Supplementary Information

Hierarchical chirality observed from chiral supramolecular assembling of racemic and enantiopure helicene derivatives on silica nanohelix surfaces

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Figure S1

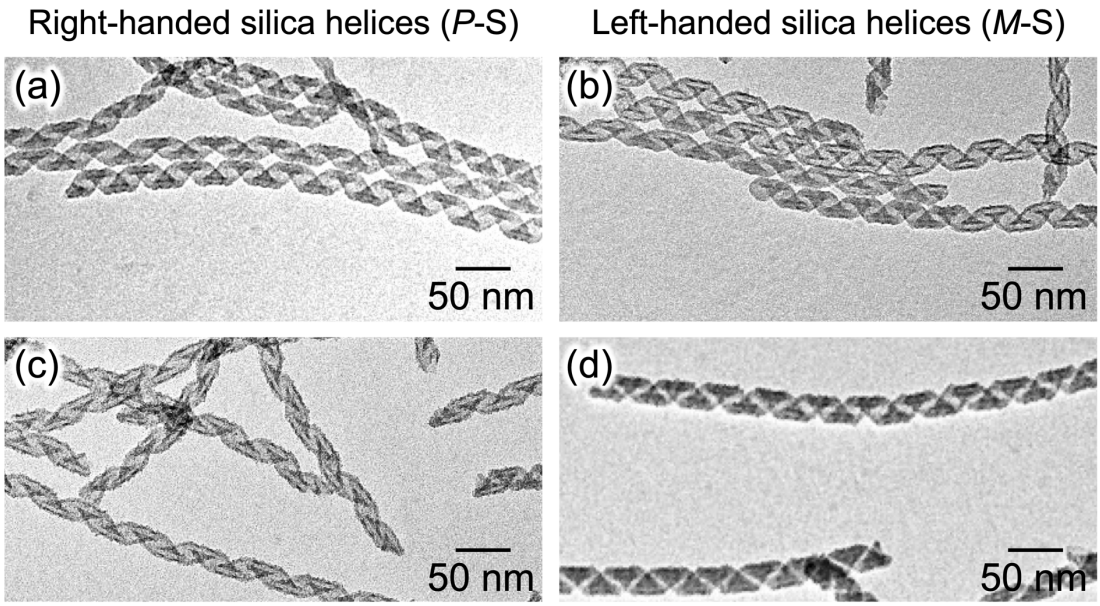


Figure S1. TEM images of silica nanoelices prepared from gemini surfactant with L- or D-tartrate before (a, b) and after (c, d) modification of (3-Aminopropyl) triethoxysilane (APTES).

Figure S2

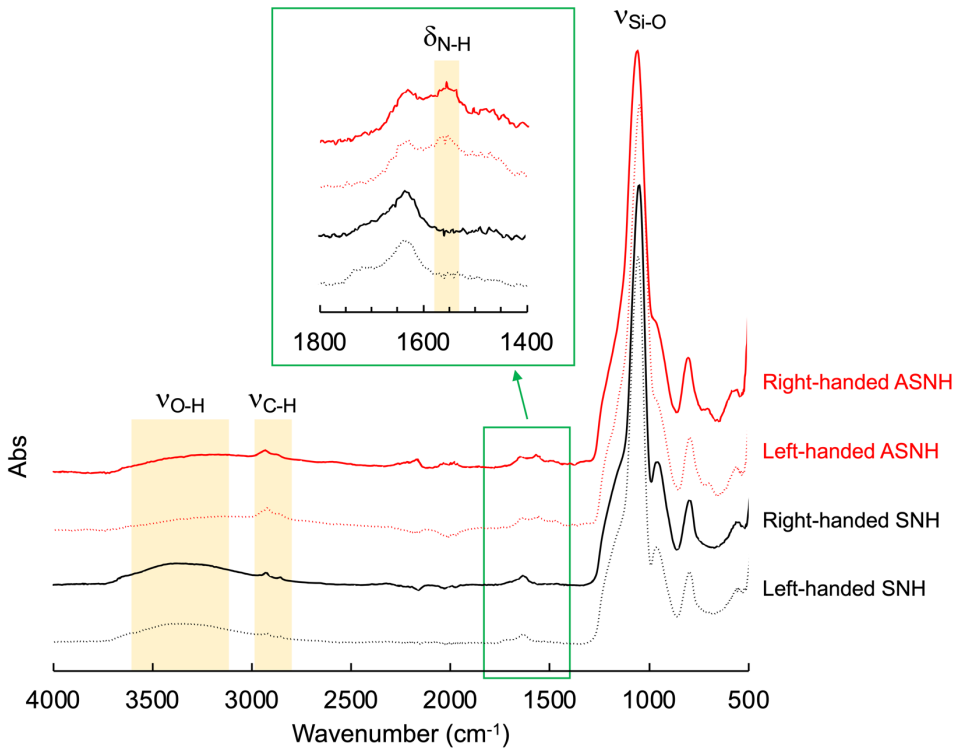


Figure S2. ATR-FTIR spectra of silica nanohelices before (SNH) and after (ASNH) modification of APTES.

Figure S3

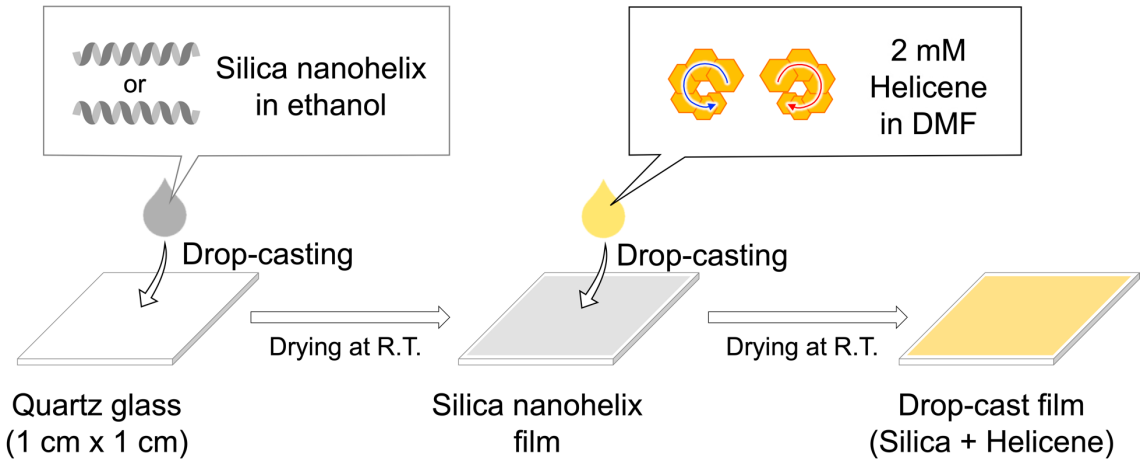


Figure S3. Schematic illustration of preparation process of drop-cast films.

Figure S4

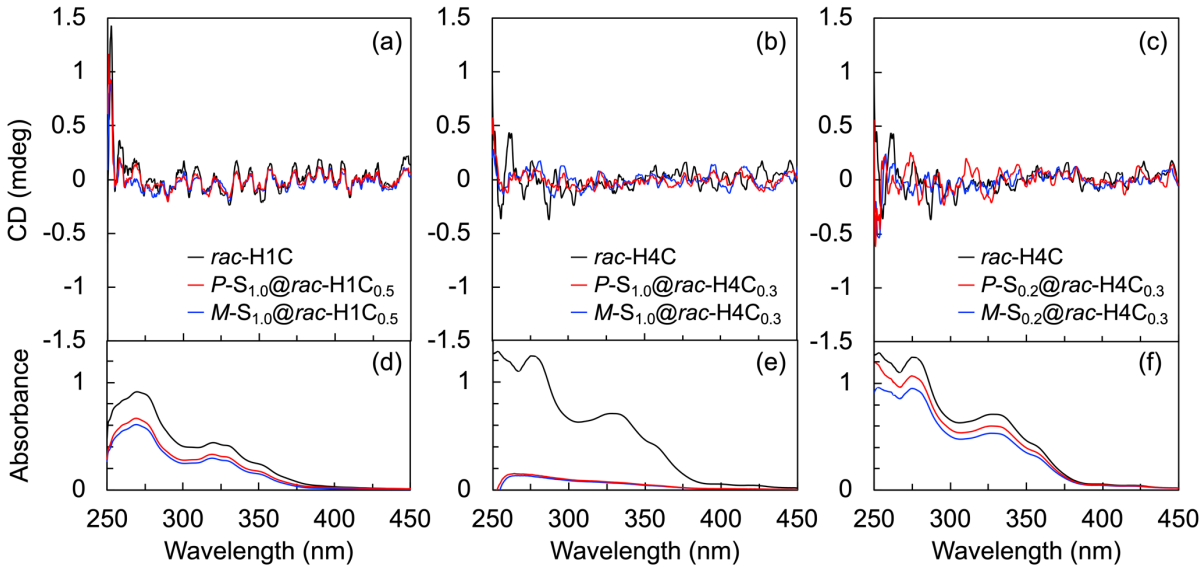


Figure S4. CD (a, b, c) and UV-vis absorption (d, e, f) spectra of supernatant of ASNH and helicenes mixture. (a, d) ASNH: 1.0 mg/mL, *rac*-H1C: 0.5 mM, (b, e) ASNH: 1.0 mg/mL, *rac*-H4C: 0.3 mM and (c, f) ASNH: 0.2 mg/mL, *rac*-H4C: 0.3 mM

Figure S5

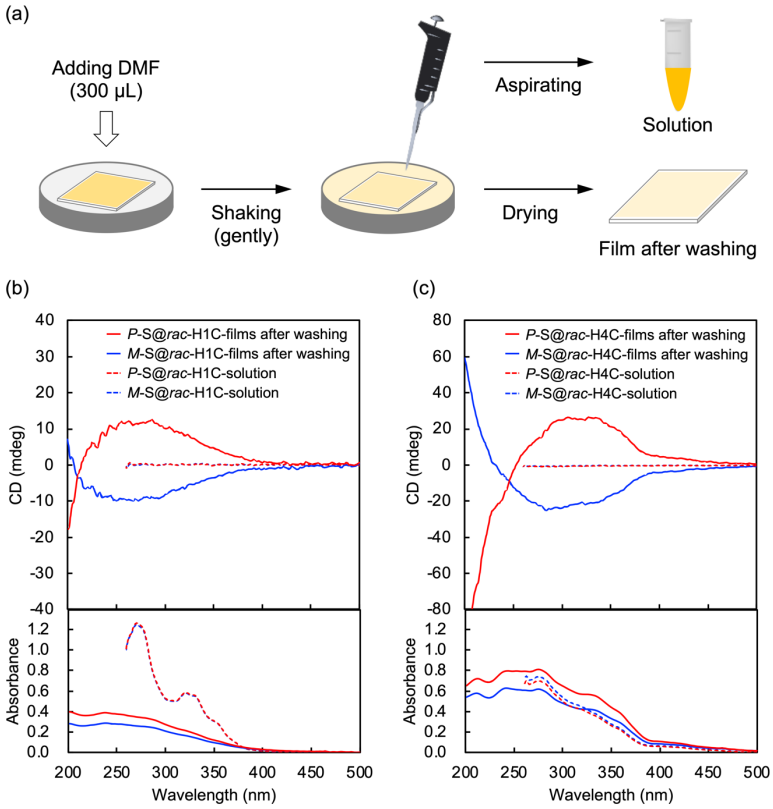


Figure S5. (a) Schematic illustration of washing process of drop-cast films and (b, c) CD and UV-vis absorption spectra of the drop-cast films and the solution after washing drop-cast films. (b) *rac*-H1C, (c) *rac*-H4C

Figure S6

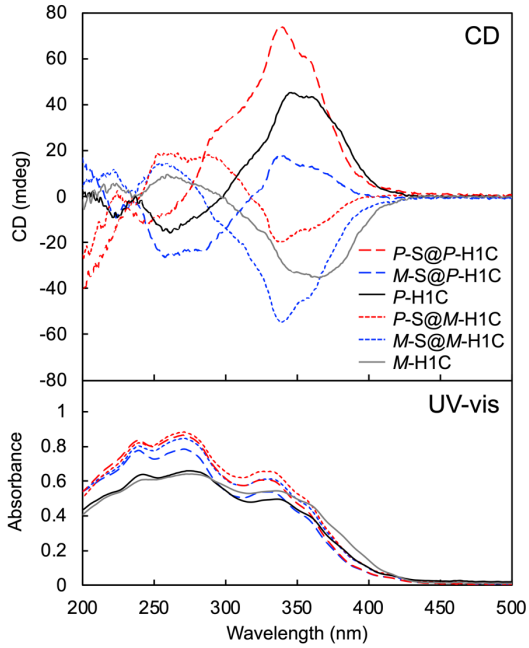


Figure S6. DRCD and UV-vis absorption spectra of drop-cast films prepared with and without ASNH and enantiomer H1C (*P*-H1C or *M*-H1C).

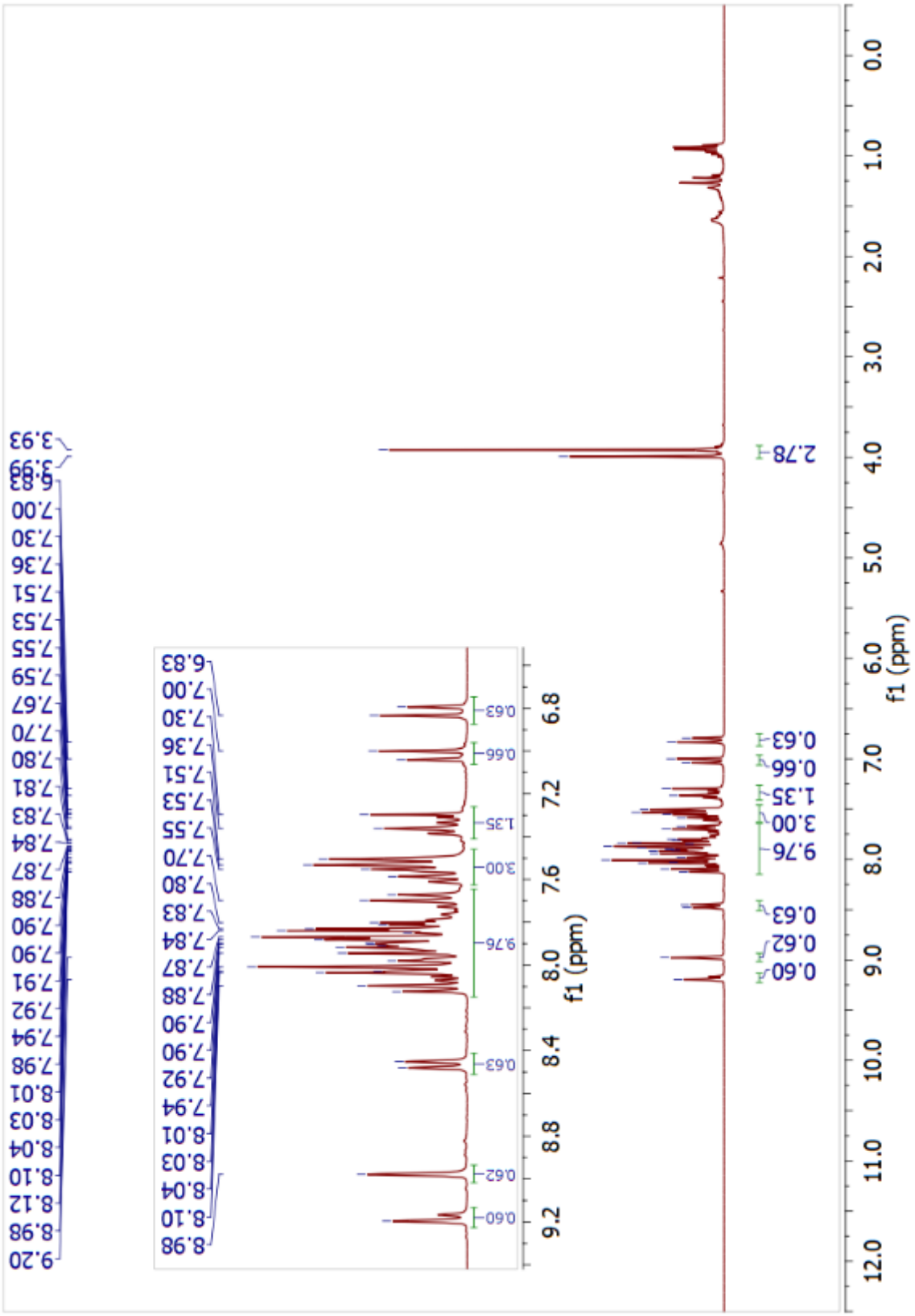


Figure S7. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of Methyl (E/Z)-[4]helicene-4-vinylbenzoate.

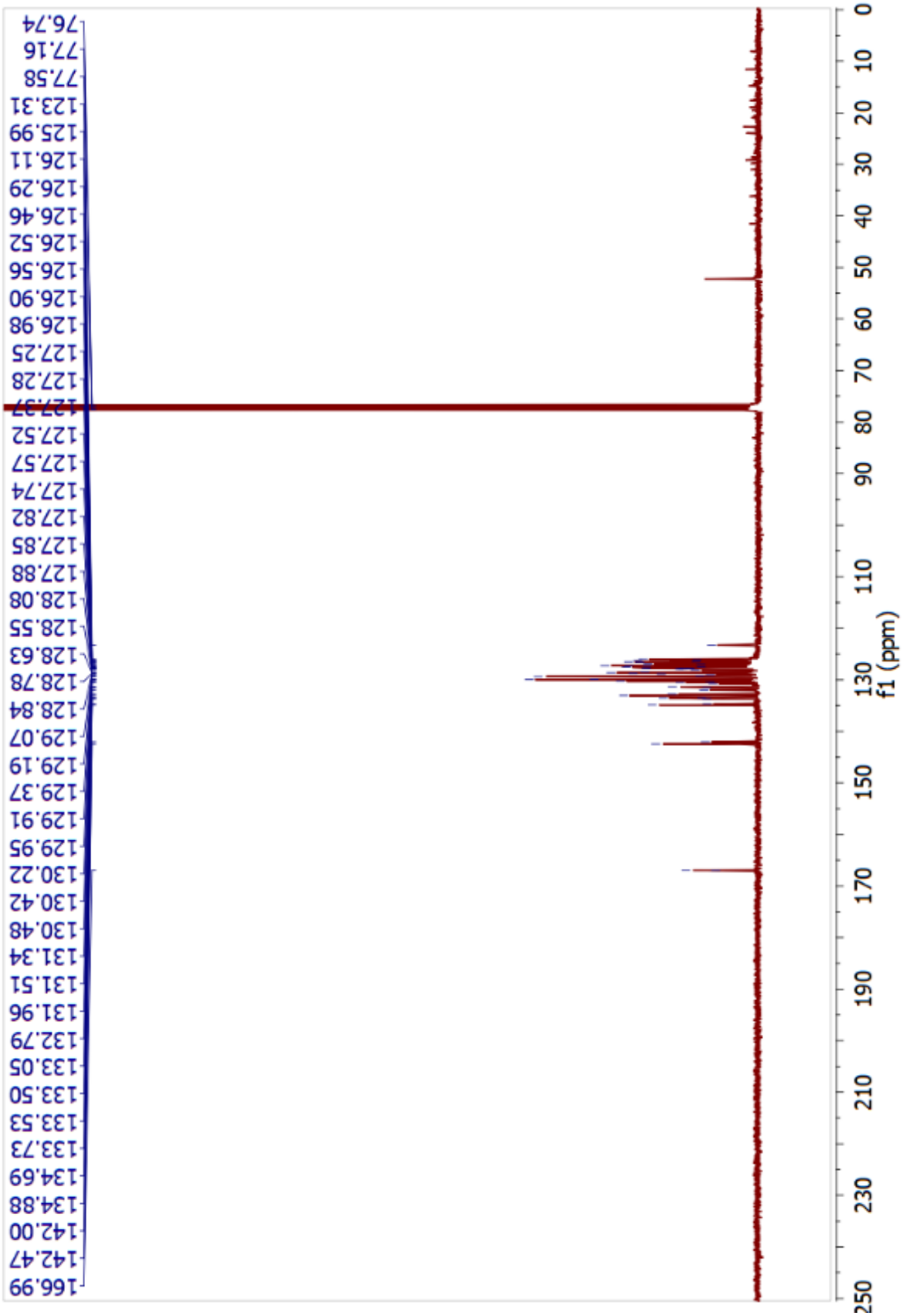


Figure S8. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of Methyl (E/Z)-[4]helicene-4-vinylbenzoate.

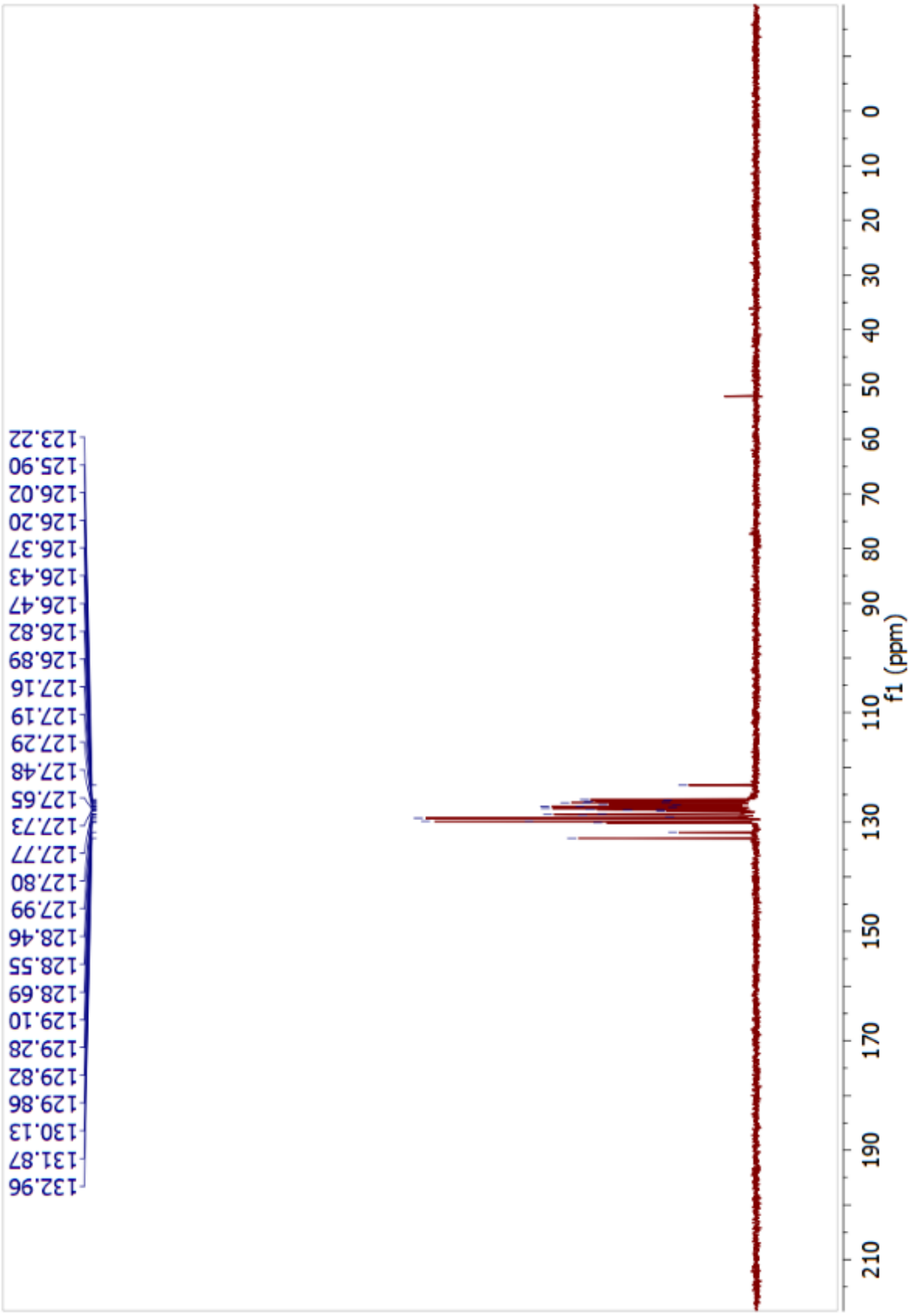


Figure S9. ^{13}C-DEPT135 NMR (75 MHz, $CDCl_3$) spectra of Methyl (E/Z)-[4]helicene-4-vinylbenzoate.

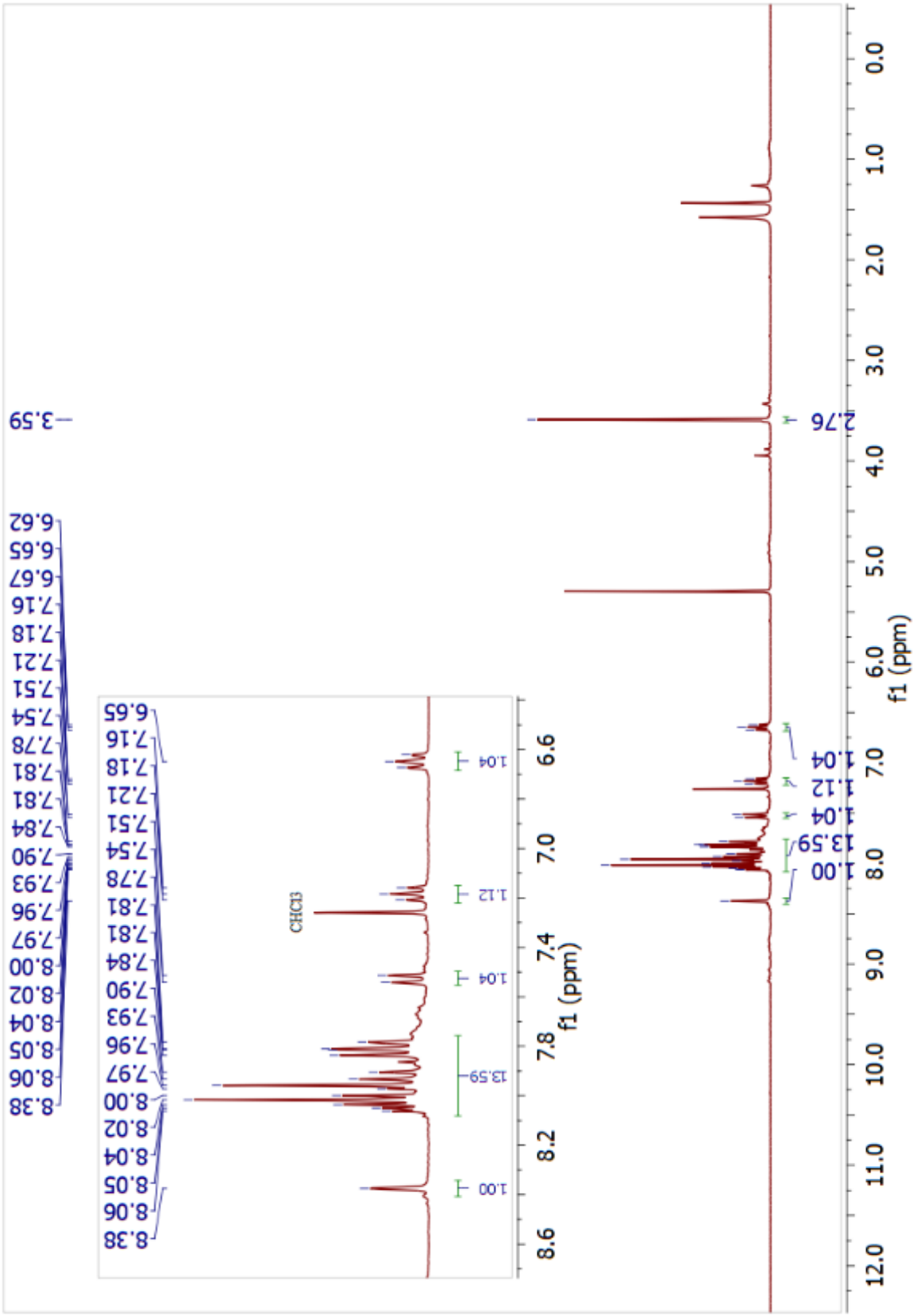


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of Methyl [6]helicene-15-carboxylate.

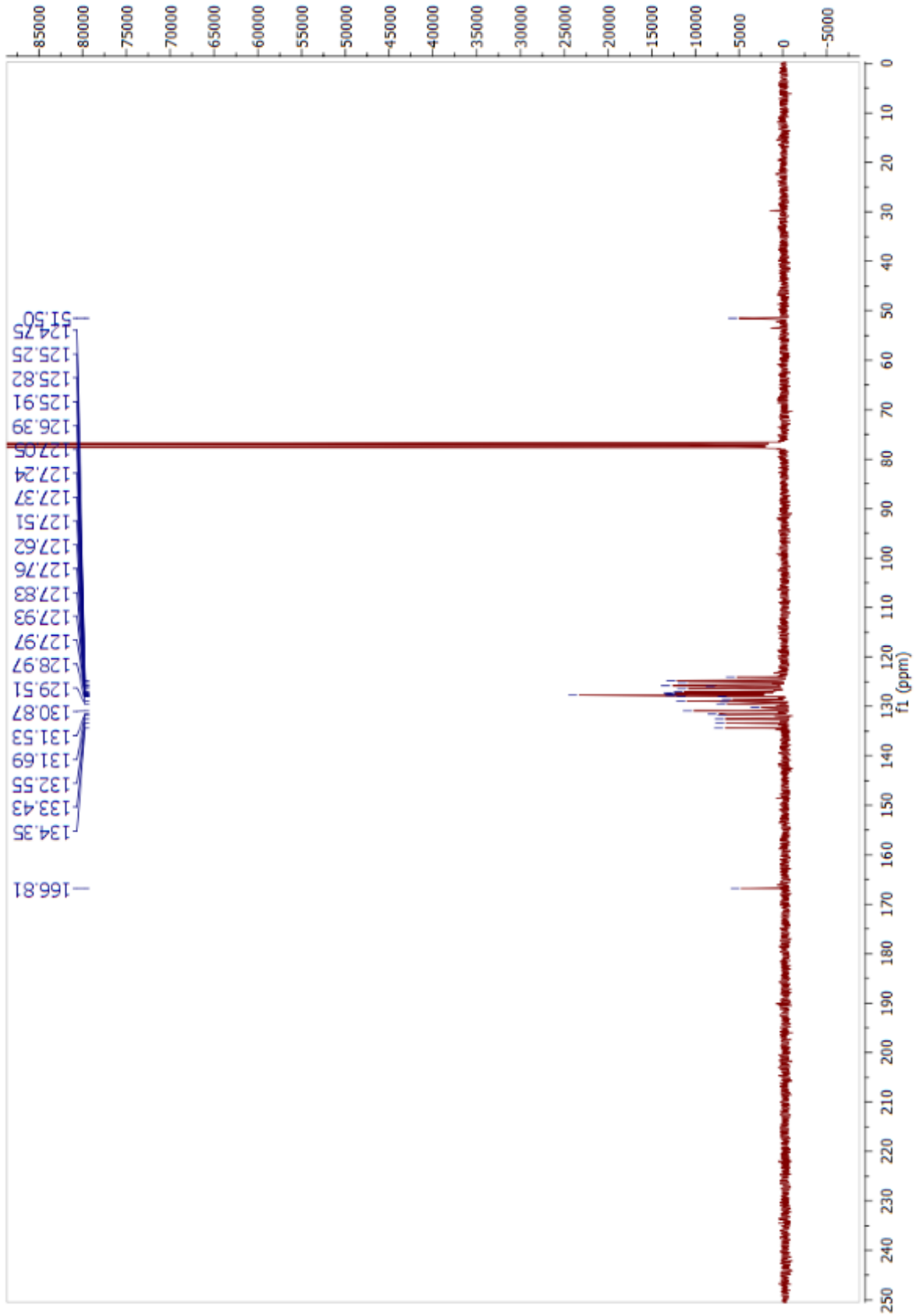


Figure S11. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of Methyl [6]helicene-15-carboxylate.

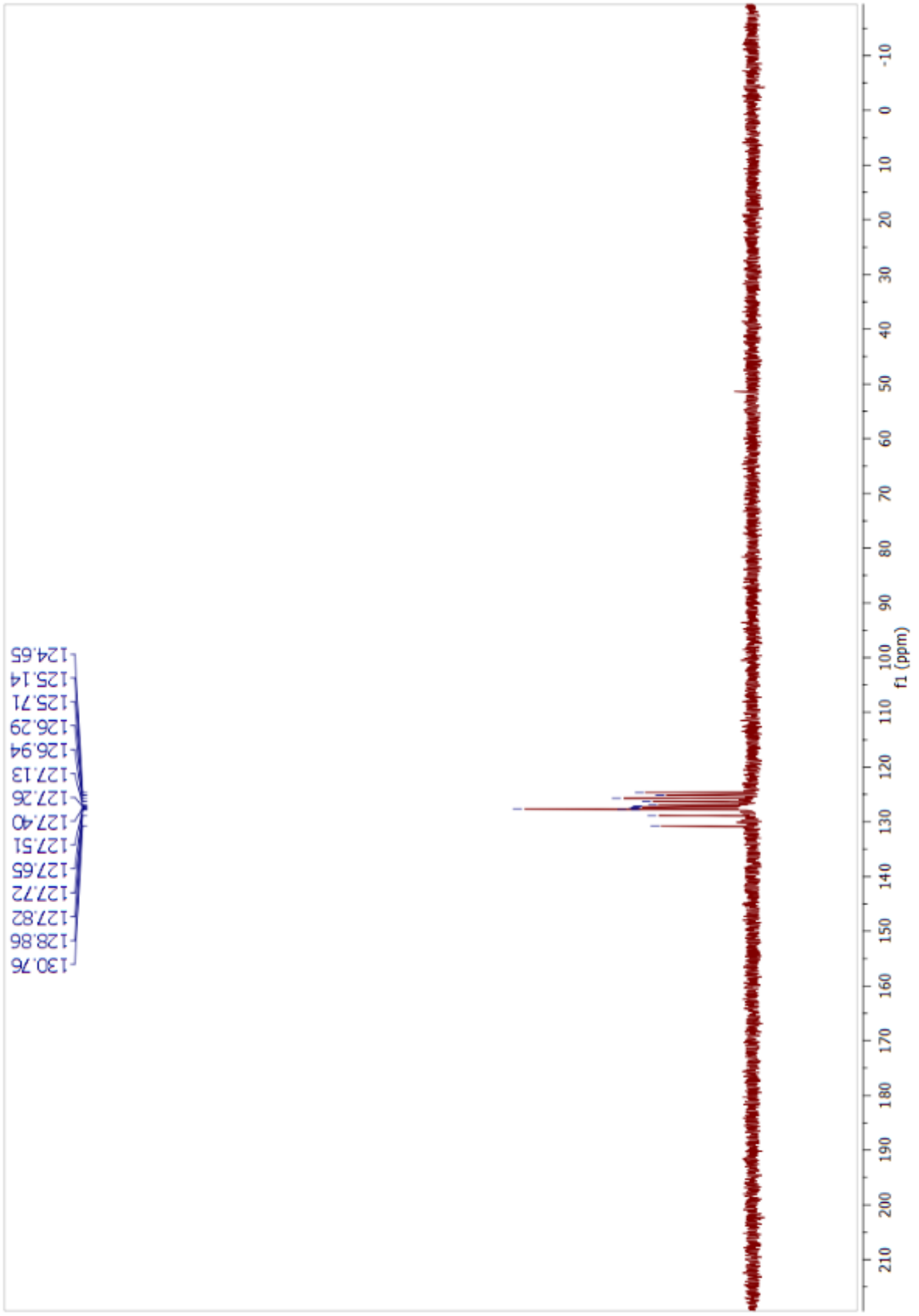


Figure S12. ^{13}C-DEPT135 NMR (75 MHz, $CDCl_3$) spectra of Methyl [6]helicene-15-carboxylate.

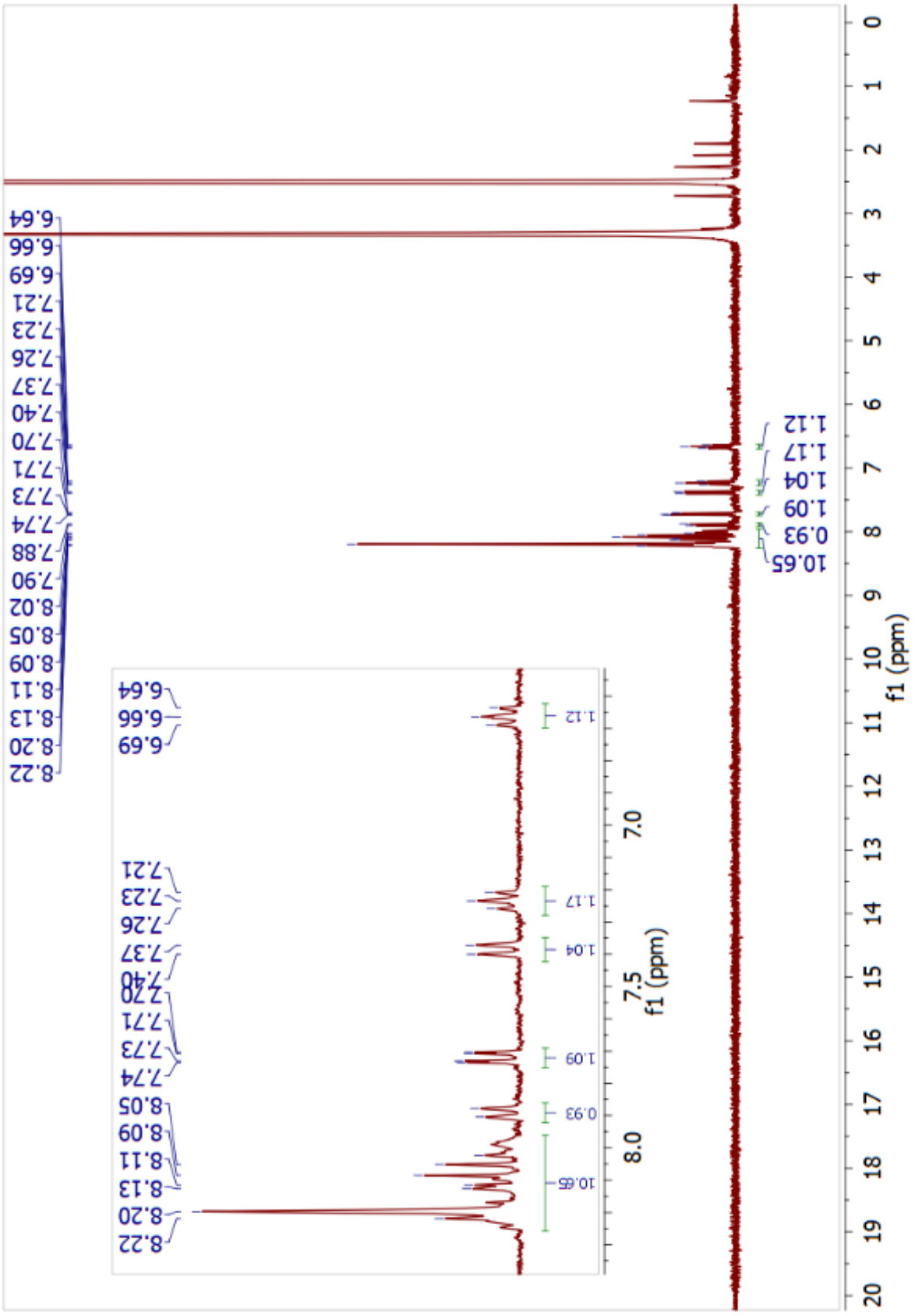
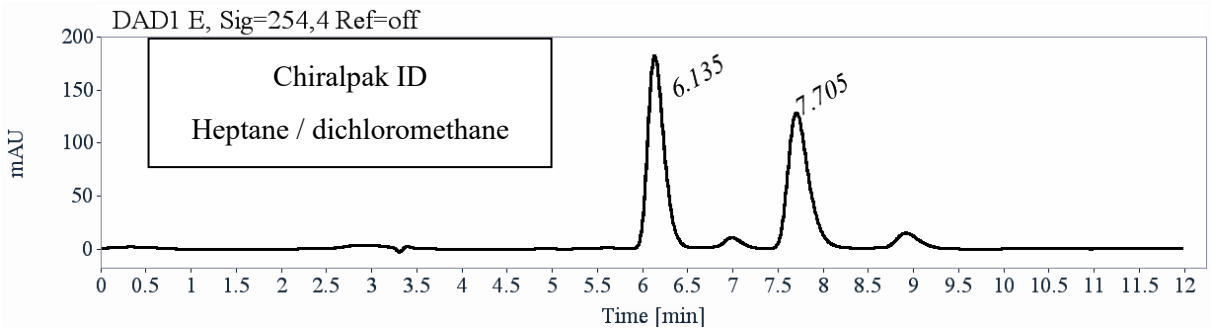


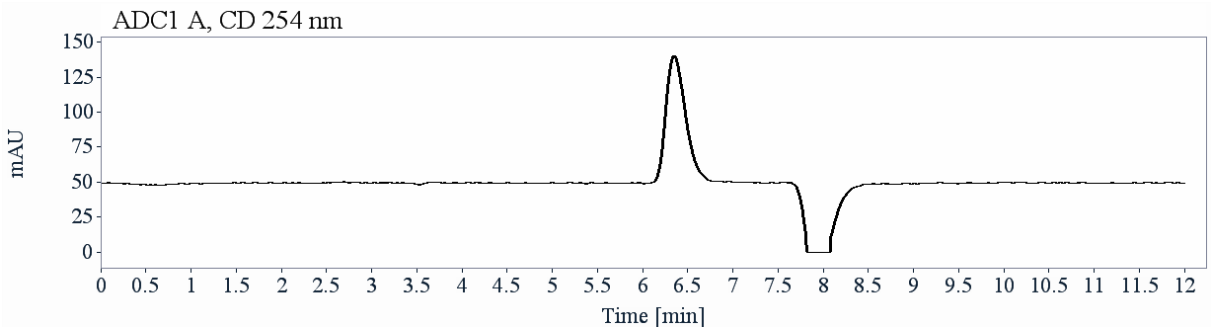
Figure S13. ^{1}H NMR (300 MHz, DMSO-*d6*) spectra of [6]helicene-15-carboxylic acid **H1C**.

Analytical chiral HPLC separation for compound **Methyl [6]helicene-15-carboxylate**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak ID	Heptane / dichloromethane (60/40)	6.13 (+)	1.08	7.70 (-)	1.61	1.49	4.17





RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
6.13	2295	52.69	1.08		
7.70	2061	47.31	1.61	1.49	4.17
Sum	4355	100.00			

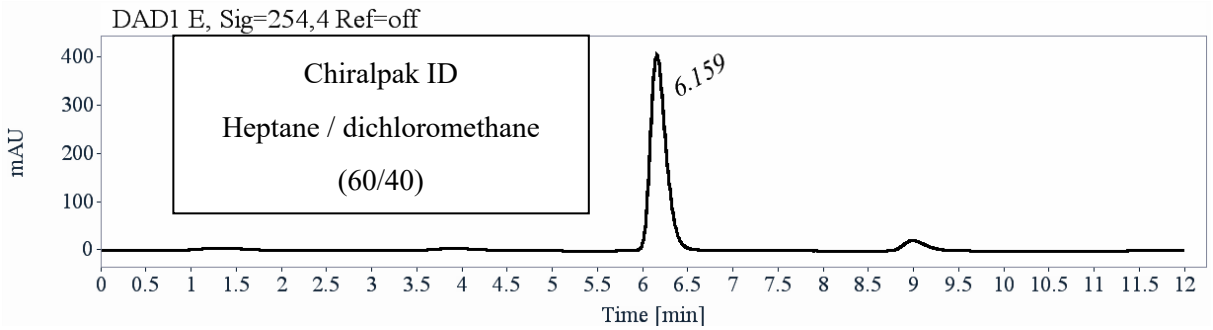
Preparative separation for compound **Methyl [6]helicene-15-carboxylate**:

• Sample preparation: About 98 mg of compound **Methyl [6]helicene-15-carboxylate** are dissolved in 4 mL of dichloromethane.

• Chromatographic conditions: Chiralpak ID (250 x 10 mm), hexane / dichloromethane (60/40) as mobile phase, flow-rate = 5 mL/min, UV detection at 290 nm.

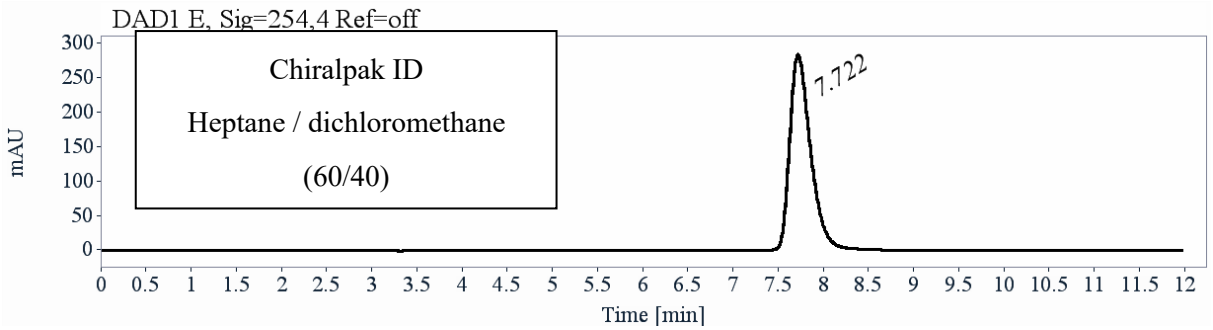
• Injections: 50 times 80 µL, every 10 minutes.

• First fraction: 32 mg of the first eluted with ee > 99.5 %



RT [min]	Area	Area%
6.16	4902	100.00
Sum	4902	100.00

• Second fraction: 35 mg of the second eluted with ee > 99.5 %



RT [min]	Area	Area%
7.72	4507	100.00
Sum	4507	100.00

Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578 and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

λ (nm)	first eluted on Chiralpak ID $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.15)	second eluted on Chiralpak ID $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.10)
589	- 3600	+ 3600

578	- 3800	+ 3800
546	- 4800	+ 4800

Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.

The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing.

first eluted enantiomer (M): green solid line, concentration = 0.233 mmol.L^{-1} in acetonitrile.

second eluted enantiomer (P): red dotted line, concentration = 0.225 mmol.L^{-1} in acetonitrile.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.