

Electronic Supplementary Information

Europium complexes: choice of efficient synthetic routes from RM1 thermodynamic quantities as figures of merit

Nathalia B.D. Lima, Anderson I.S. Silva, Vanessa F.C. Santos,
Simone M.C. Gonçalves, and Alfredo M. Simas*

*E-mail: simas@ufpe.br

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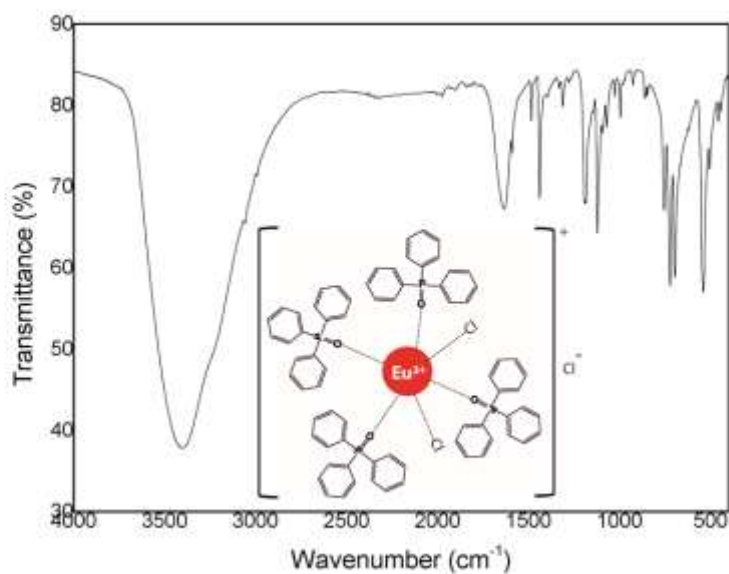
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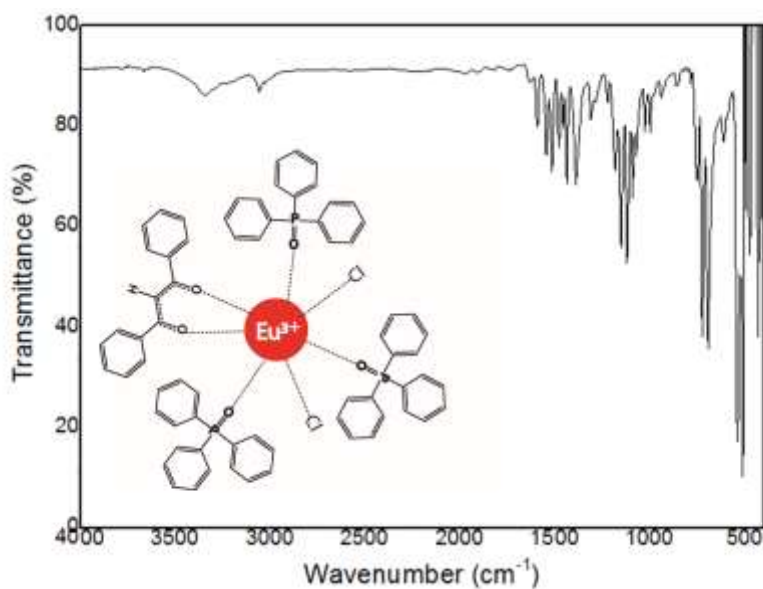
Characterization

Infrared Spectra



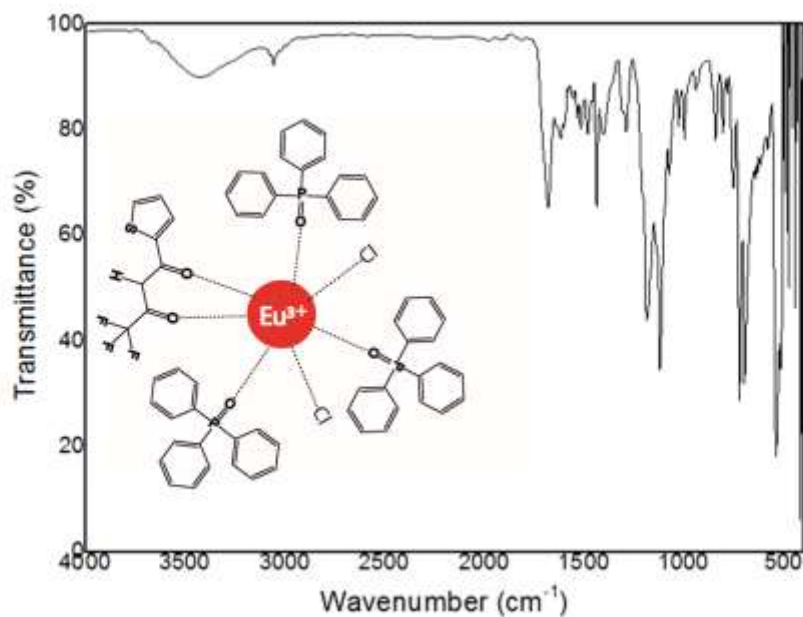
[EuCl₃(TPPO)₄].3H₂O (KBr disk): ν O-H 3461 cm⁻¹, ν C-H 3090 cm⁻¹ - 3015 cm⁻¹, and ν P=O 1087 cm⁻¹.

Figure S1. Infrared spectrum of [EuCl₂(TPPO)₄]Cl.3H₂O.



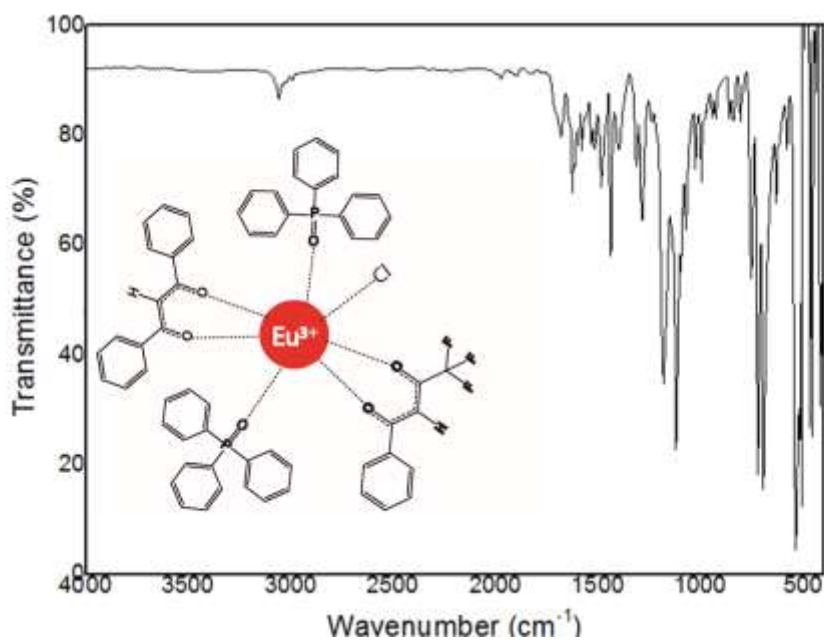
[EuCl₂(DBM)(TPPO)₃] (KBr disk): ν C-H 3062 cm⁻¹, ν C=O 1594 cm⁻¹, ν P=O 1148-1128 cm⁻¹.

Figure S2. Infrared spectrum of [EuCl₂(DBM)(TPPO)₃].



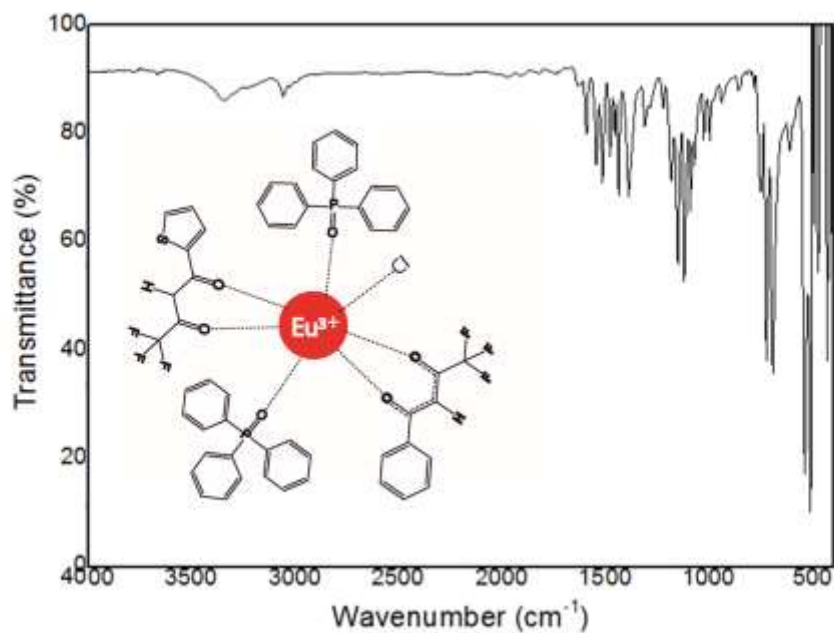
[EuCl₂(TTA)(TPPO)₃] (KBr disk): $\nu_{\text{C-H}}$ 3056 cm⁻¹, $\nu_{\text{C=O}}$ 1688 cm⁻¹, $\nu_{\text{P=O}}$ 1179-1115 cm⁻¹, $\nu_{\text{C-F}}$ 1287 cm⁻¹, and $\nu_{\text{S=C}}$ 1065 cm⁻¹.

Figure S3. Infrared spectrum of [EuCl₂(TTA)(TPPO)₃].



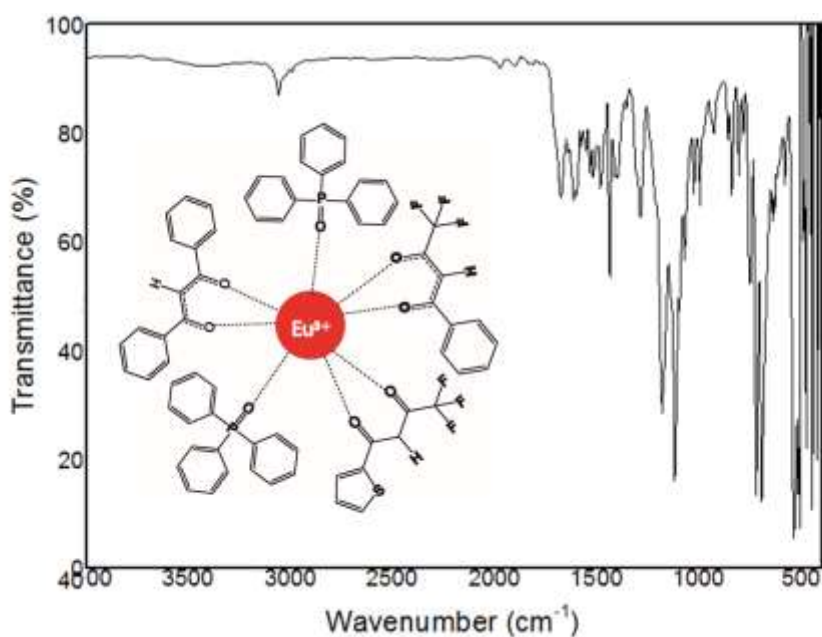
[EuCl(DBM)(BTFA)(TPPO)₂] (KBr disk): $\nu_{\text{C-H}}$ 3056 cm⁻¹, $\nu_{\text{C=O}}$ 1681 cm⁻¹, $\nu_{\text{P=O}}$ 1179-1116 cm⁻¹, and $\nu_{\text{C-F}}$ 1287 cm⁻¹.

Figure S4. Infrared spectrum of [EuCl(DBM)(BTFA)(TPPO)₂].



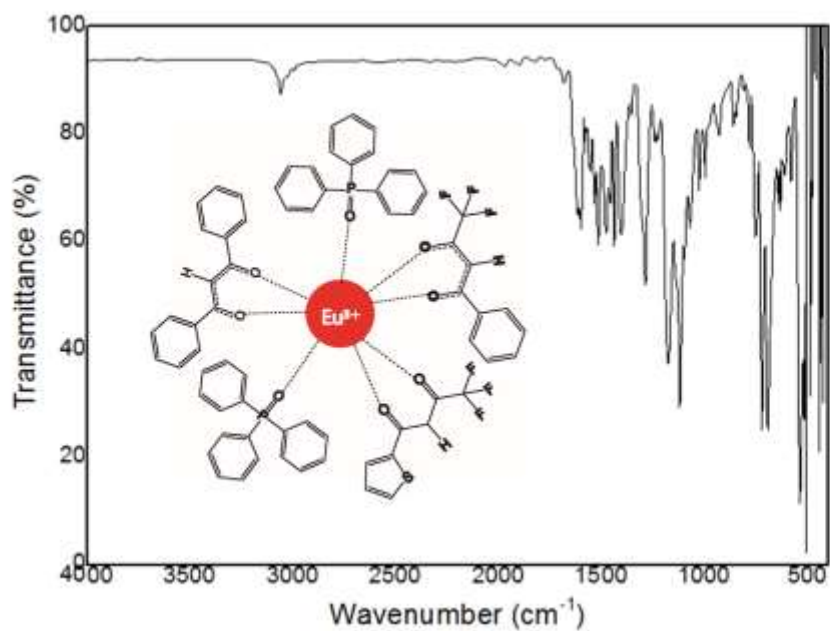
[EuCl(TTA)(BTFA)(TPPO)₂] (KBr disk): $\nu_{\text{C-H}}$ 3062 cm^{-1} , $\nu_{\text{C=O}}$ 1599 cm^{-1} , $\nu_{\text{P=O}}$ 1154-1116 cm^{-1} , $\nu_{\text{C-F}}$ 1185 cm^{-1} , and $\nu_{\text{S=C}}$ 1084 cm^{-1} .

Figure S5. Infrared spectrum of [EuCl(TTA)(BTFA)(TPPO)₂].



[Eu(DBM)(BTFA)(TTA)(TPPO)₂] (KBr disk): $\nu_{\text{C-H}}$ 3056 cm^{-1} , $\nu_{\text{C=O}}$ 1681 cm^{-1} , $\nu_{\text{P=O}}$ 1179-1116 cm^{-1} , $\nu_{\text{C-F}}$ 1294 cm^{-1} , and $\nu_{\text{S=C}}$ 1065 cm^{-1} .

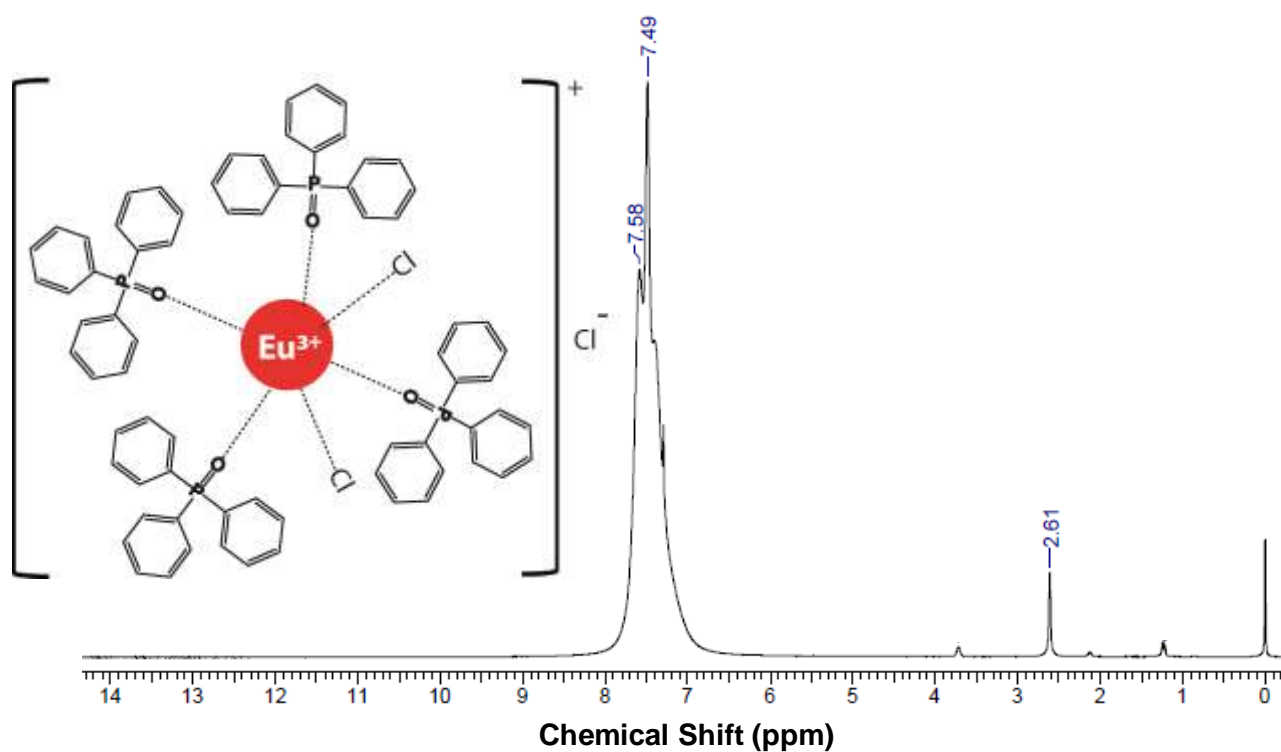
Figure S6. Infrared spectrum of [Eu(DBM)(BTFA)(TTA)(TPPO)₂] obtained via synthetic route 1.



[Eu(DBM)(BTFA)(TTA)(TPPO)₂] (KBr disk): $\nu_{\text{C-H}}$ 3056 cm⁻¹; $\nu_{\text{C=O}}$ 1612-1593 cm⁻¹; $\nu_{\text{P=O}}$ 1166-1122 cm⁻¹; $\nu_{\text{C-F}}$ 1281 cm⁻¹; $\nu_{\text{S=C}}$ 1071 cm⁻¹.

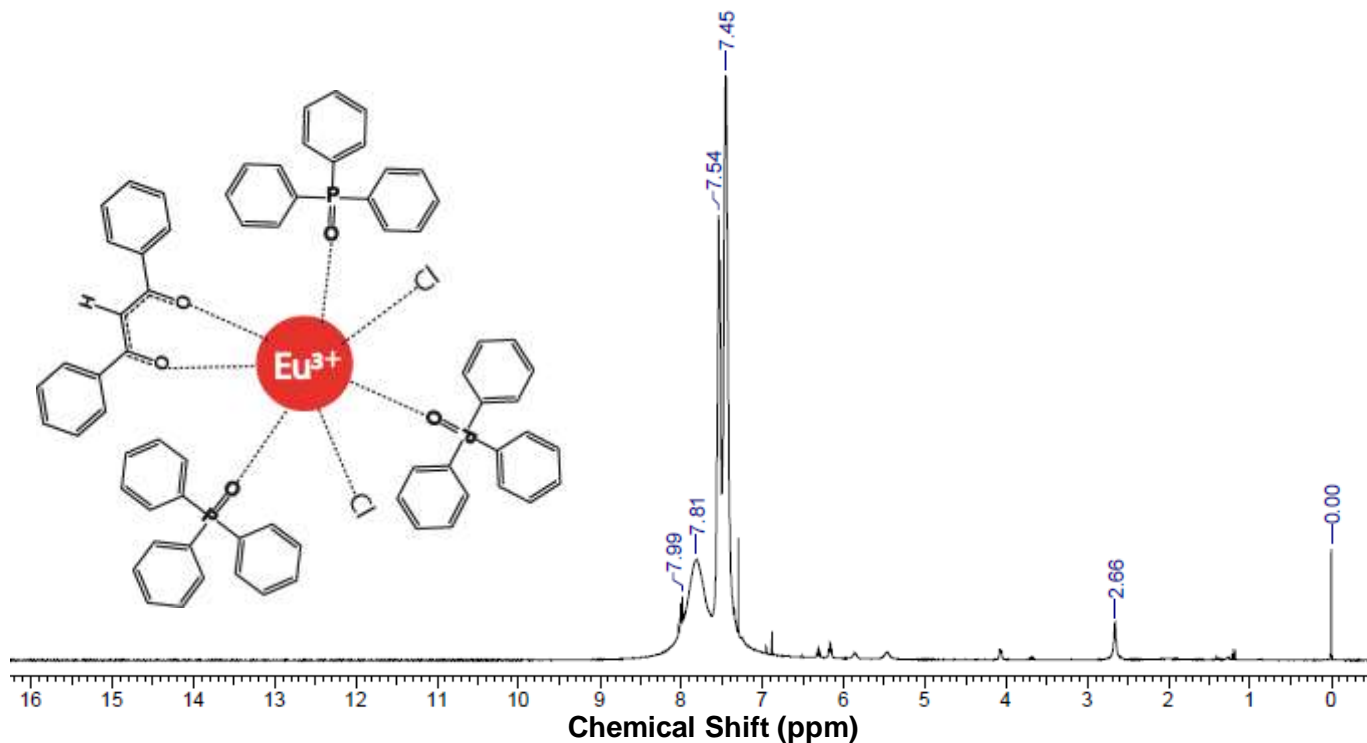
Figure S7. Infrared spectrum of [Eu(DBM)(BTFA)(TTA)(TPPO)₂] obtained via synthetic route 6.

^1H NMR Spectra



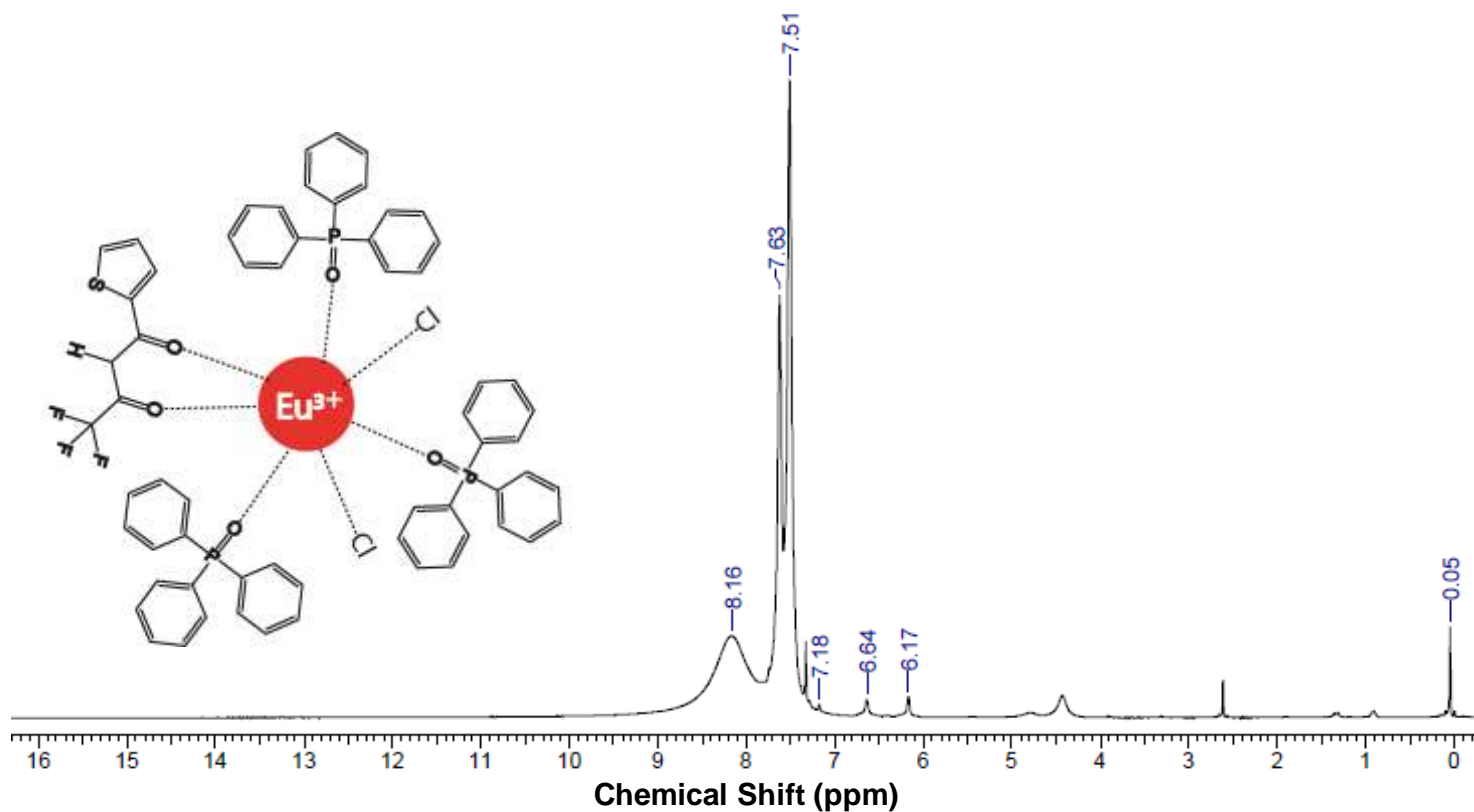
^1H NMR (400 MHz, CDCl_3): δ 7.60-7.31 ppm (m, Ar), and 2.61 ppm (s, OH).

Figure S8. ^1H NMR spectrum of $[\text{EuCl}_2(\text{TPPO})_4]\text{Cl} \cdot 3\text{H}_2\text{O}$.



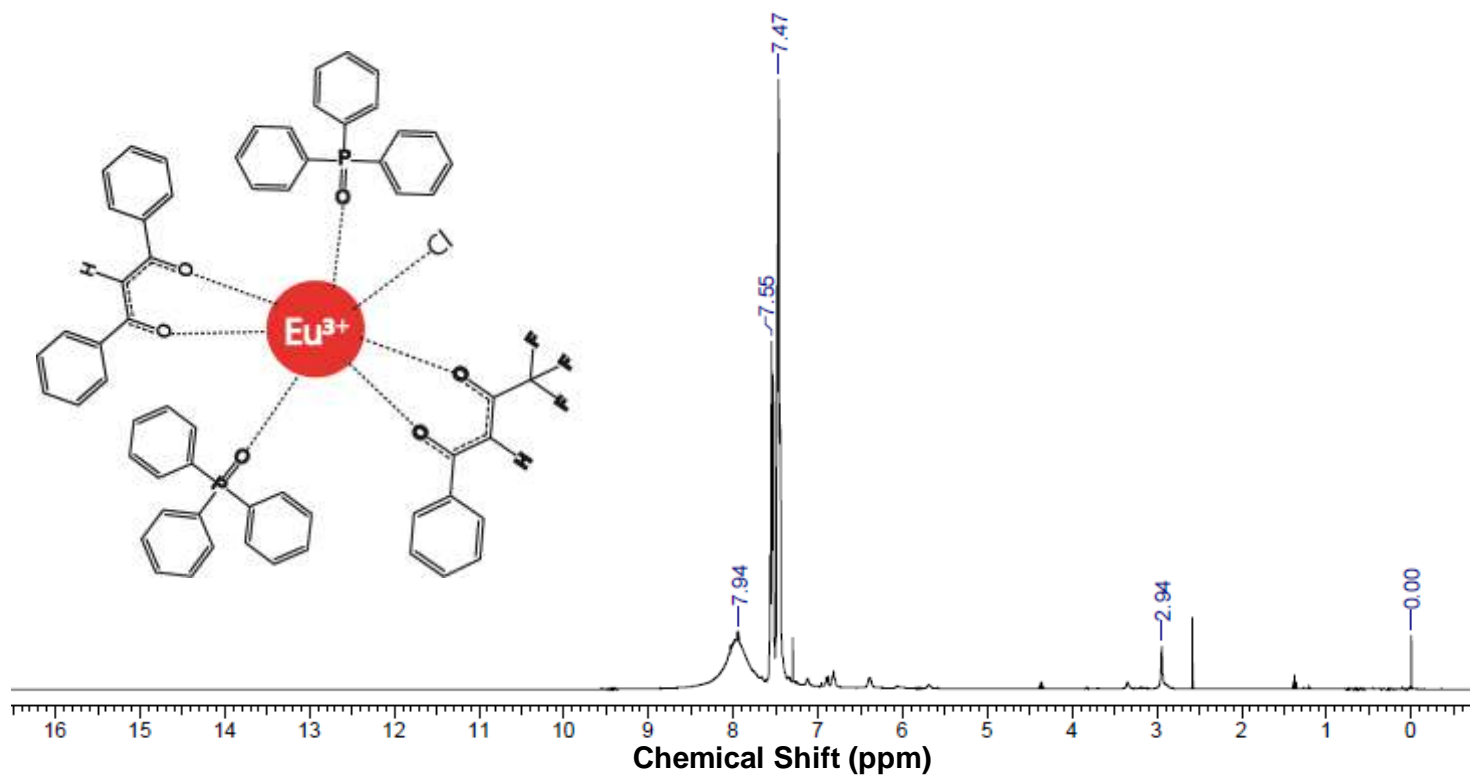
^1H NMR (400 MHz, CDCl_3): δ 7.81 ppm (s, CH), and δ 7.56–7.36 ppm (m, Ar).

Figure S9. ^1H NMR spectrum of $[\text{EuCl}_2(\text{DBM})(\text{TPPO})_3]$.



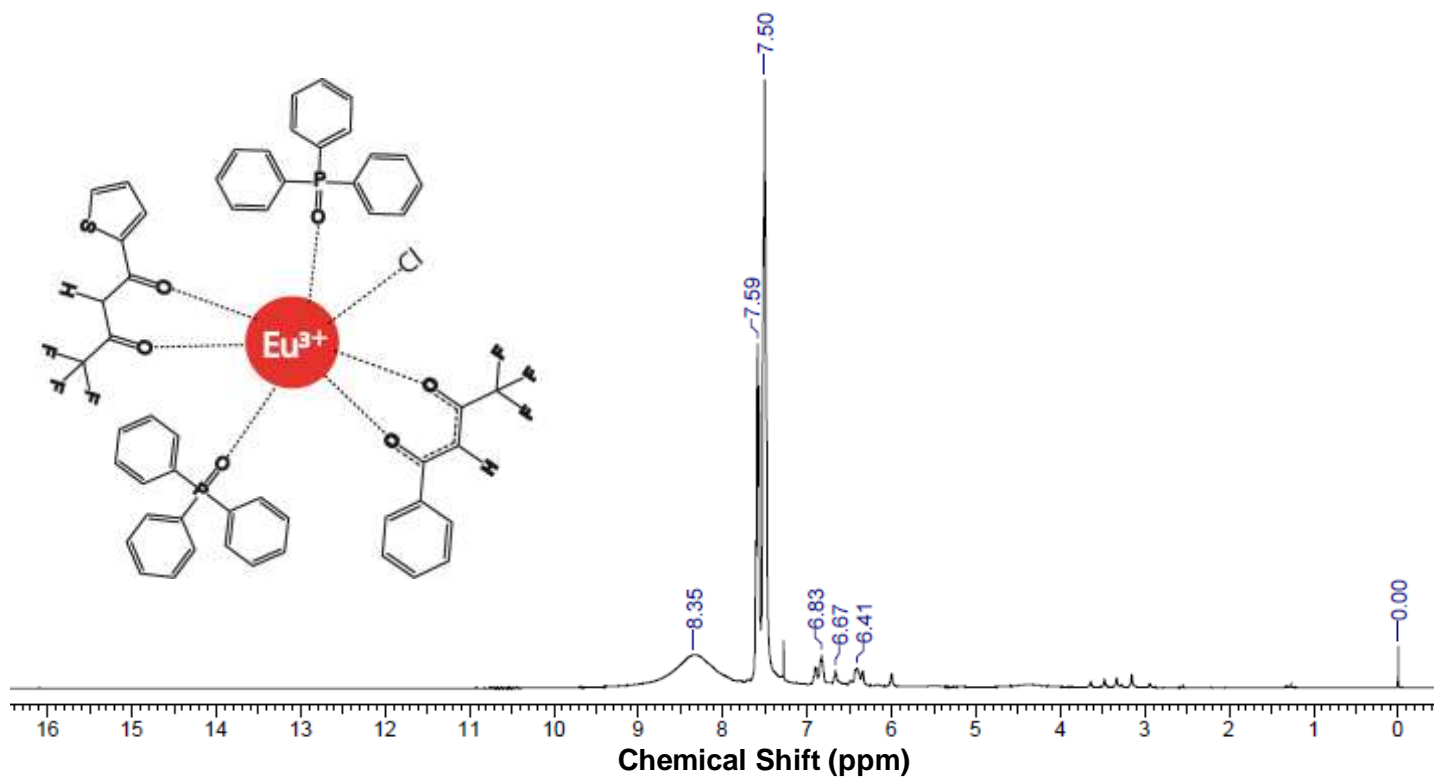
^1H NMR (400 MHz, CDCl_3): δ 8.16 ppm (s, CH), δ 7.65–6.14 ppm (m, Ar), and δ 7.21–6.14 ppm (m, Th).

Figure S10. ^1H NMR spectrum of $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_3]$.



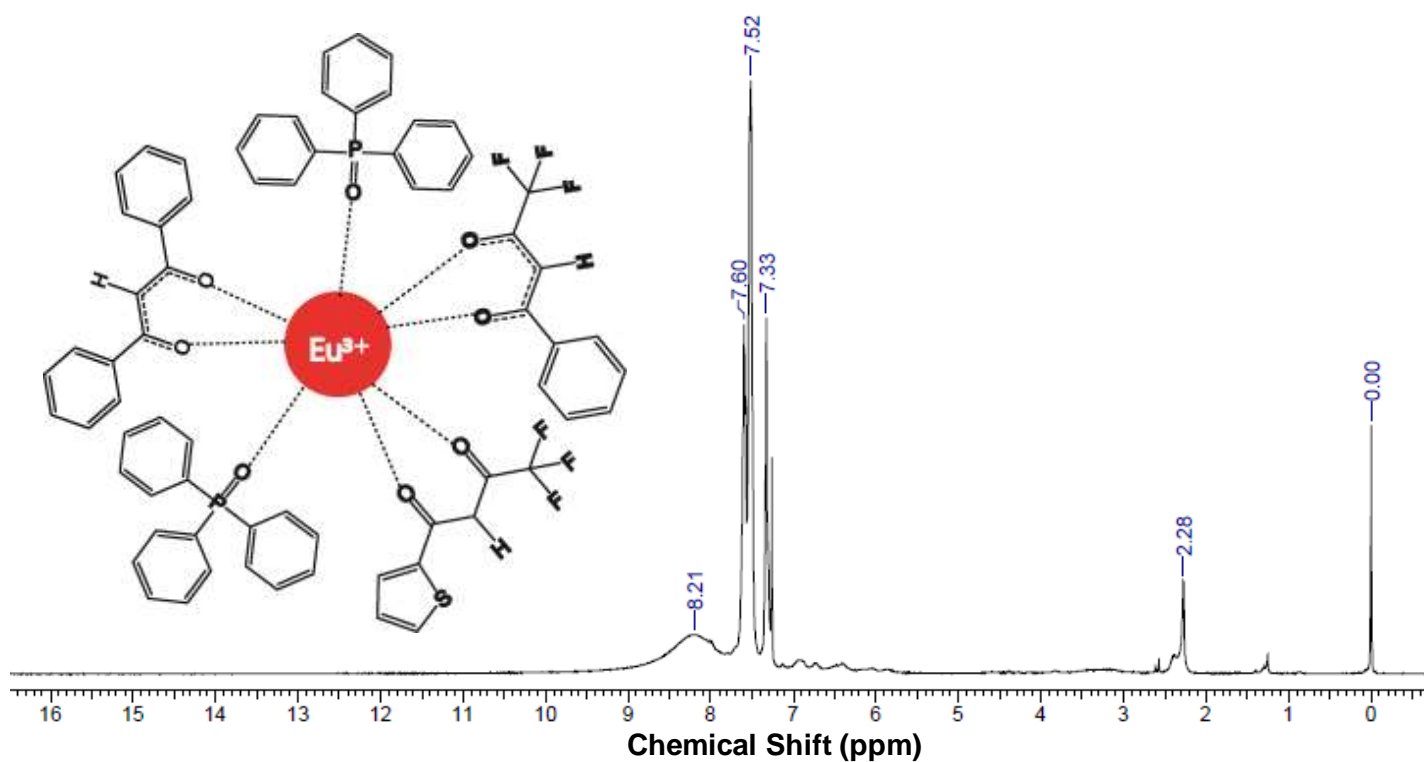
^1H NMR (400 MHz, CDCl_3): δ 7.94 ppm (s, CH) and δ 7.57–7.44 ppm (m, Ar).

Figure S11. ^1H NMR spectrum of $[\text{EuCl}(\text{DBM})(\text{BTFA})(\text{TPPO})_2]$.



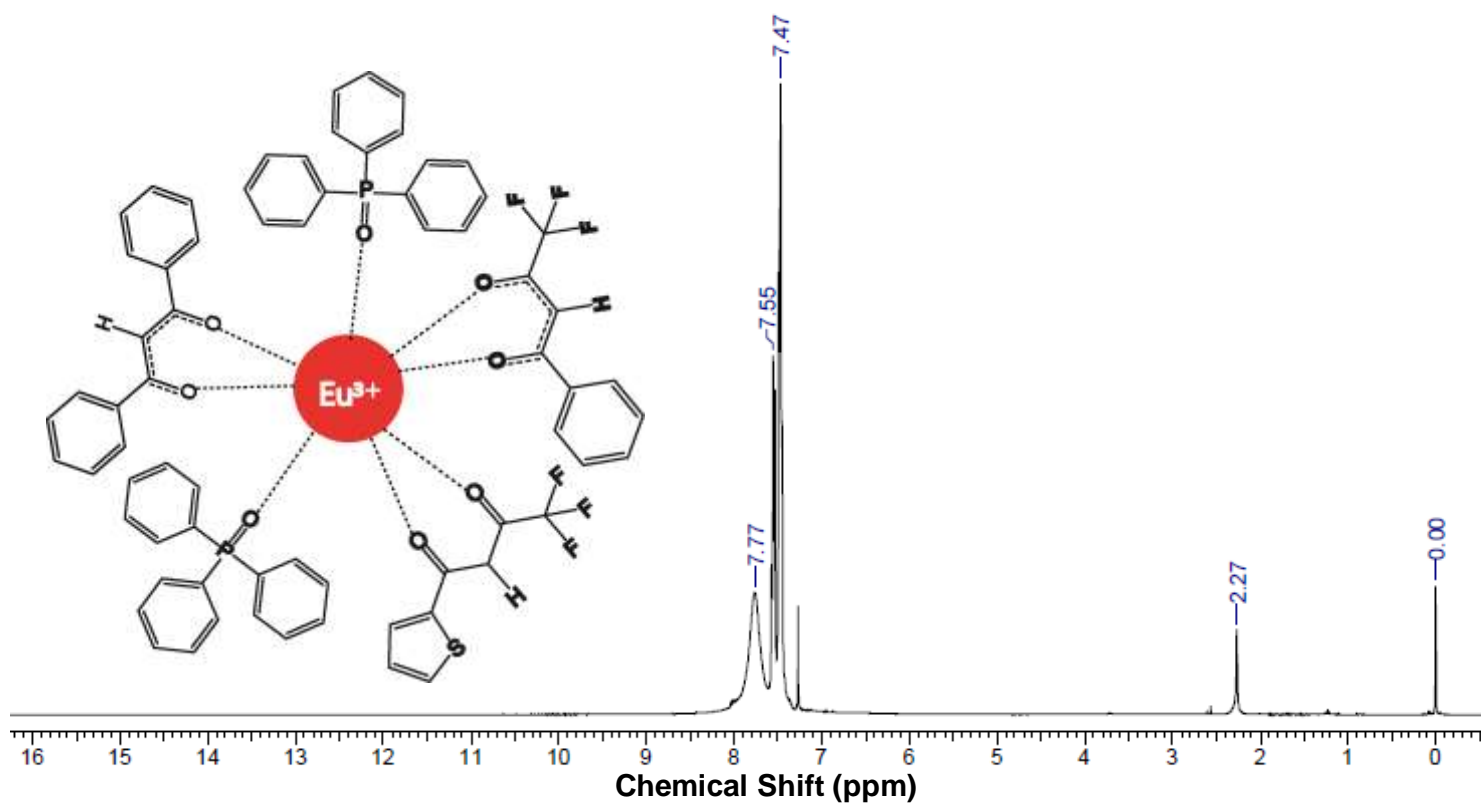
¹H NMR (400 MHz, CDCl₃): δ 8.35 ppm (s, CH), δ 7.62 – 6.39 ppm (m, Ar),
 δ 6.87–6.38 ppm (m, Th).

Figure S12. ¹H NMR spectrum of [EuCl(TTA)(BTFA)(TPPO)₂].



¹H NMR (400 MHz, CDCl₃): δ 8.21 ppm, and (s, CH), δ 7.63–7.29 ppm (m, Ar).

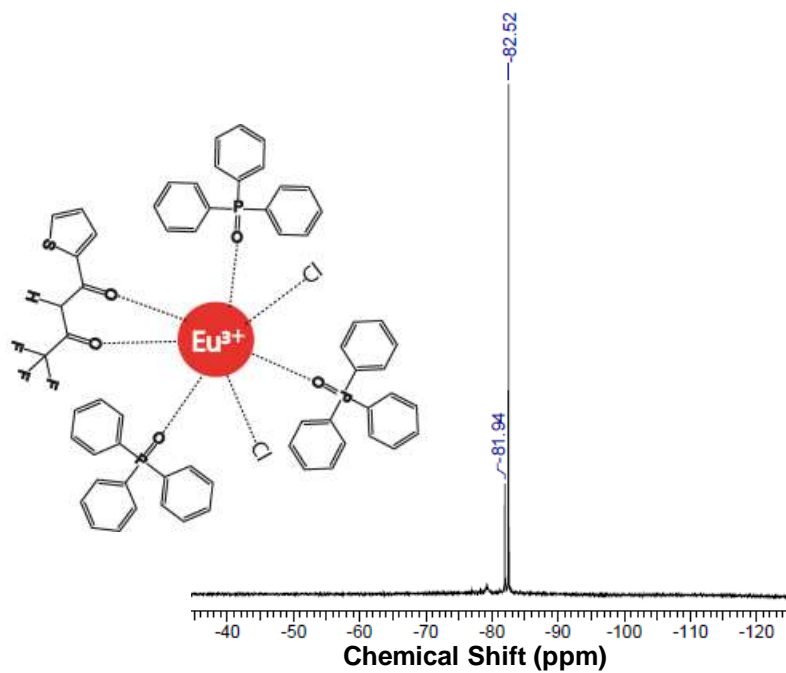
Figure S13. ¹H NMR spectrum of [Eu(DBM)(BTFA)(TTA)(TPPO)₂] obtained via synthetic route 1.



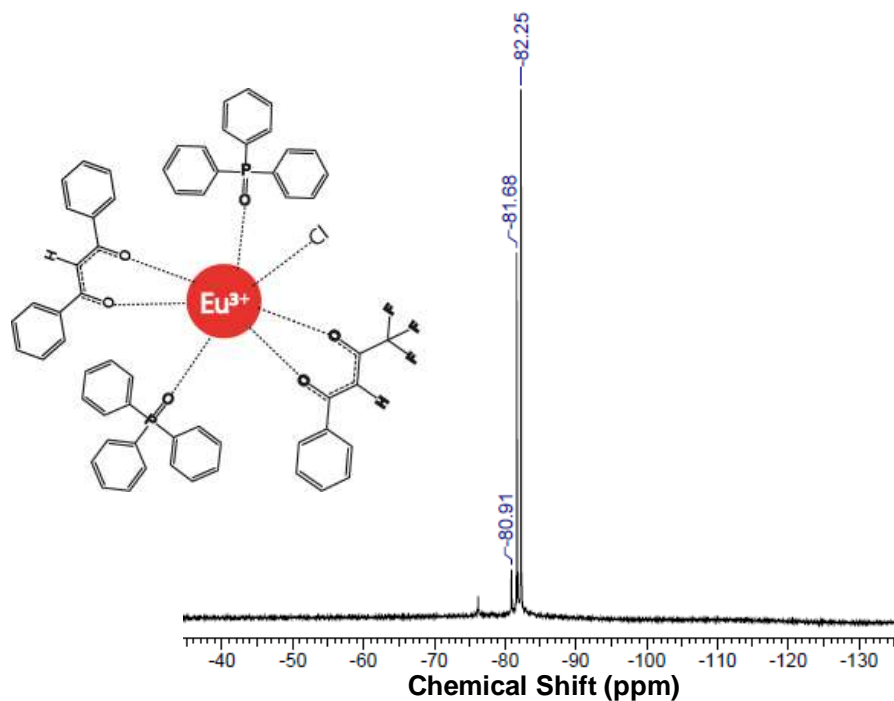
¹H NMR (400 MHz, CDCl₃): δ 7.77 ppm (s, CH), and δ 7.57–7.45 ppm (m, Ar).

Figure S14. ¹H NMR spectrum of [Eu(DBM)(BTFA)(TTA)(TPPO)₂] obtained via synthetic route 6.

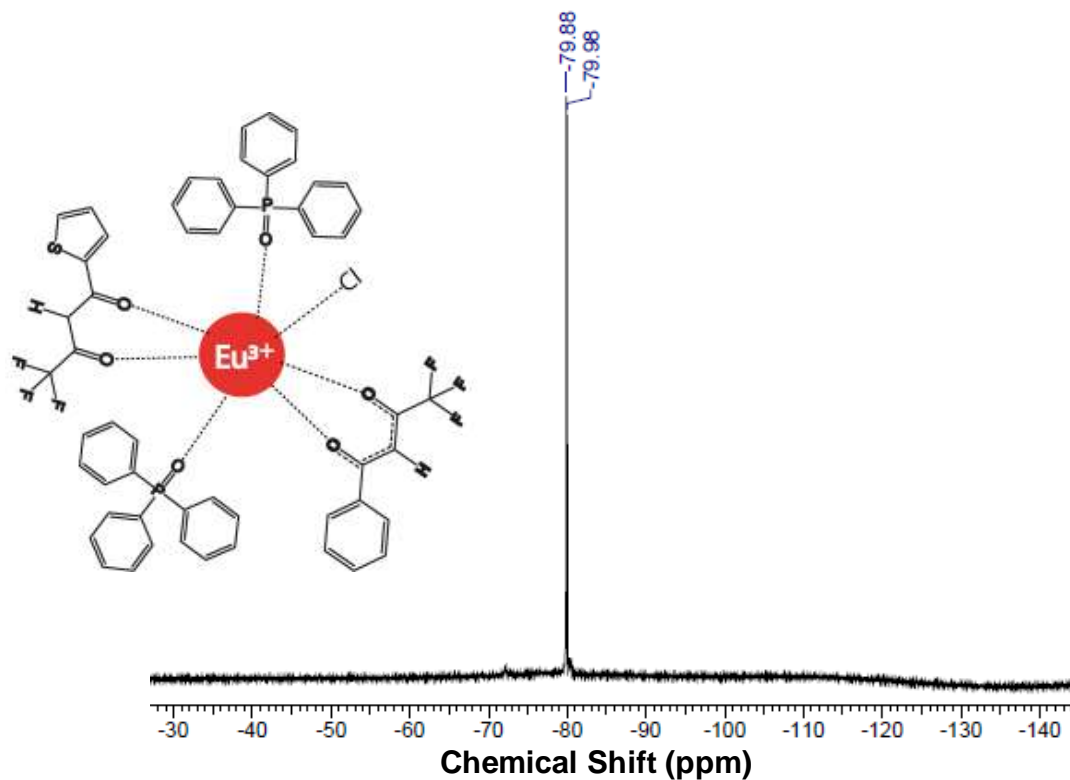
^{19}F NMR Spectra



^{19}F NMR (376 MHz, CDCl_3): δ -82 ppm, and δ -83 ppm.
Figure S15. ^{19}F NMR spectrum of $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_3]$.

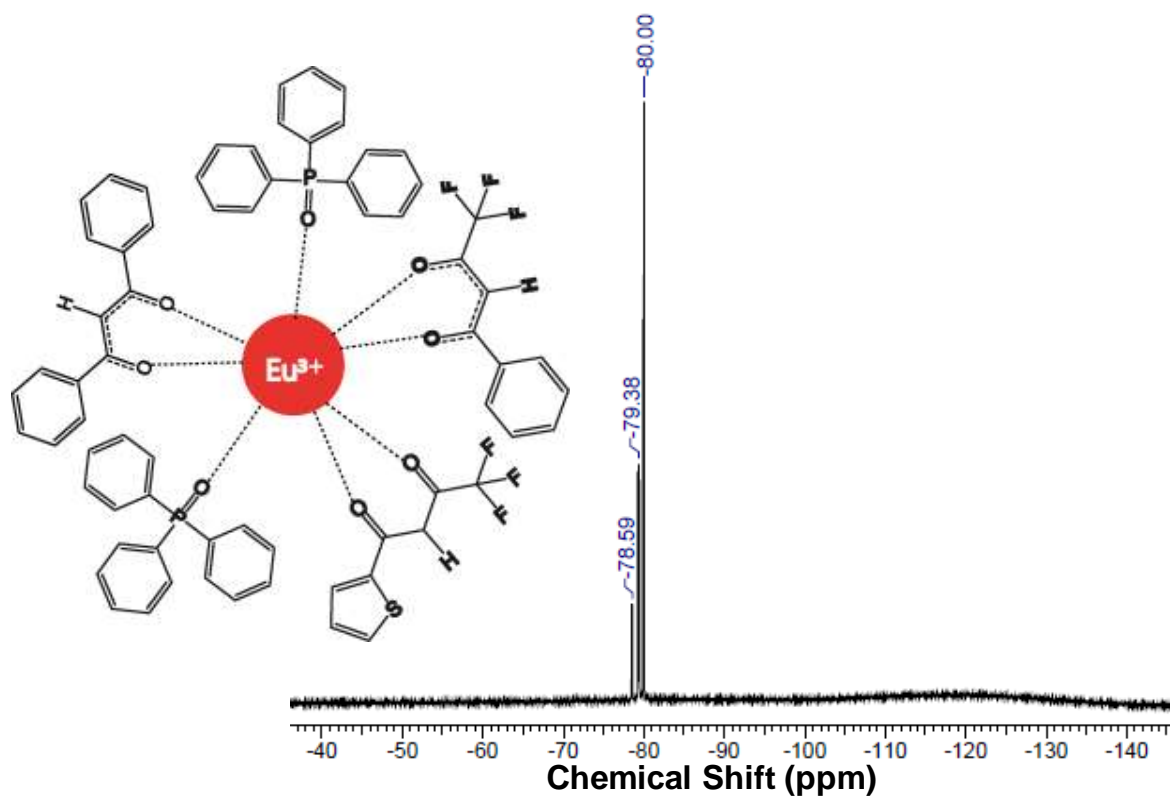


^{19}F NMR (376 MHz, CDCl_3): δ -81 ppm; and δ -82 ppm.
Figure S16. ^{19}F NMR spectrum of $[\text{EuCl}(\text{DBM})(\text{BTFA})(\text{TPPO})_2]$.



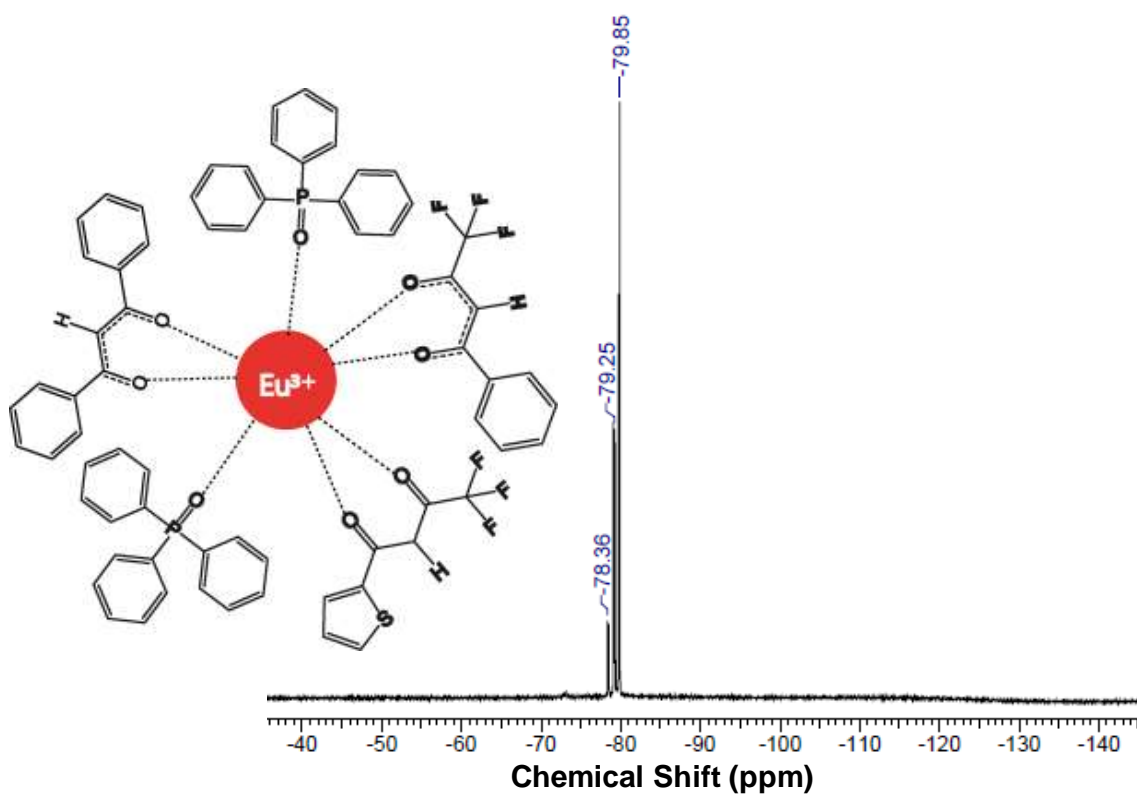
^{19}F NMR (376 MHz, CDCl_3): δ -80 ppm.

Figure S17. ^{19}F NMR spectrum of $[\text{EuCl}(\text{TTA})(\text{BTFA})(\text{TPPO})_2]$.



^{19}F NMR (376 MHz, CDCl_3): δ -79 ppm, and δ -80 ppm.

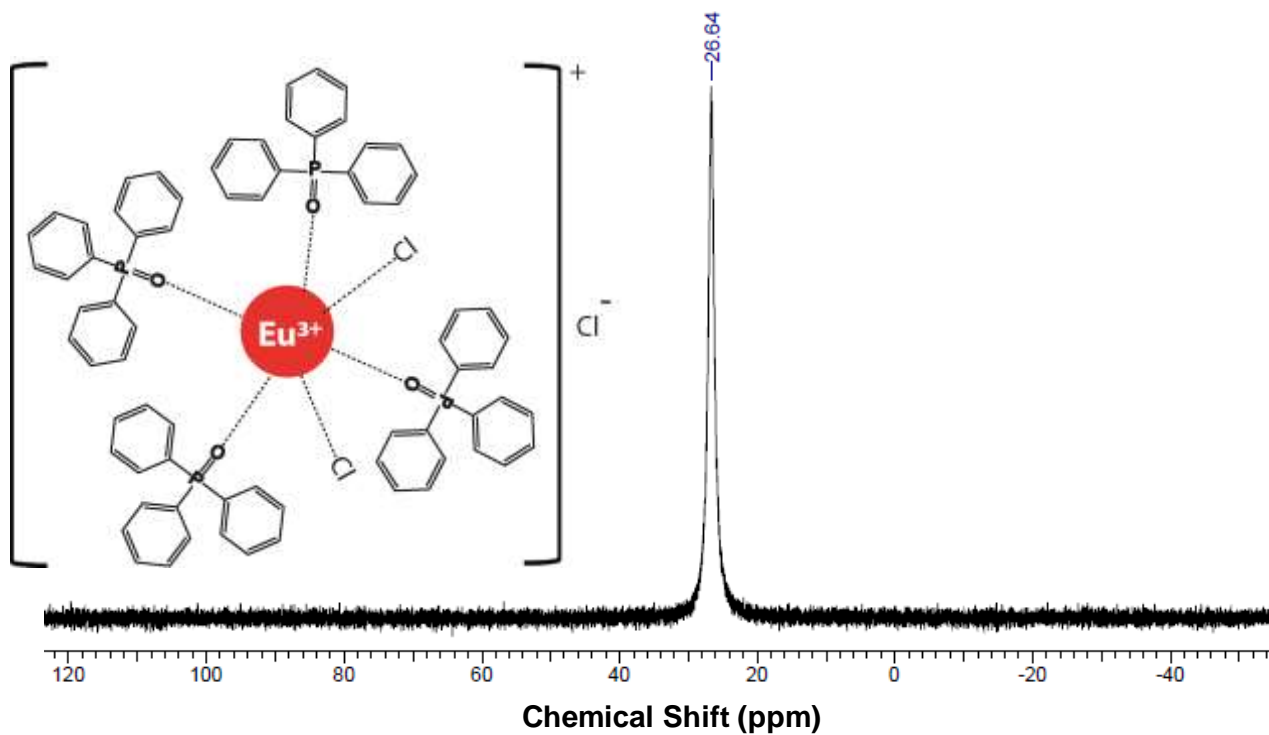
Figure S18. ^{19}F NMR spectrum of $[\text{Eu}(\text{DBM})(\text{BTFA})(\text{TTA})(\text{TPPO})_2]$ obtained via synthetic route 1.



^{19}F NMR (376 MHz, CDCl_3): δ -78 ppm, and δ -80 ppm.

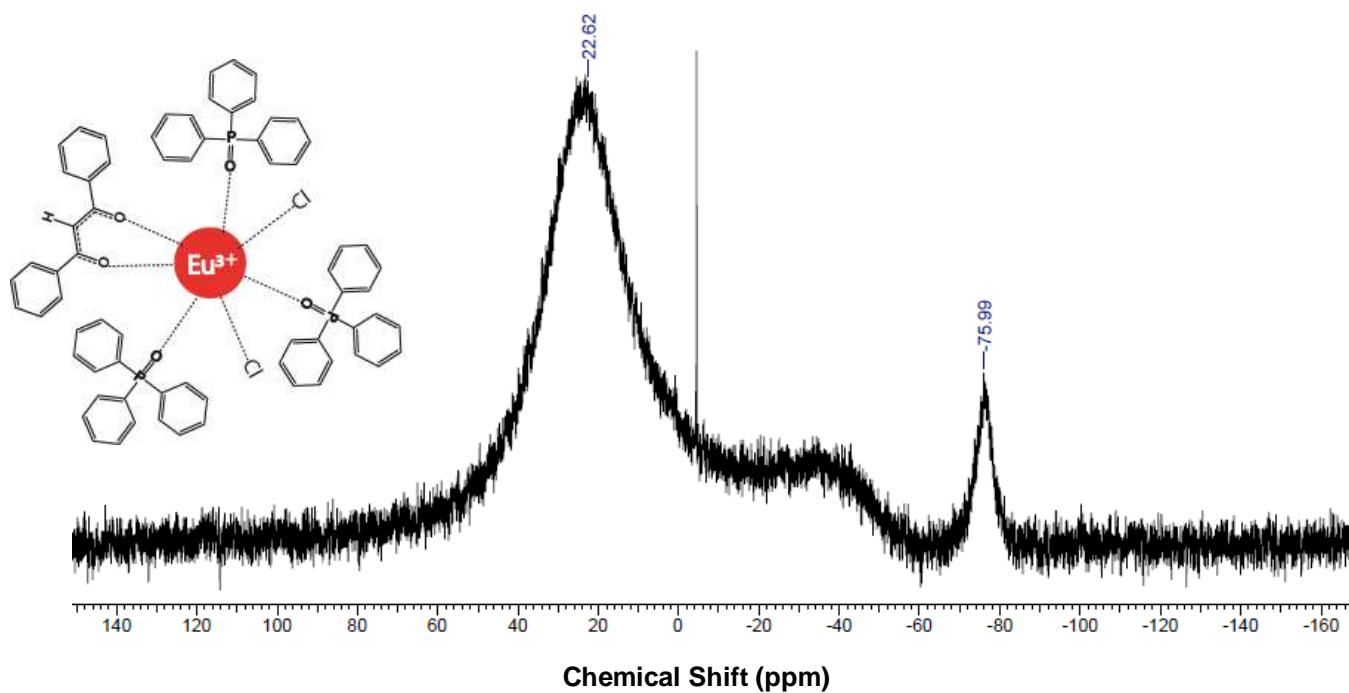
Figure S19. ^{19}F NMR spectrum of $[\text{Eu}(\text{DBM})(\text{BTFA})(\text{TTA})(\text{TPPO})_2]$ obtained via synthetic route 6.

^{31}P NMR Spectra



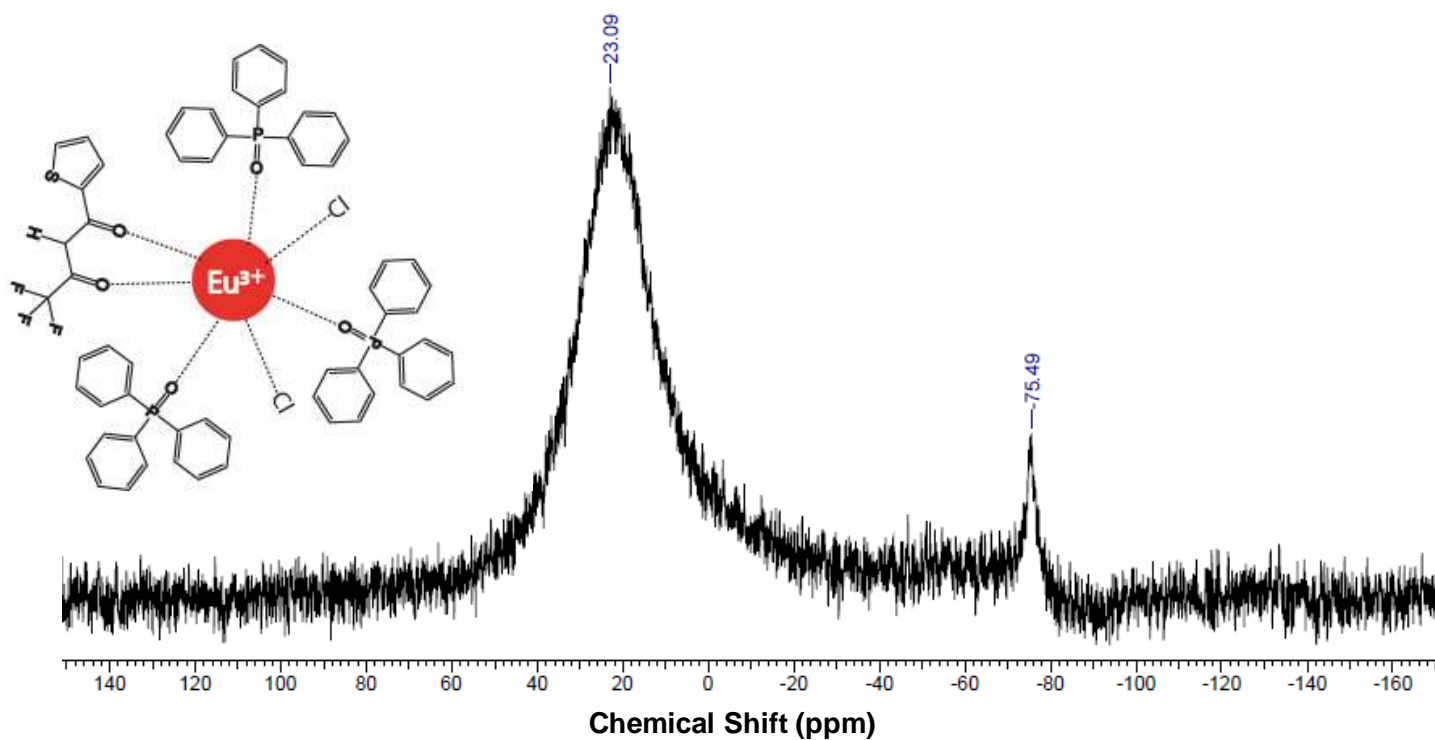
^{31}P NMR (162 MHz, CDCl_3): δ 27 ppm.

Figure S20. ^{31}P NMR spectrum of $[\text{EuCl}_2(\text{TPPO})_4]\text{Cl}\cdot 3\text{H}_2\text{O}$.

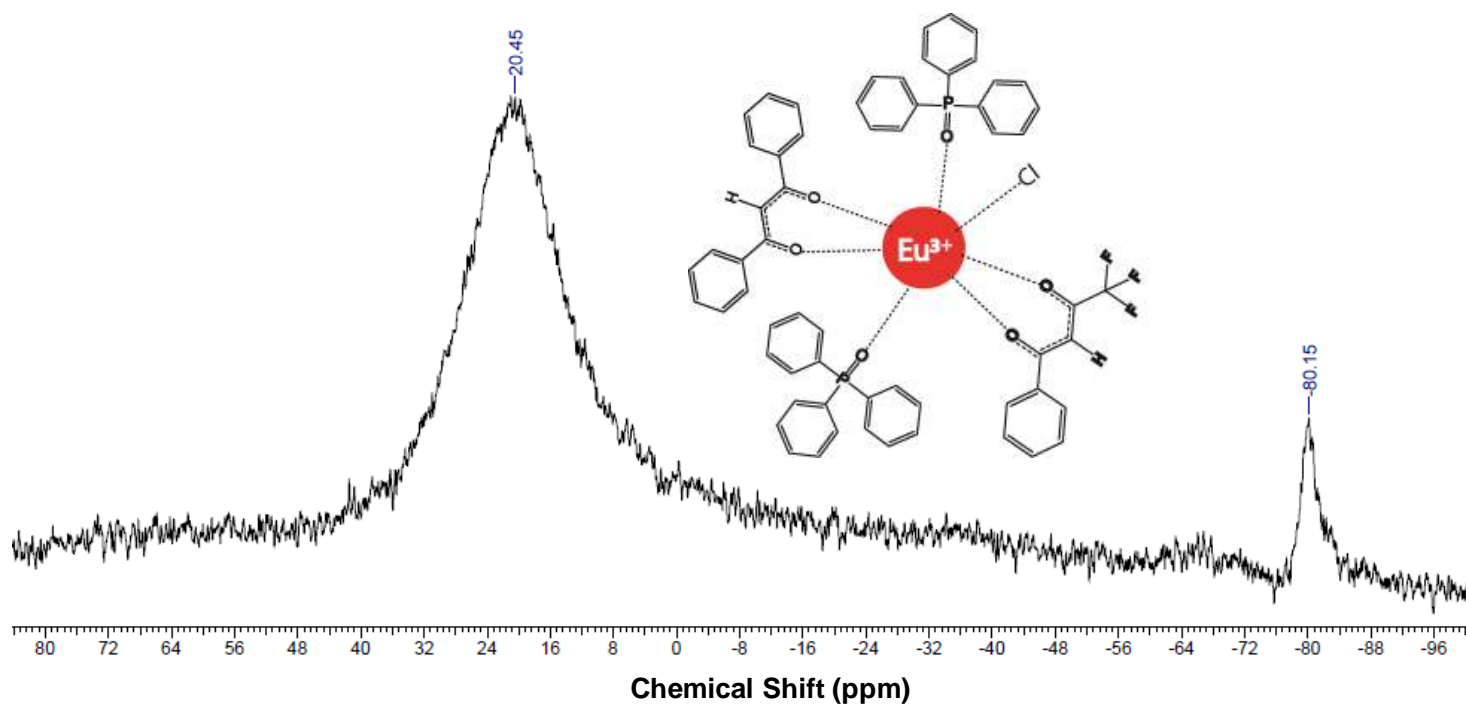


^{31}P NMR (162 MHz, CDCl_3): δ 23 ppm, and δ -76 ppm.

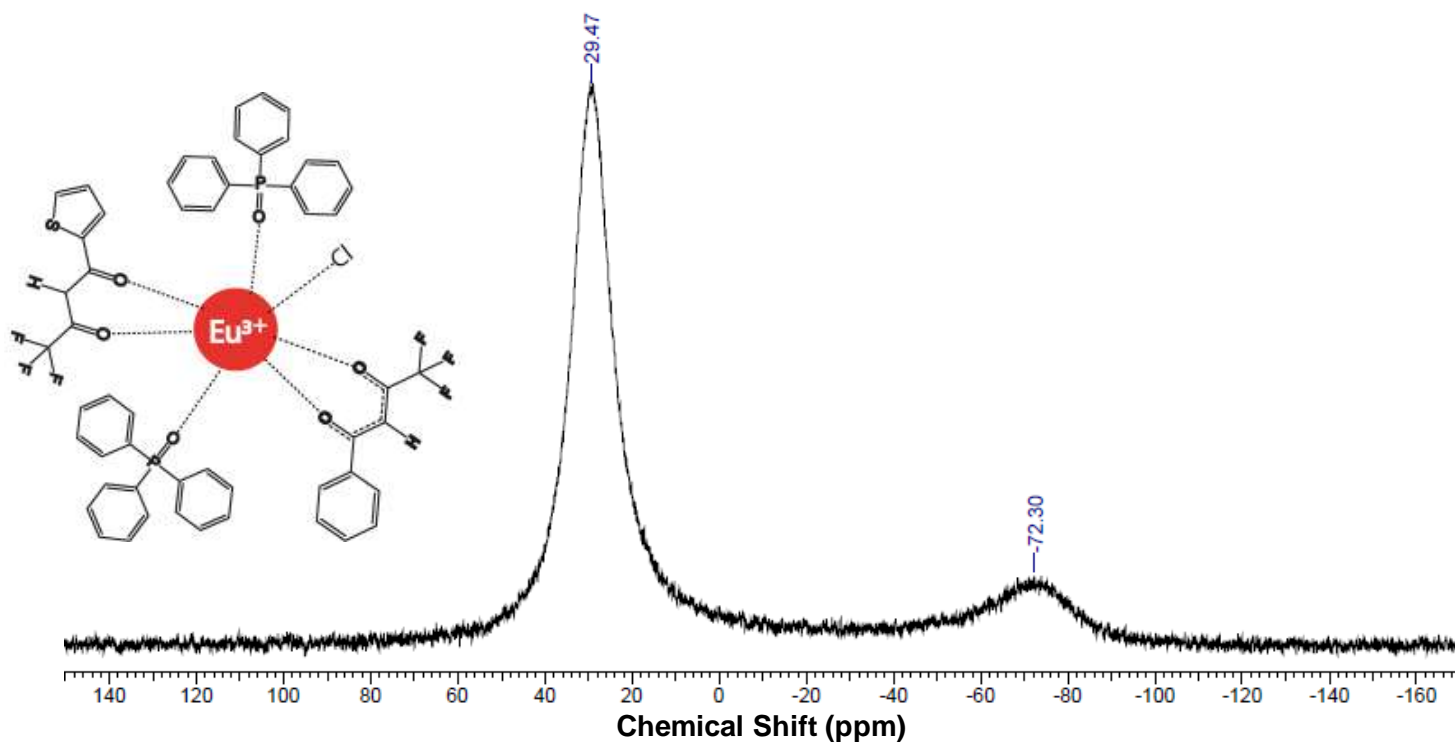
Figure S21. ^{31}P NMR spectrum of $[\text{EuCl}_2(\text{DBM})(\text{TPPO})_3]$.



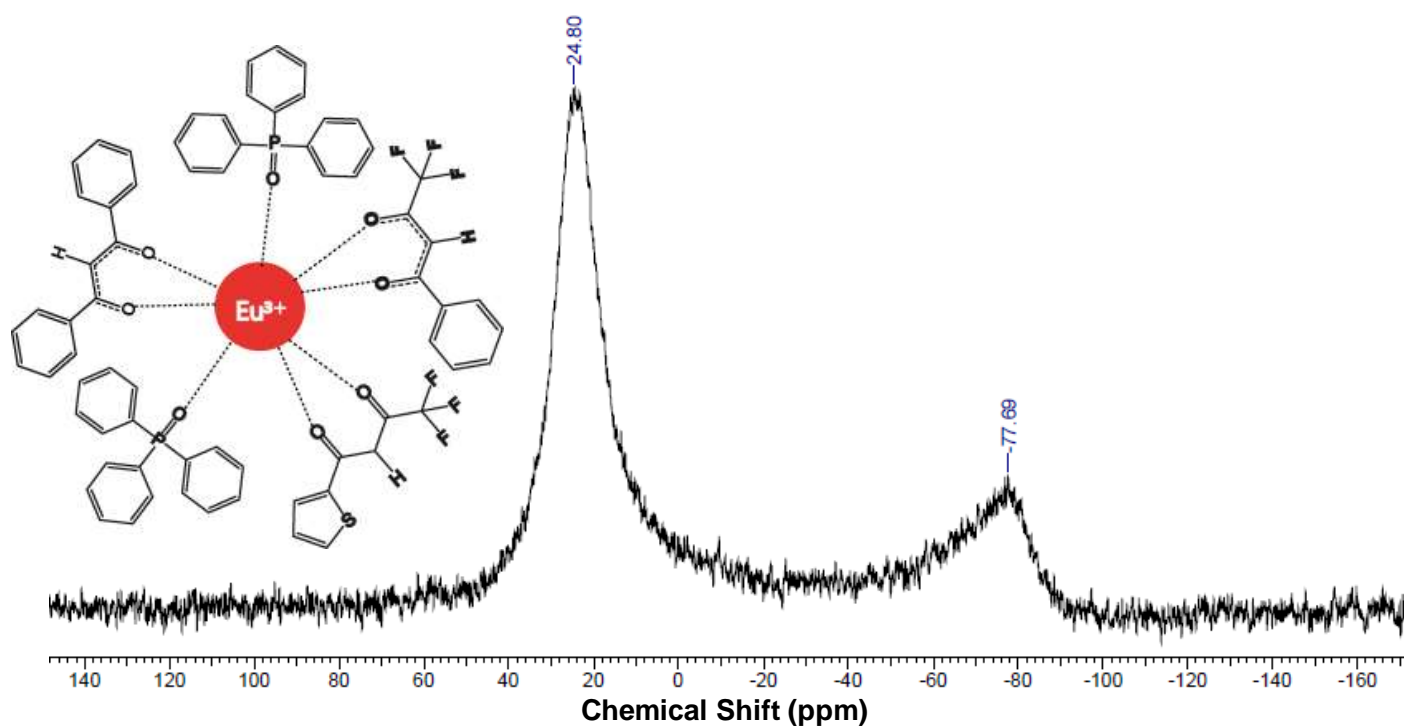
^{31}P NMR (162 MHz, CDCl_3): δ 23 ppm, and δ -75 ppm.
Figure S22. ^{31}P NMR spectrum of $[\text{EuCl}_2(\text{TTA})(\text{TPPO})_3]$.



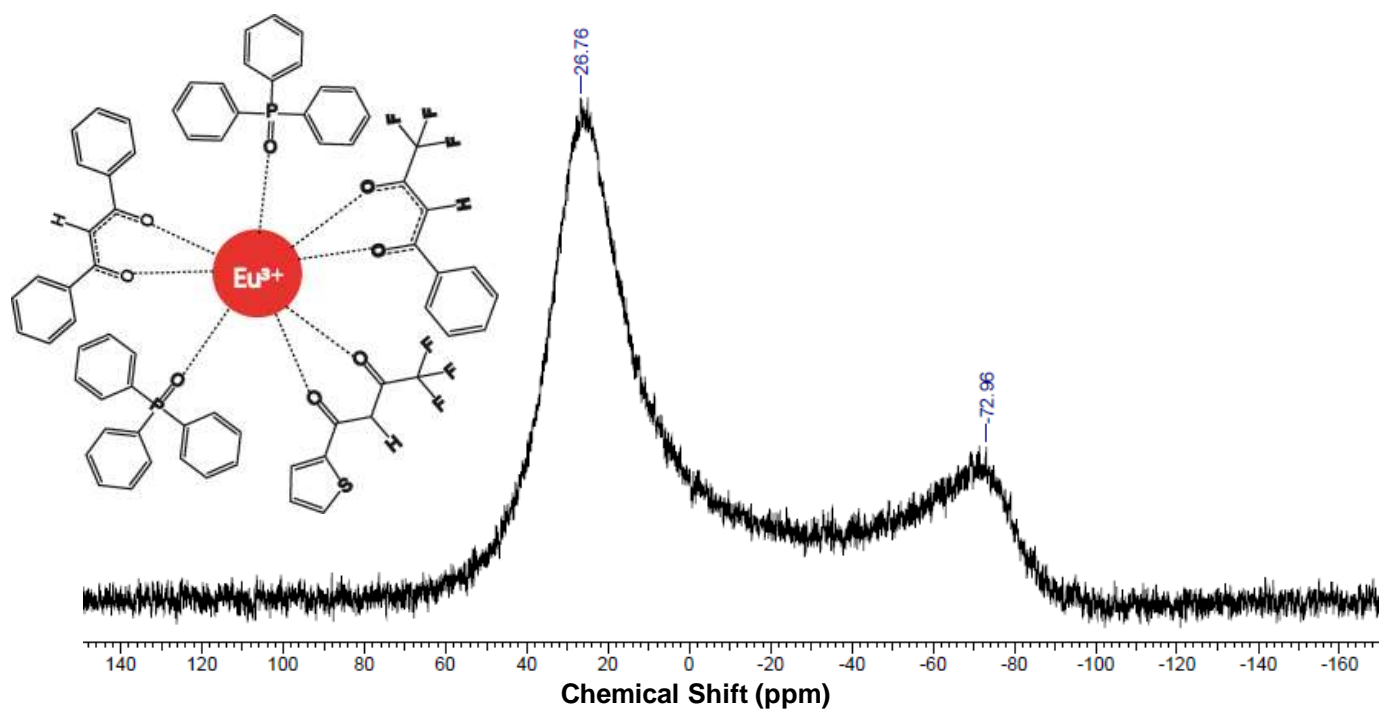
^{31}P NMR (162 MHz, CDCl_3): δ 20 ppm, and δ -80 ppm.
Figure S23. ^{31}P NMR spectrum of $[\text{EuCl}(\text{DBM})(\text{BTFA})(\text{TPPO})_2]$.



^{31}P NMR (162 MHz, CDCl_3): δ 29 ppm, and δ -72 ppm.
Figure S24. ^{31}P NMR spectrum of $[\text{EuCl}(\text{TTA})(\text{BTFA})(\text{TPPO})_2]$.



^{31}P NMR (162 MHz, CDCl_3): δ 25 ppm, and δ -78 ppm.
Figure S25. ^{31}P NMR spectrum of $[\text{Eu}(\text{DBM})(\text{BTFA})(\text{TTA})(\text{TPPO})_2]$ obtained via synthetic route 1.



³¹P NMR (162 MHz, CDCl₃): δ 27 ppm, and δ -73 ppm.

Figure S26. ³¹P NMR spectrum of [Eu(DBM)(BTFA)(TTA)(TPPO)₂] obtained via synthetic route 6.