Supporting Information for:

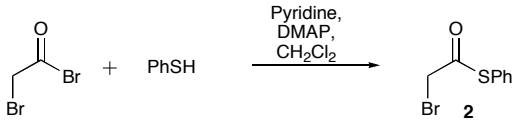
Direct Carbon-Carbon Bond Formation via Soft Enolization: Aldol Addition of α-Halogenated Thioesters to Enolizable Aldehydes

Julianne M. Yost, Rachel Alfie, Emily M. Tarsis, Elizabeth E. Calloway and Don M. Coltart*

Department of Chemistry, Duke University, Durham, North Carolina, USA. Fax: XX XXXX XXXX; Tel: XX XXXX XXXX; E-mail: don.coltart@duke.edu

General Considerations: Unless stated to the contrary, where applicable, the following conditions apply: Reactions were carried out using dried solvents (see below) and under a slight static pressure of Ar (pre-purified quality) that had been passed through a column (5 x 20 cm) of Drierite. Glassware was dried in an oven at 120 ºC for at least 12 h prior to use and then either cooled in a dessicator cabinet over Drierite or assembled quickly while hot, sealed with rubber septa, and allowed to cool under a stream of Ar. Reaction were stirred magnetically using Teflon-coated magnetic stirring bars. Teflon-coated magnetic stirring bars and syringe needles were dried in an oven at 120 ºC for at least 12 h prior to use and then cooled in a dessicator cabinet over Drierite. Hamilton microsyringes were dried in an oven at 60 ºC for at least 24 h prior to use and cooled in the same manner. Commercially available Norm-Ject disposable syringes were used. Dry benzene, toluene, Et_2O, CH_2Cl_2, THF, MeCN and DME were obtained using an Innovative Technologies solvent purification system. All other dry solvents were of anhydrous quality purchased from Sigma-Aldrich. Commercial grade solvents were used for routine purposes without further purification. Et_3N, pyridine, *i*-Pr_2NEt, 2,6-lutidene, *i*-Pr_2NH and TMEDA were distilled from CaH_2 under a N_2 atmosphere prior to use. Brine (NaCl), $NaHCO_3$, and NH_4Cl refer to saturated aqueous solutions. Flash column chromatography was performed on silica gel 60 (32-63μ) with reagent grade solvents. ^1H and ^{13}C NMR spectra were recorded on a Varian spectrometer (400 MHz and 100 MHz, respectively) at ambient temperature. All ^1H chemical shifts are reported in ppm (δ) relative to TMS (0.00); ^{13}C shifts are reported in ppm (δ) relative to $CDCl_3$. MS data were collected from Agilent 1100 Series liquid chromatography-electrospray ionization mass spectrometer.

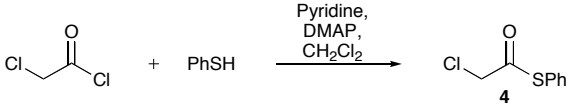
Thioester Preparation



***S*-phenyl α-bromothioacetate (2).** Pyridine (0.93 mL, 11.5 mmol) was added dropwise to a stirred solution of Bromoacetyl bromide (1.09 mL, 12.5 mmol), benzenthiol (1.12 mL, 10.9 mmol) and DMAP (0.136 g, 1.11 mmol) in CH_2Cl_2 (50 mL) at 0 ºC. The mixture was stirred at 0 ºC for 15 min, then warmed to rt and allowed to stir overnight. Reaction was quenched by the addition of saturated aqueous NH_4Cl (15 mL), diluted in EtOAc (200 mL), H_2O added to just dissolve the formed precipitate (5 mL), organic

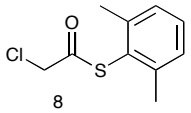
phase washed with H_2O (2 x 10 mL), brine, dried over $MgSO_4$ and evaporated. Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **2** (2.37 g; 94%) as a pure, white solid. Spectroscopic data was identical to that previously reported.[1, 2]

***The following reaction is representative of the preparation of α-chloro thioesters* 5, 8, 9, *and* 10:**



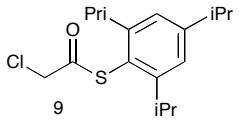
4

General procedure. *S*-phenyl α-chlorothioacetate (4). Pyridine (2.5 mL, 5% v/v was added dropwise to a stirred solution of chloroacetyl chloride (1.80 mL, 22.6 mmol), benzenthiol (2.0 mL, 19.5 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (50 mL) at 0 ºC. The mixture was stirred at 0 ºC for 15 min, then warmed to rt and allowed to stir overnight. The reaction was quenched by the addition of saturated aqueous NH_4Cl (15 mL), diluted in EtOAC (200 mL), H_2O added to just dissolve the formed precipitate (5 mL), organic phase washed with H_2O (2 x 10 mL), brine, dried over $MgSO_4$ and evaporated. Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **4** (3.45 g; 95%) as a pure, white solid. Spectroscopic data was identical to that previously reported.[3, 4]



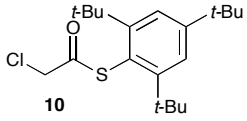
8

***S*-(2,6-Dimethyl)phenyl α-chlorothioacetate (8).** Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **8** (0.640 g; 86%) as a pure, colorless oil: **^{1}H NMR** ($CDCl_3$): δ 7.28-7.21 (m, 1H), 7.19-7.13 (m, 2H), 4.26 (s, 2H), 2.35 (s, 6H); **^{13}C NMR** ($CDCl_3$): δ 191.3, 143.0, 130.4, 128.6, 125.8, 48.0, 21.7; **ESI-MS** *m / z* $[M + H]^+$ calcd for $C_{10}H_{12}ClOS$: 215.0, found 214.9.



9

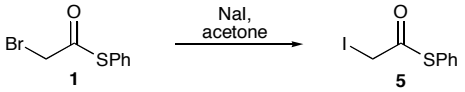
***S*-(2,4,6-triisopropyl)phenyl α-chlorothioacetate (9).** Starting from 2,4,6-Triisopropylbenzenethiol; flash chromatography over silica gel, using 3:97 EtOAc-hexanes gave **9** (0.353 g; 89%) as a pure, pale yellow solid. **^{1}H NMR** ($CDCl_3$): δ 7.10 (s, 2H), 4.28 (s, 2H) 3.35 (sept, *J* =6.8 Hz, 2H), 2.92 (sept, *J* = 6.8 Hz, 1H) 1.27 (d, *J* =6.8, 6H), 1.19 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR** ($CDCl_3$): δ 192.8, 152.7, 151.8, 122.4, 120.4, 48.0, 34.5, 32.1, 24.5, 23.6; **ESI-MS** *m / z* $[M + Na]^+$ calcd for $C_{17}H_{25}ClNaOS$: 335.1, found 335.1.



10

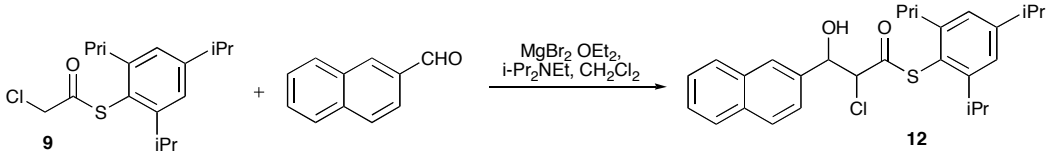
***S*-(2,4,6-tri-*tert*-butyl)phenyl α-chlorothioacetate (10).** Flash chromatography over silica gel, using 2.5:97.5 EtOAc-hexanes gave **10** (0.449 g; 70%) as a pure, colorless solid: **^{1}H NMR** ($CDCl_3$): δ 7.50 (s, 2H), 4.17 (br s, 2H) 1.45 (s, 18H), 1.34 (s, 9H); **^{13}C**

NMR ($CDCl_3$): δ 193.3 (br s), 154.8, 152.4 (br s), 123.5, 121.5 (br s), 47.8, 38.0, 35.4, 32.1, 31.4; **ESI-MS** *m / z* $[M + Na]^+$ calcd for $C_{20}H_{31}ClNaOS$: 377.2, found 377.2.

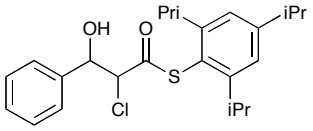


***S*-phenyl α-iodothioacetate (5).** NaI (1.69 g, 11.3 mmol) was added to a stirred solution *S*-phenyl α-bromothioacetate (**2**) (1.31 g, 5.67 mmol) in acetone (50 mL). The reaction was covered to exclude to light and allowed to stir overnight. The mixture was concentrated and then dissolved in Et_2O. Organic phase was washed with H_2O, brine, dried over MgSO4, and concentrated *in vacuo*. Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **17** (1.55 g; 98%) as a yellow light-sensitive solid: **^{1}H NMR** ($CDCl_3$): δ 7.43 (s, 5H), 4.08 (s, 2H); **^{13}C NMR** ($CDCl_3$): δ 191.2 134.5, 130.0, 129.5, 127.2, 3.6; **ESI-MS** *m / z* $[M + Na]^+$ calcd for C_8H_7INaOS: 300.9, found 300.9.

The following reaction is representative of those depicted in Table 3. All aldehydes, except for 2-naphthaldehyde, were freshly distilled prior to use. Diastereomeric ratios were determined by ^{1}H NMR analysis of the crude materials. Each reaction was run at rt for either 30 min or 1 h.

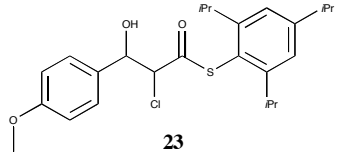


α-Chloro-β-hydroxy thioester (12). $MgBr_2OEt_2$ (0.181 g, 0.7 mmol) was added to a stirred solution of thioester **9** (0.188 g, 0.6 mmol) and 2-naphthaldehyde (0.078 g, 0.5 mmol) in CH_2Cl_2 (2.5 mL), followed by the addition of *I*-Pr_2NEt (0.18 mL, 1.0 mmol) at rt. Stirring was continued for 30 min at rt and then EtOAc (2.5 mL) and 10% (v/v) aqueous HCl (2.5 mL) were added. Stirring continued for 10 min and the mixture was then partitioned between EtOAc (10 mL) and H_2O (2 mL). The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic extracts were washed with brine, dried over MgSO4, and concentrated *in vacuo* to give a yellow oil. Flash chromatography over silica gel, using 5:95 to 10:90 EtOAc-hexanes gave **12** (0.210 g, 90%) as a yellow oil of a 5.2:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.92-7.79 (m, 4H), 7.57-7.42 (m, 3H), 7.08 – 6.90 (m, 1H, including a s at 7.04 and a s at 6.94) 5.37-5.35 [m, 1H, including a dd at 5.31 (*J* = 3.6, 6.4 Hz) and dd at 5.31 (*J* = 5.6, 6.4 Hz)], 4.88-4.81 [m, 1H including d at 4.87 (*J* = 6.4 Hz) and d at 4.81 (*J* = 6.8Hz)], 3.39 (d, OH, *J* = 5.2 Hz) 3.29 (two overlapping sept, 1 H, *J* = 6Hz), 3.08 (d, OH, 3.6Hz), 2.92-2.79 (two overlapping sept, 1H, *J* =7.2Hz), 2.56-2.42 (two overlapping sept, 1H, *J* = 6.4 Hz) 1.26-1.21 [m 1H, including a d at 1.25 (*J* = 7.2Hz) and a d at 1.22 (*J* = 6.8 Hz)], 1.20-1.10 (br s, 1H) 1.03-0.92 (br s, 1H); **^{13}C NMR** ($CDCl_3$): δ 195.4, 193.6, 152.6, 152.4, 151.8, 151.7, 136.2, 135.4, 133.5, 133.4, 133.2, 133.1, 128.6, 128.4, 128.35, 128.31, 127.7, 126.9, 126.6, 126.5, 126.48, 126.4, 124.2, 124.1, 122.2, 122.1, 120.1, 120.0, 75.7, 74.9, 68.1, 64.6, 34.4, 34.3, 31.9, 31.8, 31.7, 24.3, 24.2, 23.8, 23.6, 22.8 **ESI-MS** *m / z* $[M + Na]^+$ calcd for $C_{28}H_{33}ClNaO_2S$: 491.2, found 491.2.



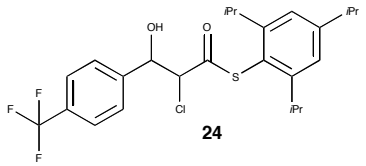
22

α-Chloro-β-hydroxy thioester (22). Stirred at rt for 30 min. Flash chromatography over silica gel, using 5:95 to 10:90 EtOAc-hexanes gave **22** (0.389 g, 96%) as a yellow oil of a 4:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.43-7.31 (m, 5H), 7.10-7.02 (m, 2H), 5.16 (dd, 1H, 4 Hz, 6.8 Hz), 5.12 (dd, 1H, *J* = 5.6 Hz, 6.6 Hz), 4.72 (d, 1H, *J* = 6.4 Hz), 4.67 (d, 1H, *J* = 7.2 Hz), 3.38-3.25 (br m, 1H), 3.22 (d, 1H, *J* =5.2 Hz), 3.00-2.71 [m including d at 2.96 (1H, *J* = 4.4Hz), sept at 2.88 (1H, *J* = 6.8 Hz), br m at 2.77 (1H)] 1.29-0.98 (m, 18H); **^{13}C NMR** ($CDCl_3$): δ 195.4, 193.7, 152.6, 151.8, 151.7, 138.8, 138.2, 128.8, 128.7, 128.5, 127.2, 127.0, 122.3, 122.2, 120.2, 120.1, 75.5, 74.7, 68.3, 64.8, 34.4, 31.9, 31.8, 31.7, 24.5, 24.3, 23.9, 23.6, 23.4, ; **ESI-MS** *m* / *z* $[M + Na]^+$ calcd for $C_{24}H_{31}ClNaO_2S$: 441.2, found 441.2.



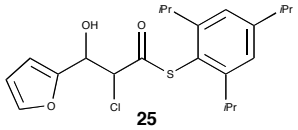
23

α-Chloro-β-hydroxy thioester (23). Stirred at rt for 1 hour. Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **23** (0.053 g, 96%) as a white solid of a 4:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.40-7.37 (m, 2H), 7.13-7.06 (m, 2H), 6.97-6.94 (m, 2H), 5.15 (d, 1H, J=7.0 Hz), 4.73-4.69 (m, 1H [containing d at 4.70 (J=7.0) and d at 4.60 (J=7.0)]), 3.85 (s, 3H), 3.39-3.33 (m, 1H), 2.95-2.90 (m, 2H), 2.79-2.76 (m, 1H), 1.31-1.27 (m, 6H [containing d at 1.30 (J=7.0) and d at 1.28 (J=7.0)]), 1.24-1.16 (m, 10H), 1.08-1.02 (m, 5H); **^{13}C NMR** ($CDCl_3$): δ 193.5, 159.9, 152.6, 151.7, 130.0, 128.6, 128.4, 122.4, 122.1, 120.0, 114.2, 113.9, 75.3, 75.0, 74.7, 74.3, 68.2, 68.0, 55.4, 55.2, 34.5, 34.3, 31.9, 31.8, 31.6, 24.5, 24.4, 23.9, 23.8, 23.5, 23.2; **ESI-MS** *m* / *z* $[M + Na]^+$ calcd for $C_{25}H_{33}ClO_3S$: 448.2, found 448.3.



24

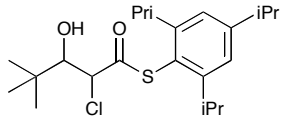
α-Chloro-β-hydroxy thioester (24). Stirred at rt for 30 min. Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **24** (0.055 g, 97%) as a white solid of a 4:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.67-7.55 (m, 4H), 7.08-7.05 (m, 2H), 5.29-5.19 (m, 1H, containing apparent dd), 4.72-4.67 (m, 1H [containing d at 4.71 (J=6.0 Hz), d at 4.68 (J=7.0 Hz)]), 3.35-3.28 (m, 1H), 3.06-3.05 (m, 1H), 2.94-2.82 (m, 2H), 1.27-1.24 (m, 7H), 1.17-1.03 (m, 14H); **^{13}C NMR** ($CDCl_3$): δ 195.4, 194.0, 152.5, 151.9, 142.0, 131.0, 130.8, 131.0, 130.8, 127.5, 127.4, 122.5, 119.7, 75.0, 74.8, 74.0, 73.9, 67.9, 67.7, 34.5, 34.3, 31.9, 31.8, 24.3, 24.2, 33.8; **ESI-MS** *m* / *z* $[M + Na]^+$ calcd for $C_{25}H_{30}ClF_3O_2S$: 487.0, found 487.0.



25

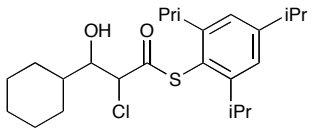
α-Chloro-β-hydroxy thioester (25). Stirred at rt for 30 min. Flash chromatography over silica gel, using 5:95 EtOAc-hexanes gave **25** (0.046 g, 83%) as a white solid of a 4:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.42-7.41 (m, 1H), 7.07-7.05 (m, 2H), 6.41-6.40 (m, 1H), 6.36 (dd, 1H, J=1.5 Hz, J=3.25 Hz), 5.25-5.14 (m, 1H [containing apparent dd at 5.24 and apparent dd at 5.15]), 4.93-4.85 (m, 1H

[containing d at 4.92 (J=5.5 Hz) and d at 4.86 (J=7.0 Hz)]), 3.33-3.31 (m, 1H), 3.09-3.05 (m, 1H), 2.93-2.84 (m, 2H), 1.24-1.22 (m, 8H), 1.14-1.09 (m, 13H); **^{13}C NMR** ($CDCl_3$): δ 194.0, 152.6, 152.5, 151.7, 150.9, 142.9, 142.8, 122.4, 122.2, 110.5, 109.0, 69.3, 69.1, 66.3, 65.0, 34.5, 34.3, 31.9, 24.4, 23.9, 23.8; **ESI-MS** *m* / *z* $[M + Na]^+$ calcd for $C_{22}H_{29}ClO_3S$: 408.2, found 408.1.



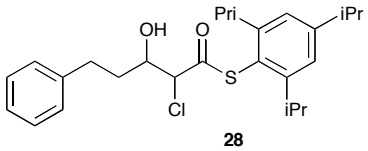
26

α-Chloro-β-hydroxy thioester (26). Stirred at rt for 30 min. Flash chromatography over silica gel, using 2:98 to 6:94 EtOAc-hexanes gave **26** (0.258 g, 76%) as a yellow oil of a 3:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.10 (s, 2H), 4.75 (d, 1H, *J* = 2.4 Hz), 4.63 (d, 1H, *J* = 4.4 Hz), 3.88 (dd, 1H, *J* = 2.4 Hz, 7.2 Hz), 3.78 (dd, 1H, *J* = 4 Hz, 7.8 Hz), 3.48-3.30 (br m, 2H), 3.18 (d, 1H, *J* = 7.6), 2.91 (sept, 1H, *J* = 6.8 Hz), 2.45 (d, 1H, *J* = 7.6 Hz), 1.26 (d, 6H, *J* = 6.4 Hz), 1.18 (d, 12H, *J* = 6.4 Hz), 1.05 (s, 9H); **^{13}C NMR** ($CDCl_3$): δ 196.3, 196.2, 152.7, 152.5, 151.8, 151.6, 122.3, 120.6, 119.9, 82.6, 77.9, 65.8, 60.4, 35.9, 35.8, 34.3, 31.9, 26.7, 26.5, 24.4, 23.8, 23.6; **ESI-MS** *m* / *z* $[M + Na]^+$ calcd for $C_{22}H_{35}ClNaO_2S$: 421.2 found 421.2.



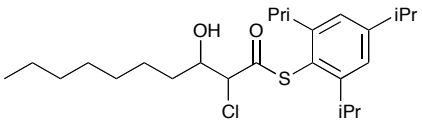
27

α-Chloro-β-hydroxy thioester (27). Stirred at rt for 1 h. Flash chromatography over silica gel, using 5:95 to 7:93 EtOAc-hexanes gave **27** (0.160 g, 73%) as a yellow oil of a 3:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.10 (s, 2H), 4.68 (d, 1H, *syn*, *J* = 3.6), 4.56 (d, 1H, *anti*, *J* = 6.4 Hz), 3.89-3.81 (m, 1H), 3.48-3.30 (br m, 2H), 2.91 (sept, 1H, *J* = 6.8 Hz), 2.51 (d, OH, *J* = 6.4 Hz), 2.27 (d, OH, *J* = 7.2 Hz), 2.05-2.00 (br m, 1H), 1.87-1.57 (m, 6H), 1.28-1.09 [m including d at 1.26 (6H, *J* = 6.8), d at 1.18 (12 H, *J* = 6 Hz), and m (4H); **^{13}C NMR** ($CDCl_3$): δ 195.9, 195.8, 152.7, 152.5, 151.7, 151.6, 122.3, 122.2, 120.6, 120.4, 67.0, 62.6, 40.6, 39.8, 34.5, 32.0, 31.9, 29.2, 28.1, 26.5, 26.24, 26.2, 26.1, 25.98, 25.9, 25.8, 24.4, 23.8, 23.6; **ESI-MS** *m* / *z* $[M + Na]^+$ calcd for C_8H_7INaOS: 425.1, found 425.3.



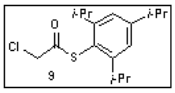
28

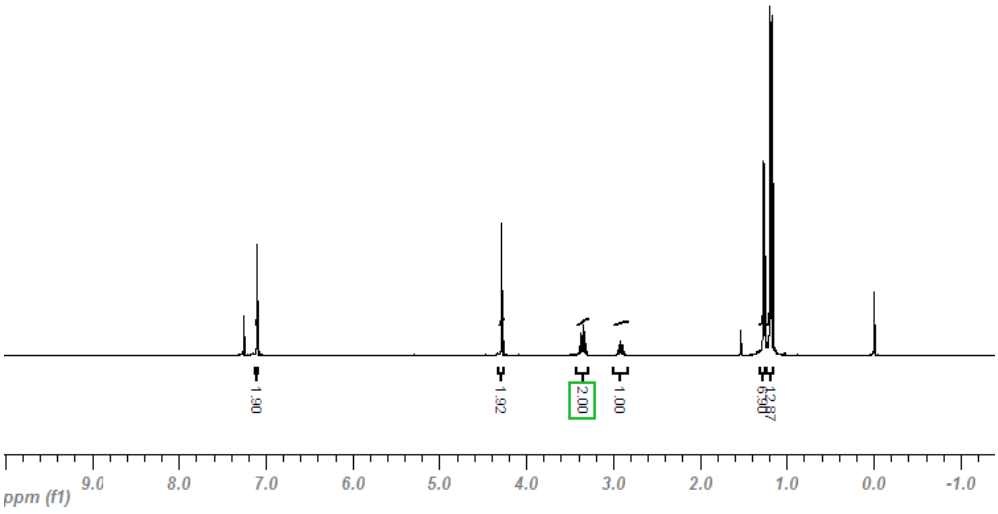
α-Chloro-β-hydroxy thioester (28). Stirred at rt for 1 h. Flash chromatography over silica gel, using 5:95 to 9:91 EtOAc-hexanes gave **28** (0.05 g, 22%) as a yellow oil of a 3:1 (*syn:anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.30-7.17 (m, 5H), 7.10 (s, 2H), 4.54-4.50 [m, 1H, including d at 4.53 (*J* = 4Hz) and d at 4.51 (*J* = 6 Hz)], 4.19-4.10 (m, 1H), 3.42-3.24 (m, 2H), 2.97-2.84 (m, 2H), 2.77-2.67 (m, 1H), 2.55-2.47 [m, 1H including d at 2.53 (*anti* OH, *J* = 6.4 Hz) and a d at 2.48 (*syn* OHJ = 6.4 Hz)], 2.12-1.86 (two overlapping m, 1H), 1.26 (d, 6H, *J* = 6.8 Hz), 1.18-1.14 (m, 12 H); **^{13}C NMR** ($CDCl_3$): δ 195.8, 195.7 151.7, 141.1, 128.5, 128.4, 126.1, 122.3, 120.3, 71.8, 68.2, 35.4, 34.3, 32.0, 31.7, 24.3, 23.82, 23.80, 23.6; **ESI-MS** m / z [M + Na]+ calcd for $C_{26}H_{35}ClNaO_2S$: 469.2, found 469.2.

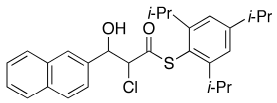


29

α-Chloro-β-hydroxy thioester (29). Stirred at rt for 1 h. Flash chromatography over silica gel, using 4:96 EtOAc-hexanes gave **29** (0.076 g, 33%) as a yellow oil of a 5:1 (*syn*:*anti*) mixture of diastereomers. **^{1}H NMR** ($CDCl_3$): δ 7.10 (s, 2H), 4.53-4.48 (overlapping d, 1H, *syn* J = 4.4 Hz), 4.18-4.08 (m, 1H, J = 4.4, 6.8 Hz), 3.42-3.29 (br m, 2H, J = 5.6Hz), 2.92 (sept, 1H, J = 7.2 Hz), 2.47-2.39 [m including d at 2.45 (*anti* OH, J = 6.8 Hz) and d at 2.42 (*syn* OH, J = 6.4 Hz)], 1.66-1.50 (m, 4H), 1.38-1.11 [m, 23H, including d at 1.26 (J = 6.8 Hz) and d at 1.18 (J = 6.8 Hz)], 0.89-0.86 (m, 6H); **^{13}C NMR** ($CDCl_3$): δ 195.9, 195.6, 152.6, 151.6, 122.3, 120.4, 120.37, 73.2, 72.7, 68.4, 66.5, 34.3, 33.7, 33.1, 32.0, 31.9, 31.8, 31.7, 29.4, 29.38, 29.2, 29.1; **ESI-MS** m / z $[M + Na]^+$ calcd for $C_{24}H_{37}ClNaO_2S$: 463.2, found 463.3.

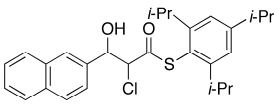





i-Pr
i-Pr
OH
O
S
Cl
i-Pr

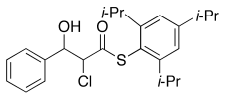
12

9
8
7
6
5
4
3
2
1
-0
ppm
4.55
3.28
2.13
1.08
1.00
1.08
2.09
0.86
15.37
6.18


i-Pr
i-Pr
OH
O
S
Cl
i-Pr

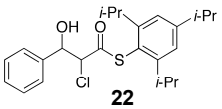
12

220
200
180
160
140
120
100
80
60
40
20
0
ppm


i-Pr
OH
O
i-Pr
S
Cl
i-Pr

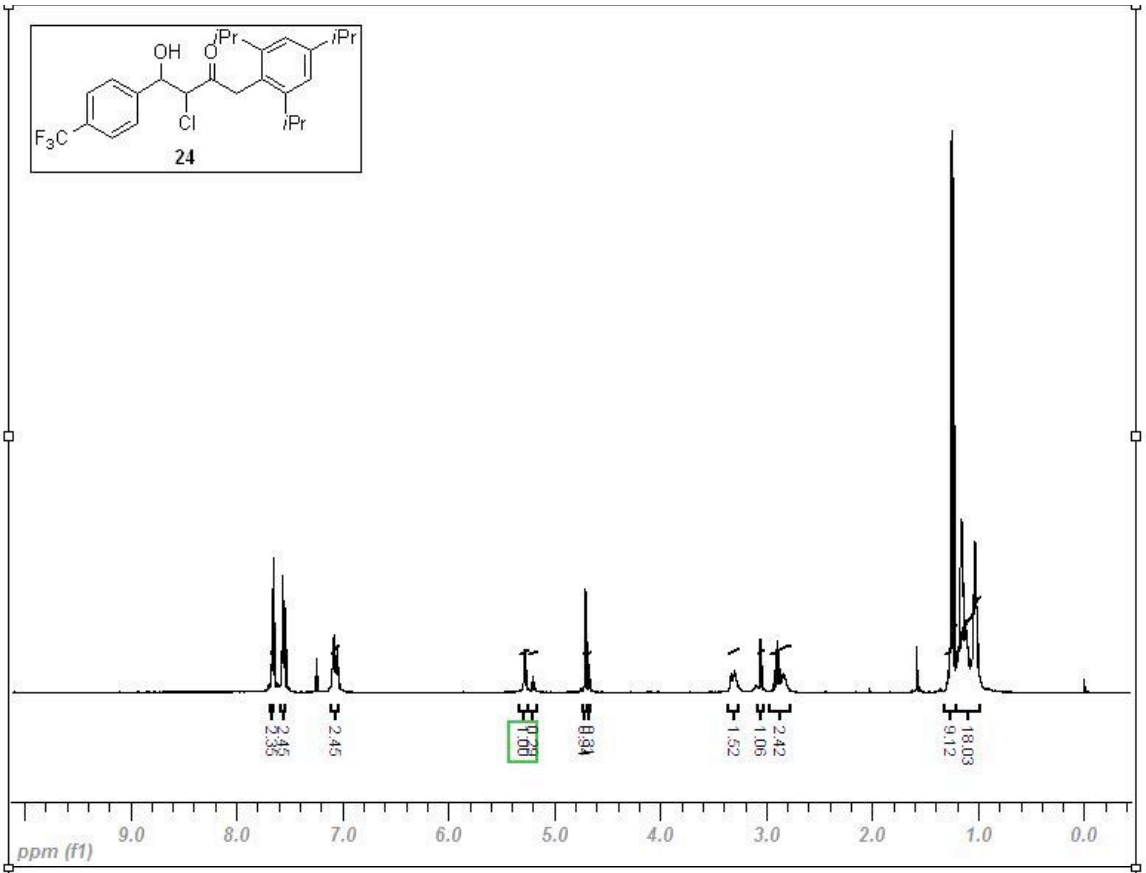
22

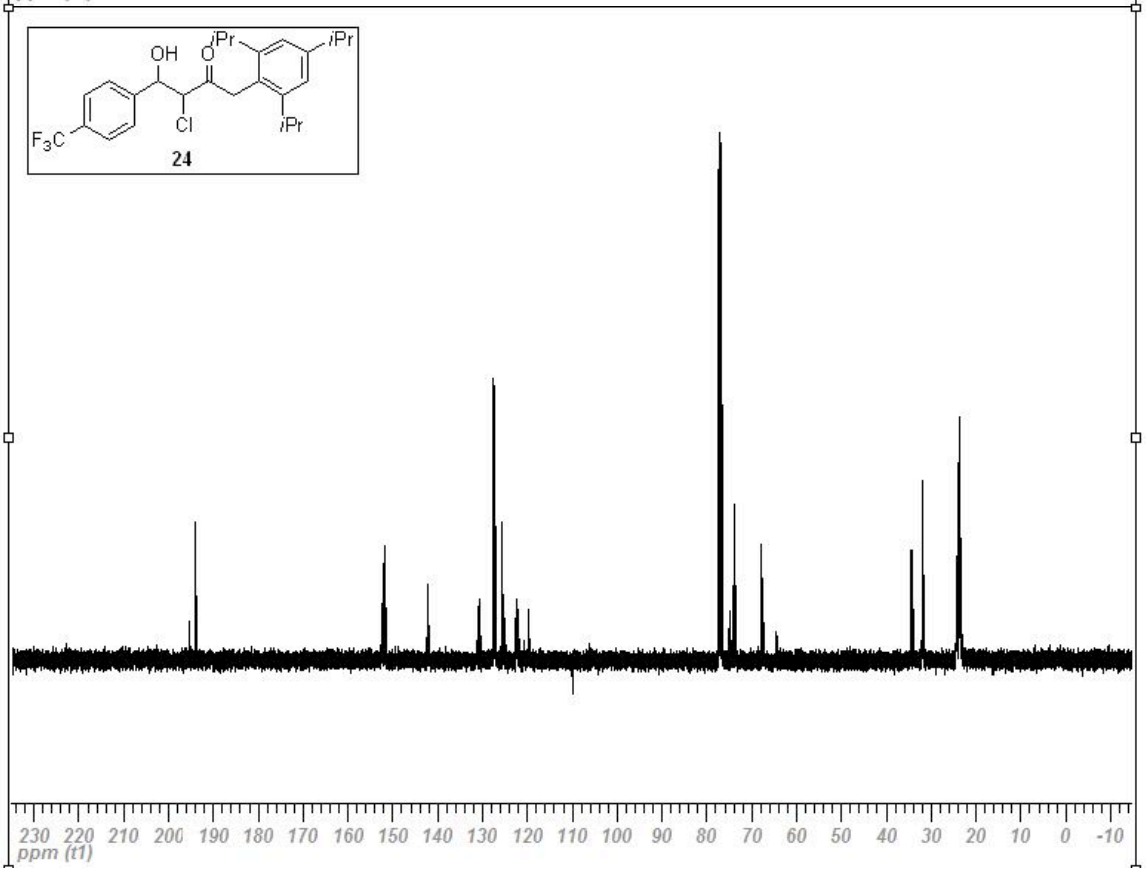
9
8
7
6
5
4
3
2
1
-0
ppm
4.84
2.00
1.00
0.93
1.72
2.18
18.54

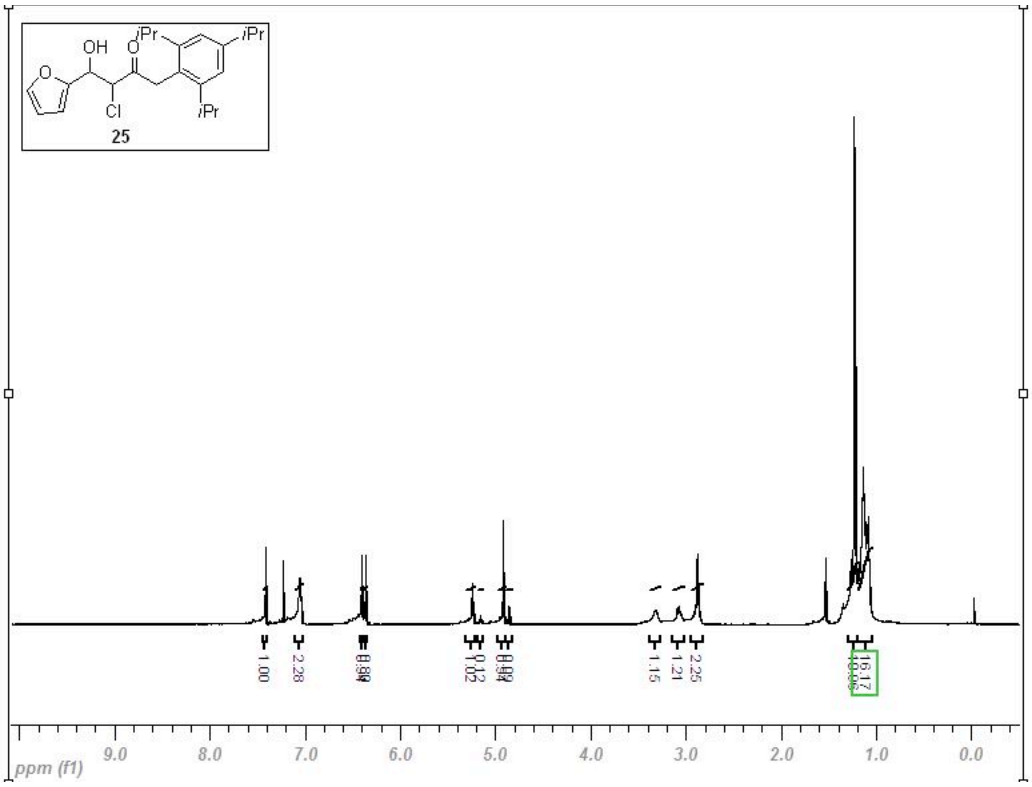

i-Pr
OH
O
i-Pr
S
Cl
i-Pr

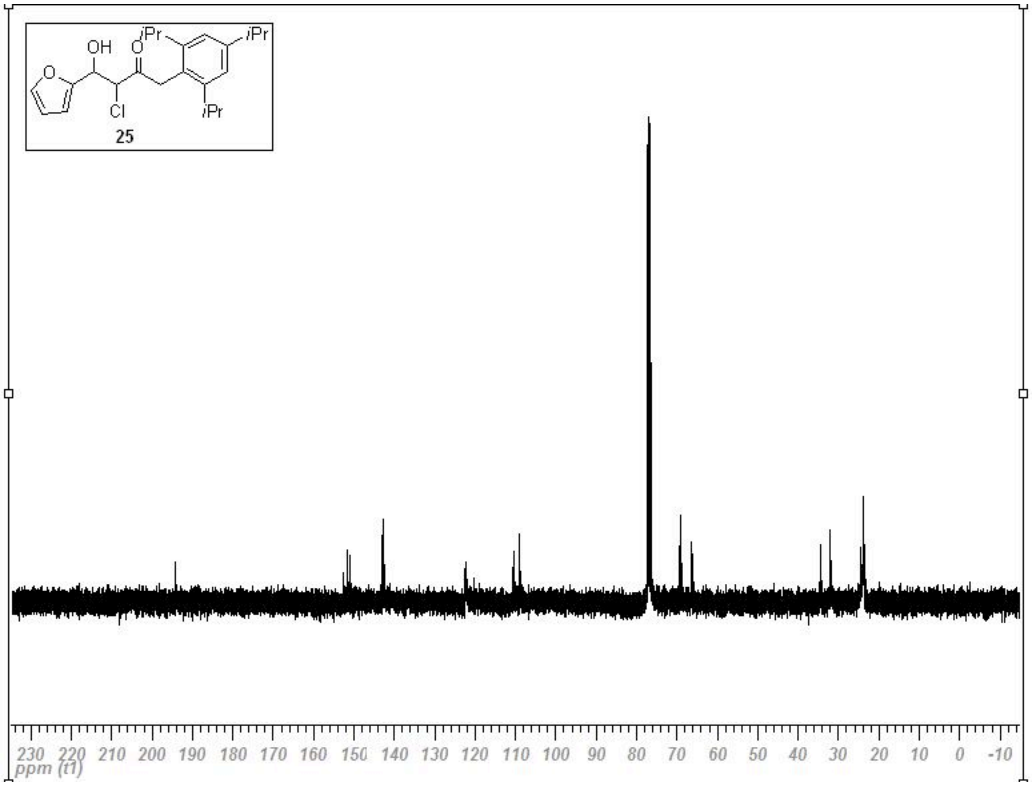
22

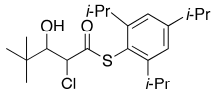
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OH
O
iPr
iPr
iPr
Cl
F3C
24
2.45
2.35
2.45
1.00
0.84
1.52
1.06
2.42
9.12
18.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


OH
O
iPr
iPr
iPr
Cl
F3C
24
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

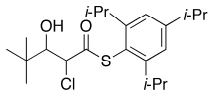

OH
O
iPr
iPr
O
Cl
iPr
25
1.00
2.28
0.89
0.89
1.15
1.21
2.25
16.17
ppm (f1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


OH
O
iPr
iPr
O
Cl
iPr
25
ppm (f1)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


i-Pr
i-Pr
OH
O
S
Cl
i-Pr

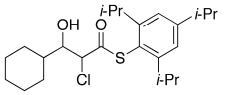
26

9
8
7
6
5
4
3
2
1
-0
ppm
2.00
0.18
0.78
0.20
0.84
0.18
2.08
1.04
0.77
12.32
6.56
5.78


i-Pr
i-Pr
OH
O
S
Cl
i-Pr

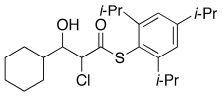
26

220
200
180
160
140
120
100
80
60
40
20
0
ppm


i-Pr
i-Pr
OH
O
S
Cl
i-Pr

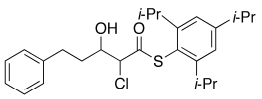
27

9
8
7
6
5
4
3
2
1
-0
ppm
2.00
0.23
0.70
1.03
2.15
0.99
0.22
0.70
0.78
6.44
27.37


i-Pr
i-Pr
OH
O
S
Cl
i-Pr

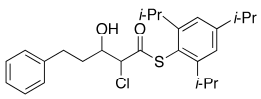
27

220
200
180
160
140
120
100
80
60
40
20
0
ppm


OH
O
i-Pr
i-Pr
S
Cl
i-Pr

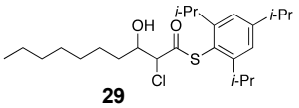
28

9
8
7
6
5
4
3
2
1
-0
ppm
2.02.00
2.90
0.96
1.01
2.05
2.13
0.98
1.17
2.13
6.87
12.07


OH
O
i-Pr
i-Pr
S
Cl
i-Pr

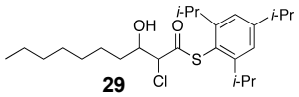
28

220
200
180
160
140
120
100
80
60
40
20
0
ppm


i-Pr
OH
O
i-Pr
S
Cl
i-Pr

29

9
8
7
6
5
4
3
2
1
-0
ppm
2.00
1.01
1.12
2.20
1.12
1.06
3.59
32.37
3.92


i-Pr
OH
O
i-Pr
S
Cl
i-Pr

29

220
200
180
160
140
120
100
80
60
40
20
0
ppm

1. Dagli, D. J.; Yu, P. S.; Wemple, J., Darzens Synthesis of Glycidic Thiol Esters - Formation of a Beta-Lactone by-Product. *J Org Chem* **1975,** 40, (22), 3173-3178.
2. Roblot, G.; Wylde, R.; Martin, A.; Parello, J., Regioselective Synthesis of Inhibitors of Histone Acetyl Transferase Covalently Linking Spermidine to the S-Terminus of Coenzyme-a and Fragments. *Tetrahedron* **1993,** 49, (29), 6381-6398.
3. Imamoto, T.; Kodera, M.; Yokoyama, M., A CONVENIENT METHOD FOR THE PREPARATION OF THIOL ESTERS. *Synthesis-Stuttgart* **1982**, (2), 134-136.
4. Silveira, C. C.; Braga, A. L.; Larghi, E. L., Synthesis of thiol, selenol, and tellurol esters by the reaction of organochalcogeno mercurials with acid chlorides. *Organometallics* **1999,** 18, (24), 5183-5186.