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)₂ (7.4 g, 100 mmol) was then 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 (MeOH:CH₂Cl₂). The NMR spectra were initially recorded in chloroform-d 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-d₆, 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 C₆H₄ unit of biphenyl are assigned as ‘’ and those of Ph part as ‘’; Ph means N-Ph. ¹H NMR (CDCl₃, DRX 250) 2.223 (s, 3H, CH₃), 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 1.1, 8.7, Ar CH), 10.595 (bs, 1H, O); ¹³C NMR (CDCl₃, DRX 250) 16.05 (CH₃), 103.67 (C₆H₄), 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 (C₆H₄), 137.32 (C₆H₄), 139.89 (C₆H₄), 144.86 (C₆H₄), 147.87 (C₆H₄), 161.69 (C₆H₄), 191.41 (C=O); ¹H NMR (benzene-d₆, II+ 600) 1.977 (s, 3H, CH₃), 6.972 (tt, 1H, J 1.0, 7.4, C=CH₂ of Ph), 7.138-7.221 (m, 5H, CH=CH₂ and CH=CH-5 of Ph and CH-3′, CH-4′ and CH-5′ of biPh), 7.339 (dd, 2H, J 1.7, 8.3, CH=CH₂ and CH=CH-5′ of biPh), 7.381 (dd, 2H, J 1.4, 8.4, CH=CH₂ and CH=CH-6′ of biPh), 7.465 (dd, 2H, J 1.8, 8.3, CH=CH₂ and CH=CH-6′ of biPh), 8.212 (dd, 2H, J 1.1, 8.7, CH=CH₂ and CH=CH-6′ of Ph), 12.237 (bs, 1H, OH); ¹³C NMR (benzene-d₆, II+ 600) 15.85 (CH₃), 103.86 (C₆H₄), 120.08 (CH=CH₂ and CH=CH-6 of Ph), 126.04 (CH=CH₂ and CH=CH-5′ of biPh), 127.20 (CH=CH-4′ of biPh), 128.00 (CH=CH₂ and CH=CH-6′ of biPh), 128.84 (CH=CH₂ and CH-5′ of Ph or CH-3′ and CH-5′ of biPh), 128.86 (CH=CH₂ and CH-5′ of Ph or CH-3′ and CH-5′ of biPh, 129.01 (CH=CH₂ and CH=CH-6′ of biPh), 129.01 (CH=CH₂ and CH=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

1.1. NMR spectra of HL:

Figure S1. 1H NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in CDCl3.
Figure S2. $^{13}$C (down) and DEPT (up) NMR spectra of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in CDCl$_3$.

Figure S3. $^1$H NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in CDCl$_3$ (up) and in benzene-d$_6$ (down).
Figure S4. $^1$H NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-$d_6$.

Figure S5. $^{13}$C (down) and DEPT (up) NMR spectra of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-$d_6$. 
Figure S6. $^1$H-$^1$H COSY NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-d$_6$.

Figure S7. $^1$H-$^1$H NOESY NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-d$_6$. 
Figure S8. $^1$H-$^{13}$C HSQC NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-$d_6$.

Figure S9. $^1$H-$^{13}$C HMBC NMR spectrum of 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one in benzene-$d_6$. 
2. NMR characterization of SIV

The quality of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(dimethylphosphinoylmethoxy)calix[4]arene (SIV) has been checked by $^1$H NMR in CDCl$_3$ (250 MHz, 25°C): $\delta = 1.074 (s, 36H, (C\text{H}_3)_3C)$, 1.532(d, $^2$J$_{HP}$=12.9 Hz, 24H, (C\text{H}_3)_2P=O), 3.268(d, $^2$J$_{HH}$=13.0 Hz, 4H, Ar-CH$_2$-Ar), 4.688(d, $^2$J$_{HP}$=1.3 Hz, 8H, CH$_2$P=O), 4.836(d, $^2$J$_{HH}$=13.0 Hz, 4H, Ar-CH$_2$-Ar), 6.800(s, 8H, Ar-H) and in CD$_3$OD (250MHz, 25°C): $\delta = 1.001 (s, 36H, (C\text{H}_3)_3C)$, 1.527(d, $^2$J$_{HP}$=13.1 Hz, 24H, (C\text{H}_3)_2P=O), 3.292(d, $^2$J$_{HH}$=13.2 Hz, 4H, Ar-CH$_2$-Ar), 4.668(d, $^2$J$_{HP}$=1.3 Hz, 8H, CH$_2$P=O), 4.780(d, $^2$J$_{HH}$=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]= 1.5×10^{-2} 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.

<table>
<thead>
<tr>
<th>Ln</th>
<th>CHCl$_3$</th>
<th>IL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HL alone</td>
<td>HL + SIV</td>
</tr>
<tr>
<td>La</td>
<td>1.02 (0.979)</td>
<td>0.968 (0.989)</td>
</tr>
<tr>
<td>Nd</td>
<td>0.972 (0.986)</td>
<td>1.00 (0.993)</td>
</tr>
<tr>
<td>Eu</td>
<td>1.00 (0.973)</td>
<td>1.02 (0.986)</td>
</tr>
<tr>
<td>Ho</td>
<td>0.968 (0.989)</td>
<td>0.984 (0.945)</td>
</tr>
<tr>
<td>Lu</td>
<td>0.990 (0.989)</td>
<td>0.984 (0.958)</td>
</tr>
</tbody>
</table>

nd: not determined.
4. Interaction between HL and S_{IV}

All samples were prepared separately by using pure dry compounds dissolved in deuterochloroform (Deutero GmbH). The spectra of the individual ligand (HL) and the synergist S_{IV}, 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](image.png)

**Figure S11.** $^1$H spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in CDCl$_3$. 
Figure S12. The aromatic area of $^1$H spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in CDCl$_3$.

Figure S13. $^{13}$C spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in CDCl$_3$. 
Figure S14. The aromatic area of $^{13}$C spectra of (from bottom to top): S, S:HL 2:1, S:HL 1:1 and HL in CDCl$_3$.

Figure S15. $^{31}$P spectra of S (bottom), S:HL 2:1 (middle) and S:HL 1:1 (top) in CDCl$_3$.
Figure S16. $^1$H-$^1$H ROESY spectrum of S:HL 2:1 mixture in CDCl$_3$. 
**Figure S17.** $^1$H-$^1$H ROESY spectrum of S:HL 1:1 mixture in CDCl$_3$.

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

**Figure S19.** Log$D_{L,S}$ vs. log[HL] for the extraction of lanthanoid(III) ions with mixtures HL–S$_{IV}$ at [S$_{IV}$] = $6 \times 10^{-4}$mol/dm$^3$ in CHCl$_3$: La, pH=3.20; Nd, pH=2.95; Eu, pH=2.95; Ho, pH=2.75; Lu, pH=2.70.
Figure S20. Log\(D_{L,S}\) vs. log[S\(_{IV}\)] for the extraction of lanthanoid(III) ions with mixtures HL–S\(_{IV}\) at [HL]= 1.5×10\(^{-2}\)mol/dm\(^3\) in CHCl\(_3\): La, pH=3.15; Nd, pH=2.95; Eu, pH=2.95; Ho, pH=2.80; Lu, pH=2.65.

5. Solvent extraction of La\(^{3+}\) ion with HL and S\(_{IV}\) used alone and IL as diluent.

Figure S21. Log\(D_L\) vs. pH for the extraction of lanthanum(III) ions with HL alone in IL. Log\(D_L\) vs. [HL] for the extraction of lanthanum(III) ions with HL alone in IL at pH=2.80. Log\(D_L\) vs. [S] for the extraction of lanthanum(III) ions with S alone in IL at pH=3.05.
Figure S22. Log\(D_L\) vs. pH for the extraction of Ln(III) ions with [HL]=7x10\(^{-3}\) mol/dm\(^3\) alone in IL.

Fig. 23. Log\(D_{L,S}\) vs. pH for La(III) extraction with mixture HL–S\(_{IV}\) at [S\(_{IV}\)]=7x10\(^{-4}\)mol/dm\(^3\) in IL.
Log\(D_{L,S}\) vs. log[HL] for La(III) ions extraction with mixture HL–S\(_{IV}\) at [S\(_{IV}\)]=7x10\(^{-4}\)mol/dm\(^3\) and pH=2.20.
Log\(D_{L,S}\) vs. log[S\(_{IV}\)] for La(III) ions extraction with mixture HL–S\(_{IV}\) at [HL]=5x10\(^{-3}\) 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.