On the supramolecular polymerization of [5]helicenes. Consequences of self-assembly on configurational stability

Jorge S. Valera Rafael Gómez, and Luis Sánchez*

Departamento de Química Orgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain; e-mail: lusamar@quim.ucm.es

Table of Contents

1. Supplementary Figures

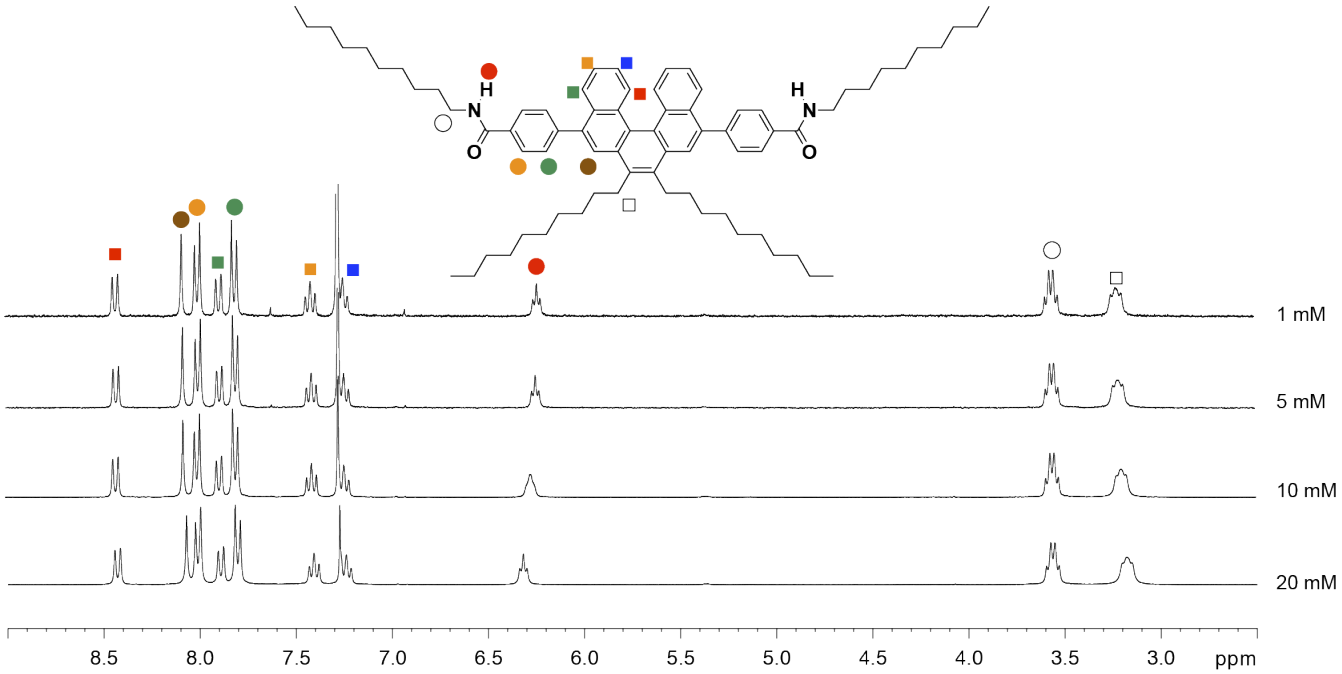


Figure S1. Concentration-dependent ^{1}H NMR spectra of **1** in $CDCl_3$ (300 MHz, 298 K) showing the aromatic, the amide and the methylene linked to the nitrogen atom and to the aromatic backbone protons.

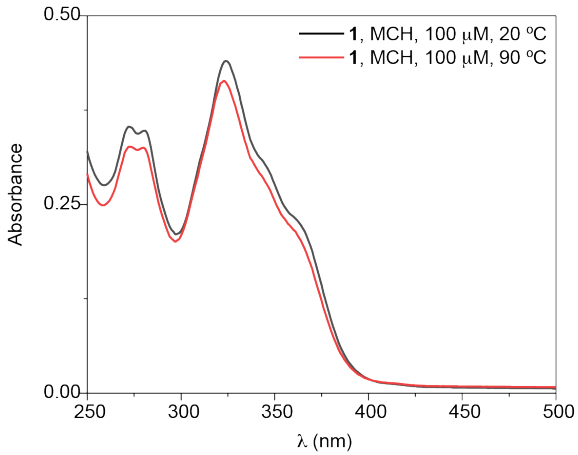


Figure S2. UV-Vis spectra of **1** in MCH at 20 ºC (black line) and 90 ºC (red line) at a concentration of 100 μM.

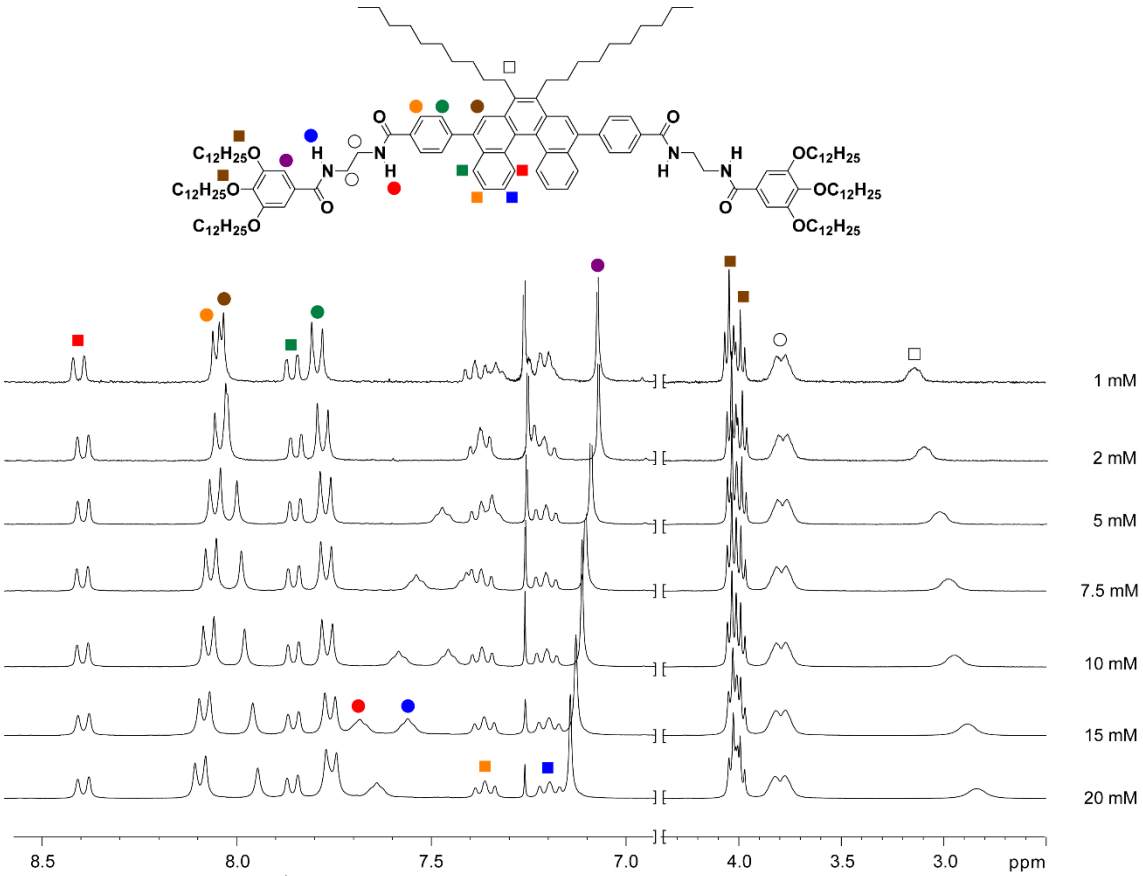


Figure S3. Concentration-dependent ^{1}H NMR spectra of **2** in $CDCl_3$ (300 MHz, 298 K) showing the aromatic, the amide and the methylene linked to the nitrogen atom and to the aromatic backbone protons.

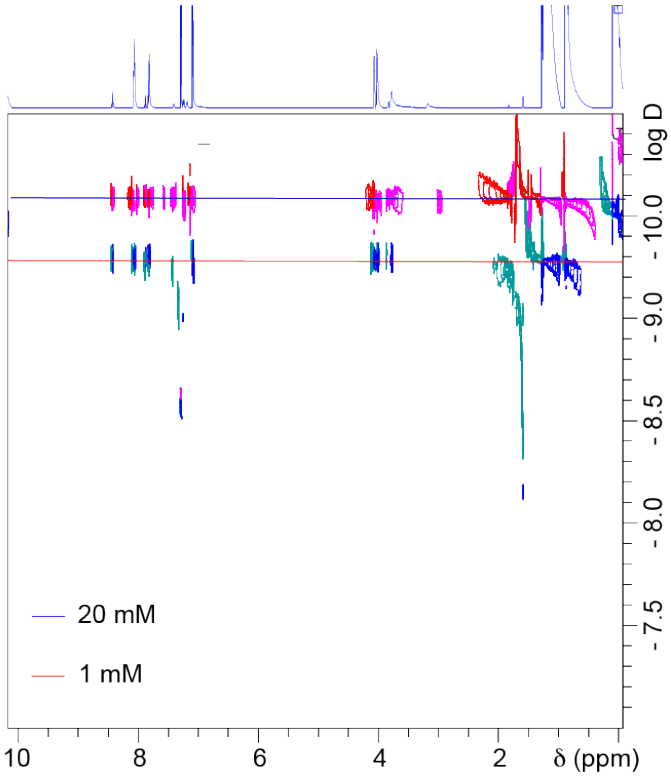


Figure S4. Partial ^{1}H DOSY NMR (Δ = 160 ms, t = 3 ms) spectra of **2** at different concentrations ($CDCl_3$, 298 K, 300 MHz).

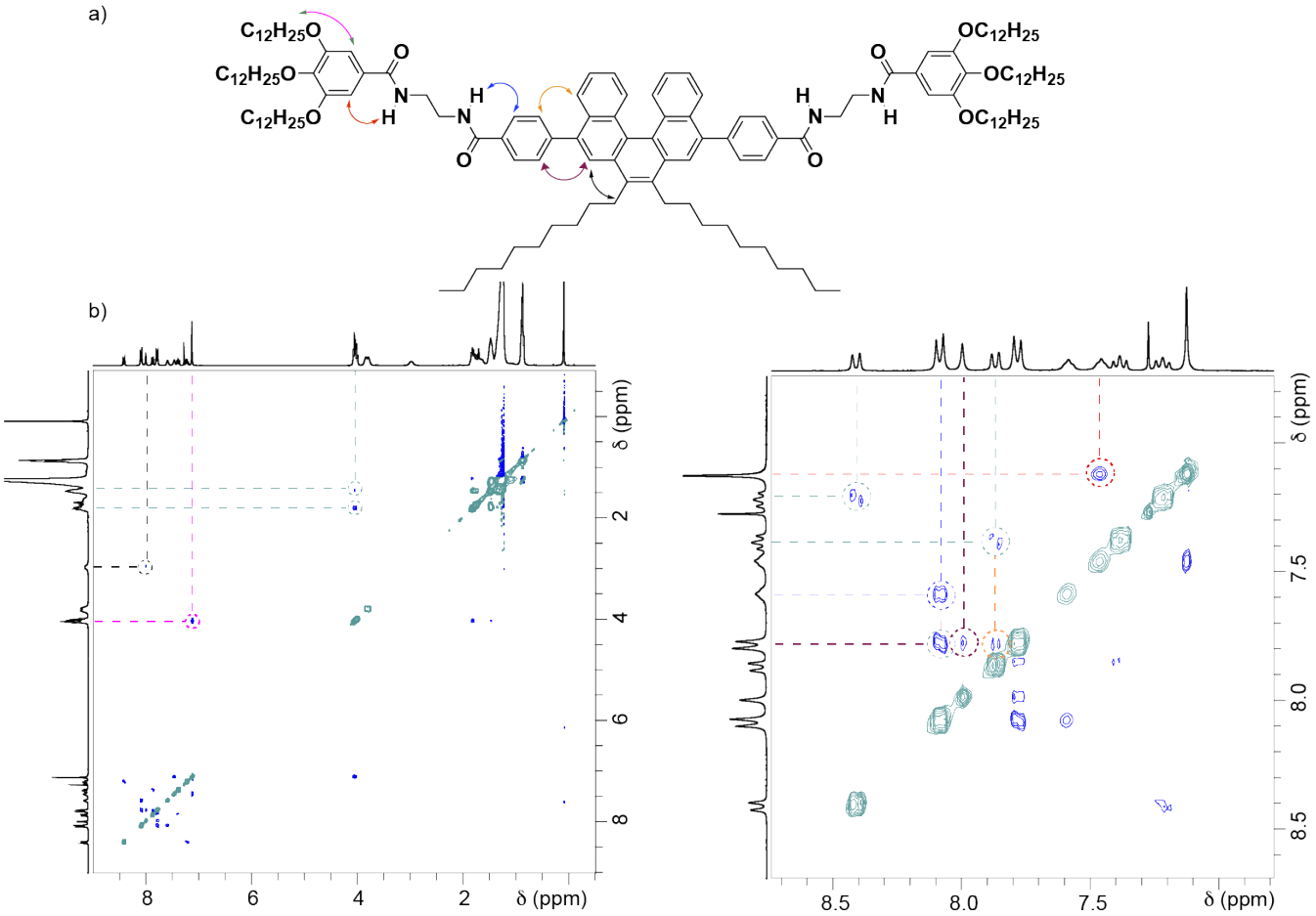


Figure S5. (a) Chemical structure of [5]helicene **2** depicting with curved arrows of different colors the intramolecular through-space coupling signals. (b) ROESY NMR spectra (CDCl3, 300 MHz, 20 x 10^{-3} M, 293 K) of **2**. The dotted coloured lines highlight the intramolecular through-space coupling signals.

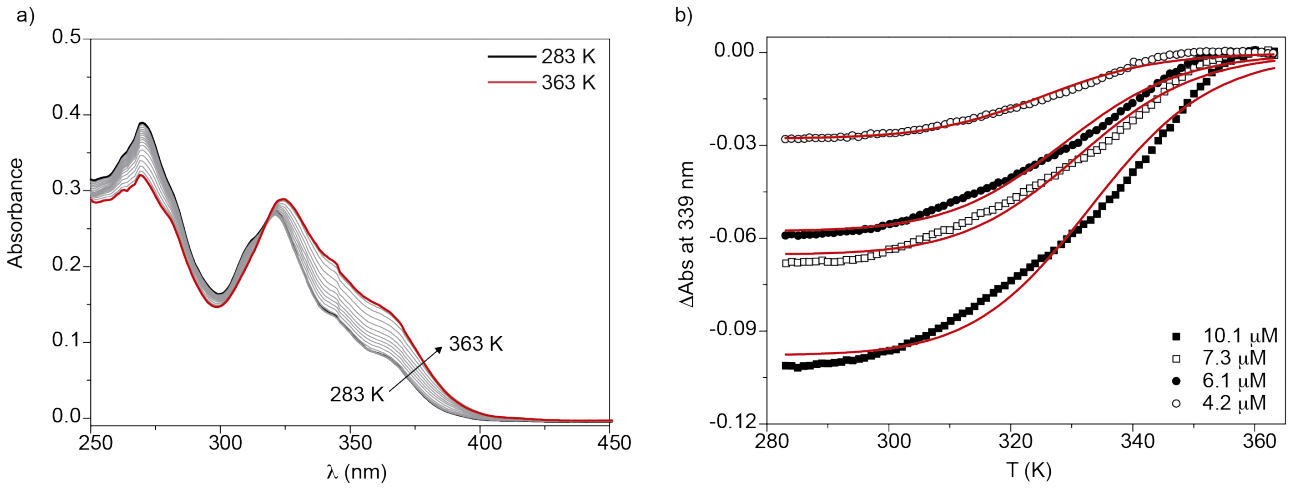


Figure S6. (a) VT-UV-Vis spectra of **2** in MCH (c_T = 10 μM; cooling rate = 1Kmin^{-1}) . (b) Plots of the variation of the absorbance at λ = 339 nm against temperature at different concentrations. The red curves represent the fit to the EQ model.

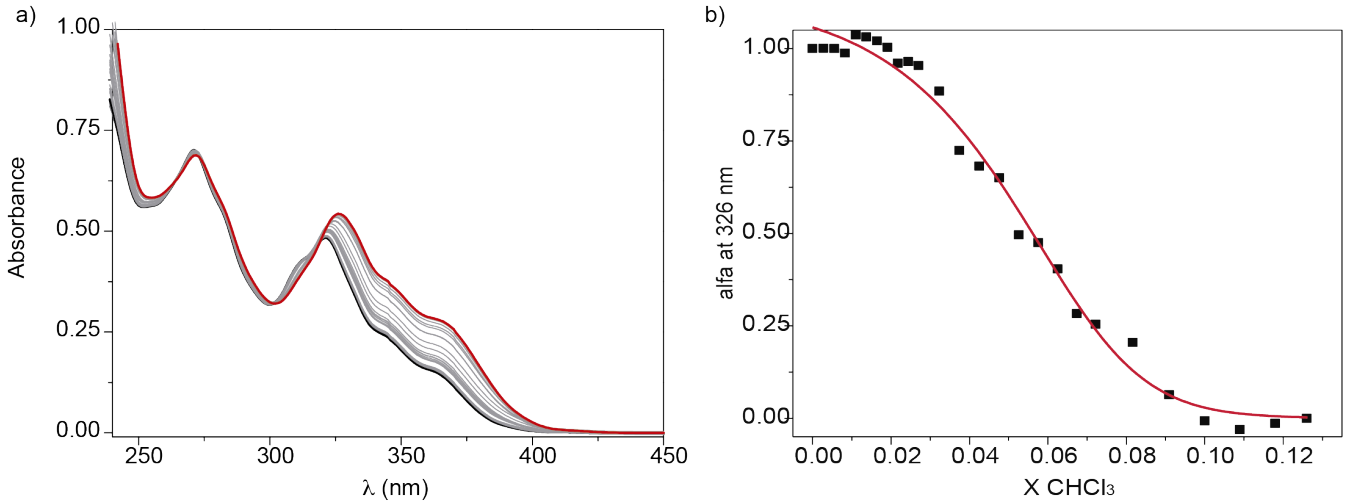


Figure S7. (a) UV-Vis spectra of **2** in MCH/$CHCl_3$ mixtures (c_T = 10 μM, 208 K). The black and red lines depict the UV-Vis spectra of **1b** in MCH and $CHCl_3$, respectively. (b) Plot of the degree of aggregation (α) versus the molar fraction of the good solvent $CHCl_3$. The red line shows the fitting to the SD model.

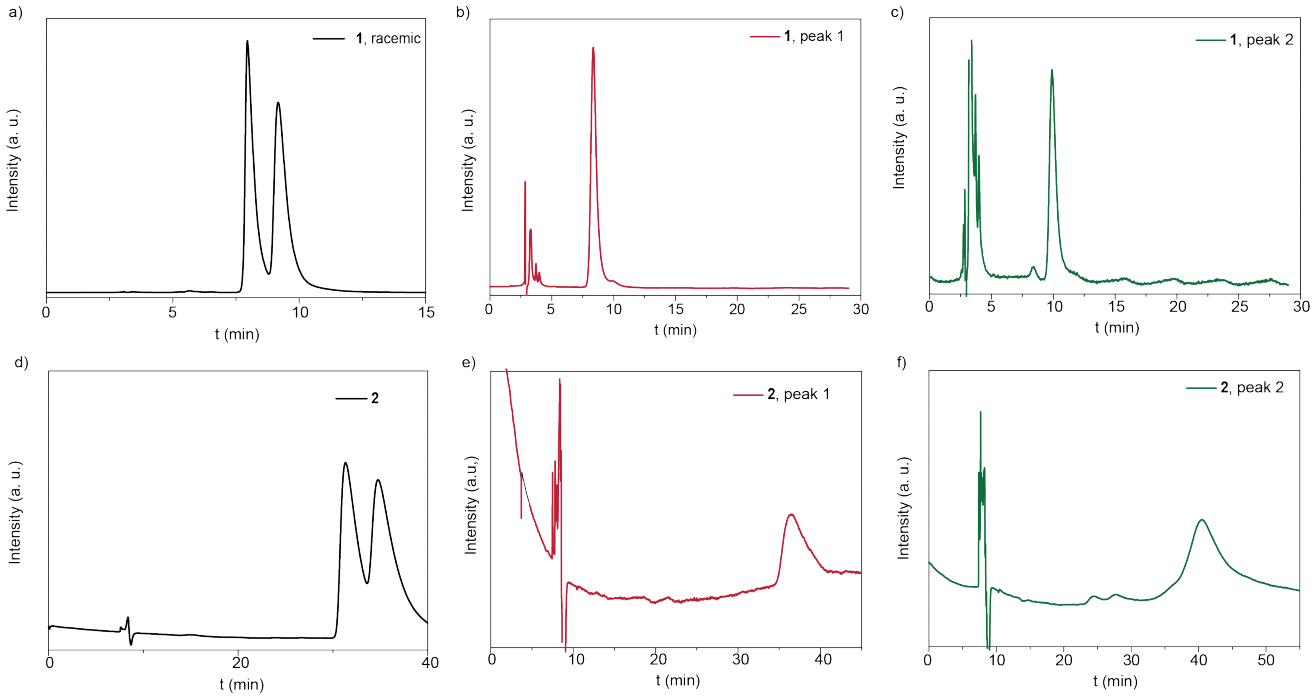


Figure S8. HPLC traces of helicenes **1** (a-c) and **2** (d-f) in their racemic (a, d) and enantiomerically enriched forms (b, c, e, f) on a (R,R)-Whelk 01 chiral column (experimental conditions for **1**: eluents: toluene/2-propanol mixture (97/3) as eluent, flow rate: 5 mL/min; for **2**: hexane/2-propanol (80/20) as eluent; flow rate 2,5 mL/min).

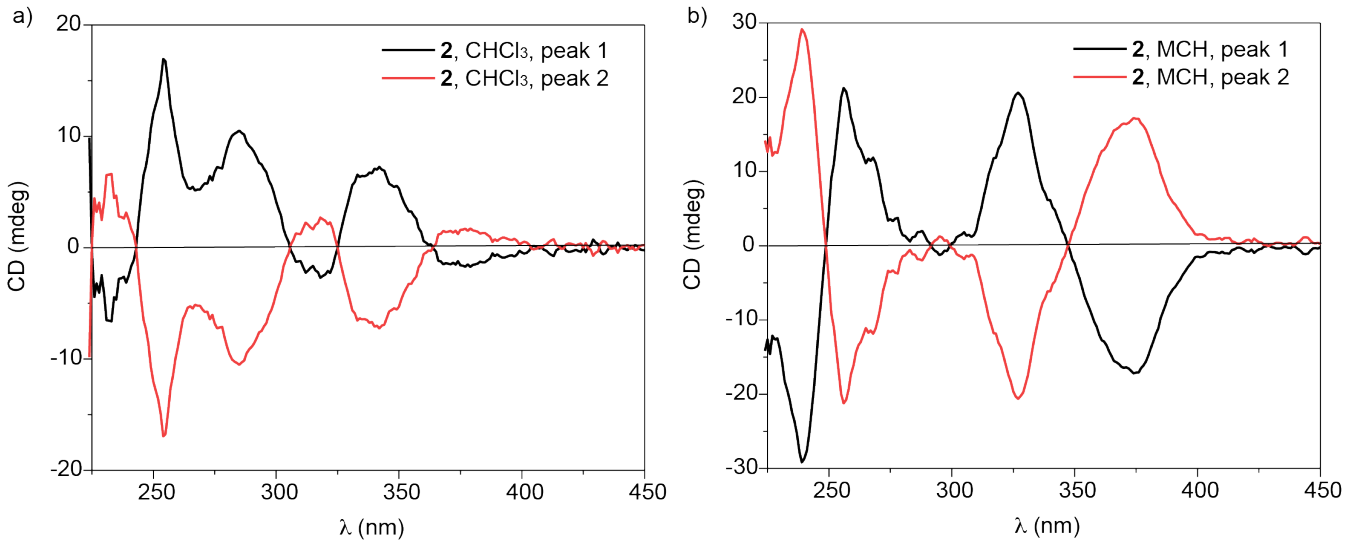


Figure S9. CD spectra of the two *M* and *P* enantiomers of **2** in a molecularly dissolved state ($CHCl_3$, 298 K, ~1 ×10^{-5} M) (a) and in the aggregated state (MCH, 298 K, ~1 × 10−5 M) (b).

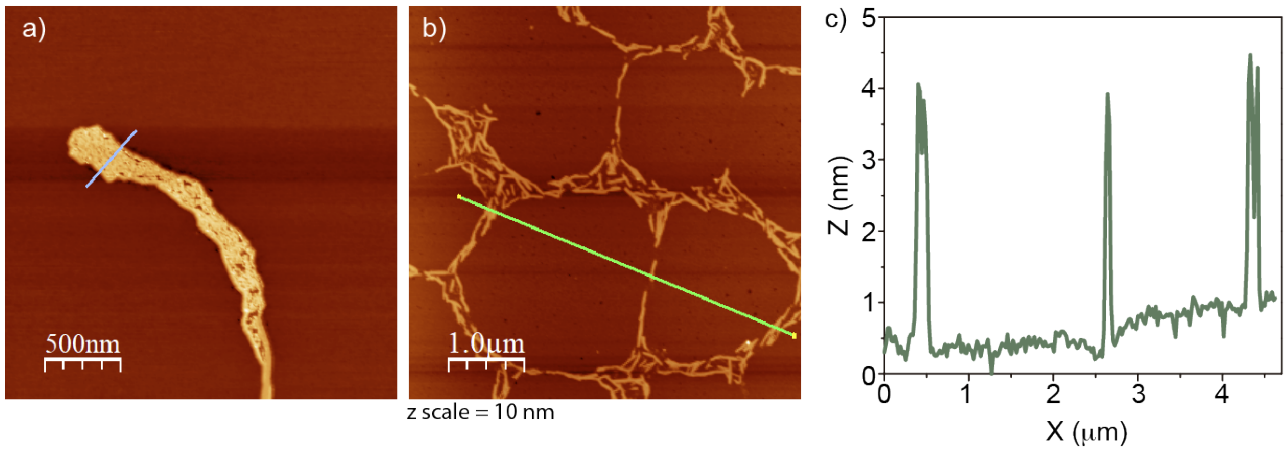


Figure S10. AFM images of the racemic mixture (a) and the *M* enantiomer (b) of **2** (10 μM, 298 K, mica as surface, z scale = 10 nm). (c) Height profile (green line in panel (b)) of the rod-like structures formed from the self-assembly of *M*-**2**.

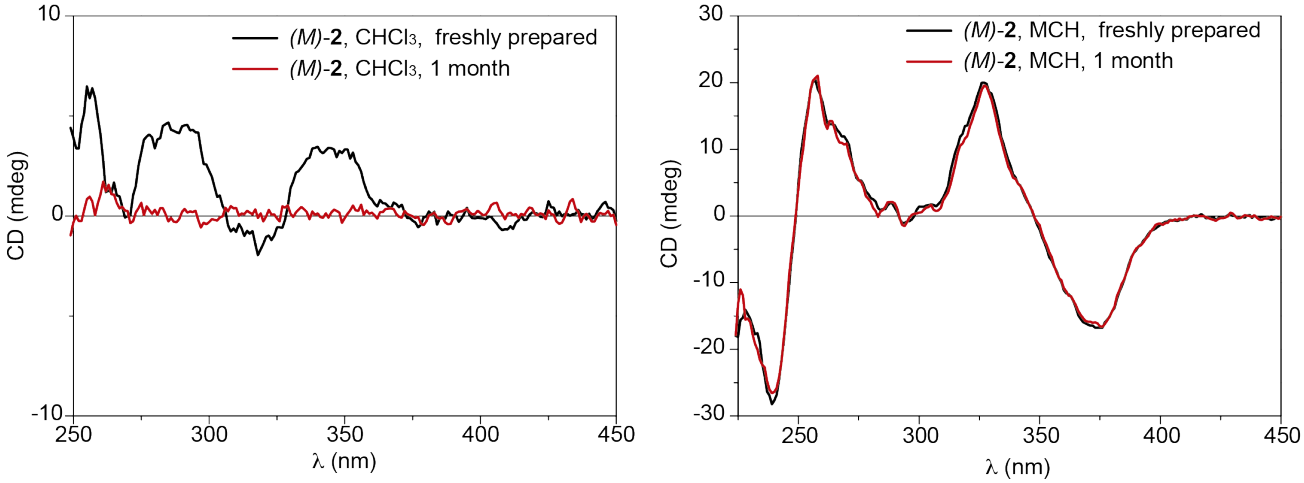


Figure S11. CD spectra of *M*-**2** in $CHCl_3$ (a) and MCH (b) (c_T = 10 mM; T = 283 K) measured at different times upon preparation.

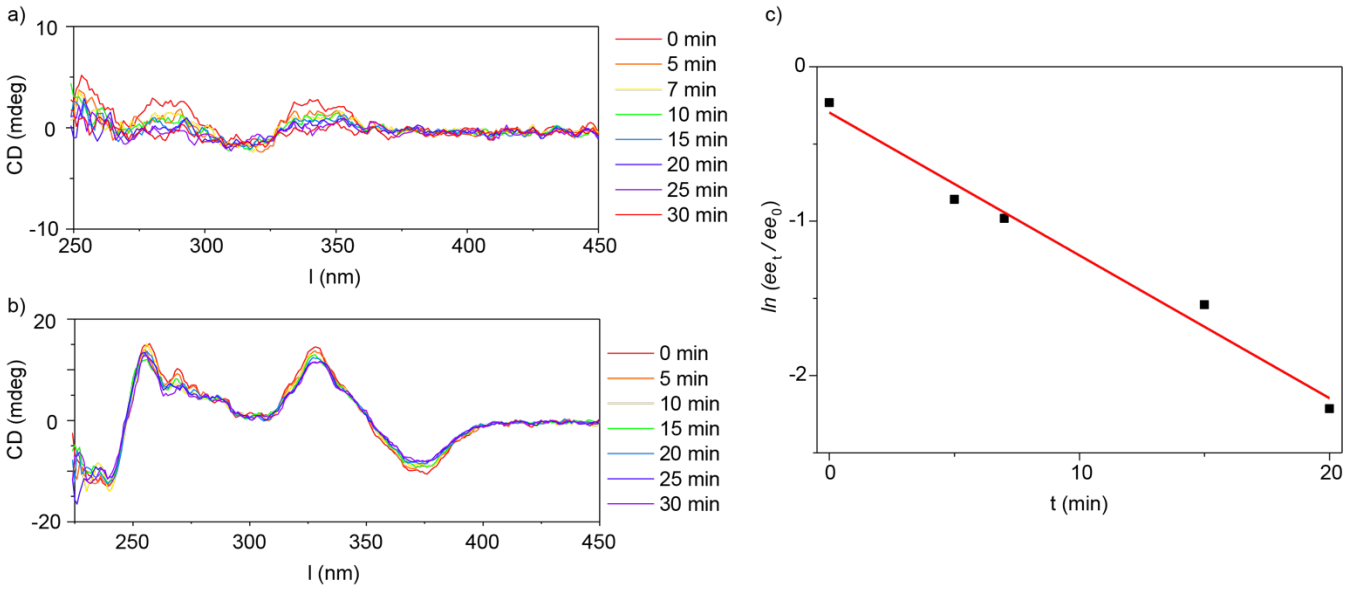


Figure S12. CD spectra of *M*-**2** in $CHCl_3$ (a) and MCH (b) (c_T = 10 mM; T = 328 K). (c) Natural logarithmic plot of the variation of enantiomeric excess of *M*-**2** in $CHCl_3$ versus time to derive the racemization constant k_{rac}.

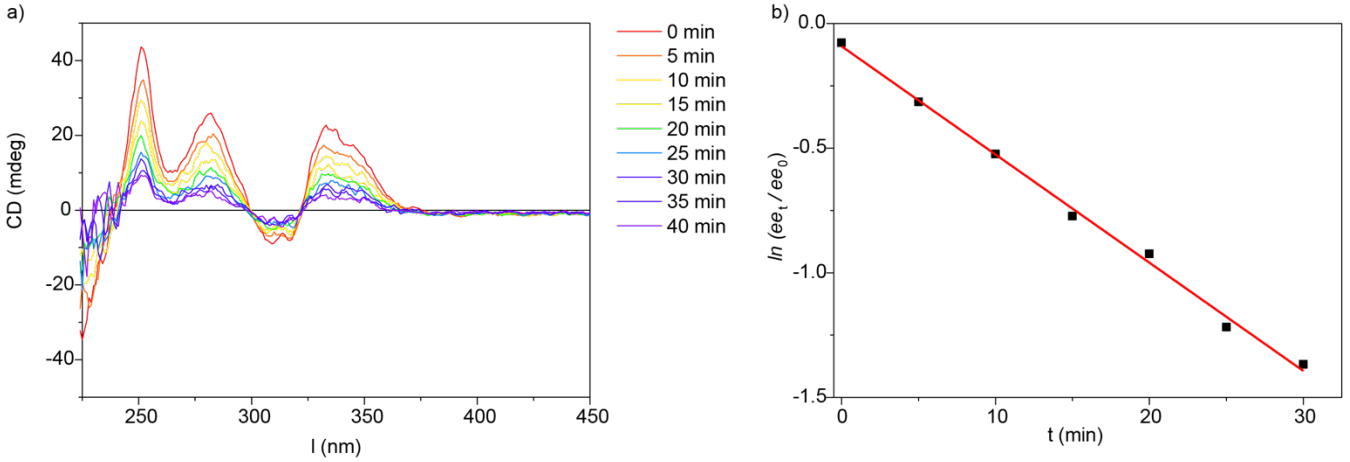


Figure S13. CD spectra of *P*-**1** in MCH (a) (c_T = 10 mM; T = 328 K). (b) Natural logarithmic plot of the variation of the variation of enantiomeric excess versus time to derive the racemization constant k_{rac}.

3. Experimental section

General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz), spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. High resolution mass spectra (HRMS) were recorded on a FTMS Bruker APEX Q IV spectrometer. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 220 and 450 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm. A 1 cm path length quartz cuvette (Hellma) was used. Thermal experiments were performed at constant heating rates of 1 K min^{-1} in methylcyclohexane. Circular dichroism (CD) measurements were performed on a Jasco-1500 dichrograph equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 220 and 450 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm. A 1 cm path length quartz cuvette (Hellma) was used. The spectra were recorded in the continuous mode between 350 and 600 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm. A 1 cm path length quartz cuvette (Hellma) was used. A 1 cm path length quartz cuvette (Hellma) was used. HPLC experiments were conducted using a (R,R)-Whelk 01 (5/100) chiral column (25 cm × 10 mm) with toluene/2-propanol mixture (97/3) for compound **1** and hexane/2-propanol (80/20) for compound **2** as eluents. Atomic Force Microscopy was performed on a SPM Nanoscope IIIa multimode microscope working on tapping mode with a RTESPA tip (Veeco) at a working frequency of ~235 kHz.

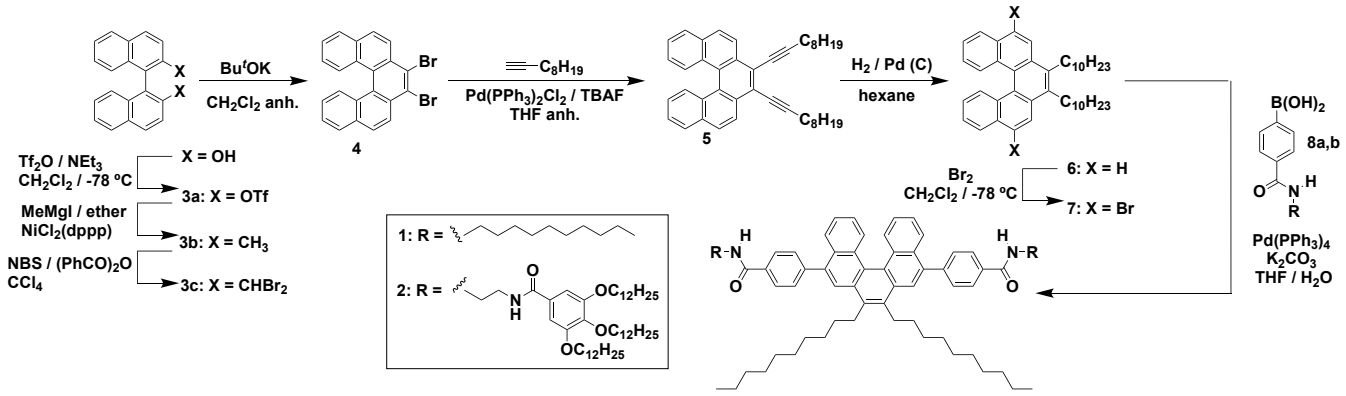
Racemization Experiments in solution

The value of the Gibbs activation energy of enantiomerization $\Delta G^{\ddagger}(T)$ for compounds *P*-**1** and *M*-**2** were obtained by resolution of the corresponding enantiomers in HPLC and by following the decay of the enantioenriched sample dissolved in MCH, for *P*-**1**, and $CHCl_3$ for *M*-**2** at a determined temperature (328 K) over time (t) by monitoring the change in the maximum (332, for , for *P*-**1**, and 349 nm for *M*-**2**) of the circular dichroism spectrum. The value ee_0 corresponds to the maximum at 349 nm at 293 K, and it relates to the enantiopure sample as shown by HPLC. Considering that the racemization process follows a first-order kinetics, the representation of $ln\ (ee_t / ee_0)$ versus t (where ee_t corresponds to the CD signal at the maximum at different times) allows to obtain the k_{rac} as these parameters are related through the equation $ln(ee_t / ee_0) = -k_{rac}t$. The constant k_{rac} is also used to calculate the half-time of the process according to $t_{½} = \ln 2 / k_{rac}$.
The free activation energy $\Delta G^{\ddagger}(328K)$ for the racemization is calculated by using the Eyring equation $\Delta G^{\ddagger}(T)=-RT\ ln(k_e h/\kappa k_B T)$ where k_e is the constant of enantiomerization ($k_e=k_{rac}/2$), *R* is the gas constant (R = 8.31441 J K^{-1}), *h* is the Planck constant (h = 6.626176.10^{-34} Js), k_B is the Boltzmann constant (k_B = 1.380662.10^{-23} JK^{-1}), and κ is the transmission coefficient (κ = 0.5). The transmission coefficient κ = 0.5 in the Eyring equation was used because the enantiomerization process is defined as a reversible first order reaction.[1]

The data derived for *P*-**1** are:
k_{rac} = (4.3 ± 0.1) x 10^{-2} min^{-1}
$t_{½}$ = 16.0 ± 0.4 min
k_e = (2.2 ± 0.1) x 10^{-2} min^{-1}
$\Delta G^{\ddagger}(328K)$ = 100 ± 3 kJ mol^{-1} = **24.0 ± 0.6 kcal mol^{-1}**

The data derived for *M*-**2** are:
k_{rac} = (9.2 ± 0.7) x 10^{-2} min^{-1}
$t_{½}$ = 7.5 ± 0.6 min
k_e = (4.6 ± 0.4)xx 10^{-2} min^{-1}
$\Delta G^{\ddagger}(328K)$ = 98 ± 8 kJ mol^{-1} = **23 ± 2 kcal mol^{-1}**
[1] a) G. Schoetz, O. Trapp, V. Schurig, *Electrophoresis* **2001**, *22*, 3185–3190. (b) K. J. Laidler, *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, **1987**.

4. Synthetic details and characterization

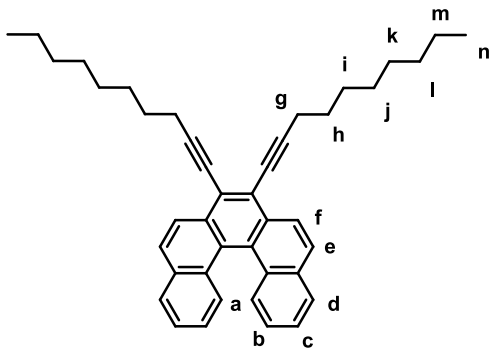


Scheme S1. Synthesis of the 5,7,8,10-tetrasubstituted [5]helicenes **1** and **2**.

Compounds **4**,[2] **8a**[3] and **8b**[4] were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties than those reported therein.

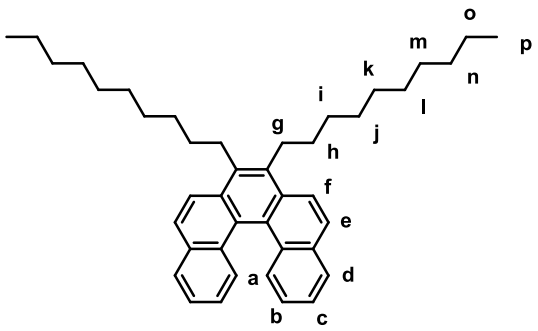
[1] a) T. Ooi, M. Kameda and K. Maruoka, *J. Am. Chem. Soc.* **2003**, *125*, 5139. b) S. Goretta, C. Tasciotti, S. Mathieu, M. Smet, W. Maes, Y. M. Chabre, W. Dehaen, R. Giasson, J. M. Raimundo, C. R. Henry, C. Barth, and M. Gingras, *Org.Lett*. **2009**, *11*, 3846.
[2] F. García, J. Buendía, S. Ghosh, A. Ajayaghosh and L. Sánchez, *Chem. Comm.* **2013**, *49*, 9278.
[3] E. E. Greciano and L. Sánchez, *Chem. Eur. J.* **2016**, *22*, 13724.

Synthesis of (±)-7,8-di(1-decynyl)[5]helicene.



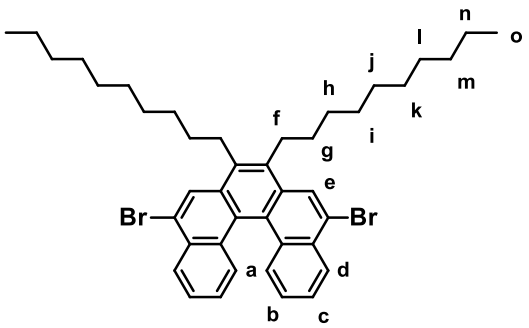
Compound **4** (290 mg, 0.67 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 9.6 $x10^{-2}$ mmol) and CuI (10 mg, $4.8x10^{-2}$ mmol) are dissolved in anhydrous THF (18 mL) under argon atmosphere and subjected to vacuum/argon cycles. Subsequently, 2 mL of a 1 M solution of tetrabutylammonium fluoride in THF (2 mmol) are added and the resulting mixture is subjected to vacuum/argon cycles. After that, 1-decyne (0.29 mL, 1.6 mmol) is charged and the solution is stirred under reflux overnight. After 24 hours, a new amount of $PdCl_2(PPh_3)_2$ (70 mg), CuI (10 mg) and 1-decyne (0.15 mL) is added and the mixture is stirred and refluxed overnight. The solvent is evaporated and the residue is redissolved in $CHCl_3$ and washed with 1M aqueous HCl, sat. NH_4Cl and brine. The organic layer is dried with $MgSO_4$, and further filtration and removal of the solvent affords a residue which is subjected to a silica gel chromatography column (hexane as eluent) obtaining **5** as a pale yellow solid in a 62% yield (230 mg, 0.42 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.49 (d, ^3J = 8.8 Hz, 2H, H_a), 8.33 (d, ^3J = 8.6 Hz, 2H, $H_{e\ or\ f}$), 7.97 (d, ^3J = 8.6 Hz, 2H, $H_{f\ or\ e}$), 7,94 (d, ^3J = 7.6 Hz, 2H, H_d) 7.51 (ddd, ^3J = 7.6 Hz, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2H, $H_{b\ or\ c}$), 7.25 (ddd, ^3J = 8.8 Hz, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 2H, $H_{c\ or\ b}$), 2.71 (t, ^3J = 7.0 Hz, 4H, H_g), 1.86-1.75 (m, 4H, H_h), 1.65-1.56 (m, 4H, H_i), 1.41-1.33 (m, 16H, H_{j-m}), 0.91 (t, ^3J = 6.5 Hz, 6H, H_n). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 132.7, 131.8, 130.7, 129.5, 128.0, 127.8, 126.6, 126.5, 124.6, 124.6, 124.1, 100.4, 78.7, 32.1, 29.5, 29.5, 29.3, 29.2, 22.9, 20.3, 14.3. FTIR ν (cm^{-1}): 2926, 2856, 2222, 1514, 1461, 1431, 1384, 1343, 1262, 817, 751, 664. HRMS m/z: $C_{42}H_{46}$ $[M]^+$ calculated 550.3600; found 550.3616.

Synthesis of compound (±)-7,8-didecyl[5]helicene.



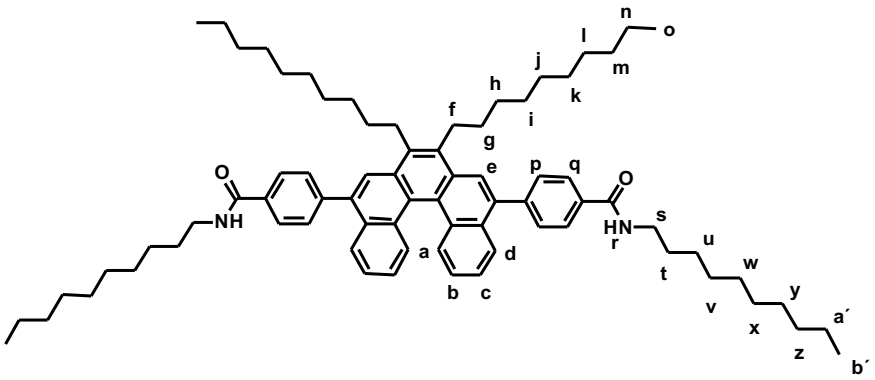
A solution of **5** (240 mg, 0.44 mmol) in CH_2Cl_2 (100 mL) is bubbled with argon for 10 minutes in absence of light. After that, 10% Pd/C (14 mg, 0.13 mmol) is added, and hydrogen is passed through the solution during 4 hours. After the removal of the catalyst with celite and subsequent elimination of the solvent, the residue is purified with a silica gel column chromatography (hexane as eluent), affording **6** as a light yellow solid in a 60% yield (140 mg, 0.25 mmol).^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.28 (d, ^3J = 8.4 Hz, 2H, H_a), 8.14 (d, ^3J = 8.9 Hz, 2H, $H_{e\ or\ f}$), 7.96 (d, ^3J = 8.9 Hz, 2H, $H_{f\ or\ e}$), 7.93 (d, ^3J = 7.4 Hz, 2H, H_d), 7.47 (ddd, ^3J = 7.9 Hz, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2H, H_c), 7.21 (ddd, ^3J = 8.4 Hz, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 2H, H_b), 3.22 (t, ^3J = 8.3 Hz, 4H, H_g), 1.77 (m, 4H, H_h), 1.62 (m, 4H, H_i), 1.51-1.25 (m, 24H, H_{j-o}), 0.93 (t, ^3J = 7.0 Hz, 6H, H_p). ^{13}C-RMN ($CDCl_3$, 75 MHz) δ (ppm): 135.1, 131.6, 131.3, 130.9, 129.9, 127.4, 127.1, 126.2, 125.9, 124.4, 122.4, 32.1, 31.5, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 22.9, 14.3. FTIR ν (cm^{-1}): 2923, 2853, 1513, 1461, 1376, 1249, 1124, 808, 750. HRMS m/z: $C_{42}H_{54}$ $[M]^+$ calculated 558.4226; found 558.4240.

Synthesis of compound (±)-5,10-dibromo-7,8-didecyl[5]helicene.



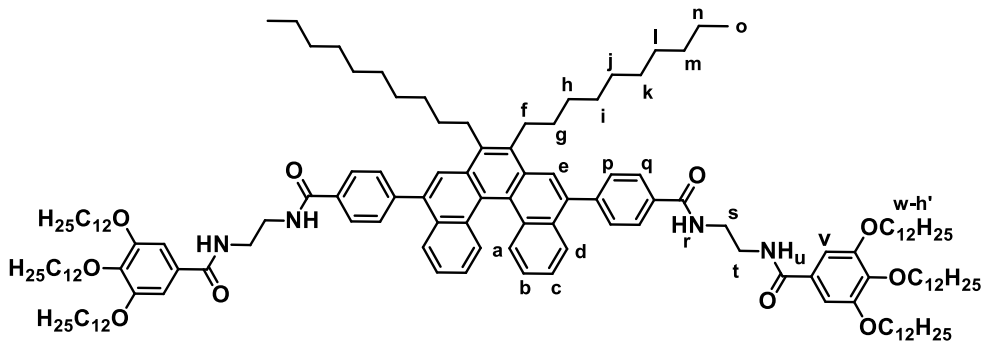
A solution of **6** (0.13 g, 0.31 mmol) in anhydrous CH_2Cl_2 (20 mL) is cooled down to -78 °C and a solution of bromine (36 µL, 0.69 mmol) in anhydrous CH_2Cl_2 (8 mL) is added dropwise. After 10 minutes, the mixture is allowed to reach room temperature and is stirred overnight. The resulting organic phase is washed with sat. $Na_2S_2O_3$ and dried with $MgSO_4$. Further filtration and removal of the solvent affords a residue that is purified by silica gel column chromatography (hexane as eluent) giving **7** as a waxy pale yellow solid in a 77% yield (171 mg, 0.24 mmol). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.34 (s, 2H, H_e), 8.29 (dd, ^3J = 8.5 Hz, ^4J = 1.6 Hz, 2H, H_a), 8.09 (d, ^3J = 7.5 Hz, 2H, H_d), 7.49 (ddd, ^3J = 7.9 Hz, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2H, H_c), 7.15 (ddd, ^3J = 8.5 Hz, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 2H, H_b), 3.07 (t, ^3J = 7.8 Hz, 4H, H_f), 1.65 (m, 4H, H_g), 1.53 (m, 4H, H_h), 1.50-1.24 (m, 24H, H_{i-n}), 0.90 (t, ^3J = 6.9 Hz, 6H, H_o). ^{13}C-RMN ($CDCl_3$, 75 MHz) δ (ppm): 135.2, 132.2, 131.5, 130.0, 129.9, 127.2, 126.9, 126.3, 125.8, 125.5, 122.3, 32.1, 31.4, 30.4, 29.9, 29.8, 29.6, 29.5, 29.4, 22.9, 14.3. FTIR ν (cm^{-1}): 2924, 2853, 1592, 1462, 1329, 1210, 865, 759. HRMS m/z: $C_{42}H_{52}Br_2$ $[M]^+$ calculated 716.2436; found 716.2466.

Synthesis of (±)-4,4´-(7,8-didecyl[5]helicene-5,10-diyl)bis(*N*-decylbenzamide).



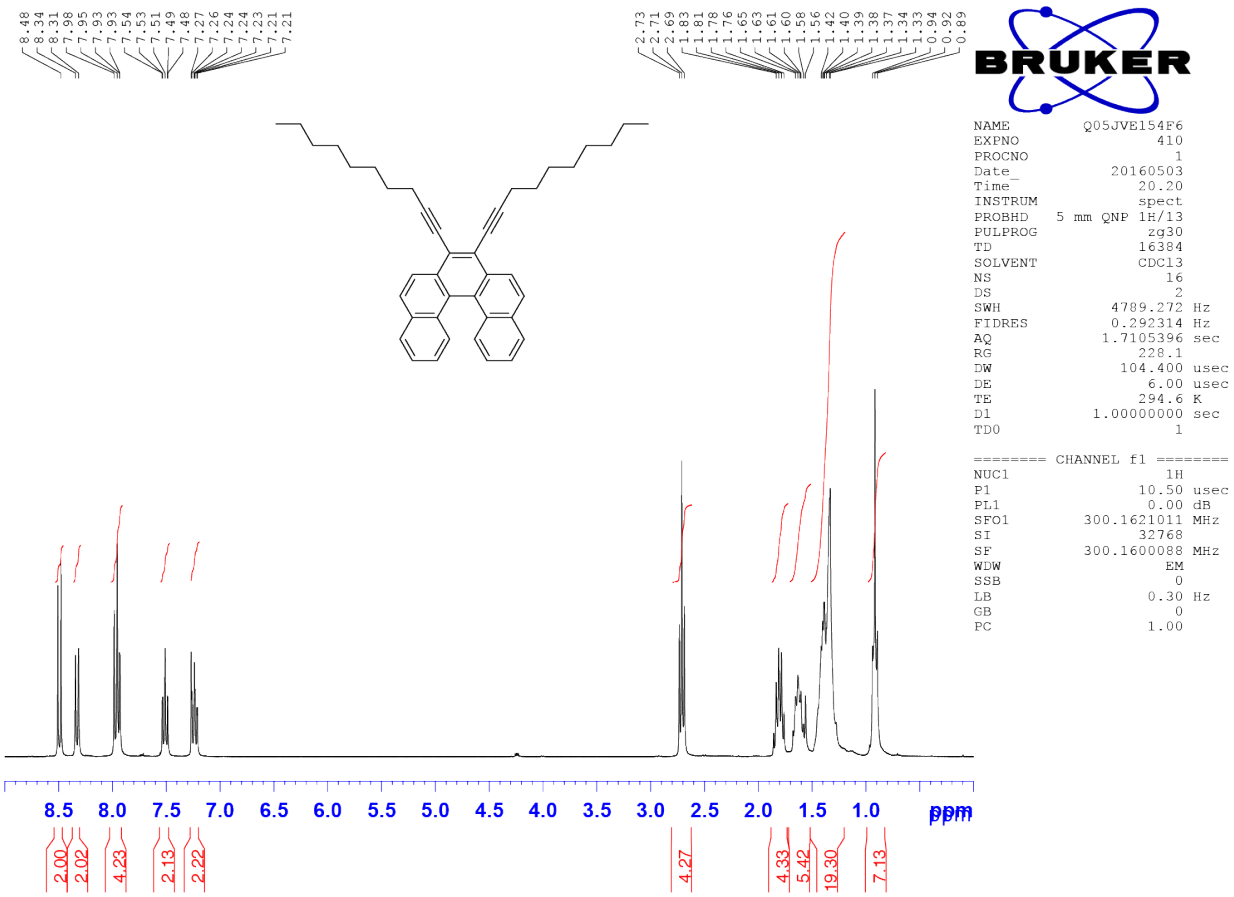
To a deoxygenated solution of **7** (80 mg, 0.11 mmol) and **8a** (86 mg, 0.28 mmol) in tetrahydrofuran (24 mL), $Pd(PPh_3)_4$ (13 mg, 1.12 x10^{-2} mmol), and an aqueous solution of K_2CO_3 (230 mg, 1.68 mmol in 4 mL of water) are added and the resulting mixture is deoxygenated again. The reaction is refluxed for 4 hours, and the crude is extracted with chloroform. The organic layer is washed with 1M aqueous HCl, NH_4Cl and brine. After drying and removal of the solvent, the crude is purified by silica gel column chromatography (gradient from chloroform to chloroform/methanol 10:0.1). The product obtained is further purified by precipitation in methanol, affording **1** as a yellow solid in a 34% yield (40 mg, 0.03 mmol). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.42 (d, ^3J = 8.2 Hz, 2H, H_a), 8.07 (s, 2H, H_e), 8.01 (d, ^3J = 8.2 Hz, 4H, H_q), 7.89 (d, ^3J = 8.3 Hz, 2H, H_d), 7.80 (d, 4H, ^3J = 8.2 Hz, H_p), 7.40 (ddd, ^3J = 8.3 Hz, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 2H, H_c), 7.24 (ddd, ^3J = 8.2 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 2H, H_b), 6.30 (t, ^3J = 5.8 Hz, 2H, H_r), 3.55 (m, 4H, H_s), 3.18 (m, 4H, H_f), 1.80-1.22 (m, 64H, $H_{g-n+t-a'}$), 0.94-0.84 (m, 12H, $H_{o+b'}$). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 167.5, 144.5, 137.9, 135.6, 134.0, 131.9, 130.5, 130.3, 130.0, 127.2, 126.2, 125.8, 125.7, 124.7, 123.2, 40.4, 32.0, 31.5, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 27.2, 22.8, 14.3. FTIR ν (cm^{-1}): 3322, 2956, 2923, 2853, 1635, 1546, 1503, 1461, 1309, 1262, 1095, 1020, 856, 801, 765. HRMS m/z: $C_{76}H_{104}N_2O_2$ $[M]^+$ calculated 1076.8098; found 1076.8046.

Synthesis of (±)-*N*,*N*'-((((4,4'-(7,8-didecyl[5]helicene-5,10-diyl)bis(benzoyl))bis-(azanediyl))bis(ethane-2,1-diyl))bis(3,4,5-tris(dodecyloxy)benzamide

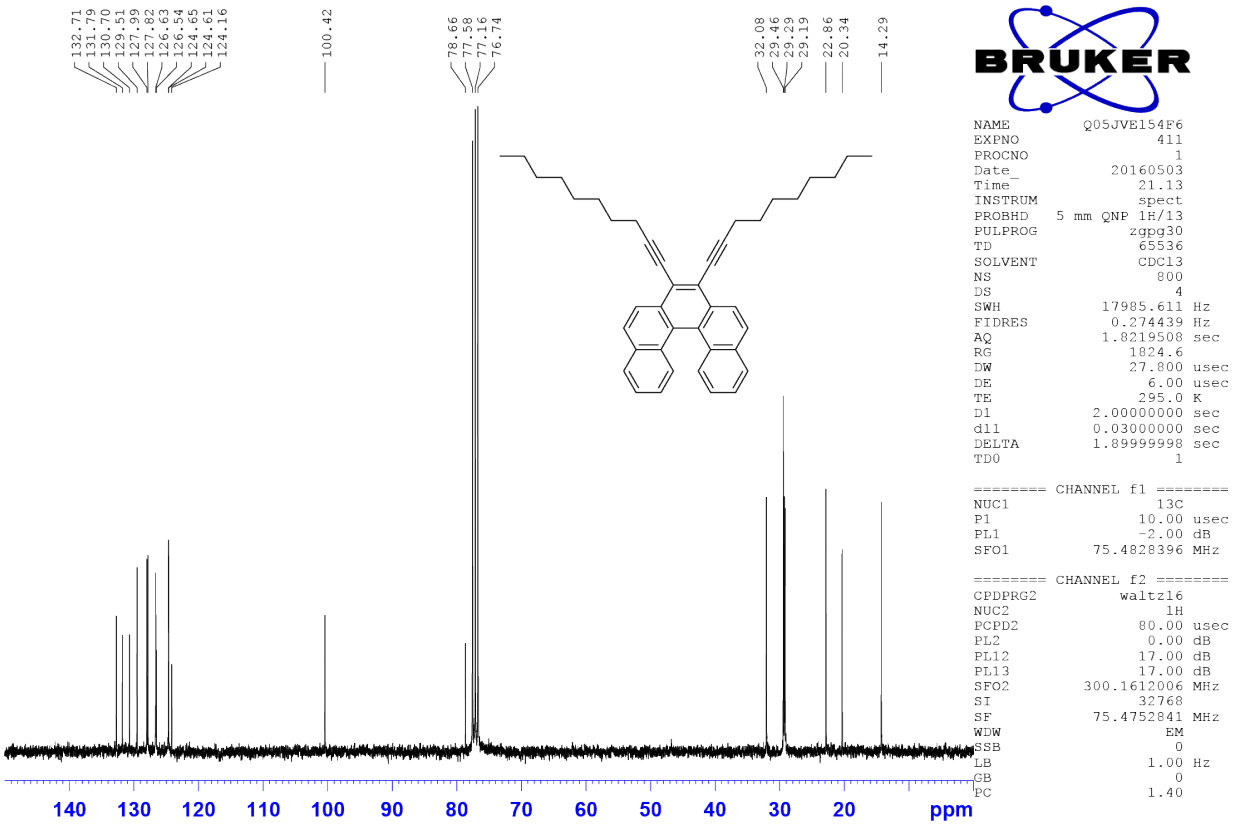


To a deoxygenated solution of **7** (50 mg, 0.07 mmol) and **8b** (150 mg, 0.17 mmol) in tetrahydrofuran (15 mL), $Pd(PPh_3)_4$ (8 mg, 7.00 x10^{-3} mmol), and an aqueous solution of K_2CO_3 (140 mg, 1.05 mmol in 3 mL of water) are added and the resulting mixture is deoxygenated again. The reaction is refluxed for 4 hours, and the crude is extracted with chloroform. The organic layer is washed with 1M aqueous HCl, NH_4Cl and brine. After drying and removal of the solvent, the crude is purified by silica gel column chromatography (gradient from chloroform to chloroform/methanol 10:0.1) and the product obtained is precipitated in methanol, affording **2** as a dark yellow solid in a 44% yield (70 mg, 0.03 mmol). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.39 (d, ^3J = 8.4 Hz, 2H, H_a), 8.09 (d, ^3J = 7.9 Hz, 4H, H_q), 7.95 (s, 2H, H_e), 7.86 (d, ^3J = 8.4 Hz, 2H, H_d), 7.76 (d, ^3J = 7.9 Hz, 4H, H_p), 7.81-7.70 (br, 2H, $H_{r\ or\ u}$), 7.61-7.69 (br, 2H, $H_{u\ or\ r}$), 7.36 (dd, ^3J = 8.4 Hz, ^3J = 7.5 Hz, 2H, H_c), 7.20 (dd, ^3J = 8.4 Hz, ^3J = 7.5 Hz, 2H, H_b), 7.14 (s, 4H, H_v), 4.3 (m, 12H, H_w), 3.81 (m, 8H, H_{s-t}), 2.86 (br, 4H, H_f), 1.81-1.13 (m, 32H + 120H, $H_{g-n\ +\ x-i'}$), 0.94-0.79 (m, 6H + 18H, $H_{o\ +\ h'}$). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 168.9, 168.8, 153.2, 144.9, 141.2, 137.7, 135.5, 132.9, 131.9, 130.5, 130.4, 130.4, 129.9, 128.8, 127.6, 126.2, 126.2, 125.8, 125.5, 124.7, 123.2, 105.7, 73.6, 69.3, 43.6, 41.4, 41.1, 32.1, 32.0, 31.3, 30.5, 30.4, 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 26.3, 26.2, 22.8, 22.8, 14.3, 14.2. FTIR v (cm^{-1}): 3307, 3020, 2923, 2853, 1631, 1581, 1544, 1498, 1467, 1344, 1304, 1265, 1215, 1115, 858, 752, 668. HRMS m/z: $C_{146}H_{226}N_4O_{10}$ $[M + Na]^+$ calculated 2218.7197; found 2218.7236.

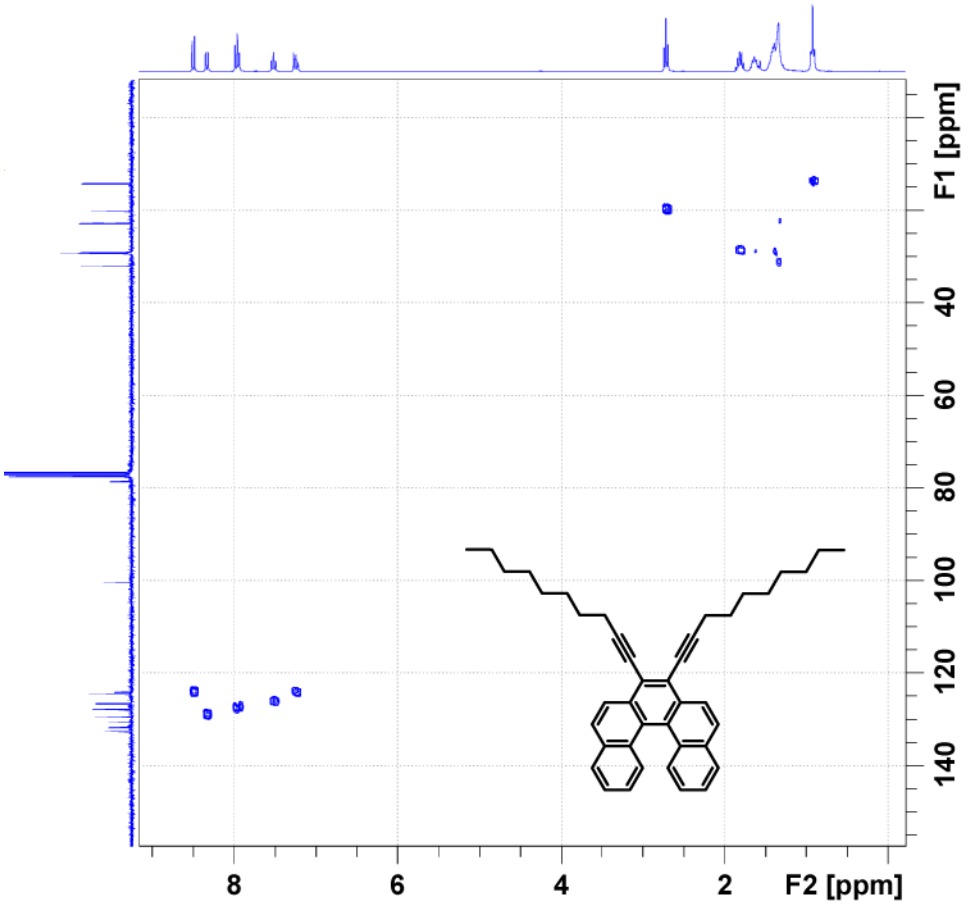
Collection of NMR spectra



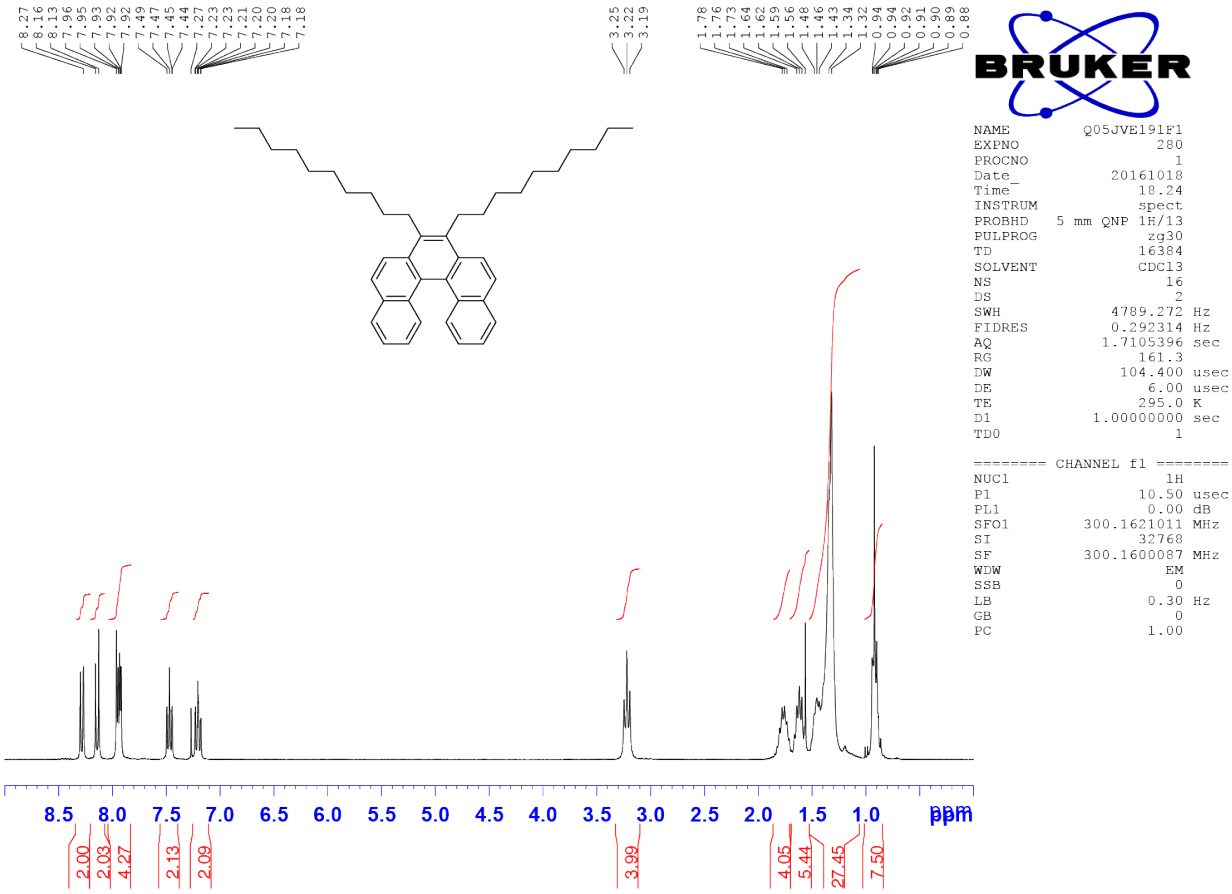
^{1}H NMR spectrum of compound **(±)-5** (300 MHz, $CDCl_3$, 298 K).



^{13}C NMR spectrum of compound **(±)-5** (75 MHz, $CDCl_3$, 298 K).

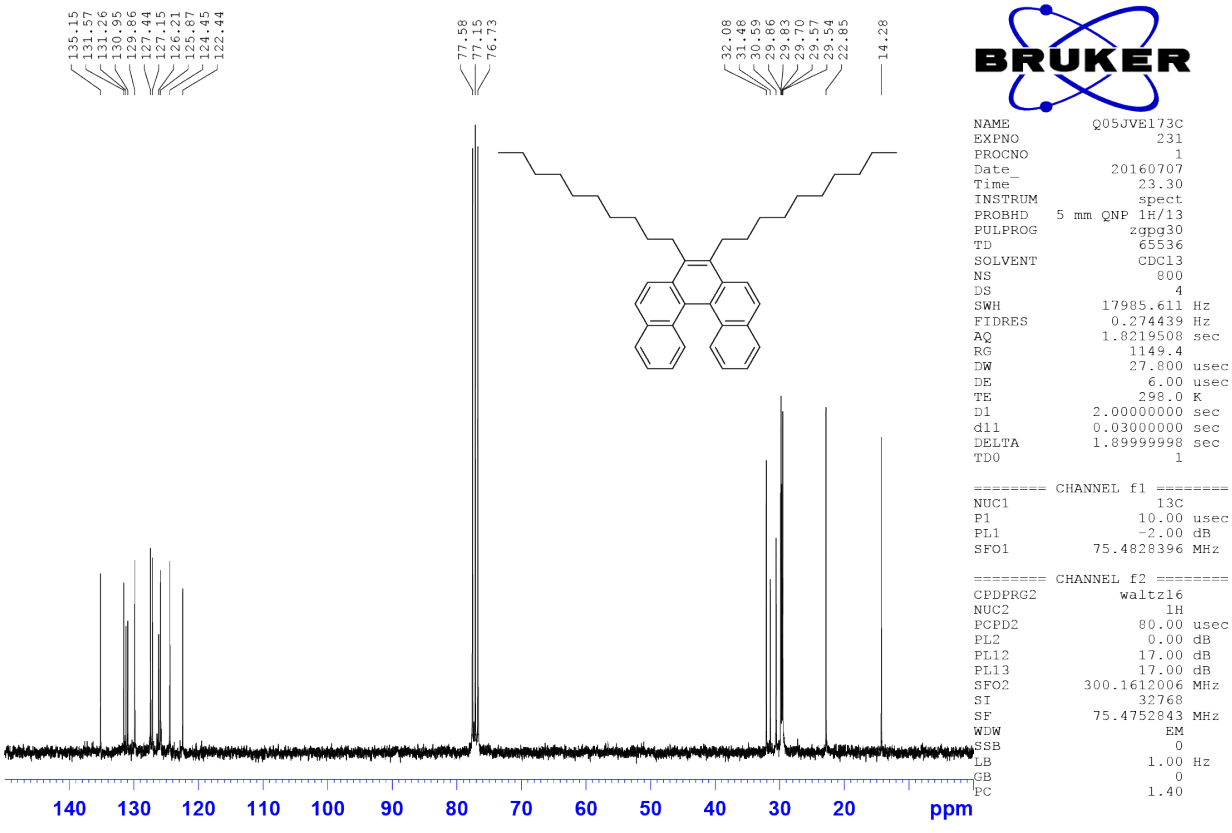


^{1}H-^{13}C HMQC spectrum of compound **(±)-5** ($CDCl_3$, 298 K).



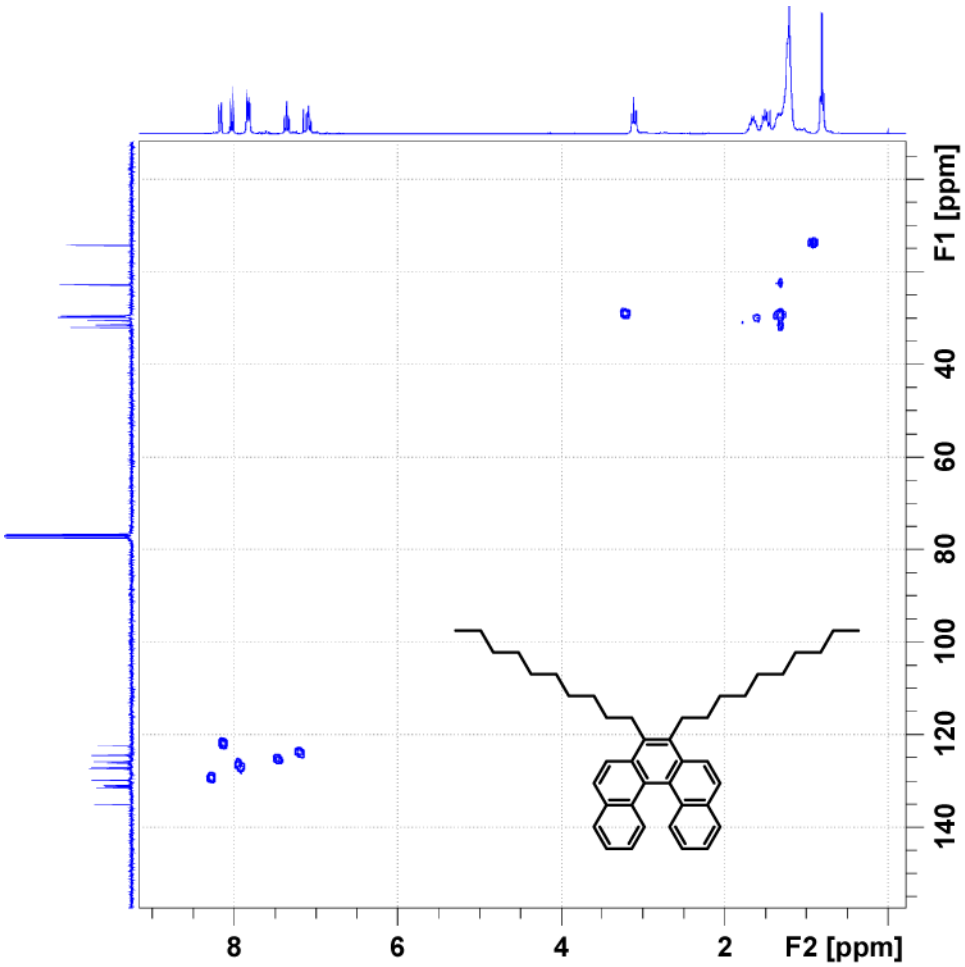

```
NAME            Q05JVE191F1
EXPNO                   280
PROCNO                    1
Date_            20161018
Time_               18.24
INSTRUM             spect
PROBHD    5 mm QNP 1H/13
PULPROG              zg30
TD                  16384
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              4789.272 Hz
FIDRES           0.292314 Hz
AQ             1.7105396 sec
RG                  161.3
DW                104.400 usec
DE                  6.00 usec
TE                 295.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.50 usec
PL1                  0.00 dB
SFO1          300.1621011 MHz
SI                  32768
SF            300.1600087 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR spectrum of compound **(±)-6** (300 MHz, $CDCl_3$, 298 K).

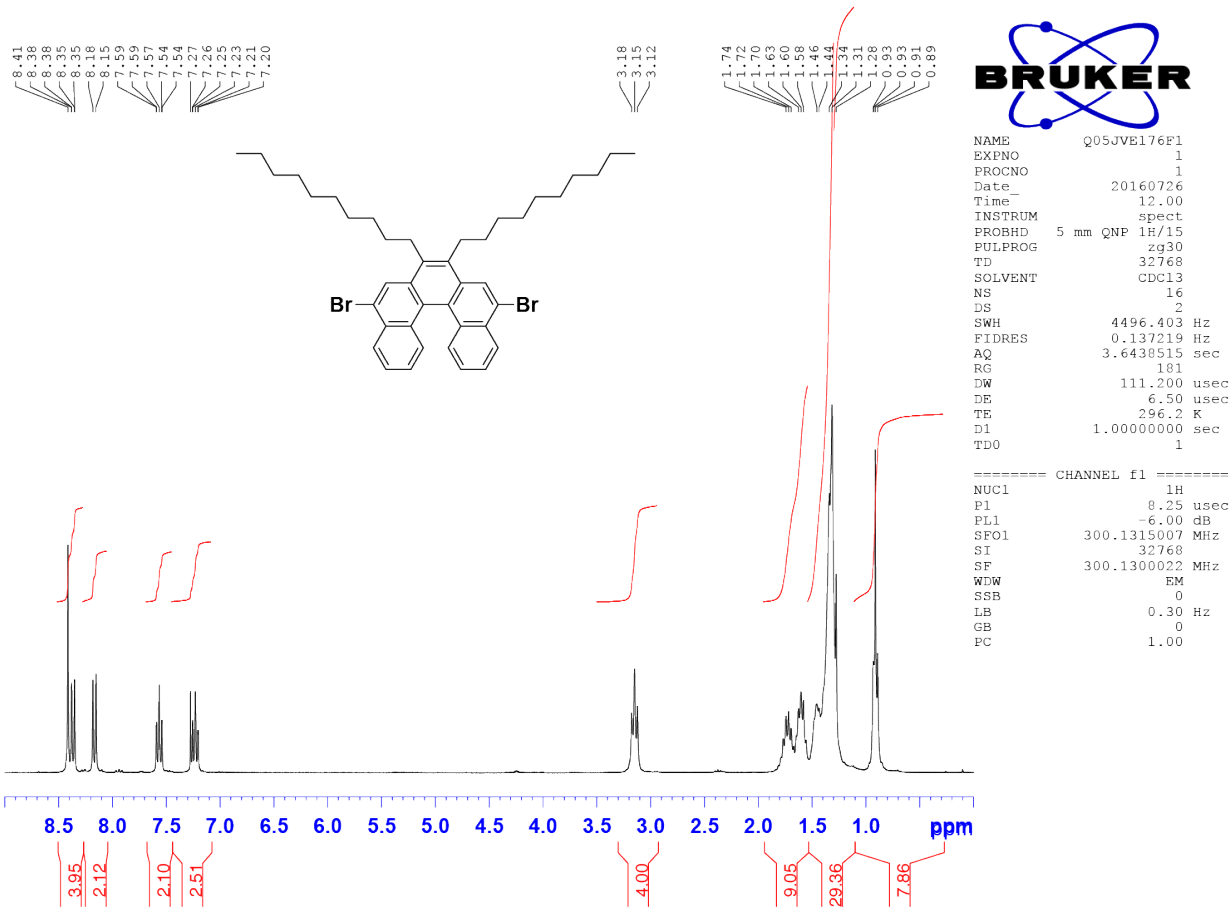



```
NAME            Q05JVE173C
EXPNO                   231
PROCNO                    1
Date_            20160707
Time_               23.30
INSTRUM             spect
PROBHD    5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    800
DS                      4
SWH             17985.611 Hz
FIDRES           0.274439 Hz
AQ             1.8219508 sec
RG                 1149.4
DW                 27.800 usec
DE                  6.00 usec
TE                 298.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                 -2.00 dB
SFO1          75.4828396 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.00 dB
PL13                17.00 dB
SFO2          300.1612006 MHz
SI                  32768
SF            75.4752843 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR spectrum of compound **(±)-6** (75 MHz, $CDCl_3$, 298 K).



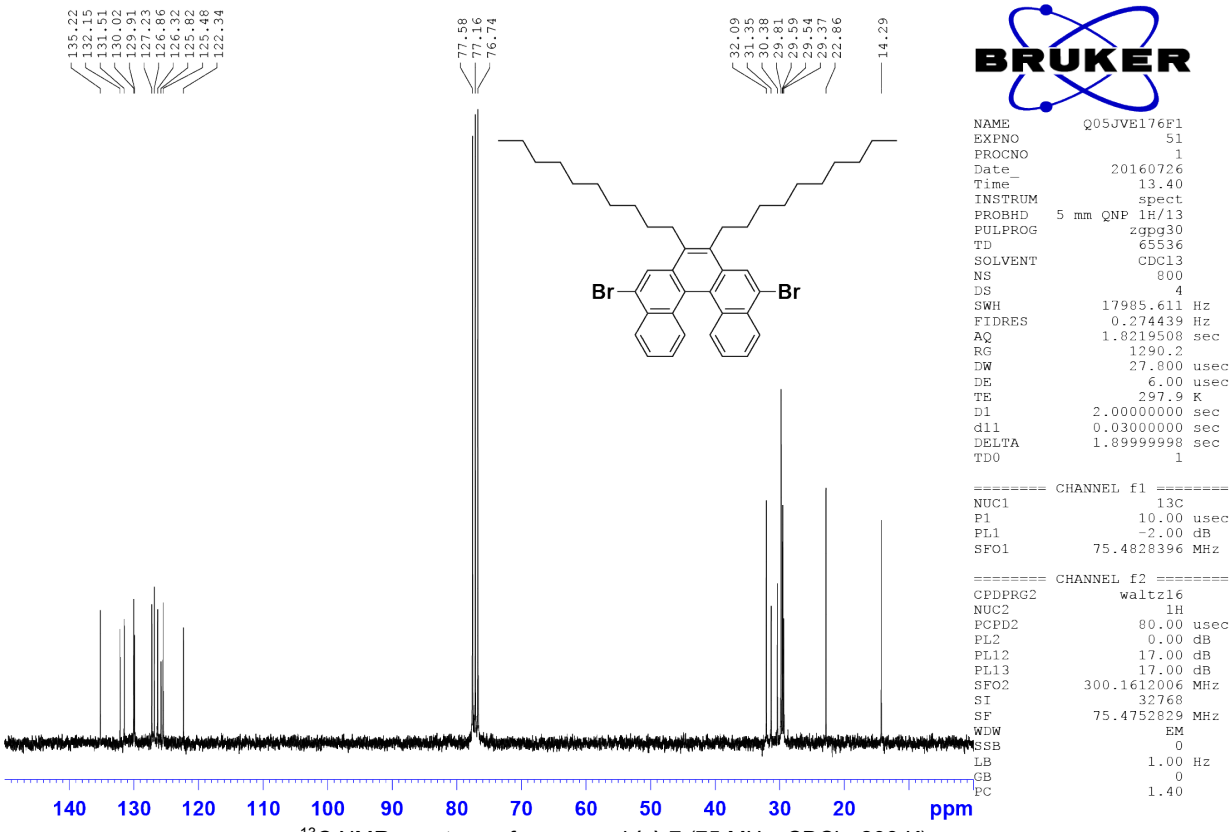
^{1}H-^{13}C HMQC spectrum of compound **(±)-6** ($CDCl_3$, 298 K).



BRUKER

```
NAME            Q05JVE176F1
EXPNO                     1
PROCNO                    1
Date_              20160726
Time                  12.00
INSTRUM               spect
PROBHD    5 mm QNP 1H/15
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                4496.403 Hz
FIDRES             0.137219 Hz
AQ                 3.6438515 sec
RG                      181
DW                  111.200 usec
DE                    6.50 usec
TE                   296.2 K
D1                 1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    8.25 usec
PL1                  -6.00 dB
SFO1           300.1315007 MHz
SI                    32768
SF             300.1300022 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

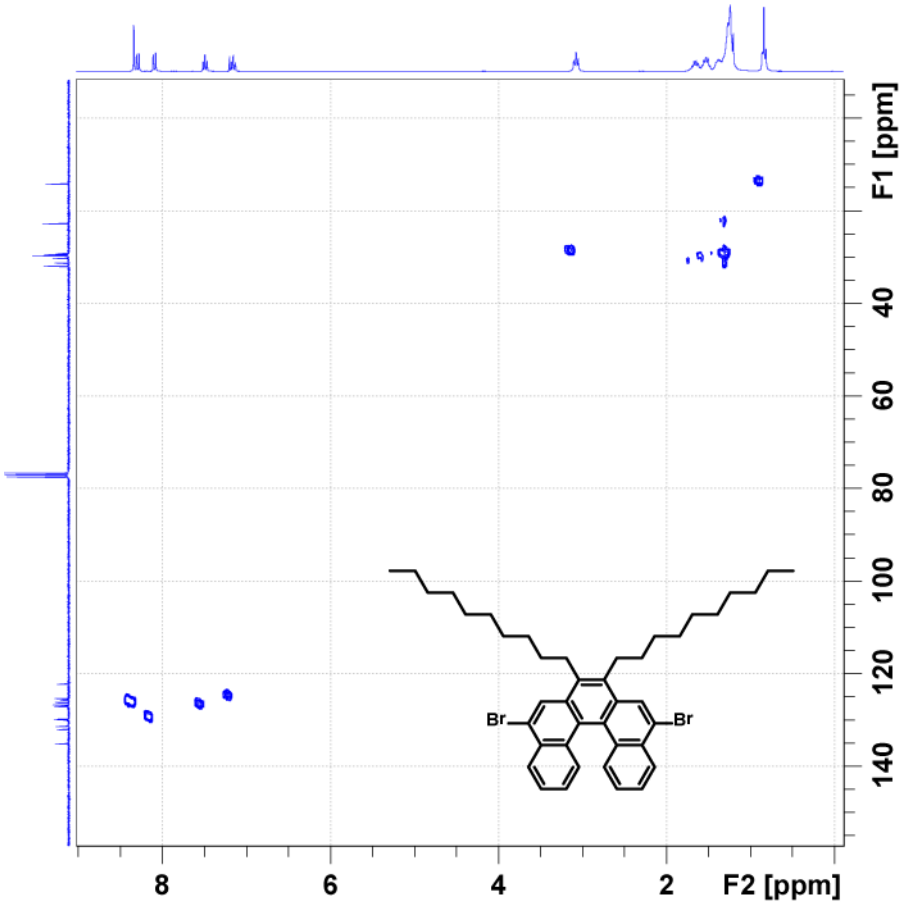
^{1}H NMR spectrum of compound **(±)-7** (300 MHz, $CDCl_3$, 298 K).



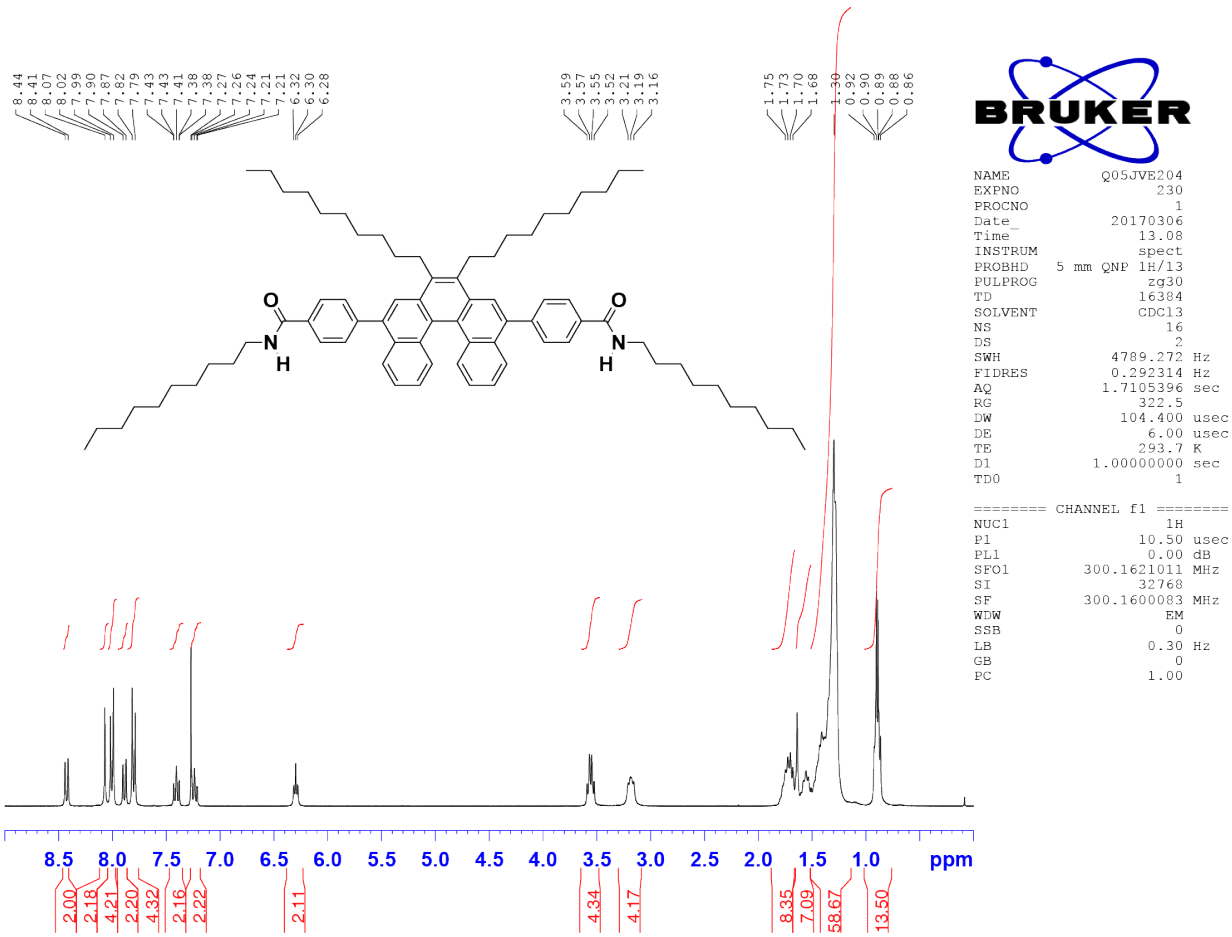
BRUKER

```
NAME            Q05JVE176F1
EXPNO                    51
PROCNO                    1
Date_              20160726
Time                  13.40
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      800
DS                        4
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                    1290.2
DW                  27.800 usec
DE                    6.00 usec
TE                   297.9 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.00 usec
PL1                  -2.00 dB
SFO1           75.4828396 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.00 dB
PL13                 17.00 dB
SFO2           300.1612006 MHz
SI                    32768
SF             75.4752829 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

^{13}C NMR spectrum of compound **(±)-7** (75 MHz, $CDCl_3$, 298 K).

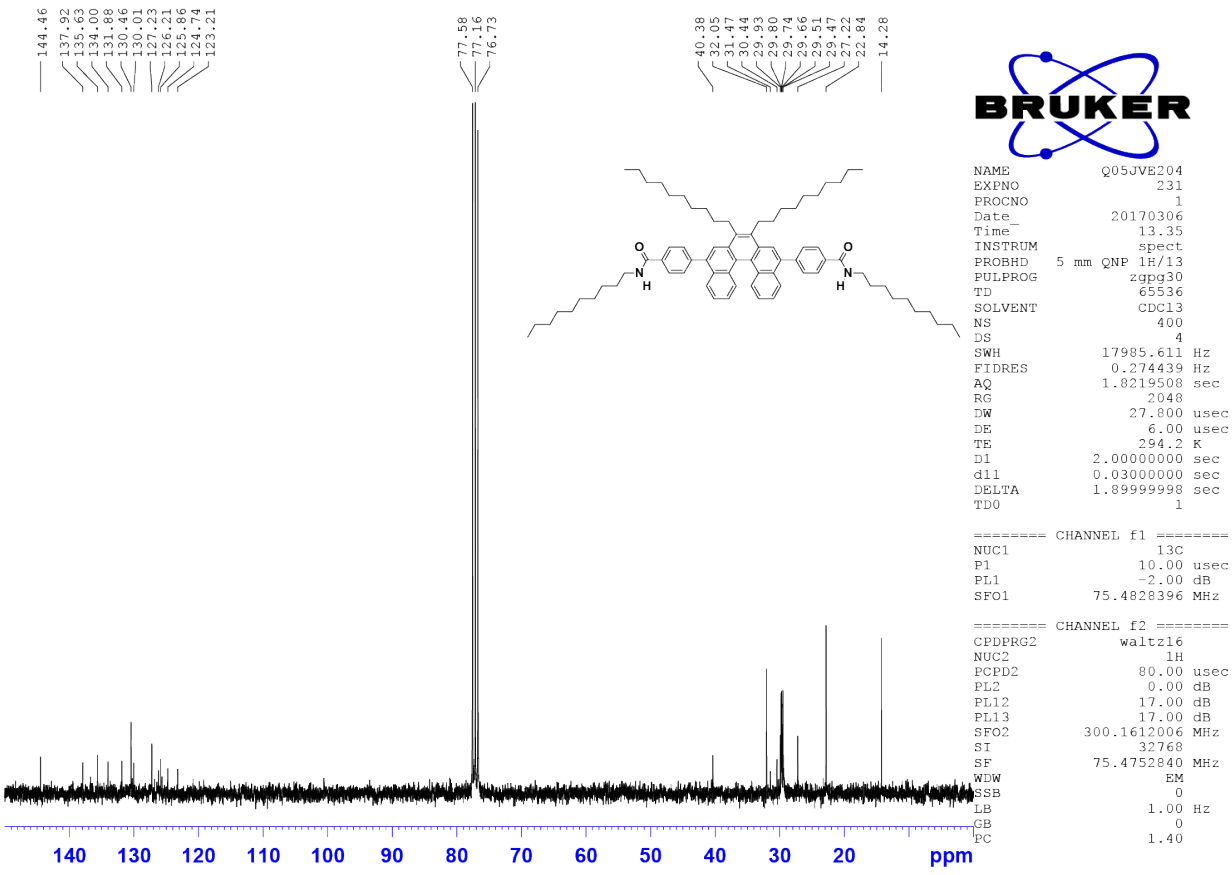


^{1}H-^{13}C HMQC spectrum of compound **(±)-7** ($CDCl_3$, 298 K).



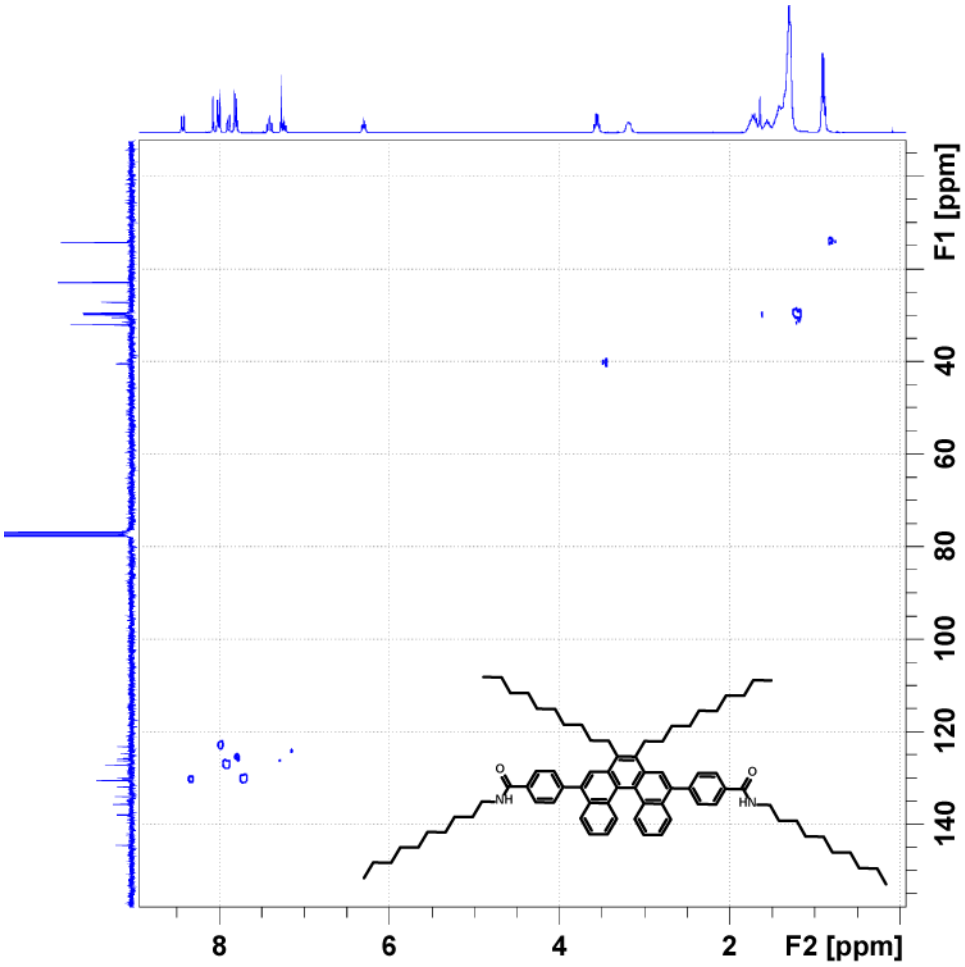

```
NAME                Q05JVE204
EXPNO                     230
PROCNO                      1
Date_                20170306
Time                    13.08
INSTRUM                 spect
PROBHD   5 mm QNP 1H/13
PULPROG                 zg30
TD                     16384
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 4789.272 Hz
FIDRES              0.292314 Hz
AQ                  1.7105396 sec
RG                      322.5
DW                    104.400 usec
DE                      6.00 usec
TE                     293.7 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      10.50 usec
PL1                      0.00 dB
SFO1             300.1621011 MHz
SI                      32768
SF               300.1600083 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

^{1}H NMR spectrum of compound **(±)-1** (300 MHz, $CDCl_3$, 298 K).

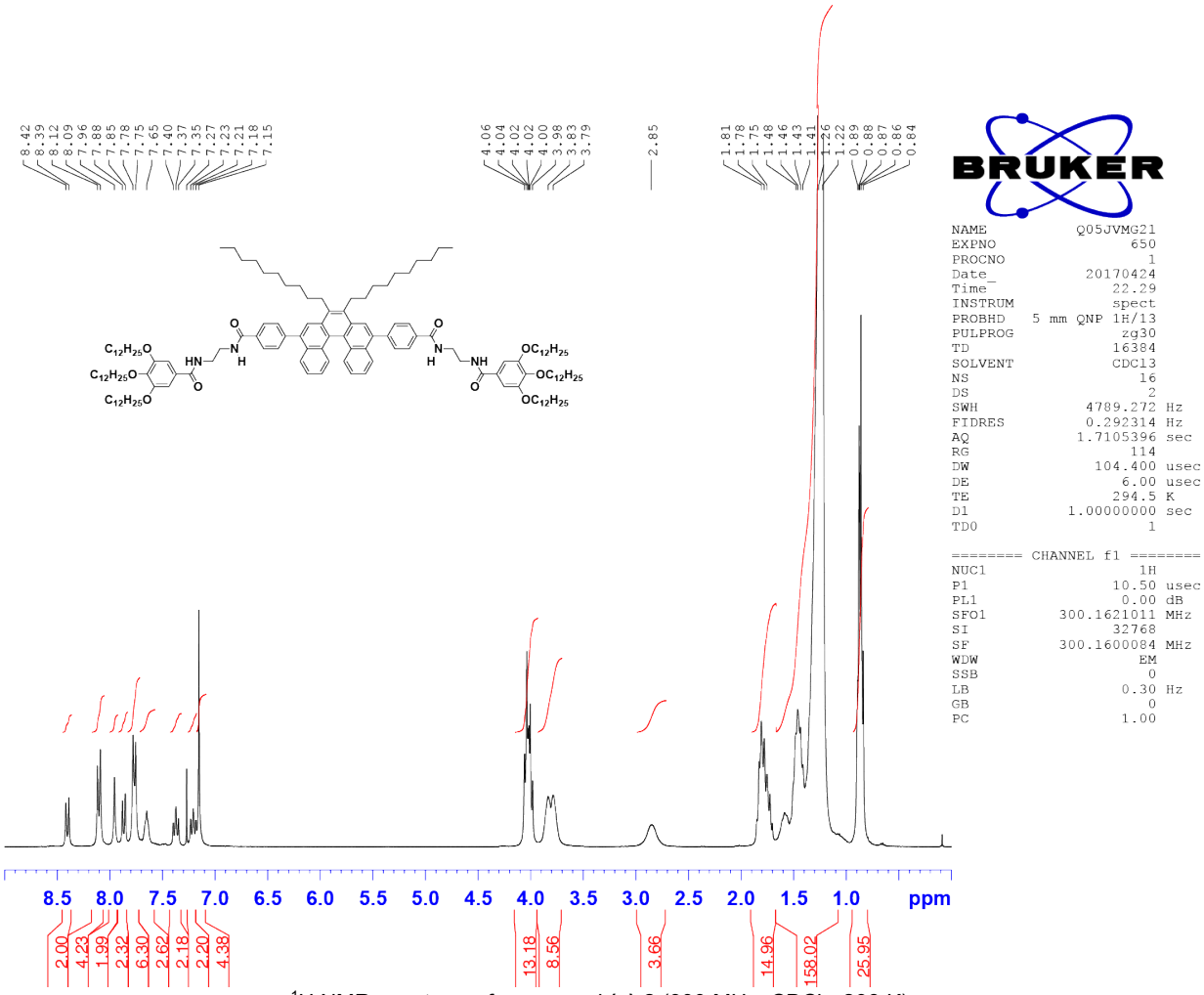



```
NAME                Q05JVE204
EXPNO                     231
PROCNO                      1
Date_                20170306
Time                    13.35
INSTRUM                 spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        400
DS                          4
SWH                17985.611 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                       2048
DW                    27.800 usec
DE                      6.00 usec
TE                     294.2 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                      10.00 usec
PL1                     -2.00 dB
SFO1             75.4828396 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    17.00 dB
PL13                    17.00 dB
SFO2             300.1612006 MHz
SI                      32768
SF               75.4752840 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

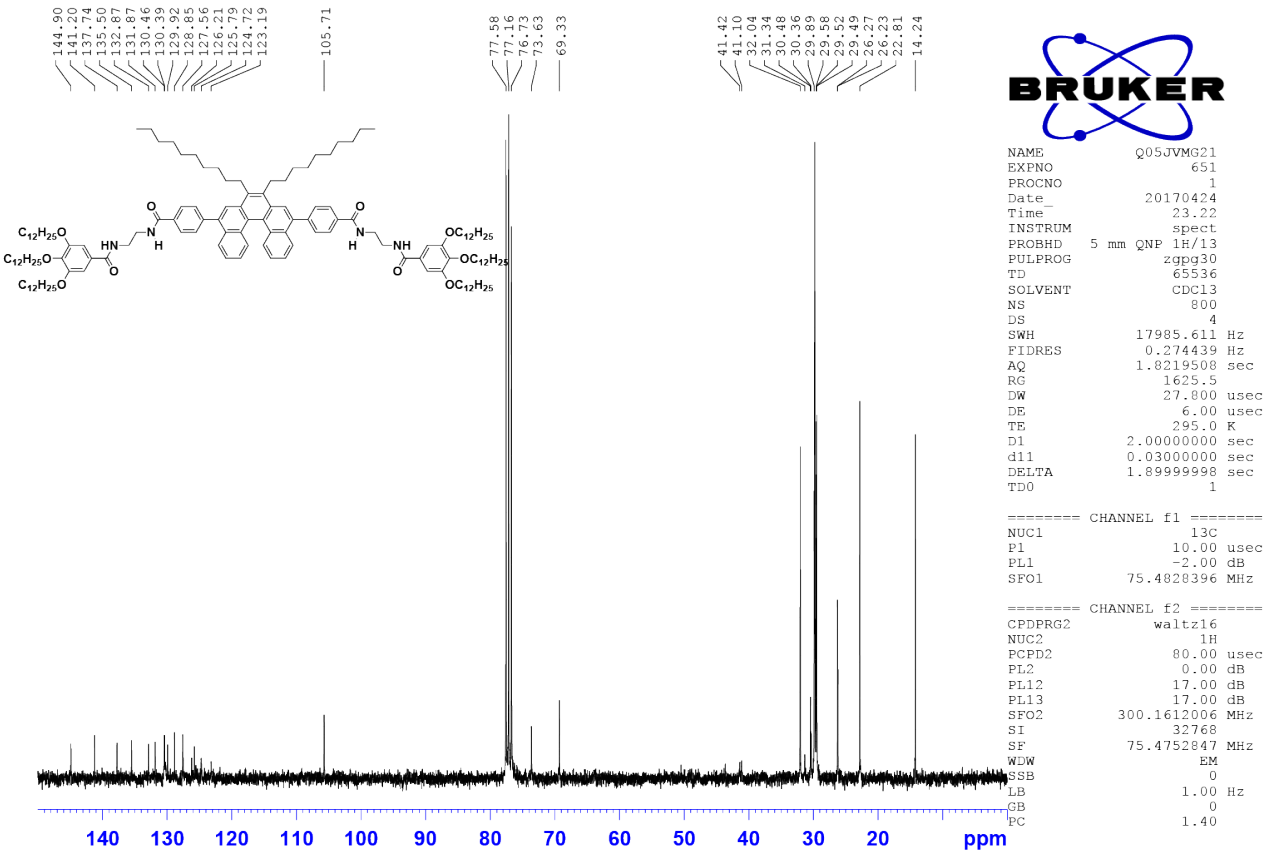
^{13}C NMR spectrum of compound **(±)-1** (75 MHz, $CDCl_3$, 298 K).



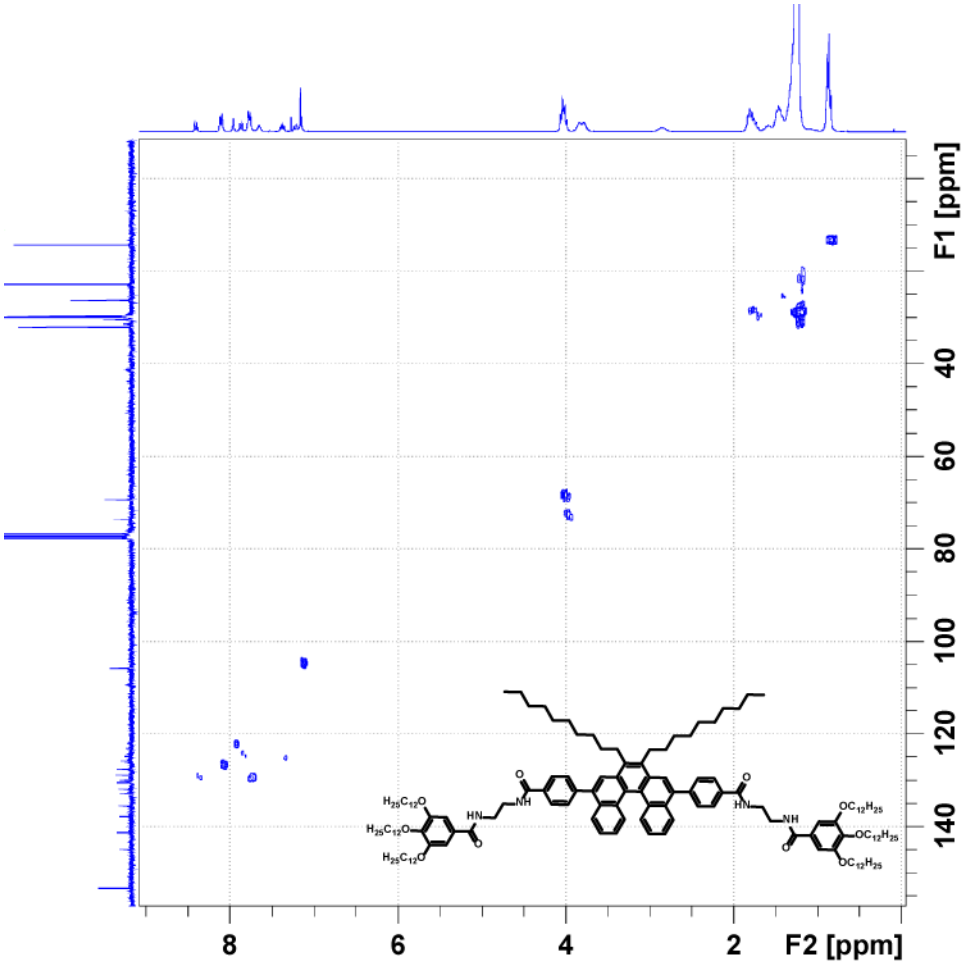
^{1}H-^{13}C HMQC spectrum of compound **(±)-1** ($CDCl_3$, 298 K).



^{1}H NMR spectrum of compound **(±)-2** (300 MHz, $CDCl_3$, 298 K).



^{13}C NMR spectrum of compound **(±)-2** (75 MHz, $CDCl_3$, 298 K).



^{1}H-^{13}C HMQC spectrum of compound **(±)-2** ($CDCl_3$, 298 K).