Supporting Information

Dimethylthiocarbamate (DMTC): An Alcohol Protecting Group

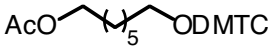
D. K. Barma,[†] A. Bandyopadhyay,[†] Jorge H. Capdevila,[‡] and J. R. Falck*,[†]

[†]*Departments of Biochemistry and Pharmacology, University of Texas Southwestern Medical Center, Dallas, Texas 75390-9038, and* [‡]*Departments of Medicine and Biochemistry, Vanderbilt University School of Medicine, Nashville, TN 37232 USA*

Dimethylthiocarbamoylation

General Method A. A solution of alcohol (5.0 mmol) in dry THF (5 mL) was added to a stirring, 0°C suspension of NaH (5.1 mmol) in dry THF (20 mL) under an argon atmosphere. After 30 min, NaI (0.1 mmol) and *N,N*-dimethylthiocarbamoyl chloride (6.0 mmol, 1.2 equiv) were added successively and the resulting mixture was stirred at room temperature for 10 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether (3 × 10 mL). The combined ethereal extracts were washed with water, brine, and dried over Na_2SO_4. Removal of all volatiles *in vacuo* and chromatographic purification of the residue on SiO_2 furnished the DMTC protected alcohol.

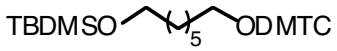
General Method B. 1,1'-Thiocarbonyldiimidazole (1.1 mmol) was added to a stirring solution of alcohol (1 mmol) in dry CH_2Cl_2 (5 mL) containing DMAP (0.1 mmol) under an argon atmosphere. After 2-10 h, the reaction mixture was filtered through a small pad of silica gel and the filter cake was washed with EtOAc (5 mL). The combined filtrate was concentrated under reduced pressure and the residue was dissolved in a 2 M THF solution of dimethylamine (4 mL). After 2-4 h, all volatiles were removed *in vacuo* and the residue was chromatographed over silica gel affording the DMTC protected alcohol.



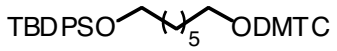
1-Acetyloxy-7-dimethylthiocarbamoyloxyheptane (1)

1-Acetyloxyheptan-1-ol[1] was converted to **1** in 98% yield according to General Method B. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32-1.44 (m, 6H), 1.58-1.76 (m, 4H), 2.04 (s, 3H), 3.10 (s, 3H), 3.56 (s, 3H), 4.04 (t, 2H, J = 6.3 Hz), 4.42 (t, 2H, J = 6.3 Hz); MS *m/z* 261 (M^+). Anal. cald for $C_{12}H_{23}NO_3S$: C, 55.14; H, 8.87; found: C, 55.10; H, 8.91.

1-(*tert*-Butyldimethylsilanyloxy)-7-dimethylthiocarbamoyloxyheptane (2)



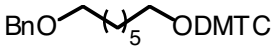
7-(tert-Butyldimethylsilanyloxy)-heptan-1-ol[2] was converted to **2** in 99% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.04 (s, 6H), 0.88 (s, 9H), 1.30-1.42 (m, 6H), 1.46-1.54 (m, 2H), 1.67-1.76 (m, 2H), 3.10 (s, 3H), 3.36 (s, 3H), 3.59 (t, 2H, J = 13.2 Hz), 4.42 (t, 2H, J = 13.2 Hz); MS *m/z* 333 (M^+). Anal. cald for $C_{16}H_{35}NO_2SSi$: C, 57.60; H, 10.57; found:



C, 57.70; H, 10.49.

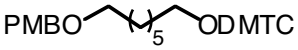
1-(*tert*-Butyldiphenylsilanyloxy)-7-dimethylthiocarbamoyloxyheptane (3)

7-(tert-Butyldiphenylsilanyloxy)-heptan-1-ol[3] was converted to **3** in 97% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.04 (s, 9H), 1.23-1.42 (m, 6H), 1.51-1.60 (m, 2H), 1.65-1.74 (m, 2H), 3.09 (s, 3H), 3.36 (s, 3H), 3.65 (t, 2H, J = 12.9 Hz), 4.42 (t, 2H, J = 13.2 Hz), 7.34-7.42 (m, 6H), 7.64-7.69 (m, 4H); MS *m/z* 457 (M^+). Anal. cald for $C_{26}H_{39}NO_2SSi$: C, 68.22; H, 8.59; found: C, 68.29; H, 8.74.



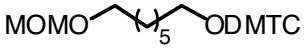
1-(Benzyloxy)-7-dimethylthiocarbamoyloxyheptane (4)

7-Benzyloxy-heptan-1-ol[4] was converted to **4** in 93% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.32-1.44 (m, 6H), 1.56-1.65 (m, 2H), 1.66-1.76 (m, 2H), 3.09 (s, 3H), 3.36 (s, 3H), 3.46 (t, 2H, J = 13.2 Hz), 4.42 (t, 2H, J = 13.2 Hz), 4.50 (s, 2H), 7.25-7.35 (m, 5H); MS *m/z* 309 (M^+). Anal. cald for $C_{17}H_{27}NO_2S$: C, 65.96; H, 8.79; found: C, 65.90; H, 8.64.



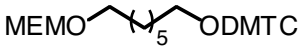
1-(4-Methoxybenzyloxy)-7-dimethylthiocarbamoyloxyheptane (5)

7-(4-Methoxybenzyloxy)-heptan-1-ol[5] was converted to **5** in 90% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.31-1.42 (m, 6H), 1.54-1.75 (m, 4H), 3.09 (s, 3H), 3.35 (s, 3H), 3.40 (t, 2H, J = 6.4 Hz), 3.79 (s, 3H), 4.38-4.44 (m, 4H), 6.86 (d, 2H, J = 6.6 Hz), 7.24 (d, 2H, J = 6.6 Hz); MS *m/z* 339 (M^+). Anal. cald for $C_{18}H_{29}NO_3S$: C, 63.68; H, 8.61; found: C, 63.77; H, 8.74.



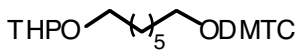
1-(Methoxymethoxy)-7-dimethylthiocarbamoyloxyheptane (6)

7-(Methoxymethoxy)heptan-1-ol[6] was converted to **6** in 96% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.32-1.44 (m, 6H), 1.54-1.63 (m, 2H), 1.67-1.77 (m, 2H), 3.08 (s, 3H), 3.35 (s, 6H), 3.51 (t, 2H, J = 6.3 Hz), 4.42 (t, 2H, J = 6.3 Hz), 4.61 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 26.06, 26.26, 28.84, 29.20, 29.79, 37.78, 42.71, 55.18, 67.84, 71.74, 96.49, 188.46; IR (neat) 2933, 1520, 1393, 1293, 1193, 1146, 1110, 1043 cm^{-1}; MS *m/z* 263 (M^+). HRMS (CI, CH_4) calcd for $C_{12}H_{26}NO_3S$ (M^++1) *m/z* 264.1633, found 264.1630.



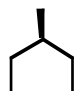
1-(2-Methoxy-ethoxymethoxy)-7-dimethylthiocarbamoyloxyheptane (7)

7-(2-Methoxy-ethoxymethoxy)-heptan-1-ol[7] was converted to **7** in 92% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.32-1.42 (m, 6H), 1.53-1.62 (m, 2H), 1.67-1.76 (m, 2H), 3.10 (s, 3H), 3.36 (s, 3H), 3.39 (s, 3H), 3.51-3.57 (m, 4H), 3.67-3.71 (m, 2H), 4.42 (t, 2H, J = 6.3 Hz), 4.71 (s, 2H); MS *m/z* 307 (M^+). Anal. cald for $C_{14}H_{29}NO_4S$: C, 54.69; H, 9.51; found: C, 54.91; H, 9.68.



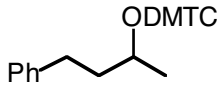
1-(Tetrahydropyran-2-yloxy)-7-dimethylthiocarbamoyloxyheptane (8)

7-(Tetrahydropyran-2-yloxy)-heptan-1-ol[8] was converted to **8** in 93% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.32-1.90 (m, 16H), 3.09 (s, 3H), 3.36 (s, 3H), 3.33-

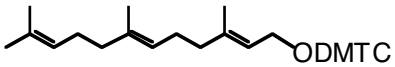


3.41 (m, 1H), 3.45-3.53 (m, 1H), 3.68-3.77 (m, 1H), 3.82-3.90 (m, 1H), 4.42 (t, 2H, J = 13.2 Hz), 4.56 (t, 1H, J = 6.9 Hz); MS *m/z* 303 (M^+). Anal. cald for $C_{15}H_{29}NO_3S$: C, 59.37; H, 9.63; found: C, 59.22; H, 9.85.

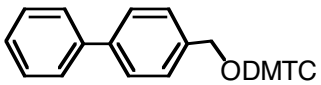
Menthyl *N,N*-dimethylthiocarbamate (9)
(-)-Menthol was converted to **9** in 95% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 0.81 (d, 3H, J = 7.5 Hz), 0.86-0.93 (m, 7H), 1.01-1.17 (m, 1H), 1.43-1.59 (m, 2H), 1.63-1.73 (m, 2H), 1.81-1.94 (m, 1H), 2.17-2.26 (m, 1H), 3.07 (s, 3H), 3.35 (s, 3H), 5.24 (dt, 1H, J = 4.5, 10.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 17.10, 20.99, 22.25, 23.75, 26.65, 31.41, 34.52, 37.72, 41.06, 42.70, 47.66, 81.64, 187.86; IR (neat) 2953, 1520, 1390, 1293, 1196 cm^{-1}; MS *m/z* 243 (M^+). HRMS (CI, CH_4) calcd for $C_{13}H_{26}NOS$ (M^++1) *m/z* 244.1735, found 244.1741.



4-Phenyl-2-butanyl *N,N*-dimethylthiocarbamate (10)
4-Phenyl-2-butanol was converted to **10** in 96% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.34 (d, 3H, J = 6.0 Hz), 1.84-2.10 (m, 2H), 2.62-2.74 (m, 2H), 3.05 (s, 3H), 3.36 (s, 3H), 5.53-5.64 (m, 1H), 7.14-7.30 (m, 5H); MS *m/z* 237 (M^+). Anal. cald for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; found: C, 65.46; H, 7.89.



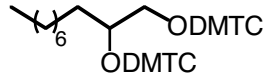
***E,E,E*-Farnesyl *N,N*-dimethylthiocarbamate (11)**
E,E,E-Farnesol was converted to **11** in 92% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 400 MHz) □ 1.59 (s, 6H), 1.67 (s, 3H), 1.71 (s, 3H), 1.93-2.16 (m, 8H), 3.09 (s, 3H), 3.36 (s, 3H), 4.96 (d, 2H, J = 6.8 Hz), 5.05-5.11 (m, 2H), 5.39-5.43 (m, 1H); MS *m/z* 309 (M^+). Anal. cald for $C_{18}H_{31}NOS$: C, 69.85; H, 10.10; found: C, 69.93; H, 10.24.



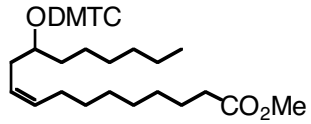
4-Biphenylmethyl *N,N*-dimethylthiocarbamate (12)
4-Biphenylmethanol was converted to **12**, mp 84ºC, in 91% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 400 MHz) □ 3.15 (s, 3H), 3.41 (s, 3H), 5.55 (s, 2H), 7.33-7.47 (m, 5H), 7.56-7.61 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) □ 38.20, 43.16, 72.93, 127.31, 127.37, 127.53, 127.71, 128.80, 129.03, 129.09, 129.65, 135.46, 140.92, 141.36, 188.25; MS *m/z* 271 (M^+). Anal. cald for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; found: C, 70.89; H, 6.55.

6-Phenylhex-2-yn-1-yl *N,N*-dimethylthiocarbamate (13)

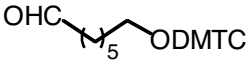
6-Phenylhex-2-yn-1-ol was converted to **13** in 93% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.73-1.89 (m, 2H), 2.21-2.27 (m, 2H), 2.72 (t, 2H, J = 7.8 Hz), 3.15 (s, 3H), 3.36 (s, 3H), 5.10-5.12 (m, 2H), 7.17-7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 18.49, 30.26, 34.96, 38.23, 43.16, 59.65, 75.24, 87.59, 126.17, 128.61, 128.79, 141.73, 187.64; MS *m/z* 261 (M^+). HRMS (CI, CH_4) calcd for $C_{15}H_{20}NOS$ (M^++1) *m/z* 262.1266, found 261.1260.



1,2-Decanediyl *N,N*-dimethylthiocarbamate (14)
Decane-1,2-diol was converted to **14** in 89% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 0.84 (t, 3H, J = 7.2 Hz), 1.19-1.41 (m, 12H), 1.58-1.77 (m, 2H), 3.08 (s, 6H), 3.32 (s, 3H), 3.33 (s, 3H), 4.50-4.61 (m, 2H), 5.70-5.86 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) □ 14.21, 22.74, 25.23, 29.28, 29.46, 29.60, 31.08, 31.92, 37.87, 38.06, 42.87, 72.19, 78.88, 187.82, 187.95; MS *m/z* 348 (M^+). HRMS (CI, CH_4) calcd for $C_{16}H_{33}N_2O_2S_2$ (M^++1) *m/z* 349.1983, found 349.1992.



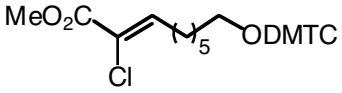
Methyl 12-dimethylthiocarbamoyloxyoctadec-9(Z)-enoate (16)
Methyl ricinoleate **(15)** was converted to **16** in 96% yield according to General Method B. ^{1}H NMR ($CDCl_3$, 400 MHz) □ 0.85 (t, 3H, J = 6.9 Hz), 1.22-1.34 (m, 16H), 1.53-1.67 (m, 4H), 1.97-2.05 (m, 2H), 2.28 (t, 2H, J = 7.8 Hz), 2.32-2.44 (m, 2H), 3.06 (s, 3H), 3.34 (s, 3H), 3.64 (s, 3H), 5.31-5.38 (m, 1H), 5.40-5.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) □ 14.30, 22.81, 25.15, 25.38, 27.64, 29.33, 29.39, 29.47, 29.75, 31.72, 31.94, 33.46, 34.30, 37.79, 42.77, 51.66, 81.52, 124.29, 132.82, 174.52, 188.10; MS *m/z* 399 (M^+). HRMS (CI, CH_4) calcd for $C_{22}H_{42}NO_3S$ (M^++1) *m/z* 400.2885, found 400.2888.



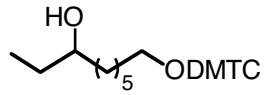
7-Dimethylthiocarbamoyloxyheptanal (Scheme 1)
Route a: PCC (1.5 mmol) was added to a stirring, room temperature solution of 7-dimethylthiocarbamoyloxyheptan-1-ol[9] (1.0 mmol) in dry CH_2Cl_2 (5 mL) under an argon atmosphere. After 2 h, the reaction mixture was filtered through a small pad of silica gel and the filter cake was washed with CH_2Cl_2. The combined filtrate was concentrated under reduced pressure and the residue was chromatographically purified over silica gel affording pure 7-dimethylthiocarbamoyloxyheptanal (91%).

Route b: To a stirred solution of oxalyl chloride (2.0 mmol) in dry CH_2Cl_2 (5 mL) at -78ºC was added DMSO (3.0 mmol) under an argon atmosphere. After 30 min at -78ºC, 7-dimethylthiocarbamoyloxyheptanol[9] (1.0 mmol) in dry CH_2Cl_2 (2 mL) was added and stirred for

another 1 h. Triethylamine (5.0 mmol) was added and the reaction mixture was slowly warmed to 0ºC, then quenched with water and extracted with CH_2Cl_2. The organic layer was washed with water, brine, and dried over Na_2SO_4. Concentration of the solvent under reduced pressure and purification of the residue by SiO_2 chromatography afforded pure aldehyde 7-dimethylthiocarbamoyloxyheptanal (97%). ^{1}H NMR ($CDCl_3$, 400 MHz) □ 1.31-1.47 (m, 4H), 1.61-1.78 (m, 4H), 2.43 (dt, 2H, J = 1.8, 7.2 Hz), 3.10 (s, 3H), 3.36 (s, 3H), 4.43 (t, 2H, J = 6.3 Hz), 9.77 (t, 1H, J = 1.8 Hz); MS *m/z* 217 (M^+). Anal. cald for $C_{10}H_{19}NO_2S$: C, 55.26; H, 8.81; found: C, 54.95; H, 8.65.

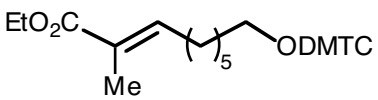


Methyl 2-chloro-9-dimethylthiocarbamoyloxynon-2(Z)-enoate (Scheme 1, Route c)
Following the procedure of Barma et al,[10] methyl trichloroacetate (1.0 mmol) and 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry THF (3 mL) were added at room temperature to a stirring suspension of anhydrous $CrCl_2$ (5.0 mmol) in dry THF (7 mL) under an argon atmosphere. After 30 min, the reaction mixture was quenched with water and extracted with Et_2O (3 □ 10 mL). The combined ethereal extracts were washed with water, brine, and dried over Na_2SO_4. Concentration of the solvent under reduced pressure and purification of the residue by SiO_2 chromatography afforded methyl 2-chloro-9-dimethylthiocarbamoyloxynon-2(Z)-enoate (99%). ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.33-1.55 (m, 6H), 1.67-1.77 (m, 2H), 2.32-2.40 (m, 2H),



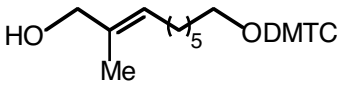
3.10 (s, 3H), 3.36 (s, 3H), 3.82 (s, 3H), 4.43 (t, 2H, J = 6.3 Hz), 7.07 (t, 1H, J = 7.2 Hz); MS *m/z* 307 (M^+). Anal. cald for $C_{13}H_{22}ClNO_3S$: C, 50.72; H, 7.20; found: C, 50.79; H, 7.24.

1-Dimethylthiocarbamoyloxynonan-3-ol (Scheme 1, Route d)
EtMgBr (1.05 mmol) was added to a stirring, 0ºC solution of 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry ether (5 mL) under an argon atmosphere. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 □ 10 mL). The ethereal extracts were washed with water, brine, and dried over Na_2SO_4. Concentration of the solvent under reduced pressure and purification of the residue by SiO_2 chromatography afforded 1-dimethylthiocarbamoyloxynon-3-ol (95%). ^{1}H NMR ($CDCl_3$, 300 MHz) □ 0.91 (t, 2H, J = 7.2 Hz), 1.28-1.52 (m, 10H), 1.65-1.74 (m, 2H), 3.07 (s, 3H), 3.33 (s, 3H), 3.45-3.53 (m, 1H), 4.40 (t, 2H, J = 6.3 Hz); MS *m/z* 247 (M^+). HRMS (CI, CH_4) calcd for $C_{12}H_{26}NO_2S$ (M^++1) *m/z* 248.1684, found 248.1677.



Ethyl 2-methyl-9-dimethylthiocarbamoyloxynon-2(E)-enoate (Scheme 1, Route e)

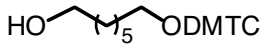
(Carbethoxyethylidene)triphenylphosphorane (1.2 mmol) was added to a stirring, room temperature solution of 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry CH_2Cl_2 (5 mL) under an argon atmosphere. After 12 h, all volatiles were removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 95% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.29 (t, 3H, J = 7.5 Hz), 1.35-1.49 (m, 6H), 1.68-1.76 (m, 2H), 1.82 (s, 3H), 2.13-2.21 (m, 2H), 3.10 (s, 3H), 3.36 (s, 3H), 4.18 (q, 2H, J = 7.5 Hz), 4.43 (t, 2H, J = 6.3 Hz), 6.74 (t, 1H, J = 7.5 Hz); MS *m/z* 301 (M^+). Anal. cald for $C_{15}H_{27}NO_3S$: C, 59.77; H, 9.03; found: C, 59.89; H, 9.17.



9-Dimethylthiocarbamoyloxynon-2(E)-en-1-ol (Scheme 1)

Route f: DIBAL-H (1.05 mmol) was added to a stirring, -78ºC solution of ethyl 2-methyl-9-dimethylthiocarbamoyloxynon-2(E)-enoate (1.0 mmol) in dry CH_2Cl_2 (5 mL) under an argon atmosphere. After 30 min, a few drops of MeOH were added and the reaction mixture was warmed to 0ºC followed by slow addition of 10% aq. HCl to pH 5. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 □ 10 mL). The combined organic layers were washed with water, brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 95% yield.

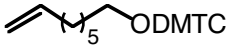
Route g: $LiAlH_4$ (1.0 mmol) was added to a stirring, room temperature solution of ethyl 2-methyl-9-dimethylthiocarbamoyloxynon-2(E)-enoate (1.0 mmol) in dry ether (5 mL) under an argon atmosphere. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl, filtered, and the filtrate was extracted with Et_2O (3 □ 10 mL). The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 93% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.30-1.41 (m, 6H), 1.50 (t, 1H, J = 4.5 Hz), 1.62 (s, 3H), 1.64-1.73 (m, 2H), 1.97-2.04 (m, 2H), 3.08 (s, 3H), 3.34 (s, 3H), 3.96 (d, 2H, J = 4.5 Hz), 4.40 (t, 2H, J = 6.3 Hz), 5.37 (t, 1H, J = 6.9 Hz); MS *m/z* 259 (M^+). HRMS (CI, CH_4) calcd for $C_{13}H_{26}NO_2S$ (M^++1) *m/z* 260.1684, found 260.1679.



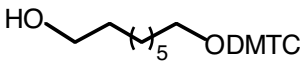
7-Dimethylthiocarbamoyloxyheptan-1-ol (Scheme 1, Route h)

$NaBH_4$ (1.0 mmol) was added to a stirring, 0ºC solution of 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry methanol (5 mL) under an argon atmosphere. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 □ 10 mL). The ethereal extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 99% yield identical with an authentic sample.[9] ^{1}H NMR ($CDCl_3$, 300 MHz) □ 1.32-1.43 (m, 6H), 1.52-1.61 (m, 2H), 1.67-1.77 (m, 2H), 3.10 (s, 3H), 3.36 (s, 3H), 3.64 (t, 2H, J = 13.2 Hz), 4.42 (t, 2H, J = 13.2 Hz); MS *m/z* 219 (M^+).

1-Dimethylthiocarbamoyloxyhept-7-ene (Scheme 1, Route i)

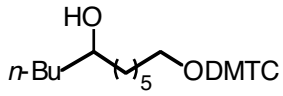


n-BuLi (1.5 mmol, 2.5M in hexane) was added to a stirring, -78ºC solution of Ph_3PCH_3Br (1.5 mmol) in dry ether (5 mL) under an argon atmosphere. After 30 min, 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry ether (1 mL) was added and the reaction mixture was slowly warmed to -20ºC and stirred for another 1h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 × 10 mL). The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 99% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31-1.45 (m, 6H), 1.67-1.77 (m, 2H), 1.99-2.08 (m, 2H), 3.10 (s, 3H), 3.35 (s, 3H), 4.43 (t, 2H, J = 6.3 Hz), 4.91-5.02 (m, 2H), 5.74-5.87 (m, 1H); MS *m/z* 215 (M^+). HRMS (CI, CH_4) calcd for $C_{11}H_{22}NOS$ (M^++1) *m/z* 216.1422, found 216.1421.



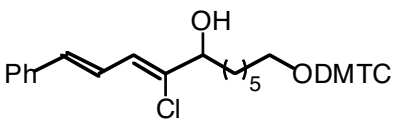
8-Dimethylthiocarbamoyloxyoctan-1-ol (Scheme 1, Route j)

Diborane dimethylsulfide complex (1.2 mmol) was added to a stirring, 0ºC solution of 1-dimethylthiocarbamoyloxyhept-7-ene in dry THF (5 mL) under an argon atmosphere. After 3 h, excess diborane was quenched with few drops of methanol and the reaction mixture was treated with 30% H_2O_2 (1 mL) and aq. NaOH (1 mL, 3 N). After 3 h at room temperature, the reaction mixture was extracted with Et_2O (3 × 10 mL). The combined ethereal extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 88% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30-1.41 (m, 1H), 1.51-1.59 (m, 2H), 1.67-1.75 (m, 2H), 3.10 (s, 3H), 3.35 (s, 3H), 3.63 (t, 2H, J = 6.3 Hz), 4.42 (t, 2H, J = 6.3 Hz); MS *m/z* 233 (M^+). HRMS (CI, CH_4) calcd for $C_{11}H_{24}NO_2S$ (M^++1) *m/z* 234.1528, found 234.1534.



1-Dimethylthiocarbamoyloxyundecan-7-ol (Scheme 1, Route k)

n-BuLi (1.05 mmol, 2.5 M in hexane) was added to a stirring, -78ºC solution of 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry THF (5 mL) under an argon atmosphere. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined ethereal extracts were washed with water, brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 95% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, 3H, J = 7.2 Hz), 1.24-1.48 (m, 14H), 1.67-1.76 (m, 2H), 3.09 (s, 3H), 3.35 (s, 3H), 3.53-3.62 (m, 1H), 4.12 (t, 2H, J = 6.3 Hz); MS *m/z* 275 (M^+). HRMS (CI, CH_4) calcd for $C_{14}H_{30}NO_2S$ (M^++1) *m/z* 276.1997, found 276.2001.



1-Dimethylthiocarbamoyloxy-8-chloro-11-phenylundec-8(Z),10(E)-diene-7-ol (Scheme 1, Route l)

Following the method of Barma *et al*,[11] (1,1,1-trichloro-4-phenylbut-3(E)-ene[11] (1.0 mmol) and 7-dimethylthiocarbamoyloxyheptanal (1.0 mmol) in dry THF (3 mL) were added to a stirring, room temperature suspension of anhydrous $CrCl_2$ (5.0 mmol) in dry THF (7 mL) under an argon atmosphere. After 12 h, the reaction mixture was quenched with water and extracted with Et_2O (3 × 10 mL). The combined ethereal extracts were washed with water, brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the title compound in 90% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32-1.44 (m, 6H), 1.64-1.78 (m, 4H), 2.14 (br s, 1H), 3.08 (s, 3H), 3.34 (s, 3H), 4.21-4.28 (m, 1H), 4.15 (t, 2H, J = 6.3 Hz), 6.50 (d, 1H, J = 10.5 Hz), 6.67 (d, 1H, J = 15.9 Hz), 7.10 (dd, 1H, J = 10.5, 15.9 Hz), 7.22-7.36 (m, 3H), 7.42-7.47 (m, 2H); MS *m/z* 381 (M^+). Anal. cald for $C_{20}H_{28}ClNO_2S$: C, 62.89; H, 7.39; found: C, 62.71; H, 7.24.

DMTC cleavage

General Method A. $NaIO_4$ (4.0 mmol) was added to a stirring, room temperature solution of DMTC protected alcohol (1.0 mmol) in MeOH/H_2O (10 mL, 20:1). The resulting solution was heated at 45ºC for 2 h, cooled to room temperature, and Na_2CO_3 (6.0 mmol) was added. Following another 2 h, the reaction mixture was extracted with Et_2O (3 × 6 mL) and the combined ethereal extracts were washed with water, brine, and dried over Na_2SO_4. All volatiles were removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the free alcohol (85-95%).

General Method B. The DMTC protected alcohol (1.0 mmol) was stirred at 50ºC with 30% H_2O_2 (1 mL) in THF or CH_3CN (2 mL). After 4 h, an aqueous solution of NaOH (2 M, 1 mL) was added and the stirring was continued at the same temperature overnight. The reaction mixture was cooled to room temperature, extracted with Et_2O (3 × 5 mL) and the combined ethereal extracts were washed with water (until the aqueous layer was negative to starch/iodine paper), brine, and dried over Na_2SO_4. All volatiles were removed under reduced pressure and the residue was purified by SiO_2 chromatography to give the free alcohol (80-90%).

References and Notes

1. Fyles, T. M.; Leznoff, C. C. *Can. J. Chem.* **1976**, *54*, 935.
2. Orita, A.; Hamada, Y.; Nakano, T.; Toyoshima, S.; Otera, J. *Chemistry A European Journal* **2001**, *7*, 3321.
3. Yu, C.; Liu, B.; Hu, L. *Tetrahedron Lett.* **2000**, *41*, 4281.
4. Mash, E. A.; Kantor, L. T. A.; Waller, S. C. *Synth. Commun.* **1997**, *27*, 507.

5. To a stirred suspension of NaH (1.1 mmol) in dry THF (3 mL) at 0ºC was added 1,7-heptanediol (1.0 mmol) in dry THF (1 mL) under an argon atmosphere. After 30 min, *n*-Bu_4NI (10 mol%) and *para*-methoxybenzyl bromide (1.2 mmol, prepared from *para*-methoxybenzyl alcohol (1.2 mmol) and PBr_3 (0.4 mmol) in dry ether (5 mL) at 0ºC) were successively added. The reaction mixture was slowly warmed to room temperature and, after 12 h, quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined ethereal extracts were washed with water, brine, and dried over Na_2SO_4. Removal of solvent under reduced pressure and purification of the residue over silica gel afforded 7-(4-methoxybenzyloxy)heptan-1-ol in 59% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31-1.41 (m, 6H), 1.51-1.63 (m, 4H), 3.43 (t,

2H, J = 6.6 Hz), 3.63 (t, 2H, J = 6.3 Hz), 3.80 (s, 3H), 4.43 (s, 2H), 6.81-6.90 (m, 2H), 7.21-7.27 (m, 2H); MS *m/z* 252 (M^+).
6. Sabitha, G.; Babu, R. S.; Rajkumar, M.; Srividya, R.; Yadav, J. S. *Org. Lett.* **2001**, *3*, 1149.
7. MEM-Cl (1.1 mmol) was added to a stirring 0°C solution of 1,7-heptanediol (1.0 mmol) and $^{i}Pr_2NEt$ (1.5 mmol) in dry CH_2Cl_2 (5 mL) under an argon atmosphere. The reaction mixture was slowly warmed to room temperature. After 6 h, the reaction was quenched with water and extracted in CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine and dried over Na_2SO_4. Removal of solvent under reduced pressure and purification of the residue over silica gel afforded 7-(2-methoxy-ethoxymethoxy)heptan-1-ol in 57% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31-1.39 (m, 6H), 1.51-1.62 (m, 4H), 3.39 (s, 3H), 3.51-3.69 (m, 8H), 4.70 (s, 2H); MS *m/z* 220 (M^+).
8. Crouch, R. D.; Mitten, J. V.; Span, A. R. *Tetrahedron Lett.* **1997**, *38*, 791.
9. 1,7-Heptanediol was converted to 7-dimethylthiocarbamoyloxyheptan-1-ol in 60% yield according to General Method A. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32-1.43 (m, 6H), 1.52-1.61 (m, 2H), 1.67-1.77 (m, 2H), 3.10 (s, 3H), 3.36 (s, 3H), 3.64 (t, 2H, J = 13.2 Hz), 4.42 (t, 2H, J = 13.2 Hz); MS *m/z* 219 (M^+). Anal. cald for $C_{10}H_{21}NO_2S$: C, 54.76; H, 9.65; found: C, 54.82; H, 9.88.
10. Barma, D. K.; Kundu, A.; Zhang, H.; Mioskowski, C.; Falck, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 3218.
11. Barma, D. K.; Baati, R.; Valleix, A.; Mioskowski, C.; Falck, J. R. *Org. Lett.* **2001**, *3*, 4237.