Supporting Information

Regioselective direct sulfenylation of glycals using arylsulfonyl chlorides in the presence of triphenylhosphine: access to C2-thioaryl glycosides

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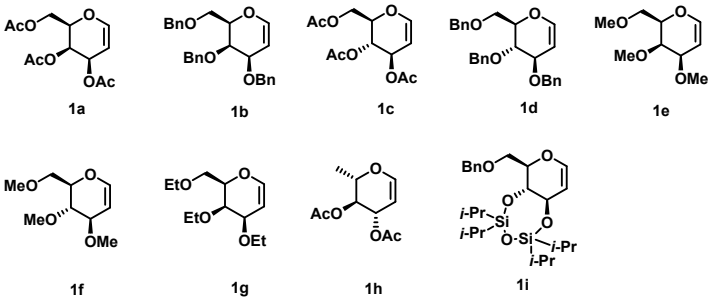
1. EXPERIMENTAL SECTION

1.1. General Experimental Information.

Unless otherwise specified, all reactions were carried out under air atmosphere in oven-dried round-bottom flasks and the heating reactions were performed in oil bath. All commercially available reagents were purchased from commercial sources and were used without further purification. All reactions were monitored by thin layer chromatography over silica gel-coated TLC plates. The spots on TLC were visualized by warming ceric sulfate [2% $Ce(SO_4)_2$ in 5% H_2SO_4 in EtOH]-sprayed plates on a hot plate. Silica gel 230-400 mesh was used for column chromatography. ^1H, ^{13}C NMR and 2D spectra were recorded on Bruker AV 400/500 MHz spectrometer. Chemical shifts δ are given in ppm relative to the residual signals of tetramethylsilane in $CDCl_3$ for ^1H and ^{13}C NMR. Coupling constants are given in hertz. The HRMS spectra were recorded as ESI-HRMS on Q-TOF mass spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions. Commercially available all the sulfonyl chlorides are used in all reactions.

1.2. List of glycal donors used in the study and preparation



The known compounds **1a**,[1] **1b**,[1] **1c**,[1] **1d**,[1] **1e**,[1] **1f**,[1] **1g**,[1] **1h**,[1] and **1i**[1d] showed characterization data in full agreement with previously reported data.

1.3. Optimization of reaction conditions for regioselective sulfenylation of galactal 1a with *p*-tolylsulfonyl chloride 2a[a]

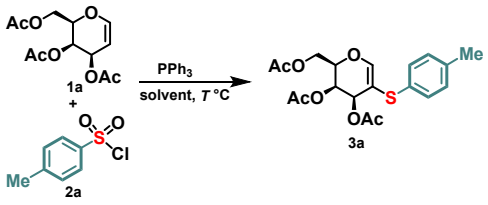
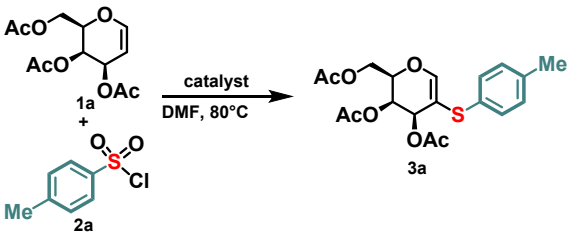


Table S1. Preliminary Screening of catalyst PPh_3 in different solvent with different temperature

Entry	**reductant (equiv.)**	**solvent**	Temp. (°C)	**Yield[b] (%) 3a**
1	PPh_3 (2)	CH_3CN	50	18
2	PPh_3 (2)	CH_3CN	80	16
3	PPh_3 (2)	DCE	50	12
4	PPh_3 (2)	Toluene	50	28
5	PPh_3 (2)	Toluene	80	29
6	PPh_3 (2)	THF	50	38
7	PPh_3 (2)	1,4-dioxane	50	33
8	PPh_3 (2)	DMF	50	59
9	PPh_3 (2)	DMF	80	76
10[c]	PPh_3 (2)	DMF	120	70

[a]Reactions were carried out using galactal **1a** (1.0 mmol, 1.0 equiv.), *p*-toluenesulfonyl chloride **2a** (1.5 mmol, 1.5 equiv.), and Triphenylphosphine (2 equiv.) in 5 mL of solvent at indicated temperature for 3 h. [b]Yield of isolated product based on reactant **1a**, [c]reaction run for 20 h.

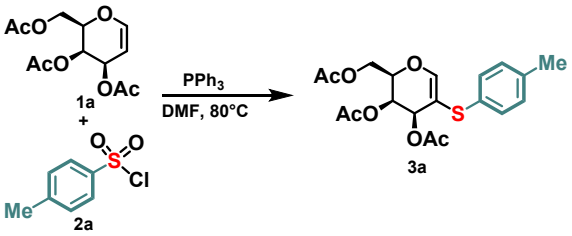
Table S2. Different phosphines in DMF



Entry	reductant (equiv.)	solvent	Temp. (°C)	Yield[b] (%) 3a
1	$P(OEt)_3$ (2)	DMF	80	26
2	PPh_2Me (2)	DMF	80	42
3	$(MeO)_2P(O)H$ (2)	DMF	80	24
4	$(EtO)_2P(O)H$ (2)	DMF	80	22

[a]Reactions were carried out using galactal **1a** (1.0 mmol, 1.0 equiv.), *p*-toluenesulfonyl chloride **2a** (1.5 mmol, 1.5 equiv.), and phosphine reductant (2 equiv.) in 5 mL of DMF at indicated temperature for 3 h. [b]Yield of isolated product based on reactant **1a**.

Table S3. Loading of triphenylphosphine in DMF

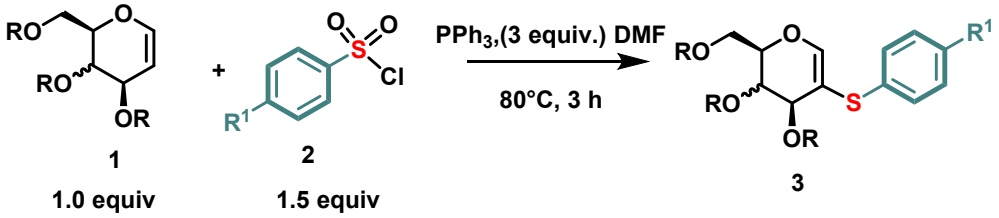


Entry	reductant (equiv.)	solvent	Temp. (°C)	Yield[b] (%) 3a
1	PPh_3 (3)	DMF	80	81
2[c]	PPh_3 (3)	DMF	80	81
3	PPh_3 (3)	DMF	120	77
4	PPh_3 (4)	DMF	80	80

[a]Reactions were carried out using galactal **1a** (1.0 mmol, 1.0 equiv.), *p*-toluenesulfonyl chloride **2a** (1.5 mmol, 1.5 equiv.), and Triphenylphosphine (X equiv.) in 5 mL of DMF at indicated temperature for 3 h. [b]Yield of isolated product based on reactant **1a**, [c]reaction run for 20 h.

1.4. General Procedure for synthesis of 2-*S*-Aryl-Glycosides (3a-3x)

A solution of glycal **1a-f** (1.0 mmol, 1.0 eq.), was charged with arylsulfonyl chloride **2a-g** (1.5 mmol, 1.5 eq.) and PPh_3 (3.0 mmol, 3 eq.) and DMF (5 mL). The resulting solution was stirred at 80 °C for 3 h. After the starting material was completely consumed (detected by TLC), cooling the reaction mixture to room temperature the solvent were removed under vacuum and the residue was purified by column chromatography to afford the corresponding arylylthiolated glycals **3a-x** Yield: 77-84% (Scheme 1).

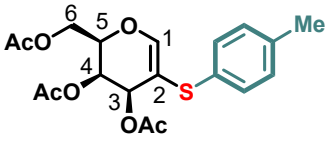


Scheme 1. Procedure for synthesis of 2-*S*-Aryl-Glycosides.

1.5. Characterization data

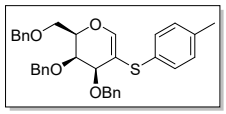
2-(*p*-tolylthio)-3,4,6-tri-*O*-acetyl-D-galactal (3a)

Synthesized according to general procedure in 1 mmol scale, afforded **3a** (319 mg, yield



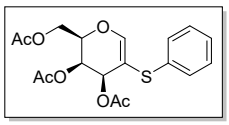
79%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2954, 1740, 1619, 1435, 1367, 1247, 1211, 1171, 1135, 1016, 912, 860, 839, 827, 753, 695 cm^{-1}; $[\alpha]_D^{25}$ +1.14 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.1 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.98 (s, 1 H, H-1), 5.62 (d, *J* = 4.3 Hz, 1 H, H-3), 5.46 (dd, *J* = 4.3, 2.3 Hz, 1 H, H-4), 4.45-4.43 (m, 1 H, H-5), 4.36-4.32 (m, 1 H, H-6_a), 4.23 (dd, *J* = 11.8, 4.9 Hz, 1 H, H-6_b), 2.30 (s, 3 H, C*H*$_3$), 2.11 (s, 3 H, COC*H*$_3$), 2.10 (s, 3 H, COC*H*$_3$), 1.76 (s, 3 H, COC*H*$_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5 (*C*OCH$_3$), 170.0 (*C*OCH$_3$), 169.8(*C*OCH$_3$), 151.9 (C-1), 136.2 (Ar$_q$), 132.7 (Ar$_q$), 129.5 (Ar), 128.4 (Ar), 104.3 (C-2), 73.4 (C-5), 65.6 (C-3), 64.6 (C-4), 61.6 (C-6), 21.0 (*C*H$_3$), 20.7 (COCH$_3$), 20.6(COCH$_3$), 20.2 (COCH$_3$); HRMS (ESI) m/z: [M + NH_4]$^+$ Calcd for $C_{19}H_{26}NO_7S$ 412.1424; Found 412.1422.

2-(*p*-tolylthio)-3,4,6-tri-*O*-benzyl-D-galactal (3b)

Synthesized according to general procedure in 1 mmol scale, afforded **3b** (452 mg, yield 

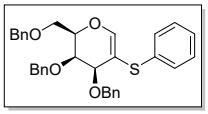
84%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2952, 2924, 1617, 1419, 1247, 1170, 1154, 1128, 1103, 1077, 1048, 1027, 827, 753, 695 cm^{-1}; $[\alpha]_D^{25}$ +3.10 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 4 H), 7.29-7.27 (m, 3 H), 7.26-7.23 (m, 3 H), 7.22-7.20 (m, 3 H), 7.17 (d, *J* = 8.2 Hz, 2 H), 7.12-7.09 (m, 2 H), 7.00 (d, *J* = 8 Hz, 2 H), 6.83 (s, 1 H), 4.74 (d, *J* = 11.7 Hz, 1 H), 4.66 (d, *J* = 11.7 Hz, 1 H), 4.62 (d, *J* = 11.7 Hz, 1 H), 4.56 (d, *J* = 1.9 Hz, 1 H), 4.53 (d, *J* = 2.2 Hz, 1 H), 4.46 (d, *J* = 11.9 Hz, 1 H), 4.40-4.37 (m, 1 H), 4.09 (d, *J* = 3.6 Hz, 1 H), 3.98 (t, *J* = 3.5 Hz, 1 H), 3.89 (dd, *J* = 10.8, 7.7 Hz, 1 H), 3.76 (dd, *J* = 10.8, 4 Hz, 1 H), 2.30 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.2, 138.5, 138.0, 135.2, 134.2, 130.5, 130.0, 129.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 105.1, 76.2, 73.8, 73.5, 73.4, 73.0, 68.1, 21.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{35}O_4S$ 539.2251; Found 539.2247.

2-(phenylthio)-3,4,6-tri-*O*-acetyl-D-galactal (3c)

Synthesized according to general procedure in 1 mmol scale, afforded **3c** (300 mg, yield 

79%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2924, 2853, 1740, 1712, 1618, 1515, 1436, 1367, 1210, 1169, 1160, 1050, 1018, 911, 778 cm^{-1}; $[\alpha]_D^{25}$ +1.30 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2 H), 7.26-7.22 (m, 2 H), 7.18-7.14 (m, 1 H), 7.00 (d, *J* = 1.3 Hz, 1 H), 5.66-5.64 (m, 1 H), 5.48 (dd, 4.4, 2.2 Hz, 1 H), 4.48-4.45 (m, 1 H), 4.37-4.32 (m, 1 H), 4.24 (dd, *J* = 11.8 5.1 Hz, 1 H), 2.12 (s, 3 H), 2.10 (s, 3 H), 1.70 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.9, 169.7, 152.6, 136.7, 128.6, 127.8, 126.1, 103.5, 73.5, 65.8, 64.4, 61.5, 20.7, 20.5, 20.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}O_7S$ 381.1003; Found 381.1001.

2-(phenylthio)-3,4,6-tri-*O*-benzyl-D-galactal (3d)

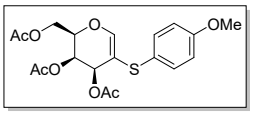
Synthesized according to general procedure in 1 mmol scale, afforded **3d** (435 mg, yield 

83%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2952, 2853, 1740, 1712, 1620, 1584, 1404, 1368, 1245, 1214, 1170, 1135, , 690 cm^{-1}; $[\alpha]_D^{25}$ +3.40 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 5 H), 7.30-7.28 (m, 4 H), 7.26-7.24 (m, 3 H), 7.22-7.19 (m, 3 H), 7.19-7.16 (m, 2 H), 7.13-7.10 (m, 1 H), 7.09-7.07 (m, 2 H), 6.84 (d, *J* = 0.8 Hz, 1 H), 4.77 (d, *J* = 11.6 Hz, 1 H), 4.67 (d, *J* = 11.7

Hz, 1 H), 4.62 (d, *J* = 11.7 Hz, 1 H), 4.57-4.53 (m, 2 H), 4.47 (d, *J* = 11.9 Hz, 1 H), 4.41-4.37 (m, 1 H), 4.13 (d, *J* = 3.7 Hz, 1 H), 4.00 (t, *J* = 3.4 Hz, 1 H), 3.90-3.86 (m, 1 H), 3.76 (dd, *J* = 10.6, 4.3 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 151.9, 138.4, 138.2, 137.9, 128.7, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 127.5, 127.3, 126.8, 125.2, 104.4, 76.4, 73.8, 73.7, 73.5, 73.2, 72.8, 68.1; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{33}O_4S$ 525.2094; Found 525.2090.

2-((4-methoxyphenyl)thio)-3,4,6-tri-*O*-acetyl-D-galactal (3e)

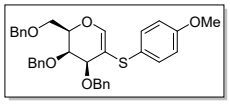
Synthesized according to general procedure in 1 mmol scale, afforded **3e** (324 mg, yield



79%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2954, 2871, 1613, 1436, 1356, 1250, 1157, 758, 669 cm^{-1}; $[\alpha]_D^{25}$ +0.92 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.28 (m, 1 H), 7.27-7.25 (m, 1 H), 6.97 (d, *J* = 1.2 Hz, 1 H), 6.83-6.79 (m, 2 H), 5.60-5.58 (m, 1 H), 5.43 (dd, *J* = 4.4, 2.5 Hz, 1 H), 4.42-4.39 (m, 1 H), 4.36-4.31 (m, 1 H), 4.22 (dd, *J* = 11.7, 4.7 Hz, 1 H), 3.78 (s, 3 H), 2.09 (s, 6 H), 1.81 (s, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 170.1, 169.7, 158.9, 151.0, 131.1, 126.4, 114.4, 105.4, 73.3, 65.4, 64.6, 61.5, 55.3, 20.7, 20.5, 20.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}O_7S$ 411.1108; Found 411.1102.

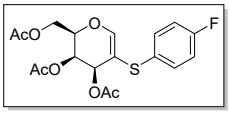
2-((4-methoxyphenyl)thio)-3,4,6-tri-*O*-benzyl-D-galactal (3f)

Synthesized according to general procedure in 1 mmol scale, afforded **3f** (460 mg, yield



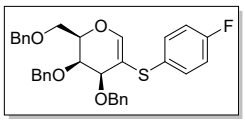
83%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2959, 2924, 2853, 1738, 1620, 1465, 1367, 1240, 1208, 1183, 1131, 1023, 944, 908, 767, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +2.80 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.27 (m, 8 H), 7.25-7.20 (m, 7 H), 7.14-7.12 (m, 2 H), 6.82 (d, *J* = 0.4 Hz, 1 H), 6.76-6.72 (m, 2 H), 4.73 (d, *J* = 11.7 Hz, 1 H), 4.65 (s, 2 H), 4.54 (d, *J* = 11.6 Hz, 2 H), 4.46 (d, *J* = 11.9 Hz, 1 H), 4.39-4.36 (m, 1 H), 4.07-4.06 (m, 1 H), 3.95 (t, *J* = 3.5 Hz, 1 H), 3.91-3.85 (m, 1 H), 3.79-3.78 (m, 0.5 H), 3.77 (s, 3 H), 3.75-3.74 (m, 0.5 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 158.2, 150.5, 138.5, 138.0, 137.9, 129.6, 128.4, 128.1, 127.9, 127.8, 127.7, 127.5, 127.3, 114.7, 114.4, 106.1, 76.2, 73.8, 73.5, 73.3, 73.0, 68.1, 55.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{35}O_5S$ 555.2200; Found 555.2197.

2-((4-fluorophenyl)thio)-3,4,6-tri-*O*-acetyl-D-galactal (3g)

Synthesized according to general procedure in 1 mmol scale, afforded **3g** (287 mg, yield 

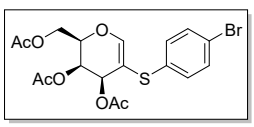
72%); eluted with 25% EtOAc in hexane; Colorless jelly, IR (neat): 2922, 1737, 1622, 1433, 1367, 1235, 1173, 1095, 1034, 978, 733, 647 cm^{-1}; $[\alpha]_D^{25}$ +1.81 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2 H), 7.00 (d, *J* = 1.2 Hz, 1 H), 6.99-6.95 (m, 2 H), 5.64-5.62 (m, 1 H), 5.46 (dd, *J* = 4.4, 2.3 Hz, 1 H), 4.46-4.43 (m, 1 H), 4.37-4.32 (m, 1 H), 4.23 (dd, *J* = 11.8, 5.0 Hz, 1 H), 2.11 (s, 3 H), 2.10 (s, 3 H), 1.76 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.9, 169.7, 161.7 (d, *J* = 244.8 Hz), 152.4, 131.5 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 8.0 Hz), 115.7 (d, *J* = 22.0 Hz), 104.1, 73.5, 65.7, 64.4, 61.4, 20.7, 20.5, 20.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}O_7S$ 399.0908; Found 399.0903.

2-((4-fluorophenyl)thio)-3,4,6-tri-*O*-benzyl-D-galactal (3h)

Synthesized according to general procedure in 1 mmol scale, afforded **3h** (428 mg, yield 

79%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2928, 1672, 1503, 1436, 1236, 1157, 758, 669 cm^{-1}; $[\alpha]_D^{25}$ +3.30 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 5 H), 7.30-7.27 (m, 3 H), 7.25-7.21 (m, 7 H), 7.09-7.06 (m, 2 H), 6.87-6.82 (m, 3 H), 4.76 (d, *J* = 11.6 Hz, 1 H), 4.64 (s, 2 H), 4.57 (d, *J* = 5.7 Hz, 1 H), 4.54 (s, 5.9 H), 4.47 (d, *J* = 11.9 Hz, 1 H), 4.38-4.35 (m, 1 H), 4.11 (d, *J* = 3.6 Hz, 1 H), 3.99 (t, *J* = 3.3 Hz, 1 H), 3.85 (dd, *J* = 10.5, 7.4 Hz, 1 H), 3.75 (dd, *J* = 10.5, 4.6 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ161.4 (d, *J* = 243.8 Hz), 151.8, 138.2, 137.9, 137.8, 133.2 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 8.0 Hz), 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.4, 115.6 (d, *J* = 21.8 Hz), 105.0, 76.4, 74.0, 73.7, 73.5, 73.4, 72.5, 68.0; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{33}H_{35}FNO_4S$ 560.2265; Found 560.2262.

2-((4-bromophenyl)thio)-3,4,6-tri-*O*-acetyl-D-galactal (3i)

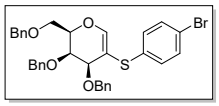
Synthesized according to general procedure in 1 mmol scale, afforded **3i** (334 mg, yield 

73%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2954, 1740, 1619, 1435, 1367, 1247, 1211, 1157, 758 cm^{-1}; $[\alpha]_D^{25}$

+1.10 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2 H), 7.19-7.16 (m, 2 H), 6.99 (d, *J* = 1.3 Hz, 1 H), 5.65-5.64 (m, 1 H), 5.48 (dd, *J* = 4.4, 2.2 Hz, 1 H), 4.49-4.45 (m, 1 H), 4.37-4.33 (m, 1 H), 4.23 (dd, *J* = 11.8, 5.1 Hz, 1 H), 2.13 (s, 3 H), 2.10 (s, 3 H), 1.74 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.4, 169.8, 169.7, 153.2, 136.4, 131.6, 129.1, 119.8, 102.9, 73.7, 65.8, 64.3, 61.4, 20.7, 20.5, 20.2; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{18}H_{23}BrNO_7S$ 476.0373; Found 476.0371.

2-((4-bromophenyl)thio)-3,4,6-tri-*O*-benzyl-D-galactal (3j)

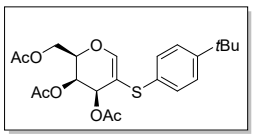
Synthesized according to general procedure in 1 mmol scale, afforded **3j** (470 mg, yield



78%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2952, 2843, 1738, 1680, 1465, 1367, 1230, 1208, 1183, 1131, 1023, 767, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +3.10 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m,8 H), 7.25-7.21 (m, 7 H), 7.15-7.11 (m, 2 H), 7.03-7.01 (m, 2 H), 6.82 (d, *J* = 0.9 Hz, 1 H), 4.77 (d, *J* = 11.5 Hz, 1 H), 4.63 (s, 2 H), 4.57 (d, *J* = 9.0 Hz, 1 H), 4.54 (d, *J* = 9.3 Hz, 1 H), 4.47 (d, *J* = 11.9 Hz, 1 H), 4.36-4.34 (m, 1 H), 4.14-4.13 (m, 1 H), 4.01-4.00 (m, 1 H), 3.84 (dd, *J* = 10.4, 7.3 Hz, 1 H), 3.75 (dd, *J* = 10.4, 4.9 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.5, 138.1, 138.0, 137.9, 137.8, 131.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.4, 127.4, 118.7, 104.1, 76.5, 74.3, 73.6, 73.5, 72.2, 68.1; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{33}H_{35}BrNO_4S$ 620.1465; Found 620.1460.

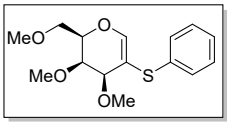
2-((4-*tert*-butylphenyl)thio)-3,4,6-tri-*O*-acetyl-D-galactal (3k)

Synthesized according to general procedure in 1 mmol scale, afforded **3k** (340 mg, yield



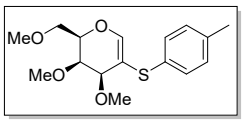
78%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2959, 2924, 2853, 1738, 1620, 1465, 1367, 1240, 1208, 1183, 1131, 1023, 944, 908, 767, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +1.14 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.9 Hz, 2 H), 7.23 (d, *J* = 8.9 Hz, 2 H), 6.98 (s, 1 H), 5.64-5.62 (m, 1 H), 5.46 (dd, *J* = 4.3, 2.3 Hz, 1 H), 4.46-4.42 (m, 1 H), 4.35 (dd, *J* = 7.7, 11.6 Hz, 1 H), 4.24 (dd, *J* = 4.9, 11.8 Hz, 1 H), 2.11 (s, 3 H), 2.10 (s, 3 H), 1.74 (s, 3 H), 1.29 (s, 9 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.9, 169.8, 152.0, 149.6, 132.8, 128.2, 125.7, 104.2, 73.4, 65.7, 64.6, 61.6, 34.4, 31.3, 20.7, 20.6, 20.1; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{32}NO_7S$ 454.1894; Found 454.1890.

2-(phenylthio)-3,4,6-tri-*O*-methyl-D-galactal (3l)

Synthesized according to general procedure in 1 mmol scale, afforded **3l** (243 mg, yield 

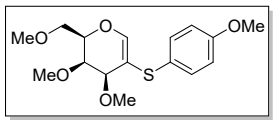
82%); eluted with 15% EtOAc in hexane; colorless jelly, IR (neat2952, 2924, 1617, 1419, 1247, 1170, 1131, 1023, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +1.20 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 3 H), 7.26-7.24 (m, 1 H), 7.17-7.13 (m, 1 H), 6.83 (s, 1 H), 4.42-4.38 (m, 1 H), 3.83-3.78 (m, 3 H), 3.66 (dd, *J* = 10.9, 3.6 Hz, 1 H), 3.53 (s, 3 H), 3.45 (s, 3 H), 3.42 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.1, 137.6, 128.8, 127.2, 125.6, 104.7, 75.7, 75.6, 74.5, 70.1, 60.0, 59.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}O_4S$ 297.1155; Found 297.1157.

2-(*p*-tolylthio)-3,4,6-tri-*O*-methyl-D-galactal (3m)

Synthesized according to general procedure in 1 mmol scale, afforded **3m** (257 mg, yield 

83%); eluted with 12% EtOAc in hexane; colorless jelly, IR (neat): 2950, 1645, 1612, 1452, 1302, 1171, 1139, 767, 733, 698 cm^{-1} ; $[\alpha]_D^{25}$ +0.28 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.21-7.19 (m, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.82 (s, 1 H), 4.40-4.36 (m, 1 H), 3.82-3.78 (m, 2 H), 3.77 (d, *J* = 3.8 Hz, 1 H), 3.64 (dd, *J* = 10.8, 3.4 Hz, 1 H), 3.51 (s, 3 H), 3.45 (s, 3 H), 3.41 (s, 3 H), 2.31 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.4, 135.7, 133.6, 129.6, 127.8, 105.4, 75.7, 75.6, 74.2, 70.1, 60.0, 59.2, 59.1, 20.9; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{23}O_4S$ 311.1312; Found 311.1310.

2-((4-methoxyphenyl)thio)-3,4,6-tri-*O*-methyl-D-galactal (3n)

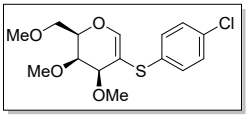
Synthesized according to general procedure in 1 mmol scale, afforded **3n** (270 mg, yield 

83%); eluted with 15% EtOAc in hexane; colorless jelly, IR (neat): 2959, 2924, 2853, 1738, 1620, 1465, 1367, 1240, 1208, 1183, 1131, 1023, 944, 908, 767, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +0.23 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2 H), 6.85-6.82 (m, 2 H), 6.81 (s, 1 H), 4.37-4.33 (m, 1 H), 3.80-3.78 (m, 1 H), 3.79 (s, 3 H), 3.76-3.72 (m, 2 H), 3.63 (dd, *J* = 10.8, 3.5 Hz, 1 H), 3.50 (s, 3 H), 3.46 (s, 3 H), 3.40 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.5, 149.3, 130.5,

127.2, 114.5, 106.7, 75.7, 75.5, 74.0, 70.0, 60.0, 59.2, 59.1, 55.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{23}O_5S$ 327.1261; Found 327.1264.

2-((4-Chlorophenyl)thio)-3,4,6-tri-*O*-methyl-D-galactal (3o)

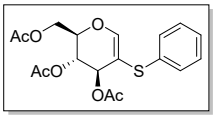
Synthesized according to general procedure in 1 mmol scale, afforded **3o** (254 mg, yield



77%); eluted with 15% EtOAc in hexane; colorless jelly, IR (neat): 2954, 2920, 1671, 1512, 1446, 1226, 1059, 760, 660 cm^{-1} ; $[\alpha]_D^{25}$ +0.31 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2 H), 7.26-7.24 (m, 1 H), 7.17-7.13 (m, 1 H), 6.84 (s, 1 H), 4.42-4.38 (m, 1 H), 3.83-3.78 (m, 3 H), 3.66 (dd, *J* = 10.8, 3.6 Hz, 1 H), 3.53 (s, 3 H), 3.45 (s, 3 H), 3.42 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.1, 137.6, 128.8, 127.2, 125.6, 104.7, 75.7, 75.6, 74.6, 70.1, 60.0, 59.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}ClO_4S$ 331.0765; Found 331.0762.

2-(phenylthio)-3,4,6-tri-*O*-acetyl-D-glucal (3p)

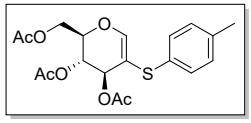
Synthesized according to general procedure in 1 mmol scale, afforded **3p** (285 mg, yield



75%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2952, 2853, 1738, 1620, 1465, 1357, 1240, 1208, 1183, 1023, 944, 908, 767, 658 cm^{-1} ; $[\alpha]_D^{25}$ +2.71 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 3 H), 7.25-7.24 (m, 1 H), 7.19-7.18 (m, 1 H), 7.05 (s, 1 H), 5.41-5.40 (m, 1 H), 5.21 (dd, *J* = 5.2, 4.6 Hz, 1 H), 4.51-4.43 (m, 2 H), 4.22-4.18 (m, 1 H), 2.11 (s, 3 H), 2.08 (s, 3 H), 1.78 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.8, 169.3, 152.8, 136.0, 128.8, 128.0, 126.3, 103.2, 74.1, 67.7, 67.4, 61.0, 20.7, 20.4; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{18}H_{24}NO_7S$ 398.1268; Found 398.1261.

2-(*p*-tolylthio)-3,4,6-tri-*O*-acetyl-D-glucal (3q)

Synthesized according to general procedure in 1 mmol scale, afforded **3q** (307 mg, yield

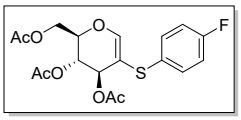


78%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2955, 2853, 1738, 1620, 1465, 1367, 1220, 1208, 1183, 1131, 1023, 944, 908, 767, 661 cm^{-1} ; $[\alpha]_D^{25}$ +2.10 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.22-

7.19 (m, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 7.03 (s, 1 H), 5.38-5.37 (m, 1 H), 5.20-5.18 (m, 1 H), 4.49-4.41 (m, 2 H), 4.21-4.17 (m, 1 H), 2.30 (s, 3 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 1.82 (s, 3 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.8, 169.3, 152.1, 136.4, 132.1, 129.6, 128.6, 104.0, 74.0, 67.5, 67.4, 61.1, 22.7, 21.0, 20.7, 20.4; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{19}H_{26}NO_7S$ 412.1424; Found 412.1422.

2-((4-fluorophenyl)thio)-3,4,6-tri-*O*-acetyl-D-glucal (3r)

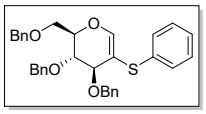
Synthesized according to general procedure in 1 mmol scale, afforded **3r** (283 mg, yield



71%); eluted with 30% EtOAc in hexane; colorless jelly, IR (neat): 2924, 2853, 1740, 1712, 1618, 1515, 1436, 1367, 1210, 1023, 944, 908, 767, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +2.32 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2 H), 7.05 (s, 1 H), 7.00-6.97 (m, 2 H), 5.38 (d, *J* = 4.4 Hz, 1 H), 5.18 (t, *J* = 5.1, 4.7 Hz, 1H), 4.48 (dd, *J* = 11.8, 6.9 Hz, 1 H), 4.44-4.41 (m, 1 H), 4.18 (dd, *J* = 11.9, 3.4 Hz, 1 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 1.83 (s, 3 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 170.4, 169.7, 169.2, 161.8 (d, *J* = 245.2 Hz), 152.5, 130.8 (d, *J* = 3.9 Hz), 130.6 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 21.9 Hz), 104.0, 74.1, 67.5, 67.4, 60.9, 20.7, 20.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}O_7S$ 399.0908; Found 399.0902.

2-(phenylthio)-3,4,6-tri-*O*-benzyl-D-glucal (3s)

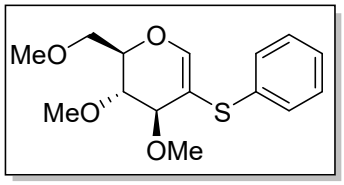
Synthesized according to general procedure in 1 mmol scale, afforded **3s** (424 mg, yield



81%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2954, 1740, 1619, 1435, 1367, 1247, 1211, 1171, 1135, 1016, 912, 648 cm^{-1} ; $[\alpha]_D^{25}$ +3.40 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.27 (m, 10 H), 7.23-7.22 (m, 5 H), 7.19-7.16 (m, 2 H), 7.15-7.09 (m, 3 H), 6.95 (s, 1 H), 4.62-4.53 (m, 4 H), 4.52-4.47 (m, 3 H), 3.95-3.94 (m, 1 H), 3.91-3.89 (m, 1 H), 3.83 (dd, *J* = 6.8, 10.6 Hz, 1 H), 3.71 (dd, *J* = 4.3, 10.6 Hz, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 152.2, 138.0, 137.9, 137.7, 137.6, 128.8, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 126.8, 125.4, 103.7, 76.5, 73.8, 73.7, 73.5, 72.9, 72.4, 68.1; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{33}H_{36}NO_4S$ 542.2360; Found 542.2364.

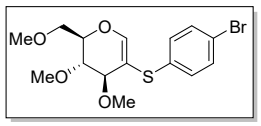
2-(phenylthio)-3,4,6-tri-*O*-methyl-D-glucal (3t)

Synthesized according to general procedure in 1 mmol scale, afforded **3t** (237 mg, yield 80%); eluted with 15% EtOAc in hexane; colorless jelly, IR (neat): 2959, 2924, 2853, 1738, 1617, 1419, 1247, 1170, 1154, 1128, 1103, 908, 767, 733, 648 cm^{-1} ; $[\alpha]_D^{25}$ +1.20 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (m, 2 H), 7.28-7.24 (m, 2 H), 7.15-7.11 (m, 1 H), 6.89 (s, 1 H), 4.40-4.36 (m, 1 H), 3.72 (dd, *J* = 6.9, 10.6 Hz, 1 H), 3.63-3.61 (m, 2 H), 3.59 (dd, *J* = 3.9, 10.6 Hz, 1 H), 3.47 (s, 3 H), 3.41 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.7, 137.4, 128.8, 126.9, 125.4, 103.9, 76.1, 75.3, 75.2, 70.4, 59.2, 58.3, 58.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{21}O_4S$ 297.1155; Found 297.1158.



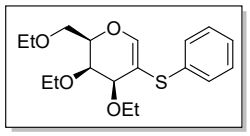
2-((4-bromophenyl)thio)- 3,4,6-tri-O-methyl-D-glucal (3u)

Synthesized according to general procedure in 1 mmol scale, afforded **3u** (288 mg, yield 77%); eluted with 15% EtOAc in hexane; colorless jelly, IR (neat): 2924, 2853, 1740, 1712, 1618, 1515, 1436, 1367, 1210, 778 cm^{-1} ; $[\alpha]_D^{25}$ +1.20 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.7 Hz, 2 H), 7.18 (d, *J* = 8.7 Hz, 2 H), 6.89 (s, 1 H), 4.41-4.37 (m, 1 H), 3.71 (dd, *J* = 6.9, 10.6 Hz, 1 H), 3.64-3.56 (m, 3 H), 3.47 (s, 3 H), 3.41 (s, 3 H) 3.39 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.2, 136.9, 131.8, 128.3, 119.1, 103.3, 76.0, 75.5, 75.1, 70.3 59.2, 58.3, 58.2; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}BrO_4S$ 375.0260; Found 375.0262.



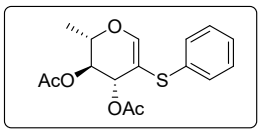
2-(phenylthio)-3,4,6-tri-*O*-ethyl-D-galactal (3v)

Synthesized according to general procedure in 1 mmol scale, afforded **3v** (267 mg, yield 79%); eluted with 15% EtOAc in hexane; colorless jelly, IR (neat): 2952, 2863, 1758, 1646, 1419, 1247, 1170, 1154, 1128, 1114, 908, 733, 691 cm^{-1} ; $[\alpha]_D^{25}$ +2.50 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.33-7.21 (m, 4 H), 7.15-7.09 (m, 1 H), 6.82 (brs, 1 H), 4.37-4.31 (m, 1 H), 3.92-3.90 (m, 1 H), 3.87-3.82 (m, 2 H), 3.79-3.70 (m, 2 H), 3.66-3.49 (m, 5 H), 1.24 (t, *J* = 7.1Hz, 3 H), 1.21 (t, *J* = 7.1Hz, 3 H), 1.01 (t, *J* = 7.1Hz, 3 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 151.3, 138.3, 128.7, 127.3, 125.5, 105.3, 76.6, 73.9, 73.8, 68.5, 67.7, 67.3, 67.0, 15.7, 15.6, 15.4; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{27}O_4S$ 339.1625; Found 339.1628.



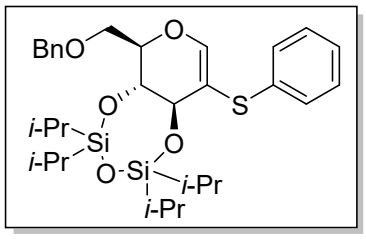
2-(phenylthio)- 3,4-di-*O*-acetyl-L-rhamnal (3w)

Synthesized according to general procedure in 1 mmol scale, afforded **3w** (258 mg, yield 80%); eluted with 10% EtOAc in hexane; colorless jelly, IR (neat): 2962, 2853, 1754, 1686, 1523, 1347, 1246, 1123, 1028, 691 cm^{-1} ; $[\alpha]_D^{25}$ +8.50 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 3 H), 7.25-7.23 (m, 1 H), 7.17-7.13 (m, 1 H), 7.02 (brs, 1 H), 5.43-5.41 (m, 1 H), 5.04 (dd, *J* = 4.7, 5.8 Hz, 1 H), 4.37-4.30 (m, 1 H), 2.08 (s, 3 H), 1.76 (s, 3 H), 1.39 (d, *J* = 6.8 Hz, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.0, 169.6, 153.7, 136.6, 128.7, 127.7, 125.9, 102.2, 72.8, 71.6, 68.5, 20.8, 20.4, 16.3; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}O_5S$ 323.0948; Found 323.051.



2-(phenylthio)-6-*O*-benzyl-3,4-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-D-glucal (3x)

Synthesized according to general procedure in 1 mmol scale, afforded **3x** (457 mg, yield 78%); eluted with 8% EtOAc in hexane; colorless jelly, IR (neat): 2928, 2863, 1734, 1656, 1533, 1357, 1236, 1122, 1028, 691 cm^{-1} ; $[\alpha]_D^{25}$ +8.50 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.33 (m, 4 H), 7.30-7.25 (m, 3 H), 7.21-7.18 (m, 2 H), 7.08-7.05 (m, 1 H), 6.89 (brs, 1 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 12.0 Hz, 1 H), 4.39 (dd, *J* = 1.2, 6.8 Hz, 1 H), 4.11-4.07 (m, 1 H), 4.02 (dd, *J* = 6.8, 10.4 Hz, 1 H), 3.87 (dd, *J* = 1.8, 10.8 Hz, 1 H), 3.76 (dd, *J* = 5.6, 10.7 Hz, 1 H), 1.04-0.74 (m, 28 H, 4 x Si(C*H*(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.1, 138.6, 137.8, 128.4, 127.9, 127.7, 126.5, 124.9, 106.3, 79.2, 75.1, 73.7, 72.8, 68.8, 17.3 (Si(CH)(*C*H_3)(CH$_3$)), 17.2 (Si(CH)(*C*H_3)(CH$_3$)), 17.1 (Si(CH)(*C*H_3)(CH$_3$)), 17.0 (Si(CH)(*C*H_3)(CH$_3$)), 16.9 (Si(CH)(*C*H_3)(CH$_3$)), 16.8 (Si(CH)(*C*H_3)(CH$_3$)), 12.9 (Si(*C*H(CH$_3$)$_2$), 12.7 (Si(*C*H(CH$_3$)$_2$), 12.3 (Si(*C*H(CH$_3$)$_2$), 12.2 (Si(*C*H(CH$_3$)$_2$); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{47}O_5SSi_2$ 587.2677; Found 587.2677.



2-(*p*-tolylthio)-D-galactal-3,4,6-triol (4)

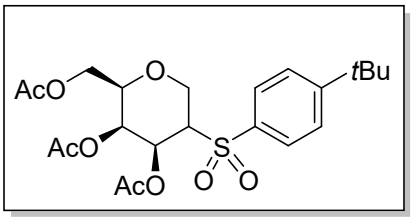
To a solution of **3a** (100 mg, 0.25 mmol) in methanol (5 mL) and K_2CO_3 (42 mg, 0.30 mmol) was added. The reaction mixture was stirred at rt until consumption of starting material (30 min). Then, acidic ion exchange resin (Dowex Wx8) was added until neutral, the resin filtered off, and the solvent removed. The crude product was purified by column chromatography (CH_2Cl_2:MeOH 13:1) to give compound **4** (249 mg, yield 93%) as a white solid. IR (neat): 3313, 2952, 2924, 1617, 1419, 1247, 1154, 1128, 1103, 1077, 1001, 915, 888, 859, 838, 823, 753, 690 cm^{-1} ; $[\alpha]_D^{25}$ +0.20 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, CD_3OD): δ 7.23 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.88 (s, 1 H), 4.18 (d, *J* = 4.3 Hz, 1 H), 4.12-4.09 (m, 1 H), 4.04 (dd, *J* = 1.9, 4.3 Hz, 1 H), 3.90 (dd, *J* = 6.9, 11.7 Hz, 1 H), 3.80 (dd, *J* = 4.8, 11.7 Hz, 1 H), 2.28 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, MeOD): δ 151.3, 135.3, 133.9, 129.1, 127.3, 107.1, 78.5, 65.9, 65.2, 60.4, 19.5; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}NaO_4S$ 291.0662; Found 291.0660.

(*2R,3S,4S*)-2-(acetoxymethyl)-5-((4-(*tert*-butyl)phenyl)sulfinyl)-3,4-dihydro-2H-pyran-3,4-diyl diacetate (5)

To a solution of KF (117 mg, 2.0 mmol) in CH_3CN–H_2O (4.0 ml; v/v 5:1), 70% *m*-CPBA (345 mg, 2.0 mmol) was added and the reaction mixture was stirred at 0ºC for 30 min. To the ice-cooled reaction mixture was added (**3k**; 440 mg, 1.0 mmol) and the mixture was stirred at 0ºC for 30 min. After completion of the reaction, it was quenched with aq $FeSO_4$ solution and extracted with CH_2Cl_2. The organic layer was washed with aq $NaHCO_3$ and water successively, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified over SiO_2 using hexane-EtOAc (6:1) as eluent to give pure compound **5** (399, 88% yield) as colorless oil; IR (neat): 2930, 2216, 1716, 1667, 1426, 1216, 1039, 760, 669 cm^{-1} ; $[\alpha]_D^{25}$ +21.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.6 Hz, 2 H), 7.74 (s, 1 H), 7.53 (d, *J* = 8.6 Hz, 2 H), 5.89-5.88 (m, 1 H), 5.35 (t, *J* = 4.1 Hz, 1 H),4.53-4.49 (m, 1

H), 4.37 (dd, *J* = 8.5, 12.3 Hz, 1 H), 4.24 (dd, *J* = 3.7, 12.4 Hz, 1 H), 2.09 (s, 3 H), 1.98 (s, 3 H), 1.74 (s, 3 H), 1.34 (s, 9 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.2, 169.1, 157.1, 155.2, 138.1, 127.4, 126.1, 114.2, 74.1, 64.1, 61.1, 35.2, 31.1, 20.7, 20.3, 20.2; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{32}NO_8S$ 470.1843; Found 470.1840.

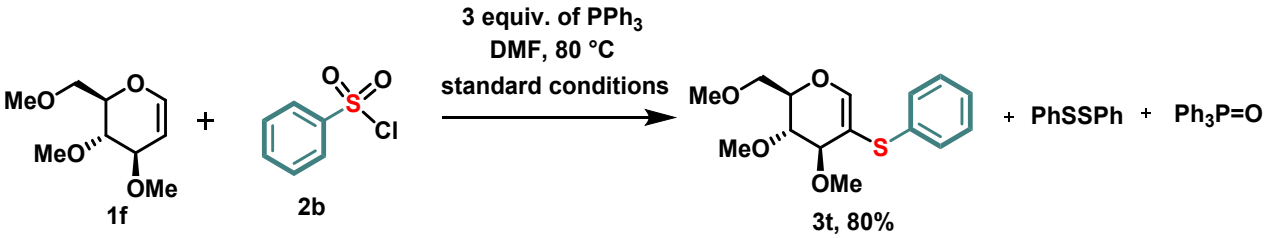
(*2R,3S,4S*)-2-(acetoxymethyl)-5-((4-(*tert*-butyl)phenyl)sulfonyl)tetrahydro-2H-pyran-3,4-diyl diacetate (6)



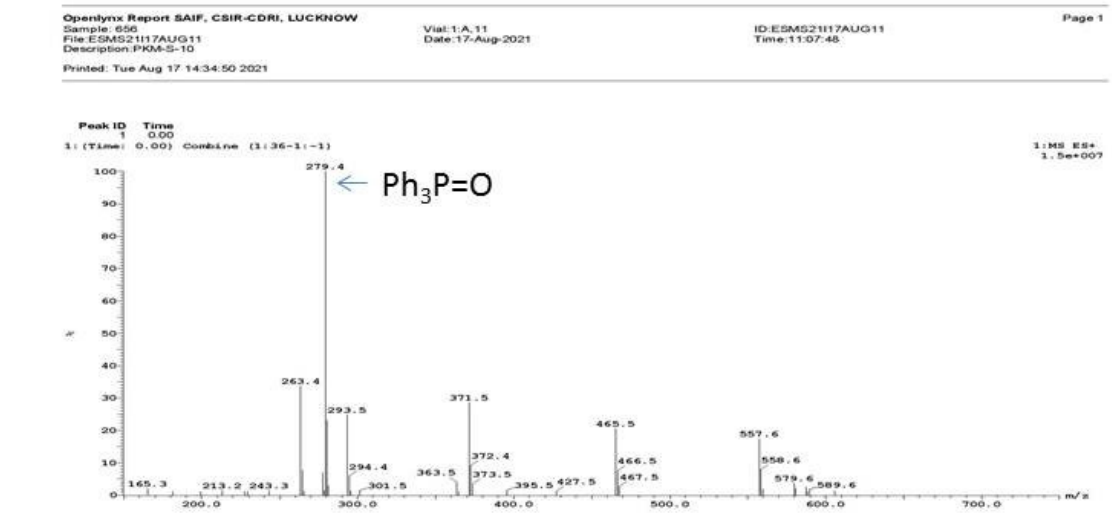
To a stirred solution of compound (**3k**, 1 equivalent) in freshly dried DCM (4 mL), 1.0 equivalent of *m*-CPBA were added to a stirred solution. The reaction mixture was cooled to −10 °C and allowed to stir for 30 min, after completion of the reaction diluted with 20 mL of DCM. The organic layer was washed with $NaHCO_3$ (aq.) and dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified over SiO_2 using hexane-EtOAc (3:1) as eluent to give pure compound **6** (330, 80% yield) as colorless oil; IR (neat): 2952, 2863, 1738, 1668, 1435, 1367, 1240, 1208, 1023, 944, 908, 767, 648 cm^{-1} ; $[\alpha]_D^{25}$ +25.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.7 Hz, 2 H), 7.59 (d, *J* = 8.7 Hz, 2 H), 5.69-5.65 (m, 1 H), 5.45-5.44 (m, 1 H), 4.99-4.96 (m, 1 H), 4.87 (d, *J* = 7.1 Hz, 1 H), 4.09 (dd, *J* = 7.5, 11.5 Hz, 1 H), 3.96 (dd, *J* = 5.2, 11.6 Hz, 1 H), 2.72 (ddd, *J* = 14.3, 5.0, 1.8 Hz, 1H), 2.40-2.32 (m, 1H), 2.11 (s, 3 H), 2.03 (s, 3 H), 2.02 (s, 3 H), 1.36 (s, 9 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 170.3, 169.9, 169.6, 158.3, 133.3, 128.9, 126.2, 88.4, 71.4, 65.9, 65.5, 62.6, 35.3, 31.0, 21.9, 20.8, 20.7, 20.6; HRMS (ESI) m/z: $[M + NH_4]^+$ Calcd for $C_{22}H_{34}NO_9S$ 488.1949; Found 488.1944.

1.6. Controlled experiments for the mechanistic investigation

It is noteworthy that no sulfonylating product was observed. In order to get some mechanistic insights, the reaction mixture was further investigated. In order to get some mechanistic insights, the reaction mixture was further investigated. Under the standard conditions, the coupling of **1f** with **2b** produced **3t** in 80% yield with a concomitant quantitative amount of triphenylphosphine oxide (Ph_3PO) and phenyldisulfide (Scheme 2). These results suggested that arylsulfonyl chloride was subjected to reduction by triphenylphosphine, which abstracted oxygen from arylsulfonyl chloride to generate the corresponding RS^+ equivalent (Scheme S3).


3 equiv. of PPh3
DMF, 80 °C
standard conditions
MeO
MeO
OMe
1f
2b
Cl
MeO
MeO
OMe
3t, 80%
PhSSPh
Ph3P=O

Scheme S2.


Openlynx Report SAIF, CSIR-CDRI, LUCKNOW
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Printed: Tue Aug 17 14:34:50 2021
Vial:1:A,11
Date:17-Aug-2021
ID:ESMS21I17AUG11
Time:11:07:48
Page 1
Peak ID Time
1 0.00
1: (Time: 0.00) Combine (1:36-1:-1)
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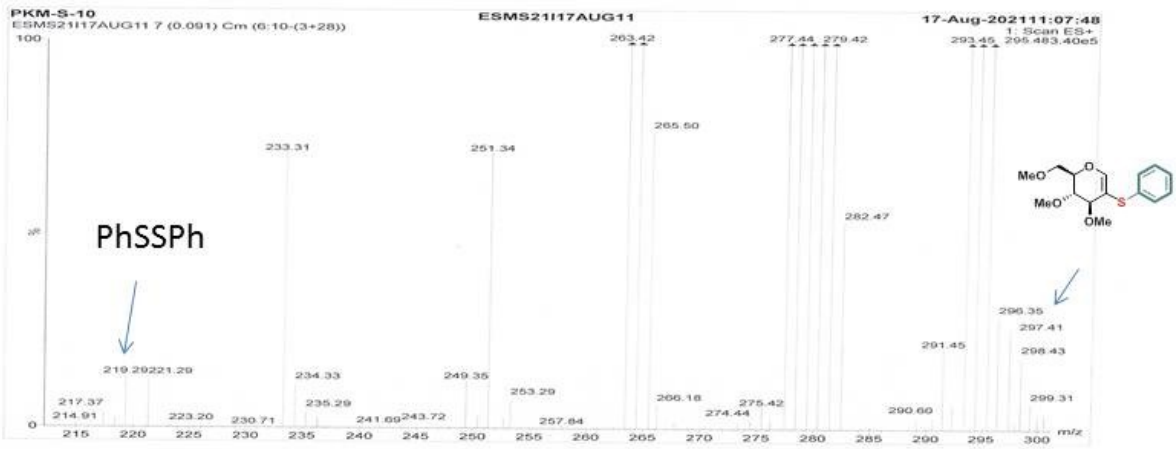
263.4
293.5
371.5
465.5
557.6
m/z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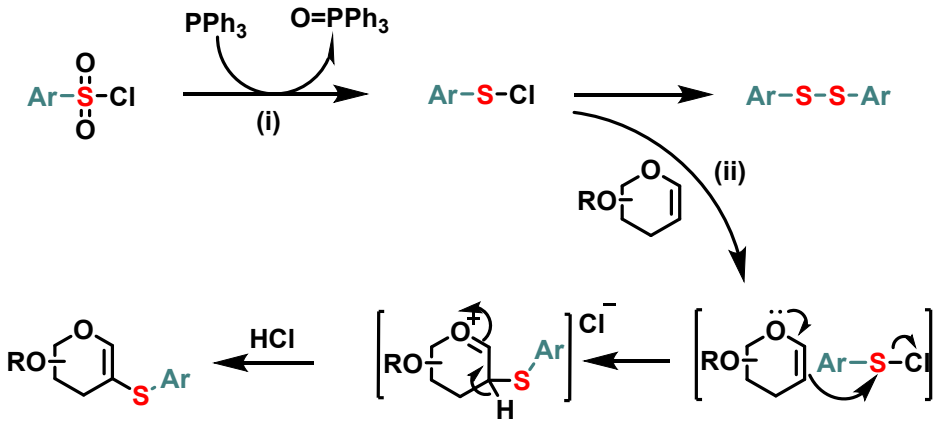
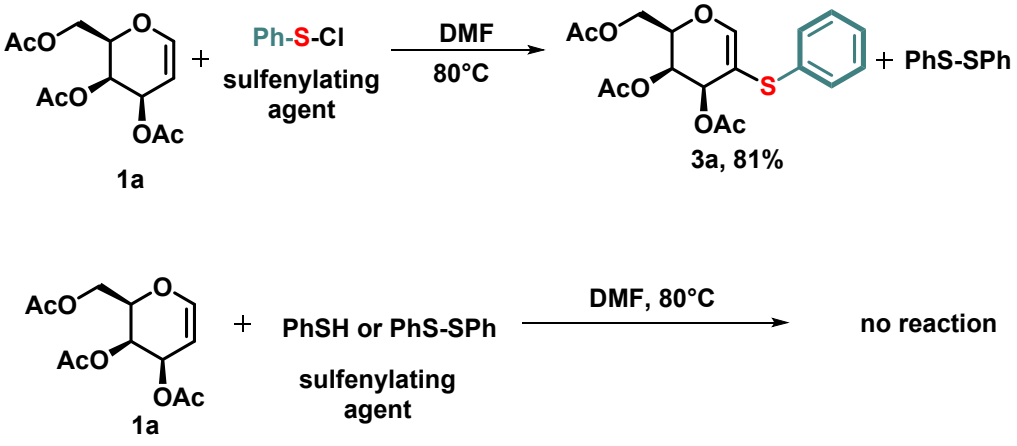
17-Aug-202111:07:48
1: Scan ES+
PhSSPh
263.42
277.44
279.42
265.50
233.31
251.34
282.47
MeO
MeO
OMe
296.35
297.41
298.43
291.45
299.31
m/z



Scheme S3. Proposed mechanism

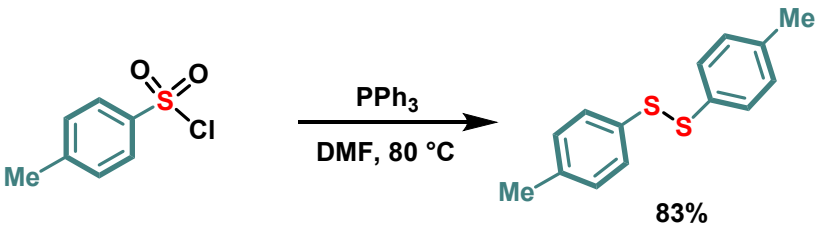
Sulfenylation of peracetylated galactal 1a with various sulfenylating agents

Under an N_2 atmosphere, a reaction tube (15 mL) equipped with a magnetic stir bar was charged with peracetylated galactal **1a** (100 mg, 0.37 mmol) sulfenylting agent (1.10 mmol), and DMF (2.5 mL). The mixture was stirred for 5 min at room temperature, and then heated at 80 °C for 3 h. Purification was via silica gel column chromatography (Scheme 4).



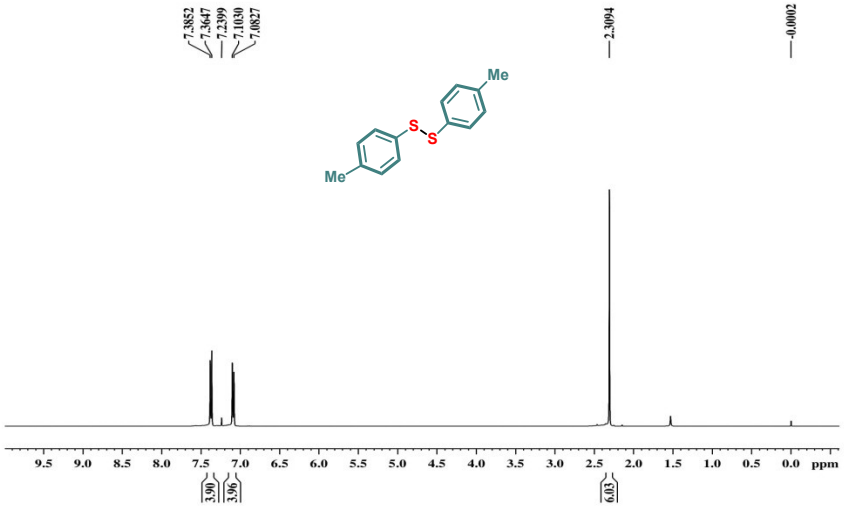
Scheme S4.

Reduction of *p*-tosylsulfonyl chloride to 1, 2-di-*p*-tolyl disulfide[2]

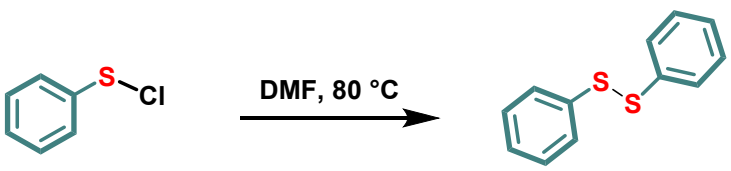


Scheme S5.

Under an N_2 atmosphere, a reaction tube with a magnetic stirring bar was charged with *p*-tolylsulfonyl chloride (100 mg, 0.5 mmol), PPh_3 (411 mg, 1.5 mmol) and DMF (2.5 mL). The mixture was stirred for 5 min at room temperature, and then heated at 80 °C for 3 h (Scheme 5). Purification via silica gel column chromatography afforded 1, 2-di-*p*-tolyl disulfide as a white solid (83% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.6 Hz, 4 H), 7.09 (d, J = 7.6 Hz, 4H), 2.31 (s, 6H).

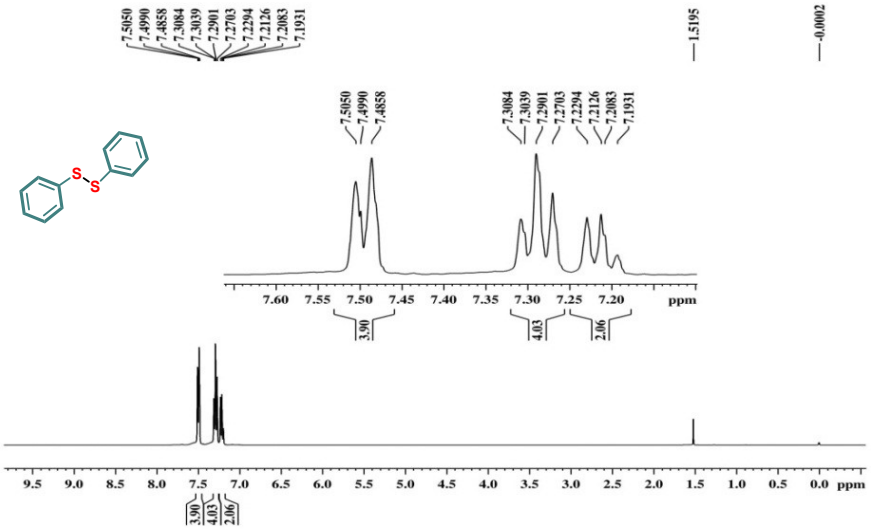


Homocoupling of benzenesulfenyl chloride[3]



Scheme S6.

Under an N_2 atmosphere, a reaction tube with a magnetic stirring bar was charged with benzenesulfenyl chloride (28.2 μL, 0.3 mmol) and DMF (1.5 mL). The mixture was stirred for 5 min at room temperature, and then heated at 80 °C for 3 h. Purification via silica gel column chromatography afforded diphenyl disulfie as a white solid (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.6 Hz, 4H), 7.29 (t, J = 7.6 Hz, 4H), 7.23-7.19 (m, 2H).



1.7. X-Ray Data Collection and Structure Refinement Details for Compound 4 [4,5]

A good quality single crystal of size 0.38 x 0.11 x 0.02 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **4** were collected on the Rigaku Kappa 3 circle diffractometer equipped with the AFC12 goniometer and enhanced sensitivity (HG) Saturn724+ CCD detector in the 4x4 bin mode using the monochromated Mo-Kα radiation generated from the microfocus sealed tube MicroMax-003 X-ray generator equipped with specially designed confocal multilayer optics. Data collection was performed using ω-scans of 0.5^o steps at 293(2) K. Cell determination, data collection and data reduction was performed using the Rigaku CrystalClear-SM Expert 2.1 b24[1] software. Structure solution and refinement were performed by using SHELX-97[2].

Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

Crystallization: The compound **4** (5mg) was dissolved in a 1ml mixture of MeOH/DCM (1:2) and placed in a cabinet to evaporate slowly. After two days, **4** was obtained as white crystals.

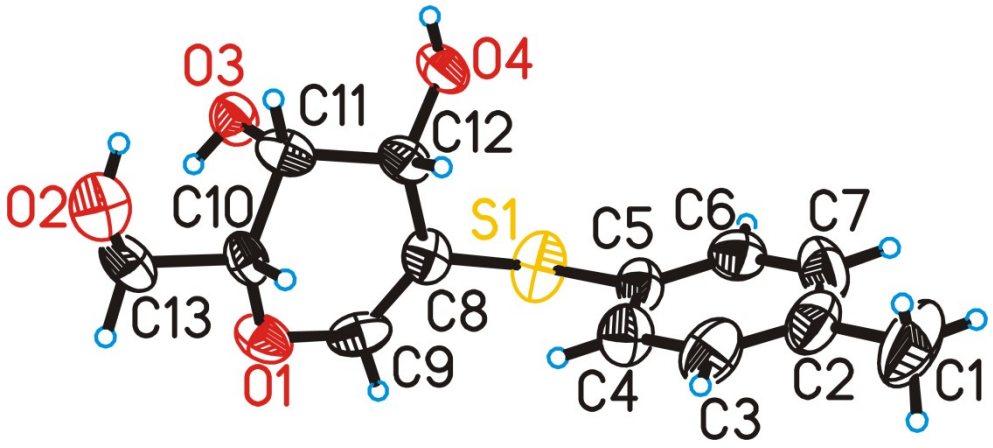
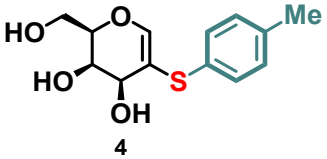


Figure S1. ORTEP diagram drawn with 50% ellipsoid probability of for non-H atoms of one molecule of the asymmetric unit of the crystal structure of compound **4** determined at 293 K.

Table S4. Crystal data and structure refinement details for **4**.



4

Compound	**4**
Empirical formula	$C_{13}H_{16}O_4S$
Formula weight	268.32
Crystal System	Monoclinic
Space group	$P\,2_1$

a (Å)	5.572(2)
b (Å)	18.599(7)
c (Å)	18.753(8)
α (°)	90.00
β (°)	92.336(8)
γ (°)	90.00
V (Å^3)	1941.8(13)
Z	6
D_c (g/cm^3)	1.377
F_{000}	852
μ (mm^{-1})	0.254
θ_{max} (°)	25.42
Total reflections	12093
Unique reflections	5586
Reflections [$I > 2\sigma(I)$]	2944
Parameters	487
R_{int}	0.1034
Goodness-of-fit	0.919
R [$F^2 > 2\sigma(F^2)$]	0.0713
wR (F^2, all data)	0.1719
CCDC No.	2102357

1.8. Computational Study (DFT and MD study)

Gaussian G09 program[6] were used for all the computational calculation by using hybrid B3LYP[7,8] functional with a 6-311G++(d,p) basic set,[9] in gaseous phase, for validating and understanding the experimental results towards the formation of regioselective 2-S-aryl-glycosides. The frequency calculations were carried out for confirming that these optimized structures are real minima on the potential energy surface with all positive frequencies and transition state (TS) with one imaginary frequency. The Intrinsic reaction coordinates (IRC) were also performed, to verify the transition states fond connected the related reactant and products. Stationary points were characterized as minima (ground state), Transition state (TS-1/TS-2) via frequency calculation. As the reaction intermediate having two electrophilic site

at C1 and C2 position in tri-*O*-acetylated galactal, we were expecting different products with different mode of electrophilic addition reaction. In order to validate the possible regioselective intermolecular electrophilic addition reaction pathway, compound 1a were taken as a reactant. Compound 1a was taken as a reactant, with two different transition states with the electrophilic addition at C1 and C2 position. The reaction pathway leading to C2 position is slightly exergonic (2.14 kcal/mol) and presents lower activation energy (9.13 kcal/mol), whereas the electrophilic addition at C2 position passes through high activation (49.59 Kcal/mol). We have noticed that the intermolecular electrophilic addition and site-selective at C2 is the preferred site for the electrophilic addition, as it proceeds with a low activation barrier and forms a stable product.

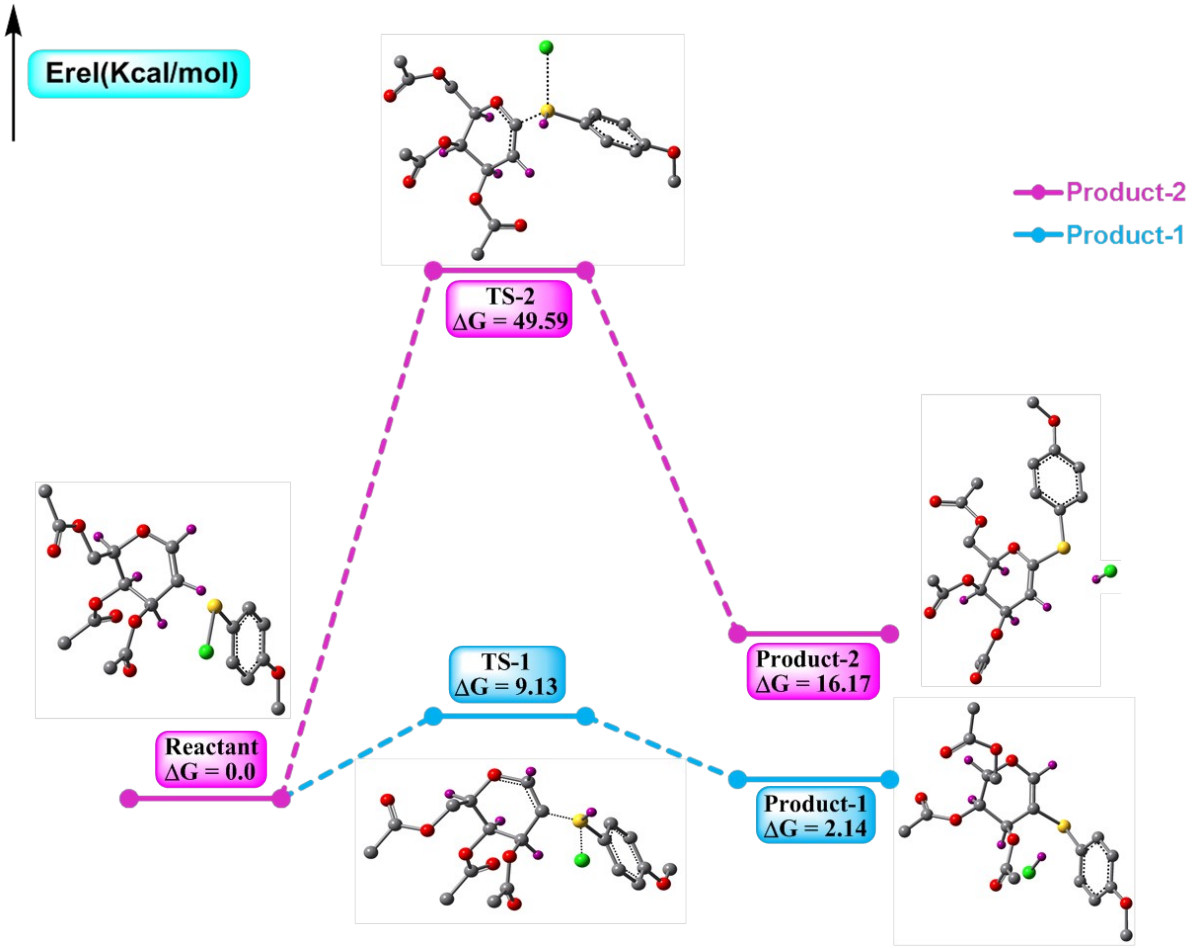
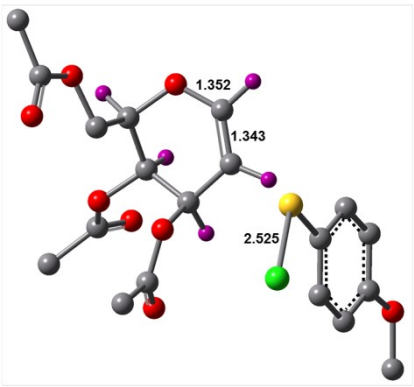


Figure S2: Comparative energy profile diagram for the agioselective intermolecular electrophilic addition reaction for **3e** at the B3LYP//6-311G++G(d,p) level of theory in the gas phase.

The absolute energy value E in Hartree, Cartesian coordinates xyz and name of the compound used in computational study

Reactant

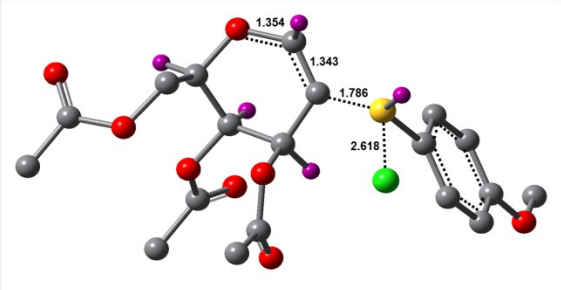


Reactant, E = -2198.517242

C	2.7092	1.4260	-0.1013
C	2.4521	0.3213	-1.1267
C	3.6806	-0.5654	-1.3259
C	4.8550	0.3655	-1.4937
C	4.8334	1.6491	-1.1059
O	3.7698	2.2513	-0.4976
C	2.9313	0.9442	1.3328
O	1.3340	-0.4245	-0.7359
O	0.7141	-0.8443	-2.8920
C	0.5423	-0.9677	-1.7003
C	-0.5915	-1.7438	-1.0613
O	3.9182	-1.4047	-0.2208
O	2.6515	-3.1026	-1.0727
C	3.3431	-2.6369	-0.1961
C	3.6711	-3.3375	1.1065
O	2.6936	2.0049	2.2241
O	2.7426	0.5700	3.9959
C	2.5891	1.6816	3.5419
C	2.2187	2.9043	4.3569
H	1.7975	2.0771	-0.0872
H	2.2261	0.8419	-2.0908
H	3.5791	-1.1687	-2.2576
H	5.7613	-0.0419	-1.9721
H	5.7175	2.2863	-1.2811
H	3.9728	0.5794	1.4838
H	2.2151	0.1218	1.5630
H	-1.3124	-2.0918	-1.8346
H	-0.1947	-2.6361	-0.5262
H	-1.1451	-1.1044	-0.3367
H	3.4510	-2.6783	1.9769
H	3.0635	-4.2637	1.2149
H	4.7464	-3.6233	1.1303
H	1.3039	3.3879	3.9447
H	3.0550	3.6393	4.3505
H	2.0092	2.6205	5.4131
C	8.6576	0.0699	-0.4017
C	8.8317	-1.3135	-0.3852
C	10.0946	-1.8489	-0.6342
C	11.1638	-0.9922	-0.9020
C	11.0253	0.4034	-0.9427
C	9.7421	0.9073	-0.6739
S	7.4247	-2.4103	-0.0337
Cl	6.7064	-3.1443	-1.7616
O	12.1372	1.1654	-1.2012
C	12.0256	2.5667	-1.1124
H	7.6678	0.5091	-0.1977
H	10.2571	-2.9387	-0.6192
H	12.1577	-1.4315	-1.0905
H	9.5475	1.9908	-0.6710
H	13.0291	3.0018	-1.3185

H	11.3176	2.9481	-1.8816
H	11.7200	2.8650	-0.0846

TS-1



TS-1, E = -2198.502699

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C	3.5596	2.2995	0.2663
C	3.7428	1.2171	-0.6883
C	4.7038	0.1490	-0.1493
C	4.9531	0.0969	1.1917
O	4.3735	0.8893	2.1546
C	1.9477	1.0222	1.8857
C	7.9589	-2.4438	-1.5219
C	7.3014	-1.2308	-1.2745
C	7.9884	-0.0543	-0.9370
C	9.3598	-0.1283	-1.2286
C	10.1349	-1.2344	-1.4828
C	9.3311	-2.3535	-1.5933
S	5.5129	-1.1822	-1.2293
Cl	4.4374	-2.7866	-0.7798
O	2.5062	3.1713	-0.0720
O	3.5659	3.9131	-2.0591
C	2.6284	3.8784	-1.2809
C	1.2678	4.5633	-1.5308
O	2.5071	0.7094	-0.9806
O	2.9283	0.1181	-3.1609
C	2.2001	0.1910	-2.1926
C	0.9625	-0.5928	-2.0422
O	0.8758	1.4124	1.1407
O	-0.5649	0.5981	2.7236
C	-0.3215	1.1817	1.7114
C	-1.3050	1.7146	0.6688
O	11.4918	-1.0350	-1.6957
C	12.2872	-2.2203	-1.8081
H	3.3110	2.6817	2.4018
H	4.5482	2.9202	0.3373
H	4.3627	1.6248	-1.5255
H	5.6496	-0.7049	1.6282
H	2.0551	-0.0901	1.6008
H	1.6571	1.1017	3.0043
H	7.3669	-3.3884	-1.6415
H	7.4903	0.8707	-0.5652
H	9.8831	0.8390	-1.2233
H	9.7827	-3.2928	-1.7839
H	5.1198	-0.8749	-2.4540
H	0.8922	5.2926	-0.7095
H	1.5368	5.0539	-2.4872
H	0.5009	3.8014	-1.7906
H	0.0220	-0.2033	-2.7490
H	1.3068	-1.6823	-2.1826
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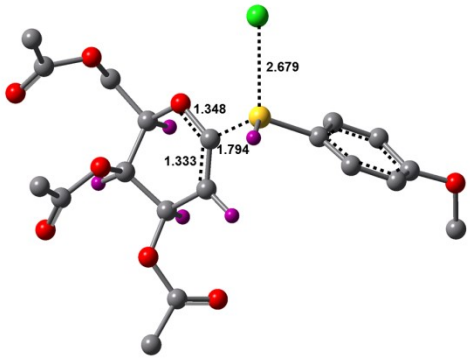
H	-2.2883	1.2285	0.7570
H	-0.9308	1.5501	-0.3229
H	-1.5772	2.8495	0.7847
H	13.3734	-2.0274	-1.5776
H	12.0010	-3.0230	-1.1939
H	12.1133	-2.6247	-2.8334

TS-2



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C	-5.1042	-1.1233	1.1097
C	-3.9695	-1.1056	0.2084
C	-3.8845	-0.3996	-0.9269
O	-4.9568	0.3396	-1.3711
C	-5.6241	1.8526	0.1167
C	-0.4977	1.6994	-1.8922
C	-1.4595	1.0393	-1.1578
C	-1.7779	1.3199	0.2188
C	-1.0682	2.3200	0.8064
C	-0.1634	3.0963	0.0401
C	0.1935	2.6939	-1.2474
S	-2.3850	-0.3961	-1.9980
Cl	-2.7133	-0.0736	-3.9278
O	0.6095	3.9603	0.7686

C	0.1348	5.2941	0.8060
O	-7.4396	-0.4642	1.0829
O	-8.5927	-2.1976	0.3251
C	-8.4382	-1.3186	1.0870
C	-9.1691	-1.2045	2.4435
O	-5.4797	-2.3788	1.5907
O	-3.6509	-2.6279	2.9678
C	-4.6193	-3.0697	2.4597
C	-5.0957	-4.5328	2.5505
O	-6.5664	2.2421	1.0769
O	-8.0652	2.8676	-0.6691
C	-7.7098	2.7258	0.5195
C	-8.6750	3.1788	1.5756
H	-6.9733	0.7558	-1.3187
H	-6.7090	-1.4338	-0.5715
H	-5.0084	-0.4212	1.9576
H	-3.1094	-1.7740	0.4641
H	-5.6193	2.6692	-0.5982
H	-4.5663	1.8695	0.4775
H	-0.2994	1.4280	-2.9757
H	-2.5251	0.7318	0.8028
H	-1.2920	2.4823	1.8516
H	0.9734	3.2983	-1.8069
H	-1.6617	-1.4823	-1.9214
H	-0.7415	5.3569	1.5084
H	1.0156	5.9600	0.9710
H	-0.1455	5.5897	-0.2263
H	-8.6997	-1.8882	3.1092
H	-9.2417	-0.1661	2.7725
H	-10.1907	-1.6067	2.4157
H	-4.5630	-5.3586	2.0839
H	-5.5636	-4.7244	3.5147
H	-5.9980	-4.6262	1.8811
H	-9.4543	2.4717	1.9441
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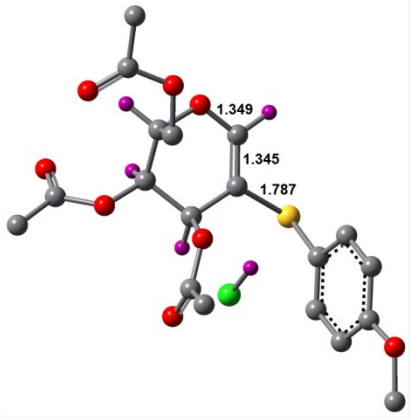
H	-9.2460	4.0405	1.3405

Product-1



Product-1, E = -2198.51383

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C	-2.9793	1.6434	-0.5469
C	-2.9331	2.5529	0.4357
O	-4.0927	3.0751	0.9977
C	-5.7584	1.3517	1.5011
C	-1.9247	-0.9832	0.7985
C	-0.9892	-0.4577	-0.0696
C	0.2108	-1.1931	-0.2973
C	0.3977	-2.4236	0.4422
C	-0.5977	-2.9296	1.2817
C	-1.7739	-2.2345	1.4344
S	-1.3318	1.1093	-1.0646
Cl	-1.3748	0.2542	-3.7299
O	-0.6063	-4.2447	1.7591
C	0.4192	-4.5646	2.6307
O	-5.9772	1.7292	2.8678
O	-8.2248	1.8223	2.4909
C	-7.2666	2.0507	3.2252
C	-7.3374	2.7017	4.5767
O	-4.6637	-0.0887	-0.8529
O	-5.5423	-0.6282	-2.8125
C	-5.2041	-1.0071	-1.7217
C	-5.4185	-2.4215	-1.1262
O	-6.5895	1.7443	-1.2775
O	-7.5262	3.7694	-0.7943
C	-7.5435	2.6956	-1.3589
C	-8.6779	2.1062	-2.2937
H	-6.0704	3.3221	0.9224
H	-5.1435	3.1512	-1.4686
H	-4.0232	1.1209	-2.3846
H	-1.9008	2.8988	0.8918
H	-6.5907	0.6924	1.1141
H	-4.9711	0.5652	1.6066
H	-2.8144	-0.3366	1.0226
H	1.0693	-0.7957	-0.8703
H	1.3294	-2.9574	0.2721
H	-2.5944	-2.6324	2.0733
H	0.2414	-5.4629	3.1937
H	1.4107	-4.6598	2.0126
H	0.4702	-3.7133	3.3351
H	-6.9365	1.9908	5.3016
H	-6.6785	3.6019	4.5098
H	-8.3844	2.9059	4.8648
H	-5.8157	-3.2115	-1.8678
H	-4.4004	-2.6928	-0.7737
H	-6.1693	-2.3994	-0.2506
H	-9.0685	2.9073	-2.8846
H	-9.4546	1.6951	-1.6363
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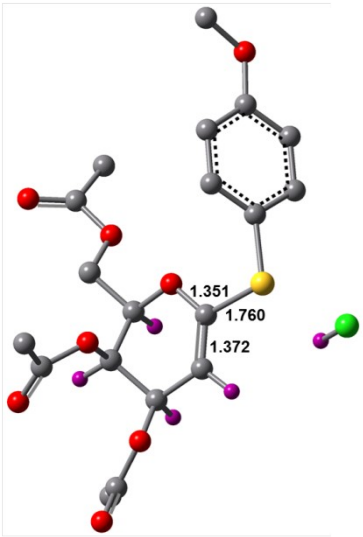
H	-0.0848	0.2544	-3.7299

Product-2



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C	2.6015	-2.2487	0.3033
C	3.8111	-3.1860	0.3229
C	5.0215	-2.3396	0.6343
C	5.0248	-1.0046	0.4442
O	3.9785	-0.2937	-0.0753
C	1.7059	-0.1317	-0.7758
S	6.5595	-0.1388	0.9283
C	6.1738	1.5612	0.4190
C	6.9134	2.1609	-0.6003
C	6.6422	3.4810	-0.9639
C	5.6346	4.2438	-0.3545
C	4.9260	3.6160	0.6829
C	5.1827	2.2980	1.0682
O	2.3061	-1.7888	1.5952
O	0.6601	-3.3407	1.8832
C	1.3260	-2.4194	2.2983
C	1.1980	-1.8077	3.6781
O	3.6731	-4.1944	1.2982
O	2.9351	-6.2192	1.9541
C	3.0571	-5.3911	1.0756
C	2.5685	-5.6647	-0.3354
O	1.9666	0.7792	-1.8126
O	-0.1533	1.5990	-1.6500
C	0.9350	1.5869	-2.1793
C	1.3310	2.4469	-3.3618
O	5.4617	5.5456	-0.7545
C	4.6293	6.3784	0.0186
H	3.2231	-1.4272	-1.5955
H	1.7213	-2.7705	-0.1344
H	4.0110	-3.6362	-0.6742
H	5.9054	-2.8586	1.0410
H	1.4865	0.4306	0.1613
H	0.8167	-0.7446	-1.0552
H	7.7224	1.6098	-1.1067
H	7.2528	3.9444	-1.7570
H	4.1401	4.1531	1.2360
H	4.6066	1.8508	1.8947
H	0.3870	-2.3077	4.2539
H	2.1494	-1.9266	4.2447
H	0.9525	-0.7241	3.6028
H	2.0206	-6.6341	-0.3617
H	1.8535	-4.8939	-0.6933
H	3.4214	-5.7641	-1.0435
H	1.6061	1.8054	-4.2299
H	0.4819	3.0990	-3.6686
H	2.1956	3.0973	-3.0980
H	4.6769	7.4031	-0.4141
H	4.9970	6.4260	1.0683
H	3.5740	6.0285	-0.0353
Cl	10.4158	-0.1313	0.1928
H	9.5366	-0.5708	-0.7214

Molecular Dynamics Study:-

Discovery studio 3.0 version,[10] using CHARMm4 force field with default parameters were used for the energy minimisation and molecular dynamics (MD) calculation. Volume integral of the Cross peak in NOESY spectra were taken as distance restrains in the simulated molecular dynamics using two-spin approximation with a reference of 1.80 Å for the geminal protons. Force constant of 10 K cal/Å and 5 K cal/Å were used for distance and torsional restraints respectively. Minimization was done with steepest descent algorithm followed by conjugate gradient methods for maximum 1000 iterations each. The molecules were initially equilibrated for 5pS and then subjected to 1 nS production run. Starting from 50 K, they were heated to 300 K in five steps increasing the temperature 50 K at each step. 10 structures were stored from the production run and are again energy minimized with the above mentioned protocol.

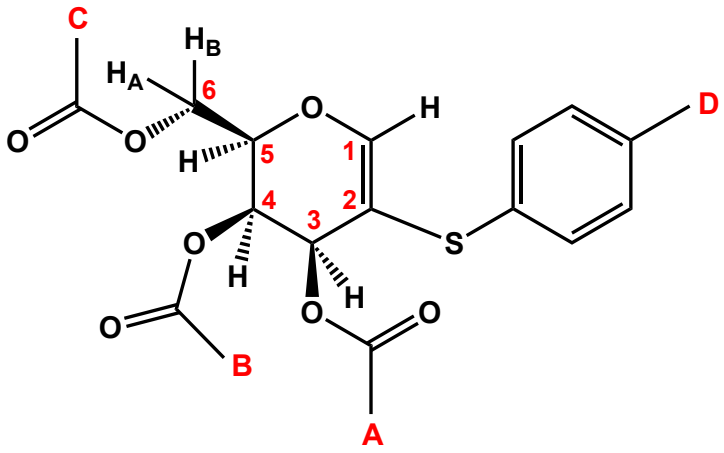


Table S5:- Distance constraints used in the MD calculation for **3a** derived from NOESY experiment in CD_3OD (500 MHz, 303K)

Residue	Atom	Residue	Atom	Upper bond	Lower bond
Sugar ring	H-3	Sugar ring	H-4	2.3	2.5
Sugar ring	H-4	Sugar ring	H-5	2.4	2.6
Sugar ring	H-5	Sugar ring	H_{6A}	2.4	2.6
Sugar ring	H-5	Sugar ring	H_{6B}	3.1	3.3
Sugar ring	H-3	Sugar ring	CH_{3A}	2.4	2.6

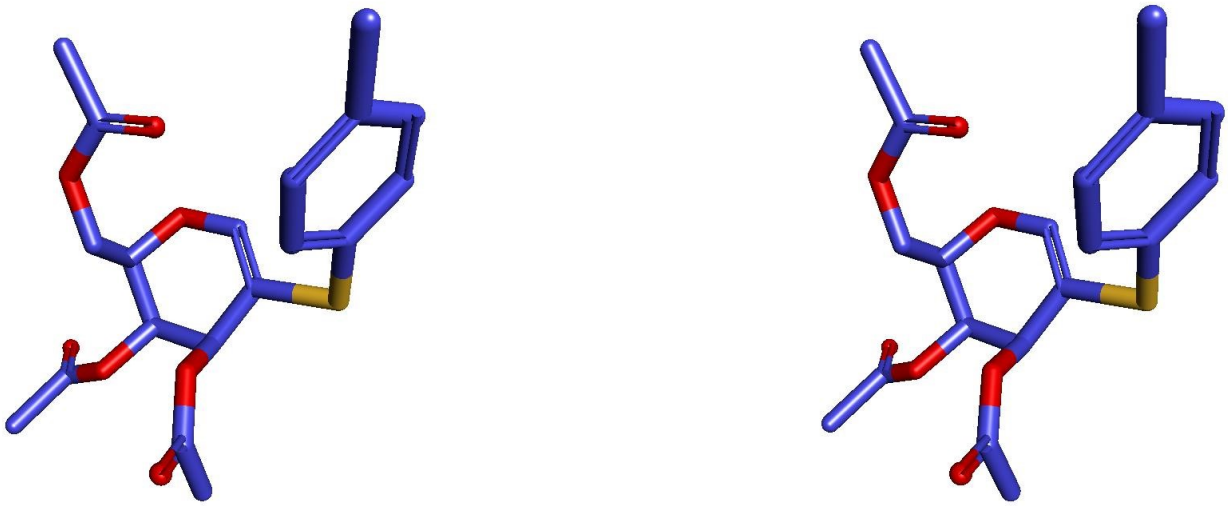


Figure S3: Stereo-view of the least energy conformations of **3a**.

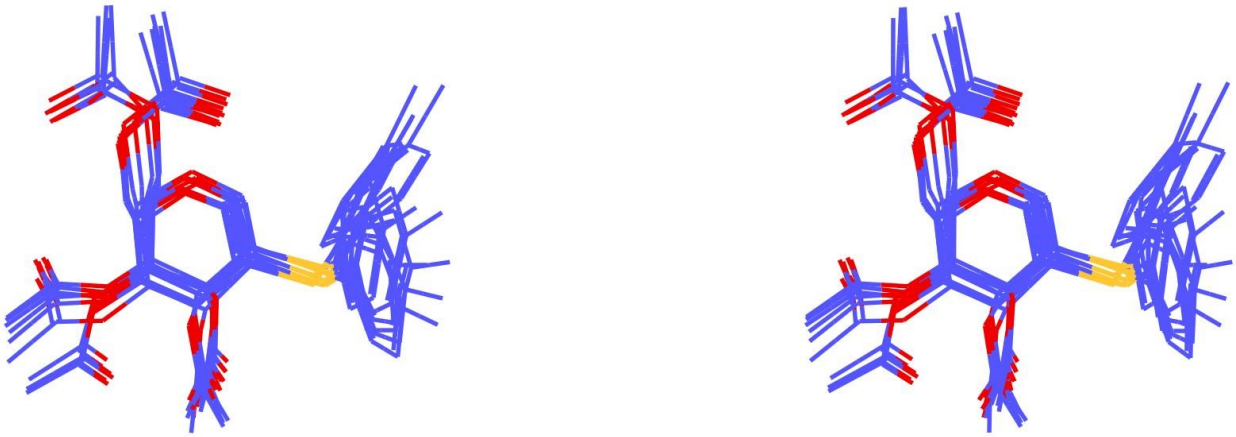
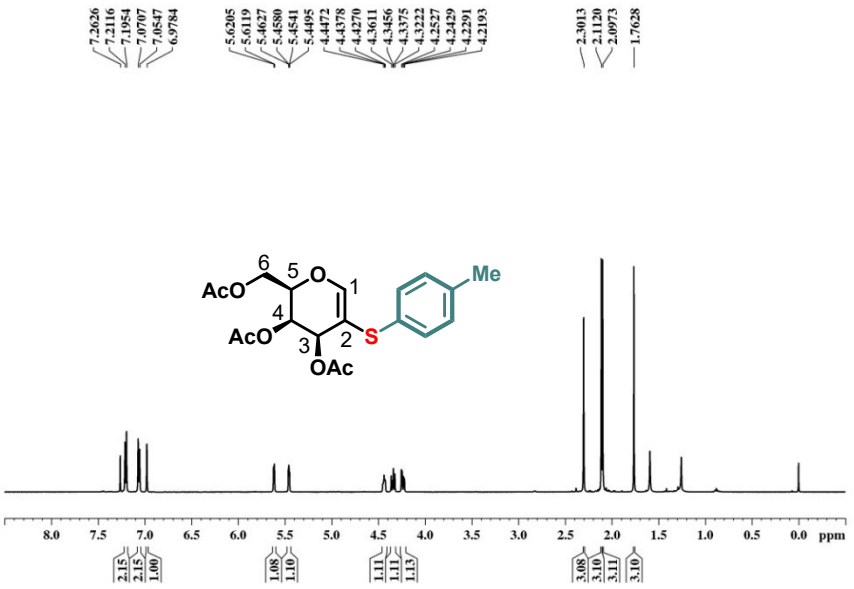


Figure S4: Stereo-view of the 10 superimposed least energy conformations of **3a**.

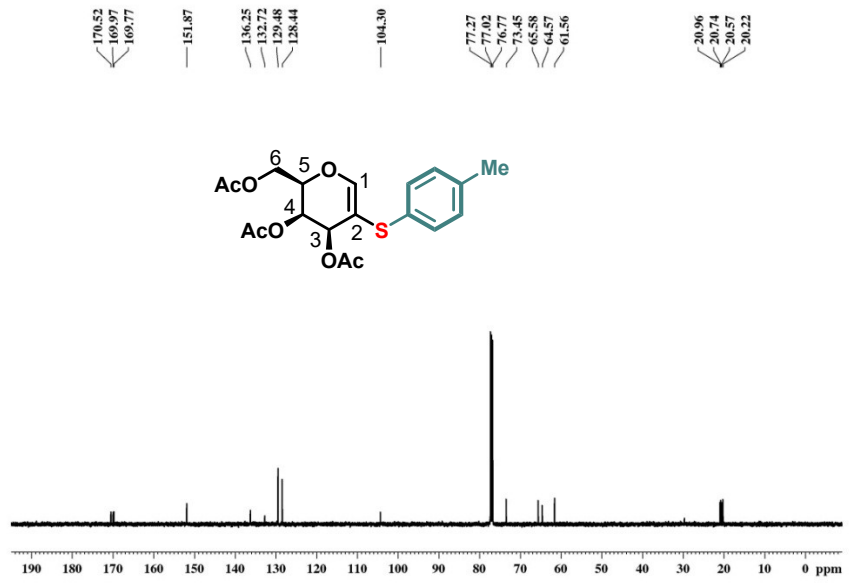
1.9. References

1. (a) Balmond, E. I.; Coe, D. M.; Galan, M. C.; McGarrigle, E. M. *Angew. Chem. Int. Ed.* **2012,** *51*, 9152-9155. (b) Wang, B.; Xiong, D. C.; Ye, X. S. *Org. Lett*., **2015**, *17*, 5698-5701. (c) Singh, A. K.; Kandasamy, J. *Org. Biomol. Chem***.**, **2018**,16, 5107-5112. (d) Balmond, E. I.; Benito-Alifonso, D.; Coe, D. M.; Alder, R. W.; McGarrigle, E. M. Galan, M. C.; *Angew. Chem. Int. Ed.***2014**, *53*, 8190-8194.
2. Liu, Y.; Zhang, Y. *Tetrahedron Lett.,* **2003**, *44*, 4291-4294.
3. Banfield, S. C.; Omori, A. T.; Leisch, H.; Hudlicky, T. *J. Org. Chem.*, **2007**, *72*, 4989-4992.
4. CrystalClear 2.1, Rigaku Corporation, Tokyo, Japan.
5. Sheldrick, G. M. Acta Crystallogr., Sect. A **2008**, *64*, 112–122.
6. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, K.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc. 2009, Wallingford CT.
7. Becke, A. D. *Phys. Rev*. A, **1988**, *38*, 3098-3100.
8. C. Lee, W. Yang and R. G. Parr, *Phys. Rev*. B: Condens. Matter, **1988**, *37*, 785- 789.
9. Hariharan P. C.; Pople, J. A.*Theort.chim. Acta*, **1973**, *28*, 213-222.
10. (a) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. CHARMM: A program for macro-molecular energy, minimization, and dynamics calculations. *J. Com-put. Chem*. **1983**, *4*, 187-217. (b) Siriwardena, A.; Pulukuri, K. K.; Kandiyal, P. S.; Roy, S.; Bande, O.; Ghosh, S.; Fernndez, J. M. G.; Martin, F. A.; Ghigo, J. M.; Beloin, C.; Ito, K.; Woods, R. J.; Ampa-pathi, R. S.; Chakraborty, T. K. Sugar-modified foldamers as conformationally defined and biologically distinct glycopeptide mimics. *Angew. Chem. Int. Ed*. **2013**, *52*, 10221-10226.

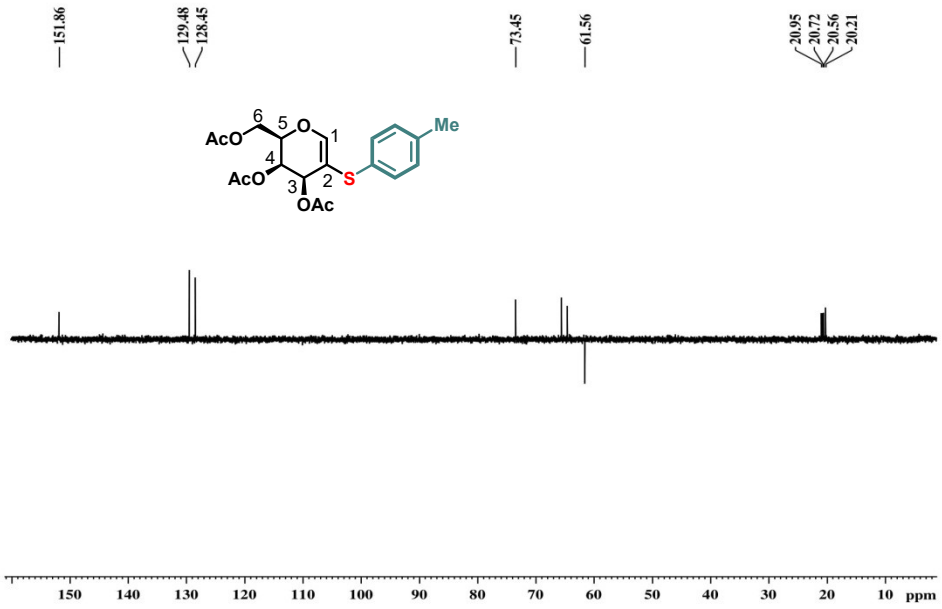
1.10. Copies of ^{1}H, ^{13}C, COSY, HSQC, and HRMS



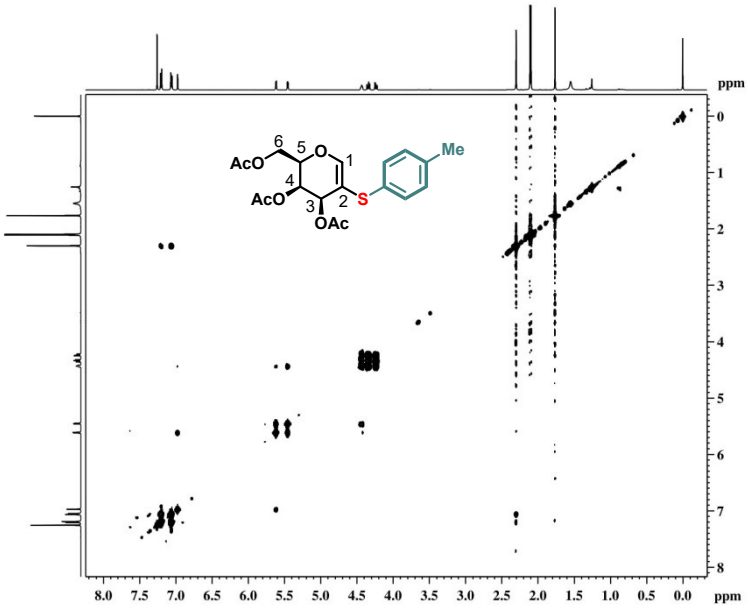
^{1}H NMR spectrum of **3a** (500 MHz, $CDCl_3$, 300 K)



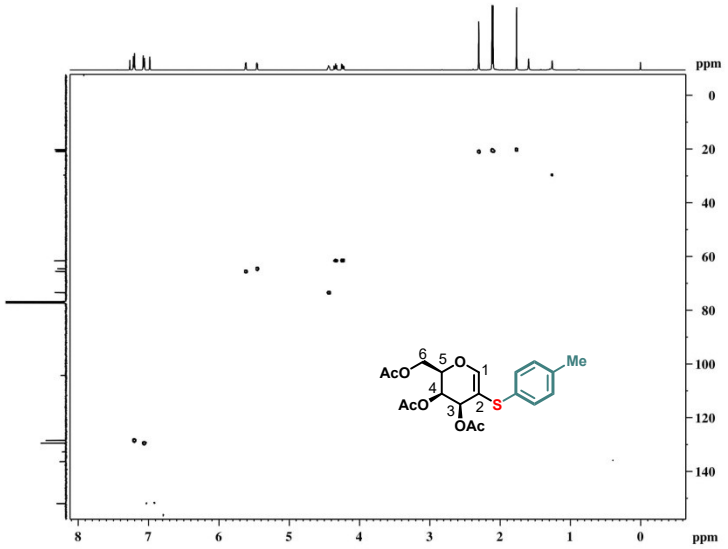
^{13}C NMR spectrum of **3a** (125 MHz, $CDCl_3$, 300 K)



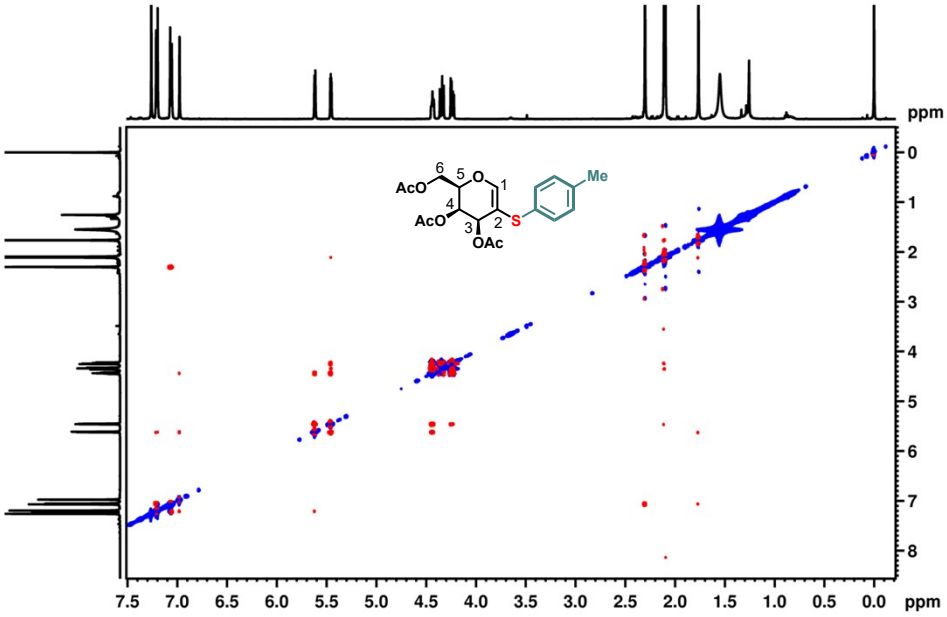
DEPT-135 NMR spectrum of **3a** (125 MHz, $CDCl_3$, 300 K)



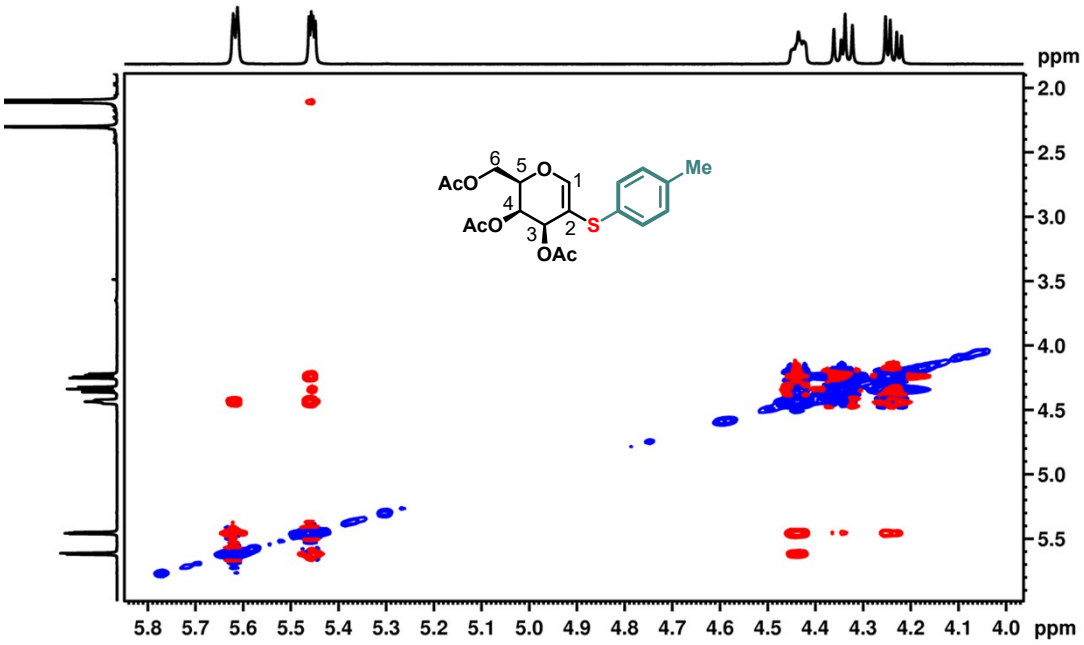
2D-COSY spectrum of **3a** (500 MHz, $CDCl_3$, 300 K)



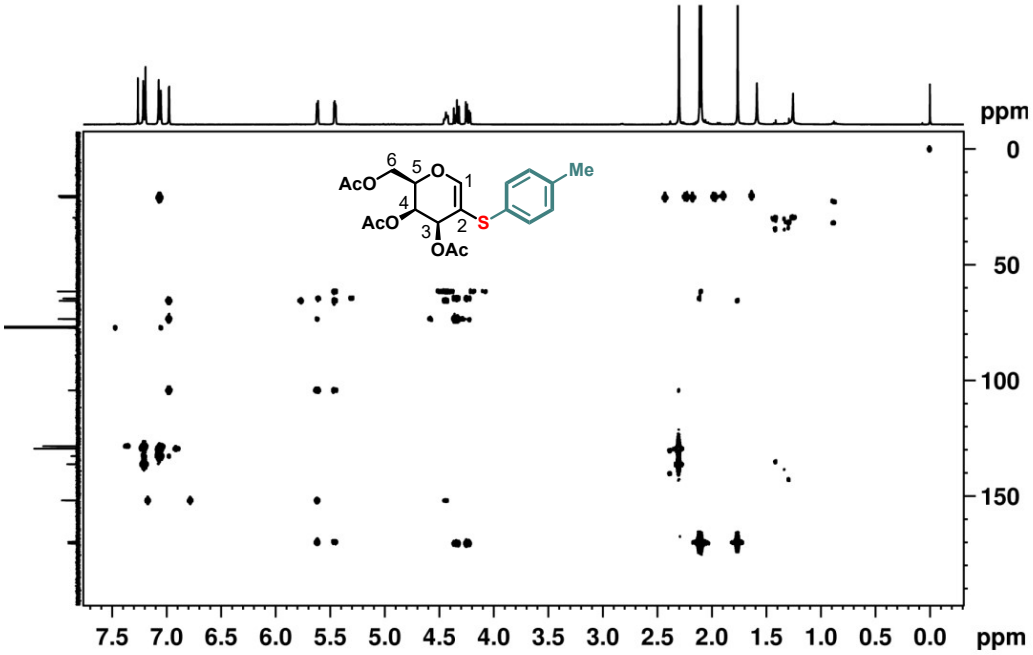
2D-HSQC spectrum of **3a** (500 MHz, $CDCl_3$, 300 K)



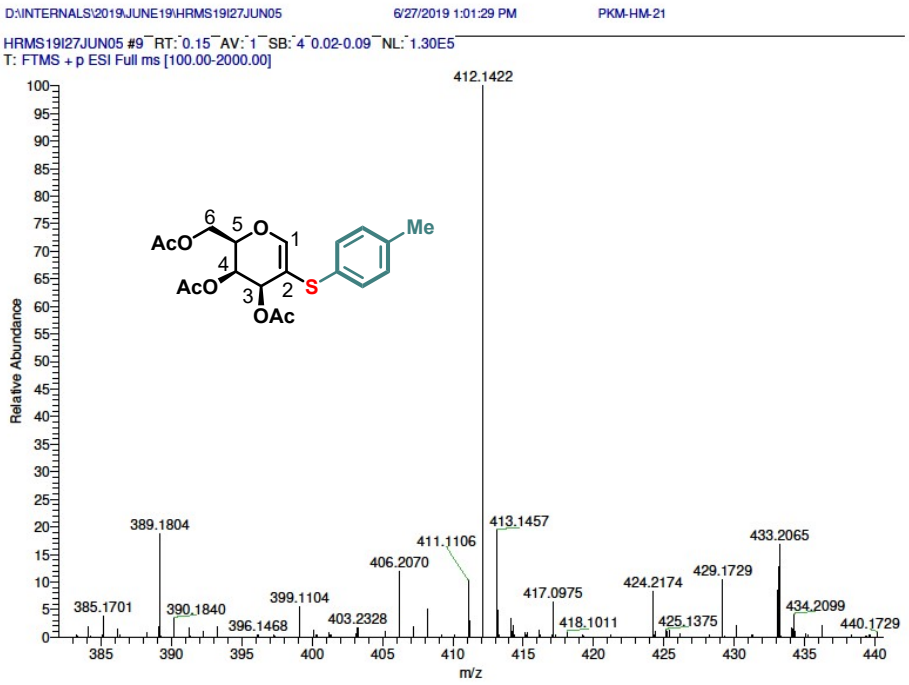
2D-NOESY spectrum of **3a** (500 MHz, $CDCl_3$, 300 K)



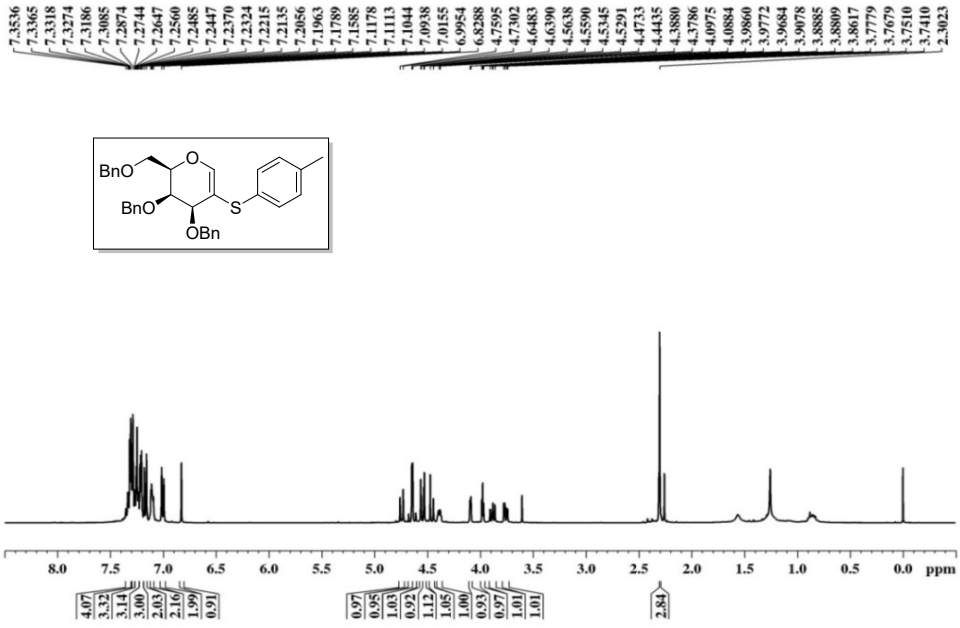
2D-NOESY Expansion spectrum of **3a** (500 MHz, $CDCl_3$, 300 K)



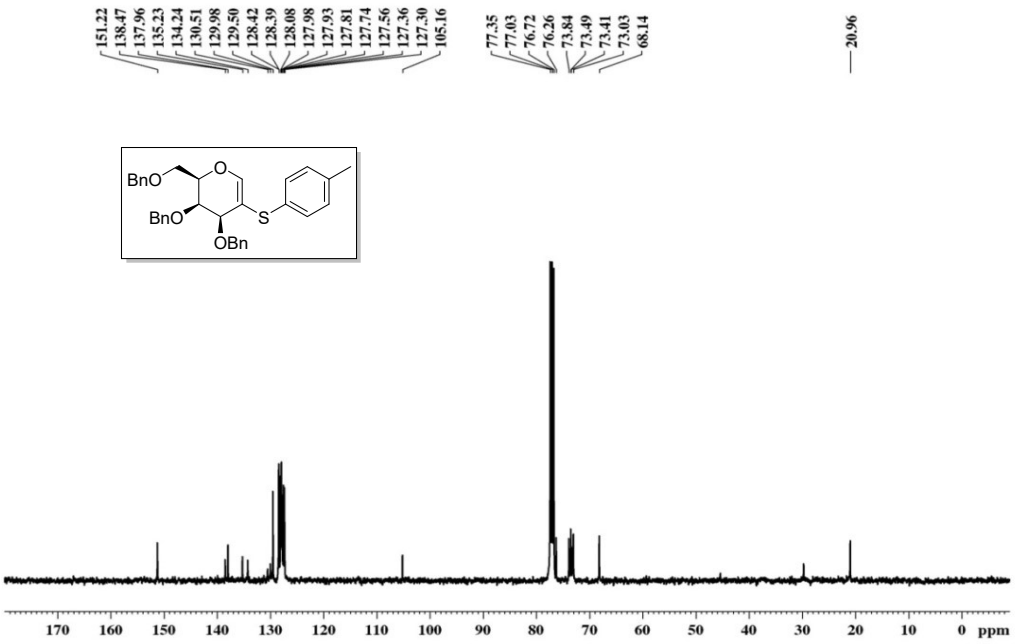
2D-HMBC spectrum of **3a** (500 MHz, $CDCl_3$, 300 K)



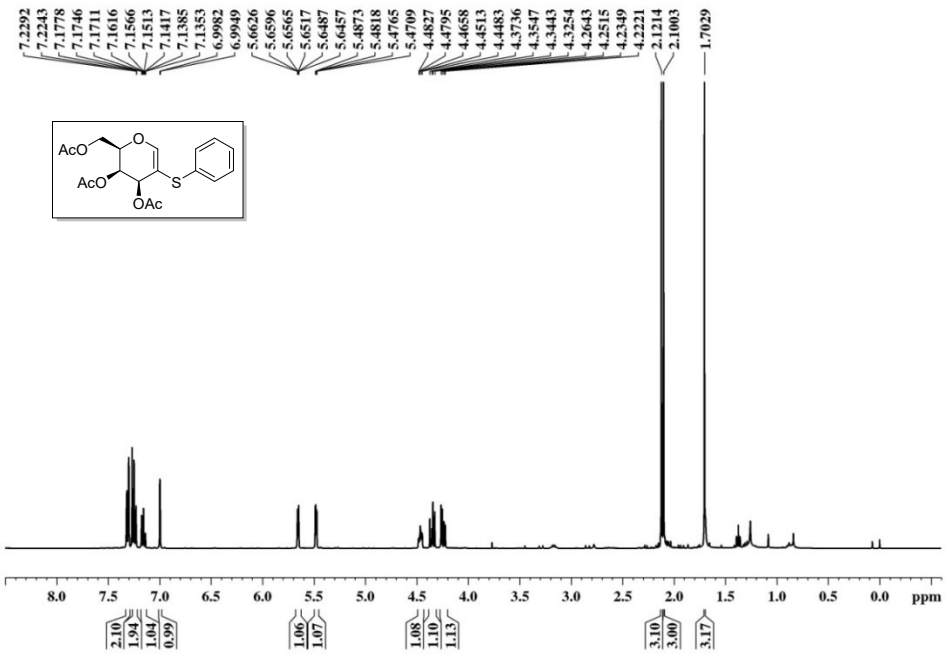
m/z: $[M + NH_4]^+$ Calcd for $C_{19}H_{26}NO_7S$ 412.1424; Found 412.1422
HRMS of **3a**



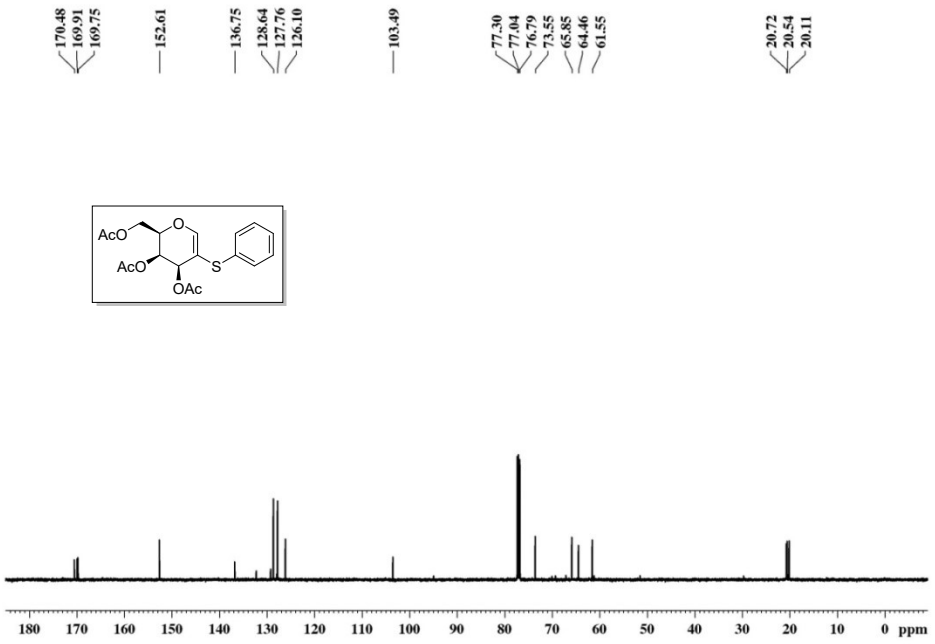
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$, 300 K)



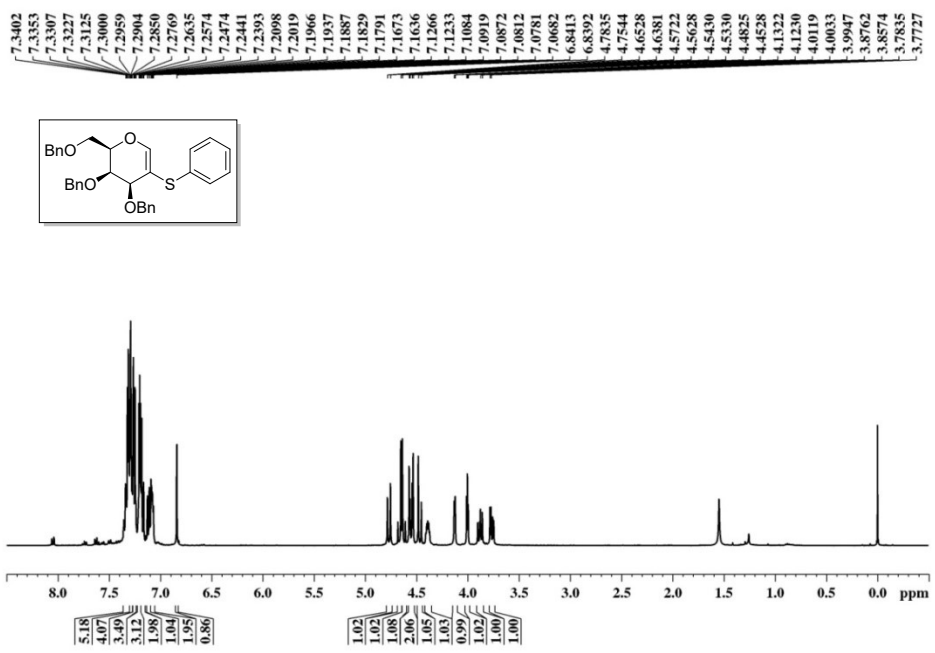
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$, 300 K)



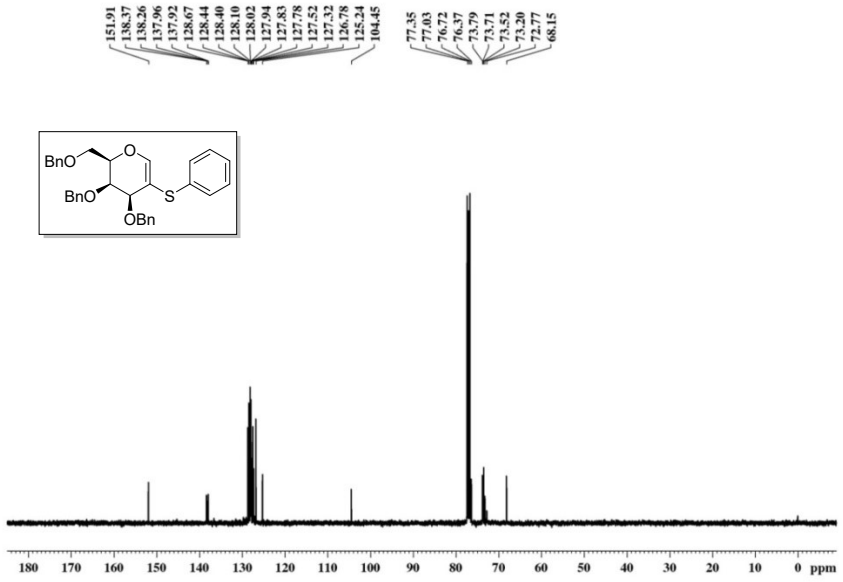
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$, 300 K)



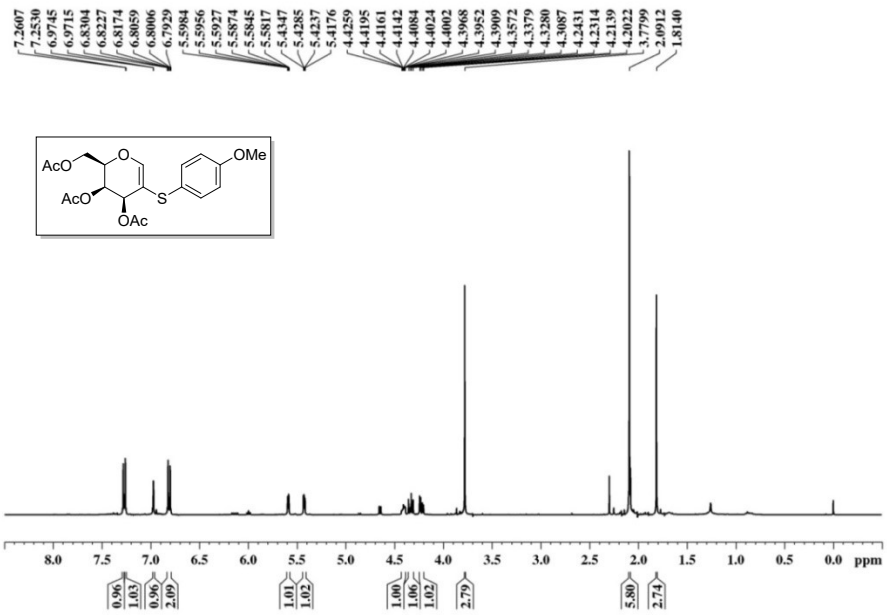
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$, 300 K)



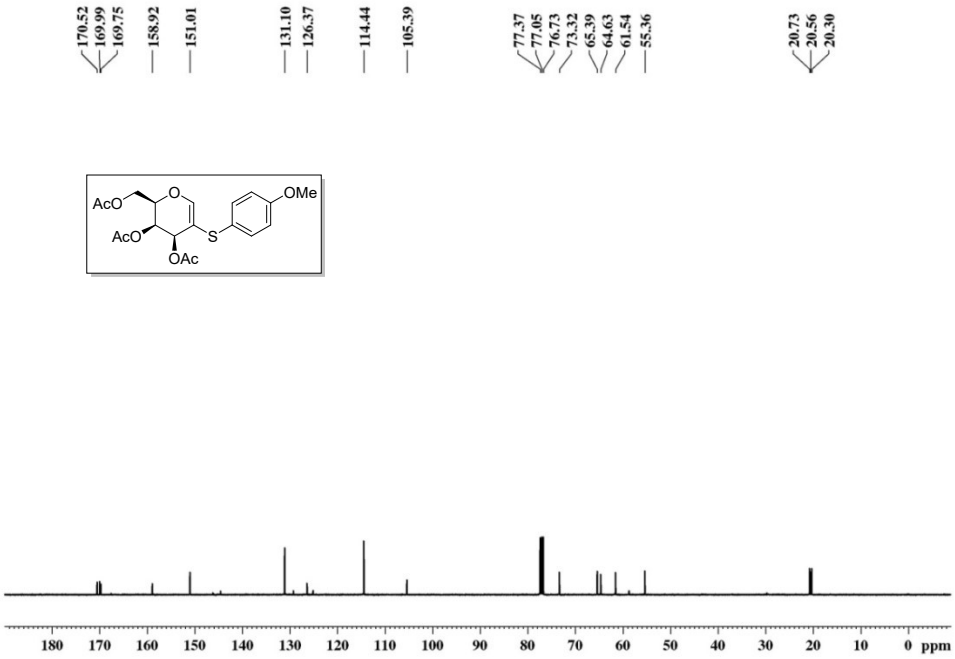
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$, 300 K)



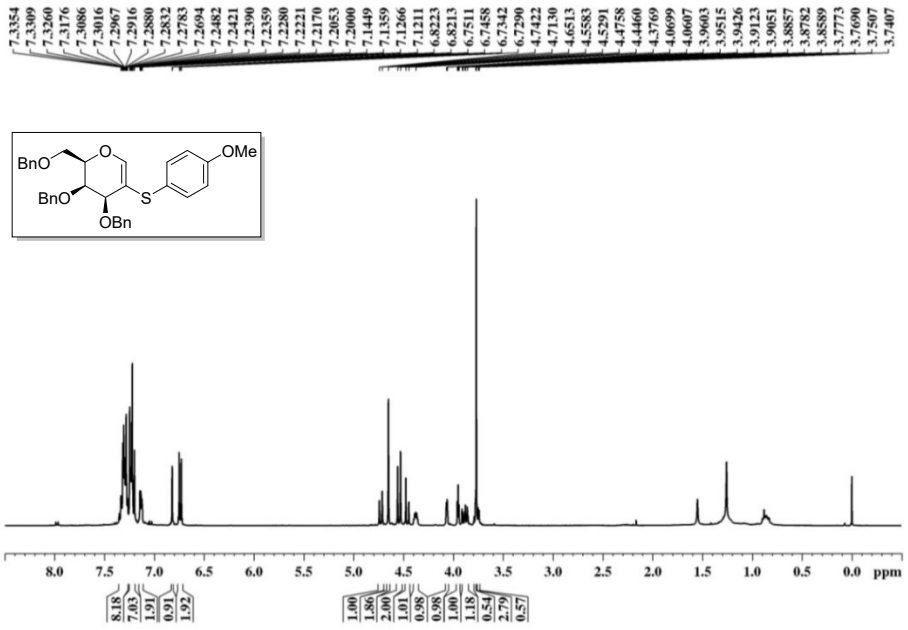
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$, 300 K)



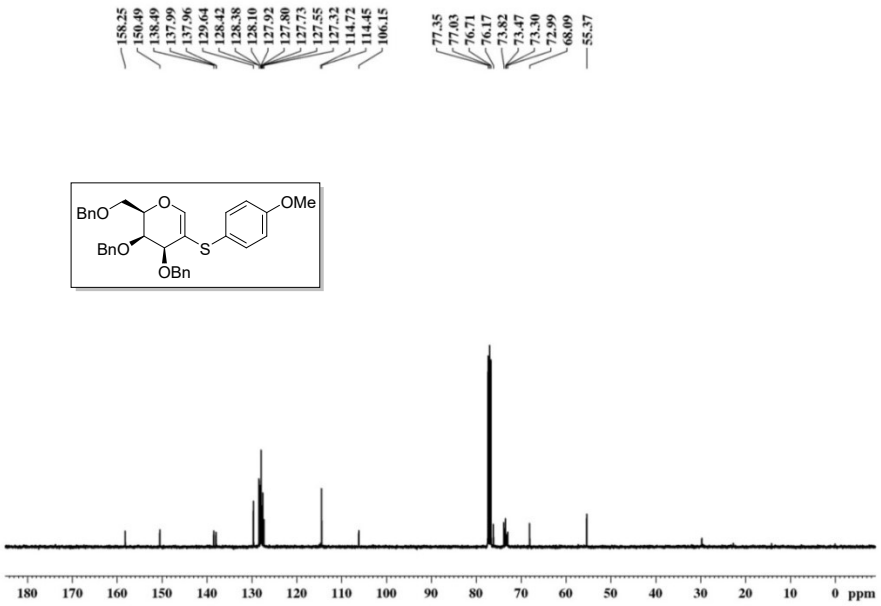
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$, 300 K)



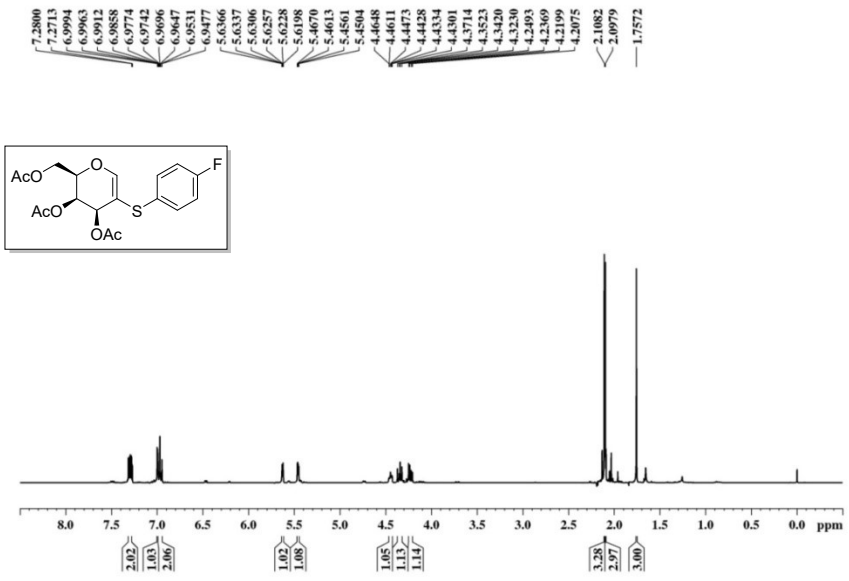
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$, 300 K)



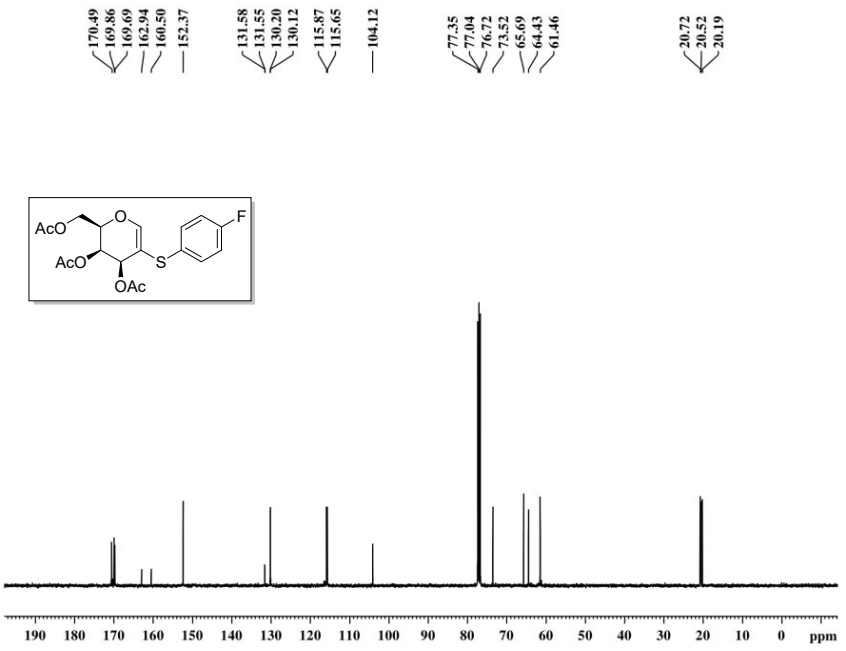
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$, 300 K)



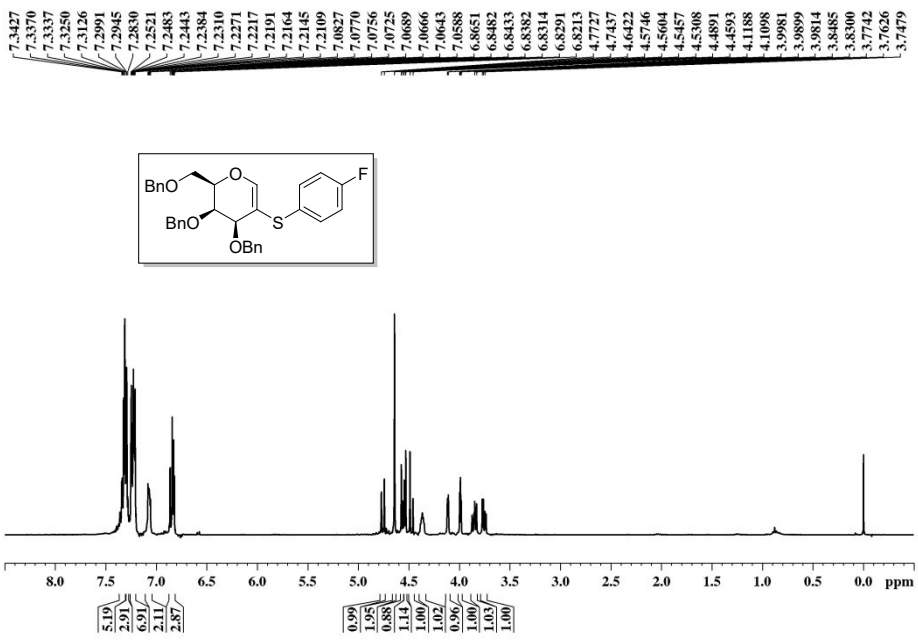
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$, 300 K)



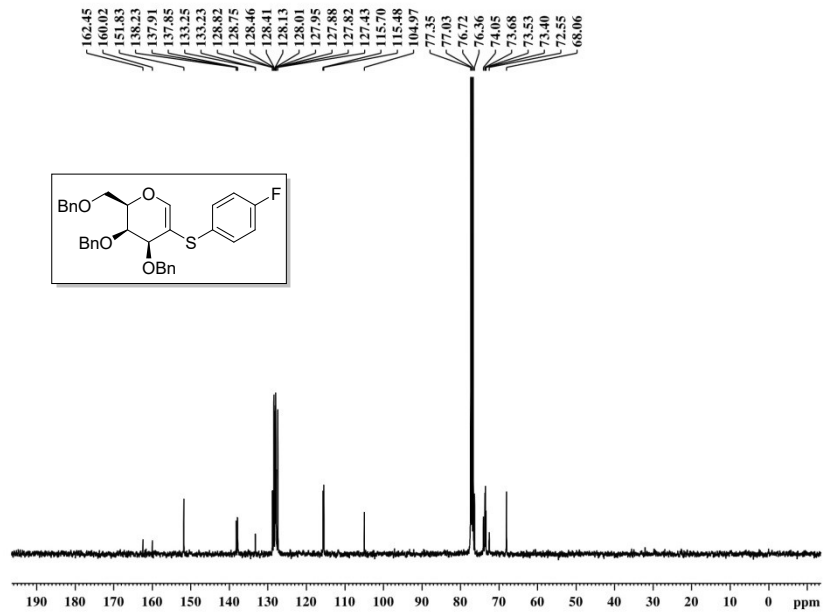
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$, 300 K)



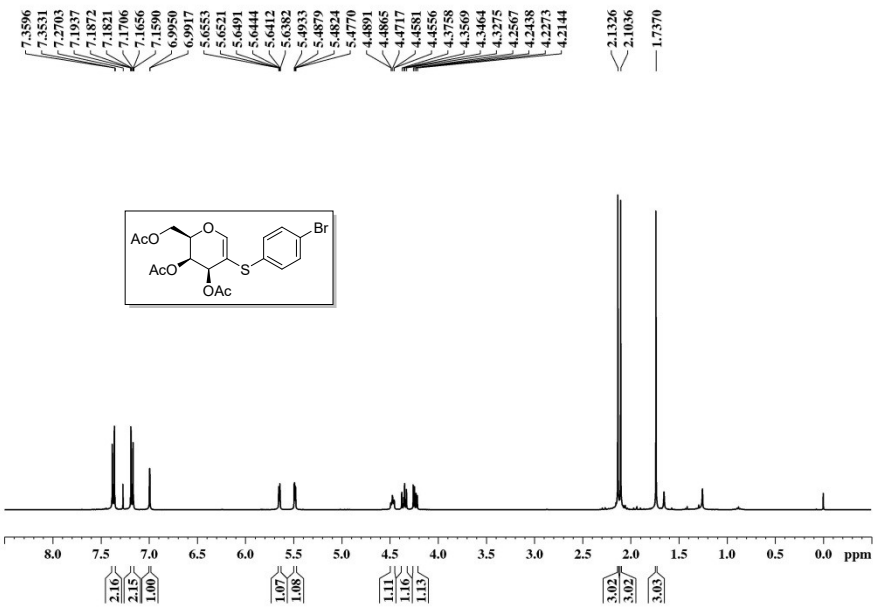
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$, 300 K)



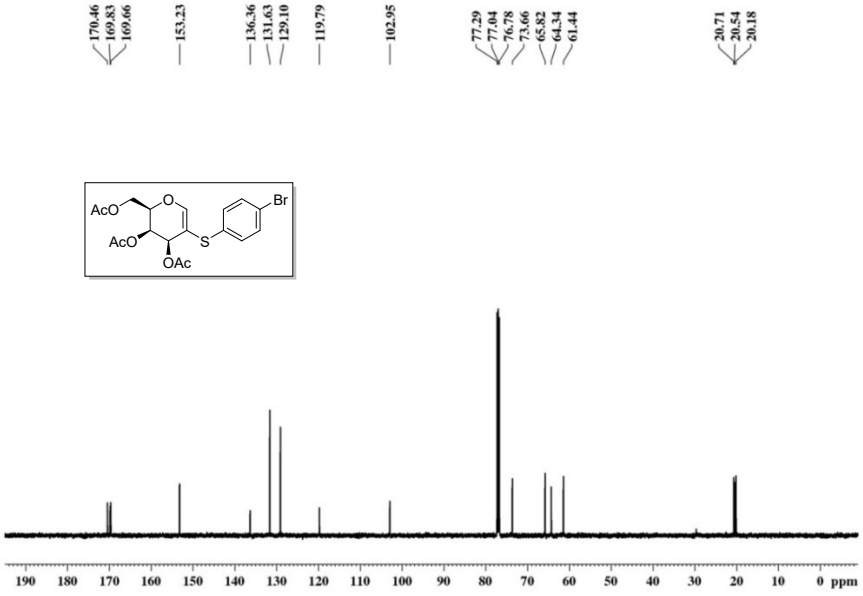
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$, 300 K)



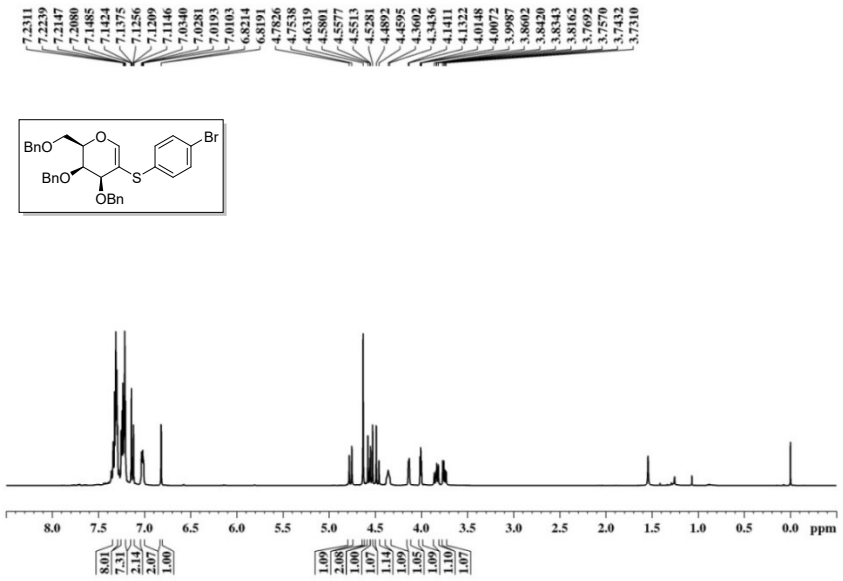
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$, 300 K)



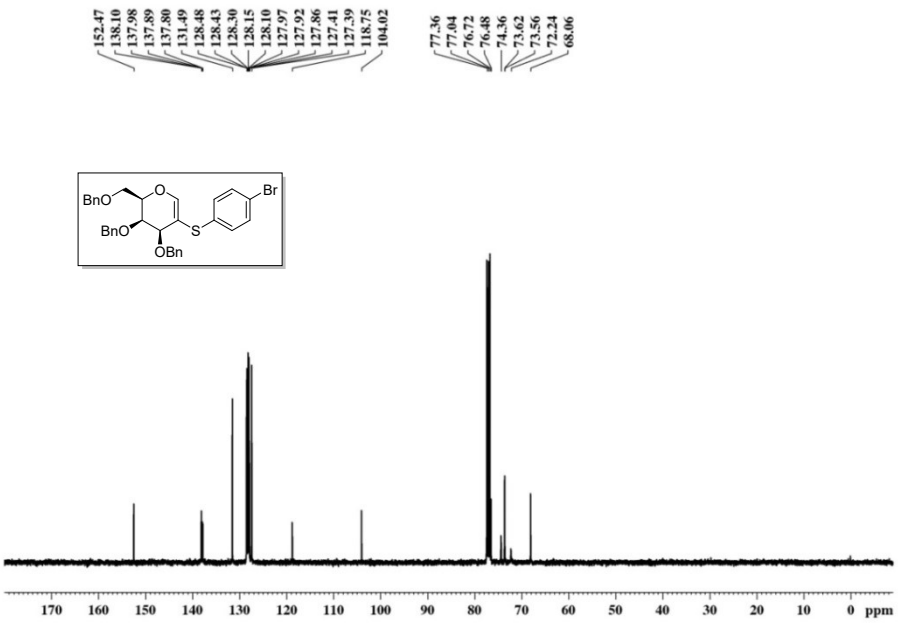
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$, 300 K)



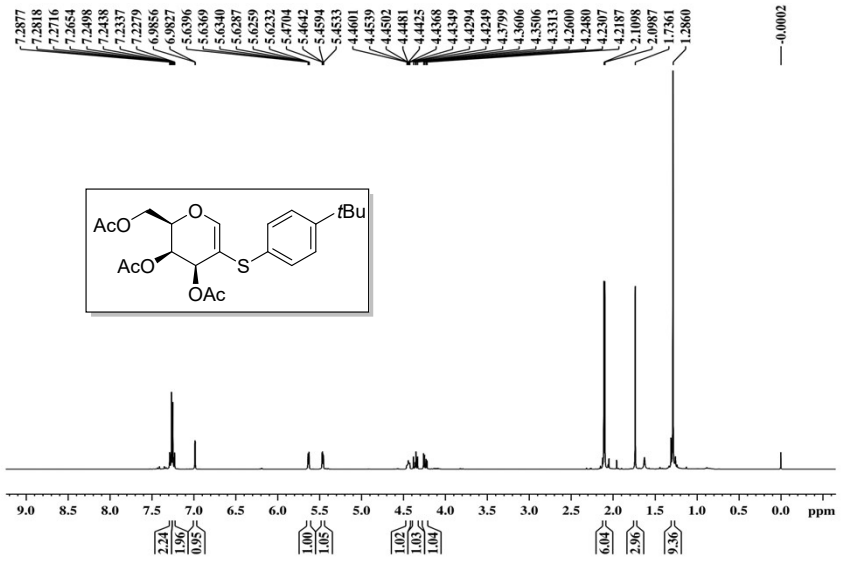
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$, 300 K)



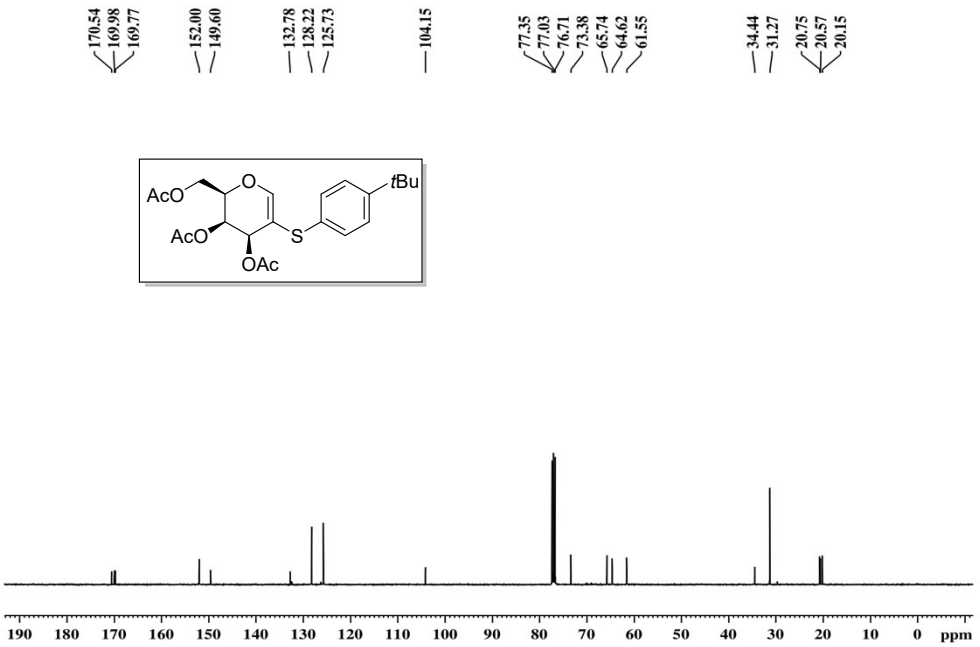
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$, 300 K)



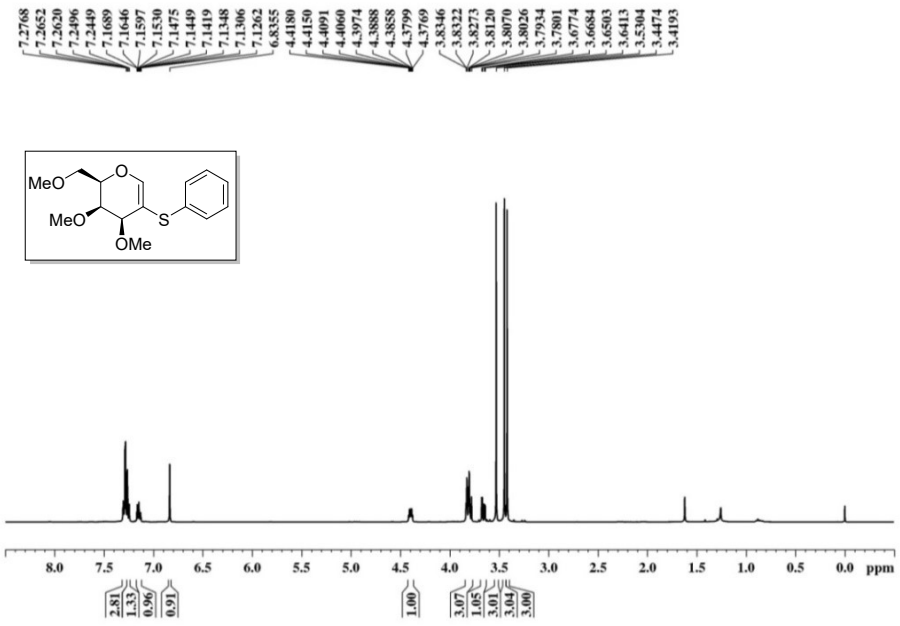
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$, 300 K)



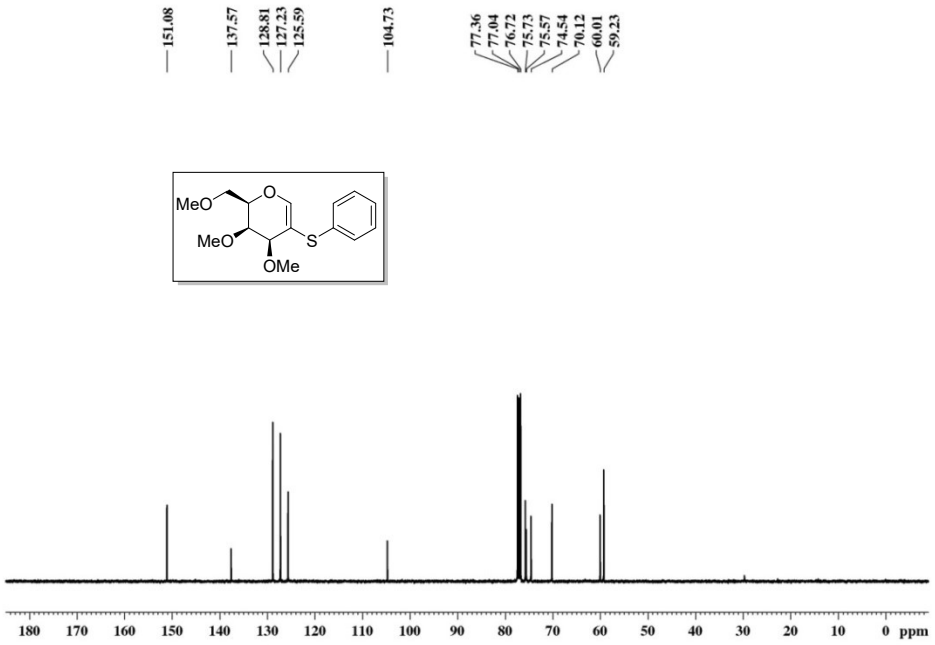
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$, 300 K)



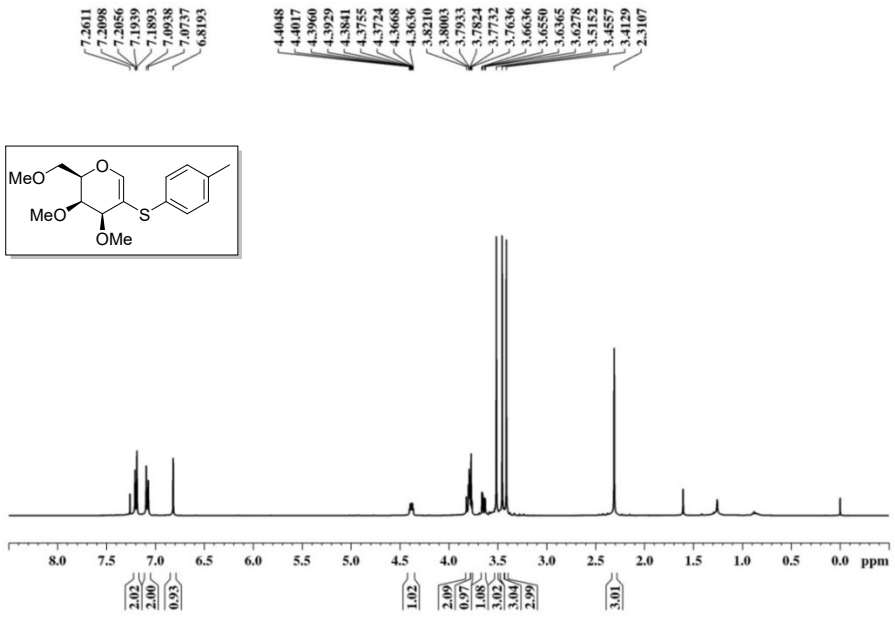
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$, 300 K)



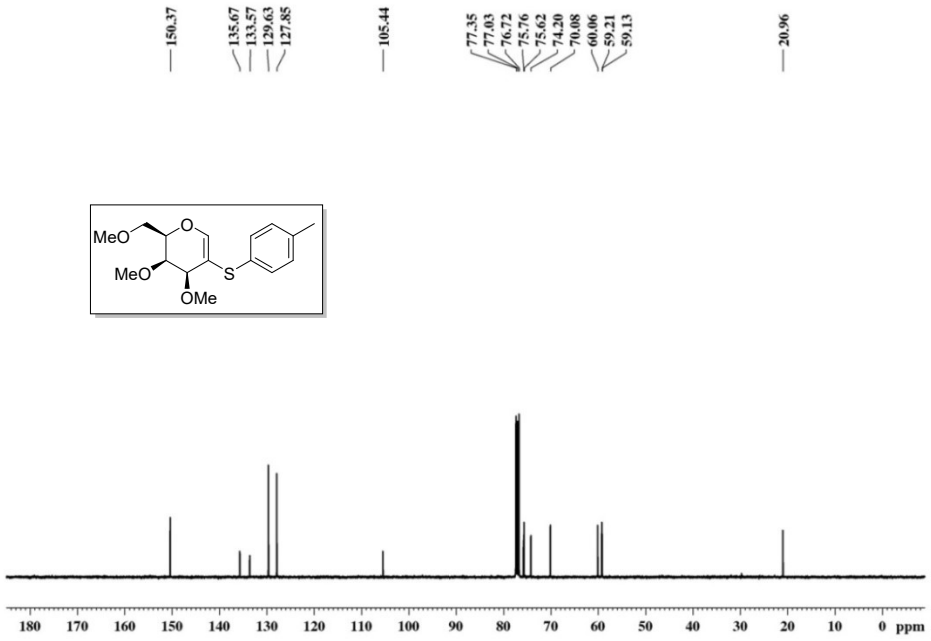
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$, 300 K)



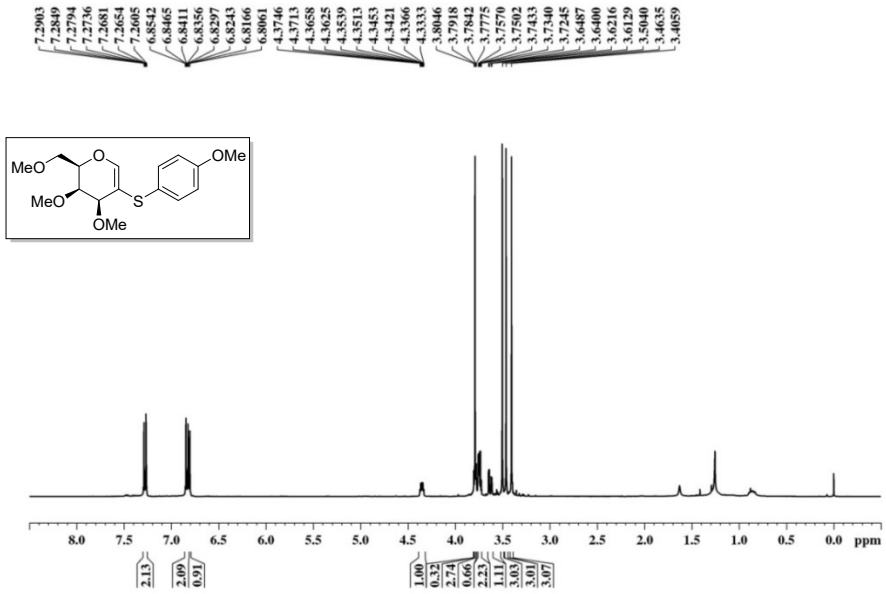
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$, 300 K)



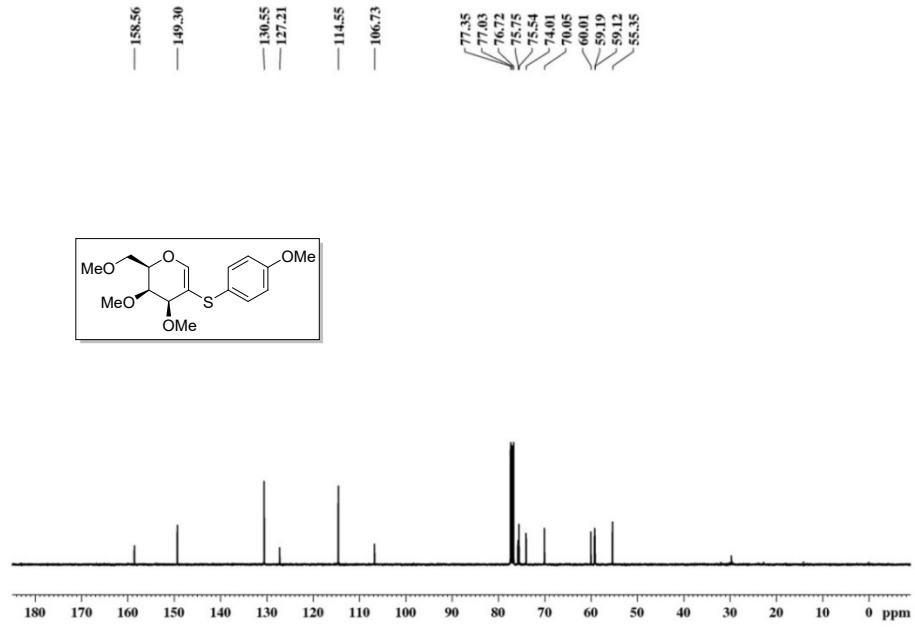
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$, 300 K)



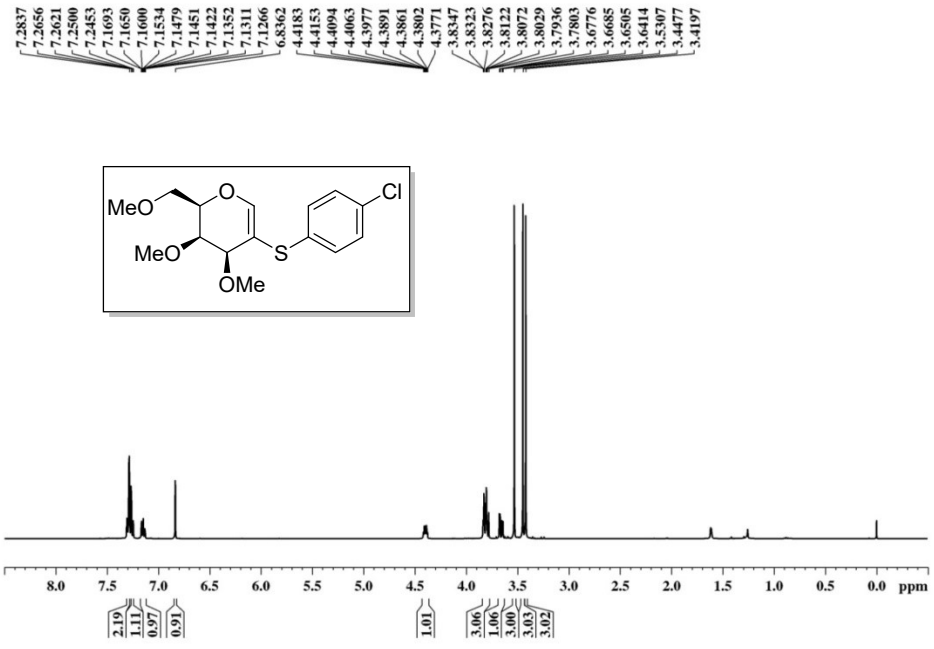
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$, 300 K)



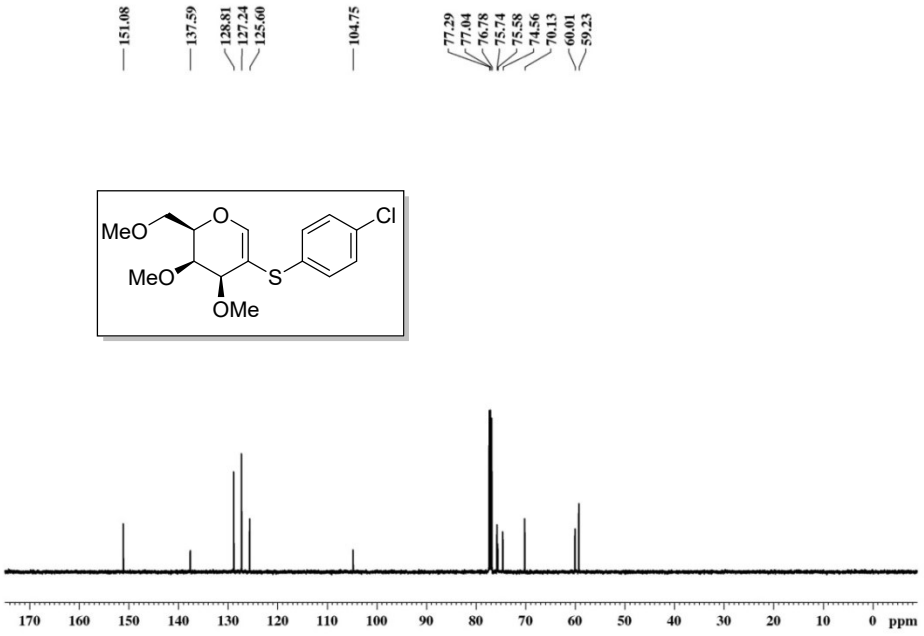
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$, 300 K)



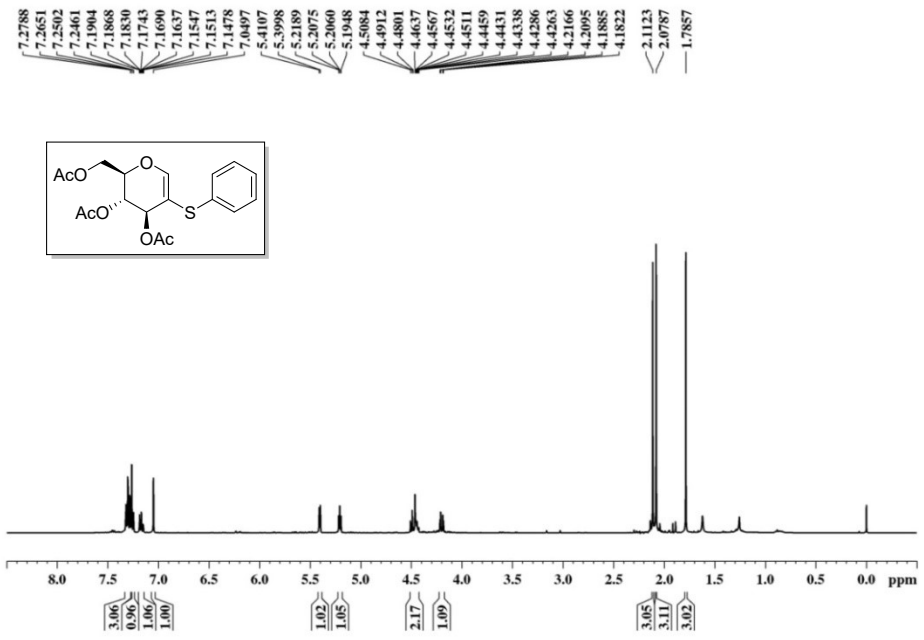
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$, 300 K)



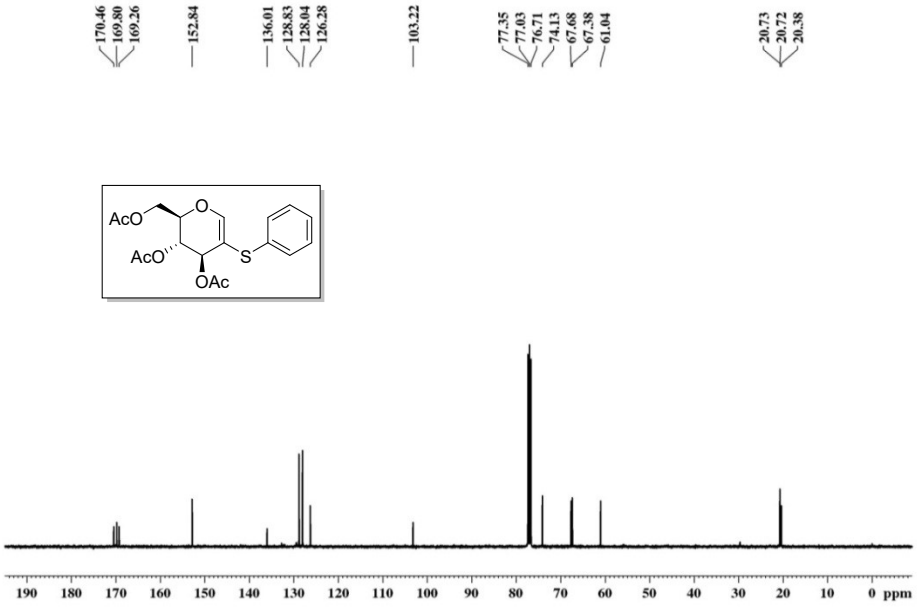
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$, 300 K)



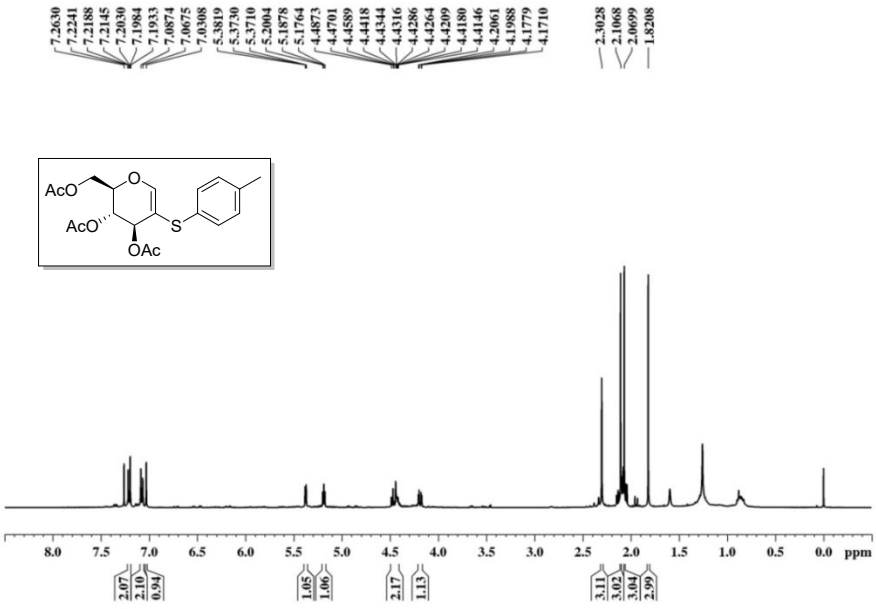
^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$, 300 K)



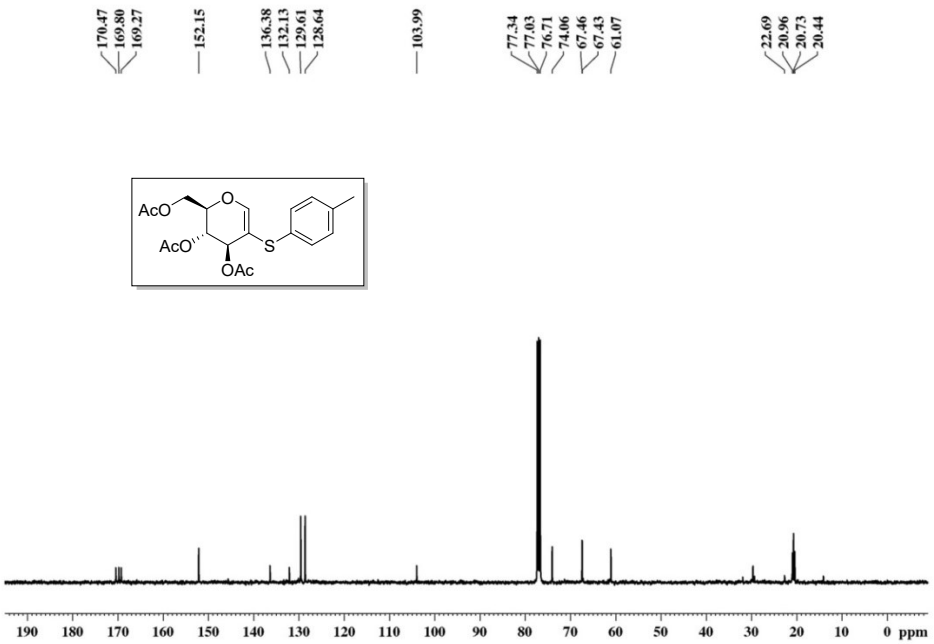
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$, 300 K)



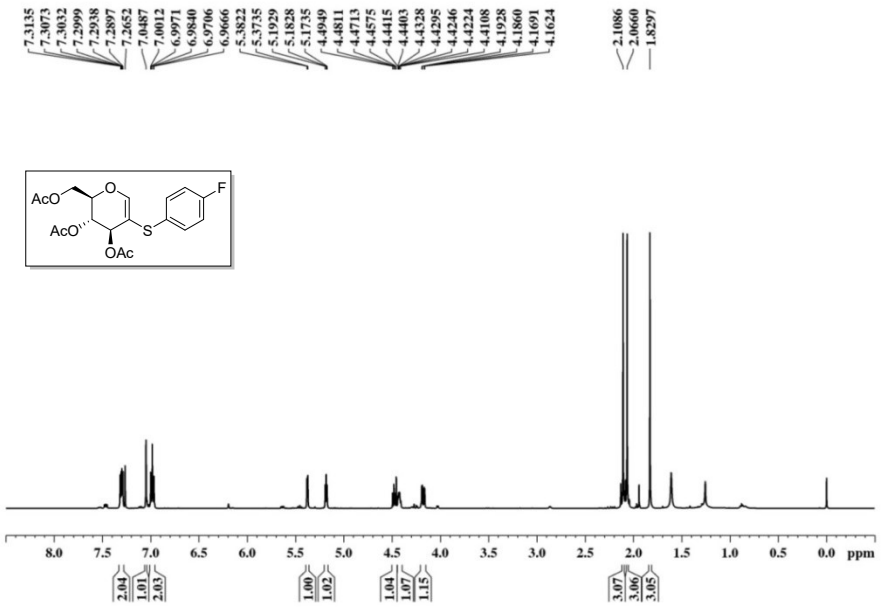
^{13}C NMR spectrum of **3p** (100 MHz, $CDCl_3$, 300 K)



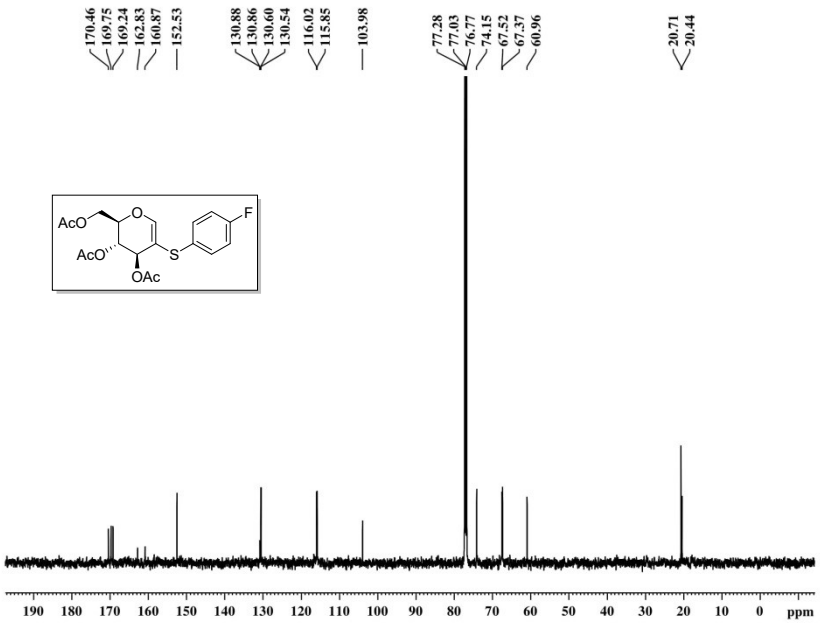
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$, 300 K)



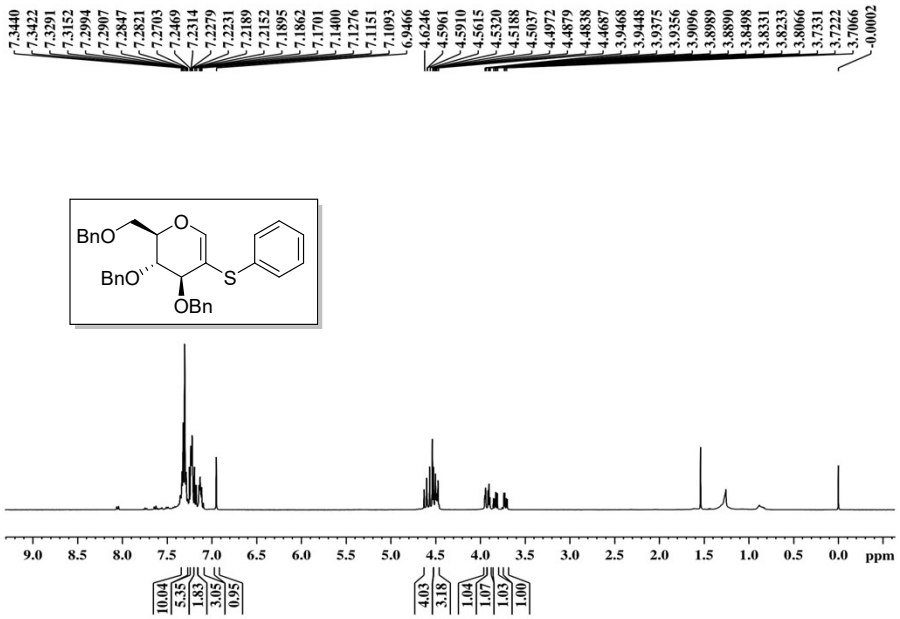
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$, 300 K)



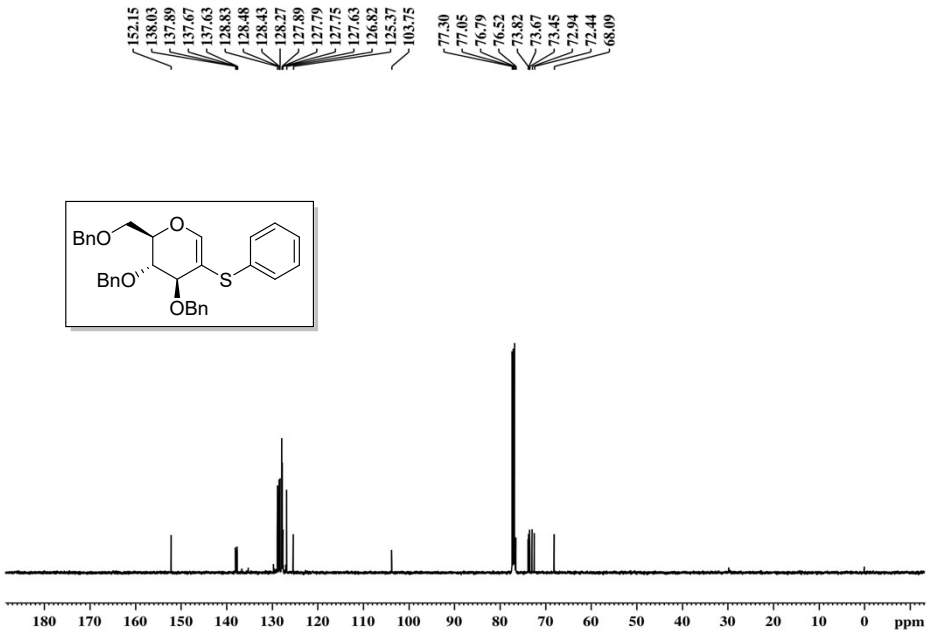
^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$, 300 K)



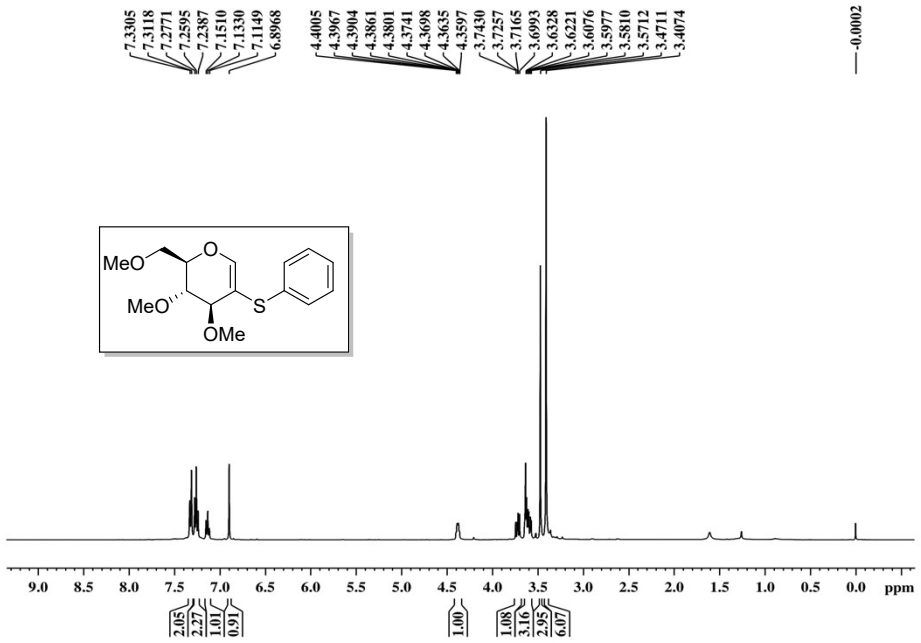
^{13}C NMR spectrum of **3r** (100 MHz, $CDCl_3$, 300 K)



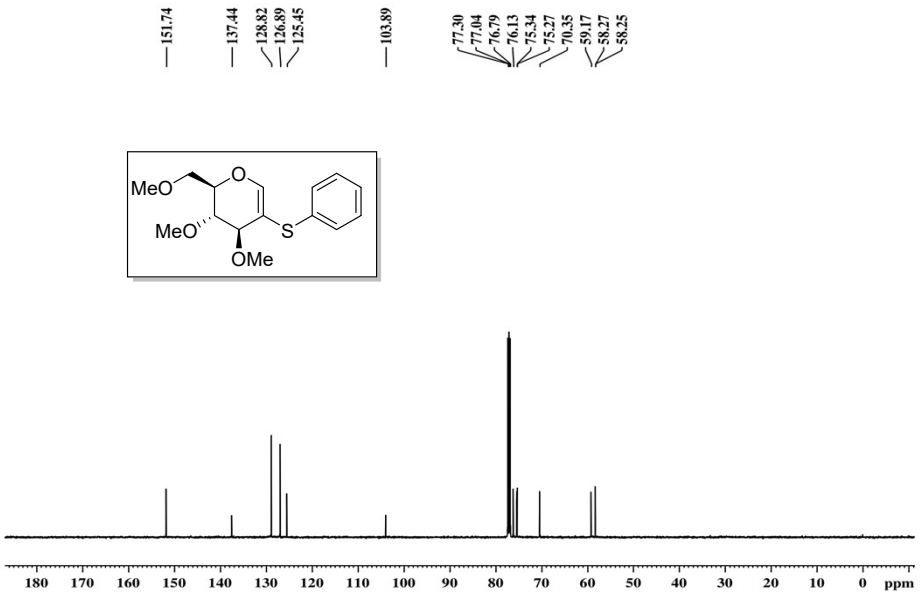
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$, 300 K)



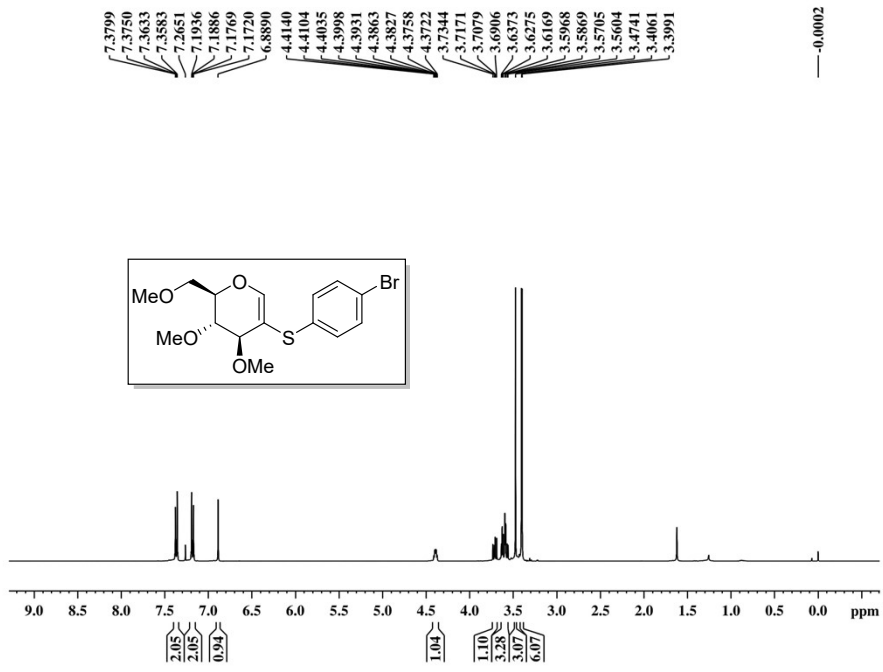
^{13}C NMR spectrum of **3s** (100 MHz, $CDCl_3$, 300 K)



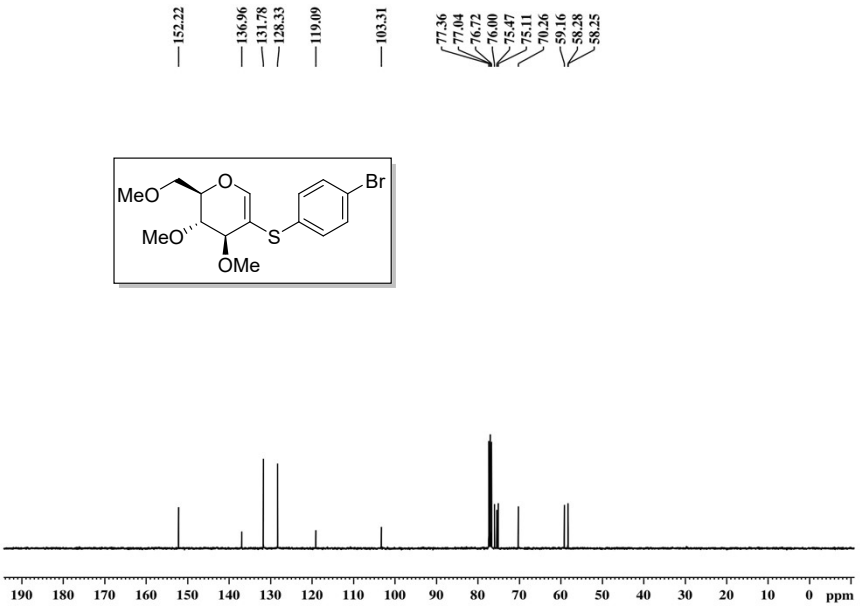
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$, 300 K)



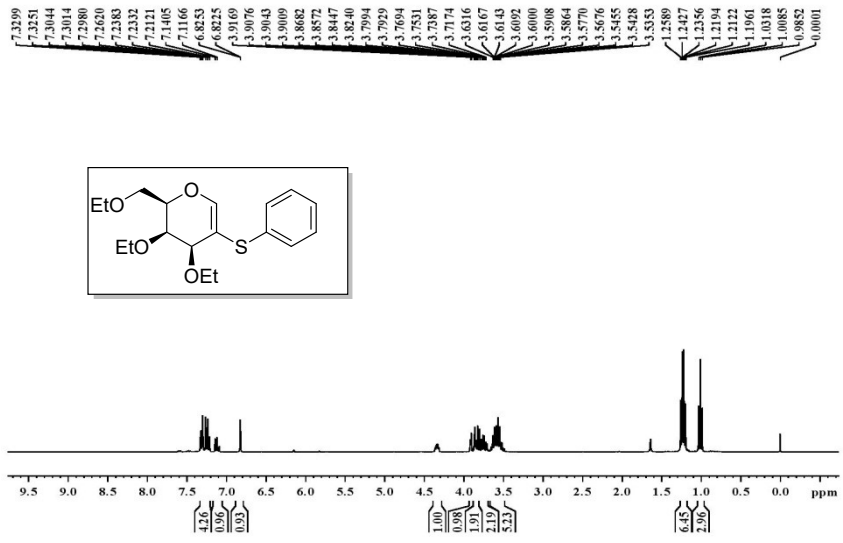
^{13}C NMR spectrum of **3t** (100 MHz, $CDCl_3$, 300 K)



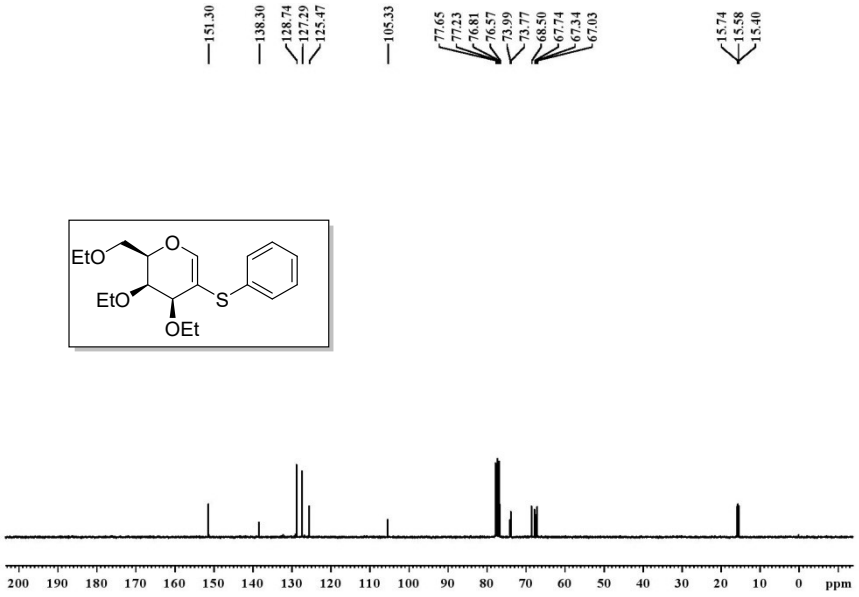
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$, 300 K)



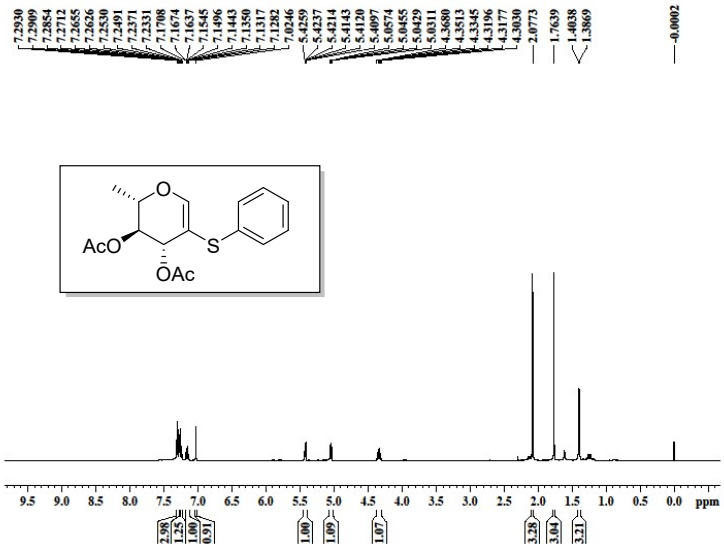
^{13}C NMR spectrum of **3u** (100 MHz, $CDCl_3$, 300 K)



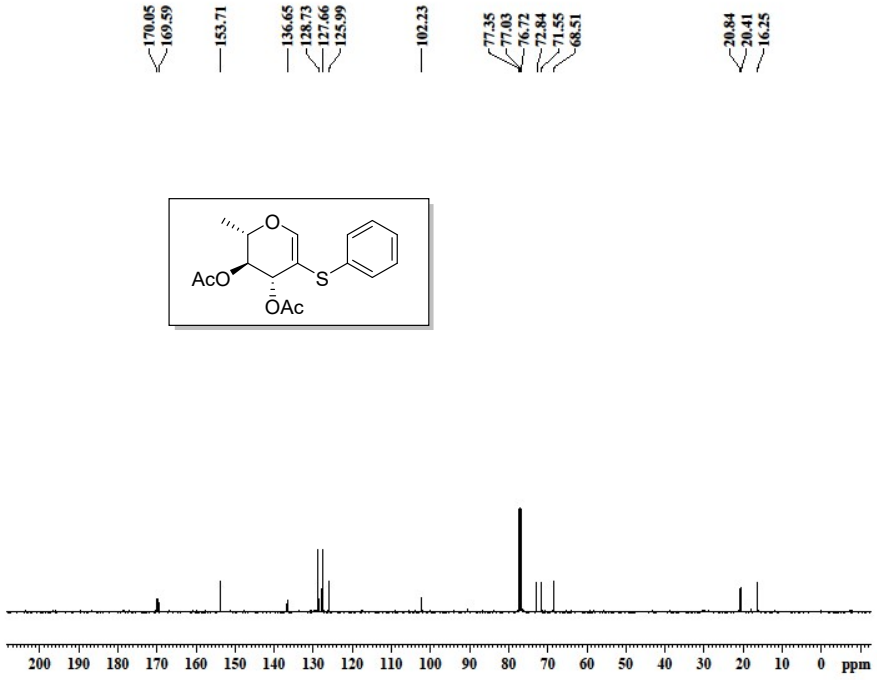
^{1}H NMR spectrum of **3v** (300 MHz, $CDCl_3$, 300 K)



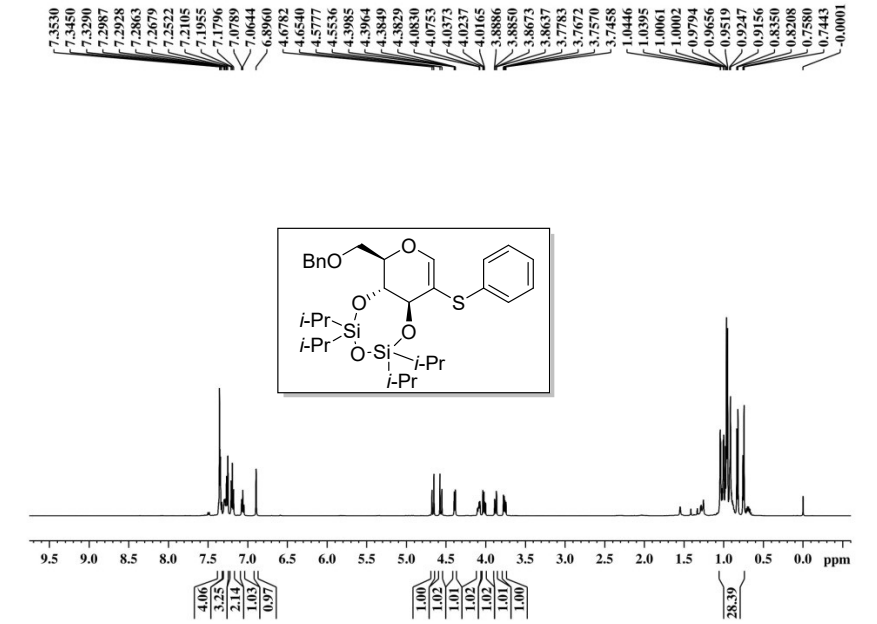
^{13}C NMR spectrum of **3v** (75 MHz, $CDCl_3$, 300 K)



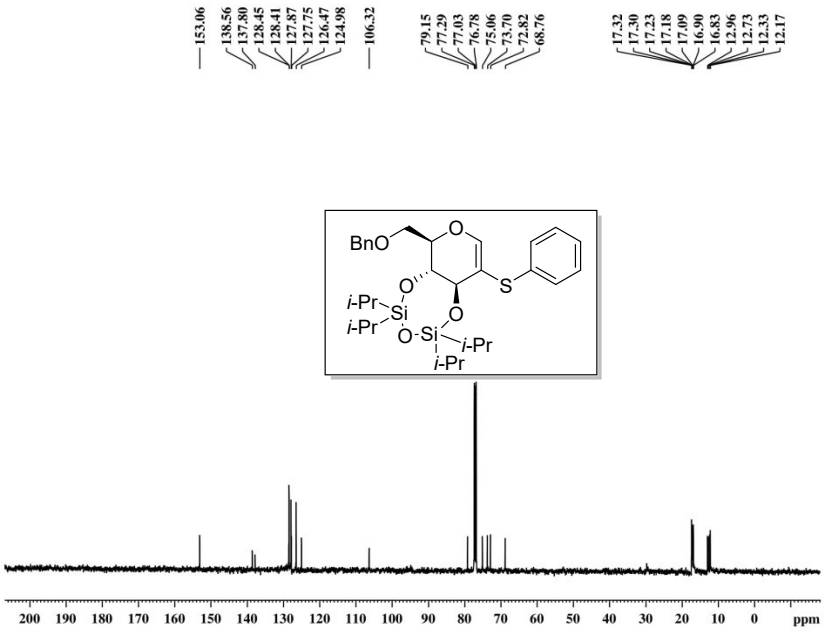
^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$, 300 K)



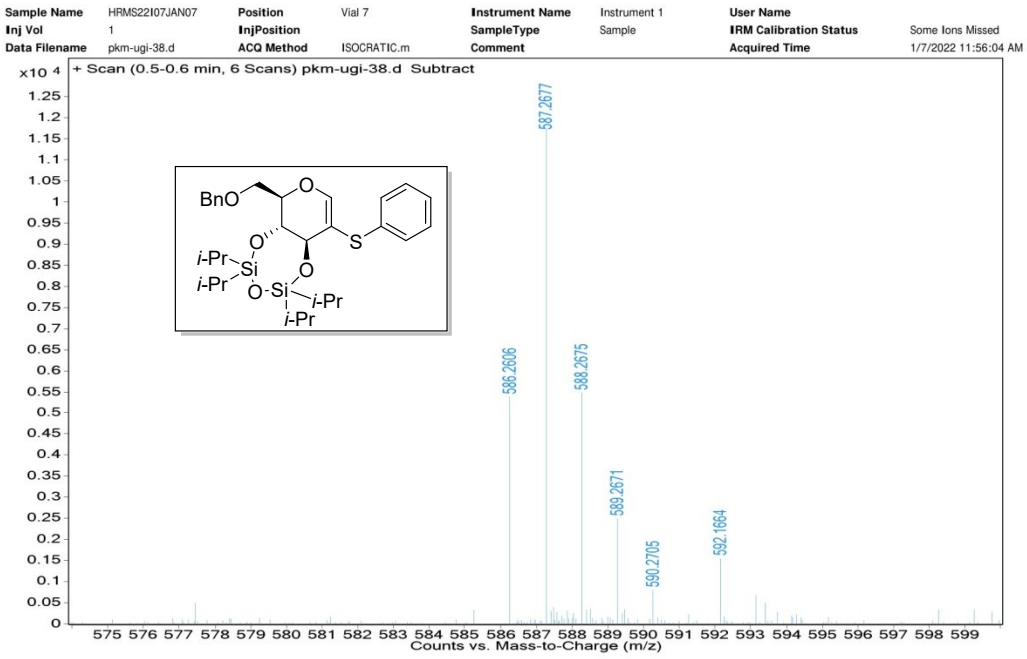
^{13}C NMR spectrum of **3w** (100 MHz, $CDCl_3$, 300 K)



^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$, 300 K)

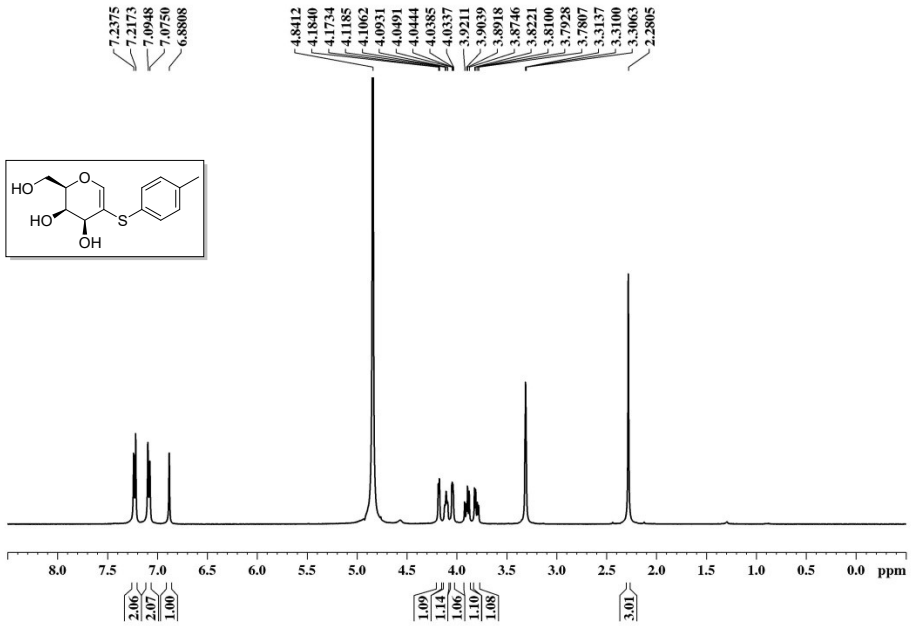


^{13}C NMR spectrum of **3x**(100 MHz, $CDCl_3$, 300 K)

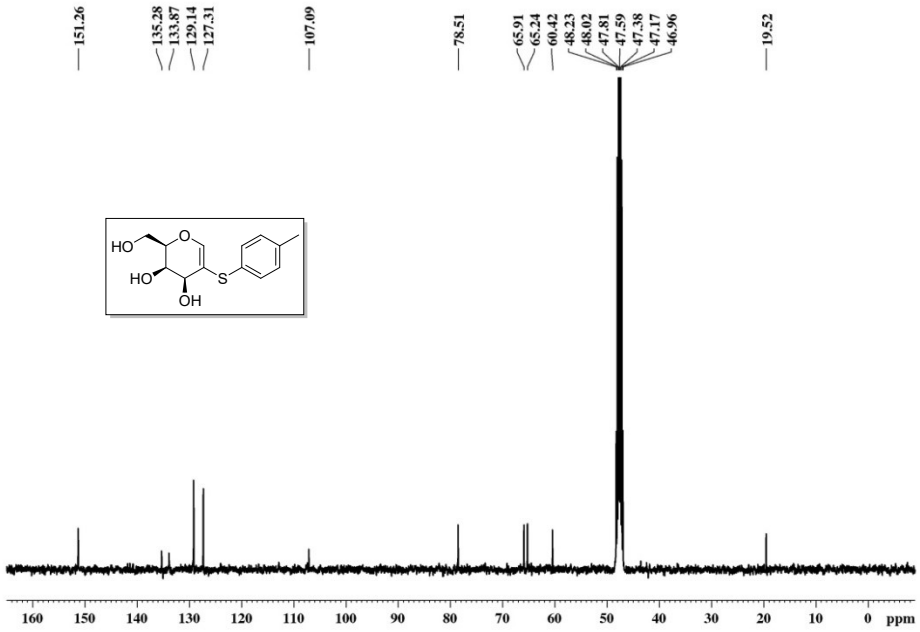


HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{47}O_5SSi_2$ 587.2677; Found 587.2677.

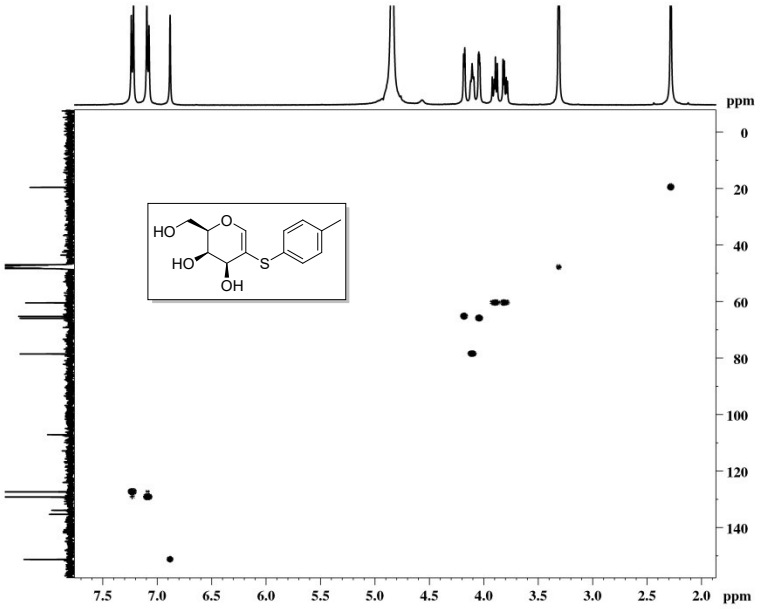
of **3x**



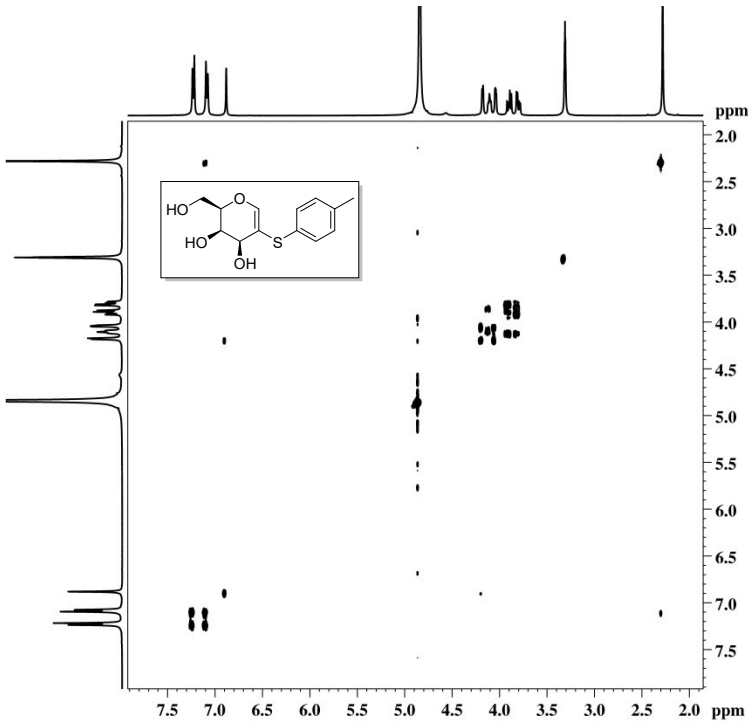
^{1}H NMR spectrum of **4** (400 MHz, MeOD, 300 K)



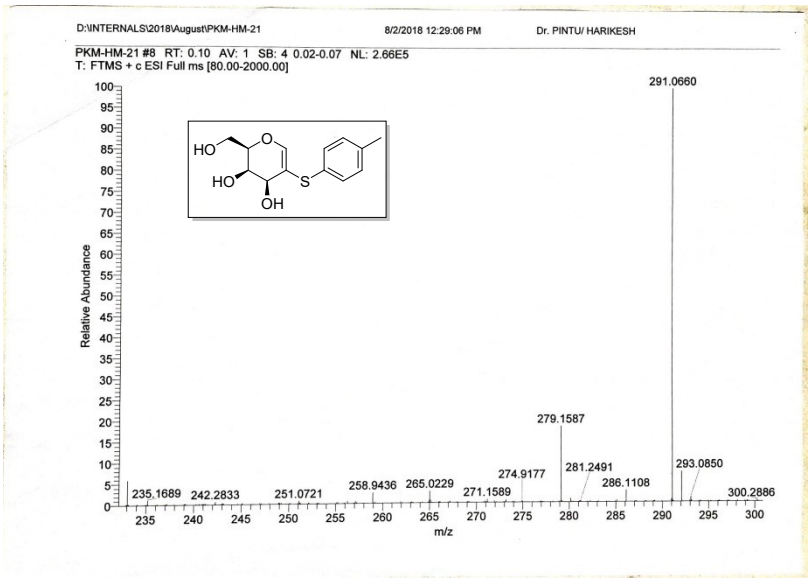
^{13}C NMR spectrum of **4** (100 MHz, MeOD, 300 K)



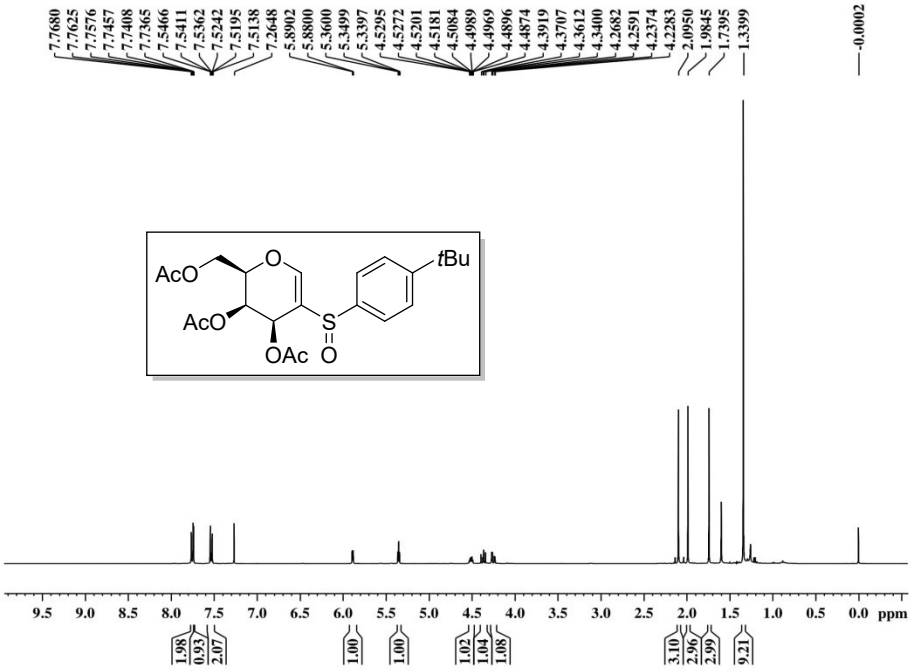
2D-HSQC spectrum of spectrum of compound **4** (400 MHz, MeOD, 300 K)



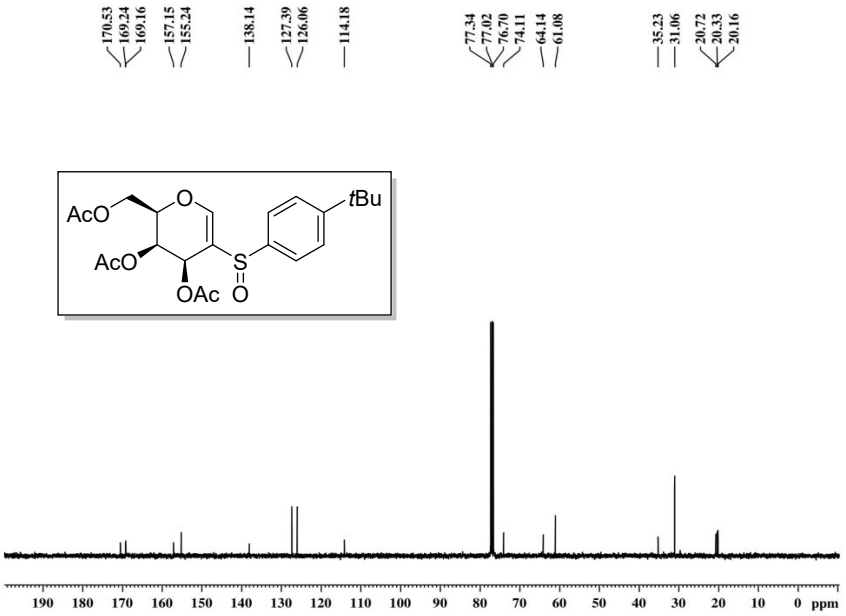
2D-COSY spectrum of spectrum of compound **4** (400 MHz, MeOD, 300 K)



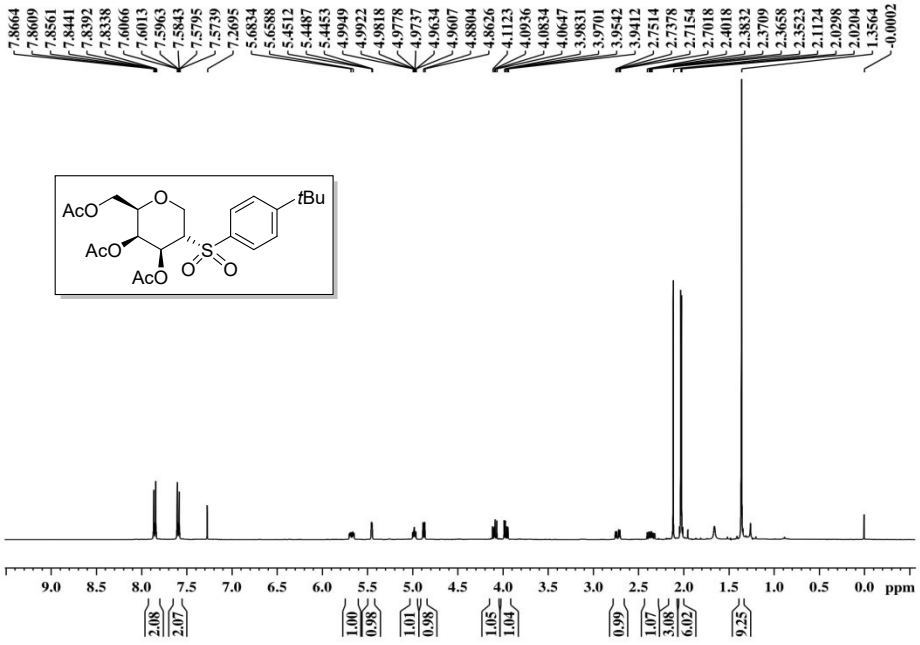
m/z: [M + Na]$^+$ Calcd for $C_{13}H_{16}NaO_4S$ 291.0662; Found 291.0660.
HRMS of **4**



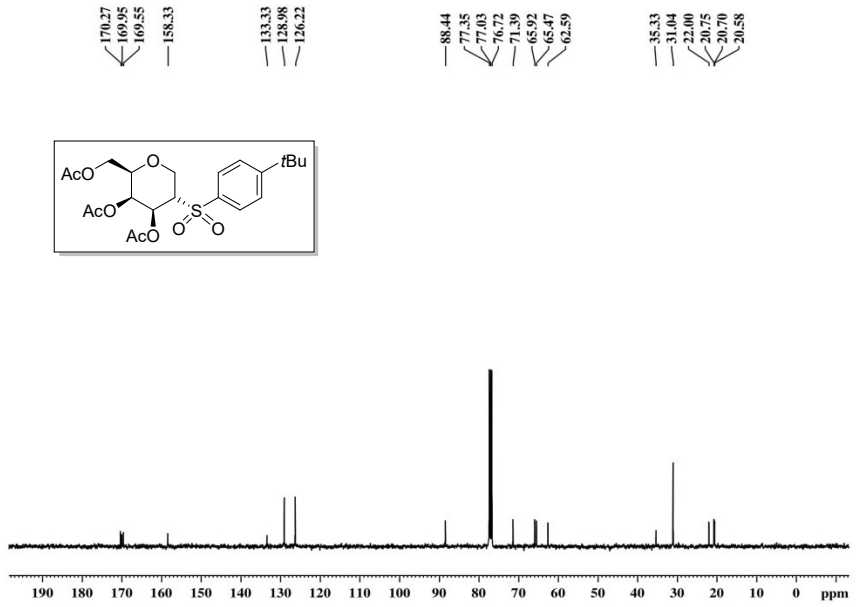
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$, 300 K)



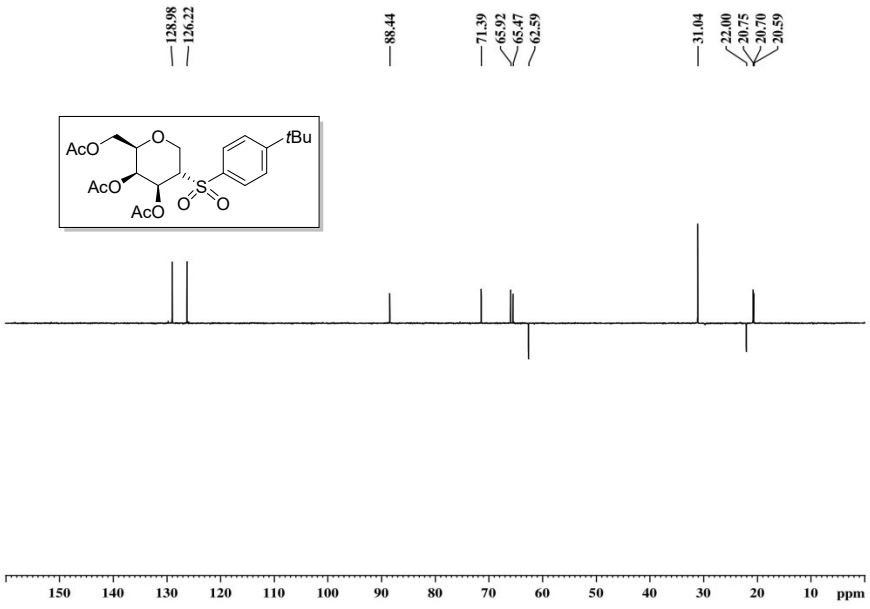
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$, 300 K)



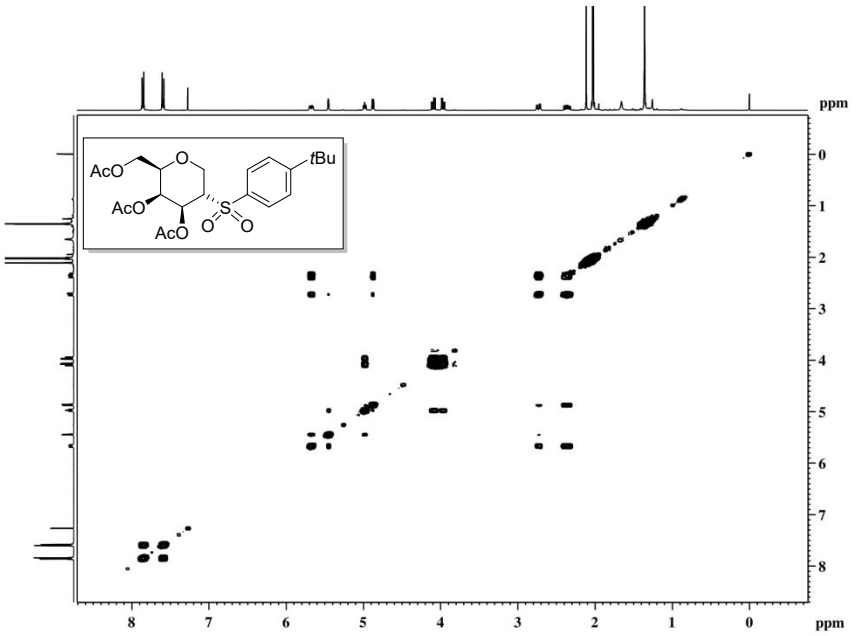
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$, 300 K)



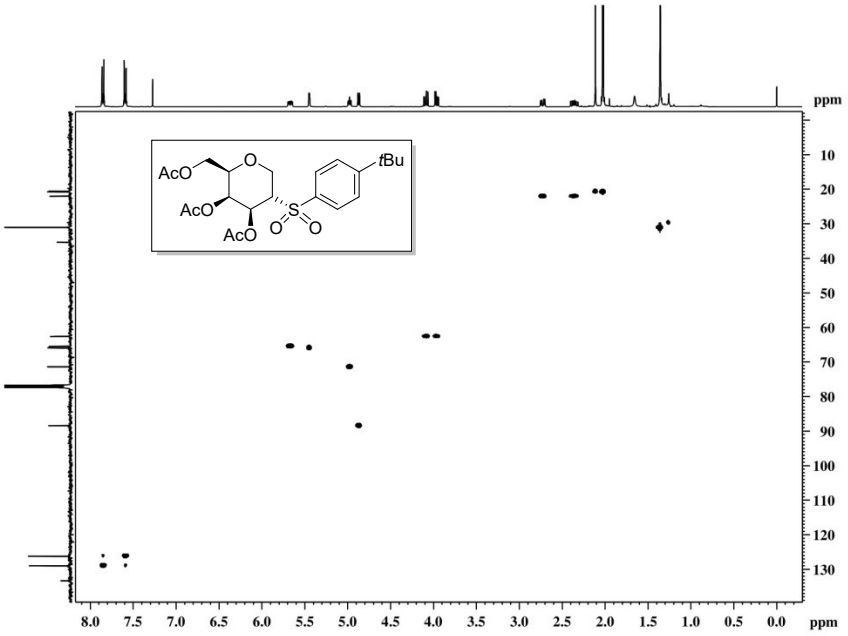
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$, 300 K)



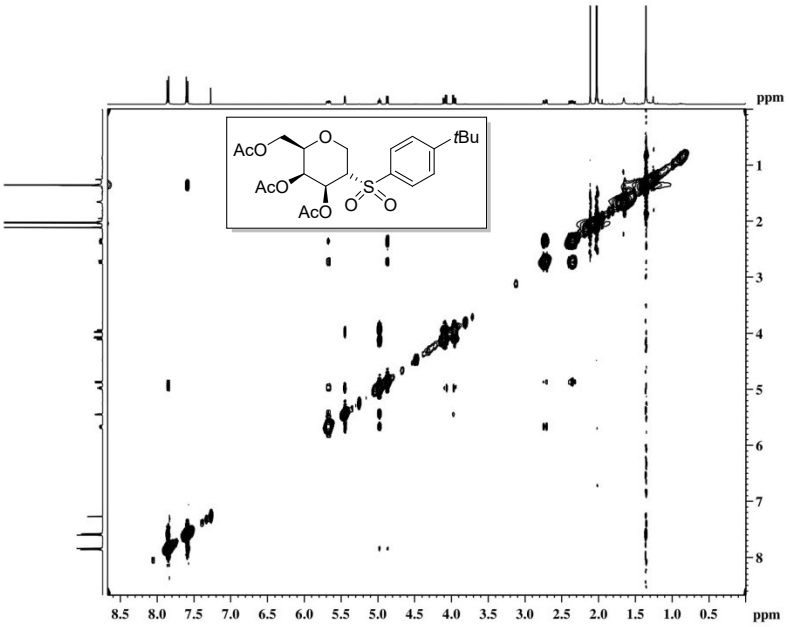
DEPT-135 NMR spectrum of **6** (100 MHz, $CDCl_3$, 300 K)



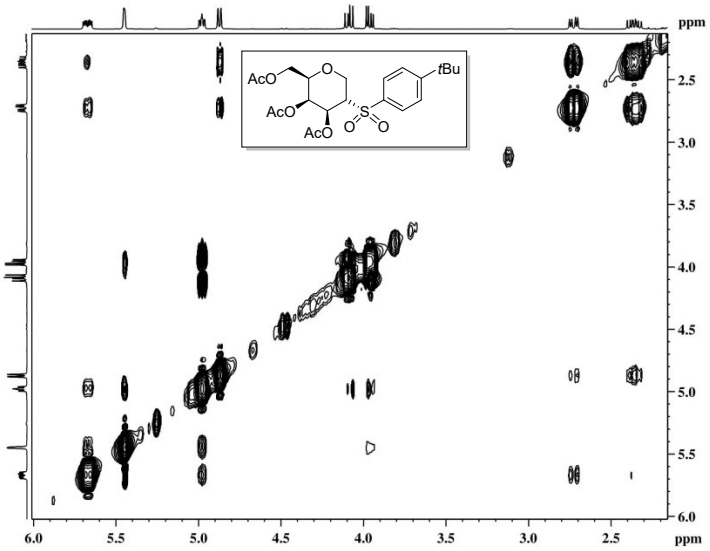
2D-COSY spectrum of **6** (400 MHz, $CDCl_3$, 300 K)



2D-HSQC spectrum of **6** (400 MHz, $CDCl_3$, 300 K)



2D-NOESY spectrum of **6** (400 MHz, $CDCl_3$, 300 K)



2D-NOESY spectrum of **6 (expansion region)** (400 MHz, $CDCl_3$, 300 K)