Supplementary Material (ESI) for Chemical Communications

Phosphine-Catalyzed Disulfide Metathesis

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General Methods

Reagents were purchased from Sigma-Aldrich, Merck and Lancaster and used as received. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 (100) MHz and/or Bruker Avance DMX 500 at 500 (125) MHz respectively. Chemical shifts are reported as δ values (ppm) with $CDCl_3$ (^{1}H-NMR δ 7.26, ^{13}C-NMR δ 77.16) or DMSO-d6 (^{1}H-NMR δ 2.50, ^{13}C-NMR δ 39.52) as an internal standard. *J* values are given in Hertz (Hz). ^{31}P-NMR spectra were recorded on a Bruker Avance DMX 500 at 200 MHz. GC-MS analysis were performed on a DB-wax column (J&W Scientific, 30m, 0.25 mm id and 0.15 μm film thickness) connected to a Finnigan SSQ 7000 mass spectrometer (EI, 70 eV, ion source temperature: 150°C).

Tricyclohexylphosphine (PCy_3).

Air exposed PCy_3 was analyzed by quantitative ^{31}P-NMR (200 MHz, $CDCl_3$) δ 9.16 (PCy_3, 55%), δ 48.25 ($OPCy_3$, 45%).

Preparation of tricyclohexylphosphine oxide ($OPCy_3$).

Tricyclohexylphosphine (PCy_3) (20 mg, 0.07 mmol) was dissolved in Toluene (5 ml). The mixture was then heated for 2h at 80°C with air bubbling. Solvent evaporation under reduced pressure led to a white powder. ^{31}P-NMR (200 MHz, $CDCl_3$) δ 48.25 ($OPCy_3$).

Methyl disulfide 1. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.40 (6H, s). ^{13}C-NMR (500 MHz, $CDCl_3$) δ 22.14. MS (EI) m/z 94.1.

Ethyl disulfide 2a. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.31 (6H, t, J = 7.25 Hz), 2.67 (4H, q, J = 7.25 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$) δ 14.48, 32.91. MS (EI) m/z 122.1.

Propyl disulfide 2b. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.99 (6H, t, J = 7.3 Hz), 1.70 (4H, sixtet, J = 7.3 Hz), 2.66 (4H, t, J = 7.3 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$) δ 13.20, 22.58, 41.25.

Phenyl disulfide 2c. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.20 (4H, t, J = 7.25 Hz), 7.28 (2H, t, J = 7.56 Hz), 7.48 (4H, d, J = 7.25 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$) δ 127.30, 127.66, 129.20, 137.17.

Allyl disulfide 2d. ^{1}H-NMR (500 MHz, DMSO-d6) δ 3.38 (4H, d, J = 7.35 Hz), 5.15 (2H, m), 5.18 (2H, dq, J = 1.35 Hz, J = 16.9 Hz), 5.80 (2H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 40.87, 118.61, 133.61.

Benzyl disulfide 2e. ^{1}H-NMR (500 MHz, DMSO-d6) δ 3.74 (4H, s), 7.28 (6H, m), 7.33 (4H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 41.61, 127.29, 128.39, 129.36, 137.29.

Ethyl methyl disulfide 3a. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.25 Hz), 2.38 (3H, s), 2.70 (2H, q, J = 7.25 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$) δ 14.48, 23.49, 32.03. MS (EI) m/z 108.

Methyl propyl disulfide 3b. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.98 (3H, t, J = 7.25 Hz), 1.70 (2H, sixtet, J = 7.25 Hz), 2.38 (3H, s), 2.67 (2H, t, J = 7.25 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$) δ. 13.20, 22.58, 23.44, 40.42.

Methyl phenyl disulfide 3c. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.42 (3H, s), 7.21 (2H, t, J = 7.25 Hz), 7.32 (1H, t, J = 7.25 Hz), 7.52 (2H, d, J = 7.25 Hz). ^{13}C-NMR (500 MHz, $CDCl_3$) δ 22.98, 126.95, 127.67, 129.10, 137.00.

Allyl methyl disulfide 3d. ^{1}H-NMR (500 MHz, DMSO-d6) δ 2.39 (3H, s), 3.40 (2H, m), 5.15 (1H, m), 5.21 (1H, dq, J = 1.30 Hz, J = 16.95 Hz), 5.84 (1H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 22.52, 40.21, 118.49, 133.74.

Benzyl methyl disulfide 3e. ^{1}H-NMR (500 MHz, DMSO-d6) δ 2.17 (3H, s), 3.98 (2H, s), 7.28 (3H, m), 7.32 (2H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 22.13, 41.31, 127.21, 128.36, 129.30, 137.55.

Ethyl propyl disulfide 4a. ^{1}H-NMR (500 MHz, DMSO-d6) δ 0.94 (3H, t, J = 7.25 Hz), 1.25 (3H, t, J = 7.25 Hz), 1.64 (2H, sixtet, J = 7.25 Hz), 2.68 (2H, t, J = 7.25 Hz), 2.70 (2H, q, J = 7.25 Hz). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 12.70, 14.22, 21.86, 31.74, 39.99.

Allyl ethyl disulfide 4b. ^{1}H-NMR (500 MHz, DMSO-d6) δ 1.24 (3H, t, J = 7.30 Hz), 2.70 (2H, q, J = 7.30 Hz), 3.37 (2H, m), 5.13 (1H, m), 5.20 (1H, dq, J = 1.35 Hz, J = 16.95 Hz), 5.80 (1H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 14.26, 31.56, 41.10, 118.44, 133.68.

Benzyl ethyl disulfide 4c. ^{1}H-NMR (500 MHz, DMSO-d6) δ 1.16 (3H, t, J = 7.25 Hz), 2.49 (2H, q, J = 7.25 Hz), 3.95 (2H, s), 7.28 (3H, m), 7.33 (2H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 14.10, 31.21, 42.19, 127.20, 128.33, 129.25, 137.56.

Allyl propyl disulfide 5a. ^{1}H-NMR (500 MHz, DMSO-d6) δ 0.94 (3H, t, J = 7.30 Hz), 1.63 (2H, sixtet, J = 7.15 Hz), 2.68 (2H, q, J = 7.15 Hz), 3.36 (2H, dt, J = 1 Hz, J = 4.85 Hz), 5.14 (1H, m), 5.21 (1H, dq, J = 1.30 Hz, J = 16.95 Hz), 5.80 (1H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 12.75, 21.84, 39.79, 41.02, 118.43, 133.68.

Benzyl propyl disulfide 5b. ^{1}H-NMR (500 MHz, DMSO-d6) δ 0.86 (3H, t, J = 7.30 Hz), 1.54 (2H, sixtet, J = 7.30 Hz), 2.44 (2H, t, J = 7.1 Hz), 3.95 (2H, s), 7.28 (3H, m), 7.33 (2H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 12.75, 21.66, 39.28, 42.13, 127.18, 128.32, 129.25, 137.57.

Allyl benzyl disulfide 6a. ^{1}H-NMR (500 MHz, DMSO-d6) δ 3.14 (4H, d, J = 7.35 Hz), 3.96 (2H, s), 5.10 (4H, m), 5.75 (2H, m), 7.28 (3H, m), 7.34 (2H, m). ^{13}C-NMR (500 MHz, DMSO-d6) δ. 40.44, 41.97, 118.57, 127.24, 128.36, 133.34, 137.40.

Reversibility control experiment

1 and **2a** (350 mM of each) were mixed together in $CDCl_3$ and in presence of 5 mol% of PCy_3. After equilibration of the reaction (**1**, **2a** and **3a** were present in solution with a ratio 1:1:2.2 respectively, Figure S1a-b), **2b** (350 mM) was added. A new equilibration was formed, indicating reversibility of the reaction (Figure S1c-d).

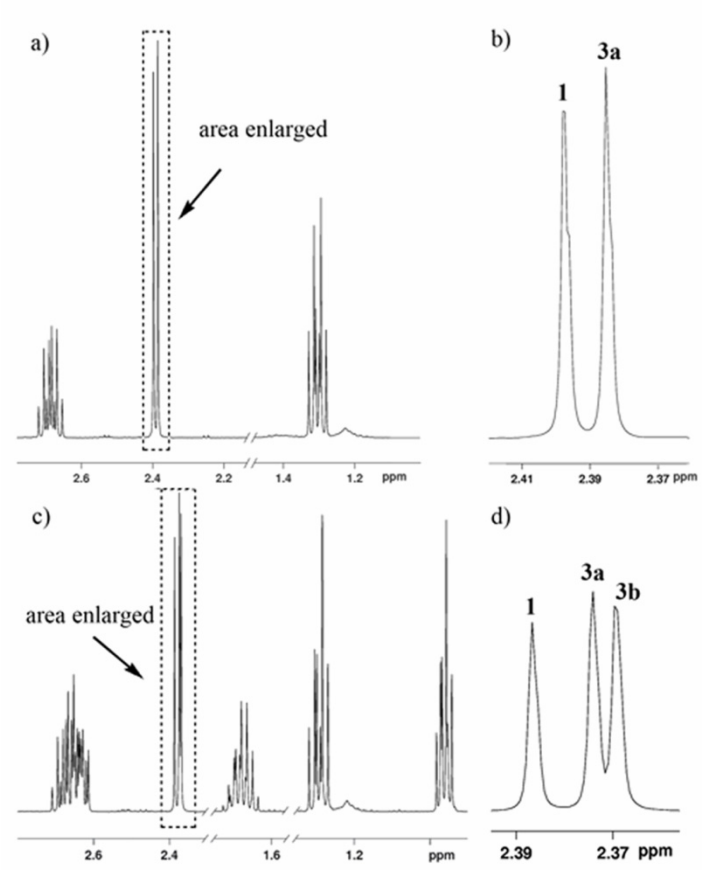

Figure S1: ^{1}H-NMR spectra of the reaction mixture: a) after equilibration between **1** and **2a**; b) enlarged area of the methyl region of a); c) after equilibration between **1**, **2a** and **2b** (50 min); d) enlarged area of the methyl region. Compound numbering as in Table 1.

GC-MS analysis of 1 and 2a after reaction.

A GC-MS analysis was performed in order to confirm the ^{1}H-NMR results and monitor the presence of the two symmetrical disulfides and the unsymmetrical disulfide resulting from the exchange reaction. A mixture of methyl disulfide **1** (0.23 mmol) and ethyl disulfide **2a** (0.23 mmol) in benzene and in presence of 5 mol% of PCy_3 was injected after 11 days of reaction (around 150 ng) for separation on a DB-wax column. The following temperature program was used: 40 ^oC (1 min), 5 ^oC/min, 225 ^oC (15 min). Injection was 220 ^oC (split closed 30 s), and the transfer was held at 230 ^oC. The GC chromatogram confirmed the ^{1}H-NMR results. The retention time of 5.41 min, 6.95 min and 8.60 min (see Figure S1) correspond to **1**, ethyl methyl disulfide **3a** and **2a** respectively. The reaction products were clearly identified by Mass Spectrometry (see Figure S2, Figure S3 and Figure S4).

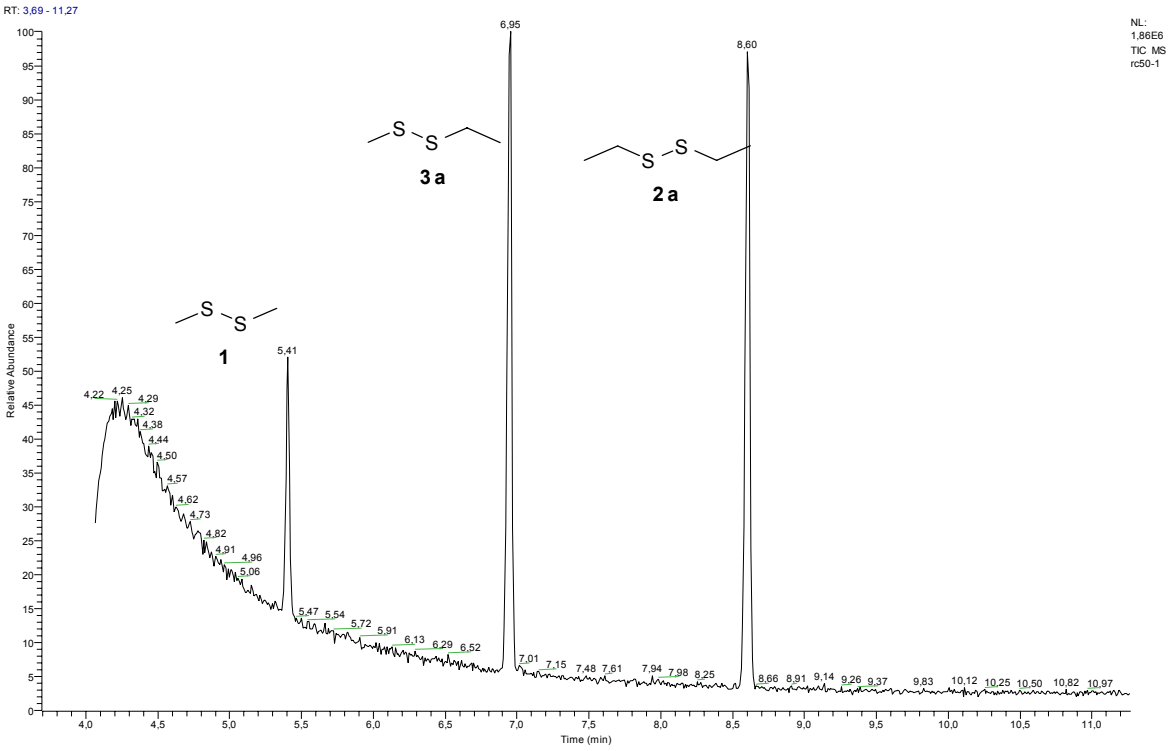

Figure S2: GC chromatogram of a mixture of **1** (0.23 mmol), **2a** (0.23 mmol) and PCy_3 (5 mol%) in benzene after 11 days. The three picks with a retention time (RT) of 5.41 min, 6.95 min and 8.60 min correspond to **1**, **3a** and **2a** respectively.

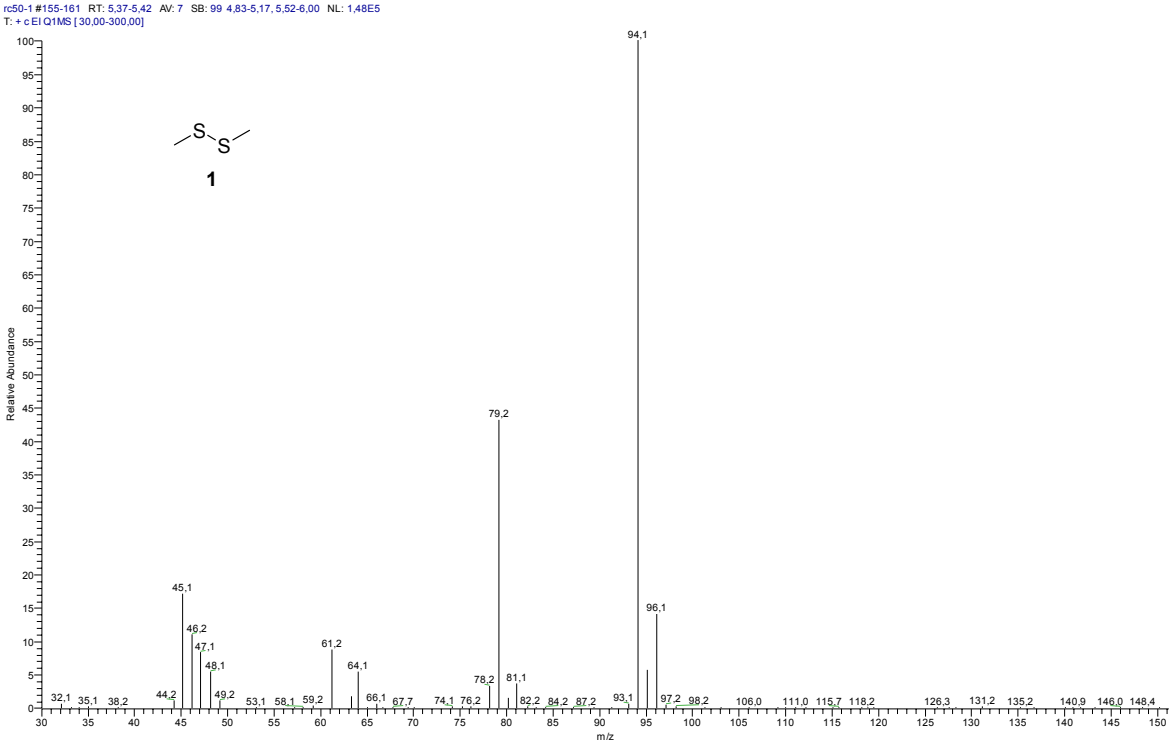

Figure S3: MS spectrum of methyl disulfide **1** (retention time: 5.41 min)

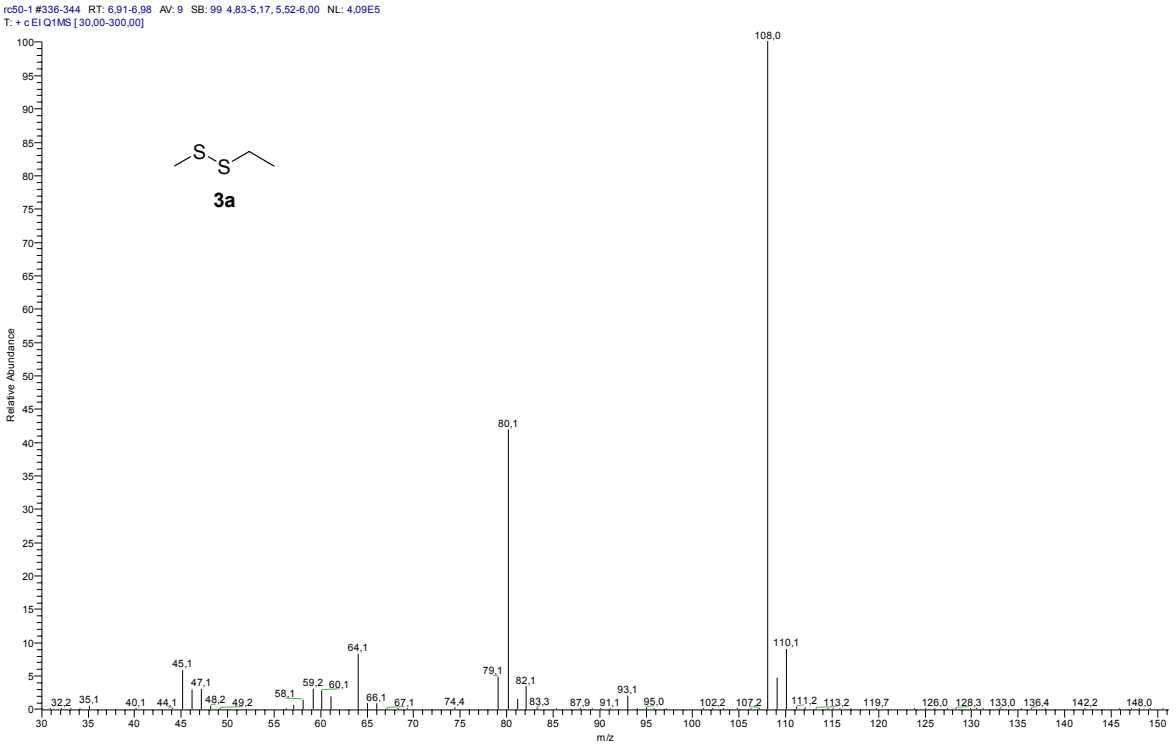

Figure S4: MS spectrum of ethyl methyl disulfide **3a** (retention time: 6.95 min)

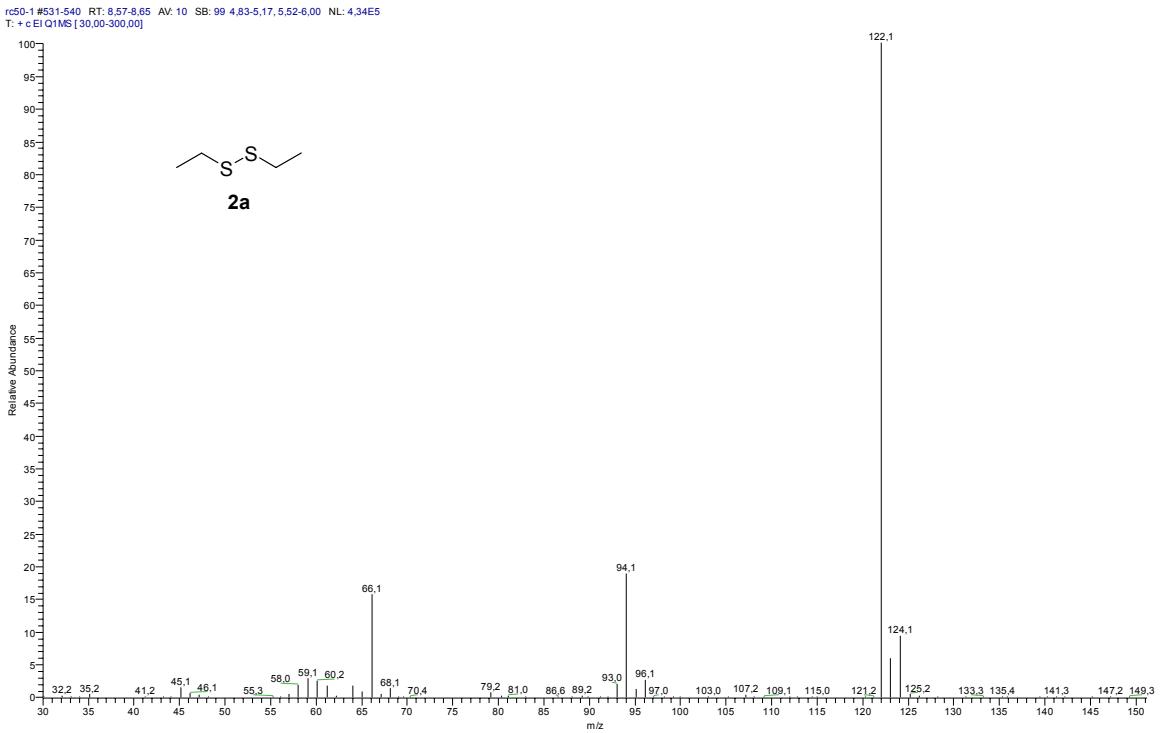

Figure S5: MS spectrum of ethyl disulfide **2a** (retention time: 8.60 min)