

## **A straightforward and versatile FeCl<sub>3</sub> catalyzed Friedel-Crafts C-glycosylation process. Application to the synthesis of new functionalized C-nucleosides.**

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## Chemistry

### *General procedures.*

All organic solvents were purchased from commercial sources and used as received or dried using standard procedures; all chemicals were purchased from Aldrich, Merck or Alfa Aesar and used without further purification.

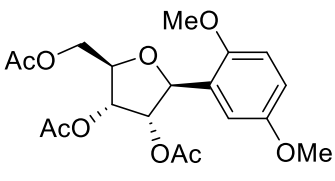
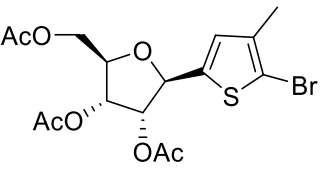
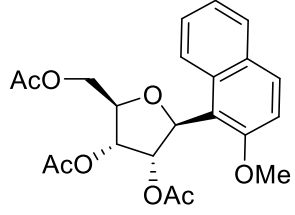
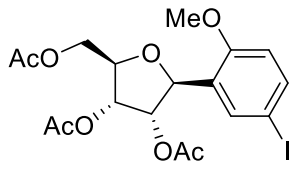
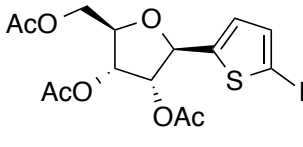
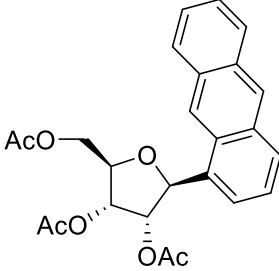
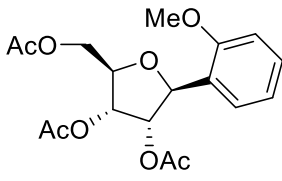
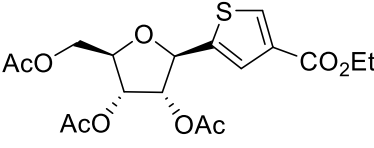
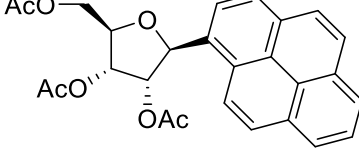
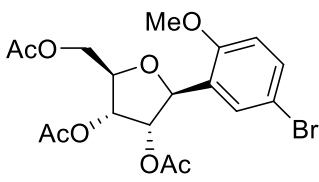
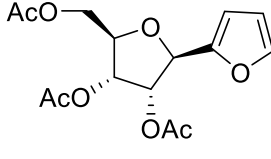
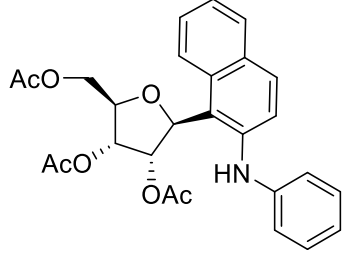
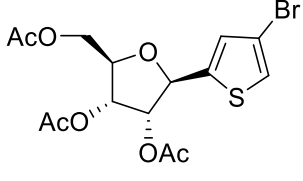
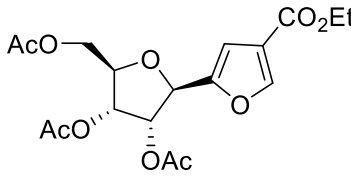
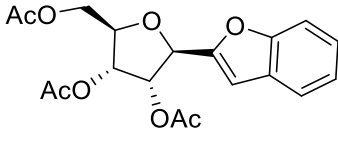
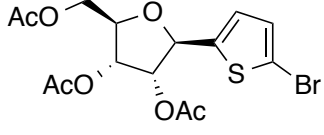
Analytical thin layer-chromatographies (TLC) have been performed on pre-coated silica gel plates (Kieselgel 60 F<sub>254</sub>, E. Merck, Germany), and chromatograms were visualized by UV- light irradiation (254 and 360 nm), then by staining with ninhydrin, *p*-anisaldehyde or H<sub>2</sub>SO<sub>4</sub>/EtOH. Purifications by column chromatography have been performed using silica gel, 100-200 mesh (Merck, Germany).

NMR spectroscopies were recorded in dry deuterated solvent (DMSO or chloroform) on a Bruker AC 200, or on a Bruker AC 500 spectrometers at 200 MHz or 400 MHz for <sup>1</sup>H NMR and 50 MHz for <sup>13</sup>C NMR;  $\delta$  is expressed in ppm related to TMS (0 ppm) as internal standard. Splitting patterns are designated as follow: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Coupling constants (*J* values) are listed in Hertz (Hz). Mass spectra (ESI-MS) were recorded on a Bruker Daltonics Esquire 3000+, and the samples were diluted in methanol.

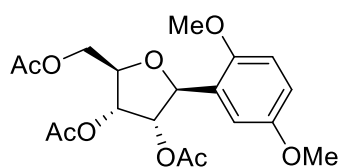
### *General procedure for the Friedel-Craft ribosylation.*

To a stirred solution of the carbohydrate (1'- $\beta$ -ribofuranose-1',2',3',5'-tetraacetate, 1 mmol) and the appropriate (hetero)aryle (2 mmol) in dichloromethane (8 mL), was added at room temperature and in one portion FeCl<sub>3</sub> (10 mol%). The resulting mixture is heated in refluxing dichloromethane and the reaction is monitored by TLC. Once the carbohydrate fully reacted (10-30 min.), 10 mL of a saturated solution of NaHCO<sub>3</sub> was added to quench the reaction. The mixture is extracted three times using dichloromethane (15 mL). The organic layers were combined, then dried over MgSO<sub>4</sub> and concentrated under reduced pressure; the crude material is purified by flash chromatography using a mixture of ethyl acetate and hexane as solvent. Importantly, samples used for the fluorescence assay have been submitted to a second purification (preparative TLC) in order to strengthen their final purities.

*List of the synthesized compounds.*

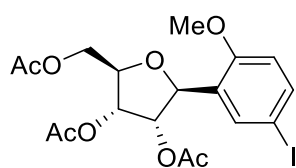
 <p><b>4a</b></p>	 <p><b>4g</b></p>	 <p><b>5a</b></p>
 <p><b>4b</b></p>	 <p><b>4h</b></p>	 <p><b>5b</b></p>
 <p><b>4c</b></p>	 <p><b>4i</b></p>	 <p><b>5c</b></p>
 <p><b>4d</b></p>	 <p><b>4j</b></p>	 <p><b>5d</b></p>
 <p><b>4e</b></p>	 <p><b>4k</b></p>	 <p><b>5e</b></p>
 <p><b>4f</b></p>		

### Characterization of compounds 4a-4k and 5a-5e



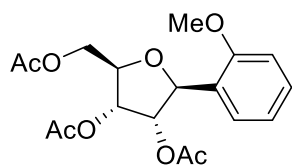
**4a**

Rf = 0.54 (Cyclohexane/AcOEt : 1-1) ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.99 (bs, 1H), 6.70-6.62 (m, 2H), 5.74 (t,  $J = 4.2$  Hz, 1H), 5.31 (t,  $J = 4.5$  Hz, 1H), 5.17 (d,  $J = 3.7$  Hz, 1H), 4.40 – 4.05 (m, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H);  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.6, 169.5, 153.7, 150.6, 127.5, 113.6, 113.1, 111.3, 79.3, 75.4, 72.0, 70.5, 63.1, 55.8, 55.5, 20.7, 20.6, 20.5 HRMS Calcd. for  $\text{C}_{19}\text{H}_{25}\text{O}_9$ : ( $[\text{M}^+]$ ): 397.1420, Found: 397.14931.



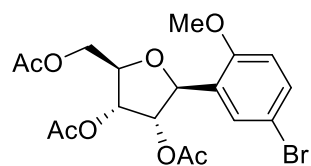
**4b**

Rf = 0.73 (Cyclohexane/AcOEt : 1-1);  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ ) :  $\delta$  7.71 (d,  $J = 1.6$  Hz, 1H), 7.47 (dd,  $J = 8.6$ ,  $J' = 2.3$  Hz, 1H), 6.50 (d,  $J = 8.6$  Hz, 1H), 5.72 (dd,  $J = 4.3$ ,  $J' = 3.3$  Hz, 1H), 5.40 (d,  $J = 3.1$  Hz, 1H), 5.34 (dd,  $J = 8.1$ , 4.4 Hz, 1H), 4.39 (t,  $J = 2.8$  Hz, 1H), 4.36 – 4.30 (m, 1H), 4.12 (dd,  $J = 12.8$ ,  $J' = 5.5$  Hz, 1H), 3.70 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H), 1.74 (s, 3H);  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.8, 169.3, 155.7, 137.4, 136.1, 126.8, 112.0, 82.3, 76.8, 76.3, 72.5, 71.8, 63.6, 55.4, 20.8, 20.5, 20.3; HRMS Calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}_8\text{I}$ : ( $[\text{M}^+]$ ): 492.0281, Found: 493.03539.



**4c**

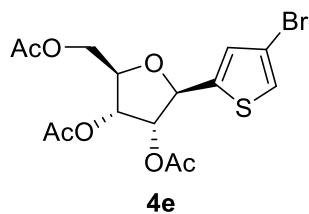
Rf = 0.64 (Cyclohexane/AcOEt : 1-1) ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 6.9$  Hz, 1H), 7.23 (t,  $J = 7.6$  Hz, 1H), 6.88 (t,  $J = 7.5$  Hz, 1H), 6.72 (d,  $J = 8.1$  Hz, 1H), 5.75 (t,  $J = 3.3$  Hz, 1H), 5.39 – 4.86 (m, 2H), 4.40 – 4.18 (m, 2H), 4.13 (dd,  $J = 12.8$ , 5.6 Hz, 1H), 3.71 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.68 (s, 3H).  $^{13}\text{C NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 169.8, 169.4, 155.8, 128.7, 127.3, 126.9, 120.0, 109.5, 79.7, 75.3, 72.7, 72.1, 63.7, 55.2, 20.8, 20.5, 20.3; HRMS Calcd. for  $\text{C}_{18}\text{H}_{23}\text{O}_8$ : ( $[\text{M}^+]$ ): 367.1315, Found: 397.13934.



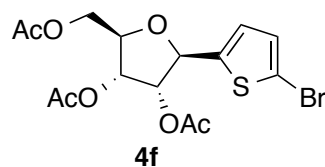
**4d**

Rf = 0.75 (Cyclohexane/AcOEt : 1-1) ;  $^1\text{H NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 2.6$  Hz, 1H), 7.28 (dd,  $J = 8.7$ ,  $J' = 2.5$  Hz, 1H), 6.61 (d,  $J = 8.7$  Hz, 1H), 5.73 (t,  $J = 3.0$  Hz, 1H),

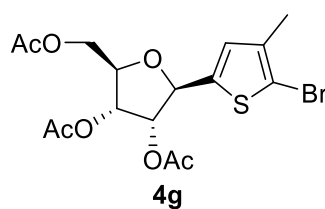
5.41 (d,  $J = 3.1$  Hz, 1H), 5.34 (dd,  $J = 8.1$ ,  $J' = 4.3$  Hz, 1H), 4.42 – 4.21 (m, 2H), 4.12 (dd,  $J = 12.8$ ,  $J' = 5.5$  Hz, 1H), 3.70 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H), 1.74 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 168.8, 168.4, 153.9, 130.3, 129.3, 125.5, 111.6, 110.4, 78.0, 75.8, 71.5, 70.9, 62.6, 54.5, 19.8, 19.5, 19.3 ; HRMS Calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}_8\text{Br}$ : ( $[\text{M}^+]$ ): 445.0420, Found: 445.04926.



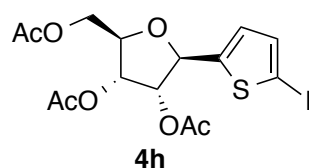
$R_f = 0.71$  (Cyclohexane/AcOEt : 1-1) ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (d,  $J = 5.1$  Hz, 1H), 6.88 (d,  $J = 5.3$  Hz, 1H), 5.31–5.19 (m, 2H), 4.42-4.02 (m, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.45, 169.68, 169.35, 136.20, 130.30, 126.04, 109.59, 79.96, 77.82, 76.01, 71.56, 63.29, 20.80, 20.55, 20.44 ; HRMS Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_7\text{BrS}$ : ( $[\text{M}^+]$ ): 420.9878, Found : 420.99533



$R_f = 0.69$  (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  6.86 (d,  $J = 3.8$  Hz, 1H), 6.76 (d,  $J = 3.8$  Hz, 1H), 5.56 – 5.16 (m, 2H), 5.08 (d,  $J = 2.7$  Hz, 1H), 4.38-4.10 (m, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H) ;  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 168.7, 168.6, 141.9, 128.7, 124.6, 111.7, 79.0, 77.7, 75.3, 70.6, 62.3, 19.8, 19.6, 19.5 ; HRMS Calcd. for  $\text{C}_{18}\text{H}_{23}\text{O}_8$ : ( $[\text{M}^+]$ ): 420.9878, Found: 420.99512.

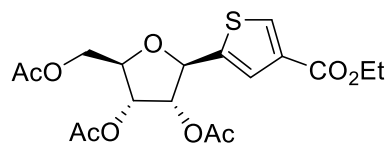


$R_f = 0.72$  (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  6.69 (s, 1H), 5.21 (t,  $J = 4.5$  Hz, 1H), 5.12–5.00 (m, 2H), 4.33 (dd,  $J = 11.7\text{Hz}$ ,  $J' = 2.8$  Hz, 1H), 4.26 – 4.19 (m, 1H), 4.13 (dd,  $J = 11.7$  Hz,  $J' = 3.7$  Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 169.7, 169.6, 140.6, 137.0, 127.2, 109.5, 79.8, 78.7, 76.2, 71.6, 63.3, 20.8, 20.5, 20.5, 15.2; HRMS Calcd. for  $\text{C}_{16}\text{H}_{20}\text{O}_7\text{BrS}$ : 435.0035, Found: 435.0112.



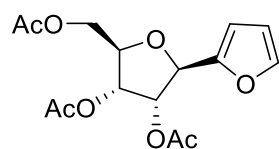
$R_f = 0.71$  (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.05 (d,  $J = 3.7$  Hz, 1H), 6.68 (d,  $J = 3.7$  Hz, 1H), 5.22 (t,  $J = 4.6$  Hz, 1H), 5.17–5.04 (m, 2H), 4.35 (dd,  $J = 11.7$  Hz,  $J' = 2.8$  Hz, 1H), 4.26-4.21 (m, 1H), 4.14 (dd,  $J = 11.7$  Hz,  $J' = 3.7$  Hz, 1H), 2.07 (s, 3H), 2.04

(s, 3H), 2.01 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 169.7, 169.6, 147.3, 136.8, 126.8, 80.0, 75.5, 76.4, 71.6, 63.3, 20.9, 20.6, 20.5; HRMS Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_7$ : 467.9740, Found: 468.9813.



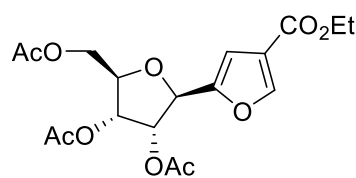
**4i**

Rf = 0.60 (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 5.3$  Hz, 1H), 7.15 (d,  $J = 5.3$  Hz, 1H), 5.87 (t,  $J = 4.3, 3.8$  Hz, 1H), 5.44 – 5.07 (m, 2H), 4.45 – 4.04 (m, 5H), 2.06 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.30 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.5, 169.1, 162.7, 148.8, 128.7, 128.3, 124.3, 78.3, 77.4, 72.3, 72.2, 63.3, 60.7, 20.8, 20.4, 20.2, 14.2; HRMS Calcd. for  $\text{C}_{18}\text{H}_{23}\text{O}_9$ : 415.0985, Found: 415.10583.



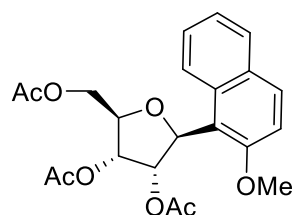
**4j**

Rf = 0.69 (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (s, 1H), 6.36 – 6.20 (m, 2H), 5.43 (t,  $J = 5.5$  Hz, 1H), 5.32 (t,  $J = 5.3$  Hz, 1H), 4.94 (d,  $J = 5.6$  Hz, 1H), 4.33 (dd,  $J = 11.6, 3.1$  Hz, 1H), 4.26 – 4.17 (m, 1H), 4.09 (dd,  $J = 11.6, 4.5$  Hz, 1H), 2.03 (s, 6H), 2.00 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 169.7, 169.6, 150.0, 143.4, 110.4, 109.4, 79.2, 76.1, 73.3, 71.7, 63.5, 20.7, 20.6, 20.5; HRMS Calcd. for  $\text{C}_{15}\text{H}_{19}\text{O}_8$ : ([M<sup>+</sup>]): 327.1002, Found: 327.10744.



**4k**

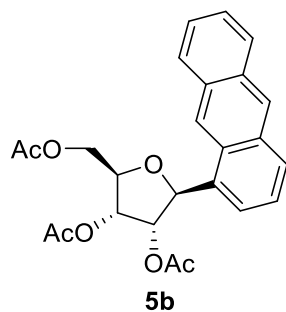
Rf = 0.61 (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (s, 1H), 6.69 (s, 1H), 5.40 (t,  $J = 5.5$  Hz, 1H), 5.28 (t,  $J = 5.2$  Hz, 1H), 4.92 (d,  $J = 5.7$  Hz, 1H), 4.34 (dd,  $J = 11.7$  Hz,  $J' = 3.1$  Hz, 1H), 4.23 (q,  $J = 7.1$  Hz, 3H), 4.10 (dd,  $J = 11.7$  Hz,  $J' = 4.2$  Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.27 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 169.7, 169.5, 162.7, 151.5, 148.0, 120.3, 109.3, 79.5, 75.9, 73.2, 71.4, 63.3, 60.6, 20.7, 20.5, 20.5, 14.3; HRMS Calcd. for  $\text{C}_{18}\text{H}_{23}\text{O}_{10}$ : 399.1213, Found: 399.1281.



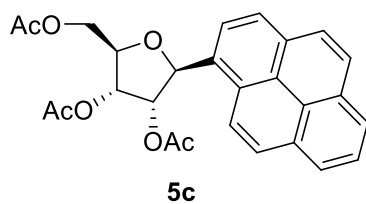
**5a**

Rf = 0.69 (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.7$  Hz, 1H), 7.76 (d,  $J = 9.1$  Hz, 1H), 7.68 (dd,  $J = 8.2$  Hz,  $J' = 1.3$  Hz, 1H), 7.39 (t,  $J = 7.8$  Hz,

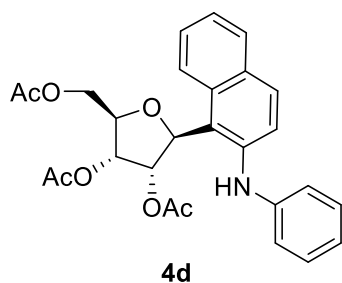
1H), 7.25 (t,  $J = 7.5$  Hz, 1H), 7.18 (d,  $J = 9.0$  Hz, 1H), 5.82 (d,  $J = 5.7$  Hz, 1H), 5.72 (t,  $J = 6.1$  Hz, 1H), 5.52 (t,  $J = 6.7$  Hz, 1H), 4.38 (dd,  $J = 11.5$  Hz,  $J' = 2.0$  Hz, 1H), 4.26–4.19 (m, 2H), 3.90 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 169.7, 169.4, 156.1, 132.8, 131.3, 123.3, 128.8, 127.0, 123.5, 122.7, 116.9, 113.5, 78.9, 77.8, 74.2, 70.9, 63.6, 56.5, 20.8 (x2), 20.6; HRMS Calcd. for  $\text{C}_{25}\text{H}_{27}\text{O}_7$ : 417.1471, Found: 417.15442.



Rf = 0.73 (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48-8.40 (m, 3H), 7.99–7.92 (m, 2H), 7.47-7.36 (m, 4H), 6.35 (d,  $J = 8.0$  Hz, 1H), 5.68-5.62 (m, 2H), 4.56 (dd,  $J = 12.2$ ,  $J' = 2.7$  Hz, 1H), 4.46 (dd,  $J = 12.3$ ,  $J' = 3.6$  Hz, 1H), 4.32 (m, 1H), 2.21 (s, 3H), 2.12 (s, 3H), 1.84 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 169.7, 169.4, 138.8, 131.5, 130.5, 129.8, 129.5, 127.8, 127.7, 127.4, 126.2, 126.1, 124.8, 124.1, 123.4, 121.1, 81.8, 78.8, 74.7, 70.3, 63.3, 20.9, 20.6, 20.3; HRMS Calcd. for  $\text{C}_{25}\text{H}_{27}\text{O}_7$ : 437.1522, Found: 437.15958.

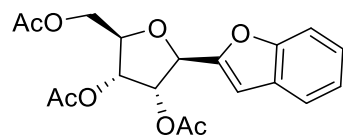


Rf = 0.31 (Cyclohexane/AcOEt : 8-2) ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 – 8.29 (m, 1H), 8.25 – 8.20 (m, 4H), 8.15 – 8.12 (m, 1H), 8.11 – 8.07 (m, 2H), 8.06 – 8.01 (m, 1H), 6.12 (d,  $J = 6.5$  Hz, 1H), 5.45 (m, 2H), 4.72 – 4.33 (m, 3H), 2.20 (s, 3H), 2.18 (s, 3H), 2.06 (s, 3H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 169.9, 169.6, 131.5, 131.5, 131.1, 130.7, 128.6, 128.0, 127.9, 127.6, 126.2, 125.7, 125.4, 125.3, 124.9, 124.8, 123.2, 122.4, 80.2, 79.3, 71.9, 63.8, 53.6, 21.1, 20.9, 20.7; HRMS Calcd. for  $\text{C}_{27}\text{H}_{24}\text{O}_7$ : ([M<sup>+</sup>]): 461.1522, Found [M+Na<sup>+</sup>]: 483.14160.



Rf = 0.70 (Cyclohexane/AcOEt : 1-1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.4$  Hz, 1H), 7.78 (d,  $J = 9.2$  Hz, 2H), 7.41–7.38 (m, 3H), 7.31 (t,  $J = 7.8$  Hz, 2H), 7.07 (t,  $J = 7.9$  Hz, 2H), 6.73 – 6.78 (m, 3H) , 6.03 (d,  $J = 8.5$  Hz, 1H), 4.95 (dd,  $J = 5.5$  Hz,  $J' = 1.9$  Hz, 1H), 4.45 (t,  $J = 7.0$  Hz, 1H), 4.14 (bs), 4.00 (d,  $J = 3.4$  Hz, 2H), 2.00 (s, 3H) , 1.99 (s, 3H) 1.84 (s, 3H);  $^{13}\text{C}$  NMR

(50 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 169.8, 169.0, 148.8, 137.7, 134.8, 133.2, 129.4, 129.1 (x2), 128.6, 128.3, 126.4 (x2) 126.0, 124.3, 120.1, 116.1 (x2), 89.2, 78.2, 71.0, 70.6, 63.9, 20.7, 20.4, 20.4; HRMS Calcd. for C<sub>27</sub>H<sub>28</sub>O<sub>7</sub>N: 478.1788, Found: 478.1859.



**5e**

R<sub>f</sub> = 0.61 (Cyclohexane/AcOEt : 1-1); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.59–7.32 (m, 2H), 7.27–7.10 (m, 2H), 6.71 (s, 1H), 5.54 (t, *J* = 5.4 Hz, 1H), 5.37 (t, *J* = 5.3 Hz, 1H), 5.08 (d, *J* = 5.4 Hz, 1H), 4.39 (dd, *J* = 11.6 Hz, *J*' = 3.2 Hz, 1H), 4.33 – 4.25 (m, 1H), 4.14 (dd, *J* = 11.7 Hz, *J*' = 4.4 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  170.6, 169.7, 169.6, 155.2, 152.6, 127.6, 124.9, 123.0, 121.3, 111.5, 106.0, 79.6, 79.5, 73.4, 71.7, 63.4, 20.8, 20.6, 20.5. HRMS Calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>8</sub>: 377.1158, Found: 377.1231.

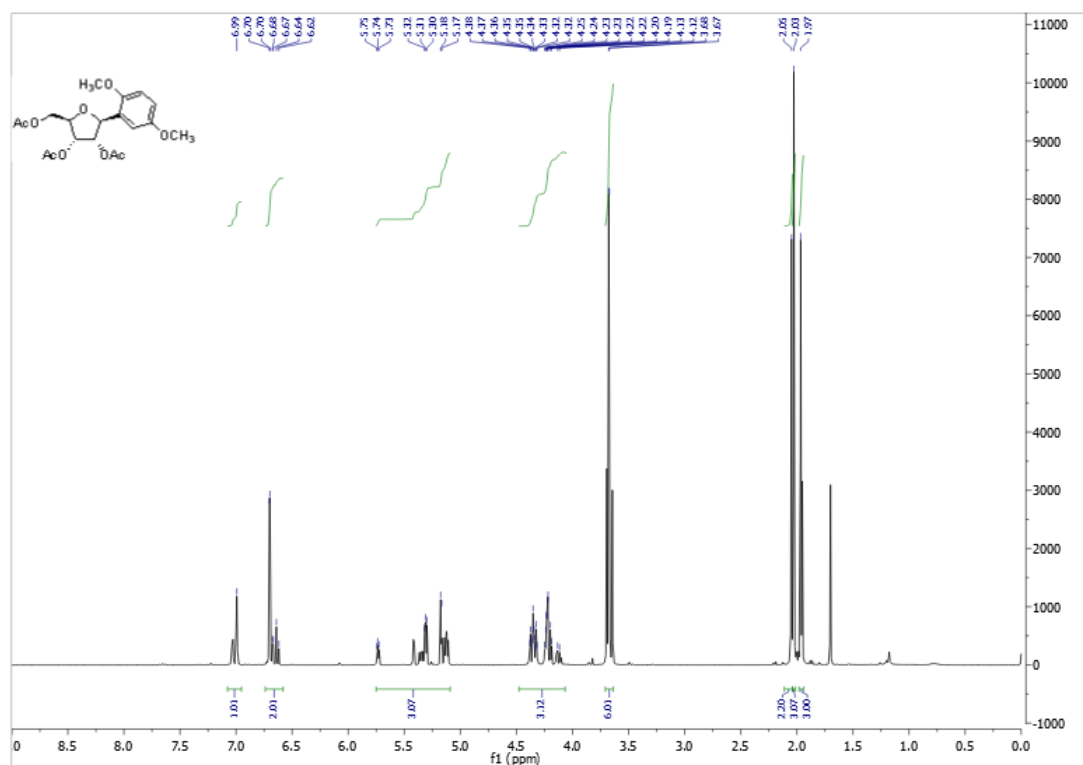


## Photophysics

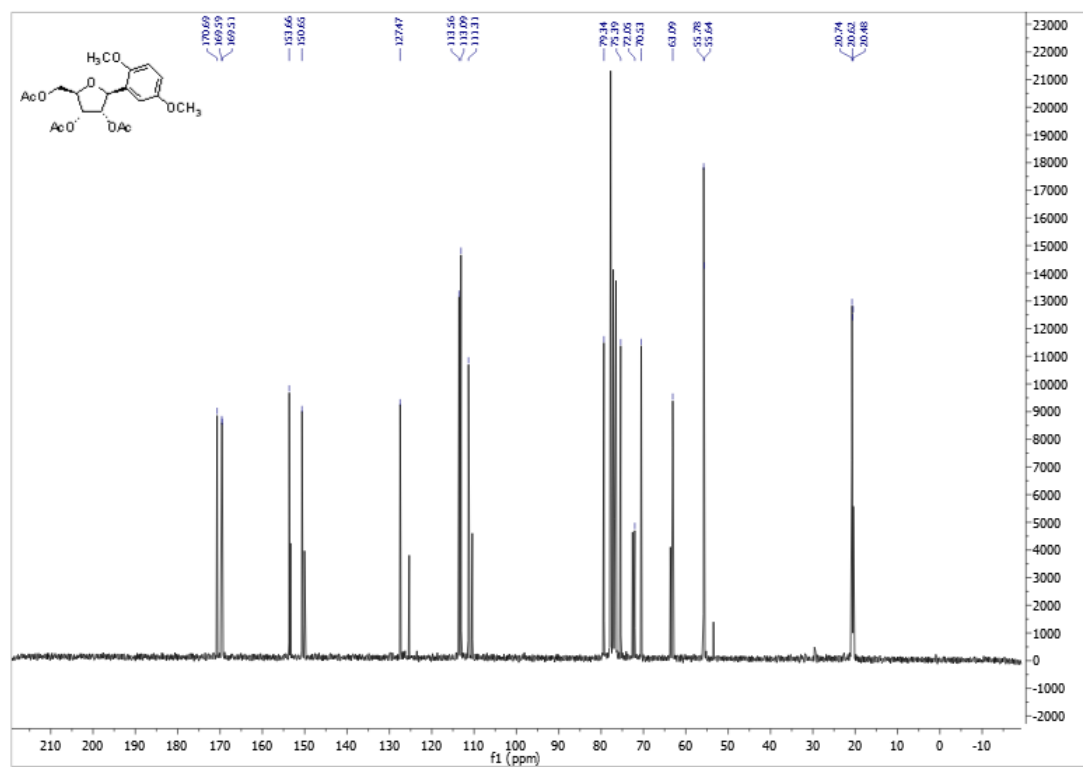
### *General procedures.*

All solvents for absorption and fluorescence experiments were of spectroscopic grade. Absorption spectra were recorded on a Cary 4 spectrophotometer (Varian) using quartz cells of 1 cm path length. Fluorescence spectra were recorded on FluoroMax 4.0 spectrofluorometer (Jobin Yvon, Horiba). Wavelengths used as the excitation wavelengths are highlighted in table 3. Stock solutions of the solvatofluorochromic dyes were prepared using 1,4- doxane. The samples used for spectroscopic measurements contained  $\approx 0.1\%$  v/v of the stock solvent. For fluorescence quantum yield measurements, the absorbance of the corresponding solution was kept below 0.05.

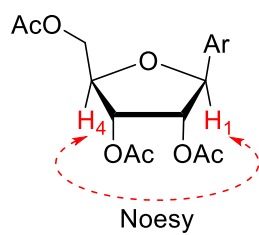
Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra



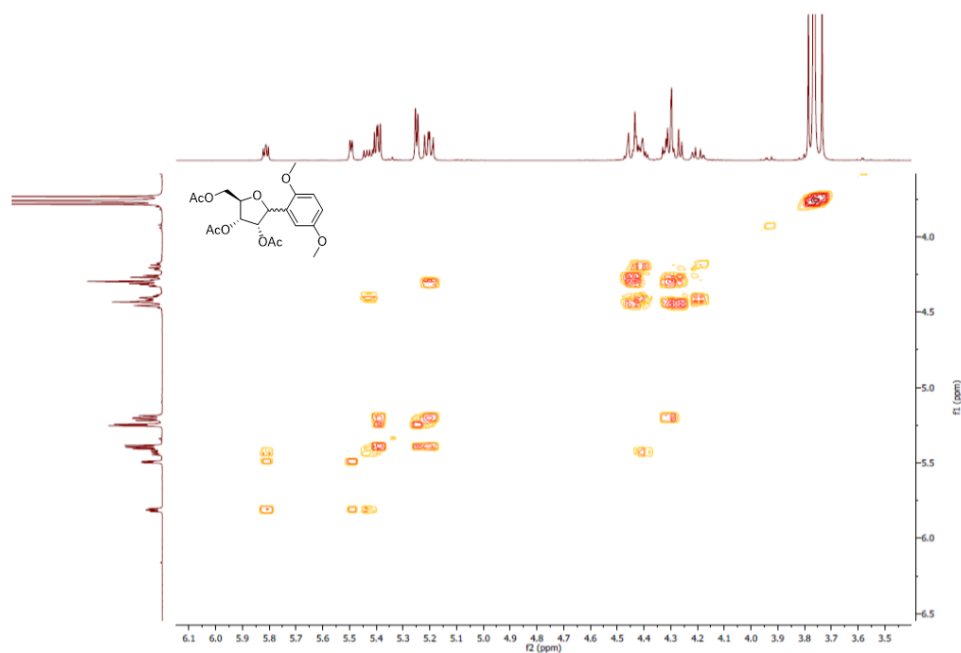
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **4a**.



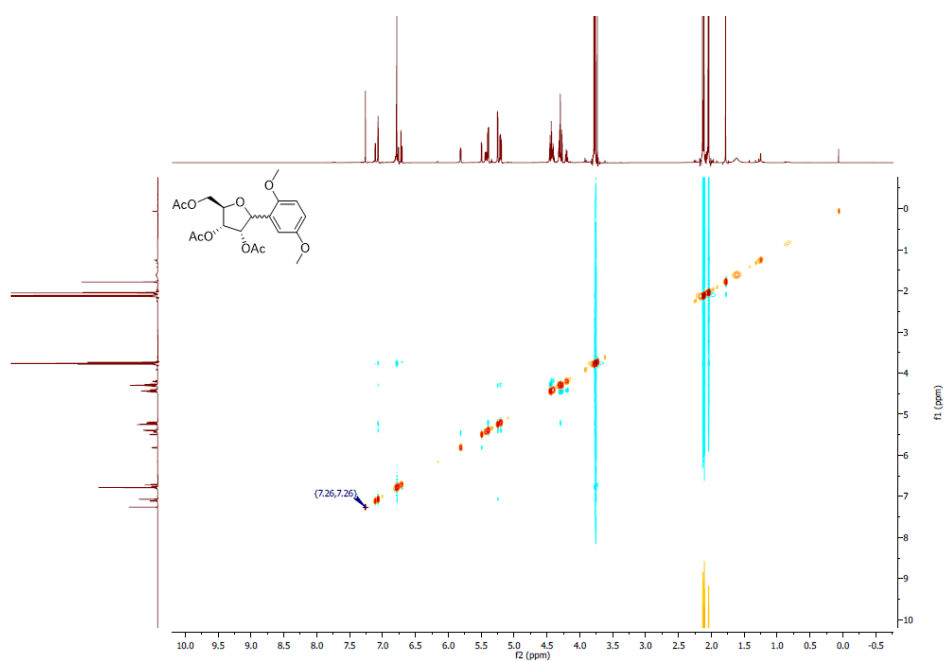
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ) spectrum of **4a**.



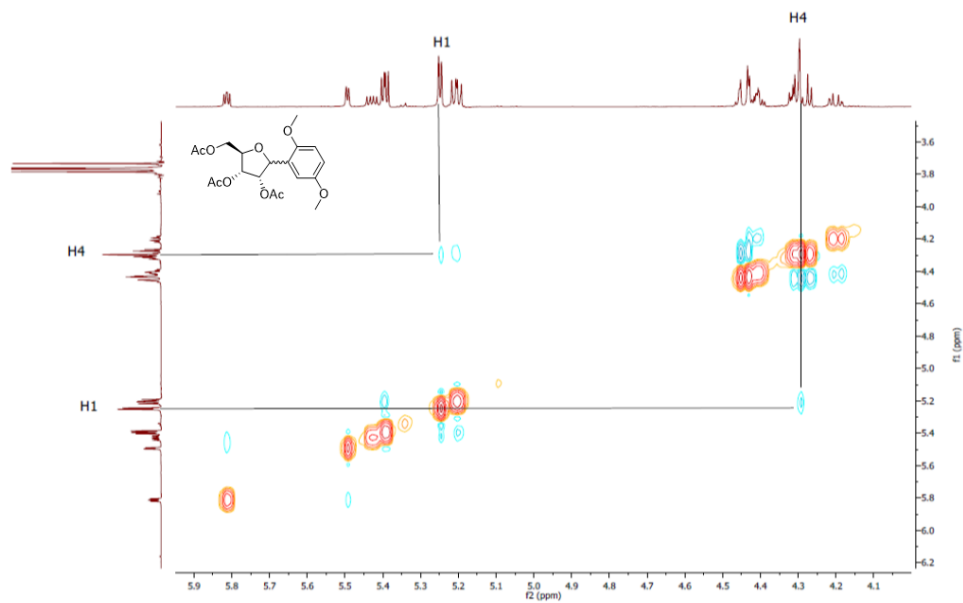
<sup>1</sup>H Noesy correlation for β-configuration.



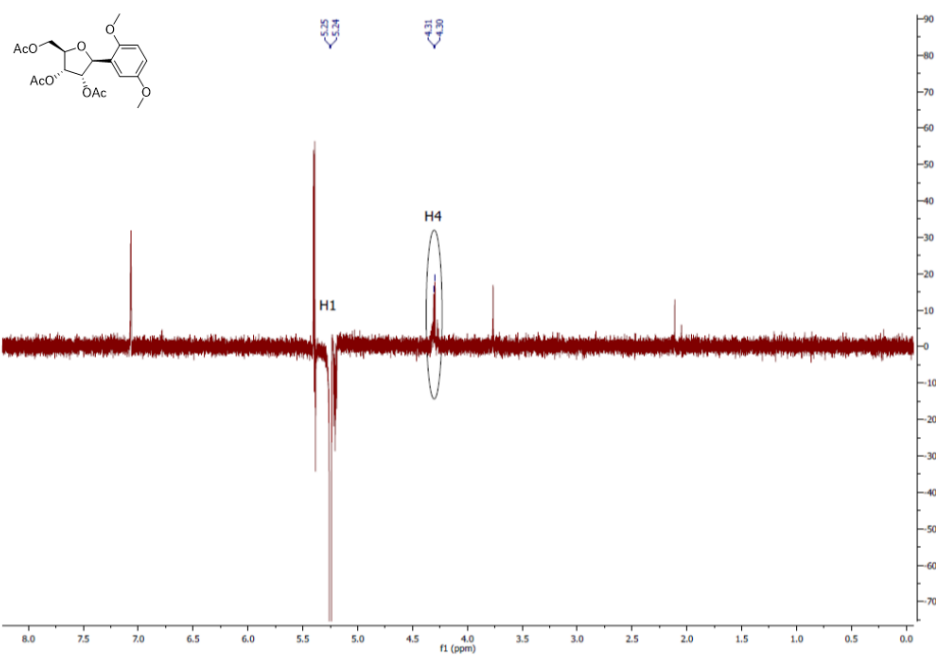
Cosy spectrum of **4a**.



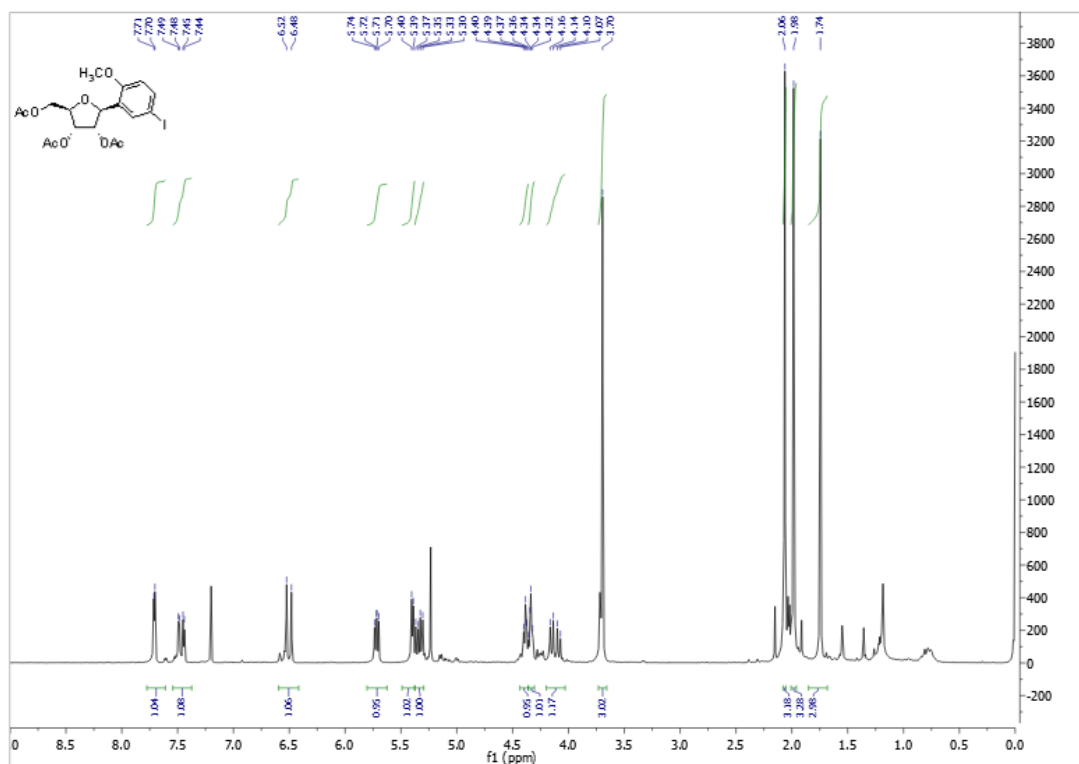
Noesy spectrum of **4a**.



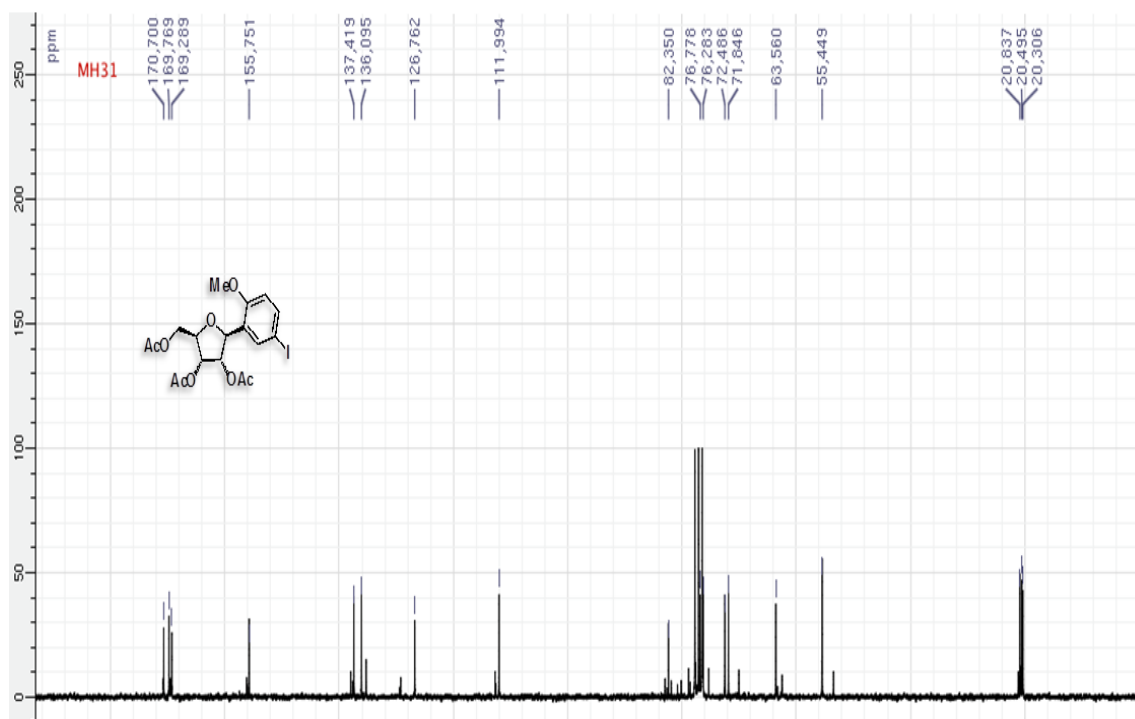
Noesy spectrum of **4a** (4 – 6 ppm).



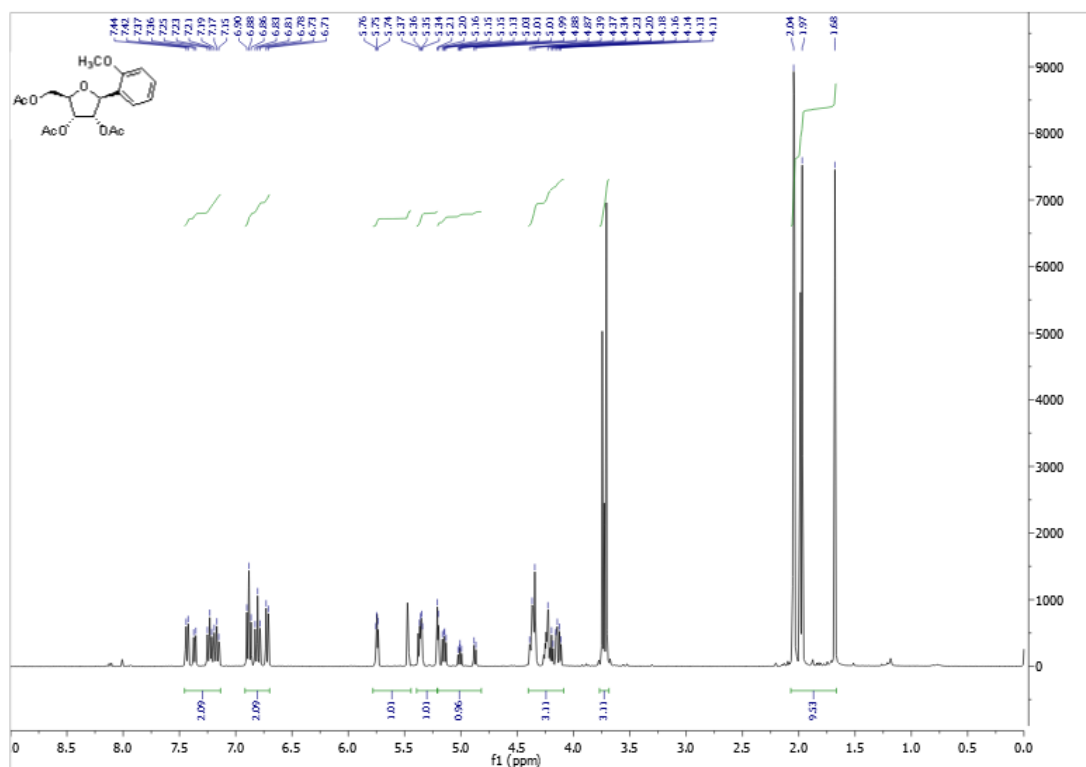
Selective noesy spectrum of **4a** (5.25 ppm,  $\beta$ -anomer).



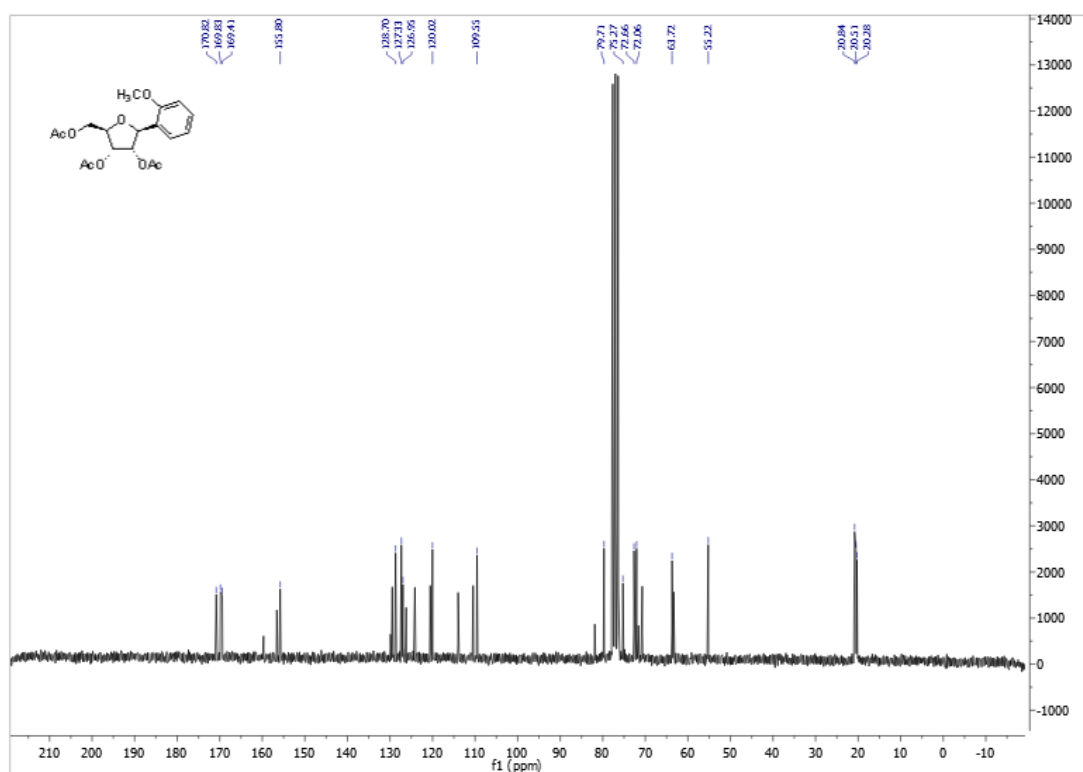
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of **4b**.



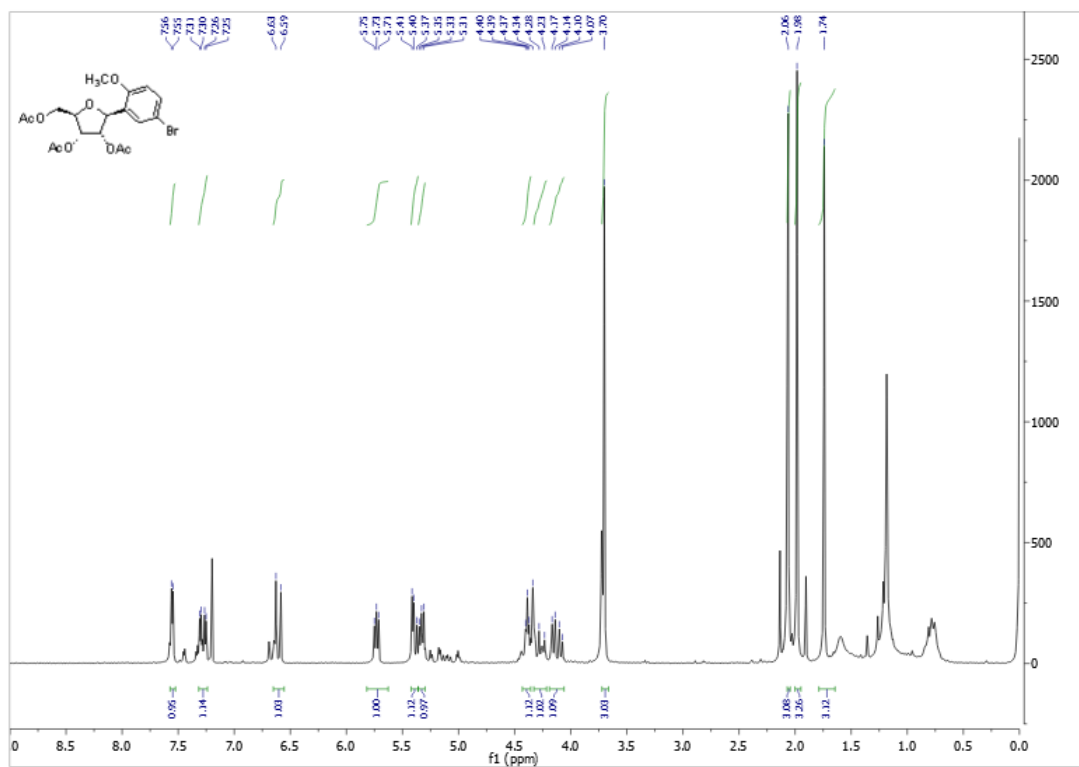
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **4b**.



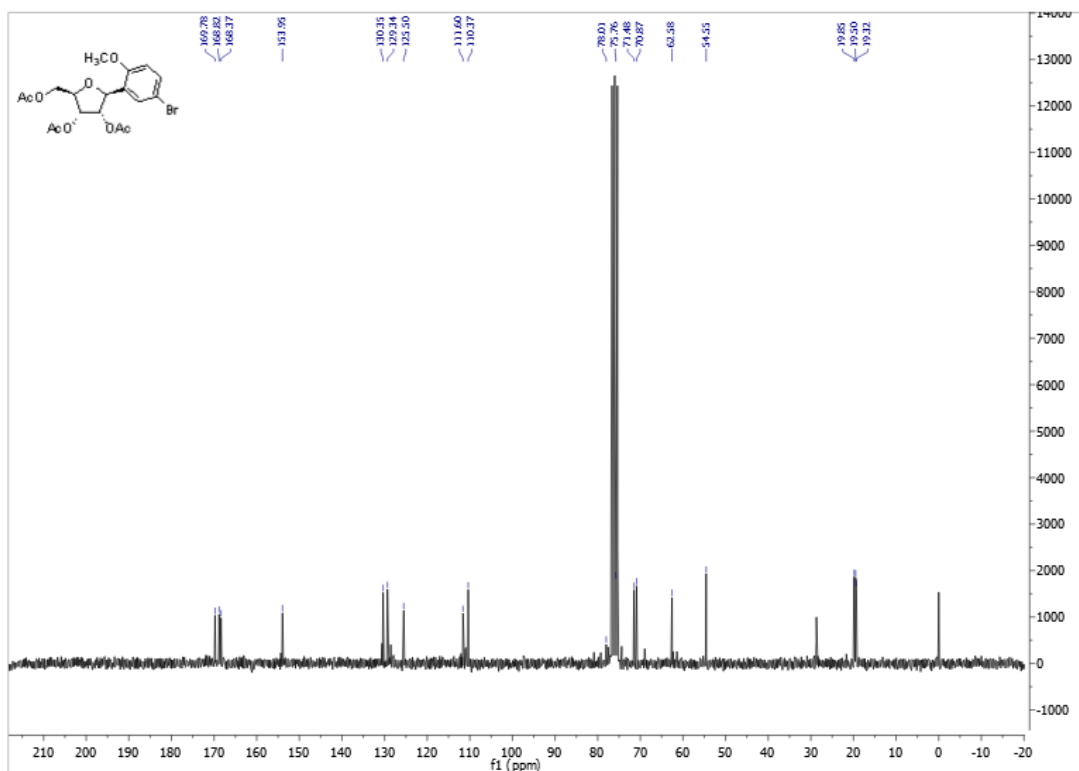
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **4c**.



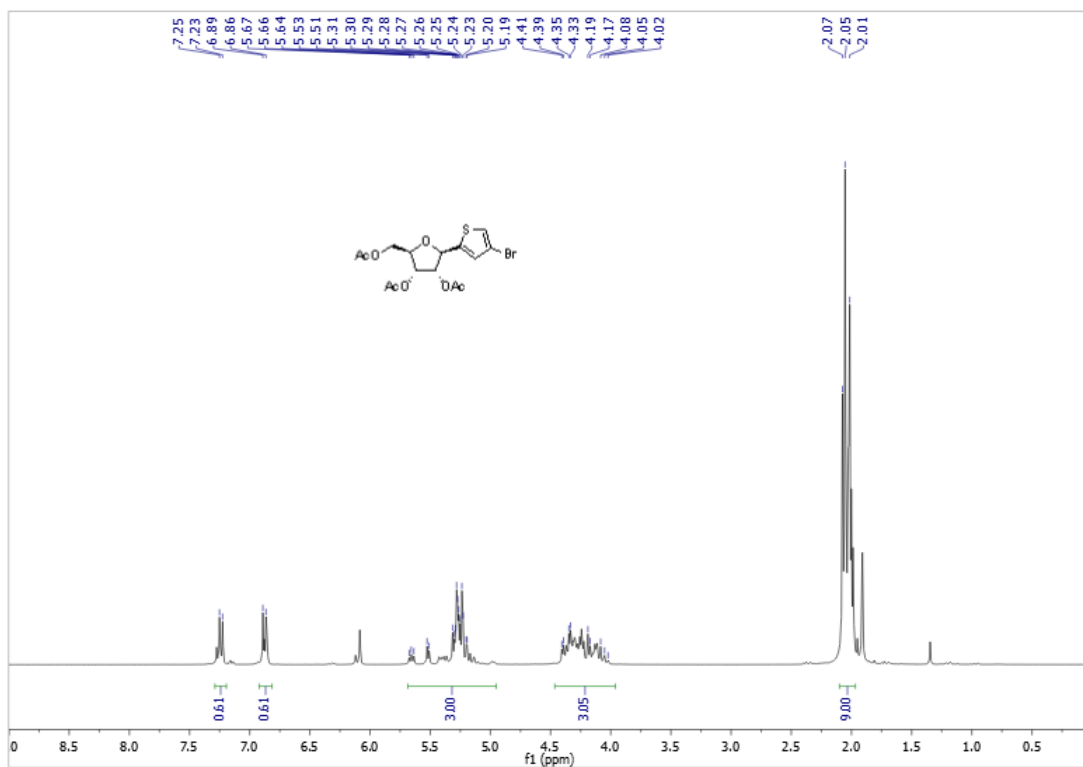
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **4c**.



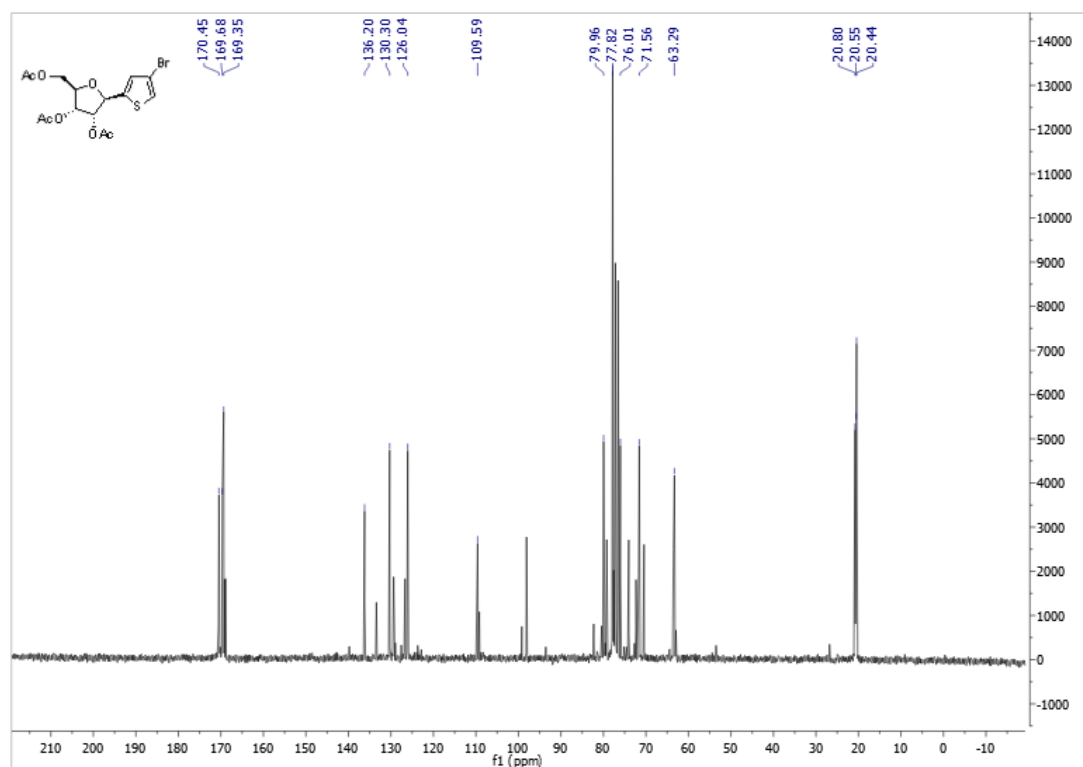
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of 4d.



<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of 4d.

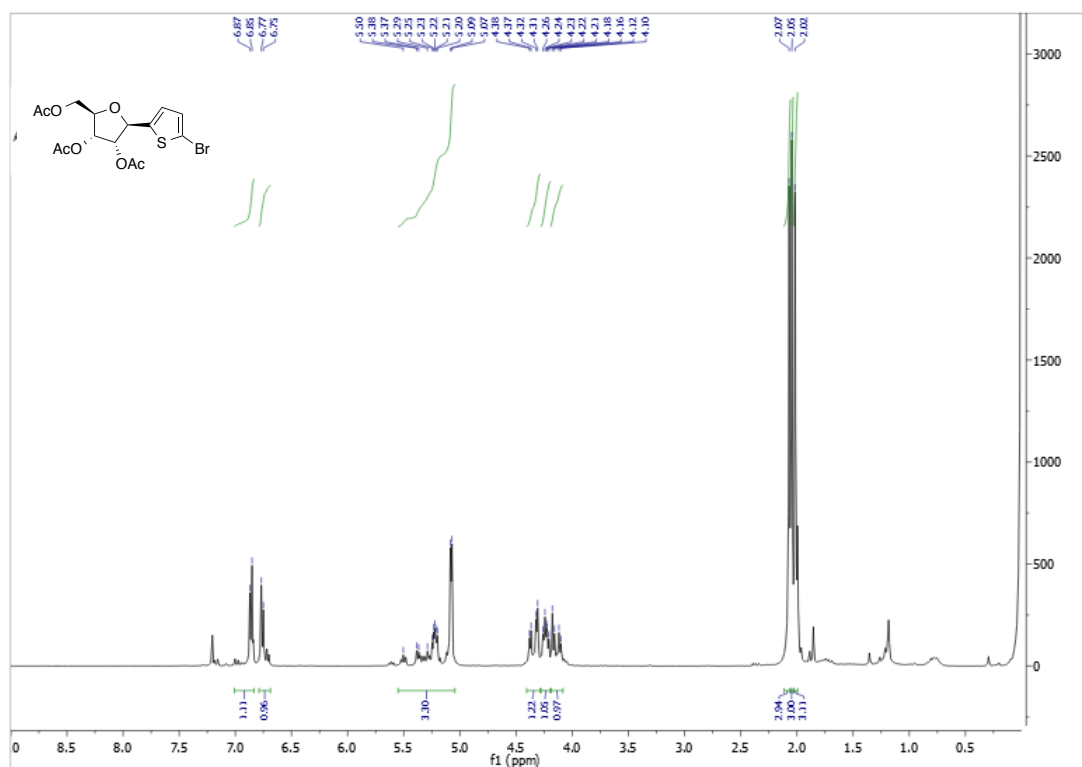


$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) spectrum of **4e**.

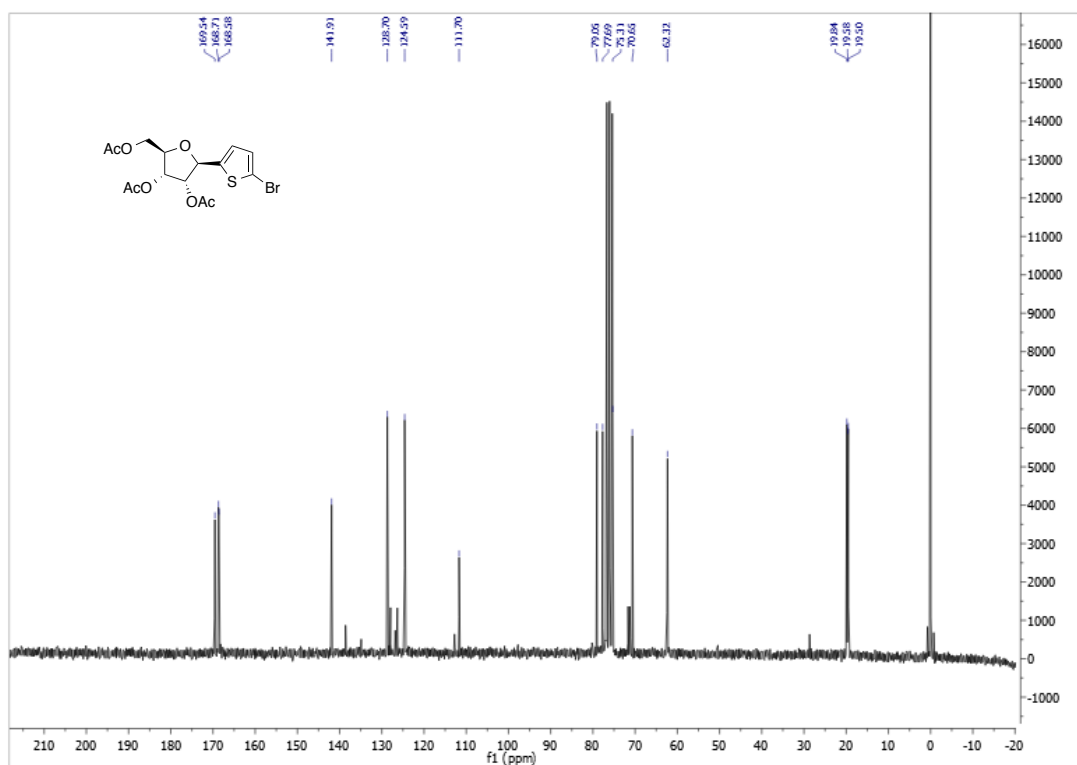


$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ) spectrum of **4e**.

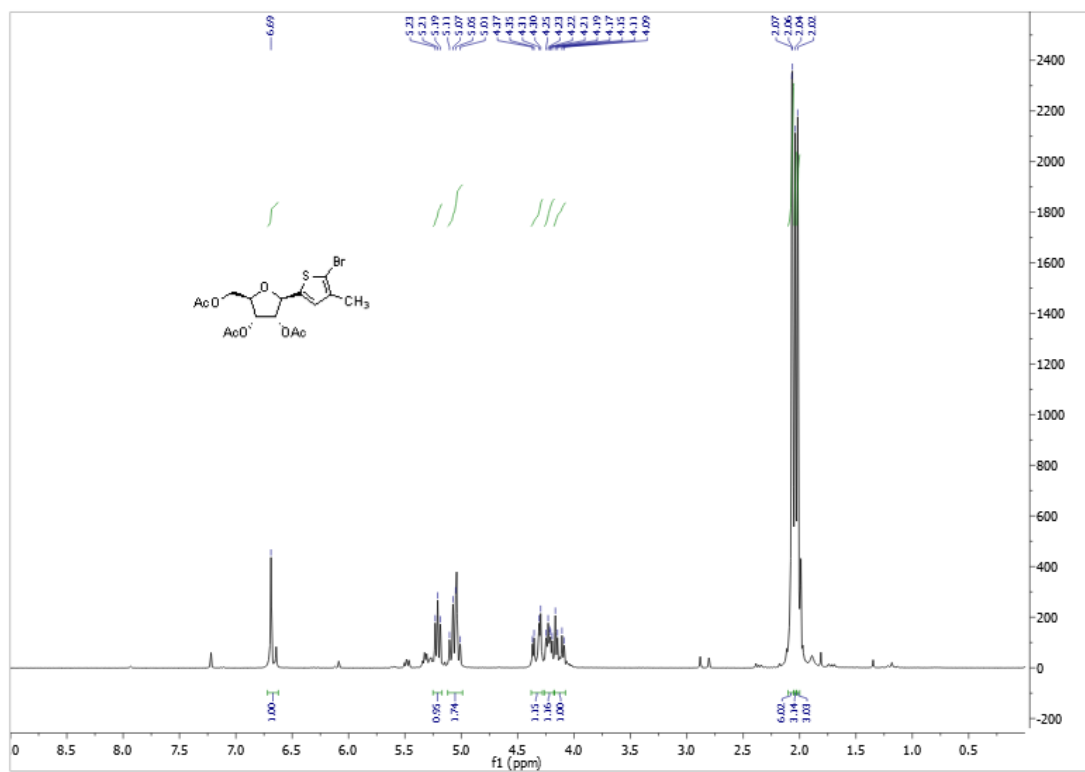




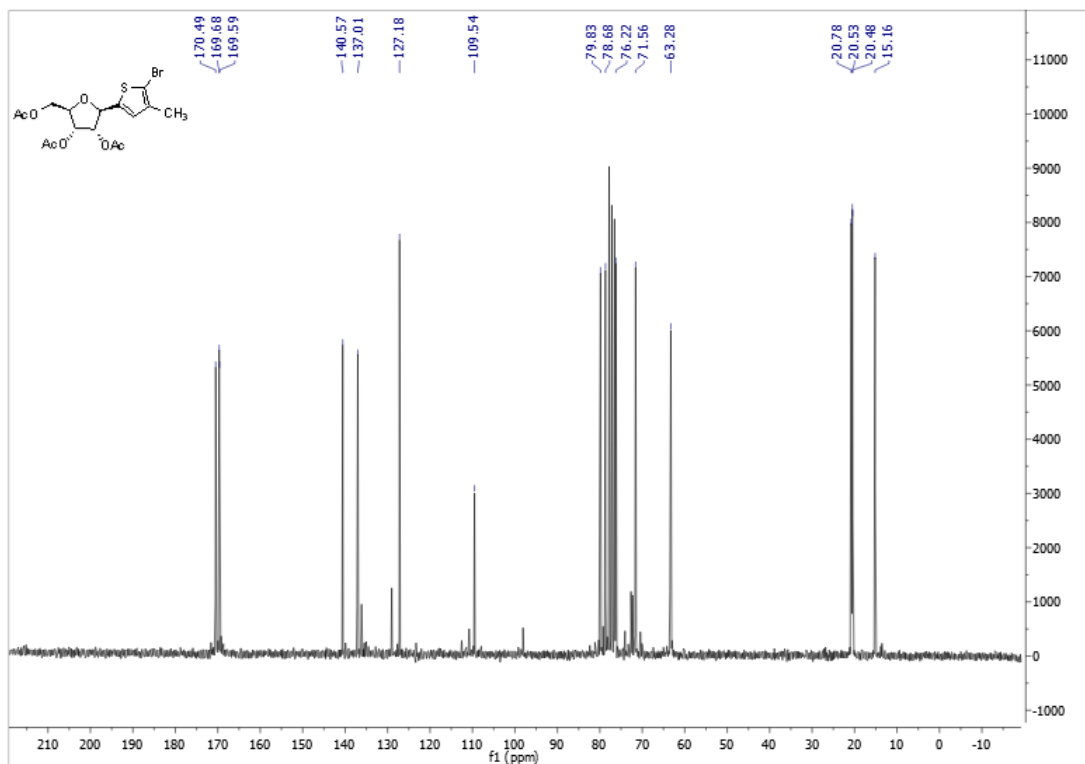
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) spectrum of **4f**.



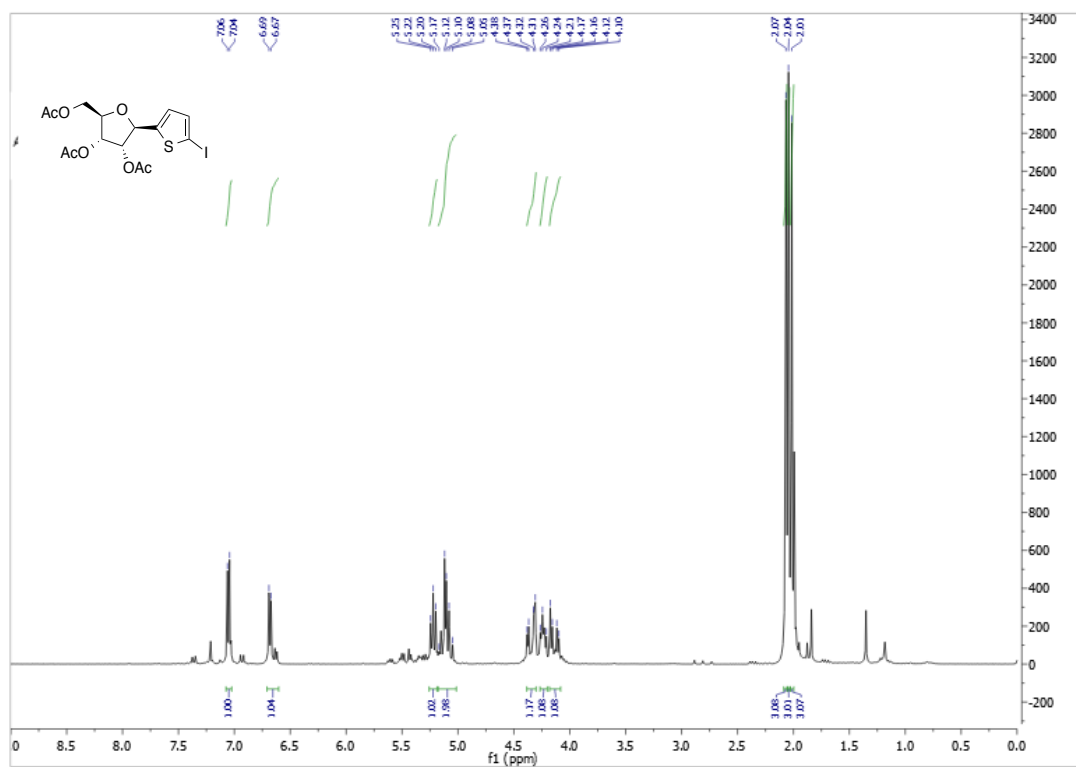
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ) spectrum of **4f**.



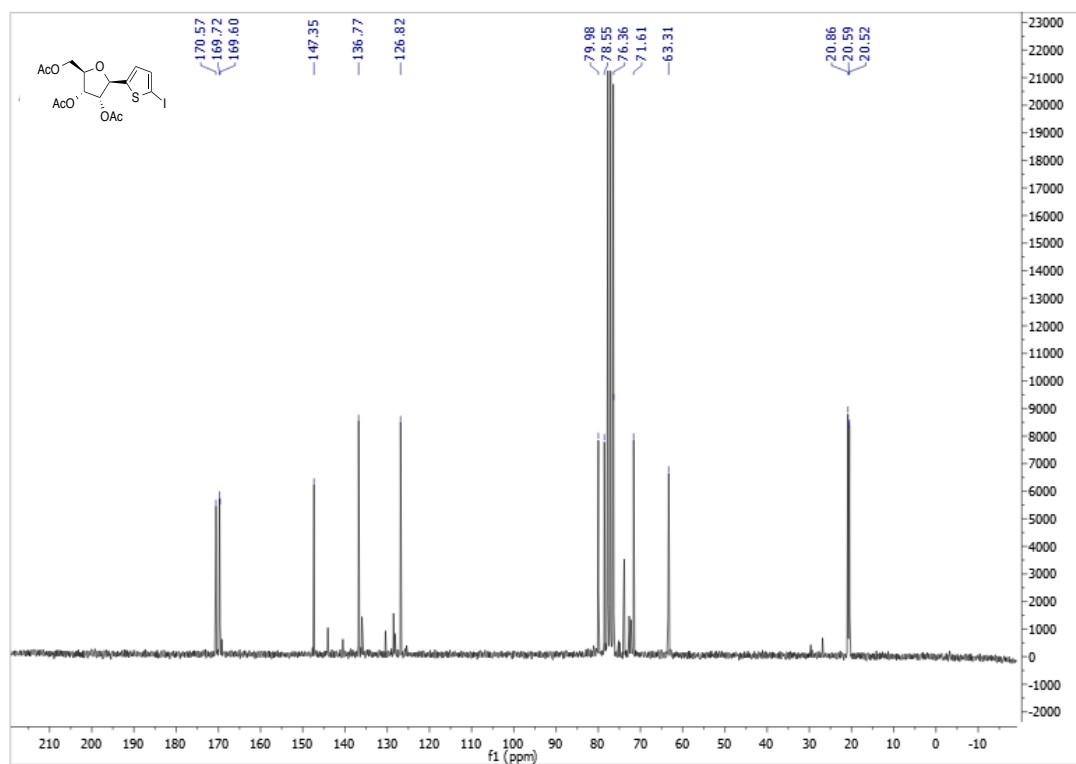
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of **4g**.



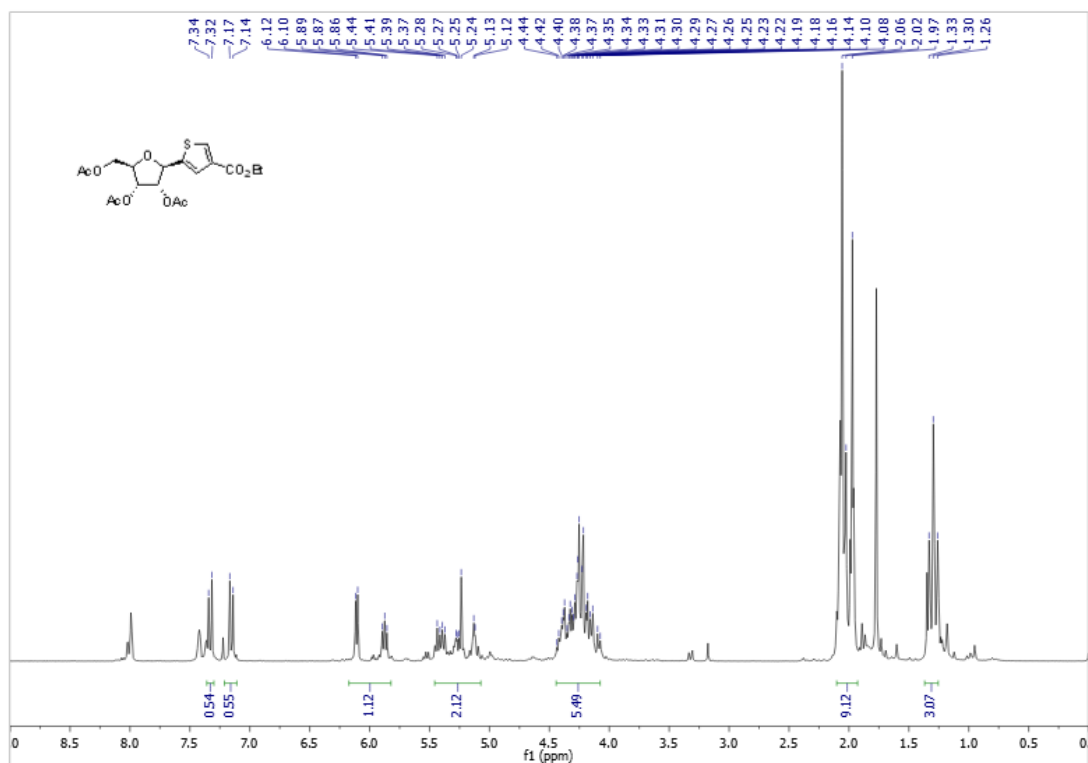
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **4g**.



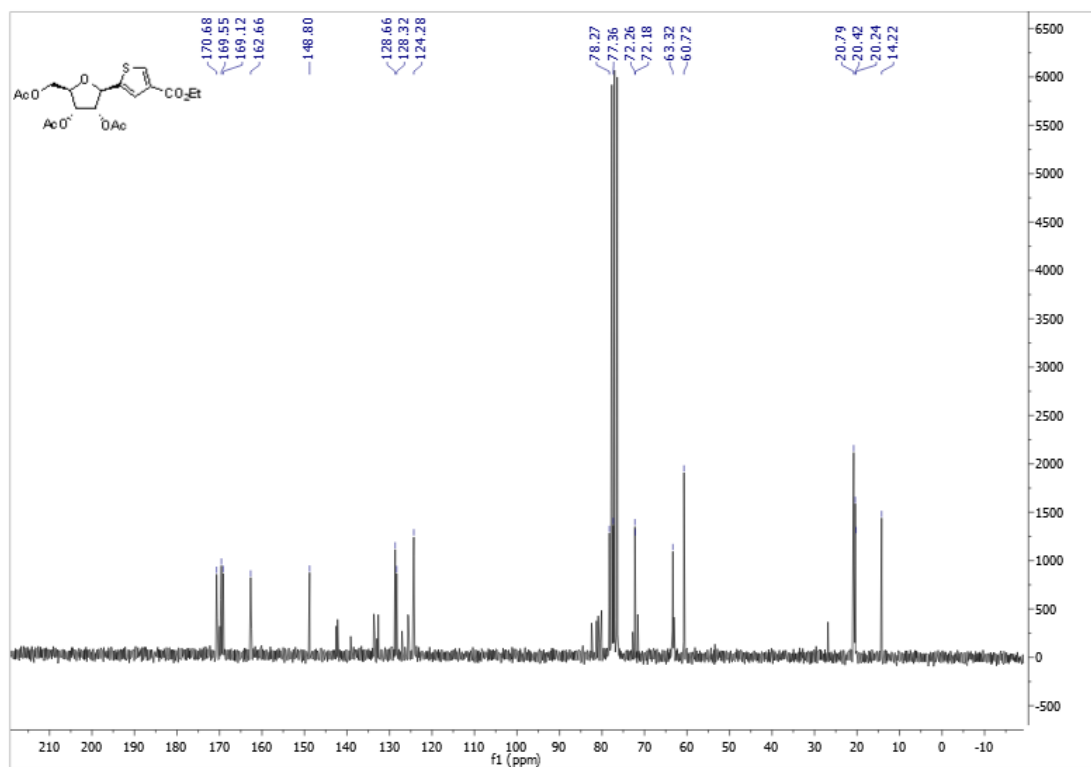
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of **4h**.



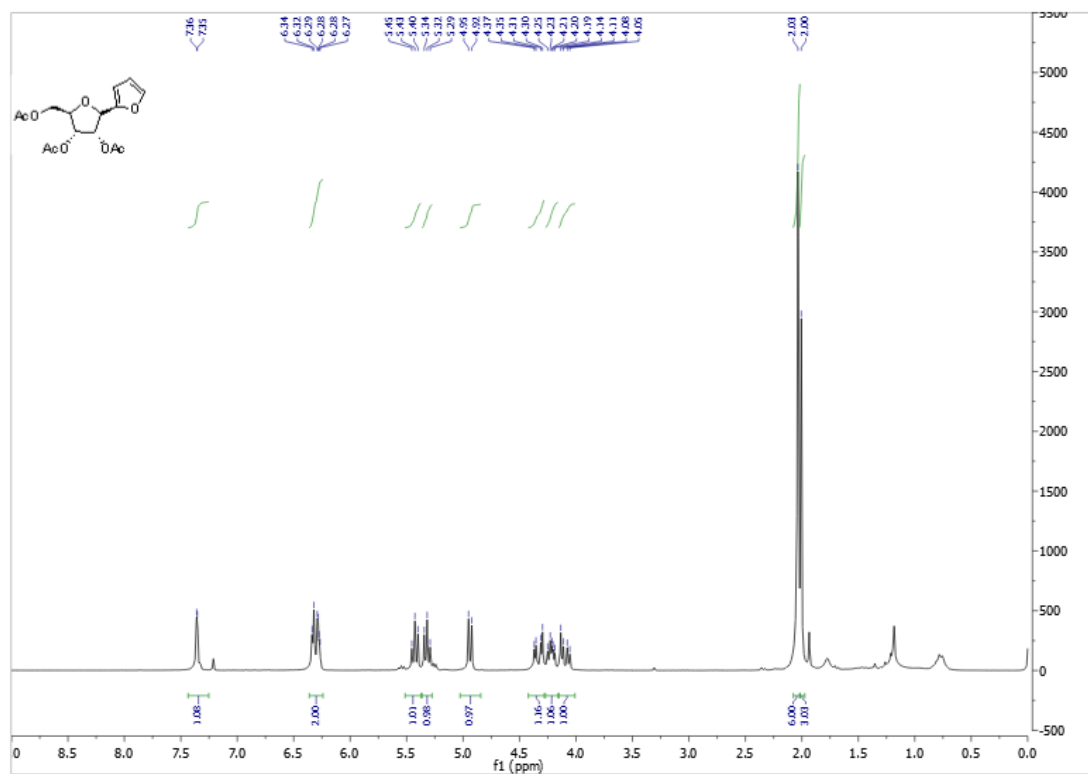
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **4h**.



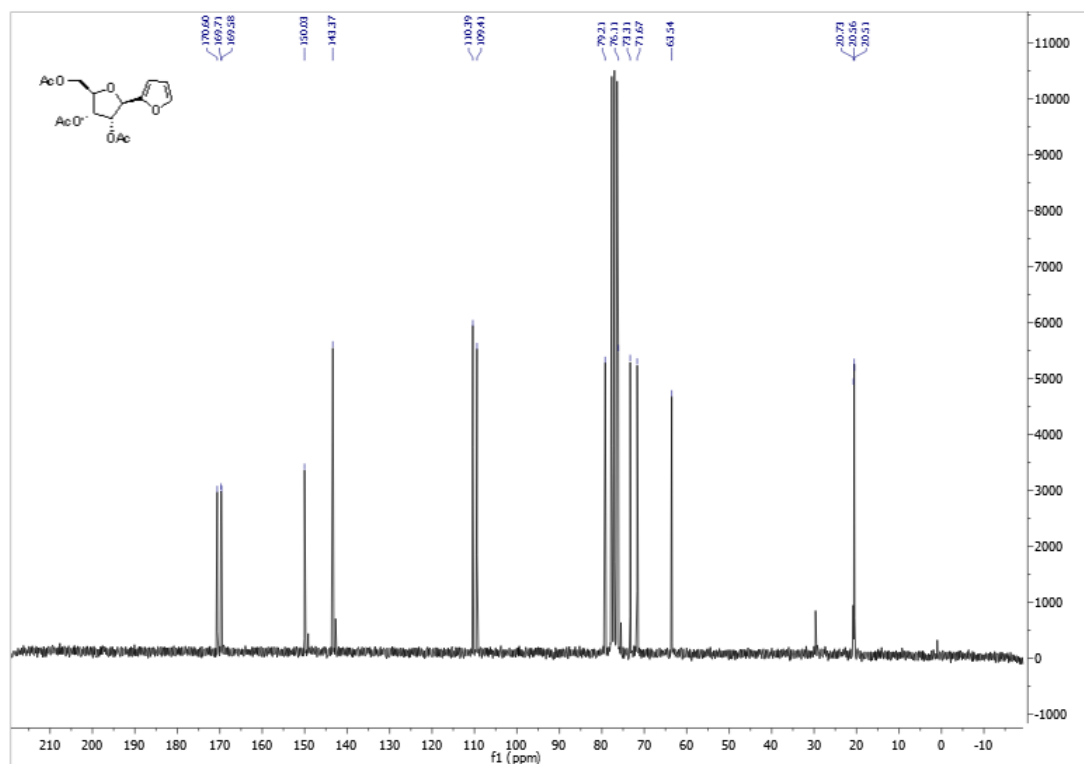
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of **4i**.



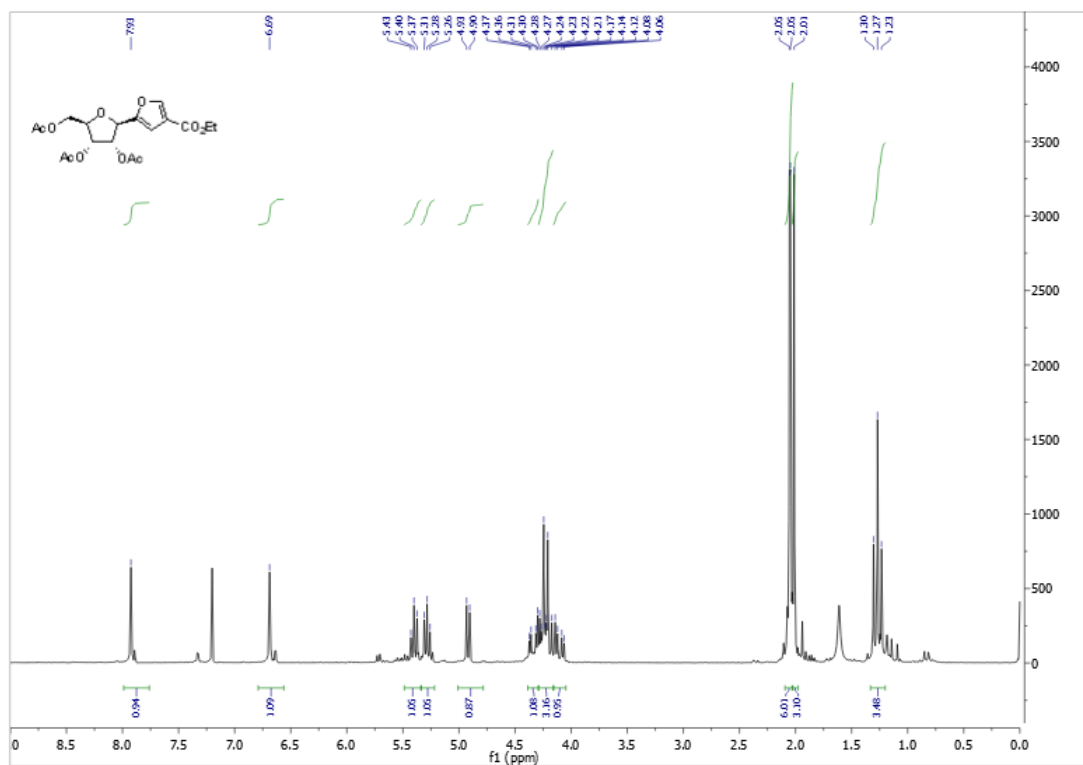
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **4i**.



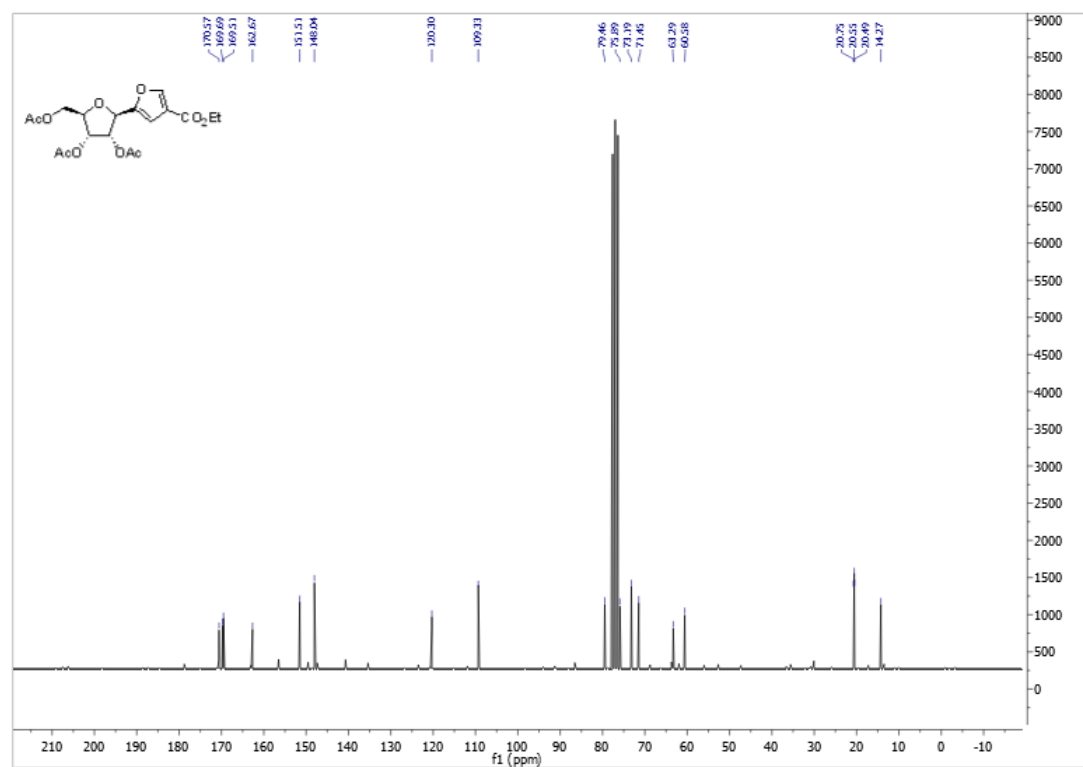
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of **4j**.



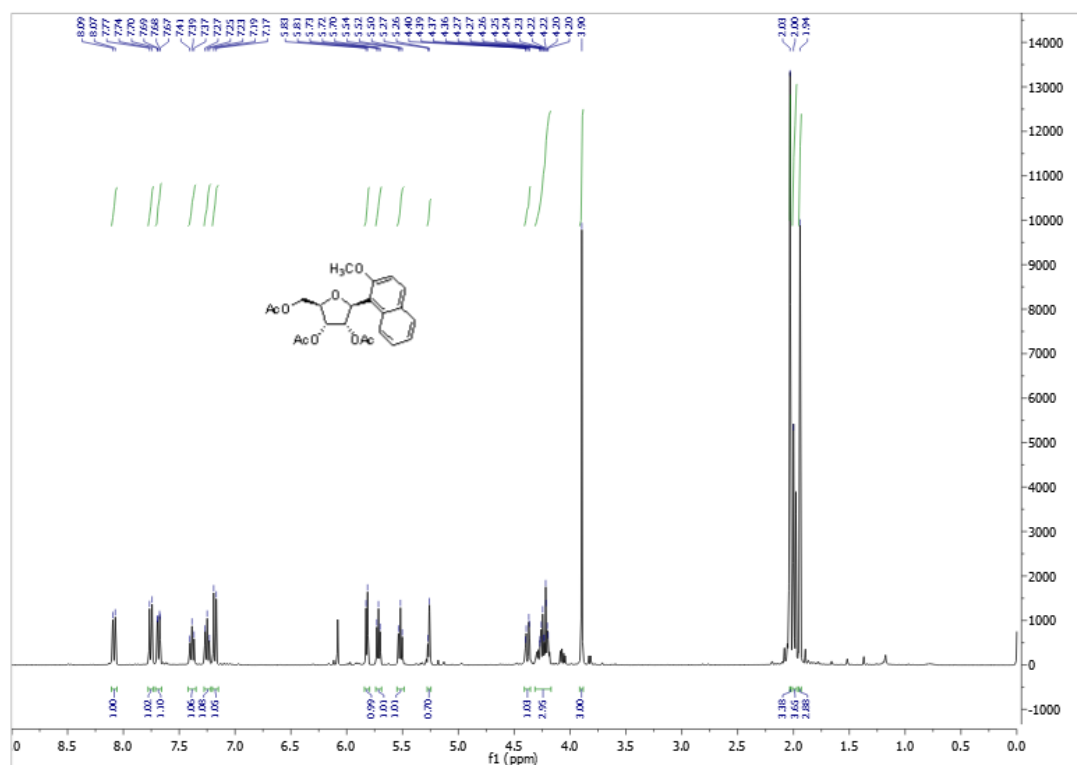
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **4j**.



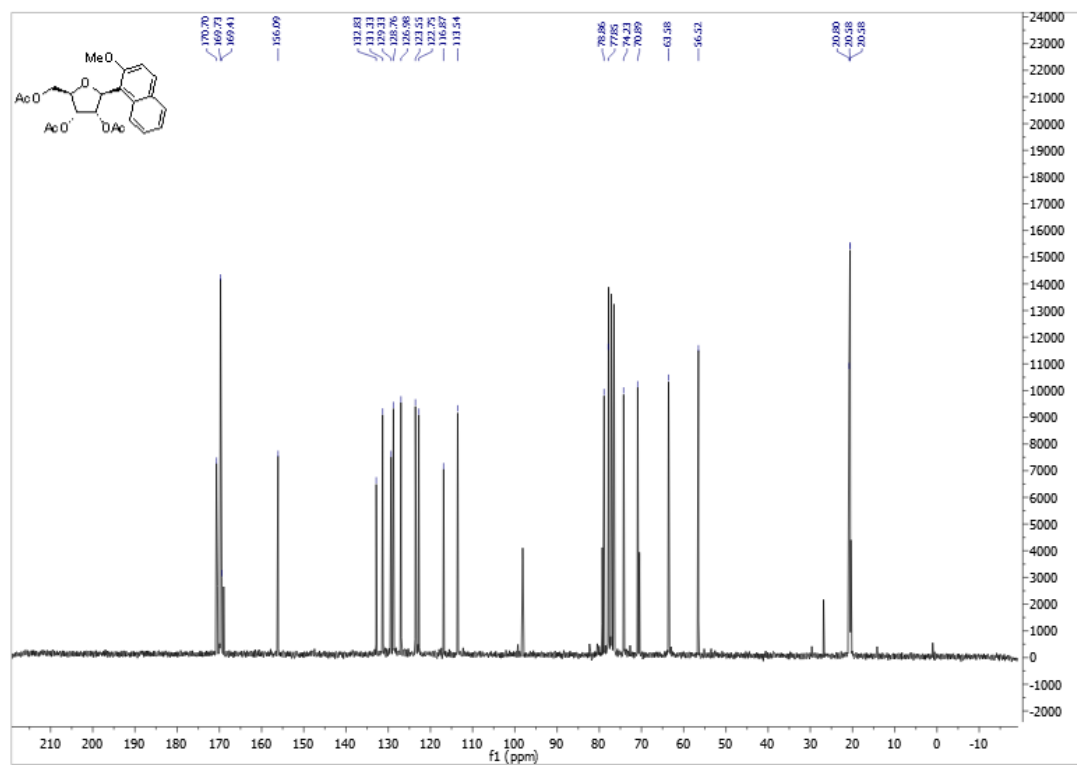
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) spectrum of **4k**.



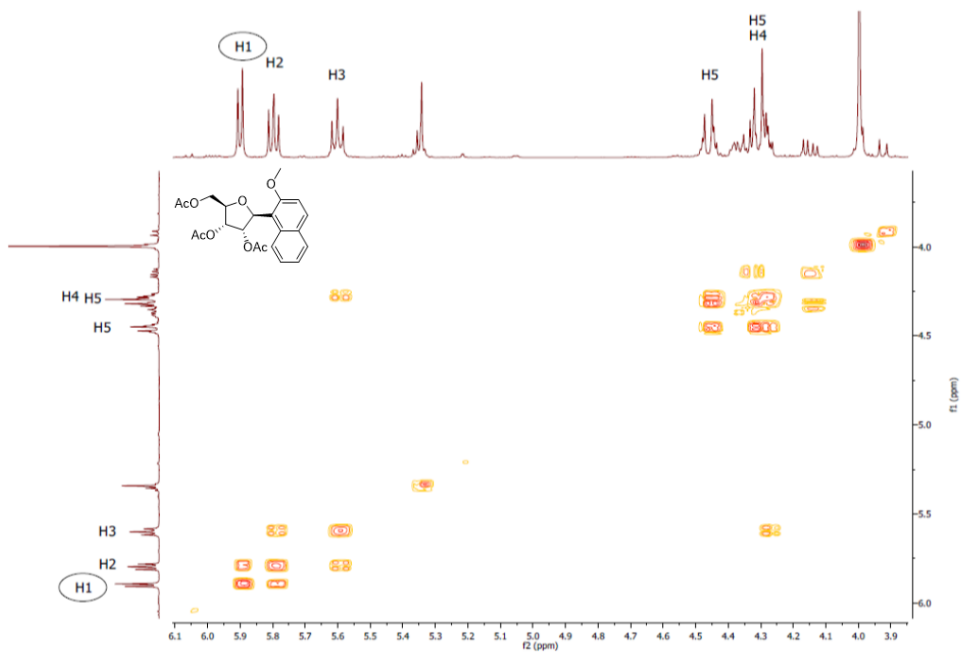
$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ) spectrum of **4k**.



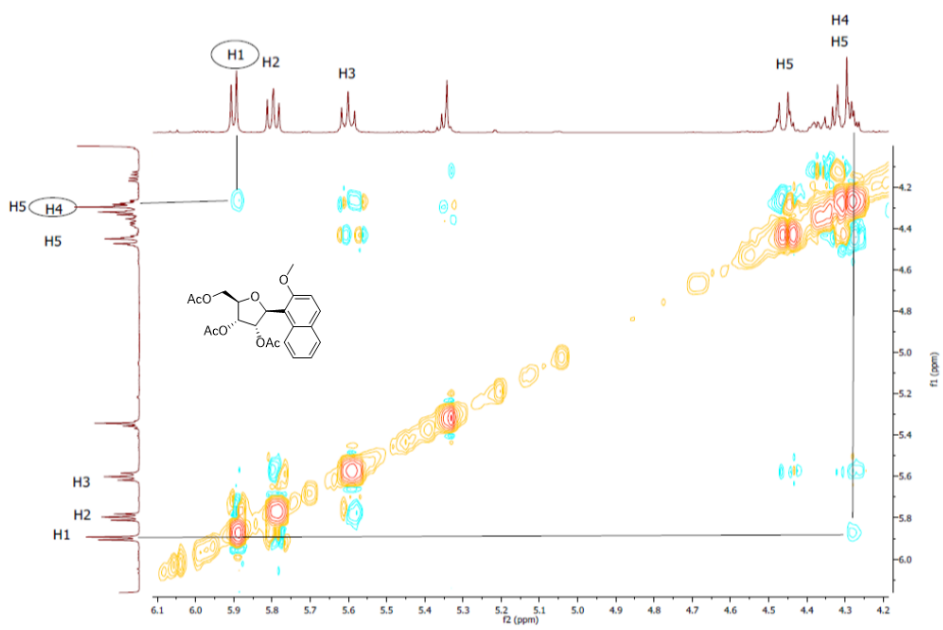
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 5a.



<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of 5a.

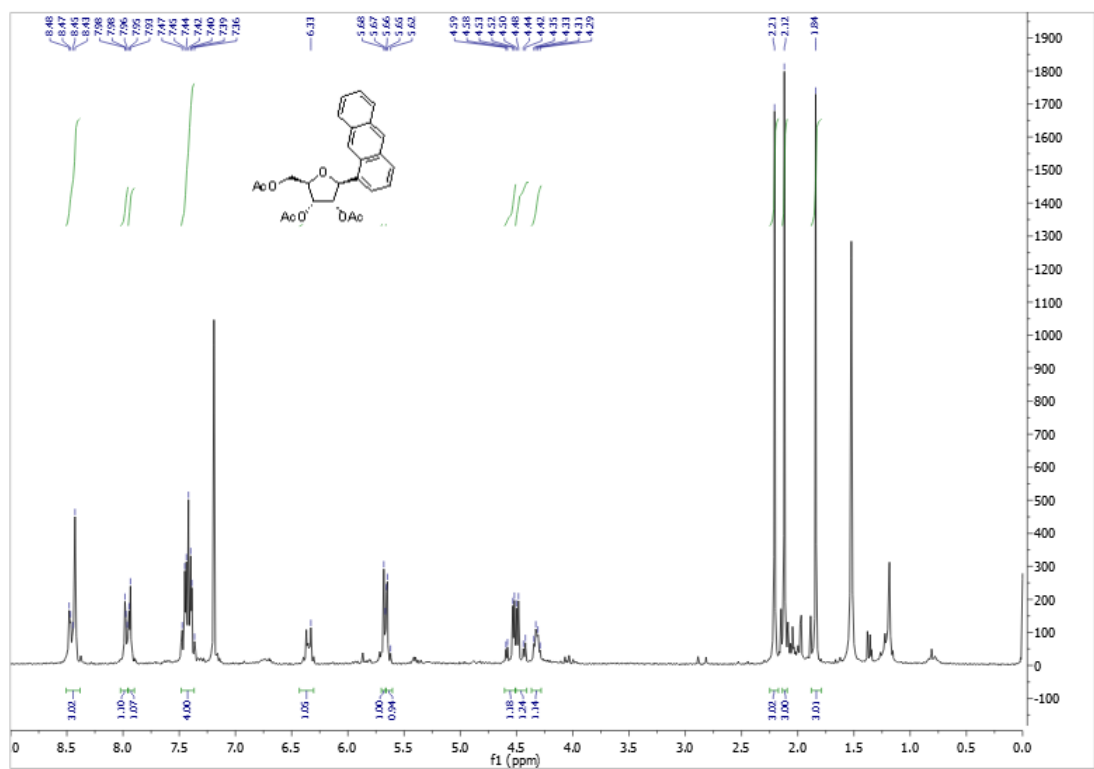


COSY spectrum of **5a**.

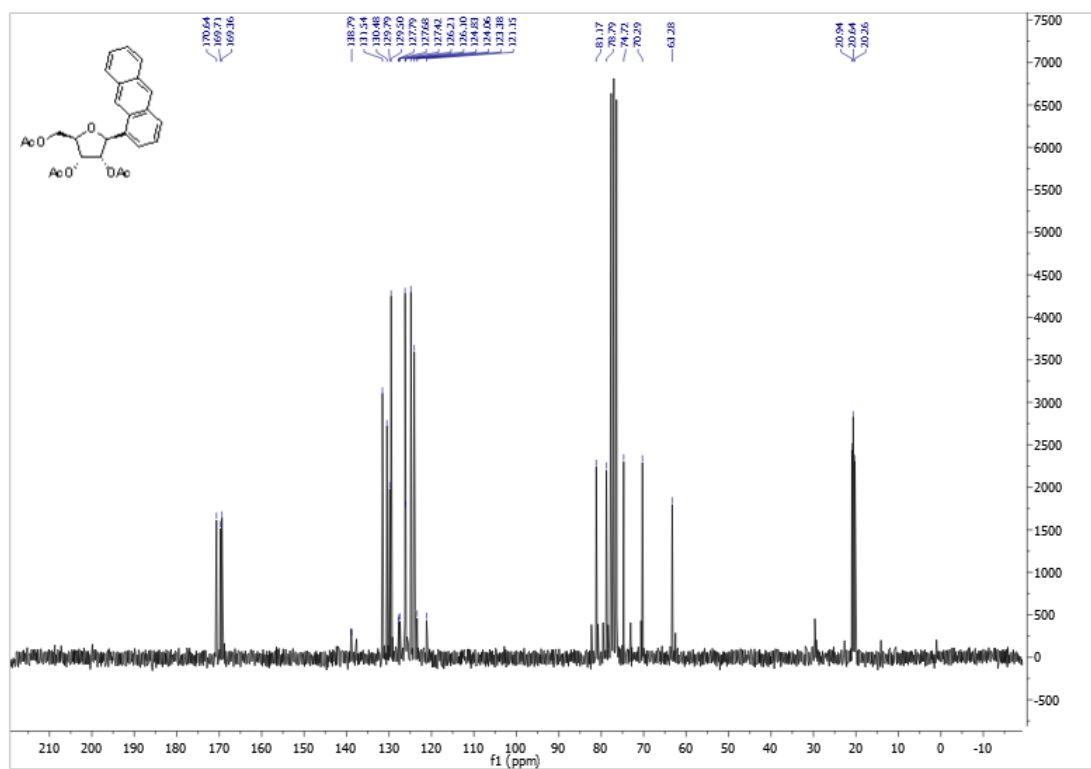


NOESY spectrum of **5a**.

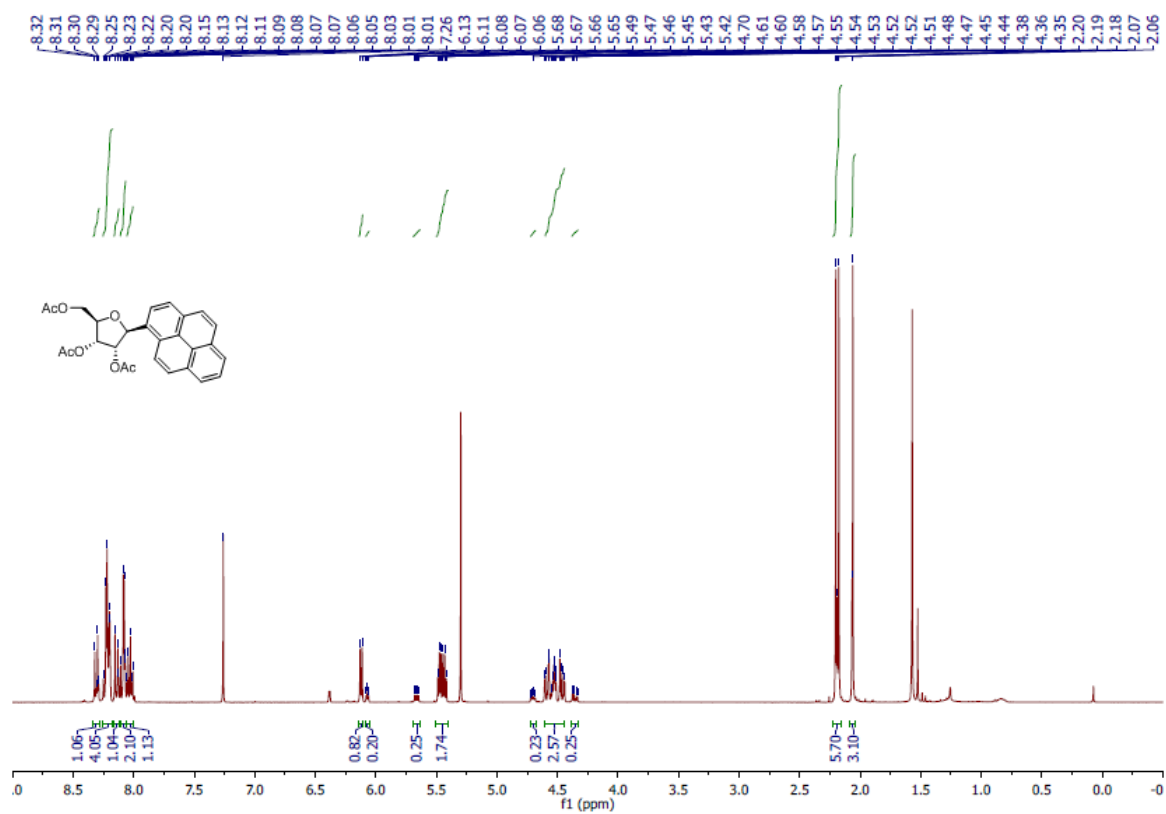




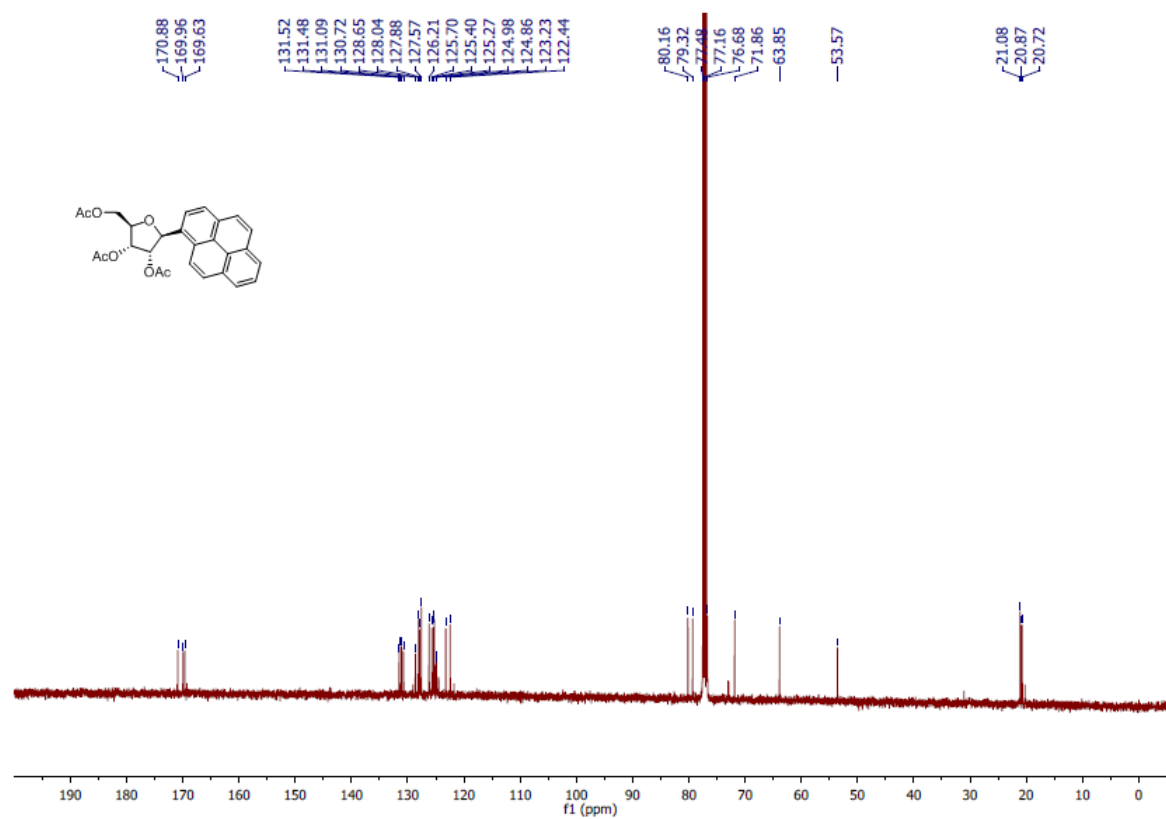
<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) spectrum of **5b**.



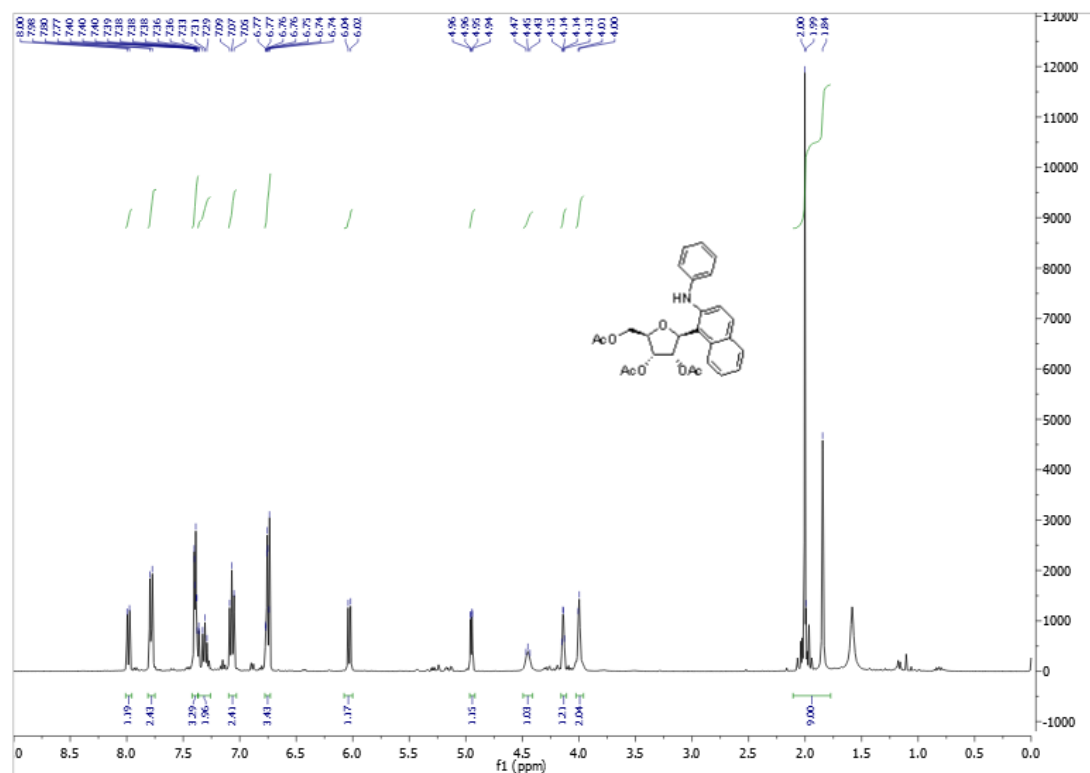
<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of **5b**.



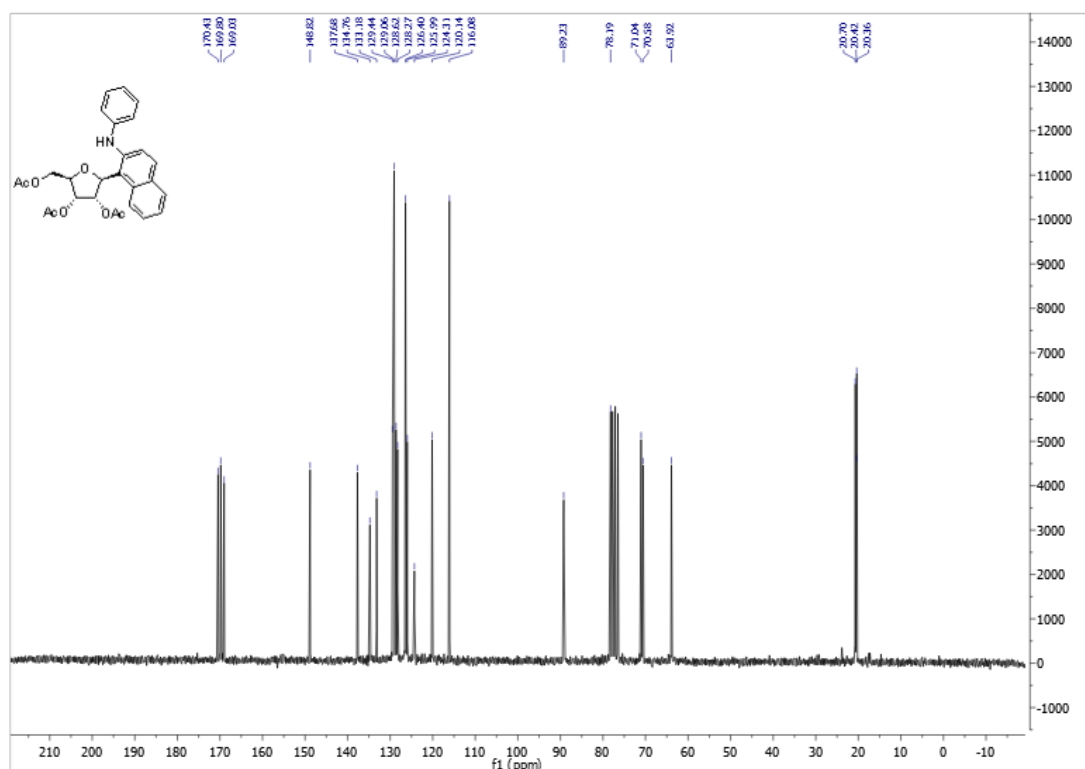
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **5c**.



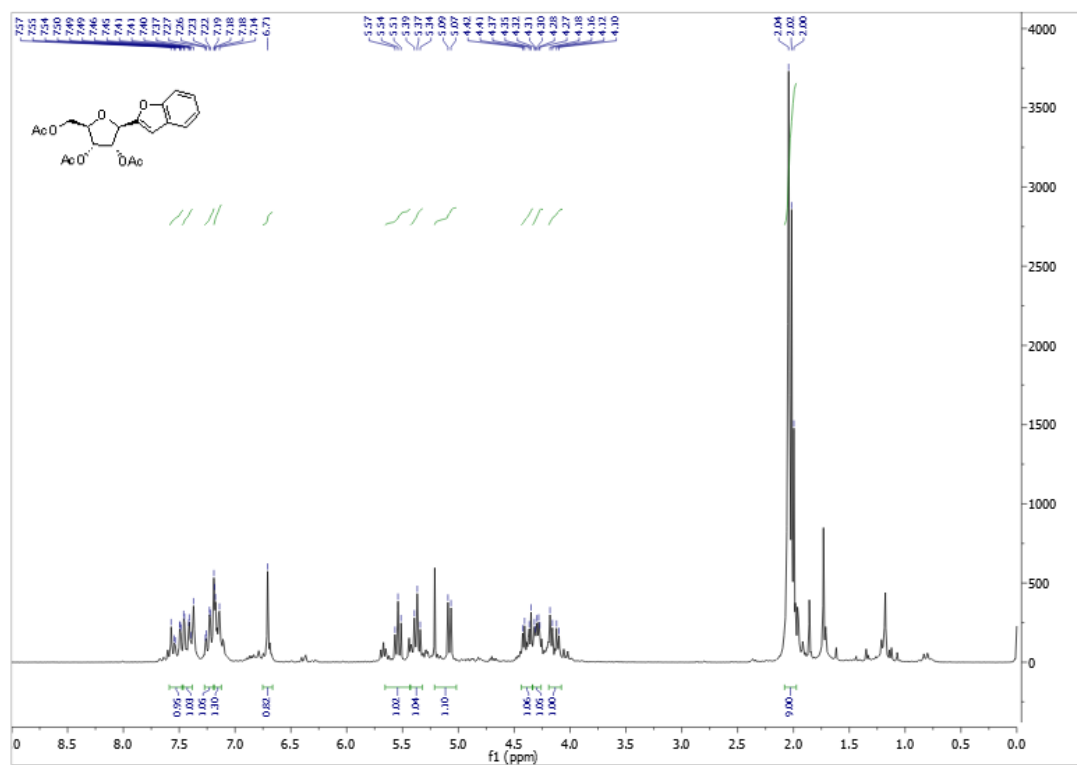
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of **5c**.



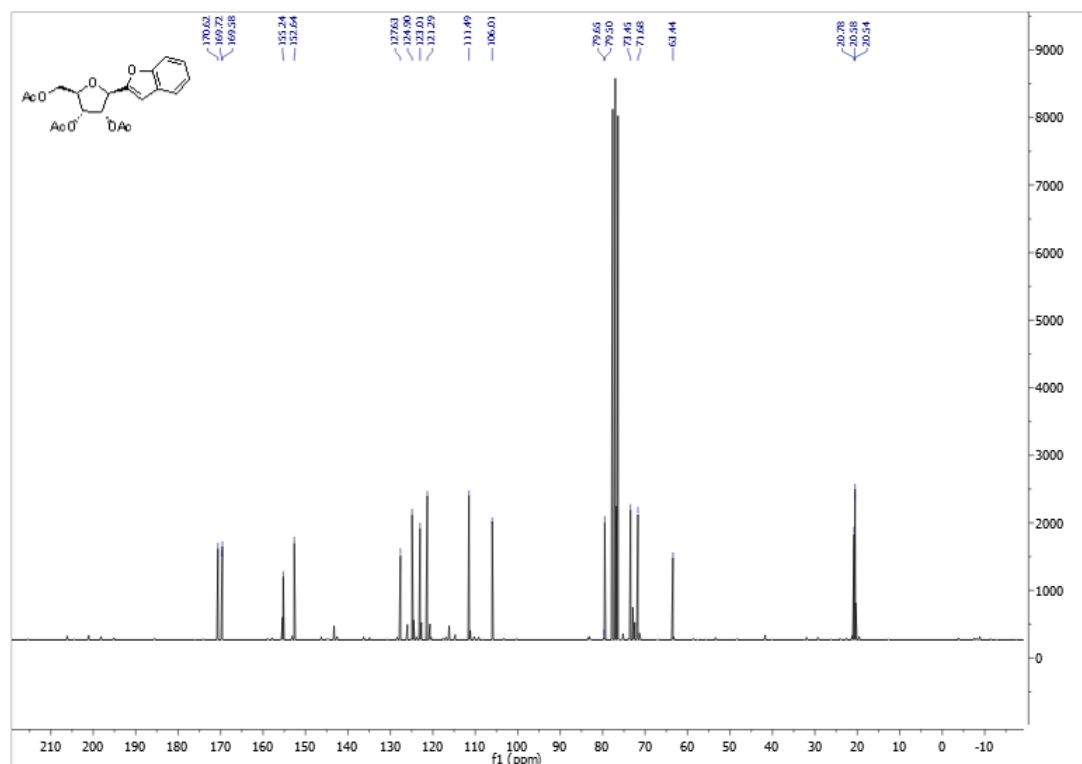
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 5d.



<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) spectrum of 5d.



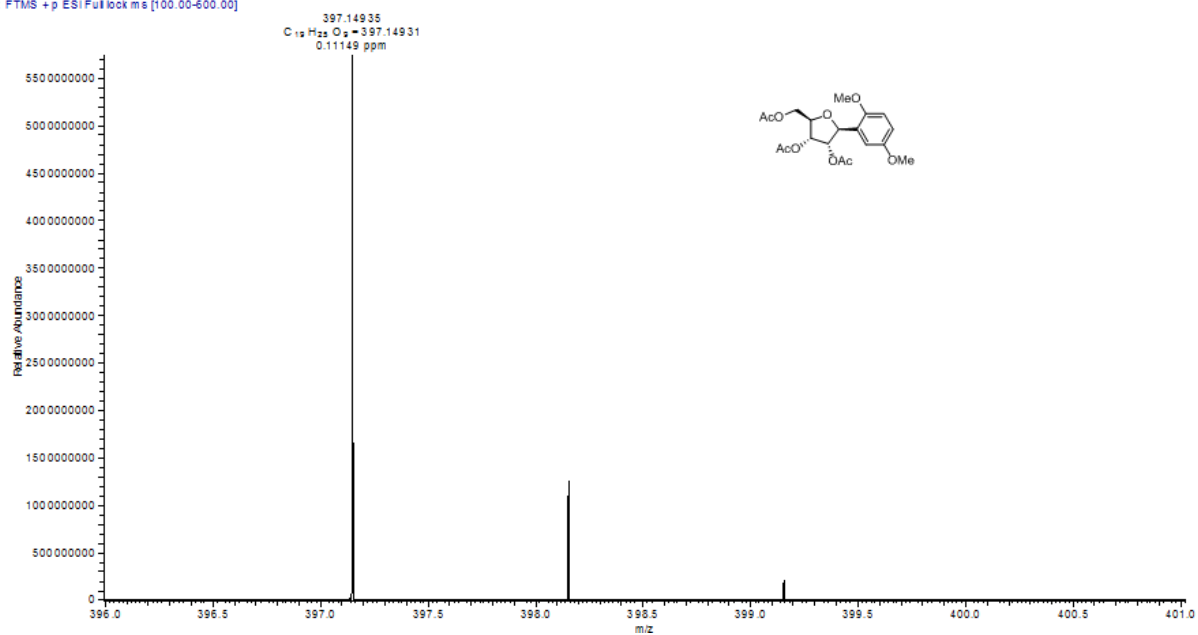
$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ) spectrum of **5e**.



$^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ) spectrum of **5e**.

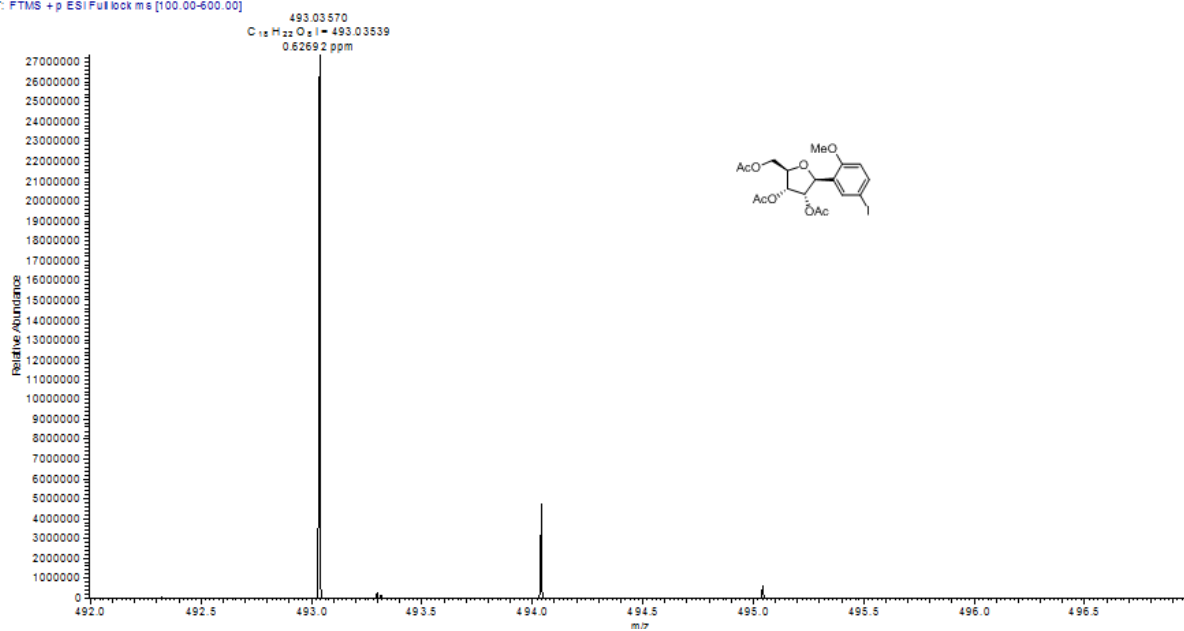
## Copies of HRMS spectra

141016W02#54 RT: 0.51 AV: 1 NL: 5.75E9  
T: FTMS + p ESI Full lock ms [100.00-600.00]



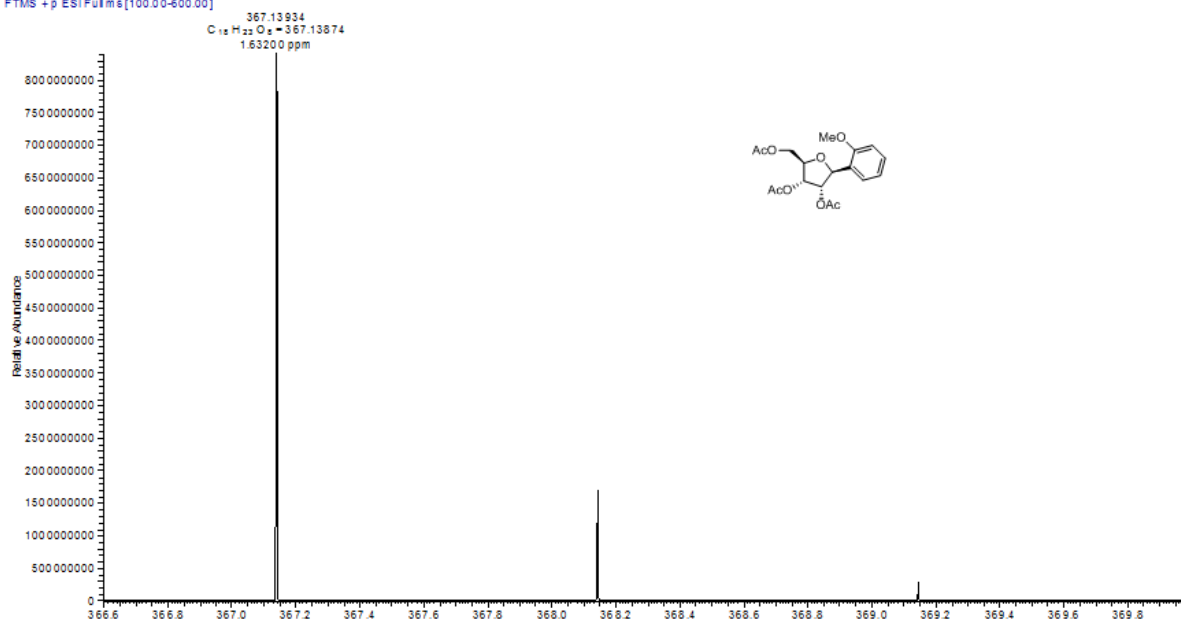
HRMS (ESI-MS) spectrum of **4a**.

141016LD01 #17-23 RT: 0.17-0.22 AV: 7 NL: 2.74E7  
T: FTMS + p ESI Full lock ms [100.00-600.00]



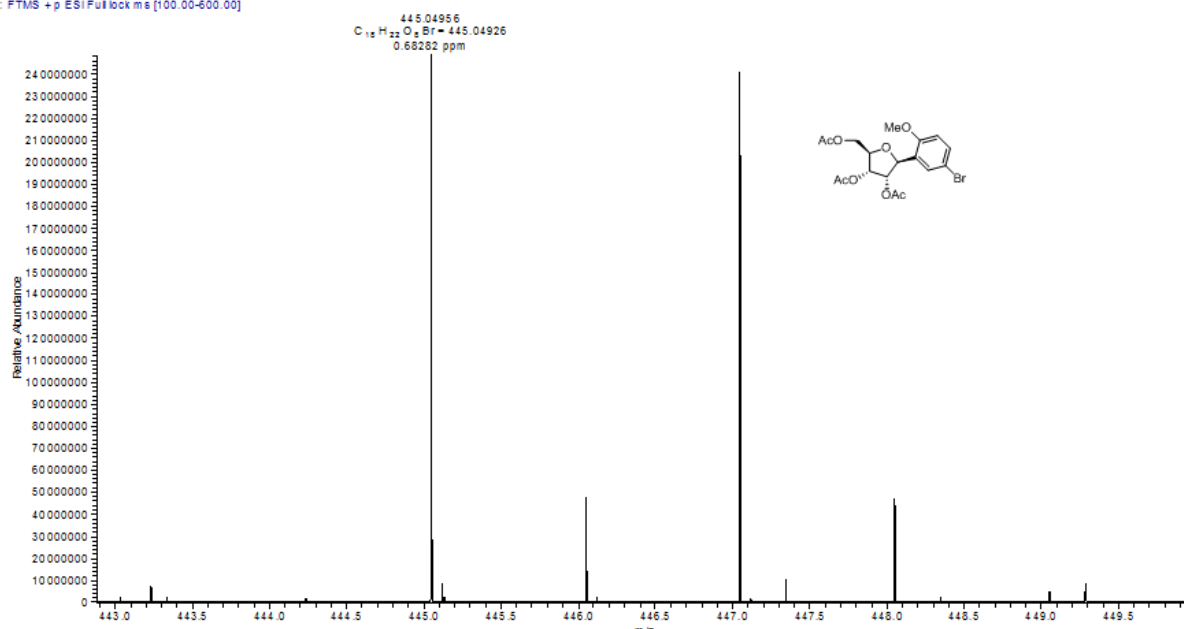
HRMS (ESI-MS) spectrum of **4b**.

1410161003#34 RT: 0.32 AV: 1 NL: 8.41E9  
T: FTMS + p ESI Full ms [100.00-600.00]

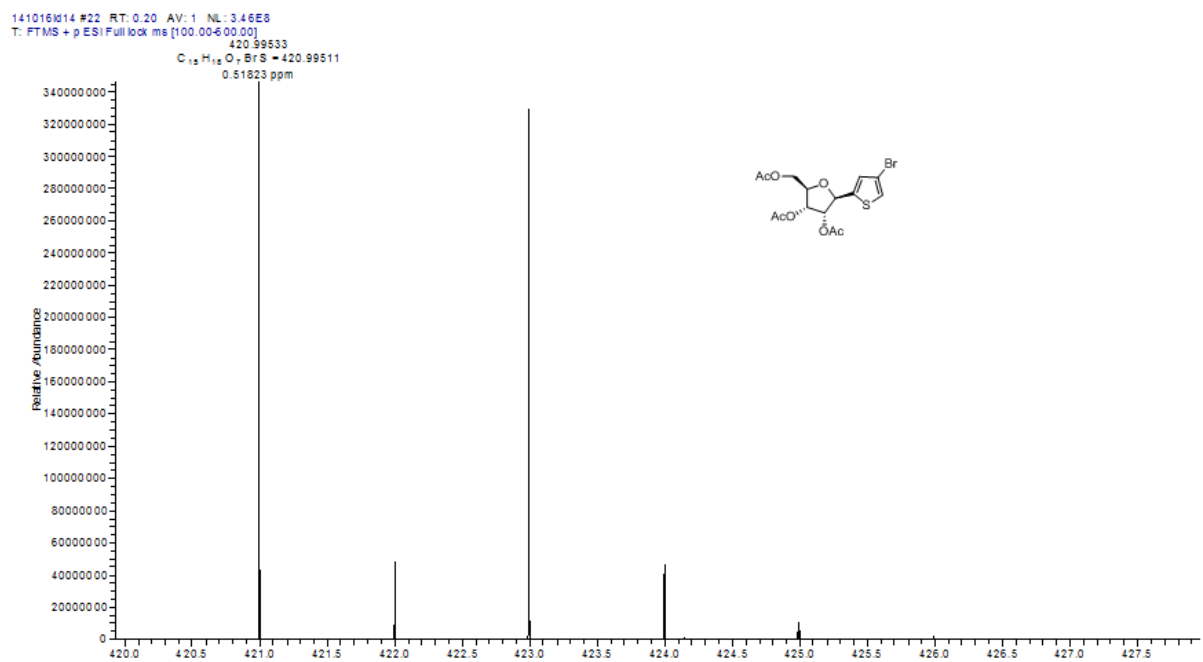


HRMS (ESI-MS) spectrum of 4c.

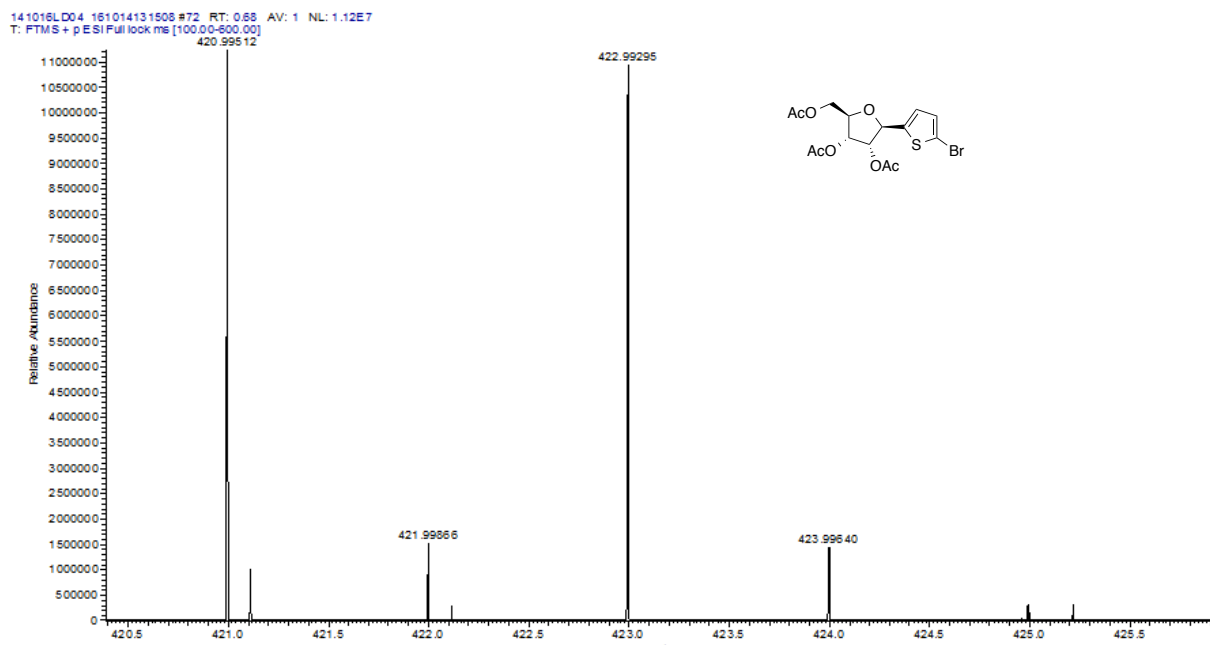
1410161006#10 RT: 0.09 AV: 1 NL: 2.49E8  
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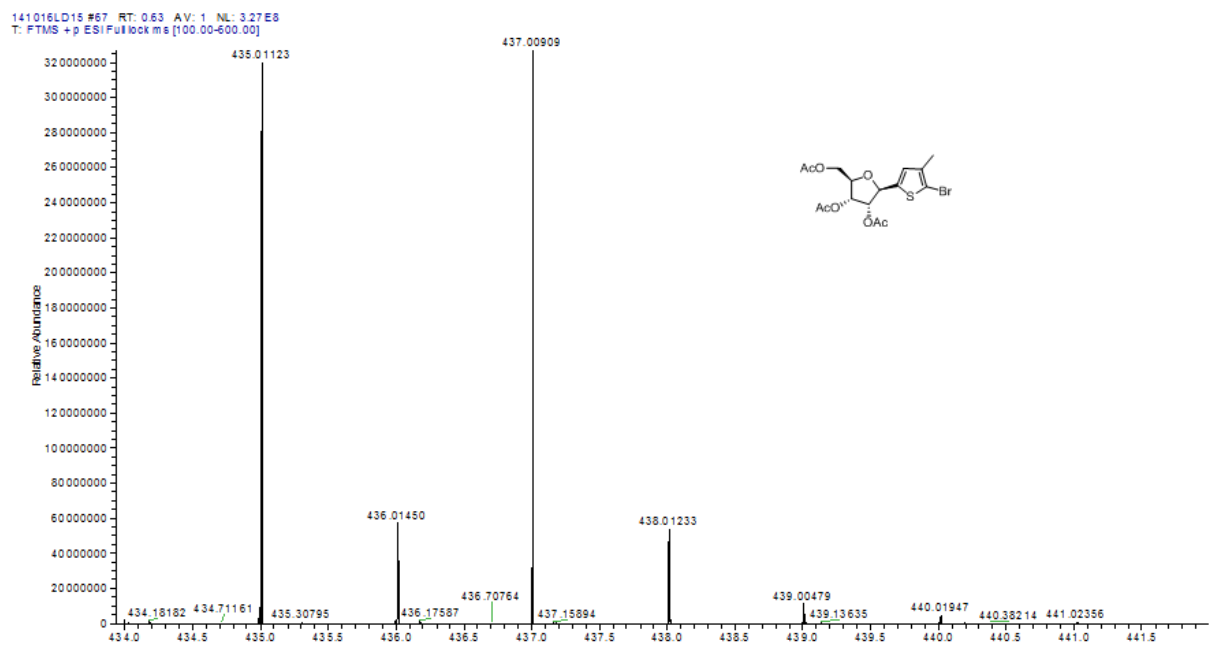
HRMS (ESI-MS) spectrum of 4d.



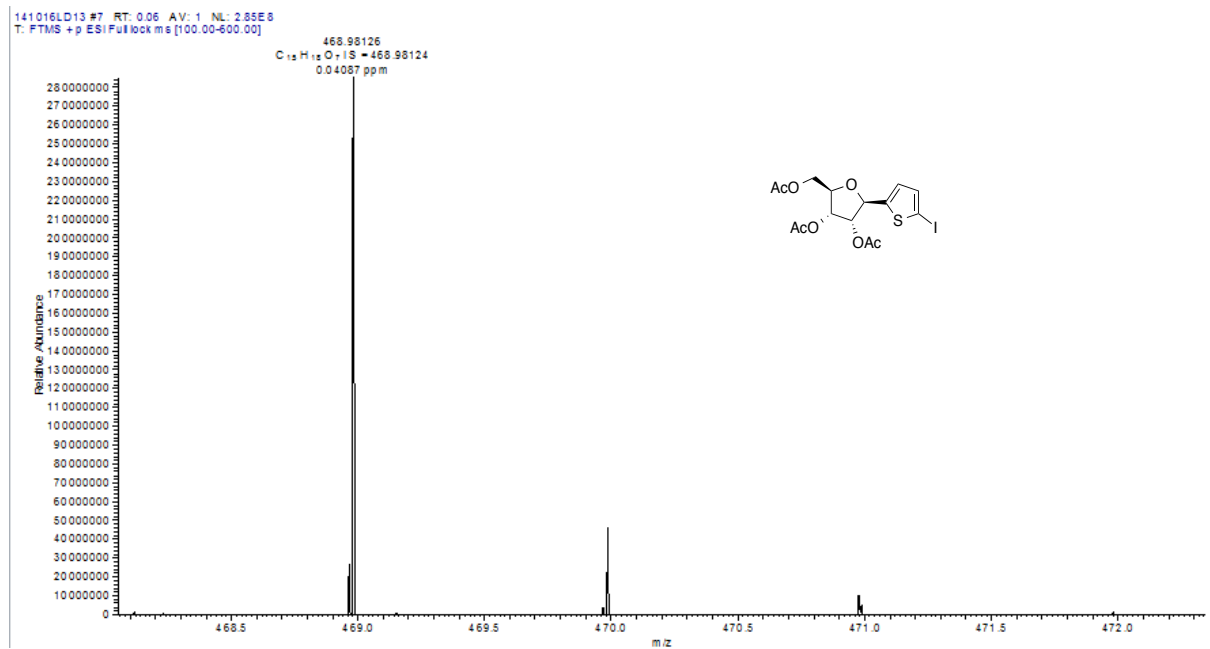
HRMS (ESI-MS) spectrum of **4e**.



HRMS (ESI-MS) spectrum of **4f**.



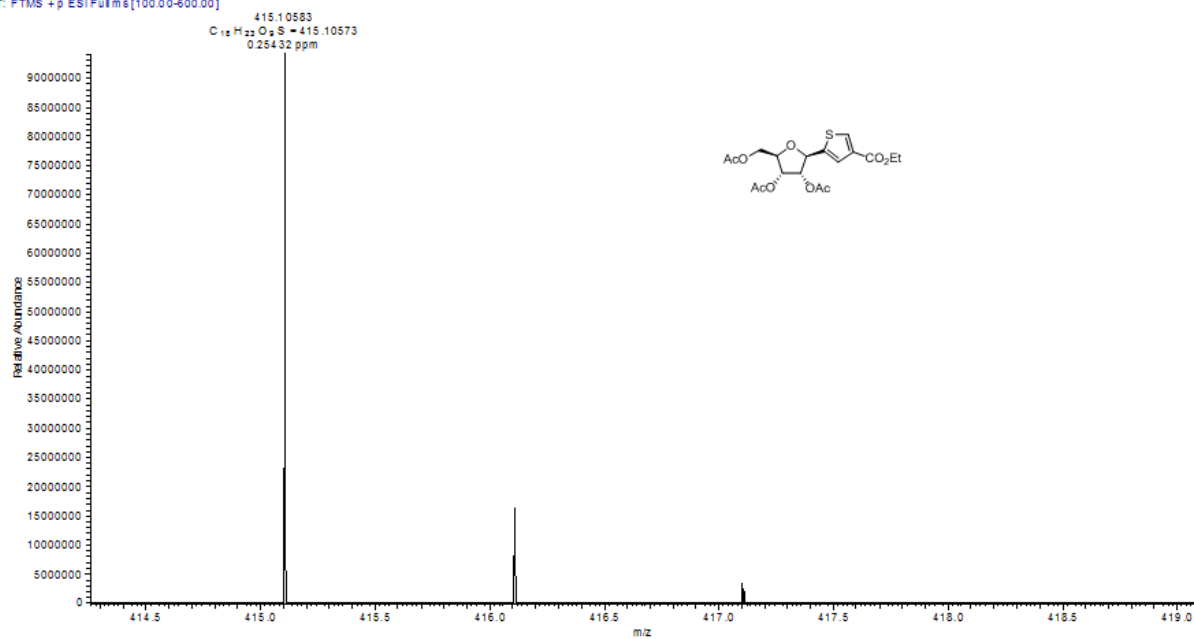
HRMS (ESI-MS) spectrum of **4g**.



HRMS (ESI-MS) spectrum of **4h**.

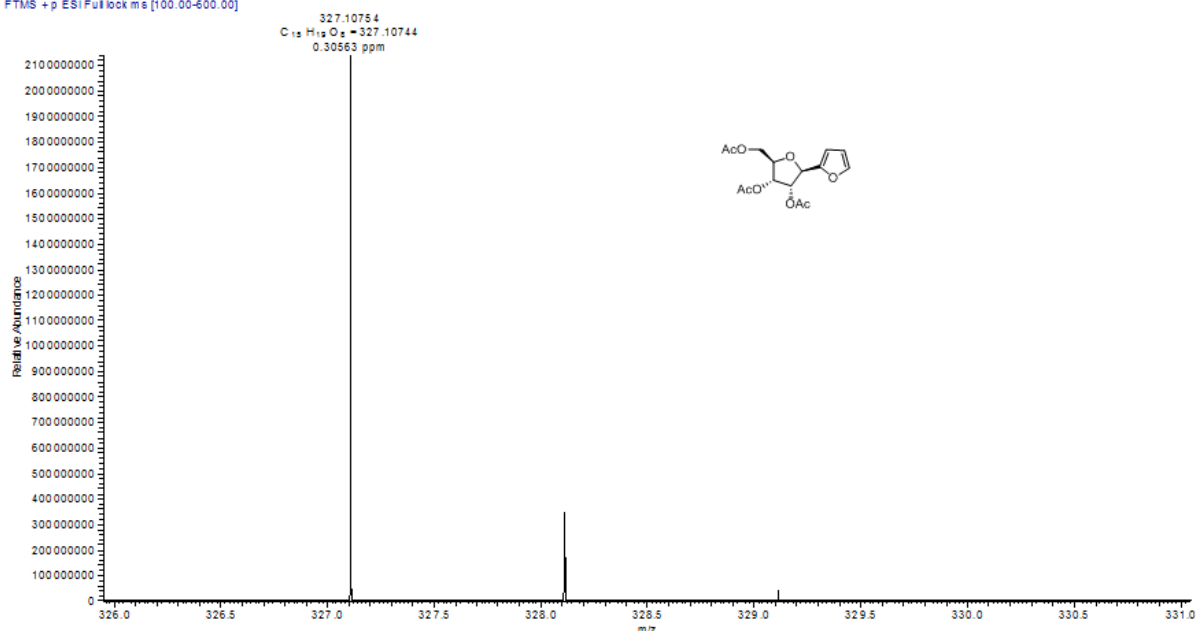


141016W09#24 RT: 0.22 AV: 1 NL: 9.42E7  
T: FTMS + p ESI Fullms [100.00-600.00]



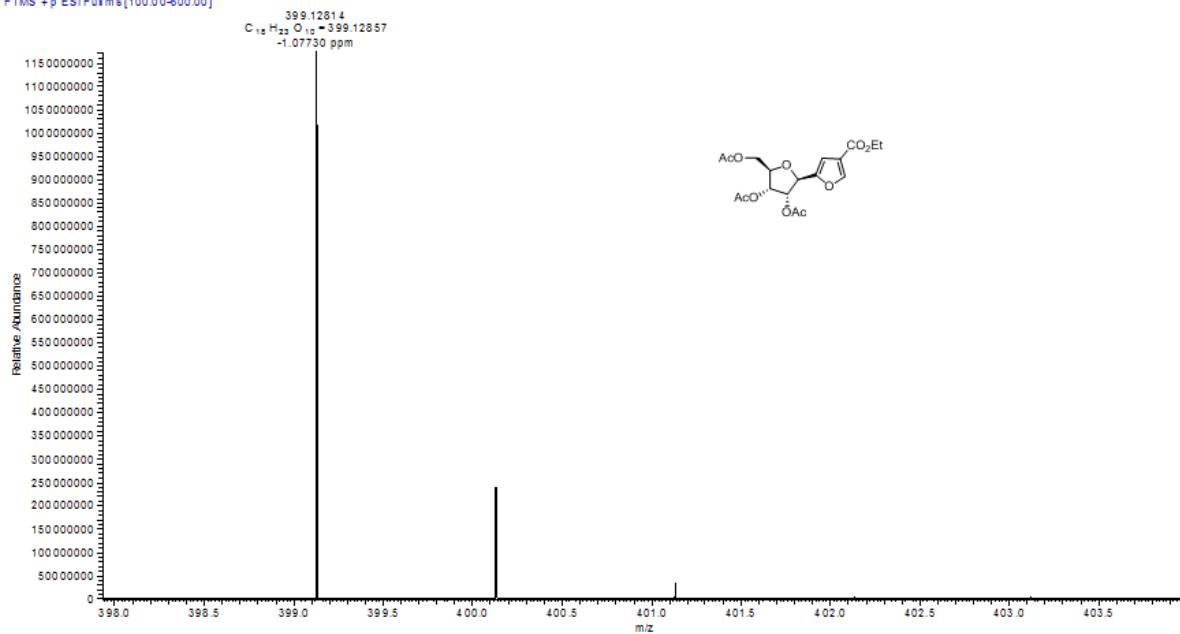
HRMS (ESI-MS) spectrum of **4i**.

141016W05#24 RT: 0.22 AV: 1 NL: 2.14E9  
T: FTMS + p ESI Full lock ms [100.00-600.00]



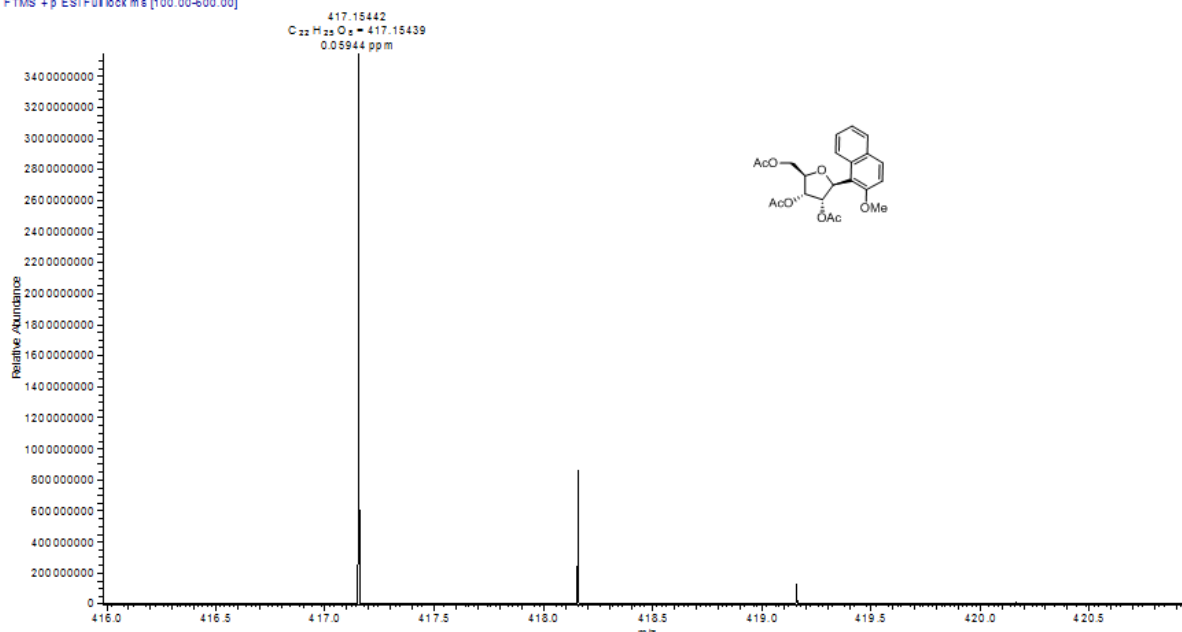
HRMS (ESI-MS) spectrum of **4j**.

1410161016#12 RT: 0.11 AV: 1 NL: 1.17E9  
T: FTMS + p ESI Full ms [100.00-600.00]



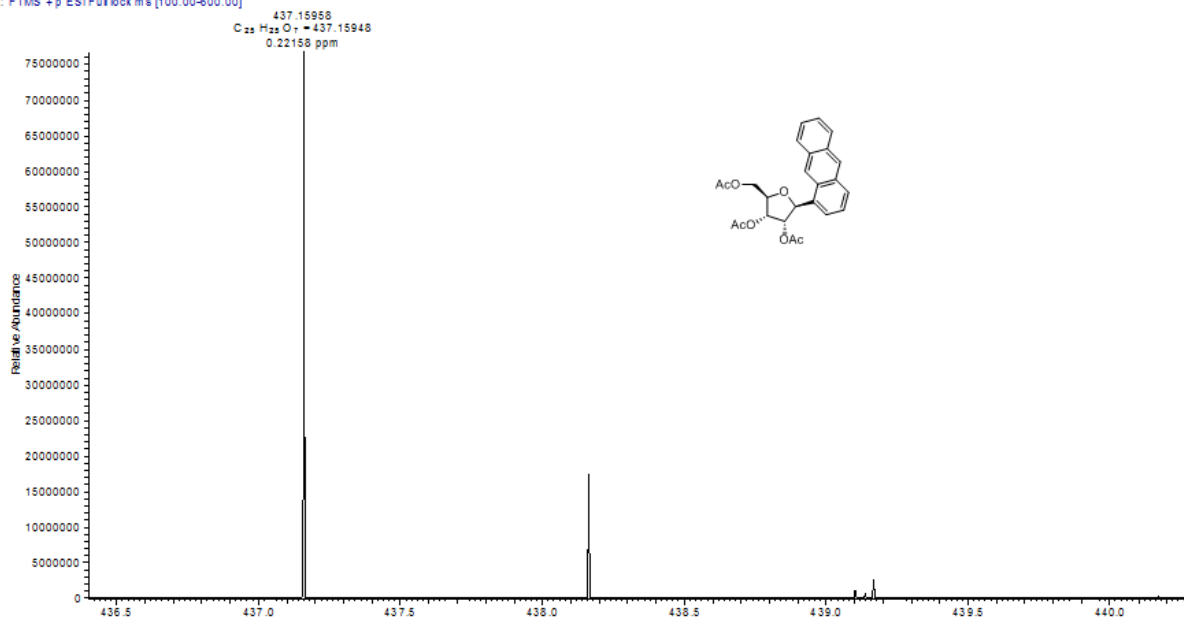
HRMS (ESI-MS) spectrum of **4k**.

1410161016#35 RT: 0.33 AV: 1 NL: 3.55E9  
T: FTMS + p ESI Full lock ms [100.00-600.00]



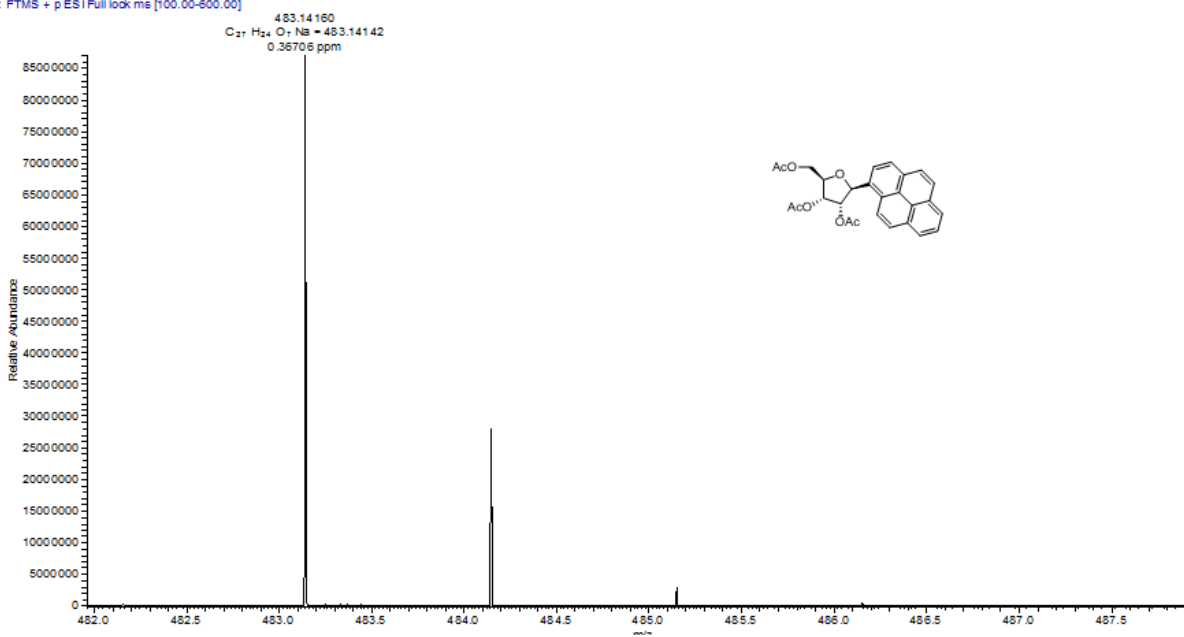
HRMS (ESI-MS) spectrum of **5a**.

1410161008 #31 RT: 0.29 AV: 1 NL: 7.68E7  
T: FTMS + p ESI Full lock ms [100.00-600.00]



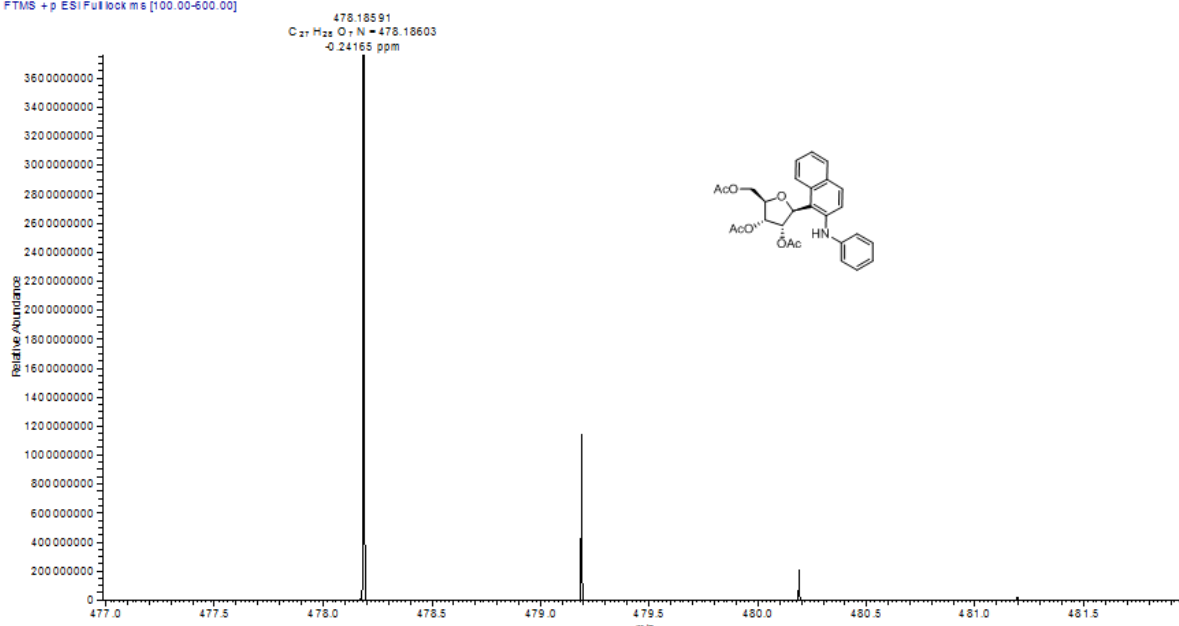
HRMS (ESI-MS) spectrum of **5b**.

1410161007 #10 RT: 0.09 AV: 1 NL: 8.71E7  
T: FTMS + p ESI Full lock ms [100.00-600.00]



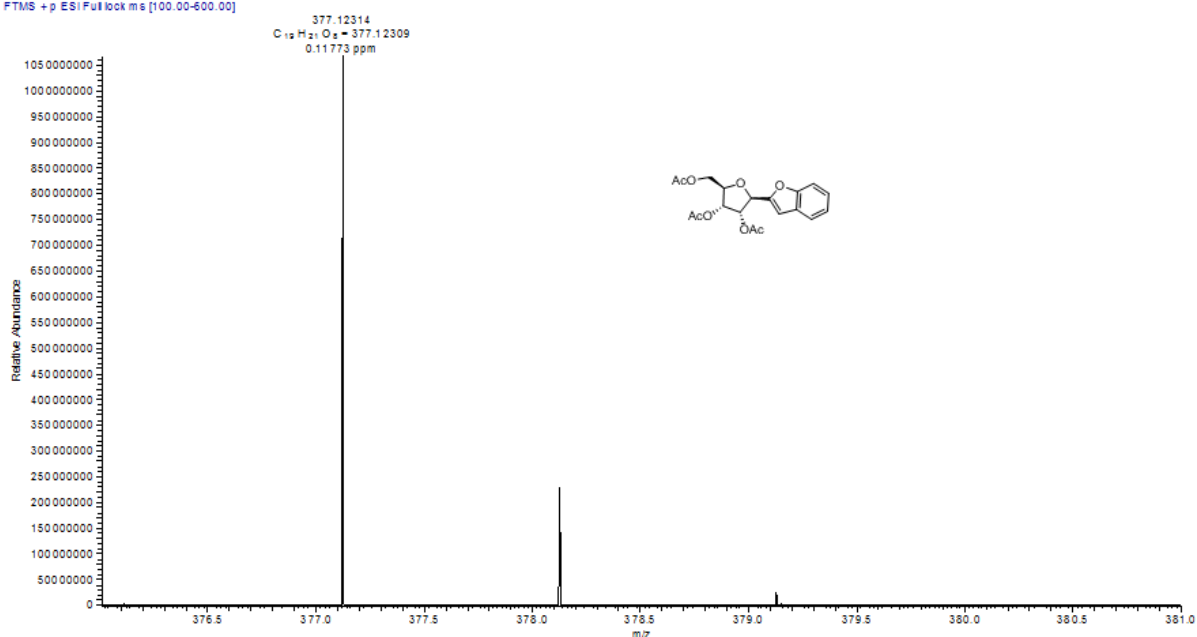
HRMS (ESI-MS) spectrum of **5c**.

141016K12 #28 RT: 0.26 AV: 1 NL: 3.76E9  
T: FTMS +p ESI Full lock m s [100.00-600.00]



HRMS (ESI-MS) spectrum of **5d**.

141016LD11 #17 RT: 0.16 AV: 1 NL: 1.07E9  
T: FTMS +p ESI Full lock m s [100.00-600.00]



HRMS (ESI-MS) spectrum of **5e**.

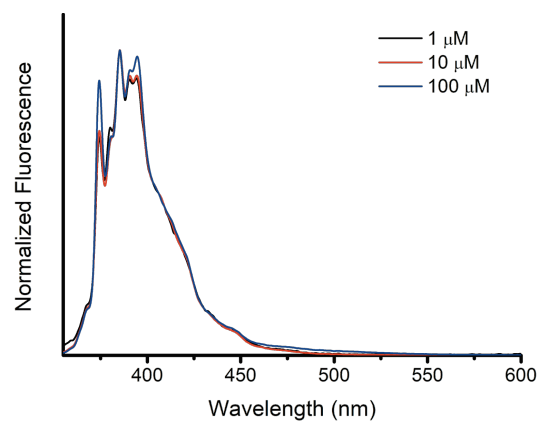


Figure S1. Fluorescence emission spectra of **5c** in different concentrations in cyclohexane.