Generation and Intermolecular Capture of Cyclopropylacyl Radicals

Markus R. Heinrich and Samir Z. Zard*

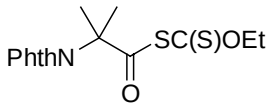
Laboratoire de Synthèse Organique associé au CRNS, Ecole Polytechnique,

91128 Palaiseau Cedex, France

General experimental

Solvents and reagents were used as received. Infra-red spectra were recorded on a Fourier transform IR spectrometer. ^{1}H NMR were recorded using a 400 MHz spectrometer using $CDCl_3$ as solvent referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm). Chemical shifts are reported in parts per million (ppm). Coupling constants are in Hertz (*J* Hz); The following abbreviations are used for the description of signals: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quadruplet), m (multiplet). ^{13}C NMR were recorded at 100.7 MHz in $CDCl_3$ using $CDCl_3$ (77.0 ppm) as standard. Chemical shifts are given in parts per million (ppm). Mass spectra were recorded using electron impact (EI) and electron spray ionization (ESI). Analytical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light, $KMnO_4$ and $(NH_4)_2Ce(NO_3)_6$ to visualise components. Silica gel (Silice 60, A C.C 40-63 μm, SDS) was used for flash column chromatography.

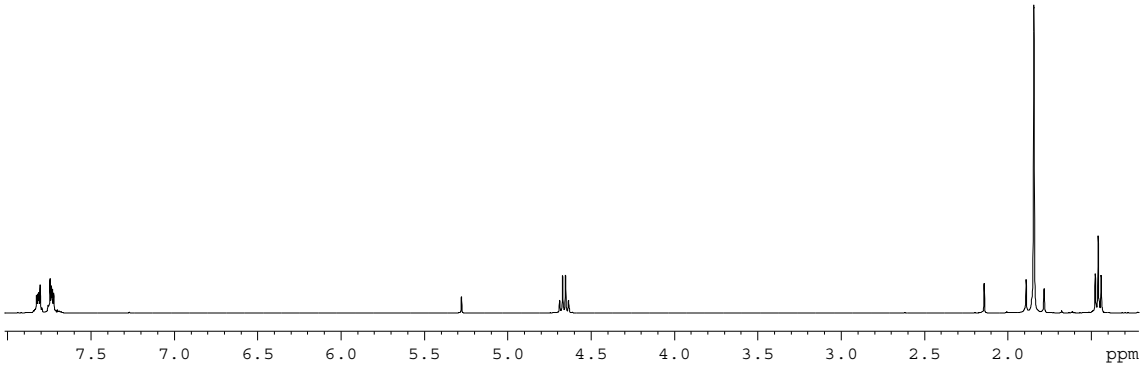
Dithiocarbonic acid [2-(1,3-dioxo-1,3-dihydroisoindol-2-yl)-2-methyl-propionyl] ester ethyl ester (3)

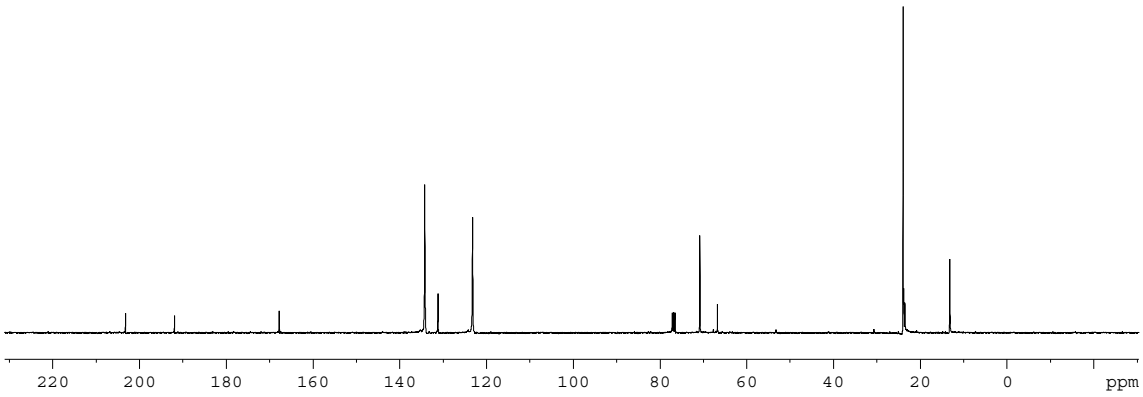


3

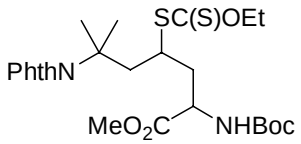
To a solution of 2-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-2-methyl-propionyl chloride **2**[1] (1.00 g, 3.97 mmol) in acetone (20 mL) at 0°C was added ethyl xanthic acid potassium salt (0.61 g, 3.81 mmol). After stirring for 15 min at 0°C the solvent was removed under reduced pressure at 0–10°C. The residue was dissolved in dichloromethane, washed with water, followed by brine and dried over Na_2SO_4. Evaporation of the solvent gave acyl xanthate **3** (1.20 g, 3.56 mmol, 94%)

R_f:	0.60 (1:4 EtOAc–hexanes)
IR:	(CCl_4): $\tilde{\nu}$ = 1781 (m), 1738 (m), 1725 (s), 1264 (m, C–S), 1041 (m, C=S) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 1.46 (t, ^3J = 7.0 Hz, 3H), 1.86 (s, 6H), 4.66 (q, ^3J = 7.0 Hz, 2H), 7.72–7.76 (m, 2H), 7.80–7.84 (m, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 13.33 (CH_3), 24.12 (2×CH_3), 66.92 (C_q), 70.98 (CH_2), 123.37 (2×CH), 131.35 (2×C_q), 134.38 (2×CH), 167.95 (2×C_q), 192.10 (C_q), 203.39 (C_q).
ESI-MS:	354 (M^++NH_3), 338 (M^++H)
	$C_{15}H_{15}NO_4S_2$ (337.42)





2-*tert*-Butoxycarbonylamino-6-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-4-ethoxythio-carbonylsulfanyl-6-methyl-heptanoic acid methyl ester (8)



8

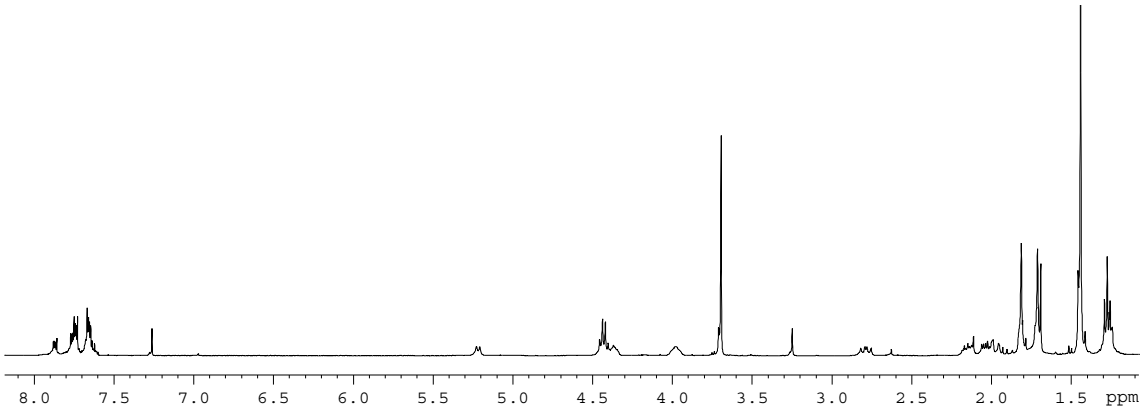
A degassed solution of xanthate **3** (0.30 g, 0.89 mmol), 2-*tert*-butoxycarbonylamino-pent-4-enoic acid methyl ester **4**[2] (0.10 g, 0.44 mmol) and DLP (0.18 g, 0.44 mmol) in 1,2-dichloroethane (1.0 mL) was stirred for 5 h at 60°C. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography (1:4 EtOAc–hexanes) to give the two separated isomers **8a** and **8b** (5 + 8 mg, 0.02 mmol, 6%).

R_f: 0.45 (**8a**), 0.35 (**8b**) (1:4 EtOAc–hexanes)

IR (**8a**): (CCl_4): $\tilde{\nu}$ = 1774 (w), 1746 (m), 1712 (s), 1220 (m, C–S), 1055 (m, C=S) cm^{-1}.

^{1}H-NMR (**8a**): (400 MHz, $CDCl_3$): δ = 1.27 (t, ^3J = 7.2 Hz, 3H), 1.44 (s, 9H), 1.71 (s, 3H), 1.81 (s, 3H), 1.95–2.07 (m, 2H), 2.11–2.18 (m, 1H), 2.79 (dd, ^3J = 15.6 Hz, ^3J = 10.4 Hz, 1H), 3.69 (s, 3H), 3.92–4.01 (m, 1H), 4.33–4.40 (m, 1H), 4.43 (q, ^3J = 7.2 Hz, 2H), 5.22 (d, ^3J = 8.4 Hz, NH), 7.62–7.86 (m, 4H).

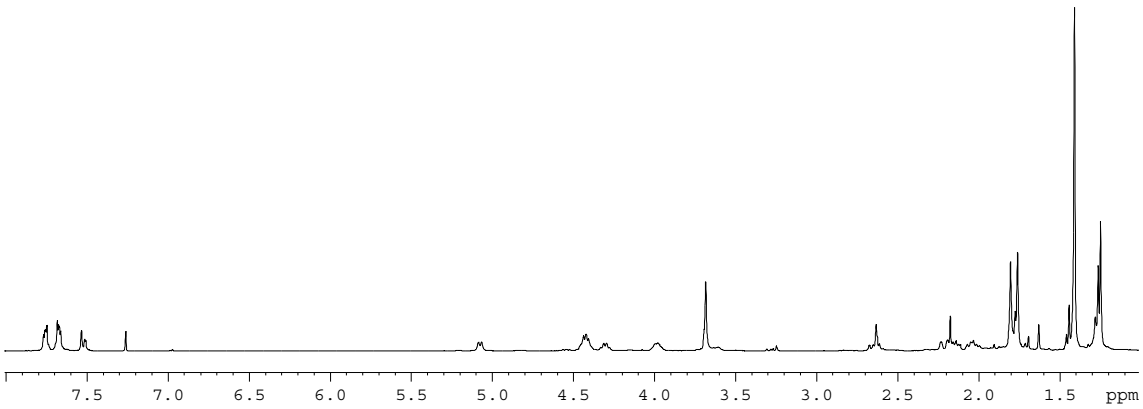
^{13}C-NMR (**8a**): (100.7 MHz, $CDCl_3$): δ = 13.23 (CH_3), 26.52 (CH_3), 27.97 (3×CH_3), 28.74 (CH_3), 39.48 (CH_2), 40.34 (CH_2), 43.05 (CH/CH_3), 51.09 (CH/CH_3), 52.27 (CH/CH_3), 59.29 (C_q), 69.78 (CH_2), 80.11 (C_q), 122.47 (2×CH), 131.76 (2×C_q), 133.63 (2×CH), 155.52 (C_q), 169.97 (2×C_q), 172.62 (C_q), 212.70 (C_q).



IR (**8b**): (CCl_4): $\tilde{\nu}$ = 1774 (w), 1746 (m), 1712 (s), 1216 (m, C–S), 1055 (m, C=S) cm^{-1}.

^{1}H-NMR (**8b**): (400 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 6.4 Hz, 3H), 1.41 (s, 9H), 1.76 (s, 3H), 1.80 (s, 3H), 1.99–2.09 (m, 1H), 2.11–2.24 (m, 2H), 2.60–2.68 (m, 1H), 3.68 (s, 3H), 3.95–4.02 (m, 1H), 4.30 (dt, ^3J = 8.0 Hz, ^3J = 6.8 Hz, 1H), 4.38–4.47 (m, 2H), 5.08 (d, ^3J = 8.0 Hz, NH), 7.50–7.76 (m, 4H).

^{13}C-NMR (**8b**): (100.7 MHz, $CDCl_3$): δ = 13.56 (CH_3), 27.75 (CH_3), 28.29 (3×CH_3), 28.82 (CH_3), 39.61 (CH_2), 42.71 (CH_2), 44.08 (CH/CH_3), 51.55 (CH/CH_3), 52.36 (CH/CH_3), 59.71 (C_q), 69.88 (CH_2), 79.96 (C_q), 122.66 (2×CH), 132.09 (2×C_q), 133.70 (2×CH), 155.03 (C_q), 169.90 (2×C_q), 172.58 (C_q), 212.70 (C_q).



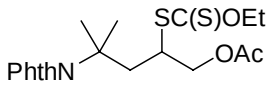
ESI-MS: 556 (M^++NH_4), 539 (M^++H).

FAB-HRMS: $C_{25}H_{34}N_2O_7S_2Na^+$, calcd.: 561.1705, found: 561.1730.

$C_{25}H_{35}N_2O_7S_2^+$, calcd.: 539.1886, found: 539.1865.

$C_{25}H_{34}N_2O_7S_2$ (538.68)

Acetic acid 4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-2-ethoxythiocarbonylsulfanyl-4-methyl-pentyl ester (9)



9

A degassed solution of xanthate **3** (454 mg, 1.35 mmol) in allyl acetate (2.50 mL) was exposed to visible light for 10 h whilst the reaction temperature was kept below 40°C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (1:4 EtOAc–hexanes) to give **9** (420 mg, 1.03 mmol, 76%).

Yield: 76%

R_f: 0.40 (1:4 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1775 (m), 1747 (s), 1713 (s), 1225 (m, C–S), 1054 (m, C=S) cm^{-1}.

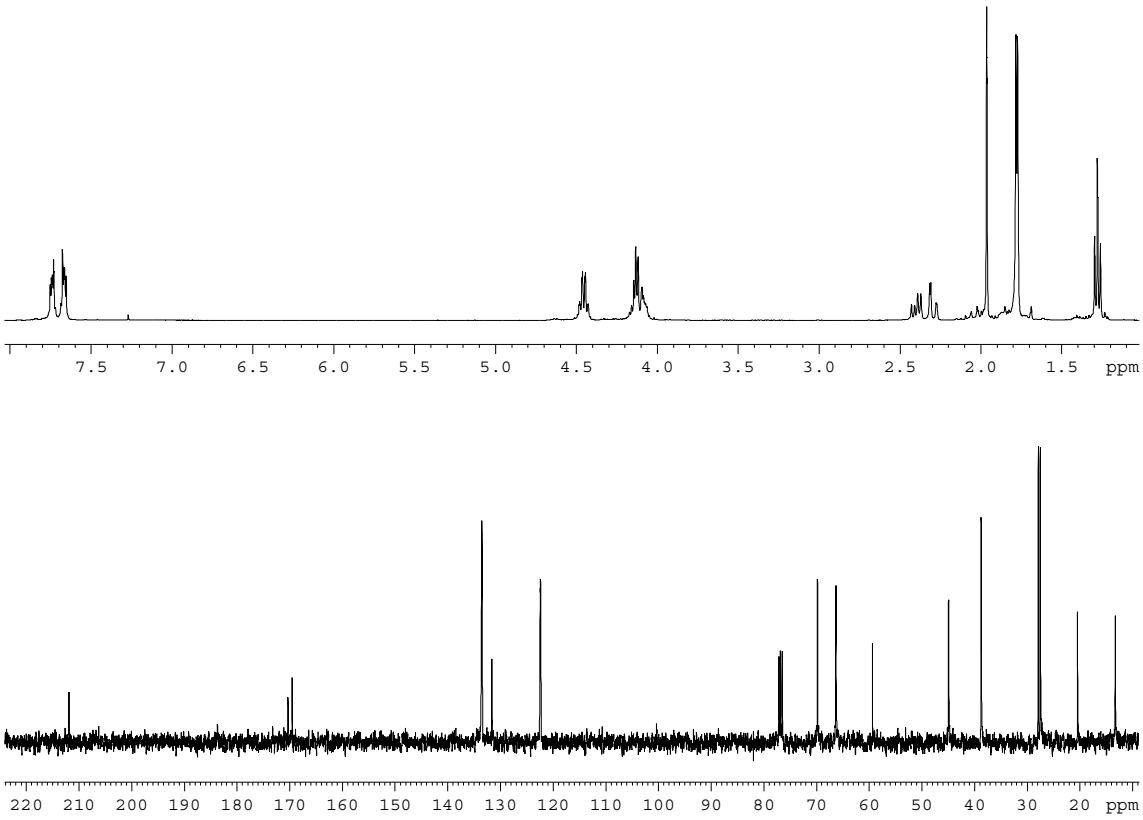
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.31 (t, ^3J = 6.8 Hz, 3H), 1.80 (s, 3H), 1.81 (s, 3H), 1.99 (s, 3H), 2.33 (dd, ^2J = 15.6 Hz, ^3J = 3.2 Hz, 1H), 2.43 (dd, ^2J = 15.6 Hz, ^3J = 8.0 Hz, 1H), 4.08–4.20 (m, 3H), 4.45–4.53 (m, 2H), 7.66–7.71 (m, 2H), 7.75–7.78 (m, 2H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 13.55 (CH_3), 20.70 (CH_3), 27.79 (CH_3), 28.18 (CH_3), 39.06 (CH_2), 45.23 (CH), 59.67 (C_q), 66.62 (CH_2), 70.07 (CH_2), 122.69 (2×CH), 131.95 (2×C_q), 133.78 (2×CH), 169.79 (2×C_q), 170.61 (C_q), 212.21 (C_q).

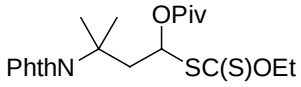
ESI-MS: 427 (M^++NH_4), 410 (M^++H), 408 (M^+–H)

EI-HRMS: $C_{19}H_{23}NO_5S_2$, calcd.: 409.1018, found: 409.1040.

$C_{19}H_{23}NO_5S_2$ (409.52)



2,2-Dimethyl-propionic acid 3-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-1-ethoxythio-carbonylsulfanyl-3-methyl-butyl ester (10)



10

A degassed solution of xanthate **3** (170 mg, 0.50 mmol) in vinyl pivalate (1.50 mL) was exposed to visible light for 2 h while the reaction temperature was kept below 40°C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (1:10 EtOAc–hexanes) to give **10** (206 mg, 0.47 mmol, 94%).

R_f: 0.70 (1:4 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1775 (m), 1735 (m), 1714 (s), 1224 (m, C–S), 1050 (m, C=S) cm^{-1}.

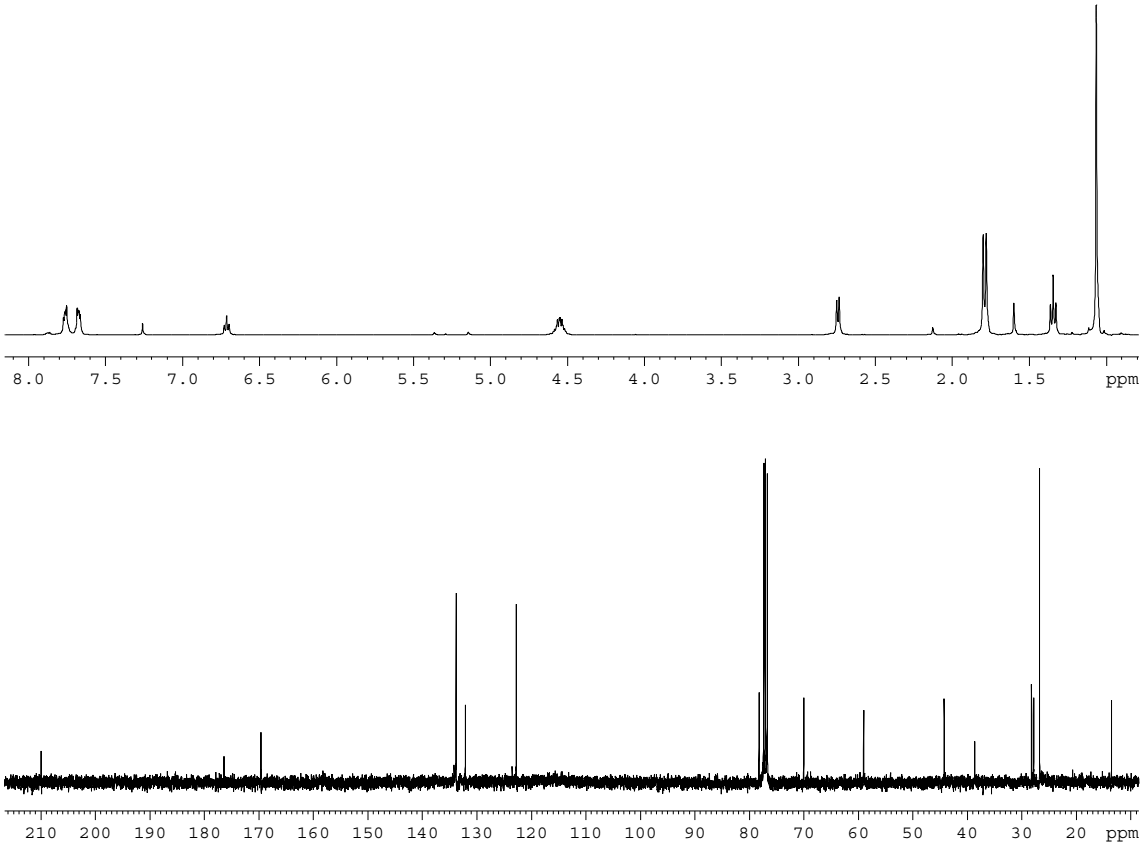
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.01 (s, 9H), 1.29 (t, ^{3}J = 7.2 Hz, 3H), 1.73 (s, 3H), 1.74 (s, 3H), 2.67–2.70 (m, 2H), 4.49 (m, 2H), 6.66 (dd, ^{3}J = 6.8 Hz, ^{3}J = 5.6 Hz, 1H), 7.62–7.65 (m, 2H), 7.68–7.72 (m, 2H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 14.02 (CH_3), 26.55 (3×CH_3), 27.64 (CH_3), 27.99 (CH_3), 38.93 (C_q), 43.96 (CH_2), 58.76 (C_q), 69.88 (CH_2), 77.95 (CH), 122.53 (2×CH), 131.82 (2×C_q), 133.69 (2×CH), 169.40 (2×C_q), 176.18 (C_q), 209.64 (C_q).

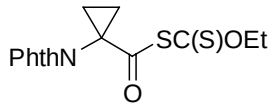
ESI-MS: 455 (M^++NH_4), 438 (M^++H)

FAB-HRMS: $C_{21}H_{27}NO_5S_2Na^+$, calcd.: 460.1229, found: 460.1199.

$C_{21}H_{27}NO_5S_2$ (437.57)



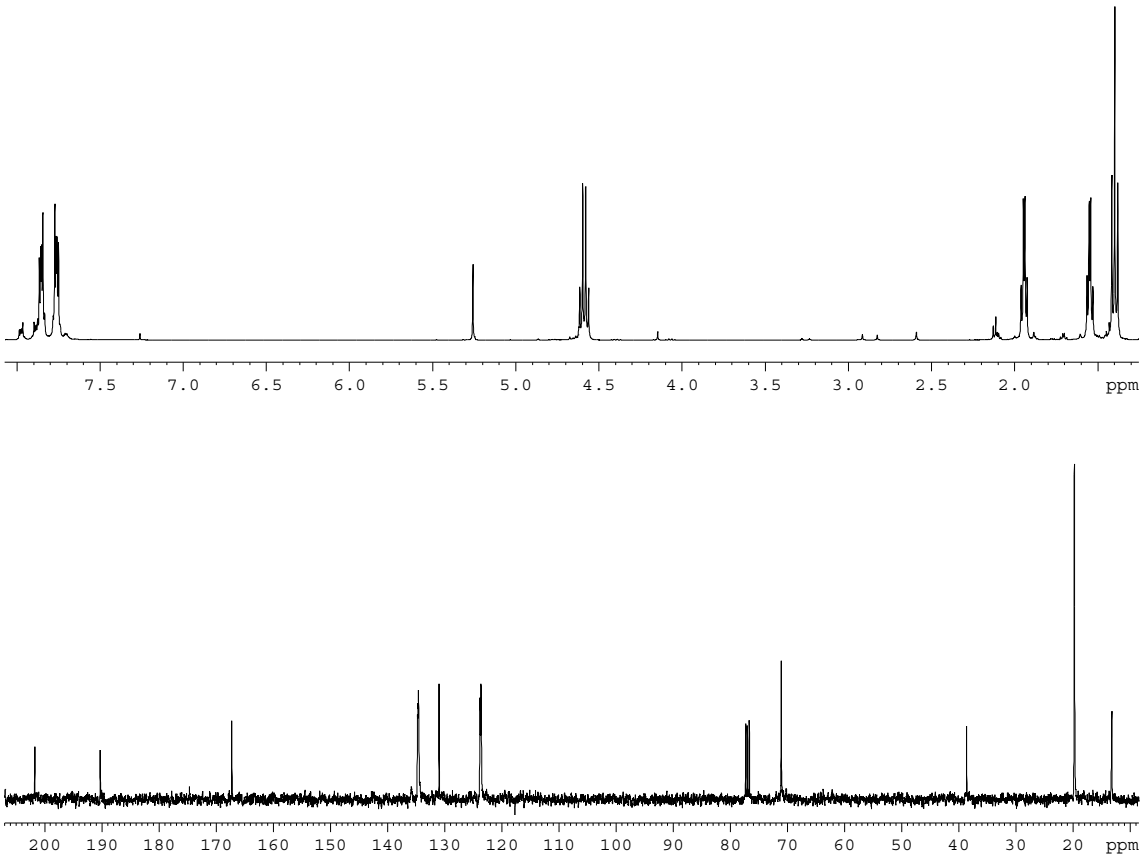
Dithiocarbonic acid [1-(1,3-dioxo-1,3-dihydroisoindol-2-yl)-cyclopropylacyl] ester ethyl ester (15)



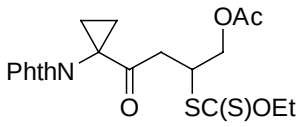
15

To a solution of 1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropanecarbonyl chloride **14**[3] (1.05 g, 4.20 mmol) in acetone (20 mL) at 0°C was added ethyl xanthic acid potassium salt (0.61 g, 3.81 mmol). After stirring for 15 min at 0°C the solvent was removed under reduced pressure at 0–10°C. The residue was dissolved in dichloromethane, washed with water, followed by brine and dried over Na_2SO_4. Evaporation of the solvent gave acyl xanthate **15** (1.15 g, 3.43 mmol, 90%)

R_f:	0.45 (1:4 EtOAc–hexanes)
m.p.:	116–118°C
IR:	(CCl_4): $\tilde{\nu}$ = 1786 (m), 1735 (s), 1391 (s), 1264 (m, C–S), 1042 (m, C=S) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 1.41 (t, ^3J = 7.2 Hz, 3H), 1.56 (dd, ^2J = 9.0 Hz, ^3J = 5.4 Hz, 2H), 1.95 (dd, ^2J = 9.0 Hz, ^3J = 5.4 Hz, 2H), 4.60 (q, ^3J = 7.2 Hz, 2H), 7.74–7.80 (m, 2H), 7.84–7.89 (m, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 13.26 (CH_3), 19.78 (2×CH_2), 38.64 (C_q), 71.09 (CH_2), 123.74 (2×CH), 130.99 (2×C_q), 134.59 (2×CH), 167.28 (2×C_q), 190.26 (C_q), 201.76 (C_q).
ESI-MS:	352 (M^++NH_3), 335 (M^+).
	$C_{15}H_{13}NO_4S_2$ (335.40)



Acetic acid 4-[1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropyl]-2-ethoxythio-carbonylsulfanyl-4-oxo-butyl ester (20)



20

A solution of xanthate **15** (151 mg, 0.45 mmol) and allyl acetate (0.10 mL, 92 mg, 0.92 mmol) in 1,2-dichloroethane (0.5 mL) was refluxed for 5 min under argon. After the addition of DLP (18 mg, 0.05 mmol, 10%) the mixture was refluxed for 1 h and concentrated under reduced pressure. Purification by column chromatography (1:4 EtOAc–hexanes) gave **20** (123 mg, 0.28 mmol, 63%).

R_f: 0.40 (1:4 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1782 (m), 1749 (s), 1728 (s), 1395 (s), 1227 (m, C–S), 1053 (m, C=S) cm^{-1}.

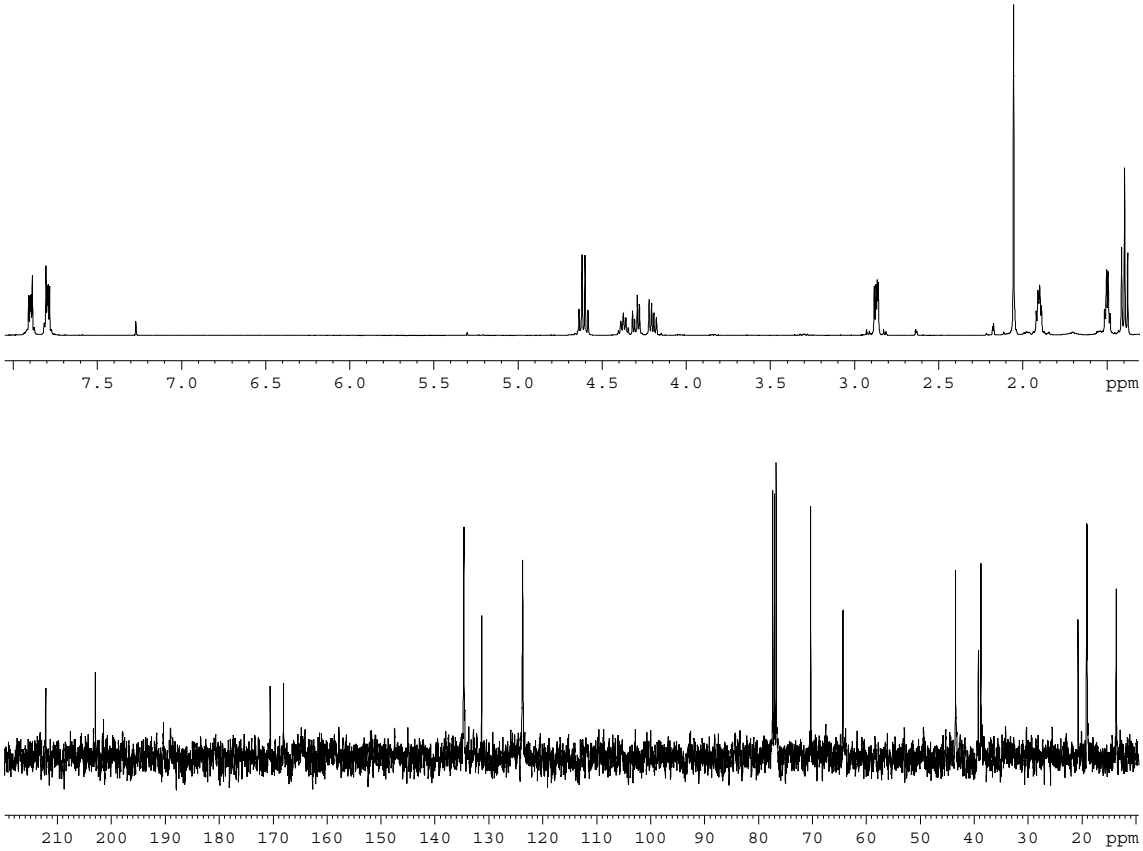
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.41 (t, ^{3}J = 7.0 Hz, 3H), 1.48–1.51 (m, 2H), 1.89–1.92 (m, 2H), 2.06 (s, 3H), 2.84 (dd, ^{2}J = 18.0 Hz, ^{3}J = 5.6 Hz, 1H), 2.90 (dd, ^{2}J = 18.0 Hz, ^{3}J = 7.0 Hz, 1H), 4.19 (dd, ^{2}J = 11.4 Hz, ^{3}J = 6.0 Hz, 1H), 4.30 (dd, ^{2}J = 11.4 Hz, ^{3}J = 5.0 Hz, 1H), 4.35–4.41 (m, 1H), 4.61 (q, ^{3}J = 7.0 Hz, 2H), 7.77–7.82 (m, 2H), 7.88–7.91 (m, 2H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 13.64 (CH_3), 19.05 (CH_2), 19.15 (CH_2), 20.69 (CH_3), 38.75 (CH_2/C_q), 39.21 (CH_2/C_q), 43.45 (CH), 64.32 (CH_2), 70.29 (CH_2), 123.71 (2×CH), 131.33 (2×C_q), 134.61 (2×CH), 168.03 (2×C_q), 170.52 (C_q), 202.91 (C_q), 212.16 (C_q).

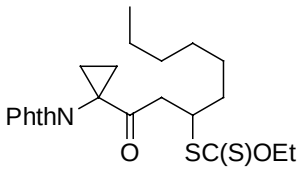
ESI-MS: 453 (M^++NH_4), 336 (M^++H).

EI-HRMS: $C_{20}H_{21}NO_6S_2$, calcd.: 435.0810, found: 435.0799.

$C_{20}H_{21}NO_6S_2$ (435.52)



Dithiocarbonic acid (1-{2-[1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropyl]-2-oxo-ethyl}-heptyl) ester ethyl ester (22)



22

A solution of xanthate **15** (168 mg, 0.50 mmol) and 1-octene (0.16 mL, 112 mg, 1.00 mmol) in 1,2-dichloroethane (0.5 mL) was refluxed for 5 min under argon. After the addition of DLP (20 mg, 0.05 mmol, 10%) the mixture was refluxed for 2.5 h while one more portion of DLP (20 mg, 0.05 mmol) was added after 1h. Concentration under reduced pressure and purification by column chromatography (1:4 EtOAc–hexanes) gave **22** (137 mg, 0.31 mmol, 61%).

R_f: 0.75 (1:4 EtOAc–hexanes)

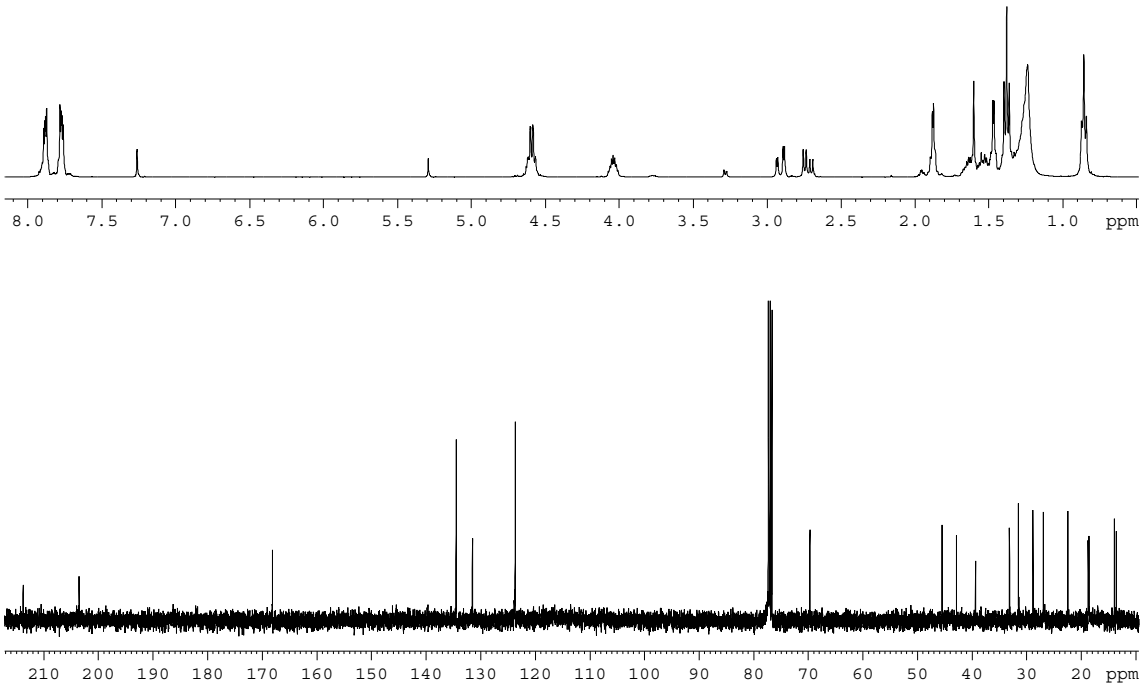
IR: (CCl_4): $\tilde{\nu}$ = 1782 (m), 1728 (s), 1710 (s), 1394 (s), 1218 (m, C–S), 1053 (m, C=S) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.82 (t, ^3J = 6.8 Hz, 3H), 1.12–1.30 (m, 8H), 1.35 (t, ^3J = 7.2 Hz, 3H), 1.41–1.45 (m, 2H), 1.45–1.60 (m, 2H), 1.81–1.85 (m, 2H), 2.70 (dd, ^2J = 18.0 Hz, ^3J = 8.4 Hz, 1H), 2.98 (dd, ^2J = 18.0 Hz, ^3J = 4.0 Hz, 1H), 3.96–4.03 (m, 1H), 4.55 (m, 2H), 7.72–7.76 (m, 2H), 7.82–7.86 (m, 2H).

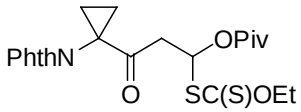
^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 13.55 (CH_3), 13.91 (CH_3), 18.57 (CH_2), 18.72 (CH_2), 22.37 (CH_2), 26.38 (CH_2), 28.72 (CH_2), 31.41 (CH_2), 32.99 (CH_2), 39.21 (C_q), 42.73 (CH_2), 45.32 (CH), 69.67 (CH_2), 123.58 (2×CH), 131.29 (2×C_q), 134.44 (2×CH), 167.98 (2×C_q), 203.47 (C_q), 213.55 (C_q).

EI-HRMS: $C_{23}H_{29}NO_4S_2$, calcd.: 447.1538, found: 447.1537.

$C_{23}H_{29}NO_4S_2$ (447.61)



2,2-Dimethyl-propionic acid 3-[1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropyl]-1-ethoxythiocarbonylsulfanyl-3-oxo-propyl ester (23)



23

A solution of xanthate **15** (168 mg, 0.50 mmol) and vinyl pivalate (0.15 mL, 131 mg, 1.02 mmol) in 1,2-dichloroethane (1 mL) was exposed to visible light and refluxed for 5 h. Concentration and purification by column chromatography (1:10 EtOAc–hexanes) gave starting material **15** (50 mg, 0.15 mmol, 30%) followed by **23** (97 mg, 0.21 mmol, 42%).

R_f: 0.20 (1:10 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1782 (m), 1729 (s), 1395 (s), 1225 (m, C–S), 1135 (s), 1053 (s, C=S) cm^{-1}.

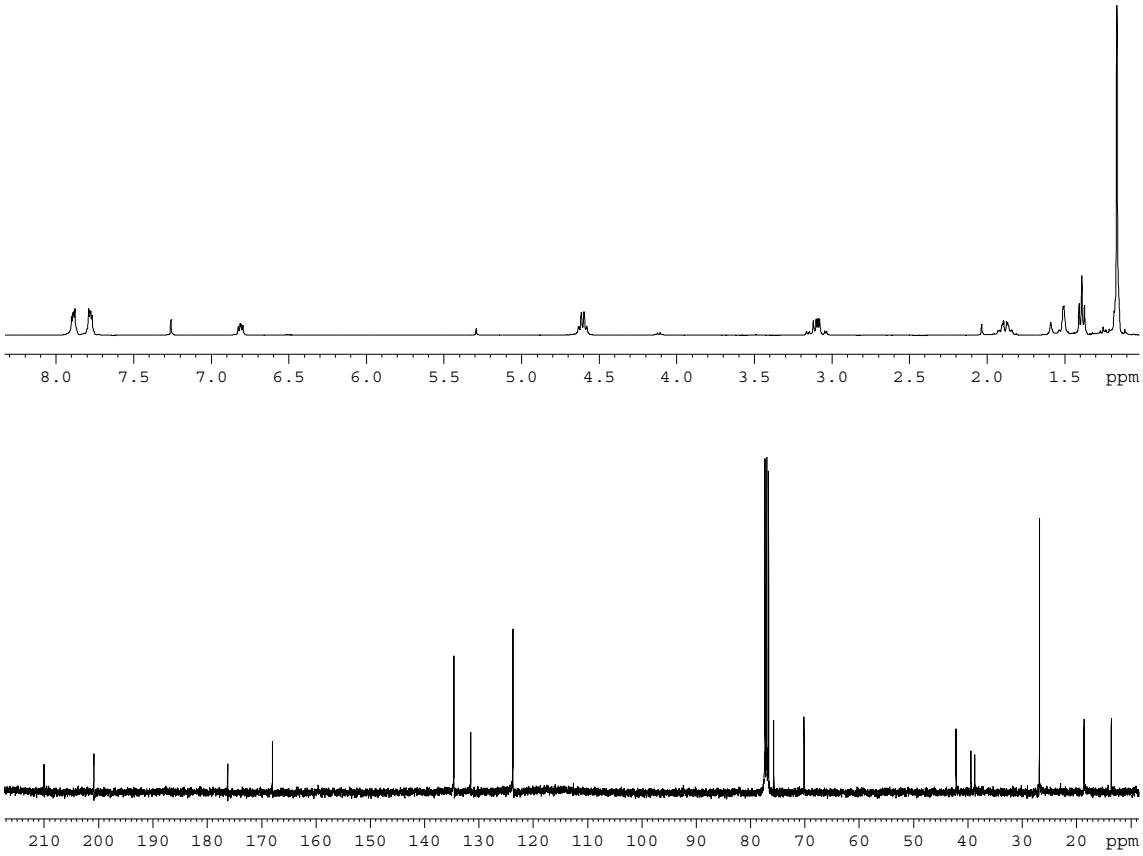
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.12 (s, 9H), 1.35 (t, ^3J = 7.2 Hz, 3H), 1.44–1.52 (m, 2H), 1.82–1.93 (m, 2H), 3.03 (dd, ^2J = 17.8 Hz, ^3J = 4.6 Hz, 1H), 3.10 (dd, ^2J = 17.8 Hz, ^3J = 7.2 Hz, 1H), 4.56 (q, ^3J = 7.2 Hz, 2H), 6.77 (dd, ^3J = 7.2 Hz, ^3J = 4.6 Hz, 1H), 7.68–7.79 (m, 2H), 7.79–7.89 (m, 2H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 13.54 (CH_3), 18.60 (CH_2), 18.66 (CH_2), 26.71 (3×CH_3), 38.74 (C_q), 39.25 (C_q), 42.01 (CH_2), 70.13 (CH_2), 75.44 (CH), 123.62 (2×CH), 131.25 (2×C_q), 134.51 (2×CH), 167.91 (2×C_q), 176.13 (C_q), 200.90 (C_q), 209.84 (C_q).

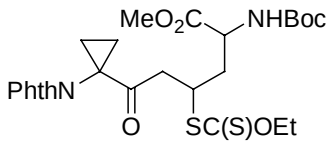
ESI-MS: 481 (M^++NH_4), 463 (M^+).

EI-HRMS: $C_{22}H_{25}NO_6S_2$, calcd.: 463.1123, found: 463.1114.

$C_{22}H_{25}NO_6S_2$ (463.57)



2-*tert*-Butoxycarbonylamino-6-[1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropyl]-4-ethoxythiocarbonylsulfanyl-6-oxo-hexanoic acid methyl ester (24), mixture of isomers



24

A solution of xanthate **15** (180 mg, 0.54 mmol) and 2-*tert*-butoxycarbonylamino-pent-4-enoic acid methyl ester **4**[2] (185 mg, 0.80 mmol) in 1,2-dichloroethane (1.0 mL) was refluxed for 5 mins under argon. After the addition of DLP (21 mg, 0.05 mmol, 10%) the mixture was refluxed for 2 h while two more portions of DLP (11 mg, 0.03 mmol) were added. Concentration under reduced pressure and purification by column chromatography (3:7 EtOAc–hexanes) gave **24** (173 mg, 0.31 mmol, 57%).

R_f: 0.45 (3:7 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1782 (m), 1726 (s, br), 1499 (s), 1391 (s), 1219 (m, C–S), 1171 (s), 1053 (s, C=S) cm^{-1}.

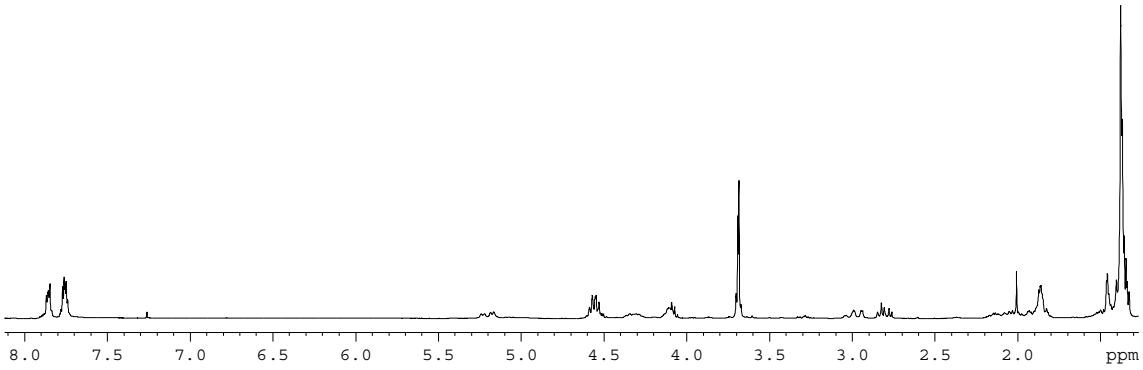
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.33–1.39 (m, 12H), 1.43–1.47 (m, 2H), 1.82–1.88 (m, 2H), 1.90–2.15 (m, 2H), 2.75–2.85 (m, 1H), 2.92–3.04 (m, 1H), 3.68, 3.69 (each s, 3H), 4.08–4.15 (m, 1H), 4.27–4.38 (m, 1H), 4.52–4.60 (m, 2H), 5.17, 5.23 (each d, ^3J = 8.0 Hz, 1H), 7.72–7.78 (m, 2H), 7.83–7.87 (m, 2H).

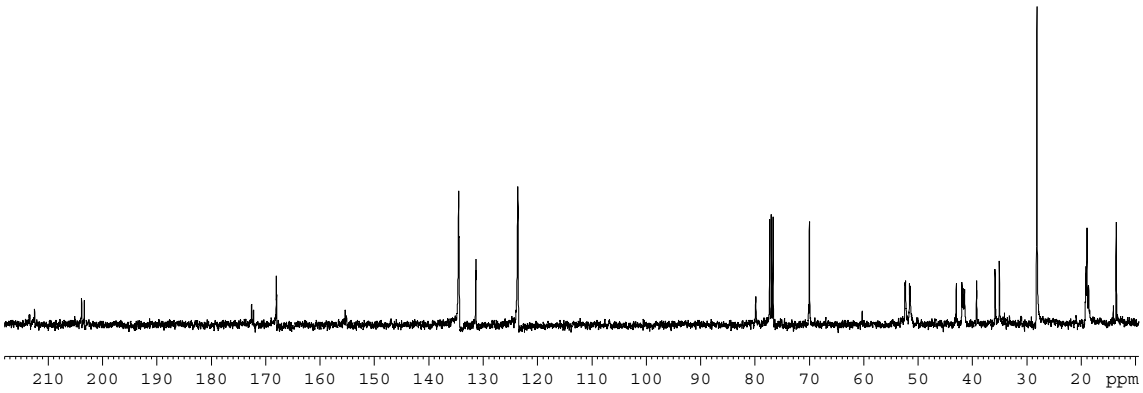
^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 13.57 (CH_3), 18.63, 18.95, 19.13 (2×CH_2), 28.15 (3×CH_3), 35.06, 35.83 (CH_2), 39.21 (C_q), 41.46, 42.99 (CH_2), 41.75, 41.93 (CH), 51.44, 51.58 (CH/CH_3), 52.32 (CH/CH_3), 69.99 (CH_2), 79.85 (C_q), 123.64 (2×CH), 131.32 (2×C_q), 134.53 (2×CH), 155.11, 155.35 (C_q), 168.02 (2×C_q), 172.21, 172.55 (C_q), 203.32, 203.83 (C_q), 212.50, 213.37 (C_q).

ESI-MS: 582 (M^++NH_4), 565 (M^++H).

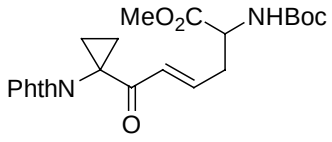
EI-HRMS: $C_{26}H_{32}N_2O_8S_2$, calcd.: 564.1600, found: 564.1607.

$C_{26}H_{32}N_2O_8S_2$ (564.67)





(*E*)-2-*tert*-Butoxycarbonylamino-6-[1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropyl]-6-oxo-hex-4-enoic acid methyl ester (25)



25

To a solution of **24** (27 mg, 0.048 mmol) in dichloromethane (4 mL) at 0°C was added DBU (ca. 0.015 mL, 0.100 mmol). After 1 h at 0°C the mixture was washed with satd. ammonium chloride, dried over Na_2SO_4 and concentrated. Purification by column chromatography (3:7 EtOAc–hexanes) gave **25** (18 mg, 0.041 mmol, 86%).

R_f: 0.30 (3:7 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1782 (w), 1727 (s, br), 1692 (w), 1495 (w), 1396 (m), 1170 (w) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.41 (m, 9H), 1.53–1.57 (m, 2H), 1.87–1.92 (m, 2H), 2.55–2.62 (m, 1H), 2.64–2.72 (m, 1H), 3.71 (s, 3H), 4.39–4.45 (m, 1H), 5.06 (d, ^3J = 7.6 Hz, 1H), 6.14 (d, ^3J = 15.2 Hz, 1H), 6.85 (ddd, ^3J = 15.2 Hz, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 1H), 7.75–7.79 (m, 2H), 7.86–7.89 (m, 2H).

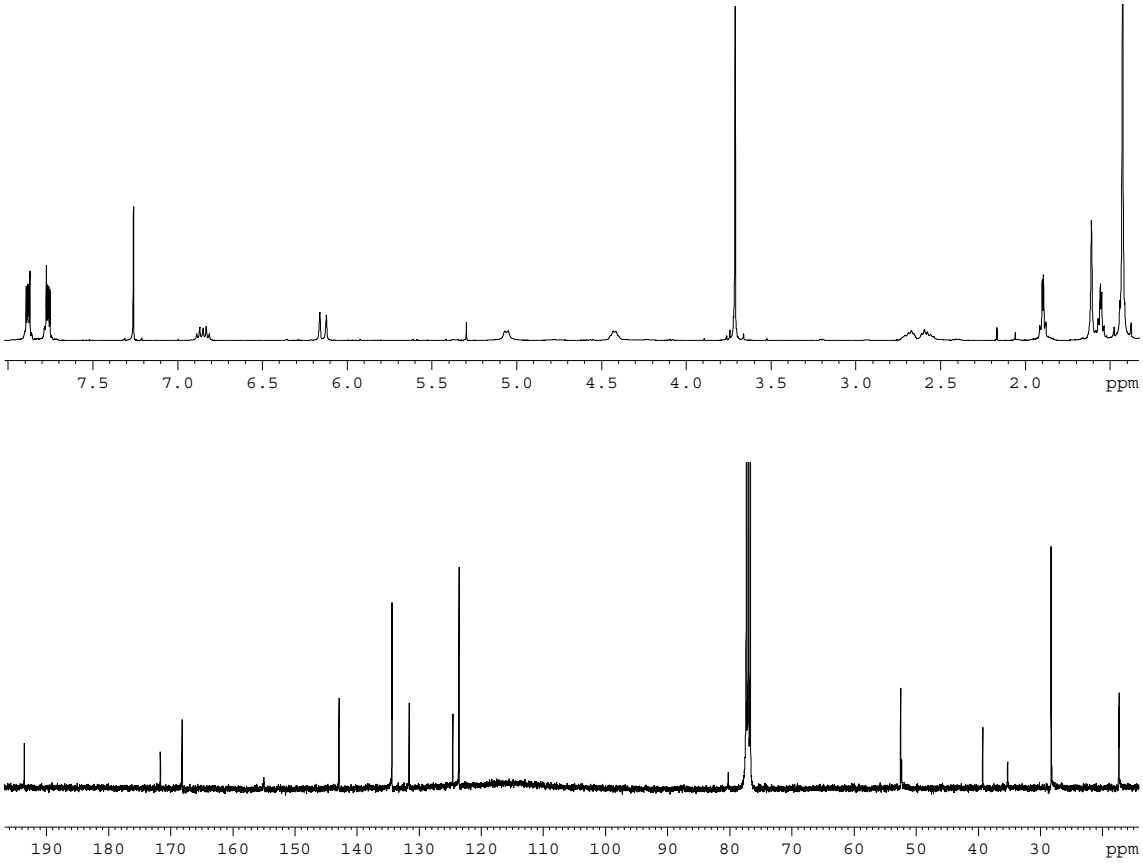
^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 17.33 (CH_2), 17.38 (CH_2), 28.26 (3×CH_3), 35.28 (CH_2), 39.29 (C_q), 52.37 (CH), 52.51 (CH_3), 80.26 (C_q), 123.60 (2×CH), 124.60 (CH), 131.62 (2×C_q), 134.37 (2×CH), 142.93 (CH), 154.99 (C_q), 168.18 (2×C_q), 171.70 (C_q), 193.54 (C_q).

ESI-MS: 460 (M^++NH_4), 443 (M^++H).

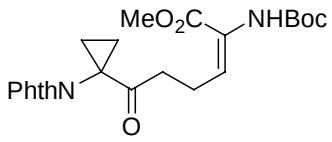
$C_{23}H_{26}N_2O_7$ (442.46)

FAB-HRMS: $C_{23}H_{26}N_2O_7Na^+$, calcd.: 465.1638, found: 465.1664.

$C_{23}H_{26}N_2O_7$ (442.46)



2-*tert*-Butoxycarbonylamino-6-[1-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-cyclopropyl]-6-oxo-hex-2-enoic acid methyl ester (27)



27

To a solution of **24** (31 mg, 0.055 mmol) in dichloromethane (10 mL) under argon was added DBU (0.017 mL, 0.110 mmol) and Na_2SO_4 (50 mg). After 48 h at r.t. the mixture was washed with satd. ammonium chloride, dried over Na_2SO_4 and concentrated. Purification by column chromatography (3:7 EtOAc–hexanes) gave a 4:1 mixture (22 mg, 0.050 mmol, 90%) of **27** (72%) and **25** (18%). Only a small amount (5 mg) of **27** could be separated of **25**.

R_f: 0.30 (3:7 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 3436 (w), 1782 (w), 1727 (s), 1492 (m), 1395 (m), 1169 (m) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.42–1.47 (m, 2H), 1.45 (s, 9H), 1.87–1.91 (m, 2H), 2.41 (dt, ^3J = 7.2 Hz, ^3J = 7.0 Hz, 2H), 2.60 (t, ^3J = 7.0 Hz, 2H), 3.75 (s, 3H), 6.29 (t, ^3J = 7.2 Hz, 1H), 6.33 (s, 1H), 7.76–7.80 (m, 2H), 7.87–7.91 (m, 2H).

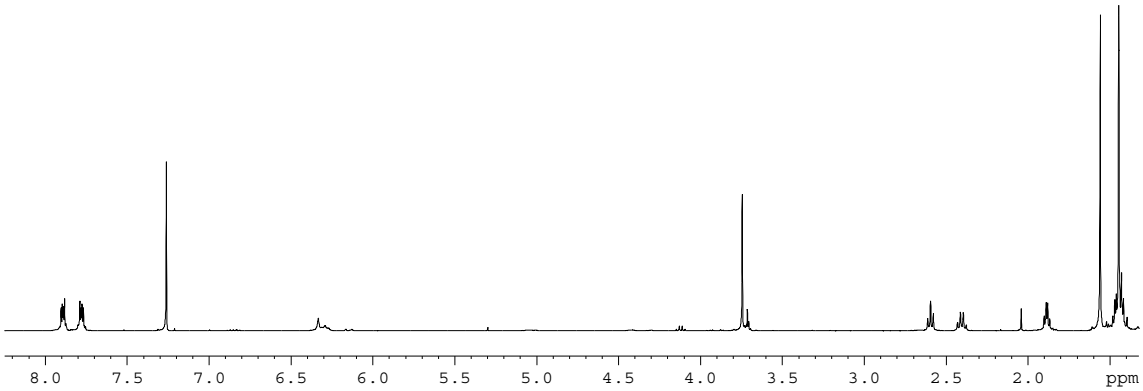
^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 18.82 (2×CH_2), 22.31 (CH_2), 28.17 (3×CH_3), 36.20 (CH_2), 39.22 (C_q), 52.23 (CH_3), 80.54 (C_q), 123.69 (2×CH), 131.52 (2×C_q), 133.23 (CH), 134.52 (2×CH), 153.35 (C_q), 168.18 (2×C_q), 205.10 (C_q). (2×C_q missing)

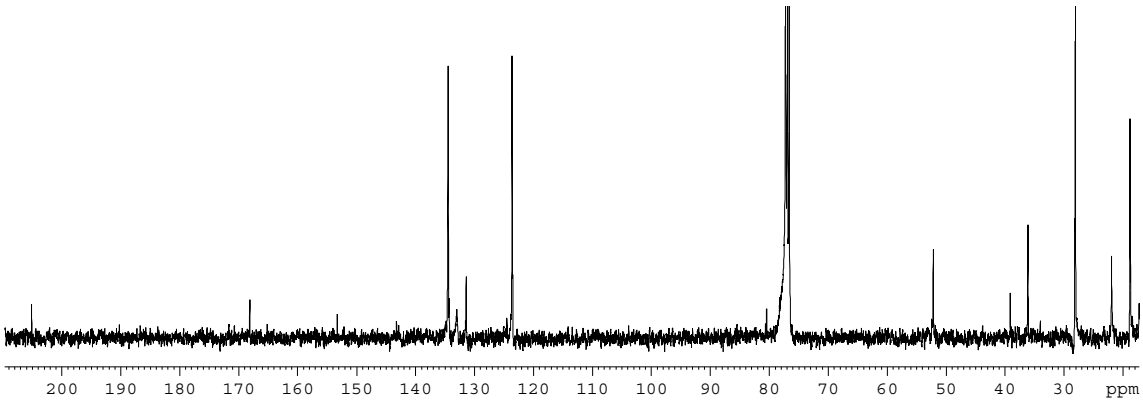
ESI-MS: 460 (M^++NH_4), 443 (M^++H).

FAB-HRMS: $C_{23}H_{26}N_2O_7Na^+$, calcd.: 465.1638, found: 465.1651.

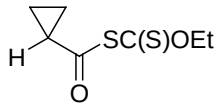
$C_{23}H_{27}N_2O_7^+$, calcd.: 443.1818, found: 443.1800.

$C_{23}H_{26}N_2O_7$ (442.46)





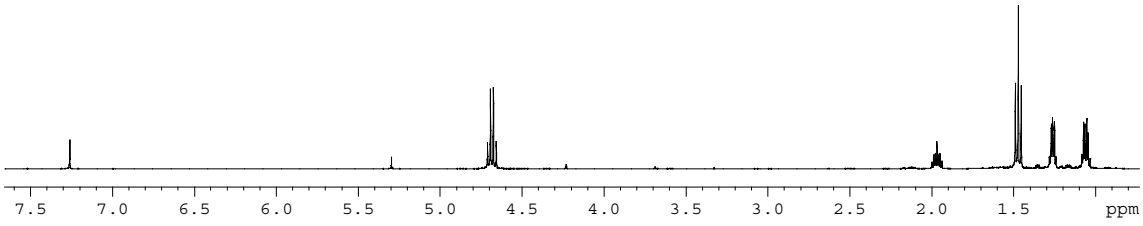
Dithiocarbonic acid (cyclopropylacyl) ester ethyl ester (28)

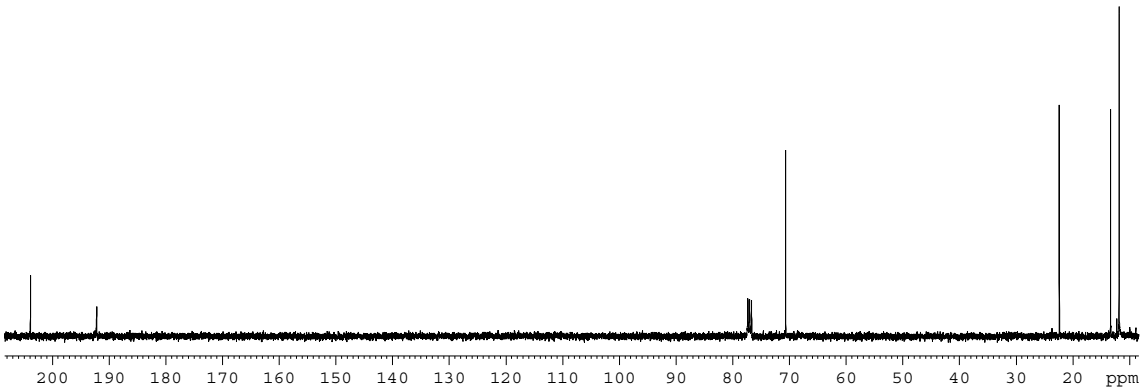


28

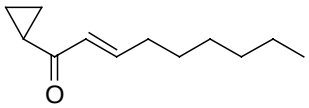
To a solution of cyclopropanecarbonyl chloride (1.60 g, 15.3 mmol) in acetone (30 mL) at 0°C was added ethyl xanthic acid potassium salt (2.45 g, 15.3 mmol). After stirring for 15 min at 0°C the solvent was removed under reduced pressure at 0–10°C. The residue was dissolved in dichloromethane, followed by water and brine and dried over Na_2SO_4. Evaporation of the solvent gave acyl xanthate **28** (2.71 g, 14.2 mmol, 93%)

R_f:	0.85 (1:10 EtOAc–hexanes)
IR:	(CCl_4): $\tilde{\nu}$ = 1721 (s), 1362 (s), 1259 (m, C–S), 1240 (s), 1038 (m, C=S) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 1.03–1.08 (m, 2H), 1.23–1.26 (m, 2H), 1.46 (t, ^3J = 7.2 Hz, 3H), 1.92–1.99 (m, 1H), 4.66 (q, ^3J = 7.2 Hz, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 12.01 (2×CH_2), 13.43 (CH_3), 22.39 (CH), 70.80 (CH_2), 192.33 (C_q), 203.89 (C_q).
ESI-MS:	208 (M^++NH_4), 191 (M^++H)
EI-HRMS:	$C_7H_{10}O_2S_2$, calcd.: 190.0122, found: 190.0118.
	$C_7H_{10}O_2S_2$ (190.29)





(*E*)-1-Cyclopropyl-non-2-en-1-one (30)[4]

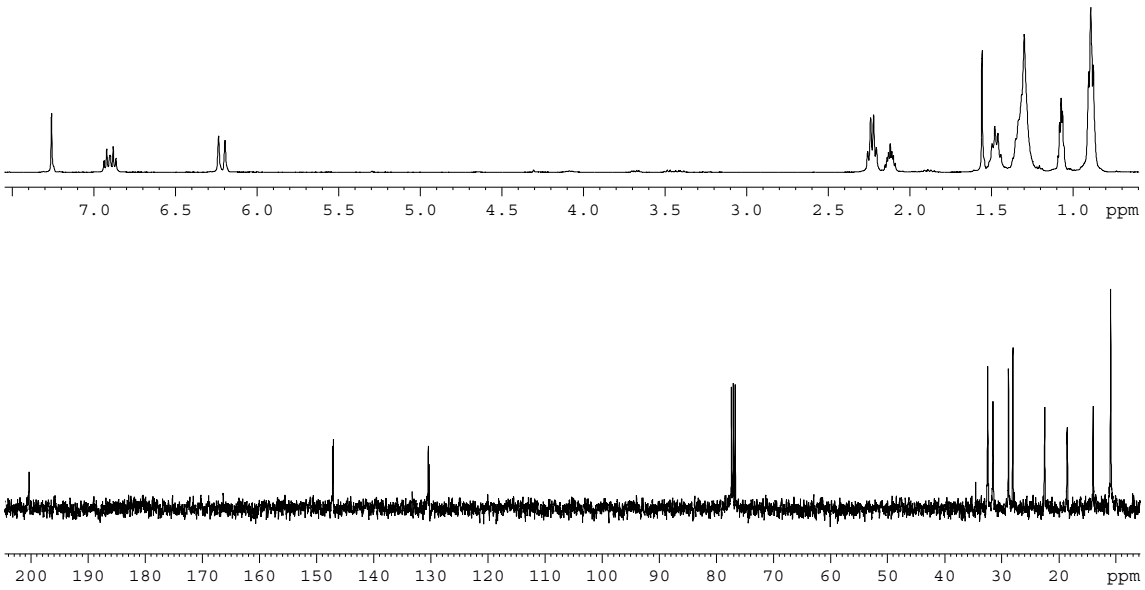


30

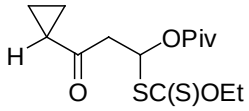
A solution of xanthate **28** (141 mg, 0.74 mmol) in 1-octene (1.50 mL) was exposed to visible light and refluxed for 2 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (5 mL). After the addition of DBU (0.14 mL, 140 mg, 0.92 mmol) the reaction mixture was stirred for 40 min at r.t. and finally quenched with satd. ammonium chloride (10 mL). Extraction with dichloromethane, drying over Na_2SO_4 and purification by column chromatography (3:97 EtOAc–hexanes) gave **30** (106 mg, 0.59 mmol, 79%).

R_f:	0.30 (3:97 EtOAc– hexanes)
IR:	(CCl_4): $\tilde{\nu}$ = 2958 (m), 2929 (s), 2856 (m), 1686 (s), 1666 (s), 1627 (s), 1387 (s) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 5H), 1.04–1.08 (m, 2H), 1.24–1.35 (m, 6H), 1.47 (tt, ^3J = 7.0 Hz, ^3J = 7.0 Hz, 2H), 2.09–2.16 (m, 1H), 2.22 (tdd, ^3J = 7.0 Hz, ^3J = 6.8 Hz, ^4J = 1.4 Hz, 2H), 6.21 (dt, ^3J = 15.6 Hz, ^4J = 1.4 Hz, 1H), 6.90 (dt, ^3J = 15.6 Hz, ^3J = 6.8 Hz, 1H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 10.93 (2×CH_2), 14.01 (CH/CH_3), 18.56 (CH/CH_3), 22.49 (CH_2), 28.06 (CH_2), 28.82 (CH_2), 31.55 (CH_2), 32.46 (CH_2), 130.36 (CH), 147.10 (CH), 200.36 (C_q).
ESI-MS:	198 (M^++NH_4), 181 (M^++H).
EI-HRMS:	$C_{12}H_{20}O$, calcd.: 180.1514, found: 180.1527.

$C_{12}H_{20}O$ (180.29)



2,2-Dimethyl-propionic acid 3-cyclopropyl-1-ethoxythiocarbonylsulfanyl-3-oxo-propyl ester (31)



31

A solution of xanthate **28** (170 mg, 0.89 mmol) in vinyl pivalate (1.50 mL) was exposed to visible light and refluxed for 7.5 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (1:20 EtOAc– hexanes and 100% CH_2Cl_2) to give **31** (102 mg, 0.16 mmol, 36%, calculated from NMR spectra) along with minor amounts of cyclopropane carboxylic acid. Due to difficulties with purification and decomposition **31** was directly converted to **32**.

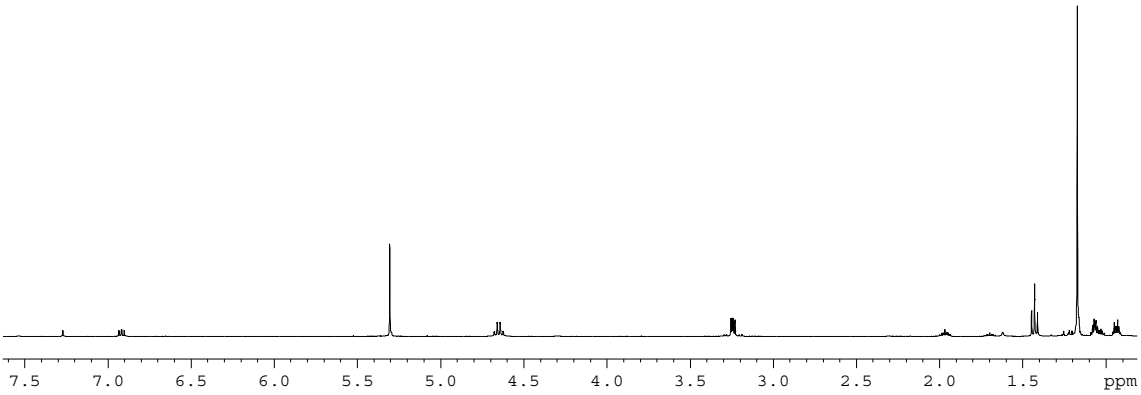
R_f: 0.25 (1:20 EtOAc–hexanes)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.91–0.96 (m, 2H), 1.03–1.09 (m, 2H), 1.17 (s, 9H), 1.43 (t, ^3J = 7.0 Hz, 3H), 1.93–2.00 (m, 1H), 3.22 (dd, ^2J = 16.4 Hz, ^3J = 7.0 Hz, 1H), 3.27 (dd, ^2J = 16.4 Hz, ^3J = 5.8 Hz, 1H), 4.65 (t, ^3J = 7.0 Hz, 2H), 6.92 (dd, ^3J = 7.0 Hz, ^3J = 5.8 Hz, 1H).

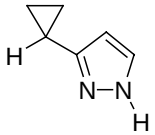
^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 11.38 (2×CH_2), 13.62 (CH_3), 20.75 (CH), 26.81 (3×CH_3), 38.79 (C_q), 47.30 (CH_2), 70.16 (CH_2), 76.27 (CH), 176.42 (C_q), 205.09 (C_q), 210.20 (C_q).

ESI-MS: 336 (M^++NH_4), 319 (M^++H).

$C_{14}H_{22}O_4S_2$ (318.45)



3-Cyclopropyl-1*H*-pyrazole (32)



32

To a solution of crude **31** (~ 0.23 mmol) in acetic acid (1 mL) was added hydrazine hydrate (0.13 mL, 2.5 mmol). The resulting mixture was stirred for 45 min at r.t. and diluted with 2N HCl (10 mL). After washing with dichloromethane (2×10 mL), the aqueous phase was basified with satd. Na_2CO_3. Extraction with dichloromethane (2×10 mL), drying over Na_2SO_4, purification by column chromatography (1:4 EtOAc–hexanes to 100% EtOAc) and sublimation under atmospheric pressure gave **32** (15 mg, 0.14 mmol, 60%).

R_f: 0.85 (100% EtOAc)

IR: (CCl_4): $\tilde{\nu}$ = 3481 (s), 3193 (s, br), 3007 (s, br), 1534 (m), 1499 (m), 1470 (m), 1369 (m), 1264 (m), 1240 (m), 1104 (m), 1026 (m) cm^{-1}.

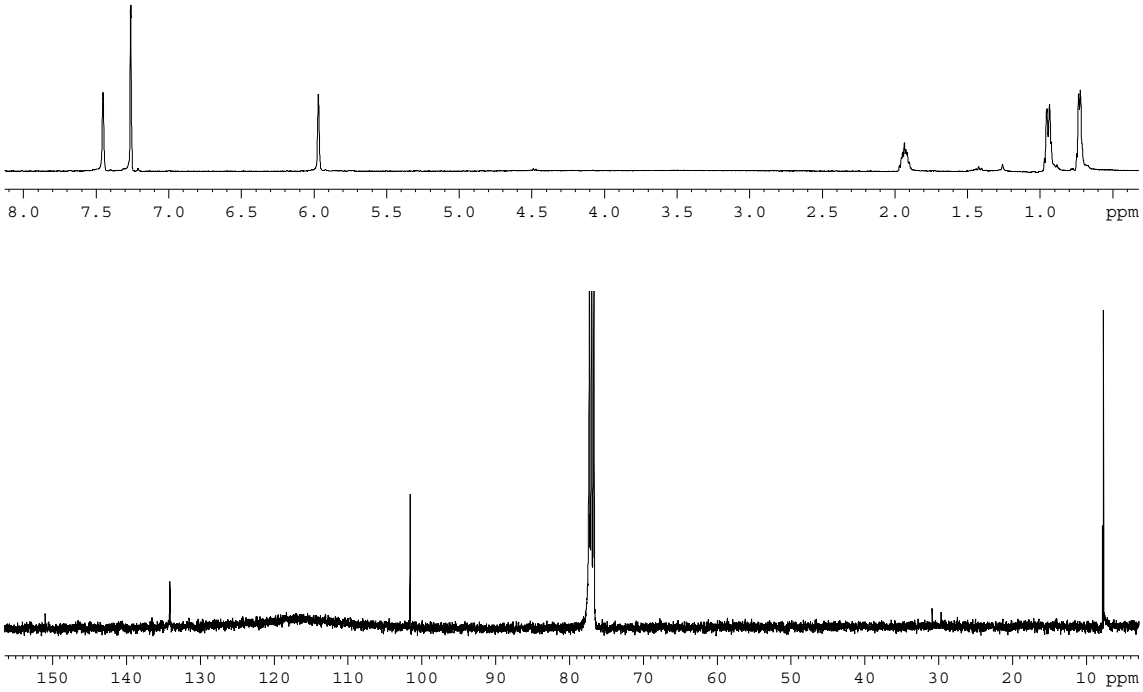
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.73 (ddd, *J* = 6.8 Hz, *J* = 6.4 Hz, *J* = 4.4 Hz, 2H), 0.94 (ddd, *J* = 8.4 Hz, *J* = 6.4 Hz, *J* = 4.4 Hz, 2H), 1.90–1.96 (m, 1H), 5.96 (d, ^3J = 2.0 Hz, 1H), 7.45 (d, ^3J = 2.0 Hz, 1H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 7.68 (2×CH_2), 7.82 (CH), 101.59 (CH), 134.10 (CH), 150.99 (C_q).

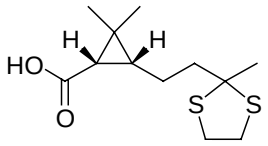
ESI-MS: 109 (M^++H).

EI-HRMS: $C_6H_8N_2$, calcd.: 108.0688, found: 108.0687.

$C_6H_8N_2$ (108.14)



(1*S*,3*R*)-2,2-Dimethyl-3-[2-(2-methyl-[1,3]dithiolan-2-yl)-ethyl]-cyclopropanecarboxylic acid (precursor for 33)



p33

p33 was prepared according to ref.[5] from (1*S*,3*R*)-2,2-dimethyl-3-(3-oxo-butyl)-cyclopropanecarboxylic acid[6] (1.37 g, 7.42 mmol), 1,2-ethanedithiol (0.62 mL, 0.70 g, 7.42 mmol) and boron trifluoride etherate (1.10 mL, 1.26 g, 8.90 mmol). Purification by column chromatography gave **p33** (1.70 g, 6.53 mmol, 88%).

R_f: 0.35 (1:10 EtOAc–hexanes)

m.p.: 97°C

α_D^{23}: +20° (c = 0.76 in MeOH)

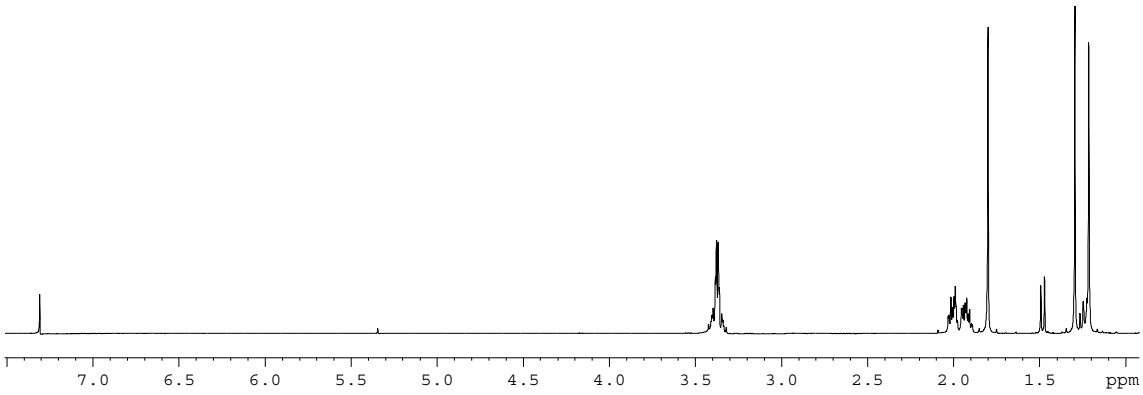
IR: (CCl_4): $\tilde{\nu}$ = 2958 (m), 2924 (m), 1695 (s), 1438 (m), 1225 (s) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.13 (s, 3H), 1.13–1.18 (m, 1H), 1.21 (s, 3H), 1.40 (d, ^3J = 8.8 Hz, 1H), 1.71 (s, 3H), 1.82–1.88 (m, 2H), 1.90–1.94 (m, 2H), 3.23–3.35 (m, 4H).

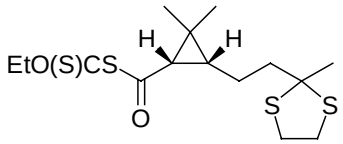
^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 14.25 (CH_3), 21.38 (CH_2), 26.86 (C_q), 28.45 (CH/CH_3), 29.12 (CH/CH_3), 31.84 (CH_3), 34.65 (CH/CH_3), 39.69 (CH_2), 39.78 (CH_2), 45.65 (CH_2), 66.50 (C_q), 178.47 (C_q).

ESI-MS: 278 (M^++NH_4), 261 (M^++H), 243 (M^+–OH).

$C_{12}H_{20}O_2S_2$ (260.42)



Dithiocarbonic acid [(1*S*,3*R*)-2,2-dimethyl-3-(3-oxo-butyl)-cyclopropylacyl] ester ethyl ester (33)

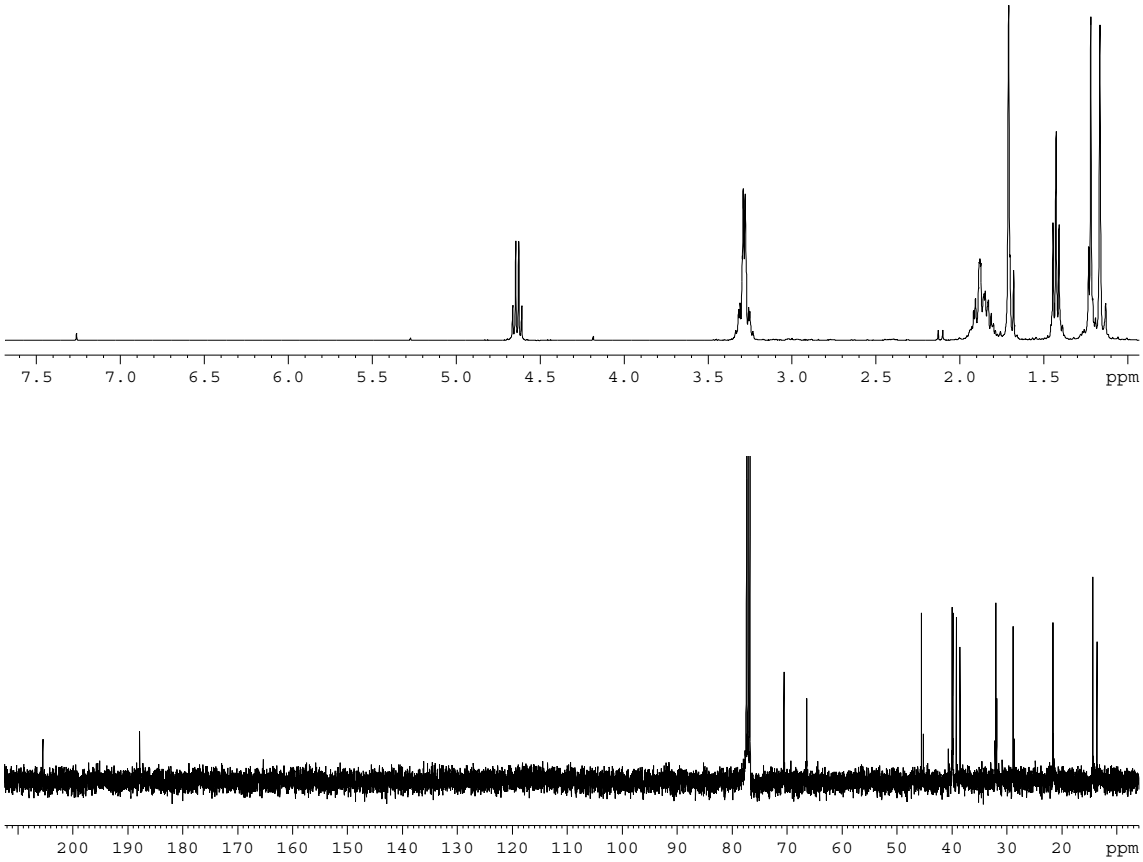


33

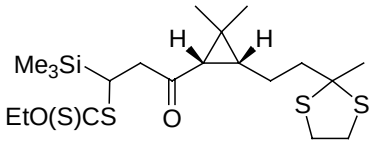
To an ice-cooled solution of acid **p33** (0.60 g, 2.30 mmol) in dichloromethane (10 mL) under argon were added oxalyl chloride (0.30 mL, 0.44 g, 3.46 mmol) and a catalytic amount of DMF. After stirring for 90 min at 0°C, the solvent was removed under reduced pressure and the residue dried *in vacuo*. The crude acid chloride was dissolved in acetone (20 mL) at 0°C and ethyl xanthic acid potassium salt (0.36 g, 2.25 mmol) was added. After stirring for 15 min at 0°C the solvent was removed under reduced pressure at 0–10°C. The residue was dissolved

in hexanes, washed with water, followed by brine and dried over Na_2SO_4. Evaporation of the solvent gave acyl xanthate **33** (0.78 g, 2.15 mmol, 93%)

R_f:	0.75 (1:10 EtOAc–hexanes)
α_D:	+40° (c = 0.25 in $CHCl_3$)
IR:	(CCl_4): $\tilde{\nu}$ = 2958 (m), 2924 (m), 1725 (s), 1255 (s, C–S), 1236 (s), 1033 (s, C=S), 983 (s) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 1.13 (s, 3H), 1.22 (s, 3H), 1.39–1.45 (m, 1H), 1.43 (t, ^3J = 7.0 Hz, 3H), 1.69 (d, ^3J = 8.8 Hz, 1H), 1.71 (s, 3H), 1.82–1.95 (m, 4H), 3.23–3.34 (m, 4H), 4.64 (q, ^3J = 7.0 Hz, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 13.46 (CH_3), 14.20 (CH_3), 21.42 (CH_2), 28.70 (CH_3), 31.68 (C_q), 31.81 (CH_3), 38.33 (CH), 39.02 (CH), 39.65 (CH_2), 39.74 (CH_2), 45.35 (CH_2), 66.20 (C_q), 70.36 (CH_2), 187.56 (C_q), 205.14 (C_q).
ESI-MS:	381 (M^++NH_3, 1%), 364 (M^+, 1%), 260 (M^++NH_3–$C_3H_5OS_2$), 243 (M^+–$C_3H_5OS_2$).
	$C_{15}H_{24}O_2S_4$ (364.61)



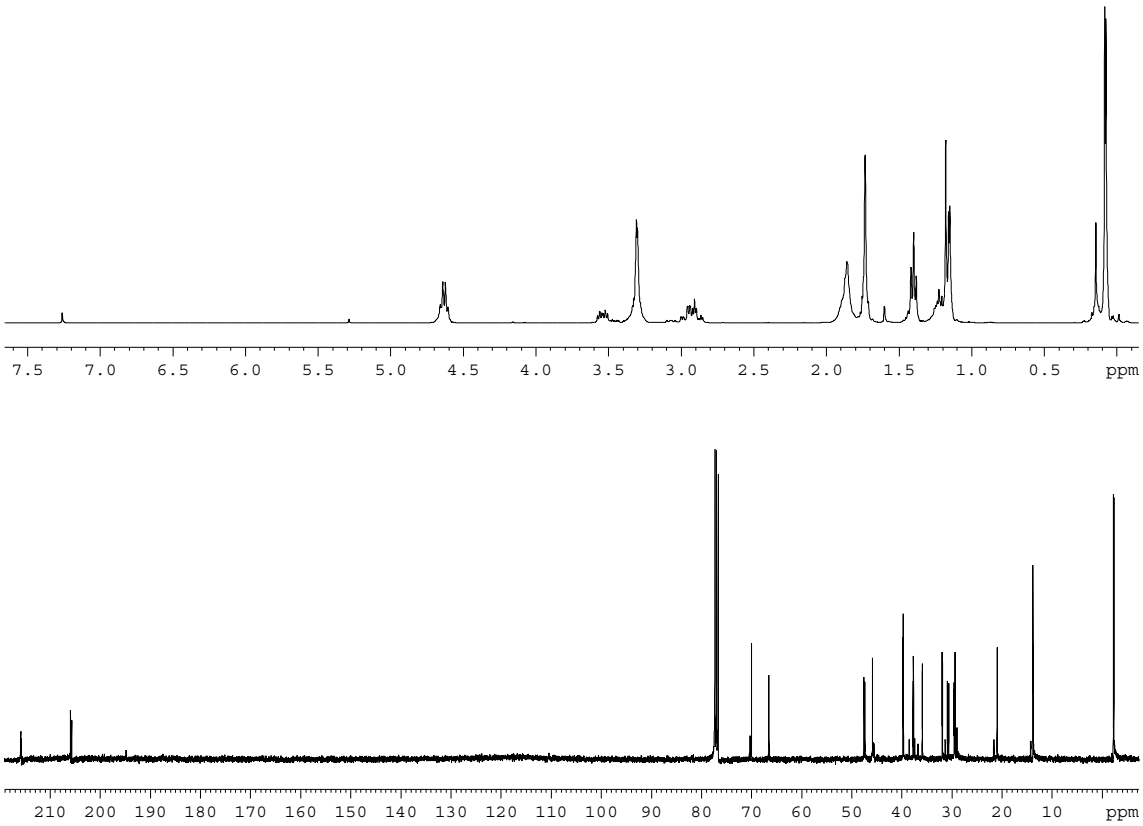
Dithiocarbonic acid (3-{(1*S*,3*R*)-2,2-dimethyl-3-[2-(2-methyl-[1,3]dithiolan-2-yl)-ethyl]-cyclopropyl}-3-oxo-1-trimethylsilanyl-propyl) ester ethyl ester (34), mixture of diastereoisomers



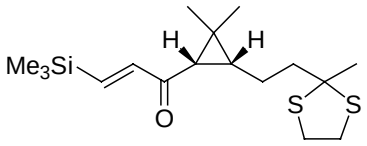
34

A solution of xanthate **33** (212 mg, 0.58 mmol) in vinyl trimethylsilane (1.5 mL) was exposed to visible light and refluxed for 8 h under argon. Concentration and purification by column chromatography (1:20 EtOAc–hexanes) gave **34** (113 mg, 0.24 mmol, 42%) along with with ca. 10% of starting material **33**.

R_f:	0.65 (1:20 EtOAc–hexanes)
IR:	(CCl_4): $\tilde{\nu}$ = 2958 (m), 2924 (m), 1694 (m), 1219 (s, C–S), 1048 (s, C=S) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 0.08, 0.09 (each s, 9H), 1.12–1.26 (m, 7H), 1.40 (t, ^3J = 7.2 Hz, 3H), 1.70–1.76 (m, 4H), 1.81–1.94 (m, 4H), 2.84–3.00 (m, 2H), 3.26–3.36 (m, 4H), 3.49–3.58 (m, 1H), 4.58–4.67 (m, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = –2.23, –2.20 (3×CH_3), 13.80 (2×CH_3), 20.98, 21.01 (CH_2), 21.03 (CH_2), 29.40, 29.42 (CH_3), 29.62, 29.67 (C_q), 31.93, 31.97 (CH_3), 35.88, 35.93 (CH), 37.72, 37.81 (CH), 39.73, 39.75, 39.81, 39.84 (2×CH_2), 45.87, 45.90 (CH_2), 47.41, 47.60 (CH_2), 66.57 (C_q), 70.11 (CH_2), 205.82, 206.03 (C_q), 215.86, 215.94 (C_q)
ESI-MS:	465 (M^++H), 341 (M^+–$C_3H_5OS_2$–H_2).
EI-HRMS:	$C_{20}H_{36}O_2S_4Si$, calcd.: 464.1367, found: 464.1321.
	$C_{20}H_{36}O_2S_4Si$ (464.85)



(*E*)-1-{(1*S*,3*R*)-2,2-Dimethyl-3-[2-(2-methyl-[1,3]dithiolan-2-yl)-ethyl]-cyclopropyl}-3-trimethylsilanyl-propenone (35)



35

A solution of **34** (25 mg, 0.05 mmol) and DBU (12 mg, 0.08 mmol) in dichloromethane (3 mL) was stirred under argon for 4 h. The solution of the crude product was washed with satd. ammonium chloride and brine and dried over Na_2SO_4. Concentration and purification by column chromatography (1:20 EtOAc–hexanes) gave **35** (15 mg, 0.04 mmol, 80%). Complete separation from bis-xanthate byproducts proved especially difficult in this case.

R_f: 0.70 (1:20 EtOAc–hexanes)

α_D: +49° (c = 1.0 in $CHCl_3$)

IR: (CCl_4): $\tilde{\nu}$ = 2958 (s), 2924 (s), 1673 (m), 1639 (w), 1450 (m), 1416 (m), 1376 (m), 1250 (s, C–S), 1205 (s), 1059 (s, C=S), 995 (m) cm^{-1}.

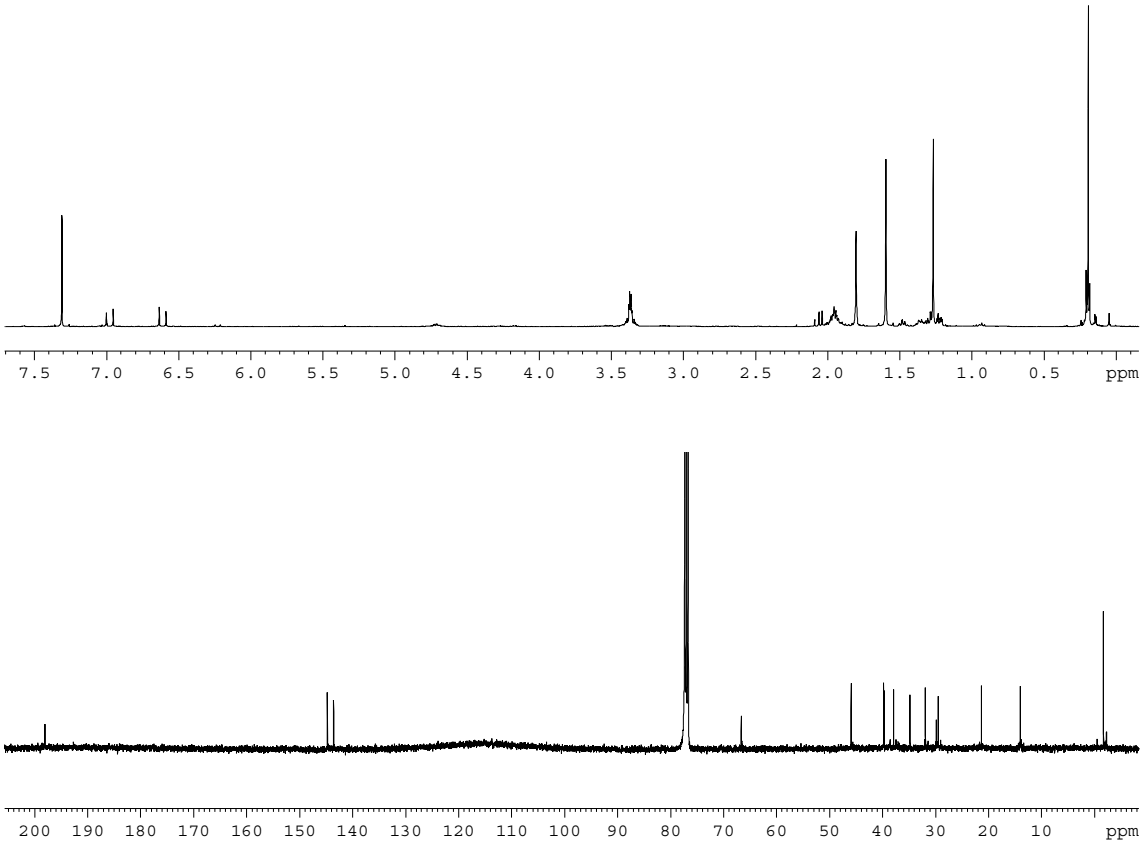
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.14 (s, 9H), 1.22 (s, 6H), 1.33–1.39 (m, 1H), 1.75 (s, 3H), 1.85–1.93 (m, 4H), 2.00 (d, ^{3}J = 8.8 Hz, 1H), 3.28–3.35 (m, 4H), 6.56 (d, ^{3}J = 18.8 Hz, 1H), 6.93 (d, ^{3}J = 18.8 Hz, 1H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = –1.71 (3×CH_3), 13.98 (CH_3), 21.32 (CH_2), 29.49 (CH_3), 29.85 (C_q), 31.90 (CH_3), 34.82 (CH), 37.92 (CH), 39.71 (CH_2), 39.78 (CH_2), 45.92 (CH_2), 66.66 (C_q), 143.58 (CH), 144.74 (CH), 198.04 (C_q).

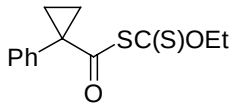
ESI-MS: 359 (M^++NH_3), 343 (M^++H), 342 (M^+).

FAB-HRMS: $C_{17}H_{31}OS_2Si^+$, calcd.: 343.1586, found: 343.1572.

$C_{17}H_{30}OS_2Si$ (342.64)



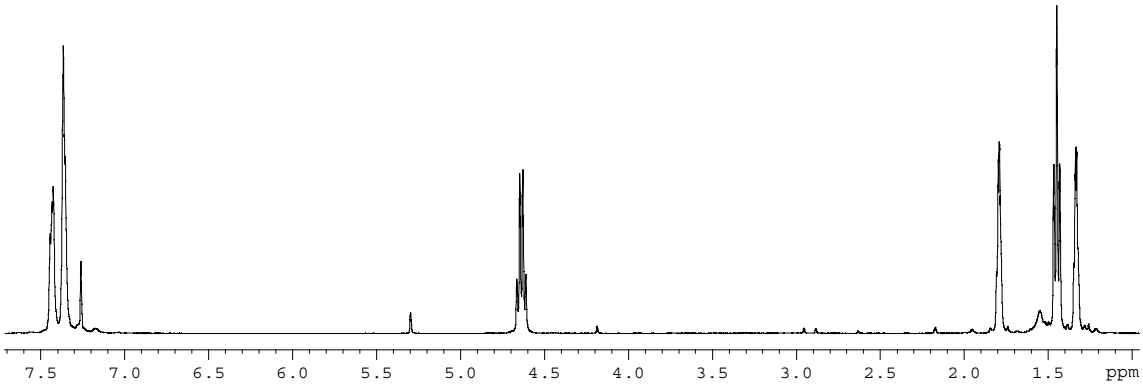
Dithiocarbonic acid ethyl ester (1-phenyl-cyclopropylacyl) ester (36)

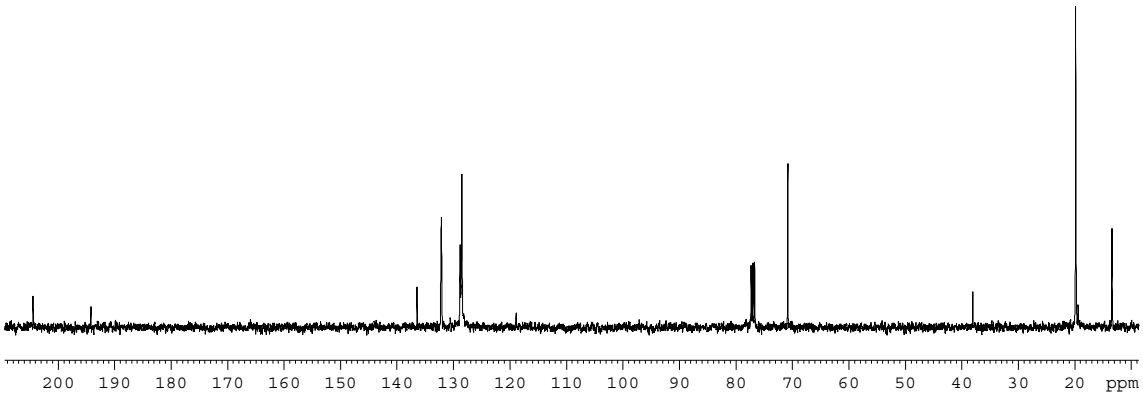


36

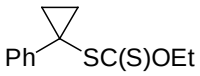
To a solution of 1-phenyl-cyclopropanecarboxylic acid (1.00 g, 5.53 mmol) in acetone (15 mL) at 0°C was added ethyl xanthic acid potassium salt (0.84 g, 5.24 mmol). After stirring for 15 min at 0°C the solvent was removed under reduced pressure at 0–10°C. The residue was dissolved in dichloromethane, washed with water and brine and dried over Na_2SO_4. Evaporation of the solvent gave acyl xanthate **36** (1.34 g, 5.03 mmol, 96%)

R_f:	0.80 (1:10 EtOAc–hexanes)
IR:	(CCl_4): $\tilde{\nu}$ =1710 (s), 1697 (s), 1257 (s, C–S), 1039 (s, C=S), 963 (s) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 1.35 (dd, ^3J = 7.2 Hz, ^2J = 3.6 Hz, 2H), 1.46 (t, ^3J = 7.0 Hz, 3H), 1.81 (dd, ^3J = 7.2 Hz, ^2J = 3.6 Hz, 2H), 4.64 (t, ^3J = 7.0 Hz, 2H), 7.36–7.38 (m, 3H), 7.44–7.46 (m, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 13.43 (CH_3), 19.83 (2×CH_2), 38.06 (C_q), 70.84 (CH_2), 128.55 (2×CH), 128.84 (CH), 132.18 (2×CH), 136.46 (C_q), 194.20 (C_q), 204.41 (C_q).
ESI-MS:	284 (M^++NH_4), 267 (M^++H).
	$C_{13}H_{14}O_2S_2$ (266.38)





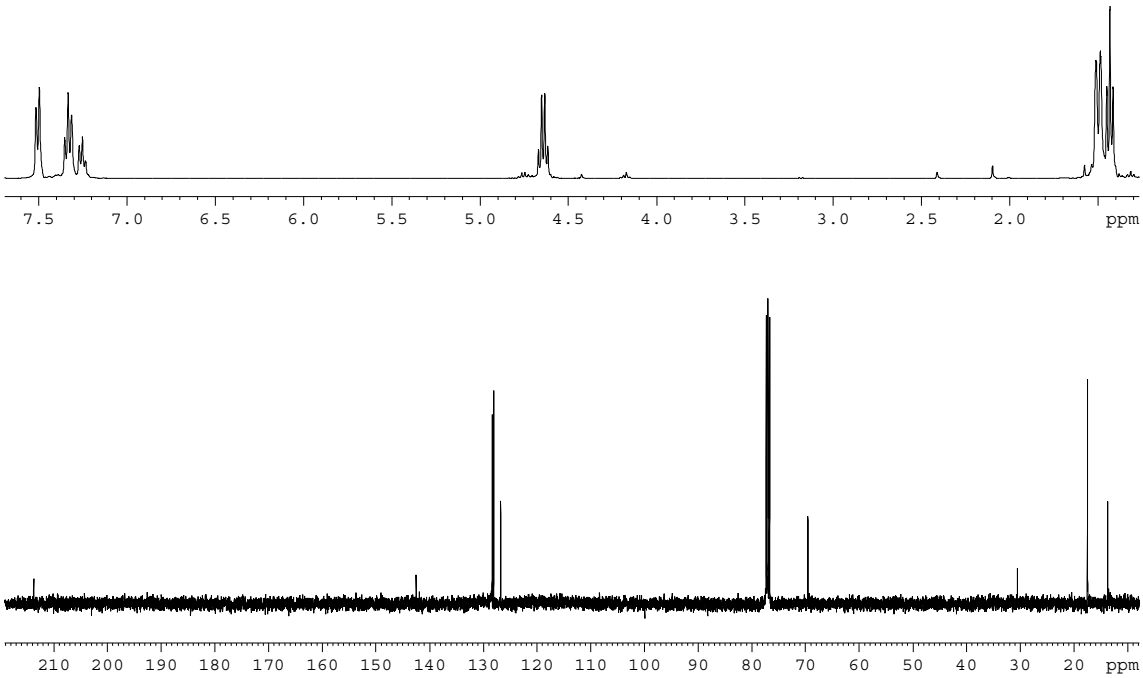
Dithiocarbonic acid ethyl ester (1-phenyl-cyclopropyl) ester (39)



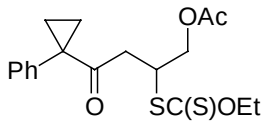
39

A solution of xanthate **36** (131 mg, 0.49 mmol) in toluene (1.5 mL) was exposed to visible light and refluxed for 4 h under argon. The solvent was removed under reduced pressure to give **39** (>85% yield). Further purification is possible by column chromatography (1:20 EtOAc–hexanes).

R_f:	0.85 (1:10 EtOAc–hexanes)
IR:	(CCl_4): $\tilde{\nu}$ = 1222 (s, C–S), 1049 (s, C=S) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 1.40 (t, ^3J = 6.8 Hz, 3H), 1.46 (dd, ^3J = 10.0 Hz, ^2J = 2.0 Hz, 2H), 1.47 (dd, ^3J = 10.0 Hz, ^2J = 2.0 Hz, 2H), 4.60 (t, ^3J = 6.8 Hz, 2H), 7.19–7.26 (m, 1H), 7.27–7.33 (m, 2H), 7.45–7.50 (m, 2H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = 13.72 (CH_3), 17.41 (2×CH_2), 30.51 (C_q), 69.60 (CH_2), 126.76 (2×CH), 128.02 (2×CH), 128.30 (CH), 142.37 (C_q), 213.71 (C_q).
ESI-MS:	239 (M^++H).
EI-HRMS:	$C_{12}H_{14}OS_2$, calcd.: 238.0486, found: 238.0485.
	$C_{12}H_{14}OS_2$ (238.37)



Acetic acid 2-ethoxythiocarbonylsulfanyl-4-oxo-4-(1-phenyl-cyclopropyl)-butyl ester (40)



40

A solution of xanthate **36** (152 mg, 0.57 mmol) in allyl acetate (1 mL) was exposed to visible light and refluxed for 1.5 h. Concentration and purification by column chromatography (1:10 EtOAc–hexanes) gave **40** (128 mg, 0.35 mmol, 61%) and also decarbonylated xanthate **39** (30 mg, 0.13 mmol, 22%).

R_f: 0.35 (1:10 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ =1748 (s), 1697 (s), 1228 (s, C–S), 1052 (s, C=S), 1024 (m) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 1.20 (dd, ^3J = 6.4 Hz, ^2J = 2.8 Hz, 2H), 1.38 (t, ^3J = 7.2 Hz, 3H), 1.64 (dd, ^3J = 6.4 Hz, ^2J = 2.8 Hz, 2H), 2.06 (s, 3H), 2.72 (d, ^3J = 6.0 Hz, 2H), 4.12–4.17 (m, 1H), 4.26–4.31 (m, 2H), 4.60 (t, ^3J = 7.2 Hz, 2H), 7.30–7.38 (m, 5H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 13.58 (CH_3), 19.19 (2×CH_2), 20.61 (CH_3), 37.28 (C_q), 42.09 (CH_2), 43.92 (CH), 64.48 (CH_2), 70.02 (CH_2), 127.64 (CH),

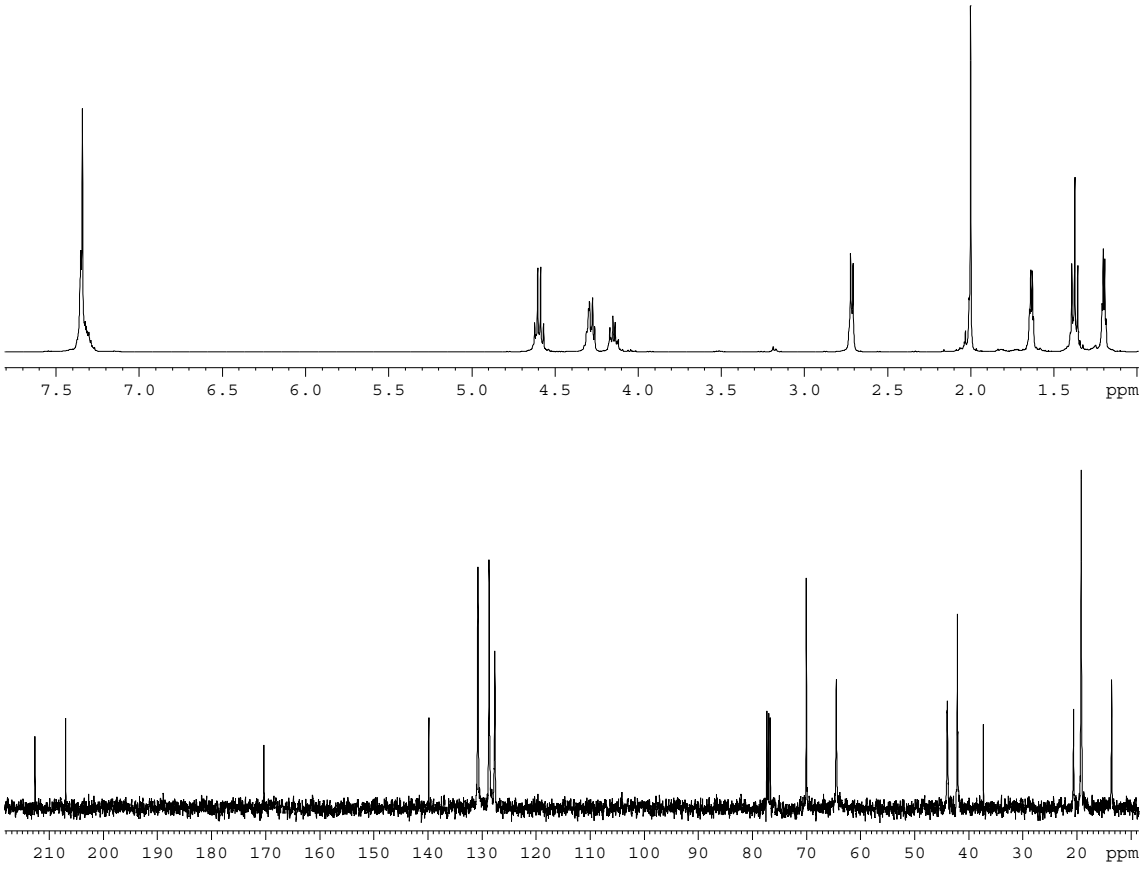
128.70 (2×CH), 130.76 (2×CH), 139.84 (C_q), 170.33 (C_q), 206.96 (C_q), 212.64 (C_q).

ESI-MS: 384 (M^++NH_4), 367 (M^++H).

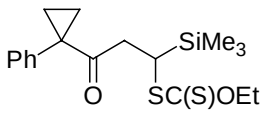
FAB-HRMS: $C_{18}H_{22}O_4S_2Na^+$, calcd.: 389.0857, found: 389.0880.

$C_{18}H_{23}O_4S_2^+$, calcd.: 367.1038, found: 367.1067.

$C_{18}H_{22}O_4S_2$ (366.50)



Dithiocarbonic acid ethyl ester [3-oxo-3-(1-phenyl-cyclopropyl)-1-trimethylsilanyl-propyl] ester (41)



41

A solution of xanthate **36** (135 mg, 0.51 mmol) in vinyl trimethylsilane (1.5 mL) was exposed to visible light and refluxed for 45 min. Concentration and purification by column chromatography (3:97 EtOAc–hexanes) gave **41** (162 mg, 0.44 mmol, 87%).

R_f: 0.75 (1:20 EtOAc–hexanes)

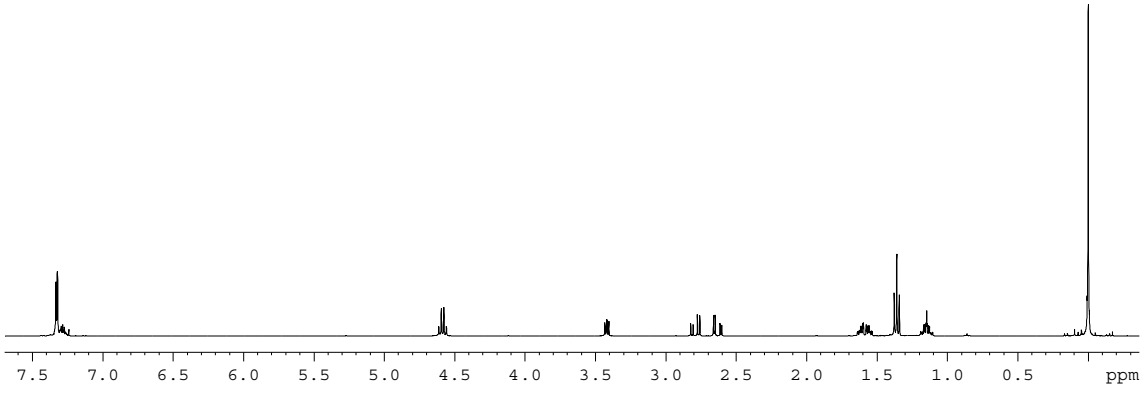
IR: (CCl_4): $\tilde{\nu}$ = 1697 (s), 1219 (s, C–S), 1050 (s, C=S) cm^{-1}.

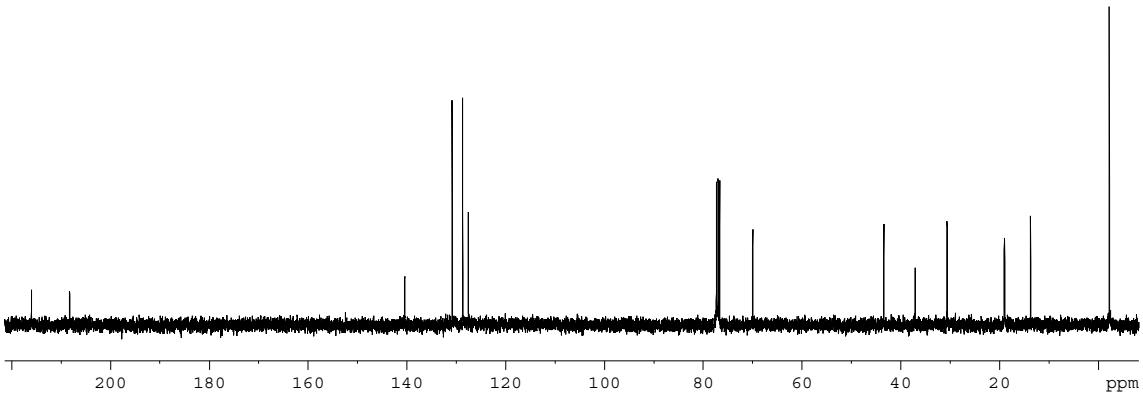
^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.01 (s, 9H), 1.12 (ddd, ^3J = 8.4 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 1.17 (ddd, ^3J = 8.4 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 1.36 (t, ^3J = 7.0 Hz, 3H), 1.55 (ddd, ^3J = 10.0 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 1.62 (ddd, ^3J = 10.0 Hz, J = 6.0 Hz, J = 2.4 Hz, 1H), 2.63 (dd, ^2J = 18.8 Hz, ^3J = 4.4 Hz, 1H), 2.79 (dd, ^2J = 18.8 Hz, ^3J = 7.0 Hz, 1H), 3.42 (dd, ^3J = 7.0 Hz, ^3J = 4.4 Hz, 1H), 4.59 (q, ^3J = 7.0 Hz, 2H), 7.28–7.34 (m, 5H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = –2.25 (3×CH_3), 13.73 (CH_3), 18.95 (CH_2), 19.06 (CH_2), 30.59 (CH), 37.09 (C_q), 43.43 (CH_2), 69.98 (CH_2), 127.55 (CH), 128.68 (2×CH), 130.83 (2×CH), 140.43 (C_q), 208.26 (C_q), 216.00 (C_q).

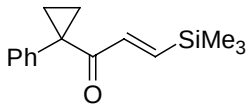
ESI-MS: 384 (M^++NH_4), 367 (M^++H).

$C_{18}H_{26}O_2S_2Si$ (366.62)





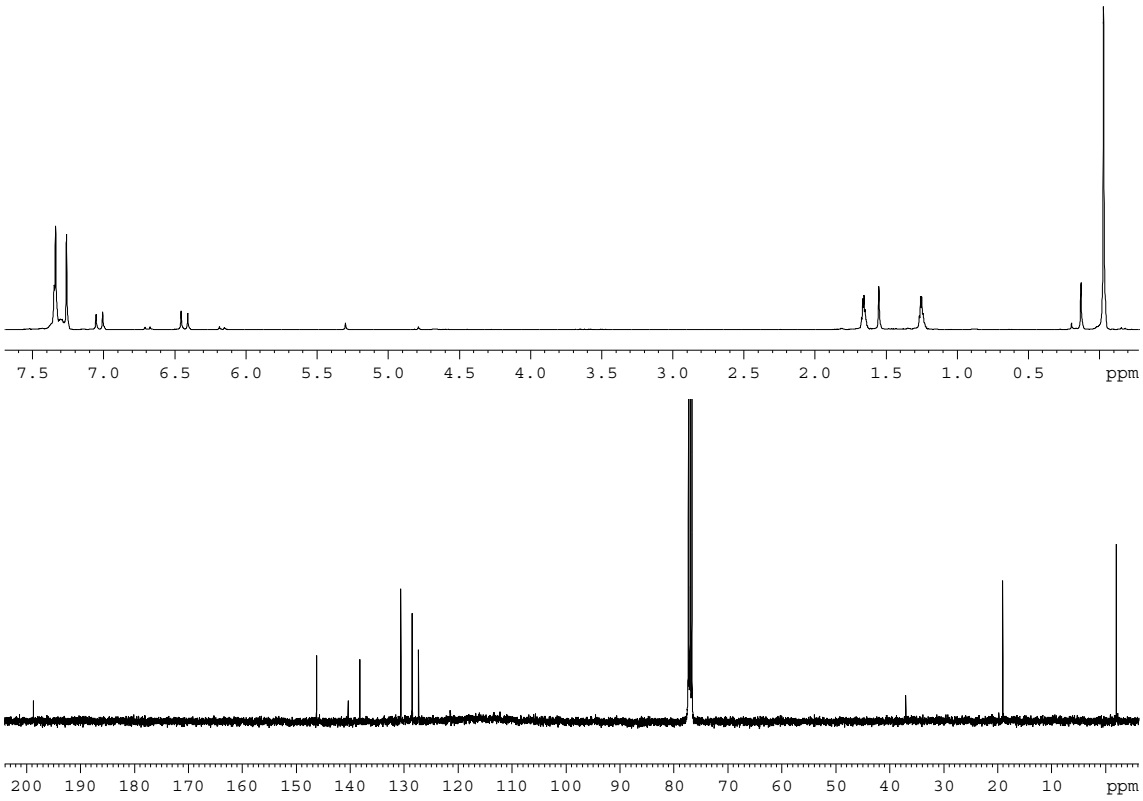
(*E*)-1-(1-Phenyl-cyclopropyl)-3-trimethylsilanyl-propenone (42)



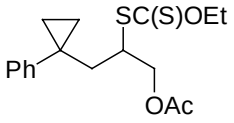
42

A solution of xanthate **36** (0.53 g, 2.0 mmol) in vinyl trimethylsilane (0.8 mL) was exposed to visible light and refluxed for 7 h under argon. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (10 mL). After the addition of DBU (0.38 mL, 0.38 g, 2.5 mmol) the reaction mixture was stirred under argon for 1.5 h. The solution of the crude product was washed with satd. ammonium chloride, followed by brine and dried over Na_2SO_4. Purification by column chromatography (4:96 Et_2O–hexanes) and sublimation (ca. 0.1 mbar) gave **42** (347 mg, 1.42 mmol, 71%). Partial isomerization occured while purification.

Yield:	71%
R_f:	0.5 (3:97 Et_2O–hexanes)
IR:	(CCl_4): $\tilde{\nu}$ = 1675 (s), 1263 (s), 1250 (s), 1070 (s) cm^{-1}.
^{1}H-NMR:	(400 MHz, $CDCl_3$): δ = 0.01 (s, 9H), 1.27 (dd, ^3J = 7.0 Hz, ^2J = 3.6 Hz, 2H), 1.68 (dd, ^3J = 7.0 Hz, ^2J = 3.6 Hz, 2H), 6.47 (d, ^3J = 18.8 Hz, 1H), 7.06 (d, ^3J = 18.8 Hz, 1H), 7.32–7.37 (m, 5H).
^{13}C-NMR:	(100.7 MHz, $CDCl_3$): δ = –2.03 (3×CH_3), 18.96 (2×CH_2), 36.98 (C_q), 127.29 (CH), 128.49 (2×CH), 130.57 (2×CH), 138.24 (CH), 140.36 (C_q), 146.13 (CH), 198.59 (C_q).
ESI-MS:	262 (M^++NH_4), 245 (M^++H).
FAB-HRMS:	$C_{15}H_{21}OSi^+$, calcd.: 245.1352, found: 245.1386.
	$C_{15}H_{20}OSi$ (244.40)



Acetic acid 2-ethoxythiocarbonylsulfanyl-3-(1-phenyl-cyclopropyl)-propyl ester (43)



43

A solution of xanthate **39** (88 mg, 0.37 mmol) and allyl acetate (0.12 mL, 111 mg, 1.11 mmol) in 1,2-dichloroethane (0.5 mL) was refluxed for 5 mins under argon. After the addition of DLP (15 mg, 0.04 mmol, 10%) the mixture was refluxed for 3 h and two further portions of DLP were added after 1 and 2 h intervals. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (1:20 to 1:4 EtOAc–hexanes) to give **43** (28 mg, 0.08 mmol, 22%) and **44** (40 mg, 0.09 mmol, 25%).

R_f: 0.8 (1:10 EtOAc–hexanes)

IR: (CCl_4): $\tilde{\nu}$ = 1747 (s), 1225 (s, C–S), 1052 (s, C=S) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.65–0.71 (m, 1H), 0.77–0.83 (m, 1H), 0.86–0.97 (m, 2H), 1.35 (t, ^3J = 7.2 Hz, 3H), 1.95 (dd, ^2J = 14.6 Hz, ^3J = 7.6 Hz, 1H),

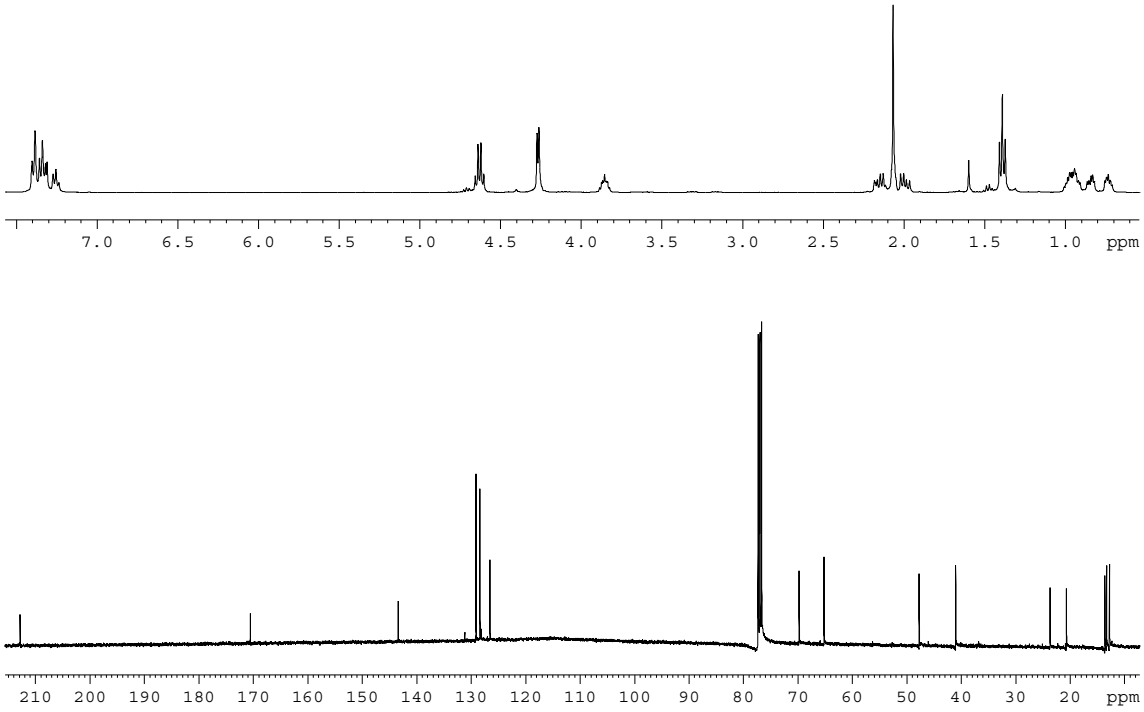
2.03 (s, 3H), 2.11 (dd, ^2J = 14.6 Hz, ^3J = 7.6 Hz, 1H), 3.77–3.84 (m, 1H), 4.22 (“d”, ^3J = 4.8 Hz, 2H), 4.58 (q, ^3J = 7.2 Hz, 2H), 7.20–7.38 (m, 5H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 12.43 (CH_2), 13.02 (CH_2), 13.32 (CH_3), 20.46 (CH_3), 23.38 (C_q), 40.63 (CH_2), 47.35 (CH), 64.88 (CH_2), 69.55 (CH_2), 126.25 (CH), 128.09 (2×CH), 128.84 (2×CH), 142.97 (C_q), 170.36 (C_q), 212.45 (C_q).

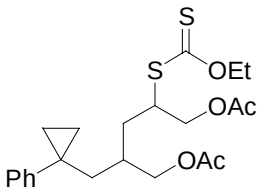
ESI-MS: 356 (M^++NH_4), 339 (M^++H).

FAB-HRMS: $C_{17}H_{23}O_3S_2^+$, calcd.: 399.1089, found: 339.1099.

$C_{17}H_{22}O_3S_2$ (338.49)



Acetic acid 5-acetoxy-4-ethoxythiocarbonylsulfanyl-2-(1-phenyl-cyclopropylmethyl)-pentyl ester (44), mixture of diastereoisomers



44

R_f: 0.4 (1:10 EtOAc–hexanes)

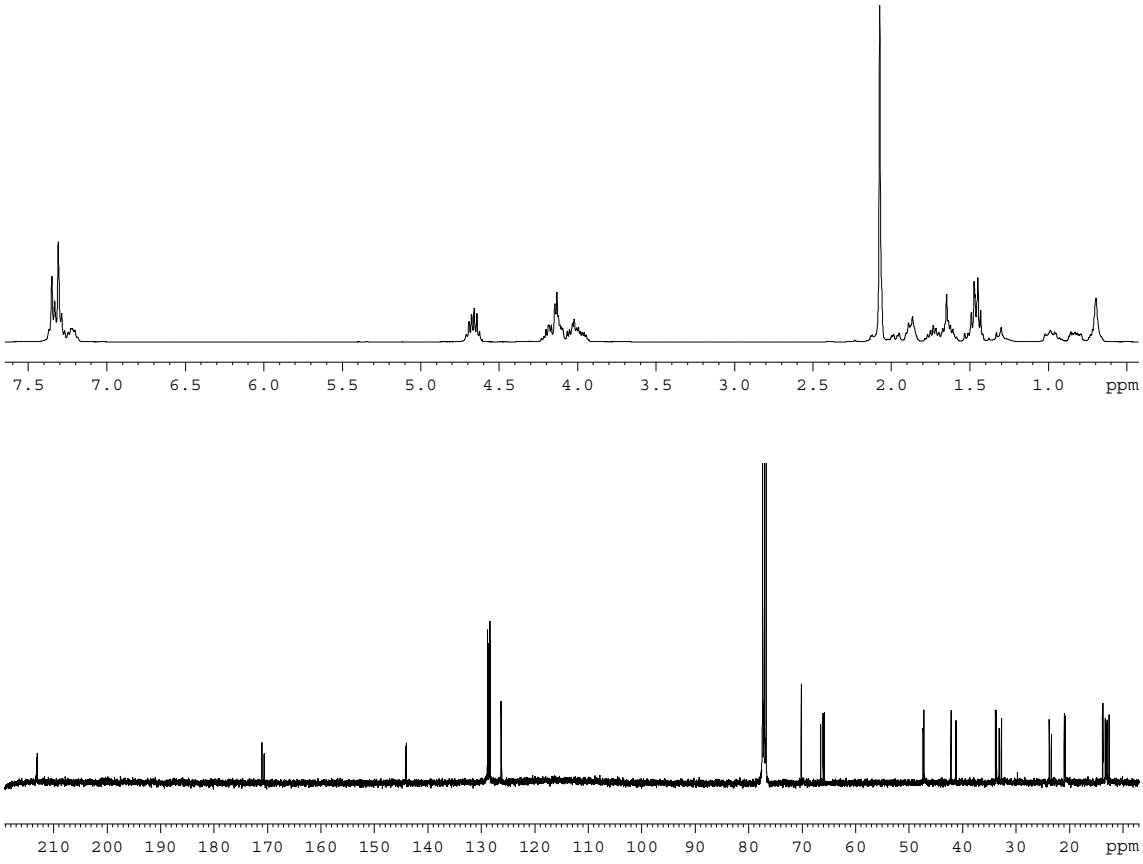
IR: (CCl_4): $\tilde{\nu}$ = 1745 (s), 1228 (s, C–S), 1051 (s, C=S) cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ = 0.62–0.70 (m, 2H), 0.73–0.84 (m, 1H), 0.90–1.00 (m, 1H), 1.38–1.45 (m, 3H), 1.55–1.65 (m, 2H), 1.66–1.74 (m, 1H), 1.80–1.96 (m, 2H), 2.08 (s, 6H), 3.90–4.17 (m, 5H), 4.58–4.68 (m, 2H), 7.15–7.32 (m, 5H).

^{13}C-NMR: (100.7 MHz, $CDCl_3$): δ = 12.60, 12.97, 13.15, 13.30 (2×CH_2), 13.76, 13.81 (CH_3), 20.77, 20.80, 20.92, 20.96 (2×CH_3), 23.40, 23.76 (C_q), 32.73, 33.15 (CH_2), 33.66, 33.81 (CH), 41.23, 42.17 (CH_2), 47.23, 47.38 (CH), 65.86, 65.91, 66.08, 66.57 (2×CH_2), 70.17 (CH_2), 126.21, 126.30 (CH), 128.36, 128.44, 128.64, 128.88 (4×CH), 144.06, 144.16 (C_q), 170.65, 171.09 (C_q), 213.05, 213.17 (C_q).

ESI-MS: 456 (M^++NH_4), 439 (M^++H).

$C_{22}H_{30}O_5S_2$ (438.60)



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   Due to the low yields reported for the preparation of acid chloride **14**, we were happy to find a more convenient modified procedure.

   Therefore 1-aminocyclopropane carboxylic acid hydrochloride was obtained from the described precursor by heating in conc. HCl at 70°C for 5 h. The cooled solution was extracted three times with diethylether and was then concentrated and dried to give the crude amino acid hydrochloride. The crude hydrochloride (2.00 g, 14.5 mmol), triethylamine (6.0 mL, 4.4 g, 43.5 mmol) and toluene (120 mL) were placed in a Dean-Stark apparatus and heated under reflux for 1.5 h. After the addition of phthalic anhydride (2.37 g, 16.0 mmol) heating was continued for 6 h. The reaction mixture was concentrated, treated with 2N HCl and extracted several times with ethyl acetate. The combined extracts were washed with brine and dried over Na_2SO_4. Recrystallization from dichloromethane gave the phthaloyl-protected amino acid (2.68 g, 11.6 mmol, 80%). Conversion to the acid chloride was achieved using the standard procedure involving oxalyl chloride and catalytic dimethylformamide in dichloromethane.
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   ^{1}H NMR data of **30** is in full accord with the data reported in ref. 4b.
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