Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Formal insertion of selenoketenes into donor-acceptor cyclopropanes: mesomeric alkynylselenolates as key starting materials

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Supporting Information

Contents

1. General Experimental

All solvents were dried and stored over molecular sieves under argon atmosphere unless otherwise stated. Air- and moisture-sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated. The heating for the catalytic reactions were done by use of a heating block with a small amount of silicon oil in the slots. All other reactions, that required heating, were proceeded in a silicon oil bath. For all purifications via column chromatography silica gel (43-60 µm particle size) was used.

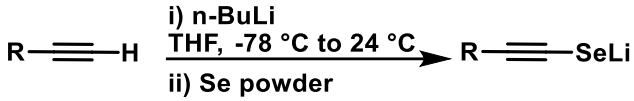
Proton (^{1}H), carbon (^{13}C) and fluorine (^{19}F) NMR spectra were recorded on a Bruker AV300, Bruker AVIII400, Bruker AVIIIHD500 or Bruker AVII600 instrument using the residual signals from $CHCl_3$, δ = 7.26 ppm and δ = 77.16 ppm, as internal reference for ^{1}H and ^{13}C chemical shifts, respectively. Additionally, tetramethylsilane (TMS; δ = 0.00 ppm; 0.03%) was added to NMR samples. The following abbreviations were used for ^{1}H and ^{13}C NMR chemical shifts: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet/quintet, oct = octet, m = multiplet and combinations thereof. ESI-HRMS mass spectrometry was carried out on an FTICR instrument. EI-HRMS mass spectrometry was carried out on JOEL AccuTOF GC JMS-T100GC instrument. IR spectra were recorded on an ATR spectrometer Tensor 27 from Bruker. Melting Points were recorded with a Büchi SMP-20 and Büchi M-560 melting point meter and are uncorrected.

2. General Procedures

2.1 General procedure for the preparation of D-A cyclopropanes (GP 1)

To a solution of the corresponding styrene (1.0 equiv), $Rh_2(OAc)_4$ (0.5 mol%) in dichloromethane was added dropwise diazomalonate (1.30 equiv) in dichloromethane over 15 h via syringe pump at ambient temperature. The solvent was removed in vacuo and silica gel column chromatography gave the desired product.[1] All donor-acceptor cyclopropanes are known to literature and were prepared according to existing procedures. **1a**[1], **1b**[1], **1c**[1], **1d**[2], **1e**[1], **1f**[6], **1g**[1], **1h**[1], **1i**[1], **1j**[3], **1k**[4], **1l**[5], **1m**[1], **1n**[7], **1o**[9], **1p**[8].

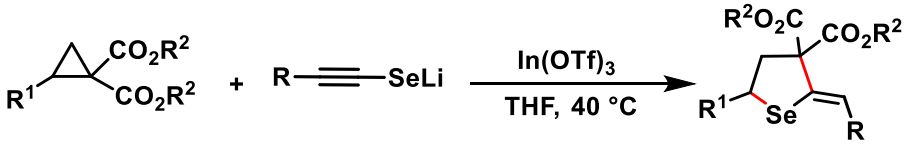
2.2 Synthesis of compound lithium alkylselenolate 2 (GP 2)



2

In a flame dried, argon-filled microwave tube was charged corresponding acetylene (2.2 equiv) in THF (0.1 M) at 0 °C. The solution was cooled to -78 °C. To this solution was added *n*-BuLi (2.0 equiv). The reaction was allowed to stir for 1 h and slowly warmed to 25 °C. To the stirring solution was added elemental selenium (2.2 equiv) in one portion. The dissolution of selenium changes the solution color from black to pale yellow to furnish **2**.

2.3 Syntheses of tetrahydroselenophenes (GP 3)

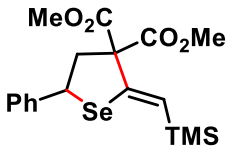


1 **2** **3**

To the *in situ* generated **2** was added a solution of cyclopropane diester **1** (100 µmol, 1.0 equiv.), and indium trifluoromethanesulfonate (80 µmol, 0.8 equiv.) dissolved in THF (0.1 M) under argon atmosphere. The solution was stirred at 40 °C (oil bath) until TLC analysis showed full conversion of cyclopropane **1**. The reaction tube is allowed to cool to the room temperature. To it was added EtOAc (10 mL), washed with saturated $NaHCO_3$ solution and extracted with EtOAc (3 x 20 mL). The organic layers were combined and dried over Na_2SO_4 and solvent was evaporated under reduced pressure. The product **3** was purified by silica gel column chromatography.

3. Preparation of Tetrahydroselenophenes (3)

Dimethyl (*Z*)-5-phenyl-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3a)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3a** (35.7 mg, 87 µmol, 87%) as yellow oil.

R_f: 0.43 in 1:20 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 – 7.42 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 6.07 (s, 1H), 4.82 (dd, *J* = 12.3, 4.6 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.10 (dd, *J* = 13.1, 4.6 Hz, 1H), 2.91 (dd, *J* = 13.2, 12.3 Hz, 1H), 0.17 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.5, 169.3, 150.3, 139.5, 128.6, 127.9, 127.7, 125.6, 73.2, 53.3, 53.0, 47.0, 46.2, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 2322, 1736, 1495, 1249, 848, 644.

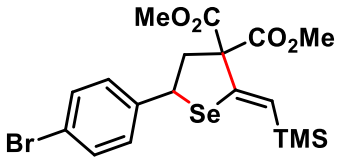
HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{24}O_4SeSiNa$**: 435.0507;

Found: 435.0502

Large scale synthesis of 3a

Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (234 mg, 1 mmol, 1.0 equiv.), and *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (449 mg, 0.8 equiv.) in THF (10.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3a** (328 mg, 87 µmol, 80%) as yellow oil.

Dimethyl (*Z*)-5-(4-bromophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3b)



Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **1b** (31 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3b** (42.6 mg, 87 µmol, 87%) as brown solid.

R_f: 0.39 in 1:20 EtOAc/Pentane

m.p. = 68-69 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.07 (s, 1H), 4.77 (dd, *J* = 12.3, 4.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.07 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.83 (dd, *J* = 13.1, 12.3 Hz, 1H), 0.16 (s, 9H).

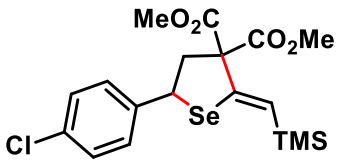
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.4, 169.2, 149.9, 138.8, 131.8, 129.6, 126.0, 121.4, 73.2, 53.3, 53.1, 47.0, 45.4, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 1731, 1434, 1240, 1134, 1064, 832.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{23}BrO_4SeSiNa$**: 512.9612.

Found: 512.9603

Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3c)



Dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate **1c** (27 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3c** (42.2 mg, 95 µmol, 95%) as brown oil.

R_f: 0.40 in 1:20 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 6.08 (s, 1H), 4.78 (dd, *J* = 12.3, 4.7 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.08 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.84 (dd, *J* = 13.2, 12.3 Hz, 1H), 0.16 (s, 9H).

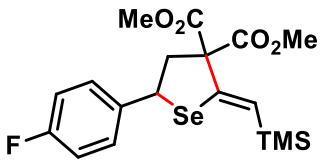
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.3, 169.2, 149.9, 138.2, 133.3, 129.2, 128.8, 126.0, 73.2, 53.3, 53.1, 47.0, 45.4, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2894, 1734, 1437, 1237,1066, 835.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{23}ClO_4SeSiNa$**: 469.0117.

Found: 469.0113.

Dimethyl (*Z*)-5-(4-fluorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3d)



Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate **1d** (25.2 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3d** (29.6 mg, 69 µmol, 69%) as yellow oil.

R_f: 0.35 in 1:20 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 – 7.38 (m, 2H), 7.03 – 6.97 (m, 2H), 6.07 (s, 1H), 4.80 (dd, *J* = 12.3, 4.7 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.08 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.84 (dd, *J* = 13.2, 12.3 Hz, 1H), 0.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5, 168.4, 162.5 (C-F, $^1J_{C\text{-}F}$ = 246.7 Hz), 150.2, 135.5 (C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.6 (C-F, $^3J_{C\text{-}F}$ = 8.2 Hz), 126.0, 115.7 (C-F, $^2J_{C\text{-}F}$ = 21.5 Hz), 73.3, 53.5, 53.2, 47.4, 45.5, -1.3.

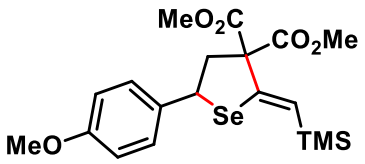
^{19}F NMR (377 MHz, $CDCl_3$): δ = -114.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2954, 2322, 1733, 1508, 1229,1150, 833.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{23}FO_4SeSiNa$**: 453.0413.

Found: 453.0410.

Dimethyl (*Z*)-5-(4-methoxyphenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3e)



Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate **1e** (26.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3e** (21.1 mg, 48 µmol, 48%) as yellow oil.

R_f: 0.27 in 1:10 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = δ 7.38 – 7.34 (m, 2H), 6.87 – 6.82 (m, 2H), 6.06 (s, 1H), 4.80 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.82 (s, 3H), 3.79 (d, *J* = 1.8 Hz, 6H), 3.06 (dd, *J* = 13.2, 4.6 Hz, 1H), 2.88 (dd, *J* = 13.1, 12.4 Hz, 1H), 0.16 (s, 9H).

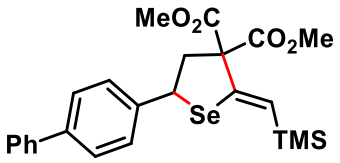
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.5, 169.3, 159.0, 150.5, 131.4, 128.9, 125.5, 114.0, 73.2, 55.3, 53.3, 53.0, 47.3, 45.9, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2952, 2322, 1732, 1510, 1240,1068, 835.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{26}O_5SeSiNa$**: 465.0613.

Found: 465.0611.

Dimethyl (*Z*)-5-([1,1'-biphenyl]-4-yl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3f)



Dimethyl 2-([1,1'-biphenyl]-4-yl)cyclopropane-1,1-dicarboxylate **1f** (31 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3f** (37 mg, 76 µmol, 76%) as yellow oil.

R_f: 0.42 in 1:20 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 – 7.50 (m, 6H), 7.46 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H), 6.09 (s, 1H), 4.88 (dd, J = 12.3, 4.7 Hz, 1H), 3.13 (dd, J = 13.1, 4.7 Hz, 1H), 2.96 (dd, J = 13.1, 12.4 Hz, 1H), 0.18 (s, 9H).

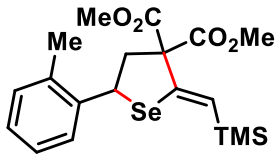
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.5, 169.3, 150.3, 140.6, 140.5, 138.6, 128.7, 128.3, 127.3, 127.3, 127.0, 125.7, 73.3, 53.3, 53.1, 47.0 45.9, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2952, 2322, 1732, 1570, 1487, 1241, 834, 730.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{24}H_{28}O_4SeSiNa$**: 511.0820

Found: 511.0813

Dimethyl (*Z*)-5-(*o*-tolyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3g)



Dimethyl 2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate **1g** (25 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3g** (34 mg, 80 µmol, 80%) as yellow oil.

R_f: 0.4 in 1:20 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 6.10 (s, 1H), 5.04 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.06 (dd, *J* = 13.1, 4.4 Hz, 1H), 2.93 (dd, *J* = 13.1, 12.4 Hz, 1H), 2.37 (s, 3H), 0.17 (s, 9H).

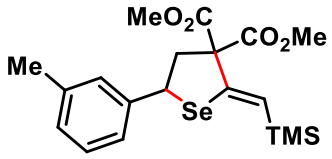
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.45, 169.41, 150.1, 137.4, 136.1, 130.4, 127.3, 126.7, 126.5, 125.9, 72.8, 53.2, 53.0, 45.9, 42.3, 19.5, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 2322, 1733, 1571, 1438, 1238, 836.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{26}O_4SeSiNa$**: 449.0664

Found: 449.0660.

Dimethyl (*Z*)-5-(*m*-tolyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3h)



Dimethyl 2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate **1h** (25 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3h** (24.2 mg, 57 µmol, 57%) as yellow solid.

R_f: 0.4 in 1:10 EtOAc/Pentane

m.p. = 96-97 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.17 (m, 3H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.07 (s, 1H), 4.79 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.81 (d, *J* = 7.9 Hz, 6H), 3.08 (dd, *J* = 13.2, 4.6 Hz, 1H), 2.90 (dd, *J* = 13.1, 12.4 Hz, 1H), 2.36 – 2.32 (m, 3H), 0.17 (s, 9H).

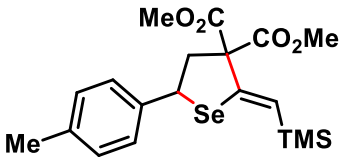
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5, 169.4, 150.4, 139.4, 138.3, 128.5, 128.5, 128.5, 125.6, 124.9, 73.2, 53.3, 53.0, 47.0, 46.3, 21.3, -1.45.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 2322, 1733, 1438, 1238, 836, 730.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{26}O_4SeSiNa$:** 449.0664

Found: 449.0660

Dimethyl (*Z*)-5-(*p*-tolyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3i)



Dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate **1i** (25 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3i** (28.4 mg, 67 µmol, 67%) as yellow oil.

R_f: 0.42 in 1:10 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 – 7.31 (m, 2H), 7.14 – 7.11 (m, 2H), 6.06 (s, 1H), 4.80 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.07 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.90 (dd, *J* = 13.2, 12.4 Hz, 1H), 2.32 (s, 3H), 0.17 (s, 9H).

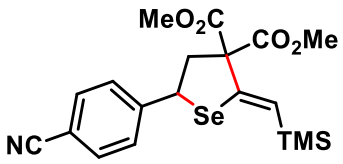
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.5, 169.3, 150.5, 137.4, 136.4, 129.3, 127.7, 125.5, 73.2, 53.2, 53.0, 47.0, 46.1, 21.0, -1.48.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 2391, 1733, 1437, 1238,1067, 833.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{26}O_4SeSiNa$:** 449.0664

Found: 449.0661

Dimethyl (*Z*)-5-(4-cyanophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3j)



Dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate **1j** (26 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3j** (40.5 mg, 93 µmol, 93%) as yellow solid.

R_f: 0.53 in 1:2 EtOAc/Pentane

m.p. = 115-116 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 – 7.54 (m, 4H), 6.11 (s, 1H), 4.84 (dd, *J* = 12.2, 4.7 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.11 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.83 (dd, *J* = 13.1, 12.2 Hz, 1H), 0.17 (s, 9H).

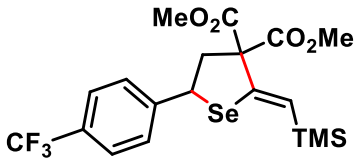
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 168.9, 149.2, 145.4, 132.4, 128.8, 126.6, 118.5, 111.5, 73.1, 53.4, 53.1, 46.6, 45.2, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 2313, 2225, 1732, 1434, 1240, 1133, 834.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{23}NO_4SeSiNa$**: 460.0460

Found: 460.04590

Dimethyl (*Z*)-5-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3k)



Dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate **1k** (30 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3k** (33.1 mg, 69 µmol, 69%) as yellow oil.

R_f: 0.27 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (s, 4H), 5.93 (s, 1H), 4.69 (dd, *J* = 12.2, 4.8 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H), 2.95 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.70 (dd, *J* = 13.1, 12.2 Hz, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.2, 169.1, 149.6, 143.9, 130.0 (C-F, $^1J_{C\text{-}F}$ = 256 Hz), 128.3, 127. 8 (C-F, $^1J_{C\text{-}F}$ = 256 Hz), 126.3, 125.68 (C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.64 (C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.6 (C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.5 (C-F, $^3J_{C\text{-}F}$ = 3.8 Hz), 125.3 (C-F, $^1J_{C\text{-}F}$ = 256 Hz), 122.6 (C-F , $^1J_{C\text{-}F}$ = 256 Hz), 73.2, 53.3, 53.1, 46.8, 45.3, -1.5.

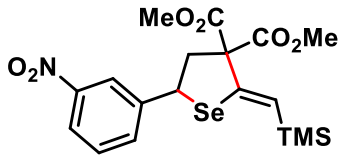
^{19}F NMR (377 MHz, $CDCl_3$): δ = -63.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2955, 2322, 1734, 1432, 1322, 1158,1118, 835.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{23}F_3O_4SeSiNa$**: 503.0381

Found: 503.0374

Dimethyl (*Z*)-5-(3-nitrophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3l)



Dimethyl 2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate **1l** (28 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3l** (41.9 mg, 92 µmol, 92%) as yellow oil.

R_f: 0.2 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (t, *J* = 2.0 Hz, 1H), 8.12 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.79 (ddd, *J* = 7.8, 1.6, 0.9 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 6.13 (s, 1H), 4.89 (dd, *J* = 12.2, 4.8 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.14 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.87 (dd, *J* = 13.1, 12.2 Hz, 1H), 0.18 (s, 9H).

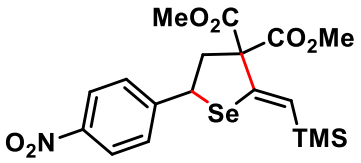
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.1, 168.9, 149.1, 142.2, 134.2 129.6, 126.7, 122.9, 122.7, 73.1, 53.4, 53.2, 46.8, 44.8, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 1732, 1520, 1437, 1343, 1242,1149, 836.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{23}NO_6SeSiNa$**: 480.0358

Found: 480.0359

Dimethyl (*Z*)-5-(4-nitrophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3m)



Dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate **1m** (28 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3m** (32.8 mg, 72 µmol, 72%) as brown oil.

R_f: 0.53 in 1:2 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 6.12 (s, 1H), 4.89 (dd, J = 12.2, 4.8 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.13 (dd, J = 13.1, 4.8 Hz, 1H), 2.85 (dd, J = 13.1, 12.2 Hz, 1H), 0.17 (s, 9H).

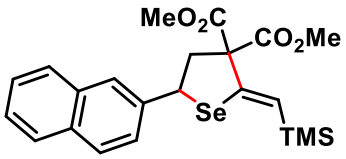
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.2, 169.0, 149.2, 147.5, 128.9, 126.8, 124.0, 73.2, 53.5, 53.3, 46.7, 44.9, -1.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 1732, 1520, 1437, 1343, 1242, 836, 691.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{23}NO_6SeSiNa$**: 480.0358

Found: 480.0359

Dimethyl (*Z*)-5-(naphthalen-2-yl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3n)



Dimethyl 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate **1n** (28 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3n** (35.5 mg, 77 µmol, 77%) as yellow solid.

R_f: 0.36 in 1:10 EtOAc/Pentane

m.p. = 112 °C -113 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 – 7.77 (m, 4H), 7.60 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.48 – 7.44 (m, 2H), 6.10 (s, 1H), 5.01 (dd, *J* = 12.2, 4.7 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.16 (dd, *J* = 13.1, 4.8 Hz, 1H), 3.03 (dd, *J* = 13.1, 12.2 Hz, 1H), 0.18 (s, 9H).

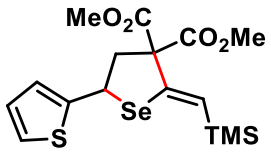
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.5, 169.3, 150.3, 136.9, 133.2, 132.9, 128.5, 127.7, 127.6, 126.6, 126.3, 126.0, 125.7, 125.7, 73.3, 53.3, 53.1, 46.9, 46.6, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2958, 2322, 1728, 1506, 1431, 1247,1170, 954,752.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{22}H_{26}O_4SeSiNa$**: 485.0664

Found: 485.0657

Dimethyl (*Z*)-5-(thiophen-2-yl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)dicarboxylate (3o)



Dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate **1e** (24 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3o** (18.7 mg, 45 µmol, 45%) as yellow oil.

R_f: 0.31 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.04 (ddd, *J* = 3.5, 1.2, 0.7 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.08 (s, 1H), 5.14 (ddd, *J* = 11.9, 4.8, 0.7 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.20 (dd, *J* = 13.1, 4.8 Hz, 1H), 2.92 (dd, *J* = 13.1, 11.9 Hz, 1H), 0.16 (s, 9H).

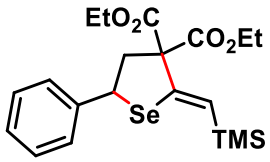
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.2, 169.0, 149.8, 144.0, 1 26.7, 126.0, 125.4, 124.8, 72.9, 53.3, 53.0, 48.2, 40.4, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2953, 1732, 1436, 1237, 1143, 1003, 835.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{16}H_{22}O_4SSeSiNa$**: 441.0071

Found: 441.0066

Diethyl (*Z*)-5-phenyl-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3p)



Diethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate **1p** (28 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(trimethylsilyl)ethyne-1-selenolate **2a** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **3p** (32.0 mg, 73 µmol, 73%) as yellow oil.

R_f: 0.5 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 – 7.43 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 6.12 (s, 1H), 4.84 (dd, *J* = 12.4, 4.7 Hz, 1H), 4.32 – 4.22 (m, 4H), 3.09 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.89 (dd, *J* = 13.2, 12.4 Hz, 1H), 1.29 (td, *J* = 7.1, 4.5 Hz, 6H), 0.16 (s, 9H).

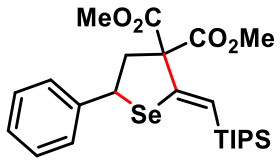
^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.9, 168.8, 150.5, 139.6, 128.6, 127.8, 127.6, 125.5, 73.1, 62.0, 61.9, 47.0, 46.2, 14.0, 13.9, -1.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2964, 2323, 1729, 1572, 1235, 1147, 1014, 839.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{20}H_{28}O_4SeSiNa$**: 463.0820.

Found: 463.0819.

Dimethyl (*Z*)-5-phenyl-2-((triisopropylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (4a)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(triisopropylsilyl)ethyne-1-selenolate (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **4a** (46.1 mg, 87 µmol, 87%) as yellow oil.

R_f: 0.5 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.42 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 6.07 (s, 1H), 4.88 (dd, *J* = 12.3, 4.7 Hz, 1H), 3.80 (d, *J* = 13.9 Hz, 6H), 3.11 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.89 (dd, *J* = 13.1, 12.3 Hz, 1H), 1.30 – 1.17 (m, 3H), 1.09 (dd, *J* = 7.3, 1.9 Hz, 18H).

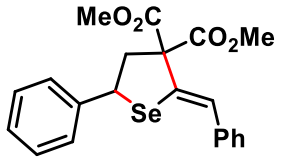
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 169.5, 151.5, 139.7, 128.6, 127.9, 127.6, 122.7, 73.9, 53.1, 52.9, 47.1, 46.5, 18.8, 18.7, 11.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2944, 2862, 2322, 1734, 1445, 1231, 1150, 1066, 666.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{21}H_{20}O_4SeNa$**: 519.1446

Found: 519.1438

Dimethyl (*Z*)-2-benzylidene-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4b)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-phenylethyne-1-selenolate **2b** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **4b** (46.1 mg, 87 µmol, 87%) as colourless solid.

R_f: 0.4 in 1:20 EtOAc/Pentane

m.p. = 114-115 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 2H), 7.40 – 7.20 (m, 8H), 6.95 (s, 1H), 4.91 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.85 (d, *J* = 2.5 Hz, 6H), 3.22 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.92 (dd, *J* = 13.1, 12.4 Hz, 1H).

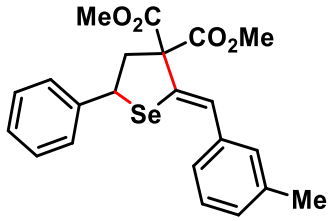
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 139.1, 137.3, 135.6, 128.7, 128.3, 128.1, 127.9, 127.8, 127.1, 126.7, 71.7, 53.4, 53.2, 47.1, 46.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2955, 2657, 2200, 1758, 1489, 1267, 1150, 1013, 744.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{21}H_{20}O_4SeNa$**: 439.0425

Found: 439.0422

Dimethyl (*Z*)-2-(3-methylbenzylidene)-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4c)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-(*m*-tolyl)ethyne-1-selenolate **2c** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **4c** (18.6 mg, 43 µmol, 43%) as yellow oil.

R_f: 0.4 in 1:20 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.44 (m, 2H), 7.32 (dd, *J* = 8.3, 6.4 Hz, 2H), 7.28 – 7.16 (m, 4H), 7.06 – 7.02 (m, 1H), 6.92 (s, 1H), 4.89 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.85 (d, *J* = 2.9 Hz, 6H), 3.21 (dd, *J* = 13.1, 4.7 Hz, 1H), 2.92 (dd, *J* = 13.1, 12.4 Hz, 1H), 2.34 (s, 3H).

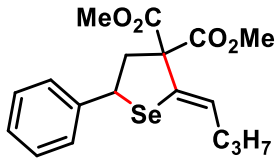
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.7, 169.7, 139.1, 137.9, 137.2, 128.8, 128.7, 128.2, 127.9, 127.8, 126.8, 125.1, 71.7, 53.4, 53.2, 47.0, 46.5, 21.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3023, 2950, 2323, 1730, 1489, 1230, 1149, 748, 690.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{21}H_{20}O_4SeNa$**: 453.0581

Found: 453.0577

Dimethyl (*Z*)-2-butylidene-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4d)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium pent-1-yne-1-selenolate **2d** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **4d** (22.0 mg, 58 µmol, 58%) as yellow oil.

R_f: 0.5 in 1:10 EtOAc/Pentane

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.43 (m, 2H), 7.34 – 7.24 (m, 3H), 5.88 (t, *J* = 7.0 Hz, 1H), 4.79 (dd, *J* = 12.3, 4.6 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.18 – 3.10 (m, 1H), 2.90 (t, *J* = 12.7 Hz, 1H), 1.97 (dt, *J* = 14.7, 7.3 Hz, 2H), 1.50 (q, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

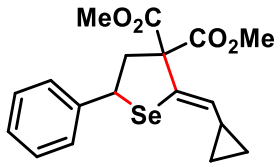
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 169.5, 139.6, 134.5, 128.6, 127.8, 127.6, 127.2, 69.6, 53.2, 53.0, 48.0, 44.9, 36.2, 30.8, 21.8, 13.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2955, 2323, 1732, 1494, 1232, 1152, 1063, 695.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{22}O_4SeNa$**: 405.0581

Found: 405.0575

Dimethyl (*Z*)-2-(cyclopropylmethylene)-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4e)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-cyclopropylethyne-1-selenolate **2e** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **4e** (17.0 mg, 45 µmol, 45%) as yellow oil.

R_f: 0.5 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.45 (m, 2H), 7.35 – 7.25 (m, 3H), 5.40 (d, *J* = 8.8 Hz, 1H), 4.84 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.13 (dd, *J* = 13.2, 4.6 Hz, 1H), 2.90 (dd, *J* = 13.1, 12.4 Hz, 1H), 1.15 (dtd, *J* = 9.4, 8.3, 4.1 Hz, 1H), 0.88 – 0.78 (m, 2H), 0.50 (td, *J* = 4.6, 2.4 Hz, 2H).

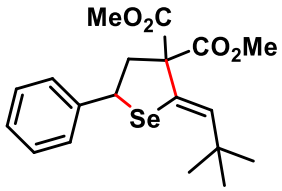
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.9, 169.5, 139.5, 131.9, 130.7, 128.6, 127.9, 127.6, 69.4, 53.3, 53.0, 48.2, 45.1, 15.8, 7.1, 6.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3004, 2951, 2323, 1729, 1232, 1150, 1014, 695.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{20}O_4SeNa$**: 403.0425

Found: 403.0419

Dimethyl (*Z*)-2-(2,2-dimethylpropylidene)-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4f)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 3,3-dimethylbut-1-yne-1-selenolate **2f** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product **4f** (20.1 mg, 51 µmol, 51%) as yellow oil.

R_f: 0.5 in 1:10 EtOAc/Pentane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.43 (m, 2H), 7.34 – 7.30 (m, 2H), 7.26 (s, 1H), 5.88 (s, 1H), 4.70 (dd, *J* = 12.5, 4.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.09 (dd, *J* = 13.1, 4.6 Hz, 1H), 2.82 (dd, *J* = 13.1, 12.4 Hz, 1H), 1.13 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.2, 170.0, 139.5, 137.4, 129.9, 128.6, 127.8, 127.6, 71.6, 53.2, 53.0, 46.7, 46.0, 33.3, 29.0.

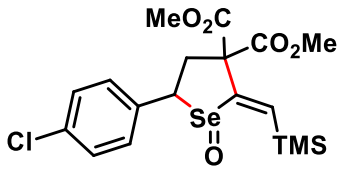
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2957, 2323, 1733, 1442, 1237, 1148, 962, 733.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{19}H_{24}O_4SeNa$**: 419.0738

Found: 419.0734

4. Follow-up reactions

Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate 1-oxide (7c)



Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2H)-dicarboxylate **3c** (44.6 mg, 100 µmol, 1.0 equiv.) was dissolved in dichloromethane (5 mL). To the stirring solution was added *meta*-chloroperoxybenzoic acid (*m*CPBA) (52 mg, 300 µmol, 3.0 equiv). The solution was allowed to stir for 5 h. To the solution was added more dichloromethane, washed with 2M NaOH solution and extracted using dichloromethane. The combined organic layers were dried using Na_2SO_4 and the solvent was evaporated off under reduced pressure gave the desired product **7c** (45.1 mg, 98 µmol,98 %) as colourless semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (dd, J = 8.4, 0.5 Hz, 2H), 7.36 – 7.33 (m, 2H), 6.95 (s, 1H), 4.36 (dd, J = 14.3, 4.5 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.54 (t, J = 14.2 Hz, 1H), 3.03 (dd, J = 14.1, 4.5 Hz, 1H), 0.31 (s, 9H).

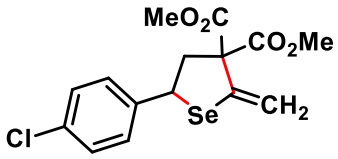
^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.4, 167.7, 159.5, 147.4, 134.8, 130.7, 130.0, 128.8, 68.1, 61.2, 53.6, 53.4, 39.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3053, 2322, 1732, 1242, 1145, 1020, 840, 703.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{18}H_{23}ClO_5SeSiNa$**: 485.0066

Found: 485.0057

Dimethyl (*Z*)-5-(4-chlorophenyl)-2-methylenedihydroselenophene-3,3(2*H*)-dicarboxylate (8c)



Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2H)-dicarboxylate **3c** (44.6 mg, 100 µmol, 1.0 equiv.) was dissolved in acetonitrile/ THF/water in a 3:3:1 ratio (5 mL). To the stirring solution was added *para*-toluenesulfonic acid (*p*TsOH) (29 mg, 150 µmol, 1.5 equiv). The solution was allowed to reflux for 5 h. To the solution was added more dichloromethane, washed with 2M NaOH solution and extracted using dichloromethane. The combined organic layers were dried using Na_2SO_4 and the solvent was evaporated off under reduced pressure. Silica gel column chromatography (*n*-pentane: EtOAc = 10:1) gave the desired product **8c** (25.4 mg, 68 µmol, 68 %) as orange solid.

R_f: 0.40 in 1:20 EtOAc/Pentane

m.p. = 102-103 °C

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41 – 7.36 (m, 2H), 7.31 – 7.26 (m, 2H), 5.71 (dd, *J* = 2.0, 0.5 Hz, 1H), 5.46 (dd, *J* = 2.0, 0.6 Hz, 1H), 4.85 (dd, *J* = 12.2, 4.7 Hz, 1H), 3.84 (d, *J* = 0.5 Hz, 3H), 3.81 (d, *J* = 0.5 Hz, 3H), 3.13 (ddd, *J* = 13.3, 4.7, 0.6 Hz, 1H), 2.88 (dd, *J* = 13.3, 12.2 Hz, 1H).

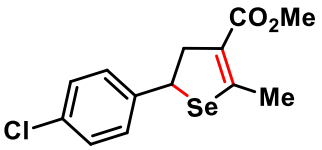
^{13}C NMR (126 MHz, $CDCl_3$): δ = 169.1, 168.8, 142.3, 137.9, 133.4, 129.2, 128.8, 112.6, 70.3, 53.4, 53.2, 48.2, 45.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2951, 2322, 1731, 1489, 1258, 1226, 885.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for **$C_{15}H_{15}ClO_4SeNa$**: 396.9722

Found: 396.9713

Methyl (*Z*)-5-(4-chlorophenyl)-2-methyl-4,5-dihydroselenophene-3-carboxylate (9c)



Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2H)-dicarboxylate **3c** (44.6 mg, 100 µmol, 1.0 equiv.) was dissolved in acetonitrile/water in a 1:1 ratio (5 mL). To the stirring solution was added aqueous NaOH (2 M, 0.2 mL). The solution was allowed to stir overnight. To the solution was added more dichloromethane, washed with 2M HCl solution and extracted using dichloromethane. The combined organic layers were dried using Na_2SO_4 and the solvent was evaporated off under reduced pressure. Silica gel column chromatography (*n*-pentane: EtOAc = 10:1) gave the desired product **9c** (28 mg, 88 µmol, 88 %) as orange oil.

R_f: 0.22 in 1:5 EtOAc/Pentane

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 – 7.29 (m, 2H), 7.26 (dt, J = 6.6, 2.3 Hz, 2H), 4.95 (dd, J = 8.7, 7.1 Hz, 1H), 3.73 (s, 3H), 3.55 (ddd, J = 16.3, 8.7, 2.0 Hz, 1H), 3.44 – 3.37 (m, 1H), 2.47 (t, J = 1.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 164.3, 155.7, 141.6, 133.1, 128.8, 128.3, 123.2, 77.2, 51.2, 46.9, 45.1, 18.7.

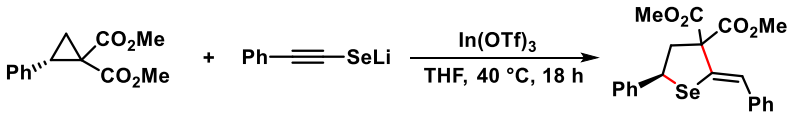
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2992, 2842, 2322, 1695, 1599, 1228, 1049, 821.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for **$C_{13}H_{14}ClO_2Se$**: 316.9847

Found: 316.9839

5. Sterospecificity Experiment

Dimethyl (*R,Z*)-2-benzylidene-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate



(*S*)-1a
98% ee

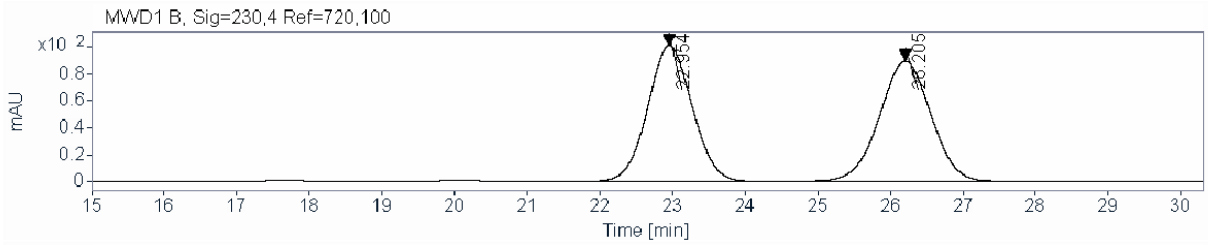
2b

(*R*)-4b
95% ee

Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (***S***)-**1a** (23.4 mg, 100 µmol, 1.0 equiv.), *in situ* generated lithium 2-phenylethyne-1-selenolate **2b** (see GP2) and indium trifluoromethanesulfonate (44.9 mg, 80.0 µmol, 0.8 equiv.) in THF (1.0 mL) were reacted according to GP 3 for 18 h. Silica gel column

chromatography (*n*-pentane: EtOAc = 20:1) gave the desired product (***R***)-**4b** (31.9 mg, 77 µmol, 77%) as yellow oil. HPLC data revealed that the reaction proceeds with high stereospecificity with only a slight loss of enantiopurity (98 to 95% ee). This prompted us to conclude that the initial nucleophilic attack by chalcogen proceeds by an S_N2-like attack with inversion at the stereocenter to form (***R***)-**4b**.

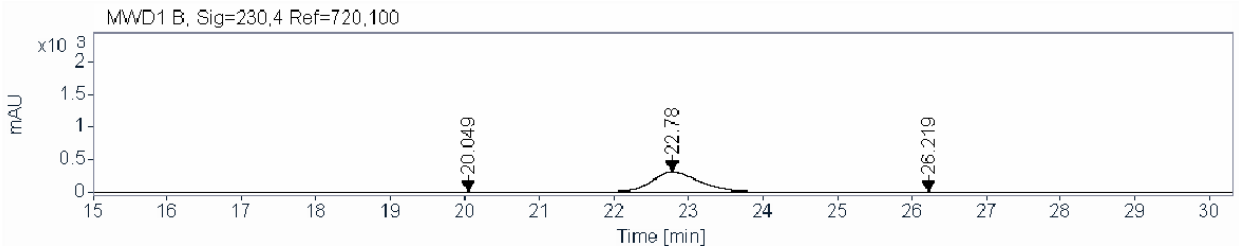
Chromatogram of (*rac*)-**4b**



Signal: MWD1 B, Sig=230,4 Ref=720,100

RT [min]	Width [min]	Height	Area	Area%
22.959	0.5667	19.7323	846.8037	49.4739
26.203	0.6163	17.4159	864.8126	50.5261
		Sum	1711.6163	

Chromatogram of (*R*)-**4b**

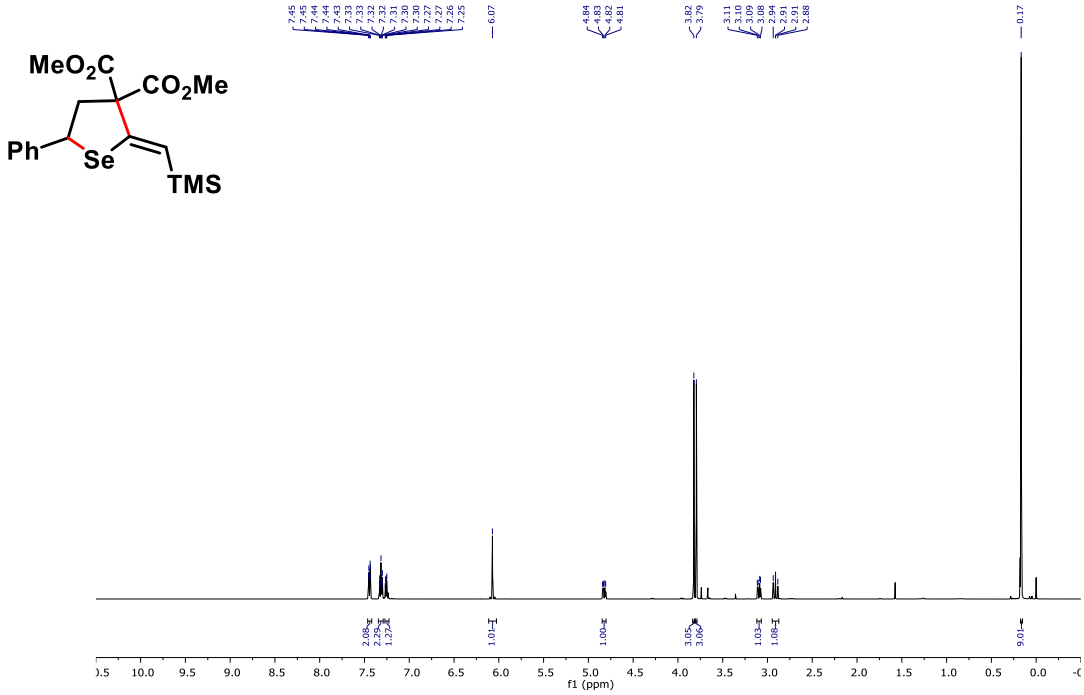


Signal: MWD1 B, Sig=230,4 Ref=720,100

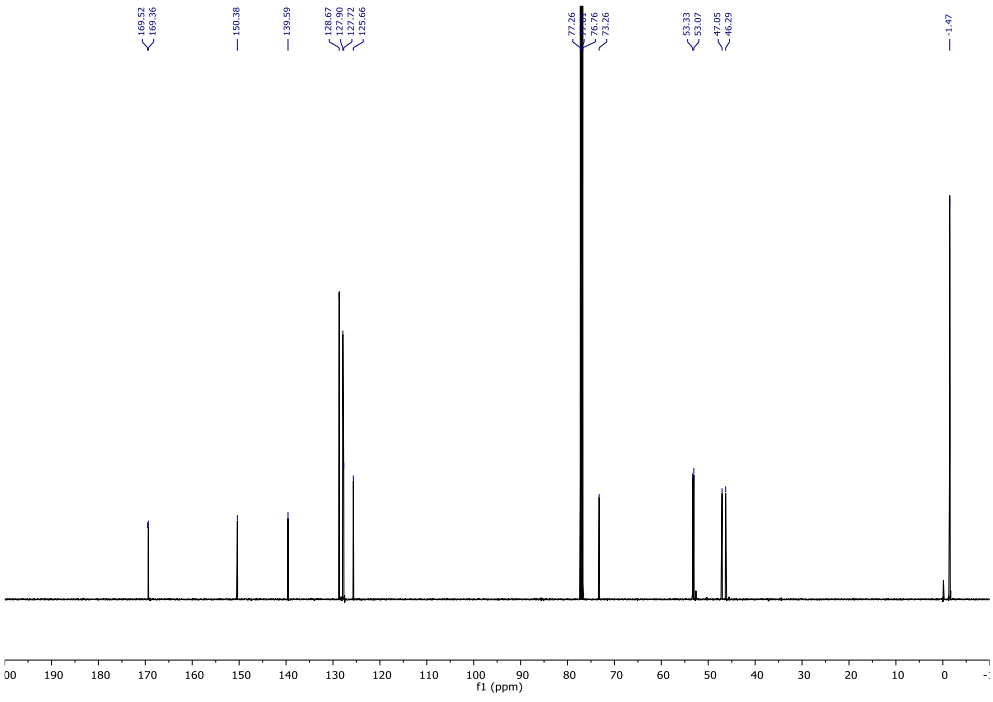
RT [min]	Width [min]	Height	Area	Area%
22.780	0.6512	307.0833	13324.0029	28.4208
26.219	0.5800	3.6918	180.3726	0.3847
		Sum	46881.1273	

6. ^{1}H and ^{13}C NMR data

Dimethyl (*Z*)-5-phenyl-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3a)

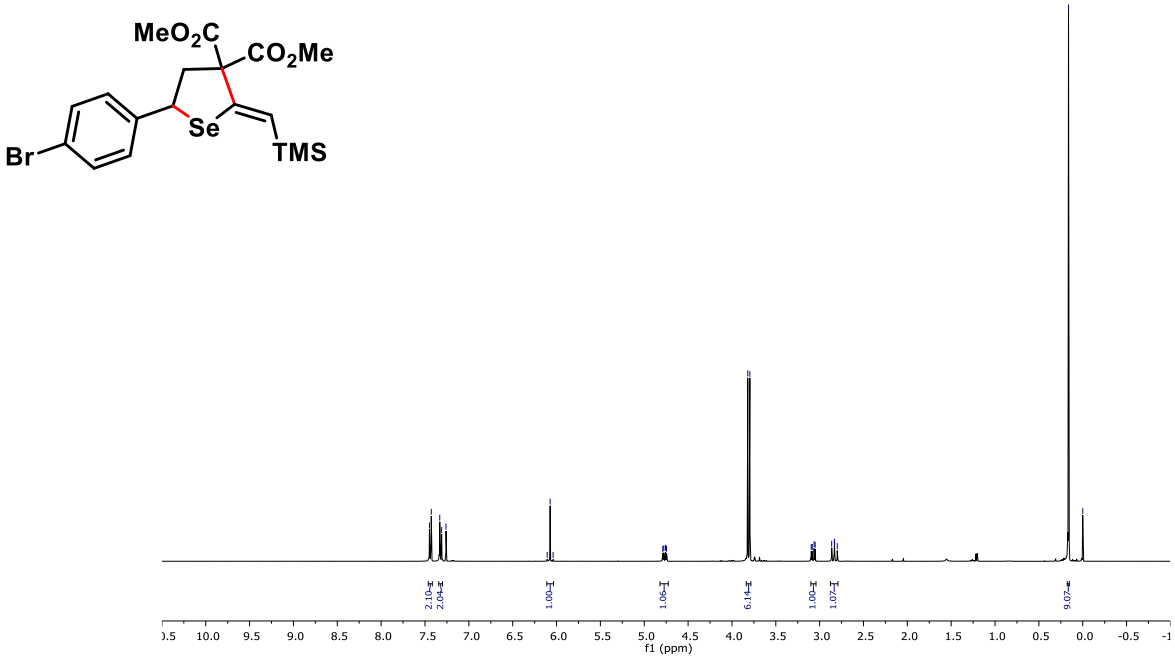


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$)

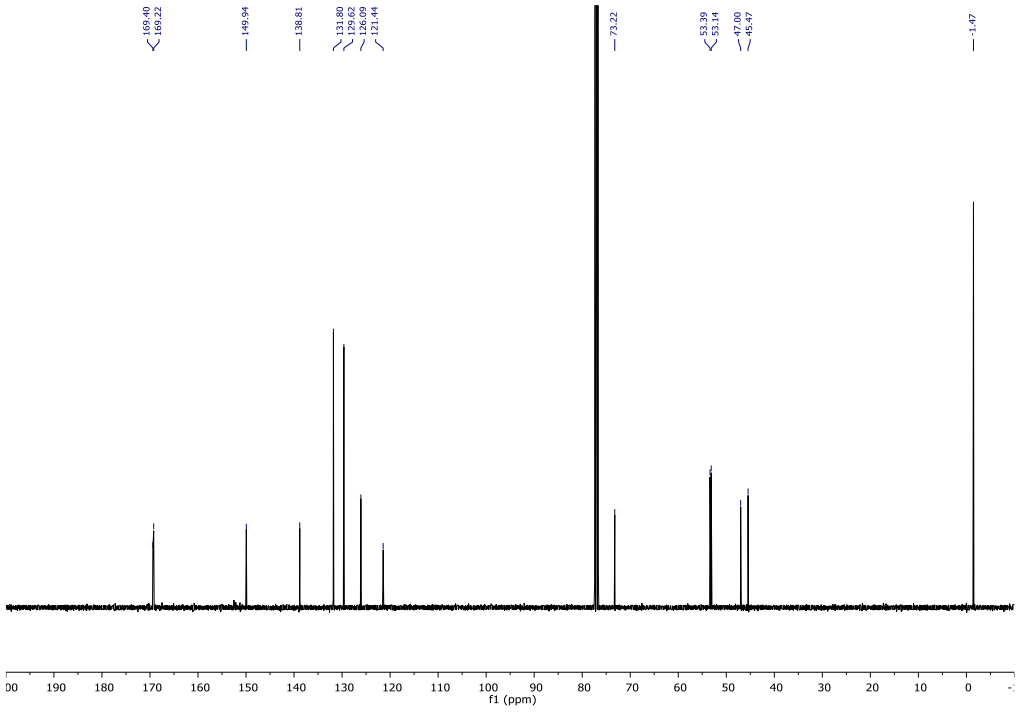


^{13}C-NMR Spectrum (150 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(4-bromophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3b)

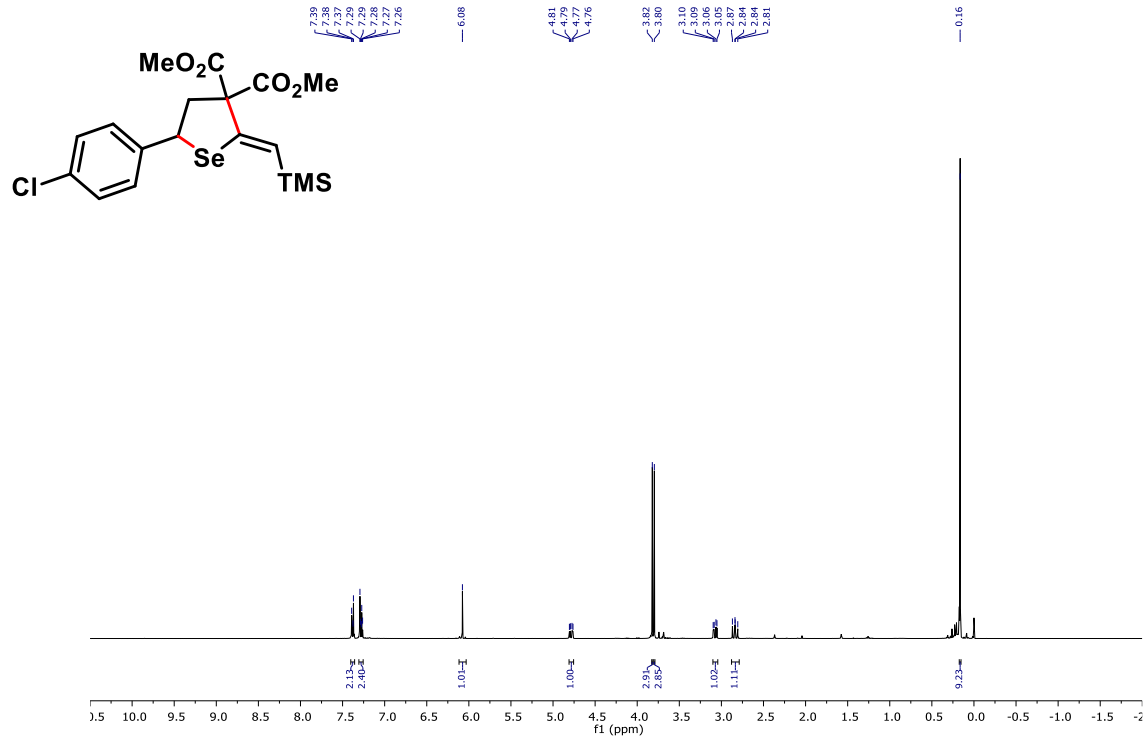


^{1}H-NMR Spectrum (600 MHz, $CDCl_3$)

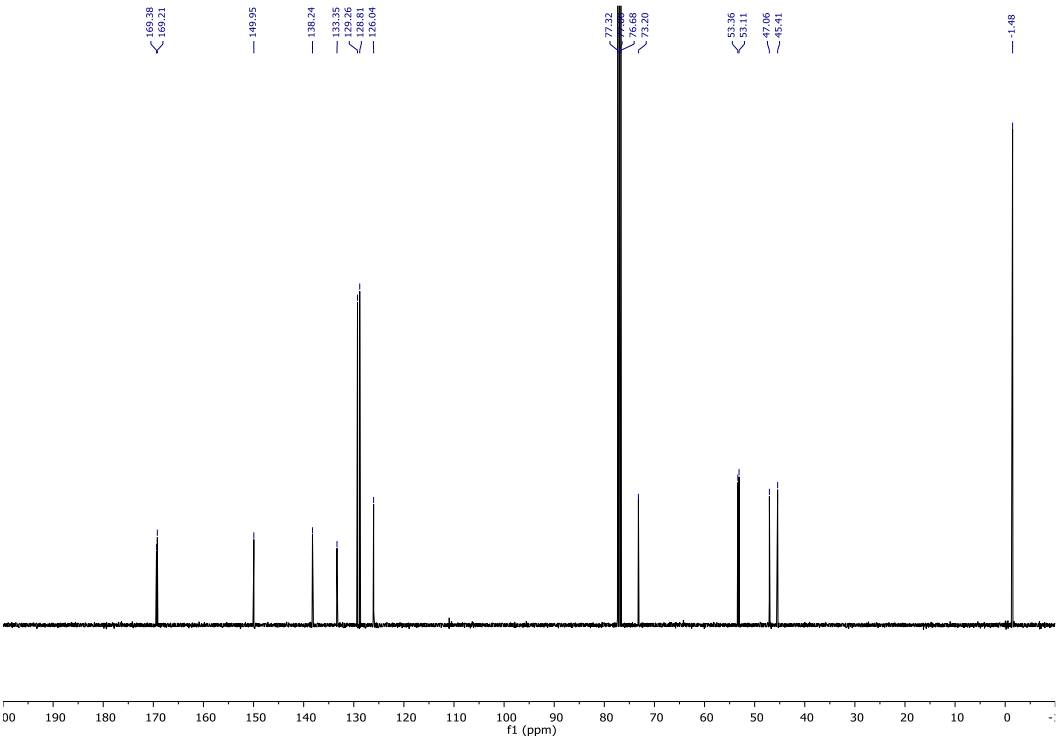


^{13}C-NMR Spectrum (150 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3c)

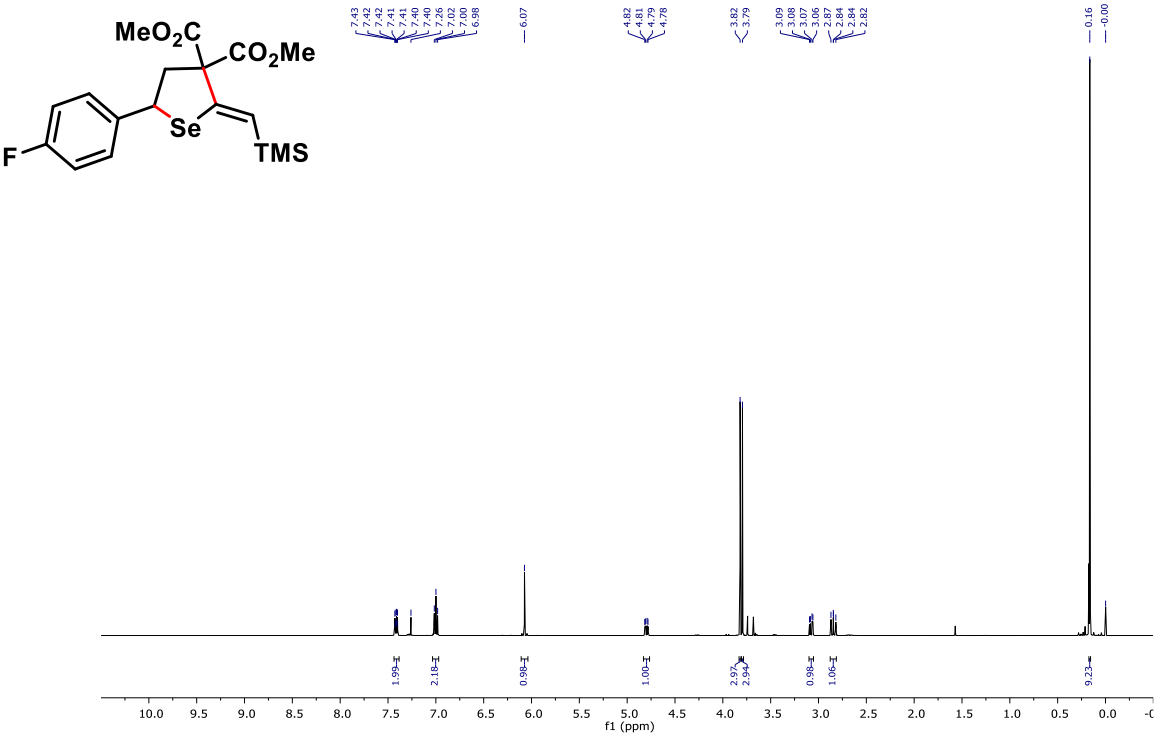


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

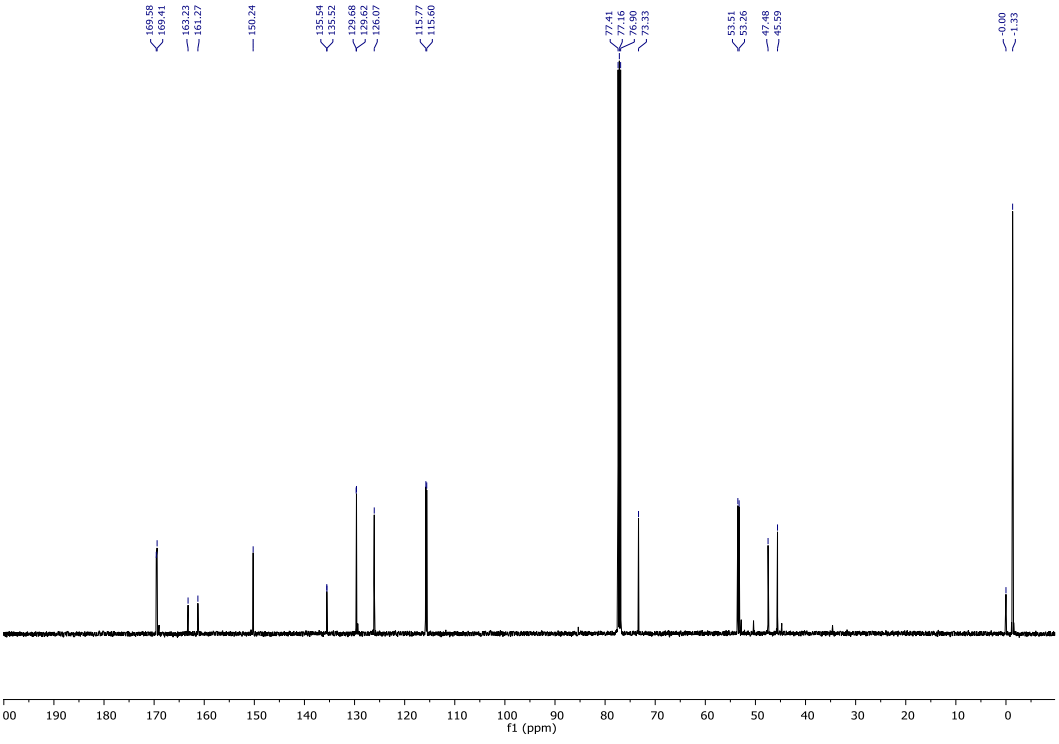


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

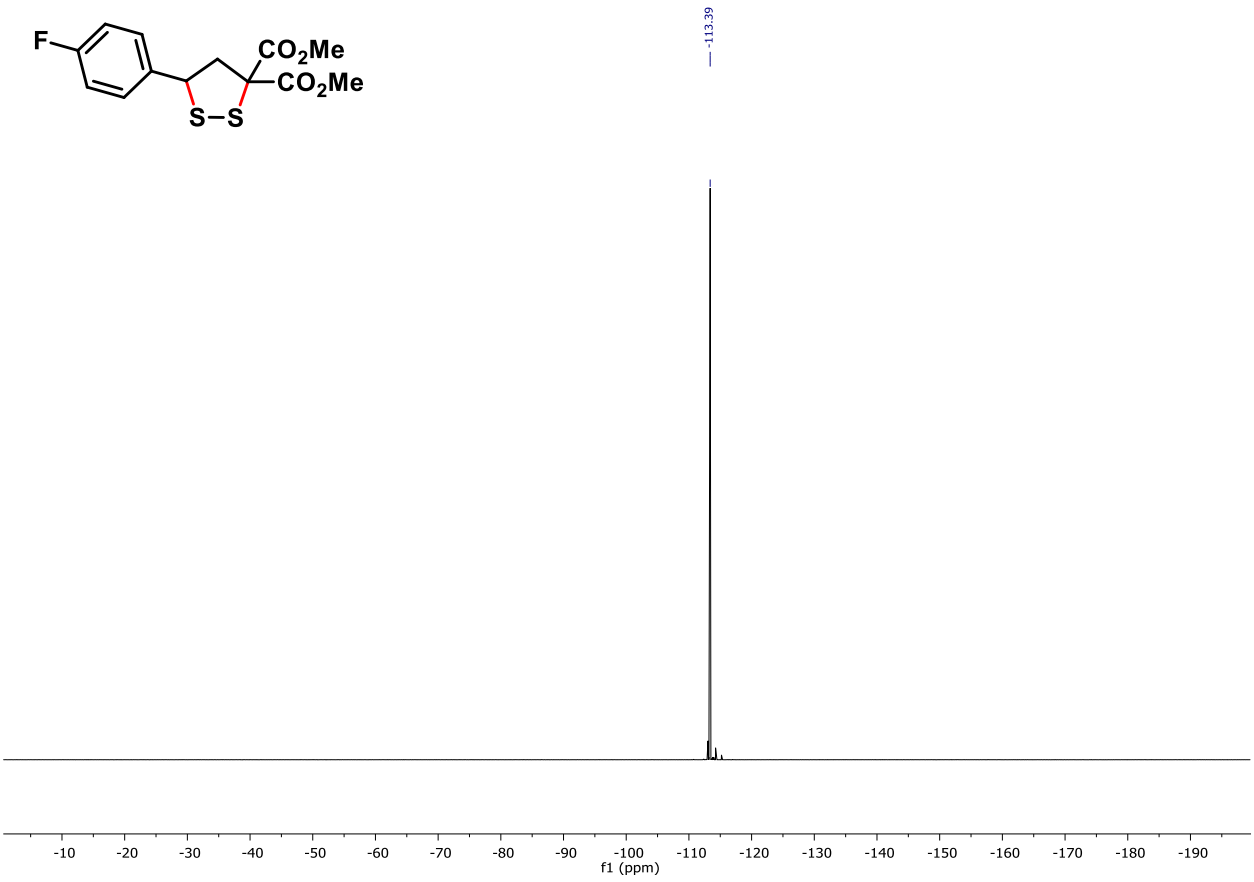
Dimethyl (*Z*)-5-(4-fluorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3d)



^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

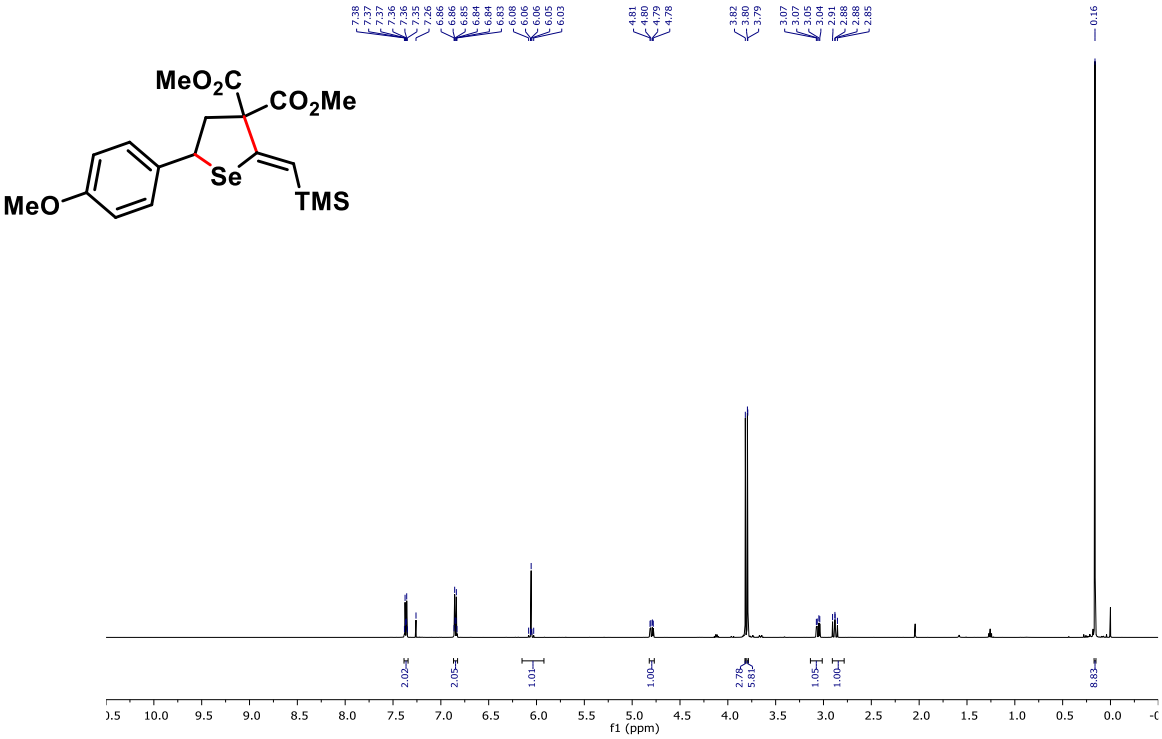


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

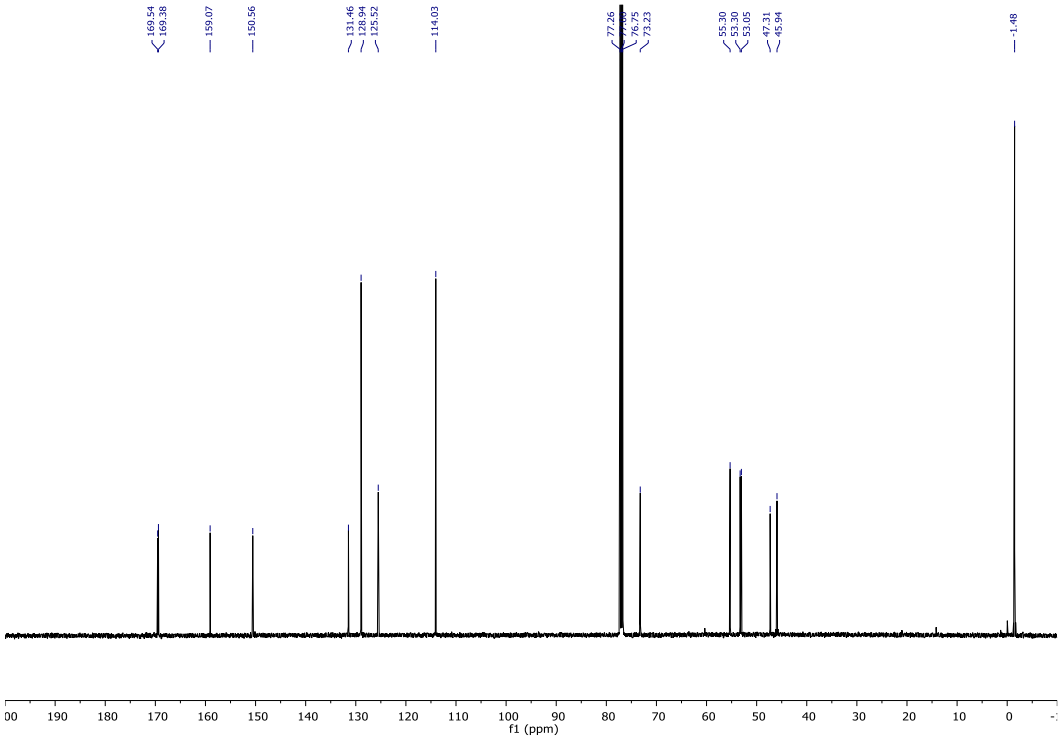


^{19}F-NMR Spectrum (377 MHz, $CDCl_3$)

Dimethyl -(*Z*)-5-(4-methoxyphenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate(3e)

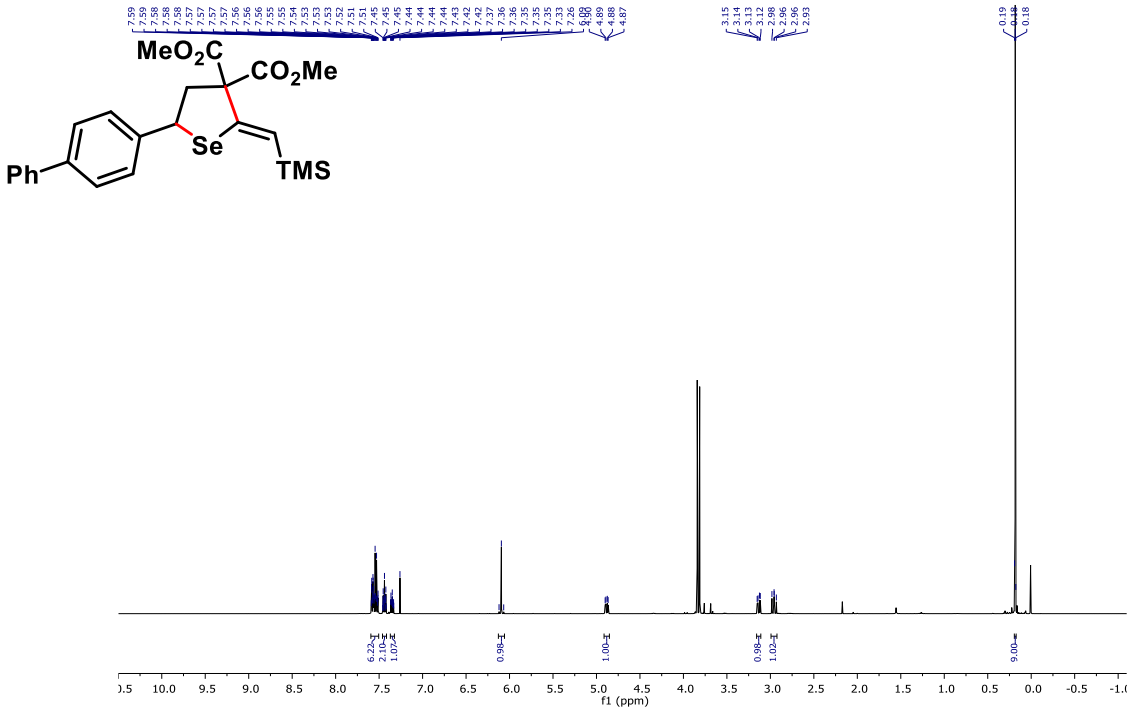


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

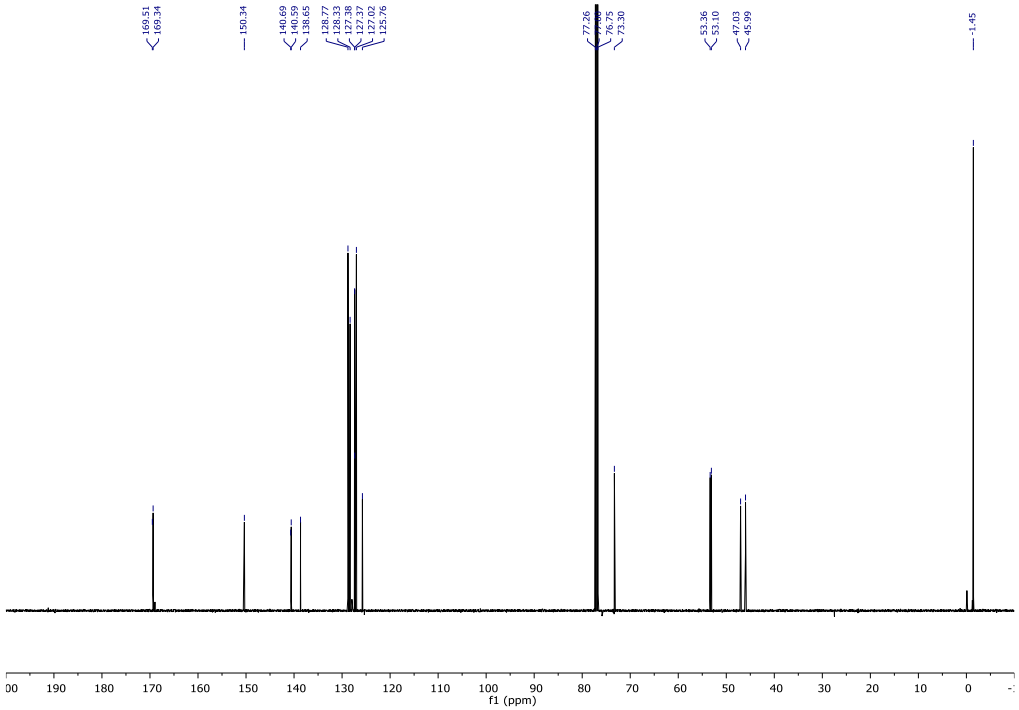


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl -(*Z*)-5-([1,1'-biphenyl]-4-yl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)dicarboxylate (3f)

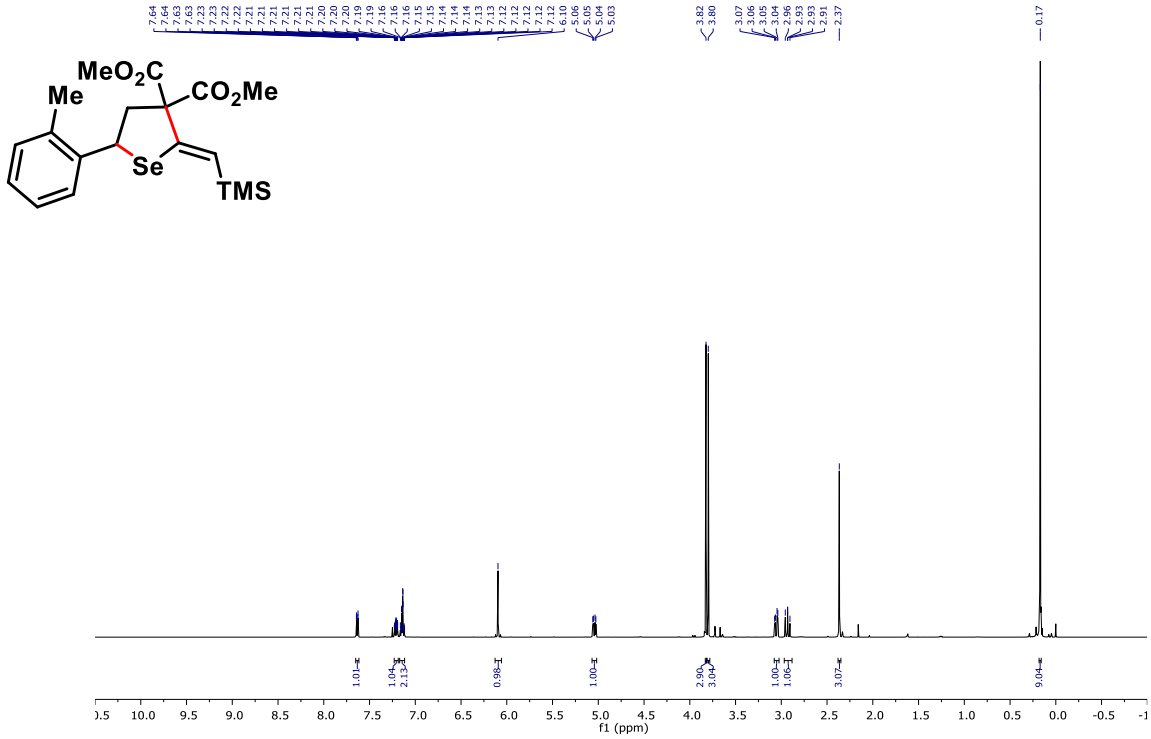


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

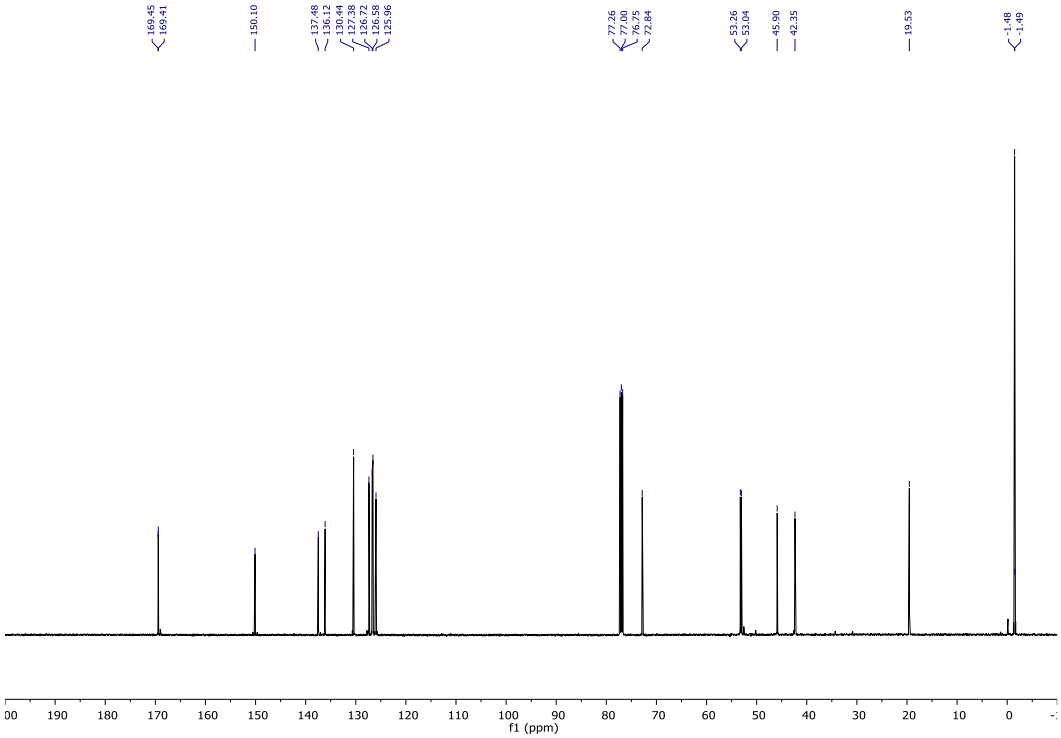


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(o-tolyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3g)

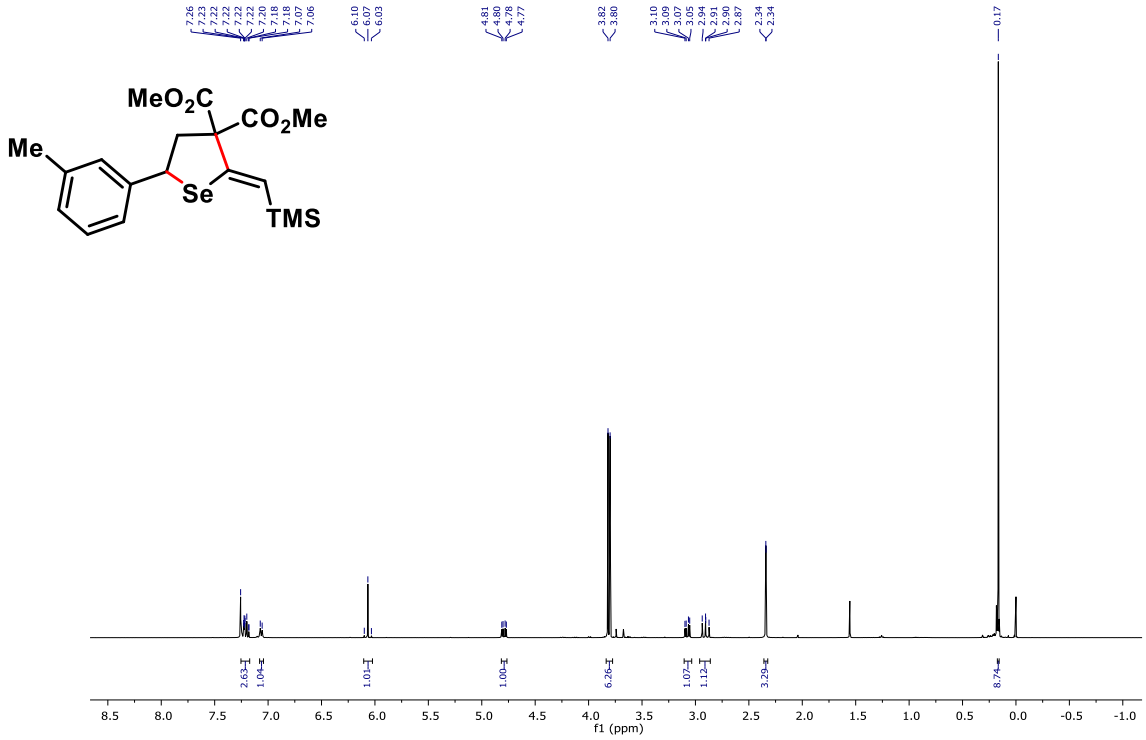


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

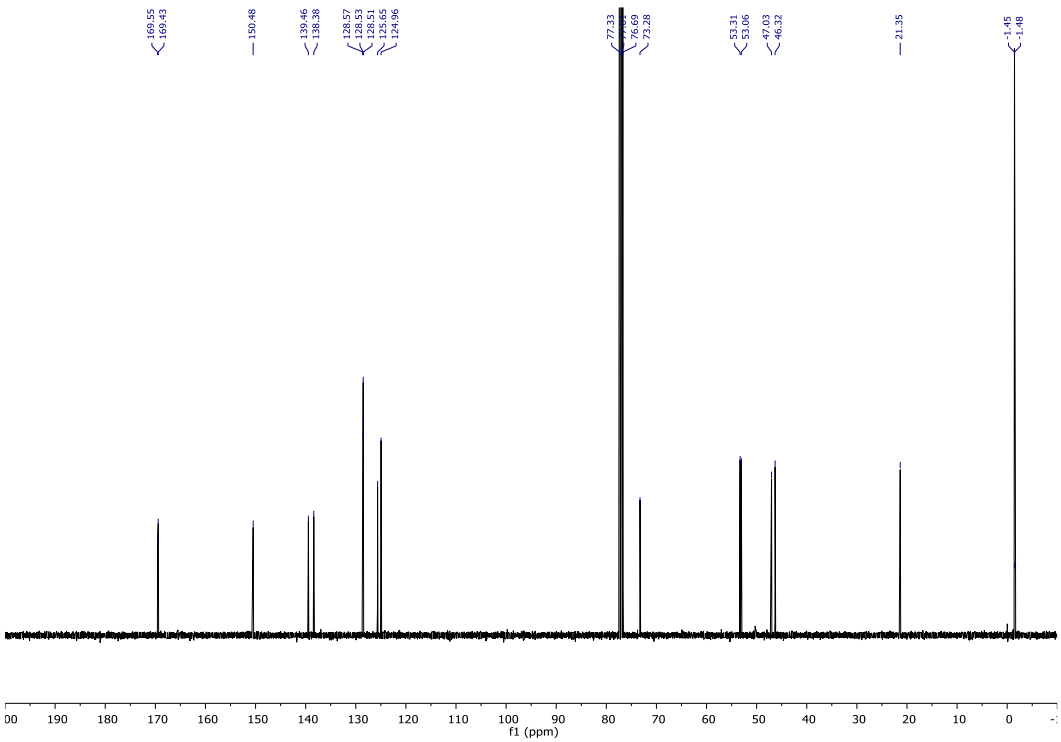


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(m-tolyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3h)

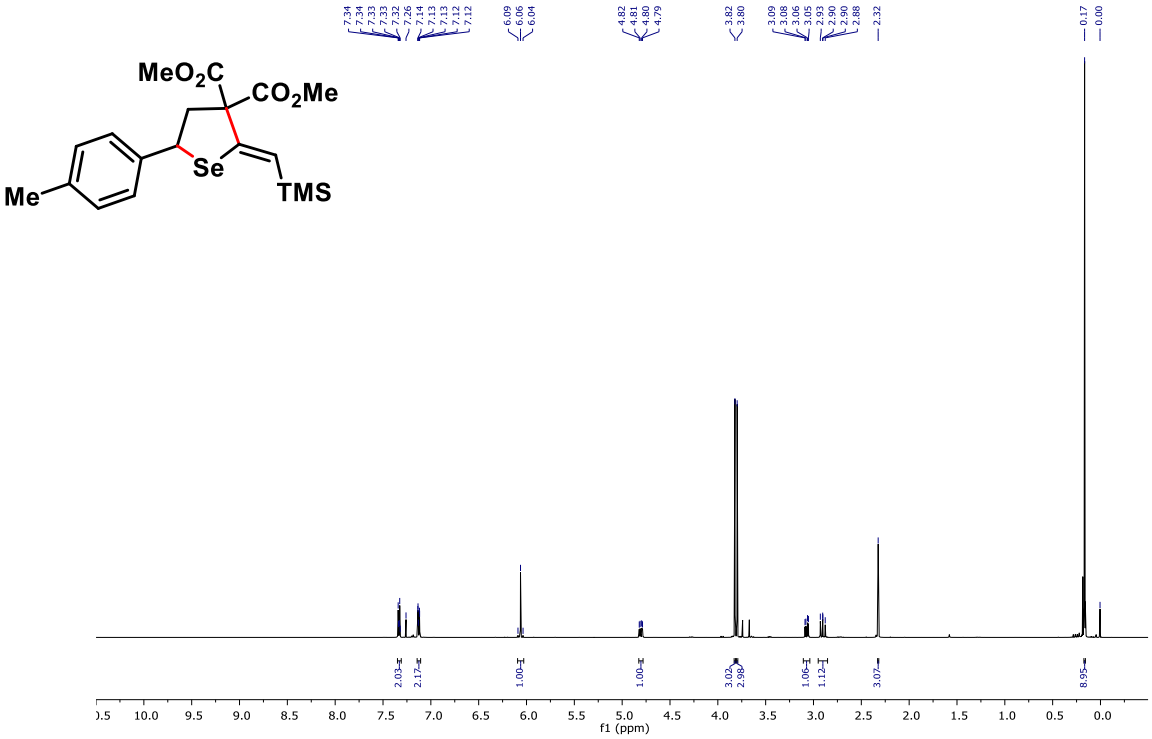


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

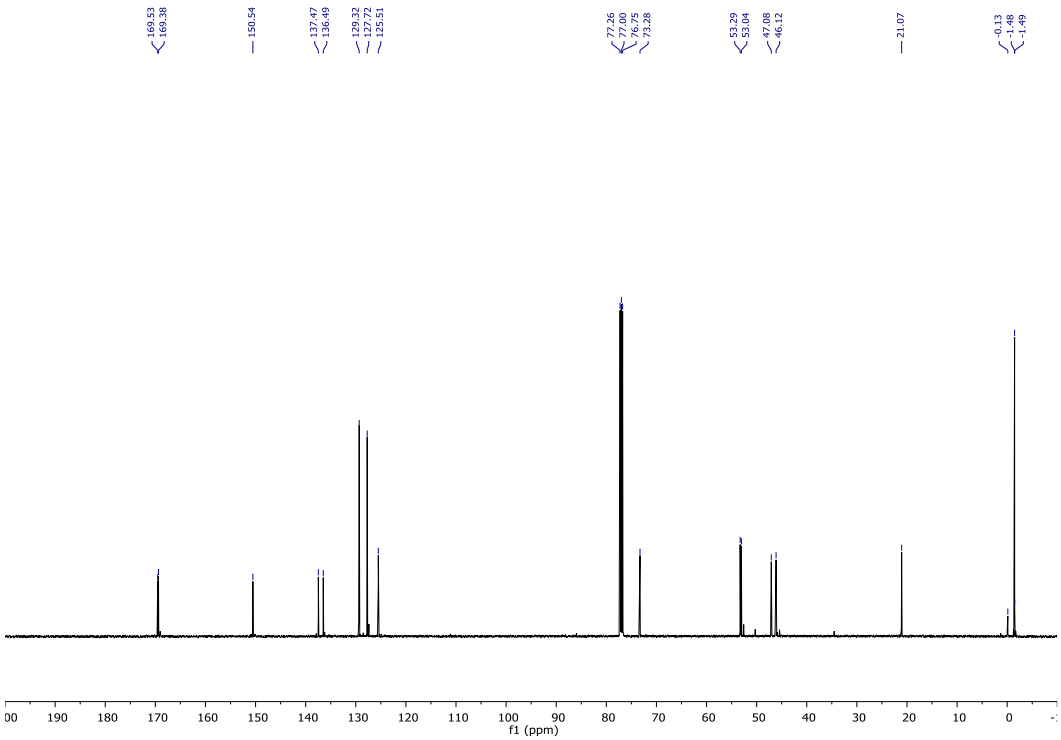


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(*p*-tolyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3i)

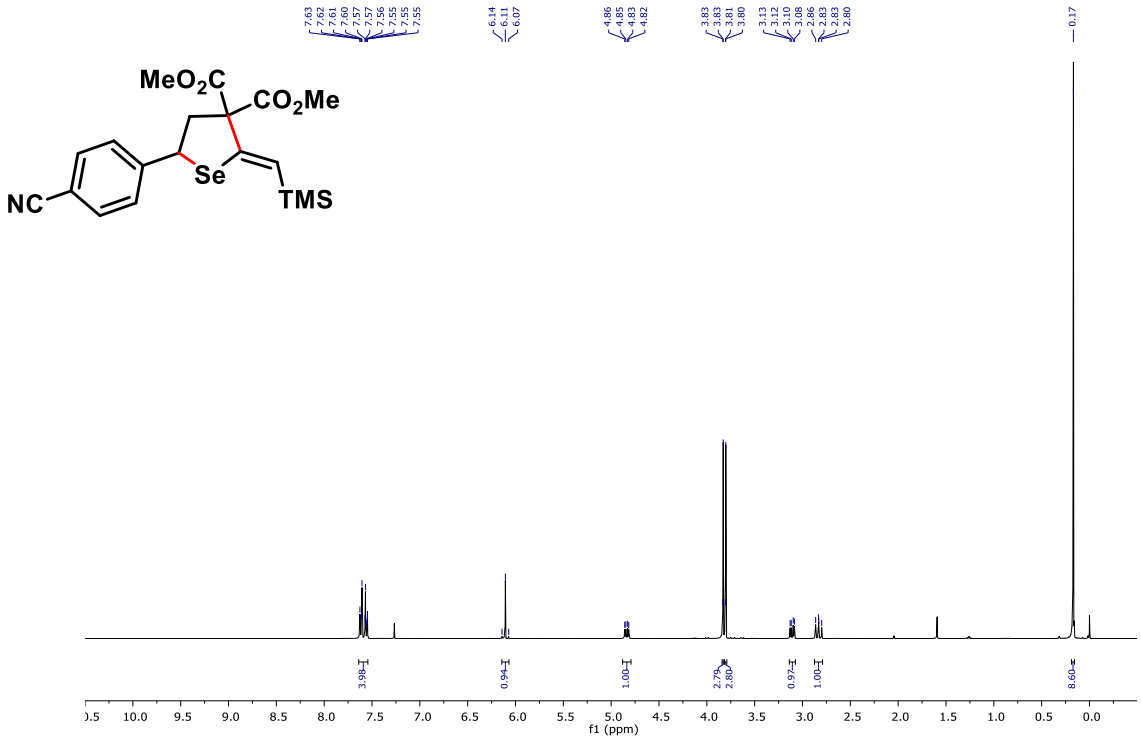


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

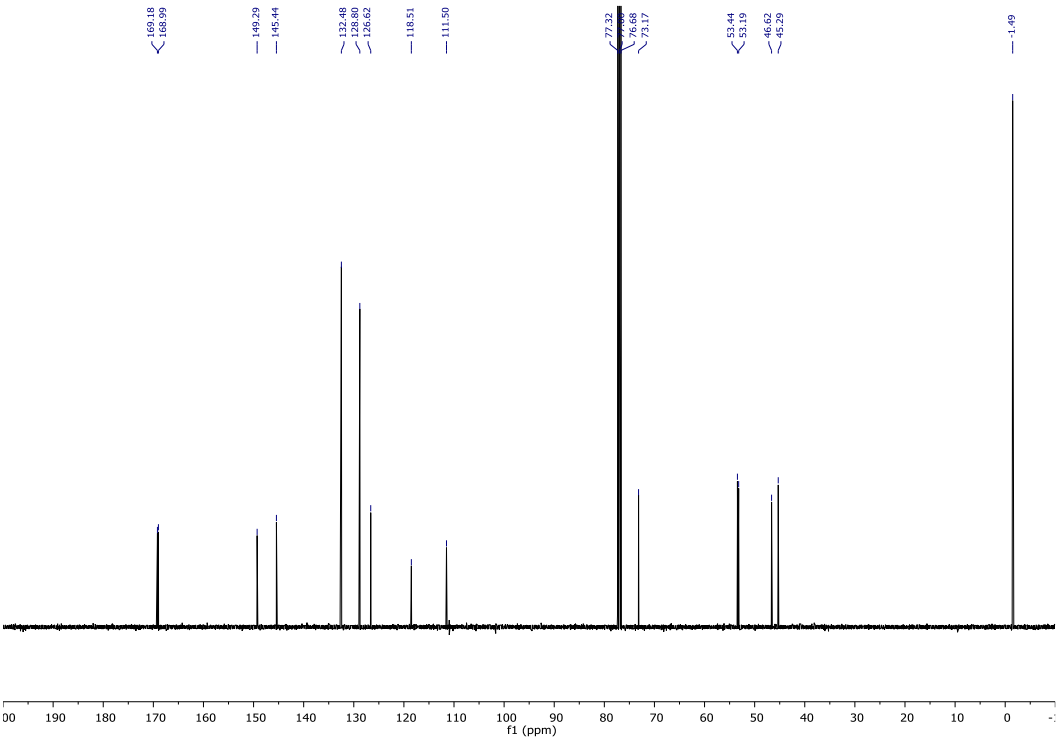


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(4-cyanophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3j)

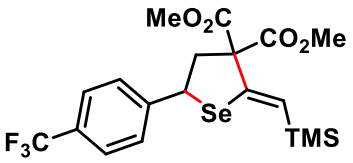


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

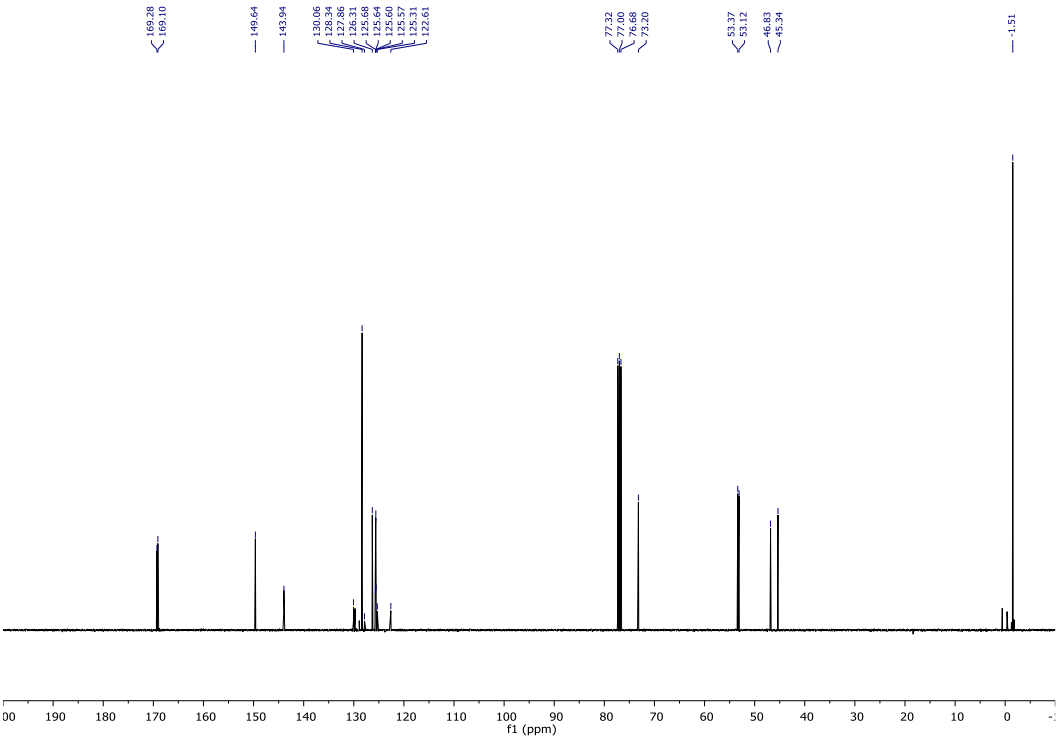


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

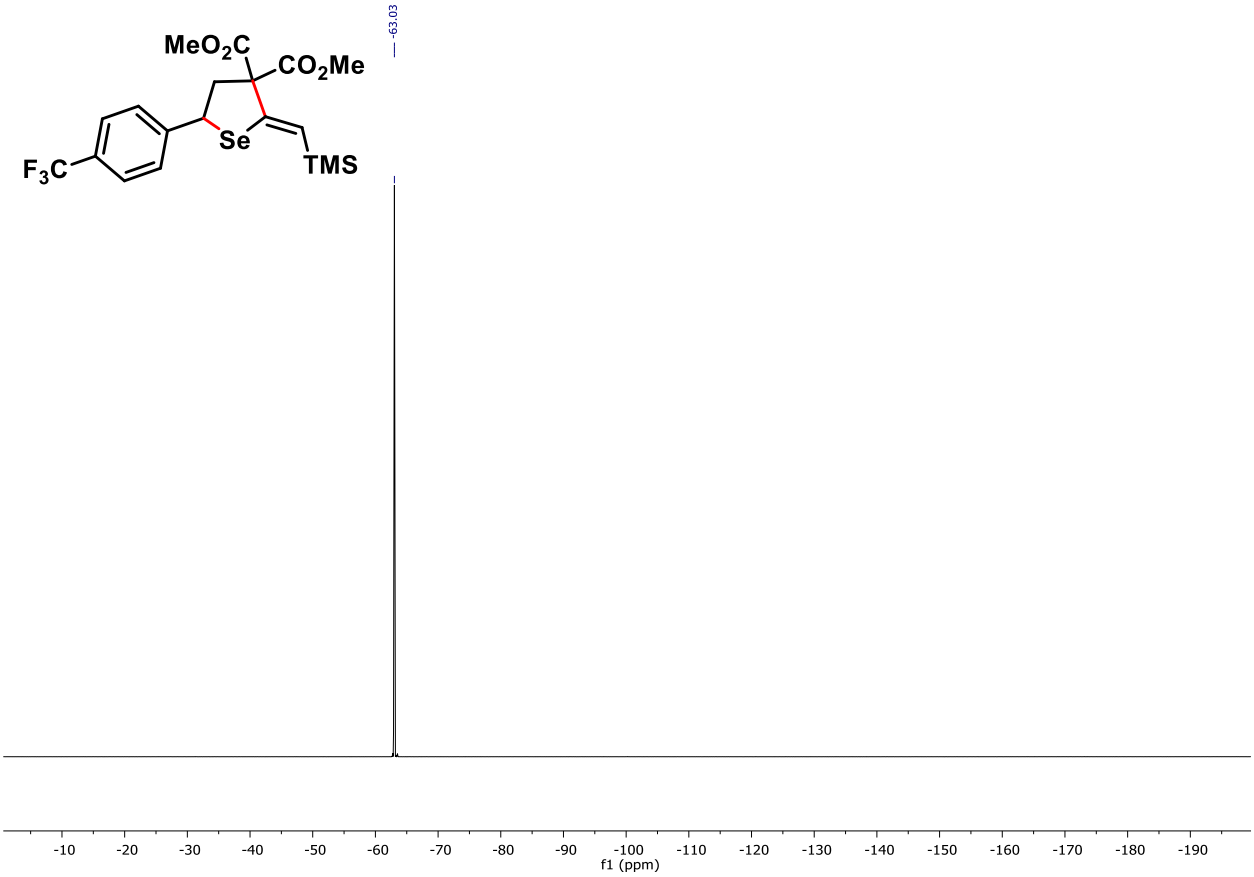
Dimethyl (*Z*)-5-(4-(trifluoromethyl)phenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*) dicarboxylate (4k)



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

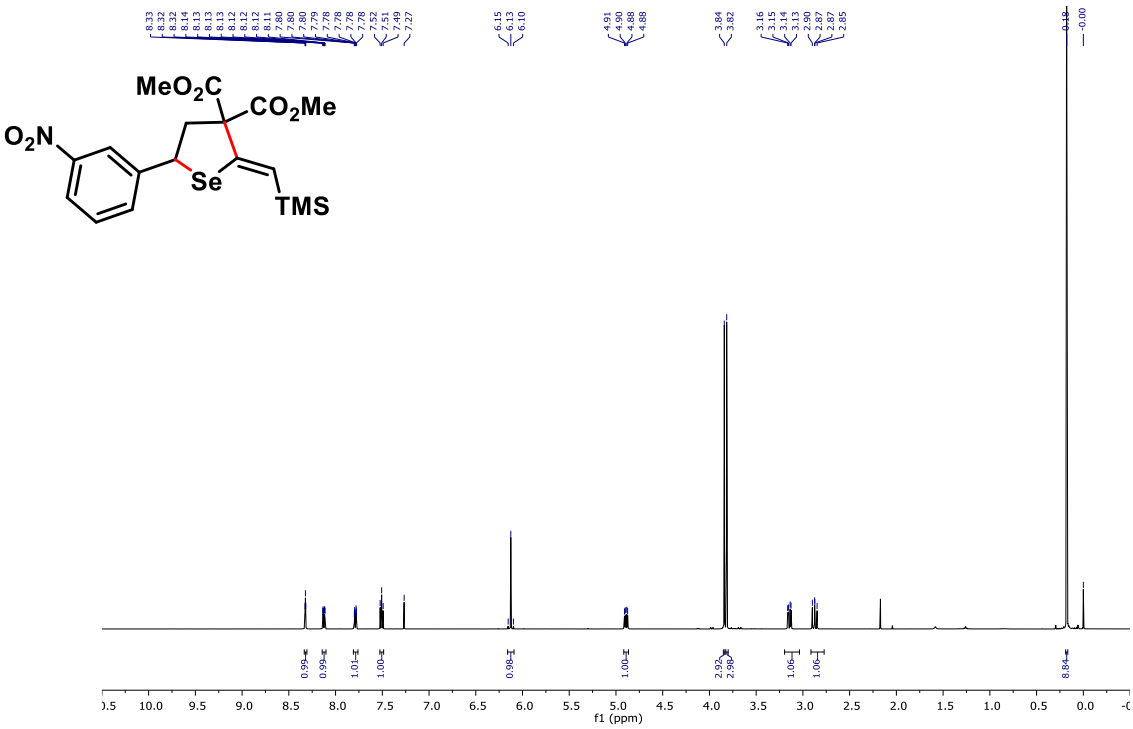


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

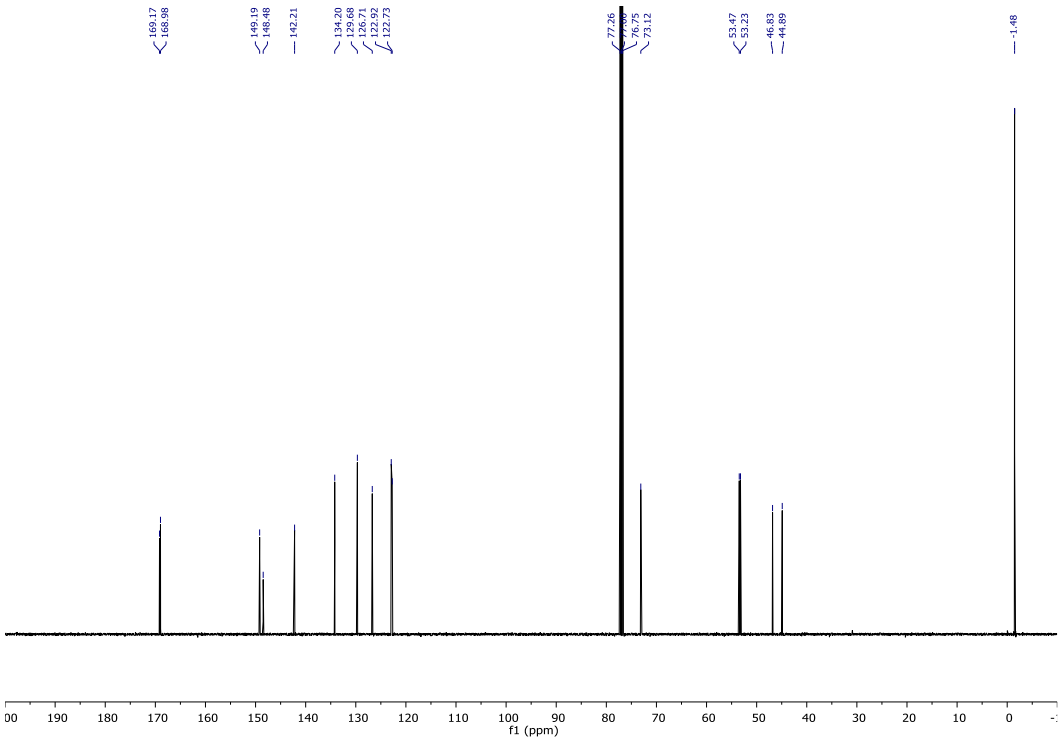


^{19}F-NMR Spectrum (377 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(3-nitrophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3l)

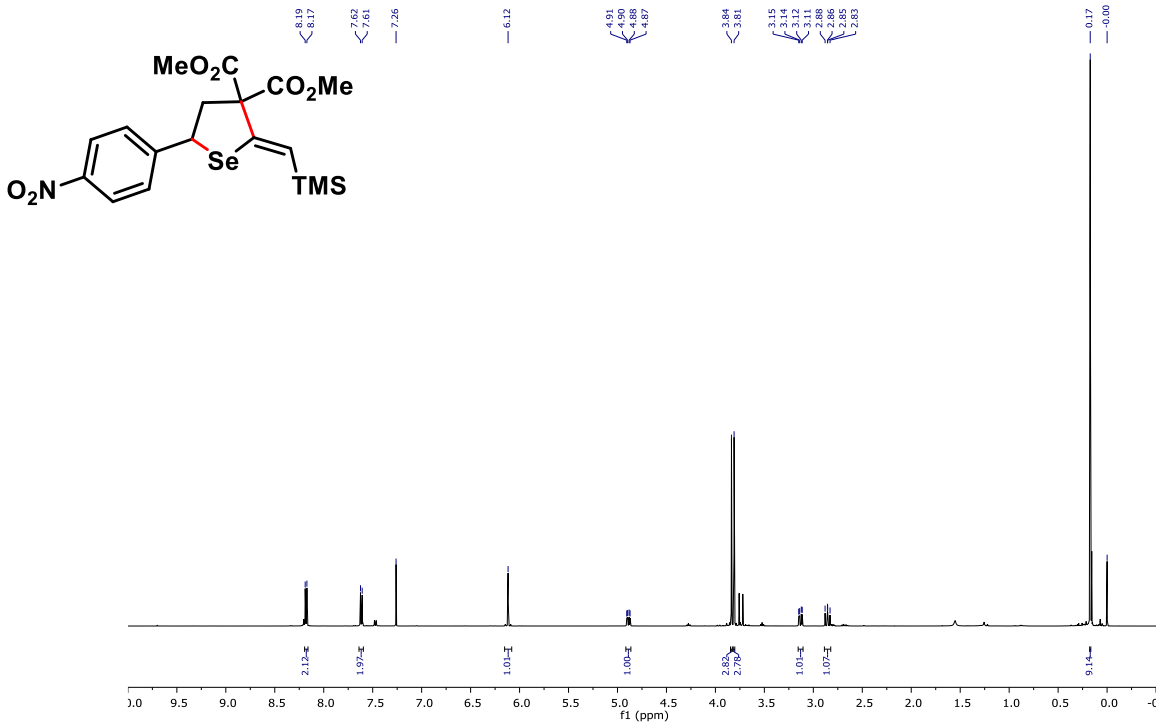


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

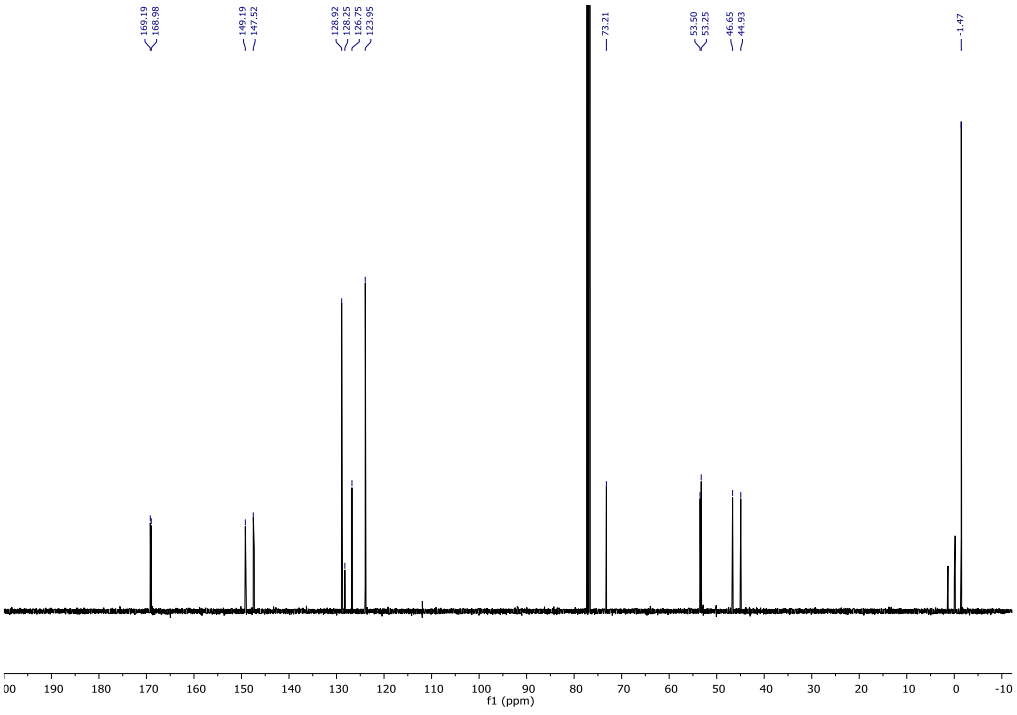


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(4-nitrophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3m)

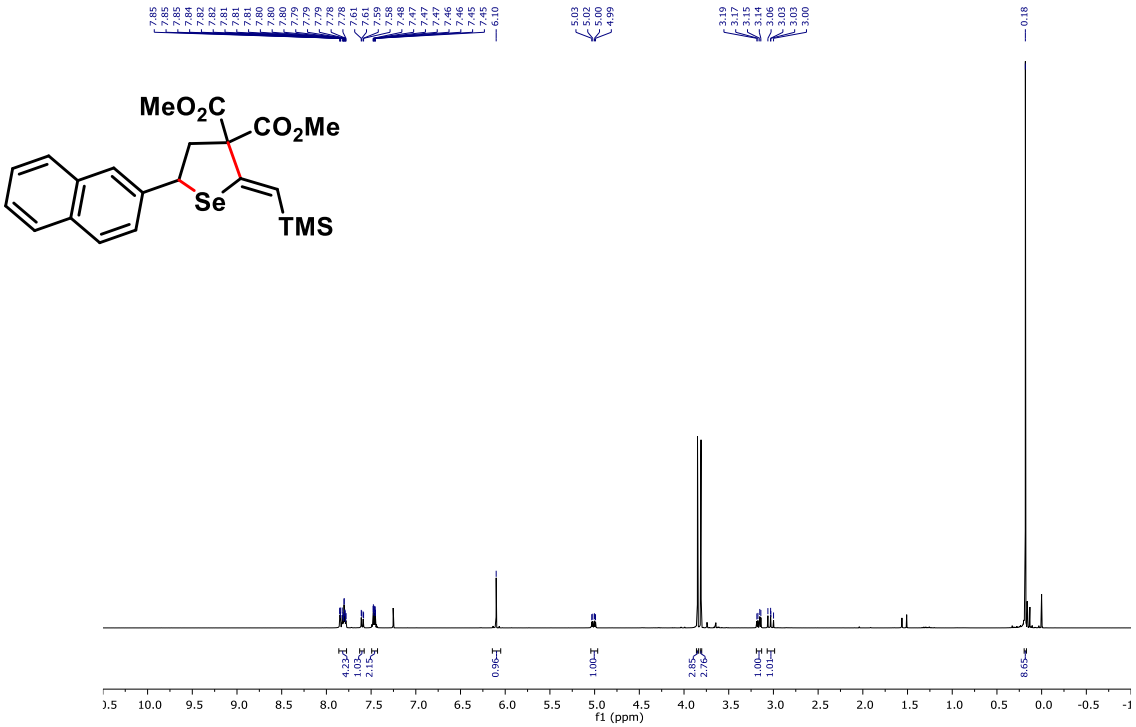


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

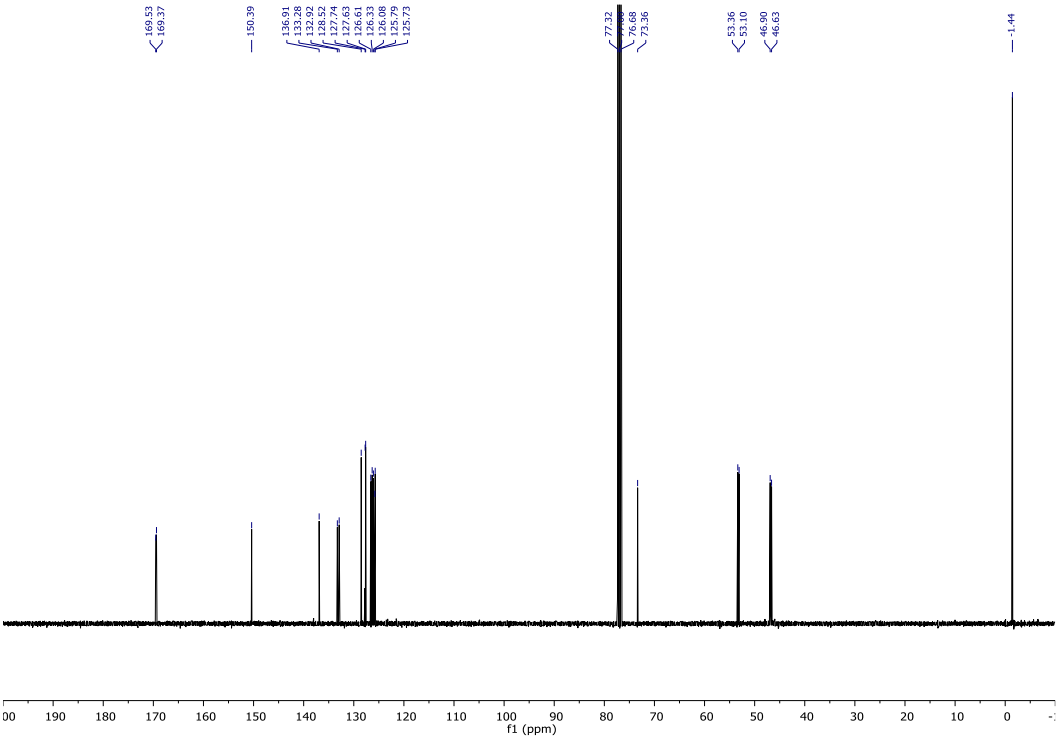


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(naphthalen-2-yl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3n)

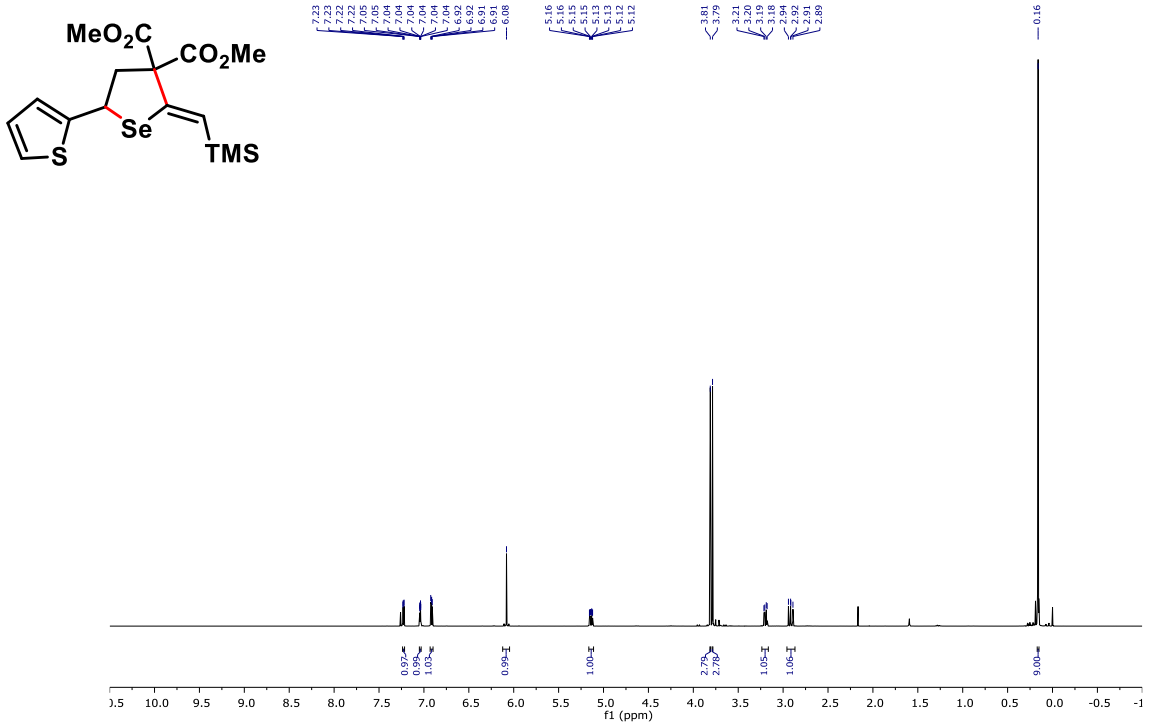


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

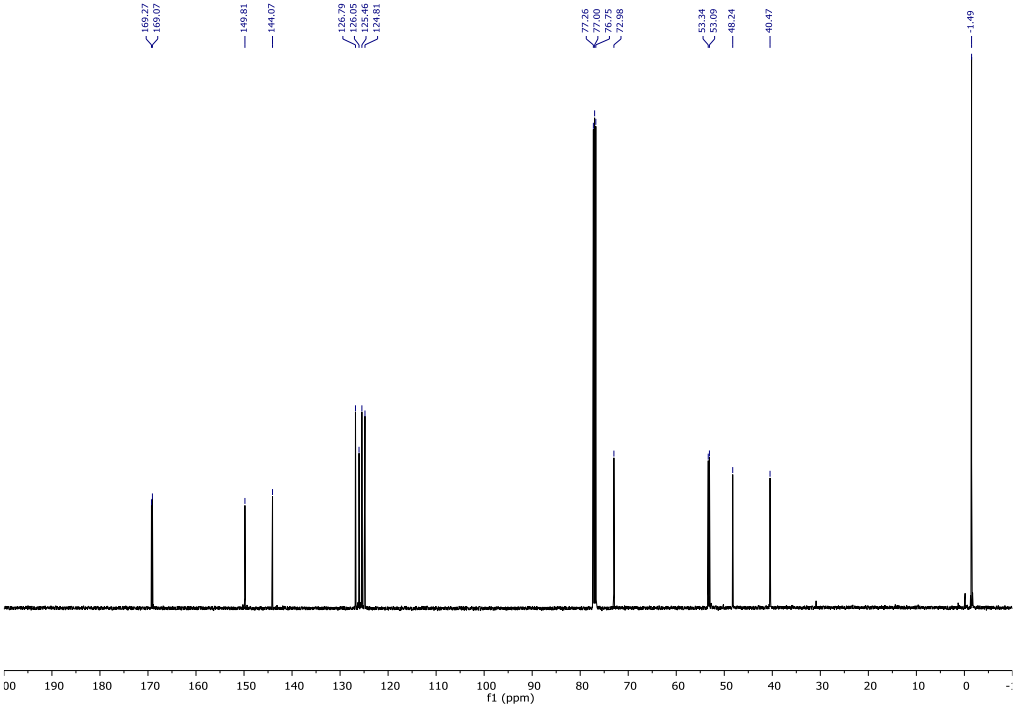


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(thiophen-2-yl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3o)

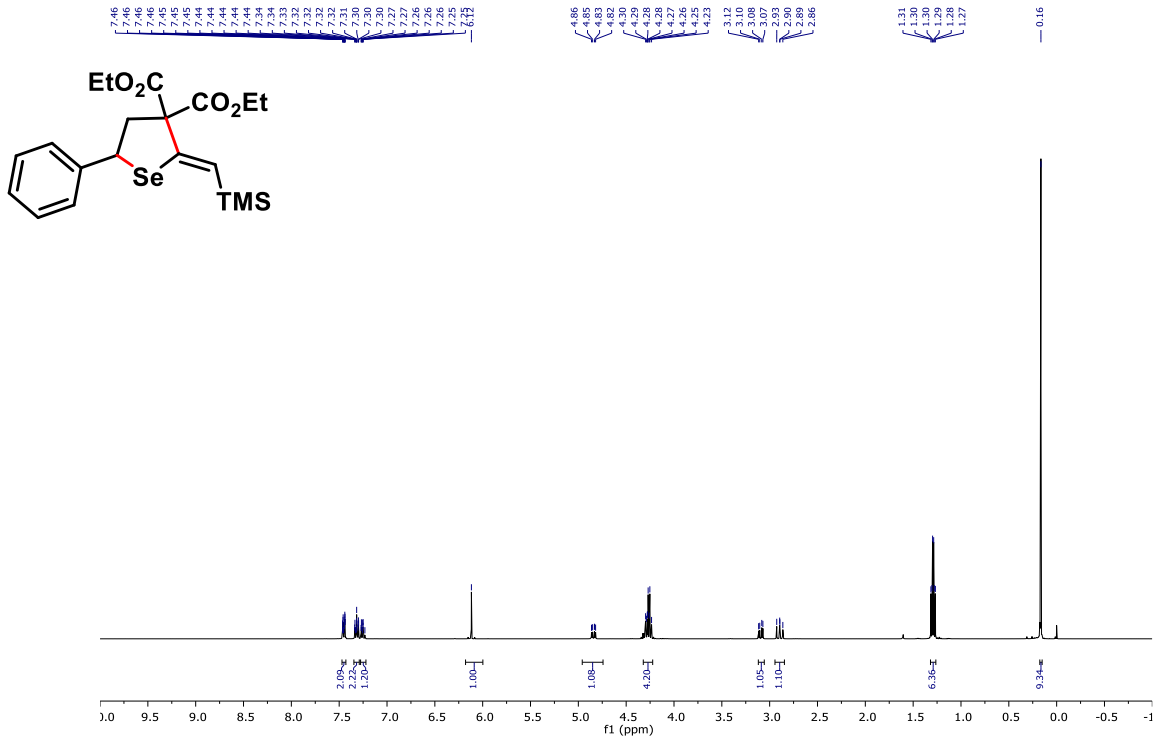


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

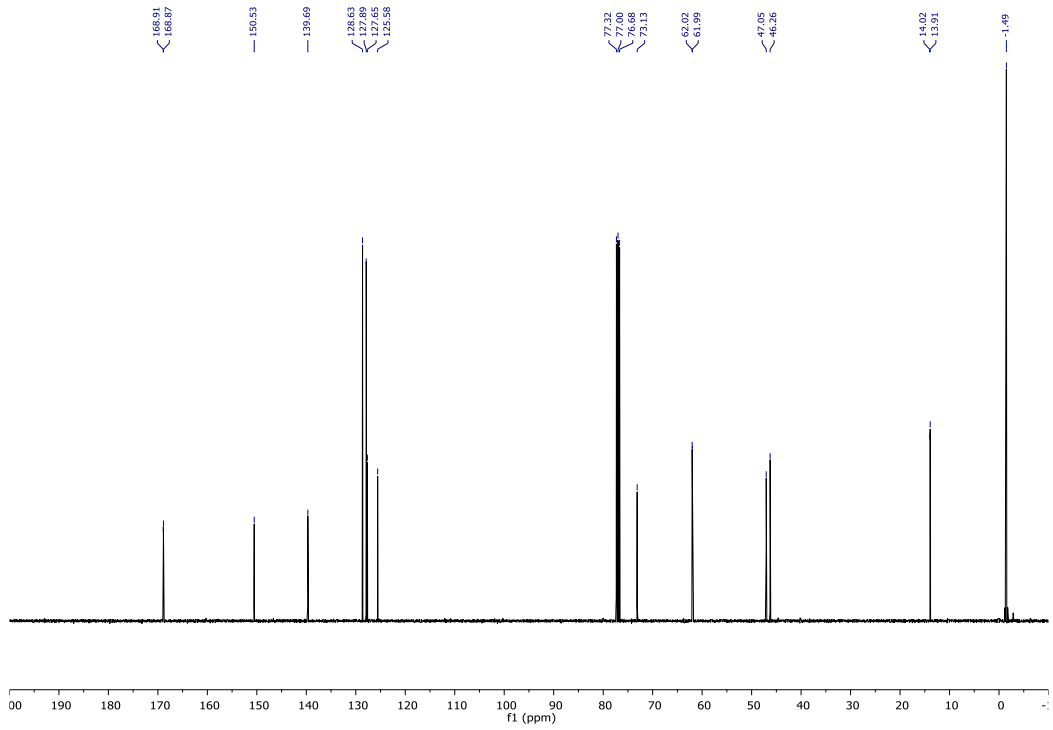


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Diethyl (*Z*)-5-phenyl-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (3p)

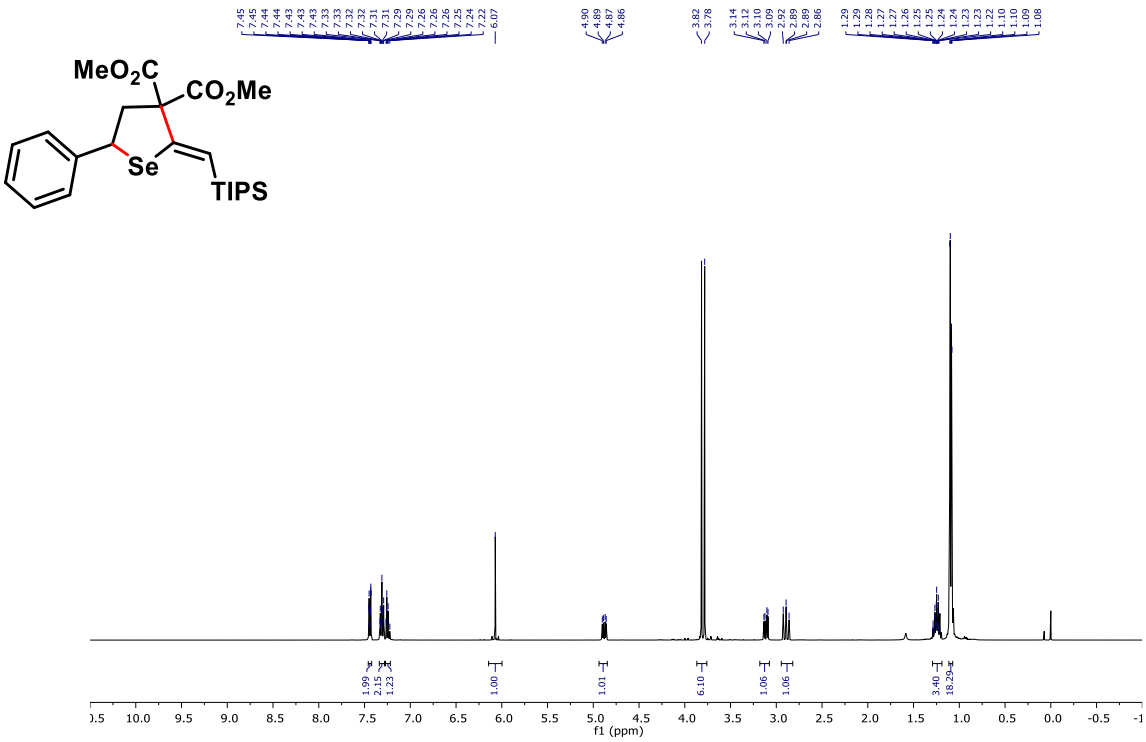


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

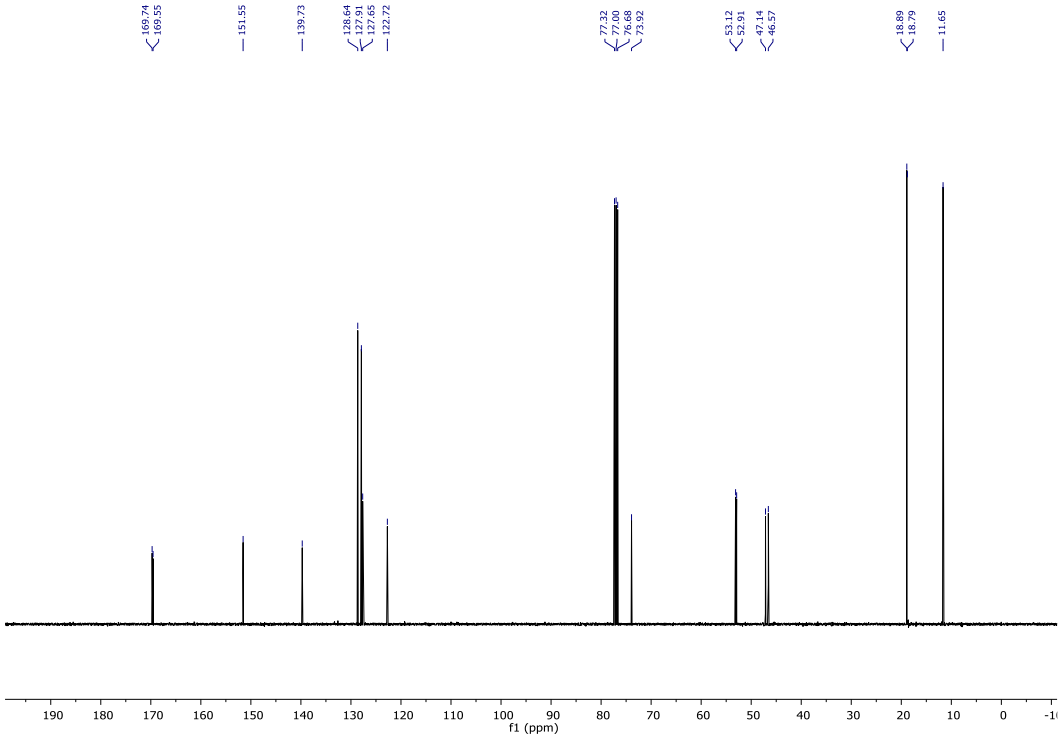


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-phenyl-2-((triisopropylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate (4a)

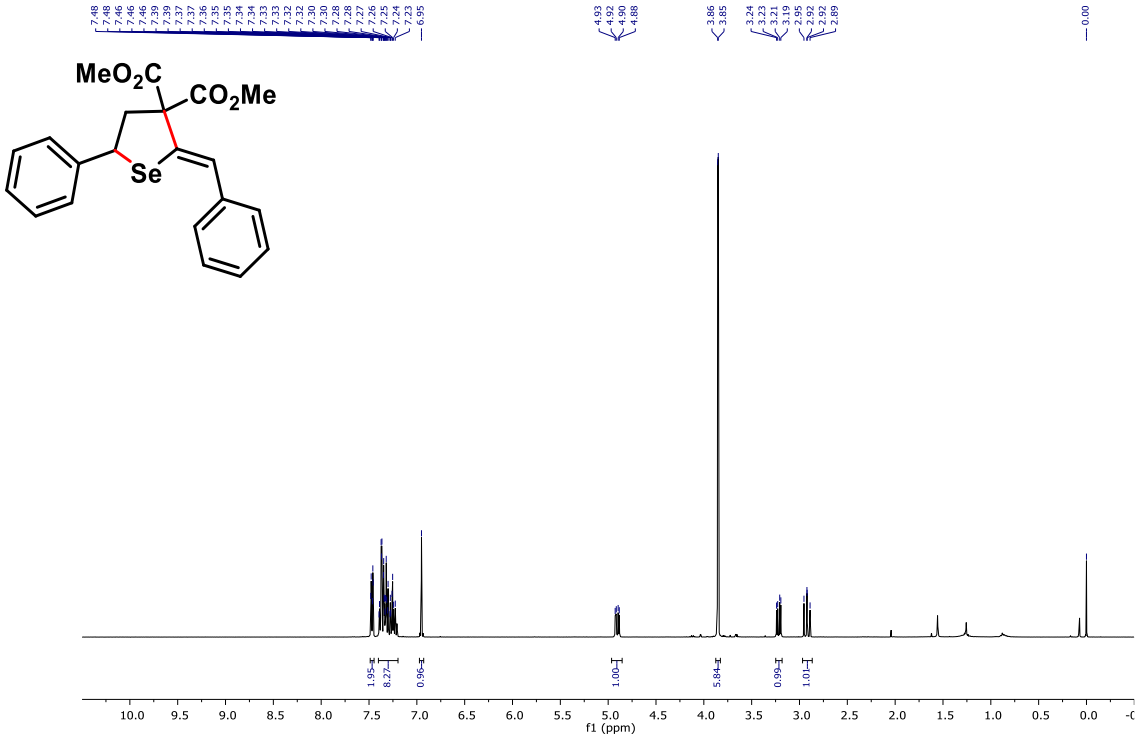


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

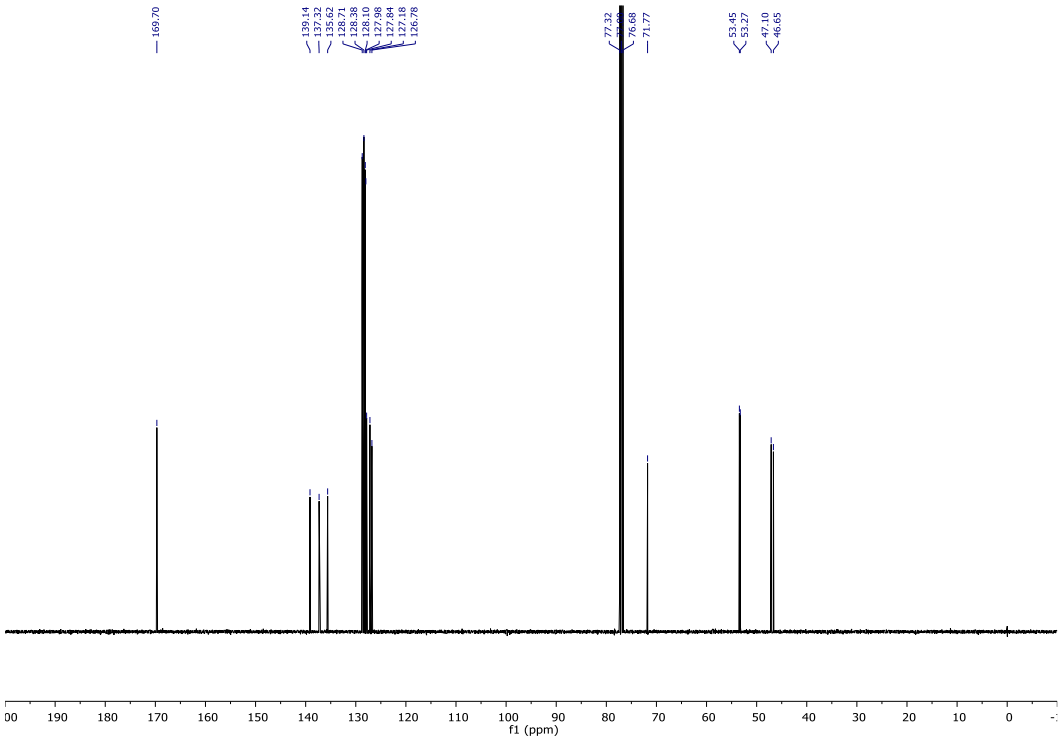


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-2-benzylidene-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4b)

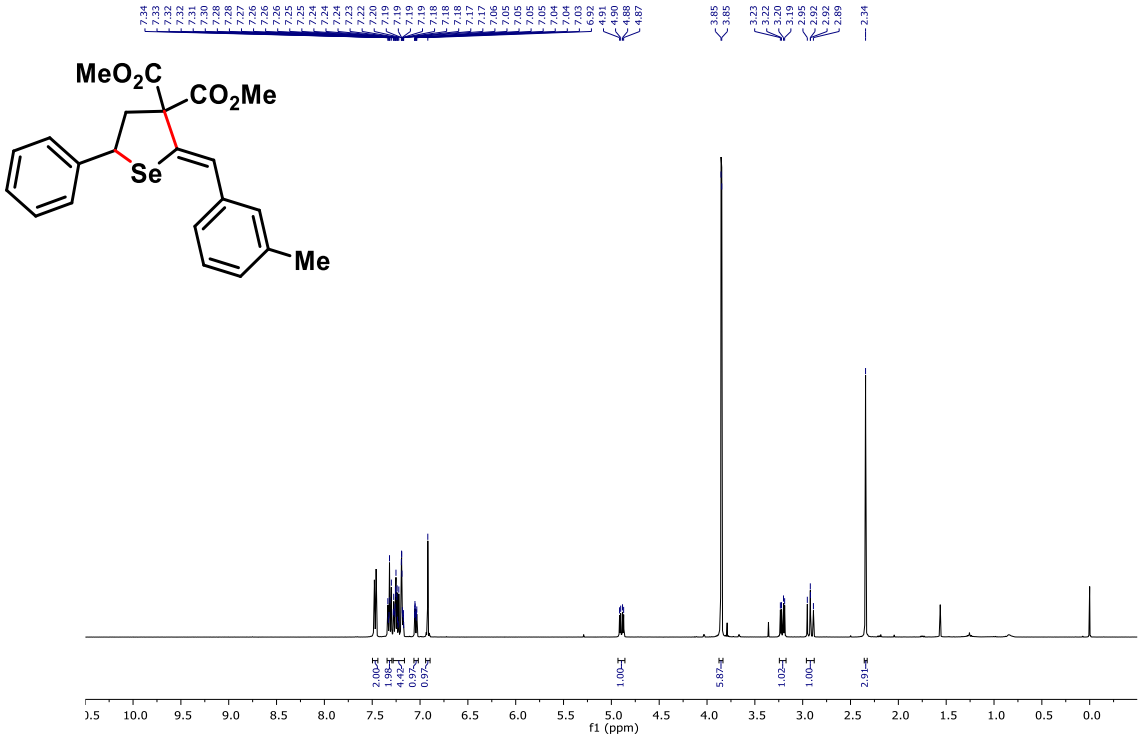


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

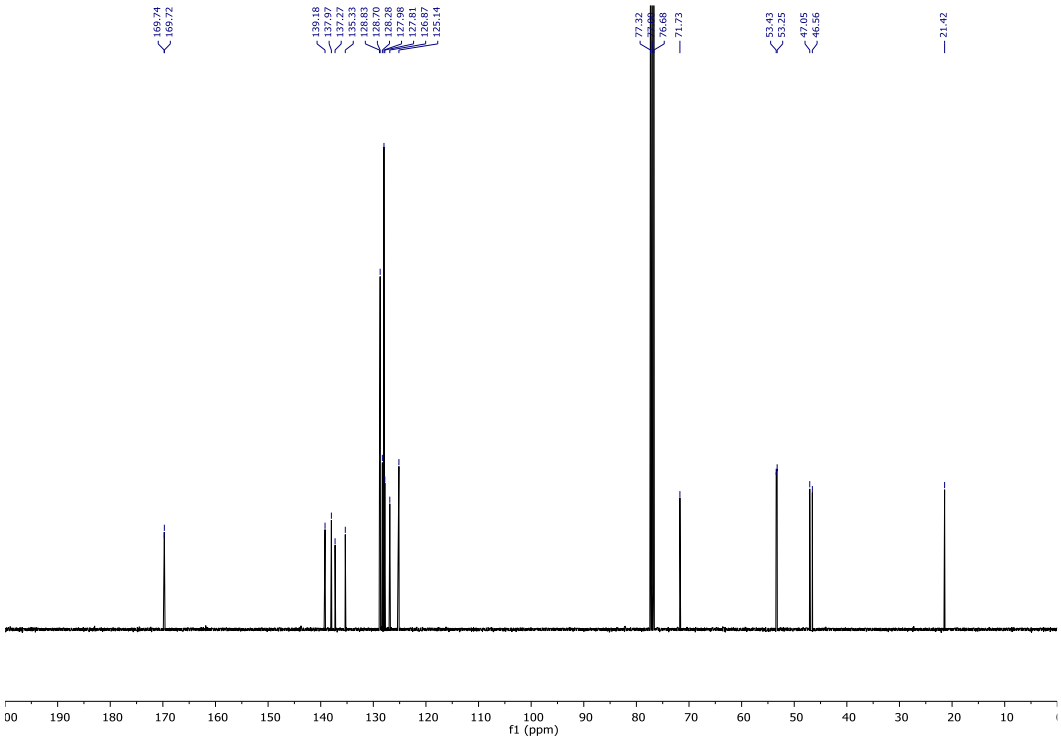


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-2-(3-methylbenzylidene)-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4c)

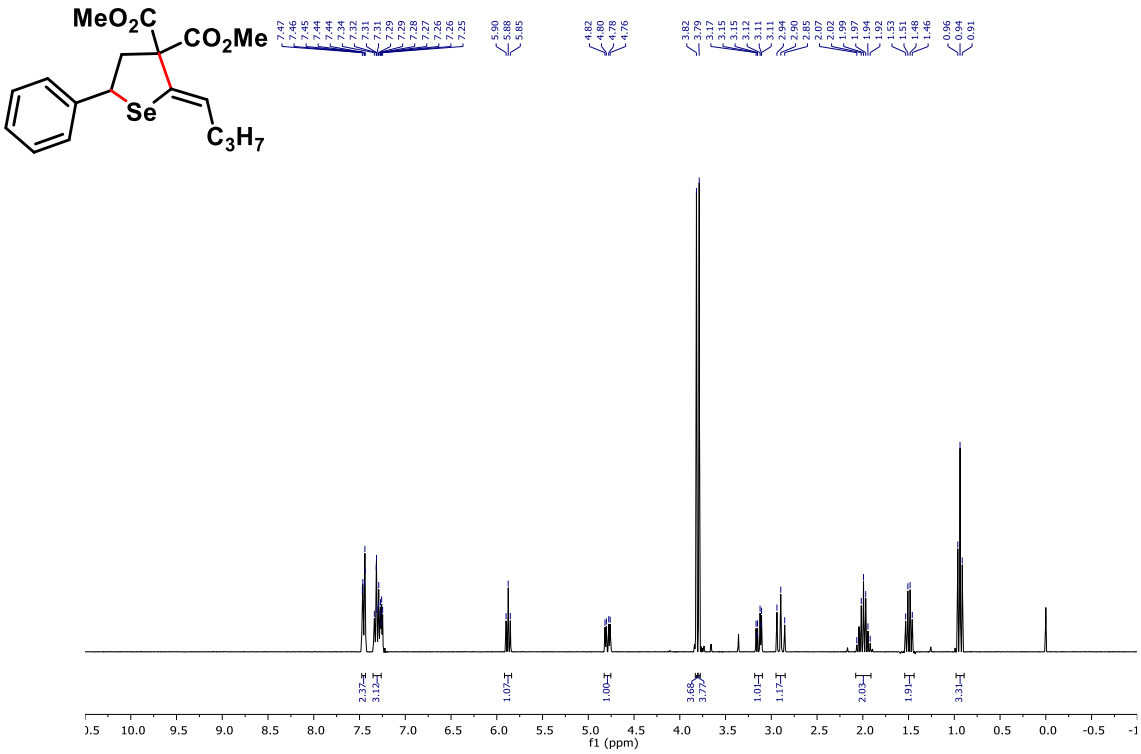


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

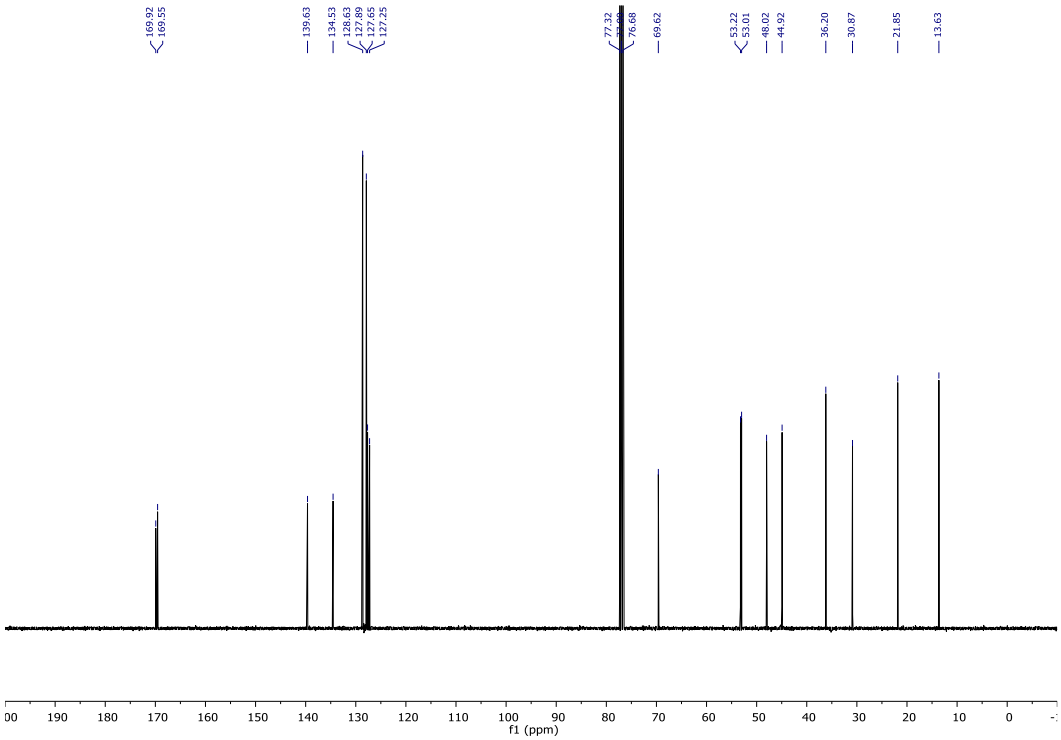


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-2-butylidene-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4d)

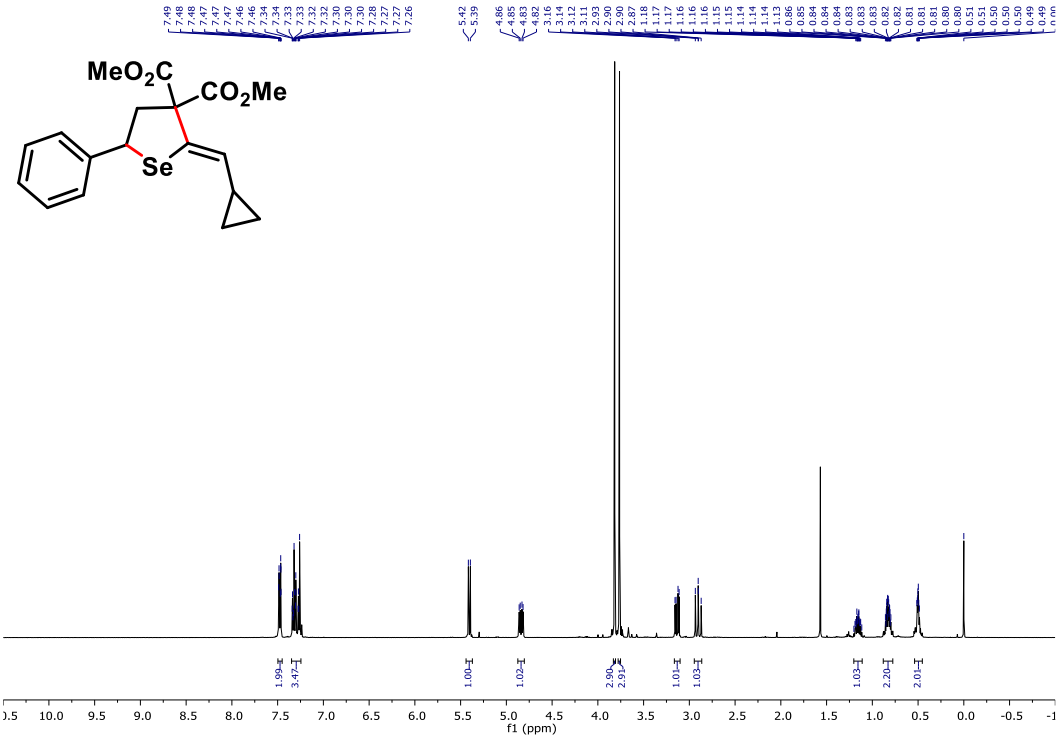


^{1}H-NMR Spectrum (300 MHz, $CDCl_3$)

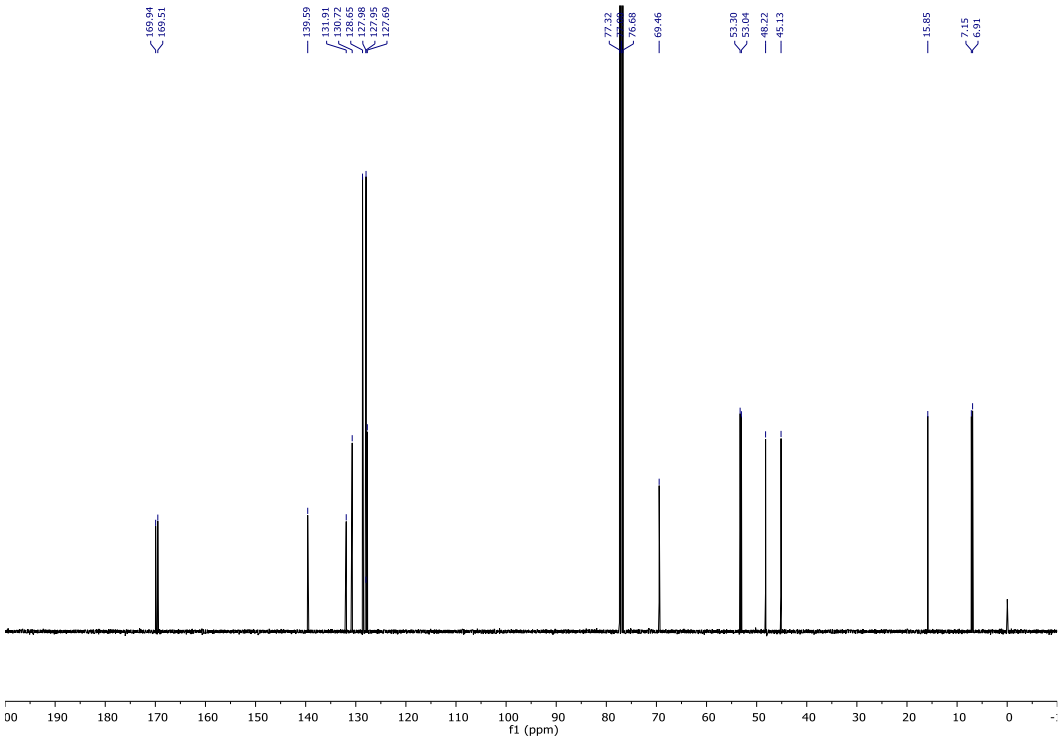


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl (*Z*)-2-(cyclopropylmethylene)-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4e)

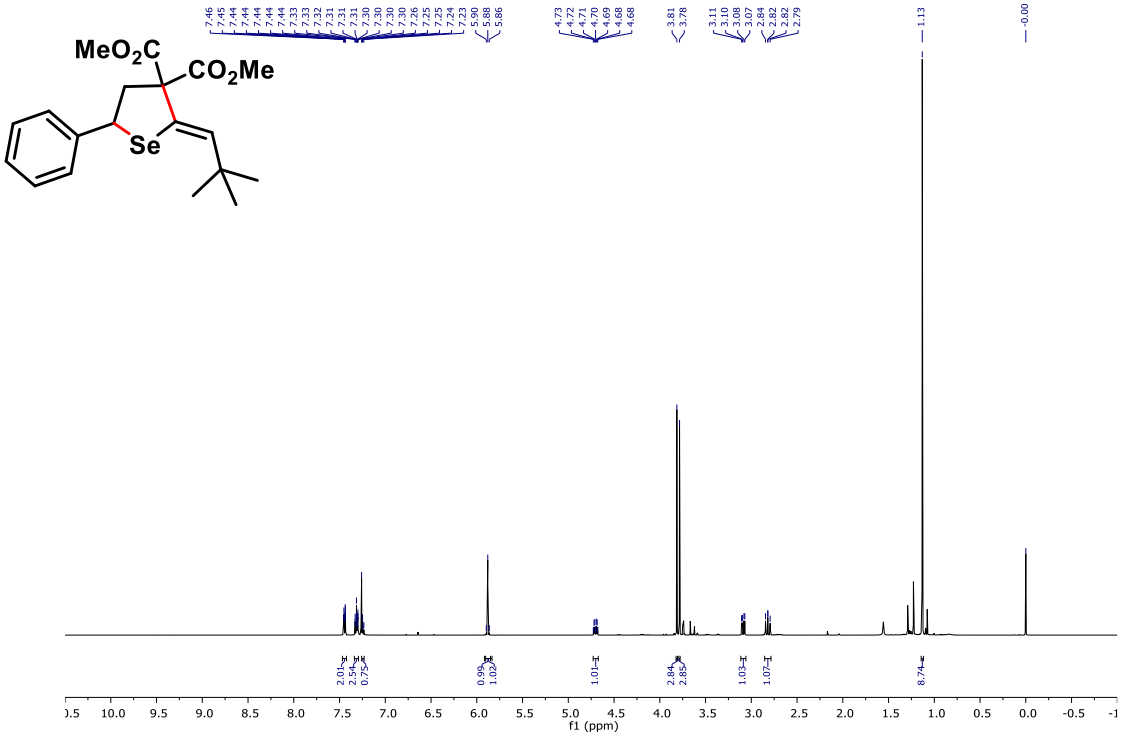


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

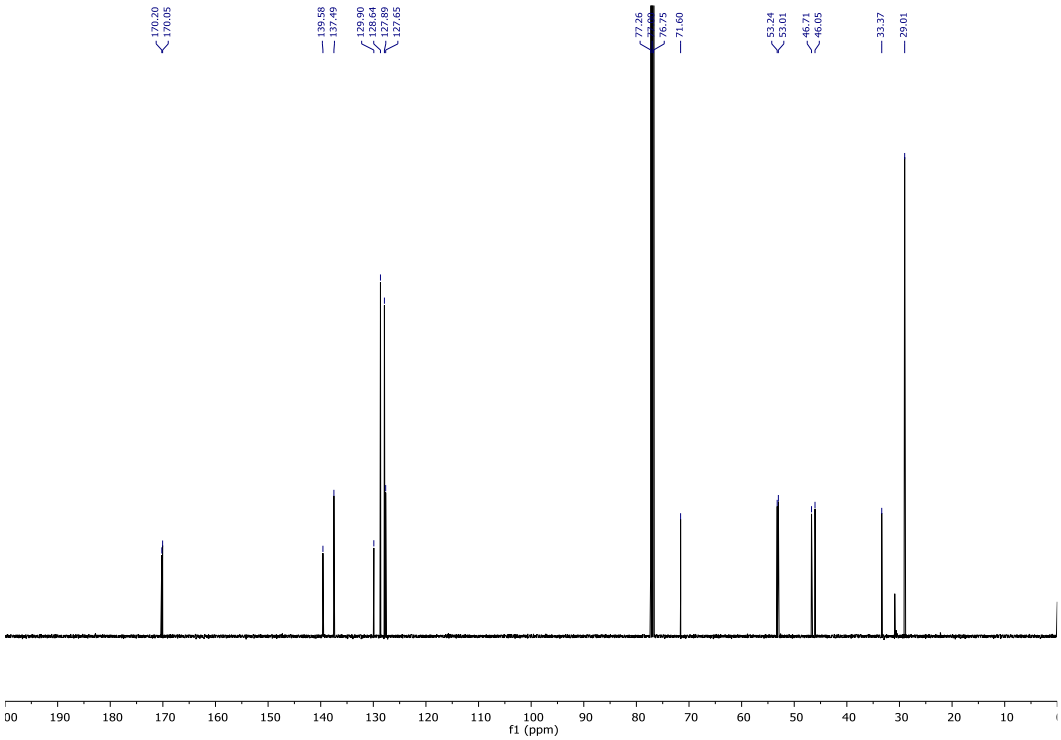


^{13}C-NMR Spectrum (101MHz, $CDCl_3$)

Dimethyl (*Z*)-2-(2,2-dimethylpropylidene)-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (4f)

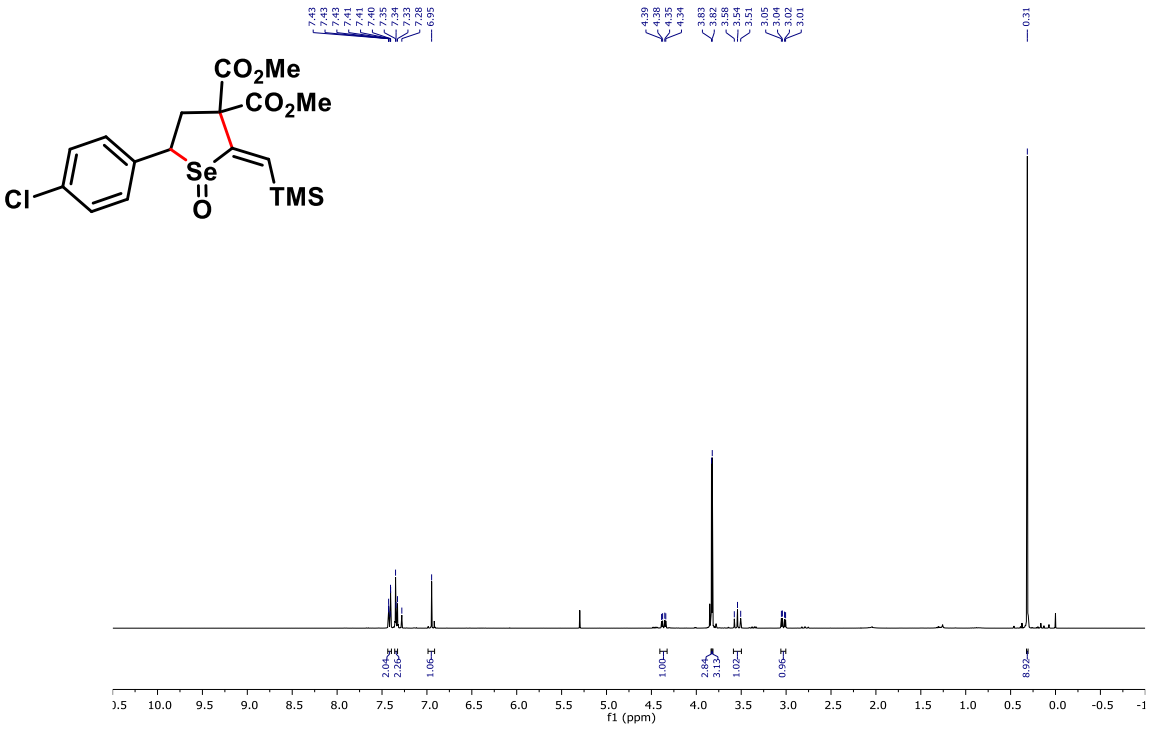


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

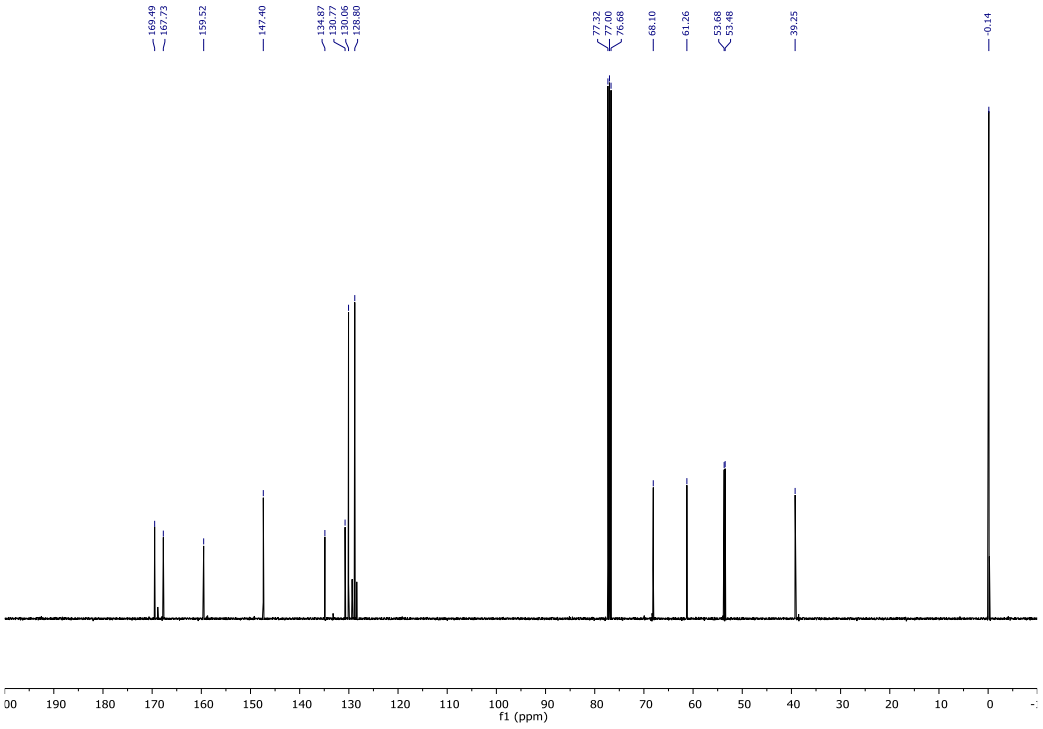


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl (*Z*)-5-(4-chlorophenyl)-2-((trimethylsilyl)methylene)dihydroselenophene-3,3(2*H*)-dicarboxylate 1-oxide (7c)

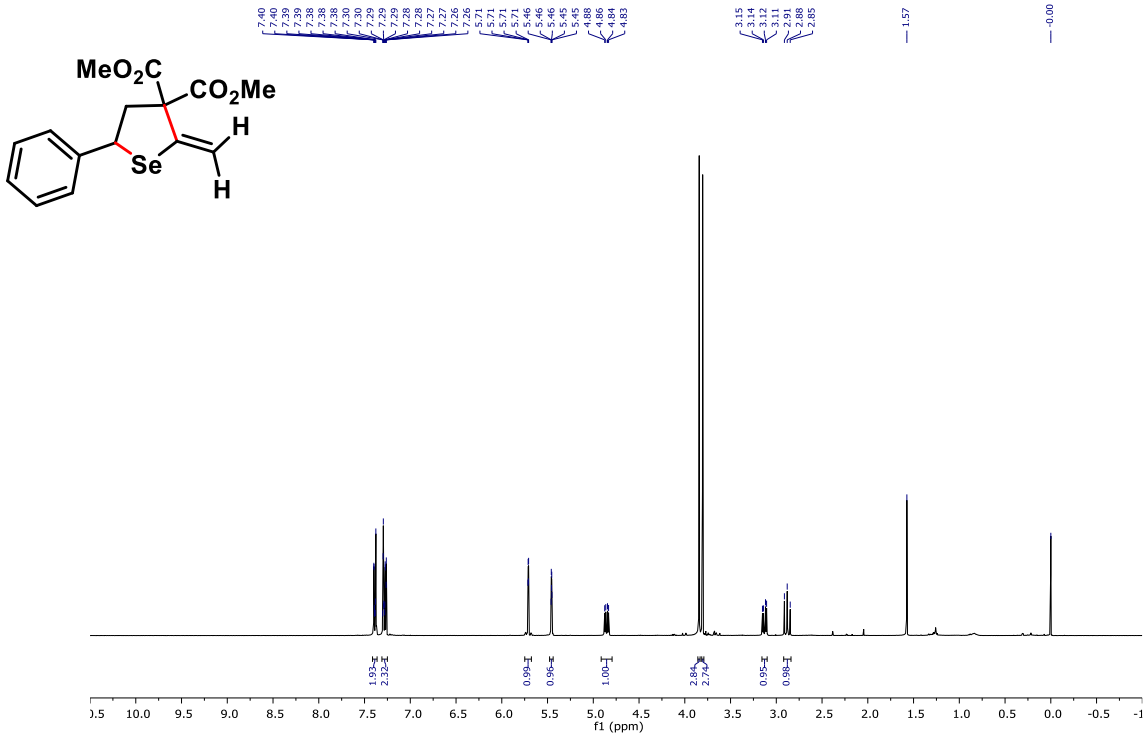


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

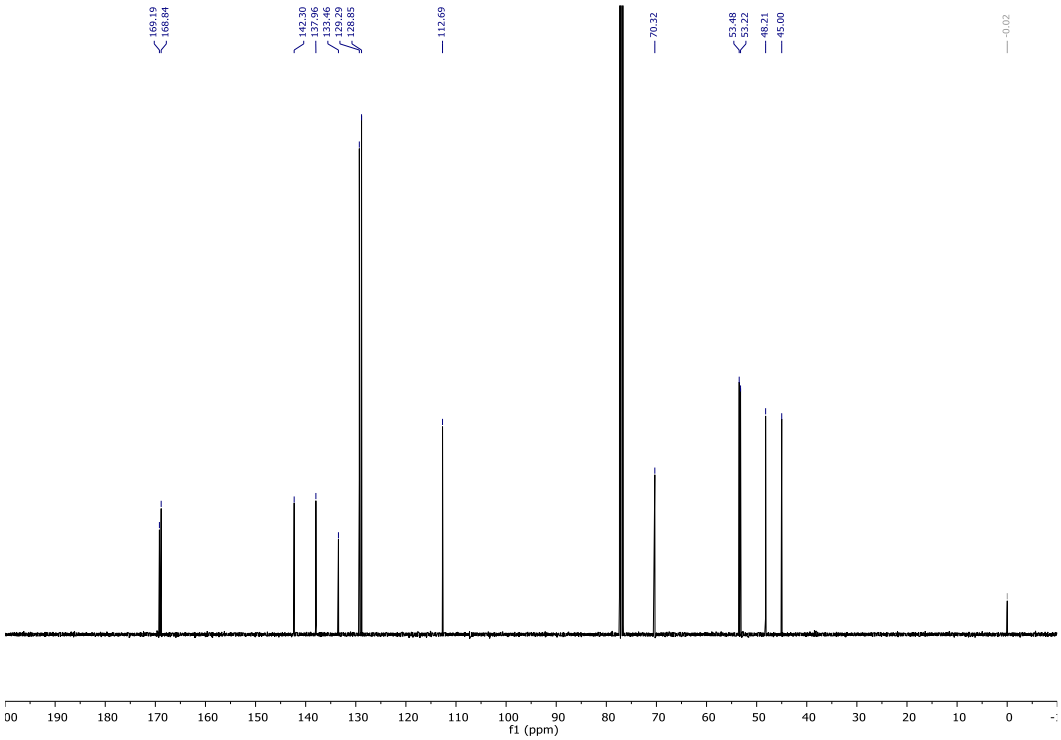


^{13}C-NMR Spectrum (126MHz, $CDCl_3$)

Dimethyl 2-methylene-5-phenyldihydroselenophene-3,3(2*H*)-dicarboxylate (8c)

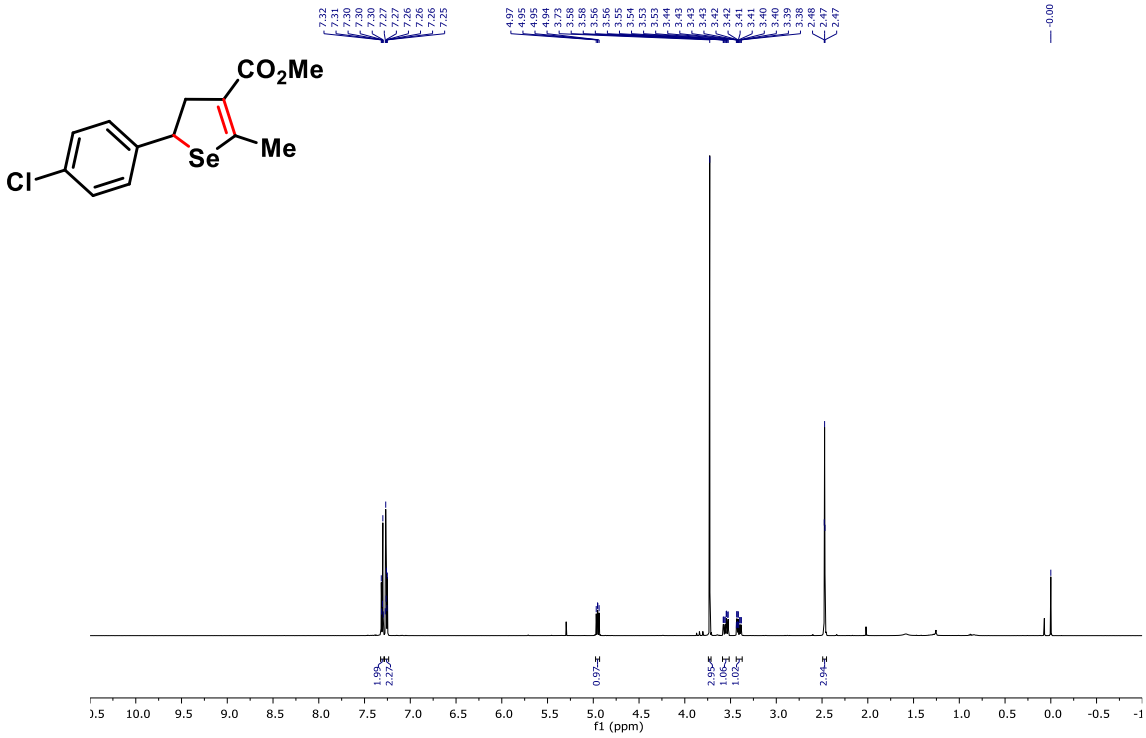


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

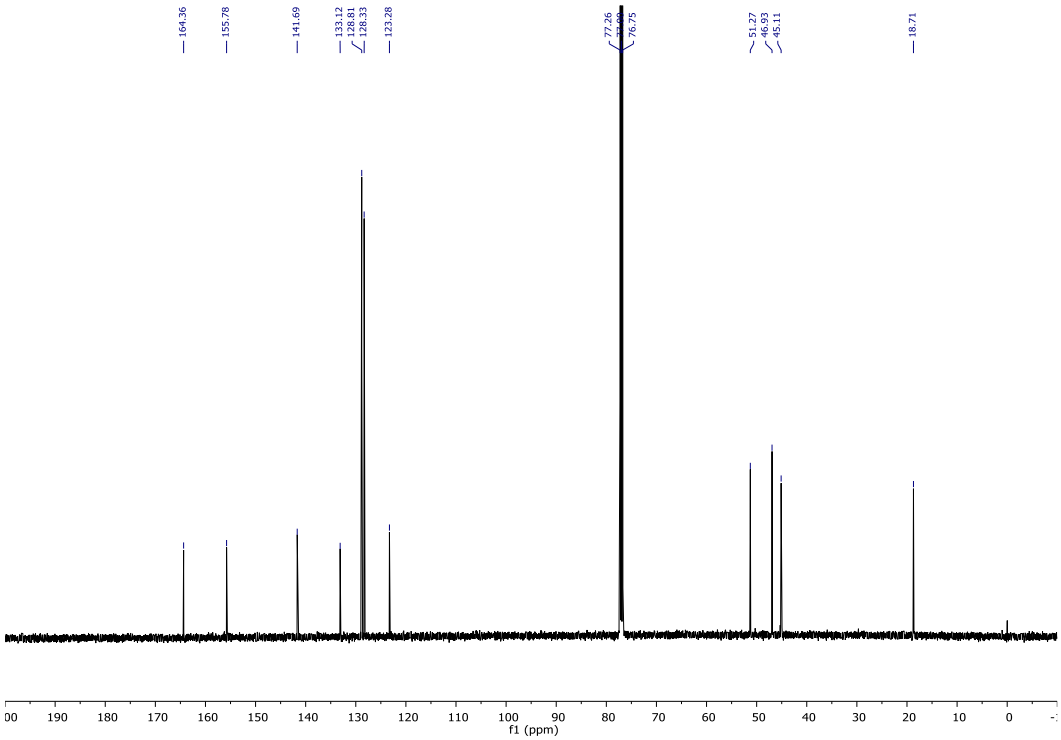


^{13}C-NMR Spectrum (101MHz, $CDCl_3$)

Methyl 5-(4-chlorophenyl)-2-methyl-4,5-dihydroselenophene-3-carboxylate (9c)



^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)



^{13}C-NMR Spectrum (126MHz, $CDCl_3$)

7. Crystal Structure Determination of Compound 8c

Crystals in the form of irregular colourless blocks were obtained by evaporation from a mixture of dichloromethane and *n*-heptane. The selected crystal was mounted in inert oil on a Hampton loop and transferred to the cold gas stream of a Rigaku/OD XtaLAB Synergy diffractometer. Mirror-focussed Mo-*K*α radiation was employed for the intensity measurements. Absorption corrections were implemented on the basis of multi-scans. The structure was refined anisotropically on F^2 using the program SHELXL-2018.[10] The hydrogen atoms of the $=CH_2$ group were refined freely, but with C–H distances restrained to be approximately equal (command "SADI"); other hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions.

Crystallographic data are summarized in Table S1, and an ellipsoid plot is presented as Fig. S1. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the number CCDC 2210773. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

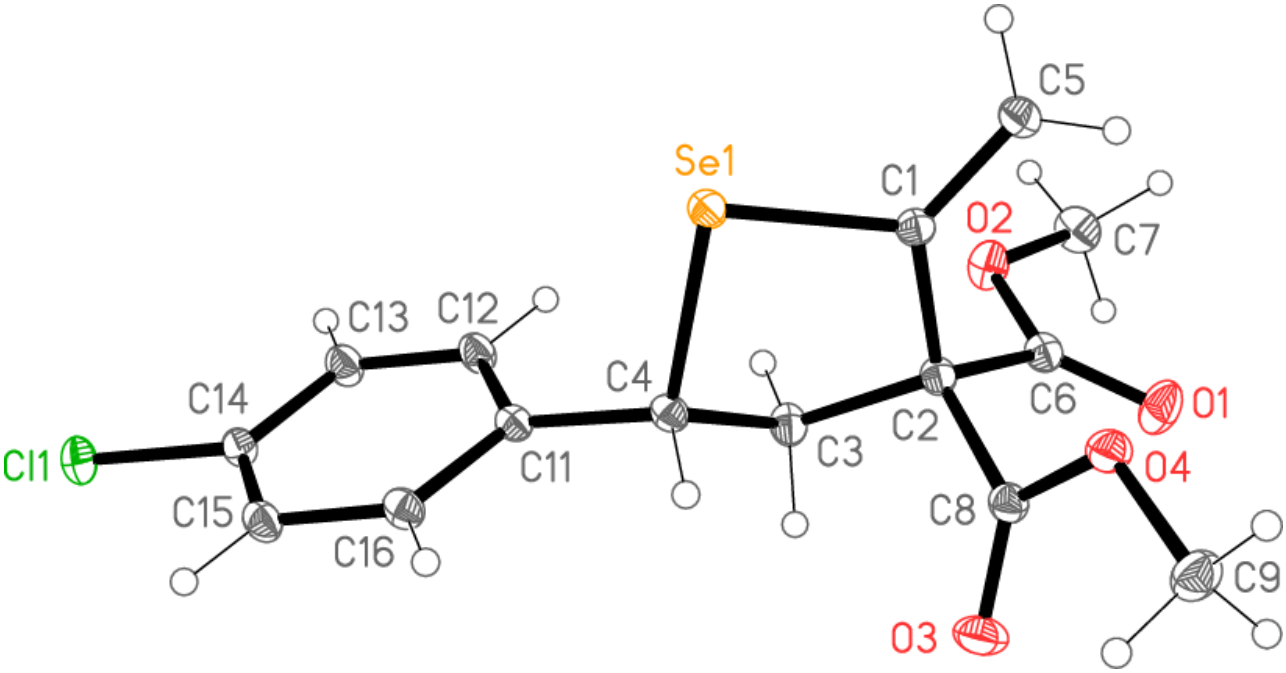


Fig. S1. The molecule of compound **8c** in the crystal. Ellipsoids correspond to 50% probability levels. Selected bond lengths (Å) and angles (°): Se1–C1 1.9093(8), Se1–C4 1.9822(8), C1–C5 1.3328(11), C1–Se1–C4 89.56(3), Se–C1–C5 123.67(6), C2–C1–C5 125.73(7). The five-membered ring displays an envelope conformation, whereby C3 lies 0.64 Å out of the plane of the other four atoms (r.m.s. deviation < 0.01 Å).

Table S1: Crystallographic data and structure refinement details for compound **8c**.

Compound	**8c**
Formula	$C_{15}H_{15}ClO_4Se$
M_r	373.68
Cryst. size (mm)	0.12 x 0.11 x 0.10
Crystal system	triclinic
Space group	*P*(-1)
Temperature (°C)	-173
a (Å)	7.85998(10)
b (Å)	9.94396(14)
c (Å)	11.27503(17)
α (°)	114.4747(13)
β (°)	96.3936(12)
γ (°)	101.6968(12)
V (Å^3)	766.31
Z	2
D_x (Mg m^{-3})	1.619
λ (Å)	0.71073
μ (mm^{-1})	2.64
Transmissions	0.895 – 1.000
F(000)	376
$2\theta_{max}$	38.3
Refl. measured	91637
Refl. indep.	8149
R_{int}	0.028
Parameters	200
Restraints	1
wR(F^2, all refl.)	0.057
R(*F*, >4σ(*F*))	0.026
S	1.12
Max. Δ*p* (e Å^{-3})	0.81, –0.52

8. References

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