**Thionation with the reagent combination of phosphorus pentasulfide
and hexamethyldisiloxane**

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O-Ethyl benzenecarbothioic acid (6b). The reaction was carried out for 8 h according to general thionation procedure, method A, using **6a** (12.9 mL, 90 mmol), P₄S₁₀ (13.3 g, 30 mmol), HMDO (32 mL, 150 mmol), and xylene (90 mL). Workup and purification as for the methyl analog **5b** gave **6b** (10.9 g, 73%) as an orange liquid, bp 80 - 85 °C/0.4 Torr (lit.⁴² bp 74 - 75 °C/0.4 Torr). Purity by GC was 99.7%.

O-(1-Methylethyl) benzenecarbothioic acid (7b). The reaction was carried out for 8 h according to general thionation procedure, method A, using **7a** (8.13 mL, 50 mmol), P₄S₁₀ (7.4 g, 16.7 mmol), HMDO (17.7 mL, 83 mmol), and xylene (50 mL). Workup and purification as for the methyl analog **5b** gave **7b** (7.46 g, 83%) as an orange liquid, bp 54 -61 °C/0.01 Torr (lit.¹⁶ bp 105 - 110 °C/15 Torr). Purity by GC was 98.3%.

O-Methyl 4-nitrobenzenecarbothioic acid (9b). The reaction was carried out for 14 h according to general thionation procedure, method A, using **9a** (0.543 g, 3 mmol), P₄S₁₀ (0.333 g, 0.75 mmol), HMDO (1.06 mL, 5 mmol) and xylene (3 mL). Workup by reaction workup procedure, method A, using benzene as the extraction solvent, followed by flash column chromatography (5% toluene in hexane) and recrystallization from hexane gave **9b** (0.127 g, 21%) as yellow needles, mp 73 - 74 °C (lit.⁴³ mp 71 - 73 °C). Purity by HPLC was 99.4%.

O-Ethyl 1-naphthalenecarbothioic acid (10b). The reaction was carried out for 10 h according to general thionation procedure, method A, using **10a** (0.55 mL, 3 mmol), P₄S₁₀ (0.333 g, 0.75 mmol), HMDO (1.06 mL, 5 mmol) and xylene (3 mL). Workup by reaction workup procedure, method A, using benzene as the extraction solvent gave a crude solid which was dissolved in benzene, filtered through a pad of silica gel (1.5 g)

plus activated carbon (1 g) and recrystallization from pentane to give **10b** (0.566 g, 87%) as an orange solid, mp 43 - 44 °C (lit.¹⁶ mp 41 °C). Purity by HPLC was 98.1%.

O-Ethyl 3-phenyl-2-propenethioic acid (11b). The reaction was carried out for 4 h according to general thionation procedure, method A, using **11a** (6.72 mL, 40 mmol), P₄S₁₀ (4.45 g, 10 mmol), HMDO (14.2 mL, 67 mmol) and toluene (40 mL). Workup by reaction workup procedure, method A, using benzene as the extraction solvent gave a dark liquid, which was dissolved in hexane, filtered through a short pad of silica gel and distilled to give **11b** (5.50 g, 72%) as an orange liquid, bp 80 - 85 °C/0.01 Torr (lit.⁴⁴ bp 80 °C/0.2 Torr). Purity by GC was 99.8%.

O-Ethyl 2-cyano-3,3-diphenyl-2-propenethioic acid (12b). The reaction was carried out for 20 h according to general thionation procedure, method A, using **12a** (0.832 g, 3 mmol), P₄S₁₀ (0.333 g, 0.75 mmol), HMDO (1.06 mL, 5 mmol) and xylene (3 mL). Workup by reaction workup procedure, method A, using benzene as the extraction solvent gave a crude solid, which was purified by flash column chromatography (1:1 toluene/hexane) and recrystallized from 2-propanol to give **12b** (0.367 g, 42%) as orange needles, mp 127 - 128 °C (lit.²² mp 126 -128 °C). Purity by HPLC was 98.9%.

O-2-Naphthenyl ethanethioic acid (13b). The reaction was carried out for 17 h according to general thionation procedure, method A, using **13a** (0.558 g, 3 mmol), P₄S₁₀ (0.333 g, 0.75 mmol), HMDO (1.06 mL, 5 mmol) and ethylbenzene (3 mL). Workup by reaction workup procedure, method A, using benzene as the extraction solvent gave a dark solid. The products from three such runs were combined, purified by flash column chromatography (4:1 hexane/toluene), followed by filtration in toluene through a short column of activated carbon, and recrystallization from hexane to give **13b** (0.545 g, 30%)

as pale yellow plates, mp 95 - 96 °C (no physical properties were reported for this substance¹⁹). Purity by HPLC was 98.9%.

O-Ethyl heptanethioic acid (14b). The reaction was carried out for 4 h according to general thionation procedure, method A, using **14a** (9.12 mL, 50 mmol), P₄S₁₀ (5.56 g, 12.5 mmol), HMDO (17.7 mL, 83 mmol) and xylene (50 mL). Workup by reaction workup procedure, method A, using benzene as the extraction solvent, followed by distillation gave **14b** (6.50 g, 75%) as a pale yellow liquid, bp 38 - 42 °C/0.01 Torr (lit.¹⁶ bp 80 - 85 °C/12 Torr). Purity by GC was 98.5%.

Tetrahydro-2H-pyran-2-thione (19b). The reaction was carried out for 45 min according to general thionation procedure, method A, using **19a** (4.64 mL, 50 mmol), P₄S₁₀ (5.56 g, 12.5 mmol), HMDO (17.7 mL, 83 mmol) and acetonitrile (50 mL). Workup and purification as for the isomeric thionolactone **18b** gave **19b** (3.79 g, 65%) as a yellow liquid, bp 86 - 87 °C/0.4 Torr (no bp was reported for this substance⁴⁵). Purity by GC was 99.5%.

2-Oxepanethione (20b). The reaction was carried out for 40 min according to general thionation procedure, method A, using **20a** (5.60 mL, 50 mmol), P₄S₁₀ (5.56 g, 12.5 mmol), HMDO (17.7 mL, 83 mmol) and acetonitrile (50 mL). Workup and purification as for thionolactone **18b** gave **20b** (5.01 g, 77%) as a yellow liquid, bp 55 - 61 °C/0.02 Torr (lit.⁴⁶ bp 52 °C/0.1 Torr). GC analysis showed no detectable impurities.

2-Oxocanethione (21b). The reaction was carried out for 45 min according to general thionation procedure, method A, using **21a** (0.365 mL, 3 mmol), P₄S₁₀ (0.333 g, 0.75 mmol), HMDO (1.06 mL, 5 mmol) and acetonitrile (3 mL). Workup by reaction workup procedure, method C, using benzene as extraction solvent gave an orange oil

which was dissolved in 3:1 hexane/benzene and filtered through silica gel. Recrystallization from pentane gave **21b** (0.317 g, 73%) as large pale yellow needles, mp 48 - 49 °C (lit.⁴⁷ mp 48.0 - 48.5 °C). Purity by GC was 99.4%.

Oxacycloheptadecane-2-thione (22b). The reaction was carried out for 4 h according to general thionation procedure, method A, using **22a** (0.763 g, 3 mmol), P₄S₁₀ (0.333 g, 0.75 mmol), HMDO (1.06 mL, 5 mmol) and xylene (3 mL). Workup by reaction workup procedure, method A, using benzene as extraction solvent, followed by distillation in a Kugelrohr apparatus gave **22b** (0.696 g, 86%) as a pale yellow oil, bp 72 - 86 °C (bath temperature)/0.01 Torr (no bp was reported for this substance⁴¹). Purity by GC was 99.9%.

5-Ethyl-3H-1,2-dithiole-3-thione (24b). The reaction was carried out for 2 h according to general thionation procedure, method B, using **23b** (3.58 mL, 25 mmol), P₄S₁₀ (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). Workup by reaction workup procedure, method A, using toluene as extraction solvent gave a dark oil, which was dissolved in benzene, filtered through a column of silica gel (11 g) plus activated carbon (7.4 g), and distilled to give **24b** (3.00 g, 74%), as a red liquid, bp 96 - 99 °C/0.02 Torr, solidifying to an orange solid, mp 18 - 20 °C (lit.⁴⁹ mp 21 °C). Purity by HPLC was 99.1%.

5-Phenyl-3H-1,2-dithiole-3-thione (24c). The reaction was carried out for 1 h according to general thionation procedure, method B, using **23c** (4.44 mL, 25 mmol), P₄S₁₀ (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). Workup by reaction workup procedure, method B, using toluene as extraction solvent gave a dark oil, which was dissolved in toluene, filtered through a

column of silica gel (11 g) plus activated carbon (10 g), and recrystallized from CCl_4 to give **24c** (3.70 g, 70%), mp 125 - 126 °C (lit.⁴⁹ mp 125 °C). Purity by HPLC was 99.0%.

5-(1,1-Dimethylethyl)-3H-1,2-dithiole-3-thione (24d). The reaction was carried out for 8 h according to general thionation procedure, method B, using **23d** (4.45 mL, 25 mmol), P_4S_{10} (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). Workup by reaction workup procedure, method B, using toluene as the extraction solvent, followed by filtration through silica gel plus activated carbon, as for the 5-ethyl derivative **24b**, and recrystallization from hexane gave **24d** (3.96 g, 83%), mp 70 - 71 °C (lit.⁵⁰ mp 70 °C). Purity by HPLC was 99.7%.

5-Tricyclo[3.3.1.1^{3,7}]dec-1-yl-3H-1,2-dithiole-3-thione (24e). The reaction was carried out for 5 h according to general thionation procedure, method B, using **23e** (0.246 mL, 1 mmol), P_4S_{10} (0.267 g, 0.6 mmol), sulfur (0.032 g, 1 mg atom), HMDO (0.64 mL, 3 mmol) and xylene (2 mL). Workup by reaction workup procedure, method A, using ethyl acetate as extraction solvent gave a brown solid which was purified by flash chromatography (3:1 hexane/toluene) and recrystallized from ethyl acetate (first crop) and cyclohexane (second crop) to give **24e** (0.187 g, 70%) as a yellow solid, mp 141 - 142 °C. Purity by HPLC was 98.0%. ^1H NMR (CDCl_3) δ 1.76 (m, 6H), 2.00 (s, 6H), 2.13 (s, 3H), 7.13 (s, 1H); ^{13}C NMR (CDCl_3) δ 28.73, 36.28, 40.91, 43.99, 136.03, 189.47, 215.86. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{S}_3$: C, 58.16; H, 6.01; S, 35.83. Found: C, 58.27; H, 6.10; S, 35.70.

(3-Thioxo-3H-1,2-dithiol-5-yl)ferrocene (24f). Because of its photosensitivity, the preparation and purification of **24f** was carried out under subdued light. The thionation reaction was conducted for 30 min according to general thionation procedure,

method B, using **23f** (0.900 g, 3 mmol), P₄S₁₀ (0.800 g, 1.8 mmol), sulfur (0.096 g, 3 mg atom), HMDO (1.9 mL, 9 mmol) and xylene (6 mL). Workup by reaction workup procedure, method A, using benzene as extraction solvent gave a brown solid which was purified by flash chromatography (1:1 hexane/toluene) and recrystallized from benzene (first crop) and cyclohexane (second crop) to give **24f** (0.349 g, 37%), mp 157 - 159 °C. Purity by HPLC was 99.1%. ¹H NMR (CDCl₃) δ 4.24 (s, 5H), 4.61 (t, *J* = 2 Hz, 2H), 4.73 (t, *J* = 2 Hz, 2H), 7.21 (s, 1H); ¹³C NMR (CDCl₃) δ 68.96, 71.41, 72.47, 75.11, 133.79, 176.96, 214.05. Anal. Calcd for C₁₃H₁₀FeS₃: C, 49.06; H, 3.17; S, 30.22. Found: C, 48.99; H, 3.28; S, 30.38.

4,5-Dimethyl-3H-1,2-dithiole-3-thione (24g). The reaction was carried out for 2 h according to general thionation procedure, method B, using **23g** (3.67 mL, 25 mmol), P₄S₁₀ (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). Workup and filtration through silica gel plus activated carbon, as for the 5-ethyl derivative **24b**, followed by recrystallization from cyclohexane gave **24g** (3.16 g, 78%), mp 95 - 96 °C (lit.⁵⁰ mp 95 - 96 °C). Purity by HPLC was 99.7%.

5-Methyl-4-(1-methylethyl)-3H-1,2-dithiole-3-thione (24h). The reaction was carried out for 2 h according to general thionation procedure, method B, using **23h** (4.58 mL, 25 mmol), P₄S₁₀ (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). Workup by reaction workup procedure, method B, using benzene as the extraction solvent, and filtration through silica gel plus activated carbon, as for the 5-ethyl derivative **24b**, followed by distillation gave **24h** (3.42 g, 72%), bp 99 - 103 °C/0.06 Torr, solidifying to a solid, mp 35 - 38 °C (lit.⁵⁰ mp 37 - 38 °C). Purity by GC was 97.7%.

4,5,6,7-Tetrahydro-3H-1,2-benzodithiole-3-thione (24i). The reaction was carried out for 1 h according to general thionation procedure, method B, using **23i** (4.21 mL, 25 mmol), P₄S₁₀ (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). The reaction mixture was worked up by reaction workup procedure, method B, using ethyl acetate as the extraction solvent. The resulting crude solid was sublimed and recrystallized from CCl₄ to give **24i** (3.96 g, 84%), mp 102 - 103 °C (lit.⁵¹ mp 102 °C). Purity by HPLC was 99.5%.

5,6-Dihydrocyclopenta-1,2-dithiole-3(4H)-thione (3). The reaction was carried out for 2 h according to general thionation procedure, method B, using **23j** (3.73 mL, 25 mmol), P₄S₁₀ (6.67 g, 15 mmol), sulfur (0.802 g, 25 mg atom), HMDO (16 mL, 75 mmol) and xylene (50 mL). Workup by reaction workup procedure, method A, using dichloromethane as extraction solvent yielded a dark solid which was sublimed and recrystallized from CCl₄ to give **3** (2.97 g, 68%), mp 122 - 123 °C (lit.⁵¹ mp 122 - 123 °C). Purity by HPLC was 99.3%.

3-Pyridinecarbothioamide (26b). Amide **26a** (0.366 g, 3 mmol), P₄S₁₀ (0.245 g, 0.55 mmol), HMDO (1.06 mL, 5 mmol), and HMPA (3 mL) were stirred at 80 °C for 23 h. The resulting pale yellow solution was cooled to room temperature, toluene (2 mL) was added, and the mixture poured with stirring into water (30 mL) containing Na₂HPO₄ (0.625 g, 4.4 mmol). After stirring at 0 °C for 30 min, the crystalline solid was filtered, washed with water, 1:1 toluene/hexane, and hexane to give **26b** (0.287 g, 69%) as pale yellow needles, mp and mixed mp with an authentic sample 188 - 189 °C. HPLC showed a purity of 99.2%.

N-Phenylethanethioamide (27b). Amide **27a** (0.406 g, 3 mmol), P_4S_{10} (0.253 g, 0.57 mmol), HMDO (1.06 mL, 5 mmol), and dichloromethane (3 mL) were stirred at room temperature for 4 h. Workup as for **25b** and recrystallization from benzene/hexane gave **27b** (0.383 g, 84%) as large yellow needles, mp 75 - 76 °C (lit.¹⁵ mp 76 °C). HPLC showed no detectable impurities.

4-(1-Thioxoethyl)-morpholine (29b). The thionation reaction was carried out for 45 min according to general thionation procedure, method B, using amide **29a** (0.347 mL, 3 mmol), P_4S_{10} (0.245 g, 0.55 mmol), HMDO (1.06 mL, 5 mmol), and chloroform (3 mL). Workup by reaction workup procedure, method D, using dichloromethane as the eluent, followed by recrystallization from cyclohexane gave **29b** (0.409 g, 94%) as white needles, mp and mixed mp with an authentic sample 90 - 91 °C. HPLC showed no detectable impurities.

2-Pyrrolidinethione (31b). Lactam **31a** (0.464 g, 6 mmol), P_4S_{10} (0.489 g, 1.1 mmol), HMDO (2.1 mL, 10 mmol), and dichloromethane (6 mL) were stirred at room temperature for 3 h. Workup as for **25b** and recrystallization from benzene/cyclohexane gave **31b** (0.502 g, 83%) as white needles, mp and mixed mp with an authentic sample 112 - 113 °C. HPLC showed greater than 99.9% purity.

Hexahydro-2H-azepine-2-thione (32b). Lactam **32a** (0.34 g, 3 mmol), P_4S_{10} (0.245 g, 0.55 mmol), HMDO (1.06 mL, 5 mmol), and dichloromethane (3 mL) were stirred at room temperature for 3 h. Workup by reaction workup, method A, using ethyl acetate as the extraction solvent, followed by solution of the crude thiolactam in dichloromethane, filtration through a short silica gel column and recrystallization from

isopropyl ether gave **32b** (0.355 g, 92%), mp and mixed mp with an authentic sample 106 - 107 °C. HPLC showed a purity of 99.6%.

(1R,4R)-1,7,7-Trimethylbicyclo[2,2,1]heptane-2-thione (35b). The thionation reaction was carried out for 12 h according to general thionation procedure, method A, using (1R)-(+)-camphor **35a** (2.74 g, 18 mmol), P₄S₁₀ (1.47 g, 3.3 mmol), HMDO (6.4 ml, 30 mmol) and toluene (18 mL). The reaction was worked up by reaction workup procedure, method D, using pentane as the eluting solvent. Recrystallization from methanol at -78 °C gave **35b** (1.64 g, 54%) as a waxy orange solid, mp 138 - 140 °C (lit.⁵² mp 135 - 136 °C). GC showed a purity of 99.9%.