

Unraveling the catalytic cycle of tertiary phosphine oxides reduction with hydrosiloxane and $\text{Ti}(\text{OiPr})_4$ through EPR and ^{29}Si NMR spectroscopy.

Supporting Information

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1. GENERAL INFORMATION	S2
2. SYNTHESIS	S2
3. SIMULATION OF EPR SPECTRA	S4
4. ^{29}Si NMR analysis of the reactions products	S6
5. DSC ANALYSIS	S8
6. RAMAN SPECTRA OF INDIVIDUAL SPECIES	S10

1. GENERAL INFORMATION

EPR spectra were recorded using a Bruker Elexsys e500 X-band (9.4 GHz) spectrometer with a standard cavity and a liquid nitrogen accessory allowing a temperature control in the range 93-373 K.

^{29}Si NMR spectra were obtained at 99.35 MHz on a Bruker Avance 500 spectrometer, using a 5mm broadband probe and standard NMR tubes. A coaxial insert filled with D_2O was used for locking without interacting with the sample. A DEPT sequence was used with a 45° reading pulse and an interpulse delay optimized for a 7Hz ^1H - ^{29}Si coupling. All data were recorded using a $7.7\mu\text{s}$ 90° pulse, a 1s recycling delay, an acquisition time of 0.35s and 6000 scans at 298K.

Experiments were performed on DSC apparatus from Mettler Toledo: DSC-30 working with glass cells. STARe software was used to acquire and evaluate data. Samples masses are between 3 to 7 mg. Mixture are prepared at room temperature.

A Kaiser RamanRXN1 process spectrometer with 300mW laser (785 nm) was used. Real-time Raman spectra were fixed in $100\text{--}3300\text{ cm}^{-1}$ spectral range with spectral resolution of 1 cm^{-1} . The MR probe head with immersion optics was used to in situ monitor the reaction. Exposition time was 1 s, while the accumulation number was 10 every 2 minutes for the first hour then every 10 minutes. Exact quantification of the raw spectra was obtained using the Classical Least Square (CLS) method. The CLS method, which is a bilinear model, is based on the assumption that mixture spectra are linear combinations of the spectra of the pure components. Therefore, the calculated concentration values will be referred to as “spectral concentrations” to avoid confusion with the real concentration values.

2. SYNTHESIS

2.1. OXIDATION OF (*S,S*)-DIPAMP

H_2O_2 (2.5 mL, 30% wt in water) was added drop wise into a solution of (*S,S*)-DIPAMP (0.21 mmol) in CH_2Cl_2 (2 mL) at 0°C . After 1h at room temperature TLC analysis showed the complete conversion of the phosphine. Water (3 mL) was then added and the organic phase was separated. The organic phase was then washed with sodium bisulfate, with brine and then dried over MgSO_4 . The organic phase was evaporated under vacuum to obtain diphosphine oxide with 96% yield (98.5 mg, ee= 100%).

^1H NMR (400 MHz, CDCl_3) δ 7.98-7.94 (2H, m), 7.75 (4H, q, J = 6.28, 5.52), 7.49-7.37 (8H, m) 7.08 (2H, t, J = 7.28) 6.82-6.80 (2H, m) 3.59 (6H, s), 2.75-2.59 (4H, m). ^{13}C NMR (100 MHz, CDCl_3) δ 160.2 (2C), 134.9, 134, 4, 134.0, 133.5, 133.0, 131.9, 131.2, 131.2, 131.1, 128.7 (2C), 128.6 (2C), 121.5 (2C), 121.3 (2C), 120.5, 120.0, 119.4, 111.1 (2C), 55.5, 21.7 (d, J = 33Hz), 21.3 (d, J = 31 Hz),

^{31}P NMR (81 MHz, CDCl_3): δ 33.84 ppm. Chiral column [Daicel Chiralpak AD, 0.46 cm \cdot 25 cm, 254 nm UV detector, r.t., eluent 75:25 (*n*-heptane:2-PrOH), flow rate 0.5 mL/min], t_R = 78.98 min. for *S,S* and 62.02 min. for *R,R*.

2.2. REDUCTION OF (*S,S*)-DIPAMP OXIDE 11

In a 5 mL dried round-bottomed flask fitted with a magnetic stirrer and a condenser were placed the (*S,S*)-DIPAMP oxide **11** (0.10 mmol, 1 equiv.), sodium sulfate and toluene (0.5 mL). Then, TMDS (0.05 mL, 0.125 mmol, 1.25 equiv.) and $\text{Ti}(\text{O}i\text{Pr})_4$ (4 μL , 0.01 mmol, 0.1 equiv.) were added to the reaction vessel. The heterogeneous mixture was stirred at 60 ° C under an argon atmosphere. Reaction can be followed up by ^{31}P NMR until complete consumption of the starting material. Silica gel was added in this mixture until the end of the gas emission, filtered on silica gel with ethyl acetate. After concentration of the filtrate, the crude residue was purified by flash chromatography (silica gel, cyclohexane 100 to cyclohexane/ethyl acetate: 20/ 80) to yield the (*S,S*)-DIPAMP **12**.

^1H NMR (300 MHz, CDCl_3) δ 7.40-7.30 (10H, m), 7.24 (2H, d, J = 1,68Hz), 6.96-6.93 (2H, m) , 6.87-6.80 (4H, m), 3.73 (6H, s), 2.26-2.23 (2H, m), 2.01-1.90 (2H, m) ^{31}P NMR (81 MHz, CDCl_3): δ - 20.69 ppm Chiral column [Daicel Chiralpak AD, 0.46 cm \cdot 25 cm, 254 nm UV detector, r.t., eluent 90:10 (*n*-heptane:2-PrOH), flow rate 0.5 mL/min], t_R = 21.9 min. for *S,S* and 16.3 min. for *R,R*.

2.3. REDUCTION OF TPO ON 100 G SCALE

In a jacketed glass reactor of 1L equipped with mechanical stirring, dropping funnel, temperature and Raman optical probes was added 100 g (0.36 mole) of triphenylphosphine oxide (TPO), 700 mL of cyclohexane, 10 g of Na_2SO_4 and 50.77 g (0.38 mole) of tetramethyldisiloxane (TMDS). The reaction mixture was stirred and heat to 60°C. Then, 10.21 g (0.035 mole) of $\text{Ti}(\text{O}i\text{Pr})_4$ was added and then the heterogenous mixture is stirred for 14 h at 60 ° C. Aliquots were taken for ^{31}P NMR analysis. The reaction mixture was then cooled, filtrated over porous glass and the solid was washed with 3 x 50 mL of pentane. The resulting white solid was recrystallized from acetone yielding 94.4g of triphenylphosphine (quantitative yield). Unreacted TMDS in the filtrate must be destroyed by carefull addition of a 3 M alcoholic solution of KOH at room temperature with rigourous stirring. TMDS decomposes on contact with bases, forming hydrogen.

m.p. 80°C (Litt. 82-83°C). ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.30 (m, 15H). ^{13}C NMR (50 MHz, CDCl_3) δ 137.6 (d, J = 9.8Hz), 134.0 (d, J = 19.1Hz, 2C), 129.1, 128.8 (d, J = 11.4Hz, 2C). ^{31}P NMR (81 MHz, CDCl_3): δ -4,2.

3. SIMULATION OF EPR SPECTRA

The Matlab-based simulation package EasySpin was used for simulating and fitting EPR spectra.

Table S1 Simulation parameters of the EPR signal measured at 135 K; accuracy of ± 1 on the last digit provided for g and A values.

Species (percentage)	g_1	g_2	g_3	g_{av}	A_1/G	A_2/G	A_3/G	A_{av}/G
C (46%)	2.000	1.954	1.936	1.964	0	19	0	6.4
A (25%)	1.968	1.944	1.925	1.946	0	25	0	8.3
B (10%)	1.975	1.961	1.925	1.954	9	16	3.3	9.4
D (6%)	1.999	1.957	1.938	1.965	35	3.3	1.7	13.3
E (3%)	2.001	1.966	1.937	1.968	11.7	20	8.3	13.3

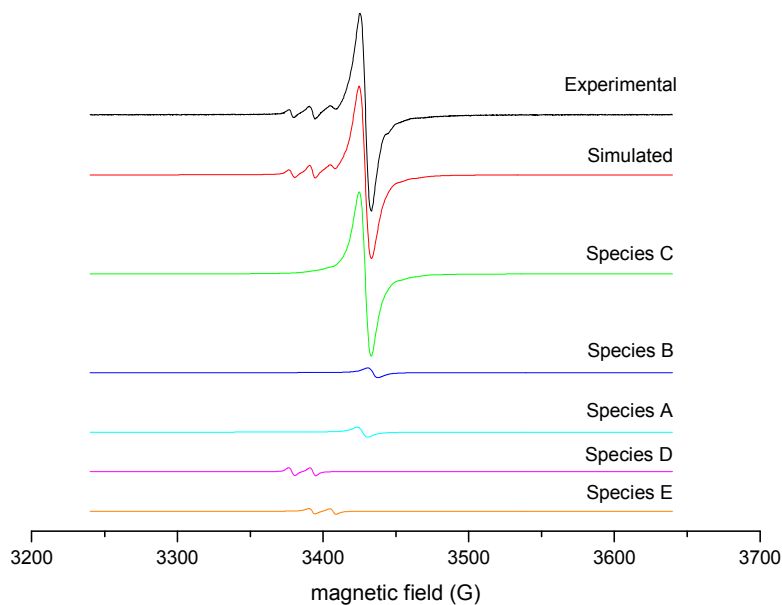


Figure S 1. Experimental EPR spectra, simulated EPR spectra and simulated spectrum for each species at 295 K.

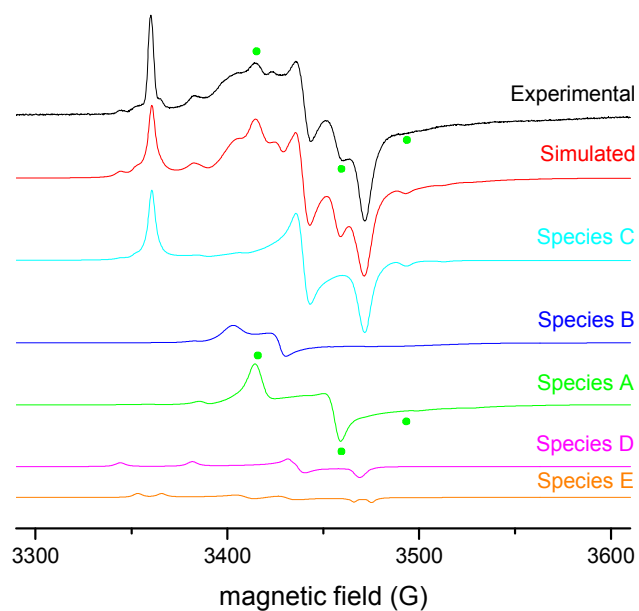


Figure S2. Experimental (black line) and simulated (red line) EPR spectrum of the TMDS/Ti(OiPr)₄ system at 135K. Individual simulated signal A, B, C, D and E provided with the intensity used for the simulation of experimental spectrum. The green spots standing for the most specific feature of signal A.

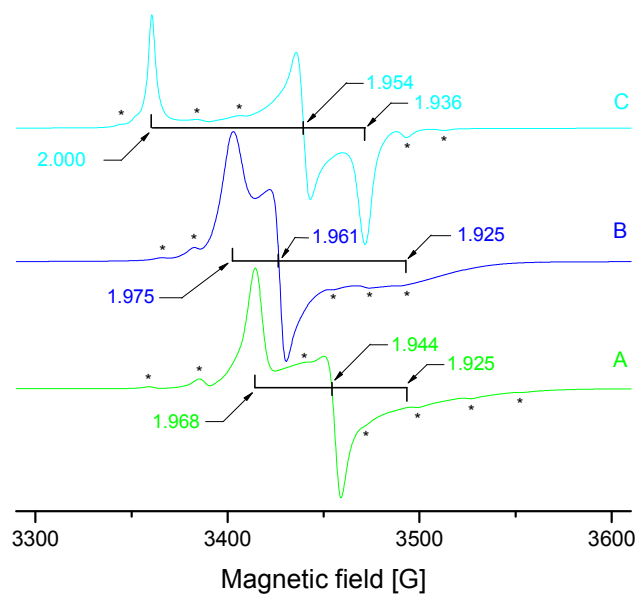


Figure S3. Full scale simulated signal A, B and C at 135K with g_1 , g_2 and g_3 assignments and stars pointing the most obvious features of the Ti hfs contributions.

4. ^{29}Si NMR analysis of the reactions products

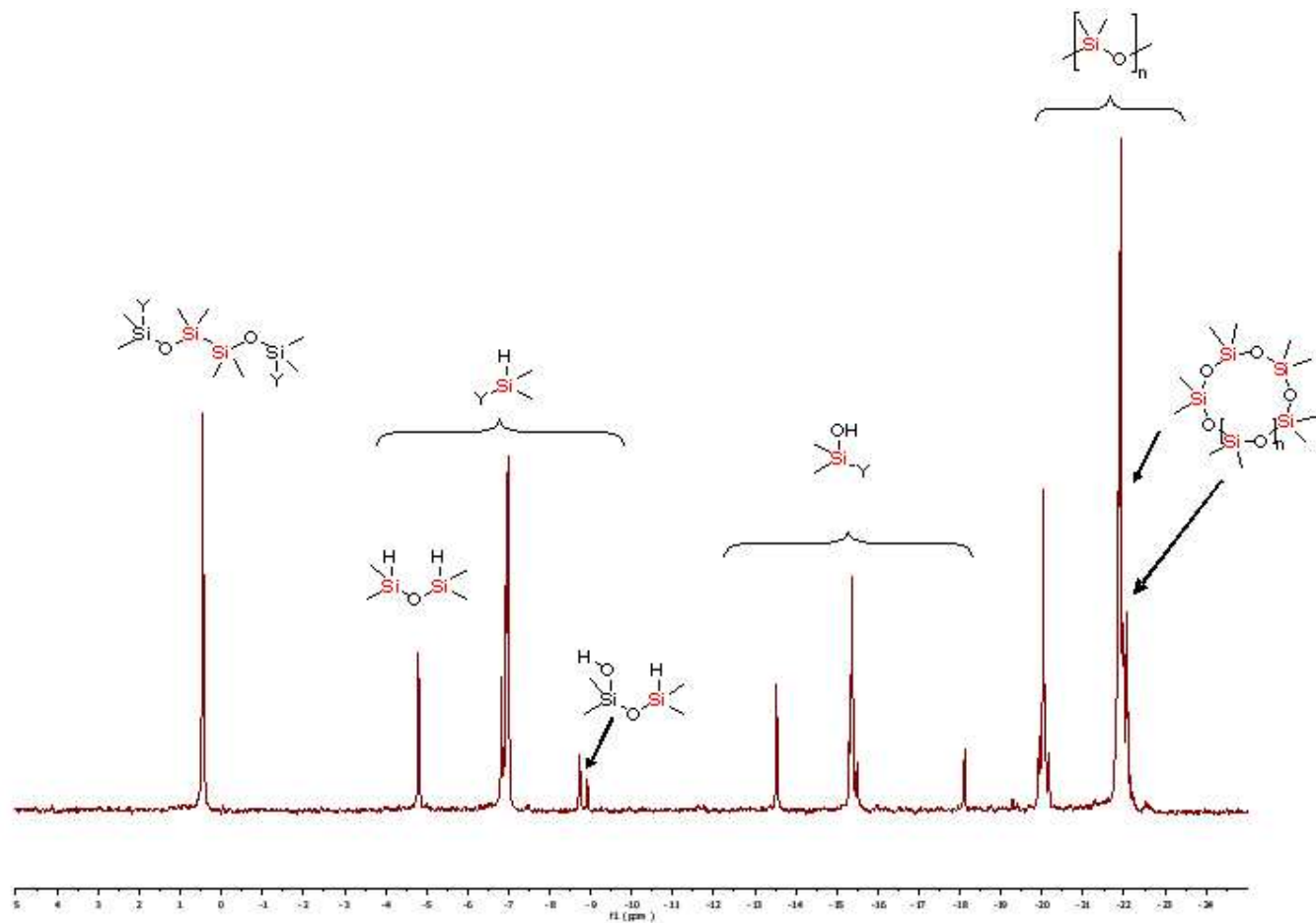
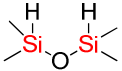
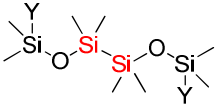
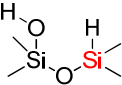
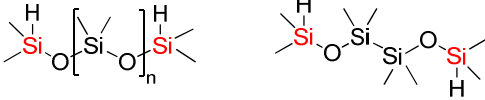
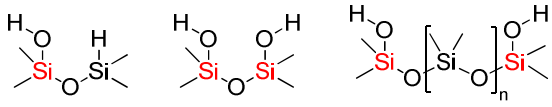
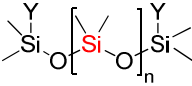
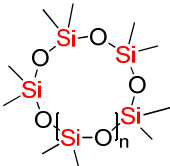


Figure S4. ^{29}Si NMR of the crude reaction mixture of TPO reduction by $\text{TMDS}/\text{Ti}(\text{OiPr})_4/\text{MCH}$ in CDCl_3 and using $\text{Cr}(\text{acac})_3$ as spin relaxant

Table S2. Structure of silicon species and chemical shift

Species ^{a)}	Structure	δ (ppm) ^{b)}
1		- 5
2		-0.2
4		- 9.0
5		- 7.0 ~ -7.5
6		-14.1 -15.9 -18.4
7	 Y = H, OH	- 20.2 ~ -20.6
8		- 22.0 ~ -22.7

^{a)} See Scheme 2

^{b)} data from i) Kintzinger, J. P.; Marsmann, H. NMR Basic Principles and Progress: Oxygen-17 and Silicon-29; Springer-Verlag: Berlin Heidelberg, 1981 and ii) Gupta, R. R.; Lechner, M. D.; Marsmann, H.; Mikhova, B.; Uhlig, F. Chemical shifts and coupling constants for Silicon-29; Springer: Berlin, 2008

5. DSC analysis

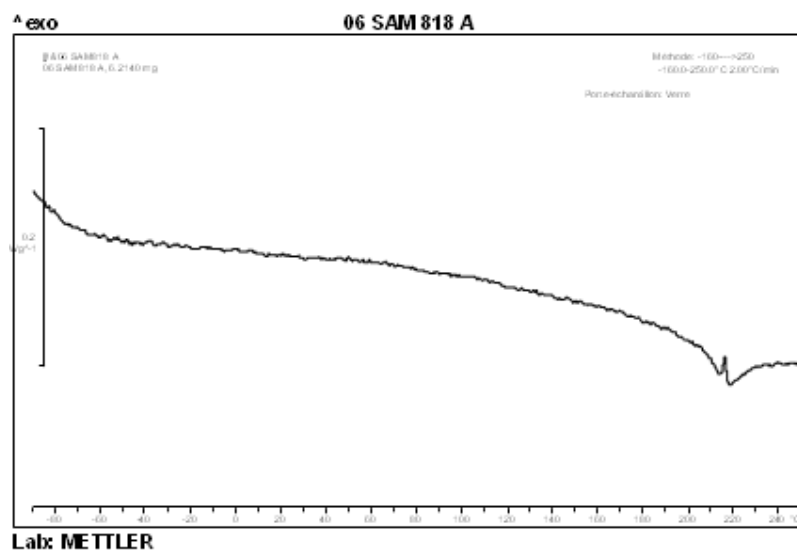


Figure S5. Dynamic DSC study of neat TMDS (-100°C to 250°C at 2°C/min.)

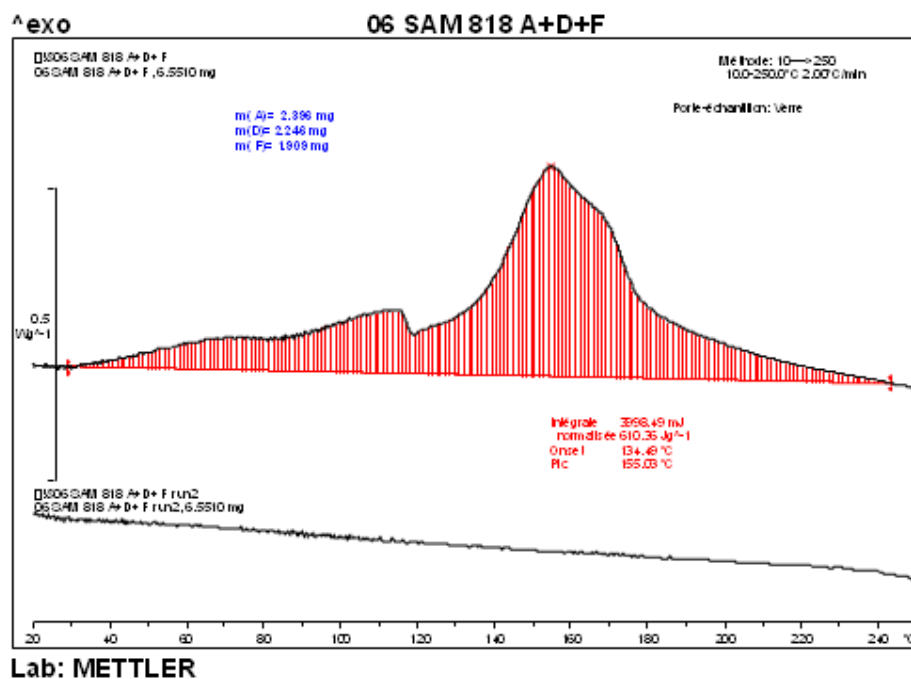


Figure S6. Dynamic DSC study of neat TMDS/Ti(OiPr)₄/MCH (1/0.4/1.2) (20°C to 250°C at 2°C/min.)

6. RAMAN SPECTRA OF INDIVIDUAL SPECIES

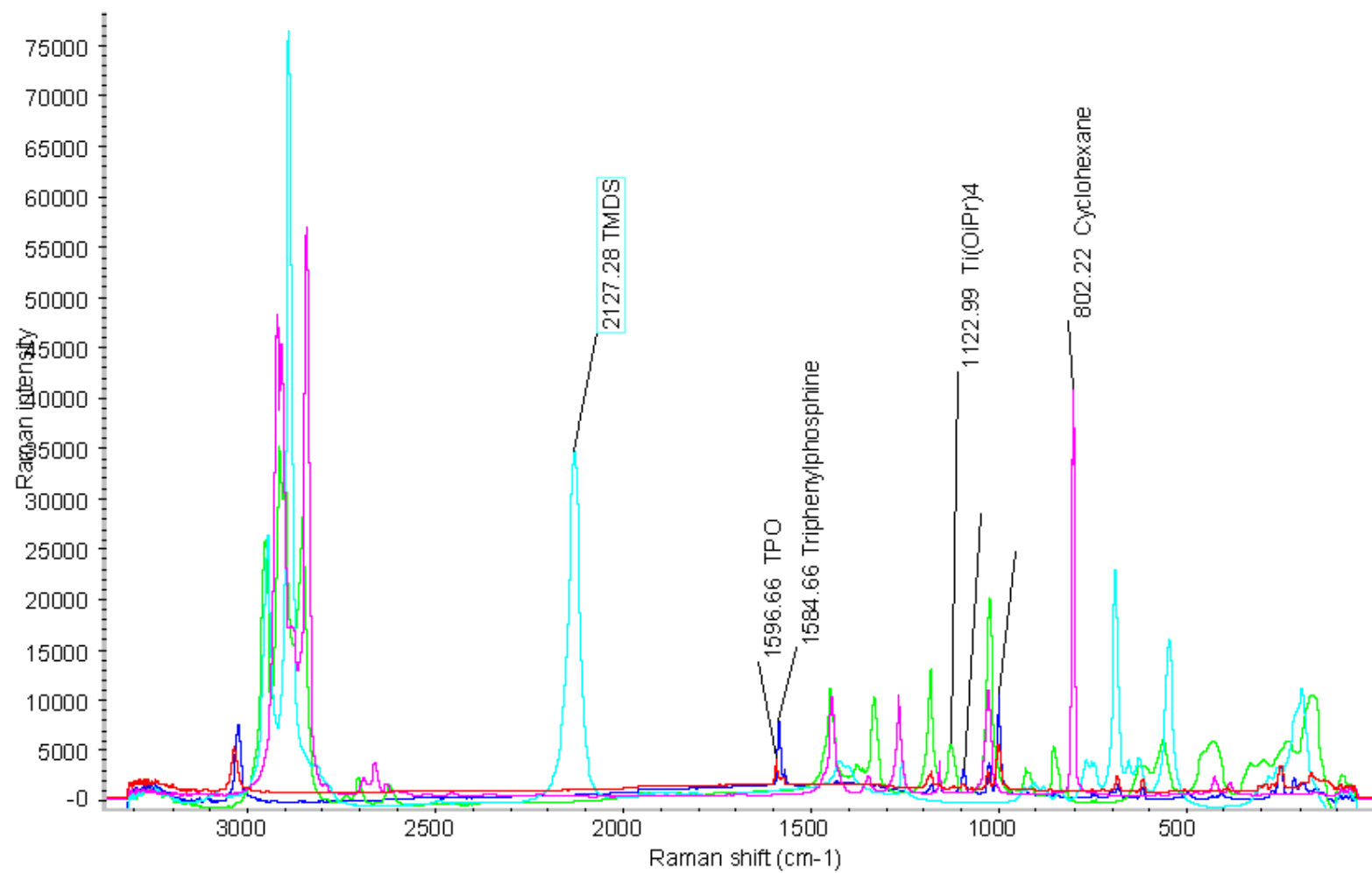


Figure S8. Superimposed Raman spectra of individual species