Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information for

Can chiral P(III) coordinate Eu(III)? Unexpected solvent dependent circularly polarised luminescence of BINAP and Eu(III)(hfa)$_3$ in chloroform and acetone

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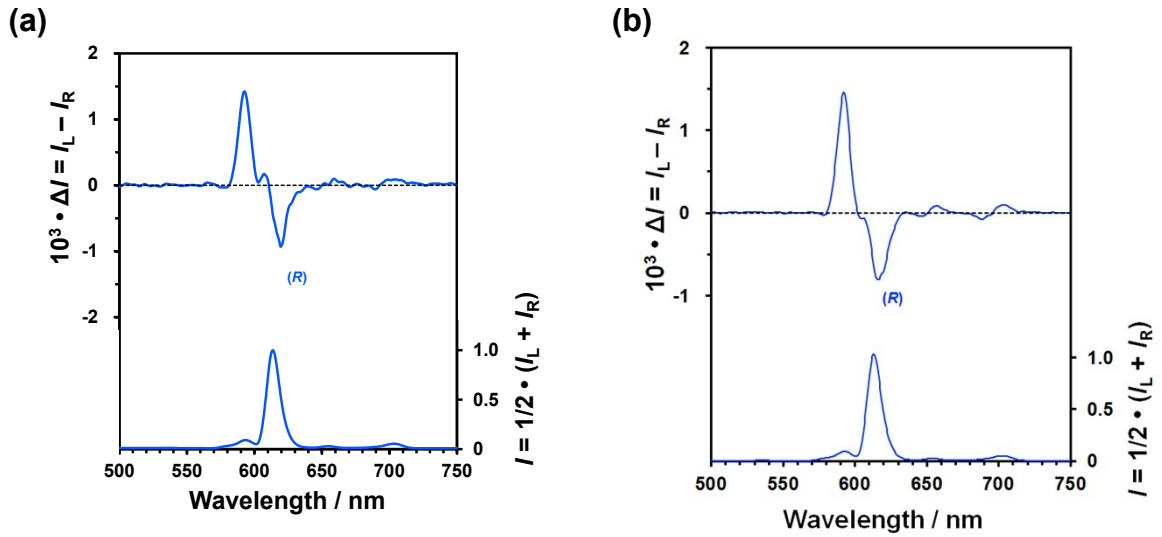


Fig. S1. Normalized CPL and PL spectra of (*R*)-BINAP:Eu(hfa)$_3$ = 1:1 in EtOH-free chloroform. Path length 1.0 mm. (a) [Eu(hfa)$_3$] = 1×10^{-5} M. λ_{ex} = 300 nm, g_{em} = $+1.6 \times 10^{-2}$ (593 nm), -0.95×10^{-3} (618nm). (b) [Eu(hfa)$_3$] = 1×10^{-4} M. λ_{ex} = 300 nm, g_{em} = $+1.4 \times 10^{-2}$ (592 nm), -0.92×10^{-3} (613 nm).

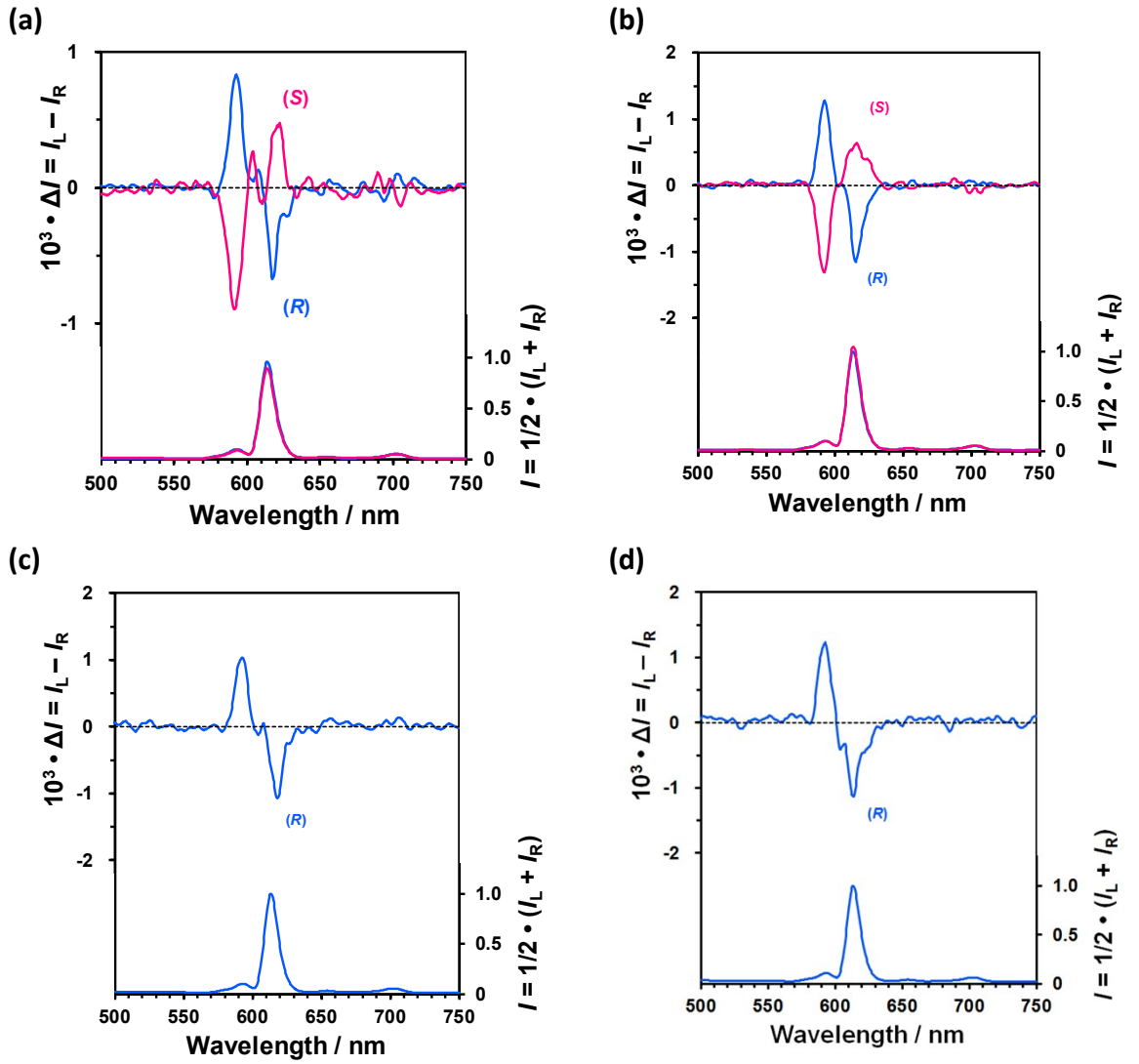


Fig. S2. Normalized CPL and PL spectra of (*R*)-BINAP:Eu(hfa)$_3$ in EtOH-free chloroform, [Eu(hfa)$_3$] = 5 × 10^{-4} M (path length 1.0 mm). (a) (*R*)- (and (*S*))-BINAP:Eu(hfa)$_3$ = 1:2, λ_{ex} = 325 nm, g_{em} for (*R*) = +0.89×10^{-2} (592 nm), –0.75×10^{-3} (617 nm), g_{em} for (*S*) = –0.89×10^{-2} (592 nm), +0.75 × 10^{-3} (617 nm). (b) (*R*)- (and (*S*))-BINAP:Eu(hfa)$_3$ = 2:1, λ_{ex} = 325 nm, g_{em} for (*R*) = +1.3 × 10^{-2} (592 nm), –1.15 × 10^{-3} (615 nm), g_{em} for (*S*) = –1.3 × 10^{-2} (592 nm), +0.85 × 10^{-3} (615 nm). (c) (*R*)-BINAP:Eu(hfa)$_3$ = 5:1, λ_{ex} = 335 nm, g_{em} = +1.0 × 10^{-2} (592 nm), –1.6 × 10^{-3} (618 nm). (d) (*R*)-BINAP:Eu(hfa)$_3$ = 10:1, λ_{ex} = 335 nm, g_{em} = +1.1×10^{-2} (592 nm), –1.1×10^{-3} (613 nm).

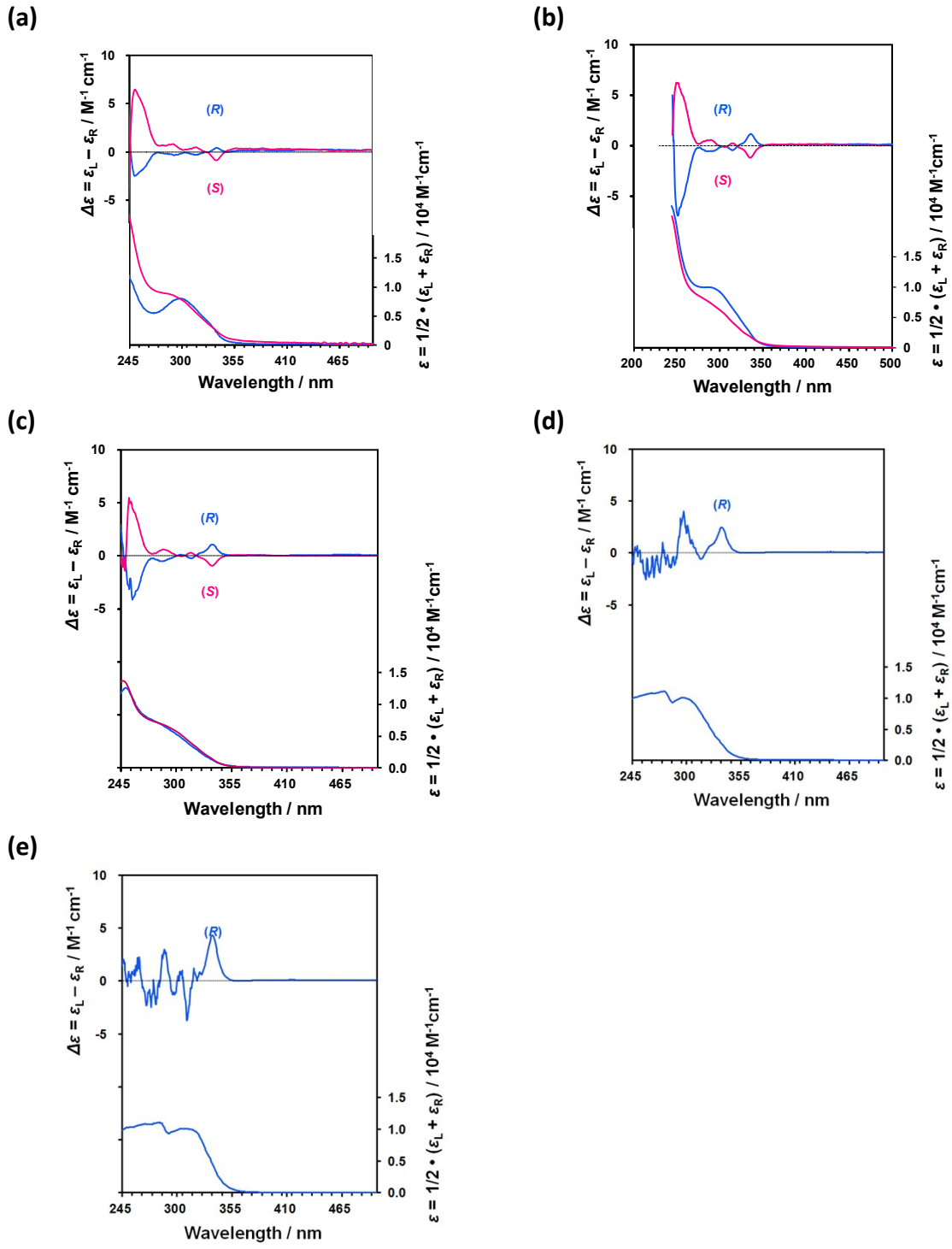
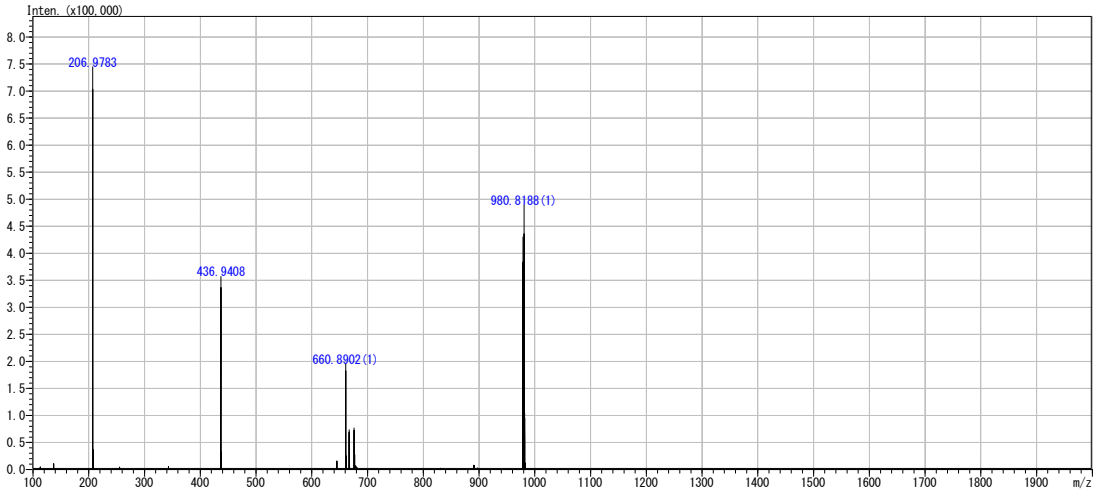


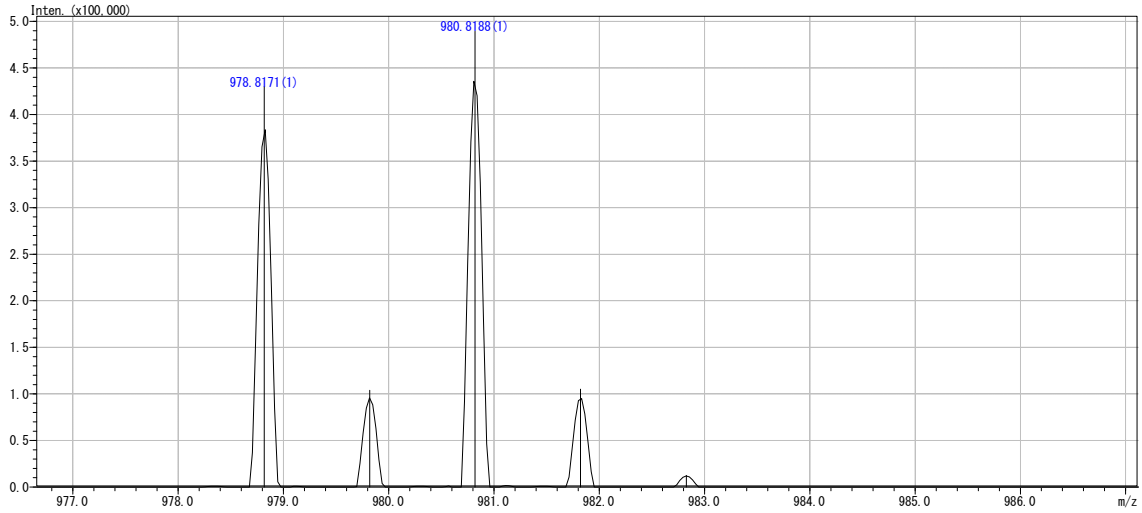
Fig. S3. Normalized CD and UV-vis spectra of (*R*)- and (*S*)-BINAP:Eu(hfa)$_3$ in EtOH-free chloroform. [Eu(hfa)$_3$] = 5 × 10^{-4} M (path length 1.0 mm). (a) (*R*)- and (*S*)-BINAP:Eu(hfa)$_3$ = 1:2, $|g_{abs}|$ = 2.6 × 10^{-4} at 336 nm. (b) (*R*)- and (*S*)-BINAP: Eu(hfa)$_3$ = 1:1, $|g_{abs}|$ = 5.8 × 10^{-4} at 336 nm. (c) (*R*)- and (*S*)-BINAP:Eu(hfa)$_3$ = 2:1, $|g_{abs}|$ = 7.4 × 10^{-4} at 336 nm. (d) (*R*)-BINAP:Eu(hfa)$_3$ = 5:1, g_{abs} = +9.0 × 10^{-4} at 335 nm. (e) (*R*)-BINAP:Eu(hfa)$_3$ = 10:1, g_{abs} = +9.4 × 10^{-4} at 335 nm.

Negative mode (full range)



m/z= 206.99: hfa, m/z= 660.89: BINAP, m/z= 980.82: BINAP+Eu+hfa

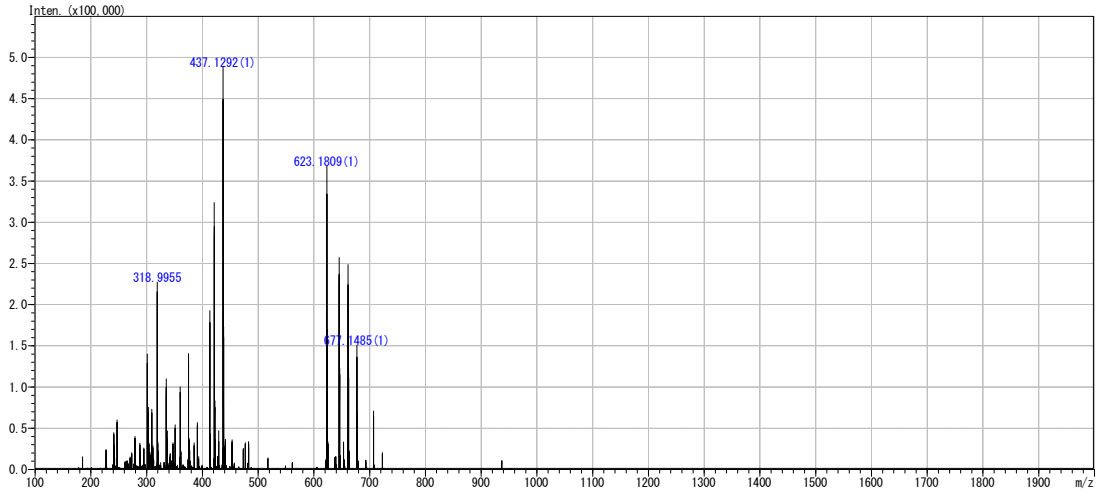
Negative mode (zoom-in)



m/z = 978.82: ^{151}Eu+BINAP+HFA, m/z= 980.82: ^{153}Eu+BINAP+HFA

Fig. S4. Negative-mode LCMS-IT-TOF spectra of (*R*)-BINAP-Eu(III). Top; full spectrum. Bottom; its zoom-in spectrum.

Positive mode (full)



Positive mode (zoom-in)

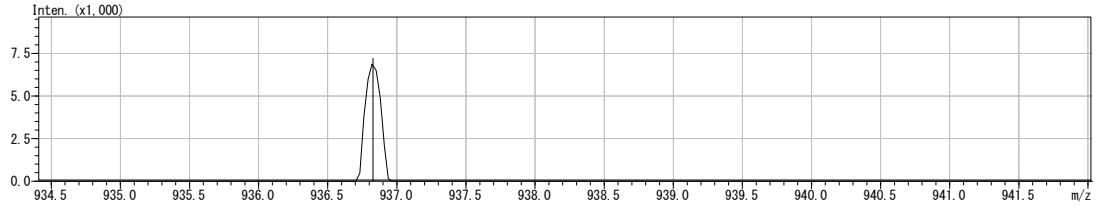
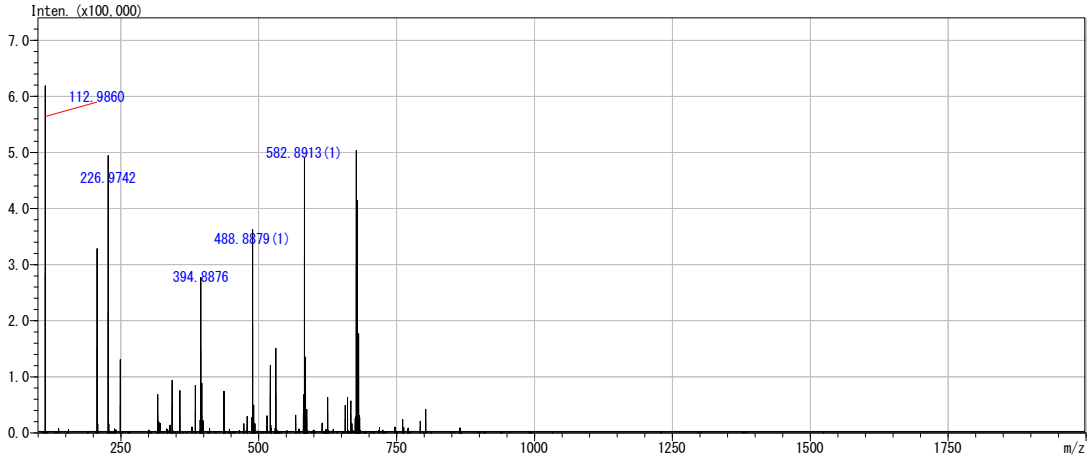


Fig. S5. Positive-mode LCMS-IT-TOF spectra of (*R*)-BINAP-Eu(III). Top; full spectrum. Bottom; its zoom-in spectrum.

Negative mode (full)



Negative mode (zoom-in)

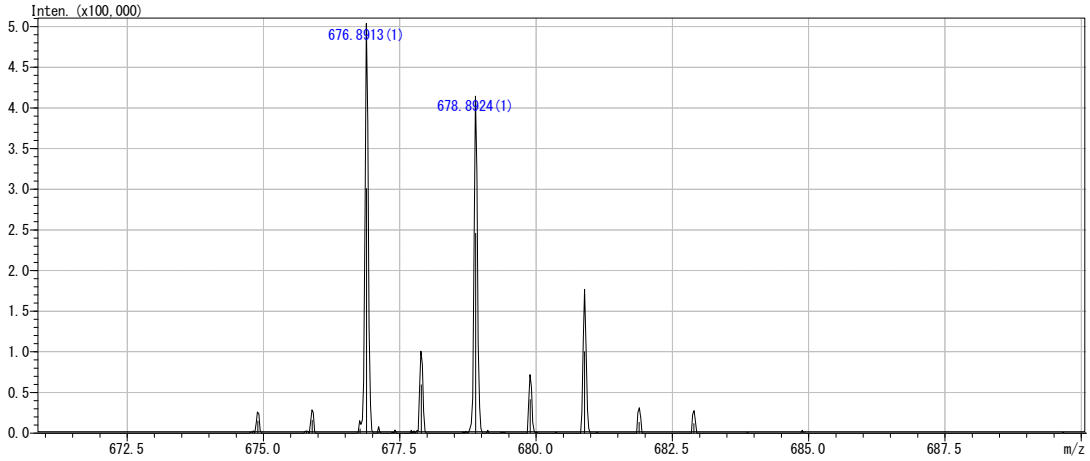


Fig. S6. Negative-mode electrospray MS spectrum of (*R*)-BINAP-Eu(III) by adding Na triflate. Two Eu(III) isotopic species with a natural abundance around m/z= 676.89 and 678.89 were observed. However, no distinct parent peaks of Eu(III)$(hfa)_3$-BINAP (m/z= 1396.08 and 1398.08) with Na^+ (m/z = 22.99) triflate (m/z = 148.95) without H_2O (m/z = 18.01) and two or three H_2O molecules as adducts were detected.

Positive mode (full)

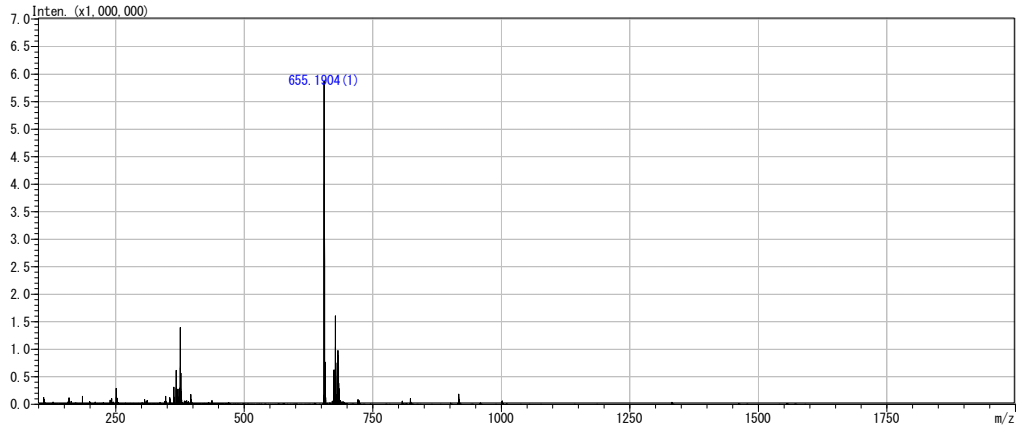


Fig. S7. Positive-mode electrospray MS spectrum of (*R*)-BINAP-Eu(III) with NaOTf. Any Eu(III) isotopic species with natural abundance around m/z= 670 and 980 were not observed. No distinct parent peaks of Eu(III)$(hfa)_3$-BINAP (m/z= 1396.08 and 1398.08) with Na^+ (m/z = 22.99) triflate (m/z = 148.95) without H_2O (m/z = 18.01) and two/three H_2O molecules as adducts were detected.

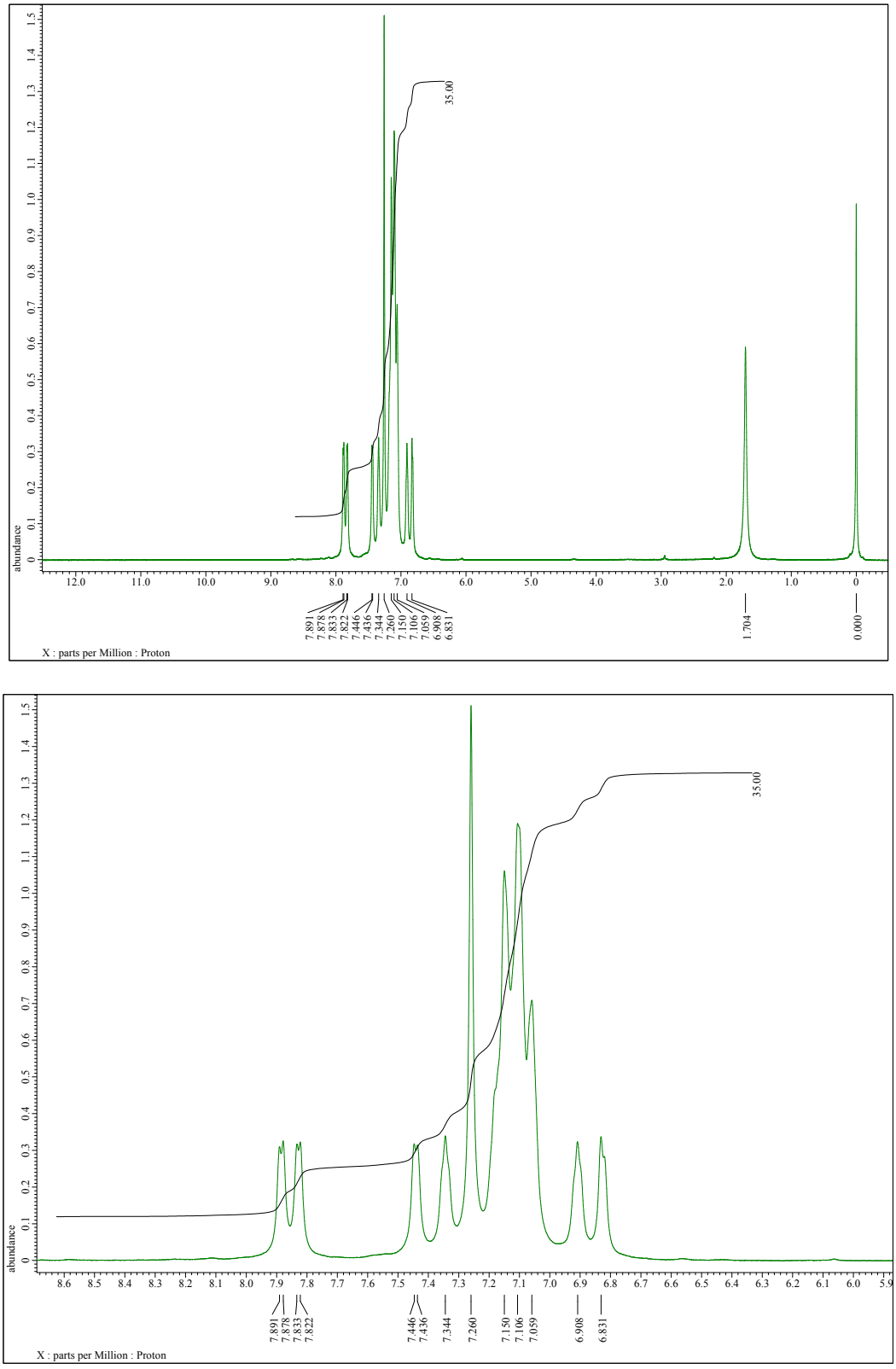


Fig. S8. ^{1}H-NMR spectra of (*R*)-BINAP with Eu(hfa)$_3$ (1:1) in $CDCl_3$.
^{1}H-NMR signals at 7.260 ppm and 1.574 ppm are due to residual $CHCl_3$ and H_2O.

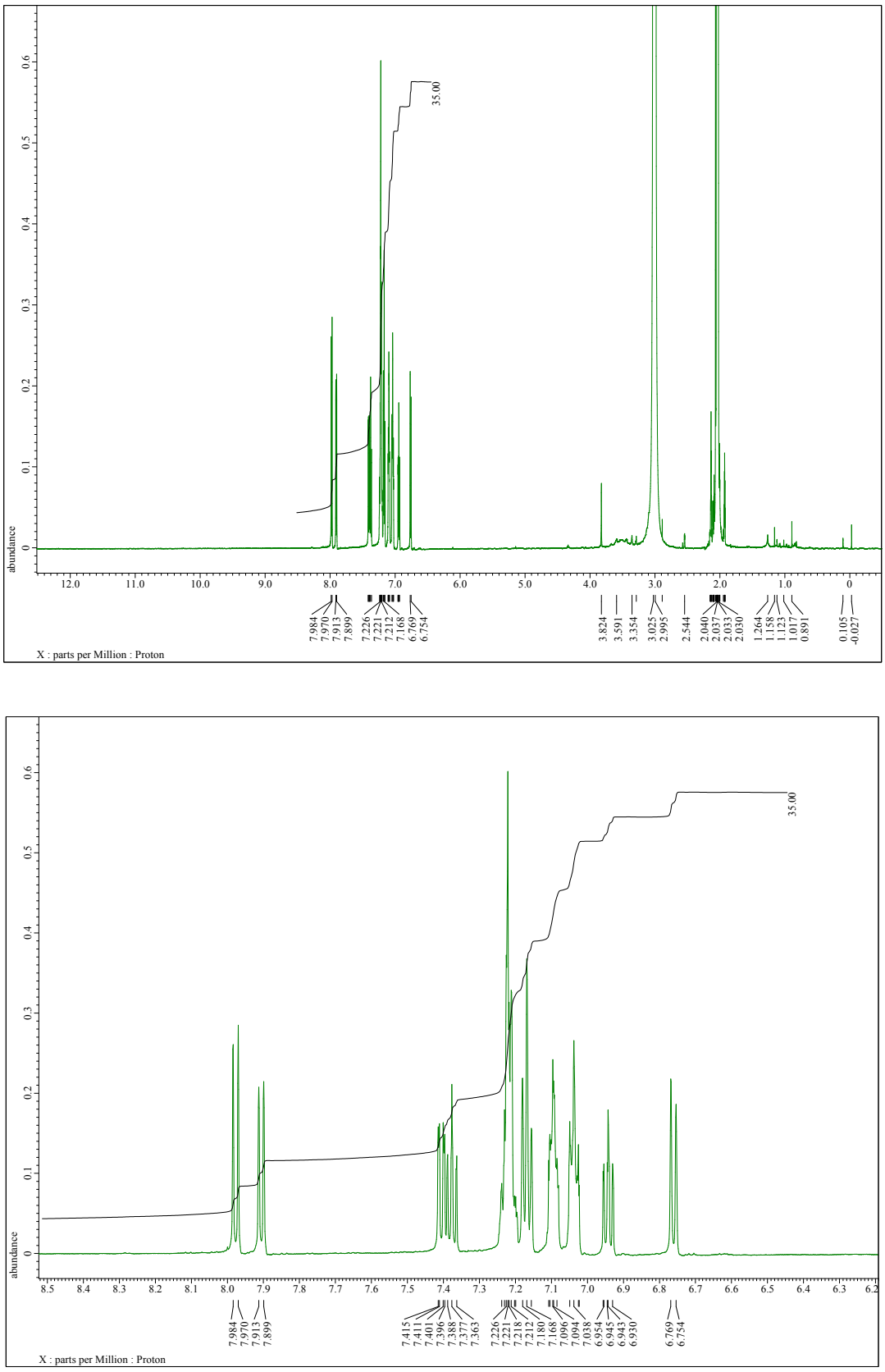


Fig. S9. ^{1}H-NMR spectra of (*R*)-BINAP with Eu(hfa)$_3$ (1:1) in acetone-d_6.

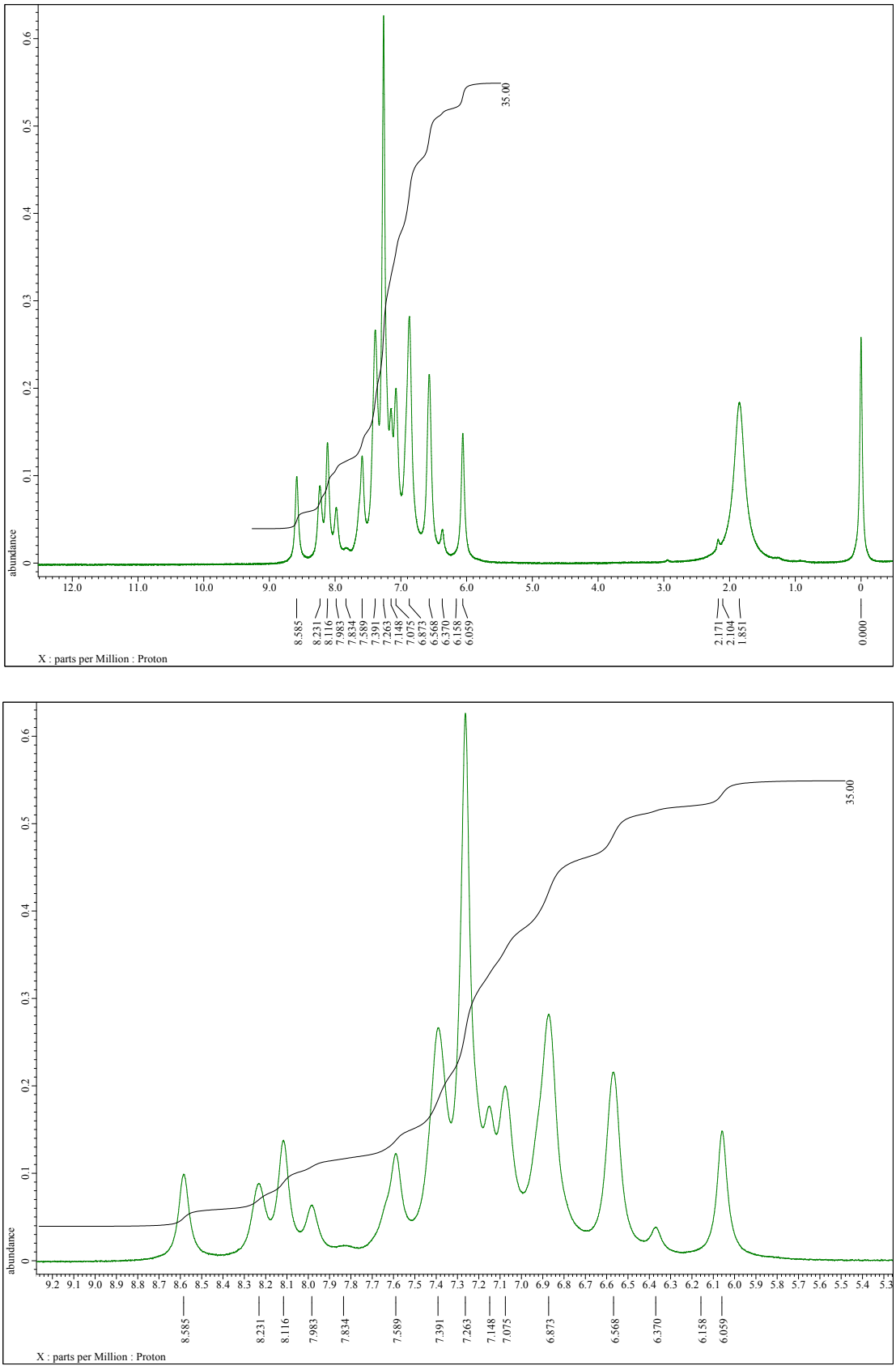


Fig. S10. ^{1}H-NMR spectra of (*R*)-BINAPO with Eu(hfa)$_3$ (1:1) in $CDCl_3$.

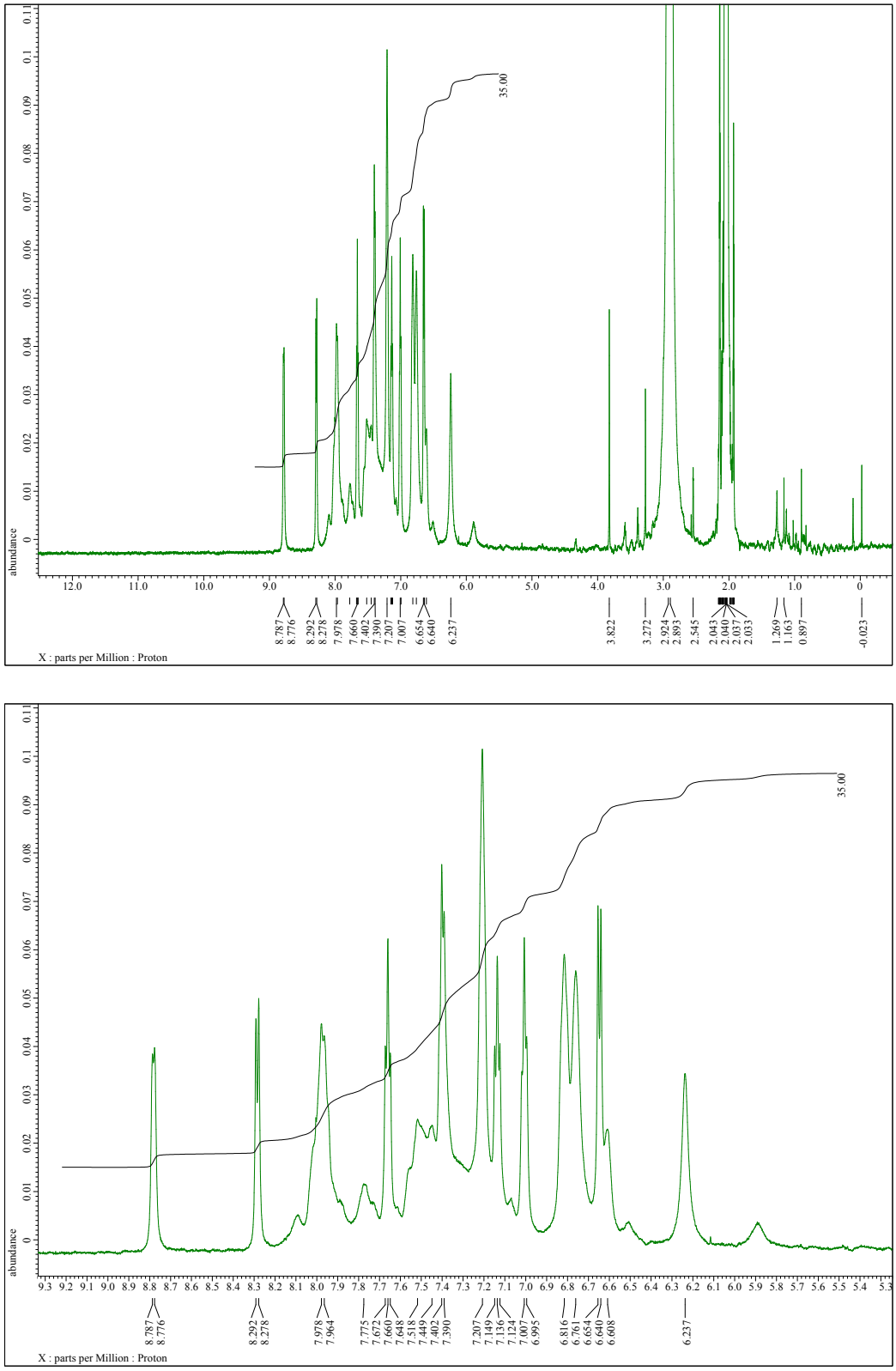


Fig. S11. ^{1}H-NMR spectra of (*R*)-BINAPO with Eu(hfa)$_3$ (1:1) in acetone-d_6.

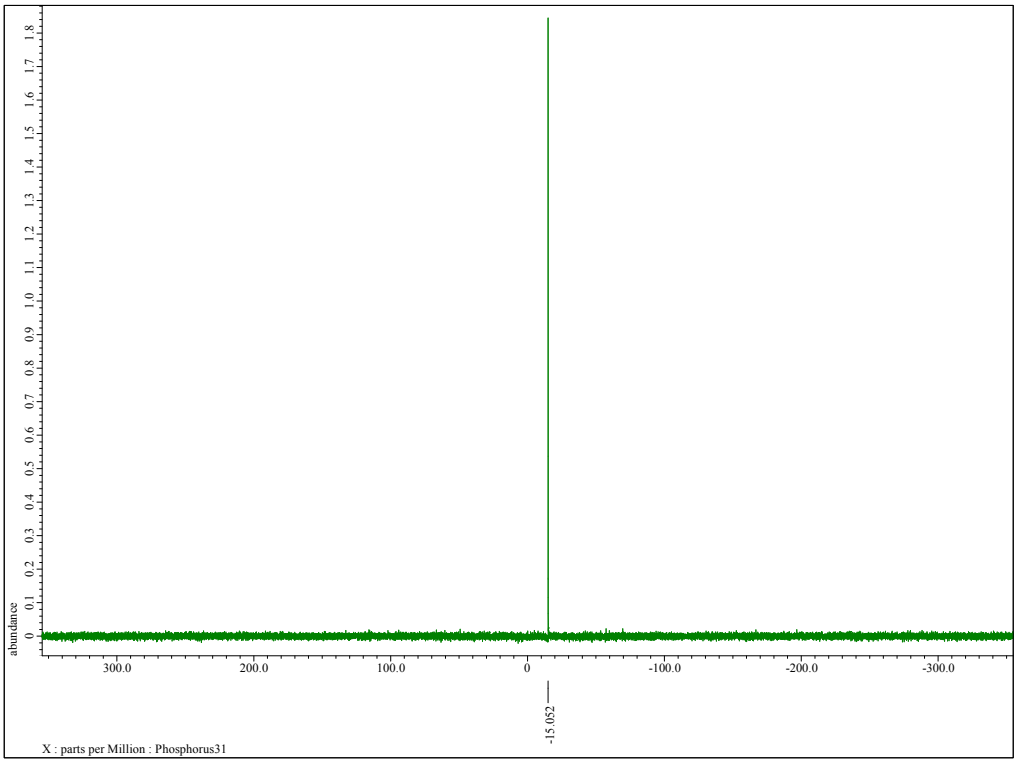


Fig. S12. ^{31}P-NMR spectrum of (*R*)-BINAP with Eu(hfa)$_3$ (1:1 in molar ratio) in $CDCl_3$. ^{31}P resonances at -15.052 ppm using a reference ^{31}P peak (at 140 ppm) of P(OMe)$_3$ in MeOD.

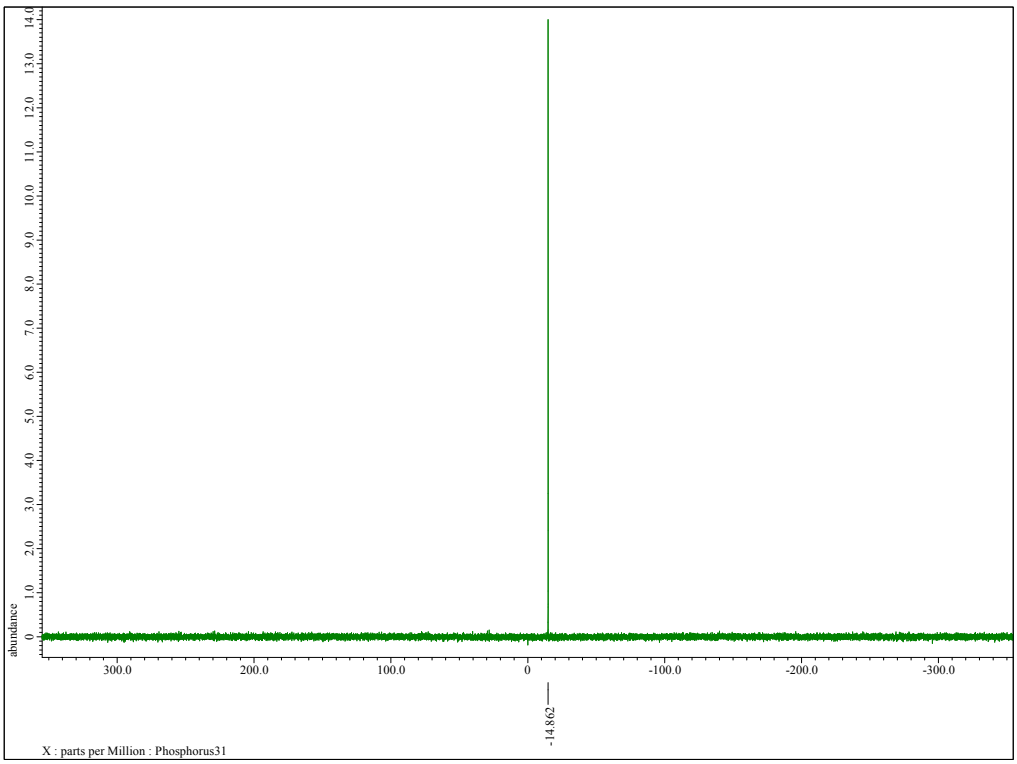


Fig. S13. ^{31}P-NMR spectrum of (*R*)-BINAP in $CDCl_3$. ^{31}P resonances at –14.862 ppm. 500-1000 acquisitions. Sample (5–10 mg) was dissolved in 0.6 mL of $CDCl_3$, corresponding to (0.6–1.2) x 10^{-2} M.

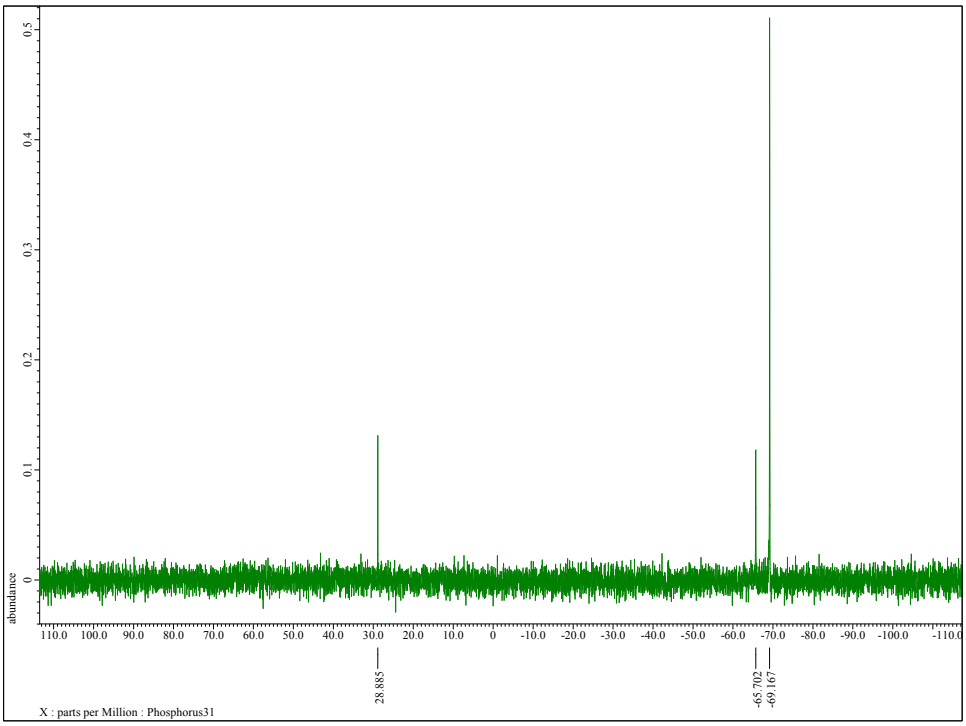


Fig. S14. ^{31}P-NMR spectrum of (*R*)-BINAPO with Eu(hfa)$_3$ (1:1 in molar ratio) in $CDCl_3$. Major ^{31}P signal at -69.167 infers the coordination of P(V)=O of BINAPO, whilst minor ^{31}P signal at +28.885 ppm is non-coordinated P(V)=O of BINAPO. The origin of minor ^{31}P-NMR signal at -65.702 ppm is unclear. 500–1000 acquisitions. Sample (5-10 mg) was dissolved in 0.6 mL of $CDCl_3$, corresponding to (0.6–1.2) x 10^{-2} M.

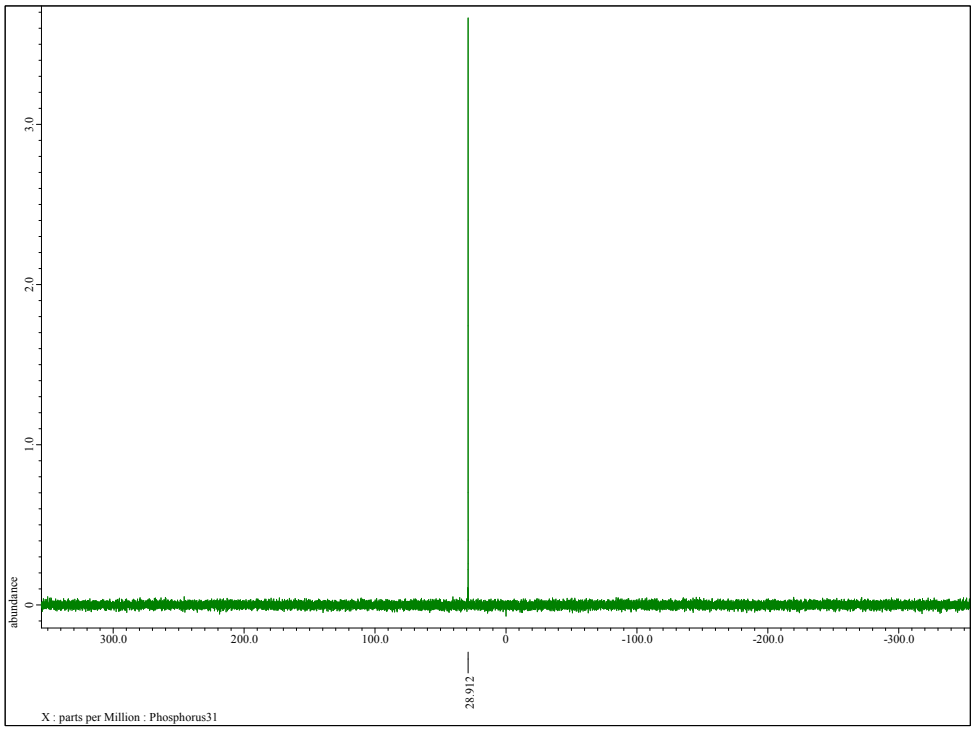


Fig. S15. ^{31}P-NMR spectrum of (*R*)-BINAPO in $CDCl_3$. ^{31}P resonances at +28.912 ppm.

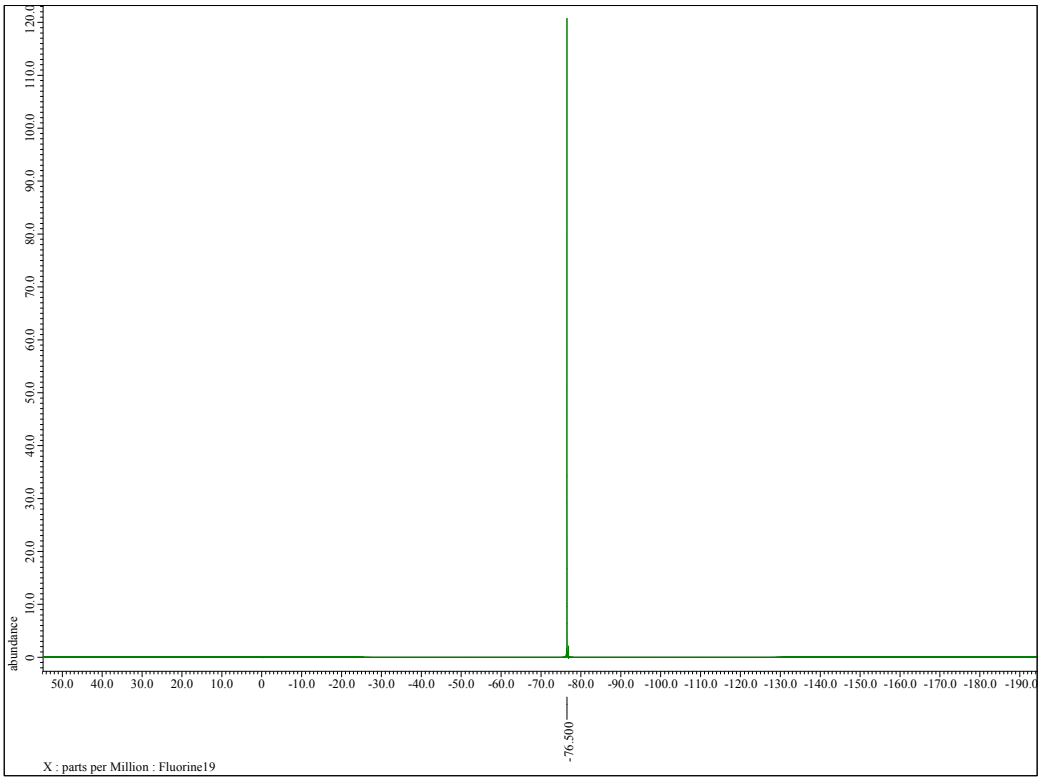


Fig. S16. ^{19}F-NMR spectrum of hfa in $CDCl_3$. ^{19}F resonances at −76.500 ppm.

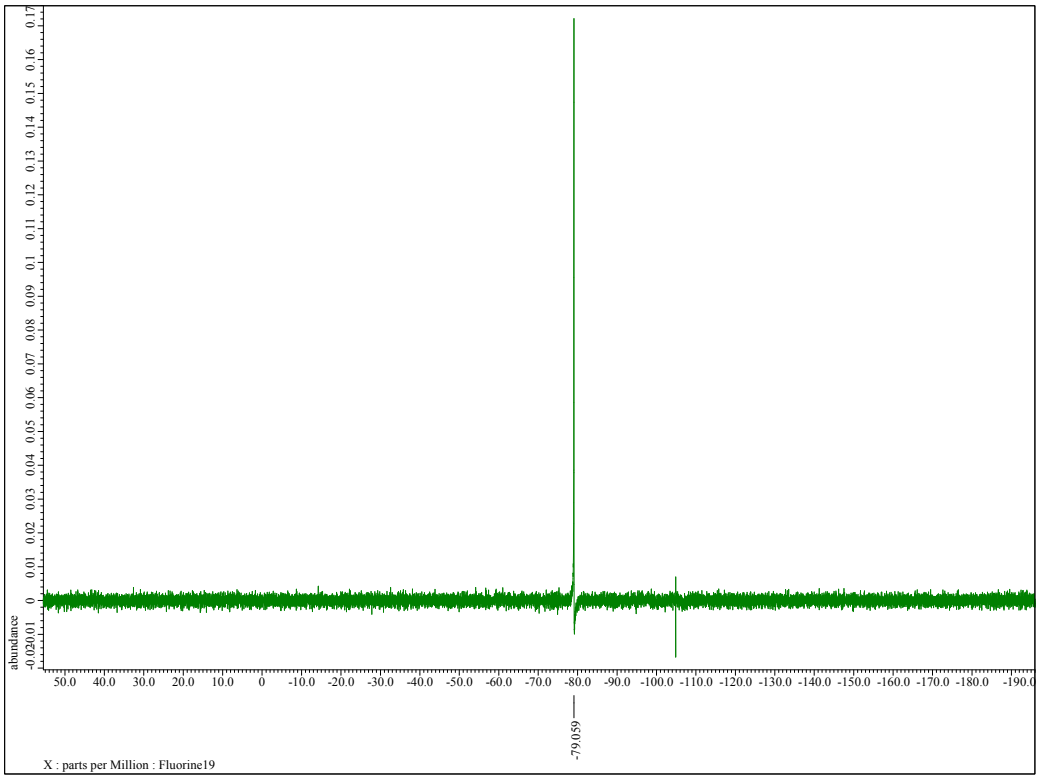


Fig. S17. ^{19}F-NMR spectrum of $Eu(hfa)_3$ in $CDCl_3$. ^{19}F resonances at −79.059 ppm.

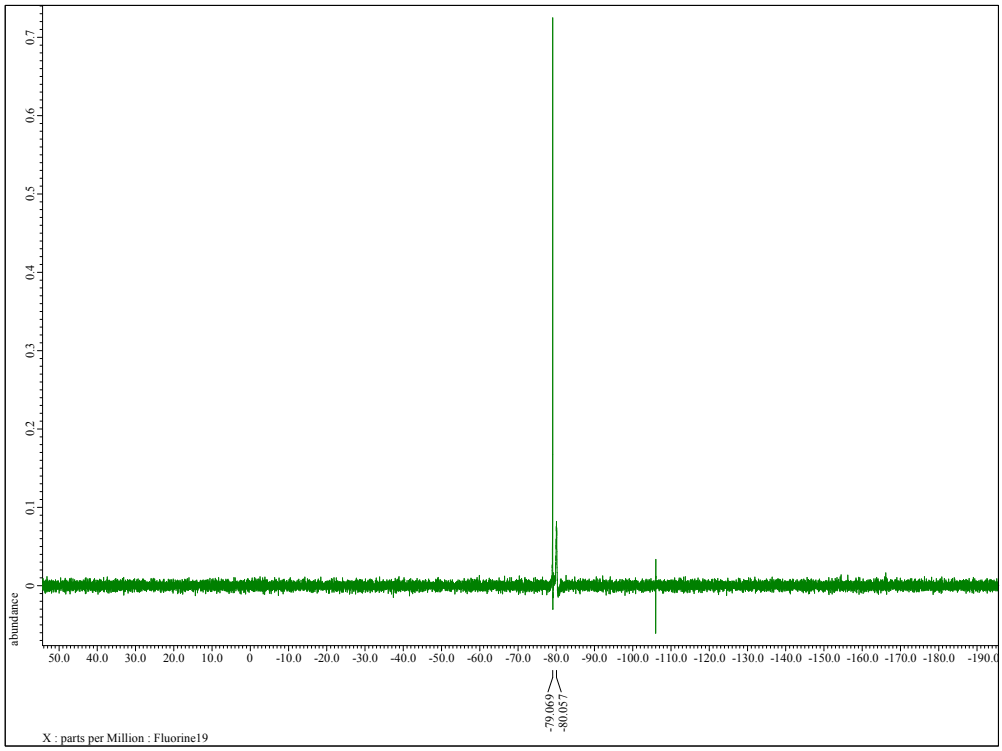


Fig. S18. ^{19}F-NMR spectrum of (*R*)-BINAP and Eu(hfa)$_3$ (= 1:1 in molar ratio) in $CDCl_3$. ^{19}F resonances at −79.099 ppm (major) and −80.057 ppm (minor).

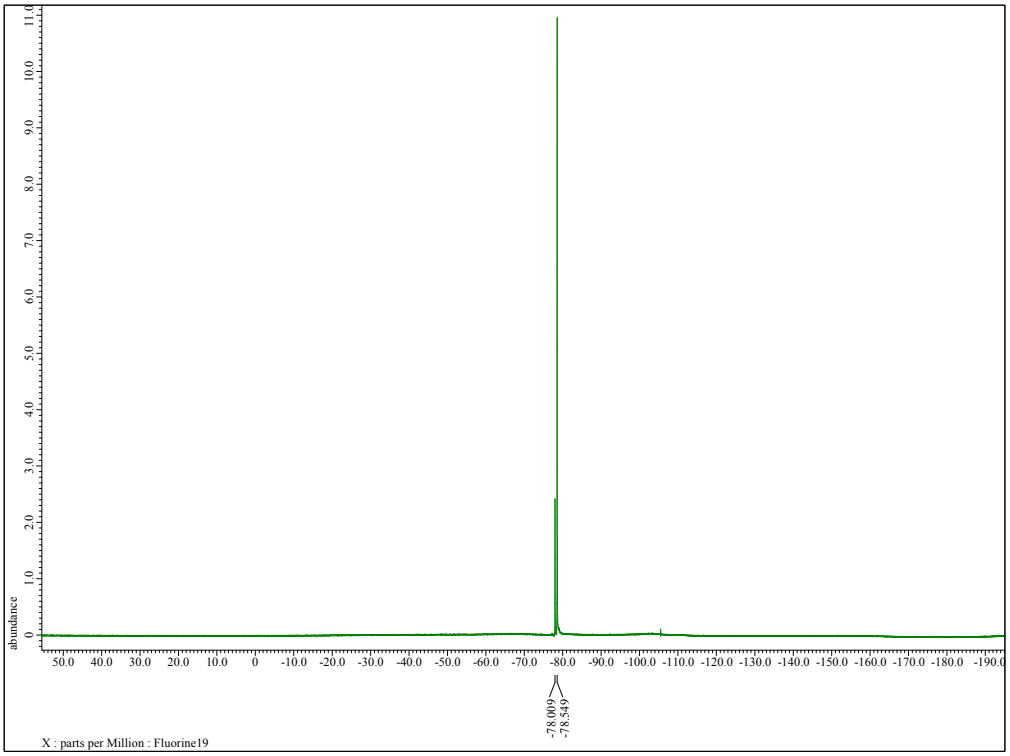


Fig. S19. ^{19}F-NMR spectrum of (*R*)-BINAPO and Eu(hfa)$_3$ (= 1:1 in molar ratio) in $CDCl_3$. ^{19}F resonances at −78.099 ppm (minor) and −78.549 ppm (major).