A Direct Xanthate Based Route to γ-Thio-lactones

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1. General Methods

All reactions were carried out in oven-dried glassware under nitrogen or open flask atmosphere with magnetic stirring, unless stated otherwise. Tetrahydrofuran, acetonitrile and dichloromethane were dried by passage over Grubbs device purification system from Braun. All chemicals were purchased from Strem, Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagal silica 40-63µm, 60 Å or using aluminium oxide, basic, Brockmann I purchased from Acros, using the solvents indicated as eluent with 0.1-0.5 bar pressure. For flash chromatography, previously distilled technical grade solvents were used. TLC was performed on Merck silica gel 60 F254 TLC glass plates or aluminium plates and visualized with UV light, and by permanganate stain, CAN stain, p-anisaldehyde stain or ninhydrin stain followed by heating. $^1$H-NMR spectra were recorded on a Brucker AMX-400 400 MHz spectrometer in CDCl$_3$, (CD$_3$)$_2$SO, CD$_2$Cl$_2$ CD$_2$OD, CD$_3$CN, or D$_2$O all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal (CD$_3$)$_2$SO signal at 2.50 ppm, the internal CD$_2$Cl$_2$ signal at 5.31 ppm, the internal CD$_2$OD signal at 3.30 ppm, the internal CD$_3$CN signal at 1.94 ppm or the internal D$_2$O signal at 4.79 ppm as standard. The data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation). $^{13}$C-NMR spectra were recorded with $^1$H-decoupling on a Brucker AMX-400 101 MHz spectrometer in CDCl$_3$, (CD$_3$)$_2$SO, CD$_2$Cl$_2$ or CD$_2$OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal (CD$_3$)$_2$SO signal at 39.5 ppm, the internal CD$_2$Cl$_2$ signal at 53.5 ppm, the internal CD$_2$OD signal at 49.0 ppm, or the internal CD$_3$CN signal at 132 ppm and 118.26 ppm as standard. Infrared spectra were recorded on a Spectrum Two™ de Perkin-Elmer spectrophotometer on NaCl support and are reported as cm$^{-1}$. High resolution mass spectrometry measurements were performed by the mass spectrometry service of LSO at École Polytechnique (France), on a JEOL JMS-GCmate II, GS/MS. The nomenclature of the new molecules was generated with Chemdraw.
2. Preparation of Xanthate Reagents

Precursor: 3-bromodihydrothiophen-2(3H)-one (13)

Following a slightly modified procedure,\(^1\) DL-homocystein thiolactone hydrochloride 1 (1.0 g, 6.5 mmol, 1.0 equiv) was suspended in 5 mL of 48% hydrobromic acid. The suspension was stirred in ice-salt bath at -20 °C while sodium nitrite (487 mg, 7.1 mmol, 1.1 equiv) in 2 mL of chilled water was added dropwise. The mixture was stirred 15 minutes, warmed up to room temperature and stirred 1 hour more. Extracted with 3 x 2.5 mL of DCM and dried over MgSO\(_4\). Concentrated \textit{in vacuo} and purified by flash column chromatography (PE:EtOAc 90:10) to afford 13 (261 mg, 1.4 mmol, 22%) as an orange oil. \(R_f\) (PE:EtOAc 8:2) = 0.52. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.49 (t, 0.5 H, \(J = 3.6\) Hz, \(CH\text{Br}\)), 4.47 (t, 0.5 H, \(J = 3.6\) Hz, \(CH\text{Br}\)), 3.66-3.59 (m, 1 H, \(CH\text{H}_2\text{CHBr}\)), 3.38-3.33 (m, 1 H, \(CH\text{H}_2\text{CHBr}\)), 2.65-2.56 (m, 1 H, \(CH\text{H}_2\text{S}\)), 2.54-2.48 (m, 1 H, \(CH\text{H}_2\text{S}\)). The values of the NMR spectra are in accordance with reported literature data.\(^1\) \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 202.3 (CO), 50.0 (CHBr), 35.7 (CH\text{H}_2\text{CHBr}), 31.1 (CH\text{H}_2\text{S}). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\(_4\)H\(_2\)BrOS [M\(^+\)] 179.9244; found 179.9236.

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O-ethyl S-(2-oxotetrahydrothiophen-3-yl) carbonodithioate (14)

Following a slightly modified procedure,2 DL-homocystein thiolactone hydrochloride 1 (10.0 g, 65.1 mmol, 1.0 equiv) was suspended in 50 mL of 48% hydrobromic acid. The suspension was stirred in icesalt bath at -20 °C while sodium nitrite (4.87 g, 70.6 mmol, 1.1 equiv) in 20 mL of chilled water was added dropwise. The mixture was stirred 15 minutes, warmed up to room temperature and stirred 1 hour more. Extracted with 3 x 50 mL of DCM and dried over MgSO₄. Concentrated in vacuo to afford 13-containing residue as an orange oil. This step was repeated one more time and the residues were gathered. The resulting residue was diluted in 167 mL of acetone and stirred in ice bath at 0 °C while KSCSOEt (14.7 g, 91.9 mmol, 0.7 equiv) was slowly added. The solution was warmed up to room temperature and stirred 45 min, filtered over a plug of silica and concentrated in vacuo. The crude was purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 14 (10.5 g, 47.1 mmol, yield = 36%) as an orange oil. \( R_f \) (PE:EtOAc 8:2) = 0.54. ¹H NMR (CDCl₃, 400 MHz) δ 4.67 (q, 1 H, J = 7.1 Hz, OCH₂CH₃), 4.67 (q, 1 H, J = 7.1 Hz, OCH₂CH₃), 4.62 (d, 0.5 H, J = 7.0 Hz, CHS), 4.59 (d, 0.5 H, J = 7.0 Hz, CHS), 3.48-3.36 (m, 2 H, CH₂CH₂S), 2.89-2.81 (m, 1 H, CH₂CH₂S), 2.41-2.31 (m, 1 H, CH₂CH₂S), 1.43 (t, 3 H, J = 7.1 Hz, OCH₂CH₃). ¹³C NMR (CDCl₃, 101 MHz) δ 211.7 (CS₂), 202.7 (CO), 71.1 (CH₂CH₃), 58.3 (CHS), 32.2 (CH₂CHS), 30.2 (CH₂S), 13.9 (CH₂CH₃). IR ν 1690 (C=O), 1230 (SC-O), 1042 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C₇H₁₀O₂S₃ [M⁺] 221.9843; found 221.9837.

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O-neopentyl S-(2-oxotetrahydrothiophen-3-yl) carbonodithioate (15)

Following a slightly modified procedure,\(^2\) DL-homocystein thiolactone hydrochloride 1 (1.0 g, 6.5 mmol, 1.0 equiv) was suspended in 5 mL of 48% hydrobromic acid. The suspension was stirred in ice-salt bath at -20 °C while sodium nitrite (487 mg, 7.1 mmol, 1.1 equiv) in 2 mL of chilled water was added dropwise. The mixture was stirred 15 minutes, warmed up to room temperature and stirred 1 hour more. Extracted with 3 x 2.5 mL of DCM and dried over MgSO₄. Concentrated in vacuo to afford 13-containing residue as an orange oil. The residue was diluted in 5.6 mL of acetone. The suspension was stirred in ice bath at 0 °C while NaSCSOoneoPent (704 mg, 3.8 mmol, 0.6 equiv) was slowly added. The solution was warmed up to room temperature and stirred 1 hour 30 minutes. 150 mL of water was added and extracted with 3 x 150 mL of EtOAc. Dried over MgSO₄ and concentrated in vacuo. The crude was purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 15 (463 mg, 1.8 mmol, 27%) as a yellow oil. \(R_f\) (PE:EtOAc 9:1) = 0.50. \(^1\)H NMR (CDCl₃, 400 MHz) \(\delta\) 4.67 (d, 0.5 H, \(J = 7.0\) Hz, CHS), 4.64 (d, 0.5 H, \(J = 7.0\) Hz, CHS), 4.27 (s, 1.7 H, CCH₂O), 4.27 (s, 0.3 H, CCH₂O), 3.48-3.37 (m, 2 H, CH₂CH₂S), 2.90-2.83 (m, 1 H, CH₂CH₂S), 2.40-2.30 (m, 1 H, CH₂CH₂S), 1.01 (s, 9 H, C(CH₃)₃). \(^13\)C NMR (CDCl₃, 101 MHz) \(\delta\) 212.0 (CS₂), 202.8 (CO), 84.5 (OCH₂), 58.2 (CHS), 32.3 (CH₂CH₂S), 32.0 (C(CH₃)₃), 30.3 (CH₂S), 26.7 (C(CH₃)₃). IR \(\nu\) 1708 (C=O), 1233 (SC), 1063 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C₁₀H₁₀O₂S₃ \([\text{M}^+\]) 264.0312; found 264.0313.
O-phenethyl S-(2-oxotetrahydrothiophen-3-yl) carbonodithioate (16)

Following a slightly modified procedure,2 DL-homocystein thiolactone hydrochloride 1 (1.0 g, 6.5 mmol, 1.0 equiv) was suspended in 5 mL of 48% hydrobromic acid. The suspension was stirred in ice-salt bath at -20 °C while sodium nitrite (487 mg, 7.1 mmol, 1.1 equiv) in 2 mL of chilled water was added dropwise. The mixture was stirred 15 minutes, warmed up to room temperature and stirred 1 hour more. Extracted with 3 x 2.5 mL of DCM and dried over MgSO₄. Concentrated in vacuo to afford 13-containing residue as an orange oil. The residue was diluted in 7.1 mL of acetone. The suspension was stirred in ice bath at 0 °C while NaSCSOCH₂CH₂Ph (928 mg, 4.2 mmol, 0.6 equiv) was slowly added. The solution was warmed up to room temperature and stirred 1 hour 15 minutes. 150 mL of water was added and extracted with 3 x 150 mL of EtOAc. Dried over MgSO₄ and concentrated in vacuo. The crude was purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 16 (613 mg, 2.1 mmol, 32%) as a yellow oil. Rₗ (PE:EtOAc 8:2) = 0.51. ¹H NMR (CDCl₃, 400 MHz) δ 7.35-7.22 (m, 5 H, ArH), 4.86-4.76 (m, 2 H, CH₃CH₂O), 4.52 (d, 0.5 H, J = 7.0 Hz, CHS), 4.689 (d, 0.5 H, J = 7.0 Hz, CHS), 3.41-3.30 (m, 2 H, CH₃CH₂S), 3.12 (t, 2 H, J = 6.8 Hz, CH₂CH₂O), 2.76-2.68 (m, 1 H, CH₂CH₂S), 2.30-2.20 (m, 1 H, CH₂CH₂S). ¹³C NMR (CDCl₃, 101 MHz) δ 211.4 (CS₂), 202.6 (CO), 137.1 (C(CHCH)₂), 129.0 (C(CHCH)₂), 128.8 (C(CHCH)₂), 127.0 (CH(CHCH)₂), 74.8 (CH₂CH₂O), 58.0 (CHS), 34.6 (CH₂CH₂O), 32.1 (CH₂CHS), 30.2 (CH₂S). COSY, HSQC and HMBC were consistent with this attribution. IR ν 1709 (C=O), 1237 (SC-O), 1063 (C=S). HRMS (El) calculated for C₁₃H₂₄O₅S₃ [M⁺] 298.0156; not found; fragmentation calculated for CH₂CH₂Ph [M⁺] 105.0704; found 105.0700.
O-octadecyl S-(2-oxotetrahydrothiophen-3-yl) carbonodithioate (17)

Following a slightly modified procedure,² DL-homocystein thiolactone hydrochloride 1 (1.0 g, 6.5 mmol, 1.0 equiv) was suspended in 5 mL of 48% hydrobromic acid. The suspension was stirred in ice-salt bath at -20 °C while sodium nitrite (487 mg, 7.1 mmol, 1.1 equiv) in 2 mL of chilled water was added dropwise. The mixture was stirred 15 minutes, warmed up to room temperature and stirred 1 hour more. Extracted with 3 x 2.5 mL of DCM and dried over MgSO₄. Concentrated in vacuo to afford 13-containing residue as an orange oil. The residue was diluted in 8.1 mL of acetone to obtain a 0.5 M solution. The suspension was stirred in ice bath at 0 °C while NaSCS(OCH₂)₃H (1.65 mg, 4.5 mmol, 0.7 equiv) was slowly added. The solution was warmed up to room temperature and stirred 30 minutes. The crude was purified by flash column chromatography (PE:EtOAc 95:05) to afford pure 17 (761 mg, 1.7 mmol, 26%) as a brown oil. Rf (PE:EtOAc 8:2) = 0.62. ¹H NMR (CDCl₃, 400 MHz) δ 4.63-4.54 (m, 3 H, CH₂CH₂O, CHS), 3.47-3.36 (m, 2 H, CH₂CH₂S), 2.88-2.81 (m, 1 H, CH₃CH₂S), 2.41-2.31 (m, 1 H, CH₂CH₂S), 1.83-1.76 (m, 2 H, CH₂CH₂O), 1.40-1.20 (m, 30 H, OCH₂CH₂(CH₃)₃CH₃), 0.89-0.82 (m, 3 H, CH₃). ¹³C NMR (CDCl₃, 101 MHz) δ 211.8 (CS₂), 202.7 (CO), 75.4 (CH₂CH₂O), 58.3 (CHS), 32.2 (CH₂CH₂S), 32.1 (CH₂CH₂O), 30.2 (CH₂S) 29.9-29.3 (OCH₂CH₂(CH₂)₃CH₂CH₂CH₃), 28.3 (CH₂CH₂CH₂CH₃), 26.0 (CH₂CH₂CH₃), 22.8 (CH₂CH₃), 14.3 (CH₃). IR ν 1710 (C=O), 1238 (SC=O), 1050 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C₂₃H₄₂O₂S₃ [M⁺] 446.2347; found 446.2355.
3. Addition to Alkenes

O-ethyl S-(5-oxo-1-(2-oxotetrahydrothiophen-3-yl)hexan-2-yl) carbonodithioate (19)

Following a slightly modified procedure, \(^3\) O-ethyl S-(5-oxo-1-(2-oxotetrahydrothiophen-3-yl)hexan-2-yl) carbonodithioate (19) (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with hex-5-en-2-one (238 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 85:15) to afford pure 19 (285 mg, 0.9 mmol, 89%) as a light yellow oil and as a mixture of diastereoisomers. \(R\) \(_f\) (PE:EtOAc 8:2) = 0.27. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.60-4.52 (m, 2 H, OCH\(_2\)CH\(_2\)), 3.78-3.71 (m, 1 H, CHS), 3.29-3.19 (m, 2 H, CH\(_2\)S), 2.65-2.46 (m, 4 H, CH\(_2\)CH\(_2\)CH\(_2\)CH), 2.22-2.08 (m, 1 H, CH\(_2\)CH\(_2\)CHS), 2.08-2.04-1.95 (s, 3 H, COCH\(_3\)), 2.04-1.95 (m, 1 H, CH\(_2\)CH\(_2\)S), 1.95-1.84 (m, 0.5 H, CH\(_2\)CH\(_2\)S), 1.84-1.73 (m, 1 H, CHCH\(_2\)CH), 1.69-1.60 (m, 1 H, CH\(_2\)CH\(_2\)CHS), 1.60-1.52 (m, 0.5 H, CH\(_2\)CH\(_2\)S), 1.37-1.32 (m, 3 H, OCH\(_2\)CH\(_2\)). \(^13\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 214.0 (CS\(_2\)), 213.5 (CS\(_2\)), 209.6 (COS), 209.4 (COS), 207.4 (COCH\(_3\)), 207.4 (COCH\(_3\)), 70.3 (OCH\(_2\)CH\(_3\)), 70.0 (OCH\(_2\)CH\(_3\)), 49.6 (CHS), 49.5 (CHS), 49.4 (CHCOS), 48.9 (CHCOS), 40.2 (CH\(_2\)COCH\(_2\)), 35.4 (CH\(_2\)CHCS), 34.8 (CH\(_2\)CHCS), 32.3 (CH\(_2\)CH\(_2\)S), 32.1 (CH\(_2\)CH\(_2\)S), 30.2 (CH\(_2\)CH\(_2\)S), 30.1 (CH\(_2\)CH\(_2\)S), 30.0 (COCH\(_3\)), 29.9 (COCH\(_3\)), 29.3 (CHCH\(_2\)CH), 26.6 (CHCH\(_2\)CH), 13.7 (OCH\(_2\)CH\(_3\)).

IR \(\nu\) 1696 (SC=O, C=O), 1219 (SC=O), 1047 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\(_{13}\)H\(_{20}\)O\(_3\)S\(_3\) [M\(^+\)] 320.0575; found 320.0574.
Diethyl 2-((ethoxycarbonothioyl)thio)-3-(2-oxotetrahydrothiophen-3-yl)propyl)malonate (20)

Following a slightly modified procedure, 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with 2-allylmalonate (404 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 20 (361 mg, 0.9 mmol, 86%) as a light yellow oil and as a mixture of diastereoisomers. Rf (PE:EtOAc 8:2) = 0.47. 1H NMR (CDCl3, 400 MHz) δ 4.61-4.48 (m, 2 H, CSOCH2CH3), 4.18-4.04 (m, 4 H, CO2CH2CH3), 3.82-3.71 (m, 1 H, CHS), 3.56-3.49 (m, 1 H, CH(CO2)2), 3.29-3.18 (m, 2 H, CH2S), 2.65-2.49 (m, 2 H, CHCOS, CH2CH3S), 2.39-2.27 (m, 1 H, CH2CHS, CH2CH2S), 2.20-2.05 (m, 1.5 H, CH2CHS, CH2CH2S), 1.97-1.76 (m, 1.5 H, CH2CH3S, CH2CH2S), 1.72-1.56 (m, 1 H, CH2CHS, CH2CH2S), 1.34 (t, 1.5 H, J = 7.1 Hz, CSOCH2CH3), 1.33 (t, 1.5 H, J = 7.1 Hz, CSOCH2CH3), 1.20-1.16 (m, 6 H, CO2CH2CH3). 13C NMR (CDCl3, 101 MHz) δ 213.4 (CS2), 212.9 (CS2), 209.2 (COS), 168.7 (CO2), 168.5 (CO2), 70.5 (CSOCH2CH3), 70.2 (CSOCH2CH3), 61.5 (CO2CH2CH3), 49.6 (CHCOS, (CHCO2)), 49.4 (CHCOS, (CHCO2)), 49.4 (CHCOS, (CHCO2)), 49.3 (CHCOS, (CHCO2)), 48.3 (CHS), 47.6 (CHS), 35.9 (CH2CHS), 35.0 (CHCH2CHCOS), 34.6 (CHCH2CHCOS), 32.3 (CH2CH2S), 31.8 (CH2CH2S), 30.2 (CH2CH2S), 30.0 (CH2CH2S), 13.9 (CO2CH2CH3), 13.6 (CO2CH2CH3). COSY, HSQC and HMBC were consistent with this attribution. IR ν 1731 (OC=O), 1697 (SC=O), 1222 (SC-O), 1048 (C=S). HRMS (EI) calculated for C17H26O5S3 [M+][+] 422.0892; found 422.0879.
S-(1,1-Diethoxy-3-(2-oxotetrahydrothiophen-3-yl)propan-2-yl) O-ethyl carbonodithioate (21)

Following a slightly modified procedure, 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with acrolein diethylacetal (318 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC, repeated 3 times. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 21 (245 mg, 0.7 mmol, 69%) as a light yellow oil and as a mixture of diastereoisomers. Rf (PE:EtOAc 8:2) = 0.76. 1H NMR (CDCl3, 400 MHz) δ 4.66-4.60 (m, 2 H, CSOCH2CH3), 4.55-4.52 (m, 1 H, CH(OCH2CH3)2) 4.34-4.29 (m, 0.5 H, CHS), 4.06-4.03 (m, 0.5 H, CHS), 3.78-3.47 (m, 4 H, CH(OCH2CH3)2), 3.27-3.24 (m, 2 H, CH2S), 2.75-2.66 (m, 1 H, CHCOS), 2.62-2.47 (m, 1 H, CH2CH2S), 2.42-2.35 (m, 0.5 H, CHCH2CH22), 2.27-2.19 (m, 0.5 H, CHCH2CH2), 2.02-1.92 (m, 0.5 H, CHCH2CH2), 1.92-1.83 (m, 1 H, CH2CH2S), 1.64-1.57 (m, 0.5 H, CHCH2CH2), 1.41 (t, 1.5 H, J = 7.0 Hz, CSOCH2CH3), 1.40 (t, 1.5 H, J = 7.0 Hz, CSOCH2CH3), 1.24-1.16 (m, 6 H, CH(OCH2CH3)2). 13C NMR (CDCl3, 101 MHz) δ 215.1 (CS2), 214.2 (CS2), 210.0 (COS), 209.7 (COS), 203.2 (CH(OCH2CH3)2), 104.0 (CH(OCH2CH3)2). 70.6 (CSOCH2CH3), 70.3 (CSOCH2CH3), 65.0 (CH(OCH2CH3)2), 64.8 (CH(OCH2CH3)2), 64.0 (CH(OCH2CH3)2), 63.8 (CH(OCH2CH3)2), 53.0 (CHS), 51.7 (CHS), 49.5 (CHCOS), 49.1 (CHCOS), 33.0 (CH2CH2S), 32.5 (CH2CH2S), 30.3 (CH2CH2S), 30.2 (CH2CH2S), 28.7 (CHCH2CH2), 28.3 (CHCH2CH2), 15.4 (CH(OCH2CH3)2), 15.3 (CH(OCH2CH3)2), 15.2 (CH(OCH2CH3)2), 13.9 (CSOCH2CH3), 13.8 (CSOCH2CH3). IR ν 1695 (C=O), 1220 (SC-O), 1053 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C14H20O4S3 [M+] 352.0837; found 352.0843.
Following a slightly modified procedure,3 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with 1,1,1-trifluoro-2-(trifluoromethyl)-4-penten-2-ol (307 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC, repeated 2 times. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 22 (208 mg, 0.7 mmol, 72%) as a light yellow oil and as a mixture of diastereoisomers. 

Rf (PE:EtOAc 8:2) = 0.53. 1H NMR (CDCl3, 400 MHz) δ 5.13 (s, 0.6 H, OH), 4.83 (s, 0.4 H, OH), 4.67-4.61 (m, 2 H, OCH2CH3), 4.18-4.10 (m, 0.4 H, CHS), 4.06-3.99 (m, 0.6 H, CHS), 3.35-3.25 (m, 2 H, CH2S), 2.74-2.61 (m, 1 H, CHCOS), 2.61-2.59 (m, 1.5 H, CH2CH2S), 2.45-2.40 (m, 0.5 H, CH2COH), 2.34-2.19 (m, 2.1 H, CH2COH, CHCH2CH2), 2.05-1.96 (m, 1 H, CH2COH), 1.94-1.86 (m, 0.5 H, CH2CH2S), 1.75-1.67 (m, 0.4 H, CHCH2CH2), 1.43-1.38 (m, 3 H, OCH2CH3). 13C NMR (CDCl3, 101 MHz) δ 212.4 (CS2), 212.1 (COH), 211.8 (COH), 211.5 (COS), 127.2 (CF3), 124.3 (CF3), 121.5 (CF3), 118.6 (CF3), 70.7 (OCH2CH3), 49.9 (CHCOS), 44.3 (CHS), 43.0 (CHS), 36.0 (CHCH2CH), 35.7 (CHCH2CH), 34.2 (CH2COH), 34.0 (CH2COH), 32.4 (CH2CH2S), 32.1 (CH2CH2S), 30.6 (CH2CH2S), 30.4 (CH2CH2S), 13.6 (OCH2CH3). IR ν 3333 (C-OH), 1676 (C=O), 1217 (SC-O), 1047 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C11H16F4O5S3 [M+] 430.0166; not found, fragmentation calculated for C10H11F5O2S [M+] 309.079; found 309.0384.

\[ O\text{-ethyl S-(5,5,5-trifluoro-4-hydroxy-1-(2-oxotetrahydrothiophen-3-yl)-4-(trifluoromethyl)-pentan-2-yl) carbonodithioate (22)} \]
2-((Ethoxycarbonothioyl)thio)-3-(2-oxotetrahydrothiophen-3-yl)propyl acetate (23)

Following a slightly modified procedure, 3 14 (111 mg, 0.5 mmol, 1.0 equiv) was dissolved in 500 µL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with allyl acetate (108 µL, 1.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (20 mg, 0.05 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 80:20) to afford pure 23 (103 mg, 0.3 mmol, 64%) as a light yellow oil and as a mixture of diastereoisomers. \( R_f \) (PE:EtOAc 8:2) = 0.28. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 4.62-4.56 (m, 2 H, OCH\(_2\)CH\(_3\)), 4.34-4.24 (m, 2 H, OCH\(_2\)CH), 4.24-4.22 (m, 0.5 H, CHS), 4.17-4.09 (m, 0.5 H, CHS), 3.35-3.25 (m, 2 H, CH\(_3\)S), 2.89-2.81 (m, 1 H, CH\(_3\)CHBr), 2.76-2.62 (m, 1 H, CHCOS), 2.62-2.54 (m, 1 H, CH\(_2\)CH\(_2\)S), 2.31-2.23 (m, 1 H, CHCH\(_2\)CH), 2.08 (s, 1.5 H, CCH\(_2\)), 2.07 (s, 1.5 H, CCH\(_2\)), 2.02-1.85 (m, 1 H, CH\(_2\)CH\(_2\)S), 1.77-1.63 (m, 1 H, CHCH\(_2\)CH), 1.44 (t, 1.5 H, \( J = 7.2 \) Hz, OCH\(_2\)CH\(_2\)), 1.43 (t, 1.5 H, \( J = 7.2 \) Hz, OCH\(_2\)CH\(_2\)). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \( \delta \) 213.2 (CS\(_2\)), 212.8 (CS\(_2\)), 209.4 (COS), 170.8 (COO), 70.8 (OCH\(_2\)CH\(_2\)), 70.6 (OCH\(_2\)CH\(_2\)), 66.3 (OCH\(_2\)CH), 65.4 (OCH\(_2\)CH), 49.4 (CHCOS), 48.4 (CHS), 48.0 (CHS), 32.6 (CH\(_2\)CH\(_2\)S), 32.2 (CH\(_2\)CH\(_2\)S), 31.5 (CHCH\(_2\)CH), 31.1 (CHCH\(_2\)CH), 30.6 (CH\(_2\)SCH\(_2\)S), 20.9 (CCH\(_2\)), 13.9 (OCH\(_3\)CH\(_3\)). IR \( \nu \) 1743 (OC=O), 1695 (SC=O), 1229 (SC-O), 1047 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for \( \text{C}_{12}\text{H}_{19}\text{O}_{5}\text{S} \) \([\text{M}^+\]) 322.0367; found 322.0356; fragmentation calculated for \( \text{C}_{10}\text{H}_{13}\text{O}_{4}\text{S} \) \([\text{M}^+\]) 201.0580; found 201.0577.

Following a slightly modified procedure,\textsuperscript{3} 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with 4-phenyl-1-butene (311 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC, repeated 2 times. The crude was concentrated \textit{in vacuo} and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 24 (342 mg, 1.0 mmol, 97\%) as a light yellow oil and as a mixture of diastereoisomers. $R_f$ (PE:EtOAc 8:2) = 0.71. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) $\delta$ 7.29-7.24 (m, 2 H, ArH), 7.21-7.16 (m, 3 H, ArH), 4.67-4.59 (m, 2 H, OCH\textsubscript{2}CH\textsubscript{2}), 3.88-3.79 (m, 1 H, CHS), 3.29-3.17 (m, 2 H, CH\textsubscript{2}S), 2.86-2.65 (m, 2.5 H, ArCH\textsubscript{2}, CHCOS), 2.60-2.49 (m, 1 H, CHCOS, CH\textsubscript{2}CH\textsubscript{2}S), 2.39-2.32 (m, 0.5 H, CHCOS, CH\textsubscript{2}CH\textsubscript{2}S), 2.30-2.17 (m, 1 H, CHCH\textsubscript{2}CH), 2.06-1.91 (m, 2 H, CH\textsubscript{2}CH\textsubscript{2}S), 1.91-1.77 (m, 1 H, CH\textsubscript{2}CH\textsubscript{2}S), 1.74-1.65 (m, 1 H, CHCH\textsubscript{2}CH), 1.41 (t, 1.5 H, J = 7.1 Hz, OCH\textsubscript{2}CH\textsubscript{2}), 1.40 (t, 1.5 H, J = 7.1 Hz, OCH\textsubscript{2}CH\textsubscript{2}). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) $\delta$ 214.1 (CS\textsubscript{2}), 213.7 (CS\textsubscript{2}), 209.7 (COS), 141.1 (Ar), 128.5 (ArH), 126.1 (ArH), 70.3 (OCH\textsubscript{2}CH\textsubscript{2}S), 70.0 (OCH\textsubscript{2}CH\textsubscript{2}S), 49.8 (CHCOS), 49.7 (CHCOS), 49.6 (CHS), 48.9 (CHS), 37.7 (CH\textsubscript{2}CH\textsubscript{2}CHS), 35.4 (CH\textsubscript{2}CH\textsubscript{2}CHS), 35.1 (CHCH\textsubscript{2}CH), 34.3 (CHCH\textsubscript{2}CH), 33.0 (CH\textsubscript{2}CH\textsubscript{2}CHS), 32.4 (CH\textsubscript{2}CH\textsubscript{2}S), 32.2 (CH\textsubscript{2}CH\textsubscript{2}S), 30.3 (CH\textsubscript{2}CH\textsubscript{2}S), 30.2 (CH\textsubscript{2}CH\textsubscript{2}S), 13.8 (OCH\textsubscript{2}CH\textsubscript{2}). IR $\nu$ 1696 (C=O), 1218 (SC-O), 1049 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\textsubscript{17}H\textsubscript{22}O\textsubscript{2}S\textsubscript{3} [M$^+$] 354.0782; not found, fragmentation calculated for C\textsubscript{14}H\textsubscript{17}OS [M$^+$] 233.1000; found 233.1008.
S-(1-cyano-3-(2-oxotetrahydrothiophen-3-yl)propan-2-yl) O-ethyl carbonodithioate (25)

Following a slightly modified procedure, 3 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with allyl cyanide (164 μL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC, repeated 2 times. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 25 (208 mg, 0.7 mmol, 72%) as a light yellow oil and a mixture of diastereoisomers. \( R_f \) (PE:EtOAc 7:3) = 0.44. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 4.63 (q, 1 H, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 4.62 (q, 1 H, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 4.20-4.19 (m, 0.5 H, CHS), 3.95-3.93 (m, 0.5 H, CHS), 3.34-3.23 (m, 2 H, CH\(_2\)S), 2.99-2.81 (m, 2 H, CH\(_2\)CN), 2.72-2.61 (m, 1 H, CHCOS), 2.56-2.49 (m, 1 H, CH\(_2\)CH\(_2\)S), 2.35-2.28 (m, 0.5 H, CHCH\(_2\)CH), 2.20-2.14 (m, 0.5 H, CHCH\(_2\)CH), 1.99-1.87 (m, 1 H, CH\(_2\)CH\(_2\)S), 1.85-1.76 (m, 1 H, CHCH\(_2\)CH), 1.41 (t, 1.5 H, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 1.40 (t, 1.5 H, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)). \(^1\)C NMR (CDCl\(_3\), 101 MHz) \( \delta \) 211.7 (CS\(_2\)), 211.3 (CS\(_2\)), 209.2 (COS), 208.7 (COS), 116.9 (CN), 116.8 (CN), 70.9 (OCH\(_2\)CH\(_3\)), 70.7 (OCH\(_2\)CH\(_3\)), 49.1 (CHCOS), 48.9 (CHCOS), 45.2 (CHS), 44.6 (CHS), 32.9 (CHCH\(_2\)CH), 32.7 (CHCH\(_2\)CH), 32.5 (CH\(_2\)CH\(_2\)S), 31.9 (CH\(_2\)CH\(_2\)S), 30.2 (CH\(_2\)CH\(_2\)S), 30.1 (CH\(_2\)CH\(_2\)S), 24.5 (CHCN), 24.3 (CHCN), 13.7 (OCH\(_2\)CH\(_3\)). IR \( \nu \) 2250 (CN), 1693 (C=O), 1229 (SC-O), 1048 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\(_{11}\)H\(_{15}\)NO\(_2\)S\(_3\) [M\(^+\)] 289.0265; not found, fragmentation calculated for C\(_4\)H\(_{10}\)NOS [M\(^+\)] 168.0478; found 168.0475.
Following a slightly modified procedure, $^3$ 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with 2-allylsindolin-1,3-dione (374 mg, 2.0 mmol, 2.0 equiv) was added and the solution was stirred for 1 hour and monitored by TLC. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 80:20 to 70:30) to afford pure 26 (370 mg, 0.9 mmol, 90%) as a light yellow oil and as a mixture of diastereoisomers. $R_f$(PE:EtOAc 8:2) = 0.12. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.84-7.80 (m, 2 H, ArH), 7.73-7.69 (m, 2 H, ArH), 4.60-4.49 (m, 2 H, OCH$_2$CH$_2$), 4.27-4.15 (m, 1 H, CHS), 4.03-3.88 (m, 2 H, CH$_2$N), 3.35-3.20 (m, 2 H, CH$_2$S), 2.78-2.64 (m, 1.5 H, CH$_2$CH$_2$S, CHCOS), 2.60-2.54 (m, 1 H, CH$_2$CH$_2$S), 2.28-2.18 (m, 1 H, CHCH$_2$CH), 2.05-1.95 (m, 0.5 H, CH$_2$CHS), 1.92-1.81 (m, 0.5 H, CH$_2$CH$_2$S), 1.75-1.65 (m, 1 H, CHCH$_2$CH), 1.38 (t, 1.5 H, $J$ = 7.1 Hz, OCH$_2$CH$_3$), 1.37 (t, 1.5 H, $J$ = 7.1 Hz, OCH$_2$CH$_3$). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 212.5 (CS$_2$), 212.3 (CS$_2$), 209.3 (COS), 209.2 (COS), 168.1 (N(CO)$_2$), 134.2 (ArH), 131.7 (ArH), 123.5 (ArH), 70.6 (OCH$_2$CH$_3$), 70.4 (OCH$_2$CH$_3$), 49.5 (CHCOS), 48.3 (CHS), 41.8 (CH$_2$N), 40.3 (CH$_2$N), 32.7 (CH$_2$CH$_2$S), 32.4 (CH$_2$CH$_2$S), 32.1 (CHCH$_2$CH), 31.8 (CHCH$_2$CH), 30.3 (CH$_2$CH$_2$S), 30.2 (CH$_2$CH$_2$S), 13.7 (OCH$_2$CH$_3$). COSY, HSQC and HMBC were consistent with this attribution. IR ν 1773 (NC=O), 1718 (SC=O, NC=O), 1223 (SC-O), 1048 (C=S). HRMS (EI) calculated for C$_{18}$H$_{16}$NO$_3$S [M$^+$] 409.0476; found 409.0481, fragmentation calculated for C$_{18}$H$_{14}$NO$_3$S [M$^+$] 288.0694; found 288.0689.

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S-(1-(1,3-dioxoisindolin-2-yl)-3-(2-oxotetrahydrothiophen-3-yl)propan-2-yl) O-ethyl carbonodithioate (26)
S-(1-(benzo[d][1,3]dioxol-5-yl)-3-(2-oxotetrahydrothiophen-3-yl)propan-2-yl) O-ethyl carbonodithioate (28)

Following a slightly modified procedure, \(^3\) 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with β-pinene 27 (312 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 28 (231 mg, 0.6 mmol, 65%) as a light yellow oil and as a mixture of diastereoisomers. \(R_f\) (PE:EtOAc 8:2) = 0.59 \(^1^H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 5.42 (s, 1 H, \(\text{CH}_2\text{CH})), 4.66-4.60 (q, 2 H, \(J = 7.0\) Hz, OCH\(_{\text{CH}}\)), 3.26-3.22 (m, 2 H, \(\text{CH}_2\text{S}\)), 2.61-2.52 (m, 1 H, CHCOS), 2.51-2.42 (m, 1 H, CCH\(_2\)CH), 2.37-2.29 (m, 1 H, CH\(_2\text{CH}_2\)S), 2.14-2.10 (m, 1 H, CHCH\(_2\)CH), 2.01-2.07 (m, 7 H, CH\(_3\)CH\(_2\)S, CH\(_2\)CHCH\(_2\)CH=CHC, CCH\(_2\)CH), 1.45-1.39 (m, 9 H, OCH\(_2\text{CH}_3\), C(CH\(_3\))\(_2\), 1.32-1.19 (m, 1 H, CHCH\(_2\text{CH}_2\)CH), \(^{13}^C\) NMR (CDCl\(_3\), 101 MHz) \(\delta\) 214.2 (CS=O), 210.3 (COS), 134.7 (CH\(_2\text{CH}\)), 123.0 (CH\(_2\text{CH}_{\text{CH}}\)), 69.3 (OCH\(_2\text{CH}_3\)), 59.0 (C(CH\(_3\))\(_2\)), 50.2 (CHCOS), 49.9 (CHCOS), 42.7 (CH\(_2\text{CH}(\text{CH}_3)\)), 38.1 (CCH\(_2\)CH), 37.3 (CCH\(_2\)CH), 31.6 (CH\(_2\text{CH}_2\)S), 31.3 (CH\(_2\text{CH}_2\)S), 30.3 (CH\(_2\text{CH}_3\), 29.3 (CH\(_2\text{CH}_2\text{CH}_2\)), 29.1 CH\(_2\text{CH}_2\text{CH}_2\)), 27.1 ((CH\(_3\))\(_2\)CCH), 25.2 (C(CH\(_3\))\(_2\)), 25.1 (C(CH\(_3\))\(_2\)), 24.9 (C(CH\(_3\))\(_2\)), 24.9 (C(CH\(_3\))\(_2\)), 24.7 (CHCH\(_2\text{CH}_2\)CH), 24.4 (CHCH\(_2\text{CH}_2\)CH), 13.8 (OCH\(_2\text{CH}_3\)). IR \(\nu\) 1695 (C=O), 1234 (SC-O), 1040 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\(_{14}\)H\(_{26}\)O\(_2\)S\(_3\) [M\(^+\)] 358.1095; not found, fragmentation calculated for C\(_{14}\)H\(_{25}\)OS [M\(^+\)] 237.1308; found 237.1306.
Methyl 10-((ethoxycarbonothioyl)thio)-11-(2-oxotetrahydrothiophen-3-yl)undecanoate (29)

Following a slightly modified procedure, 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with methyl-10-undecenoate (468 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 29 (262 mg, 0.6 mmol, 62%) as a light yellow oil and as a mixture of diastereoisomers. \( R_j \) (PE:EtOAc 9:1) = 0.28. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) 4.62 (q, 1 H, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 4.56 (q, 1 H, \( J = 7.1 \) Hz, OCH\(_2\)CH\(_3\)), 3.84-3.71 (m, 1 H, CHS), 3.61 (s, 1 H, OCH\(_3\)), 3.27-3.21 (m, 2 H, CH\(_2\)S), 2.66-2.47 (m, 2 H, CH\(_2\)CH\(_2\)S, CHCOS), 2.24 (t, 2 H, \( J = 7.5 \) Hz, CH\(_2\)CO\(_2\)), 2.19-2.09 (m, 1 H, CHCH\(_2\)CH), 2.02-1.91 (m, 0.5 H, CH\(_2\)CH\(_2\)S), 1.88-1.78 (m, 0.5 H, CH\(_2\)CH\(_2\)S), 1.67-1.62 (m, 2 H, CH\(_2\)CH\(_2\)CH\(_2\)CO\(_2\)), 1.60-1.54 (m, 3 H, CHCH\(_2\)CH, CH\(_2\)CH\(_2\)CO\(_2\)), 1.40-1.35 (m, 5 H, CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CO\(_2\), OCH\(_2\)CH\(_3\)), 1.23 (br, 8 H, CHCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \( \delta \) 214.6 (CS), 214.1 (CS), 209.7 (CO\(_2\)), 174.2 (CO\(_2\)), 70.1 (OCH\(_2\)CH\(_3\)), 69.9 (OCH\(_2\)CH\(_3\)), 51.4 (OCH\(_3\)), 50.2 (CHS), 49.8 (CHS), 49.7 (CHCOS), 49.6 (CHCOS), 35.8 (CH\(_2\)CH\(_2\)CH\(_2\)CO\(_2\)), 35.0 (CH\(_2\)CH\(_2\)CO\(_2\)), 34.4 (CH\(_2\)CH\(_2\)CO\(_2\)), 34.0 (CH\(_2\)CO\(_2\)), 33.6 (CH\(_2\)CO\(_2\)), 32.5 (CH\(_2\)CH\(_2\)S), 32.3 (CH\(_2\)CH\(_2\)S), 30.3 (CH\(_2\)CH\(_2\)S), 30.2 (CH\(_2\)CH\(_2\)S), 29.3 (CHCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)), 29.2 (CHCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)), 29.1 (CHCH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)), 29.0 (CHCH\(_2\)CH), 26.6 (CHCH\(_2\)CH), 24.9 (CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CO\(_2\)), 13.8 (OCH\(_3\)CH\(_3\)). IR \( \nu \) 1738 (OC=O), 1698 (C=O), 1215 (SC=O), 1049 (C=S), COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\(_{19}\)H\(_{35}\)O\(_3\)S\(_3\) [M\(^+\)] 420.1463; found 420.1457.
S-(1-(benzo[d][1,3]dioxol-5-yl)-3-(2-oxotetrahydrothiophen-3-yl)propan-2-yl) O-ethyl carbonodithioate (30)

Following a slightly modified procedure, 3 14 (222 mg, 1.0 mmol, 1.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with safrole (305 µL, 2.0 mmol, 2.0 equiv). After 15 minutes of reflux under nitrogen, DLP (40 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour and monitored by TLC, repeated 3 times. The crude was concentrated in vacuo and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 30 (134 mg, 0.3 mmol, 35%) as a light yellow oil. Rf (PE:EtOAc 8:2) = 0.35. 1H NMR (CDCl3, 400 MHz) δ 6.78-6.67 (m, 3 H, ArH), 5.93 (s, 2 H, OCH2O), 4.61 (q, 2 H, J = 7.0 Hz, OCH2CH3), 4.15-4.08 (m, 1 H, CHS), 3.26-3.23 (m, 2 H, CH2S), 3.00 (dd, 1 H, J = 6.7 Hz, J = 7.5 Hz, CH2CH3), 2.83 (dd, 1 H, J = 6.7 Hz, J = 7.5 Hz, CH2CH3), 2.64-2.56 (m, 1 H, CHCOS), 2.54-2.47 (m, 1 H, CH2CH3S), 2.21-2.15 (m, 1 H, CHCH2CH), 2.01-1.91 (m, 1 H, CH2CH3S), 1.66-1.59 (m, 1 H, CHCH2CH), 1.41 (t, 3 H, J = 7.0 Hz, OCH2CH3). 13C NMR (CDCl3, 101 MHz) δ 213.5 (COS), 209.5 (CS2), 147.7 (Ar), 146.5 (Ar), 131.7 (Ar), 122.5 (ArH), 109.7 (ArH), 108.3 (ArH), 70.1 (OCH2CH3), 50.6 (CHS), 49.7 (CHCOS), 40.7 (CH2CH3S), 33.7 (CHCH2CH), 32.6 (CH2CH3S), 30.3 (CH2CH3S), 13.9 (OCH2CH3). IR ν 1694 (SC=O), 1247 (C-O-C), 1219 (SC-O), 1046 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C14H20O2S3 [M+] 384.0524; not found, fragmentation calculated for C14H14O3S [M+] 262.0664; found 262.0666.
4. Addition to Dialkenes

\[
\text{S,S'}-(1,8\text{-bis(2-oxotetrahydrothiophen-3-yl)octane-2,7-diyl)} \ O,O'\text{-diethyl dicarbonodithioate (32)}
\]

Following a slightly modified procedure, \textsuperscript{3} \textbf{14} (222 mg, 1.0 mmol, 3.0 equiv) was dissolved in 1 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with 1,7-octadiene \textbf{31} (50 \mu L, 0.3 mmol, 1.0 equiv). After 15 minutes of reflux under nitrogen, DLP (13 mg, 0.04 mmol, 0.1 equiv) was added and the solution was stirred 1 hour monitored by TLC, repeated 5 times. The crude was concentrated \textit{in vacuo} and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure \textbf{32} (170 mg, 0.3 mmol, 92%) as a light yellow oil and as a mixture of diastereoisomers. \textit{R} \text{f} (PE:EtOAc 8:2) = 0.48. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz) \delta 4.68-4.62 (m, 4 H, OCH\textsubscript{2}CH\textsubscript{3}), 3.85-3.72 (m, 2 H, CHS), 3.28-3.22 (m, 4 H, CH\textsubscript{2}S), 2.68-2.48 (m, 4 H, CH\textsubscript{2}CH\textsubscript{2}S), 2.19-2.08 (m, 2 H, CH\textsubscript{2}CH), 2.01-1.91 (m, 1 H, CH\textsubscript{2}CH\textsubscript{2}S), 1.89-1.78 (m, 1 H, CH\textsubscript{2}CH\textsubscript{2}S), 1.68-1.64 (m, 4 H, CH\textsubscript{2}CHCH\textsubscript{2}CH\textsubscript{2}S), 1.62-1.35 (m, 2 H, CH\textsubscript{2}CH\textsubscript{2}S), 1.45-1.36 (m, 10 H, SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH, OCH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 101 MHz) \delta 214.4 (CS\textsubscript{2}), 213.9 (CS\textsubscript{2}), 209.6 (COS), 70.2 (OCH\textsubscript{2}CH\textsubscript{3}), 70.0 (OCH\textsubscript{2}CH\textsubscript{3}), 49.9 (CHCOS), 49.7 (CHS), 49.5 (CHS), 35.5 (CH\textsubscript{2}CH\textsubscript{2}S), 34.9 (CH\textsubscript{2}CH\textsubscript{2}S), 34.3 (CH\textsubscript{2}CH\textsubscript{2}S), 33.4 (CH\textsubscript{2}CH\textsubscript{2}S), 32.5 (CH\textsubscript{2}CH\textsubscript{2}S), 32.3 (CH\textsubscript{2}CH\textsubscript{2}S), 30.3 (CH\textsubscript{2}CH\textsubscript{2}S), 30.2 (CH\textsubscript{2}CH\textsubscript{2}S), 26.3 (SCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}S), 13.8 (OCH\textsubscript{2}CH\textsubscript{2}S). IR \nu 1695 (C=O), 1217 (SC-O), 1048 (C=S). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\textsubscript{22}H\textsubscript{38}O\textsubscript{3}S\textsubscript{8} [M\textsuperscript{+}] 554.0781; found 554.0793.
Bis(2-((ethoxycarbonothioyl)thio)-3-(2-oxotetrahydrothiophen-3-yl)propyl) carbonate (34)

Following a slightly modified procedure,\(^3\) 14 (666 mg, 3.0 mmol, 3.0 equiv) was dissolved in 3 mL of ethyl acetate to obtain a 1 M solution. The solution was warmed up to 80 °C with diallyl carbonate 33 (145 \(\mu\)L, 1.0 mmol, 1.0 equiv). After 15 minutes of reflux under nitrogen, DLP (13 mg, 0.04 mmol, 0.1 equiv) was added and the solution was stirred 1 hour monitored by TLC, repeated 5 times. The crude was concentrated \(\text{in vacuo}\) and purified by flash column chromatography (PE:EtOAc 90:10) to afford pure 34 (542 mg, 0.9 mmol, 93%) as a light yellow oil and as a mixture of diastereoisomers. \(R_f\) (PE:EtOAc 7:3) = 0.32. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 4.67-4.61 (m, 4 H, OCH\(_2\)CH\(_3\)), 4.41-4.26 (m, 4 H, OCH\(_2\)CHSH), 4.26-4.20 (m, 1 H, CHS), 4.08-4.01 (m, 1 H, CHS), 3.34-3.24 (m, 4 H, CH\(_2\)S), 2.76-2.62 (m, 2 H, CHCOS), 2.59-2.52 (m, 2 H, CH\(_2\)CH\(_2\)S), 2.29-2.18 (m, 2 H, CHCH\(_2\)CH), 2.03-1.86 (m, 2 H, CH\(_2\)CH\(_2\)S), 1.82-1.65 (m, 2 H, CHCH\(_2\)CH), 1.42 (t, 1.5 H, J = 7.1 Hz, OCH\(_2\)CH\(_3\)), 1.41 (t, 1.5 H, J = 7.1 Hz, OCH\(_2\)CH\(_3\)). \(^1\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 212.7 (COS), 212.2 (COS), 209.3 (CS\(_2\)), 154.5 (CO\(_2\)), 70.9 (OCH\(_2\)CH\(_3\)), 70.6 (OCH\(_2\)CH\(_3\)), 69.6 (CH\(_2\)CHS), 69.2 (CH\(_2\)CHS), 49.3 (CHCOS), 48.0 (CHS), 47.6 (CHS), 32.6 (CH\(_2\)CH\(_2\)S), 32.1 (CH\(_2\)CH\(_2\)S), 31.2 (CHCH\(_2\)CH), 30.7 (CHCH\(_2\)CH), 30.3 (CH\(_2\)CH\(_2\)S), 13.9 (OCH\(_2\)CH\(_3\)). COSY, HSQC and HMBC were consistent with this attribution. IR \(\nu\) 1751 (OC=O), 1694 (SC=O), 1240 (SC-O, OC-O), 1047 (C=S). HRMS (EI) calculated for C\(_{34}\)H\(_{30}\)O\(_7\)S\(_6\) [M\(^+\)] 586.0316; not found.
5. Dexanthylation

\[ \text{S,S'}-(1,8-\text{bis}(2-\text{oxotetrahydrothiophen}-3-\text{yl})\text{octane}-2,7-\text{diyl}) \text{ O,O'}-\text{diethyl dicarbonodithioate} (36) } \]

\[
\begin{array}{c}
\text{O} \\
\text{Et} \\
\text{S} \\
\text{OEt} \\
\text{Et} \\
\text{H}_3\text{PO}_2, \text{ Et}_3\text{N} \\
\text{AIBN} (10 \text{ mol% per hour}) \\
1,4-\text{dioxane, reflux} \\
\end{array}
\]

Following a slightly modified procedure, \( \text{319} \) (1.14 g, 13.6 mmol, 1.0 equiv) was dissolved in 35 mL of dioxane to obtain a 0.1 M solution. \( \text{Et}_3\text{N} \) (1.63 mL, 11.7 mmol, 3.3 equiv) was added, then \( \text{H}_3\text{PO}_2 \) (as a 50% solution in water; 552 \( \mu \text{L} \), 10.7 mmol, 3.0 equiv) was added and the solution was warmed up to 100 °C. After 15 minutes of reflux under nitrogen, AIBN (58 mg, 0.7 mmol, 0.1 equiv) was added and the solution was stirred 1 hour monitored by TLC, repeated 2 times. Crude was concentrated \textit{in vacuo}, 40 mL of EtOAc were added, washed with 3x40 mL of water and dried over MgSO\(_4\). Concentrated \textit{in vacuo} and purified by flash column chromatography (PE:EtOAc 90:10 to 80:20) to afford pure \( \text{36} \) (659 mg, 3.3 mmol, 93%) as a yellow oil. \( \text{R}_f \) (PE:EtOAc 7:3) = 0.38. \( ^1\text{H} \text{NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \) 3.24-3.20 (m, 2 H, CH\(_2\)S), 2.45-2.34 (m, 4 H, CH\(_2\)CH\(_2\)S, CH\(_2\)COCH\(_3\)), 2.07 (s, 3 H, COCH\(_3\)), 1.88-1.72 (m, 2 H, CH\(_2\)CH\(_2\)S, CH\(_2\)CH\(_2\)COCH\(_3\)), 1.58-1.46 (m, 2 H, CH\(_2\)CHCOS), 1.35-1.25 (m, 3 H, CH\(_2\)CH\(_2\)CH\(_2\)COCH\(_3\)). \( ^{13}\text{C} \text{NMR} \) (CDCl\(_3\), 101 MHz) \( \delta \) 210.5 (C=O), 208.8 (COS), 154.1 (CHCOS), 43.2 (CH\(_2\)COCH\(_3\)), 31.7 (CH\(_2\)CH\(_3\)), 30.3 (CH\(_2\)CH\(_3\)), 30.0 (COCH\(_3\)), 29.6 (CH\(_2\)CH\(_2\)COCH\(_3\)), 26.8 (CH\(_2\)CH\(_2\)CHCOS), 23.4 (CH\(_2\)CHCOS). IR \( \nu \) 1701 (SC=O, C=O). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C\(_{10}\)H\(_{16}\)O\(_2\)S [M\(^+\)] 200.0871; found 200.0878.
Following a slightly modified procedure, \(^3\) 32 (525 mg, 0.9 mmol, 1.0 equiv) was dissolved in 9.5 mL of dioxane to obtain a 0.1 M solution. Et\(_3\)N (870 \(\mu\)L, 6.2 mmol, 6.6 equiv) was added, then H\(_3\)PO\(_2\) (as a 50\% solution in water; 294 \(\mu\)L, 5.7 mmol, 3.0 equiv) was added and the solution was warmed up to 100 °C. After 15 minutes of reflux under nitrogen, AIBN (31 mg, 0.2 mmol, 0.2 equiv) was added and the solution was stirred 1 hour monitored by TLC, repeated 2 times. Crude was concentrated \textit{in vacuo}, 15 mL of EtOAc were added, washed with 3x15 mL of water and dried over MgSO\(_4\). Concentrated \textit{in vacuo} and recrystallized in EtOAc to afford pure 37 (228 mg, 0.7 mmol, 77\%) as a white solid (1:1 mixture of meso and dl diastereoisomers). Mp: ~73 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 3.25-3.21 (m, 4 H, \(CH_2\)S), 2.46-2.34 (m, 4 H, \(CHCH_2CH_2\)S), 1.79-1.71 (m, 2 H, \(CH_2\)CHCOS), 1.29-1.23 (br, 14 H, \(CH_2CH_2\)CH\(_2\)CH\(_2\)CHCOS). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 210.6 (COS), 51.6 (CHCOS), 31.8 (CH\(_2\)CHS), 30.4 (CH\(_2\)CHS), 29.8 (CH\(_2\)CHCOS), 29.4 (CH\(_2\)CH\(_2\)CHCOS), 29.3 (CH\(_2\)CH\(_2\)CH\(_2\)CHCOS), 27.3 (CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)CHCOS). IR \(\nu\) 1693 (SC=O). COSY, HSQC and HMBC were consistent with this attribution. HRMS (El) calculated for C\(_{16}\)H\(_{26}\)O\(_2\)S\(_2\) [M\(^{+}\)] 314.1374; found 314.1377.
Following a slightly modified procedure, 34 (542 mg, 0.9 mmol, 1.0 equiv) was dissolved in 9.2 mL of dioxane to obtain a 0.1 M solution. Et$_3$N (425 µL, 3.0 mmol, 3.3 equiv) was added, then H$_3$PO$_2$ (as a 50% solution in water; 144 µL, 2.8 mmol, 3.0 equiv) was added and the solution was warmed up to 100 °C. After 15 minutes of reflux under nitrogen, AIBN (15 mg, 0.1 mmol, 0.1 equiv) was added and the solution was stirred 1 hour monitored by TLC. Crude was concentrated in vacuo, 20 mL of EtOAc were added, washed with 3x20 mL of water and dried over MgSO$_4$. Concentrated in vacuo and recrystallized in EtOAc to afford pure 38 (193 mg, 0.6 mmol, 60%) as a white solid (1:1 mixture of meso and dl diastereoisomers).

$^1$H NMR (CDCl$_3$, 400 MHz) δ 4.07 (t, 4 H, J = 6.4 Hz, OCH$_2$), 3.25-3.22 (m, 4 H, CH$_2$S), 2.47-2.37 (m, 4 H, CH$_2$CH$_2$S, CH$_2$CHCOS), 1.75-1.64 (m, 4 H, OCH$_2$CH$_2$), 1.44-1.35 (m, 2 H, CH$_2$CHCOS).

$^{13}$C NMR (CDCl$_3$, 101 MHz) δ 209.9 (COS), 155.0 (CO$_3$), 67.4 (OCH$_2$), 51.0 (CHCOS), 31.7 (CH$_2$CH$_2$S), 30.2 (CH$_2$CH$_2$S), 26.4 (OCH$_2$CH$_2$), 26.1 (CH$_2$CHCOS). IR ν 1743 (OC=O), 1694 (SC=O), 1258 (OC-O). COSY, HSQC and HMBC were consistent with this attribution. HRMS (EI) calculated for C$_{15}$H$_{22}$O$_5$S$_2$ [M$^+$] 348.0909; found 346.0916.
7. NMR Spectra for New Compounds
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (101 MHz, CDCl$_3$)

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