

## Electronic Supplementary Information

### 2-Trifluoromethylthiolation of Glycals

Yang Yu, De-Cai Xiong and Xin-Shan Ye\*

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*State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Road No. 38, Beijing 100191, China.*

*E-mail: [xinshan@bjmu.edu.cn](mailto:xinshan@bjmu.edu.cn)*

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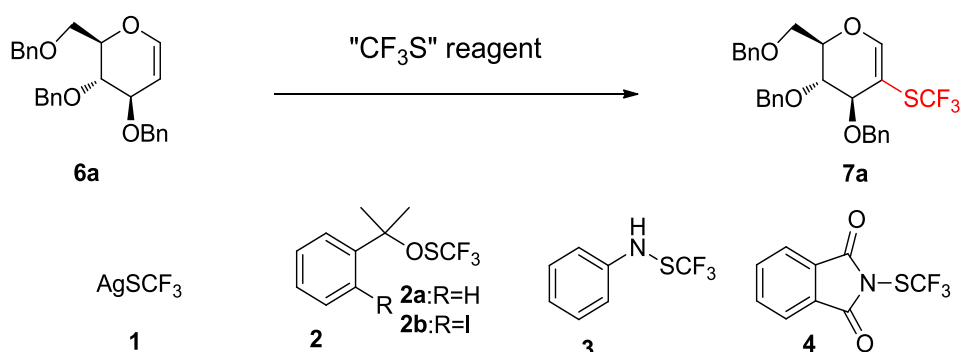
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## 1. General Information

All reagents and solvents were purchased from commercial suppliers and were used without further purification unless otherwise specified. All reactions were performed in an atmosphere of dry argon. All organic extracts were dried over sodium sulfate and concentrated under vacuum. Column chromatographic purification was carried out over silica gel (200—300 mesh). Analytical thin-layer chromatography was performed with silica gel-coated aluminum plates (60 F<sub>254</sub>, E. Merck) and visualized by UV light and/or by staining with acidic ceric ammonium molybdate. High resolution mass spectra were recorded with Fourier transform ion cyclotron resonance mass spectrometer. <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C NMR spectra were recorded at the Avance III 400 or Avance III 600 instruments from Bruker at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane ( $\delta = 0$  ppm for <sup>1</sup>H), CDCl<sub>3</sub> ( $\delta = 77.16$  ppm for <sup>13</sup>C) in deuterated chloroform. The following standard abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and br = broad.

## 2. Optimization Studies

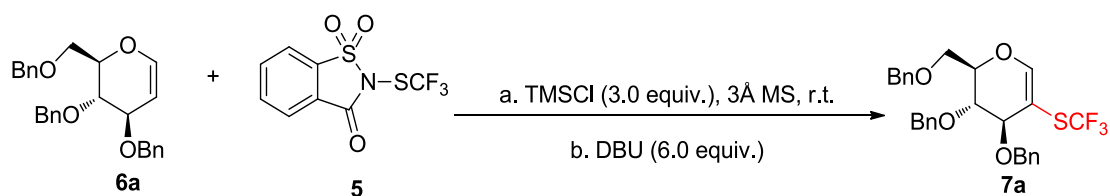
**Table S1.** Screening of trifluoromethylthiolating reagents **1-4**<sup>a</sup>



Entry	“CF <sub>3</sub> S” reagent	Additive (eq.) and condition	Yield <sup>b</sup> (%)
1	<b>1</b>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (3.0), CH <sub>3</sub> CN, 70 °C	0
2	<b>1</b>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (3.0), CH <sub>3</sub> CN/DMF (1:1), 70 °C	0
3	<b>1</b>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (3.0), CH <sub>3</sub> CN, 70 °C	0
4	<b>1</b>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (3.0), CH <sub>3</sub> CN/H <sub>2</sub> O/DCE (6:2:1), 70 °C	0
5	<b>2a</b>	CSA (0.10), CH <sub>3</sub> CN, 70 °C	0
6	<b>2b</b>	CSA (0.10), CH <sub>3</sub> CN, 70 °C	0
7	<b>2b</b>	TMSCl (0.10), CH <sub>3</sub> CN, 70 °C	0
8	<b>3</b>	TsOH (5.0), CH <sub>3</sub> CN, 70 °C	0
9	<b>4</b>	K <sub>2</sub> CO <sub>3</sub> (2.0), CH <sub>3</sub> CN, 70 °C	0
10	<b>4</b>	DBU (2.0), CH <sub>3</sub> CN, 70 °C	0
11	<b>4</b>	TMSCl (3.0), CH <sub>3</sub> CN, 70 °C	0

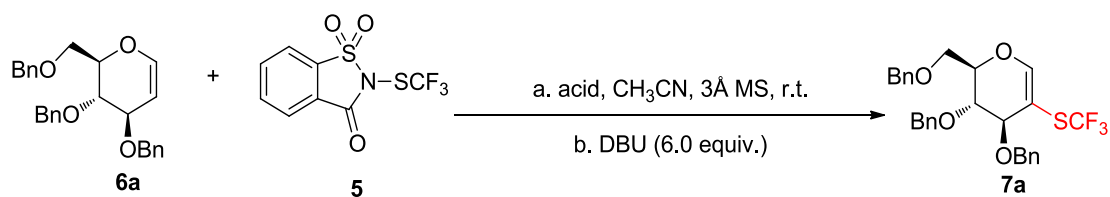
<sup>a</sup>General conditions: **6a** (1.0 eq.), **1-4** (1.1 eq.) in 3.0 mL of solvent at an atmosphere of argon for 10 hours. <sup>b</sup>Yield was determined by <sup>19</sup>F NMR using  $\alpha,\alpha,\alpha$ -trifluorotoluene as an internal standard.

**Table S2.** Screening of solvents



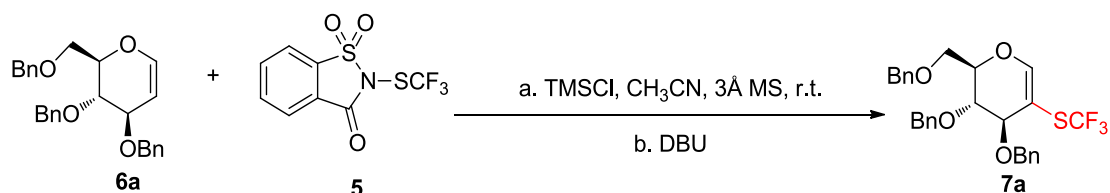
Entry	“CF <sub>3</sub> S” reagent	Additive (eq.) and condition	Yield (%)
1	<b>5</b>	a. TMSCl (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	92
2	<b>5</b>	a. TMSCl (3.0), CH <sub>2</sub> Cl <sub>2</sub> ; b. DBU (6.0)	0
3	<b>5</b>	a. TMSCl (3.0), THF; b. DBU (6.0)	0
4	<b>5</b>	a. TMSCl (3.0), Et <sub>2</sub> O; b. DBU (6.0)	0

General conditions: a. **6** (1.0 eq.), **5** (1.1 eq.), anhydrous solvent (3.0 mL), TMSCl (3.0 eq.), 3Å molecular sieves (300 mg), room temperature, 10 hours; b. DBU (6.0 eq.); isolated yield.

**Table S3.** Screening of acids

Entry	Additive (eq.) and condition	Yield (%)
1	a. TMSCl (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	92
2	a. BF <sub>3</sub> ·Et <sub>2</sub> O (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	0
3	a. TfOH (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	0
4	a. TsOH (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	0
5	a. CuCl (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	0
6	a. Cu(OTf) <sub>2</sub> (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	0

General conditions: a. **6** (1.0 eq.), **5** (1.1 eq.), anhydrous CH<sub>3</sub>CN (3.0 mL), acid, 3Å molecular sieves (300 mg), room temperature, 10 hours; b. DBU (6.0 equiv.); isolated yield.

**Table S4.** Screening of equivalents of TMSCl and DBU

Entry	Additive (eq.) and condition	Yield (%)
1	a. TMSCl (3.0), CH <sub>3</sub> CN; b. DBU (6.0)	92
2	a. TMSCl (2.0), CH <sub>3</sub> CN; b. DBU (6.0)	62
3	a. TMSCl (4.0), CH <sub>3</sub> CN; b. DBU (6.0)	93
4	a. TMSCl (3.0), CH <sub>3</sub> CN; b. DBU (4.0)	76
5	a. TMSCl (3.0), CH <sub>3</sub> CN; b. DBU (8.0)	92

General conditions: a. **6** (1.0 eq.), **5** (1.1 eq.), anhydrous solvent (3.0 mL), TMSCl, 3Å molecular sieves (300 mg), room temperature, 10 hours; b. DBU; isolated yield.

### 3. General Procedure for the Synthesis of **7**

A solution of glycal **6**<sup>1-3</sup> (0.10 mmol, 1.0 eq.), *N*-trifluoromethylthiosaccharin (**5**)<sup>4</sup> (0.11 mmol, 1.1 eq.) and activated 3 Å powdered molecular sieves (300 mg, 3.0 g/mmol) in anhydrous CH<sub>3</sub>CN (3.0 mL) was stirred at an atmosphere of dry argon at room temperature for 2 hours before trimethyl chlorosilane (0.30 mmol, 3.0 eq.) was added. The reaction mixture was then stirred for 10 hours (24 hours for **6m**) at the same temperature. After the starting material was completely consumed (detected by TLC), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (6.0 mmol, 6.0 eq.) was added and the reaction mixture was stirred for another 5 hours, and then diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through Celite, washed with water and saturated NaCl solution, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate to afford the desired trifluoromethylthiolated product **7**.

### 4. Deprotection of **7d**

To a solution of **7d** (0.10 mmol, 1.0 eq.) in 1,4-dioxane was added Pd(OH)<sub>2</sub> (0.010 mmol, 0.10 eq.) and the reaction was stirred at an atmosphere of H<sub>2</sub> for 1 hour under atmospheric pressure at room temperature. After TLC showed the reaction was completed, the mixture was filtered through Celite and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH to afford the desired deprotected product **10**.

### 5. Deprotection of **7e**

To a solution of **7e** (0.10 mmol, 1.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (10/1, 2 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (0.45 mmol, 4.5 eq.). The reaction was stirred at room temperature for 2 hours. After TLC showed the reaction was completed, the

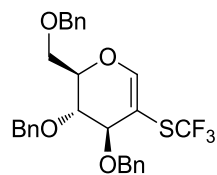
mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH to afford the desired deprotected product **10**.

## 6. Deprotection of **7m**

To a solution of **7m** (0.10 mmol, 1.0 eq.) in MeOH was added catalytic amount of NaOMe/MeOH and the reaction was stirred for 0.5 hour. After TLC showed the reaction was completed, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH<sub>2</sub>Cl<sub>2</sub>/MeOH to afford the desired deprotected product **10**.

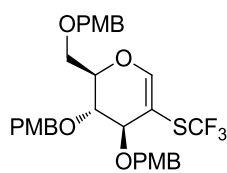
## 7. Compound Characterization Data of **7a-7n** and **10**

### 3,4,6-Tri-*O*-benzyl-2-trifluoromethylthio-D-glucal (**7a**)



Colorless oil; 92% yield (47.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (20:1 to 15:1);  $[\alpha]_{\text{D}}^{25} = 2.3$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 – 7.30 (m, 15H, Ar-H), 6.99 (s, 1H, H-1), 4.75 (d,  $J = 11.0$  Hz, 1H), 4.67 (d,  $J = 11.5$  Hz, 1H), 4.61 (d,  $J = 11.2$  Hz, 1H), 4.56 (d,  $J = 11.6$  Hz, 1H), 4.51 (brs, 2H), 4.42 – 4.34 (m, 1H), 4.12 (brd,  $J = 3.2$  Hz, 1H), 3.93 – 3.87 (m, 1H), 3.81 – 3.73 (m, 1H), 3.72 – 3.65 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 137.84, 137.80, 137.6, 129.9 (q,  $J = 309.8$  Hz, SCF<sub>3</sub>), 128.7, 128.57, 128.56, 128.1, 128.04, 127.97, 127.9, 127.9, 98.7 (d,  $J = 1.78$  Hz), 77.3, 76.1, 73.6, 73.5, 73.1, 67.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -43.92; HRMS (ESI) calcd for C<sub>28</sub>H<sub>27</sub>F<sub>3</sub>NaO<sub>4</sub>S [M + Na]<sup>+</sup> 539.1474, found 539.1486.

### 3,4,6-Tri-*O*-(*p*-methoxybenzyl)-2-trifluoromethylthio-D-glucal (**7b**)



Colorless oil; 94% yield (57.0 mg); column chromatography

conditions: petroleum ether/ethyl acetate (15:1 to 9:1);  $[\alpha]_{\text{D}}^{25} = 0.54$

(c 0.10,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 8.54$  Hz,

2H, Ar-H), 7.22 – 7.15 (m, 4H, Ar-H), 6.92 – 6.81 (m, 7H), 4.72 (d,  $J = 11.6$  Hz, 1H),

4.70 (brs, 2H), 4.51 (d,  $J = 11.5$  Hz, 1H), 4.43 (d,  $J = 11.5$  Hz, 1H), 4.33 (d,  $J = 11.5$  Hz,

1H), 4.31 – 4.27 (m, 1H), 4.16 (d,  $J = 3.57$  Hz, 1H), 3.94 (t,  $J = 3.3$  Hz, 1H), 3.81 (s,

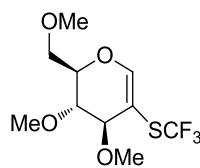
3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.71 (dd,  $J = 7.7, 10.5$  Hz, 1H), 3.61 (dd,  $J = 4.3, 10.5$

Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 159.5, 159.4, 155.8, 130.3, 130.0 (q,  $J = 309.7$  Hz,  $\text{SCF}_3$ ), 130.01, 129.95, 129.84, 129.7, 113.9, 113.9, 99.2, 77.0, 73.8, 73.6,

73.2, 73.2, 71.7, 67.7, 55.4, 55.4;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.28; HRMS (ESI)

calcd for  $\text{C}_{31}\text{H}_{33}\text{F}_3\text{NaO}_7\text{S}$   $[\text{M} + \text{Na}]^+$  629.1791, found 629.1802.

### 3,4,6-Tri-*O*-methyl-2-trifluoromethylthio-D-glucal (7c)



Colorless oil; 91% yield (26.0 mg); column chromatography

conditions: petroleum ether/ethyl acetate (15:1 to 12:1);  $[\alpha]_{\text{D}}^{25} = 3.4$

(c 1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.95 (s, 1H, H-1), 4.34

– 4.27 (m, 1H), 3.81 (d,  $J = 4.5$  Hz, 1H), 3.68 (dd,  $J = 3.7, 10.7$  Hz, 1H), 3.62 – 3.56 (m,

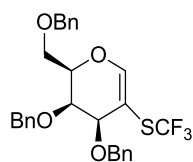
2H), 3.55 (s, 3H), 3.52 (s, 3H), 3.40 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8,

129.8 (q,  $J = 309.54$  Hz,  $\text{SCF}_3$ ), 98.7 (d,  $J = 1.67$  Hz), 77.8, 76.9, 75.3, 70.2, 59.3,

58.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.19; HRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{15}\text{F}_3\text{NaO}_4\text{S}$

$[\text{M} + \text{Na}]^+$  311.0535, found 311.0547.

### 3,4,6-Tri-*O*-benzyl-2-trifluoromethylthio-D-galactal (7d)



Colorless oil; 92% yield (47.0 mg); column chromatography

conditions: petroleum ether/ethyl acetate (20:1 to 15:1);  $[\alpha]_{\text{D}}^{25} = 3.3$  (c

1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.20 (m, 15H,

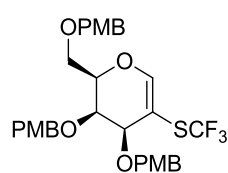
Ar-H), 6.90 (s, 1H, H-1), 4.84 – 4.72 (m, 3H), 4.57 (d,  $J = 11.7$  Hz, 1H), 4.48 (d,  $J =$

11.8 Hz, 1H), 4.39 (d,  $J = 12.1$  Hz, 1H), 4.37 – 4.32 (m, 1H), 4.23 – 4.15 (m, 1H),



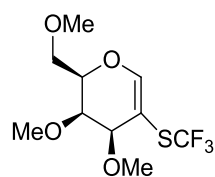
4.02 – 3.94 (m, 1H), 3.84 – 3.73 (m, 1H), 3.69 (dd,  $J = 10.2, 3.7$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 138.2, 137.9, 137.9, 130.0 (q,  $J = 309.89$  Hz,  $\text{SCF}_3$ ), 128.5, 128.5, 128.5, 128.1, 128.0, 128.0, 127.89, 127.85, 99.1, 74.2, 73.9, 73.6, 73.5, 72.4, 68.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.16; HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{27}\text{F}_3\text{NaO}_4\text{S}$   $[\text{M} + \text{Na}]^+$  539.1474, found 539.1464.

### 3,4,6-Tri-*O*-(*p*-methoxybenzyl)-2-trifluoromethylthio-D-galactal (7e)

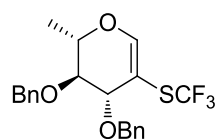


Colorless oil; 96% yield (58.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (15:1 to 9:1);  $[\alpha]_{\text{D}}^{25} = 0.011$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.18 (m, 4H, Ar-H), 7.16 – 7.12 (m, 2H, Ar-H), 6.96 (s, 1H, H-1), 6.88 – 6.83 (m, 6H, Ar-H), 4.68 (d,  $J = 10.8$  Hz, 1H), 4.57 (dd,  $J = 16.6, 11.0$  Hz, 2H), 4.47 (d,  $J = 11.3$  Hz, 1H), 4.45 (brs, 2H), 4.32 (dd,  $J = 9.8, 5.3$  Hz, 1H), 4.07 (d,  $J = 4.5$  Hz, 1H), 3.86 – 3.75 (m, 10H), 3.72 (dd,  $J = 10.7, 6.1$  Hz, 1H), 3.63 (dd,  $J = 10.7, 3.9$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 159.6, 159.5, 156.1, 130.2, 130.0, 129.96 (q,  $J = 310.19$  Hz,  $\text{SCF}_3$ ), 129.85, 129.74, 129.61, 129.55, 114.0, 98.8 (d,  $J = 1.58$  Hz), 77.5, 75.9, 73.4, 73.3, 73.2, 72.7, 67.6, 55.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.04; HRMS (ESI) calcd for  $\text{C}_{31}\text{H}_{33}\text{F}_3\text{NaO}_7\text{S}$   $[\text{M} + \text{Na}]^+$  629.1791, found 629.1794.

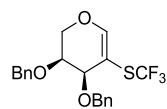
### 3,4,6-Tri-*O*-methyl-2-trifluoromethylthio-D-galactal (7f)



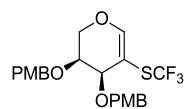
Colorless oil; 93% yield (27.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (15:1 to 12:1);  $[\alpha]_{\text{D}}^{25} = 0.22$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (s, 1H, H-1), 4.38 – 4.33 (m, 1H), 3.98 (d,  $J = 3.4$  Hz, 1H), 3.83 (t,  $J = 3.38$  Hz, 1H), 3.75 – 3.63 (m, 2H), 3.59 (s, 3H), 3.57 (s, 3H), 3.41 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 130.0 (q,  $J = 310.19$  Hz,  $\text{SCF}_3$ ), 98.9 (d,  $J = 1.57$  Hz), 76.4, 75.7, 74.3, 70.2, 59.9, 59.8, 59.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.40; HRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{15}\text{F}_3\text{NaO}_4\text{S}$   $[\text{M} + \text{Na}]^+$  311.0535, found 311.0540.

**3,4-Di-*O*-benzyl-2-trifluoromethylthio-L-rhamninal (7g)**

Colorless oil; 96% yield (39.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (20:1 to 15:1);  $[\alpha]_{\text{D}}^{25} = 0.29$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.24 (m, 10H, Ar-H), 6.94 (s, 1H, H-1), 4.83 (d,  $J = 11.2$  Hz, 1H), 4.71 (d,  $J = 11.6$  Hz, 1H), 4.66 (d,  $J = 11.2$  Hz, 1H), 4.58 (d,  $J = 11.6$  Hz, 1H), 4.33 – 4.24 (m, 1H), 4.14 (d,  $J = 4.7$  Hz, 1H), 3.55 (dd,  $J = 6.1, 4.9$  Hz, 1H), 1.38 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 138.0, 137.7, 130.1 (q,  $J = 311.08$  Hz,  $\text{SCF}_3$ ), 128.7, 128.6, 128.1, 128.00, 127.97, 98.7, 78.2, 74.8, 73.8, 73.4, 16.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.13; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{21}\text{F}_3\text{NaO}_3\text{S}$   $[\text{M} + \text{Na}]^+$  433.1056, found 433.1050.

**3,4-Di-*O*-benzyl-2-trifluoromethylthio-L-arabinal (7h)**

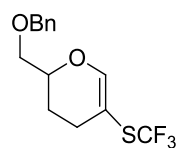
Colorless oil; 87% yield (34.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (20:1 to 15:1);  $[\alpha]_{\text{D}}^{25} = 2.1$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.26 (m, 10H, Ar-H), 6.92 (s, 1H, H-1), 4.91 (d,  $J = 11.3$  Hz, 1H), 4.76 (d,  $J = 11.3$  Hz, 1H), 4.69 (d,  $J = 11.9$  Hz, 1H), 4.62 (d,  $J = 11.9$  Hz, 1H), 4.22 (d,  $J = 2.9$  Hz, 1H), 4.14 – 4.04 (m, 2H), 3.90 – 3.83 (m, 1H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 138.4, 137.7, 129.9 (q,  $J = 308.2$  Hz,  $\text{SCF}_3$ ), 128.7, 128.5, 128.3, 128.2, 127.9, 127.8, 97.9 (d,  $J = 1.6$  Hz), 74.3, 74.2, 73.1, 71.9, 63.1;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.63; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NaO}_3\text{S}$   $[\text{M} + \text{Na}]^+$  419.0899, found 419.0904.

**3,4-Di-*O*-(*p*-methoxybenzyl)-2-trifluoromethylthio-L-arabinal (7i)**

Colorless oil; 88% yield (40.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (15:1 to 9:1);  $[\alpha]_{\text{D}}^{25} = 8.7$  (c 1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.23 (m, 4H, Ar-H), 6.92 – 6.84 (m, 5H), 4.83 (d,  $J = 10.9$  Hz, 1H), 4.68 (d,  $J = 10.9$  Hz, 1H), 4.61 (d,  $J = 11.6$  Hz, 1H),

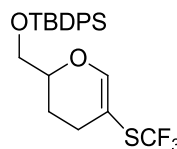
4.53 (d,  $J = 11.6$  Hz, 1H), 4.18 (d,  $J = 2.9$  Hz, 1H), 4.09 – 3.99 (m, 2H), 3.87 – 3.75 (m, 7H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 159.5, 157.4, 129.9, 129.9 (q,  $J = 309.61$  Hz,  $\text{SCF}_3$ ), 129.5, 114.1, 113.9, 98.0, 73.9, 73.9, 72.8, 71.6, 63.2, 55.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.59; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{23}\text{F}_3\text{NaO}_5\text{S}$  [ $\text{M} + \text{Na}$ ] $^+$  479.1111, found 479.1109.

### 2-Benzyloxymethyl-5-trifluoromethylthio-3,4-dihydro-2H-pyran (7j)



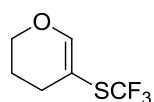
Colorless oil; 82% yield (25.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (20:1 to 15:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.27 (m, 5H, Ar-H), 6.95 (s, 1H, H-1), 4.69 – 4.51 (m, 2H), 4.15 – 4.07 (m, 1H), 3.64 – 3.54 (m, 2H), 2.50 – 2.38 (m, 1H), 2.34 – 2.24 (m, 1H), 2.02 – 1.92 (m, 1H), 1.89 – 1.76 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 137.9, 130.1 (q,  $J = 310.2$  Hz,  $\text{SCF}_3$ ), 128.6, 128.0, 127.9, 98.1 (d,  $J = 1.7$  Hz), 74.8, 73.7, 71.5, 27.1, 24.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -43.97; HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{NaO}_2\text{S}$  [ $\text{M} + \text{Na}$ ] $^+$  327.0637, found 327.0633.

### 2-*t*-butyldiphenylsilyloxymethyl-5-trifluoromethylthio-3,4-dihydro-2H-pyran (7k)



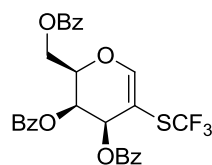
Colorless oil; 99% yield (45.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (25:1 to 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.63 (m, 4H, Ar-H), 7.45 – 7.32 (m, 6H, Ar-H), 6.90 (s, 1H, H-1), 4.04 – 3.97 (m, 1H), 3.79 (dd,  $J = 10.8, 5.1$  Hz, 1H), 3.71 (dd,  $J = 10.8, 5.4$  Hz, 1H), 2.47 – 2.36 (m, 1H), 2.33 – 2.22 (m, 1H), 2.05 – 1.97 (m, 1H), 1.91 – 1.77 (m, 1H), 1.06 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.7, 135.8, 133.4, 130.2 (q,  $J = 311.08$  Hz,  $\text{SCF}_3$ ), 130.0, 127.9, 97.8 (d,  $J = 1.7$  Hz), 76.0, 65.3, 27.0, 24.4, 19.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -43.98; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{27}\text{F}_3\text{NaO}_2\text{SSi}$  [ $\text{M} + \text{Na}$ ] $^+$  475.1345, found 475.1338.

### 5-Trifluoromethylthio-3,4-dihydro-2H-pyran (7l)



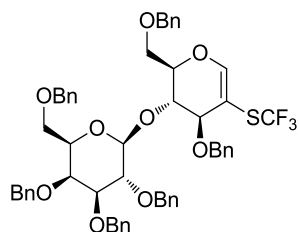
Colorless oil; 76% yield (14.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (20:1 to 15:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93 (s, 1H), 4.10 – 3.97 (m, 2H), 2.35 (t,  $J = 6.1$  Hz, 2H), 2.06 – 1.85 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 130.2 (q,  $J = 309.88$  Hz,  $\text{SCF}_3$ ), 98.1, 65.9, 27.5, 22.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -44.10; MS (EI) calcd for  $\text{C}_6\text{H}_7\text{F}_3\text{OS}$  [ $\text{M}^+$ ] 184.02, found 184.00.

### 3,4,6-Tri-*O*-benzoyl-2-trifluoromethylthio-*D*-galactal (7m)



Colorless oil; 64% yield (35.7 mg); column chromatography conditions: petroleum ether/ethyl acetate (12:1 to 9:1);  $[\alpha]_{\text{D}}^{25} = 1.13$  (c 1.0,  $\text{CDCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 8.00 (m, 2H), 7.96 – 7.87 (m, 4H), 7.61 – 7.49 (m, 3H), 7.42 (dd,  $J = 13.9, 7.7$  Hz, 4H), 7.35 (t,  $J = 7.8$  Hz, 2H), 7.27 (s, 1H), 6.12 (d,  $J = 4.3$  Hz, 1H), 6.01 (dd,  $J = 4.3, 2.1$  Hz, 1H), 4.87 (d,  $J = 5.1$  Hz, 1H), 4.79 (dd,  $J = 11.7, 7.7$  Hz, 1H), 4.55 (dd,  $J = 11.8, 4.7$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 165.7, 165.4, 157.4, 133.8, 133.5, 133.5, 130.1, 129.95, 129.92, 129.38, 129.36 (q,  $J = 310.49$  Hz,  $\text{SCF}_3$ ), 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 127.9, 97.5, 74.6, 66.0, 64.8, 62.2, 53.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -43.89; HRMS (ESI) calcd for  $\text{C}_{28}\text{H}_{25}\text{F}_3\text{NO}_7\text{S}$  [ $\text{M} + \text{NH}_4$ ] $^+$  576.1298, found 576.1302.

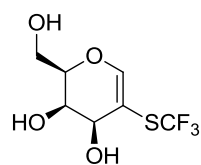
### 3,6-Di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- $\beta$ -*D*-galactopyranosyl)-2-trifluoromethylthio-*D*-glucal (7n)



Colorless oil; 92% yield (87.0 mg); column chromatography conditions: petroleum ether/ethyl acetate (15:1 to 12:1);  $[\alpha]_{\text{D}}^{25} = 0.02$  (c 0.10,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.21 (m, 30H, Ar-H), 6.99 (s, 1H, H-1), 4.95 (d,  $J = 11.6$  Hz, 1H), 4.80 (d,  $J = 10.9$  Hz, 1H), 4.76 – 4.63 (m, 5H), 4.63 – 4.57 (m, 1H), 4.52 – 4.41 (m, 4H), 4.41 – 4.31 (m, 2H), 4.26 (t,  $J = 3.5$  Hz, 1H), 4.16 (d,  $J = 2.8$  Hz, 1H), 3.88 (d,  $J = 2.7$  Hz, 1H), 3.82 – 3.74 (m, 2H), 3.60 (dd,  $J = 10.7, 4.2$  Hz, 1H), 3.53 –

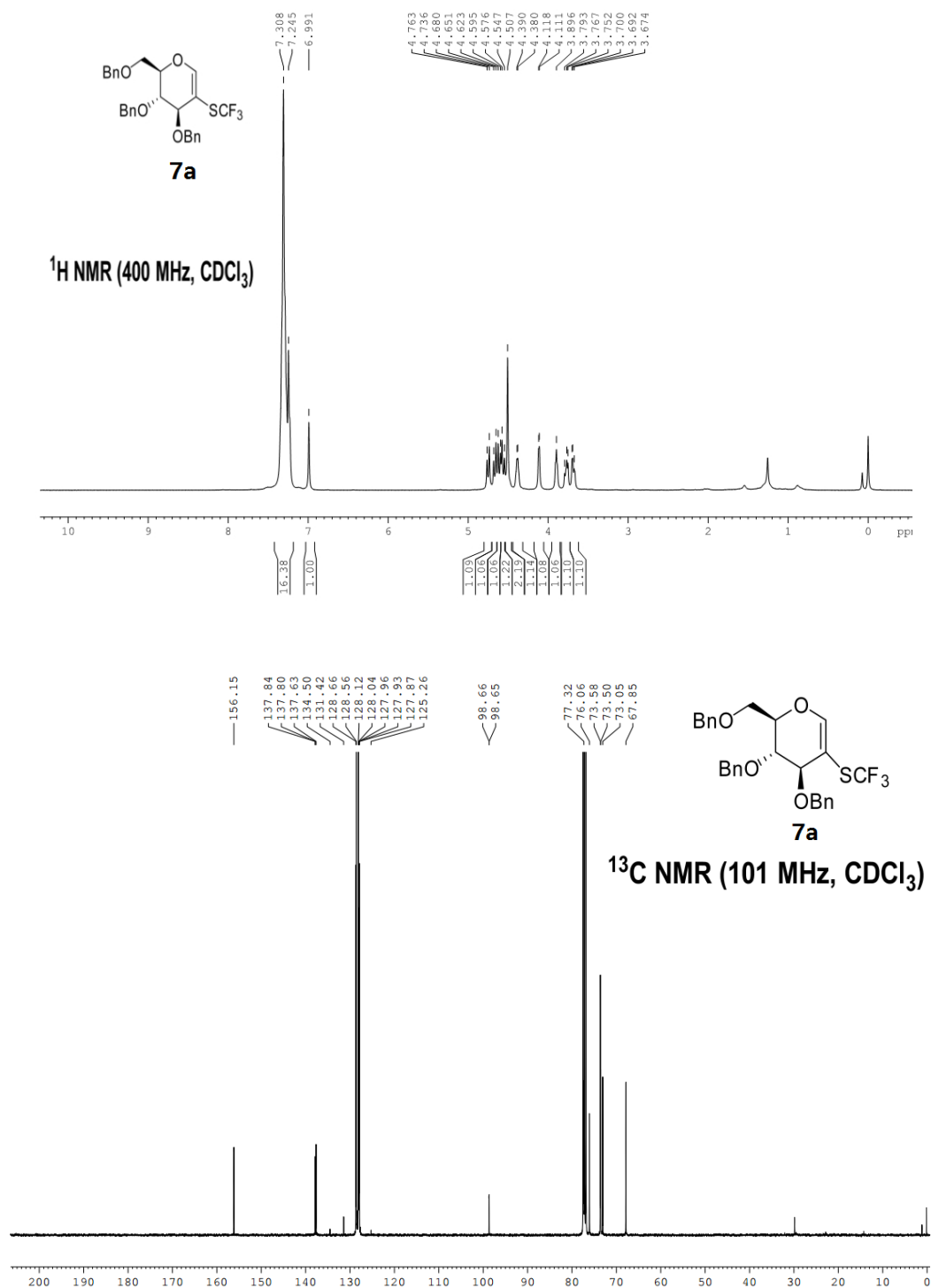
3.42 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 138.8, 138.7, 138.6, 138.2, 138.0, 137.9, 129.8 (q,  $J = 309.92$  Hz,  $\text{SCF}_3$ ), 128.54, 128.49, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.70, 127.68, 127.66, 127.63, 102.6, 98.5 (d,  $J = 1.6$  Hz), 82.2, 79.4, 76.3, 75.5, 75.3, 74.7, 73.7, 73.69, 73.65, 73.4, 73.2, 73.0, 72.4, 68.8, 67.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -43.75; HRMS (ESI) calcd for  $\text{C}_{55}\text{H}_{55}\text{F}_3\text{NaO}_9\text{S}$   $[\text{M} + \text{Na}]^+$  971.3411, found 971.3433.

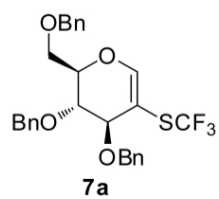
### 2-Trifluoromethylthio-D-galactal (10)



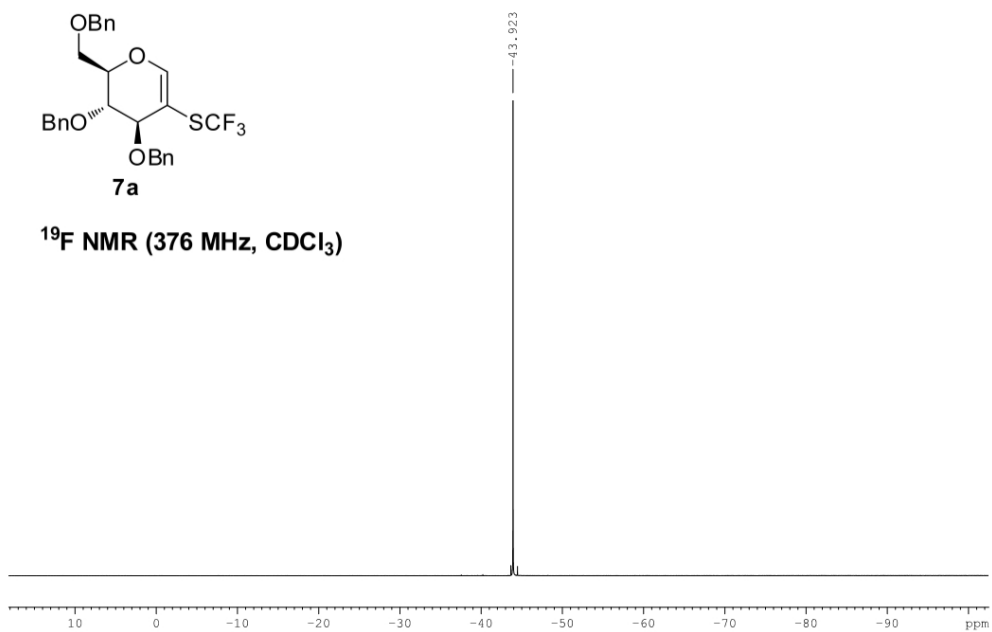
Colorless oil; column chromatography conditions:  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (12:1);  $[\alpha]_D^{25} = 0.129$  (c 1.0, MeOH);  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.03 (s, 1H), 4.33 (d,  $J = 4.3$  Hz, 1H), 4.13 (t,  $J = 6.0$  Hz, 1H), 4.08 (dd,  $J = 4.4, 1.6$  Hz, 1H), 3.89 (dd,  $J = 11.7, 6.9$  Hz, 1H), 3.81 (dd,  $J = 11.7, 5.1$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, MeOD)  $\delta$  157.4, 131.7 (q,  $J = 308.45$  Hz,  $\text{SCF}_3$ ) 102.0, 80.5, 67.2, 66.7, 61.8;  $^{19}\text{F}$  NMR (376 MHz, MeOD)  $\delta$  -46.22; HRMS (ESI) calcd for  $\text{C}_7\text{H}_8\text{F}_3\text{O}_4\text{S}$   $[\text{M} - \text{H}]^-$  245.0101, found 245.0092.

## 8. NMR Spectra of 7a-7n and 10

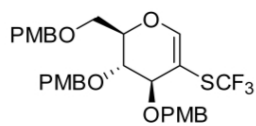




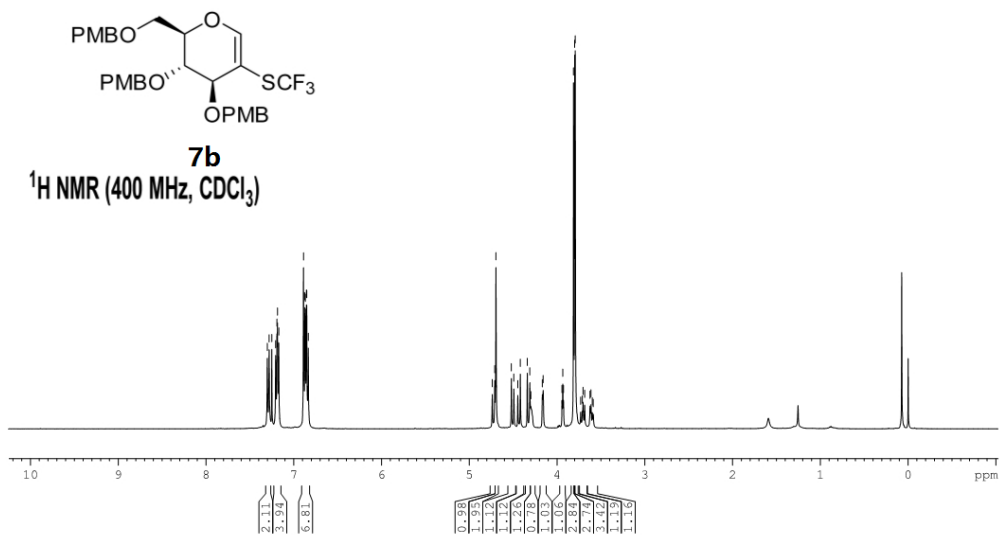
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

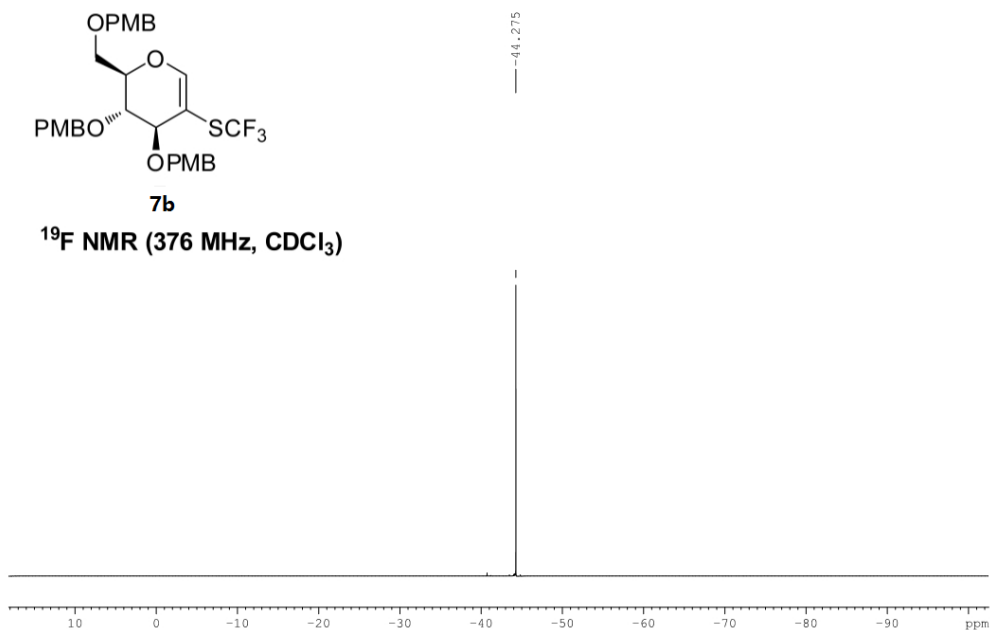
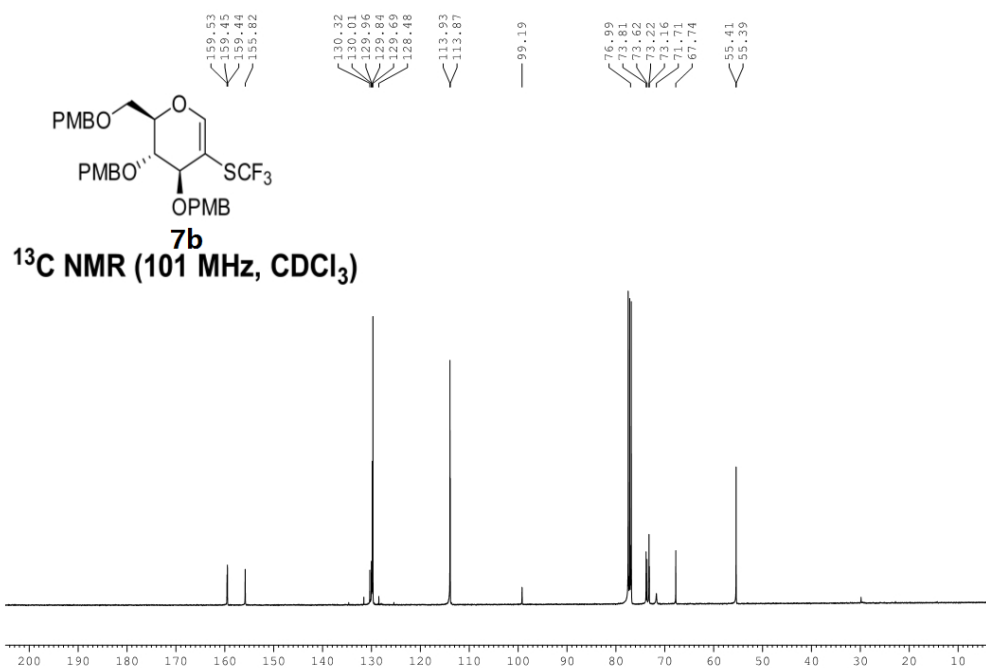


7.302  
7.280  
7.251  
7.207  
7.192  
7.195  
7.196  
6.889  
6.873  
6.868  
6.856  
6.852  
6.835  
4.739  
4.730  
4.697  
4.521  
4.493  
4.448  
4.419  
4.390  
4.381  
4.298  
4.167  
4.159  
3.944  
3.935  
3.927  
3.813  
3.799  
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3.705  
3.686  
3.625  
3.614  
3.595  
3.587

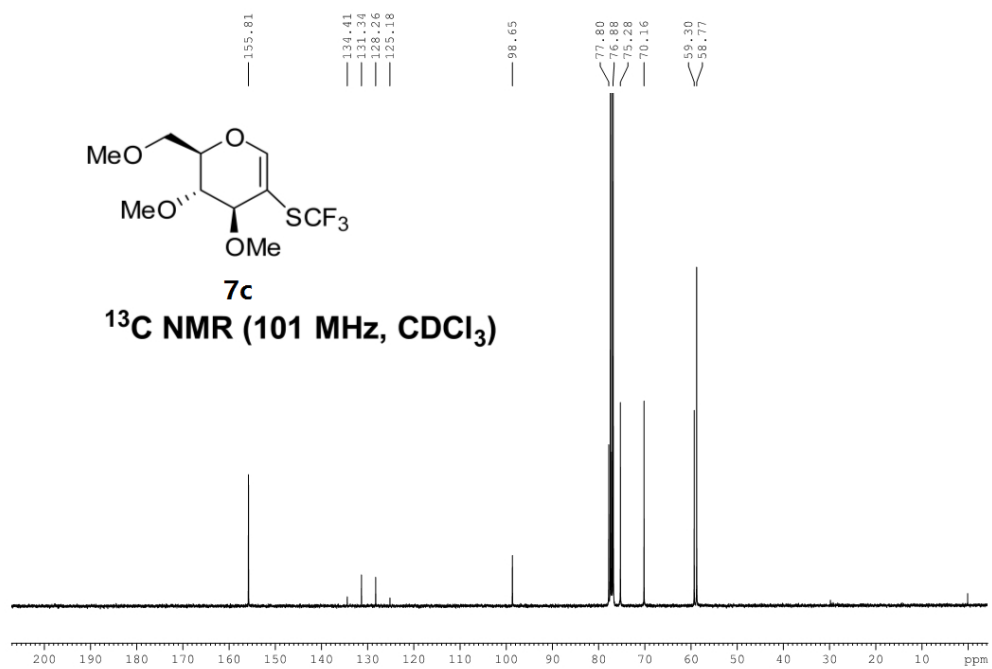
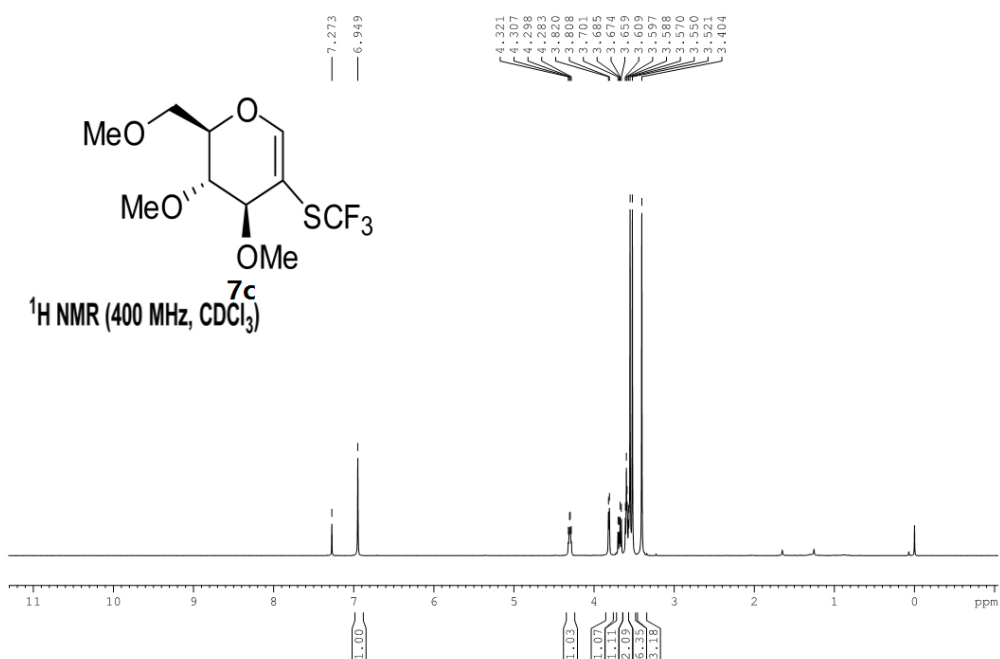


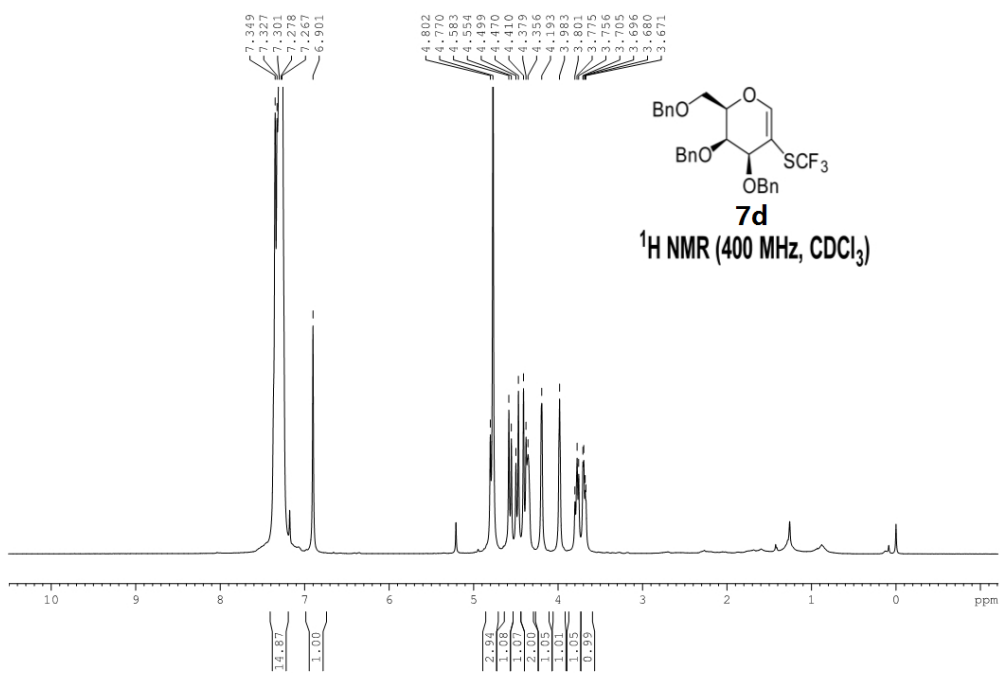
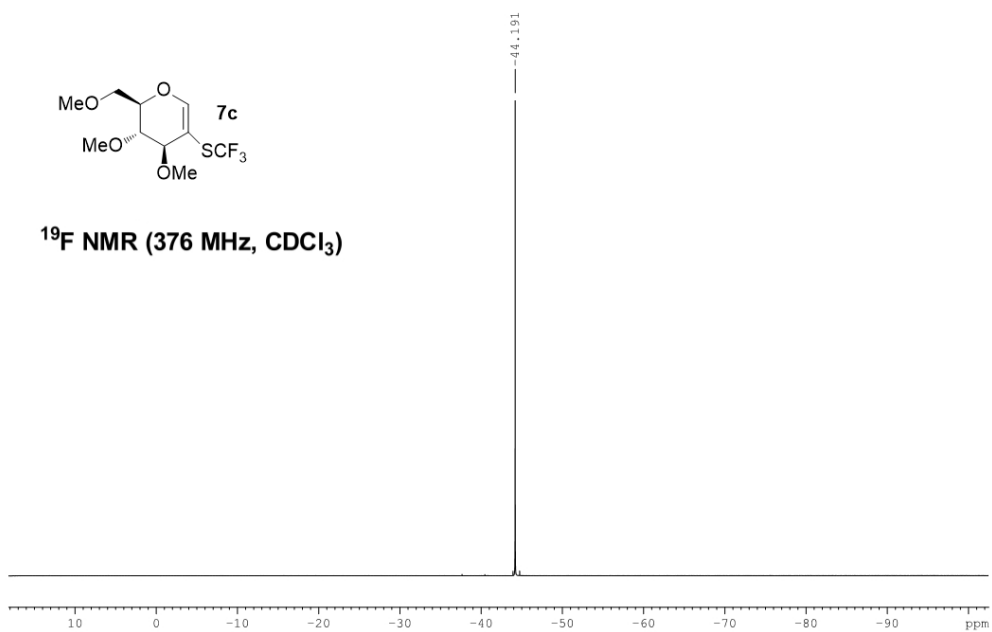
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



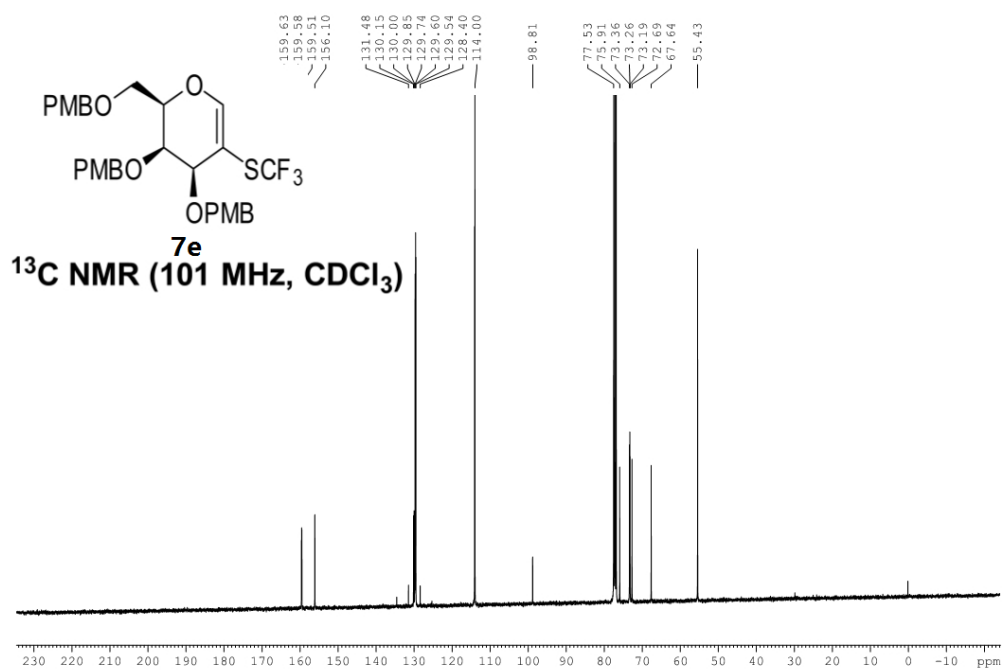
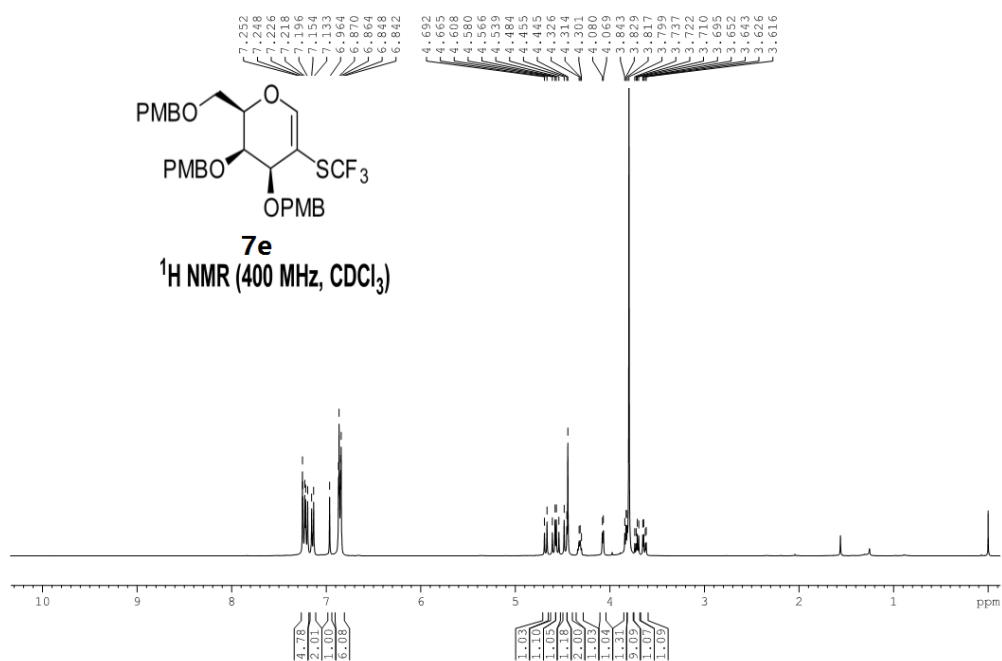


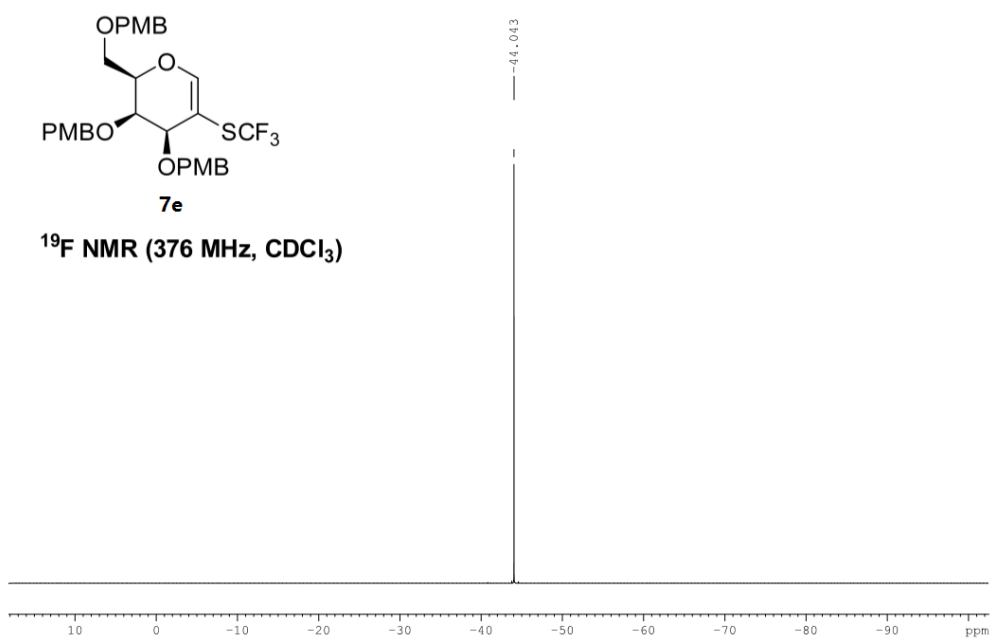


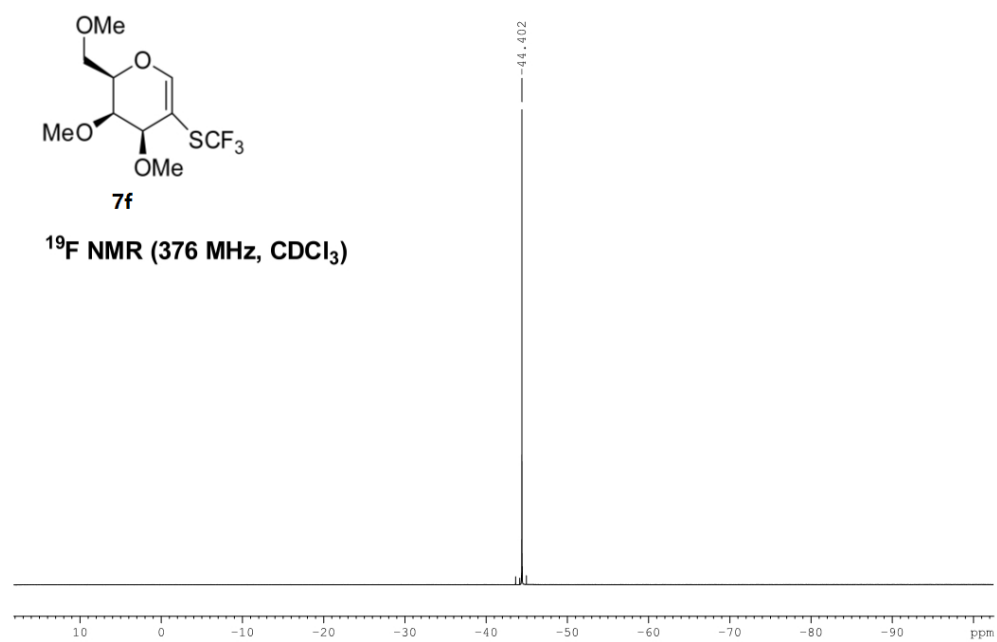
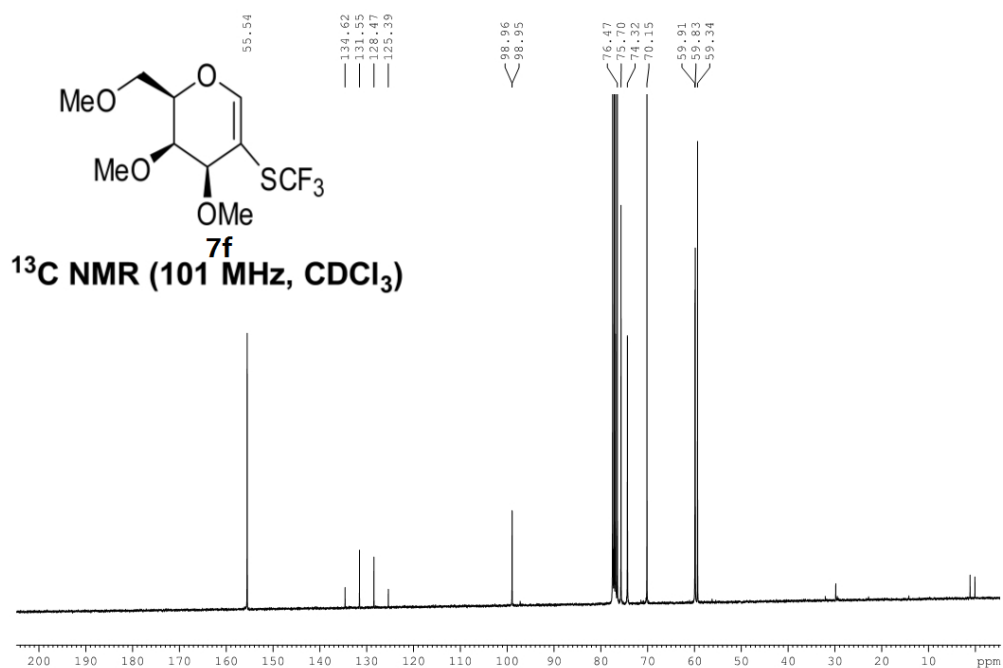


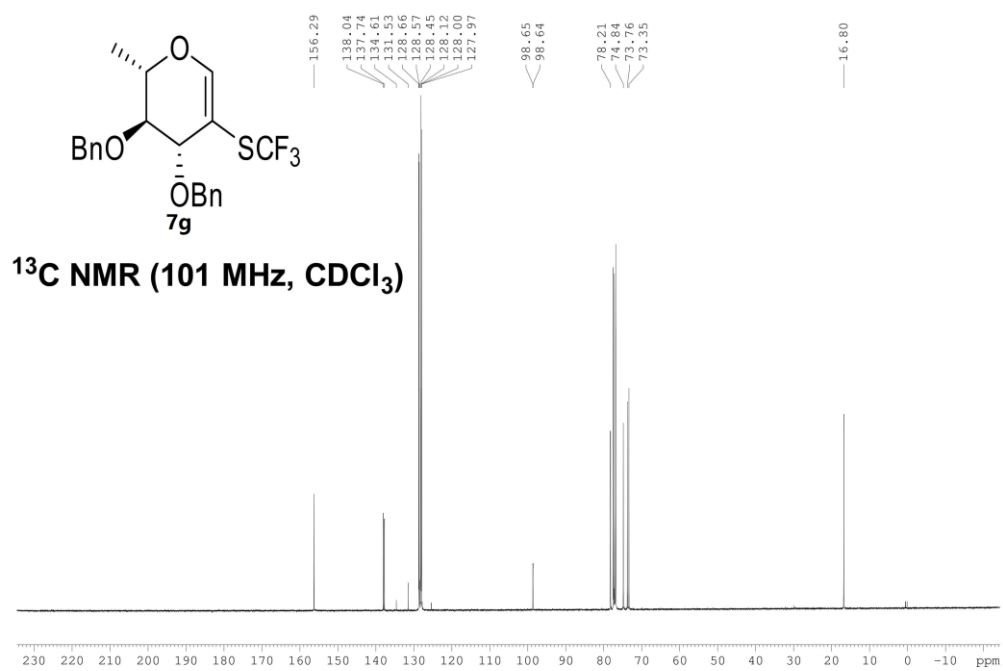
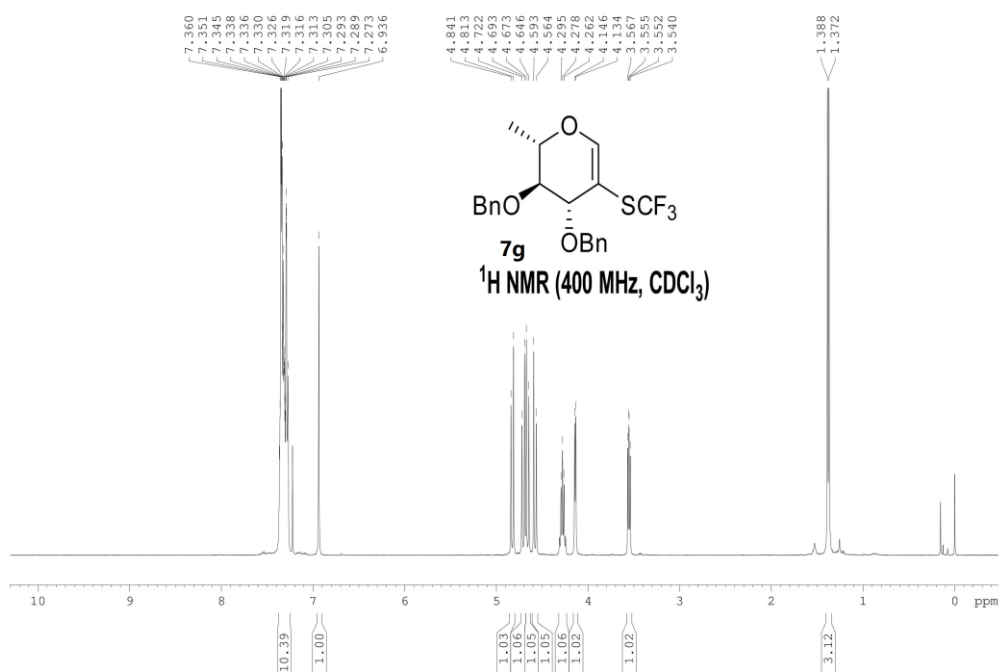


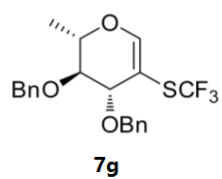




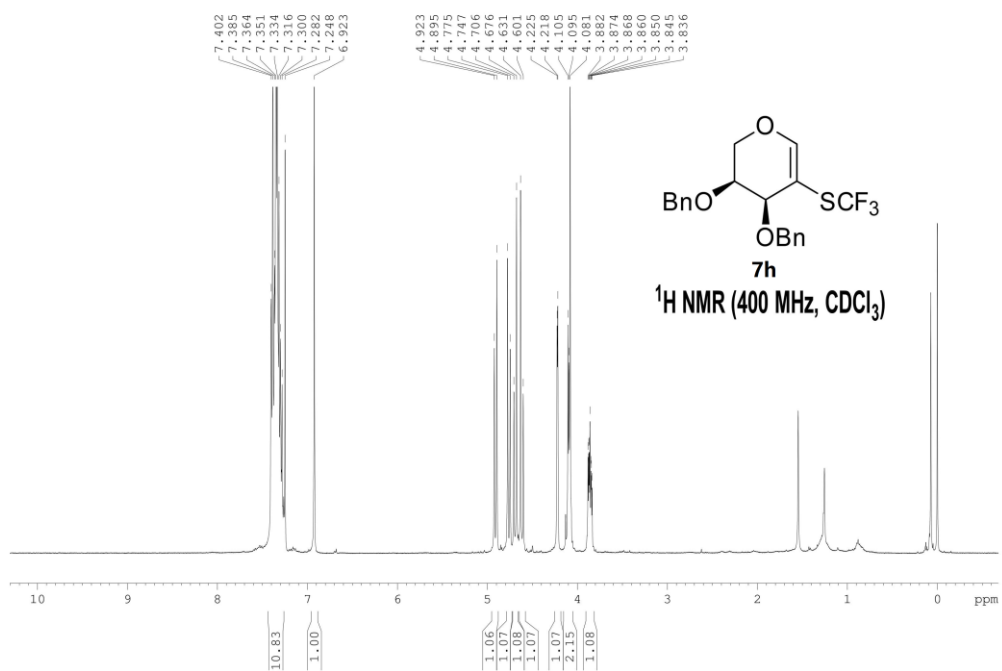
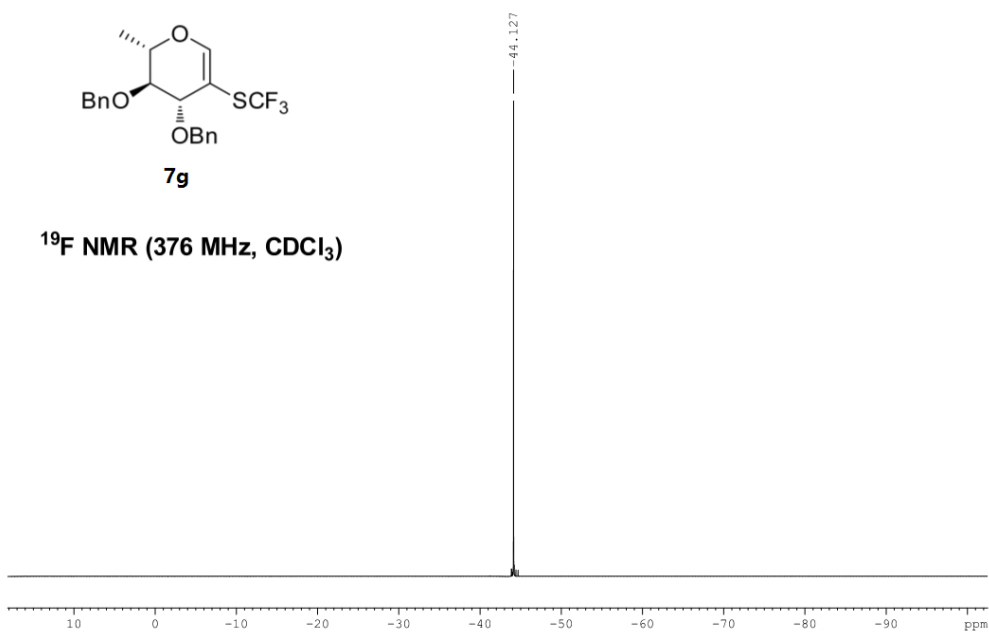




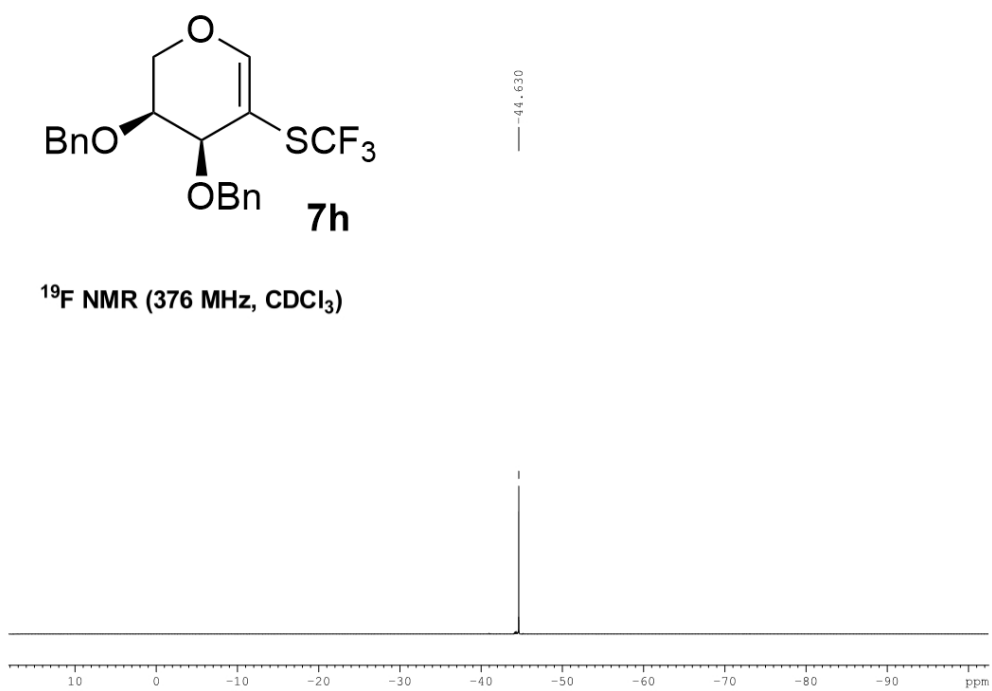
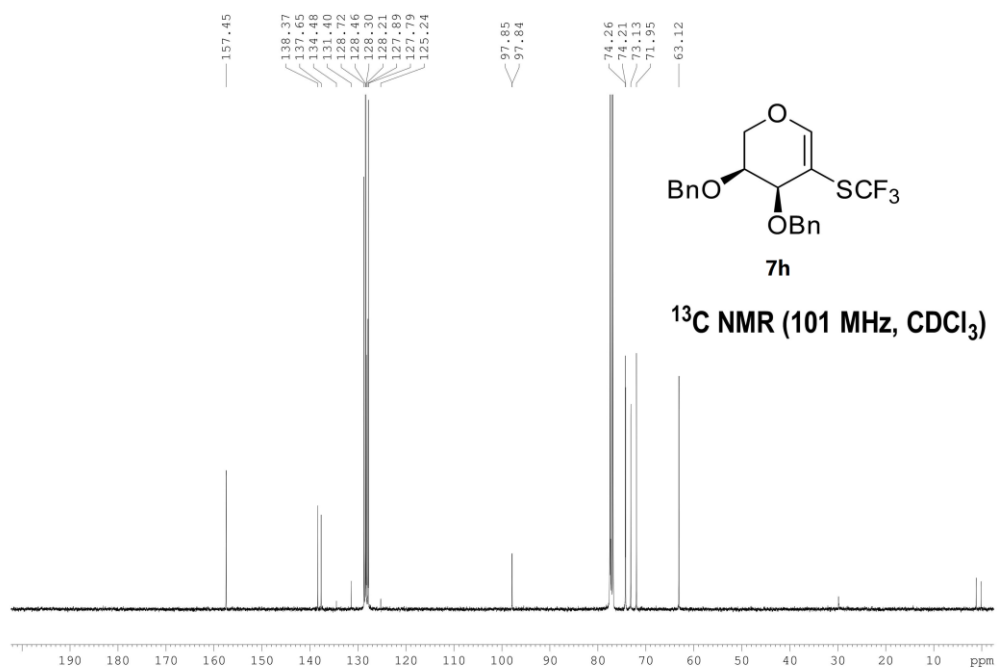


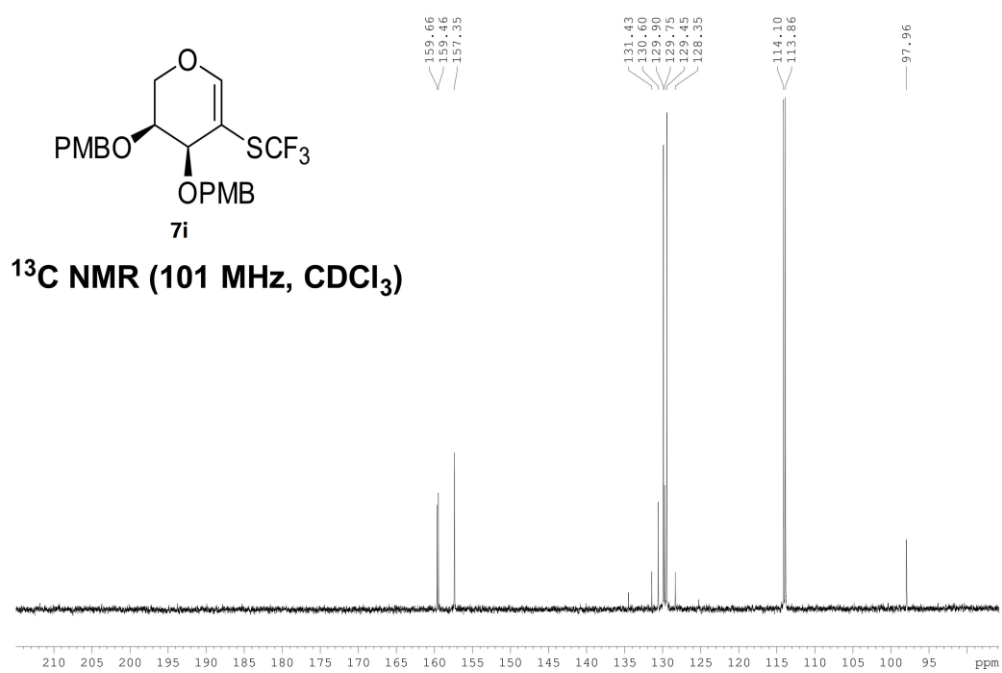
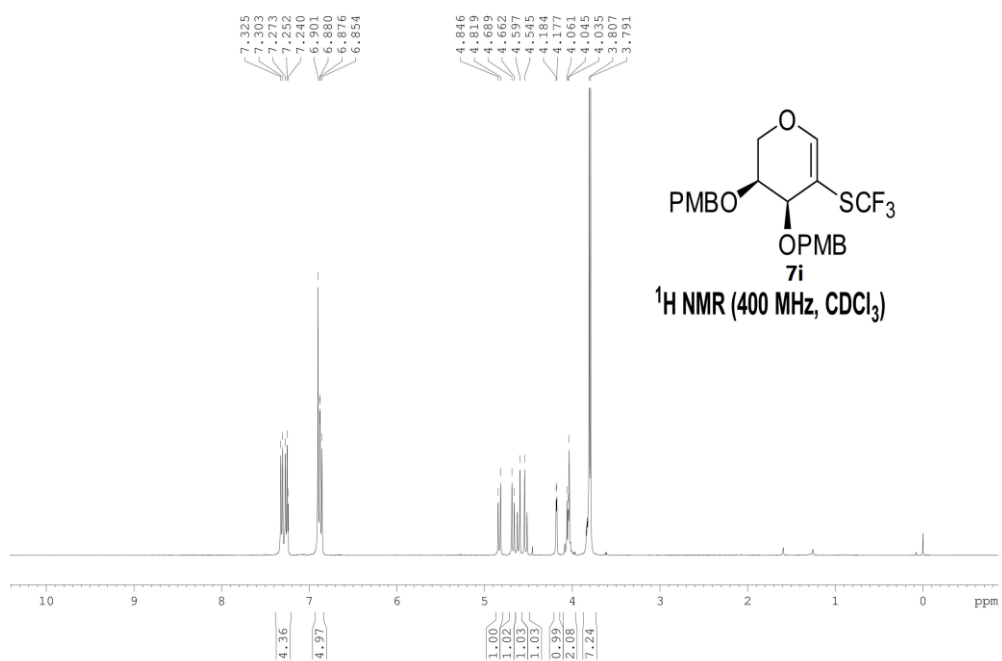


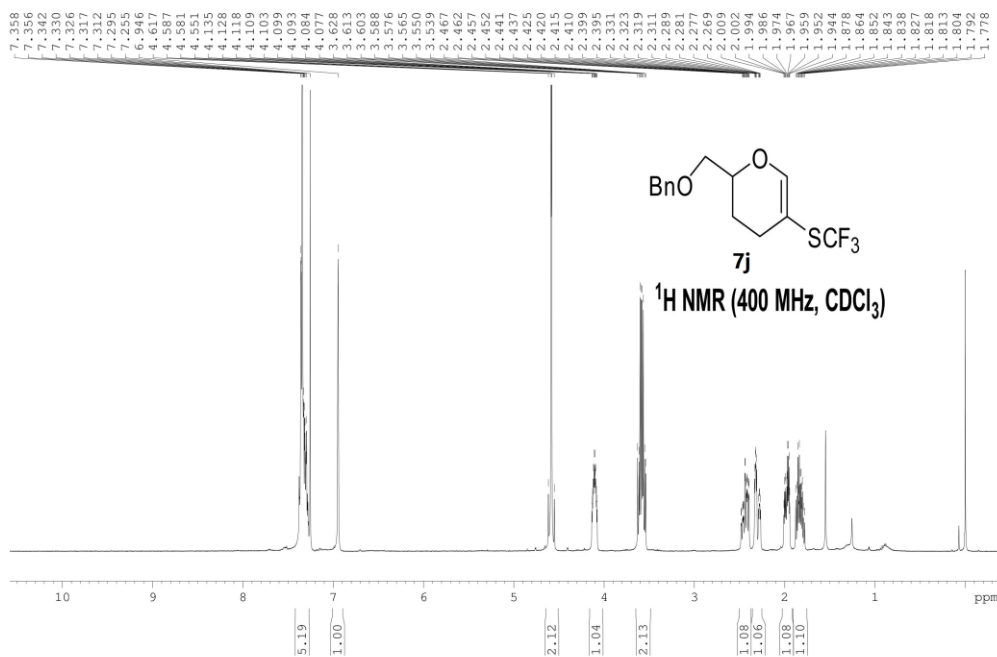
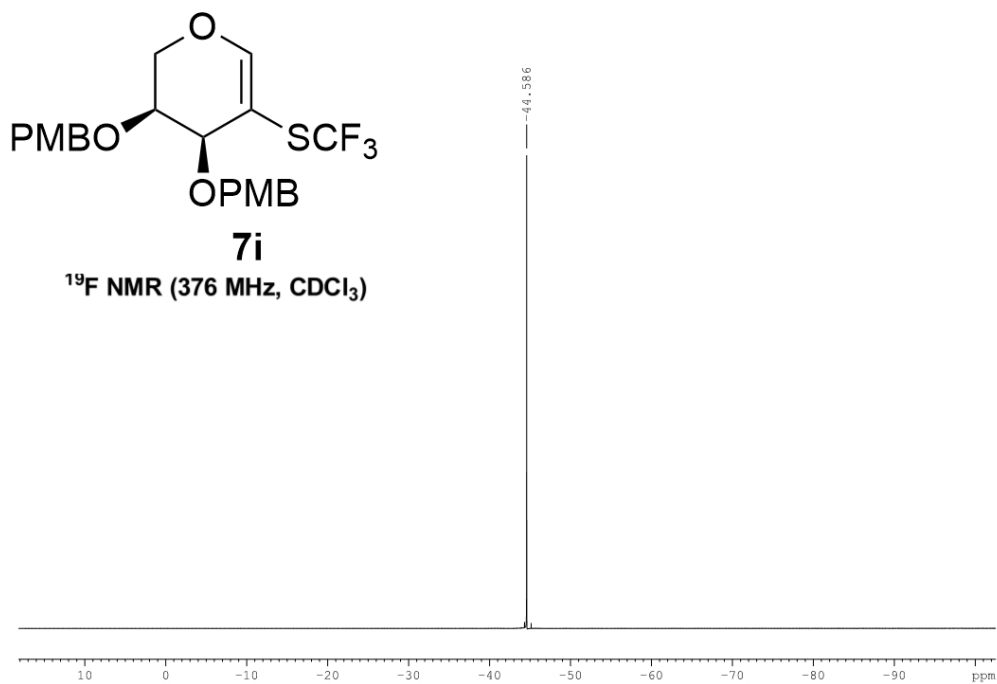
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

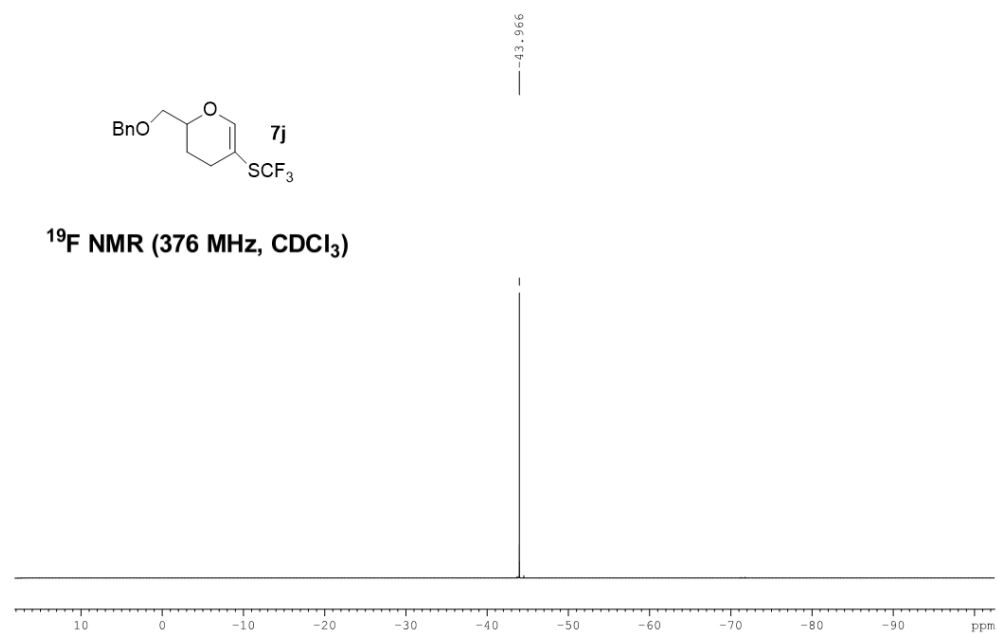
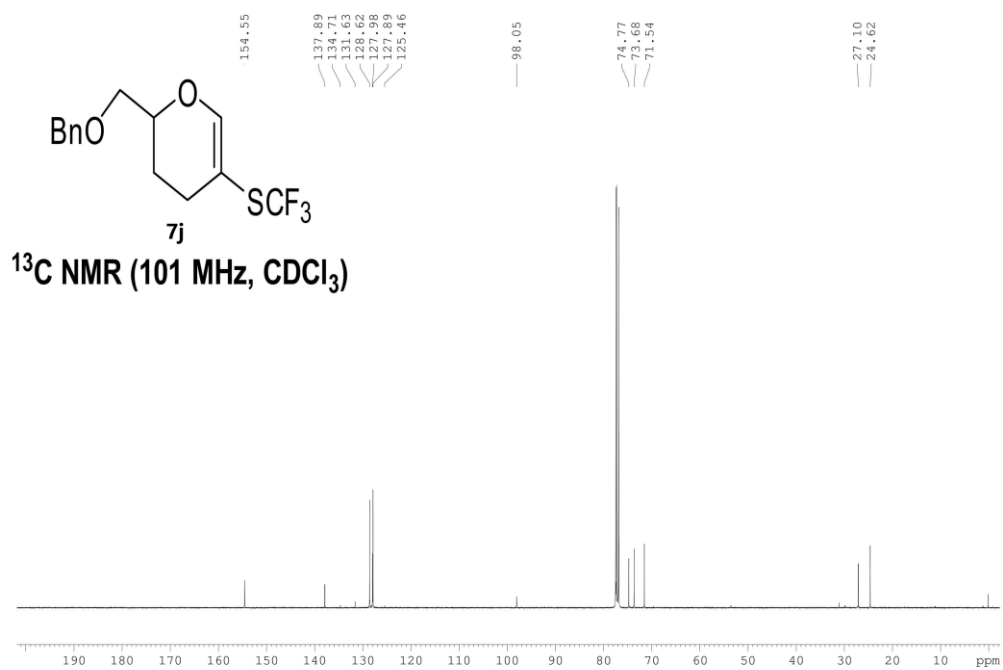




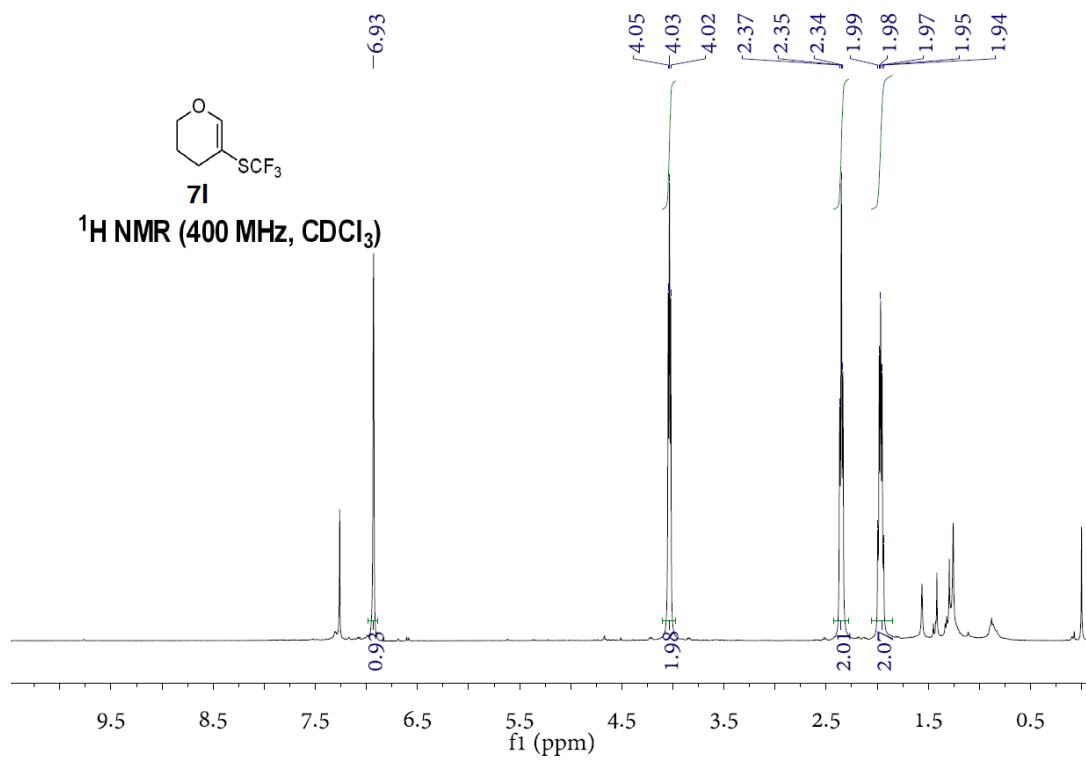
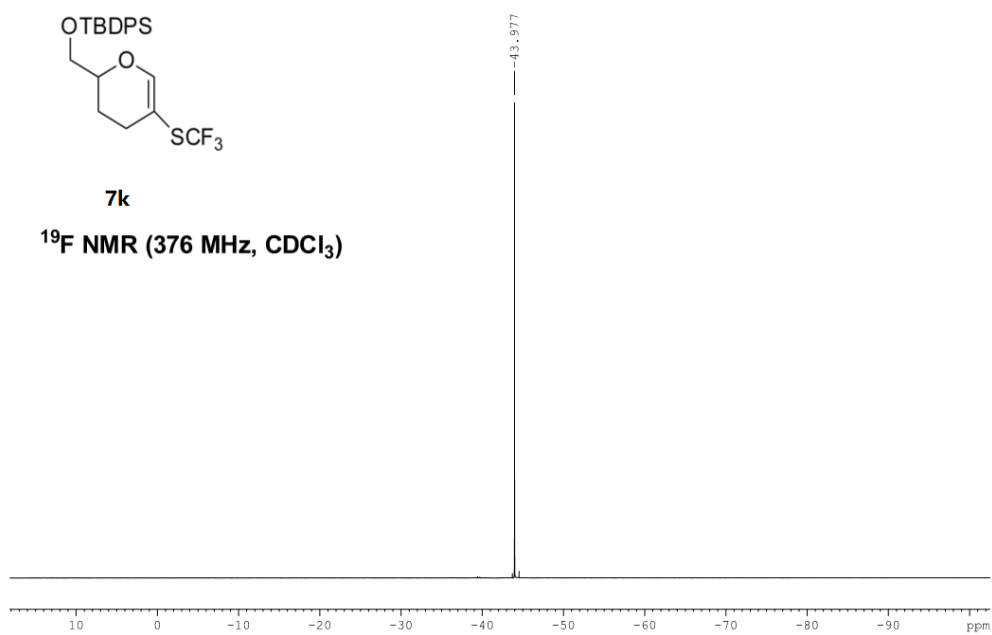




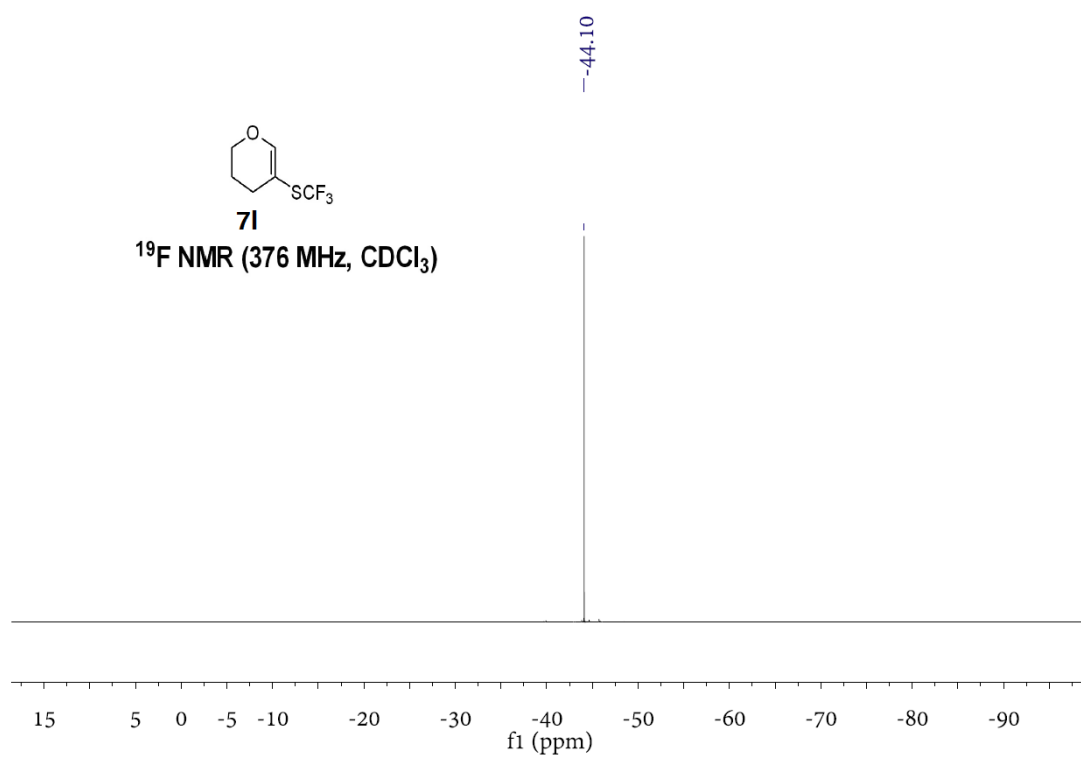
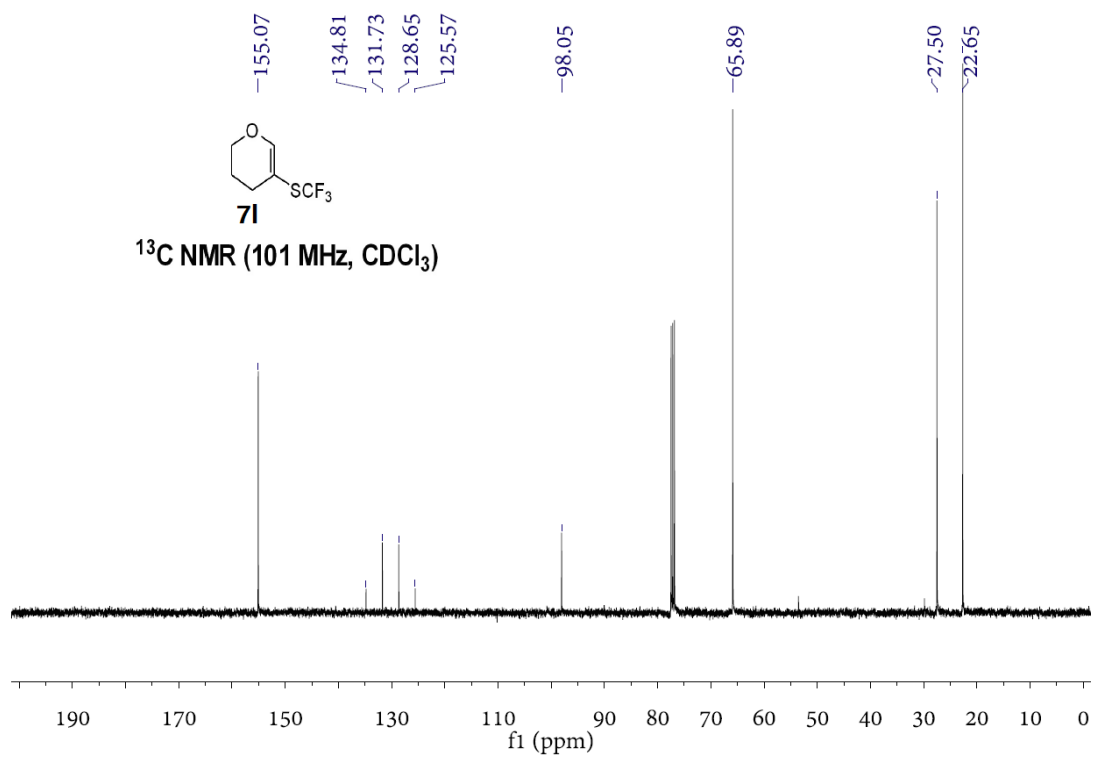




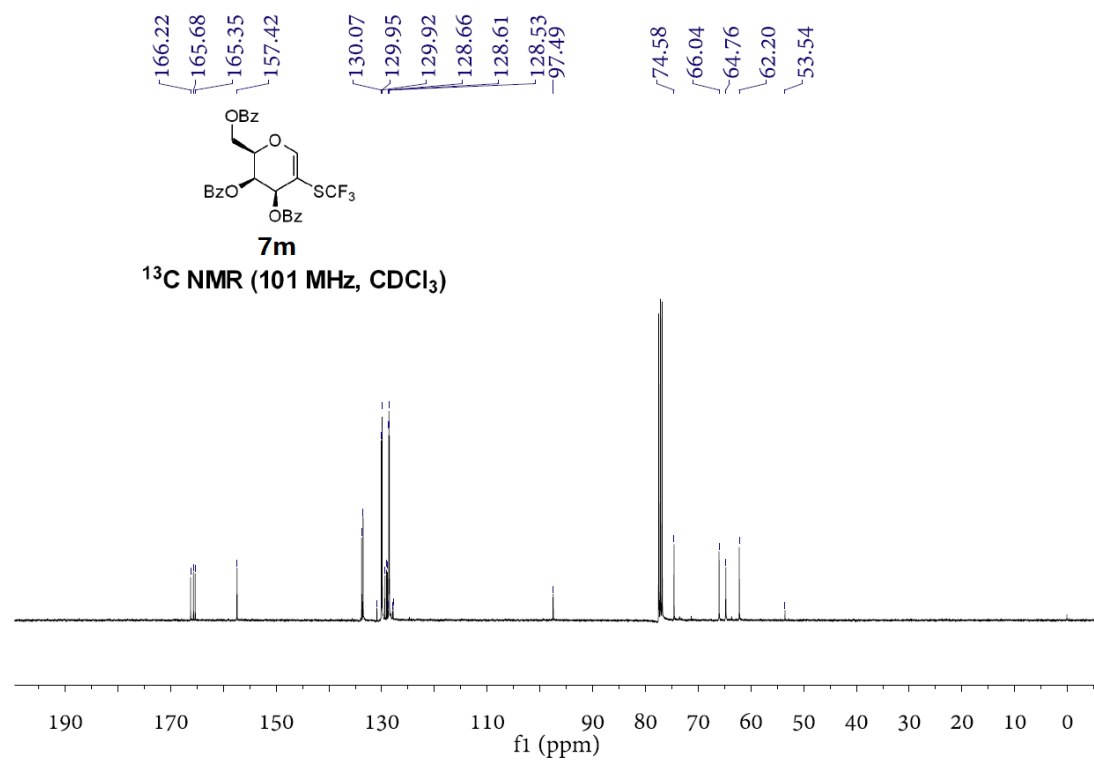
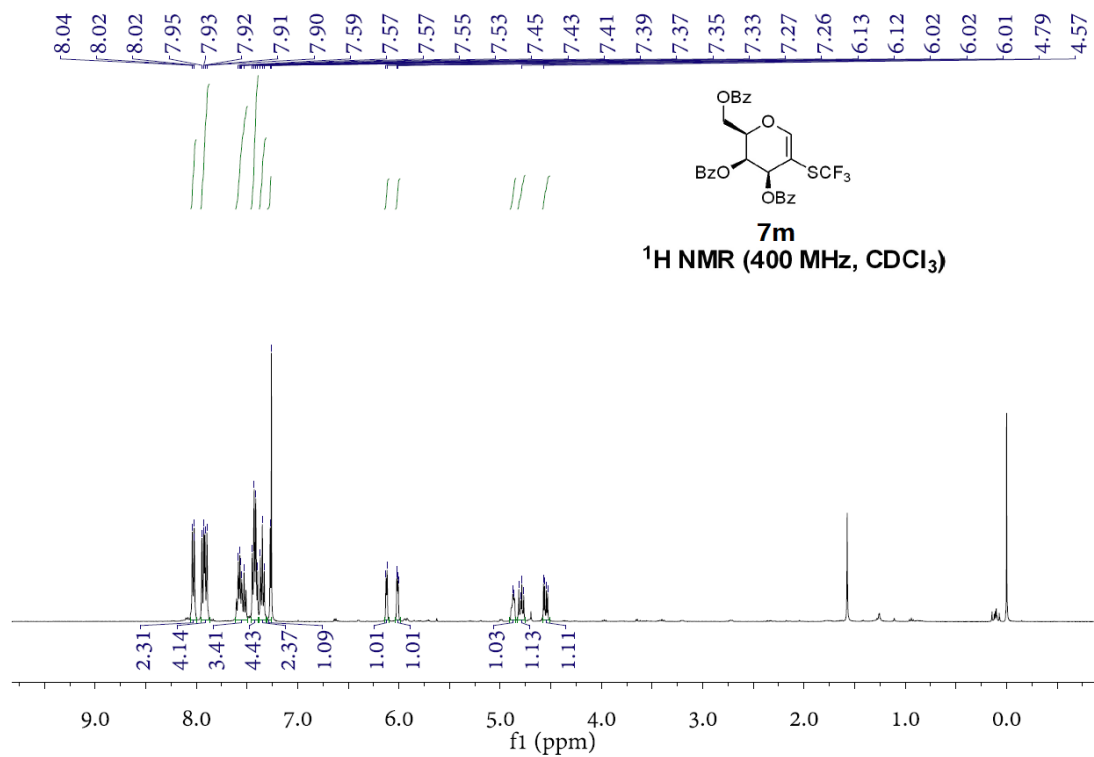




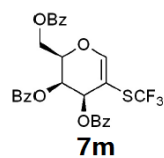
Journal Name COMMUNICATION



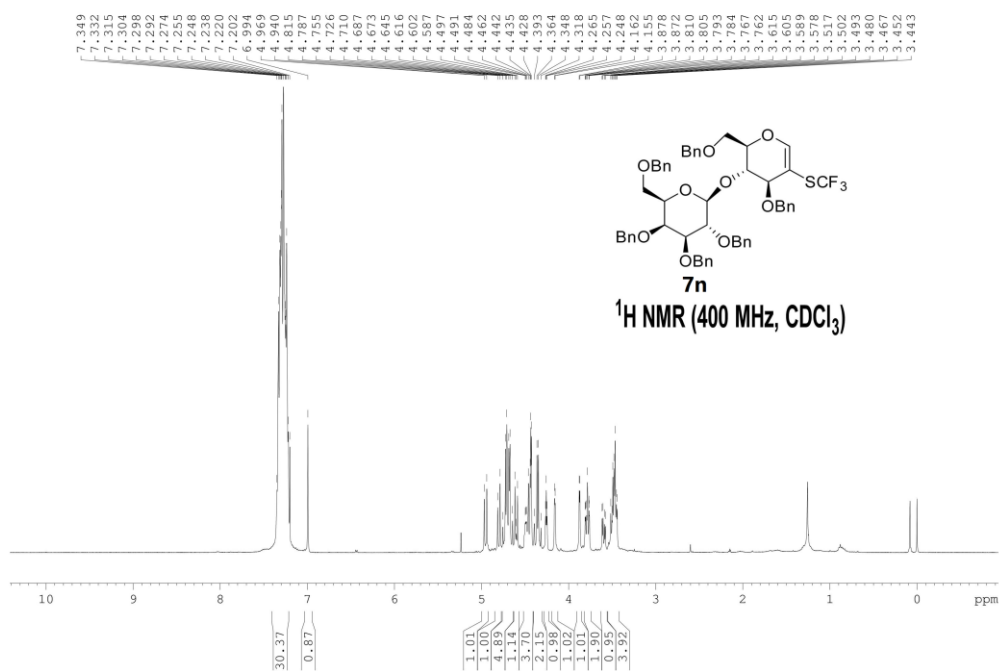
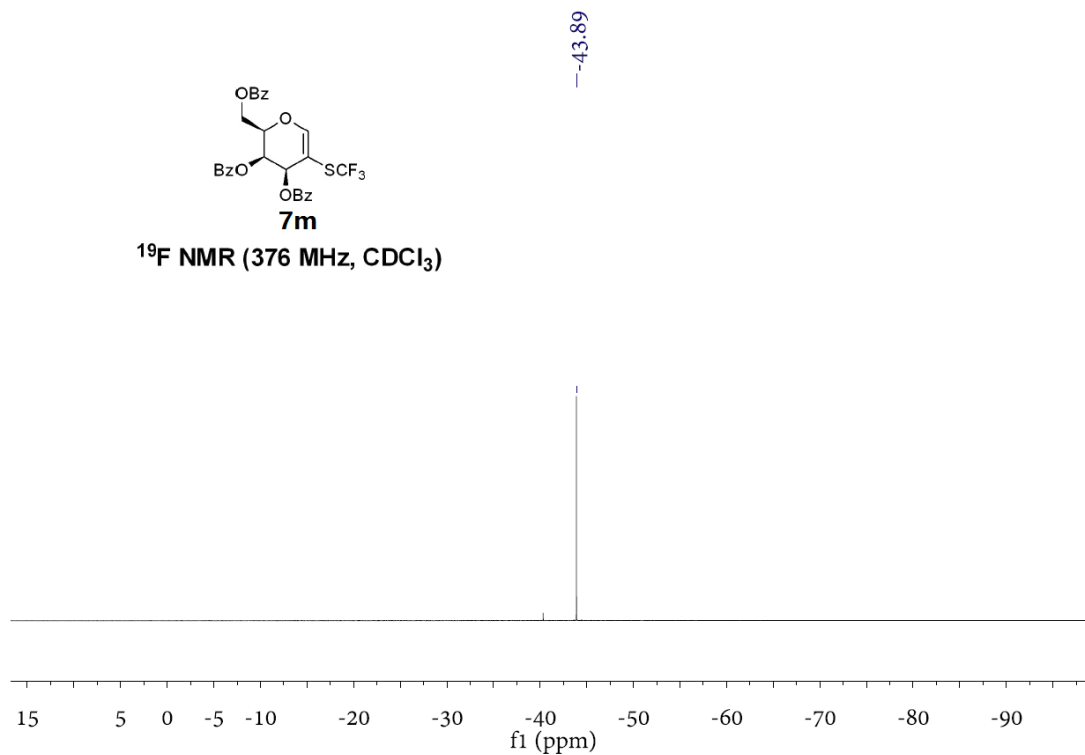
Journal Name COMMUNICATION

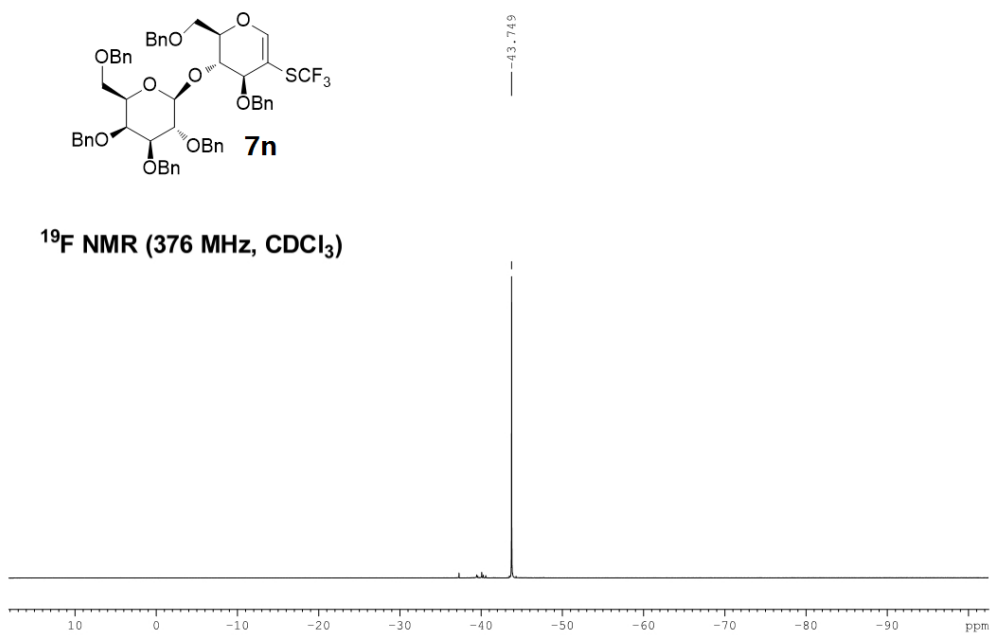
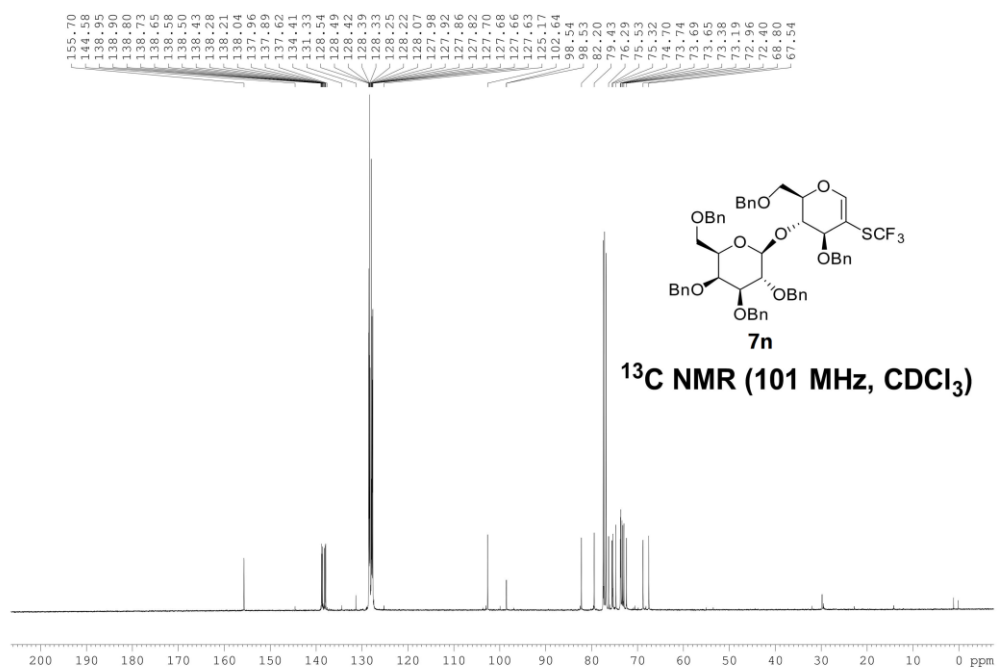


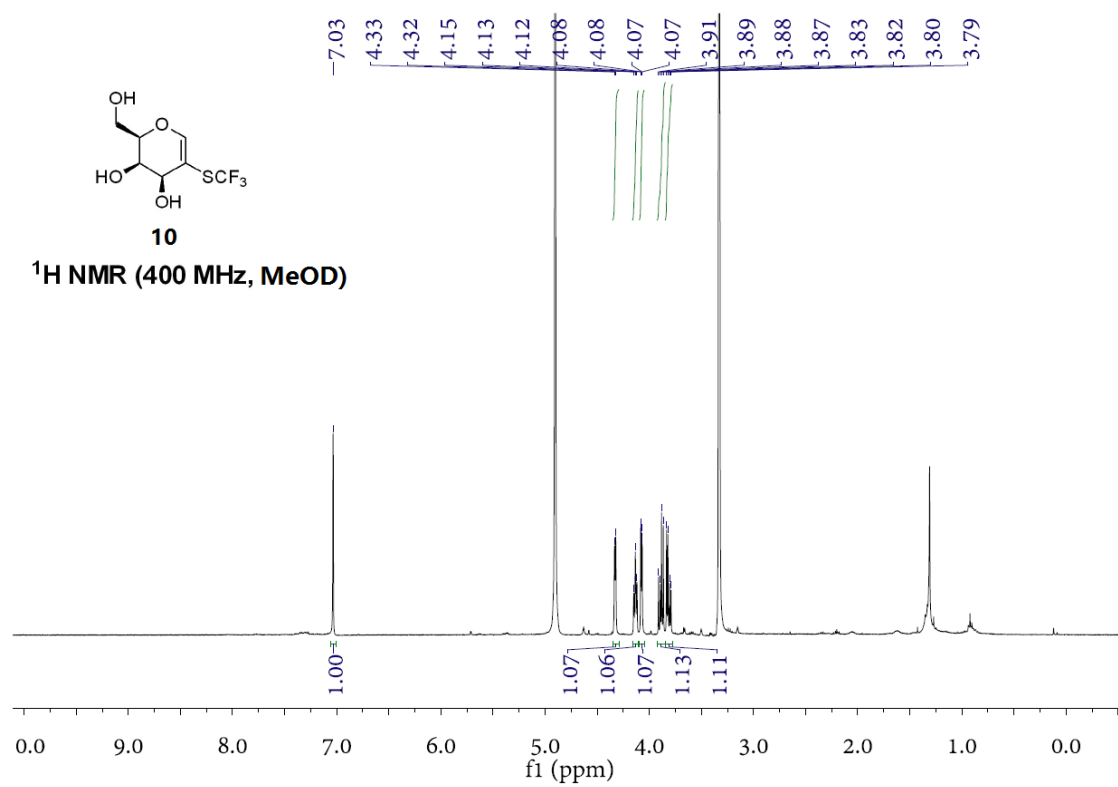


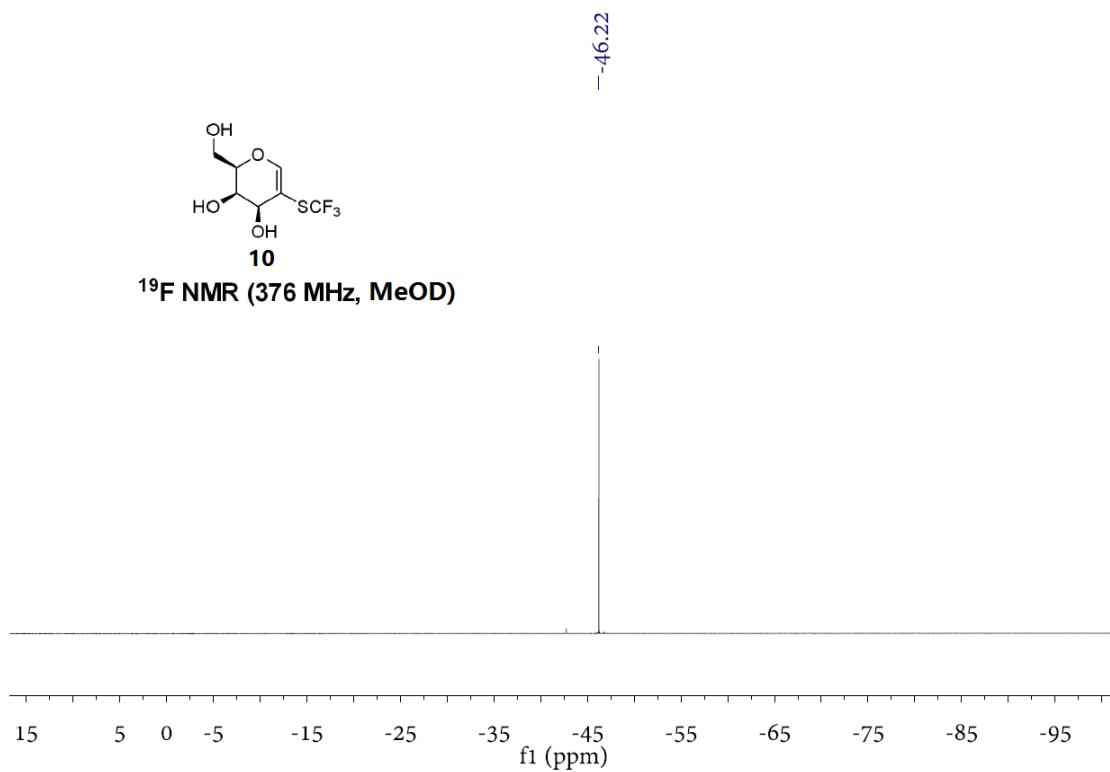
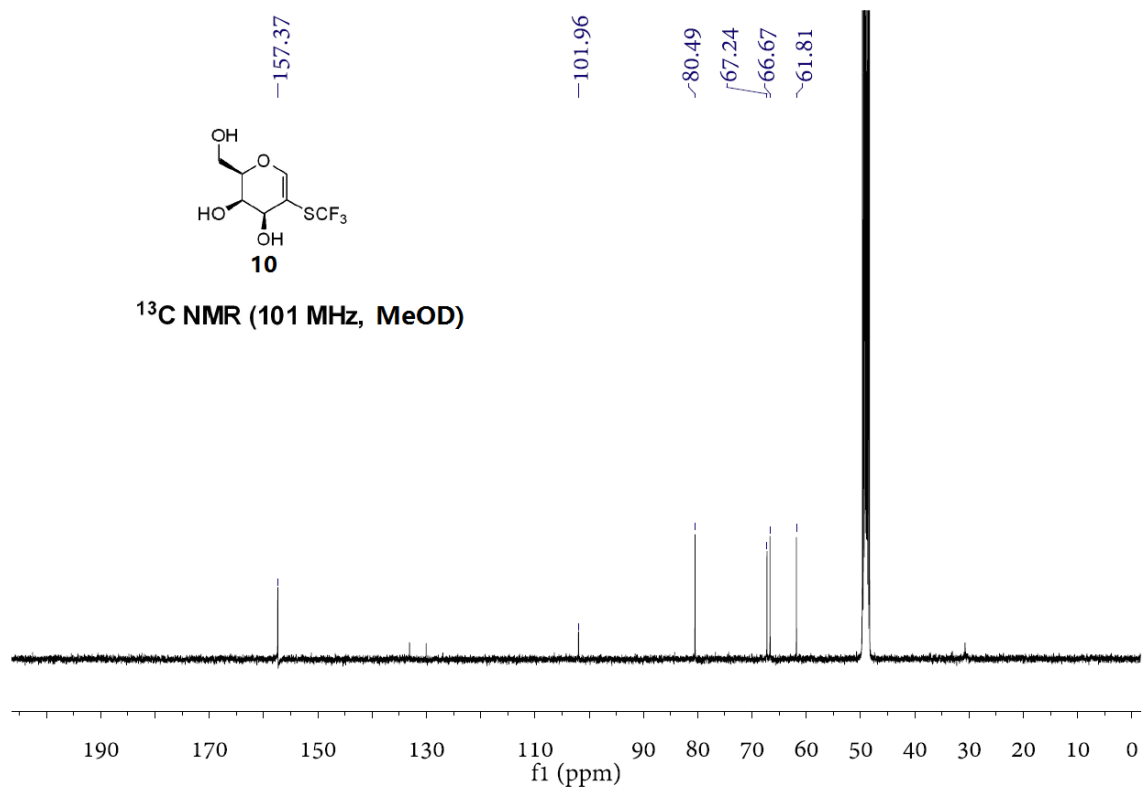


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )





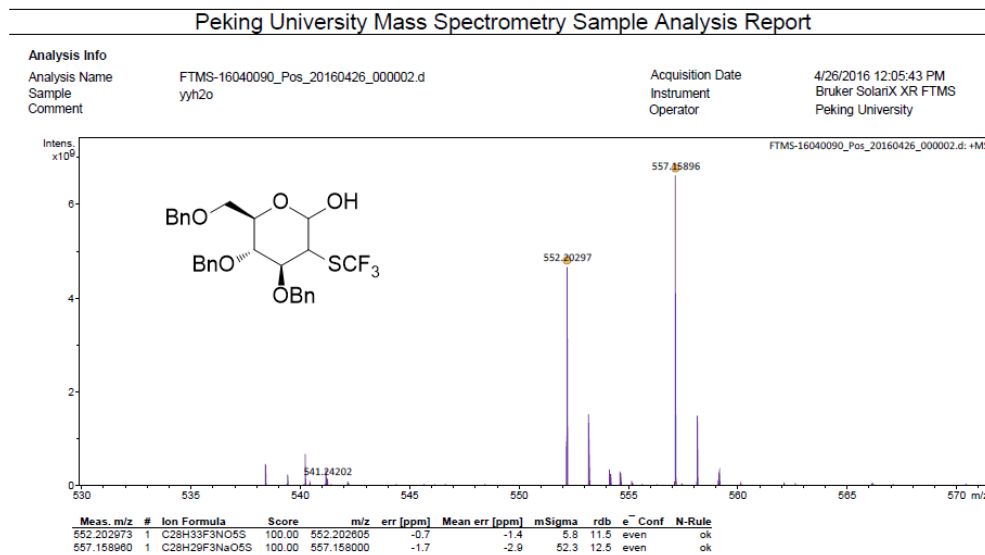




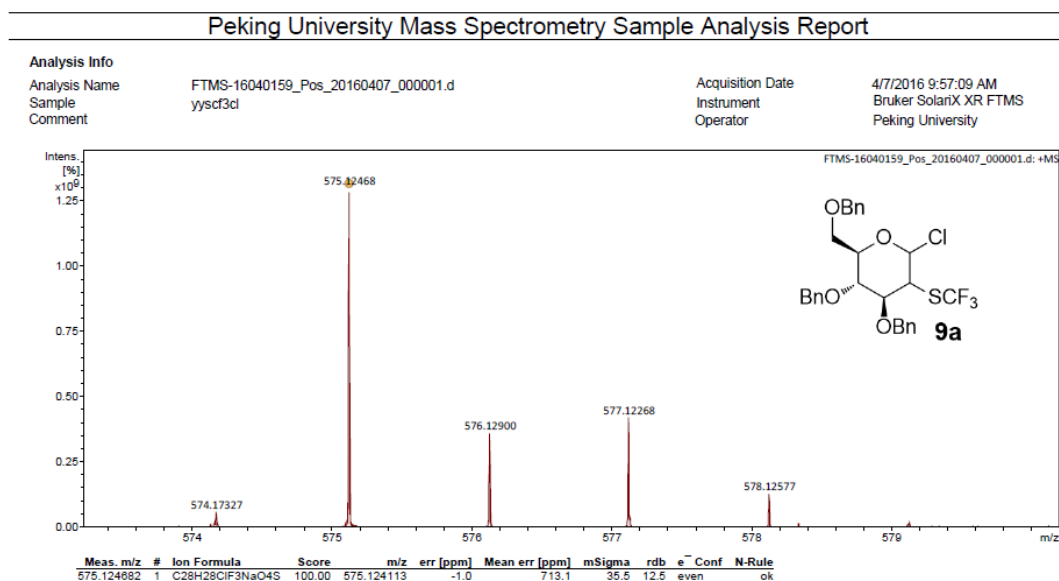


before use) to afford **9a** as colorless oil (17.0 mg, 31% yield). HRMS (ESI) calcd for  $C_{28}H_{28}ClF_3NaO_4S$   $[M + Na]^+$  575.1241, found 575.1247.

## 11. The HRMS Analysis Report of **8a**



## 12. The HRMS Analysis Report of **9a**



### 13. References

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