Electronic Supplementary Material (ESI) for Chemical Communications

Phosphine Oxide Functionalised Imidazolium Ionic Liquids as Tuneable Ligands for Lanthanide Complexation

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Electronic Supplementary Information

Materials and general methods

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purifications. 1,2-Dimethylimidazole, 98%, was purchased from Acros.

^{1}H and ^{13}C NMR spectra were recorded at 27 °C, using a Bruker DRX 300 spectrometer, a Bruker Avance III 400 spectrometer, or a Bruker DRX 500 spectrometer.

Phase transitions were determined using differential scanning calorimetry (DSC) analysis. All scans were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS) and an autosampler. The samples were sealed in TA Tzero aluminium pans with hermetic lids. The temperature was ramped, with modulation, from 120 to -90 °C, at 5 °C min^{-1}, then stabilised at -90 °C for 10 min and subsequently heated to 12 °C, at 5 °C min^{-1}, then stabilised for 5 min, and the whole cycle was repeated twice. The DSC chamber was filled with dry nitrogen gas.

Exact mass was obtained using high-resolution mass spectrometry with electrospray ionisation (ESI-MS). The ESI-MS experiments were carried out using a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an *m/z* range of 50 to 1500. Samples were injected as dilute solutions in acetonitrile.

Infrared spectra of neat samples were recorded on a Perkin Elmer Spectrum 100 Series FT-IR spectrometer with a universal ATR accessory.

Titration experiments and binding constant determination

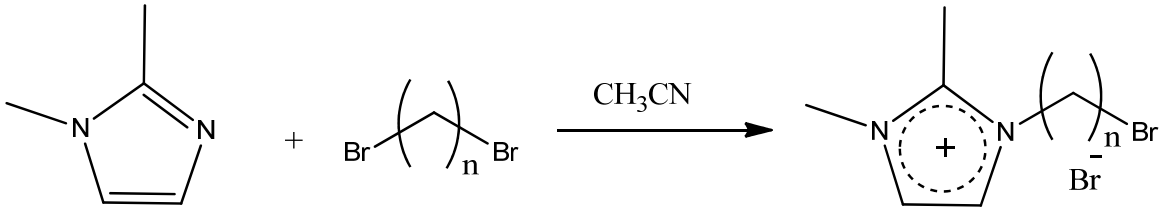
A phosphine oxide-functionalised ionic liquid, POFIL, (*ca.* 80 mg) was placed in a volumetric flask (2 cm^3) and dissolved in d_4-methanol to prepare stock solution 1. $La(OTf)_3 \cdot 6H_2O$ (ca. 350 mg) was placed in a volumetric flask and dissolved into stock solution 1 (1 cm^3), to obtain stock solution 2. Stock solution 1 (0.5 cm^3), measured with a syringe, was poured into a standard NMR tube (5mm, borosilicate glass) and titrated 10 times with 5 µl portions of stock solution 2 using a microsyringe. Exact amounts of the materials are listed in Table 1.

Table 1: Amounts of the materials used for the NMR titration to determine the binding constants.

n	m_{POIL} / mg for stock solution 1	$m_{La(OTf)3}$ / mg for stock solution 2
2	79	371
3	79	377
4	80	369
6	82	364
8	93	395

Synthesis of the ionic liquids

a) Synthesis of ionic liquids with bromoalkyl chains



Scheme 1: General procedure for the synthesis of ionic liquids with bromoalkyl chains.

A dibromoalkane has been poured into a round-bottomed flask (250 cm^3) equipped with a reflux and a dropping funnel, and dissolved in 8-fold excess of acetonitrile (by volume) under an argon atmosphere. The solution has been heated to 60 °C. A solution of 1,2-dimethylimidazole in acetonitrile was poured into the dropping funnel, and added drop-wise into the vigorously stirred solution of dibromoalkane. The reaction was carried out overnight. A white precipitate (by-product) was removed by filtration under reduced pressure, and washed with small portions of acetonitrile. The solutions from filtration and washes were combined, and the solvent was removed under reduced pressure using a rotary evaporator. The crude product was washed with ethyl acetate (x 3) and diethyl ether (x 3), and then dried (overnight, 60 °C, high vacuum). Subsequently, it has been recrystallised from a mixture of methanol and ethyl acetate, and the purified product was dried again (overnight, 60 °C, high vacuum). Yields and exact amounts of the materials are listed in Table 2. The purity of the products has been checked using ^{1}H NMR spectroscopy (see below Table 2).

Table 2: Amounts of the materials used for the synthesis of ionic liquids with bromoalkyl chains and yields of the synthesis.

n	**amount of $Br(CH_2)_nBr$**		**amount of DMIm**		**yield**
	/ cm^3	**/ mmol**	**/ g**	**/ mmol**	**%**
2	63	728	10	104	61
3	22	216	10	104	80
4	87	728	10	104	87
6	112	728	10	104	82
8	67 g	245	10	104	47

^{1}H NMR spectroscopy analysis

***n* = 2**: ^{1}H NMR (300 MHz, DMSO) *δ* 7.76 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 4.62 (t, *J* = 5.9 Hz, 2H), 3.91 (t, *J* = 5.9 Hz, 2H), 3.80 (s, *J* = 18.9 Hz, 3H), 2.65 (s, 3H).

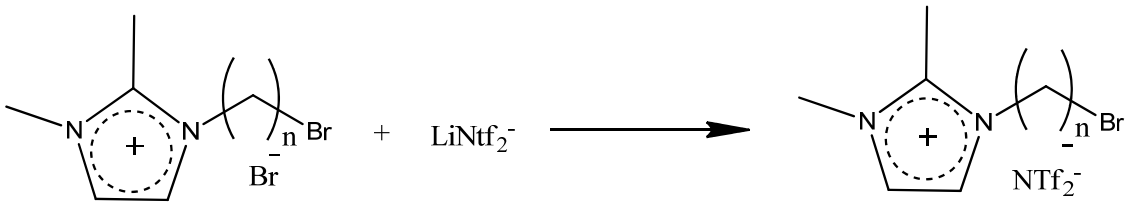
***n* = 3:** ^{1}H NMR (300 MHz, DMSO) δ 7.67 (d, *J* = 5.0 Hz, 2H), 4.23 (t, *J* = 6.9 Hz, 2H), 3.75 (s, 3H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.60 (s, *J* = 18.0 Hz, 3H), 2.38 – 2.15 (m, 2H).

***n* = 4**: ^{1}H NMR (300 MHz, DMSO) δ 7.63 (dd, *J* = 9.1, 2.0 Hz, 2H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.74 (s, 3H), 3.57 (t, *J* = 5.9 Hz, 2H), 2.57 (s, *J* = 6.4 Hz, 3H), 1.91 – 1.62 (m, 4H).

***n* = 6**: ^{1}H NMR (300 MHz, DMSO) *δ* 7.63 (d, J = 9.2 Hz, 2H), 4.11 (t, J = 7.1 Hz, 2H), 3.76 (s, 3H), 3.54 (t, J = 6.6 Hz, 2H), 2.59 (s, 3H), 1.93 – 1.62 (m, 4H), 1.54 – 1.21 (m, 4H).

***n* = 8**: ^{1}H NMR (300 MHz, DMSO) *δ* 7.62 (d, J = 8.8 Hz, 2H), 4.09 (t, J = 7.1 Hz, 2H), 3.74 (s, 3H), 3.52 (t, J = 6.6 Hz, 2H), 2.57 (s, J = 14.9 Hz, 3H), 1.94 – 1.56 (m, 4H), 1.51 – 1.09 (m, J = 26.5 Hz, 8H).

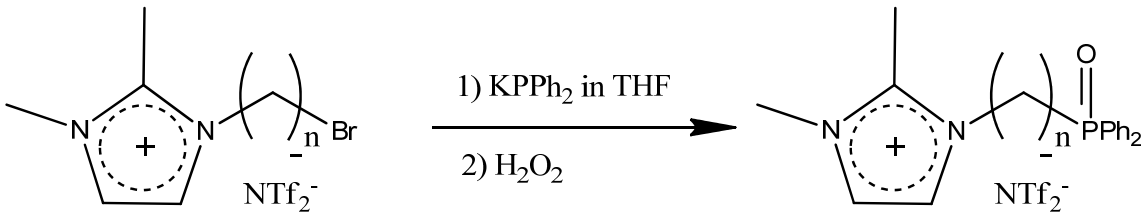
b) Anion exchange



Scheme 2: Anion exchange of bromide to bis(trifluoromethylsulfonyl)imide

An ionic liquid with bromoalkyl chain was poured into a round-bottomed flask (250 cm^3) and dissolved in deionised water (25 cm^3). An equimolar amount of lithium bis(trifluoromethylsulfonyl)imide, dissolved deionised water (25 cm^3), was added to the vigorously stirred solution of an ionic liquid. The mixture was allowed to react (ambient temperature, 3 h), and subsequently, the top layer was decanted and the bottom layer was washed with deionised water (8 x 10 cm^3). Finally, the product was dried (overnight, 60 °C, high vacuum), and immediately used for the further synthesis.

c) Synthesis of phosphine oxide functionalised ionic liquids



Scheme 3: The synthesis of the phosphine oxide functionalised ionic liquids.

In an argon filled glove-box, an ionic liquid with bromoalkyl chain and bis(trifluoromethylsulfonyl)imide anion was added to a Schlenk flask (100 cm^3) equipped with a stirring bar. The Schlenk flask was then flushed with argon. Tetrahydrofuran, THF (30 cm^3) was added to the ionic liquid, and the solution was degased three times using the freeze-thaw method. A pressure-equalising dropping funnel was attached to the Schlenk tube, the system was flushed with argon, and taken out of the glovebox. The vigorously stirred solution was cooled to -78 °C in an acetone dry ice bath. A solution of potassium diphenylphosphine in THF (0.5 M) was poured into the pressure-equalising dropping funnel, and added drop-wise to the cooled, vigorously stirred ionic liquid solution. Subsequently, the reaction mixture was stirred for an hour at -78 °C, and then left stirring overnight, slowly reaching room temperature. The solvent was removed by reduced-pressure distillation, and the intermediate product was treated with an aqueous solution of hydrogen peroxide. The oxidised product was washed with ethyl acetate (x3) and diethyl ether (x3), dried (overnight, 60 °C, high vacuum), and analysed by NMR spectroscopy, ESI-MS and FT-IR; yields and analytical results are listed below.

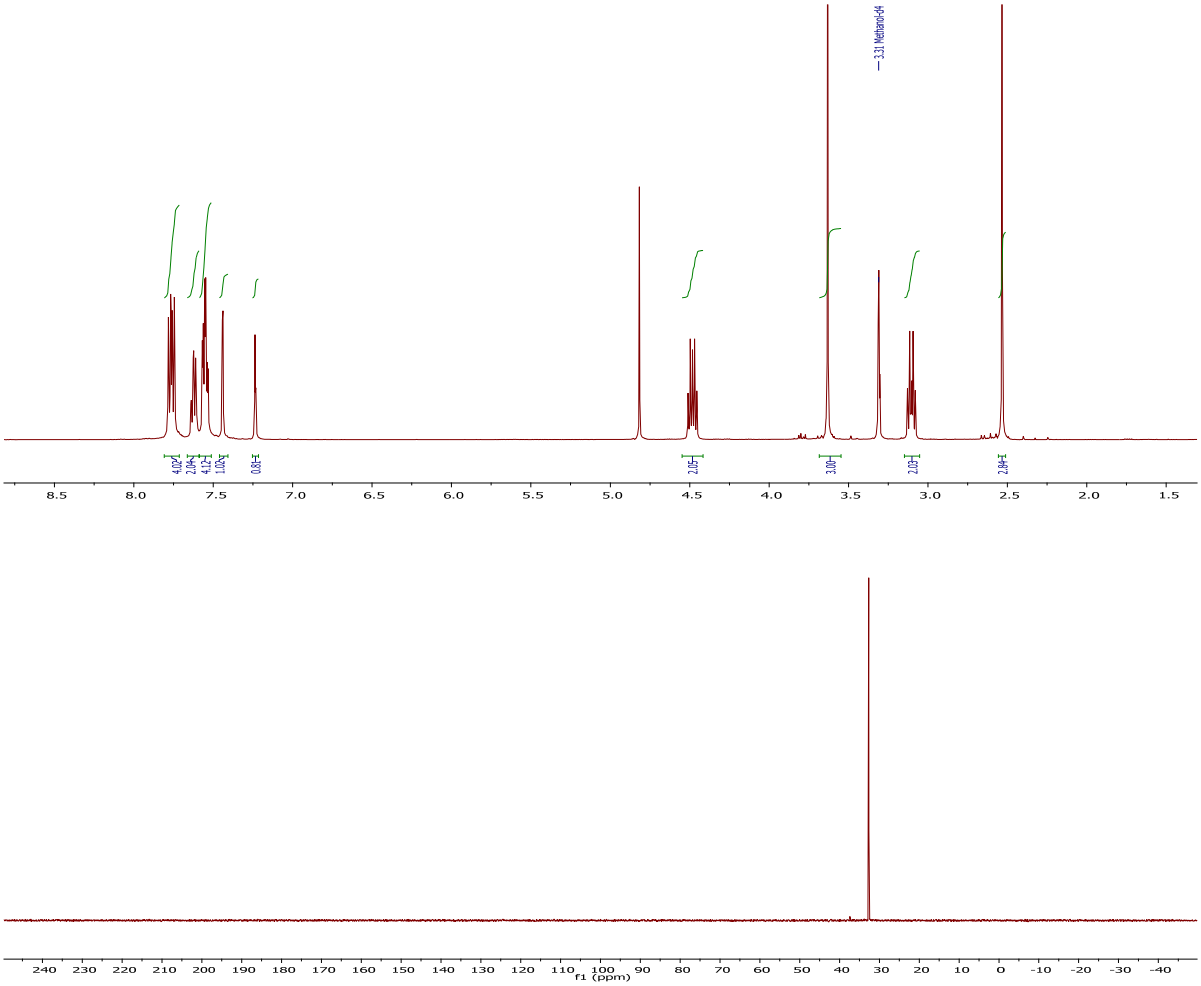


Figure S1: ^{1}H (top) and ^{31}P NMR (bottom) NMR spectra of $[DMImC_2P(O)Ph_2][Tf_2N]$.

***n* = 2**: Yield: 71% ESI-MS: $[C_{19}H_{22}N_2PO]^+$ 325.145; $[C_2S_2NF_6O_4]^-$ 279.912. FT-IR: 613, 669, 601, 718, 1052, 1120, 1139, 1178, 1348 cm^{-1}. ^1H NMR (300 MHz, DMSO) δ 7.76 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 1.9 Hz, 1H), 4.62 (t, J = 5.9 Hz, 2H), 3.91 (t, J = 5.9 Hz, 2H), 3.80 (s, J = 18.9 Hz, 3H), 2.65 (s, 3H). 31P NMR (202 MHz, MeOD) δ 32.67 (s).^1H NMR (500 MHz, CDCl3) δ 7.81 – 7.71 (m, 4H), 7.66 – 7.59 (m, 2H), 7.59 – 7.51 (m, 4H), 7.44 (s, J = 2.2 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H), 4.48 (dt, J = 13.8, 7.0 Hz, 2H), 3.63 (s, 3H), 3.10 (dt, J = 10.8, 7.0 Hz, 2H), 2.53 (s, 3H). ^{31}P NMR (202 MHz, MeOD) δ 32.67 (s). ^{13}C NMR (126 MHz, MeOD) δ 128.37 (s), 116.36 (d, *J* = 2.3 Hz), 115.14 (s), 114.33 (s, *J* = 7.2 Hz), 114.07 (d, *J* = 10.0 Hz), 112.70 (d, *J* = 12.1 Hz), 107.52 (s, *J* = 13.2 Hz), 106.27 (s), 104.97 (s), 104.63 (s), 102.42 (s, *J* = 37.3 Hz), 99.87 (s, *J* = 15.3 Hz), 25.40 (d, *J* = 2.4 Hz), 17.78 (s), 13.02 (s), 12.46 (s), -7.74 (s).

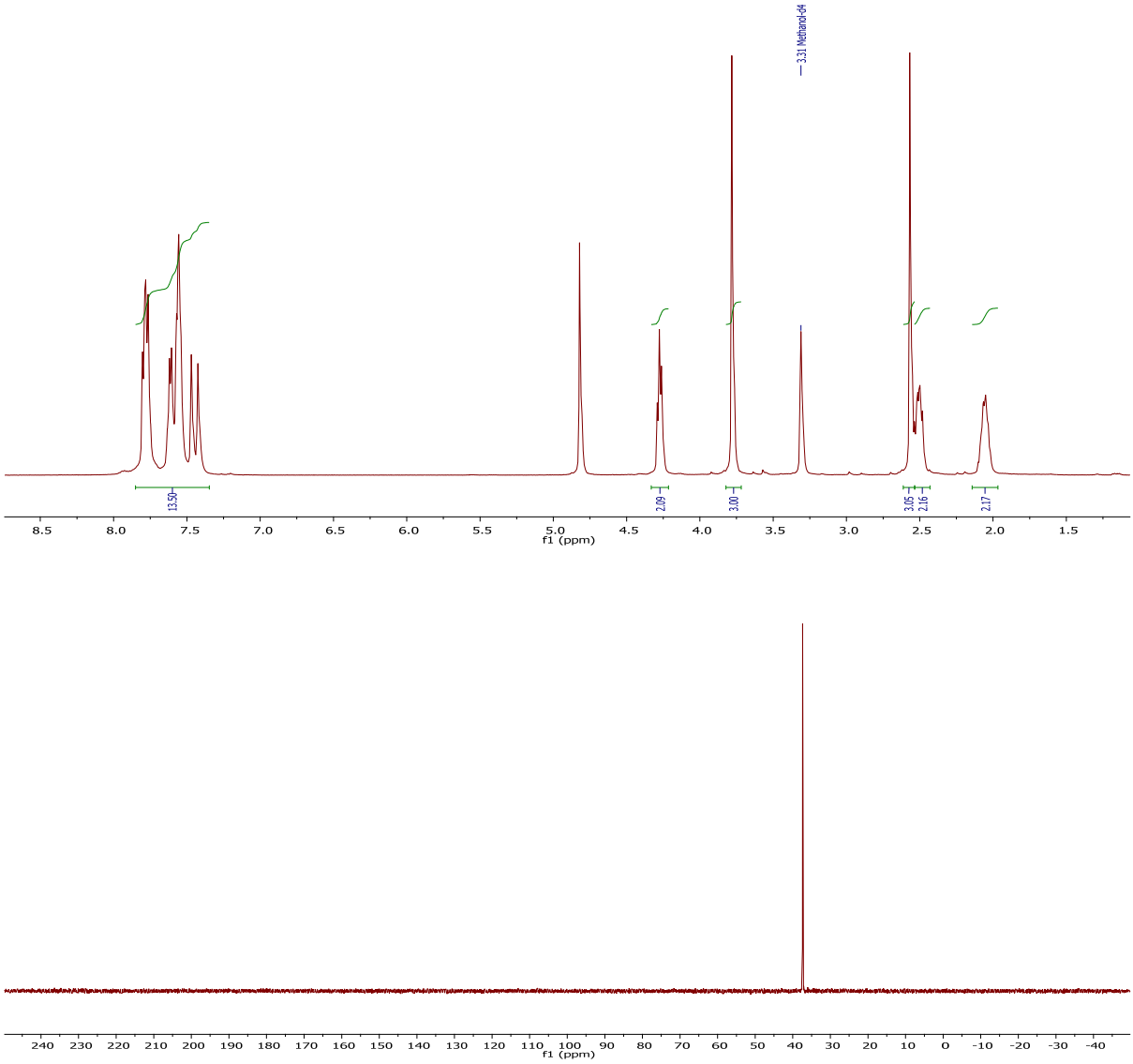


Figure S2: ^1H (top) and ^{31}P NMR (bottom) NMR spectra of $[DMImC_3P(O)Ph_2][Tf_2N]$.

***n* = 3**: Yield 65%. ESI-MS: $[C_{20}H_{24}N_2PO]^+$ 339.163; $[C_2S_2NF_6O_4]^-$ 279.918. FT-IR: 600, 659, 719, 793, 1053, 1134, 1179, 1348, 1440, 1539, 1597 cm^{-1}. ^1H NMR (500 MHz, MeOD) δ 7.82 – 7.42 (m, 12H), 4.28 (t, J = 7.3 Hz, 2H), 3.78 (s, 3H), 2.57 (s, 3H), 2.54 – 2.47 (m, 2H), 2.06 (dd, J = 20.1, 12.7 Hz, 2H). 31P NMR (202 MHz, MeOD) δ 37.38 (s). ^1H NMR (500 MHz, MeOD) δ 7.82 – 7.42 (m, 12H), 4.28 (t, J = 7.3 Hz, 2H), 3.78 (s, 3H), 2.57 (s, 3H), 2.54 – 2.47 (m, 2H), 2.06 (dd, J = 20.1, 12.7 Hz, 2H). ^{31}P NMR (202 MHz, MeOD) δ 37.38 (s). ^{13}C NMR (126 MHz, MeOD) δ 128.53 (s, *J* = 41.4 Hz), 116.10 (s, *J* = 26.1 Hz), 115.56 (s, *J* = 24.3 Hz), 115.16 (s), 114.76 (s), 114.29 (d, *J* = 9.6 Hz), 112.65 (d, *J* = 11.9 Hz), 112.01 (s), 111.91 (s), 107.50 (s), 106.29 (s), 104.95 (s), 104.43 (s, *J* = 21.2 Hz), 102.40 (s), 99.85 (s), 17.92 (s), 9.07 (s), 8.50 (s), 5.80 (s), -8.03 (s).

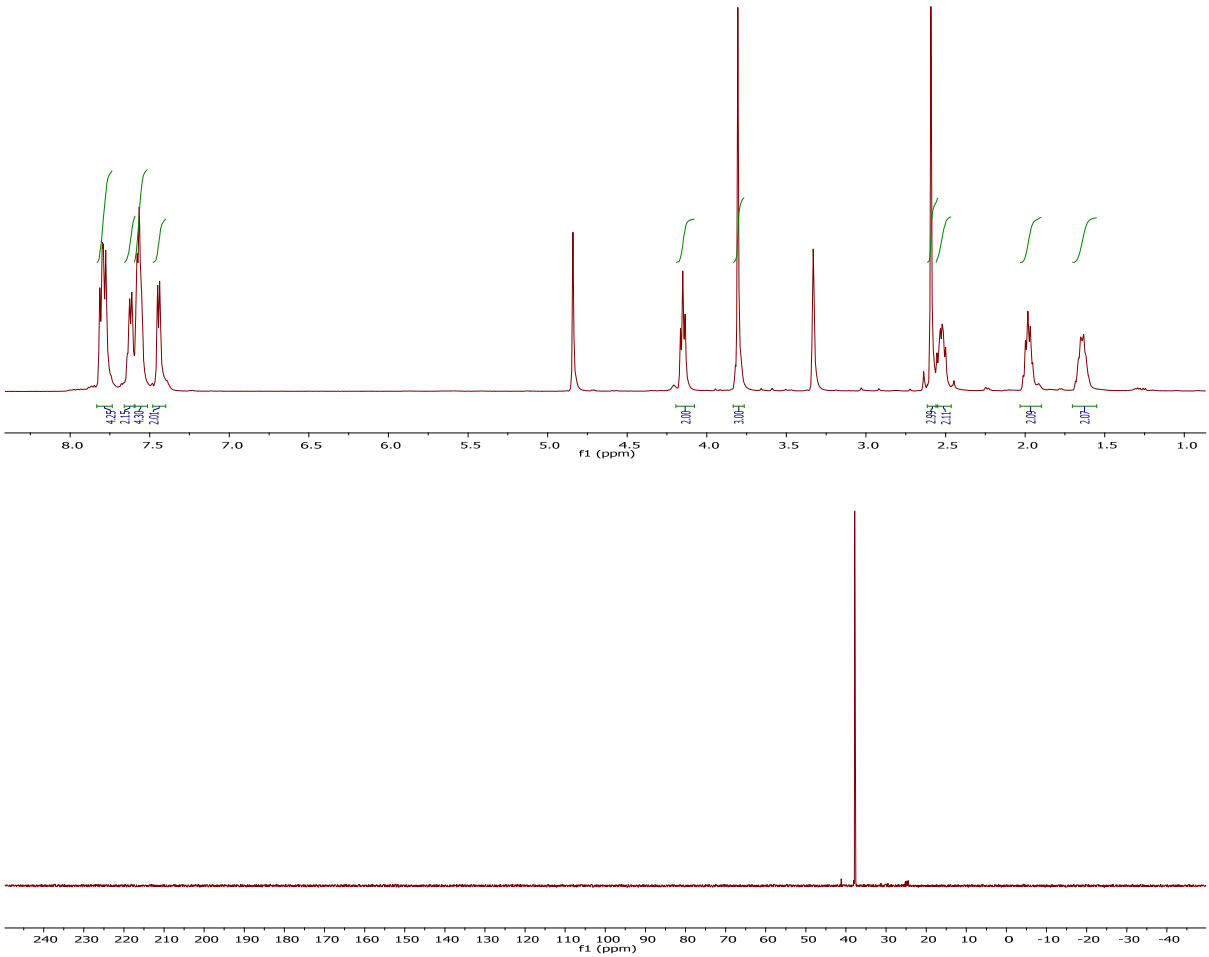


Figure S3: ^1H (top) and ^{31}P NMR (bottom) NMR spectra of $[DMImC_4P(O)Ph_2][Tf_2N]$.

***n* = 4**: Yield: 75%. ESI-MS: $[C_{21}H_{26}N_2PO]^+$ 353.178; $[C_2S_2NF_6O_4]$- 279.913. FT-IR: 568, 611, 698, 717, 790, 998, 1049, 1120, 1136, 1176, 1352, 1443, 1539, 1591 cm^{-1}. ^1H NMR (500 MHz, MeOD) δ 7.83 – 7.73 (m, 4H), 7.62 (d, J = 6.4 Hz, 2H), 7.60 – 7.51 (m, 4H), 7.44 (d, J = 5.8 Hz, 2H), 4.15 (t, J = 7.3 Hz, 2H), 3.80 (s, J = 7.5 Hz, 3H), 2.59 (s, J = 19.1 Hz, 3H), 2.53 (dd, J = 16.1, 11.0 Hz, 2H), 2.03 – 1.90 (m, 2H), 1.70 – 1.55 (m, 2H).^1H NMR (500 MHz, MeOD) δ 7.83 – 7.73 (m, 4H), 7.62 (d, J = 6.4 Hz, 2H), 7.60 – 7.51 (m, 4H), 7.44 (d, J = 5.8 Hz, 2H), 4.15 (t, J = 7.3 Hz, 2H), 3.80 (s, J = 7.5 Hz, 3H), 2.59 (s, J = 19.1 Hz, 3H), 2.53 (dd, J = 16.1, 11.0 Hz, 2H), 2.03 – 1.90 (m, 2H), 1.70 – 1.55 (m, 2H). ^{31}P NMR (202 MHz, MeOD) δ 37.81 (s). ^{13}C NMR (126 MHz, MeOD) δ 126.38 (s, *J* = 12.5 Hz), 113.96 (d, *J* = 2.4 Hz), 113.20 (s), 112.30 (d, *J* = 9.6 Hz), 110.56 (d, *J* = 11.9 Hz), 109.58 (s), 104.10 (s, *J* = 20.2 Hz), 102.97 (s, *J* = 21.3 Hz), 102.60 (s, *J* = 20.8 Hz), 100.43 (s), 29.24 (s), 15.84 (s), 11.84 (d, *J* = 13.7 Hz), 9.73 (s, *J* = 16.8 Hz), 9.16 (s), 7.95 (s), 0.01 (d, *J* = 3.7 Hz), -10.17 (s).

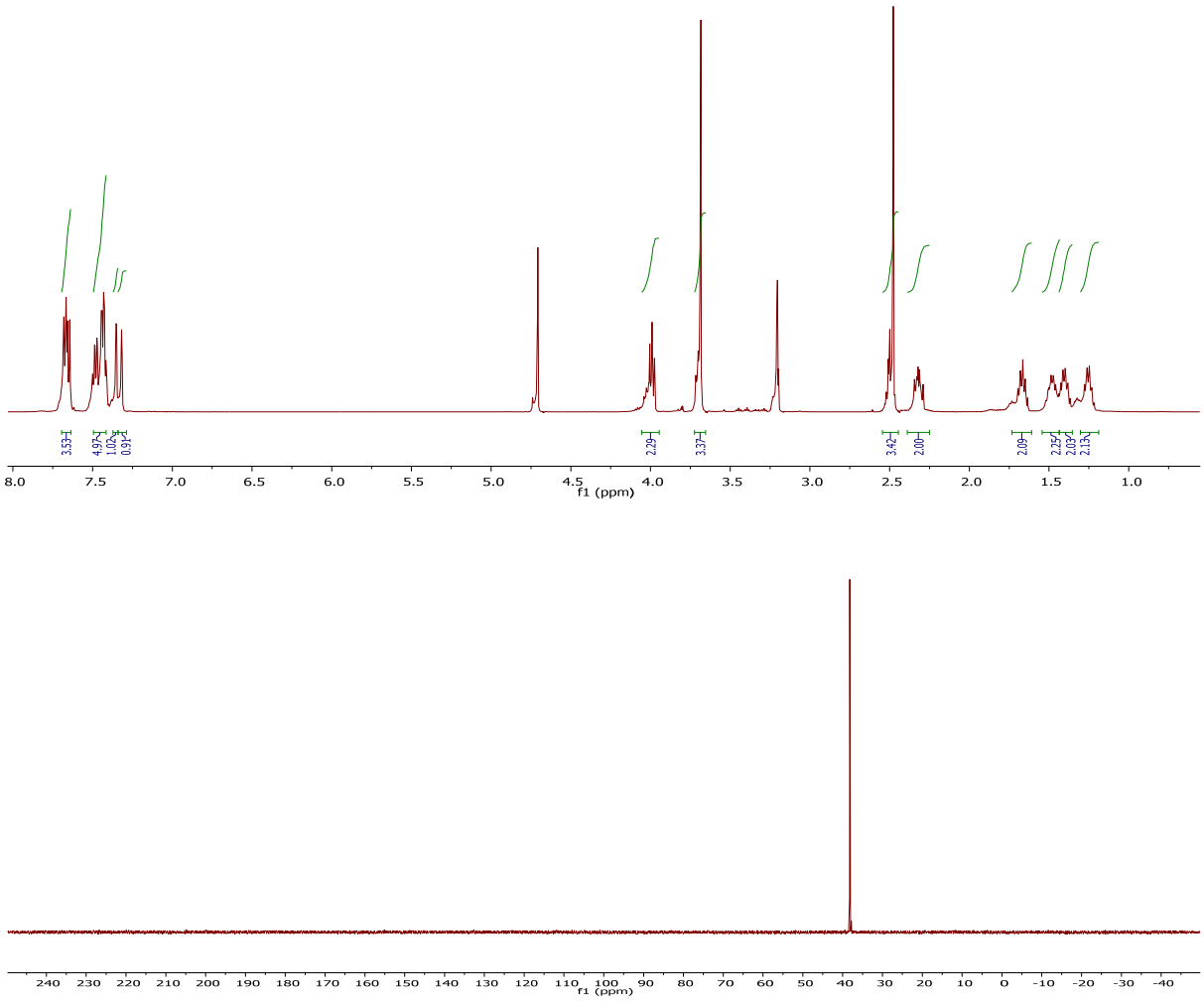


Figure S4: ^1H (top) and ^{31}P NMR (bottom) NMR spectra of $[DMImC_6P(O)Ph_2][Tf_2N]$.

***n* = 6**: Yield: 71%. ESI-MS: $[C_{23}H_{30}N_2PO]^+$ 381.206; $[C_2S_2NF_6O_4]$- 279.915. FT-IR: 570, 612, 740, 1059, 1120, 1137, 1176, 1339, 1350, 1440, 1543, 1594 cm^{-1}. ^1H NMR (500 MHz, MeOD) δ 7.69 – 7.64 (m, 3H), 7.50 – 7.41 (m, 5H), 7.35 (d, J = 2.1 Hz, 1H), 7.32 (d, J = 2.1 Hz, 1H), 4.05 – 3.95 (m, 2H), 3.68 (s, J = 15.6 Hz, 3H), 2.48 (s, J = 5.6 Hz, 3H), 2.39 – 2.25 (m, 2H), 1.73 – 1.61 (m, 2H), 1.54 – 1.43 (m, 2H), 1.44 – 1.35 (m, 2H), 1.25 (dt, J = 14.8, 7.4 Hz, 2H). ^{31}P NMR (202 MHz, MeOD) δ 38.22 (s). ^1H NMR (500 MHz, MeOD) δ 7.69 – 7.64 (m, 3H), 7.50 – 7.41 (m, 5H), 7.35 (d, J = 2.1 Hz, 1H), 7.32 (d, J = 2.1 Hz, 1H), 4.05 – 3.95 (m, 2H), 3.68 (s, J = 15.6 Hz, 3H), 2.48 (s, J = 5.6 Hz, 3H), 2.39 – 2.25 (m, 2H), 1.73 – 1.61 (m, 2H), 1.54 – 1.43 (m, 2H), 1.44 – 1.35 (m, 2H), 1.25 (dt, J = 14.8, 7.4 Hz, 2H). ^{13}C NMR (126 MHz, MeOD) δ 126.17 (s), 114.27 (s, *J* = 14.4 Hz), 113.81 (d, *J* = 2.3 Hz), 113.48 (s), 112.26 (d, *J* = 9.6 Hz), 110.50 (d, *J* = 11.8 Hz), 104.03 (s), 102.96 (s), 102.55 (s), 100.41 (s), 15.85 (s), 11.43 (d, *J* = 14.1 Hz), 10.82 (s, *J* = 6.4 Hz), 10.26 (s), 9.69 (s, *J* = 14.7 Hz), 7.12 (s, *J* = 6.7 Hz), 2.74 (d, *J* = 3.9 Hz), -0.01 (d, *J* = 3.6 Hz), -10.04 (s, *J* = 4.8 Hz).

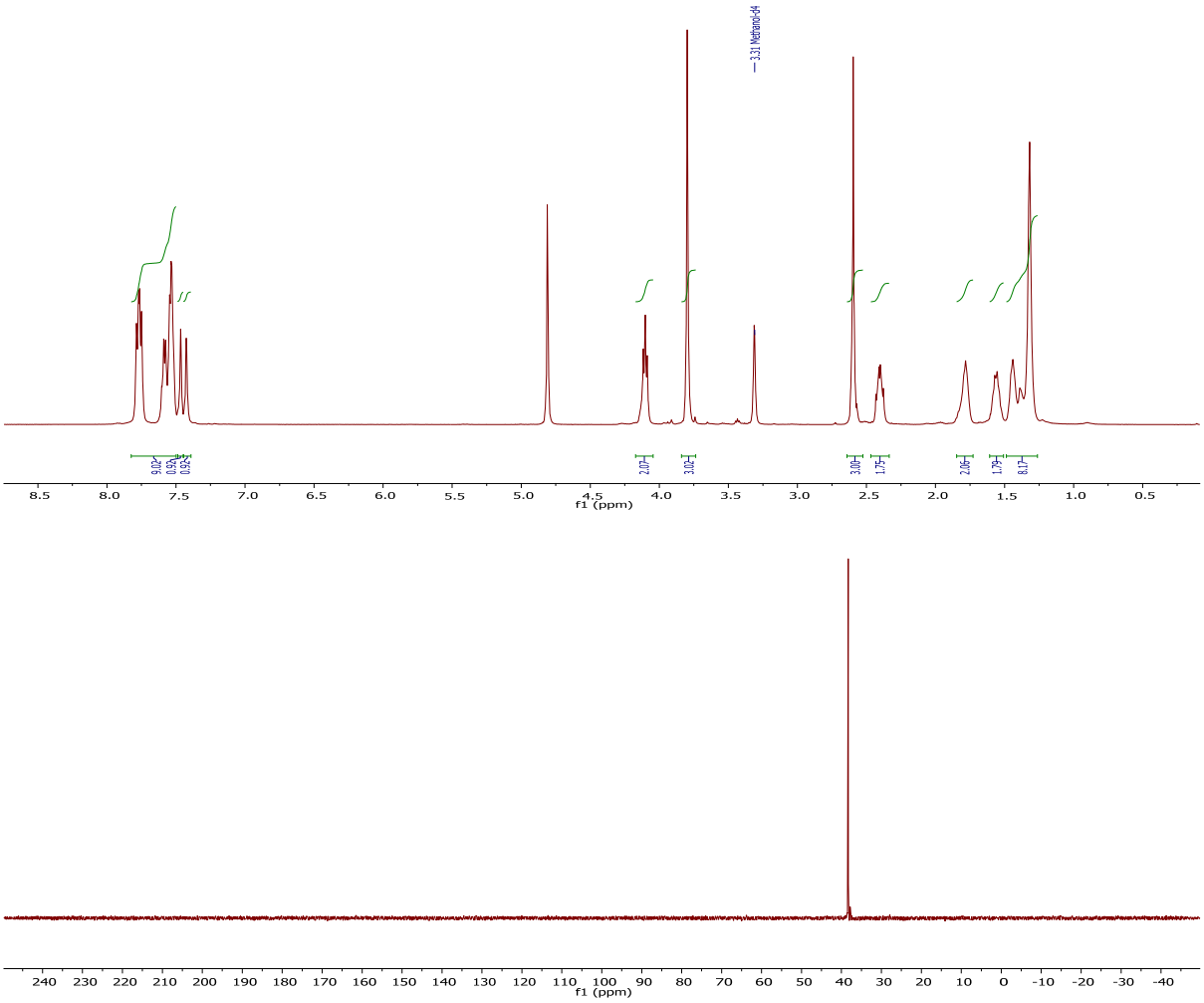


Figure S5: ^1H (top) and ^{31}P NMR (bottom) NMR spectra of $[DMImC_8P(O)Ph_2][Tf_2N]$.

***n* = 8**: Yield: 70%. ESI-MS: $[C_{25}H_{34}N_2PO]^+$ 409.240; $[C_2S_2NF_6O_4]$- 279.917. FT-IR: 569, 599, 613, 697, 1053, 1120, 1134, 1177, 1349, 1440 cm^{-1}. ^{1}H NMR (500 MHz, CDCl3) δ 7.82 – 7.50 (m, 10H), 7.46 (d, J = 1.9 Hz, 1H), 7.42 (d, J = 1.9 Hz, 1H), 4.10 (t, J = 7.4 Hz, 2H), 3.79 (s, 3H), 2.59 (s, J = 4.5 Hz, 3H), 2.40 (dd, J = 16.0, 11.1 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.61 – 1.50 (m, 2H), 1.48 – 1.26 (m, 8H). ^{31}P NMR (202 MHz, MeOD) δ 38.29 (s). ^{1}H NMR (500 MHz, CDCl3) δ 7.82 – 7.50 (m, 10H), 7.46 (d, J = 1.9 Hz, 1H), 7.42 (d, J = 1.9 Hz, 1H), 4.10 (t, J = 7.4 Hz, 2H), 3.79 (s, 3H), 2.59 (s, J = 4.5 Hz, 3H), 2.40 (dd, J = 16.0, 11.1 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.61 – 1.50 (m, 2H), 1.48 – 1.26 (m, 8H). ^{31}P NMR (202 MHz, MeOD) δ 38.29 (s). ^{13}C NMR (126 MHz, MeOD) δ 128.17 (s), 116.31 (s), 115.77 (s), 115.52 (s), 114.26 (d, *J* = 9.5 Hz), 112.46 (d, *J* = 11.7 Hz), 106.03 (s), 104.96 (s), 104.56 (s), 102.41 (s), 31.89 (s, *J* = 6.8 Hz), 17.83 (s), 16.95 (s), 16.32 (s), 14.02 (s), 13.91 (s), 13.09 (s, *J* = 45.0 Hz), 12.41 (s), 12.28 (s), 12.21 (s), 11.84 (s), 9.57 (s), 4.86 (d, *J* = 3.6 Hz), -8.06 (s).

Table 3: ESI mass spectrometry assignments to species for solutions of the ionic liquids and $La(OTf)_3$. L = $[DMImC_nP(O)Ph_2]^+$ (n = 2, 3, 4, 6, 8); A = $[OTf]^-$; B = $[Tf_2N]^-$; C = H_2O.

Assigned species	chainlength 2	chainlength 3	chainlength 4	chainlength 6	chainlength 8
L^+	325.14	339.16	352.12	381.20	409.24
$[LaL_1A_1B_2]^+$				1228.52	1256.94
$[LaL_2A_2B_2]^+$	1646.95	1674.97			1815.13
$[LaL_2A_1B_3]^+$	1777.92	1805.94		1890.56	
$[LaL_3A_3C_1]^{2+}$		541.22			
$[LaL_3A_3B_1C_1]^{2+}$	929.55				
$[LaL_3A_3B_1C_2]^{2+}$		959.14			
$[LaL_4A_3B_2C_1]^{2+}$	1232.09				
$[LaL_4B_6C_1Na]^+$		1608.05			
$[LaL_4A_3B_1C_2]^{3+}$		752.78	771.21		
$[LaL_4A_2B_3]^{2+}$		1316.61			
$[LaL_4A_5C_1]^{2+}$			1157.2		
$[LaL_4A_2B_2C_5]^{3+}$			833.46		
$[LaL_5A_2B_4C_3]^{2+}$				1758.94	
$[LaL_6A_2B_2]^{5+}$				657.09	
$[LaL_6A_1B_5C_1]^{3+}$					1386.97

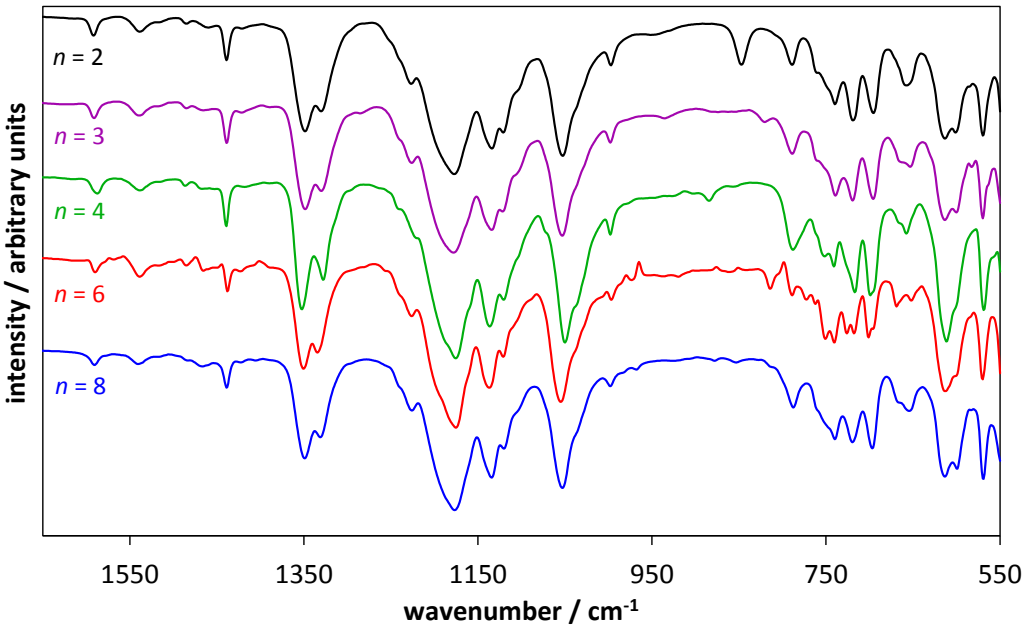


Figure 1: IR data for [DMImC_nP(O)Ph_2][Tf_2N] ionic liquids (n = 2, 3, 4, 6, 8).

Crystallography

Crystal data for $[DMImC_3P(O)Ph_2][PF_6]$ (**2A**), and $Eu(hfa)_4(DMImC_3P(O)Ph_2)$ (**3**) were collected using a Bruker Nonius Kappa CCD diffractometer with a FR591 rotating anode and a molybdenum target at *ca.* 120 K in a nitrogen stream. Lorentz and polarisation corrections were applied. The structures were solved by direct methods. Hydrogen-atom positions were located from difference Fourier maps and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded, 1.5 for methyl), was used for subsequent refinements. The function minimised was $\Sigma[\omega(|F_0|^2 - |F_c|^2)]$ with reflection weights $\omega^1 = [\sigma^2 |F_0|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max|F_0|^2 + 2|F_c|^2]/3$. The SHELXTL package and OLEX2 were used for structure solution and refinement.[i,ii] Due to poor diffraction of the crystals of $Eu(hfa)_4(DMImC_3P(O)Ph_2)$ (**3**) at higher angles (tested for a number of crystals), in this structure only the europium and the phosphorus atom have been refined anisotropically (otherwise a number of NPDs were obtained).

Table 4: Crystallographic data.

	$[DMImC_3P(O)Ph_2][PF_6]$ (2A)	**$Eu(hfa)_4(DMImC_3P(O)Ph_2)$ (3)**
Formula	$C_{20}H_{24}N_2F_6PO_1$	$C_{40}H_{28}EuF_{24}N_2O_9P$
MW / g	484.35	1319.57
Dimensions / mm^3	0.16×0.06×0.03	0.06×0.05×0.01
Crystal system	Triclinic	Monoclinic
Spacegroup	P-1	Cc
a / Å	5.9974(1)	20.278(6)
b / Å	8.5870(2)	12.748(5)
c / Å	22.1778(6)	19.529(9)
α / °	97.619(1)	90.00
β / °	91.789(1)	105.33(2)
γ / °	107.244(1)	90.00
V / $Å^3$	1078.18(4)	4869(3)
Z	2	4
D_{calc} / g cm^{-3}	1.492	1.804
Crystal shape	Plate	Plate
Crystal color	colourless	Light blue
μ / mm^{-1}	0.268	1.470
F(000)	500	2592
Meas. reflections	14475	36124
Unique reflections	4916	14097
Parameters refined	337	697
Flack parameter	-	0.003(16)
Goof on F^2	1.112	1.181
R_1	0.0519	0.0865
wR_2	0.1203	0.1778
CCDC	869702	869703

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[ii] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339.