Electronic Supporting Information (ESI) for

Unveiling controlled breaking of the mirror symmetry of $Eu(fod)_3$ with α-/β-pinene and BINAP by circularly polarised luminescence (CPL), CPL excitation, and ^{19}F-/$^{31}P\{^{1}H\}$-NMR spectra and Mulliken charges

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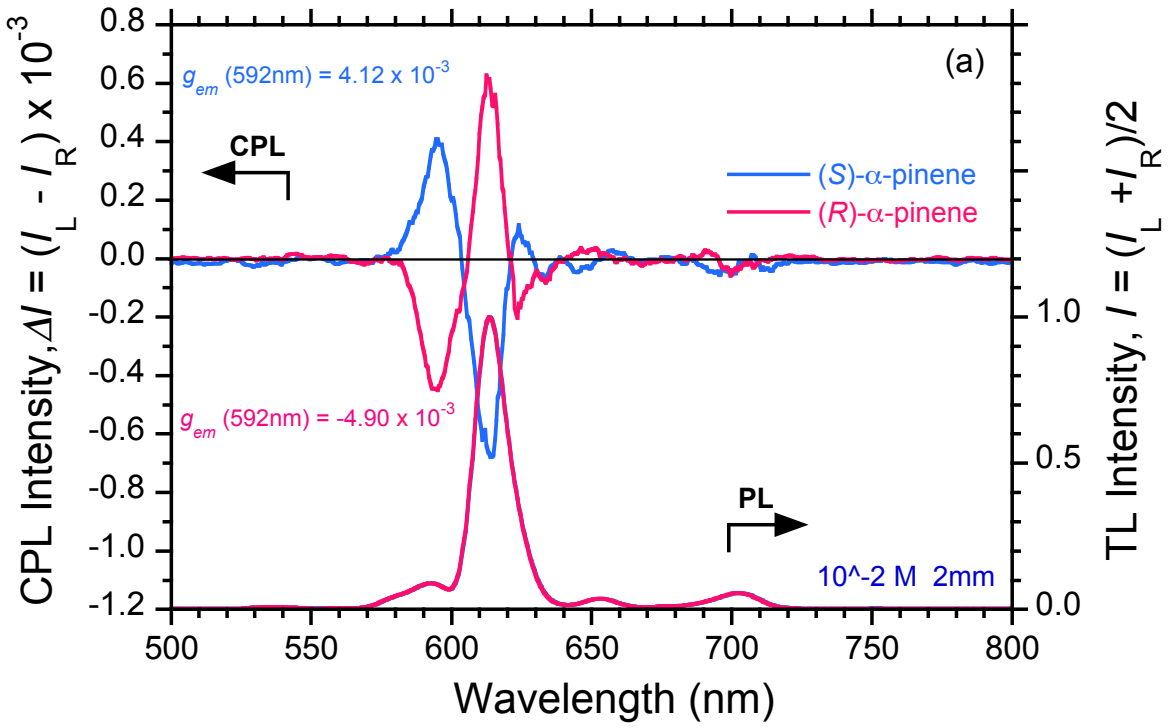
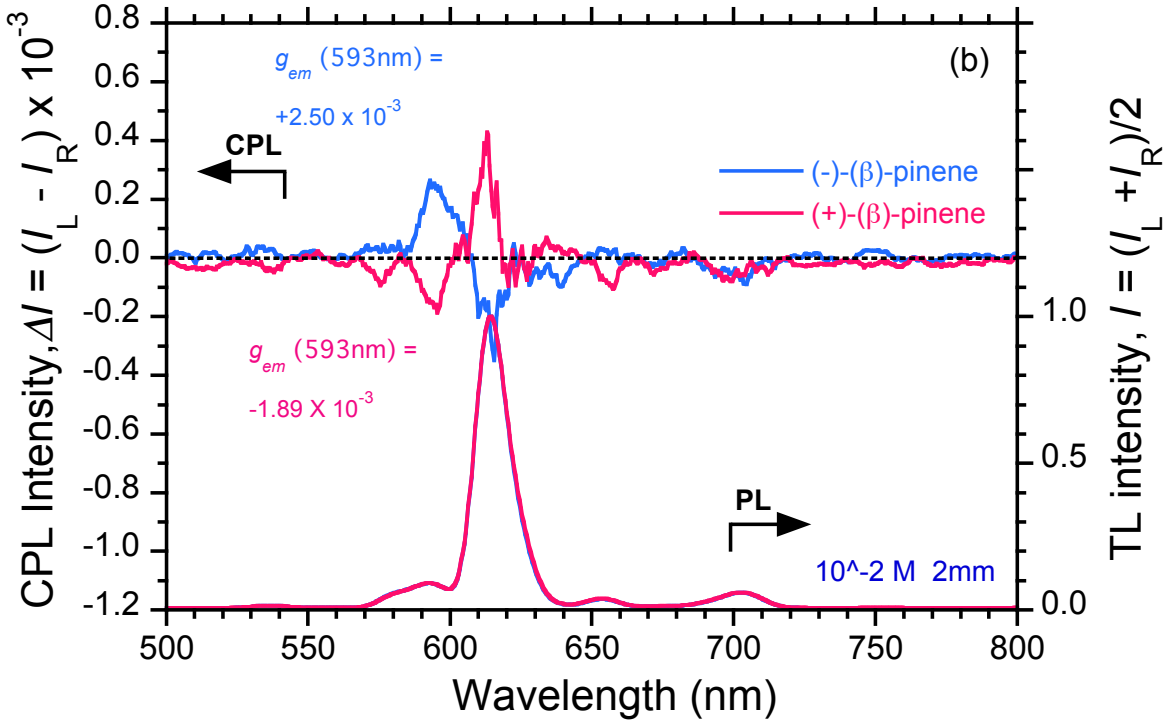

(a)
g_{em} (592nm) = 4.12 x 10^{-3}
CPL
(S)-α-pinene
(R)-α-pinene
g_{em} (592nm) = -4.90 x 10^{-3}
PL
10^-2 M 2mm
CPL Intensity,ΔI = (I_L - I_R) x 10^{-3}
TL Intensity, I = (I_L +I_R)/2
Wavelength (nm)


(b)
g_{em} (593nm) =
+2.50 x 10^{-3}
CPL
(-)-(β)-pinene
(+)-(β)-pinene
g_{em} (593nm) =
-1.89 X 10^{-3}
PL
10^-2 M 2mm
CPL Intensity,ΔI = (I_L - I_R) x 10^{-3}
TL intensity, I = (I_L +I_R)/2
Wavelength (nm)

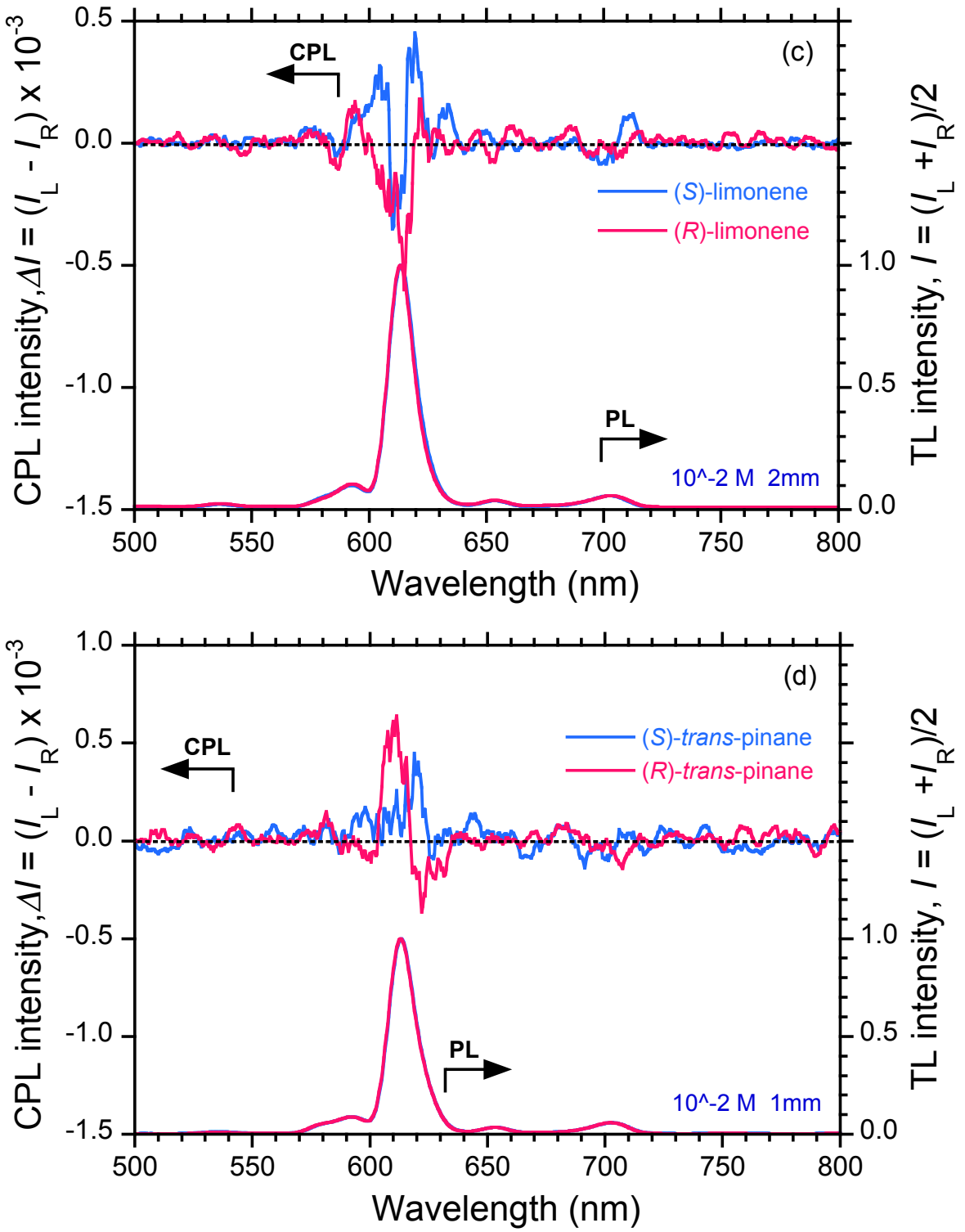


Fig. S1. CPL/PL spectra of $Eu(fod)_3$ dissolved in neat (a) (*S*)-/(*R*)-α-pinene excited at 345 nm, (b) (*S*)-/(*R*)-β-pinene excited at 335 nm, (c) (*S*)-/(*R*)-limonene excited at 335 nm and (d) (*S*)-/(*R*)-*trans*-pinane excited at 330 nm.

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Calculation Method = RMP2-FC
Basis Set = 6-311G
Charge = 0
Spin = Singlet
E(MP2) = -4457.07894629 a.u.
RMS Gradient Norm = a.u.
Imaginary Freq =
Dipole Moment = 11.7577 Debye
Point Group = C3
Job cpu time: 0 days 22 hours 38 minutes 20.5 seconds.

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Basis Set = 6-311G
Charge = 0
Spin = Singlet
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RMS Gradient Norm = a.u.
Imaginary Freq =
Dipole Moment = 6.4797 Debye
Point Group = C1
Job cpu time: 0 days 22 hours 45 minutes 36.9 seconds.

Fig. S2. Brief log data of (top) *fac*- and (bottom) *mer*-Sc(fod)$_3$ as models of *fac*- and *mer*-Eu(fod)$_3$ in a vacuum, obtained with Gaussian 09 (rev.D.01)[S1]

Ref. S1) Gaussian 09, Rev. D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

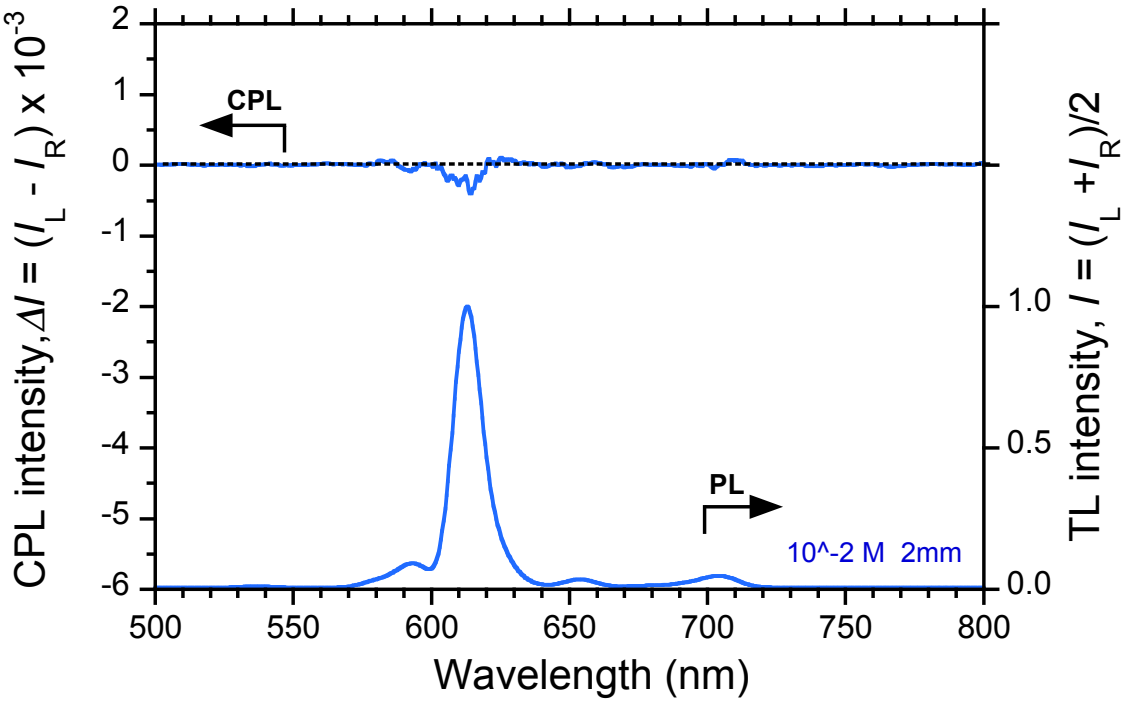


Fig. S3. CPL/PL spectra of $Eu(fod)_3$ in EtOH-free anhydrous chloroform excited at 335 nm.

Table S1. PL quantum yield, ϕ_{PL}, of $Eu(fod)_3$ in EtOH-free dehydrated chloroform, in neat (*S*)-/(*R*)-α-pinene, (*R*)-BINAP (1:1 nominal molar ratio in the chloroform), (*R*)-BINAPO (1:1 nominal molar ratio in the chloroform), (*S*)-BINAPO (1:1 nominal molar ratio in the chloroform).

Solvents	Quantum yield, ϕ_{PL} (%)[S2,S3]	
	$^5D_0 \rightarrow {}^7F_1$ transition	$^5D_0 \rightarrow {}^7F_2$ transition
chloroform	0.3	3.9
(1*S*)-α-pinene	0.3	3.4
(1*R*)-α-pinene	0.2	2.8
(*R*)-BINAP in chloroform	0.1	1.9
(*R*)-BINAPO in chloroform	0.6	7.5
(*S*)-BINAPO in chloroform	0.3	3.9

[S2] A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem., Int. Ed.*, 2007, **46**, 4273–4276.

[S3] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, Heidelberg, 3rd edn, 2006.

The binding constant, *K*, can be obtained from the solution equilibria illustrated below:

$$EuFOD + P^* \overset{K}{\leftrightarrow} EuFOD \bullet P^* \qquad eq\ 1$$

$$K = \frac{[EuFOD \bullet P^*]}{[EuFOD][P^*]} \qquad eq\ 2$$

where

$$[P^*] = [P^*]_0 - [EuFOD \bullet P^*]$$
$$[EuFOD] = [EuFOD]_0 - [EuFOD \bullet P^*] \qquad eq\ 3$$

considering that

$$[P^*]_0 \rangle\rangle [EuFOD]_0 \qquad eq\ 4$$

thus,

$$[P^*] = [P^*]_0 \qquad eq\ 5$$

and *K* can be written as *eq* 6,

$$K = \frac{[EuFOD \bullet P^*]}{([EuFOD]_0 - [EuFOD \bullet P^*])[P^*]} \qquad eq\ 6$$

The definition of g_{em} in concentration is given in *eq* 7,

$$g_{em}(apparent) = \frac{[EuFOD \bullet P^*]}{[EuFOD] + [EuFOD \bullet P^*]} \text{ x } g_{em}(EuFOD100\%)[EuFOD \bullet P^*] \qquad eq\ 7$$

since

$$[EuFOD]_0 = [EuFOD] + [EuFOD \bullet P^*] \qquad eq\ 8$$

the equation can be rewritten as *eqs* 9,

$$\frac{g_{em}(apparent)}{g_{em}(EuFOD100\%)}[EuFOD \bullet P^*]^{-1} = \frac{[EuFOD \bullet P^*]}{[EuFOD]_0} \qquad eq\ 9$$

From *eqs* 6 and 9, it can be arranged to *eq*10,

$$\frac{g_{em}(apparent)}{g_{em}(EuFOD100\%)}[EuFOD \bullet P^*]^{-1} = \frac{1}{\mathrm{K}[P^*]} + 1 \qquad eq\ 10$$

The fitting of *eq* 10 to the plots in Fig. 3 gives the *K* values when 1/[EuFOD•*P**] versus 1/[P*] is plotted. The calculated binding constants, *K* values, given by the fitting of the plots of Eu(fod)$_3$ in both (*S*)- and (*R*)-α-pinene are as low as ≈ 10^{-3}.

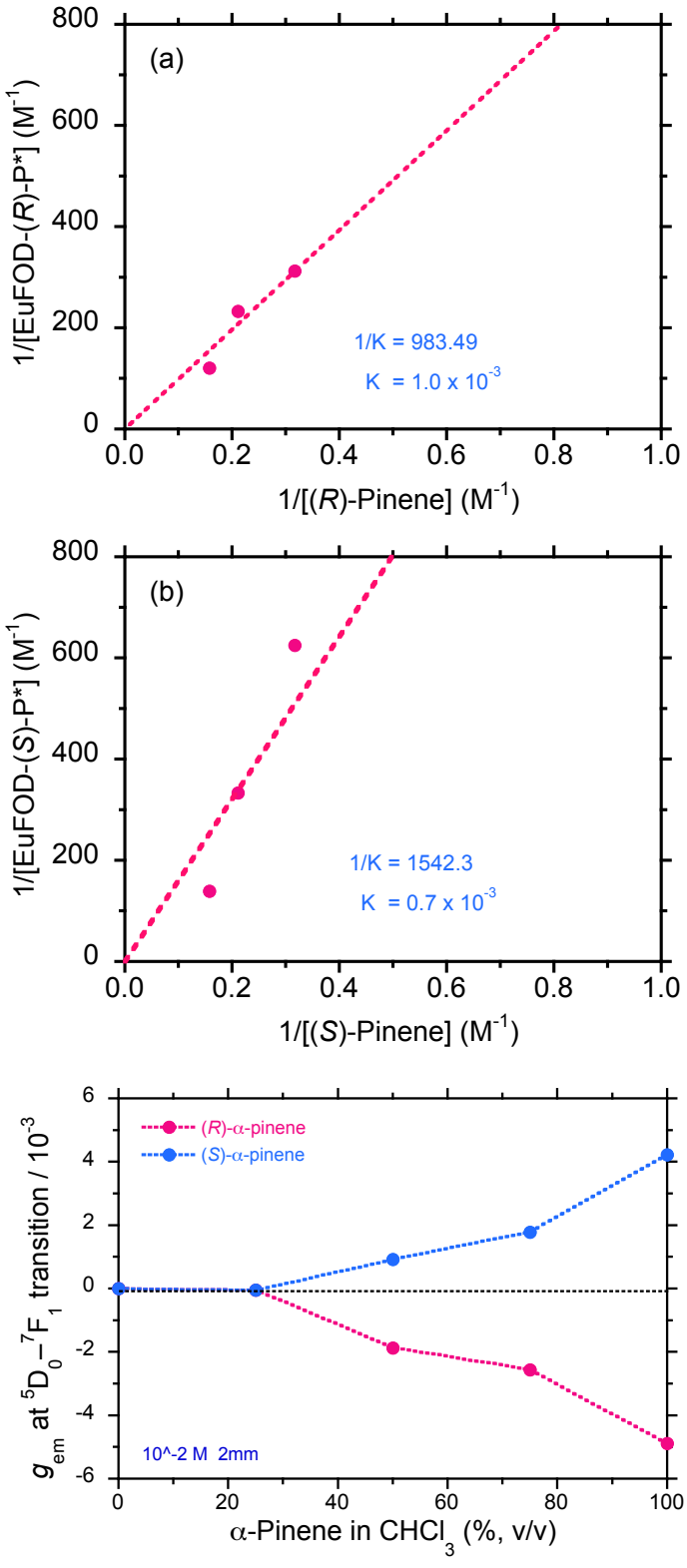


Fig. S4. The fitting plots of 1/[Eu(fod)$_3$//α-pinene] M^{-1} *versus* (a) 1/[(*R*)-α-pinene] in M^{-1} and (b) 1/[(*S*)-α-pinene] in M^{-1} associated with (c) the g_{em} value at 593 nm as a function of volume fraction of α-pinene in EtOH-free anhydrous chloroform.

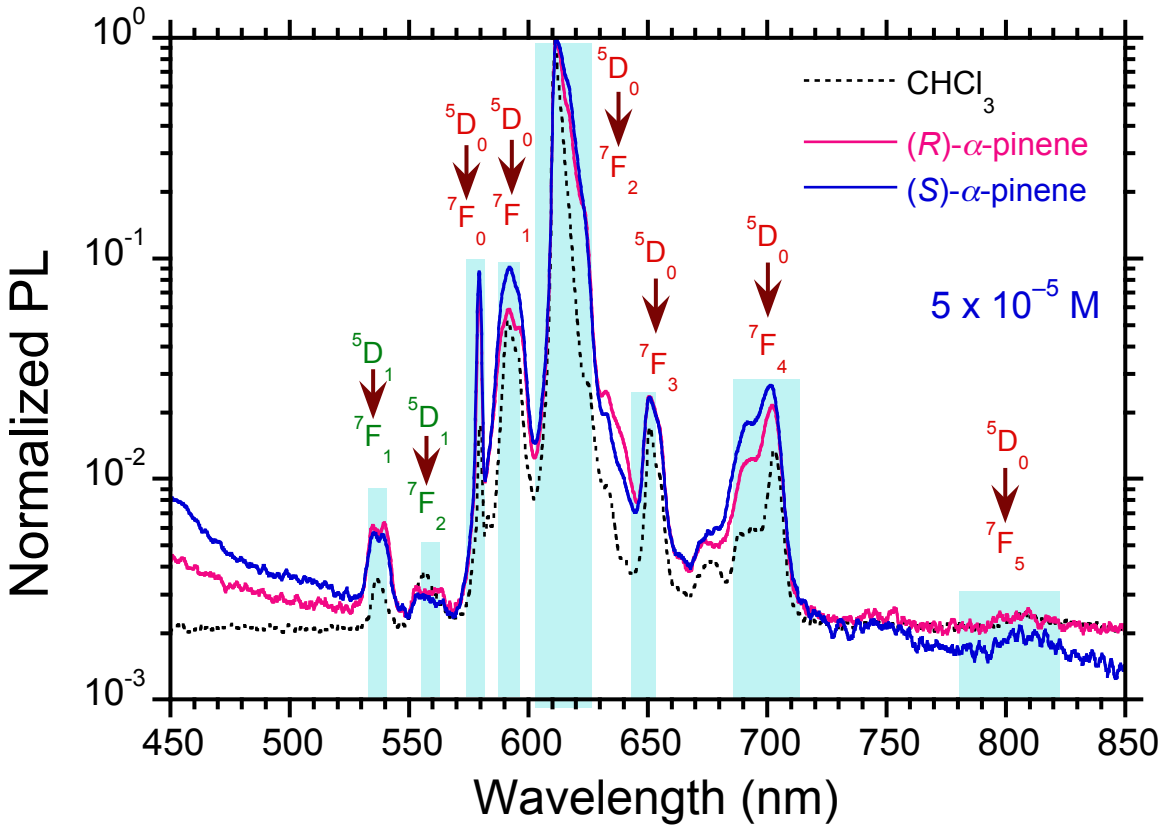


Fig. S5. Semilog plot of the PL spectra of $Eu(fod)_3$ in chloroform (λ_{ex} 278 nm; 5.0×10^{-6} M) and in (*S*)-/(*R*)-α-pinene (λ_{ex} 317 nm; 5.0×10^{-5} M). Measurement conditions: 10 nm bandwidth for excitation; 1 nm bandwidth for emission; PMT in high-sensitivity mode; 1 second response time; 0.2 nm data interval; and one scan collected at a rate of 100 nm min^{-1}. Under these conditions, no stray light (556 nm and 634 nm) from the two gratings of the spectrometer and Raman band Stokes line (≈ 3000 cm^{-1}) by the chloroform solvent was observed.

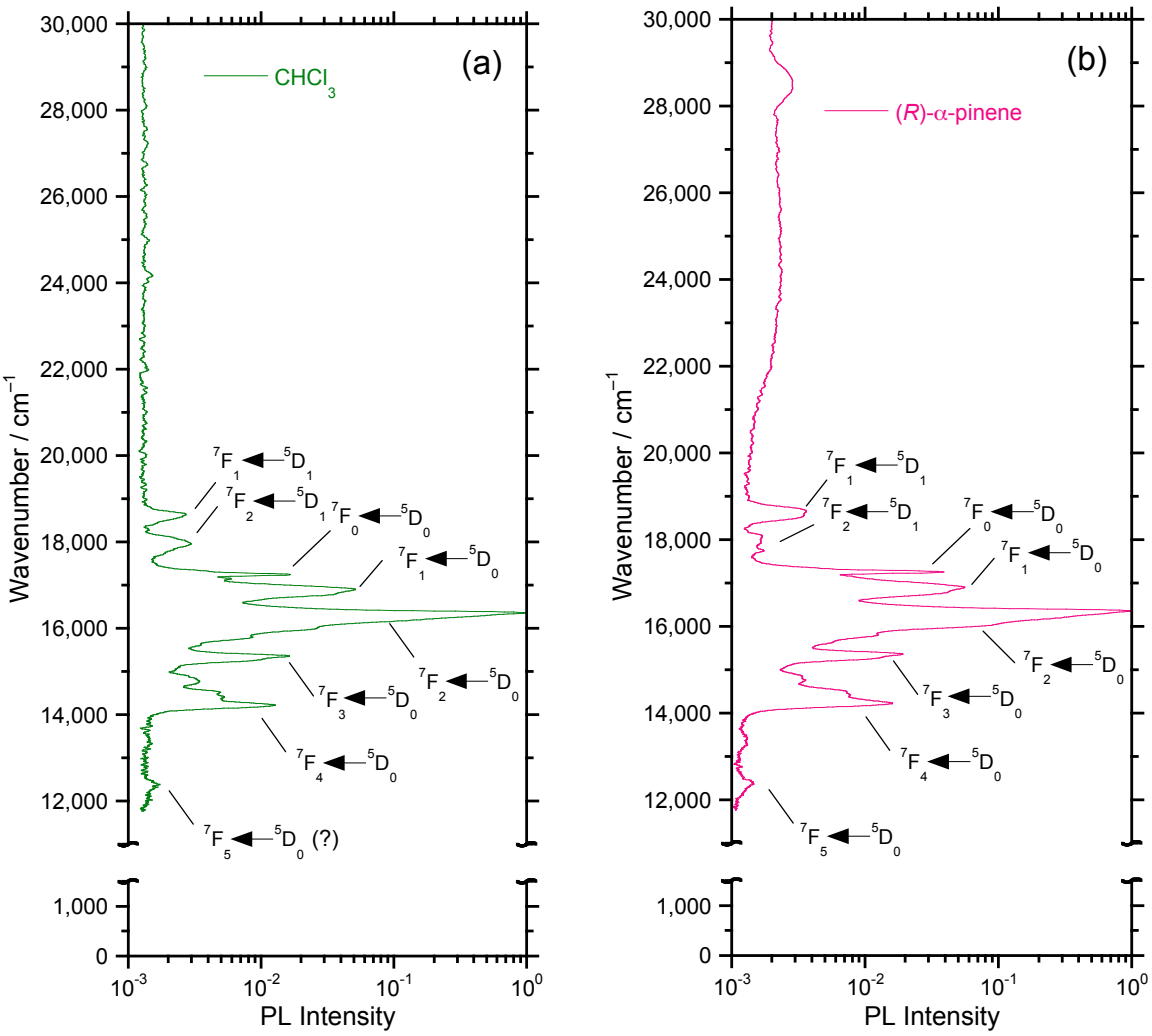


Fig. S6. PL spectra (in cm^{-1}) of $Eu(fod)_3$ in (a) chloroform (λ_{ex} 278 nm, 35,970 cm^{-1}) and (b) in neat (*R*)-α-pinene (l_{ex} 317 nm, 31,450 cm^{-1}). In (b), the small bump at 28,400 cm^{-1} is attributed to the Raman C–H vibration band of α-pinene. All data were taken from Fig. S5.

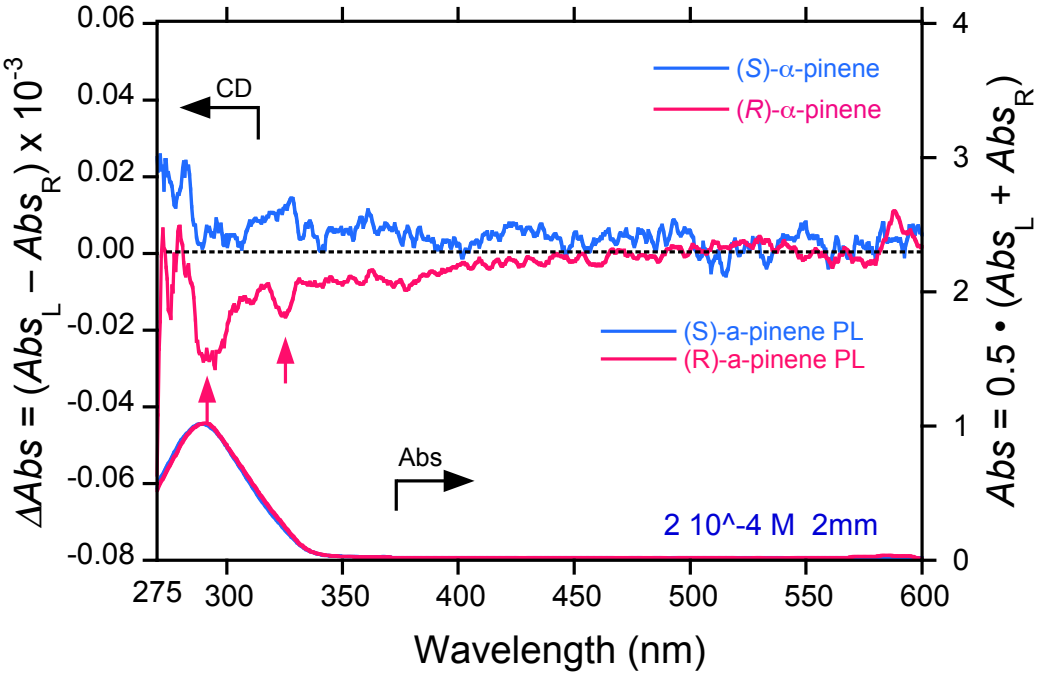


Fig. S7. CD and UV-vis spectra of Eu(fod)$_3$ in neat (*S*)-/(*R*)-α-pinene at 2.0×10^{-4} M (path length: 2.0 mm) obtained by subtracting the spectra of (*S*)-/(*R*)-α-pinene.

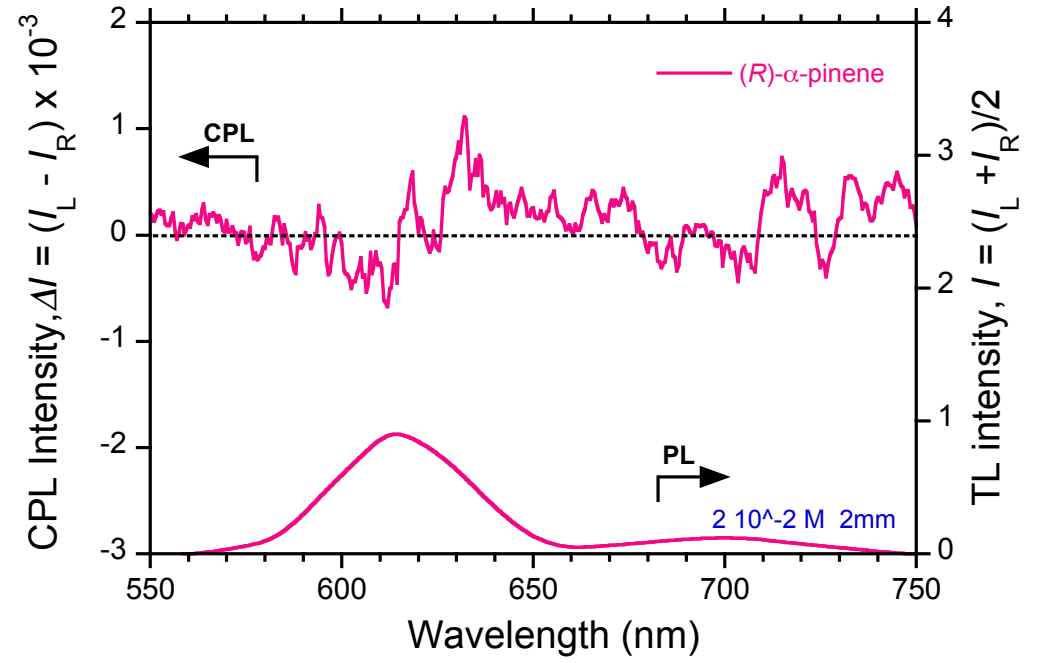


Fig. S8. CPL/PL spectra of Eu(dpm)$_3$ dissolved in neat (*S*)-/(*R*)-α-pinene excited at 345 nm (2.0×10^{-2} M, path length: 2.0 mm).

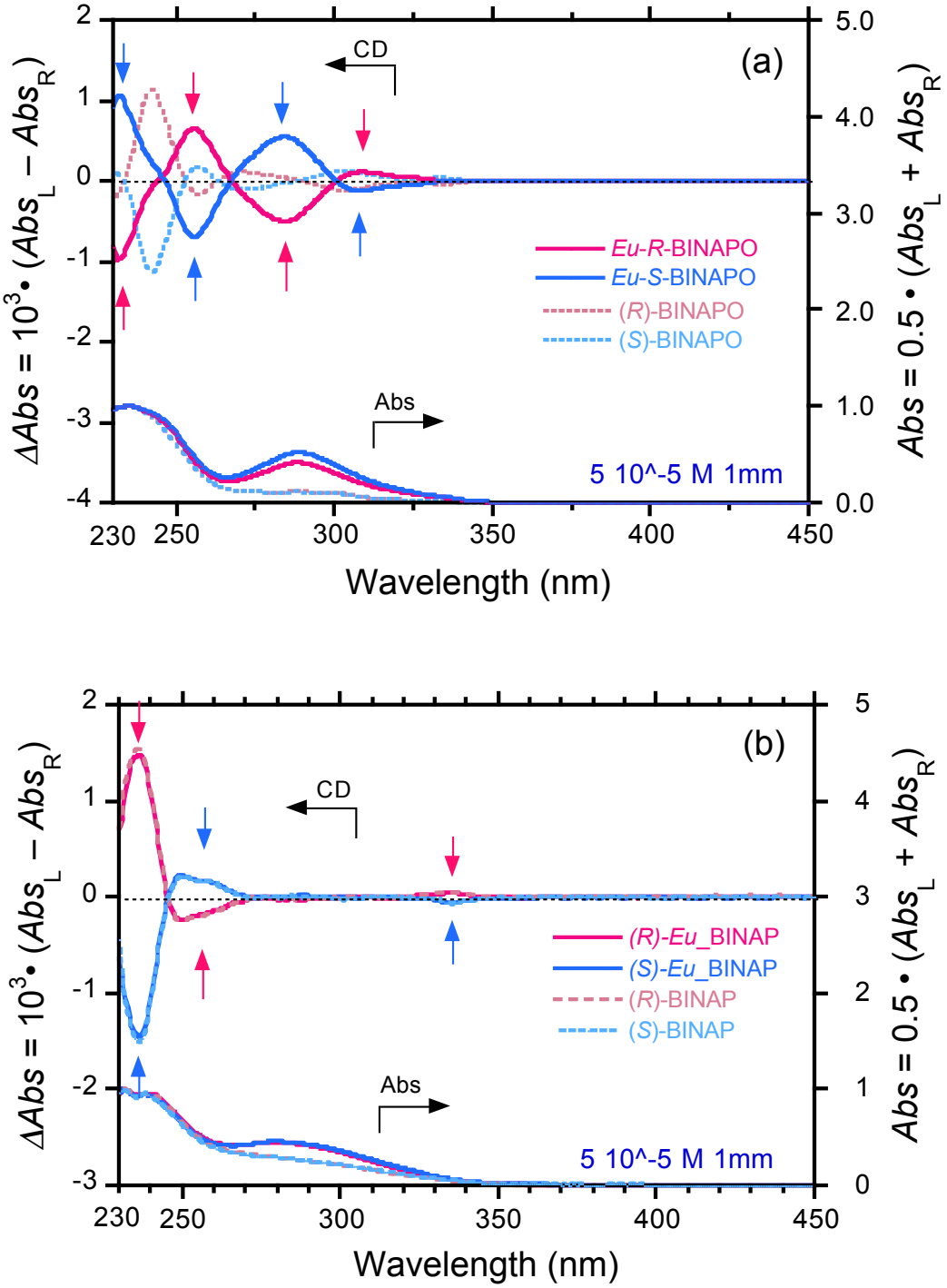


Fig. S9. CD and UV-vis spectra of (a) Eu(fod)$_3$ with (*S*)-/(*R*)-BINAPO (1:1) and (b) (*S*)-/(*R*)-BINAP (1:1) at 5.0 × 10^{-5} M (path length: 1.0 mm).

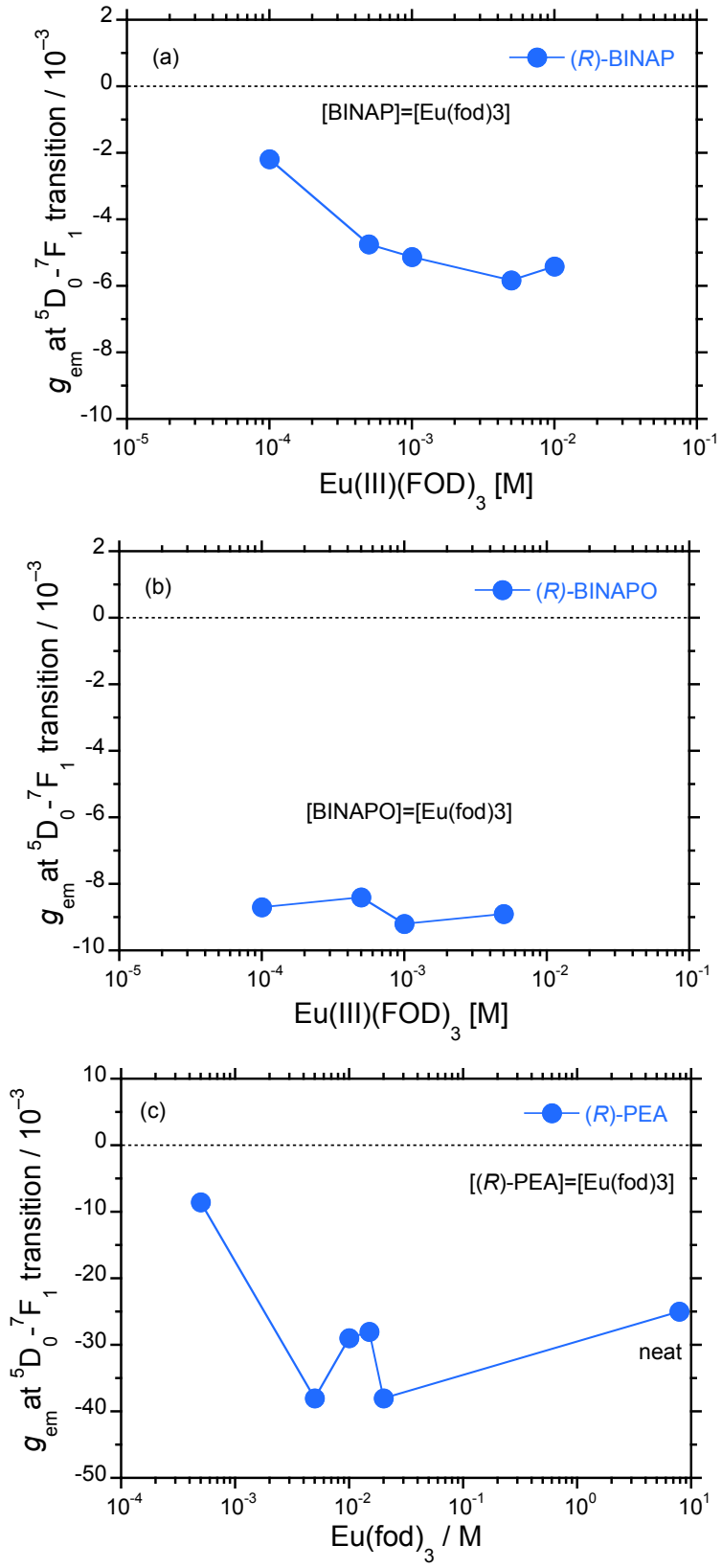


Fig. S10. Variation in the g_{em} values at the $^5D_0 \rightarrow {}^7F_1$ transition of $Eu(fod)_3$ as a function of (a) (*R*)-BINAP (1:1) and (b) (*R*)-BINAPO (1:1) ranging from $[Eu(fod)_3]_0 = 10^{-4}$ and 10^{-2} M. (c) $Eu(fod)_3$ in (*R*)-PEA at concentrations ranging from $[Eu(fod)_3]_0 = 5 \times 10^{-4}$ and 7.86 (neat) M.

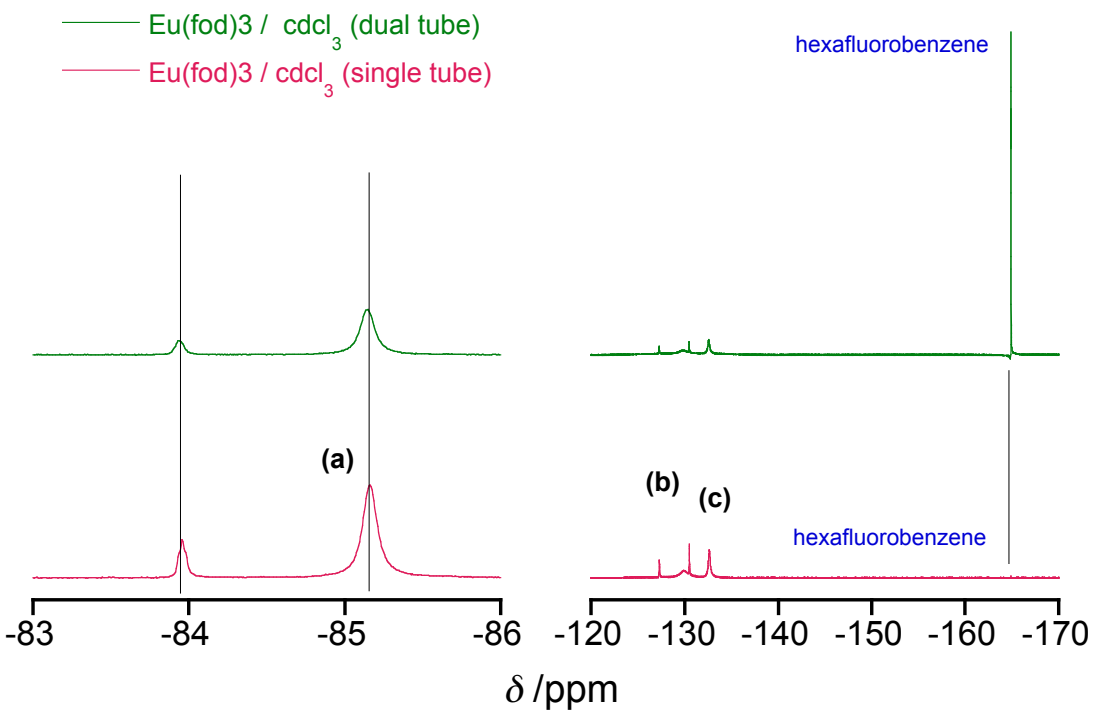


Fig. S11. Comparison of the ^{19}F-NMR spectra of Eu(fod)$_3$ in $CDCl_3$ and hexafluorobenzene (HFB) as a reference by using a single NMR tube and using a reference insert tube.

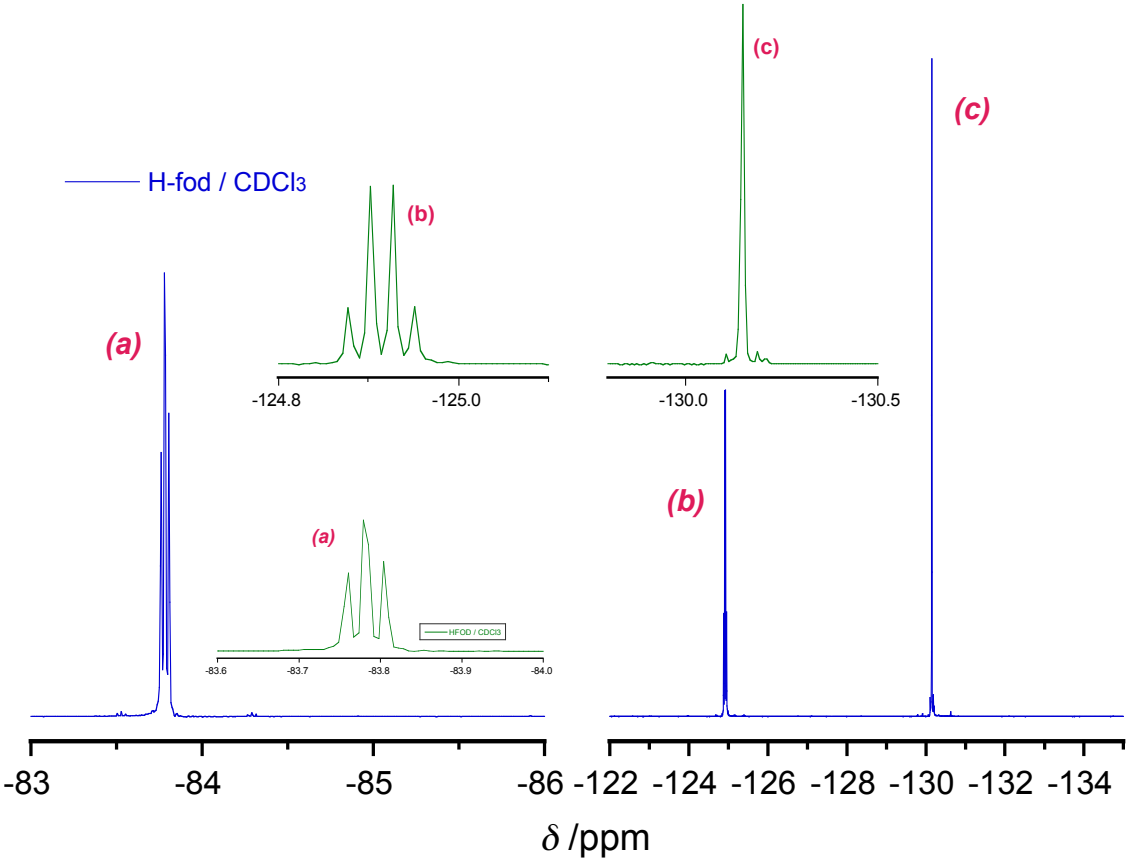


Fig. S12. ^{19}F-NMR spectra and magnified regions of H-fod in $CDCl_3$.

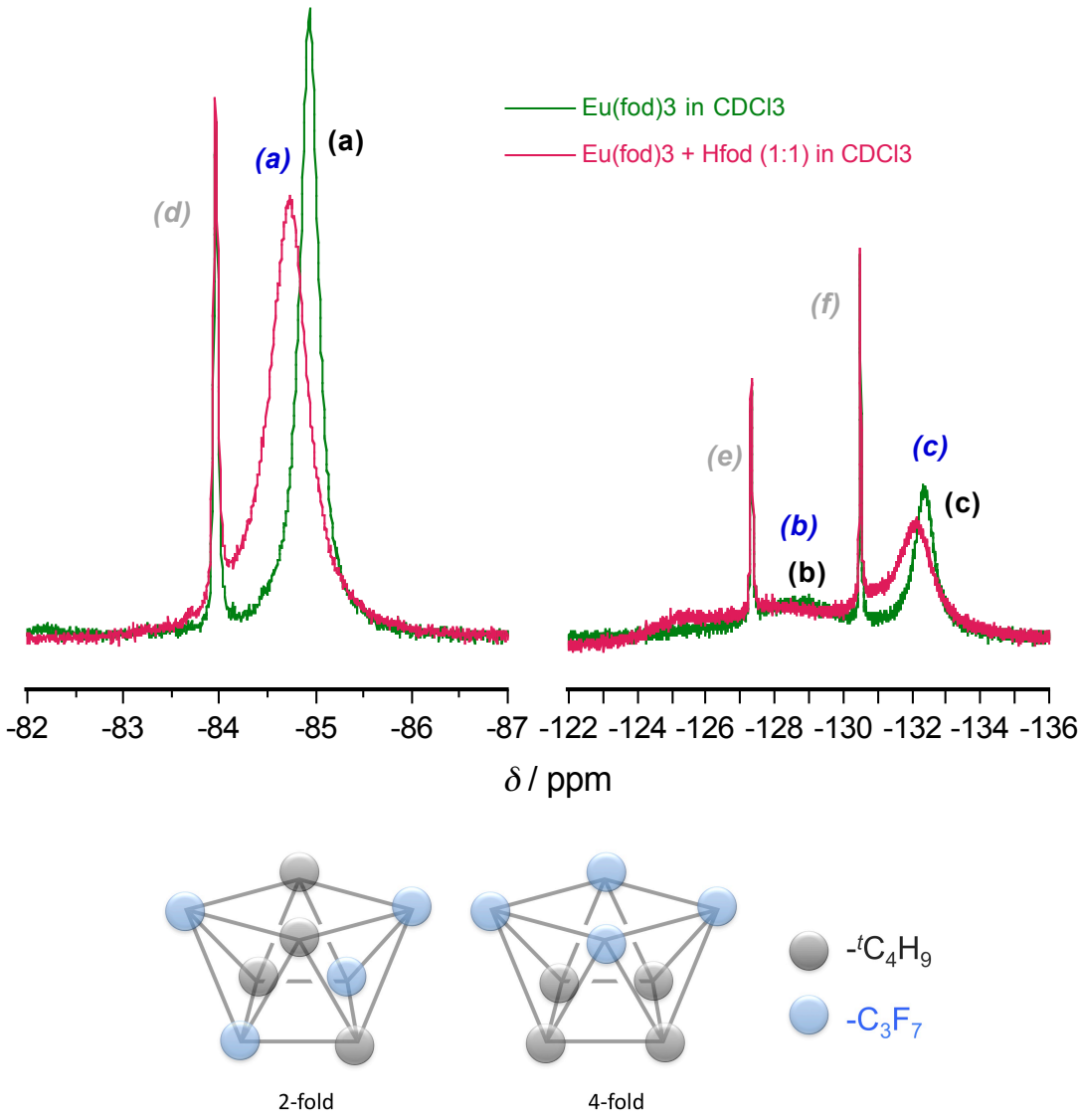


Fig. S13. ^{19}F-NMR spectra of Eu(fod)$_3$ with H-fod (1:1 molar ratio) in $CDCl_3$ and proposed square anti-prism (SAP)-like geometries (bottom left; pseudo-2-fold and bottom right; pseudo-4-fold symmetry) of $Eu^{3+}(fod^{-})_4$ with H^+.

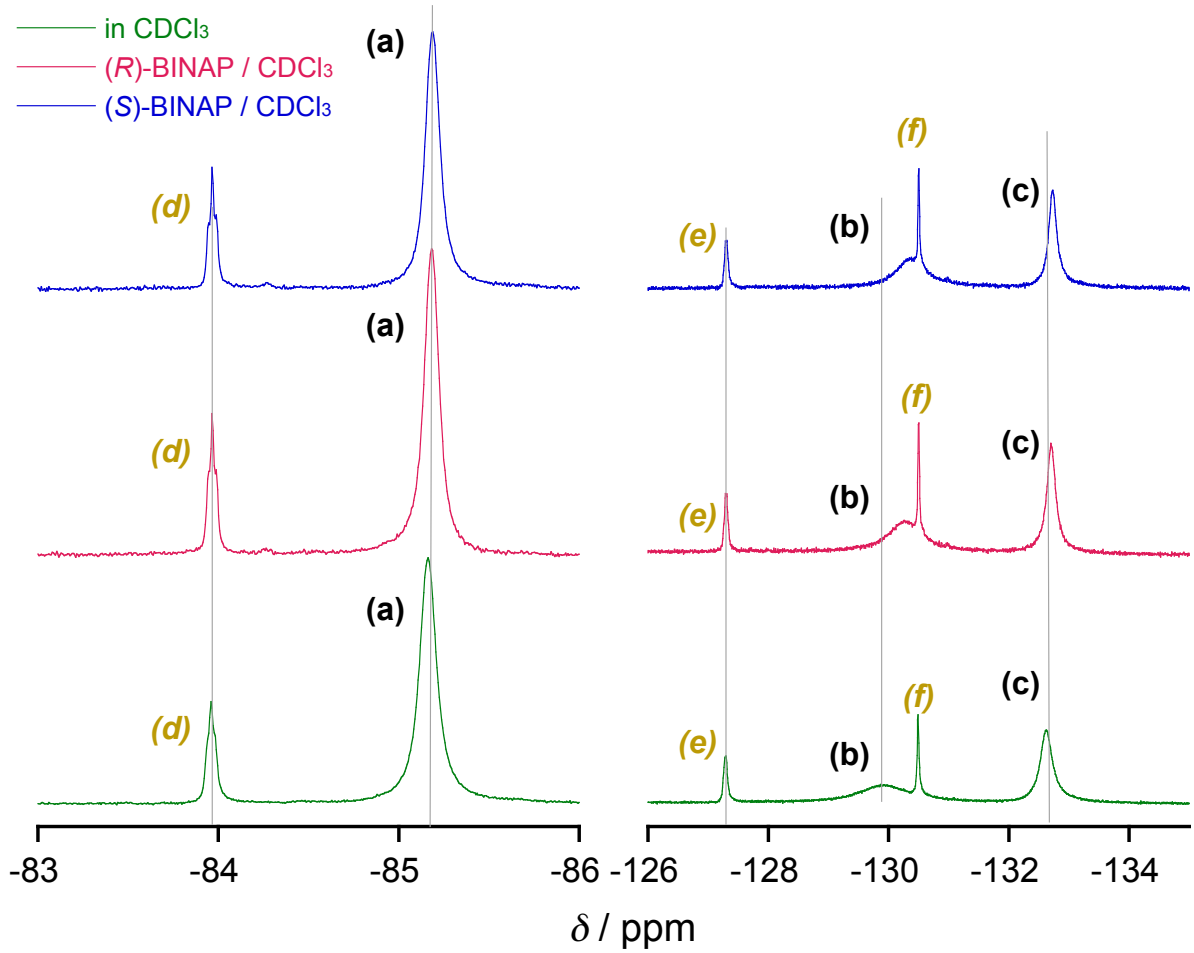


Fig. S14. A comparison of the ^{19}F-NMR spectra of Eu(fod)$_3$ with (*S*)-BINAP (1:1, green line) and (*R*)-BINAP (1:1, red line) and without BINAP (green line) in $CDCl_3$. HFB was used as an internal standard in the same NMR tube.

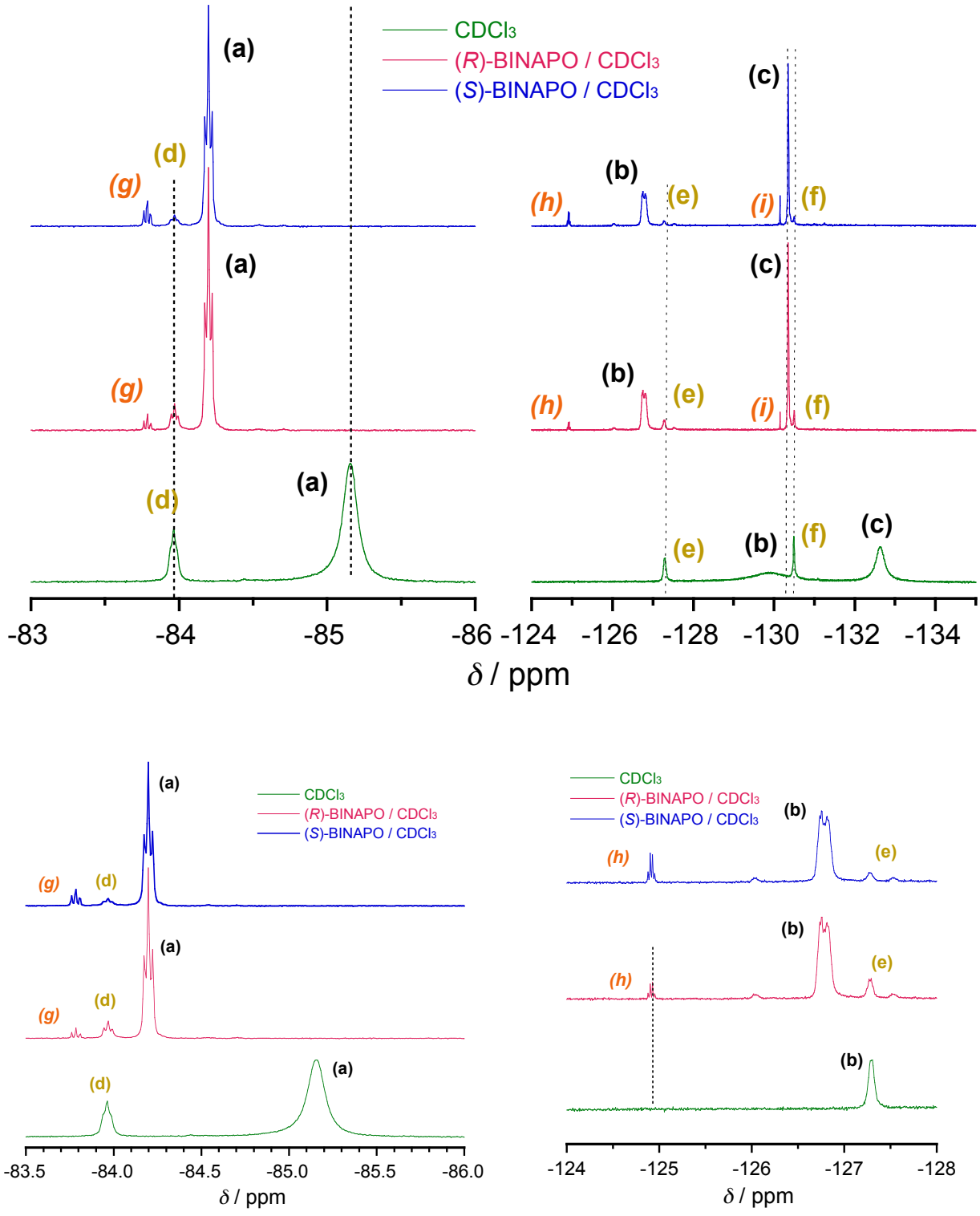


Fig. S15. A comparison of the ^{19}F-NMR spectra and magnified regions of the spectra of Eu(fod)$_3$ with (*S*)-BINAPO (1:1, green line) and (*R*)-BINAP (1:1, red line) and without BINAPO (green line) in $CDCl_3$. HFB was used as an internal standard in the same NMR tube.

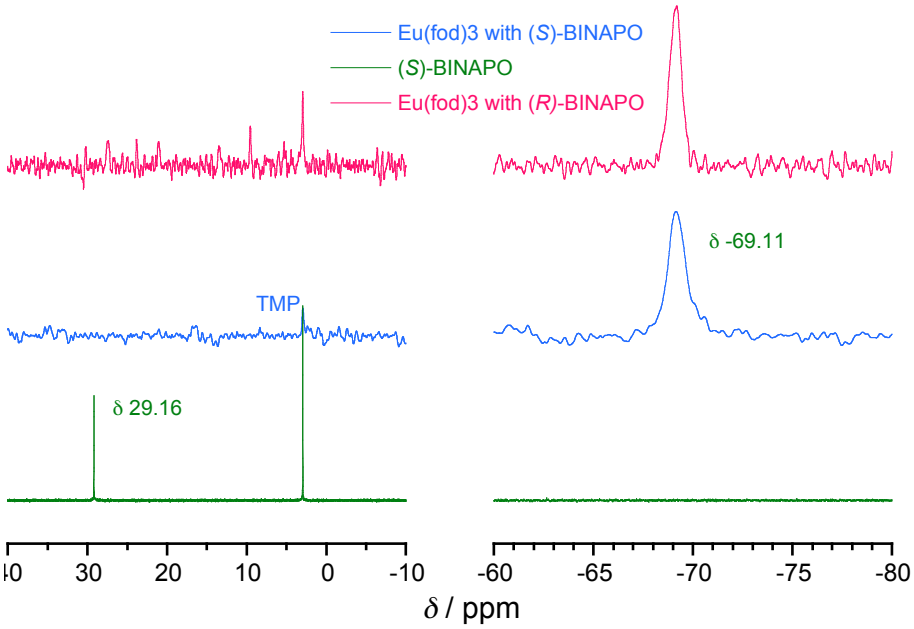


Fig. S16. $^{31}P\{^{1}H\}$-NMR spectra of (*S)*-BINAPO (green line), Eu(fod)$_3$ with (*S)*-BINAPO (1:1, blue line) and Eu(fod)$_3$ with (*R)*-BINAPO (1:1, red line) in $CDCl_3$. TMP was used as an internal standard in the same NMR tube for (*S)*-BINAPO and a reference insert was used for samples containing Eu(fod)$_3$.

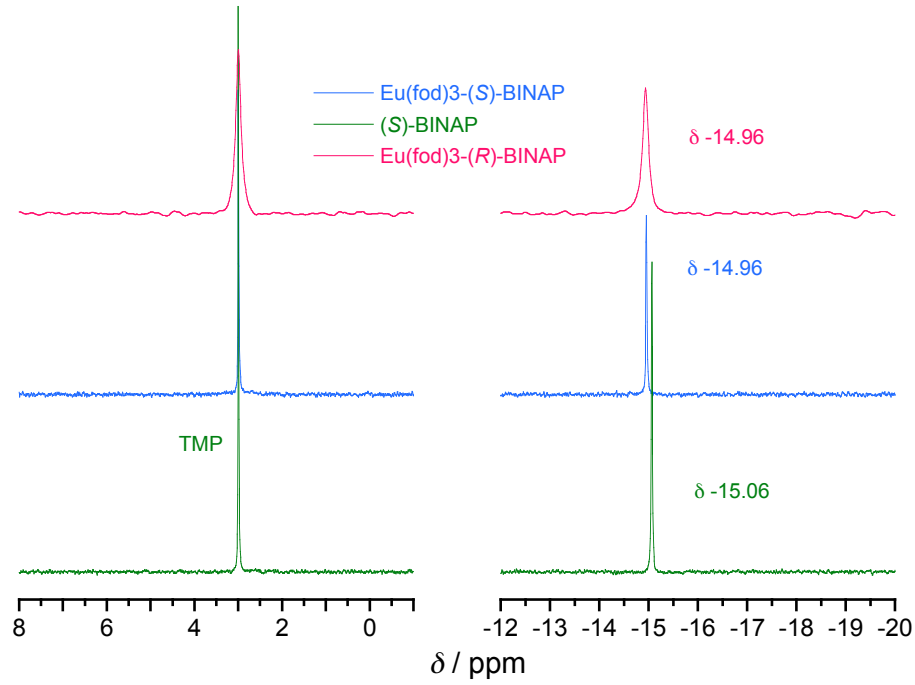


Fig. S17. $^{31}P\{^{1}H\}$-NMR spectra of (*S)*-BINAP (green line), Eu(fod)$_3$ with (*S)*-BINAP (1:1) in $CDCl_3$ (blue line) and (*R)*-BINAP (1:1) in $CDCl_3$ (red line). TMP was used as an internal standard in the same NMR tube for (*S)*-BINAP and a reference insert was used for samples containing Eu(fod)$_3$.

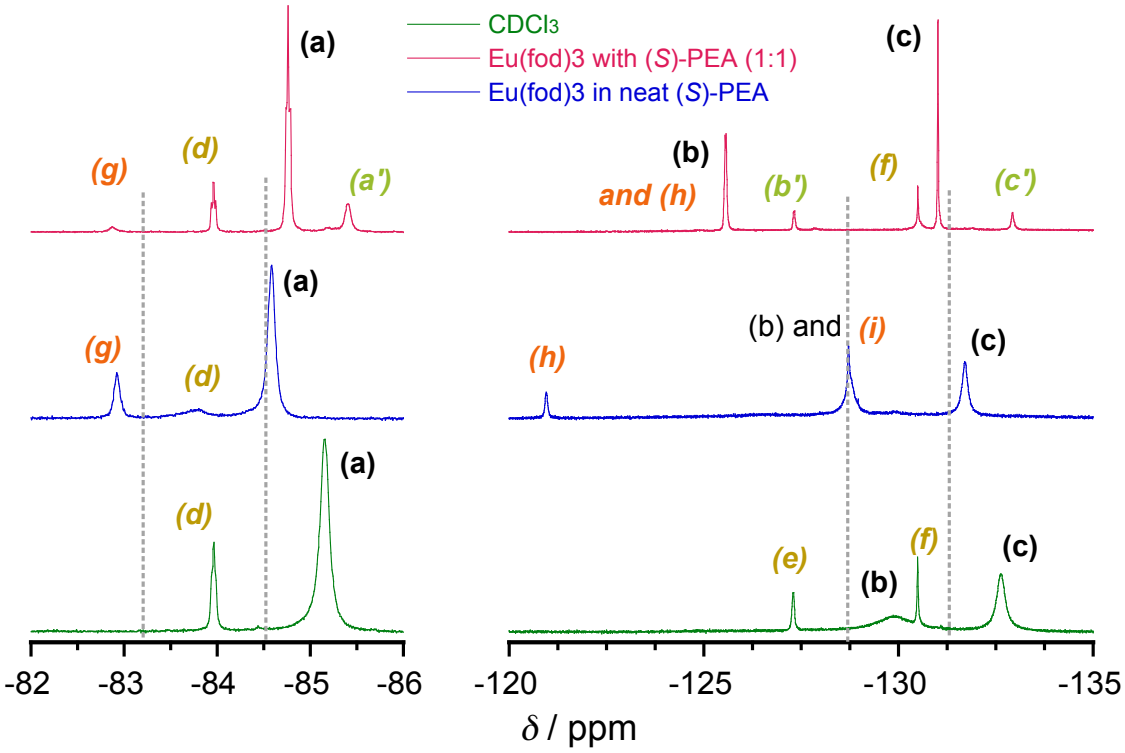


Fig. S18. A comparison of the ^{19}F-NMR spectra and magnified regions of the spectra of Eu(fod)$_3$ in neat (*S*)-PEA (blue line), with (*R*)-PEA (1:1, red line) in $CDCl_3$ and in pure $CDCl_3$ (green line). HFB was used as an external standard in a reference insert for neat solvent spectra, and as an internal standard for the sample in $CDCl_3$.

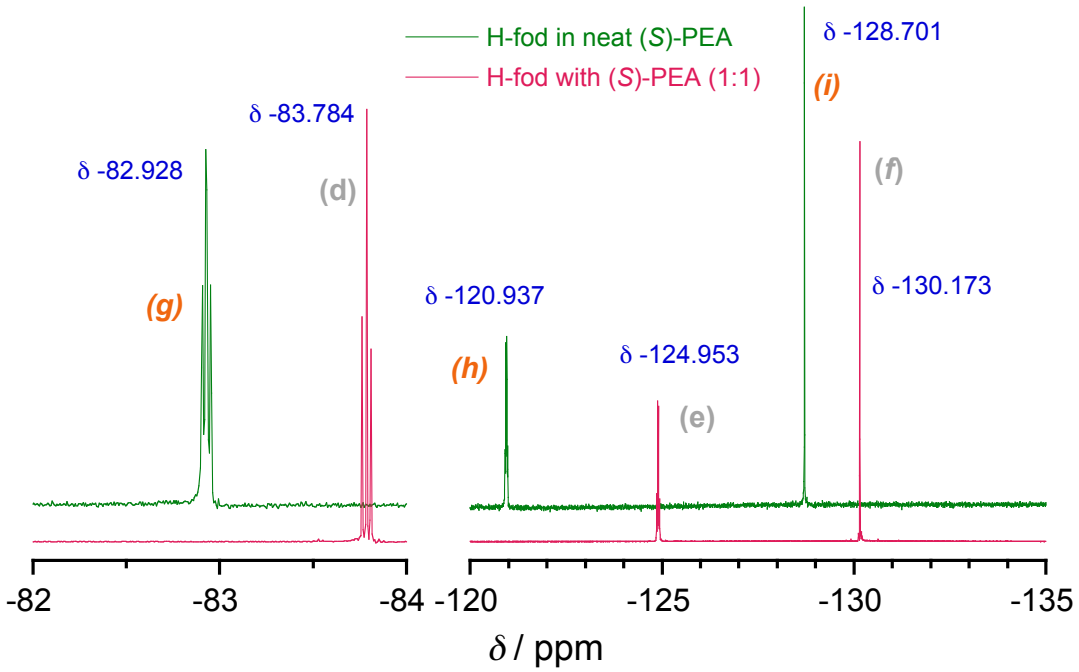


Fig. S19. A comparison of the ^{19}F-NMR spectra of H-fod in neat (*S*)-PEA (green line) and with (*S*)-PEA (1:1, red line) in $CDCl_3$. HFB was used as an external standard in a reference insert for neat solvent spectra, and as an internal standard for the sample in $CDCl_3$.

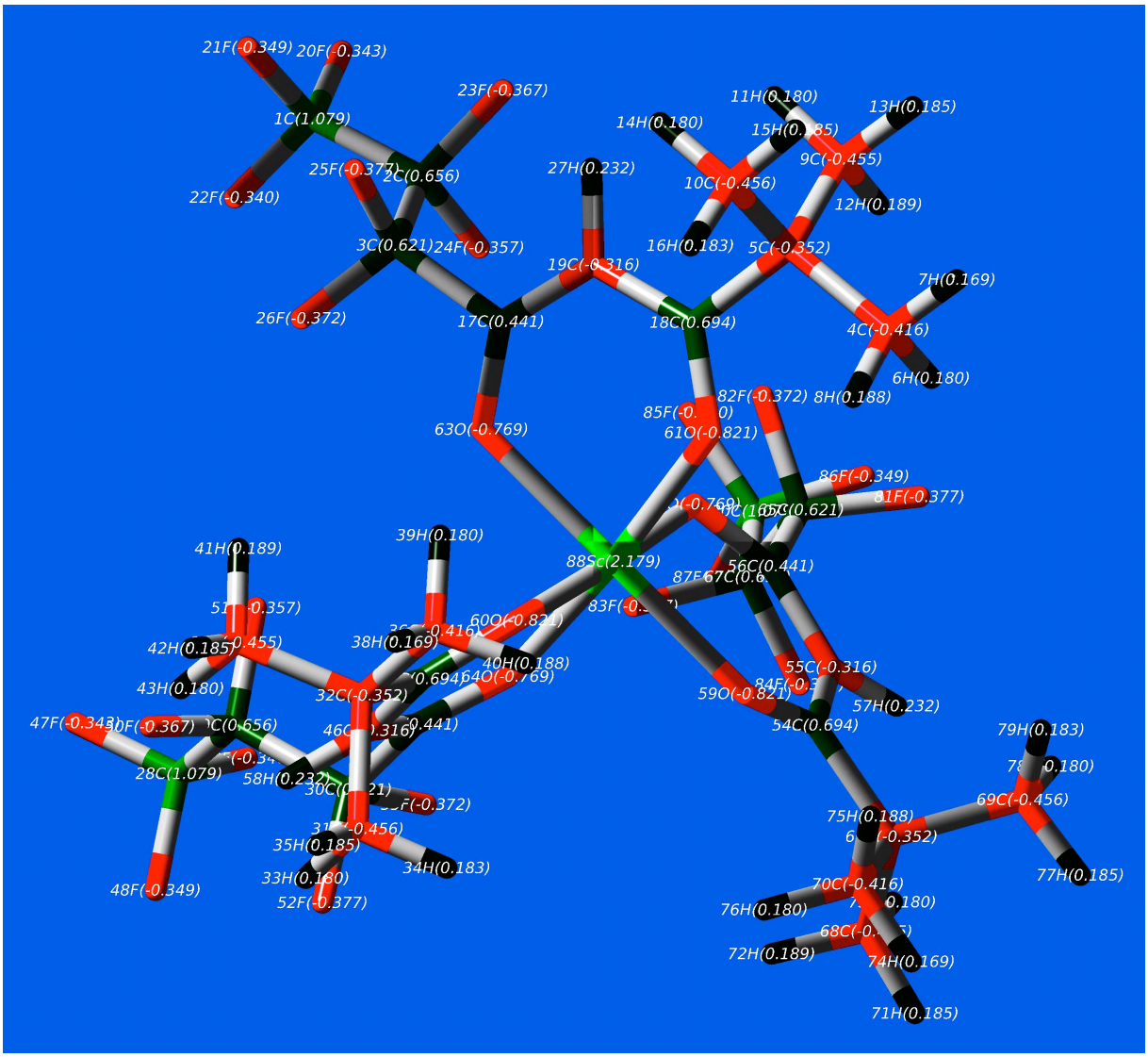


Fig. S20. Mulliken charge distribution of *fac*-Sc(fod)$_3$ obtained with MP2 (6-311G).

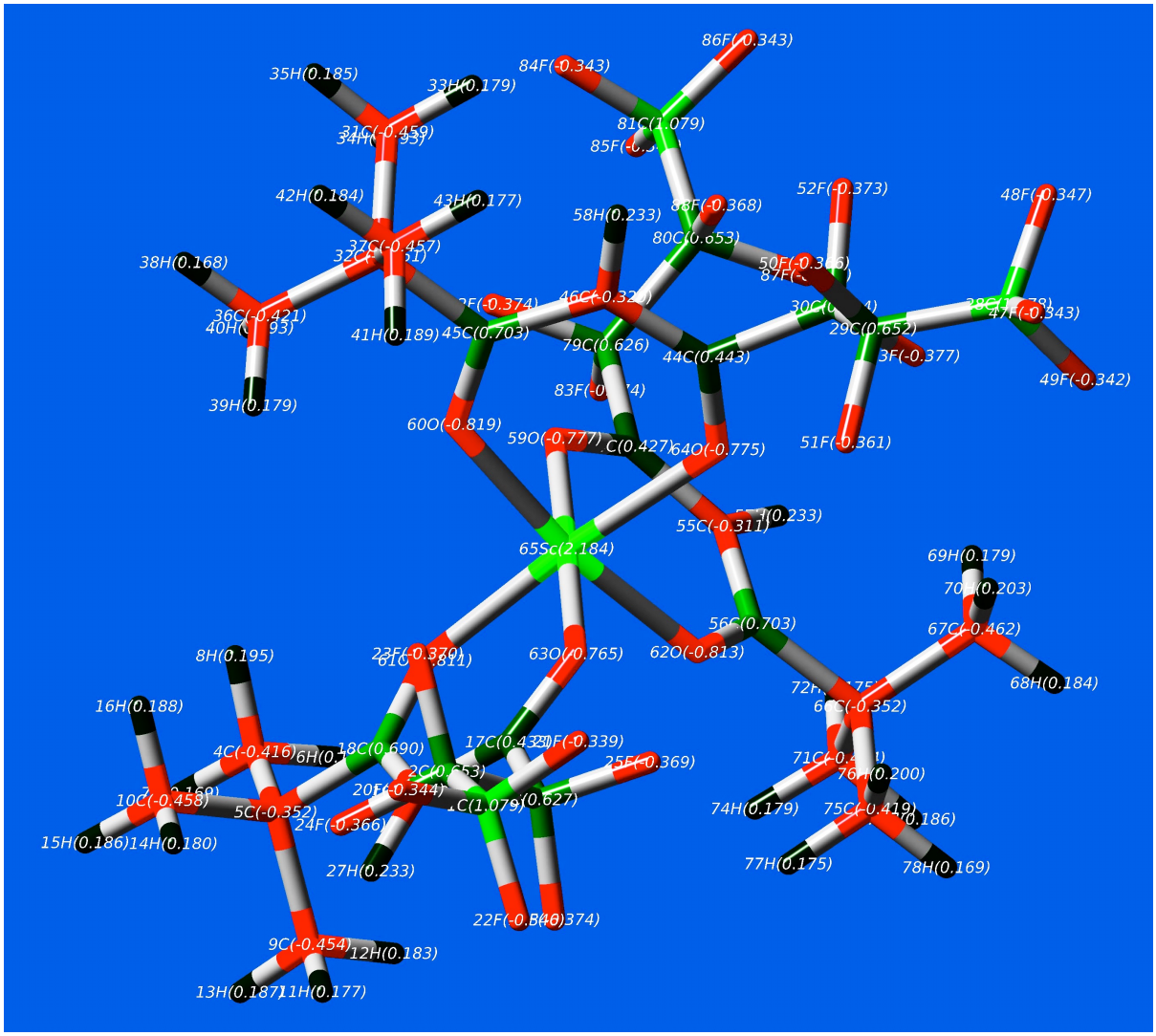


Fig. S21. Mulliken charge distribution of *mer*-Sc(fod)$_3$ obtained with MP2 (6-311G).

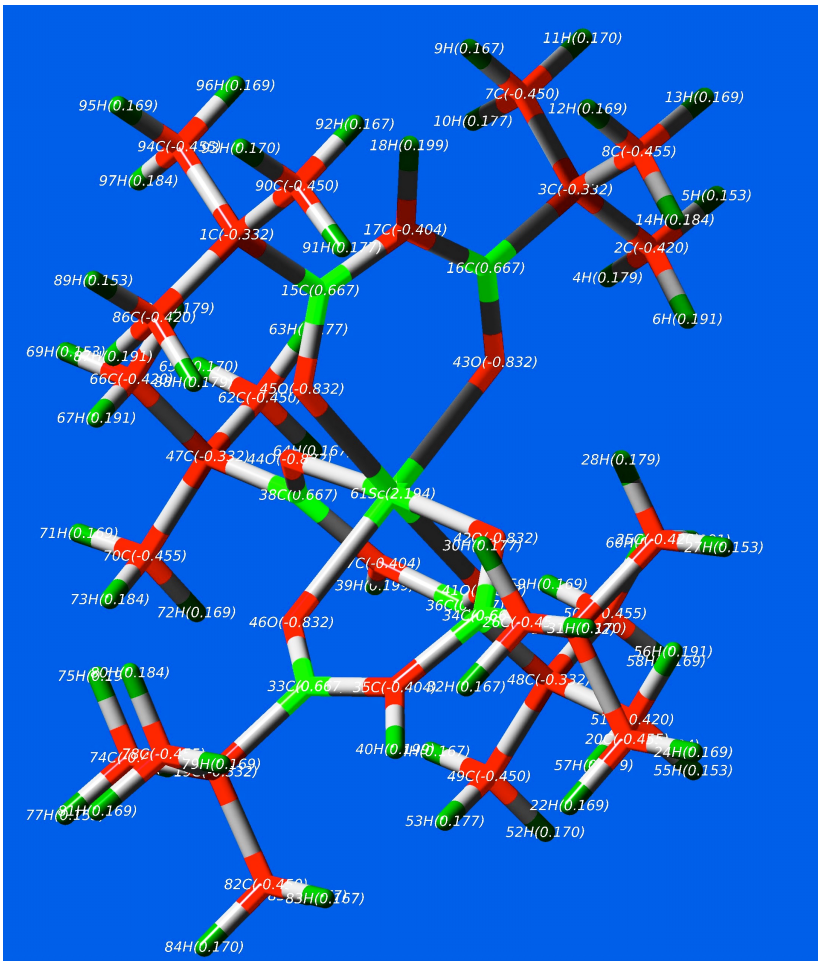


Fig. S22. Mulliken charge distribution of $Sc(dpm)_3$ obtained with MP2 (6-311G).

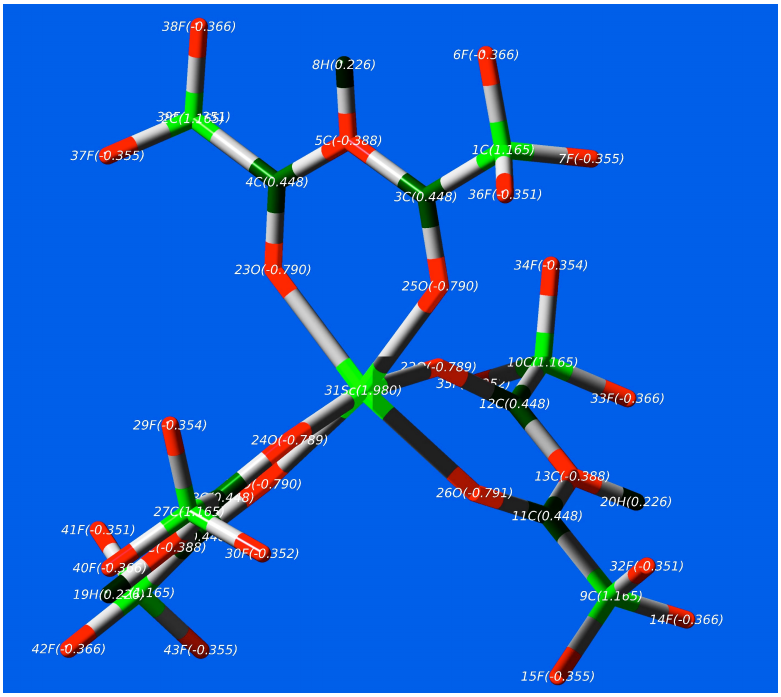


Fig. S23. Mulliken charge distribution of $Sc(hfa)_3$ obtained with MP2 (6-311G).

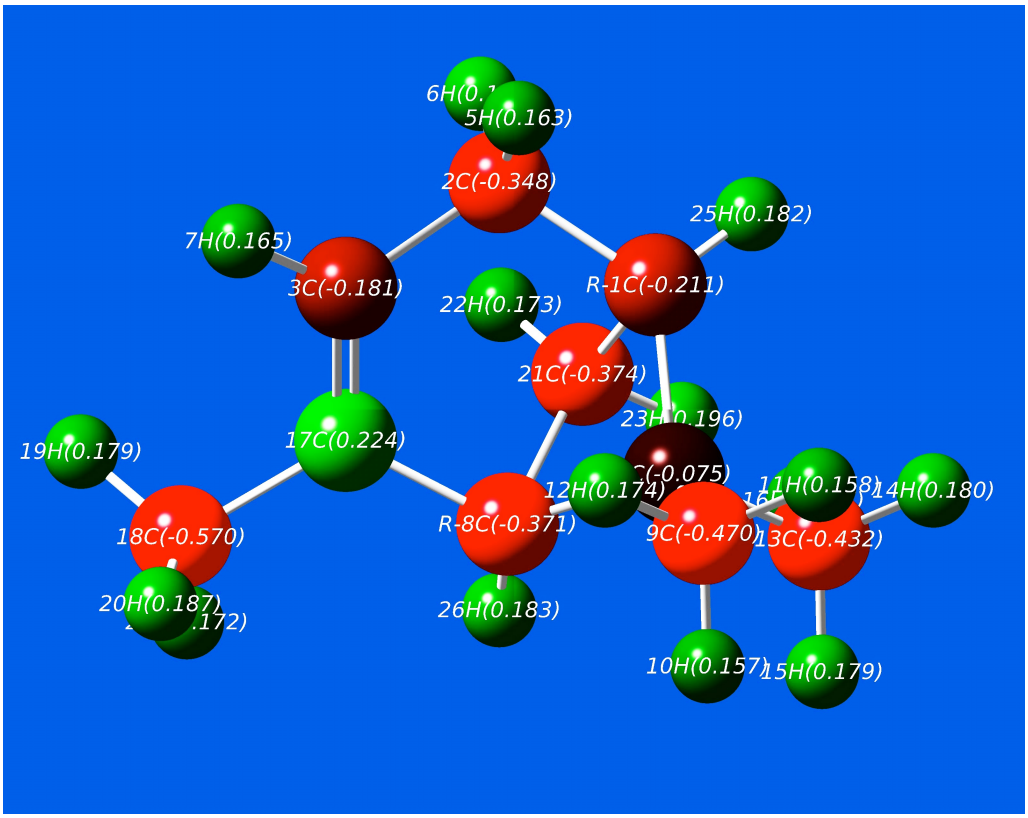


Fig. S24. Mulliken charge distribution of (*R*)-α-pinene obtained with MP2 (6-311G).

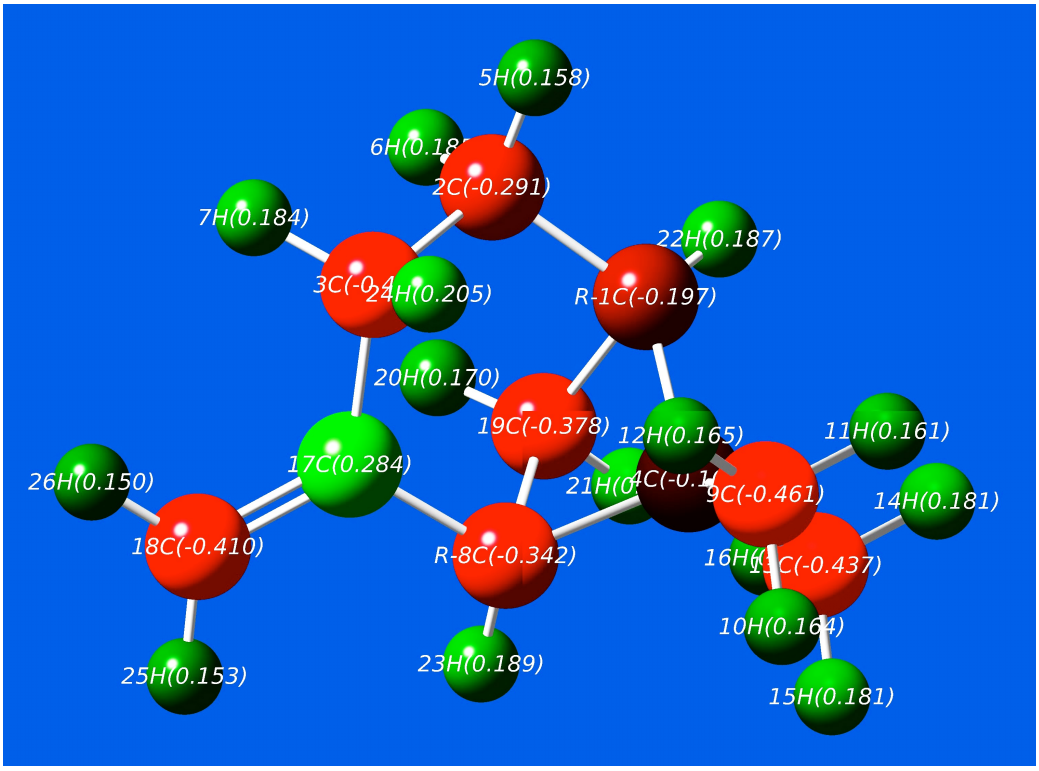


Fig. S25. Mulliken charge distribution of (*R*)-β-pinene obtained with MP2 (6-311G).

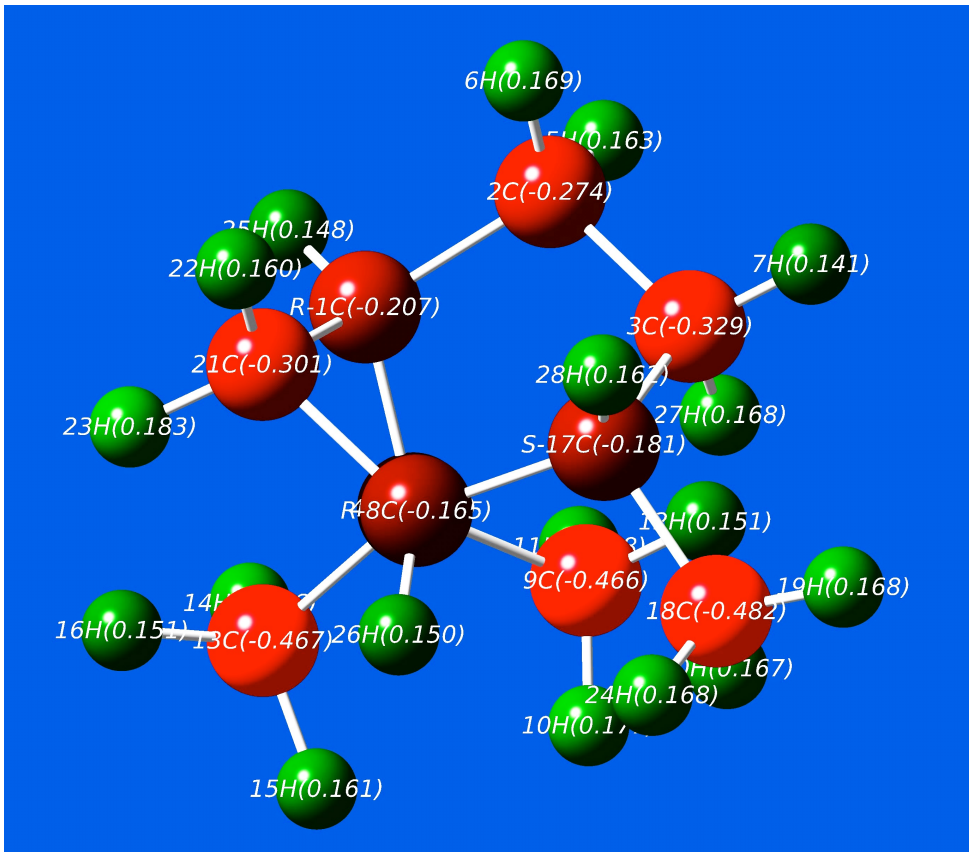


Fig. S26. Mulliken charge distribution of (*R*)-*trans*-pinane obtained with MP2 (6-311G).

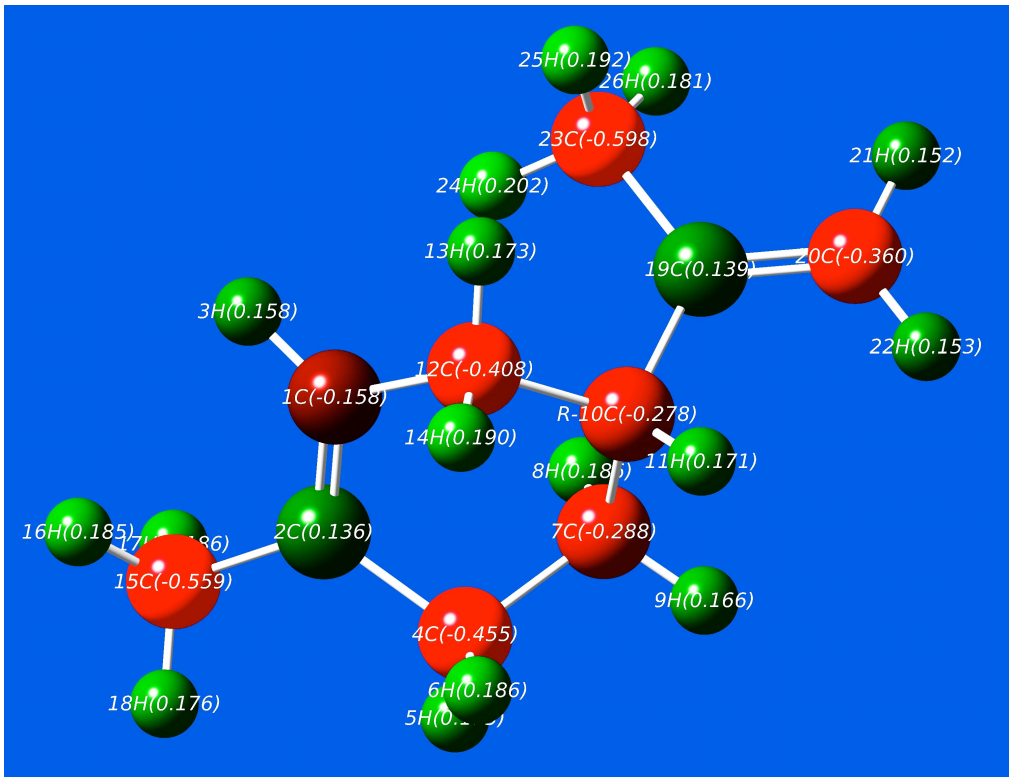


Fig. S27. Mulliken charge distribution of (*R*)-limonene obtained with MP2 (6-311G).

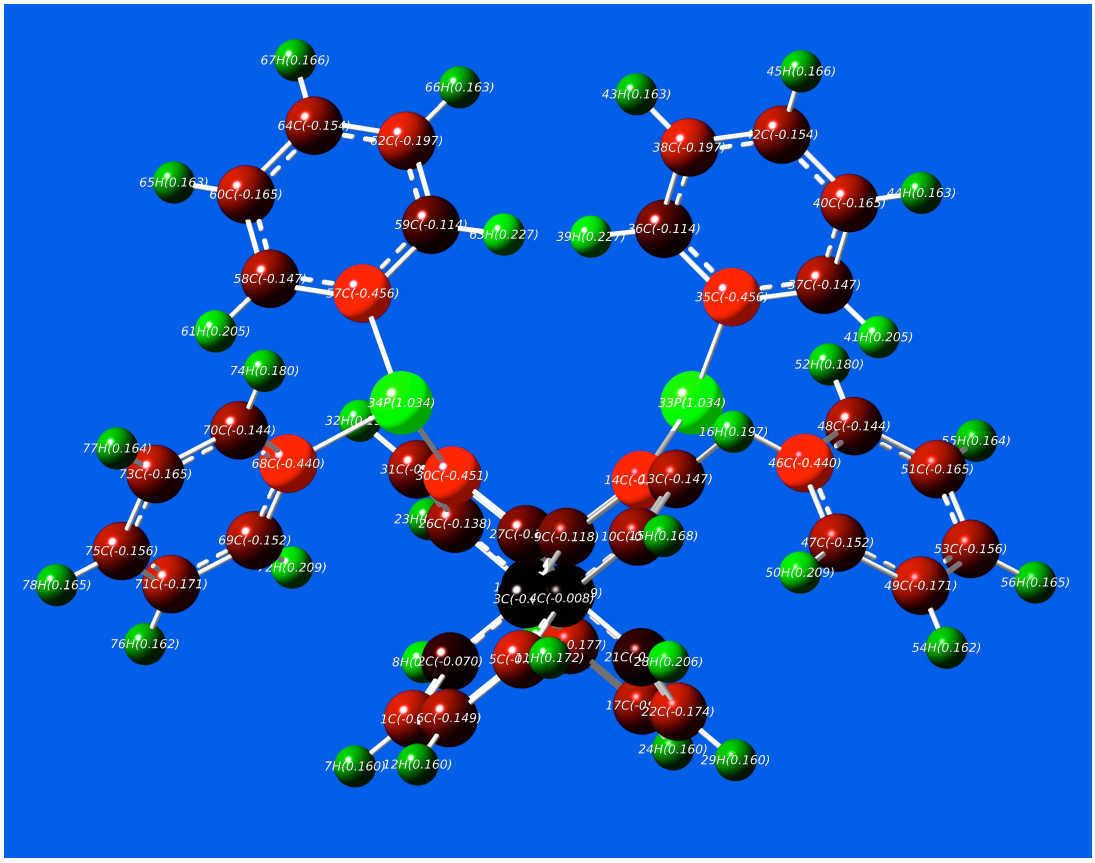


Fig. S28. Mulliken charge distribution of (*R*)-BINAP obtained with MP2 (6-311G).

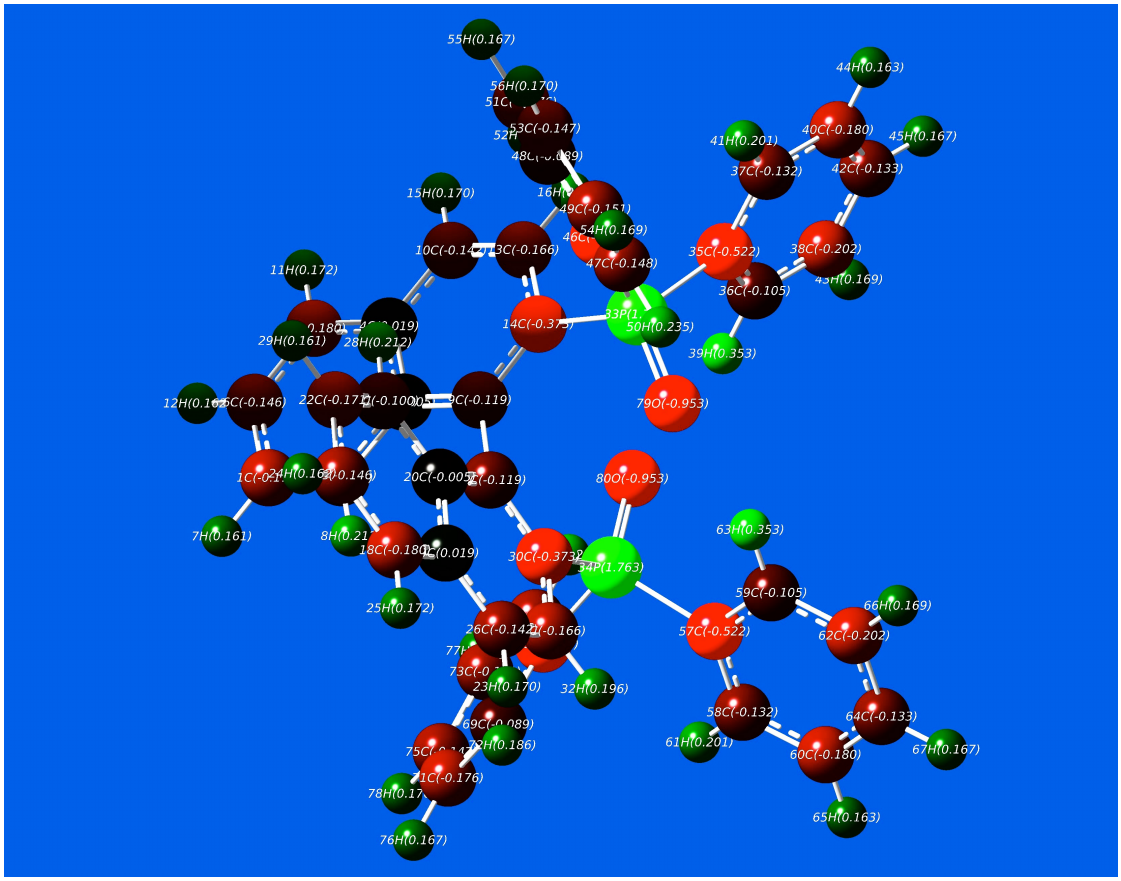


Fig. S29. Mulliken charge distribution of (*R*)-BINAPO obtained with MP2 (6-311G).

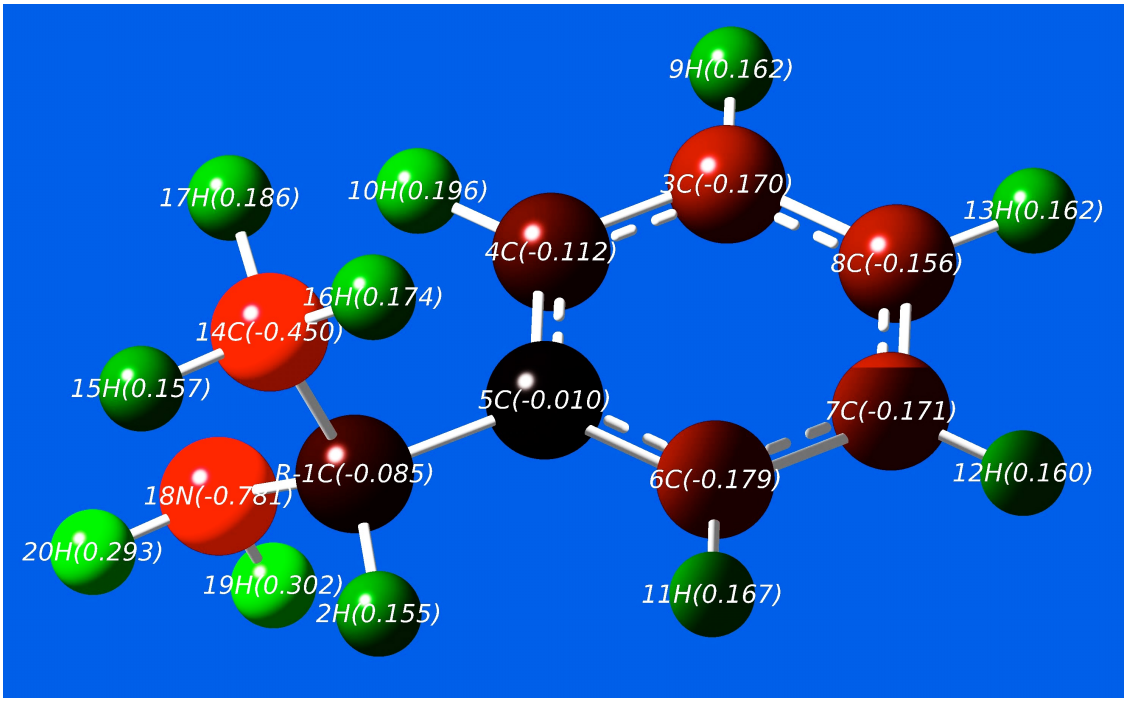


Fig. S30. Mulliken charge distribution of (*R*)-α-PEA obtained with MP2 (6-311G).

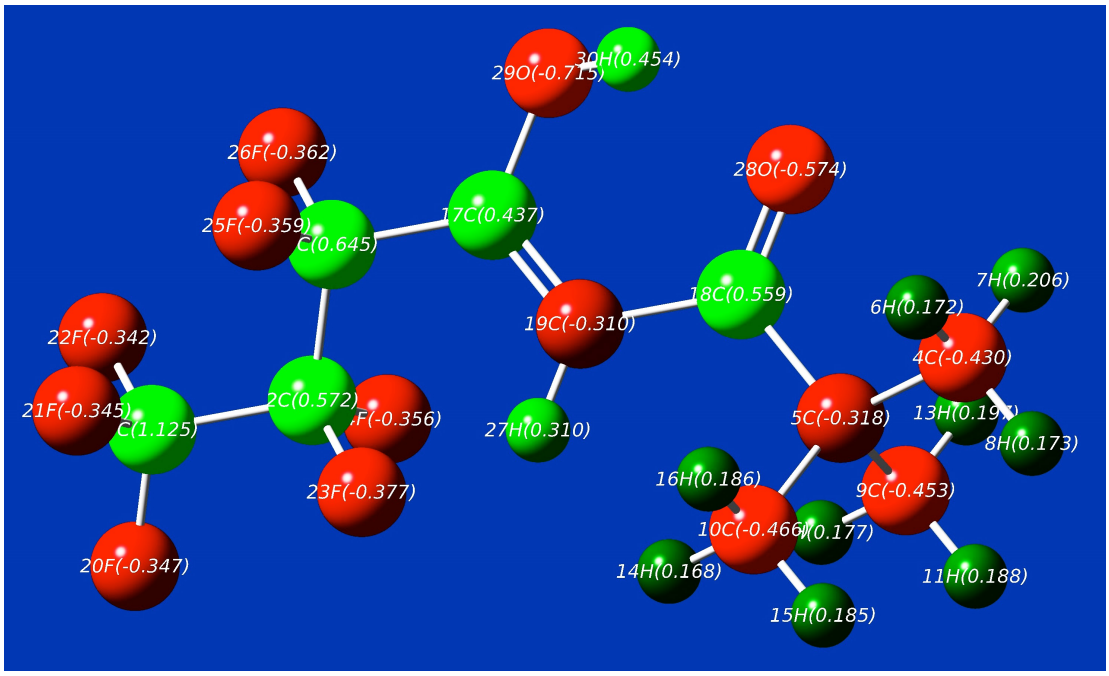


Fig. S31. Mulliken charge distribution of H-fod obtained with MP2 (6-311G).

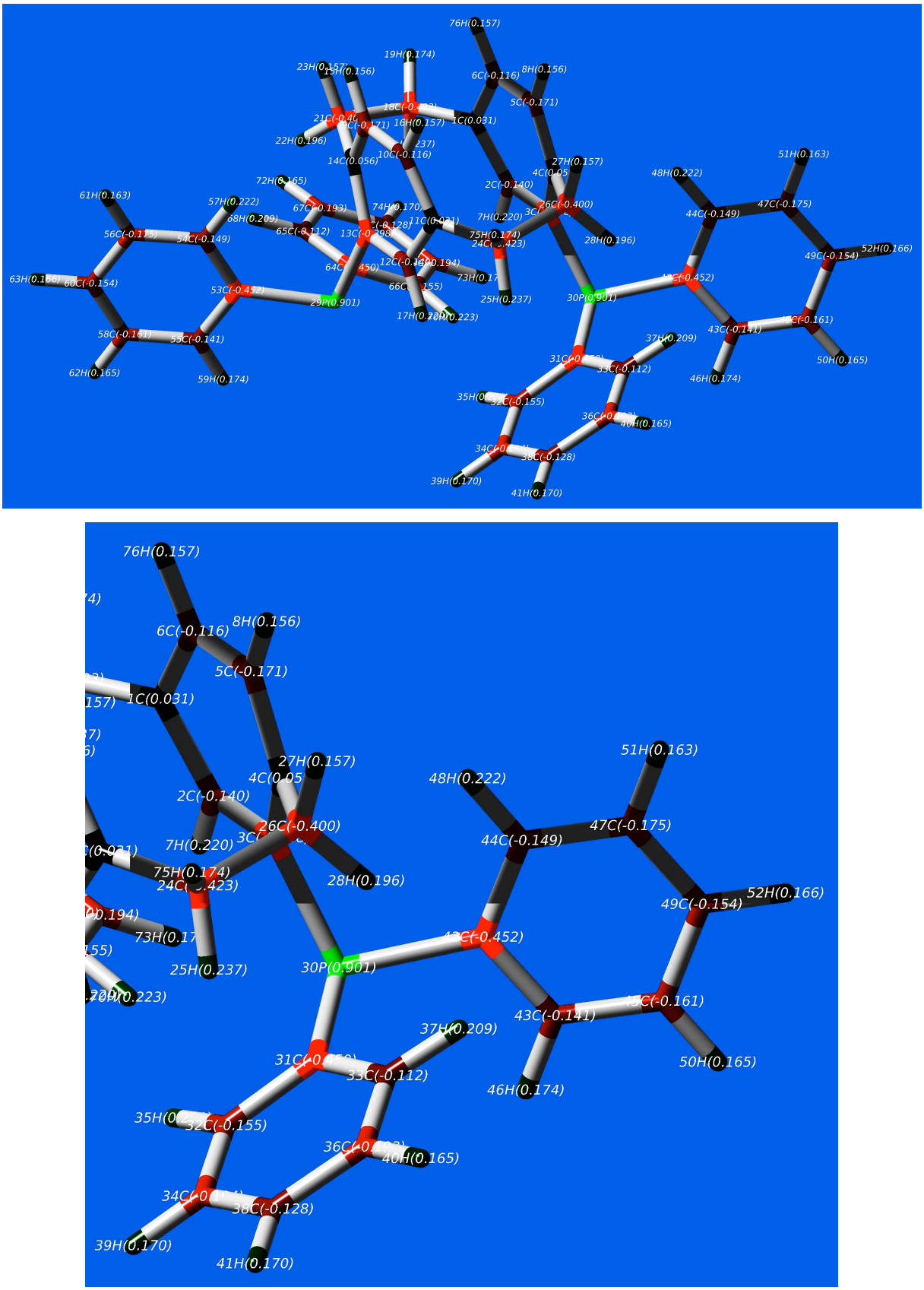


Fig. S32. Mulliken charge distribution of (*R*)-Phanephos obtained with MP2 (6-311G).

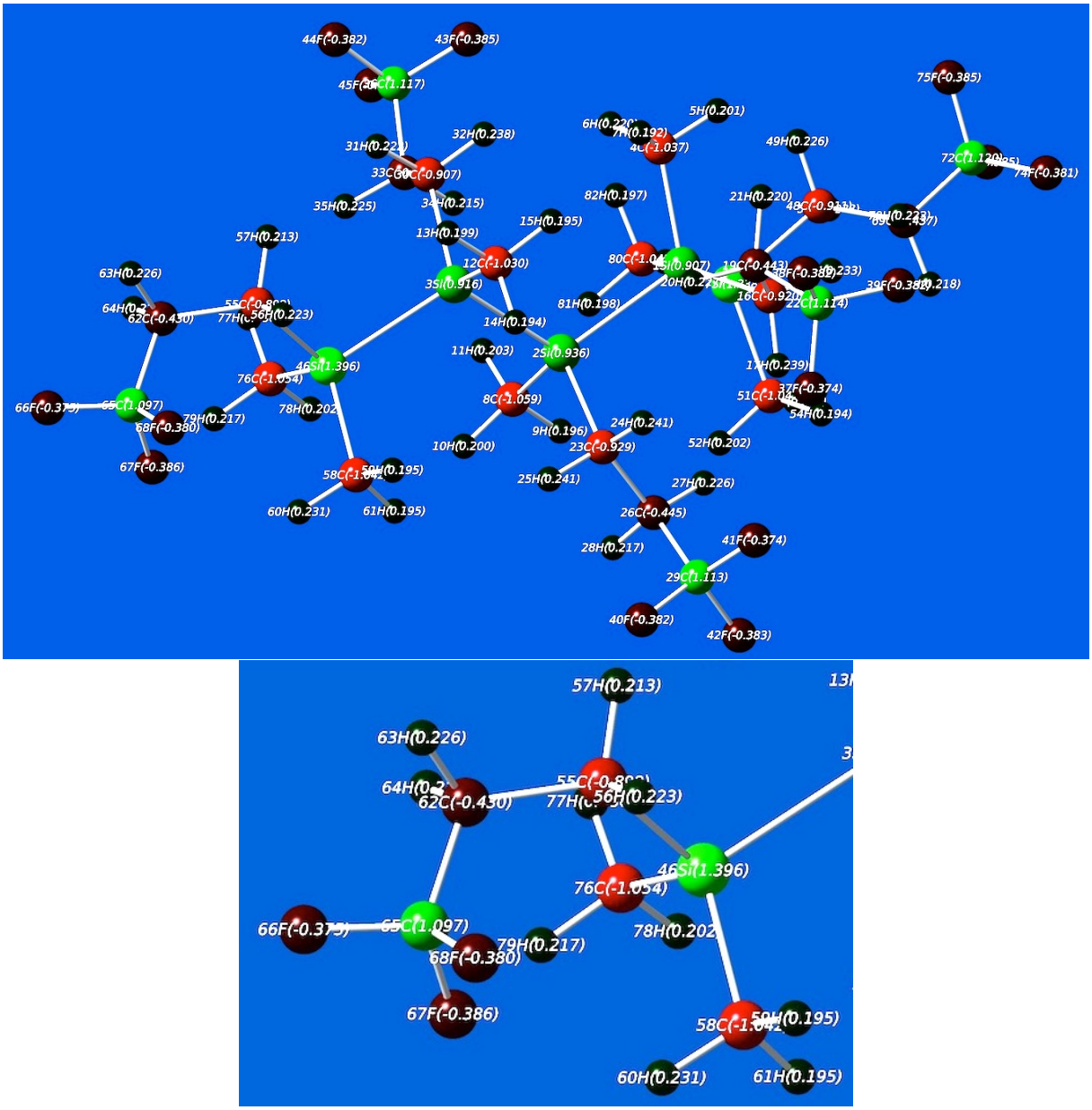


Fig. S33. Mulliken charge distribution of CH_3-(CH_3-Si-$CH_2CH_2CF_3$)$_5$-CH_3 obtained with MP2 (6-311G).

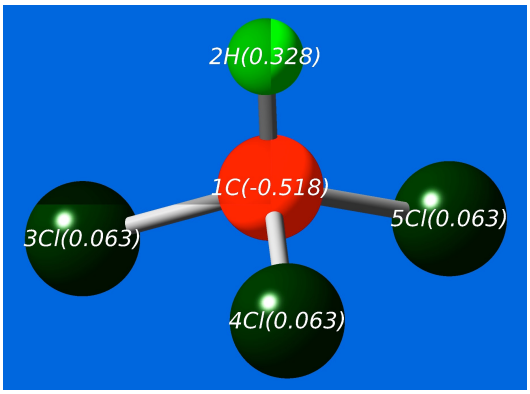


Fig. S34. Mulliken charge distribution of $CHCl_3$ obtained with MP2 (6-311G).

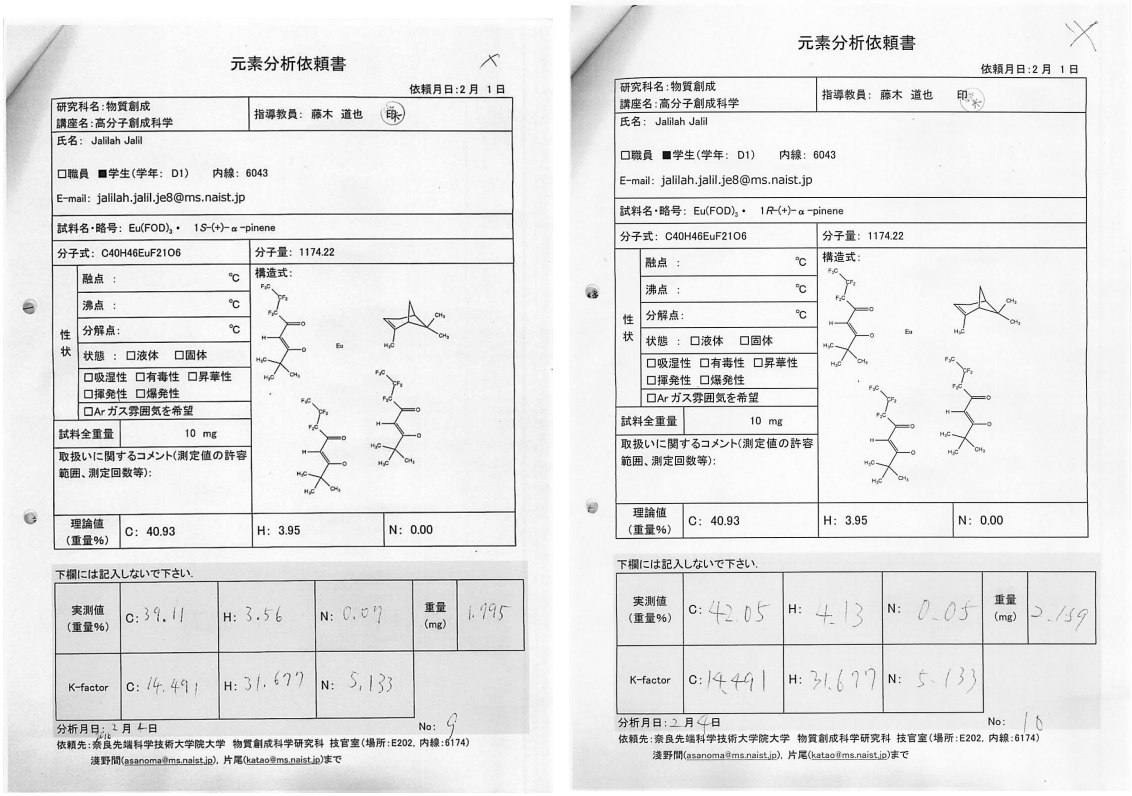
レポートが作成されました: 30-MAR-2018 10:56:08

Filename	= 19F_EuFOD_CDCl3_180315-5.jdf
Author	= delta
Experiment	= single_pulse.exp
Sample_Id	= 1
Solvent	= CHLOROFORM-D
Creation_Time	= 15-MAR-2018 10:28:41
Revision_Time	= 30-MAR-2018 10:55:48
Current_Time	= 30-MAR-2018 10:56:08
Comment	= Single Pulse Experiment
Data_Format	= 1D COMPLEX
Dim_Size	= 32768
Dim_Title	= 19F
Dim_Units	= [ppm]
Dimensions	= X
Site	= ECP400
Spectrometer	= DELTA_NMR
Field_Strength	= 9.38977[T] (400[MHz])
X_Acq_Duration	= 0.43254[s]
X_Domain	= 19F
X_Freq	= 376.17105[MHz]
X_Offset	= -100[ppm]
X_Points	= 32768
X_Prescans	= 0
X_Resolution	= 2.31194[Hz]
X_Sweep	= 75.75758[kHz]
Clipped	= FALSE
Scans	= 64
Total_Scans	= 64
Relaxation_Delay	= 4[s]
Recvr_Gain	= 17
Temp_Get	= 20.6[dC]
X_90_Width	= 14[us]
X_Acq_Time	= 0.43254[s]
X_Angle	= 45[deg]
X_Pulse	= 7[us]
Initial_Wait	= 1[s]
Phase_Preset	= 3[us]
Unblank_Time	= 2[us]

レポートが作成されました: 30-MAR-2018 10:58:07

Filename	= EuFOD_SBINAPO_cdcl3_dualTMP171214-1-2.jdf
Author	= delta
Experiment	= carbon.jxp
Sample_Id	= S#564892
Solvent	= CHLOROFORM-D
Creation_Time	= 14-DEC-2017 15:41:50
Revision_Time	= 30-MAR-2018 10:57:47
Current_Time	= 30-MAR-2018 10:58:08
Comment	= single pulse decoupled gated NOE
Data_Format	= 1D COMPLEX
Dim_Size	= 26214
Dim_Title	= Phosphorus31
Dim_Units	= [ppm]
Dimensions	= X
Site	= JNM-ECA600
Spectrometer	= DELTA2_NMR
Field_Strength	= 14.09637[T] (600[MHz])
X_Acq_Duration	= 0.53477[s]
X_Domain	= 31P
X_Freq	= 242.95404[MHz]
X_Offset	= 0[ppm]
X_Points	= 32768
X_Prescans	= 4
X_Resolution	= 1.86995[Hz]
X_Sweep	= 61.27451[kHz]
X_Sweep_Clipped	= 49.01961[kHz]
Irr_Domain	= Proton
Irr_Freq	= 600.1723[MHz]
Irr_Offset	= 5[ppm]
Clipped	= FALSE
Scans	= 64
Total_Scans	= 64
Relaxation_Delay	= 2[s]
Recvr_Gain	= 58
Temp_Get	= 19.6[dC]
X_90_Width	= 10.9[us]
X_Acq_Time	= 0.53477[s]
X_Angle	= 30[deg]
X_Atn	= 9[dB]
X_Pulse	= 3.63333[us]

Fig. S35. Detailed measurement conditions of ^{19}F- and ^{31}P{H}-NMR.



元素分析依頼書

依頼月日:2 月 1 日

研究科名:物質創成
講座名:高分子創成科学
指導教員: 藤木 道也 印

氏名: Jalilah Jalil

□職員 ■学生(学年: D1) 内線: 6043

E-mail: jalilah.jalil.je8@ms.naist.jp

試料名・略号: Eu(FOD)$_3$・ 1*S*-(+)-α-pinene

分子式: C40H46EuF21O6 分子量: 1174.22

構造式:

性状: 融点 : ℃ / 沸点 : ℃ / 分解点: ℃ / 状態 : □液体 □固体 / □吸湿性 □有毒性 □昇華性 □揮発性 □爆発性 / □Ar ガス雰囲気を希望

試料全重量 10 mg

取扱いに関するコメント(測定値の許容範囲、測定回数等):

理論値(重量%) C: 40.93 H: 3.95 N: 0.00

下欄には記入しないで下さい.

実測値(重量%)	C: 39.11	H: 3.56	N: 0.07	重量(mg)	1.995
K-factor	C: 14.491	H: 31.677	N: 5.133		

分析月日: 2 月 4 日 No: 9

依頼先:奈良先端科学技術大学院大学 物質創成科学研究科 技官室(場所:E202, 内線:6174)
淺野間(asanoma@ms.naist.jp), 片尾(katao@ms.naist.jp)まで

元素分析依頼書

依頼月日:2 月 1 日

研究科名:物質創成
講座名:高分子創成科学
指導教員: 藤木 道也 印

氏名: Jalilah Jalil

□職員 ■学生(学年: D1) 内線: 6043

E-mail: jalilah.jalil.je8@ms.naist.jp

試料名・略号: Eu(FOD)$_3$・ 1*R*-(+)-α-pinene

分子式: C40H46EuF21O6 分子量: 1174.22

構造式:

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試料全重量 10 mg

取扱いに関するコメント(測定値の許容範囲、測定回数等):

理論値(重量%) C: 40.93 H: 3.95 N: 0.00

下欄には記入しないで下さい.

実測値(重量%)	C: 42.05	H: 4.13	N: 0.05	重量(mg)	2.159
K-factor	C: 14.491	H: 31.677	N: 5.133		

分析月日: 2 月 4 日 No: 10

依頼先:奈良先端科学技術大学院大学 物質創成科学研究科 技官室(場所:E202, 内線:6174)
淺野間(asanoma@ms.naist.jp), 片尾(katao@ms.naist.jp)まで

Fig. S36. Raw elemental analysis data of the viscous residual oils after removal of volatile *α*-pinene from Eu(fod)$_3$ dissolved in (left) (*S*)-*α*-pinene and (right) (*R*)-*α*-pinene (samples were placed in a vacuum oven at 60 °C overnight (in Japanese)). The oils suggested that Eu(fod)$_3$ and *α*-pinene formed 1:1 adducts.