

## Supporting Information

### **Metal-Free C-Se Cross-Coupling Enabled by Photoinduced Intermolecular Charge Transfer**

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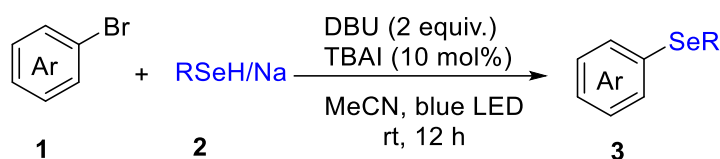
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## 1. General Information

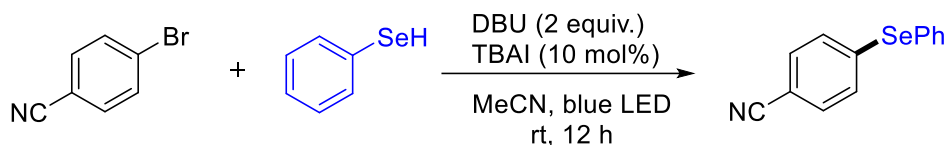
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were HPLC grade. Anhydrous and degassed CH<sub>3</sub>CN used in reactions was purchased from Sigma-Aldrich in Sure/Seal™ bottle. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed on silica gel (particle size 0.043–0.063 mm) by using Interchim PuriFlash® 430 automatic purification system. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on Bruker DRX-500 and AMX-400 instruments in CDCl<sub>3</sub> and are reported relative to the solvent residual peaks. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). Mass spectra (EI-MS, 70 eV) were conducted on a Agilent 7890 gas chromatograph equipped with 5975C EI-MSD Triple-Axis Detector using DB5MS and HP5MS columns. HRMS analysis was performed using a Thermo LTQ Velos Orbitrap mass spectrometer (Thermo Scientific, Pittsburgh, PA, USA) equipped with an ESI source.

## 2. General Procedure for the Photoinduced C-Se Bond Formation Reactions



A dry 5 mL vial equipped with a stirring bar was charged with an aryl bromide (0.2 mmol, 1 equiv.), TBAI (7.4 mg, 0.02 mmol, 10 mol%), and selenide salt<sup>1</sup> (if applied, 2 equiv., without the addition of DBU) in glovebox. Anhydrous and degassed CH<sub>3</sub>CN (1.0 mL), phenylselenol (if applied, 42.5 uL, 0.4 mmol, 2 equiv.) and DBU (59.7 uL, 0.4 mmol, 2 equiv.) was added subsequently via syringe. The reaction mixture was stirred for 12 h under the irradiation of 440 nm blue LED with fan cooling. After the reaction is completed, the mixture was concentrated under vacuum and the product was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent.

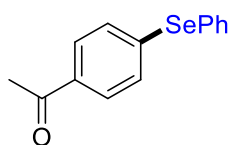
### 3. General Procedure for the Scale up Reaction



A dry 100 mL flask equipped with a stirring bar was charged with 4-bromobenzonitrile (1.09g, 6 mmol, 1 equiv.), TBAI (0.22 g, 0.6 mmol, 10 mol%) in glovebox. Anhydrous and degassed CH<sub>3</sub>CN (50 mL), phenylselenenol (1.29 mL, 12 mmol, 2 equiv.) and DBU (1.79 mL, 12 mmol, 2 equiv.) was added subsequently via syringe. The reaction mixture was sealed and stirred for 18 h under irradiation of two 440 nm blue LED with fan cooling. After the reaction is completed, the mixture was concentrated under vacuum and the product was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent. The desired product 4-(phenylselanyl)benzonitrile was isolated as yellow oil with 73% yield (1.13g).

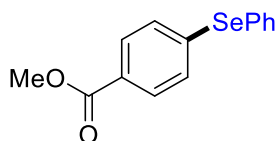
### 4. Spectroscopic Data of the Products

#### 1-(4-(phenylselanyl)phenyl)ethan-1-one (3a)



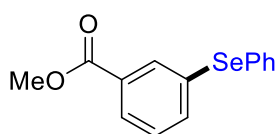
Yield: 85% (46.8 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.39 (t, *J* = 8.2 Hz, 5H), 2.57 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 197.3, 140.3, 135.2, 135.1, 130.3, 129.8, 128.9, 128.7, 128.5, 26.5. Data in accordance with the literature<sup>2</sup>.

#### Methyl 4-(phenylselanyl)benzoate (3b)



Yield: 98% (57 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.87 (m, 2H), 7.62 – 7.58 (m, 2H), 7.38 (tq, *J* = 8.8, 2.5 Hz, 5H), 3.91 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.7, 139.6, 134.9, 130.3, 130.1, 129.7, 128.7, 128.5, 128.2, 52.1. Data in accordance with the literature<sup>1</sup>.

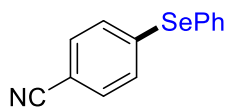
#### Methyl 3-(phenylselanyl)benzoate (3c)



Yield: 89% (52 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.19 (t, *J* = 1.8 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.5 Hz, 1H),

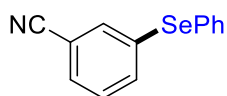
7.63 (dt,  $J = 7.8, 1.5$  Hz, 1H), 7.54 – 7.50 (m, 2H), 7.36 (d,  $J = 7.7$  Hz, 1H), 7.33 – 7.31 (m, 3H), 3.92 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 136.9, 133.6, 133.4, 132.0, 131.1, 130.3, 129.5, 129.2, 128.42, 127.8, 52.2. HRMS (ESI) for  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{Se}$ : calculated for  $[\text{M}+\text{Na}]^+$  314.98947, found 314.98944.

#### 4-(phenylselanyl)benzonitrile (3d)



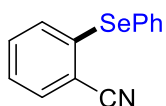
Yield: 87% (45 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.61 (m, 2H), 7.48 – 7.39 (m, 5H), 7.37 – 7.34 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 135.6, 132.4, 130.2, 129.9, 129.1, 127.5, 118.8, 109.6. Data in accordance with the literature<sup>1</sup>.

#### 3-(phenylselanyl)benzonitrile (3e)



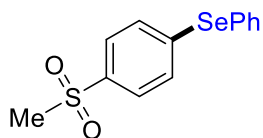
Yield: 87% (45 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.56 (m, 4H), 7.51 (dt,  $J = 7.7, 1.4$  Hz, 1H), 7.42 – 7.32 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  135.4, 134.7, 134.4, 134.25, 130.2, 129.9, 129.6, 128.7, 128.4, 118.2, 113.4. Data in accordance with the literature<sup>1</sup>.

#### 2-(phenylselanyl)benzonitrile (3f)



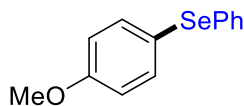
Yield: 76% (39 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.61 (m, 3H), 7.43 – 7.36 (m, 4H), 7.34 – 7.29 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 135.3, 135.2, 133.7, 133.0, 132.3, 129.8, 128.9, 128.0, 127.0, 117.5, 114.8. Data in accordance with the literature<sup>3</sup>.

#### (4-(methylsulfonyl)phenyl)(phenyl)selane (3g)



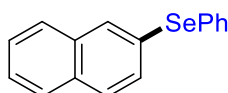
Yield: 88% (55 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.5$  Hz, 2H), 7.66 – 7.61 (m, 2H), 7.46 – 7.38 (m, 5H), 3.04 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.9, 138.1, 135.6, 130.3, 129.9, 129.1, 127.8, 127.5, 44.5. HRMS (ESI) for  $\text{C}_{13}\text{H}_{12}\text{SO}_2\text{Se}$ : calculated for  $[\text{M}+\text{Na}]^+$  334.96154, found 334.96152.

#### (4-methoxyphenyl)(phenyl)selane (3h)



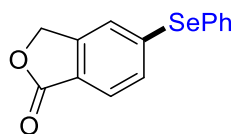
Yield: 44% (23.2 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (dd,  $J = 8.6, 1.6$  Hz, 2H), 7.36 (dt,  $J = 8.0, 1.7$  Hz, 2H), 7.27 – 7.19 (m, 3H), 6.89 (dd,  $J = 8.6, 1.6$  Hz, 2H), 3.84 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 136.5, 133.2, 130.9, 129.2, 129.1, 126.4, 119.9, 115.1, 55.3. Data in accordance with the literature<sup>1</sup>.

#### Naphthalen-2-yl(phenyl)selane (3i)



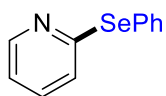
Yield: 62% (35 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (s, 1H), 7.85 – 7.82 (m, 1H), 7.77 (d,  $J = 7.9$  Hz, 2H), 7.57 – 7.50 (m, 5H), 7.33 – 7.30 (m, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0, 132.9, 132.4, 132.0, 131.2, 130.5, 129.4, 128.8, 128.4, 127.8, 127.4, 127.3, 126.5, 126.2. Data in accordance with the literature<sup>2</sup>.

#### 5-(phenylselanyl)isobenzofuran-1(3H)-one (3j)



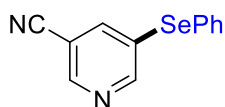
Yield: 47% (27 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.0$  Hz, 1H), 7.65 (dd,  $J = 7.6, 1.8$  Hz, 2H), 7.47 – 7.40 (m, 4H), 7.34 (s, 1H), 5.23 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 147.5, 142.5, 135.7, 130.5, 130.0, 129.1, 127.6, 125.9, 123.7, 122.9, 69.1. HRMS (ESI) for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{Se}$ : calculated for  $[\text{M}+\text{Na}]^+$  312.97382, found 312.97334.

#### 2-(phenylselanyl)pyridine (3k)



Yield: 73% (34.2 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (dd,  $J = 5.1, 1.9$  Hz, 1H), 7.76 – 7.70 (m, 2H), 7.42 (dtd,  $J = 10.3, 5.2, 2.7$  Hz, 4H), 7.07 – 7.00 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 149.9, 136.6, 136.2, 129.7, 128.9, 127.9, 124.3, 120.4. Data in accordance with the literature<sup>4</sup>.

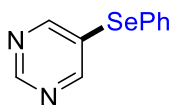
#### 5-(phenylselanyl)nicotinonitrile (3l)



Yield: 97% (50 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (d,  $J = 2.1$  Hz, 1H), 8.68 (d,  $J = 1.8$  Hz, 1H), 7.80 (t,  $J = 2.0$  Hz, 1H), 7.63 – 7.58 (m, 2H), 7.46 – 7.38 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 149.8,

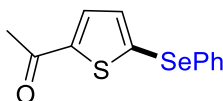
140.5, 135.2, 131.3, 130.2, 129.4, 126.7, 116.1, 110.6. HRMS (ESI) for  $C_{12}H_8N_2Se$ : calculated for  $[M+Na]^+$  282.97449, found 282.97487.

### 5-(phenylselanyl)pyrimidine (3m)



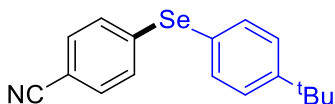
Yield: 97% (45.7 mg);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.07 (s, 1H), 8.72 (s, 2H), 7.55 (dd,  $J = 7.6, 2.0$  Hz, 2H), 7.39 – 7.32 (m, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  159.1, 156.8, 134.2, 129.9, 128.8, 128.4, 127.7. HRMS (ESI) for  $C_{10}H_8N_2Se$ : calculated for  $[M-H]^-$  234.97690, found 234.97636.

### 1-(5-(phenylselanyl)thiophen-2-yl)ethan-1-one (3n)



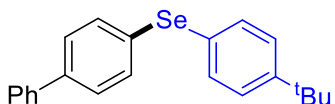
Yield: 92% (52 mg);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.57 – 7.52 (m, 3H), 7.32 (dd,  $J = 5.0, 1.8$  Hz, 3H), 7.21 (d,  $J = 3.8$  Hz, 1H), 2.53 (s, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  189.8, 148.1, 136.7, 134.3, 132.9, 132.6, 130.6, 129.6, 128.2, 26.7. HRMS (ESI) for  $C_{12}H_{10}SOSe$ : calculated for  $[M+Na]^+$  304.95098, found 304.95051.

### 4-((4-(tert-butyl)phenyl)selanyl)benzonitrile (3o)



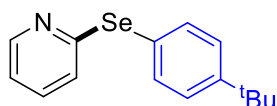
Yield: 84% (26.5 mg);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.56 (dd,  $J = 8.3, 1.4$  Hz, 2H), 7.45 (ddd,  $J = 13.7, 8.3, 1.4$  Hz, 4H), 7.35 (dd,  $J = 8.3, 1.4$  Hz, 2H), 1.37 (s, 9H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  152.6, 141.5, 135.6, 132.3, 129.8, 127.1, 123.7, 118.9, 109.3, 34.8, 31.2. HRMS (ESI) for  $C_{17}H_{17}NSe$ : calculated for  $[M+Na]^+$  338.04184, found 338.04250.

### [1,1'-biphenyl]-4-yl(4-(tert-butyl)phenyl)selane (3p)



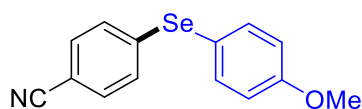
Yield: 55% (20.2 mg);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.60 (d,  $J = 7.9$  Hz, 2H), 7.55 – 7.43 (m, 8H), 7.40 – 7.35 (m, 3H), 1.36 (s, 9H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  150.8, 140.4, 140.0, 133.3, 132.8, 130.8, 128.8, 127.9, 127.4, 127.0, 126.9, 126.5, 34.6, 31.3. HRMS (ESI) for  $C_{22}H_{22}Se$ : calculated for  $[M]^+$  366.08812, found 366.08804.

### 2-((4-(tert-butyl)phenyl)selanyl)pyridine (3q)



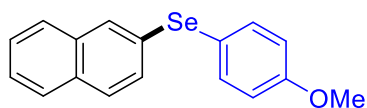
Yield: 41% (12 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (dd,  $J = 4.7, 1.7$  Hz, 1H), 7.65 – 7.62 (m, 2H), 7.41 (dd,  $J = 8.5, 1.5$  Hz, 3H), 7.02 – 6.98 (m, 2H), 1.34 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 152.2, 149.8, 136.6, 136.0, 126.8, 124.2, 124.1, 120.2, 34.7, 31.2. HRMS (ESI) for  $\text{C}_{15}\text{H}_{17}\text{NSe}$ : calculated for  $[\text{M}+\text{Na}]^+$  314.04184, found 314.04185.

### 4-((4-methoxyphenyl)selanyl)benzonitrile (3r)



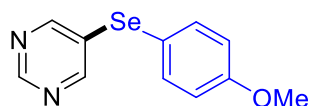
Yield: 80% (23 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J = 8.4, 1.4$  Hz, 2H), 7.46 – 7.42 (m, 2H), 7.27 (dd,  $J = 8.4, 1.5$  Hz, 2H), 6.98 – 6.93 (m, 2H), 3.87 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7, 142.4, 138.1, 132.2, 129.0, 118.9, 116.9, 115.6, 109.0, 55.3. Data in accordance with the literature<sup>5</sup>.

### (4-methoxyphenyl)(naphthalen-2-yl)selane (3s)



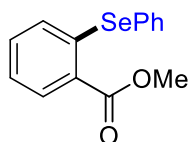
Yield: 70% (22 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (s, 1H), 7.82 – 7.78 (m, 1H), 7.72 (d,  $J = 8.2$  Hz, 2H), 7.58 (dd,  $J = 8.5, 1.5$  Hz, 2H), 7.46 (ddt,  $J = 10.0, 6.4, 1.7$  Hz, 3H), 6.91 (dd,  $J = 8.5, 1.4$  Hz, 2H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 136.4, 134.0, 132.0, 130.6, 129.5, 128.9, 128.5, 127.7, 127.2, 126.4, 125.8, 120.0, 115.2, 55.3. Data in accordance with the literature<sup>6</sup>.

### 5-((4-methoxyphenyl)selanyl)pyrimidine (3t)



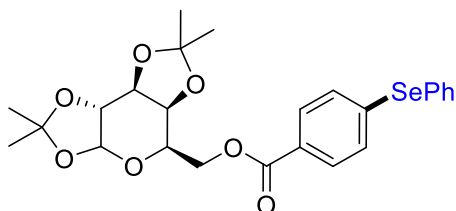
Yield: 89% (23.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.01 (s, 1H), 8.62 (s, 2H), 7.58 – 7.54 (m, 2H), 6.91 (dd,  $J = 8.5, 1.4$  Hz, 2H), 3.84 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 157.7, 156.3, 137.2, 129.8, 116.8, 115.6, 55.4. HRMS (ESI) for  $\text{C}_{11}\text{H}_{10}\text{OSe}$ : calculated for  $[\text{M}-\text{H}]^-$  264.98746, found 264.98849.

### Methyl 2-(phenylselanyl)benzoate (3u)



Yield: 67% (39.1 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 7.5$  Hz, 1H), 7.74 (d,  $J = 7.2$  Hz, 2H), 7.46 (dt,  $J = 14.3, 7.0$  Hz, 3H), 7.20 (dt,  $J = 20.5, 7.3$  Hz, 2H), 6.98 – 6.89 (m, 1H), 4.00 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 140.5, 137.6, 132.7, 131.4, 129.8, 129.2, 129.1, 128.9, 127.1, 124.8, 52.3.

**((5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(phenylselanyl)benzoate (8)**



Yield: 82% (42.6 mg), 0.10 mmol scale;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.4$  Hz, 2H), 7.57 (dt,  $J = 7.2, 1.2$  Hz, 2H), 7.39 – 7.31 (m, 5H), 5.55 (d,  $J = 5.0$  Hz, 1H), 4.64 (dd,  $J = 7.9, 2.5$  Hz, 1H), 4.50 (dd,  $J = 11.5, 4.8$  Hz, 1H), 4.40 (dd,  $J = 11.5, 7.6$  Hz, 1H), 4.34 (dd,  $J = 5.0, 2.5$  Hz, 1H), 4.30 (dd,  $J = 7.9, 1.9$  Hz, 1H), 4.15 (ddd,  $J = 7.1, 4.8, 1.8$  Hz, 1H), 1.50 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 139.8, 134.9, 130.3, 130.2, 129.7, 128.7, 128.5, 128.1, 109.7, 108.8, 96.3, 71.1, 70.7, 70.5, 66.1, 63.9, 26.0, 25.9, 24.9, 24.5. HRMS (ESI) for  $\text{C}_{25}\text{H}_{28}\text{O}_7\text{Se}$ : calculated for  $[\text{M}+\text{Na}]^+$  543.08924, found 543.08982.

## 5. References

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## 6. Copies of NMR Spectra

