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Supporting Information

Ring-Opening 1,3-Aminochalcogenation of Donor–Acceptor Cyclopropanes: A Three-Component Approach

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Supporting Information

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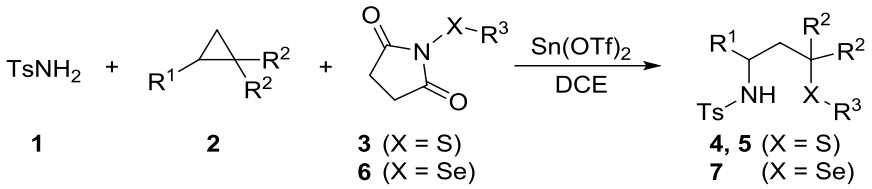
1) General Experimental

All solvents were used without further purification or drying. 1,2-Dichloroethane (DCE) was purchased from Acros Organics (99.8%, Extra Dry, Water <50ppm). Tin(II) trifluoromethanesulfonate was preheated before usage for 45 min at 200 °C. 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.

Proton (^{1}H), carbon (^{13}C) and fluorine (^{19}F) NMR spectra were recorded on a *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, m = multiplet. ESI-HRMS mass spectroscopy was carried out on an FTICR instrument. IR spectra were recorded on an ATR spectrometer Tensor 27 from *Bruker*. Preparative HPLC were conducted using an Agilent 1260 Infinity Series II system with an Agilent Pursuit XRs 10 C18 column (250 x 21.2 mm) at a flow rate of 25 mL/min using MeCN/H_2O (isocratic 70/30) eluent mixture. Enantiomeric excess was determined using an Agilent 1260 Infinity system with a Chiralpak IG column (150 x 4.6 mm) at a flow rate of 1.0 ml/min with MeCN/H_2O (isocratic 50/50) eluent mixture.

2) General Procedure

General Procedure (GP 1) for the Preparation of Compounds 4, 5 and 7



1 **2** **3** (X = S), **6** (X = Se) **4, 5** (X = S), **7** (X = Se)

In a glovebox the respective cyclopropane **2** (1.00 equiv.) and $Sn(OTf)_2$ (0.10 equiv.) were dissolved in DCE (1.5 mL) and prestirred for 5 min. Subsequently, compound **3** or **6** (1.70 equiv.) and tosylamide (**1**) (1.10 equiv.) were added to the reaction vessel and the mixture was stirred overnight at room temperature. The crude mixture was prepared for preparative HPLC and purified by reverse phase column chromatography (C18).

3) Preparation of Starting Materials

Synthesis of Donor-Acceptor Cyclopropanes 2

All D-A cyclopropanes **2a-n** were synthesized according to literature procedures.[1]

Synthesis of *N*-(arylthio)succinimide and *N*-(alkylthio)succinimide derivatives 3

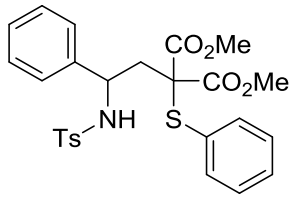
N-(Arylthio)succinimide and *N*-(alkylthio)succinimde derivatives **3a-f** were synthesized according to literature procedures.[2]

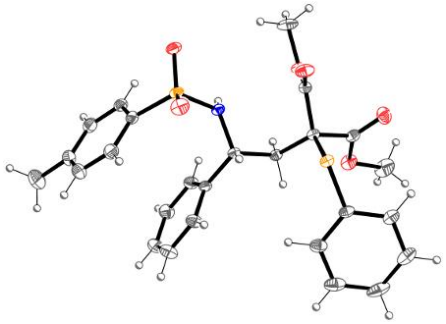
Synthesis of *N*-(phenylseleno)succinimde 6

N-(Phenylseleno)succinimide **6** was synthesized according to literature procedures.[3]

4) Preparation of Compounds 4, 5, 7 and 8

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylthio)malonate (4a)





Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4a** (95.2 mg, 185 µmol, 93%) as a colorless solid.

Single crystals were obtained by evaporation from $CDCl_3$.

m.p.: 124 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.39 (dd, *J* = 15.1, 6.0 Hz, 1H), 2.58 (dd, *J* = 15.1, 8.1 Hz, 1H), 3.39 (s, 3H), 3.77 (s, 3H), 4.99 (td, *J* = 8.1, 6.0 Hz, 1H), 5.18 – 5.21 (m, 1H), 6.93 – 6.96 (m, 2H), 6.98 – 6.99 (m, 2H), 7.02 – 7.09 (m, 3H), 7.29 – 7.34 (m, 2H), 7.36 – 7.43 (m, 3H), 7.49 – 7.53 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.3, 41.1, 53.0, 53.5, 55.0, 63.3, 126.9 (2C), 127.1 (2C), 127.4, 128.3(2C), 128.98, 129.03 (2C), 129.1 (2C), 130.1, 136.9 (2C), 137.4, 139.5, 142.7, 168.1, 168.6 ppm.

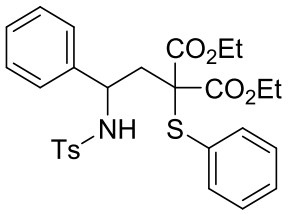
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3260, 1731, 1437, 1329, 1229, 1153, 1072.

MS (ESI): *m*/*z* = 531.2 $[M+NH_4]^+$.

$C_{26}H_{27}NO_6S_2$ (MW 513.62) calcd.: 536.11720

found: 536.11738 $[M+Na]^+$ (ESI-HRMS).

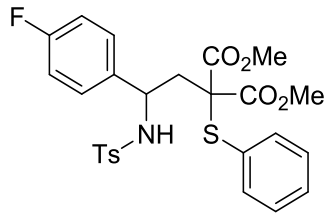
Diethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylthio)malonate (4b)



Diethyl 2-phenylcyclopropane-1,1-dicarboxylate (52.5 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4b** (82.9 mg, 153 µmol, 77%) as a colorless semi-solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.10 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 2.31 (s, 3H), 2.39 (dd, *J* = 15.1, 6.0 Hz, 1H), 2.55 (dd, *J* = 15.1, 7.8 Hz, 1H), 3.72 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.85 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.14 – 4.29 (m, 2H), 4.94 (td, *J* = 7.8, 6.0 Hz, 1H), 5.03 (d, *J* = 7.8 Hz, 1H), 6.93 – 6.97 (m, 2H), 6.99 – 7.03 (m, 2H), 7.04 – 7.11 (m, 3H), 7.29 – 7.34 (m, 2H), 7.36 – 7.42 (m, 3H), 7.51 – 7.55 (m, 2H) ppm.
^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.6, 13.8, 21.4, 40.9, 55.1, 62.3, 62.7, 63.2, 126.9 (2C), 127.1 (2C), 127.5, 128.2 (2C), 129.0 (2C), 129.1 (2C), 129.3, 130.0, 136.9 (2C), 137.4, 139.8, 142.8, 167.8, 168.2 ppm.
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3282, 2982, 1727, 1440, 1327, 1251, 1219, 1156, 1090, 1021.
MS (ESI): *m*/*z* = 559.2 $[M+NH_4]^+$.
$C_{28}H_{31}NO_6S_2$ (MW 541.68) calcd.: 564.14850
found: 564.14872 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-(4-fluorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4c)



Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (50.5 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4c** (100 mg, 189 µmol, 94%) as a colorless solid.

m.p.: 143 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.32 – 2.36 (m, 1H), 2.33 (s, 3H), 2.49 – 2.56 (m, 1H), 3.45 (s, 3H), 3.78 (s, 3H), 4.95 – 4.98 (m, 2H), 6.74 – 6.77 (m, 2H), 6.91 – 6.94 (m, 2H), 7.04 – 7.05 (m, 2H), 7.31 – 7.34 (m, 2H), 7.39 – 7.42 (m, 3H), 7.47 – 7.49 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 41.1, 53.1, 53.6, 54.3, 63.1, 115.1 (d, *J* = 21.7 Hz, 2C), 127.1 (2C), 128.6 (d, *J* = 8.2 Hz, 2C), 128.9, 129.1 (2C), 129.2 (2C), 130.3, 135.5 (d, *J* = 3.2 Hz), 136.8 (2C), 137.4, 143.1, 162.0 (d, *J* = 247.0 Hz), 168.1, 168.6 ppm.

^{19}F-NMR (471 MHz, $CDCl_3$): δ = -114.7 ppm.

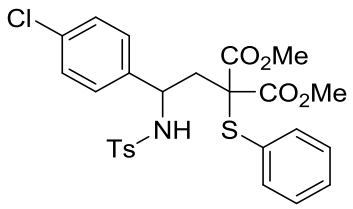
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3262, 1729, 1436, 1223, 1154, 1082.

MS (ESI): *m*/*z* = 549.1 $[M+NH_4]^+$.

$C_{26}H_{26}FNO_6S_2$ (MW 531.61) calcd.: 554.10778

found: 554.10790 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4d)



Dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (53.3 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4d** (103 mg, 188 µmol, 94%) as a colorless solid.

m.p.: 172 °C

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.27 – 2.37 (m, 1H), 2.34 (s, 3H) 2.52 (dd, *J* = 15.1, 8.3 Hz, 1H), 3.46 (s, 3H), 3.78 (s, 3H), 4.95 (td, *J* = 8.3, 5.7 Hz, 1H), 5.11 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.91 (m, 2H), 6.98 – 7.06 (m, 4H), 7.29 – 7.35 (m, 2H), 7.36 – 7.43 (m, 3H), 7.45 – 7.51 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.4, 41.0, 53.1, 53.6, 54.4, 63.1, 127.1 (2C), 128.3 (2C), 128.4 (2C), 128.9, 129.15 (2C), 129.18 (2C), 130.3, 133.4, 136.8 (2C), 137.3, 138.1, 143.2, 168.1, 168.6 ppm.

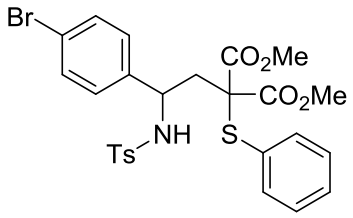
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3254, 1733, 1438, 1227, 1152, 1074.

MS (ESI): *m*/*z* = 565.1 $[M+NH_4]^+$.

$C_{26}H_{26}ClNO_6S_2$ (MW 548.07) calcd.: 570.07823

found: 570.07861 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-(4-bromophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4e)



Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (62.6 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4e** (108 mg, 182 µmol, 91%) as a colorless solid.

m.p.: 170 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.32 (dd, *J* = 15.2, 5.7 Hz, 1H), 2.35 (s, 3H), 2.51 (dd, *J* = 15.2, 8.3 Hz, 1H), 3.46 (s, 3H), 3.79 (s, 3H), 4.94 (td, *J* = 8.3, 5.7 Hz, 1H), 5.08 – 5.10 (m, 1H), 6.79 – 6.83 (m, 2H), 7.01 – 7.06 (m, 2H), 7.14 – 7.19 (m, 2H), 7.29 – 7.40 (m, 5H), 7.45 – 7.49 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 40.8, 53.1, 53.6, 54.5, 63.1, 121.5, 127.1 (2C), 128.7 (2C), 128.8, 129.1 (2C), 129.2 (2C), 130.3, 131.3 (2C), 136.8 (2C), 137.2, 138.5, 143.2, 168.1, 168.6 ppm.

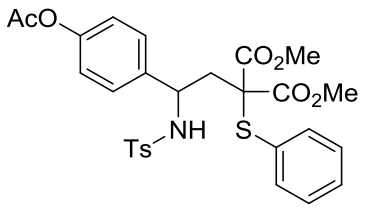
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3259, 1734, 1436, 1332, 1229, 1153, 1071.

MS (ESI): *m*/*z* = 609.1 $[M+NH_4]^+$.

$C_{26}H_{26}BrNO_6S_2$ (MW 592.52) calcd.: 614.02771

found: 614.02809 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-(4-acetoxyphenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4f)



Dimethyl 2-(4-acetoxyphenyl)cyclopropane-1,1-dicarboxylate (58.6 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4f** (101 mg, 177 µmol, 88%) as a colorless solid.

m.p.: 164 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.30 (s, 3H), 2.38 (dd, *J* = 15.1, 6.3 Hz, 1H), 2.55 (dd, *J* = 15.1, 7.8 Hz, 1H), 3.41 (s, 3H), 3.77 (s, 3H), 5.00 (td, *J* = 7.8, 6.3 Hz, 1H), 5.28 (d, *J* = 8.5 Hz, 1H), 6.73 – 6.80 (m, 2H), 6.93 – 6.98 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.43 (m, 5H), 7.48 – 7.53 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.0, 21.3, 41.1, 53.1, 53.5, 54.4, 63.3, 121.4 (2C), 127.0 (2C), 128.0 (2C), 128.9, 129.1 (2C), 129.2 (2C), 130.2, 136.9 (2C), 137.1, 137.3, 143.1, 150.0, 168.0, 168.6, 169.0 ppm.

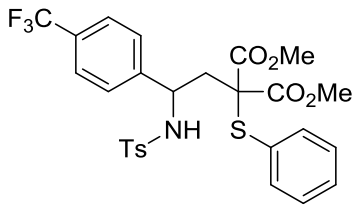
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3257, 1733, 1432, 1327, 1221, 1150, 1071.

MS (ESI): *m*/*z* = 589.2 $[M+NH_4]^+$.

$C_{28}H_{29}NO_8S_2$ (MW 571.66) calcd.: 594.12323

found: 594.12299 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(4-(trifluoromethyl)phenyl)ethyl)-2-(phenylthio)malonate (4g)



Dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate (60.5 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4g** (101 mg, 174 µmol, 86%) as a colorless solid.

m.p.: 183 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 2.32 (dd, J = 15.2, 5.2 Hz, 1H), 2.53 (dd, *J* = 15.2, 8.5 Hz, 1H), 3.48 (s, 3H), 3.82 (s, 3H), 5.05 (td, *J* = 8.5, 5.2 Hz, 1H), 5.15 (d, *J* = 8.5 Hz, 1H), 6.94 – 6.99 (m, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.36 (m, 6H), 7.38 – 7.43 (m, 1H), 7.46 – 7.50 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.2, 40.9, 53.2, 53.7, 54.6, 62.9, 125.2, 125.2, 127.0 (2C), 127.3 (2C), 128.8, 129.1 (2C), 129.2 (2C), 129.9, 130.3, 136.8 (2C), 137.2, 143.3, 143.5, 168.2, 168.7 ppm; 1x *C*-F_3 signal is missing.

^{19}F-NMR (377 MHz, $CDCl_3$): δ = -63.1 ppm.

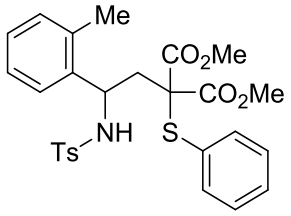
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3252, 2959, 1738, 1436, 1322, 1151, 1122, 1066.

MS (ESI): *m*/*z* = 599.0 $[M+NH_4]^+$.

$C_{27}H_{26}F_3NO_6S_2$ (MW 581.62) calcd.: 604.10458

found: 604.10491 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*o*-tolyl)ethyl)-2-(phenylthio)malonate (4h)



Dimethyl 2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate (49.7 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4h** (94.2 mg, 179 µmol, 89%) as a colorless solid.

m.p.: 162 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 2.29 (s, 3H), 2.50 (dd, *J* = 15.1, 6.1 Hz, 1H), 2.61 – 2.69 (m, 1H), 3.33 (s, 3H), 3.72 (s, 3H), 5.20 (q, *J* = 6.8 Hz, 2H), 6.87 – 7.01 (m, 6H), 7.29 – 7.35 (m, 2H), 7.36 – 7.42 (m, 3H), 7.49 – 7.55 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.2, 21.4, 41.1, 53.0, 53.3, 63.4, 126.09, 126.14, 126.9 (2C), 127.4, 129.0 (2C), 129.1 (2C), 129.2, 130.1, 130.47, 130.52, 135.7, 136.9 (2C), 137.4, 137.8, 168.1, 168.6 ppm; 1x *C* signal (~ 54 ppm) is missing.

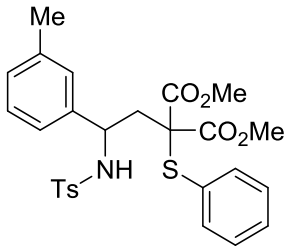
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3282, 2954, 1739, 1435, 1255, 1225, 1155, 1089.

MS (ESI): *m*/*z* = 545.2 $[M+NH_4]^+$.

$C_{27}H_{29}NO_6S_2$ (MW 527.65) calcd.: 550.13340

found: 550.13306 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*m*-tolyl)ethyl)-2-(phenylthio)malonate (4i)



Dimethyl 2-(*m*-tolyl)cyclopropane-1,1-dicarboxylate (49.7 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4i** (84.5 mg, 160 µmol, 80%) as a colorless solid.

m.p.: 144 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 2.29 (s, 3H), 2.38 (dd, *J* = 15.2, 5.8 Hz, 1H), 2.56 (dd, *J* = 15.2, 8.4 Hz, 1H), 3.41 (s, 3H), 3.79 (s, 3H), 4.94 (td, *J* = 8.4, 5.8 Hz, 1H), 5.08 (d, *J* = 8.6 Hz, 1H), 6.61 – 6.62 (m, 1H), 6.75 – 6.78 (m, 1H), 6.84 – 6.87 (m, 1H), 6.94 – 7.00 (m, 3H), 7.29 – 7.36 (m, 2H), 7.36 – 7.43 (m, 3H), 7.49 – 7.55 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.0, 21.3, 41.1, 52.9, 53.5, 54.9, 63.3, 123.9, 127.1 (2C), 127.5, 128.1, 128.2, 128.9 (2C), 129.1 (3C), 130.1, 136.9 (2C), 137.4, 137.8, 139.3, 142.6, 168.2, 168.7 ppm.

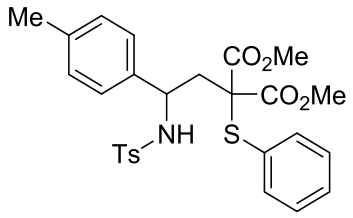
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3262, 2956, 1732, 1434, 1332, 1233, 1153, 1071.

MS (ESI): *m*/*z* = 545.2 $[M+NH_4]^+$.

$C_{27}H_{29}NO_6S_2$ (MW 527.65) calcd.: 550.13285

found: 550.13308 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*m*-tolyl)ethyl)-2-(phenylthio)malonate (4j)



Dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate (49.7 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4j** (69.4 mg, 132 µmol, 66%) as a colorless solid.

m.p.: 175 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3H), 2.31 (s, 3H), 2.38 (dd, *J* = 15.2, 6.1 Hz, 1H), 2.57 (dd, *J* = 15.2, 8.1 Hz, 1H), 3.39 (s, 3H), 3.76 (s, 3H), 4.94 (td, *J* = 8.1, 6.0 Hz, 1H), 5.04 (d, *J* = 8.5 Hz, 1H), 6.81 – 6.87 (m, 4H), 6.97 – 7.04 (m, 2H), 7.28 – 7.35 (m, 2H), 7.36 – 7.44 (m, 3H), 7.48 – 7.54 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 20.9, 21.4, 41.0, 52.9, 53.5, 54.8, 63.4, 126.8 (2C), 127.1 (2C), 128.9 (2C), 129.0 (2C), 129.05, 129.08 (2C), 130.1, 136.5, 136.9 (2C), 137.3, 137.4, 142.7, 168.1, 168.6 ppm.

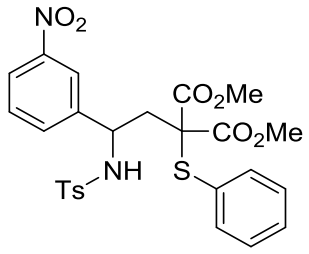
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3278, 2954, 1729, 1435, 1328, 1224, 1155, 1086.

MS (ESI): *m*/*z* = 545.2 $[M+NH_4]^+$.

$C_{27}H_{29}NO_6S_2$ (MW 527.65) calcd.: 550.13285

found: 550.13311 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(3-nitrophenyl)ethyl)-2-(phenylthio)malonate (4k)



Dimethyl 2-(3-nitrophenyl)cyclopropane-1,1-dicarboxylate (55.9 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4k** (92.1 mg, 165 µmol, 82%) as a colorless semi-solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.32 (dd, *J* = 15.2, 4.9 Hz, 1H), 2.59 (dd, *J* = 15.2, 8.9 Hz, 1H), 3.54 (s, 3H), 3.84 (s, 3H), 5.10 (td, *J* = 8.9, 4.9 Hz, 1H), 5.71 (d, *J* = 8.3 Hz, 1H), 6.94 – 7.00 (m, 2H), 7.27 – 7.36 (m, 3H), 7.38 – 7.43 (m, 4H), 7.45 – 7.49 (m, 2H), 7.68 – 7.70 (m, 1H), 7.92 (ddd, *J* = 8.3, 2.3, 1.0 Hz, 1H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.2, 40.9, 53.3, 53.8, 54.4, 62.9, 121.8, 122.3, 127.0 (2C), 128.7, 129.2 (2C), 129.26 (2C), 129.30, 130.4, 133.1, 136.7 (2C), 137.2, 141.8, 143.3, 147.9, 168.3, 168.6 ppm.

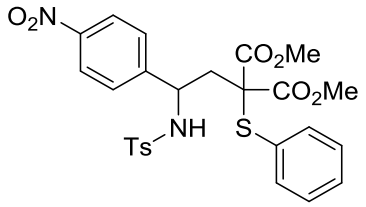
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3280, 2955, 1729, 1529, 1436, 1346, 1225, 1157, 1085.

MS (ESI): *m/z* = 576.1 $[M+NH_4]^+$.

$C_{26}H_{26}N_2O_8S_2$ (MW 558.62) calcd.: 581.10228

found: 581.10251 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(4-nitrophenyl)ethyl)-2-(phenylthio)malonate (4l)



Dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (55.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4l** (93.5 mg, 167 µmol, 84%) as a colorless solid.

m.p.: 182 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 2.32 (dd, *J* = 15.1, 5.0 Hz, 1H), 2.58 (dd, *J* = 15.1, 8.8 Hz, 1H), 3.52 (s, 3H), 3.81 (s, 3H), 5.07 (td, *J* = 8.8, 5.0 Hz, 1H), 5.74 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.20 (m, 2H), 7.32 (dd, *J* = 8.0, 6.7 Hz, 2H), 7.38 – 7.47 (m, 5H), 7.87 – 7.93 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.3, 40.9, 53.3, 53.7, 54.4, 62.9, 123.4 (2C), 127.1 (2C), 127.8 (2C), 128.7, 129.20 (2C), 129.24 (2C), 130.4, 136.7 (2C), 137.1, 143.6, 147.0, 147.1, 168.2, 168.5 ppm.

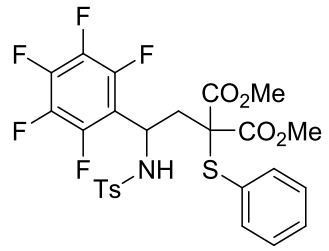
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3277, 2955, 1729, 1520, 1436, 1343, 1255, 1223, 1157, 1083.

MS (ESI): *m*/*z* = 576.1 $[M+NH_4]^+$.

$C_{26}H_{26}N_2O_8S_2$ (MW 558.62) calcd.: 581.10228

found: 581.10243 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(perfluorophenyl)ethyl)-2-(phenylthio)malonate (4m)



Dimethyl 2-(perfluorophenyl)cyclopropane-1,1-dicarboxylate (64.8 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4m** (64.9 mg, 108 µmol, 54%) as a colorless solid.

m.p.: 138 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.23 (dd, *J* = 15.2, 4.5 Hz, 1H), 2.35 (s, 3H), 2.74 (dd, *J* = 15.2, 10.3 Hz, 1H), 3.66 (s, 3H), 3.87 (s, 3H), 4.94 (d, *J* = 10.6 Hz, 1H), 5.45 (td, *J* = 10.3, 4.5 Hz, 1H), 7.13 – 7.18 (m, 2H), 7.28 – 7.33 (m, 2H), 7.36 – 7.44 (m, 3H), 7.54 – 7.60 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.3, 38.1, 45.4, 53.3, 53.9, 62.8, 113.4 (t, *J* = 16 Hz.0), 127.0 (2C), 128.5, 129.25 (2C), 129.26 (2C), 130.3, 136.4 (2C), 136.7, 137.2 (d, *J* = 254.0 Hz), 140.7 (d, *J* = 255.2 Hz), 144.0, 168.0, 168.3 ppm; 1x *C*-F signal is missing.

^{19}F-NMR (283 MHz, $CDCl_3$): δ = -161.76, -154.73 (tt, *J* = 20.6, 2.2 Hz), -144.09, -141.39 ppm.

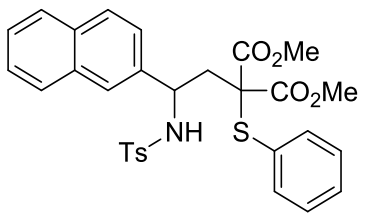
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3265, 3955, 1732, 1434, 1332, 1153, 1070.

MS (ESI): *m*/*z* = 621.1 $[M+NH_4]^+$.

$C_{26}H_{22}F_5NO_6S_2$ (MW 603.58) calcd.: 626.07009

found: 626.07022 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(naphthalene-2-yl)ethyl)-2-(phenylthio)malonate (4n)



Dimethyl 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (56.9 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylthio)succinimide (70.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **4n** (96.9 mg, 172 µmol, 86%) as a colorless solid.

m.p.: 193 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.45 – 2.53 (m, 1H), 2.61 – 2.70 (m, 1H), 3.28 (s, 3H), 3.80 (s, 3H), 5.12 – 5.20 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 7.06 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.27 – 7.46 (m, 8H), 7.50 – 7.61 (m, 4H), 7.67 – 7.72 (m, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.0, 40.9, 52.9, 53.5, 55.2, 63.3, 123.9, 126.1, 126.2, 126.6, 127.0 (2C), 127.4, 127.8, 128.3, 128.8 (2C), 129.0, 129.2 (2C), 130.2, 132.6, 132.7, 136.2, 136.9 (2C), 137.2, 142.8, 168.1, 168.7 ppm.

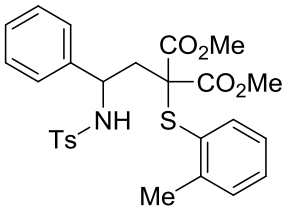
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3261, 1731, 1439, 1334, 1233, 1152, 1070.

MS (ESI): *m*/*z* = 581.2 $[M+NH_4]^+$.

$C_{30}H_{29}NO_6S_2$ (MW 563.68) calcd.: 586.13285

found: 586.13295 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(*o*-tolylthio)malonate (5a)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(*o*-tolylthio)succinimide (75.2 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **5a** (68.5 mg, 129 µmol, 65%) as a colorless solid.

m.p.: 143 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 2.48 (dd, *J* = 15.1, 5.4 Hz, 1H), 2.49 (s, 3H), 2.68 (dd, *J* = 15.1, 8.2 Hz, 1H), 3.40 (s, 3H), 3.71 (s, 3H), 4.82 – 4.99 (m, 2H), 6.89 – 6.96 (m, 2H), 6.96 – 7.03 (m, 2H), 7.03 – 7.14 (m, 4H), 7.21 – 7.26 (m, 2H), 7.34 – 7.42 (m, 2H), 7.47 – 7.54 (m, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.0, 21.4, 42.1, 52.9, 53.3, 55.2, 62.8, 126.4 (2C), 126.8 (2C), 127.1, 127.5, 128.3 (2C), 128.9, 129.1 (2C), 130.0, 130.7, 137.5, 137.7, 139.7, 142.8, 143.9, 168.4, 168.8 ppm.

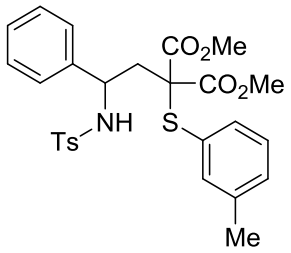
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3279, 2954, 1729, 1434, 1326, 1251, 1225, 1156, 1088.

MS (ESI): *m/z* = 545.0 $[M+NH_4]^+$.

$C_{27}H_{29}NO_6S_2$ (MW 527.65) calcd.: 550.13285

found: 550.13294 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(*m*-tolylthio)malonate (5b)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(*m*-tolylthio)succinimide (75.2 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **5b** (72.0 mg, 136 µmol, 69%) as a colorless solid.

m.p.: 139 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.31 (s, 3H), 2.36 (dd, *J* = 15.2, 5.9 Hz, 1H), 2.57 (dd, *J* = 15.2, 8.1 Hz, 1H), 3.40 (s, 3H), 3.78 (s, 3H), 5.01 (td, *J* = 8.1, 5.9 Hz, 1H), 5.12 (d, *J* = 8.1 Hz, 1H), 6.93 – 7.00 (m, 4H), 7.02 – 7.08 (m, 3H), 7.17 – 7.23 (m, 2H), 7.27 (dt, *J* = 3.8, 1.6 Hz, 1H), 7.36 – 7.42 (m, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.1, 21.3, 41.0, 52.9, 53.5, 55.0, 63.4, 126.9 (2C), 127.1 (2C), 127.5, 128.3 (2C), 128.6, 128.9, 129.0 (2C), 131.0, 133.8, 137.4, 137.6, 139.0, 139.7, 142.7, 168.1, 168.7 ppm.

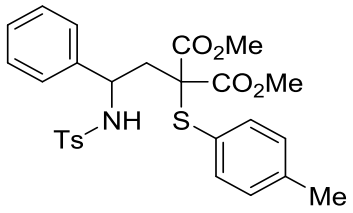
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3280, 2954, 1729, 1435, 1326, 1224, 1156, 1086.

MS (ESI): *m/z* = 545.0 $[M+NH_4]^+$.

$C_{27}H_{29}NO_6S_2$ (MW 527.65) calcd.: 550.13285

found: 550.13291 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(*p*-tolylthio)malonate (5c)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(*p*-tolylthio)succinimide (75.2 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **5c** (90.9 mg, 172 µmol, 86%) as a colorless semi-solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.32 (s, 3H), 2.37 (dd, *J* = 15.1, 6.0 Hz, 1H), 2.55 (dd, *J* = 15.1, 8.2 Hz, 1H), 3.40 (s, 3H), 3.77 (s, 3H), 4.99 (td, *J* = 8.2, 5.9 Hz, 1H), 5.21 (d, *J* = 8.2 Hz, 1H), 6.95 – 6.99 (m, 4H), 7.02 – 7.09 (m, 3H), 7.10 – 7.14 (m, 2H), 7.36 – 7.42 (m, 4H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.3, 21.3, 40.9, 52.9, 53.5, 55.0, 63.3, 125.3, 126.9 (2C), 127.1 (2C), 127.4, 128.2 (2C), 129.0 (2C), 129.9 (2C), 136.9 (2C), 137.4, 139.6, 140.5, 142.7, 168.1, 168.7 ppm.

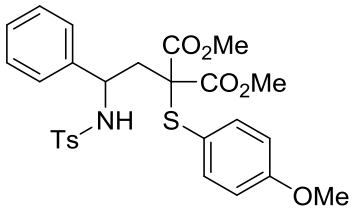
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3282, 2953, 1730, 1434, 1254, 1224, 1155, 1086.

MS (ESI): *m*/*z* = 545.2 $[M+NH_4]^+$.

$C_{27}H_{28}NO_6S_2$ (MW 527.65) calcd.: 550.13285

found: 550.13301 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-((4-methoxyphenyl)thio)-2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)malonate (5d)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-((4-methoxyphenyl)thio)succinimide (80.7 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **5d** (103 mg, 190 µmol, 95%) as a colorless solid.

m.p.: 156 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.39 (dd, *J* = 15.1, 6.3 Hz, 1H), 2.57 (dd, *J* = 15.1, 7.8 Hz, 1H), 3.37 (s, 3H), 3.75 (s, 3H), 3.77 (s, 3H), 4.99 (td, *J* = 7.8, 6.2 Hz, 1H), 5.33 (d, *J* = 8.5 Hz, 1H), 6.79 – 6.85 (m, 2H), 6.96 – 6.99 (m, 4H), 7.01 – 7.08 (m, 3H), 7.39 – 7.44 (m, 4H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.3, 41.0, 52.9, 53.3, 55.0, 55.3, 63.4, 114.6 (2C), 119.4, 126.9 (2C), 127.1 (2C), 127.4, 128.2 (2C), 129.0 (2C), 137.4, 138.6 (2C), 139.6, 142.7, 161.2, 168.1, 168.6 ppm.

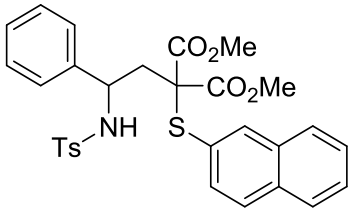
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3275, 2954, 1740, 1708, 1594, 1431, 1232, 1159, 1098, 1070.

MS (ESI): *m/z* = 560.9 $[M+NH_4]^+$.

$C_{27}H_{29}NO_7S_2$ (MW 543.65) calcd.: 566.12776

found: 566.12794 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(naphthalen-2-ylthio)malonate (5e)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-((2-naphthyl)thio)succinimide (87.5 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **5e** (83.4 mg, 148 µmol, 74%) as a colorless solid.

m.p.: 122 °C.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 2.44 (dd, *J* = 15.1, 6.1 Hz, 1H), 2.63 (dd, *J* = 15.1, 7.4 Hz, 1H), 3.36 (s, 3H), 3.76 (s, 3H), 5.05 – 5.13 (m, 1H), 5.16 (d, *J* = 8.8 Hz, 1H), 6.95 – 6.98 (m, 4H), 7.02 – 7.10 (m, 3H), 7.38 – 7.45 (m, 2H), 7.46 – 7.55 (m, 3H), 7.74 – 7.85 (m, 3H), 8.15 (d, *J* = 2.0 Hz, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.3, 41.1, 53.0, 53.5, 55.1, 63.6, 126.1, 126.6, 126.9 (2C), 127.1 (2C), 127.4, 127.5, 127.6, 128.1, 128.3 (2C), 128.6, 129.1 (2C), 132.6, 133.4, 133.6, 137.4, 137.6, 139.5, 142.8, 168.0, 168.6 ppm.

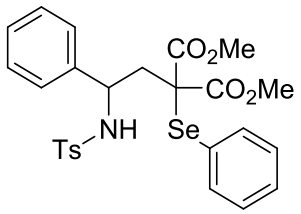
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3242, 2952, 1730, 1434, 1327, 1251, 1216, 1153, 1073.

MS (ESI): *m*/*z* = 581.2 $[M+NH_4]^+$.

$C_{30}H_{29}NO_6S_2$ (MW 563.68) calcd.: 586.13285

found: 586.13303 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylselanyl)malonate (7a)



Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (46.9 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylseleno)succinimide (86.4 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **7a** (98.9 mg, 177 µmol, 88%) as a pale yellow solid.

m.p.: 178 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.32 (dd, *J* = 15.1, 5.7 Hz, 1H), 2.35 (s, 3H), 2.52 (dd, *J* = 15.1, 8.4 Hz, 1H), 3.45 (s, 3H), 3.79 (s, 3H), 4.94 (td, *J* = 8.4, 5.7 Hz, 1H), 5.24 (d, *J* = 8.4 Hz, 1H), 6.79 – 6.84 (m, 2H), 7.00 – 7.05 (m, 2H), 7.13 – 7.18 (m, 2H), 7.29 – 7.35 (m, 2H), 7.36 – 7.42 (m, 3H), 7.45 – 7.49 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 40.8, 53.1, 53.6, 54.5, 63.1, 121.5, 127.1 (2C), 128.7 (2C), 128.8, 129.1 (2C), 129.2 (2C), 130.3, 131.3 (2C), 136.8 (2C), 137.2, 138.5, 143.2, 168.1, 168.6 ppm.

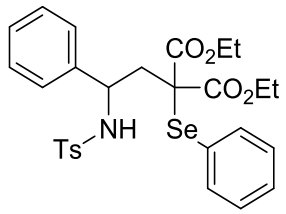
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3262, 1727, 1437, 1329, 1228, 1153, 1073.

MS (ESI): *m*/*z* = 579.1 $[M+NH_4]^+$.

$C_{26}H_{27}NO_6SSe$ (MW 560.52) calcd.: 584.06165

found: 584.06184 $[M+Na]^+$ (ESI-HRMS).

Diethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylselanyl)malonate (7b)



Diethyl 2-phenylcyclopropane-1,1-dicarboxylate (52.5 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylseleno)succinimide (86.4 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **7b** (91.2 mg, 155 µmol, 77%) as a colorless semi-solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 2.28 – 2.36 (m, 1H), 2.29 (s, 3H), 2.50 (dd, *J* = 15.3, 8.2 Hz, 1H), 3.77 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.90 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.21 (qd, *J* = 7.1, 3.7 Hz, 2H), 4.93 (td, *J* = 8.2, 5.8 Hz, 1H), 5.12 (d, *J* = 8.2 Hz, 1H), 6.90 – 6.95 (m, 2H), 6.97 – 7.09 (m, 5H), 7.28 – 7.34 (m, 2H), 7.37 – 7.43 (m, 3H), 7.59 – 7.65 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 13.7, 13.8, 21.4, 41.0, 56.1, 57.3, 62.2, 62.6, 126.0, 126.8 (2C), 127.1 (2C), 127.4, 128.2 (2C), 129.0 (2C), 129.1 (2C), 129.8, 137.6, 137.8 (2C), 139.9, 142.7, 168.7, 168.9 ppm.

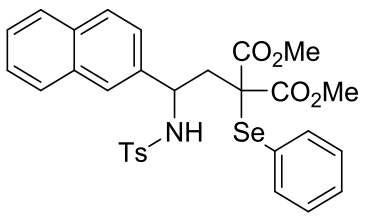
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3281, 2983, 1722, 1445, 1250, 1219, 1156, 1090, 1022.

MS (ESI): *m*/*z* = 606.9 $[M+NH_4]^+$.

$C_{28}H_{31}NO_6SSe$ (MW 588.58) calcd.: 612.09295

found: 612.09327 $[M+Na]^+$ (ESI-HRMS).

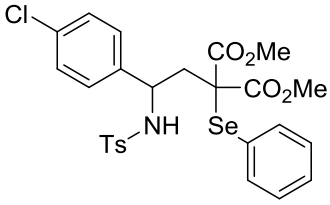
Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(naphthalene-2-yl)ethyl)-2-(phenylseleno)malonate (7c)

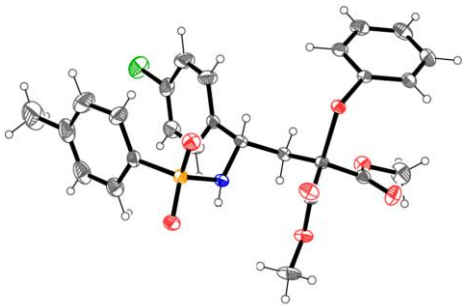


Dimethyl 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (56.9 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylseleno)succinimide (86.4 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **7c** (47.6 mg, 78.0 µmol, 39%) as a pale yellow semi-solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3H), 2.38 – 2.47 (m, 1H), 2.54 – 2.66 (m, 1H), 3.35 (s, 3H), 3.79 (s, 3H), 5.06 – 5.17 (m, 2H), 6.71 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.29 – 7.33 (m, 4H), 7.37 – 7.45 (m, 3H), 7.50 – 7.60 (m, 2H), 7.60 – 7.66 (m, 2H), 7.66 – 7.72 (m, 1H) ppm.
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 21.0, 41.1, 53.0, 53.5, 56.2, 57.2, 123.9, 125.8, 126.0, 126.1, 126.4, 127.0 (2C), 127.3, 127.7, 128.3, 128.8 (2C), 129.2 (2C), 130.0, 132.6, 132.7, 136.4, 137.3, 137.9 (2C), 142.8, 169.1, 169.4 ppm.
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3260, 2954, 1728, 1434, 1294, 1235, 1151, 1073.
MS (ESI): *m*/*z* = 628.9 $[M+NH_4]^+$.
$C_{30}H_{29}NO_6SSe$ (MW 610.58) calcd.: 634.07730
found: 634.07739 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylseleno)malonate (7d)





Dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (53.7 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylseleno)succinimide (86.4 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **7d** (97.2 mg, 163 µmol, 82%) as a colorless pale yellow solid.

Single crystals were obtained by diffusing *n*-pentane vapour into an ethyl acetate solution of the compound.

m.p.: 144 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.26 (dd, *J* = 15.3, 5.5 Hz, 1H), 2.34 (s, 3H), 2.47 (dd, *J* = 15.3, 8.7 Hz, 1H), 3.50 (s, 3H), 3.78 (s, 3H), 4.92 (td, *J* = 8.5, 5.5 Hz, 1H), 5.11 (d, *J* = 8.5 Hz, 1H), 6.81 – 6.86 (m, 2H), 6.98 – 7.05 (m, 4H), 7.29 – 7.34 (m, 2H), 7.36 – 7.43 (m, 3H), 7.56 – 7.58 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 41.1, 53.2, 53.6, 55.4, 56.9, 125.7, 127.1 (2C), 128.2 (2C), 128.3 (2C), 129.1 (2C), 129.2 (2C), 130.1, 133.3, 137.3, 137.8 (2C), 138.2, 143.2, 169.1, 169.3 ppm.

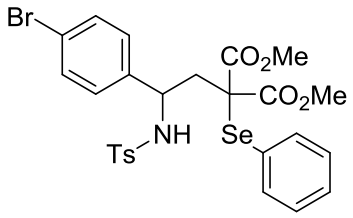
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3277, 2953, 1725, 1435, 1331, 1253, 1223, 1156, 1084.

MS (ESI): *m*/*z* = 612.8 $[M+NH_4]^+$.

$C_{26}H_{26}ClNO_6SSe$ (MW 594.97) calcd.: 618.02268

found: 618.02282 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-(4-bromophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylselanyl)malonate (7e)



Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate (62.6 mg, 200 µmol, 1.00 equiv.), *p*-toluene-sulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylseleno)succinimide (86.4 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **7e** (78.1 mg, 122 µmol, 61%) as a colorless solid.

m.p.: 168 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.25 (dd, *J* = 15.3, 5.3 Hz, 1H), 2.35 (s, 3H), 2.46 (dd, *J* = 15.3, 8.6 Hz, 1H), 3.51 (s, 3H), 3.79 (s, 3H), 4.91 (td, *J* = 8.6, 5.3 Hz, 1H), 5.06 (d, *J* = 8.5 Hz, 1H), 6.75 – 6.80 (m, 2H), 7.00 – 7.05 (m, 2H), 7.13 – 7.18 (m, 2H), 7.29 – 7.42 (m, 5H), 7.57 (dd, *J* = 8.1, 1.4 Hz, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 41.0, 53.2, 53.6, 55.5, 56.8, 121.4, 125.7, 127.0 (2C), 128.5 (2C), 129.1 (2C), 129.2 (2C), 130.1, 131.3 (2C), 137.3, 137.8 (2C), 138.7, 143.2, 169.1, 169.3 ppm.

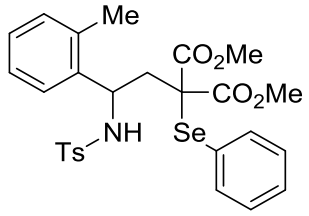
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3257, 1730, 1434, 1332, 1228, 1152, 1072.

MS (ESI): *m*/*z* = 657.0 $[M+NH_4]^+$.

$C_{26}H_{26}BrNO_6SSe$ (MW 639.42) calcd.: 661.97216

found: 661.97242 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*o*-tolyl)ethyl)-2-(phenylselanyl)malonate (7f)



Dimethyl 2-(*o*-tolyl)cyclopropane-1,1-dicarboxylate (49.7 mg, 200 µmol, 1.00 equiv.), *p*-toluenesulfonamide (37.7 mg, 220 µmol, 1.10 equiv.), *N*-(phenylseleno)succinimide (86.4 mg, 340 µmol, 1.70 equiv.) and $Sn(OTf)_2$ (8.3 mg, 20.0 µmol, 0.10 equiv.) in DCE (1.5 mL) were reacted according to GP1 overnight. Reverse phase column chromatography (C18, MeCN:H_2O = 70/30) gave the desired product **7f** (69.6 mg, 121 µmol, 61%) as a colorless semi-solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 2.29 (s, 3H), 2.46 (dd, *J* = 15.1, 5.8 Hz, 1H), 2.61 (dd, *J* = 15.1, 7.7 Hz, 1H), 3.40 (s, 3H), 3.72 (s, 3H), 5.07 – 5.21 (m, 2H), 6.86 – 6.94 (m, 2H), 6.94 – 7.00 (m, 4H), 7.28 – 7.35 (m, 2H), 7.35 – 7.44 (m, 3H), 7.57 – 7.65 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 19.2, 21.4, 41.3, 53.0, 53.3, 57.1, 126.0, 126.1, 126.8 (2C), 127.3, 129.0 (2C), 129.1 (2C), 130.0, 130.4, 135.4, 137.4, 137.82, 137.87 (2C), 137.9, 142.7, 169.1, 169.2 ppm; 1x *C* signal (~63 ppm) is missing.

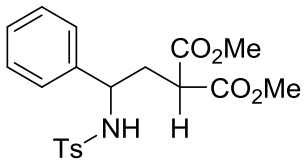
IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3285, 2954, 1725, 1436, 1253, 1225, 1156, 1071.

MS (ESI): *m*/*z* = 593.0 $[M+NH_4]^+$.

$C_{27}H_{29}NO_6SSe$ (MW 574.55) calcd.: 598.07743

found: 598.07757 $[M+Na]^+$ (ESI-HRMS).

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)malonate (8)



Side product **8** was collected during screening and optimization studies by reverse phase column chromatography on a preparative HPLC (C18, MeCN:H_2O = 70/30) as a colorless solid.

m.p.: 145 °C

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.25 – 2.37 (m, 5H), 3.54 (t, *J* = 7.0 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.40 (td, *J* = 8.9, 5.9 Hz, 1H), 5.10 (d, *J* = 8.6 Hz, 1H), 6.94 – 7.00 (m, 2H), 7.06 – 7.11 (m, 2H), 7.11 – 7.17 (m, 3H), 7.46 – 7.52 (m, 2H) ppm.

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 21.4, 36.3, 48.8, 52.7, 52.8, 56.7, 126.2 (2C), 127.0 (2C), 127.7, 128.6 (2C), 129.3 (2C), 137.3, 139.7, 143.1, 169.3, 169.9 ppm.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3249, 2950, 1750, 1731, 1440, 1312, 1147.

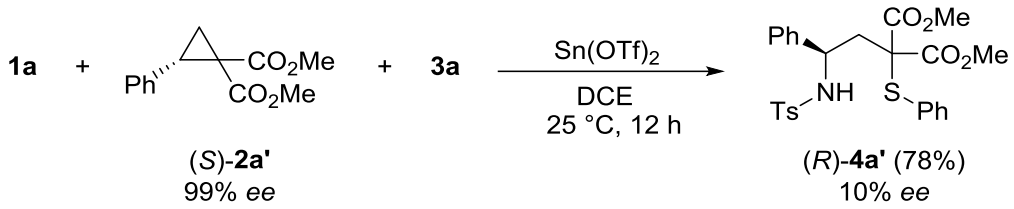
MS (ESI): *m/z* = 423.2 $[M+NH_4]^+$.

$C_{20}H_{23}NO_6S$ (MW 405.47) calcd.: 428.13183

found: 428.11422 $[M+Na]^+$ (ESI-HRMS).

5) Mechanistic Investigations

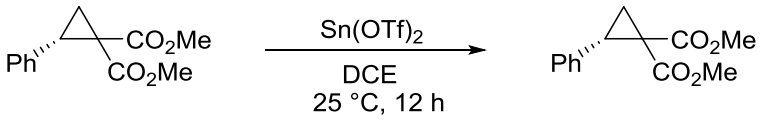
To gain insights into a plausible mechanism for our transformation we conducted several control experiments. Highly enantioenriched D-A cyclopropane (*S*)-**1a'** (>99% *ee*) was subjected to our standard reaction conditions. Unfortunately, the desired compound (*R*)-**4a'** could only be isolated in an enantiomeric excess of 10%.



(*S*)-**2a'**
99% *ee*

(*R*)-**4a'** (78%)
10% *ee*

To test whether our enantioenriched D-A cyclopropane (*S*)-**2a'** is stable or not under the given conditions, we subjected compound (*S*)-**2a'** (>99% *ee*) to our standard conditions without any reaction partner (**1** and **3a**). Indeed, a major loss of enantiomeric excess to 8% *ee* was observed. Detailed information can be found in the literature.[4]



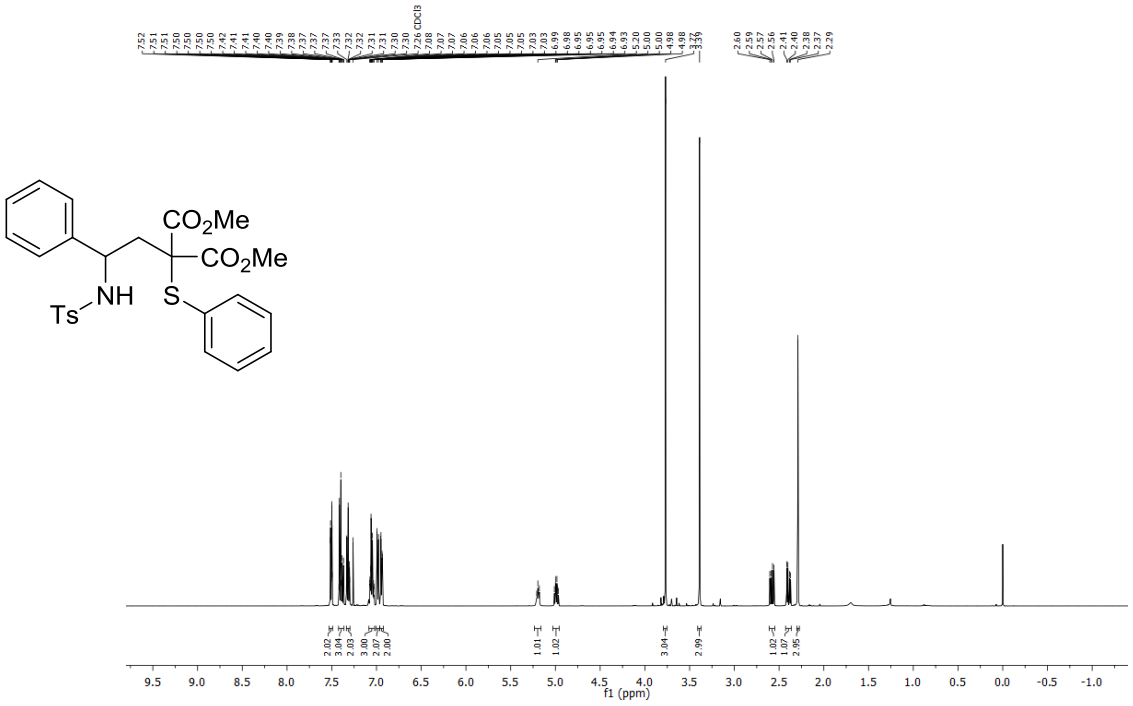
(*S*)-**2a'**
99% *ee*

(*S*)-**2a'**
8% *ee*

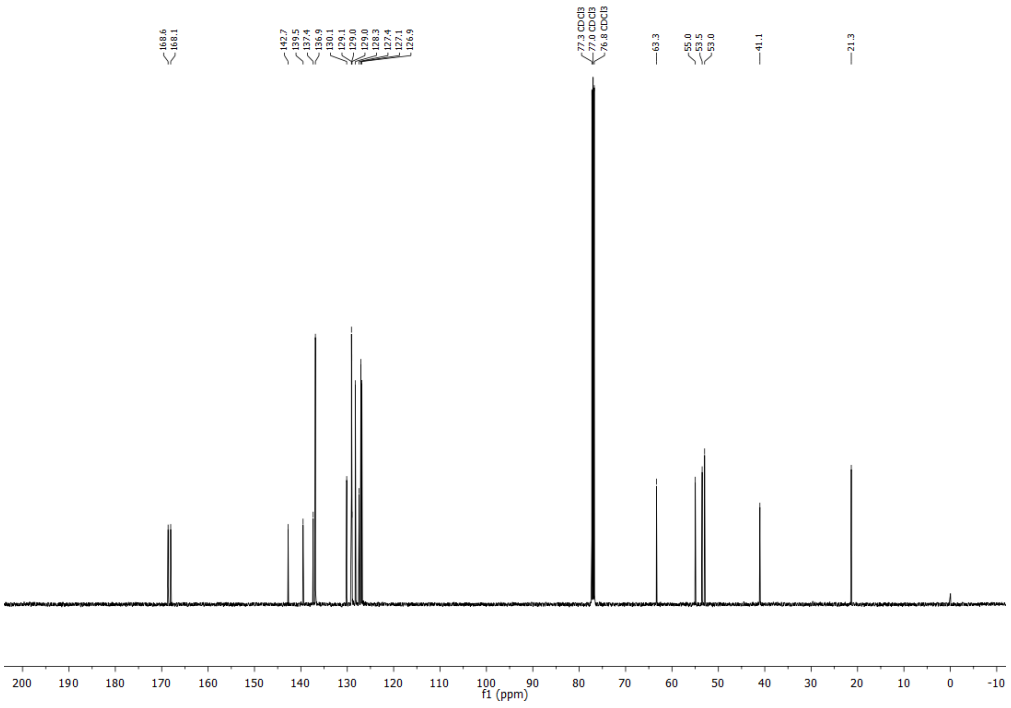
As consequence of those two experiments, we strongly believe that the background racemization of D-A cyclopropane (*S*)-**2a'** is fast in comparison to the nucleophilic attack of $TsNH_2$ (**1**) so that a significant loss of stereoinformation is observed.

6) ^{1}H- and ^{13}C-NMR Spectra

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylthio)malonate (4a)

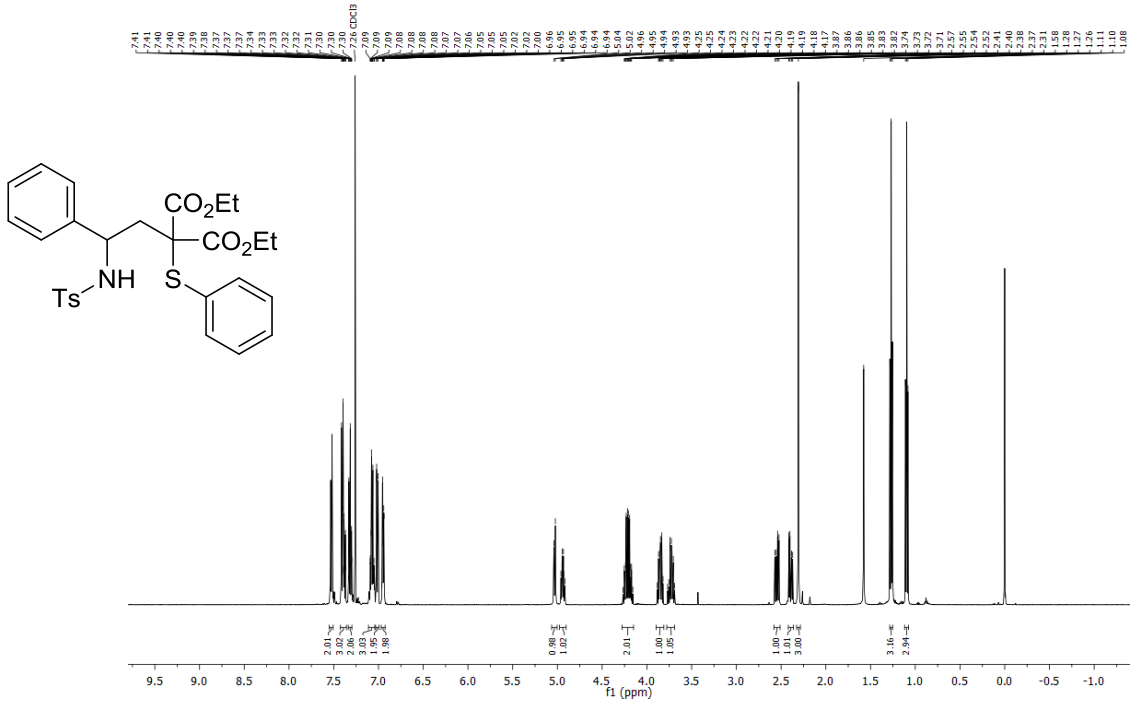


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

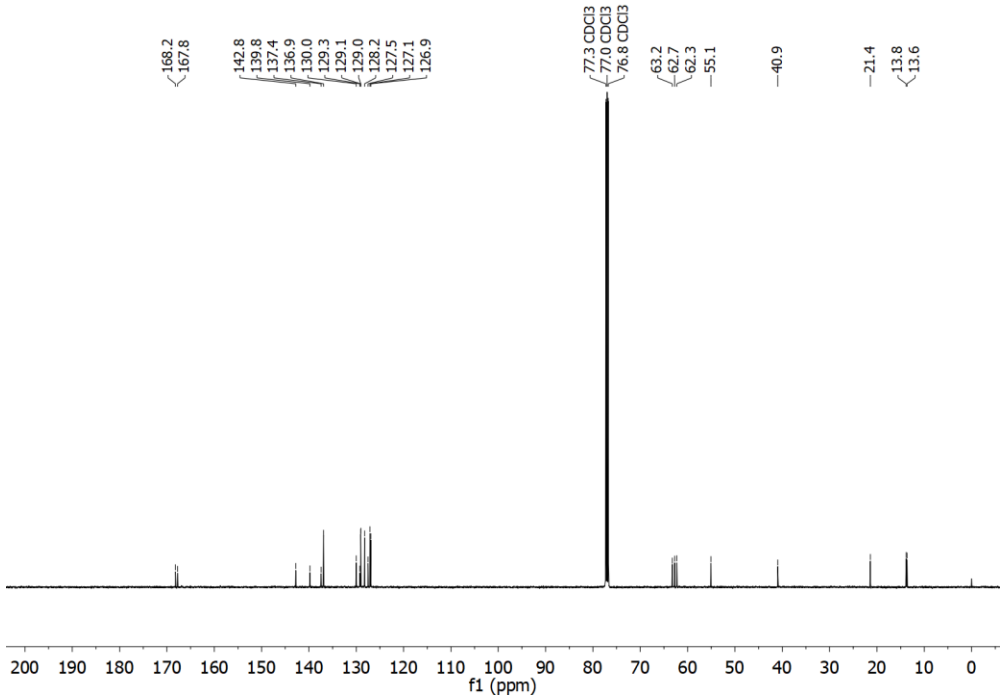


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Diethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylthio)malonate (4b)

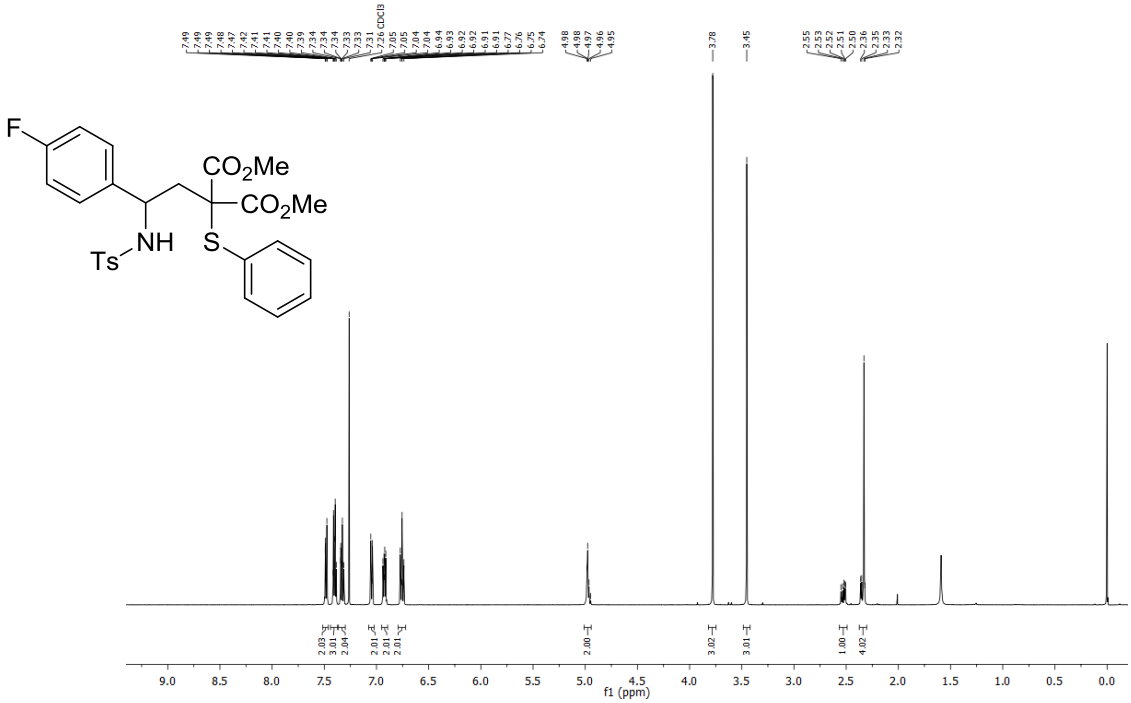


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

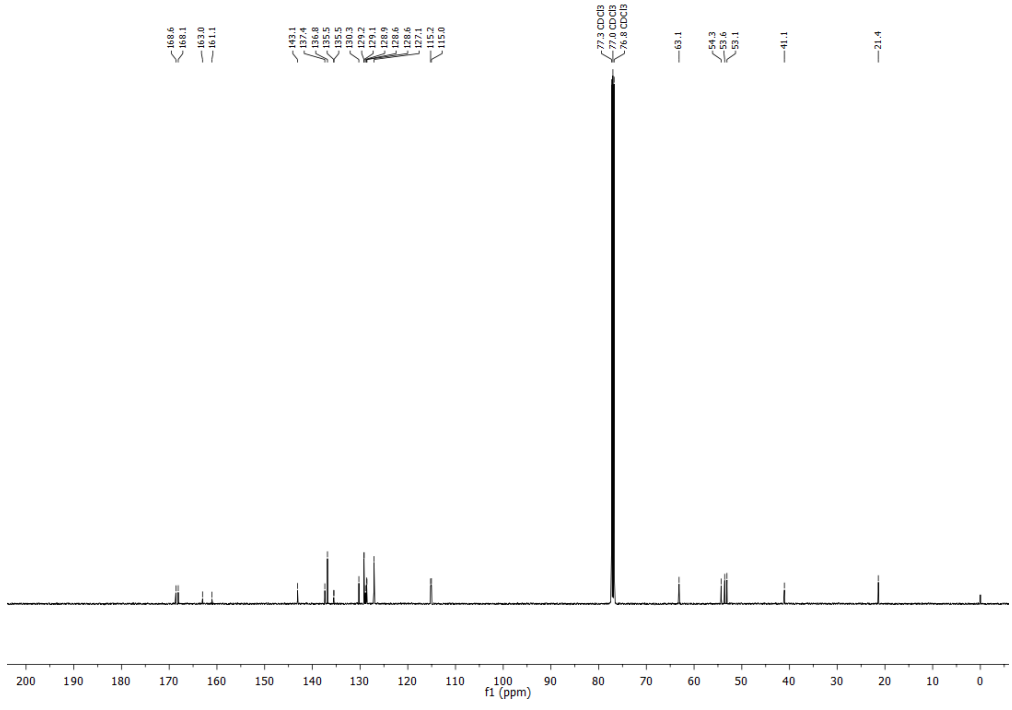


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

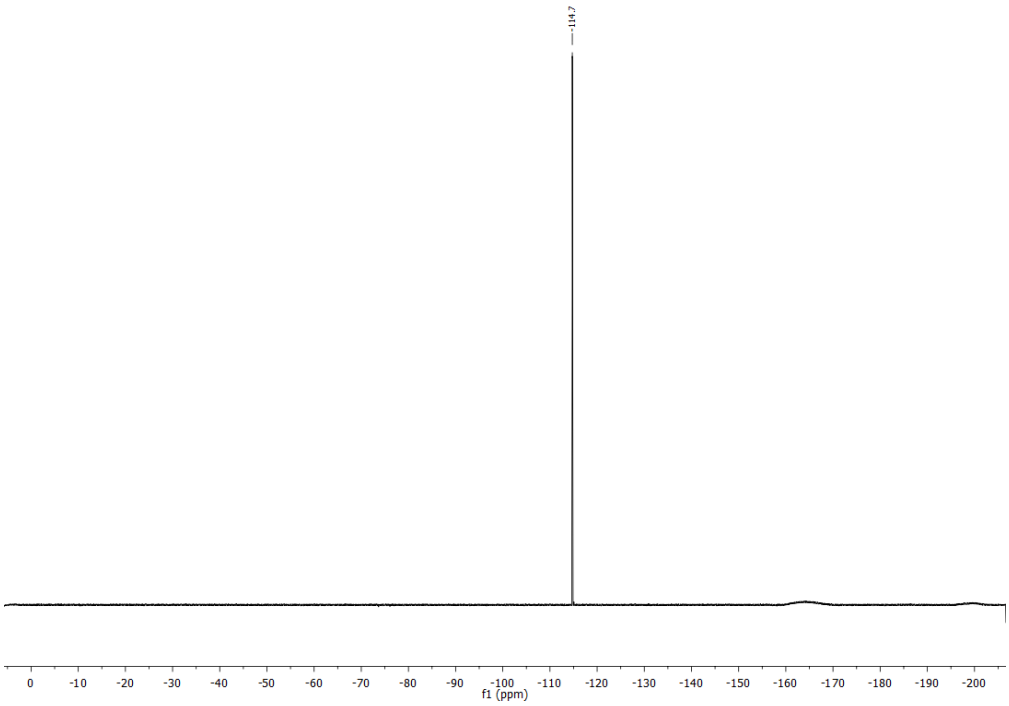
Dimethyl 2-(2-(4-fluorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4c)



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

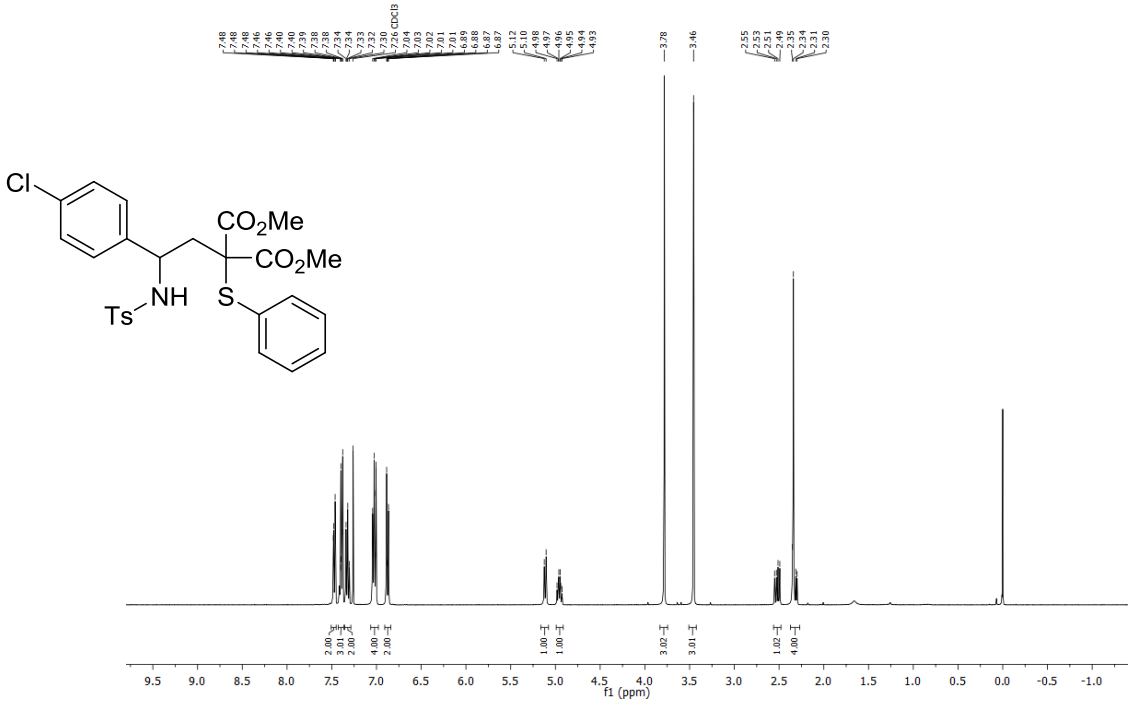


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

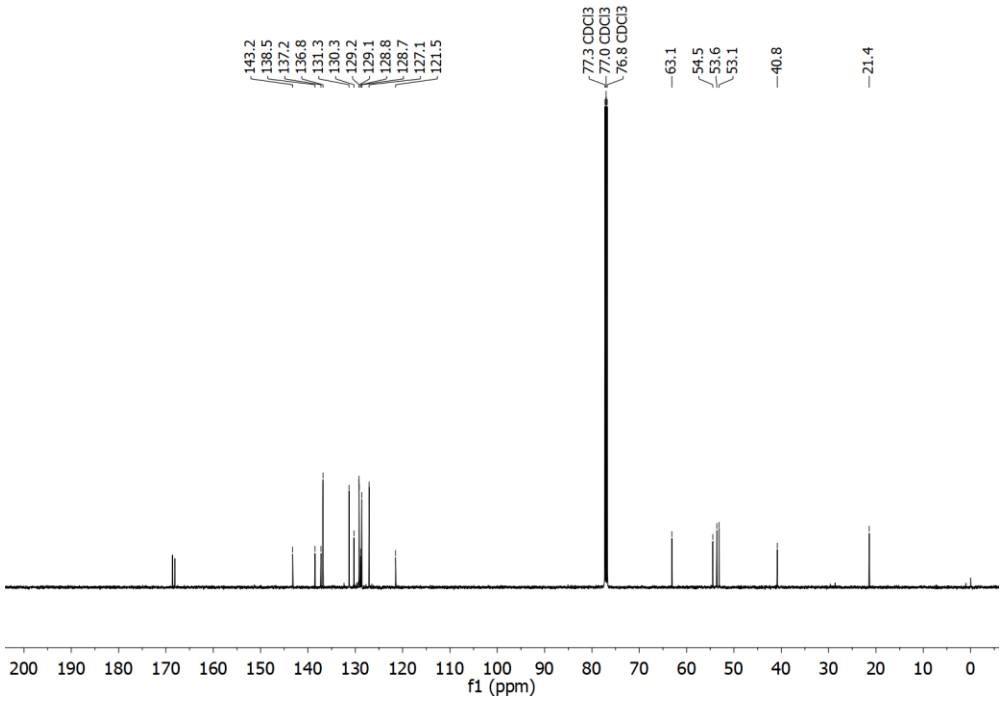


^{19}F-NMR Spectrum (471 MHz, $CDCl_3$)

Dimethyl 2-(2-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4d)

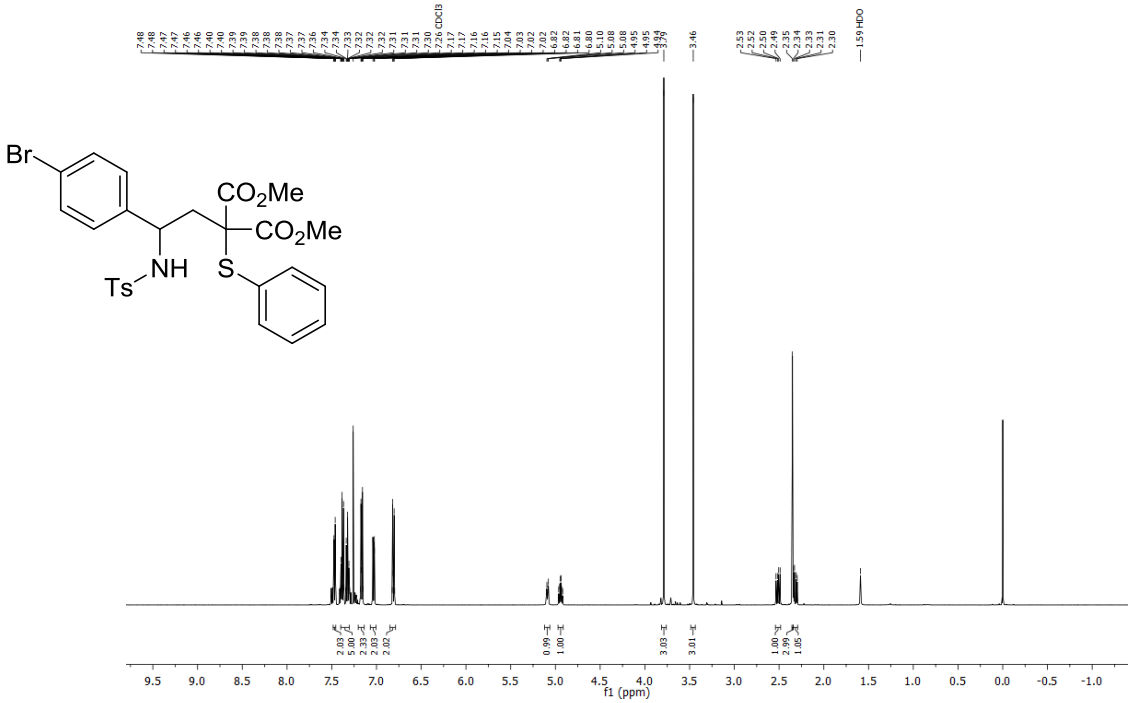


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

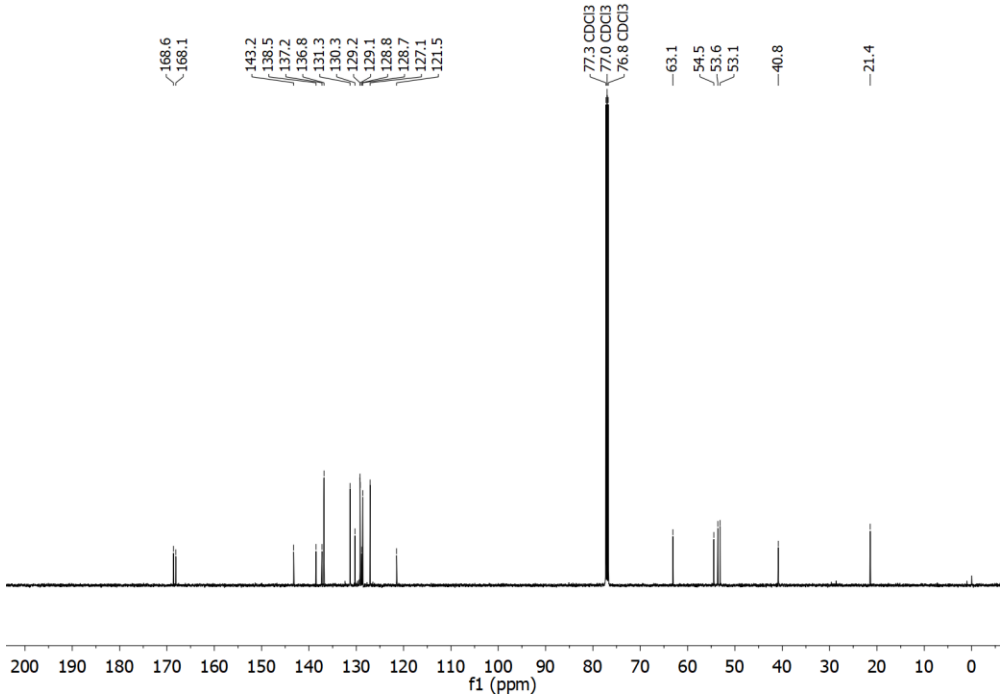


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl 2-(2-(4-bromophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4e)

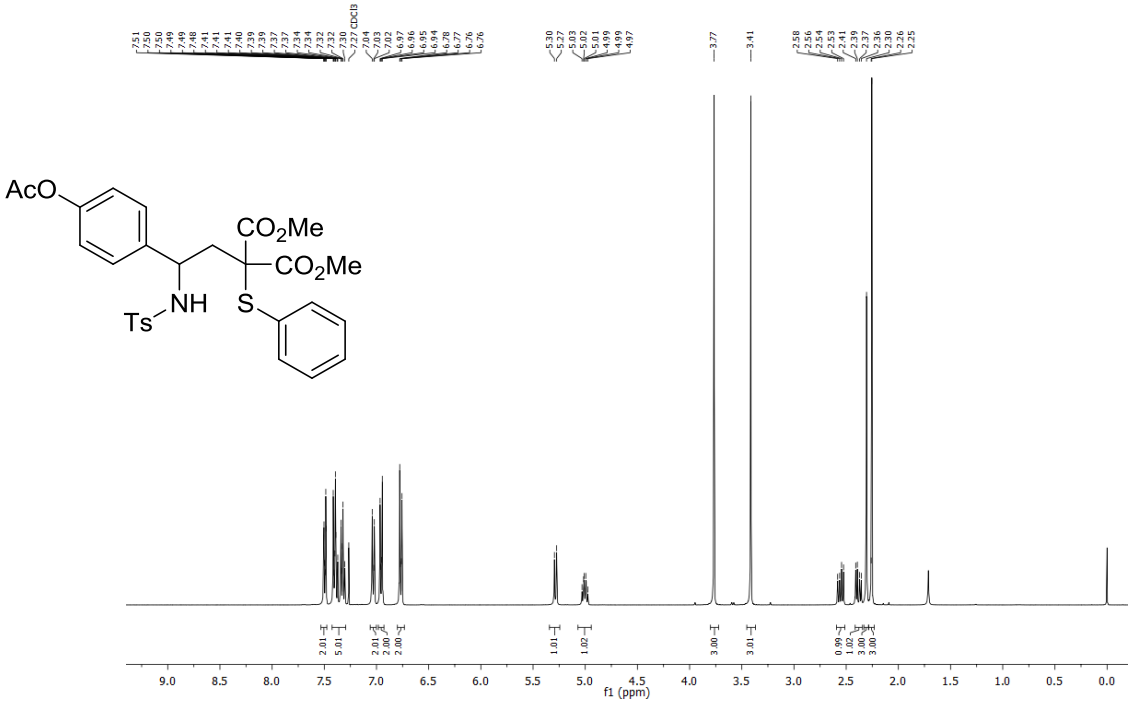


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

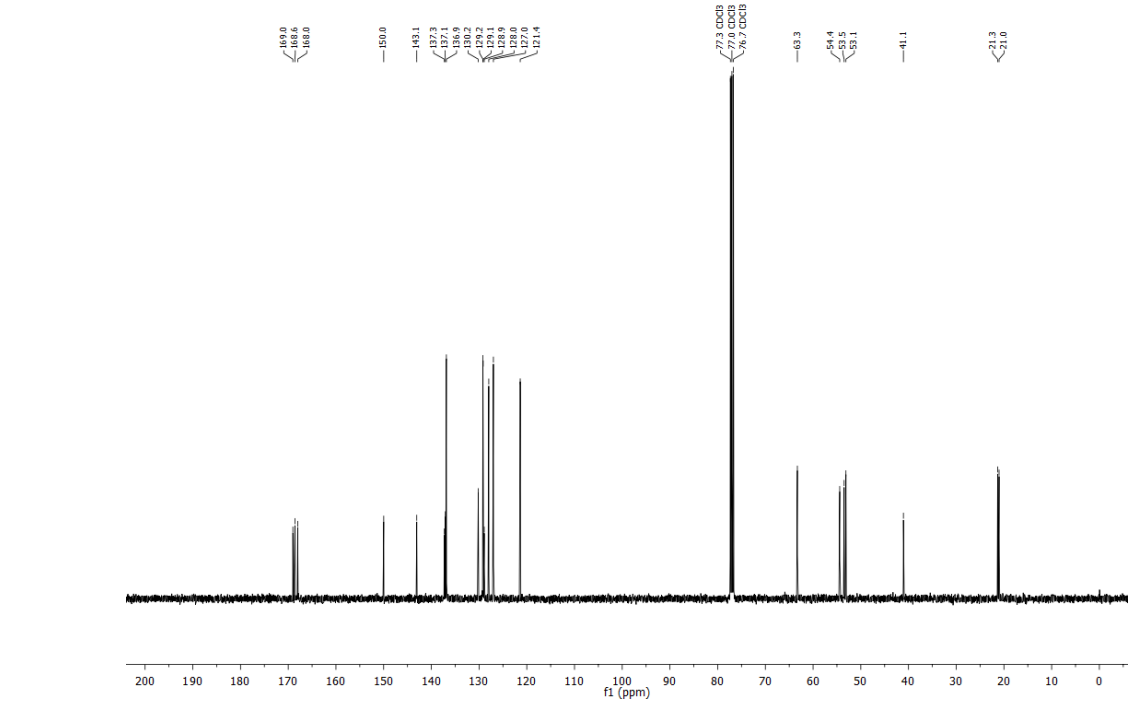


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl 2-(2-(4-acetoxyphenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylthio)malonate (4f)

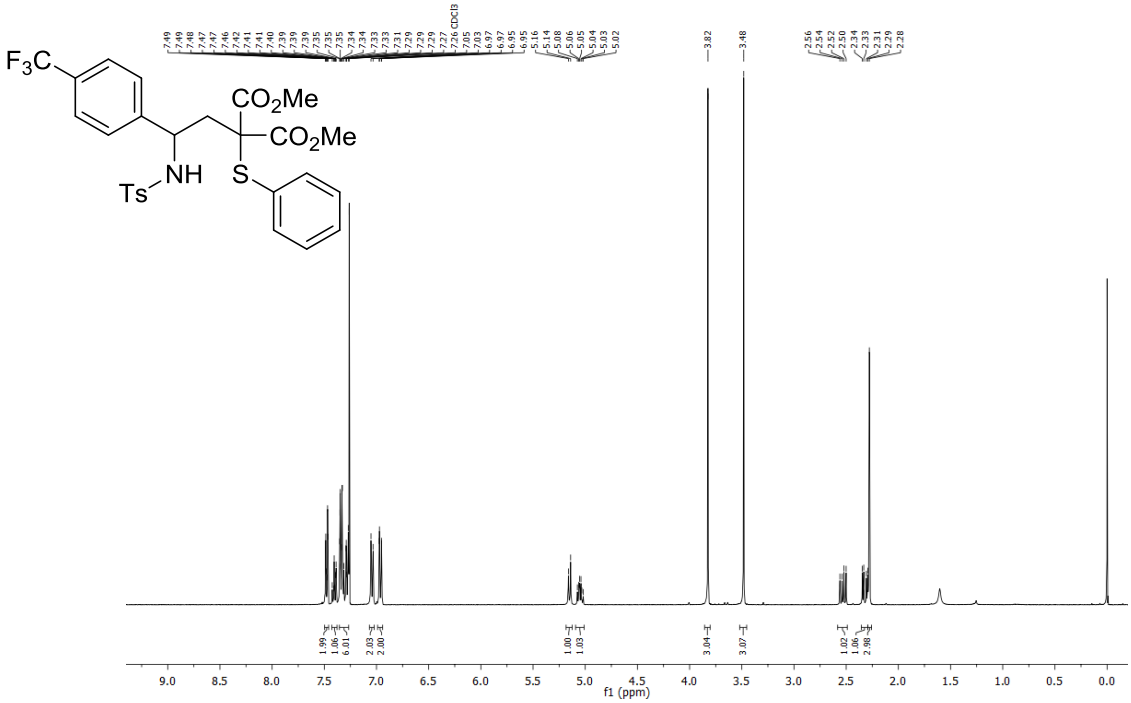


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

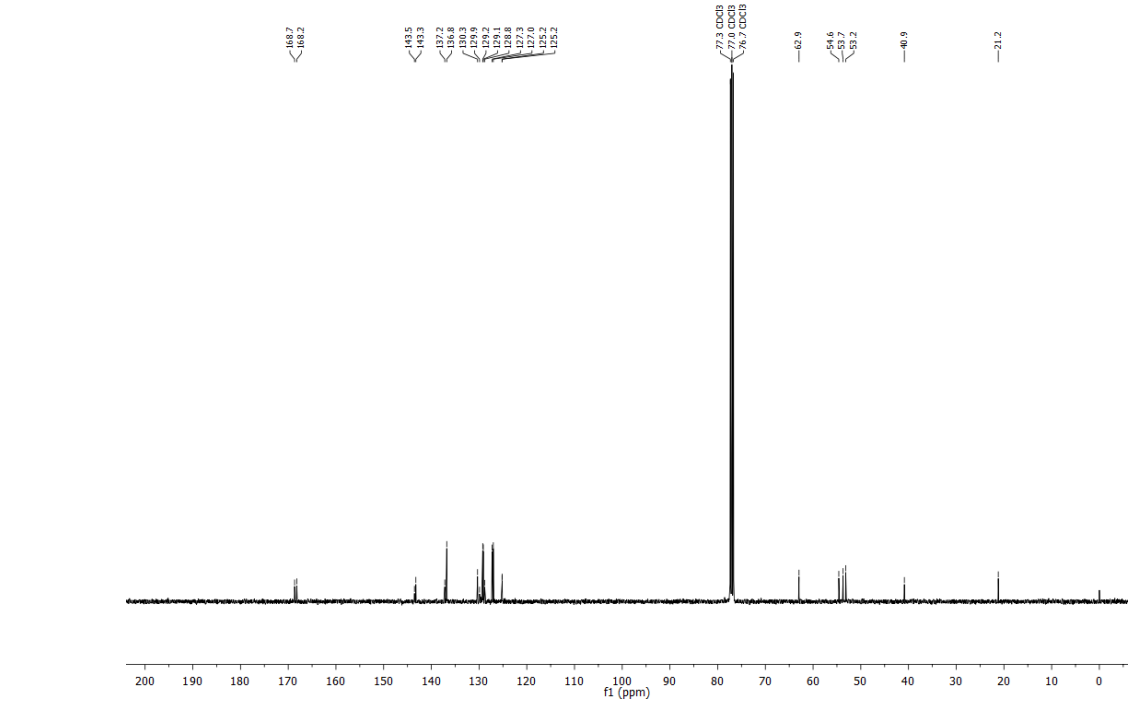


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

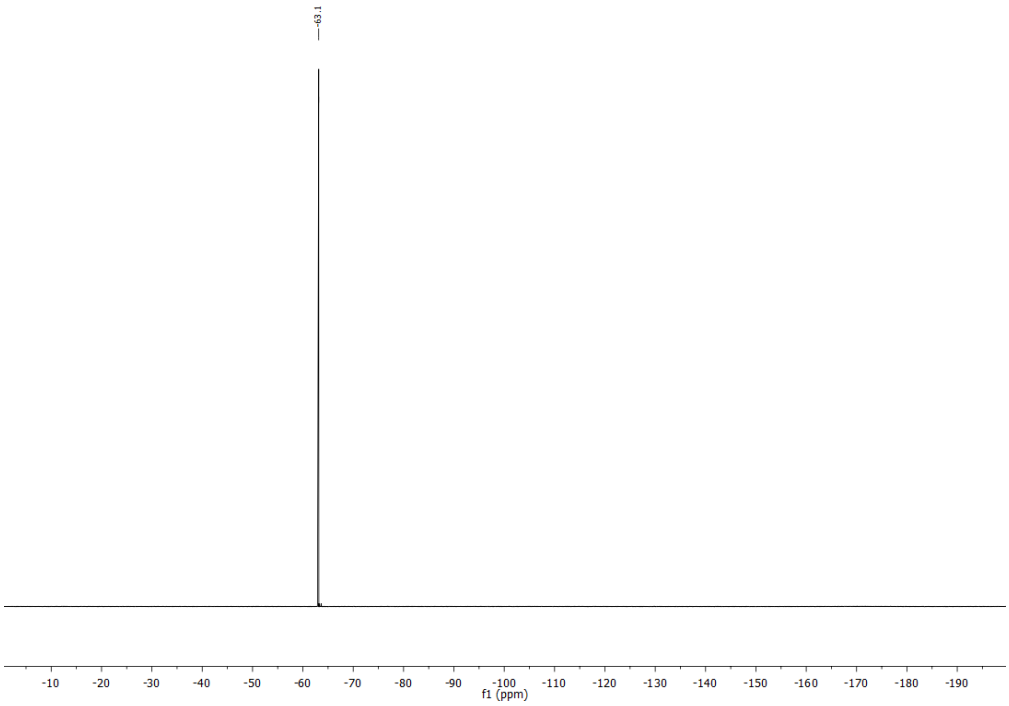
Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(4-(trifluoromethyl)phenyl)ethyl)-2-(phenylthio)malonate (4g)



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

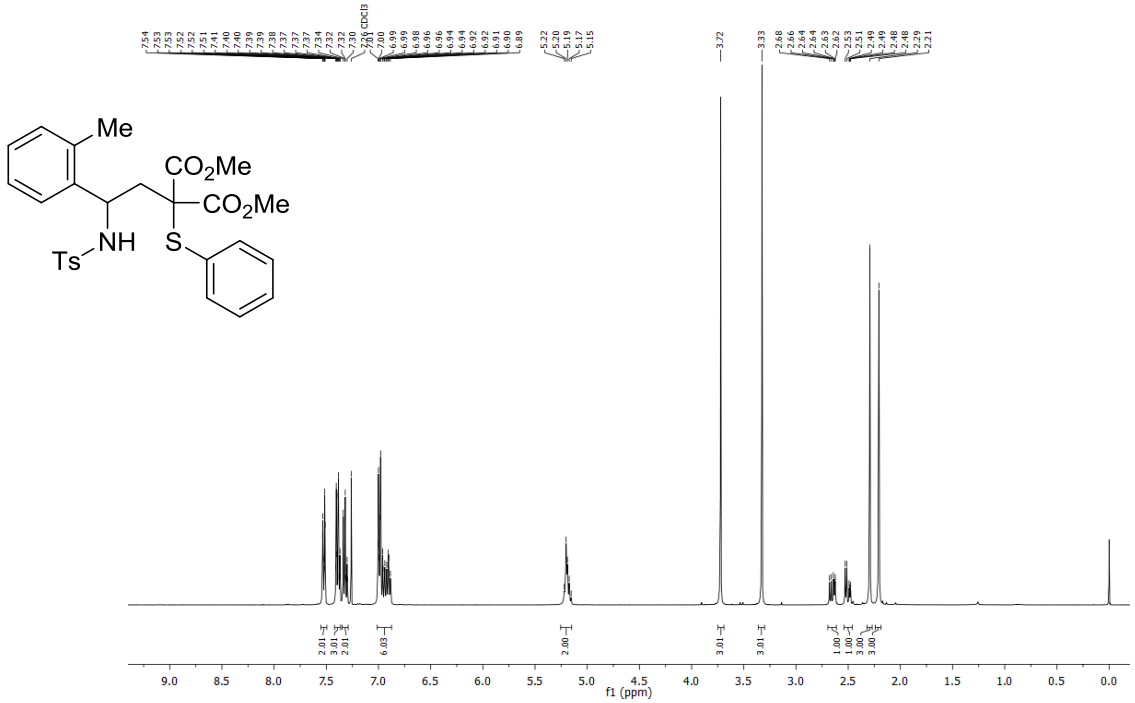


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

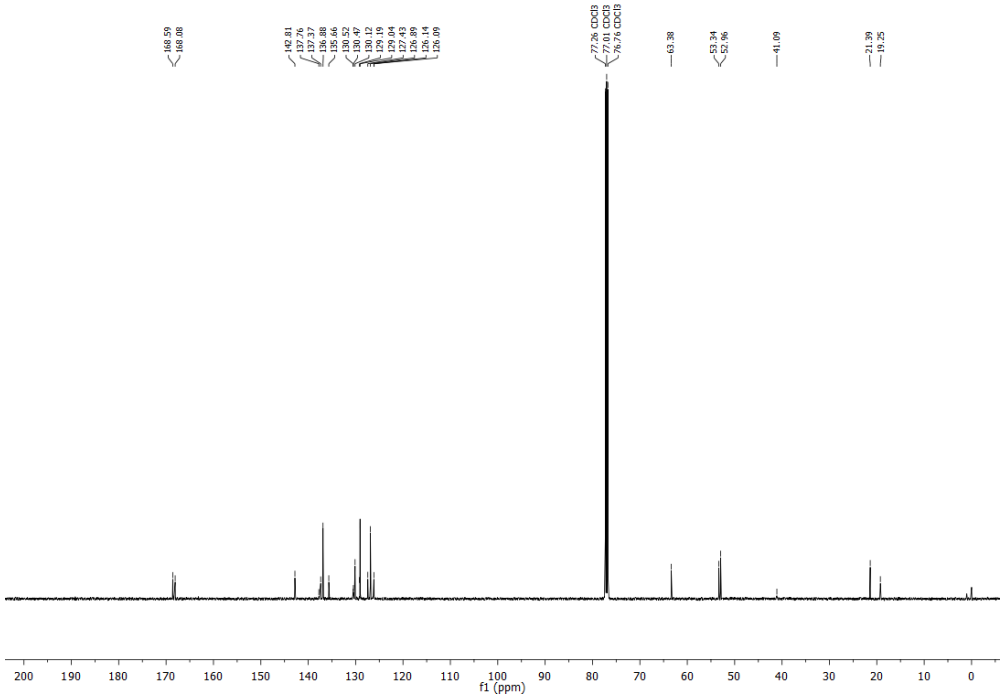


^{19}F-NMR Spectrum (377 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*o*-tolyl)ethyl)-2-(phenylthio)malonate (4h)

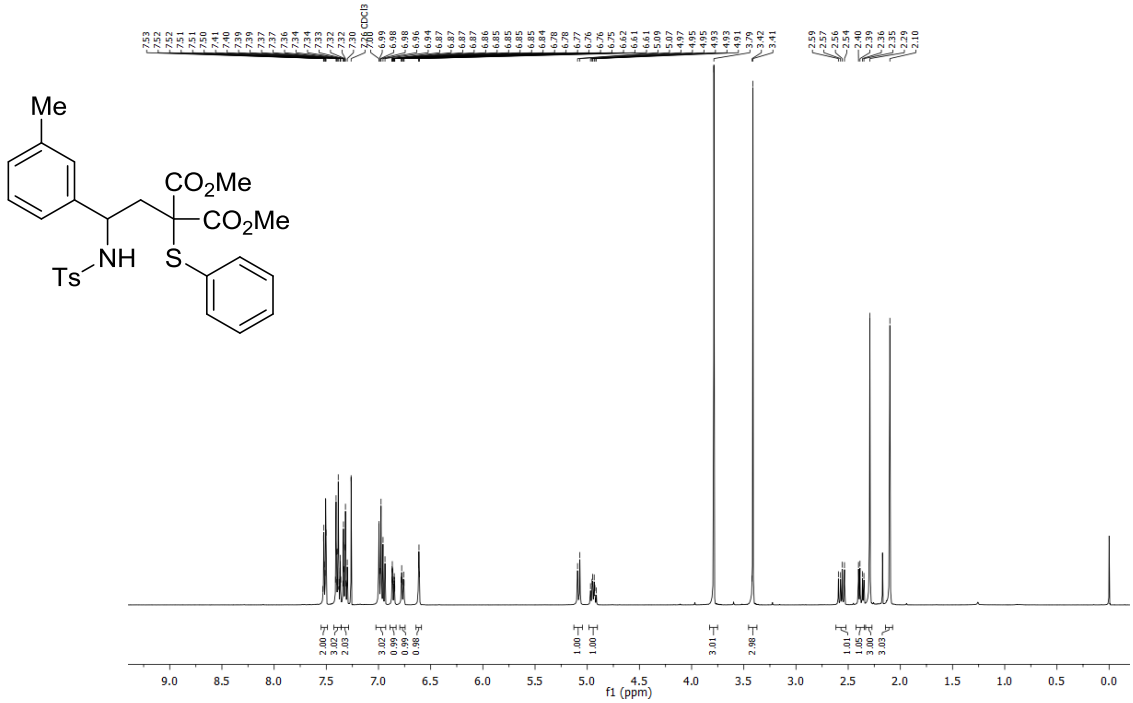


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

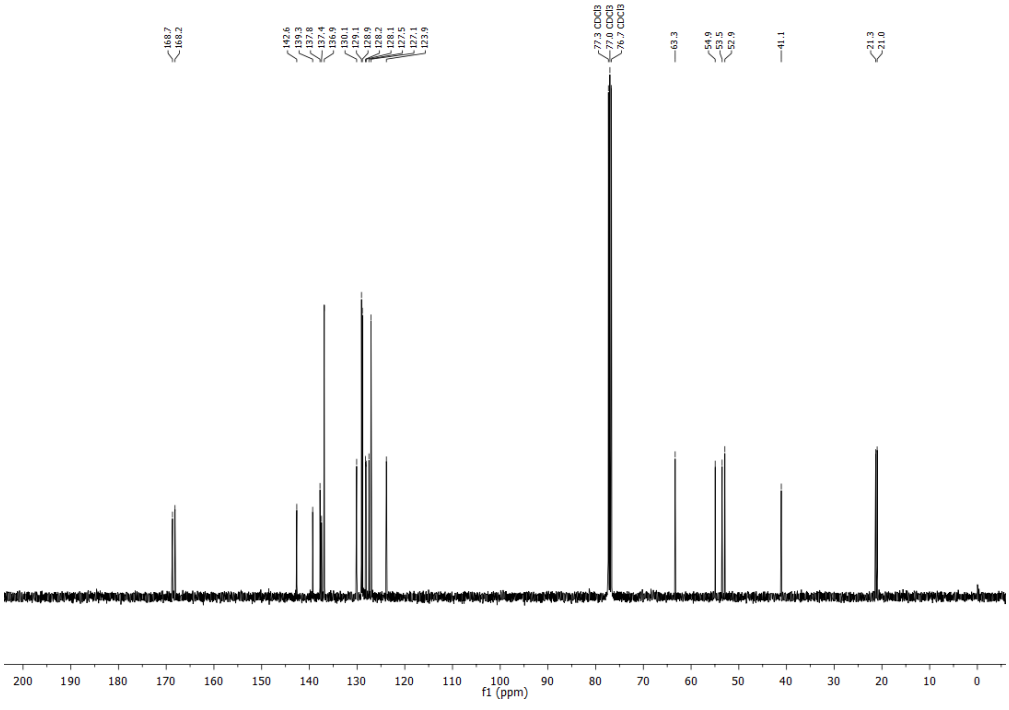


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*m*-tolyl)ethyl)-2-(phenylthio)malonate (4i)

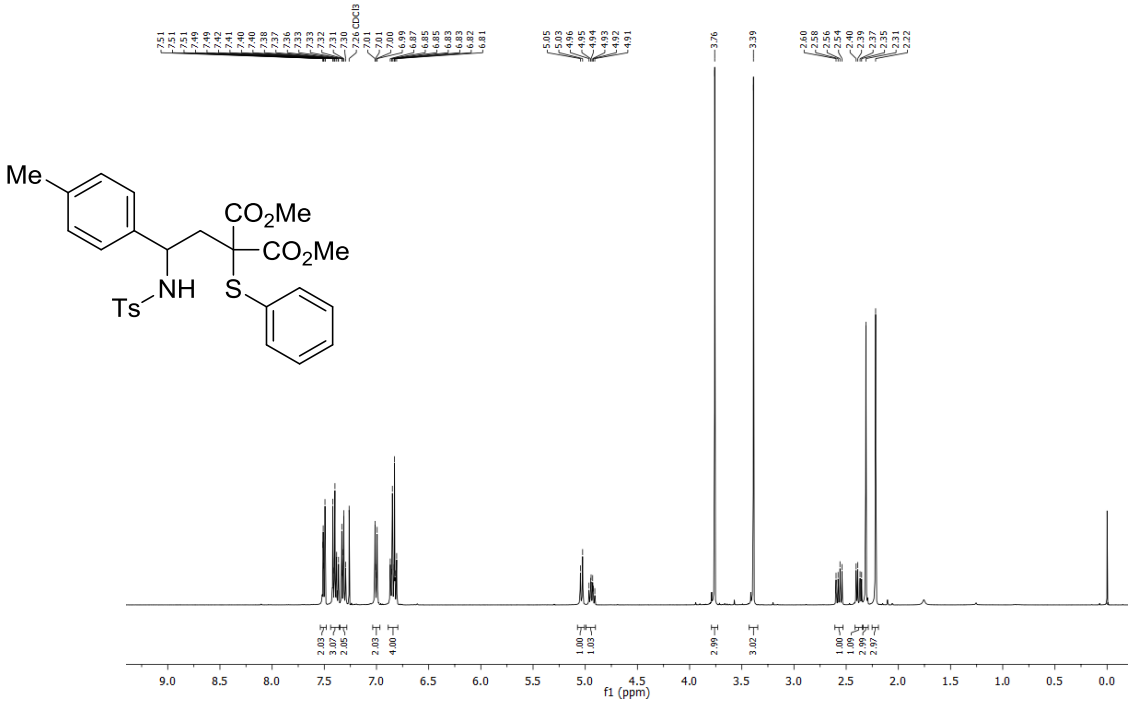


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

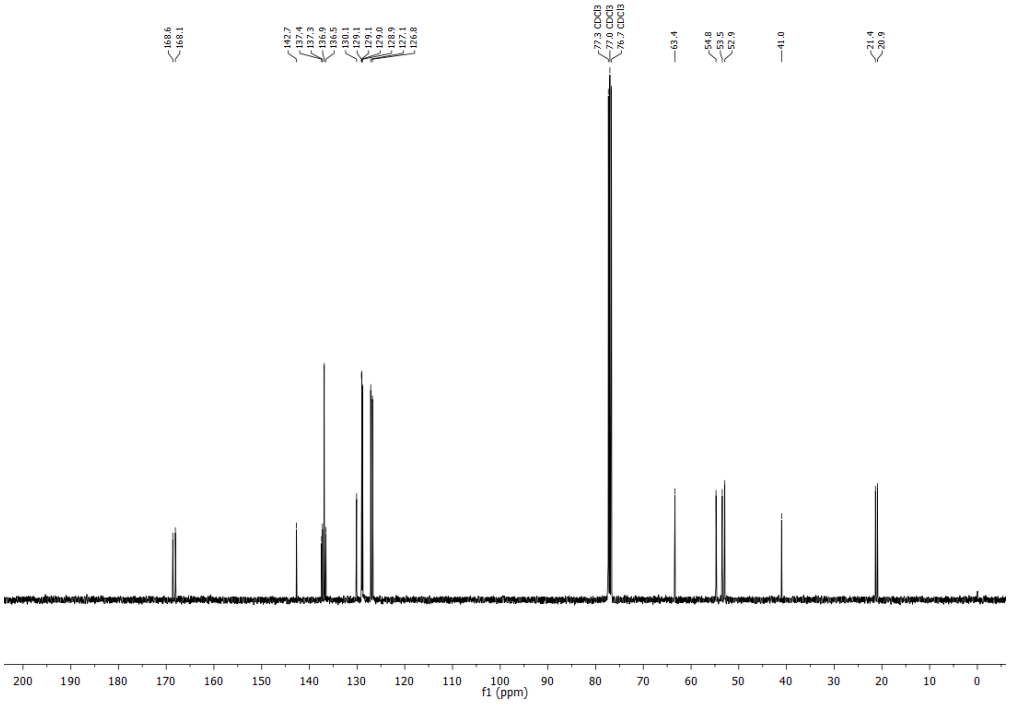


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*p*-tolyl)ethyl)-2-(phenylthio)malonate (4j)

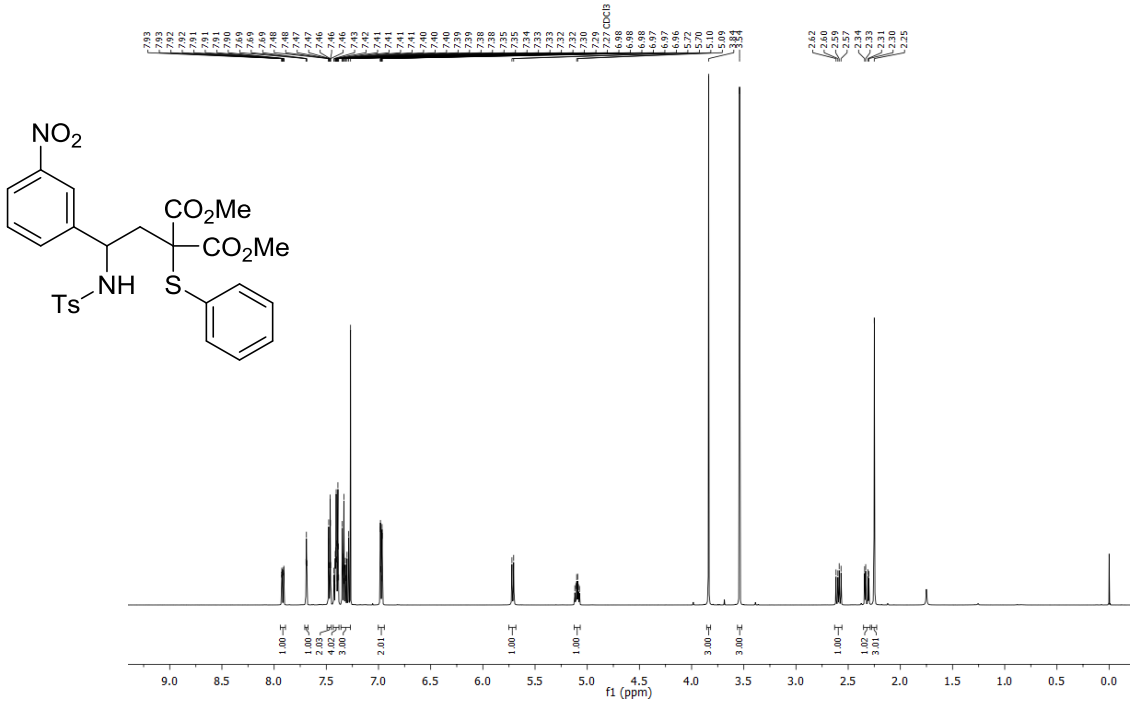


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

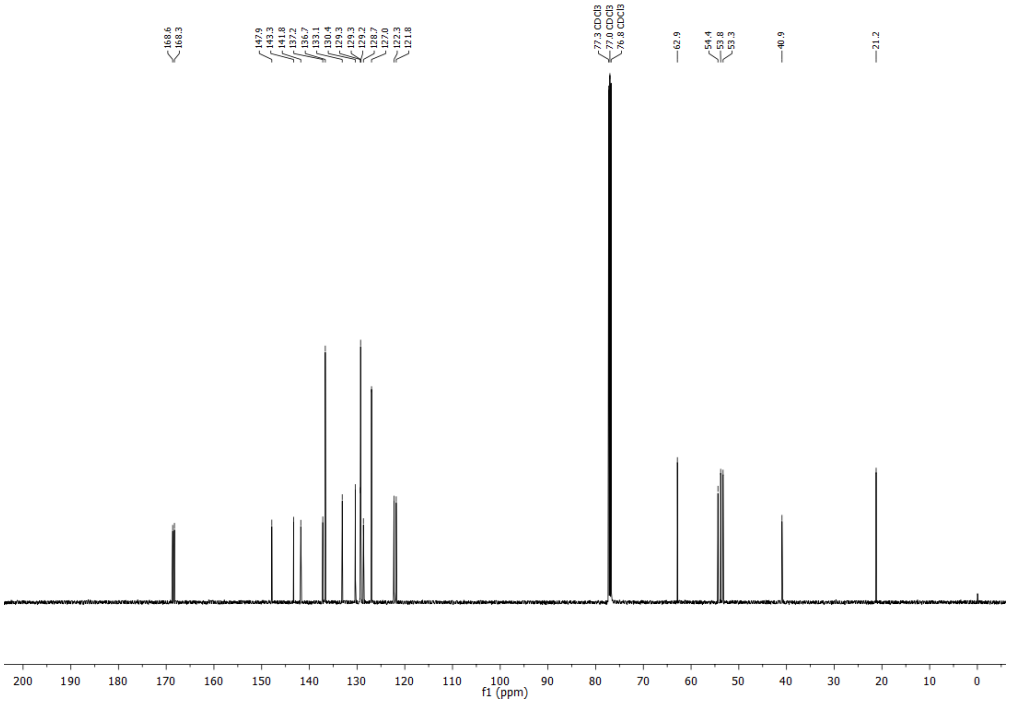


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(3-nitrophenyl)ethyl)-2-(phenylthio)malonate (4k)

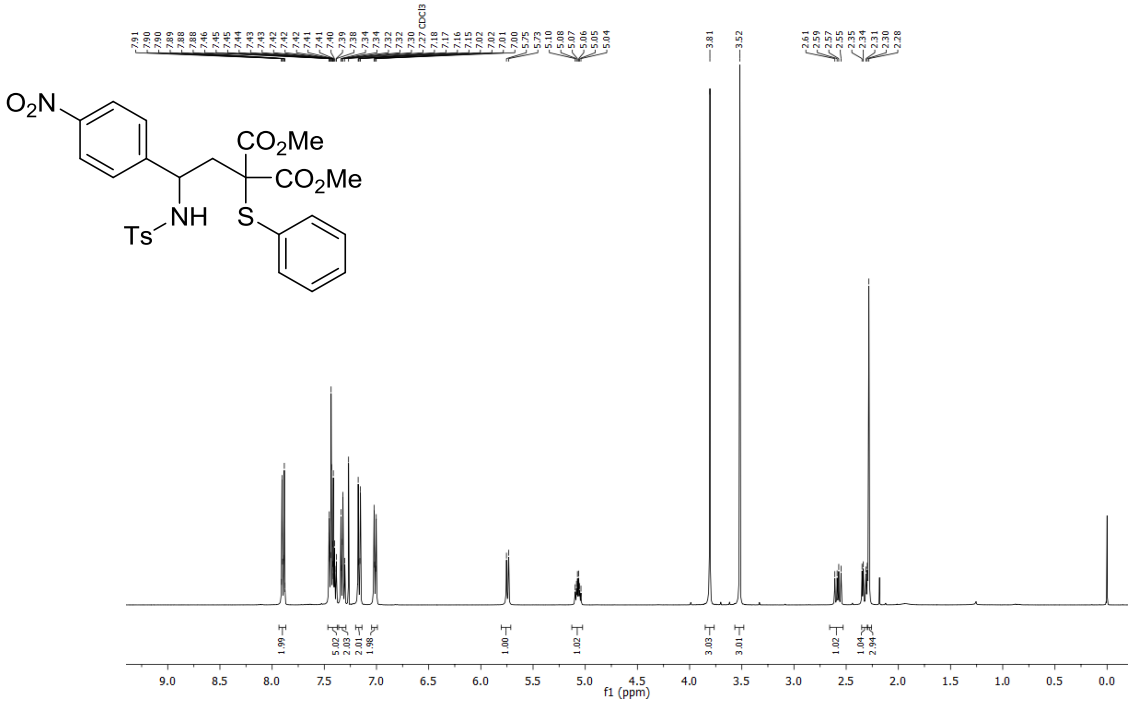


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

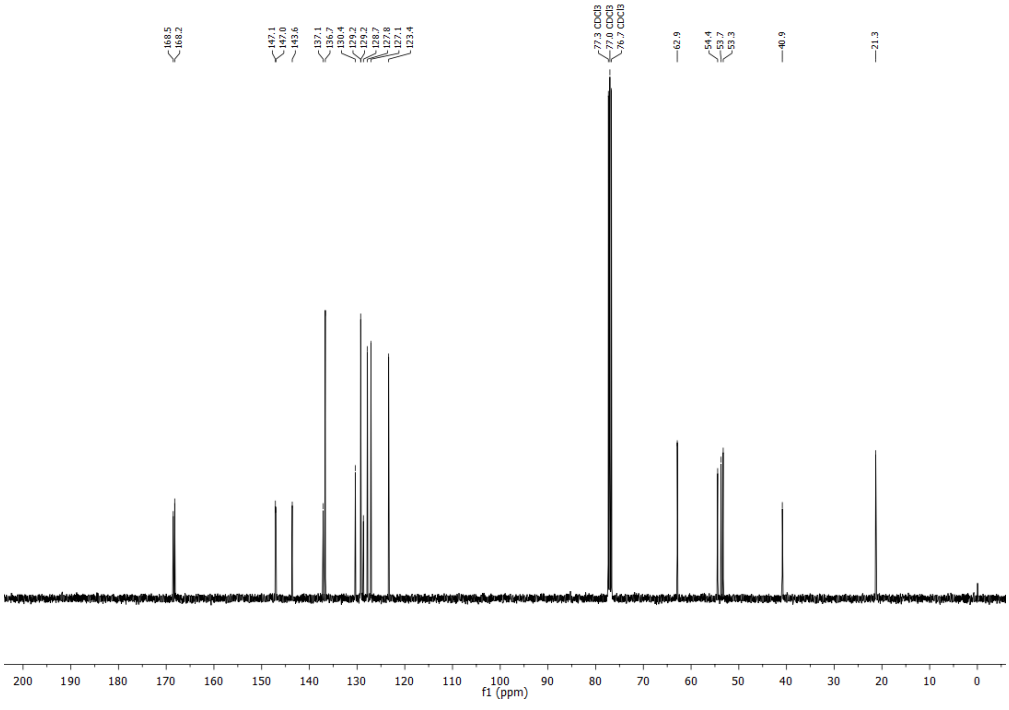


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(4-nitrophenyl)ethyl)-2-(phenylthio)malonate (4l)

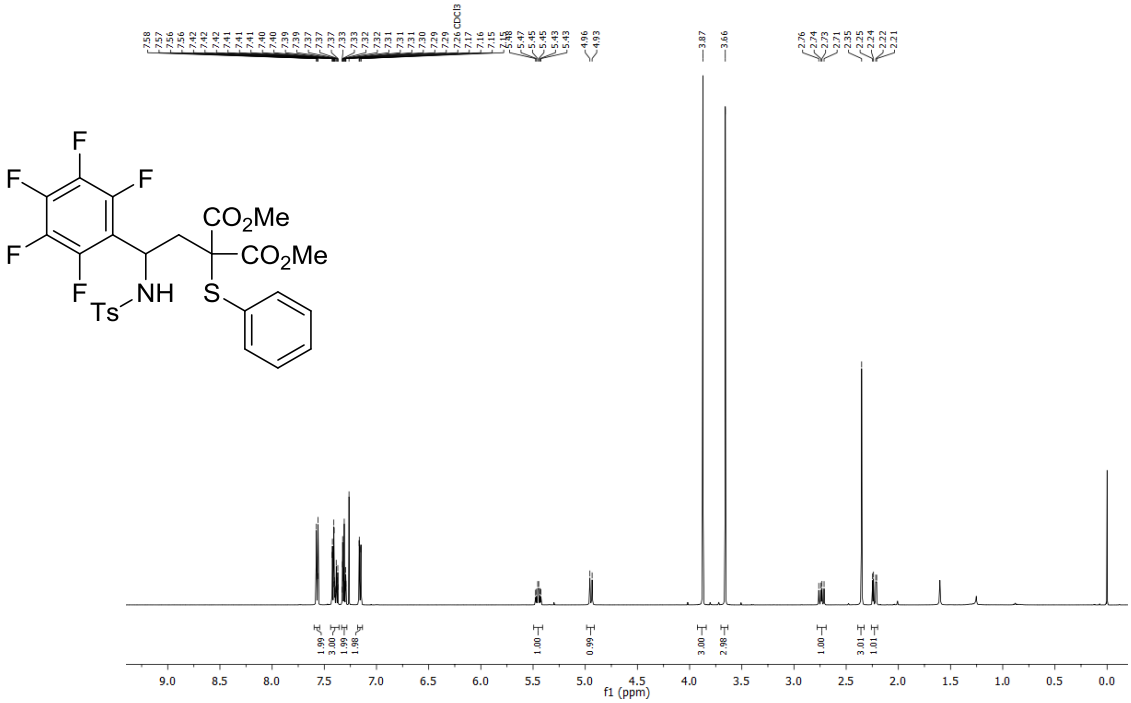


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

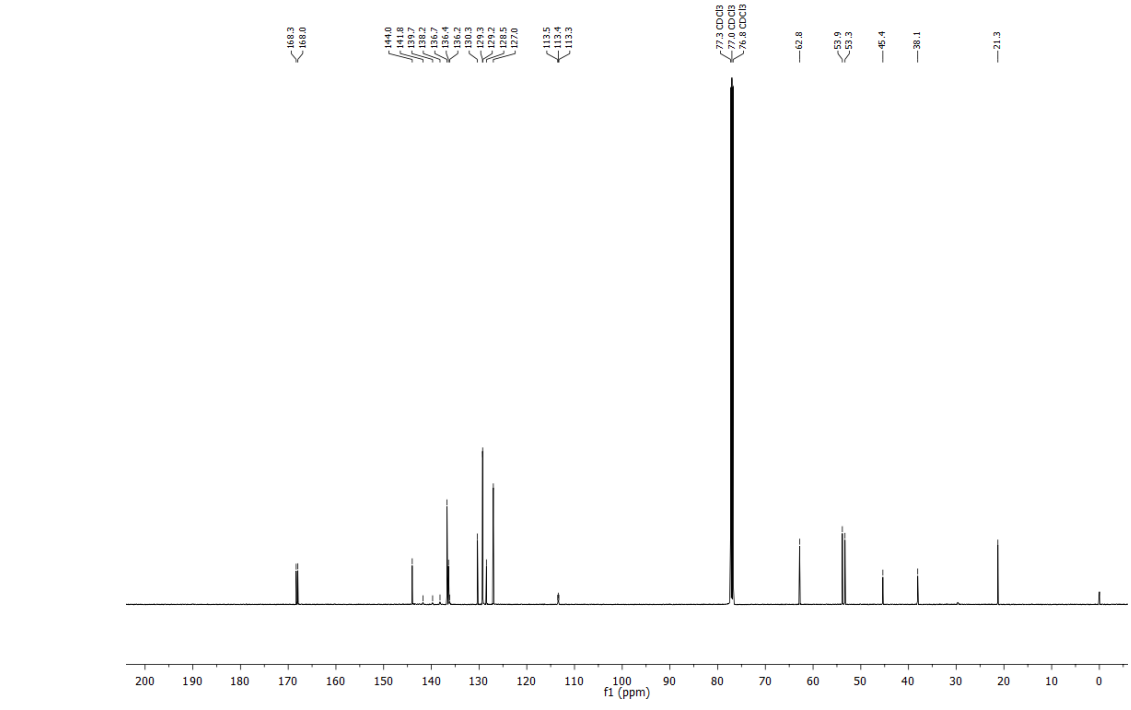


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

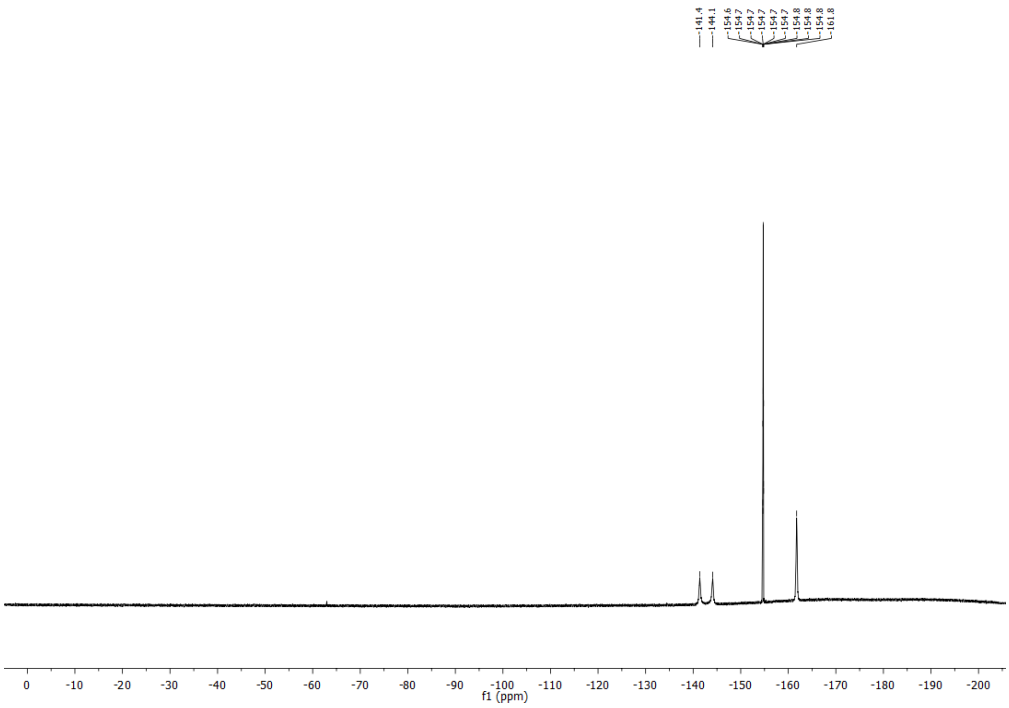
Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(perfluorophenyl)ethyl)-2-(phenylthio)malonate (4m)



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

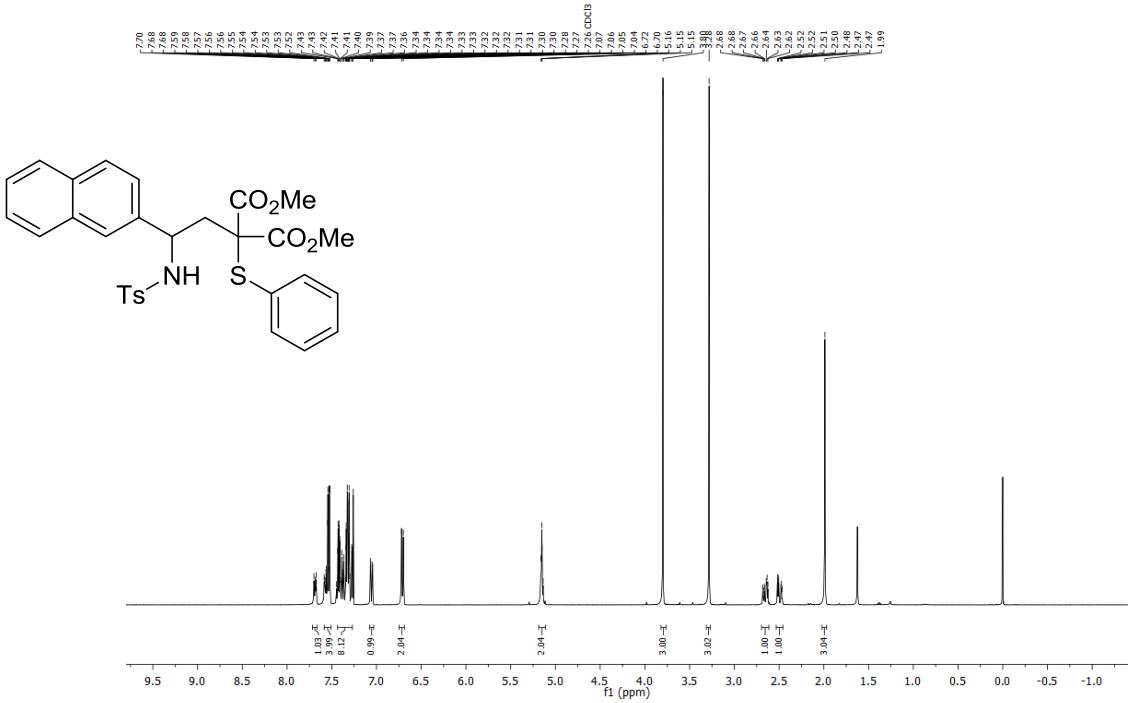


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

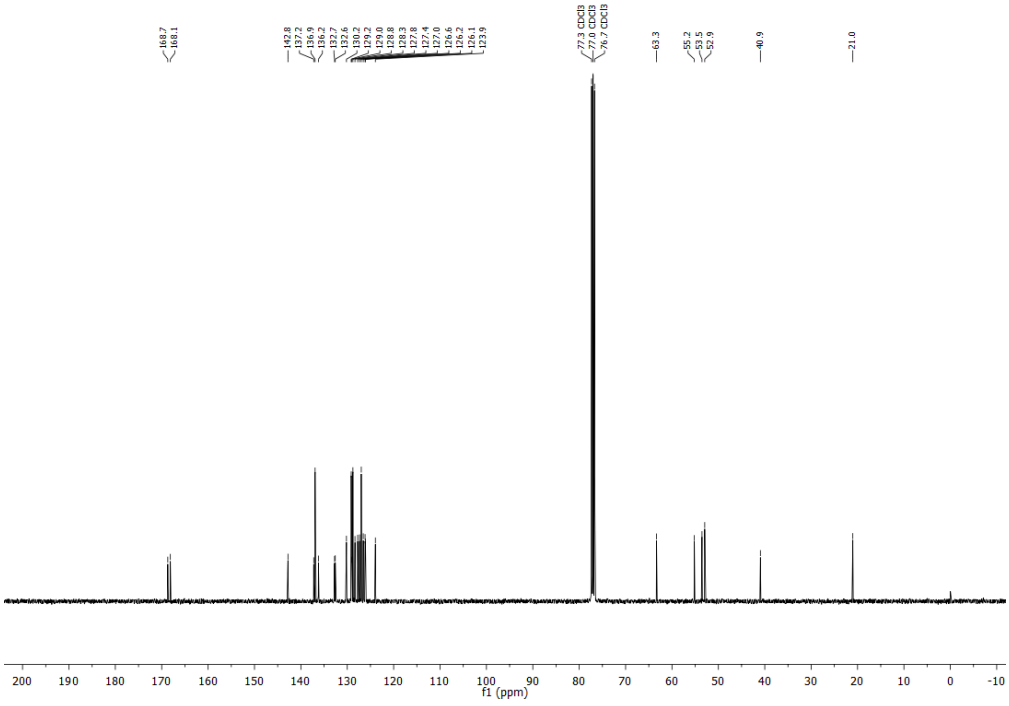


^{19}F-NMR Spectrum (283 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(naphthalene-2-yl)ethyl)-2-(phenylthio)malonate (4n)

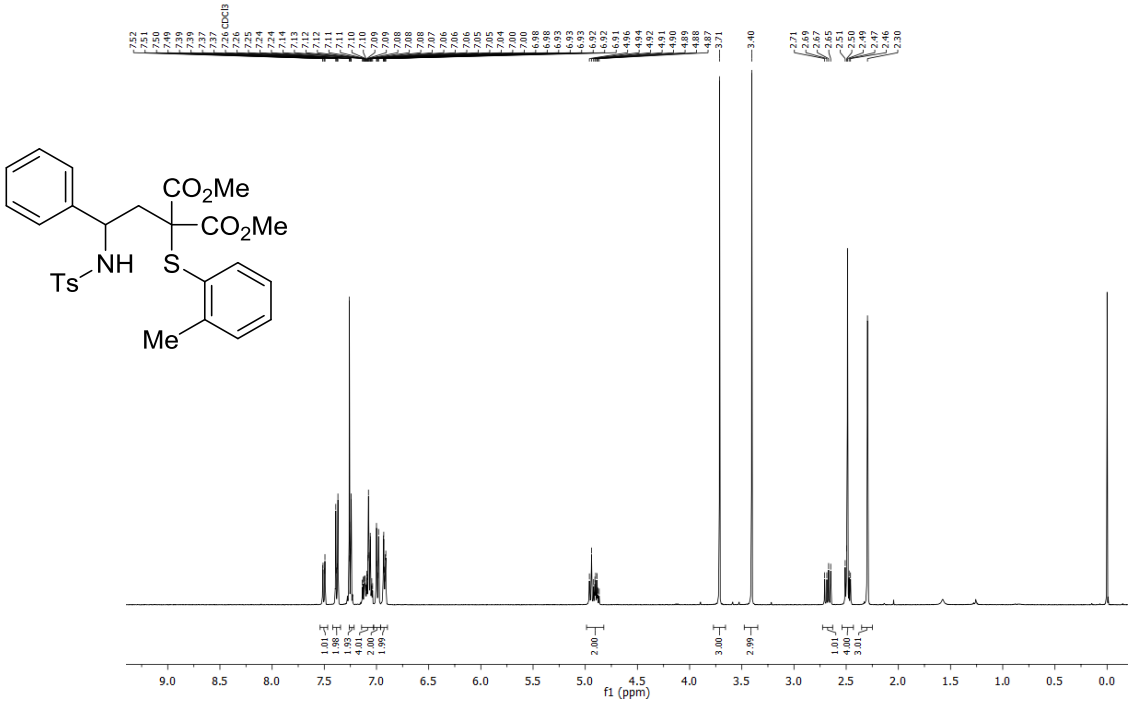


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

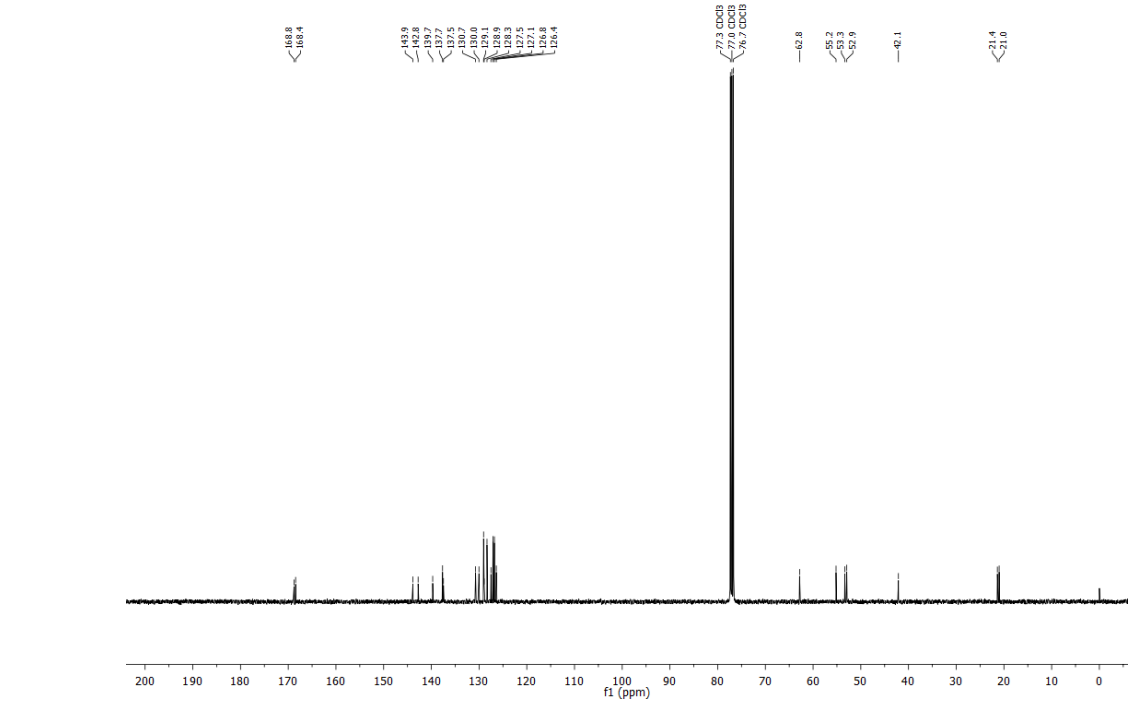


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(*o*-tolylthio)malonate (5a)

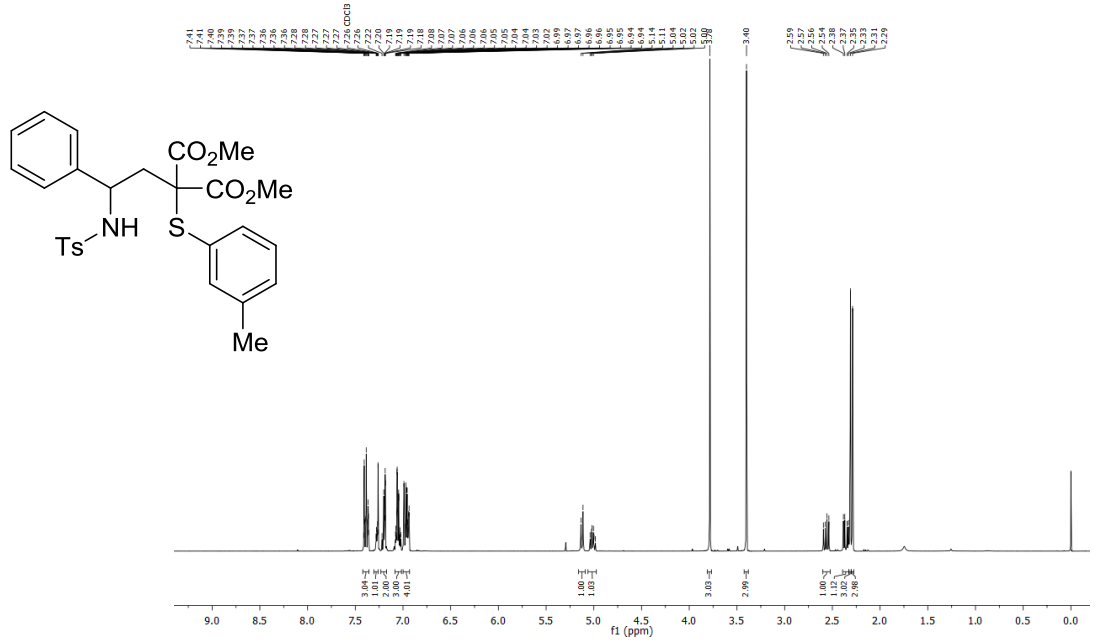


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

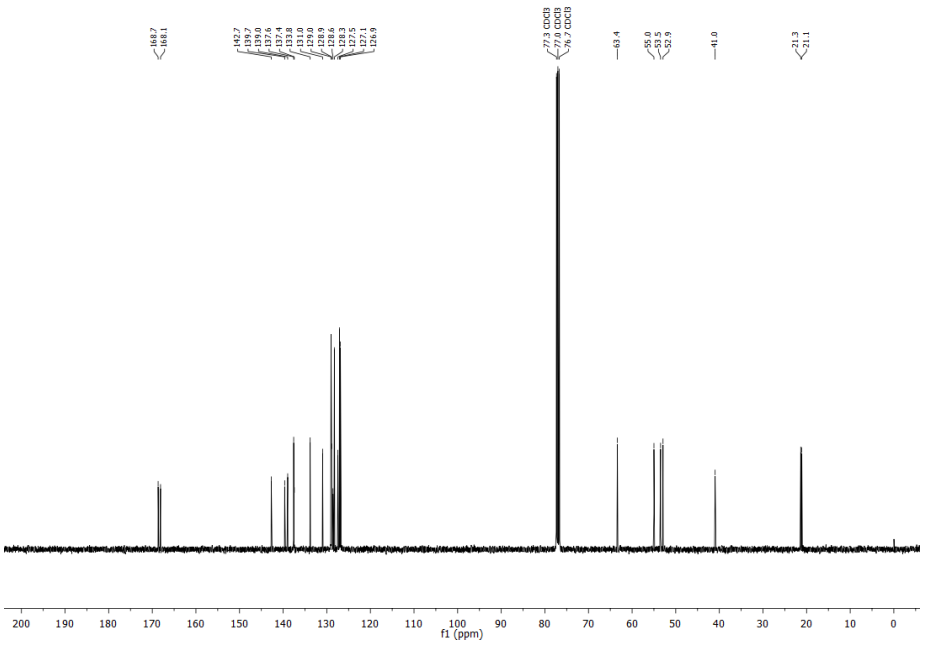


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(*o*-tolylthio)malonate (5b)

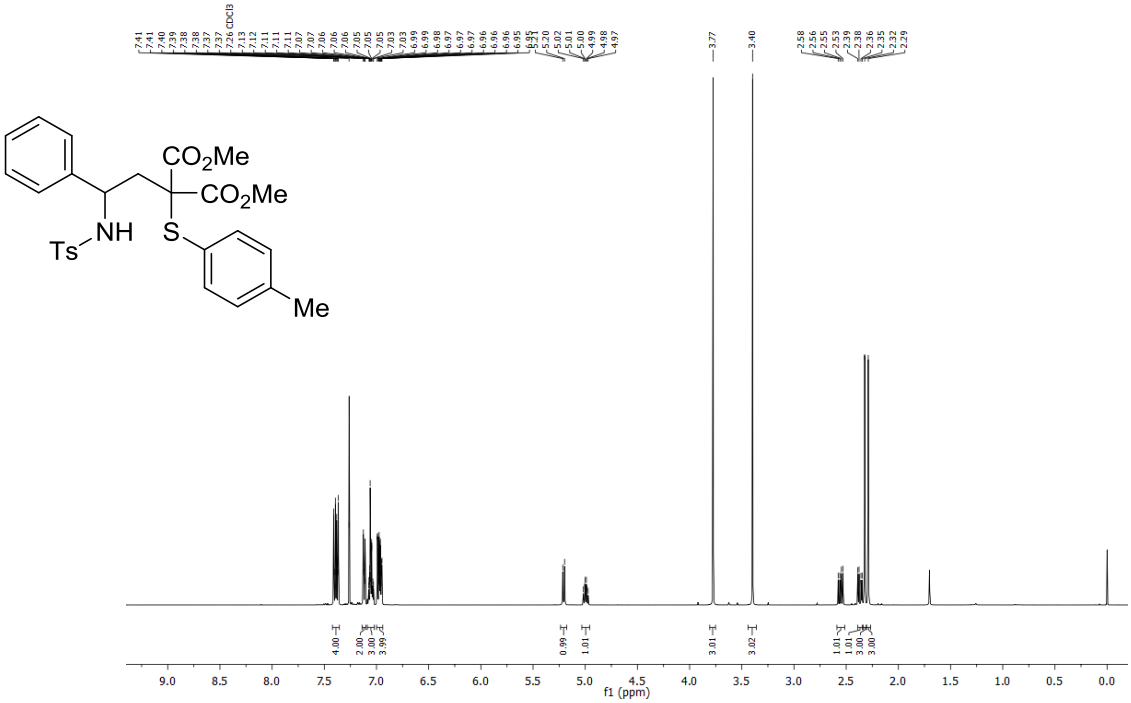


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

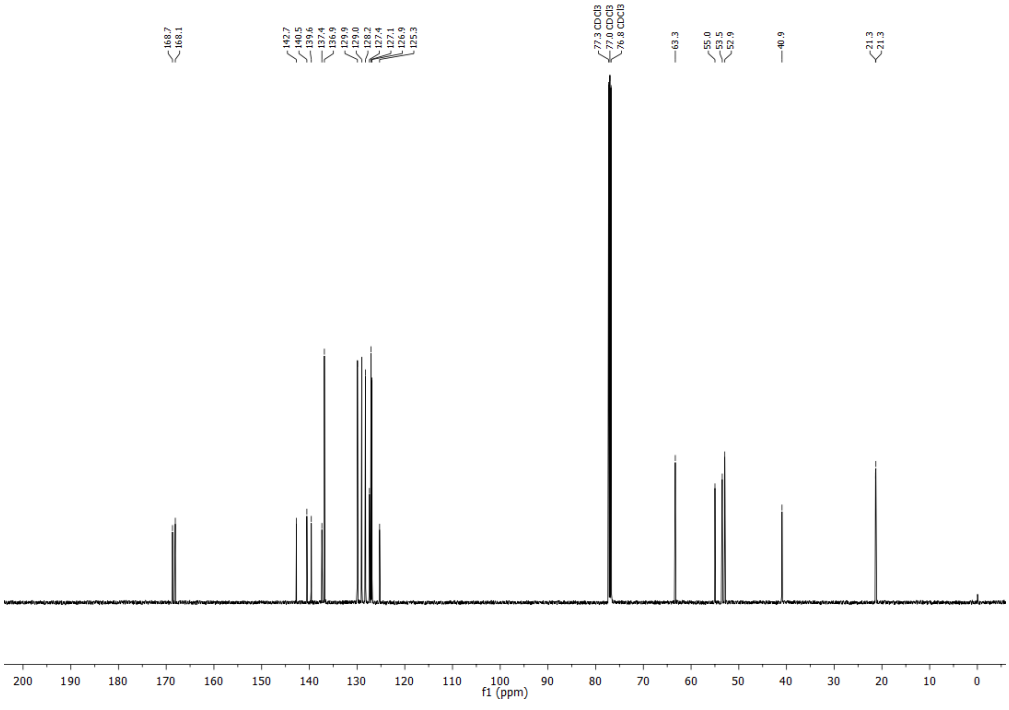


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(*p*-tolylthio)malonate (5c)

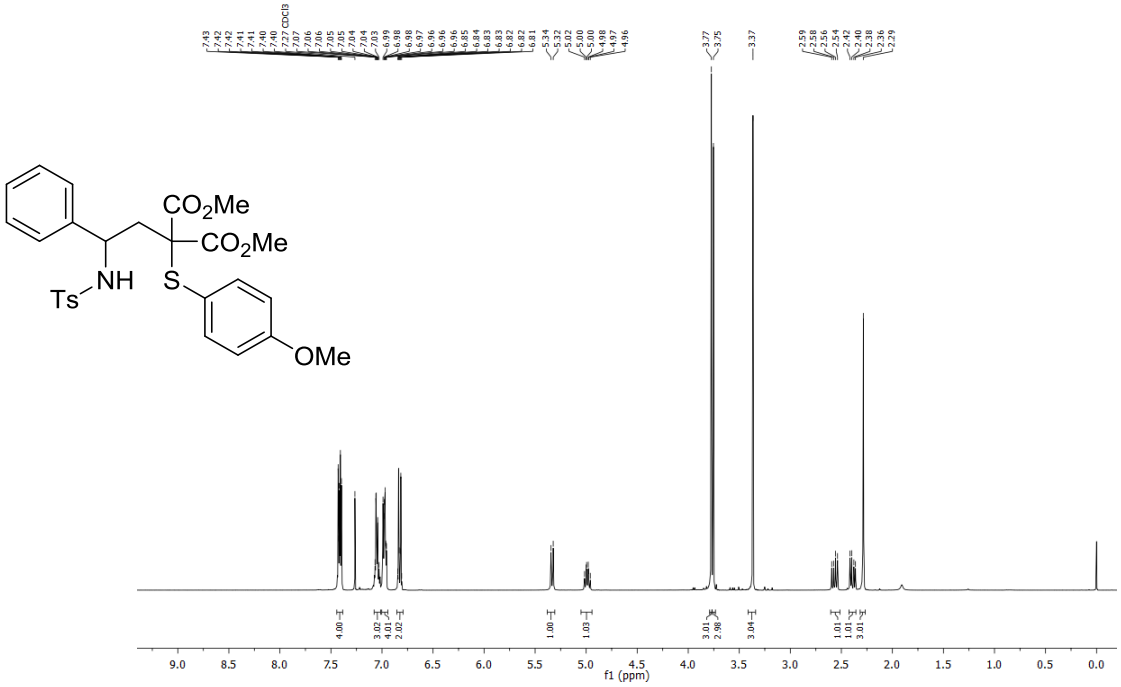


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

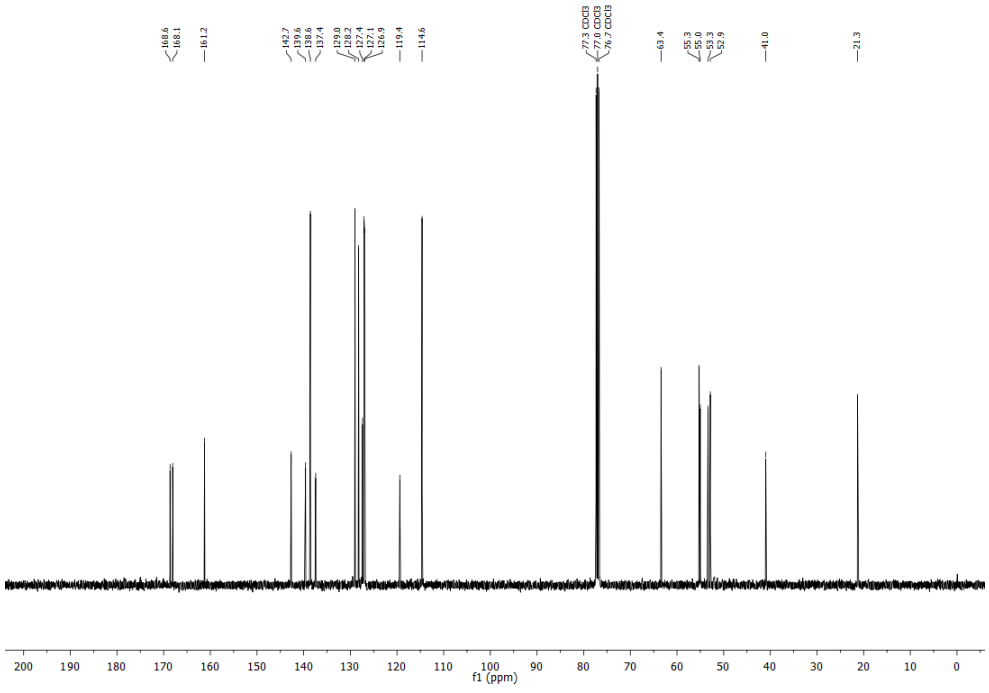


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl 2-((4-methoxyphenyl)thio)-2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)malonate (5d)

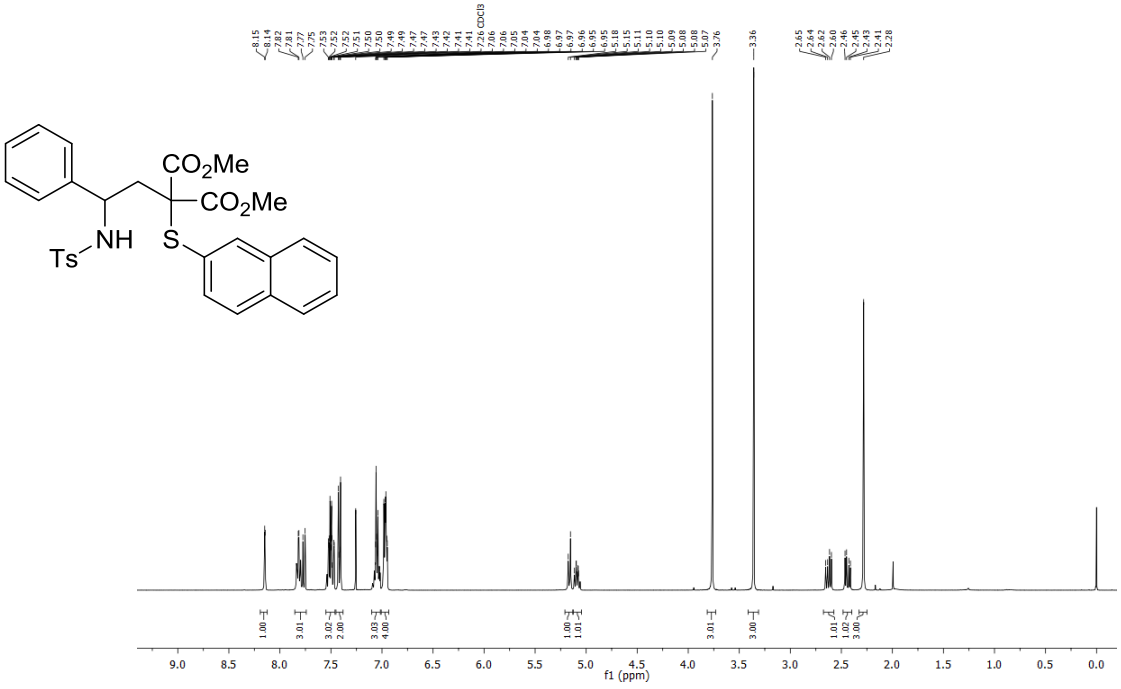


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

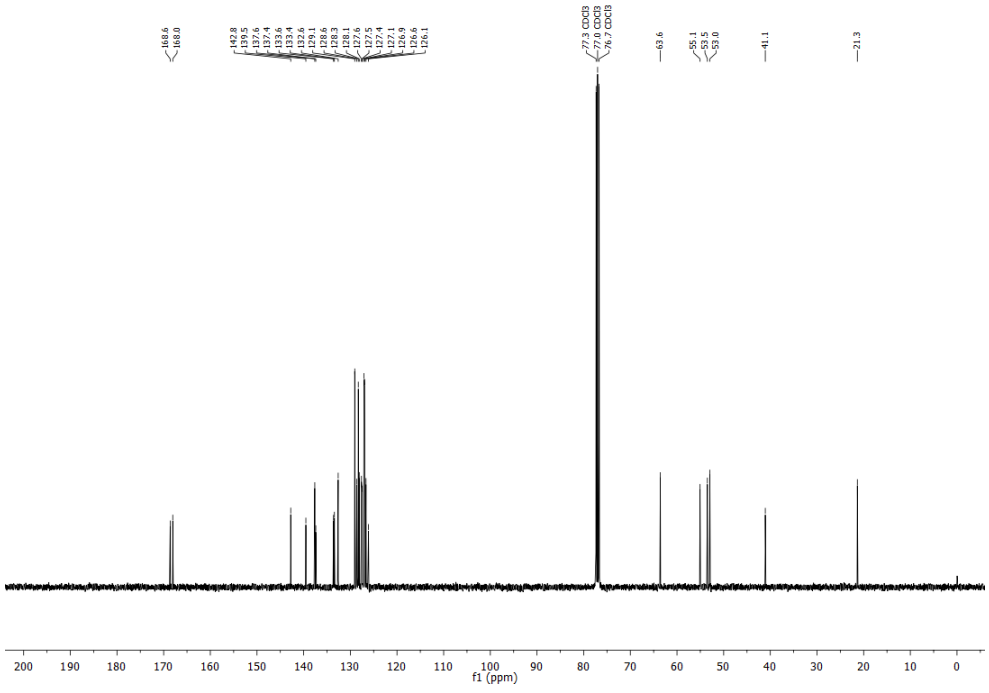


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(naphthalen-2-ylthio)malonate (5e)

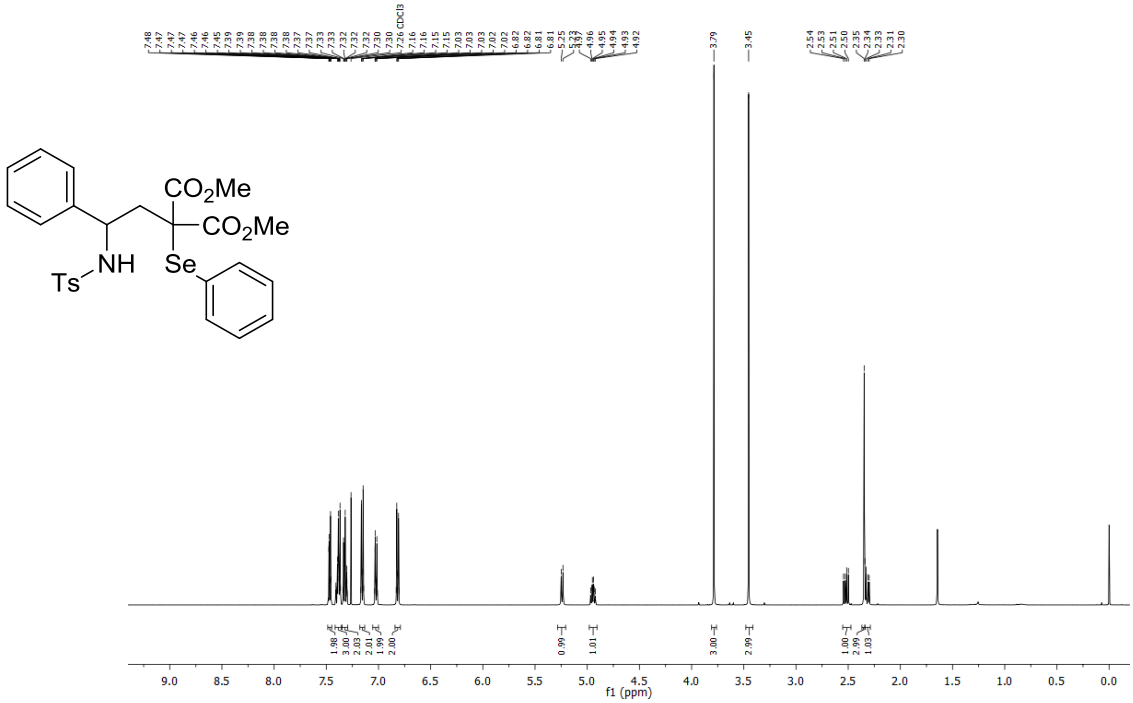


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

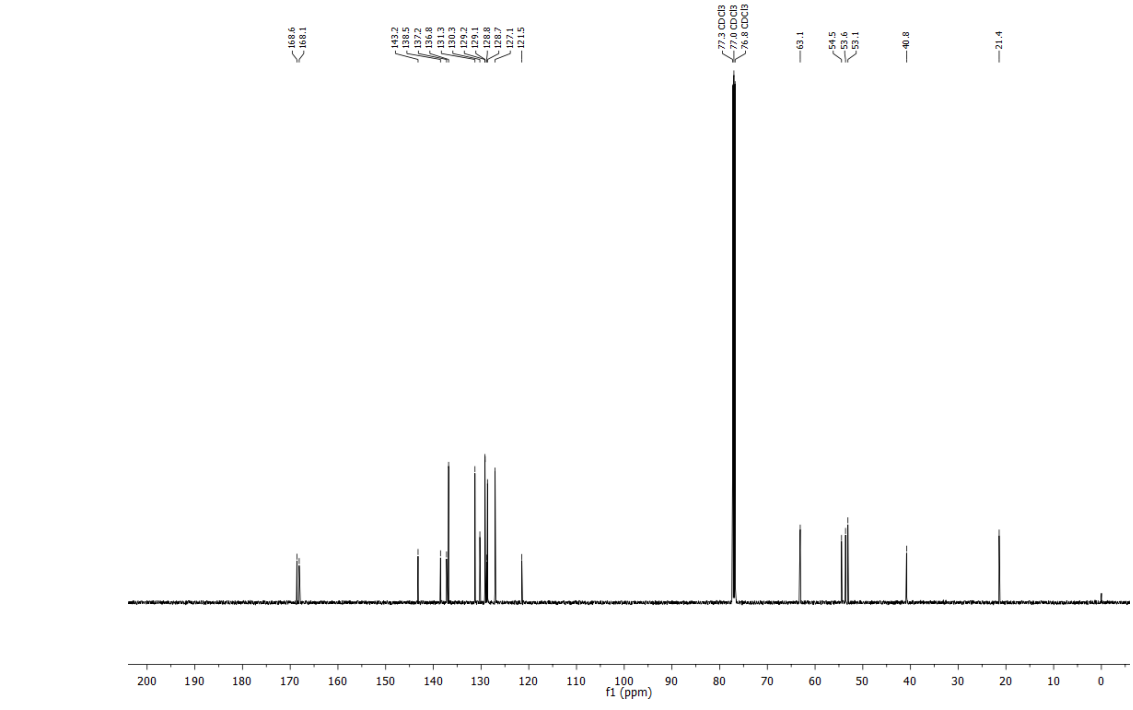


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylselanyl)malonate (7a)

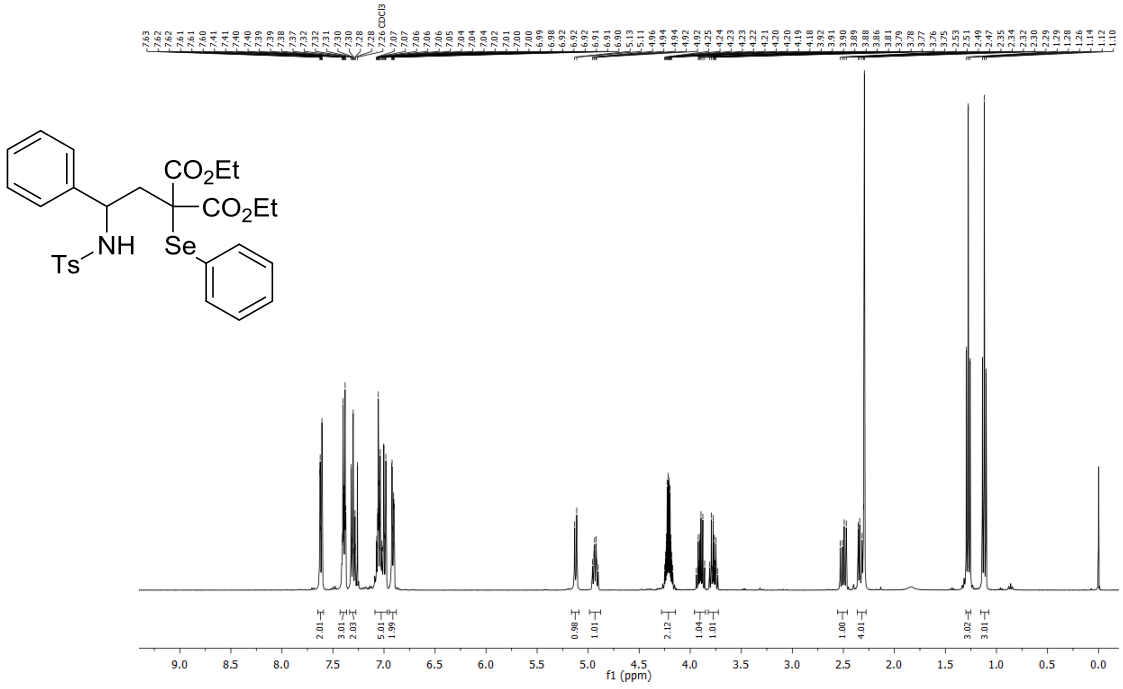


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

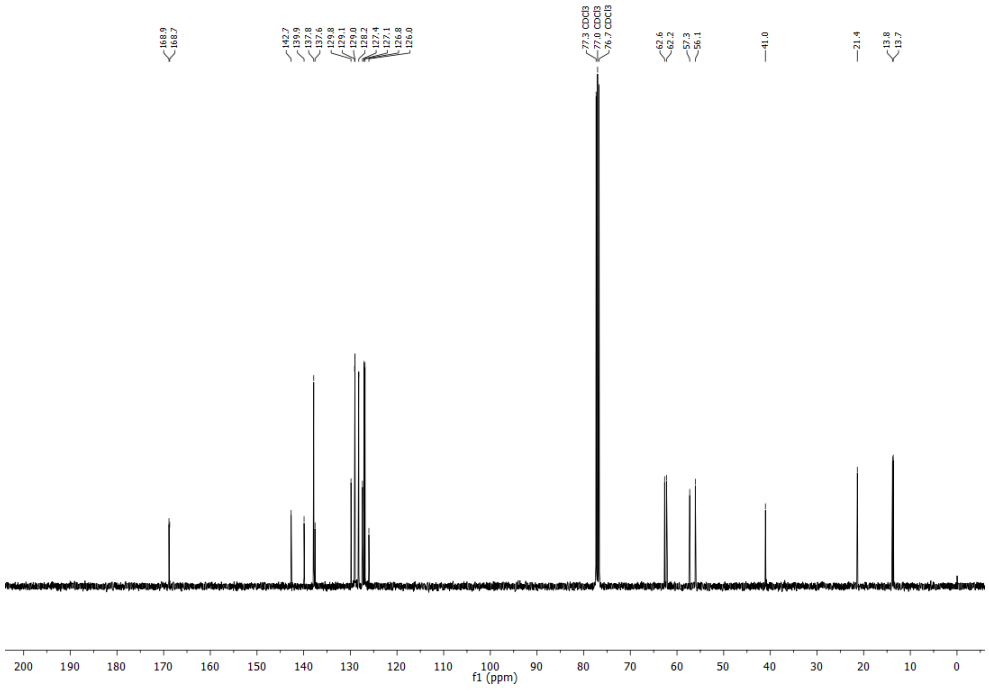


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Diethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylselanyl)malonate (7b)

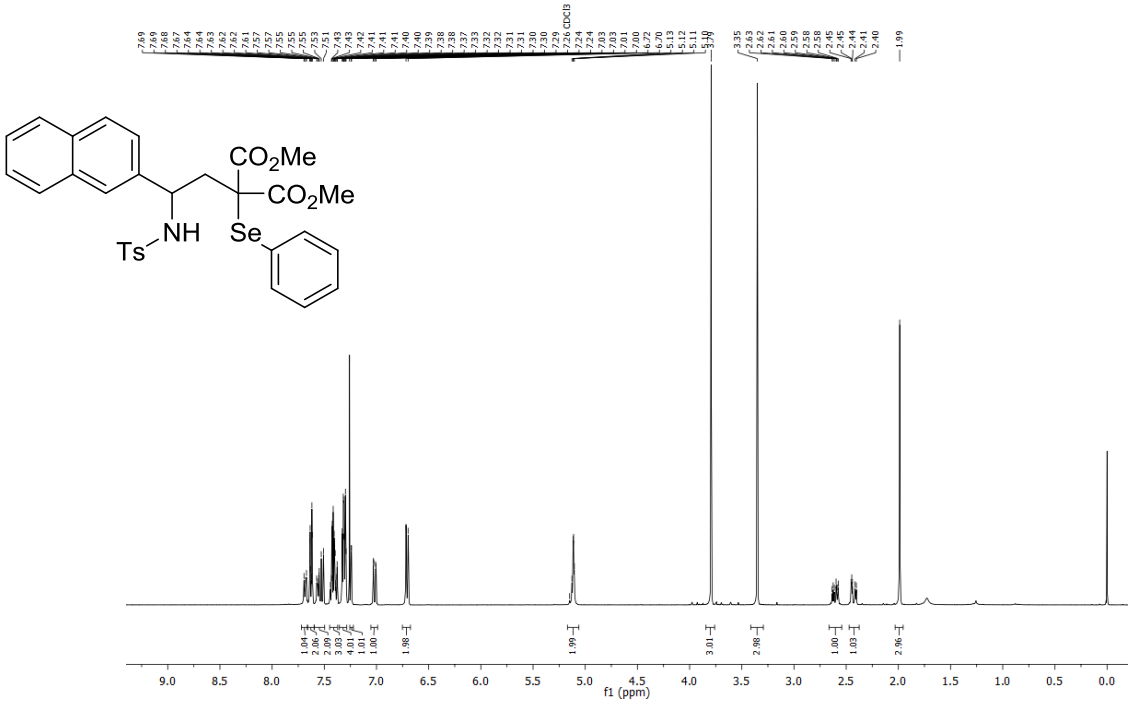


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

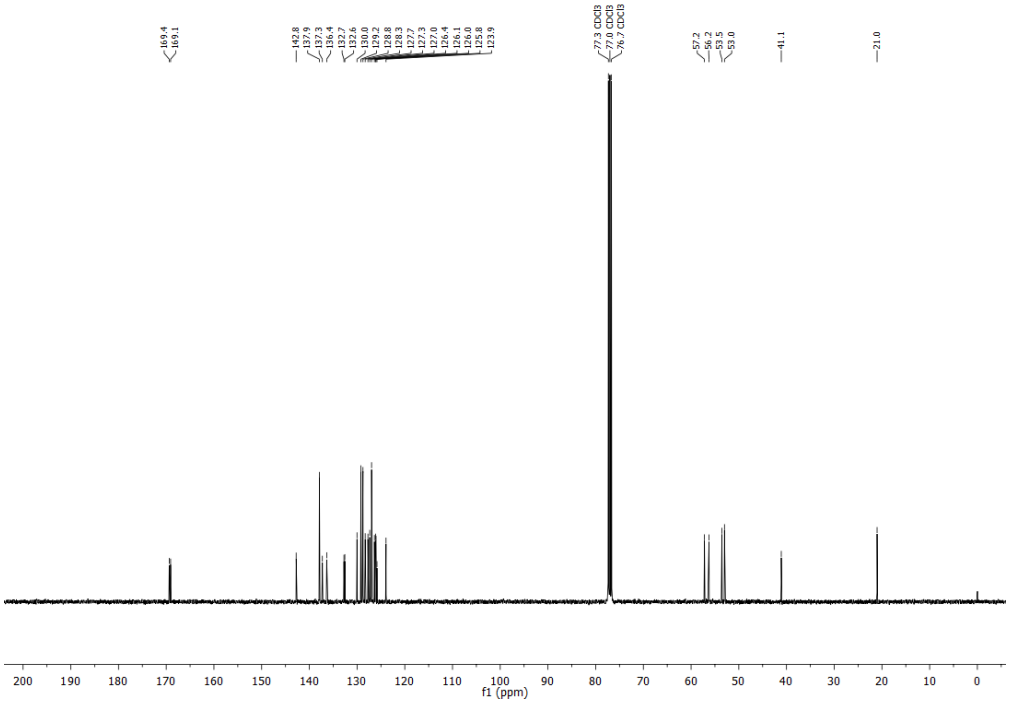


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(naphthalene-2-yl)ethyl)-2-(phenylthio)malonate (7c)

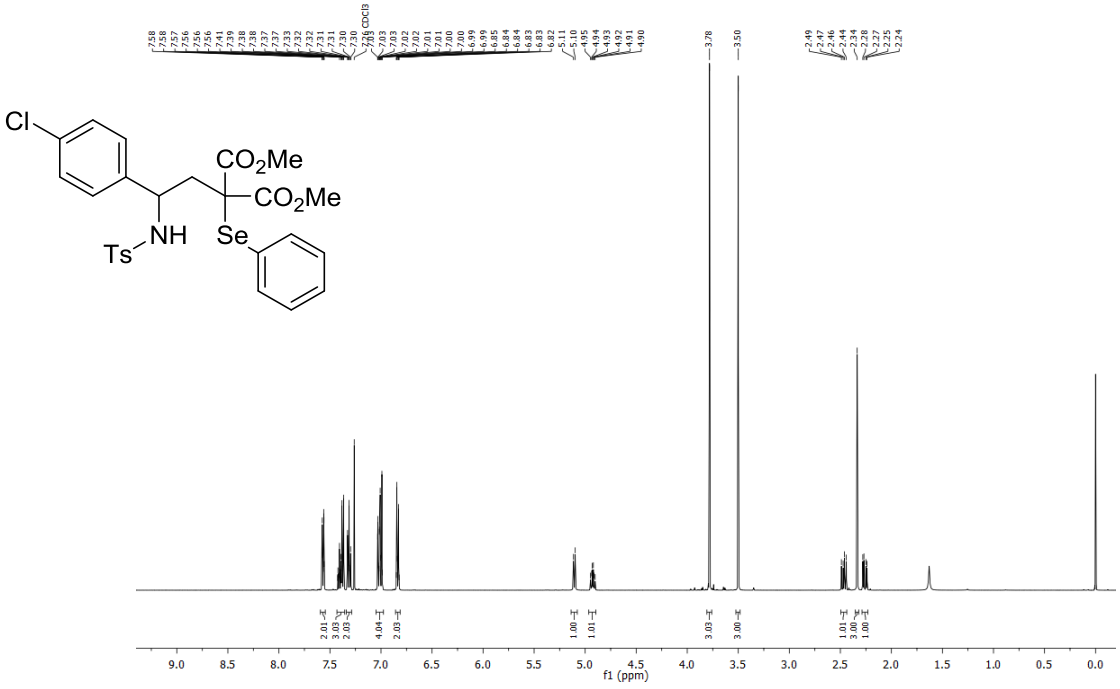


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

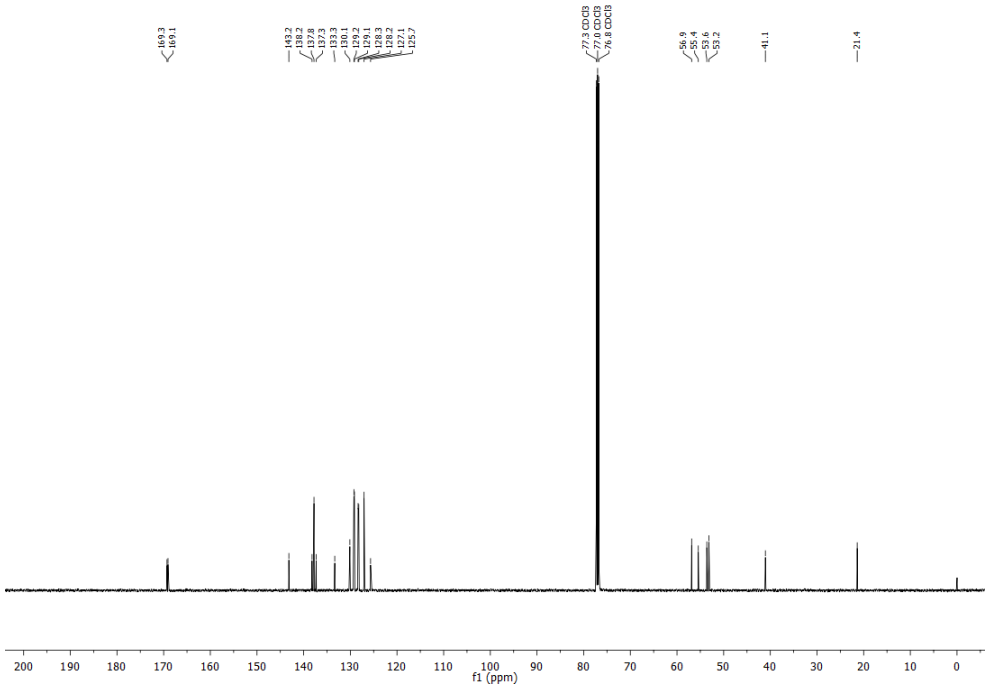


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylseleno)malonate (7d)

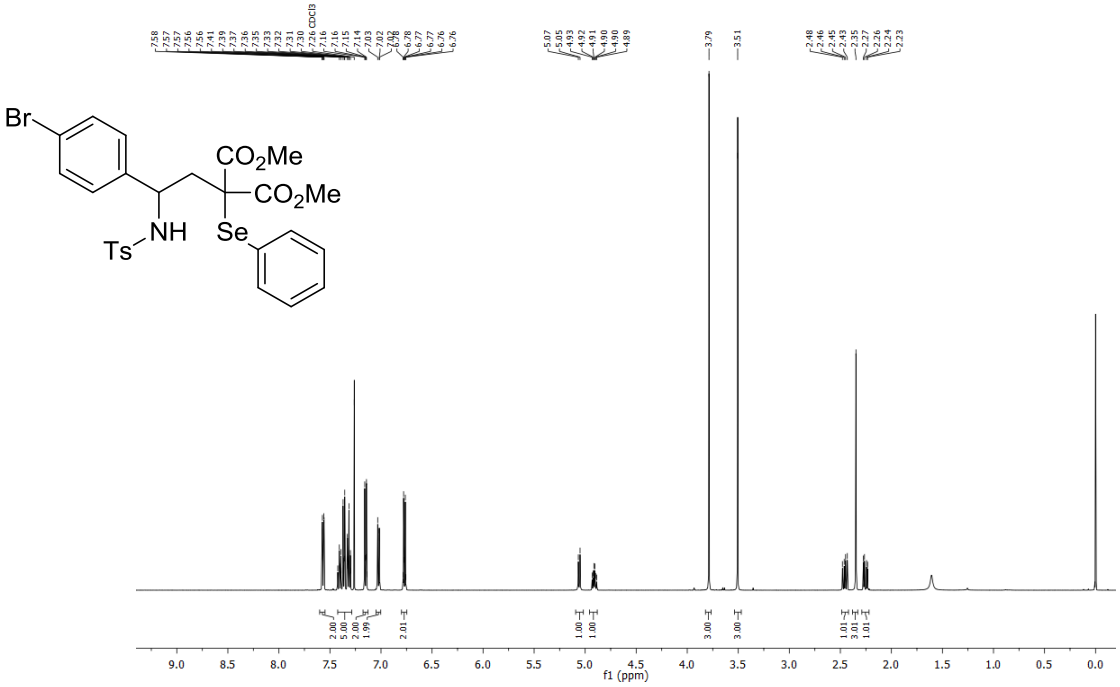


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

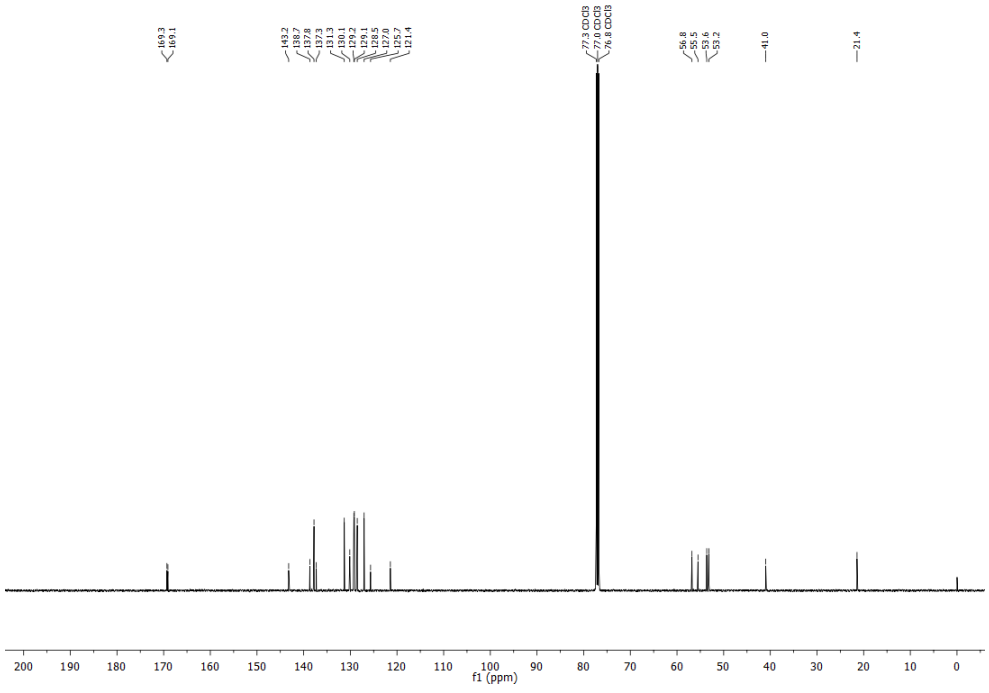


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl 2-(2-(4-bromophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylselanyl)malonate (7e)

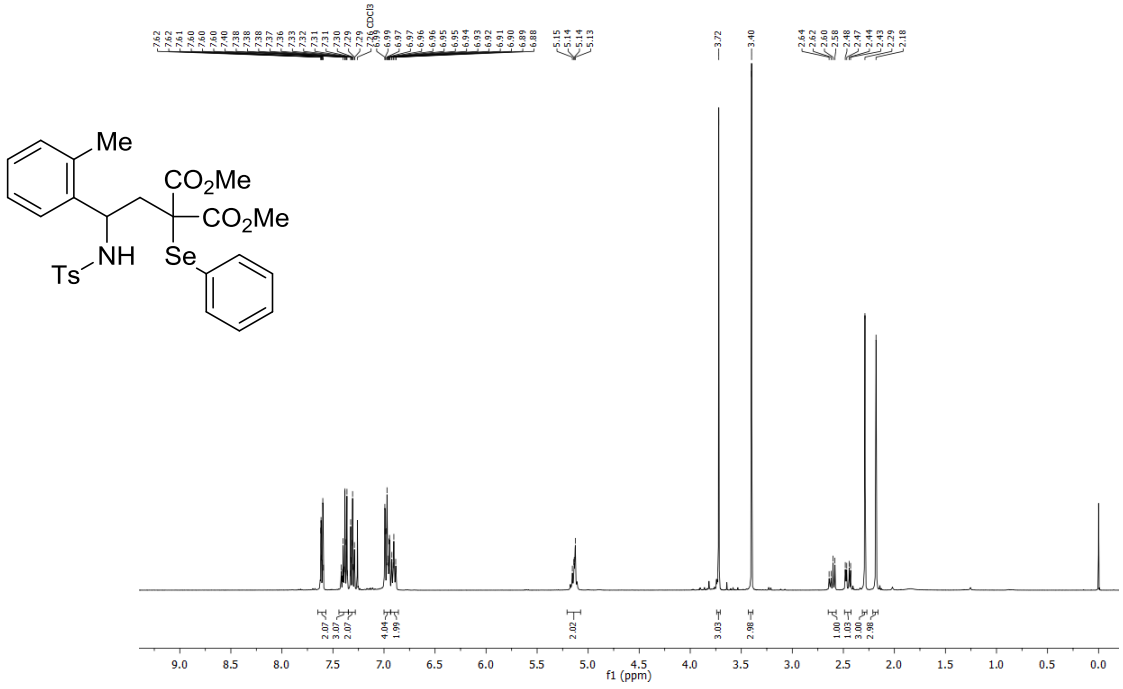


^{1}H-NMR Spectrum (500 MHz, $CDCl_3$)

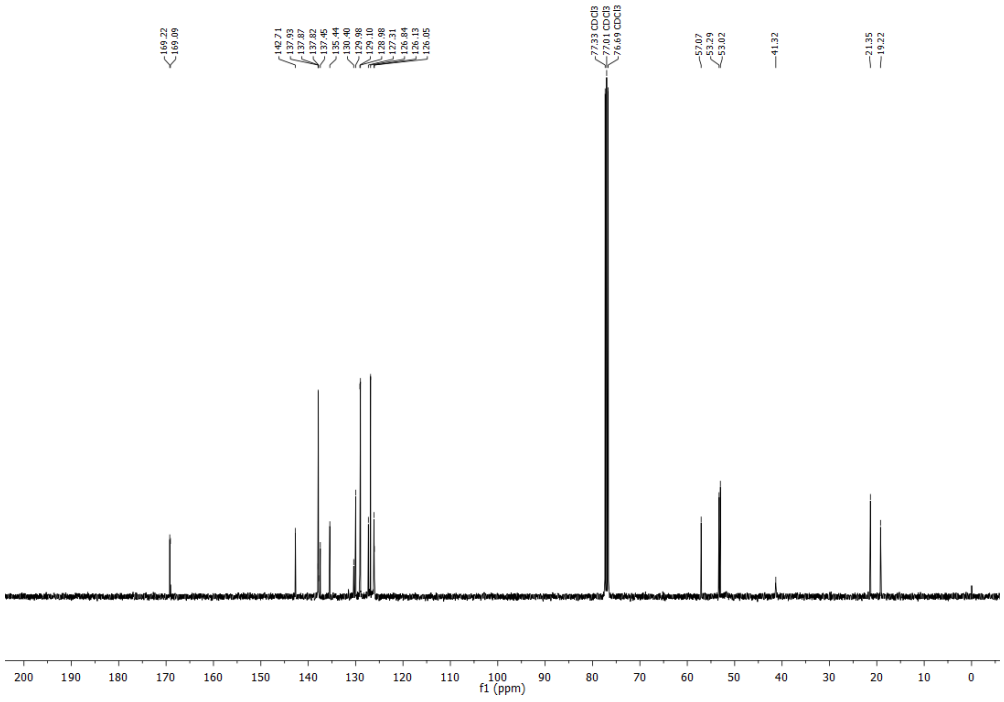


^{13}C-NMR Spectrum (126 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-(*o*-tolyl)ethyl)-2-(phenylselanyl)malonate (7f)

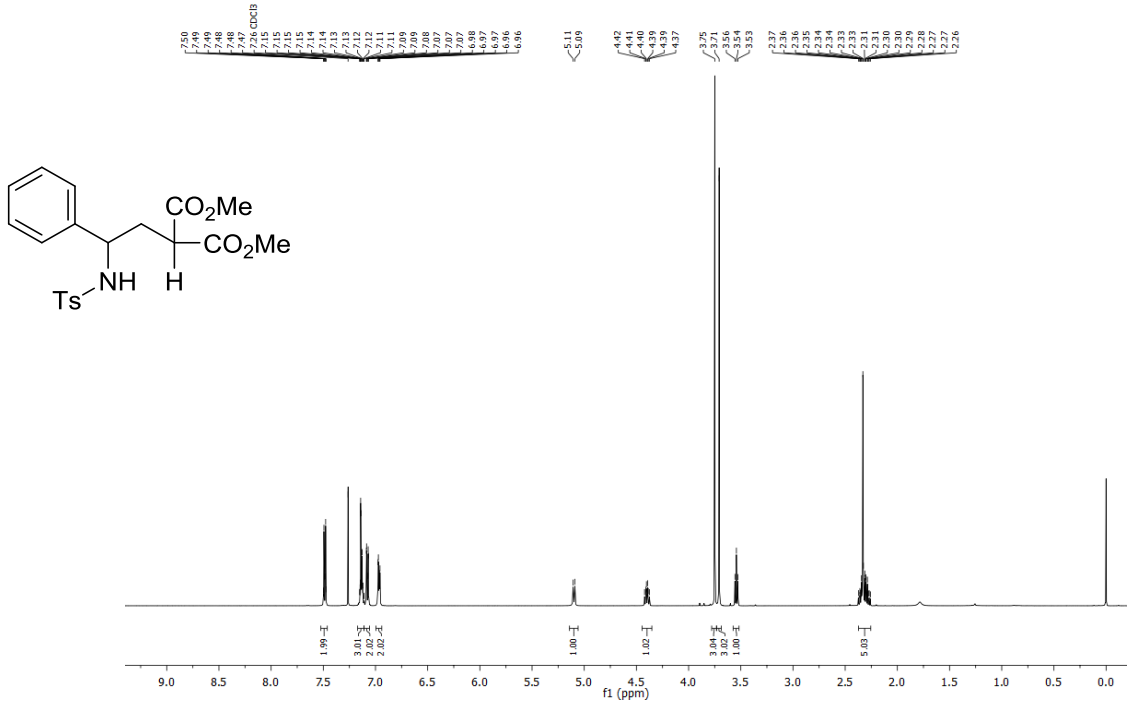


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$)

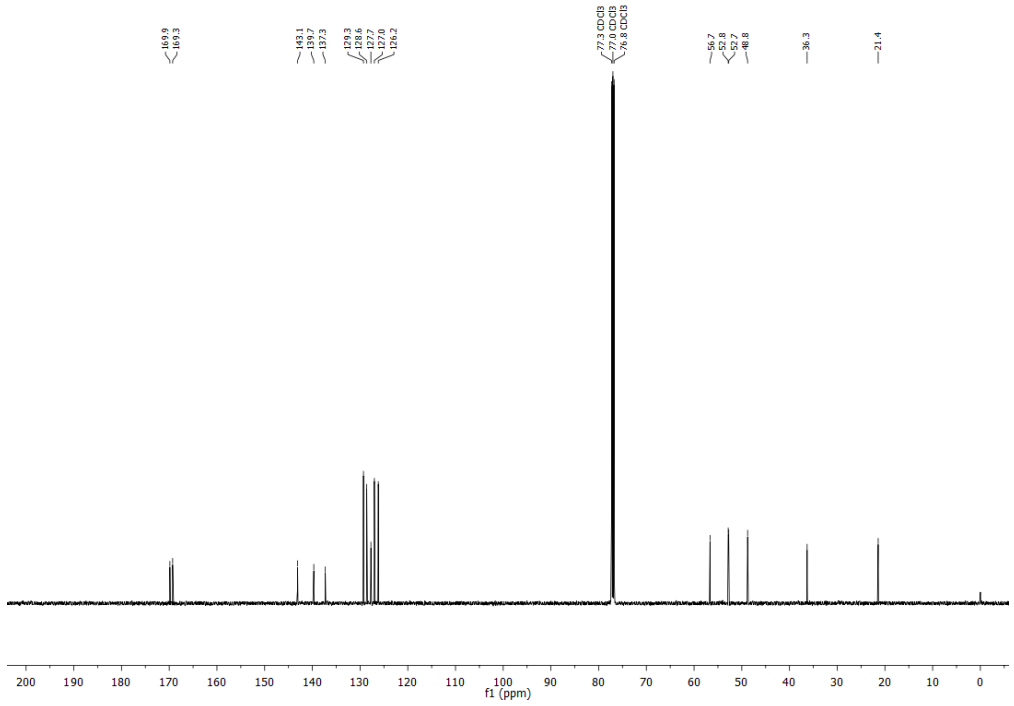


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$)

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)malonate (8)



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



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

7) Crystal Structure Determinations

Numeric data are summarized in Table 1. Crystals were mounted in inert oil on a glass fibre (**4a**) or a plastic ring mount (**7d**) and transferred to the cold gas stream of the diffractometer (Oxford Diffraction Xcalibur E with monochromated Mo Kα radiation for **4a**, Rigaku/Oxford XtaLAB Synergy with mirror-focussed Mo Kα radiation for **7b**). Absorption corrections were implemented on the basis of multi-scans. The structures were refined anisotropically on F^2 using the program SHELXL-97 [5] for **4a** and SHELXL-2017 [6] for **7d**. NH hydrogens were refined freely. Other hydrogens were refined using rigid idealized methyl groups allowed to rotate but not tip, or a riding model starting from calculated positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-1915047 (**4a**) and -1915048 (**7d**). Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Exceptions and special features. Compound **4a**: The compound crystallizes as a deuteriochloroform solvate; the $CDCl_3$ molecule is well-ordered. The maxima at the methyl carbon C20 were indistinct and a model of a rigid hexagon of half-occupied hydrogens ("AFIX 127") was used instead of the standard methyl group ("AFIX 137"); this model should however be interpreted with caution. Compound **7d**: The crystals lose solvent rapidly on exposure to the air. A region of significant residual electron density around an inversion centre was interpreted as disordered *n*-pentane, but no satisfactory refinement was achieved. For this reason the routine SQUEEZE (part of the PLATON suite [7]) was employed to remove mathematically the effects of the solvent. For calculating the molecular mass and related parameters, the solvent content per cell was assumed to be two pentane molecules (i.e. the compound is a ¼-solvate). Two significant peaks (just over 1 electron per cubic Angstrom) near C6 and C11 were related arithmetically to the coordinates of the selenium atoms and are probably the result of an unidentified minor twinning component.

Table 1: Crystallographic data and structure refinement.

Compound	**4a·CDCl$_3$**	**7d·¼C$_5$H$_{12}$**
Formula	$C_{27}H_{27}DCl_3NO_6S_2$	$C_{27.25}H_{29}ClNO_6SSe$
M_r	633.98	612.98
Cryst. size (mm^3)	0.35 x 0.30 x 0.20	0.30 x 0.20 x 0.20
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
Temperature (°C)	-173	-173
a (Å)	14.4394(4)	7.91721(12)
b (Å)	27.2581(7)	27.5321(4)
c (Å)	8.05640(17)	26.0203(15)
α (°)	90	90
β (°)	105.285(3)	90.8639(14)
γ (°)	90	90
V (Å^3)	3058.76(13)	5671.19(15)
Z	4	8
D_x (Mg/m^{-3})	1.377	1.436
λ (Å)	0.71073	0.71073
μ (mm^{-1})	0.48	1.53
Transmissions	0.938 – 1.000	0.881 – 1.000
F(000)	1312	2516
$2\theta_{max}$	61.3	63
Refl. measured	144295	302394
Refl. indep.	9063	18332
R_{int}	0.049	0.054
Parameters	359	663
wR(F^2, all refl.)	0.0879	0.0911
R(*F*, >4σ(*F*))	0.0368	0.0354
S	1.05	1.02
max. Δ*p* (e Å^{-3})	0.63	1.4

Dimethyl 2-(2-((4-methylphenyl)sulfonamido)-2-phenylethyl)-2-(phenylthio)malonate (4a)

Fig. S1 shows the structure of the chloroform solvate of compound **4a**; ellipsoids correspond to 50% probability levels. Note the hydrogen bond from the chloroform hydrogen to O3 (H···O 2.35 Å).

Figure S2 shows the molecular packing of **4a**; the molecules are linked by a classical hydrogen bond from the NH group to O6, via the *c* glide plane, to form spiral chains parallel to the *c* axis at *y* ≈ ¼, ¾.

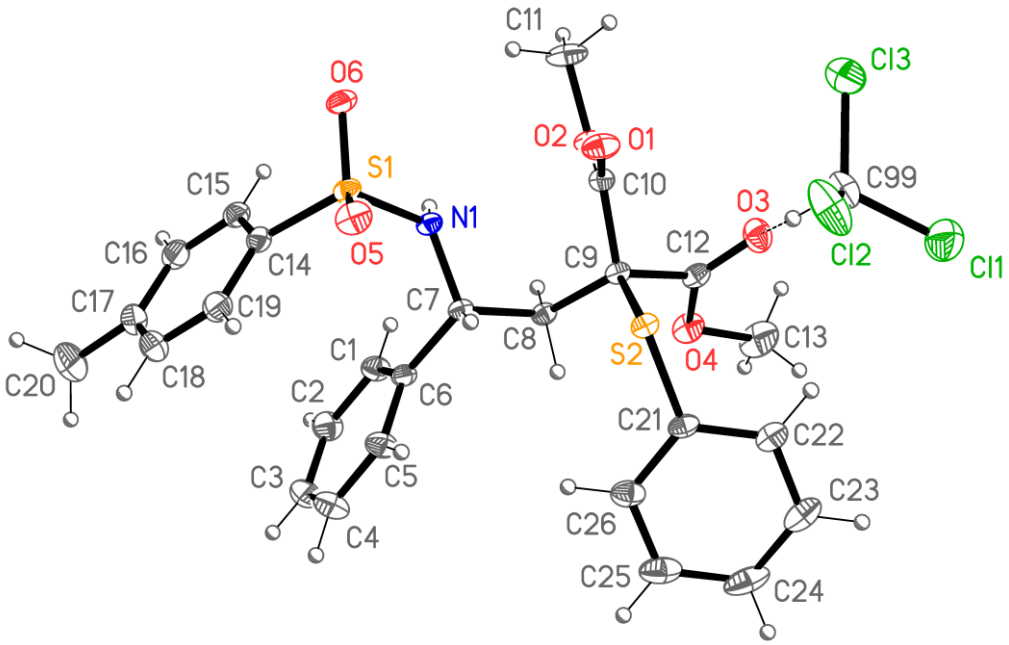


Figure S1. The structure of compound **4a** in the crystal. Ellipsoids indicate 50% probability levels.

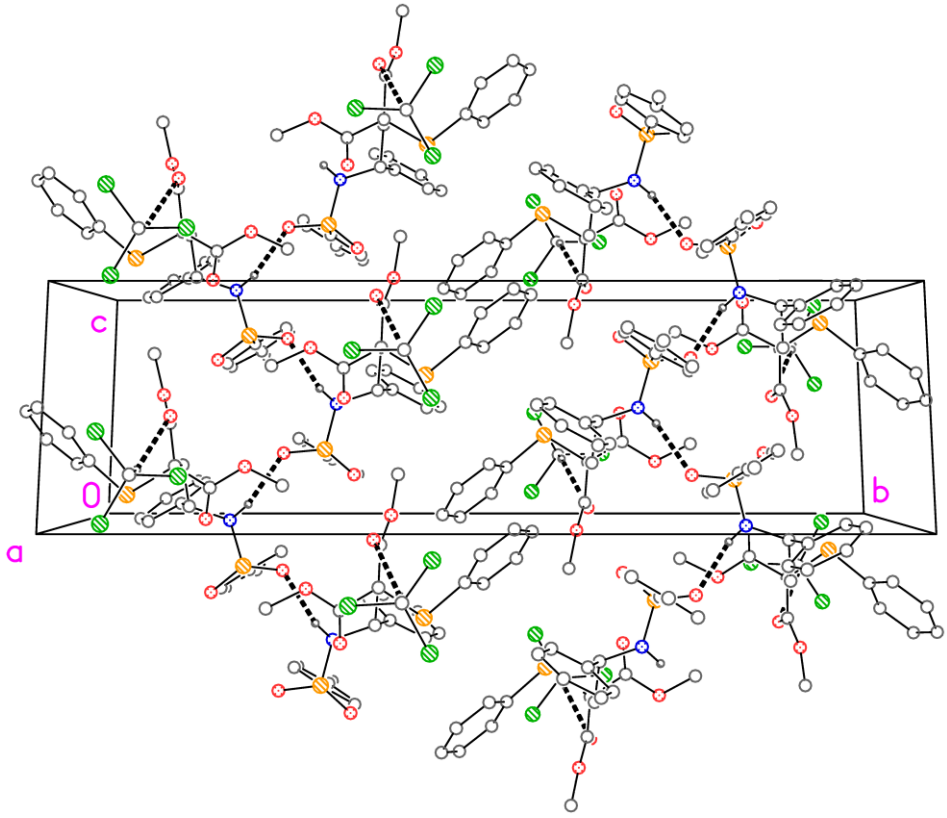


Figure S2. Packing diagram of compound **4a** viewed parallel to the *a* axis. Hydrogen bonds are indicated by dashed lines.

Dimethyl 2-(2-(4-chlorophenyl)-2-((4-methylphenyl)sulfonamido)ethyl)-2-(phenylseleno)malonate (7d)

Fig. S3 shows the structure of compound **7d**; ellipsoids correspond to 50% probability levels. There are two molecules in the asymmetric unit; a least-squares fit of all non-H atoms shows an r.m.s. deviation of only 0.14 Å.

Fig. S4 shows the molecular packing of **7d** (disordered solvent is omitted); the molecules are linked by classical hydrogen bonds from the NH groups of each molecule to the atom O6 of the other molecule to form zigzag chains parallel to the *a* axis [N1'–H···O6 within the asymmetric unit, H···O = 2.08(2) Å; N1–H···O6' (*x*-1, *y*, *z*) H···O = 2.15(2) Å].

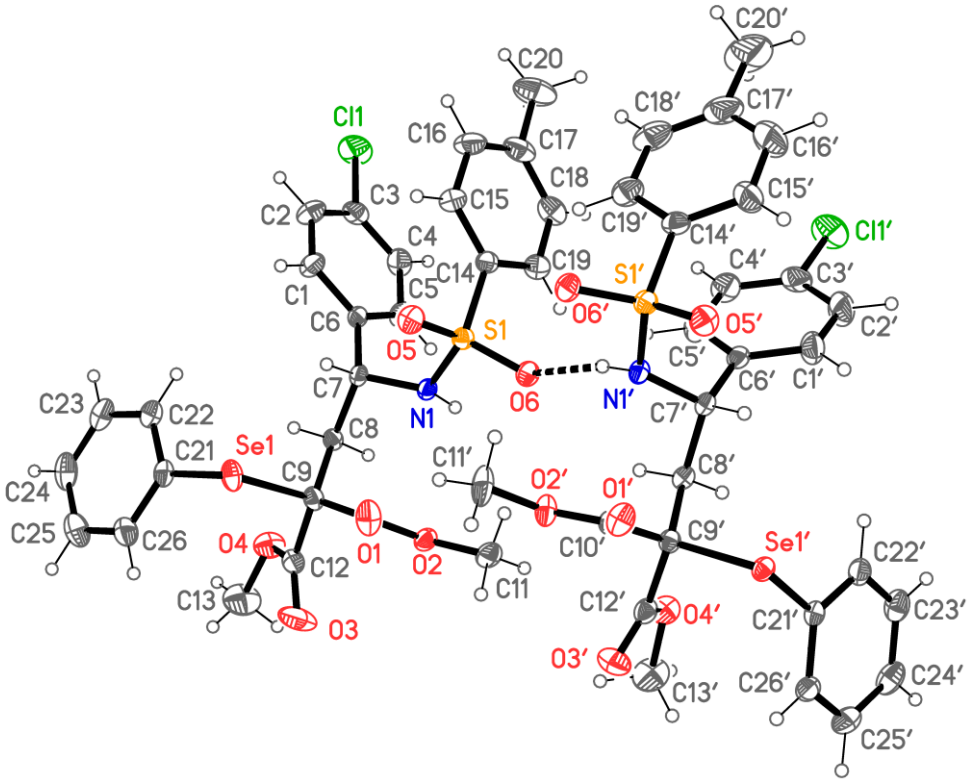


Figure S3. The structure of compound **7d** in the crystal. Ellipsoids indicate 50% probability levels. The dashed line indicates a hydrogen bond.

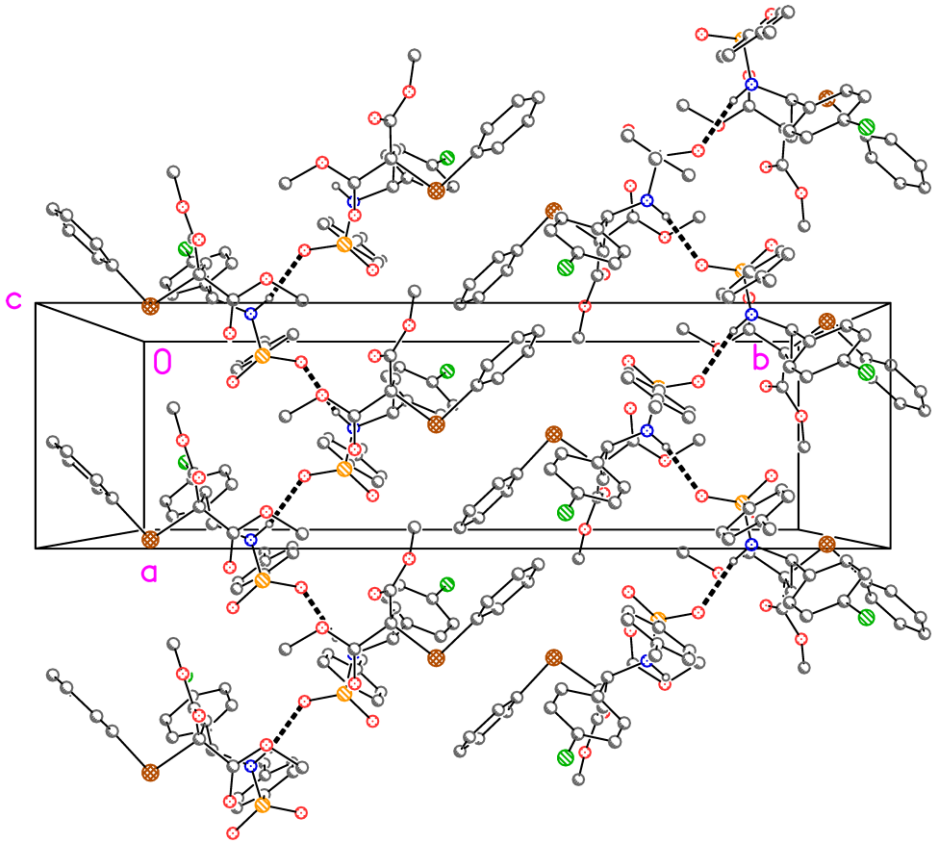


Figure S4. Packing diagram of compound **7d** viewed perpendicular to the *ab* plane in the region $z \approx ¾$. Hydrogen bonds are indicated by dashed lines.

8) References

[1] A. U. Augustin, M. Busse, P. G. Jones, D. B. Werz, *Org. Lett.* **2018**, *20*, 820.

[2] T. Hostier, V. Ferey, G. Ricci, D. Gomez Pardo, J. Cossy, *Chem. Comm.* **2015**, *51*, 13898.

[3] T. Hori, K. B. Sharpless, *J. Org. Chem.* **1979**, *44*, 4204.

[4] P. D. Pohlhaus, S. D. Sanders, A. T. Parsons, W. Li, J. S. Johnson, *J. Am. Chem. Soc.* **2008**, *130*, 8642.

[5] G. M. Sheldrick, *Acta Crystallographica, Section A, Foundations of Crystallography*, **2008**, *64*, 112.

[6] G. M. Sheldrick, *Acta Crystallographica, Section C, Structural Chemistry,* **2015***, 71*, 3.

[7] A. L. Spek, *Acta Crystallographica, Section D, Structural Biology,* **2009***, 65*, 148.