

Supplementary Material

Typical experimental procedure:

Synthesis of 1a: To an ice-cooled solution of trifluoroacetic anhydride (13.3 ml; 90.1 mmol) in anhydrous acetonitrile (40 ml) is added dropwise a solution of sodium *O*-phenethyl xanthate (10g; 45.0 mmol) in anhydrous acetonitrile under an inert atmosphere. Once the addition is complete, the mixture is heated to reflux for 15 min., then three portions of lauroyl peroxide (907 mg; 4.5 mmol) are added at intervals of 1.5 hrs. The solvent is then evaporated under reduced pressure and the residue taken up in dichloromethane. The organic layer was washed with saturated sodium bicarbonate, dried and evaporated. Chromatography of the residue on silica (heptane) did not give a totally pure material, so further purification was accomplished by distillation in a Kugelrohr (80°C / 0.1 torr) to give the desired xanthate in 38% yield as a pale yellow oil.

General procedure for the radical additions to olefin: A solution of the xanthate (1mmol) and olefin (2-5 mmol) in 1,2-dichloroethane (ca 1 ml) is heated to reflux for 15 min, then lauroyl peroxide (2.5 mol%) are added every 1.5 hrs until almost complete consumption of the xanthate. The solvent is then removed under reduced pressure and the residue purified by chromatography on silica.

Dithiocarbonic acid-*O*-phenetyl ester *S*-trifluoromethyl ester 1a. ¹H NMR (200 MHz, CDCl₃) δ: 7.39-7.23 (m, 5H arom.), 4.88 (t, *J* = 7.0 Hz, 2H, OCH₂), 3.15 (t, *J* = 7.0 Hz, OCH₂CH₂). ¹³C NMR (50 MHz, CDCl₃) δ: 201.3 (C=S), 136.5 (Cq arom.), 129.0, 128.8, 127.1 (5 CH arom), 126.8 (q, *J* = 311.4 Hz, CF₃), 75.4 (OCH₂), 34.4 (OCH₂CH₂). IR (cm⁻¹) ν: 3031 ν(Csp³-H), 2955, 2924 ν(Csp²-H), 1606, 1497 ν(C=C), 1455 δa(Csp³-H, CH₂), 1382, 1271, 1237 ν(O-CS), 1164, 1119, 1030 ν(C=S), 951, 927, 905, 836. Anal. Calc. for C₁₀H₉F₃OS₂: C, 45.10, H, 3.41. Found: C, 45.33, H, 3.36. 38% yield (pale yellow oil).

Acetic acid 12.12.12-trifluoro-10-phenethyloxythiocarbonylsulfanyl-dodecyl ester 4a. ¹H NMR (300 MHz, CDCl₃) δ: 7.34-7.22 (m, 5H, *H* arom.), 4.81 (t, *J* = 7.0 Hz, 2H, OCH₂CH₂Ph), 4.05 (t, *J* = 6.8 Hz, 2H, CH₃COOCH₂), 3.93-3.84 (m, 1H, CHS), 3.11 (t, *J* = 7.0 Hz, OCH₂CH₂Ph), 2.67-2.32 (2m, 2H, CHHCF₃), 2.04 (s, 3H, CH₃), 1.82-1.27 (m, 16H, alkyl chain). ¹³C NMR (75 MHz, CDCl₃) δ: 212.7 (C=S), 171.3 (C=O), 137.1 (Cq arom.), 129.0, 128.8, 126.9 (3 CH arom.), 126.2 (q, *J*_{C-F} = 279.8 Hz, CF₃), 74.1 (OCH₂CH₂Ph), 64.7 (CH₃COOCH₂), 44.4 (CHS), 38.6 (q, *J*_{C-F} = 28.1 Hz, CH₂CF₃), 34.6, 32.9, 29.4, 29.3, 28.7, 26.6, 26.0 (7CH₂), 21.1 (CH₃). IR (cm⁻¹): 2929, 2857 ν(Csp³-H), 1737 ν(C=O), 1605, 1498, 1455 ν(C=C), 1433 δa (C-H), 1368 δs (C-H, CH₃CO), 1243 ν(O-C=S), 1178, 1141, 1062 ν(C=S), 908, 839, 750, 700. Anal. Calc. for C₂₃H₃₃F₃O₃S₂: C, 57.22, H, 6.95. Found: C, 57.91, H, 6.94. 82% yield (colorless oil).

Dithiocarbonic acid *O*-phenethyl ester *S*-(3.3.3-trifluoro-1-trimethylsilanyl) ester 4b. ¹H NMR (250 MHz, CDCl₃) δ: 7.18-7.03 (m, 5H, *H* arom.), 4.64 (t, *J* = 7.2 Hz, 1H, OCHH), 4.63 (t, *J* = 7.2 Hz, 1H, OCHH), 3.17 (dd, *J* = 4.4 Hz, *J* = 8.0 Hz, 1H, CHS), 2.95 (t, *J* = 7.1 Hz, 2H, OCH₂CH₂), 2.38-2.11 (m, 2H, CH₂CF₃), -0.52 (s, 9H, Si(CH₃)₃). ¹³C NMR (62.5 MHz, CDCl₃) δ: 214.0 (C=S), 137.2 (Cq arom.), 129.0, 128.7, 126.9 (3 CH arom.), 74.4 (OCH₂CH₂Ph), 126.7 (q, *J*_{C-F} = 277.2 Hz, CF₃), 35.2 (q, *J*_{C-F} = 28.5 Hz, CH₂CF₃), 34.6

(OCH₂CH₂Ph), 29.3 (CHS), -2.6 (3CH₃). IR (cm⁻¹) ν : 2956 ν (Csp³-H), 1605, 1498, 1455 ν (C=C), 1433, 1290, 1255 δ (Si-CH₃), 1231 ν (O-CS), 1179, 1140, 1060 ν (C=S), 916, 848, 750. Anal. Calc. for C₁₅H₂₁F₃OS₂ Si : C, 49.15, H, 5.77. Found: C, 49.03, H, 5.63. MS (CI, NH₃) m/z : 367 (M+H)⁺, 384 (M+NH₄)⁺. 44% yield (colorless oil).

Dithiocarbonic acid O-phenethyl ester S-(3.3.3-trifluoro-1-trimethylsilanyl-methyl-propyl) ester 4c. ¹H NMR (250 MHz, CDCl₃) δ : 7.27-7.14 (m, 5H, **H** arom.), 4.73 (t, J = 7.0 Hz, 2H, OCH₂CH₂Ph), 3.92-3.80 (m, 1H, CHS), 3.03 (t, J = 7.0 Hz, 2H, OCH₂CH₂Ph), 2.56 (dq, J = 4.7 Hz, J = 10.9 Hz, J = 15.2 Hz, 1H, CHHCF₃), 2.30 (dq, J = 8.2 Hz, J = 10.3 Hz, J = 15.2 Hz, 1H, CHHCF₃), 1.10 (dd, J = 5.4 Hz, J = 15.4 Hz, SiCHH), 0.93 (dd, J = 10.0 Hz, J = 15.4 Hz, SiCHH), -0.02 (s, 9H, Si(CH₃)₃). ¹³C NMR (75 MHz, CDCl₃) δ : 212.6 (C=S), 137.1 (Cq arom.), 129.0, 128.8, 127.0 (3CH arom.), 125.9 (q, J_{C-F} = 277.8 Hz, CF₃), 74.0 (OCH₂CH₂Ph), 41.7 (q, J_{C-F} = 27.0 Hz, CH₂CF₃), 41.5 (CHS), 34.6 (OCH₂CH₂Ph), 21.4 (CH₂SiMe₃), -0.8 (Si(CH₃)₃). IR (cm⁻¹) ν : 3066, 3031 ν (Csp²-H), 2954, 2856 ν (Csp³-H), 1606, 1498, 1455 ν (C=C), 1431 δ_a (C-H), 1371, 1329, 1251 δ (Si-CH₃), 1220 ν (O-CS), 1177, 1138, 1086, 1064 ν (C=S), 986, 839, 749. MS (CI, NH₃) m/z : 381 (M+H)⁺, 398 (M+NH₄)⁺. 61% yield (colorless oil).

4.4.4-trifluoro-2-phenethyloxythiocarbonylsulfanyl-butyl)-phosphonic acid diethyl ester 4d. ¹H NMR (300 MHz, CDCl₃) δ : 7.35-7.22 (m, 5H, **H** arom.), 4.81 (t, J = 7.1 Hz, 2H, OCH₂CH₂Ph), 4.23-4.06 (m, 5H, CHS + 2 OCH₂CH₃), 3.12 (t, J = 7.1 Hz, 2H, OCH₂CH₂Ph), 2.98-2.80 (m, 1H, CHHCF₃), 2.71-2.52 (m, 1H, CHHCF₃), 2.35 (ddd, J = 7.9 Hz, J = 15.7 Hz, J = 19.4 Hz, 1H, CHHP(O)(OEt)₂), 2.25 (ddd, J = 7.9 Hz, J = 15.7 Hz, J = 17.4 Hz, 1H, CHHP(O)(OEt)₂), 1.34, 1.33 (2t, J = 7.0 Hz, 6H, 2 OCH₂CH₃). ¹³C NMR (75 MHz, CDCl₃) δ : 211.5 (C=S), 136.9 (Cq arom.), 128.9, 128.7, 127.6 (3CH arom.), 125.7 (q, J_{C-F} = 275.9 Hz, CF₃), 74.3 (OCH₂Ph), 62.23, 62.15 (2 OCH₂CH₃), 38.8 (CHS), 37.4 (q, J = 24.2 Hz, CH₂CF₃), 34.6 (OCH₂CH₂Ph), 30.6 (q, J_{C-P} = 138.0 Hz, CH₂P), 16.5, 16.4 (2 OCH₂CH₃). IR (cm⁻¹) ν : 3030 ν (Csp²-H), 2984 ν (Csp³-H), 1605, 1498, 1455 ν (C=C), 1391 δ_s (Csp³-H), 1245 ν (O-CS), 1175, 1141, 1049 ν (C=S), 966, 860, 793, 700. Anal. Calc. for C₁₇H₂₄F₃O₄S₂ P: C, 45.94, H, 5.44. Found: C, 45.81, H, 5.47. MS (CI, NH₃) m/z : 445 (M+H)⁺, 462 (M+NH₄)⁺. 60% yield (colorless oil).

Dithiocarbonic acid S-[1-(dodecanoylamino-methyl)-3.3.3-trifluoro-propyl]-ester O-phenethyl ester 4e ¹H NMR (250 MHz, CDCl₃) δ : 7.37-7.23 (m, 5H, **H** arom.), 5.80 (bt, J = 6.1 Hz, 1H, NH), 4.85-4.76 (m, 2H, OCH₂CH₂Ph), 4.00 (quint., J = 6.5 Hz, 1H, CHS), 3.69-3.58 (m, 1H, NCHH), 3.50-3.39 (m, 1H, NCHH), 3.12 (t, J = 7.0 Hz, OCH₂CH₂Ph), 2.59-2.39 (m, 2H, CHHCF₃), 1.60 (t, J = 6.8 Hz, 2H, -COCH₂-), 1.62-1.57 (m, 2H, CH₂), 1.26 (bs, 16H, 8CH₂), 0.88 (t, J = 6.5 Hz, 3H, CH₃). ¹³C NMR (62.5 MHz, CDCl₃) δ : 211.6 (C=S), 173.7 (C=O), 137.0 (Cq arom.), 128.9, 128.8, 127.0 (3CH arom.), 125.7 (q, J_{C-F} = 275.8 Hz, CF₃), 74.4 (OCH₂), 44.5 (CHS), 41.9, 36.7 (2 CH₂), 36.1 (q, J_{C-F} = 28.6 Hz, CH₂CF₃), 34.5, 32.0, 29.7, 29.6, 29.4, 25.7, 22.7 (7 CH₂), 14.2 (CH₃). IR (cm⁻¹) ν : 3292 ν (N-H), 3067, 3031 ν (Csp²-H), 2926, 2855 ν (Csp³-H), 1651 ν (C=O), 1550 ν (N-CO), 1498 ν (C=C), 1456, 1381 δ_s (CH₃), 1263-1229 ν (O-CS), 1147, 1062 ν (C=S), 900, 834, 749. Anal. Calc. for C₂₅H₃₈F₃NO₂S₂ C, 59.38, H, 7.57. Found: C, 59.11, H, 7.42. 67% yield (colorless oil).

2-Acetylamino-2-(4.4.4-trifluoro-2-phenethyloxythiocarbonylsulfanyl-butyl)-malonic acid diethyl ester 4f. ¹H NMR (250 MHz, CDCl₃) δ : 7.36-7.23 (m, 5H, H arom.), 6.81 (bs, 1H, NH), 4.90-4.75 (m, 2H, OCH₂CH₂Ph), 4.29-4.10 (m, 4H, 2COOCH₂CH₃), 3.84-3.74 (m, 1H, CHS), 3.12 (t, J = 6.9 Hz, OCH₂CH₂Ph), 3.01 (dd, J = 2.4 Hz, J = 15.8 Hz, 1H, NH-

CHH), 2.73 (dd, $J = 11.1$ Hz, $J = 15.8$ Hz, 1H, NH-**CHH**), 2.61-2.34 (m, 2H, CF₃**CHH**), 1.99 (s, 3H, CO**CH**₃), 1.25, 1.24 (2t, $J = 7.1$ Hz, 6H, 2 COOCH₂**CH**₃). ¹³C NMR (62.5 MHz, CDCl₃) δ : 211.7 (C=S), 169.5 (CO**CH**₃), 167.7, 167.2 (2 CO₂Et), 136.9 (Cq. arom.), 128.9, 128.7, 126.9 (3 **CH** arom.), 125.5 (q, $J_{C-F} = 276.9$ Hz, CF₃), 74.4 (OCH₂CH₂Ph), 65.1 (Cq), 63.2, 62.9 (2 COOCH₂CH₃), 40.4 (q, $J_{C-F} = 27.6$ Hz, CH₂CF₃), 40.0 (**CHS**), 34.6, 34.5 (NH-CH₂ + OCH₂CH₂Ph), 22.9 (CO**CH**₃), 13.9, 13.8 (2 COOCH₂CH₃). IR (cm⁻¹) ν : 3401 ν (N-H), 3030, 2984, 1739, 1682 ν (C=O), 1605, 1583, 1496, 1445 ν (C=C), 1372 ν (C-O-C), 1223 ν (O-CS), 1140 ν (C-O-C), 1061 ν (C=S), 955, 860, 751, 701. MS (CI, NH₃) m/z : 524 (M+H)⁺, 541 (M+NH₄)⁺. 60% (80%) yield (pale yellow oil).

Acetic acid 4.4.4-trifluoro-2-phenethoxythiocarbonylsulfanyl-butyl ester 4g. ¹H NMR (300 MHz, CDCl₃) δ : 7.34-7.21 (m, 5H arom.), 4.81 (t, $J = 6.9$ Hz, 2H, OCH₂), 4.31 (dd, $J = 4.8$ Hz, $J = 11.7$ Hz, 1H, **CHHOCOCH**₃), 4.25 (dd, $J = 5.3$ Hz, $J = 11.7$ Hz, 1H, **CHHOCOCH**₃), 4.19-4.11 (m, 1H, **CHS**), 3.11 (t, $J = 6.9$ Hz, 2H, OCH₂**CH**₂), 2.65-2.46 (m, 2H, **CH**₂CF₃), 2.07 (s, 3H, **CH**₃). ¹³C NMR (75 MHz, CDCl₃) δ : 211.0 (C=S), 170.3 (C=O), 136.9 (Cq arom.), 128.9, 128.8, 127.0 (3 **CH** arom.), 125.6 (q, $J_{C-F} = 276.2$ Hz, CF₃), 74.5 (OCH₂CH₂Ph), 64.4 (CO-OCH₂), 42.7 (**CHS**), 35.2 (q, $J_{C-F} = 28.8$ Hz, CH₂CF₃), 34.5 (OCH₂CH₂Ph), 20.6 (**CH**₃). IR (cm⁻¹) ν : 3066, 3031 ν (Csp²-H), 2955 ν (Csp³-H), 1749 ν (C=O), 1605, 1498, 1455 ν (C=C), 1434 δ (C-H), 1384 δ s(C-H, CH₃), 1232 ν (O-CS), 1148, 1058 ν (C=S), 978, 834, 750, 700. Anal. Calc. for C₁₅H₁₇F₃O₃S₂: C, 49.17, H, 4.68. Found: C, 48.91, H, 4.84. 55% yield (pale yellow oil).

Dithiocarbonic acid S-(1-cyanomethyl-3.3.3-trifluoro-propyl) ester O-phenetyl ester 4h. ¹H NMR (250 MHz, CDCl₃) δ : 7.36-7.21 (m, 5H, **H** arom.), 4.81 (t, $J = 6.9$ Hz, 2H, OCH₂CH₂Ph), 4.07 (ddd, $J = 5.6$ Hz, $J = 7.6$ Hz, $J = 11.5$ Hz, 1H, **CHS**), 3.10 (t, $J = 6.9$ Hz, 2H, OCH₂**CH**₂Ph), 2.87 (dd, $J = 5.3$ Hz, $J = 17.4$ Hz, 1H, **CHHCN**), 2.79 (dd, $J = 5.3$ Hz, $J = 17.4$ Hz, 1H, **CHHCN**), 2.69-2.53 (m, 2H, **CH**₂CF₃). ¹³C NMR (62.5 MHz, CDCl₃) δ : 209.8 (C=S), 136.8 (Cq arom.), 128.9, 128.8, 127.0 (3 **CH** arom.), 125.1 (q, $J_{C-F} = 276.2$ Hz, CF₃), 116.1 (C $\equiv$ N), 74.8 (OCH₂CH₂Ph), 39.7 (**CHS**), 36.5 (q, $J_{C-F} = 29.3$ Hz, CH₂CF₃), 34.4 (OCH₂CH₂Ph), 23.0 (CH₂CN). IR (cm⁻¹) ν : 3065, 3030, 2954, 2251 ν (C $\equiv$ N), 1604, 1498, 1455 ν (C=C), 1433, 1384, 1336, 1317, 1250 ν (O-CS), 1148, 1111, 1058 ν (C=S), 992, 932, 751, 701. Anal. Calc. for C₁₄H₁₄F₃NOS₂: C, 50.44, H, 4.23. Found: C, 50.61, H, 4.34. 64% yield (colorless oil).

Dithiocarbonic acid S-(1-benzenesulfonyl-3.3.3-trifluoro-propyl)ester O-phenethyl ester 4i. ¹H NMR (300 MHz, CDCl₃) δ : 7.91 (d, $J = 5.9$ Hz, 2H, **CH** arom.), 7.63 (t, $J = 7.2$ Hz, 1H, **CH** arom.), 7.47 (t, $J = 7.9$ Hz, 2H, **CH** arom.), 7.38-7.23 (m, 3H, **CH** arom.), 7.18 (d, $J = 6.8$ Hz, 2H, **CH** arom.), 5.42 (dd, $J = 1.9$ Hz, $J = 11.1$ Hz, 1H, **CHS**), 4.67 (dt, $J = 6.7$ Hz, $J = 10.8$ Hz, 1H, OCH₂**HH-CH**₂), 4.46 (dt, $J = 7.1$ Hz, $J = 10.8$ Hz, 1H, OCH₂**HH-CH**₂), 3.27 (dq, $J = 2.1$ Hz, $J = 9.7$ Hz, $J = 15.5$ Hz, 1H, **CHHCF**₃), 2.98 (t, $J = 6.9$ Hz, 2H, OCH₂**CH**₂), 2.71-2.56 (m, 1H, **CHHCF**₃). ¹³C NMR (75 MHz, CDCl₃) δ : 207.1 (C=S), 136.8, 135.2 (2 Cq arom.), 134.7, 130.3, 129.2, 129.0, 128.9, 127.2 (10 **CH** arom.), 125.1 (q, $J_{C-F} = 276.3$ Hz, CF₃), 75.5 (OCH₂CH₂), 65.2 (**CHS**), 34.5 (OCH₂CH₂), 32.0 (q, $J_{C-F} = 30.9$ Hz, CH₂CF₃). IR (cm⁻¹) ν : 3065, 3031 ν (Csp²-H), 2955, 2927, 2856 ν (Csp³-H), 1604, 1585, 1498 ν (C=C), 1448, 1433 δ a (C-H), 1381, 1329, 1302, 1260 ν (O-CS) + ν (S=O), 1188, 1153 ν (S=O), 1107, 1084, 1050 ν (C=S), 1000, 985, 955, 923, 848, 749. 12%(17%) yield (colorless oil).

Dithiocarbonic acid O-phenethylester S-(3.3.3-trifluoro-1-[(4-fluoro-phenyl)-methanesulfonyl-amino]-methyl)-propyl) ester 4j. ¹H NMR (300 MHz, CDCl₃) δ : 7.55-

7.04 (m, 9H arom.), 4.72 (t, $J = 6.9$ Hz, 2H, OCH₂), 4.01-3.66 (m, 3H, NCH₂ + CHS), 3.04 (t, $J = 6.9$ Hz, 2H, OCH₂CH₂), 2.87 (s, 3H, SO₂CH₃), 2.82-2.70 (m, 1H, CF₃CHH), 2.59-2.32 (m, 1H, CF₃CHH). ¹³C NMR (75 MHz, CDCl₃) δ : 211.0 (C=S), 162.5 (d, $J_{C-F} = 248.0$ Hz, 2 CH arom.), 136.9, 133.9 (2 Cq arom.), 130.8 (d, $J_{C-F} = 8.6$ Hz, 2 CH arom.), 129.0, 128.8, 127.0 (3 CH arom.), 125.7 (q, $J_{C-F} = 276.1$ Hz, CF₃), 116.8 (d, $J_{C-F} = 22.6$ Hz, 2CH arom.), 74.4 (OCH₂), 53.1 (CH₂N), 42.2 (CHS), 37.3 (q, $J_{C-F} = 28.7$ Hz, CH₂CF₃), 34.4 (CH₂Ph). IR (cm⁻¹) ν : 2930 ν (Csp³-H), 1602, 1507 ν (C=C), 1455 δ_a (Csp²-H), 1387, 1346 ν (SO₂Me), 1236, 1153 ν (S=O), 1058 ν (C=S), 963, 871, 840, 812, 762, 701. Anal. Calc. for C₂₀H₂₁F₄NO₃S₃: C, 48.47, H, 4.27. Found: C, 47.94, H, 4.32. MS (CI, NH₃) m/z : 513 (MNH₄)⁺. 64% yield (colorless oil).

5-Fluoro-1-methanesulfonyl-3-(2,2,2-trifluoro-ethyl)-2,3-dihydro-1H-indole 10. ¹H NMR (300 MHz, CDCl₃) δ : 7.38 (dd, $J = 4.4$ Hz, $J = 8.7$ Hz, Cq-CH-CH-CF), 7.00-6.91 (m, 2H, CH arom.), 4.22 (dd, $J = 8.9$ Hz, $J = 9.9$ Hz, CHHN), 3.81-3.68 (m, 2H, CHHN + CHCH₂N), 2.89 (s, 3H, SO₂CH₃), 2.71-2.54 (m, 1H, CHHCF₃), 2.47-2.29 (m, 1H, CHHCF₃). ¹³C NMR (75 MHz, CDCl₃) δ : 159.8 (d, $J_{C-F} = 242.0$ Hz, CqF), 137.7 (Cq-CH-CHCF), 134.0 (d, $J_{C-F} = 7.6$ Hz, Cq-CH-CF), 126.0 (q, $J_{C-F} = 275.6$ Hz, CF₃), 115.8 (d, $J_{C-F} = 23.5$ Hz, CH-CF), 115.1 (d, $J_{C-F} = 8.2$ Hz, CH-CH-CF), 112.0 (d, $J_{C-F} = 24.4$ Hz, CH-CF), 56.4 (CH₂N), 38.2 (q, $J_{C-F} = 28.0$ Hz, CH₂-CF₃), 34.8 (SO₂CH₃ + CHCH₂N). IR (cm⁻¹) ν : 1610 ν (C=C), 1488 δ_a (Csp³-H), 1334 ν (SO₂Me), 1255, 1179, 1153, 1068, 1011, 970, 892, 870, 822, 782. HRMS. Calc. for C₁₁H₁₁F₄NO₂S: 297.0452. Found: 297.0447. MS (CI, NH₃) m/z : 298 (M+H)⁺, 315 (M+NH₄)⁺. 60% yield (colorless oil).