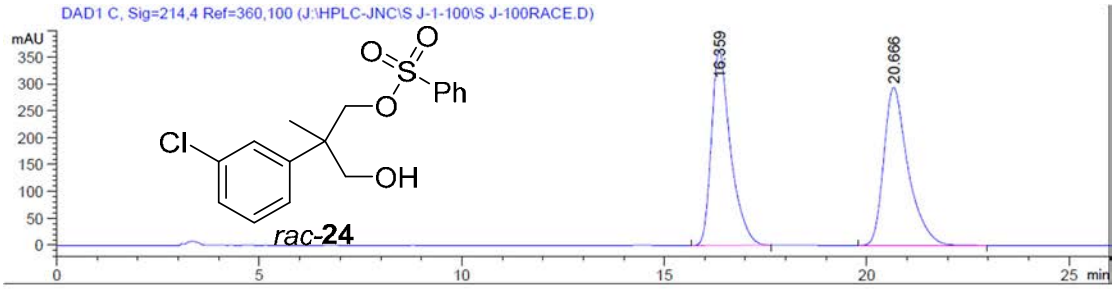
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.431	VB	0.4069	3.00337e4	1112.82178	49.8426
2	17.208	BB	0.5322	3.02234e4	859.51923	50.1574
Totals :				6.02571e4	1972.34100	



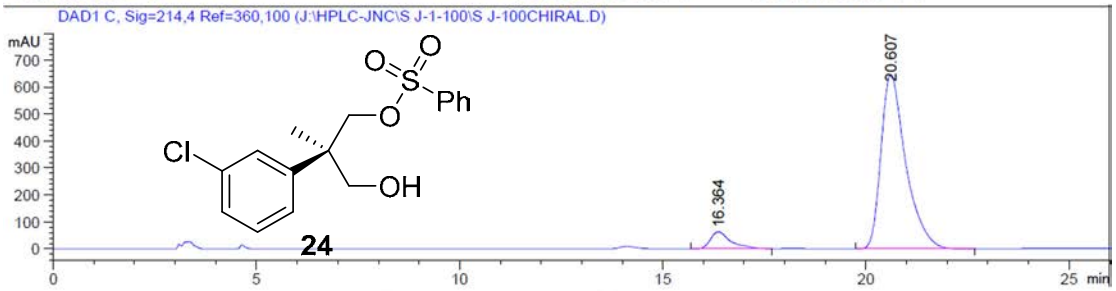
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.464	BB	0.4175	4041.71436	143.11044	5.9220
2	17.146	BB	0.5609	6.42076e4	1746.52466	94.0780
Totals :				6.82493e4	1889.63510	



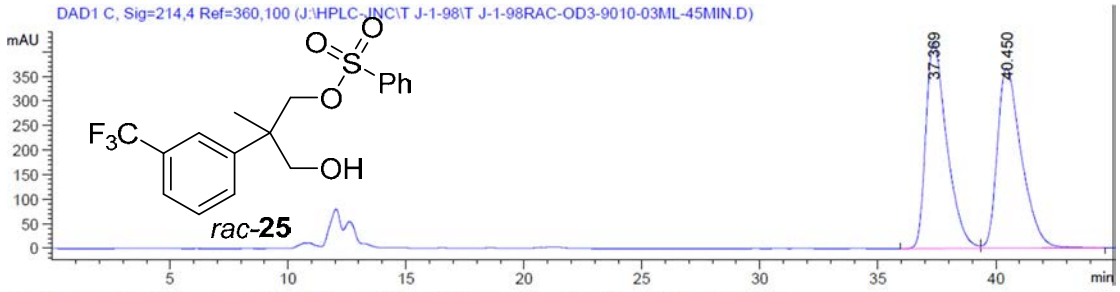
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.359	BB	0.4930	1.19515e4	362.14798	49.2865
2	20.666	BB	0.6239	1.22975e4	294.03146	50.7135
Totals :				2.42491e4	656.17944	



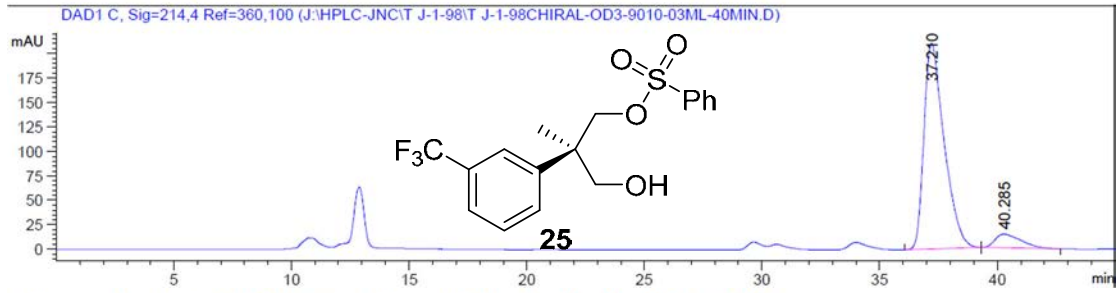
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.364	BB	0.5167	2231.01001	63.68486	7.5066
2	20.607	BB	0.6386	2.74896e4	648.39532	92.4934
Totals :				2.97206e4	712.08019	



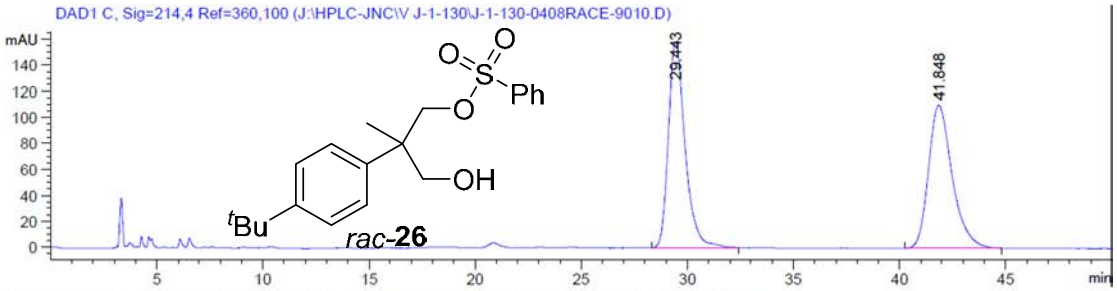
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.369	BV	0.9164	2.60903e4	421.33765	49.9609
2	40.450	VB	1.0544	2.61312e4	367.12762	50.0391
Totals :				5.22215e4	788.46527	



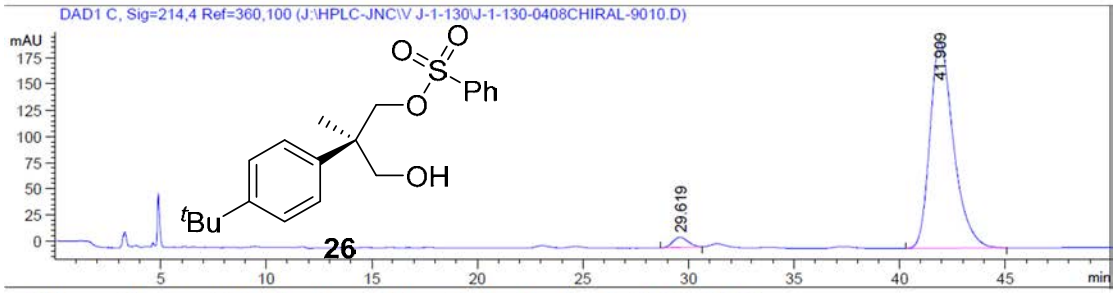
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.210	BB	0.8851	1.25468e4	210.58719	92.0208
2	40.285	BB	1.0576	1087.94312	14.17150	7.9792
Totals :				1.36348e4	224.75869	



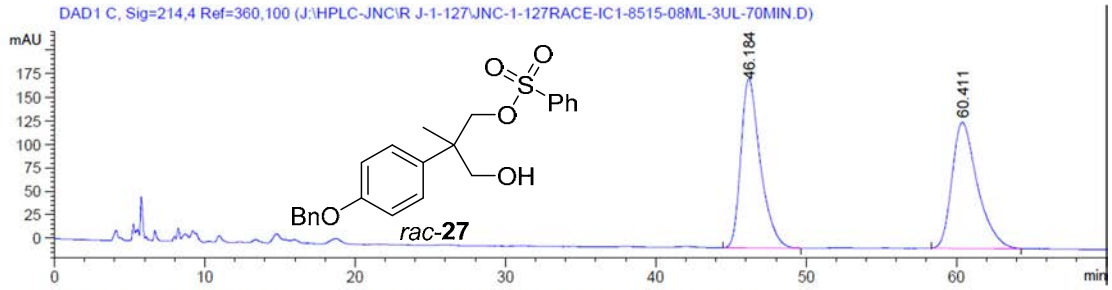
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.443	BB	0.8305	8666.94141	158.35564	50.3687
2	41.848	BB	1.1140	8540.05371	110.21272	49.6313
Totals :				1.72070e4	268.56835	



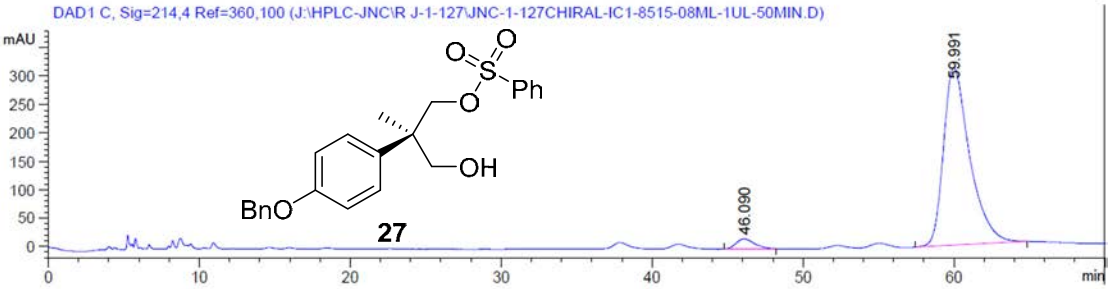
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.619	BB	0.5906	484.02200	9.69248	3.0644
2	41.909	BB	1.1662	1.53110e4	196.68939	96.9356
Totals :				1.57950e4	206.38187	



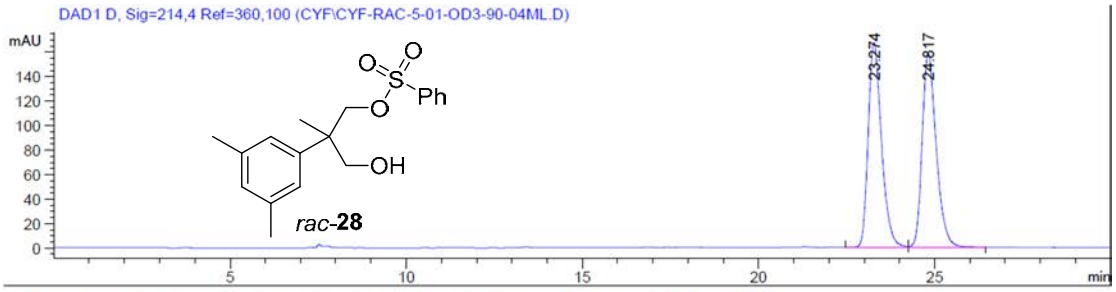
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.184	BB	1.2733	1.62088e4	179.53838	50.6514
2	60.411	BB	1.3983	1.57919e4	134.25790	49.3486
Totals :				3.20008e4	313.79628	



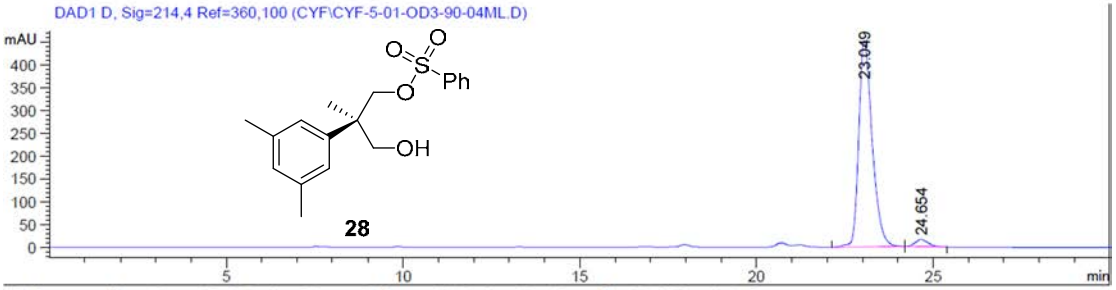
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.090	BB	0.9952	1519.08008	18.02513	3.8625
2	59.991	BB	1.6451	3.78102e4	312.15445	96.1375
Totals :				3.93293e4	330.17958	



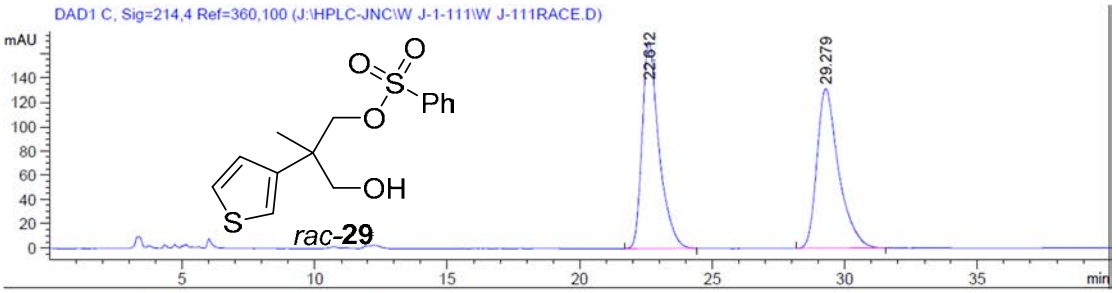
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.274	BV	0.3998	4392.04834	167.58720	49.9583
2	24.817	VB	0.4238	4399.38037	158.51543	50.0417
Totals :				8791.42871	326.10263	



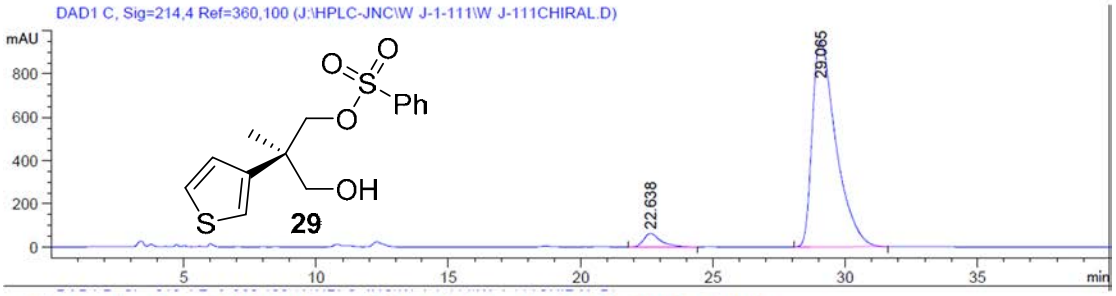
Signal 4: DAD1 D, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.049	BB	0.4028	1.19484e4	451.41046	96.7776
2	24.654	BB	0.3897	397.85120	15.28601	3.2224
Totals :				1.23463e4	466.69647	



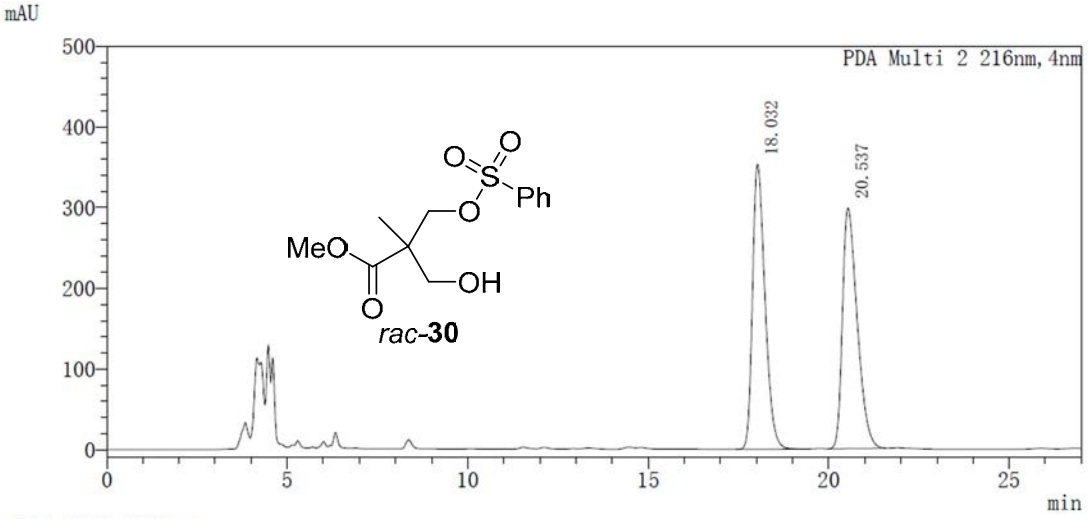
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.612	BB	0.6586	7538.25537	170.22421	50.1406
2	29.279	BB	0.8446	7495.96533	131.19647	49.8594
Totals :				1.50342e4	301.42068	



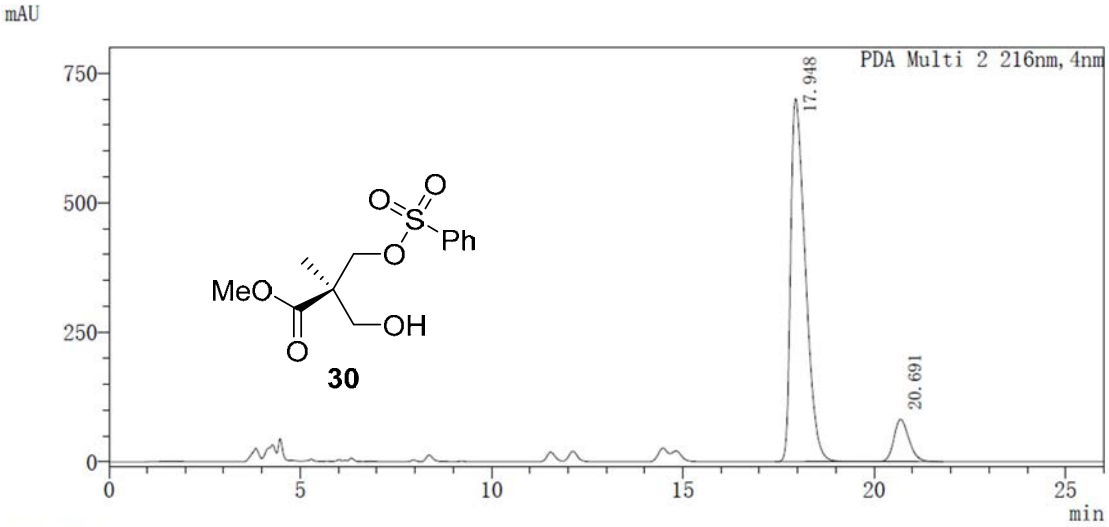
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.638	BB	0.6518	2808.64746	62.80257	4.5239
2	29.065	BB	0.9275	5.92758e4	953.26880	95.4761
Totals :				6.20844e4	1016.07137	



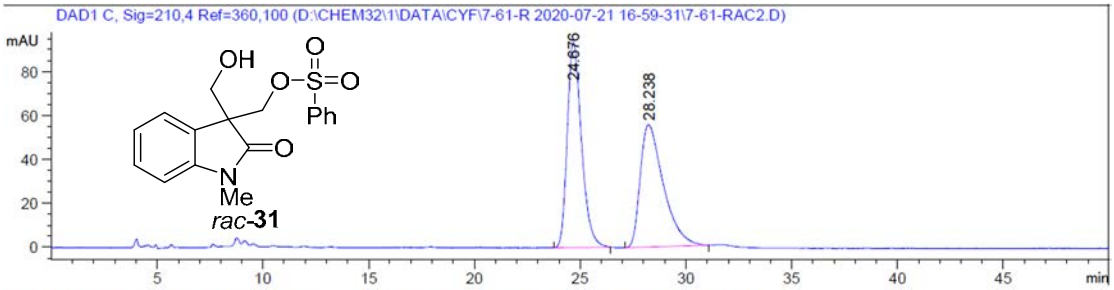
PDA Ch2 216nm

Peak#	Ret. Time	Area	Area%
1	18.032	8502427	50.071
2	20.537	8478254	49.929



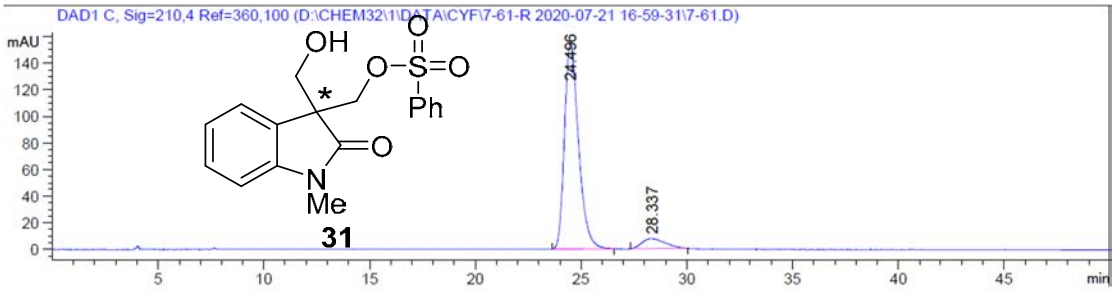
PDA Ch2 216nm

Peak#	Ret. Time	Area	Area%
1	17.948	18703727	89.359
2	20.691	2227374	10.641



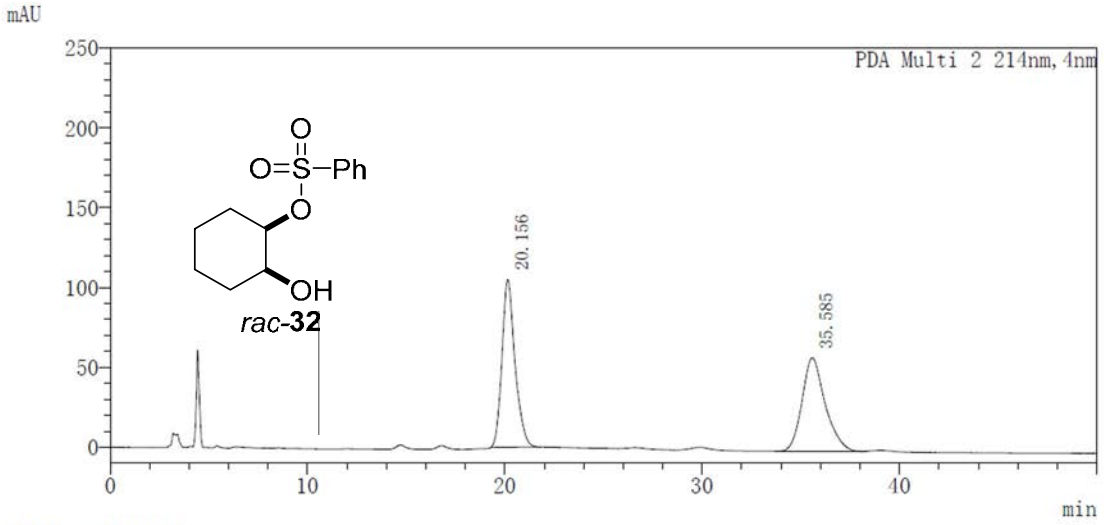
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.676	BB	0.6711	4358.09082	93.27851	50.6129
2	28.238	BB	0.9044	4252.54053	55.72058	49.3871
Totals :				8610.63135	148.99910	



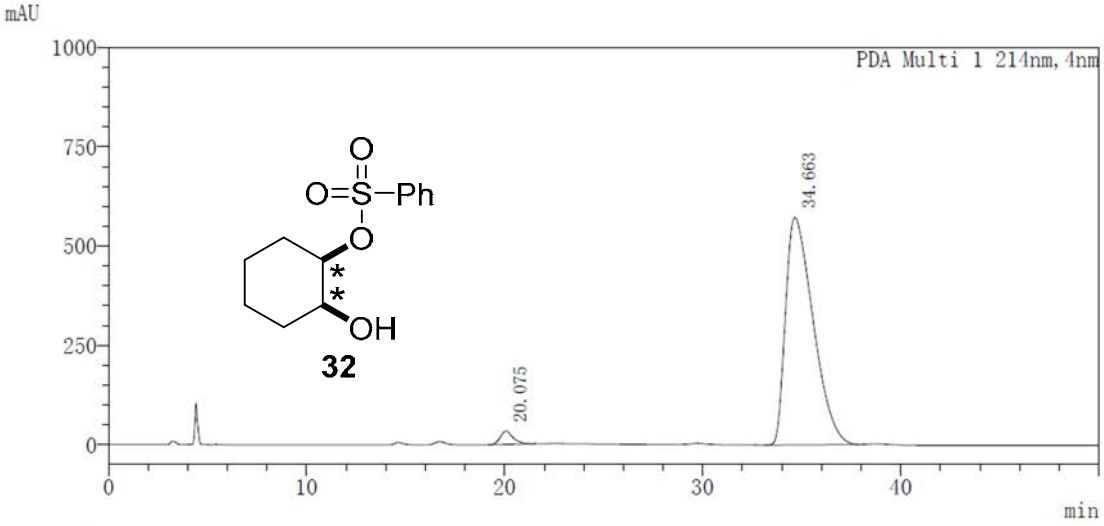
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.496	BB	0.6814	7145.81738	154.56819	92.5157
2	28.337	BB	0.9032	578.07666	7.56759	7.4843
Totals :				7723.89404	162.13578	



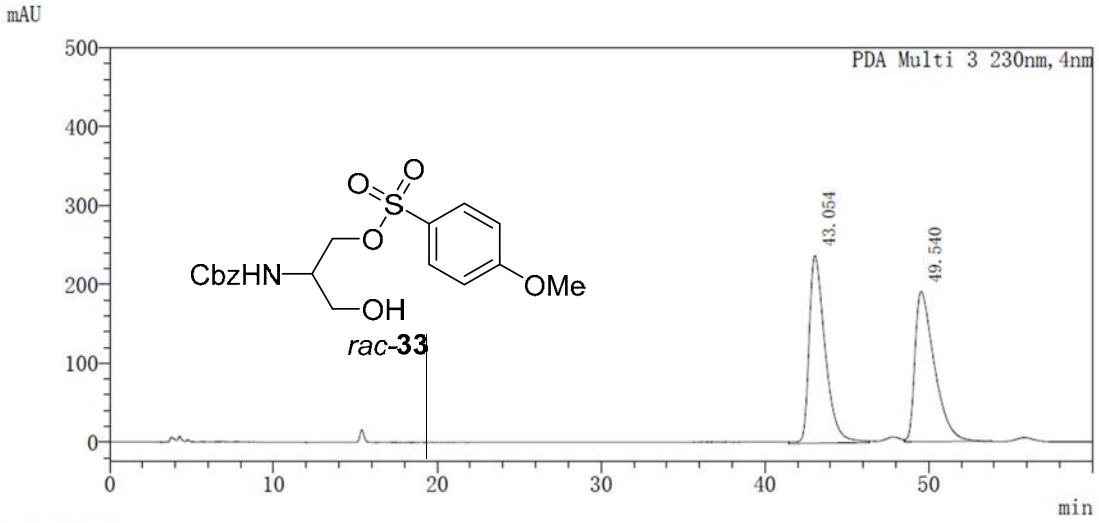
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	20.156	4817879	50.226
2	35.585	4774471	49.774



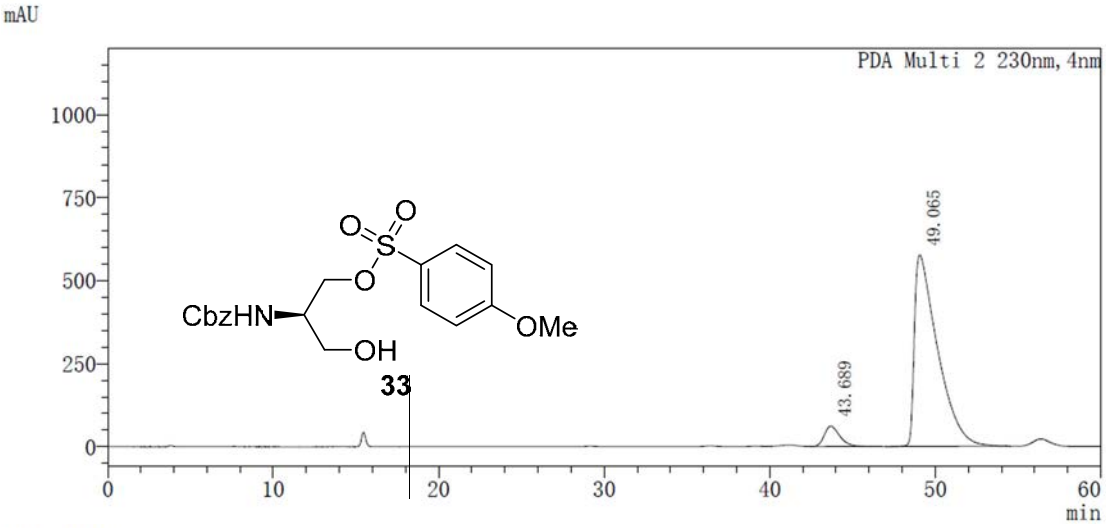
PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	20.075	1508858	2.650
2	34.663	55419143	97.350



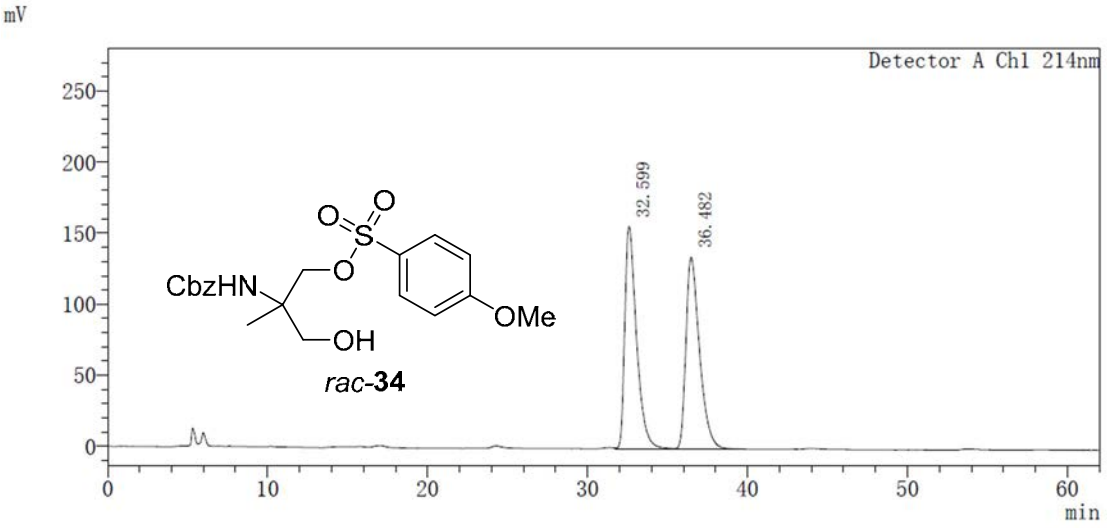
PDA Ch3 230nm

Peak#	Ret. Time	Area	Area%
1	43.054	16181251	50.797
2	49.540	15673499	49.203



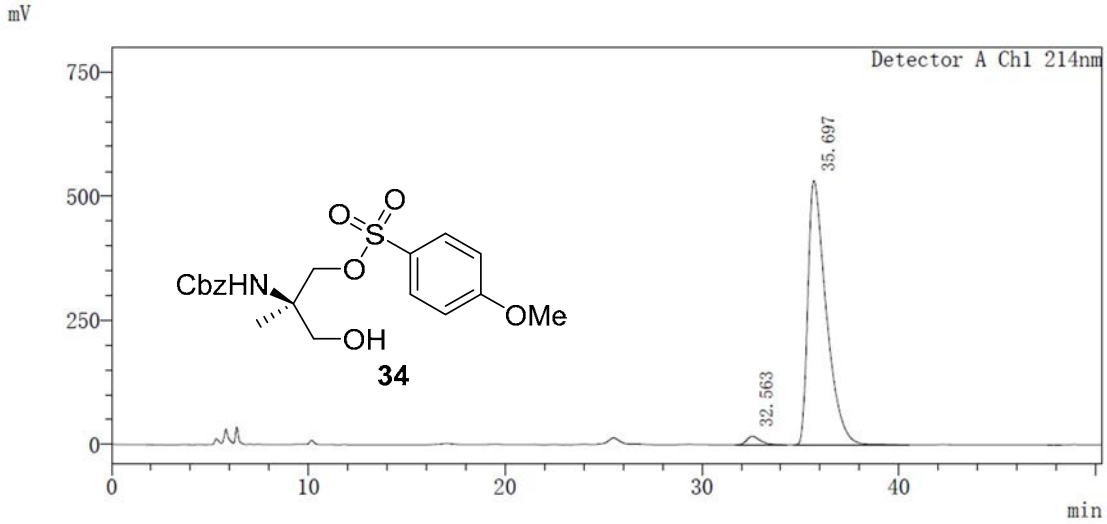
PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	43.689	3970147	6.606
2	49.065	56127057	93.394



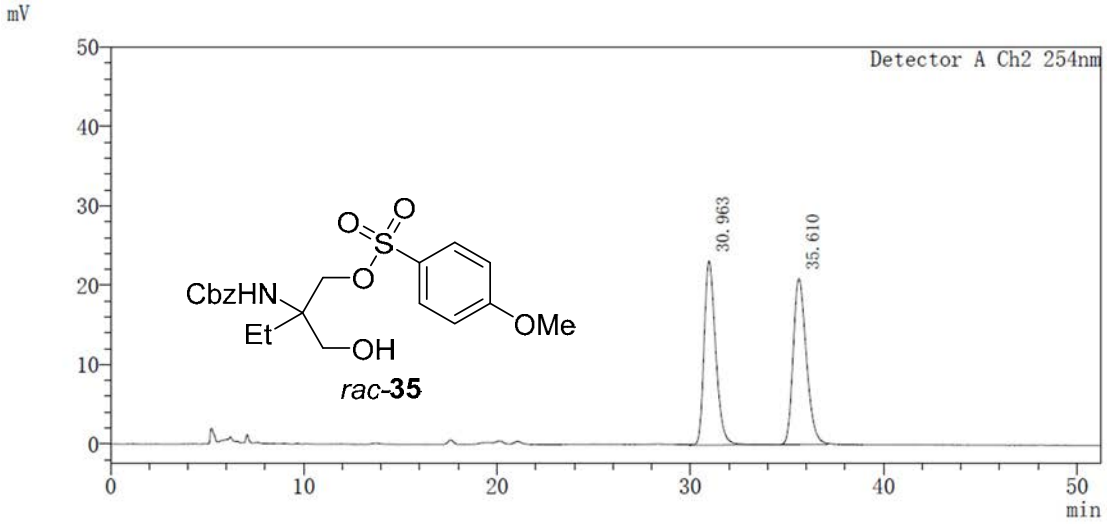
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	32.599	7974609	50.027
2	36.482	7965842	49.973



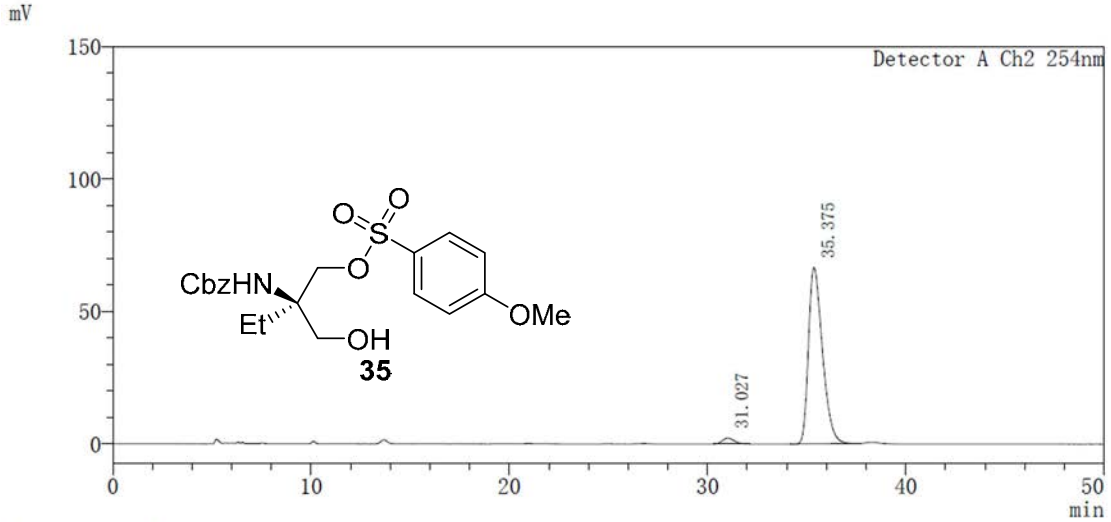
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	32.563	799560	2.267
2	35.697	34465827	97.733



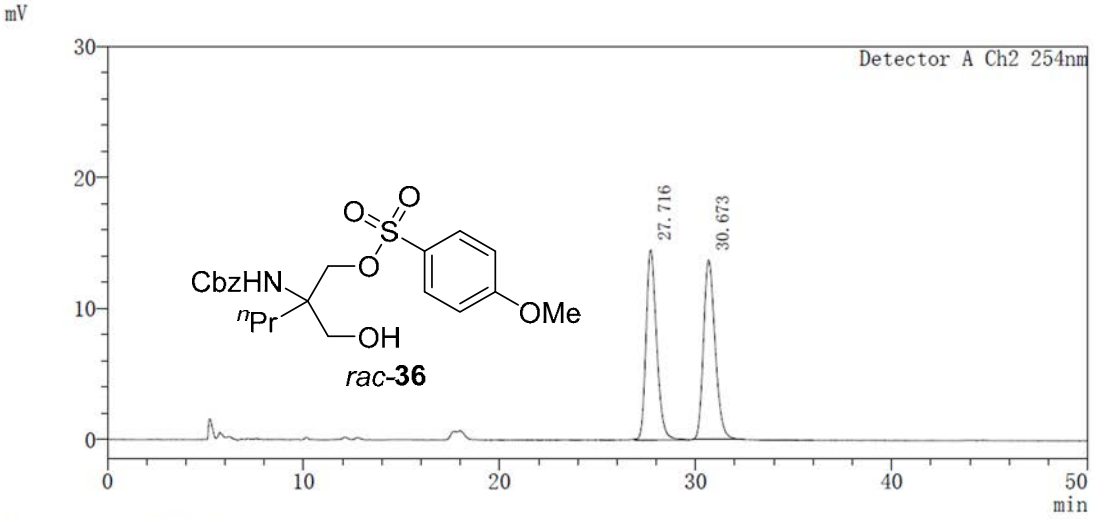
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	30.963	966334	49.344
2	35.610	992047	50.656



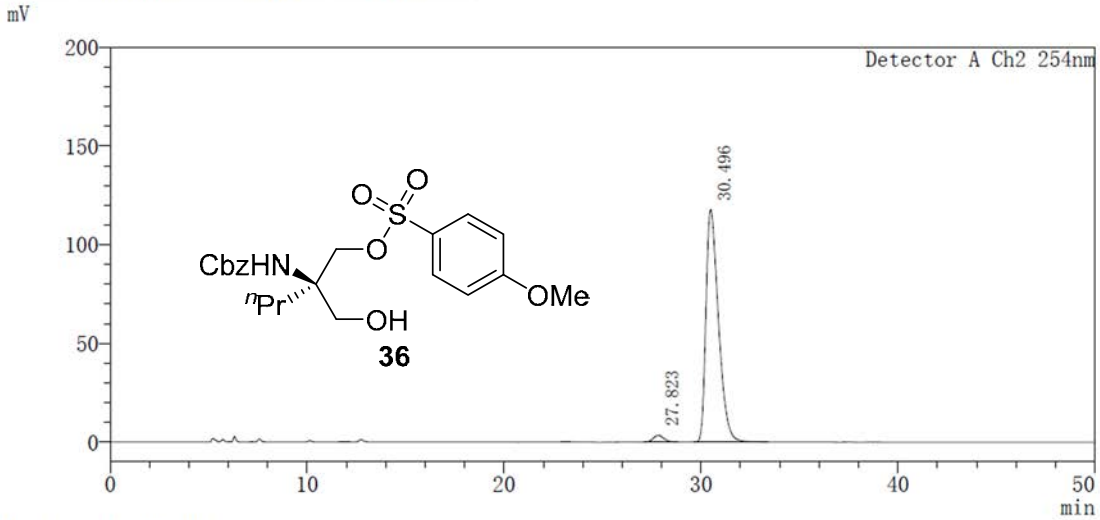
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	31.027	93811	2.789
2	35.375	3269394	97.211



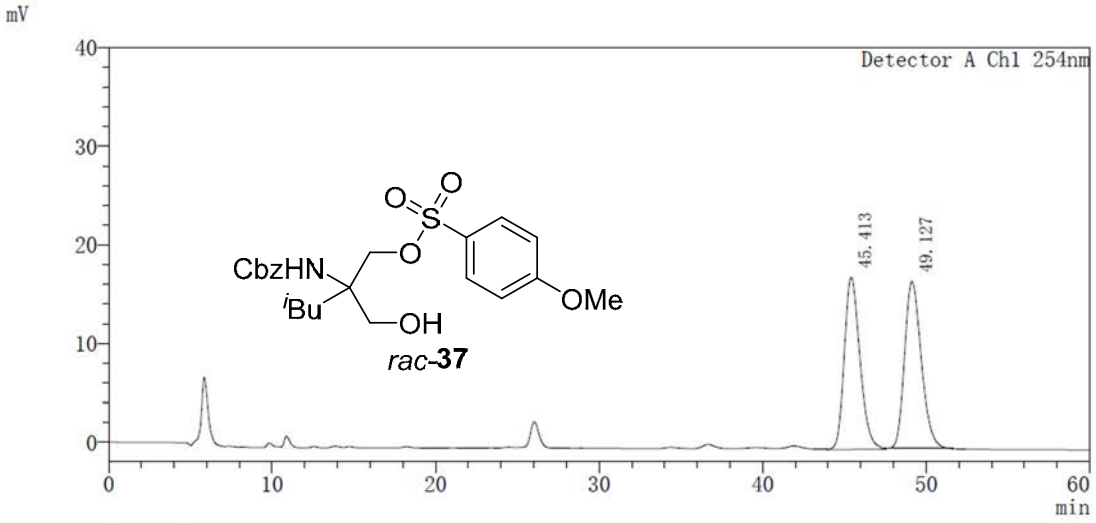
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	27.716	543738	48.918
2	30.673	567791	51.082



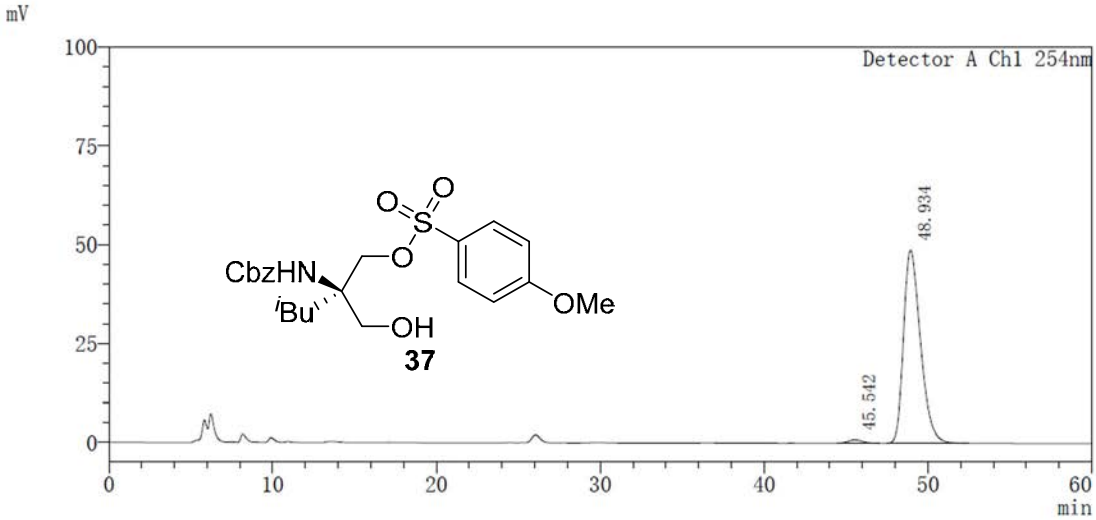
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	27.823	126589	2.372
2	30.496	5209174	97.628



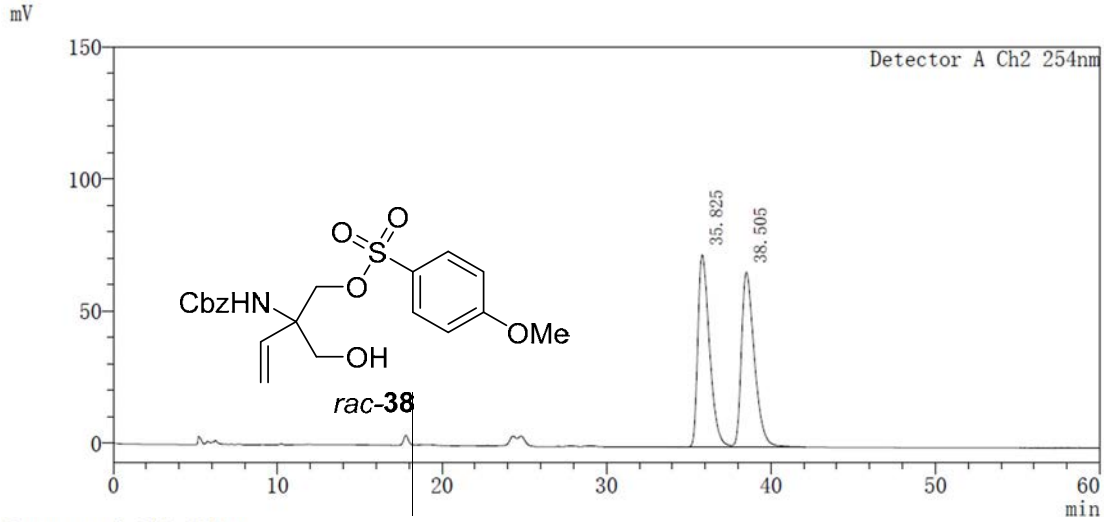
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	45.413	1164442	49.167
2	49.127	1203885	50.833



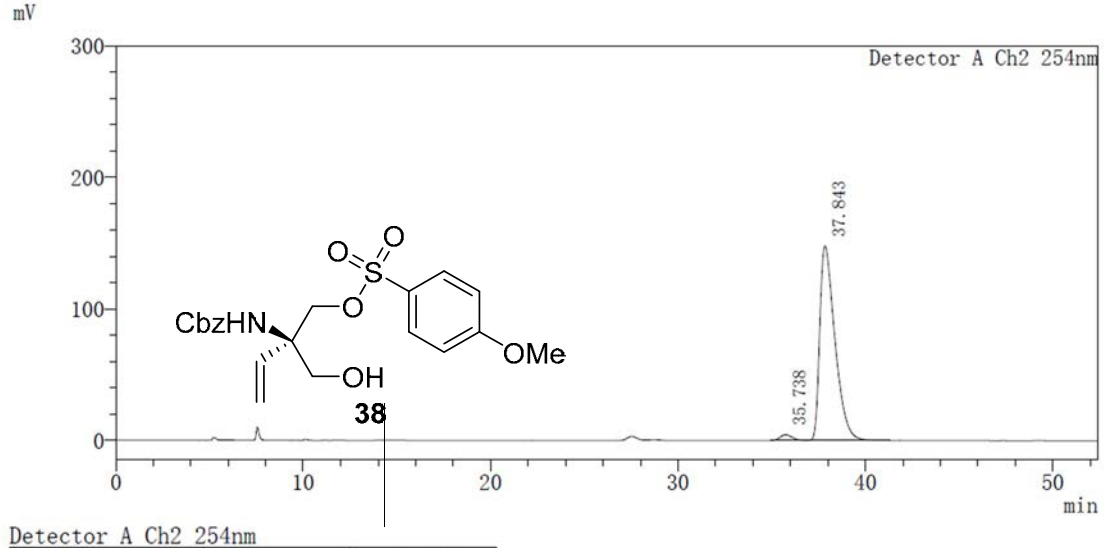
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	45.542	52850	1.478
2	48.934	3522880	98.522



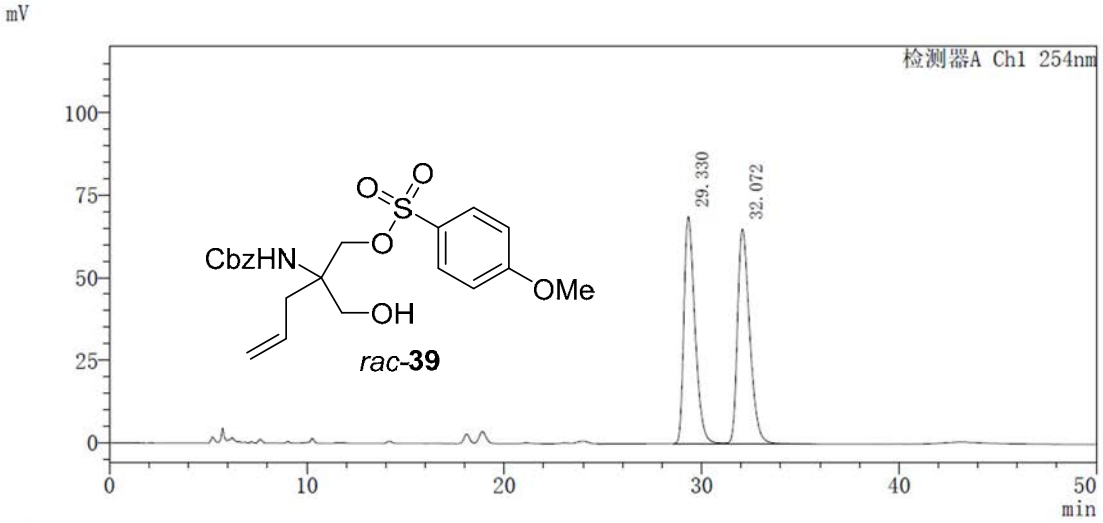
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	35.825	3561601	49.490
2	38.505	3635070	50.510



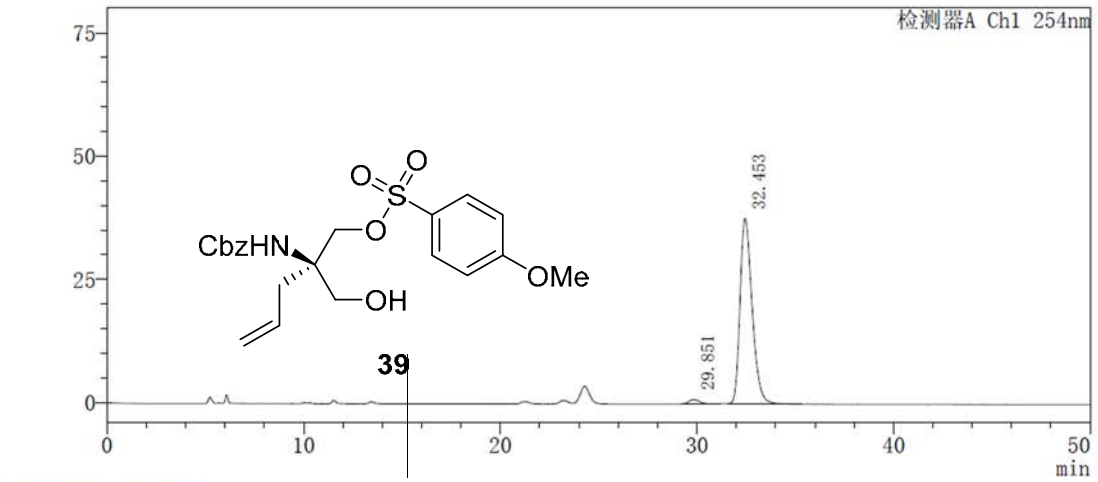
Detector A Ch2 254nm

Peak#	Ret. Time	Area	Area%
1	35.738	203033	2.377
2	37.843	8337897	97.623



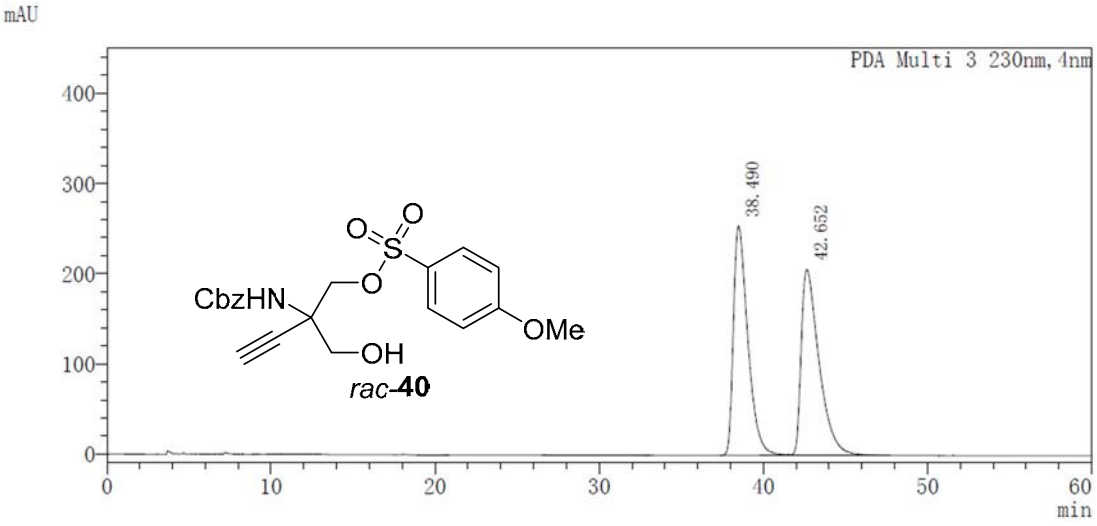
检测器A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.330	2687842	49.065
2	32.072	2790274	50.935



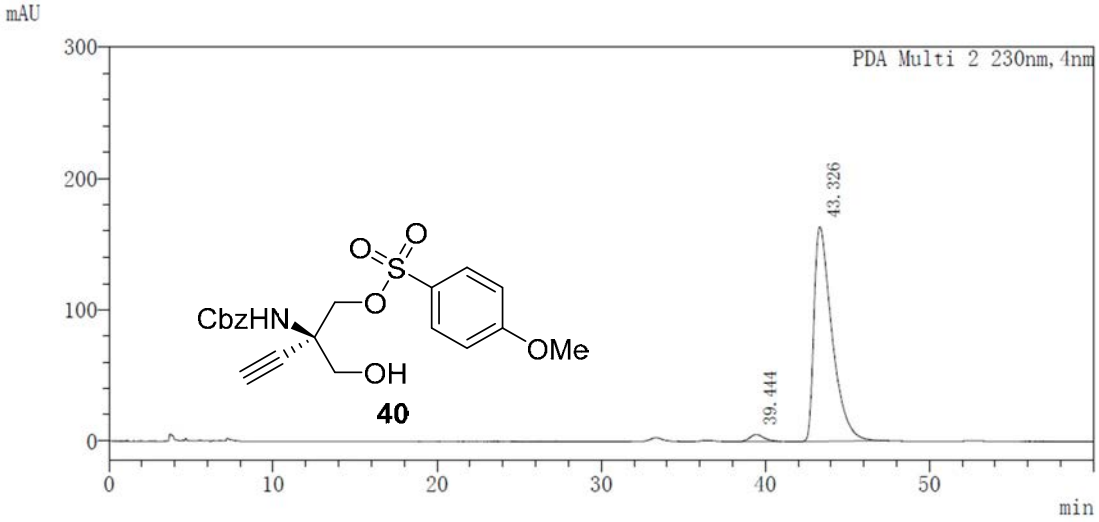
检测器A Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.851	38751	2.336
2	32.453	1619786	97.664



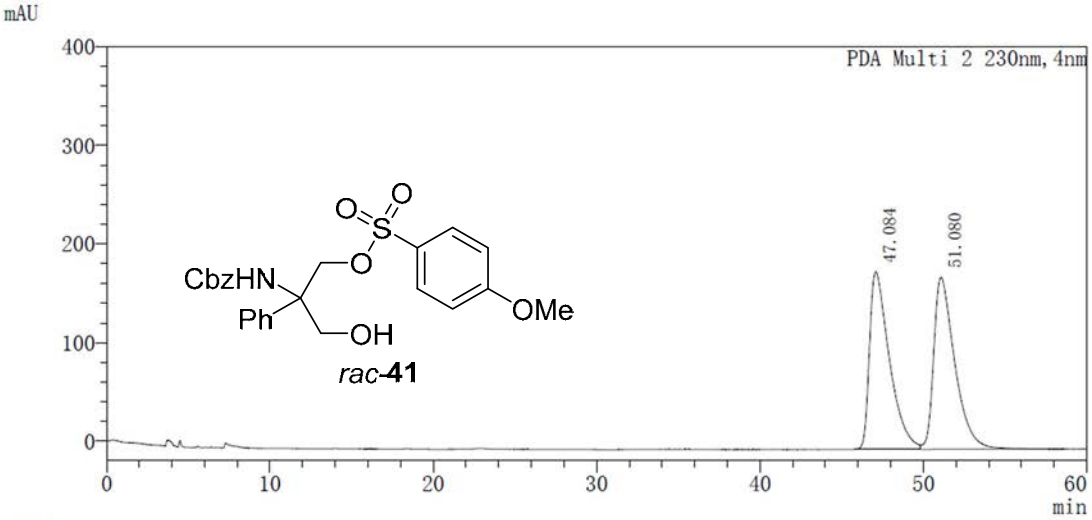
PDA Ch3 230nm

T	Hight	Area	Area%
38.490	254394	15535634	49.951
42.652	206255	15566355	50.049



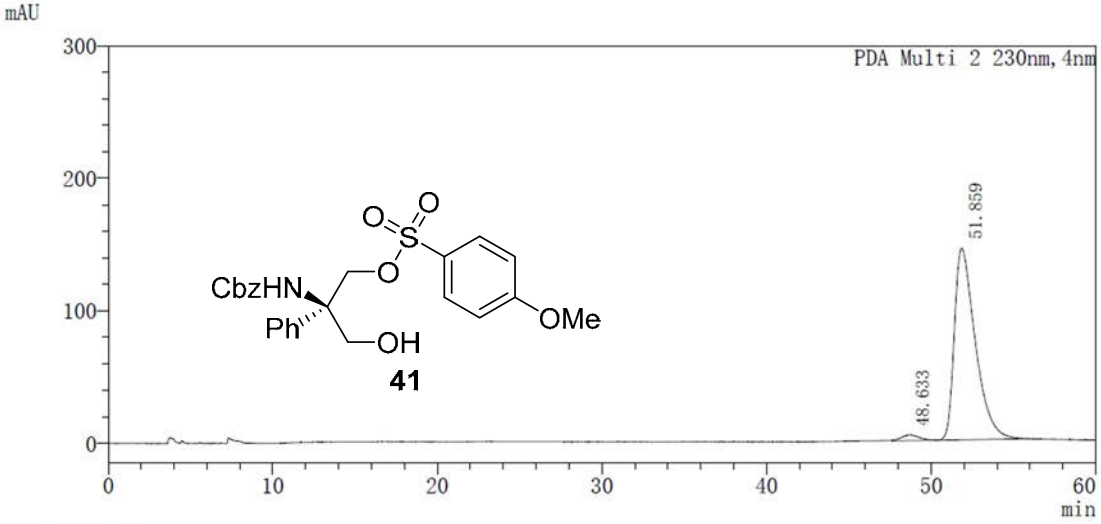
PDA Ch2 230nm

T	Hight	Area	Area%
39.444	5180	307519	2.420
43.326	163374	12400571	97.580



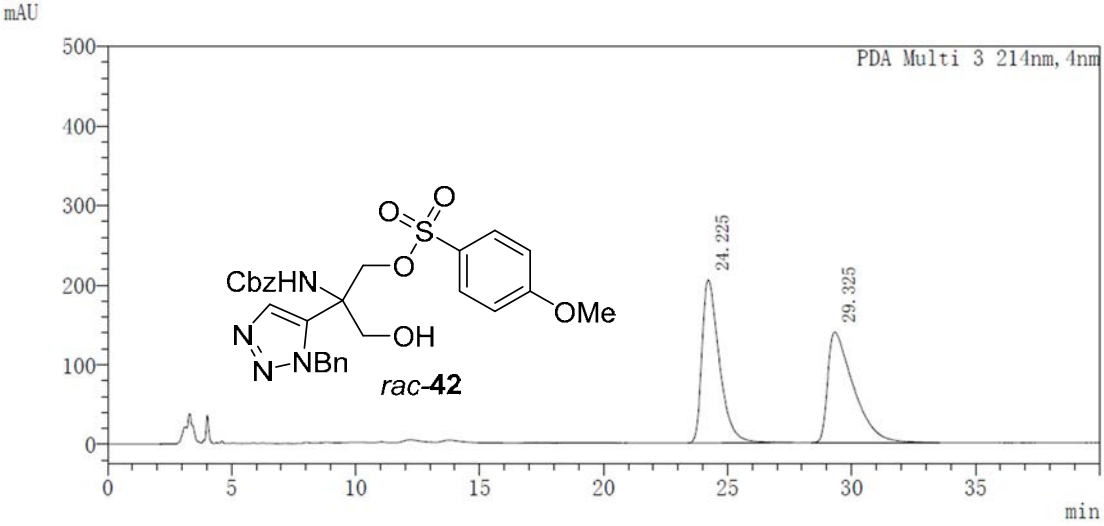
PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	47.084	15275420	49.355
2	51.080	15674870	50.645



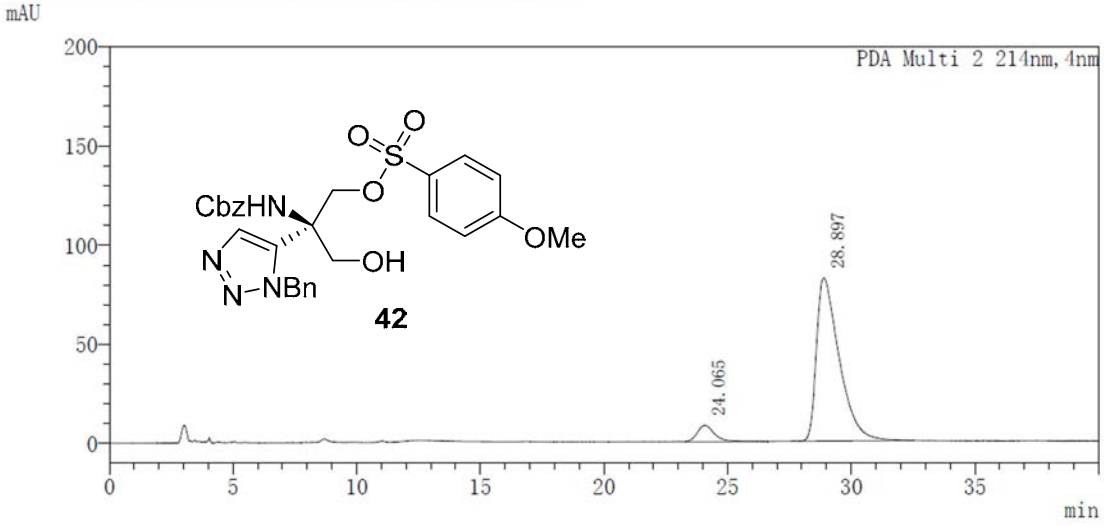
PDA Ch2 230nm

Peak#	Ret. Time	Area	Area%
1	48.633	316202	2.409
2	51.859	12811977	97.591



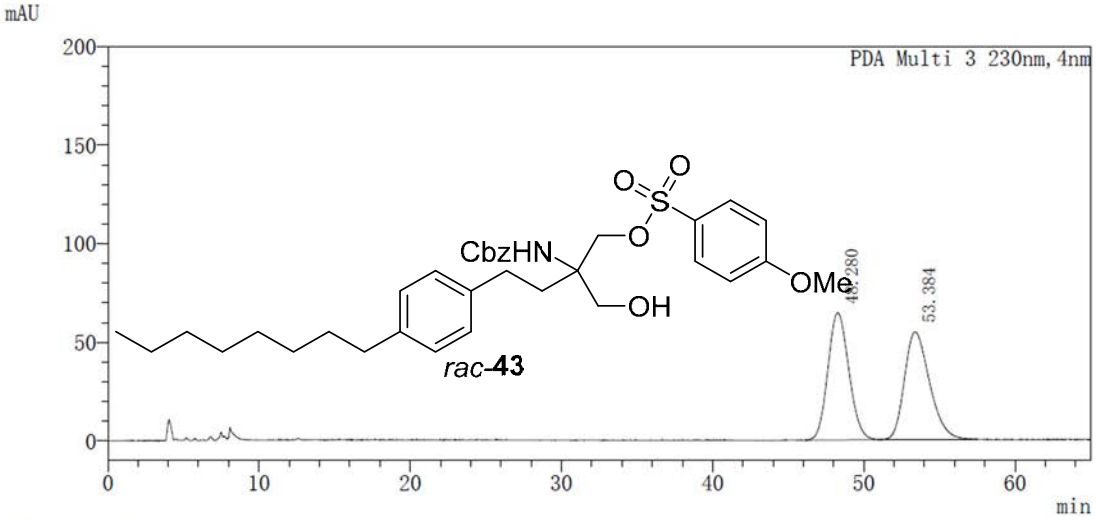
PDA Ch3 214nm

T	Hight	Area	Area%
24.225	204902	10007288	50.022
29.325	138923	9998410	49.978



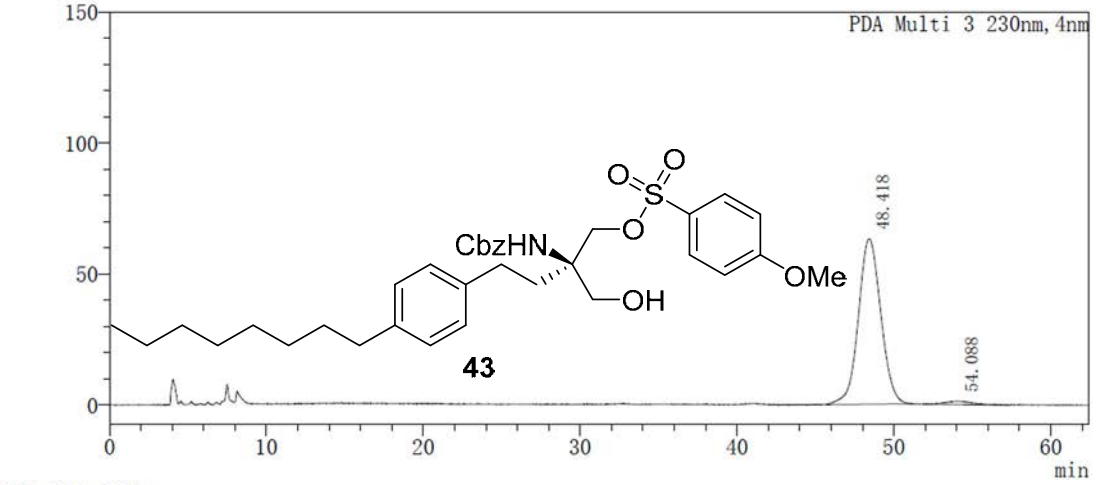
PDA Ch2 214nm

T	Hight	Area	Area%
24.065	8291	392913	6.947
28.897	82324	5262570	93.053



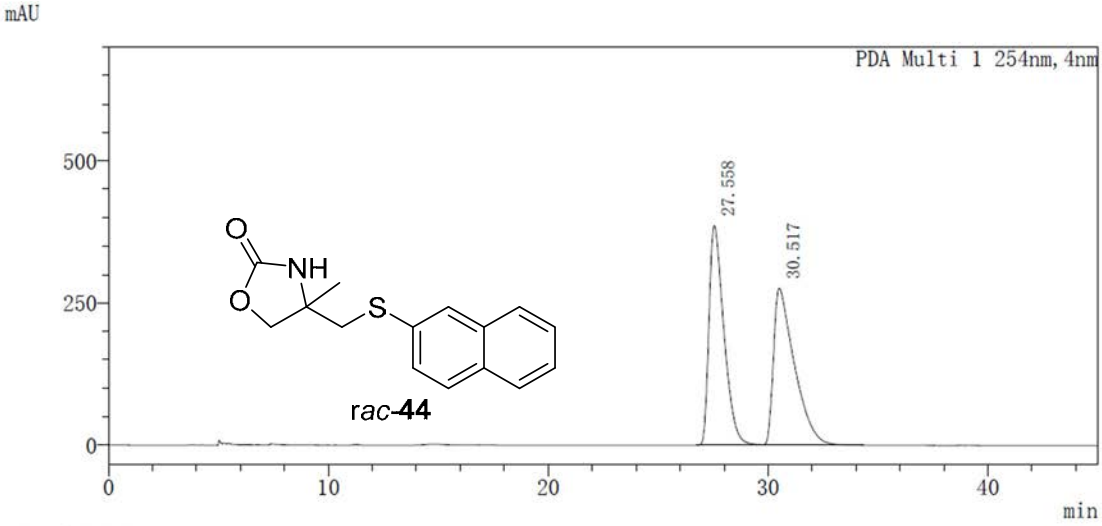
PDA Ch3 230nm

Peak#	Ret. Time	Area	Area%
1	48.280	6243254	49.688
2	53.384	6321764	50.312



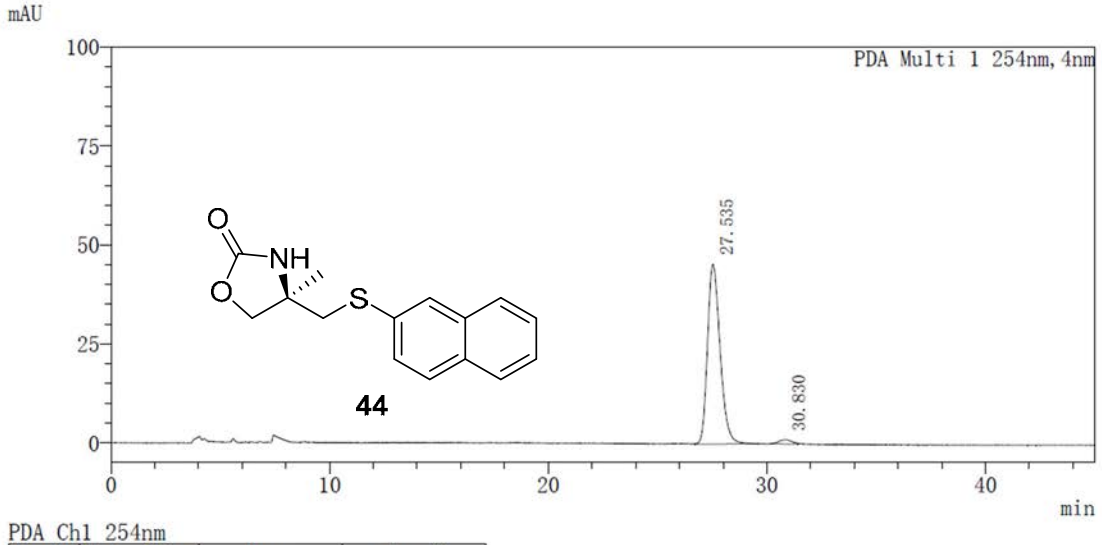
PDA Ch3 230nm

Peak#	Ret. Time	Area	Area%
1	48.418	6293819	97.605
2	54.088	154437	2.395



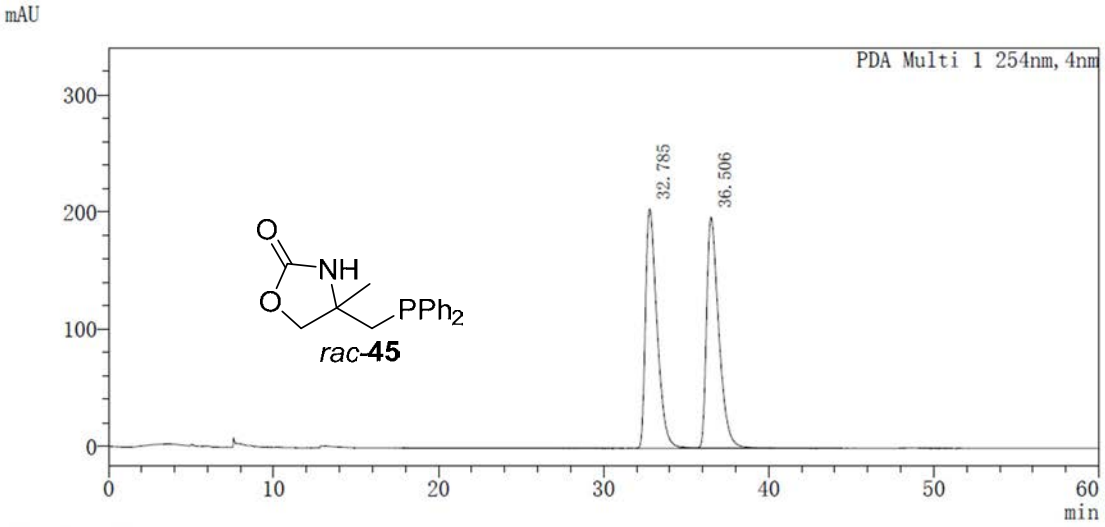
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.558	18195120	49.866
2	30.517	18293159	50.134



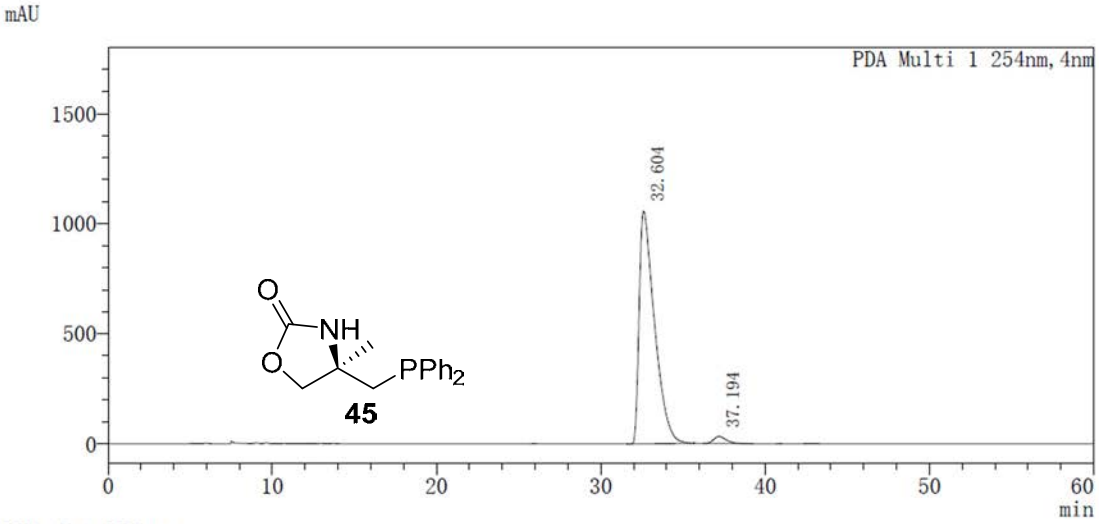
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.535	1818170	97.544
2	30.830	45769	2.456



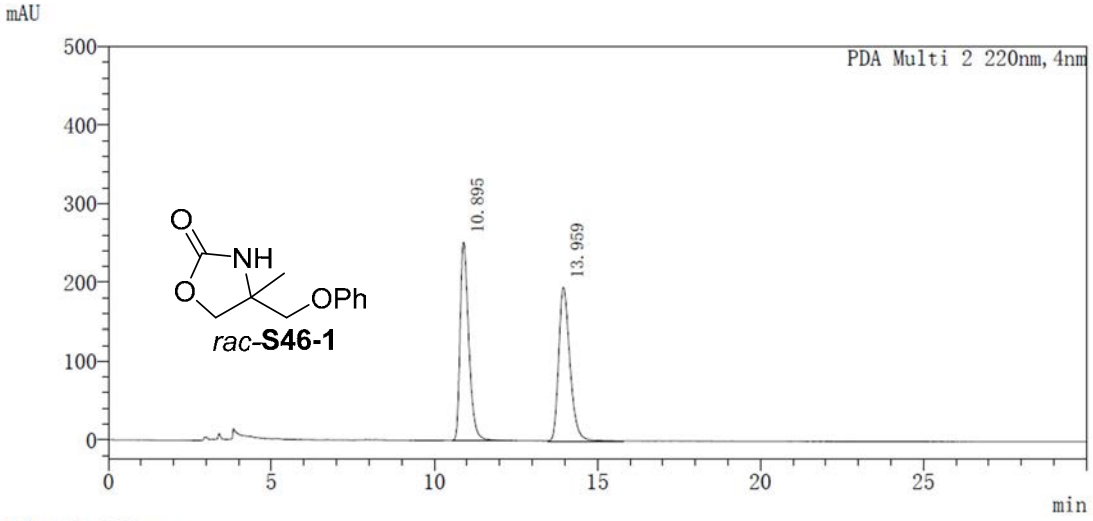
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	32.785	9918386	49.477
2	36.506	10127922	50.523



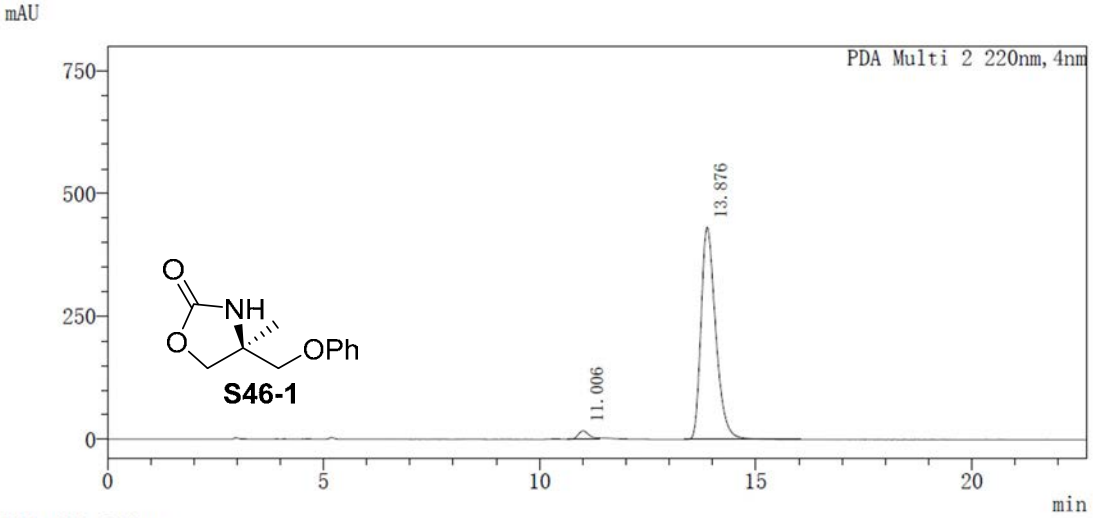
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	32.604	68505060	97.605
2	37.194	1681033	2.395



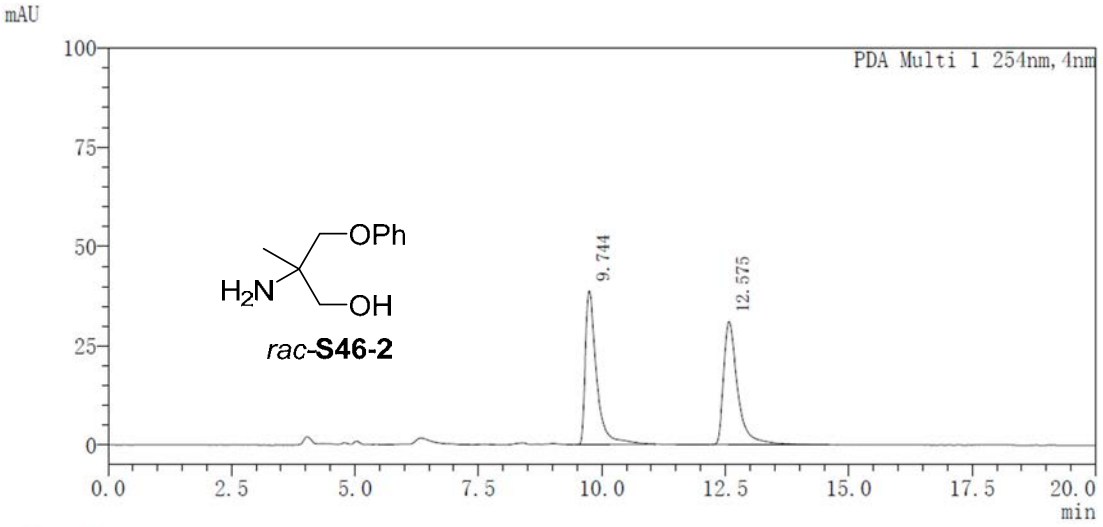
PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	10.895	4642491	49.778
2	13.959	4683967	50.222



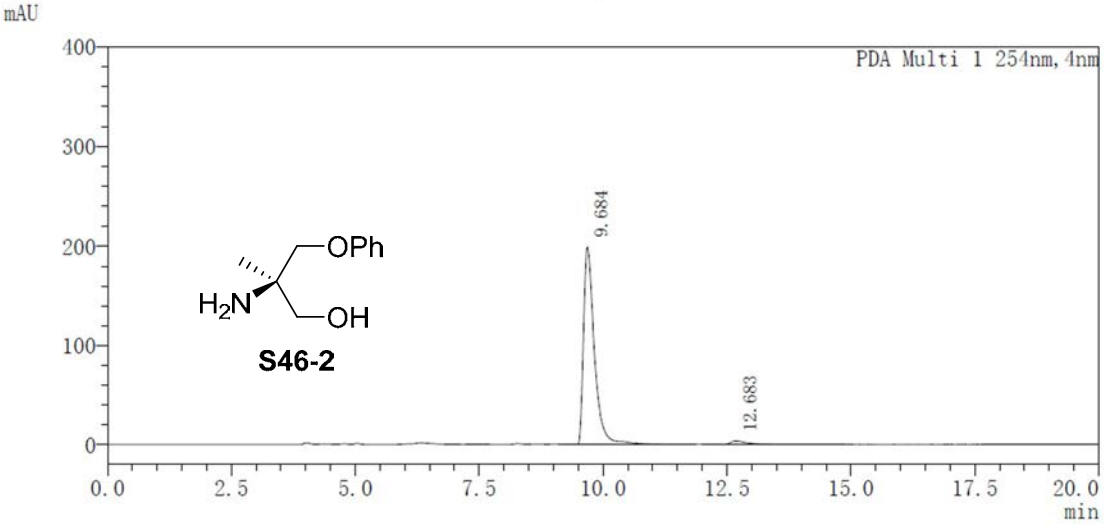
PDA Ch2 220nm

Peak#	Ret. Time	Area	Area%
1	11.006	311125	2.954
2	13.876	10221706	97.046



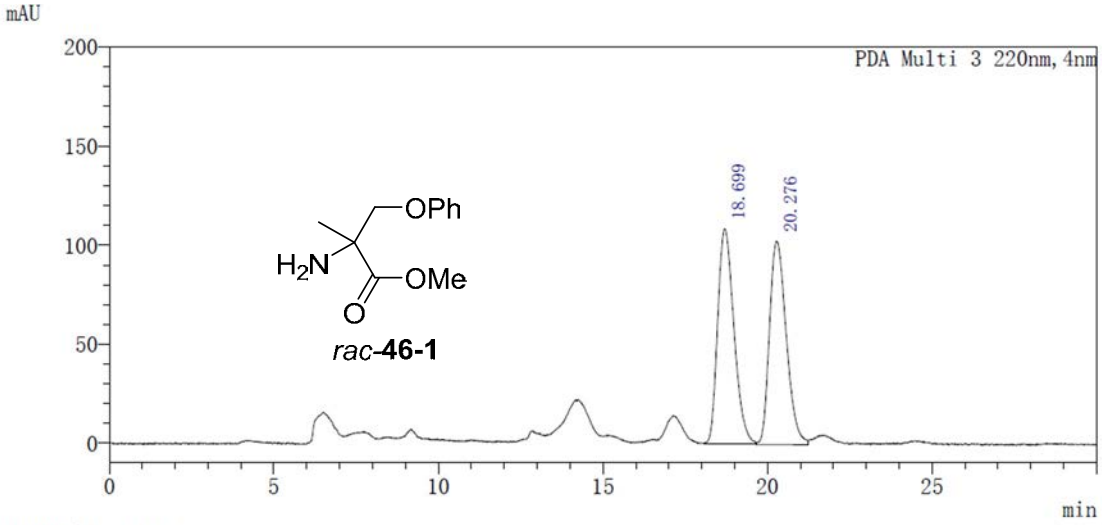
PDA Ch1 254nm

T	Hight	Area	Area%
9.744	38777	615862	50.091
12.575	31033	613628	49.909



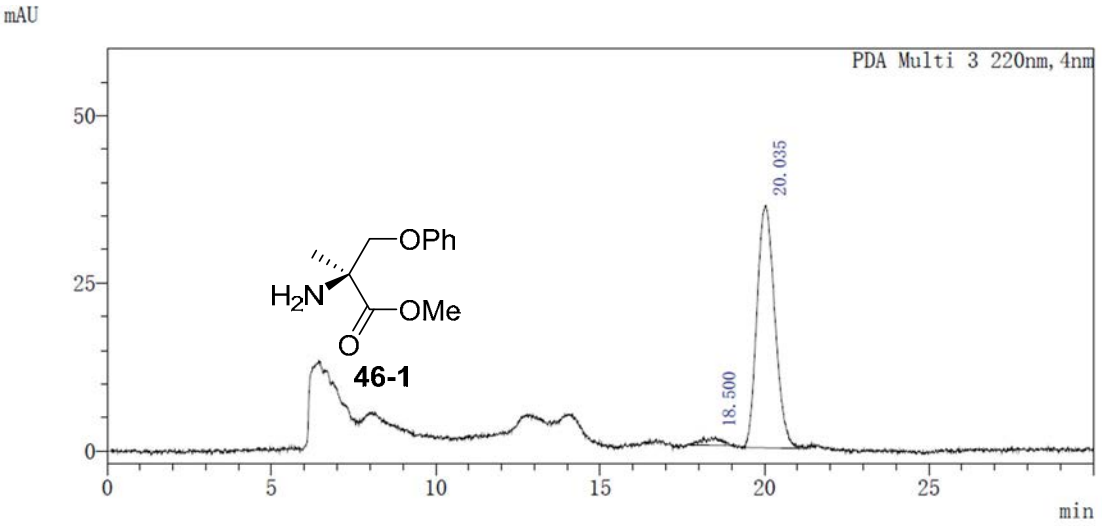
PDA Ch1 254nm

T	Hight	Area	Area%
9.684	198870	3031553	97.493
12.683	3519	77949	2.507



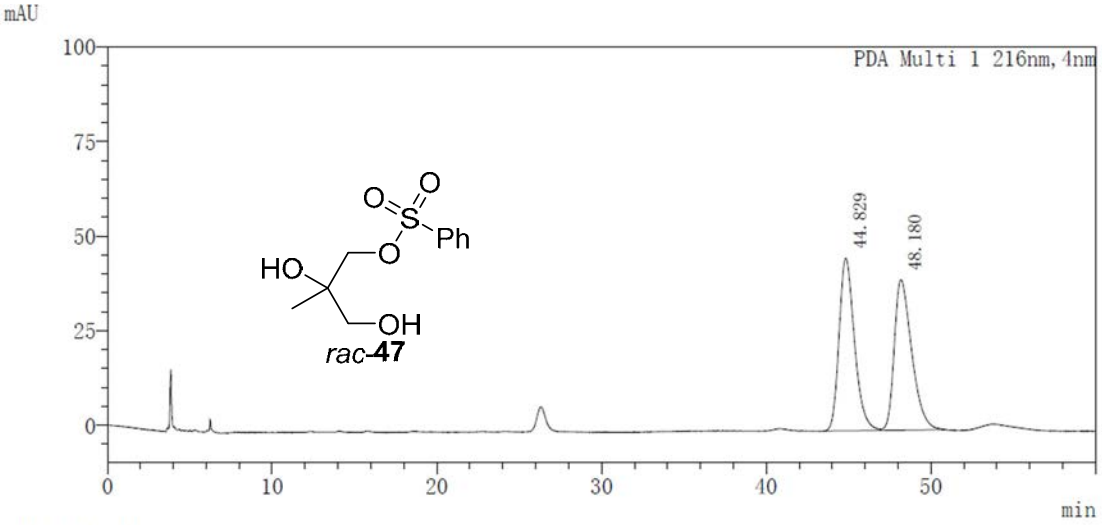
PDA Ch3 220nm

T	Hight	Area	Area%
18.699	108309	3705920	50.421
20.276	102720	3644095	49.579



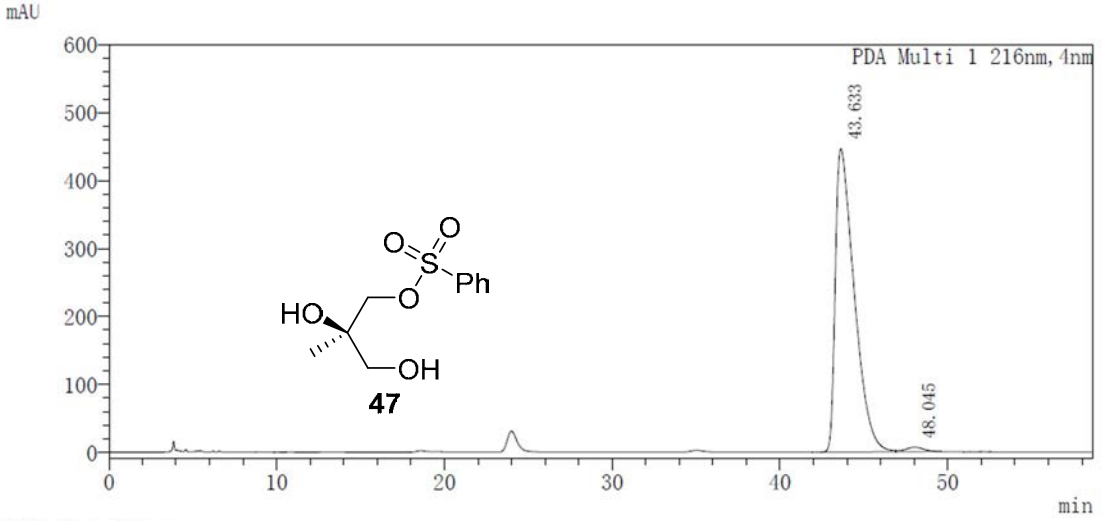
PDA Ch3 220nm

T	Hight	Area	Area%
18.500	1280	44099	3.121
20.035	36139	1368896	96.879



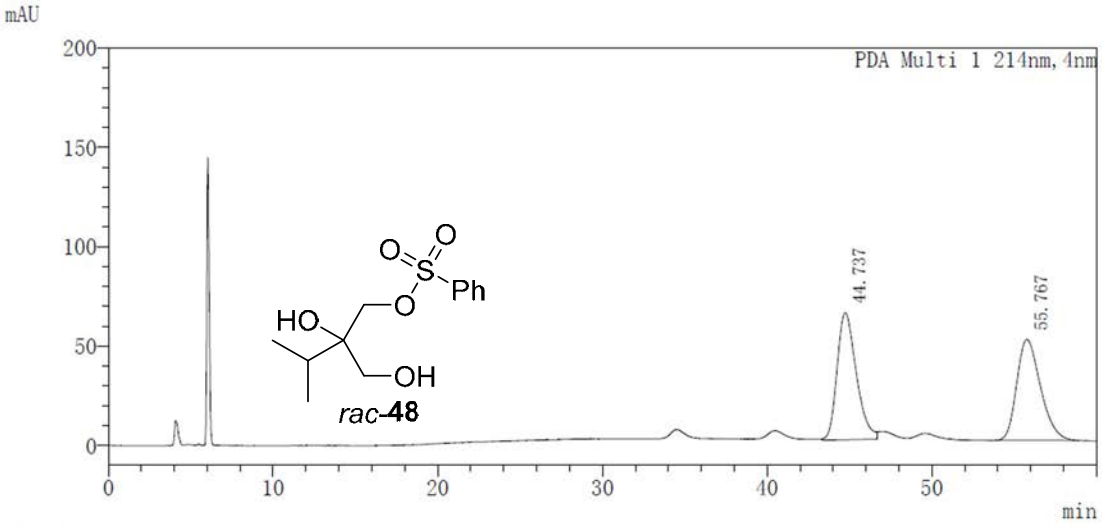
PDA Ch1 216nm

T	Hight	Area	Area%
44.829	45687	2970689	50.336
48.180	39799	2931023	49.664



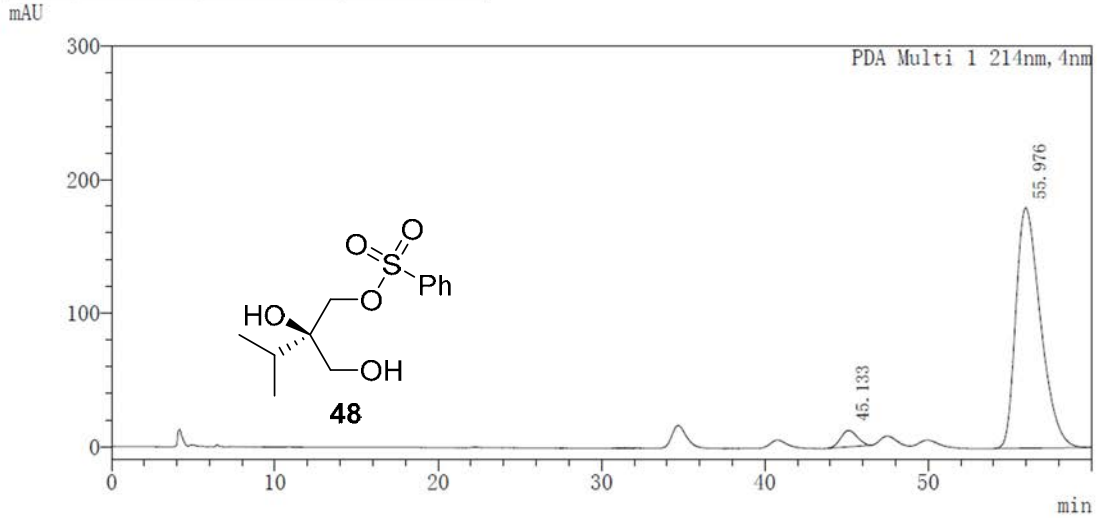
PDA Ch1 216nm

T	Hight	Area	Area%
43.633	446816	35084052	98.563
48.045	6508	511615	1.437



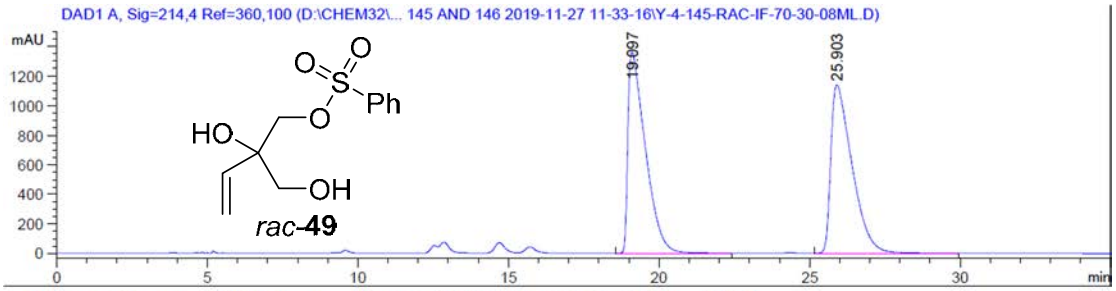
PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	44.737	5170923	50.422
2	55.767	5084411	49.578



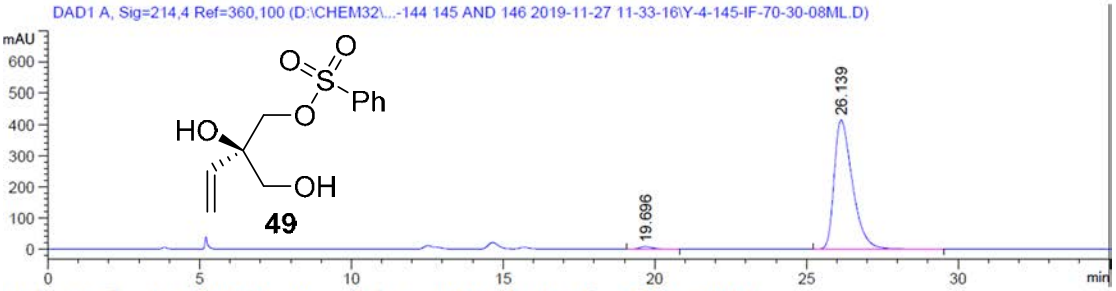
PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	45.133	862927	4.354
2	55.976	18957529	95.646



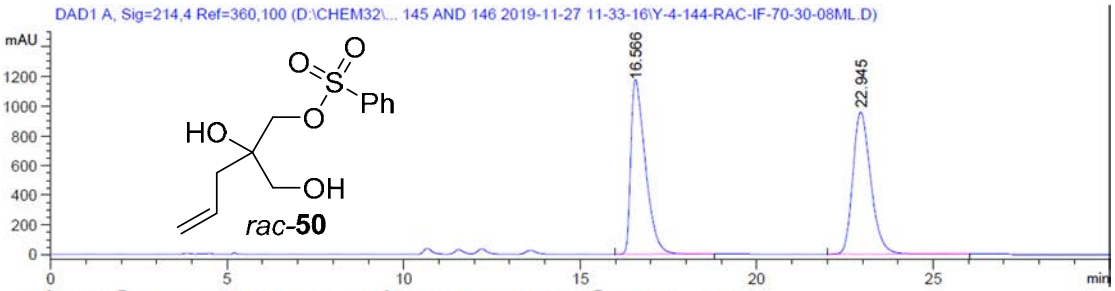
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.097	BB	0.5927	5.49300e4	1361.50183	49.6119
2	25.903	BB	0.7202	5.57893e4	1137.53833	50.3881
Totals :				1.10719e5	2499.04016	



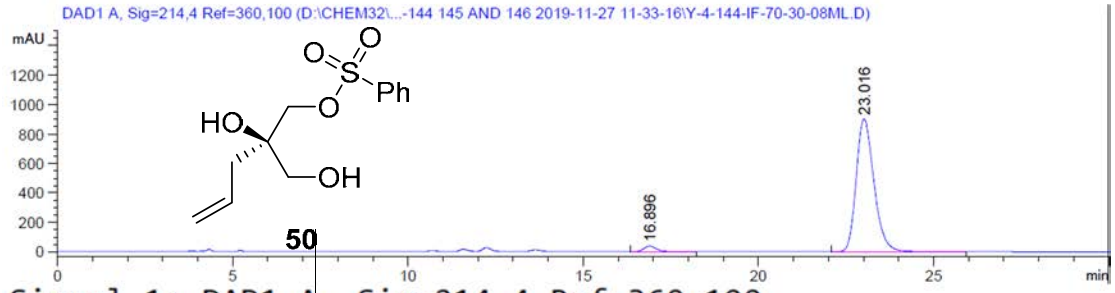
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.696	BB	0.4271	223.91586	7.44110	1.2765
2	26.139	BB	0.6353	1.73174e4	414.63785	98.7235
Totals :				1.75413e4	422.07895	



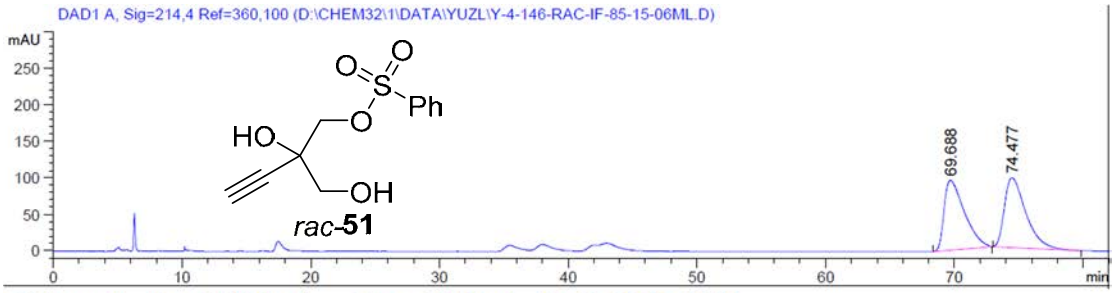
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.566	BB	0.4341	3.36574e4	1175.45862	49.7711
2	22.945	BB	0.5477	3.39670e4	957.85992	50.2289
Totals :				6.76245e4	2133.31854	



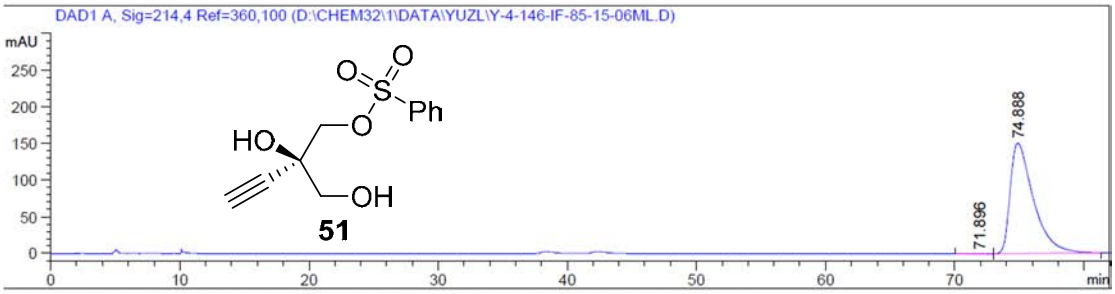
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.896	BB	0.3851	994.24774	39.03794	3.0223
2	23.016	BB	0.5443	3.19023e4	902.72003	96.9777
Totals :				3.28966e4	941.75797	



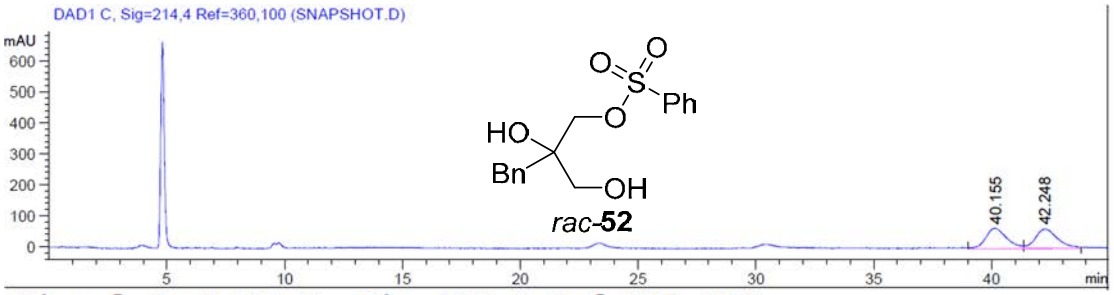
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	69.688	BB	1.4905	1.04227e4	95.26035	48.6567
2	74.477	BB	1.5120	1.09982e4	95.32996	51.3433
Totals :				2.14210e4	190.59031	



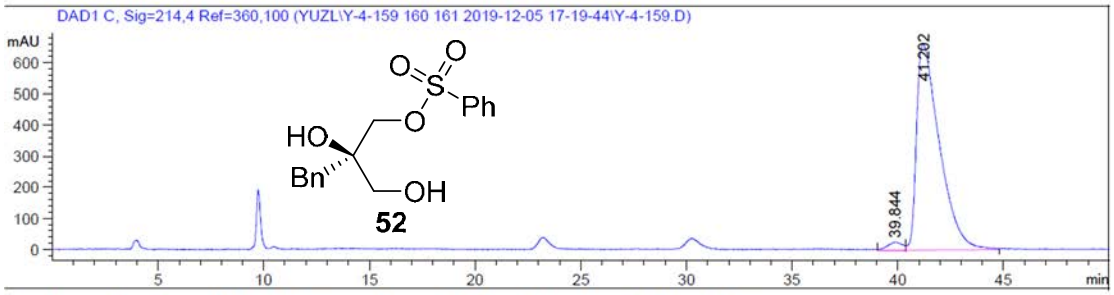
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	71.896	MM R	1.6864	36.91464	3.64819e-1	0.1953
2	74.888	BB R	1.7048	1.88659e4	150.87593	99.8047
Totals :				1.89028e4	151.24075	



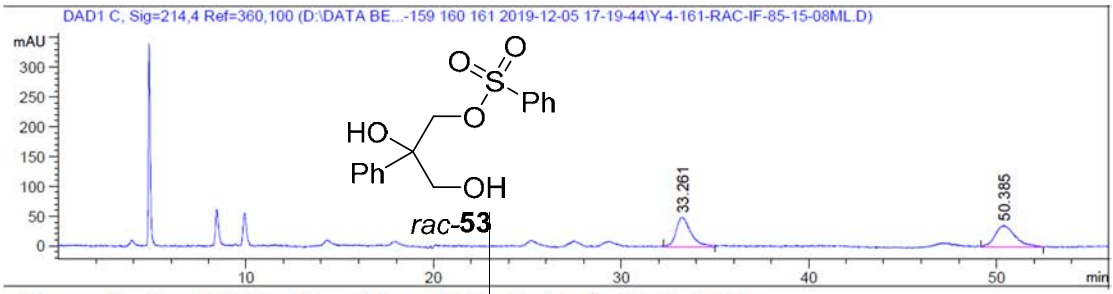
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.155	MF R	1.0439	4132.74365	65.98158	50.2760
2	42.248	FM R	1.0789	4087.36255	63.13996	49.7240
Totals :				8220.10620	129.12153	



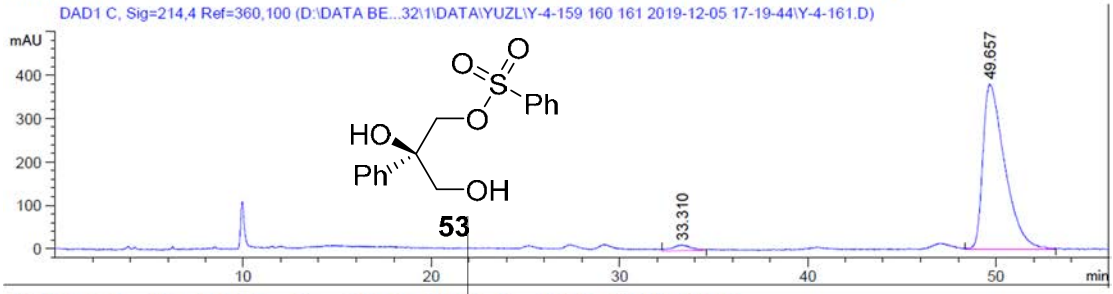
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.844	MF R	0.8243	1289.43713	26.07094	2.5085
2	41.202	FM R	1.2568	5.01140e4	664.55450	97.4915
Totals :				5.14034e4	690.62545	



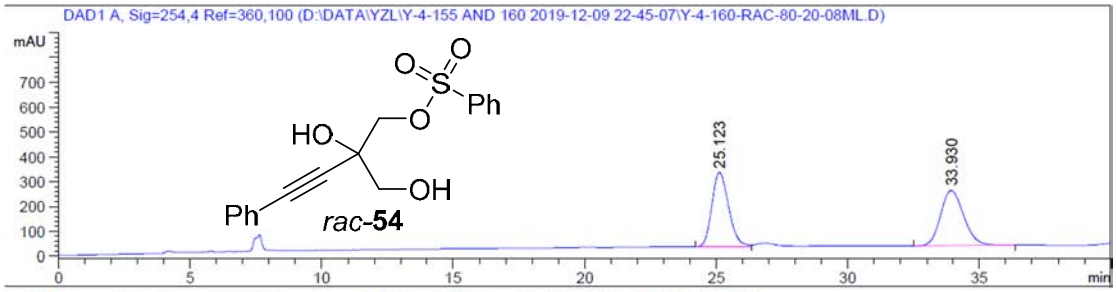
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.261	MM R	0.9470	2851.12207	50.17986	50.7037
2	50.385	MM R	1.2603	2771.98584	36.65672	49.2963
Totals :				5623.10791	86.83659	



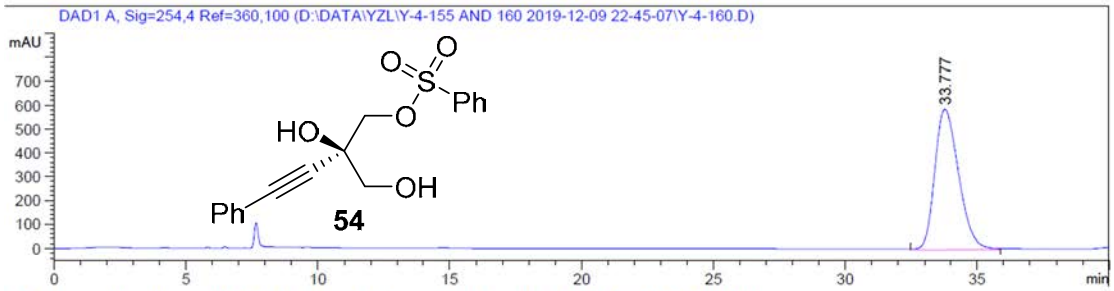
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.310	MM R	1.1787	903.11511	12.76951	2.8688
2	49.657	MM R	1.3411	3.05780e4	380.00366	97.1312
Totals :				3.14811e4	392.77317	



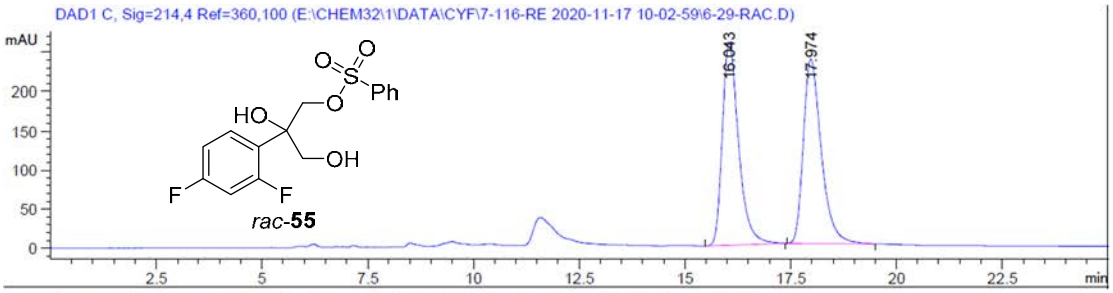
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.123	MM R	0.7431	1.34045e4	300.64035	49.7959
2	33.930	BB	0.9485	1.35144e4	222.52800	50.2041
Totals :				2.69190e4	523.16835	



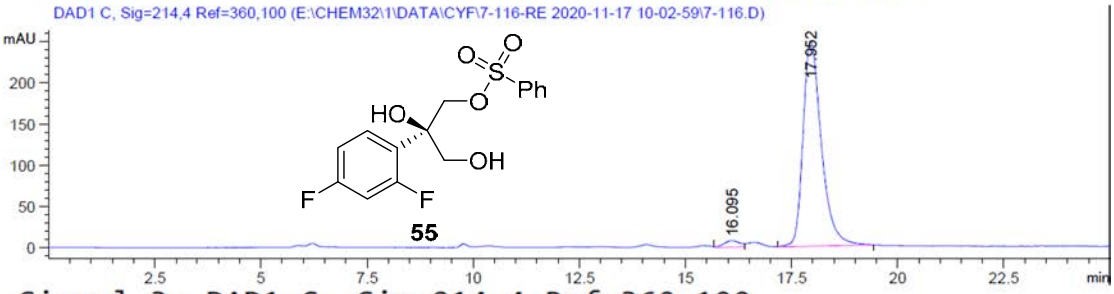
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.777	MM R	1.0497	3.71312e4	589.54926	100.0000
Totals :				3.71312e4	589.54926	



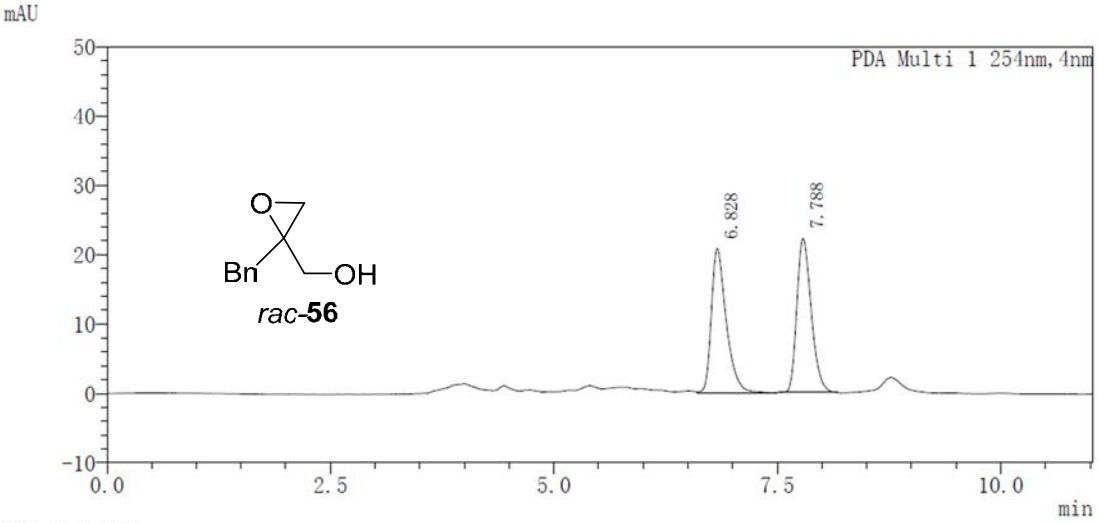
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.043	BB	0.4042	6933.35449	259.12103	49.8665
2	17.974	BB	0.4415	6970.48145	235.35799	50.1335
Totals :				1.39038e4	494.47902	



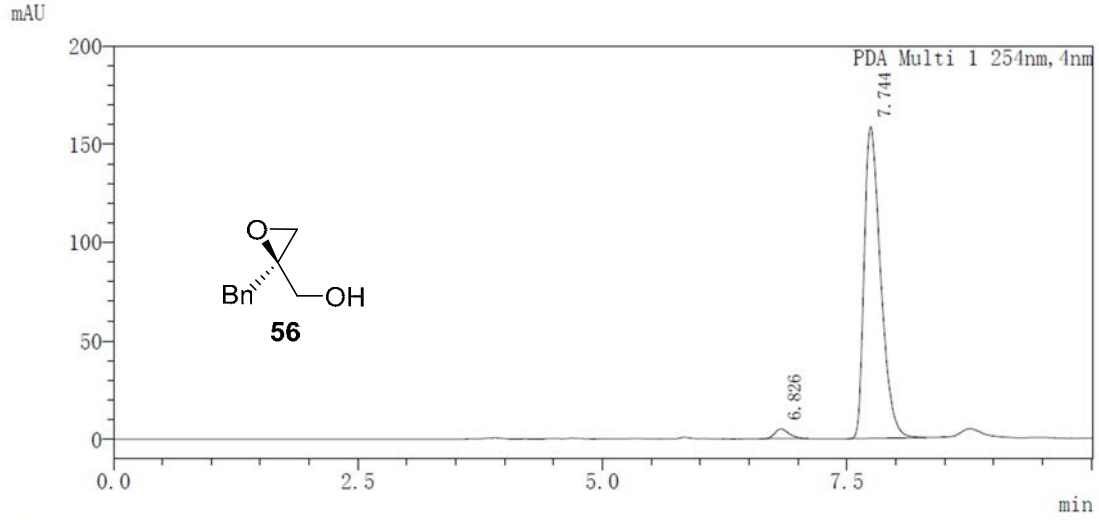
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.095	VV	0.3044	201.24348	8.08368	2.6139
2	17.952	BB	0.4581	7497.80273	249.85152	97.3861
Totals :				7699.04622	257.93520	



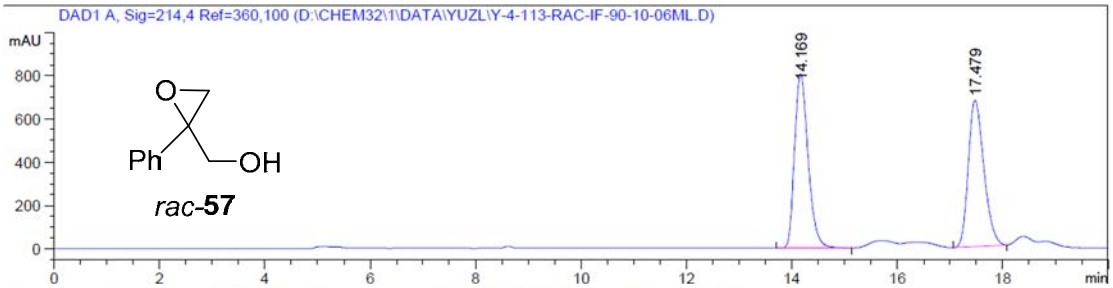
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.828	239232	49.007
2	7.788	248929	50.993



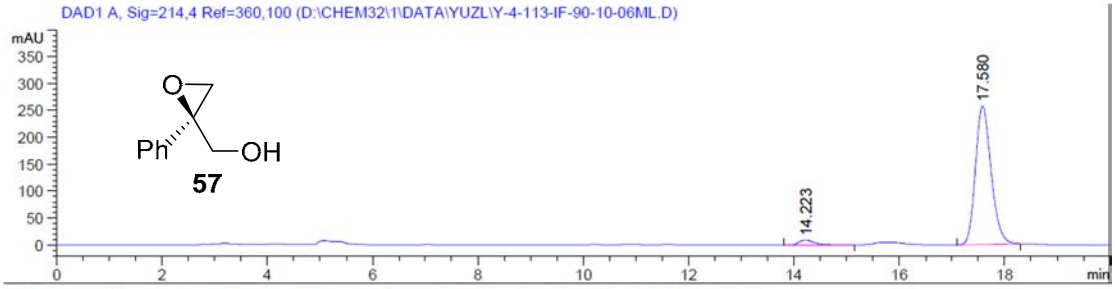
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.826	50295	2.633
2	7.744	1859928	97.367



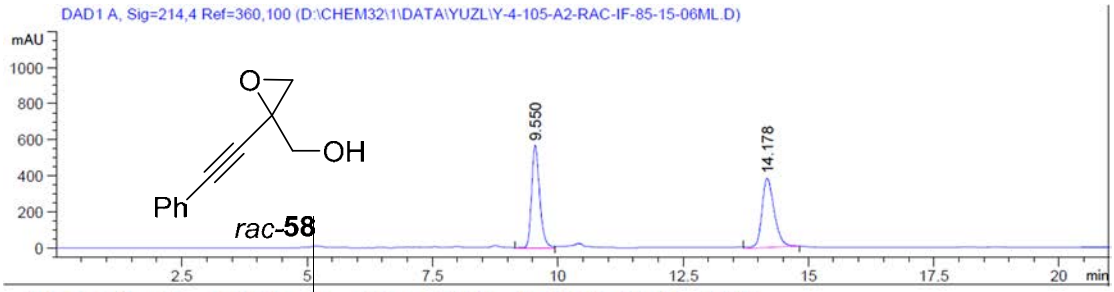
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.169	BB	0.2844	1.43686e4	804.36670	50.8227
2	17.479	BB	0.3178	1.39034e4	676.29822	49.1773
Totals :				2.82719e4	1480.66492	



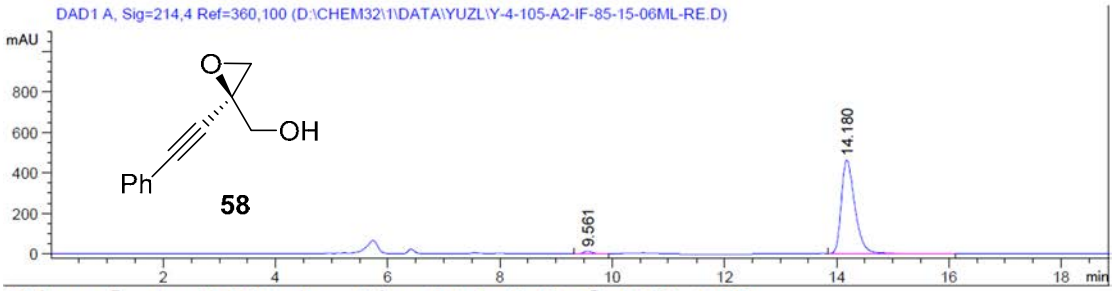
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.223	BB	0.3046	175.96741	9.05875	3.2035
2	17.580	BB	0.3187	5317.02051	257.68738	96.7965
Totals :				5492.98792	266.74612	



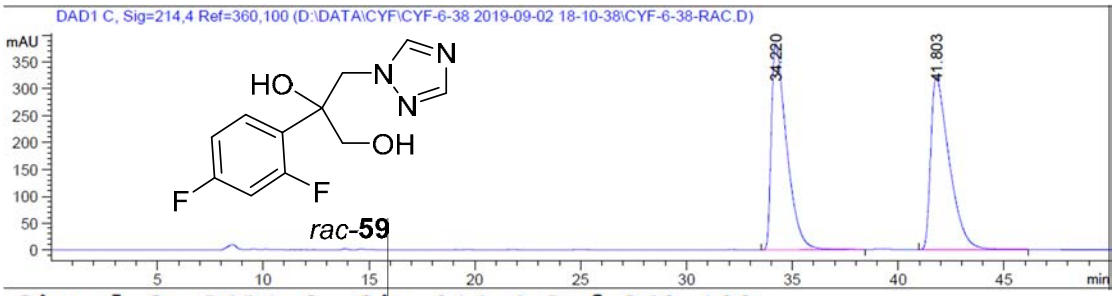
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.550	BV	0.1723	6344.29980	568.22705	49.1477
2	14.178	MM R	0.2850	6564.34619	383.89737	50.8523
Totals :				1.29086e4	952.12442	



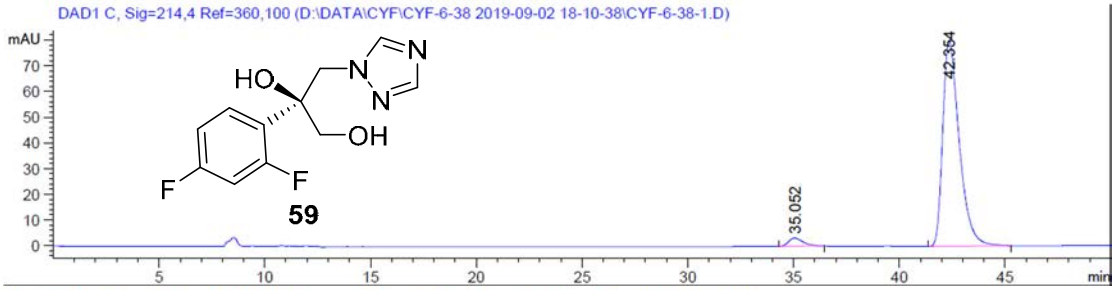
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.561	BB	0.1653	150.32806	13.78107	1.8749
2	14.180	VB	0.2574	7867.64990	465.09219	98.1251
Totals :				8017.97797	478.87326	



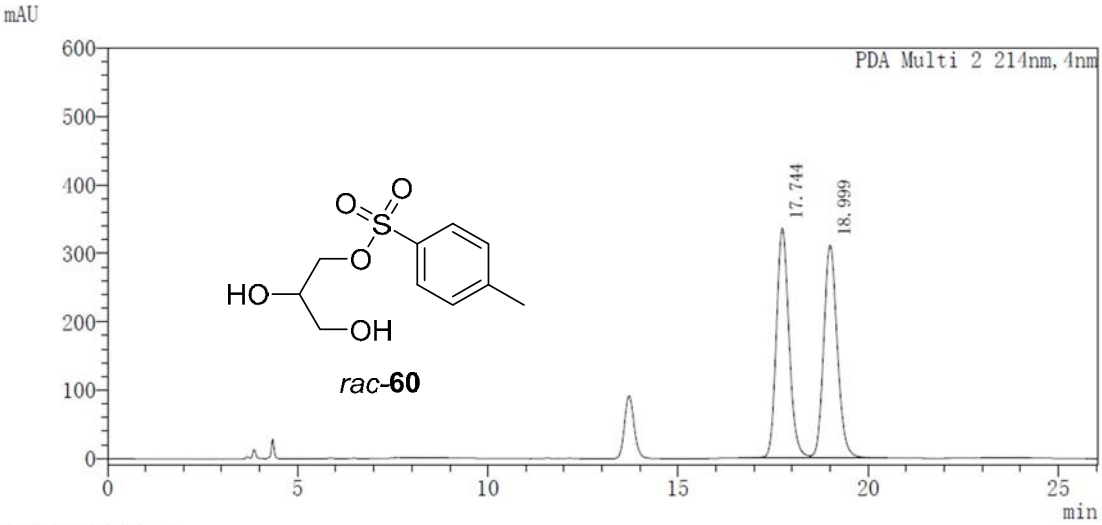
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.220	BB	0.7497	1.93434e4	383.97079	49.8087
2	41.803	BB	0.8924	1.94920e4	321.02356	50.1913
Totals :				3.88354e4	704.99435	



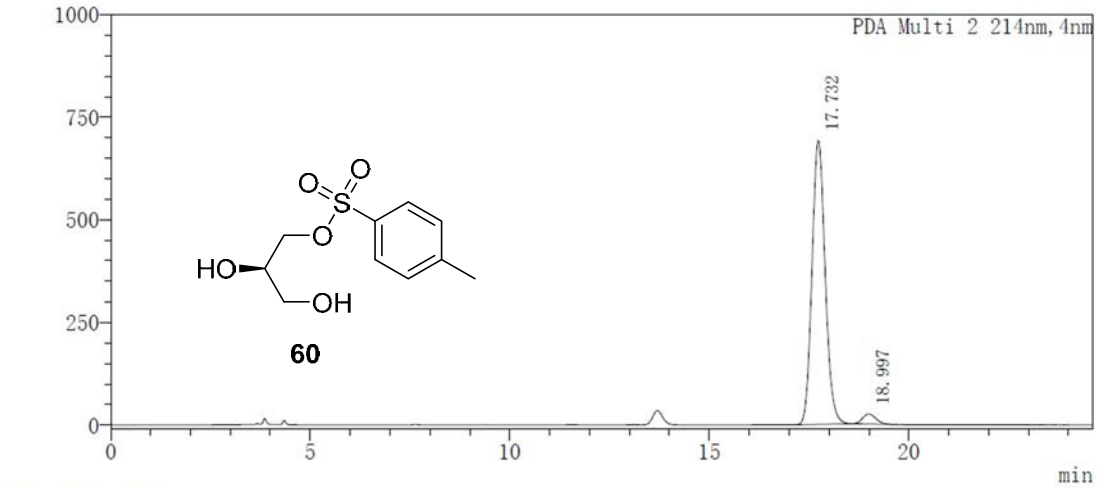
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.052	BB	0.5761	152.75999	3.22813	3.4050
2	42.354	BB	0.8174	4333.64697	79.82232	96.5950
Totals :				4486.40697	83.05045	



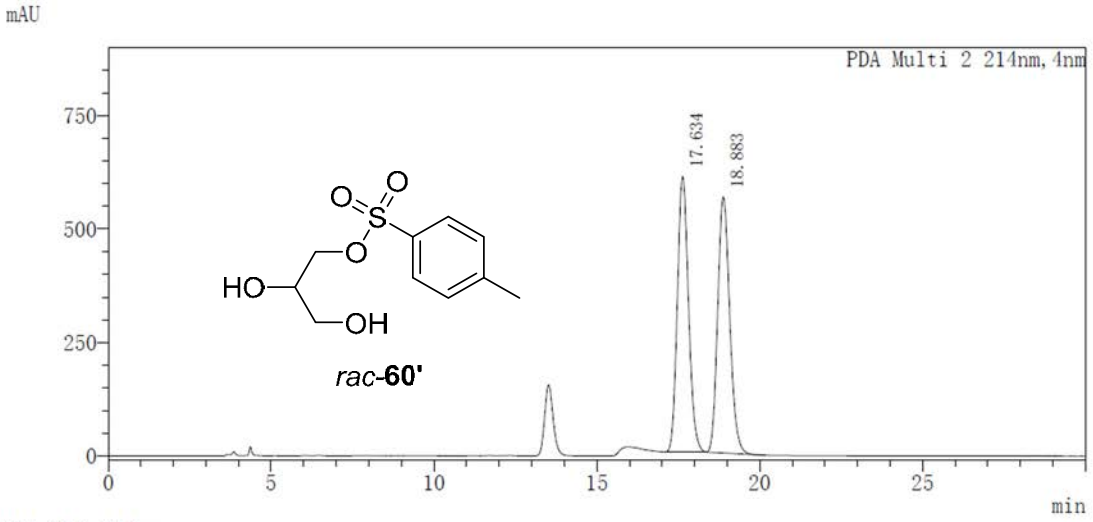
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	17.744	7770885	50.093
2	18.999	7741996	49.907



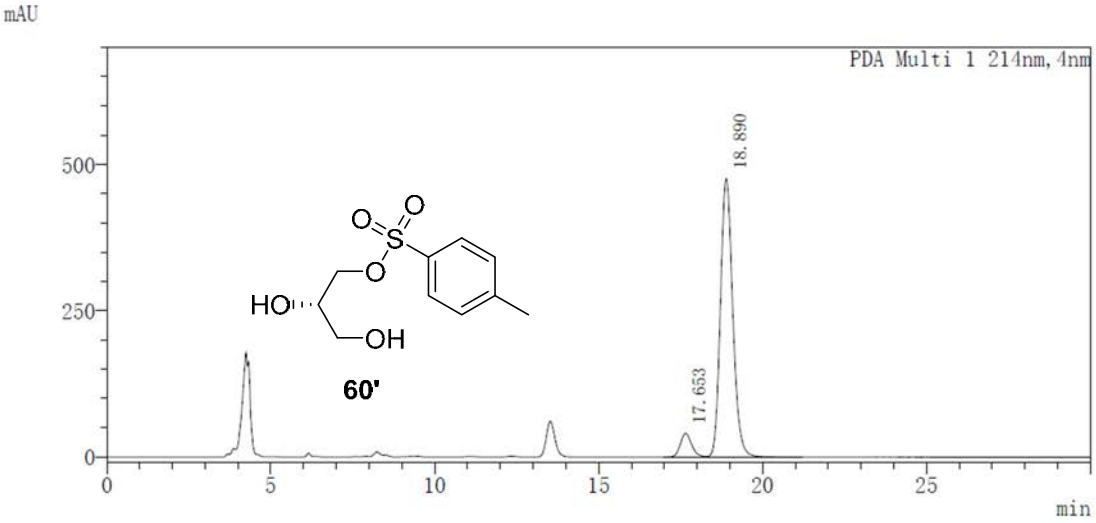
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	17.732	15825448	96.517
2	18.997	571060	3.483



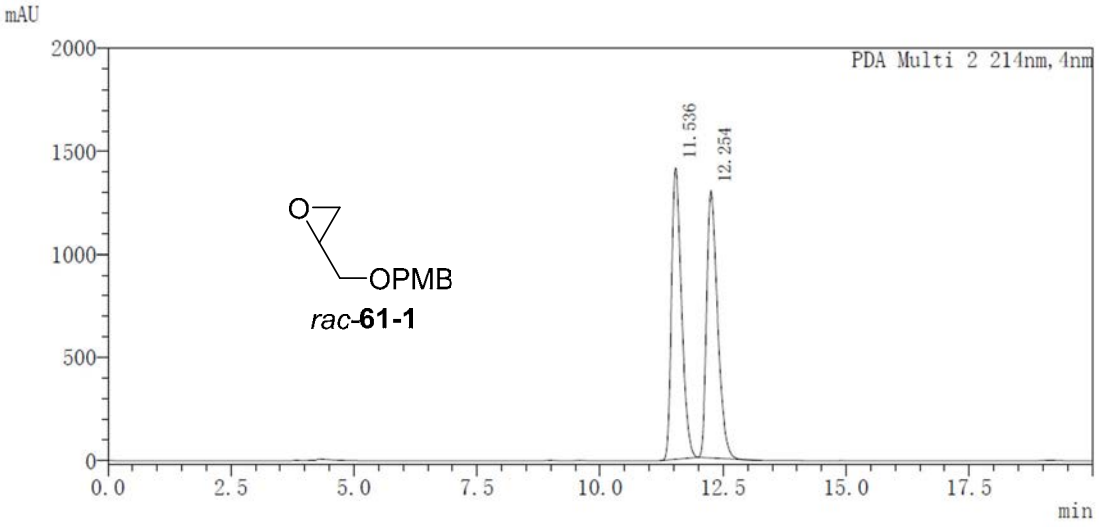
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	17.634	14452992	49.968
2	18.883	14471286	50.032



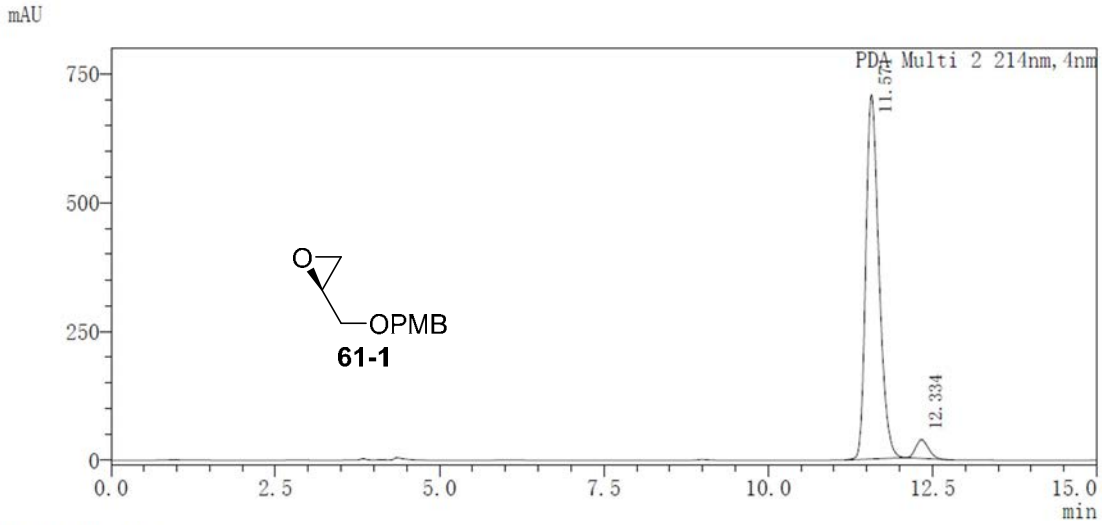
PDA Ch1 214nm

Peak#	Ret. Time	Area	Area%
1	17.653	967526	7.243
2	18.890	12390772	92.757



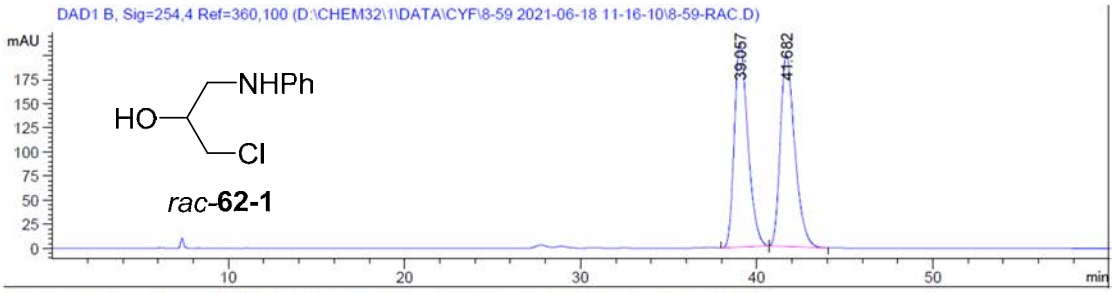
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	11.536	20014504	49.983
2	12.254	20028468	50.017



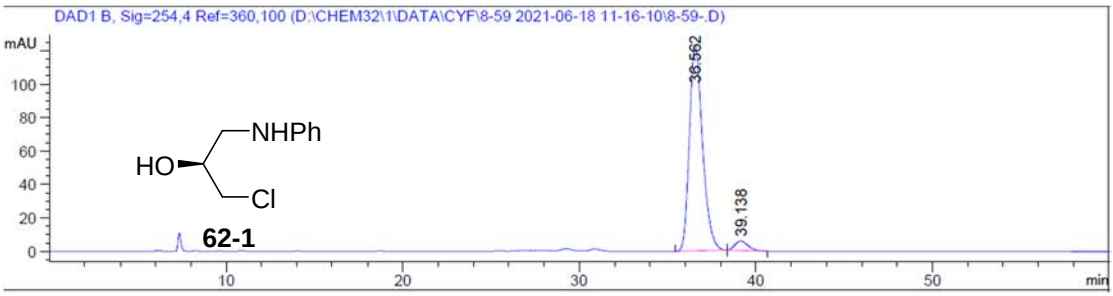
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	11.571	9836666	95.202
2	12.334	495774	4.798



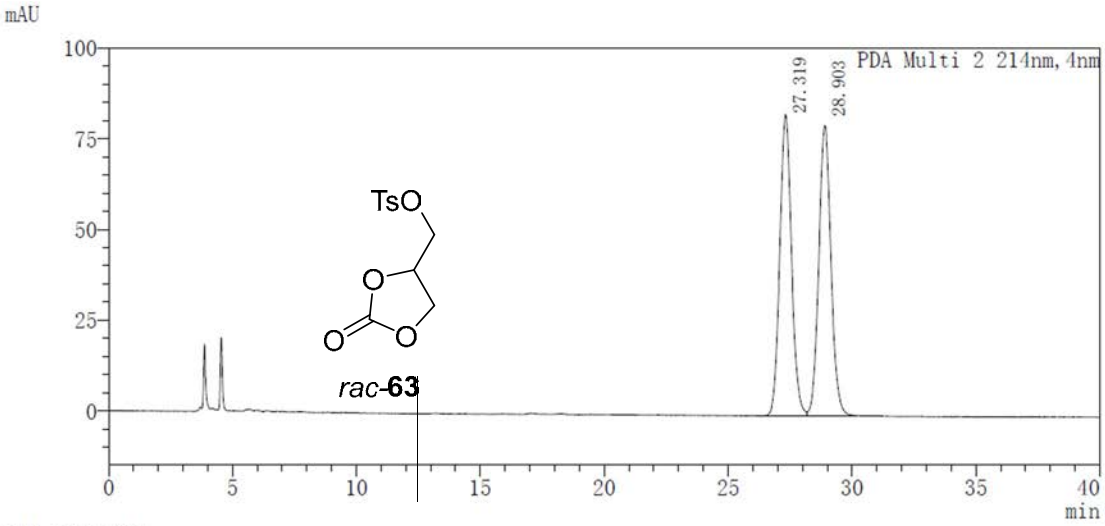
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	39.057	BB	0.8159	1.13314e4	212.56741	49.9013
2	41.682	BB	0.8492	1.13762e4	198.90997	50.0987
Totals :				2.27076e4	411.47739	



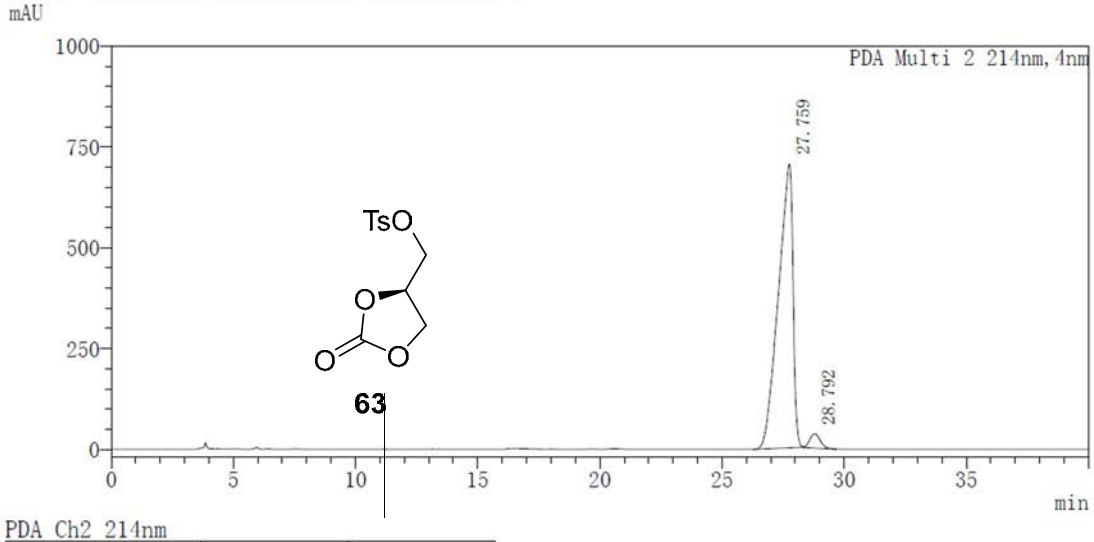
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.562	BB	0.7683	6347.69092	122.96014	95.6414
2	39.138	BB	0.6199	289.28012	5.64447	4.3586
Totals :				6636.97104	128.60460	



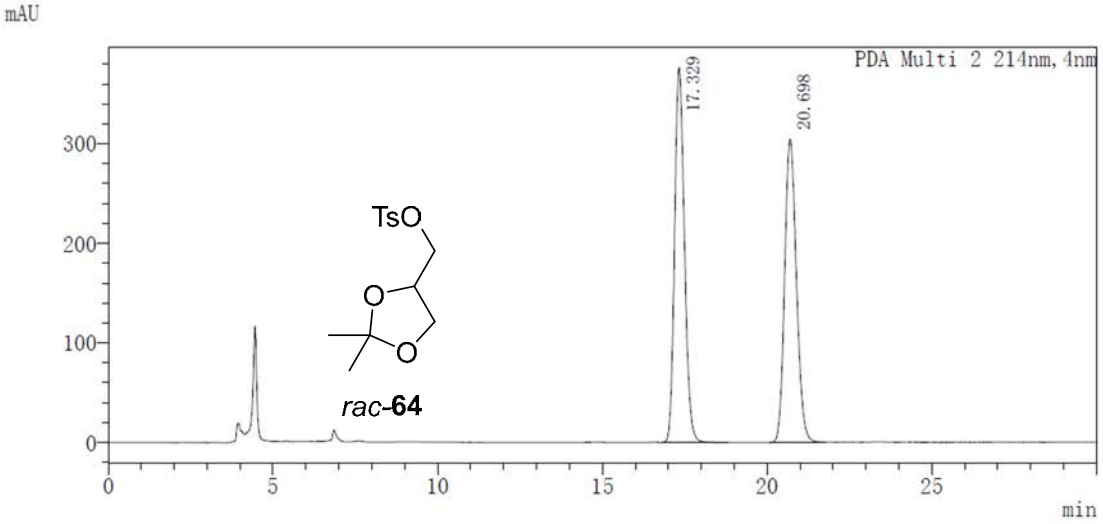
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	27.319	2732185	49.952
2	28.903	2737405	50.048



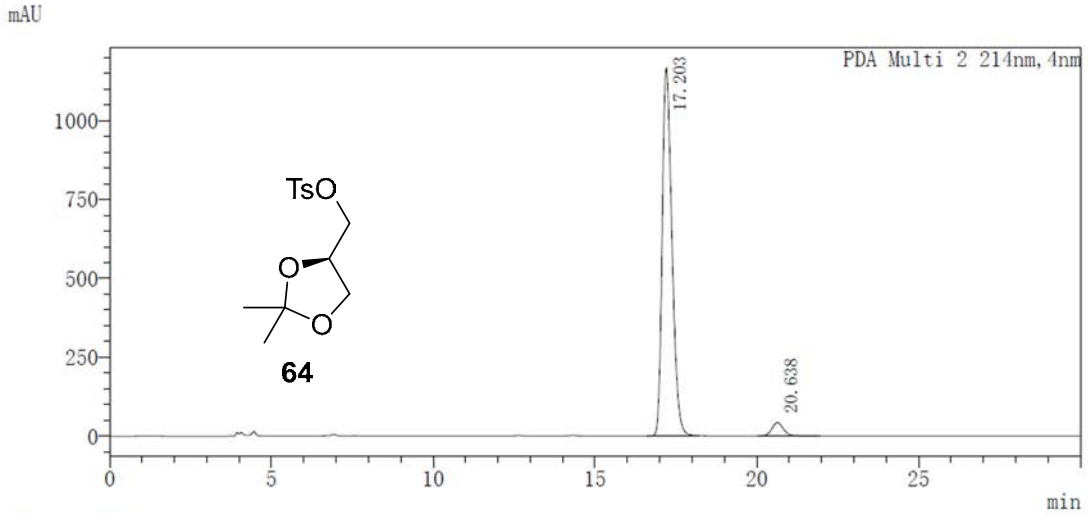
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	27.759	29203039	96.530
2	28.792	1049921	3.470



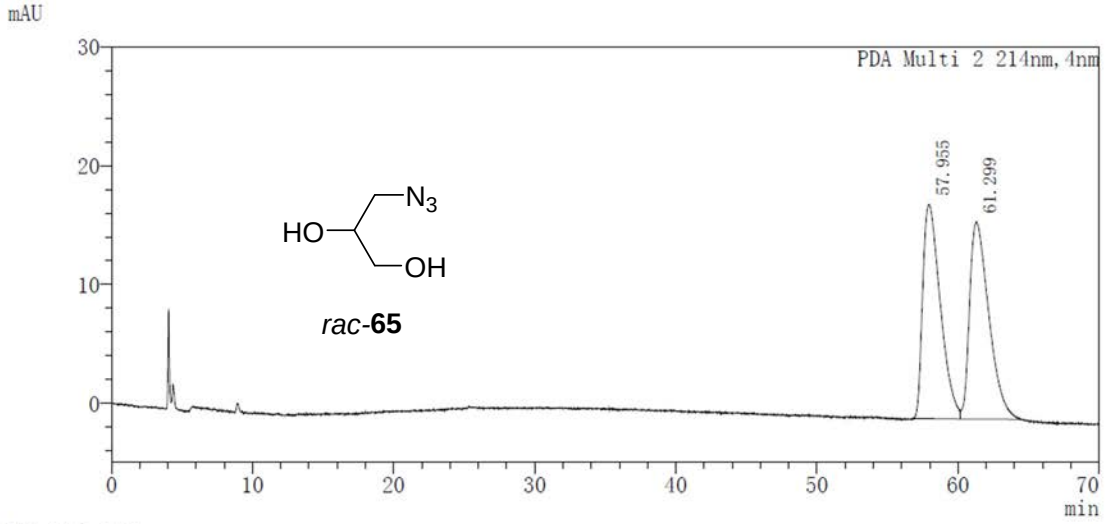
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	17.329	7818800	50.859
2	20.698	7554659	49.141



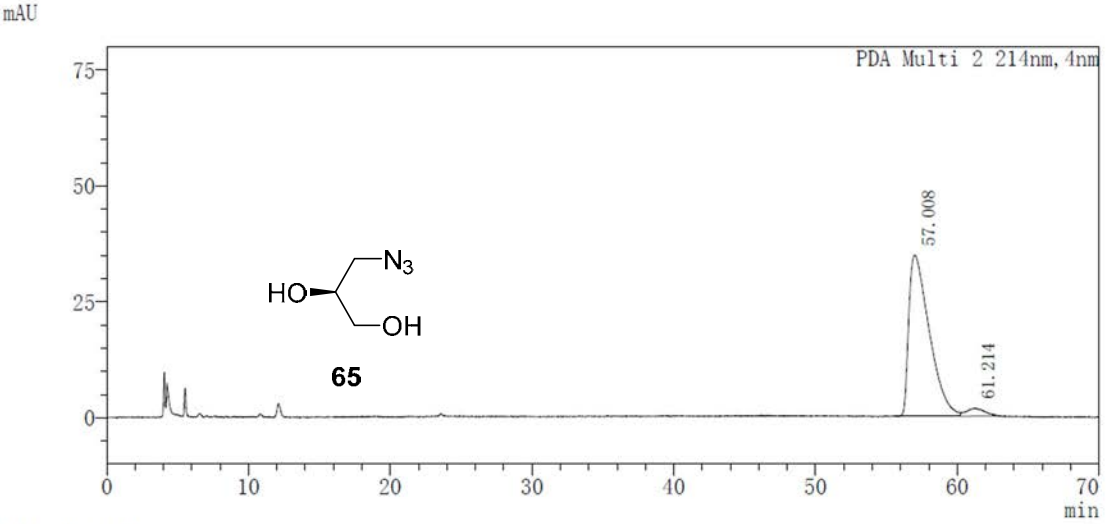
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	17.203	24403595	95.953
2	20.638	1029377	4.047



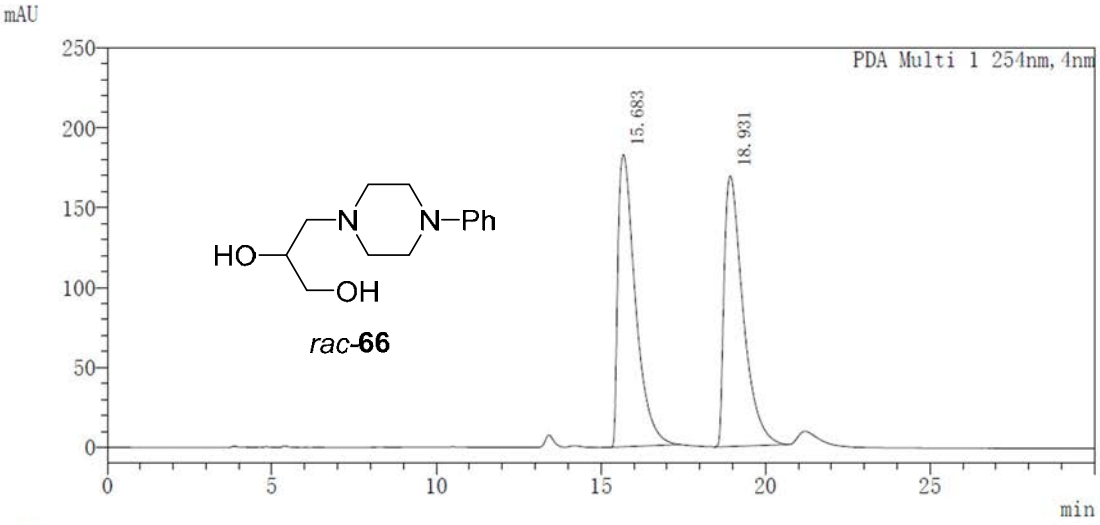
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	57.955	1567218	49.776
2	61.299	1581338	50.224



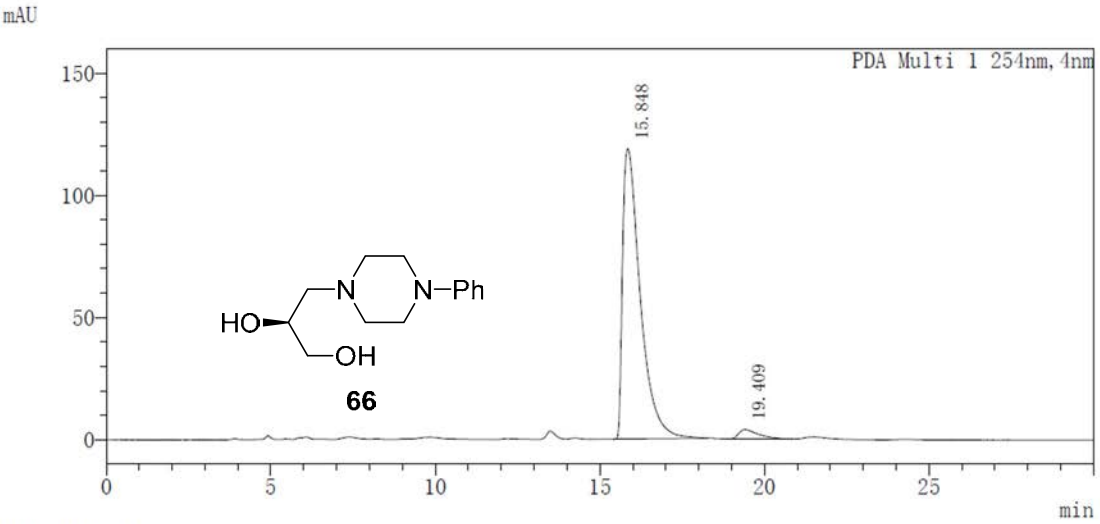
PDA Ch2 214nm

Peak#	Ret. Time	Area	Area%
1	57.008	3500135	95.790
2	61.214	153849	4.210



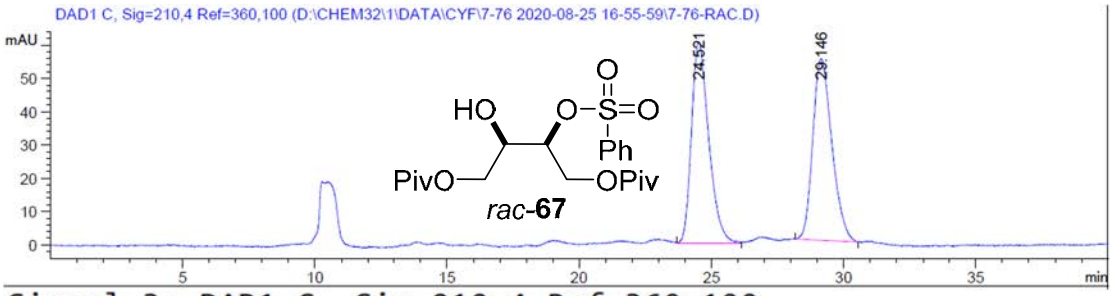
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.683	6787469	50.041
2	18.931	6776370	49.959



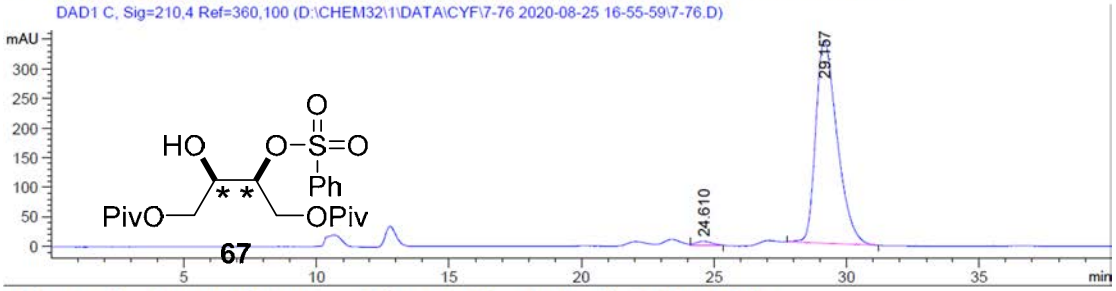
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	15.848	4443892	96.584
2	19.409	157150	3.416



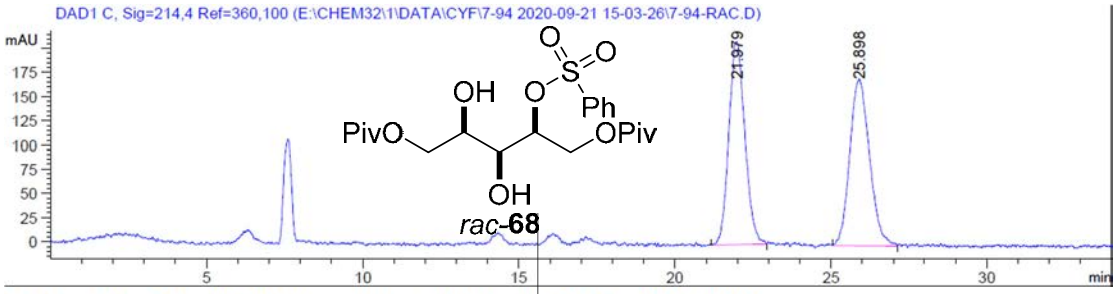
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.521	MM R	0.7550	2737.22607	60.42809	49.9650
2	29.146	BB	0.5999	2741.06470	54.57893	50.0350
Totals :				5478.29077	115.00702	



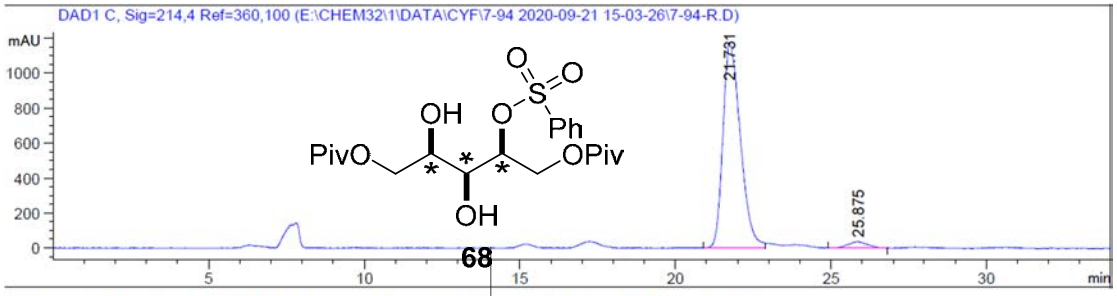
Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.610	VBA	0.4859	284.42828	6.88627	1.4559
2	29.157	BB	0.7737	1.92518e4	342.54050	98.5441
Totals :				1.95362e4	349.42676	



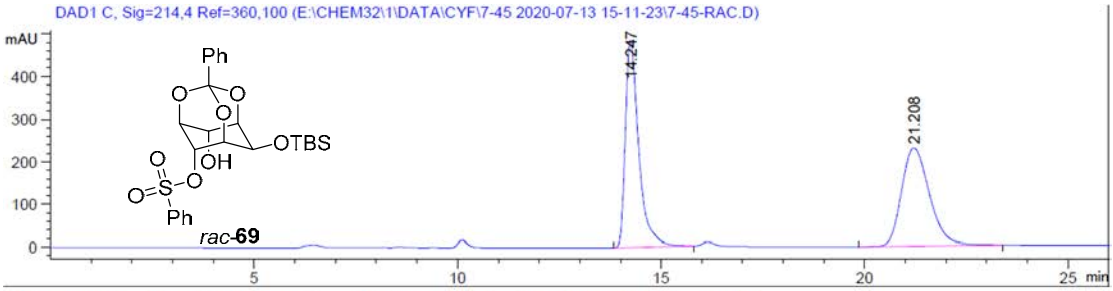
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.979	VV R	0.4243	7495.18896	210.41428	49.7485
2	25.898	VV R	0.5297	7570.98486	172.54945	50.2515
Totals :				1.50662e4	382.96373	



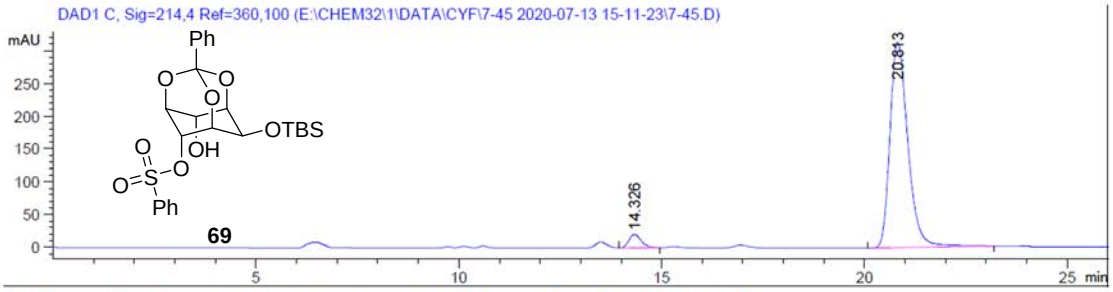
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.731	MF R	0.6522	4.60241e4	1176.15613	96.5065
2	25.875	MM R	0.7466	1666.04968	37.19242	3.4935
Totals :				4.76901e4	1213.34855	



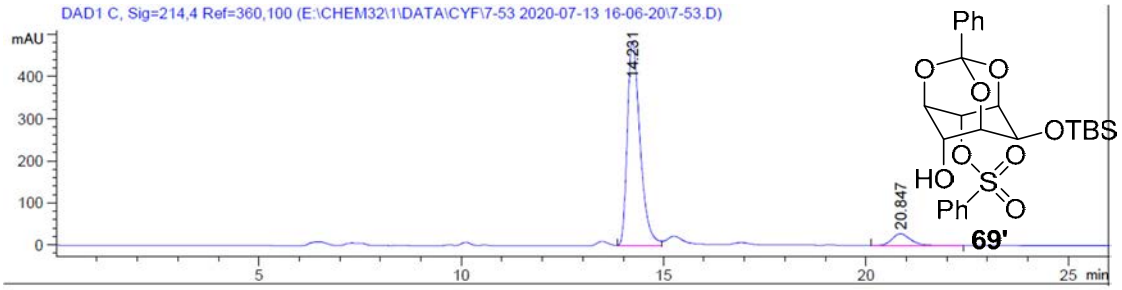
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.247	BB	0.3478	1.11356e4	485.09732	50.2792
2	21.208	BB	0.7362	1.10119e4	230.99066	49.7208
Totals :				2.21475e4	716.08798	



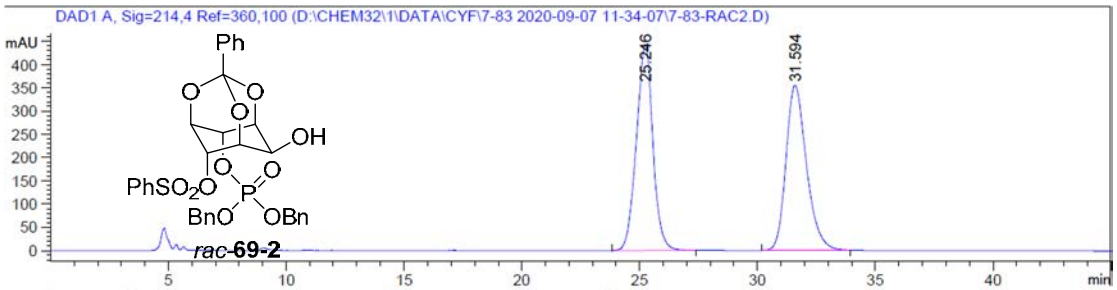
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.326	VB	0.3219	431.55362	20.64451	4.2794
2	20.813	MM R	0.5120	9652.83691	314.24161	95.7206
Totals :				1.00844e4	334.88612	



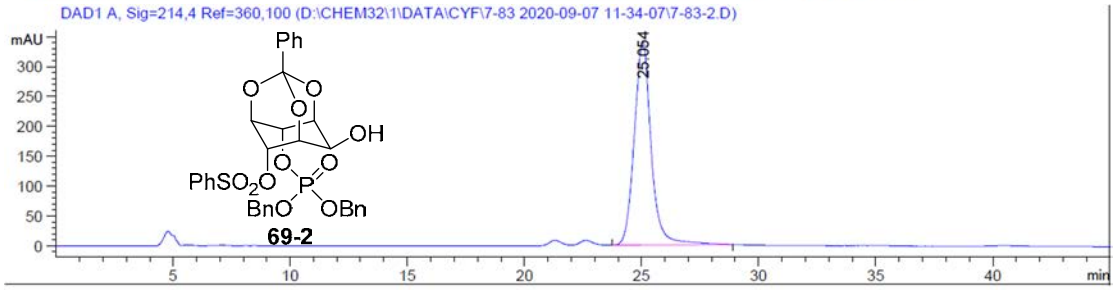
Signal 3: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.231	FM R	0.3634	1.06069e4	486.45728	92.3635
2	20.847	BB	0.4886	876.96826	27.60643	7.6365
Totals :				1.14838e4	514.06371	



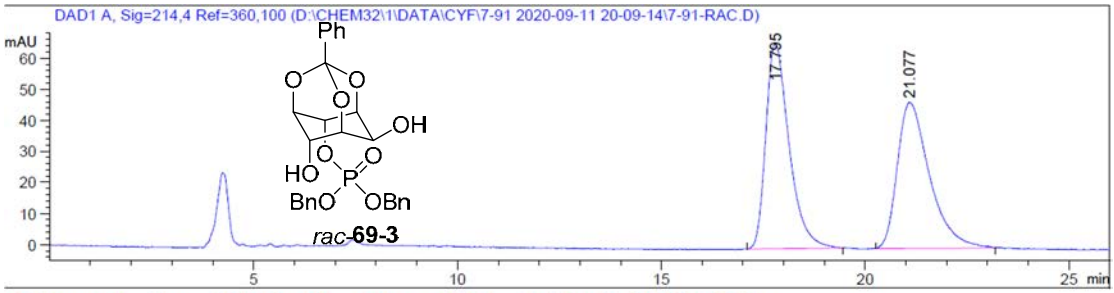
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.246	BB	0.7178	2.15957e4	443.73969	50.0919
2	31.594	BB	0.8804	2.15164e4	355.35165	49.9081
Totals :				4.31121e4	799.09134	



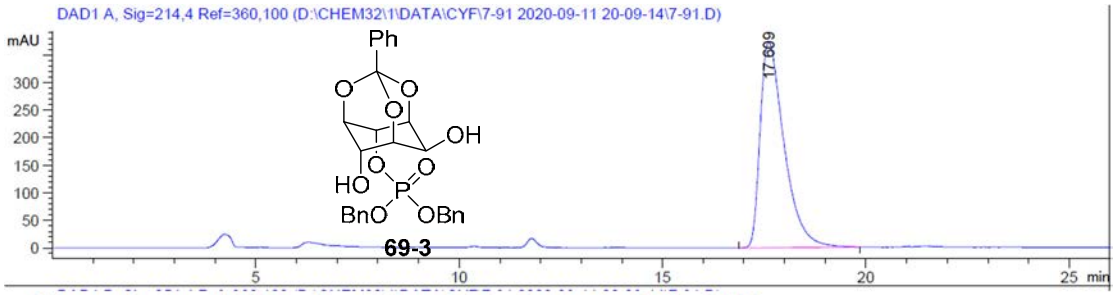
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.054	BB	0.7288	1.71626e4	341.24591	100.0000
Totals :				1.71626e4	341.24591	



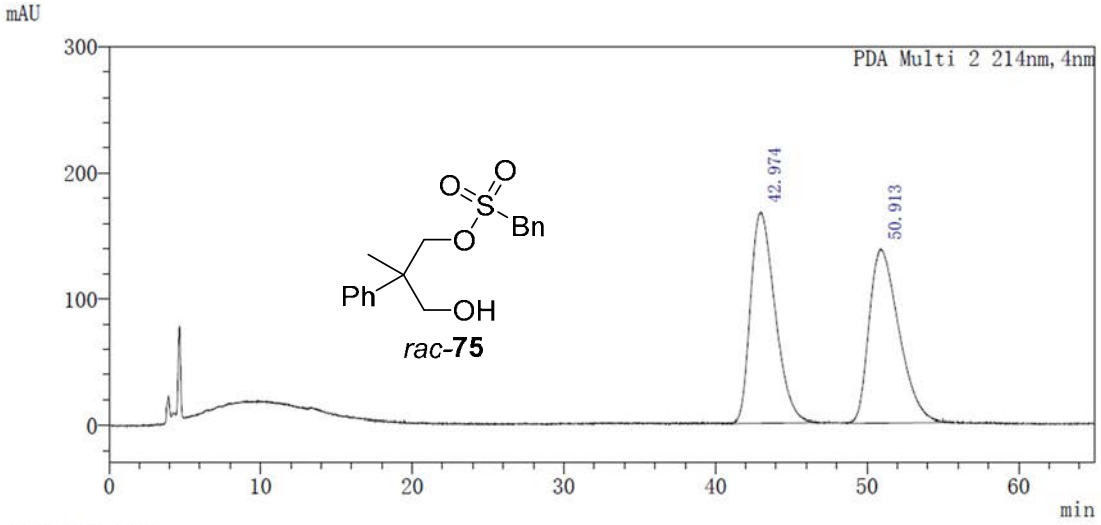
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.795	BB	0.5492	2627.13843	66.17142	50.4671
2	21.077	BB	0.6600	2578.50488	47.00665	49.5329
Totals :				5205.64331	113.17807	



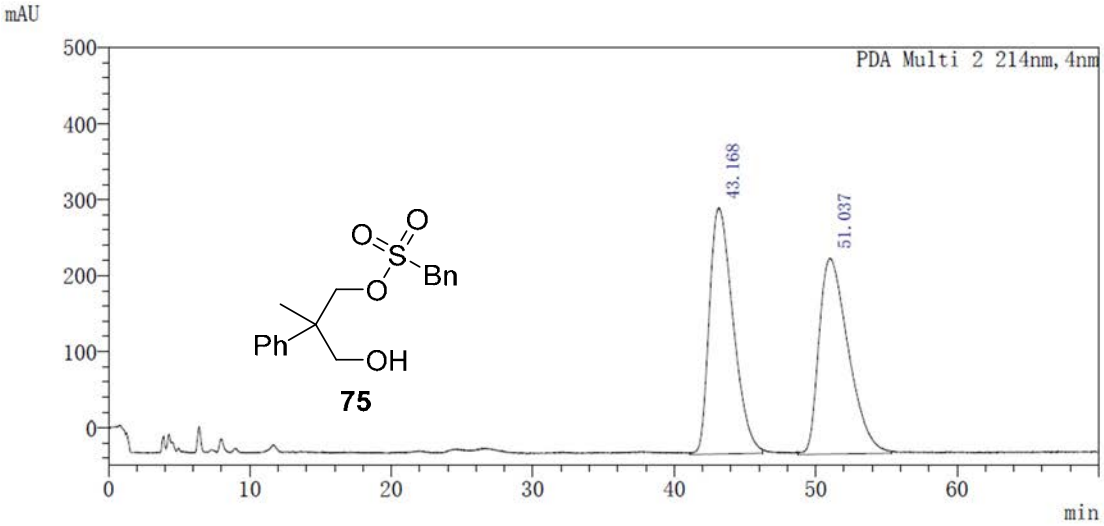
Signal 1: DAD1 A, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.609	BB	0.6034	1.52800e4	373.41321	100.0000
Totals :				1.52800e4	373.41321	



PDA Ch2 214nm

T	Hight	Area	Area%
42.974	167425	18864266	50.069
50.913	137467	18812123	49.931



PDA Ch2 214nm

T	Hight	Area	Area%
43.168	323381	37814858	50.432
51.037	257676	37167756	49.568

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