Supporting information

Enhanced circularly polarized luminescence of chiral Eu(III) coordination polymers with structural strain

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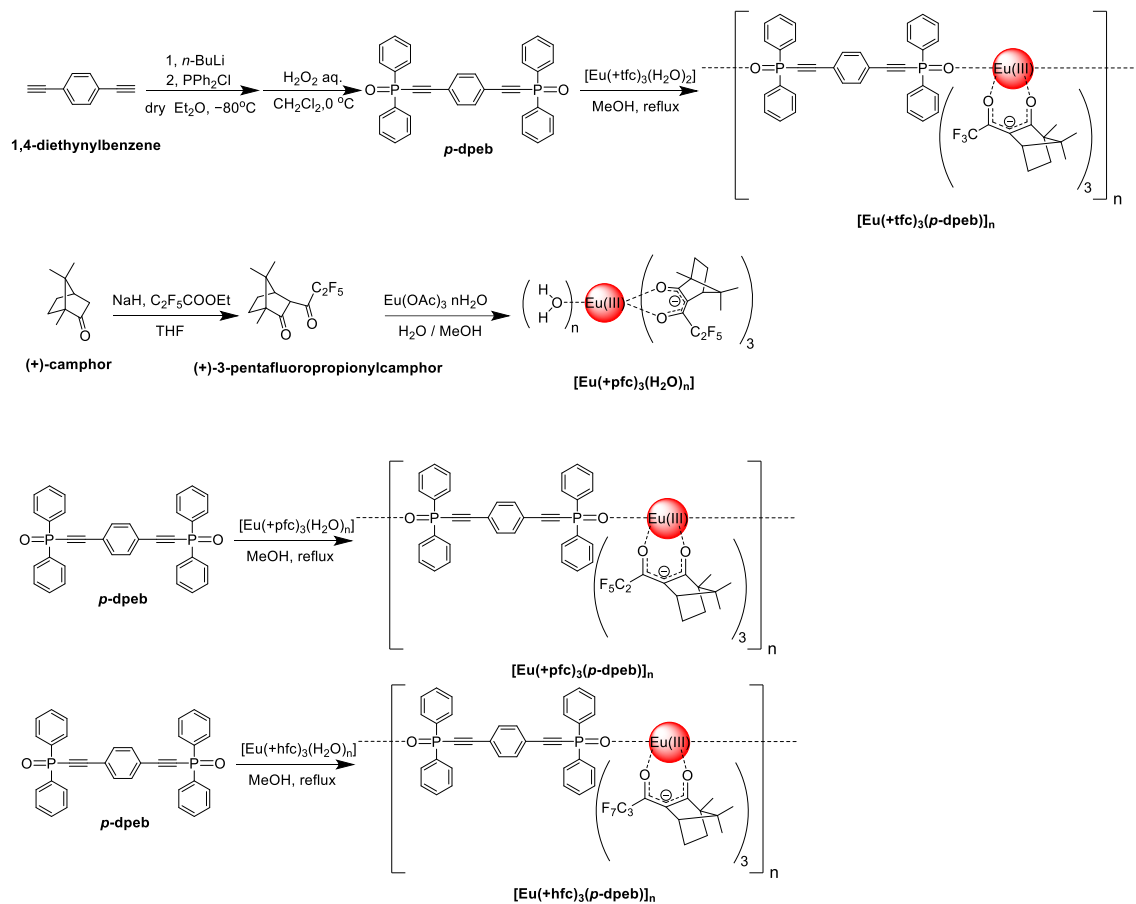
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Scheme S1. Synthetic scheme of chiral Eu(III) coordination polymers.

Preparation of [Eu(−tfc)$_3$(p-dpeb)]$_n$, [Eu(−pfc)$_3$(p-dpeb)]$_n$, and [Eu(−hfc)$_3$(p-dpeb)]$_n$

[Eu(−tfc)$_3$(p-dpeb)]$_n$, [Eu(−pfc)$_3$(p-dpeb)]$_n$, and [Eu(−hfc)$_3$(p-dpeb)]$_n$ were synthesized by the similar procedure to that described for the [Eu(+tfc)$_3$(p-dpeb)]$_n$, [Eu(+pfc)$_3$(p-dpeb)]$_n$, and [Eu(+hfc)$_3$(p-dpeb)]$_n$, respectively. (−)-3-Triflouroacetylcamphor, (−)-3-(Pentafluoropropionyl)camphor, and (−)-3-(Heptafluorobutyryl)camphor were used as starting materials.

[Eu(−tfc)$_3$(p-dpeb)]$_n$: ESI-MS (m/z): [M−tfc]$^+$ calcd. for C$_{58}$H$_{52}$EuF$_6$O$_6$P$_2$, 1173.24; found, 1173.23. Elemental analysis: calcd. for C$_{70}$H$_{66}$EuF$_9$O$_8$P$_2$, C 59.20, H 4.68; found, C 58.93, H 4.56%.

[Eu(−pfc)$_3$(p-dpeb)]$_n$: ESI-MS (m/z): [M−pfc]$^+$ calcd. for C$_{60}$H$_{52}$EuF$_{10}$O$_6$P$_2$, 1273.23; found, 1273.22. Elemental analysis: calcd. for C$_{73}$H$_{66}$EuF$_{15}$O$_8$P$_2$, C 55.84, H 4.24; found, C 55.59, H 4.14%.

[Eu(−hfc)$_3$(p-dpeb)]$_n$: ESI-MS (m/z): [M−hfc]$^+$ calcd. for C$_{62}$H$_{52}$EuF$_{14}$O$_6$P$_2$, 1373.22; found, 1373.24. Elemental analysis: calcd. for C$_{76}$H$_{66}$EuF$_{21}$O$_8$P$_2$, C 53.06, H 3.87; found, C 52.32, H 3.82%.
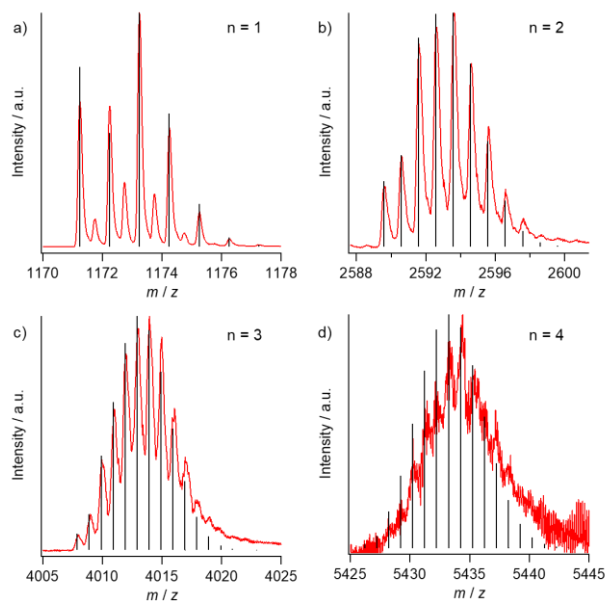
Figure S1. ESI-MS spectra (red) and simulated mass pattern (black) of $[Eu_n(+tfc)_{3n-1}(p\text{-dpeb})_n]^+$

(a) n = 1, b) n = 2, c) n = 3, d) n = 4).

Figure S2. ESI-MS spectra (red) and simulated mass pattern (black) of $[Eu_n(+pfc)_{3n-1}(p\text{-dpeb})_n]^+$

(a) n = 1, b) n = 2, c) n = 3, d) n = 4).

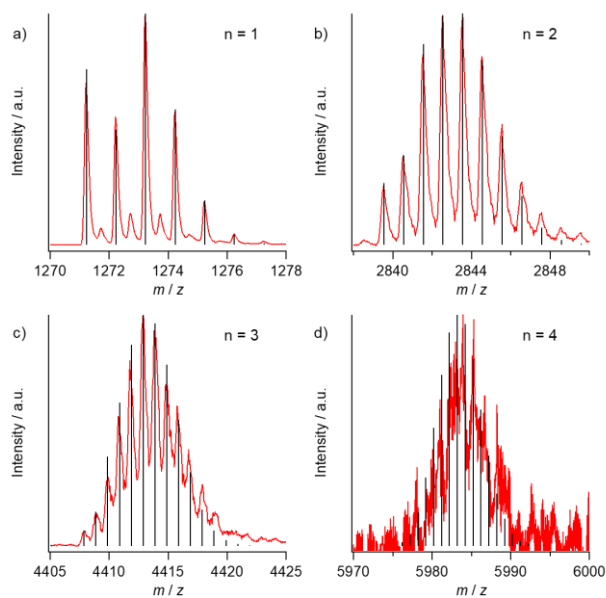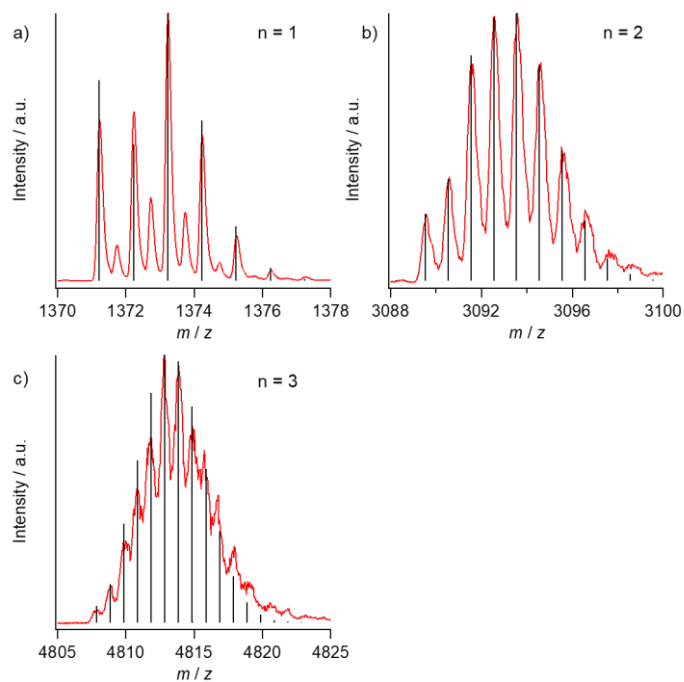**Figure S3.** ESI-MS spectra (red) and simulated mass pattern (black) of $[Eu_n(+hfc)_{3n-1}(p\text{-dpeb})_n]^+$
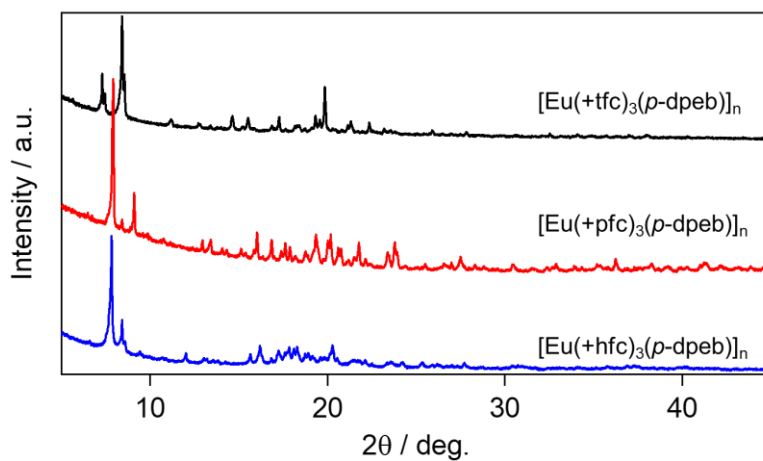
(a) n = 1, b) n = 2, c) n = 3).

Figure S4. PXRD patterns of $[Eu(+tfc)_3(p\text{-dpeb})]_n$ (black), $[Eu(+pfc)_3(p\text{-dpeb})]_n$ (red), and $[Eu(+hfc)_3(p\text{-dpeb})]_n$ (blue).

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Table S1. Crystallographic data of chiral Eu(III) coordination polymers.

Compounds	$[Eu(+pfc)_3(p\text{-}dpeb)]_n$	$[Eu(+hfc)_3(p\text{-}dpeb)]_n$
Chemical formula	$C_{73}H_{66}EuF_{15}O_8P_2$	$C_{76}H_{66}EuF_{21}O_8P_2$
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a / Å	17.7325(3)	17.6036(3)
b / Å	19.2862(3)	20.5986(5)
c / Å	21.0290(3)	20.7174(5)
β / deg.	90	90
Volume / $Å^3$	7191.76(19)	7512.3(3)
Z	4	4
ρ_{calc} / g cm^{-3}	1.450	1.521
Temperature / K	123	123
μ (Mo Kα) / mm^{-1}	1.009	0.984
max 2θ / deg.	62.164	61.978
No. of reflns collected	67773	57738
No. of independent reflns	17870	19014
R_1	0.0576	0.0648
wR_2	0.1546	0.1828
Flack parameter	−0.004(7)	0.000(6)

The CShM factor (S_{CShM}) expresses the degree of deviation from the ideal coordination structure and is determined using the following equation:

$$S_{\text{CShM}} = \min \frac{\sum_k^N |Q_k - P_k|^2}{\sum_k^N |Q_k - Q_0|^2} \times 100 \qquad (S1)$$

where N, Q_k, Q_0, and P_k are the number of vertices, vertices of the actual structure, position vectors of the geometrical center, and vertices of the ideal structure, respectively.

Figure S5. Emission spectra ($\lambda_{\text{ex}} = 360$ nm) of a) [Eu(+tfc)$_3$(p-dpeb)]$_n$ (black), [Eu(+pfc)$_3$(p-dpeb)]$_n$ (red), and [Eu(+hfc)$_3$(p-dpeb)]$_n$ (blue) expanded in the region of $^5D_0 \rightarrow {}^7F_{0,\,1}$ (left) and $^5D_0 \rightarrow {}^7F_2$ (right) transitions.

The temperature-dependent emission lifetimes in the solid state measured in the range of 150–350 K are shown in Figure S6a. The energy transfer rate constants (k_{EnT}) between Eu(III) and LMCT states were estimated using kinetic Arrhenius analysis (Figure S6b). The k_{EnT} was defined by the following equation:[S1–S3]

$$\ln\left(\frac{1}{\tau_{obs}} - \frac{1}{\tau_{150K}}\right) = \ln k_{EnT} = \ln A - \frac{\Delta E_a}{RT} \tag{S2}$$

where τ_{obs}, τ_{150K}, A, ΔE_a, R, and T are the observed emission lifetime, standard emission lifetime at 150 K, frequency factor, activation energy, gas constant, and temperature, respectively. The calculated ΔE_a and A values are summarized in Table S2. The Arrhenius plots were well fitted to the equation (S1) with high coefficient of determination ($R^2 = 0.996$ ([Eu(+pfc)$_3$(p-dpeb)]$_n$), and 0.999 ([Eu(+hfc)$_3$(p-dpeb)]$_n$)), indicating the single temperature-dependent quenching state.
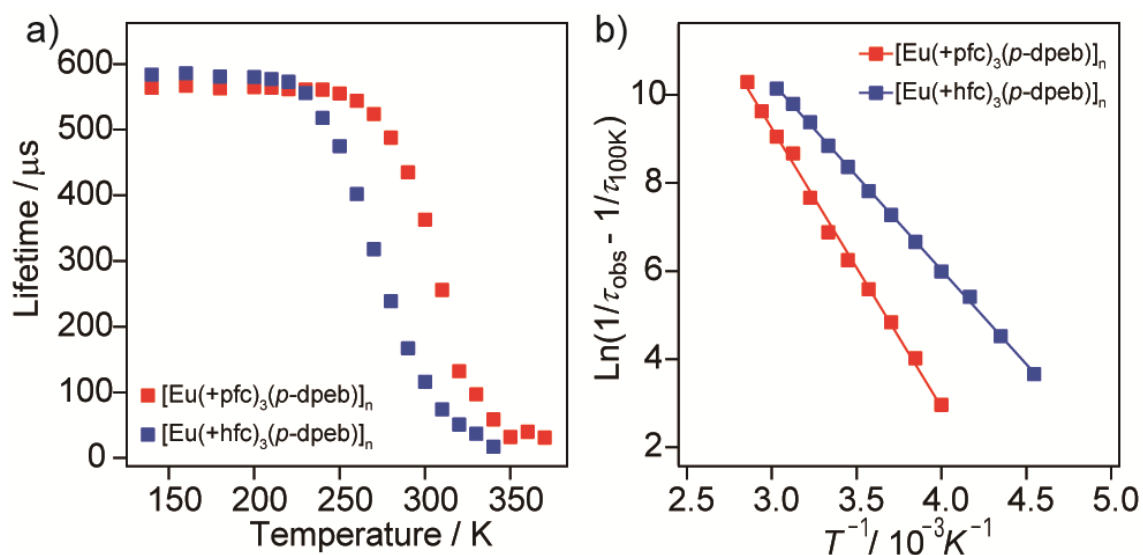

Figure S6. a) Temperature-dependent emission lifetimes and b) Arrhenius plots of [Eu(+pfc)$_3$(p-dpeb)]$_n$ (red) and [Eu(+hfc)$_3$(p-dpeb)]$_n$ (blue) (λ_{ex} = 355 nm, λ_{em} = 610 nm). c) Selected α-spin molecular orbitals of [Eu(+pfc)$_3$(p-dpeb)]$_n$ and [Eu(+hfc)$_3$(p-dpeb)]$_n$.

Table S2. Arrhenius parameters of chiral Eu(III) coordination polymers.

Compounds	ΔE_a / cm^{-1}	A / s^{-1}
[Eu(+pfc)$_3$(p-dpeb)]$_n$	4.4×10^3	4.0×10^{11}
[Eu(+hfc)$_3$(p-dpeb)]$_n$	3.0×10^3	1.1×10^{10}

Figure S7. Diffuse reflection spectra of [Eu(+tfc)$_3$(p-dpeb)]$_n$ (black), [Eu(+pfc)$_3$(p-dpeb)]$_n$ (red), and [Eu(+hfc)$_3$(p-dpeb)]$_n$ (blue).
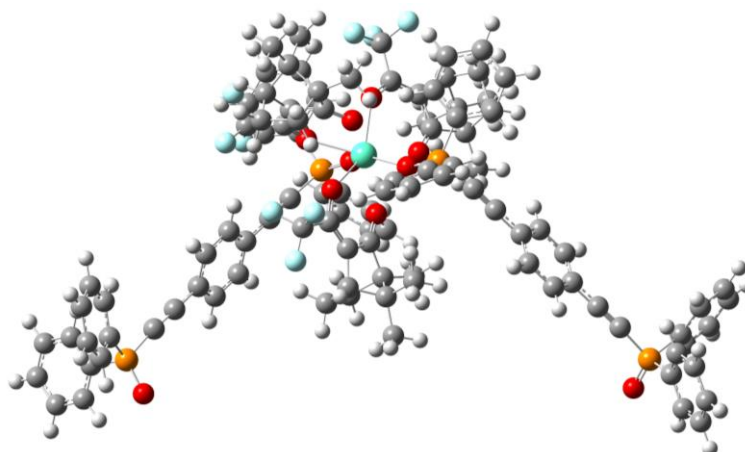
Figure S8. Optimized structure of [Eu(+tfc)₃(*p*-dpeb)₂] obtained by DFT calculations.

Table S3. Cartesian coordinates (in Å) of [Eu(+tfc)₃(*p*-dpeb)₂] for optimized structure obtained by DFT calculations.

Atom	X	Y	Z	Atom	X	Y	Z
P	-9.19144	6.46651	0.060322	H	4.269938	-1.41087	1.588213
P	-1.73203	-1.82383	3.306254	H	5.213164	-2.16582	2.895127
O	-8.49847	7.781126	-0.14049	C	5.709428	0.957488	-1.48149
C	-11.5897	7.929844	3.017292	C	3.99269	-5.69766	1.15331
H	-11.7295	8.893318	3.500071	H	4.751975	-6.39063	1.532707
C	-4.63744	1.27532	2.179704	H	3.64865	-6.08255	0.190533
C	-10.0071	5.846056	-1.44979	C	0.594008	-5.06216	0.763562
C	-10.4522	6.551627	1.381444	C	-1.71186	0.858623	-1.36092
C	-10.2946	4.49232	-1.67385	C	2.804381	-5.54233	2.147546
H	-9.98789	3.742445	-0.94974	H	2.44606	-6.48076	2.576663
C	-8.14622	5.125639	0.560394	C	-2.55008	-3.80656	-3.96462
C	-3.71372	0.274856	2.597052	C	9.813183	4.12604	0.221181
C	-5.38555	1.097582	0.997373	C	12.27974	4.065834	1.612245
H	-5.26891	0.190066	0.417034	C	0.68665	3.509383	-0.33214
C	-7.35857	4.265651	0.913279	C	2.329699	-4.05394	4.225561
C	-12.3592	6.832652	3.4075	H	2.740093	-3.26454	4.866716
H	-13.1007	6.94063	4.194766	H	2.061448	-4.89546	4.876707
C	-4.80466	2.454309	2.934729	H	1.409981	-3.67147	3.776299
H	-4.22672	2.591698	3.84301	C	2.212574	-0.39366	-6.68836
C	-6.272	2.081628	0.581453	H	2.872556	-0.41024	-7.55135
H	-6.838	1.948315	-0.33455	C	1.889228	2.349745	1.748417
C	-10.6369	7.792045	2.005681	H	1.687275	1.681995	2.592606
H	-10.0277	8.634013	1.691208	H	2.277292	3.293773	2.148884
C	-6.44362	3.259229	1.336767	H	2.674219	1.880598	1.145628
C	-2.92964	-0.59434	2.932619	C	6.497938	0.572889	-0.37791
C	-0.87057	-1.19095	4.781109	H	6.278413	-0.35839	0.134045
C	-10.9497	4.099939	-2.84151	C	-4.50594	-3.79038	-2.79576
H	-11.1658	3.048873	-3.013	H	-5.43002	-4.16658	-2.35313
C	-5.69822	3.431956	2.521124	C	-2.80091	1.288586	-2.3539

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Atom	x	y	z	Atom	x	y	z
H	-5.8269	4.338765	3.102921	C	0.159907	-6.53858	0.779095
C	-11.2269	5.45159	1.776667	C	4.539625	-4.2404	1.058317
H	-11.0897	4.484369	1.300721	H	4.47224	-3.82789	0.046435
C	-2.64857	-3.32031	3.759744	H	5.591569	-4.17849	1.360059
C	0.348583	-0.52544	4.580312	C	4.261542	-3.52152	-3.20369
H	0.745927	-0.4349	3.573448	H	4.979328	-2.71311	-3.31087
C	-12.1772	5.593106	2.786775	C	-1.53324	3.748579	0.632793
H	-12.7753	4.738194	3.090611	H	-1.63541	4.838256	0.675965
C	1.037235	0.002352	5.673468	H	-2.5378	3.324671	0.708903
H	1.981041	0.517817	5.517567	C	11.80664	5.965342	-0.59804
C	-11.021	6.403584	-3.57925	C	-0.56896	3.216539	1.736649
H	-11.2942	7.145966	-4.32422	H	-1.03857	2.475733	2.392434
C	-2.67334	-5.73834	3.88334	H	-0.19738	4.022102	2.379705
H	-2.18744	-6.68889	3.686065	C	12.56986	4.230279	2.972913
C	-11.3164	5.055376	-3.79261	H	12.06178	5.013088	3.527827
H	-11.8235	4.747319	-4.70309	C	4.681828	-4.84535	-3.33543
C	-2.02049	-4.55482	3.54042	H	5.722258	-5.06135	-3.5622
H	-1.03651	-4.59039	3.086345	C	-3.26726	-6.07467	-2.89135
C	-3.9473	-5.69342	4.453749	H	-2.63968	-6.71617	-3.52265
H	-4.45682	-6.61635	4.717512	H	-4.14148	-6.66787	-2.5948
C	-10.3667	6.800139	-2.41237	H	-2.70331	-5.84132	-1.98434
H	-10.1139	7.842937	-2.24552	C	13.49964	3.393974	3.594357
C	-3.93367	-3.278	4.318053	H	13.72208	3.523868	4.650011
H	-4.43985	-2.32618	4.451017	C	0.078014	0.167605	-5.68997
C	-4.57611	-4.46493	4.671383	H	-0.91834	0.592353	-5.76466
H	-5.57436	-4.43087	5.098862	C	12.95272	7.886589	-1.53011
C	-1.38792	-1.33079	6.076128	H	13.35743	8.88796	-1.41158
H	-2.32165	-1.86173	6.238749	C	0.928803	0.151159	-6.79605
C	0.517503	-0.1336	6.962998	H	0.593891	0.561226	-7.74515
H	1.05771	0.276138	7.812355	C	-3.54469	-2.93494	-0.49303
C	-0.69314	-0.80122	7.163922	C	12.33488	7.255879	-0.44966
H	-1.09338	-0.91538	8.167594	H	12.24095	7.761053	0.506971
Eu	-0.39327	-1.98933	-0.11325	C	13.04359	7.23553	-2.76239
P	2.307823	-1.53709	-2.73721	H	13.52323	7.728765	-3.60363
P	11.0548	5.208037	0.881819	C	1.645149	3.009961	-1.4281
O	0.246398	0.155438	0.715752	H	2.6874	3.07914	-1.09315
F	1.122215	-7.34245	0.259232	H	1.547916	3.633409	-2.32601
O	10.55702	6.214951	1.874901	H	1.454722	1.974226	-1.72074
O	1.184283	-1.3942	-1.73797	C	-3.34055	-2.57517	-4.54142
O	-0.17708	-4.28037	0.12209	H	-3.4762	-2.69862	-5.62196
F	-5.7889	-2.11244	-0.56651	H	-2.78922	-1.64282	-4.38958
F	-0.96249	-6.75102	0.083921	C	-3.71532	-4.82293	-3.66785
O	1.791263	-2.35834	0.836142	C	-3.43267	-3.35374	-1.80604
F	-3.02525	2.617448	-2.40544	C	-2.20614	-3.35546	-2.53808
F	-4.94921	-2.48537	1.400508	C	4.613129	-4.97704	3.940677
O	-1.64629	-0.40923	-1.25824	H	5.438108	-5.28763	3.295278
O	-1.05555	-3.01443	-2.16895	H	4.357507	-5.83002	4.582036
O	-2.61019	-2.54057	0.274011	H	4.9884	-4.18102	4.595258
C	0.006772	1.320197	0.320347	C	0.50521	-0.35965	-4.46921
F	-2.47555	0.891653	-3.61356	H	-0.15389	-0.36296	-3.60847
C	2.434852	-5.60968	-2.8566	C	-4.95179	-2.92952	0.133997
H	1.729711	-6.42036	-2.69693	C	11.88842	5.320747	-1.84044
C	7.822436	2.595653	-0.60285	H	11.44997	4.335356	-1.97341
C	1.794239	-0.8984	-4.35935	C	1.056267	4.972818	-0.03325
C	1.755171	-4.70825	1.425341	H	0.476324	5.422361	0.775911
C	2.919202	-3.23935	-2.90763	H	0.903	5.587672	-0.92915
C	3.36413	-4.50181	3.178322	H	2.115838	5.053307	0.237976

Atom	x	y	z	Atom	x	y	z
C	2.647982	-0.91697	-5.47229	C	-1.37146	-4.25761	-4.8094
H	3.646624	-1.33908	-5.39382	H	-1.6976	-4.53891	-5.81776
C	3.728571	-0.58501	-2.30524	H	-0.86144	-5.11968	-4.36462
C	0.626329	2.580932	0.937277	H	-0.63441	-3.45336	-4.9063
C	8.892045	3.423997	-0.15682	C	12.50816	5.954562	-2.91802
C	7.030738	2.981351	-1.70377	H	12.56591	5.452732	-3.88018
H	7.24173	3.919075	-2.20735	C	-4.69679	-2.59446	-3.77455
C	-0.90851	1.765186	-0.69194	H	-4.87753	-1.66624	-3.22731
C	-0.82611	3.287965	-0.67545	C	-4.47435	-5.30325	-4.91695
H	-1.17256	3.791274	-1.5781	H	-4.80513	-4.49505	-5.57342
C	4.638599	0.128941	-1.9232	H	-5.36473	-5.87072	-4.6176
C	3.769684	-5.88894	-3.15906	H	-3.84695	-5.9768	-5.51353
H	4.101641	-6.91969	-3.25026	C	12.9275	3.061601	0.878477
C	2.279538	-3.37791	1.373024	H	12.71263	2.928363	-0.1784
C	7.539887	1.380917	0.054686	C	14.14128	2.394503	2.861133
H	8.143854	1.085169	0.90623	H	14.86538	1.744596	3.345338
C	5.988894	2.173615	-2.13766	C	13.85515	2.228806	1.502597
H	5.379015	2.474033	-2.9834	H	14.35593	1.452148	0.930852
C	2.001151	-4.28812	-2.73684	O	-0.7114	-2.06543	2.210701
H	0.962604	-4.07215	-2.50346	F	-3.97831	0.7001	-2.04976
C	3.650719	-3.42396	2.064421	F	-5.51755	-4.15789	0.136967
C	4.210037	-2.06933	2.462166	F	-0.06153	-6.97015	2.052854
H	3.567286	-1.56882	3.194749				

Figure S9. CPL spectra of a) [Eu(+tfc)$_3$(*p*-dpeb)]$_n$ (solid) and [Eu(−tfc)$_3$(*p*-dpeb)]$_n$ (dotted), b) [Eu(+pfc)$_3$(*p*-dpeb)]$_n$ (solid) and [Eu(−pfc)$_3$(*p*-dpeb)]$_n$ (dotted), and c) [Eu(+hfc)$_3$(*p*-dpeb)]$_n$ (solid) and [Eu(−hfc)$_3$(*p*-dpeb)]$_n$ (dotted).
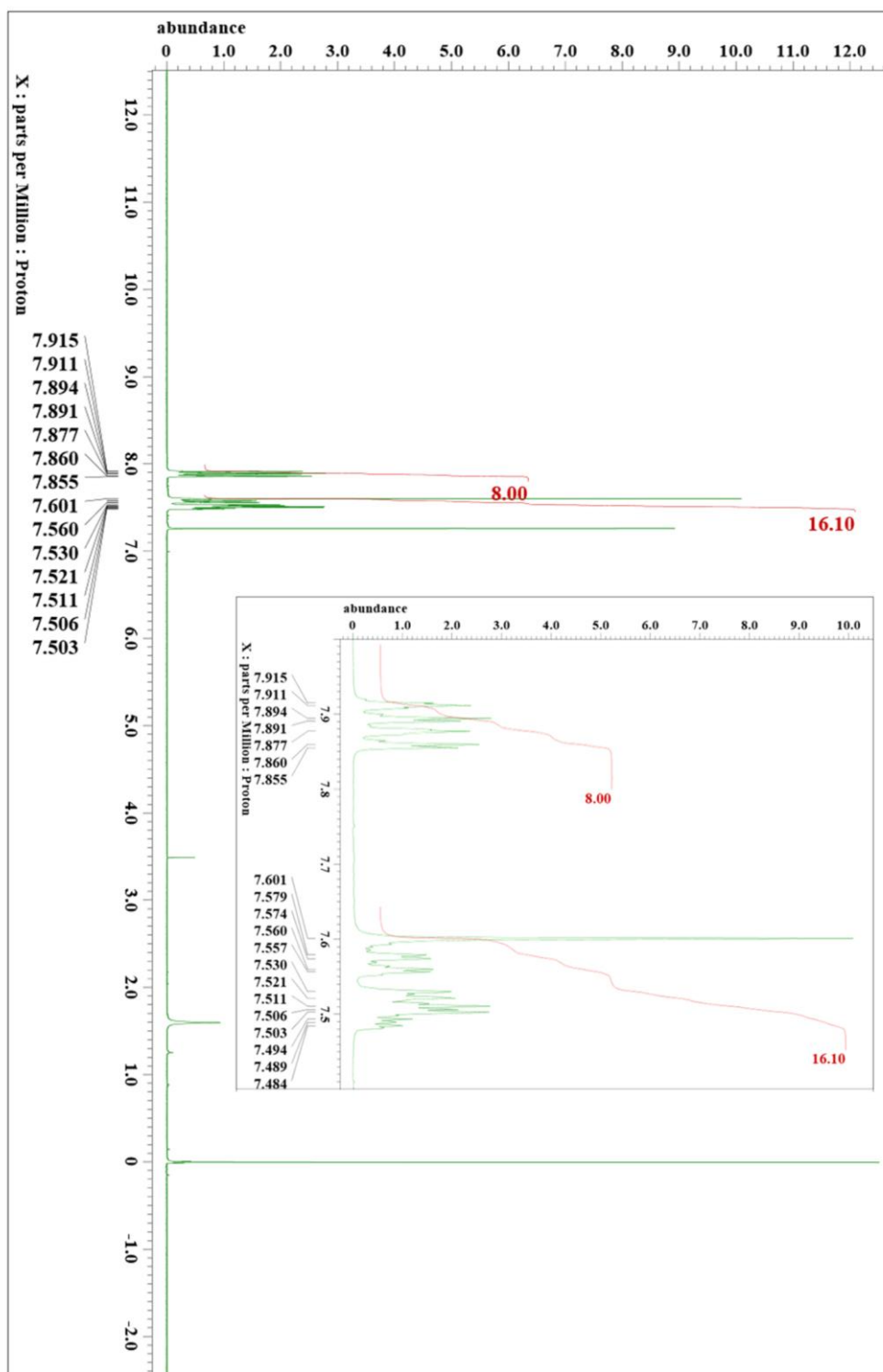
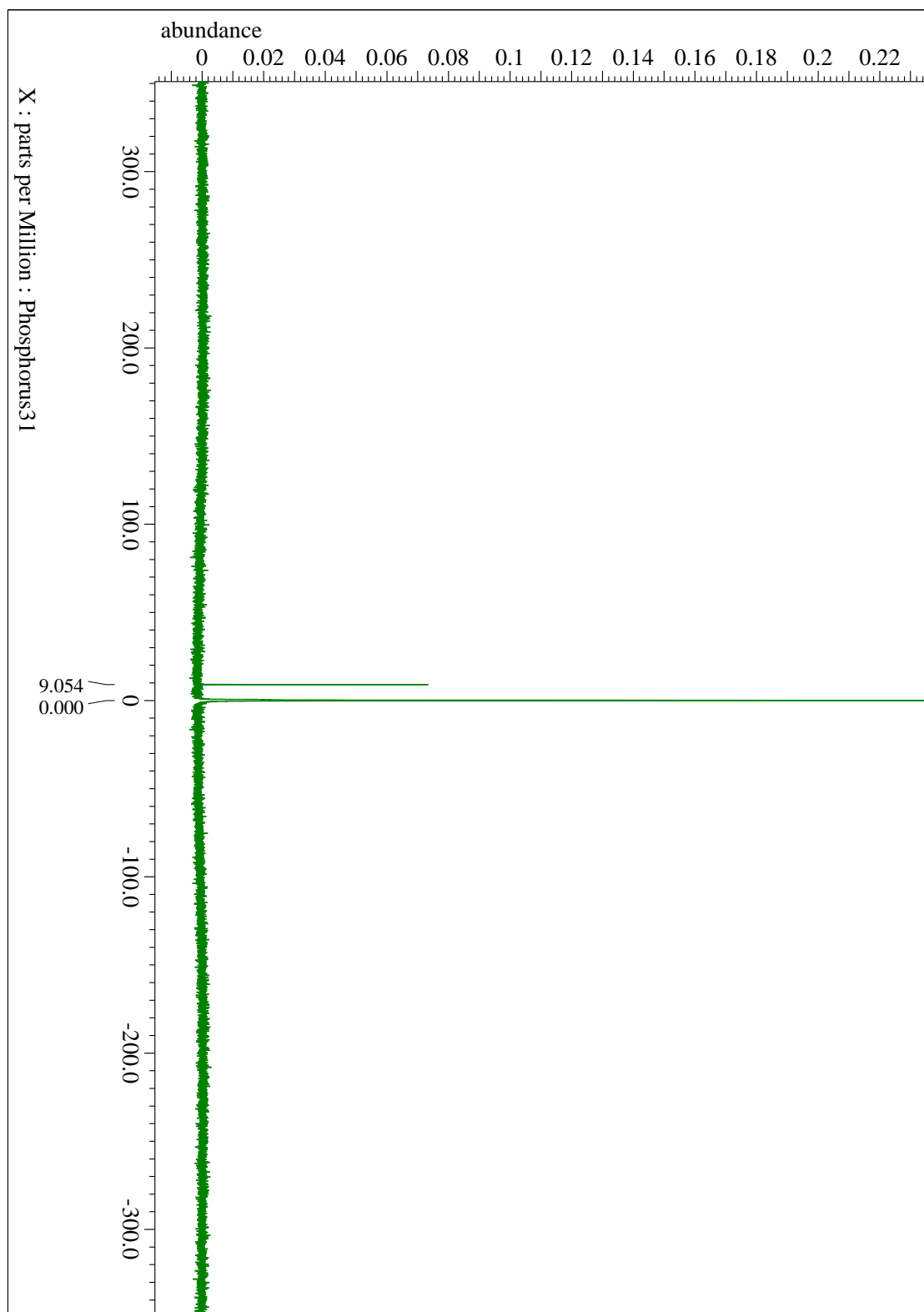**Figure S10.** ^{1}H NMR spectra of *p*-dpeb in CDCl$_3$ with TMS as an internal standard (400 MHz).

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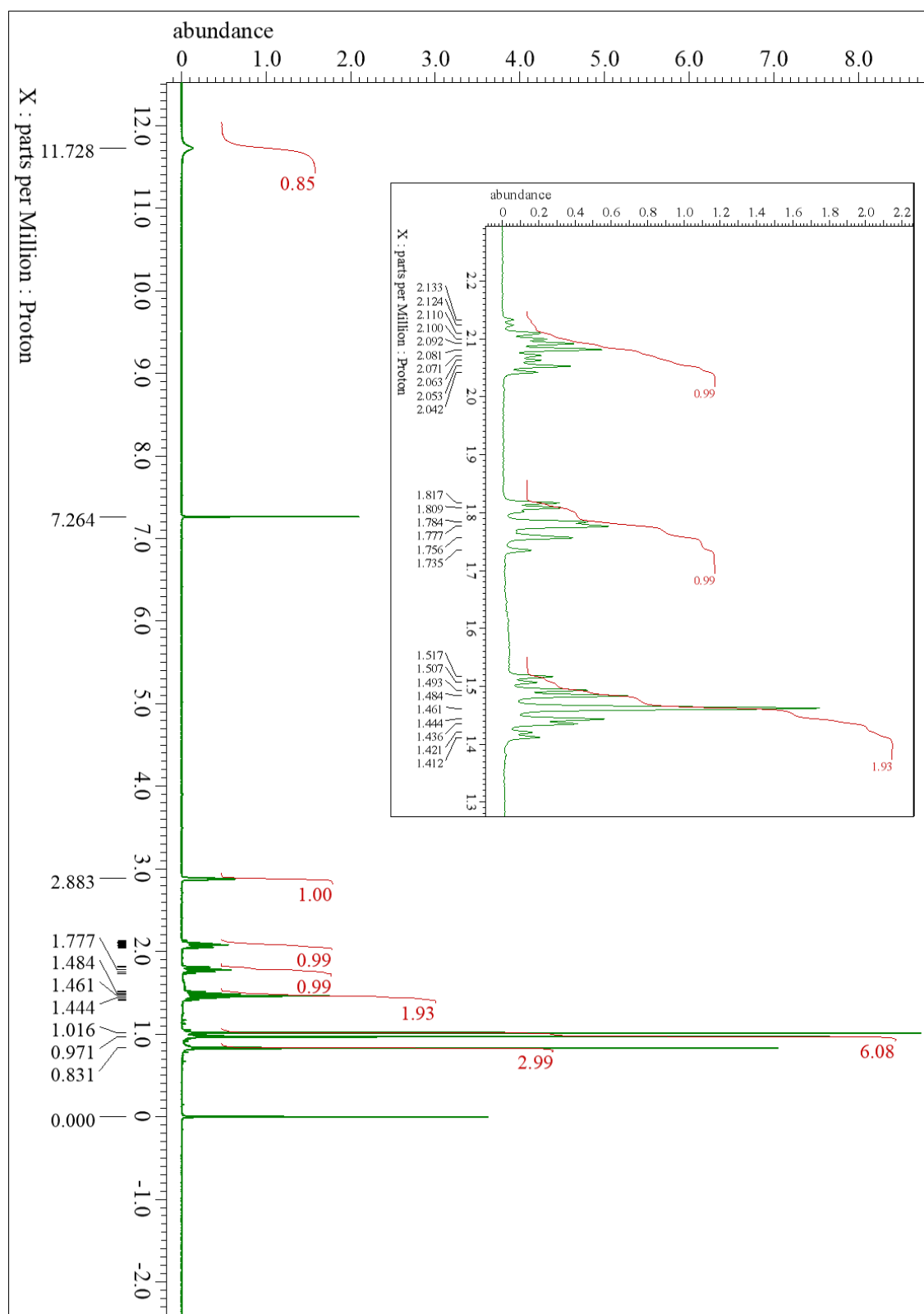**Figure S11.** ³¹P NMR spectrum of *p*-dpeb in CDCl₃ with phosphoric acid as an external standard (162 MHz).

Figure S12. ^{1}H NMR spectra of (+)-3-(pentafluoropropionyl)camphor in CDCl$_3$ with TMS as an internal standard (400 MHz).
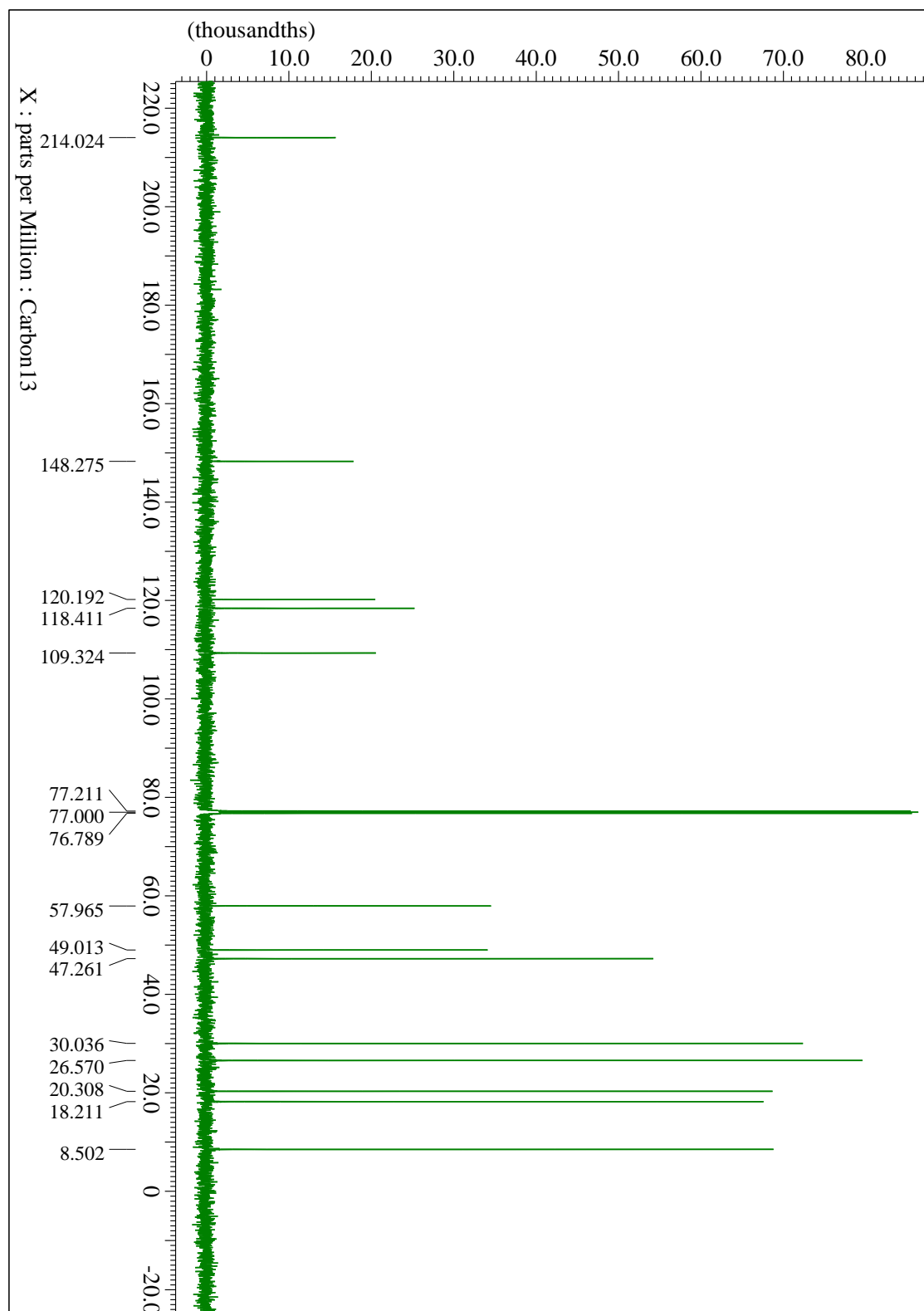
Figure S13. ^{13}C {^{1}H, ^{19}F} NMR spectrum of (+)-3-(pentafluoropropionyl)camphor in CDCl$_3$ (151 MHz).
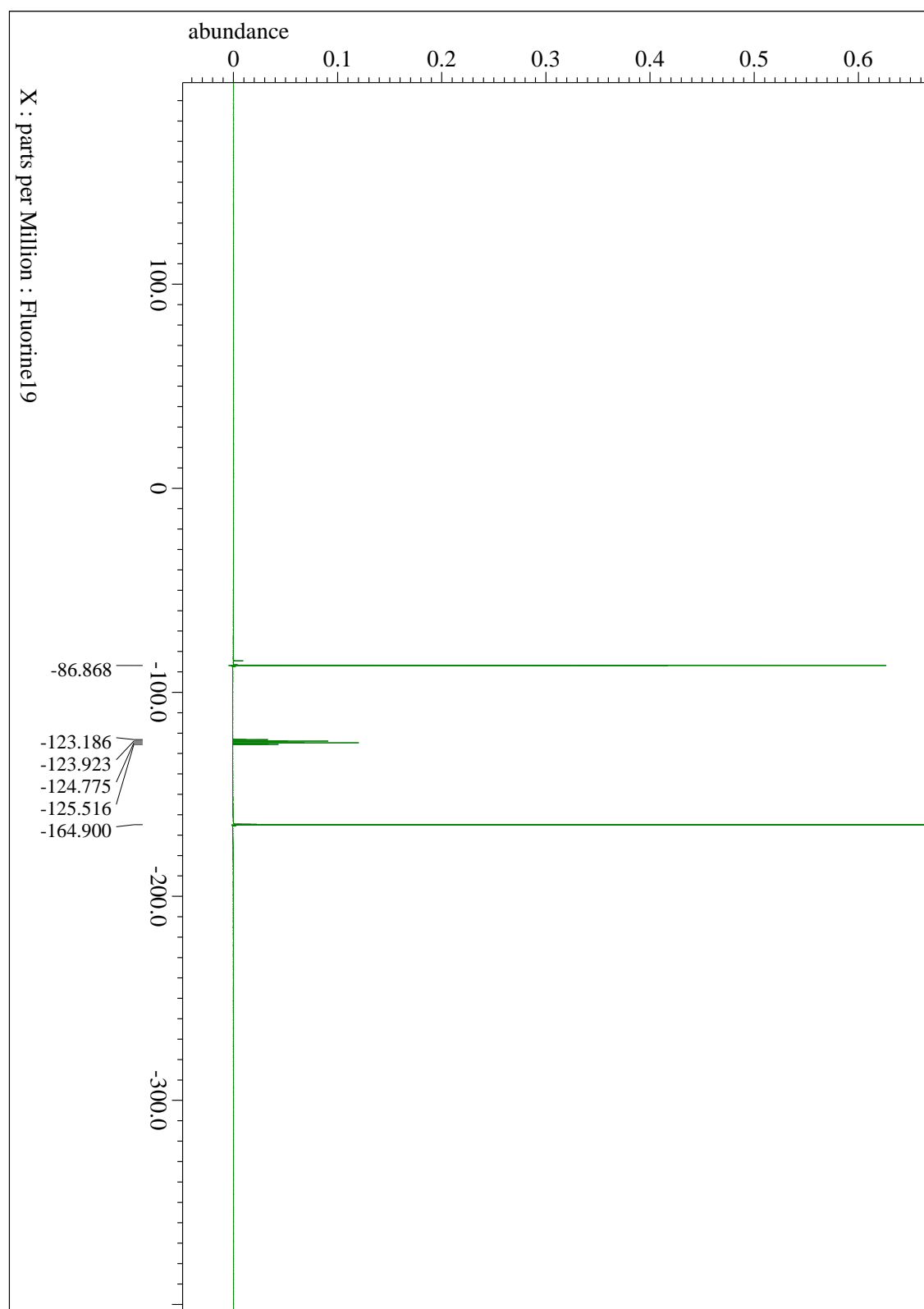
Figure S14. ¹⁹F NMR spectrum of (+)-3-(pentafluoropropionyl)camphor in CDCl₃ with hexafluorobenzene as an internal standard (376 MHz).

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