Supporting Information
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Supplementary Data for

Convenient and Rapid Synthesis of
3-Selenocyanato-4H-chromen-4-ones

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1-General remarks.

Melting points were determined with a Büchi B-540 apparatus and are uncorrected. HRMS were carried out at the Spectropole, Faculté des Sciences et Techniques de Saint-Jérôme, Marseille. $^1$H NMR (250 MHz, reference CDCl$_3$ δ = 7.26 or DMSO-$_d_6$ δ = 2.50) and $^{13}$C NMR spectra (62.5 MHz, reference CDCl$_3$ δ = 77.16 or DMSO-$_d_6$ δ = 39.5) were recorded on a Bruker ARX 200 spectrometer in CDCl$_3$ at the Faculté de Pharmacie de Marseille. The following adsorbent was used for column chromatography: silica gel 60 (Merck, particle size 0.063-0.200 mm, 70-230 mesh ASTM). TLC was performed on 5 cm × 10 cm aluminum plates coated with silica gel 60F-254 (Merck) using an appropriate eluent. Petroleum ether (PE) used in this study refers to the fraction boiling in the range 40-65 °C. HRMS spectra were recorded on QStar Elite (Applied Biosystems SCIEX) spectrometer. PEG was the matrix for HRMS. LC/MS analyses were performed at the Faculté de Pharmacie de Marseille on an Accela High System ® chain U-HPLC coupled with a Thermo MSQ Plus ® simple quadrupole. A Thermo Hypersil Gold ® 50 × 2.1 mm chromatographic column was used (SiO$_2$ C18) with 1.9 μm diameter particles. The volume of sample injected on the column was 1 μL. The analysis was an eight-minute run with a MeOH-H$_2$O gradient eluent from 50:50 to 95:05, with following solvent gradient: t = 0 min, H$_2$O-MeOH 50:50; 0 < t < 4 min, linear increase in the proportion of H$_2$O to a ratio H$_2$O-MeOH 95:5; 4 < t < 6 min, H$_2$O-MeOH 95:5; 6 < t < 7 min, linear decrease in the proportion of H$_2$O to return to a ratio H$_2$O-MeOH 50:50; 6 < t < 7 min, H$_2$O-MeOH 50:50. The H$_2$O used was buffered with 5 mM NH$_4$OAc.

2-General procedure for the sequential one-pot selenocyanation of $o$-hydroxyacetophenone:

A mixture of $o$-hydroxyacetophenone 1a (136 mg, 1 mmol, 1 equiv.) and dimethylformamide dimethylacetal (120 mg, 1 mmol, 1 equiv.) was heated for 2 hours at 100°C. After cooling to 25°C, a pre-prepared solution of malononitrile (66 mg, 1 mmol, 1 equiv.) and SeO$_2$ (332 mg, 3 mmol, 3 equiv.) in DMSO (1 mL), stirred at 25°C for 20 min, was added at 25 °C. The reaction mixture was stirred for a further 30 min, then water was added (3 mL). The resulting precipitate was filtered off, washed with water (3 x 10 mL) and dried under a fume hood overnight at 25°C to give pure product 3a.
3- Data of 3-selenocyanato-4H-chromen-4-one (3a-3p):

3-selenocyanato-4H-chromen-4-one (3a)

![Chemical Structure](image)

Yield: 76%, brown solid, mp 136-137°C.

$^1$H NMR (250 MHz, CDCl$_3$) δ ppm 8.26 (s, 1H), 8.20 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.79 (dt, $J = 8.4$ 1.7 Hz, 1H), 7.56 (dt, $J = 8.4$ Hz, 1H), 7.51 (dt, $J = 7.1$, 1.1 Hz, 1H).

$^{13}$C NMR (62.5 MHz, CDCl$_3$) δ ppm 174.3 (CO), 156.7 (C), 153.1 (CH), 135.1 (CH), 126.5 (CH), 125.9 (CH), 122.0 (C), 118.6 (CH), 112.7 (C), 100.0 (CN).

HRMS (ESI): m/z calcd for [C$_{10}$H$_5$NO$_2$Se+H]$^+$: 251.9559, found: 251.9557.

6-fluoro-3-selenocyanato-4H-chromen-4-one (3b)

![Chemical Structure](image)

Yield: 71%, pinkish solid, mp 165-166°C.

$^1$H NMR (250 MHz, CDCl$_3$) δ ppm 8.27 (s, 1H), 7.83 (dd, $J = 7.8$, 3.0 Hz, 1H), 7.62-7.45 (m, 2H).

$^{13}$C NMR (62.5 MHz, DMSO-$_d_6$) δ ppm 170.5 (d, $^4$J$_{C-F}$ = 2.3 Hz, CO), 160.8 (CH), 159.4 (d, $^1$J$_{C-F}$ = 245.8 Hz, C), 152.4 (C), 123.8 (d, $^3$J$_{C-F}$ = 7.6 Hz, C), 123.3 (d, $^2$J$_{C-F}$ = 25.5 Hz, CH), 121.7 (d, $^3$J$_{C-F}$ = 8.5 Hz, CH), 110.7 (C), 110.2 (d, $^2$J$_{C-F}$ = 24.0 Hz, CH), 103.7 (CN).

HRMS (ESI): m/z calcd for [C$_{10}$H$_4$NO$_2$FSe+H]$^+$: 269.9464, found: 269.9462.

6-chloro-3-selenocyanato-4H-chromen-4-one (3c)

![Chemical Structure](image)

Yield: 75%, pinkish solid, mp 184-186°C.

$^1$H NMR (250 MHz, CDCl$_3$) δ ppm 8.26 (s, 1H), 8.16 (d, $J = 2.5$ Hz, 1H), 7.72 (dd, $J = 9.0$, 2.6 Hz, 1H), 7.53 (d, $J = 9.0$ Hz, 1H).

$^{13}$C NMR (62.5 MHz, DMSO-$_d_6$): δ ppm 172.1 (CO), 160.8 (CH), 154.5 (C), 135.0 (CH), 130.9 (C), 124.4 (CH), 123.7 (C), 121.3 (CH), 111.4 (C), 103.7 (CN).

HRMS (ESI): m/z calcd for [C$_{9}$H$_5$ClNO$_2$Se+H]$^+$: 285.9166, found: 285.9163.
6-bromo-3-selenocyanato-4H-chromen-4-one (3d)

![Chemical Structure](image)

Yield: 69%, pinkish solid, mp 200-202°C.

$^1$H NMR (250 MHz, DMSO-$d_6$) δ ppm 8.97 (s, 1H), 8.18 (d, $J = 2.4$ Hz, 1H), 8.05 (dd, $J = 9.0, 2.5$ Hz, 1H), 7.74 (d, $J = 9.0$ Hz, 1H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$) δ ppm 171.9 (CO), 160.8 (CH), 154.9 (C), 137.7 (CH), 127.5 (CH), 124.0 (C), 121.4 (CH), 118.9 (C), 111.4 (C), 103.6 (CN).

HRMS (ESI): m/z calcd for [C$_{10}$H$_4$NO$_2$BrSe+H]$^+$: 329.8660, found: 329.8658.

6-methyl-3-selenocyanato-4H-chromen-4-one (3e)

![Chemical Structure](image)

Yield: 75%, yellow solid, mp = 145°C.

$^1$H NMR (250 MHz, CDCl$_3$) δ ppm 8.23 (s, 1H), 7.97 (s, 1H), 7.60 (d, $J = 8.7, 2.0$ Hz, 1H), 7.57 (d, $J = 8.6$ Hz, 1H), 2.49 (s, 3H).

$^{13}$C NMR (62.5 MHz, CDCl$_3$): δ ppm 174.3 (C), 155.1 (C), 153.0 (CH), 136.8 (CH), 136.4 (CH), 125.1 (CH), 121.8 (C), 118.3 (CH), 112.5 (C), 100.1 (C), 21.1 (CH$_3$).

HRMS (ESI): m/z calcd for [C$_{11}$H$_8$NO$_2$Se+H]$^+$: 265.9715, found: 265.9716.

6-methoxy-3-selenocyanato-4H-chromen-4-one (3f)

![Chemical Structure](image)

Yield: 77%, pinkish solid, mp 145-146°C

$^1$H NMR (250 MHz, CDCl$_3$) δ ppm 8.25 (s, 1H), 7.52 (dd, $J = 9.2, 3.0$ Hz, 2H), 7.35 (dd, $J = 9.2$, 3.0 Hz, 1H), 3.91 (s, 3H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$) δ ppm 168.7 (C), 156.1 (CH), 153.2 (CH), 146.7 (CH), 120.2 (CH), 119.3 (C), 116.4 (CH), 106.5 (C), 101.1 (CH), 99.8 (CN), 51.9 (OCH$_3$).

HRMS (ESI): m/z calcd for [C$_{11}$H$_7$NO$_3$Se+H]$^+$: 281.9664, found: 281.9667.
6-cyano-3-selenocyanato-4H-chromen-4-one (3g)

Yield: 72%, orange solid, mp 230°C.

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm 8.55 (d, $J = 2.1, 1$H), 8.29 (s, 1H), 8.00 (dd, $J = 8.8, 2.1$ Hz, 1H), 7.69 (d, $J = 8.8$ Hz, 1H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ ppm 171.9 (CO), 160.9 (CH), 159.5 (C), 157.9 (CH), 137.6 (CH), 131.3 (CH), 123.0 (C), 120.7 (CH), 117.6 (C), 112.2 (C), 109.5 (CN), 103.6 (CN).

HRMS (ESI): m/z calcd for [C$_{11}$H$_{14}$N$_2$O$_2$Se+H]$^+$: 276.9511, found: 276.9511.

3-selenocyanato-4H-benzo[h]chromen-4-one (3h)

Yield: 81%, dark brown, mp 137-139°C.

$^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ ppm 9.07 (s, 1H), 8.45 (dd, $J = 7.3, 2.1$ Hz, 1H), 8.16 (dd, $J = 7.1, 1.9$ Hz, 1H), 8.01 (s, 2H), 7.86-7.80 (m, 2H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$): $\delta$ ppm 172.8 (CO), 159.0 (CH), 153.4 (C), 135.5 (C), 130.2 (C), 128.4 (CH), 128.1 (CH), 126.5 (CH), 123.0 (C), 121.9 (CH), 120.1 (CH), 118.8 (C), 113.2 (C), 103.5 (CN).

HRMS (ESI): m/z calcd for [C$_{14}$H$_7$NO$_2$Se+H]$^+$: 301.9715, found: 301.9718.

7-fluoro-3-selenocyanato-4H-chromen-4-one (3i)

Yield: 73%, pinking solid, mp 172-173°C.

$^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ ppm 8.94 (s, 1H), 8.17 (dd, $J = 8.9, 6.3$ Hz 1H), 7.74 (dd, $J = 9.5, 2.4$ Hz, 1H), 7.47 (dt, $J = 8.8, 2.4$ Hz, 1H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$) $\delta$ ppm 172.2 (CO), 165.3 (d, $^1$J$_{C-F} = 253.4$ Hz, C), 160.7 (CH), 157.0 (d, $^3$J$_{C-F} = 14.1$ Hz, C), 128.5 (d, $^3$J$_{C-F} = 11.1$ Hz, CH), 119.7 (d, $^4$J$_{C-F} = 2.3$ Hz, C), 115.2 (d, $^2$J$_{C-F} = 23.2$ Hz, CH), 111.6 (C), 105.9 (d, $^2$J$_{C-F} = 26.1$ Hz, CH), 103.6 (CN).

HRMS (ESI): m/z calcd for [C$_{10}$H$_4$NO$_2$FSe+H]$^+$: 269.9464, found: 269.9462.
7-chloro-3-selenocyanato-4\(H\)-chromen-4-one (3j)

Yield: 75\%, pinking solid, mp 198-200\(^\circ\)C.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 8.22 (s, 1H), 8.14 (d, \(J = 2.5\) Hz 1H), 7.69 (dd, \(J = 8.9, 2.6\) Hz, 1H), 7.50 (d, \(J = 8.6\) Hz, 1H).

\(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)) \(\delta\) ppm 172.4 (CO), 160.6 (CH), 156.1 (C), 139.3 (C), 127.3 (CH), 127.1 (CH), 121.4 (C), 118.7 (CH), 111.7 (C), 103.6 (CN).

HRMS (ESI): m/z calcd for \([C_{10}H_4NO_2ClSe+H]^+\): 285.9166, found: 285.9167.

7-bromo-3-selenocyanato-4\(H\)-chromen-4-one (3k)

Yield: 64\%, pinkish solid, mp 205\(^\circ\)C.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 8.22 (s, 1H), 8.06 (d, \(J = 8.5\) Hz, 1H), 7.76 (d, \(J = 1.7\) Hz, 1H), 7.62 (dd, \(J = 8.5, 1.7\) Hz, 1H).

\(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)) \(\delta\) ppm 172.5 (CO), 160.6 (CH), 156.0 (C), 129.9 (CH), 128.2 (C), 127.3 (CH), 121.7 (C), 121.6 (CH), 111.7 (C), 103.6 (CN).

HRMS (ESI): m/z calcd for \([C_{10}H_4BrNO_2Se+H]^+\): 329.8660, found: 329.8659.

7-methyl-3-selenocyanato-4\(H\)-chromen-4-one (3l)

Yield: 76\%, pinking solid, mp 161-162\(^\circ\)C.

\(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) ppm 8.21 (s, 1H), 8.07 (d, \(J = 2.5\) Hz, 1H), 7.35-7.30 (m, 2H), 2.53 (s, 3H).

\(^{13}\)C NMR (62.5 MHz, DMSO-\(d_6\)) \(\delta\) ppm 172.7 (CO), 160.1 (C), 156.0 (C), 146.3 (CH), 127.9 (CH), 125.2 (CH), 120.3 (C), 118.2 (CH), 111.2 (C), 103.7 (CN), 21.3 (CH\(_3\)).

HRMS (ESI): m/z calcd for \([C_{11}H_7NO_2Se+H]^+\): 265.9715, found: 265.9717.
7-methoxy-3-selenocyanato-4H-chromen-4-one (3m)

Yield: 78%, orange solid, mp 166-167°C.

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm 8.16 (s, 1H), 8.09 (d, $J = 9.0$ Hz, 1H), 7.06 (dd, $J = 9.0$, 2.4 Hz, 1H), 6.91 (d, $J = 2.3$ Hz, 1H), 3.94 (s, 3H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$) $\delta$ ppm 172.2 (CO), 164.4 (CH), 159.7 (C), 157.8 (C), 126.9 (CH), 116.2 (C), 115.8 (CH), 111.3 (C), 103.7 (CN), 101.0 (CH), 56.3 (OCH$_3$).

HRMS (ESI): m/z calcd for [C$_{11}$H$_7$NO$_3$Se+H]$^+$: 281.9664, found: 281.9664.

6,8-dibromo-3-selenocyanato-4H-chromen-4-one (3n)

Yield: 65%, brown solid, mp 135 °C.

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm 8.34 (s, 1H), 8.27 (d, $J = 2.3$ Hz, 1H), 8.12 (d, $J = 2.3$ Hz, 1H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$) $\delta$ ppm 171.6 (CO), 160.8, 151.9, 139.9, 127.3, 124.8, 118.9, 113.3, 111.9, 103.6 (CN).

HRMS (ESI): m/z calcd for [C$_{10}$H$_3$Br$_2$NO$_2$Se+H]$^+$: 409.7748, found: 409.7748.

6,7-dimethoxy-3-selenocyanato-4H-chromen-4-one (3o)

Yield: 56%, brown solid, mp 216-218°C.

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm 8.17 (s, 1H), 7.45 (s, 1H), 6.93 (s, 1H), 4.00 (s, 3H), 3.97 (s, 3H).

$^{13}$C NMR (62.5 MHz, CDCl$_3$) $\delta$ ppm 173.2 (CO), 155.6 (C), 153.3 (C), 151.8 (CH), 148.6 (C), 115.5 (C), 112.5 (C), 103.9 (CH), 100.3 (CN), 99.8 (CH), 56.8 (OCH$_3$), 56.6 (OCH$_3$).

HRMS (ESI): m/z calcd for [C$_{12}$H$_9$NO$_4$Se+H]$^+$: 311.9770, found: 311.9771.
6-chloro-7-methyl-3-selenocyanato-4H-chromen-4-one (3p)

Yield: 75%, pinking brown, mp 191-192°C.

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm 8.21 (s, 1H), 8.14 (s, 1H), 7.45 (s, 1H), 2.54 (s, 3H).

$^{13}$C NMR (62.5 MHz, DMSO-$d_6$) $\delta$ ppm 171.9 (CO), 160.6 (CH), 154.4 (C), 143.8 (C), 131.7 (C), 124.6 (CH), 121.7 (CH), 121.0 (C), 111.2 (C), 103.7 (CN), 20.2 (CH$_3$).

HRMS (ESI): m/z calcd for [C$_{11}$H$_6$NO$_2$Se+H]$^+$: 299.9323, found: 299.9321.

Procedure for the synthesis of 3-selenocyanato-4H-chromen-4-one (5a):

To a solution of 3-selenocyanato-4H-chromen-4-one (3a) (125 mg, 0.5 mmol, 1 equiv.) in MeOH (2 mL) was added NaBH$_4$ (24 mg, 1.26 mmol, 1.25 equiv.) at 25 °C. After 10 min stirring, acetylchloride (90 ml, 1.3 mmol, 2.6 equiv.) was added. The reaction mixture was stirred for a further 30 min, then a saturated ammonium chloride solution was added (5 mL). The product was extracted with dichloromethane (2 x 10 mL). The organic layers were dried over sodium sulfate filtered and then evaporated under vacuum to give the pure product Se-(4-oxo-4H-chromen-3-yl)ethaneselenoate (108 mg, 80% yield) (5a).

Se-(4-oxo-4H-chromen-3-yl)ethaneselenoate (5a)

Yield: 80%, orange solid, 107-108°C.

$^1$H NMR (250 MHz, CDCl$_3$) $\delta$ ppm 8.23 (dd, $J = 8.0, 1.3$ Hz, 1H), 8.15 (s, 1H), 7.45 (dt, $J = 7.1, 1.7, 1H$), 7.39-7.49 (m, 2H), 2.51 (s, 3H).

$^{13}$C NMR (62.5 MHz, CDCl$_3$) $\delta$ ppm 194.6 (CO), 174.8 (C), 160.0 (CH), 156.4 (C), 134.2 (CH), 126.6 (CH), 125.9 (CH), 123.8 (C), 118.2 (CH), 113.8 (CN), 34.0 (CH$_3$).

HRMS (ESI): m/z calcd for [C$_{11}$H$_8$O$_3$Se+H]$^+$: 268.9712, found: 268.9716.
Procedure for the synthesis of $o$-hydroxybenzoic acid (6a):

To a solution of 3-selenocyanato-4H-chromen-4-one (3a) (250 mg, 1 mmol, 1 equiv.) in DCM (10 mL) was added slowly H$_2$O$_2$ (35% w/w aq. sol. stab.) (0.1 mL, 1 equiv.) at 25 °C. After overnight stirring, other H$_2$O$_2$ (35% w/w aq. sol. stab.) (0.1 mL, 1 equiv.) was added at 25 °C. The reaction mixture was stirred for a further 6 h, then water was added (10 mL). The product was extracted with dichloromethane (2 x 10 mL). The organic layers were dried over sodium sulfate filtered and then evaporated under vacuum to give the pure product $o$-hydroxybenzoic acid (6a). The structure and purity of 6a were confirmed by comparison of their spectral data to the literature (NMR, mass spectrum and fusion point).