Supporting Information

A Direct Approach to α -Trifluoromethyl Amines.

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General Considerations

All reactions were carried out under an atmosphere of dry argon. Commercial reagents were used as received without further purification. All products were purified by flash column chromatography using silica gel SDS 60 C.C. 40-63. NMR spectra were recorded in CDCl₃ with TMS as an internal standard at ambient temperature on a Bruker AMX400 operating at 400 MHz for ¹H and 100 MHz for ¹³C. Infrared Absorption spectra were recorded as a solution in CCl₄ with a Perkin-Elmer 1600 Fourier Transform Spectrophotometer. Mass spectra were recorded with a HP 5989B mass spectrometer. Melting points were determined by Reichert microscope apparatus and were uncorrected.

Experimental Section

Synthesis of xanthate 6

Dithiocarbonic acid *S*-(1-acetylamino-2,2,2-trifluoro-ethyl) ester *O*-ethyl ester (6). To a solution of *N*-(1-chloro-2,2,2-trifluoro-ethyl)-acetamide* (208 mg, 1.18 mmol) in 5 ml of acetone was added portionwise ethylxanthic acid potassium salt (208 mg, 1.29 mmol). The resulting mixture was stirred at room temperature for 15 min and concentrated under reduced pressure. Ether was then added to the residue to precipitate the excess of ethylxanthic acid potassium salt which were removed by filtration. The organic filtered layer was concentrated and purified by flash column chromatography (silica gel, AcOEt-petroleum ether, 2:8) to give **6** (305 mg, 99%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.44 (t, *J*= 7.0 Hz, 3H), 2.09 (s, 3H), 4.69 (q, *J*= 7.0 Hz, 2H), 6.59 (qd, *J*= 7.6, 10.0 Hz, 1H), 6.89 (d, *J*= 10.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.7, 23.0, 57.8 (q, *J*= 38 Hz), 71.4, 123.5 (q, *J*= 280 Hz), 169.6, 206.9. IR(CCl₄) 3441, 2983, 1714, 1489, 1368, 1331, 1270, 1234, 1196, 1122, 1047. cm⁻¹.

MS (CI+NH₃) m/z 262 (MH⁺), 279 (MNH₄⁺). MP (Ethyl acetate-heptane) 84-86°C. Anal. calcd. for C₇H₁₀F₃NO₂S₂: C, 32.18; H, 3.86, found: C, 32.57; H, 3.91.

* *N*-(1-chloro-2,2,2-trifluoro-ethyl)-acetamide was synthesised according to procedure reported by Tanaka & coworkers (Tanaka, K.; Ishiguro, Y.; Mitsuhashi, K. *Bull. Chem. Soc. Jpn.* **1993**, 66, 661).

Typical procedure for the synthesis of radical adducts 8a-k

Acetic acid 3-acetylamino-1-ethoxythiocarbonylsulfanyl-4,4,4-trifluoro-butyl ester (8a).

A solution of Dithiocarbonic acid *S*-(1-acetylamino-2,2,2-trifluoro-ethyl) ester *O*-ethyl ester **6** (200 mg, 0.77 mmol) and vinyl acetate** (85 µl, 0.92 mmol) in 1.5 ml of 1,2-dichloroethane was refluxed for 15 min under argon. Lauroyl peroxide was then added portionwise (2 to 5 mol% / **6** per hour) to the refluxing solution. When **6** was totally consumed (after a global addition of 6 mg of lauroyl peroxide (0.015 mmol)), the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, AcOEt-petroleum ether, 2:8 to 3:7) to give radical adduct **8a** (4:6 mixture of inseparable diastereoisomers, 254 mg, 95%) as a pale yellow oil. *For the mixture of diastereoisomers*: ¹H NMR (400 MHz, CDCl₃) δ 1.38 (t, *J*= 7.6 Hz, 3H), 1.39 (t, *J*= 7.0 Hz, 3H), 2.03 (s, 6H), 2.06 (s, 3H), 2.07 (s, 3H), 2.12-2.22 (m, 2H), 2.38-2.51 (m, 2H), 4.60 (q, *J*= 7.0 Hz, 2H), 4.61 (q, *J*= 7.6 Hz, 2H), 4.70-4.83 (m, 2H), 6.53 (dd, *J*= 10.0, 2.9 Hz, 1H), 6.62 (d, *J*= 9.4 Hz, 1H), 6.64 (dd, *J*= 8.2, 4.7 Hz, 1H), 6.78 (d, *J*= 10.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 20.7, 20.8, 22.8, 23.0, 32.7, 33.3, 47.4 (q, *J*= 32 Hz), 47.6 (q, *J*= 32 Hz), 70.4, 70.7, 76.0, 78.3, 124.6 (q, *J*= 281 Hz), 124.7 (q, *J*= 281 Hz), 168.9, 169.7, 170.5, 170.7, 209.3, 209.9. IR(CCl₄) 3429, 2982, 1767, 1706, 1503, 1369, 1235, 1188, 1137, 1049 cm⁻¹. MS (CI+NH₃) m/z 288 (M-AcOH+H⁺), 348 (MH⁺), 365 (MNH₄⁺). Anal. calcd. for C₁₁H₁₆F₃NO₄S₂: C, 38.03; H, 4.64, found: C, 37.79; H, 4.51.

** A two fold excess of olefin was used in the case of olefins 7b-k.

Dithiocarbonic acid *S*-[1-(2-acetylamino-3,3,3-trifluoro-propyl)-4-oxo-pentyl] ester *O*-ethyl ester (8b). Pale yellow oil (88%, 1:1 mixture of diastereoisomers). Silica gel, AcOEt-Petroleum ether, 1:1. *For the mixture of diastereoisomers*: ¹H NMR (400 MHz, CDCl₃)

δ 1.37 (t, J = 7.0 Hz, 3H), 1.39 (t, J = 7.0 Hz, 3H), 1.67-1.86 (m, 2H), 1.90-2.16 (m, 6H), 1.98 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.51-2.70 (m, 4H), 3.64 (m, 1H), 3.87 (m, 1H), 4.58 (q, J = 7.0 Hz, 2H), 4.61 (q, J = 7.0 Hz, 2H), 4.75 (m, 1H), 4.81 (m, 1H), 6.35 (d, J = 9.4 Hz, 1H), 6.57 (d, J = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 23.1, 25.6, 29.2, 30.0, 30.1, 32.7, 34.2, 40.2, 40.6, 46.5, 47.1, 48.3 (q, J = 32 Hz), 48.6 (q, J = 30 Hz), 70.5, 70.6, 124.9 (q, J = 281 Hz), 125.1 (q, J = 281 Hz), 170.4, 170.8, 207.3, 208.1, 213.7, 214.1. IR(CCl_4) 3442, 2983, 1714, 1703, 1504, 1443, 1369, 1238, 1185, 1133, 1112, 1050. cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 360 (MH^+), 377 (MNH_4^+). Anal. calcd. for $\text{C}_{13}\text{H}_{20}\text{F}_3\text{NO}_3\text{S}_2$: C, 43.44; H, 5.61, found: C, 43.65; H, 5.77.

Acetic acid 4-acetylamino-2-ethoxythiocarbonylsulfanyl-5,5,5-trifluoro-pentyl ester (8c).

Pale yellow oil (84%, 1:1 mixture of diastereoisomers). Silica gel, AcOEt-Petroleum ether, 3:7. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.38 (t, J = 7.0 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H), 1.89-2.15 (m, 2H), 1.99 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.20-2.27 (m, 2H), 3.92-3.98 (m, 1H), 4.09-4.15 (m, 1H), 4.24-4.41 (m, 4H), 4.60 (q, J = 7.0 Hz, 2H), 4.62 (q, J = 7.0 Hz, 2H), 4.72-4.91 (m, 2H), 6.50 (d, J = 9.4 Hz, 1H), 6.64 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 20.7, 20.8, 23.0, 29.0, 30.1, 45.6, 46.0, 48.4 (q, J = 30 Hz), 48.5 (q, J = 30 Hz), 64.0, 65.9, 70.7, 70.8, 124.7 (q, J = 281 Hz), 125.0 (q, J = 281 Hz), 170.5, 170.6, 170.7, 170.9, 212.4, 212.9. IR(CCl_4) 3442, 2984, 1752, 1703, 1506, 1442, 1381, 1367, 1340, 1227, 1186, 1137, 1112, 1052. cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 302 ($\text{M}-\text{HOAc}+\text{H}^+$), 362 (MH^+), 379 (MNH_4^+). Anal. calcd. for $\text{C}_{12}\text{H}_{18}\text{F}_3\text{NO}_4\text{S}_2$: C, 39.88; H, 5.02, found: C, 40.08; H, 5.07.

Dithiocarbonic acid *S*-(3-acetylamino-4,4,4-trifluoro-1-trimethylsilanylmethyl-butyl) ester *O*-ethyl ester (8d).

Crystals (95%, 4:6 mixture of separable diastereoisomers). Silica gel, AcOEt-Petroleum ether, 1:9 to 2:8. *Major diastereoisomer:* ^1H NMR (400 MHz, CDCl_3) δ 0.03 (s, 9H), 0.85-1.16 (m, 2H), 1.42 (t, J = 7.0 Hz, 3H), 1.93-2.16 (m, 2H), 2.11 (s, 3H), 3.64 (m, 1H), 4.63 (q, J = 7.0 Hz, 2H), 4.71 (m, 1H), 6.00 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ -0.8, 13.9, 19.5, 23.1, 37.4, 43.8, 48.4 (q, J = 32 Hz), 70.3, 125.0 (q, J = 281 Hz), 170.3, 215.1. IR(CCl_4) 3432, 2956, 1701, 1507, 1250, 1218, 1184, 1130, 1112, 1051 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 254 ($\text{M}-\text{HSCSOEt}+\text{H}^+$), 376 (MH^+), 393 (MNH_4^+). Anal. calcd. for $\text{C}_{13}\text{H}_{24}\text{F}_3\text{NO}_2\text{S}_2\text{Si}$: C, 41.58; H, 6.44, found: C, 41.48; H, 6.41. *Minor diastereoisomer:* ^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H), 1.04-1.19 (m, 2H), 1.40 (t, J = 7.0 Hz, 3H), 1.94-2.21

(m, 2H), 2.03 (s, 3H), 4.02 (m, 1H), 4.63 (q, $J = 7.0$ Hz, 2H), 4.84 (m, 1H), 6.03 (d, $J = 10.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ -0.7, 13.9, 23.28, 23.3, 35.1, 45.0, 48.5 (q, $J = 28$ Hz), 70.1, 125.1 (q, $J = 281$ Hz), 170.1, 213.5. IR(CCl_4) 3441, 2955, 1704, 1441, 1367, 1251, 1217, 1183, 1129, 1112, 1048 cm^{-1} . MS ($\text{CI} + \text{NH}_3$) m/z 254 ($\text{M} - \text{HSCSOEt} + \text{H}^+$), 376 (MH^+), 393 (MNH_4^+). Anal. calcd. for $\text{C}_{13}\text{H}_{24}\text{F}_3\text{NO}_2\text{S}_2\text{Si}$: C, 41.58; H, 6.44, found: C, 41.49; H, 6.45.

Dithiocarbonic acid S-(3-acetylamino-1-cyanomethyl-4,4,4-trifluoro-butyl) ester O-ethyl ester (8e). Pale yellow oil (87%, 4:6 mixture of inseparable diastereoisomers). Silica gel, AcOEt-Petroleum ether, 3:7. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.39 (t, $J = 7.0$ Hz, 3H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.99 (s, 3H), 2.06 (s, 3H), 2.02-2.31 (m, 4H), 2.82-3.02 (m, 4H), 3.92 (m, 1H), 4.01 (m, 1H), 4.61 (q, $J = 7.0$ Hz, 2H), 4.63 (q, $J = 7.0$ Hz, 2H), 4.73 (m, 1H), 4.82 (m, 1H), 6.90 (d, $J = 10.0$ Hz, 1H), 7.01 (d, $J = 9.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 22.3, 22.8, 24.2, 30.4, 31.4, 42.5, 43.1, 48.2 (q, $J = 30$ Hz), 48.3 (q, $J = 30$ Hz), 71.0, 71.1, 116.5, 116.9, 124.5 (q, $J = 281$ Hz), 124.7 (q, $J = 281$ Hz), 170.9, 171.2, 211.2, 211.3. IR(CCl_4) 3438, 2984, 1701, 1505, 1442, 1369, 1237, 1191, 1139, 1112, 1049 cm^{-1} . MS ($\text{CI} + \text{NH}_3$) m/z 329 (MH^+), 346 (MNH_4^+). Anal. calcd. for $\text{C}_{11}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_2\text{S}_2$: C, 40.23; H, 4.60, found: C, 40.39; H, 4.53.

Dithiocarbonic acid S-(3-acetylamino-1-diethoxymethyl-4,4,4-trifluoro-butyl) ester O-ethyl ester (8f). Pale yellow oil (95%, 1:1 mixture of inseparable diastereoisomers). Silica gel, AcOEt-Petroleum ether, 3:7. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.16 (t, $J = 7.0$ Hz, 3H), 1.17 (t, $J = 7.0$ Hz, 3H), 1.20 (t, $J = 7.0$ Hz, 3H), 1.21 (t, $J = 7.0$ Hz, 3H), 1.38 (t, $J = 7.0$ Hz, 6H), 1.80-2.19 (m, 3H), 1.98 (s, 3H), 2.05 (s, 3H), 2.49 (m, 1H), 3.43-3.76 (m, 8H), 3.95-4.05 (m, 2H), 4.52 (d, $J = 3.0$ Hz, 1H), 4.59 (d, $J = 3.0$ Hz, 1H), 4.61 (q, $J = 7.0$ Hz, 4H), 4.73-4.91 (m, 2H), 6.19 (d, $J = 9.4$ Hz, 1H), 6.31 (d, $J = 9.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 15.1, 15.1, 15.3, 23.0, 23.1, 25.8, 28.5, 48.4 (q, $J = 30$ Hz), 49.1 (q, $J = 30$ Hz), 49.9, 50.4, 64.1, 64.3, 64.8, 65.5, 70.5, 70.6, 102.7, 103.9, 124.9 (q, $J = 281$ Hz), 125.2 (q, $J = 283$ Hz), 170.1, 171.3, 213.9, 214.8. IR(CCl_4) 3443, 2979, 2930, 2875, 1741, 1703, 1508, 1443, 1370, 1341, 1284, 1218, 1185, 1135, 1112, 1054 cm^{-1} . MS ($\text{CI} + \text{NH}_3$) m/z 346 ($\text{M} - \text{EtOH} + \text{H}^+$).

(4-Acetylamino-2-ethoxythiocarbonylsulfanyl-5,5,5-trifluoro-pentyl)-phosphonic acid diethyl ester (8g). Pale yellow oil (86%, 4:6 mixture of inseparable diastereoisomers). Silica

gel, Dichloromethane-Methanol, 99:1. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.29 (t, J = 7.6 Hz, 6H), 1.30 (t, J = 7.0 Hz, 6H), 1.25 (t, J = 7.0 Hz, 3H), 1.36 (t, J = 7.0 Hz, 3H), 1.99 (s, 3H), 2.02 (s, 3H), 2.06-2.45 (m, 8H), 3.92-4.16 (m, 10 H), 4.53-4.61 (m, 4H), 4.65-4.79 (m, 2H), 7.05 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.7 (m), 16.3 (m), 22.9, 29.0 (d, J = 138 Hz), 31.3, 31.4, 31.7 (d, J = 135 Hz), 41.5, 42.1, 48.4 (q, J = 30 Hz), 48.7 (q, J = 30 Hz), 62.2 (m), 70.3, 124.8 (q, J = 281 Hz), 170.5, 170.7, 212.2, 212.9. IR(CCl_4) 3309, 2983, 1699, 1532, 1442, 1390, 1368, 1291, 1227, 1186, 1135, 1112, 1048, 1028 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 318 ($\text{M}-\text{HSCSOEt}+\text{H}^+$), 440 (MH^+), 457 (MNH_4^+). Anal. calcd. for $\text{C}_{14}\text{H}_{25}\text{F}_3\text{NO}_5\text{PS}_2$: C, 38.26; H, 5.73, found: C, 38.01; H, 5.81.

Dithiocarbonic acid *S*-[5-(1-acetylamino-2,2,2-trifluoro-ethyl)-2-oxo-[1,3]dioxolan-4-yl] ester *O*-ethyl ester (8h). Crystals (72%, 1:1 mixture of separable diastereoisomers). Silica gel, Ether-Petroleum ether, 4:6 to 6:4. *Less polar diastereoisomer:* ^1H NMR (400 MHz, CDCl_3) δ 1.46 (t, J = 7.0 Hz, 3H), 2.16 (s, 3H), 4.69 (q, J = 7.0 Hz, 2H), 5.12 (d, J = 5.3 Hz, 1H), 5.17 (qd, J = 7.6, 10.0 Hz, 1H), 6.04 (d, J = 5.3 Hz, 1H), 7.38 (d, J = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 22.6, 51.2 (q, J = 29 Hz), 71.5, 77.7, 83.5, 123.2 (q, J = 283 Hz), 152.9, 171.9, 205.7. IR(CCl_4) 3432, 3343, 2959, 1842, 1816, 1741, 1709, 1500, 1371, 1273, 1236, 1192, 1141, 1047 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 348 (MH^+), 365 (MNH_4^+). Anal. calcd. for $\text{C}_{10}\text{H}_{12}\text{F}_3\text{NO}_5\text{S}_2$: C, 34.58; H, 3.48, found: C, 34.28; H, 3.47. *More polar diastereoisomer:* ^1H NMR (400 MHz, CDCl_3) δ 1.48 (t, J = 7.0 Hz, 3H), 2.13 (s, 3H), 4.72 (q, J = 7.0 Hz, 2H), 4.85 (dd, J = 5.3, 5.3 Hz, 1H), 5.19 (qdd, J = 7.6, 5.3, 10.0 Hz, 1H), 6.06 (d, J = 10.0 Hz, 1H), 6.35 (d, J = 5.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 22.4, 52.9 (q, J = 30 Hz), 72.7, 77.3, 85.6, 125.0 (q, J = 283 Hz), 153.7, 173.7, 208.7. IR(CCl_4) 3258, 3064, 2985, 1818, 1686, 1549, 1442, 1360, 1298, 1255, 1135, 1076, 1047 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 348 (MH^+), 365 (MNH_4^+). Anal. calcd. for $\text{C}_{10}\text{H}_{12}\text{F}_3\text{NO}_5\text{S}_2$: C, 34.58; H, 3.48, found: C, 34.81; H, 3.44.

Dithiocarbonic acid *S*-[3-acetylamino-4,4,4-trifluoro-1-(2-oxo-pyrrolidin-1yl)-butyl] ester *O*-ethyl ester (8i). Pale yellow oil (62%, 4:6 mixture of inseparable diastereoisomers). Silica gel, Dichloromethane-Methanol, 98:2. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.41 (t, J = 7.0 Hz, 3H), 1.42 (t, J = 7.0 Hz, 3H), 2.02-2.26 (m, 7H), 2.07 (s, 3H), 2.09 (s, 3H), 2.35-2.42 (m, 4H), 2.60-2.67 (m, 1H), 3.41-3.57 (m, 4H), 4.50-4.62 (m, 1H), 4.64 (q, J = 7.0 Hz, 2H), 4.65 (q, J = 7.0 Hz, 2H), 4.74-4.86 (m, 1H), 5.90 (dd, J = 12.3,

4.1 Hz, 1H), 6.02 (dd, J = 8.2, 7.6 Hz, 1H), 6.69 (d, J = 10.0 Hz, 1H), 7.29 (d, J = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 13.8, 18.0, 18.1, 22.9, 23.0, 30.7, 30.8, 31.1, 31.2, 44.9, 45.2, 47.5 (q, J = 30 Hz), 48.1 (q, J = 32 Hz), 58.3, 59.0, 70.6, 70.7, 124.7 (q, J = 281 Hz), 124.8 (q, J = 282 Hz), 170.5, 170.9, 175.5, 175.6, 210.1, 211.8. IR(CCl_4) 3439, 3298, 2984, 1703, 1501, 1416, 1368, 1286, 1265, 1226, 1183, 1132, 1111, 1049 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 251 ($\text{M}-\text{HSCSOEt}+\text{H}^+$), 268 ($\text{M}-\text{HSCSOEt}+\text{NH}_4^+$), 373 (MH^+), 390 (MNH_4^+).

Dithiocarbonic acid *S*-[3-acetylamino-1-(1,3-dioxo-1,3-dihydro-isoindol-2-ylmethyl)-4,4,4-trifluoro-butyl] ester *O*-ethyl ester (8j). Crystals (77%, 4:6 mixture of inseparable diastereoisomers). Silica gel, AcOEt-Petroleum ether, 4:6. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.33 (t, J = 7.0 Hz, 3H), 1.37 (t, J = 7.0 Hz, 3H), 2.02-2.24 (m, 4H), 2.02 (s, 3H), 2.19 (s, 3H), 3.93-4.06 (m, 4H), 4.16-4.23 (m, 1H), 4.23-4.30 (m, 1H), 4.51 (q, J = 7.0 Hz, 2H), 4.57 (q, J = 7.0 Hz, 2H), 4.90-5.11 (m, 2H), 6.44 (d, J = 10.0 Hz, 1H), 6.53 (d, J = 10.0 Hz, 1H), 7.70-7.73 (m, 4H), 7.79-7.84 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.6, 13.7, 23.1, 23.2, 24.0, 30.4, 39.0, 41.6, 45.9, 46.3, 48.2 (q, J = 31 Hz), 48.6 (q, J = 31 Hz), 70.7, 70.7, 123.5, 123.6, 124.8 (q, J = 279 Hz), 125.0 (q, J = 280 Hz), 131.7, 131.7, 134.4, 168.2, 168.2, 170.3, 170.7, 211.9, 212.7. IR(CCl_4) 3441, 2983, 1776, 1722, 1504, 1468, 1441, 1392, 1366, 1227, 1187, 1134, 1112, 1050 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 449 (MH^+), 366 (MNH_4^+). Anal. calcd. for $\text{C}_{18}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_4\text{S}_2$: C, 48.21; H, 4.27, found: C, 48.61; H, 4.42.

Dithiocarbonic acid *S*-[3-acetylamino-1-[(4-bromo-phenyl)-methanesulfonyl-amino]-methyl]-4,4,4-trifluoro-butyl) ester *O*-ethyl ester (8k). Foam (77%, 1:1 mixture of inseparable diastereoisomers). Silica gel, AcOEt-Petroleum ether, 4:6. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 1.29 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H), 1.86 (s, 3H), 1.90-2.04 (m, 2H), 1.94 (s, 3H), 2.19-2.30 (m, 2H), 2.83 (s, 6H), 3.56-3.70 (m, 2H), 3.81-3.96 (m, 4H), 4.44-4.57 (m, 4H), 4.70-4.83 (m, 2H), 6.50 (d, J = 9.4 Hz, 1H), 6.67 (d, J = 9.4 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.5, 13.6, 22.6, 22.7, 28.2, 29.5, 36.7, 37.0, 44.8, 45.7, 48.0 (q, J = 32 Hz), 51.4, 53.4, 70.6, 122.6, 124.6 (q, J = 281 Hz), 124.8 (q, J = 281 Hz), 130.3, 130.4, 132.7, 137.1, 137.3, 170.4, 170.7, 211.5, 212.5. IR(CCl_4) 3437, 2984, 1700, 1488, 1442, 1358, 1227, 1187, 1162, 1140, 1112, 1050, 1012 cm^{-1} . MS

(CI+NH₃) m/z 552 (MH⁺), 569 (MNH₄⁺). Anal. calcd. for C₁₇H₂₂BrF₃N₂O₄S₃: C, 37.03; H, 4.02, found: C, 37.06; H, 4.11.

Ionic Transformations of radical adducts 8a & 8i

N-(3,3-Dimethoxy-1-trifluoromethyl-propyl)-acetamide (9). To a solution of **8a** (200 mg, 0.57 mmol) in 10 ml of methanol was added 10-camphorsulfonic acid (7 mg, 0.02 mmol). The reaction was refluxed for 24h. The crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, AcOEt-Petroleum ether, 7:3) to give **9** (95 mg, 72%) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.90 (ddd, *J*= 14.4, 10.0, 4.0 Hz, 1H), 2.04 (ddd, *J*= 14.4, 7.6, 3.3 Hz, 1H), 2.02 (s, 3H), 3.31 (s, 3H), 3.33 (s, 3H), 4.43 (dd, *J*= 7.6, 4.0 Hz, 1H), 4.66-4.78 (m, 1H), 6.66 (d, *J*= 9.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 23.0, 31.7, 47.5 (q, *J*= 31 Hz), 53.3, 53.9, 101.5, 125.1 (q, *J*= 281 Hz), 170.5. IR(CCl₄) 3444, 2936, 2833, 1704, 1505, 1434, 1371, 1285, 1248, 1188, 1138, 1065 cm⁻¹. MS (CI+NH₃) m/z 198 (M-MeOH+H⁺), 230 (MH⁺). MP (Ethyl acetate-heptane) 56-58°C. Anal. calcd. for C₈H₁₄F₃NO₃: C, 41.92; H, 6.16, found: C, 41.84; H, 6.09.

N-[3-(2-Oxo-pyrrolidin-1-yl)-1-trifluoromethyl-allyl] acetamide (10). A solution of **8i** (170 mg, 0.45 mmol) in 5 ml of 1,2-dichlorobenzene was refluxed for 2h under argon. The crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, Dichloromethane-Methanol, 98:2) to give **10** (111 mg, 100%) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 2.03 (s, 3H), 2.06-2.14 (m, 2H), 2.46 (dd, *J*= 7.3, 7.3 Hz, 2H), 3.49 (dd, *J*= 7.3, 7.3 Hz, 2H), 4.87 (dd, *J*= 14.7, 6.4 Hz, 1H), 5.22 (qdd, *J*= 9.4, 7.6, 6.4 Hz, 1H), 7.20 (d, *J*= 14.7 Hz, 1H), 7.43 (d, *J*= 9.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 17.3, 22.8, 31.0, 45.1, 50.6 (q, *J*= 30 Hz), 101.5, 124.5 (q, *J*= 281 Hz), 128.6, 170.3, 173.8. IR(CCl₄) 3444, 2980, 1708, 1667, 1558, 1497, 1400, 1262, 1235, 1186, 1131 cm⁻¹. MS (CI+NH₃) m/z 251 (MH⁺), 268 (MNH₄⁺). Anal. calcd. for C₁₀H₁₃F₃N₂O₂: C, 48.00; H, 5.24, found: C, 47.62; H, 5.31.

Radical Transformations of radical adducts 8h, 8j & 8k

Dithiocarbonic acid S-{2-[5-(1-acetylamino-2,2,2-trifluoro-ethyl)-2-oxo-[1,3]dioxolan-4-yl]-1-trimethylsilanylmethyl-ethyl} ester O-ethyl ester (11). A solution of the major diastereoisomer of **8h** (130 mg, 0.37 mmol) and allyltrimethylsilane (178 μ l, 1.12 mmol) in 1 ml of 1,2-dichloroethane was refluxed for 15 min under argon. Lauroyl peroxide was then added portionwise (2 to 5 mol% / **8h** per hour) to the refluxing solution. When **8h** was totally consumed (after a global addition of 8 mg of lauroyl peroxide (0.018 mmol)), the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, Ether-petroleum ether, 3:7) to give radical adduct **11** (1:1 mixture of inseparable diastereoisomers, 123 mg, 72%) as a pale yellow oil. *For the mixture of diastereoisomers:* ^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H), 0.08 (s, 9H), 0.96-1.15 (m, 4H), 1.41 (t, J = 7.0 Hz, 3H), 1.42 (t, J = 7.0 Hz, 3H), 2.12 (s, 6H), 2.14-2.35 (m, 4H), 3.83-3.90 (m, 1H), 3.90-3.97 (m, 1H), 4.54-4.62 (m, 2H), 4.63 (q, J = 7.0 Hz, 2H), 4.64 (q, J = 7.0 Hz, 2H), 4.75 (d, 1H, J = 5.8 Hz, 1H), 4.84 (d, J = 6.6 Hz, 1H), 4.93-5.04 (m, 2H), 7.45 (d, J = 10.5 Hz, 1H), 7.47 (d, J = 10.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ -0.8 to -0.6 (m), 13.8, 21.0, 22.6, 22.9, 41.3, 42.1, 43.7, 44.3, 50.7 (q, J = 32 Hz), 70.2, 70.3, 76.7, 77.2, 77.8, 78.0, 123.4 (q, J = 283 Hz), 154.0, 154.1, 171.7, 171.8, 213.1, 213.2. IR(CCl_4) 3435, 3328, 2954, 1807, 1697, 1502, 1371, 1301, 1277, 1251, 1221, 1189, 1142, 1111, 1050 cm^{-1} . MS ($\text{CI}+\text{NH}_3$) m/z 340 ($\text{M}-\text{HSCSOEt}+\text{H}^+$), 463 (MH^+), 480 (MNH_4^+).

N-[1-(5-Bromo-1-methanesulfonyl-2,3-dihydro-1H-indol-3-ylmethyl)-2,2,2-trifluoro-ethyl]-acétamide (12). A solution of **8k** (396 mg, 0.72 mmol) in 4 ml of 1,2-dichloroethane was refluxed for 15 min under argon. Lauroyl peroxide was then added portionwise (10 mol% / **8k** per hour) to the refluxing solution. When **8k** was totally consumed (after a global addition of 315 mg of lauroyl peroxide (0.79 mmol)), the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, AcOEt-petroleum ether, 1:1) to give cyclised product **12** (6:4 mixture of inseparable diastereoisomers, 278 mg, 90%) as crystals. *Major diastereoisomer:* ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 1.92-2.10 (m, 1H), 1.97 (s, 3H), 2.18-2.24 (m, 1H), 3.01 (s, 3H), 3.52-3.63 (m, 1H), 3.83 (d, J = 10.3, 5.4 Hz, 1H), 4.15 (dd, J = 10.3, 10.0 Hz, 1H), 4.80-4.95 (m, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.41 (d, J = 8.6 Hz, 1H), 7.66 (s, 1H), 7.76 (d, J = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 22.8, 33.2, 34.8, 37.4, 49.3 (q, J = 30 Hz), 57.1, 115.8, 116.3, 126.4 (q, J = 281 Hz), 129.5, 132.1, 137.3, 142.5, 170.7. *Minor diastereoisomer:* ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 1.96-2.07 (m, 1H), 2.03 (s, 3H), 2.20-2.27 (m, 1H), 3.02 (s,

3H), 3.57-3.66 (m, 1H), 3.82 (dd, J = 10.0, 7.5 Hz, 1H), 4.11 (dd, J = 10.0, 9.5 Hz, 1H), 4.74-4.87 (m, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.40 (d, J = 8.5 Hz, 1H), 7.41 (s, 1H), 7.67 (d, J = 9.3 Hz, 1H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 22.8, 32.9, 34.7, 36.7, 49.0 (q, J = 30 Hz), 56.4, 115.9, 116.2, 126.5 (q, J = 281 Hz), 128.5, 132.0, 137.8, 142.8, 170.9. *For the mixture of diastereoisomers*: IR(nujol) 3285, 1759, 1549, 1352, 1307, 1269, 1214, 1161, 1128, 1112 cm^{-1} . MS (CI+ NH_3) m/z 430 (MH^+), 447 (MNH_4^+). Anal. calcd. for $\text{C}_{14}\text{H}_{16}\text{BrF}_3\text{N}_2\text{O}_3\text{S}$: C, 39.17; H, 3.76, found: C, 38.73; H, 3.69.

***N*-[4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-1-trifluoromethyl-butyl] acetamide (13).** A solution of **8j** (250 mg, 0.56 mmol) in 4 ml of propan-2-ol was refluxed for 15 min under argon. Lauroyl peroxide was then added portionwise (10 mol% / **8j** per hour) to the refluxing solution. When **8k** was totally consumed (after a global addition of 245 mg of lauroyl peroxide (0.62 mmol)), the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by flash column chromatography (silica gel, AcOEt-petroleum ether, 4:6) to give reduced product **13** (144 mg, 78%) as crystals. ^1H NMR (400 MHz, CDCl_3) δ 1.48-1.60 (m, 1H), 1.74-1.89 (m, 3H), 2.05 (s, 3H), 3.69 (t, J = 6.8 Hz, 2H), 4.59-4.72 (m, 1H), 6.40 (d, J = 9.3 Hz, 1H), 7.69-7.71 (m, 2H), 7.79-7.81 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 23.0, 24.7, 25.1, 37.2, 50.2 (q, J = 30 Hz), 123.3, 125.0 (q, J = 281 Hz), 131.9, 134.2, 168.5, 170.5. IR(CCl_4) 3445, 2932, 1774, 1717, 1505, 1438, 1396, 1369, 1244, 1187, 1136 cm^{-1} . MS (CI+ NH_3) m/z 329 (MH^+), 345 (MNH_4^+). MP (Ethyl acetate-heptane) 179-180°C. Anal. calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_3$: C, 54.88; H, 4.61, found: C, 54.84; H, 4.58.

Dimerisation of xanthate 6

***N*-(2-acetylamino-3,3,3-trifluoro-1-trifluoromethyl-propyl)-acetamide (14).** A solution of **6** (522 mg, 2 mmol) in 16 ml of 1,2-dichlorobenzene was refluxed for 15 min under argon. Lauroyl peroxide was then added portionwise (10 mol% / **8j** per 10 min) to the refluxing solution. When **6** was totally consumed (after a global addition of 955 mg of lauroyl peroxide (2.4 mmol)), the crude mixture was cooled to room temperature, concentrated under reduced pressure and purified by precipitation (Ether-petroleum ether, 1:9) to give dimer **14** (7:5 mixture of meso and dl isomers, 221 mg, 79%) as a white solid. *Major isomer*: ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 1.90 (s, 6H), 4.90-5.03 (m, 2H), 8.86 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 22.2, 47.8 (q, J = 29 Hz), 124.0 (q, J = 282 Hz), 169.6. *Minor isomer*:

^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 1.98 (s, 6H), 5.17 (qd, $J = 8.2, 9.2$ Hz, 2H), 8.41 (d, $J = 9.2$ Hz, 2H). ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 22.4, 47.2 (q, $J = 29$ Hz), 123.9 (q, $J = 282$ Hz), 169.5. *For the mixture of isomers:* IR (nujol) 3284, 3072, 1674, 1547, 1340, 1301, 1255, 1238, 1181, 1153, 1108 cm^{-1} . MS (CI+ NH_3) m/z 281 (MH^+), 298 (MNH_4^+). Anal. calcd. for $\text{C}_8\text{H}_{10}\text{F}_6\text{N}_2\text{O}_2$: C, 34.30; H, 3.60, found: C, 33.67; H, 3.63.