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which should be cited to refer to this work.

Simulant Synthesis:

[2-(2-Diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA)

To diisopropylaminoethan-2-thiol (1.6 g, 10 mmol, 1 equiv.) in methanol (40 mL), a solution of aqueous H_2O_2 (30 %, 20 μL) was added at room temperature. Dry air was bubbled through the solution and after 1 h a new portion of H_2O_2 (30 %, 40 μL) was added. The reaction was followed by GC-MS measurement. After completion, the solvent was evaporated under reduce pressure and the crude product was purified by Kugelrohr (bulb to bulb) vacuum distillation. Bp 142 °C / $2.8 \cdot 10^{-4}$ mbar. Yield: 75 %, purity >98 % ^{1}H-NMR.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.01 (sep, 4H, 4 x C*H*, *J* = 8 Hz), 2.76-2.69 (m, 8H, 2 x NCH_2CH_2S), 1.02 (d, 24H, 8 x CH_3, *J* = 8 Hz). **^{13}C-NMR (100 MHz, $CDCl_3$)** δ 49.3 (s, *C*H), 45.8 (s, NCH_2), 40.5 (s, SCH_2), 20.8 (s, CH_3). **GC (Rt)** 18.61 min, **MS** 193, 160, 144, 114 (100%), 102, 84, 72, 56, 43.

General Synthetic Procedure

To the OP ester chloride (27.0 mmol, 1 equiv.) in MeCN (25 mL) was added dropwise under ice bath cooling and inert atmosphere (N_2) a solution of the appropriate alcohol (1.1 equiv.) and 4-(dimethylamino)pyridine (1.1 equiv.) in MeCN (35 mL). The reaction mixture was further stirred within 0 and 10 °C for 4 h and then at room temperature overnight. After filtration (removal of the white precipitate), the solvent was evaporated under reduced pressure. The residue was dissolved in hexane (20 ml) and washed with HCl_{aq} (0.1 mol dm^{-3}, 2 x 10 mL) and brine (1 x 10 mL). The organic phase was dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by Kugelrohr (bulb to bulb) vacuum distillation.

Phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE)

Following the general procedure, using diethyl phosphorochloridate (4.65 g, 27.0 mmol, 1 equiv.), 2-ethoxyethanol (2.7 g, 29.7 mmol, 1.1 equiv.), 4-(dimethylamino)pyridine (3.6 g, 29.7 mmol, 1.1 equiv.). Bp 90 °C/$2.0 \cdot 10^{-2}$ mbar. Yield 53 %, purity >98 %, ^{31}P-NMR.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.19-4.10 (m, 6H, 2 x POCH_2CH$_3$, and POCH_2CH$_2$O), 3.65 (t, 2H, POCH$_2$$CH_2$O, *J* = 4 Hz), 3.55 (q, 2H, OCH_2CH$_3$, *J* = 8 Hz), 1.34 (t, 6H, 2 x POCH$_2$$CH_3$, *J* = 8 Hz), 1.21 (t, 3H, OCH$_2$$CH_3$, *J* = 8 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)** δ -0.9. **^{13}C-NMR (100 MHz, $CDCl_3$)** δ 69.3 (d, O*C*H$_2$CH$_3$, *J* = 7 Hz), 66.6 (d, POCH$_2$*C*H$_2$O, *J* = 6 Hz), 66.5 (d, PO*C*H$_2$CH$_2$O, *J* = 6 Hz), 63.7 (d, PO*C*H$_2$CH$_3$, *J* = 5 Hz), 16.1 (d, POCH$_2$*C*H$_3$, *J* = 7 Hz), 15.1 (s, OCH$_2$*C*H$_3$). **GC (Rt)** 14.00 min, **MS** 227 (M^+), 182, 162, 155 (100%), 142, 125, 113, 108, 99, 82, 72, 59, 45. **TOF MS ES$^+$ calc**: $C_8H_{19}O_5P$ 226.10, **found [M+Na]$^+$** 249.0868.

Phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE)

Following the general procedure, using diethyl phosphorochloridate (4.65 g, 27.0 mmol, 1 equiv.), 2-(ethylthio)ethanol (3.2 g, 29.7 mmol, 1.1 equiv.), 4-(dimethylamino)pyridine (3.6 g, 29.7 mmol, 1.1 equiv.). Bp 90 °C/$5.0 \cdot 10^{-3}$ mbar. Yield 61 %, purity >98 % ^{31}P-NMR.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.18-4.10 (m, 6H, 2 x POCH_2CH$_3$, and POCH_2CH$_2$S), 2.81 (t, 2H, POCH$_2$$CH_2$S, *J* = 8 Hz), 2.59 (q, 2H, SCH_2CH$_3$, *J* = 8 Hz), 1.35 (t, 6H, 2 x POCH$_2$$CH_3$, *J* = 8 Hz), 1.27 (t, 3H, SCH$_2$$CH_3$, *J* = 8 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)** δ -1.2. **^{13}C-NMR (100 MHz, $CDCl_3$)** δ 66.5 (d, POCH$_2$*C*H$_2$O, *J* = 6 Hz), 63.8 (d, PO*C*H$_2$CH$_3$, *J* = 6 Hz), 31.3 (d, POCH$_2$*C*H$_2$S, *J* = 7 Hz), 26.3 (d, S*C*H$_2$CH$_3$, *J* = 7 Hz), 16.1 (d, POCH$_2$*C*H$_3$, *J* = 7 Hz), 14.8 (s, SCH$_2$*C*H$_3$). **GC (Rt)** 15.87 min, **MS** 197, 155, 141, 127, 109, 99, 88 (100%), 81, 60. **TOF MS ES$^+$ calc**: $C_8H_{19}O_4SP$ 242.07, **found [M+Na]$^+$** 265.0639.

Simulant Characterisation:

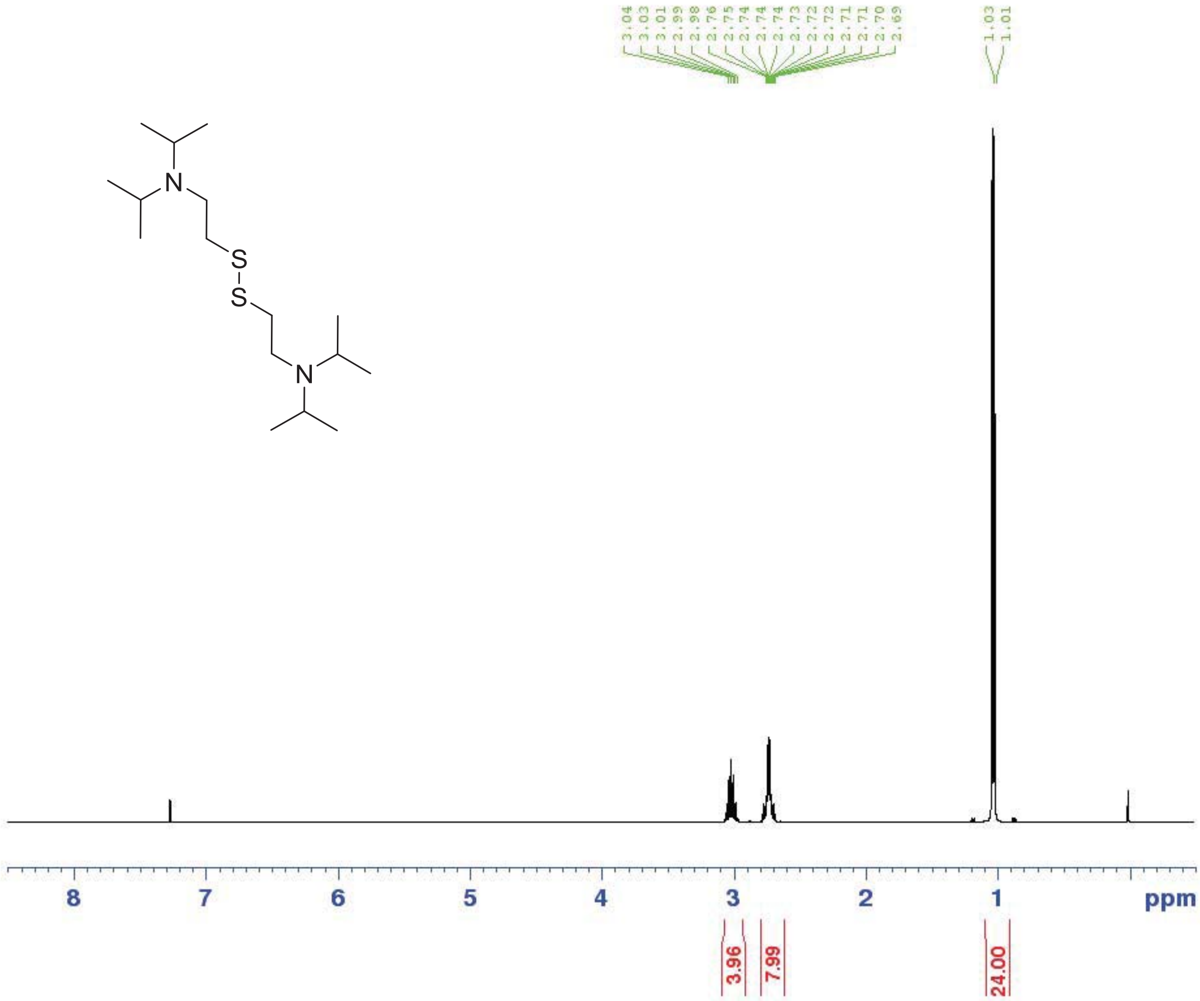


Figure S1: ^{1}H NMR spectrum of the synthesised [2-(2-Diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA) used in this study in $CDCl_3$.

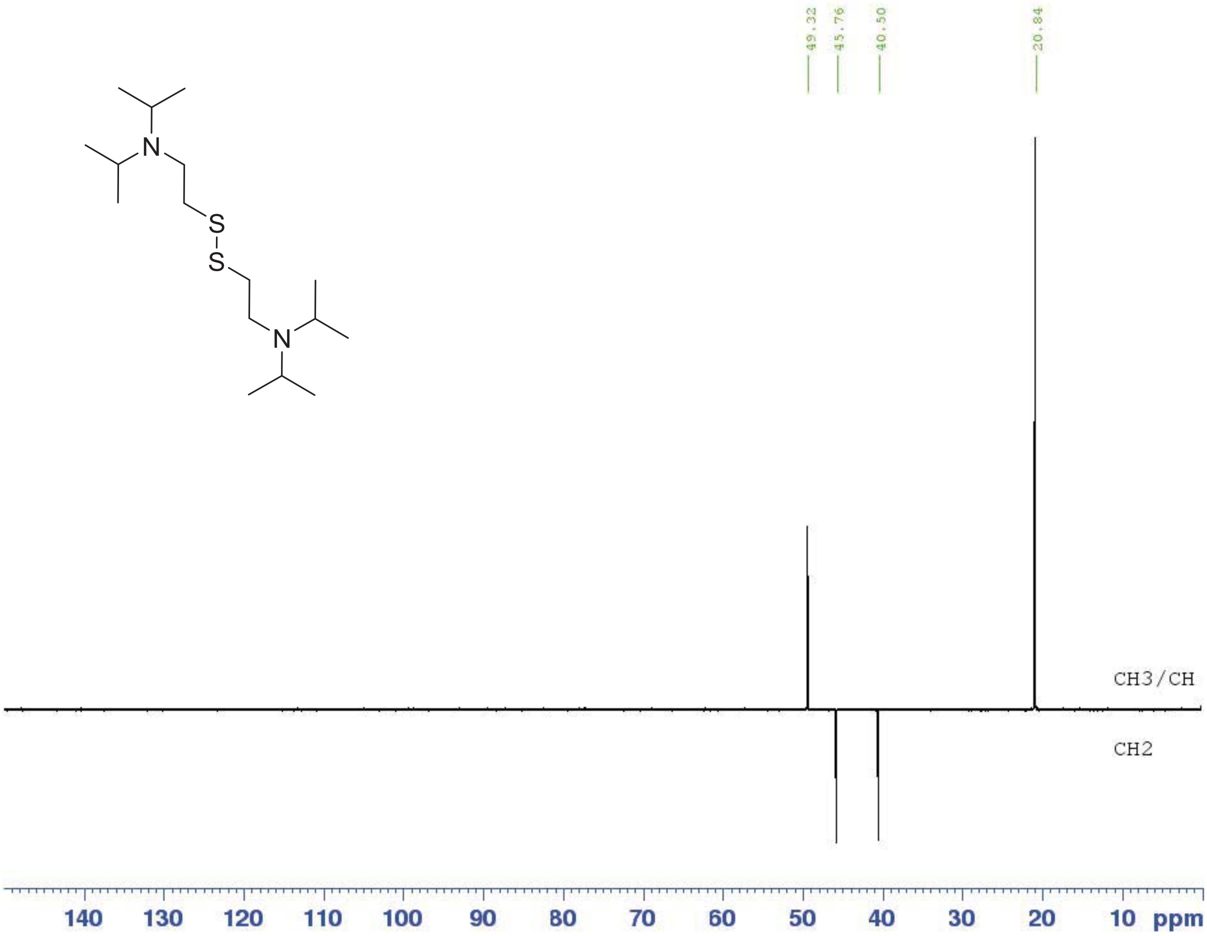
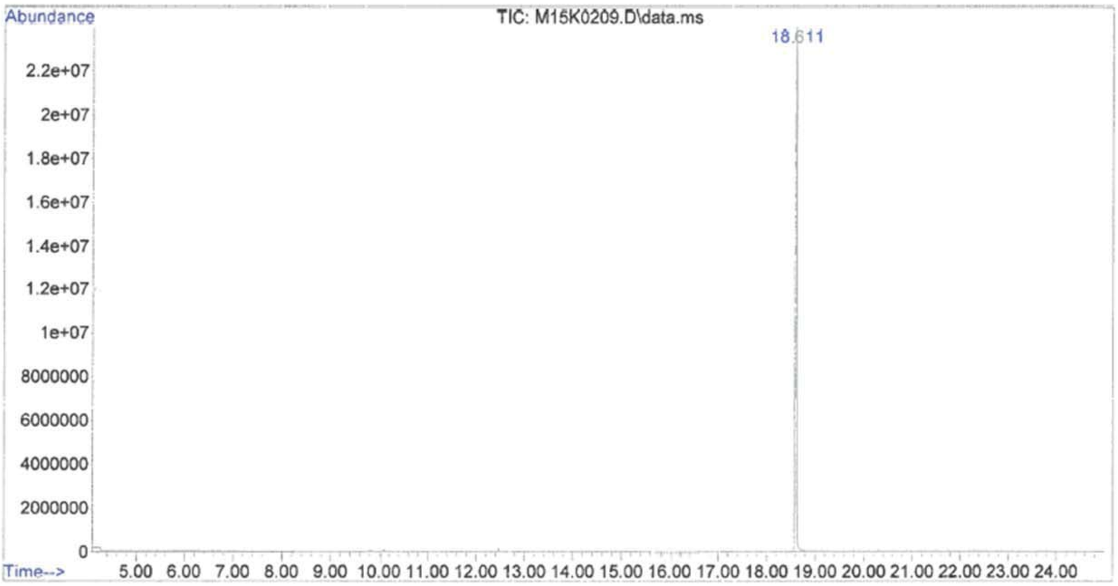


Figure S2: ^{13}C DEPT NMR spectrum of the synthesised [2-(2-Diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA) used in this study in $CDCl_3$.



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Sorted by Signal

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Wed Mar 04 12:51:55 2015

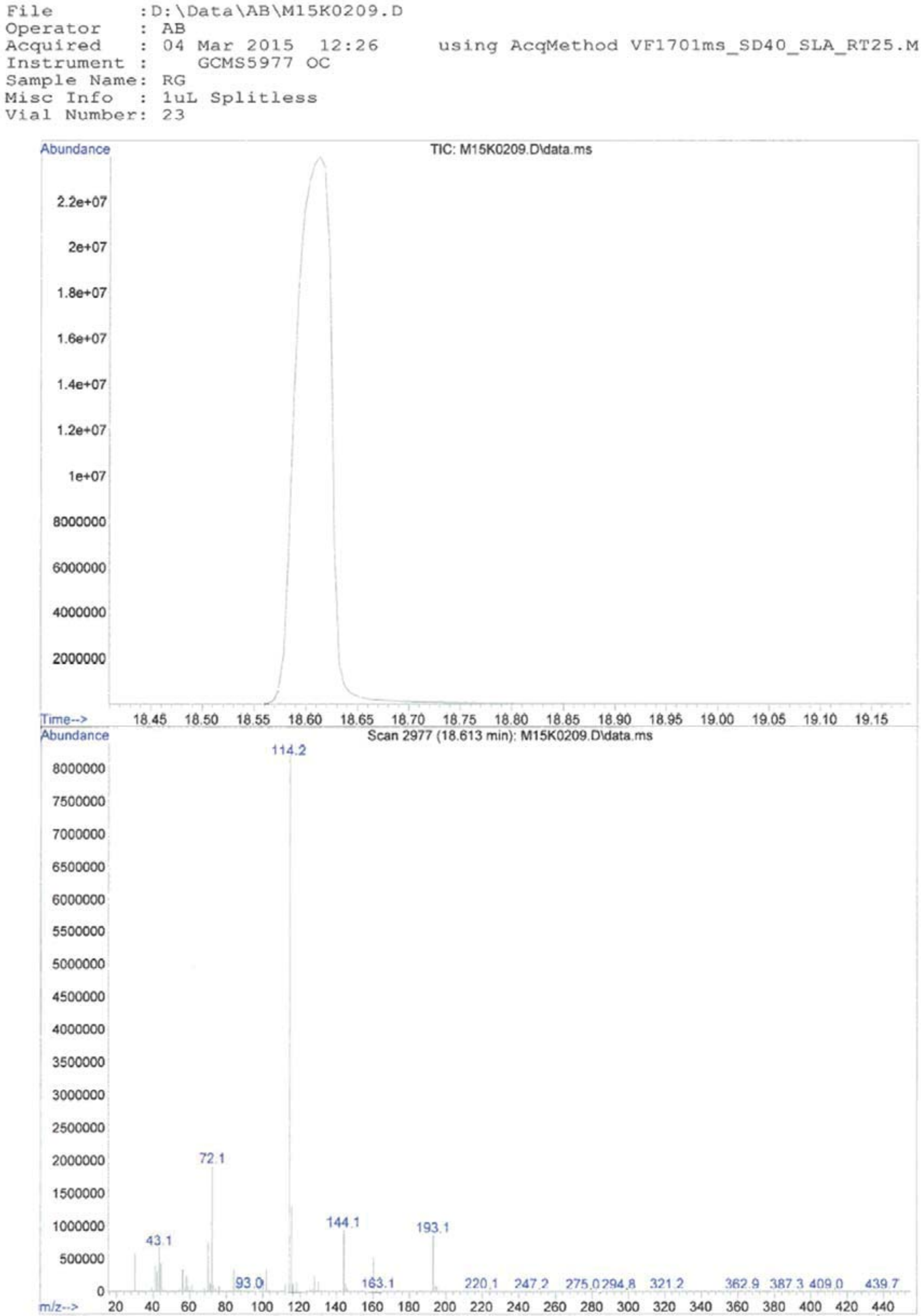


Figure S3: GC-MS analyses of the synthesised [2-(2-Diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA) used in this study.

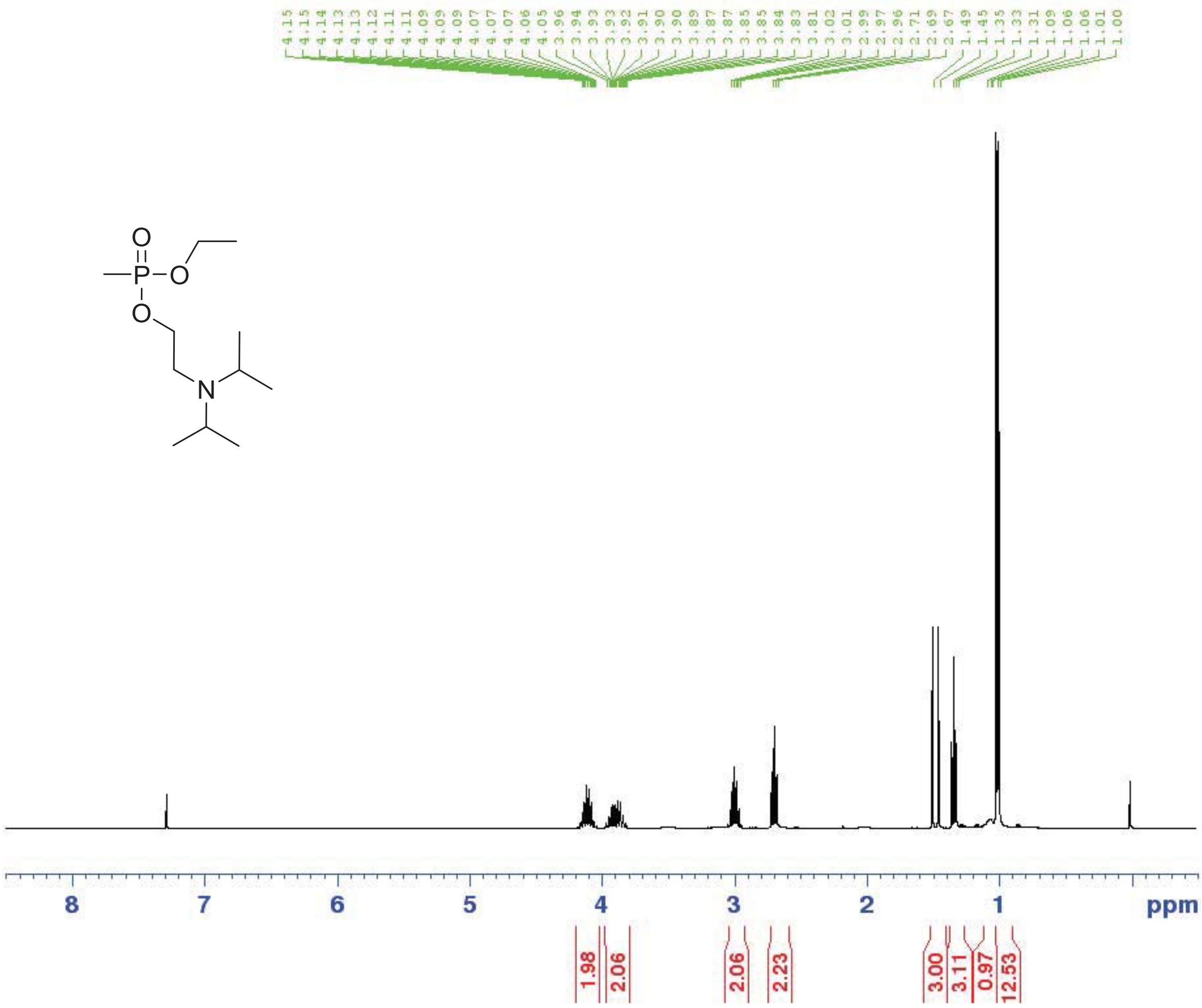


Figure S4: [1]H NMR spectrum of the synthesised 2-diisopropylaminoethyl ethyl methylphosphonate (VO) used in this study in $CDCl_3$.

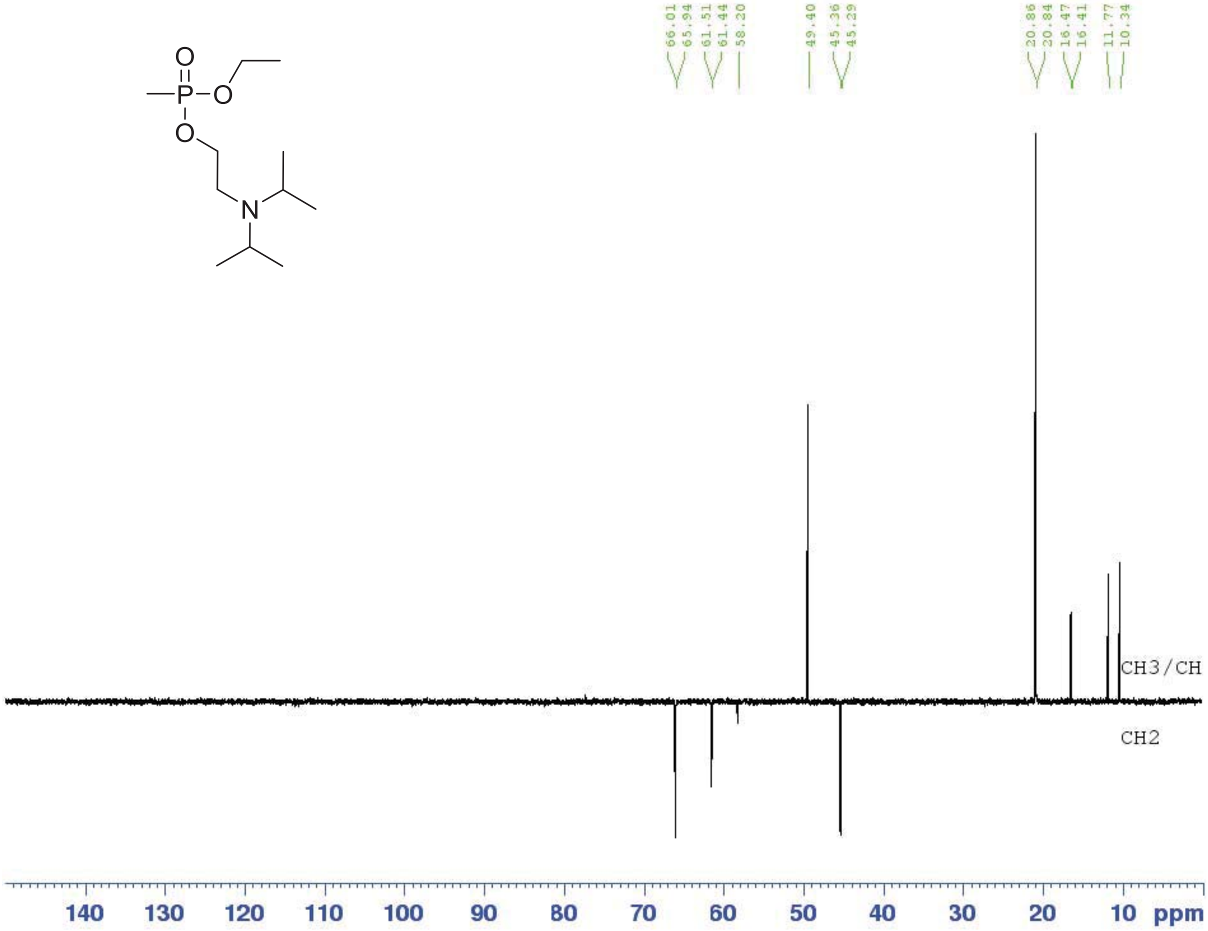


Figure S5: ^{13}C DEPT NMR spectrum of the synthesised 2-diisopropylaminoethyl ethyl methylphosphonate (VO) used in this study in $CDCl_3$.

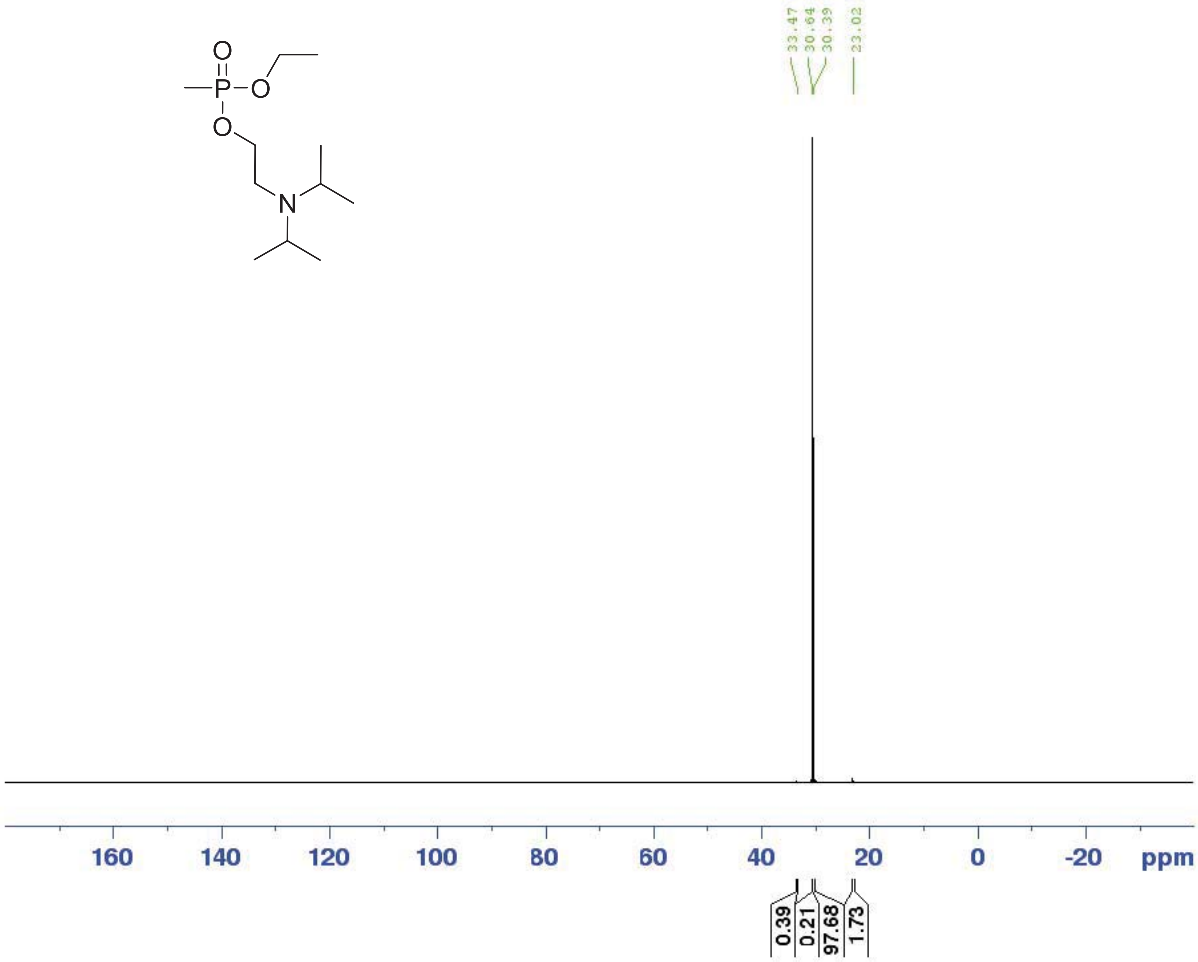
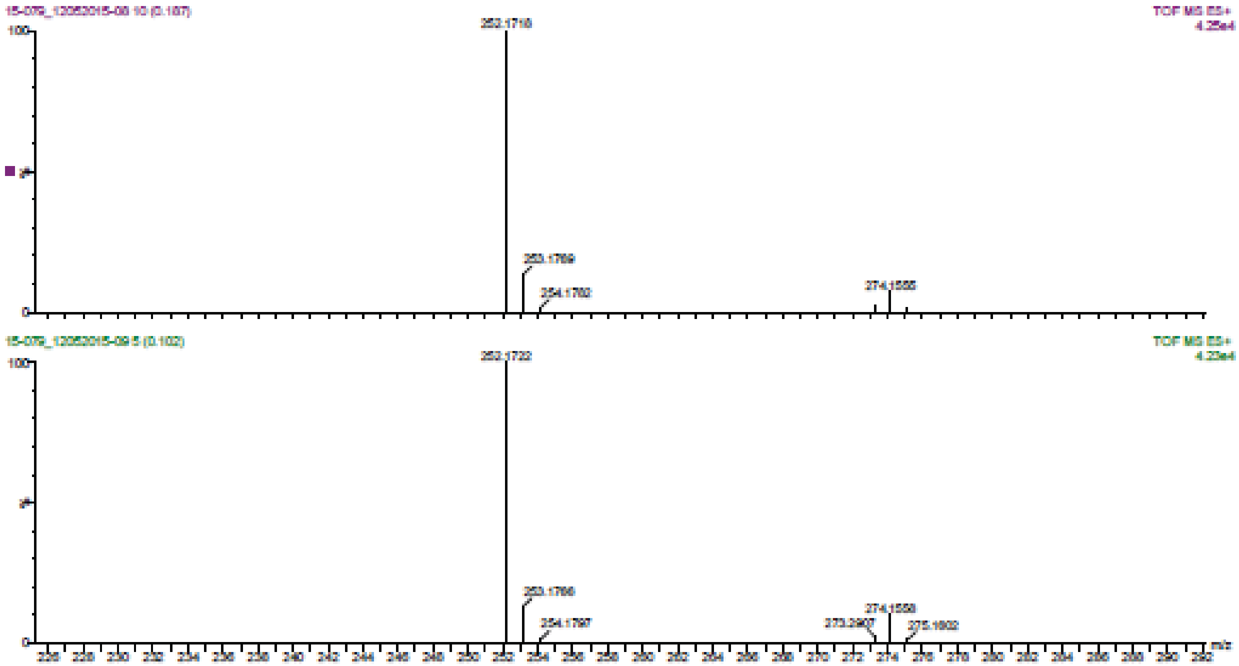


Figure S6: ^{31}P NMR spectrum of the synthesised 2-diisopropylaminoethyl ethyl methylphosphonate (VO) used in this study in $CDCl_3$.

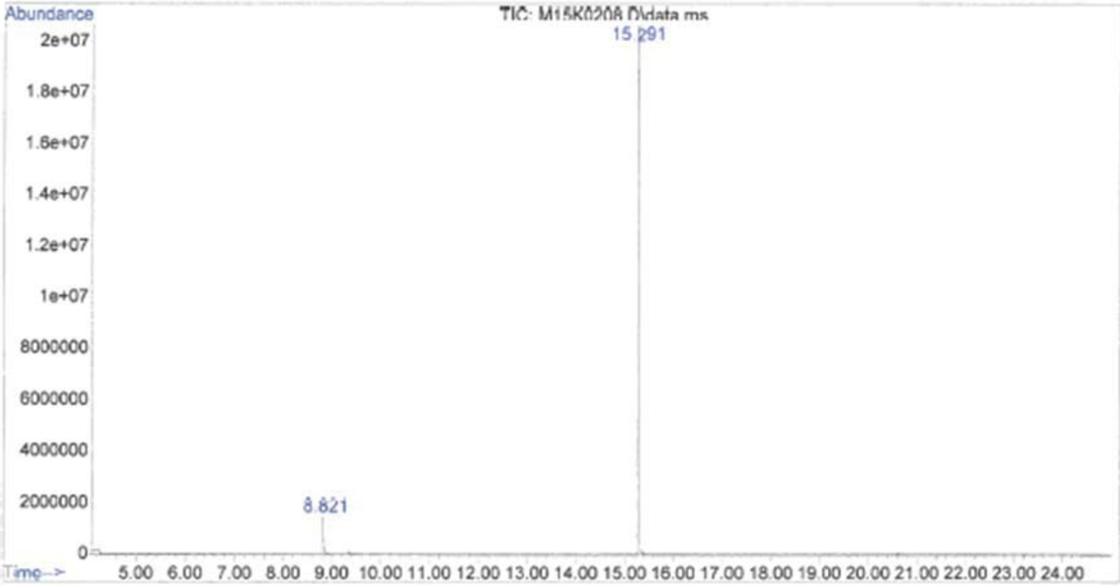
High Resolution Spectra
Positive ion



Accurate Mass Data

Observed Mass	Formula [M+H]+	Calculated mass	Difference (ppm)	iFiT (norm)
252.1722	C11H27NO3P	252.1729	-2.8	0.7
252.1718	C11H27NO3P	252.1729	-4.4	1.0

Figure S7: High resolution mass spectrum (ES^+) of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) used in this study.



Area Percent Report
Sorted by Signal

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Total Ion Chromatogram

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Wed Mar 04 12:20:11 2015

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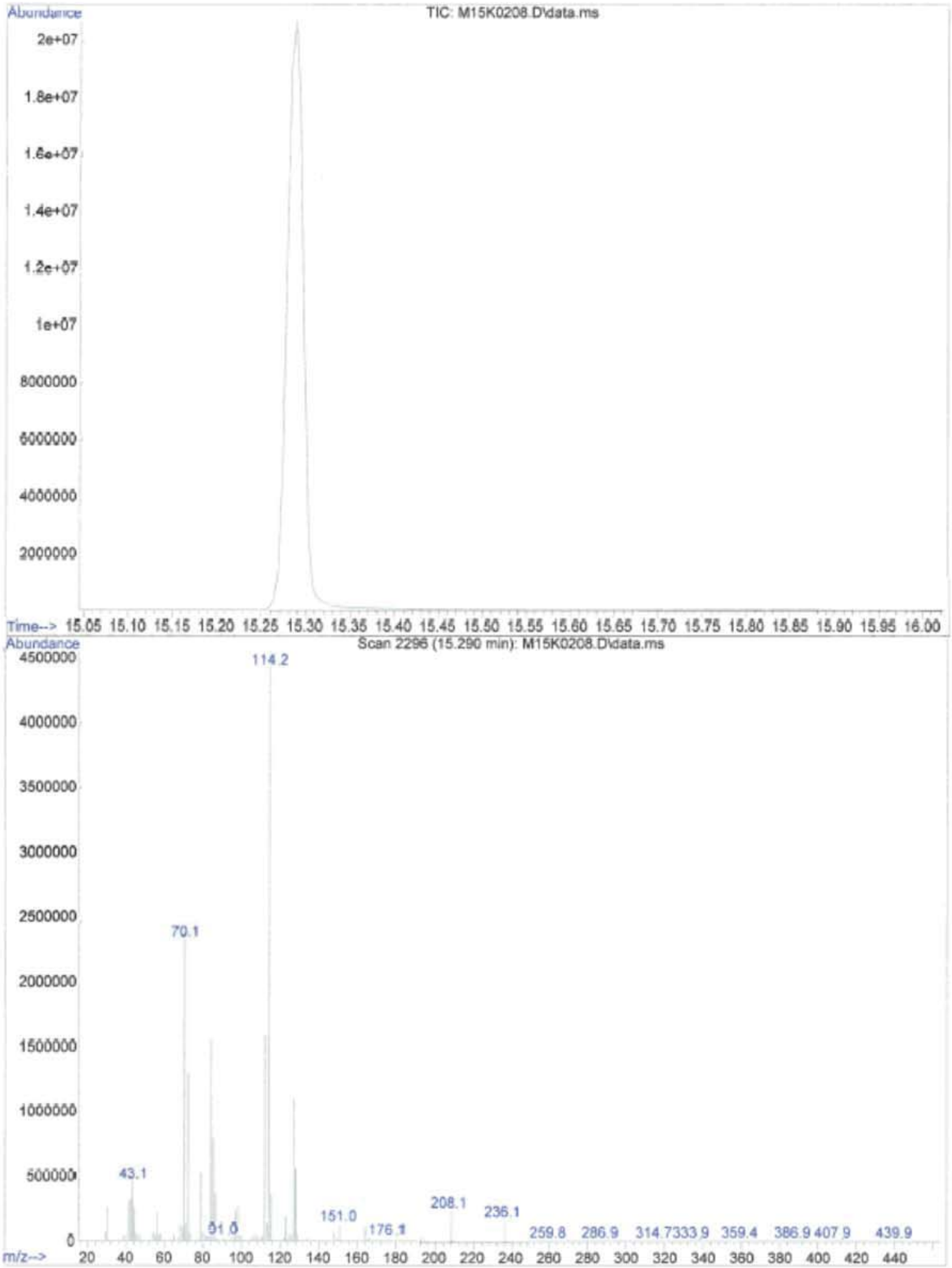


Figure S8: GC-MS analyses of the synthesised 2-diisopropylaminoethyl ethyl methylphosphonate (VO) used in this study .

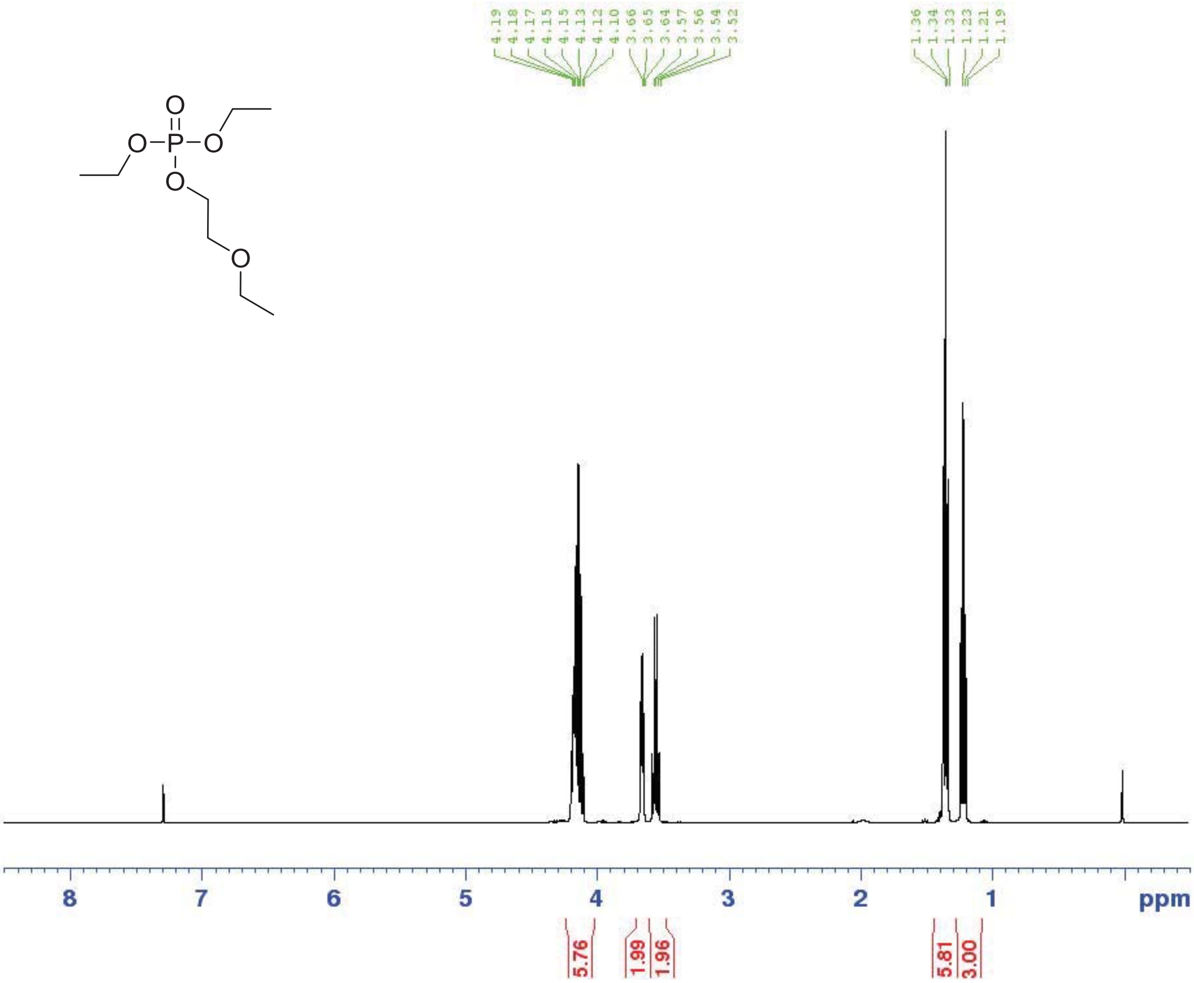


Figure S9: ^{1}H NMR spectrum of the synthesised phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE) used in this study in $CDCl_3$.

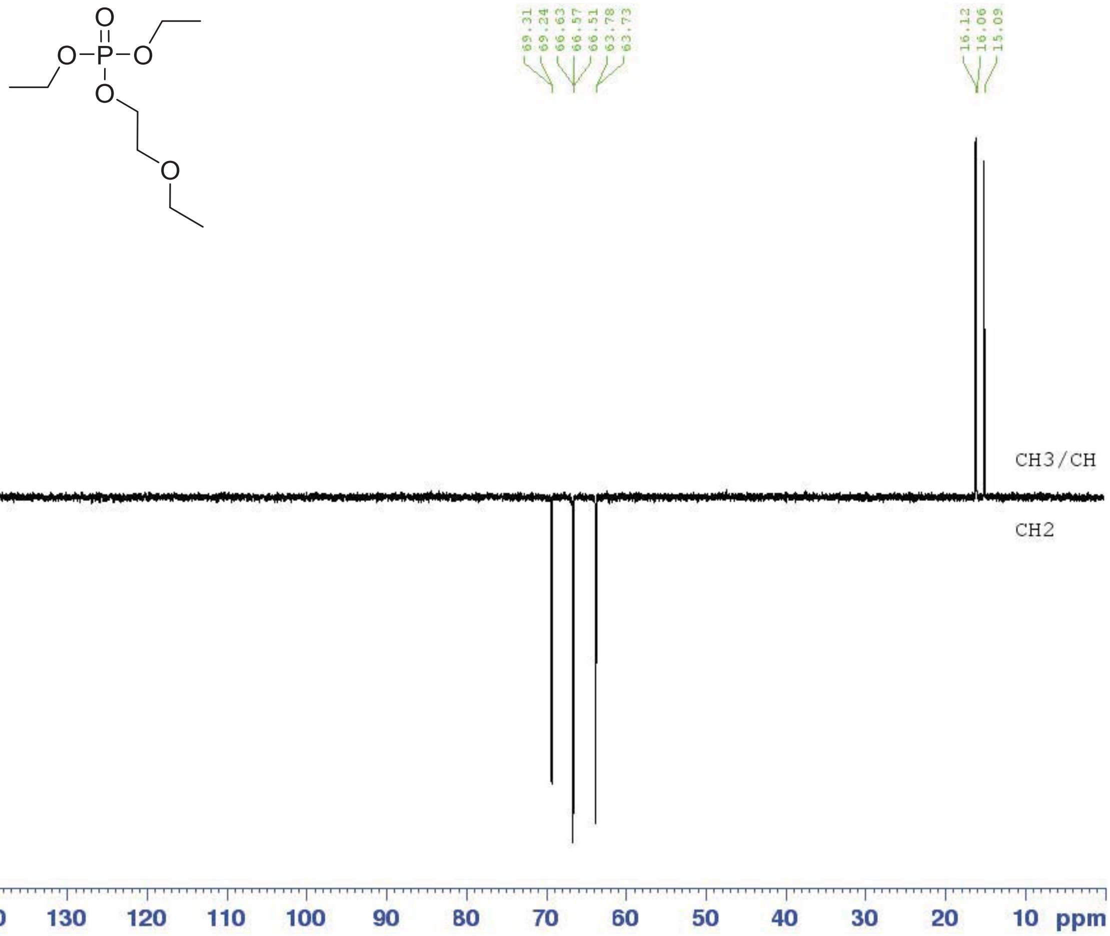


Figure S10: ^{13}C DEPT NMR spectrum of the synthesised phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE) used in this study in $CDCl_3$.

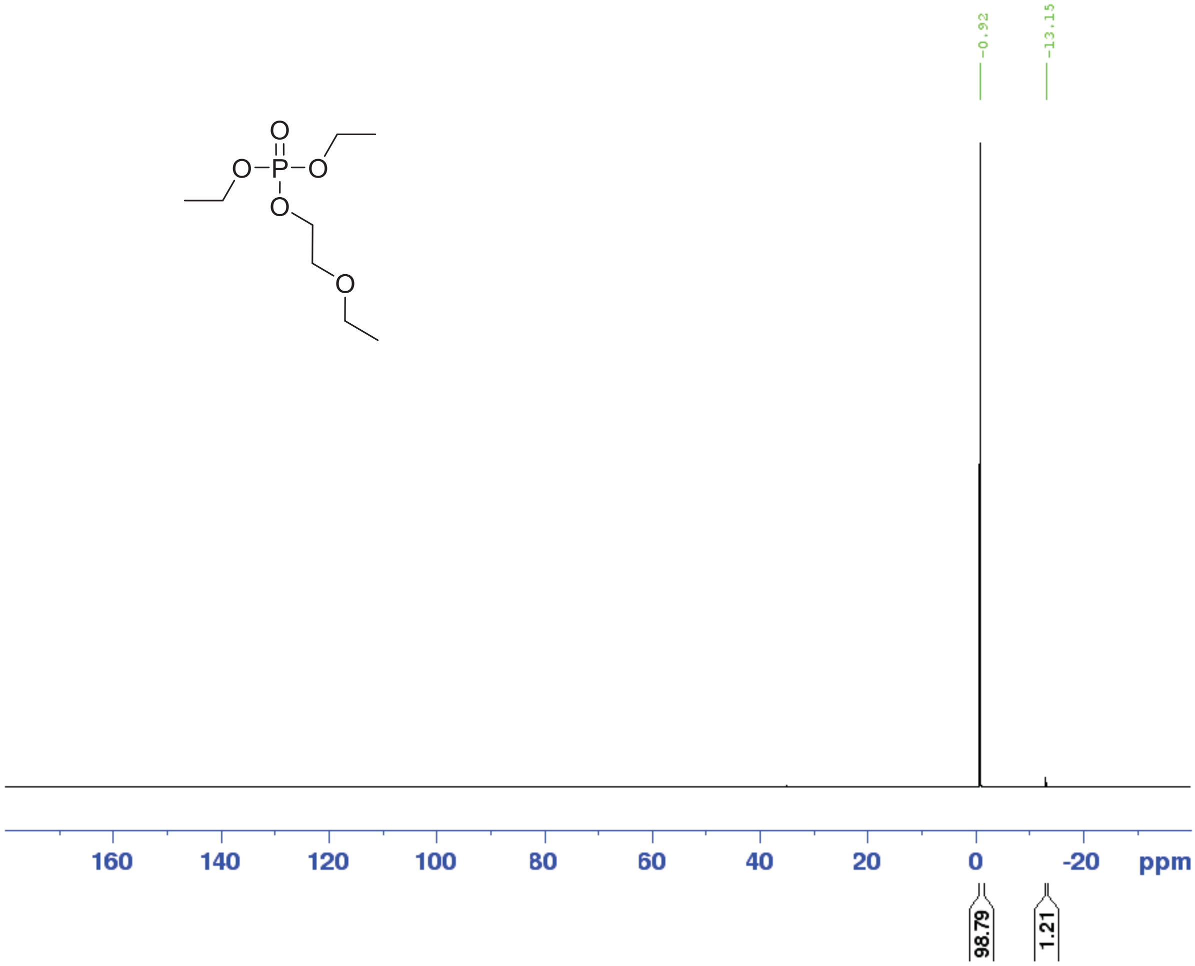
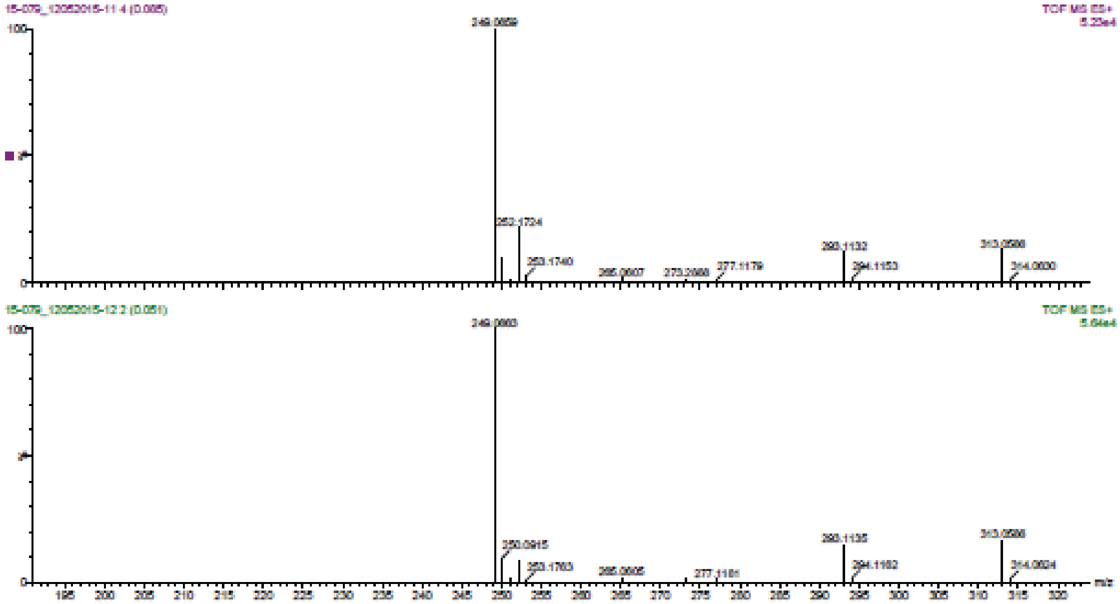


Figure S11: ^{31}P NMR spectrum of the synthesised phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE) used in this study in $CDCl_3$.

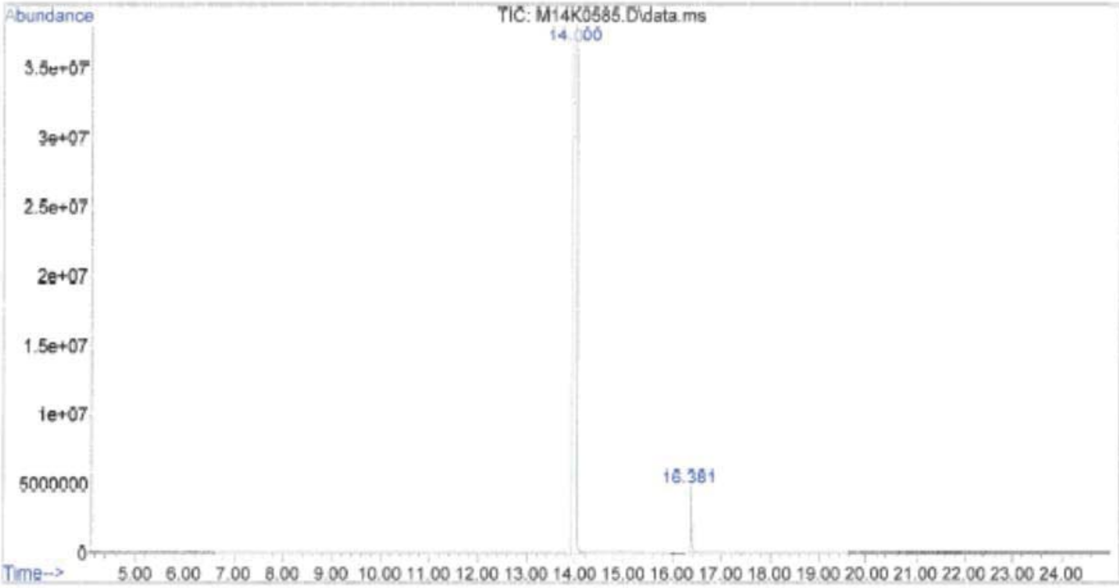
High Resolution Spectra
Positive ion



Accurate Mass Data

Observed Mass	Formula [M+Na]+	Calculated mass	Difference (ppm)	iFiT (norm)
249.0863	C8H19O5PNa	249.0868	-2.0	0.0
249.0859	C8H19O5PNa	249.0868	-3.6	0.0

Figure S12: High resolution mass spectrum (ES$^+$) of phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE) used in this study.



Area Percent Report
Sorted by Signal

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Total Ion Chromatogram

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Mon Mar 02 13:54:57 2015

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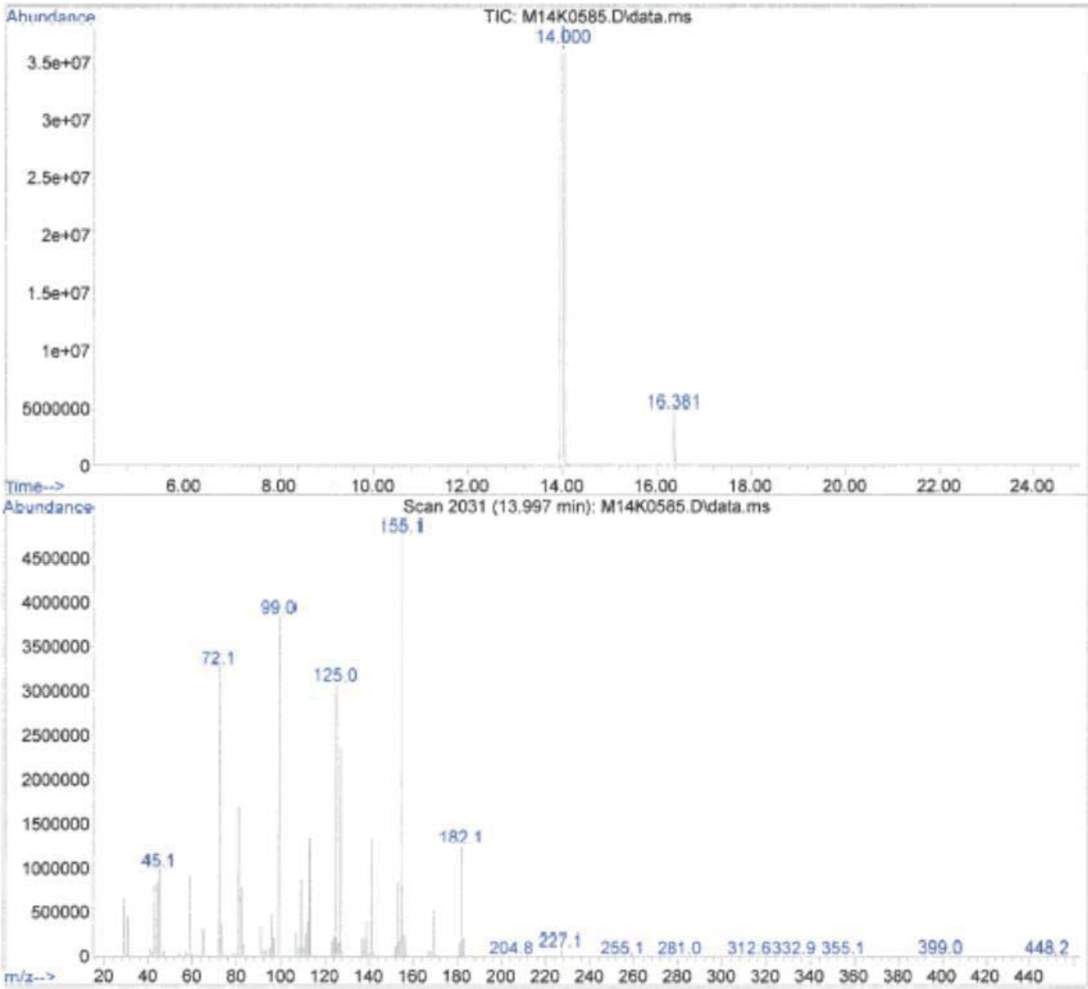


Figure S13: GC-MS analyses of the synthesised of phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE) used in this study.

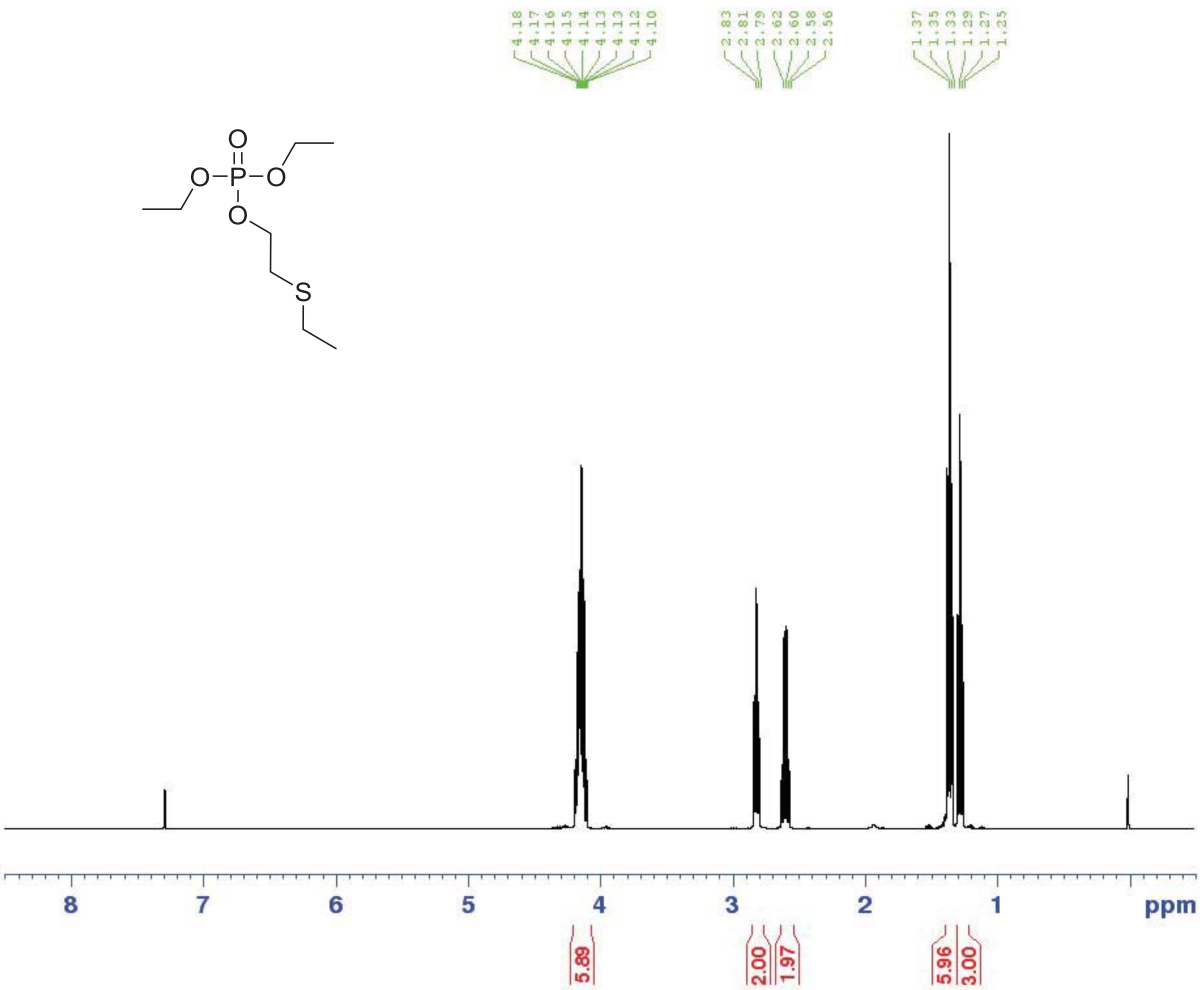


Figure S14: ^{1}H NMR spectrum of the synthesised phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE) used in this study in $CDCl_3$.

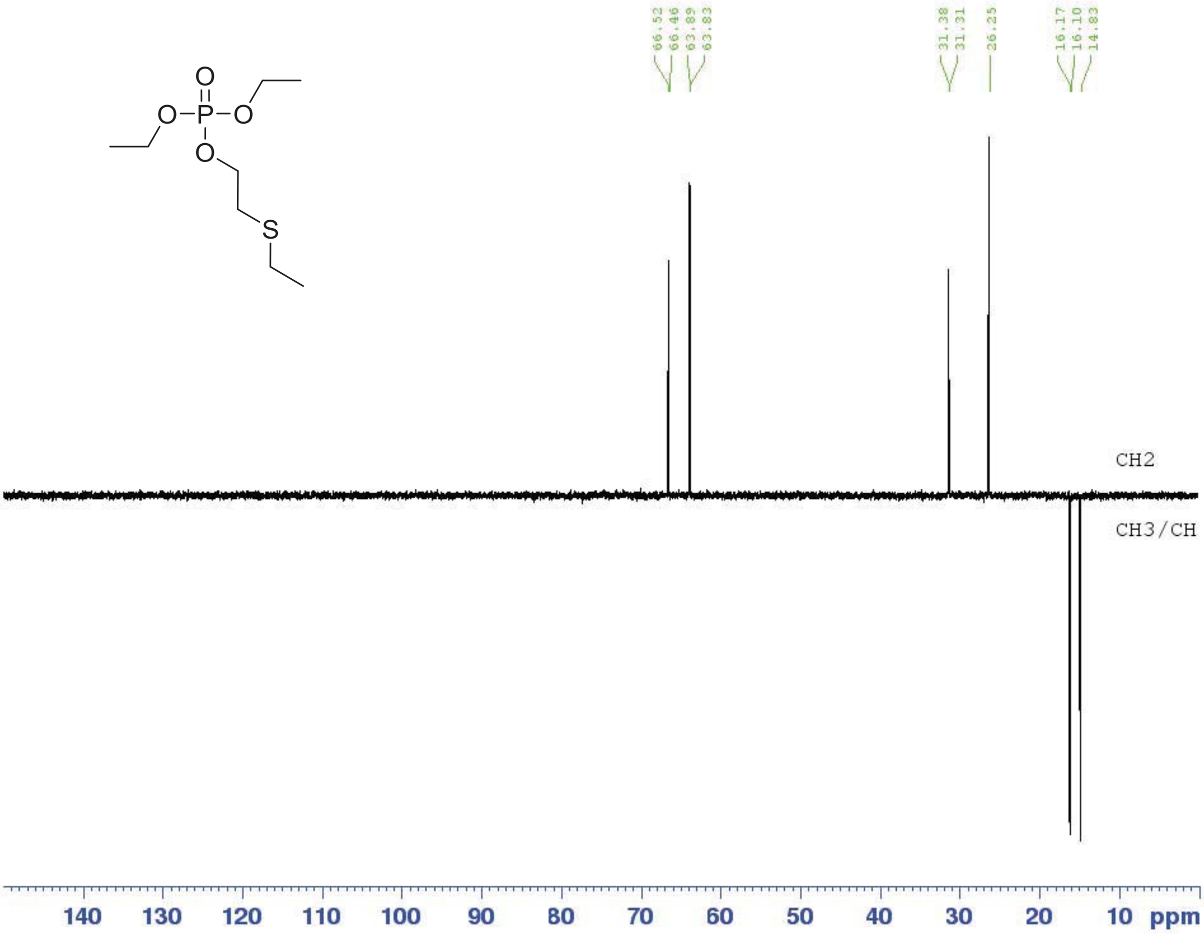


Figure S15: ^{13}C DEPT NMR spectrum of the synthesised phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE) used in this study in $CDCl_3$.

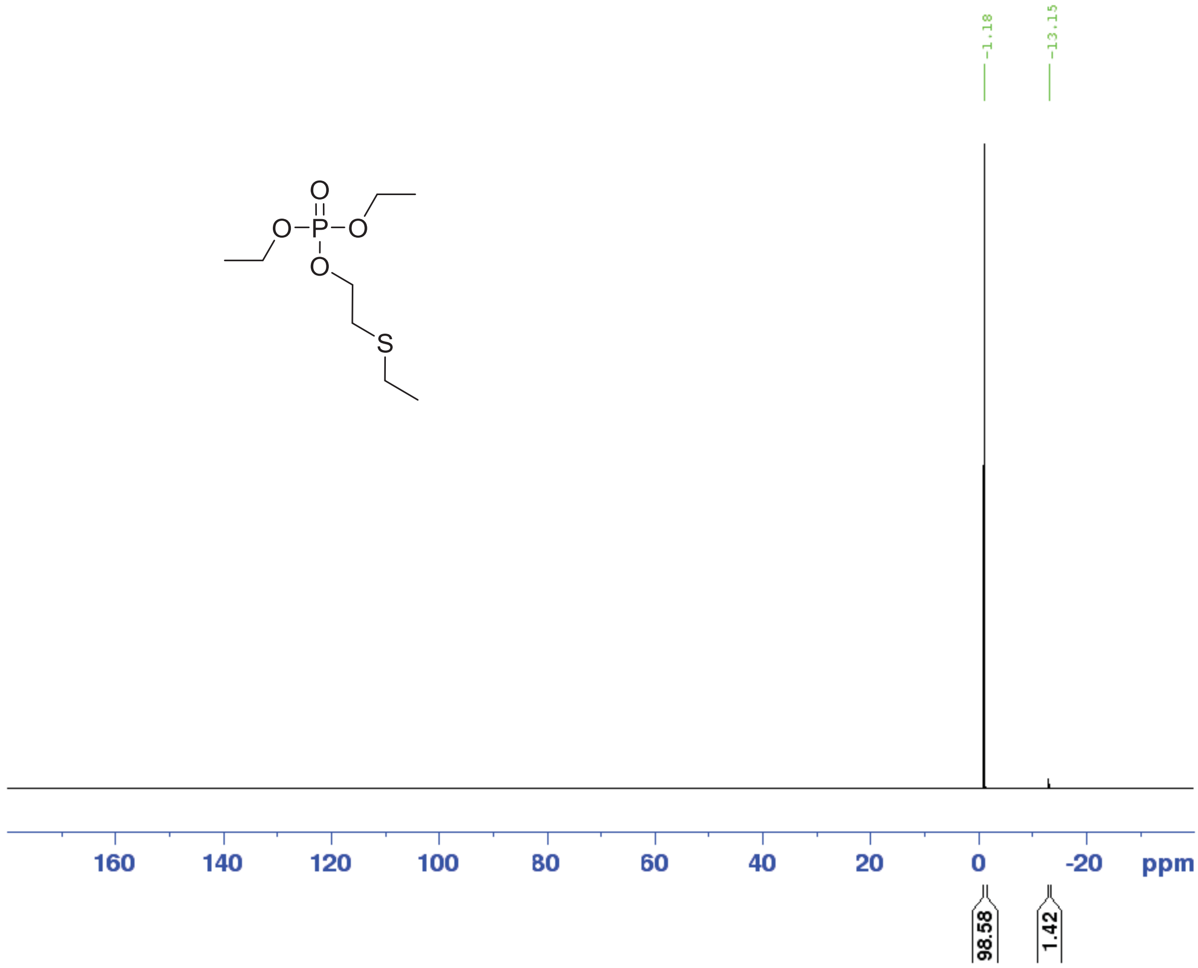
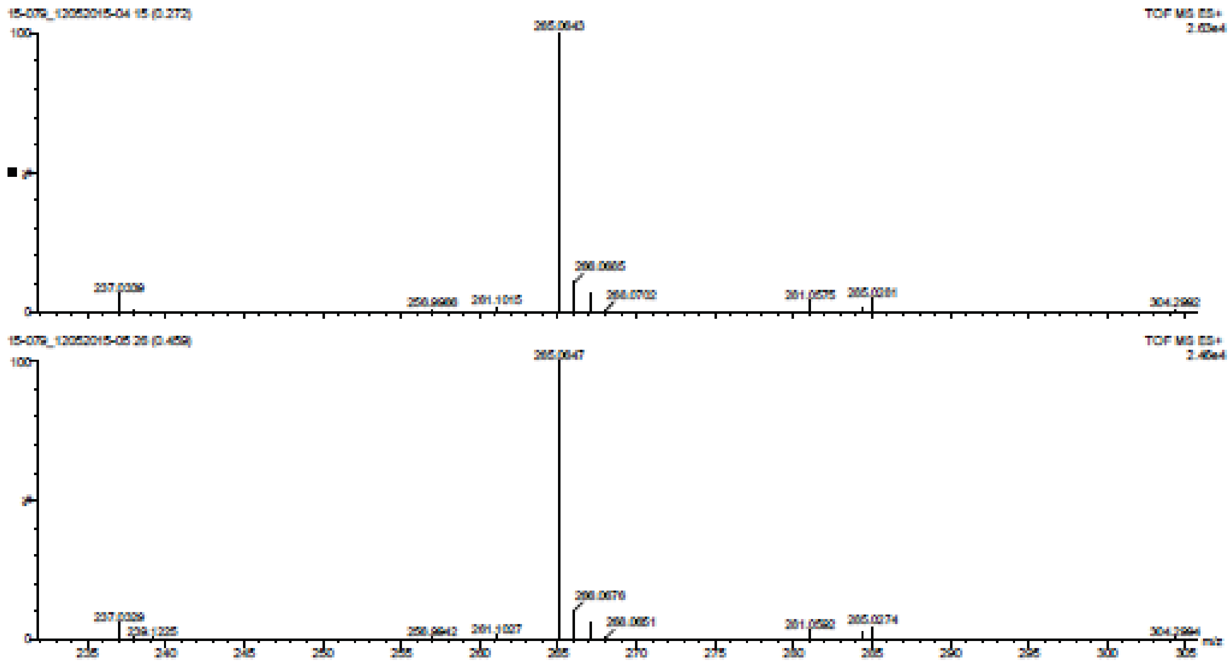


Figure S16: ^{31}P NMR spectrum of the synthesised Phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE) used in this study in $CDCl_3$.

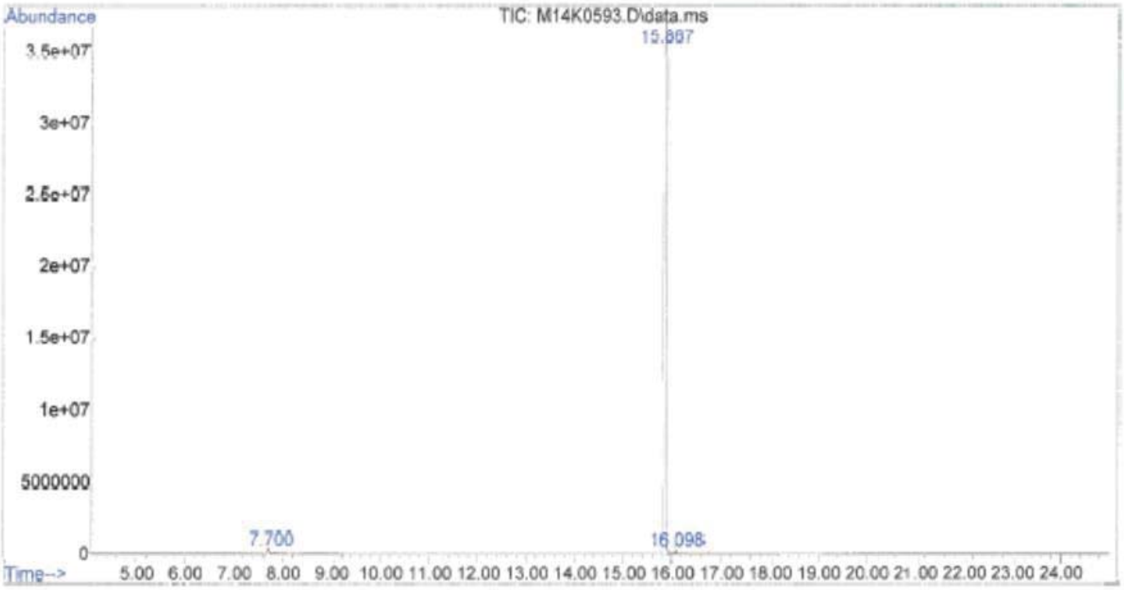
High Resolution Spectra
Positive ion



Accurate Mass Data

Observed Mass	Formula $[M+Na]^+$	Calculated mass	Difference (ppm)	iFiT (norm)
265.0647	C8H19O4SPNa	265.0639	3.0	0.0
265.0643	C8H19O4SPNa	265.0639	1.5	0.0

Figure S17: High resolution mass spectrum (ES^+) of phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE) used in this study.



Area Percent Report
Sorted by Signal

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Mon Mar 02 13:54:46 2015

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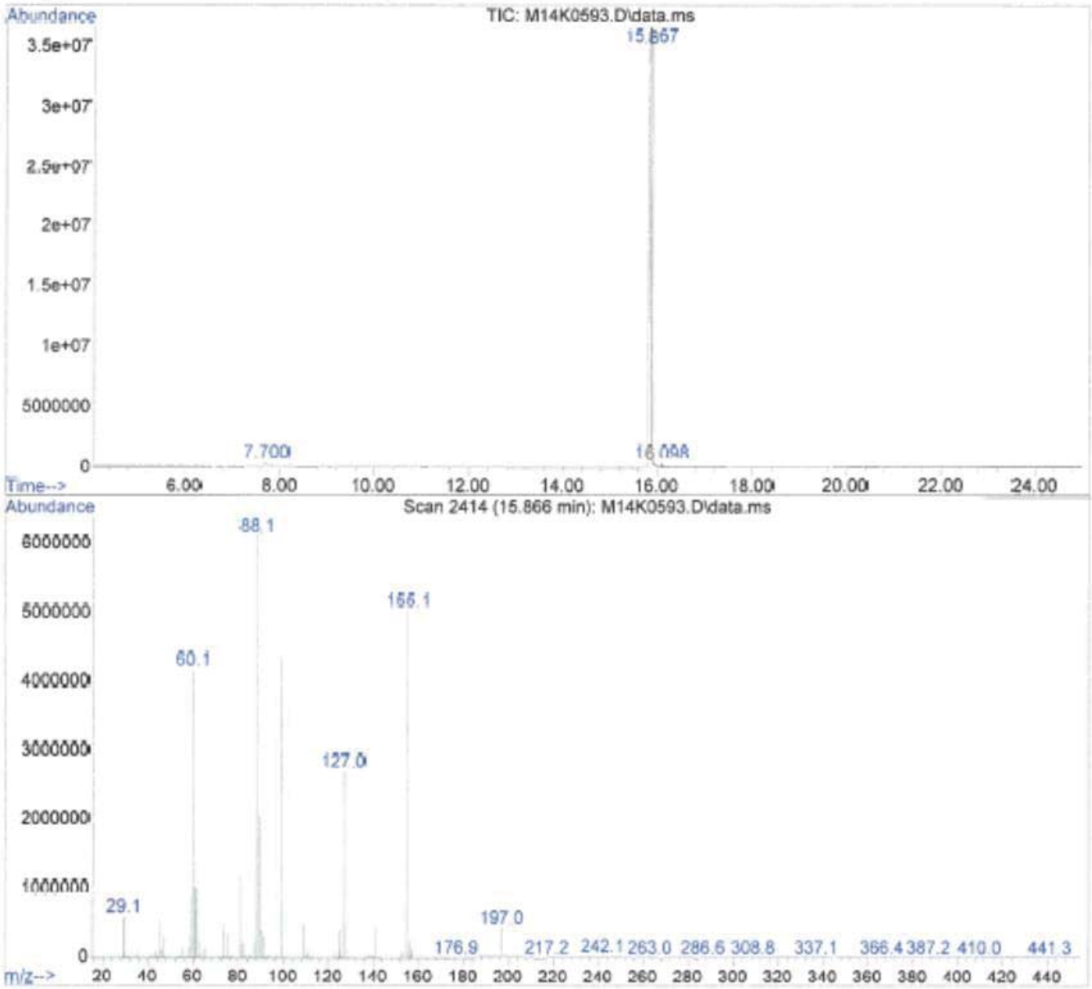


Figure S18: GC-MS analyses of the synthesised of phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE) used in this study .

Luminescence Spectral Plots:

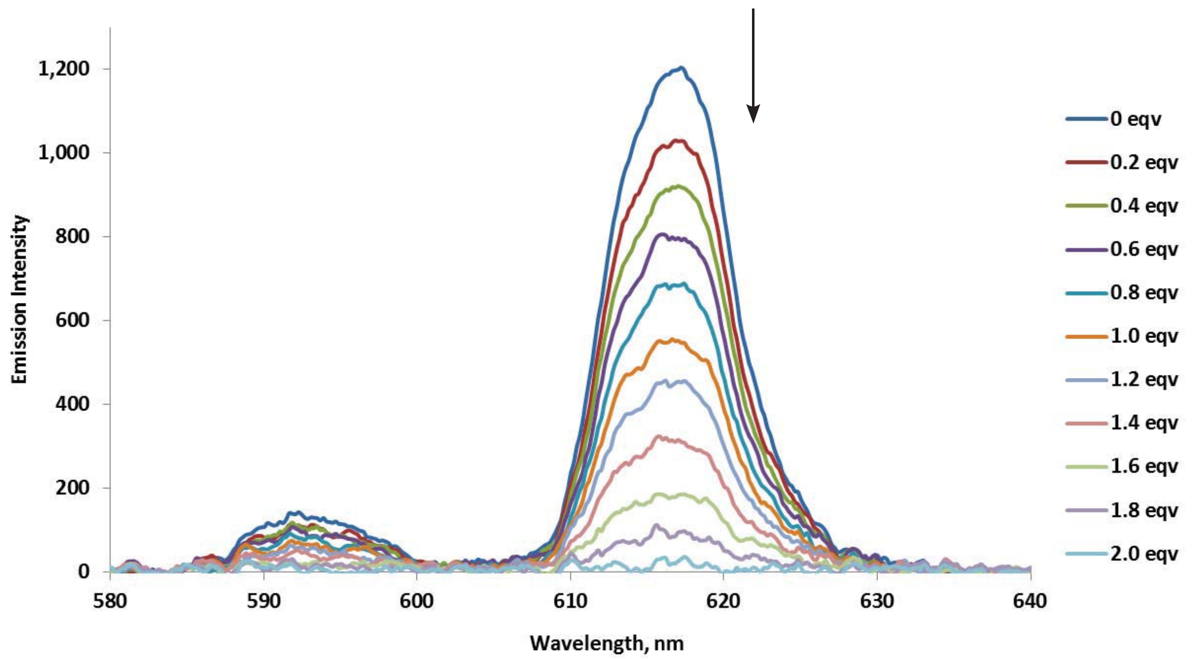


Figure S19: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of N,N,N',N'-tetramethyl-1,4-butanediamine (TMBD); [complex] = 1×10^{-5} mol dm^{-3}, 293 K.

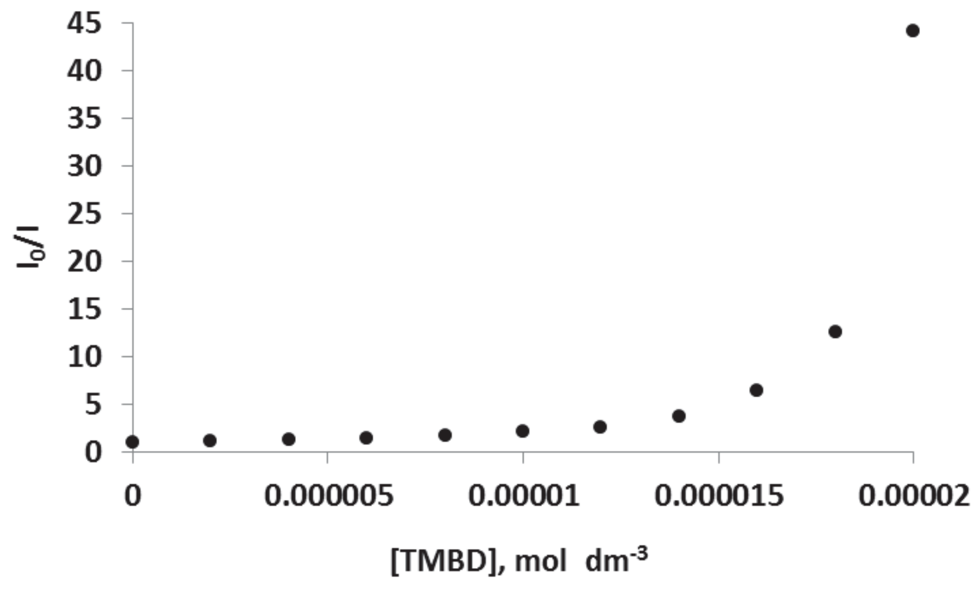


Figure S20: Stern-Volmer plot of the luminescent quenching titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with up to 2 mol equivalents of N,N,N',N'-tetramethyl-1,4-butanediamine (TMBD) where λ_{em} = 617 nm; [complex] = 1×10^{-5} mol dm^{-3}, 293K.

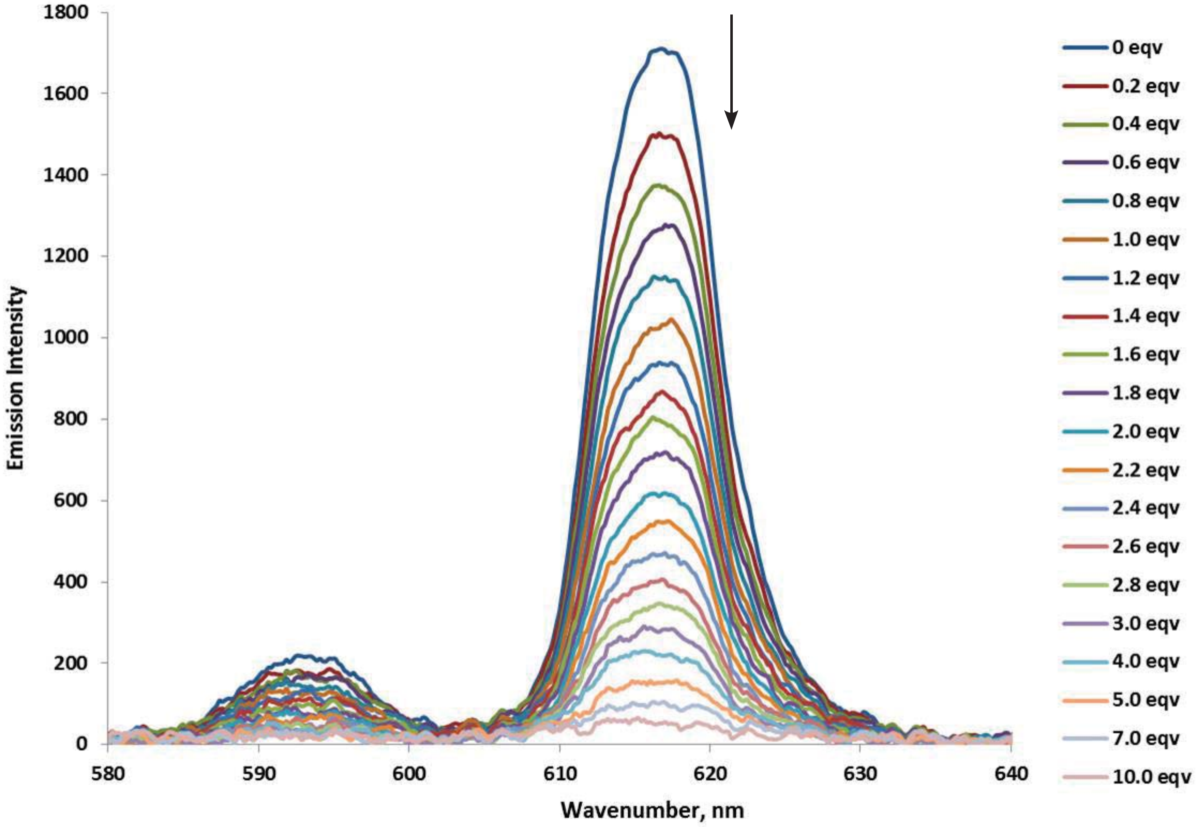


Figure S21: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of [2-(2-diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

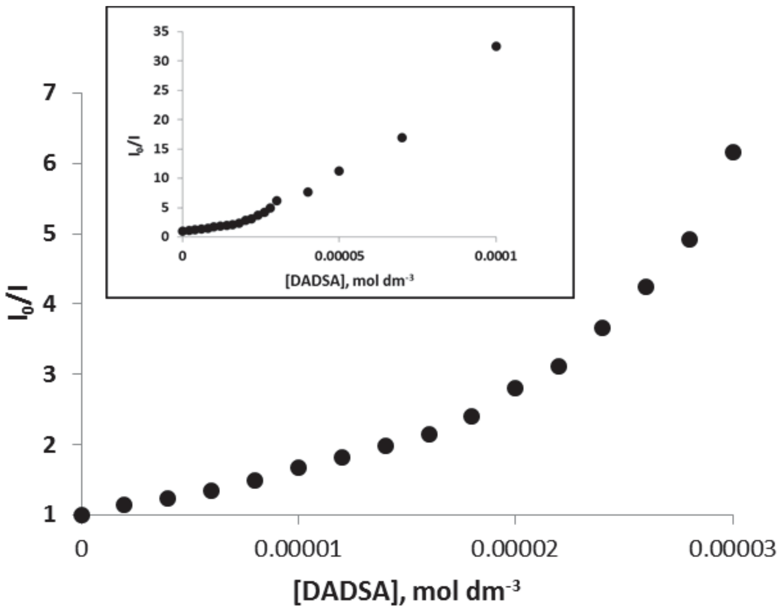


Figure S22: Stern-Volmer plot of the luminescent quenching titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with up to 3 mol equivalents of [2-(2-diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA) where λ_{em} = 617 nm; [complex] = 1 x 10^{-5} mol dm^{-3}, 293K. Inset: Stern-Volmer plot over the whole titration range (10 mol equivalents).

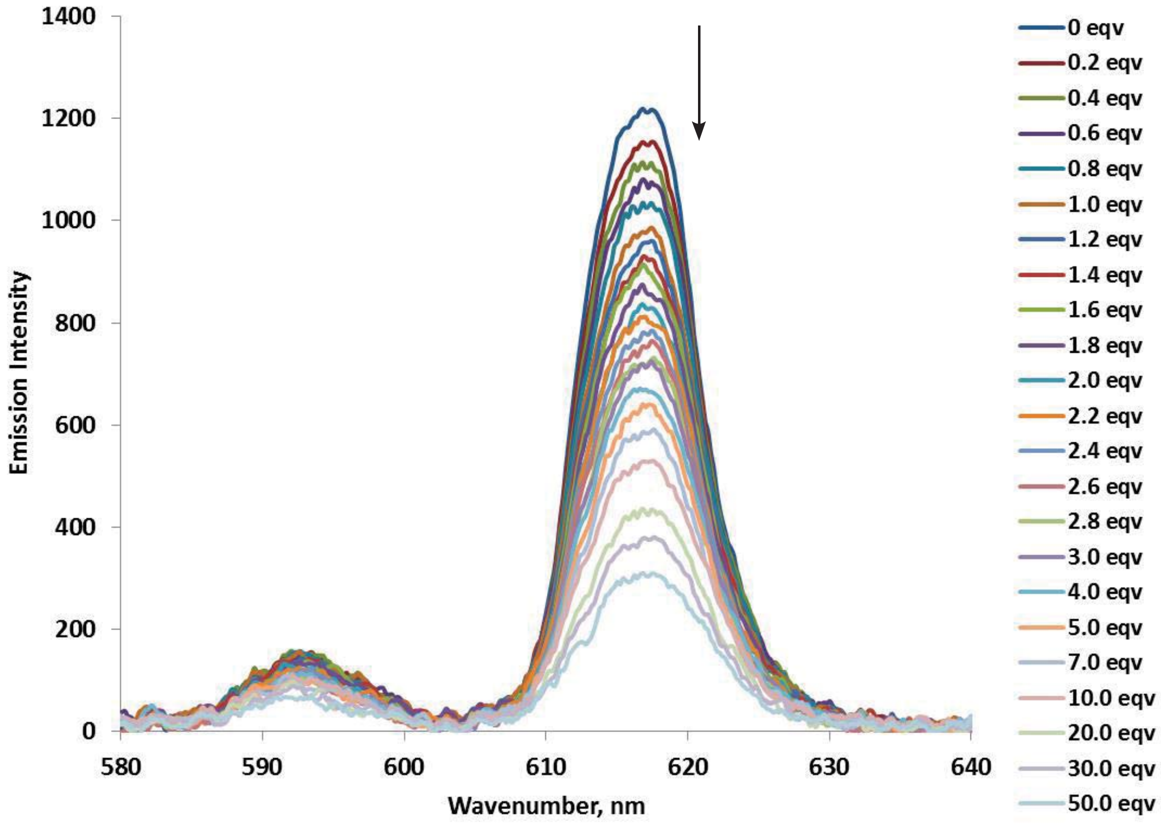


Figure S23: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of tetraethyl ethylenediphosphonate (TEEP); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

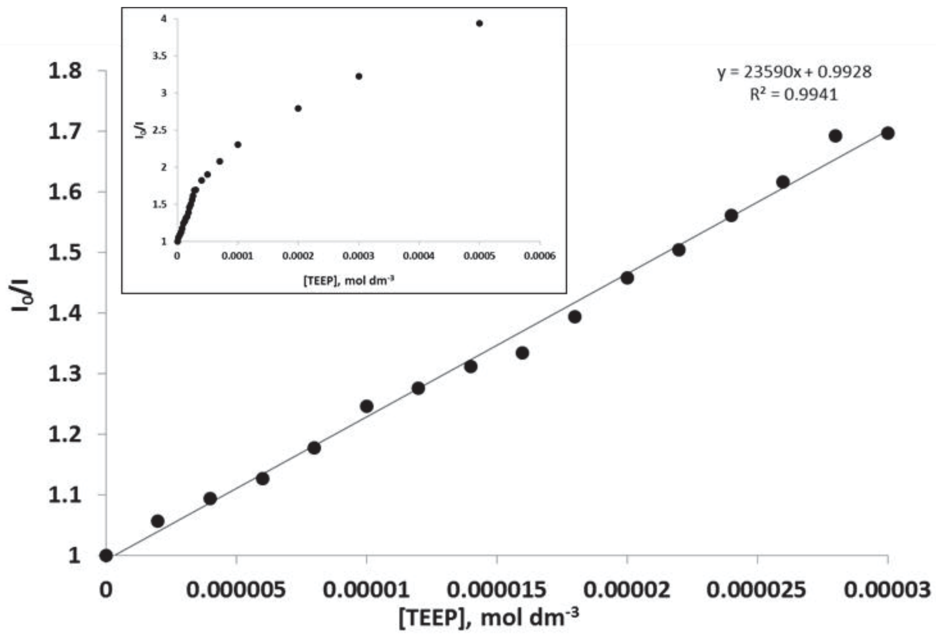


Figure S24: Stern-Volmer plot of the luminescent quenching titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with up to 3 mol equivalents of tetraethyl ethylenediphosphonate (TEEP) where λ_{em} = 617 nm; [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K. Inset: Stern-Volmer plot over the whole titration range (50 mol equivalents).

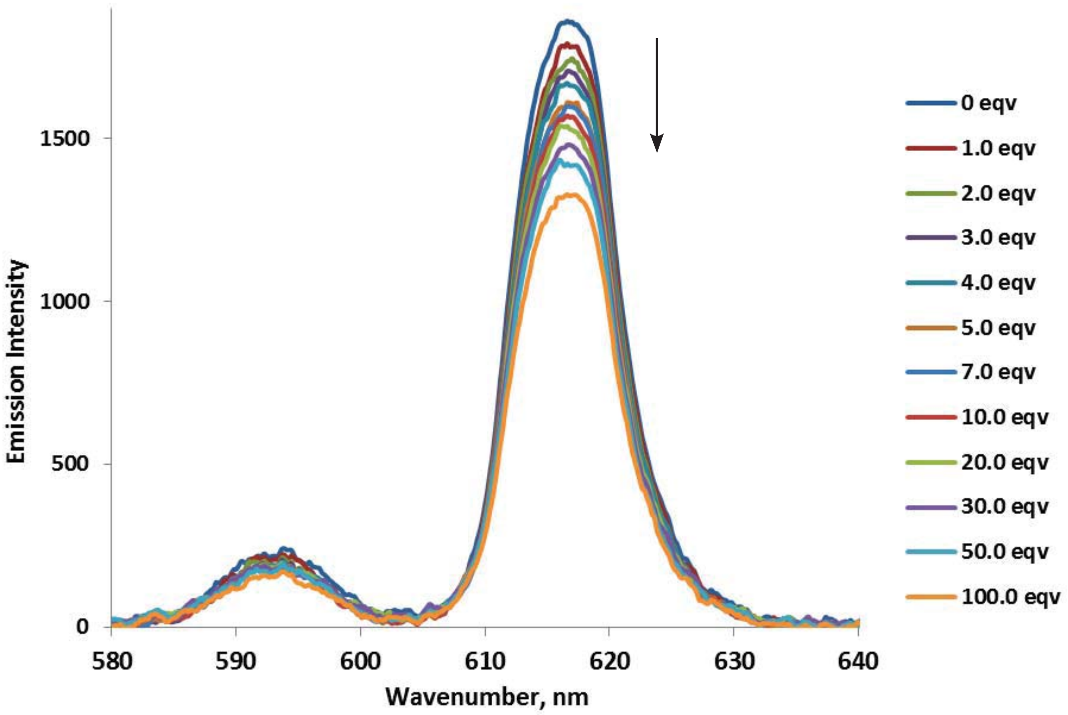


Figure S25: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of phosphoric acid, diethyl 2-ethoxyethyl ester (DEPATEXE); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

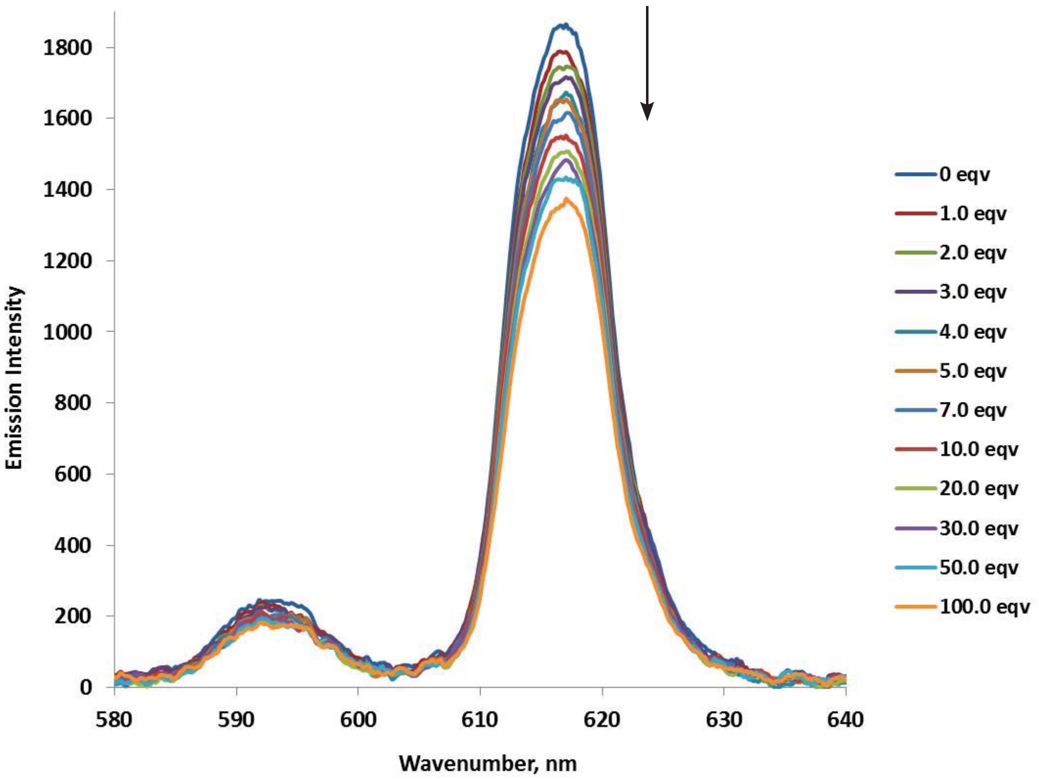


Figure S26: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

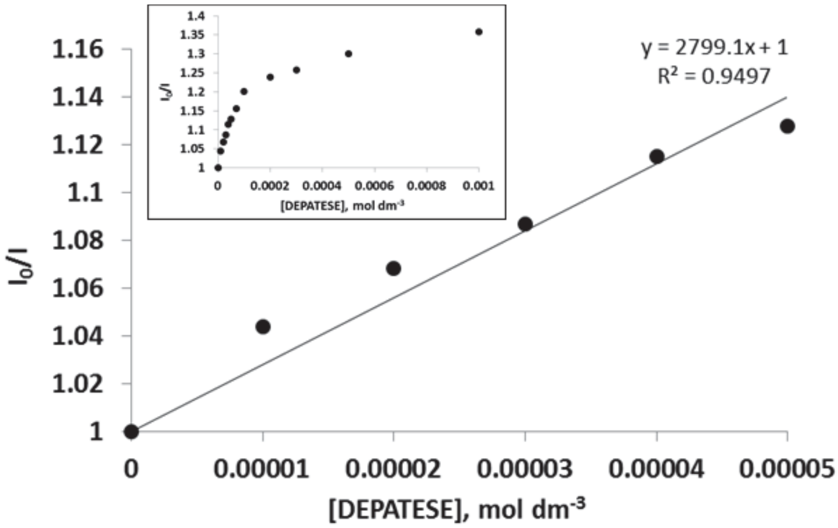


Figure S27: Stern-Volmer plot of the luminescent quenching titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with up to 5 mol equivalents of phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE) where λ_{em} = 617 nm; [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K. Inset: Stern-Volmer plot over the whole titration range (100 mol equivalents).

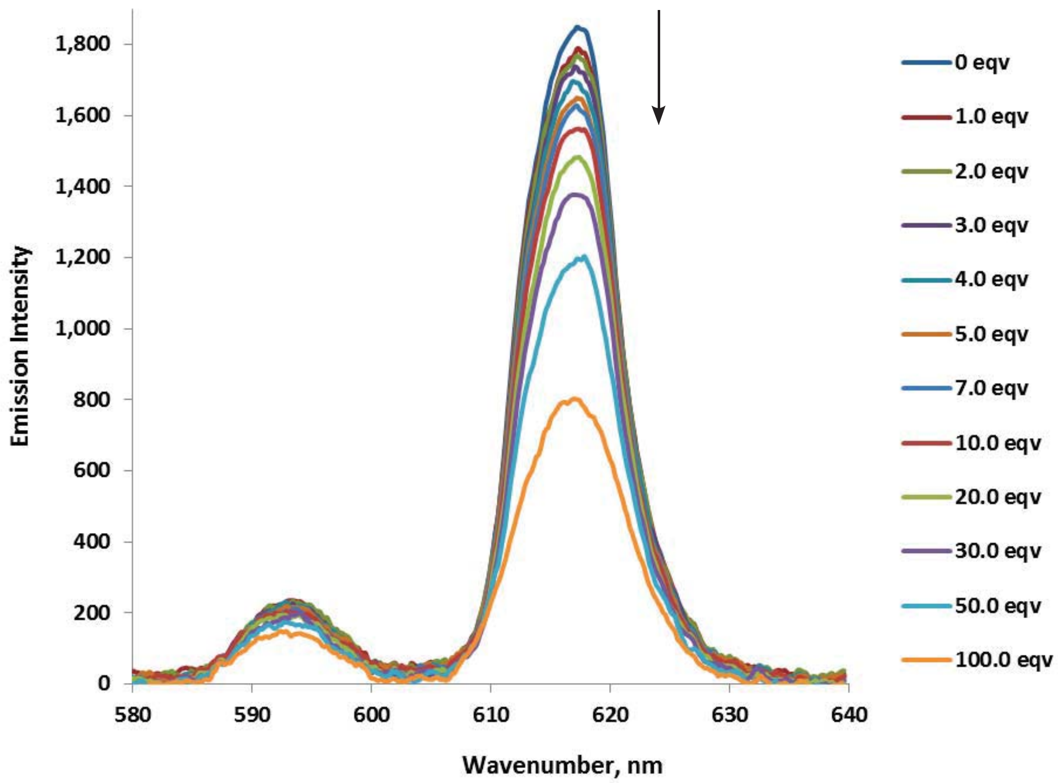


Figure S28: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of methyl N-acetyl-O-(ethoxy(methyl)phosphonyl)-L-serinate (Ac-Ser(MPE)-OMe; [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

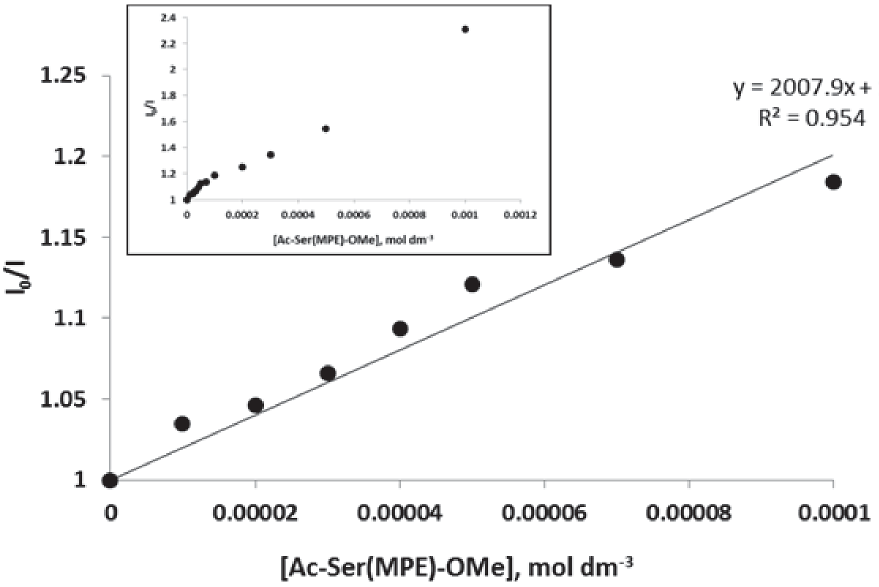


Figure S29: Stern-Volmer plot of the luminescent quenching titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with up to 10 mol equivalents of methyl N-acetyl-O-(ethoxy(methyl)phosphonyl)-L-serinate (Ac-Ser(MPE)-OMe where λ_{em} = 617 nm; [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K. Inset: Stern-Volmer plot over the whole titration range (100 mol equivalents).

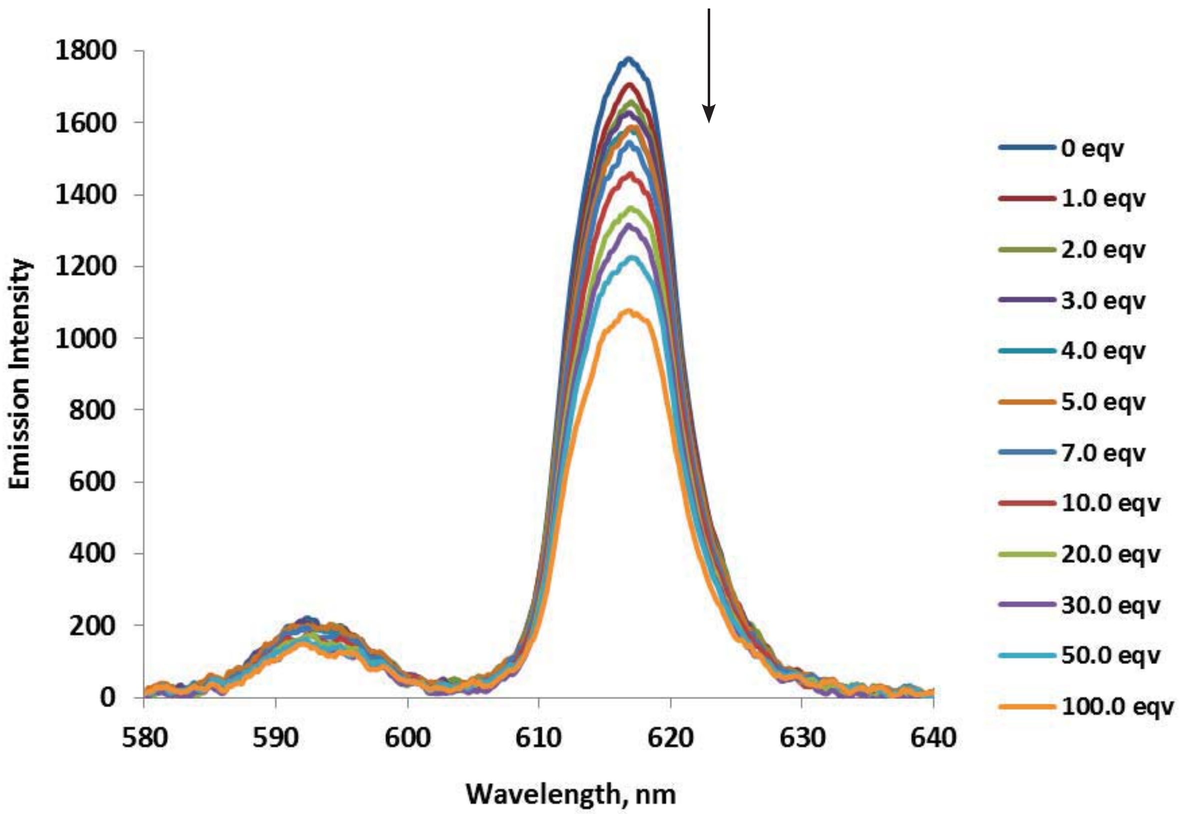


Figure S30: Quenching of the luminescent emission of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon addition of benzyl N-((benzyloxy)carbonyl)-O-(ethoxy(methyl)phosphonyl)-L-serinate (Cbz-Ser(MPE)-OBn); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

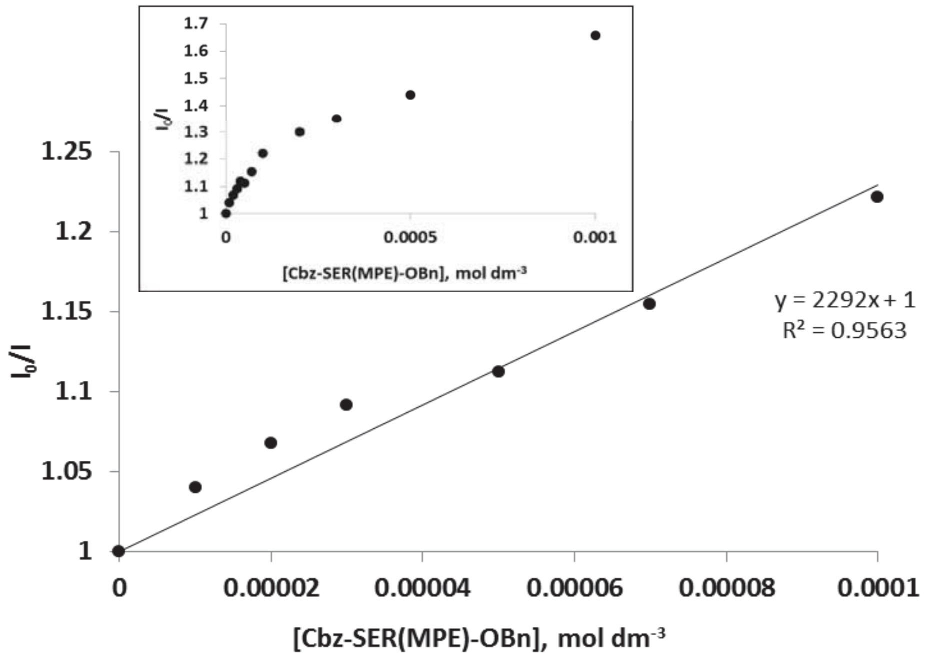


Figure S31: Stern-Volmer plot of the luminescent quenching titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with up to 10 mol equivalents of benzyl N-((benzyloxy)carbonyl)-O-(ethoxy(methyl)phosphonyl)-L-serinate (Cbz-Ser(MPE)-OBn) where λ_{em} = 617 nm; [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K. Inset: Stern-Volmer plot over the whole titration range (100 mol equivalents).

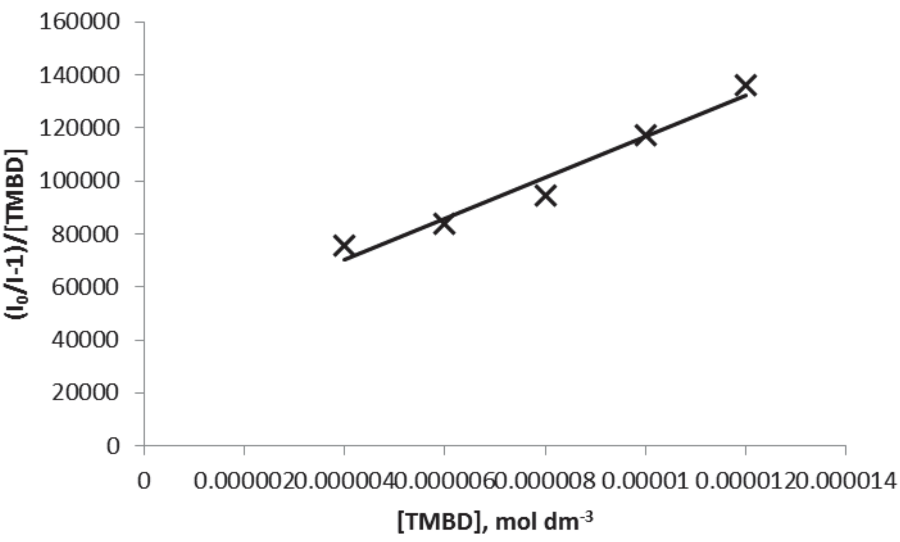


Figure S32: Extended Stern-Volmer plot of the luminescence titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with TMBD for the TMBD concentration range from 4 x 10^{-6} mol dm^{-3} to 1 x 10^{-5} mol dm^{-3}. Slope = 7.72 x 10^9, R^2 = 0.963.

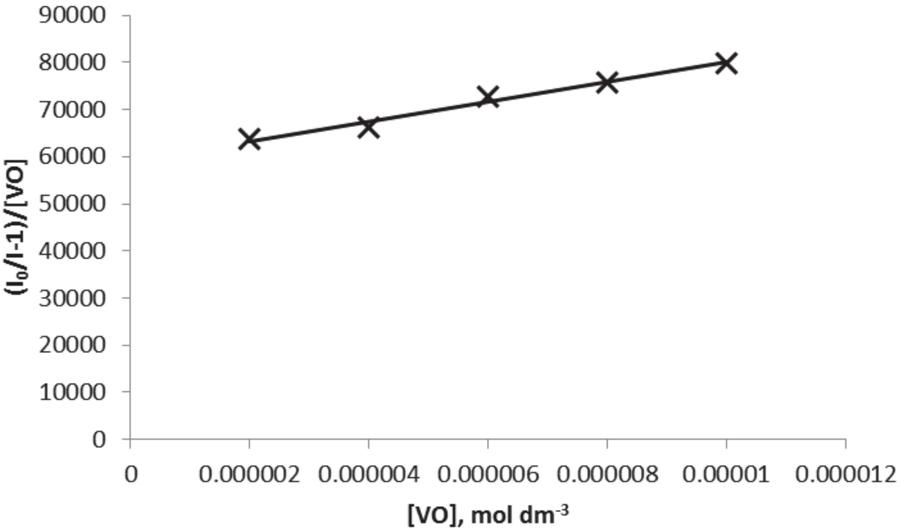


Figure S33: Extended Stern-Volmer plot of the luminescence titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with VO for the VO concentration range up to 1 x 10^{-5} mol dm^{-3}. Slope = 2.10 x 10^9, R^2 = 0.985.

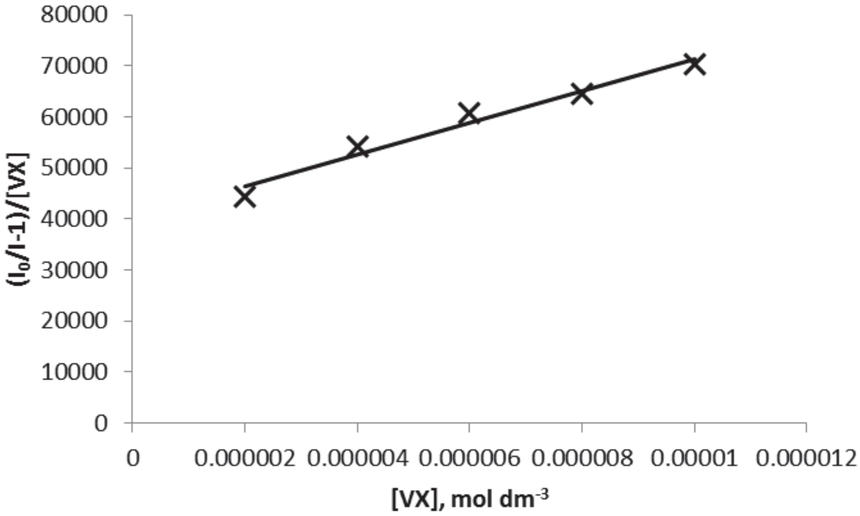


Figure S34: Extended Stern-Volmer plot of the luminescence titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with VX for the VX concentration range up to 1 x 10^{-5} mol dm^{-3}. Slope = 3.12 x 10^9, R^2 = 0.971.

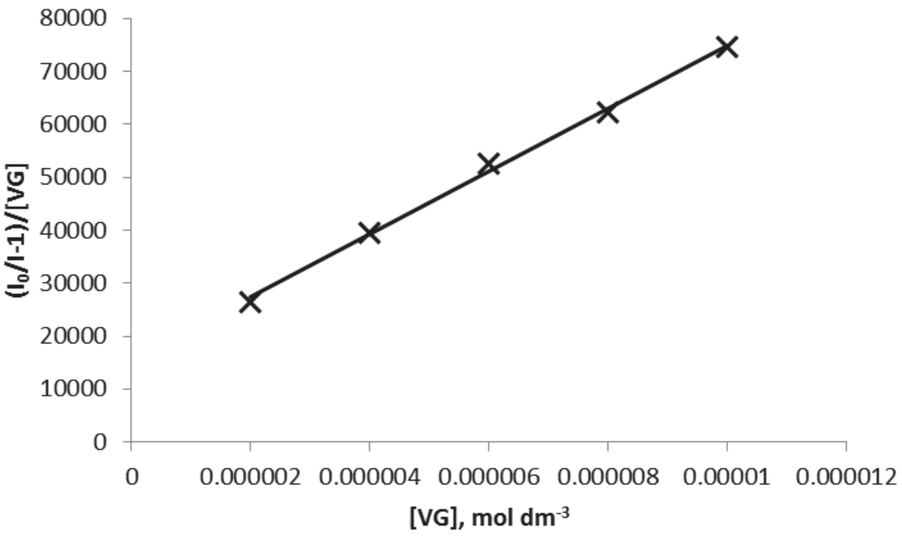


Figure S35: Extended Stern-Volmer plot of the luminescence titration of $Eu(phen)_2(NO_3)_3(H_2O)_3$ with VG for the VG concentration range up to 1×10^{-5} mol dm^{-3}. Slope = 5.94×10^9, $R^2 = 0.997$.

UV-Vis Spectral Plots:

Live OP CWA: Thermo Scientific Evolution 201 UV-vis spectrophotometer. Absorbance, band width = 2 nm, Integration time 0.05 secs, data interval 1.00 nm, scan speed 1200 nm/min, connected to cuvette stage (in the fumecupboard) with fibre optic cables. [1,2]

Simulant studies: Varian Cary 50-Bio UV-vis Spectrophotometer. Absorbance, Dual beam, band width = 1.5 nm, data interval 1.00 nm, scan speed 600 nm/min, integration time 0.1 secs.

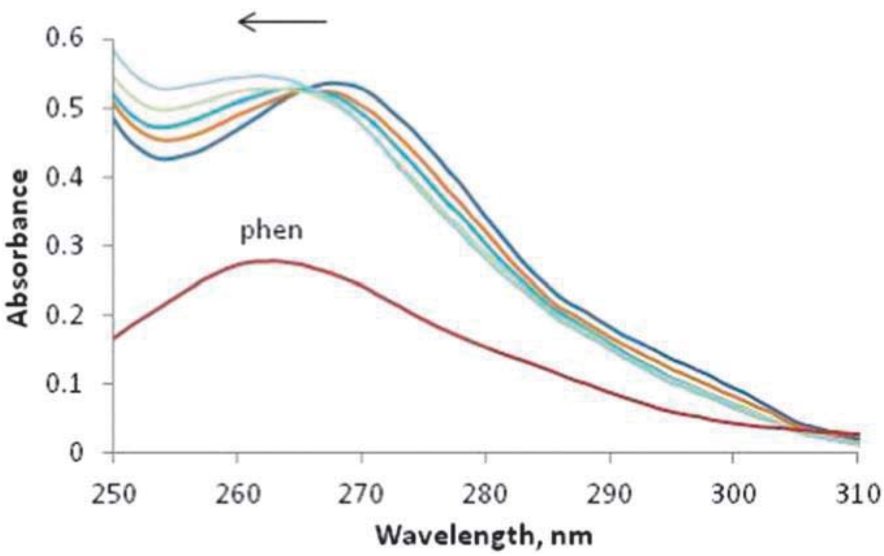


Figure S36: Selected UV-vis absorbance spectra of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon additions of VX (complex, 1, 2, 5 and 10 mol eqv). These spectra were obtained on a Thermo Scientific Evolution UV-vis spectrophotometer used in our previous work with live OP CWA. [1,2] The low absorbance red trace is free 1,10-phenanthroline. $[complex]_{inital} = 1 \times 10^{-5}$M mol dm^{-3}, 293K.

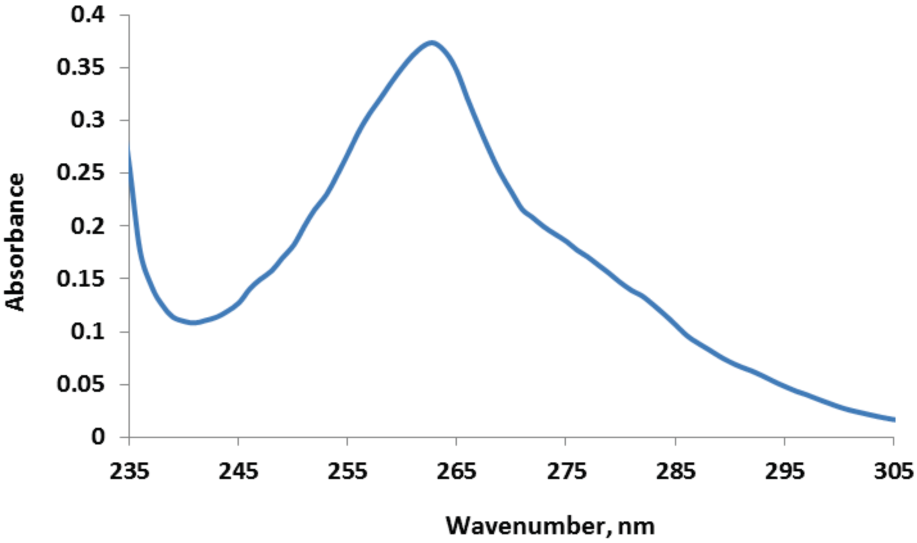


Figure S37: The UV-vis absorbance spectrum of 1,10-phenanthroline obtained on the Varian Cary 50-Bio UV-vis spectrophotometer used in this study [phen] = 1 x 10^{-5}M mol dm^{-3}, 293K.

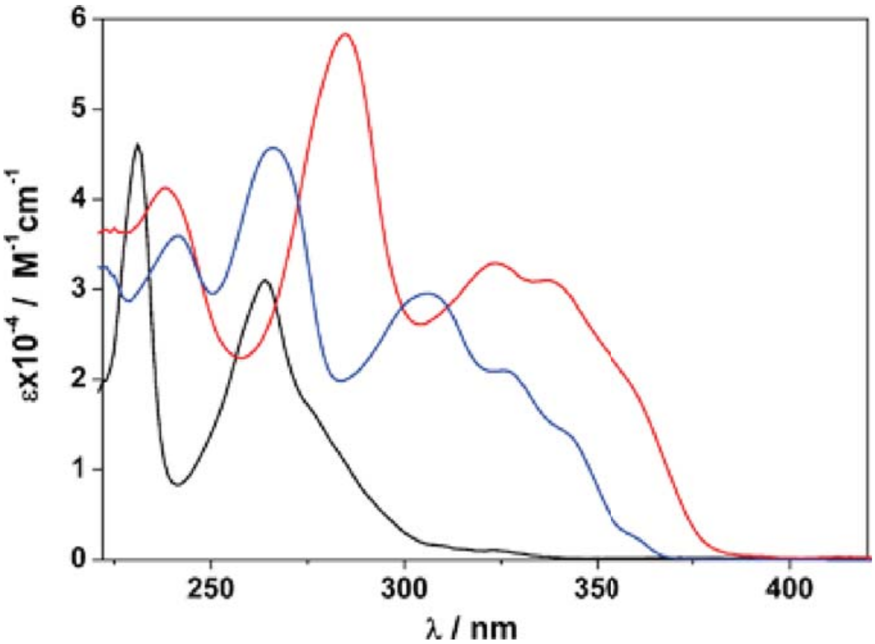


Figure S38: The UV-vis absorbance spectrum of 1,10-phenanthroline (black) in CH_2Cl_2 obtained from the literature.[3] The blue and red traces are of 2,9-aromatic substituted 1,10-phenanthrolines. Image reproduced with permission from *Chem. Soc. Rev.*, 2009, **38**, 1690-1700.

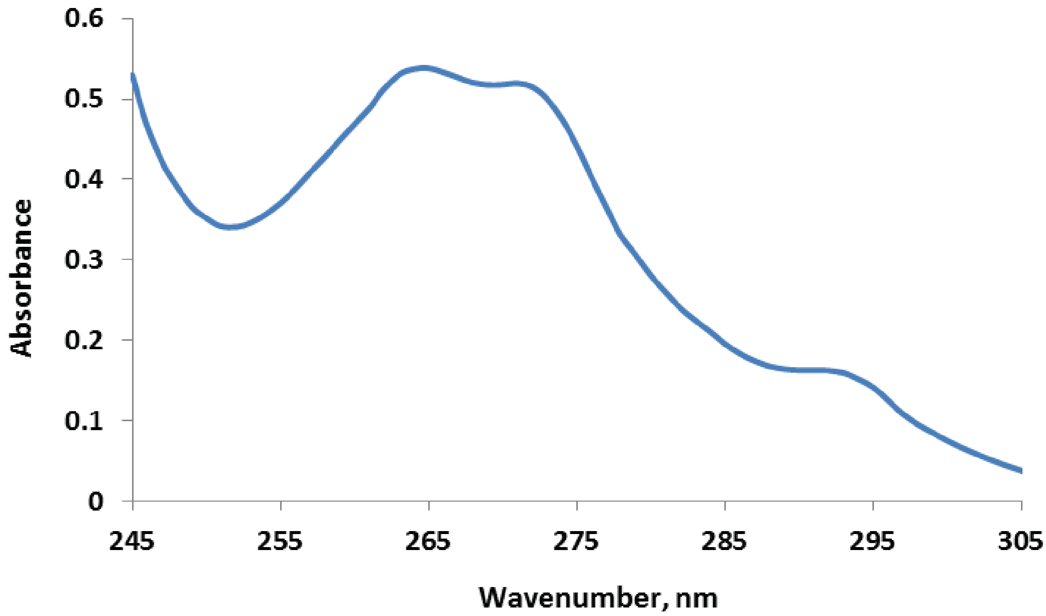


Figure S39: The UV-vis absorbance spectrum of Eu(phen)$_2$(NO$_3$)$_3$(H$_2$O)$_3$ obtained on the Varian Cary 50-Bio UV-vis spectrophotometer used this study. [complex] = 1 x 10^{-5}M mol dm^{-3}, 293 K.

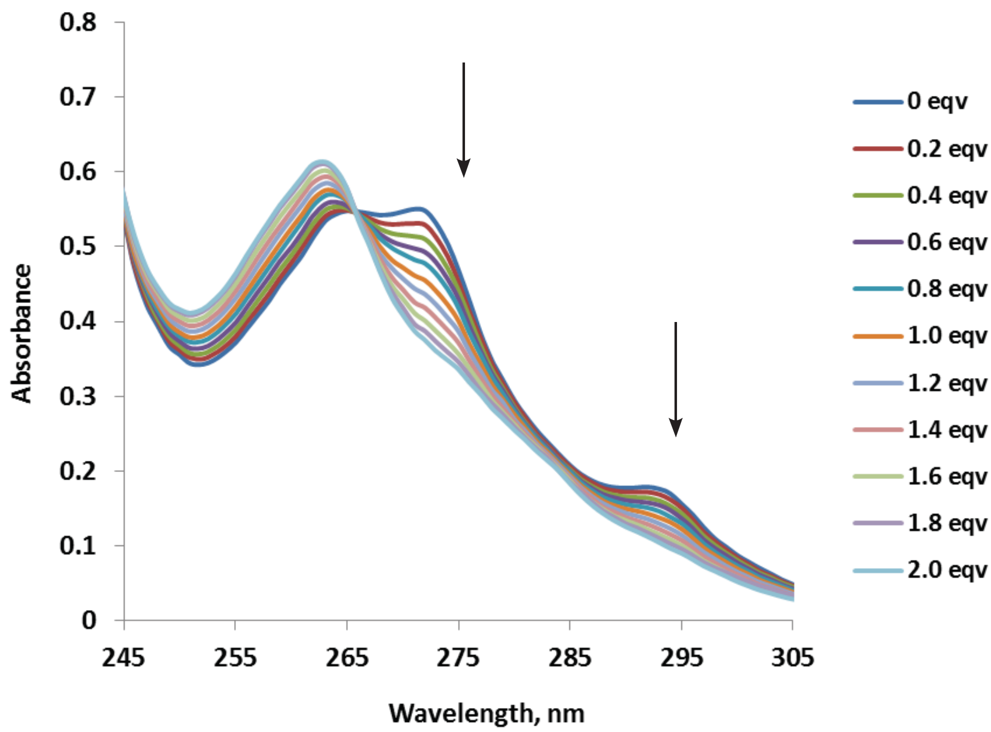


Figure S40: The UV-vis absorbance spectrum of Eu(phen)$_2$(NO$_3$)$_3$(H$_2$O)$_3$ upon titration of up to 2 mol equivalents of N,N,N',N'-tetramethyl-1,4-butanediamine (TMBD); [complex] = 1 x 10^{-5} mol dm^{-3}, 293K.

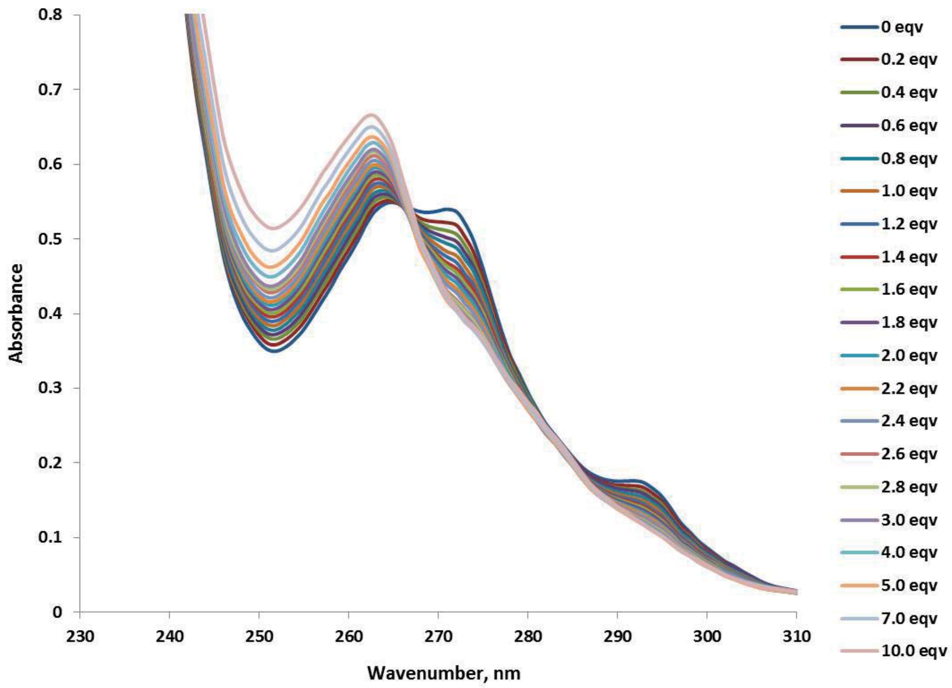


Figure S41: The UV-vis absorbance spectrum of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon titration of up to 10 mol equivalents of [2-(2-diisopropylamino-ethyldisulfanyl)-ethyl]-diisopropylamine (DADSA); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

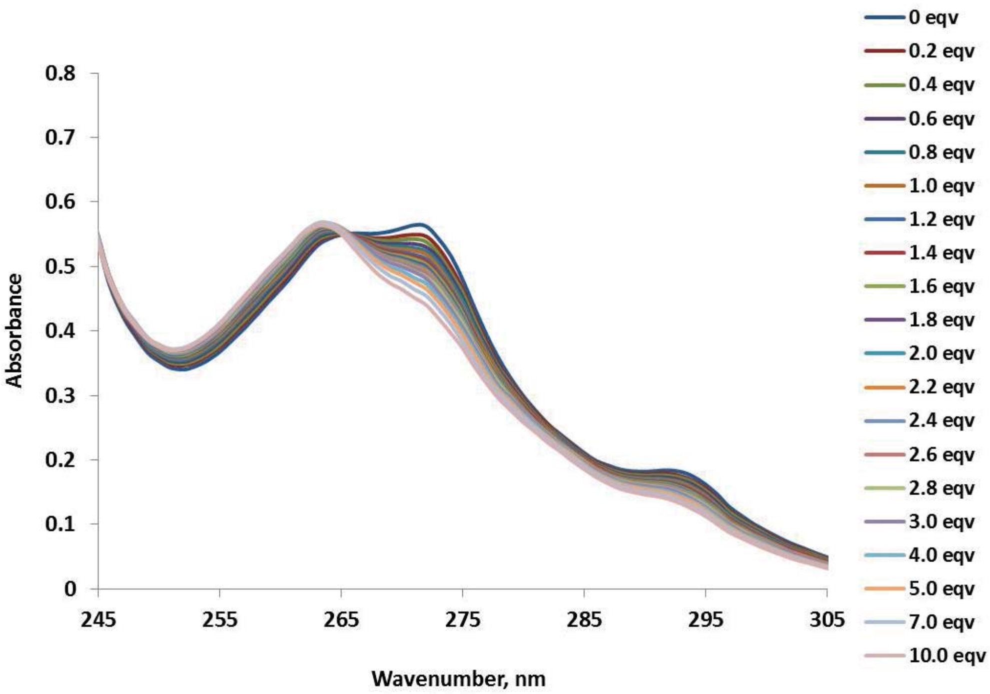


Figure S42: The UV-vis absorbance spectrum of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon titration of up to 10 mol equivalents of tetraethyl ethylenediphosohonate (TEEP); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

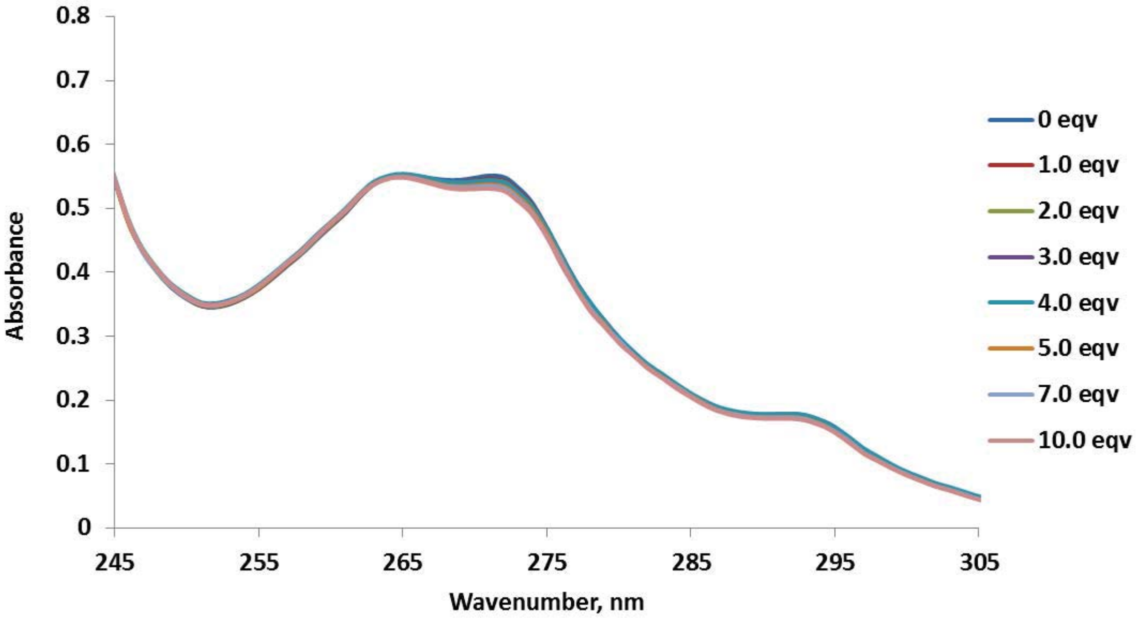


Figure S43: The UV-vis absorbance spectrum of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon titration of up to 10 mol equivalents of phosphoric acid, diethyl 2-(ethylthio)ethyl ester (DEPATESE); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

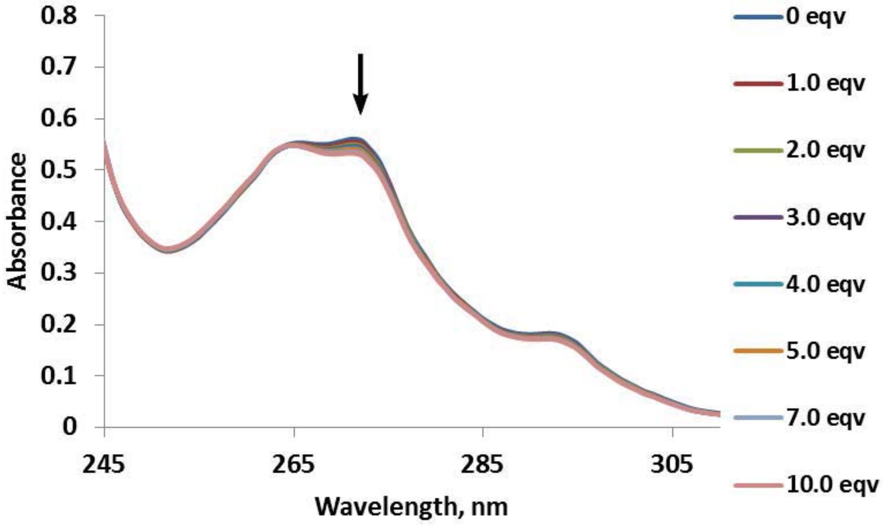


Figure S44: Selected UV-vis absorbance spectra from the titration of [Eu(phen)2(NO3)3]·2H2O with DEPATEXE (up to ten equivalents), where [complex] = 1 x 10-5 mol dm-3, 293 K.

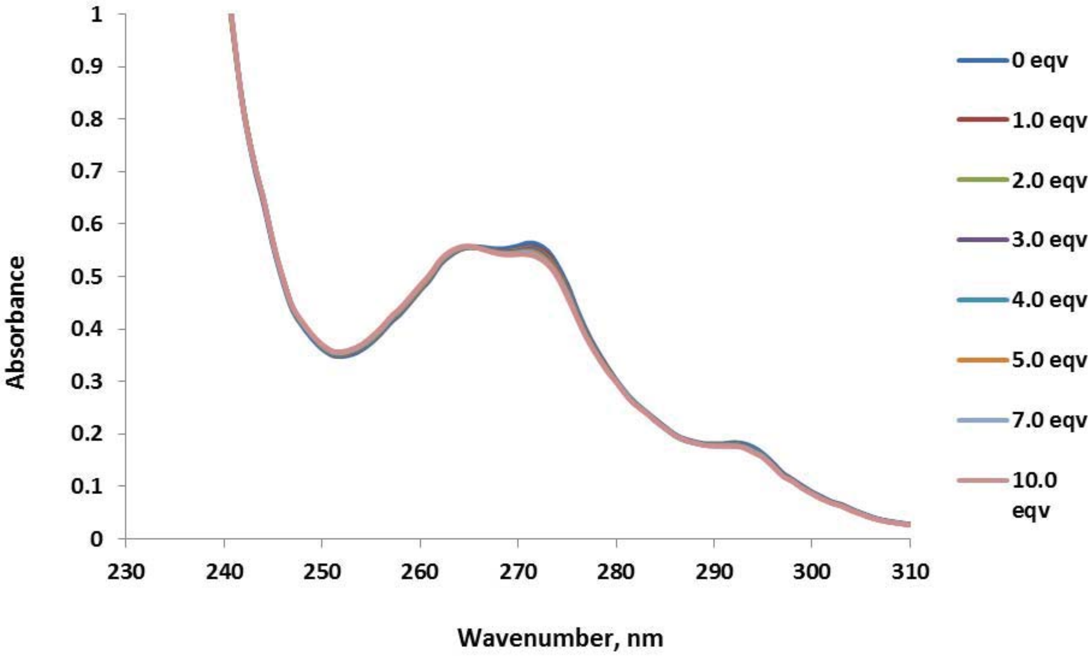


Figure S45: The UV-vis absorbance spectrum of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon titration of up to 10 mol equivalents (Ac-Ser(MPE)-OMe); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

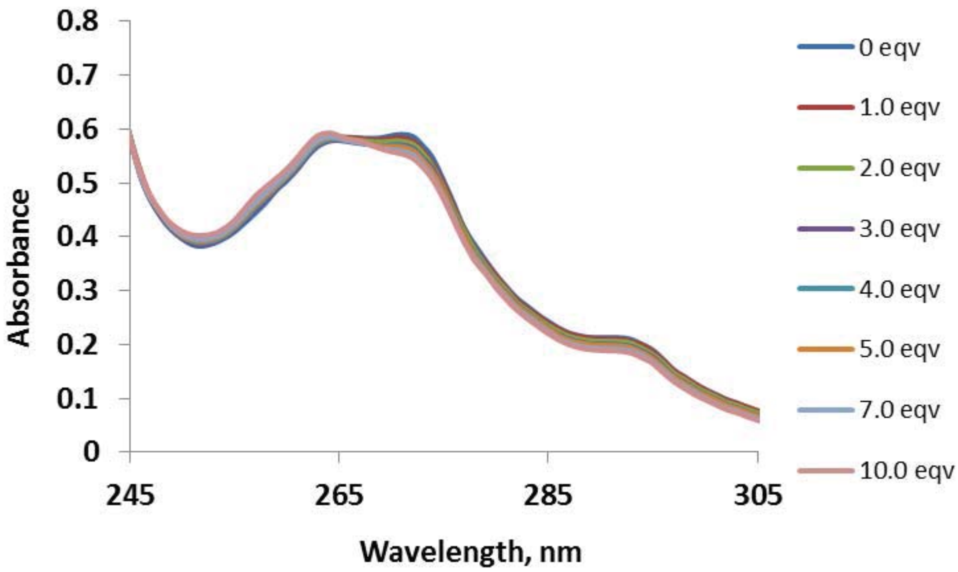


Figure S46: The UV-vis absorbance spectrum of $Eu(phen)_2(NO_3)_3(H_2O)_3$ upon titration of up to 10 mol equivalents (Cbz-Ser(MPE)-OBn); [complex] = 1 x 10^{-5} mol dm^{-3}, 293 K.

NMR Titration Spectra:

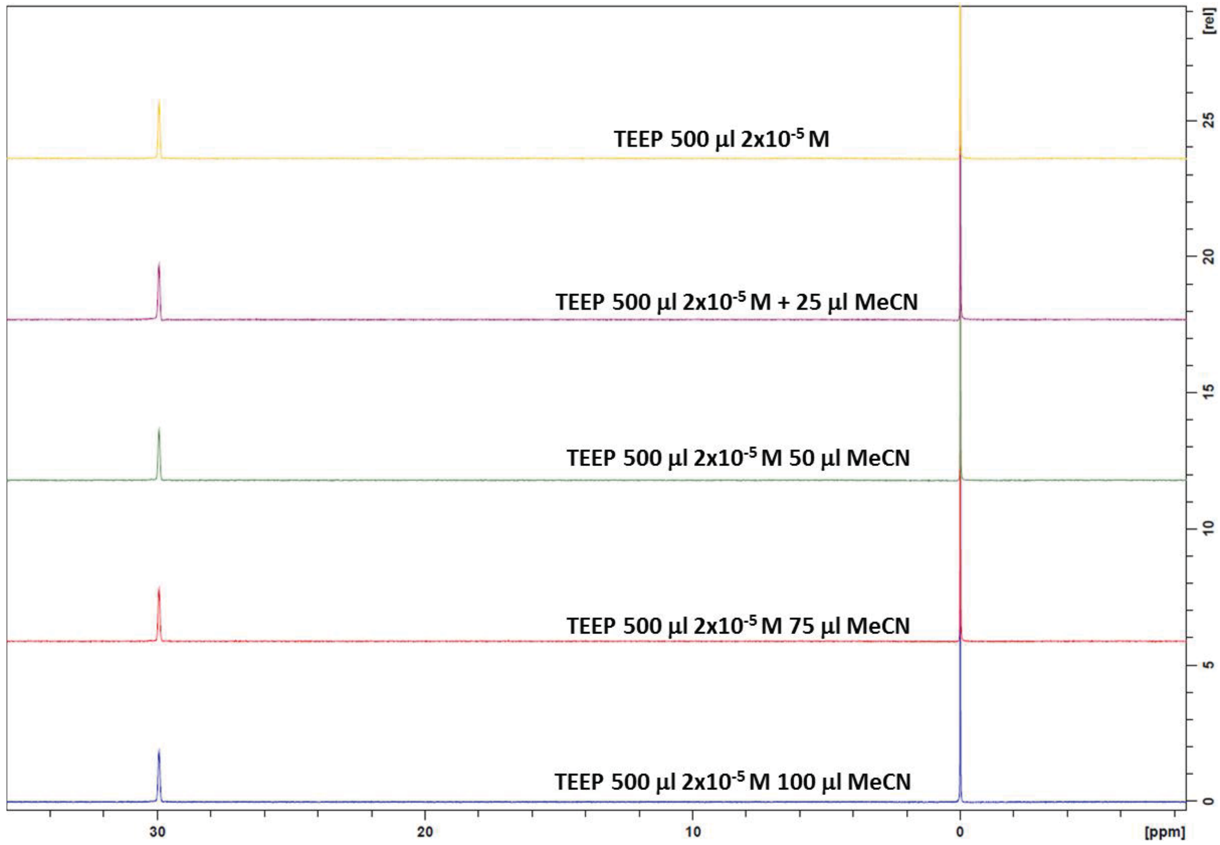


Figure S47: ^{31}P NMR spectra of blank acetonitrile (solvent) additions to tetraethyl ethylenediphosphonate in acetonitrile, Internal standard: phosphoric acid in D_2O. [TEEP] = 2 x 10^{-5} mol dm^{-3}, 293 K.

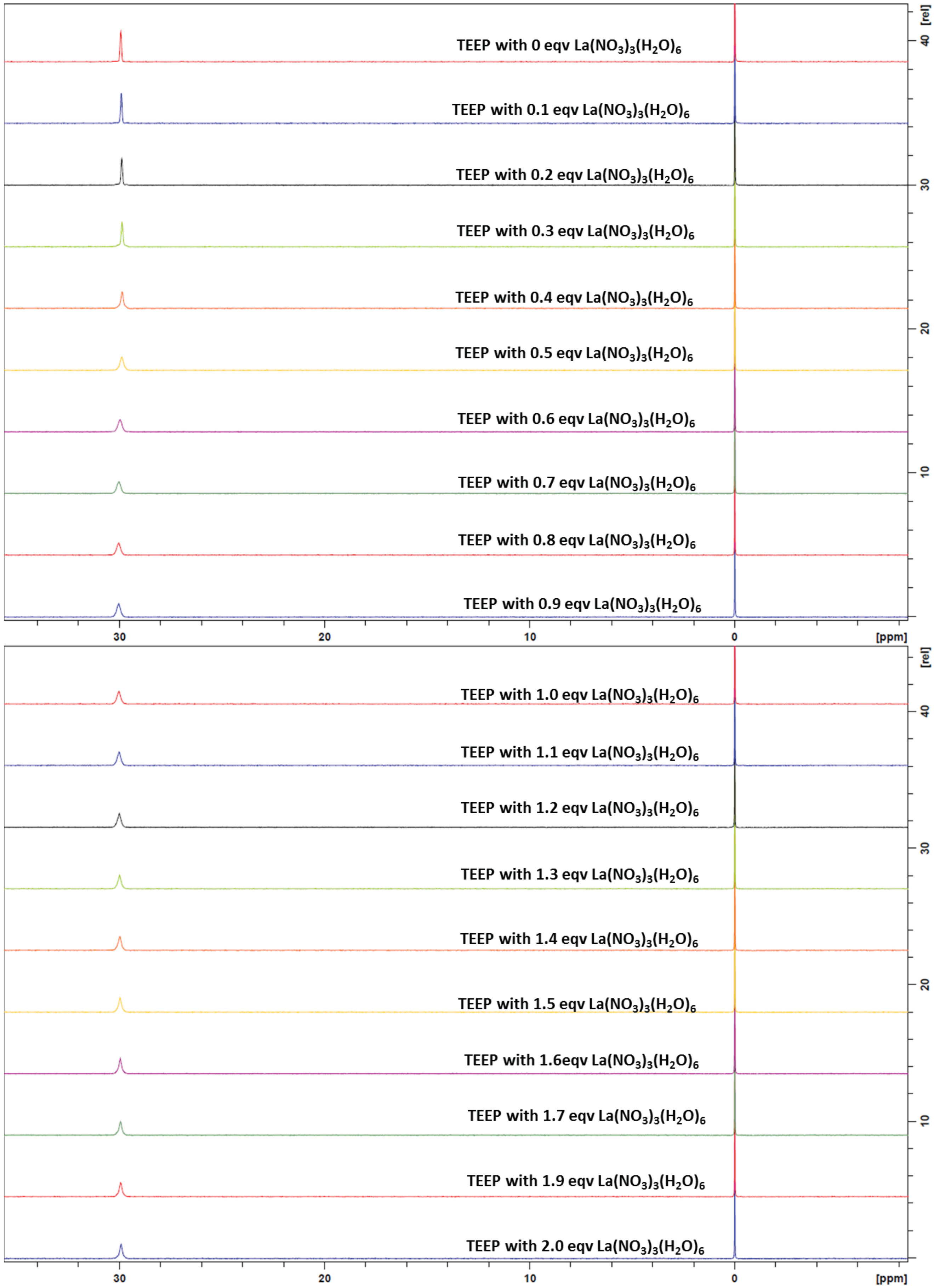


Figure S48: ^{31}P NMR spectra of tetraethyl ethylenediphosphonate (TEEP) upon 0.1 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in acetonitrile. Internal standard phosphoric acid in D_2O: [TEEP] = 2×10^{-5} mol dm^{-3}, 293 K.

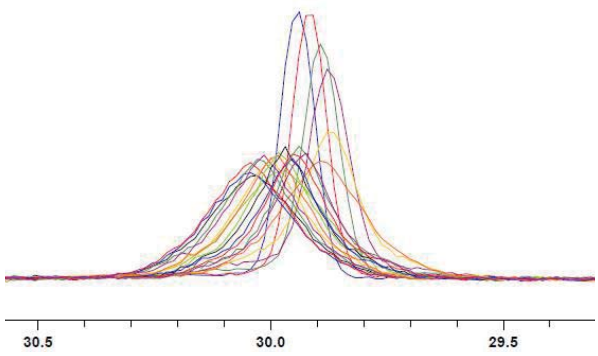


Figure S49: Overlay of the ^{31}P NMR spectra of tetraethyl ethylenediphosphonate (TEEP) upon 0.1 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in MeCN where $[TEEP]_{inital}$ = 2 x 10^{-5} mol dm^{-3}, 293 K

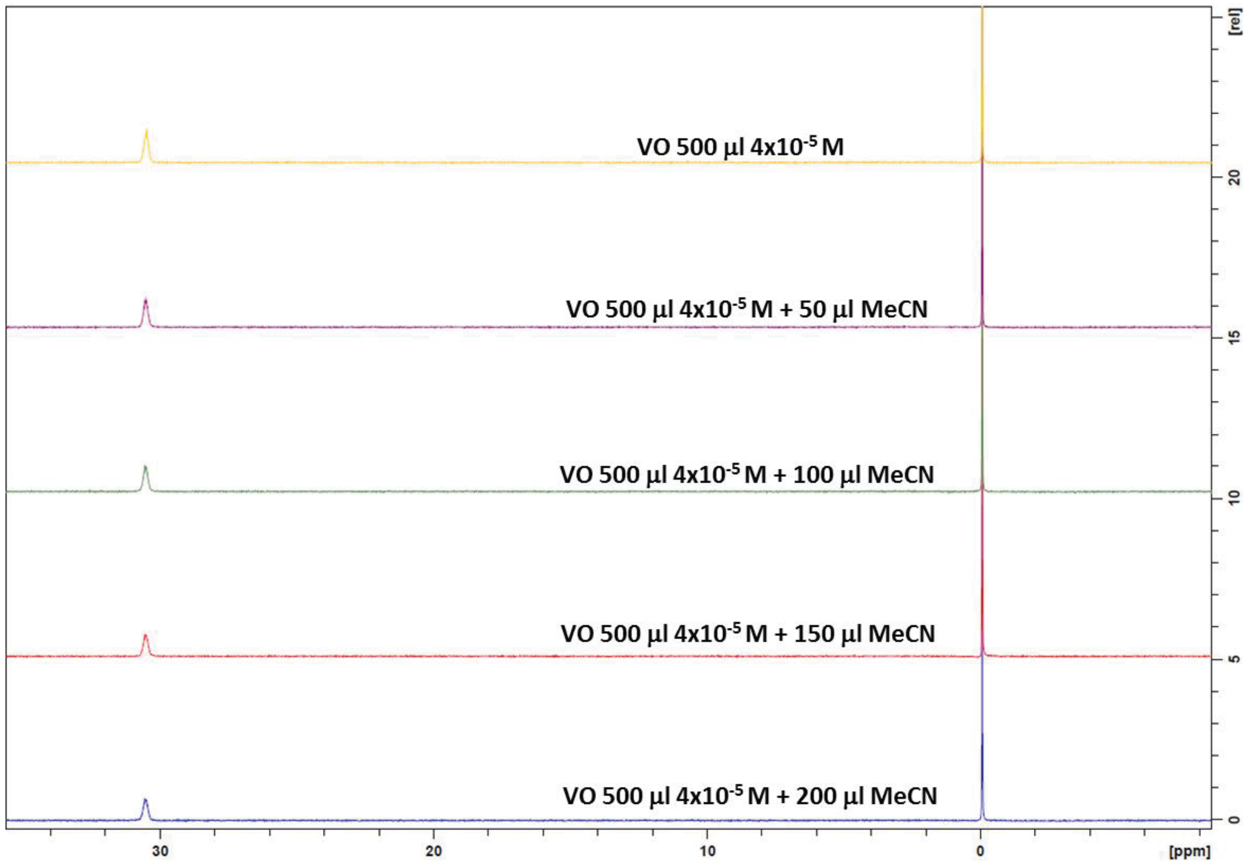


Figure S50: ^{31}P NMR spectra of blank acetonitrile (solvent) additions to 2-diisopropylaminoethyl ethyl methylphosphonate (VO) in acetonitrile, Internal standard: phosphoric acid in D_2O. [VO] = 4 x 10^{-5} mol dm^{-3}, 293 K.

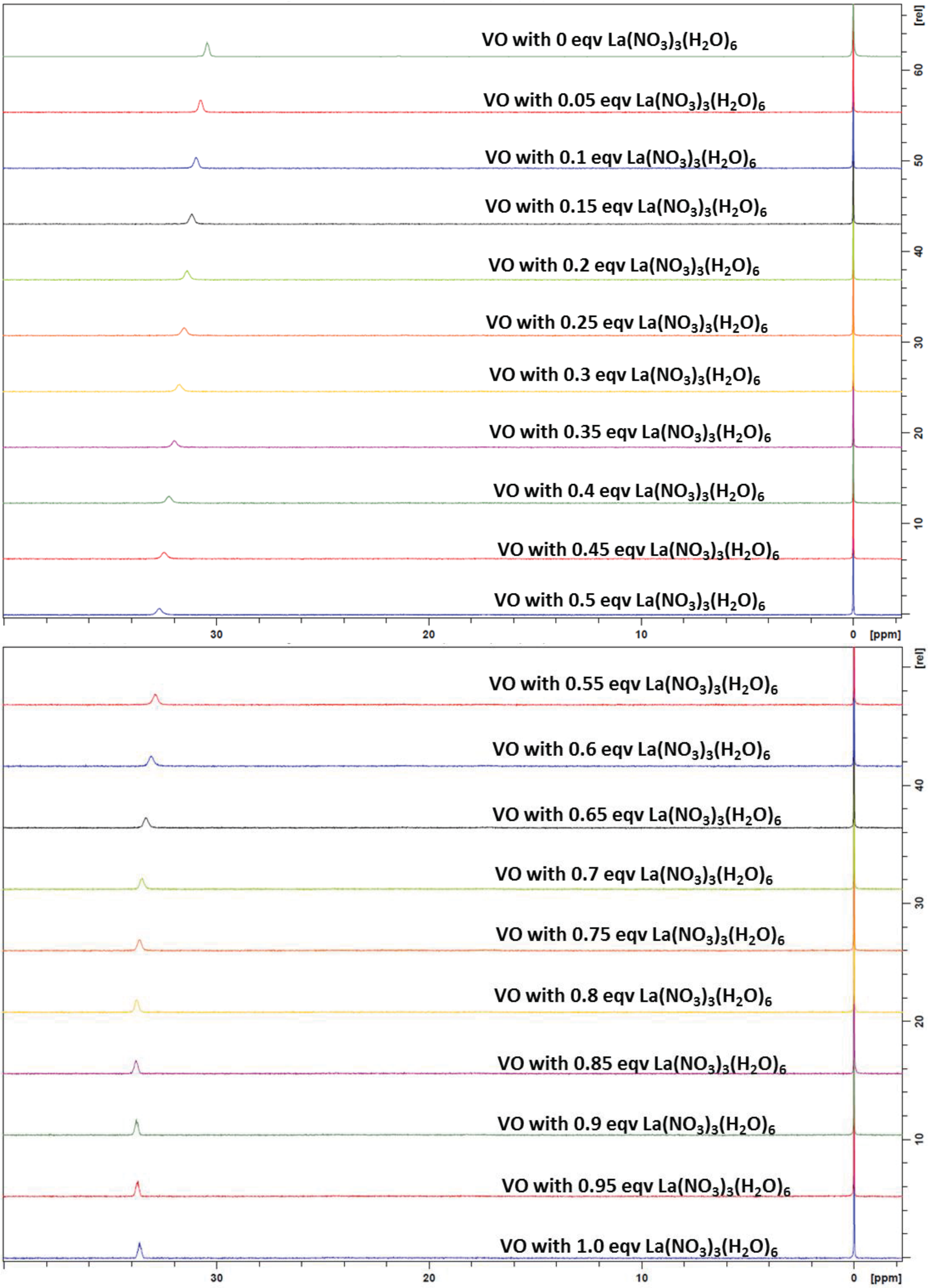


Figure S51: ^{31}P NMR spectra of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) upon 0.05 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in acetonitrile. Internal standard phosphoric acid in D_2O: [VO] = 4 x 10^{-5} mol dm^{-3}, 293 K.

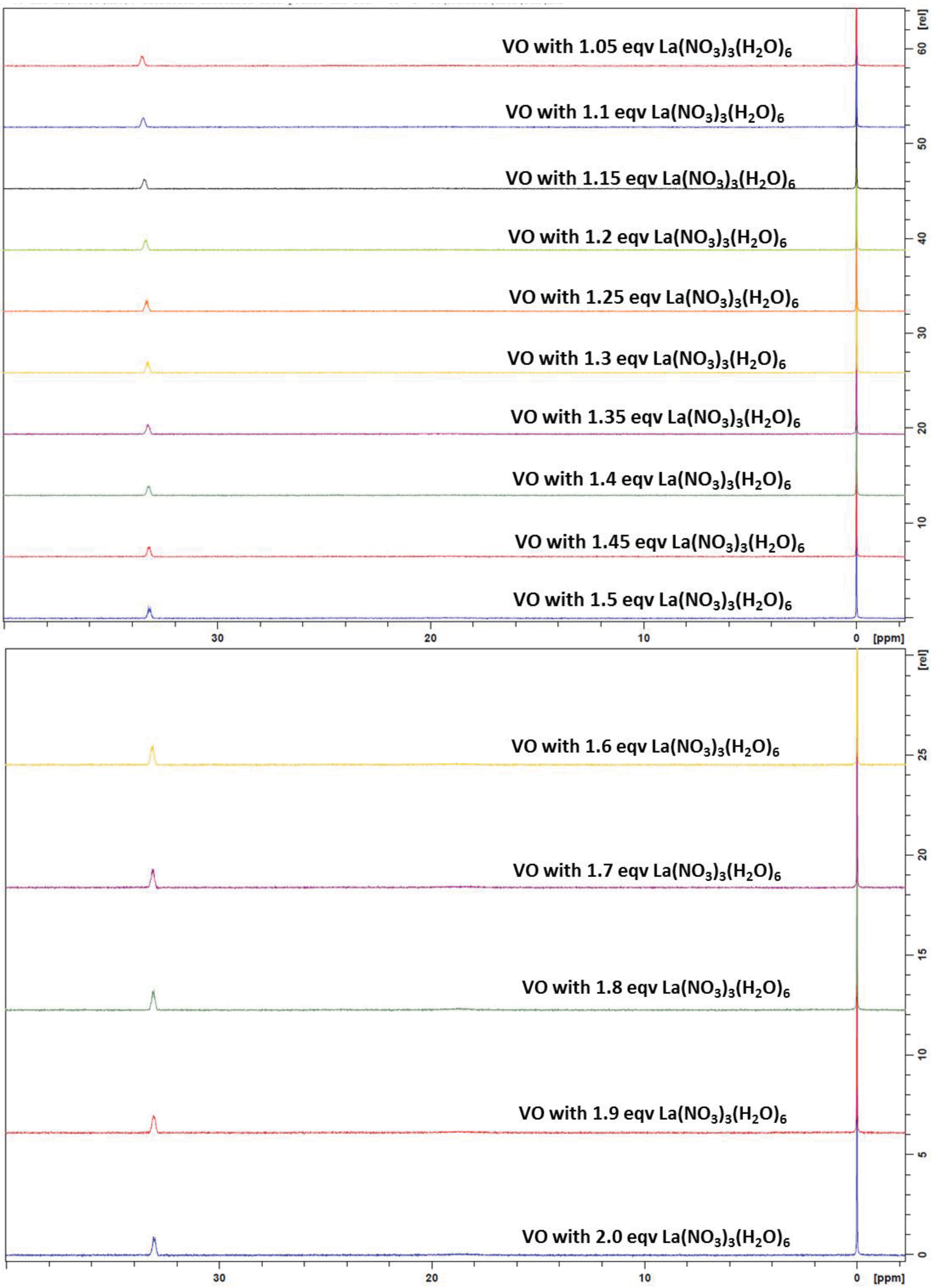


Figure S52: ^{31}P NMR spectra of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) upon 0.05 and 0.1 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in acetonitrile. Internal standard phosphoric acid in D_2O: [VO] = 4 x 10^{-5} mol dm^{-3}, 293 K.

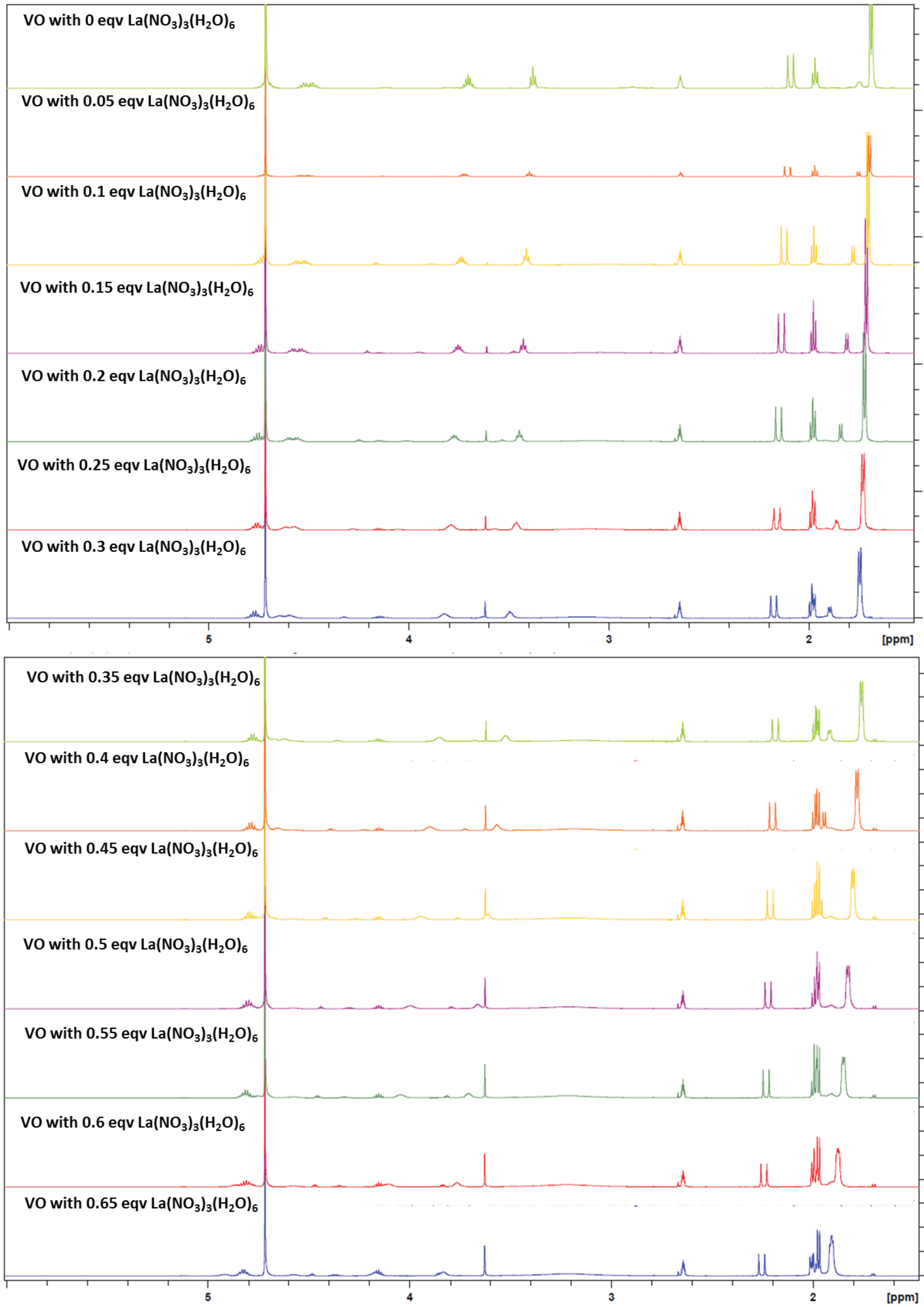


Figure S53: ^{1}H NMR spectra of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) upon 0.05 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in acetonitrile. Internal standard phosphoric acid in D_2O: [VO] = 4×10^{-5} mol dm^{-3}, 293 K.

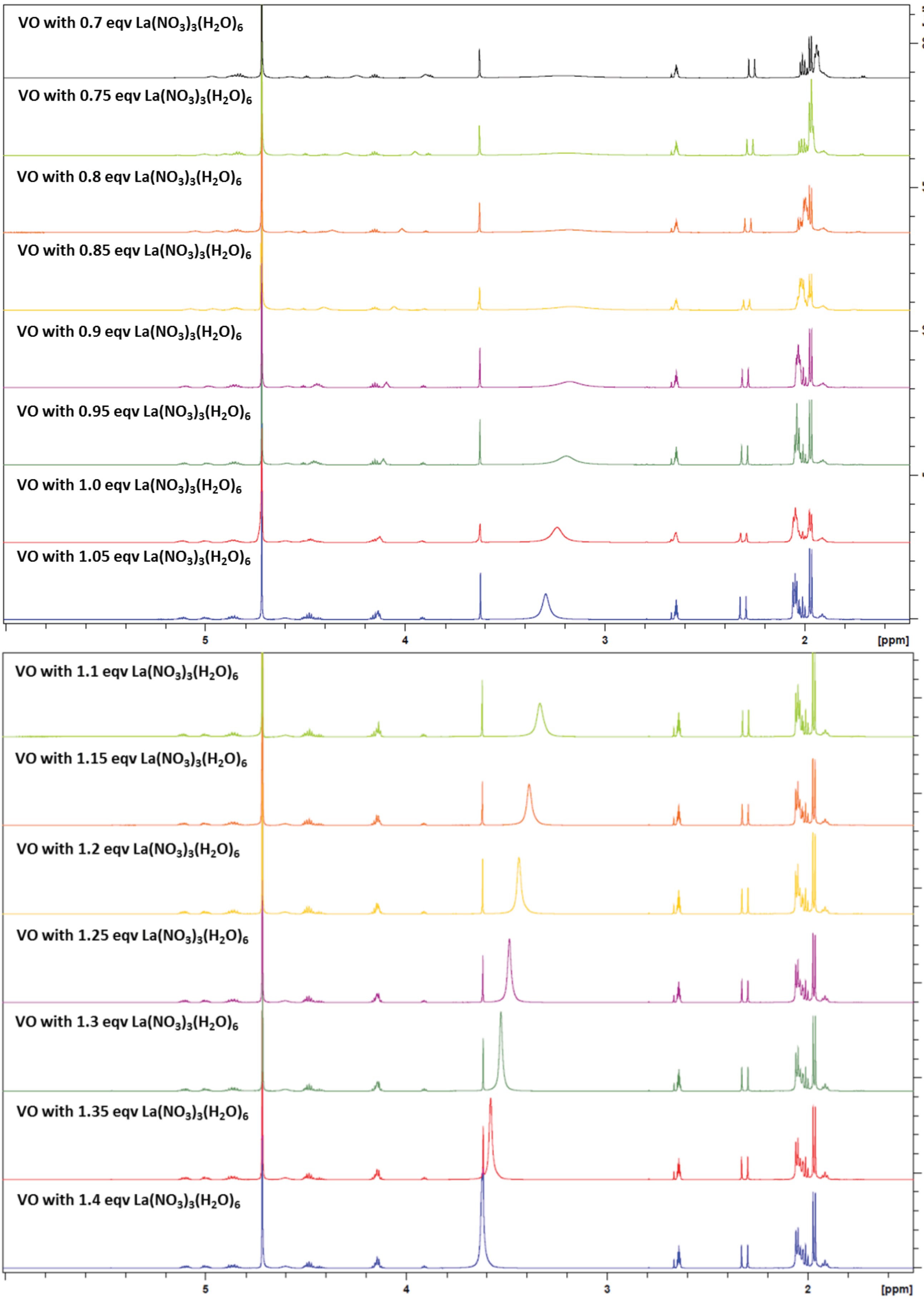


Figure S54: ^{1}H NMR spectra of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) upon 0.05 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in acetonitrile. Internal standard phosphoric acid in D_2O: [VO] = 4 x 10^{-5} mol dm^{-3}, 293 K.

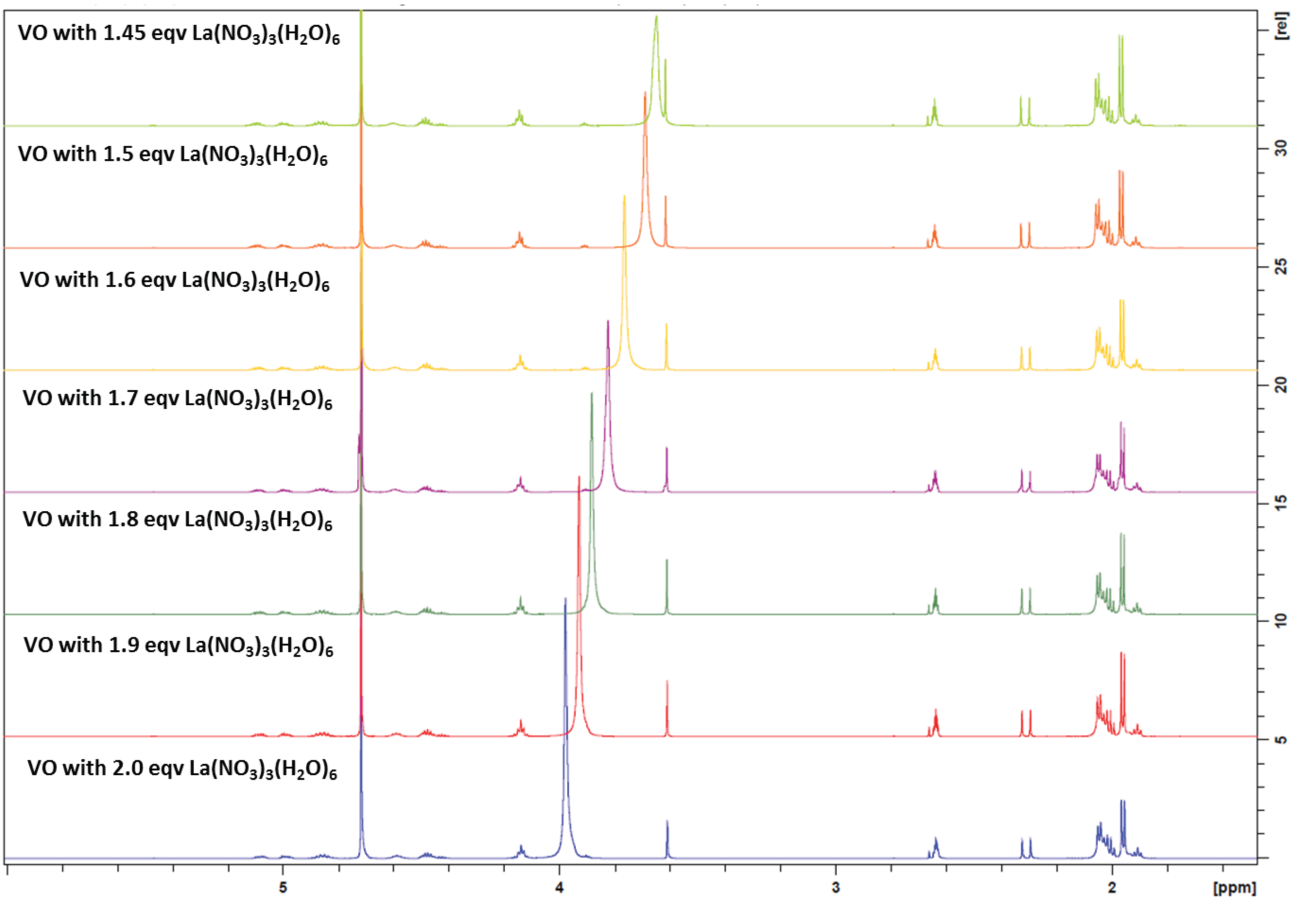


Figure S55: ^{1}H NMR spectra of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) upon 0.05 and 0.1 mol equivalent additions of $La(NO_3)_3(H_2O)_6$ in acetonitrile. Internal standard phosphoric acid in D_2O: [VO] = 4 x 10^{-5} mol dm^{-3}, 293 K.

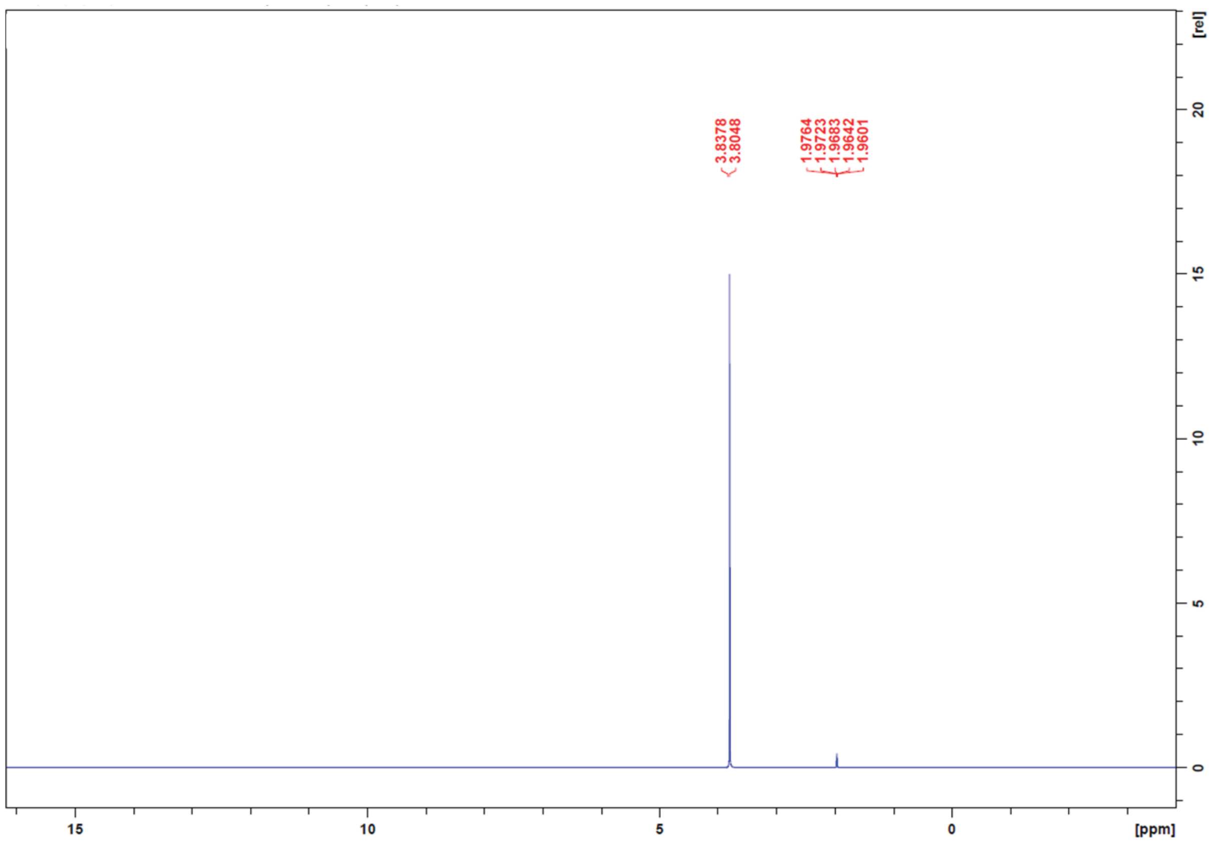


Figure S56: ^{1}H NMR spectra of $La(NO_3)_3(H_2O)_6$ in d_3-acetonitrile.

Table S1: Chemical shift data for the ^{31}P and ^{1}H NMR titration of $La(NO_3)_3(H_2O)_5$ to VO, where $[VO]_{initial}$ = 4 x 10^{-5} mol dm^{-3}, 293 K.

Molar Equivalents of $La(NO_3)_3(H_2O)_5$	**^{31}P**	**^{1}H ($P-CH_3$ signal)**
0	30.435	2.1063
0.05	30.7458	2.1211
0.1	30.9569	2.1382
0.15	31.1638	2.1521
0.2	31.3845	2.1661
0.25	31.5156	2.1743
0.3	31.7381	2.1909
0.35	31.9946	2.2019
0.4	32.2702	2.2159
0.45	32.4613	2.2268
0.5	32.6906	2.2383
0.55	32.8955	2.2474
0.6	33.0759	2.2577
0.65	33.3366	2.2696
0.7	33.5352	2.2802
0.75	33.6246	2.289
0.8	33.7643	2.2993
0.85	33.7905	2.3056
0.9	33.7609	2.3124
0.95	33.7401	2.3157
1.0	33.6172	2.3202
1.05	33.5317	2.323
1.1	33.4891	2.3246
1.15	33.4263	2.3264
1.2	33.3622	2.3276
1.25	33.3242	2.3281
1.3	33.2744	2.3282
1.35	33.2543	2.3293
1.4	33.2628	2.3295
1.45	33.2207	2.3296
1.5	33.2055	2.3294
1.6	33.1425	2.3274
1.7	33.1268	2.3262
1.8	33.0986	2.3262
1.9	33.0703	2.3251
2.0	33.0559	2.3251

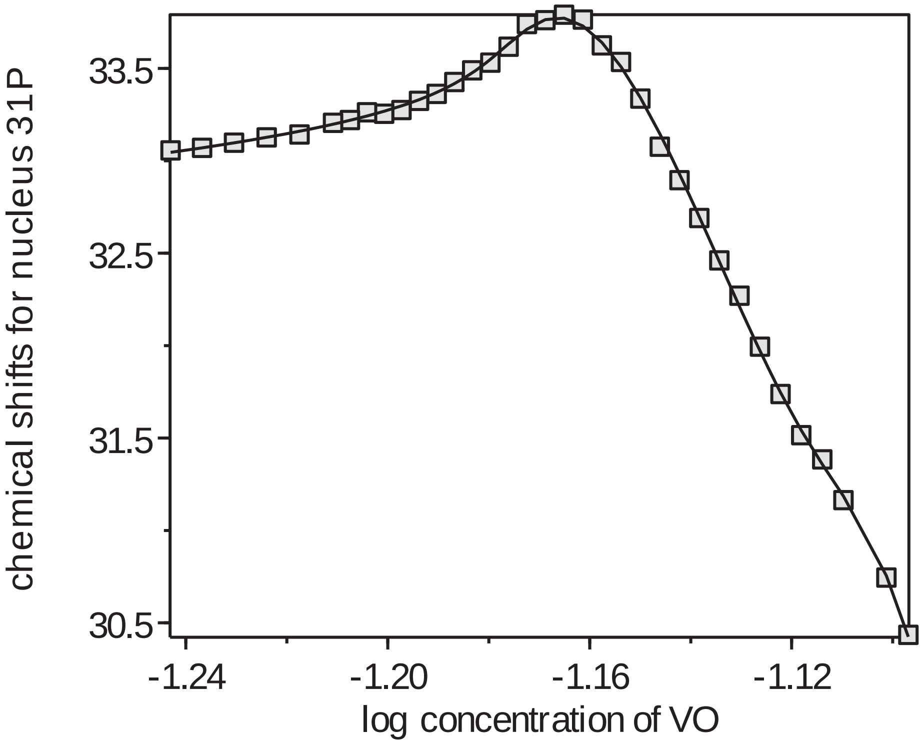


Figure S57: HypNMR visual fit of ^{31}P titration data upon addition of $La(NO_3)_3(H_2O)_6$ to VO.

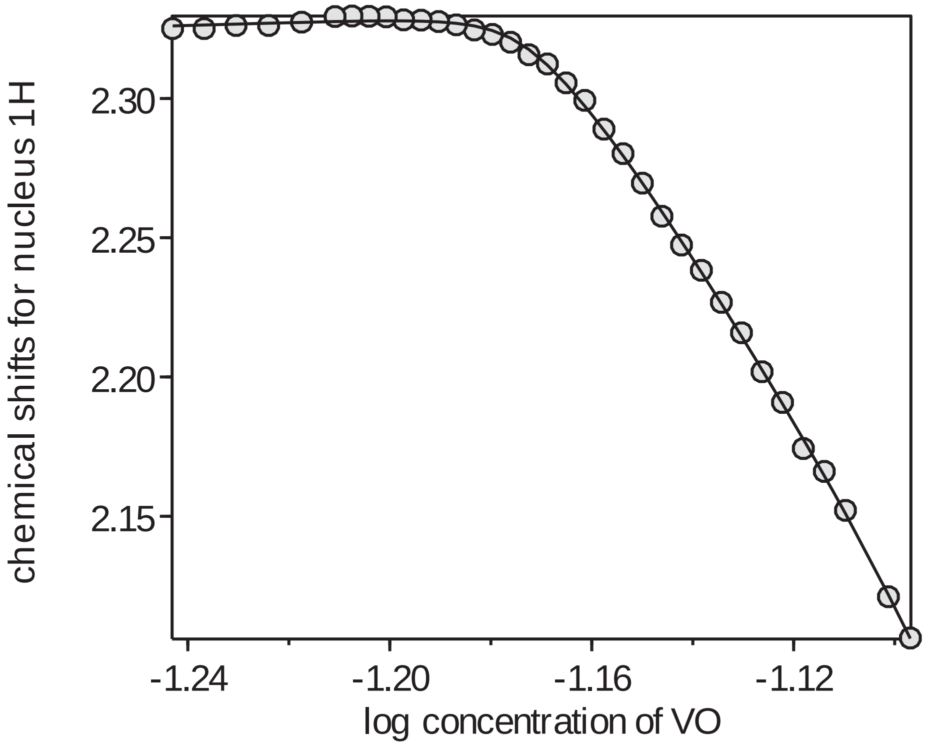
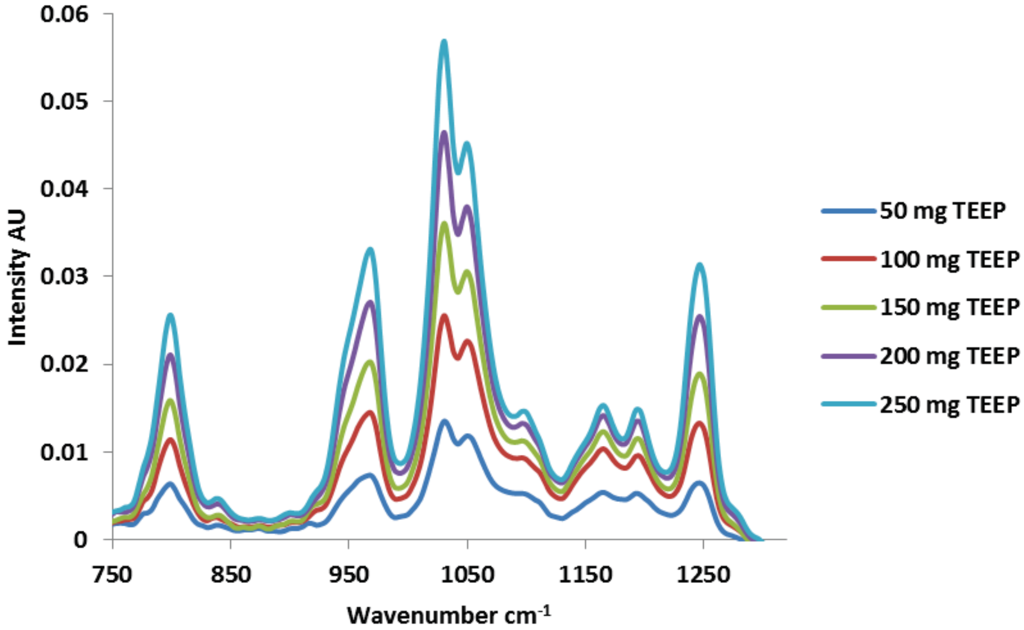


Figure S58: HypNMR visual fit of ^{1}H titration data of the P-CH_3 proton signal upon addition of $La(NO_3)_3(H_2O)_6$ to VO a



b

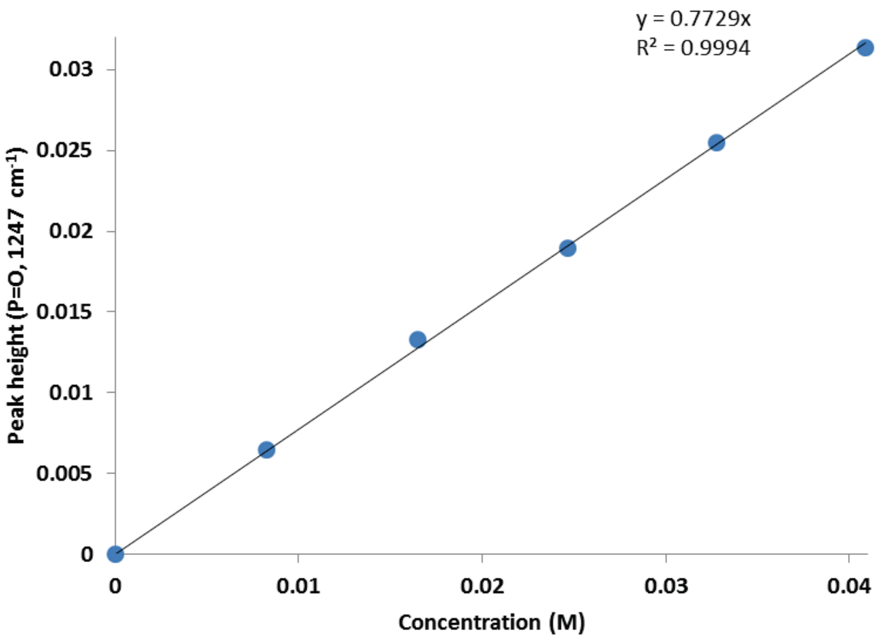


Figure S59: a) Fingerprint region of the IR spectrum of tetraethyl ethylenediphosphonate (TEEP) in dry acetonitrile at various concentrations. b) Concentration curve for tetraethyl ethylenediphosphonate (TEEP) in dry MeCN.

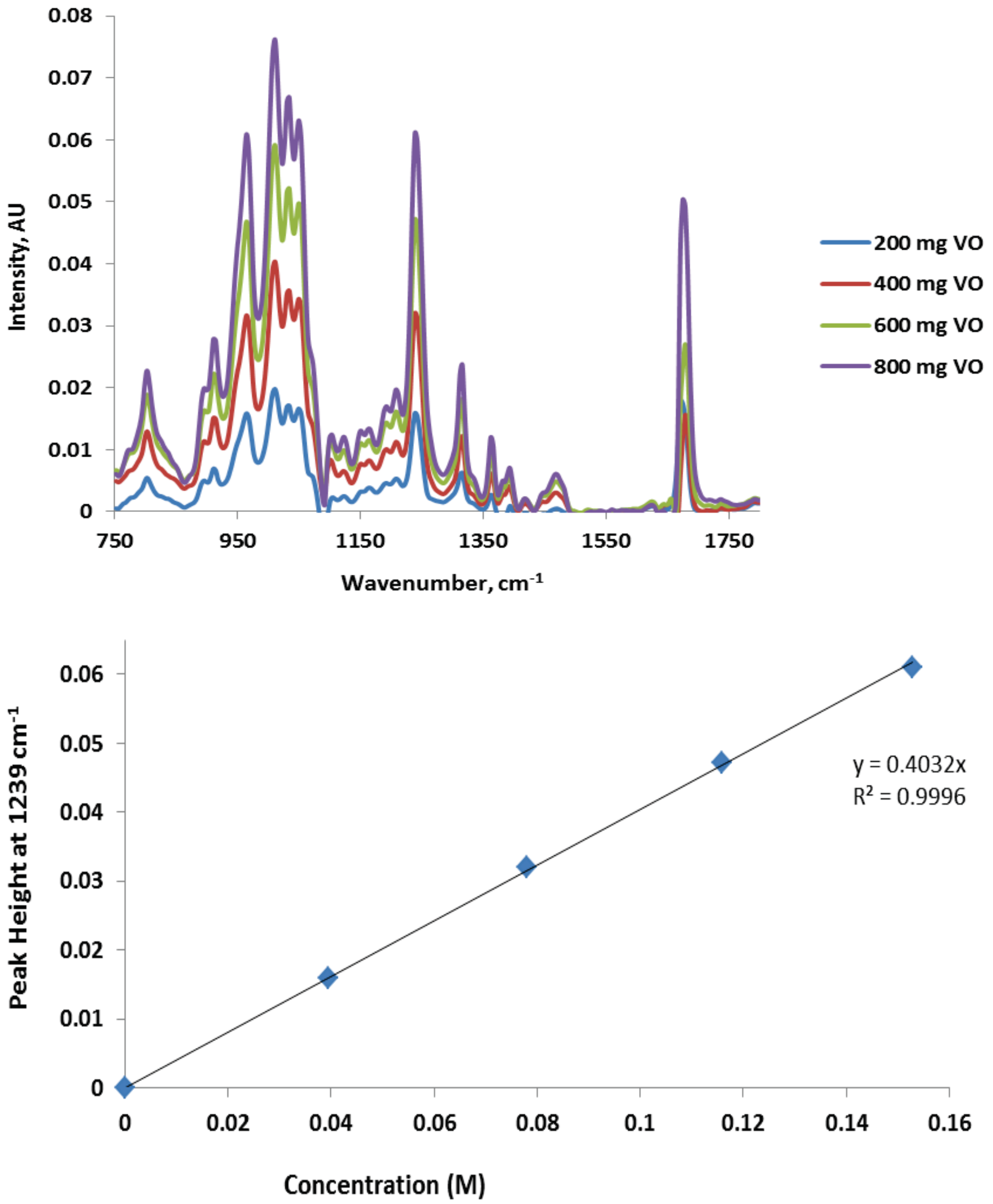


Figure S60: a) Fingerprint region of the IR spectrum of 2-diisopropylaminoethyl ethyl methylphosphonate (VO) in dry MeCN / DMF at various concentrations. b) Concentration curve for 2-diisopropylaminoethyl ethyl methylphosphonate (VO) in dry MeCN / DMF.

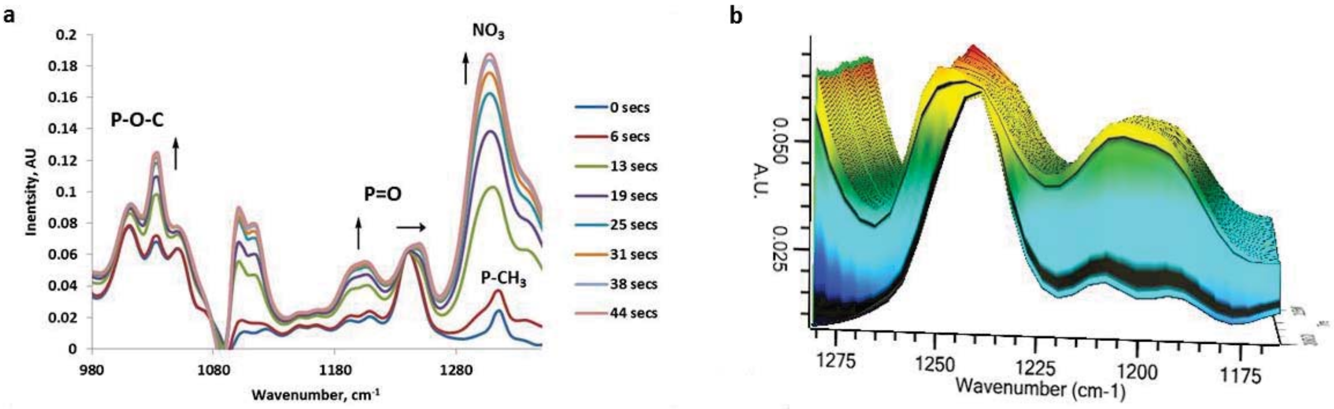


Figure 61: a) Overlay of the characteristic region of the IR spectrum of VO (time 0) and after the 1 equivalent addition of $Eu(NO_3)_3(H_2O)_5$ (at 6, 13, 19, 25, 31, 38 and 44 seconds) in MeCN:DMF. b) 3D waterfall image (where x-axis = wavenumber, y = peak intensity and z = time) of the characteristic phosphonyl stretches. In this reaction the addition of the $Eu(NO_3)_3(H_2O)_5$ solution was made at time = 1 minute, which has been termed time point zero in the kinetic calculations.

References:

1. G. H. Dennison, M. R. Sambrook and M. R. Johnston, Chem. Commun., 2014, **50**, 195-197.
2. G. H. Dennison, M. R. Sambrook and M. R. Johnston, *RSC Adv*., 2014, *4*, 55524-55528.
3. G. Accorsi, A. Listorti, K. Yoosaf and N. Armaroli., *Chem Soc. Rev.,* 2009, **38**, 1690-1700