Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Chiroptical Properties of Cryptophane-111

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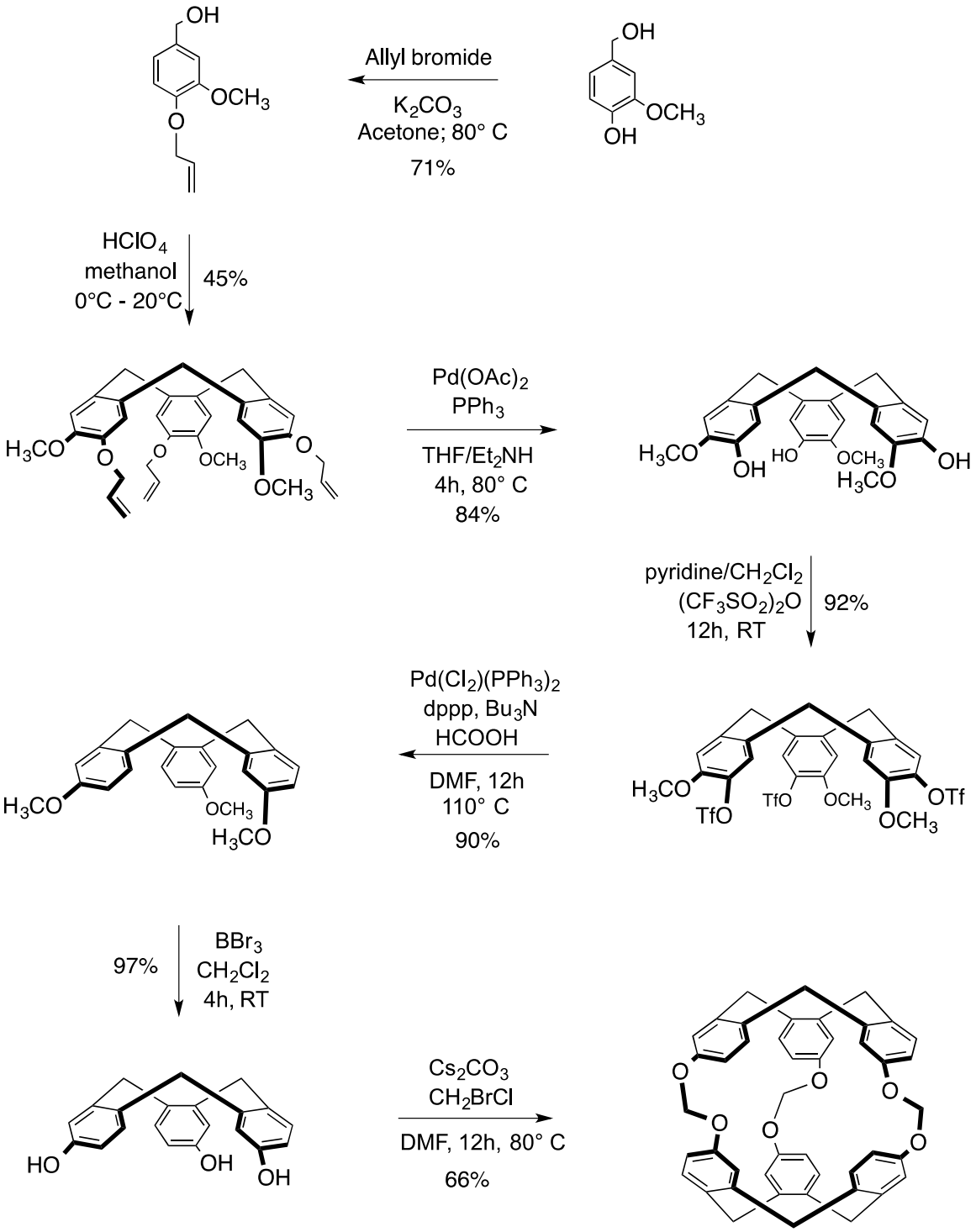

Figure S1. Synthesis of the (*rac*)-**1**.

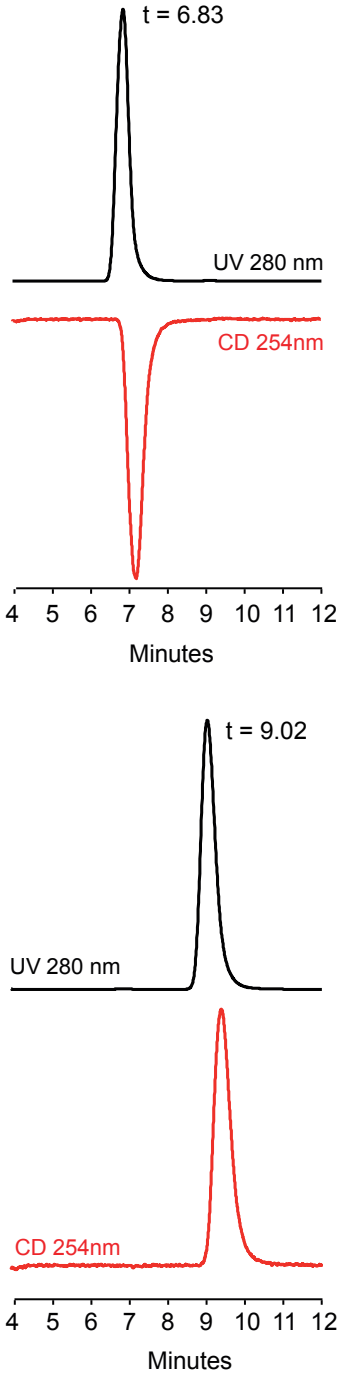

Figure S2. Chromatograms (Chiralpak ID, 250 × 4.6 mm, heptane/EtOH/$CHCl_3$ 50/30/20, 1 mL/min) of the collected enantiomers of **1** after a semipreparative separation of 350 mg of racemate on Chiralpak ID (250 × 10 mm, Hexane/EtOH/$CHCl_3$ 50/10/40, 5 mL/min). Top: detection by UV-vis spectroscopy (280 nm). Bottom: detection by CD at 254 nm.

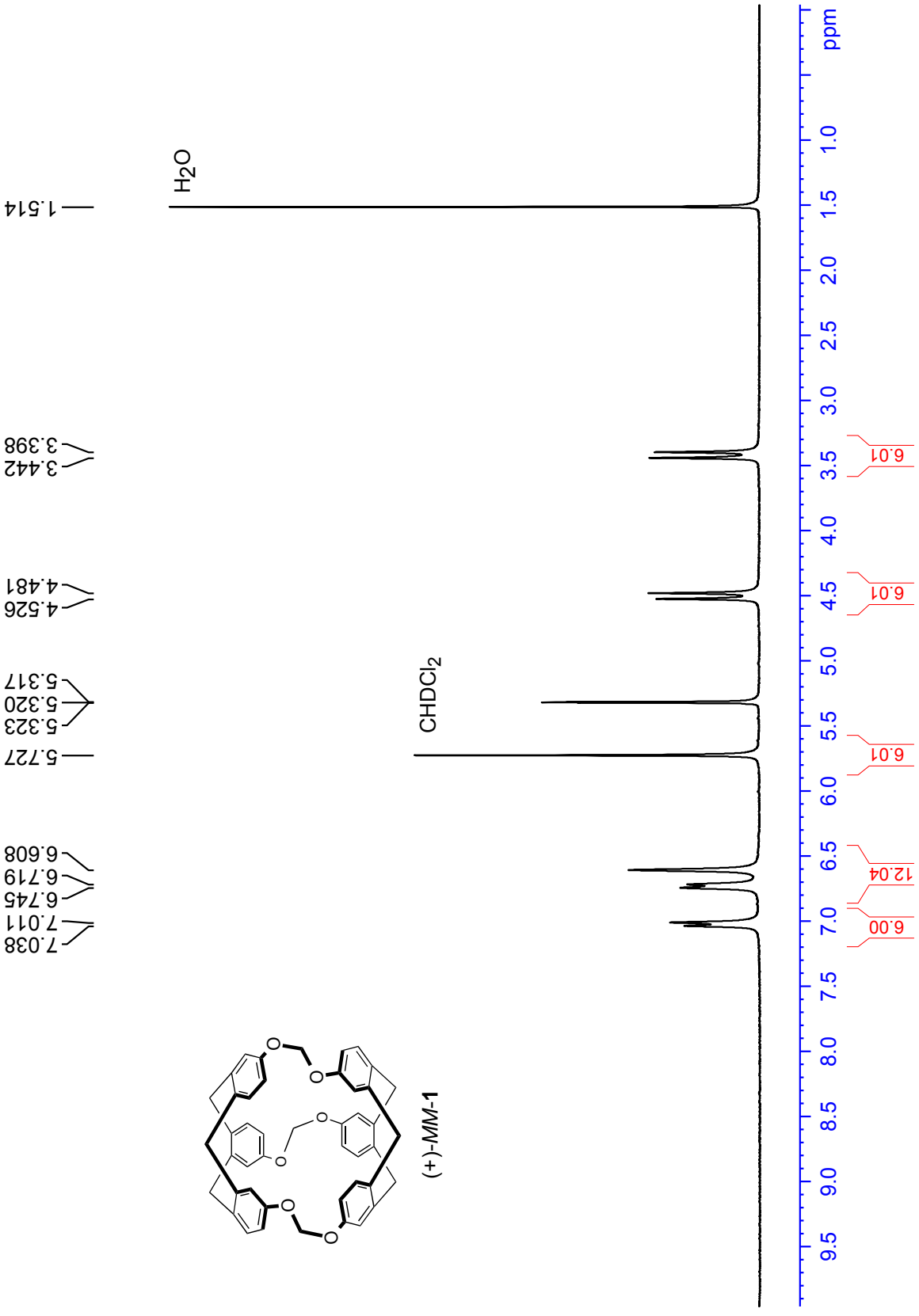

Figure S3. ^{1}H NMR (500 MHz) spectrum of (+)-*MM*-**1** complex in CD_2Cl_2 at 298 K.

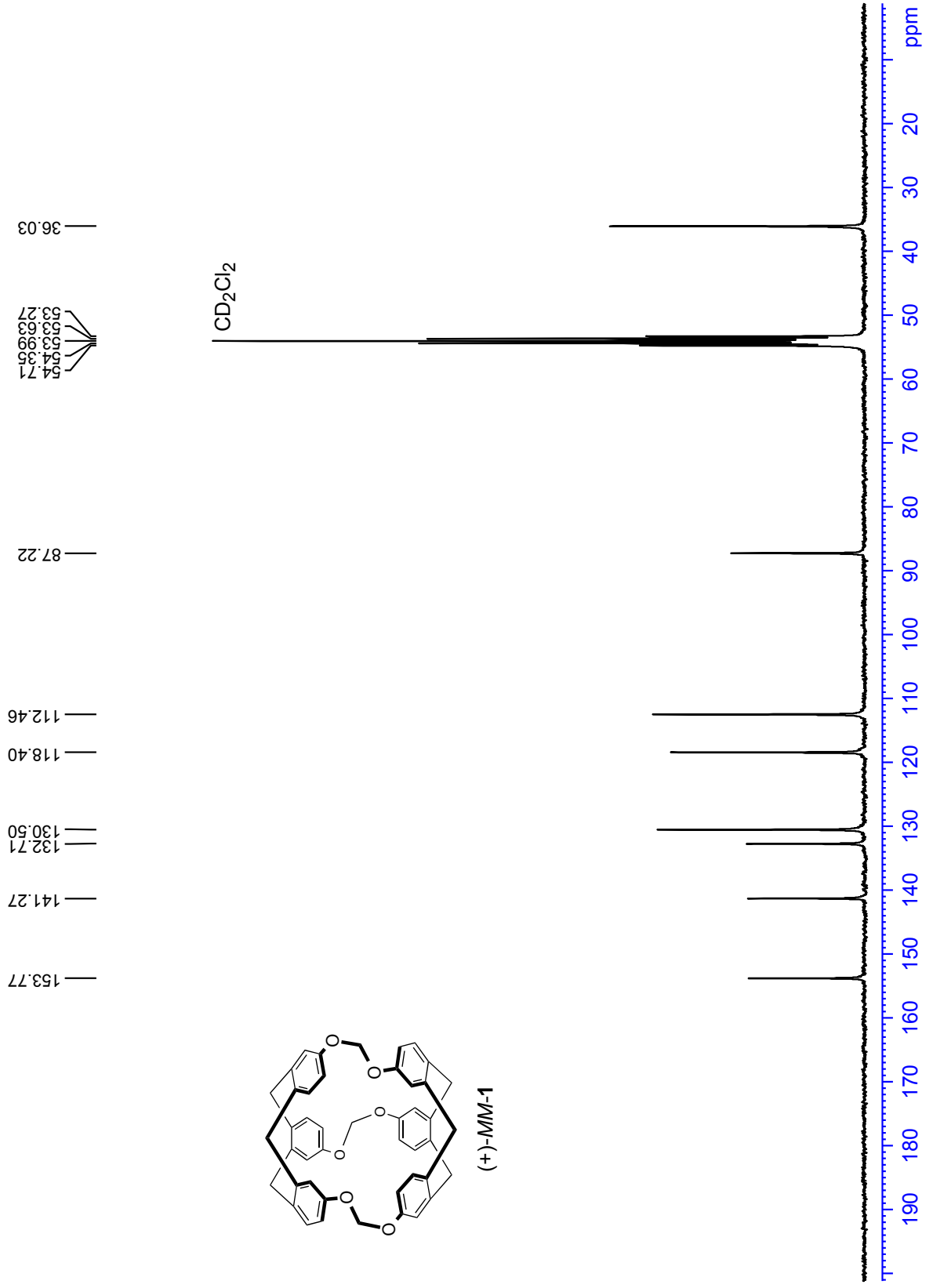

Figure S4. ^{13}C NMR (126.7 MHz) spectrum of (+)-*MM*-**1** complex in CD_2Cl_2 at 298 K.

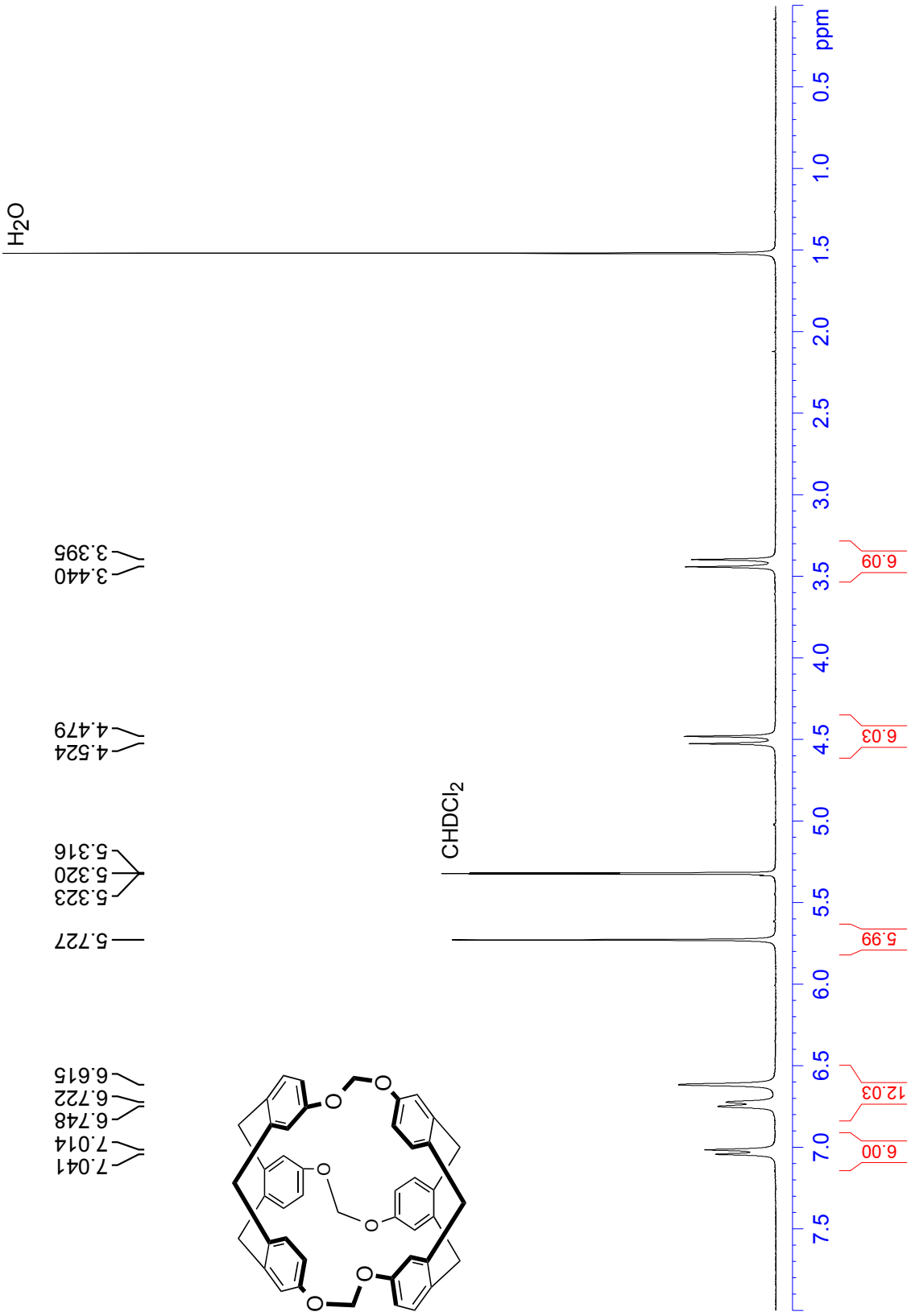

Figure S5. ^{1}H NMR (500 MHz) spectrum of (–)-*PP*-**1** complex in CD_2Cl_2 at 298 K.

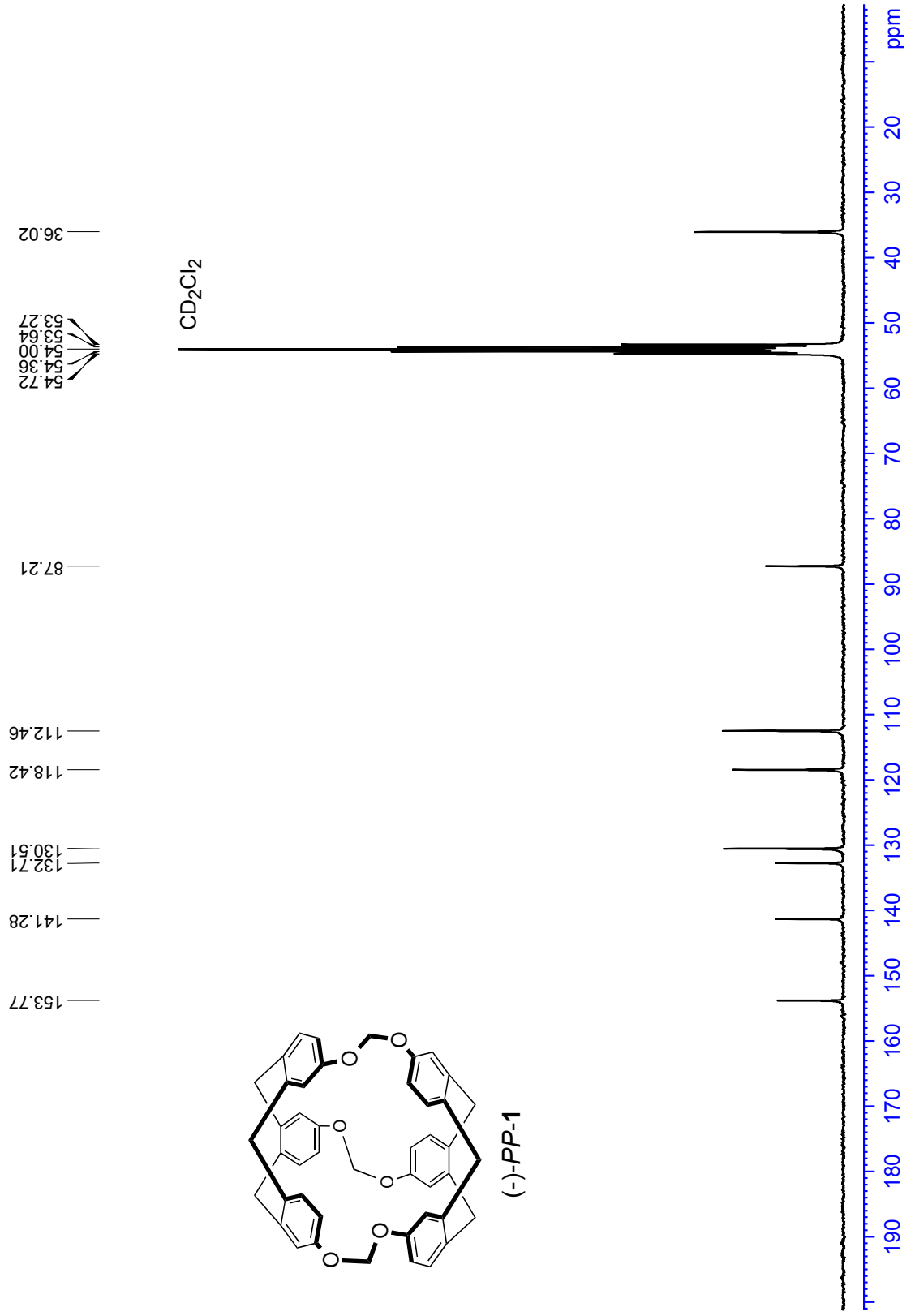

Figure S6. ^{13}C NMR (126.7 MHz) spectrum of (–)-*PP*-**1** complex in CD_2Cl_2 at 298 K.

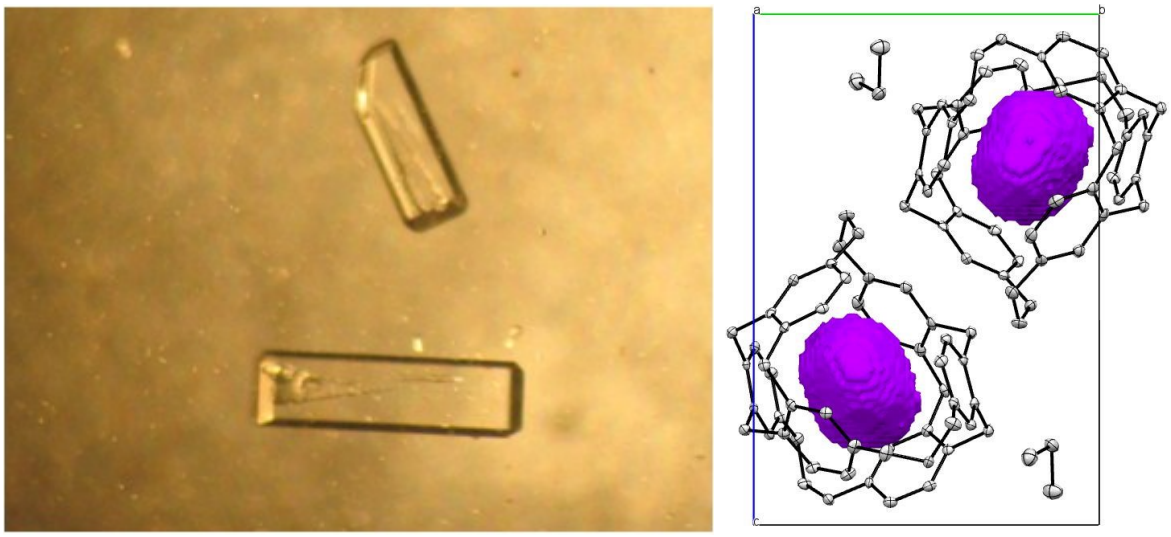

Figure S7a. Picture of the X-ray single crystals for the [CD(+)$_{254}$]-**1** derivative. View of the crystal packing of [CD(+)$_{254}$]-**1** along the a axis of the unit cell. The volume accessible by a guest molecule is represented by the purple zone.

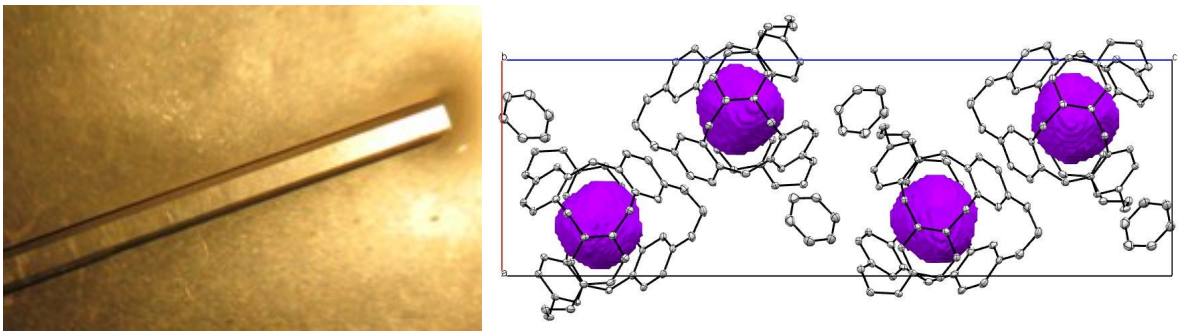

Figure S7b. Picture of the X-ray single crystals for the [CD(−)$_{254}$]-**1** derivative. View of the crystal packing of [CD(+)$_{254}$]-**1** along the b axis of the unit cell. The volume accessible by a guest molecule is represented by the purple zone.

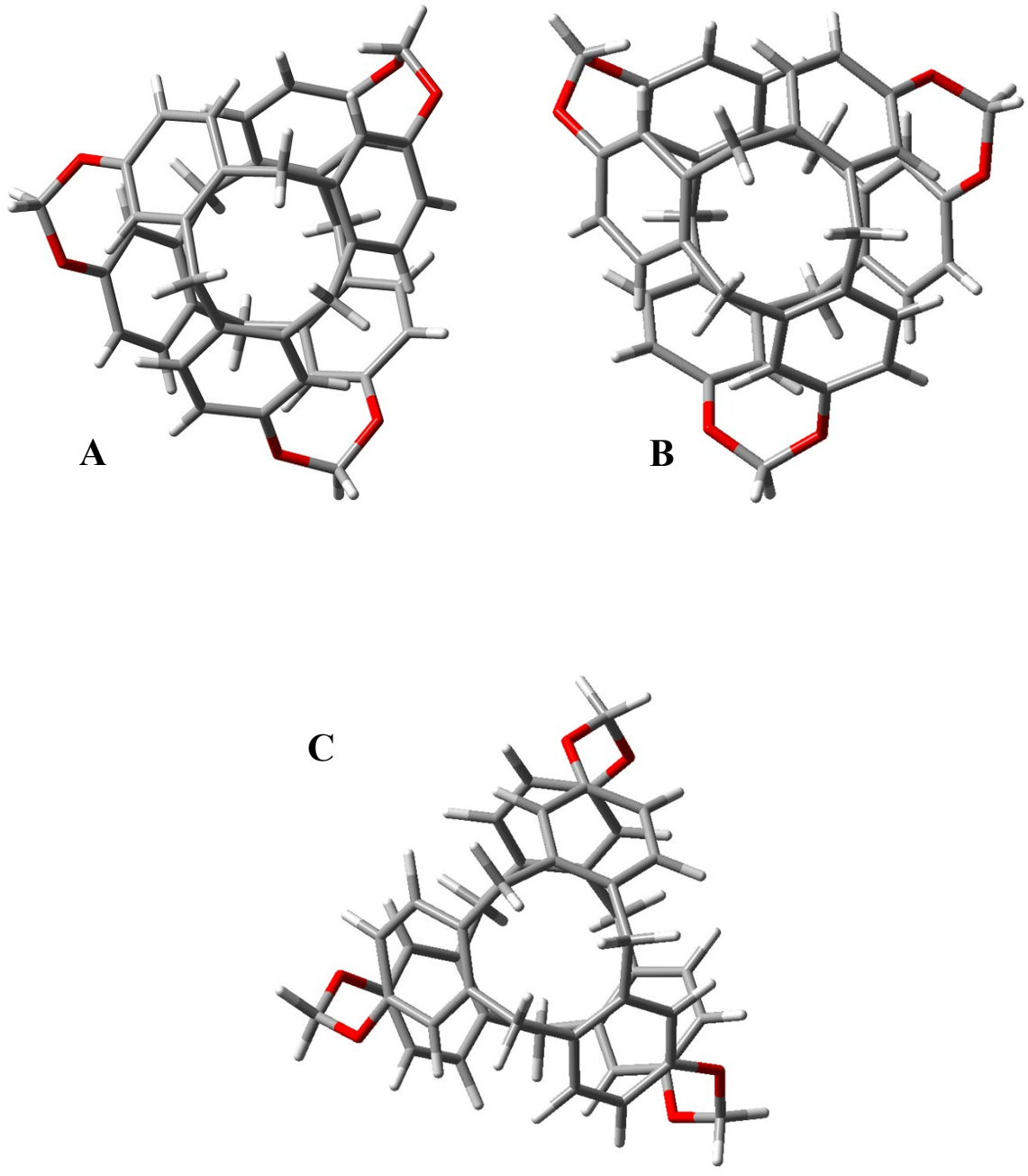

Figure S8. Top view of A) [CD(+)$_{254}$]-**1** , B) [CD(−)$_{254}$]-**1**, and C) (rac)-**1** geometries obtained from X-ray structures.

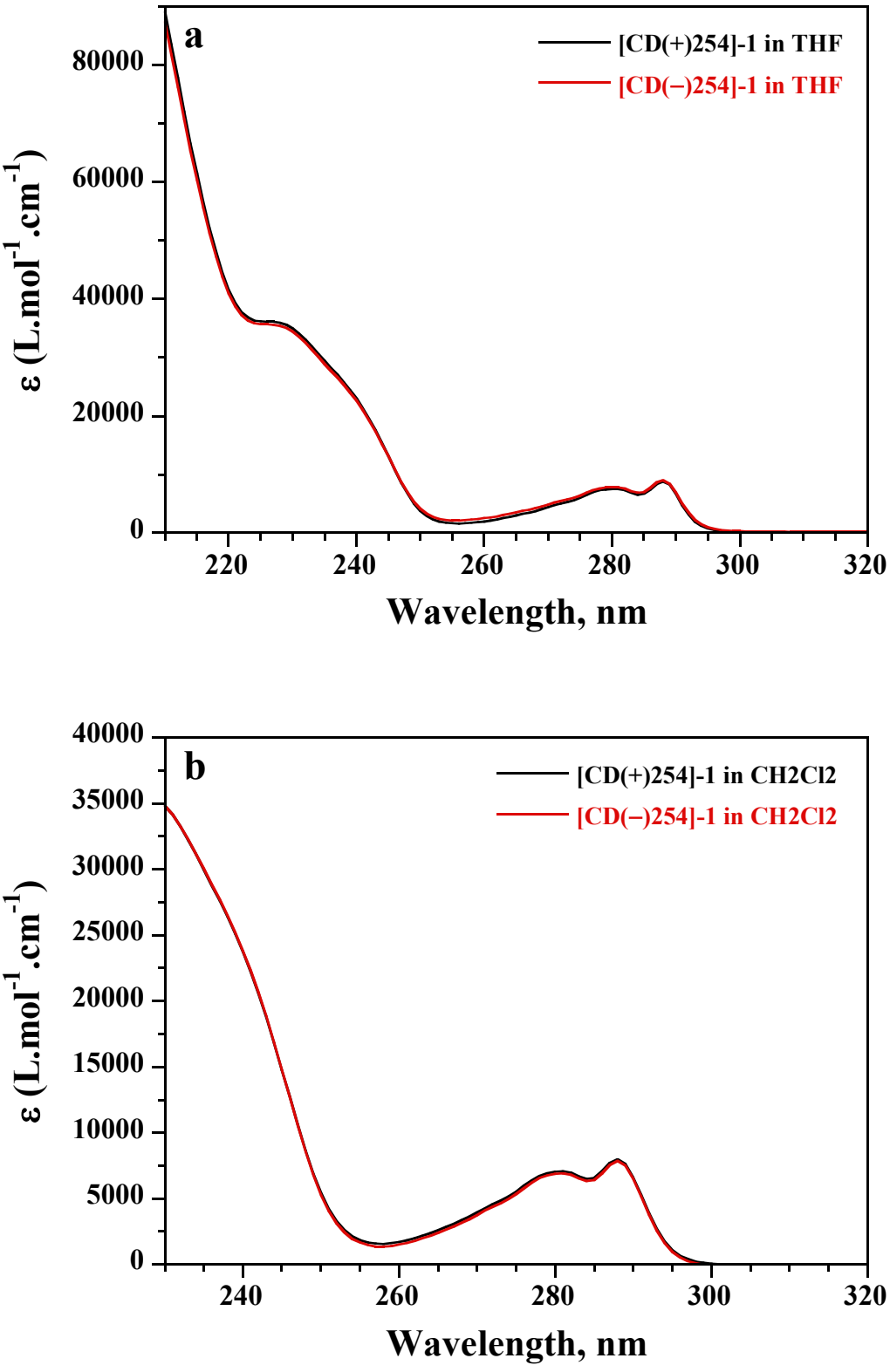

Figure S9. UV-vis spectra of [CD(+)254]-**1** (black spectra) and [CD(−)254]-**1** (red spectra) in THF and CH_2Cl_2 solvents at 298 K. Concentration used for [CD(−)254]-**1** and [CD(+)254]-**1** are in the range 6.5 - 8.0 10^{-5} M.

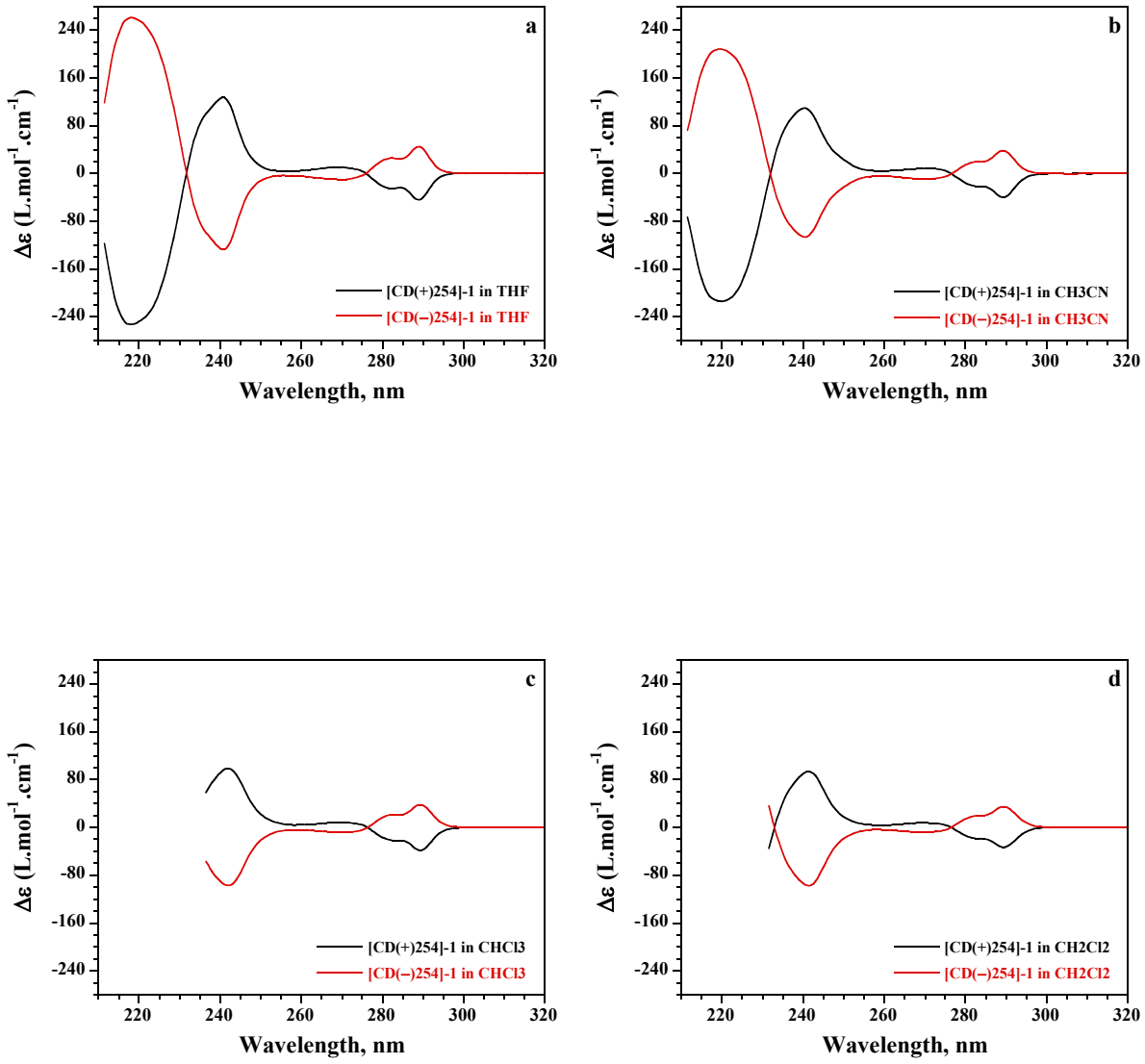

Figure S10. ECD spectra of [CD(+)254]-**1** (black spectra) and [CD(−)254]-**1** (red spectra) in a) THF, b) CH_3CN, c) $CHCl_3$ and d) CH_2Cl_2 solvents at 298 K.

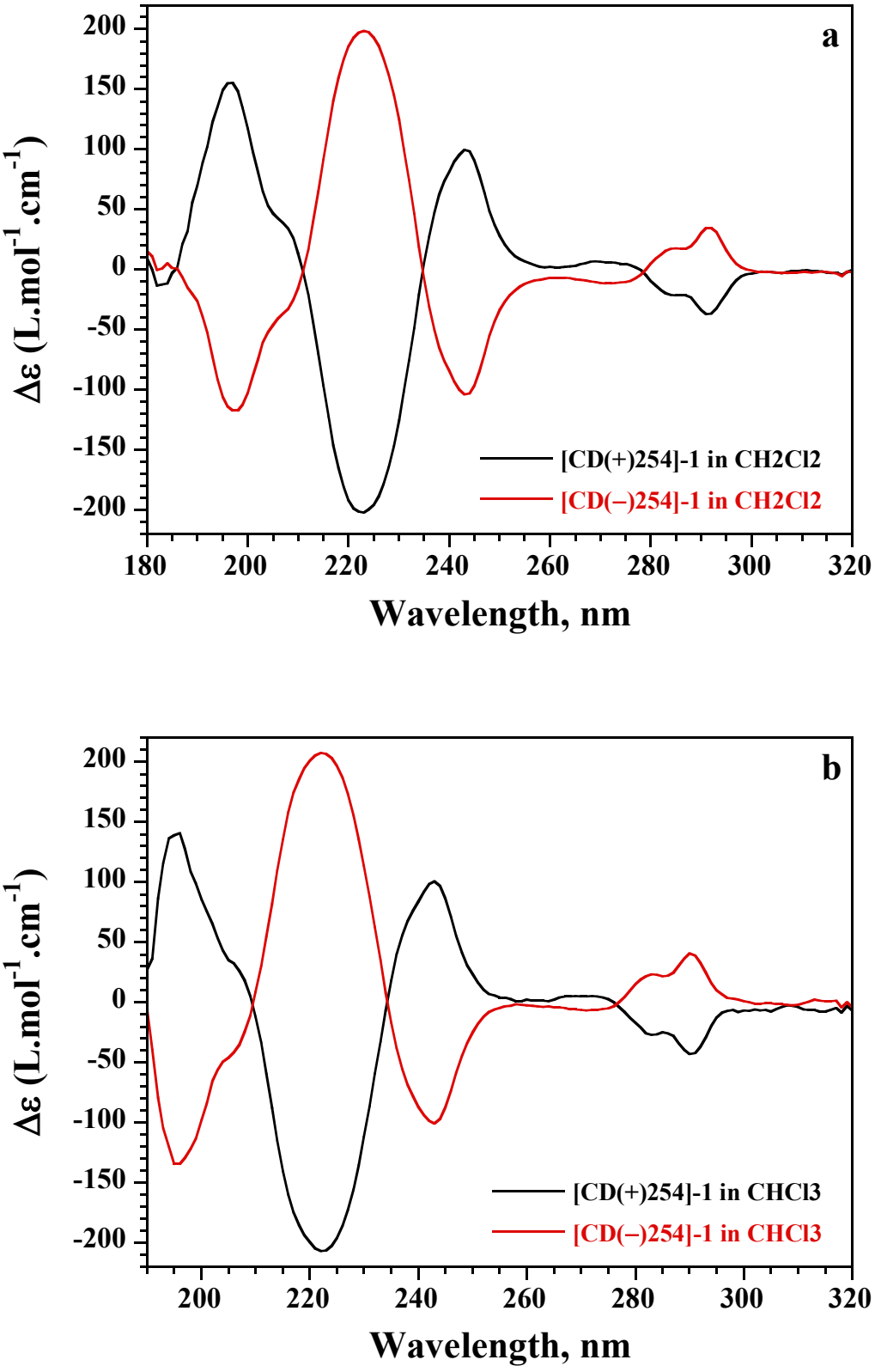

Figure S11. SRCD spectra of [CD(+)254]-**1** (black spectra) and [CD(−)254]-**1** (red spectra) in a) CH_2Cl_2 and b) $CHCl_3$ solvents at 298 K.

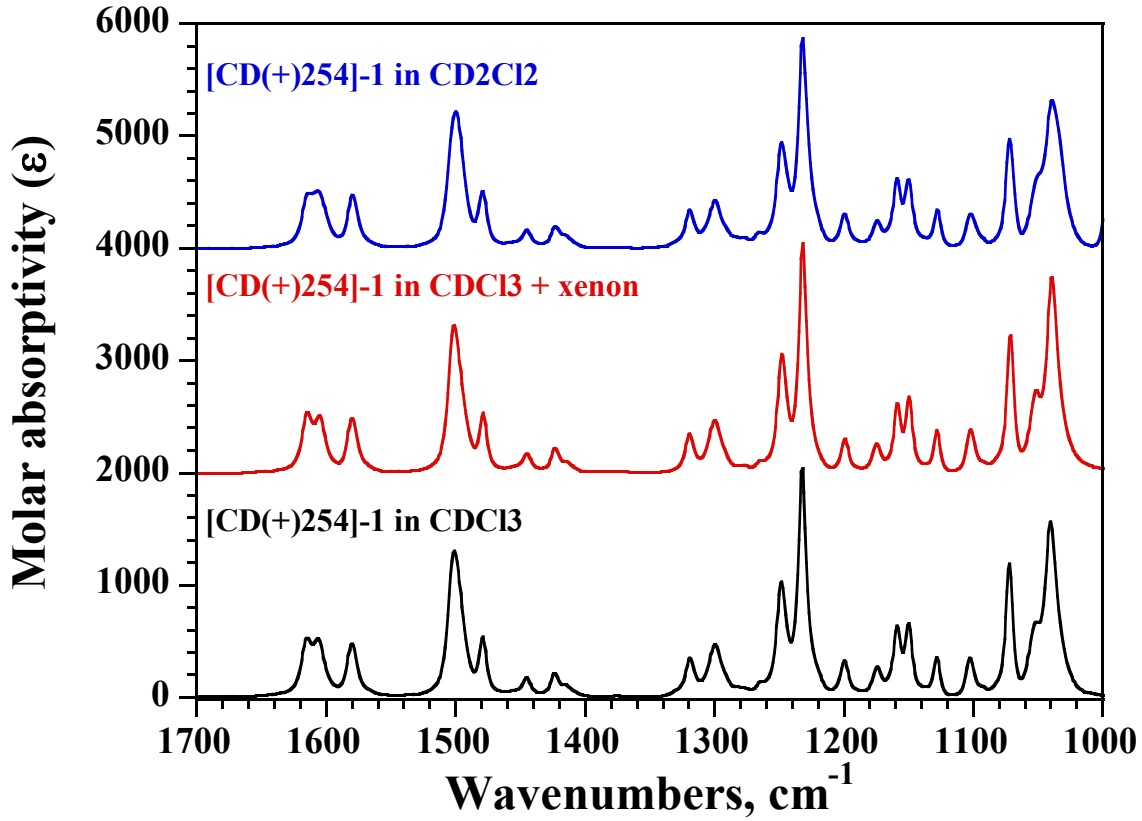

Figure S12. IR spectra of [CD(+)254]-**1** in CD_2Cl_2 (blue spectrum), in $CDCl_3$ with xenon (red spectrum) and in $CDCl_3$ (black spectrum) solutions.

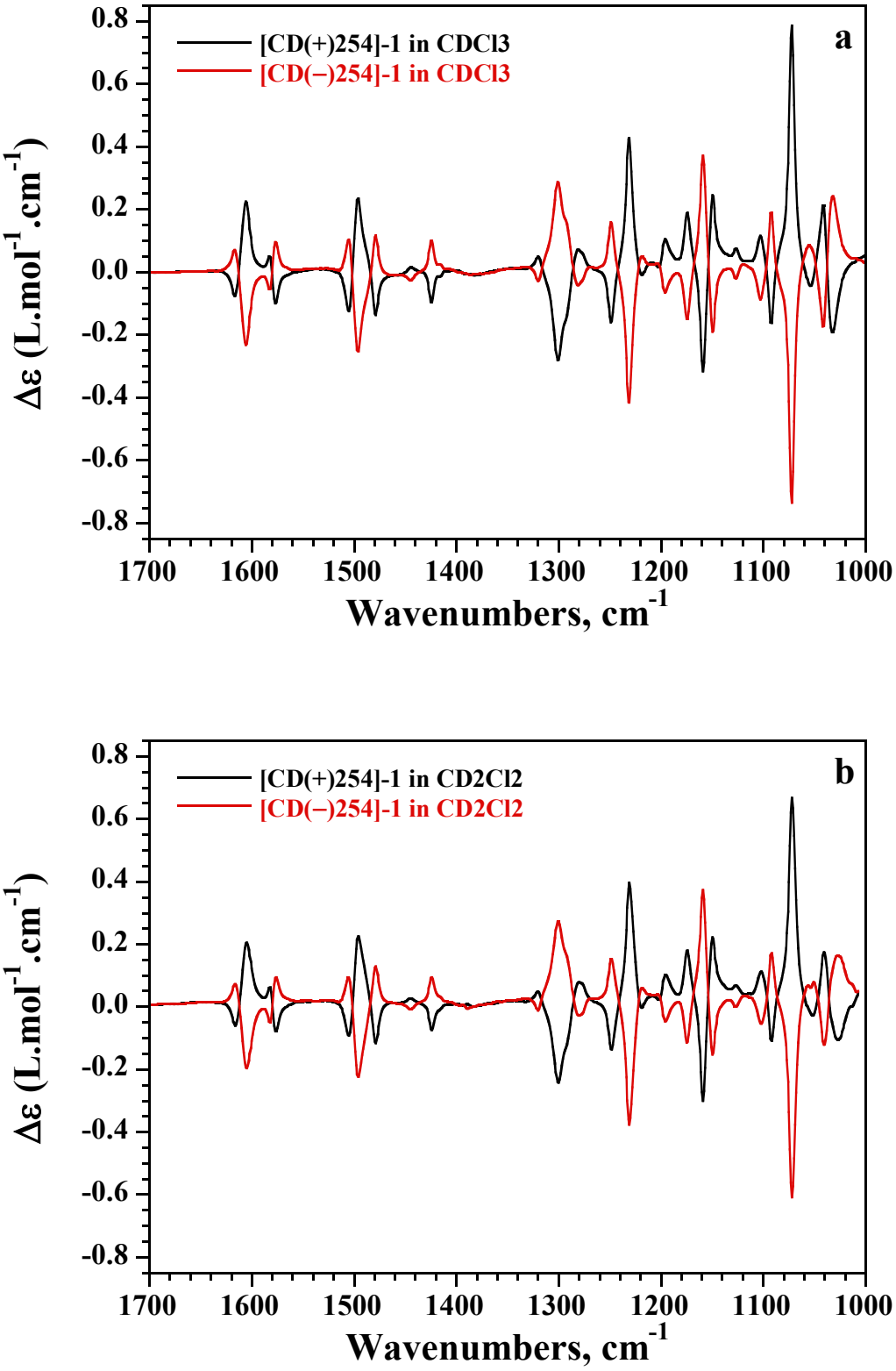

Figure S13. VCD spectra of [CD(+)254]-**1** (black spectra) and [CD(−)254]-**1** (red spectra) in a) $CDCl_3$ and b) CD_2Cl_2 solutions.

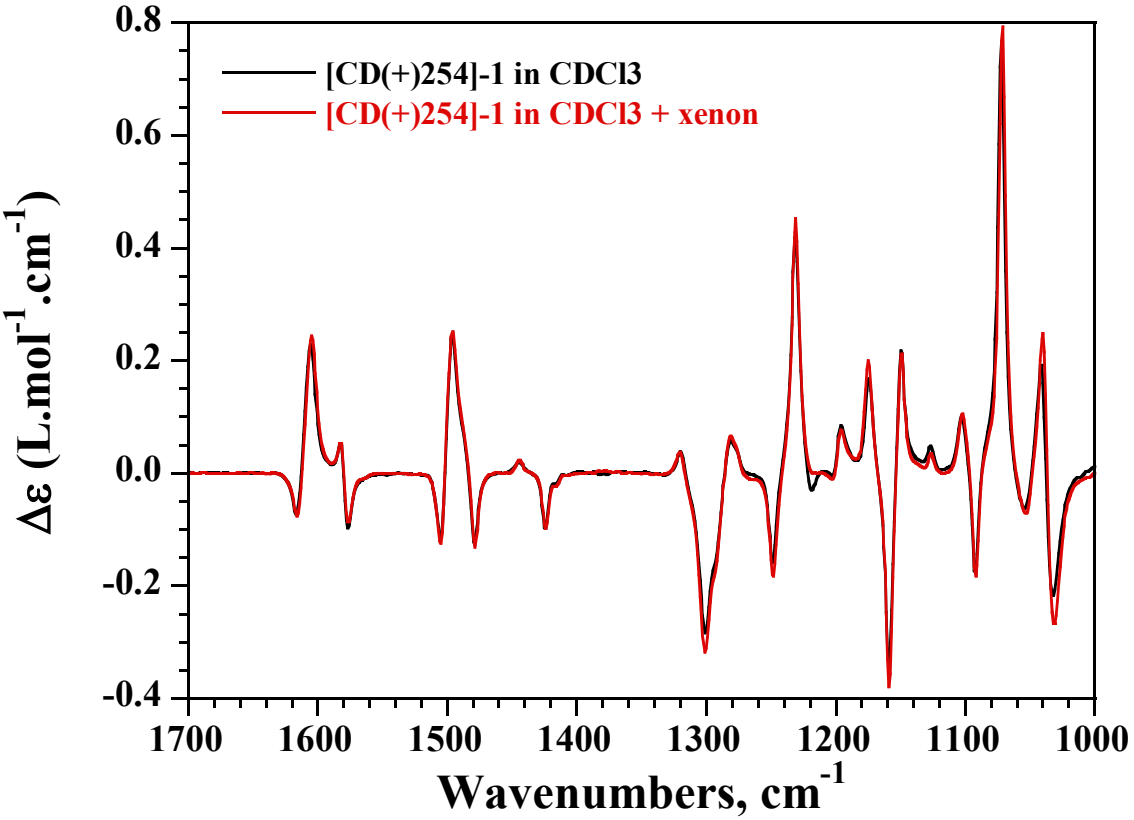

Figure S14. Comparison of experimental VCD spectra of [CD(+)$_{254}$]-**1** in $CDCl_3$ in presence (red spectrum) or not (black spectrum) of xenon.

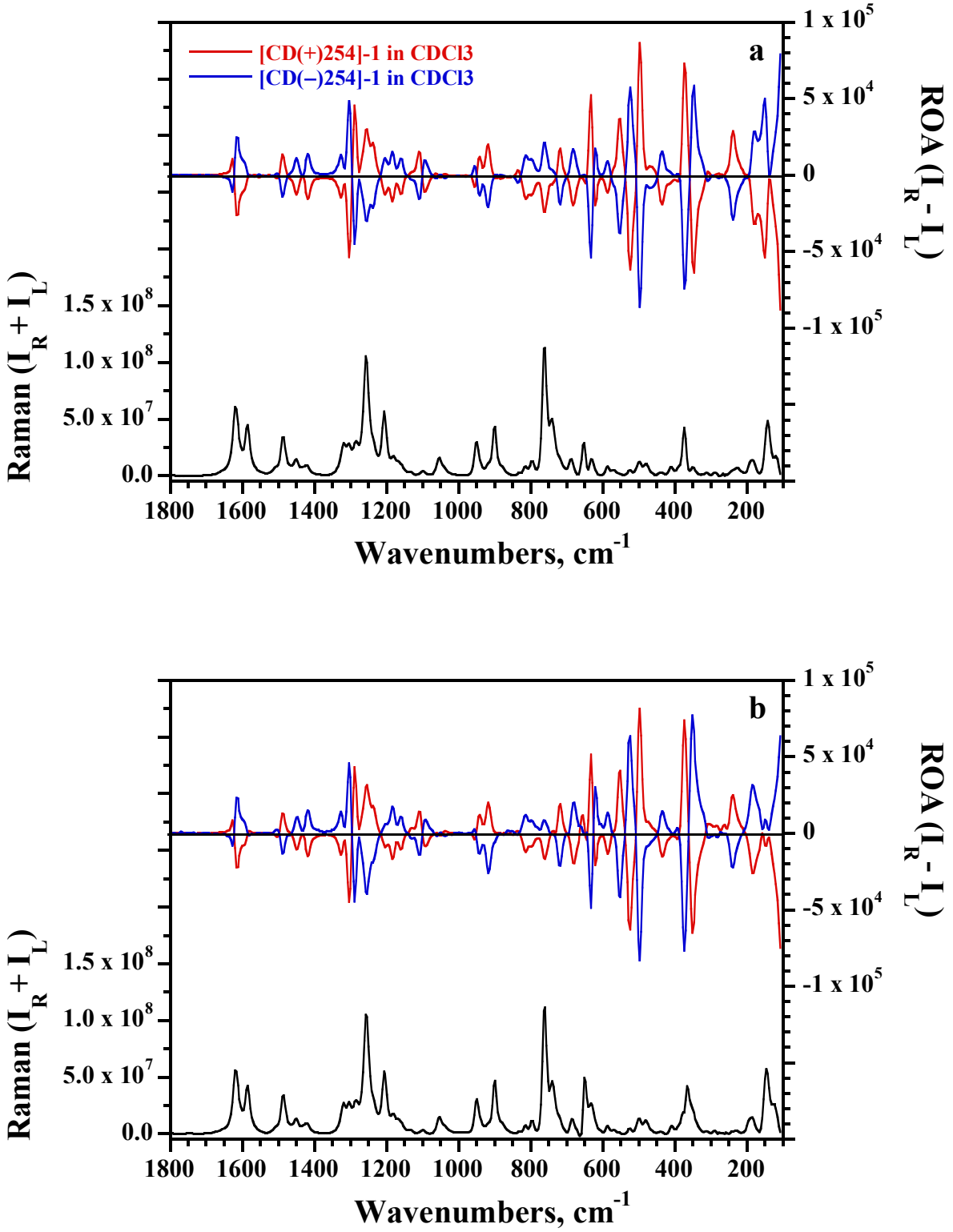

Figure S15. ROA spectra of [CD(+)254]-**1** (red spectra) and [CD(–)254]-**1** (blue spectra) in a) $CDCl_3$ and b) $CDCl_3$ in presence of xenon.

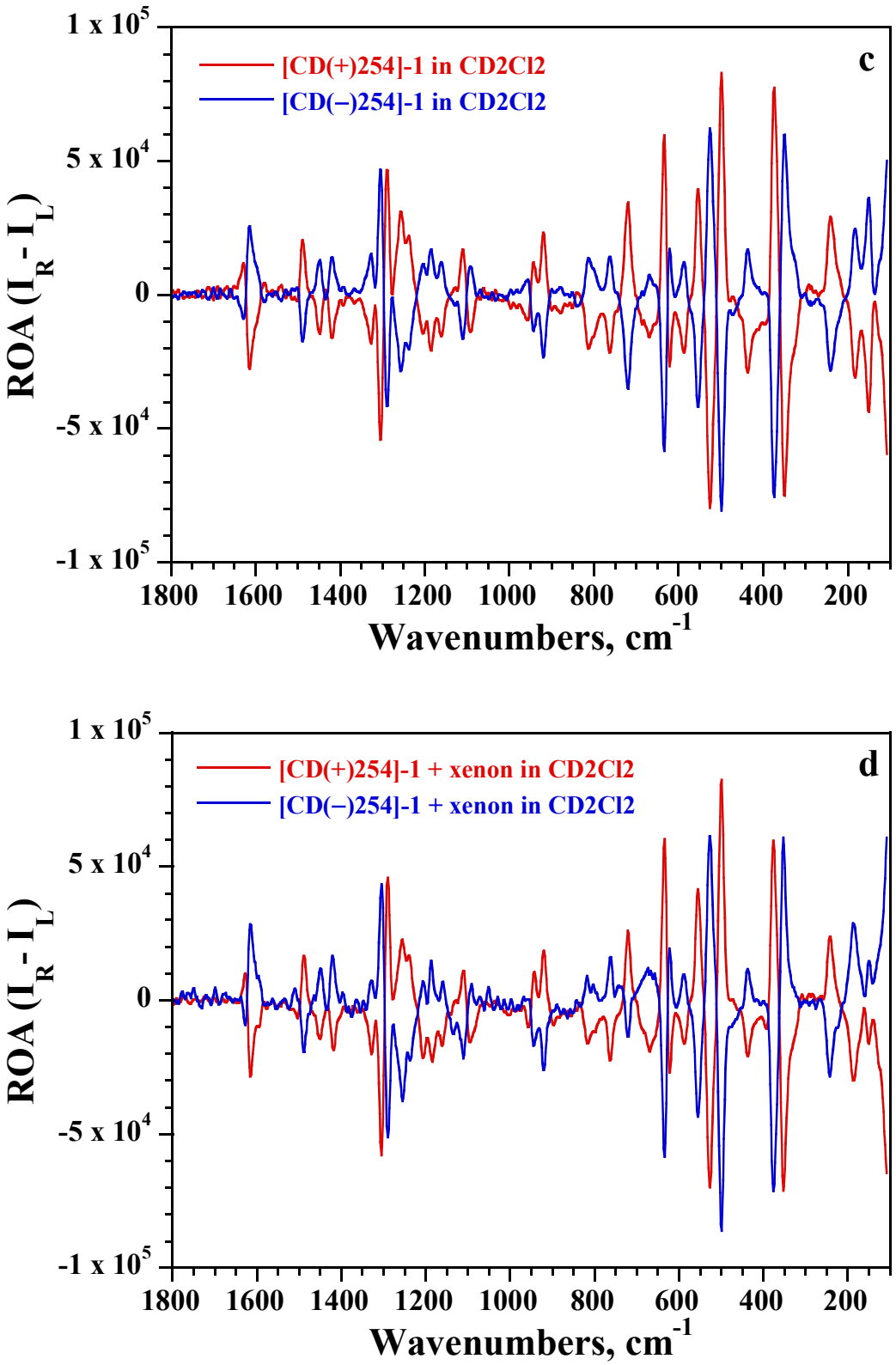

Figure S15. ROA spectra of [CD(+)254]-**1** (red spectra) and [CD(−)254]-**1** (blue spectra) in c) CD_2Cl_2 and d) CD_2Cl_2 in presence of xenon.

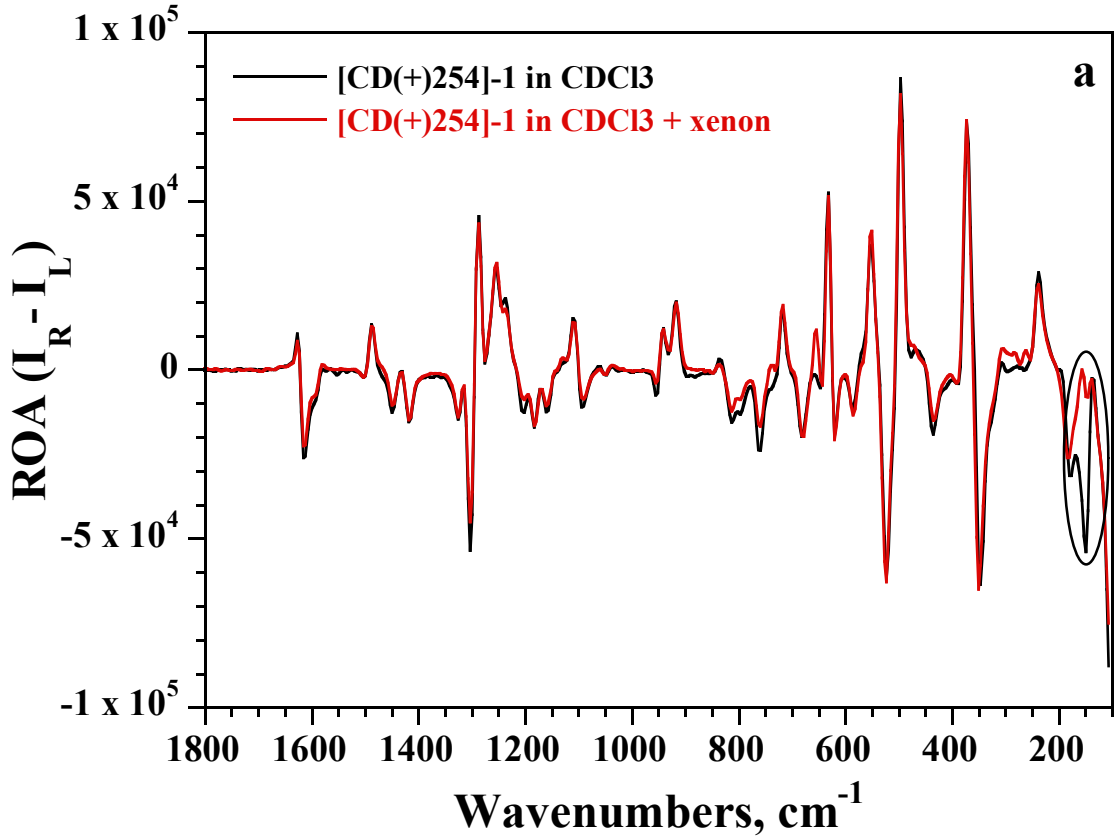

Figure S16. Comparison of experimental ROA spectra of [CD(+)$_{254}$]-**1** in $CDCl_3$ solution in presence (red spectrum) or not (black spectrum) of xenon.

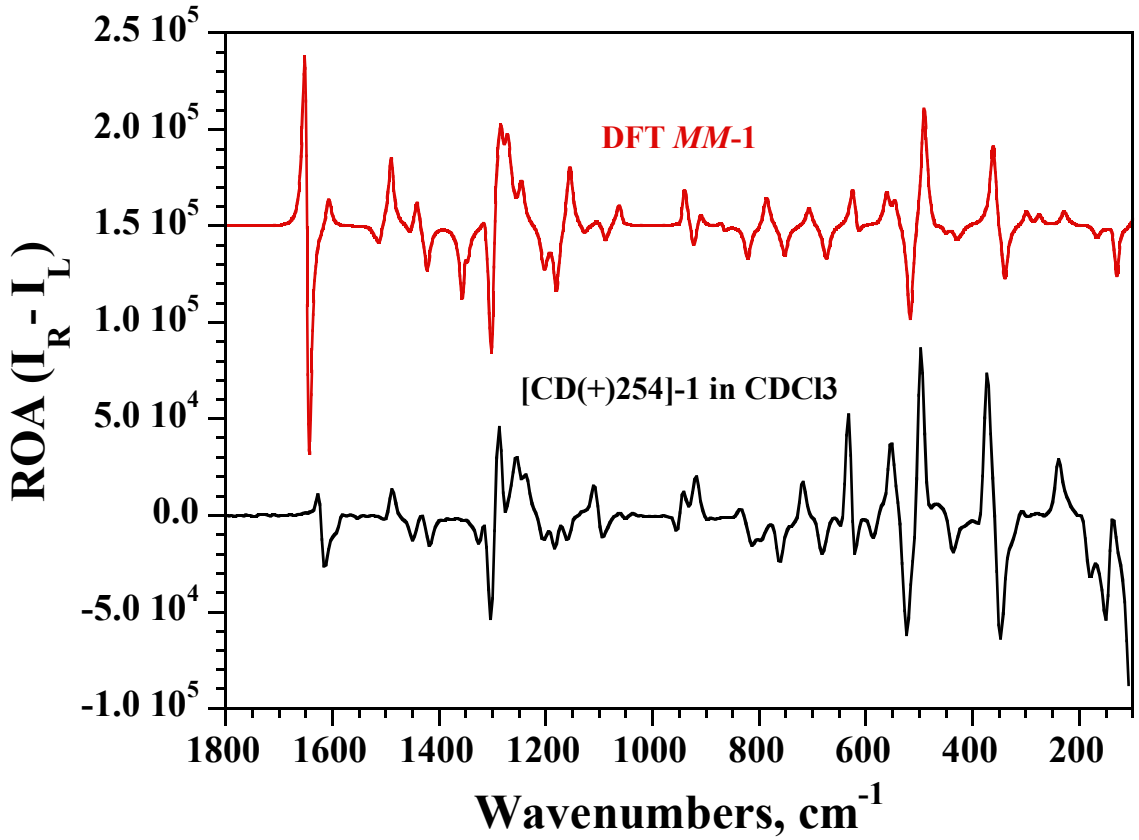

Figure S17. Comparison of the experimental ROA spectrum of [CD(+)254]-**1** recorded in $CDCl_3$ solution with the calculated spectrum at the B3PW91/6-31G** level for conformer A of *MM*-**1**.

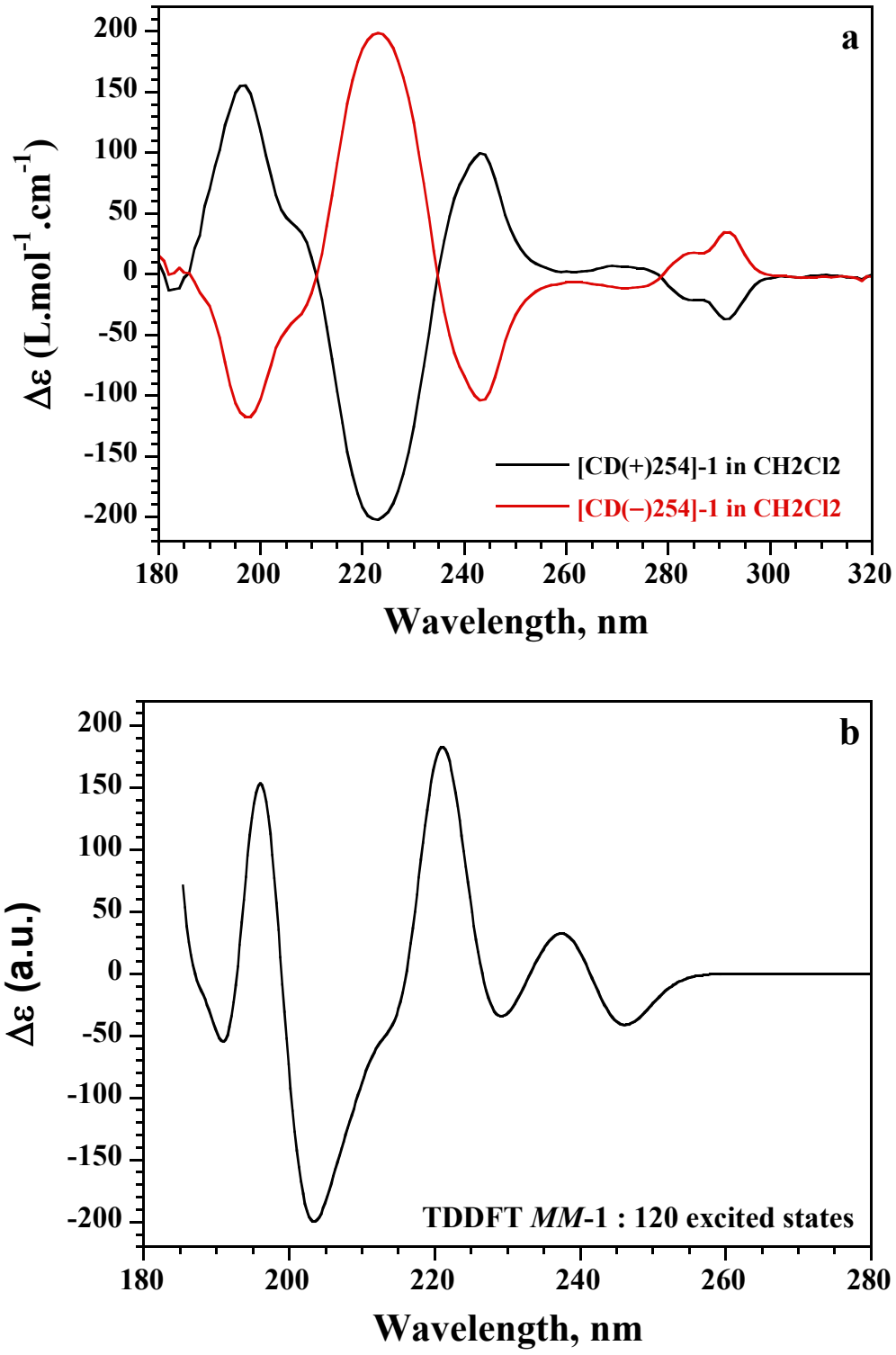

Figure S18. Comparison of experimental a) SRCD spectra of [CD(+)254]-**1** (black spectra) and [CD(−)254]-**1** (red spectra) recorded in CH_2Cl_2 solution with b) the predicted spectrum calculated by TDDFT for the *MM* configuration of **1**.

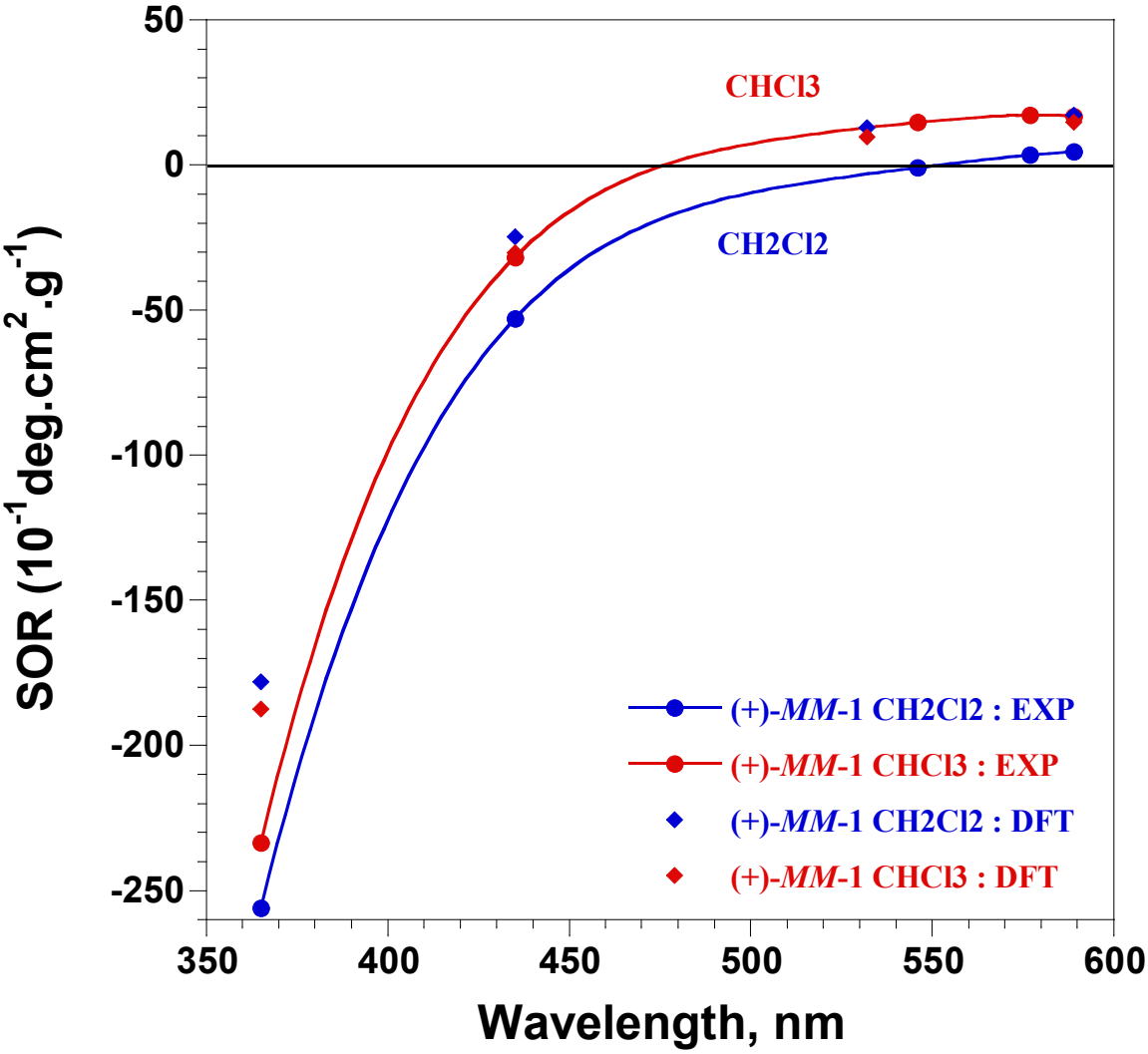

Figure S19. Specific optical rotation values (10^{-1} deg cm^2 g^{-1}) of [CD(+)254]-**1** recorded at several wavelengths (365, 435.8, 546.1, 577 and 589 nm) in $CHCl_3$ and CH_2Cl_2 solvents. Specific optical rotation calculated at the B3PW91/6-31G** level (IEFPCM=$CHCl_3$ and CH_2Cl_2) for conformer A of *MM*-**1**.

compound	[CD(−)$_{254}$]-**1**	[CD(+)$_{254}$]-**1**
formula	$C_{45}H_{36}O_6$, C_5H_5N	$C_{45}H_{36}O_6$, CH_2Cl_2
formula weight	751.84	757.66
crystal habit	prism	rhombohedral
crystal colour	clear intense colourless	clear intense colourless
crystal size [mm]	0.3230×0.1838×0.0921	0.3378×0.2757×0.0873
crystal system	Orthorhombic	Monoclinic
space group	$P2_12_12_1$	$P2_1$
a (Å)	10.5518(5)	10.6304(4)
b (Å)	10.7827(5)	10.6493(5)
c (Å)	32.7161(13)	16.3294(8)
α (°)	90	90
β (°)	90	104.655(5)
γ (°)	90	90
V (Å^3)	3722.3(3)	1788.45(14)
Z	4	2
D_{calc} (g.cm^{-1})	1.342	1.407
T (K)	80	100
λ(Kα)	1.54184	1.54184
μ (mm^{-1})	0.701	2.065
θ max (°)	67.790	66.893
θ min (°)	4.317	4.299
limiting indices	$-12 \le h \le 12$ $-12 \le k \le 12$ $-36 \le l \le 38$	$-12 \le h \le 11$ $-12 \le k \le 12$ $-19 \le l \le 19$
F (000)	1584	792
reflns measured	63817	25119
unique reflns.	6606	6318
reflns used $I>2\sigma(I)$	6606	6318
no. of parameters	515	488
restraints	0	1
GOF on F^2	1.069	1.038
R_1 [$I > 2\sigma(I)$]	0.0526	0.0476
wR_2	0.1197	0.1224
max $\Delta\rho$ [eÅ^{-3}]	0.292	0.327
min $\Delta\rho$ [eÅ^{-3}]	-0.263	-0.373
Flack parameter (x)	-0.04(11)	-0.031(13)
Hooft parameter (y)	-0.05(9)	-0.018(8)

Table S1. Crystal data and structure refinement of [CD(+)$_{254}$]-**1** and [CD(−)$_{254}$]-**1**

Compd.	solvent	Conc.[a]	$[\alpha]_{589}^{25}$	$[\alpha]_{577}^{25}$	$[\alpha]_{546}^{25}$	$[\alpha]_{436}^{25}$	$[\alpha]_{365}^{25}$
[CD(+)254]-**1**	CH_2Cl_2	0.27	+ 4.5	+ 3.4	- 0.9	- 52.9	- 256.1
[CD(−)$_{254}$]-**1**	CH_2Cl_2	0.27	- 4.1	- 3.7	+ 1.7	+ 53.6	+ 255.0
[CD(+)254]-**1**	$CHCl_3$	0.22	+ 16.9	+ 17.2	+ 14.7	- 31.7	- 233.6
[CD(−)$_{254}$]-**1**	$CHCl_3$	0.23	- 15.8	- 15.8	- 14.0	+ 30.9	+ 228.5

[a] g/100 mL.

Table S2. Optical rotations (10^{-1} deg cm^2 g^{-1}) of the two enantiomers of compound **1** recorded at several wavelengths in CH_2Cl_2 or $CHCl_3$.