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Electronic supplementary information

Highly contorted superhelicene hits near-infrared circularly polarized luminescence

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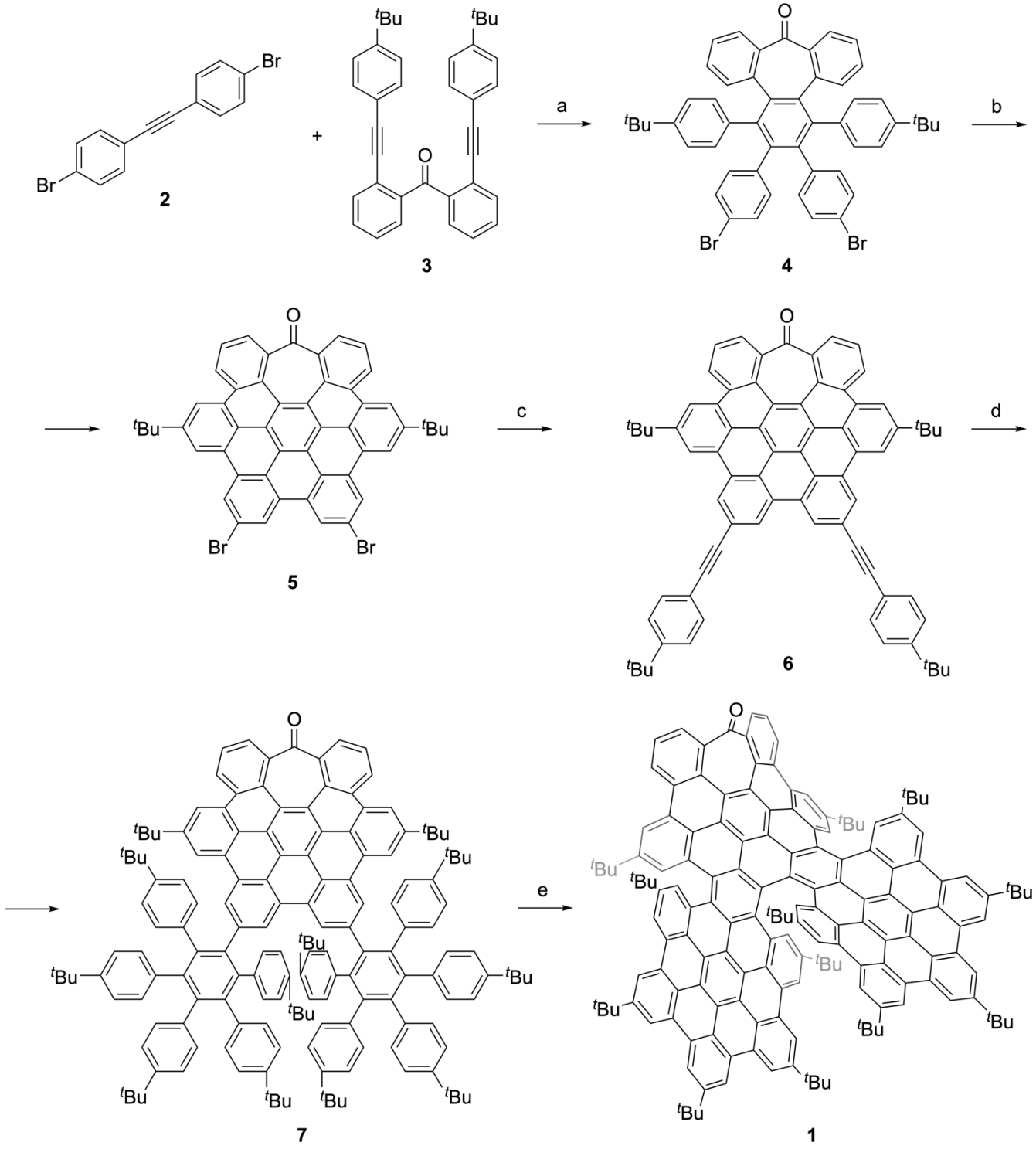
General Details

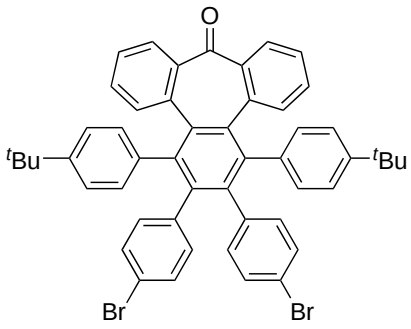
Unless otherwise stated, all reagents and solvents were purchased from commercial sources and used without further purification. HPLC grade solvents (hexane, CH_2Cl_2) were purchased from VWR. Dry toluene, CH_2Cl_2 and EtOH were purchased from Scharlau, THF was purchased from Honeywell, Ph_2O was purchased from Apollo Scientific and $MeNO_2$ was purchased from TCI. Flash column chromatography was carried out using Silica gel 40-63 µm (230-400 mesh, SILICYCLE, Canada) as the stationary phase. Analytical TLC was performed on aluminium sheets coated with silica gel with fluorescent indicator UV_{254} (Sigma-Aldrich) and observed under UV light (254 or 365 nm) and/or stained with phosphomolybdic acid (5% ethanol solution). All ^{1}H and ^{13}C NMR spectra were recorded on Bruker Nanobay Avance III HD 400 MHz, Bruker Avance NEO 400 MHz, Bruker Avance NEO 500 MHz, Varian Direct Drive 500 MHz or Varian Direct Drive 600 MHz spectrometers, at a constant temperature of 298 K. Chemical shifts are reported in ppm and referenced to residual solvent. Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, b = broad. Assignment of the ^{13}C NMR signals was accomplished by DEPT, HSQC and HMBC techniques. ESI-TOF mass spectra were recorded on a Waters XEVO GL-XS QTof mass spectrometer. IR-ATR spectra were recorded on a Perkin Elmer Spectrum Two IR Spectrometer. Melting points were measured on a Stuart SMP3. Chiral stationary phase (CSP-HPLC) resolution of compound **1** was accomplished using a semipreparative Chiralpak® IA column (particle size 5 µm, dimensions 10 mm diameter × 250 mm length) from Daicel Chiral Technologies (*n*-Hex:DCM 8:2, flow = 3.8 mL min^{-1}). Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) were carried out on a PGSTAT2014 potentiostat/galvanostat (Metrohm Autolab B. V.) with a three electrode cell under Ar atmosphere at 25°C. A Pt-wire counterelectrode, an Ag wire quasireference electrode and a glassy carbon disk working electrode were used. Freshly distilled THF was used as solvent to prepare a 0.1 M solution of tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) which was used as work solution. The scan rate was 0.05 V/s. Potential values are referred to the ferrocenium/ferrocene ($FeCp_2$+/$FeCp_2$) system, Fc was added as an internal reference after each measurement. Films formed via spin-coating were obtained using a Laurell Technologies Corporation spin-coater (Model WS-400BZ-6NPP/LITE). As substrates for the thin film formation, quartz microscope slides from Thermo Scientific (76 × 26 mm) were used. For optical characterization of macrohelicene films Optical Microscopy (OM) OLYMPUS BX51 was used, with the following configuration: Microscope stand BX51. Lenses: 2x (Apo), 4x, 10x, 20x, 40x (Plan Fluor), 60x and immersion 100x (Plan Fluor). Photographic system PM10SP1. Digital camera DP50, effective resolution 2.776x2.074 pixels. Prism DIC for transmitted light, DIC analyzer, DIC prisms for PF 20x, 40x, 60x and 100x. For morphological study of nanostructured macrohelicene films Tapping-mode Atomic Force Microscopy (AFM) NX20 (Park Systems) was employed. Motorized slide (XY: 150 mm; Z: 25 mm); vacuum sample immobilization and multisample slide up to 16 samples. XY scanner: XY simple flexion module scanner with closed loop controller. Coupled optical microscopy window (842 x 631 μm^2). Scanning range: 100 µm x 100µm. 20-bit position controller and 24-bit position sensor. Z scanner: Z-stacked piezoelectric scanner with high guided force. Scanning range: 15 µm. 20-bit position controller and 24-bit position sensor. Lenses: 10× (0.21 NA) for extra-long working distance. Lens on sample surface vision axis and cantilever (ACTA, tapping mode, Set point = 14.379E3 nm, Amplitude = 28.048E3 nm, Sel. Frequency = 290.48E3 Hz, Scan rate = 0.6 Hz, unless otherwise specified). Coupled with 10x lens: 840 × 630 µm. CCD: 5M pixel. Glassware and quartz plates used as substrate in the thin film formation were sonicated in acetone for 5 min, then with isopropanol for 5 min, and finally dried with Ar flow while heated with the heatgun.

Synthesis



Scheme S1. Synthesis of compound **1**. Compounds **2** and **3** were prepared according to literature procedures.[S1, S2] a) $Co_2(CO)_8$, toluene, 110°C, 16 h, 20%; b) DDQ, CF_3SO_3H, CH_2Cl_2, 0°C, 10 min, 83%; c) 4-*tert*-butylphenylacetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, THF, r.t., 16 h, 65%; d) 2,3,4,5-*tetrakis*(4-*tert*-butylphenyl)cyclopentadienone, Ph_2O, 259°C, 23%; e) DDQ, CF_3SO_3H, CH_2Cl_2, 0°C, 10 min, 50%. (*M,M,P*)-**1** enantiomer is shown.

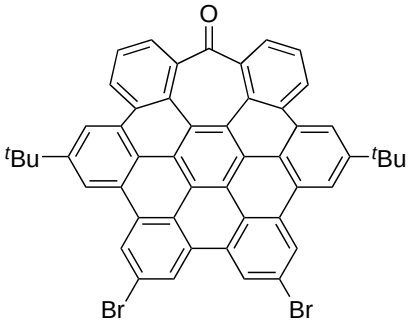
Compound 4



4

In a glovebox, compound **3** (350 mg, 0.71 mmol) and $Co_2(CO)_8$ (315 mg, 0.92 mmol) were placed in a round bottom flask and capped properly, the solids were dissolved in dry toluene (6 mL) and the reaction mixture placed in an oil bath at 110°C for 30 min. Then a degassed suspension of **2** (350 mg, 1.04 mmol) in dry toluene (2 mL) was added dropwise over the reaction mixture and the resulting solution was stirred at 110°C overnight. The solvent was removed in the rotavapor and the crude material purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) affording **4** (120 mg, 20%) as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.35 (d, *J*=7.5, 2H), 7.25 (d, *J*=8.1, 2H), 7.21 (d, *J*=7.9, 2H), 7.09 (t, *J*=7.4, 2H), 7.03 (s, 4H), 6.93 (d, *J*=7.7, 2H), 6.84 (t, *J*=7.9, 4H), 6.79 (t, *J*=7.6, 2H), 6.36 (d, *J*=8.0, 2H), 6.32 (d, *J*=7.9, 2H), 1.17 (s, 14H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 200.04 (C), 149.30 (C), 146.48 (C), 141.78 (C), 141.46 (C), 139.86 (C), 137.71 (C), 136.45 (C), 135.09 (C), 133.72 (CH), 133.29 (CH), 132.66 (CH), 132.54 (CH), 130.45 (CH), 129.80 (CH), 128.75 (CH), 127.39 (CH), 124.54 (CH), 124.45 (CH), 123.97 (CH), 120.10 (C), 34.52 (C), 31.33 (CH_3). HR-MS (ESI-TOF): m/z calcd. for $C_{51}H_{42}Br_2NaO$ $[M+Na]^+$: 853.1480, found: 853.1503. IR (ATR): 3067, 3033, 3961, 3904, 3866, 1907, 1781, 1684 cm^{-1}.

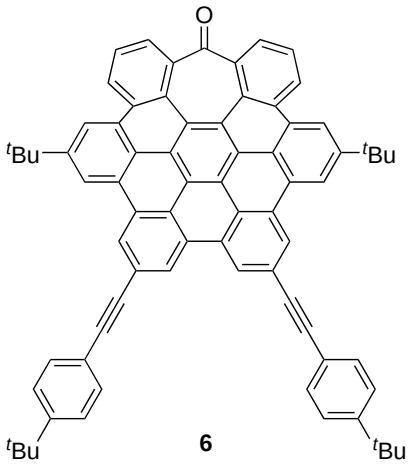
Compound 5



5

To a solution of polyphenylene **4** (110 mg, 0.13 mmol) and DDQ (170 mg, 0.75 mmol) in dry CH_2Cl_2 (6 mL) placed in an ice-water bath, then trifluoromethanesulfonic acid (0.15 mL) was slowly added and the reaction mixture stirred for 10 min under Ar atmosphere. The mixture was then diluted with CH_2Cl_2 (10 mL) and silica gel was added. The solvent was removed in the rotavapor and the crude material purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2, 3:2) giving rise to **5** (89 mg, 83%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (dd, *J* = 8.7, 1.5 Hz, 2H), 8.76 (dd, *J* = 7.9, 1.7 Hz, 4H), 8.68 (dd, *J* = 6.1, 1.7 Hz, 4H), 7.84 (dd, *J* = 7.2, 1.4 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 1.68 (s, 18H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): 202.2, 150.3, 142.5,132.3, 131.2, 130.4, 128.4, 128.2, 127.7, 127.1, 126.3, 125.2, 125.1, 124.4, 124.3, 123.3, 123.2, 122.9, 122.3, 121.0, 120.2, 119.1, 35.8, 32.0 ppm. HR-MS (ESI-TOF): m/z calcd. for : $C_{51}H_{32}Br_2NaO$ $[M+Na]^+$; 843.0697, found: 843.0745. IR (ATR): 2956, 2925, 2855, 1725, 1681, 1576 cm^{-1}.

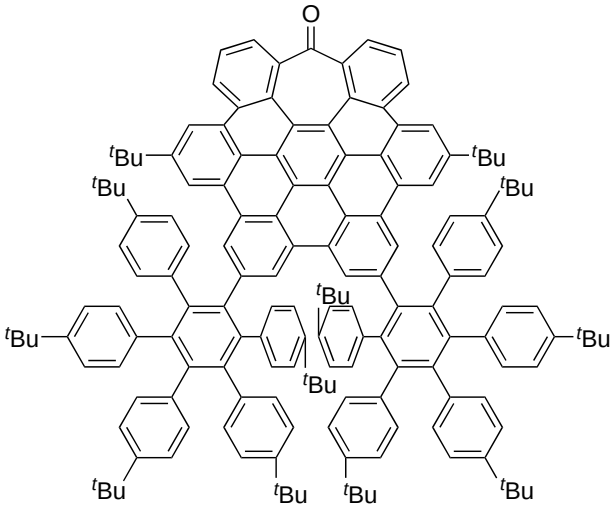
Compound 6



6

Compound **5** (270 mg, 0.33 mmol), $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) and CuI (15 mg, 0.08 mmol) were placed into a round bottom flask, capped properly and purged with Ar. The solids were suspended with a mixture of freshly distilled THF (2 mL) and NEt_3 (4 mL) and bubbled with Ar. The reaction mixture was placed at 70°C and *p-tert*-butylphenylacetylene (0.18 mL, 0.99 mmol) was added dropwise. The reaction mixture was kept at this temperature for 16 h. Once cooled to room temperature, the crude was diluted with CH_2Cl_2 (100 mL) and washed with $NH_4Cl_{(sat)}$ (2 × 100 mL). The organic layer was separated, dried with anhydrous Na_2SO_4, filtered and the solvent removed at the rotavapor. The crude was purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2, 1:1) affording **6** (208 mg, 65%) as a yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.69 (s, 2H), 8.54 (s, 2H), 8.49 (s, 2H), 8.44 (d, *J*=7.7, 2H), 8.27 (s, 1H), 7.67 (d, *J*=7.2, 2H), 7.52 (d, *J*=8.0, 4H), 7.40 (d, *J*=8.0, 4H), 7.33 (t, *J*=7.1, 2H), 1.68 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 202.37 (C), 152.13 (C), 150.06 (C), 142.45 (C), 131.95 (CH), 131.12 (C), 130.49 (C), 129.05 (C), 129.00 (C), 128.34 (C), 127.32 (C), 127.00 (C), 125.93 (CH), 124.89 (C), 124.71 (CH), 124.28 (CH), 124.04 (CH), 123.70 (C), 123.11 (C), 123.09 (C), 122.24 (C), 121.12 (CH), 120.64 (C), 120.39 (C), 118.91 (CH), 90.92 (C), 89.74 (C), 35.94 (C), 35.13 (C), 32.12 (CH_3), 31.36 (CH_3). HR-MS (MALDI dctb + PPG790): m/z calcd. for $C_{75}H_{58}O$ $[M]^+$: 974.4488, found: 974.4482. IR (ATR): 3076, 3036, 2956, 2904, 2866, 1913, 1740, 1678, 1609, 1584 cm^{-1}.

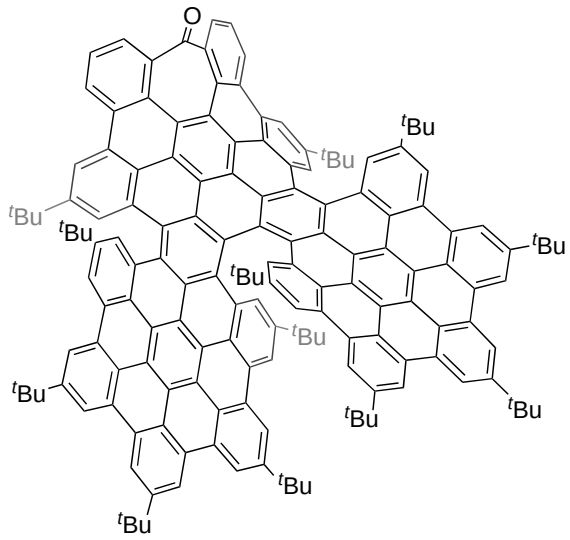
Compound 7



7

A solution of **6** (67 mg, 68.70 µmol) and 2,3,4,5-*tetrakis*-(*p-tert*-butyl-phenyl)-cyclopentadienone (84 mg, 137.4 µmol) in Ph_2O (2 mL) was placed in a sand bath and refluxed overnight. The reaction mixture was cooled down to room temperature, diluted with hexane (10 mL) and purified by flash column chromatography (SiO_2, hexane/CH_2Cl_2, 3:2) giving rise to **7** (44 mg, 30%) as a glassy yellow solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.62 (d, *J*=7.7, 2H), 8.49 (s, 2H), 8.32 (s, 5H), 7.92 (s, 2H), 7.62 (d, *J*=7.0, 2H), 7.54 (t, *J*=7.5, 2H), 7.05 (d, *J*=7.9, 4H), 6.99 – 6.90 (m, 14H), 6.89 – 6.78 (m, 17H), 6.75 (d, *J*=7.9, 4H), 6.61 (d, *J*=7.8, 4H), 1.54 (s, 18H), 1.17 (s, 18H), 1.16 (s, 36H), 0.69 (s, 36H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 202.64 (C), 149.99 (C), 148.46 (C), 148.38 (C), 148.35 (C), 142.49 (C), 141.61 (C), 141.36 (C), 141.04 (C), 140.36 (C), 140.00 (C), 138.62 (C), 138.60 (C), 138.36 (C), 131.89 (CH), 131.81 (CH), 131.57 (CH), 131.50 (CH), 131.42 (CH), 129.78 (C), 129.50 (C), 128.79 (C), 128.44 (C), 127.56 (CH), 127.36 (C), 127.05 (CH), 126.90 (CH), 126.22 (CH), 124.49 (C), 123.80 (CH), 123.71 (CH), 123.13 (C), 123.03 (C), 122.28 (C), 121.06 (C), 120.57 (CH), 117.88 (CH), 35.74 (C), 34.46 (C), 34.13 (C), 31.96 (CH_3), 31.40 (CH_3), 31.00 (CH_3). HR-MS (ESI-TOF): m/z calcd. for $C_{163}H_{162}NaO$ $[M+Na]^+$: 2159.2557, found: 2159.2610. IR (ATR): 3089, 3058, 3026, 2954, 2904, 2866, 1687, 1609, 1587, 1511 cm^{-1}.

Compound 1



1

In a round bottom flask, compound **7** (34 mg, 16 µmol) and DDQ (50 mg, 0.22 mmol) were purged with Ar and dissolved with dry CH_2Cl_2 (6 mL). The reaction mixture was placed in an ice-water bath and trifluoromethanesulfonic acid (0.15 mL) were added dropwise and stirred for 10 min. The mixture was diluted with CH_2Cl_2 (10 mL), silica gel was added and the solvent removed under vacuo. The crude material was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexane, 3:2) affording **1** as a dark green solid in a 50% yield. (*M,M,P/P,P,M*)-**1**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.71 (s, 1H), 9.48 – 9.22 (m, 13H), 9.15 (d, *J*=6.7, 3H), 9.01 (s, 1H), 8.84 (s, 1H), 8.78 (s, 1H), 8.49 (s, 1H), 8.29 – 8.04 (m, 7H), 8.00 (s, 1H), 7.68 (s, 1H), 1.94 (s, 9H), 1.90 (s, 18H), 1.89 (s, 9H), 1.59 (s, 9H), 1.55 (s, 9H), 1.45 (s, 9H), 1.43 (s, 9H), 1.41 (s, 9H), 0.13 (s, 9H), -0.26 (s, 9H). HR-MS (ESI-TOF): *m/z* calc. for $C_{163}H_{139}O$ $[M+H]^+$: 2112.0781; found: 2112.0757. (*M,M,M/P,P,P*): ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.61 (s, 2H), 9.47 (s, 2H), 9.46 – 9.41 (m, 6H), 9.33 (s, 2H), 9.31 – 9.26 (m, 4H), 9.17 (s, 2H), 8.93 (s, 2H), 8.45 (s, 2H), 8.23 (s, 2H), 8.15 – 8.02 (m, 4H), 7.93 (s, 2H), 1.92 (s, 18H), 1.86 (s, 18H), 1.50 (s, 18H), 1.49 (s, 18H), 1.31 (s, 18H), -0.22 (s, 18H). HR-MS (ESI-TOF): *m/z* calc. for $C_{163}H_{138}O$ $[M]^+$: 2111.0748; found: 2111.0757. IR (ATR): 3076, 2955, 2924, 2855, 1734, 1681, 1602, 1579 cm^{-1}.

^{1}H, ^{13}C and 2D NMR spectra of new compounds

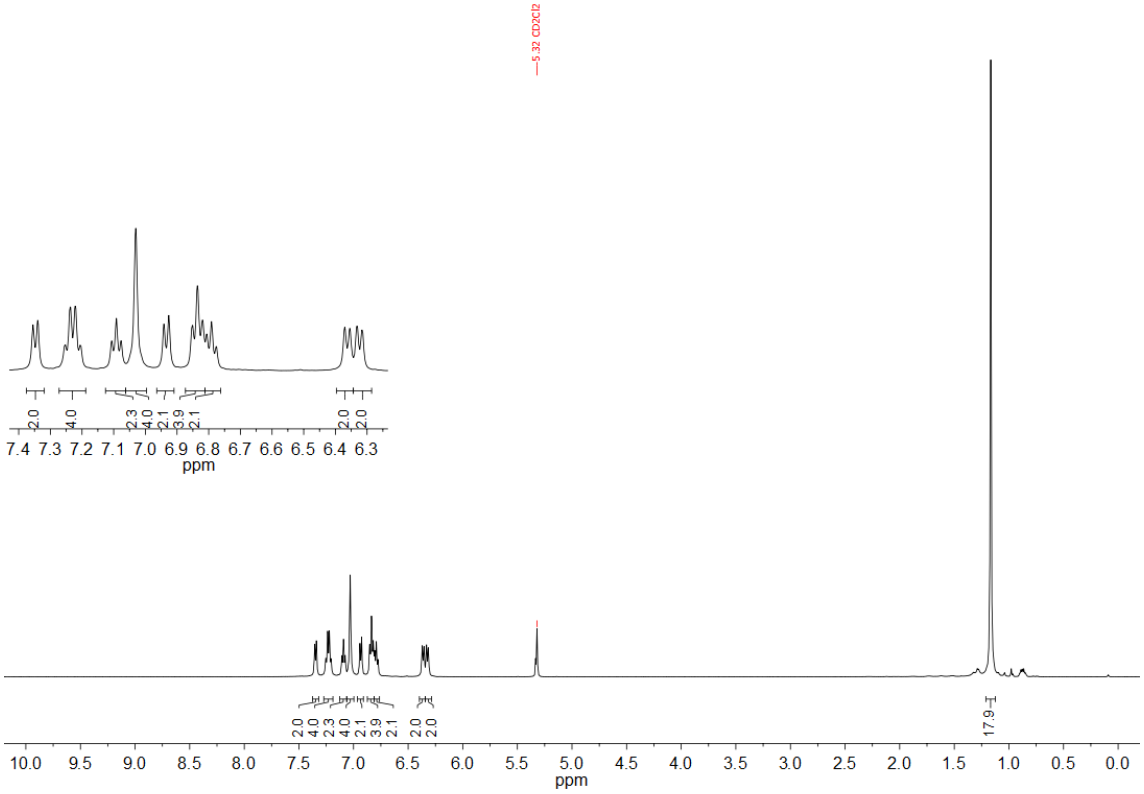


Figure S1. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of compound **4**.

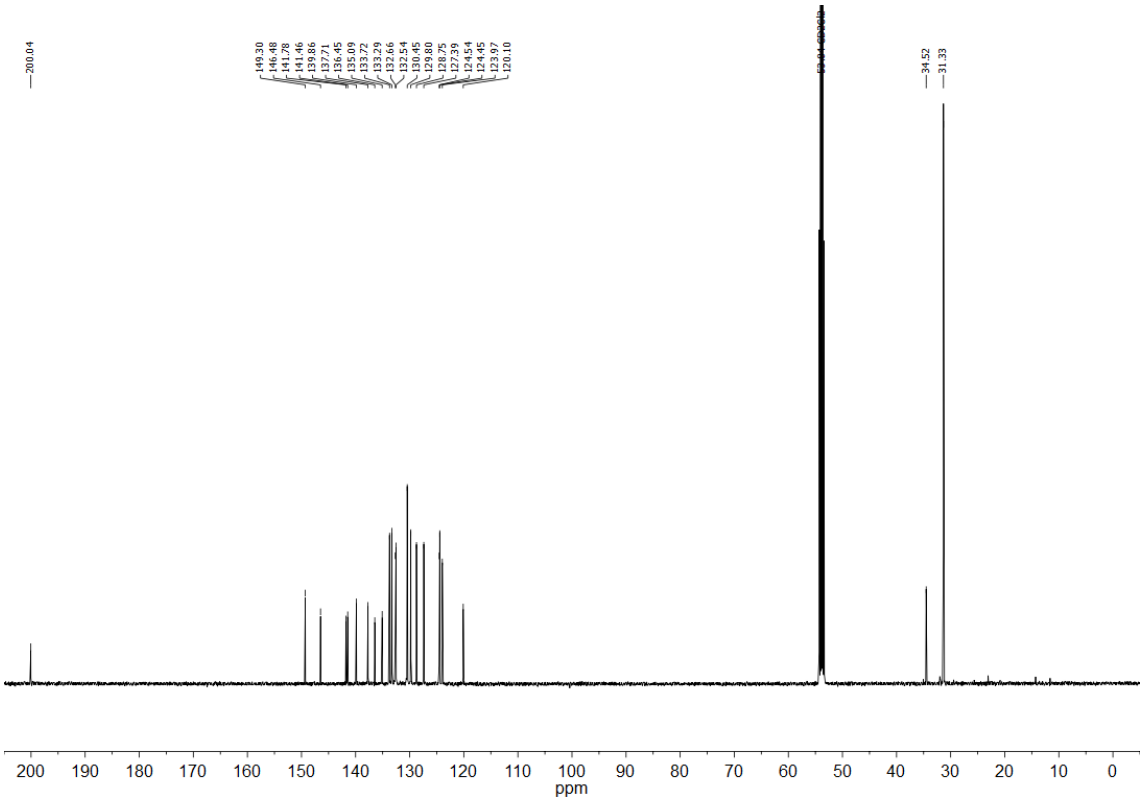


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **4**.

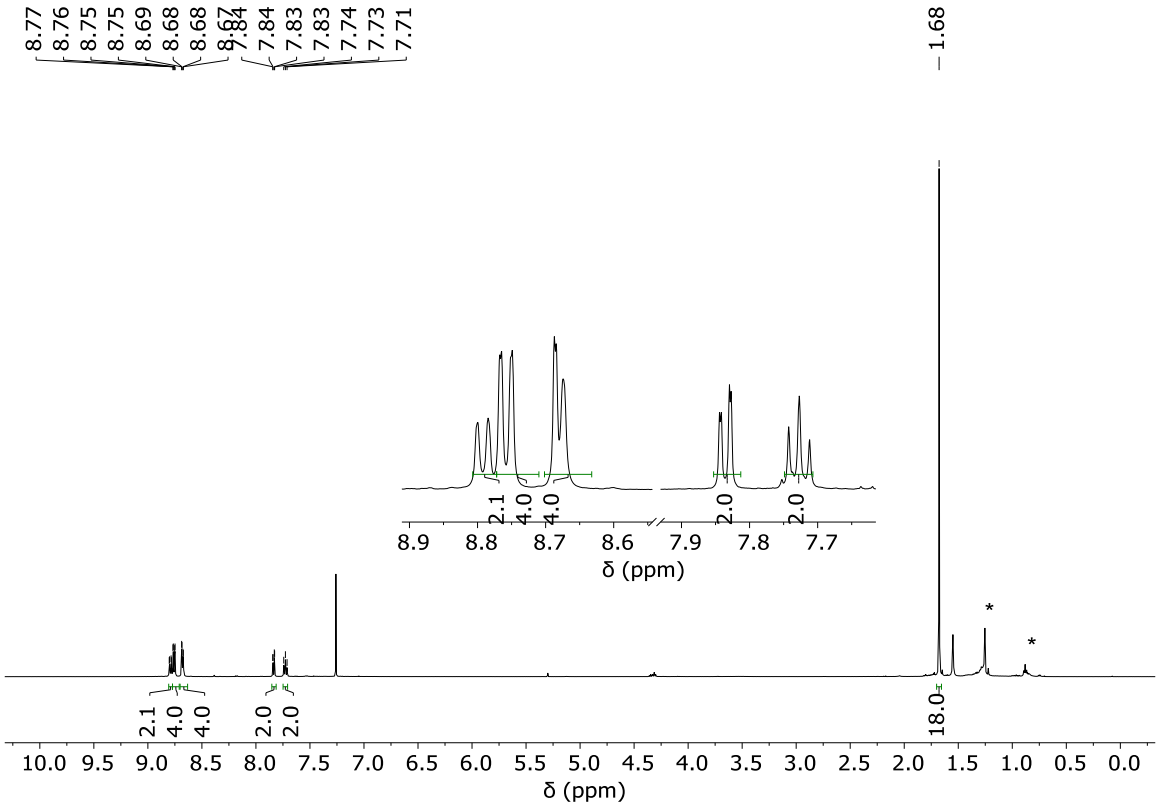


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5.**

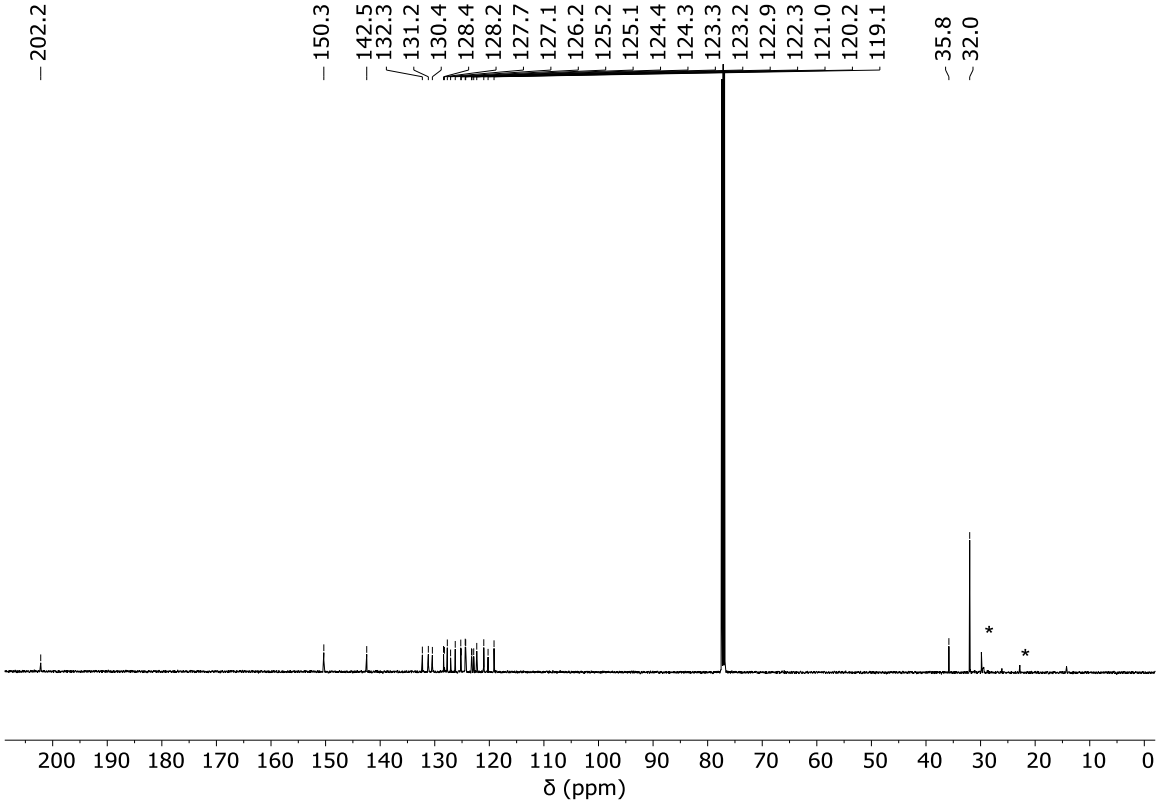


Figure S4. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **5.**

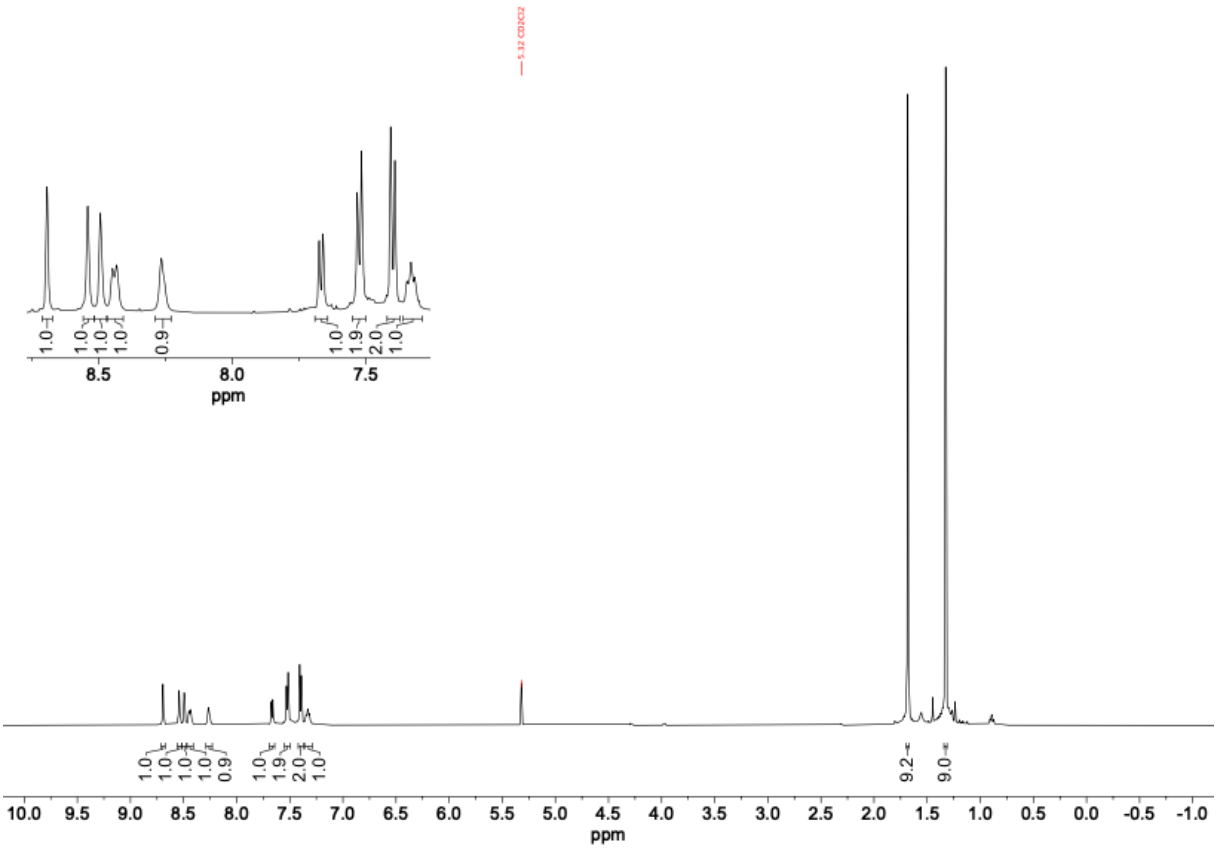


Figure S5. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of compound **6**.

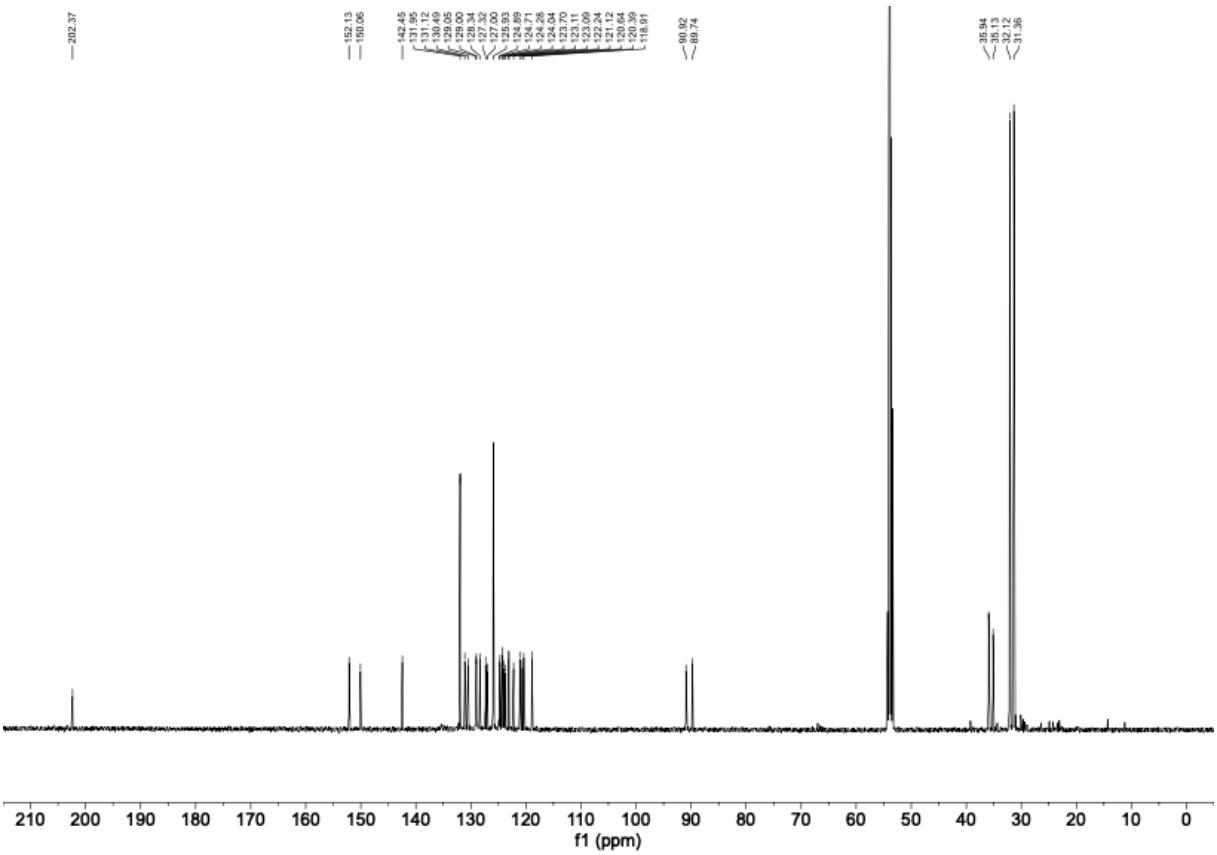


Figure S6. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of compound **6**.

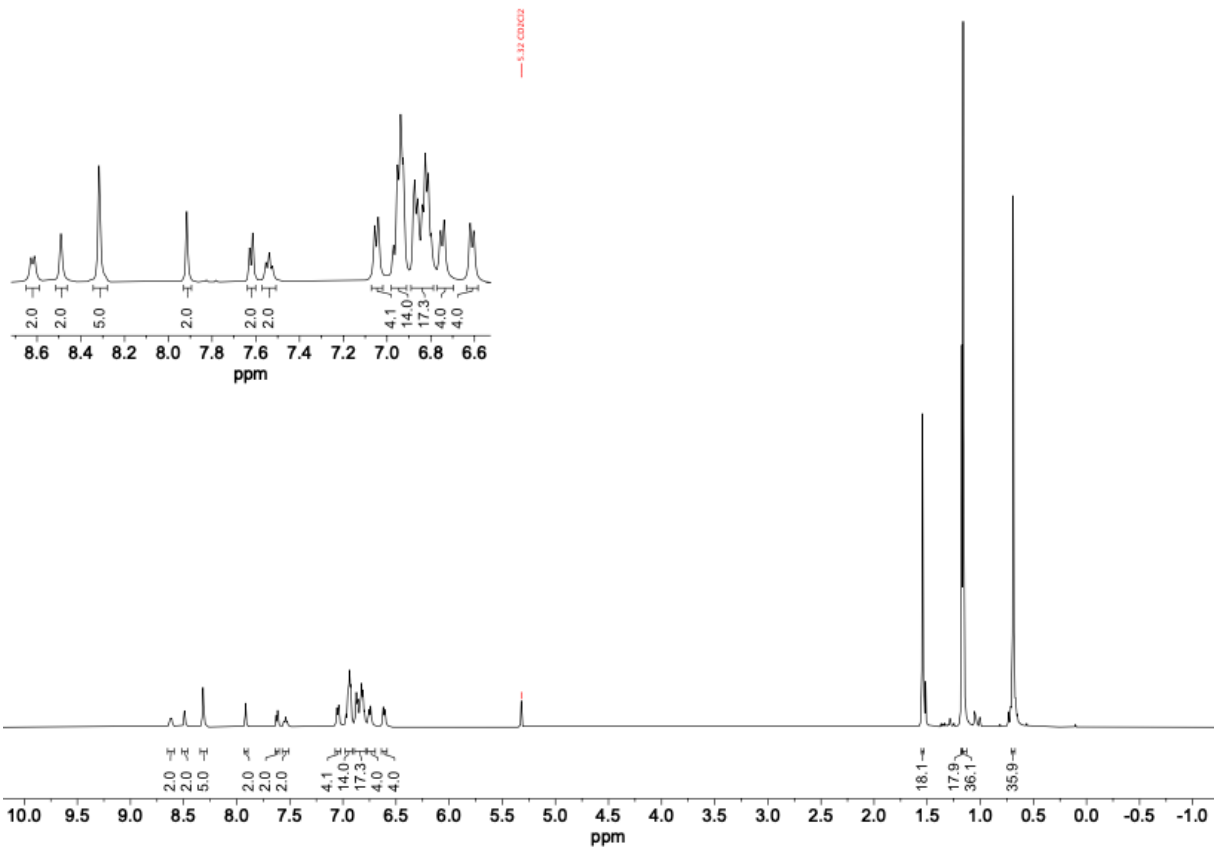


Figure S7. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of compound **7**.

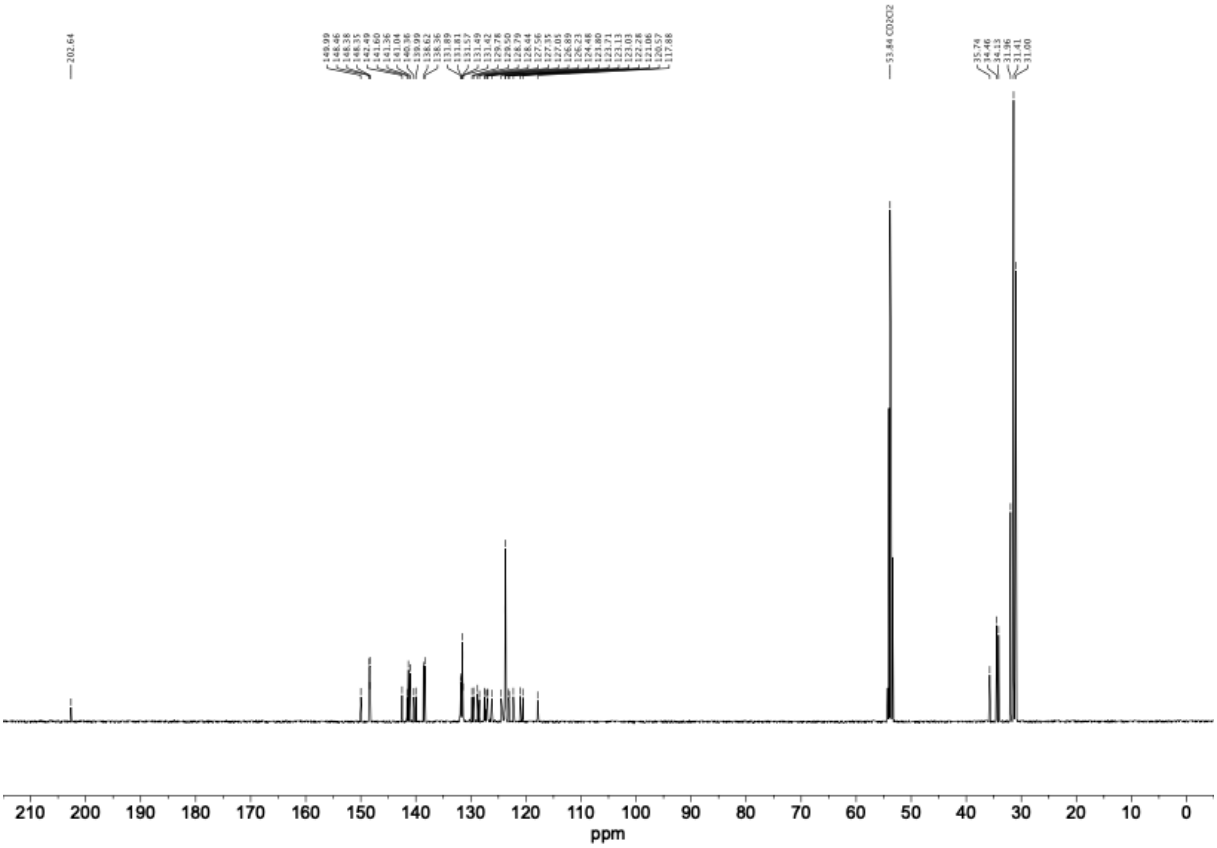


Figure S8. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of compound **7**.

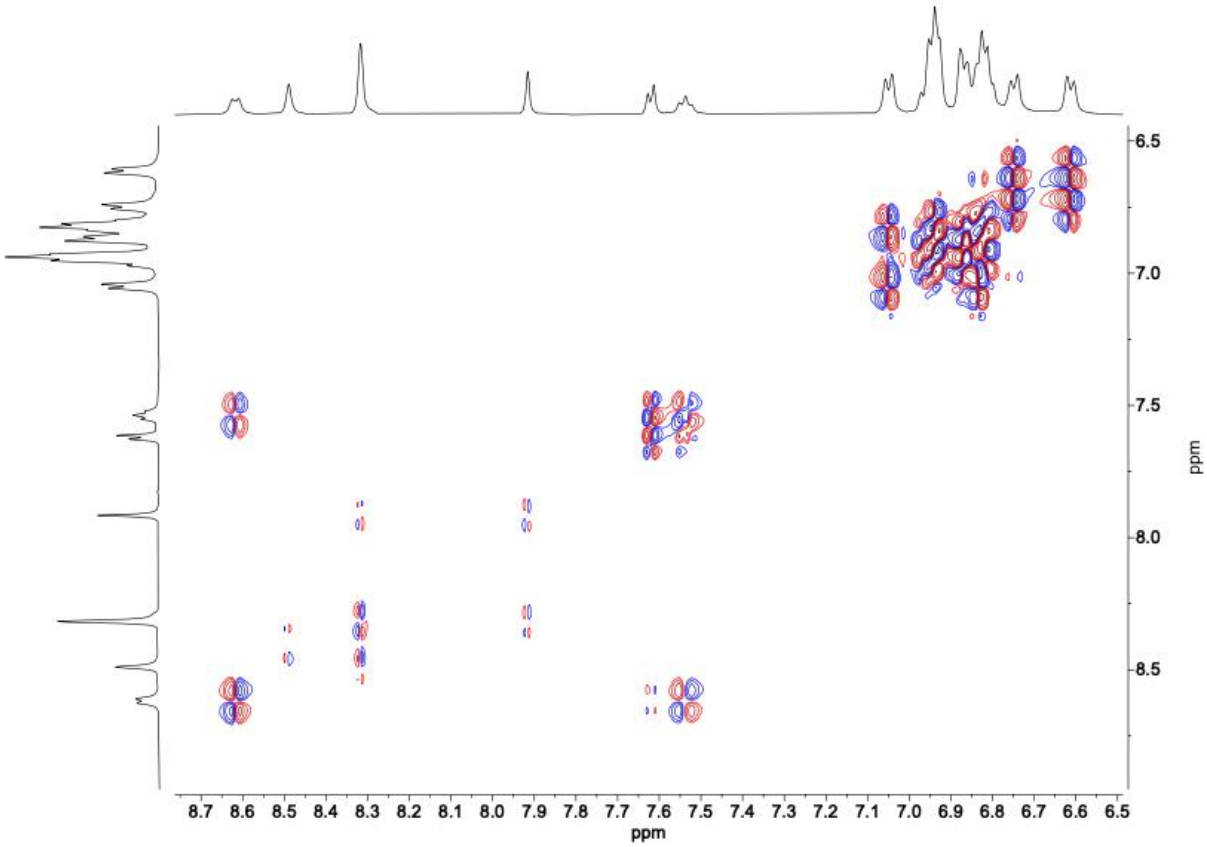


Figure S9. ^{1}H-^{1}H COSY (500 MHz, CD_2Cl_2) spectrum of compound **7**.

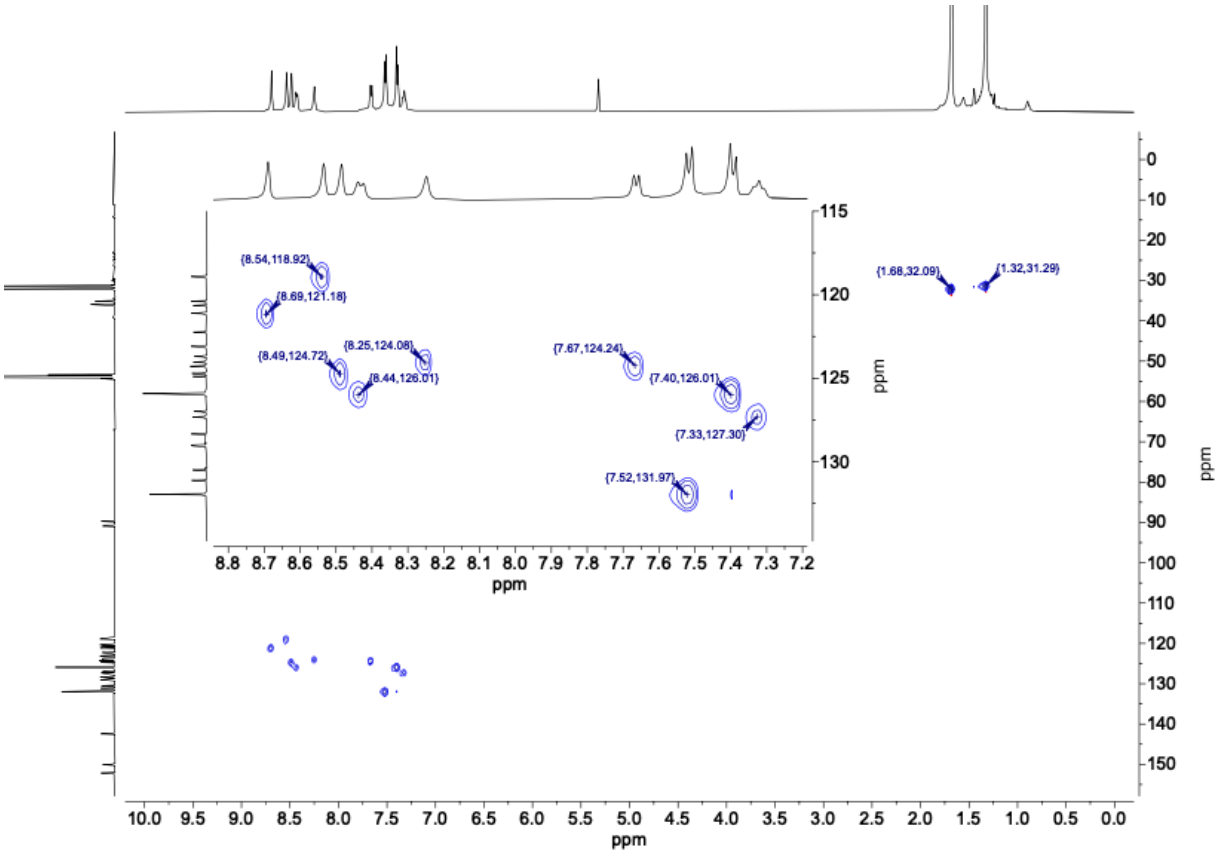


Figure S10. ^{1}H-^{13}C HSQC (500 MHz, 126 MHz, CD_2Cl_2) spectrum of compound **7**.

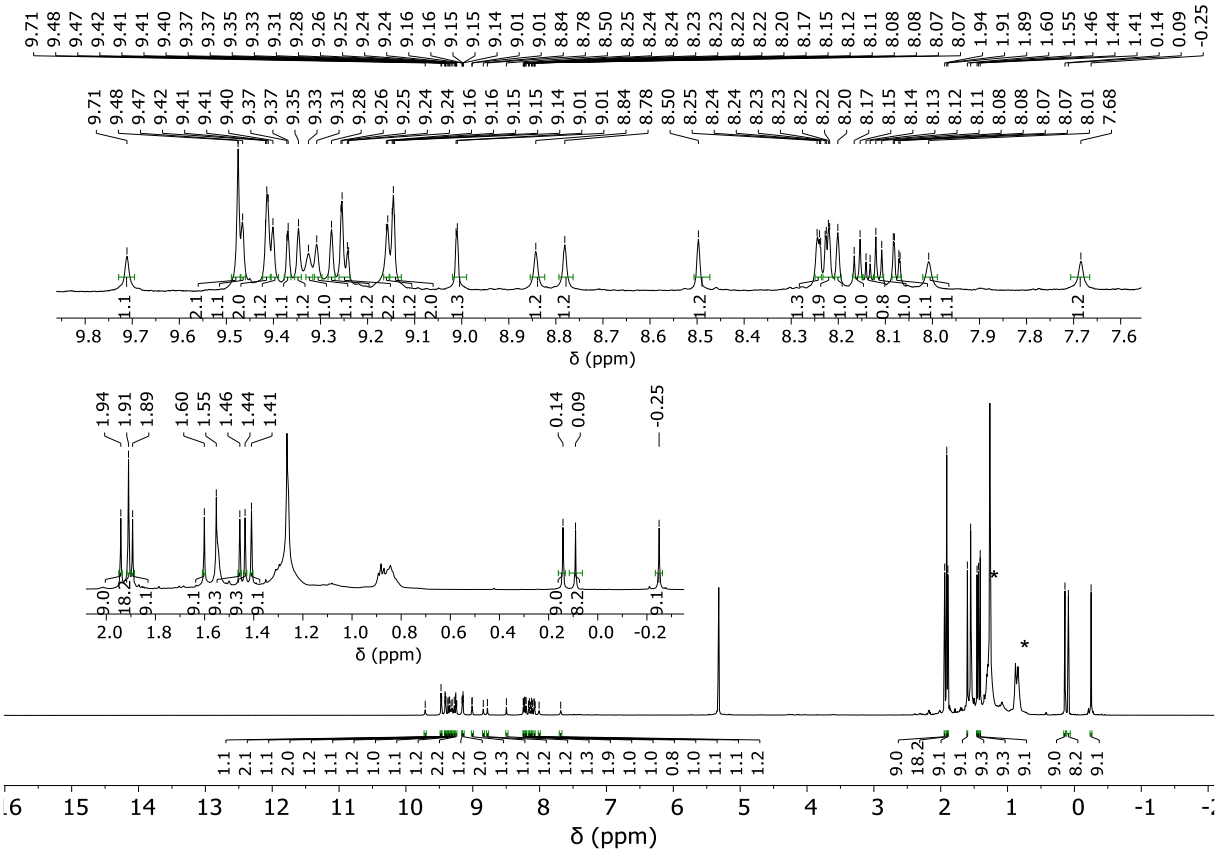


Figure S11. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**. * Grease traces.

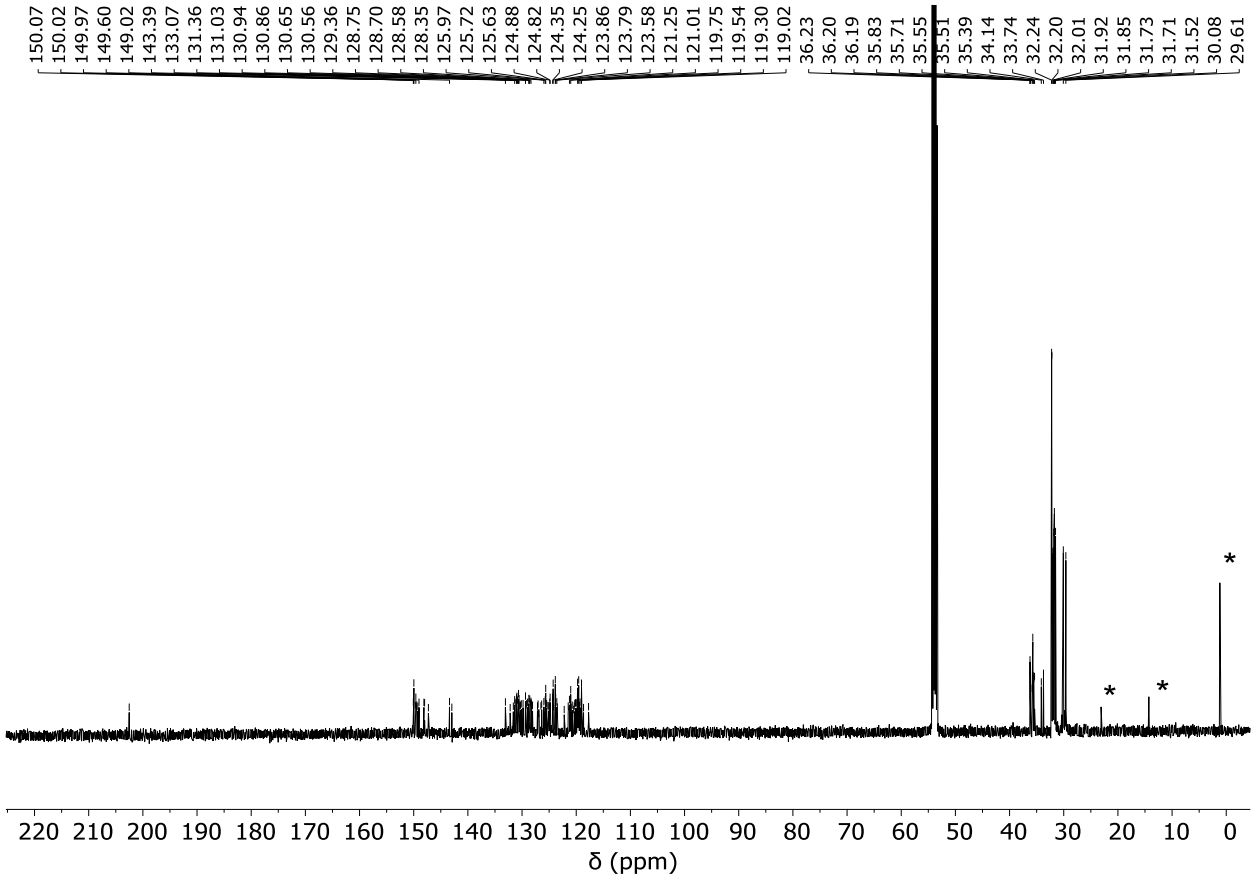


Figure S12. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.* Grease traces.

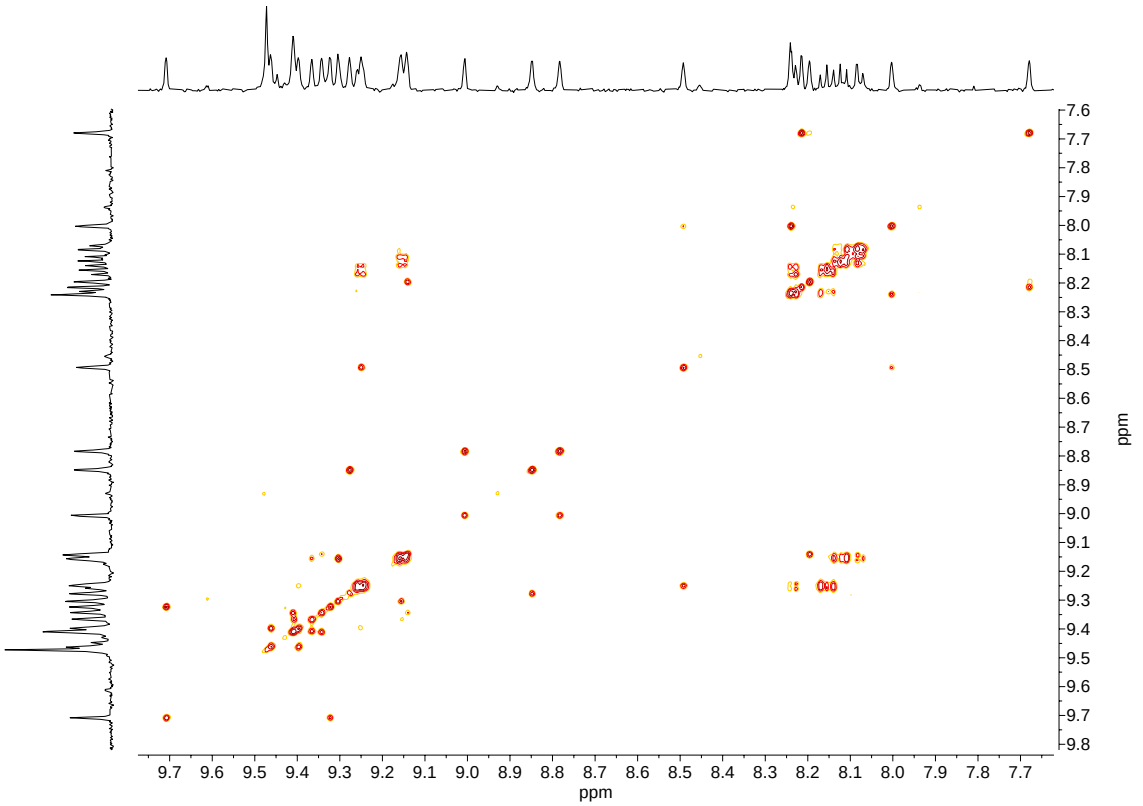


Figure S13. Partial ^{1}H-^{1}H COSY (500 MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

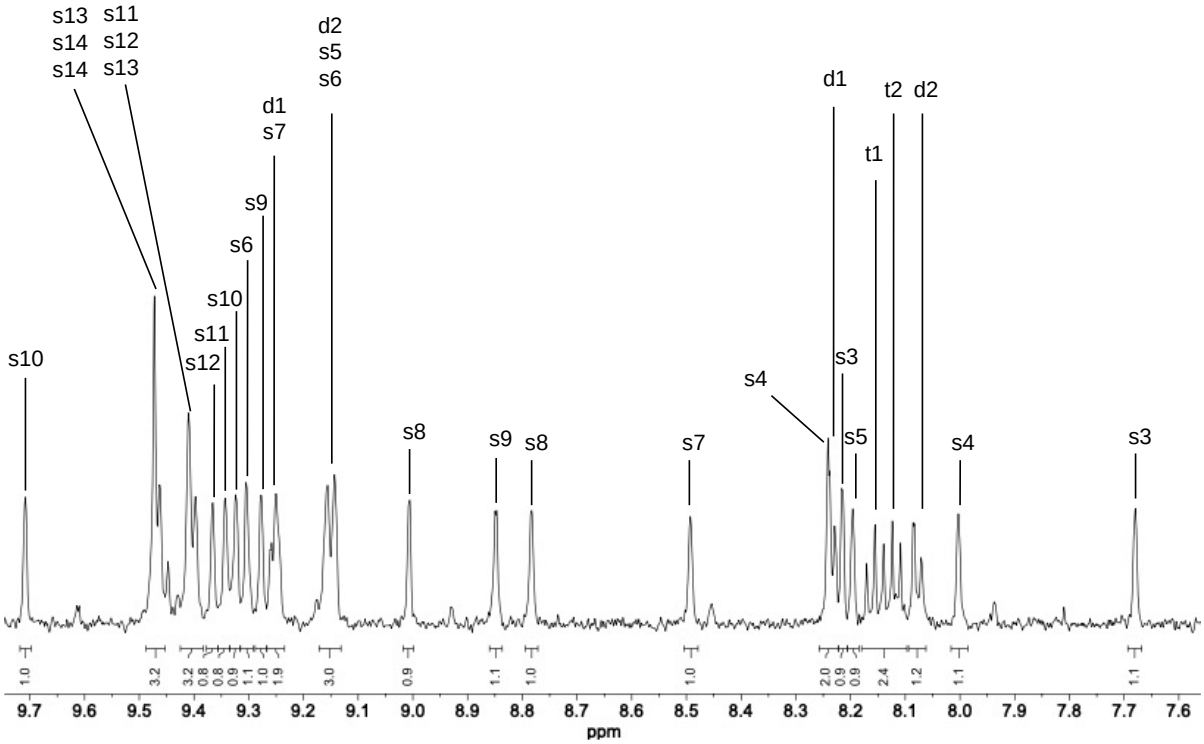


Figure S14. Partial ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum showing the coupling systems observed in Figure S13.

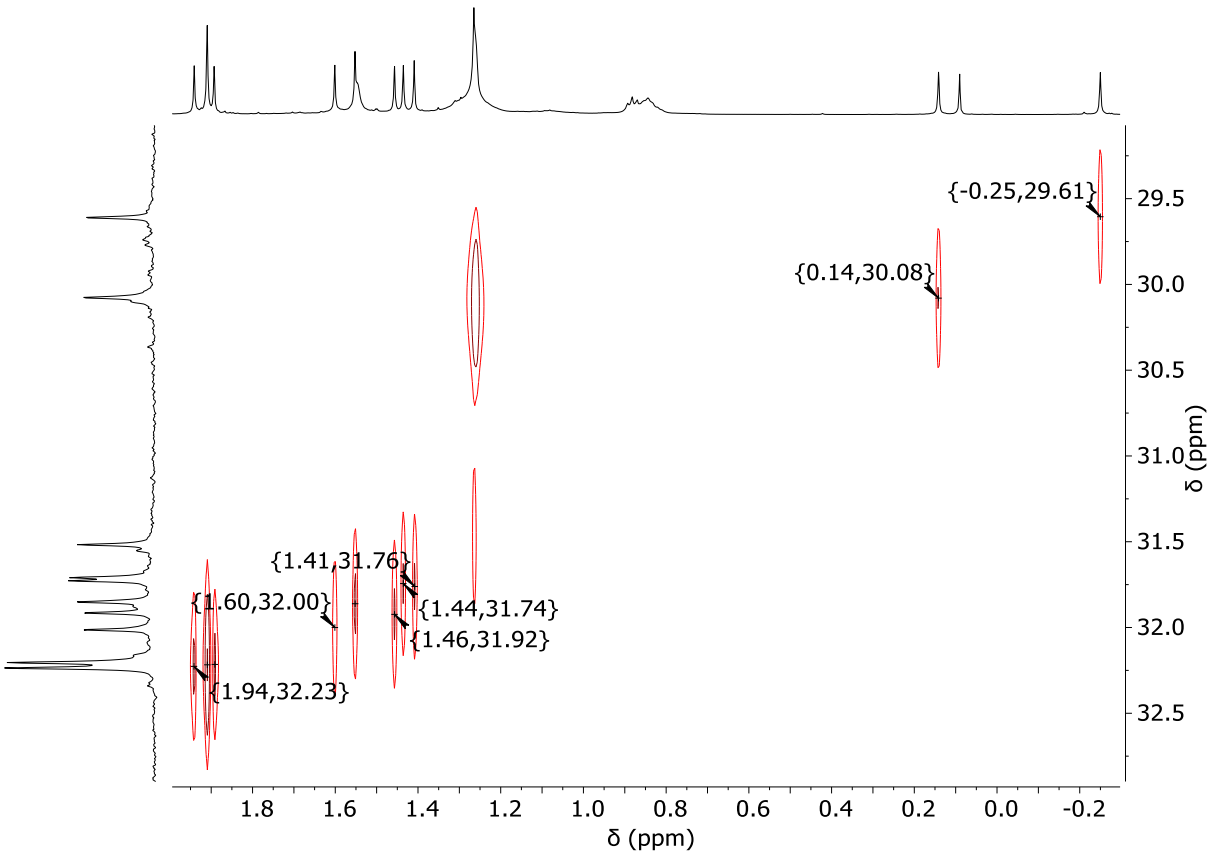


Figure S15. Partial ^{1}H-^{13}C HSQC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

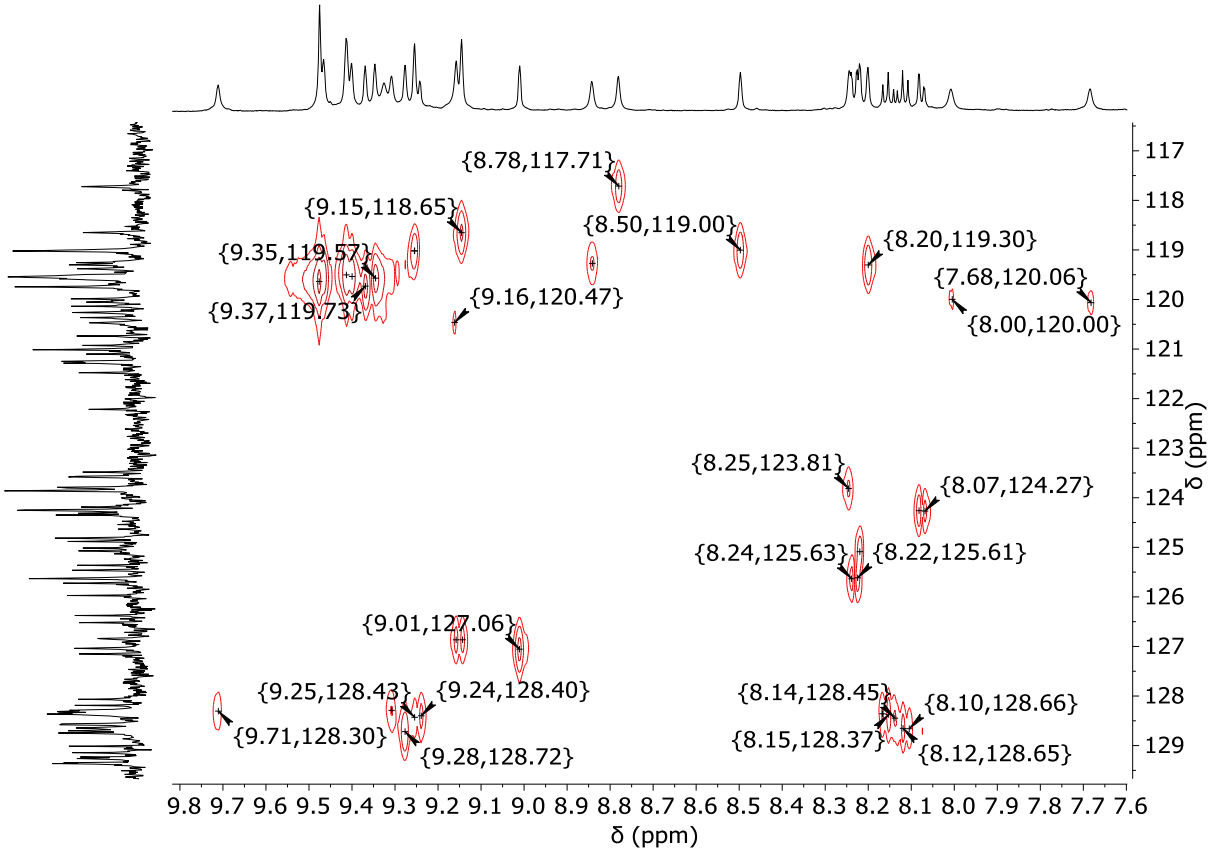


Figure S16. Partial ^{1}H-^{13}C HSQC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

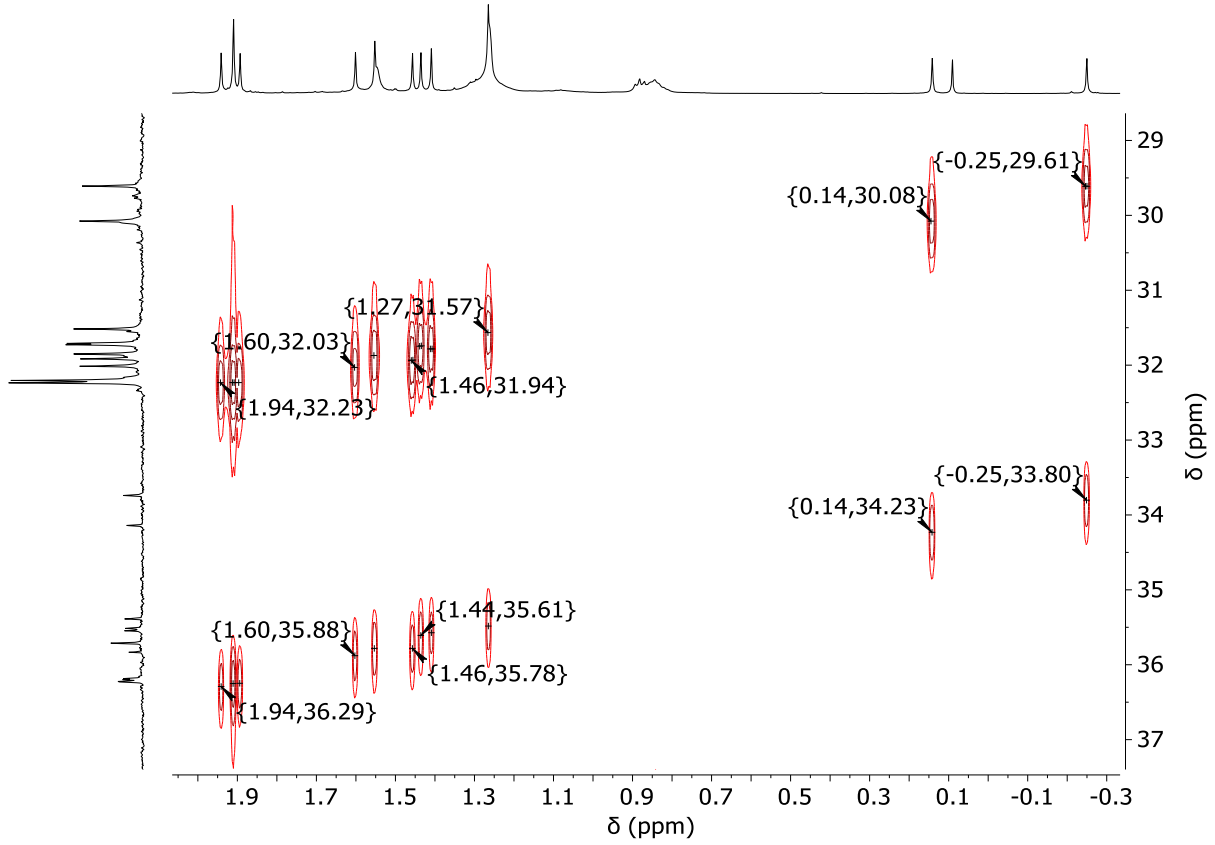


Figure S17. Partial ^{1}H-^{13}C HMBC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

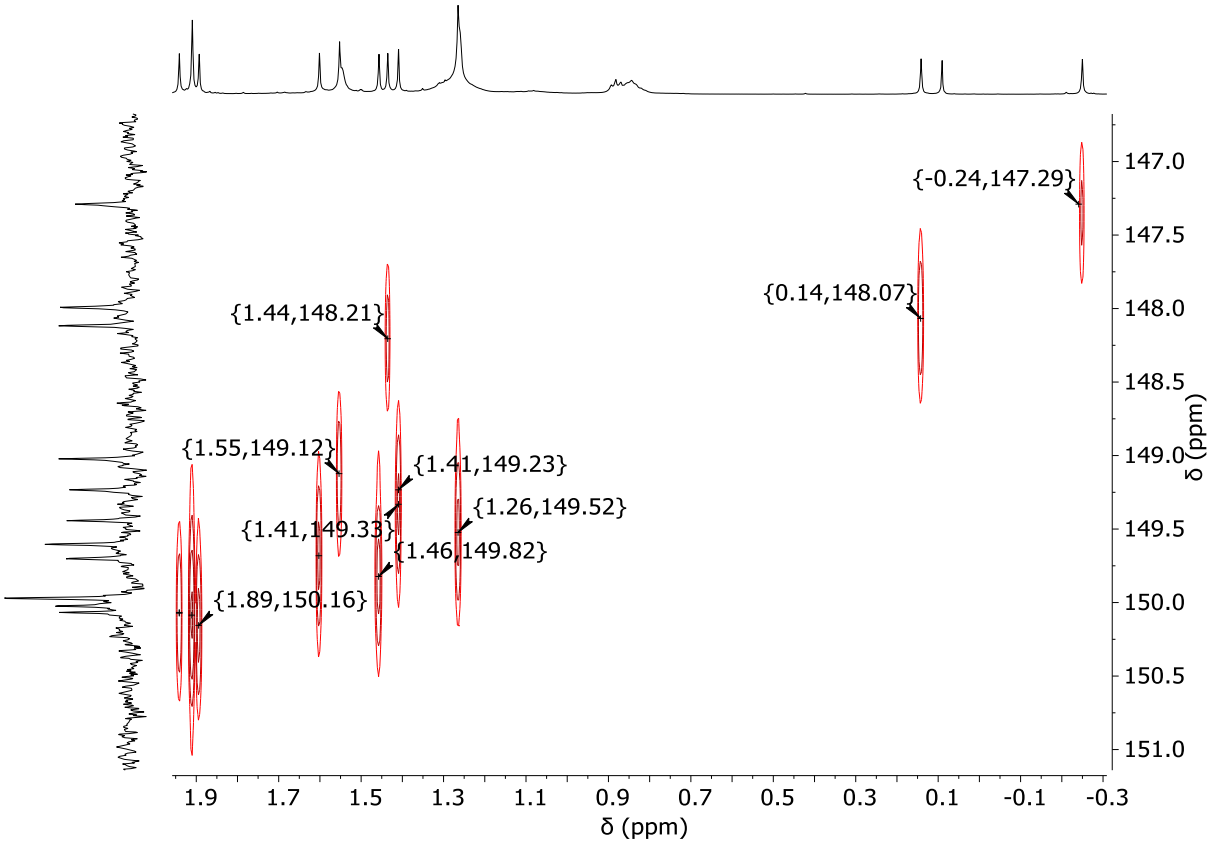


Figure S18. Partial ^{1}H-^{13}C HMBC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

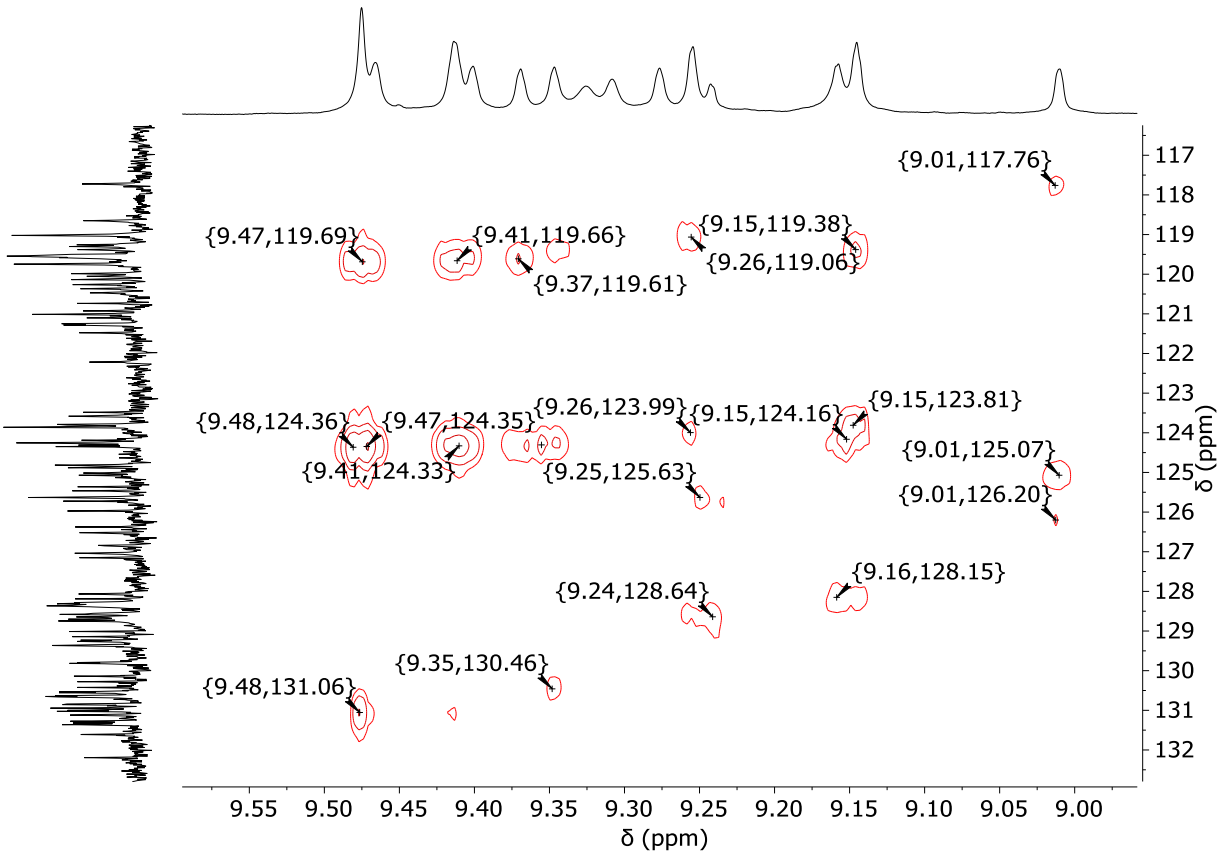


Figure S19. Partial ^{1}H-^{13}C HMBC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

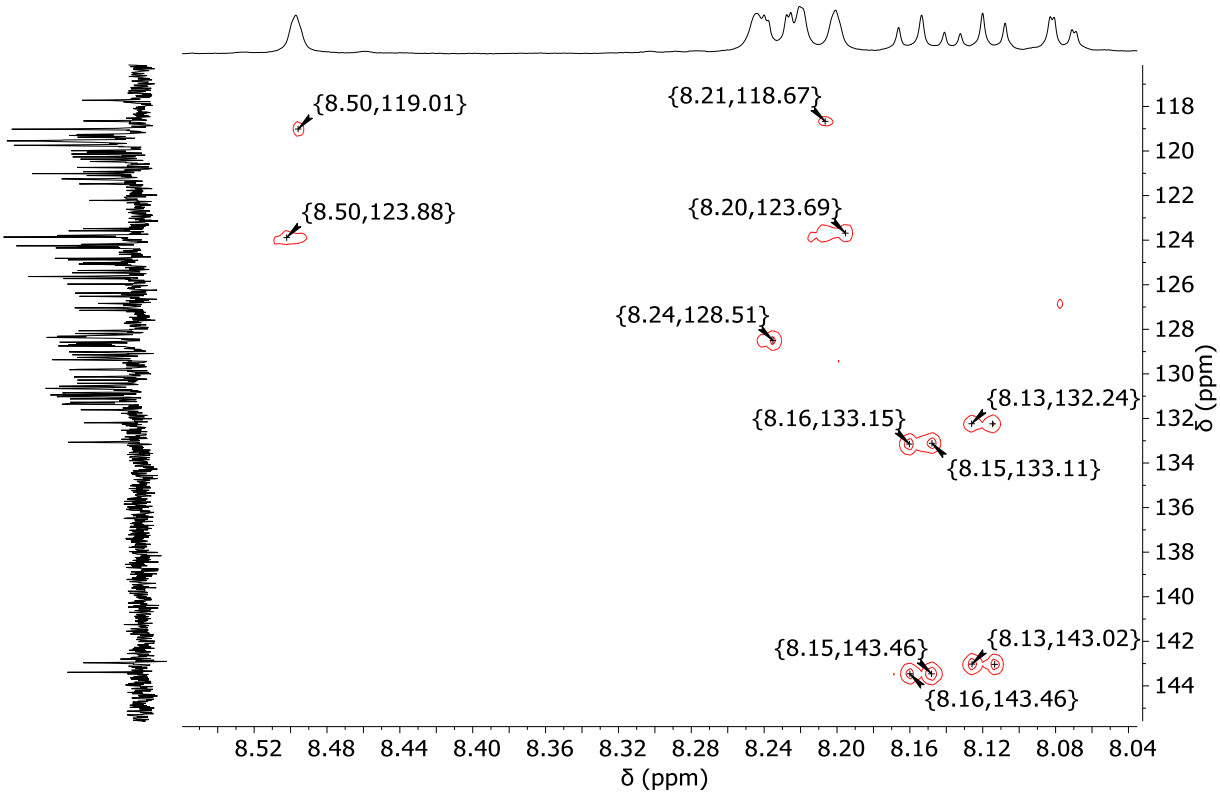


Figure S20. Partial ^{1}H-^{13}C HMBC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

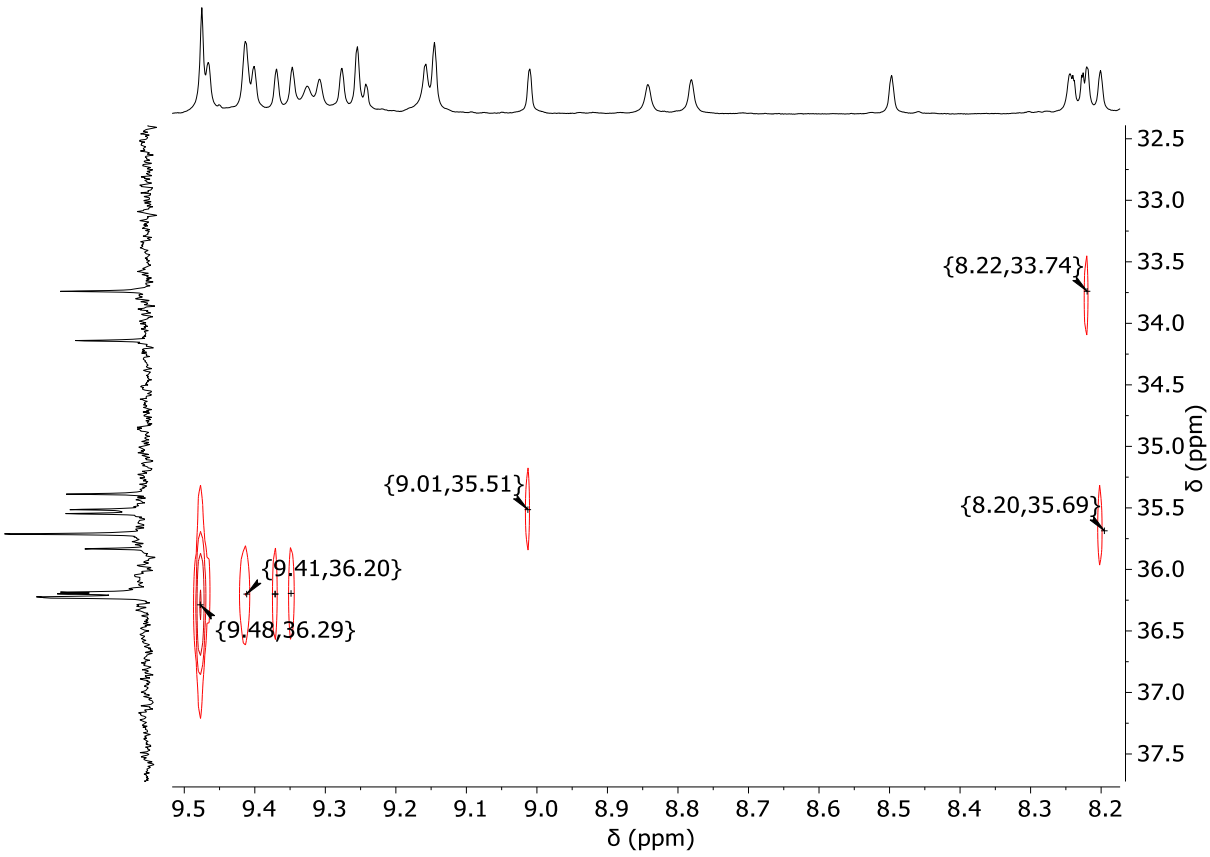


Figure S21. Partial ^{1}H-^{13}C HMBC (500 MHz, 126 MHz, MHz, CD_2Cl_2) spectrum of compound (*P*,*P*,*M*)-**1**.

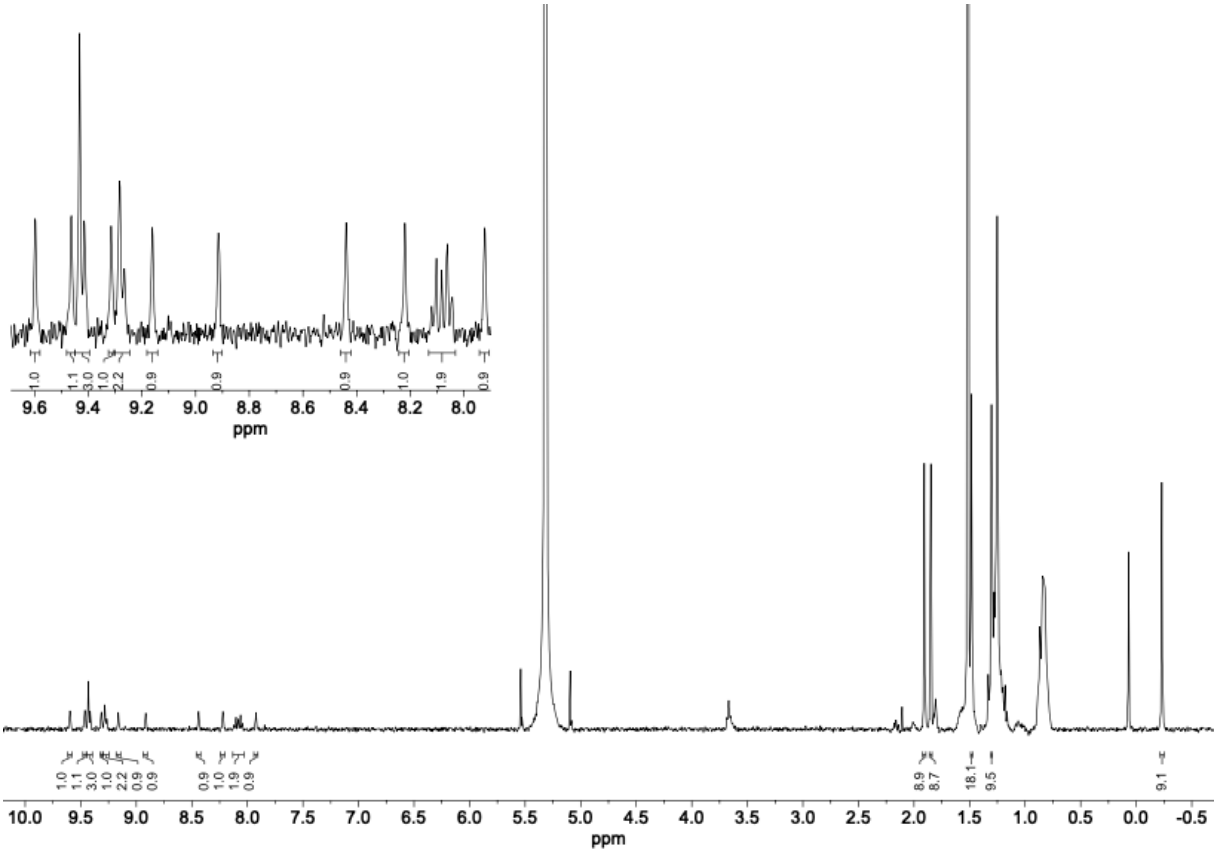


Figure S22. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of compound (*M*,*M*,*M*)-**1**.

ESI-TOF-HRMS spectra of compound 1

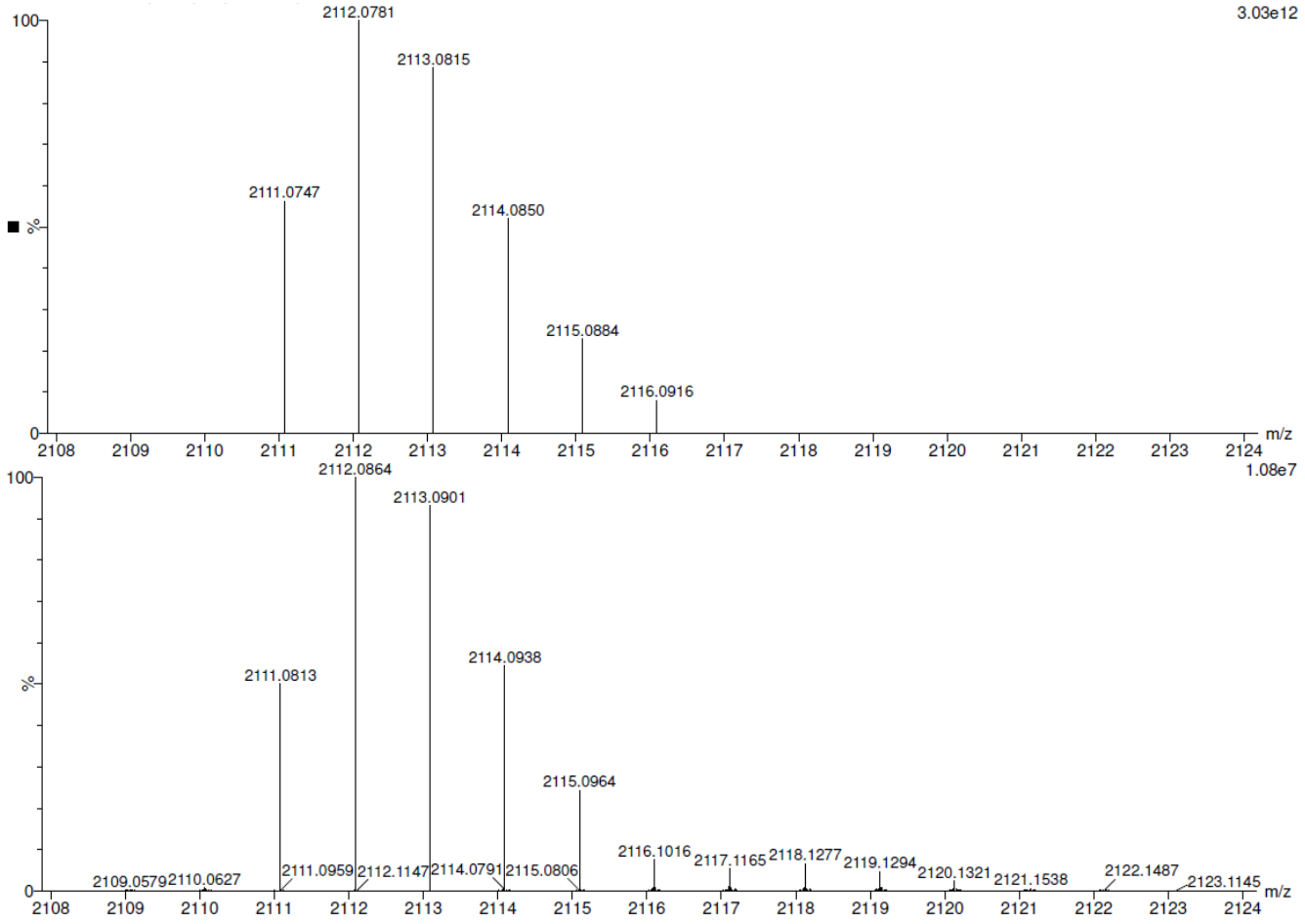


Figure S23. Theoretical (top) and experimental (bottom) ESI-TOF HRMS spectra of $[M]^+$ of compound **1**.

Single Crystal X-Ray Diffraction Structure

Single crystals of compound racemic (*P*,*P*,*M*/*M*,*M*,*P*)-**1** were obtained by slow evaporation of a solution of the compound in a mixture of dichloromethane and hexane. The diffraction measurements were carried out with Bruker D8 Venture diffractometer with a Mo radiation source and equipped with a PHOTON III detector. The structure was solved using SHELXT[S3] and refined by means of the full-matrix least-squares against F^2 procedure, using SHELX 2018[S4] and the WinGX32[S5] interface. C–H hydrogen atoms were placed in idealized positions (U_{eg}(H) = 1.2U_{eg}(C) or U_{eg}(H) = 1.5U_{eg}(C)) and were allowed to ride on their parent atoms.

Unfortunately, the quality of the crystals was low and the X-ray diffraction data collected were of a too poor quality (R_{int} = 0.28) for the adequate refinement of the structure, precluding the publication of the structure as a cif file. In this sense, after solving the structure the identity of the compound, the position of the atoms and its structure was unambiguously established. However, after applying anisotropy, a series of nearly 2D thermal ellipsoids or with an excessive prolate or oblate shape were observed in the main structure, probably due to the low quality of the data. Attempts to grow crystals of better quality or improve the diffraction data using a Cu radiation source proved unsuccessful.

Moreover, although a molecule of hexane and another one of chloroform could be located and modeled, a large amount of residual electron density was still present in the voids of the structure and could not be assigned to solvent molecules, despite it probably corresponds to disordered molecules of these solvents, especially chloroform, which has Cl atoms that have a higher electron density. Therefore, the SQUEEZE[S6] routine included in PLATON[S7] was applied and a density of 289 e^- in an approximately 1063 Å^3 volume was identified. This could correspond to around 6 molecules of dichloromethane per asymmetric unit. This density was removed, and the data refined against the model.

Summary of the X-ray diffraction measurement and refinement data: Chemical formula, $C_{170}H_{154}Cl_2O$; *Mr*, 2283.82; crystal size [mm^3], 0.185 x 0.104 x 0.103; temperature, 100(2) K; wavelength [Å], 0.71073 (Mo Kα), crystal system, triclinic; space group, *P*-1; *a* [Å], 19.498(2); *b* [Å], 19.742(2); *c* [Å], 21.334(2); α [°], 81.337(4); β [°], 74.395(4); γ [°], 60.717(4); *V* [Å^3], 6896.7(13); *Z*, 2; ρ_{calcd} [Mg m^{-3}], 1.100; μ [mm^{-1}], 0.100; F(000), 2432; ϑ range [°], 2.169 to 28.471; *hkl* ranges, -26/26, -26/26, -28/28; reflections collected, 174202; independent reflections, 34092; R_{int}, 0.2838; completeness to ϑ = 25.242°, 98.8%); absorption correction, numerical; refinement method; full-matrix least-squares on F^2; Final *R* indices [$I>2\sigma(I)$], R_1 = 0.1361, wR_2 = 0.3010; *R* indices (all data), R_1 = 0.2590, wR_2 = 0.3595; goodness-of-fit on F^2, 1.034.

The unit cell of the crystal structure contains the two enantiomers, (*M*,*M*,*P*)- and (*P*,*P*,*M*)-**1**, held together by the interplay of two C-H···π interactions ($d_{C\cdots\pi\ centroid}$ = 3.570 Å) between the two terminal HBCs. The overall network is formed by alternation of homoenantiomeric layers with disordered solvent (hexane and CH_2Cl_2 molecules) between them. Same configuration molecules within the same layer are also interacting through C-H···π interactions, but in this case between one terminal HBC *tert*-butyl and one of the benzene rings attached to the carbonyl of the tropone ($d_{C\cdots\pi\ centroid}$ = 3.583 Å). When looking to a single (*M*,*M*,*P*/*P*,*P*,*M*)-**1** molecule, it is worth mentioning the angle between the terminal HBC moieties of ca. 30º, and the feasibility of intramolecular parallel displaced π–π ($d_{C\cdots\pi\ centroid}$ = 3.634 Å) and C–H···π ($d_{C\cdots\pi\ centroid}$ = 3.701 Å) interactions.

Table S1. Atomic coordinates for the solid-state structure of **1**.

Atom	X	Y	Z	H	25.2106	7.3614	7.7574
C	31.4724	15.5577	4.2543	H	25.1092	8.9325	8.0446
C	30.7551	16.5177	5.1315	C	19.8819	13.7113	1.1216
C	23.2561	8.0473	7.7794	H	20.6706	13.4833	0.5856
C	28.9752	17.2852	6.5530	H	19.5143	14.5657	0.8145
C	29.5408	16.2229	5.7970	H	19.2051	13.0090	1.0196
C	29.8725	7.1076	1.6495	C	28.7873	14.9625	5.6512
C	19.0348	14.1992	3.4265	C	30.6263	5.7682	1.7358
H	18.3339	13.5288	3.2829	H	30.6457	5.4628	2.6677
H	18.7063	15.0790	3.1446	H	31.5448	5.8891	1.4142
H	19.2697	14.2276	4.3770	H	30.1718	5.1001	1.1828
C	21.3074	14.9536	2.7506	C	30.7654	8.1474	2.3213
H	21.6093	14.9963	3.6827	H	30.3594	9.0353	2.2296
H	20.8950	15.8068	2.5020	H	31.6470	8.1470	1.8918
H	22.0752	14.7790	2.1671	H	30.8649	7.9304	3.2711
C	24.7536	8.1928	7.5103	C	22.5319	21.1705	4.6076
H	24.8978	8.3753	6.5594	H	21.5685	21.3423	4.6492

H	22.9650	21.8675	4.0704	C	28.4994	12.5439	5.2999
H	22.9054	21.1782	5.5134	C	27.0969	12.6884	5.2938
C	29.6339	7.4901	0.2136	C	26.5195	13.9373	5.6204
H	29.0199	6.8458	-0.1979	C	27.3768	15.0483	5.8628
H	30.4851	7.4852	-0.2712	C	26.7749	16.2043	6.4975
H	29.2401	8.3863	0.1751	C	27.5948	17.2200	7.0193
C	22.1096	19.7286	2.6048	C	27.0459	18.1953	7.8821
H	22.3233	18.8721	2.1791	H	27.6176	18.8490	8.2647
H	22.4309	20.4630	2.0426	C	25.6887	18.2193	8.1820
H	21.1384	19.8034	2.7174	C	24.8733	17.2726	7.5904
C	24.2805	19.6473	3.8024	H	23.9415	17.2972	7.7710
H	24.7015	19.6132	4.6866	C	25.3689	16.2768	6.7317
H	24.6346	20.4118	3.3014	C	24.4893	15.2385	6.2017
H	24.4751	18.8195	3.3155	C	25.0869	14.0219	5.7806
C	29.3644	13.6704	5.3924	C	24.2849	12.8709	5.5957
C	30.8212	13.3540	5.3348	C	20.2809	13.8257	2.5966
C	31.8005	14.2450	4.8377	C	24.8414	11.7433	4.8480
C	31.4018	17.7415	5.2609	C	26.2354	11.5783	4.9384
H	32.1936	17.9139	4.7678	C	26.8104	10.3095	4.6446
C	30.8865	18.7096	6.1113	C	25.0774	19.2724	9.1372
H	31.3601	19.5209	6.2575	C	22.7821	19.7990	3.9626
C	29.6992	18.4843	6.7317	C	26.1369	20.1865	9.7330
H	29.3448	19.1537	7.3039	H	25.7108	20.8261	10.3424
C	33.1619	13.9144	4.8398	H	26.5911	20.6736	9.0145
H	33.7962	14.5243	4.4819	H	26.7900	19.6499	10.2285
C	33.5856	12.7054	5.3595	C	24.3442	18.5458	10.2773
H	34.5121	12.5142	5.4373	H	24.9784	17.9828	10.7666
C	32.6468	11.7795	5.7601	H	23.6315	17.9861	9.9024
H	32.9411	10.9332	6.0776	H	23.9535	19.2059	10.8870
C	31.2649	12.0522	5.7149	C	24.0865	20.1442	8.3258
C	30.3139	10.9593	5.8874	H	23.6718	20.8039	8.9192
C	30.6364	9.6933	6.4030	H	23.3929	19.5724	7.9361
H	31.5048	9.5469	6.7581	H	24.5700	20.6063	7.6095
C	29.7166	8.6413	6.4092	C	23.0650	7.7867	9.2708
C	28.5061	8.8522	5.7621	H	23.6047	7.0146	9.5388
H	27.9020	8.1222	5.6835	H	22.1195	7.6042	9.4516
C	28.1336	10.0815	5.2239	H	23.3484	8.5761	9.7776
C	28.9920	11.1910	5.4006	C	29.9801	7.2892	7.0748

C	22.7478	6.8492	6.9597	C	25.5574	4.6010	2.5842
H	22.9222	7.0061	6.0088	C	26.1235	3.3303	2.3562
H	21.7841	6.7414	7.1023	H	27.0662	3.2550	2.2717
H	23.2132	6.0359	7.2479	C	25.3472	2.1948	2.2494
C	31.2844	7.2282	7.8020	C	23.9698	2.3292	2.3295
H	32.0200	7.3258	7.1612	H	23.4285	1.5551	2.2265
H	31.3633	6.3671	8.2616	C	23.3488	3.5621	2.5555
H	31.3266	7.9548	8.4591	C	21.8755	3.7093	2.5924
C	29.9169	6.1867	5.9901	C	21.2959	4.9899	2.7999
H	30.6481	6.3165	5.3506	C	19.8830	5.1321	2.7671
H	29.0589	6.2368	5.5219	C	19.2866	6.4726	2.9540
H	30.0075	5.3068	6.4143	C	17.8973	6.6745	2.8985
C	28.8608	7.0168	8.1224	H	17.3329	5.9284	2.7369
H	28.9860	6.1256	8.5087	C	17.3194	7.9217	3.0731
H	27.9860	7.0652	7.6850	C	18.1646	9.0133	3.2231
H	28.9092	7.6909	8.8328	H	17.7851	9.8796	3.3094
C	26.0405	9.3295	4.0304	C	19.5616	8.8797	3.2519
C	24.6341	9.5086	3.8784	C	20.1241	7.5794	3.1676
C	24.0449	10.7710	4.1906	C	21.5669	7.4174	3.2375
C	22.6561	10.9852	3.7675	C	22.1402	6.1298	3.0279
C	22.1604	12.2680	3.4593	C	23.5491	5.9972	3.0259
H	22.7424	13.0168	3.5207	C	24.1512	4.7162	2.7280
C	20.8360	12.4674	3.0670	C	25.9738	0.7821	2.0645
C	19.9791	11.3504	3.0875	C	27.5119	0.8516	1.9392
H	19.0514	11.4868	2.9354	H	27.8887	1.2639	2.7442
C	20.4342	10.0574	3.3237	H	27.7517	1.3901	1.1547
C	21.8280	9.8629	3.5559	H	27.8734	-0.0531	1.8353
C	22.3882	8.5388	3.4840	C	25.6481	-0.0734	3.2929
C	23.7956	8.3831	3.5251	H	26.0495	-0.9608	3.1870
C	24.3720	7.1135	3.2744	H	24.6767	-0.1611	3.3795
C	25.8037	6.9975	3.1697	H	26.0114	0.3564	4.0951
C	26.3977	5.8016	2.6767	C	25.4076	0.1386	0.7970
C	27.7313	5.8439	2.2658	H	25.5686	0.7267	0.0305
H	28.1339	5.0490	1.9341	H	24.4422	0.0000	0.9047
C	28.4928	7.0075	2.3233	H	25.8450	-0.7251	0.6444
C	27.9414	8.1267	2.9252	C	18.7058	1.5217	2.1795
H	28.4666	8.9131	3.0158	C	17.9626	1.2794	3.4922
C	26.6130	8.1221	3.4080	H	17.3830	0.4939	3.3997

H	17.4176	2.0637	3.7091	C	20.9440	14.1365	6.6598
H	18.6110	1.1228	4.2107	C	20.2403	12.9321	6.9269
C	17.7030	1.7906	1.0559	C	20.9536	11.6739	6.9536
H	18.1873	1.9641	0.2207	C	20.2854	10.4701	7.3233
H	17.1569	2.5705	1.2846	C	21.0540	9.3189	7.5082
H	17.1242	1.0081	0.9398	H	20.6078	8.5090	7.7308
C	19.4853	0.2499	1.8324	C	22.4475	9.3004	7.3767
H	18.8565	-0.4873	1.6804	C	23.0675	10.4825	6.9597
H	20.0823	0.0199	2.5757	H	24.0132	10.4974	6.8737
H	20.0142	0.4005	1.0227	C	22.3419	11.6450	6.6639
C	15.7992	8.1359	2.9540	C	23.0046	12.8539	6.2120
C	15.4721	8.4245	1.4790	C	22.3554	14.1074	6.3620
H	15.7687	7.6713	0.9252	C	18.8450	10.5032	7.5698
H	15.9356	9.2400	1.1940	C	18.1713	11.7573	7.5904
H	14.5056	8.5448	1.3753	C	18.8568	12.9739	7.2514
C	15.0206	6.8978	3.4059	C	18.1789	14.2105	7.2638
H	15.1923	6.1592	2.7848	C	18.8647	15.4097	6.9187
H	14.0616	7.1003	3.4150	C	18.1478	16.6635	6.8509
H	15.3091	6.6413	4.3063	C	18.7967	17.8231	6.3558
C	15.3176	9.3462	3.7798	C	18.0968	19.0399	6.3270
H	14.3383	9.3728	3.7808	H	18.5390	19.8200	6.0099
H	15.6661	10.1727	3.3832	C	16.7707	19.1339	6.7502
H	15.6435	9.2641	4.7004	C	16.1496	17.9697	7.1980
C	19.0968	3.9997	2.5657	H	15.2436	18.0221	7.4748
H	18.1516	4.0962	2.5543	C	16.7876	16.7416	7.2597
C	19.6467	2.7281	2.3809	C	16.1226	15.5284	7.7486
C	21.0230	2.6097	2.3952	C	16.7926	14.2769	7.6869
H	21.4082	1.7520	2.2641	C	16.1262	13.0965	8.1019
C	23.0724	15.3056	6.2017	C	16.8013	11.7984	7.9602
C	22.3156	16.5239	5.9347	C	16.1260	10.6006	8.2169
C	22.9004	17.5997	5.2362	H	15.2036	10.6338	8.4412
H	23.8255	17.5589	5.0232	C	16.7612	9.3542	8.1532
C	22.1721	18.7153	4.8459	C	18.1143	9.3364	7.8246
C	20.8291	18.7795	5.2465	H	18.5606	8.4996	7.7720
H	20.3298	19.5619	5.0418	C	14.8541	13.2142	8.6627
C	20.1943	17.7429	5.9306	H	14.4102	12.4287	8.9631
C	20.9289	16.5576	6.2058	C	14.2066	14.4449	8.7942
C	20.2474	15.3708	6.6434	C	14.8425	15.5669	8.3073

H	14.3917	16.4024	8.3544	H	16.2814	7.3630	6.4949
C	16.0011	20.4686	6.7605	H	14.8704	8.0900	6.6988
C	16.8071	21.6070	6.1606	H	15.0913	6.6033	7.2484
H	16.2697	22.4260	6.1671	C	14.8022	8.2831	9.3694
H	17.0513	21.3830	5.2385	H	14.4069	7.4243	9.6271
H	17.6203	21.7451	6.6898	H	14.1304	8.8262	8.9065
C	15.7022	20.8289	8.2231	H	15.1085	8.7557	10.1712
H	16.5447	20.8982	8.7213	O	31.9453	15.9069	3.1800
H	15.1434	20.1313	8.6244	C	19.1138	4.9112	6.0867
H	15.2310	21.6869	8.2594	H	19.7165	4.3791	5.5084
C	14.6962	20.3183	5.9778	H	19.1707	5.8553	5.7932
H	14.2194	21.1743	5.9708	Cl	17.4704	4.3455	5.8696
H	14.1376	19.6352	6.4018	Cl	19.6651	4.7966	7.7373
H	14.8984	20.0501	5.0563	C	28.0149	11.6217	8.9030
C	12.8305	14.5758	9.4782	H	28.4605	12.3550	8.4305
C	11.8426	15.2813	8.5456	H	28.2525	10.7691	8.4823
H	11.7135	14.7432	7.7365	H	28.3042	11.6141	9.8404
H	12.1977	16.1612	8.2986	C	26.5363	11.8132	8.8414
H	10.9827	15.3938	9.0029	H	26.1025	11.0570	9.3096
C	12.9999	15.4277	10.7498	H	26.2562	11.7750	7.8920
H	13.4252	16.2798	10.5159	C	26.0199	13.1131	9.4433
H	13.5632	14.9473	11.3913	H	26.3858	13.8705	8.9208
H	12.1221	15.5994	11.1482	H	26.3673	13.1929	10.3670
C	12.2421	13.2222	9.8480	C	24.4777	13.2432	9.4844
H	11.3362	13.3451	10.2016	H	24.1279	13.1343	8.5643
H	12.8039	12.7983	10.5300	H	24.1137	12.5021	10.0312
H	12.2076	12.6521	9.0521	C	23.9726	14.5403	10.0390
C	16.0000	8.0362	8.4285	H	22.9918	14.5764	9.9127
C	16.9114	7.0031	9.1126	H	24.3690	15.2818	9.5159
H	17.6587	6.7837	8.5169	C	24.2820	14.7648	11.5099
H	16.3981	6.1920	9.3055	H	23.9317	14.0149	12.0356
H	17.2594	7.3778	9.9483	H	23.8620	15.5975	11.8090
C	15.5185	7.4723	7.0994	H	25.2525	14.8248	11.6346

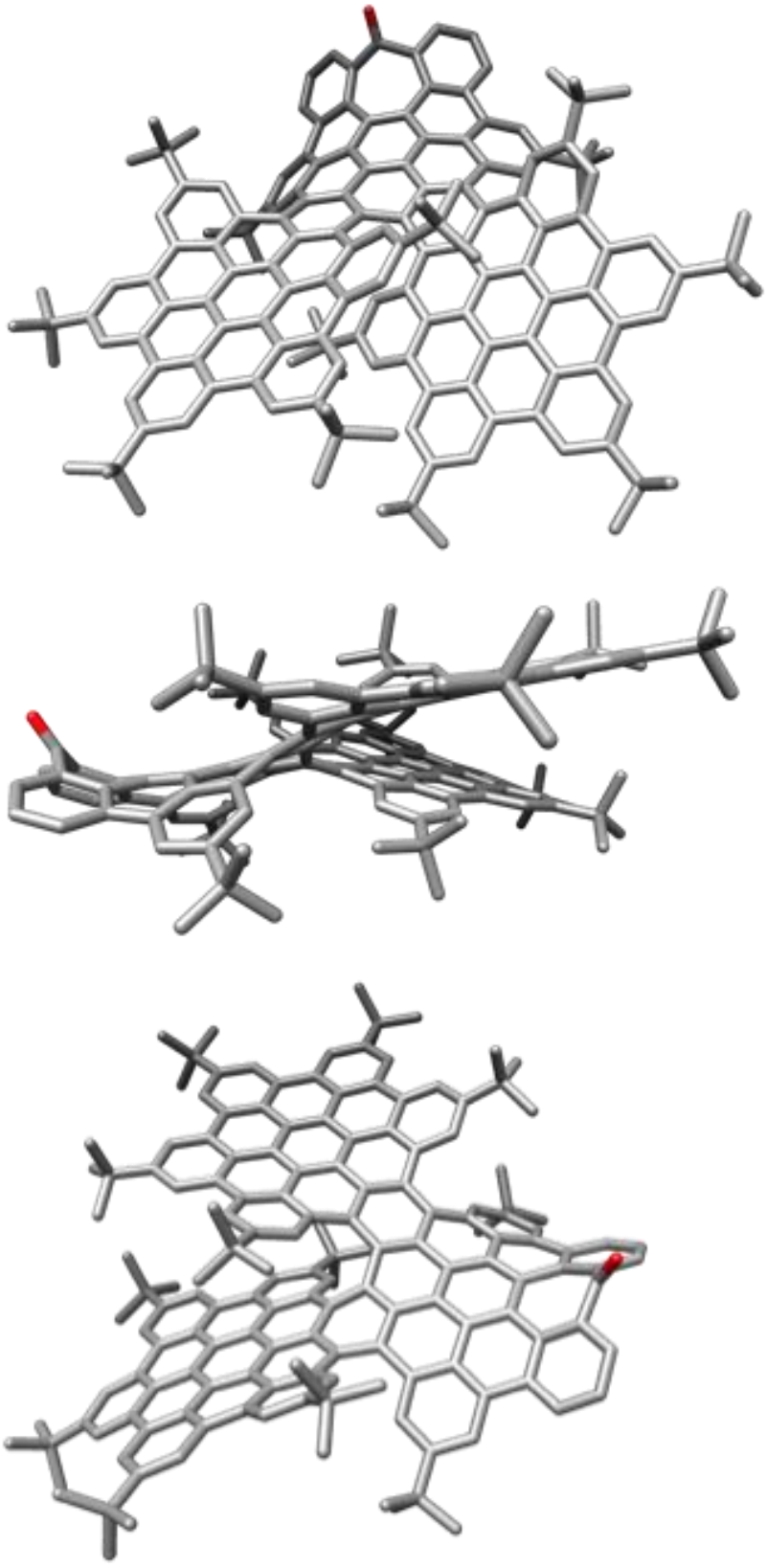


Figure S24. Front (top), side (middle) and top (bottom) views of compound (*P*,*P*,*M*)-**1** extracted from XRD. H atoms and solvent molecules have been omitted for clarity.

CSP-HPLC traces of compound 1

Diastereomeric resolution was neither possible by flash column chromatography, nor preparative Thin Layer Chromatography. In addition, normal phase High Performance Liquid Chromatography (HPLC) did not afford any separation. Chiral stationary phase HPLC (CSP-HPLC) was used to perform both diastereomeric and racemic resolution simultaneously.

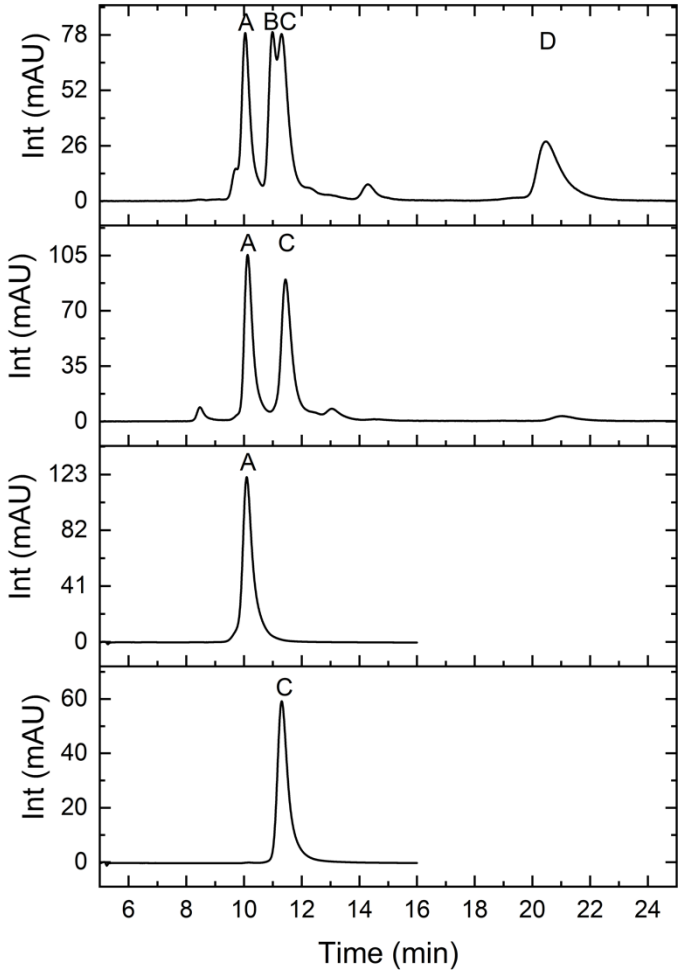


Figure S25. CSP-HPLC traces of compound **1**. From top to bottom, First: chromatogram before reflux of **1** in toluene, containing a mixture of four main compounds: A = (*P*,*P*,*M*)-**1**, B = (*P*,*P*,*P*)-**1**, C = (*M*,*M*,*P*)-**1**, and D = (*M*,*M*,*M*)-**1**. Second: chromatogram after reflux of **1** in toluene; Third: traces of the collected fraction A; Fourth: traces of the collected fraction C. Conditions: Chiralpak® IA, *n*-Hex:DCM 8:2, flow = 3.8 mL min^{-1}.

Optical properties

The linear absorption spectra were recorded in a JASCO V-540 spectrophotometer. The fluorescence spectra were recorded using a Horiba Jobin Yvon Fluorlog 3-22 Spectrofluorometer with a xenon lamp of 450 W as the excitation source. The absorption and emission spectra were recorded at μM concentrations either in spectroscopic grade dimethyl sulfoxide (DMSO) or chloroform (CH_3Cl). The excitation independent emission and the overlap between the absorption and excitation spectra confirmed the purity of the samples and the absence of aggregates (Figure **S26**).

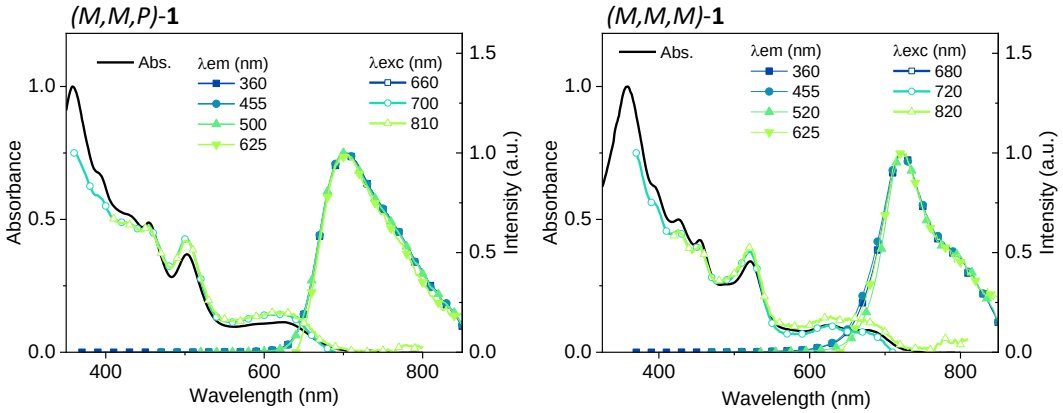


Figure 26. Excitation wavelength independent emission specra (⍰exc at 660-810 nm) and emission wavenlength independent excitation spectra (lem at 360-625 nm) for the enantiomers pairs isolated in DMSO. The excitation spectra show a good overlap with the corresponding absorption spectra.

Quantum Yield (φ_F)

The fluorescence quantum yields were measured using Tetraphenylporphirine (TPP) in toluene as standard ($\phi_F = 0.11$).[58] For each sample, several solutions were prepared in the 0.06-1 μM concentration range. To avoid non-linear effects the absorbances in the 5 mm quartz cuvettes were kept bellow 0.06 at the excitation wavelength (590 nm for CH_3Cl and 514 for DMSO). The fluorescence spectra were measured for each sample and standard at the same conditions. The plots of the absorbance versus integrated fluorescence intensity showed a good linear correlation, as illustrated in Figure **S27** for the compounds in CH_3Cl. The slopes (*m*) obtained from the linear fit were used to calculate ϕ_F according to the following equation:

$$\phi_F = \phi_S \cdot \frac{m}{m_S} \cdot \frac{n^2}{n_S{}^2} \qquad (1)$$

where the subscripts *S* denote the standard, *m* is the slope from the plot of integrated fluorescence intensity versus the absorbance (Figure S24), and η the refractive index of the solvent.

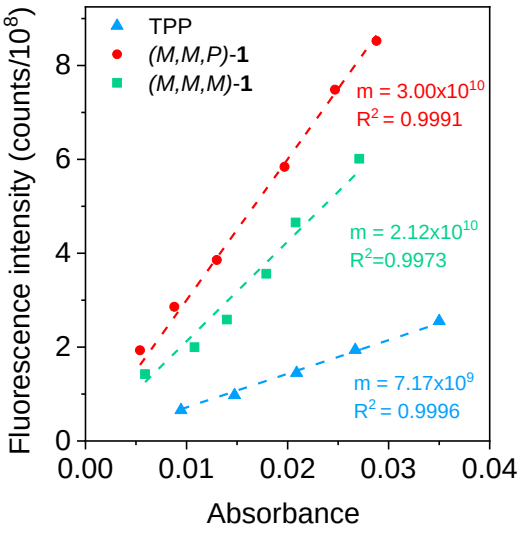


Figure S27. Integrated fluorescence intensity vs absorbance plots for the compounds (*M,M,M/P,P,P*)-**1** and (*M,M,P/P,P,M*)-**1** in CH_3Cl and the standard (TPP) fitted by a linear fit with intercept equal to zero. The legend includes the R-square and the slope.

Emission lifetimes (τ)

The emission lifetimes were measured by the Single-Photon Timing technique in a home-built setup using a linear excitation source operating at 330 nm with a 4 MHz repetition rate (second harmonic of a Coherent Radiation Dye laser 700 series, 560-610 nm, 130 mW, 5 ps, 4 MHz), an Hamamatsu R2809U-01 MCP-PMT as the detector and an SPC-160 photon counting board from Becker & Hickl GmbH. The emission at 680 nm (*(M,M,P)*-**1**, peak A) and 715 nm (*(M,M,M)*-**1,** peak B) was collected at the magic angle. The instrument response functions (IRF) for deconvolution (140 ps FWHM) were generated by scattering dispersions of colloidal silica in water. The solution was kept under gentle stirring during the data collection. Blank decays were acquired to ensure that dark photon counts were negligible. Decay curves were stored in 1024 channels with 39.06 ps per channel and an accumulation of 10k counts in the peak channel. The fluorescence decays were analyzed by a non-linear least-squares reconvolution method using the TRFA DP software by SSTC (Scientific Software Technologies Center, Belarusian State University, Minsk, Belarus). In both DMSO and CH_3Cl, (*M,M,P*)-**1** showed a slightly longer lifetime (6-7 ns) than (M,M,M)-1 (5 ns) as illustrated in Figure S28.

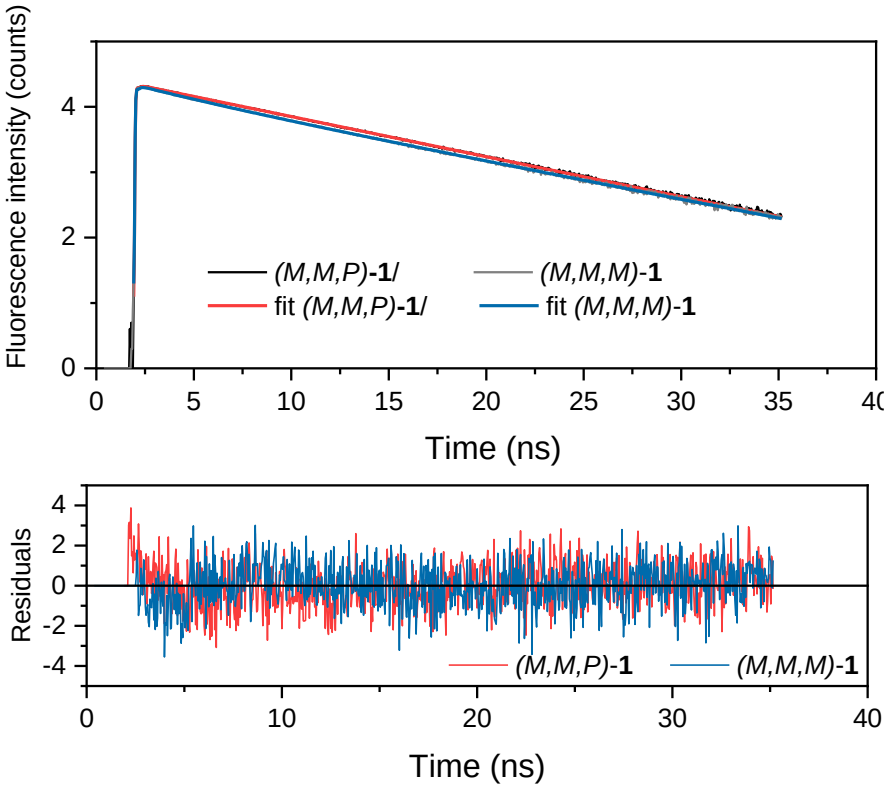


Figure S28. Fluorescence emission decays of compounds (*M,M,M/P,P,P*)-**1** (peak D) and (*M,M,P/P,P,M*)-**1** (peak A) in DMSO (black and gray, respectively). The exponential fitting of the decay is shown in red (A) and blue (D). For a better judgment of the quality of the fits, the corresponding residuals are presented.

$$\Phi_F = \frac{k_f}{k_f + k_{nr}} = k_f \tau_{av}$$

Table S2. Summary of photophysical properties for compound **1** diastereoisomers and undecabenzo[7]helicene reported by Campaña and coworkers (*Angew. Chem. Int. Ed.*, 2018, **57**, 14782–14786), including calculated fluorescence emission rate constant (k_f) and nonradiative decay rate constant (k_{nr})

Compound	Φ	τ_{av} (ns)	k_f (ns^{-1})	k_{nr} (ns^{-1})
(*M,M,P*)-**1**	0.43	6.1	0.070	0.093
(*M,M,M*)-**1**	0.30	5.3	0.057	0.132
Undezabenzo[7]helicene (Campaña)	0.098	18.0	0.005	0.050

Two-photon absorption cross-section (σ_2)

The TPA spectra were measured by two-photon induced fluorescence (TPF) using Zn-2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine as a standard to account for the collection efficiency and excitation pulse characteristics. The two-photon absorption cross-section of the reference was taken from reference.[S9] The excitation source was a Ti:sapphire laser (Tsunami BB, Spectra-Physics, 710-990 nm, 1.7 W, 100 fs, 82 MHz). A modified setup that follows the one described by Xu and Webb was used to estimate the TPA cross-section in the 710-920 nm region.[S10] The two-photon absorption cross-section was calculated from the following equation:

$$\sigma_2 = \left(\frac{F_2}{\phi C n}\right)_s \left(\frac{\phi C n \sigma_2}{F_2}\right)_{ref} \quad (2)$$

where F_2 stands for two-photon induced fluorescence intensity, ϕ is the one-photon excited fluorescence quantum yield, *n* refers to the refractive index in solution, *C* is the concentration and *s* and *ref* are relative to the sample and the TPA reference, respectively. The two-photon emission was measured within a narrow wavelength bandwidth centered at 700 nm selected by the H20Vis Jobin Yvon monochromator placed at the entrance of a PMC-100-4 photomultiplier tube (Becker and Hickl GmbH). The integrated intensity over the entire emission band was extrapolated using the emission spectra corrected by the detector sensitivity recorded by commercial spectrofluorometer. The emission intensity dependence on the excitation power was checked to be quadratic (Figure **S29**). Figure **S30** shows the experimental one-photon absorption (OPA, black), one-photon emission (OPE, dashed black), two-photon absorption (TPA, red line with symbols) and two-photon emission (TPE, dashed red) spectra of for the racemic mixture of the high energy enantiomers *(M,M,P/P,P,M)*-**1** measured in $CHCl_3$ at ca. 1×10^{-6} M, λ_{exc} = 370 nm for OPE and λ_{exc} = 900 nm for TPE.

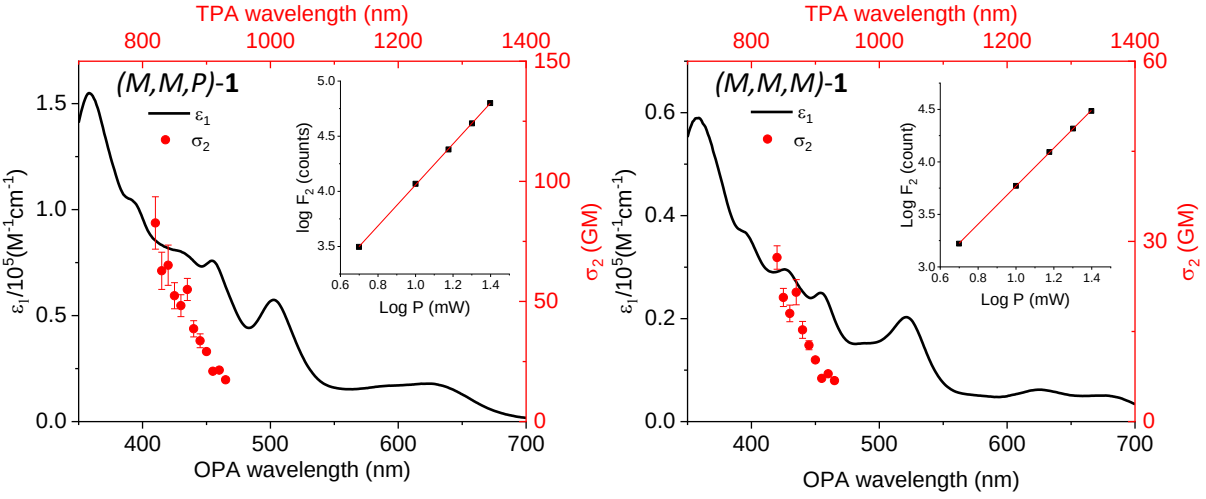


Figure S29. Linear molar absorptivity (ε_1, black line) and two photon absorption cross-section (σ_2, red dots) for *(M,M,P/P,P,M)*-**1** (peak A) and *(M,M,M/P,P,P)*-**1** (peak D) in DMSO. The insert shows the power dependence of the two-photon emission upon excitation at 820 nm in a log-log plot. The experimental data (squares) is well represented by a linear fit with a slope ~2 (1.9 for (*M,M,P/P,P,M)*-**1** and 1.8 for *(M,M,M/P,P,P)*-**1**).

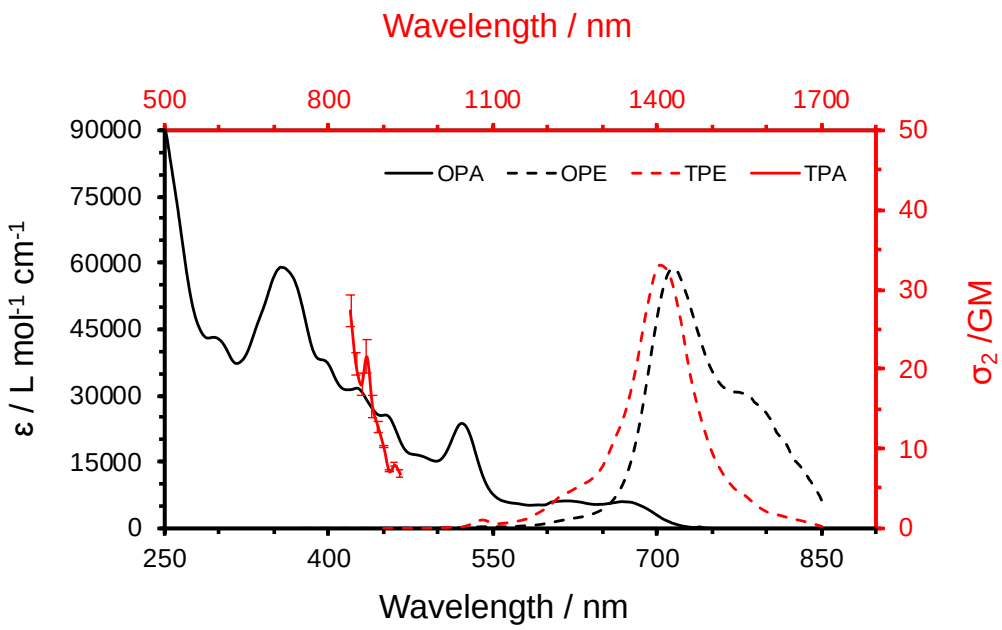


Figure S30. Experimental OPA (black), OPE (black, dashed), TPA (red line plus symbol) and TPE (red, dashed) spectra of (*M*,*M*,*M*/*P*,*P*,*P*)-**1**. Measured in $CHCl_3$ at ca. 1×10^{-6} M, λ_{exc} = 370 nm for OPE, λ_{exc} = 900 nm for TPE.

A summary of the optical properties of the isolated enantiomer pairs is given in Table S1.

Table S3 Summary of optical properties studied for *(M,M,P/P,P,M)*-**1** and *(M,M,M/P,P,P)*-**1**

compound	solvent	ϕ_F	τ (ns)	ε_1 ($M^{-1}cm^{-1}$)/10^5	σ_2(GM)	$\phi_F\,\sigma_2$
M,M,P-1/P,P,M-1	CH_3Cl	0.43	6.1	1.55	110 ± 5	47
	DMSO	0.50	7.1	1.45	63 ± 7	32
M,M,M-1/P,P,P-1	CH_3Cl	0.30	5.3[a)]	0.59	30 ± 3	9
	DMSO	0.39	5.4[a)]	0.59	27 ± 2	10

[a)]Average decay estimated from a biexponential fit

Electrochemistry

Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV) were carried out on a PGSTAT2014 potentiostat/galvanostat (Metrohm Autolab B. V.) with a three-electrode cell under Ar atmosphere at 25ºC. A Pt-wire counterelectrode, an Ag wire quasireference electrode and a glassy carbon disk working electrode were used. Freshly distilled THF was used as solvent to prepare a 0.1 M solution of tetra-*n*-butylammonium hexfluorophosphate ($TBAPF_6$) which was used as work solution. The scan rate was 0.05 V/s. Potential values are referred to the ferrocenium/ferrocene ($FeCp_2^+/FeCp_2$) system, Fc was added as an internal reference after each measurement.

Electrochemical measurements of a THF solution of (*M*,*M*,*P*/*P*,*P*,*M*)-**1** show oxidation waves at 0.74 (quasi-reversible) and 0.45 V (reversible), three reductions centered at −1.50 (reversible), −1.70 (quasi-reversible), −1.95 V (quasi-reversible), and another three irreversible reductions with potentials at −2.28, −2.44, and −2.76 V respectively. The estimated electrochemical bandgap is in perfect agreement with the optical bandgap (1.95 eV).

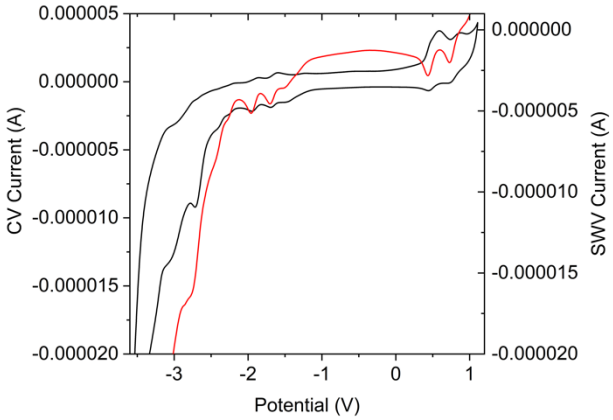


Figure S31. Cyclic (black) and square wave (red) voltammetry of (*M*,*M*,*P*/*P*,*P*,*M*)-**1** measured in THF at ca. 1×10^{-3} M (internal standard Fc/Fc+, v = 0.05 Vs^{-1}).

Theoretical Calculations

All the calculations were performed by using the Gaussian09 suite.[S11] Geometry optimizations of (*M,M,M*)-**1**, (*M,M,P*)-**1** and (*P,M,P*)-**1** were carried out at DFT-CAMB3LYP/6-31G(d,p) level of theory (lateral ^{t}Bu groups that are not taking part of any helicene moiety were removed for reducing calculation costs). Harmonic frequencies were calculated in order to corroborate that found geometries were true minima. Electronic transitions were studied by TDDFT method at the same level of theory.

Table S4. DFT-CAMB3LYP/6-31G(d,p) energies for (*MMM*)-**1***, (*MMP*)-**1*** and (*PMP*)-**1*** (*without lateral ^{t}Bu groups).

Compound	SCF Energy (au)	Relative energy (kcal mol^{-1})
(*M,M,M*)-**1**	–5736.055601	3.32
(*M,M,P*)-**1**	–5736.060894	0.00
(*P,M,P*)-**1**	–5736.044078	10.55

Optimized structures

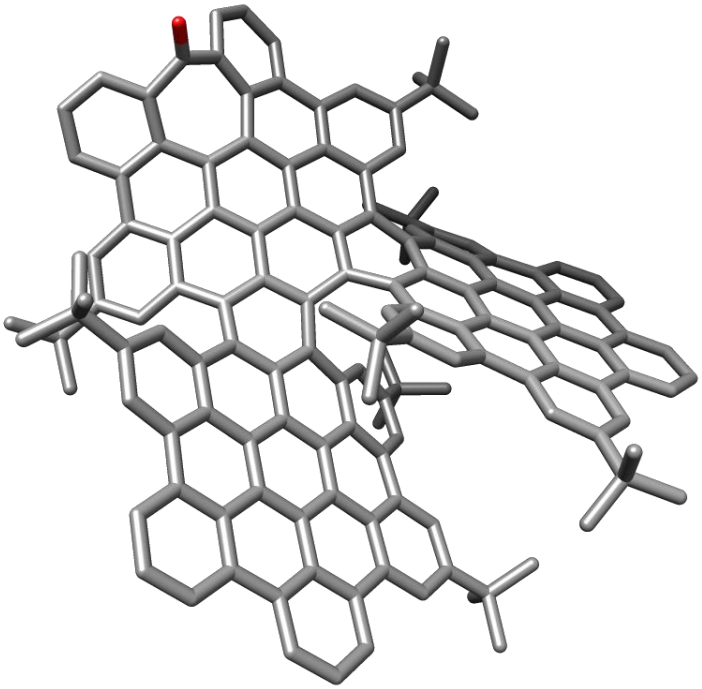


Figure S32. Optimized geometry of (*M,M,M*)-**1**.

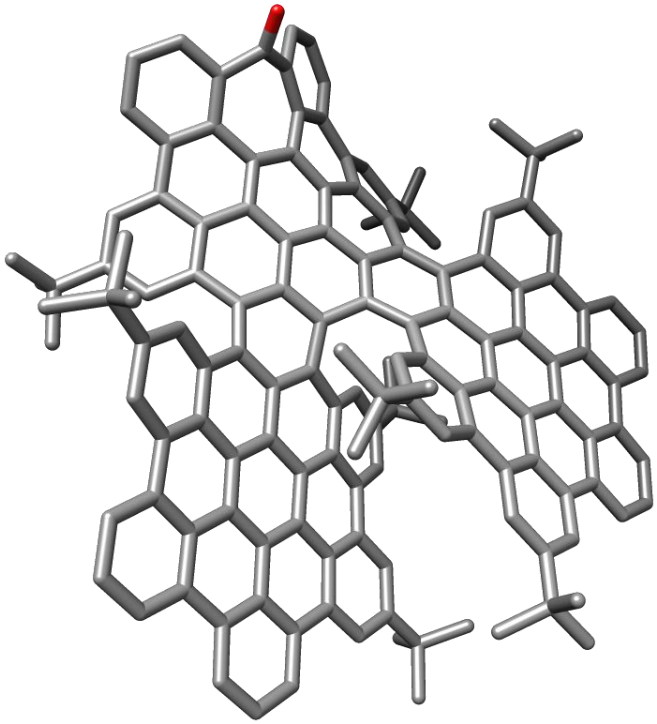


Figure S33. Optimized geometry of (*M,M,P*)-**1**.

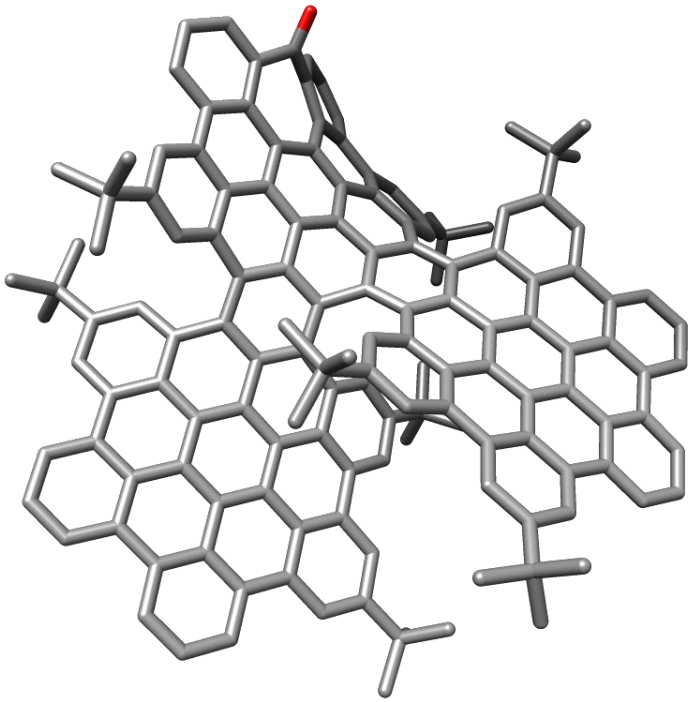


Figure S34. Optimized geometry of (*P,M,P*)-**1**.

Frontier molecular orbitals of (*M,M,M*)-1

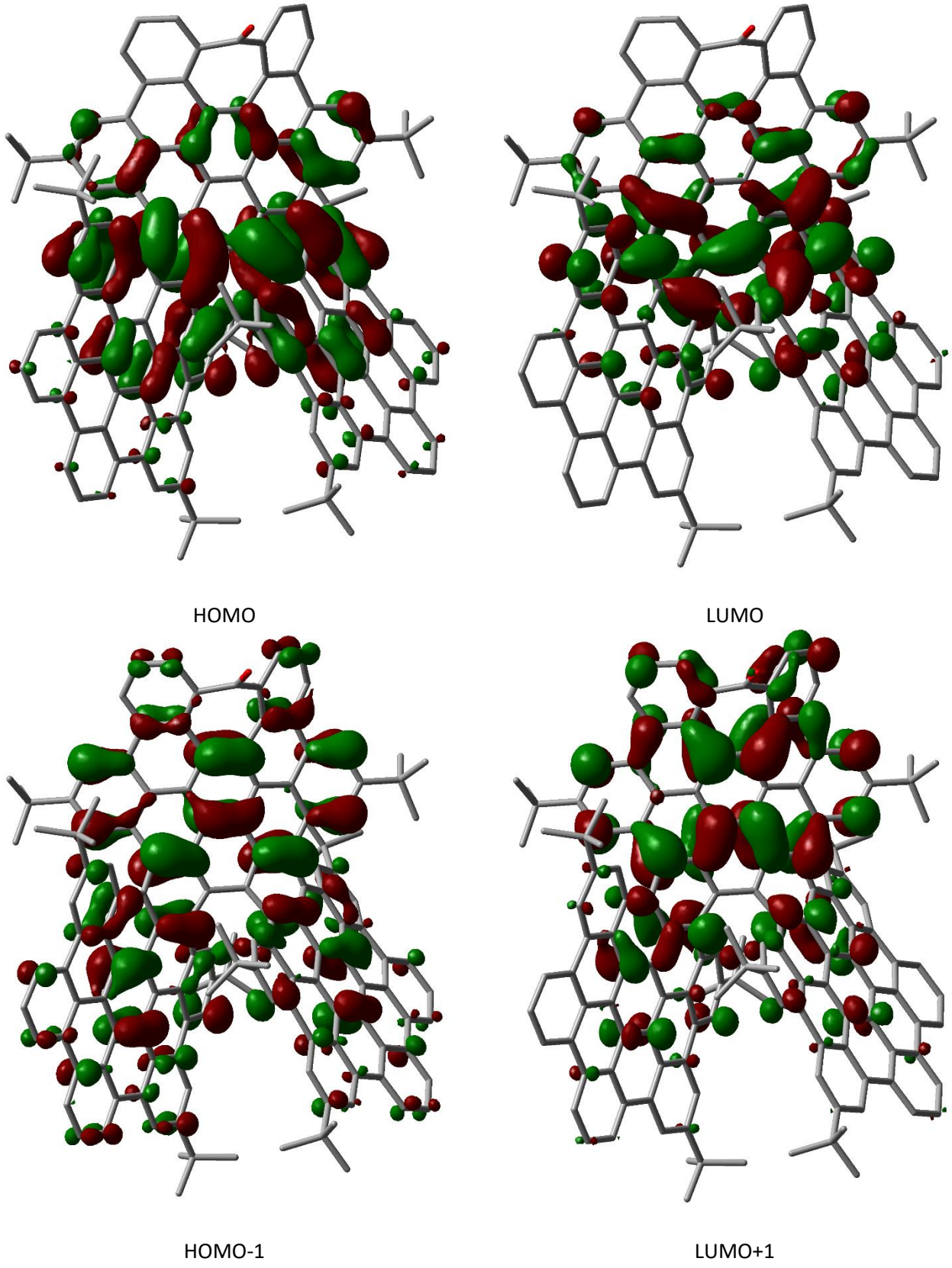


Figure S35. Frontier molecular orbitals of (*M,M,M*)-**1**

Frontier molecular orbitals of (*M,M,P*)-1

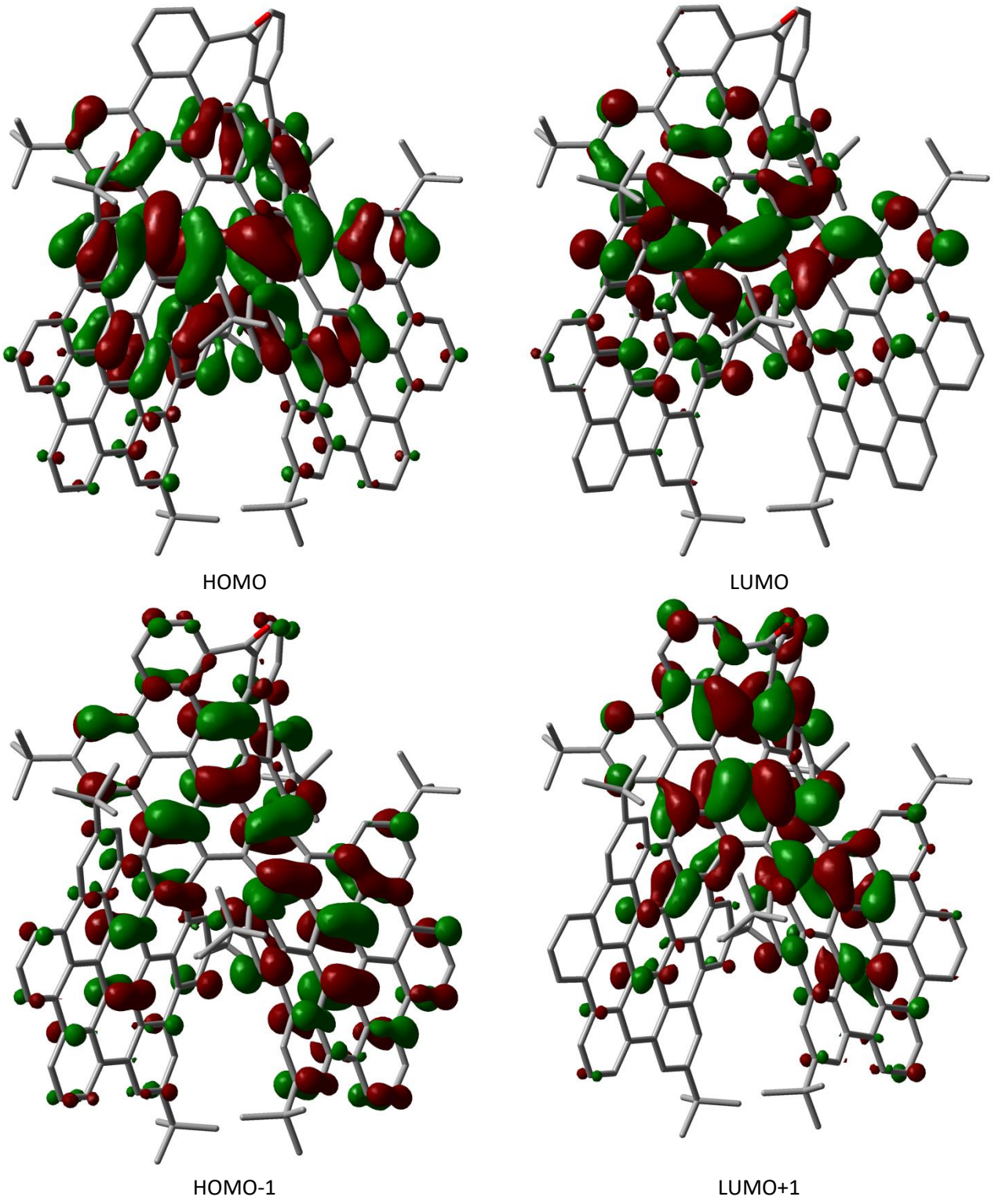


Figure S36. Frontier molecular orbitals of (*M,M,P*)-**1**

Frontier molecular orbitals of (*P,M,P*)-1

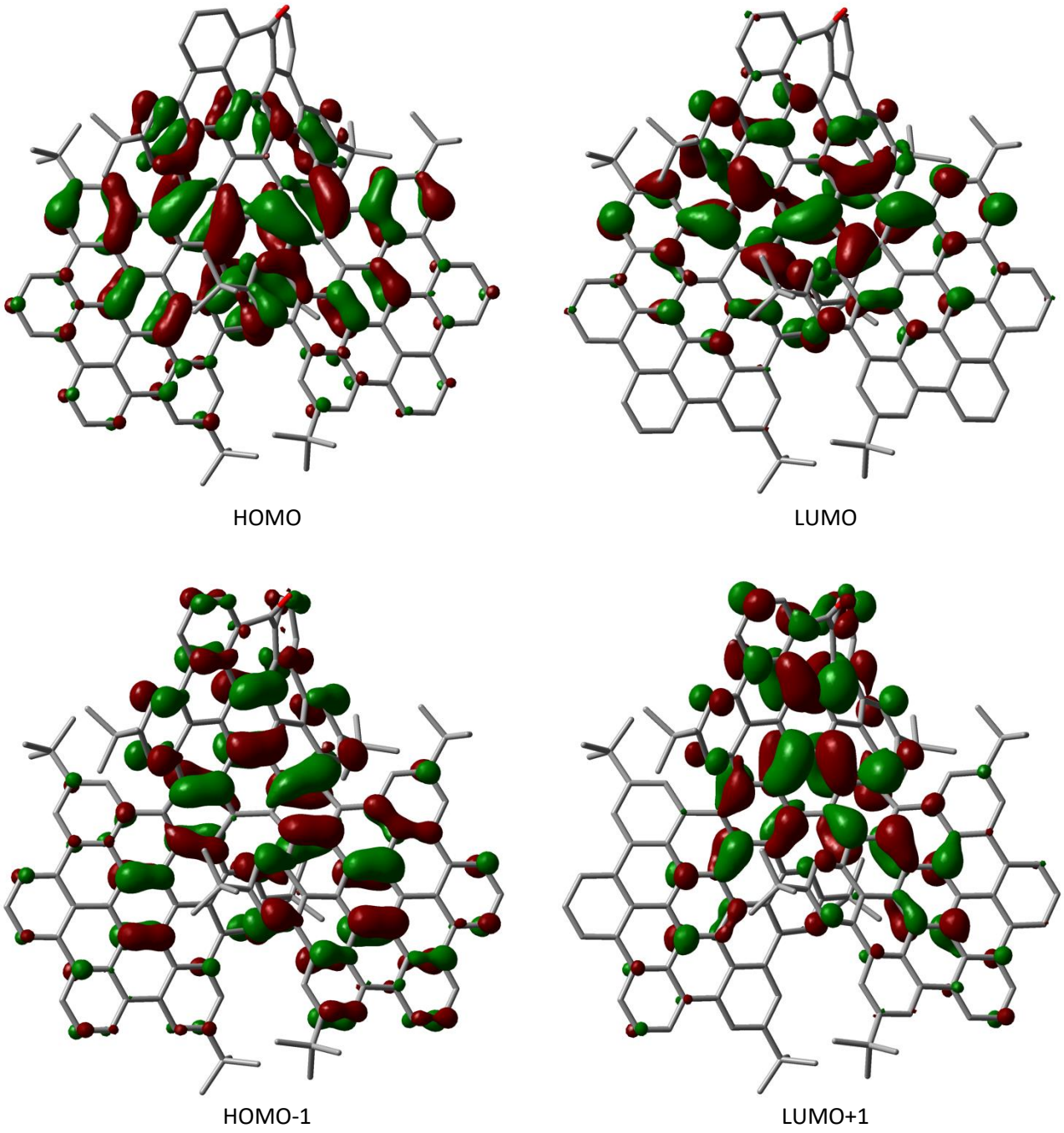


Figure S37. Frontier molecular orbitals of (*P,M,P*)-**1**

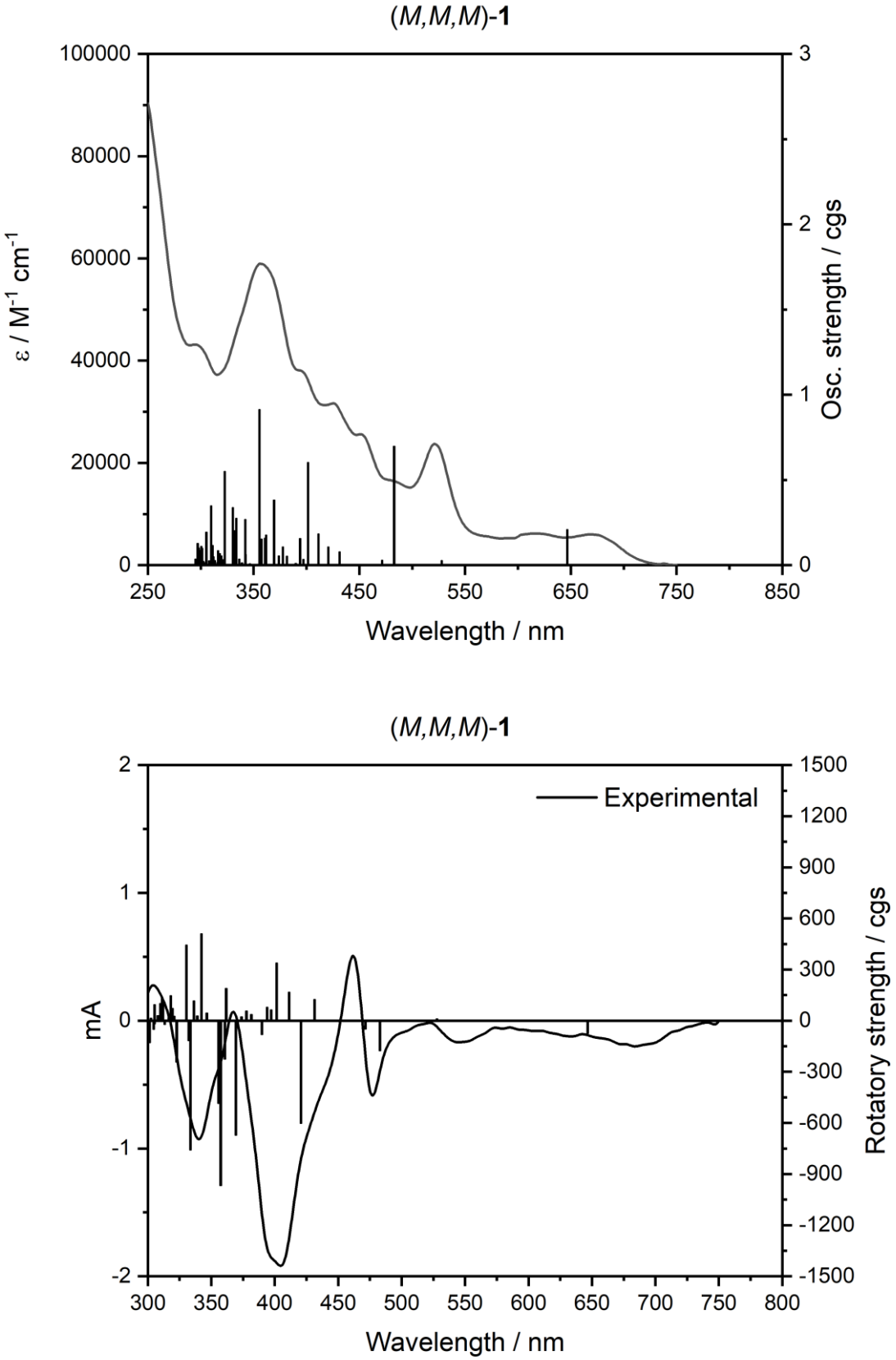


Figure S38. Top: Experimental (gray) UV-Vis spectrum of compound (*M,M,M*)-**1** (fraction D in Figure S22) and calculated oscillatory strength for the first 50 electronic transitions (black bars). Bottom: Experimental (black) ECD spectrum of compound (*M,M,M*)-**1** and calculated rotatory strength for the first 50 electronic transitions (black bars).

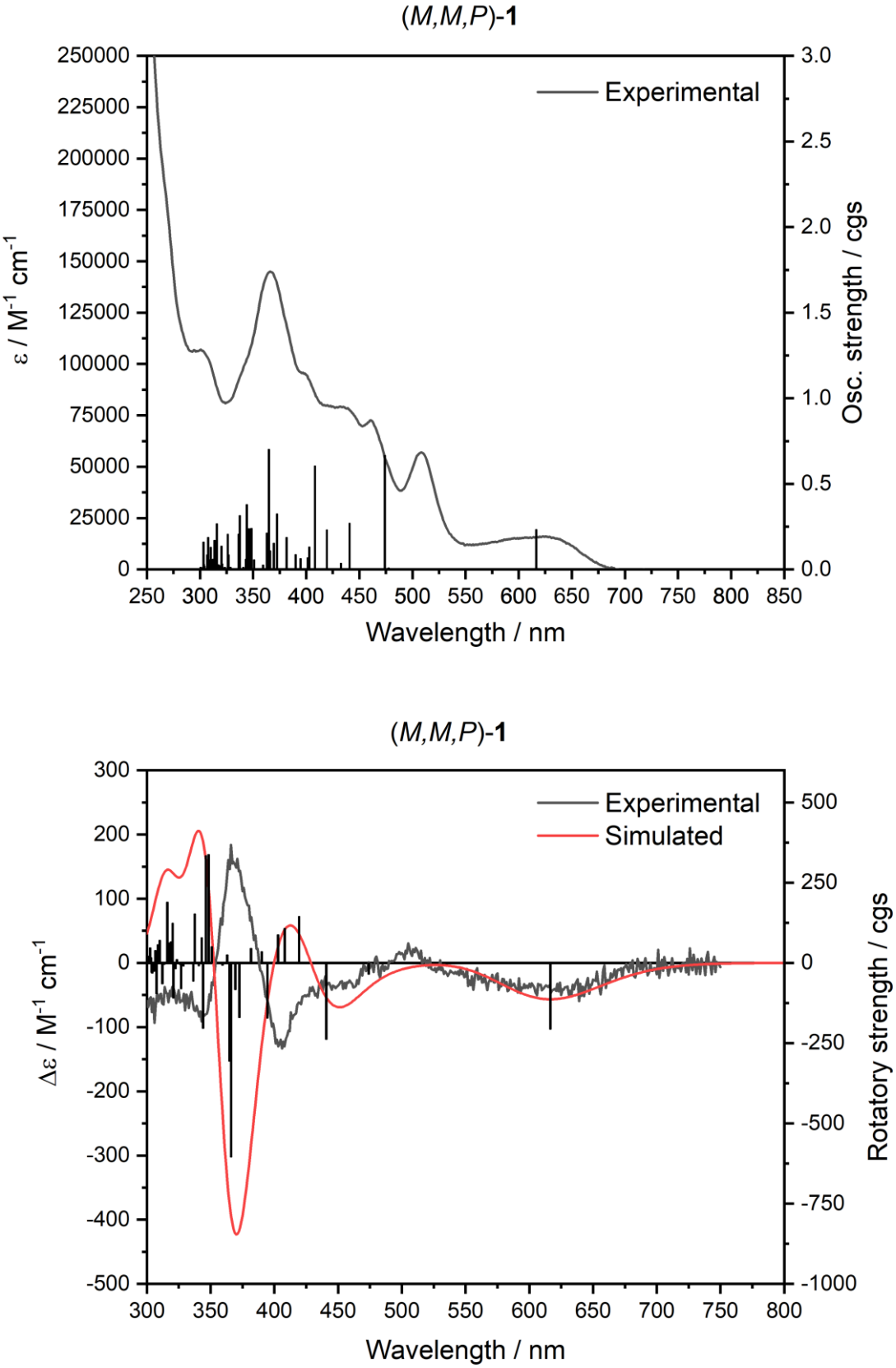


Figure S39. Top: Experimental (gray) and simulated (red) UV-Vis spectra of compound (*M,M,P*)-**1** and calculated oscillatory strength for the first 50 electronic transitions (black bars). Bottom: Experimental (gray) and simulated (red) ECD spectra of compound (*M,M,P*)-**1** and calculated rotatory strength for the first 50 electronic transitions (black bars).

Analysis of the lowest energy transition of (*M,M,M*)-1

Wavelength (nm)	**Orbitals Contributing to the lowest energy transition**	**% Contribution** (gaussian coefficient)	**Oscillator strength (f)**
646.62	H -> L	100% (0.67239)	0.2090

Transition electric dipole moment (esu cm)	**Transition magnetic dipole moment (erg G^{-1})**	**Angle between moments (°)**	**Dipole Strength (esu^2 cm^2)**	**Calculated g_{abs} value**
4.9299×10^{-18}	2.0545×10^{-20}	93.3385	2.4303×10^{-35}	9.7078×10^{-4}

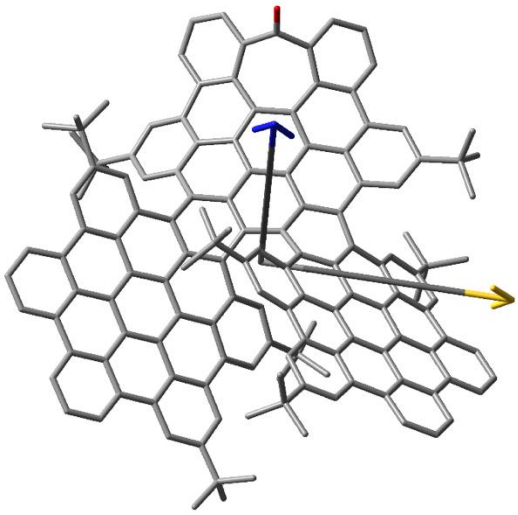


Figure S40. Calculated electric (yellow headed arrow) and magnetic (blue headed arrow) transition dipole moments for the lowest energy transition of (*M,M,P*)-**1**.

Analysis of the lowest energy transition of (*M,M,P*)-1

Wavelength (nm)	**Orbitals Contributing to the lowest energy transition**	**% Contribution** (gaussian coefficient)	**Oscillator strength (f)**
616.55	H -> L	100% (0.66609)	0.2338

Transition electric dipole moment (esu cm)	**Transition magnetic dipole moment (erg G^{-1})**	**Angle between moments (°)**	**Dipole Strength (esu^2 cm^2)**	**Calculated g_{abs} value**
5.0052×10^{-18}	2.2230×10^{-20}	99.3042	2.5052×10^{-35}	2.8723×10^{-3}

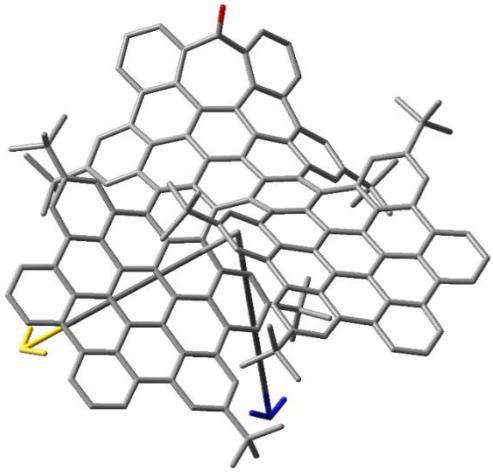


Figure S41. Calculated electric (yellow headed arrow) and magnetic (blue headed arrow) transition dipole moments for the lowest energy transition of (*M,M,P*)-**1**.

Analysis of the lowest energy transition of (*P,M,P*)-1

Wavelength (nm)	**Orbitals Contributing to the lowest energy transition**	**% Contribution to excitation** (gaussian coefficient)	**Oscillator strength (f)**
562.56	H -> L H-1 -> L+1	97% (0.65422) 3% (0.10941)	0.2566

Transition electric dipole moment (esu cm)	**Transition magnetic dipole moment (erg G^{-1})**	**Angle between moments (°)**	**Dipole Strength (esu^2 cm^2)**	**Calculated g_{abs} value**
5.0489×10^{-18}	2.1678×10^{-20}	112.3508	2.5491×10^{-35}	6.5311×10^{-3}

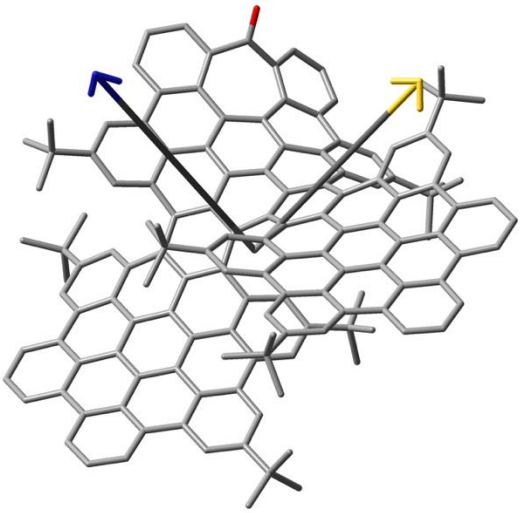


Figure S42. Calculated electric (yellow headed arrow) and magnetic (blue headed arrow) transition dipole moments for the lowest energy transition of (*P,M,P*)-**1**.

Geometries

(*M,M,M*)-**1**

C	3.48310800	1.69499800	-0.25554000
C	3.85800100	0.35800100	-0.05423100
C	5.23211000	0.02284000	-0.02779800
C	6.22974600	0.94106400	-0.44902700
C	5.83841400	2.29321500	-0.73684900
C	4.47943600	2.67250500	-0.50357500
C	7.61354200	0.39571400	-0.46770400
C	8.62725600	0.81034400	-1.35196500
C	8.45565600	1.87414800	-2.35617200
C	7.98608100	3.17455700	-1.83838800
C	6.76151800	3.37023600	-1.16314000
C	8.87113400	4.21146300	-2.10404100
C	8.59909900	5.49330700	-1.65589700
C	7.35335600	5.74075300	-1.12581200
C	6.39422100	4.72679900	-0.98382500
C	7.94796900	-0.70387100	0.36642900
C	9.26303600	-1.18423200	0.41397200
C	10.25004300	-0.69869400	-0.41584400
C	9.90644300	0.26598700	-1.34503300
O	8.89345600	1.76585600	-3.48602500
C	5.57860900	-1.23674200	0.59777100
C	4.05102900	4.05444600	-0.58980500
C	2.07859300	2.04941000	-0.22698800
C	2.84853500	-0.65150300	0.18939600
C	4.99263700	5.08098900	-0.80378000
C	4.56471500	6.38950500	-1.01317600
C	3.21773700	6.73296400	-1.06258000
C	2.30241300	5.72612900	-0.81012900
C	2.68457900	4.41477300	-0.49966500
C	4.59295500	-2.18591600	0.91743000
C	4.89407200	-3.22921200	1.80109000
C	6.15794500	-3.38395100	2.35023600
C	7.15522500	-2.50693500	1.91953100
C	6.89767700	-1.47497600	1.02307100
C	1.47691900	-0.31092300	0.18751000
C	0.56214400	-1.27546200	0.68115500
C	0.91587900	-2.63741300	0.54948400
C	2.26097800	-2.99935400	0.31728300
C	3.23382500	-1.98159700	0.44275400
C	1.67728500	3.39929000	-0.22161500
C	0.30028700	3.67152400	-0.00384900
C	-0.62344000	2.69747000	-0.44136900
C	-0.19016800	1.38049200	-0.70584100
C	1.09902100	1.02442400	-0.24229100
C	-2.02038400	3.04006000	-0.58835800
C	-0.10115100	-3.66044700	0.65625600
C	-2.48881200	4.29718100	-0.15272000
C	-3.85200700	4.63479600	-0.29036200
C	-4.74065300	3.73037500	-0.91179200
C	-4.27197200	2.47041100	-1.34634000
C	-2.91868200	2.11495700	-1.15777300
C	-1.41472200	-3.30822300	1.02638600
C	-2.41590600	-4.29738300	1.11469900
C	-2.11631500	-5.63728600	0.78722200
C	-0.79812200	-5.99453100	0.42456000
C	0.21347200	-5.00832700	0.38159900
C	-1.59025300	5.17883500	0.54738000
C	-4.33234600	5.90291200	0.21009000
C	-6.12481800	4.09562600	-1.10914400
C	-5.17751000	1.53733600	-1.97399500
C	-2.42873200	0.84185000	-1.62468900
C	-1.69280600	-1.95569000	1.43834600
C	1.55442900	-5.35922000	-0.01386600
C	-0.47973100	-7.36870500	0.10903700
C	-3.16109700	-6.63554300	0.81863400

C	-3.74597400	-3.93310300	1.54159000
C	-0.22716800	4.84501000	0.68717800
C	0.55841000	5.56026000	1.60075200
C	0.06356700	6.64294400	2.31183100
C	-1.25202800	7.03590300	2.05720300
C	-2.08317300	6.34030000	1.18461600
C	-3.46147500	6.76176600	0.92505900
C	-3.93383900	8.00072300	1.35659300
C	-5.24359200	8.38181700	1.12397100
C	-6.10743200	7.52968600	0.46101000
C	-5.67686300	6.28588300	-0.00658800
C	-6.58811700	5.36939700	-0.69641000
C	-7.91692700	5.71758500	-0.94277800
C	-8.77985700	4.83737700	-1.56928600
C	-8.33693200	3.58534900	-1.95368800
C	-7.01764100	3.18728200	-1.73004000
C	-6.53998400	1.86356500	-2.13687100
C	-7.40768800	0.91659200	-2.68914800
C	-6.97633900	-0.33658700	-3.09814400
C	-5.62087100	-0.62642800	-2.96190500
C	-4.71078700	0.28085300	-2.42862000
C	-3.28382400	-0.03818900	-2.32613300
C	-2.74127700	-1.16869000	-2.92817700
C	-1.38181300	-1.47268400	-2.86762100
C	-0.57199600	-0.63789000	-2.11250600
C	-1.07361300	0.48889900	-1.44964500
C	-0.69578600	-0.96300300	1.35443400
C	-0.86968300	0.23484700	2.06010200
C	-2.02638300	0.50312500	2.78010300
C	-3.06547100	-0.42423700	2.70078100
C	-2.93159200	-1.63783700	2.03629600
C	-4.02044900	-2.61505400	1.97612700
C	-5.32133500	-2.27260100	2.32823800
C	-6.36762700	-3.19249900	2.30536000
C	-6.07102100	-4.49241800	1.92183800
C	-4.78463400	-4.88580700	1.53864100
C	-4.48903500	-6.26806500	1.15337200
C	-5.48563600	-7.24498700	1.12549400
C	-5.19391200	-8.55380500	0.78801500
C	-3.89617400	-8.91945100	0.48203100
C	-2.86235200	-7.98174900	0.49755100
C	-1.48512900	-8.36297300	0.17708000
C	-1.13801800	-9.69333300	-0.06615200
C	0.16060600	-10.04479700	-0.38439800
C	1.13743400	-9.07106600	-0.48783100
C	0.83993500	-7.72716200	-0.26001000
C	1.86237000	-6.68653700	-0.39355400
C	3.12407300	-6.96821400	-0.90884500
C	4.10097200	-5.98832200	-1.07654200
C	3.79652600	-4.70212000	-0.65982200
C	2.56278300	-4.37195100	-0.08531100
C	6.48712900	-4.46373100	3.38744200
C	6.91083200	-3.78383900	4.70153800
C	7.64116100	-5.34434200	2.87626600
C	5.28675100	-5.37204700	3.67706300
C	2.80543200	8.16140200	-1.43563800
C	3.27869300	8.46585400	-2.86858000
C	1.28620300	8.35971700	-1.37777100
C	3.46021500	9.15898400	-0.46414900
C	0.88689600	7.38109700	3.37470900
C	0.89823100	8.89150000	3.08139600
C	2.33986200	6.89346400	3.42305600
C	0.24721900	7.13955200	4.75404600
C	-2.19013200	1.73454400	3.68012600
C	-2.43167500	1.26709900	5.12748500
C	-0.94548400	2.62737900	3.67500400
C	-3.39410000	2.56883400	3.20993000
C	-0.84227300	-2.68206700	-3.64167600
C	0.66910800	-2.86169700	-3.46078300
C	-1.54286800	-3.96107700	-3.15004200

C	-1.12514200	-2.48994200	-5.14271500
C	5.44481700	-6.35374400	-1.71851900
C	6.40439100	-5.15933300	-1.77684600
C	5.20424800	-6.85186000	-3.15478500
C	6.11787000	-7.46945600	-0.89966400
H	9.78106300	3.98550100	-2.64683300
H	9.32180500	6.29322000	-1.77356400
H	7.09991200	6.75220000	-0.83747100
H	9.49850500	-2.01334800	1.06754900
H	11.25433500	-1.10632500	-0.37894300
H	10.61729000	0.62037000	-2.08177300
H	5.29512100	7.15288000	-1.23977800
H	1.24956300	5.94717400	-0.86595500
H	4.09585700	-3.90359600	2.07592400
H	8.15788300	-2.63198800	2.30706500
H	1.57526400	5.23281600	1.75879800
H	-1.65220300	7.88273600	2.59899800
H	-3.27087600	8.69047400	1.86291800
H	-7.12968400	7.84893600	0.30919200
H	-8.29359100	6.68839100	-0.65015400
H	-9.03371700	2.92152700	-2.44732600
H	-8.45400300	1.16048400	-2.78790400
H	-5.27064000	-1.60402100	-3.26478700
H	-3.38495900	-1.81548700	-3.50903200
H	0.48690800	-0.83730900	-2.05147600
H	-0.05024900	0.93884600	2.07887000
H	-3.98495300	-0.21695700	3.23232500
H	-5.53457400	-1.24925900	2.60877500
H	-6.86533700	-5.22268100	1.91763100
H	-6.50923000	-6.99085600	1.36554300
H	-3.69908100	-9.94915200	0.21605700
H	-1.88116600	-10.47583400	0.00697200
H	2.14725500	-9.37411100	-0.73085400
H	3.34716200	-7.97512400	-1.23480800
H	4.52366300	-3.91752900	-0.79370800
H	6.10415400	-3.15940500	5.09538200
H	7.78871000	-3.14730100	4.56357600
H	7.15842200	-4.53636800	5.45675800
H	8.55326700	-4.76771500	2.70394600
H	7.87618600	-6.12140900	3.60994300
H	7.37358000	-5.83541500	1.93629700
H	4.94399900	-5.89192700	2.77782800
H	4.44343800	-4.81217300	4.09043700
H	5.56975900	-6.13036800	4.41208400
H	4.36431600	8.38286000	-2.96446400
H	2.82689800	7.77329600	-3.58402700
H	2.99463300	9.48354200	-3.15447800
H	0.88340400	8.14818100	-0.38330200
H	0.76570400	7.72248800	-2.09797500
H	1.04237200	9.39693400	-1.62362700
H	3.15189000	8.96466700	0.56699400
H	4.55143000	9.11041300	-0.49942100
H	3.16751500	10.18222100	-0.71877700
H	-0.10611600	9.32155400	3.09262300
H	1.33893400	9.10088900	2.10278600
H	1.48850400	9.41707500	3.83813300
H	2.40680400	5.83986000	3.70752300
H	2.84413300	7.01829700	2.46038400
H	2.89541300	7.46901100	4.16852300
H	0.23164900	6.07270100	4.99451200
H	-0.78228700	7.50530600	4.79043000
H	0.81520500	7.65621900	5.53422400
H	-1.59052800	0.67028200	5.49149700
H	-2.54645200	2.13207300	5.78838700
H	-3.33535500	0.65904000	5.21619100
H	-0.72136200	3.01252700	2.67869600
H	-0.06486600	2.09423700	4.04537100
H	-1.11037800	3.48862900	4.32872700
H	-3.25901500	2.91062200	2.18149400
H	-4.32589600	1.99896500	3.25379700

H	-3.51503800	3.44984700	3.84780300
H	1.22776700	-1.99687100	-3.83024100
H	1.00347000	-3.73571700	-4.02625300
H	0.93849300	-3.02464400	-2.41438600
H	-2.62470800	-3.91710500	-3.29962400
H	-1.16824600	-4.83118800	-3.69800900
H	-1.35874600	-4.12554900	-2.08551200
H	-2.19468600	-2.39921100	-5.34867700
H	-0.74848000	-3.34624400	-5.71083500
H	-0.63458000	-1.58863400	-5.52104500
H	6.62065800	-4.76026500	-0.78162900
H	6.00691300	-4.34664100	-2.39093700
H	7.35251100	-5.47225300	-2.22277100
H	4.55898200	-7.73392300	-3.17740200
H	4.73018600	-6.07586500	-3.76210800
H	6.15379000	-7.12093500	-3.62795000
H	5.50803800	-8.37549400	-0.86185800
H	6.29716800	-7.14585500	0.12977300
H	7.08126400	-7.73688600	-1.34444000
H	0.41376400	-11.08613100	-0.55353400
H	-5.98506800	-9.29588100	0.76468700
H	-9.80726100	5.12980800	-1.75918400
H	-5.59439600	9.35068500	1.46355200
C	-7.78015000	-2.74426100	2.69976400
C	-7.76620800	-2.22622700	4.14902700
H	-8.76737600	-1.89749500	4.44491100
H	-7.44687300	-3.01029500	4.84136300
H	-7.08884600	-1.37755500	4.27064100
C	-8.23881400	-1.61604600	1.75872400
H	-7.57744400	-0.74786100	1.80683700
H	-8.25960300	-1.95898400	0.72030000
H	-9.24585400	-1.28261600	2.02835900
C	-8.80117600	-3.88430900	2.61110600
H	-8.55058200	-4.70888800	3.28467200
H	-9.78907600	-3.51393700	2.89807500
H	-8.88055400	-4.28139000	1.59499400
C	-7.92332800	-1.38988200	-3.68638600
C	-7.45868800	-1.75796300	-5.10692600
H	-8.12490200	-2.50978700	-5.54141400
H	-7.46373900	-0.88056900	-5.75974500
H	-6.44671500	-2.17010000	-5.11060200
C	-9.37029700	-0.89061600	-3.77328000
H	-9.45906000	-0.00955000	-4.41537800
H	-10.00290100	-1.67372900	-4.20001000
H	-9.77484900	-0.64107500	-2.78819700
C	-7.90288200	-2.64833300	-2.80080500
H	-6.90174000	-3.07882800	-2.72470500
H	-8.24306200	-2.41673100	-1.78730900
H	-8.56505300	-3.41514300	-3.21501200

Zero-point correction= 2.108276 (Hartree/Particle)
Thermal correction to Energy= 2.221509
Thermal correction to Enthalpy= 2.222453
Thermal correction to Gibbs Free Energy= 1.961811
Sum of electronic and zero-point Energies= -5736.055601
Sum of electronic and thermal Energies= -5735.942368
Sum of electronic and thermal Enthalpies= -5735.941424
Sum of electronic and thermal Free Energies= -5736.202066

(*M,M,P*)-**1**

C	-3.63999300	1.31831600	-0.04216600
C	-3.84547900	-0.06562000	0.00515000
C	-5.15949400	-0.56211600	0.10421900
C	-6.28726200	0.27396100	-0.08004600
C	-6.07974900	1.68173600	-0.21106500
C	-4.75563500	2.18435100	-0.05999800
C	-7.59720200	-0.40784800	-0.00092700
C	-8.74983800	0.00973500	-0.68987800

C	-8.77644200	1.14434800	-1.64111300
C	-8.33026000	2.46267700	-1.13612000
C	-7.13395600	2.69783900	-0.42455100
C	-9.24271400	3.47784800	-1.40306300
C	-9.02765300	4.76292900	-0.93693100
C	-7.85802500	5.02962300	-0.25916700
C	-6.89882600	4.03687100	-0.02245900
C	-7.70519000	-1.61881200	0.73356000
C	-8.95407000	-2.22875500	0.89681800
C	-10.08725800	-1.74358500	0.27659400
C	-9.96596500	-0.65339100	-0.56743800
C	-4.51293100	3.57210000	0.26893400
C	-5.28617200	-1.92003900	0.58270200
C	-2.72749600	-0.98020300	-0.10370900
C	-2.29095000	1.83341000	0.04210600
C	-5.60116500	4.42998100	0.51755500
C	-5.39653200	5.63345300	1.18159200
C	-4.12372700	6.05669400	1.56889000
C	-3.04830800	5.26513400	1.19511200
C	-3.20920500	4.05085700	0.51466500
C	-4.16933800	-2.77140900	0.65218400
C	-4.22185400	-3.88361900	1.49856500
C	-5.36597400	-4.20989100	2.21768000
C	-6.51352300	-3.44687100	1.99035900
C	-6.50126100	-2.33388900	1.15624800
C	-1.44291900	-0.45874700	-0.34999100
C	-0.45254400	-1.31016900	-0.88388500
C	-0.65785000	-2.70708500	-0.83427000
C	-1.92416900	-3.24813700	-0.49108500
C	-2.93738200	-2.37423500	-0.04296400
C	-2.05989900	3.21446100	0.18397600
C	-0.72274400	3.67838900	0.08583500
C	0.30512400	2.77448900	0.43362400
C	0.02059600	1.39645700	0.57601100
C	-1.20604700	0.92645300	0.05893800
C	1.66014800	3.24804600	0.61934600
C	0.47717200	-3.59061400	-1.01421400
C	1.98713600	4.59011500	0.33136600
C	3.31774800	5.04405600	0.47627400
C	4.31638700	4.16235800	0.94565800
C	3.98363900	2.82506300	1.25632100
C	2.66238400	2.36511100	1.07437500
C	1.75652700	-3.06014400	-1.26997900
C	2.88493200	-3.90262900	-1.30302300
C	2.74129900	-5.28293600	-1.05785800
C	1.45291000	-5.82954000	-0.88216500
C	0.32705100	-4.98182100	-0.85464100
C	0.97807800	5.46331000	-0.21333300
C	3.65099500	6.41263500	0.15073500
C	5.67793000	4.62203200	1.10258400
C	4.99475400	1.92338400	1.75790400
C	2.30697500	1.01887800	1.44992000
C	1.88464300	-1.66912800	-1.61188800
C	4.18294300	-3.35054800	-1.60327100
C	3.90833800	-6.12765700	-0.97979900
C	1.28279600	-7.25592100	-0.74440000
C	-0.99816700	-5.53665100	-0.77743300
C	3.25317600	0.17782800	2.07669000
C	2.82441000	-1.01980000	2.63965800
C	1.49180700	-1.42763100	2.60675400
C	0.59737600	-0.63489000	1.90238900
C	0.98759000	0.55578400	1.27763800
C	0.76474700	-0.82111100	-1.53829500
C	0.81145300	0.41561000	-2.19120000
C	1.96071300	0.86695100	-2.82926200
C	3.10849100	0.07924500	-2.73108800
C	3.10208700	-1.17257200	-2.12523800
C	6.33554800	2.34429000	1.87443800
C	7.30010000	1.43626800	2.32359400
C	6.98743200	0.12918200	2.66890500

C	5.65360700	-0.25902400	2.57205300
C	4.65219100	0.60544100	2.14251300
C	6.00924900	5.96801000	0.81126200
C	7.33421100	6.38462100	0.94940200
C	7.99536000	4.19564300	1.66578700
C	6.68616000	3.72753500	1.54205400
C	2.66031600	7.28274000	-0.36620600
C	2.98336700	8.62030100	-0.59353700
C	5.24453200	8.23544600	0.10165100
C	4.96744800	6.88987300	0.35373500
C	-0.34418400	5.00411700	-0.39810200
C	-1.23166700	5.77693400	-1.15811300
C	-0.88907600	7.02438200	-1.65611400
C	0.38422200	7.51005200	-1.35813400
C	1.32009000	6.76481300	-0.64786400
C	-1.18344500	-6.93410300	-0.86590200
C	-2.46472800	-7.42724700	-1.09503400
C	-3.57154800	-6.58827800	-1.22556900
C	-3.38037600	-5.22829300	-1.01313700
C	-2.12230200	-4.68646800	-0.72909700
C	2.41732000	-8.09552900	-0.64445600
C	2.22366400	-9.47233300	-0.51390300
C	-0.16013700	-9.19330700	-0.58221800
C	-0.01884200	-7.81428600	-0.73443100
C	5.20074700	-5.56530900	-1.13144100
C	6.31403600	-6.38307900	-0.93108500
C	4.90602600	-8.28303200	-0.51565900
C	3.76016700	-7.50917400	-0.70487500
C	4.30509400	-2.00357000	-2.01908000
C	5.56844500	-1.49517400	-2.29989800
C	6.72382400	-2.26895800	-2.20656800
C	6.58156400	-3.59480200	-1.81848200
C	5.33696200	-4.15554900	-1.51316500
C	-5.39589400	-5.34522800	3.24826600
C	-6.57088100	-6.29706200	2.96339700
C	-5.57473200	-4.73158500	4.64898500
C	-4.10193900	-6.16820400	3.24033600
C	-3.96173000	7.34332500	2.38673300
C	-2.48895800	7.70529900	2.61063800
C	-4.63077200	7.14885000	3.75939500
C	-4.63765200	8.51773900	1.65730400
C	-1.83575200	7.85646700	-2.52958900
C	-2.03505100	9.24723300	-1.90181600
C	-3.21274400	7.19968200	-2.68126800
C	-1.21757300	8.01695800	-3.93015800
C	-4.93051100	-7.17948300	-1.62232200
C	-6.05009700	-6.13192700	-1.59775900
C	-5.31451300	-8.31418700	-0.65681700
C	-4.82714600	-7.74638000	-3.05003200
C	1.07165900	-2.69913000	3.35503700
C	-0.42532600	-2.99484000	3.20745000
C	1.85714200	-3.90443900	2.80892500
C	1.37971400	-2.52649600	4.85368200
C	2.00520700	2.16097200	-3.65207400
C	2.31628400	1.80594800	-5.11795700
C	0.67387000	2.91939800	-3.61723000
C	3.10543500	3.09051500	-3.11141300
H	-10.12076300	3.23081700	-1.98728300
H	-9.74457800	5.55243200	-1.13420700
H	-7.64650400	6.04815400	0.03985300
H	-9.02388200	-3.14638200	1.46697700
H	-11.04025000	-2.24655600	0.39945100
H	-10.80582700	-0.29940000	-1.15324300
H	-6.25347600	6.24265200	1.43974100
H	-2.04509800	5.56842500	1.45390200
H	-3.32841000	-4.48022700	1.60893200
H	-7.42937900	-3.71258500	2.50284100
H	3.53758800	-1.63634000	3.17022900
H	-0.44257300	-0.91941700	1.85666700
H	-0.08767600	1.01346300	-2.22352600

H	4.02029500	0.43469800	-3.19320300
H	8.32614300	1.75977300	2.40452800
H	5.39330800	-1.27800000	2.82472700
H	7.61621300	7.40276800	0.71780800
H	8.78476600	3.53538800	1.99836300
H	2.22703100	9.31239100	-0.94039700
H	6.23600000	8.63242600	0.27276900
H	-2.20641700	5.36740600	-1.37244700
H	0.66763900	8.48114800	-1.74159200
H	-2.59989300	-8.49180000	-1.23637200
H	-4.22117000	-4.55676200	-1.08780900
H	3.07206200	-10.14116000	-0.45190000
H	-1.14636700	-9.63712700	-0.53024000
H	7.31337300	-5.97478000	-1.00658700
H	4.82361800	-9.33437200	-0.27291100
H	5.66132400	-0.45569700	-2.58560900
H	7.46210000	-4.21720800	-1.76514800
H	-6.49548700	-6.73053500	1.96261500
H	-7.53779200	-5.79353000	3.03669700
H	-6.57449900	-7.11645300	3.68852300
H	-4.74789800	-4.05706800	4.88810300
H	-5.60390000	-5.51814800	5.40974200
H	-6.50354000	-4.15940400	4.72064600
H	-3.23369800	-5.56357400	3.51674000
H	-3.90770100	-6.61386400	2.26038100
H	-4.17973800	-6.98034800	3.96826000
H	-1.95693300	7.84748000	1.66549600
H	-1.96367500	6.93766700	3.18529500
H	-2.42286900	8.63943600	3.17510300
H	-5.69567100	6.92230500	3.66083500
H	-4.16383800	6.32612400	4.30788000
H	-4.53506500	8.05751400	4.36203400
H	-5.70942000	8.35516000	1.51977000
H	-4.19445600	8.67578300	0.67008300
H	-4.51701000	9.43942400	2.23456400
H	-1.09554700	9.79866700	-1.81597500
H	-2.46680900	9.16801000	-0.90007100
H	-2.71332400	9.84588300	-2.51744100
H	-3.14867800	6.23008900	-3.18264000
H	-3.70250300	7.05150200	-1.71447400
H	-3.85924200	7.83938300	-3.28831200
H	-1.06776300	7.04277900	-4.40391200
H	-0.24831200	8.52085400	-3.89005800
H	-1.87691300	8.60975500	-4.57194800
H	-5.87457900	-5.33016100	-2.32014000
H	-6.16543300	-5.67962100	-0.60853200
H	-6.99991200	-6.60520100	-1.86166200
H	-6.29092500	-8.72619900	-0.92920500
H	-4.59487300	-9.13609000	-0.67912000
H	-5.37457000	-7.95201700	0.37308900
H	-4.06704400	-8.52905600	-3.11866700
H	-4.56261500	-6.96096900	-3.76333500
H	-5.78412700	-8.17868900	-3.35900700
H	-1.04234400	-2.18829500	3.61380300
H	-0.67155600	-3.90750100	3.75808600
H	-0.70781000	-3.15055400	2.16326500
H	2.93604700	-3.77631900	2.92732600
H	1.57171900	-4.81489600	3.34513800
H	1.65353400	-4.05829800	1.74639400
H	2.44407200	-2.35589500	5.03393100
H	0.83051200	-1.67761800	5.27077400
H	1.08846500	-3.42538500	5.40615400
H	1.54464600	1.15239400	-5.53467000
H	2.35865200	2.71439000	-5.72711700
H	3.27639900	1.29299400	-5.21651100
H	0.39794700	3.21345700	-2.60188000
H	-0.14254200	2.32601400	-4.03893300
H	0.75775300	3.83302400	-4.21231100
H	2.91922700	3.35584600	-2.06843400
H	4.09515000	2.63059400	-3.16865800

H	3.13794900	4.01475100	-3.69651600
C	8.08065100	-1.64840500	-2.56332200
C	8.30174100	-0.36007200	-1.75072200
C	9.24937300	-2.59852700	-2.27685100
C	8.09264900	-1.30616900	-4.06435000
H	7.54499300	0.39779200	-1.96480900
H	8.27263200	-0.55805900	-0.67582100
H	9.27739200	0.07304800	-1.99196500
H	9.19281900	-3.50949100	-2.87929400
H	10.19288800	-2.10357500	-2.52241700
H	9.28966700	-2.88599900	-1.22197800
H	9.04904600	-0.85403300	-4.34576300
H	7.94828100	-2.20432700	-4.67141400
H	7.29954300	-0.59922100	-4.32096000
C	8.03470800	-0.87279300	3.17143800
C	8.01885200	-2.13435200	2.29022700
C	9.45388500	-0.29351700	3.14823400
C	7.69810700	-1.26487400	4.62181200
H	7.04463400	-2.62810200	2.29419700
H	8.26164400	-1.89240900	1.25185000
H	8.75749500	-2.85619800	2.65256500
H	9.55026000	0.57663700	3.80380100
H	10.16380900	-1.04754000	3.49886800
H	9.75553100	0.00107300	2.13878500
H	8.43344300	-1.98009400	5.00367500
H	7.70391400	-0.38818800	5.27552400
H	6.71156400	-1.72927300	4.69586100
C	0.95046300	-10.01279900	-0.47268300
H	0.82247600	-11.08401600	-0.35746000
C	6.16731300	-7.72245400	-0.61542000
H	7.04581500	-8.33760500	-0.45092100
C	8.31636500	5.50768900	1.37055800
C	4.26094300	9.09386100	-0.35336700
H	4.49216300	10.14004200	-0.52400000
H	9.34123000	5.84966300	1.46971900
O	-9.34947900	1.04053000	-2.71040000

Zero-point correction= 2.108405 (Hartree/Particle)
Thermal correction to Energy= 2.221477
Thermal correction to Enthalpy= 2.222421
Thermal correction to Gibbs Free Energy= 1.963624
Sum of electronic and zero-point Energies= -5736.060894
Sum of electronic and thermal Energies= -5735.947822
Sum of electronic and thermal Enthalpies= -5735.946878
Sum of electronic and thermal Free Energies= -5736.205675

(*P,M,P*)-**1**

C	3.24715500	1.83886900	0.06341600
C	3.70045300	0.57586400	-0.30093800
C	5.06385200	0.39584600	-0.63110100
C	5.98942500	1.48176000	-0.61507200
C	5.55812700	2.70216600	0.03584500
C	4.18532200	2.84996100	0.33570100
C	7.30814300	1.23100900	-1.24902800
C	8.27729500	2.22611600	-1.54415500
C	8.18687200	3.66737900	-1.22979200
C	7.70580200	4.09440300	0.09713700
C	6.42359200	3.77491000	0.57440100
C	8.55665200	4.96962600	0.76072000
C	8.16513200	5.54881600	1.95505000
C	6.85751500	5.38361100	2.36177000
C	5.95441700	4.58386800	1.65100900
C	7.62753100	-0.07185700	-1.73260100
C	8.90066500	-0.34996800	-2.25238900
C	9.83805600	0.63088400	-2.46505700
C	9.49003600	1.93274100	-2.15932900
C	3.66110200	3.97489100	1.07723200
C	5.41926200	-0.93077600	-1.08448200

C	2.77049300	-0.53102300	-0.18038000
C	1.82727500	2.11171900	0.07540800
O	8.67437600	4.49766200	-1.97766800
C	4.52043300	4.71121300	1.90018900
C	3.97625300	5.59547100	2.83779100
C	2.60581100	5.79255100	2.95027400
C	1.77673100	5.13562700	2.03907200
C	2.27553800	4.24563700	1.09289500
C	4.51788700	-2.01381800	-0.95993200
C	4.76012200	-3.18678200	-1.67620500
C	5.90930700	-3.36787800	-2.43522400
C	6.85788700	-2.35186700	-2.40694200
C	6.64542400	-1.14958700	-1.72848400
C	1.41082200	-0.27676900	0.10192000
C	0.62568400	-1.30596700	0.66541200
C	1.14069500	-2.62527100	0.68120400
C	2.49036900	-2.88786800	0.33631500
C	3.26632300	-1.84562500	-0.21244300
C	1.38035700	3.43317200	0.25243800
C	0.10158900	3.78827600	-0.21369800
C	-0.77732500	2.76026600	-0.65252200
C	-0.34484500	1.41403500	-0.73535700
C	0.92519900	1.07640900	-0.21813600
C	-2.17058800	3.07472300	-0.90637800
C	0.24852000	-3.73557700	0.95499100
C	-2.64792500	4.38982900	-0.72694300
C	-4.02381500	4.67567700	-0.85158800
C	-4.93255000	3.64137400	-1.15542500
C	-4.45034300	2.34044200	-1.41162100
C	-3.07585800	2.05647300	-1.27351800
C	-1.11534800	-3.50291500	1.21813500
C	-2.00873100	-4.58454900	1.35551200
C	-1.54438000	-5.90763000	1.20885800
C	-0.16707700	-6.14651700	1.02688800
C	0.72234300	-5.06154700	0.89607200
C	-1.70613900	5.45981500	-0.52488100
C	-4.49737100	6.03004000	-0.68147400
C	-6.35134400	3.90957700	-1.19314900
C	-5.35777300	1.30559300	-1.84555800
C	-2.57375000	0.74895300	-1.60446400
C	-1.56137100	-2.15827300	1.47221600
C	-3.39261300	-4.33662100	1.67538200
C	-2.47512800	-7.00968800	1.24096500
C	0.33660200	-7.49917000	0.99405700
C	2.14002400	-5.29500000	0.82918100
C	-3.42467400	-0.21513000	-2.19246300
C	-2.86053500	-1.37118300	-2.72405100
C	-1.48762800	-1.60931000	-2.70581000
C	-0.68401200	-0.69218200	-2.04188600
C	-1.20572900	0.45548500	-1.43572000
C	-0.66840400	-1.07836700	1.32548000
C	-0.99396800	0.14288000	1.92745500
C	-2.21226500	0.35349800	2.56211900
C	-3.14822100	-0.67949600	2.52703200
C	-2.85399000	-1.92988800	1.99419800
C	-6.74675200	1.55986800	-1.91315000
C	-7.59323800	0.56904400	-2.40353100
C	-7.12934100	-0.68292300	-2.79948400
C	-5.76551700	-0.92391200	-2.69957400
C	-4.86585500	0.04576300	-2.24999200
C	-6.83572300	5.20327200	-0.88320300
C	-8.21467400	5.40508300	-0.80233800
C	-9.10061200	4.36996300	-1.04121300
C	-8.62967100	3.11779800	-1.39533500
C	-7.26073600	2.86728600	-1.49492400
C	-3.57126200	7.09124800	-0.53889300
C	-4.04942100	8.38733400	-0.34808400
C	-5.40898300	8.64674200	-0.33003200
C	-6.31629900	7.61709600	-0.50402400
C	-5.88614000	6.29978700	-0.67741500

C	-0.33254600	5.17979600	-0.38790700
C	0.58473700	6.22587100	-0.53739700
C	0.18446600	7.54407900	-0.71817500
C	-1.18346400	7.81306400	-0.68484100
C	-2.13616900	6.80399200	-0.57694900
C	2.65438600	-6.59549100	1.02646600
C	4.01635400	-6.74839200	1.26796700
C	4.89138000	-5.66171600	1.30391000
C	4.37992200	-4.41012700	0.98371300
C	3.02748600	-4.21139900	0.68509100
C	-0.56555100	-8.58888100	0.99138700
C	-0.05125100	-9.88683400	0.95746700
C	1.31342600	-10.11267200	0.91971700
C	2.19785300	-9.04756700	0.93777200
C	1.73305100	-7.73388800	0.99087200
C	-3.85929000	-6.76130200	1.41155400
C	-4.75046400	-7.83056500	1.30756600
C	-4.29585900	-9.11627800	1.07255600
C	-2.93958500	-9.36833500	0.96218500
C	-2.00777900	-8.33369100	1.05561400
C	-3.82555500	-3.02844800	1.99613300
C	-5.16524700	-2.81895400	2.30712100
C	-6.09336000	-3.85796600	2.35503000
C	-5.64422500	-5.13775900	2.05999500
C	-4.31669800	-5.40096300	1.70980400
C	6.13250500	-4.60251200	-3.31742500
C	7.51134100	-5.22187200	-3.03043100
C	6.07341600	-4.17006100	-4.79390300
C	5.06651300	-5.68000000	-3.08418600
C	1.98428800	6.69246500	4.02614100
C	1.24055500	7.85954700	3.35521200
C	0.99111200	5.86753300	4.86450400
C	3.03545900	7.27780300	4.97616000
C	-8.11595800	-1.71813600	-3.35443300
C	-7.44659700	-3.06820300	-3.63673200
C	-8.70716300	-1.18700800	-4.67304300
C	-9.25467400	-1.95297800	-2.34703800
C	1.18082600	8.67470500	-1.00631400
C	0.90704400	9.88340000	-0.09487100
C	2.63422200	8.23469500	-0.79044400
C	1.01451600	9.10661800	-2.47504000
C	-7.55043200	-3.55607600	2.72688500
C	-8.41380600	-4.82171400	2.78280200
C	-8.15401100	-2.60904000	1.67517900
C	-7.60131100	-2.88386600	4.11049800
C	6.35161100	-5.87401500	1.72351200
C	7.19726700	-4.60763800	1.54210200
C	6.98793600	-6.99790800	0.88737100
C	6.38444500	-6.27331300	3.21009600
C	-0.92472400	-2.84611200	-3.41825500
C	0.60224800	-2.93549500	-3.31310700
C	-1.52609700	-4.11815600	-2.79445700
C	-1.29794500	-2.78453200	-4.91054500
C	-2.55148200	1.64826100	3.31278000
C	-2.82617900	1.31226700	4.79029100
C	-1.40954700	2.66966300	3.26486700
C	-3.80451900	2.29528500	2.69716300
H	9.52003000	5.18958300	0.31667600
H	8.84265500	6.18217300	2.51707500
H	6.51358600	5.92641600	3.23233000
H	9.15733600	-1.37112900	-2.49641000
H	10.81111800	0.39278000	-2.88015000
H	10.16001200	2.75663000	-2.36840200
H	4.63551800	6.13920800	3.49724300
H	0.70646300	5.29278600	2.08132100
H	4.00981700	-3.96186500	-1.64812800
H	7.75754100	-2.47999900	-2.99105000
H	-3.49968400	-2.09181000	-3.21633500
H	0.38243900	-0.84910600	-2.01353700
H	-0.25561400	0.92965700	1.92798700

H	-4.11329800	-0.51887200	2.98957600
H	-8.64933300	0.78162200	-2.50222500
H	-5.38675700	-1.89579000	-2.97768400
H	-8.61129600	6.37552800	-0.53462600
H	-9.34428800	2.32518700	-1.57483200
H	-3.35730300	9.20525200	-0.19273800
H	-7.37208300	7.85360400	-0.51222500
H	1.63657100	5.98729400	-0.53982400
H	-1.51622100	8.83539800	-0.80709400
H	4.40063300	-7.73443900	1.49471800
H	5.03545600	-3.55302400	0.97840600
H	-0.71708600	-10.73975400	0.97091400
H	3.26114300	-9.24686900	0.89147400
H	-5.81640300	-7.66400000	1.39222600
H	-2.61342900	-10.38502600	0.78631200
H	-5.50435100	-1.81154800	2.51099300
H	-6.34085400	-5.96019700	2.11968400
H	7.60163600	-5.51855900	-1.98209600
H	8.32895000	-4.53201100	-3.25303200
H	7.65854600	-6.11221400	-3.64907400
H	5.09931800	-3.73543400	-5.03473300
H	6.23409600	-5.03107200	-5.45051400
H	6.83799800	-3.42354300	-5.02478900
H	4.06713900	-5.32952200	-3.35630700
H	5.03926300	-6.00881400	-2.04128300
H	5.28559800	-6.55277400	-3.70543100
H	0.75324200	8.48513900	4.10965600
H	0.47219800	7.51132600	2.66058600
H	1.93842800	8.48842500	2.79466500
H	1.49437600	5.02857000	5.35330900
H	0.54135500	6.49379700	5.64117000
H	0.18078300	5.46160600	4.25457400
H	3.59139700	6.49444600	5.49933800
H	2.54198500	7.89420100	5.73242100
H	3.75105800	7.91628400	4.45019500
H	-7.00325800	-3.49837300	-2.73399600
H	-6.66520000	-2.98504500	-4.39725700
H	-8.19188400	-3.77589300	-4.00991900
H	-9.23601700	-0.24175800	-4.52664200
H	-7.92068900	-1.01738200	-5.41366000
H	-9.41824300	-1.90754700	-5.08955500
H	-9.81621200	-1.03864400	-2.14151000
H	-8.86528000	-2.32569300	-1.39597600
H	-9.96025100	-2.69185000	-2.73944600
H	0.99199400	9.61139500	0.96005700
H	-0.08847500	10.30483400	-0.25347200
H	1.63159400	10.67697800	-0.30063500
H	2.80419200	7.87554900	0.22868100
H	2.92924700	7.44279400	-1.48385800
H	3.30323700	9.08200100	-0.96380400
H	1.21436200	8.27173900	-3.15232900
H	0.00038300	9.46305600	-2.67471700
H	1.71116200	9.91568900	-2.71668800
H	-8.04760600	-5.53098500	3.53060400
H	-8.45393300	-5.33097600	1.81567400
H	-9.43820500	-4.55420200	3.05569900
H	-7.60160600	-1.66886300	1.60567200
H	-8.14200600	-3.07500700	0.68590200
H	-9.19210200	-2.37030800	1.92708500
H	-7.04582400	-1.94331800	4.12826300
H	-7.17676100	-3.53718100	4.87791400
H	-8.63694000	-2.66228400	4.38668200
H	6.84870100	-3.79013400	2.17892900
H	7.19158500	-4.25790900	0.50561700
H	8.23412400	-4.81664400	1.81960900
H	8.03659900	-7.12922500	1.17070000
H	6.48792900	-7.95792200	1.03592200
H	6.95167000	-6.76513900	-0.18023400
H	5.82239400	-7.19341200	3.39087000
H	5.94898600	-5.48819400	3.83436800

H	7.41547200	-6.43774800	3.53923400
H	1.09347700	-2.07013900	-3.76719900
H	0.95142900	-3.82734200	-3.84135900
H	0.93542600	-3.01440200	-2.27513800
H	-2.61554400	-4.13801400	-2.88025000
H	-1.13788900	-5.00712600	-3.30140000
H	-1.27347800	-4.19354800	-1.73376200
H	-2.38034000	-2.76630900	-5.05992100
H	-0.88102000	-1.88987100	-5.38161600
H	-0.90466700	-3.66056800	-5.43577800
H	-1.94980800	0.85299200	5.25640700
H	-3.06984700	2.22292200	5.34651300
H	-3.66448000	0.62018500	4.90240900
H	-1.17911200	2.97626600	2.24175500
H	-0.49502500	2.28063600	3.72180100
H	-1.70092000	3.56499200	3.82190800
H	-3.63947000	2.55437700	1.64870000
H	-4.67162500	1.63170000	2.74523300
H	-4.05994100	3.21183300	3.23806500
H	-10.16845900	4.54165800	-0.95527000
H	-5.76452600	9.66114300	-0.18273400
H	-5.00571300	-9.93165000	0.98049900
H	1.69143800	-11.12888900	0.88030600

Zero-point correction= 2.108694 (Hartree/Particle)
Thermal correction to Energy= 2.221774
Thermal correction to Enthalpy= 2.222718
Thermal correction to Gibbs Free Energy= 1.963162
Sum of electronic and zero-point Energies= -5736.044078
Sum of electronic and thermal Energies= -5735.930998
Sum of electronic and thermal Enthalpies= -5735.930054
Sum of electronic and thermal Free Energies= -5736.189610

Thin Films

Preliminary studies using the racemic superhelicene (*M*,*M*,*P*/*P*,*P*,*M*)-**1** were conducted to obtain thin films on quartz plates as substrate by three different deposition techniques: home-made Langmuir-Blodgett-type, spin-coating and drop casting. Posterior optical and morphological examination of the deposited samples via optical (OM) and tapping-mode atomic force microscopy (AFM) was carried out to analyze the suitability of the conditions and deposition technique employed through the morphology inspection. Solutions of (*M*,*M*,*P*/*P*,*P*,*M*)-**1** in $CHCl_3$/toluene mixtures ranging from 0 to 100% toluene were tested. While fast evaporation of mixtures containing $CHCl_3$ led to amorphous material deposits using Langmuir-Blodgett and spin-coating, toluene-containing samples were not suitable for spin-coating deposition, due to the lack of solution/substrate interactions. Solutions ranging from 1 to 0.2 mg mL−1 were too concentrated yielding amorphous materials. The best results in terms of thin film formation via drop casting were obtained for 0.1 mg mL^{-1} solutions in pure toluene (Figure S43). For samples grown under these conditions, AFM revealed wide homogeneous areas of ca. 100×100 µm constituted by stacked flakes (ca. 5 µm) where height profiles of ca. 1.6 to 2.4 nm (coincident with superhelicene dimensions) hint at the presence of stacked monolayers (Figures S44-S46).

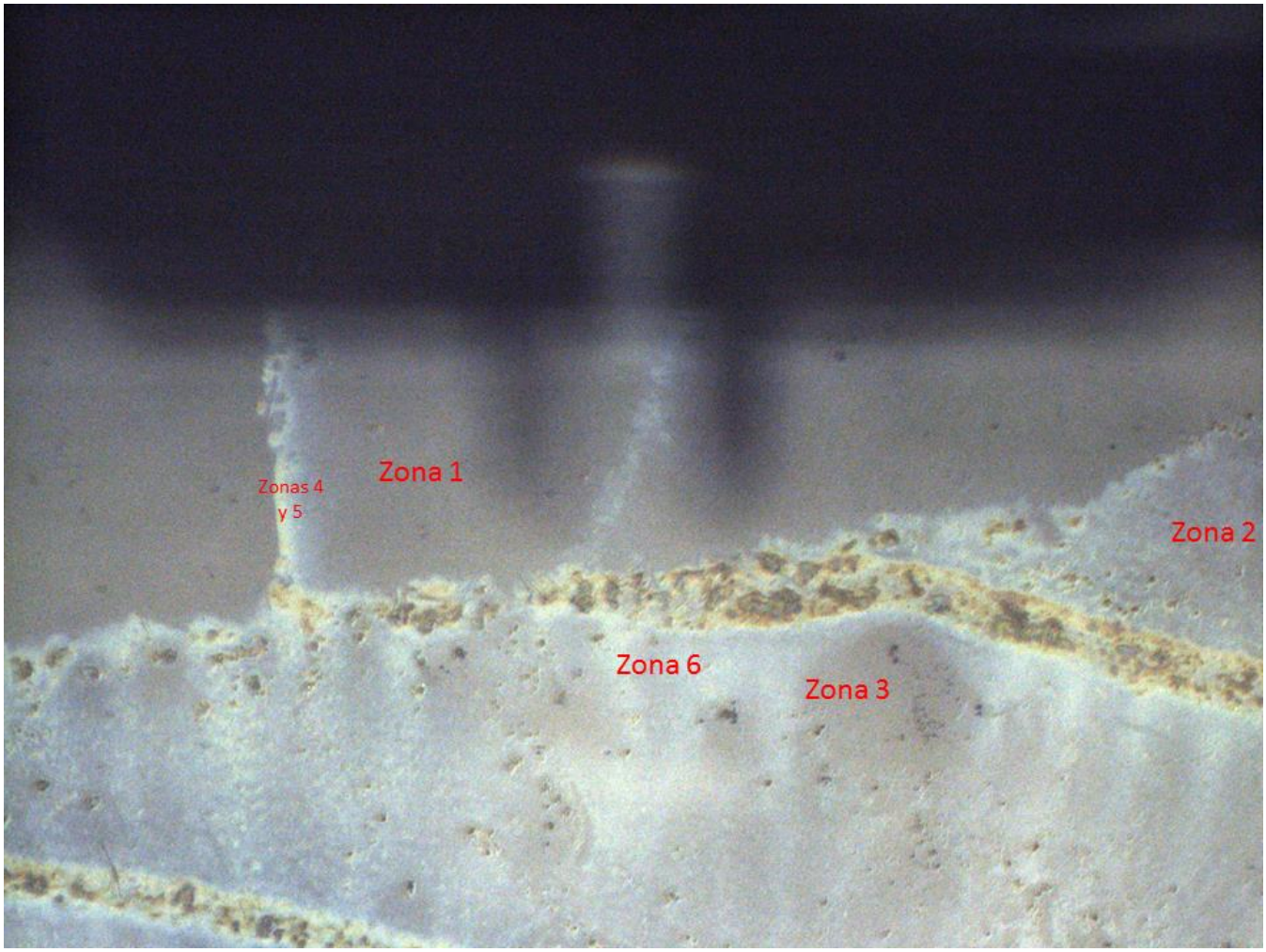


Figure S43. Optical Microscopy (coupled to AFM) of several zones to be explored by tapping-mode AFM of racemic (*P*,*P*,*M*)/(*M*,*M*,*P*)-**1** thin films deposited on a quartz plate via drop casting (dark zones are sample-concentrated and brighter zones correspond to the ones bearing less amount of compound or lower thickness). *c* = 0.1 mg mL^{-1}, solvent = toluene. Window size 842 x 631 μm^2.

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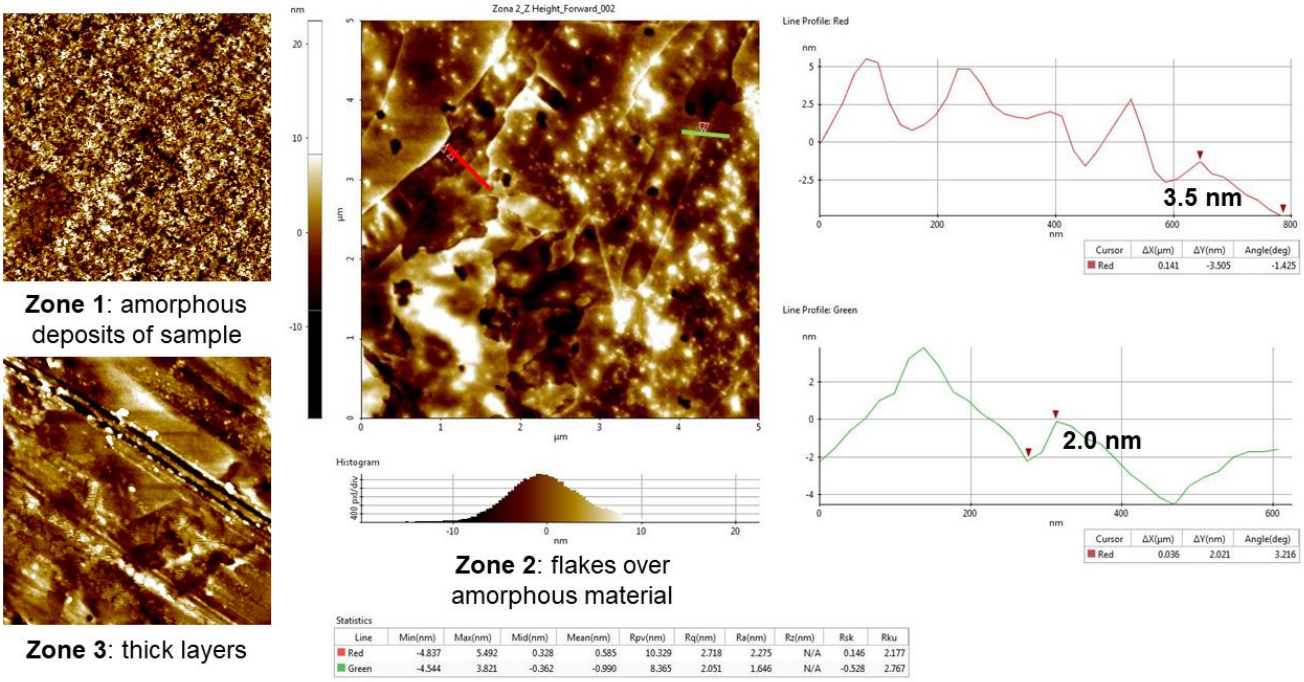


Figure S44. Tapping-mode AFM of racemic (*P*,*P*,*M*)/(*M*,*M*,*P*)-**1** thin films from zones 1 to 3 with corresponding height. c = 0.1 mg mL^{-1}, solvent = toluene, substrate = quartz plate.

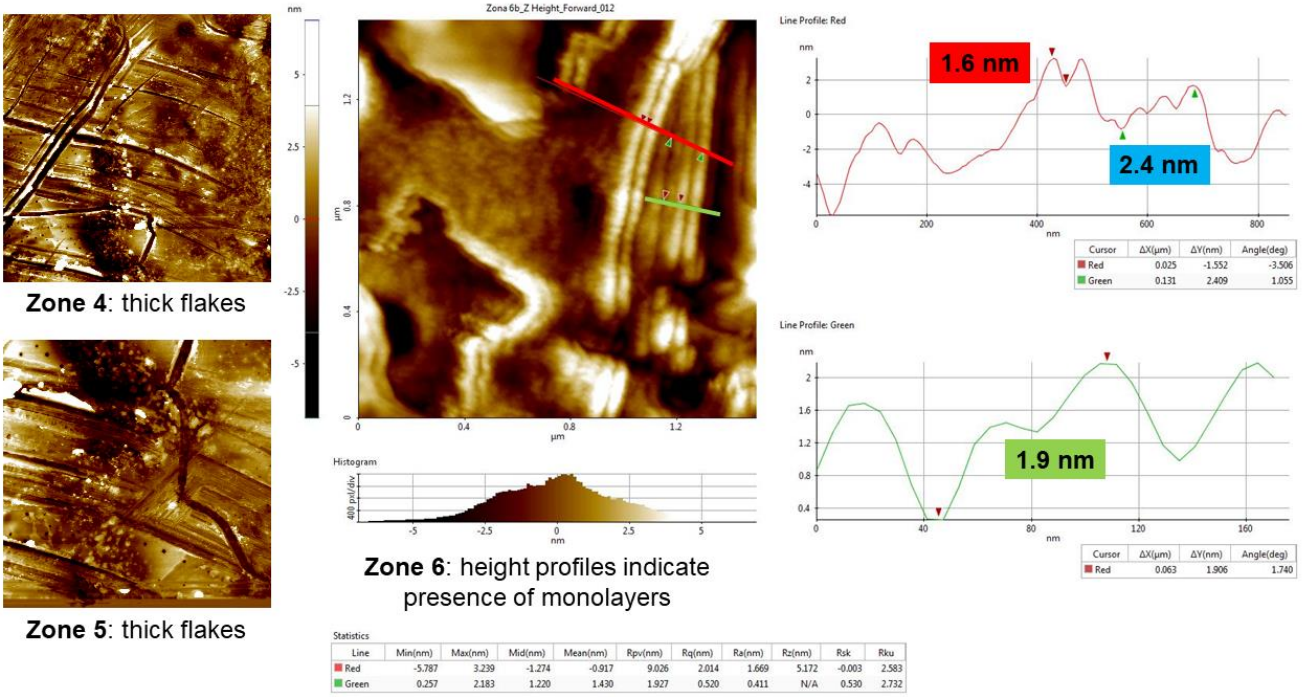


Figure S45. Tapping-mode AFM of racemic (*P*,*P*,*M*)/(*M*,*M*,*P*)-**1** thin films from zones 4 to 6 with corresponding height. c = 0.1 mg mL^{-1}, solvent = toluene, substrate = quartz plate.

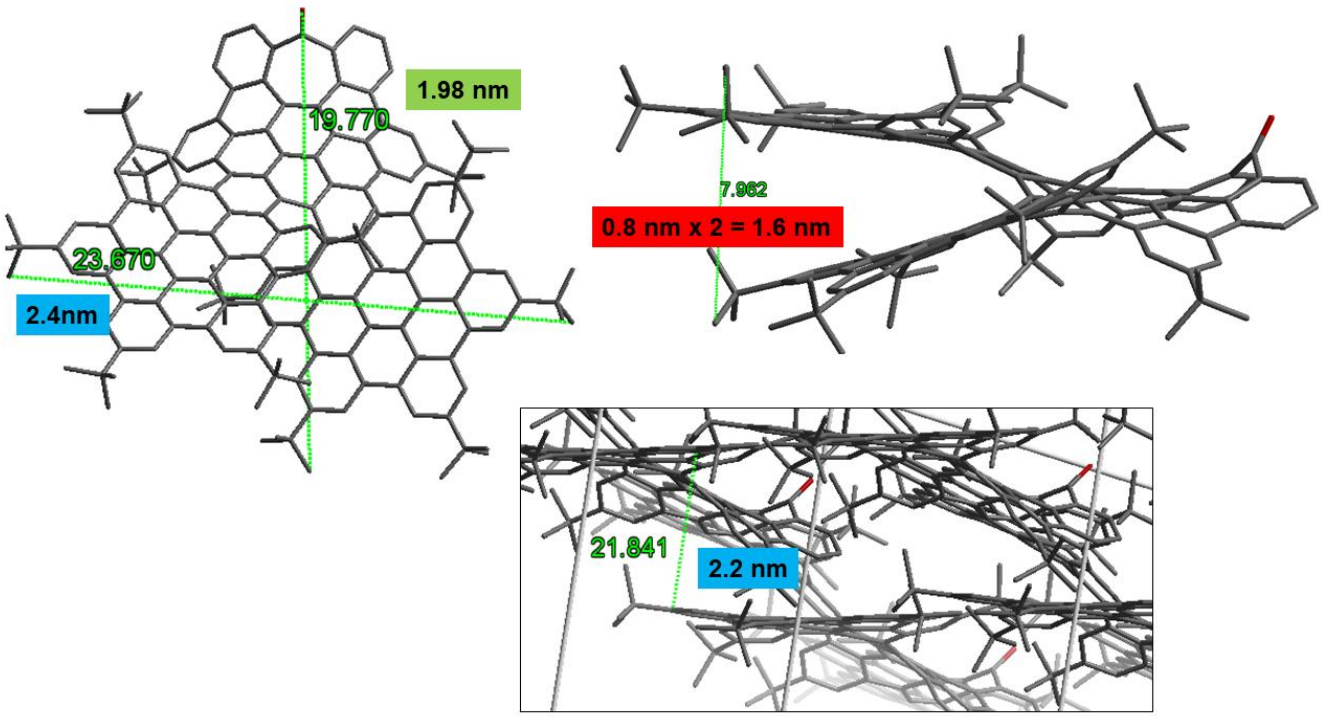


Figure S46. Racemic macrohelicene (*M*,*M*,*P*/*P*,*P*,*M*)-**1** crystal with molecular dimensions (left), distance between terminal HBCs (right) and interlayer distance (bottom) (distances in green are displayed in Å).

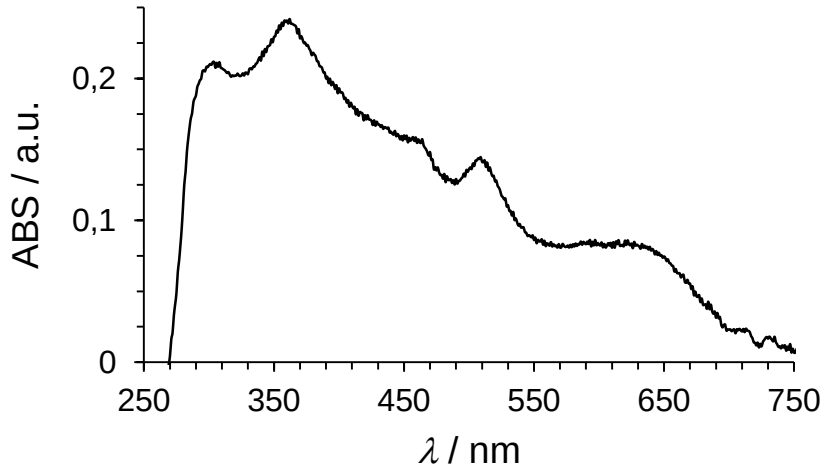


Figure S47. Absorption spectrum of enantiopure (*P*,*P*,*M*)-**1** thin film formed via drop-casting from a chloroform solution (ca. 5 mg mL^{-1}).

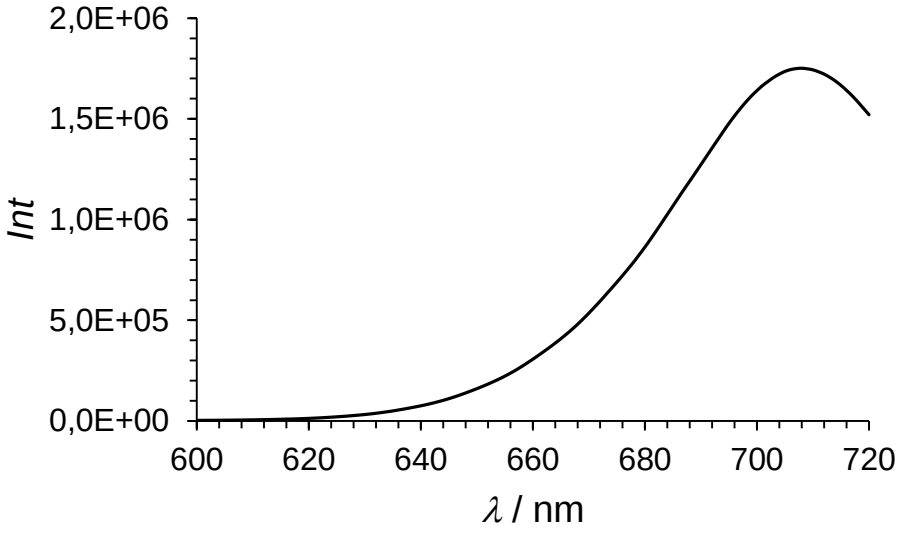


Figure S48. Emission spectrum of enantiopure (*P*,*P*,*M*)-**1** thin film formed via drop-casting from a chloroform solution (ca. 5 mg mL^{-1}).

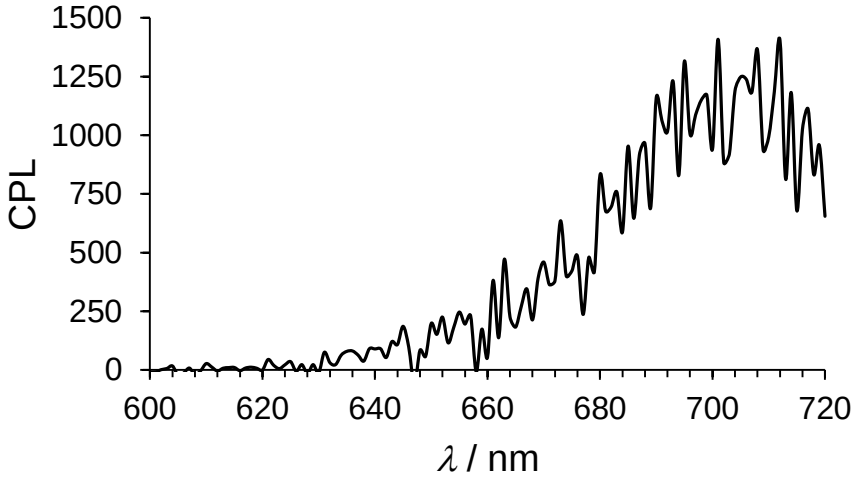


Figure S49. CPL spectrum of (*P*,*P*,*M*)-**1** thin film formed via drop-casting from a chloroform solution (ca. 5 mg mL^{-1}).

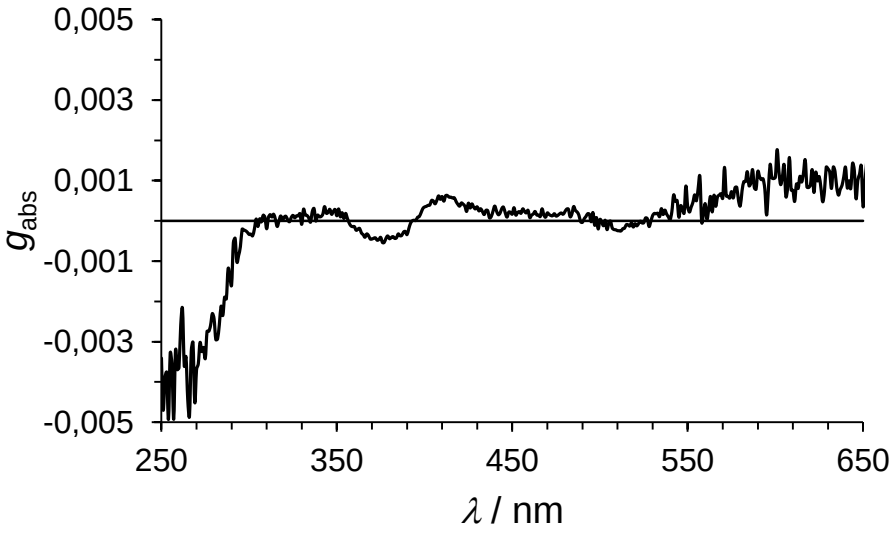


Figure S50. Absorption dissymmetry factor vs wavelength of (*P*,*P*,*M*)-**1** thin film formed via drop-casting from a chloroform solution (ca. 5 mg mL^{-1}).

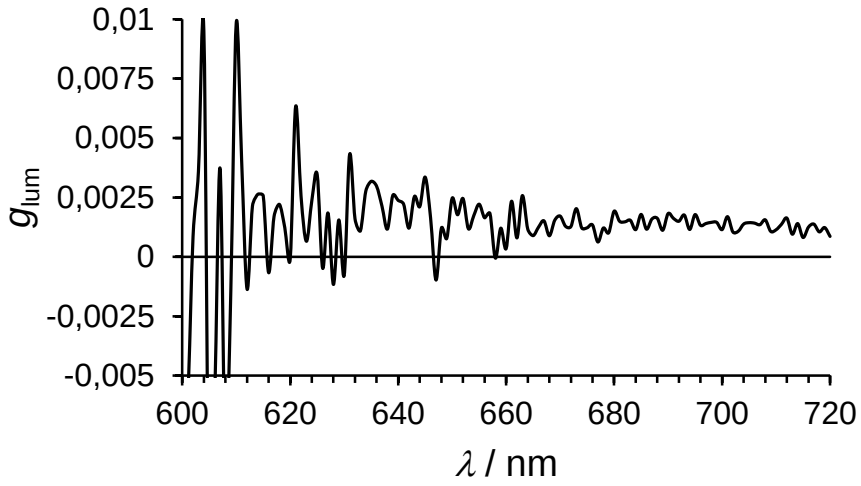


Figure S51. Emission dissymmetry factor vs wavelength of (*P*,*P*,*M*)-**1** thin film formed via drop-casting from a chloroform solution (ca. 5 mg mL^{-1}).

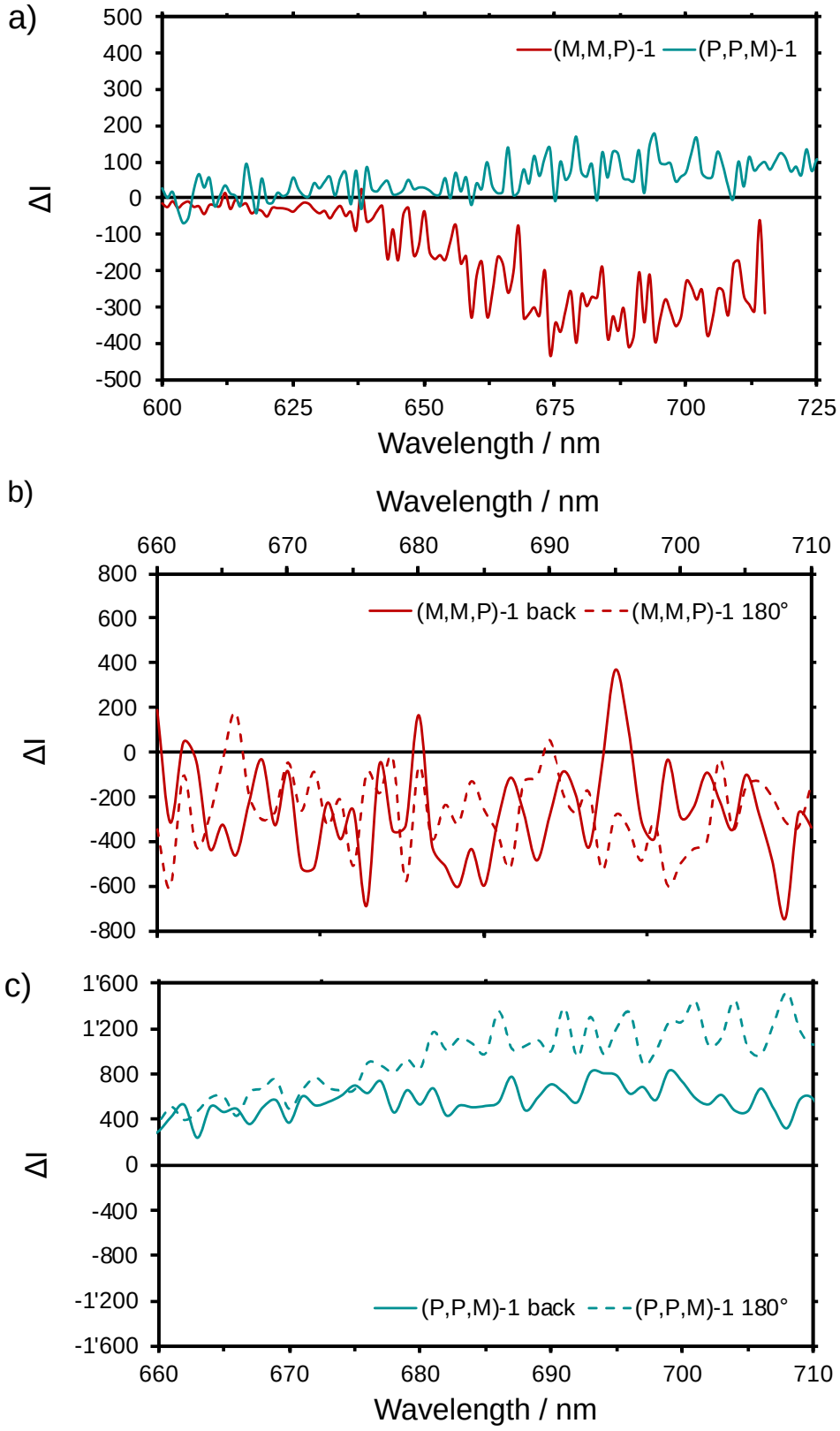
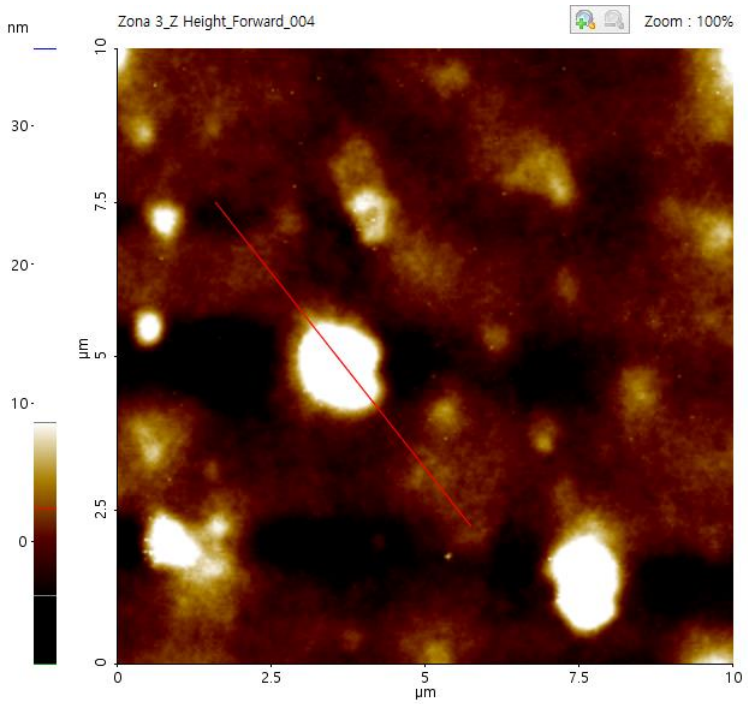


Figure 52. a) Experimental CPL spectra (λ_{exc} = 370 nm) of (*M*,*M*,*P*)-**1** (red) and (*P*,*P*,*M*)-**1** (turquoise) on quartz substrates from $CHCl_3$ solutions at ca. 5 mg mL^{-1}; b) CPL spectra of (*M*,*M*,*P*)-**1** film rotated at an angle of 180° (dashed line) and backside-flipped (solid line). c) CPL of (*P*,*P*,*M*)-**1** film rotated at an angle of 180º (dashed line) and backside-flipped (solid line).

For the enantiopure films, given that the sample concentration to obtain a thickness enough for the detection of chiroptical responses are ca. fifty times higher than those used for AFM characterization of the racemate, neither flake structure nor hint of multilayers were found in the corresponding images (Figure S56).

a)



b)

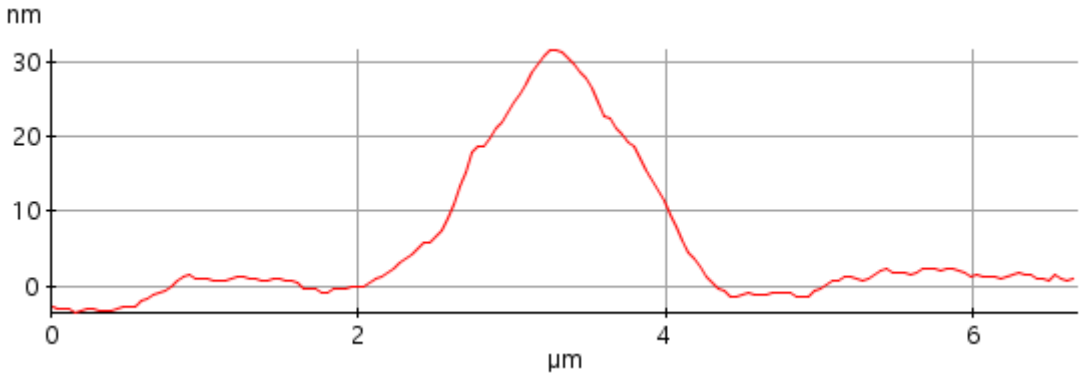


Figure S53. Non-contact mode AFM image (a) and height profile (b) of enantiopure (*P,P,M*)-**1** thin film deposited on a quartz plate via drop-casting from a toluene solution (ca. 0.1 mg mL^{-1}).

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