SUPPORTING INFORMATION

Enantioselective Synthesis of Inherently Chiral Molecular Nanographenes

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1. General

Unless otherwise noted, all materials including solvents were obtained from commercial suppliers and used without further purification. 97% 1,3-indandione, 98% potassium *tert*-butoxide, 96% 4-*tert*-butylphenylacetylene, 99 % tetrakis(triphenylphosphine)palladium(0), 99% CuI, 95% 4-methoxyphenylboronic acid and 98% DDQ from Aldrich; 98% TfOH from Alfa Aesar; 98% 2-iodobenzyl bromide, 98% (*S*)-(−) and (*R*)-(+) α,α-Diphenyl-2-pyrrolidinemethanol from TCI; and 99% triphenylphosphine oxide from ThermoScientific. Tetra-2,3,4,5-tetrakis[4-(1,1-dimethylethyl)phenyl]2,4-cyclopentadien-1-one (**4**) was prepared according to the procedure reported in the literature.[1] Unless otherwise noted, all reactions were performed with dry solvents (dried by filtration through alumina according to the method described)[2] and under an atmosphere of argon in dried glassware with standard vacuum-line techniques. Mechanochemical reactions were performed in a Retsch MM 200 mixer mill, using a zirconium oxide grinding jar and zirconium oxide 4 mm grinding balls.

All work-up and purification procedures were carried out with reagent-grade solvents in air. Silica column chromatography was conducted with Scharlau 40-60 µm silica gel. Analytical thin-layer chromatography (TLC) was performed using E. Silica gel 60 F254-coated aluminum sheets (Merck). Developed plates were visualized using UV light at wavelength of 254 and 365 nm. Flash chromatography was performed on Silica gel 60 (0.040-0.063 mm, Merck).

^{1}H NMR spectra were recorded at 300 (Bruker AVIII) MHz and ^{13}C NMR spectra were recorded at 75 (Bruker AV) MHz. Chemical shifts for ^{1}H NMR and ^{13}C NMR are expressed in parts per million (ppm). Deuterated chloroform ($CDCl_3$) was used as NMR solvent for all the compounds, the residual solvent signal ($CDCl_3$ δ 7.26 ppm for ^{1}H and δ 77.16 ppm for ^{13}C) was used for referencing of NMR spectra. Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constant (Hz), and integration.

MALDI-ToF matrix was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) and mass analysis were performed in a Bruker Ultraflex II using a LTB MNL 106 laser source.

Electrochemical measurements were performed using a standard one-compartment, three-electrode electrochemical cell connected to an electrochemical analyzer (Metrohm Autolab). The working electrode was a glassy carbon electrode (3 mm diameter) that was freshly polished with a suspension of Al_2O_3 in distilled water and sonically rinsed with acetone before each measurement. Silver (Ag/0.1 M $AgNO_3$ in CH_3CN) and platinum wires were used as reference and counter electrodes, respectively. Electrochemical grade (Aldrich) tetrabutylammonium hexaflurophosphate 0.1 M in toluene:acetonitrile (1:1) was used as supporting electrolyte. All measurements were conducted under dry argon. Solutions were saturated with argon for deoxygenation and to maintain an argon blanket for at least 10 minutes prior to each measurement. All measurements are referenced to Fc/Fc^+ added as internal reference.

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[1] Lungerich, D.; Hitzenberger, J. F.; Marcia, M.; Hampel, F.; Drewello, T.; Jux, N. *Angewandte Chemie International Edition* **2014**, 53 (45), 12231.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 15 (5), 1518.

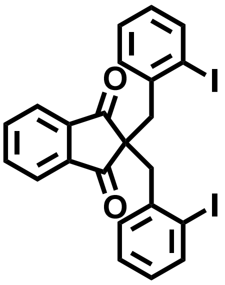
UV-vis data was obtained on a Shimadzu UV-3600 spectrometer. Optical rotations were measured using an Anton Paar MCP 100 Polarimeter.

HPLC analyses were performed on JASCO LC-4000 series, doted with a JASCO PU-4180 RHPLC pump, a JASCO AS-4050 autosampler, and a JASCO CO-4061 column oven; all connected to a JASCO CD-4095 UV-vis and CD detector. The HPLC analytical columns used were Reflect I-Cellulose B (5 µm, 25 cm x 4.6 mm ID) and (*R*,*R*) Whelk-O2 (5 µm, 25 cm x 4.6 mm ID).

The ECD spectra were measured on a JASCO J-1500 CD Spectrometer, over a spectral range of 250 nm to 550 nm in chloroform (ca. 10^{-5} M solutions). Measurements were made in a quartz cell with a 1 cm path length using a scanning speed of 50 nm/min, a response time of 4 seconds and standard instrument sensitivity. The CPL spectra were measured on a JASCO CPL-300 with a 180º geometry. The following parameters were used: excitation and emission slit width of 1 nm, integration time of 4 seconds, scan speed of 50 nm/min, with 20 accumulations. (ca. 10^{-5} M solutions).

2. Synthetic procedures

2,2-bis(2-iodobenzyl)-1,3-indandione – 2

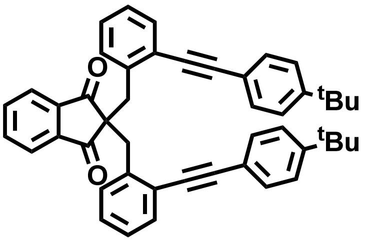


1,3-indandienone (6.74 mmol, 985 mg), 2-iodobenzyl bromide (16.80 mmol, 5 g) and potassium *tert*-butoxide (16.80 mmol, 1.89 g) were placed in a 25 mL zirconium oxide ball mill jar along with twenty-one zirconium oxide grinding balls (⌀ = 4 mm). The reaction was carried out in a miller at 25 Hz for 4 hours. Upon completion, the reaction crude was filtered through a small-plug of Celite-S and washed with ethyl acetate. The solvent was removed under reduced pressure, and the mixture purified by silica gel column chromatography using Hexane:AcOEt (4:1) as eluent. After removal of the solvents under reduced pressure, **2** was afforded as a yellow solid (2 g, 51%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.81 (dd, J = 5.7, 3.1 Hz, 2H), 7.72 (dd, J = 8.0, 1.1 Hz, 2H), 7.68 (dd, J = 5.7, 3.1 Hz, 2H), 7.06 – 6.97 (m, 4H), 6.73 (ddd, J = 8.0, 6.5, 2.5 Hz, 2H), 3.51 (s, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 201.75, 142.47, 140.22, 138.82, 135.62, 130.24, 128.67, 127.99, 123.25, 102.81, 60.43, 44.45.

HRMS (MALDI-TOF): Calc. for $C_{23}H_{16}I_2O_2$: $[M]^+$ = 577,9240 m/z, Calc. for $C_{23}H_{16}I_2O_2Na$: $[M+Na]^+$ = 600.9138 m/z; found: $[M+Na]^+$ = 600,7949 m/z.

2,2-bis[2-(4-tert-butylphenylethynyl)benzyl]-1,3-indandione – 3

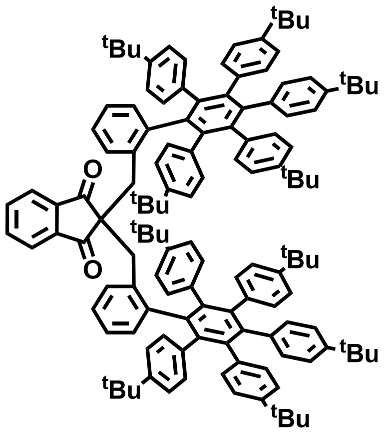


In a dried 100 mL Schlenk flask, $Pd(PPh_3)_4$ (0.078 mmol, 90 mg), copper iodide (0.078 mmol, 15 mg) and **2** (1.73 mmol, 1 g) were placed along with a magnetic stir bar under Ar atmosphere. The flask was evacuated and backfilled with Ar three times to exclude moisture and air. Anhydrous THF (15 mL) and anhydrous triethylamine (15 mL) were added under Ar atmosphere, followed by 4-(*tert*-butyl) phenylacetylene (6.92 mmol, 1,25 mL), stirring the mixture for 16 h at 70ºC. The resulting mixture was diluted with DCM and washed with a saturated solution of NH_4Cl and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (2:1) as eluent. After removal of the solvents under reduced pressure, **3** was afforded as a yellow solid (1.08 g, 98%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.71 (dd, J = 5.7, 3.1 Hz, 2H), 7.48 (dd, J = 5.7, 3.1 Hz, 2H), 7.41 – 7.26 (m, 10H), 7.15 (dd, J = 7.1, 2.0 Hz, 2H), 7.09 – 6.99 (m, 4H), 3.63 (s, 4H), 1.33 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 202.05, 151.42, 142.09, 137.89, 135.10, 132.36, 131.46, 130.48, 127.81, 126.79, 125.31, 124.58, 123.02, 120.53, 94.18, 87.81, 60.20, 38.65, 34.91, 31.37.

HRMS (MALDI-TOF): Calc. for $C_{47}H_{42}O_2$: $[M]^+$ = 638.3185 m/z, Calc. for $C_{47}H_{42}O_2K$: $[M+K]^+$ = 677.2822 m/z; found: $[M]^+$ = 638.3159 m/z, $[M+K]^+$ = 677.0019 m/z

2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandione – 5



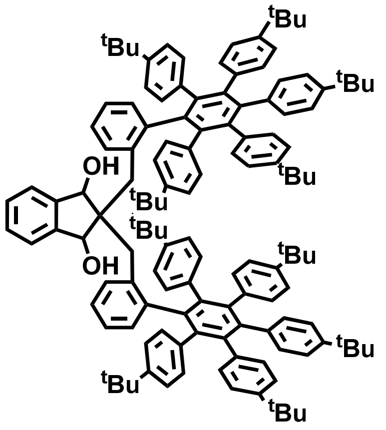
In a 25 mL Schlenk flask, **3** (0.271 mmol, 173 mg) and **4** (0.821 mmol, 500 mg) were placed along with a magnetic stir bar. The flask was evacuated for 30 minutes to keep a low-pressure atmosphere. Both solids were stirred for 40 h at 280ºC. After the mixture was warmed to room temperature, the resulting solid was collected with DCM and purified by silica gel column chromatography using Hexane:DCM (4:1) as eluent. After removal of the solvents under reduced pressure, **5** was afforded as a white solid (405 mg, 83%).

^{1}H-NMR (300 MHz, CDCl$_3$) δ (ppm) = 7.90 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.7, 3.1 Hz, 2H), 6.98 – 6.65 (m, 32H), 6.57 (m, 12H), 6.42 (td, *J* = 7.6, 1.5 Hz, 2H), 6.22 (dd, *J* = 7.9, 1.2 Hz, 2H), 2.75 (s, 4H), 1.13 (s, 36H), 1.09 (s, 36H) , 1.07 (s, 18H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ (ppm) = 203.80, 147.63, 147.37, 147.31, 143.89, 140.92, 140.86, 140.83, 140.76, 138.66, 138.08, 137.86, 137.79, 135.00, 134.40, 133.74, 132.47, 132.04, 131.70, 131.37, 131.12, 127.40, 125.52, 124.49, 123.21, 123.05, 122.74, 77.58, 77.16, 76.74, 61.28, 41.68, 34.19, 31.46, 31.36.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{146}O_2$: [M]$^+$ = 1799.1323 m/z; found: [M]$^+$ = 1799.1300 m/z.

ATR-FTIR ν (C=O) = 1712 cm^{-1}.

Racemic (S,S) + (R,R) 2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – trans-6



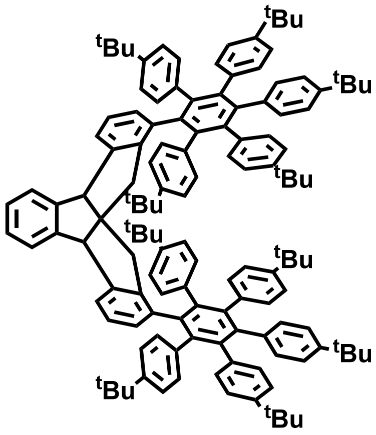
In a 100 mL dried round bottom flask provided with a magnetic stir bar, LiAlH$_4$ (95%, 3.75 mmol, 150 mg) was placed under Ar atmosphere. Anhydrous THF (30 mL) was slowly added with stirring, forming a dispersion where a solution of **5** (0,20 mmol, 360 mg) in anhydrous THF (10 mL) was added dropwise. The mixture was stirred for 4 h at reflux, cooled in an ice bath and diluted with diethyl ether to perform a classic Fieser workup. The mixture was filtered to remove the aluminium salts and the MgSO$_4$, and solvents were removed under reduced pressure. The crude was further purified by silica gel column chromatography using Hexane:DCM (3:2) as eluent. After removal of the solvents under reduced pressure, ***trans*-6** was obtained as a white solid (332 mg, 92%).

^{1}H-NMR (300 MHz, CDCl$_3$) δ (ppm) = 7.35 – 7.23 (m, 2H), 7.21 – 7.15 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.00 – 6.50 (m, 42H), 6.43 (t, *J* = 7.5 Hz, 2H), 6.28 (d, *J* = 7.9 Hz, 2H), 4.67 (s, 2H), AB system (δ_A = 2.84, δ_B = 2.70, *J* = 16.8 Hz, 4H), 1.09 (s, 18H), 1.09 (s, 36H), 1.08 (s, 18H), 1.07 (s, 18H). ^{13}C-NMR (75 MHz, CDCl$_3$) δ (ppm) = 148.10, 147.96, 147.53, 147.52, 147.42, 143.95, 141.30, 141.21, 141.00, 140.72, 140.61, 139.72, 139.22, 138.31, 138.20, 138.00, 137.94, 136.91, 133.34, 131.85, 131.53, 131.37, 131.17, 130.99, 130.87, 128.85, 126.11, 124.90, 123.82, 123.19, 123.08, 122.92, 79.60, 57.57, 39.67, 34.24, 34.21, 34.19, 34.16, 31.39, 31.37, 31.31.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{150}O_2$: $[M]^+$ = 1803.1636 m/z, Calc. for $C_{135}H_{150}O_2Na$: $[M+Na]^+$ = 1826.1534 m/z, Calc. for $C_{135}H_{150}O_2K$: $[M+K]^+$ = 1842.1273 m/z; found: $[M+Na]^+$ = 1826.1480 m/z, $[M+K]^+$ = 1842.1444 m/z.

ATR-FTIR ν (O-H) = 3568 cm^{-1}.

Racemic (S,S,S_a) + (R,R.R_a) bis-2-[penta(4-tert-butylphenyl)benzene]centrotriindan – Rac-7

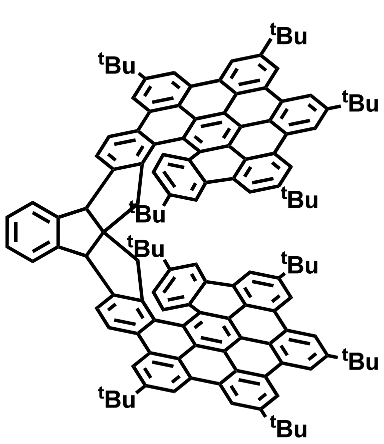


The Hendrickson salt was prepared in a regular dried vial provided with a magnetic stir bar, where freshly distilled trifluoromethanesulfonic anhydride (0.297 mmol, 50 μL) was added to a solution of triphenylphosphine oxide (0.683 mmol, 190 mg) in anhydrous DCM (1 mL) at 0ºC. The mixture was stirred for 20 minutes, upon complete formation of a white precipitate. Separately, in a 25 mL dried round bottom flask provided with a magnetic stir bar, ***trans*-6** (0.139 mmol, 250 mg) was dissolved with anhydrous DCM (5 mL) under Ar atmosphere at 0ºC. The white precipitate was quickly added to the solution, stirring the reaction mixture for 30 minutes at room temperature under Ar atmosphere. The reaction was quenched with a saturated solution of $NaHCO_3$, diluted in DCM and washed with more $NaHCO_3$ solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (5:1) as eluent. After removal of the solvents under reduced pressure, **Rac-7** was afforded as a white solid (183 mg, 74%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.04 – 6.45 (m, 48H), 6.34 (d, *J* = 7.8 Hz, 2H), 6.18 (d, *J* = 8.0 Hz, 2H), 3.49 (s, 2H), AB system (δ_A = 2.71, δ_B = 2.56, *J* = 16.6 Hz, 4H), 1.16 (s, 18H), 1.12 (s, 18H), 1.10 (s, 18H), 1.07 (s, 18H), 1.01 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 147.80, 147.51, 147.49, 147.48, 147.45, 147.32, 144.62, 143.23, 141.71, 140.39, 140.31, 140.27, 140.18, 140.13, 139.09, 138.36, 138.24, 138.15, 138.07, 137.52, 131.38, 131.34, 131.16, 130.91, 130.71, 130.54, 130.32, 126.37, 125.19, 124.28, 123.12, 123.03, 121.95, 61.80, 60.89, 43.23, 34.27, 34.21, 34.20, 34.13, 34.08, 31.59, 31.37, 31.35, 31.32.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{146}$: $[M]^+$ = 1767.1425 m/z; found: $[M]^+$ = 1767.1471 m/z.

Racemic (S,S,S_a,M,M) + (R,R.R_a,P,P) Rac-1

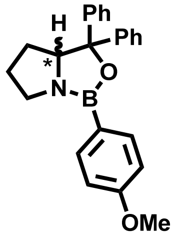


In a 100 mL dried round bottom flask provided with a magnetic stir bar, DDQ (0.370 mmol, 84 mg) and **Rac-7** (0.031 mmol, 55 mg) were dissolved with anhydrous DCM (40 mL) under Ar atmosphere. The solution was stirred and cooled down to -78ºC in a dry ice bath, where trifluoromethanesulfonic acid was added (3.70 mmol, 325 μL), stirring for 90 minutes at -78ºC with an Ar flow. The reaction was quenched with a saturated solution of $NaHCO_3$, warmed up to room temperature and washed with more $NaHCO_3$ solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (10:1) as eluent. After removal of the solvents under reduced pressure, **Rac-1** was afforded as a yellow solid (24 mg, 45%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 9.09 (bs, 2H), 9.07 (bs, 2H), 9.05 (bs, 2H), 9.04 (bs, 2H), 9.03 (bs, 2H), 8.94 (bs, 2H), 8.86 (bs, 2H), 8.78 (d, *J* = 8.4 Hz, 2H), 8.64 (bs, 2H), 8.51 (bs, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.60 (dd, *J* = 5.1, 3.4 Hz, 2H), 7.42 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.93 (dd, *J* = 8.7, 1.4 Hz, 2H), 3.72 (s, 2H), AB system (δ_A = 2.48, δ_B = 1.59, *J* = 17.2 Hz, 4H), 1.81 (s, 18H), 1.75 (s, 18H), 1.65 (s, 18H), 1.49 (s, 18H), 1.45 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 149.53, 149.38, 148.78, 148.76, 148.61, 144.67, 143.33, 141.64, 130.98, 130.43, 130.37, 130.18, 130.15, 130.13, 130.04, 129.89, 129.83, 129.24, 127.60, 127.32, 124.73, 124.42, 123.97, 123.72, 123.65, 123.57, 123.47, 123.11, 122.99, 122.79, 121.54, 120.42, 120.28, 120.02, 119.25, 119.02, 118.96, 118.69, 118.66, 118.58, 118.44, 62.83, 60.41, 47.49.

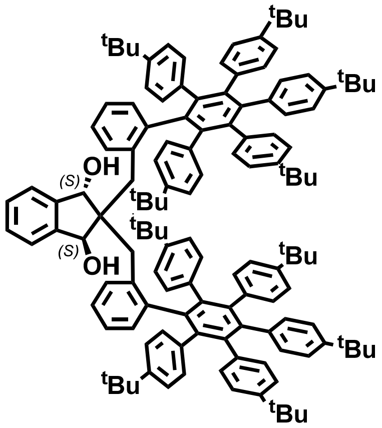
HRMS (MALDI-TOF): Calc. for $C_{135}H_{126}$: $[M]^+$ = 1746.9860 m/z; found: $[M]^+$ = 1746.9818 m/z.

General procedure for the synthesis of Corey-Bakshi-Shibata pMPOAB catalysts:



In a 50 mL round bottom flask provided with a magnetic stir bar, (*S*)-(−) or (*R*)-(+) α,α-Diphenyl-2-pyrrolidinemethanol (2.22 mmol, 563 mg) and 4-methoxyphenylboronic acid (95%, 2.22 mmol, 355 mg) and anhydrous toluene (25 mL) were placed under Ar atmosphere. A 50 mL addition funnel provided with activated 4 Å molecular sieves was placed in the neck of the flask, acting as a Soxhlet extractor to dry out water from the system. The mixture was stirred and heated to reflux under Ar atmosphere overnight (ca. 16 h). The funnel's key was closed to remove most of the solvent and concentrate the catalyst solution (ca. 3 mL), to be warmed up to room temperature and stored under Ar atmosphere prior to any use.

(S,S)-2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – (S,S)-6

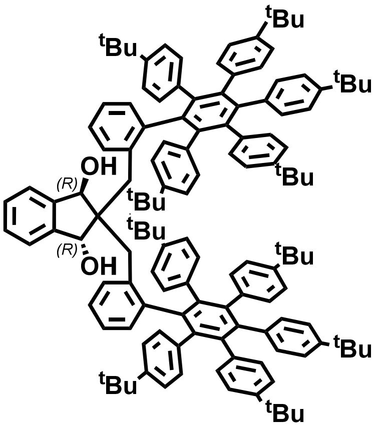


To a solution of (*S*)-*p*MPOAB (ca. 2.22 mmol) in toluene (ca. 3 mL) a solution of $BH_3 \cdot THF$ in THF (1 M, 2.2 mmol, 2.2 mL) was added at room temperature under Ar atmosphere. The mixture was stirred for 30 minutes to form the catalytic complex, and **5** (0.089 mmol, 160 mg) was added. The reaction was stirred for 2 h, cooled in an ice bath and diluted with diethyl ether before adding water in a dropwise manner to quench it. The mixture was washed with a HCl 0.1 M solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude -a mixture of two diastereomers- was purified by silica gel column chromatography using Hexane:DCM (5:1) as eluent. After removal of the solvents under reduced pressure, optically active trans diol **(*S,S*)-6** was obtained (98 mg, 61%), as well as cis diol **meso-6** as a byproduct (46 mg, 28%), both white solids (*dl*/meso 68/32, $[\alpha]^{20}_D$ = -62 (c = 1 g/100 mL), ≥97% *ee*).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.30 (dd, *J* = 5.6, 3.1 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.13 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.01 – 6.50 (m, 42H), 6.48 – 6.38 (m, 2H), 6.29 (d, *J* = 8.0 Hz, 2H), 4.68 (d, *J* = 6.8 Hz, 2H), AB system (δ_A = 2.85, δ_B = 2.71, *J* = 16.8 Hz, 4H), 1.51 (d, *J* = 7.1 Hz, 2H), 1.09 (s, 18H), 1.09 – 1.08 (m, 36H), 1.08 (s, 18H), 1.07 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 148.10, 147.95, 147.53, 147.52, 147.42, 143.96, 141.30, 141.21, 141.00, 140.72, 140.61, 139.72, 139.22, 138.32, 138.20, 138.00, 137.94, 136.91, 133.34, 131.85, 131.55, 131.53, 131.50, 131.36, 131.18, 131.17, 131.00, 130.87, 128.85, 126.11, 124.90, 123.82, 123.22, 123.20, 123.10, 123.08, 79.59, 34.24, 34.22, 34.19, 34.16, 31.39, 31.37, 31.32.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{150}O_2$: $[M]^+$ = 1803.1636 m/z, Calc. for $C_{135}H_{150}O_2Na$: $[M+Na]^+$ = 1826.1534 m/z, Calc. for $C_{135}H_{150}O_2K$: $[M+K]^+$ = 1842.1273 m/z; found: $[M+Na]^+$ = 1826.1525 m/z, $[M+K]^+$ = 1842.1133 m/z.

(R,R)-2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – (R,R)-6

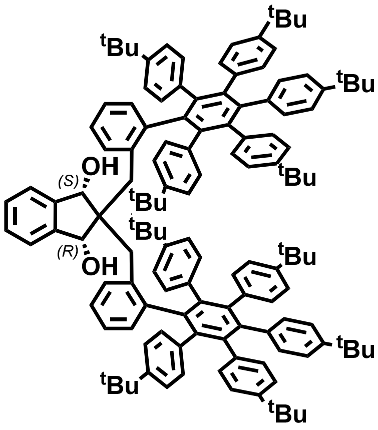


To a solution of (*R*)-*p*MPOAB (ca. 2.22 mmol) in toluene (ca. 3 mL) a solution of $BH_3 \cdot THF$ in THF (1 M, 2.2 mmol, 2.2 mL) was added at room temperature under Ar atmosphere. The mixture was stirred for 30 minutes to form the catalytic complex, and **5** (0.081 mmol, 145 mg) was added. The reaction was stirred for 2 h, cooled in an ice bath and diluted with diethyl ether before adding water in a dropwise manner to quench it. The mixture was washed with a HCl 0.1 M solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude -a mixture of two diastereomers- was purified by silica gel column chromatography using Hexane:DCM (5:1) as eluent. After removal of the solvents under reduced pressure, optically active trans diol **(*R,R*)-6** was obtained (107 mg, 73%), as well as cis diol **meso-6** as a byproduct (35 mg, 24%), both white solids (*dl*/meso 75/25, $[\alpha]^{20}_{D}$ = +69 (c = 1 g/100 mL), ≥98% *ee*).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.30 (dd, *J* = 5.6, 3.1 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.13 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.01 – 6.49 (m, 42H), 6.43 (t, *J* = 7.5 Hz, 2H), 6.28 (d, *J* = 7.9 Hz, 2H), 4.67 (s, 2H), AB system (δ_A = 2.84, δ_B = 2.70, *J* = 16.8 Hz, 4H), 1.09 (s, 18H), 1.09 – 1.08 (m, 36H), 1.08 (s, 18H), 1.07 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 147.96, 147.53, 147.52, 147.42, 141.79, 141.30, 141.22, 141.00, 140.72, 139.22, 138.31, 138.20, 138.00, 137.94, 136.91, 132.23, 131.85, 131.36, 131.03, 130.87, 128.88, 128.85, 126.11, 124.90, 124.71, 124.61, 123.82, 123.27, 123.23, 123.19, 123.12, 123.08, 34.24, 34.21, 34.19, 34.16, 31.39, 31.36, 31.31.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{150}O_2$: $[M]^+$ = 1803.1636 m/z, Calc. for $C_{135}H_{150}O_2Na$: $[M+Na]^+$ = 1826.1534 m/z, Calc. for $C_{135}H_{150}O_2K$: $[M+K]^+$ = 1842.1273 m/z; found: $[M+Na]^+$ = 1826.1596 m/z, $[M+K]^+$ = 1842.1321 m/z.

(S,R)-2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – meso-6



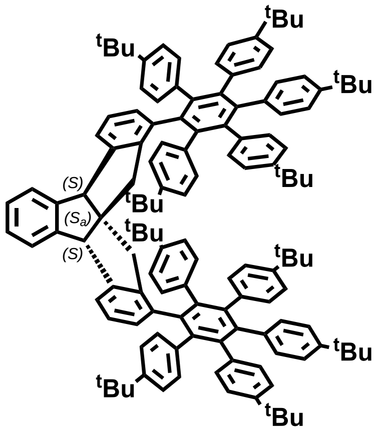
The molecule was attained as a white solid, and as a byproduct of the enantioselective reduction of **5.** and.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.40 – 7.30 (m, 4H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.96 – 6.43 (m, 45H), 6.24 (d, *J* = 7.8 Hz, 1H), 4.82 (s, 2H), 3.02 (s, 2H), 2.53 (s, 2H), 1.14 – 1.03 (m, 90H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 147.88, 147.79, 147.51, 147.45, 147.40, 147.34, 144.30, 141.29, 141.24, 141.06, 140.91, 140.84, 140.69, 140.36, 140.11, 138.97, 138.68, 138.26, 138.25, 138.02, 137.83, 137.79, 136.66, 133.89, 133.68, 131.75, 131.70, 130.99, 130.87, 128.80, 127.80, 126.37, 125.04, 124.03, 123.83, 123.58, 123.15, 123.11, 123.05, 80.41, 56.29, 34.21, 34.18, 34.16, 34.15, 31.38, 31.35, 31.30.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{150}O_2$: $[M]^+$ = 1803.1636 m/z, Calc. for $C_{135}H_{150}O_2Na$: $[M+Na]^+$ = 1826.1534 m/z, Calc. for $C_{135}H_{150}O_2K$: $[M+K]^+$ = 1842.1273 m/z; found: $[M+Na]^+$ = 1826.1508 m/z, $[M+K]^+$ = 1842.1185 m/z.

ATR-FTIR ν (O-H) = 3560 cm^{-1}.

(S,S,S$_a$)-bis-2-[penta(4-tert-butylphenyl)benzene]centrotriindan – (S,S,S$_a$)-7

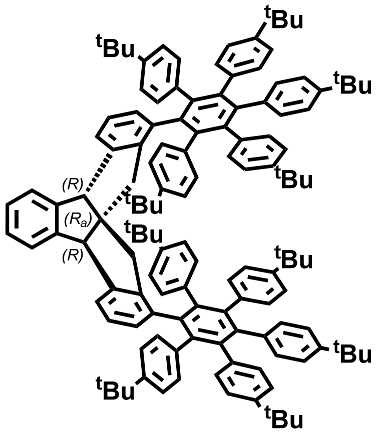


The Hendrickson salt was prepared in a regular dried vial provided with a magnetic stir bar, where freshly distilled trifluoromethanesulfonic anhydride (0.083 mmol, 14 µL) was added to a solution of triphenylphosphine oxide (0.169 mmol, 47 mg) in anhydrous DCM (1 mL) at 0ºC. The mixture was stirred for 20 minutes, upon complete formation of a white precipitate. Separately, in a 25 mL dried round bottom flask provided with a magnetic stir bar, **(*S,S*)-6** (0.041 mmol, 75 mg) was dissolved with anhydrous DCM (2 mL) under Ar atmosphere at 0ºC. The white precipitate was quickly added to the solution, stirring the reaction mixture for 30 minutes at room temperature under Ar atmosphere. The reaction was quenched with a saturated solution of $NaHCO_3$, diluted in DCM and washed with more $NaHCO_3$ solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (5:1) as eluent. After removal of the solvents under reduced pressure, **(*S,S,S$_a$*)-7** was afforded as a white solid (54 mg, 73%, $[\alpha]^{20}_D$ = +82 (c = 1 g/100 mL), ≥97% *ee*).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.04 – 6.43 (m, 48H), 6.34 (d, *J* = 8.1 Hz, 2H), 6.18 (d, *J* = 8.1 Hz, 2H), 3.49 (s, 2H), AB system (δ_A = 2.71, δ_B = 2.56, *J* = 16.6 Hz, 4H), 1.16 (s, 18H), 1.13 (s, 18H), 1.10 (s, 18H), 1.07 (s, 18H), 1.02 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 147.81, 147.51, 147.46, 147.33, 144.62, 143.23, 141.71, 140.39, 140.31, 140.27, 140.18, 140.13, 139.09, 138.36, 138.24, 138.15, 138.07, 137.52, 131.39, 131.35, 131.31, 131.17, 126.38, 125.19, 124.29, 123.25, 123.19, 123.12, 123.04, 121.95, 61.80, 60.90, 43.25, 34.28, 34.21, 34.20, 34.13, 34.09, 31.60, 31.38, 31.35, 31.32.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{146}$: $[M]^+$ = 1767.1425 m/z; found: $[M]^+$ = 1767.1432 m/z.

(R,R.R$_a$)-bis-2-[penta(4-tert-butylphenyl)benzene]centrotriindan – (R,R.R$_a$)-7

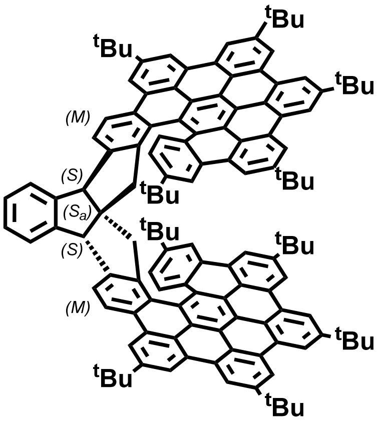


The Hendrickson salt was prepared in a regular dried vial provided with a magnetic stir bar, where freshly distilled trifluoromethanesulfonic anhydride (0.083 mmol, 14 µL) was added to a solution of triphenylphosphine oxide (0.169 mmol, 47 mg) in anhydrous DCM (1 mL) at 0ºC. The mixture was stirred for 20 minutes, upon complete formation of a white precipitate. Separately, in a 25 mL dried round bottom flask provided with a magnetic stir bar, **(*R,R*)-6** (0.041 mmol, 75 mg) was dissolved with anhydrous DCM (2 mL) under Ar atmosphere at 0ºC. The white precipitate was quickly added to the solution, stirring the reaction mixture for 30 minutes at room temperature under Ar atmosphere. The reaction was quenched with a saturated solution of $NaHCO_3$, diluted in DCM and washed with more $NaHCO_3$ solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (5:1) as eluent. After removal of the solvents under reduced pressure, **(*R,R,R$_a$*)-7** was afforded as a white solid (60 mg, 81%, $[\alpha]^{20}_D$ = -84 (c = 1 g/100 mL), ≥98% *ee*).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.04 – 6.44 (m, 48H), 6.34 (d, *J* = 8.1 Hz, 2H), 6.18 (d, *J* = 8.1 Hz, 2H), 3.49 (s, 2H), AB system (δ_A = 2.71, δ_B = 2.56, *J* = 16.6 Hz, 4H), 1.16 (s, 18H), 1.12 (s, 18H), 1.10 (s, 18H), 1.07 (s, 18H), 1.01 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 147.99, 147.80, 147.51, 147.49, 147.45, 147.33, 144.62, 143.22, 141.71, 140.41, 140.39, 140.31, 140.27, 140.18, 140.13, 139.09, 138.36, 138.24, 138.15, 138.07, 137.52, 131.43, 131.41, 131.39, 131.36, 131.35, 131.34, 131.33, 131.16, 126.38, 126.37, 123.13, 123.11, 123.03, 61.80, 60.88, 43.23, 34.27, 34.21, 34.19, 34.13, 34.08, 31.59, 31.38, 31.35, 31.32.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{146}$: $[M]^+$ = 1767.1425 m/z; found: $[M]^+$ = 1767.1474 m/z.

(S,S,S_a,M,M)-1

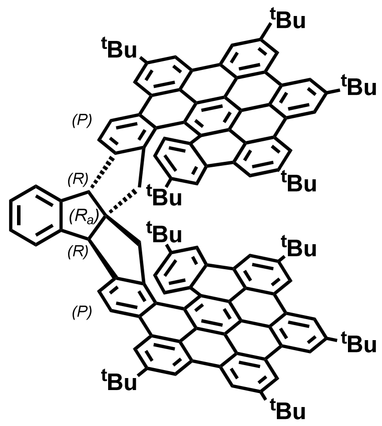


In a 100 mL dried round bottom flask provided with a magnetic stir bar, DDQ (0.158 mmol, 36 mg) and **(*S,S,S$_a$*)-7** (0.014 mmol, 25 mg) were dissolved with anhydrous DCM (30 mL) under Ar atmosphere. The solution was stirred and cooled down to -78ºC in a dry ice bath, where trifluoromethanesulfonic acid was added (1,59 mmol, 140 μL), stirring for 90 minutes at -78ºC with an Ar flow. The reaction was quenched with a saturated solution of $NaHCO_3$, warmed up to room temperature and washed with more $NaHCO_3$ solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (10:1) as eluent. After removal of the solvents under reduced pressure, **(*S,S,S$_a$,M,M*)-1** was afforded as a yellow solid (8 mg, 32%, $[\alpha]^{20}_D$ = -504 (c = 1 g/100 mL), 97% *ee*).

^{1}H-NMR (700 MHz, $CDCl_3$) δ (ppm) = 9.07 (s, 2H), 9.04 (s, 2H), 9.03 (s, 2H), 9.02 (s, 2H), 9.01 (d, *J* = 1.6 Hz, 2H), 8.91 (s, 2H), 8.84 (s, 2H), 8.76 (d, *J* = 8.4 Hz, 2H), 8.61 (s, 2H), 8.49 (s, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.41 (dd, *J* = 5.5, 2.8 Hz, 2H), 6.90 (dd, *J* = 8.4, 1.9 Hz, 2H), 3.69 (s, 2H), 2.46 (d, *J* = 17.4 Hz, 2H), 1.79 (s, 18H), 1.73 (s, 18H), 1.63 (s, 18H), 1.47 (s, 18H), 1.43 (s, 18H). ^{13}C-NMR (176 MHz, $CDCl_3$) δ (ppm) = 149.51, 149.36, 148.76, 148.74, 148.58, 144.65, 143.31, 141.62, 130.96, 130.41, 130.34, 130.15, 130.13, 130.10, 130.02, 129.87, 129.81, 129.21, 127.58, 127.31, 124.71, 124.40, 123.96, 123.70, 123.63, 123.54, 123.45, 123.09, 122.97, 122.77, 121.52, 120.40, 120.25, 120.00, 119.23, 119.01, 118.95, 118.68, 118.64, 118.58, 118.55, 118.43, 62.80, 60.39, 47.47, 35.85, 35.78, 35.69, 35.44, 35.10, 32.23, 32.12, 32.08, 32.06, 32.01, 31.84, 31.77, 31.59.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{126}$: $[M]^+$ = 1746.9860 m/z; found: $[M]^+$ = 1746.9903 m/z.

(R,R,R_a,P,P)-1



In a 100 mL dried round bottom flask provided with a magnetic stir bar, DDQ (0.311 mmol, 71 mg) and ***(R,R,R_a)*-7** (0.028 mmol, 50 mg) were dissolved with anhydrous DCM (40 mL) under Ar atmosphere. The solution was stirred and cooled down to -78ºC in a dry ice bath, where trifluoromethanesulfonic acid was added (3.11 mmol, 273 μL), stirring for 90 minutes at -78ºC with an Ar flow. The reaction was quenched with a saturated solution of $NaHCO_3$, warmed up to room temperature and washed with more $NaHCO_3$ solution and water. After drying the organic phase with $MgSO_4$ and further removal of the solvent under reduced pressure, the crude was purified by silica gel column chromatography using Hexane:DCM (10:1) as eluent. After removal of the solvents under reduced pressure, ***(R,R,R_a,P,P)*-1** was afforded as a yellow solid (20 mg, 40%, $[\alpha]^{20}_{D}$ = +516 (c = 1 g/100 mL), 98% *ee*).

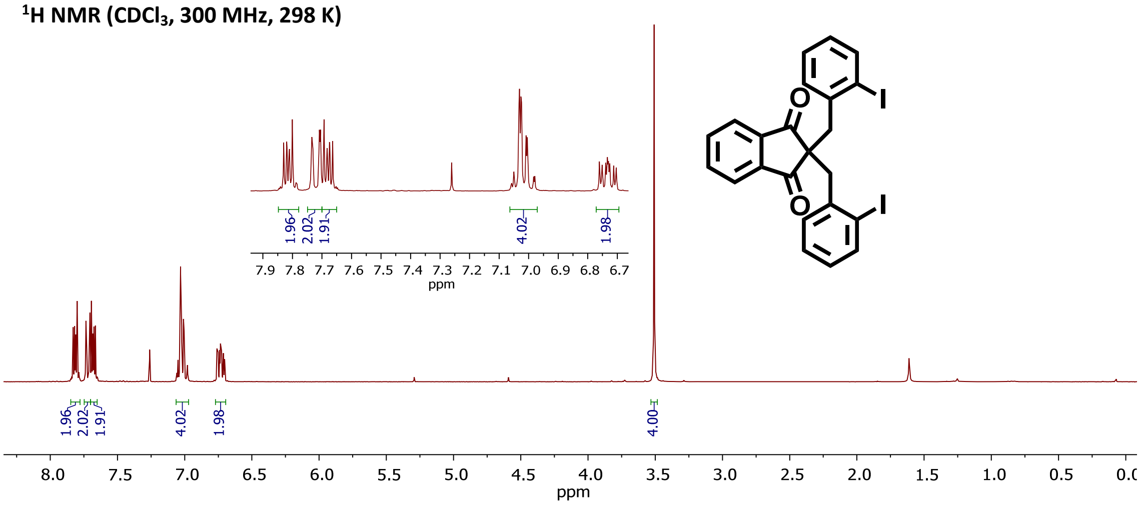
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) = 9.09 (bs, 1H), 9.08 (bs, 1H), 9.06 (bs, 1H), 9.05 (bs, 1H), 9.04 (bs, 1H), 8.94 (bs, 2H), 8.87 (bs, 2H), 8.79 (d, *J* = 8.4 Hz, 2H), 8.65 (bs, 2H), 8.52 (d, *J* = 2.0 Hz, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 5.4, 3.3 Hz, 2H), 7.43 (dd, *J* = 5.6, 3.1 Hz, 2H), 6.93 (dd, *J* = 8.7, 1.9 Hz, 2H), 3.72 (s, 2H), AB system (δ_A = 2.49, δ_B = 1.59, *J* = 17.2 Hz, 4H), 1.82 (s, 18H), 1.75 (s, 18H), 1.65 (s, 18H), 1.50 (s, 18H), 1.46 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) = 149.53, 149.38, 148.78, 148.76, 148.60, 144.66, 143.33, 141.64, 130.98, 130.43, 130.36, 130.18, 130.15, 130.13, 130.04, 129.89, 129.83, 129.24, 127.61, 127.32, 124.73, 124.42, 123.97, 123.72, 123.65, 123.56, 123.47, 123.11, 122.99, 122.79, 121.54, 120.42, 120.27, 120.02, 119.25, 119.02, 118.96, 118.69, 118.65, 118.58, 118.44, 62.83, 60.41, 47.49, 35.86, 35.79, 35.70, 35.46, 35.11, 32.24, 32.14, 32.03, 31.85, 31.79.

HRMS (MALDI-TOF): Calc. for $C_{135}H_{126}$: $[M]^+$ = 1746.9860 m/z; found: $[M]^+$ = 1746.9881 m/z.

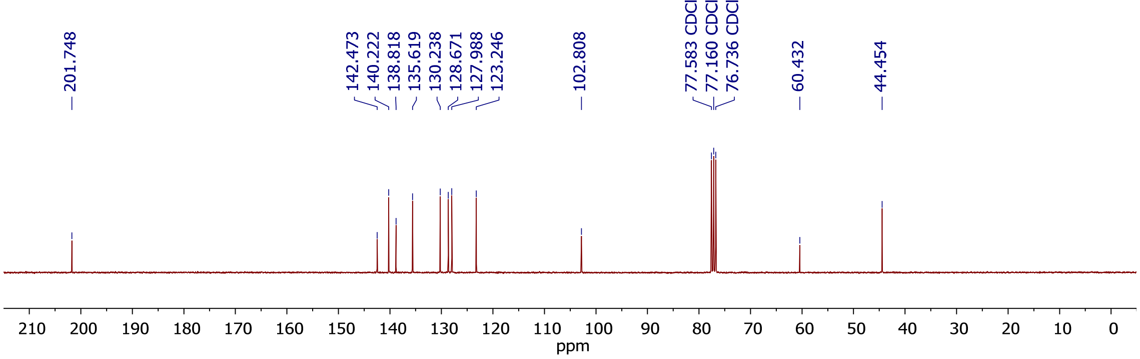
3. NMR and MS spectra

2,2-bis(2-iodobenzyl)-1,3-indandione – 2

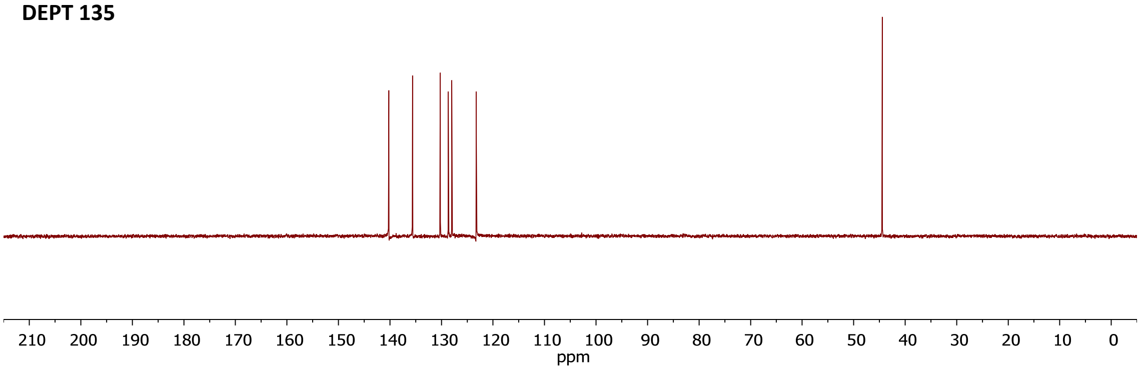
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K)



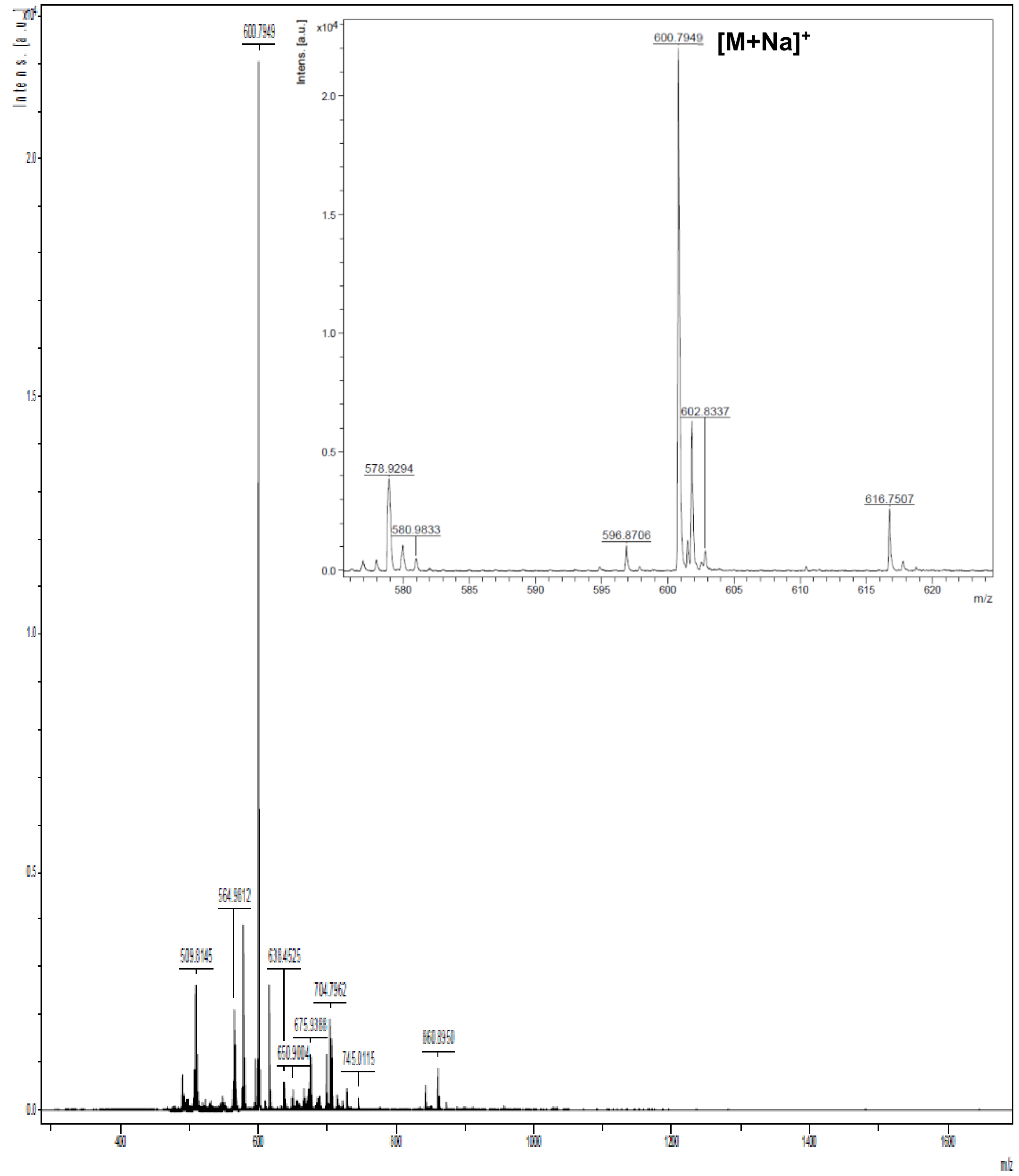
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K)



DEPT 135

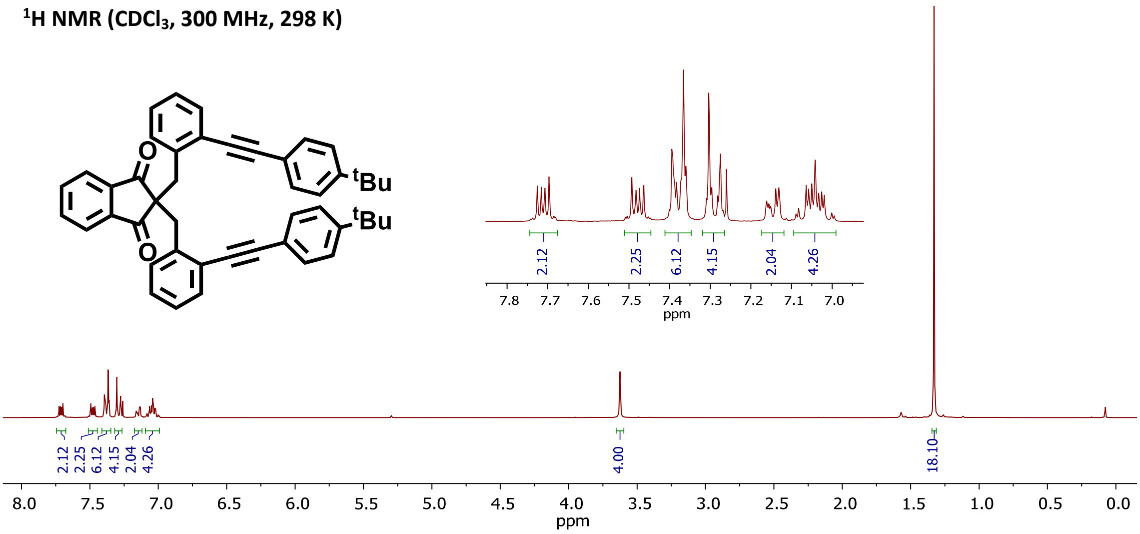


HRMS MALDI-TOF (DCTB)

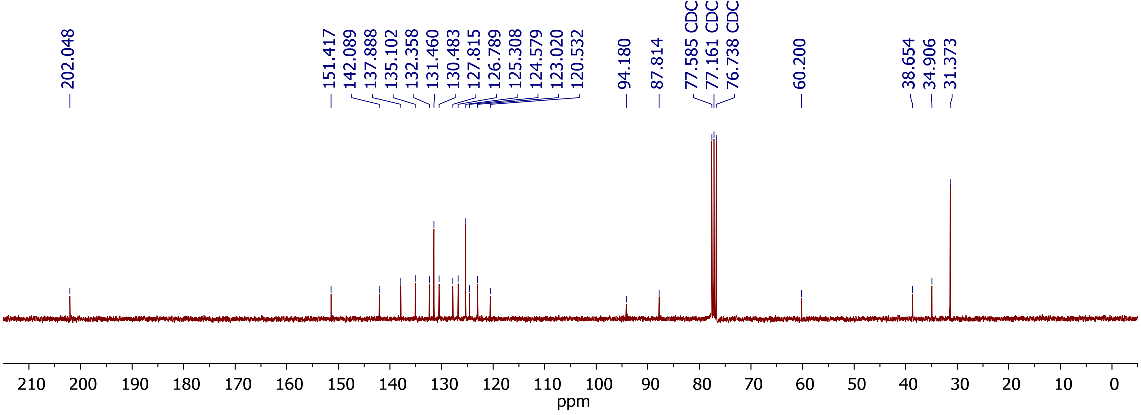


2,2-bis[2-(4-tert-butylphenylethynyl)benzyl]-1,3-indandione – 3

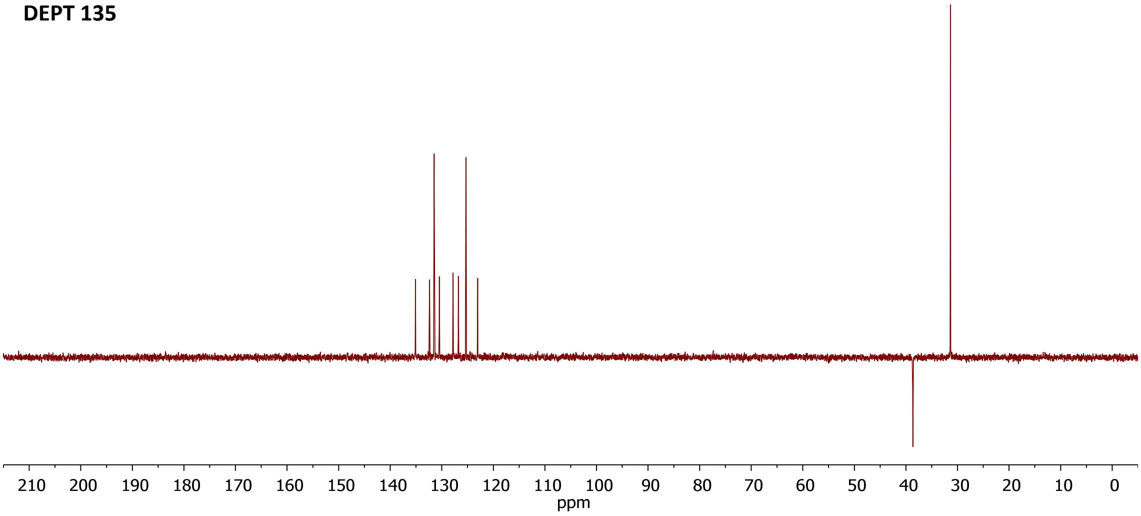
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



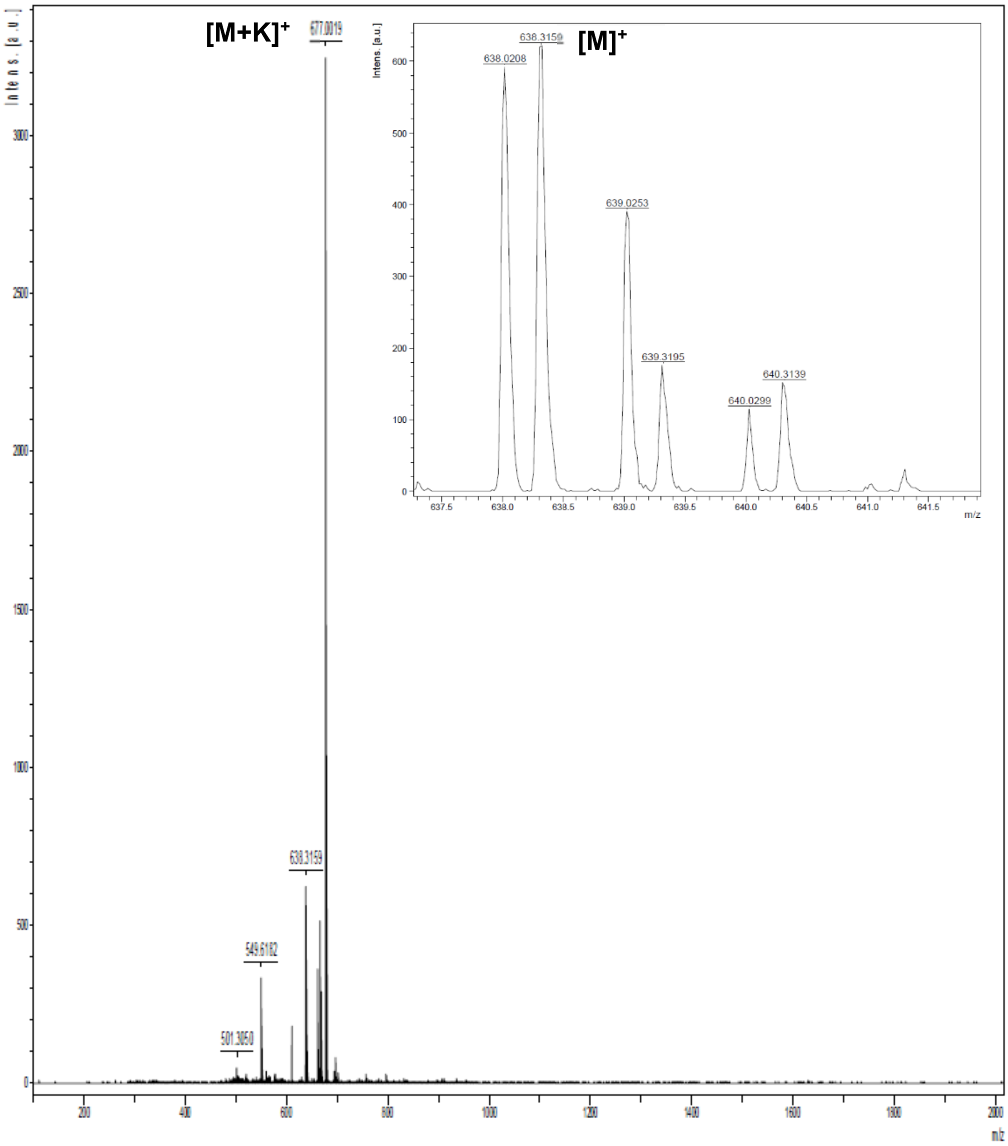
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

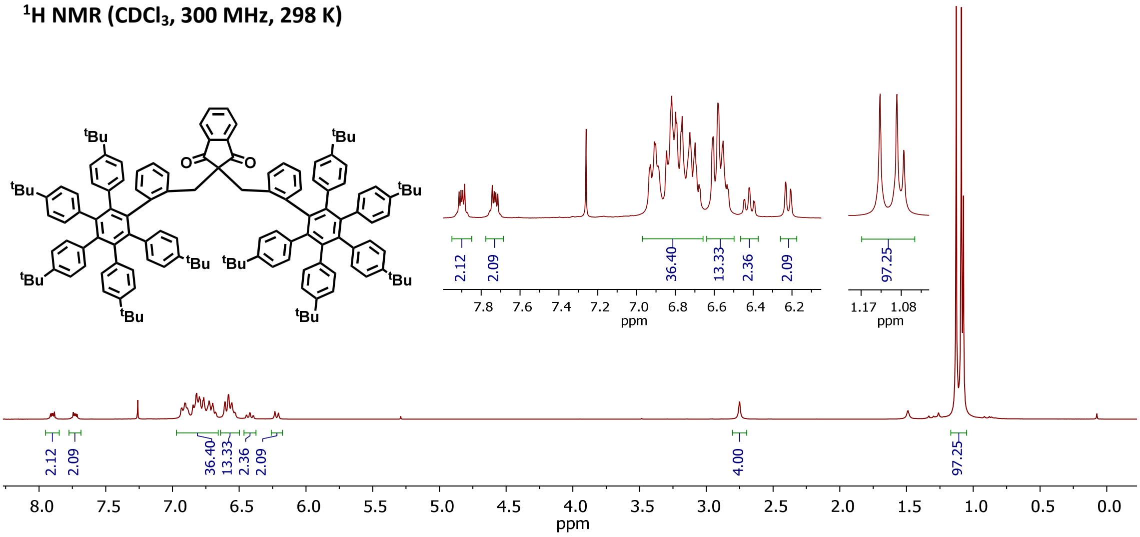


HRMS MALDI-TOF (DCTB)

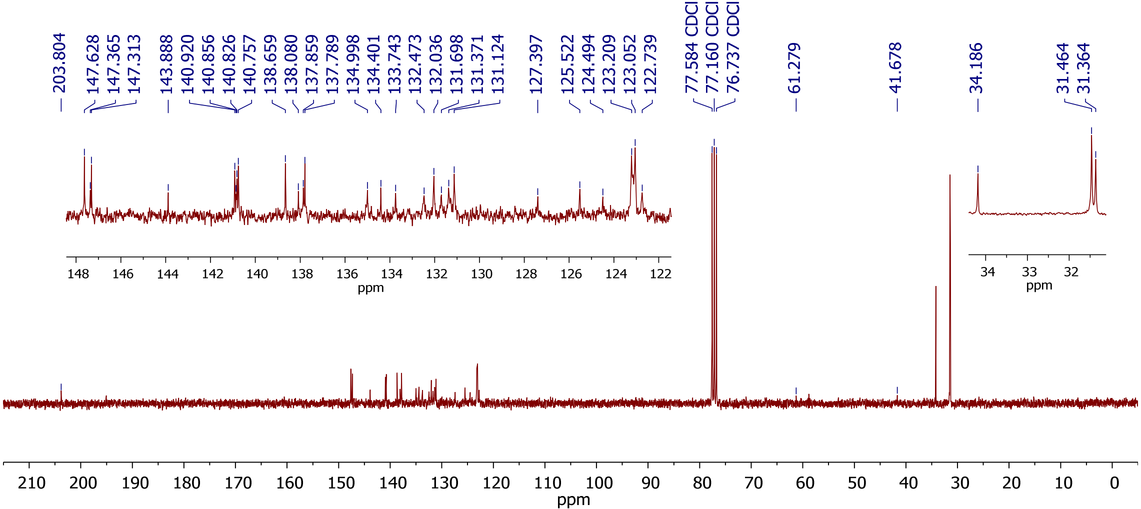


2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandione – 5

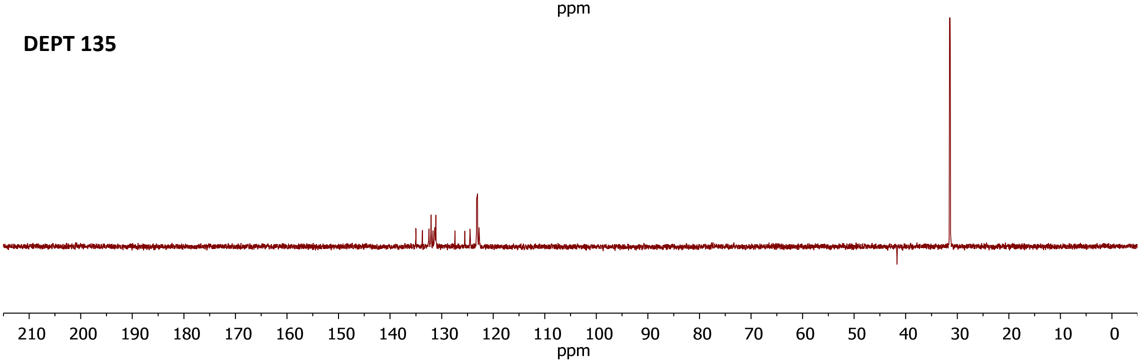
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



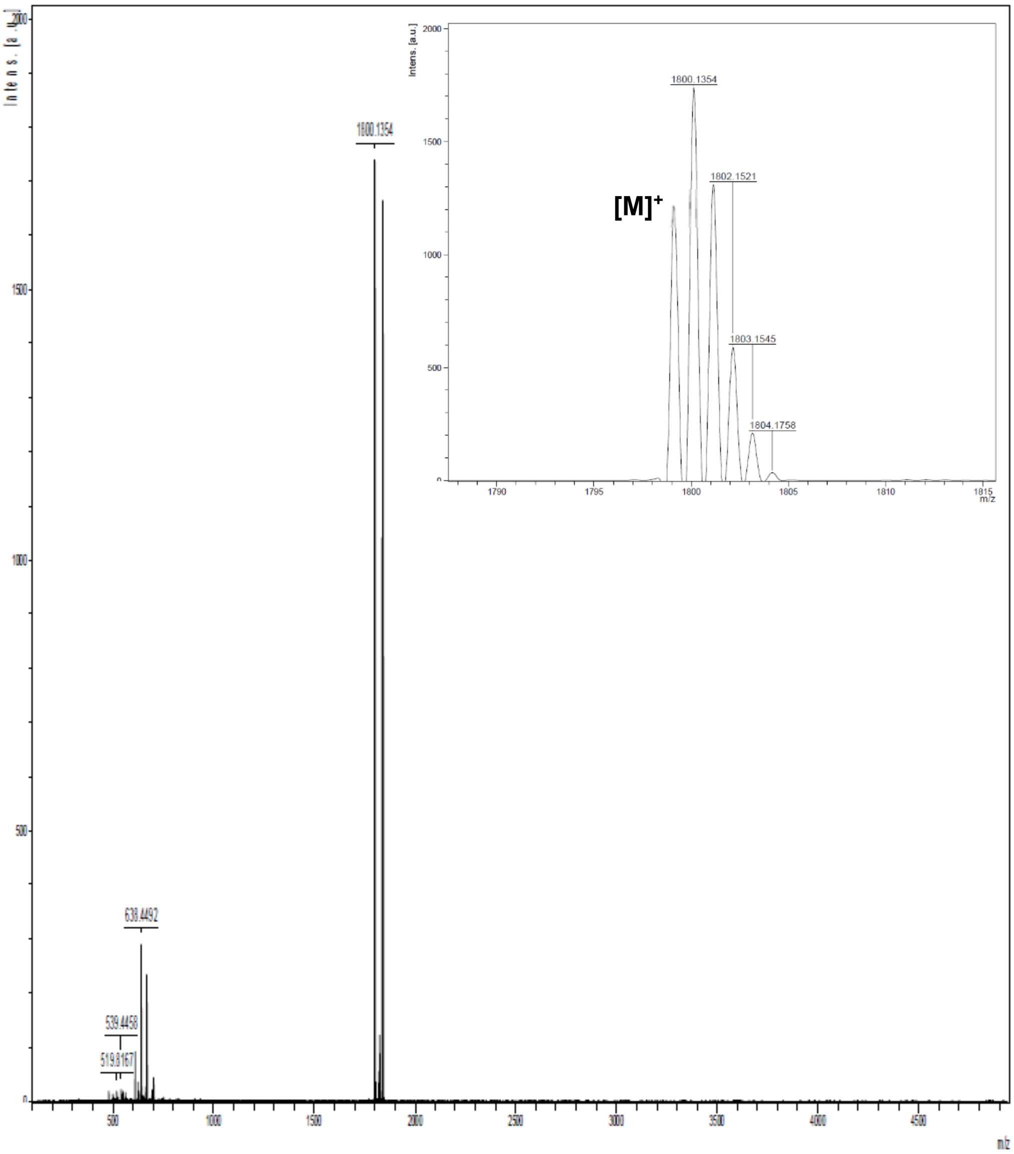
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

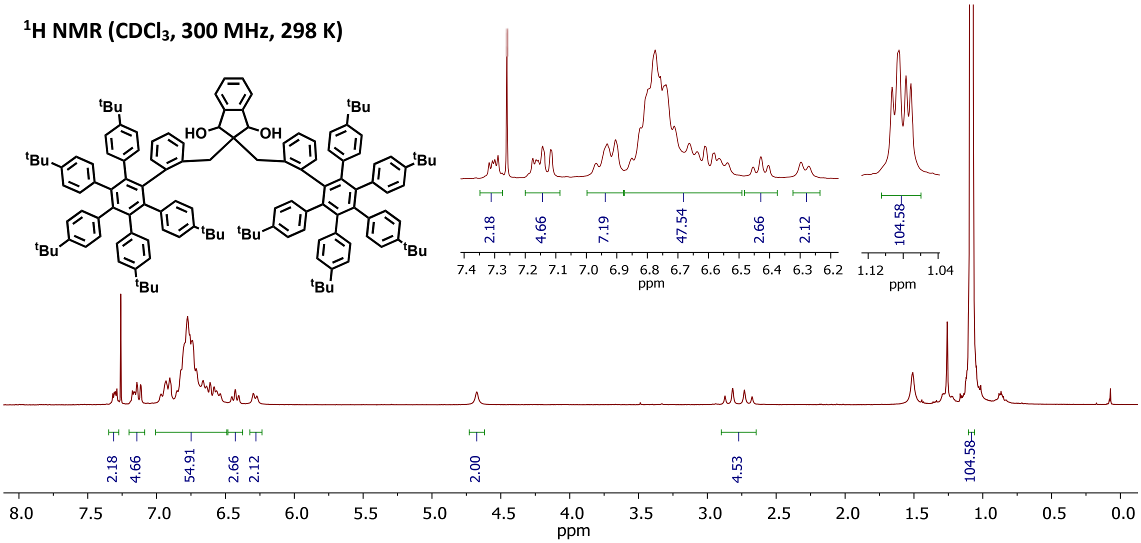


HRMS MALDI-TOF (DCTB)

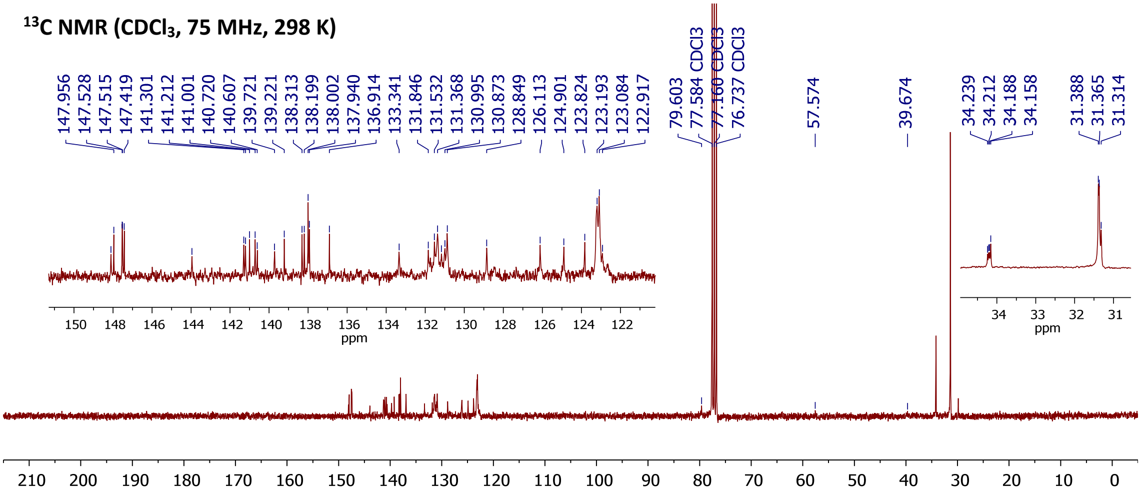


Racemic (S,S) + (R,R) 2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – trans 6

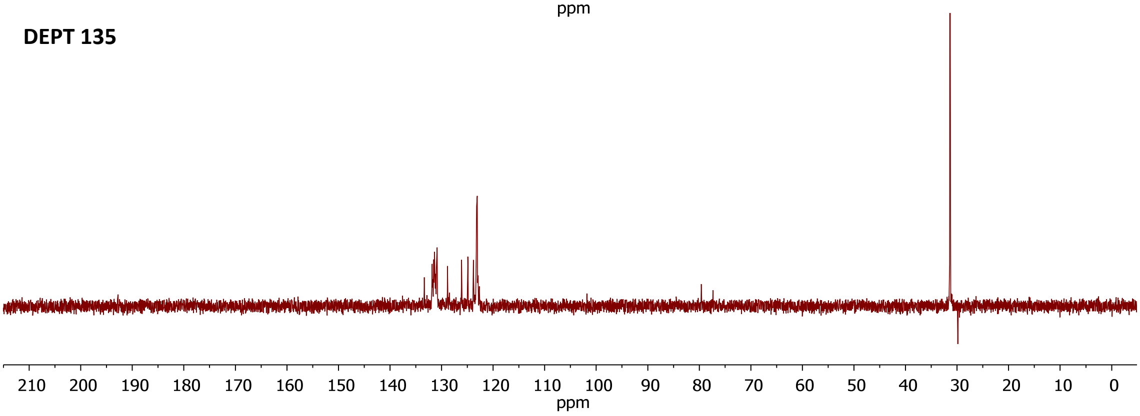
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K)



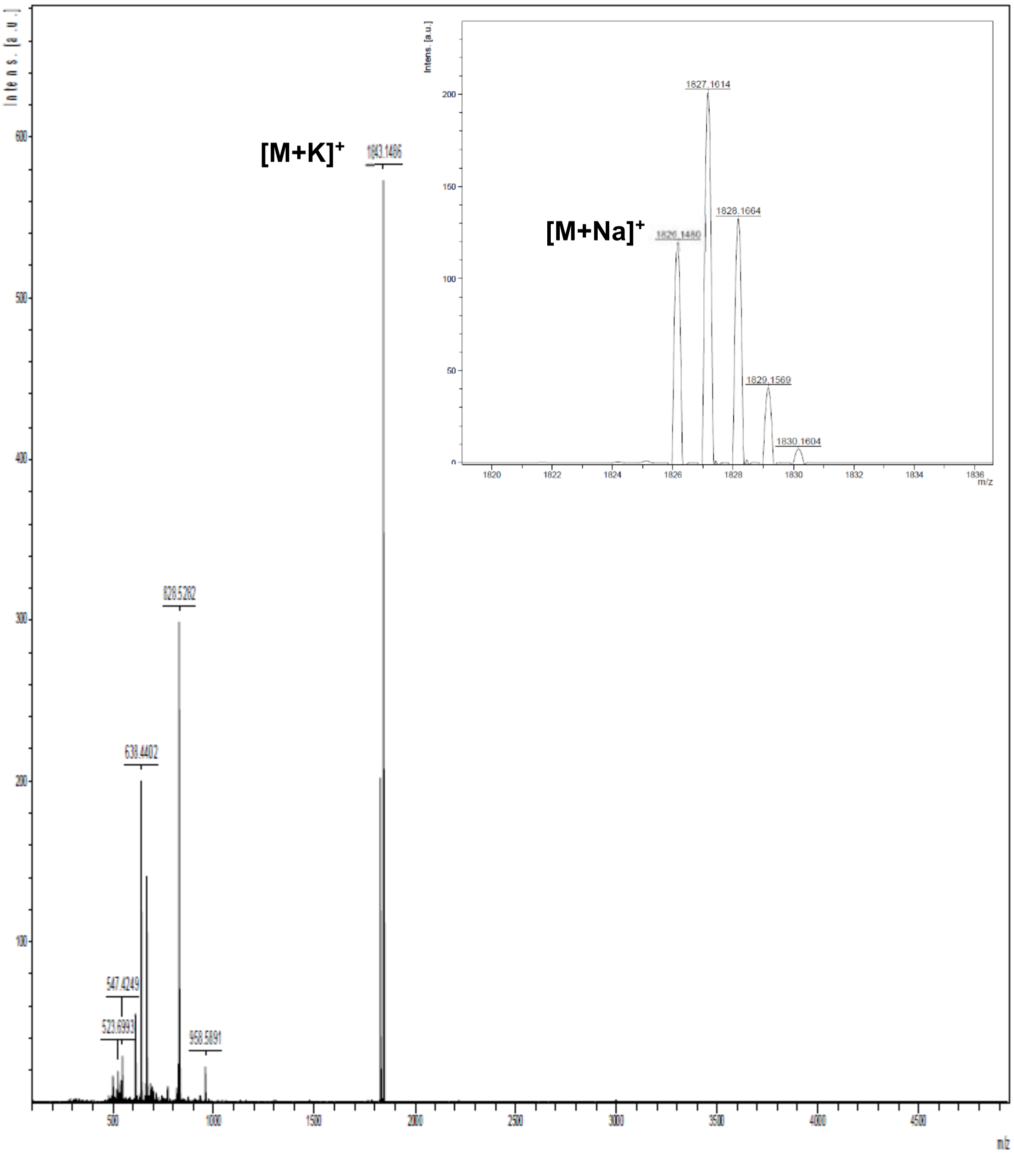
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K)



DEPT 135

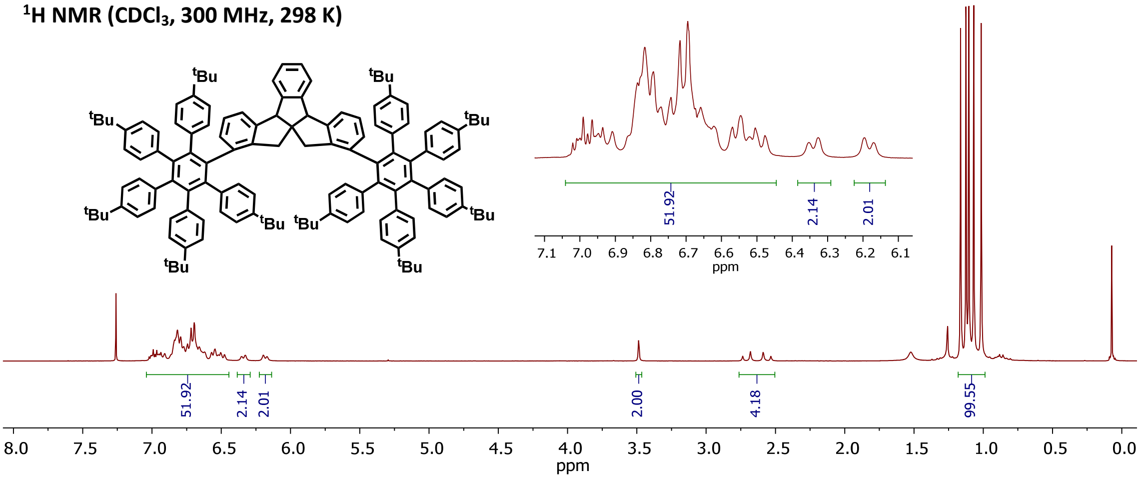


HRMS MALDI-TOF (DCTB)

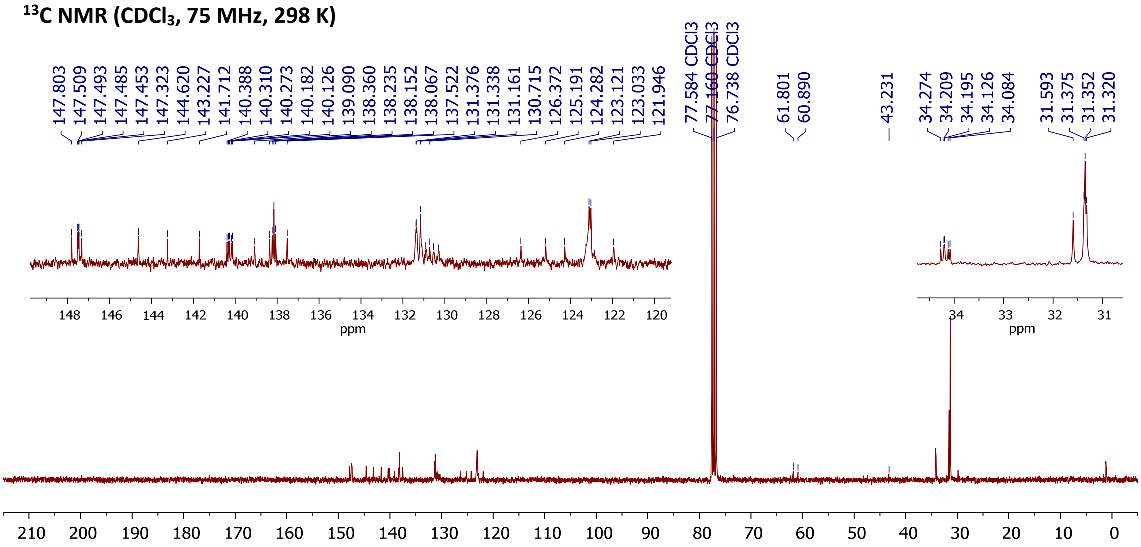


Racemic (S,S,S$_a$) + (R,R.R$_a$) bis-2-[penta(4-tert-butylphenyl)benzene]centrotriindan – Rac-7

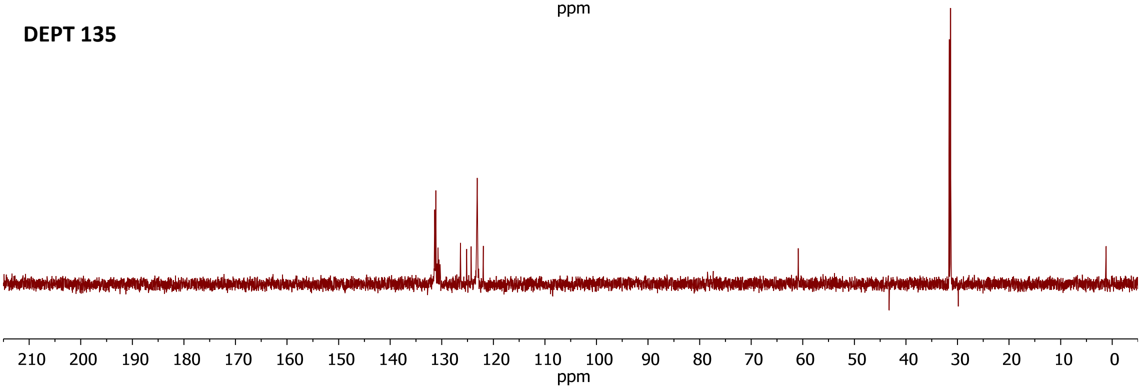
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



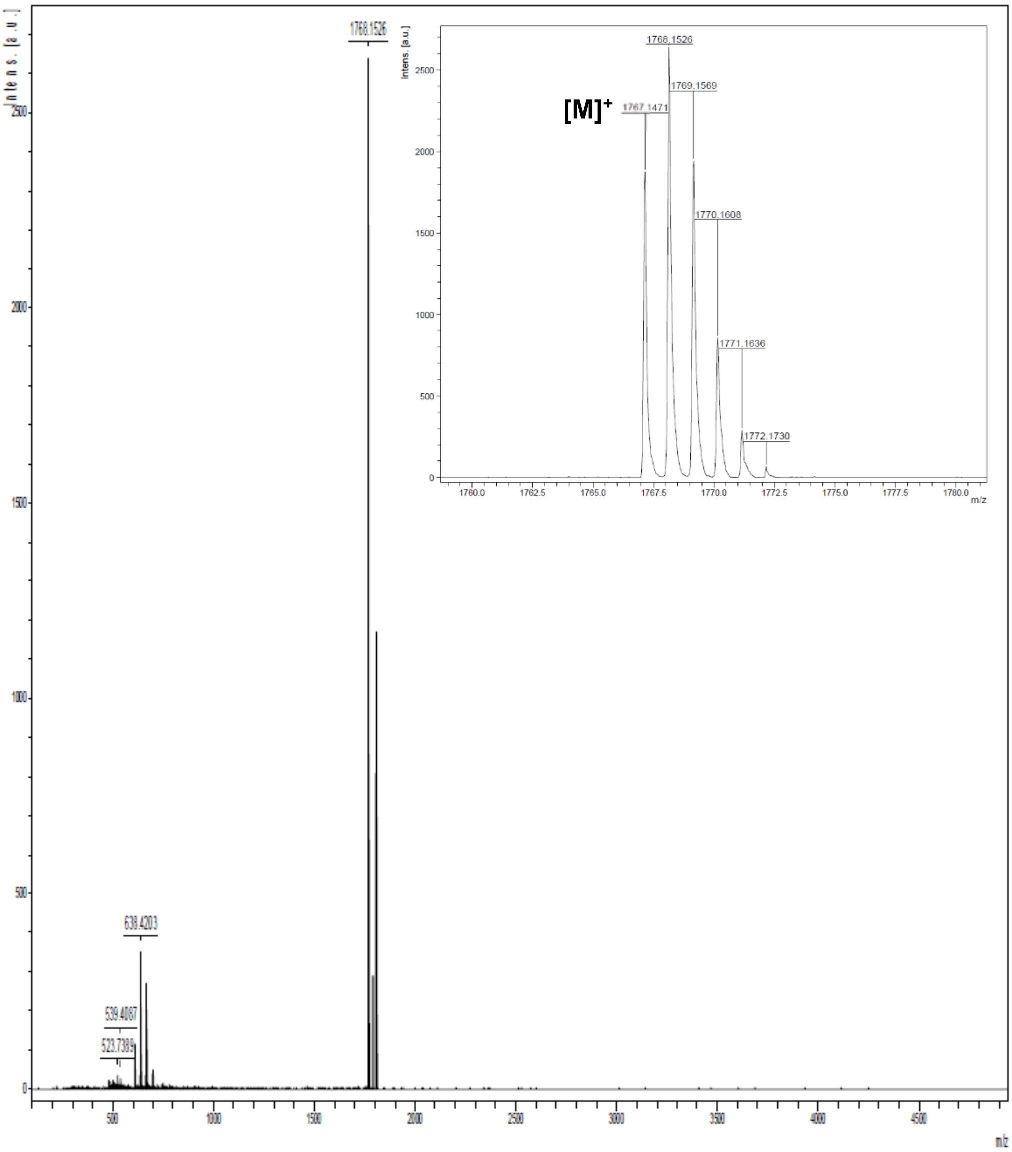
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

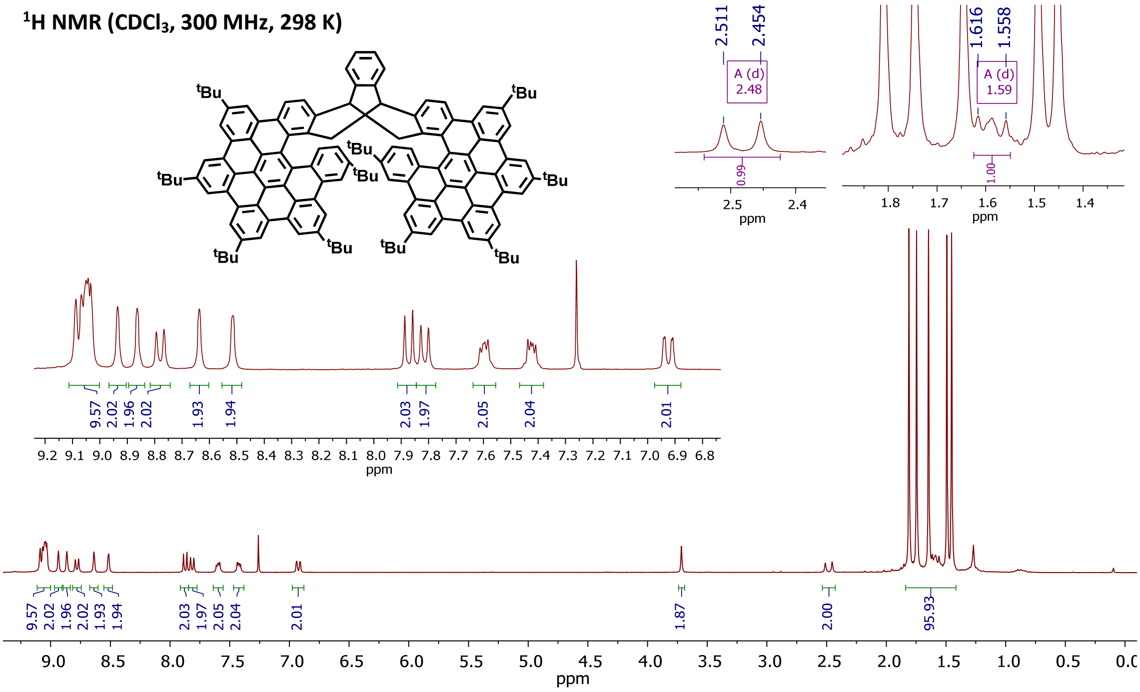


HRMS MALDI-TOF (DCTB)

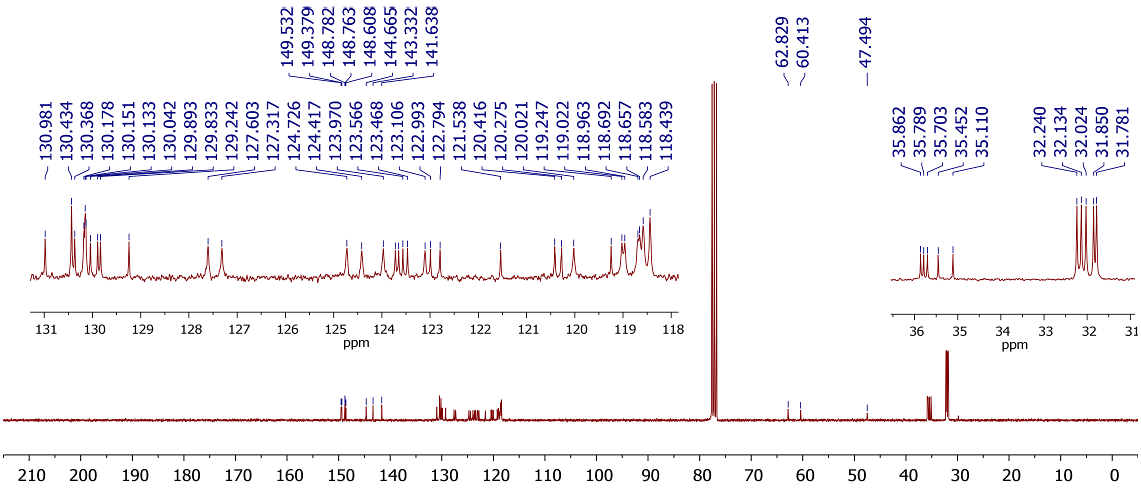


Racemic (S,S,S$_a$,M,M) + (R,R,R$_a$,P,P) Rac-1

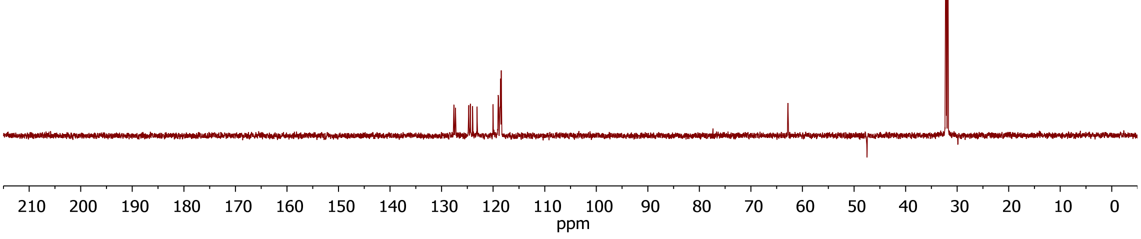
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



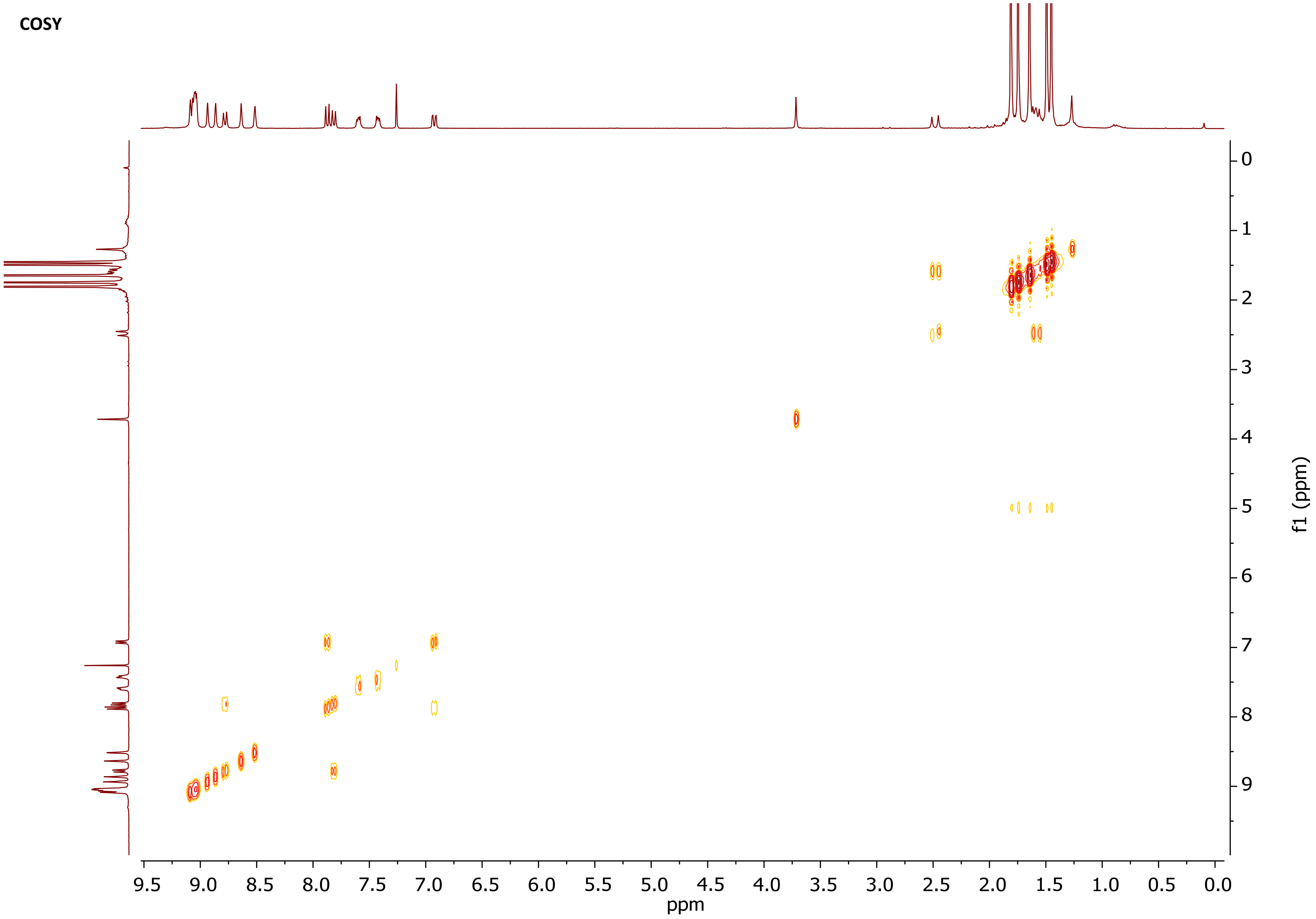
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



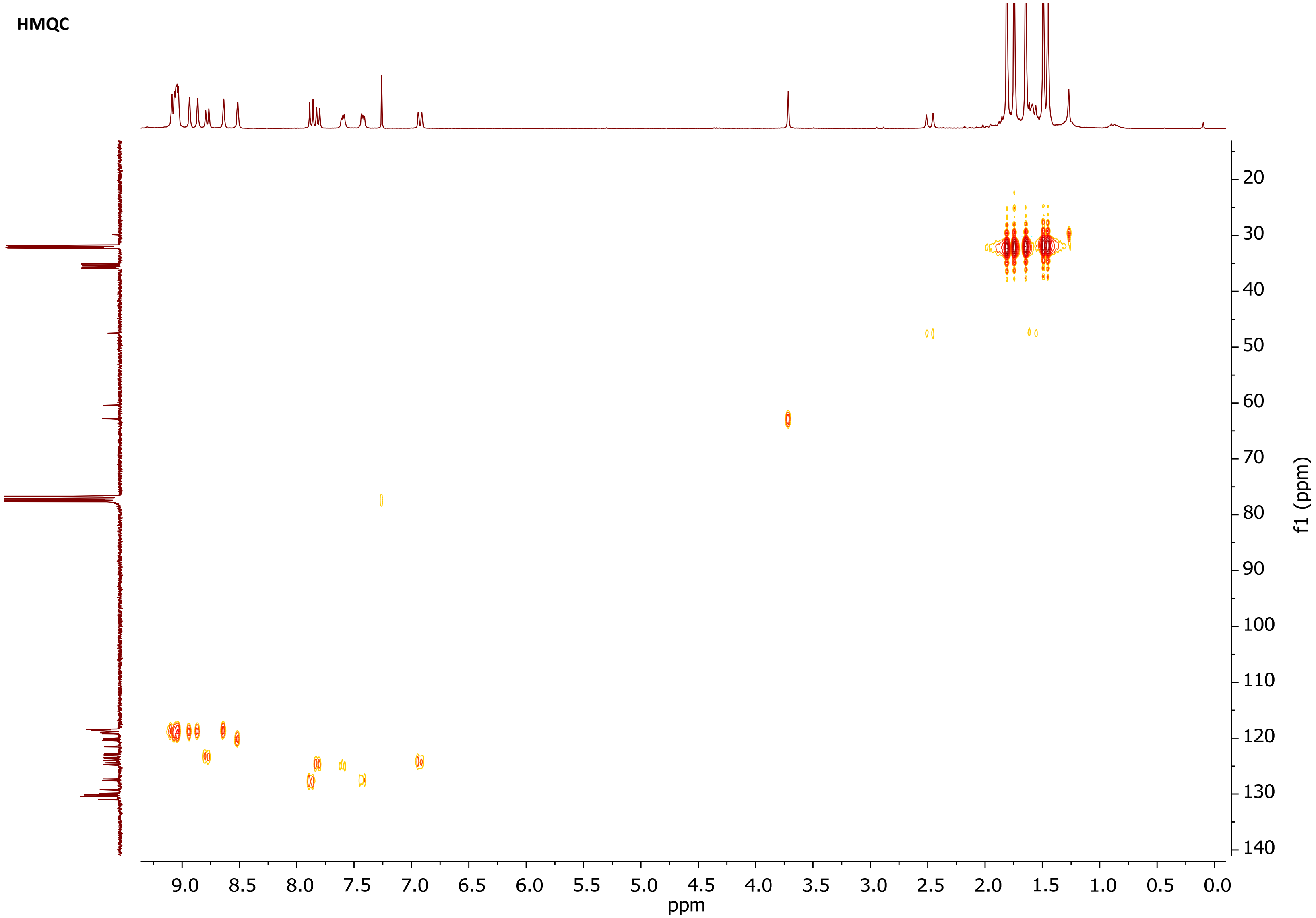
DEPT 135



COSY


9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

HMQC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3.0
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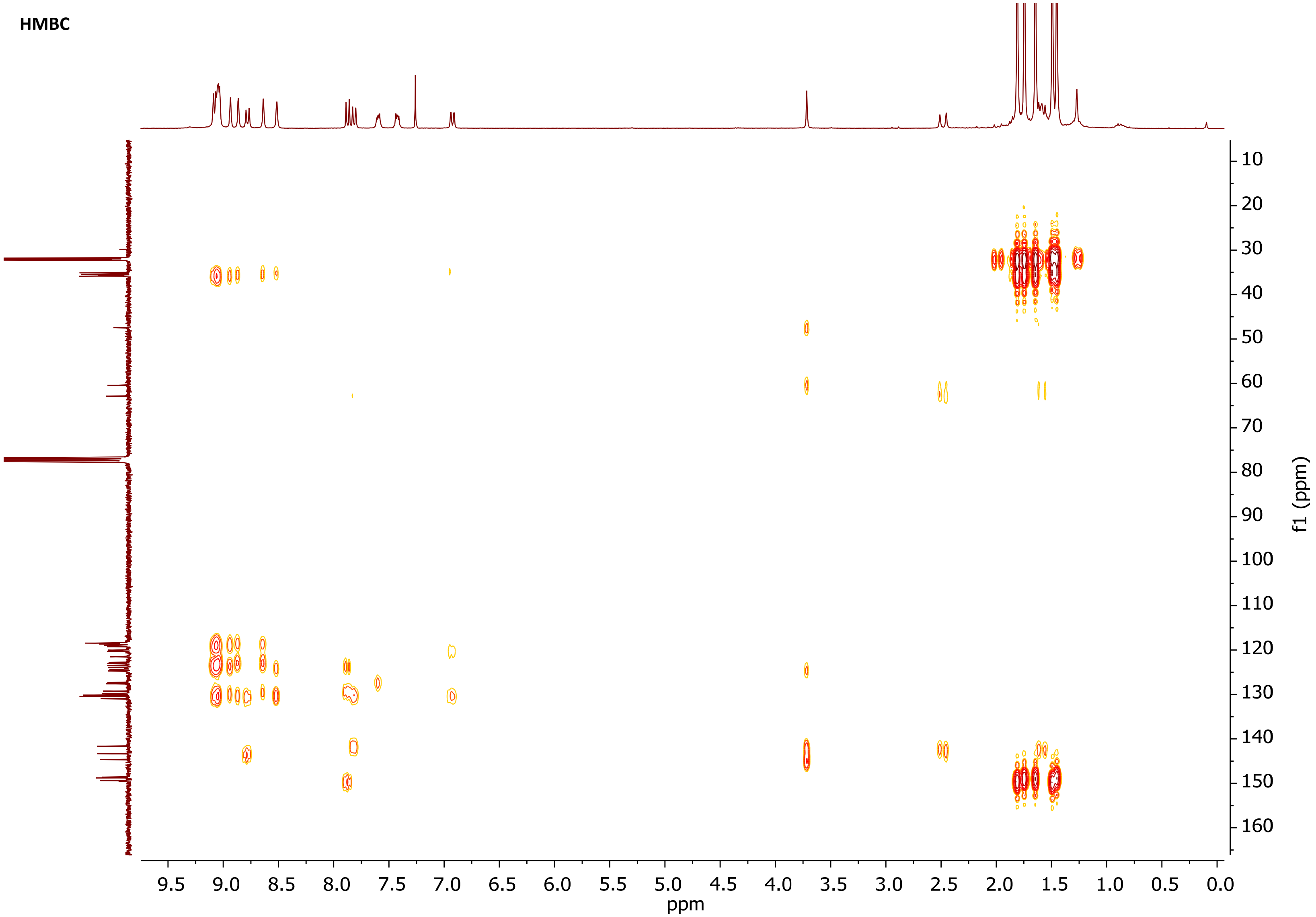
2.0
1.5
1.0
0.5
0.0
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

HMBC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20
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110
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130
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150
160
f1 (ppm)
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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0.5
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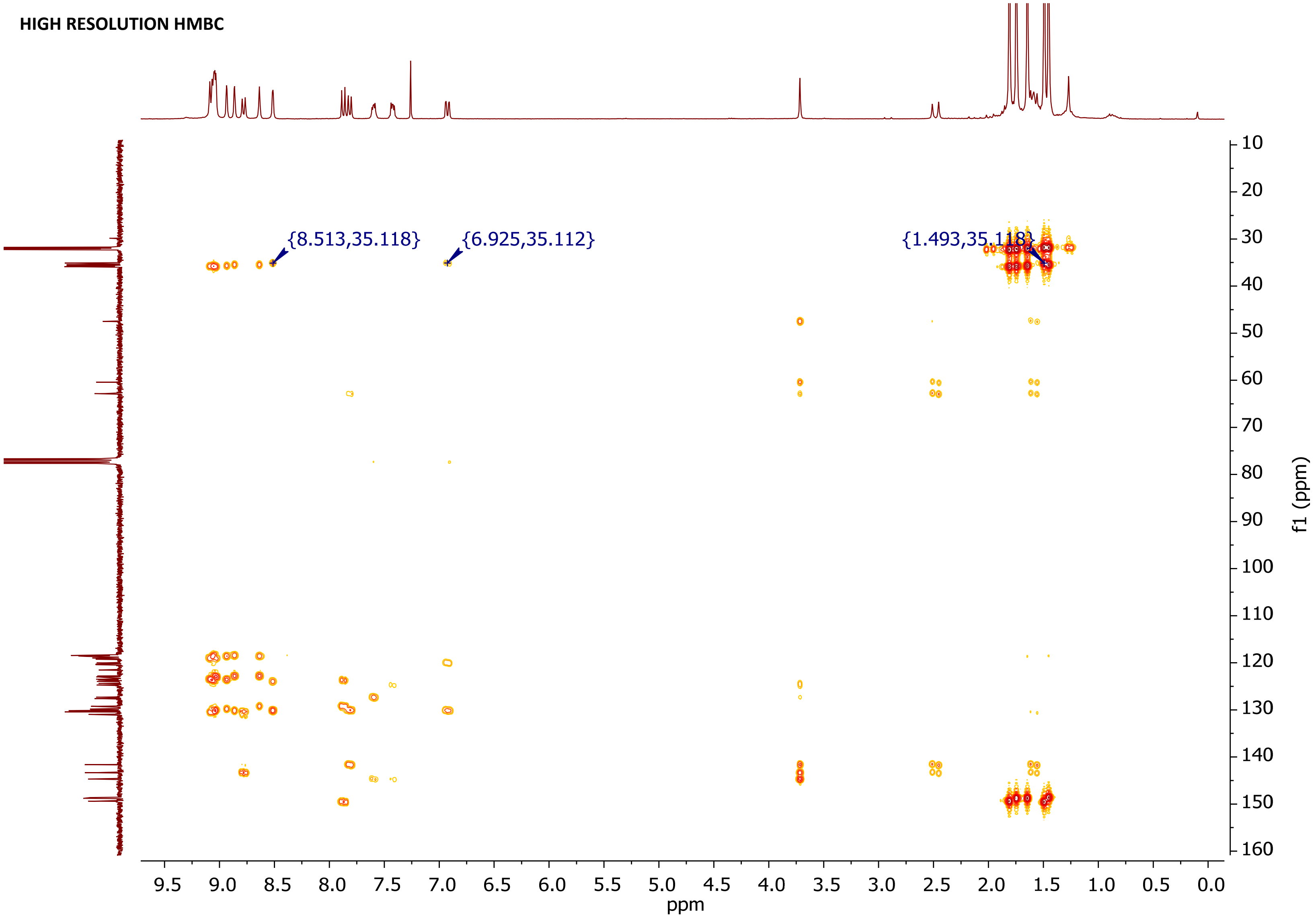
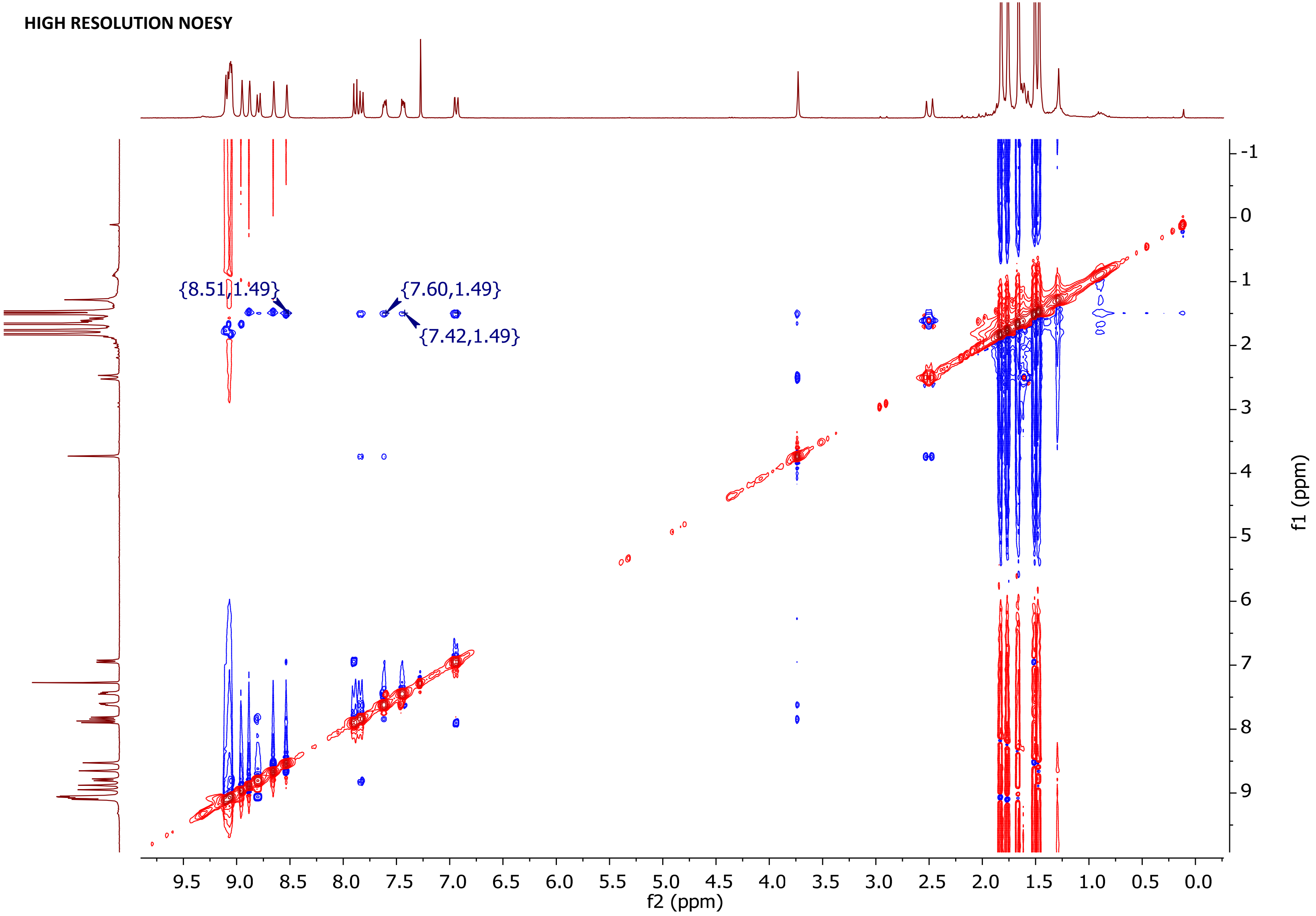
ppm

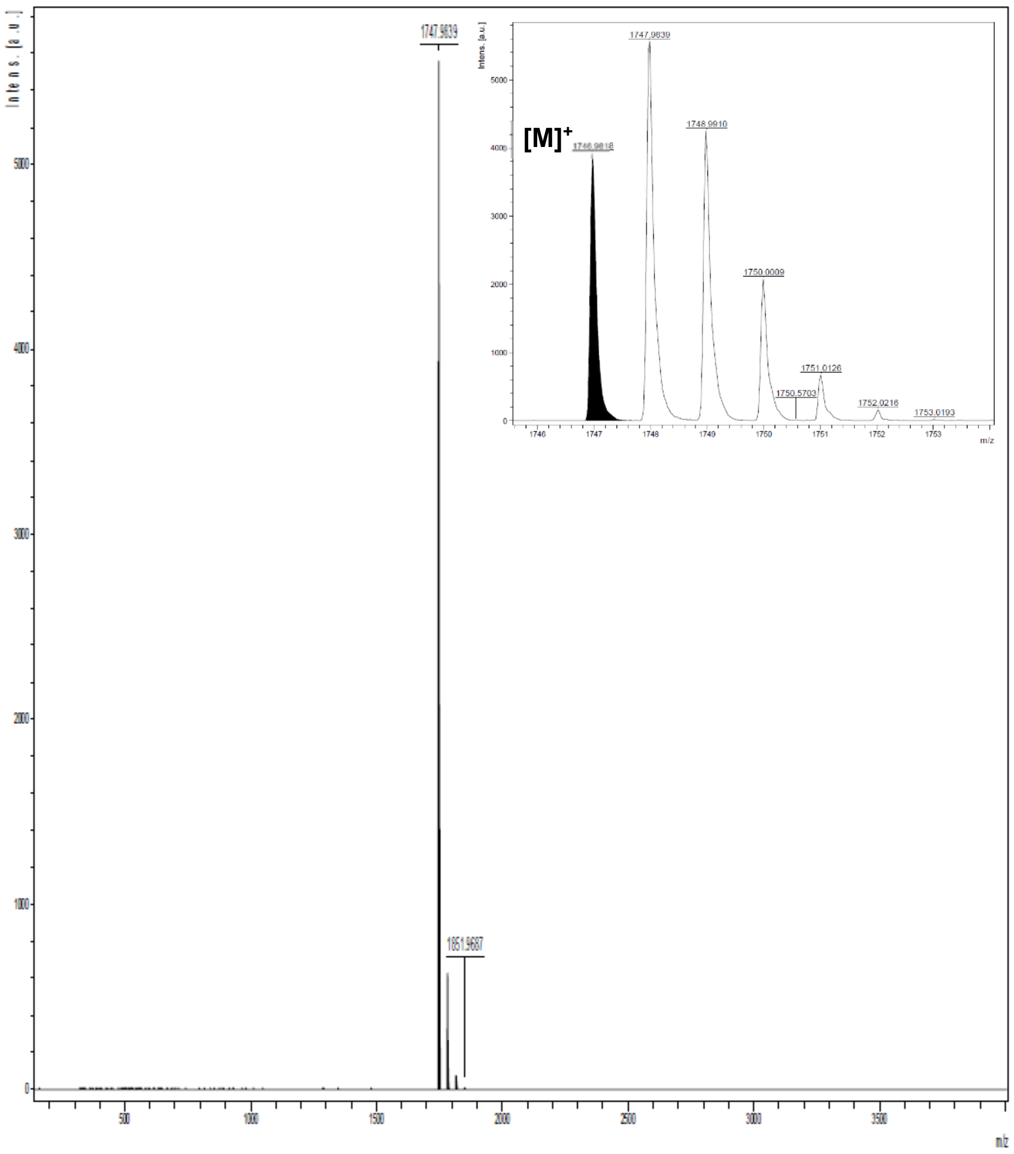
HIGH RESOLUTION HMBC



HIGH RESOLUTION NOESY

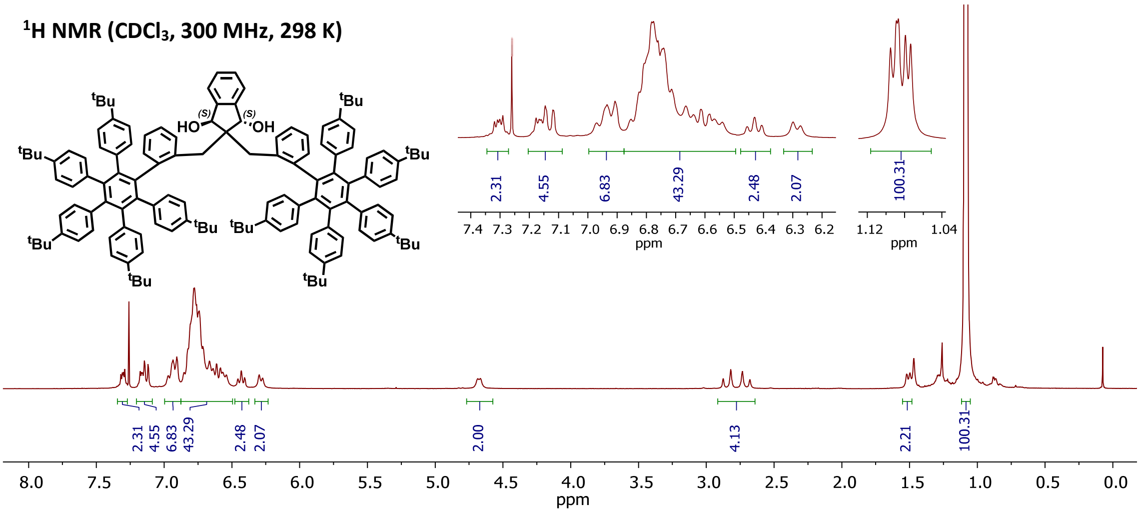


HRMS MALDI-TOF (DCTB)

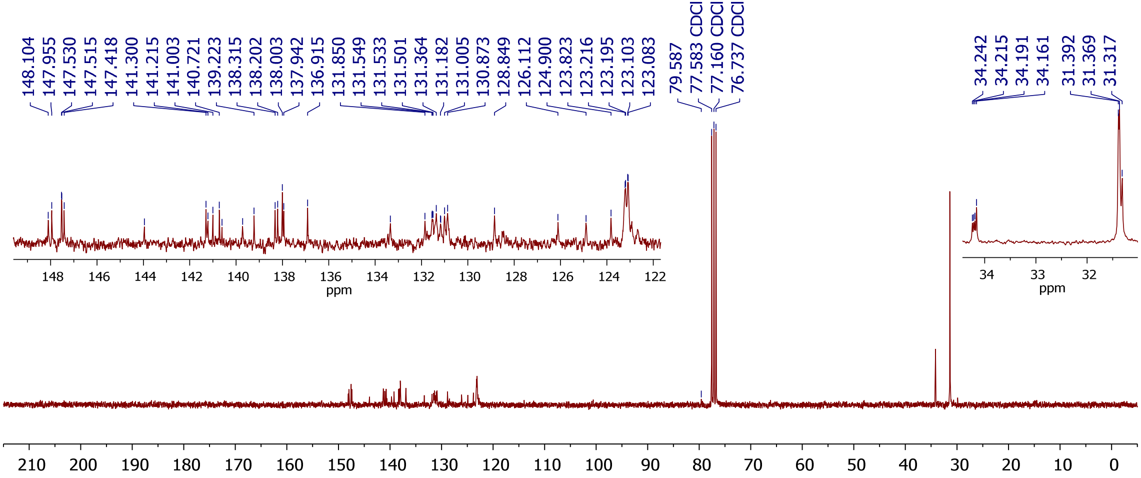


(S,S)-2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – (S,S)-6

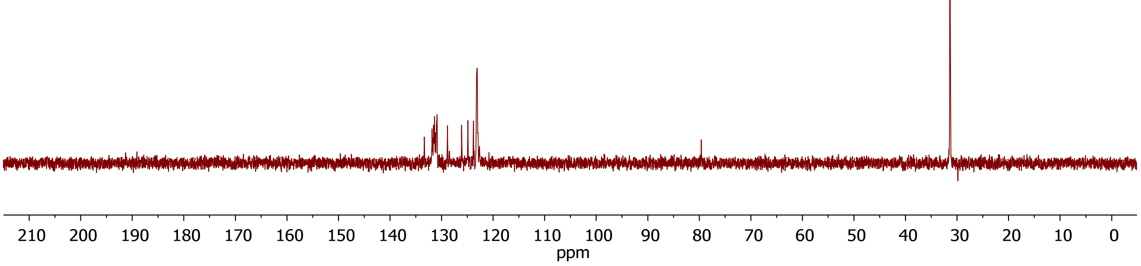
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K)



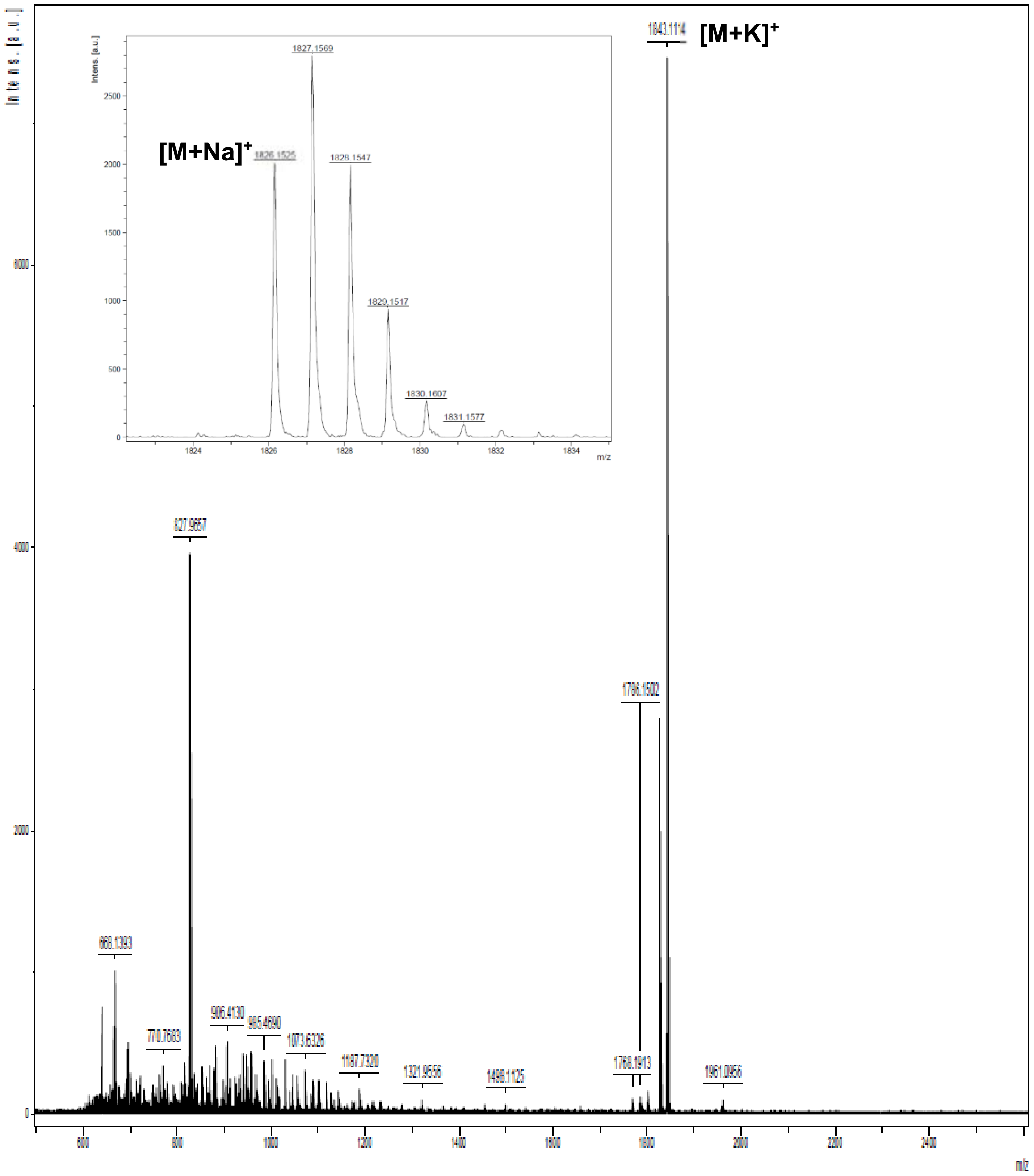
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K)



DEPT 135

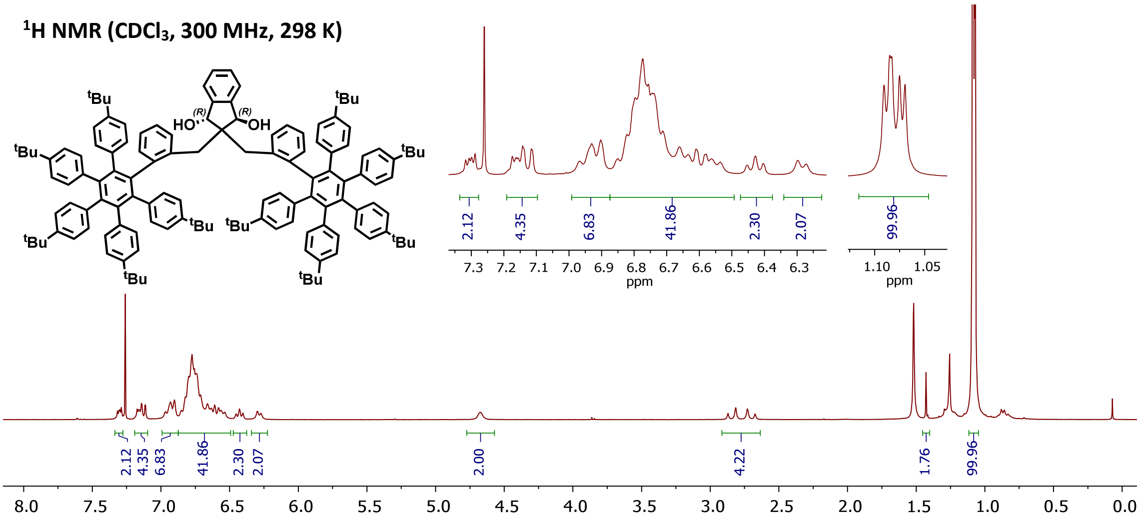


HRMS MALDI-TOF (DCTB)

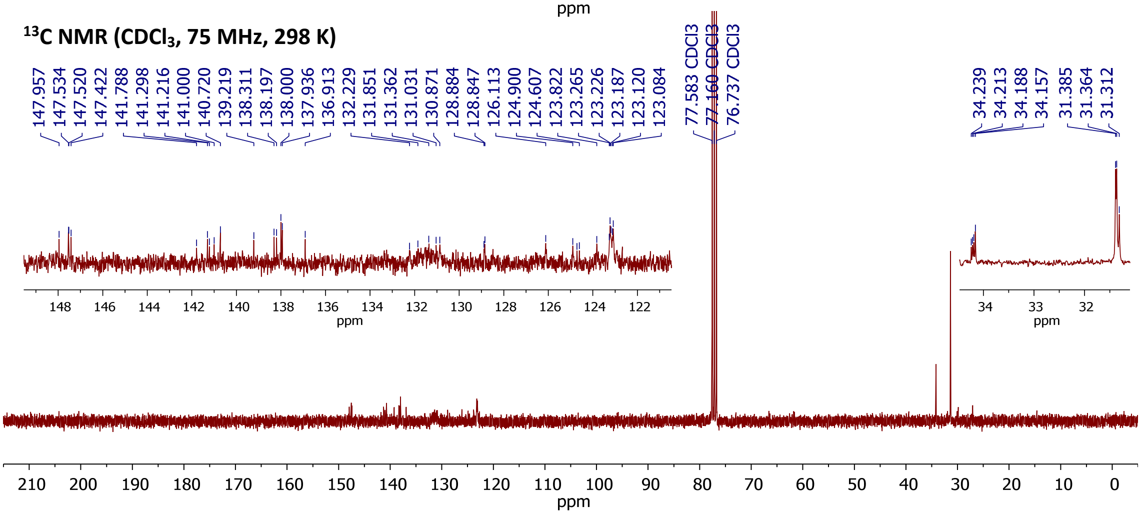


(R,R)-2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – (R,R)-6

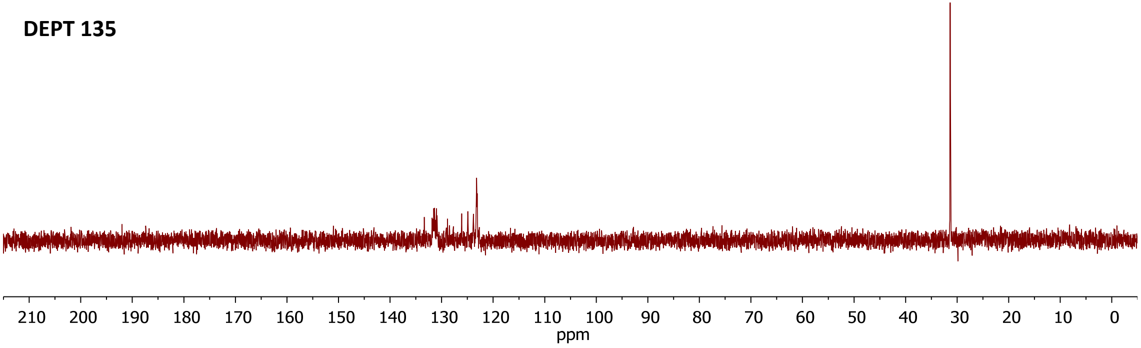
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K)



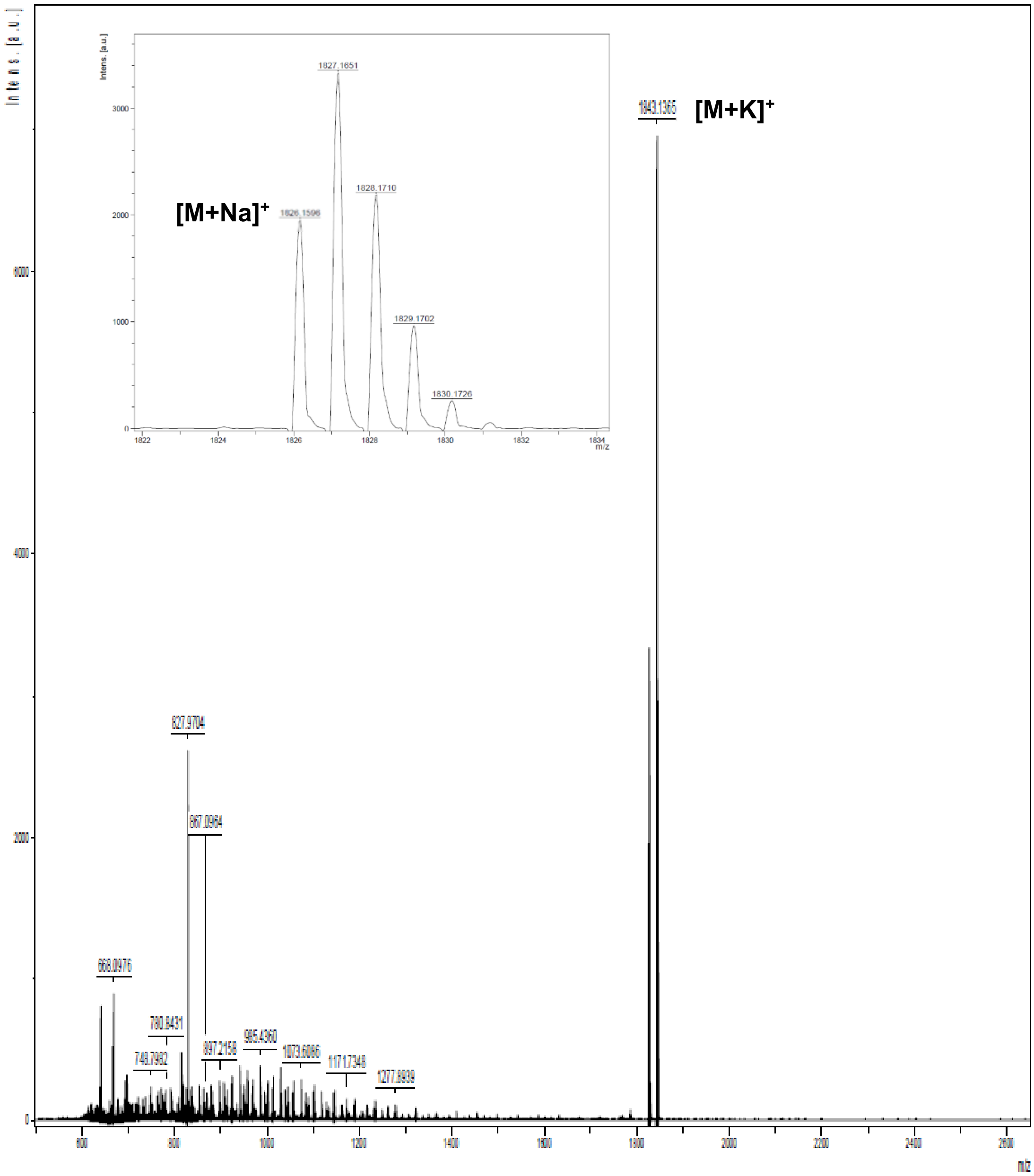
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K)



DEPT 135

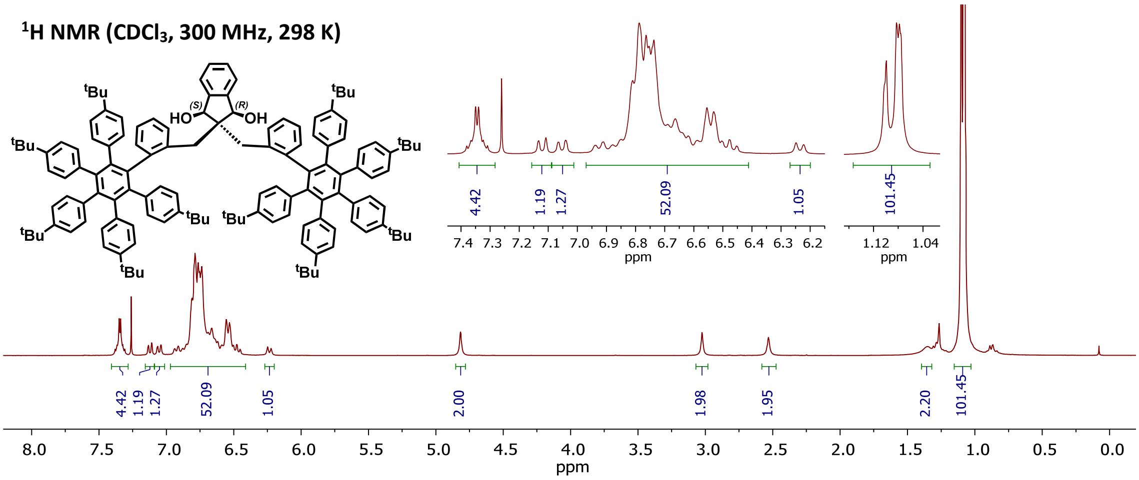


HRMS MALDI-TOF (DCTB)

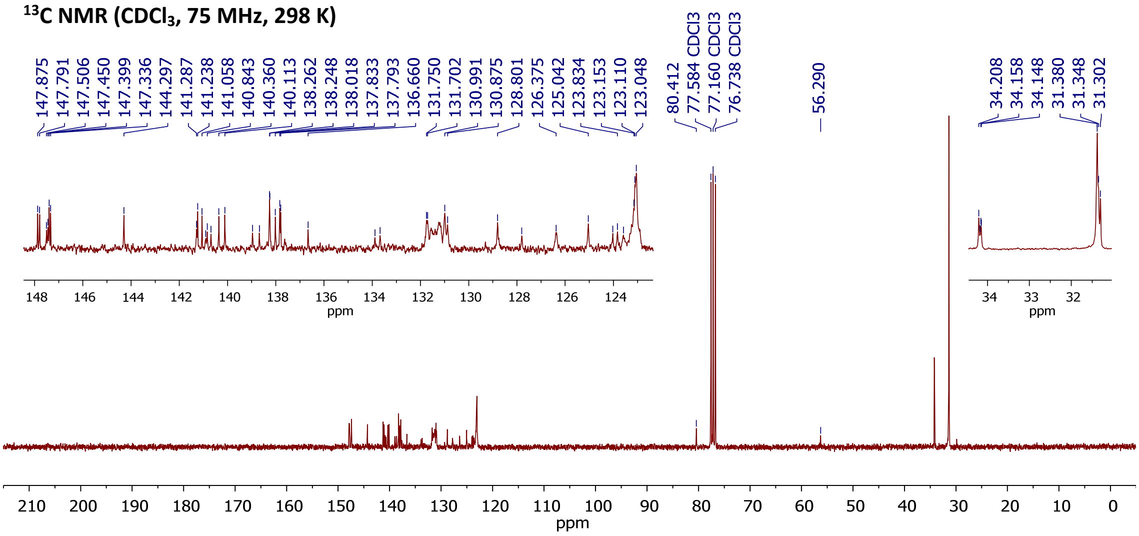


(S,R)-2,2-bis[2-[penta(4-tert-butylphenyl)benzene]benzyl]-1,3-indandiol – meso-6

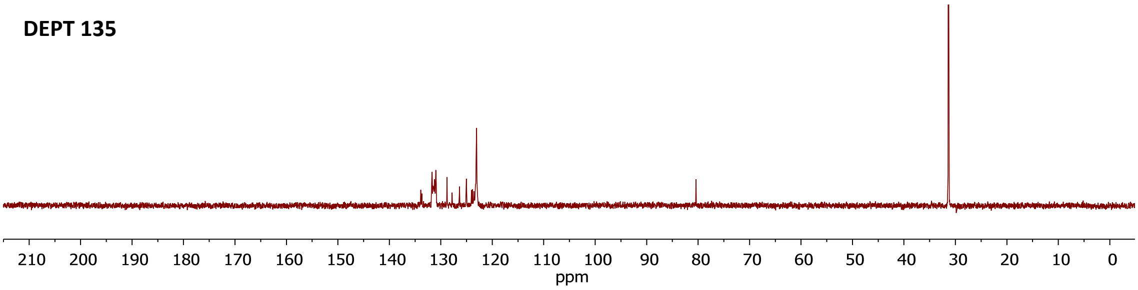
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



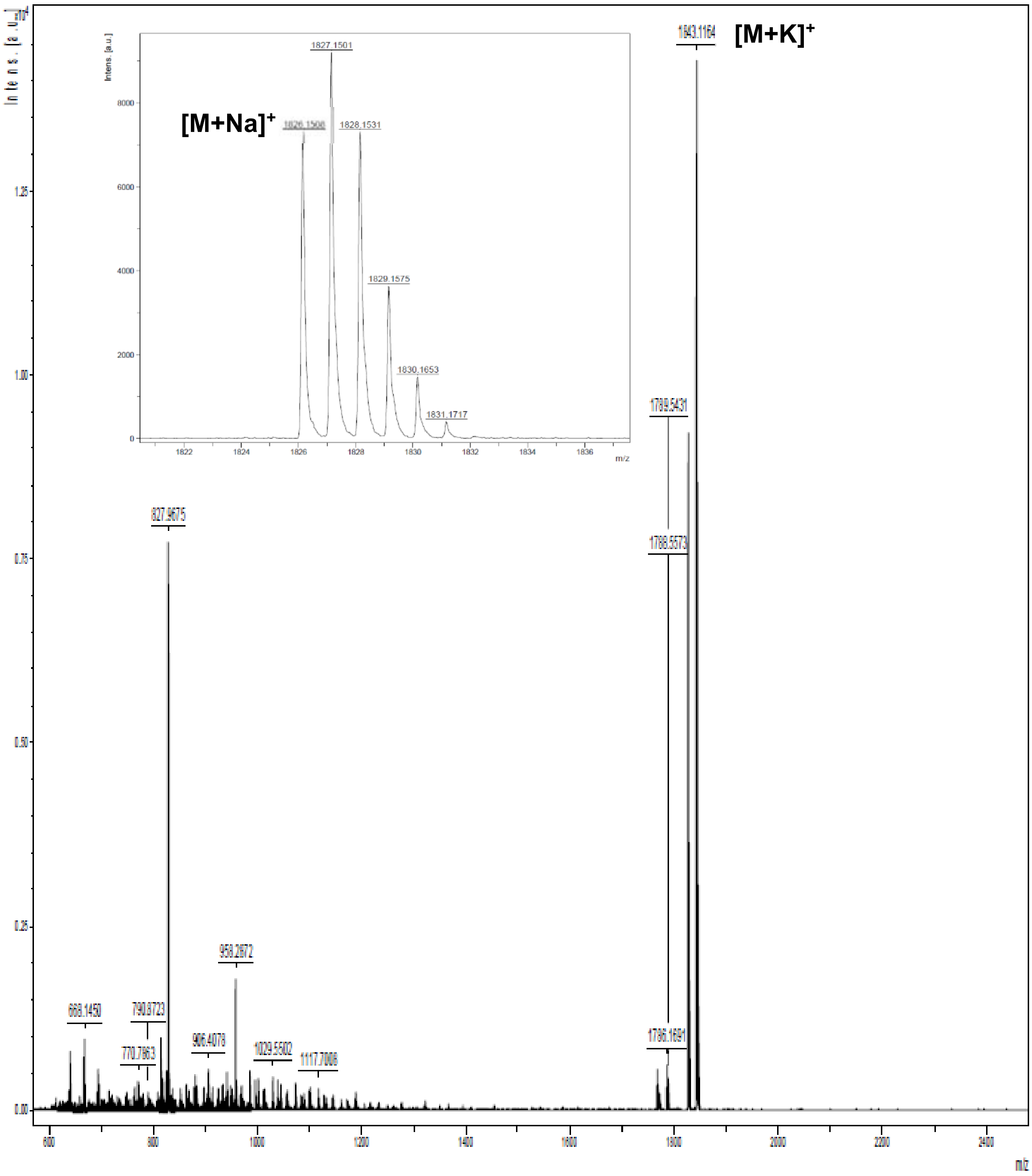
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

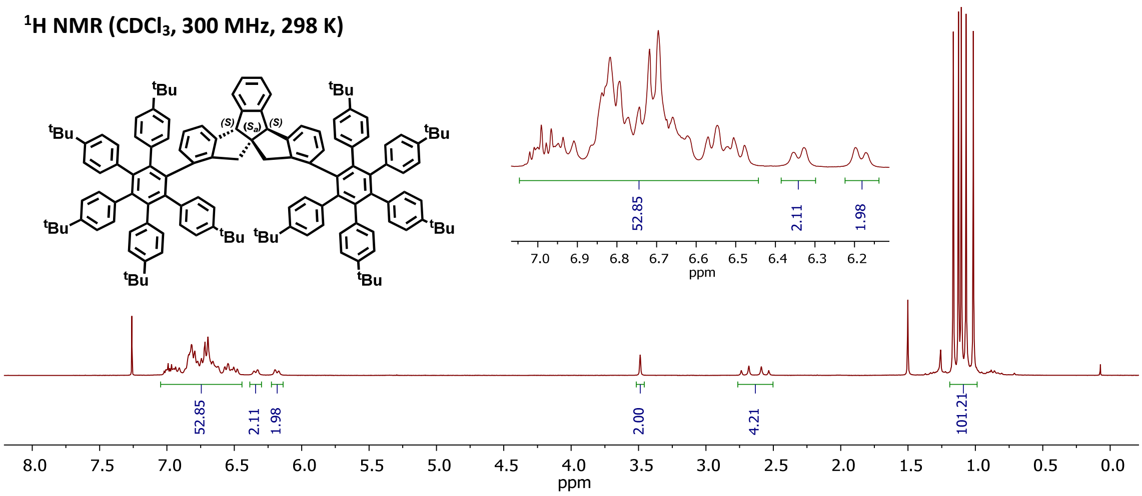


HRMS MALDI-TOF (DCTB)

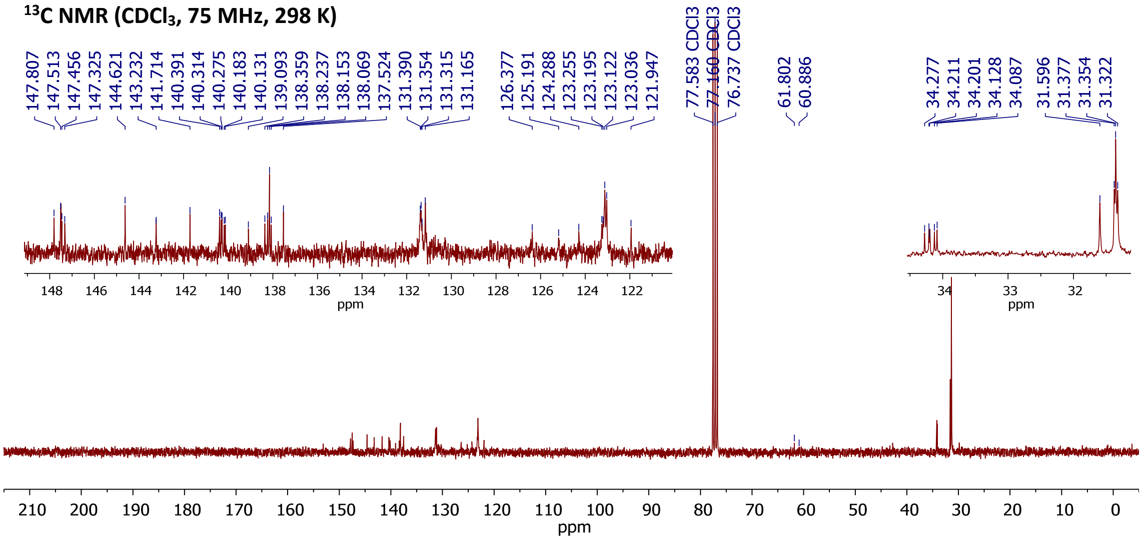


(S,S,S$_a$)-bis-2-[penta(4-tert-butylphenyl)benzene]centrotriindan – (S,S,S$_a$)-7

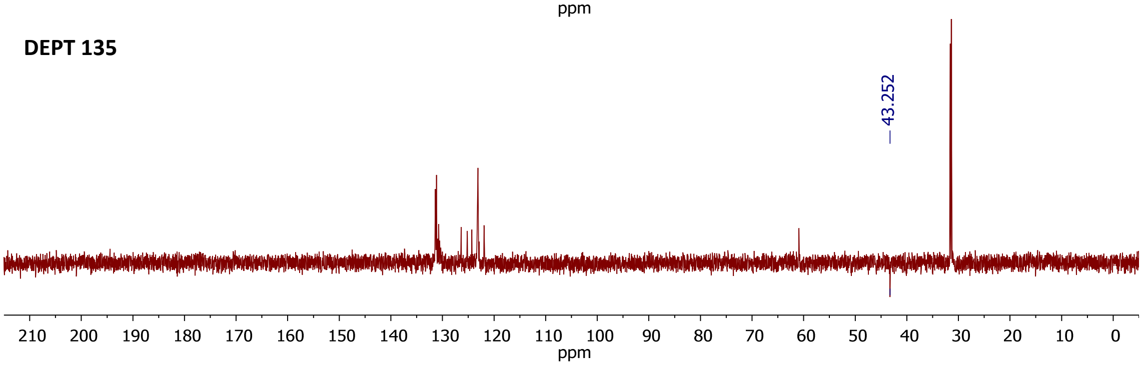
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



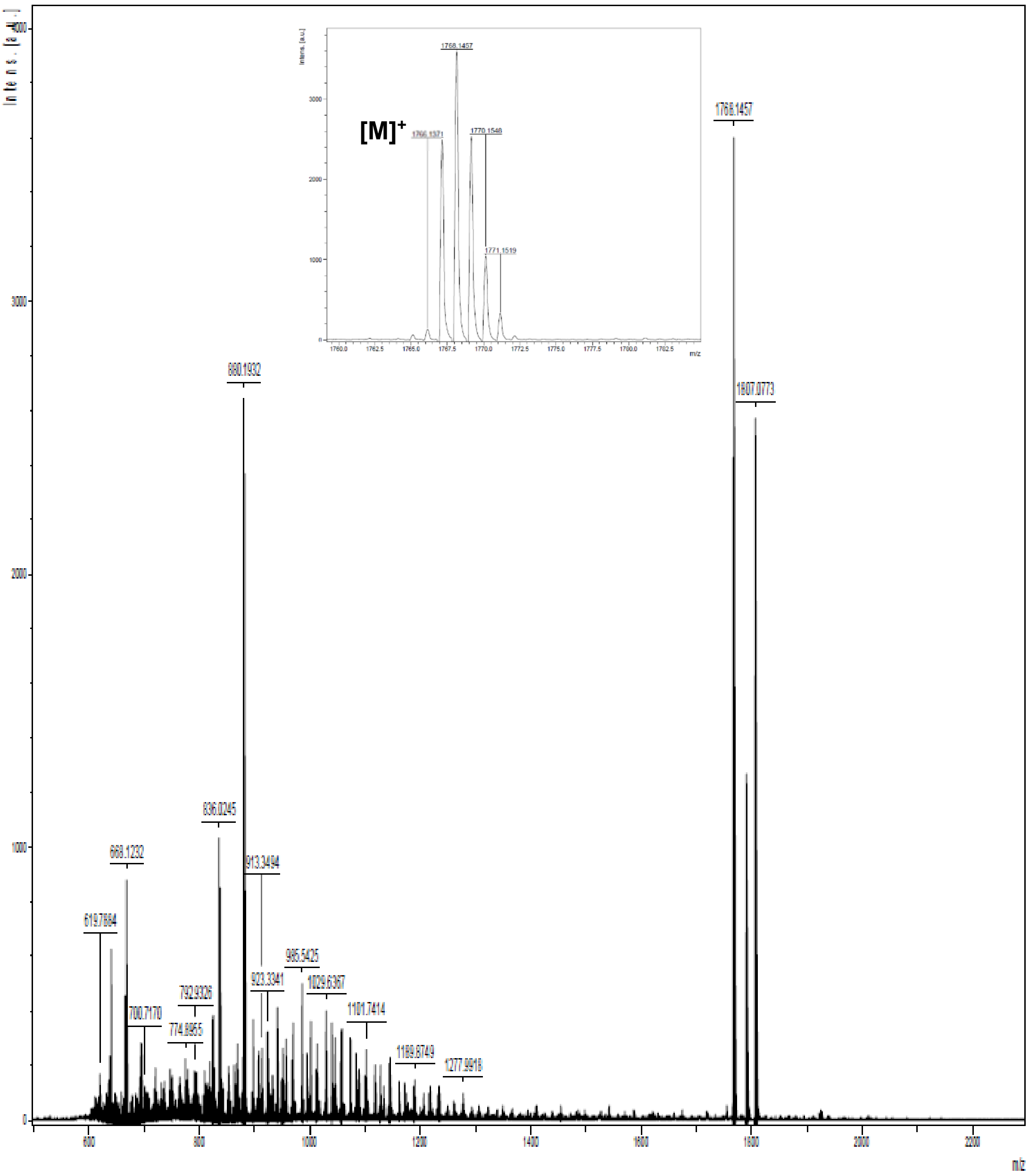
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

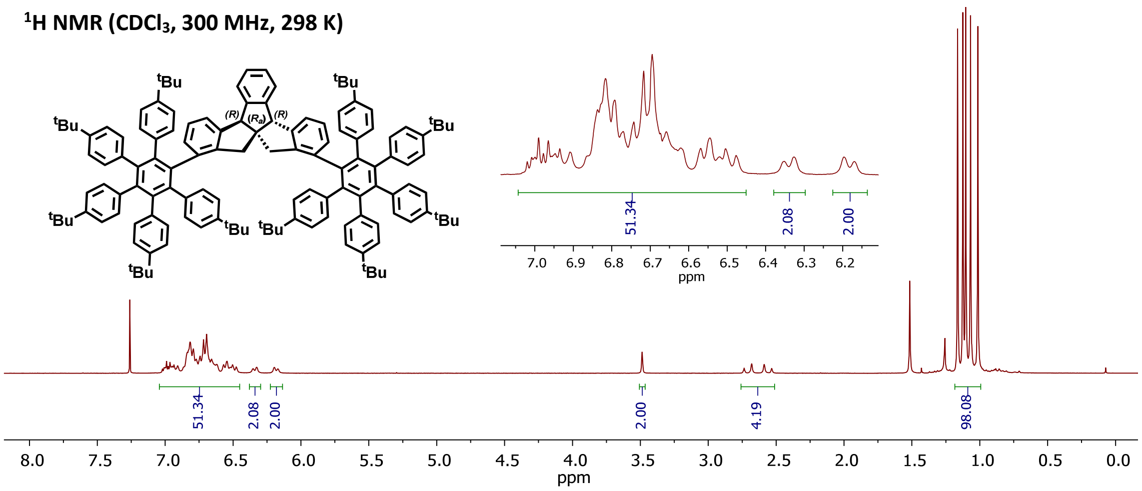


HRMS MALDI-TOF (DCTB)

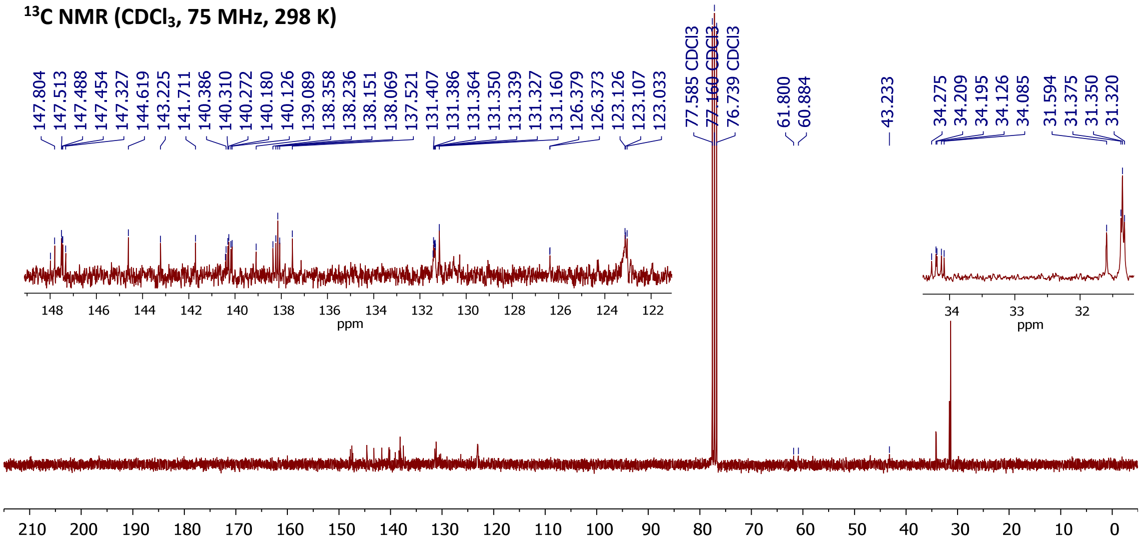


(R,R.R$_a$)-bis-2-[penta(4-tert-butylphenyl)benzene]centrotriindan – (R,R.R$_a$)-7

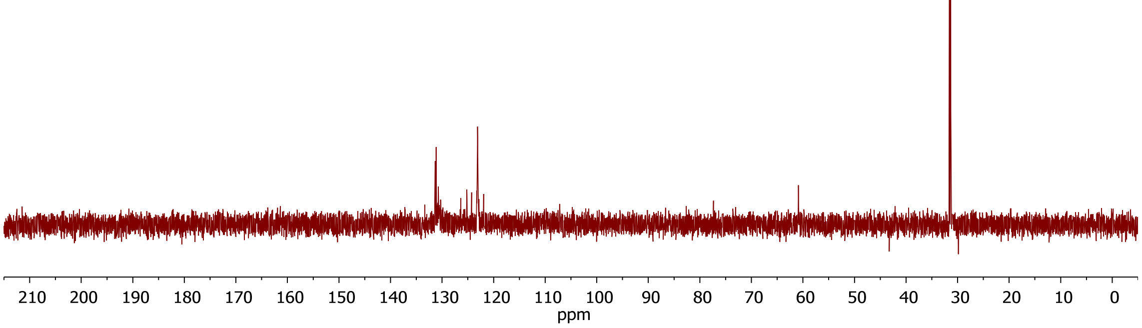
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



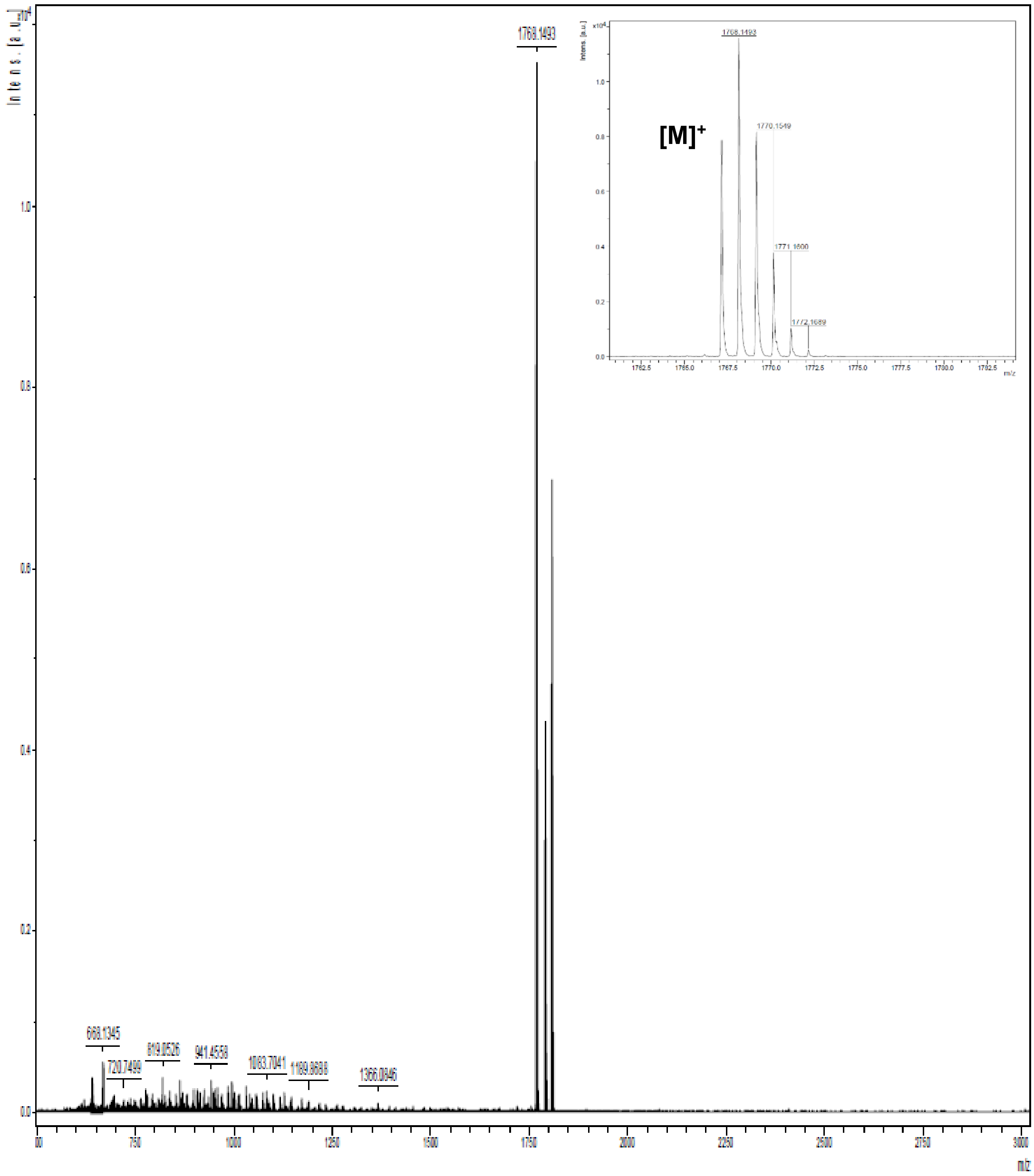
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

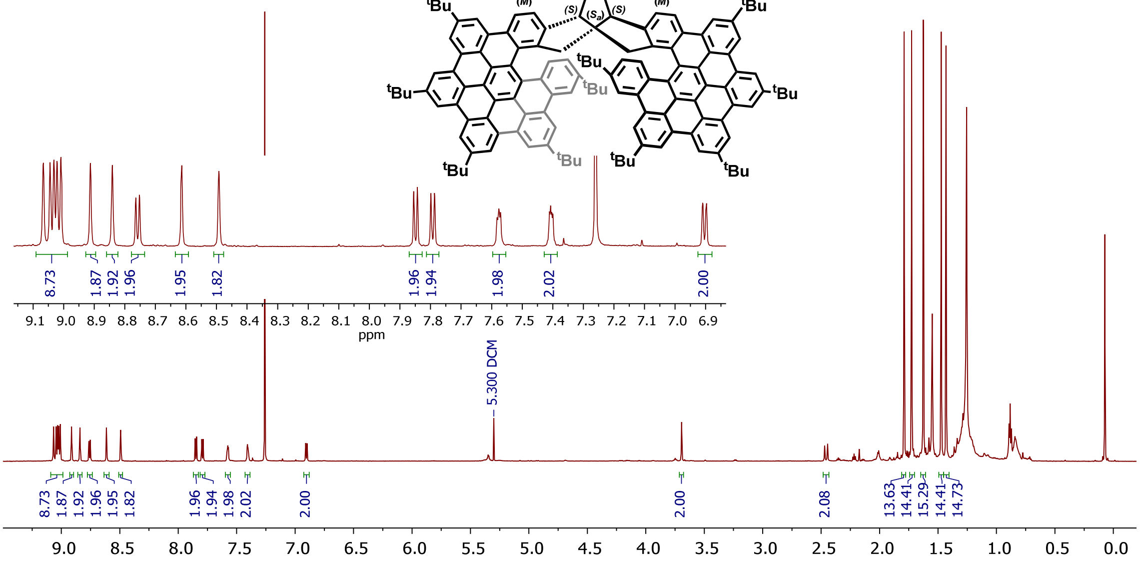


HRMS MALDI-TOF (DCTB)

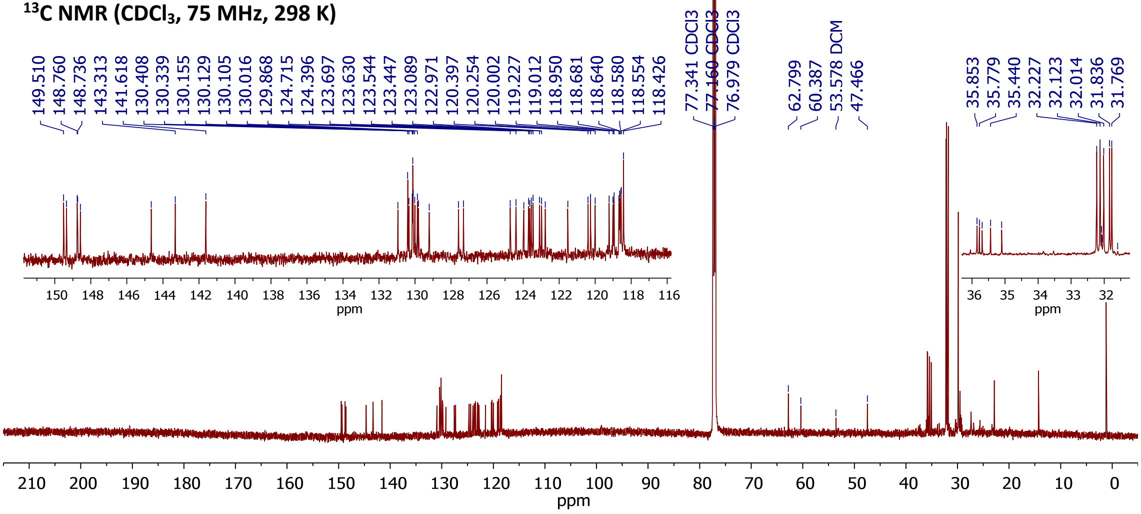


(S,S,S$_a$,M,M)-1

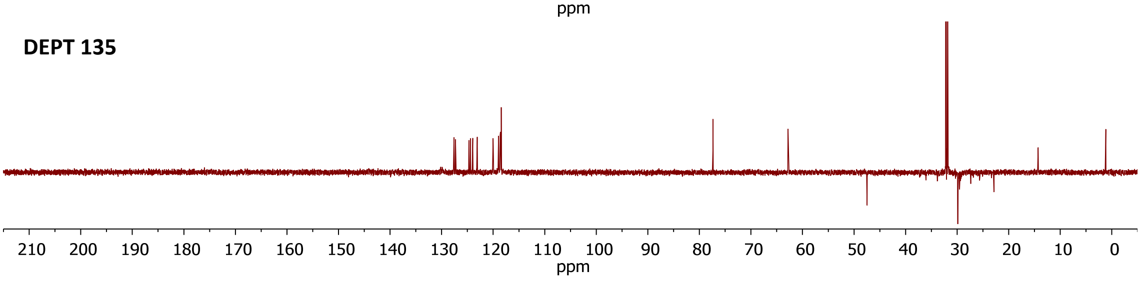
^{1}H NMR (CDCl$_3$, 300 MHz, 298 K)



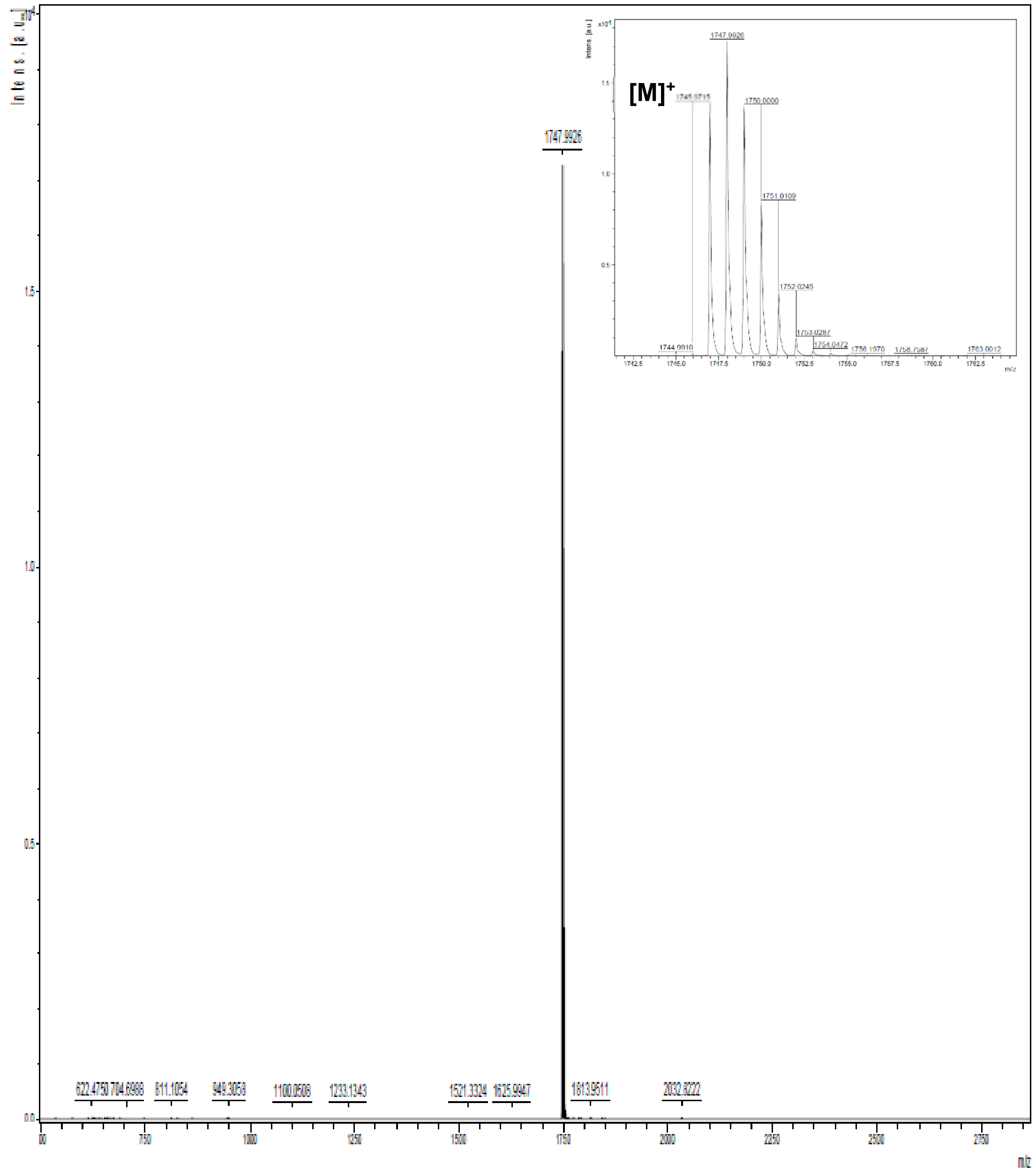
^{13}C NMR (CDCl$_3$, 75 MHz, 298 K)



DEPT 135

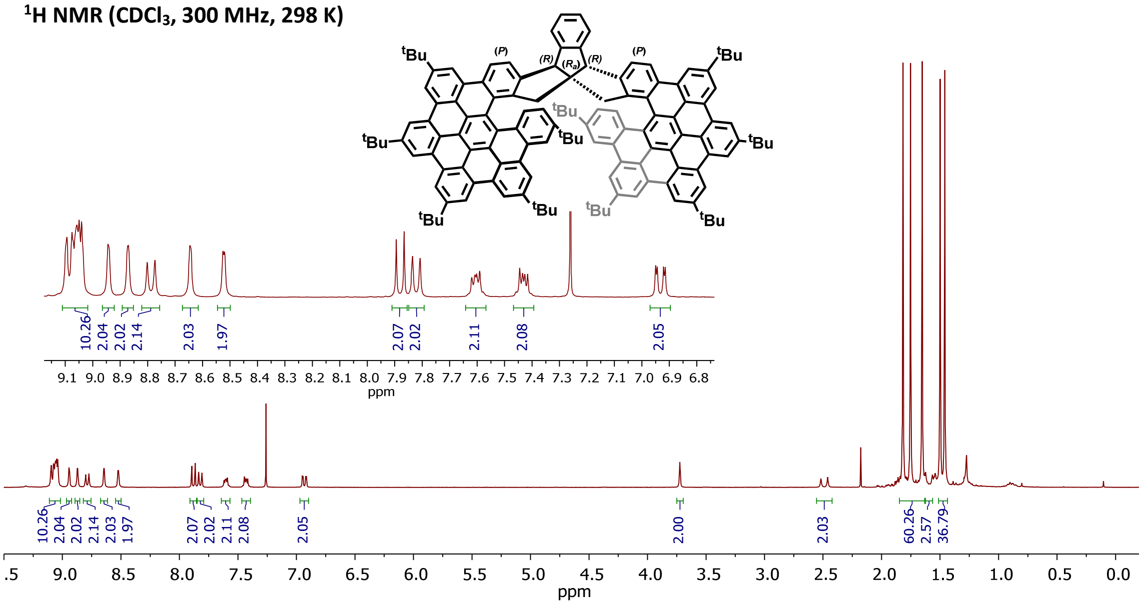


HRMS MALDI-TOF (DCTB)

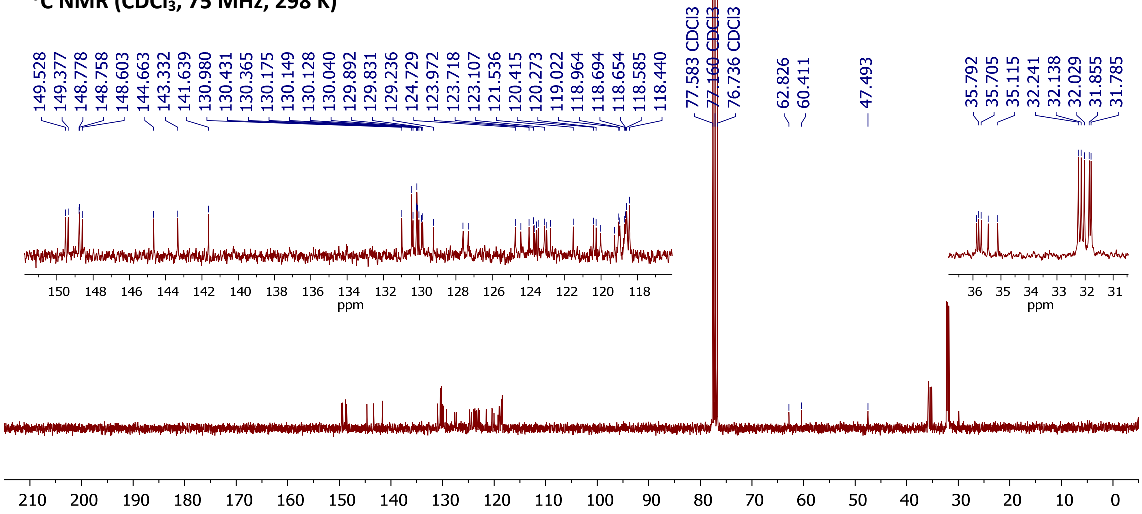


(R,R,Rα,P,P)-1

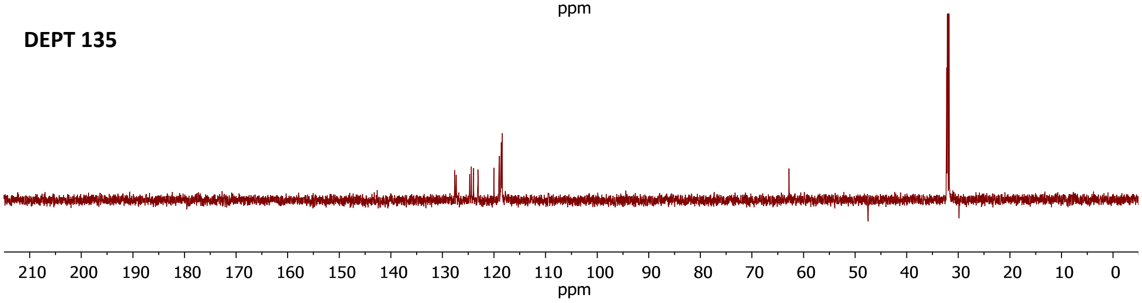
^{1}H NMR ($CDCl_3$, 300 MHz, 298 K)



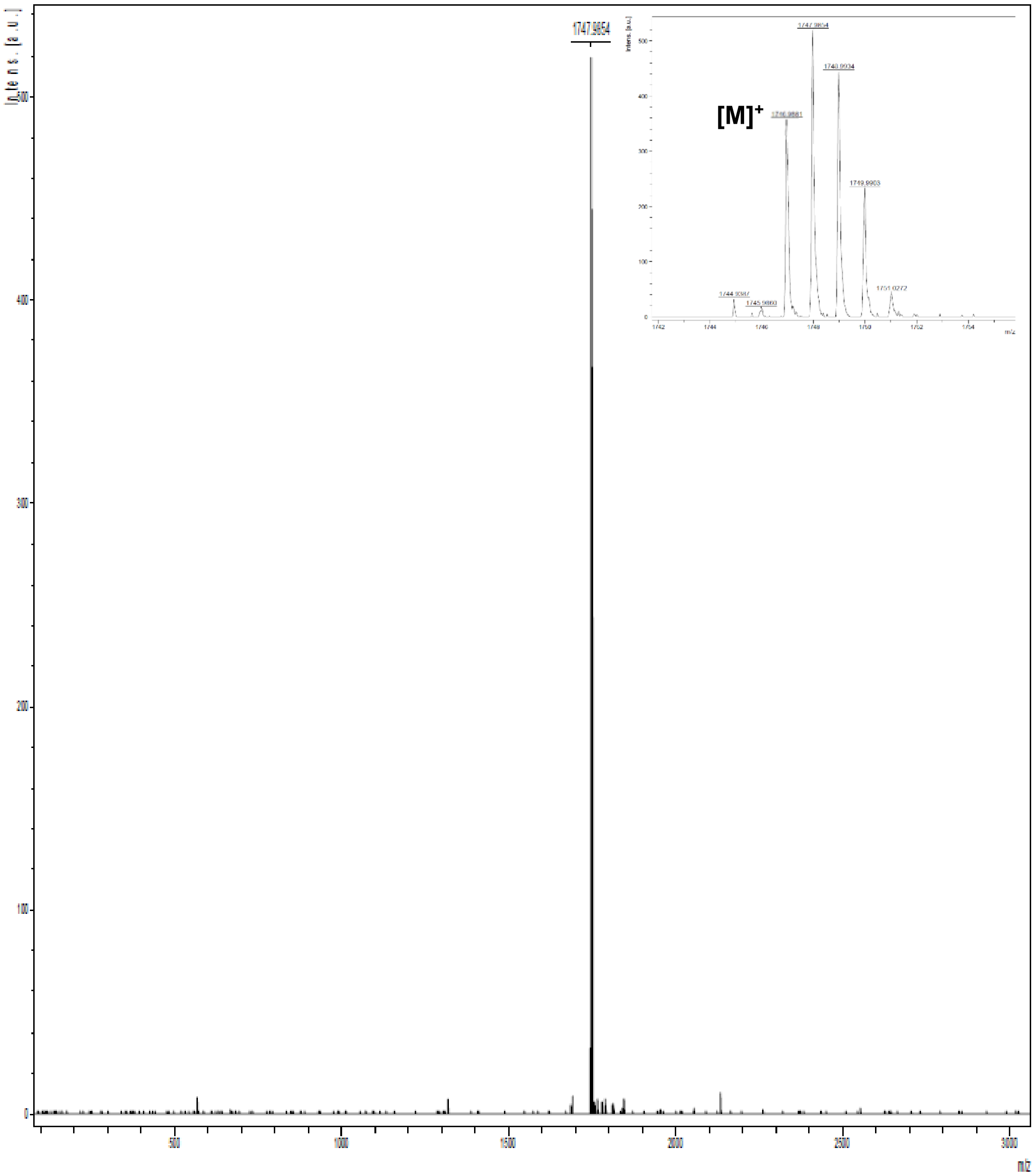
^{13}C NMR ($CDCl_3$, 75 MHz, 298 K)



DEPT 135



HRMS MALDI-TOF (DCTB)



4. Single Crystal X-ray Diffraction Data

Single crystals suitable for X-ray diffraction analysis were obtained for compounds ***(S,S)*-6, *meso*-6, *rac*-7, (*S,S,S$_a$,M,M*)-1 and *rac*-1**. In all of the cases, the packing of these molecules displays large voids that contain disordered solvent molecules. The crystals were found to be very unstable out of their mother liquors due to the loss of these interstitial solvent molecules. Additionally, many of the peripheral *tert*-butyl groups are also heavily disordered and were modelled with two alternative sets of positions.

Comments and responses for A- and B-level alerts in the CheckCIF reports for the structures have been included in the structural .cif files for the five compounds, which have been deposited in the CSD database with CCDC numbers 2278583 (***(S,S)*-6**), 2278584 (***meso*-6**), 2278585 (***rac-7***), 2278586 (**(*S,S,S$_a$,M,M*)-1**) and 2278587 (***rac*-1**).

A. Compounds 6

- ***(S,S)*-6,** with CCDC numbers 2278583

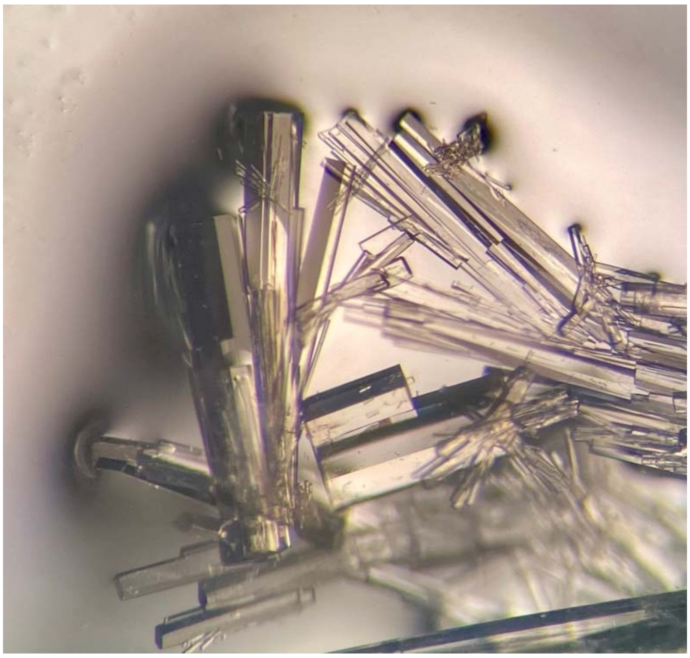


Figure RX1. Detail of hexagonal prismatic crystals from compound **(S,S)-6**

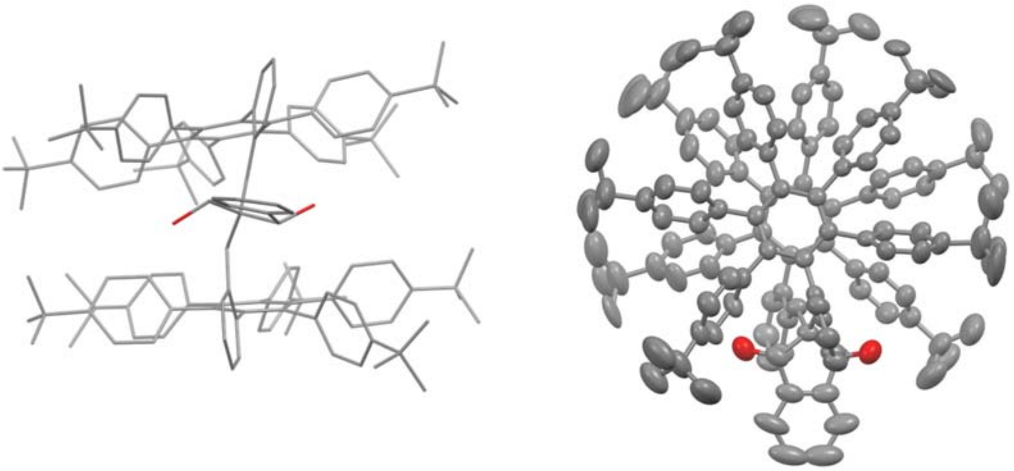


Figure RX2. Molecular plot of compound ***(S,S)*-6** (hydrogen atoms have been removed for clarity). Left: capped sticks lateral view, and right, zenithal ellipsoid plot.

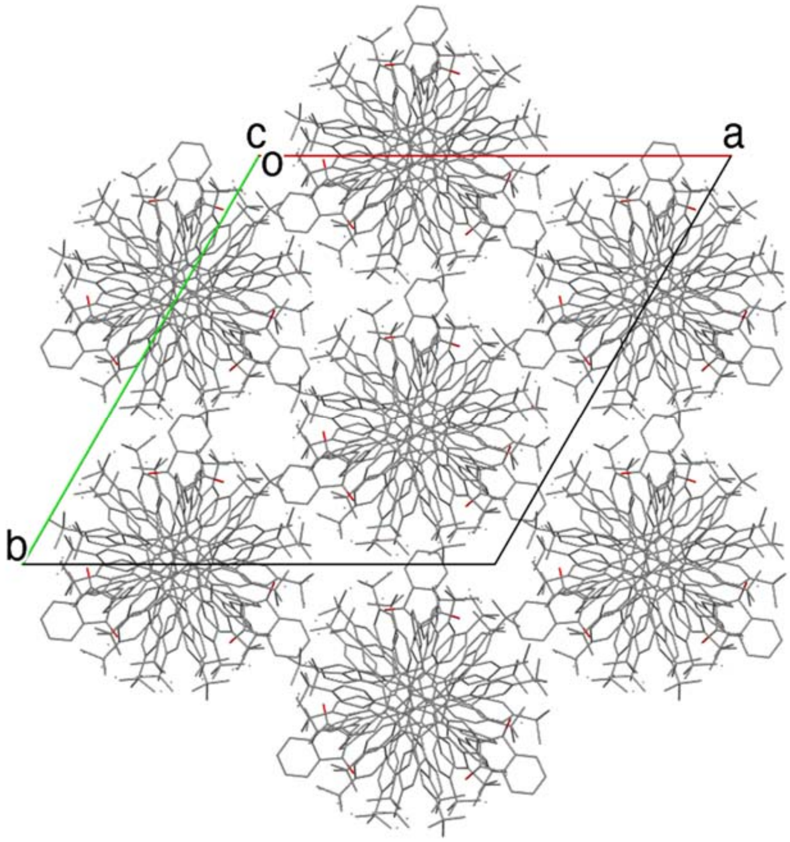


Figure RX3. Hexagonal packing of the columns of molecules in ***(S,S)*-6**

Table RX1. Sample and crystal data for *(S,S)*-6

CCDC number	2278583	
Chemical formula	$C_{135}H_{150}O_{2.50}$	
Formula weight	1812.54 g/mol	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal size	0.106 x 0.198 x 0.280 mm	
Crystal habit	clear colourless prism	
Crystal system	trigonal	
Space group	*R*3	
Unit cell dimensions	a = 30.4475(11) Å	α = 90°
	b = 30.4475(11) Å	β = 90°
	c = 34.9074(17) Å	γ = 120°
Volume	28025.(2) Å^3	
Z	9	
Density (calculated)	0.967 g/cm^3	
Absorption coefficient	0.055 mm^{-1}	
F(000)	8820	

Table RX2. Data collection and structure refinement for *(S,S)*-6

Theta range for data collection	1.40 to 25.04°
Index ranges	-36<=h<=36, -36<=k<=36, -41<=l<=34
Reflections collected	211987
Independent reflections	21060 [R(int) = 0.0584]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9940 and 0.9850

Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	21060 / 1327 / 1393	
Goodness-of-fit on F^2	1.041	
Final R indices	14865 data; $I>2\sigma(I)$	$R_1 = 0.1115$, $wR_2 = 0.2592$
	all data	$R_1 = 0.1520$, $wR_2 = 0.3002$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.2300P)^2+1.9700P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0052(4)	
Largest diff. peak and hole	1.418 and -0.922 eÅ^{-3}	
R.M.S. deviation from mean	0.242 eÅ^{-3}	

- ***meso*-6** with CCDC number 2278584

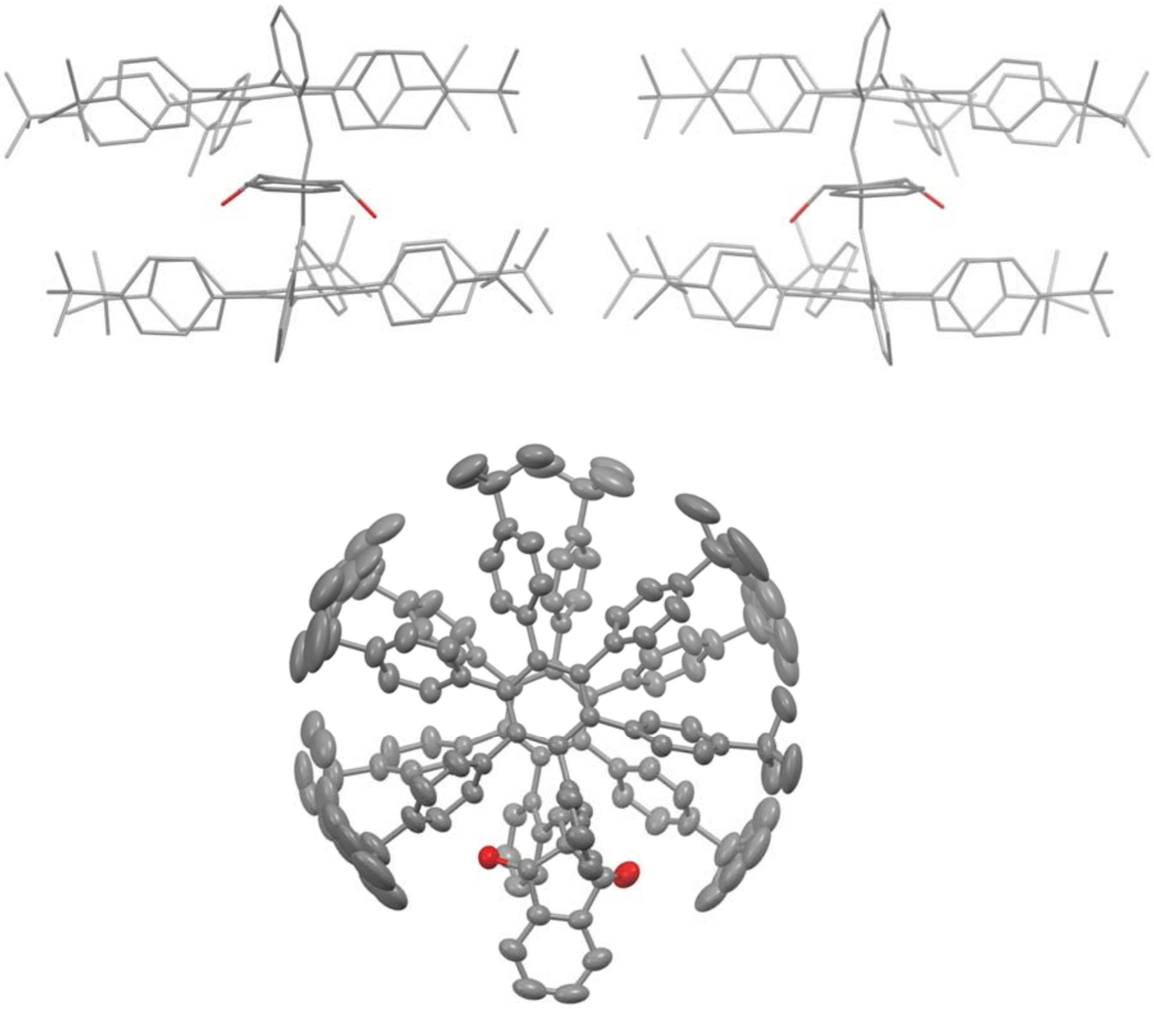


Figure RX4. Top: the two enantiomers present in the crystal of compound ***meso*-6** (left*, S,R*; and right, *R,S*). Bottom: ellipsoid plot of the enantiomer in the asymmetric unit. Hydrogen atoms have been removed for clarity.

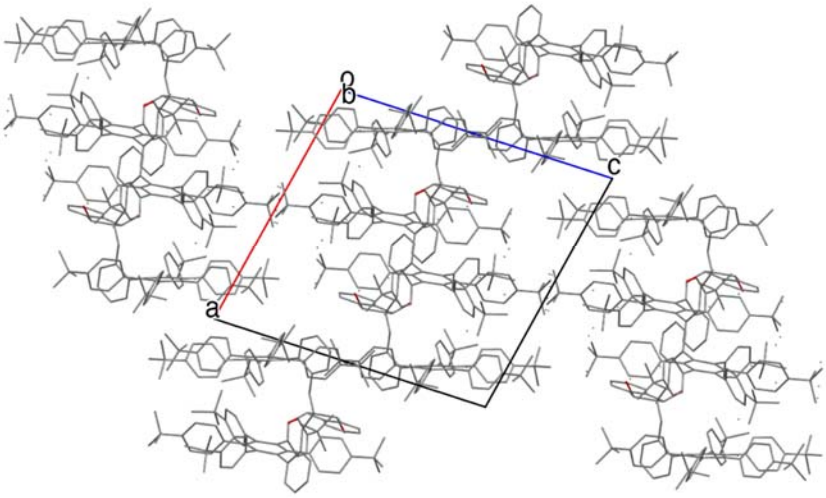


Figure RX5. Packing of the molecules in ***meso*-6.**

Table RX3. Sample and crystal data for *meso*-6

CCDC number	2278584	
Chemical formula	$C_{135}H_{150}O_2$	
Formula weight	1804.54 g/mol	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal size	0.098 x 0.188 x 0.193 mm	
Crystal habit	clear colourless prism	
Crystal system	triclinic	
Space group	*P*-1	
	a = 17.9613(10) Å	α = 92.927(2)°
Unit cell dimensions	b = 18.8711(14) Å	β = 100.038(2)°
	c = 19.0895(14) Å	γ = 102.761(2)°
Volume	6186.9(7) Å^3	
Z	2	
Density (calculated)	0.969 g/cm^3	
Absorption coefficient	0.055 mm^{-1}	
F(000)	1952	

Table RX4. Data collection and structure refinement for *meso*-6		
Theta range for data collection	1.42 to 25.05°	
Index ranges	-21<=h<=21, -22<=k<=22, -22<=l<=22	
Reflections collected	252289	
Independent reflections	21861 [R(int) = 0.0884]	
Coverage of independent reflections	99.6%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9950 and 0.9890	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	21861 / 1382 / 1429	
Goodness-of-fit on F^2	1.062	
Final R indices	11820 data; I>2σ(I)	R_1 = 0.0851, wR_2 = 0.2086
	all data	R_1 = 0.1575, wR_2 = 0.2762
Weighting scheme	w=1/[σ^2(F_o^2)+(0.1619P)^2+0.6203P] where P=(F_o^2+2F_c^2)/3	
Extinction coefficient	0.0380(20)	
Largest diff. peak and hole	0.932 and -0.640 eÅ^{-3}	
R.M.S. deviation from mean	0.209 eÅ^{-3}	

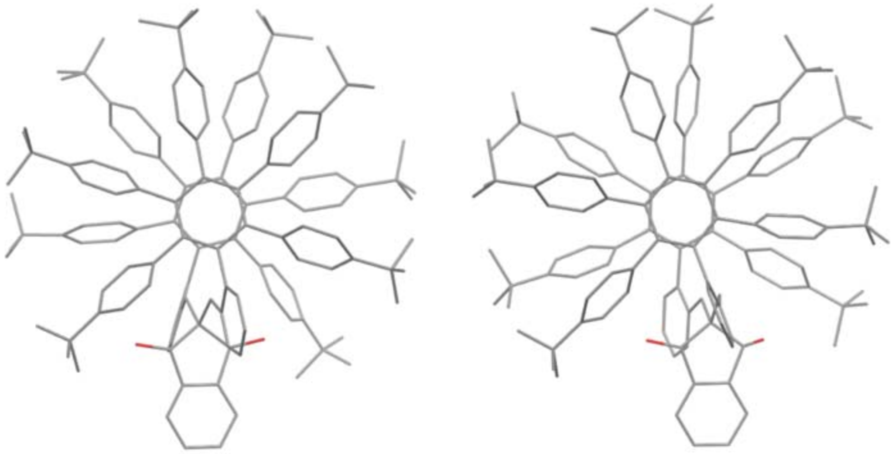


Figure RX6. Zenithal view of the molecules of compound **6** in the crystal structures: left, ***(S,S)*-6**; and right ***(S,R)*-6** in ***meso*-6**.

B. Compound *rac*-7 with CCDC number 2278585

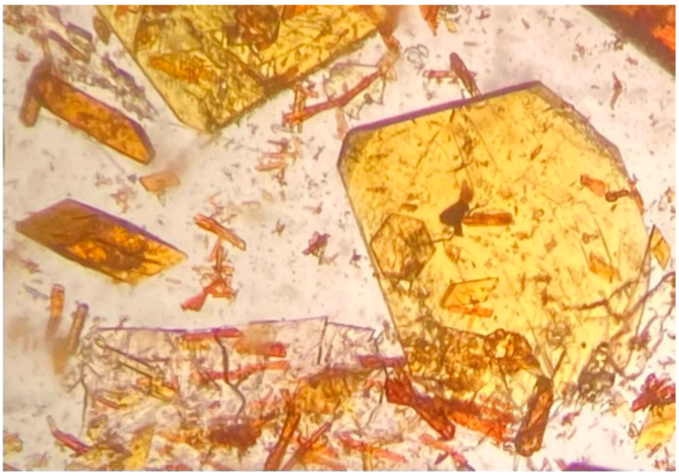


Figure RX7. Detail of the crystals of compound ***rac*-7.**

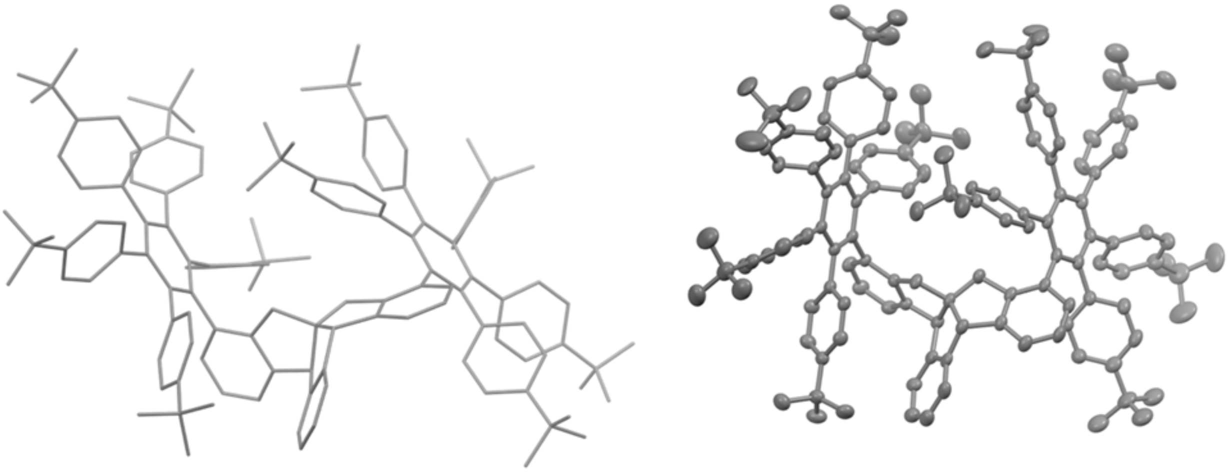


Figure RX8. Molecular structure of compound ***rac*-7**; left: capped sticks representation; right: ellipsoid plot. Hydrogen atoms have been omitted for clarity.

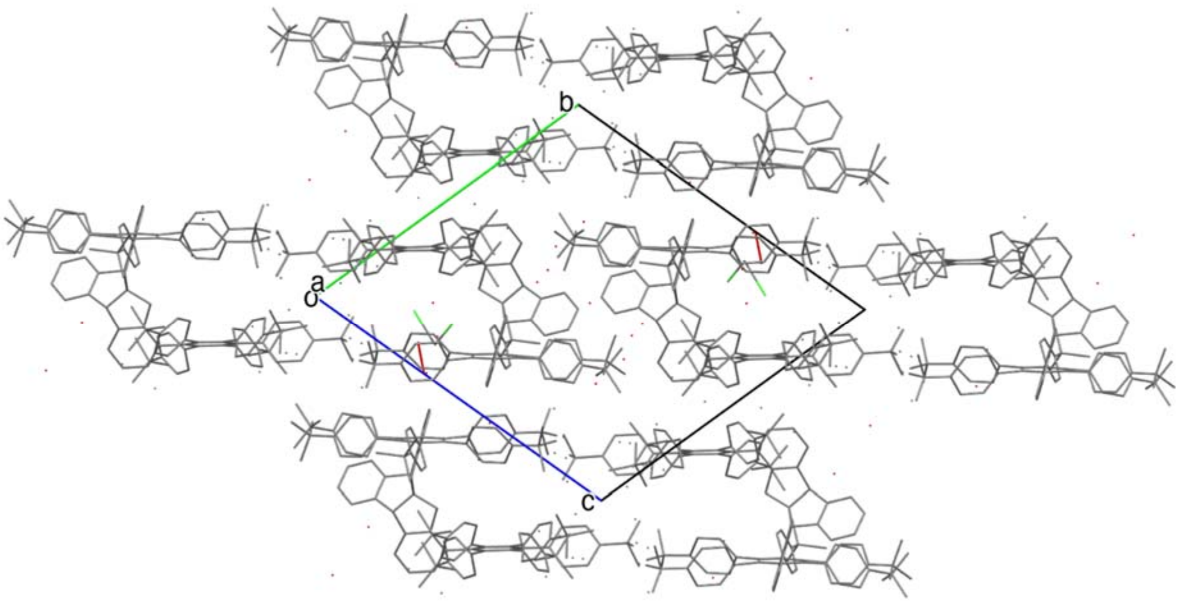


Figure RX9. Packing of the molecules in the crystal structure of ***rac*-7.**

Table RX5. Sample and crystal data for *rac*-7

CCDC number	2278585	
Chemical formula	$C_{136.50}H_{149}Cl_{1.50}O_{5.50}$	
Formula weight	1930.72 g/mol	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.095 x 0.121 x 0.243 mm	
Crystal habit	clear intense yellow plate	
Crystal system	triclinic	
Space group	*P*-1	
	a = 18.1535(10) Å	α = 69.349(2)°
Unit cell dimensions	*b* = 18.5923(10) Å	β = 76.233(2)°
	c = 20.1771(10) Å	γ = 77.152(2)°
Volume	6117.2(6) $Å^3$	
Z	2	
Density (calculated)	1.048 g/cm^3	
Absorption coefficient	0.093 mm^{-1}	
F(000)	2075	

Table RX6. Data collection and structure refinement for *rac*-7

Theta range for data collection	1.46 to 25.02°
Index ranges	-21<=h<=21, -22<=k<=22, -24<=l<=24
Reflections collected	65325
Independent reflections	21559 [R(int) = 0.0665]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9910 and 0.9780
Structure solution technique	direct methods

Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	21559 / 2377 / 1474	
Goodness-of-fit on F^2	1.064	
Final R indices	12531 data; $I>2\sigma(I)$	$R_1 = 0.1134$, $wR_2 = 0.3027$
	all data	$R_1 = 0.1767$, $wR_2 = 0.3599$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.2300P)^2+1.9700P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0360(30)	
Largest diff. peak and hole	2.024 and -0.630 eÅ^{-3}	
R.M.S. deviation from mean	0.222 eÅ^{-3}	

C. Compound 1

- ((***S*,*S*,*S*$_a$,*M*,*M***)-**1**) with CCDC number 2278586

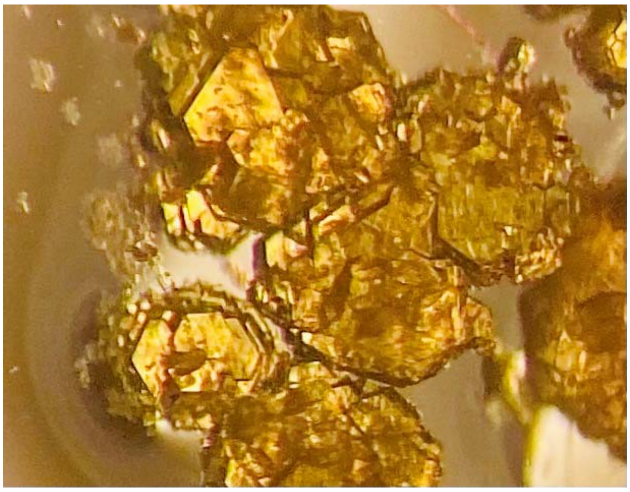


Figure RX10. Detail of the aggregates of hexagonal plates of TING (***S*,*S*,*S*$_a$,*M*,*M***)-**1.**

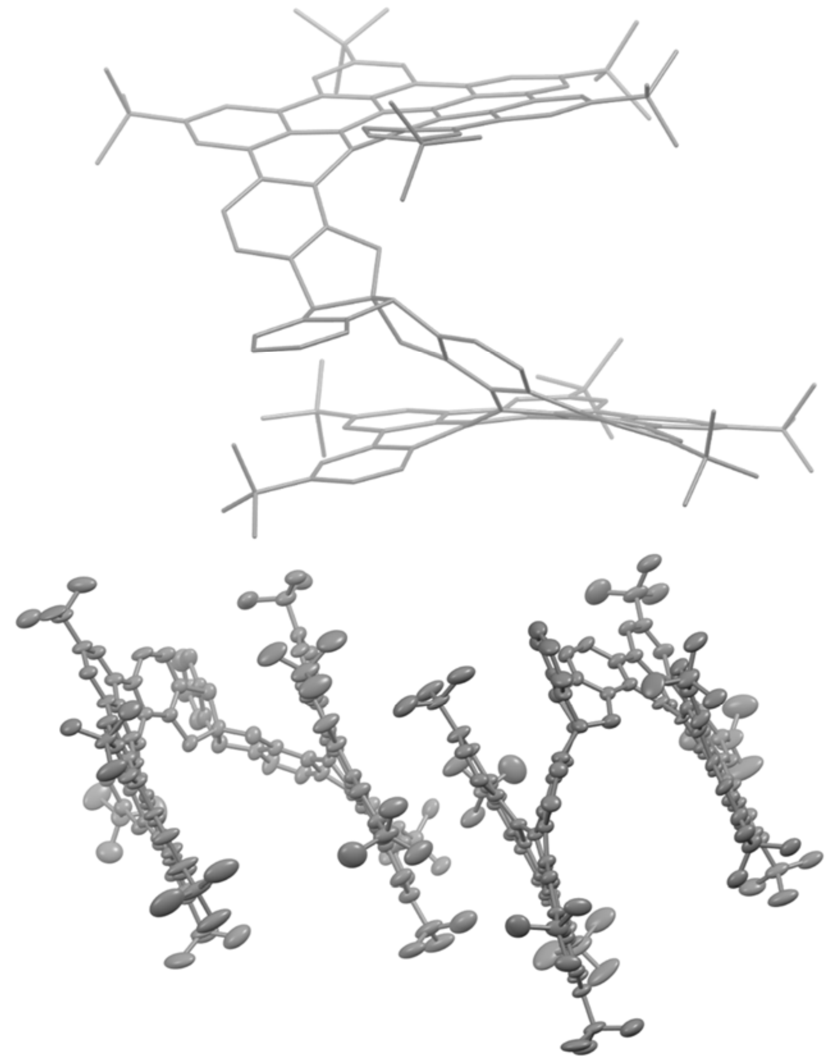


Figure RX11. Top: Schematic view of one of the molecules in the crystal structure of of TING **(*S*,*S*,*S*$_a$,*M*,*M*)-1.** Bottom: ellipsoid plot of the two molecules of TING **(*S*,*S*,*S*$_a$,*M*,*M*)-1** in the asymmetric unit. Hydrogen atoms have been removed for clarity.

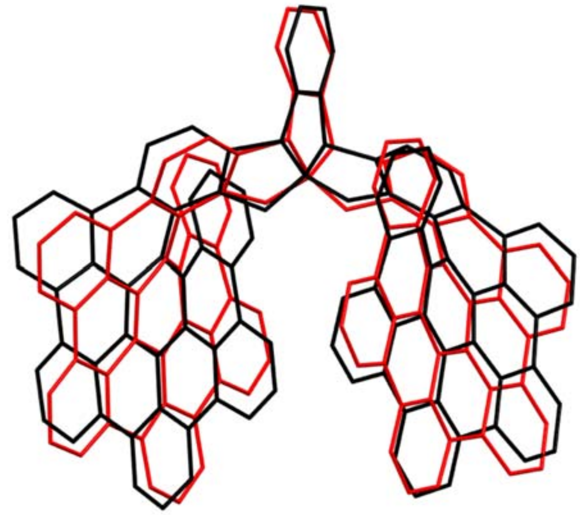


Figure RX12. Overlay of the two molecules (in black and red) present in the asymmetric unit of TING **(*S*,*S*,*S*$_a$,*M*,*M*)-1** (*t*-Bu substituents and hydrogen atoms have been omitted for clarity).

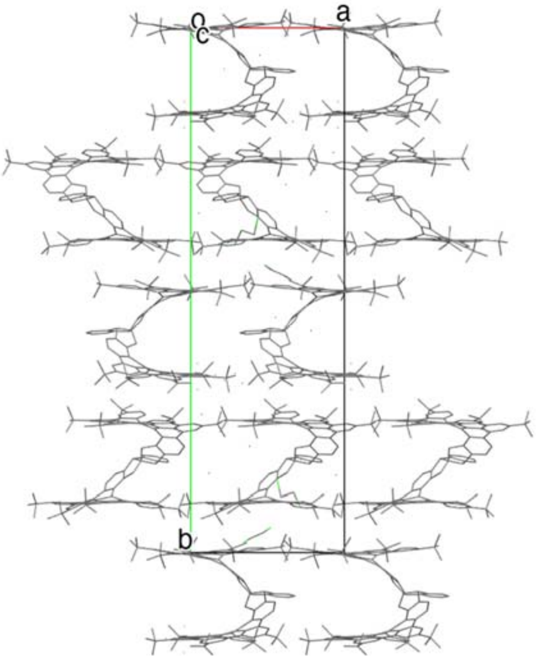


Figure RX13. Packing of the molecules in the crystal structure of TING **(*S*,*S*,*S*$_a$,*M*,*M*)-1.**

Table RX7. Sample and crystal data for (*S*,*S*,*S*$_a$,*M*,*M*)-1

CCDC number	2278586

Chemical formula	$C_{90.67}H_{85.33}Cl_{0.67}O_{3.33}$	
Formula weight	1251.88 g/mol	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal size	0.159 x 0.201 x 0.205 mm	
Crystal habit	clear intense yellow-orange prism	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 17.3119(9) Å	α = 90°
	b = 51.540(3) Å	β = 119.4220(10)°
	c = 17.4144(9) Å	γ = 90°
Volume	13534.1(12) Å^3	
Z	6	
Density (calculated)	0.922 g/cm^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	4004	

Table RX8. Data collection and structure refinement for (S,S,S_a,M,M)-1

Theta range for data collection	1.40 to 25.11°
Index ranges	-20<=h<=20, -61<=k<=49, -20<=l<=20
Reflections collected	158366
Independent reflections	43883 [R(int) = 0.0902]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9880 and 0.9850
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	43883 / 2865 / 2665	
Goodness-of-fit on F^2	1.213	
Final R indices	24943 data; I>2σ(I)	R_1 = 0.1593, wR_2 = 0.4105
	all data	R_1 = 0.2411, wR_2 = 0.4654
Weighting scheme	w=1/[σ^2(F_o^2)+(0.2850P)^2+1.9700P] where P=(F_o^2+2F_c^2)/3	
Absolute structure parameter	0.08(6)	
Largest diff. peak and hole	1.853 and -0.828 eÅ^{-3}	
R.M.S. deviation from mean	0.257 eÅ^{-3}	

- (***rac*-1**) with CCDC number 2278587

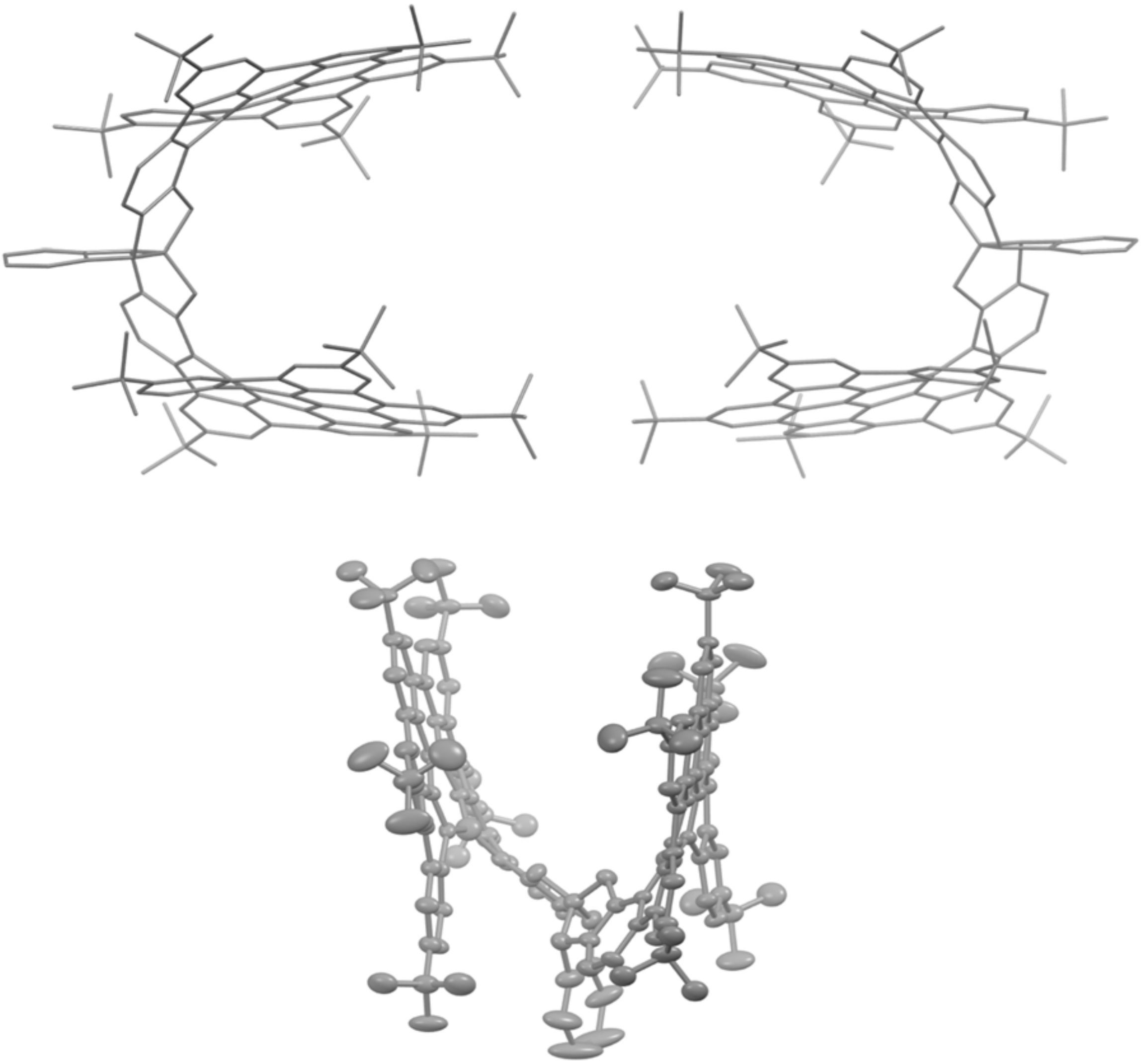


Figure RX14. Top: detail of the two enantiomers in the crystal structure of ***rac*-1** (left *(R,R,R$_a$,P,P)* and right *(S,S,S$_a$,M,M)*). Bottom: ellipsoid plot of the molecule of TING **1** in the asymmetric unit. Hydrogen atoms have been removed for clarity.

Table RX9. Sample and crystal data for *rac*-1	
CCDC number	2278587
Chemical formula	$C_{68.50}H_{64}Cl_3O_{2.75}$
Formula weight	1037.54 g/mol
Temperature	250(2) K
Wavelength	0.71073 Å

Crystal size	0.124 x 0.187 x 0.400 mm	
Crystal habit	clear intense yellow prismatic	
Crystal system	monoclinic	
Space group	*C*2/*c*	
	a = 17.4117(11) Å	α = 90°
Unit cell dimensions	b = 30.801(3) Å	β = 108.0678(19)°
	c = 27.597(2) Å	γ = 90°
Volume	14070.(2) Å^3	
Z	8	
Density (calculated)	0.980 g/cm^3	
Absorption coefficient	0.168 mm^{-1}	
F(000)	4384	

Table RX10. Data collection and structure refinement for *rac*-1

Theta range for data collection	1.32 to 24.99°
Index ranges	-20<=h<=20, -36<=k<=36, -32<=l<=32
Reflections collected	142786
Independent reflections	12354 [R(int) = 0.0425]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9790 and 0.9360
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	Σ w(F$_o^2$ - F$_c^2$)^2
Data / restraints / parameters	12354 / 24 / 760

Goodness-of-fit on F^2	1.050	
Final R indices	9084 data; $I>2\sigma(I)$	$R_1 = 0.1836$, $wR_2 = 0.5305$
	all data	$R_1 = 0.2156$, $wR_2 = 0.5890$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.5900P)^2+2.9700P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.725 and -0.706 eÅ^{-3}	
R.M.S. deviation from mean	0.247 eÅ^{-3}	

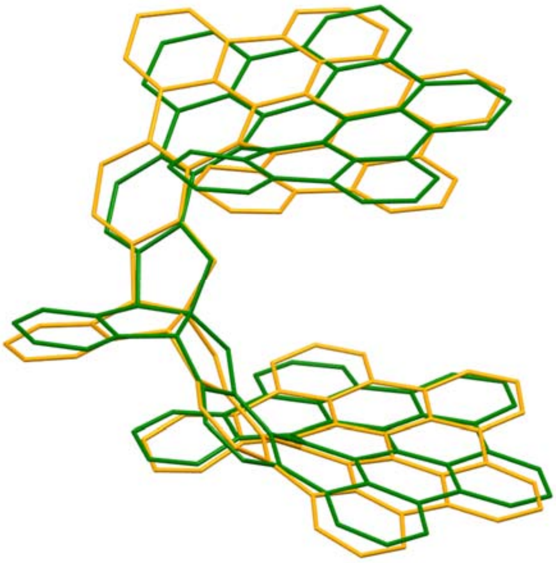


Figure RX15. Overlay of the (*S*,*S*,*S*$_a$,*M*,*M*) isomer in **1-*rac*** (orange) with one of the molecules in the enantiopure crystal of **(*S*,*S*,*S*$_a$,*M*,*M*)-1** (green).

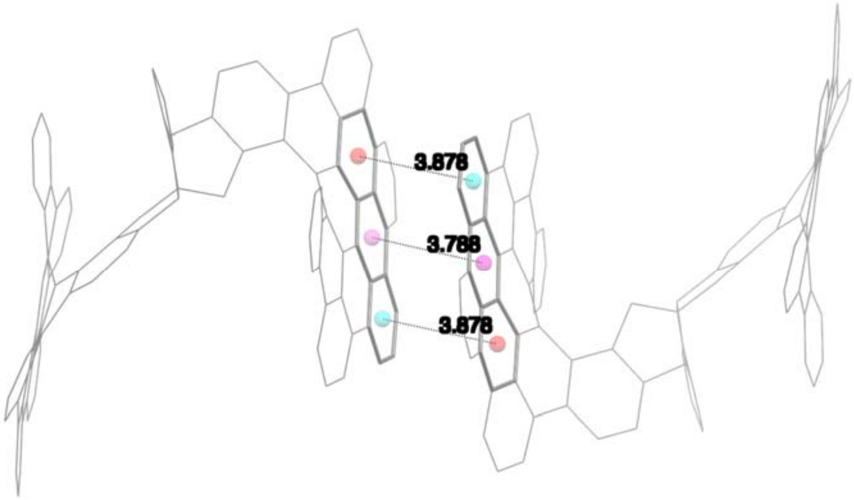


Figure RX16. Distances between centroids of closest rings in adjacent molecules in **1-*rac*.**

5. Electrochemical measurements

Electrochemical measurements were performed using a standard one-compartment, three-electrode electrochemical cell connected to an electrochemical analyzer (Metrohm Autolab). The working electrode was a glassy carbon electrode (3 mm diameter) that was freshly polished with a suspension of Al_2O_3 in distilled water and sonically rinsed with acetone before each measurement. Silver (Ag/0.1 M $AgNO_3$ in CH_3CN) and platinum wires were used as reference and counter electrodes, respectively. Electrochemical grade (Aldrich) tetrabutylammonium hexaflurophosphate 0.1 M in toluene:acetonitrile (1:1) was used as supporting electrolyte. All measurements were conducted under dry argon. Solutions were saturated with argon for deoxygenation and to maintain an argon blanket for at least 10 minutes prior to each measurement. All measurements are referenced to Fc/Fc^+ added as internal reference.

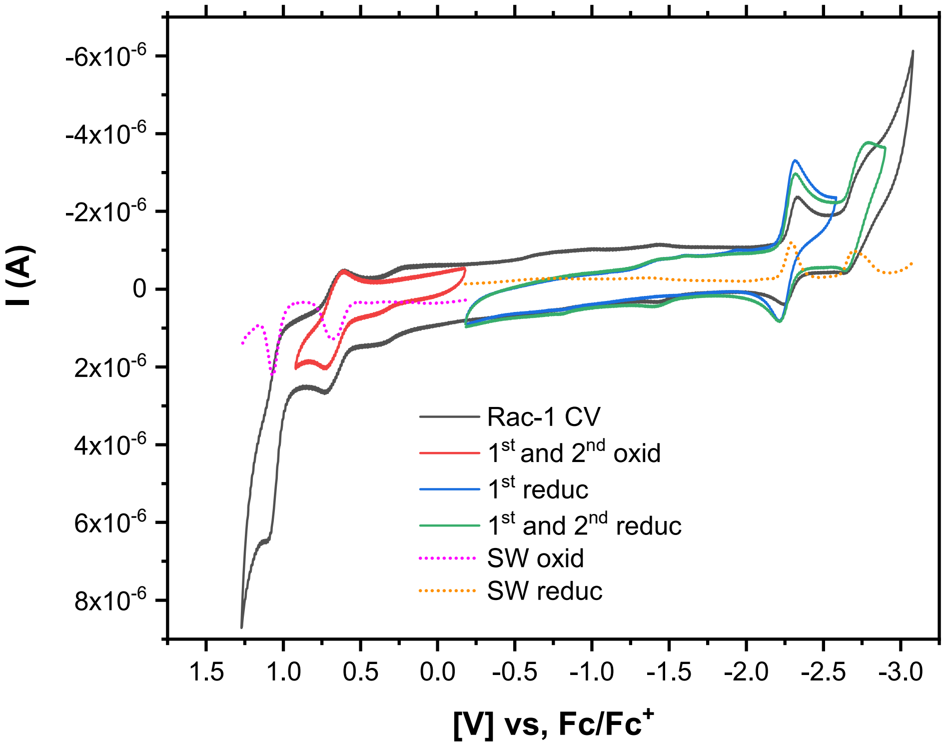


Figure S17. Cyclic Voltammetry and Square Wave voltammograms of **Rac-1** vs Fc/Fc^+ (Tol:AcN 1:1).

Table 2. First and Second Oxidation and Reduction Potential Values of ^{t}Bu-HBC and **Rac-1**.

	E_{ox}^1 (V)	E_{ox}^2 (V)	E_{red}^1 (V)	E_{red}^2 (V)
^{t}Bu-HBC	0.75		-2.24	-2.40
Rac-1	0.86	1.25	-2.11	-2.52

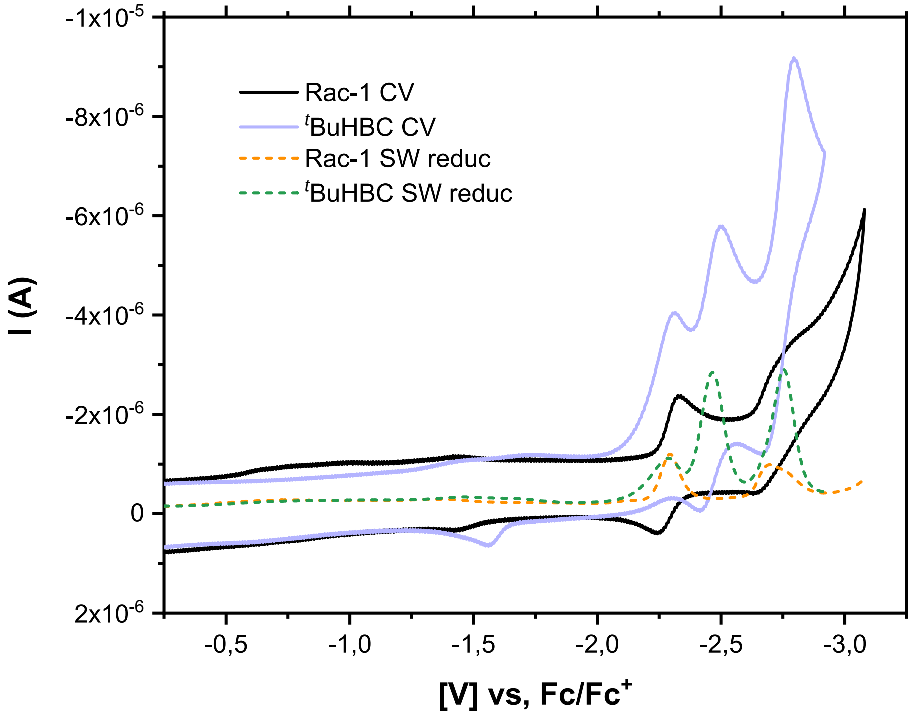


Figure S18. Reduction processes of **Rac-1** vs tBuHBC (vs Fc/Fc^{+}) (Tol:AcN 1:1)

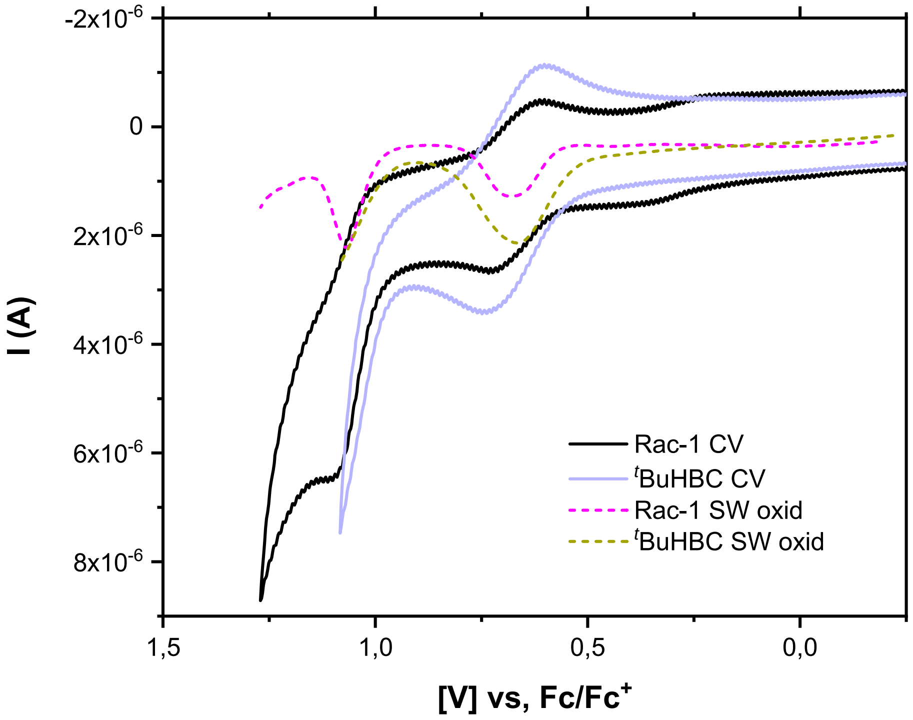
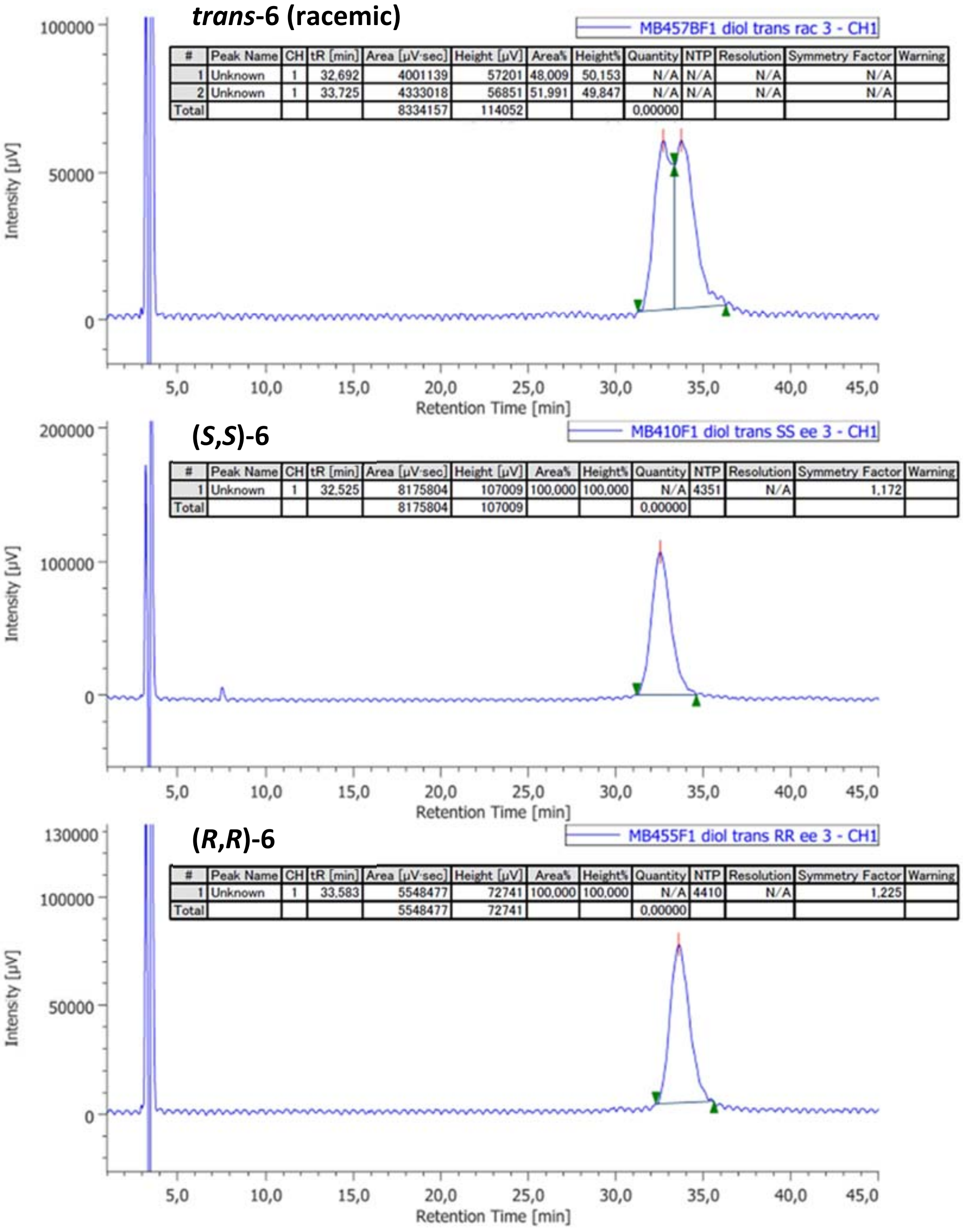


Figure S19. Oxidation processes of **Rac-1** vs tBuHBC (vs Fc/Fc^{+}) (Tol:AcN 1:1)

6. HPLC characterization



***trans*-6 (racemic)**

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	32,692	4001139	57201	48,009	50,153	N/A	N/A	N/A	N/A	
2	Unknown	1	33,725	4333018	56851	51,991	49,847	N/A	N/A	N/A	N/A	
Total				8334157	114052			0,00000				

(*S*,*S*)-6

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	32,525	8175804	107009	100,000	100,000	N/A	4351	N/A	1,172	
Total				8175804	107009			0,00000				

(*R*,*R*)-6

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	33,583	5548477	72741	100,000	100,000	N/A	4410	N/A	1,225	
Total				5548477	72741			0,00000				

Figure S20. UV-vis chromatograms for ***trans***-6, (*S*,*S*)-6 and (*R*,*R*)-6 (Control Method: Reflect I-Cellulose B 5 μm, AcN:H_2O (92:8), 1 mL/min, 20 ºC, λ = 254 nm).

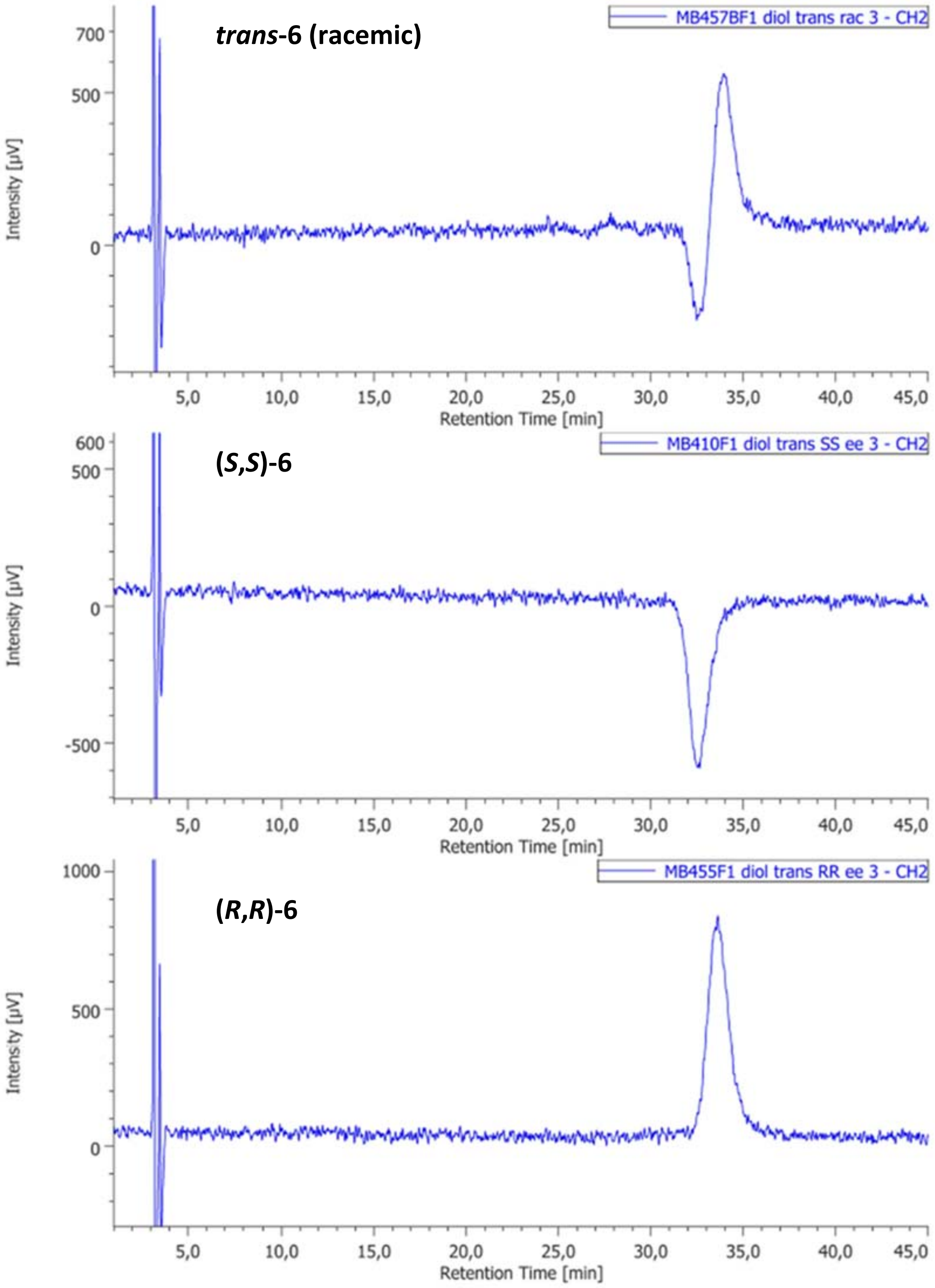
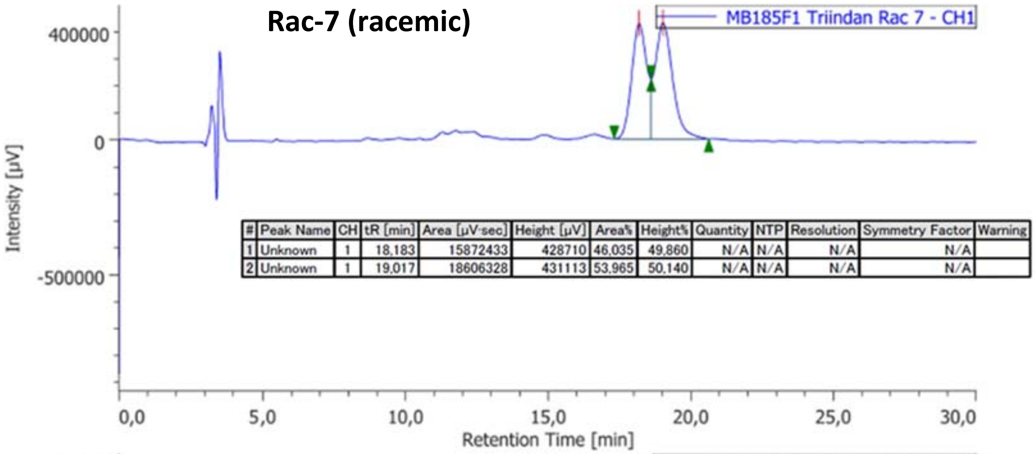
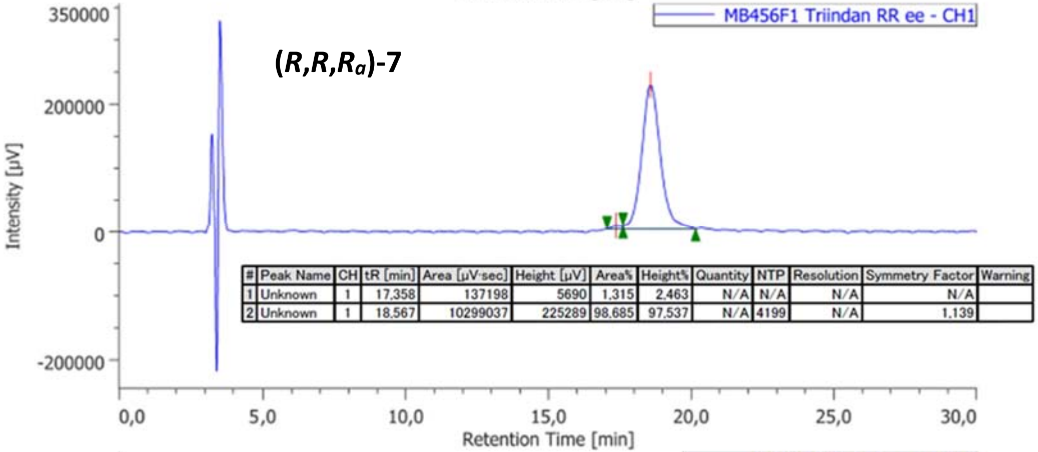


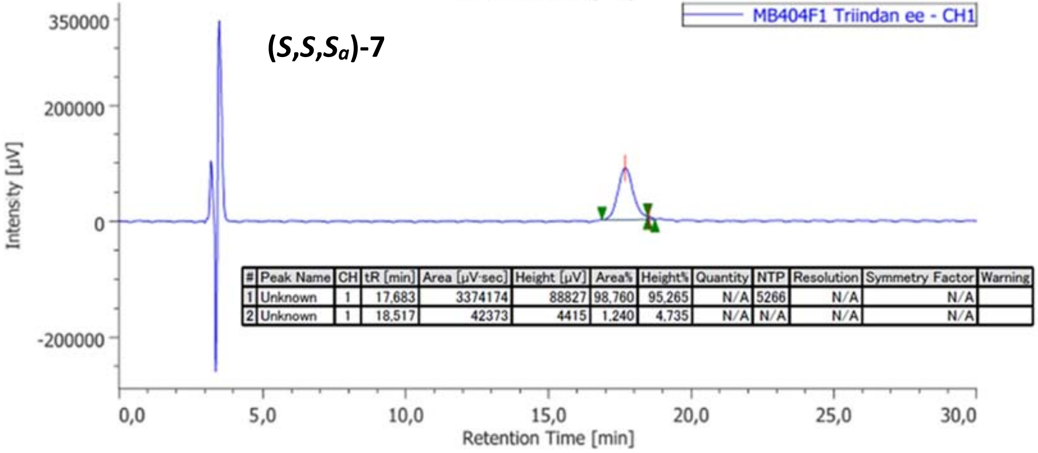
Figure S21. Circular Dichroism chromatograms for *trans*-6, (*S*,*S*)-6 and (*R*,*R*)-6 (Control Method: Reflect I-Cellulose B 5 µm, AcN:H2O (92:8), 1 mL/min, 20 ºC, λ = 254 nm).



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	18,183	15872433	428710	46,035	49,860	N/A	N/A	N/A	N/A	
2	Unknown	1	19,017	18606328	431113	53,965	50,140	N/A	N/A	N/A	N/A	



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	17,358	137198	5690	1,315	2,463	N/A	N/A	N/A	N/A	
2	Unknown	1	18,567	10299037	225289	98,685	97,537	N/A	4199	N/A	1,139	



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	17,683	3374174	88827	98,760	95,265	N/A	5266	N/A	N/A	
2	Unknown	1	18,517	42373	4415	1,240	4,735	N/A	N/A	N/A	N/A	

Figure S22. UV-vis chromatograms for Rac-7, (*S*,*S*,*S*$_a$)-7 and (*R*,*R*,*R*$_a$)-7 (Control Method: Reflect I-Cellulose B 5 µm, AcN:H_2O (95:5), 1 mL/min, 20 ºC, λ = 254 nm).

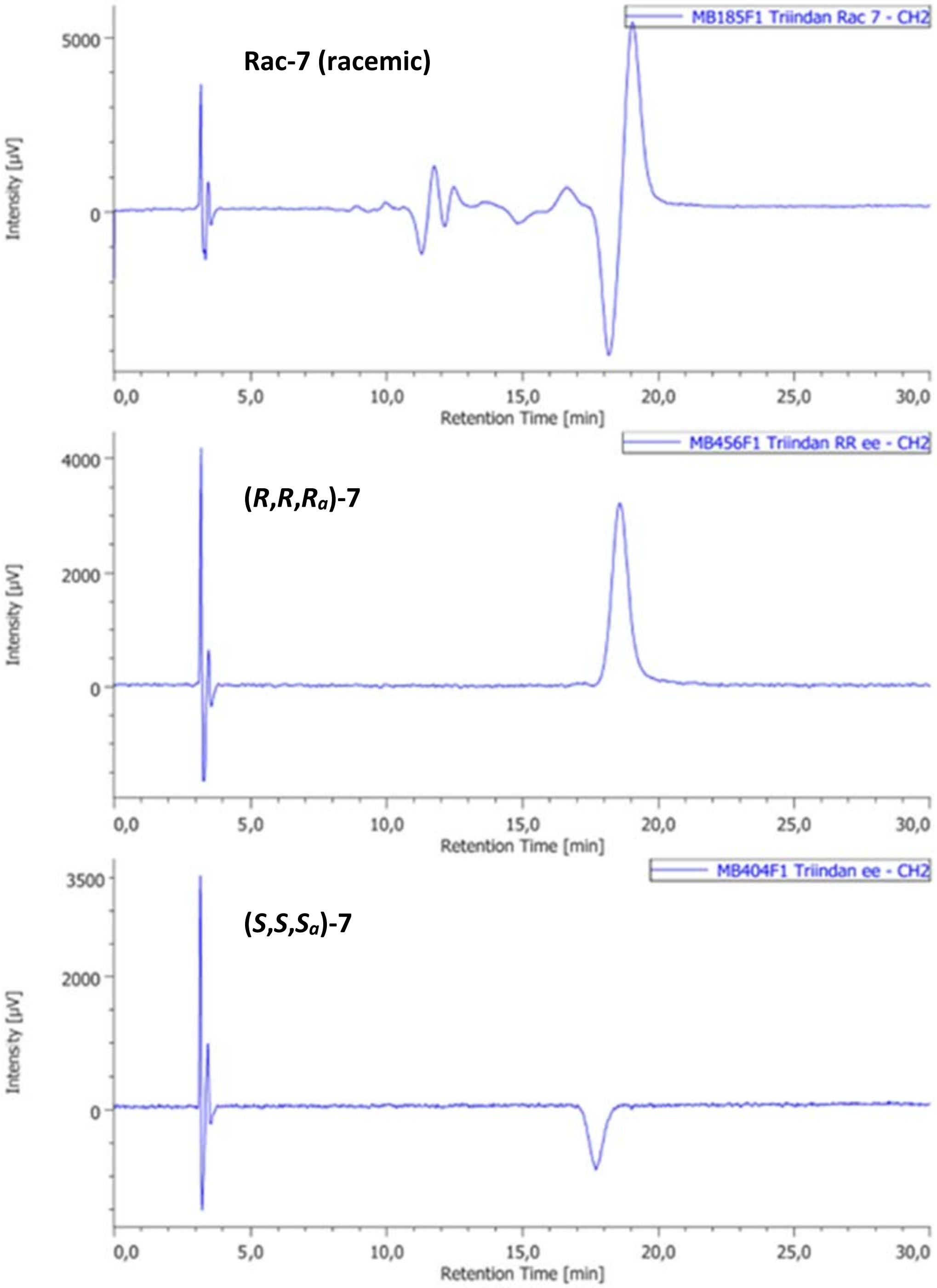
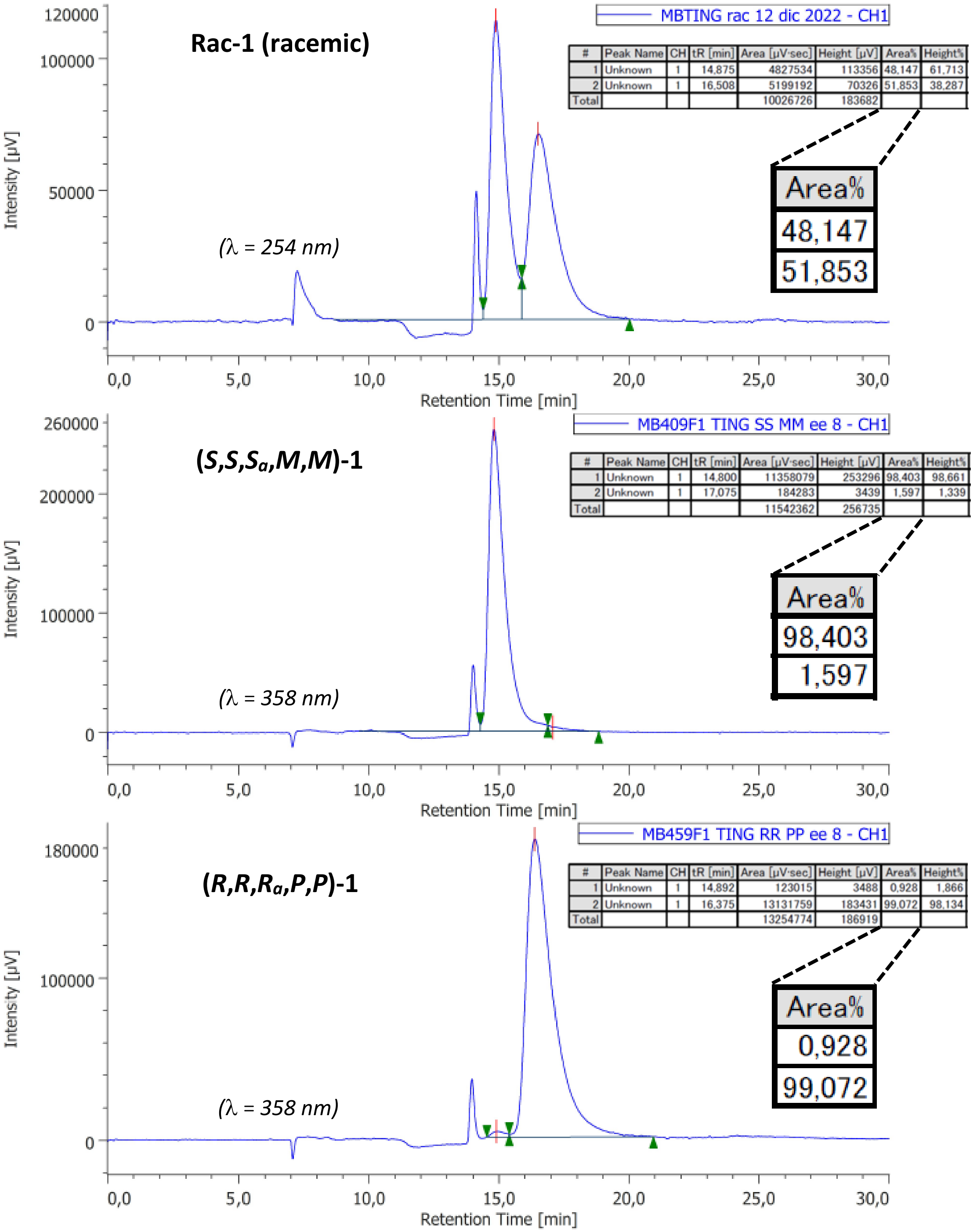


Figure S23. Circular Dichroism chromatograms for Rac-7, (*S*,*S*,*S*$_a$)-7 and (*R*,*R*,*R*$_a$)-7 (Control Method: Reflect I-Cellulose B 5 µm, AcN:H_2O (95:5), 1 mL/min, 20 ºC, λ = 254 nm).



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	1	14,875	4827534	113356	48,147	61,713
2	Unknown	1	16,508	5199192	70326	51,853	38,287
Total				10026726	183682		

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	1	14,800	11358079	253296	98,403	98,661
2	Unknown	1	17,075	184283	3439	1,597	1,339
Total				11542362	256735		

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	1	14,892	123015	3488	0,928	1,866
2	Unknown	1	16,375	13131759	183431	99,072	98,134
Total				13254774	186919		

Figure S24. UV-vis chromatograms for **Rac-1**, **(*S*,*S*,*S*$_a$,*M*,*M*)-1** and **(*R*,*R*,*R*$_a$,*P*,*P*)-1** ((*R*,*R*) Whelk-O 2 5 µm, Hex:THF:IPA (96:2:2), 0.5 mL/min, 40 ºC).

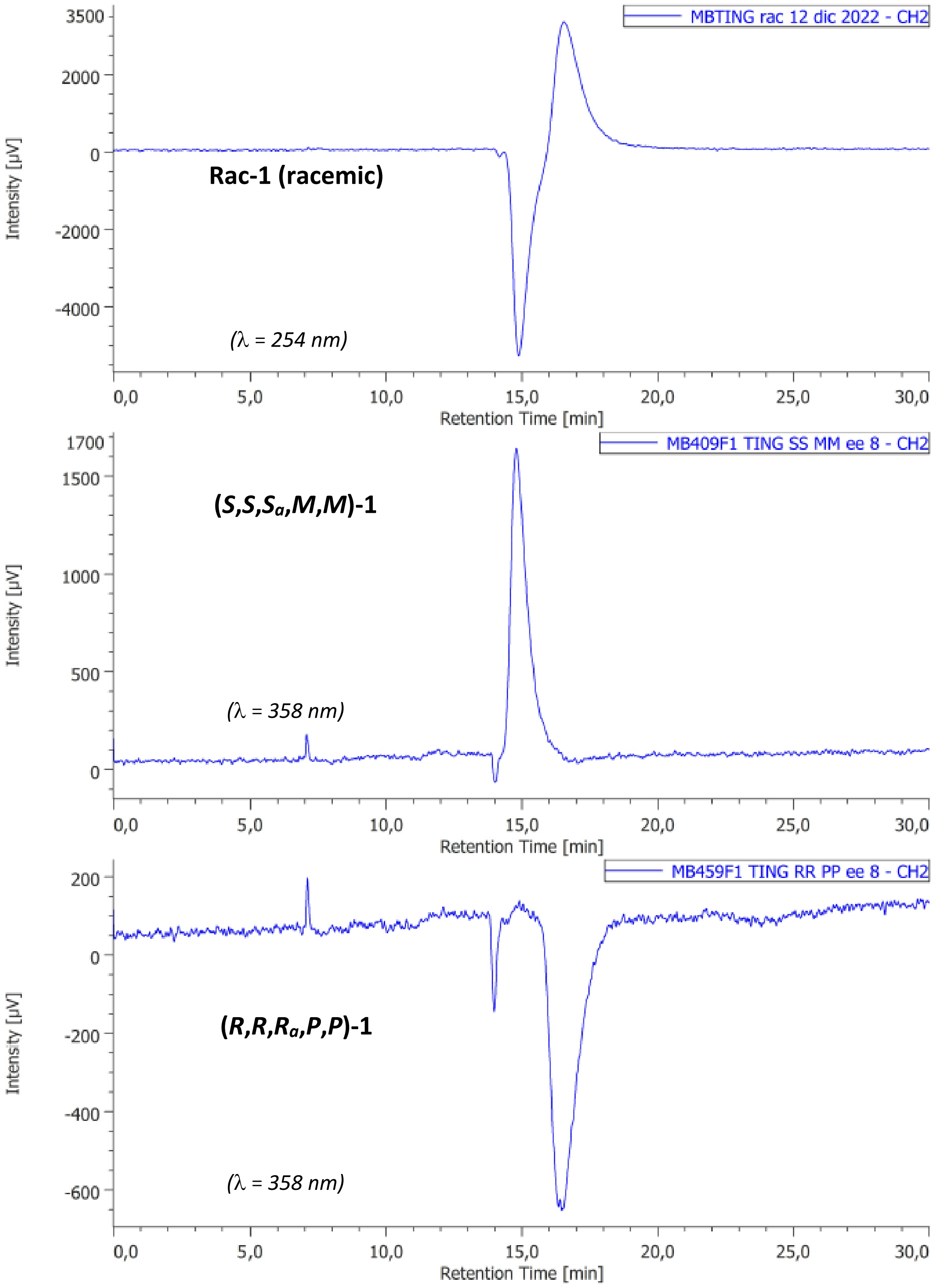


Figure S25. Circular Dichroism chromatograms for Rac-1, (*S*,*S*,*S*$_a$,*M*,*M*)-1 and (*R*,*R*,*R*$_a$,*P*,*P*)-1 ((S,S) Whelk-O 2 5 µm, Hex:THF:IPA (96:2:2), 0.5 mL/min, 40 ºC).

7. Circular Dichroism and CPL spectra

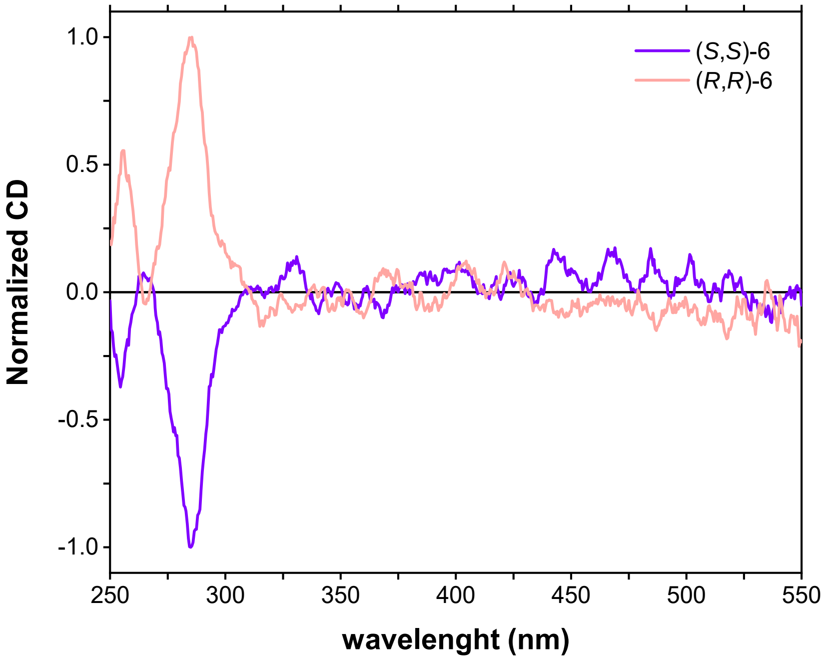


Figure S26. Circular Dichroism spectroscopic data of diols (*S*,*S*)-6 and (*R*,*R*)-6 (10 μM, $CHCl_3$, 20ºC, 10 mm).

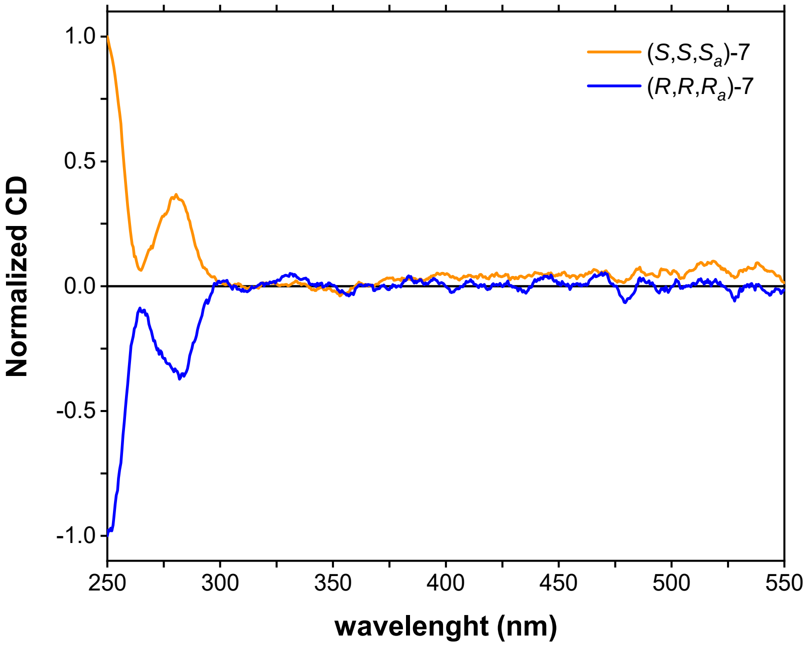


Figure S27. Circular Dichroism spectroscopic data of triindans (*S*,*S*,*S*$_a$)-7 and (*R*,*R*,*R*$_a$)-7 (10 μM, $CHCl_3$, 20ºC, 10 mm).

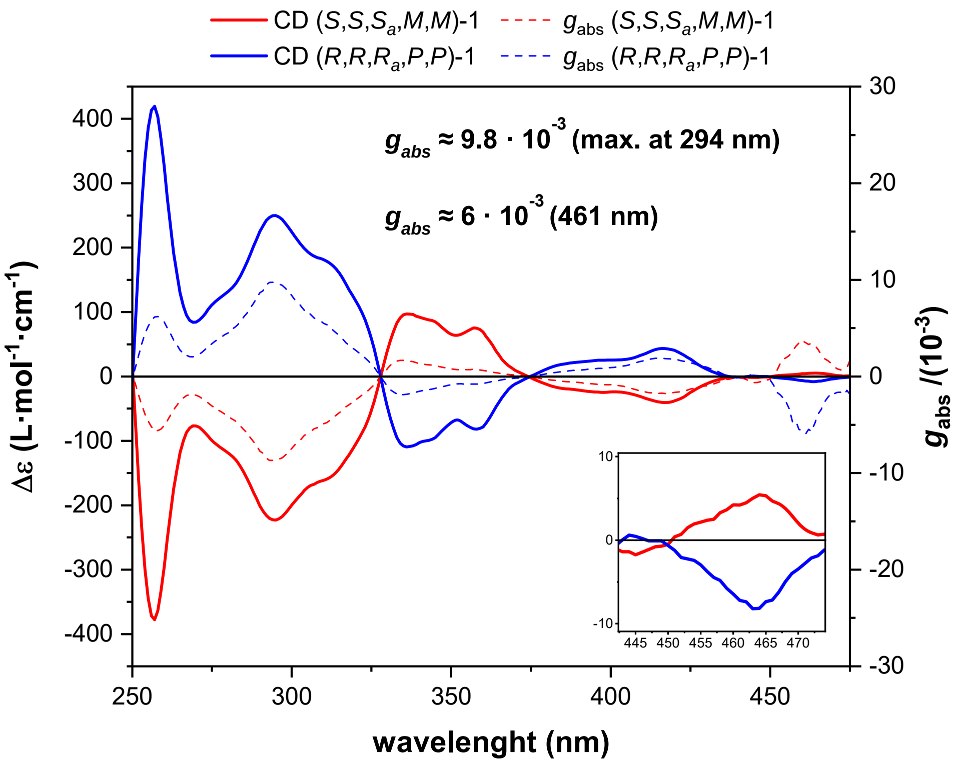


Figure S28. Circular Dichroism spectroscopic data and absorptive dissymmetry factor (g_{abs}) values of (*S,S,S$_a$,M,M*)-1 and (*R,R,R$_a$,P,P*)-1 (10 μM, $CHCl_3$, 20ºC, 10 mm).

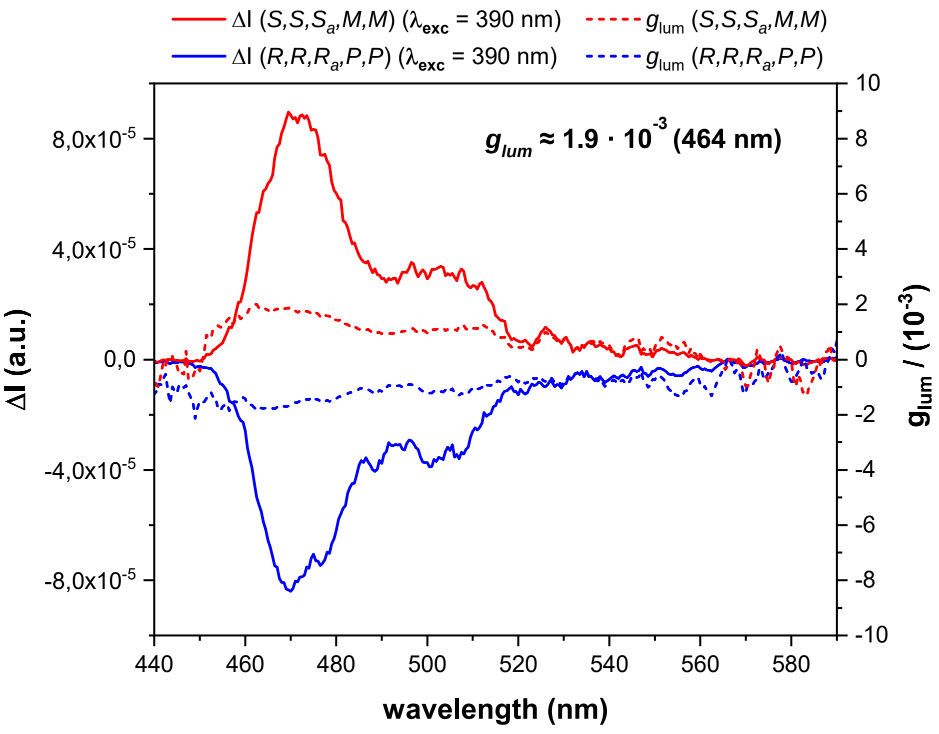


Figure S29. Circularly Polarized Luminescence spectroscopic data and luminescence dissymmetry factor (g_{lum}) value of (*S,S,S$_a$,M,M*)-1 and (*R,R,R$_a$,P,P*)-1 (ca. 10 μM, $CHCl_3$, 20ºC, 10 mm).