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Synthesis of 3-selenyl-isoflavones from 2-hydroxyphenyl enaminones using trichloroisocyanuric acid (TCCA): a sustainable approach

Carlos V. Doerner,[a] José S. S. Neto,[b] Climei R. Cabreira,[c] Sumbal Saba,[b] Louis P Sandjo,[a] Jamal Rafique,[b,c*], Antonio L. Braga[a*] and Francisco F. de Assis[a*]

[a] *Department of Chemistry, Federal University of Santa Catarina (UFSC), Campus Trindade, 8804-900, Florianópolis-SC, Brazil.*

[b] *Institute of Chemistry, Federal University of Goiás (UFG), 74690-900, Goiânia-GO, Brazil.*

[c] *Institute of Chemistry (INQUI), Federal University of Mato Grosso do Sul (UFMS), 79074-460, Campo Grande-MS, Brazil.*

Contents

1. General Remarks

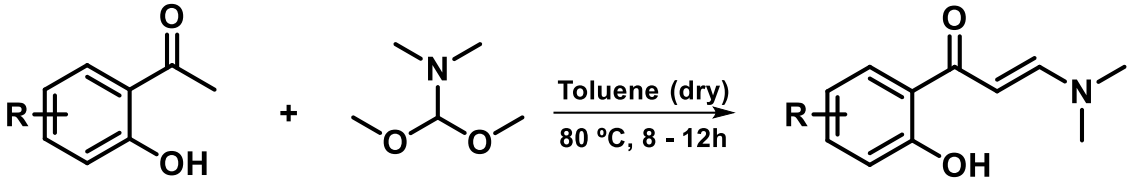
Starting materials obtained from commercial suppliers unless stated otherwise. Column chromatography was performed using silica gel 60 (diameter 0.05 - 0.10 mm) Macherey-Nagel. Thin layer chromatography (TLC) was performed using Macherey-Nagel pre-coated TLC sheets ALUGRAM Ⓡ Xtra SIL with layer of 0.20 mm. Visualization was achieved by UV fluorescence, iodine chamber and acidic vanillin**.**

The melting points were taken on a MQAPF-301 melting pointapparatus, uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Varian NMR AS 400 spectrometer and, with the samples dissolved in $CDCl_3$ or DMSO-d_6. Chemical shifts are informed in ppm downfield from the signal of TMS, used as internal standard, and the coupling constants (J) are expressed in Hertz (Hz). High-resolution mass spectral data were obtained on a Bruker microTOF-Q IIT instrument and Xevo G2-S QTOF (Waters) on ESI + mode.

2. General Procedures

2.1. General procedure for the synthesis of 2-hydroxyphenyl enaminones:

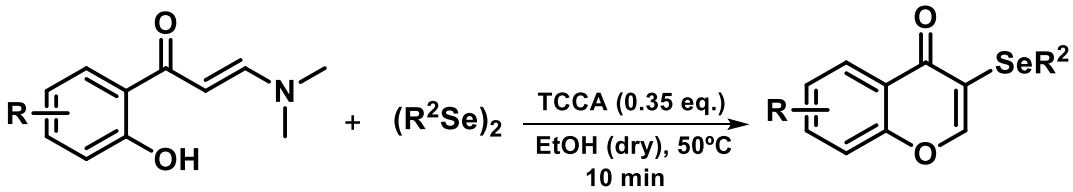
All the 2-hydroxyphenyl enaminones were synthesized using a method already described in the literature.[1]



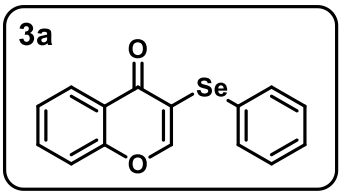
An oven dried sealed tube equipped with a stirring bar, filled with ketones (2.0 mmol), followed by of *N*,*N*-Dimethylformamide dimethyl acetal (DMF-DMA) (8.0 mmol) in toluene (2 mL). The reaction was kept under magnetic agitation at 80 °C for 8 – 12 h until the complete conversion of starting material as monitored by TLC. The reaction mixture was then concentrated and was purified by flash column chromatography (sílica gel, hexane/EtOAc).

2.2. General procedure for obtaining the 3-selenyl isoflavanoids (3):

To a test tube equipped with a magetic stirring bar were added the trichloroisocyanuric acid (8 mg, 0,034 mmol), the corresponding disselenide (0,05 mmol) and the dry etanol (2 mL). The system was then stirred at room temperature for approximately 5 minutes, until all of the trichloroisocyanuric acid was dissolved. After that, the corresponding *o*-hydroxyarylenaminone (0,1 mmol) was added and the system allowed to react for 5 minutes at 50 ºC. The reaction mixture was then concentrated and the desired product was obtained through flash column chromatography (silica gel, hexane:EtOAc).

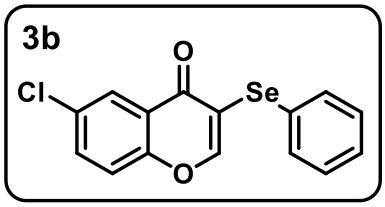


3. Characterization Data:



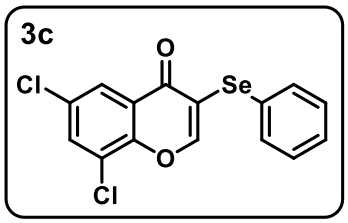
3-(phenylselanyl)-4*H*-chromen-4-one (3a):

Yield: (27 mg, 90%); **Physical Appearance**: White Solid; **mp:** 59–60 ºC (lit.,[2] 59-60 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.82 (s, 1H), 7.62 – 7.49 (m, 3H), 7.34 (d, *J* = 8.0, 2H), 7.27 – 7.18 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.2, 156.4, 155.8, 133.9, 133.8, 129.6, 128.2, 128.1, 126.4, 125.6, 123.2, 118.1, 117.9.



6-chloro-3-(phenylselanyl)-4*H*-chromen-4-one (3b):

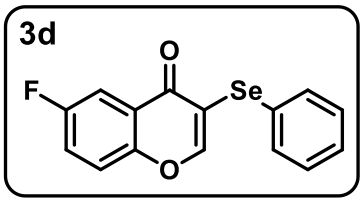
Yield: (21 mg, 63%); **Physical Appearance**: White Solid; mp: 105 -107 ºC (lit.,[2] 105-106°C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 2.6 Hz, 1H), 7.77 (s, 1H), 7.57 – 7.51 (m, 3H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.28 – 7.21 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.1, 155.4, 154.6, 134.1, 134.0, 131.4, 129.6, 128.3, 127.5, 125.6, 123.9, 119.8, 118.1.



6,8-dichloro-3-(phenylselanyl)-4*H*-chromen-4-one (3c):

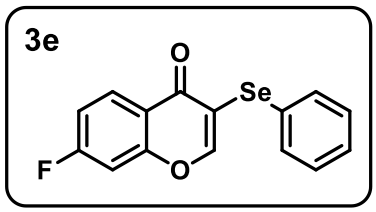
Yield: (28 mg, 76%); **Physical Appearance:** White Solid; **mp:** 114-116 ºC (lit.,[2] 113-115 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 2.5 Hz, 1H), 7.70 (s, 1H), 7.64 (d, *J* = 2.5 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.33 – 7.21 (m, 3H). **^{13}C NMR**

(100 MHz, $CDCl_3$) *δ* 173.6, 154.2, 150.7, 134.8, 134.0, 131.1, 129.8, 128.8, 126.7, 124.5, 124.4, 119.4.



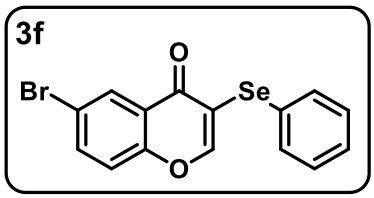
6-fluoro-3-(phenylselanyl)-4*H*-chromen-4-one (3d):

Yield: (26 mg, 81%); **Physical Appearance:** White Solid; **mp:** 120-121 ºC (lit.,[3] 120-121 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.90 – 7.84 (m, 2H), 7.64 – 7.58 (m, 2H), 7.48 – 7.29 (m, 5H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ* 174.6, 159.2 (d, $J_{C\text{-}F}$ = 247.7 Hz), 155.7, 152.5 (d, $J_{C\text{-}F}$ = 32.0 Hz) , 134.0, 129.6, 128.3, 127.8, 124.2 (d, $J_{C\text{-}F}$ = 9.8 Hz), 122.2 (d, $J_{C\text{-}F}$ = 27.5 Hz) , 120.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 117.4, 111.1 (d, $J_{C\text{-}F}$ = 24.0 Hz).



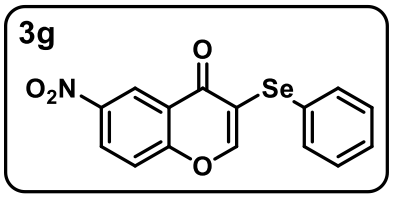
7-fluoro-3-(phenylselanyl)-4*H*-chromen-4-one (3e):

Yield: (25 mg, 80%); **Physical Appearance:** Light Brown Solid; **mp:** 105-107 ºC (lit.,[2] 105-107 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 8.27 (dd, *J* = 8.9, 6.3 Hz, 1H), 7.82 (s, 1H), 7.66 – 7.59 (m, 2H), 7.33 (m, 3H), 7.22 – 7.08 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ* 174.3, 165.6 (d, $J_{C\text{-}F}$ = 256.1 Hz), 157.3 (d, $J_{C\text{-}F}$ = 12.0 Hz), 155.3, 134.2, 129.7, 129.0 (d, $J_{C\text{-}F}$ = 10.4 Hz), 128.4, 127.7, 119.9 (d, $J_{C\text{-}F}$ = 2.7 Hz), 118.5, 114.4 (d, $J_{C\text{-}F}$ = 22.8 Hz), 104.7 (d, $J_{C\text{-}F}$ = 25.3 Hz).



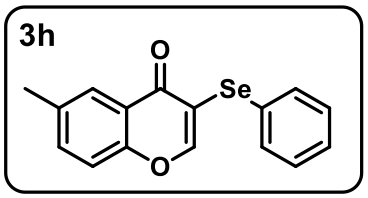
6-bromo-3-(phenylselanyl)-4*H*-chromen-4-one (3f):

Yield: (24 mg, 60%); **Physical Appearance:** White Solid; **mp:** 104-106 ºC (lit.,[2] 104-105 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36 (d, J = 2.5 Hz, 1H), 7.85 (s, 1H), 7.75 (dd, J = 8.9, 2.5 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.34 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.0, 155.4, 155.1, 136.8, 134.2, 129.7, 128.9, 128.4, 127.6, 124.3, 120.1, 118.9, 118.3.



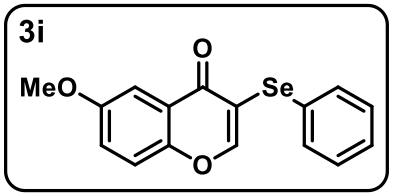
6-nitro-3-(phenylselanyl)-4*H*-chromen-4-one (3g):

Yield: (24 mg, 69%); **Physical Appearance:** Green Solid; **mp**: 115-116 ºC (lit.,[3] 115-116 °C); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.76 – 8.65 (m, 2H), 8.58 (dt, J = 9.2, 2.4 Hz, 1H), 7.94 (dd, J = 9.2, 1.8 Hz, 1H), 7.49 (dt, J = 7.0, 1.6 Hz, 2H), 7.36 – 7.24 (m, 3H). **^{13}C NMR (100 MHz, DMSO)** δ 173.9, 159.8, 159.4, 145.1, 132.0, 130.0, 129.2, 129.1, 127.9, 123.1, 122.1, 121.4, 116.1.



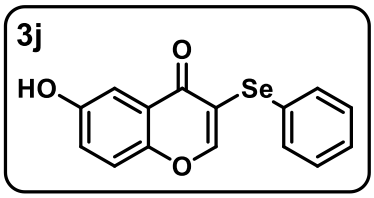
6-methyl-3-(phenylselanyl)-4*H*-chromen-4-one (3h):

Yield: (17 mg, 54%); **Physical Appearance**: Beige Solid; **mp**: 99-100 ºC (lit.,[2] 100-101 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (s, 1H), 7.83 (s, 1H), 7.54 – 7.49 (m, 2H), 7.40 (dd, J = 8.6, 2.3 Hz, 1H), 7.28 – 7.18 (m, 4H), 2.37 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.2, 155.9, 154.6, 135.6, 135.0, 133.6, 129.4, 128.3, 127.9, 125.5, 122.8, 117.7, 117.4, 20.9.



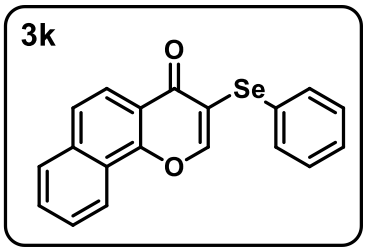
6-methoxy-3-(phenylselanyl)-4*H*-chromen-4-one (3i):

Yield: (17 mg, 53%); **Physical Appearance:** Beige Solid; **mp:** 100-101 ºC (lit.,[2] 99-101 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.60 (dd, J = 6.5, 2.9 Hz, 3H), 7.38 (d, J = 9.1 Hz, 1H), 7.34 – 7.23 (m, 4H), 3.90 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.0, 157.4, 151.3, 134.4, 129.8, 129.2, 127.1, 124.5, 124.1, 119.6, 119.0, 105.5, 56.0.



6-hydroxy-3-(phenylselanyl)-4*H*-chromen-4-one (3j):

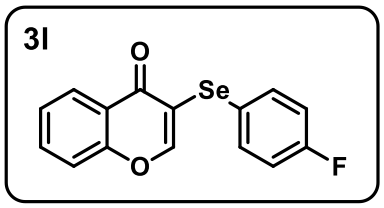
Yield: (11 mg, 36%); **Physical Appearance:** White Solid; **mp:** 186-187 ºC; **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.14 (s, 1H), 8.58 (s, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.42 (m, 2H), 7.29 (m, 5H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 174.4, 159.6, 155.7, 150.2, 131.4, 130.2, 129.9, 127.5, 124.2, 123.9, 120.4, 113.9, 108.4. **HR-MS** *m/z* calcd for $C_{15}H_{10}O_3Se$ $[M + Na]^+$ 340.9688; found, 340.9688.



3-(phenylselanyl)-4*H*-benzo[h]chromen-4-one (3k):

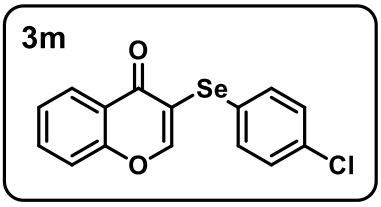
Yield: (21 mg, 61%); **Physical Appearance:** Brown Solid; **mp:** 111-113 ºC (lit.,[2] 111-113 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 – 8.38 (m, 1H), 8.17 (d, J =

8.8 Hz, 1H), 7.99 – 7.89 (m, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.63 (m, 4H), 7.43 – 7.31 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 175.0, 153.9, 135.8, 134.5, 129.7, 129.5, 128.4, 128.2, 127.6, 127.3, 125.7, 123.9, 122.2, 121.1, 120.2, 119.2



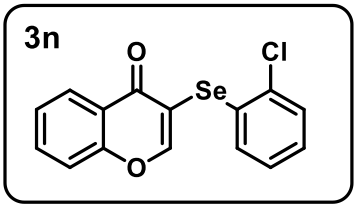
3-((4-fluorophenyl)selanyl)-4*H*-chromen-4-one (3l):

Yield: (23 mg, 72%); **Physical Appearance:** White Solid; **mp:** 85-87 ºC (lit.,[2] 84-85 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 8.24 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.75 – 7.58 (m, 3H), 7.54 – 7.39 (m, 2H), 7.08 – 6.96 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ* 175.20, 162.9 (d, $J_{C\text{-}F}$ = 242.3 Hz), 156.4, 155.6, 152.1, 136.4 (d, $J_{C\text{-}F}$ = 8.2 Hz), 133.9, 126.3, 125.7, 123.2, 122.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 118.1, 116.8 (d, $J_{C\text{-}F}$ = 21.6 Hz).



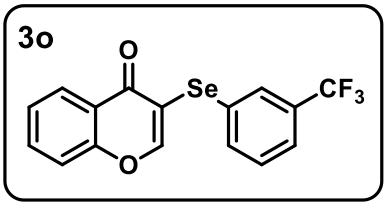
3-((4-chlorophenyl)selanyl)-4*H*-chromen-4-one (3l):

Yield: (21 mg, 63%); **Physical Appearance:** Beige Solid; **mp:** 83-85 ºC (lit.,[2] 84-85 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 8.24 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.03 (s, 1H), 7.75 – 7.68 (m, 1H), 7.56 – 7.41 (m, 4H), 7.29 – 7.24 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** *δ* 175.1, 156.5, 156.4, 134.8, 134.4, 134.0, 129.7, 126.7, 126.4, 125.8, 123.3, 118.1, 117.2.



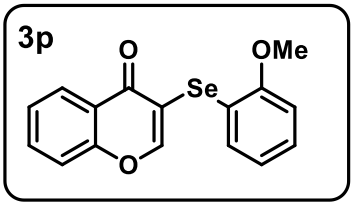
3-((2-chlorophenyl)selanyl)-4*H*-chromen-4-one (3n):

Yield: (18 mg, 54%)**; Physical Appearance:** Off-White Solid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (dd, J = 8.0, 1.7 Hz, 1H), 8.02 (s, 1H), 7.69 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.48 – 7.41 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.1, 156.5, 156.4, 134.8, 134.4, 134.0, 129.7, 126.7, 126.4, 125.7, 123.3, 118.1, 117.2.



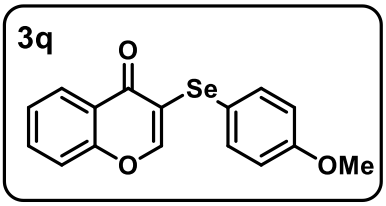
3-((3-(trifluoromethyl)phenyl)selanyl)-4*H*-chromen-4-one (3o):

Yield: (21 mg, 58%); **Physical Appearance:** White Solid; **mp:** 108-110 ºC (lit.,[2] 110-111 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (dd, J = 8.0, 1.7 Hz, 1H), 8.17 (d, J = 0.9 Hz, 1H), 7.83 (s, 1H), 7.79 – 7.70 (m, 2H), 7.58 – 7.37 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 174.9, 157.5, 156.4, 136.1, 134.1, 131.63 (q, J_{C-F} = 32.5 Hz), 130.2, 129.7, 129.30 (q, J_{C-F} = 3.3 Hz),126.4, 125.8, 124.58 (q, J_{C-F} = 3.5 Hz), 126.3 (q, J_{C-F} = 271Hz), 123.4, 118.2, 116.3



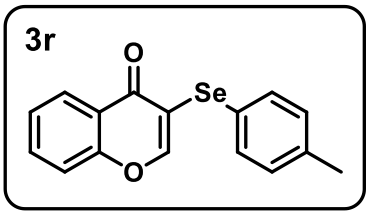
3-((2-methoxyphenyl)selanyl)-4*H*-chromen-4-one (3p):

Yield: (17 mg, 51%); **Physical Appearance:** Beige Solid; **mp:** 110-111 ºC (lit.,[2] 110-111 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (m, 1H), 8.10 (s, 1H), 7.75 – 7.67 (m, 1H), 7.52 – 7.42 (m, 2H), 7.30 – 7.15 (m, 2H), 6.91 – 6.81 (m, 2H), 3.91 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.4, 157.7, 157.5, 156.5, 133.8, 131.8, 128.6, 126.5, 125.6, 123.4, 121.8, 118.5, 118.1, 114.9, 110.8, 56.0.



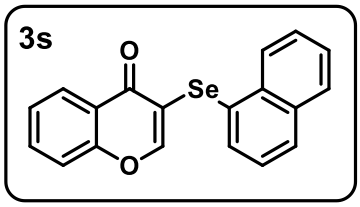
3-((4-methoxyphenyl)selanyl)-4*H*-chromen-4-one (3q):

Yield: (18 mg, 54%)**; Physical Appearance:** Beige Solid; **mp:** 92-94 ºC (lit.,[2] 92-94 °C)**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.69 – 7.61 (m, 4H), 7.46 – 7.38 (m, 2H), 6.89 (d, *J* = 4.8, 3.3 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.3, 160.2, 156.3, 153.9, 137.1, 133.7, 126.2, 125.4, 122.9, 119.4, 118.0, 117.1, 115.4, 55.3.



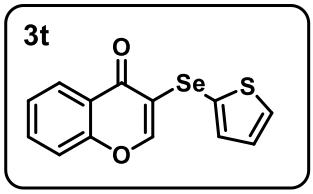
3-(p-tolylselanyl)-4*H*-chromen-4-one (3r):

Yield: (15 mg, 48%)**; Physical Appearance:** White Solid; **mp:** 87-89 ºC (lit.,[2] 88-89 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.79 (s, 1H), 7.68 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.46 – 7.39 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.3, 156.4, 154.8, 138.5, 134.6, 133.7, 130.4, 126.3, 125.5, 123.9, 123.1, 118.6, 118.0, 21.2.



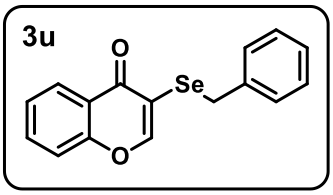
3-(naphthalen-1-ylselanyl)-4*H*-chromen-4-one (3s):

Yield: (12 mg, 34%); **Physical Appearance:** Brown Solid; **mp:** 66-68 ºC (lit.,[2] 67-68 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 – 8.39 (m, 1H), 8.28 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.99 (m, 1H), 7.96 – 7.86 (m, 2H), 7.71 – 7.51 (m, 3H), 7.50 – 7.29 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.5, 156.3, 153.4, 135.4, 134.3, 134.2, 133.7, 130.2, 128.8, 127.8, 127.5, 126.6, 126.2, 126.0, 125.4, 122.8, 118.5, 118.0.



3-(thiophen-2-ylselanyl)-4*H*-chromen-4-one (3t):

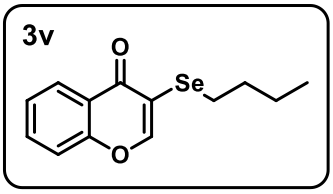
Yield: (26 mg, 84%)**; Physical Appearance:** White Solid; **mp:** 114-116 ºC (lit.,[2] 114-116 °C) **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 – 8.18 (m, 1H), 7.67 (ddd, *J* = 8.8, 7.1, 1.7 Hz, 1H), 7.60 (s, 1H), 7.51 (dd, *J* = 5.3, 1.2 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.08 (dd, *J* = 5.3, 3.5 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.1, 156.3, 153.3, 138.0, 133.8, 132.8, 128.6, 126.1, 125.5, 122.8, 120.0, 119.9, 118.1.



3-(benzylselanyl)-4*H*-chromen-4-one (3u):

Yield: (12 mg, 38%)**; Physical Appearance:** White Solid; **mp:** 95-97 ºC (lit.,[2] 95-96 °C)[1]**H NMR (400 MHz, $CDCl_3$)** δ 8.29 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.89 (s, 1H),

7.69 (m, 1H), 7.49 – 7.41 (m, 2H), 7.27 – 7.16 (m, 5H), 4.12 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.8, 157.6, 156.3, 138.5, 133.8, 129.0, 128.4, 126.9, 126.4, 125.6, 123.4, 118.1, 114.3, 29.8.

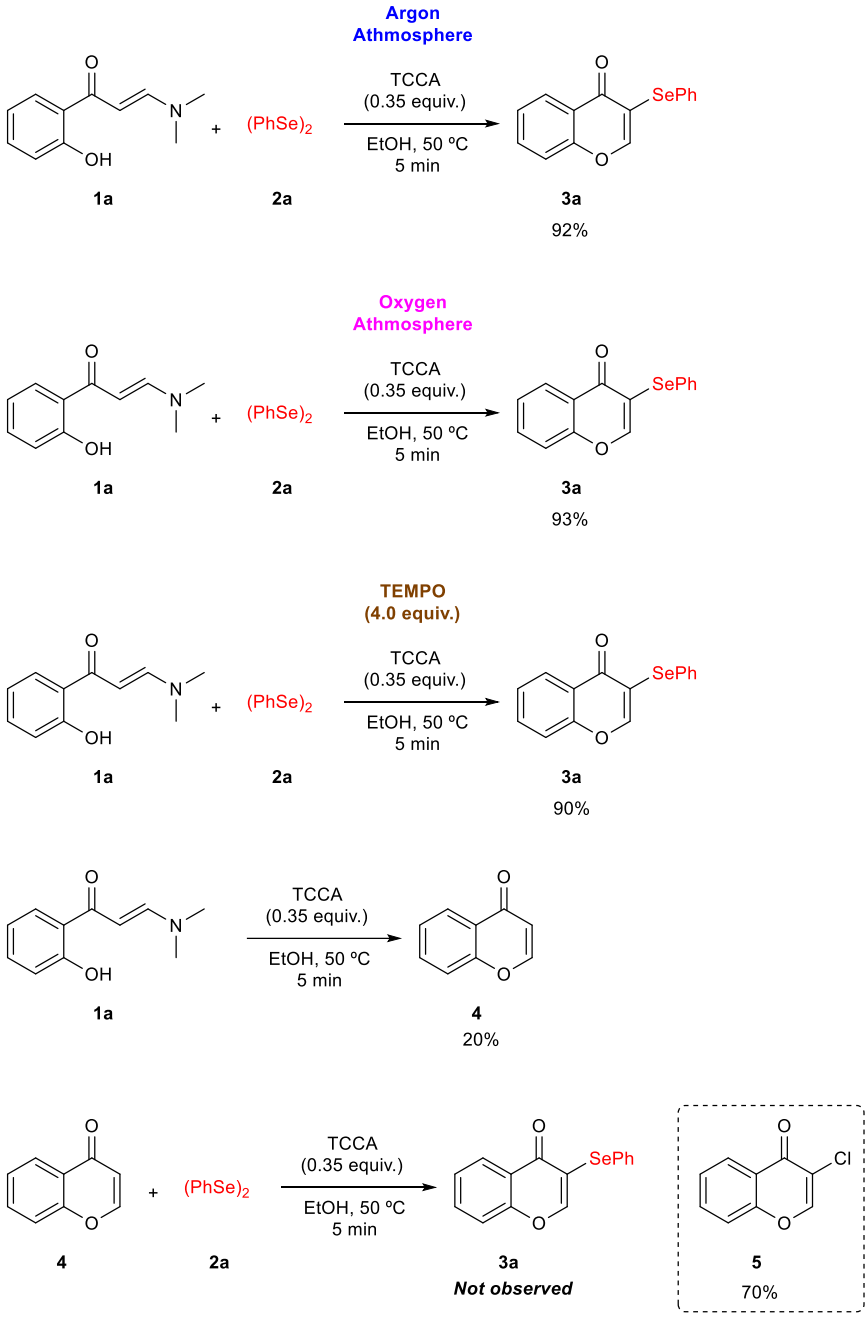


3-(butylselanyl)-4*H*-chromen-4-one (3v):

Yield: (20 mg, 71%) **;** **Physical Appearance:** Off-White Solid; **mp:** 54-55 ºC (lit.,[2] 54-55 °C); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17 (dd, J = 7.9, 1.7 Hz, 1H), 8.11 (s, 1H), 7.61 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.40 – 7.32 (m, 2H), 2.81 (t, 2H), 1.58 (p, J = 7.4 Hz, 2H), 1.34 (h, J = 7.3 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.9, 156.4, 156.3, 133.7, 126.3, 125.5, 123.2, 118.1, 114.8, 32.2, 26.0, 22.8, 13.6.

4. Control Experiments

To propose a tentative mechanism, some control experiments were also performed, which are shown in the scheme bellow.



When the reaction was carried out in the complete absence of oxygen (argon atmosphere), or with an atmosphere of pure O_2, no differences were observed compared to results on open air. This result indicates that no external oxidant is required along the conversion of substrates **1** and **2** into isoflavone **3**.

We also carried out an experiment using excess of TEMPO to probe an eventual formation of radical intermediates, however product **3a** was formed in 90% yield, suggesting that probably an ionic mechanism is involved. We also wonder whether the chalcogen moiety is introduced before or after the cyclization with the hydroxyl group at position 2'. We also performed an experiment in the absence of diselenide **2a**, which led to chromone **4** as the only product in 20% yield and major amount of unreacted **1a**. Performing the reaction with chromone **4** instead of enaminone **1a** did not afford 3-selenyl-isoflavone **3a**, as expected, and chlorinated derivative **5** was observed as single product with 70% yield. These last two experiments indicate that chalcogen introduction probably occurs before the cyclization step that assembles the chromone ring.

5. References

1. (a) Wan, J.-P.; Zhong, S.; Xie, L.; Cao, X.; Liu, Y.; Wei, L. *Org. Lett*. 2016, **18**, 584−587. (b) Xiang, H.; Yang, C. A. *Org. Lett.* 2014, **16**, 5686. (c) Mutai, P.; Pavadai, E.; Wiid, I.; Ngwane, A.; Baker, B.; Chibale, K. *Bioorg. Med. Chem. Lett*. 2015, **25**, 2510. (d) Levchenko, K. S.; Semenova, I. S.; Yarovenko, V. N.; Shmelin, P. S.; Krayushkin, M. M. *Tetrahedron Lett*. 2012, **53**, 3630.

2. Rafique J.; Saba, S.; Schneider, A. R.; Franco, M. S.; Silva, S. M.; Braga, A. L. *ACS Omega,* 2017, **2**, 2280

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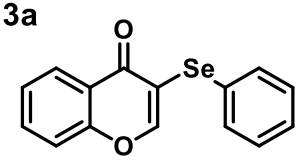
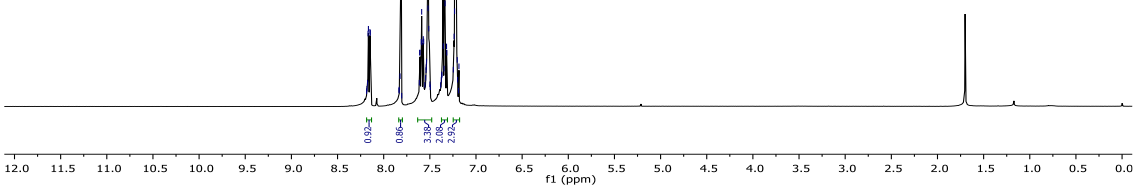
6. NMR Data

3a



^{1}H NMR (400 MHz, CDCl3)



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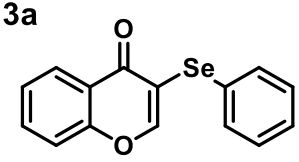

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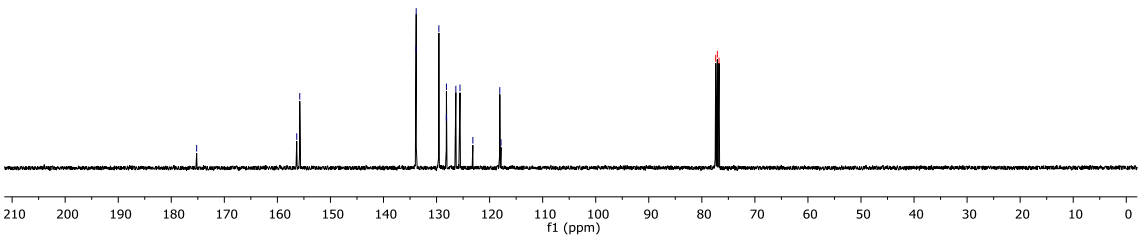

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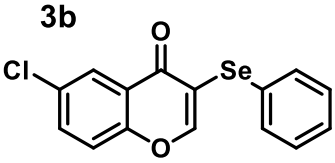
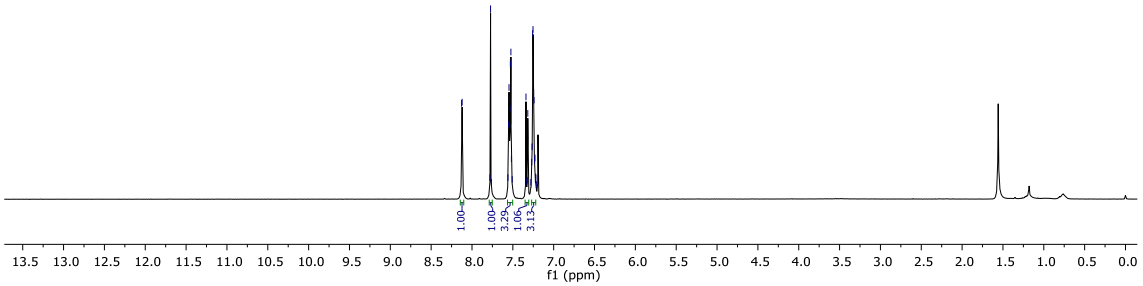


^{1}H NMR (400 MHz, $CDCl_3$)



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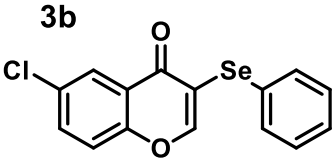

^{13}C NMR (100 MHz, $CDCl_3$)

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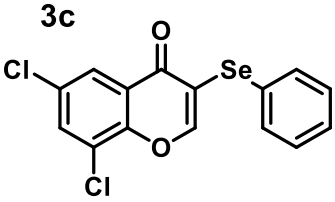

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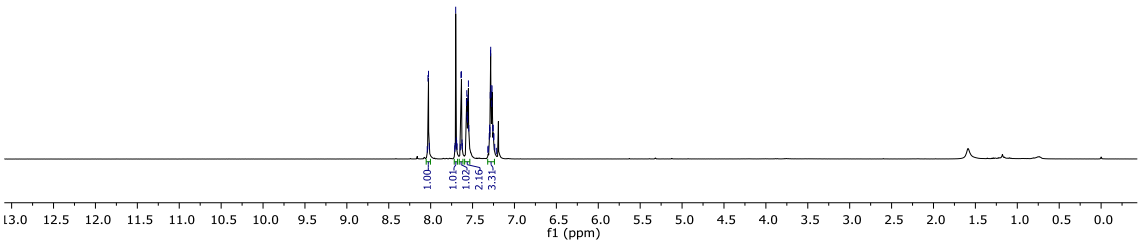

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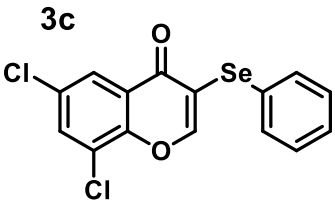

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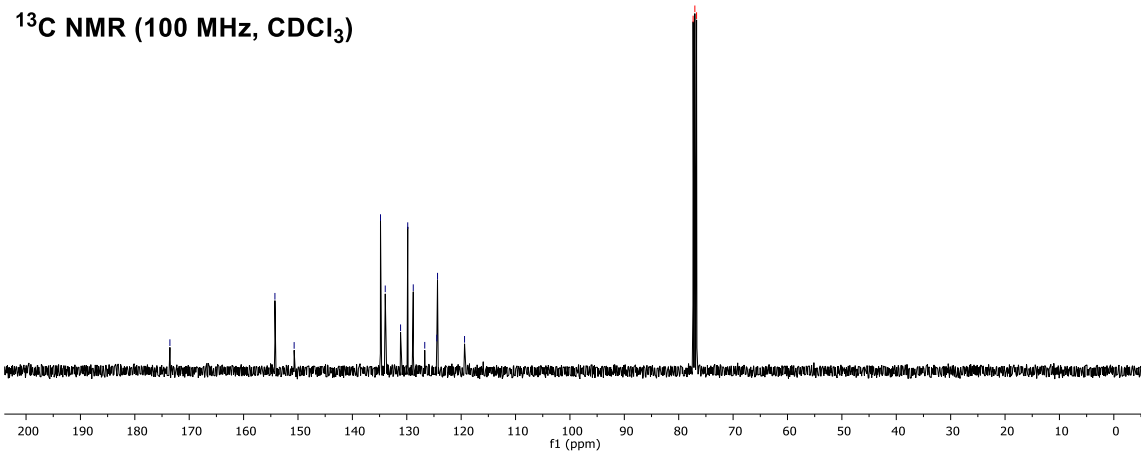

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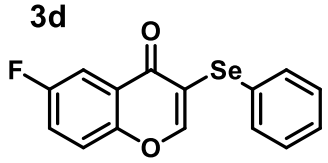

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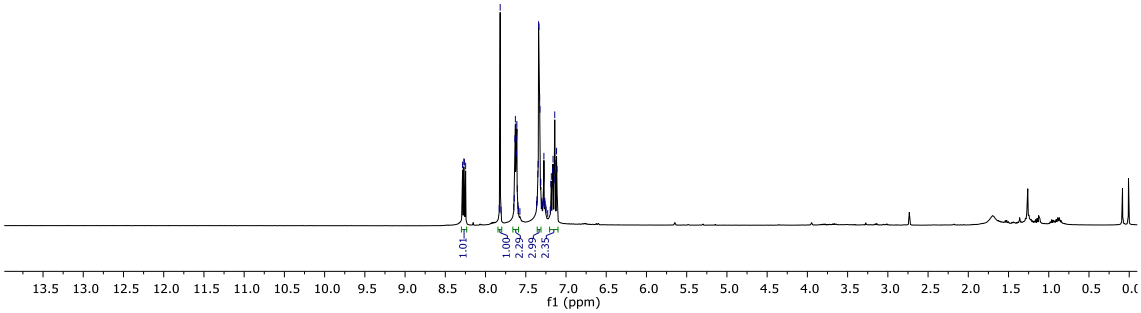

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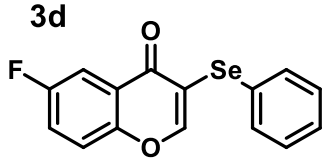

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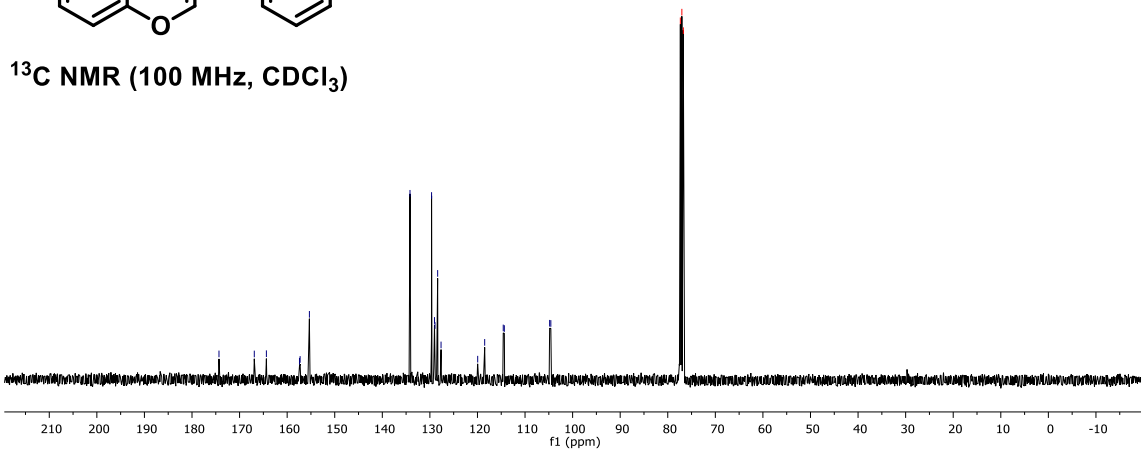

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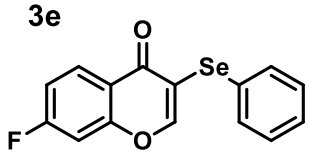

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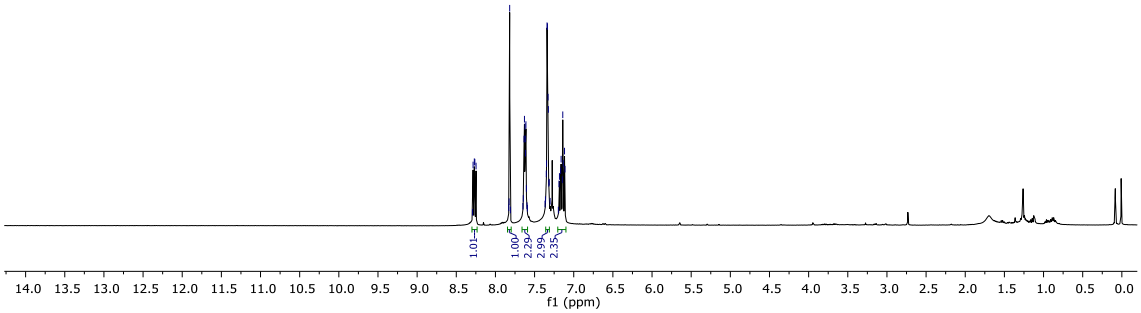

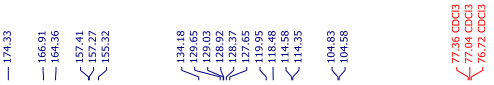

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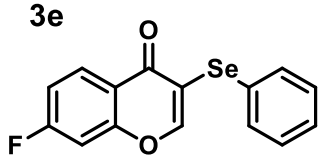

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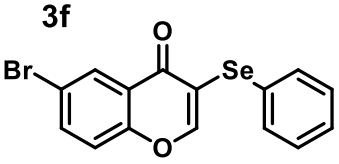

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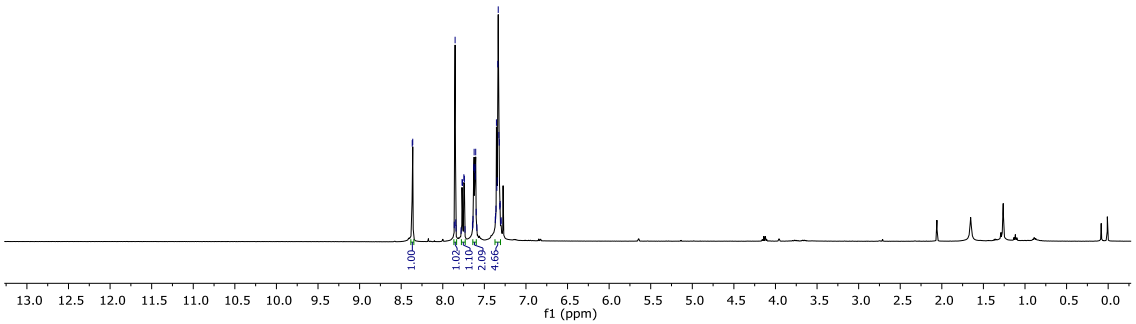

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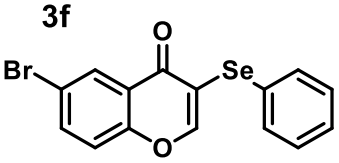

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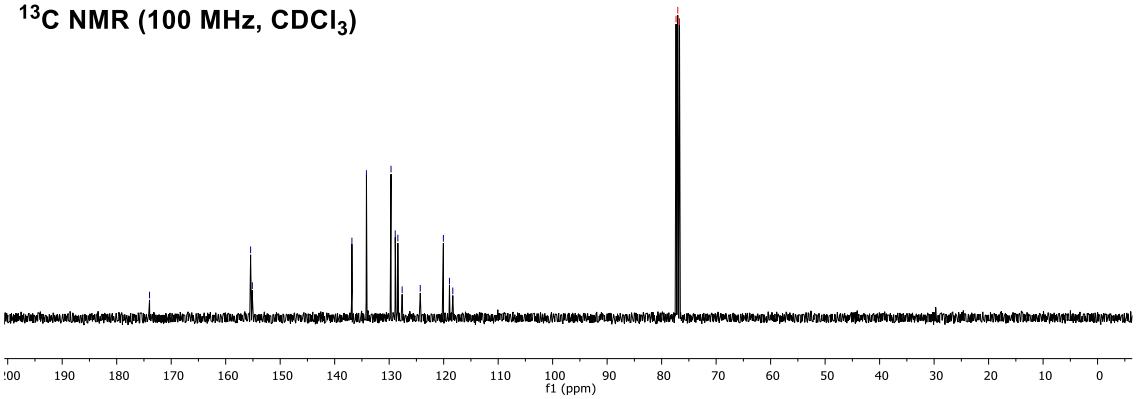

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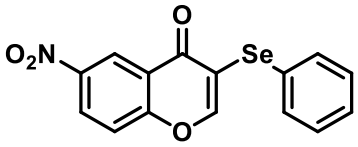

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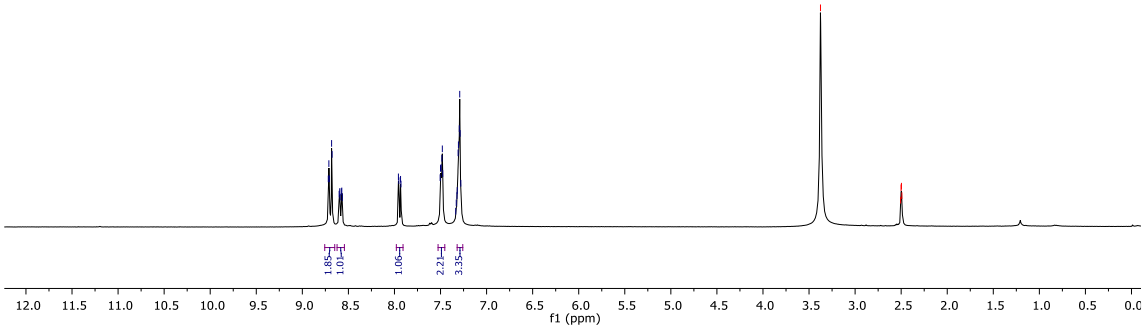

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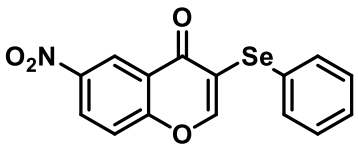

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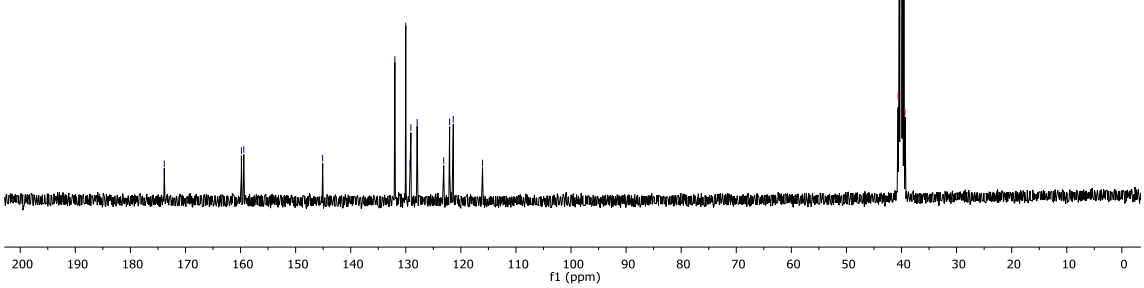

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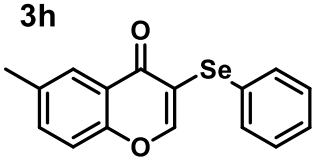

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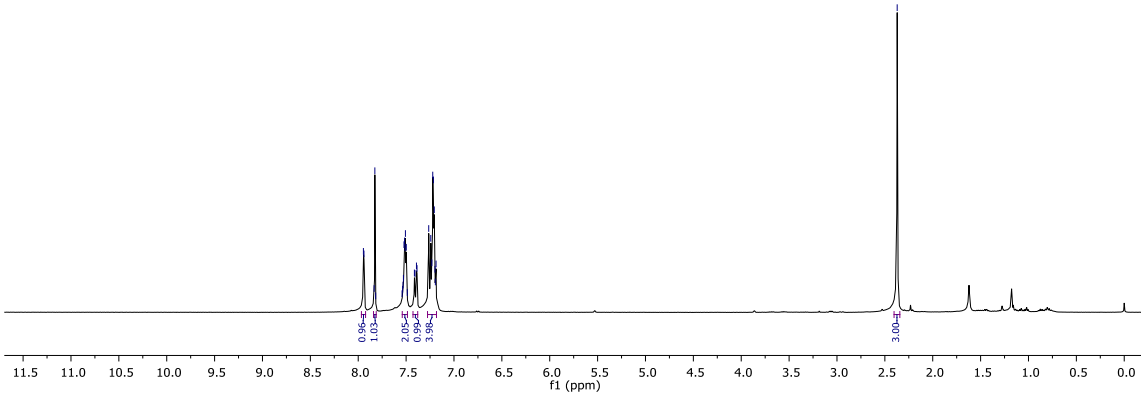

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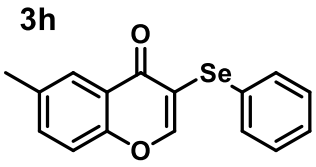

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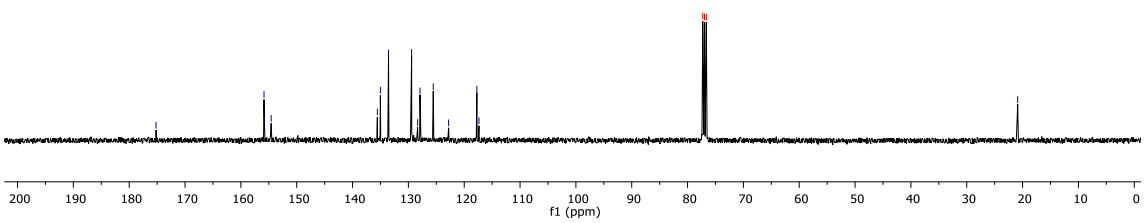

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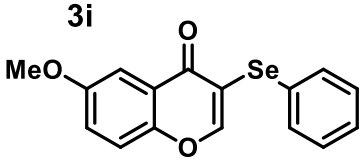

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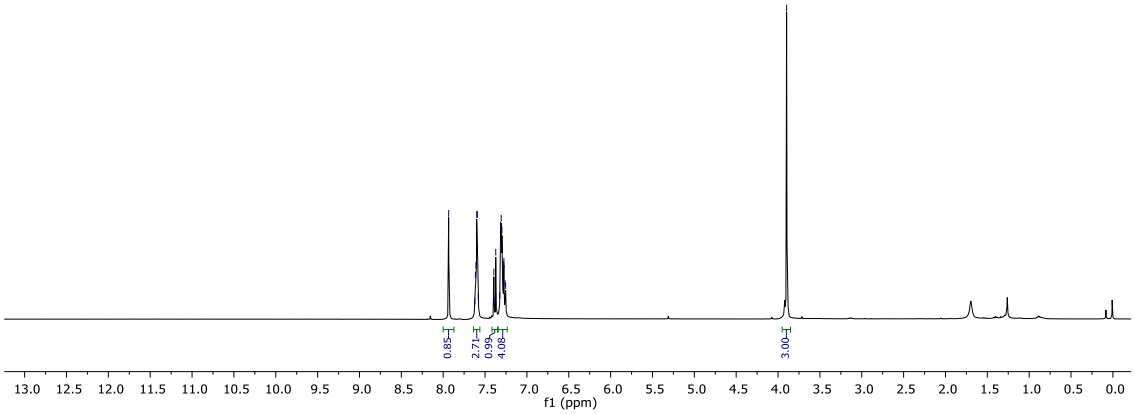

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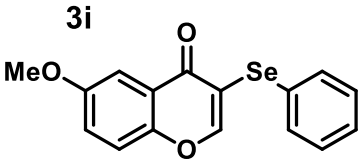

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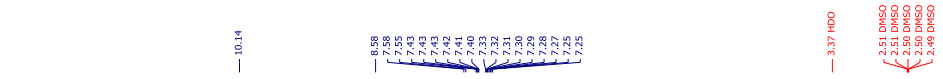

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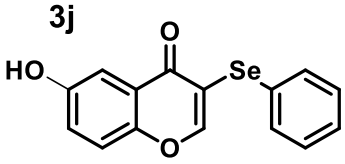

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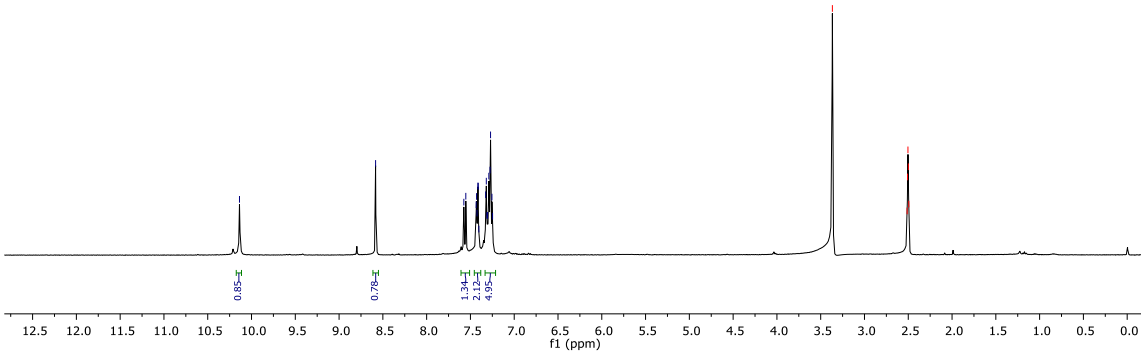

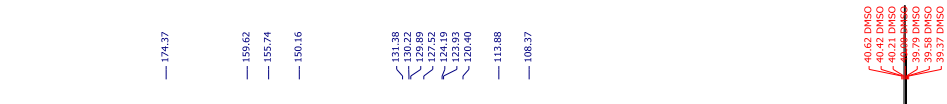

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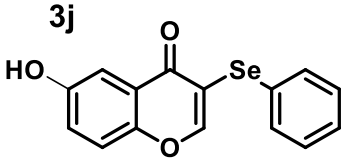

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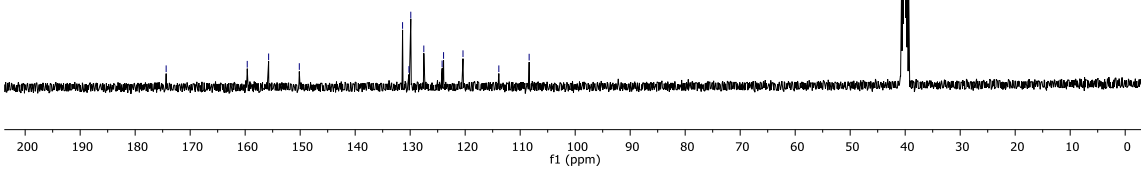

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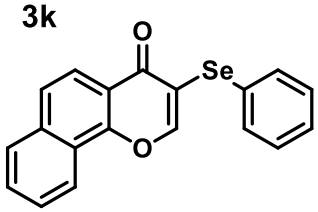

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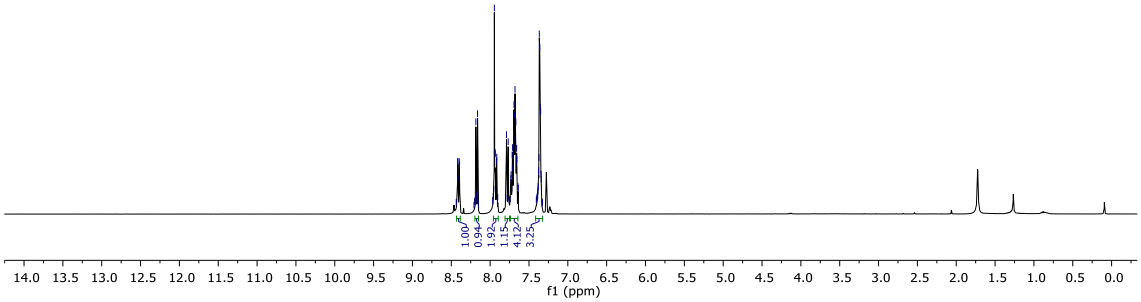
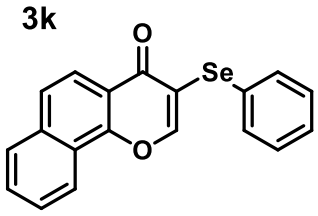
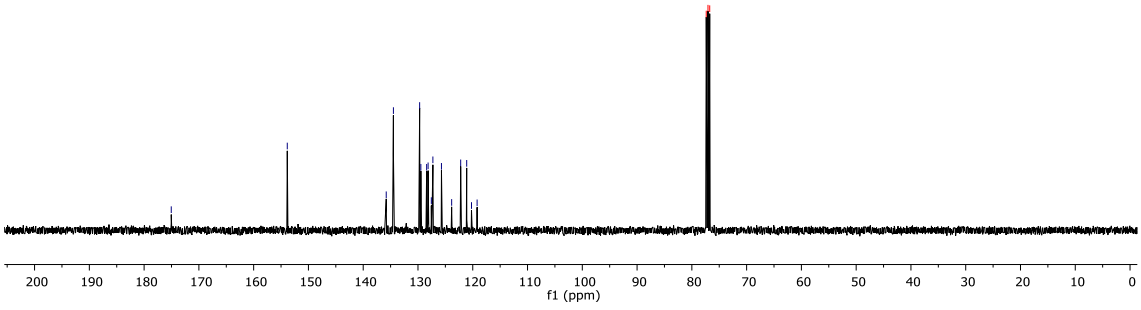


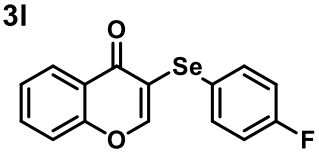
3k



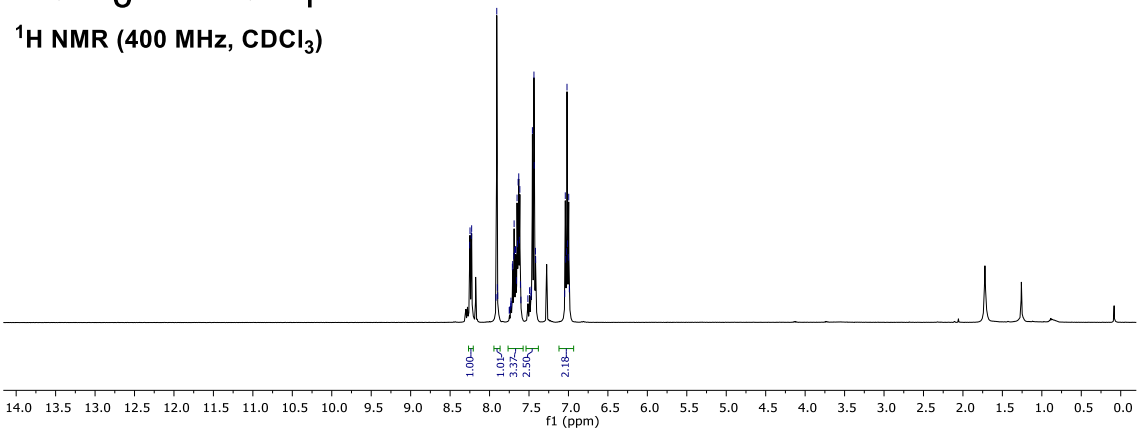
^{13}C NMR (100 MHz, $CDCl_3$)

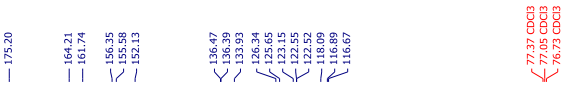


3l

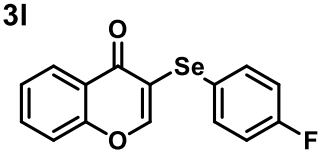


^{1}H NMR (400 MHz, $CDCl_3$)

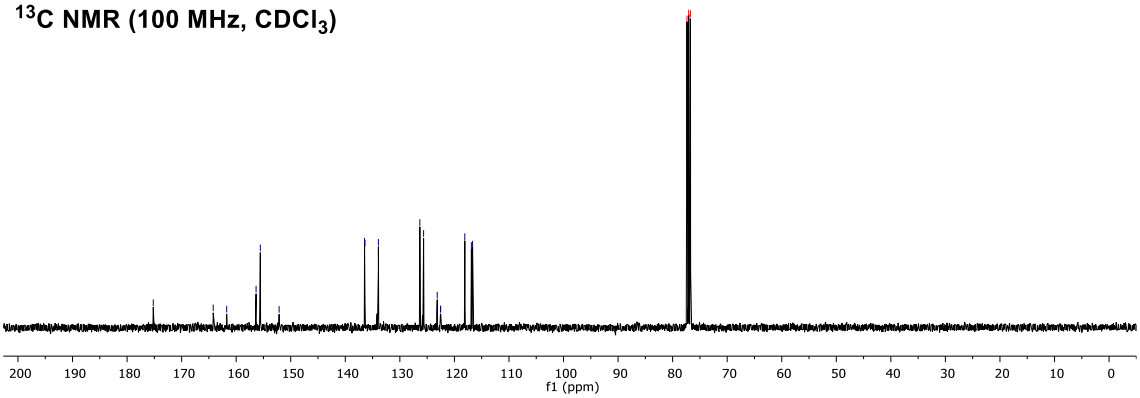




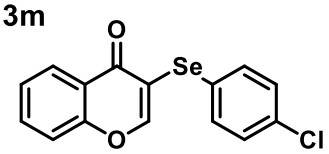
3l



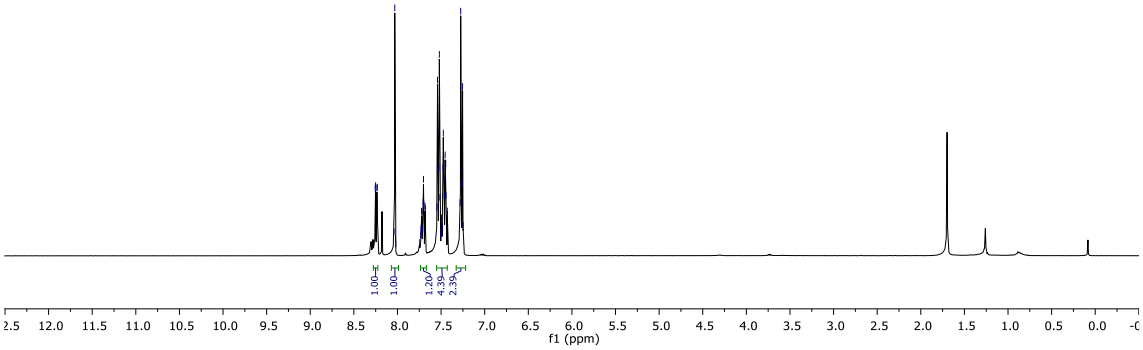
^{13}C NMR (100 MHz, $CDCl_3$)



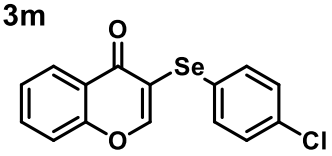
3m



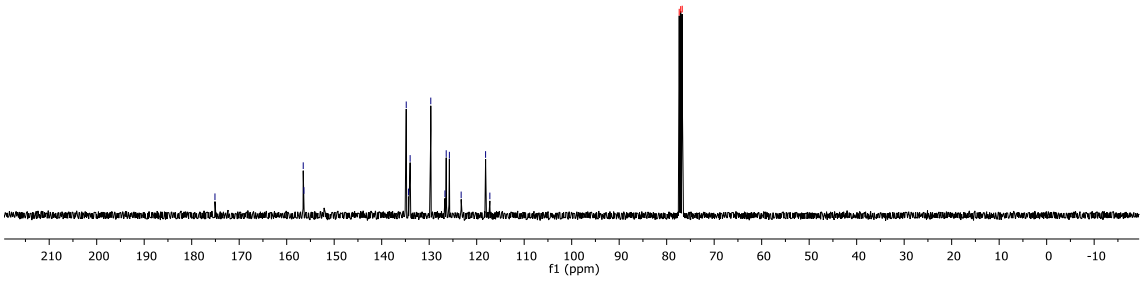
^{1}H NMR (400 MHz, $CDCl_3$)

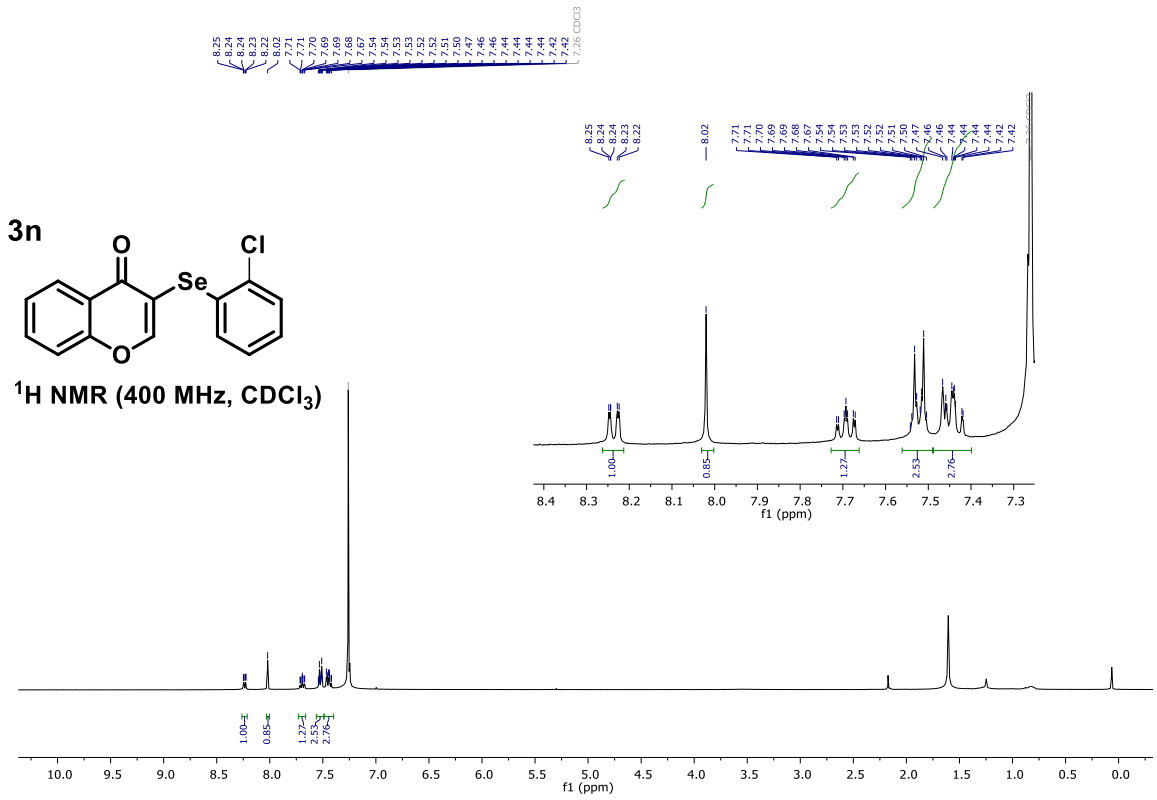


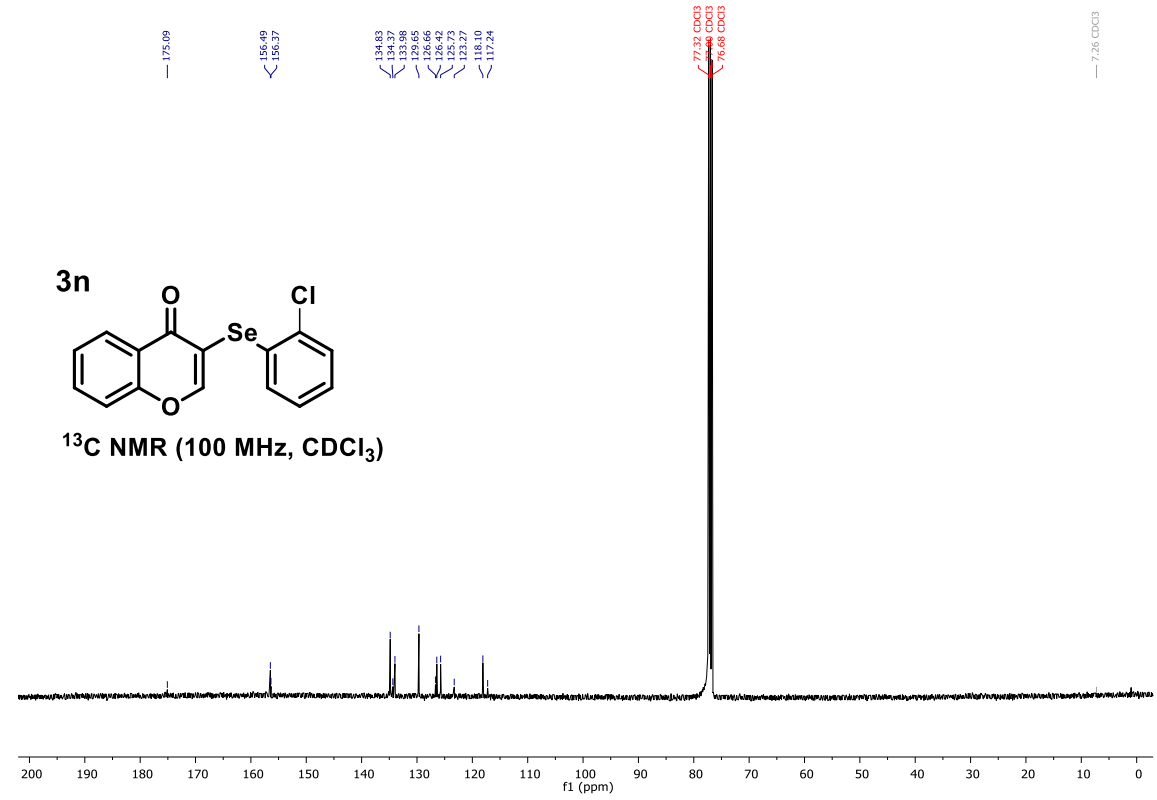
3m



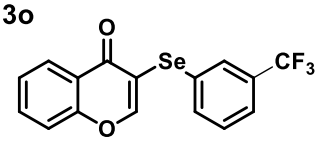
^{13}C NMR (100 MHz, $CDCl_3$)



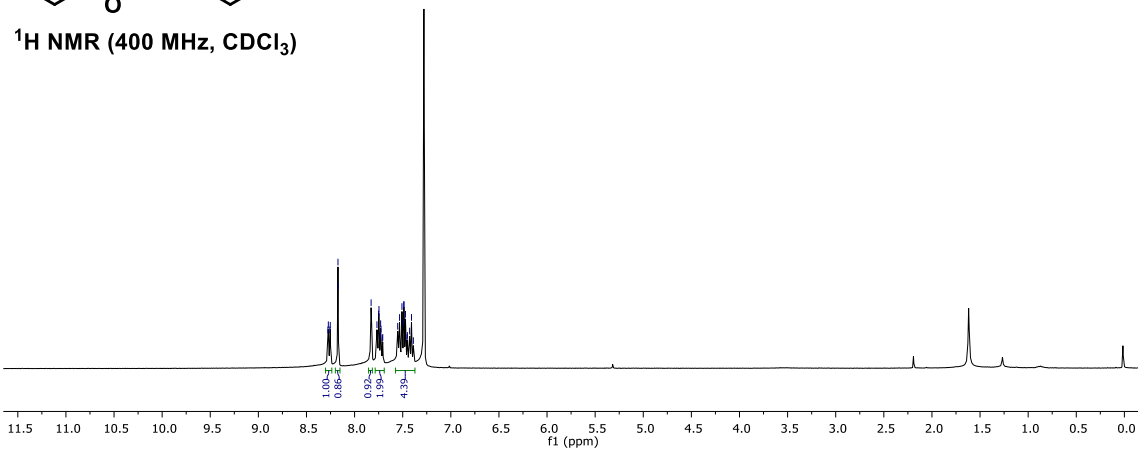

3n
O
Cl
Se
O
1H NMR (400 MHz, CDCl3)
8.25
8.24
8.24
8.23
8.22
8.02
7.71
7.71
7.70
7.69
7.68
7.68
7.67
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.47
7.46
7.46
7.44
7.44
7.44
7.42
7.42
7.26 CDCl3
1.00
0.85
1.27
2.53
2.76
f1 (ppm)


3n
O
Cl
Se
O
13C NMR (100 MHz, CDCl3)
175.09
156.49
156.37
134.83
134.37
133.98
129.65
126.66
126.42
125.73
123.27
118.10
117.24
77.32 CDCl3
76.68 CDCl3
7.26 CDCl3
f1 (ppm)

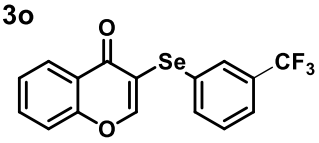
3o



^{1}H NMR (400 MHz, $CDCl_3$)

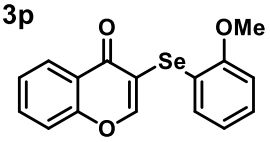


3o



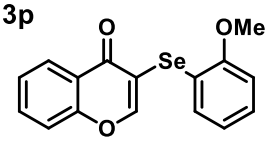
^{13}C NMR (400 MHz, $CDCl_3$)

3p

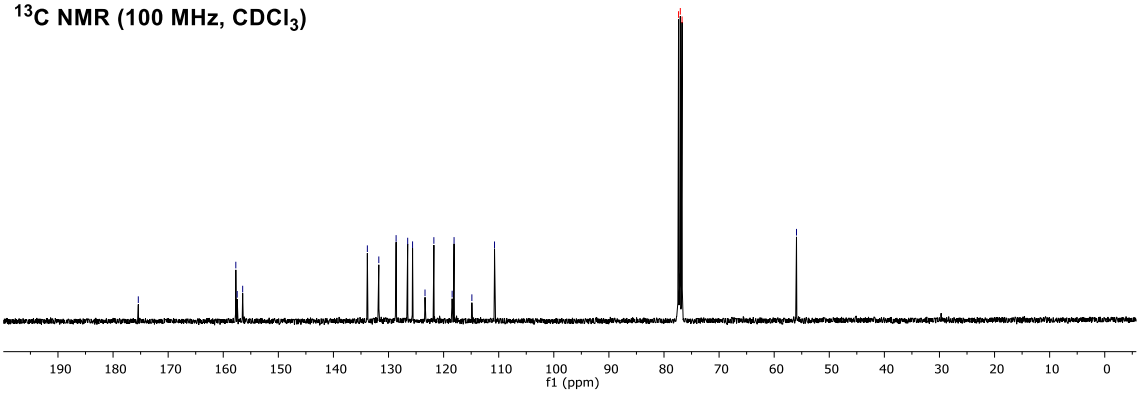


^{1}H NMR (400 MHz, $CDCl_3$)

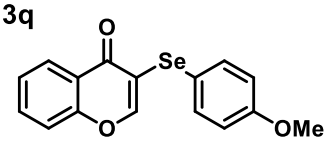
3p



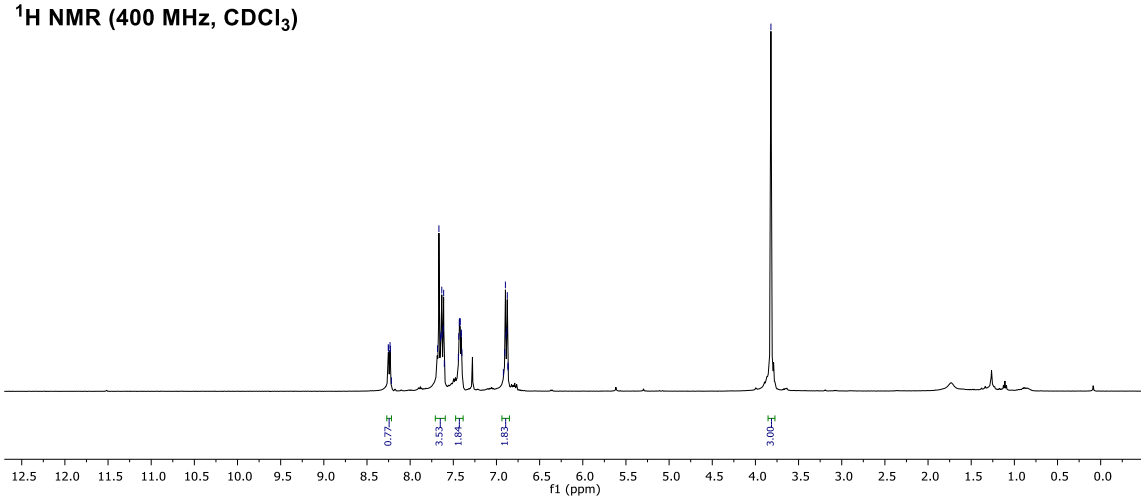
^{13}C NMR (100 MHz, $CDCl_3$)



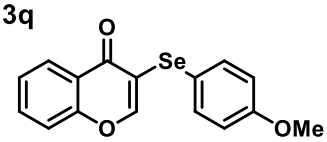
3q



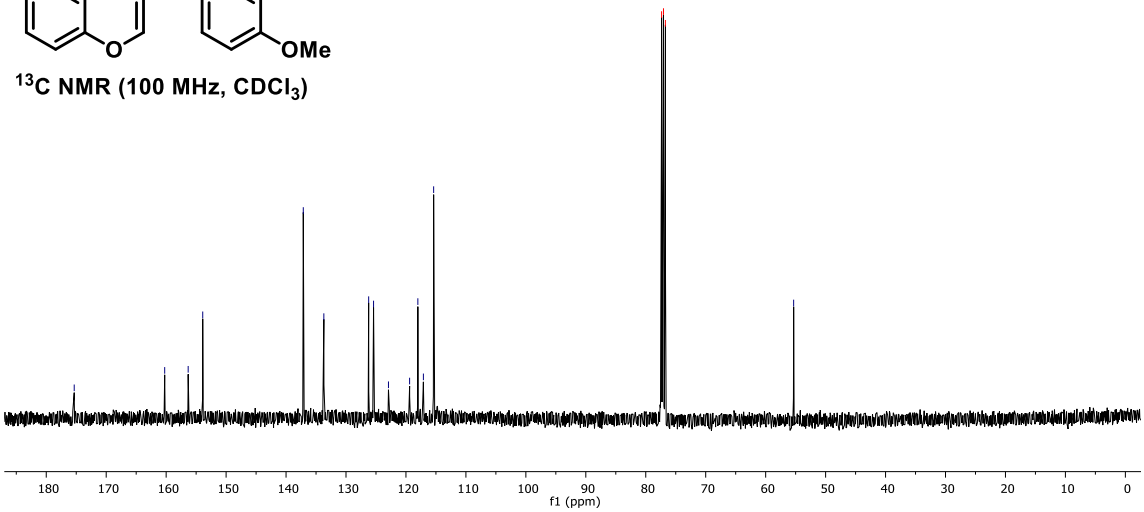
^{1}H NMR (400 MHz, $CDCl_3$)



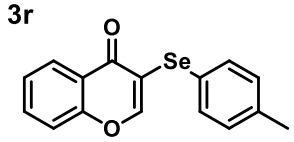
3q



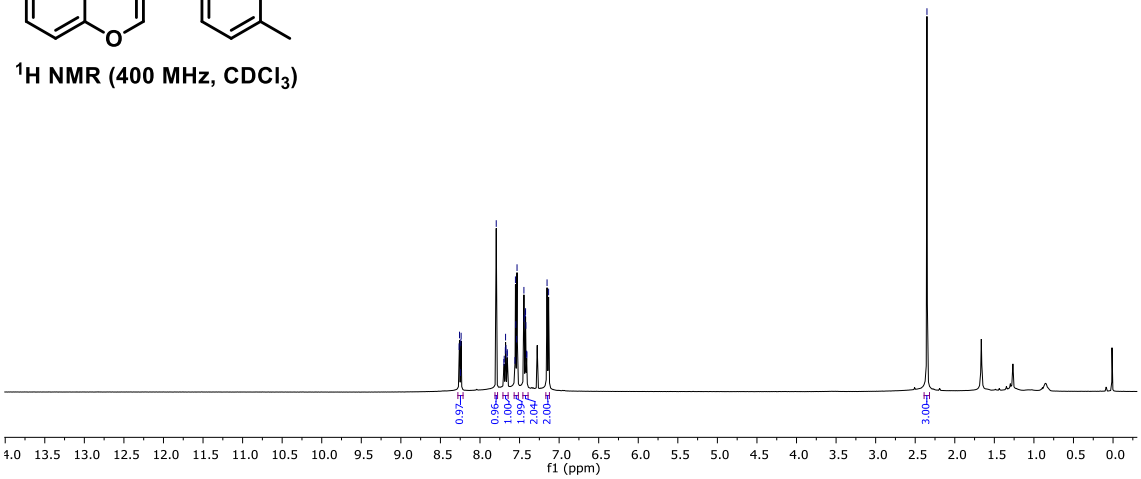
^{13}C NMR (100 MHz, $CDCl_3$)



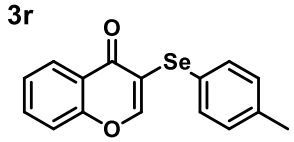
3r



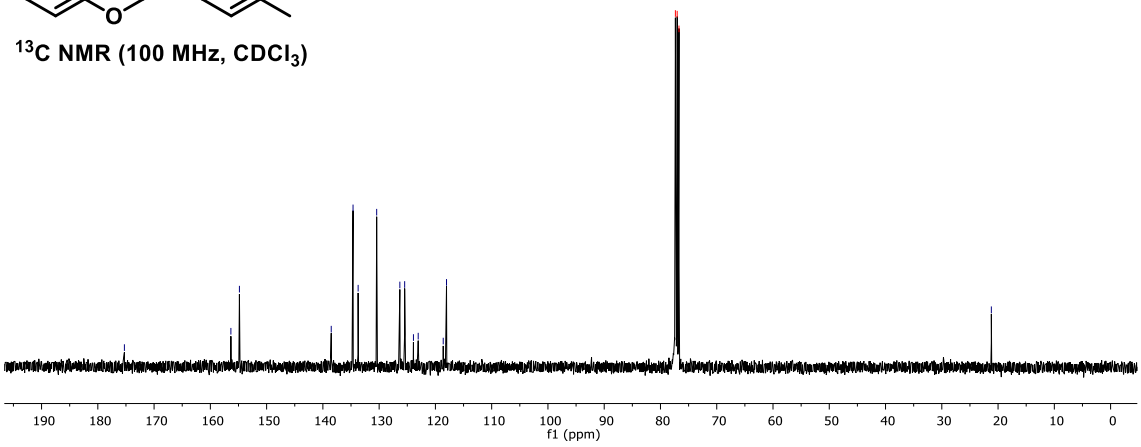
^{1}H NMR (400 MHz, $CDCl_3$)



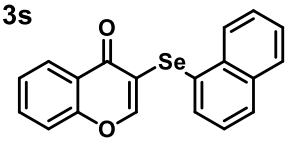
3r



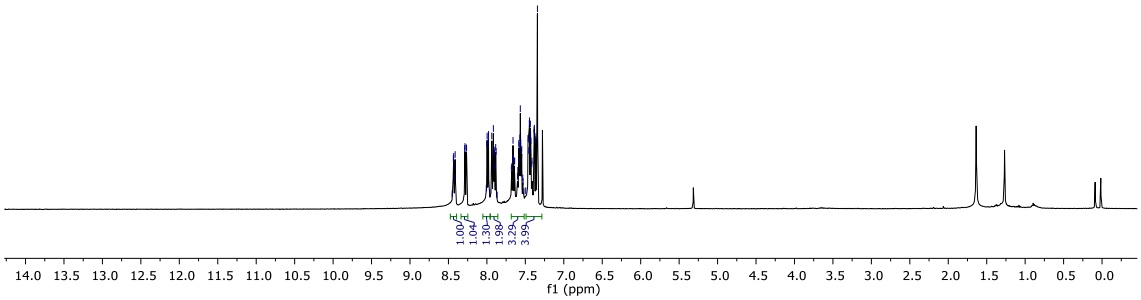
^{13}C NMR (100 MHz, $CDCl_3$)



3s

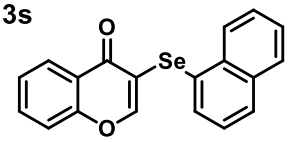


^{1}H NMR (400 MHz, $CDCl_3$)



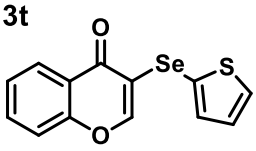
CarlosD_CD280_CDCl3.2.fid

3s

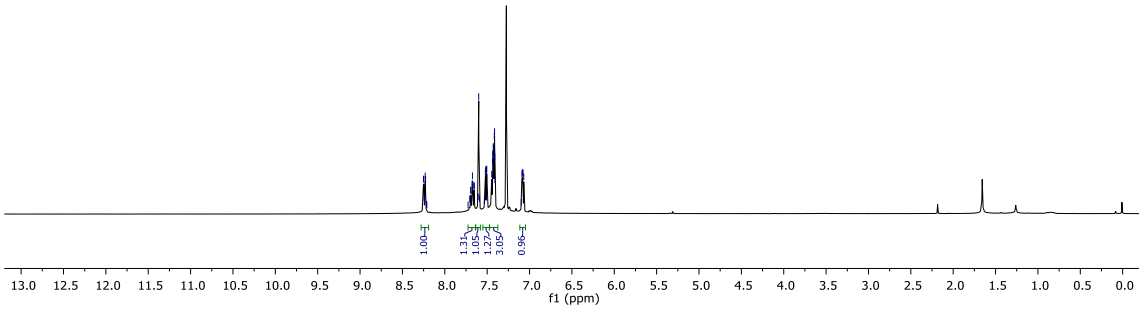


^{13}C NMR (100 MHz, $CDCl_3$)

3t



^{1}H NMR (400 MHz, $CDCl_3$)



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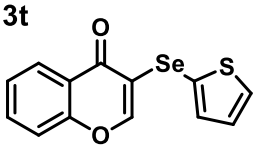
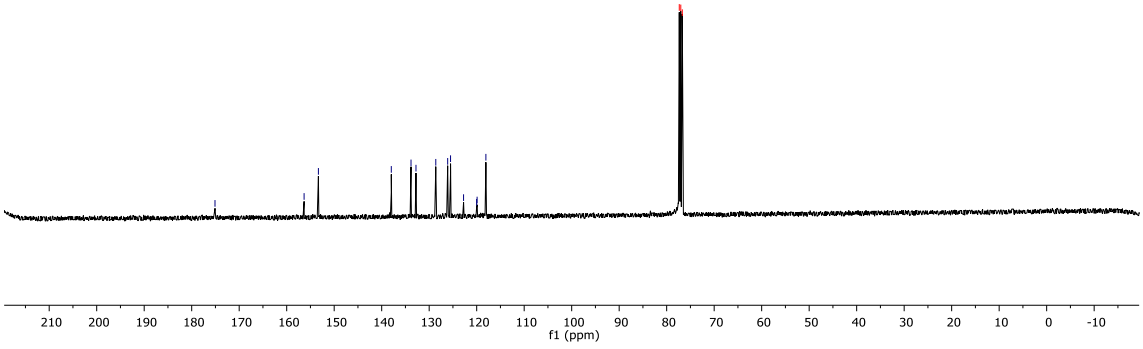
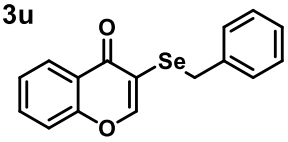


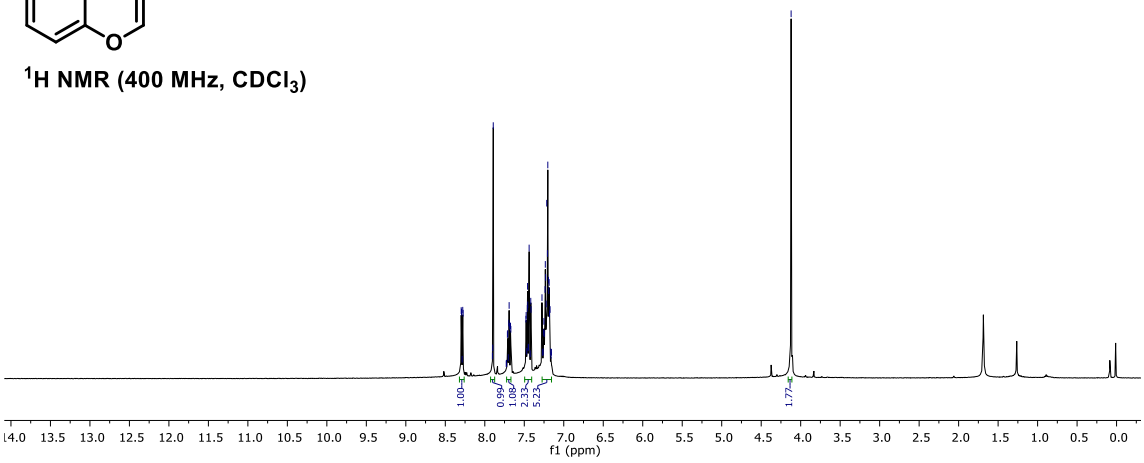
^{13}C NMR (100 MHz, $CDCl_3$)



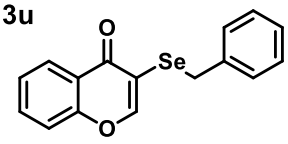
3u



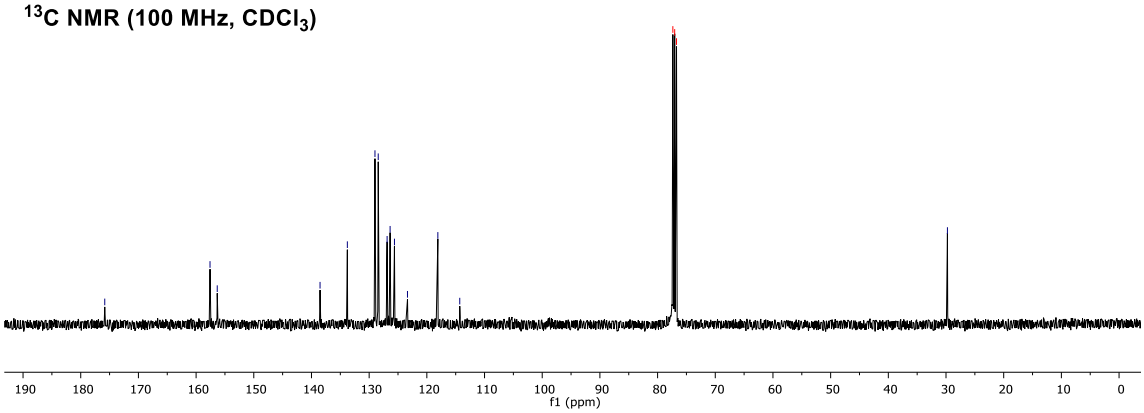
^{1}H NMR (400 MHz, $CDCl_3$)



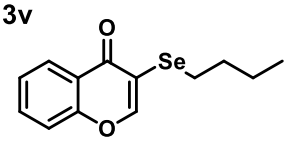
3u



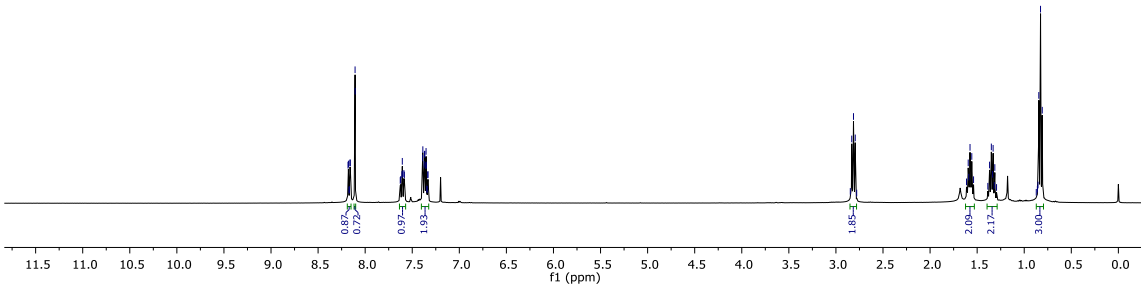
^{13}C NMR (100 MHz, $CDCl_3$)



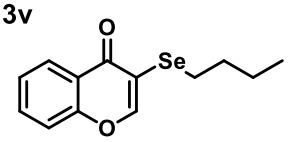
3v



^{1}H NMR (400 MHz, $CDCl_3$)



3v



^{13}C NMR (100 MHz, $CDCl_3$)