

## New Journal of Chemistry

### ELECTRONIC SUPPLEMENTARY INFORMATION

#### Are fancy acidic or neutral ligands really needed for synergism in ionic liquids? A comparative study of lanthanoids extraction in CHCl<sub>3</sub> and an ionic liquid.

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#### 1. Synthesis and characterization of HL.

The pyrazolone derivative, 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one (**HL**) [1], was obtained according to an adapted literature procedure [2] in excellent yield. Shortly, 3-methyl-1-phenyl-1H-pyrazol-5-one (8.7 g, 50 mmol) was dissolved in dry dioxane (60 ml) under gentle heating. Ca(OH)<sub>2</sub> (7.4 g, 100 mmol) was added and the mixture was stirred at room temperature for 0.5 h. 4-Phenylbenzoyl chloride (6.5 ml, 50 mmol) was then added and the mixture was refluxed with stirring for 2 h. The reaction mixture was cooled to room temperature and poured into 10 % aq. HCl (250 ml). The solid phase formed was filtered off, washed with water, dried on air, and recrystallized from ethanol/acetone to give pure product in 86-94 % yield. Second recrystallization from ethanol afforded the analytically pure compound: 71-76 % yield; m. p. 151.1-151.5°C; R<sub>f</sub> 0.51 (MeOH:CH<sub>2</sub>Cl<sub>2</sub> 5:95). The NMR spectra were initially recorded in chloroform-d<sub>3</sub> as 0.01 M solutions. However, the proton spectrum of the ligand showed overlapped signal for 5 aromatic protons. Also, four protons appeared as a sharp singlet due to non-first order spectrum. This pattern made the assignment of the signals impossible. So, the spectra were recorded in benzene-d<sub>6</sub>, where the most part of the protons give separate and well defined signals. The full assignment was accomplished by analysing the interactions in 2D experiments. For simplicity, the nuclei of C<sub>6</sub>H<sub>4</sub> unit of biphenyl are assigned as ‘ and those of Ph part as ‘; Ph means N-Ph. <sup>1</sup>H NMR (CDCl<sub>3</sub>, DRX 250) 2.223 (s, 3H, CH<sub>3</sub>), 7.343 (ddt, 1H, J 1.2, 6.8, 8.1, Ar CH), 7.444-7.561 (m, 5H Ar CH), 7.699 (dd, 2H, J 1.6, 6.8, Ar CH), 7.778 (s, 4H, Ar CH, non-first order spectrum), 7.935 (dd, 2H, J 1.2, 8.7, Ar CH), 10.595 (bs, 1H, OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, DRX 250) 16.05 (CH<sub>3</sub>), 103.67 (C<sub>q</sub>), 120.78 (2 x CH), 126.68 (CH), 127.07 (2 x CH), 127.26 (2 x CH), 128.22 (CH), 128.67 (2 x CH), 129.01 (2 x CH), 129.14 (2 x CH), 136.24 (C<sub>q</sub>), 137.32 (C<sub>q</sub>), 139.89 (C<sub>q</sub>), 144.86 (C<sub>q</sub>), 147.87 (C<sub>q</sub>), 161.69 (C<sub>q</sub>), 191.41 (C=O); <sup>1</sup>H NMR (benzene-d<sub>6</sub>, II+ 600) 1.977 (s, 3H, CH<sub>3</sub>), 6.972 (tt, 1H, J 1.0, 7.4, CH-4 of Ph), 7.138-7.221 (m, 5H, CH-3 and CH-5 of Ph and CH-3’’, CH-4’’ and CH-5’’ of biPh), 7.339 (dd, 2H, J 1.7, 8.3, CH-3’ and CH-5’ of biPh), 7.381 (dd, 2H, J 1.4, 8.4, CH-2’’ and CH-6’’ of biPh), 7.465 (dd, 2H, J 1.8, 8.3, CH-2’ and CH-6’ of biPh), 8.212 (dd, 2H, J 1.1, 8.7, CH-2 and CH-6 of Ph), 12.237 (bs, 1H, OH); <sup>13</sup>C NMR (benzene-d<sub>6</sub>, II+ 600) 15.85 (CH<sub>3</sub>), 103.86 (C<sub>q-4</sub>), 120.08 (CH-2 and CH-6 of Ph), 126.04 (CH- 4 of Ph), 126.74 (CH-3’ and CH-5’ of biPh), 127.20 (CH-4’’ of biPh), 128.00 (CH-2’’ and CH-6’’ of biPh), 128.84 (CH-3 and CH-5 of Ph or CH-3’’ and CH-5’’ of biPh), 128.86 (CH-3 and CH-5 of Ph or CH-3’’ and CH-5’’ of biPh), 129.01 (CH-2’ and CH-6’ of biPh),

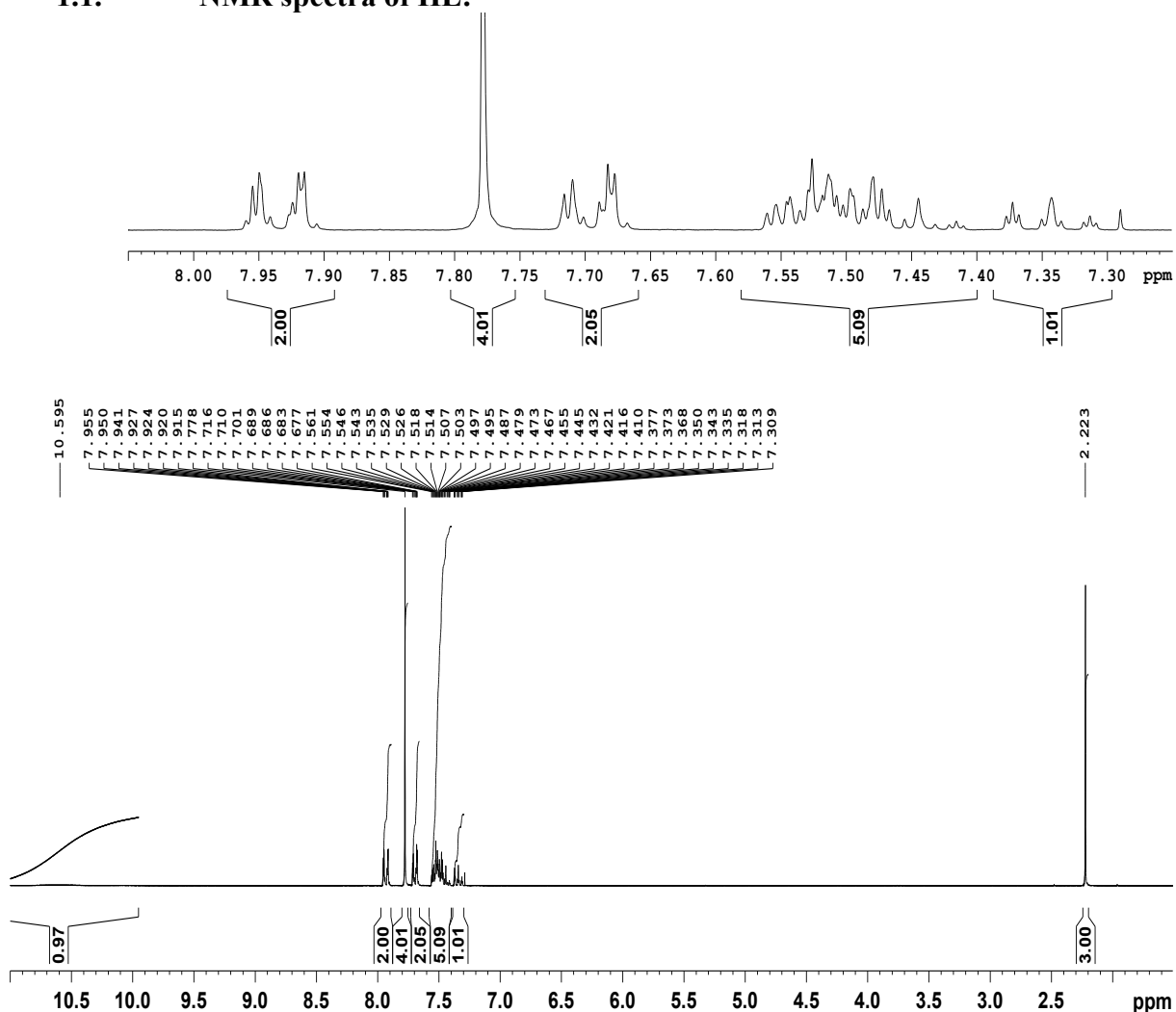
135.94 ( $C_{q-1'}$  of biPh), 138.03 ( $C_{q-1}$  of Ph), 139.92 ( $C_{q-1''}$  of biPh), 144.56 ( $C_{q-4'}$  of biPh), 147.17 ( $C_{q-3}$ ), 162.74 ( $C_{q-5}$ ), 189.99 ( $C=O$ ); COSY cross peaks: 6.972/7.138-7.221, 7.138-7.221/7.381, 7.138-7.221/8.212, 7.339/7.465; NOESY cross peaks: 1.977/7.465, 6.972/7.138-7.221, 7.138-7.221/7.381, 7.138-7.221/8.212, 7.339/7.465; HSQC cross peaks: 1.977/15.85, 6.972/126.04, 7.138-7.221/127.20, 7.138-7.221/128.84, 7.138-7.221/128.86, 7.339/126.74, 7.381/128.00, 7.465/129.01, 8.212/120.08; HMBC cross peaks: 1.977/103.86, 1.977/147.17, 6.972/120.08, 6.972/128.84 or 128.86, 6.972/138.03, 7.138-7.221/120.08, 7.138-7.221/128.00, 7.138-7.221/128.84, 7.138-7.221/128.86, 7.138-7.221/138.03, 7.138-7.221/139.92, 7.339/126.74, 7.339/135.94, 7.339/139.92, 7.381/127.20, 7.381/128.00, 7.381/144.56, 7.465/129.01, 7.465/144.56, 7.465/189.99, 8.212/120.08, 8.212/126.04, 8.212/138.03 (weak).

## References

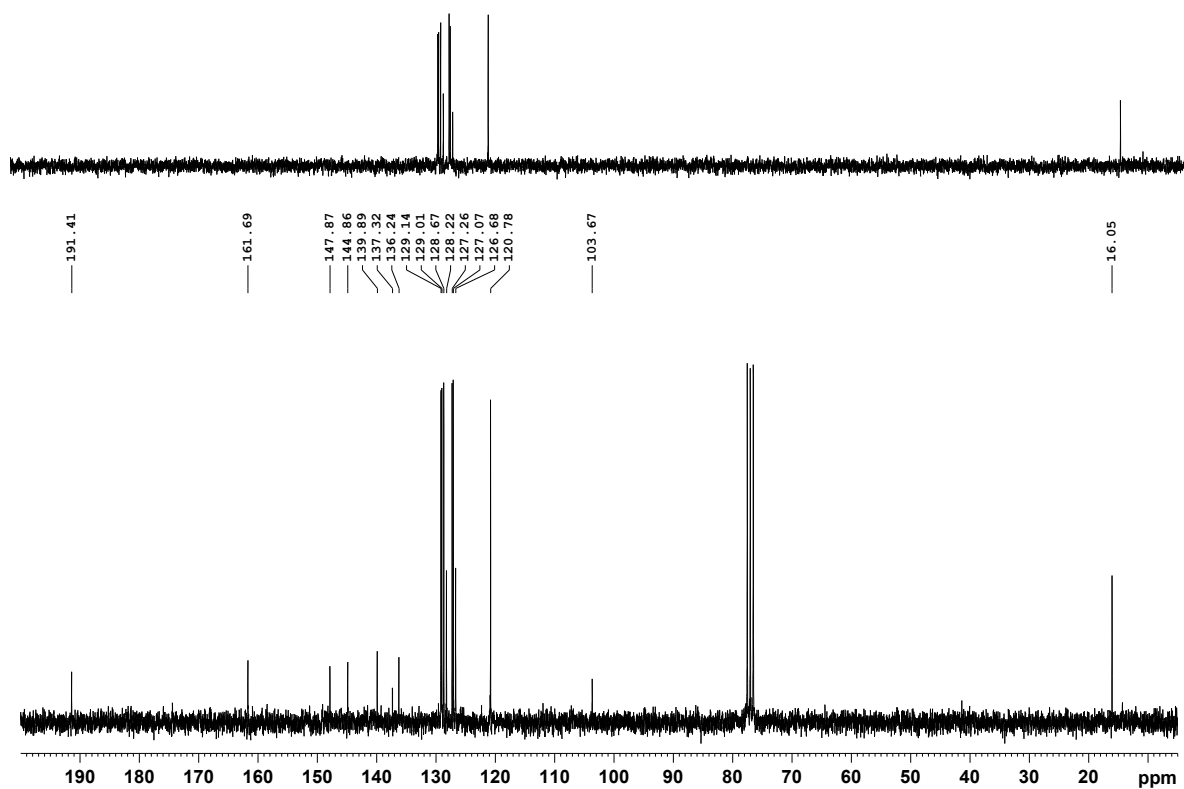
[1] F. Manetti, M. Magnani, D. Castagnolo, L. Passalacqua, M. Botta, F. Corelli, M. Saggi, D. Deidda, A. De Logu, Ligand-based virtual screening, parallel solution-phase and microwave-assisted synthesis as tools to identify and synthesize new inhibitors of Mycobacterium tuberculosis, *ChemMedChem* 1 (2006) 973-989.

[2] B.S. Jensen, The synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolones-5, *Acta Chim. Scand.* 13 (1959) 1668-1670.

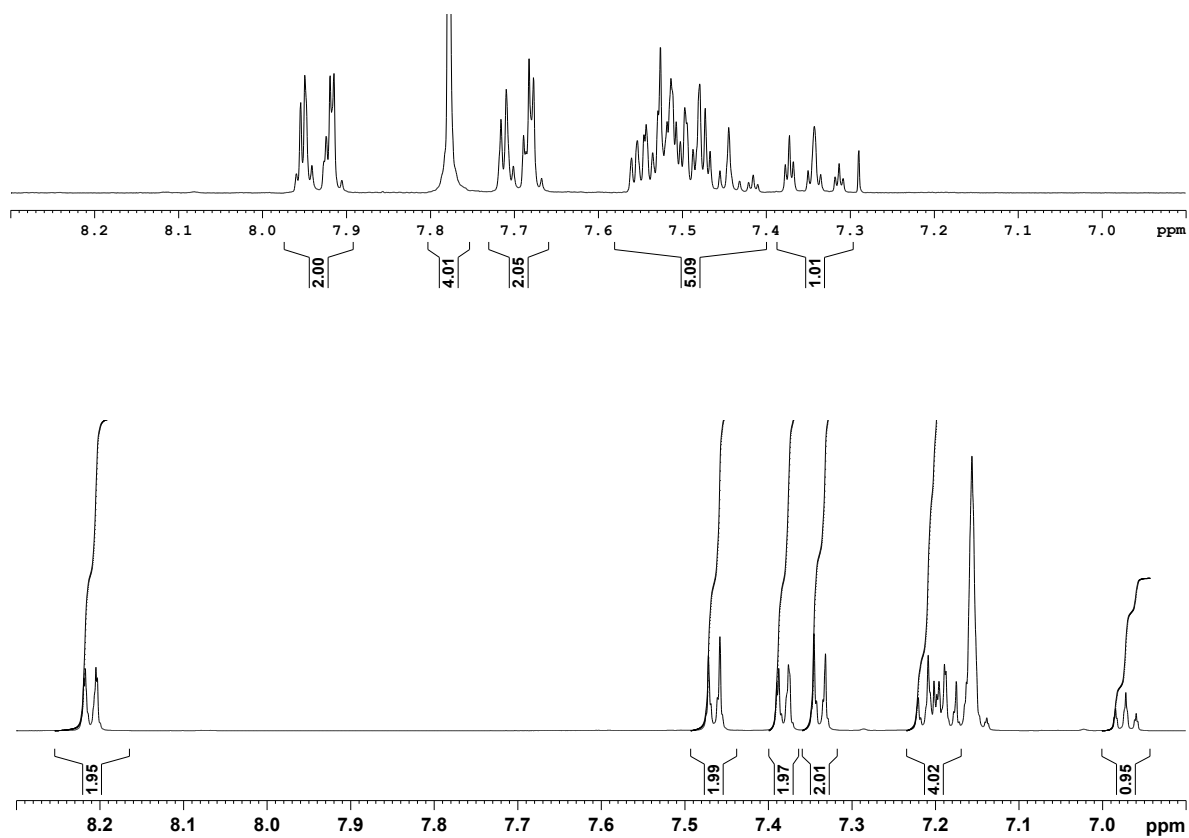
### 1.1. NMR spectra of HL:



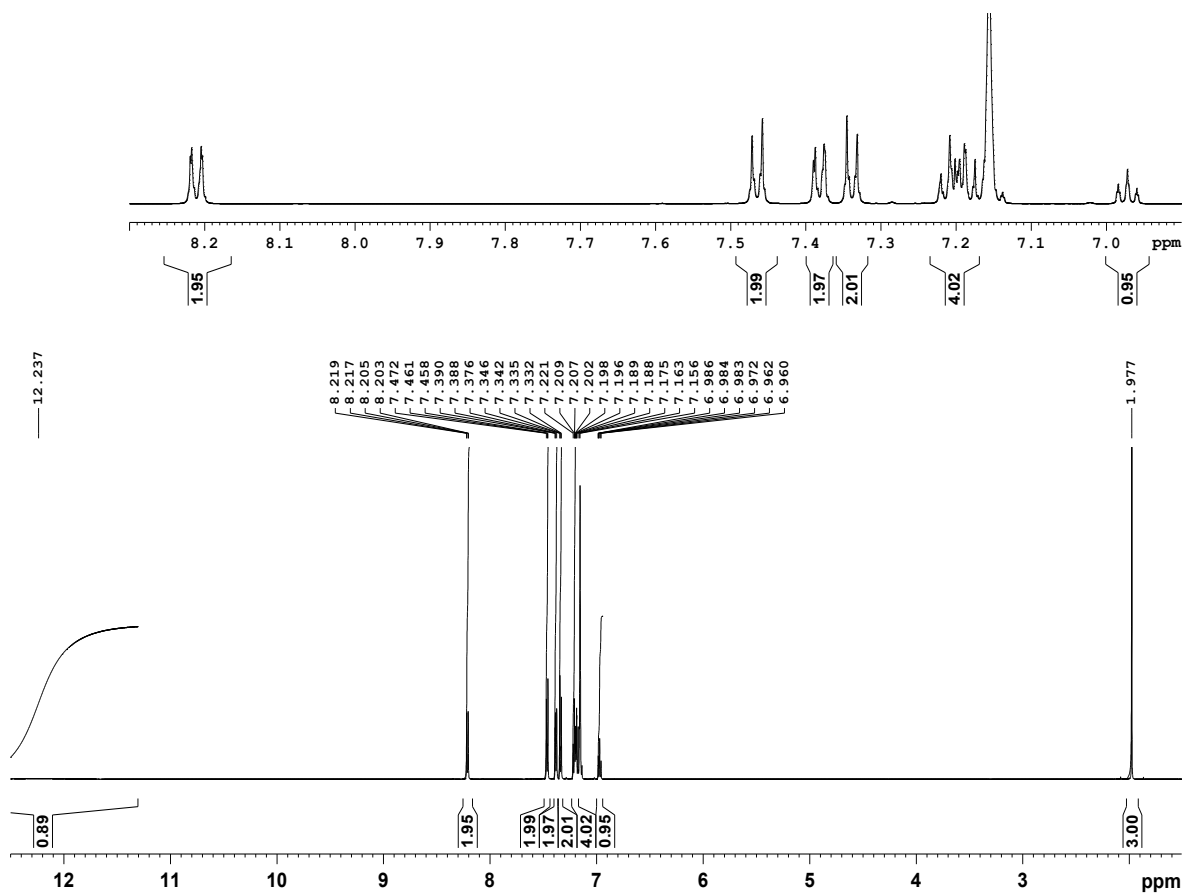
**Figure S1.**  $^1\text{H}$  NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in  $\text{CDCl}_3$ .



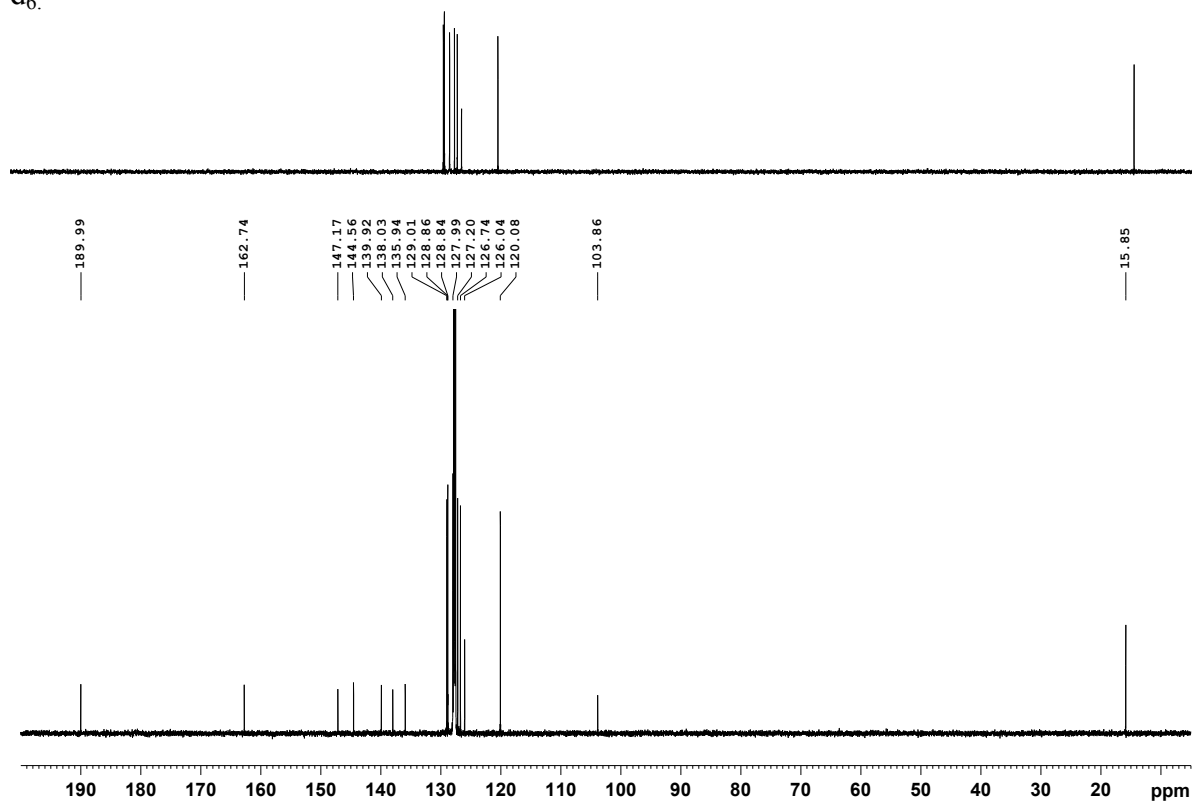
**Figure S2.**  $^{13}\text{C}$  (down) and DEPT (up) NMR spectra of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in  $\text{CDCl}_3$ .



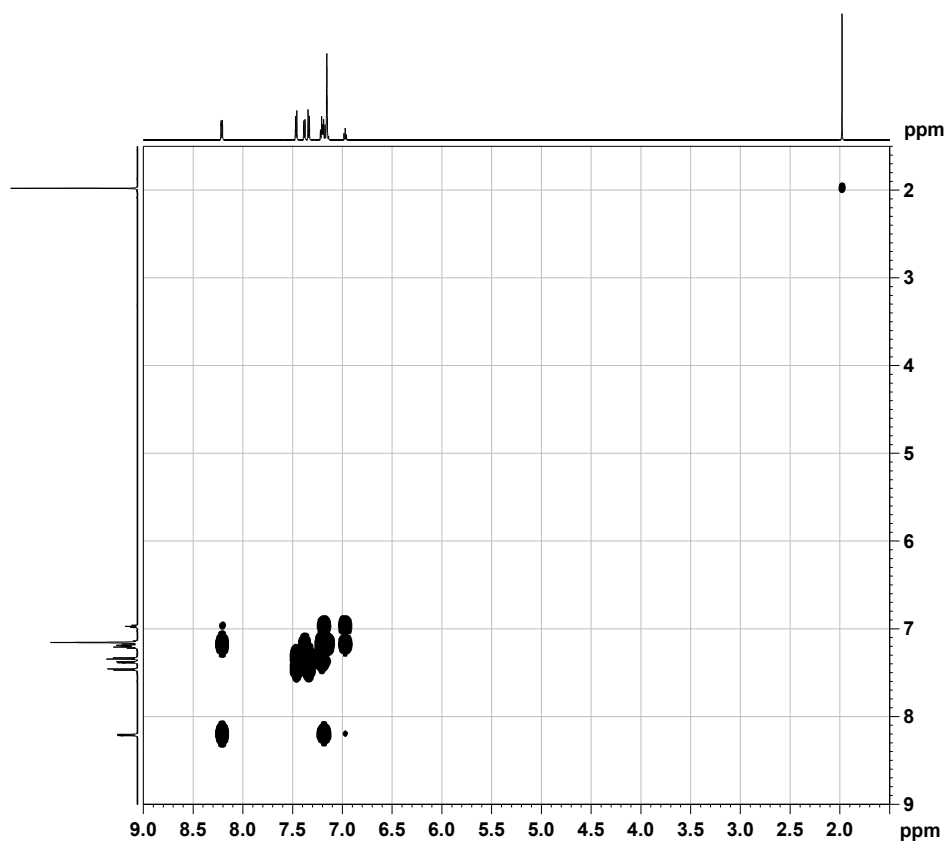
**Figure S3.**  $^1\text{H}$  NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in  $\text{CDCl}_3$  (up) and in benzene- $\text{d}_6$  (down).



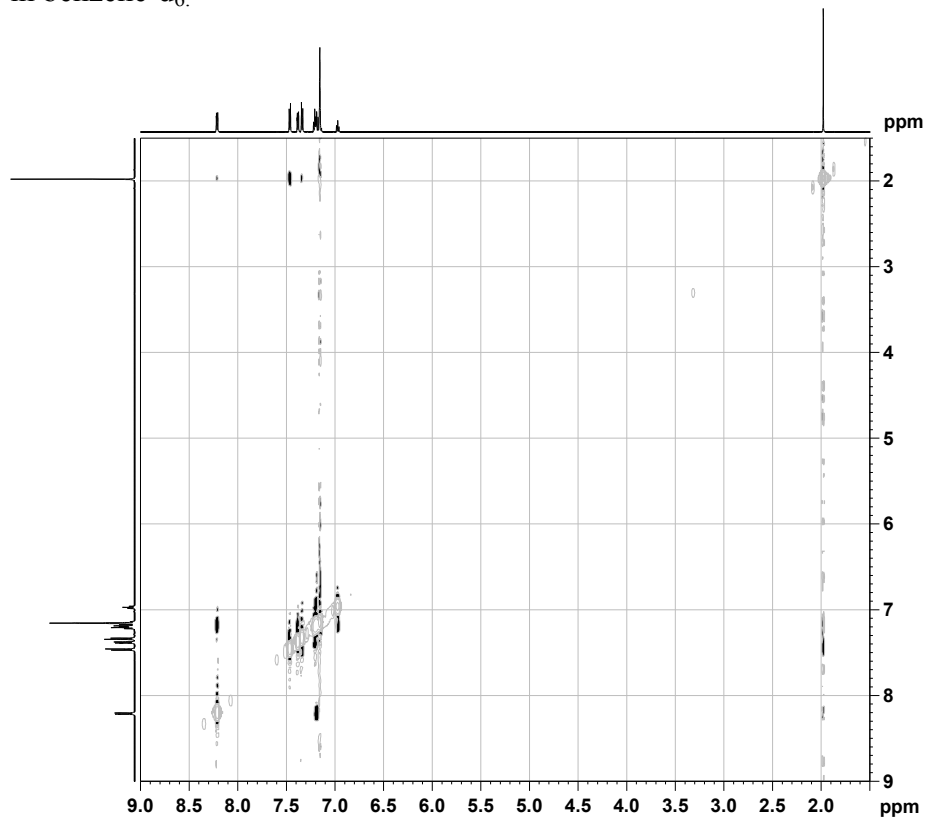
**Figure S4.**  $^1\text{H}$  NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene- $\text{d}_6$ .



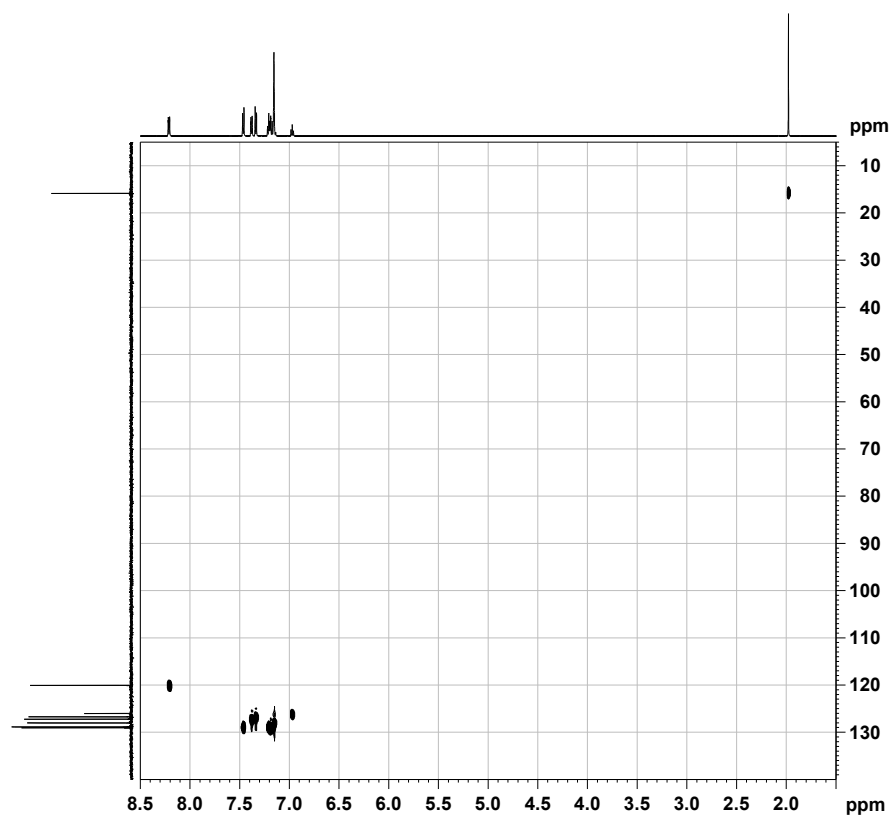
**Figure S5.**  $^{13}\text{C}$  (down) and DEPT (up) NMR spectra of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene- $\text{d}_6$ .



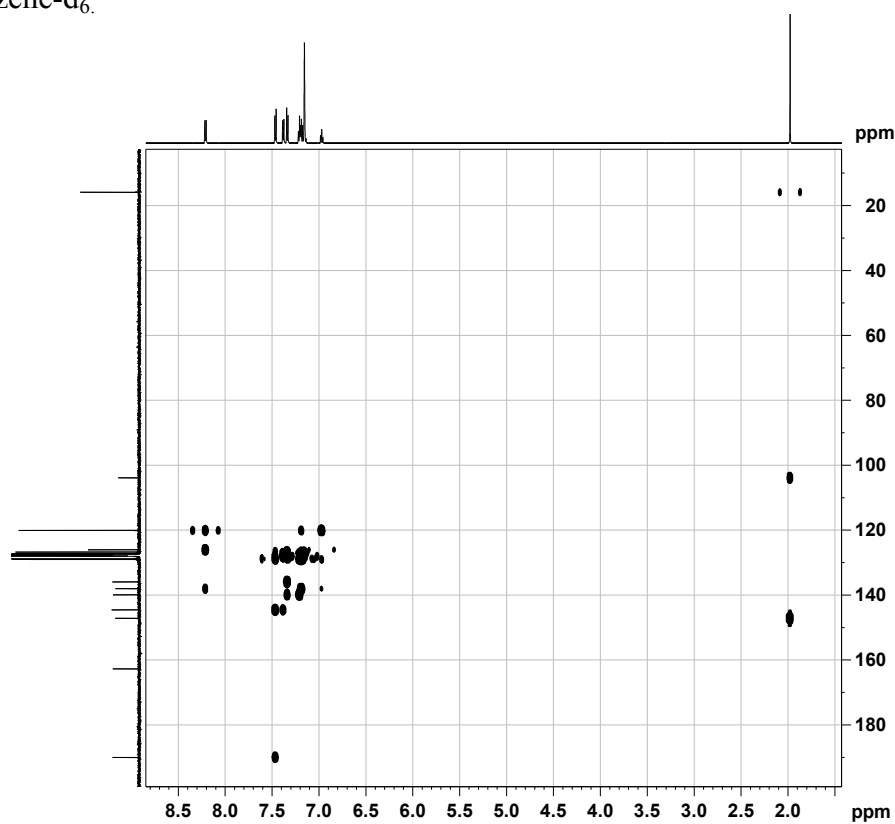
**Figure S6.** <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-d<sub>6</sub>.



**Figure S7.** <sup>1</sup>H-<sup>1</sup>H NOESY NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-d<sub>6</sub>.



**Figure S8.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene- $\text{d}_6$ .

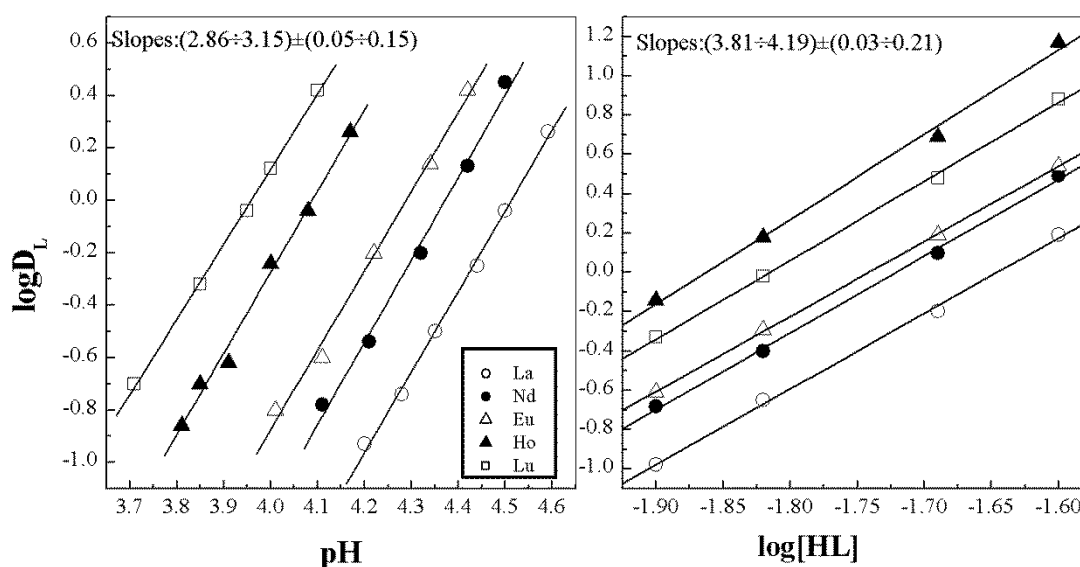


**Figure S9.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene- $\text{d}_6$ .

## 2. NMR characterization of $S_{IV}$

The quality of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(dimethylphosphinoylmethoxy)calix[4]arene ( $S_{IV}$ ) has been checked by  $^1H$  NMR in  $CDCl_3$  (250 MHz, 25°C):  $\delta = 1.074$ (s, 36H,  $(CH_3)_3C$ ), 1.532(d,  $^2J_{HP}=12.9$  Hz, 24H,  $(CH_3)_2P=O$ ), 3.268(d,  $^2J_{HH}=13.0$  Hz, 4H, Ar- $CH_2$ -Ar), 4.688(d,  $^2J_{HP}=1.3$  Hz, 8H,  $CH_2P=O$ ), 4.836(d,  $^2J_{HH}=13.0$  Hz, 4H, Ar- $CH_2$ -Ar), 6.800(s, 8H, Ar- $H$ ) and in  $CD_3OD$  (250MHz, 25°C):  $\delta = 1.001$ (s, 36H,  $(CH_3)_3C$ ), 1.527(d,  $^2J_{HP}=13.1$  Hz, 24H,  $(CH_3)_2P=O$ ), 3.292(d,  $^2J_{HH}=13.2$  Hz, 4H, Ar- $CH_2$ -Ar), 4.668(d,  $^2J_{HP}=1.3$  Hz, 8H,  $CH_2P=O$ ), 4.780(d,  $^2J_{HH}=13.2$  Hz, 4H, Ar- $CH_2$ -Ar), 6.891(s, 8H, Ar- $H$ ).

## 3. Solvent extraction of $Ln^{3+}$ ions with HL alone using $CHCl_3$ as diluent.



**Figure S10.**  $\log D_L$  vs. pH for the extraction of lanthanoid(III) ions with HL alone at  $[HL] = 1.5 \times 10^{-2} \text{ mol/dm}^3$  in  $CHCl_3$ .

$\log D_L$  vs.  $[HL]$  for the extraction of lanthanoid(III) ions with HL alone in  $CHCl_3$ : La, pH=4.30; Nd, pH=4.25; Eu, pH=4.25; Ho, pH=4.15; Lu, pH=3.95.

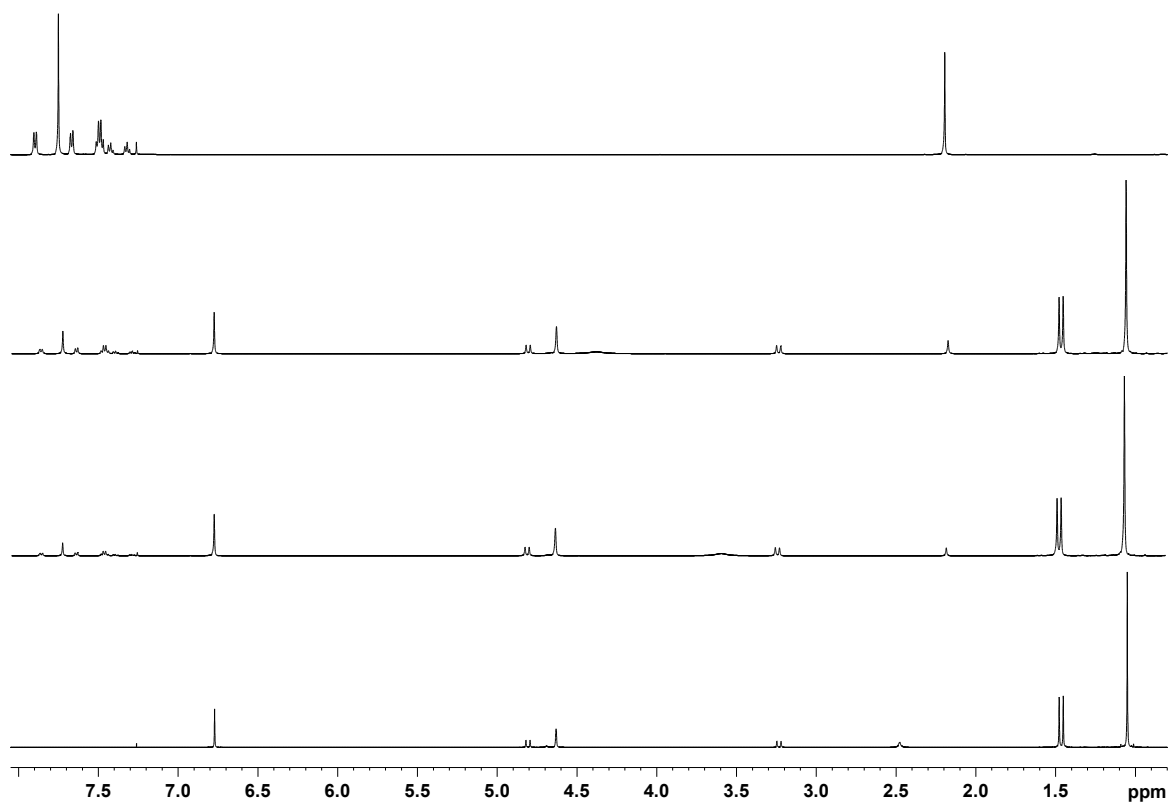
**Table S1:** Ratio and linear correlation coefficient (in parenthesis) between experimental and fitted D values.

Ln	$CHCl_3$		IL	
	HL alone	HL + $S_{IV}$	HL alone	HL + $S_{IV}$
La	1.02 (0.979)	0.968 (0.989)	0.983 (0.974)	0.985 (0.996)
Nd	0.972 (0.986)	1.00 (0.993)	nd	nd
Eu	1.00 (0.973)	1.02 (0.986)	nd	nd
Ho	0.968 (0.989)	0.984 (0.945)	nd	nd
Lu	0.990 (0.989)	0.984 (0.958)	nd	nd

nd: not determined.

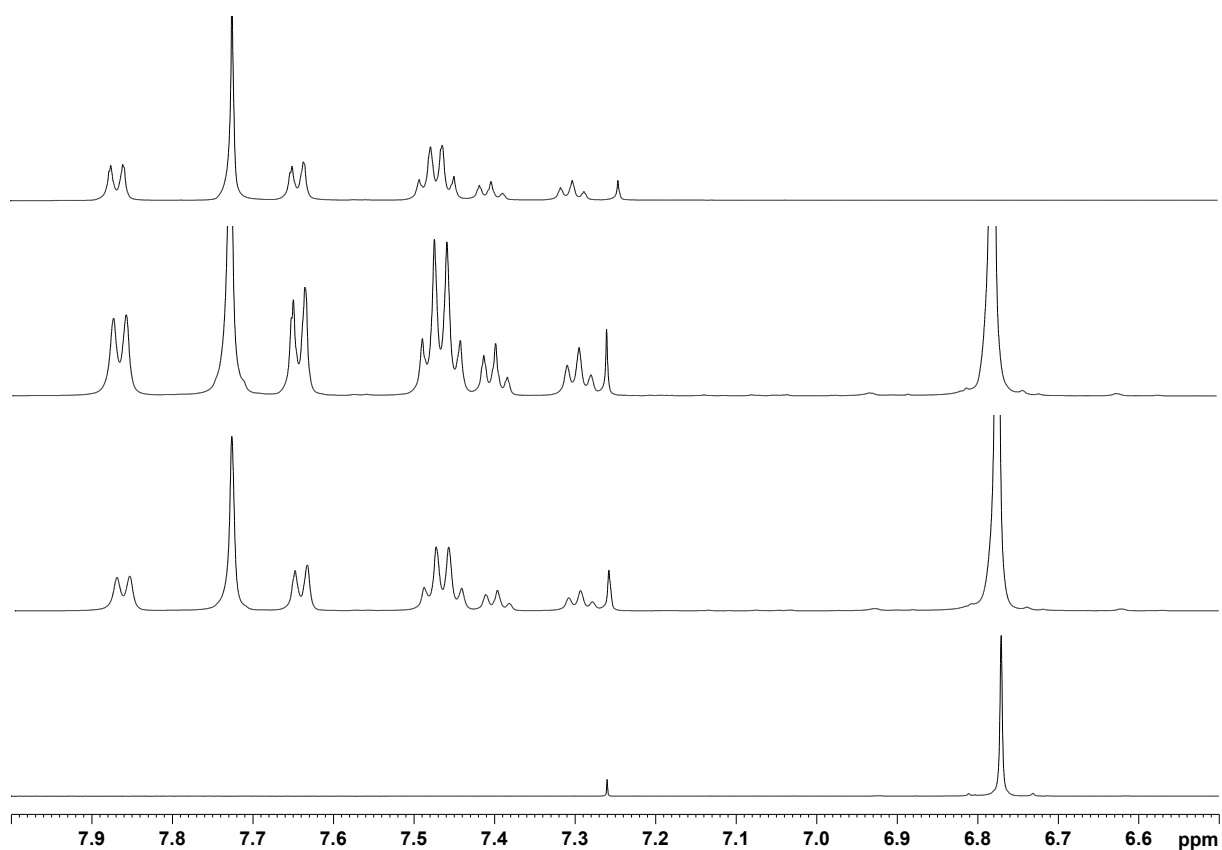
#### 4. Interaction between HL and S<sub>IV</sub>

All samples were prepared separately by using pure dry compounds dissolved in deuteriochloroform (Deutero GmbH). The spectra of the individual ligand (HL) and the synergist S<sub>IV</sub>, assigned as S in figures captions for simplicity, were recorded in 0.05 M concentrations. The spectra of the 2:1 and 1:1 S:HL mixtures were recorded as 0.05 M calixarene and 0.025 M and 0.05 M pyrazolone, respectively.

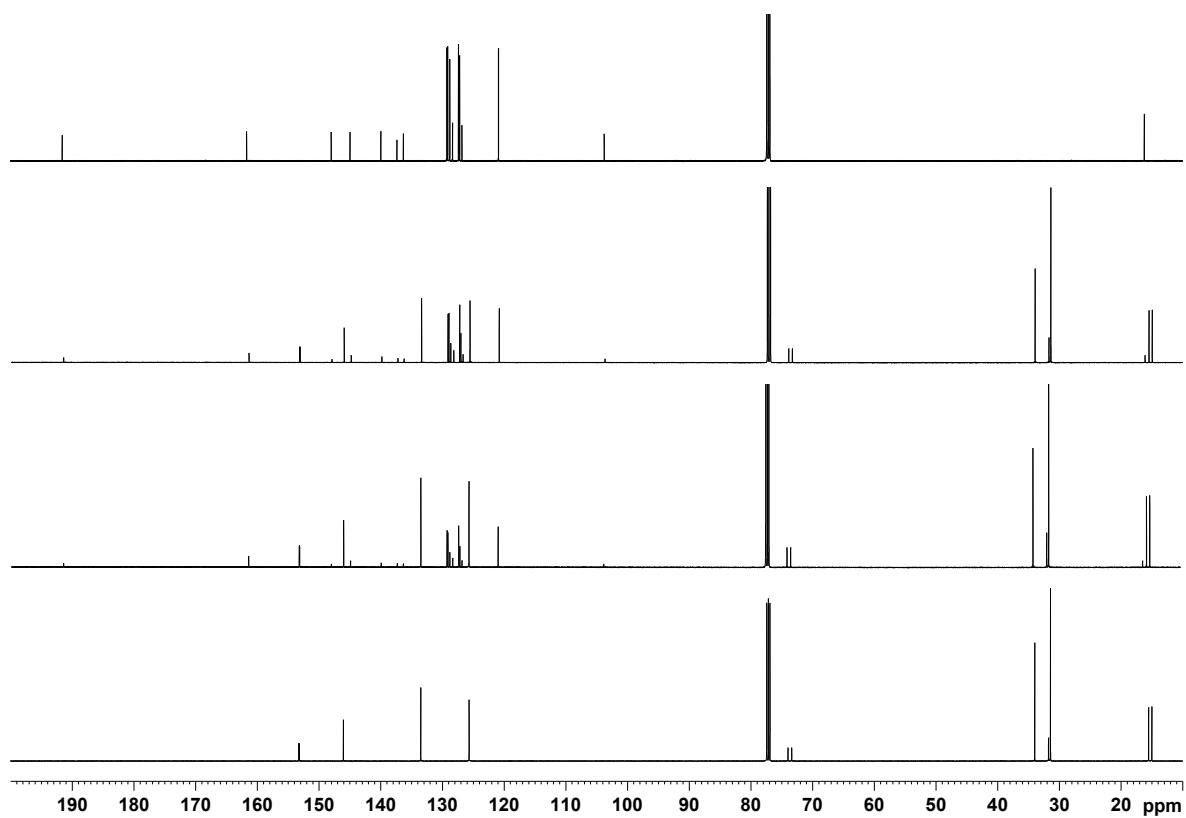


**Figure S11.** <sup>1</sup>H spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in CDCl<sub>3</sub>.

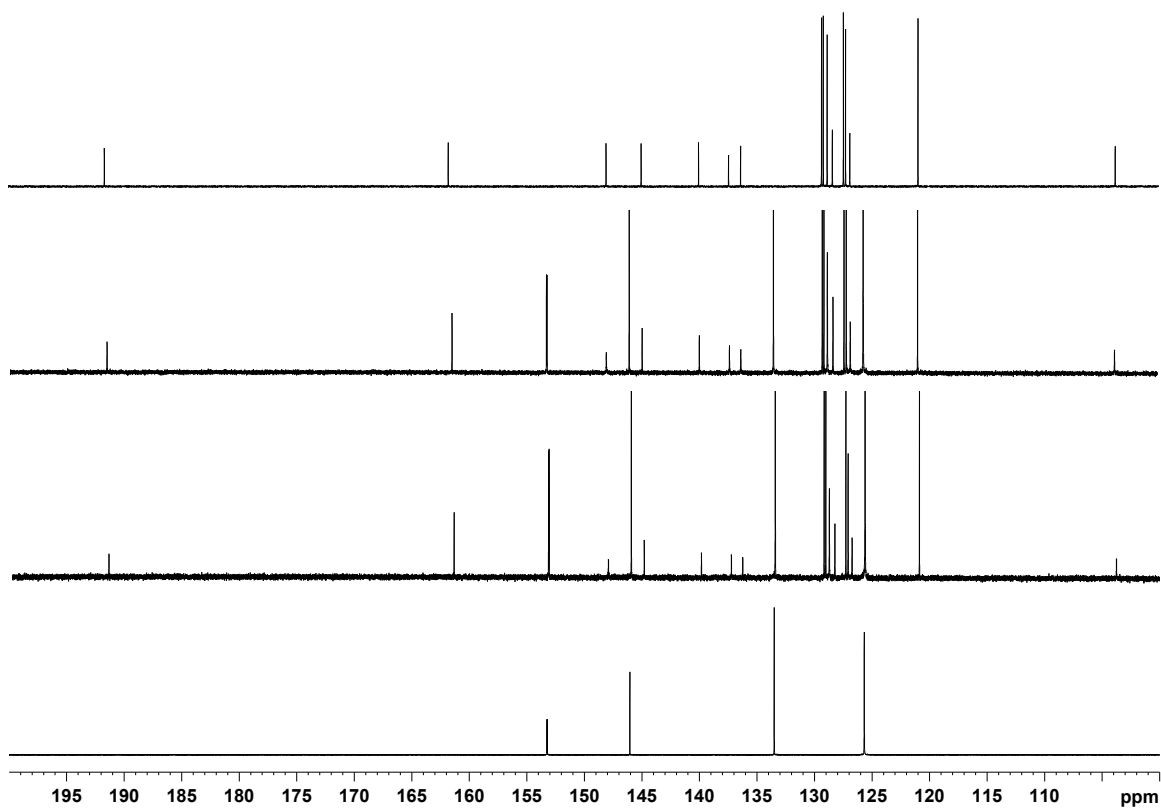




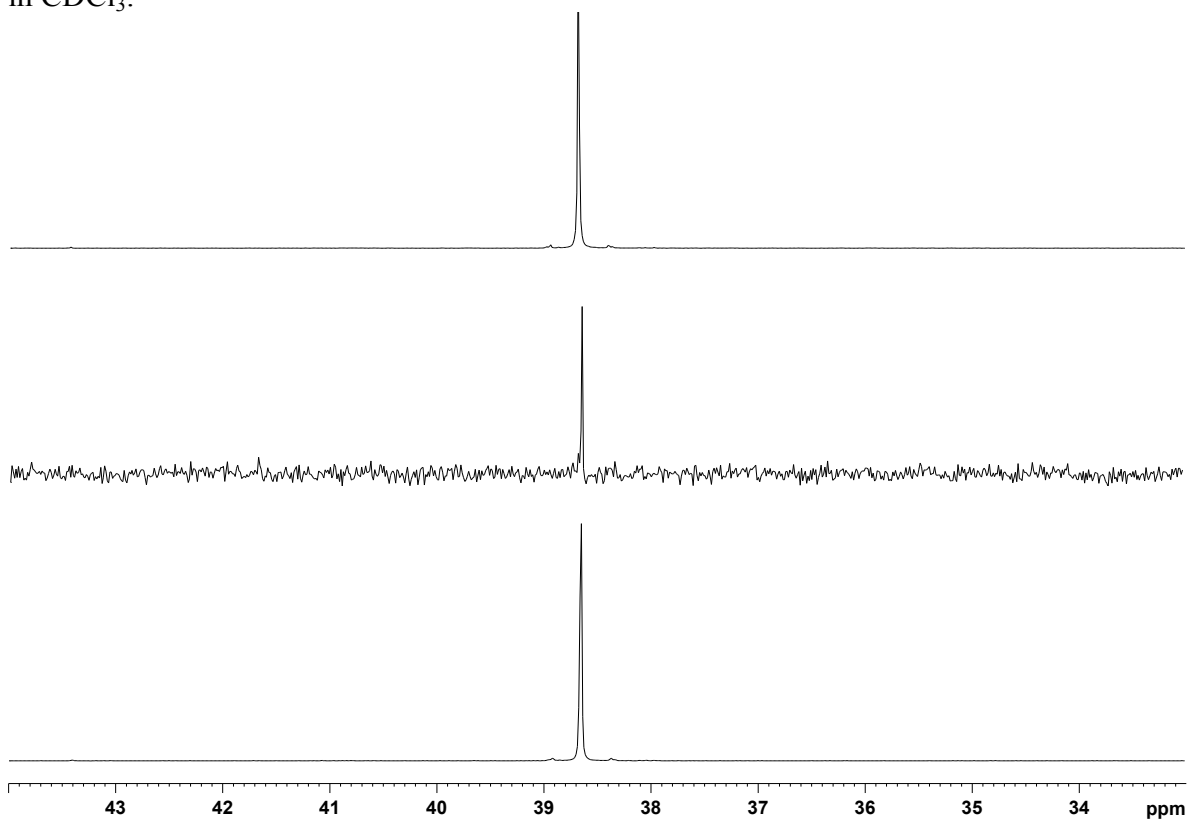
**Figure S12.** The aromatic area of  $^1\text{H}$  spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in  $\text{CDCl}_3$ .



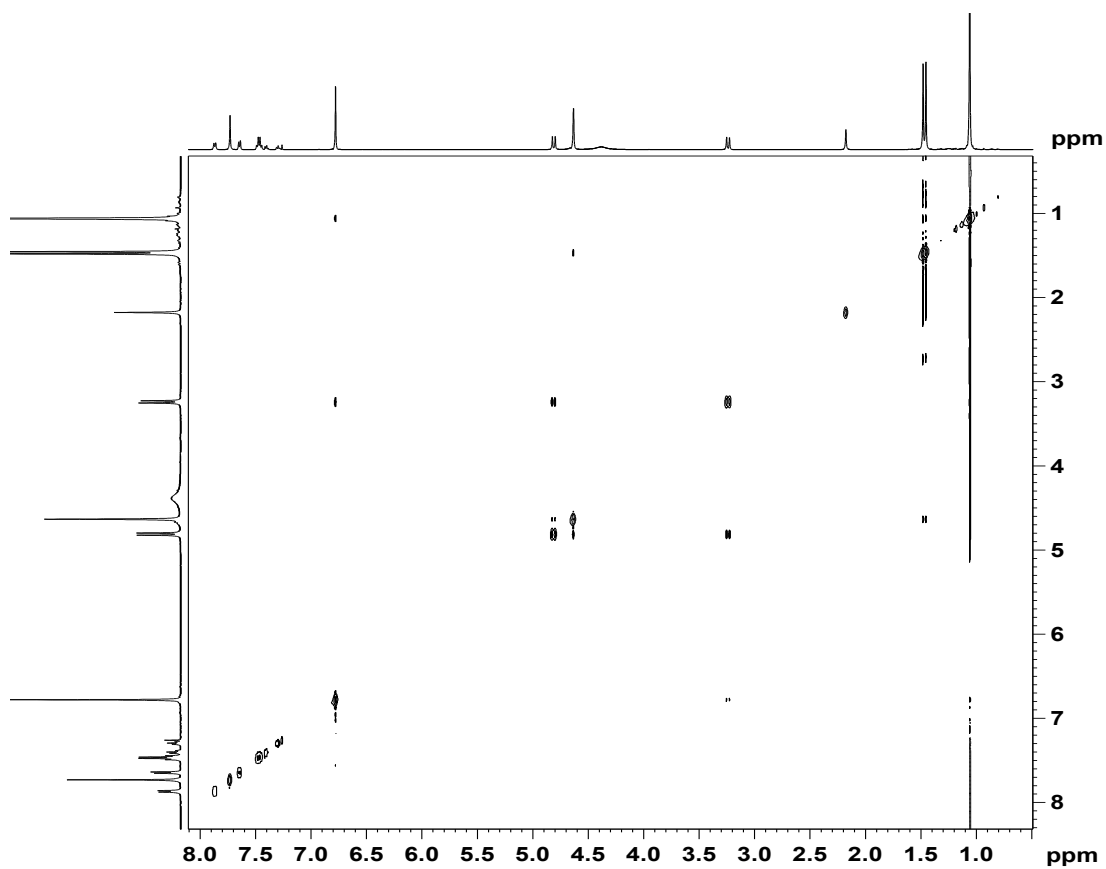
**Figure S13.**  $^{13}\text{C}$  spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in  $\text{CDCl}_3$ .



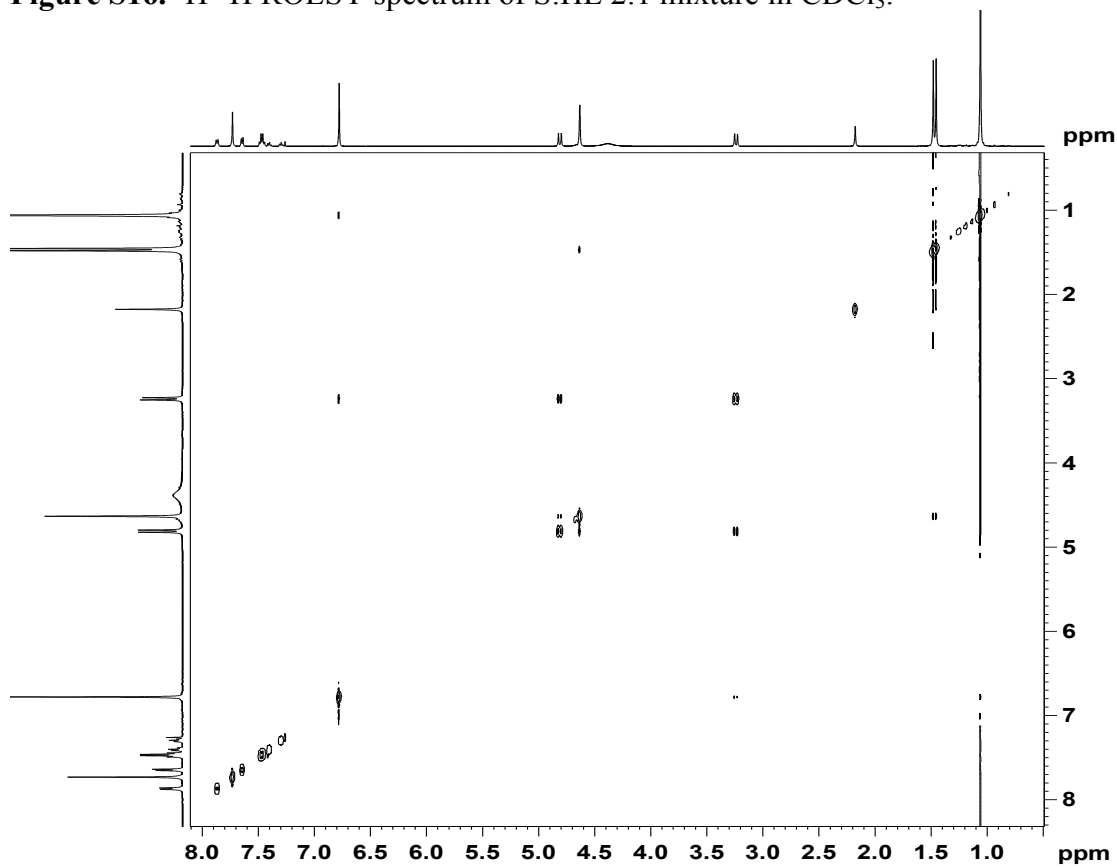
**Figure S14.** The aromatic area of  $^{13}\text{C}$  spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in  $\text{CDCl}_3$ .



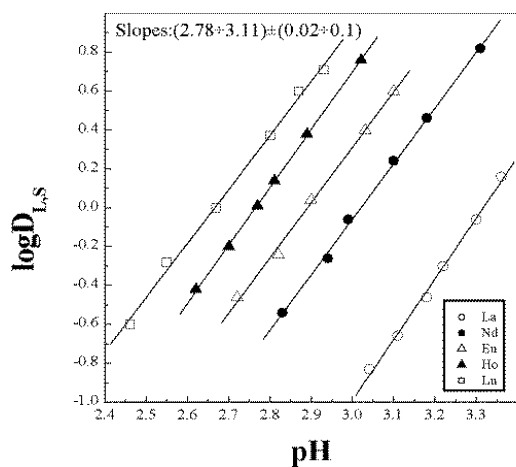
**Figure S15.**  $^{31}\text{P}$  spectra of S (bottom), S:HL 2:1 (middle) and S:HL 1:1 (top) in  $\text{CDCl}_3$ .



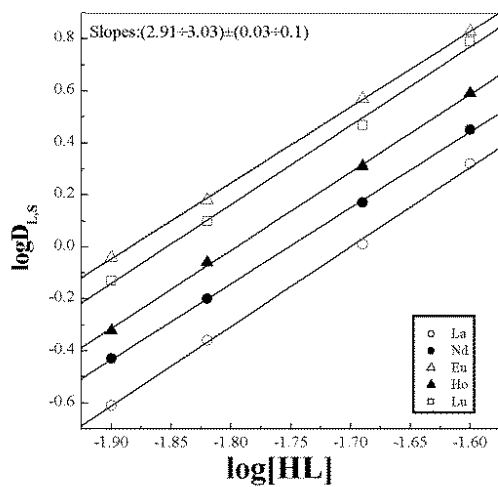
**Figure S16.**  $^1\text{H}$ - $^1\text{H}$  ROESY spectrum of S:HL 2:1 mixture in  $\text{CDCl}_3$ .



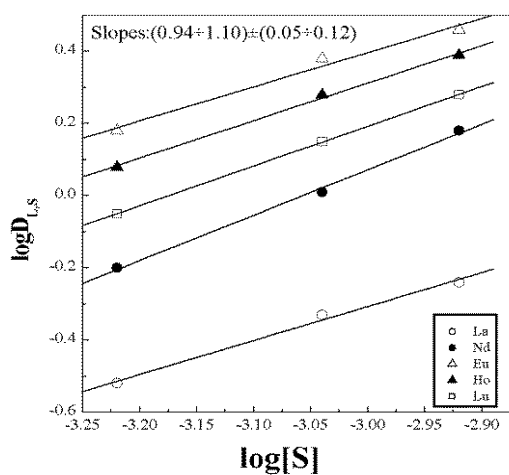
**Figure S17.**  $^1\text{H}$ - $^1\text{H}$  ROESY spectrum of S:HL 1:1 mixture in  $\text{CDCl}_3$ .



**Figure S18.**  $\log D_{L,S}$  vs. pH for the extraction of lanthanoid(III) ions with mixtures HL-S<sub>IV</sub> at  $[\text{HL}] = 1.5 \times 10^{-2} \text{ mol/dm}^3$  and  $[\text{S}_{IV}] = 6 \times 10^{-4} \text{ mol/dm}^3$  in  $\text{CHCl}_3$ .

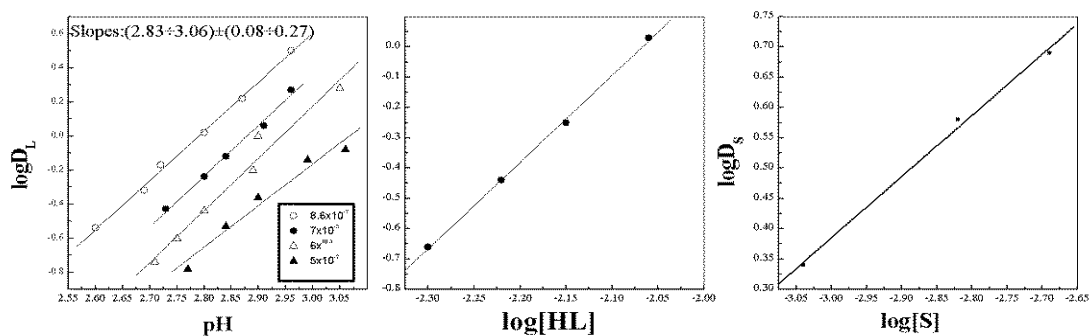


**Figure S19.**  $\log D_{L,S}$  vs.  $\log[\text{HL}]$  for the extraction of lanthanoid(III) ions with mixtures HL-S<sub>IV</sub> at  $[\text{S}_{IV}] = 6 \times 10^{-4} \text{ mol/dm}^3$  in  $\text{CHCl}_3$  : La, pH=3.20; Nd, pH=2.95; Eu, pH=2.95; Ho, pH=2.75; Lu, pH=2.70.

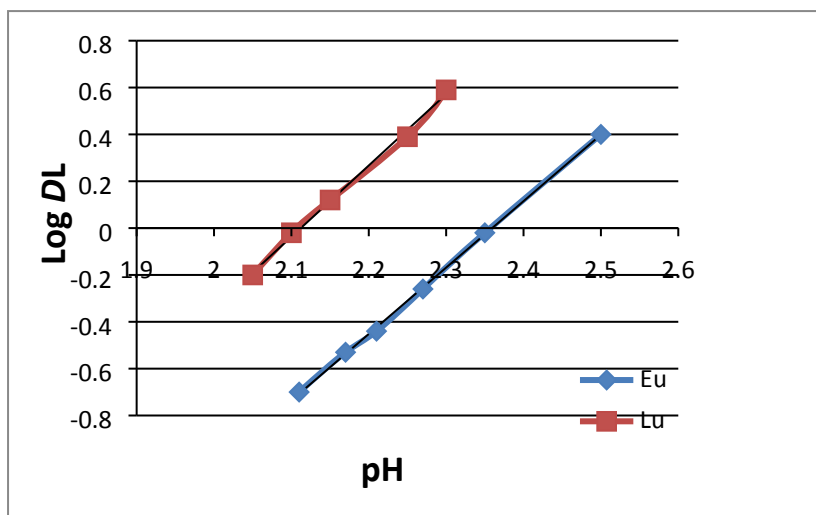


**Figure S20.**  $\text{Log}D_{L,S}$  vs.  $\text{log}[S_{IV}]$  for the extraction of lanthanoid(III) ions with mixtures HL– $S_{IV}$  at  $[\text{HL}] = 1.5 \times 10^{-2} \text{ mol/dm}^3$  in  $\text{CHCl}_3$ : La,  $\text{pH}=3.15$ ; Nd,  $\text{pH}=2.95$ ; Eu,  $\text{pH}=2.95$ ; Ho,  $\text{pH}=2.80$ ; Lu,  $\text{pH}=2.65$ .

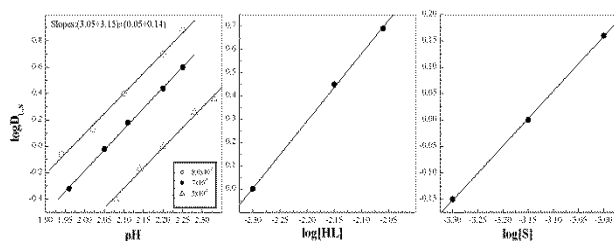
### 5. Solvent extraction of $\text{La}^{3+}$ ion with HL and $S_{IV}$ used alone and IL as diluent.



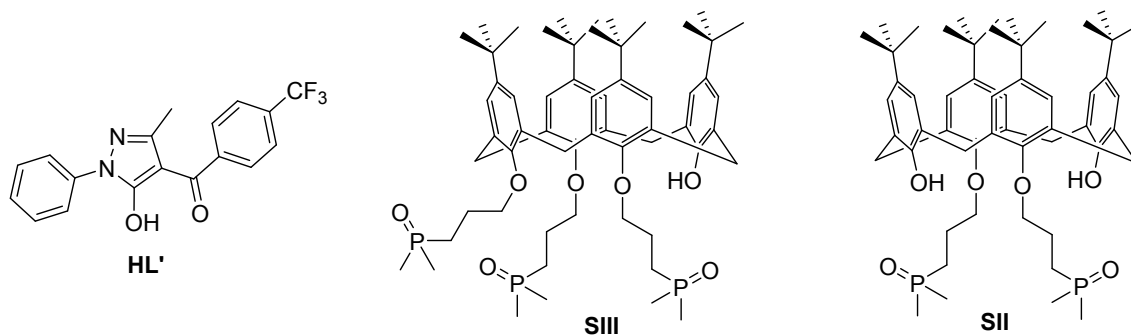
**Figure S21.**  $\text{Log}D_L$  vs.  $\text{pH}$  for the extraction of lanthanum(III) ions with HL alone in IL.  $\text{Log}D_L$  vs.  $[\text{HL}]$  for the extraction of lanthanum(III) ions with HL alone in IL at  $\text{pH}=2.80$ .  $\text{Log}D_L$  vs.  $[\text{S}]$  for the extraction of lanthanum(III) ions with S alone in IL at  $\text{pH}=3.05$ .



**Figure S22.**  $\text{Log}D_L$  vs. pH for the extraction of Ln(III) ions with  $[\text{HL}]=7 \times 10^{-3} \text{ mol/dm}^3$  alone in IL.



**Fig. 23.**  $\text{Log}D_{L,S}$  vs. pH for La(III) extraction with mixture HL-S<sub>IV</sub> at  $[\text{S}_{IV}]=7 \times 10^{-4} \text{ mol/dm}^3$  in IL.  
 $\text{Log}D_{L,S}$  vs.  $\log[\text{HL}]$  for La(III) ions extraction with mixture HL-S<sub>IV</sub> at  $[\text{S}_{IV}]=7 \times 10^{-4} \text{ mol/dm}^3$  and pH=2.20.  
 $\text{Log}D_{L,S}$  vs.  $\log[\text{S}_{IV}]$  for La(III) ions extraction with mixture HL-S<sub>IV</sub> at  $[\text{HL}]=5 \times 10^{-3} \text{ mol/dm}^3$  and pH=2.20.



**Figure S24.** Chemical structures of 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one, HL' and partially substituted calix[4]arenes by phosphinoyl functions.