

# Room Temperature Pd-Catalyzed Synthesis of 1-(Hetero)aryl Selenoglycosides

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## 1. General information

Solvents and reagents are obtained from commercial suppliers and were used without further purification. Analytical TLC was performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by UV light or by staining upon heating with vanillin solution (15 g of vanillin in 250 mL ethanol and 2.5 mL of concentrated sulfuric acid). For silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230-400 mesh) and p.a. grade solvents unless otherwise noted. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in either CDCl<sub>3</sub> or MeOD-d4 on Bruker Avance 300 spectrometers. The chemical shifts of <sup>1</sup>H and <sup>13</sup>C are reported in ppm relative to the solvent residual peaks. IR spectra were measured on a Bruker Vector 22 spectrophotometer.

Merck silica gel 60 (0.015–0.040 mm) was used for column chromatography. Melting points were recorded on a Büchi B-450 apparatus and are uncorrected. High resolution mass spectra (HR-MS) were recorded on a MicroMass LCT Premier Spectrometer spectrometer, mass analyzer type: Time of Flight Mass Spectrometer (TOF). Optical rotations were obtained with a PolAAr 32 polarimeter.

All Selenosugars were synthesized as according the following protocols.<sup>1, 2, 3</sup>

## 2. General Procedures

### 0.1 mmol scale reaction

An vial (5 mL) with a stir bar was charged with selenosugar (0.1 mmol, 1 eq), aryl halide (if solid) (0.2 mmol, 2eq), PdG3-Xantphos (0.01 mmol, 10 mol%), piperazine (0.12 mmol, 1.2 eq) and Cs<sub>2</sub>CO<sub>3</sub> (0.3 mmol, 3 eq). The vial was then evacuated and backfilled with an argon balloon. And then, aryl halide (if liqued) (0.2 mmol, 2 eq), 1 mL dry THF was added. The reaction mixture stir intensely under Ar and room temperature for two hours. After the reaction finished, the reaction mixture was extracted with DCM, and the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified with column chromatography on silica gel (from pure n-hexane to EtOAc:n-hexane = 3/7) to give the product.

### 1 mmol scale reaction:

An vial (20 mL) with a stir bar was charged with **1a** (1 mmol, 529.4 mg, 1 eq), **2a** (2 mmol, 468.0 mg, 2eq), PdG3-Xantphos (0.1 mmol, 78.0 mg, 10 mol%), piperazine (1.2 mmol, 103.4 mg, 1.2 eq) and Cs<sub>2</sub>CO<sub>3</sub> (3 mmol, 977.5 mg, 3 eq). The vial was then evacuated and backfilled with an argon balloon. And then, 5 mL dry THF was added. The reaction mixture stir intensely under Ar and room temperature for two hours. After the reaction finished, the reaction mixture was extracted with DCM, and the organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified with column chromatography on silica gel (from pure n-hexane to EtOAc:n-hexane = 3/7) to give the **3a** (92%, 475.7 mg).

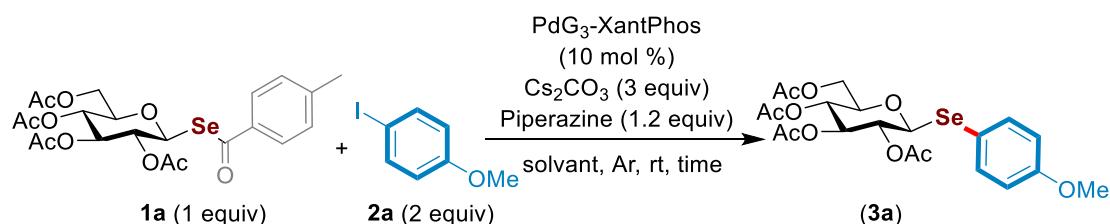
### 3. Condition screening

#### Catalyst and ligand effects:



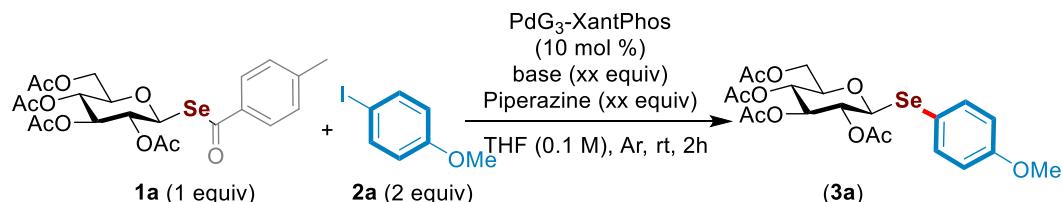
Entry	Catalyst	Ligand	Yields
1	PdG <sub>3</sub> Xantphos 10 mol%	-	95%
2	-	-	0%
3	PdG <sub>3</sub> Xantphos 5 mol%	-	81%
4	Pd(OAc) <sub>2</sub> 10 mol%	Xantphos 10 mol%	trace
5	PdCl <sub>2</sub> 10 mol%	Xantphos 10 mol%	trace

#### Reaction time and solvent effects:



Entry	Solvent	Time	Yields
1	THF	2h	95%
2	THF	1h	85%
3	THF	3h	95%
4	Dioxane	2h	95%
5	DCE	2h	83%
6	DMF	2h	89%

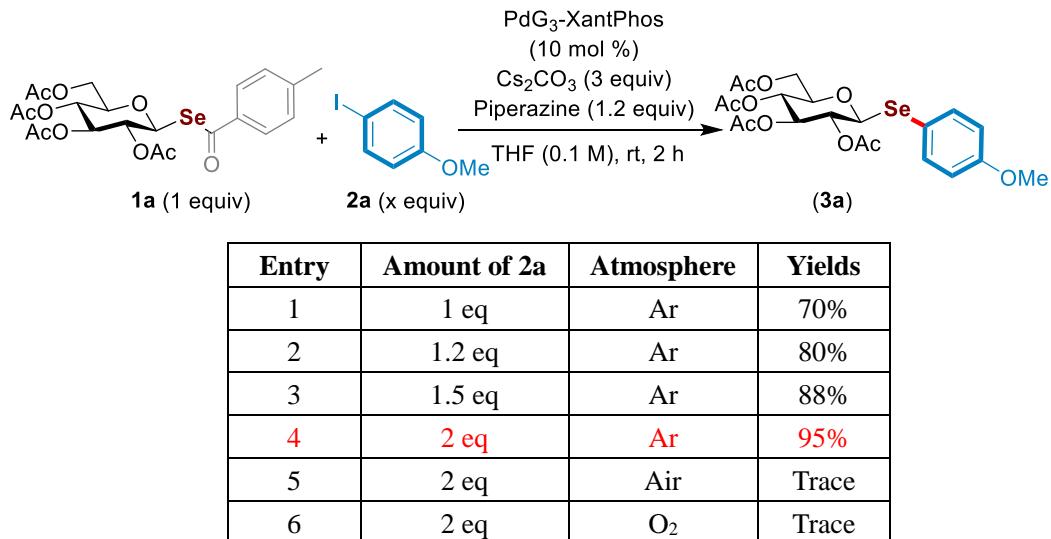
#### Base effects:



Entry	Base1	Base2	Yields
1	Cs <sub>2</sub> CO <sub>3</sub> 3eq	Piperazine 1.0 eq	72%
2	Cs <sub>2</sub> CO <sub>3</sub> 3eq	Piperazine 1.5 eq	95%
2	Cs <sub>2</sub> CO <sub>3</sub> 3eq	Piperazine 1.2 eq	95%
3	Cs <sub>2</sub> CO <sub>3</sub> 2eq	Piperazine 1.2 eq	72%
4	Cs <sub>2</sub> CO <sub>3</sub> 4eq	Piperazine 1.2 eq	95%

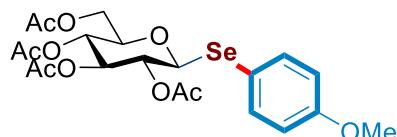
5	CsF 3eq	Piperazine 1.2 eq	83%
6	NaOAc 3eq	Piperazine 1.2 eq	65%

**Amount of 2a (xx equiv) effects:**



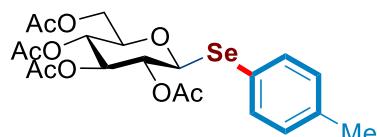
**4. Experimental data**

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((4-methoxyphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3a**)



Rf = 0.3 (EtOAc /cyclohexane: 3/7); 49.2 mg, 95%, White solid. m. p.: 103.9-104.8 °C; [α]<sub>D</sub><sup>18</sup> = -23.5 (c, 0.75, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, (CD<sub>3</sub>)<sub>2</sub>CO-d<sub>6</sub>) δ 7.54-7.58 (m, 2H), 6.87-6.93 (m, 2H), 5.27 (t, J = 9.0 Hz, 1H), 5.11 (d, J = 12.0 Hz, 1H), 4.88-4.99 (m, 2H), 4.13-4.24 (m, 2H), 3.92-3.97 (m, 1H), 3.83 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.93 (s, 3H); <sup>13</sup>C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO-d<sub>6</sub>) δ 170.6 (C), 170.2 (C), 169.9 (C), 169.7 (C), 161.3 (C), 138.2 (2CH), 117.6 (C), 115.5 (2CH), 81.2 (CH), 77.2 (CH), 74.4 (CH), 71.7 (CH), 69.2 (CH), 62.9 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1754, 1746, 1591, 1492, 1461, 1440, 1366, 1287, 1247, 1215, 117, 1059, 1030, 911, 828, 733 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>21</sub>H<sub>30</sub>NO<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 536.1029; found 536.1039.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(p-tolylselanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3b**)



Rf = 0.3 (EtOAc /cyclohexane: 3/7); 50.1 mg, 99%, White solid. m. p.: 125.1-126.0 °C; [α]<sub>D</sub><sup>18</sup> = -

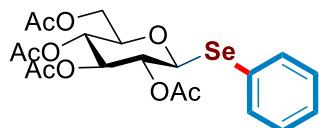
22.6 (c, 0.31,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.50 (m, 2H), 7.09-7.11 (m, 2H), 5.17 (t,  $J = 9.0$  Hz, 1H), 4.93-5.03 (m, 2H), 4.82 (d,  $J = 9.0$  Hz, 1H), 4.17-4.18 (m, 2H), 3.63-3.69 (m, 1H), 2.35 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5 (C), 170.1 (C), 169.3 (C), 169.2 (C), 138.8 (C), 135.7 (2CH), 129.8 (2CH), 122.9 (C), 80.8 (CH), 76.8 (CH), 73.9 (CH), 70.8 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 1755, 1479, 1439, 1367, 1249, 1217, 1088, 1060, 1038, 911, 743, 693 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for  $\text{C}_{21}\text{H}_{30}\text{NO}_9\text{Se} [\text{M}+\text{NH}_4]^+$  520.1080; found 520.1085.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((3-methoxyphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3c**)



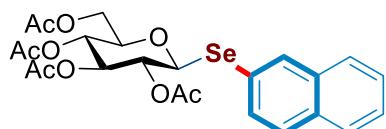
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 37.7 mg, 73%, White solid. m. p.: 124.6-125.1 °C;  $[\alpha]_D^{18} = -16.7$  (c, 0.36,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15-7.23 (m, 3H), 6.86-6.89 (m, 1H), 5.19 (t,  $J = 9.0$  Hz, 1H), 5.02 (dt,  $J = 3.0, 9.0$  Hz, 2H), 4.91 (d,  $J = 9.0$  Hz, 1H), 4.14-4.24 (m, 2H), 3.81 (s, 3H), 3.67-3.73 (m, 1H), 2.06 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6 (C), 170.1 (C), 169.3 (C), 169.2 (C), 159.6 (C), 129.7 (CH), 127.8 (C), 127.2 (CH), 120.5 (CH), 114.3 (CH), 81.0 (CH), 76.9 (CH), 73.9 (CH), 70.8 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 55.3 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 20.6 (3CH<sub>3</sub>); IR (neat): 2360, 2341, 2327, 1754, 1589, 1478, 1367, 1247, 1038, 911, 733 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for  $\text{C}_{21}\text{H}_{30}\text{NO}_{10}\text{Se} [\text{M}+\text{NH}_4]^+$  536.1029; found 536.1031.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(phenylselanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3d**)<sup>4</sup>



$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 43.9 mg, 90%, White solid. m. p.: 133.2-133.6 °C;  $[\alpha]_D^{18} = -38.1$  (c, 0.21,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61-7.64 (m, 2H), 7.28-7.40 (m, 3H), 5.21 (t,  $J = 9.0$  Hz, 1H), 5.02 (td,  $J = 6.0, 12.0$  Hz, 2H), 4.91 (d,  $J = 12.0$  Hz, 1H), 4.15-4.26 (m, 2H), 3.47-3.68 (m, 1H), 2.09 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H). IR (neat): 1755, 1479, 1439, 1367, 1249, 1217, 1088, 1060, 1038, 911, 743, 693 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for  $\text{C}_{20}\text{H}_{28}\text{NO}_9\text{Se} [\text{M}+\text{NH}_4]^+$  506.0924; found 506.0920.

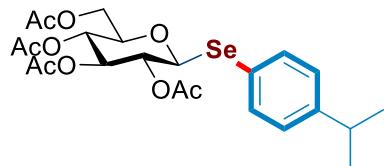
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(naphthalen-2-ylselanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3e**)



$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 39.4 mg, 73%, White solid. m. p.: 103.5-103.8 °C;  $[\alpha]_D^{18} = -$

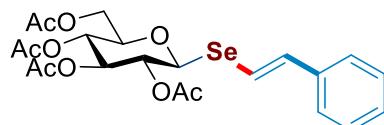
41.4 (c, 0.29,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04-8.20 (m, H), 7.61-7.84 (m, 4H), 7.49-7.52 (m, 2H), 5.20 (t,  $J = 9.0$  Hz, 1H), 4.89-5.08 (m, 3H), 3.98-4.37 (m, 2H), 3.60-3.72 (m, 1H), 2.09 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5 (C), 170.1 (C), 169.3 (2C), 135.1 (CH), 133.7 (C), 133.0 (C), 132.2 (CH), 128.4 (CH), 127.7 (2CH), 126.8 (CH), 126.5 (CH), 124.1 (C), 81.0 (CH), 77.0 (CH), 73.9 (CH), 70.9 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 20.8 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>); IR (neat): 2360, 1754, 1746, 1586, 1501, 1432, 1367, 1248, 1214, 1060, 911, 817, 747  $\text{cm}^{-1}$ ; HRMS (ESI): m/z calc. for  $\text{C}_{24}\text{H}_{30}\text{NO}_9\text{Se} [\text{M}+\text{NH}_4]^+$  556.1080; found 556.1093.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((4-isopropylphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3f**)



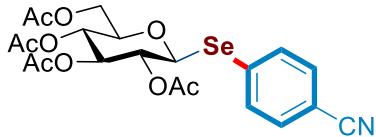
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 46.2 mg, 87%, White solid. m. p.: 120.0-121.3 °C;  $[\alpha]_D^{18} = -23.5$  (c, 0.34,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.53 (m, 2H), 7.14-7.16 (m, 2H), 5.18 (t,  $J = 9.0$  Hz, 1H), 5.01 (td,  $J = 6.0, 9.0$  Hz, 2H), 4.85 (d,  $J = 9.0$  Hz, 1H), 4.18 (d,  $J = 3.0$  Hz, 2H), 3.65-3.70 (m, 1H), 2.85-2.94 (m, 1H), 2.06 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5 (C), 170.1 (C), 169.4 (C), 169.3 (C), 149.6 (C), 135.6 (2CH), 127.2 (2CH), 123.5 (C), 81.0 (CH), 76.8 (CH), 73.9 (CH), 70.9 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 33.9 (CH) 23.8 (2CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2961, 2360, 2341, 1755, 1366, 1248, 1217, 1060, 1039, 910, 826, 773, 670  $\text{cm}^{-1}$ ; HRMS (ESI): m/z calc. for  $\text{C}_{23}\text{H}_{34}\text{NO}_9\text{Se} [\text{M}+\text{NH}_4]^+$  548.1393; found 548.1386.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((*E*)-styryl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3g**)



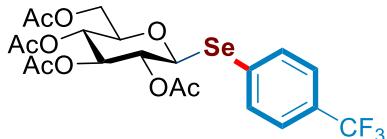
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 33.4 mg, 65%, White solid. m. p.: 103.5-103.8 °C;  $[\alpha]_D^{18} = -41.4$  (c, 0.29,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.35 (m, 5H), 7.08 (d,  $J = 15.0$  Hz, 1H), 6.96 (d,  $J = 15.0$  Hz, 1H), 5.11-5.29 (m, 3H), 4.87 (d,  $J = 15.0$  Hz, 1H), 4.14-4.29 (m, 2H), 3.71-3.79 (m, H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6 (C), 170.1 (C), 169.3 (C), 169.3 (C), 138.9 (CH), 136.7 (CH), 128.7 (2CH), 128.1 (CH), 126.3 (2CH), 113.8 (CH), 79.0 (CH), 77.2 (CH), 73.8 (CH), 70.9 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 61.2 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.6 (2CH<sub>3</sub>); IR (neat): 2925, 2360, 2326, 1755, 1367, 1216, 1087, 1060, 1034, 773  $\text{cm}^{-1}$ ; HRMS (ESI): m/z calc. for  $\text{C}_{22}\text{H}_{30}\text{NO}_9\text{Se} [\text{M}+\text{NH}_4]^+$  532.1080; found 532.1088.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-cyanophenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3h**)



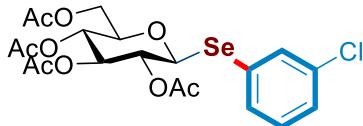
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 50.9 mg, 99%, White solid. m. p.: 164.1-165.3 °C;  $[\alpha]_D^{18} = -36.4$  (c, 0.22, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.68-7.71 (m, 2H), 7.53-7.57 (m, 2H), 5.21 (t, *J* = 12.0 Hz, 1H), 4.97-5.06 (m, 3H), 4.15-4.25 (m, 2H), 3.72-3.77 (m, 1H), 2.07 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.3 (C), 170.0 (C), 169.3 (C), 169.2 (C), 134.7 (2CH), 134.1 (C), 132.2 (2CH), 118.3 (C), 112.1 (C), 80.5 (CH), 77.1 (CH), 73.6 (CH), 70.5 (CH), 68.0 (CH), 62.0 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1754, 1433, 1367, 1217, 1060, 1041, 911, 769 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>21</sub>H<sub>23</sub>NO<sub>9</sub>NaSe [M+Na]<sup>+</sup> 536.0436; found 536.0446.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-(trifluoromethyl)phenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3i**)



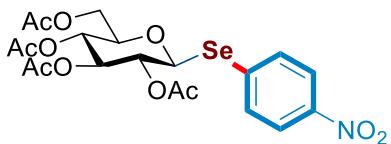
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 52.7 mg, 95%, White solid. m. p.: 150.1-151.3 °C;  $[\alpha]_D^{18} = -25.0$  (c, 0.40, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.71-7.73 (m, 2H), 7.52-7.55 (m, 2H), 5.21 (t, *J* = 9.0 Hz, 1H), 4.91-5.06 (m, 3H), 4.18-4.20 (m, 2H), 3.69-3.74 (m, 1H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.4 (C), 170.1 (C), 169.3 (2C), 135.1 (2CH), 131.7 (C), 125.6 (2CH, *J* = 3 Hz), 121.9 (C, *J* = 30 Hz), 110.35 (C, *J* = 277 Hz), 80.5 (CH), 77.0 (CH), 73.6 (CH), 70.6 (CH), 68.0 (CH), 62.0 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.6 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 2326, 1752, 1603, 1368, 1248, 1166, 1080, 1059, 911, 773 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>21</sub>H<sub>23</sub>F<sub>3</sub>NaO<sub>9</sub>Se [M+Na]<sup>+</sup> 579.0357; found 579.0347.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-(trifluoromethyl)phenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3j**)



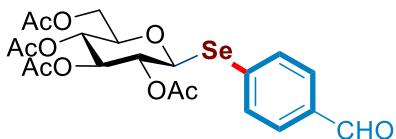
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 51.7 mg, 99%, White solid. m. p.: 77.2-77.4 °C;  $[\alpha]_D^{18} = -36.4$  (c, 0.66, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.63 (s, 1H), 7.46-7.49 (m, 1H), 7.20-7.34 (m, 2H), 5.20 (t, *J* = 9.0 Hz, 1H), 4.88-5.06 (m, 3H), 4.14-4.25 (m, 2H), 3.68-3.74 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.6 (C), 170.1 (C), 169.3 (C), 169.2 (C), 134.7 (CH), 134.4 (CH), 133.1 (CH), 130.0 (CH), 128.8 (CH), 128.4 (C), 80.9 (CH), 77.0 (CH), 73.7 (CH), 70.7 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1748, 1570, 1461, 1367, 1248, 1215, 1085, 1060, 1040, 911, 775, 681 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>20</sub>H<sub>27</sub>NO<sub>9</sub>ClSe [M+NH<sub>4</sub>]<sup>+</sup> 540.0540; found 540.0539.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-nitrophenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3k**)



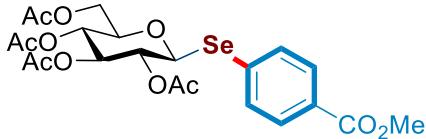
$R_f = 0.3$  (EtOAc /cyclohexane: 1/1); 42.4 mg, 85%, White solid. m. p.: 166.4-167.1 °C;  $[\alpha]_D^{18} = -36.8$  (c, 0.76, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10-8.13 (m, 2H), 7.72-7.75 (m, 2H), 5.18-5.29 (m, 1H), 5.00-5.06 (m, 3H), 4.11-4.26 (m, 2H), 3.73-3.79 (m, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.3 (C), 170.0 (C), 169.2 (2C), 147.7 (C), 136.7 (C), 134.4 (2CH), 123.7 (2CH), 80.5 (CH), 77.2 (CH), 73.5 (CH), 70.5 (CH), 68.0 (CH), 62.0 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 1746, 1598, 1576, 1520, 1368, 1346, 1247, 1034, 911, 773, 683 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>20</sub>H<sub>27</sub>N<sub>2</sub>O<sub>11</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 551.0775; found 551.0785.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-formylphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3l**)



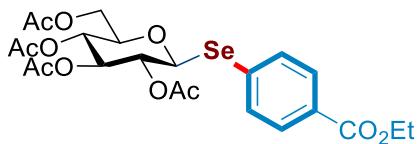
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 45.9 mg, 89%, White solid. m. p.: 74.6-75.6 °C;  $[\alpha]_D^{18} = -10.3$  (c, 0.29, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.99 (s, 1H), 7.60-7.79 (m, 4H), 5.22 (t, *J* = 9.0 Hz, 1H), 4.99-5.08 (m, 3H), 4.16-4.24 (m, 2H), 3.71-3.79 (m, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 191.4 (CH), 170.4 (C), 170.0 (C), 169.3 (C), 169.2 (C), 136.2 (C), 134.1 (2CH), 129.8 (2CH), 80.7 (CH), 77.1 (CH), 73.6 (CH), 70.6 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1748, 1699, 1589, 1564, 1433, 1367, 1248, 1213, 1172, 1060, 1039, 911, 835, 817, 773, 681 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>21</sub>H<sub>28</sub>NO<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 534.0873; found 534.0888.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-(methoxycarbonyl)phenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3m**)



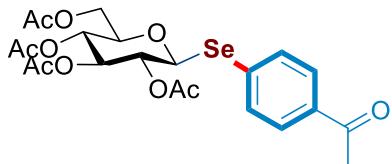
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 50.7 mg, 93%, White solid. m. p.: 140.3-142.4 °C;  $[\alpha]_D^{18} = -26.1$  (c, 0.69, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.92-7.94 (m, 2H), 7.63-7.66 (m, 2H), 5.21 (t, *J* = 9.0 Hz, 1H), 4.95-5.06 (m, 3H), 4.14-4.24 (m, 2H), 3.91 (s, 3H), 3.70-3.75 (m, H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 170.1 (C), 169.3 (C), 169.2 (C), 166.6 (C), 139.8 (C), 133.9 (2CH), 129.9 (2C), 127.7 (C), 80.8 (CH), 77.0 (CH), 73.7 (CH), 70.7 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 52.2 (CH<sub>3</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1749, 1593, 1435, 1367, 1247, 1109, 1059, 911, 825, 759 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>22</sub>H<sub>30</sub>NO<sub>11</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 564.0979; found 564.0995.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-(ethoxycarbonyl)phenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3n**)



$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 49.7 mg, 89%, White solid. m. p.: 123.2-123.3 °C;  $[\alpha]_D^{18} = -25.6$  (c, 0.43, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.92-7.95 (m, 2H), 7.63-7.66 (m, 2H), 5.20 (t, *J* = 9.0 Hz, 1H), 4.94-5.06 (m, 3H), 4.37 (q, *J* = 6.0 Hz, 2H), 4.15-4.24 (m, 2H), 3.69-3.74 (m, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.39 (t, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 170.1 (C), 169.3 (C), 169.2 (C), 166.1 (C), 134.0 (2CH), 133.5 (C), 130.3 (C), 129.9 (2CH), 80.7 (CH), 77.0 (CH), 73.7 (CH), 70.7 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 61.1 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>), 14.3 (CH<sub>3</sub>); IR (neat): 2998, 2360, 2341, 1753, 1715, 1593, 1367, 1285, 1107, 1058, 911, 774, 759, 670 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>23</sub>H<sub>32</sub>NO<sub>11</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 578.1135; found 578.1138.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-acetylphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3o**)



$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 48.8 mg, 92%, White solid. m. p.: 129.5-130.2 °C;  $[\alpha]_D^{18} = -21.7$  (c, 0.46, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.83-7.86 (m, 2H), 7.65-7.67 (m, 2H), 5.20 (t, *J* = 9.0 Hz, 1H), 4.94-5.06 (m, 3H), 4.10-4.25 (m, 2H), 3.68-3.78 (m, 1H), 2.58 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.3 (C), 170.4 (C), 170.0 (C), 169.3 (C), 169.2 (C), 136.7 (C), 134.2 (2CH), 134.0 (C), 128.6 (2CH), 80.6 (CH), 77.0 (CH), 73.7 (CH), 70.6 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 26.5 (CH<sub>3</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 2326, 1753, 1683, 1588, 1433, 1375, 1247, 1217, 1085, 1059, 1040, 958, 911, 773 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>22</sub>H<sub>26</sub>O<sub>10</sub>NaSe [M+Na]<sup>+</sup> 553.0589; found 553.0592.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((3-(methoxycarbonyl)phenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3p**)



$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 47.0 mg, 86%, White solid. m. p.: 97.5-98.7 °C;  $[\alpha]_D^{18} = -29.2$  (c, 0.48, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.37 (t, *J* = 6.0 Hz, 1H), 5.19 (t, *J* = 12.0 Hz, 1H), 4.89-5.06 (m, 3H), 4.13-4.25 (m, 2H), 3.92 (s, 3H), 3.65-3.73 (m, 1H), 20.7 (s, 3H), 20.6 (s, 3H), 20.0 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 170.1 (C), 169.3 (C), 169.3 (C), 166.2 (C), 139.4 (CH), 136.1 (CH), 131.0 (C), 129.6 (CH), 128.9 (CH), 127.4 (C), 80.9 (CH), 77.0 (CH), 73.8 (CH), 70.8 (CH), 68.1

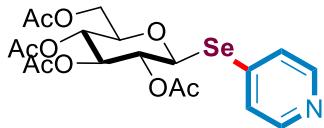
(CH), 62.1 (CH<sub>2</sub>), 52.3 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2954, 2360, 2341, 1755, 1722, 1367, 1285, 1264, 1088, 977, 773, 750 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>22</sub>H<sub>30</sub>NO<sub>11</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 564.0979; found 564.0980.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((3-(ethoxycarbonyl)phenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3q**)



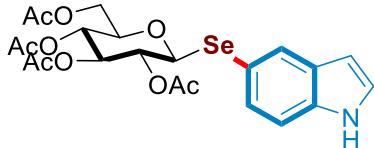
R<sub>f</sub> = 0.3 (EtOAc /cyclohexane: 3/7); 49.2 mg, 88%, White solid. m. p.: 86.4-87.3 °C; [α]<sub>D</sub><sup>18</sup> = -24.1 (c, 0.29, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.27 (s, 1H), 8.01 (d, *J* = 6.0 Hz, 1H), 7.78 (d, *J* = 6.0 Hz, 1H), 7.37 (t, *J* = 6.0 Hz, 1H), 5.19 (t, *J* = 9.0 Hz, 1H), 4.97-5.06 (m, 2H), 4.98 (d, *J* = 9.0 Hz, 1H), 4.38 (q, *J* = 6.0 Hz, 1H), 4.12-4.25 (m, 2H), 3.67-3.72 (m, H), 2.07 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.39 (t, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 170.1 (C), 169.3 (C), 169.2 (C), 165.7 (C), 139.3 (CH), 136.0 (CH), 131.0 (C), 129.6 (CH), 128.9 (CH), 127.3 (C), 80.9 (CH), 77.0 (CH), 73.8 (CH), 70.8 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 61.2 (CH<sub>2</sub>), 20.7 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>), 14.3 (CH<sub>3</sub>); IR (neat): 2360, 2327, 1755, 1718, 1367, 1262, 1088, 910, 773, 750 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>23</sub>H<sub>32</sub>NO<sub>11</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 578.1135; found 578.1147.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(pyridin-4-ylselanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3r**)



R<sub>f</sub> = 0.3 (EtOAc /cyclohexane: 1/1); 42.6 mg, 87%, White solid. m. p.: 120.5-121.9 °C; [α]<sub>D</sub><sup>18</sup> = -22.1 (c, 0.95, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.44-8.46 (m, 2H), 7.42-7.44 (m, 2H), 5.20-5.27 (m, 1H), 5.03-5.12 (m, 3H), 4.14-4.25 (m, 2H), 3.74-3.80 (m, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.4 (C), 170.0 (C), 169.3 (C), 169.3 (C), 149.7 (2CH), 139.7 (C), 127.2 (2CH), 80.2 (CH), 77.2 (CH), 73.5 (CH), 70.5 (CH), 68.1 (CH), 62.1 (CH<sub>2</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1746, 1570, 1543, 1407, 1248, 1212, 1086, 1060, 1039, 911, 806, 773 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>19</sub>H<sub>24</sub>NO<sub>9</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 490.0616; found 490.0610.

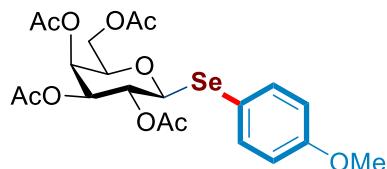
(2*S*,3*R*,4*S*,5*R*,6*R*)-2-((1*H*-indol-5-yl)selanyl)-6-(acetoxymethyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3s**)



R<sub>f</sub> = 0.3 (EtOAc /cyclohexane: 1/1); 44.6 mg, 85%, White solid. m. p.: 128.9-129.4 °C; [α]<sub>D</sub><sup>18</sup> = -33.3 (c, 0.45, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.30-8.38 (m, 1H), 7.94-7.96 (m, 1H), 7.23-

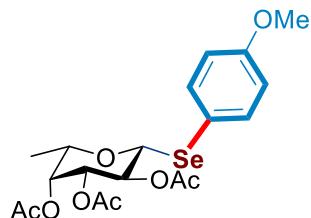
7.46 (m, 3H), 6.54-6.59 (m, 1H), 4.84-5.22 (m, 4H), 4.20-4.21 (m, 2H), 3.64-3.68 (m, 1H), 2.11 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6 (C), 170.2 (C), 169.4 (2C), 135.9 (C), 129.8 (CH), 129.3 (CH), 128.8 (C), 125.0 (CH), 116.1 (C), 111.5 (CH), 102.7 (CH), 81.3 (CH), 76.8 (CH), 74.0 (CH), 71.0 (CH), 68.3 (CH), 62.2 (CH<sub>2</sub>), 20.9 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 20.6 (2CH<sub>3</sub>); IR (neat): 2360, 2341, 1755, 1454, 1366, 1250, 1219, 1062, 1039, 912, 772, 669 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for  $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_9\text{Se} [\text{M}+\text{NH}_4]^+$  545.1038; found 545.1031.

(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-((4-methoxyphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3t**)



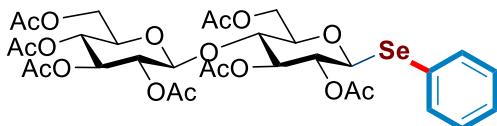
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 33.8 mg, 65%, White solid. m. p.: 102.3-102.9 °C;  $[\alpha]_D^{18} = -7.9$  (c, 0.38,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54-7.57 (m, 2H), 6.82-6.85 (m, 2H), 5.37-5.39 (m, 1H), 5.21 (t,  $J = 9.0$  Hz, 1H), 4.97-5.02 (m, 1H), 4.78 (d,  $J = 9.0$  Hz, 1H), 4.04-4.18 (m, 2H), 3.84-3.88 (m, 1H), 3.80 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3 (C), 170.1 (C), 170.0 (C), 169.4 (C), 160.3 (C), 137.5 (2CH), 117.2 (C), 114.5 (2CH), 81.7 (CH), 75.4 (CH), 71.9 (CH), 68.1 (CH), 67.3 (CH), 61.5 (CH<sub>2</sub>), 55.3 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>); IR (neat): 2360, 2341, 2325, 1748, 1492, 1373, 1247, 1219, 1081, 1054, 826, 773, 669 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for  $\text{C}_{21}\text{H}_{30}\text{NO}_{10}\text{Se} [\text{M}+\text{NH}_4]^+$  536.1029; found 536.1033.

(2*R*,3*S*,4*R*,5*R*,6*S*)-2-((4-methoxyphenyl)selanyl)-6-methyltetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3u**)



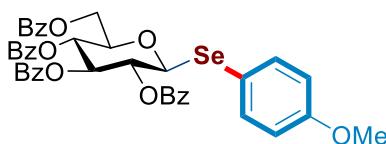
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 37.1 mg, 81%, White solid. m. p.: 69.5-70.6 °C;  $[\alpha]_D^{18} = +21.7$  (c, 0.23,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54-7.57 (m, 2H), 6.82-6.85 (m, 2H), 5.16-5.22 (m, 2H), 4.97-5.01 (m, 1H), 4.76 (d,  $J = 9.0$  Hz, 1H), 3.80 (s, 3H), 3.72-3.76 (m, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.95 (s, 3H), 1.17-1.22 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5 (C), 170.1 (C), 169.5 (C), 160.1 (C), 137.3 (2CH), 117.7 (C), 114.5 (2CH), 81.9 (CH), 74.2 (CH), 72.3 (CH), 70.5 (CH), 68.2 (CH), 55.2 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 20.6 (2CH<sub>3</sub>), 16.4 (CH<sub>3</sub>); IR (neat): 2922, 2359, 2340, 1749, 1492, 1368, 1287, 1246, 1082, 10591030, 913, 759, 626 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for  $\text{C}_{19}\text{H}_{28}\text{NO}_8\text{Se} [\text{M}+\text{NH}_4]^+$  478.0980; found 478.0980.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(((2*R*,3*R*,4*S*,5*R*,6*S*)-4,5-diacetoxy-2-(acetoxymethyl)-6-(phenylselanyl)tetrahydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3v**)<sup>5</sup>



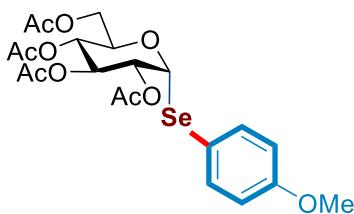
$R_f = 0.3$  (EtOAc /cyclohexane: 1/1); 63.6 mg, 82%, White solid. m. p.: 186.5-189.1 °C;  $[\alpha]_D^{18} = -22.9$  (c, 0.35, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89-7.92 (m, 1H), 7.58-7.60 (m, 1H), 7.23-7.34 (m, 3H), 4.83-5.23 (m, 5H), 4.35-4.58 (m, 3H), 3.87-4.17 (m, 4H), 3.62-3.71 (m, 2H), 2.11 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H); IR (neat): 2460, 2369, 2340, 1749, 1702, 1481, 1373, 1301, 1287, 1246, 1082, 1060, 1059, 1030, 928, 773, 619 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>32</sub>H<sub>44</sub>NO<sub>17</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 794.1769; found 794.1776.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((benzoyloxy)methyl)-6-((4-methoxyphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl tribenzoate (**3w**)



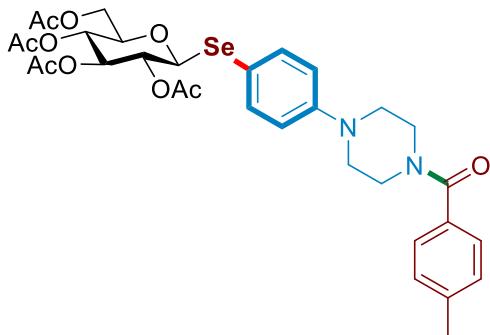
$R_f = 0.3$  (EtOAc /cyclohexane: 2/8); 65.3 mg, 85%, White solid. m. p.: 100.0-100.4 °C;  $[\alpha]_D^{18} = +24.5$  (c, 0.16, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.87-8.07 (m, 10H), 7.21-7.56 (m, 14H), 6.30-6.34 (m, 1H), 6.03-6.08 (m, 1H), 5.81-5.91 (m, 1H), 4.66-4.71 (m, 1H), 4.51-4.56 (m, 1H), 4.40-4.45 (m, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 166.1 (C), 165.7 (C), 165.1 (C), 164.6 (C), 144.7 (C), 133.5 (CH), 133.4 (CH), 133.3 (CH), 133.0 (CH), 131.8 (C), 130.7 (C), 130.2 (CH), 129.8 (2CH), 129.6 (CH), 128.7 (C), 128.4 (2CH), 128.3 (2CH), 125.7 (C), 124.6 (C), 92.6 (CH), 73.2 (CH), 72.9 (CH), 70.9 (CH), 69.2 (CH), 62.7 (CH<sub>2</sub>), 21.7 (CH<sub>3</sub>). IR (neat): 2365, 2343, 2325, 1732, 1266, 1069, 773 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>41</sub>H<sub>34</sub>NO<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 784.1655; found 784.1652.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-((4-methoxyphenyl)selanyl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**3x**)



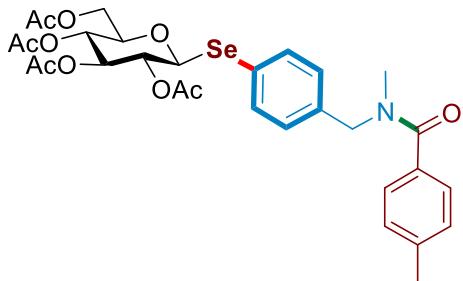
$R_f = 0.3$  (EtOAc /cyclohexane: 3/7); 46.6 mg, 90%, White solid. m. p.: 129.5-130.2 °C;  $[\alpha]_D^{18} = +226.1$  (c, 0.23, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.44-7.48 (m, 2H), 6.80-6.85 (m, 2H), 6.06 (d, *J* = 6.0 Hz, 1H), 5.39 (t, *J* = 9.0 Hz, 1H), 5.00-5.11 (m, 2H), 4.49-4.55 (m, 1H), 4.25-4.30 (m, 1H), 3.96-4.01 (m, 1H), 3.79 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 169.9 (C), 169.7 (C), 169.5 (C), 136.7 (2CH), 135.0 (C), 117.2 (C), 115.0 (2CH), 83.3 (CH), 71.3 (CH), 71.1 (CH), 69.6 (CH), 68.4 (CH), 61.9 (CH<sub>2</sub>), 55.3 (CH<sub>3</sub>), 20.8 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>), 20.6 (CH<sub>3</sub>); IR (neat): 2460, 2362, 1749, 1244, 1223, 1038, 778 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>21</sub>H<sub>26</sub>NO<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 536.1029; found 536.1029

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-(4-methylbenzoyl)piperazin-1-yl)phenyl)selanyl tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**6a**)



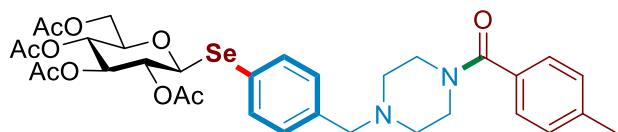
$R_f = 0.2$  (EtOAc /cyclohexane: 1/1); 62.0 mg, 90 %, White solid. m. p.: 135.1-136.1 °C;  $[\alpha]_D^{18} = -29.2$  (c, 0.24, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50-7.52 (m, 2H), 7.35-7.38 (m, 2H), 7.24-7.28 (m, 2H), 6.82-6.85 (m, 2H), 5.18 (t, *J* = 12.0 Hz, 1H), 4.91-5.03 (m, 2H), 4.76-4.79 (m, 1H), 4.13-4.20 (m, 2H), 3.65-3.78 (m, 5H), 3.22-3.33 (m, 4H), 2.41 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.6 (C), 170.5 (C), 170.2 (C), 169.4 (C), 169.2 (C), 151.3 (C), 140.1 (C), 137.7 (2CH), 132.5 (C), 129.2 (2CH), 127.3 (2CH), 116.4 (2CH), 115.2 (2CH), 80.4 (CH), 76.8 (CH), 73.9 (CH), 70.7 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 49.0 (2CH<sub>2</sub>), 48.9 (2CH<sub>2</sub>), 21.4 (CH<sub>3</sub>), 20.8 (2CH<sub>3</sub>), 20.6 (CH<sub>3</sub>); IR (neat): 2360, 2341, 2327, 1755, 1589, 1366, 1290, 1156, 1058, 1040, 910, 830, 773 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>32</sub>H<sub>39</sub>N<sub>2</sub>O<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 691.1770; found 691.1785.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-((N,4-dimethylbenzamido)methyl)phenyl)selanyl) tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**6b**)



$R_f = 0.2$  (EtOAc /cyclohexane: 1/1); 58.3 mg, 95%, White solid. m. p.: 157.6-158.1 °C;  $[\alpha]_D^{18} = -8.5$  (c, 0.59, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.59-7.62 (m, 2H), 7.20-7.38 (m, 6H), 5.21 (t, *J* = 9.0 Hz, 1H), 4.88-5.08 (m, 2H), 4.91-4.98 (m, 1H), 4.51-4.88 (m, 2H), 4.12-4.27 (m, 2H), 3.69-3.75 (m, 1H), 2.81-3.09 (m, 3H), 2.38 (s, 3H), 2.09 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 170.1 (C), 169.6 (C), 169.4 (C), 167.7 (C), 139.9 (C), 135.6 (2CH), 133.1 (C), 129.1 (4CH), 127.0 (2CH), 125.9 (C), 124.8 (C), 80.9 (CH), 76.9 (CH), 73.8 (CH), 70.8 (CH), 68.2 (CH), 62.1 (CH<sub>2</sub>), 29.7 (CH<sub>2</sub>), 21.3 (CH<sub>3</sub>), 20.8 (2CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>); IR (neat): 2360, 2341, 1755, 1606, 1368, 1326, 1248, 1213, 1126, 1095, 1063, 1037, 1014, 980, 914, 830, 776 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>30</sub>H<sub>36</sub>NO<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 650.1520; found 650.1520.

(*2R,3R,4S,5R,6S*)-2-(acetoxymethyl)-6-((4-((4-methylbenzoyl)piperazin-1-yl)methyl)phenyl)selanyl tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**6c**)

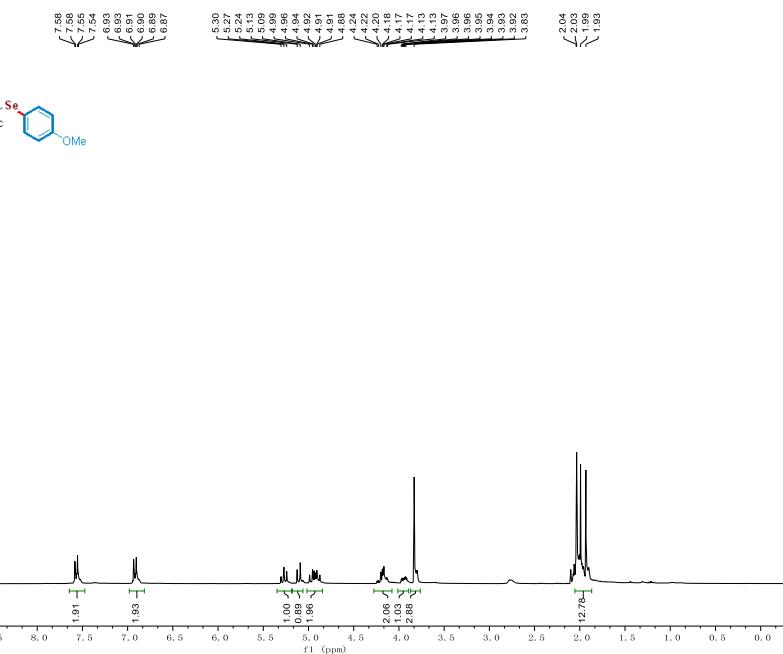


$R_f = 0.2$  (EtOAc /cyclohexane: 1/1); 57.9 mg, 82%, White solid. m. p.: 133.3-134.4 °C;  $[\alpha]_D^{18} = -8.3$  (c, 0.24, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54-7.57 (m, 2H), 7.18-7.32 (m, 6H), 5.20 (t, *J* = 9.0 Hz, 1H), 4.96-5.06 (m, 2H), 4.86-4.90 (m, 1H), 4.11-4.25 (m, 2H), 3.53-3.73 (m, 7H), 2.41-2.55 (m, 4H), 2.37 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 170.5 (C), 170.5 (C), 170.1 (C), 169.4 (C), 169.2 (C), 139.8 (C), 138.5 (C), 135.3 (2CH), 132.9 (C), 129.6 (2CH), 129.0 (2CH), 127.2 (2CH), 125.5 (C), 80.9 (CH), 76.9 (CH), 73.8 (CH), 70.7 (CH), 68.2 (CH), 62.4 (CH<sub>2</sub>), 62.1 (CH<sub>2</sub>), 53.1 (4CH<sub>2</sub>), 21.3 (CH<sub>3</sub>), 20.7 (2CH<sub>3</sub>), 20.5 (CH<sub>3</sub>); IR (neat): 2360, 2341, 2327, 1755, 1632, 1459, 1299, 1248, 1059, 1040, 1001, 911, 753 cm<sup>-1</sup>; HRMS (ESI): m/z calc. for C<sub>33</sub>H<sub>41</sub>N<sub>2</sub>O<sub>10</sub>Se [M+NH<sub>4</sub>]<sup>+</sup> 705.1917; found 705.1917.

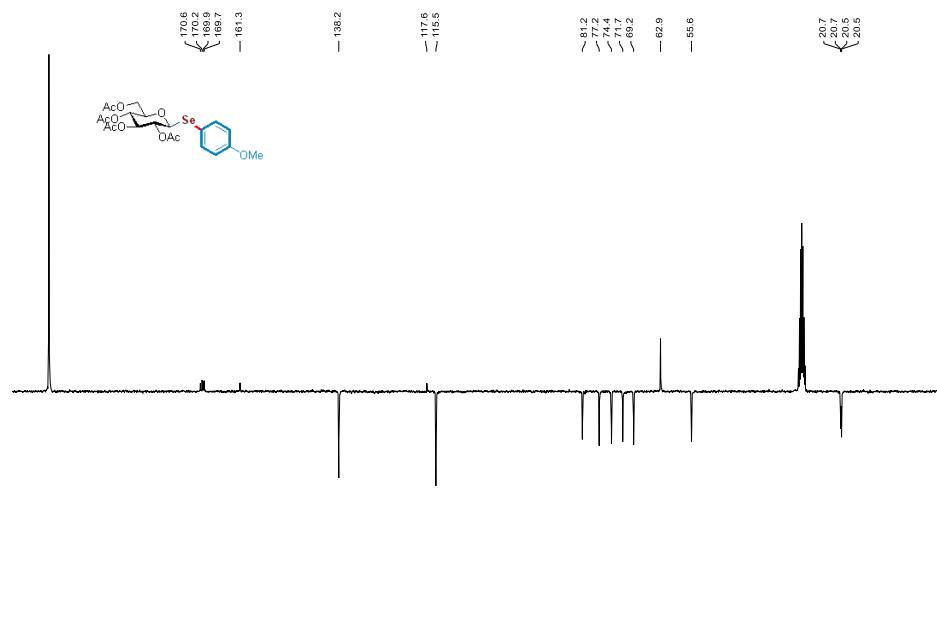
#### 4. Reference

1. A. W. McDonagh, M. F. Mahon, P. V. Murphy, *Org. Lett.* **2016**, *18*, 552–555.
2. Y. Kawai, H. Ando, H. Ozeki, M. Koketsu, H. Ishihara, *Org. Lett.* **2005**, *7*, 4653-4656.
3. M. Nanamia, H. Andob, Y. Kawaia, M. Koketsub, H. Ishihara, *Tetrahedron Lett.* **2007**, *48*, 1113-1116.
4. S. Valerio, A. Iadonisi, M. Adinolfi, A. Ravidà, *J. Org. Chem.* **2007**, *72*, 6097–6106
5. A. Sau, A. K. Misra, *Synlett* **2011**, *13*, 1905-1911.

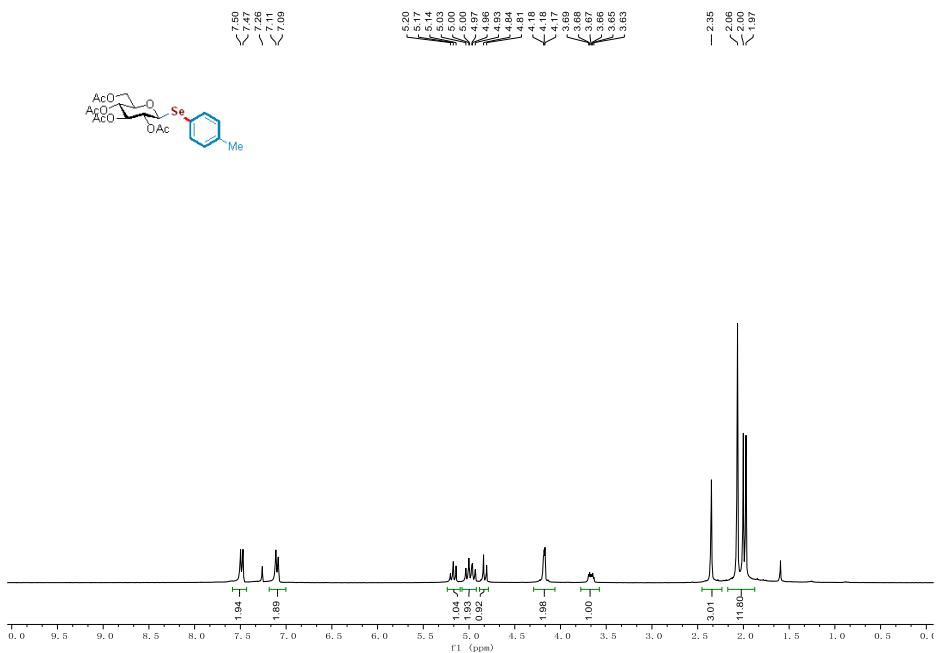
## NMR spectra



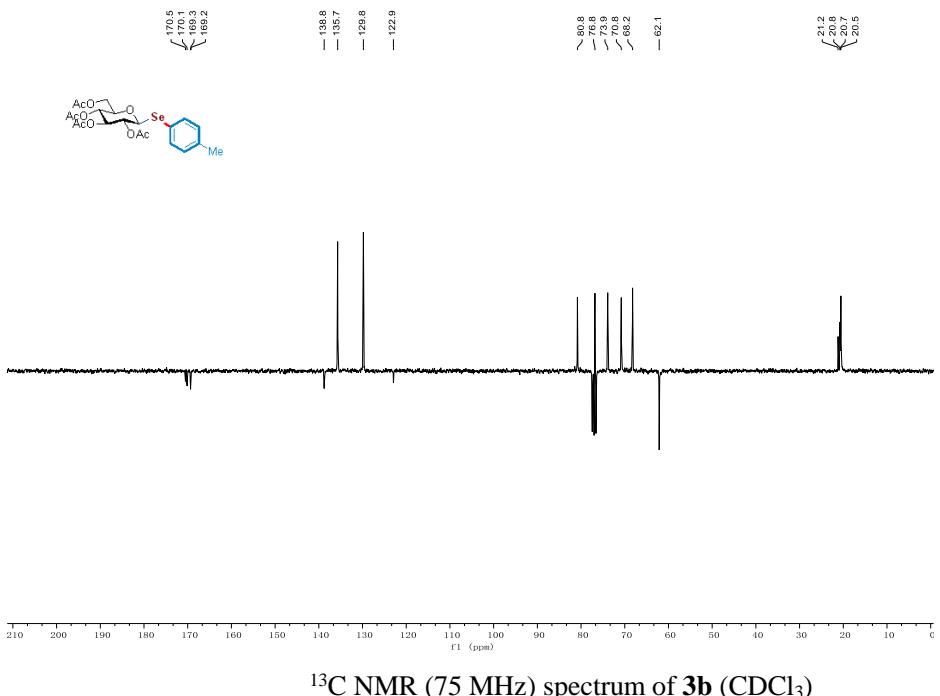
<sup>1</sup>H NMR (300 MHz) spectrum of 3a ((CD<sub>3</sub>)<sub>2</sub>CO-d<sub>6</sub>)



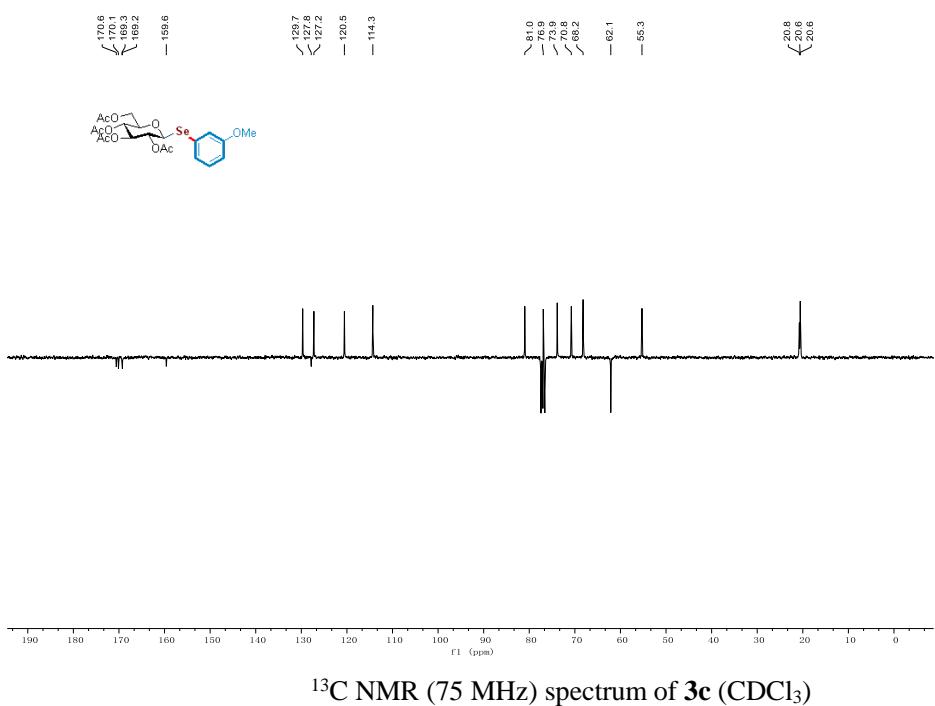
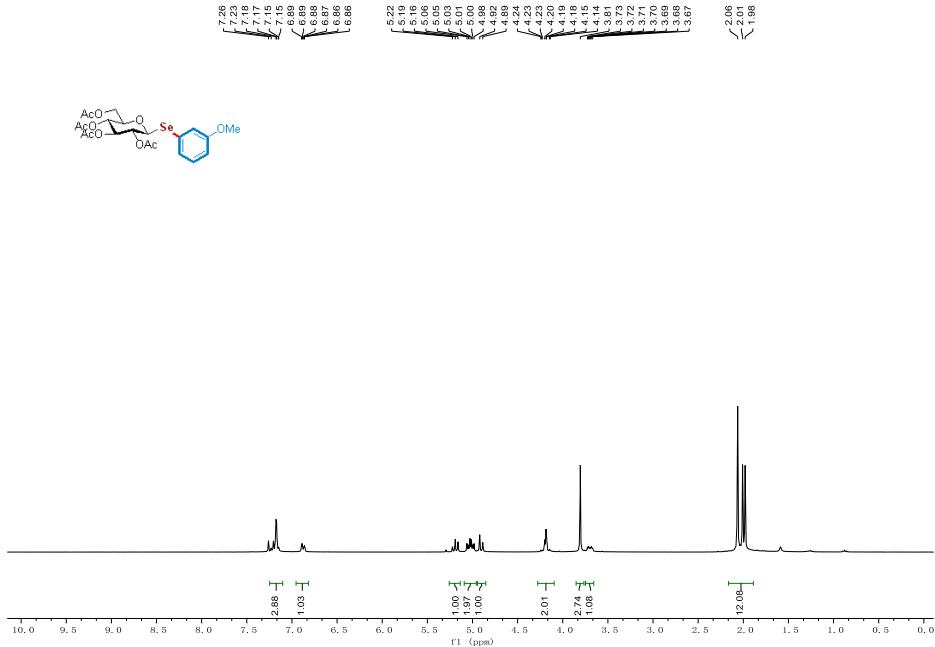
<sup>13</sup>C NMR (75 MHz) spectrum of 3a ((CD<sub>3</sub>)<sub>2</sub>CO-d<sub>6</sub>)

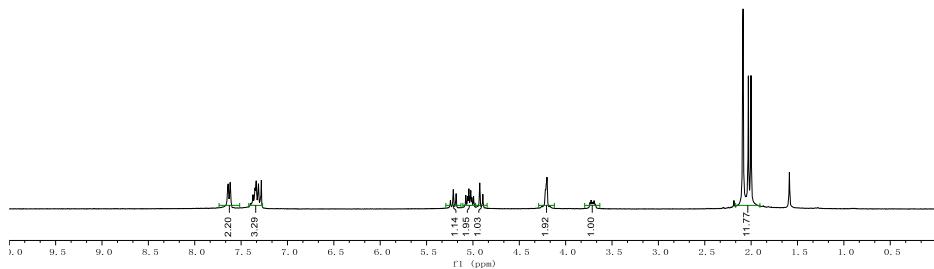
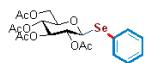


<sup>1</sup>H NMR (300 MHz) spectrum of **3b** (CDCl<sub>3</sub>)

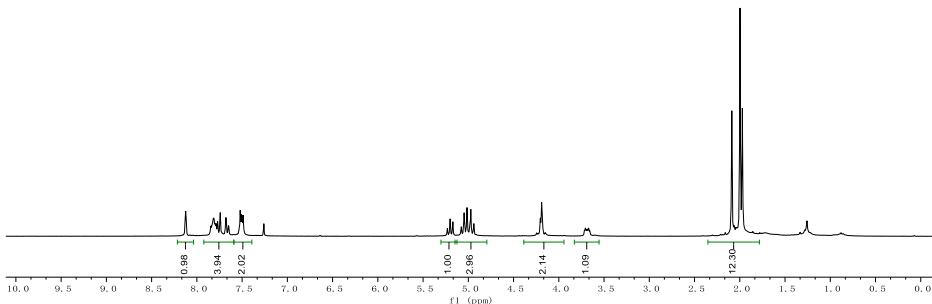
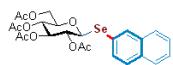


<sup>13</sup>C NMR (75 MHz) spectrum of **3b** (CDCl<sub>3</sub>)

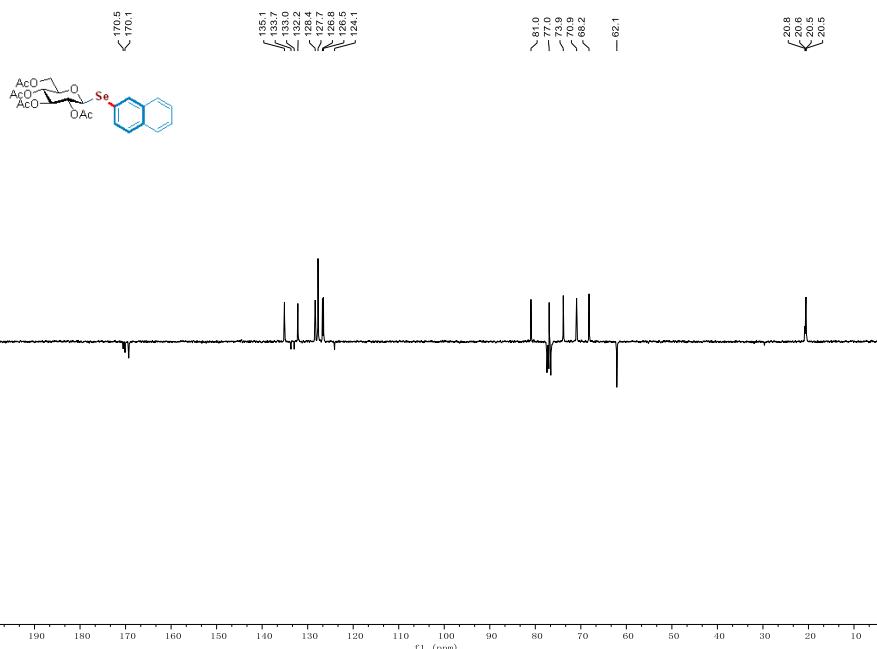




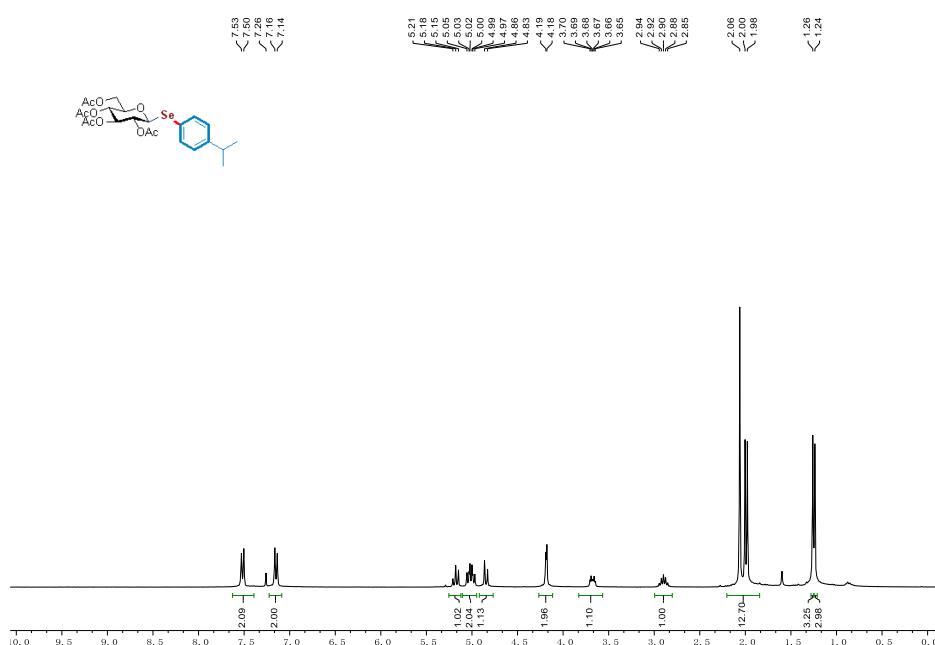
<sup>1</sup>H NMR (300 MHz) spectrum of **3d** (CDCl<sub>3</sub>)



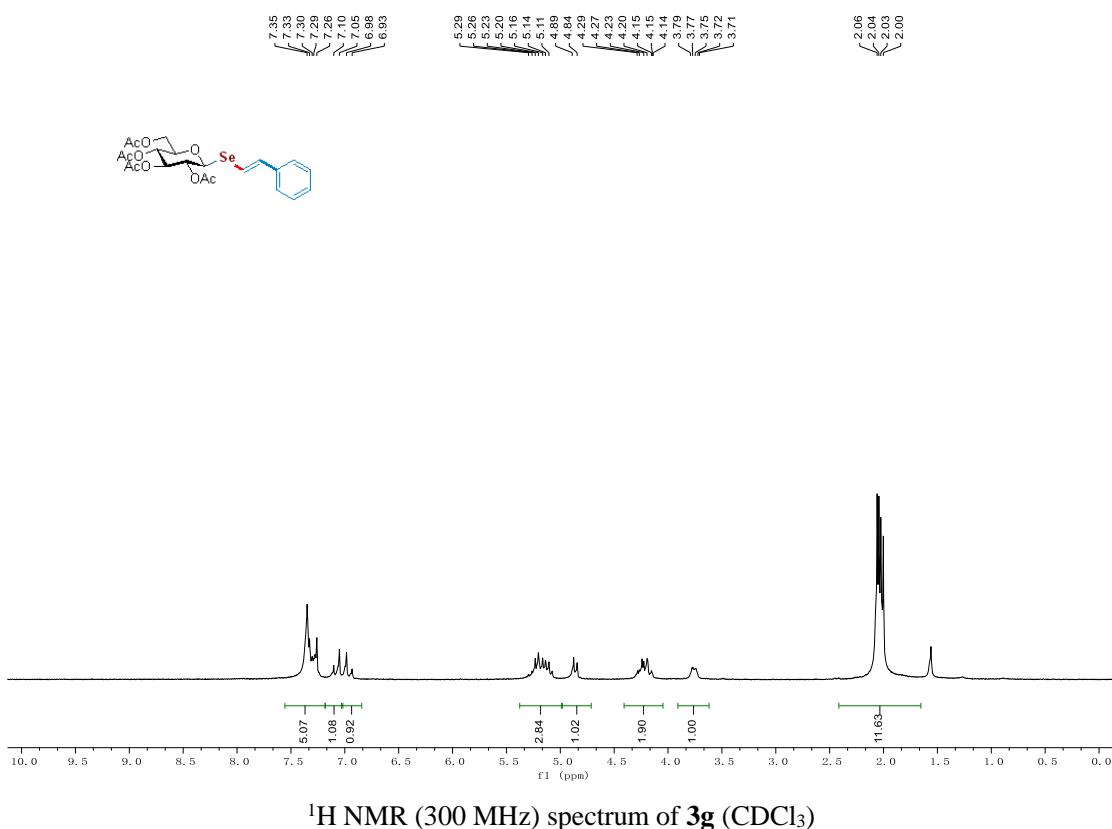
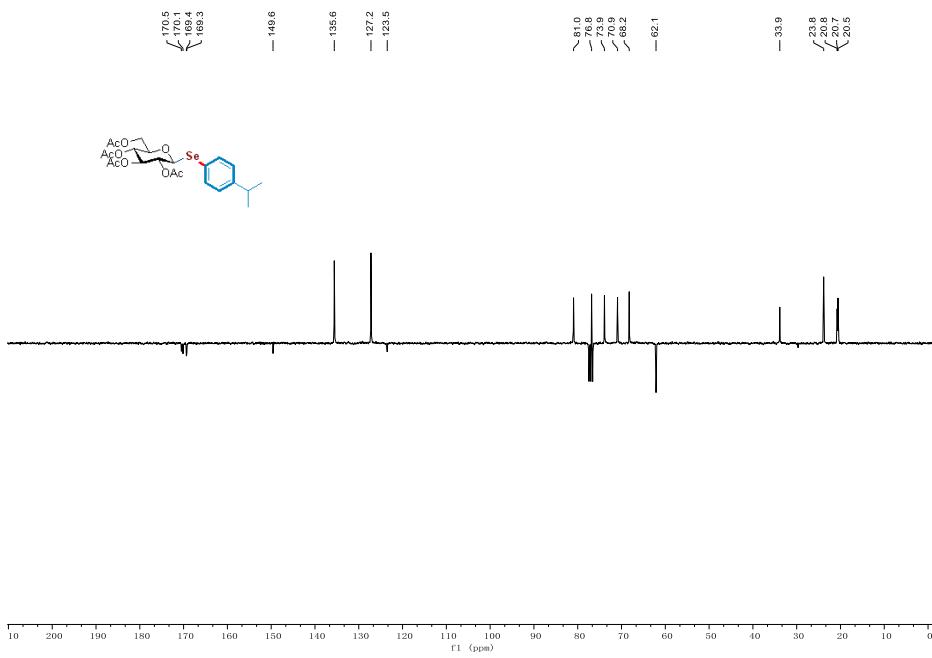
<sup>1</sup>H NMR (300 MHz) spectrum of **3e** (CDCl<sub>3</sub>)

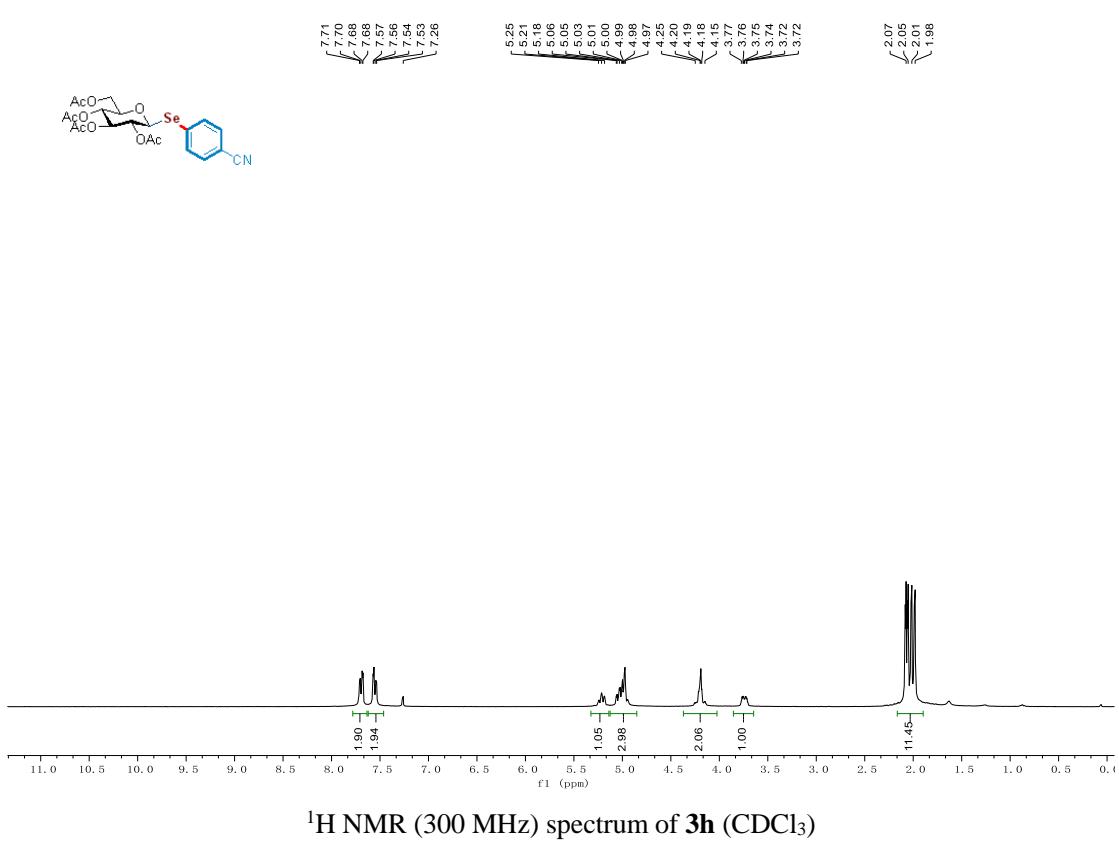
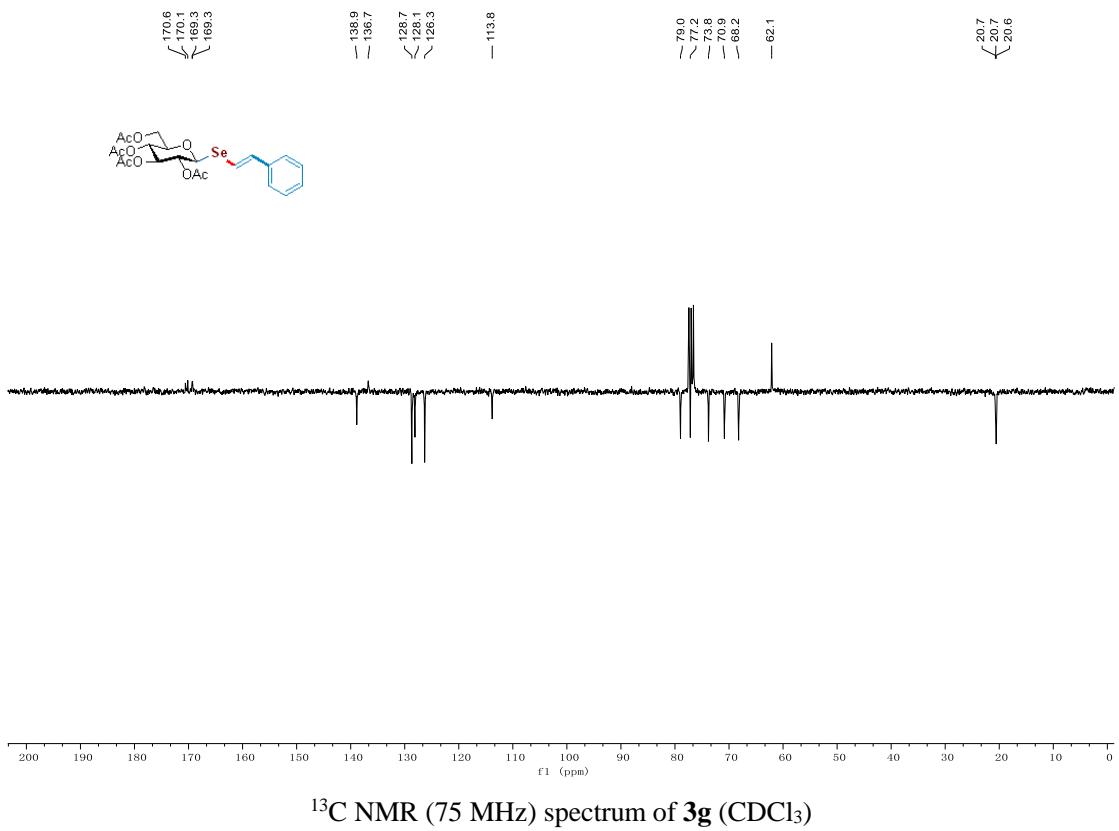


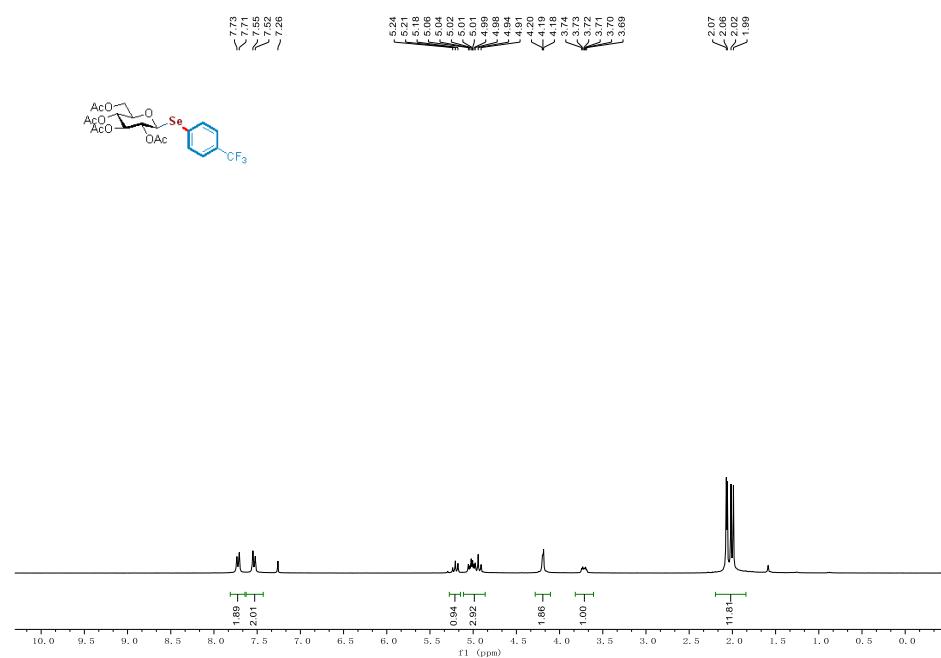
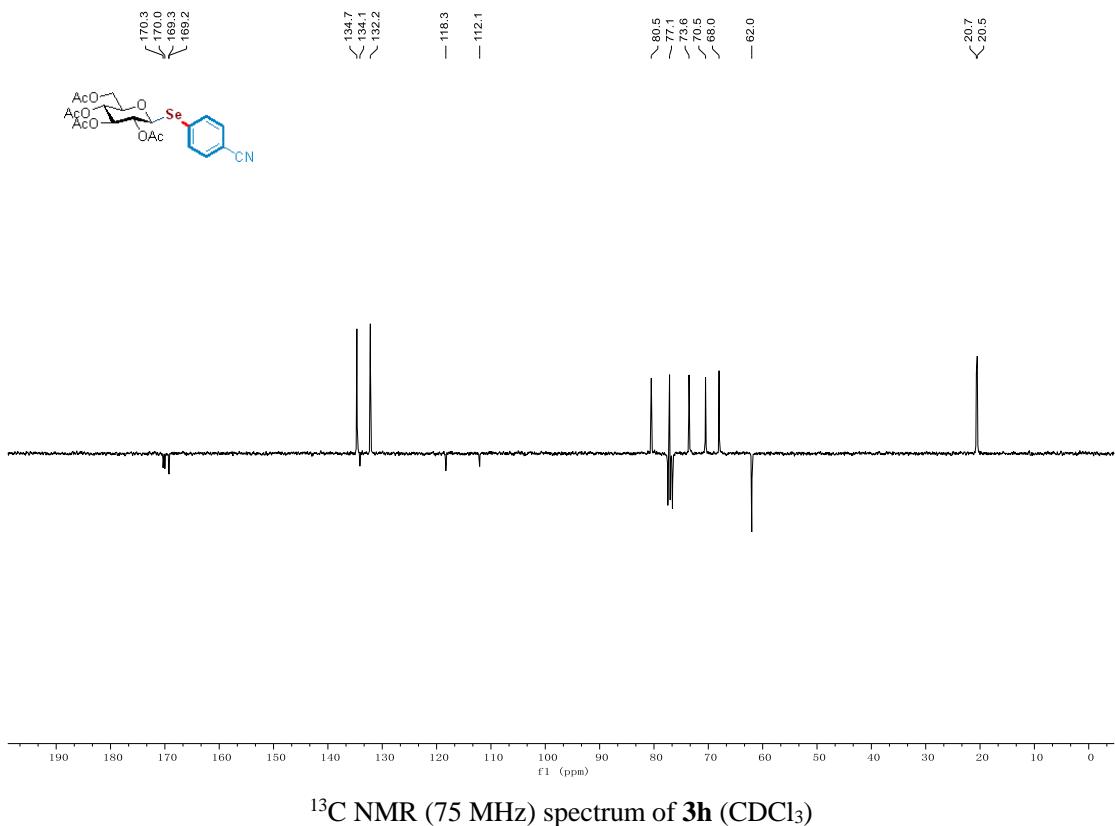
<sup>13</sup>C NMR (75 MHz) spectrum of **3e** ( $\text{CDCl}_3$ )

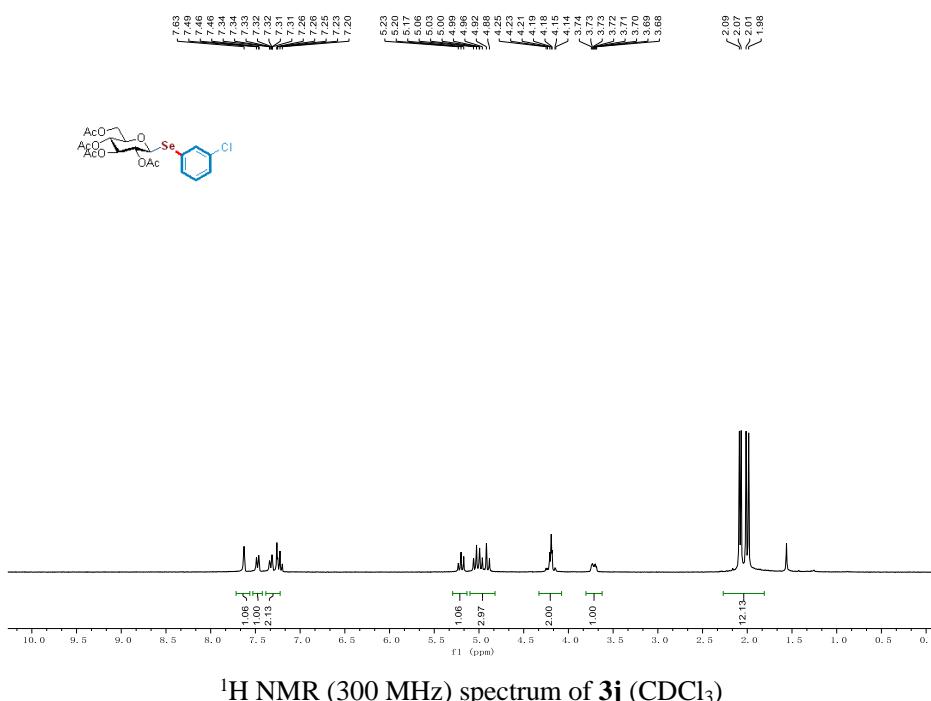
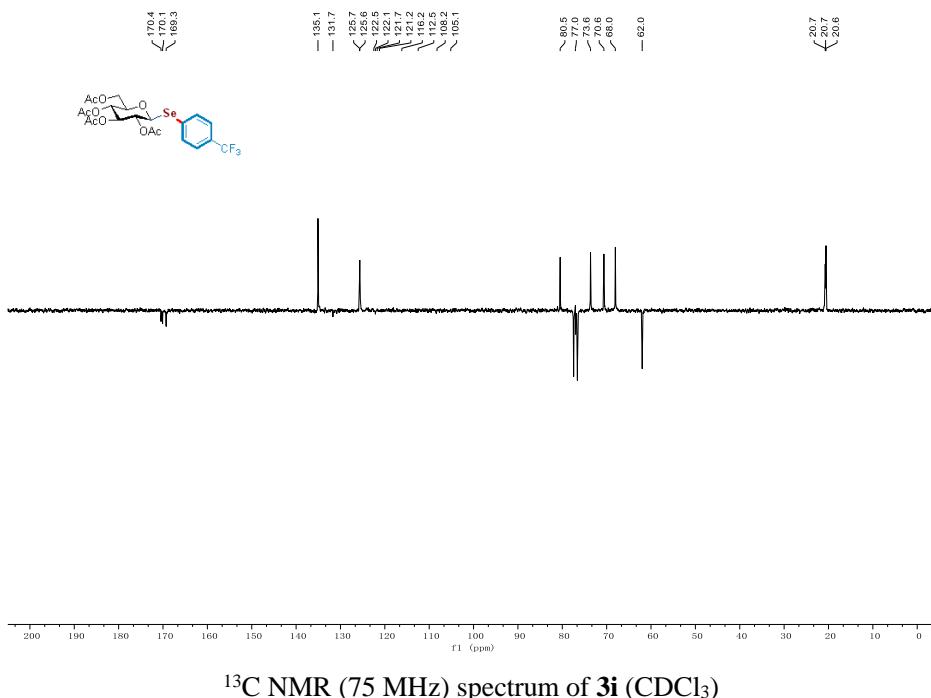


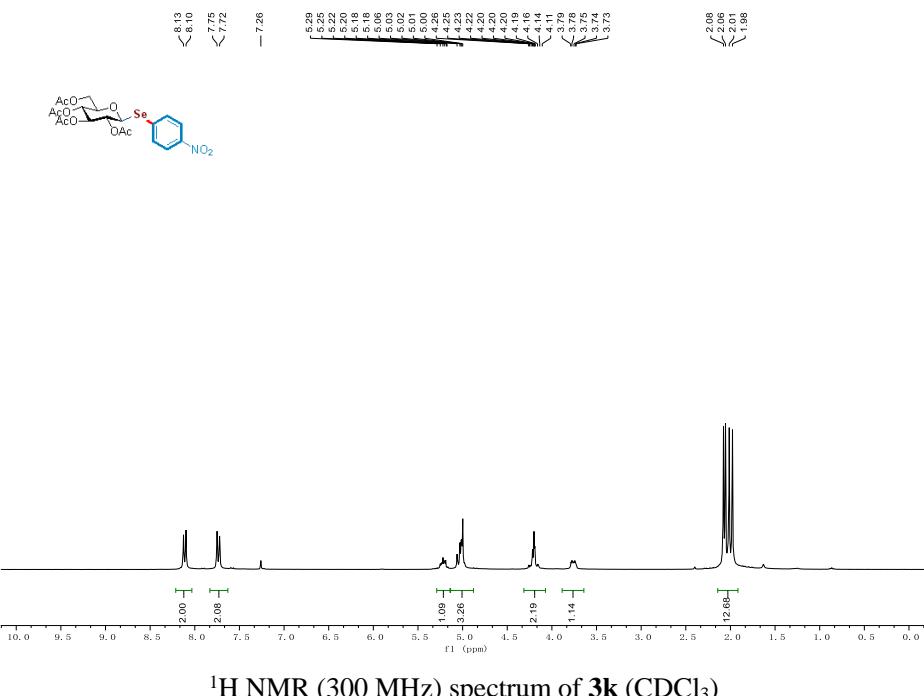
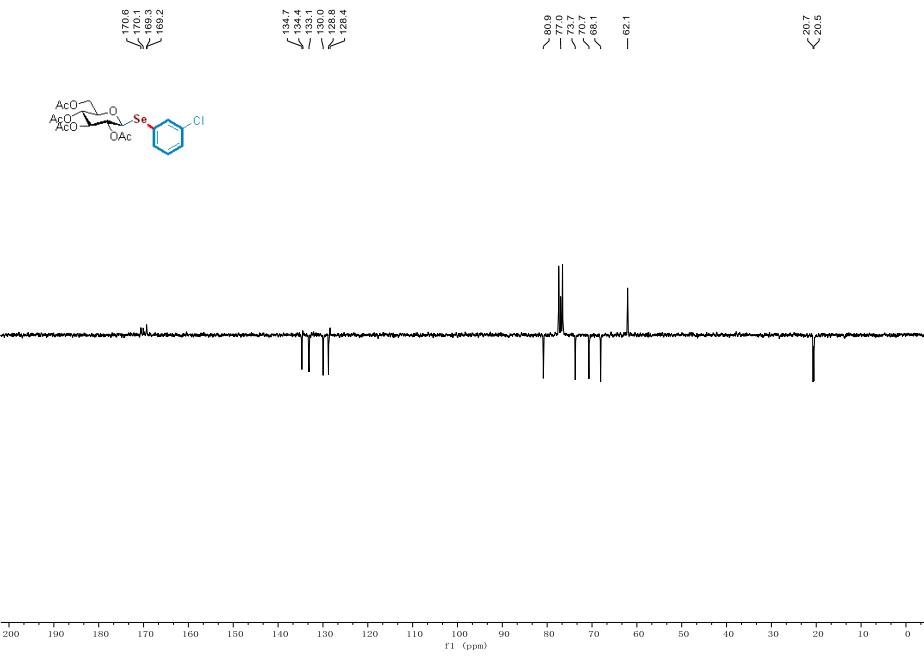
<sup>1</sup>H NMR (300 MHz) spectrum of **3f** ( $\text{CDCl}_3$ )

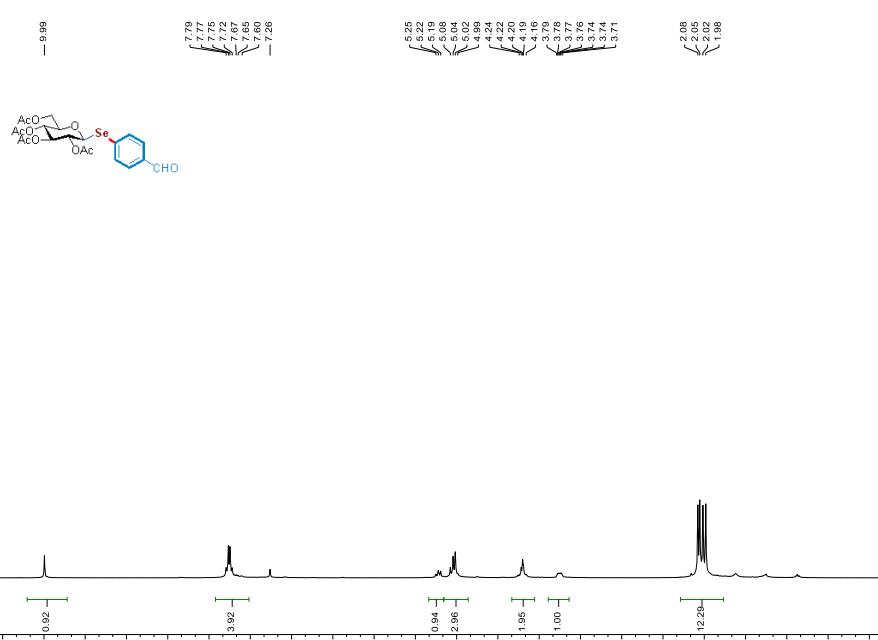
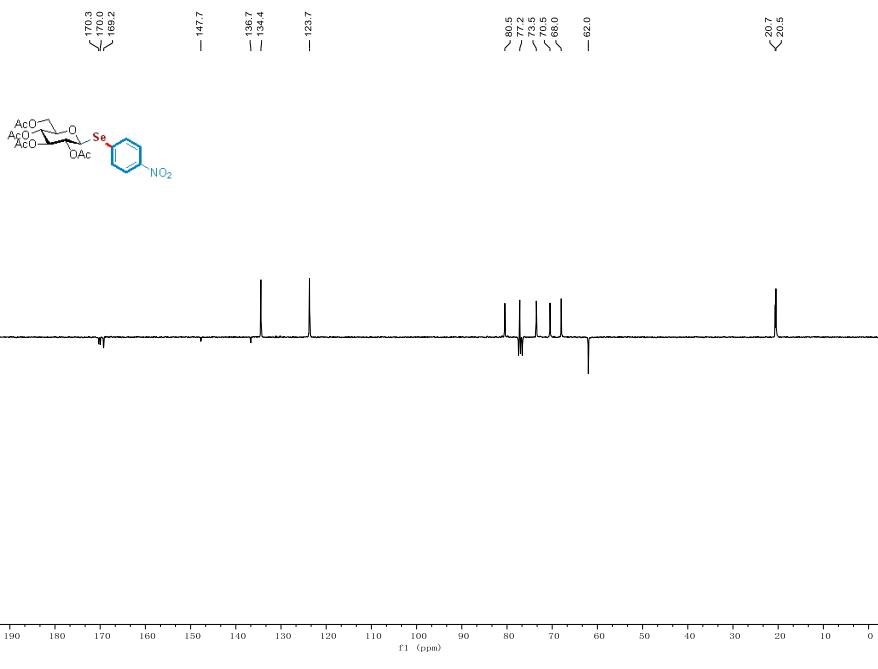




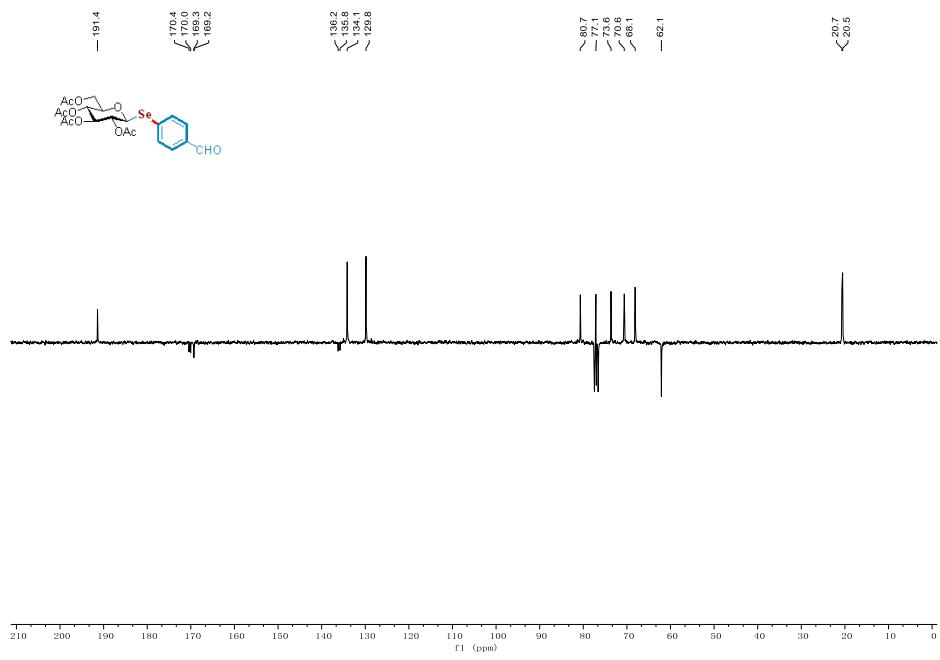




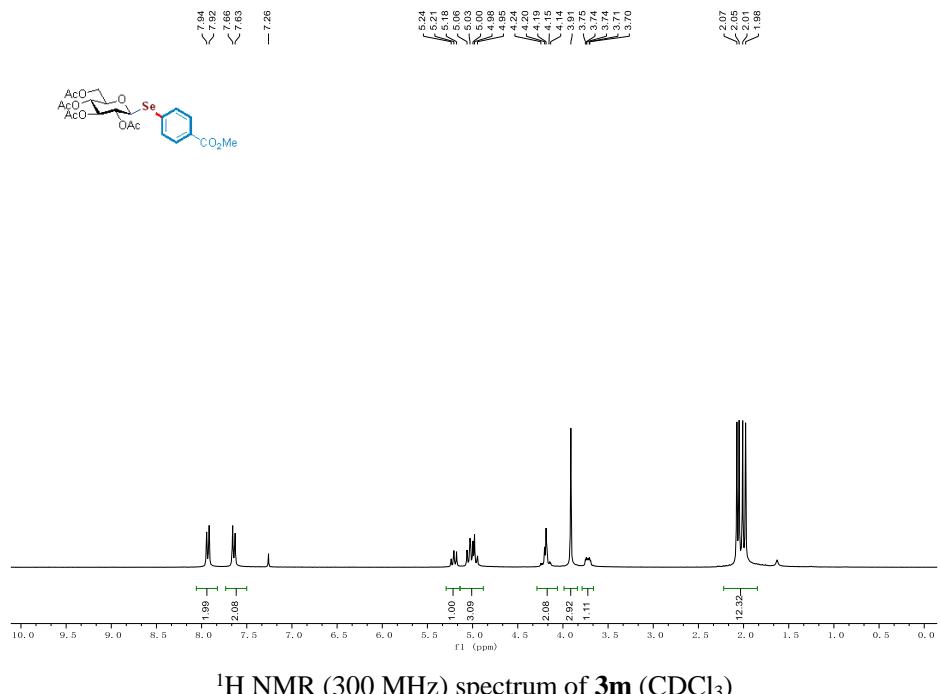




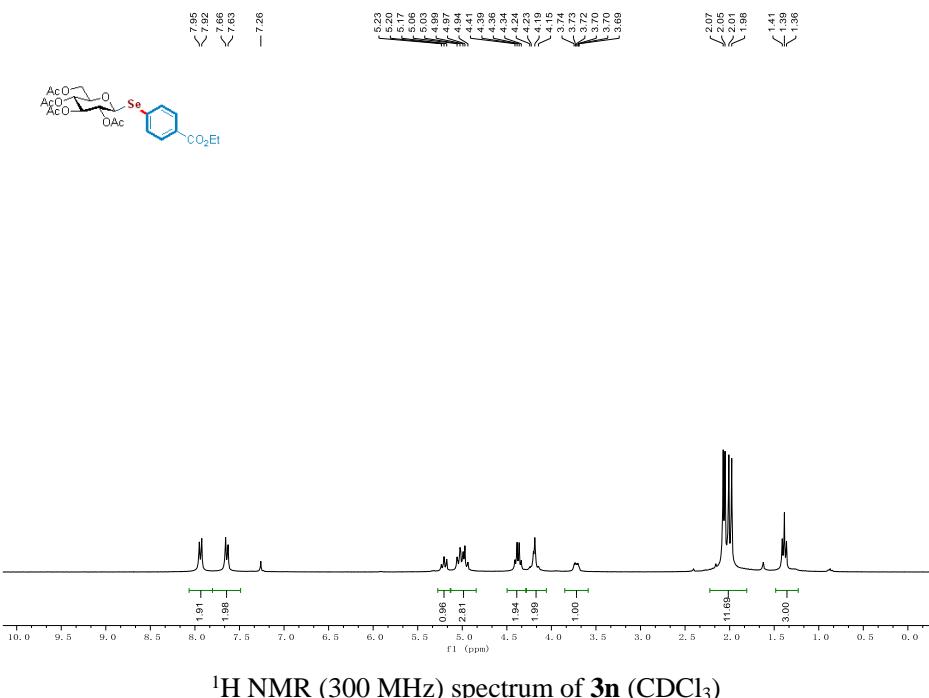
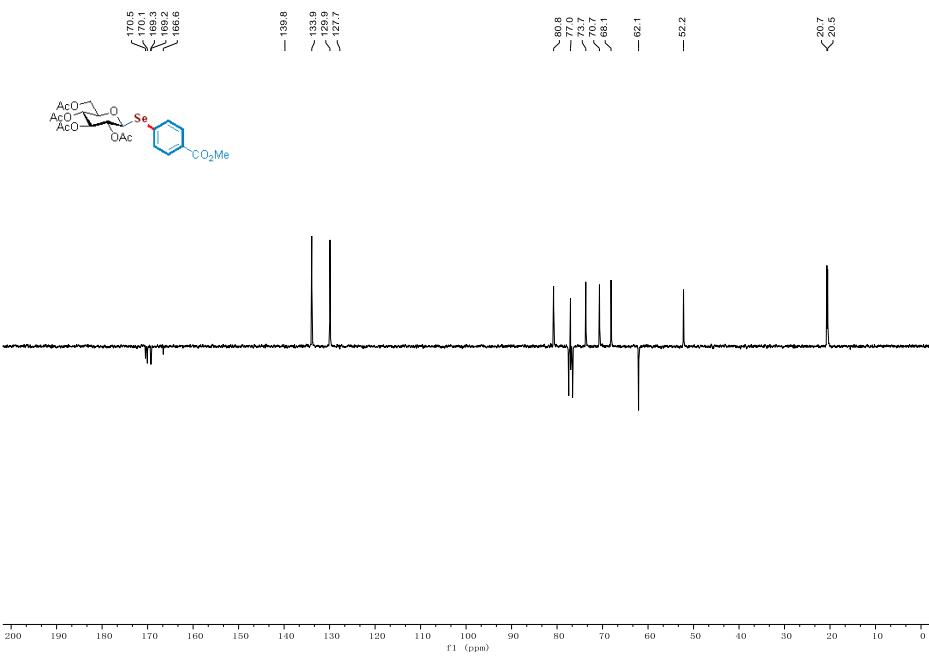
<sup>1</sup>H NMR (300 MHz) spectrum of **3l** ( $\text{CDCl}_3$ )

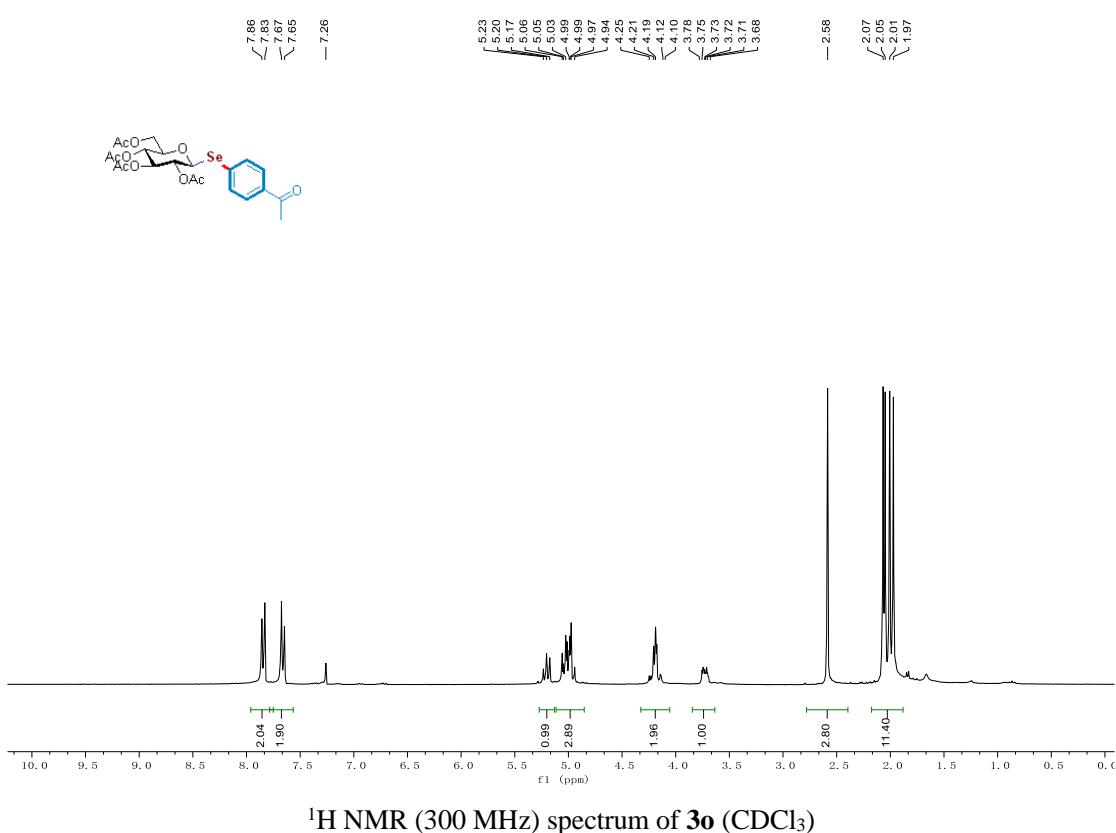
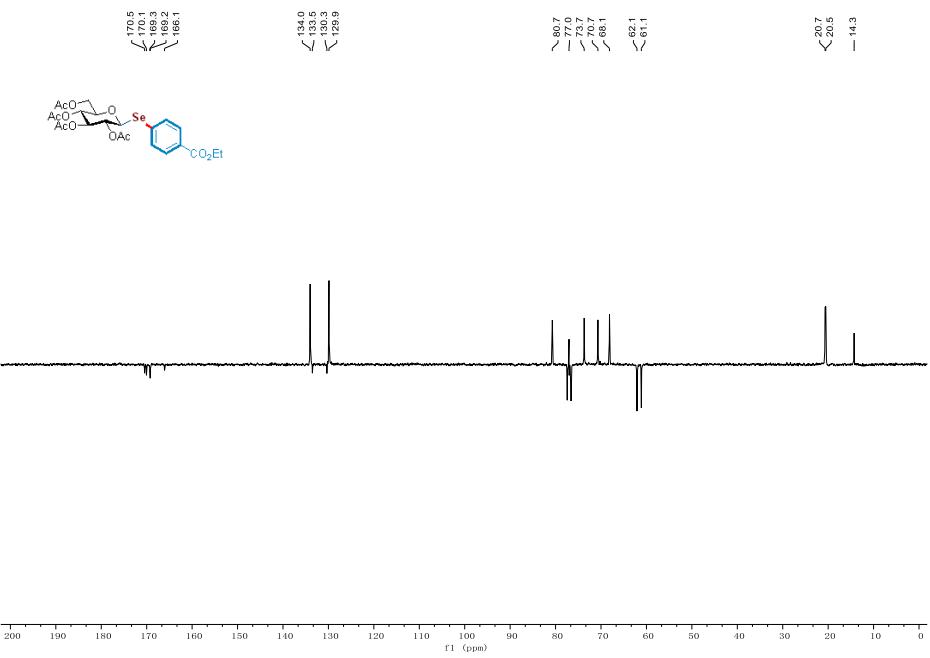


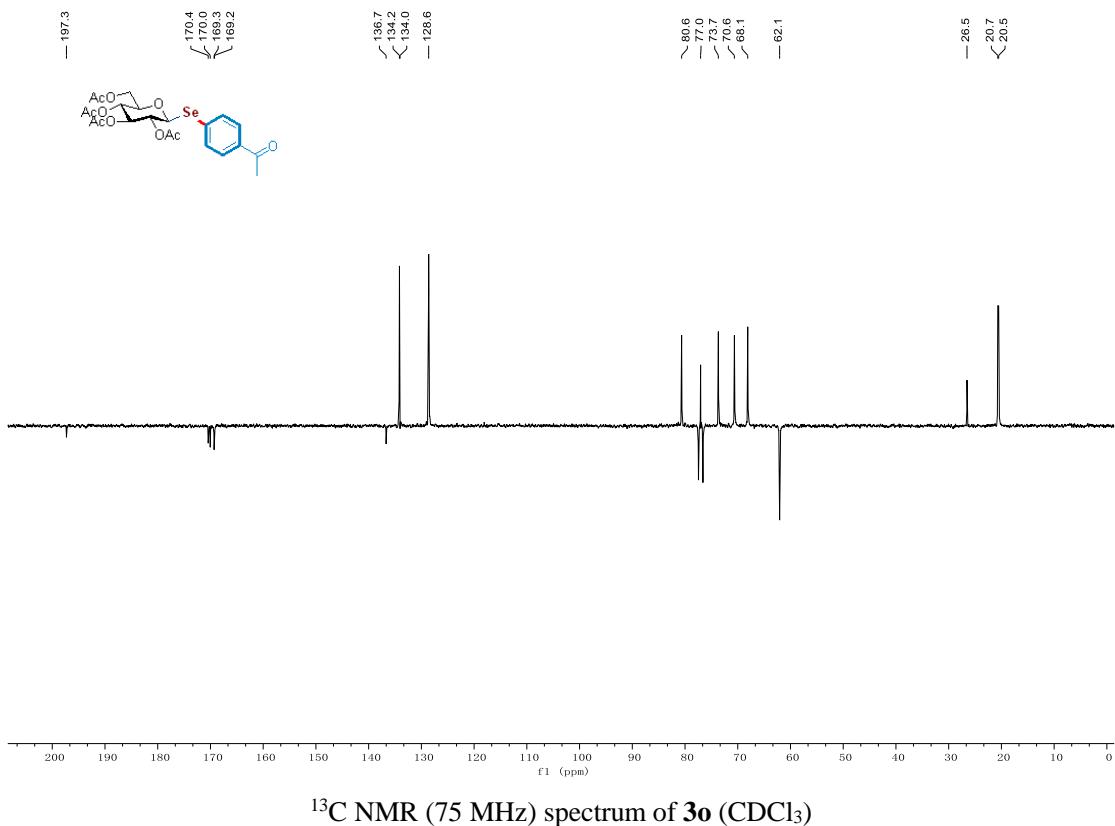
<sup>13</sup>C NMR (75 MHz) spectrum of **3l** ( $\text{CDCl}_3$ )



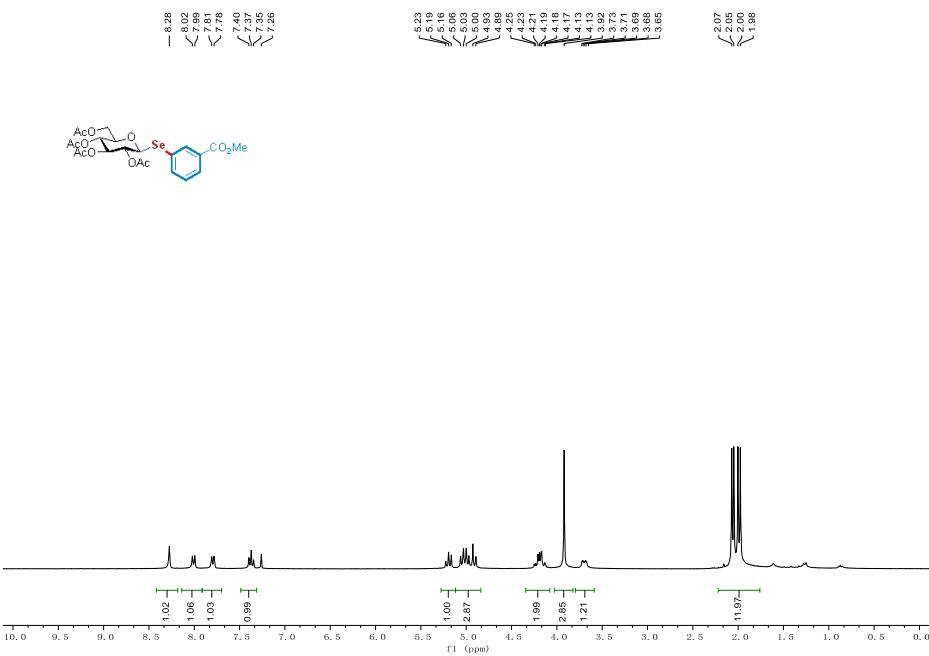
<sup>1</sup>H NMR (300 MHz) spectrum of **3m** ( $\text{CDCl}_3$ )



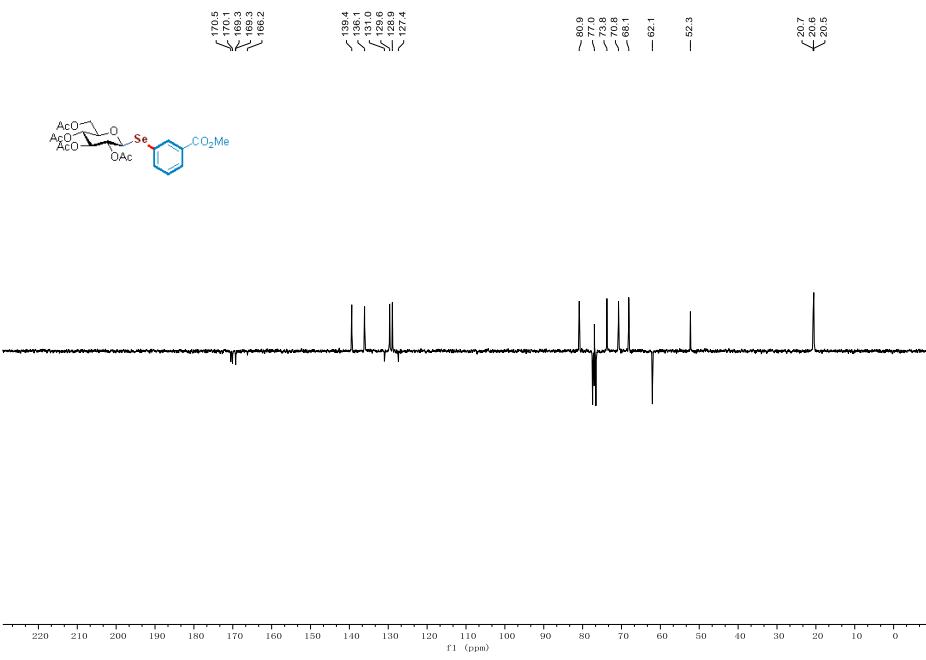




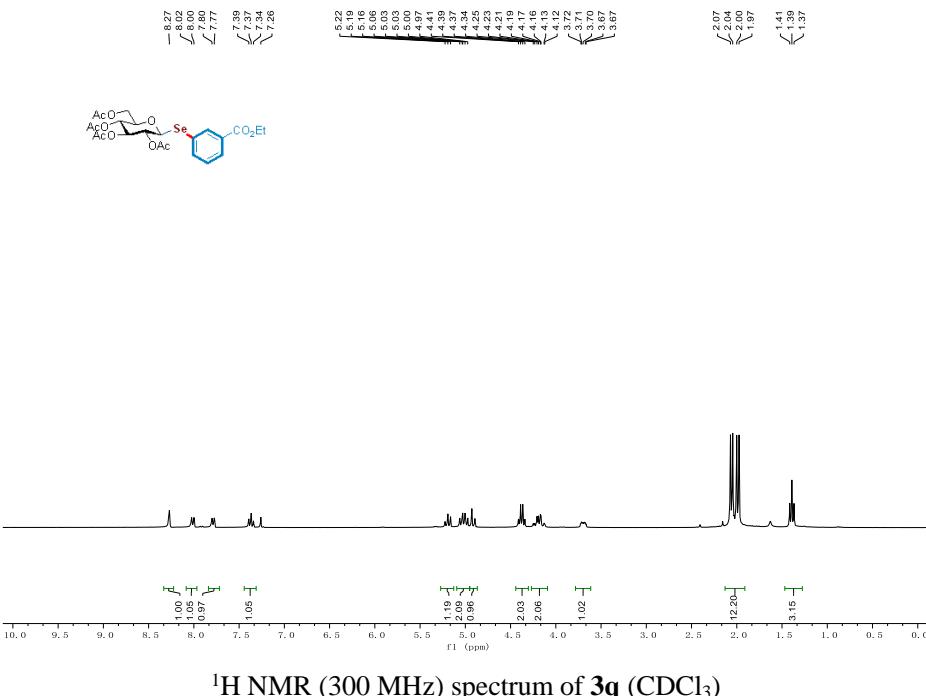
<sup>13</sup>C NMR (75 MHz) spectrum of **3o** ( $\text{CDCl}_3$ )



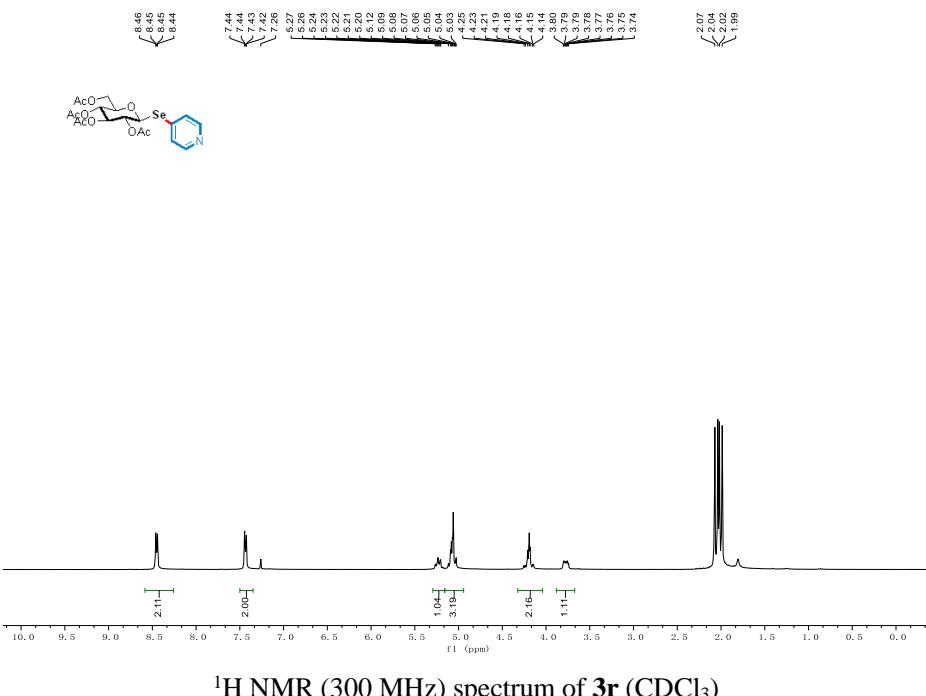
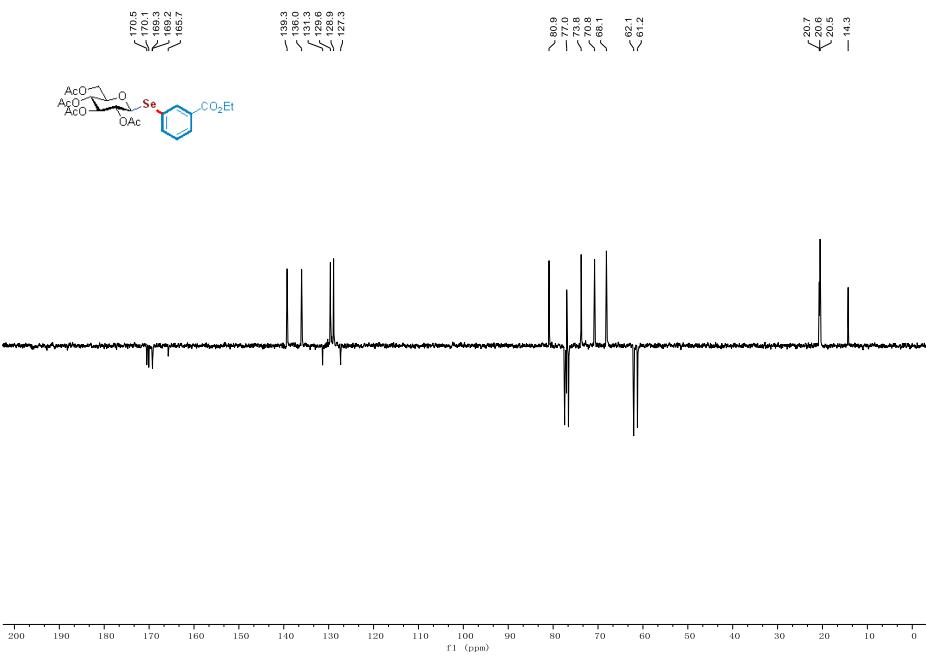
<sup>1</sup>H NMR (300 MHz) spectrum of **3p** ( $\text{CDCl}_3$ )

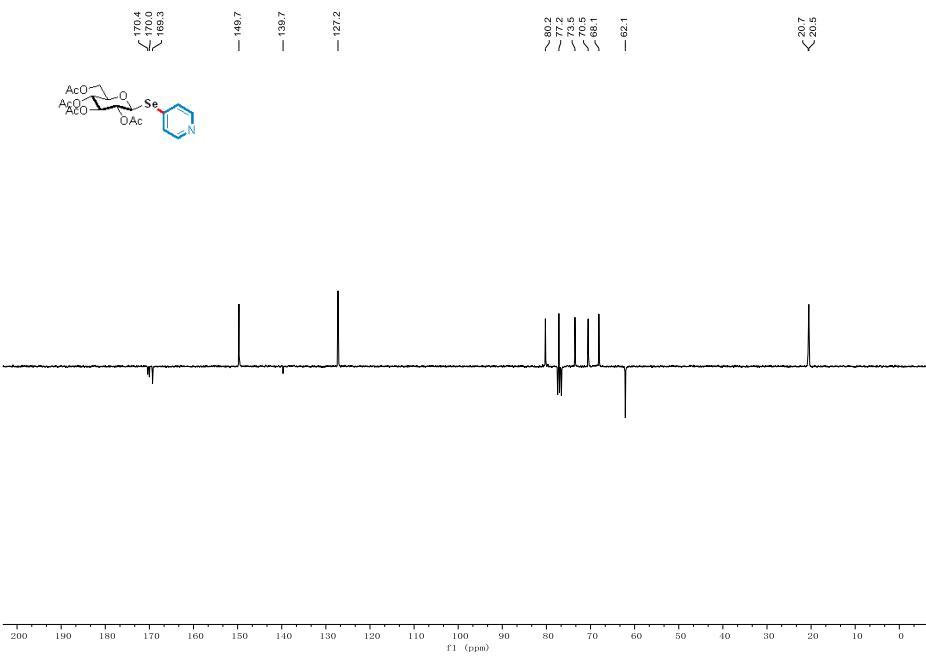


<sup>13</sup>C NMR (75 MHz) spectrum of **3p** ( $\text{CDCl}_3$ )

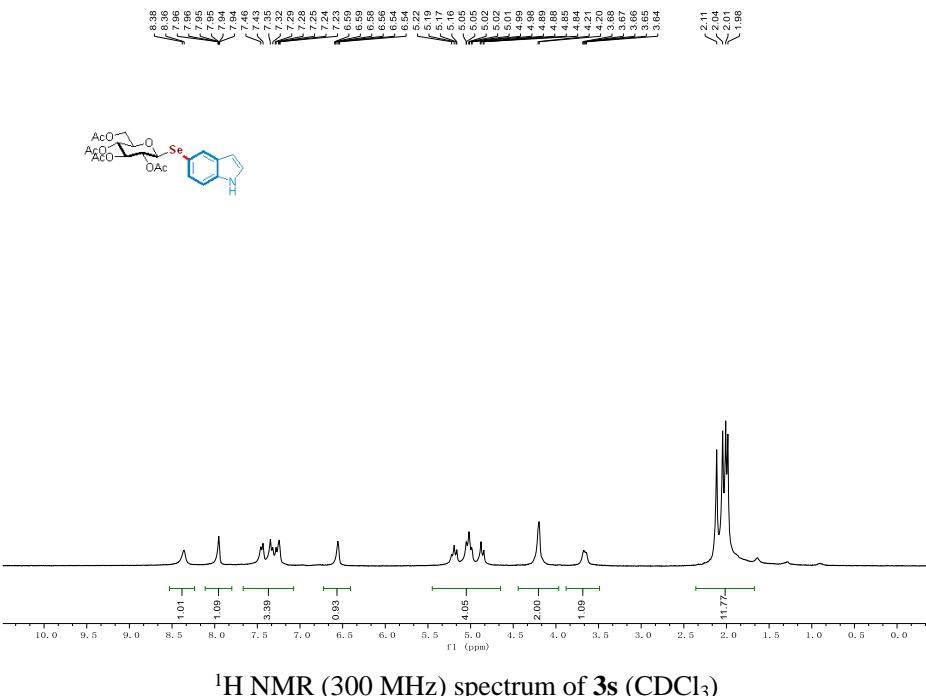


<sup>1</sup>H NMR (300 MHz) spectrum of **3q** ( $\text{CDCl}_3$ )

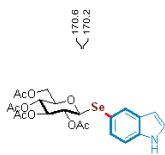




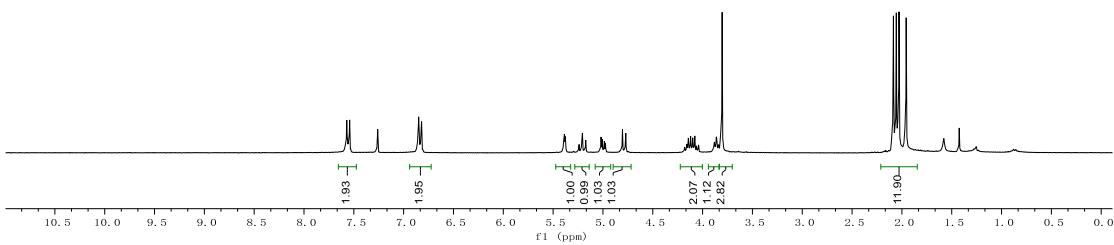
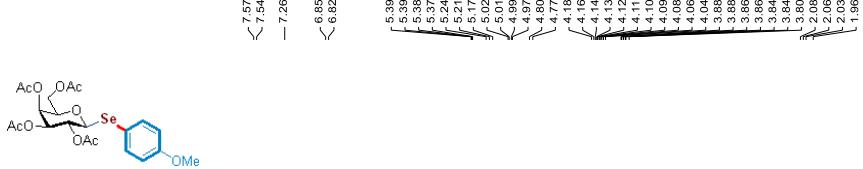
<sup>13</sup>C NMR (75 MHz) spectrum of **3r** ( $\text{CDCl}_3$ )



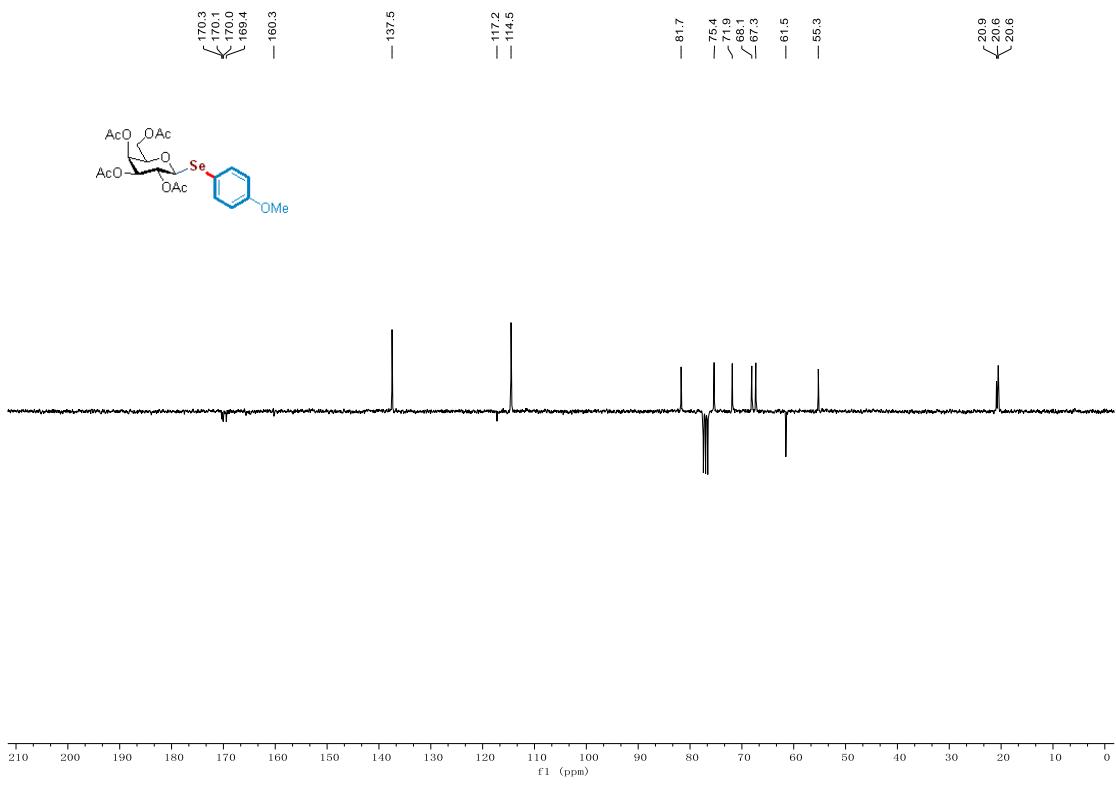
<sup>1</sup>H NMR (300 MHz) spectrum of **3s** ( $\text{CDCl}_3$ )



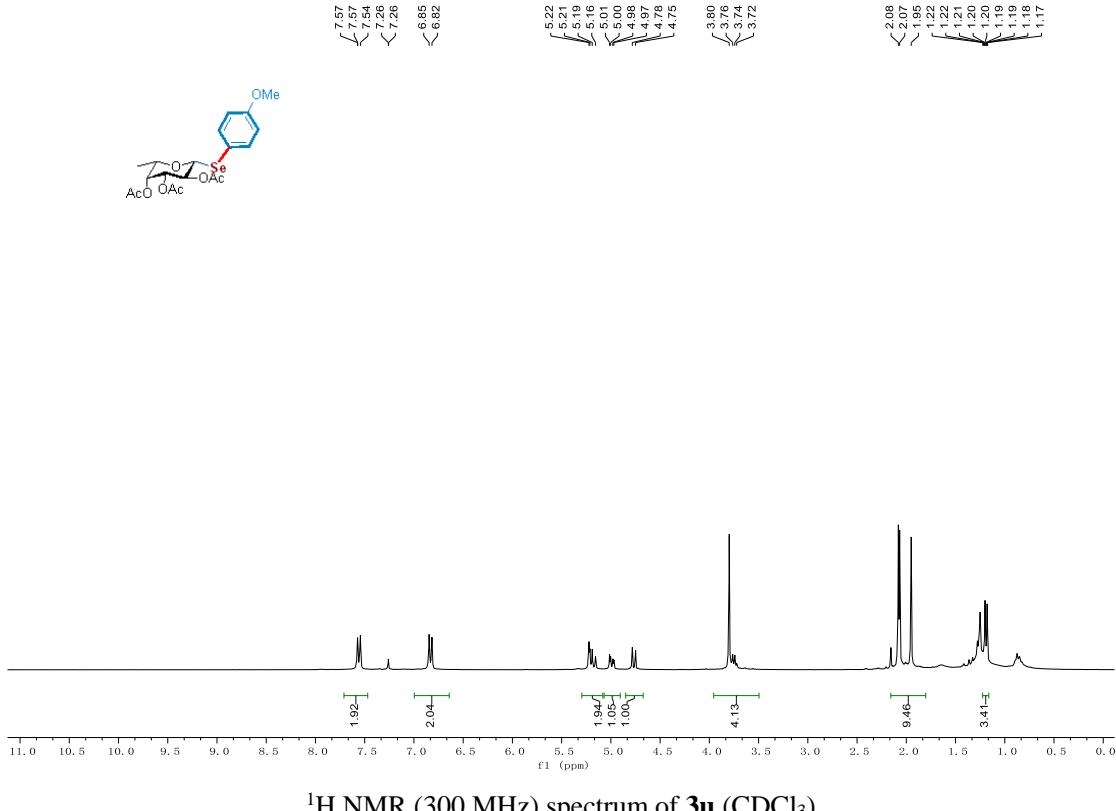
A horizontal ruler scale representing the concentration of f1 in ppm. The scale starts at 200 and ends at 0, with major tick marks labeled every 10 units: 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, and 0.



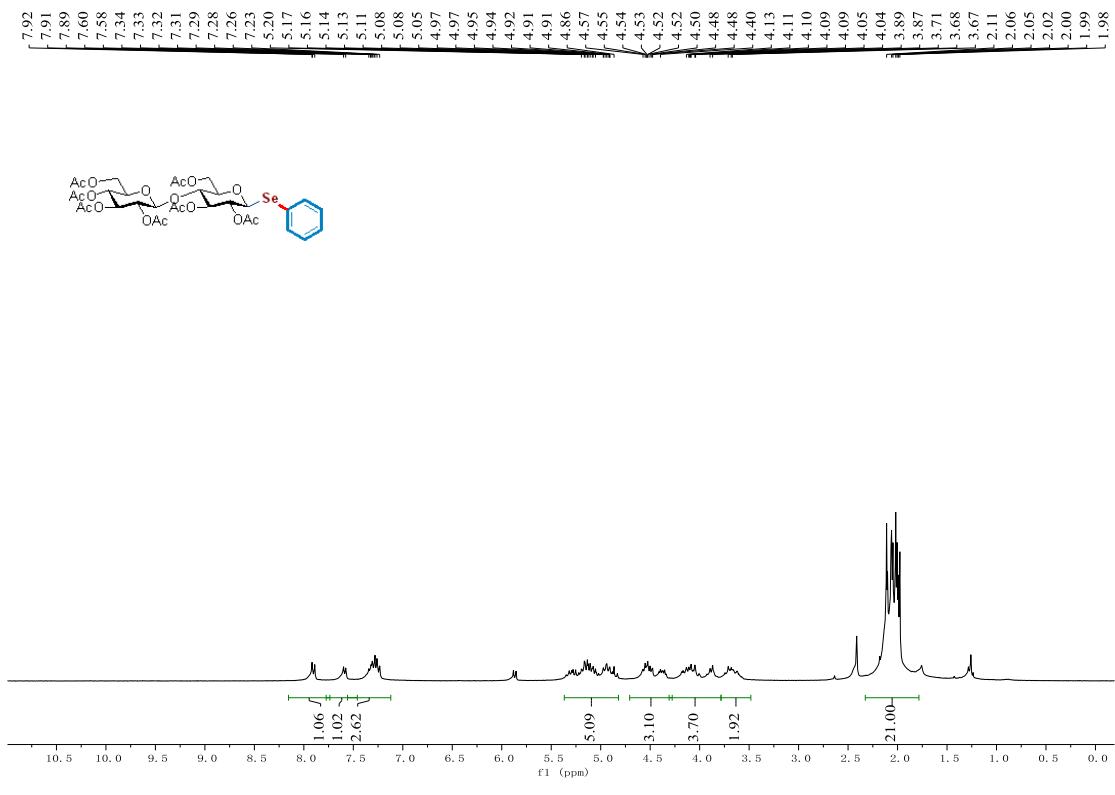
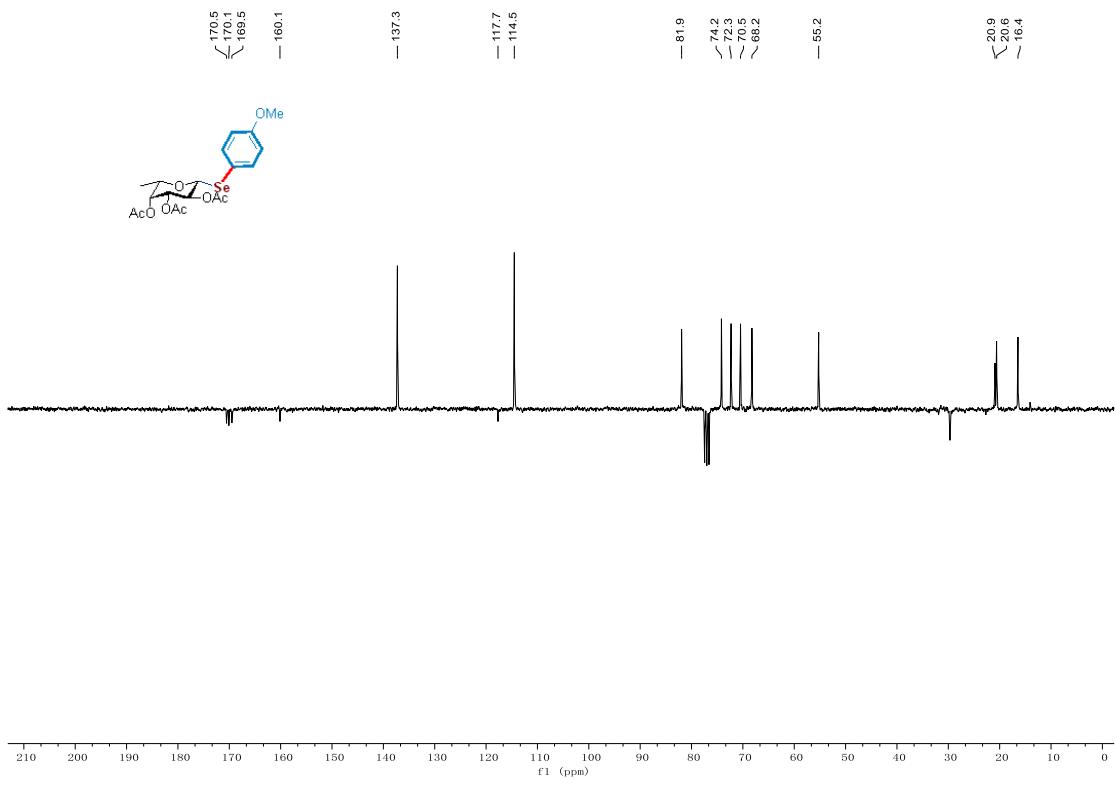
<sup>1</sup>H NMR (300 MHz) spectrum of **3t** ( $\text{CDCl}_3$ )

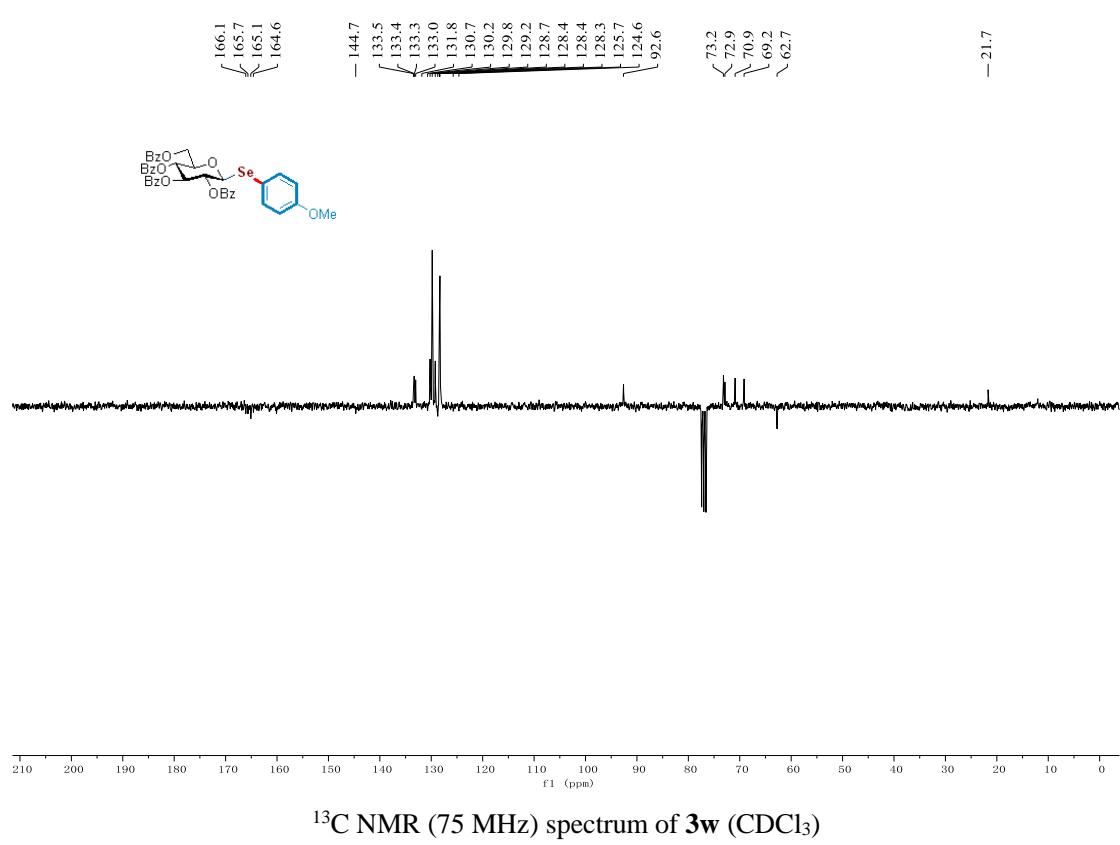
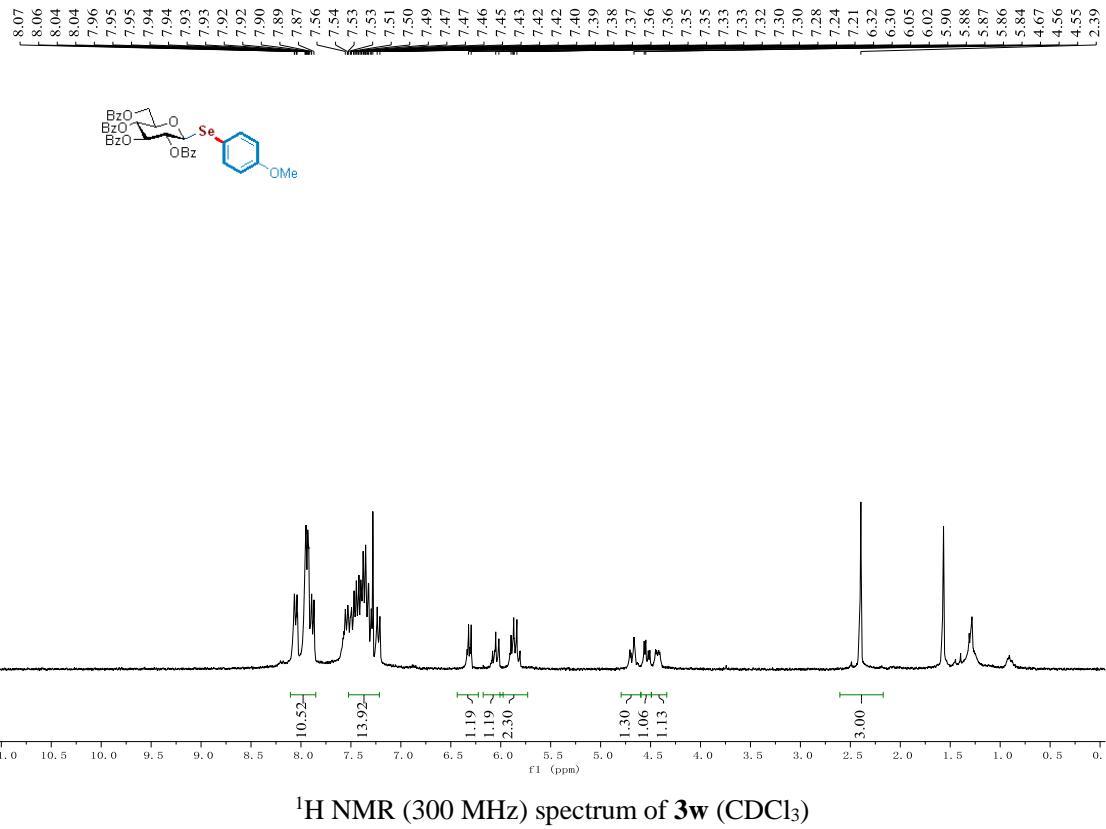


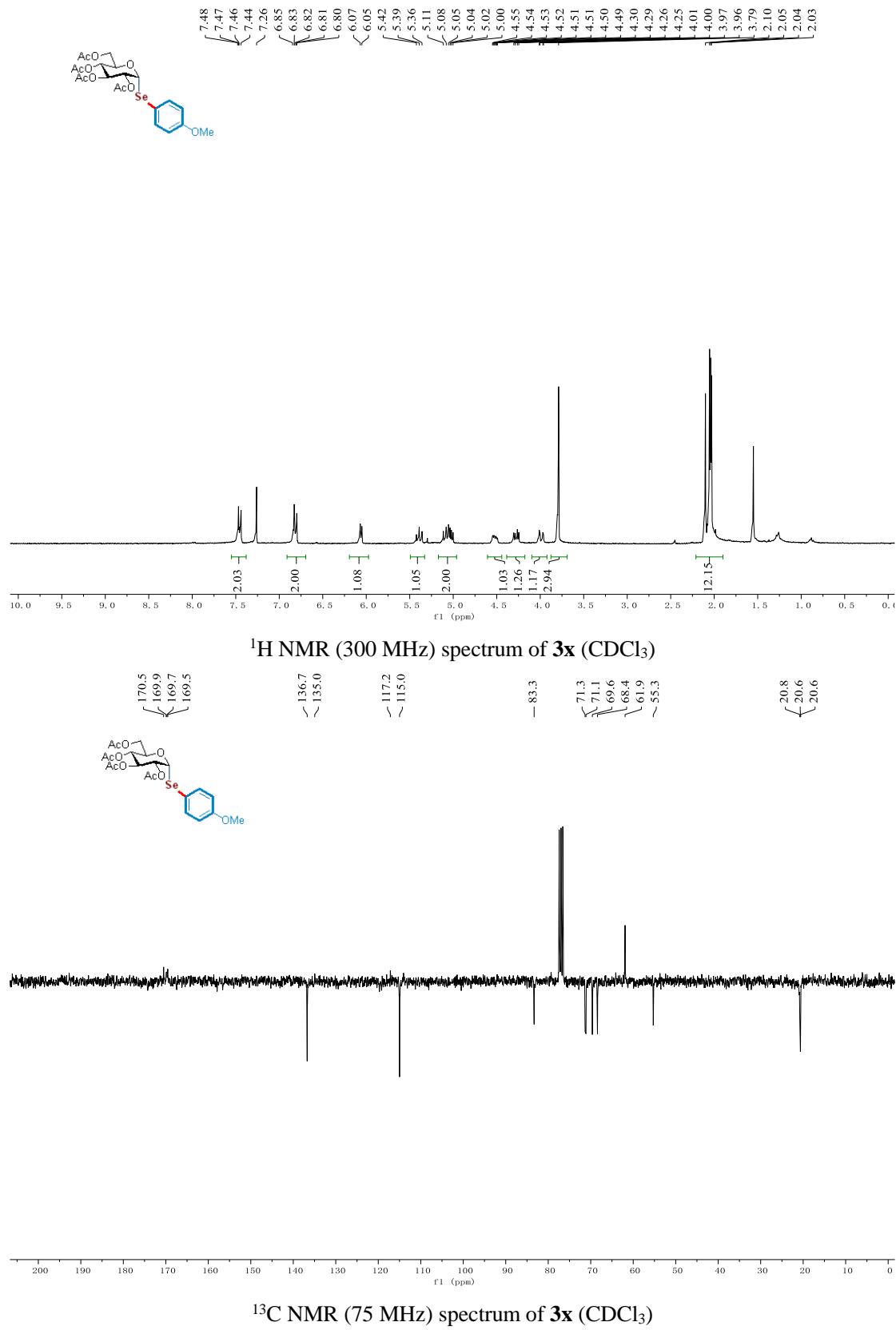
<sup>13</sup>C NMR (75 MHz) spectrum of **3t** ( $\text{CDCl}_3$ )

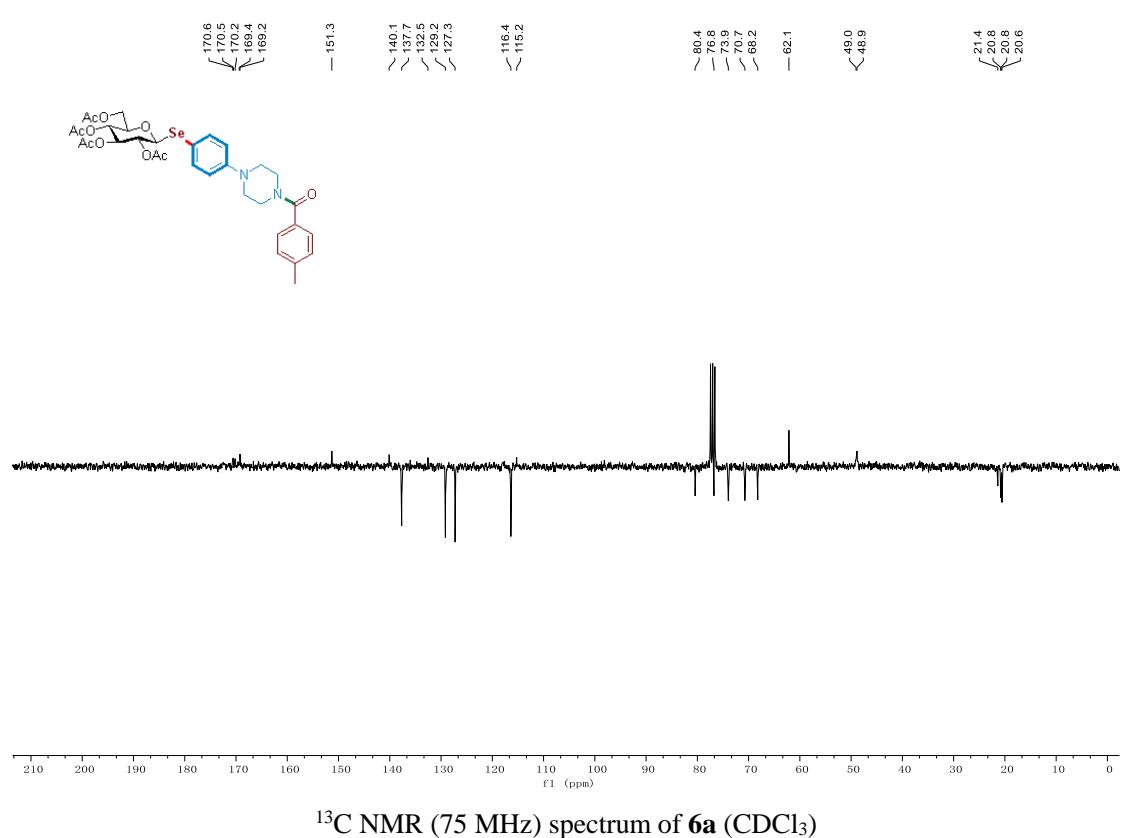
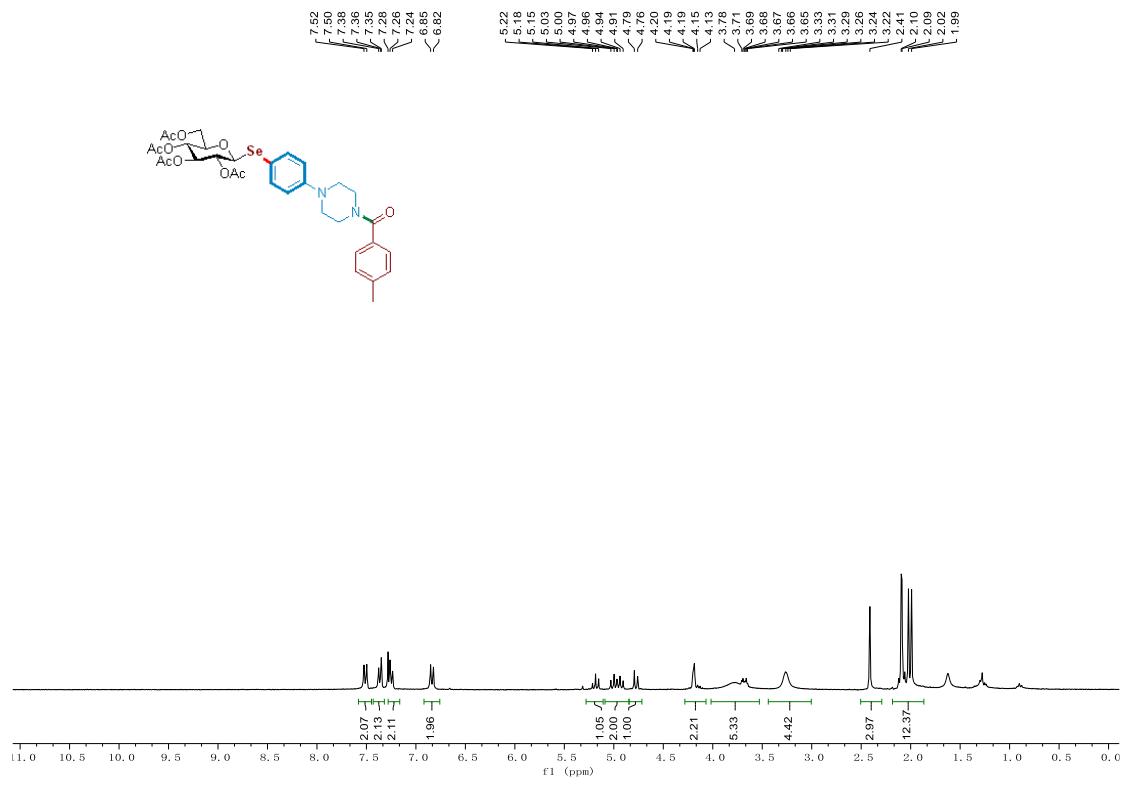


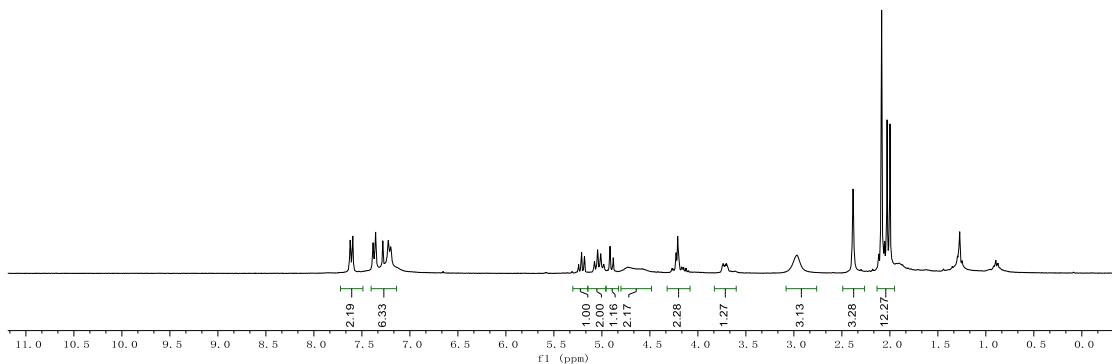
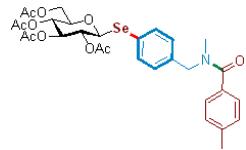
<sup>1</sup>H NMR (300 MHz) spectrum of **3u** ( $\text{CDCl}_3$ )



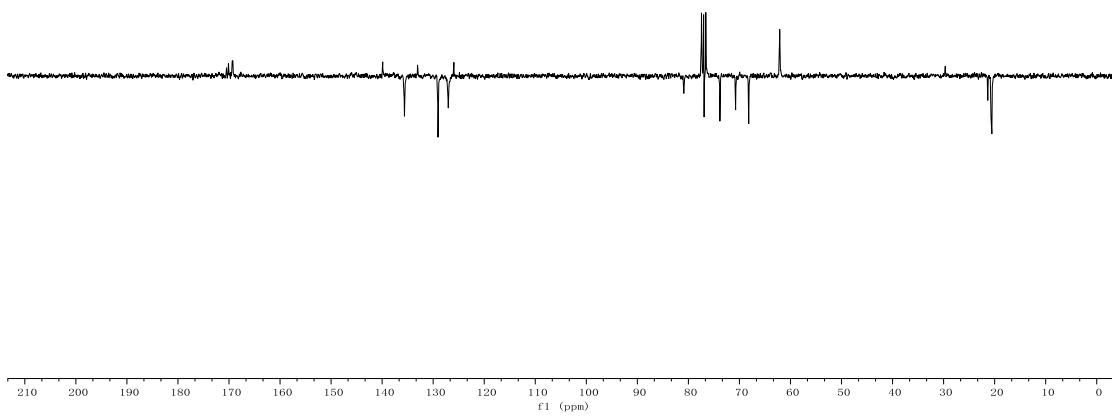
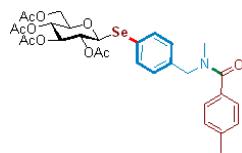




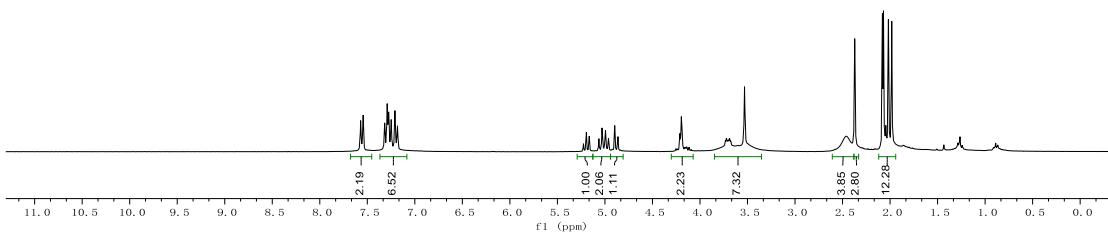
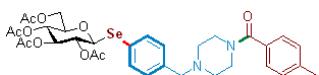




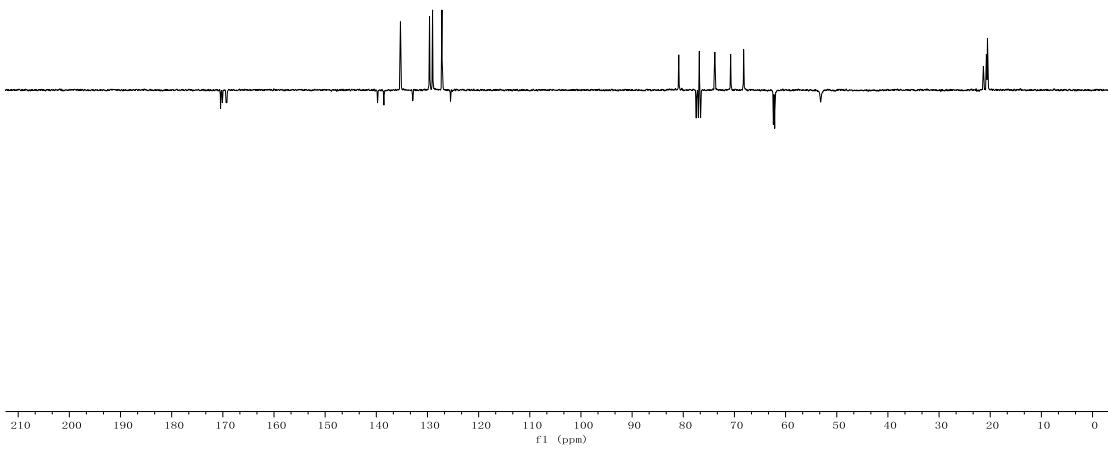
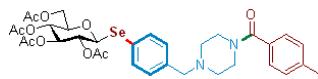
<sup>1</sup>H NMR (300 MHz) spectrum of **6b** (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz) spectrum of **6b** (CDCl<sub>3</sub>)



<sup>1</sup>H NMR (300 MHz) spectrum of **6c** (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz) spectrum of **6c** (CDCl<sub>3</sub>)