Supplementary Material (ESI) for Chemical Communications

AN UNEXPECTED SYNTHESIS OF KETENE MONOTHIOACETALS
SUPPORTING INFORMATION

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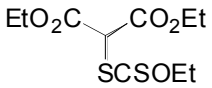
General conditions
All reactions were carried out under an inert atmosphere. Commercial reagents were used as received without further purification. All products were purified by using silica gel (SDS, Silice 60 A. C. C. 40-63 μm) or by crystallization. Analitical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light, 1% aq. $KMnO_4$ solution to visualise components. NMR spectra were recorded in $CDCl_3$ using a Bruker AMX400 operating at 400 MHz for ^1H and 100 MHz for ^{13}C. The chemical shifts are expressed in parts per million (ppm) referenced to residual chloroform. ^1H NMR data are reported as follows: δ, chemical shift; multiplicity (recorded as: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quadruplet; qt, quintuplet; ht, heptuplet; dd, double doublet; ddd, double double doublet; dddd, double double double doublet; dt, double triplet; ddt, double double triplet; dq, double quadruplet; tt, triple triplet; td; triple doublet; tdd, triple double doublet; m, multiplet), coupling constants (*J* are given in Hertz, Hz) and integration. Infrared Absorption spectra were recorded as a solution in CCl_4 with a Perkin-Elmer 1600 Fourier Transform Spectrophotometer. Mass spectra were recorded with an HP 5989B mass spectrometer via direct introduction for chemical positive ionization (CI) using ammonia as the reagent gas. Melting points were determined by Reichert microscope apparatus and were uncorrected. HRMS were performed on JEOL JMS-GcMate II, GC/MS system spectrometer.



Diethyl 2-ethoxythiocarbonylsulfanylmalonate 1

To a stirred solution of diethyl chloromalonate (5 mL, 30.9 mmol) in DMF (31 mL) was added dropwise a suspension of potassium ethylxanthogenate (5 g, 30.9 mmol) in DMF (31 mL), and stirred at room temperature overnight. After that time, the reaction mixture was diluted with EtOAc, and washed several times with H_2O and Brine. The organic layer was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 95:5), to furnish the desired xanthate as a yellow oil (8.28 g, 96%).
IR (CCl_4) ν_{max}/cm^{-1} 1746 (CO), 1238 (O-CS), 1049 (C=S).
^{1}H-NMR ($CDCl_3$) δ 1.30 (t, *J*=7.2 Hz, 6 H, 2 CH_3), 1.42 (t, *J*=7.2 Hz, 3 H, CH_3), 4.27 (q, *J*=7.2 Hz, 4 H, 2 OCH_2), 4.64 (q, *J*=7.2 Hz, 2 H, OCH_2 xanthate), 5.29 (s, 1 H, CHS).
^{13}C-NMR ($CDCl_3$) δ 13.3 (CH_3), 13.7 (2 CH3), 56.0 (CHS), 62.6 (2 OCH_2), 70.8 (OCH_2 xanthate), 164.8 (2 CO), 209.8 (CS).
MS (CI) *m/z* 281 (MH^+), 298 (MNH_4^+).
HRMS calculated for $C_{10}H_{16}O_5S_2$ 280.0439 found 280.0444.

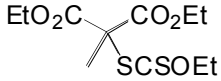
*Optimised method for the C-alkylation of xanthate **1***
To a cooled (0 ºC) solution of xanthate **1** (1 equiv.) in acetone (1 mL/mmol) was added the corresponding alkyl halide (5 equiv.) and K_2CO_3 (1.2 equiv.) and stirred at that temperature for 1 h. After that time, the reaction mixture was filtrated and concentrated. The residue was purified by flash column chromatography.

Genaral methods for the synthesis of the ketene monothioacetals

Method A. To a solution of xanthate (1 equiv.) in acetone (2 mL/mmol) was added K_2CO_3 (1.5 equiv.) and stirred for 30 min (except for compound **17** that required 15 h). Then it was added the corresponding alkyl halide (1.2 equiv.) and stirred for a further 30 min. After that time, the reaction mixture was filtrated and concentrated, and the residue was purified by flash column chromatography.

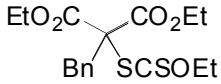
Method B. To a cooled (0 ºC) solution of xanthate (1 equiv.) in THF (2 mL/mmol) was added NaH (1.5 equiv.) and stirred for 15 min. at room temperature. Then it was added the corresponding alkyl halide (1.2 equiv.) and stirred for a further 30 min. After that time, the reaction was quenched by addition of saturated aqueous NH_4Cl solution, and it was extracted with EtOAc. The organic extracts were dried and evaporated, and the obtained residue was purified by flash column chromatography.

Method C. To a solution of xanthate (1 equiv.) in EtOH (2 mL/mmol) was added finely powdered KOH (1.1 equiv.) and heated to reflux temperature for 1 h. Then it was cooled down and it was added the corresponding alkyl halide (1.1 equiv.) and stirred for a further 30 min. After that time, the reaction was quenched by addition of saturated aqueous NH_4Cl solution, and it was extracted with EtOAc. The organic extracts were dried and evaporated, and the obtained residue was purified by flash column chromatography.



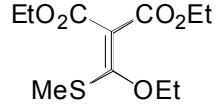
Diethyl 2-ethoxythiocarbonylsulfanyl-2-methylmalonate 2a

Yellow oil, petol:EtOAc 9:1.
IR (CCl_4) ν_{max}/cm^{-1} 1742 (CO), 1255 (O-CS), 1027 (C=S).
^{1}H-NMR ($CDCl_3$) δ 1.28 (t, *J*=7.2 Hz, 6 H, 2 CH_3), 1.39 (t, *J*=7.2 Hz, 3 H, CH_3 xanthate), 1.95 (s, 3 H, CH_3), 4.24 (q, *J*=7.2 Hz, 4 H, 2 OCH_2), 4.60 (q, *J*=7.2 Hz, 2 H, OCH_2 xanthate).
^{13}C-NMR ($CDCl_3$) δ 12.9 (CH_3 xanthate), 13.7 (2 CH_3), 22.7 (CH_3), 62.4 (2 OCH_2), 69.9 (OCH_2 xanthate), 167.3 (CO), 209.0 (CS).
MS (CI) *m/z* 295 (MH^+), 311 (MNH_4^+).



Diethyl 2-benzyl-2-ethoxythiocarbonylsulfanylmalonate 2b

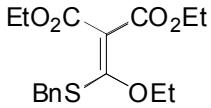
Yellow oil, petrol:EtOAc 9:1.
IR (CCl_4) ν_{max}/cm^{-1} 1740 (CO), 1255 (O-CS), 1029 (C=S).
^{1}H-NMR ($CDCl_3$) δ 1.22 (t, *J*=7.2 Hz, 6 H, 2 CH_3), 1.41 (t, *J*=7.2 Hz, 3 H, CH_3 xanthate), 3.68 (s, 2 H, CH_2Ph), 4.19 (q, *J*=7.2 Hz, 4 H, 2 OCH_2), 4.60 (q, *J*=7.2 Hz, 2 H, OCH_2 xanthate), 7.15-7.35 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 13.1 (CH_3), 13.7 (2 CH_3), 40.2 (CH_2Ph), 62.6 (2 OCH_2), 68.1 (C), 70.0 (OCH_2 xanthate), 127.3 (CH Ar), 128.0 (CH Ar), 130.4 (CH Ar), 134.6 (C-*ipso*), 166.4 (2 CO), 209.2 (CS).
MS (CI) *m/z* 370 (MH^+), 387 (MNH_4^+).



Diethyl 2-(1-ethoxy-1-methylsulfanylmethylene)malonate 3a

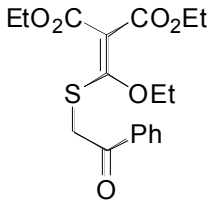
Yellow oil, petrol:EtOAc 9:1, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1724 (CO), 1563 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.20 (bm, 6 H, 2 CH_3 ester), 1.27 (t, *J*=7 Hz, 3 H, CH_3 acetal), 2.22 (s, 3 H, SCH_3), 4.04 (q, *J*=7.2 Hz, 2 H, OCH_2 acetal), 4.20 (bm, 4 H, 2 OCH_2 ester).

^{13}C-NMR ($CDCl_3$) δ 13.4, 13.9 and 14.7 (2 CH_3 ester, CH_3 acetal and SCH_3), 60.7 and 60.9 (2 OCH_2 ester), 71.0 (OCH_2 acetal), 111.3 (C=), 164.4 and 164.5 (2 CO), 172.9 (C=).
MS (CI) *m/z* 263 (MH^+).
HRMS calculated for $C_{18}H_{11}O_5S$ 262.0875 found 262.0878.



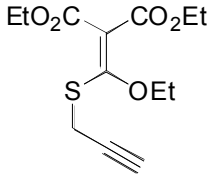
Diethyl 2-(1-benzylsulfanyl-1-ethoxymethylene)malonate 3b

Yellow oil, petrol:EtOAc 9:1, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1725 (CO), 1563 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.28 (bm, 6 H, 2 CH_3), 1.32 (t, *J*= 7 Hz, 3 H, CH_3), 4.04 (s, 2 H, SCH_2), 4.13 (q, *J*= 7.2 Hz, 2 H, OCH_2), 4.25 (bm, 4 H, 2 OCH_2), 7.20-7.40 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 13.9 (2 CH_3), 14.7 (CH_3), 35.4 (SCH_2), 60.8 (OCH_2 ester), 61.0 (OCH_2 ester), 70.8 (OCH_2 acetal), 111.6 (C=), 127.3, 128.4 and 128.7 (CH Ar), 136.2 (C Ar), 164.3 (CO), 164.6 (CO), 171.1 (C=).
MS (CI) *m/z* 339 (MH^+).
HRMS calculated for $C_{17}H_{22}O_5S$ 338.1188 found 338.1187.



Diethyl 2-[1-ethoxy-1-(2-oxo-2-phenylethylsulfanyl)methylene]malonate 3c

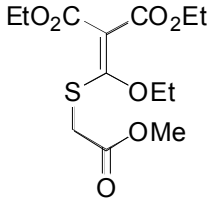
Yellow oil, petrol:EtOAc 8:2, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1738 (CO ester), 1693 (CO ketone), 1558 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.22 (t, *J*= 7 Hz, 3 H, CH_3), 1.26 (t, *J*= 7.4 Hz, 3 H, CH_3), 1.30 (t, *J*= 7.4 Hz, 3 H, CH_3), 4.12 (q, *J*= 6.8 Hz, 2 H, OCH_2 acetal), 4.16-4.28 (m, 4 H, 2 OCH_2 ester), 4.27 (s, 2 H, SCH_2), 7.49 (t, *J*= 7.6 Hz, 2 H, ArH), 7.60 (t, *J*= 6.8 Hz, 1 H, ArH), 7.96 (d, *J*= 8 Hz, 2 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.0 (2 CH_3 ester), 14.4 (CH_3 acetal), 59.0 (SCH_2), 60.7 (OCH_2 ester), 61.0 (OCH_2 ester), 62.5 (OCH_2 acetal), 100.0 (C=), 125.0, 129.0 and 129.7 (CH Ar), 133.7 (C Ar), 164.0 (2 CO ester), 178.8 (C=), 194.2 (CO ketone).
MS (CI) *m/z* 321 (MH^+-OEt).
HRMS calculated for $C_{18}H_{22}O_6S$ 366.1137 found 366.1140.



Diethyl 2-[1-ethoxy-1-(prop-2-ynylsulfanyl)methylene]malonate 3d

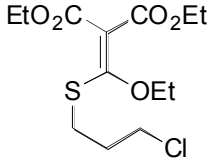
Yellow oil, petrol:EtOAc 9:1, method A.
IR (CCl_4) ν_{max}/cm^{-1} 3400 (C-H), 1743 (CO), 1552 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.28 (t, *J*= 7 Hz, 3 H, CH_3), 1.31 (t, *J*= 7 Hz, 3 H, CH_3), 1.39 (t, *J*= 7 Hz, 3 H, CH_3), 2.30 (t, *J*= 2.8 Hz, 1 H, CH), 3.59 (d, *J*= 2.8 Hz, 2 H, SCH_2), 4.21 (q, *J*= 7 Hz, 2 H, OCH_2), 4.20-4.35 (m, 4 H, 2 OCH_2).
^{13}C-NMR ($CDCl_3$) δ 13.9 (CH_3), 14.1 (CH_3), 14.9 (CH_3), 19.0 (SCH_2), 61.1 (OCH_2 ester), 61.4 (OCH_2 ester), 71.88 (CH), 71.92 (OCH_2 acetal), 90.0 (C alkyne), 111.6 (C=), 164.4 (CO), 164.7 (CO), 170.6 (C=).

MS (CI) *m/z* 287 (MH^+), 304 (MNH_4^+).
HRMS calculated for $C_{13}H_{18}O_5S$ 286.0875 found 386.0863.



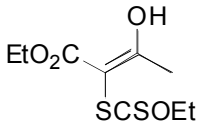
Diethyl 2-[1-ethoxy-1-(2-methoxycarbonylmethylsulfanyl)methylene]malonate 3e

Yellow oil, petrol:EtOAc 8:2, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1718 (CO), 1566 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.33 (t, *J*= 7.4 Hz, 3 H, CH_3), 1.36 (t, *J*= 7.2 Hz, 3 H, CH_3), 1.38 (t, *J*= 7 Hz, 3 H, CH_3), 3.56 (s, 2 H, SCH_2), 3.73 (s, 3 H, OCH_3), 4.19 (q, *J*= 7.2 Hz, 2 H, OCH_2), 4.28 (q, *J*= 7.2 Hz, 2 H, OCH_2), 4.30 (q, *J*= 7.2 Hz, 2 H, OCH_2).
^{13}C-NMR ($CDCl_3$) δ 14.0 (CH_3 ester), 14.1 (CH_3 ester), 14.8 (CH_3 acetal), 32.5 (SCH_2), 52.6 (OCH_3), 61.0 (OCH_2), 61.4 (OCH_2), 71.8 (OCH_2 acetal), 110.3 (C=), 164.6 (CO), 164.8 (CO), 169.2 (CO), 170.7 (C=).
MS (CI) *m/z* 321 (MH^+), 328 (MNH_4^+).
HRMS calculated for $C_{13}H_{20}O_7S$ 320.0930 found 320.0928.



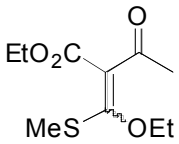
Diethyl 2-[1-(3-chloropropylsulfanyl)-1-ethoxymethylene]malonate 3f

Yellow oil, petrol:EtOAc 9:1, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1726 (CO), 1569 (C=C), 1080 (C-Cl).
^{1}H-NMR ($CDCl_3$) δ 1.29 (t, *J*= 7 Hz, 6 H, 2 CH_3 ester), 1.37 (t, *J*= 7 Hz, 3 H, CH_3 acetal), 2.15 (qn, *J*= 6.4 Hz, 2 H, CH_2), 2.99 (t, *J*= 7 Hz, 2 H, CH_2), 3.70 (t, *J*= 6.2 Hz, 2 H, CH_2, 4.16 (q, *J*= 7.2 Hz, 2 H, OCH_2 acetal), 4.24 (q, *J*= 7.2 Hz, 4 H, 2 OCH_2 ester).
HRMS calculated for $C_{13}H_{21}ClO_5S$ 324.0798 found 324.0795.



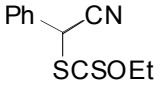
Ethyl (*E*)-2-ethoxythiocarbonylsulfanyl-3-hydroxy-but-2-enoate 9

To a stirred solution of ethyl 2-chloro-3-oxobutirate (10 mL, 72.3 mmol) in DMF (72 mL) was added dropwise a suspension of potassium ethylxanthogenate (11.6 g, 72.3 mmol) in DMF (72 mL), and stirred at room temperature overnight. After that time, the reaction mixture was diluted with EtOAc, and washed several times with H_2O and Brine. The organic layer was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 99:1), to furnish the desired xanthate as a yellow oil (6.60 g, 37%).
IR (CCl_4) ν_{max}/cm^{-1} 1729 (CO ester), 1636 (CO enol), 1228 (O-CS), 1045 (C=S).
^{1}H-NMR ($CDCl_3$) δ 1.28 (t, *J*= 7 Hz, 3 H, CH_3), 1.41 (t, *J*= 7.2 Hz, 3 H, CH_3), 2.24 (s, 3 H, CH_3C=), 4.20-4.30 (m, 2 H, OCH_2 ester), 4.64 (qd, *J*= 1.4, 7.2 Hz, 2 H, OCH_2 xanthate).
^{13}C-NMR ($CDCl_3$) δ 13.6 (CH_3), 13.8 (CH_3), 20.5 (CH_3C=), 61.4 (OCH_2 ester), 70.3 (OCH_2 xanthate), 93.1 (C=), 171.6 (CO), 184.6 (=C-OH), 213.5 (CS).
HRMS calculated for $C_9H_{14}O_4S_2$ 250.0334 found 250.0336.



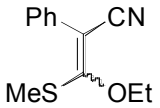
Ethyl 2-(1-ethoxy-1-methylsulfanylmethylene)-3-oxobutyrate 10

Yellow oil, petrol:EtOAc 8:2, 2 isomers A:B 6:1, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1723 (CO), 1582 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.21 (t, *J*= 7.2 Hz, 0.43 H, CH_3 ester isomer B), 1.26 (t, *J*= 7.2 Hz, 2.57 H, CH_3 ester isomer A), 1.31 (t, *J*= 7.2 Hz, 2.57 H, CH_3 acetal isomer A), 1.36 (t, *J*= 7.2 Hz, 0.43 H, CH_3 acetal isomer B), 2.14 (s, 0.43 H, SCH_3 isomer B), 2.23 (s, 2.57 H, SCH_3 isomer A), 2.25 (s, 2.57 H, CH_3 acetyl isomer A), 2.45 (s, 2.57 H, CH_3 acetyl isomer B), 4.05 (q, *J*= 7.2 Hz, 2 H, OCH_2 acetal), 4.21 (q, *J*= 7.2 Hz, 2 H, OCH_2 ester).
^{13}C-NMR ($CDCl_3$) δ 13.7 (SCH_3), 13.9 (CH_3 ester isomer A), 14.0 (CH_3 ester isomer B), 14.8 (CH_3 acetal isomer A), 15.0 (CH_3 acetal isomer B), 23.8 (CH_3 acetyl isomer B), 29.9 (CH_3 acetyl isomer A), 60.8 (OCH_2 ester isomer B), 61.0 (OCH_2 ester isomer A), 71.5 (OCH_2 acetal isomer A), 72.6 (OCH_2 acetal isomer B), 100.8 (C= isomer B), 119.7 (C= isomer A), 159.8 (CO ester isomer A), 160.2 (CO ester isomer B), 165.9 (C= isomer A), 167.2 (C= isomer B), 194.0 (CO isomer B), 195.1 (CO isomer A).
MS (CI) *m/z* 233 (MH^+).
HRMS calculated for $C_{10}H_{16}O_4S$ 232.0769 found 232.0774.



Dithiocarbonic acid *O*-ethyl ester *S*-(1-cyano-1-phenylmethyl) ester 11

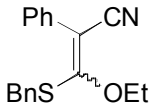
To a solution of mandelonitrile (3 mL, 22.5 mmol) in CH_2Cl_2 (17 mL) cooled to 0 ºC was added carefully PCl_5 (5.63 g, 27.0 mmol) and stirred at room temperature for 1 h. After that time the reaction mixture was concentrated, the residue was redissolved in acetone (113 mL) and cooled to 0 ºC. Potassium ethylxanthogenate (4.69 g, 29.3 mmol) was added, and the reaction mixture was stirred at room temperature for 2 h. Then, it was concentrated, the residue redissolved in Et_2O, and it was washed three times with H_2O. The organic phase was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 98:2), obtaining the desired xanthate as a yellow oil (3.76 g, 71%).
IR (CCl_4) ν_{max}/cm^{-1} 2361 (CN), 1242 (O-CS), 1047 (C=S).
^{1}H-NMR ($CDCl_3$) δ 1.48 (t, *J*=7.2 Hz, 3 H, CH_3), 4.65-4.79 (m, 2 H, OCH_2), 5.66 (s, 1 H, CH), 7.30-7.60 (m, 5 H, Ar-H).
^{13}C-NMR ($CDCl_3$) δ 13.5 (CH_3), 41.7 (CH), 71.2 (OCH_2), 117.1 (CN), 127.9, 129.2 and 129.4 (CH Ar), 129.8 (C Ar), 208.4 (CS).
MS *m/z* (CI) 238 (MH^+).
HRMS calculated for $C_{11}H_{11}NOS_2$ 237.0282 found 237.0282.



3-Ethoxy-3-methylsulfanyl-2-phenylacrylonitrile 12a

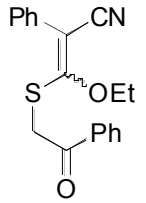
Yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 13:1, method B.
IR (CCl_4) ν_{max}/cm^{-1} 2212 (CN), 1555 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.26 (t, *J*= 7 Hz, 2.79 H, CH_3 isomer A), 1.44 (t, *J*= 7.2 Hz, 0.21 H, CH_3 isomer B), 2.20 (s, 0.21 H, SCH_3 isomer B), 2.40 (s, 2.79 H, SCH_3 isomer A), 4.11 (q, *J*= 7 Hz, 1.86 H, OCH_2 isomer A), 4.30 (q, *J*= 7 Hz, 0.14 H, OCH_2 isomer B), 7.25 (d, *J*= 7 Hz, 1 H, ArH), 7.33 (t, *J*= 7.6 Hz, 2 H, ArH), 7.61 (d, *J*= 7.6 Hz, 2 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.0 (CH_3 isomer B), 14.7 (CH_3 isomer A), 15.6 (SCH_3), 68.7 (OCH_2 isomer A), 69.9 (OCH_2 isomer B), 97.3 (C= isomer B), 100.2 (C= isomer A),

118.6 (CN), 127.6, 127.7 and 128.1 (CH Ar), 131.6 (C Ar), 166.8 (C= isomer A), 169.4 (C= isomer B).
MS (CI) *m/z* 220 (MH^+), 237 (MNH_4^+).



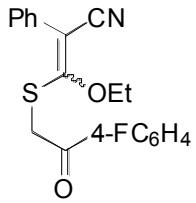
3-Benzylsulfanyl-3-ethoxy-2-phenylacrylonitrile 12b

Yellow oil, petrol:EtOAc 95:5, 2 isomers A:B 7:1, method C.
IR (CCl_4) ν_{max}/cm^{-1} 2212 (CN), 1554 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.23 (t, *J*= 7 Hz, 2.625 H, CH_3 isomer A), 1.45 (t, *J*= 7 Hz, 0.375 H, CH_3 isomer B), 3.90 (s, 0.25 H, SCH_2 isomer B), 4.08 (q, *J*= 7.2 Hz, 1.75 H, OCH_2 isomer A), 4.13 (s, 1.75 H, SCH_2 isomer A), 4.35 (q, *J*= 7.2 Hz, 0.25 H, OCH_2 isomer B), 7.20-7.60 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.6 (CH_3 isomer A), 14.7 (CH_3 isomer B), 36.0 (SCH_2 isomer B), 38.2 (SCH_2 isomer A), 68.2 (OCH_2 isomer A), 69.3 (OCH_2 isomer B), 99.4 (C= isomer B), 103.0 (C= isomer A), 127.5, 127.7, 127.8, 128.06, 128.12, 128.3, 128.4, 128.6, 128.85, 128.92, 129.0 and 129.1 (CH Ar), 130.9, 131.4, 131.5 and 136.0 (C Ar), 167.1 and 167.4 (C=).
MS (CI) *m/z* 296 (MH^+), 313 (MNH_4^+).
HRMS calculated for $C_{18}H_{17}NOS$ 295.1031 found 295.1030.



3-Ethoxy-3-(2-oxo-2-phenylethylsulfanyl)-2-phenylacrylonitrile 12c

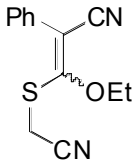
Yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 2:1, method B.
IR (CCl_4) ν_{max}/cm^{-1} 2256 (CN), 1686 (CO), 1601 (C=C).
^{1}H-NMR ($CDCl_3$) δ 0.88 (t, *J*= 7 Hz, 1 H, CH_3 isomer B), 1.25 (t, *J*= 7.2 Hz, 2 H, CH_3 isomer A), 4.12 (q, *J*= 7.2 Hz, 0.67 H, OCH_2 isomer B), 4.17 (q, *J*= 7.2 Hz, 1.33 H, OCH_2 isomer A), 4.20 (s, 0.67 H, SCH_2 isomer B), 4.38 (s, 1.33 H, SCH_2 isomer A), 7.30-8.00 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 13.2 (CH_3), 15.0 (CH_3), 28.5 (SCH_2), 29.7 (SCH_2), 69.4 (OCH_2), 70.9 (OCH_2), 100.0 (C=), 126.2, 128.1, 128.3, 128.4, 128.5, 128.57, 128.58, 128.6, 128.8, 128.9, 129.2 and 129.6 (CH Ar), 139.96 and 139.99 (C Ar), 196.5 (CO).
MS (CI) *m/z* 324 (MH^+), 341 (MNH_4^+).
HRMS calculated for $C_{19}H_{17}NO_2S$ 323.0980 found 323.0982.



3-Ethoxy-3-[2-oxo-2-(4-fluorophenyl)ethylsulfanyl]-2-phenylacrylonitrile 12d

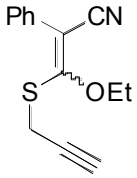
Yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 7:1, method B.
IR (CCl_4) ν_{max}/cm^{-1} 2256 (CN), 1683 (CO), 1600 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.26 (t, *J*= 7 Hz, 2.625 H, CH_3 isomer A), 1.38 (t, *J*= 7 Hz, 0.375 H, CH_3 isomer B), 3.95 (s, 0.25 H, SCH_2 isomer B), 4.12 (q, *J*= 7 Hz, 0.25 H, OCH_2 isomer B), 4.17 (q, *J*= 7 Hz, 1.75 H, OCH_2 isomer A), 4.33 (s, 1.75 H, SCH_2 isomer A), 7.20-8.05 (m, 5 H, ArH).

^{13}C-NMR ($CDCl_3$) δ 14.9 (CH_3), 15.0 (CH_3), 29.7 (SCH_2), 70.9 (OCH_2), 98.5 (C=), 116.1 (CN), 116.3 (CN), 128.3, 128.5, 128.6, 128.7, 129.2 and 129.6 (CH Ar), 131.1 (d, *J*= 9.6 Hz, CH Ar), 131.2 (d, *J*= 9.7 Hz, CH Ar), 143.9 (d, *J*= 70 Hz, C-F), 144.8 (d, *J*= 77 Hz, C-F), 204.8 (CO).
MS (CI) *m/z* 342 (MH^+), 359 (MNH_4^+).



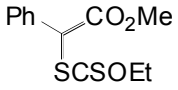
3-Cyanomethylsulfanyl-3-ethoxy-2-phenylacrylonitrile 12e

Dark yellow oil, petrol:EtOAc 9:1, 2 isomers A:B 9:1, method B.
IR (CCl_4) ν_{max}/cm^{-1} 2213 (CN), 1559 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.35 (t, *J*= 7 Hz, 3 H, CH_3), 3.48 (s, 0.2 H, SCH_2 isomer B), 3.70 (s, 1.8 H, SCH_2 isomer A), 4.12 (q, *J*= 7.2 Hz, 0.2 H, OCH_2 isomer B), 4.19 (q, *J*= 7.2 Hz, 1.8 H, OCH_2 isomer A), 7.20-7.70 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.8 (CH_3 isomer A), 14.9 (CH_3 isomer B), 16.3 (SCH_2 isomer B), 18.1 (SCH_2 isomer A), 70.3 (OCH_2 isomer A), 71.9 (OCH_2 isomer B), 99.8 (C= isomer B), 104.2 (C= isomer A), 115.4 (CN), 117.8 (CN), 128.3, 128.6, 128.9, 129.1 and 129.6 (CH Ar), 130.8 (C Ar), 161.3 (C=).
MS (CI) *m/z* 245 (MH^+), 262 (MNH_4^+).
HRMS calculated for $C_{13}H_{12}N_2OS$ 244.0670 found 244.0668.



3-Ethoxy-2-phenyl-3-(prop-2-ynylsulfanyl)acrylonitrile 12f

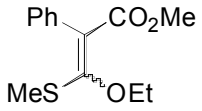
Yellow oil, petrol:EtOAc 95:5, 2 isomers A:B 13:1, method B.
IR (CCl_4) ν_{max}/cm^{-1} 3311 (C-H), 2213 (CN), 1554 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.32 (t, *J*= 7 Hz, 2.79 H, CH_3 isomer A), 1.49 (t, *J*= 7 Hz, 0.21 H, CH_3 isomer B), 2.35 (t, *J*= 2.6 Hz, 1 H, CH), 3.44 (d, *J*= 2.8 Hz, 0.14 H, SCH_2 isomer B), 3.66 (d, *J*= 2.8 Hz, 1.86 H, SCH_2 isomer A), 4.22 (q, *J*= 7.2 Hz, 2 H, OCH_2), 7.32 (d, *J*= 7.2 Hz, 1 H, ArH), 7.38 (t, *J*= 7.4 Hz, 2 H, ArH), 7.66 (t, *J*= 7.2 Hz, 2 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 13.2 (CH_3), 14.9 (SCH_2), 70.4 (OCH_2), 80.9 (CH), 92.5 (C alkyne), 117.7 (CN), 126.5, 128.5 and 128.9 (CH Ar), 136.7 (C Ar).



Methyl 2-(ethoxythiocarbonylsulfanyl)phenylacetate 13

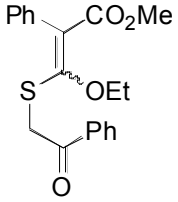
To a solution of methyl mandelate (3.32 g, 20.0 mmol) in CH_2Cl_2 (15 mL) cooled to 0 ºC was added carefully PCl_5 (5.0 g, 24.0 mmol) and stirred at room temperature for 2 h. After that time the reaction mixture was concentrated, the residue was redissolved in EtOH (80 mL) and cooled to 0 ºC. Potassium ethylxanthogenate (3.85 g, 24.0 mmol) was added, and the reaction mixture was stirred at room temperature for 4 h. Then, it was concentrated, the residue redissolved in Et_2O, and it was washed three times with H_2O. The organic phase was dried and evaporated, and the residue was purified by flash column chromatography (petrol:EtOAc 95:5), obtaining the desired xanthate as a yellow oil (3.10 g, 57%).
IR (CCl_4) ν_{max}/cm^{-1} 1746 (CO), 1226 (O-CS), 1054 (C=S).
^{1}H-NMR ($CDCl_3$) δ 1.40 (t, *J*=7 Hz, 3 H, CH_3 xanthate), 3.75 (s, 3 H, OCH_3), 4.58-4.68 (m, 2 H, OCH_2), 5.47 (s, 1 H, CH), 7.30-7.45 (m, 5 H, ArH).

^{13}C-NMR ($CDCl_3$) δ 13.5 (CH_3 xanthate), 53.0 (CH), 56.8 (OCH_3), 70.2 (OCH_2), 128.5 (CH Ar), 128.7 (CH Ar), 128.9 (CH Ar), 133.1 (C Ar), 169.7 (CO), 211.5 (CS).
MS (CI) *m/z* 271 (MH^+), 288 (MNH_4^+).
HRMS calculated for $C_{12}H_{14}O_3S_2$ 270.0385 found 270.0384.



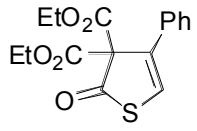
Methyl 3-ethoxy-3-methylsulfanyl-2-phenylacrylate 14a

Yellow oil, petrol:EtOAc 98:2, 2 isomers A:B 2:1, method B.
IR (CCl_4) ν_{max}/cm^{-1} 1726 and 1751 (CO), 1544 (C=C).
^{1}H-NMR ($CDCl_3$) δ 1.07 (t, *J*= 7 Hz, 2 H, CH_3 isomer A), 1.48 (t, *J*= 7 Hz, 1 H, CH_3 isomer B), 2.21 (s, 1 H, SCH_3 isomer B), 2.35 (s, 2 H, SCH_3 isomer A), 3.68 (q, *J*= 7.2 Hz, 1.33 H, OCH_2 isomer A), 3.74 (s, 1 H, OCH_3 isomer B), 3.76 (s, 2 H, OCH_3 isomer A), 4.21 (q, *J*= 7 Hz, 0.67 H, OCH_2 isomer B), 7.20-7.50 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 13.9 (SCH_3 isomer B), 14.0 (SCH_3 isomer A), 14.8 (CH_3 isomer A), 15.1 (CH_3 isomer B), 51.8 (OCH_3 isomer B), 51.9 (OCH_3 isomer A), 69.6 (OCH_2 isomer A), 69.8 (OCH_2 isomer B), 117.9 (C= isomer A), 118.8 (C= isomer B), 127.1, 127.7, 127.9, 128.2, 130.15 and 130.22 (CH Ar), 134.9 and 135.6 (C Ar), 164.2, 165.9, 167.0 and 168.4 (CO and C=).
HRMS calculated for $C_{13}H_{16}O_3S$ 252.0820 found 252.0824.



Methyl 3-ethoxy-3-(2-oxo-2-phenylethylsulfanyl)-2-phenylacrylate 14b

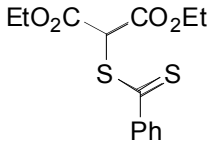
Yellow oil, petrol:EtOAc 85:15, 2 isomers A:B 2:1, method B.
^{1}H-NMR ($CDCl_3$) δ 0.90 (t, *J*= 7.2 Hz, 2 H, CH_3 isomer A), 1.34 (t, *J*= 7 Hz, 1 H, CH_3 isomer B), 3.58 (q, *J*= 7.2 Hz, 1.33 H, OCH_2 isomer A), 3.65 (s, 2 H, OCH_3 isomer A), 3.65 (s, 1 H, OCH_3 isomer B), 4.09 (s, 0.67 H, SCH_2 isomer B), 4.16 (q, *J*= 7.2 Hz, 0.67 H, OCH_2 isomer B), 4.23 (s, 1.33 H, SCH_2 isomer A), 7.15-7.35 (m, 1 H, ArH), 7.48 (t, *J*= 7.6 Hz, 1.33 H, ArH isomer A), 7.58 (t, *J*= 7.2 Hz, 0.66 H, ArH isomer B), 7.89 (t, *J*= 8 Hz, 0.66 H, ArH isomer B), 7.99 (t, *J*= 7.6 Hz, 1.33 H, ArH isomer A).
^{13}C-NMR ($CDCl_3$) δ 14.6 (CH_3 isomer A), 14.8 (CH_3 isomer B), 37.3 (SCH_2 isomer A), 37.5 (SCH_3 isomer B), 51.8 (OCH_3 isomer B), 51.9 (OCH_3 isomer A), 69.8 (OCH_2 isomer A), 70.0 (OCH_2 isomer B), 119.0 (C= isomer A), 120.6 (C= isomer B), 128.42, 128.44, 128.65, 128.68, 130.0 and 130.1 (CH Ar), 133.4 and 133.5 (C Ar), 160.9, 163.5, 165.9 and 168.2 (CO ester and C=), 193.5 and 193.9 (CO ketone).
MS (CI) *m/z* 357 (MH^+), 374 (MNH_4^+).



Diethyl 2-oxo-4-phenylthiophene-3,3-dicarboxylate 15

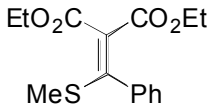
To a solution of ketene acetal **3c** (40 mg, 0.11 mmol) in CH_2Cl_2 (0.11 mL) was added triflic acid (48 μL, 0.55 mmol) and stirred at room temperature for 3 h and then heated at reflux temperature for another 3 h. After that time, the reaction mixture was diluted with CH_2Cl_2 and washed with aqueous saturated $NaHCO_3$ solution. The organic layer was dried and evaporated. The residue was purified by flash column chromatography (petrol:EtOAc 9:1) and the desired heterocycle was obtained as a yellow oil (18 mg, 51%).

IR (CCl_4) ν_{max}/cm^{-1} 1714 (CO), 1666 (CO).
^{1}H-NMR ($CDCl_3$) δ 1.36 (t, *J*= 7 Hz, 3 H, CH_3), 1.42 (t, *J*= 7.2 Hz, 3 H, CH_3), 4.33 (q, *J*= 7.2 Hz, 2 H, OCH_2), 4.39 (q, *J*= 7.2 Hz, 2 H, OCH_2), 6.71 (s, 1 H, =CH), 7.20-7.25 (m, 2 H, ArH), 7.28-7.45 (m, 2 H, ArH), 7.68 (d, *J*= 6.8 Hz, 1 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.4 (CH_3), 61.0 (OCH_2), 95.6 (C=), 100.0 (=CH), 124.9 (CH Ar), 127.4 (C=), 128.9 (CH Ar), 129.7 (CH Ar), 152.3 (CO), 178.9 (CO ester).
HRMS calculated for $C_{16}H_{16}O_5S$ 320.0718 found 320.0721.



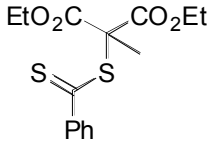
Diethyl 2-thiobenzoylsulfanylmalonate 16

The title compound was synthesised by reaction of freshly prepared phenylmagnesium bromide with CS_2 and diethyl bromomalonate in THF.
Red oil, petrol:EtOAc 98:2.
IR (CCl_4) ν_{max}/cm^{-1} 1743 (CO, CS).
^{1}H-NMR ($CDCl_3$) δ 1.37 (t, *J*= 7.2 Hz, 6 H, 2 CH_3), 4.35 (q, *J*= 7.2 Hz, 4 H, 2 OCH_2), 5.70 (s, 1 H, CHS), 7.46 (t, *J*= 8 Hz, 2 H, ArH), 7.62 (t, *J*= 7.2 Hz, 1 H, ArH), 8.08 (dd, *J*= 1.2, 8.4 Hz, 2 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.0 (CH_3), 57.8 (CHS), 63.0 (OCH_2), 127.1, 128.5 and 133.1 (CH Ar), 143.7 (C Ar), 166.1 (2 CO), 223.8 (C=S).
MS (CI) *m/z* 313 (MH^+), 330 (MNH_4^+).
HRMS calculated for $C_{14}H_{16}O_4S_2$ 312.0490 found 312.0492.



Diethyl 2-(1-methylsulfanyl-1-phenylmethylene)malonate 17

Yellow oil, petrol:EtOAc 9:1, method A.
IR (CCl_4) ν_{max}/cm^{-1} 1718 (CO), 1557 (C=C).
1H-NMR ($CDCl_3$) δ 0.94 (t, *J*= 7 Hz, 3 H, CH_3), 1.37 (t, *J*= 7.2 Hz, 3 H, CH_3), 1.85 (s, 3 H, SCH_3), 3.92 (q, *J*= 7.2 Hz, 2 H, OCH_2), 4.35 (q, *J*= 7.2 Hz, 2 H, OCH_2), 7.20-7.50 (m, 5 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 13.6 (CH_3), 14.2 (CH_3), 16.2 (SCH_3), 61.0 (OCH_2), 61.1 (OCH_2), 128.1, 128.4 and 128.8 (CH Ar), 135.5 (C Ar), 162.7, 164.0 and 165.3 (2 CO and C=).
MS (CI) *m/z* 295 (MH^+).
HRMS calculated for $C_{15}H_{18}O_4S$ 294.0926 found 294.0929.



Diethyl 2-methyl-2-thiobenzoylsulfanylmalonate 18

Red oil, petrol:EtOAc 95:5.
IR (CCl_4) ν_{max}/cm^{-1} 1734 (CO).
^{1}H-NMR ($CDCl_3$) δ 1.33 (t, *J*= 7.2 Hz, 6 H, 2 CH_3), 4.25-4.40 (m, 4 H, 2 OCH_2), 2.17 (s, 3 H, SCH_3), 7.43 (t, *J*= 6.8 Hz, 2 H, ArH), 7.59 (t, *J*= 7.4 Hz, 1 H, ArH), 8.00 (dd, *J*= 1.6, 8 Hz, 2 H, ArH).
^{13}C-NMR ($CDCl_3$) δ 14.0 (2 CH_3), 20.7 (SCH_3), 63.0 (2 OCH_2), 64.7 (C), 126.7, 128.4 and 132.7 (CH Ar), 144.8 (C Ar), 167.5 (2 CO), 224.8 (C=S).
MS (CI) *m/z* 327 (MH^+), 344 (MNH_4^+).
HRMS calculated for $C_{15}H_{18}O_4S_2$ 326.0647 found 326.0647.