Supporting Information

Tandem Conjugate Addition-Elimination Reaction Promoted by Chiral Pyrrolidinyl Sulphonamide (CPS)

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1. General procedures and methods.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF300 (300 MHz), DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm). The residual solvent peak was used as an internal reference. Low resolution mass spectra were obtained on a VG Micromass 7035 spectrometer in EI mode, a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Infrared spectra were recorded on a BIO-RAD FTS 165 FTIR spectrometer. Enantiomeric excesses were measured *via* chiral HPLC analyses on Hewlett Packard Ti Series 1050 or a set of Jasco HPLC units, including a Jasco DG-980-50 Degasser, a LG-980-02 Ternary Gradient Unit, a PU-980 Intelligent HPLC Pump, UV-975 Intelligent UV/VIS Detectors, and an AS-950 Intelligent Sampler. Optical rotations were recorded on a Jasco DIP-1000 polarimeter. Melting points were determined on a BÜCHI B-540 melting point apparatus. Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063 mm) mesh silica gel. Toluene was distilled from sodium/benzophenone and stored under N_2 atmosphere. THF was freshly distilled from sodium/benzophenone before use. All other reagents and solvents are commercial grade and were used as supplied without further purification, unless otherwise stated. Crystals were grown from hexane and dichloromethane solutions and mounted on glass fibres. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo-K_α radiation at indicated temperatures, with the SMART suite of Programs(1). Data were processed and corrected for Lorentz and polarisation effects with SAINT(2), and for absorption effect with SADABS(3). Structural solution and refinement were carried out with the SHELXTL, suite of programs(4). The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All H-atoms were put at calculated positions.

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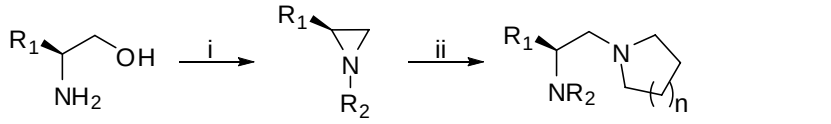
1. *SMART* version 5.628, **2001**. Bruker AXS Inc., Madison, Wisconsin, USA
2. *SAINT+* version 6.22a, **2001** Bruker AXS Inc., Madison, Wisconsin,USA
3. *SADABS*, version 2.10, **2001** G. W. Sheldrick, University of Göttingen,.
4. *SHELXTL*, Version 6.14, **2000,** Bruker AXS Inc., Madison, Wisconsin, USA

2. General procedure for the synthesis of Chiral Pyrrolidinyl Sulphonamides (CPS) 1a-d.



13a-d

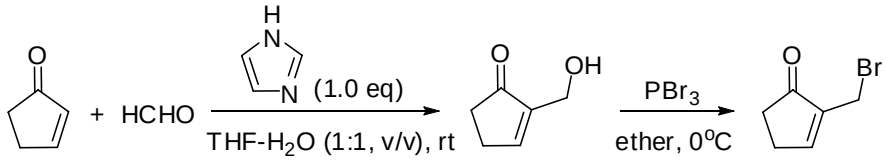
1a, R_1= Bn, R_2= Ts, n= 1
1b, R_1= ^{t}Bu, R_2= Ts, n= 1
1c, R_1= ^{t}Bu, R_2= Ts, n= 2
1d, R_1= ^{t}Bu, R_2= SO_2Mes, n= 1

i) Aziridines **13a-d** were prepared according to a reported procedure.[1]

ii) General procedure for the ring-opening of aziridines **12a-d**.

To a dry sealed tube containing benzyl aziridine **12a** (766 mg, 2.7 mmol) was added anhydrous CH_3CN (2 mL). Pyrrolidine (0.345 mL, 4.0 mmol, 1.5 eq.) was then added and the reaction mixture was refluxed (85^{o}C oil bath) and monitored by TLC. Upon completion, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel to yield promoter **1a**.

3. General procedure and characterization of substrate 2.



2

i) Substrates **2, 5b, 5c** were prepared by Baylis-Hillman reactions[2] followed by bromination[3]. Substrate **5a** was prepared by chlorination of Baylis-Hillman product using AcCl and MeOH.

ii) Characterization of **2**:

[1] W. Ye, D. Leow, L. M. S. Goh, C-T. Tan, C-T. Chian, C-T. Tan, *Tetrahedron Lett.* 2006, **47**, 1007.
[2] S. Luo, B. Zhang, J. He, A. Janczuk, P. G. Wang and J-P. Cheng, *Tetrahedron Lett.* 2002, **43**, 7369.
[3] H-K. Yim, Y. Liao and H. N. C. Wong, *Tetrahedron* 2003, **59**, 1877.

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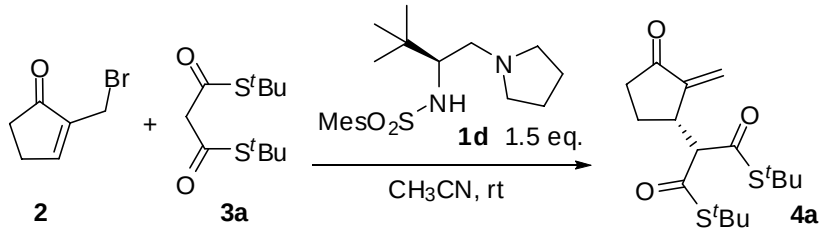
Pale yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ 2.46-2.49 (m, 2H), 2.64-2.65 (m, 2H), 4.03 (d, 2H, *J* = 1.0 Hz), 7.68-7.70 (dd, 1H, *J* = 2.4, 1.0 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 21.6, 26.5, 34.6, 120.8, 142.6, 162.0, 206.5.

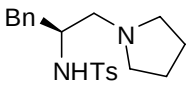
4. General procedure for the tandem conjugate addition-elimination reaction.



To a 5 mL round bottom flask containing 2- (bromomethyl) cyclopent-2-enone **2** (18 mg, 0.1 mmol) and *S*,*S*-di-*tert*-butyl dithiomalonate **3a** (50 mg, 0.2 mmol, 2 eq.), anhydrous CH_3CN (1 mL) followed by promoter **1d** (53 mg, 0.15 mmol, 1.5 eq.) were added and the mixture was stirred at room temperature. Upon completion or after the indicated reaction time, the reaction was quenched by adding 1 M HCl solution (0.5 mL) and extracted with ethyl acetate (2.0 mL × 2). The aqueous layer was basified with 1 M NaOH (0.5 mL) and extracted with CH_2Cl_2 (2.0 mL × 2) to recover the promoter **1d**. The combined organic layers was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate as eluent to give the desired product. The enantiomeric excess was determined by HPLC analyses using a chiral column.

5. Characterization of Chiral Pyrrolidinyl Sulphonamides (CPS) 1a-d.

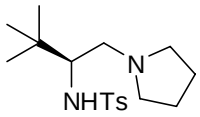
(1a)(S)-4-Methyl-*N*-(1-phenyl-3-(pyrrolidin-1-yl)propan-2-yl)benzenesulphon-amide



Pale yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ 1.51-1.64 (m, 4H), 2.00-2.08 (m, 2H), 2.11-2.18 (m, 3H), 2.39-2.47 (m, 4H), 2.73-2.80 (dd, 1H, *J* = 13.5, 7.9 Hz), 3.12-3.25 (m, 2H), 7.12-7.31 (m, 7H), 7.77 (d, 2H, *J* = 8.2 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 21.5, 23.4, 39.6, 53.1, 53.4, 57.4, 126.3, 127.2, 128.2, 129.5, 129.6,

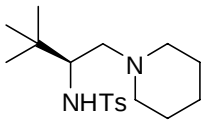
136.6, 137.2, 143.2; **IR** (film, cm^{-1}) 3375, 2970, 1599, 1475, 1341, 1162, 1092; **LRMS** (ESI) *m/z* 359.2 $[M+H]^+$; **HRMS** (ESI) calcd. for $[C_{20}H_{26}N_2O_2S+H]^+$ requires *m/z* 359.1793. Found 359.1796. $[\alpha]_D^{24}$ +83.6 (c = *6.44*, $CHCl_3$).

(1b)(S)-*N*-(3,3-Dimethyl-1-(pyrrolidin-1-yl)butan-2-yl)-4-methylbenzenesulphonamide



Pale yellow crystal. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ 0.88 (s, 9H), 1.52 (bs, 4H), 2.20-2.24 (m, 2H), 2.33-2.40 (m, 6H), 2.45-2.53 (m, 1H), 3.21 (dd, 1H, *J* = 9.1, 4.2 Hz), 7.22 (d, 2H, *J* = 8.3 Hz), 7.78 (d, 2H, *J* = 8.3 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 21.4, 23.4, 26.8, 34.3, 54.0, 56.8, 61.5, 127.0, 128.9, 139.5, 142.3; **IR** (KBr, cm^{-1}) 3433, 2969, 1600, 1457, 1321, 1153, 1086; **LRMS** (ESI) *m/z* 325.2 $[M+H]^+$; **HRMS** (ESI) calcd. for $[C_{17}H_{28}N_2O_2S+H]^+$ requires *m/z* 325.1950. Found 325.1950. $[\alpha]_D^{24}$ +56.4 (c = *4.57*, $CHCl_3$).

(1c)(S)-*N*-(3,3-Dimethyl-1-(piperidin-1-yl)butan-2-yl)-4-methylbenzenesulphonamide



Pale yellow sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ 0.84 (s, 9H), 1.33-1.39 (m, 6H), 2.11-2.19 (m, 3H), 2.27-2.34 (m, 3H), 2.38 (s, 3H), 3.27 (dd, 1H, *J* = 9.0, 4.8 Hz), 7.23 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 2H, *J* = 8.1 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 21.4, 24.1, 25.5, 26.7, 34.3, 54.7, 59.4, 59.7, 127.0, 129.1, 139.5, 142.4; **IR** (film, cm^{-1}) 3395, 2940, 1600, 1475, 1316, 1155, 1094; **LRMS** (ESI) *m/z* 339.3 $[M+H]^+$; **HRMS** (ESI) calcd. for $[C_{18}H_{30}N_2O_2S+H]^+$ requires *m/z* 339.2106. Found 339.2107. $[\alpha]_D^{24}$ +34.1 (c = *5.42*, $CHCl_3$).

(1d)(S)-*N*-(3,3-Dimethyl-1-(pyrrolidin-1-yl)butan-2-yl)-2,4,6-trimethylbenzenesulphonamide

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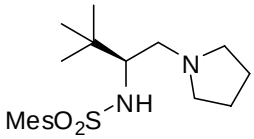
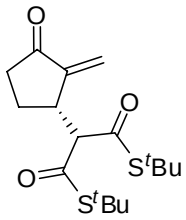


Pale yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 0.83 (s, 9H), 1.50-1.55 (m, 4H), 2.22-2.28 (m, 5H), 2.37 (dd, 1H, *J* = 12.6, 3.8 Hz), 2.46-2.57 (m, 3H), 2.65 (s, 6H), 3.28 (dd, 1H, *J* = 10.1, 4.4 Hz), 6.90 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 20.8, 23.0, 23.5, 26.8, 34.3, 54.1, 56.4, 61.4, 131.5, 136.8, 138.2, 141.1; **IR** (film, cm^{-1}) 3392, 2958, 1602, 1477, 1338, 1156, 1053; **LRMS** (ESI) *m/z* 353.3 $[M+H]^+$; **HRMS** (ESI) calcd. for $[C_{19}H_{32}N_2O_2S+H]^+$ requires *m/z* 353.2263. Found 353.2260. **$[\alpha]_D^{24}$** +57.7 (c = *4.79*, $CHCl_3$).

6. Characterization of tandem conjugate addition-elimination products.

(4a) (S)-*S,S'*-di-*tert*-Butyl 2-(2-methylene-3-oxocyclopentyl)propanebis(thioate)



White crystal. 90% ee; **Melting point**: 100.0-100.6°C; **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.47 (s, 9H), 1.49 (s, 9H), 1.71-1.78 (m, 1H), 2.06-2.13 (1H, m), 2.27-2.42 (m, 2H), 3.67 (d, 1H, *J* = 10.0 Hz), 3.69-3.73 (m, 1H), 5.31 (d, 1H, *J* = 1.9 Hz), 6.06 (d, 1H, *J* = 1.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 23.7, 29.5, 29.6, 36.3, 41.3, 49.5, 49.6, 72.4, 119.5, 145.1, 192.4, 192.5, 205.2; **IR** (film, cm^{-1}); 3021, 2926, 2855, 2401, 1690, 1216; **LRMS** (ESI) *m/z* 365.1 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{17}H_{26}O_3S_2Na]^+$ requires *m/z* 365.1221. Found 365.1222. **$[\alpha]_D^{24}$** -298 (c = *0.52*, $CHCl_3$); **HPLC conditions:** Chiralcel AD-H column (Diacel); 98/2 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 17.2 min (minor), 18.4 min (major).

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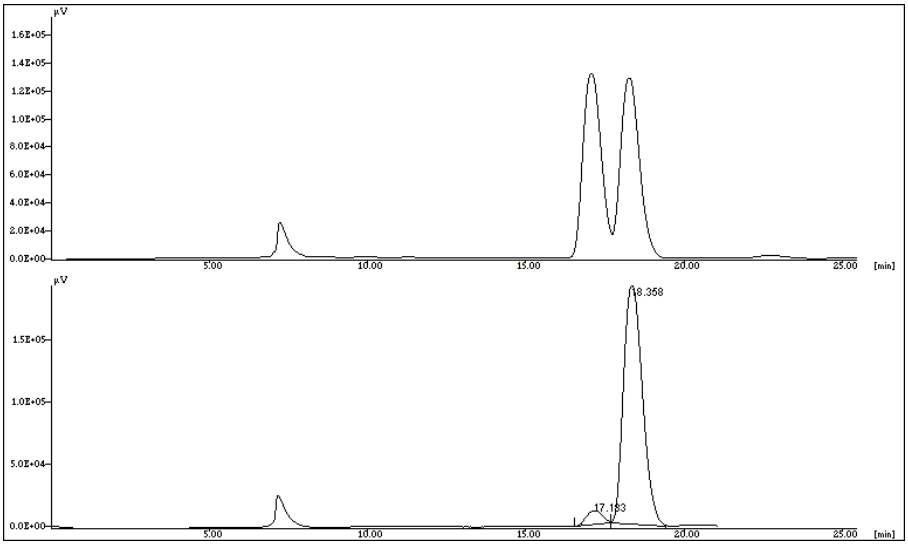
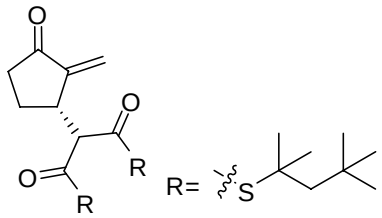


(4b) (S)-*S,S*'-bis(2,4,4-Trimethylpentan-2-yl) 2-(2-methylene-3-oxocyclopentyl) propanebis(thioate)



Yellow oil. 94% ee; **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.00 (s, 9H), 1.02 (s, 9H), 1.53-1.59 (m, 14H), 1.70-1.80 (m, 3H), 1.87-1.91 (dd, 2H, *J* = 15.2, 5.7 Hz), 2.06-2.12 (m, 1H), 2.27-2.42 (m, 2H), 3.66 (d, 1H, *J* = 10.1 Hz), 3.69-3.74 (m, 1H), 5.31 (d, 1H, *J* = 1.9 Hz), 6.05 (d, 1H, *J* = 2.5 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 23.7, 29.1, 29.2, 29.5, 31.6, 32.6 (two peaks), 36.3, 41.3, 53.2, 53.3, 54.7 (two peaks), 72.4, 119.6, 145.2, 192.0, 192.1, 205.4; **IR** (film, cm^{-1}) 3021, 2401, 1688, 1216; **LRMS** (ESI) *m/z* 477.05 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{17}H_{26}O_3S_2Na]^+$ requires *m/z* 477.2473. Found 477.2476. $[\alpha]_D^{25}$ -23.1 (c = *2.26*, $CHCl_3$); **HPLC conditions:** Two Chiralcel AD-H columns (Diacel); 95/5 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 22.8 min (minor), 23.6 min (major).

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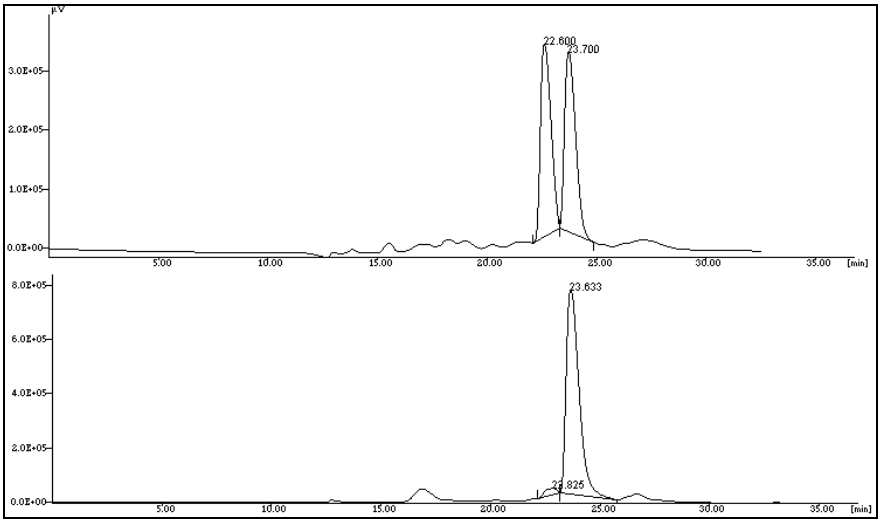
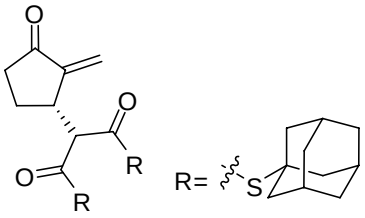


(4c) (S)-*S,S*'-di-Adamantanyl-2-(2-methylene-3-oxocyclopentyl)propanebis-(thioate)



White solid. 94% ee; **Melting point**: decomposes at 203.0-204.2 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.70-1.77 (m, 14H), 2.06-2.16 (m, 18H), 2.26-2.41 (m, 2H), 3.61 (d, 1H, *J* = 10.1 Hz), 3.65-3.69 (m, 1H), 5.33 (d, 1H, *J* = 1.9 Hz), 6.06 (d, 1H, *J* = 2.5 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 23.7, 29.8, 36.2 (two peaks), 36.3, 41.4, 41.5, 52.6 (two peaks), 72.6, 119.6, 145.1, 192.1, 192.3, 205.3; **IR** (KBr, cm^{-1}) 2906, 1689, 1451, 1259; **LRMS** (ESI) *m/z* 521.3 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{29}H_{38}O_3S_2Na]^+$ requires *m/z* 521.2160. Found 521.2158. $[\alpha]_D^{25}$ -40.4 (c = *1.16*, $CHCl_3$); **HPLC conditions:** Chiralpak IA column (Diacel); 98/2 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 23.9 min (major), 26.5 min (minor).

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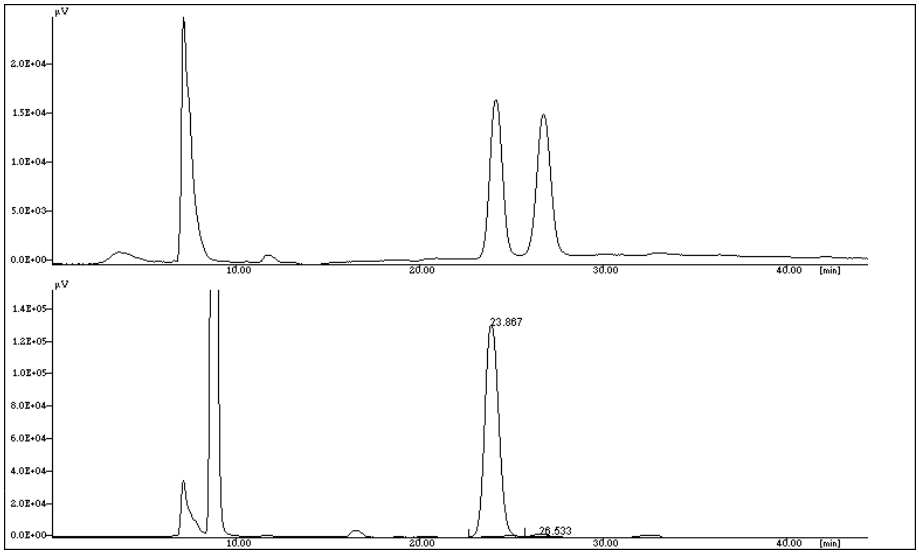
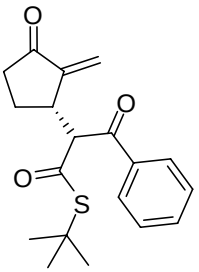


(4d) (S)-*S*-*tert*-butyl 2-((S)-2-methylene-3-oxocyclopentyl)-3-oxo-3-phenylpropanethioate



Pale yellow oil. 94, 94% ee; d.r. 3:2; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ (Mixture of two diastereomers) 1.41 (d, 23 H, *J* = 3.1 Hz), 1.51-1.59 (m, 1H), 1.85-1.95 (m, 2H), 2.03-2.49 (m, 9H), 3.90-3.95 (m, 1H each for two diastereomers), 4.61 (d, 1H, *J* = 9.8 Hz, major diastereomer), 4.73 (d, 1H, *J* = 9.8 Hz, minor diastereomer), 5.03 (d, 1H, *J* = 2.4 Hz, major diastereomer), 5.39 (d, 1H, *J* = 1.5 Hz, minor diastereomer), 5.92 (d, 1.5H, *J* = 2.4 Hz), 6.10 (d, 1H, *J* = 2.5 Hz), 7.46-7.52 (m, 6H), 7.58-7.61 (m, 3H), 8.01-8.05 (m, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 23.7, 24.3, 29.5, 36.2, 36.6, 41.5, 41.6, 49.7, 66.1, 66.8, 119.0, 119.4, 128.8, 128.9, 133.9 (two peaks), 136.4, 136.5, 145.5, 145.9, 192.6, 192.8, 193.4 (two peaks), 205.4, 205.5; **IR** (film, cm^{-1}) 3021, 1725, 1693, 1657, 1216; **LRMS** (ESI) *m/z* 353.0 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{19}H_{22}O_3SNa]^+$ requires *m/z* 353.1187. Found 353.1183. $[\alpha]_D^{25}$ -108 (c = *0.54*, $CHCl_3$); **HPLC conditions:** Chiralcel AD-H+AS-H columns (Diacel); 90/10

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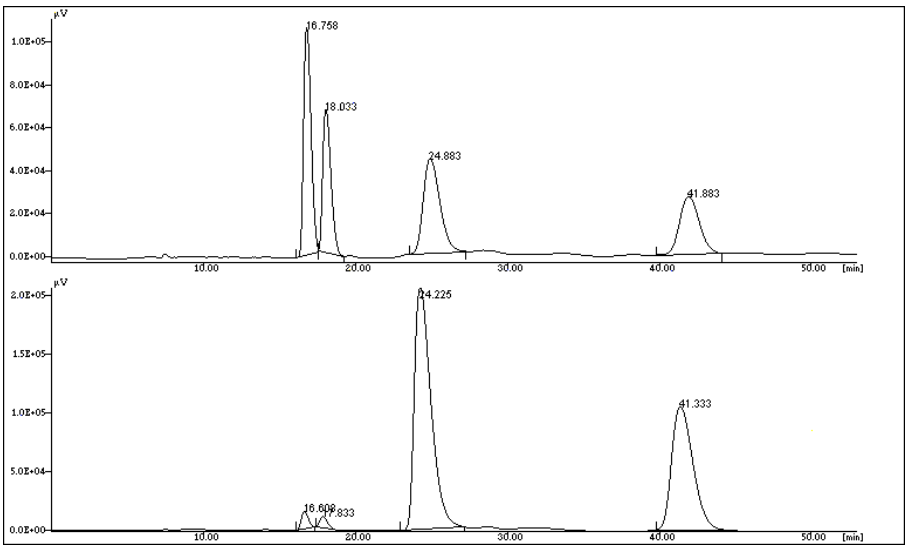
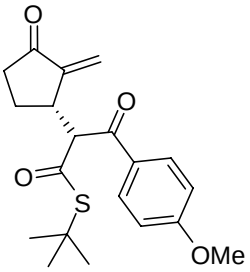
hexane/2-propanol; Flow rate 1.0 mL/min; λ = 254 nm; 16.6 min (minor), 17.8 min (minor), 24.2 (major), 41.3 (major).



(4e) (S)-*S*-*tert*-Butyl 3-(4-methoxyphenyl)-2-((S)-2-methylene-3-oxocyclopentyl)-3-oxopropanethioate



Pale yellow oil. 98, 95% ee, d.r. 3:2; **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ (Mixture of two diastereomers) 1.41 (d, 26H, *J* = 6.3 Hz), 1.52-1.54 (m, 1H, major diastereomer), 1.84-1.90 (m, 1H, major diastereomer), 2.02-2.09 (m, 1H, minor diastereomer), 2.18-2.48 (m, 8H), 3.87-3.93 (m, 12H), 4.55 (d, 1H, *J* = 9.4 Hz, major diastereomer), 4.61 (d, 1H, *J* = 10.1 Hz, minor diastereomer), 5.02 (d, 1H, *J* = 2.5 Hz, major diastereomer), 5.38 (d, 1H, *J* = 1.9 Hz, minor diastereomer), 5.90 (d, 1H, *J* = 2.5 Hz, major diastereomer), 6.09 (d, 1H, *J* = 2.5 Hz, minor diastereomer), 6.94-6.97 (m, 5H), 8.01-8.04 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 23.8, 24.3, 29.5, 36.3, 36.6, 41.5, 41.6, 49.6, 55.5 (two peaks), 65.8, 66.5, 114.1 (two peaks), 119.0, 119.3, 129.4,

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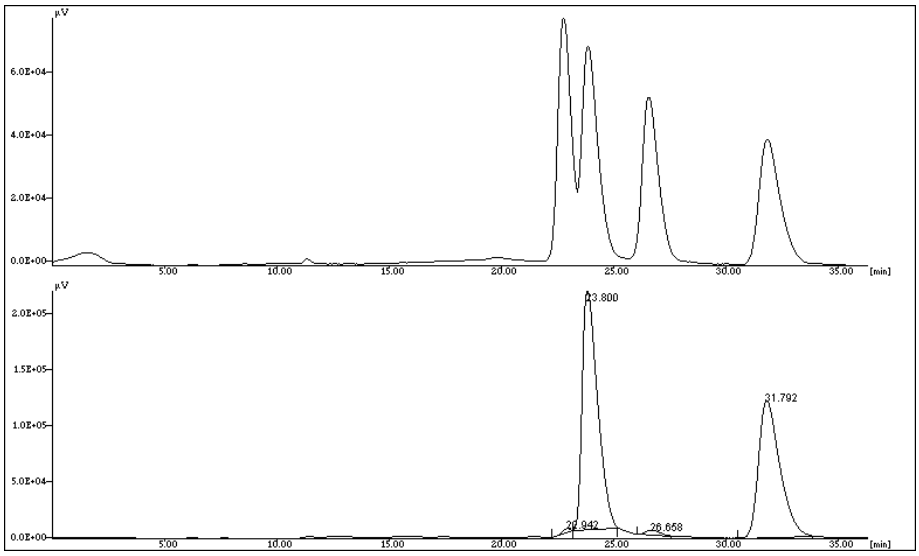
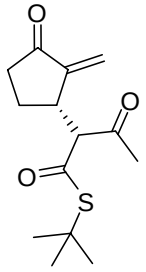
129.6, 131.3, 131.3, 145.7, 146.0, 164.2 (two peaks), 190.8, 191.0, 193.6, 193.7, 205.5, 205.6; **IR** (film, cm^{-1}) 3015, 2963, 1740, 1689, 1597, 1511, 1459; **LRMS** (ESI) *m/z* 360.8 $[M]^+$; **HRMS** (ESI) calcd. for $[C_{20}H_{24}O_4S]^+$ requires *m/z* 361.1474. Found 361.1478. $[\alpha]_D^{25}$ -11.3 (c = *2.86*, $CHCl_3$); **HPLC conditions:** Chiralcel OD-H+IA columns (Diacel); 90/10 hexane/2-propanol; Flow rate 1.0 mL/min; λ = 254 nm; 22.9 min (minor), 23.8 min (major), 26.6 (minor), 31.8 (major).



(4f) (S)-*S*-*tert*-Butyl 2-((S)-2-methylene-3-oxocyclopentyl)-3-oxobutanethioate



Pale yellow oil. 94, 94% ee, d.r. 1:1; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ (Mixture of two diastereomers) δ = 1.47 (s, 9H), 1.48 (s, 9H), 1.57-1.61 (m, 1H), 1.73-1.81 (m, 1H), 2.04-2.39 (m, 16H), 3.64-3.73 (m, 3H), 3.74 (d, 1H, *J* = 9.5 Hz), 5.14 (d, 1H, *J* = 2.5 Hz), 5.31 (d, 1H, *J* = 1.9 Hz), 6.02 (d, 1H, *J* = 2.5 Hz), 6.06 (d, 1H, *J* = 2.5 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 23.6, 24.0, 29.3, 29.4, 29.5 (two peaks), 29.9, 36.1, 36.3, 40.3, 40.4, 49.7, 49.8, 72.2, 72.6, 118.9, 119.6, 145.0, 145.8, 193.8, 194.3, 200.5, 200.6, 205.2, 205.4; **IR** (film, cm^{-1}) 3021, 2967, 1724, 1671, 1217; **LRMS**

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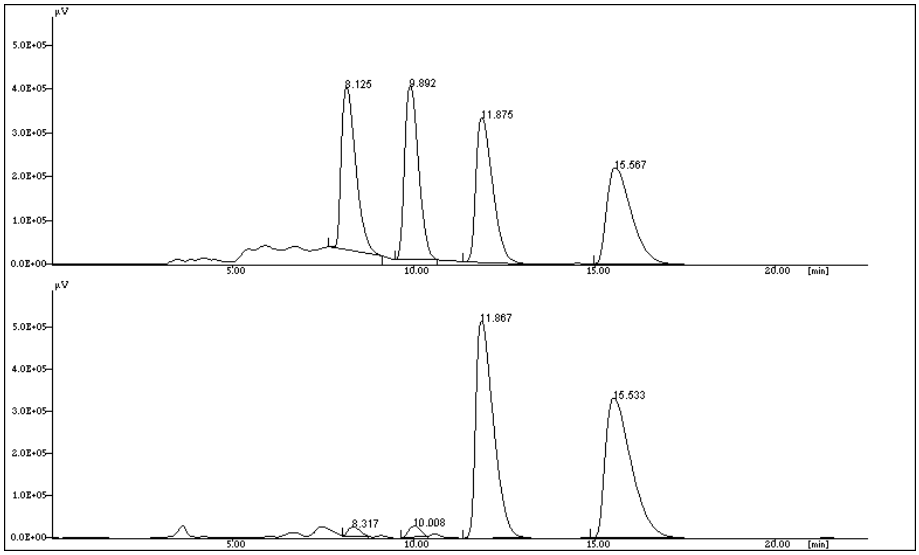
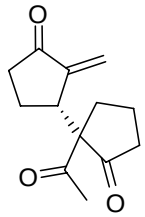
(ESI) *m/z* 267.0 $[M]^-$; **HRMS** (ESI) calcd. for $[C_{14}H_{20}O_3SNa]^+$ requires *m/z* 291.1031. Found 291.1036. $[\alpha]_D^{25}$ -464 (c = *0.25*, $CHCl_3$); **HPLC conditions:** Chiralcel AS-H column (Diacel); 80/20 hexane/2-propanol; Flow rate 1.0 mL/min; λ = 254 nm; 8.3 min (minor), 10.0 min (minor), 11.9 (major), 15.5 (major).



(4g) (1R,1'R)-1-Acetyl-2'-methylenebi(cyclopentane)-2,3'-dione



Colorless oil. 98, 95% ee, d.r. 2:1; **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ (Mixture of two diastereomers) 1.44-1.76 (m, 13H), 1.87-2.22 (m, 14H), 2.26 (s, 3H), 2.27-2.46 (m, 15H), 2.55-2.65 (m, 1H), 2.71-2.75 (m, 2H), 3.74-3.79 (m, 2H), 3.90-3.92 (m, 1H), 4.99 (d, 2H, *J* = 3.2 Hz), 5.20 (d, 1H, *J* = 1.9 Hz), 6.03 (d, 2H, *J* = 3.2 Hz), 6.11 (d, 1H, *J* = 1.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 19.6 (two peaks), 22.3, 22.7, 25.6, 26.0, 26.1, 26.2, 36.2, 36.6, 39.4, 39.5, 43.1, 44.8, 72.0, 74.7, 118.4, 120.8, 144.3, 144.6, 201.8, 203.3, 204.9, 205.8, 214.1, 214.9; **IR** (film, cm^{-1}) 3022, 2401, 1707, 1217; **LRMS** (ESI) *m/z* 237.9 $[M+H_2O]$; **HRMS** (ESI) calcd. for $[C_{13}H_{16}O_3Na]^+$ requires *m/z* 243.0977. Found 243.1010. $[\alpha]_D^{25}$ +29.1 (c = *1.06*, $CHCl_3$); **HPLC conditions:** Chiralcel OJ-H column (Diacel); 90/10 hexane/2-

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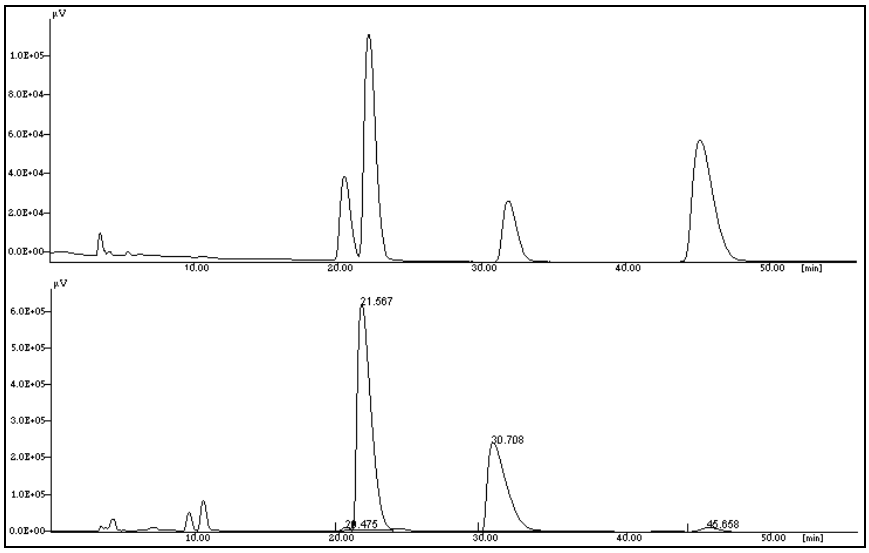
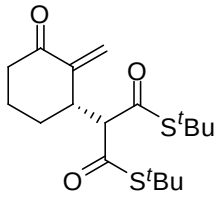
propanol; Flow rate 1.0 mL/min; λ = 210 nm; 20.5 min (minor), 21.6 min (major), 30.7 (major), 45.6 (minor).

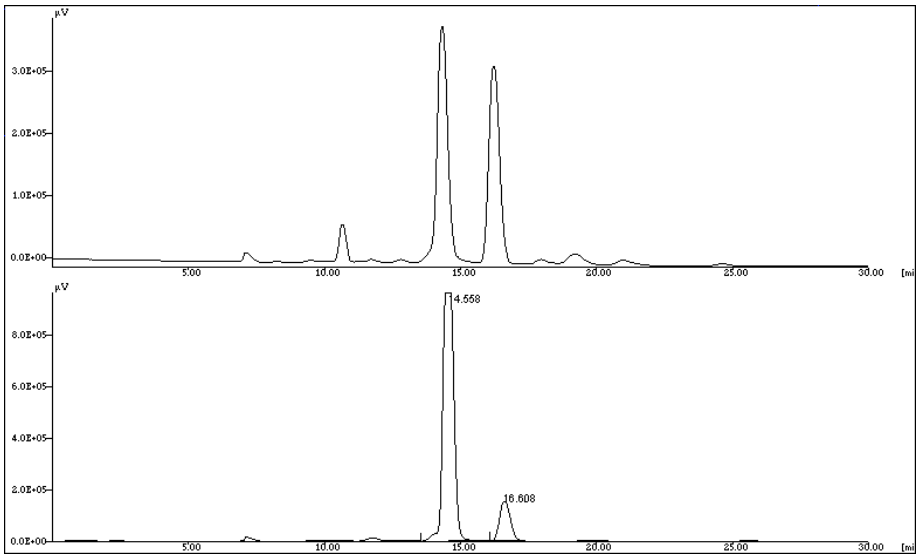


(6a) (S)-*S*,*S*'-di-*tert*-Butyl 2-(2-methylene-3-oxocyclohexyl)propanebis(thioate)

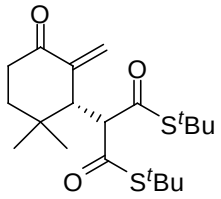


Pale yellow oil. 74% ee; **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.42 (s, 9H), 1.47 (s, 9H), 1.75-1.78 (m, 1H), 1.83-1.96 (m, 3H), 2.35-2.42 (m, 1H), 2.49-2.54 (m, 1H), 3.59-3.63 (m, 1H), 3.77 (d, 1H, *J* = 10.8 Hz), 5.19 (s, 1H), 5.82 (s, 1H);**^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 20.2, 26.6, 29.4, 29.5, 40.1, 42.8, 49.5 (two peaks), 70.9, 122.9, 145.1, 192.2, 192.4, 201.1; **IR** (film, cm^{-1}) 3020, 2400, 1726, 1691, 1216; **LRMS** (ESI) *m/z* 379.1 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{18}H_{28}O_3S_2Na]^+$ requires *m/z* 379.2379 Found 379.1372. $[\alpha]_D^{25}$ -30.9 (c = *0.56*, $CHCl_3$); **HPLC conditions:** Chiralcel AD-H column (Diacel); 98/2 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 14.6 min (major), 16.6 min (minor).

Supporting Information

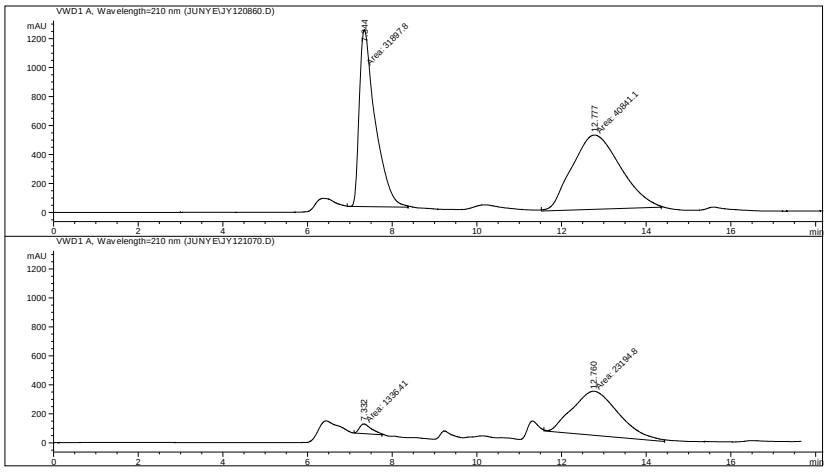


(6b) (R)-*S*,*S*'-di-*tert*-Butyl 2-(2,2-dimethyl-6-methylene-5-oxocyclohexyl)-propanebis(thioate)

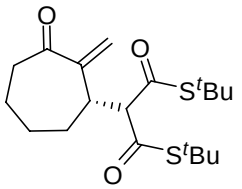


Pale yellow oil. 88% ee; **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.00 (s, 3H), 1.06 (s, 3H), 1.40 (s, 9H), 1.46 (s, 9H), 1.92-1.99 (m, 1H), 2.34-2.42 (m, 1H), 2.48-2.54 (m, 1H), 3.31-3.34 (dd, 1H, *J* = 8.2, 1.9 Hz), 3.86 (d, 1H, *J* = 8.2 Hz), 5.19 (d, 1H, *J* = 1.2 Hz), 5.95 (d, 1H, *J* = 1.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 27.3, 28.4, 29.2, 29.5, 29.6, 31.9, 33.8, 35.6, 49.2, 49.7, 52.1, 69.5, 126.3, 142.6, 192.9, 193.1, 199.6; **IR** (film, cm^{-1}) 3019, 2400, 1642, 1216; **LRMS** (ESI) *m/z* 407.1 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{20}H_{32}O_3S_2Na]^+$ requires *m/z* 407.1691 Found 407.1685. $[\alpha]_D^{25}$ -59.2 (c = *0.12*, $CHCl_3$); **HPLC conditions:** Chiralcel AS-H column (Diacel); 95/5 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 7.3 min (minor), 12.8 min (major).

Supporting Information

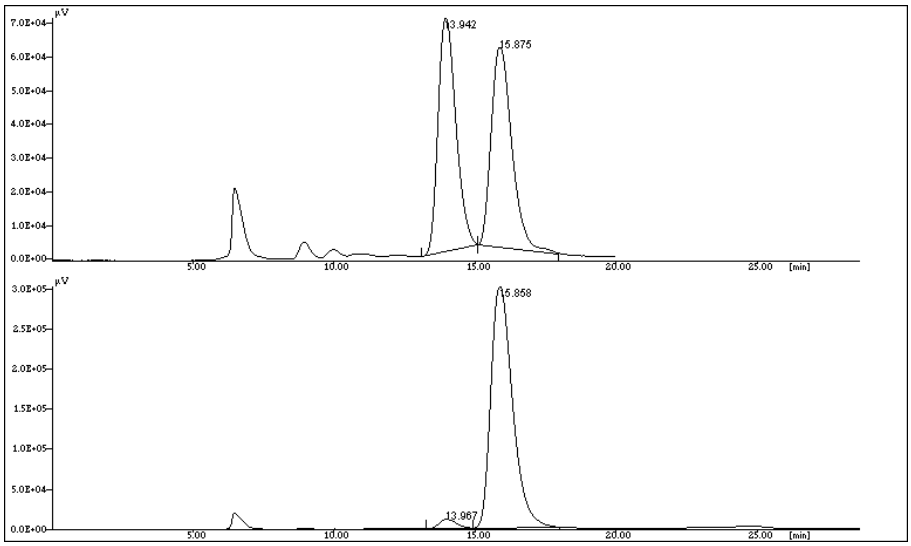


(6c) (S)-*S*,*S*'-di-*tert*-Butyl 2-(2-methylene-3-oxocycloheptyl)propanebis(thioate)



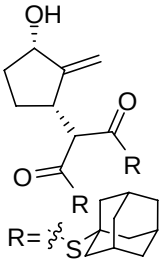
Pale yellow oil. 94% ee; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) δ 1.39 (s, 9H), 1.49 (s, 9H), 1.66-1.82 (m, 6H), 2.52-2.60 (m, 1H), 2.74-2.80 (m, 1H), 3.46-3.52 (dd, 1H, *J* = 11.6, 8.4 Hz), 4.01 (d, 1H, *J* = 11.6 Hz), 5.30 (s, 1H), 6.01 (s, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$, ppm) δ 24.5, 27.9, 29.4, 29.5, 33.7, 42.6, 42.7, 49.4, 49.5, 71.8, 122.6, 148.2, 192.2, 192.9, 202.5; **IR** (film, cm^{-1}) 3020, 2930, 1690, 1453, 1220; **LRMS** (ESI) *m/z* 393.1 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{19}H_{30}O_3S_2Na]^+$ requires *m/z* 393.1534 Found 393.1527. $[\alpha]_D^{25}$ +23.2 (c = *0.12*, $CHCl_3$); **HPLC conditions:** Chiralcel OF column (Diacel); 95/5 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 14.0 min (minor), 15.8 min (major).

Supporting Information



7. Preparation and characterization of compounds 7-12.

(7) *S,S*'-di-Adamamtanyl 2-[(1S,3S)-3-hydroxy-2-methylenecyclopentyl] propane-bis(thioate)



To a dry rbf containing C-AE product **4c** (10.0 mg, 0.02 mmol) was added CH_2Cl_2/MeOH (1:1 0.2 mL) and the reaction flask was cool to 0^oC using an ice-water bath. $CeCl_3 \cdot 7H_2O$ (5.4 mg, 0.022 mmol, 1.1 equiv.) was then added followed by $NaBH_4$ (1.0 mg, 0.022 mmol, 1.1 equiv.). Upon completion, 0.1 M HCl (1.0 mL) was added to rbf and the mixture was extracted by CH_2Cl_2 (2 mL×2). The crude product was purified by flash chromatography on silica gel to yield compound **7** as a white solid (8.6 mg, 86% yield). **Melting point**: 179.5-180.5 ^oC **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.68-1.76 (m, 14H), 2.04 (bs, 6H), 2.14 (d, 14H, *J* = 3.8 Hz), 3.42-3.44 (m, 1H), 3.50 (d, 1H, *J* = 10.1 Hz), 4.41 (d, 1H, *J* = 6.3 Hz), 5.03 (t, 1H, *J* = 1.9 Hz), 5.20 (t, 1H, *J* = 1.9 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 25.6, 29.8, 33.8, 36.2, 41.5, 42.2, 52.2 (two peaks), 73.5, 74.6, 109.8, 154.3, 192.6, 192.9; **IR** (film, cm^{-1}) 3446, 3021, 2914, 2401, 1703, 1216; **LRMS** (ESI) *m/z* 501.2 $[M+H]^+$; **HRMS**

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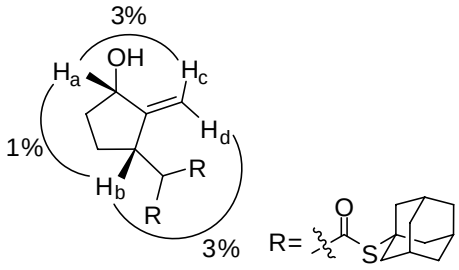
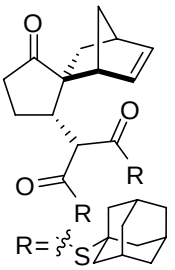
(ESI) calcd. for $[C_{29}H_{40}O_3S_2+Na]^+$ requires *m/z* 523.2317 Found 523.2314. $[\alpha]_D^{25}$ -40.5 (c = *0.86*, $CHCl_3$). The relative stereochemistry of **7** was determined by NOE studies.



(8) *S,S'*-di-Adamantanyl-2-((1R,1'S,4R,5'S)-2'-oxospiro[bicyclo[2.2.1]hept[5]-ene-2,1'-cyclopentane]-5'-yl)propanebis(thioate)

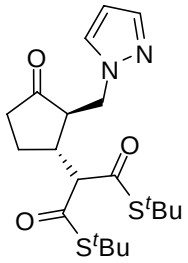


To a dry rbf containing CA-E product **4c** (10.0 mg, 0.02 mmol) was added CH_2Cl_2 (0.5 mL) and the reaction flask was cool to 0°C using an ice-water bath. $Yb(OTf)_3$ (1.2 mg, 0.002 mmol, 0.1 equiv.) was then added followed by cyclopentadiene (0.1 mL, co-solvent). The reaction was monitored by TLC. Upon completion, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel to yield compound **8** as a white solid (11.0 mg, 97% yield). **Melting point**: decomposes at 180.0-181.9 °C **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 0.84-0.90 (m, 2H), 0.96-0.99 (m, 1H), 1.18-1.21 (m, 1H), 1.67-1.76 (m, 12H), 2.02 (bs, 8H), 2.10 (d, 12H, *J* = 2.5 Hz), 2.27-2.38 (m, 2H), 2.75 (t, 1H, *J* = 7.6 Hz), 2.78 (bs, 1H), 2.88 (bs, 1H), 3.38 (d, 1H, *J* = 8.2 Hz), 6.14-6.16 (dd, 1H, *J* = 5.7, 3.2 Hz), 6.35-6.36 (dd, 1H, *J* = 5.7, 3.2 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 21.9, 29.8 (two peaks), 31.9, 33.9, 36.2, 41.4, 41.5, 43.0, 45.0, 45.4, 50.6, 52.1, 52.4, 62.7, 70.9, 133.3, 140.8, 192.8, 193.5, 219.3; **IR** (film, cm^{-1}) 2911, 2852, 1727, 1679, 1452,

Supporting Information

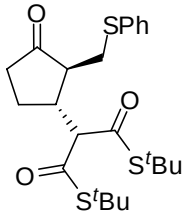
1253; **LRMS** (ESI) *m/z* 565.2 $[M+H]^+$; **HRMS** (ESI) calcd. for $[C_{34}H_{44}O_3S_2Na]^+$ requires *m/z* 587.2630 Found 587.2624. $[\alpha]_D^{25}$ -14.2 (c = *0.86*, $CHCl_3$).

(9) *S,S'*-di-*tert*-Butyl 2-((1R,2R)-2-((1H-pyrazol-1-yl)methyl)-3-oxocyclopentyl) propanebis(thioate)



The CH_2Cl_2 (0.2 mL) solution of CA-E product **4a** (10.0 mg, 0.029 mmol) and pyrazole (6.1 mg, 0.090 mmol, 3 equiv.) was stirred at room temperature. The reaction was monitored by TLC. Upon completion, the mixture was directly purified by silica gel column to yield the product **9** as colorless oil (7.6 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.46 (s, 9H), 1.49 (s, 9H), 1.64-1.69 (m, 1H), 1.93-1.99 (m, 1H), 2.07-2.15 (m, 1H), 2.27-2.35 (m, 2H), 2.49-2.56 (m, 1H), 3.74 (d, 1H, *J* = 8.2 Hz), 4.15-4.19 (dd, 1H, *J* = 14.5, 5.0 Hz), 4.61-4.64 (dd, 1H, *J* = 13.8, 3.2 Hz), 6.20 (s, 1H), 7.41 (d, 1H, *J* = 2Hz), 7.45 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 24.6, 29.5, 29.6, 37.4, 38.6, 49.5 (two peaks), 50.0, 52.4, 72.1, 105.5, 130.7, 139.8, 192.7, 193.4, 216.4; **IR** (film, cm^{-1}) 3019, 2969, 2400, 1744, 1690, 1366, 1216; **LRMS** (ESI) *m/z* 411.0 $[M+H]^+$; **HRMS** (ESI) calcd. for $[C_{20}H_{30}O_3N_2S_2+H]^+$ requires *m/z* 411.1776 Found 411.1771. $[\alpha]_D^{25}$ +19.6 (c = *0.76*, $CHCl_3$).

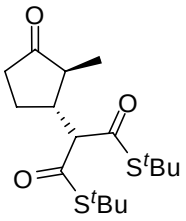
(10) *S,S'*-di-*tert*-Butyl 2-((1R,2S)-3-oxo-2-(phenylthiomethyl)cyclopentyl) propanebis(thioate)



Supporting Information

Et_3N (4.0 μL, 0.029 mmol, 1 equiv.) was added dropwise at rt to a stirring CH_2Cl_2 (0.2 mL) solution of CA-E product **4a** (10.0 mg, 0.029 mmol) and thiophenol (6 μL, 0.058 mmol, 2 equiv.). The reaction was monitored by TLC. Upon completion, the mixture was directly purified by silica gel column to give the thio-Michael product **10** as pale yellow oil and later solidified when stored in a -20°C fridge (9.2 mg, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.44 (s, 9H), 1.45 (s, 9H), 1.70-1.78 (m, 1H), 2.09-2.22 (m, 2H), 2.29-2.37 (m, 2H), 3.01-3.08 (m, 1H), 3.20 (d, 2H, *J* = 4.4 Hz), 3.73 (d, 1H, *J* = 8.2 Hz), 7.16 (t, 1H, *J* = 7.6 Hz), 7.26 (t, 2H, *J* = 7.6 Hz), 7.37 (d, 2H, *J* = 7.6 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 24.5, 29.5 (two peaks), 33.2, 37.4, 41.1, 49.4, 49.5, 52.2, 72.2, 126.3, 128.9, 129.8, 136.1, 192.8, 192.9, 216.5; **IR** (film, cm^{-1}) 3019, 2967, 2400, 1743, 1690, 1658, 1366, 1217; **LRMS** (ESI) *m/z* 451.0 $[M-H]^-$; **HRMS** (ESI) calcd. for $[C_{23}H_{32}O_3S_3Na]^+$ requires *m/z* 475.1411 Found 475.1406. $[\alpha]_D^{25}$ +26.1 (c = *0.92*, $CHCl_3$).

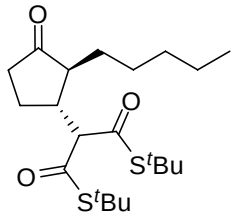
(11) *S,S*'-di-*tert*-Butyl 2-((1R,2S)-2-methyl-3-oxocyclopentyl)propanebis(thioate)



The ethyl acetate (0.2 mL) solution of CA-E product **4a** (6.9 mg, 0.02 mmol) and palladium on carbon (2.1 mg, 30% w/w) was stirred at 0°C with a H_2 balloon. Upon completion, the reaction mixture was filtered through a silica gel column to yield product **11** as a sticky colorless crystal (5.6 mg, 81% yield). Major diastereomer: **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 1.07 (d, 3H, *J* = 6.9 Hz), 1.49 (s, 18H), 1.59-1.63 (m, 1H), 1.88-1.91 (m, 1H), 2.11-2.18 (m, 2H), 2.32-2.36 (m, 1H), 2.56-2.62 (m, 1H), 3.60 (d, 1H, *J* = 5.7 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 14.0, 25.0, 29.5, 29.6 (two peaks), 36.6, 44.9, 48.5, 49.4 (two peaks), 73.7, 192.6, 192.7, 218.8; **IR** (film, cm^{-1}) 3020, 2400, 1738, 1692, 1216; **LRMS** (ESI) *m/z* 367.0 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{17}H_{28}O_3S_2Na]^+$ requires *m/z* 367.1378 Found 367.1372.

(12) *S,S*'-di-*tert*-Butyl 2-((1R,2S)-3-oxo-2-pentylcyclopentyl)propanebis(thioate)

Supporting Information



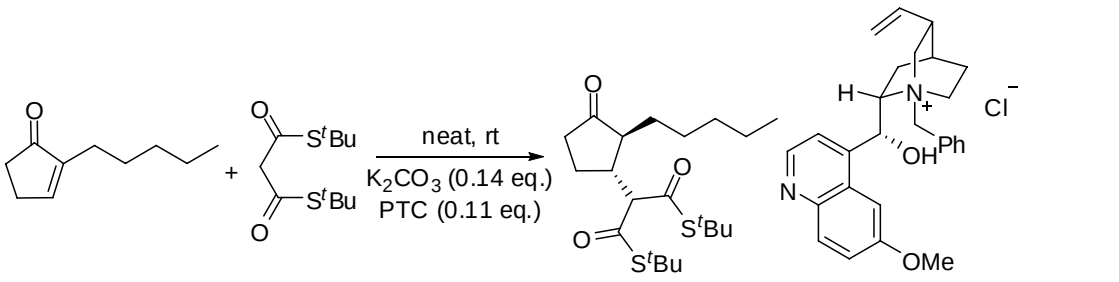
To a flame-dried rbf containing CuI (22.8 mg, 0.12 mmol, 3 equiv.) was added anhydrous THF(0.5 mL) and the reaction flask was cool to -78^{o}C. The hexane solution of *n*BuLi (1.6 M, 0.15 mL, 0.24 mmol, 6 equiv.) was then added and stirred for 30 min at -78^{o}C. The mixture of CA-E product **4a** (13.7 mg, 0.04 mmol) and TMSCl (30.4 μL, 0.24 mmol, 6 equiv.) was then added slowly to the rbf at -78^{o}C. The reaction was monitored by TLC. Upon completion, saturated NH_4Cl solution (2 mL) was added to rbf and the mixture was extracted by ether (2 mL×2). The crude product was purified by flash chromatography on silica gel to yield compound **12** as a sticky colorless crystal (10.4 mg, 65% yield). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 0.86 (t, 3H, *J* = 7.6 Hz), 1.12-1.30 (m, 5H), 1.34-1.45 (m, 2H), 1.47 (s, 9H), 1.48 (s, 9H), 1.59-1.67 (m, 2H), 1.92-1.96 (m, 1H), 2.04-2.16 (m 2H), 2.28-2.34 (m, 1H), 2.80-2.87 (m, 1H), 3058 (d, 1H, *J* = 9.4 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$, ppm) δ 14.0, 22.4, 24.7, 25.7, 28.8, 29.5, 29.6, 32.0, 37.2, 41.2, 49.4 (two peaks), 52.9, 73.5, 192.6, 192.8, 219.2; **IR** (film, cm^{-1}) 3021, 2966, 2928, 2401, 1737, 1693, 1660, 1457, 1216; **LRMS** (ESI) *m/z* 423.2 $[M+Na]^+$; **HRMS** (ESI) calcd. for $[C_{21}H_{36}O_3S_2Na]^+$ requires *m/z* 423.2004 Found 423.1998. $[\alpha]_D^{25}$ +31.7 (c = *0.06*, $CHCl_3$). **HPLC conditions:** Chiralcel AS-H column (Diacel); 98/2 hexane/2-propanol; Flow rate 0.5 mL/min; λ = 210 nm; 7.3 min (minor), 12.5 min (major).

8. Determination of absolute configuration.

The absolute configuration was determined by single crystal X-ray analyses of compound **11** (see page 53) and comparing with the literature values.[4]

[4] T. Perrard, J.-C. Plaquevent, J.-R. Desmurs and D. Hébrault, *Org. Lett.*, 2000, **2**, 2959.

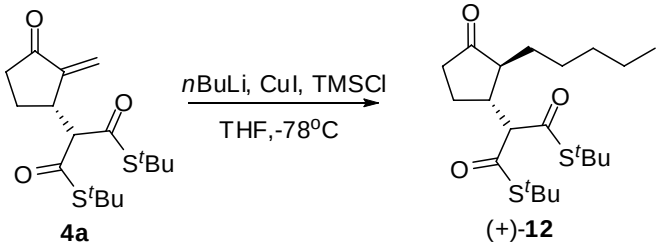
Supporting Information



(+)-**12** PTC: *N*-benzylquininium chloride

$[\alpha]_D^{25}$ +35.0 (c = *0.10*, $CHCl_3$)

93% ee



4a (+)-**12**

$[\alpha]_D^{25}$ +31.7 (c = *0.06*, $CHCl_3$)

88% ee

9. Copies of NMR spectrum.

Supporting Information

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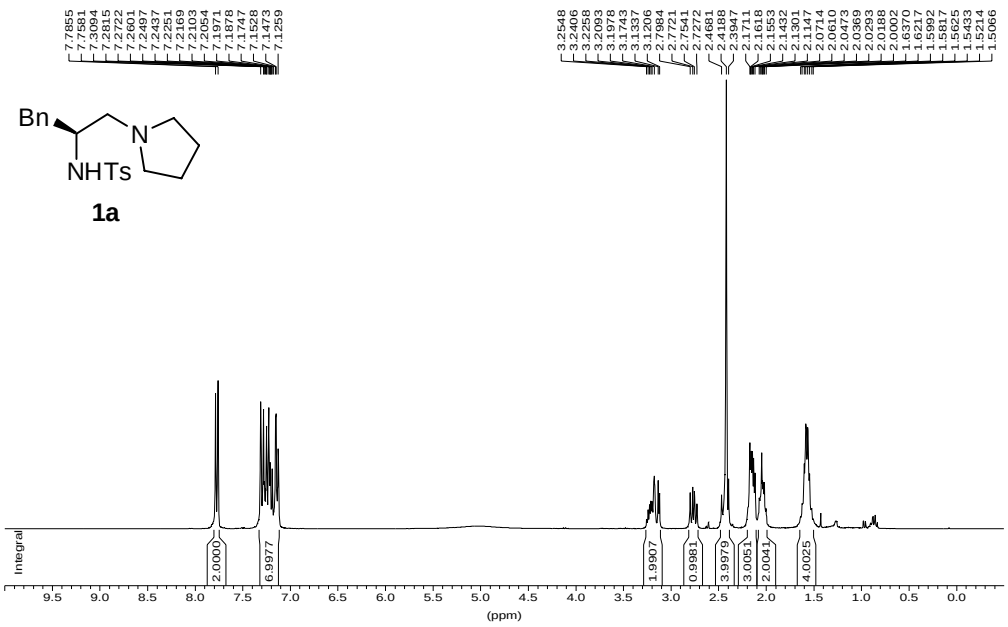

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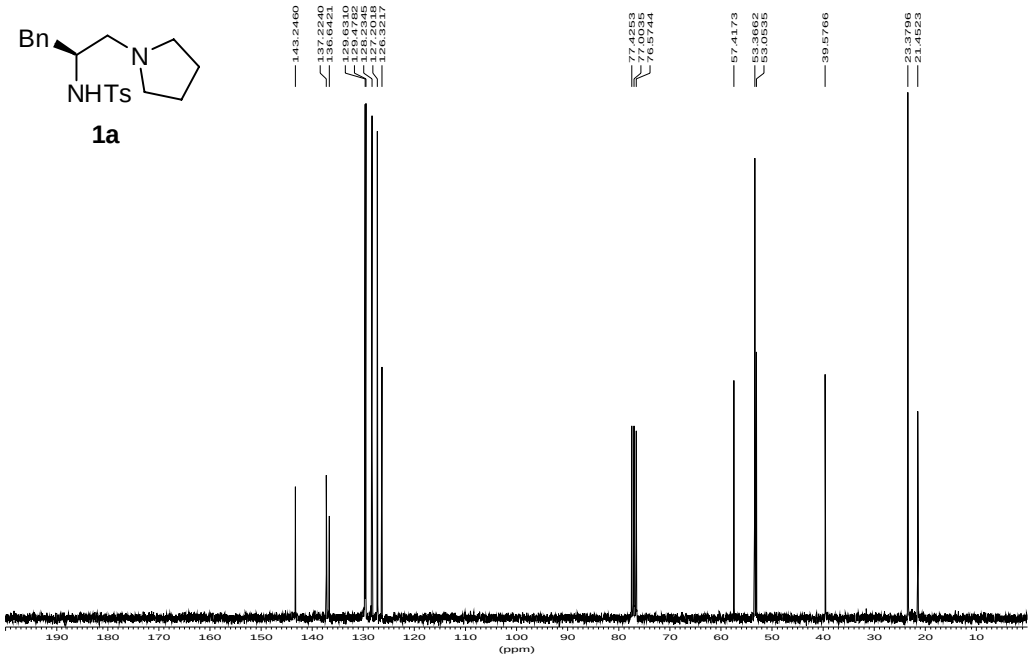

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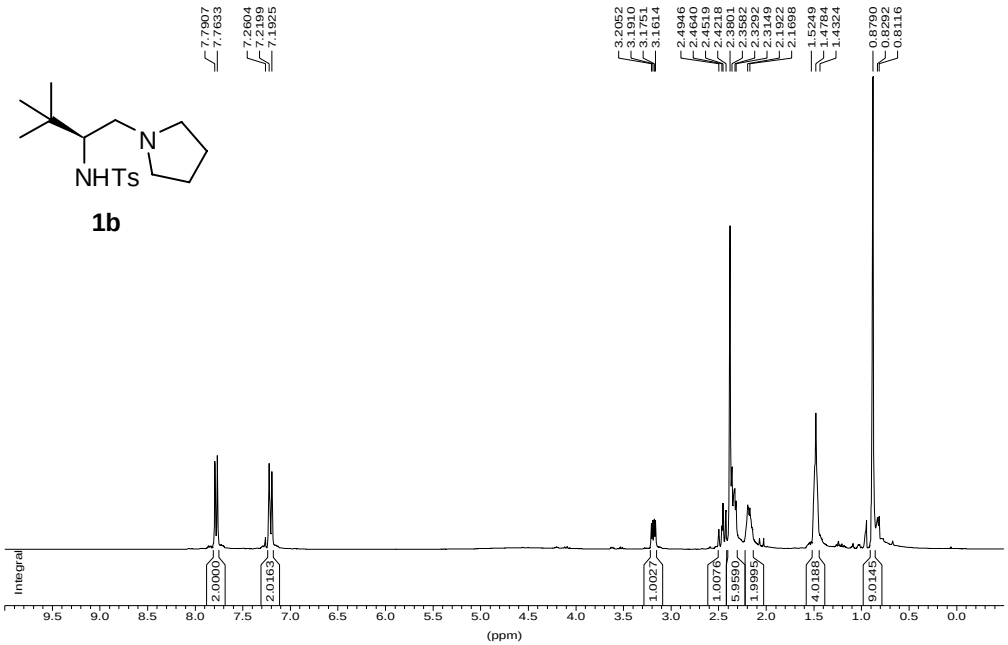

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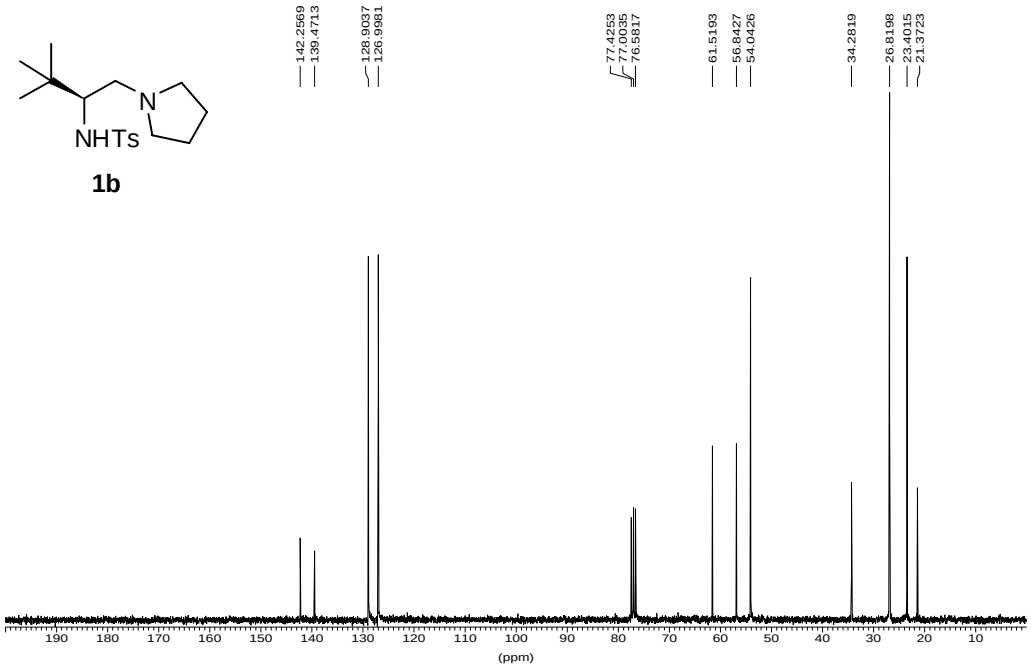

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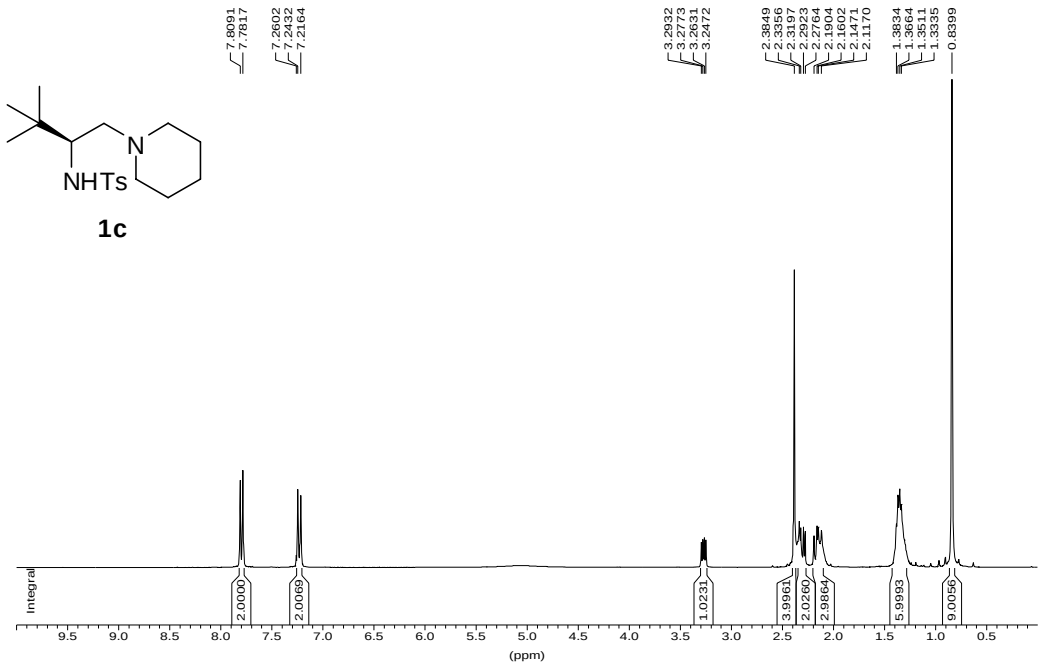

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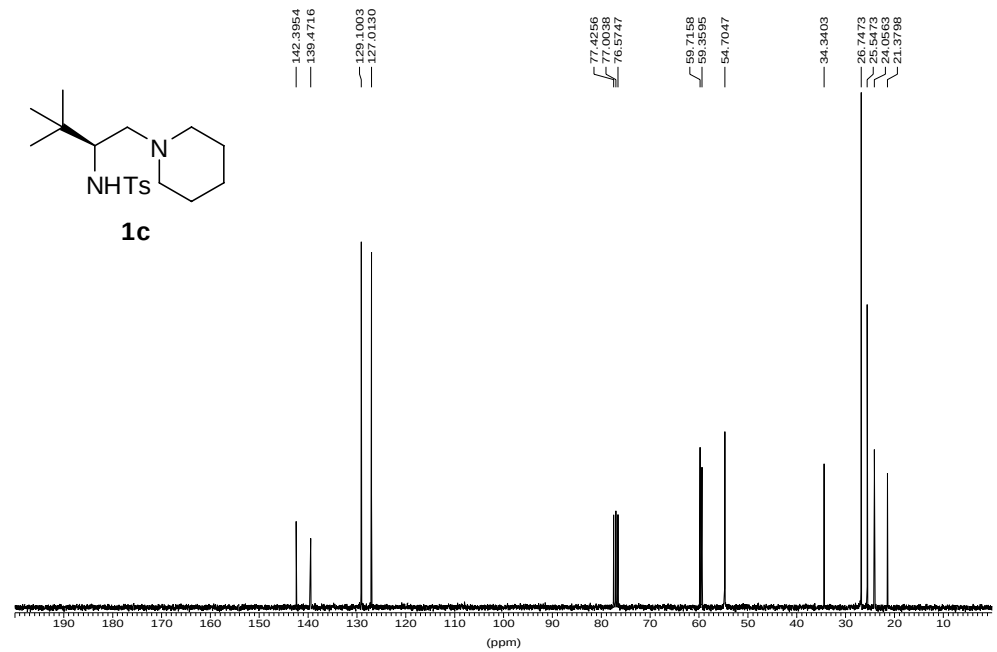

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Supporting Information

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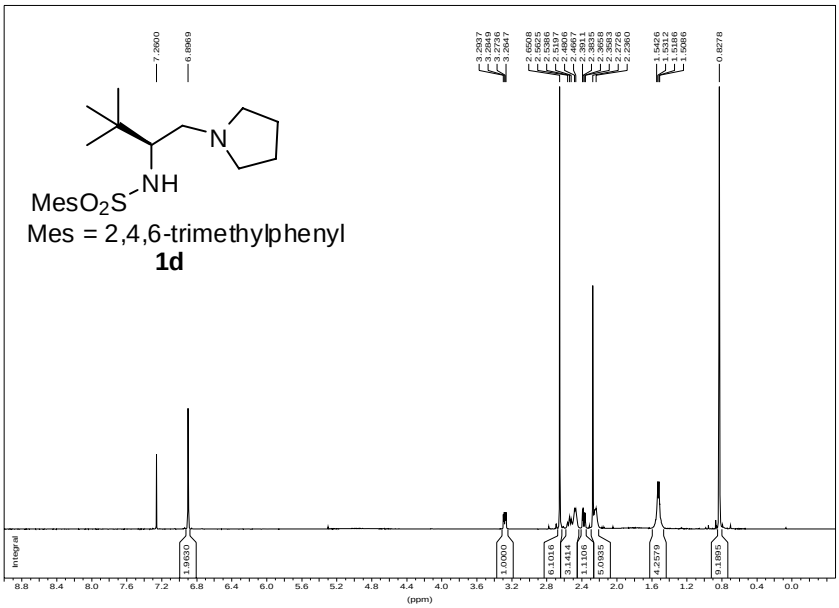

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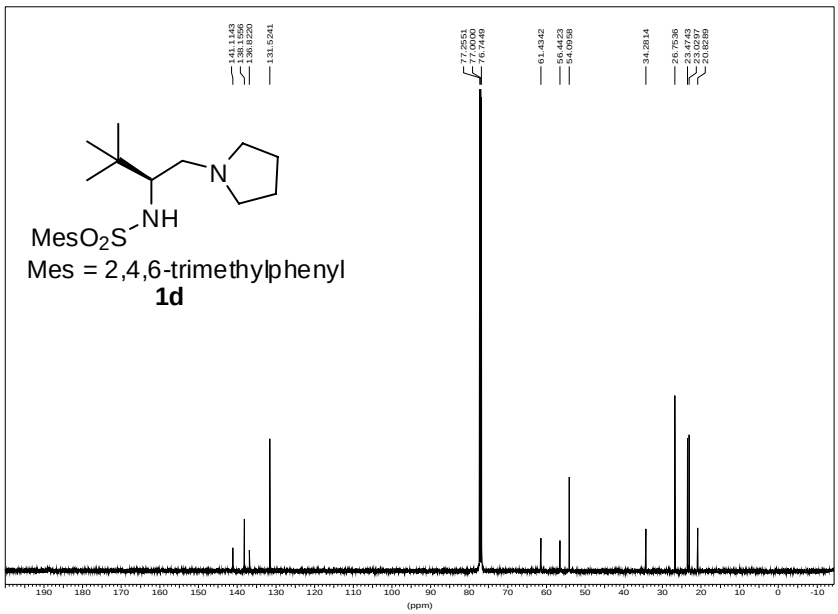

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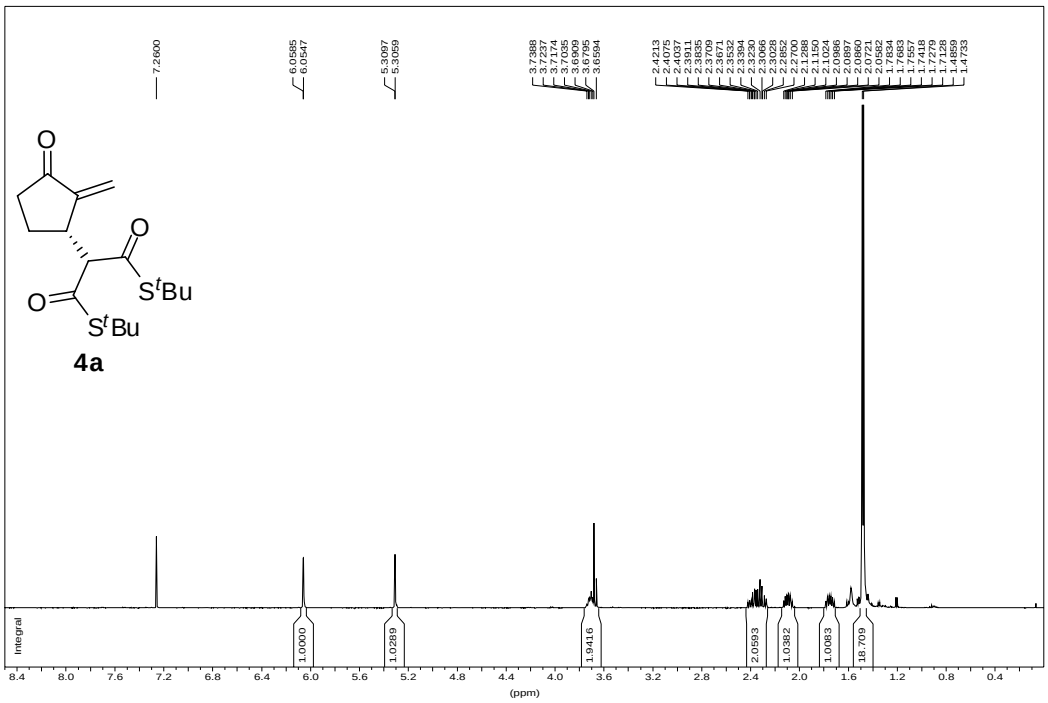

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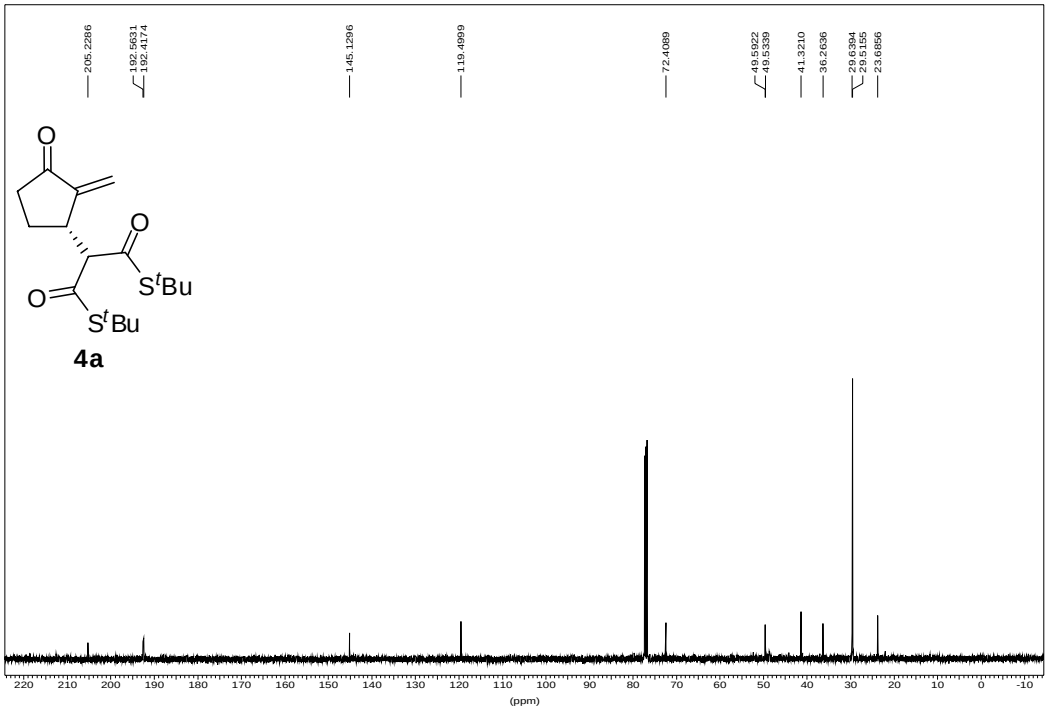

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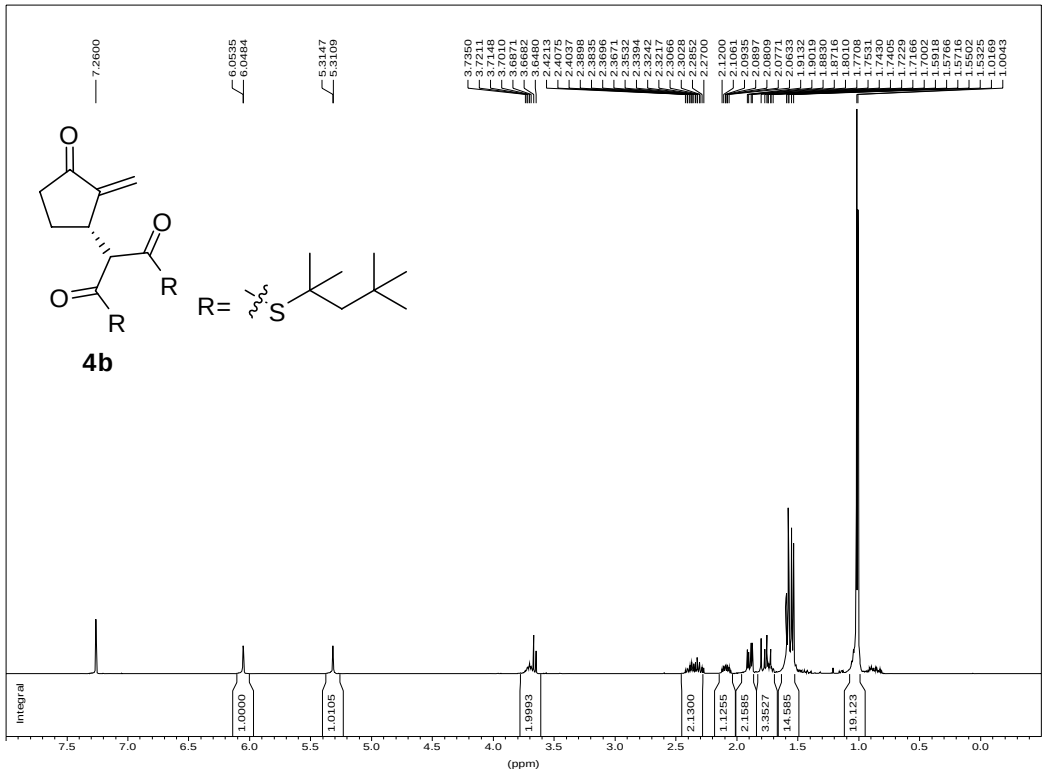

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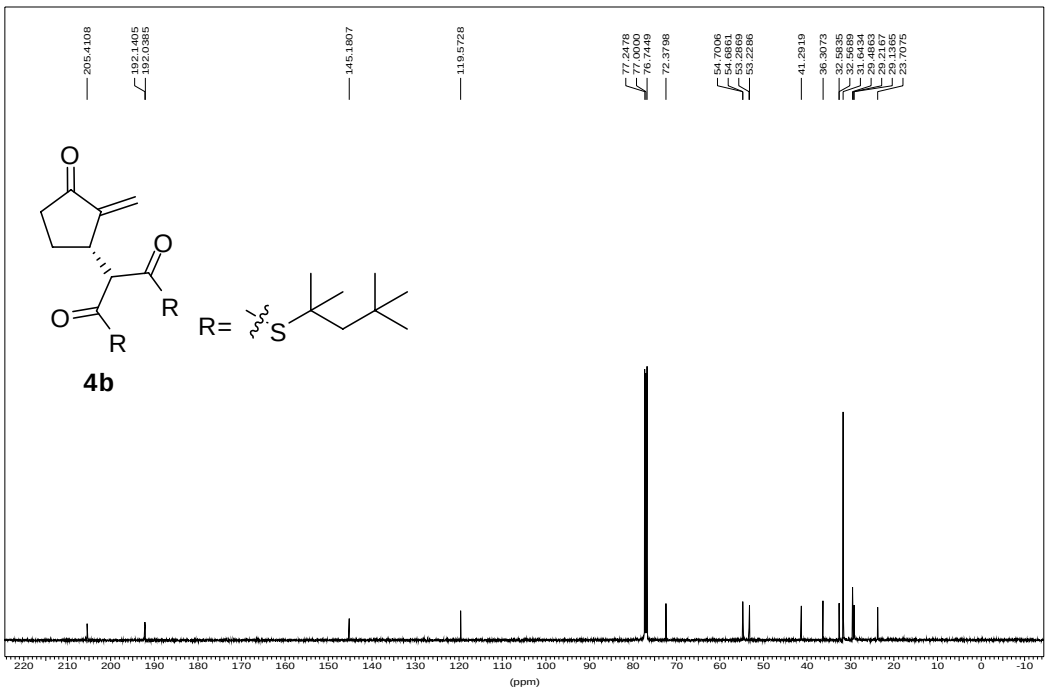

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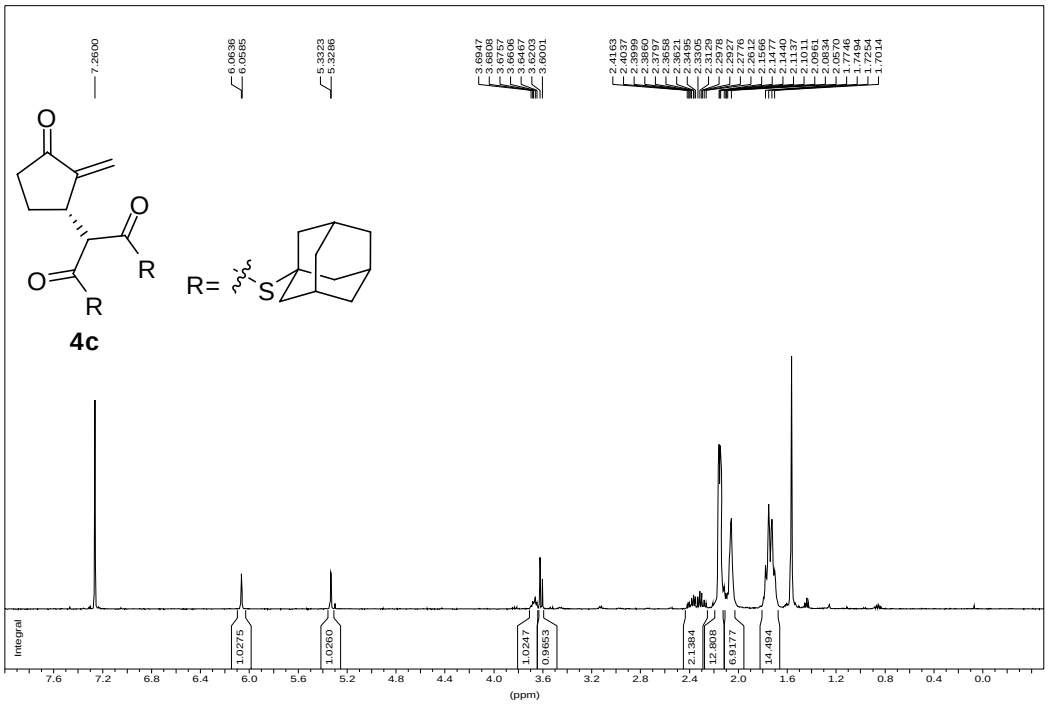

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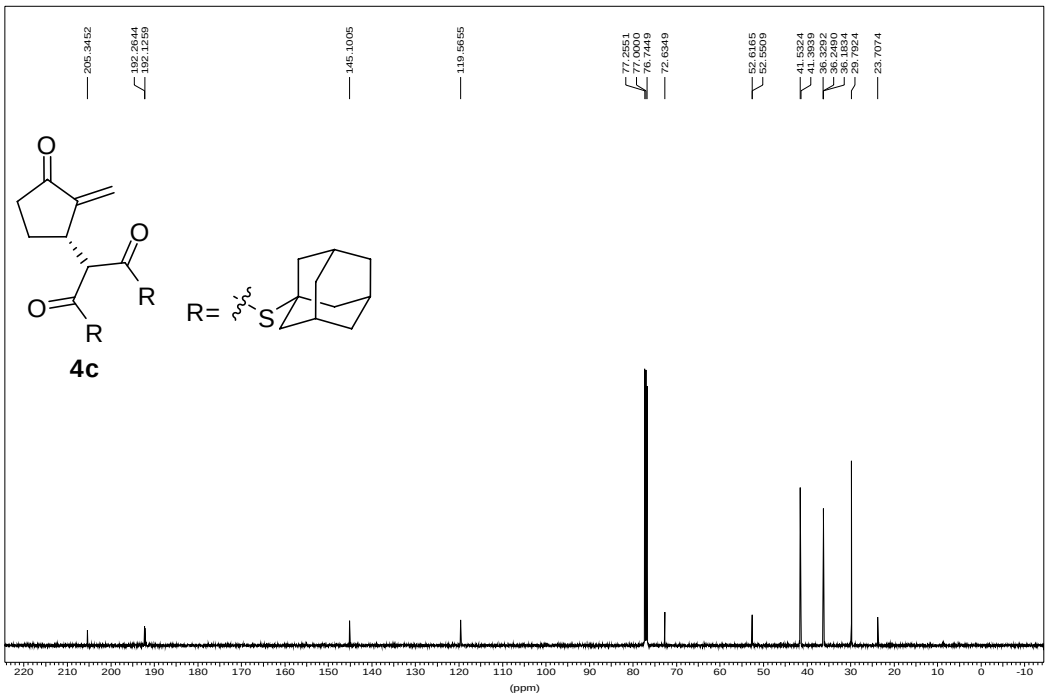

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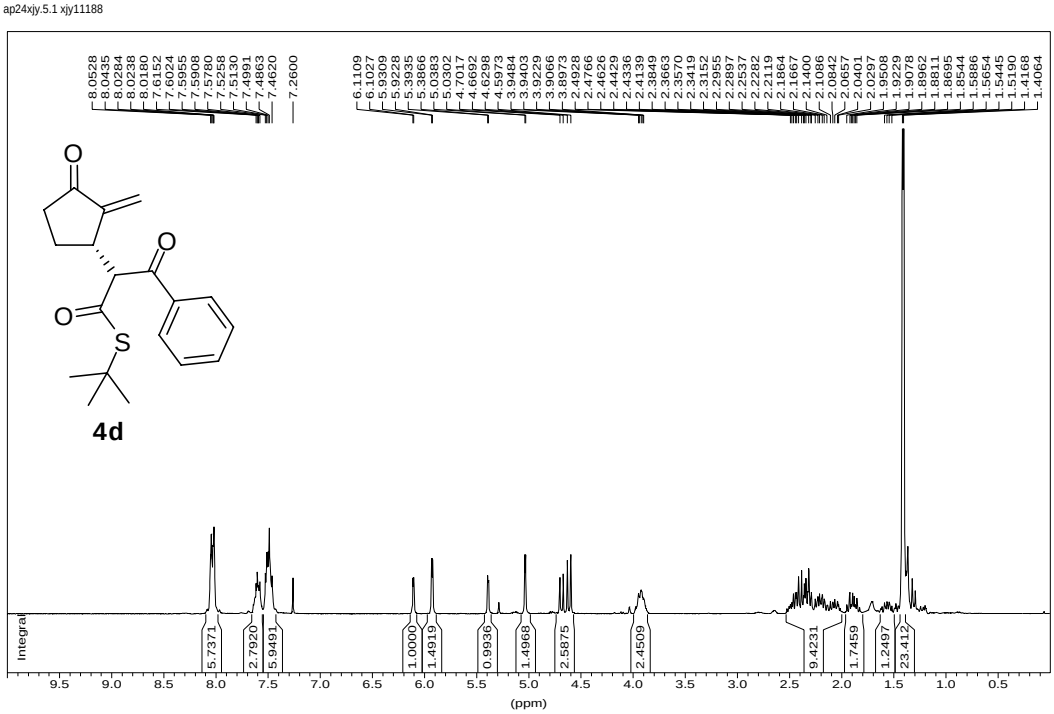

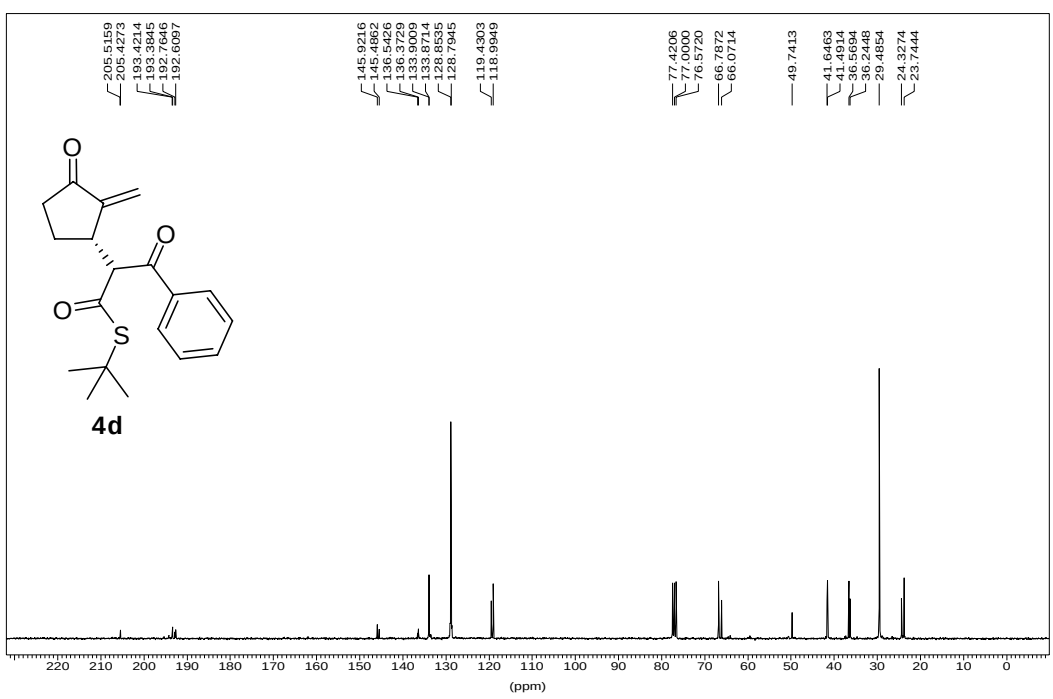

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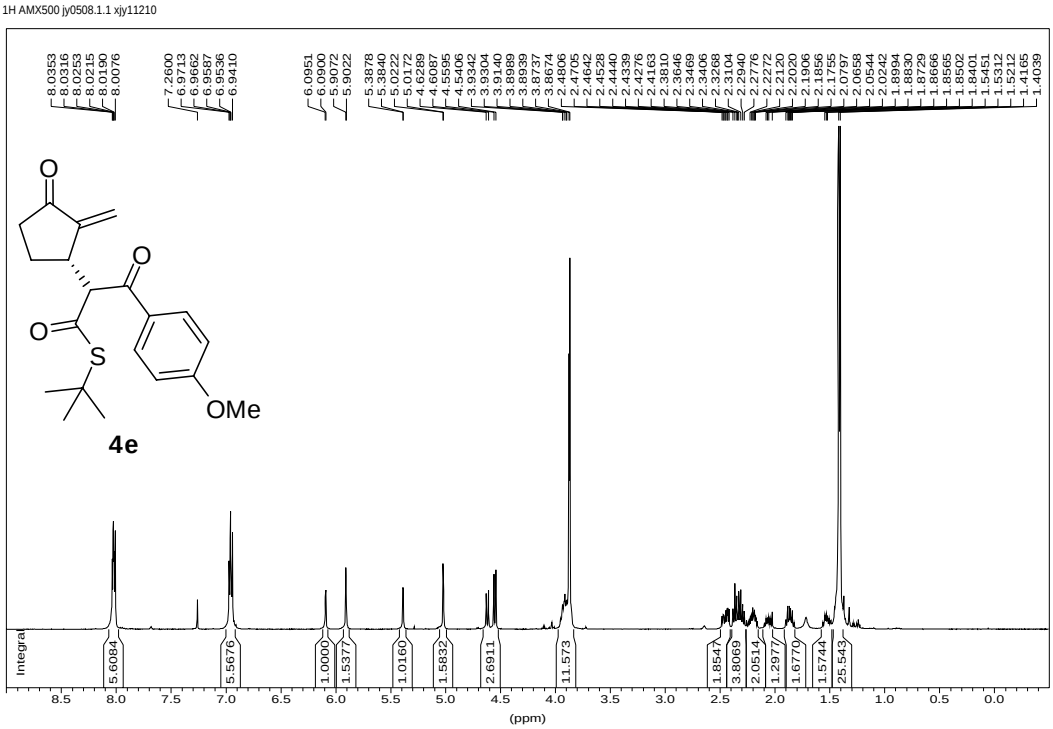

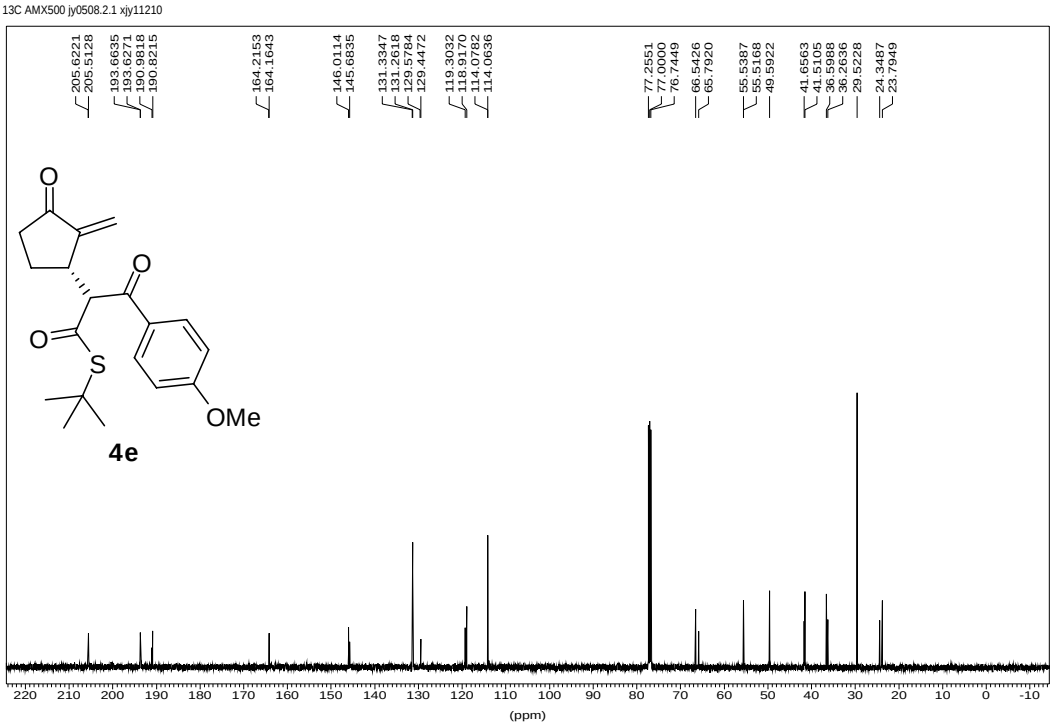

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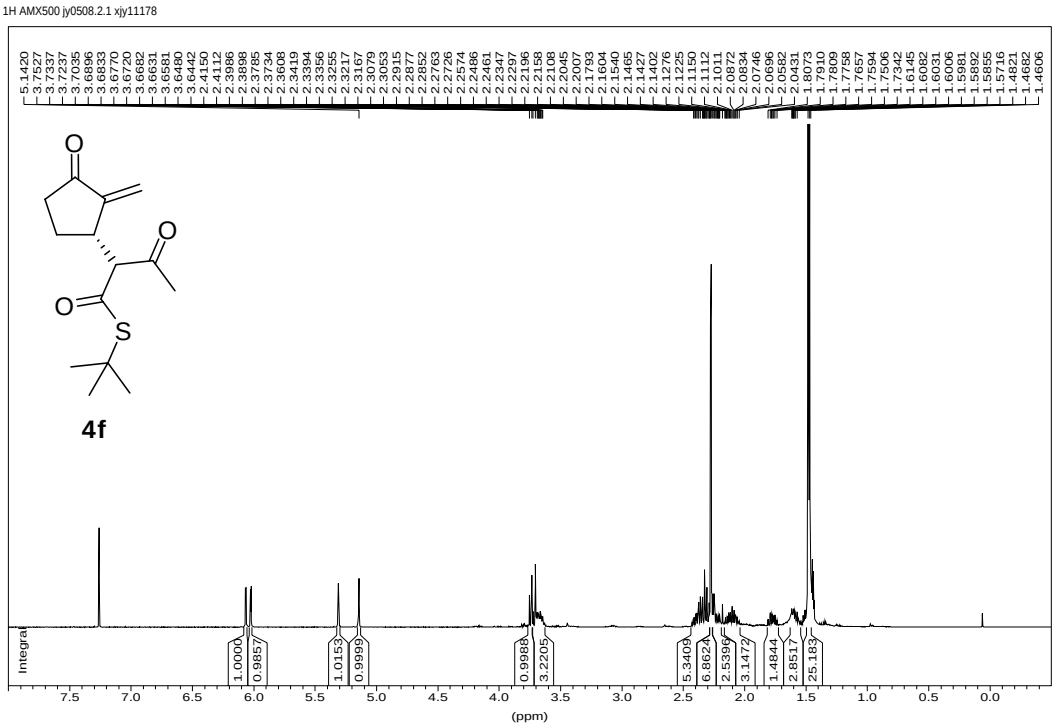

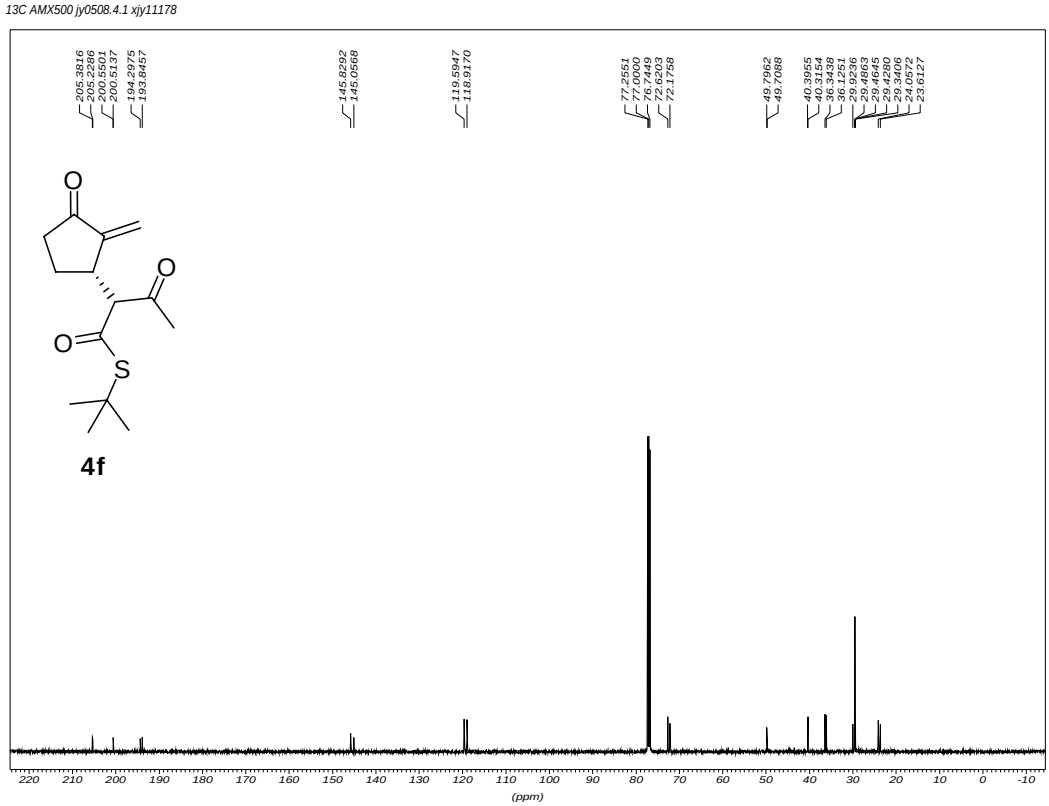

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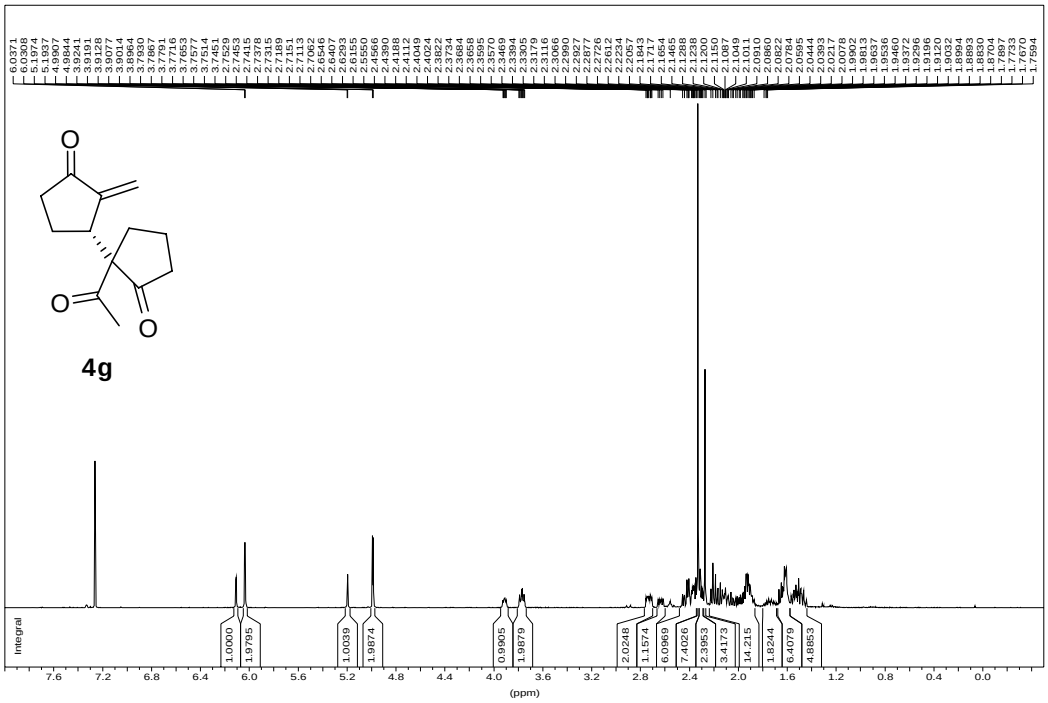

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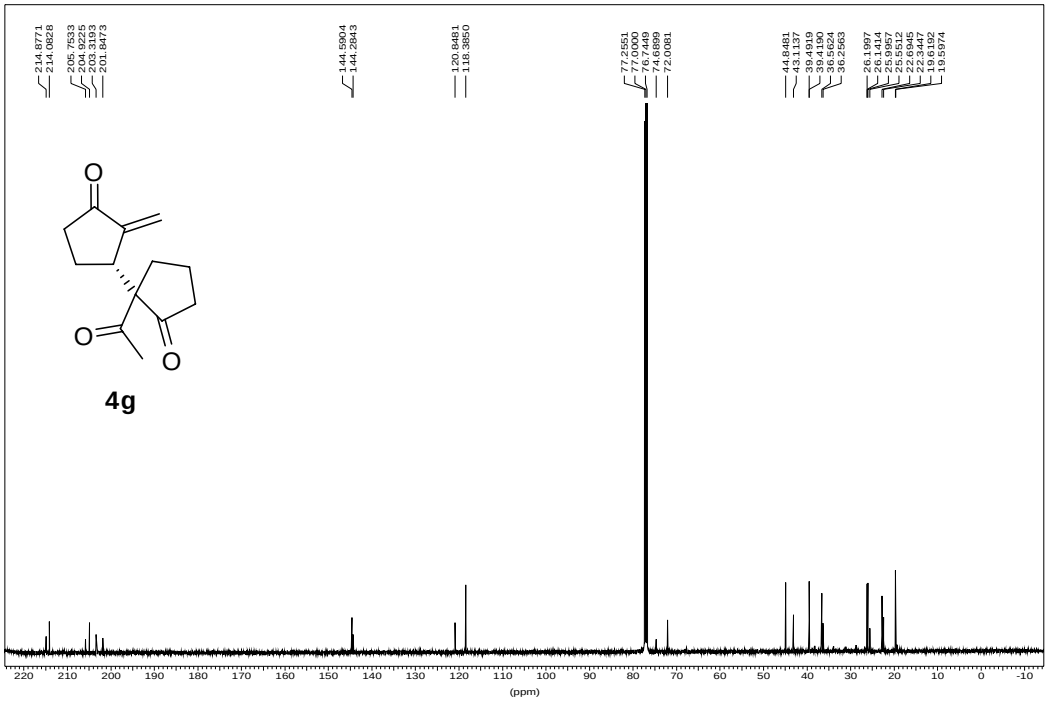

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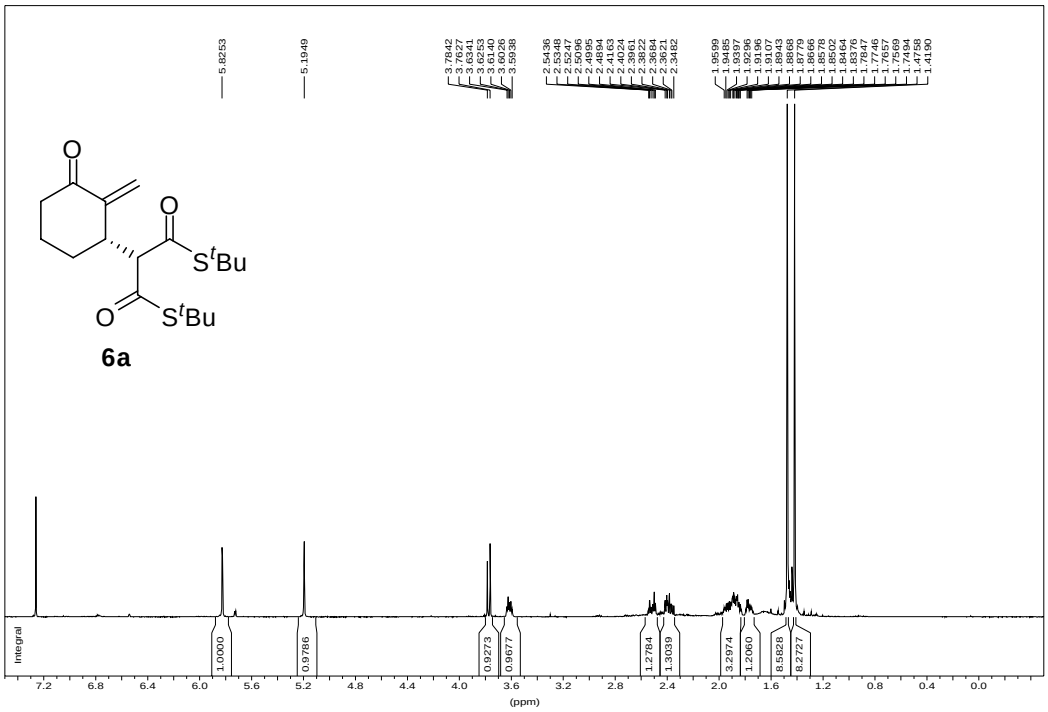

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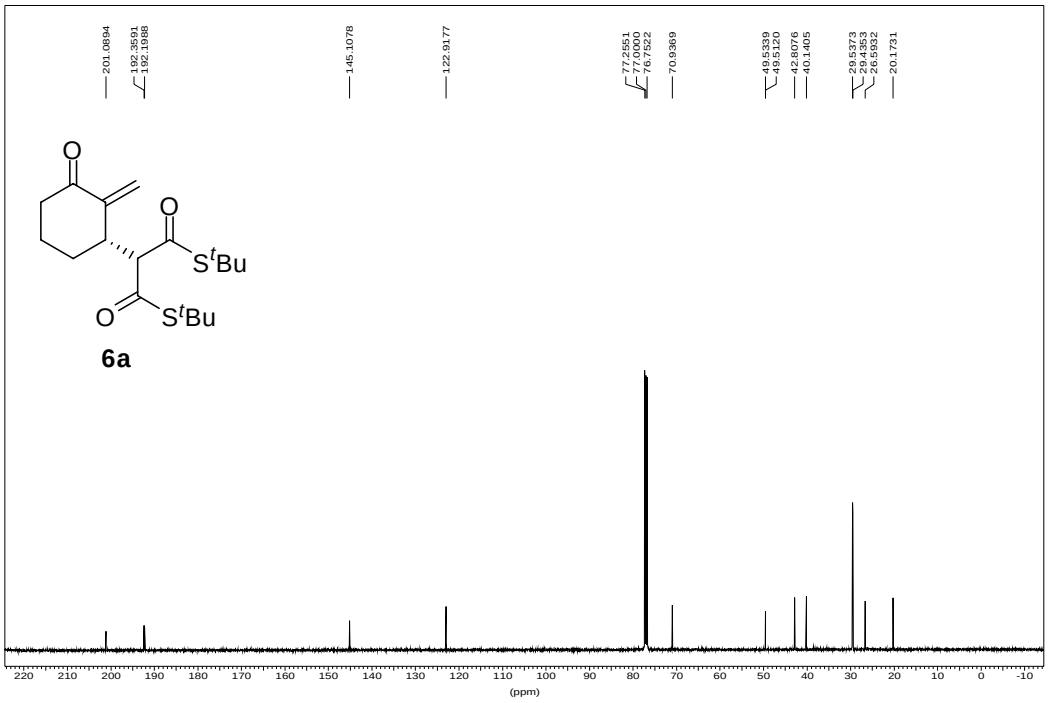

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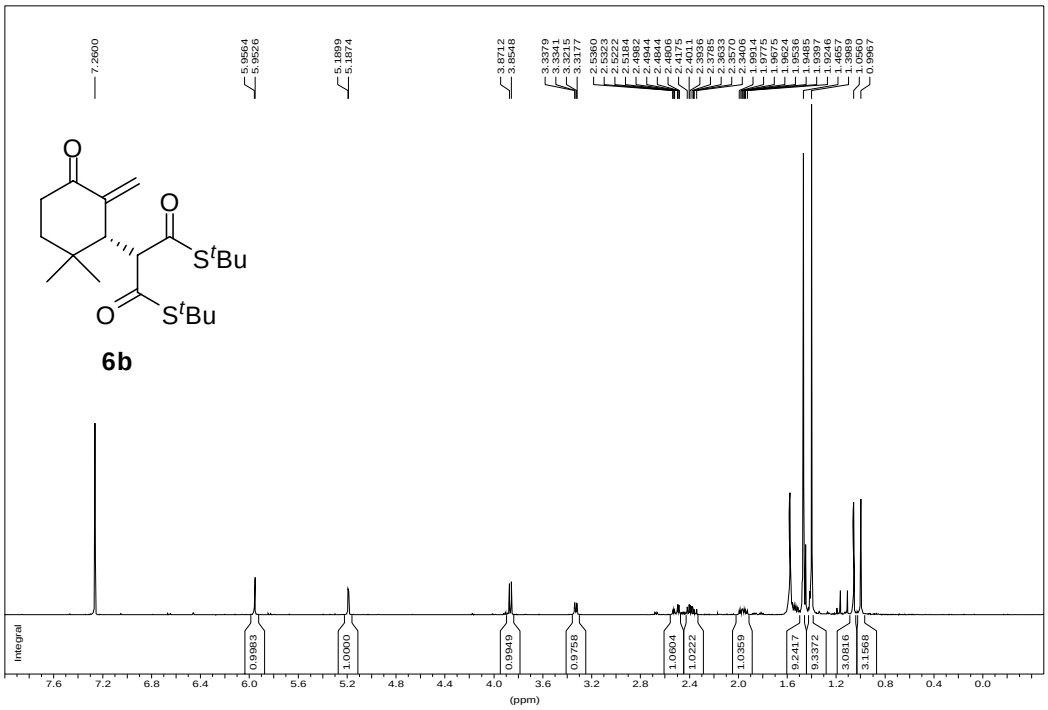

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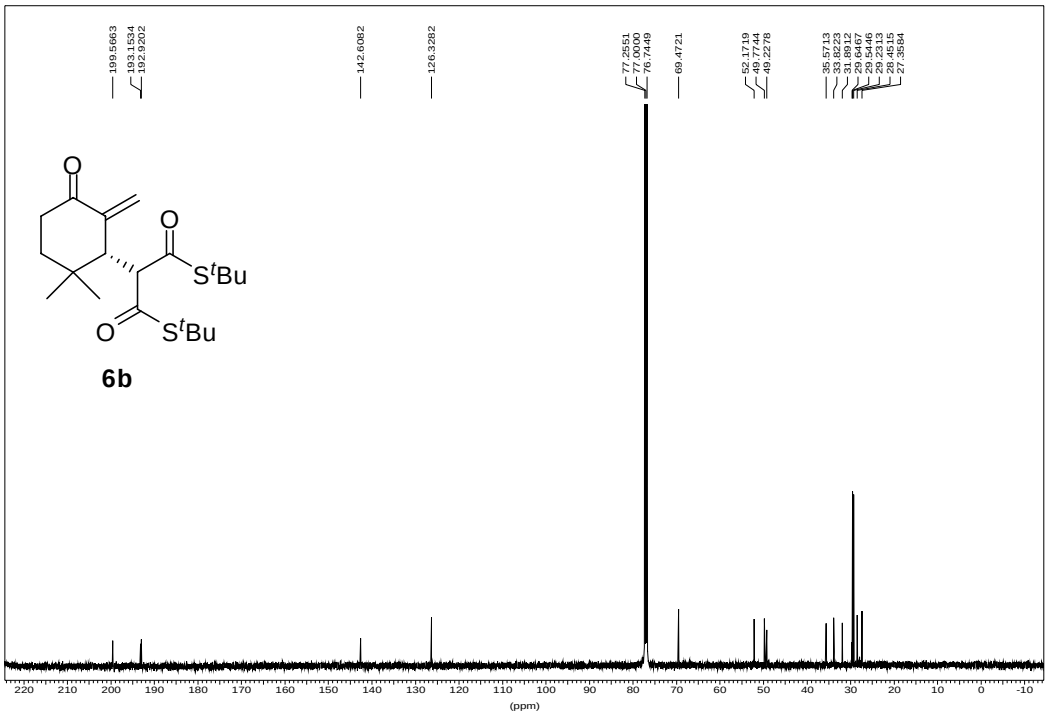

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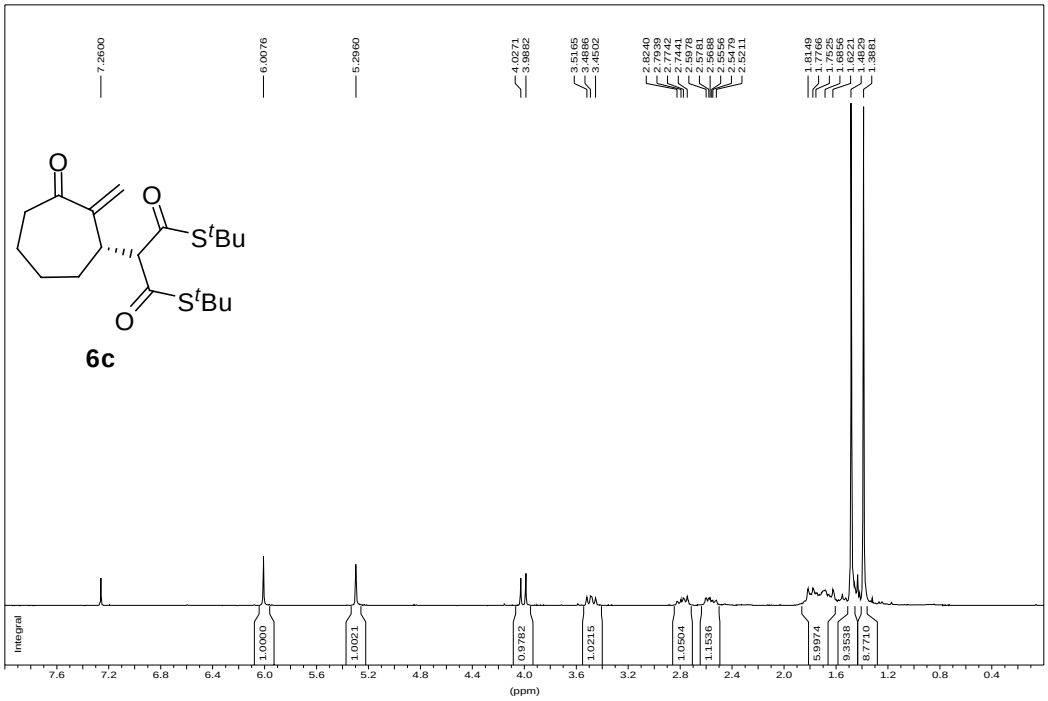

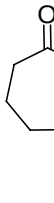

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13C Standard AC300 jl09xjy.4.1 xjy11280-2 13c

6c

Supporting Information

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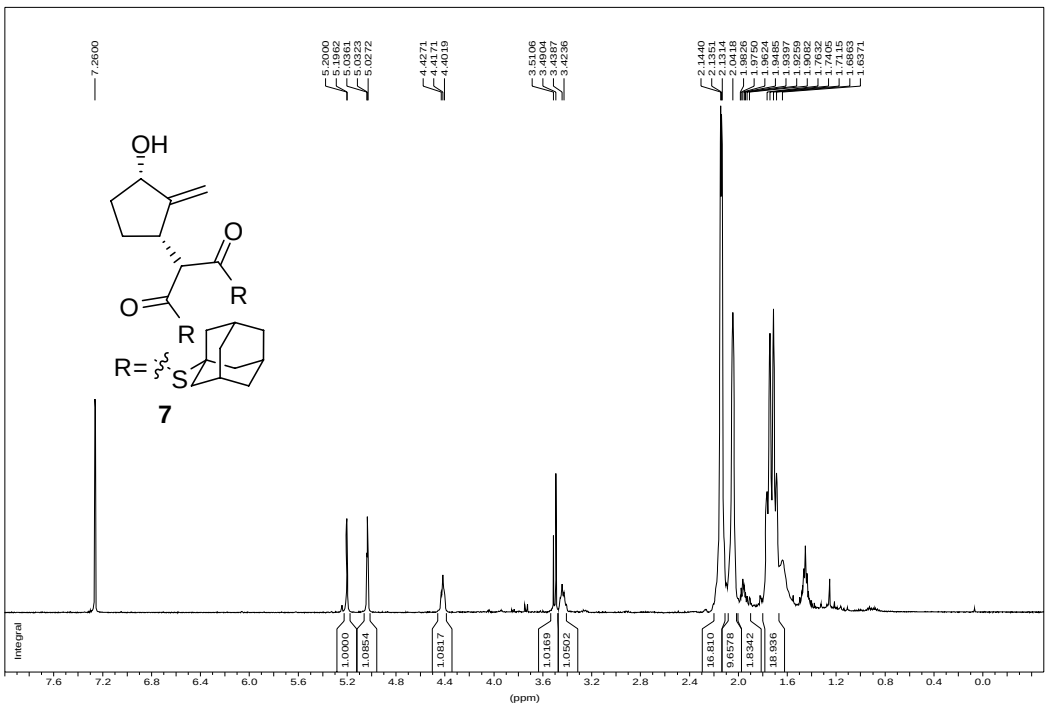

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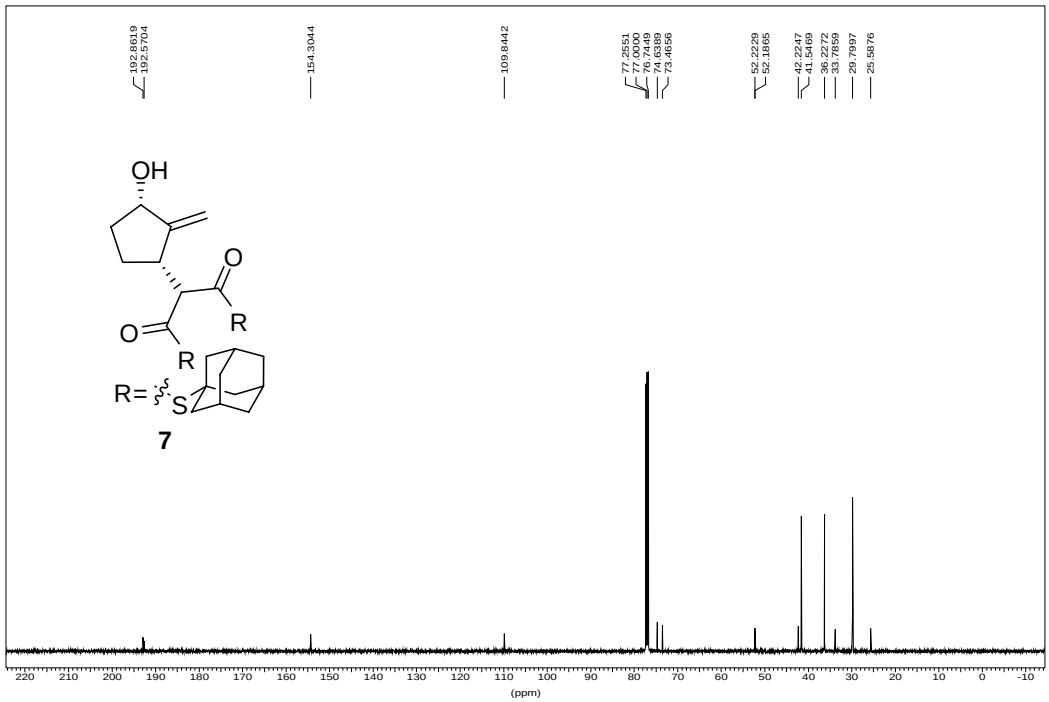

Supporting Information

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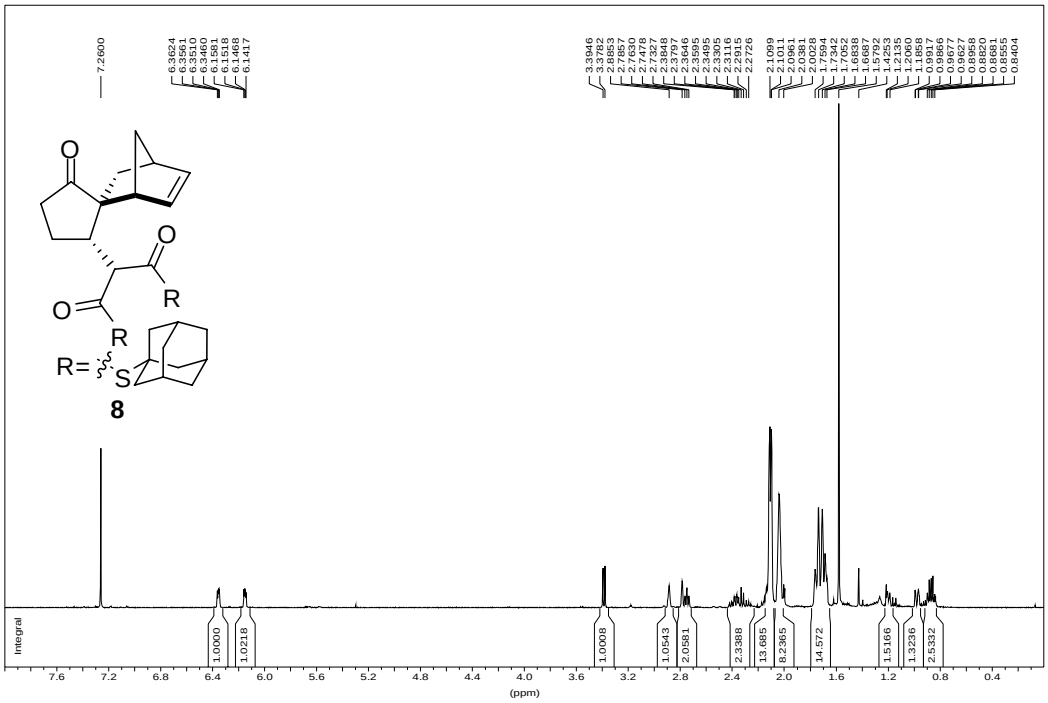

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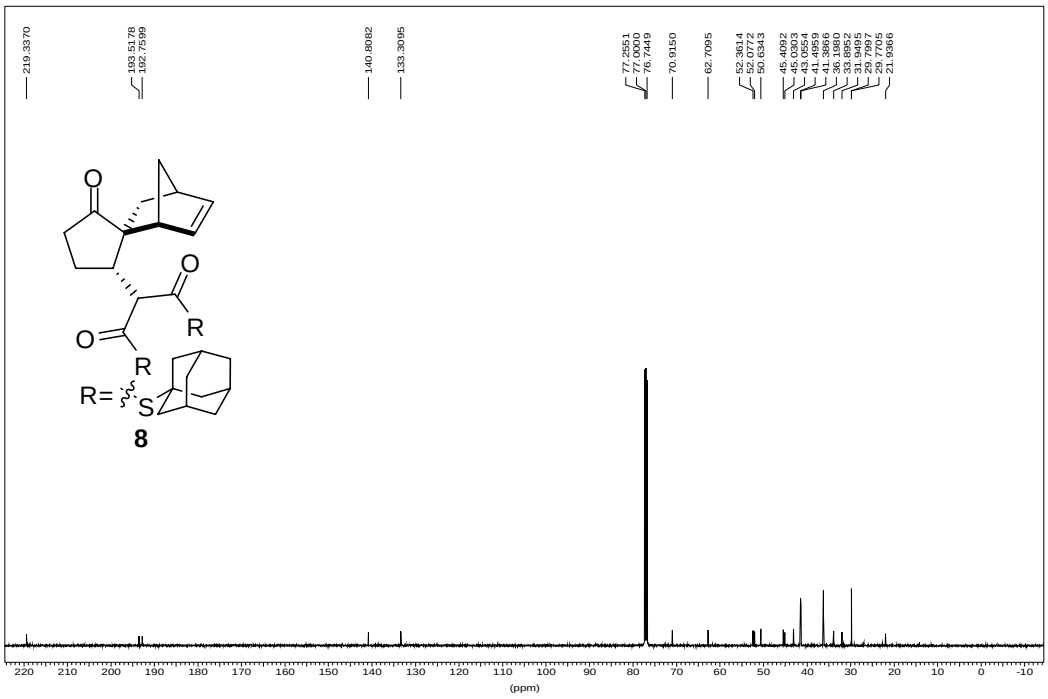

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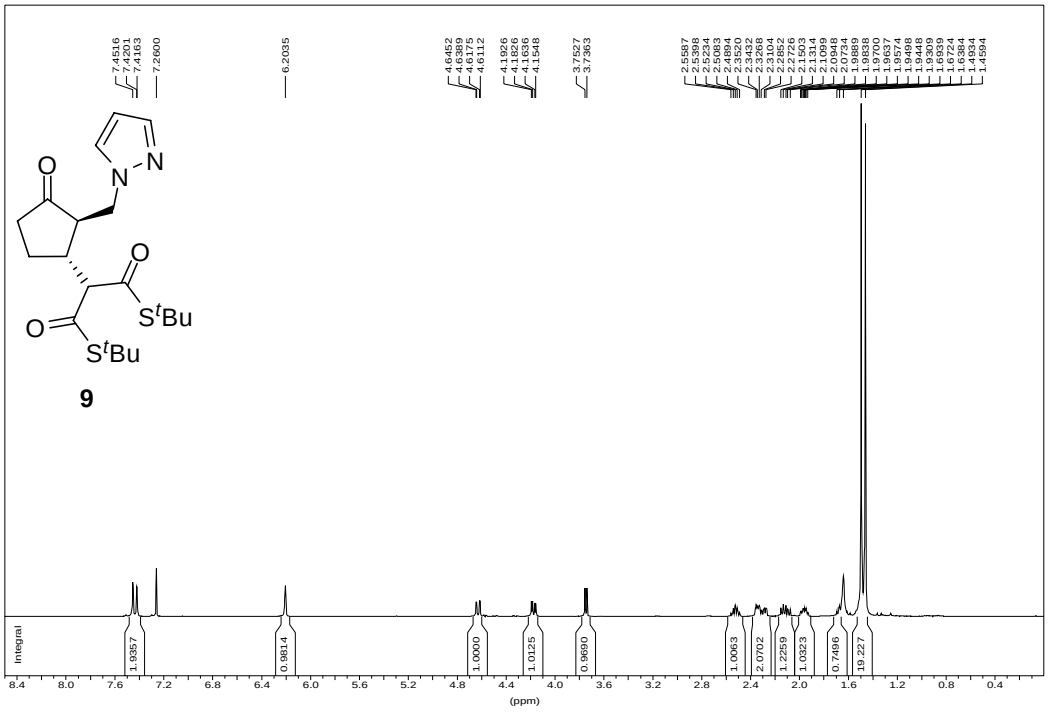

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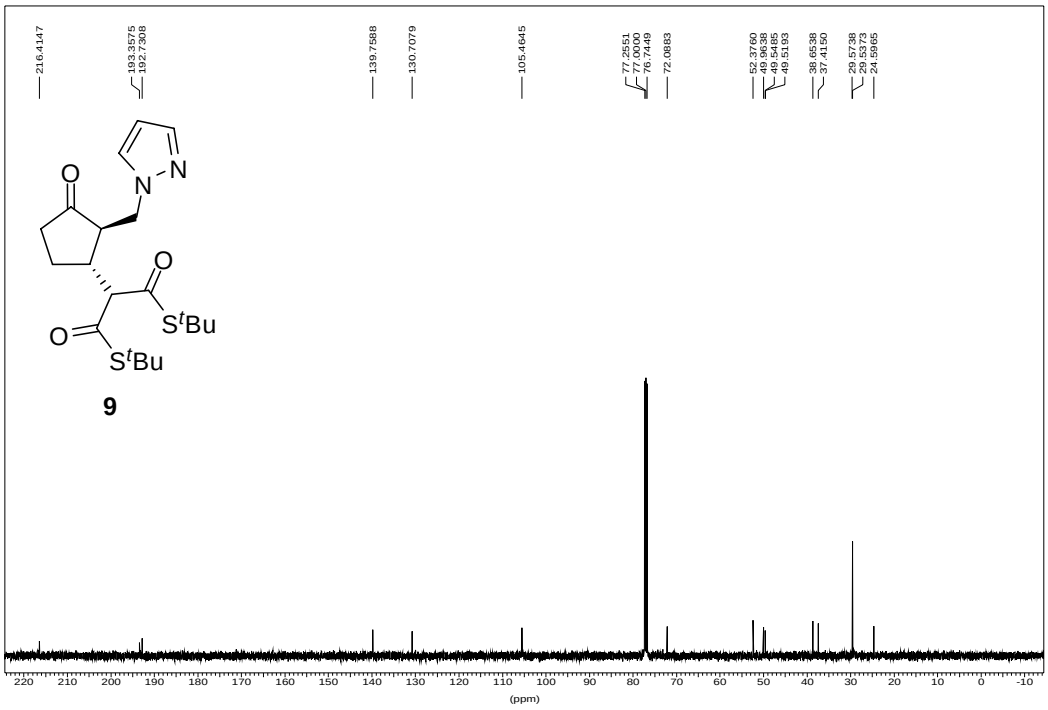

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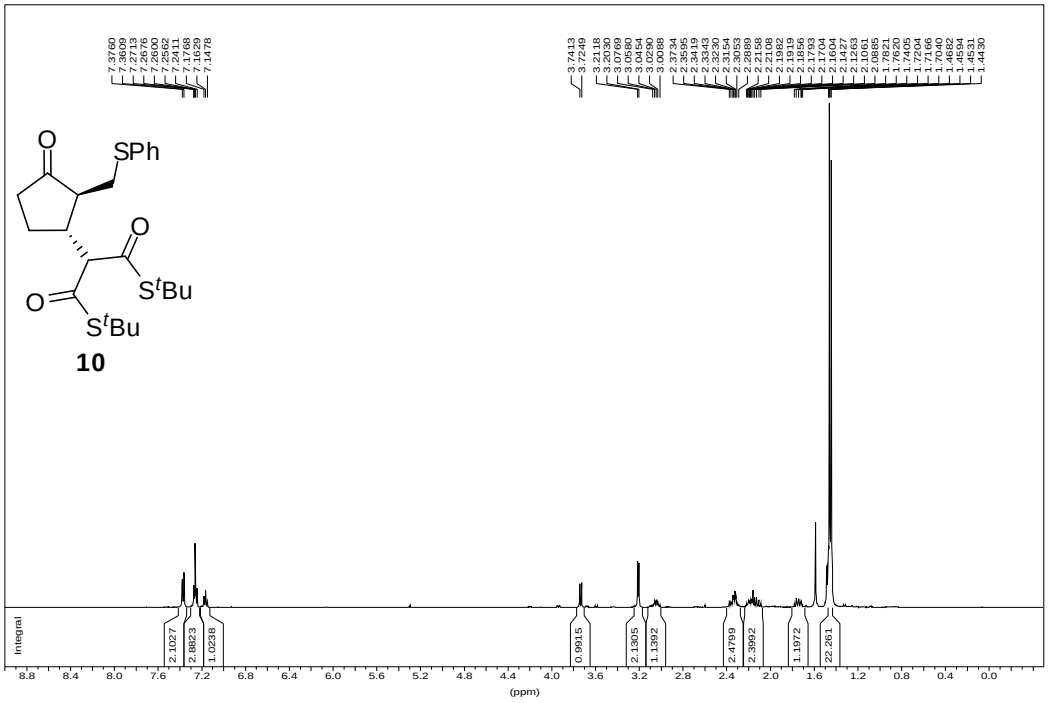

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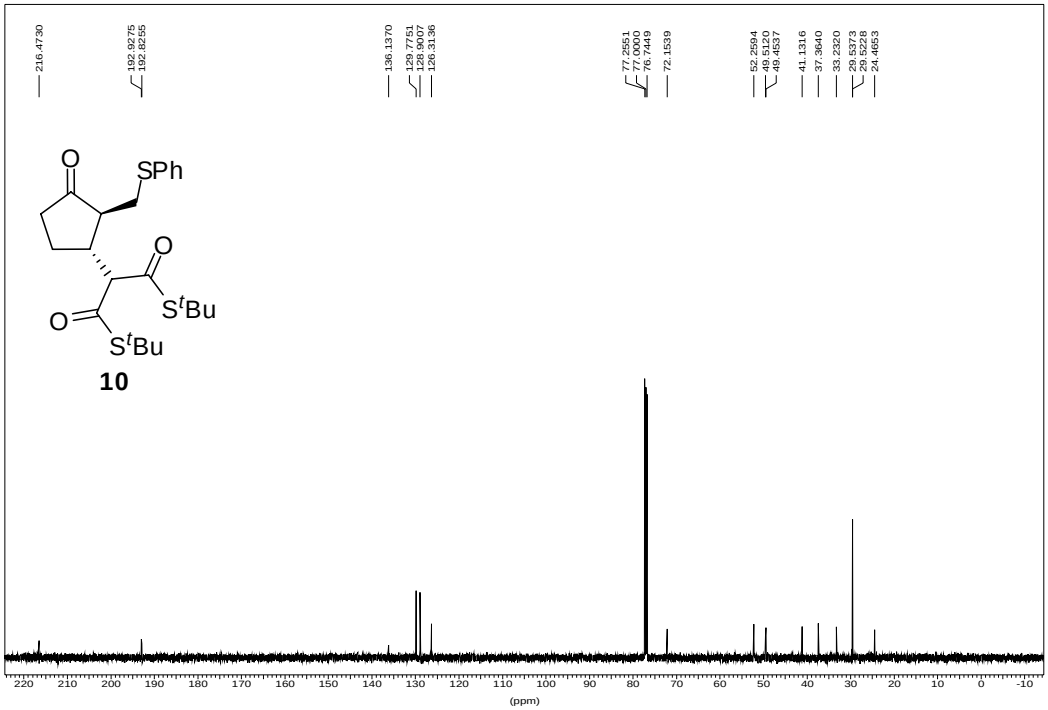

Supporting Information

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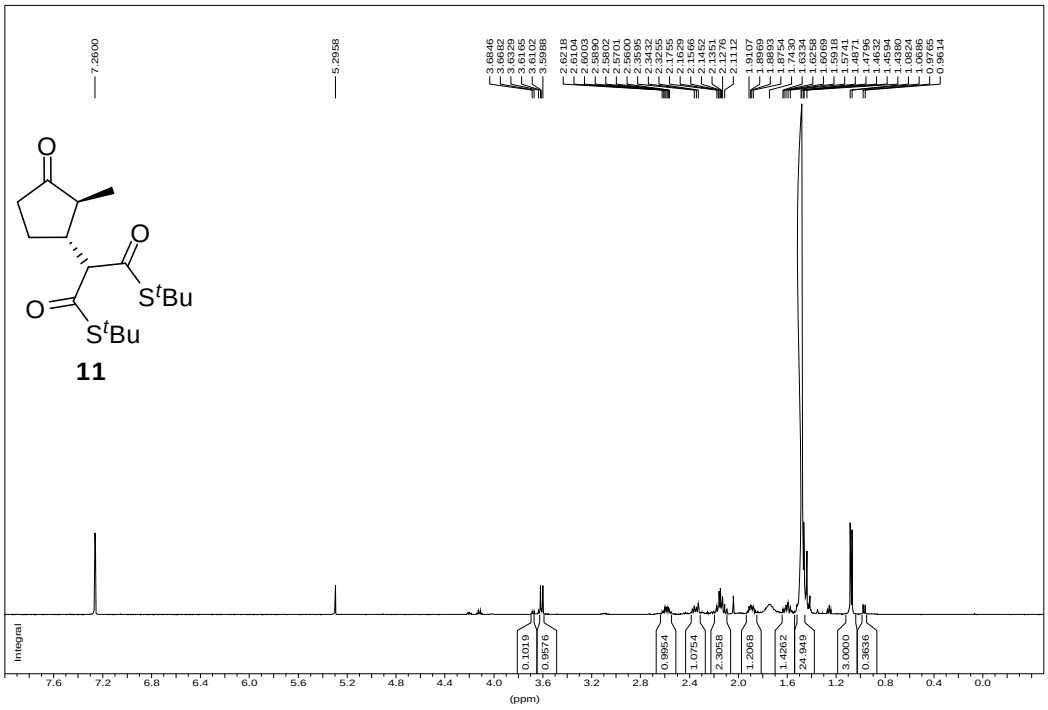

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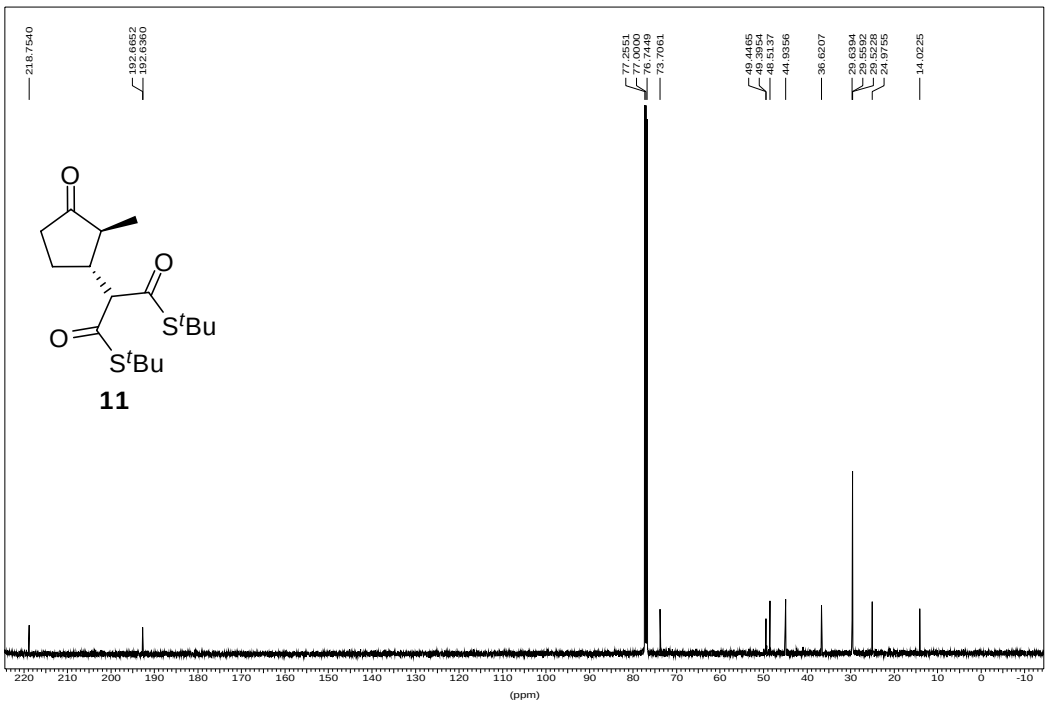

Supporting Information

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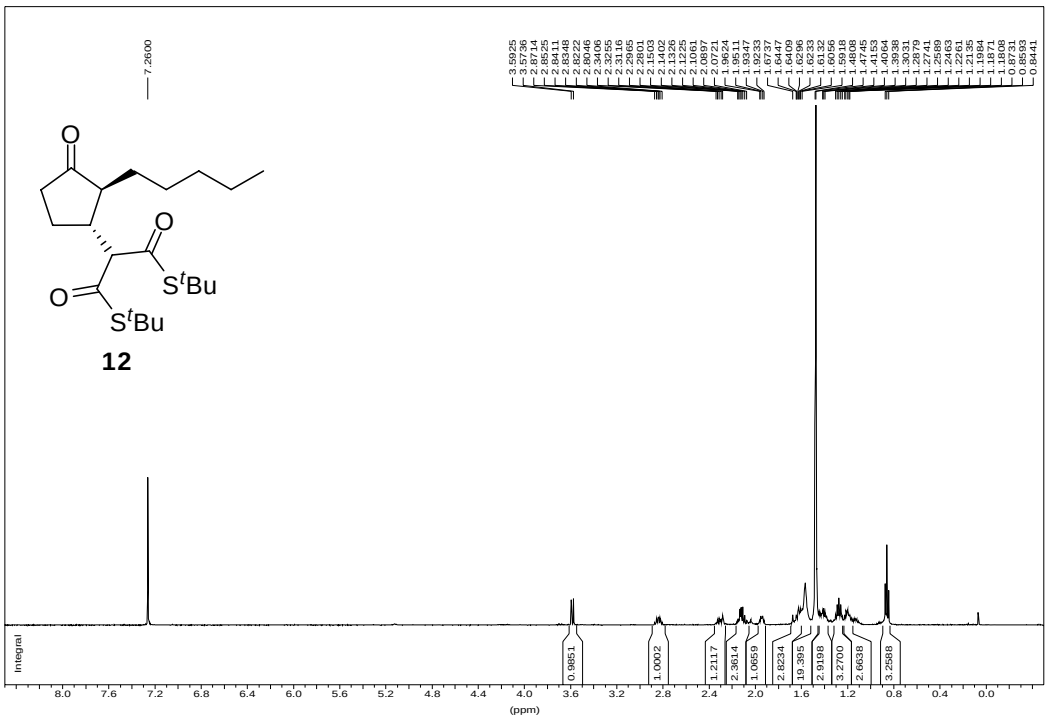

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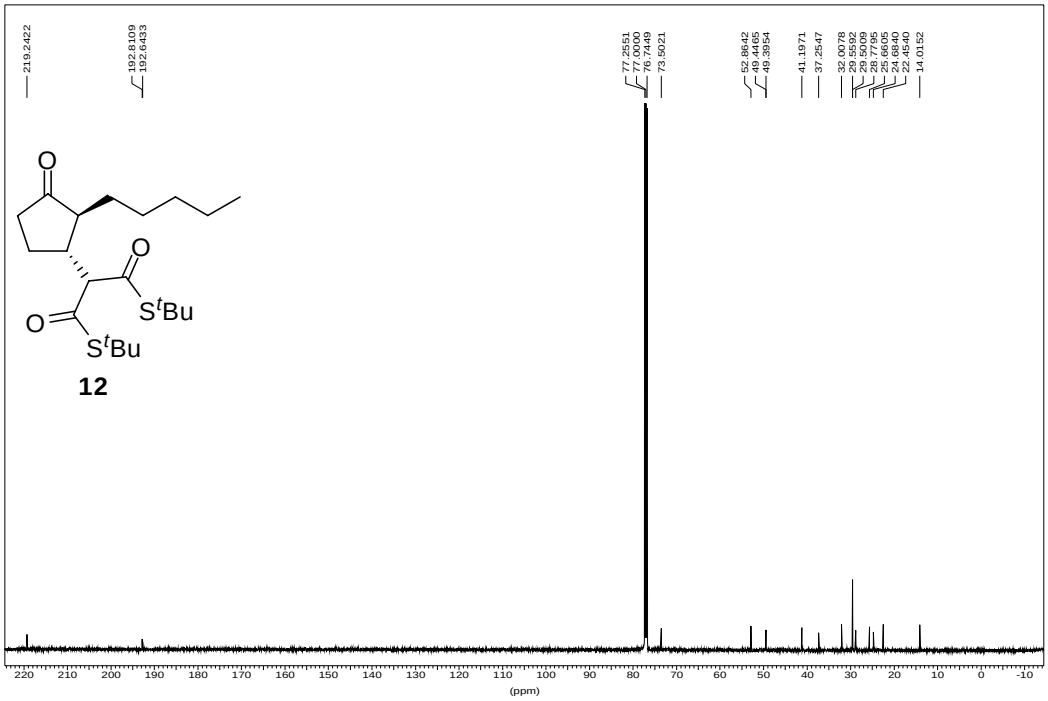
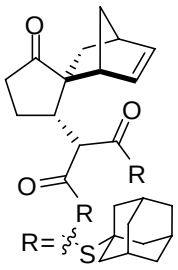


Supporting Information

10. Single Crystal X-ray Analyses for compounds 8, 11, 12 and reference 21

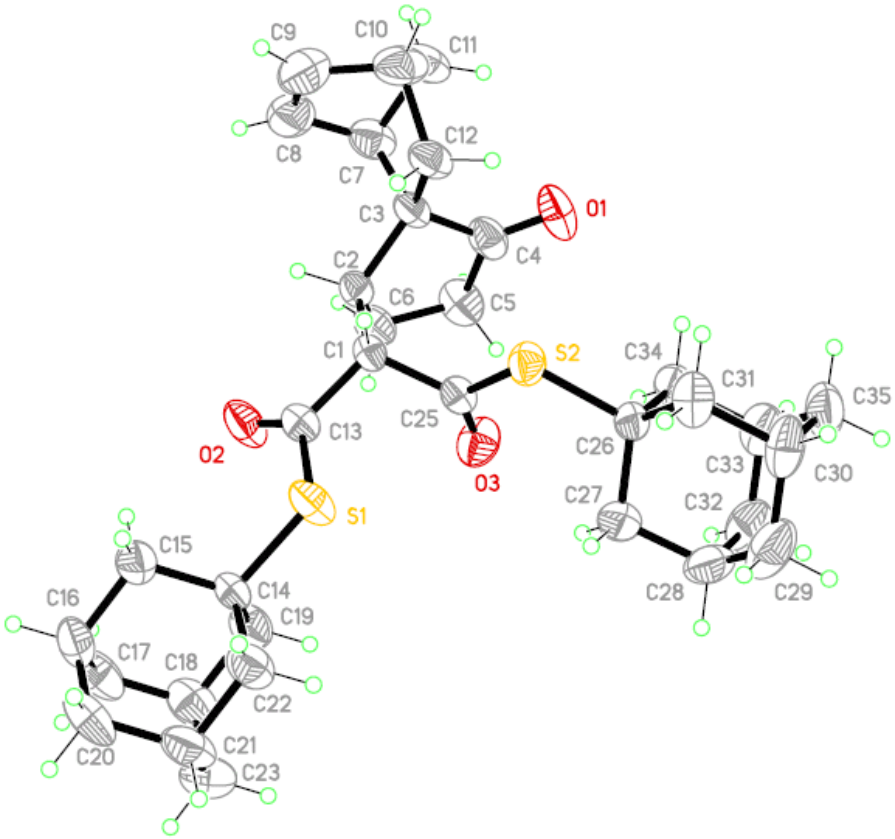
1). Compound 8 (racemic)



8

The crystal is monoclinic, space group P2(1)/c. The asymmetric unit contains one molecule of the compound $C_{34}H_{44}O_3S_2$, (as expected) Final R values are R1=0.0666 and wR2=0.1418 for 2-theta up to 55º.

The ORTEP diagram for compound **8** (The probability level of the thermal ellipsoids is 50%):



Supporting Information

Table 1. Crystal data and structure refinement for 8058a.

Identification code	8058a	
Empirical formula	C34 H44 O3 S2	
Formula weight	564.81	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.7796(12) Å	α = 90°.
	b = 13.0947(8) Å	β = 94.651(2)°.
	c = 11.9738(7) Å	γ = 90°.
Volume	2934.8(3) $Å^3$	
Z	4	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	1216	
Crystal size	0.34 x 0.20 x 0.14 mm^3	
Theta range for data collection	1.90 to 27.50°.	
Index ranges	-20<=h<=24, -16<=k<=17, -15<=l<=10	
Reflections collected	19592	
Independent reflections	6730 [R(int) = 0.0577]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9705 and 0.9304	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6730 / 0 / 352	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1418	
R indices (all data)	R1 = 0.1132, wR2 = 0.1599	
Largest diff. peak and hole	0.411 and -0.183 $e.Å^{-3}$	

Supporting Information

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 8058a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2429(1)	5450(1)	7921(1)	48(1)
S(2)	2094(1)	7008(1)	10555(1)	40(1)
O(1)	3533(1)	6831(2)	13140(2)	68(1)
O(2)	3735(1)	4829(2)	8573(2)	57(1)
O(3)	2498(1)	5080(2)	10821(2)	53(1)
C(1)	3263(1)	6105(2)	9766(2)	32(1)
C(2)	3987(1)	6031(2)	10481(2)	33(1)
C(3)	4111(1)	6859(2)	11395(2)	37(1)
C(4)	3794(2)	6383(2)	12400(2)	46(1)
C(5)	3864(2)	5238(2)	12323(2)	53(1)
C(6)	4100(2)	5024(2)	11153(2)	46(1)
C(7)	4944(2)	6980(2)	11768(3)	50(1)
C(8)	5284(2)	7330(3)	10758(3)	63(1)
C(9)	5079(2)	8273(3)	10544(3)	66(1)
C(10)	4594(2)	8582(2)	11425(3)	61(1)
C(11)	4935(2)	7979(2)	12425(3)	59(1)
C(12)	3890(2)	7976(2)	11144(2)	45(1)
C(13)	3246(2)	5366(2)	8766(2)	39(1)
C(14)	2436(1)	4411(2)	6882(2)	35(1)
C(15)	2997(2)	4560(2)	6056(2)	49(1)
C(16)	2919(2)	3716(2)	5163(2)	54(1)
C(17)	3008(2)	2683(2)	5728(3)	60(1)
C(18)	2438(2)	2542(2)	6540(3)	58(1)
C(19)	2516(2)	3371(2)	7438(2)	49(1)
C(20)	2183(2)	3794(2)	4541(2)	63(1)
C(21)	1616(2)	3644(2)	5361(3)	59(1)
C(22)	1691(2)	4488(2)	6251(2)	51(1)
C(23)	1703(2)	2606(3)	5918(3)	73(1)
C(25)	2617(1)	5903(2)	10433(2)	35(1)
C(26)	1354(1)	6626(2)	11377(2)	36(1)
C(27)	929(2)	5734(2)	10839(2)	52(1)

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C(28)	289(2)	5518(3)	11514(3)	64(1)
C(29)	-190(2)	6461(3)	11478(3)	74(1)
C(30)	224(2)	7350(3)	12015(3)	60(1)
C(31)	875(2)	7576(2)	11368(3)	52(1)
C(32)	550(2)	5263(3)	12721(3)	66(1)
C(33)	957(2)	6167(3)	13239(2)	58(1)
C(34)	1613(1)	6382(2)	12585(2)	45(1)
C(35)	474(2)	7103(3)	13217(3)	65(1)

Supporting Information

Table 3. Bond lengths [Å] and angles [°] for 8058a.

S(1)-C(13)	1.771(3)
S(1)-C(14)	1.844(2)
S(2)-C(25)	1.762(3)
S(2)-C(26)	1.836(3)
O(1)-C(4)	1.200(3)
O(2)-C(13)	1.195(3)
O(3)-C(25)	1.202(3)
C(1)-C(25)	1.528(3)
C(1)-C(13)	1.537(3)
C(1)-C(2)	1.551(3)
C(2)-C(3)	1.545(3)
C(2)-C(6)	1.550(3)
C(3)-C(4)	1.519(4)
C(3)-C(12)	1.542(3)
C(3)-C(7)	1.601(4)
C(4)-C(5)	1.508(4)
C(5)-C(6)	1.529(4)
C(7)-C(8)	1.484(5)
C(7)-C(11)	1.527(4)
C(8)-C(9)	1.312(5)
C(9)-C(10)	1.505(5)
C(10)-C(11)	1.530(5)
C(10)-C(12)	1.556(4)
C(14)-C(15)	1.516(4)
C(14)-C(19)	1.519(3)
C(14)-C(22)	1.537(4)
C(15)-C(16)	1.535(4)
C(16)-C(17)	1.516(4)
C(16)-C(20)	1.520(4)
C(17)-C(18)	1.515(5)
C(18)-C(23)	1.516(5)
C(18)-C(19)	1.527(4)
C(20)-C(21)	1.519(5)
C(21)-C(23)	1.518(5)

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C(21)-C(22)	1.533(4)
C(26)-C(34)	1.521(4)
C(26)-C(27)	1.527(4)
C(26)-C(31)	1.535(4)
C(27)-C(28)	1.529(4)
C(28)-C(32)	1.524(4)
C(28)-C(29)	1.527(5)
C(29)-C(30)	1.515(5)
C(30)-C(35)	1.512(4)
C(30)-C(31)	1.528(4)
C(32)-C(33)	1.515(4)
C(33)-C(35)	1.524(4)
C(33)-C(34)	1.539(4)

C(13)-S(1)-C(14)	106.65(12)
C(25)-S(2)-C(26)	105.83(12)
C(25)-C(1)-C(13)	109.3(2)
C(25)-C(1)-C(2)	113.4(2)
C(13)-C(1)-C(2)	110.7(2)
C(3)-C(2)-C(6)	102.90(19)
C(3)-C(2)-C(1)	114.95(19)
C(6)-C(2)-C(1)	114.7(2)
C(4)-C(3)-C(12)	115.3(2)
C(4)-C(3)-C(2)	103.1(2)
C(12)-C(3)-C(2)	120.3(2)
C(4)-C(3)-C(7)	104.9(2)
C(12)-C(3)-C(7)	101.6(2)
C(2)-C(3)-C(7)	110.7(2)
O(1)-C(4)-C(5)	125.1(3)
O(1)-C(4)-C(3)	126.4(3)
C(5)-C(4)-C(3)	108.5(2)
C(4)-C(5)-C(6)	105.8(2)
C(5)-C(6)-C(2)	106.4(2)
C(8)-C(7)-C(11)	100.3(3)
C(8)-C(7)-C(3)	106.1(2)
C(11)-C(7)-C(3)	100.2(2)

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C(9)-C(8)-C(7)	108.2(3)
C(8)-C(9)-C(10)	107.5(3)
C(9)-C(10)-C(11)	99.9(3)
C(9)-C(10)-C(12)	105.2(3)
C(11)-C(10)-C(12)	101.5(2)
C(7)-C(11)-C(10)	93.5(2)
C(3)-C(12)-C(10)	103.4(2)
O(2)-C(13)-C(1)	123.5(2)
O(2)-C(13)-S(1)	124.8(2)
C(1)-C(13)-S(1)	111.64(18)
C(15)-C(14)-C(19)	110.6(2)
C(15)-C(14)-C(22)	108.9(2)
C(19)-C(14)-C(22)	109.2(2)
C(15)-C(14)-S(1)	112.87(18)
C(19)-C(14)-S(1)	111.80(17)
C(22)-C(14)-S(1)	103.14(17)
C(14)-C(15)-C(16)	109.2(2)
C(17)-C(16)-C(20)	110.0(3)
C(17)-C(16)-C(15)	109.3(2)
C(20)-C(16)-C(15)	109.0(2)
C(18)-C(17)-C(16)	109.7(2)
C(17)-C(18)-C(23)	109.9(3)
C(17)-C(18)-C(19)	109.4(3)
C(23)-C(18)-C(19)	109.8(3)
C(14)-C(19)-C(18)	109.2(2)
C(21)-C(20)-C(16)	109.4(2)
C(23)-C(21)-C(20)	110.1(3)
C(23)-C(21)-C(22)	109.9(3)
C(20)-C(21)-C(22)	109.0(3)
C(21)-C(22)-C(14)	108.9(2)
C(18)-C(23)-C(21)	109.1(3)
O(3)-C(25)-C(1)	122.5(2)
O(3)-C(25)-S(2)	125.5(2)
C(1)-C(25)-S(2)	111.94(18)
C(34)-C(26)-C(27)	110.9(2)
C(34)-C(26)-C(31)	108.6(2)

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C(27)-C(26)-C(31)	109.3(2)
C(34)-C(26)-S(2)	111.63(18)
C(27)-C(26)-S(2)	111.93(18)
C(31)-C(26)-S(2)	104.11(18)
C(26)-C(27)-C(28)	108.9(2)
C(32)-C(28)-C(29)	110.3(3)
C(32)-C(28)-C(27)	109.7(3)
C(29)-C(28)-C(27)	108.8(3)
C(30)-C(29)-C(28)	109.2(3)
C(35)-C(30)-C(29)	110.4(3)
C(35)-C(30)-C(31)	109.0(3)
C(29)-C(30)-C(31)	109.8(3)
C(30)-C(31)-C(26)	109.4(2)
C(33)-C(32)-C(28)	109.3(3)
C(32)-C(33)-C(35)	109.9(3)
C(32)-C(33)-C(34)	109.5(3)
C(35)-C(33)-C(34)	110.2(3)
C(26)-C(34)-C(33)	108.3(2)
C(30)-C(35)-C(33)	109.1(3)

Symmetry transformations used to generate equivalent atoms:

Supporting Information

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 8058a. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	51(1)	50(1)	41(1)	-17(1)	-8(1)	13(1)
S(2)	42(1)	36(1)	44(1)	0(1)	12(1)	3(1)
O(1)	84(2)	80(2)	43(1)	-19(1)	16(1)	12(1)
O(2)	49(1)	72(1)	50(1)	-29(1)	-3(1)	17(1)
O(3)	55(1)	40(1)	65(1)	14(1)	19(1)	4(1)
C(1)	37(1)	29(1)	29(1)	-3(1)	5(1)	3(1)
C(2)	35(1)	31(1)	34(1)	-4(1)	4(1)	4(1)
C(3)	37(2)	35(1)	36(2)	-11(1)	-1(1)	5(1)
C(4)	46(2)	56(2)	34(2)	-9(1)	-5(1)	8(1)
C(5)	66(2)	50(2)	40(2)	7(1)	-2(1)	9(1)
C(6)	57(2)	36(2)	44(2)	-4(1)	-1(1)	8(1)
C(7)	45(2)	43(2)	61(2)	-10(1)	-6(1)	8(1)
C(8)	44(2)	65(2)	79(3)	-14(2)	6(2)	-4(2)
C(9)	55(2)	62(2)	80(3)	3(2)	8(2)	-9(2)
C(10)	51(2)	34(2)	98(3)	-12(2)	2(2)	0(1)
C(11)	52(2)	60(2)	63(2)	-25(2)	-14(2)	-1(2)
C(12)	46(2)	37(1)	51(2)	-12(1)	-1(1)	4(1)
C(13)	44(2)	38(1)	33(2)	-4(1)	1(1)	0(1)
C(14)	43(2)	35(1)	26(1)	-6(1)	2(1)	1(1)
C(15)	58(2)	48(2)	41(2)	-3(1)	11(1)	-9(1)
C(16)	65(2)	62(2)	38(2)	-11(1)	15(1)	3(2)
C(17)	73(2)	54(2)	51(2)	-20(2)	-6(2)	23(2)
C(18)	90(3)	32(2)	51(2)	0(1)	3(2)	1(2)
C(19)	72(2)	39(2)	35(2)	3(1)	5(1)	-4(1)
C(20)	94(3)	62(2)	32(2)	-13(1)	-8(2)	14(2)
C(21)	55(2)	65(2)	55(2)	-23(2)	-15(2)	5(2)
C(22)	47(2)	59(2)	46(2)	-13(1)	-6(1)	8(1)
C(23)	77(3)	63(2)	79(3)	-19(2)	4(2)	-23(2)
C(25)	38(2)	35(1)	31(1)	-3(1)	1(1)	3(1)
C(26)	35(1)	41(1)	31(1)	-3(1)	6(1)	-2(1)
C(27)	48(2)	65(2)	43(2)	-12(1)	3(1)	-13(1)

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C(28)	50(2)	84(2)	58(2)	-9(2)	2(2)	-29(2)
C(29)	38(2)	128(3)	57(2)	12(2)	4(1)	-5(2)
C(30)	44(2)	78(2)	60(2)	9(2)	17(2)	21(2)
C(31)	52(2)	58(2)	46(2)	5(1)	11(1)	12(2)
C(32)	59(2)	75(2)	65(2)	12(2)	18(2)	-9(2)
C(33)	56(2)	85(2)	33(2)	9(2)	3(1)	2(2)
C(34)	42(2)	59(2)	33(2)	-3(1)	-1(1)	1(1)
C(35)	57(2)	94(3)	45(2)	-12(2)	17(1)	6(2)

Supporting Information

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 8058a.

	x	y	z	U(eq)
H(1)	3219	6800	9466	38
H(2)	4370	6087	9976	40
H(5A)	3411	4909	12421	63
H(5B)	4217	4988	12894	63
H(6A)	3816	4479	10796	55
H(6B)	4599	4824	11198	55
H(7)	5173	6398	12168	60
H(8)	5588	6947	10348	75
H(9)	5211	8676	9955	79
H(10)	4541	9318	11541	74
H(11A)	5409	8221	12678	71
H(11B)	4635	7948	13047	71
H(12A)	3521	8194	11612	54
H(12B)	3719	8061	10363	54
H(15A)	3470	4531	6445	59
H(15B)	2938	5224	5701	59
H(16)	3286	3803	4634	65
H(17A)	2968	2147	5167	72
H(17B)	3477	2637	6127	72
H(18)	2496	1871	6897	69
H(19A)	2154	3284	7963	58
H(19B)	2982	3319	7850	58
H(20A)	2125	4459	4188	76
H(20B)	2131	3277	3960	76
H(21)	1141	3688	4958	71
H(22A)	1325	4410	6772	61
H(22B)	1632	5152	5897	61
H(23A)	1338	2510	6437	87
H(23B)	1650	2072	5355	87
H(27A)	1231	5133	10829	62

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H(27B)	765	5903	10072	62
H(28)	19	4938	11182	77
H(29A)	-347	6625	10707	89
H(29B)	-609	6327	11878	89
H(30)	-84	7954	11998	72
H(31A)	1141	8146	11712	62
H(31B)	721	7761	10602	62
H(32A)	145	5108	13147	79
H(32B)	858	4668	12737	79
H(33)	1118	6006	14018	69
H(34A)	1881	6955	12917	54
H(34B)	1924	5790	12610	54
H(35A)	65	6967	13640	78
H(35B)	733	7679	13558	78

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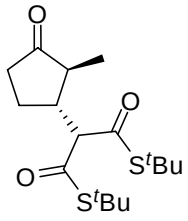
#==========END==========#

Supporting Information

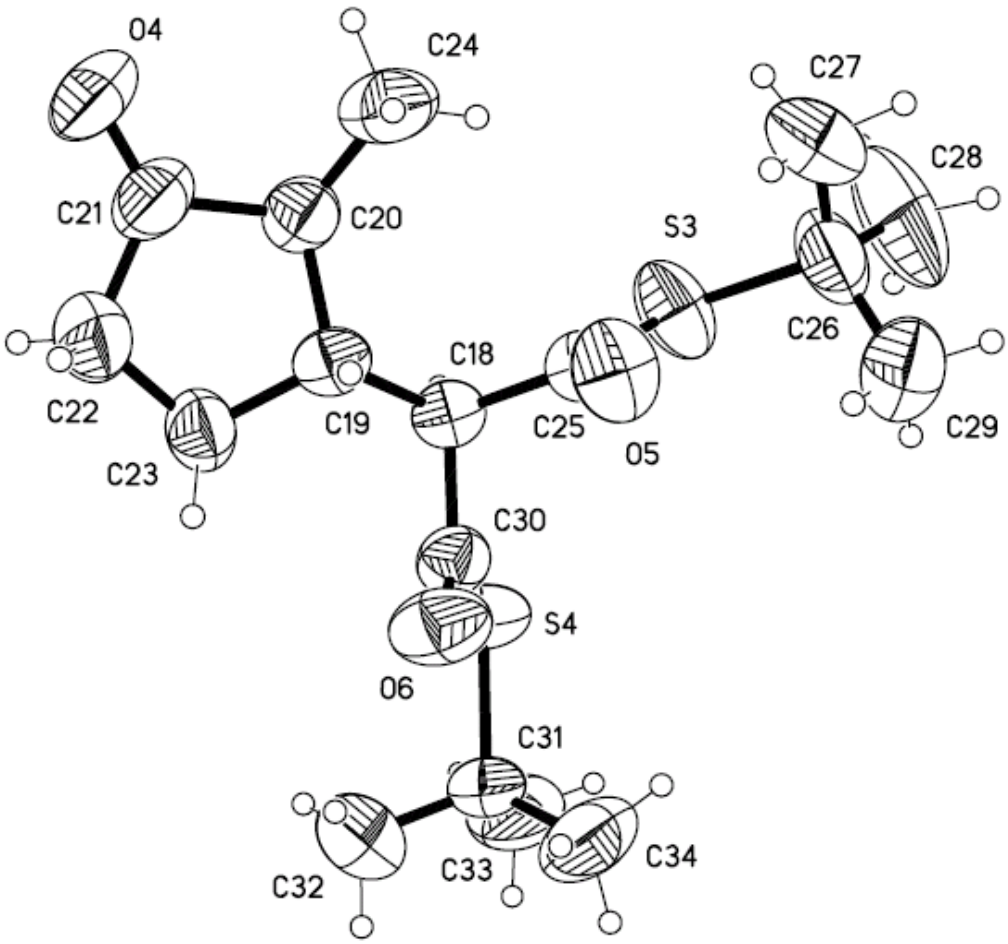
2). Compound 11 (chiral)



11

The crystal is triclinic, space group P1. The asymmetric unit contains two molecules of the compound $C_{17}H_{28}O_3S_2$. As this is a chiral space group, the crystal contains only one hand molecules. Flack parameter = 0.17 with esd 0.11 indicates that the reported structure is likely to be the correct hand. Final R values for 2-theta max of 52º are: R1= 0.0860, wR2=0.1925.

The ORTEP diagram for compound **11** (The probability level of the thermal ellipsoids is 50%):



Supporting Information

Table 1. Crystal data and structure refinement for 8430.

Identification code	8430	
Empirical formula	C17 H28 O3 S2	
Formula weight	344.51	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.7296(18) Å	α= 65.152(4)°.
	b = 11.309(2) Å	β= 68.166(4)°.
	c = 11.780(2) Å	γ = 64.564(4)°.
Volume	1032.7(3) $Å^3$	
Z	2	
Density (calculated)	1.108 Mg/m^3	
Absorption coefficient	0.266 mm^{-1}	
F(000)	372	
Crystal size	0.34 x 0.10 x 0.04 mm^3	
Theta range for data collection	1.96 to 26.00°.	
Index ranges	-11<=h<=11, -13<=k<=13, -14<=l<=14	
Reflections collected	11759	
Independent reflections	7994 [R(int) = 0.0335]	
Completeness to theta = 26.00°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9894 and 0.9149	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7994 / 3 / 411	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0860, wR2 = 0.1925	
R indices (all data)	R1 = 0.1174, wR2 = 0.2129	
Flack parameter	0.17(11)	
Largest diff. peak and hole	0.462 and -0.215 $e.Å^{-3}$	

Supporting Information

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 8430. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	8550(2)	7534(2)	8475(2)	76(1)
S(2)	10618(2)	3816(2)	7933(2)	77(1)
S(3)	6270(2)	5243(2)	4818(2)	86(1)
S(4)	4710(2)	9242(2)	4323(2)	75(1)
O(1)	9989(12)	8770(7)	1951(6)	160(3)
O(2)	6661(5)	8048(5)	7076(4)	84(1)
O(3)	7792(5)	4857(5)	7553(5)	88(1)
O(4)	3164(9)	4925(7)	10870(5)	147(3)
O(5)	3239(5)	5653(5)	5648(4)	79(1)
O(6)	1985(5)	8804(5)	5380(4)	83(1)
C(1)	9215(5)	6458(5)	6580(5)	48(1)
C(2)	9113(6)	6849(5)	5204(5)	52(1)
C(3)	9711(7)	8036(6)	4253(6)	64(1)
C(4)	9992(10)	7860(8)	2964(6)	92(2)
C(5)	10129(10)	6418(7)	3180(6)	90(2)
C(6)	10069(7)	5702(6)	4583(5)	62(1)
C(7)	8797(9)	9463(6)	4306(7)	78(2)
C(8)	7940(6)	7461(6)	7266(5)	56(1)
C(9)	6793(8)	8574(8)	9396(7)	79(2)
C(10)	6326(13)	10028(9)	8579(11)	134(4)
C(11)	5478(9)	8007(11)	9879(8)	108(3)
C(12)	7380(10)	8421(12)	10506(10)	126(4)
C(13)	8984(6)	5049(6)	7394(5)	56(1)
C(14)	10086(9)	2240(8)	8939(8)	97(3)
C(15)	9674(14)	1745(11)	8179(15)	156(5)
C(16)	11591(13)	1240(10)	9340(15)	171(6)
C(17)	8722(14)	2551(12)	10064(10)	157(5)
C(18)	4123(5)	6968(5)	6197(5)	48(1)
C(19)	3145(6)	6703(5)	7577(5)	52(1)
C(20)	4001(7)	5442(6)	8569(6)	63(1)
C(21)	3115(8)	5739(8)	9836(7)	82(2)

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C(22)	2153(9)	7244(7)	9552(7)	86(2)
C(23)	2611(7)	7884(6)	8133(6)	68(2)
C(24)	4245(11)	4021(7)	8617(8)	95(2)
C(25)	4312(6)	5928(5)	5595(5)	54(1)
C(26)	6259(10)	4036(8)	4151(8)	94(2)
C(27)	5734(14)	2886(9)	5212(11)	129(3)
C(28)	7978(14)	3519(14)	3456(15)	178(6)
C(29)	5250(15)	4795(10)	3202(9)	131(3)
C(30)	3342(6)	8381(6)	5351(5)	58(1)
C(31)	3623(8)	10931(6)	3353(6)	73(2)
C(32)	2515(13)	11774(9)	4200(10)	126(3)
C(33)	4956(11)	11536(8)	2474(8)	105(3)
C(34)	2854(12)	10798(10)	2561(8)	110(3)

Supporting Information

Table 3. Bond lengths [Å] and angles [°] for 8430.

S(1)-C(8)	1.777(5)
S(1)-C(9)	1.857(6)
S(2)-C(13)	1.726(5)
S(2)-C(14)	1.847(7)
S(3)-C(25)	1.760(5)
S(3)-C(26)	1.844(7)
S(4)-C(30)	1.763(6)
S(4)-C(31)	1.844(6)
O(1)-C(4)	1.205(9)
O(2)-C(8)	1.188(6)
O(3)-C(13)	1.203(6)
O(4)-C(21)	1.181(8)
O(5)-C(25)	1.186(6)
O(6)-C(30)	1.188(6)
C(1)-C(8)	1.515(7)
C(1)-C(2)	1.520(7)
C(1)-C(13)	1.540(8)
C(2)-C(3)	1.522(8)
C(2)-C(6)	1.530(8)
C(3)-C(7)	1.486(9)
C(3)-C(4)	1.523(9)
C(4)-C(5)	1.494(10)
C(5)-C(6)	1.495(9)
C(9)-C(10)	1.480(12)
C(9)-C(11)	1.492(10)
C(9)-C(12)	1.532(10)
C(14)-C(15)	1.469(15)
C(14)-C(16)	1.512(12)
C(14)-C(17)	1.524(13)
C(18)-C(30)	1.519(7)
C(18)-C(19)	1.524(7)
C(18)-C(25)	1.529(7)
C(19)-C(23)	1.538(8)
C(19)-C(20)	1.548(8)

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C(20)-C(24)	1.500(10)
C(20)-C(21)	1.516(9)
C(21)-C(22)	1.507(10)
C(22)-C(23)	1.491(10)
C(26)-C(29)	1.495(13)
C(26)-C(27)	1.498(13)
C(26)-C(28)	1.534(14)
C(31)-C(32)	1.478(10)
C(31)-C(34)	1.479(10)
C(31)-C(33)	1.546(11)

C(8)-S(1)-C(9)	106.6(3)
C(13)-S(2)-C(14)	106.7(3)
C(25)-S(3)-C(26)	105.6(3)
C(30)-S(4)-C(31)	107.1(3)
C(8)-C(1)-C(2)	112.3(4)
C(8)-C(1)-C(13)	105.1(4)
C(2)-C(1)-C(13)	111.2(4)
C(1)-C(2)-C(3)	114.9(4)
C(1)-C(2)-C(6)	114.5(4)
C(3)-C(2)-C(6)	102.8(4)
C(7)-C(3)-C(2)	119.9(5)
C(7)-C(3)-C(4)	114.0(5)
C(2)-C(3)-C(4)	102.3(5)
O(1)-C(4)-C(5)	125.8(7)
O(1)-C(4)-C(3)	125.0(7)
C(5)-C(4)-C(3)	109.1(6)
C(4)-C(5)-C(6)	105.2(5)
C(5)-C(6)-C(2)	104.4(5)
O(2)-C(8)-C(1)	123.9(5)
O(2)-C(8)-S(1)	124.5(4)
C(1)-C(8)-S(1)	111.4(3)
C(10)-C(9)-C(11)	110.8(8)
C(10)-C(9)-C(12)	111.1(8)
C(11)-C(9)-C(12)	111.4(7)
C(10)-C(9)-S(1)	109.9(6)

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C(11)-C(9)-S(1)	110.9(5)
C(12)-C(9)-S(1)	102.6(5)
O(3)-C(13)-C(1)	121.1(5)
O(3)-C(13)-S(2)	125.5(4)
C(1)-C(13)-S(2)	113.2(4)
C(15)-C(14)-C(16)	110.5(10)
C(15)-C(14)-C(17)	110.7(9)
C(16)-C(14)-C(17)	113.5(10)
C(15)-C(14)-S(2)	110.8(7)
C(16)-C(14)-S(2)	102.1(6)
C(17)-C(14)-S(2)	108.9(7)
C(30)-C(18)-C(19)	110.8(4)
C(30)-C(18)-C(25)	106.3(4)
C(19)-C(18)-C(25)	112.0(4)
C(18)-C(19)-C(23)	114.3(5)
C(18)-C(19)-C(20)	114.5(4)
C(23)-C(19)-C(20)	103.0(4)
C(24)-C(20)-C(21)	113.8(6)
C(24)-C(20)-C(19)	119.2(5)
C(21)-C(20)-C(19)	103.7(5)
O(4)-C(21)-C(22)	125.9(7)
O(4)-C(21)-C(20)	125.7(7)
C(22)-C(21)-C(20)	108.4(6)
C(23)-C(22)-C(21)	106.5(5)
C(22)-C(23)-C(19)	104.5(5)
O(5)-C(25)-C(18)	122.5(5)
O(5)-C(25)-S(3)	125.6(4)
C(18)-C(25)-S(3)	111.9(4)
C(29)-C(26)-C(27)	111.9(8)
C(29)-C(26)-C(28)	110.0(9)
C(27)-C(26)-C(28)	111.7(8)
C(29)-C(26)-S(3)	109.9(6)
C(27)-C(26)-S(3)	110.3(6)
C(28)-C(26)-S(3)	102.7(7)
O(6)-C(30)-C(18)	122.7(5)
O(6)-C(30)-S(4)	125.9(4)

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C(18)-C(30)-S(4)	111.4(3)
C(32)-C(31)-C(34)	112.7(7)
C(32)-C(31)-C(33)	110.4(7)
C(34)-C(31)-C(33)	109.9(6)
C(32)-C(31)-S(4)	109.5(5)
C(34)-C(31)-S(4)	112.3(5)
C(33)-C(31)-S(4)	101.5(5)

Symmetry transformations used to generate equivalent atoms:

Supporting Information

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 8430. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	56(1)	105(1)	79(1)	-54(1)	-22(1)	-8(1)
S(2)	60(1)	65(1)	95(1)	2(1)	-37(1)	-21(1)
S(3)	57(1)	89(1)	122(2)	-65(1)	-3(1)	-18(1)
S(4)	68(1)	62(1)	85(1)	2(1)	-30(1)	-26(1)
O(1)	295(10)	98(4)	55(3)	-6(3)	-12(4)	-78(5)
O(2)	54(2)	116(4)	77(3)	-47(3)	-29(2)	6(2)
O(3)	57(3)	91(3)	106(4)	1(3)	-26(2)	-40(2)
O(4)	193(7)	119(5)	47(3)	-12(3)	-25(3)	6(4)
O(5)	62(2)	97(3)	102(3)	-45(3)	-13(2)	-40(2)
O(6)	53(2)	89(3)	84(3)	-8(2)	-24(2)	-15(2)
C(1)	36(2)	55(3)	53(3)	-22(2)	-11(2)	-10(2)
C(2)	42(2)	57(3)	57(3)	-15(2)	-16(2)	-14(2)
C(3)	58(3)	62(3)	70(4)	-9(3)	-22(3)	-24(3)
C(4)	125(6)	89(5)	43(4)	-16(4)	-4(4)	-36(4)
C(5)	136(6)	73(4)	54(4)	-25(3)	-5(4)	-37(4)
C(6)	67(3)	57(3)	60(3)	-18(3)	-19(3)	-15(3)
C(7)	97(5)	59(4)	73(4)	-15(3)	-25(4)	-21(3)
C(8)	41(3)	67(3)	52(3)	-18(3)	-13(2)	-9(2)
C(9)	72(4)	101(5)	73(4)	-53(4)	-8(3)	-19(4)
C(10)	137(8)	76(6)	155(9)	-47(6)	-25(7)	-1(5)
C(11)	75(5)	171(9)	82(5)	-53(6)	-2(4)	-44(5)
C(12)	93(6)	188(10)	137(8)	-122(8)	-25(5)	-13(6)
C(13)	49(3)	62(3)	44(3)	-7(2)	-8(2)	-18(2)
C(14)	82(5)	69(4)	101(6)	12(4)	-16(4)	-31(4)
C(15)	159(10)	95(7)	227(14)	-48(8)	-34(9)	-63(7)
C(16)	135(9)	86(6)	224(14)	49(8)	-89(9)	-31(6)
C(17)	166(10)	140(9)	79(6)	9(6)	4(6)	-46(8)
C(18)	36(2)	56(3)	56(3)	-14(2)	-14(2)	-19(2)
C(19)	39(2)	58(3)	56(3)	-11(2)	-15(2)	-15(2)
C(20)	53(3)	69(4)	60(3)	-19(3)	-14(3)	-14(3)
C(21)	83(4)	90(5)	51(4)	-14(4)	-17(3)	-16(4)

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C(22)	83(4)	88(5)	77(5)	-38(4)	-15(4)	-10(4)
C(23)	61(3)	75(4)	68(4)	-35(3)	-13(3)	-11(3)
C(24)	133(7)	67(4)	79(5)	2(4)	-42(5)	-36(4)
C(25)	49(3)	56(3)	54(3)	-16(2)	-10(2)	-18(2)
C(26)	112(6)	78(5)	99(6)	-54(5)	-9(5)	-24(4)
C(27)	189(10)	61(4)	128(7)	-30(5)	-48(7)	-24(5)
C(28)	150(10)	169(11)	221(15)	-156(12)	27(9)	-22(8)
C(29)	200(10)	116(7)	84(6)	-36(5)	-38(7)	-49(7)
C(30)	50(3)	65(3)	58(3)	-18(3)	-18(2)	-14(3)
C(31)	95(5)	50(3)	64(4)	-5(3)	-34(3)	-12(3)
C(32)	152(9)	82(5)	113(7)	-41(5)	-32(6)	2(5)
C(33)	135(7)	76(5)	88(5)	9(4)	-33(5)	-48(5)
C(34)	141(7)	110(6)	86(5)	-5(5)	-64(5)	-40(5)

Supporting Information

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 8430.

	x	y	z	U(eq)
H(1)	10241	6423	6577	57
H(2)	8013	7111	5205	62
H(3)	10743	7824	4378	76
H(5A)	11109	5977	2665	108
H(5B)	9271	6408	2956	108
H(6A)	11114	5264	4737	74
H(6B)	9563	5008	4917	74
H(7A)	7710	9637	4402	118
H(7B)	9168	10106	3525	118
H(7C)	8923	9569	5025	118
H(10A)	5949	10098	7900	202
H(10B)	7213	10347	8217	202
H(10C)	5512	10583	9093	202
H(11A)	4688	8399	10524	162
H(11B)	5864	7024	10244	162
H(11C)	5037	8234	9178	162
H(12A)	8308	8681	10166	189
H(12B)	7616	7480	11049	189
H(12C)	6585	9005	10999	189
H(15A)	9756	792	8608	234
H(15B)	10376	1843	7343	234
H(15C)	8620	2275	8089	234
H(16A)	11523	326	9726	256
H(16B)	11752	1494	9951	256
H(16C)	12451	1266	8598	256
H(17A)	7771	3060	9770	235
H(17B)	8903	3085	10414	235
H(17C)	8633	1702	10717	235
H(18)	5159	6916	6187	58
H(19)	2211	6557	7600	63

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H(20)	5044	5500	8379	75
H(22A)	1045	7355	9825	103
H(22B)	2367	7672	10001	103
H(23A)	3456	8240	7907	82
H(23B)	1729	8630	7814	82
H(24A)	4726	3355	9312	143
H(24B)	4912	3865	7820	143
H(24C)	3254	3934	8749	143
H(27A)	4648	3241	5608	193
H(27B)	6344	2481	5842	193
H(27C)	5874	2201	4865	193
H(28A)	8606	2964	4078	267
H(28B)	8327	4293	2889	267
H(28C)	8077	2978	2966	267
H(29A)	5277	4167	2837	197
H(29B)	5632	5511	2531	197
H(29C)	4193	5194	3629	197
H(32A)	1982	12666	3689	189
H(32B)	3078	11873	4654	189
H(32C)	1765	11329	4806	189
H(33A)	5651	10994	1913	157
H(33B)	5527	11523	2994	157
H(33C)	4519	12468	1969	157
H(34A)	1866	10671	3071	165
H(34B)	3509	10017	2260	165
H(34C)	2687	11617	1837	165

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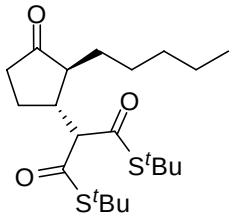
#==========END==========#

Supporting Information

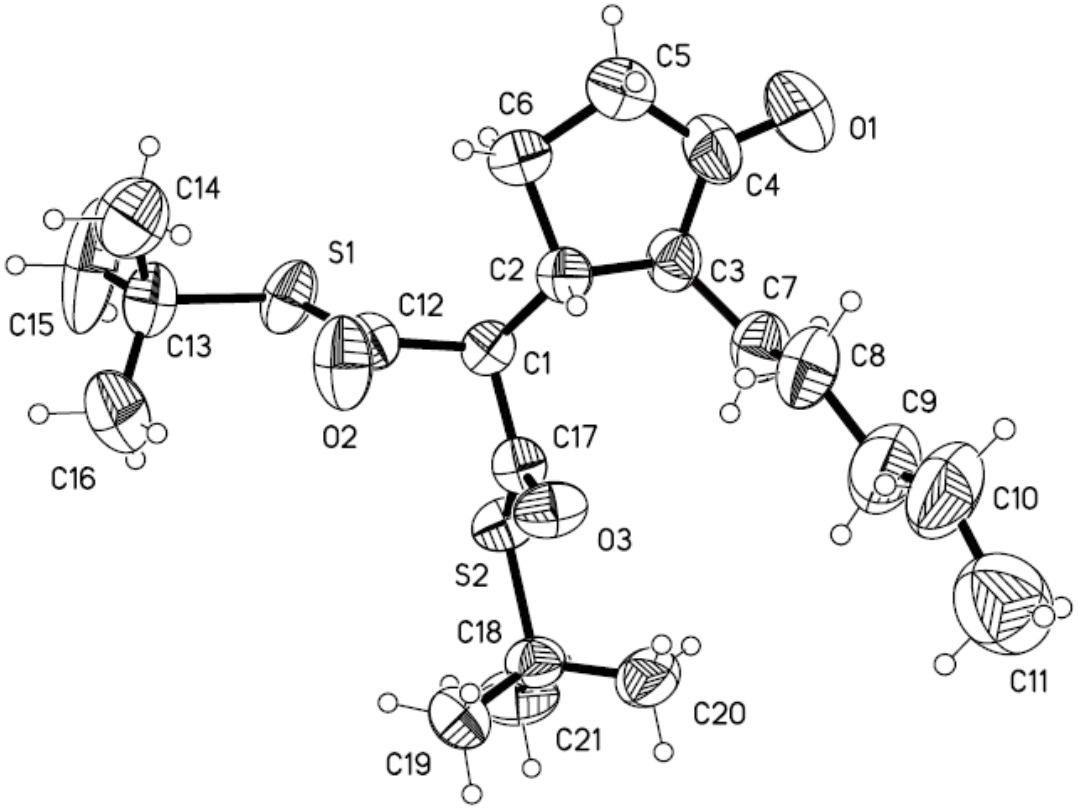
3). Compound 12 (racemic)



12

The crystal is monoclinic, space group Cc. The asymmetric unit contains one molecule of the compound $C_{21}H_{36}O_3S_2$. Final R values are R1=0.0595 and wR2= 0.1237 for 2-theta up to 55º.

The ORTEP diagram for compound **12** (The probability level of the thermal ellipsoids is 50%):



Supporting Information

Table 1. Crystal data and structure refinement for 8372.

Identification code	8372	
Empirical formula	C21 H36 O3 S2	
Formula weight	400.62	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 18.8390(19) Å	α= 90°.
	b = 12.6378(14) Å	β= 95.756(3)°.
	c = 10.2009(10) Å	γ = 90°.
Volume	2416.4(4) Å^3	
Z	4	
Density (calculated)	1.101 Mg/m^3	
Absorption coefficient	0.236 mm^{-1}	
F(000)	872	
Crystal size	0.36 x 0.04 x 0.04 mm^3	
Theta range for data collection	1.94 to 27.49°.	
Index ranges	-24<=h<=16, -16<=k<=15, -13<=l<=13	
Reflections collected	8416	
Independent reflections	4012 [R(int) = 0.0523]	
Completeness to theta = 27.49°	100.0 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9906 and 0.9199	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4012 / 2 / 242	
Goodness-of-fit on F^2	0.949	
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1237	
R indices (all data)	R1 = 0.1009, wR2 = 0.1394	
Absolute structure parameter	0.02(11)	
Largest diff. peak and hole	0.234 and -0.160 e.Å^{-3}	

Supporting Information

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 8372. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7423(1)	2638(1)	6625(1)	66(1)
S(2)	6783(1)	5736(1)	6341(1)	55(1)
O(1)	10204(2)	5968(4)	8649(5)	113(2)
O(2)	7965(2)	3415(3)	4548(3)	77(1)
O(3)	7762(2)	5855(2)	4651(3)	59(1)
C(1)	8007(2)	4590(3)	6397(4)	44(1)
C(2)	8805(2)	4819(3)	6497(4)	47(1)
C(3)	9043(2)	5696(4)	7484(4)	55(1)
C(4)	9799(3)	5421(5)	7962(5)	74(2)
C(5)	9967(3)	4330(4)	7470(7)	84(2)
C(6)	9253(2)	3857(4)	7006(5)	67(1)
C(7)	8939(3)	6852(4)	7077(5)	67(1)
C(8)	9344(3)	7188(4)	5954(6)	81(2)
C(9)	9159(4)	8281(5)	5408(9)	110(2)
C(10)	9619(4)	8625(6)	4295(9)	116(3)
C(11)	9352(4)	9563(8)	3597(9)	139(3)
C(12)	7826(2)	3562(3)	5652(4)	48(1)
C(13)	7197(3)	1488(4)	5555(6)	71(1)
C(14)	7863(4)	979(5)	5168(8)	119(3)
C(15)	6829(6)	752(6)	6474(10)	166(4)
C(16)	6707(3)	1796(6)	4360(8)	114(2)
C(17)	7571(2)	5448(3)	5627(4)	46(1)
C(18)	6294(2)	6714(4)	5249(4)	56(1)
C(19)	6105(3)	6259(4)	3886(5)	64(1)
C(20)	6721(3)	7719(4)	5198(5)	75(2)
C(21)	5623(3)	6885(5)	5943(6)	84(2)

Supporting Information

Table 3. Bond lengths [Å] and angles [°] for 8372.

S(1)-C(12)	1.753(5)
S(1)-C(13)	1.842(5)
S(2)-C(17)	1.756(4)
S(2)-C(18)	1.848(4)
O(1)-C(4)	1.202(6)
O(2)-C(12)	1.195(5)
O(3)-C(17)	1.207(5)
C(1)-C(2)	1.525(6)
C(1)-C(12)	1.527(6)
C(1)-C(17)	1.528(6)
C(2)-C(3)	1.533(6)
C(2)-C(6)	1.540(6)
C(3)-C(4)	1.499(7)
C(3)-C(7)	1.526(7)
C(4)-C(5)	1.512(8)
C(5)-C(6)	1.504(7)
C(7)-C(8)	1.500(8)
C(8)-C(9)	1.517(8)
C(9)-C(10)	1.557(11)
C(10)-C(11)	1.448(10)
C(13)-C(14)	1.499(8)
C(13)-C(16)	1.505(8)
C(13)-C(15)	1.533(9)
C(18)-C(20)	1.506(7)
C(18)-C(19)	1.514(6)
C(18)-C(21)	1.524(7)

C(12)-S(1)-C(13)	106.1(2)
C(17)-S(2)-C(18)	106.3(2)
C(2)-C(1)-C(12)	111.4(3)
C(2)-C(1)-C(17)	112.0(3)
C(12)-C(1)-C(17)	105.5(3)
C(1)-C(2)-C(3)	113.7(3)
C(1)-C(2)-C(6)	112.1(4)

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C(3)-C(2)-C(6)	103.6(3)
C(4)-C(3)-C(7)	113.7(4)
C(4)-C(3)-C(2)	104.6(4)
C(7)-C(3)-C(2)	119.5(4)
O(1)-C(4)-C(3)	125.7(5)
O(1)-C(4)-C(5)	125.2(5)
C(3)-C(4)-C(5)	109.1(4)
C(6)-C(5)-C(4)	104.9(4)
C(5)-C(6)-C(2)	103.6(4)
C(8)-C(7)-C(3)	114.7(5)
C(7)-C(8)-C(9)	115.0(5)
C(8)-C(9)-C(10)	113.4(6)
C(11)-C(10)-C(9)	113.4(7)
O(2)-C(12)-C(1)	122.8(4)
O(2)-C(12)-S(1)	125.3(3)
C(1)-C(12)-S(1)	111.9(3)
C(14)-C(13)-C(16)	111.1(6)
C(14)-C(13)-C(15)	110.0(7)
C(16)-C(13)-C(15)	112.0(7)
C(14)-C(13)-S(1)	110.1(4)
C(16)-C(13)-S(1)	111.2(4)
C(15)-C(13)-S(1)	102.0(4)
O(3)-C(17)-C(1)	122.5(4)
O(3)-C(17)-S(2)	126.1(3)
C(1)-C(17)-S(2)	111.4(3)
C(20)-C(18)-C(19)	111.5(4)
C(20)-C(18)-C(21)	111.5(4)
C(19)-C(18)-C(21)	110.5(4)
C(20)-C(18)-S(2)	110.4(3)
C(19)-C(18)-S(2)	110.9(3)
C(21)-C(18)-S(2)	101.7(3)

Symmetry transformations used to generate equivalent atoms:

Supporting Information

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 8372. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	97(1)	46(1)	58(1)	-1(1)	28(1)	-7(1)
S(2)	56(1)	60(1)	53(1)	9(1)	20(1)	13(1)
O(1)	99(3)	110(4)	121(4)	-23(3)	-37(3)	-22(3)
O(2)	107(3)	76(2)	54(2)	-21(2)	33(2)	-34(2)
O(3)	57(2)	70(2)	52(2)	19(2)	17(1)	11(2)
C(1)	51(3)	45(2)	38(2)	1(2)	11(2)	1(2)
C(2)	49(3)	49(3)	44(2)	-2(2)	6(2)	1(2)
C(3)	67(3)	51(3)	48(3)	-11(2)	4(2)	-4(2)
C(4)	72(4)	74(4)	72(4)	-10(3)	-13(3)	-16(3)
C(5)	67(4)	73(4)	106(5)	-2(3)	-14(3)	5(3)
C(6)	61(3)	54(3)	85(4)	3(3)	-6(3)	9(2)
C(7)	81(4)	58(3)	63(3)	-14(3)	8(3)	-5(2)
C(8)	94(4)	58(3)	93(4)	3(3)	24(3)	-14(3)
C(9)	108(5)	71(4)	154(7)	8(4)	24(4)	-10(4)
C(10)	136(6)	76(5)	137(7)	27(4)	27(5)	-20(4)
C(11)	127(7)	164(9)	126(7)	11(6)	8(5)	-22(6)
C(12)	43(2)	54(3)	48(3)	-6(2)	7(2)	-1(2)
C(13)	86(4)	53(3)	73(3)	-15(3)	14(3)	-10(3)
C(14)	118(6)	89(5)	147(7)	-55(5)	-14(5)	34(4)
C(15)	278(11)	77(5)	160(8)	-35(5)	100(7)	-90(7)
C(16)	89(5)	100(5)	145(6)	-22(4)	-26(4)	-22(4)
C(17)	50(2)	51(3)	39(2)	-2(2)	10(2)	-3(2)
C(18)	54(3)	55(3)	58(3)	1(2)	2(2)	11(2)
C(19)	63(3)	72(3)	56(3)	-6(2)	0(2)	-3(2)
C(20)	97(4)	55(3)	71(4)	-4(3)	-7(3)	13(3)
C(21)	69(4)	99(4)	86(4)	9(3)	16(3)	38(3)

Supporting Information

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 8372.

	x	y	z	U(eq)
H(1)	7852	4537	7294	53
H(2)	8939	5019	5617	57
H(3)	8764	5592	8246	66
H(5A)	10269	4375	6745	100
H(5B)	10212	3904	8180	100
H(6A)	9042	3508	7732	81
H(6B)	9296	3342	6300	81
H(7A)	8430	6976	6830	81
H(7B)	9086	7300	7840	81
H(8A)	9256	6671	5240	97
H(8B)	9855	7169	6250	97
H(9A)	9225	8797	6128	132
H(9B)	8655	8292	5063	132
H(10A)	10108	8757	4681	139
H(10B)	9633	8042	3664	139
H(11A)	8872	9433	3192	209
H(11B)	9659	9737	2921	209
H(11C)	9346	10149	4211	209
H(14A)	8156	747	5952	179
H(14B)	8128	1487	4695	179
H(14C)	7738	375	4605	179
H(15A)	6675	113	6003	249
H(15B)	6419	1109	6772	249
H(15C)	7162	571	7228	249
H(16A)	6961	2248	3796	171
H(16B)	6299	2175	4634	171
H(16C)	6545	1165	3879	171
H(19A)	5799	6750	3363	97
H(19B)	5857	5592	3956	97
H(19C)	6538	6142	3466	97

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H(20A)	6458	8224	4621	113
H(20B)	7173	7564	4864	113
H(20C)	6806	8016	6077	113
H(21A)	5754	7151	6826	126
H(21B)	5371	6219	5991	126
H(21C)	5316	7395	5452	126

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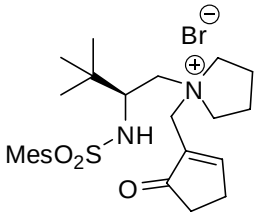
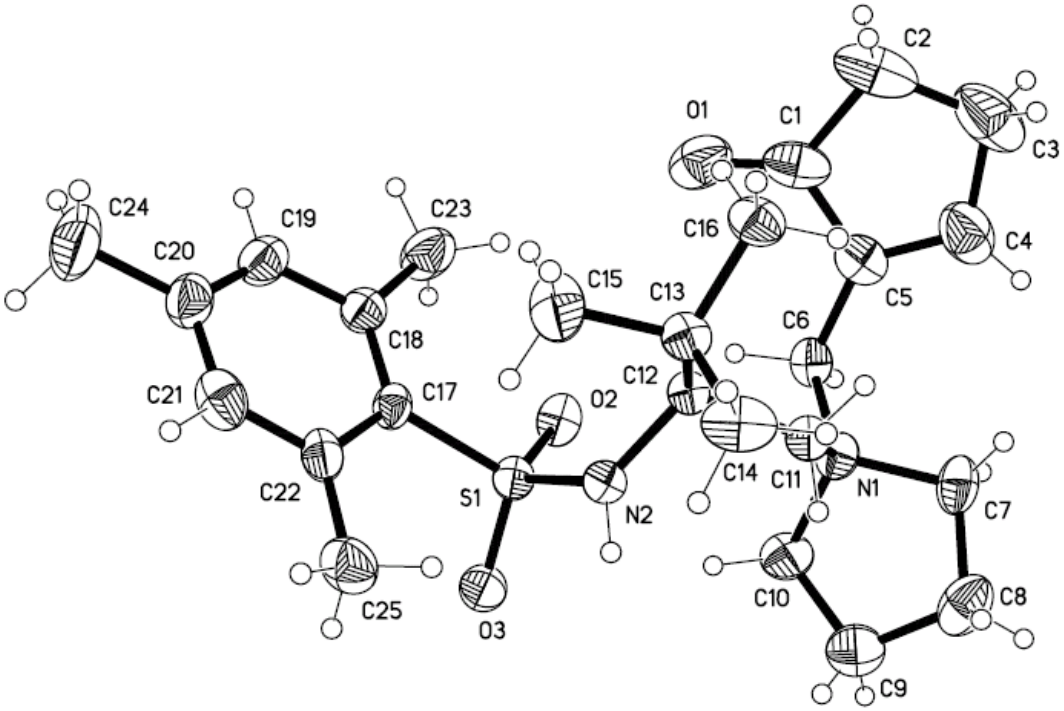
#==========END==========#

Supporting Information

4). Reference 21



The crystal is orthorhombic, space group P2(1)2(1)2(1). In the asymmetric unit there are one molecule of title cation, one Br anion and one disordered dichloromethane[5]. The final R values are: R1= 0.0579 and wR2= 0.1430. The Flack parameter is x= 0.008 (11). The ORTEP diagram for reference 21[6] (The probability level of the thermal ellipsoids is 50%):



[5] The carbon atom and one of the Cl atoms of the dichloromethane solvent was disordered into two positions with occupancy ratio 70:30. The part with smaller occupancy was refined isotropically.

[6] The asymmetric unit also contains one Br anion and one disordered dichloromethane, which are not presented in the ORTEP diagram.

Supporting Information

Table 1. Crystal data and structure refinement for 6373.

Identification code	6373	
Empirical formula	C26 H41 Br Cl2 N2 O3 S	
Formula weight	612.48	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.1010(7) Å	α = 90°.
	b = 12.7221(10) Å	β = 90°.
	c = 28.619(2) Å	γ = 90°.
Volume	2949.5(4) $Å^3$	
Z	4	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	1.675 mm^{-1}	
F(000)	1280	
Crystal size	0.54 x 0.06 x 0.06 mm^3	
Theta range for data collection	1.42 to 27.50°.	
Index ranges	-10<=h<=10, -15<=k<=16, -37<=l<=30	
Reflections collected	20732	
Independent reflections	6762 [R(int) = 0.0662]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9062 and 0.4649	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6762 / 5 / 329	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1430	
R indices (all data)	R1 = 0.0796, wR2 = 0.1549	
Flack parameter	0.008(11)	
Largest diff. peak and hole	0.699 and -0.662 $e.Å^{-3}$	

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Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6373. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	1818(1)	3028(1)	2477(1)	53(1)
S(1)	4274(1)	4477(1)	1289(1)	27(1)
O(1)	2518(5)	7790(3)	921(1)	56(1)
O(2)	5102(3)	5459(2)	1237(1)	34(1)
O(3)	5122(4)	3638(2)	1519(1)	37(1)
N(1)	3344(4)	6752(3)	2228(1)	30(1)
N(2)	2628(4)	4684(2)	1594(1)	26(1)
C(1)	2160(6)	8372(4)	1231(2)	46(1)
C(2)	981(8)	9301(4)	1205(3)	73(2)
C(3)	918(9)	9760(5)	1693(3)	79(2)
C(4)	2114(8)	9104(4)	1966(2)	60(2)
C(5)	2775(5)	8312(3)	1715(2)	39(1)
C(6)	3989(5)	7501(3)	1866(2)	32(1)
C(7)	2998(6)	7309(4)	2688(2)	41(1)
C(8)	3113(7)	6466(4)	3055(2)	50(1)
C(9)	4306(10)	5656(5)	2866(2)	70(2)
C(10)	4689(5)	5981(4)	2377(2)	40(1)
C(11)	1762(5)	6196(3)	2077(1)	27(1)
C(12)	1712(4)	5676(3)	1592(1)	24(1)
C(13)	-139(4)	5521(3)	1446(2)	29(1)
C(14)	-1115(6)	4975(4)	1835(2)	44(1)
C(15)	-195(6)	4851(4)	1007(2)	51(1)
C(16)	-937(5)	6575(3)	1333(2)	37(1)
C(17)	3704(5)	4014(3)	720(1)	28(1)
C(18)	4082(5)	4607(3)	321(1)	33(1)
C(19)	3666(6)	4160(4)	-112(2)	41(1)
C(20)	2931(6)	3198(4)	-156(2)	42(1)
C(21)	2559(6)	2650(4)	253(2)	43(1)
C(22)	2951(5)	3019(3)	688(2)	35(1)
C(23)	4833(7)	5704(4)	303(2)	53(1)
C(24)	2518(9)	2748(5)	-628(2)	67(2)

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C(25)	2516(7)	2355(4)	1097(2)	45(1)
Cl(1A)	4330(3)	10055(2)	329(1)	119(1)
C(1S)	5486(16)	8935(8)	413(3)	91(3)
Cl(1B)	6345(4)	9005(5)	976(2)	140(3)
C(2S)	5200(30)	8791(13)	229(7)	86(8)
Cl(2B)	6638(11)	8304(7)	641(4)	107(3)

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Table 3. Bond lengths [Å] and angles [°] for 6373.

S(1)-O(2)	1.427(3)
S(1)-O(3)	1.429(3)
S(1)-N(2)	1.615(3)
S(1)-C(17)	1.794(4)
O(1)-C(1)	1.191(6)
N(1)-C(6)	1.501(5)
N(1)-C(7)	1.521(5)
N(1)-C(11)	1.526(5)
N(1)-C(10)	1.527(5)
N(2)-C(12)	1.464(5)
C(1)-C(5)	1.474(7)
C(1)-C(2)	1.522(7)
C(2)-C(3)	1.515(10)
C(3)-C(4)	1.498(9)
C(4)-C(5)	1.349(7)
C(5)-C(6)	1.490(6)
C(7)-C(8)	1.504(7)
C(8)-C(9)	1.512(8)
C(9)-C(10)	1.490(8)
C(11)-C(12)	1.540(5)
C(12)-C(13)	1.569(5)
C(13)-C(15)	1.520(6)
C(13)-C(16)	1.523(5)
C(13)-C(14)	1.532(6)
C(17)-C(18)	1.401(6)
C(17)-C(22)	1.408(6)
C(18)-C(19)	1.404(6)
C(18)-C(23)	1.524(6)
C(19)-C(20)	1.366(7)
C(20)-C(21)	1.396(7)
C(20)-C(24)	1.504(7)
C(21)-C(22)	1.367(6)
C(22)-C(25)	1.486(6)
Cl(1A)-C(1S)	1.722(8)

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Cl(1A)-C(2S)	1.780(10)
C(1S)-Cl(1B)	1.755(8)
C(2S)-Cl(2B)	1.766(10)

O(2)-S(1)-O(3)	118.50(17)
O(2)-S(1)-N(2)	107.54(17)
O(3)-S(1)-N(2)	105.72(18)
O(2)-S(1)-C(17)	108.23(19)
O(3)-S(1)-C(17)	107.25(19)
N(2)-S(1)-C(17)	109.36(18)
C(6)-N(1)-C(7)	111.4(3)
C(6)-N(1)-C(11)	113.0(3)
C(7)-N(1)-C(11)	107.8(3)
C(6)-N(1)-C(10)	110.6(3)
C(7)-N(1)-C(10)	100.9(3)
C(11)-N(1)-C(10)	112.4(3)
C(12)-N(2)-S(1)	123.9(3)
O(1)-C(1)-C(5)	125.8(4)
O(1)-C(1)-C(2)	126.9(5)
C(5)-C(1)-C(2)	107.3(5)
C(3)-C(2)-C(1)	106.0(5)
C(4)-C(3)-C(2)	104.1(5)
C(5)-C(4)-C(3)	113.3(6)
C(4)-C(5)-C(1)	109.2(5)
C(4)-C(5)-C(6)	128.6(5)
C(1)-C(5)-C(6)	122.2(4)
C(5)-C(6)-N(1)	114.3(3)
C(8)-C(7)-N(1)	105.0(4)
C(7)-C(8)-C(9)	106.0(4)
C(10)-C(9)-C(8)	106.2(4)
C(9)-C(10)-N(1)	107.0(4)
N(1)-C(11)-C(12)	118.5(3)
N(2)-C(12)-C(11)	110.6(3)
N(2)-C(12)-C(13)	112.2(3)
C(11)-C(12)-C(13)	108.6(3)
C(15)-C(13)-C(16)	107.8(4)

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C(15)-C(13)-C(14)	109.4(4)
C(16)-C(13)-C(14)	109.5(3)
C(15)-C(13)-C(12)	108.5(3)
C(16)-C(13)-C(12)	110.5(3)
C(14)-C(13)-C(12)	111.0(3)
C(18)-C(17)-C(22)	121.7(4)
C(18)-C(17)-S(1)	120.5(3)
C(22)-C(17)-S(1)	117.7(3)
C(17)-C(18)-C(19)	116.6(4)
C(17)-C(18)-C(23)	127.5(4)
C(19)-C(18)-C(23)	115.9(4)
C(20)-C(19)-C(18)	123.3(4)
C(19)-C(20)-C(21)	117.7(4)
C(19)-C(20)-C(24)	121.4(5)
C(21)-C(20)-C(24)	120.9(5)
C(22)-C(21)-C(20)	122.8(4)
C(21)-C(22)-C(17)	117.9(4)
C(21)-C(22)-C(25)	117.8(4)
C(17)-C(22)-C(25)	124.2(4)
C(1S)-Cl(1A)-C(2S)	19.7(5)
Cl(1A)-C(1S)-Cl(1B)	107.6(5)
Cl(2B)-C(2S)-Cl(1A)	118.2(9)

Symmetry transformations used to generate equivalent atoms:

Supporting Information

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 6373. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	38(1)	63(1)	57(1)	29(1)	7(1)	10(1)
S(1)	21(1)	32(1)	29(1)	-3(1)	-2(1)	2(1)
O(1)	72(3)	52(2)	45(2)	8(2)	-7(2)	-13(2)
O(2)	23(1)	45(2)	36(2)	-7(1)	2(1)	-6(1)
O(3)	33(2)	43(2)	36(2)	-2(1)	-4(1)	11(1)
N(1)	26(2)	35(2)	29(2)	-5(2)	-4(2)	-5(2)
N(2)	23(2)	27(2)	28(2)	1(1)	2(1)	-1(1)
C(1)	36(3)	40(2)	63(3)	21(3)	-2(2)	-8(2)
C(2)	58(4)	53(3)	107(6)	31(4)	-10(4)	5(3)
C(3)	74(4)	52(3)	111(6)	31(4)	46(4)	18(3)
C(4)	66(4)	46(3)	69(4)	8(3)	27(3)	7(3)
C(5)	31(2)	35(2)	50(3)	5(2)	5(2)	-4(2)
C(6)	29(2)	31(2)	36(2)	-5(2)	3(2)	-6(2)
C(7)	42(3)	47(2)	34(2)	-16(2)	-2(2)	-3(2)
C(8)	59(3)	55(3)	37(2)	-6(2)	1(3)	-19(3)
C(9)	93(5)	71(4)	47(3)	2(3)	-15(3)	34(4)
C(10)	31(2)	48(2)	40(3)	-1(2)	-16(2)	2(2)
C(11)	19(2)	31(2)	30(2)	-1(2)	-3(2)	-1(2)
C(12)	18(2)	26(2)	28(2)	-1(2)	0(2)	-2(2)
C(13)	19(2)	35(2)	35(2)	-1(2)	-3(2)	0(2)
C(14)	27(2)	48(3)	58(3)	15(2)	-7(2)	-10(2)
C(15)	32(2)	64(3)	58(3)	-26(3)	-24(2)	10(2)
C(16)	27(2)	39(2)	45(2)	2(2)	-7(2)	4(2)
C(17)	25(2)	33(2)	27(2)	-7(2)	-4(2)	2(2)
C(18)	31(2)	36(2)	33(2)	0(2)	0(2)	2(2)
C(19)	40(2)	50(3)	32(2)	0(2)	1(2)	4(2)
C(20)	42(2)	48(3)	36(2)	-7(2)	1(2)	8(2)
C(21)	34(2)	37(2)	57(3)	-10(2)	-7(2)	-3(2)
C(22)	37(2)	31(2)	37(2)	-9(2)	-1(2)	2(2)
C(23)	74(4)	49(3)	36(3)	6(2)	2(2)	-12(3)
C(24)	70(4)	80(4)	51(3)	-29(3)	-11(3)	5(3)

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C(25)	51(3)	33(2)	52(3)	2(2)	1(2)	-7(2)
Cl(1A)	99(2)	117(2)	142(2)	31(2)	18(2)	1(2)
Cl(1B)	72(2)	221(6)	126(4)	77(4)	-11(2)	-51(3)

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Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 6373.

	x	y	z	U(eq)
H(2A)	1385	9826	982	87
H(2B)	-119	9070	1107	87
H(3A)	1255	10500	1692	95
H(3B)	-196	9706	1824	95
H(4)	2378	9231	2281	73
H(6A)	4966	7856	1992	38
H(6B)	4340	7097	1592	38
H(7A)	3816	7862	2745	49
H(7B)	1895	7625	2686	49
H(8A)	2028	6148	3110	60
H(8B)	3522	6758	3350	60
H(9A)	5314	5640	3055	84
H(9B)	3804	4956	2870	84
H(10A)	4696	5367	2171	47
H(10B)	5775	6319	2363	47
H(11A)	862	6709	2091	32
H(11B)	1520	5651	2310	32
H(12)	2239	6157	1364	29
H(14A)	-1217	5445	2100	66
H(14B)	-540	4341	1930	66
H(14C)	-2205	4793	1721	66
H(15A)	349	4184	1065	77
H(15B)	367	5215	755	77
H(15C)	-1335	4726	919	77
H(16A)	-2078	6465	1243	55
H(16B)	-345	6907	1078	55
H(16C)	-894	7024	1607	55
H(19)	3906	4541	-385	49
H(21)	2016	1999	228	51
H(23A)	4226	6168	510	80

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H(23B)	4774	5972	-14	80
H(23C)	5978	5672	401	80
H(24A)	1370	2892	-700	101
H(24B)	2698	1994	-624	101
H(24C)	3219	3067	-863	101
H(25A)	1699	1837	1005	68
H(25B)	2068	2795	1343	68
H(25C)	3498	2000	1210	68
H(1S1)	6362	8890	178	110
H(1S2)	4785	8310	386	110
H(2S1)	4295	8285	208	104
H(2S2)	5748	8805	-76	104
H(1N)	2540(60)	4200(20)	1814(11)	32

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#==========END==========#