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 vanilin solution (15 g of vanilin 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 $^1$H NMR and $^{13}$C NMR spectra were recorded in either CDCl$_3$ or MeOD-d$_4$ on Bruker Avance 300 spectrometers. The chemical shifts of $^1$H and $^{13}$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.$^{1,2,3}$

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$_2$CO$_3$ (0.3 mmol, 3 eq). The vial was then evacuated and backfilled with an argon balloon. And then, aryl halide (if liquid) (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$_2$SO$_4$ 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$_2$CO$_3$ (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$_2$SO$_4$ 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:

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<tr>
<td>1</td>
<td>PdG₃Xantphos 10 mol%</td>
<td>-</td>
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<tr>
<td>2</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3</td>
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<td>Pd(OAc)₂ 10 mol%</td>
<td>Xantphos 10 mol%</td>
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</tr>
<tr>
<td>5</td>
<td>PdCl₂ 10 mol%</td>
<td>Xantphos 10 mol%</td>
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Reaction time and solvent effects:

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<tr>
<td>2</td>
<td>THF</td>
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<tr>
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<tr>
<td>6</td>
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Base effects:

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<td>Piperazine 1.0 eq</td>
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<tr>
<td>2</td>
<td>Cs₂CO₃ 3eq</td>
<td>Piperazine 1.5 eq</td>
<td>95%</td>
</tr>
<tr>
<td>2</td>
<td>Cs₂CO₃ 3eq</td>
<td>Piperazine 1.2 eq</td>
<td>95%</td>
</tr>
<tr>
<td>3</td>
<td>Cs₂CO₃ 2eq</td>
<td>Piperazine 1.2 eq</td>
<td>72%</td>
</tr>
<tr>
<td>4</td>
<td>Cs₂CO₃ 4eq</td>
<td>Piperazine 1.2 eq</td>
<td>95%</td>
</tr>
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<td></td>
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<tr>
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<tr>
<td>5</td>
<td>CsF 3eq</td>
<td>Piperazine 1.2 eq</td>
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<td>6</td>
<td>NaOAc 3eq</td>
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Amount of 2a (xx equiv) effects:

4. Experimental data

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

\[
R_f = 0.3 \text{ (EtOAc /cyclohexane: 3/7); 49.2 mg, 95%, White solid. m. p.: 103.9-104.8 °C; } [\alpha]_D^{18} = -23.5 \text{ (c, 0.75, CHCl}_3); \]
\[
^1H \text{ NMR (300 MHz, (CD}_3)_2CO-d_6) \delta 7.54-7.58 (m, 2H), 6.87-6.93 (m, 2H), 5.27 (t, } J = 9.0 \text{ Hz, 1H), 5.11 (d, } J = 12.0 \text{ 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); } ^{13}C \text{ NMR (75 MHz, (CD}_3)_2CO-d_6) \delta 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), 55.6 (CH), 20.7 (2CH), 20.5 (2CH); IR (neat): 2360, 2341, 1754, 1746, 1591, 1492, 1461, 1440, 1366, 1287, 1247, 1215, 117, 1059, 1030, 911, 828, 733 cm\(^{-1}\); HRMS (ESI): m/z calc. for C\(_{21}\)H\(_{30}\)NO\(_6\)Se [M+NH\(_4\)]\(^+\) 536.1029; found 536.1039.

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

\[
R_f = 0.3 \text{ (EtOAc /cyclohexane: 3/7); 50.1 mg, 99%, White solid. m. p.: 125.1-126.0 °C; } [\alpha]_D^{18} = -
22.6 (c, 0.31, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 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); ¹³C NMR (75 MHz, CDCl₃) δ 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 (CH₂), 21.2 (CH₃), 20.8 (CH₃), 20.5 (2CH); IR (neat): 1755, 1479, 1439, 1367, 1247, 1038, 911, 743, 693 cm⁻¹; HRMS (ESI): m/z calc. for C₂₃H₂₈NO₈Se [M+NH₄]⁺ 520.1080; found 520.1085.

(2R,3R,4S,5R,6S)-2-(acetoxyethyl)-6-((3-methoxyphenyl)selanyltetrahydro-2H-pyran-3,4,5-triyl triacetate (3c)

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 37.7 mg, 73%, White solid. m. p.: 124.6-125.1 °C; [α]D¹⁸ = −16.7 (c, 0.36, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 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); ¹³C NMR (75 MHz, CDCl₃) δ 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),73.9 (CH), 70.8 (CH), 68.2 (CH), 62.1 (CH₂), 55.3 (CH₃), 20.8 (CH₃), 20.6 (CH₃); IR (neat): 2360, 2341, 2327, 1754, 1589, 1478, 1367, 1247, 1038, 911, 733 cm⁻¹; HRMS (ESI): m/z calc. for C₂₁H₂₃NO₈Se [M+NH₄]⁺ 536.1029; found 536.1031.

(2R,3R,4S,5R,6S)-2-(acetoxyethyl)-6-(phenylselanyltetrahydro-2H-pyran-3,4,5-triyl triacetate (3d)

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 43.9 mg, 90%, White solid. m. p.: 133.2-133.6 °C; [α]D¹⁸ = −38.1 (c, 0.21, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.61-7.74 (m, 2H), 7.26-7.40 (m, 2H), 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⁻¹; HRMS (ESI): m/z calc. for C₂₀H₂₆NO₈Se [M+NH₄]⁺ 506.0924; found 506.0920.

(2R,3R,4S,5R,6S)-2-(acetoxyethyl)-6-(naphthalen-2-yldiselenyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3e)

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 39.4 mg, 73%, White solid. m. p.: 103.5-103.8 °C; [α]D¹⁸ = −
41.4 (c, 0.29, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 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), 1.97 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 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 (CH₂), 20.8 (CH₃), 20.6 (CH₃), 20.5 (CH₃); IR (neat): 2360, 1754, 1746, 1586, 1501, 1432, 1367, 1248, 1214, 1060, 911, 817, 747 cm⁻¹; HRMS (ESI): m/z calc. for C₂₃H₃₀NO₅Se [M+NH₄]⁺ 556.1080; found 556.1093.

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

Rf = 0.3 (EtOAc /cyclohexane: 3:7); 46.2 mg, 87%, White solid. m. p.: 120.0-121.3 °C; [α]D¹⁸ = −23.5 (c, 0.34, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.53 (m, 2H), 7.14-7.16 (m, 2H), 5.18 (t, J = 9.0 Hz, 1H), 5.01 (dd, 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); ¹³C NMR (75 MHz, CDCl₃) δ 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 (CH₂), 33.9 (CH) 23.8 (2CH₃), 20.8 (CH₃), 20.7 (CH₃), 20.5 (2CH₃); IR (neat): 2961, 2360, 2341, 1755, 1366, 1248, 1217, 1060, 1039, 910, 826, 773, 670 cm⁻¹; HRMS (ESI): m/z calc. for C₂₃H₃₀NO₅Se [M+NH₄]⁺ 548.1393; found 548.1386.

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

Rf = 0.3 (EtOAc /cyclohexane: 3:7); 33.4 mg, 65%, White solid. m. p.: 103.5-103.8 °C; [α]D¹⁸ = −41.4 (c, 0.29, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 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); ¹³C NMR (75 MHz, CDCl₃) δ 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 (CH₂), 61.2 (CH₂), 20.7 (2CH₃), 20.6 (2CH₃); IR (neat): 2925, 2360, 2326, 1755, 1367, 1216, 1087, 1060, 1034, 773 cm⁻¹; HRMS (ESI): m/z calc. for C₂₃H₃₀NO₅Se [M+NH₄]⁺ 532.1080; found 532.1088.
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-cyanophenyl)selanyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3h)

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 50.9 mg, 99%, White solid. m. p.: 164.1-165.3 °C; [α]D 18 = –36.4 (c, 0.22, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 20.7 (2CH3), 20.5 (2CH3); IR (neat): 2360, 2341, 1754, 1433, 1367, 1217, 1060, 1041, 911, 769 cm⁻¹; HRMS (ESI): m/z calc. for C21H23NO6NaSe [M+Na]+ 536.0436; found 536.0446.

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

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 52.7 mg, 95%, White solid. m. p.: 150.1-151.3 °C; [α]D 18 = –25.0 (c, 0.40, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 20.7 (2CH3), 20.6 (2CH3); IR (neat): 2360, 2341, 2326, 1752, 1603, 1368, 1248, 1166, 1080, 1059, 911, 773 cm⁻¹; HRMS (ESI): m/z calc. for C21H17F3NaO6Se [M+Na]+ 579.0357; found 579.0347.

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

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 51.7 mg, 99%, White solid. m. p.: 77.2-77.4 °C; [α]D 18 = –36.4 (c, 0.66, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 20.7 (2CH3), 20.5 (2CH3); IR (neat): 2360, 2341, 1748, 1570, 1461, 1367, 1248, 1215, 1085, 1060, 1040, 911, 775, 681 cm⁻¹; HRMS (ESI): m/z calc. for C20H17NO6ClSe [M+NH4]+ 540.0540; found 540.0539.
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-nitrophenyl)selanyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3k)

Rf = 0.3 (EtOAc /cyclohexane: 1/1); 42.4 mg, 85%. White solid. m. p.: 166.4-167.1 °C; [α]D 18 = −36.8 (c, 0.76, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 20.7 (2CH3), 20.5 (2CH3); IR (neat): 2360, 1746, 1598, 1576, 1520, 1368, 1346, 1247, 1034, 911, 773, 683 cm⁻¹; HRMS (ESI): m/z calc. for C29H27N3O11Se [M+NH4]⁺ 551.0775; found 551.0785.

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

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 45.9 mg, 89%. White solid. m. p.: 74.6-75.6 °C; [α]D 18 = −10.3 (c, 0.29, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 20.7 (2CH3), 20.5 (2CH3); IR (neat): 2360, 2341, 1748, 1699, 1589, 1564, 1433, 1367, 1248, 1213, 1172, 1060, 1039, 911, 835, 817, 773, 681 cm⁻¹; HRMS (ESI): m/z calc. for C25H21NO10Se [M+NH4]⁺ 534.0873; found 534.0888.

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

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 50.7 mg, 93%. White solid. m. p.: 140.3-142.4 °C; [α]D 18 = −26.1 (c, 0.69, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 52.2 (CH3), 20.7 (2CH3), 20.5 (2CH3); IR (neat): 2360, 2341, 1749, 1593, 1435, 1367, 1247, 1109, 1059, 911, 825, 759 cm⁻¹; HRMS (ESI): m/z calc. for C22H18NO11Se [M+NH4]⁺ 564.0979; found 564.0995.
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-ethoxycarbonyl)phenyl)selanyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3n)

Rf = 0.3 (EtOAc / cyclohexane: 3/7); 49.7 mg, 89%. White solid. m. p.: 123.2-123.3 °C; [α]D 18 = −25.6 (c, 0.43, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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, 2H), 2.05 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.39 (t, J = 6.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 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 (CH₂), 61.1 (CH₂), 20.7 (CH₂), 20.5 (CH₂), 14.3 (CH₃); IR (neat): 2998, 2360, 2341, 1753, 1715, 1593, 1367, 1285, 1107, 1058, 911, 774, 759, 670 cm⁻¹; HRMS (ESI): m/z calc. for C₃₂H₃₂NO₁₁Se [M+NH₄]⁺ 578.1135; found 578.1138.

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

Rf = 0.3 (EtOAc / cyclohexane: 3/7); 48.8 mg, 92%. White solid. m. p.: 129.5-130.2 °C; [α]D 18 = −21.7 (c, 0.46, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 197.3 (C), 170.3 (C), 170.0 (C), 169.3 (C), 169.2 (C), 163.7 (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 (CH₂), 26.5 (CH₃), 20.7 (CH₂), 20.5 (CH₂); IR (neat): 2360, 2341, 2326, 1753, 1683, 1588, 1433, 1375, 1247, 1217, 1085, 1059, 1040, 958, 911, 773 cm⁻¹; HRMS (ESI): m/z calc. for C₃₂H₃₂O₁₀NaSe [M+Na]⁺ 553.0589; found 553.0592.

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

Rf = 0.3 (EtOAc / cyclohexane: 3/7); 47.0 mg, 86%. White solid. m. p.: 97.5-98.7 °C; [α]D 18 = −29.2 (c, 0.48, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 (CH2), 52.3 (CH3), 20.7 (CH3), 20.6 (CH3), 20.5 (2CH3); IR (neat): 2954, 2360, 2341, 1755, 1722, 1367, 1285, 1264, 1088, 977, 773, 750 cm⁻¹; HRMS (ESI): m/z calc. for C22H30NO11Se [M+NH₄]⁺ 564.0979; found 564.0980.

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

Rf = 0.3 (EtOAc /cyclohexane: 3/7); 49.2 mg, 88%, White solid. m. p.: 86.4-87.3 °C; [α]D 18 = -24.1 (c, 0.29, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 (CH₂), 61.2 (CH₂), 20.7 (CH₃), 20.6 (CH₃), 20.5 (2CH₃), 14.3 (CH₂); IR (neat): 2360, 2327, 1755, 1718, 1367, 1262, 1088, 910, 773, 750 cm⁻¹; HRMS (ESI): m/z calc. for C₂₂H₃₁NO₁₁Se [M+NH₄]⁺ 578.1135; found 578.1147.

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

Rf = 0.3 (EtOAc /cyclohexane: 1/1); 42.6 mg, 87%, White solid. m. p.: 120.5-121.9 °C; [α]D 18 = -22.1 (c, 0.95, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 (CH₂), 20.7 (2CH₃), 20.5 (2CH₃); IR (neat): 2360, 2341, 1746, 1570, 1543, 1407, 1248, 1212, 1086, 1060, 1039, 911, 806, 773 cm⁻¹; HRMS (ESI): m/z calc. for C₁₉H₂₃NO₁₁Se [M+NH₄]⁺ 490.0616; found 490.0610.

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

Rf = 0.3 (EtOAc /cyclohexane: 1/1); 44.6 mg, 85%, White solid. m. p.: 128.9-129.4 °C; [α]D 18 = -33.3 (c, 0.45, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 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$_2$), 20.9 (CH$_3$), 20.7 (CH$_3$), 20.6 (2CH$_3$); IR (neat): 2360, 2341, 1755, 1454, 1366, 1250, 1219, 1062, 1039, 912, 772, 669 cm$^{-1}$; HRMS (ESI): m/z calc. for C$_{23}$H$_{30}$NO$_3$Se [M+NH$_4$]$^+$ 545.1038; found 545.1031.

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

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\text{Rf} = 0.3 \text{ (EtOAc /cyclohexane: 3/7); 33.8 mg, 65\%, White solid. m. p.: 102.3-102.9 °C; } [\alpha]_D^{18} = -7.9 \text{ (c, 0.38, CHCl}_3\text{);} \quad \text{H NMR (300 MHz, CDCl}_3\text{) δ 7.54-7.57 (m, 2H), 6.82-6.85 (m, 2H), 5.37-5.39 (m, 1H), 5.21 (t, } J = 9.0 \text{ Hz, 1H), 4.97-5.02 (m, 1H), 4.78 (d, } J = 9.0 \text{ 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); \text{C NMR (75 MHz, CDCl}_3\text{) δ 170.3 (C), 170.1 (C), 170.0 (C), 169.4 (C), 160.3 (C), 137.5 (2CH), 117.2 (C), 114.5 (2CH), 75.4 (CH), 71.9 (CH), 68.1 (CH), 67.3 (CH), 61.5 (CH$_2$), 55.3 (CH$_3$), 20.9 (CH$_3$), 20.6 (CH$_3$), 20.6 (CH$_3$); IR (neat): 2360, 2341, 2325, 1748, 1492, 1373, 1247, 1219, 1081, 1054, 826, 773, 669 cm$^{-1}$; HRMS (ESI): m/z calc. for C$_{21}$H$_{29}$NO$_3$Se [M+NH$_4$]$^+$ 536.1029; found 536.1033.}

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

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\text{Rf} = 0.3 \text{ (EtOAc /cyclohexane: 3/7); 37.1 mg, 81\%, White solid. m. p.: 69.5-70.6 °C; } [\alpha]_D^{18} = +21.7 \text{ (c, 0.23, CHCl}_3\text{);} \quad \text{H NMR (300 MHz, CDCl}_3\text{) δ 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 \text{ 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); \text{C NMR (75 MHz, CDCl}_3\text{) δ 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$_3$), 20.9 (CH$_3$), 20.6 (2CH$_3$), 16.4 (CH$_3$); IR (neat): 2922, 2359, 2340, 1749, 1492, 1368, 1287, 1246, 1082, 10591030, 913, 759, 626 cm$^{-1}$; HRMS (ESI): m/z calc. for C$_{19}$H$_{28}$NO$_3$Se [M+NH$_4$]$^+$ 478.0980; found 478.0980.}

Rf = 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, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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), 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, 2340, 1749, 1702, 1481, 1373, 1301, 1287, 1246, 1082, 1060, 1059, 1030, 928, 773, 619 cm⁻¹; HRMS (ESI): m/z calc. for C₃₂H₄₄NO₁₇Se \([M+NH₄]^+\) 794.1769; found 794.1776.

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

Rf = 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, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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), 4.40-4.45 (m, 1H), 2.39 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl₃) 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), 71.0 (CH), 69.2 (CH), 62.7 (CH₂), 21.7 (CH₃). IR (neat): 2365, 2343, 2325, 1732, 1266, 1069, 773 cm⁻¹; HRMS (ESI): m/z calc. for C₄₁H₃₄NO₁₀Se \([M+NH₄]^+\) 784.1655; found 784.1652.

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

Rf = 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, CHCl₃); ¹H NMR (300 MHz, CDCl₃) 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); \(^{13}\)C NMR (75 MHz, CDCl₃) δ 170.5 (C), 169.9 (C), 169.7 (C), 169.5 (C), 136.7 (2CH₂), 135.0 (CH), 117.2 (C), 115.0 (2CH), 83.3 (CH), 71.3 (CH), 71.1 (CH), 69.6 (CH), 68.4 (CH), 61.9 (CH₂), 55.3 (CH₃), 20.8 (CH₃), 20.6 (CH₃), 20.6 (CH₃), 20.6 (CH₂); IR (neat): 2460, 2362, 1749, 1244, 1223, 1038, 778 cm⁻¹; HRMS (ESI): m/z calc. for C₂₁H₂₃NO₁₀Se \([M+NH₄]^+\) 536.1029; found 536.1029
(2R,3R,4S,5R,6S)-2-(acetoxyethyl)-6-((4-(4-(methylbenzoyl)piperazin-1-yl)phenyl)selanyl)tetrahydro-2H-pyran-3,4,5-triy triacetate (6a)

Rf = 0.2 (EtOAc /cyclohexane: 1/1); 62.0 mg, 90%. White solid. m. p.: 135.1-136.1 °C; [α]D 18 = –29.2 (c, 0.24, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 49.0 (2CH2), 48.9 (2CH2), 21.4 (CH3), 20.8 (2CH3), 20.6 (CH3); IR (neat): 2360, 2341, 2327, 1755, 1589, 1361, 1290, 1156, 1058, 1040, 910, 830, 773 cm⁻¹; HRMS (ESI): m/z calc. for C62H59N2O10Se [M+NH4]⁺ 691.1770; found 691.1785.

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

Rf = 0.2 (EtOAc /cyclohexane: 1/1); 58.3 mg, 95%. White solid. m. p.: 157.6-158.1 °C; [α]D 18 = –8.5 (c, 0.59, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 29.7 (CH2), 21.3 (CH3), 20.8 (2CH2), 20.7 (CH3), 20.5 (CH3), 20.5 (CH3), 20.5 (CH3); IR (neat): 2360, 2341, 1755, 1606, 1368, 1326, 1248, 1213, 1126, 1095, 1063, 1037, 1014, 980, 914, 830, 776 cm⁻¹; HRMS (ESI): m/z calc. for C30H36NO10Se [M+NH4]⁺ 650.1520; found 650.1520.

(2R,3R,4S,5R,6S)-2-(acetoxyethyl)-6-((4-(4-(methylbenzoyl)piperazin-1-yl)methyl)phenyl)selanyl)tetrahydro-2H-pyran-3,4,5-triy triacetate (6c)
Rf = 0.2 (EtOAc / cyclohexane: 1/1); 57.9 mg, 82%, White solid. m. p.: 133.3–134.4 °C; [α]D 18 = – 8.3 (c, 0.24, CHCl3); 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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 (CH2), 62.1 (CH2), 53.1 (4CH2), 21.3 (CH3), 20.7 (2CH3), 20.5 (CH3); IR (neat): 2360, 2341, 2327, 1755, 1632, 1459, 1299, 1248, 1059, 1040, 1001, 911, 753 cm⁻¹; HRMS (ESI): m/z calc. for C33H41N2O10Se [M+NH4]+ 705.1917; found 705.1917.

4. Reference

NMR spectra

\(^1\)H NMR (300 MHz) spectrum of 3a ((CD\(_3\)_2CO-d\(_6\))

\(^{13}\)C NMR (75 MHz) spectrum of 3a ((CD\(_3\)_2CO-d\(_6\))
$^1$H NMR (300 MHz) spectrum of 3b (CDCl$_3$)

$^{13}$C NMR (75 MHz) spectrum of 3b (CDCl$_3$)
**H NMR (300 MHz) spectrum of 3c (CDCl₃)**

**13C NMR (75 MHz) spectrum of 3c (CDCl₃)**
$^1$H NMR (300 MHz) spectrum of 3d (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3e (CDCl$_3$)
\[1^3\text{C NMR (75 MHz) spectrum of } 3e \text{ (CDCl}_3)\]

\[1^\text{H NMR (300 MHz) spectrum of } 3f \text{ (CDCl}_3)\]
$^{13}$C NMR (75 MHz) spectrum of 3f (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3g (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3g (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3h (CDCl$_3$)
C

C NMR (75 MHz) spectrum of 3h (CDCl₃)

H NMR (300 MHz) spectrum of 3i (CDCl₃)
$^{13}$C NMR (75 MHz) spectrum of 3i (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3j (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3j (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3k (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3k (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3l (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3l (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3m (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3m (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3n (CDCl$_3$)
$^{13}\text{C NMR (75 MHz) spectrum of 3n (CDCl}_3\text{)}$

$^1\text{H NMR (300 MHz) spectrum of 3o (CDCl}_3\text{)}$
$^{13}$C NMR (75 MHz) spectrum of $3o$ (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of $3p$ (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3p (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3q (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3q (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3r (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3r (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3s (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3s (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3t (CDCl$_3$)
$^{13}$C NMR (75 MHz) spectrum of 3u (CDCl$_3$)

$^1$H NMR (300 MHz) spectrum of 3v (CDCl$_3$)
$^1$H NMR (300 MHz) spectrum of 3w (CDCl$_3$)

$^{13}$C NMR (75 MHz) spectrum of 3w (CDCl$_3$)
$^1$H NMR (300 MHz) spectrum of 3x (CDCl$_3$)

$^{13}$C NMR (75 MHz) spectrum of 3x (CDCl$_3$)
$^1$H NMR (300 MHz) spectrum of 6a (CDCl$_3$)

$^{13}$C NMR (75 MHz) spectrum of 6a (CDCl$_3$)
$^{1}$H NMR (300 MHz) spectrum of 6b (CDCl$_3$)

$^{13}$C NMR (75 MHz) spectrum of 6b (CDCl$_3$)
$^{1}H$ NMR (300 MHz) spectrum of 6c (CDCl$_3$)

$^{13}C$ NMR (75 MHz) spectrum of 6c (CDCl$_3$)