Supporting Information for

Oxygen mediated conversion of $\{Fe(NO)_2\}^9$ dinitrosyl iron complexes to Roussin's red esters

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General considerations. Unless otherwise specified, all reactions and manipulations were carried out under an inert atmosphere of nitrogen using an MBraun glovebox (< 0.1 ppm O_2, < 0.1 ppm H_2O) or standard Schlenk line techniques. Diphenyldisulfide (PhSSPh), di-*tert*-butyldisulfide (^{t}BuSS^{t}Bu), diethyldisulfide (EtSSEt), triphenylphosphine sufide (Ph_3PS), and PPNCl were purchased from Aldrich and used as received. Solvents were purified by passage over an alumina column under an Ar atmosphere and stored over activated molecular sieves (4Å). Diethyl ether and tetrahydrofuran were additionally dried over sodium prior to use. Nitric oxide (Matheson, 99%) was purified following the literature method,[1] in which the NO gas stream is passed through an Ascarite column, and then distilled at –80 °C.

Physical Measurements. Unless otherwise specified, samples for spectroscopic measurement were prepared inside a nitrogen glovebox. Infrared spectra were recorded on a Bruker Tensor 27 FT- IR spectrometer equipped with a Fiber Optic Immersion Probe. UV-visible spectra were recorded on a Varian Cary 50 Bio spectrometer. GC-MS data were recorded on a Hewlett-Packard (Agilent) GCD 1800C GC-MS spectrometer. Elemental microanalyses for C, H, and N were performed by Columbia Analytical Services (Tucson, AZ). For complex **6**, residual solvent is present in the microanalysis and is consistent with what is observed in the ^{1}H NMR spectrum of this compound.

Synthesis. The compounds Ph_3CSNO,[2] $(PPN)_2[FeCl_4]$,[3] $(Et_4N)_2[FeCl_4]$,[3] $(PPN)[Fe(S^tBu)_2(NO)_2]$ (**1**),[4] $(PPN)[Fe(SEt)_2(NO)_2]$ (**2**),[5] and $(Et_4N)[Fe(SPh)_2(NO)_2]$ (**3**)[6] were prepared according to published literature procedures or slight modifications thereof.

General reaction of (cation)[Fe(SR)$_2$(NO)$_2$] (1: cation = PPN, R = ^{t}Bu; 2: cation = PPN, R = Et; 3: cation = Et$_4$N, R = Ph) and O$_{2(g)}$. A solution of $(PPN)[Fe(S^tBu)_2(NO)_2]$ (65 mg, 0.078 mmol) in 4 mL of dichloromethane was transferred to a 10 ml Schlenk flask covered in Al-foil, to which $O_{2(g)}$ (19.5 mL, 0.78 mmol) was injected via gas-tight syringe at room temperature. The reaction was allowed to proceed for 1 h over which time the colour of the solution changed from red-brown to brown. The volatiles were removed *in vacuo* and the residue was dissolved in 0.5 mL of MeCN. This solution was cooled to -38 °C for 12 hours over which time a dark brown fine precipitate formed. The solid was dissolved in pentane and filtered through silica. The filtrate was cooled to -38 °C for 2 days over which time a dark brown microcrystalline precipitate formed This precipitate was filtered and washed with cold Et_2O to afford 9.2 mg (0.022 mmol, 60%) of $Fe_2(S^tBu)_2(NO)_4$. Physical characterization (UV-vis and IR spectroscopy) was in good agreement with previously reported data[7] (Figures S2-S3).

In an analogous manner, reaction of complexes (**2**) and (**3**) with $O_{2(g)}$ led to formation of the corresponding $Fe_2(SR)_2(NO)_4$ in a 63% and 70% yield, respectively. Physical characterization (UV-vis and IR spectroscopy) confirmed formation of $Fe_2(SEt)_2(NO)_4$[8] (Figures S4-S5) and $Fe_2(SPh)_2(NO)_4$[6] (figures S6-S7), respectively.

Preparation of authentic Fe$_2$(SR)$_2$(NO)$_4$ (4: R = ^{t}Bu; 5: R = Et; 6: R = Ph).[6-8] $Fe_2(S^tBu)_2(NO)_4$ (**4**), was prepared according to a previously reported procedure. Briefly, $[Fe(S^tBu)_4](NEt_4)_2$ (100 mg, 0.149 mmol) was dissolved in 5 mL MeCN.

To this solution was added $NOBF_4$ (34.7 mg, 0.297 mmol). The reaction was allowed to proceed for 1 h. The solution was concentrated to 2 mL *in vacuo* and then stored at -38 ºC for 12 h to yield 25 mg (0.052 mmol, 70%) of black crystalline solid. Spectroscopic characterization was consistent with that previously reported and bulk purity was confirmed via combustion analysis. Anal. Calc. for $C_8H_{18}Fe_2N_4O_4S_4$: C 23.43, H 4.42, N 13.66. Found: C 23.74, H 4.30, N 13.12. Compound **4** has been previously crystallographically characterized.[7]

Compounds $Fe_2(SEt)_2(NO)_4$ (**5**) and $Fe_2(SPh)_2(NO)_4$ (**6**) were prepared in an analogous manner, although the preparation of (**6**) involved an additional purification in which the black crystalline material was washed with pentane and then recrystallized from dichloromethane. Bulk purity was confirmed via combustion analysis, where the presence of the solvate molecules co-crystallized with **6** was further confirmed by ^{1}H NMR spectroscopy. (**5**): Anal. Calc. for $C_4H_{10}Fe_2N_4O_4S_4$: C 13.57, H 2.85, N 15.83. Found: C 13.91, H 2.83, N 15.51. (**6**): Anal. Calc. for $C_{12}H_{10}Fe_2N_4O_4S_4$•$CH_2Cl_2$•$0.75C_5H_{12}$: C 34.15, H 3.59, N 9.41. Found: C 34.44, H 4.01, N 10.06. Complexes **5** and **6** have been previously crystallographically characterized.[9,10]

Disulfide formation and quantification (GC-MS analysis). Calibration curves were prepared for ^{t}BuSS^{t}Bu, EtSSEt, and PhSSPh by using EtSSEt (1.4 mM), ^{t}BuSS^{t}Bu (0.50 mM), and Ph_3PS (0.82 mM), respectively as internal standards. Calibration curves (Figures S2-S4) were based on the ratio of peak area of the analyte to that of the internal standard. A typical experiment is described below.

Compound (**1**) was allowed to react with 10 eq. of $O_{2(g)}$ for 1 h. The reaction mixture was purified by passage through a silica column, which was washed with an additional 1.0 mL of CH_2Cl_2. The washing were collected and combined with the original filtrate. To account for volume changes due to washing, as well as solvent evaporation during the course of the experiment, the total volume of the combined filtrates was then measured and used to calculate a correction factor for the concentration of compound (**1**). A 0.2 mL aliquot of the filtered reaction mixture was added to 1.3 mL of a 1.6 mM EtSSEt solution in CH_2Cl_2. This solution (1.4 mM EtSSEt, 21 mM initial (**1**)) was used without further modification for GC-MS analysis. Using this method of analysis it was found that ^{t}BuSS^{t}Bu was formed in a 20% yield. A 100% yield would have corresponded to ½ eq. of ^{t}BuSS^{t}Bu per 1 eq. of compound (**1**).

In an analogous manner, the EtSSEt and PhSSPh yields were found to be 80% and 50%, respectively.

Conversion of $(Et_4N)[Fe(SPh)_2(NO)_2]$ (3) into $[Fe_2(\mu\text{-}SPh)_2(NO)_4]$. UV-vis spectroscopy. A 0.15 mM solution of (**3**) was prepared in CH_2Cl_2. A 3.0 mL aliquot was transferred to a quartz cell (1 cm path length) equipped with a Schlenk arm and sealed with a rubber septum. $O_{2(g)}$ was bubbled through the solution which caused a decrease in the absorbencies at 480 nm and 800 nm and a concurrent increase in the absorbance at 400 nm as monitored for 2 h (Figure 1). The final product (red trace, Figure 1) is consistent with formation of $[Fe_2(\mu\text{-}SPh)_2(NO)_4]$.[6]

Conversion of $(Et_4N)[Fe(S^tBu)_2(NO)_2]$ (1) into $[Fe_2(\mu\text{-}S^tBu)_2(NO)_4]$. IR spectroscopy.
A 40 mM solution of (**1**) was prepared in CH_2Cl_2. $O_{2(g)}$ was bubbled through the solution at room temperature and the spectral changes were monitored for 2 h.

During this time, the ν_{NO} bands at 1680 cm^{-1} (s) and 1715 cm^{-1}(s) decayed with concomitant appearance of ν_{NO} bands at 1806 cm^{-1} (w), 1772 cm^{-1} (vs) and 1745 cm^{-1} (vs), indicative of formation of *[$Fe_2(\mu$-$S^tBu)_2(NO)_4$]*.[7]

Electronic Structure Calculations. Electronic structure calculations were performed using the software package ORCA v. 2.9.[11] Geometry optimizations were initially performed using the BP86-VWN5 functional,[12-17] the TZVPP basis set[18] and employed broken symmetry formalism.[19] Final geometry optimizations and single point calculations were performed as above, but utilized the B2PLYP double hybrid functional. Atomic orbital contributions to the molecular orbitals are given as Löwdin populations.[20] Molecular orbital plots were generated in Molekel.[21]

Table S1. Löwin Population Analysis[a]

Orbital (spin)	Fe	S1	S2	N1	O1	N2	O2
LUMO+1(α)	10.1	2.4	4.1	48.4	21.3	1.2	0.7
LUMO (α)	8.1	1.0	0.3	41.0	28.0	11.0	8.8
SOMO (α)	9.2	48.9	33.4	0.6	1.0	0.0	0.2
HOMO-1 (α)	11.2	36.9	19.2	0.9	0.6	1.5	1.2
HOMO-1 (β)	7.7	28.3	9.2	2.6	1.5	28.7	19.7
HOMO-2 (α)	12.2	31.3	42.3	0.9	3.2	0.3	1.4
HOMO-2 (β)	4.9	0.5	0.8	12.0	8.4	40.9	31.0
HOMO-3 (α)	18.8	29.1	32.6	2.9	4.3	0.2	2.2
HOMO-3 (β)	18.4	12.4	41.4	0.2	0.2	16.4	10.3
HOMO-4 (α)	32.6	28.3	9.2	1.9	1.9	0.2	1.2
HOMO-4 (β)	16.0	45.6	17.1	5.3	5.3	1.5	1.4

[a] sum of the contributions from the valence AOs for the Fe, S, and N-O atoms.

Table S2. Computational Derived vs. Experimental Metric Parameters for $[Fe(SEt)_2(NO)_2]^-$. Bond lengths are given in Å and bond lengths in degrees.

	Computational	Experimental
Fe-N(1)	1.708	1.676
Fe-N(2)	1.688	1.676
Fe-S(1)	2.277	2.273
Fe-S(2)	12.266	2.273
N-O(1)	1.201	1.186
N-O(2)	1.202	1.186
N(1)-Fe-N(1)	123.1	122.3
S(1)-Fe-S(1)	105.4	106.9
N(1)-Fe-S(1)	103.7	107.8
N(2)-Fe-S(1)	104.4	108.6
N(1)-Fe-S(2)	105.8	110.7
N(2)-Fe-S(2)	100.2	99.6
Fe-N-O(1)	168.4	172.1
Fe-N-O(2)	171.7	172.1

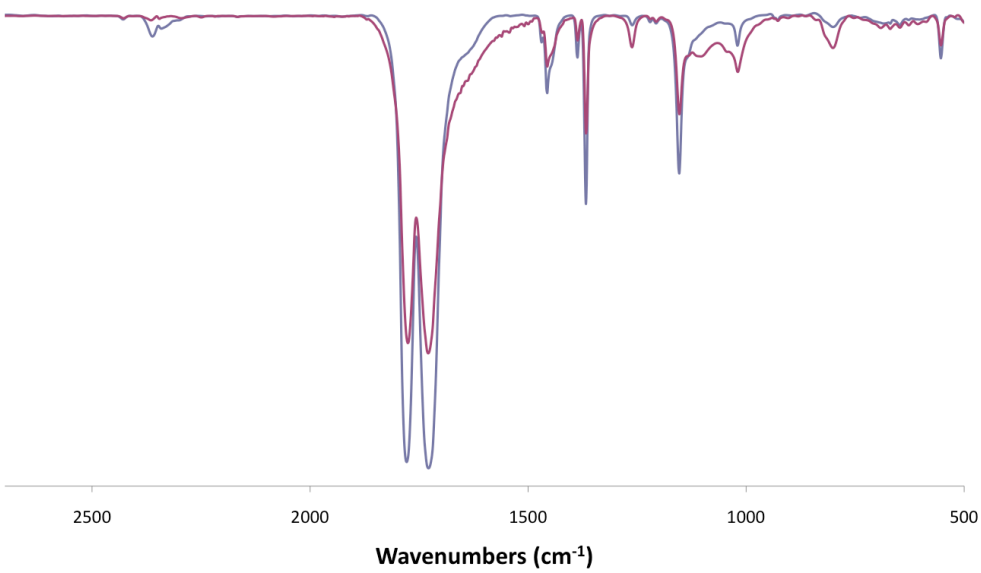

Figure S1. FTIR Spectra (KBr) of the reaction product of (PPN)[Fe(S^tBu)$_2$(NO)$_2$] (**1**) and $O_{2(g)}$ (gray trace) and authentic $Fe_2(S^tBu)_2(NO)_4$ (**4**) (red trace).

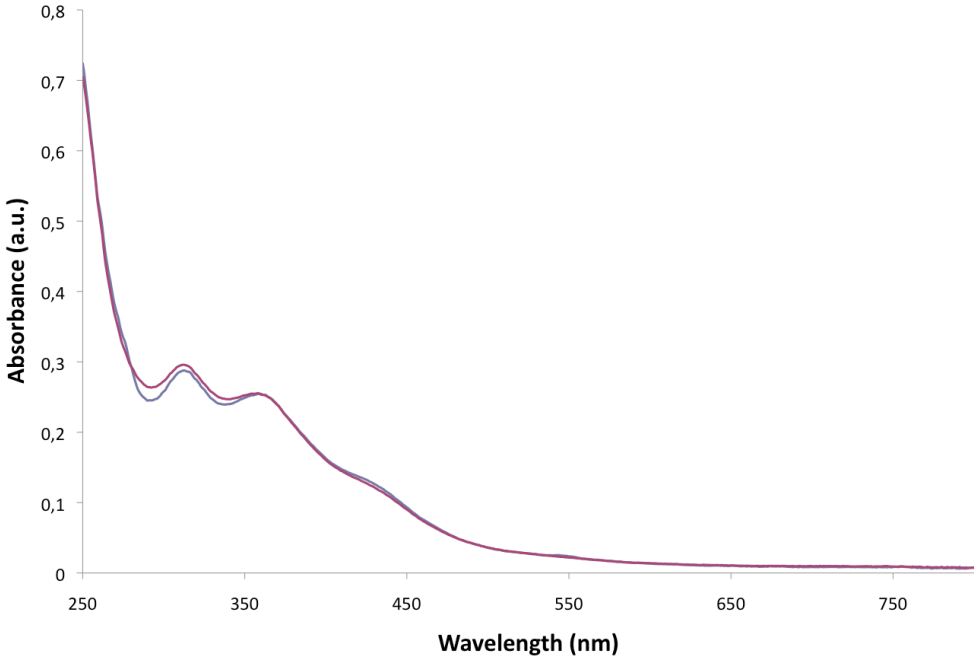

Figure S2. UV-Vis Spectra (CH_2Cl_2) of the reaction product of (PPN)[Fe(S^tBu)$_2$(NO)$_2$] (**1**) and $O_{2(g)}$ (red trace) and authentic $Fe_2(S^tBu)_2(NO)_4$ (**4**) (gray trace).

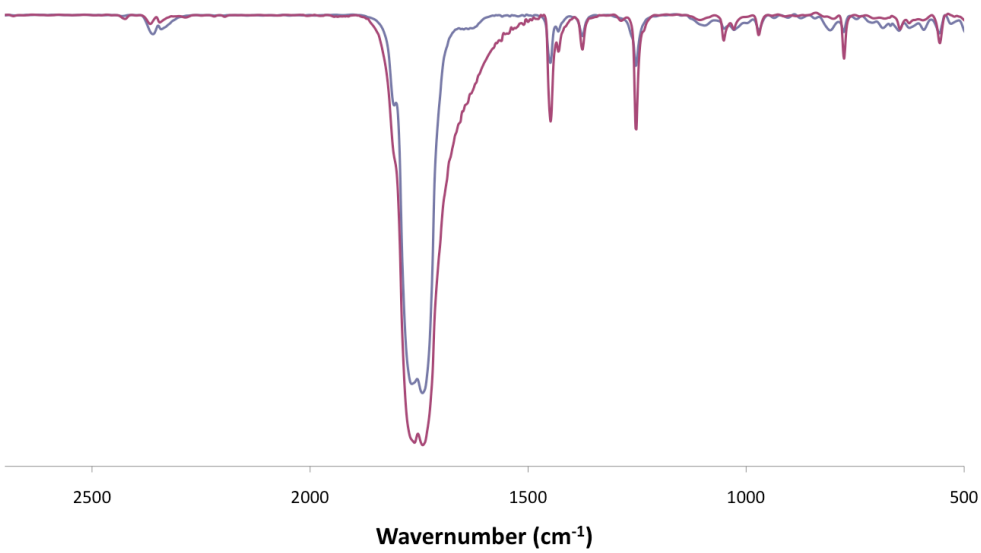

Figure S3. FTIR Spectra (KBr) of the reaction product of (PPN)[$Fe(SEt)_2(NO)_2$] (**2**) and $O_{2(g)}$ (gray trace) and authentic $Fe_2(SEt)_2(NO)_4$ (**5**) (red trace).

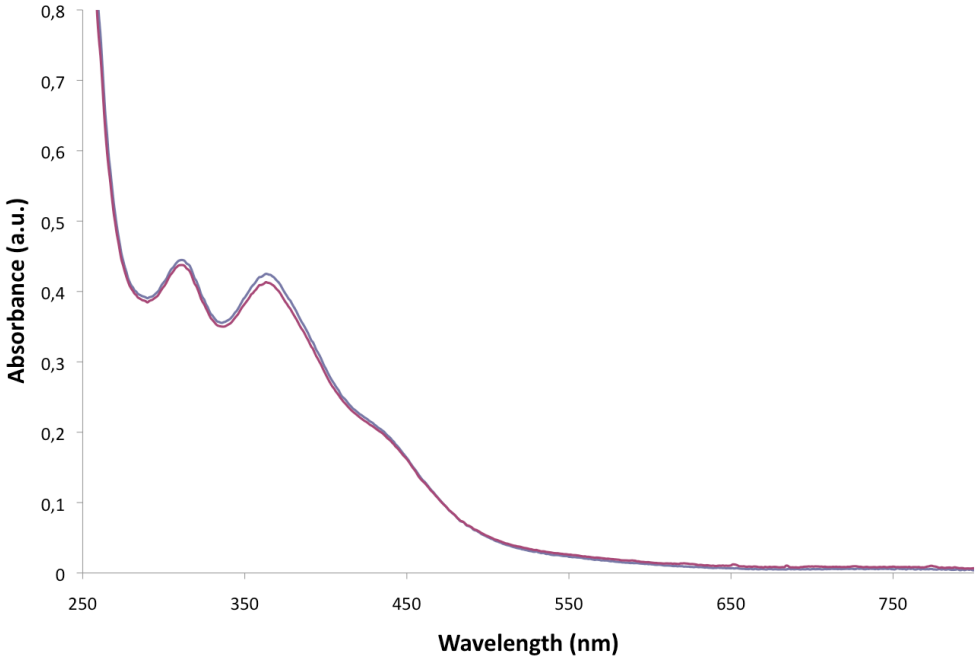

Figure S4. UV-Vis Spectra (CH_2Cl_2) of the reaction product of (PPN)[$Fe(SEt)_2(NO)_2$] (**2**) and $O_{2(g)}$ (red trace) and authentic $Fe_2(SEt)_2(NO)_4$ (**5**) (gray trace).

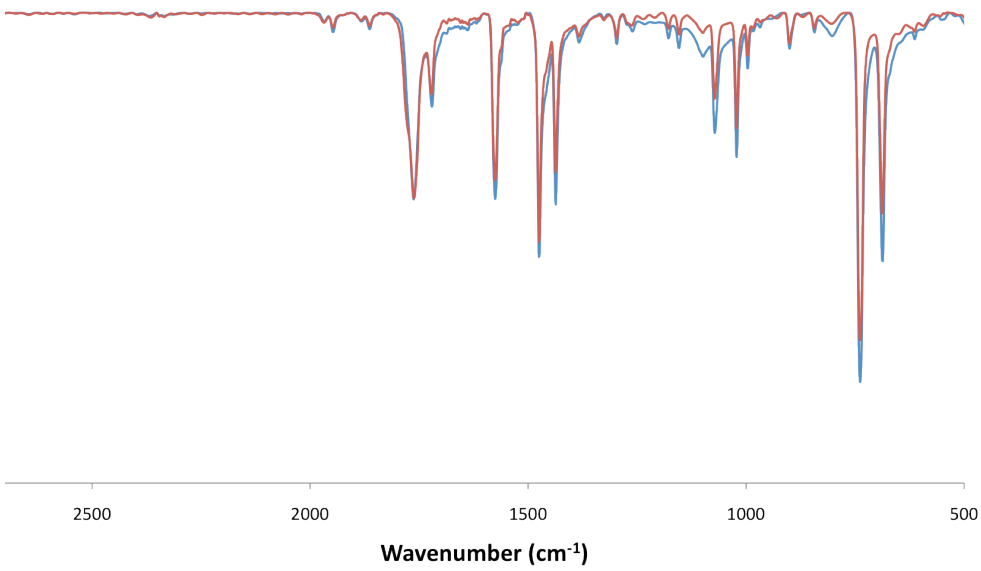

Figure S5. FTIR Spectra (KBr) of the reaction product of (PPN)[$Fe(SPh)_2(NO)_2$] (**3**) and $O_{2(g)}$ (blue trace) and authentic $Fe_2(SPh)_2(NO)_4$ (**6**) (red trace).

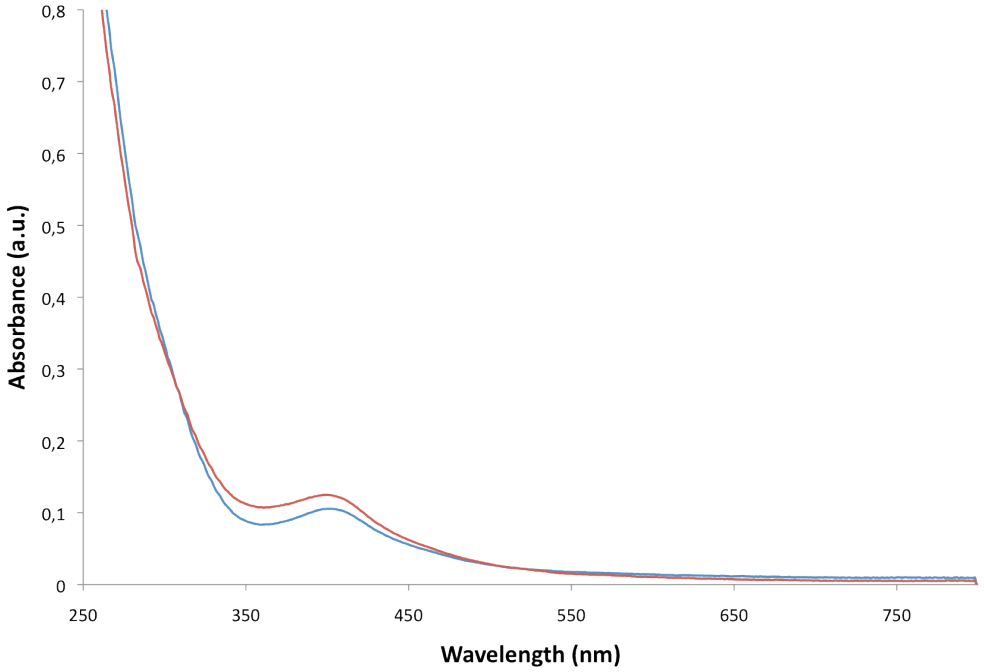

Figure S6. UV-Vis Spectra (CH_2Cl_2) of the reaction product of (Et_4N)[$Fe(SPh)_2(NO)_2$] (**3**) and $O_{2(g)}$ (blue trace) and authentic $Fe_2(SPh)_2(NO)_4$ (**6**) (red trace).

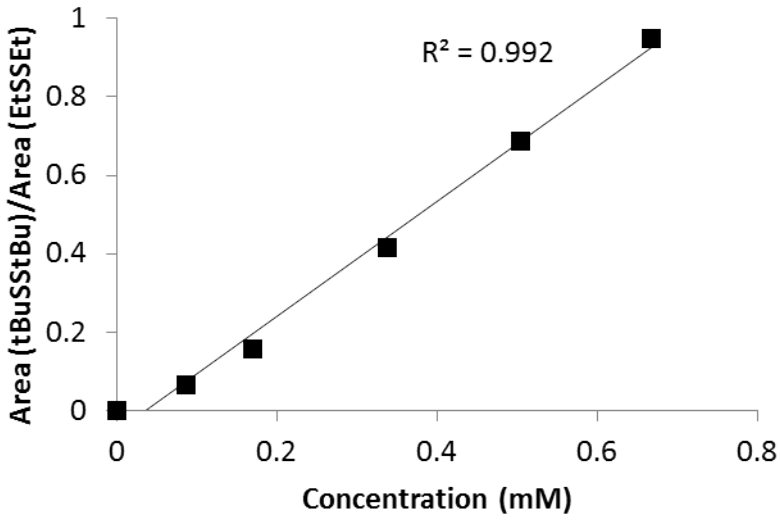

Figure S7. Calibration curve for di-tert-butyldisulfide (^{t}BuSS^{t}Bu)

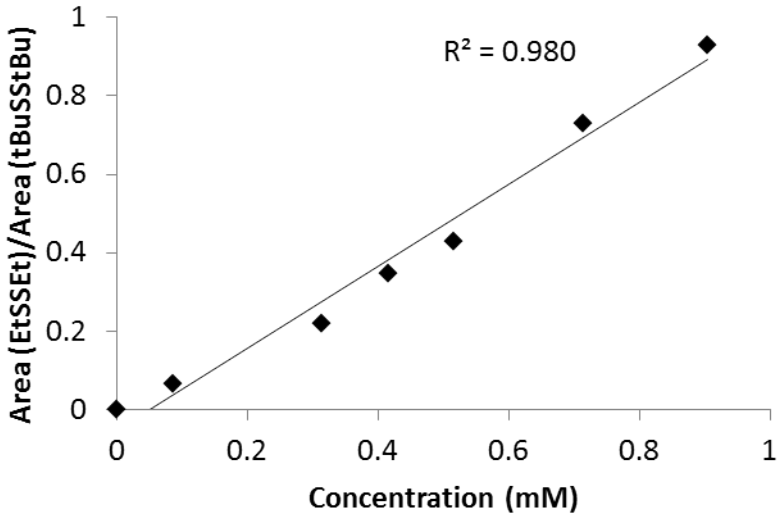

Figure S8. Calibration curve for diethyldisulfide (EtSSEt)

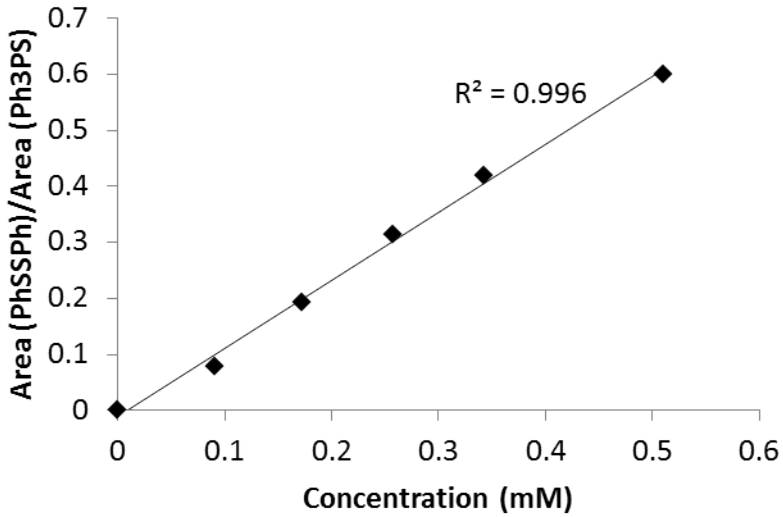

Figure S9. Calibration curve for diphenyldisulfide (PhSSPh)

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