Supporting Information

Photochemical Unmasking of Polyyne Rotaxanes

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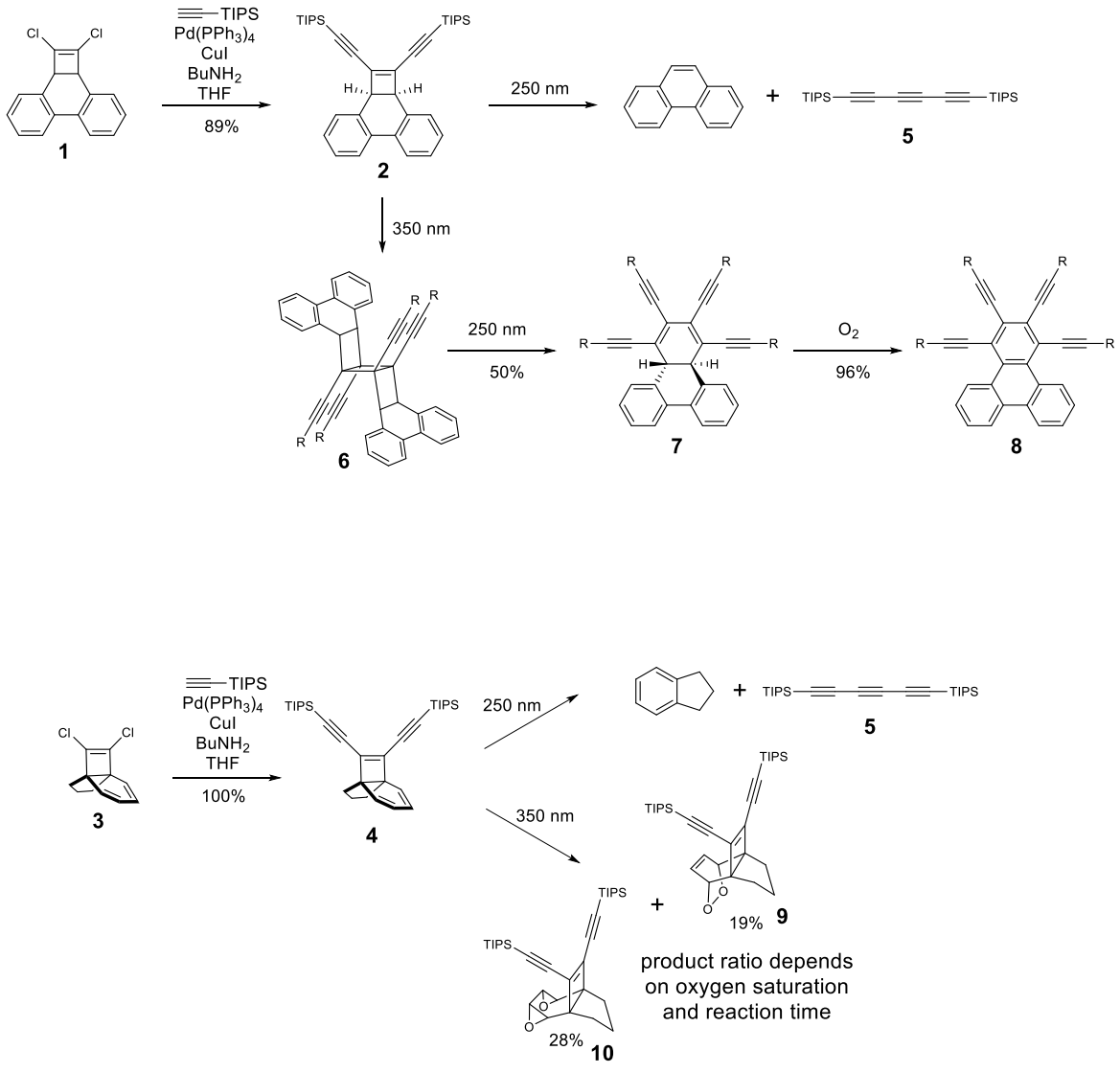
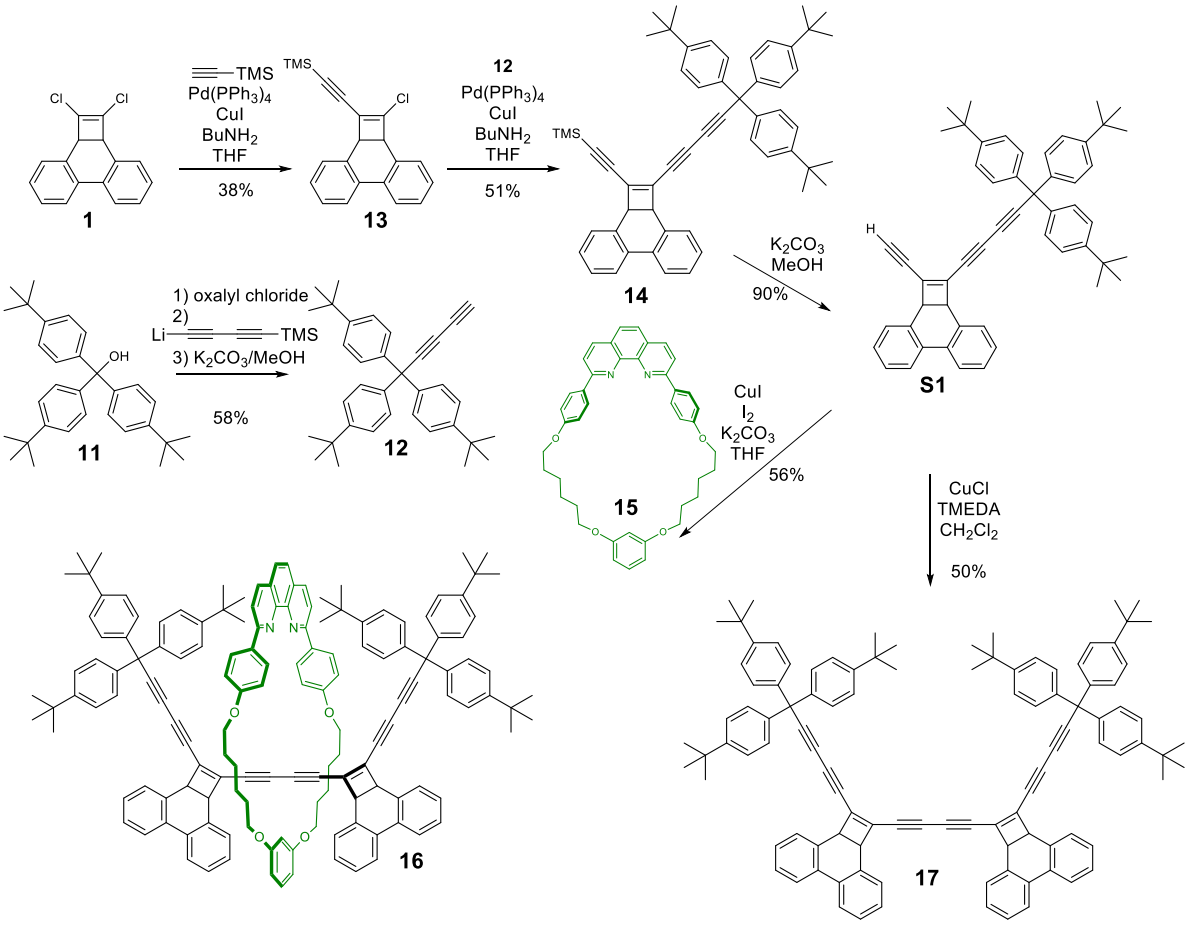
S1. General Experimental Section

All reagents and solvents were purchased from Alfa Aesar, Sigma-Aldrich Chemicals, TCI and Fluorochem and used without further purification. Dry solvents were obtained by passing through an activated alumina column on an MBraun MB-SPS-5-Bench Top system. All other solvents were purchased in p.a. quality. Petroleum ether (PE) had a boiling point range of 40-60 °C. NMR spectra were recorded on a BrukerAvance III HD 400 and a BrukerAvance III HD 500. Chemical shifts are reported in parts per million (ppm) from high to low frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet, br = broad, app = apparent. ^{1}H assignments were made using 2D NMR methods (COSY, NOESY, HSQC, HMBC). NMR tubes used were Norell® Select 5 mm and Wilmad® quartz 5 mm. Low resolution ESI mass spectrometry was performed on a Waters LCT (TOF). High resolution ESI (electrospray ionization), EI (electron ionization), and APCI (atmospheric-pressure chemical ionization) mass spectrometry were carried out by the mass spectrometry services at the University of Oxford or by the mass spectrometry services at the EPSRC National Mass Spectrometry Service Centre, Swansea, UK. Photochemical experiments were carried out in Rayonet RMR-600 photochemical reactor using RMR-2537A (for 250 nm) and RMR-3500A (for 350 nm) lamps. Single crystal X-ray diffraction data were collected using an Rigaku Oxford Diffraction SuperNova diffractometer fitted with an Oxford Cryosystems Cryostream 700 plus open flow nitrogen cooling device.[S1] Single crystal X-ray diffraction data for 2 was collected at beamline I19, Diamond Light Source.[S2] The CrysAlisPro software was used for data collection and integration. In general, structures were solved using SuperFlip[S3] within the CRYSTALS suite.[S4,S5] The structures were then modified, improved and optimised by full-matrix least squares on F2.). Full refinement details are given in the Supporting Information (CIF); Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2003495-99) and can be obtained via www. ccdc.cam.ac.uk/data_request/cif.

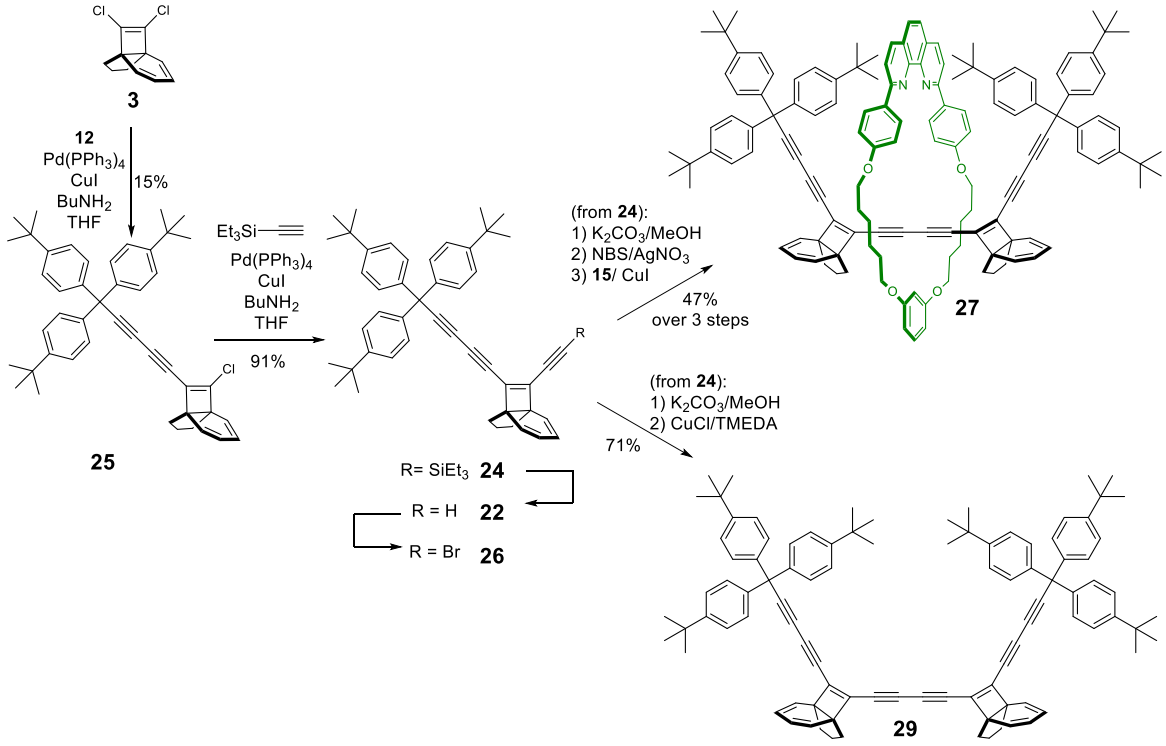
S2. Synthesis overview



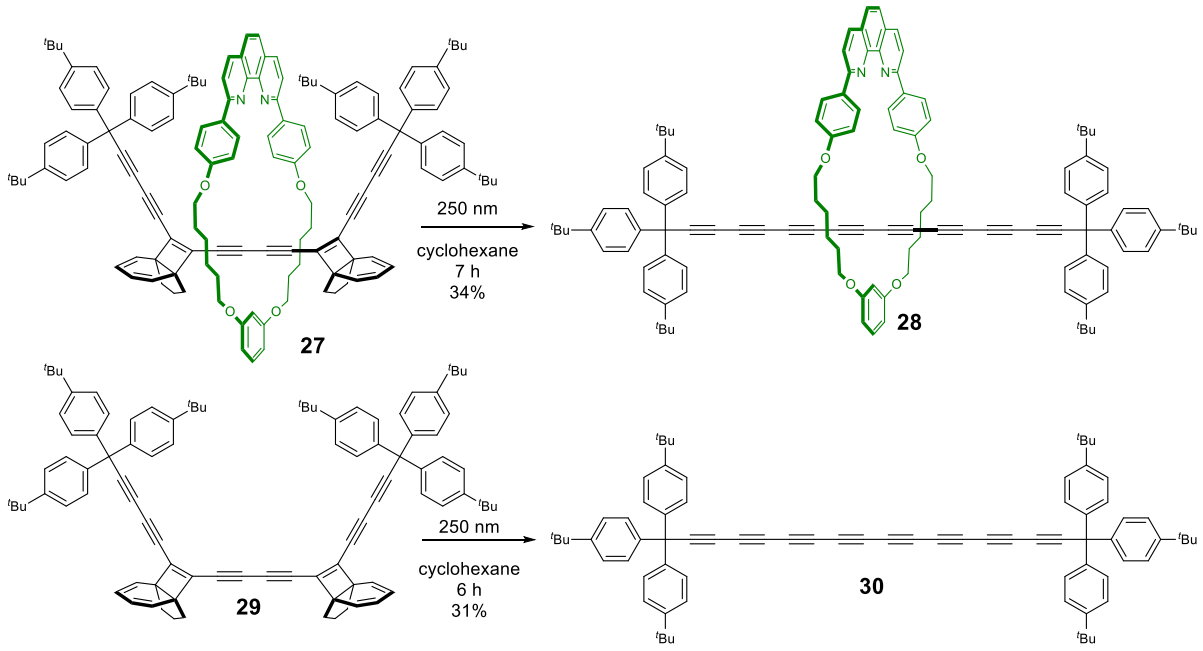
Scheme S1. Synthesis of model compounds **2** and **4** and their photochemical products



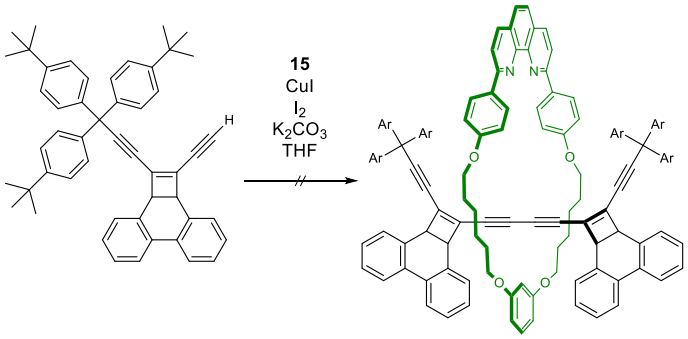
Scheme S2. Synthesis of phenanthrene rotaxane **16** and axle **17**.



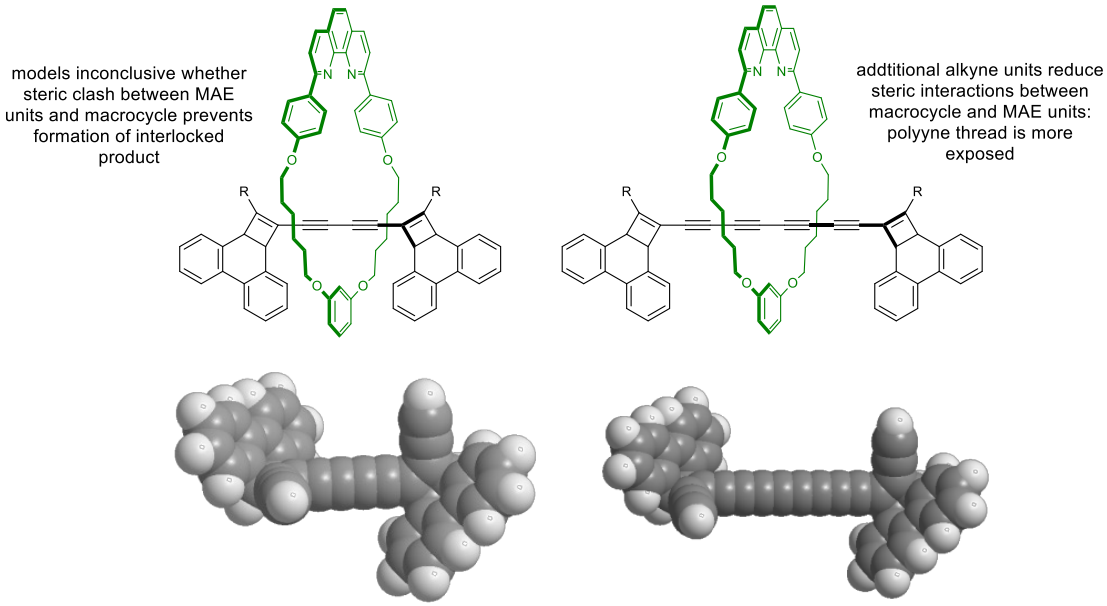
Scheme S3. Synthesis of indane rotaxane **27** and axle **29**.



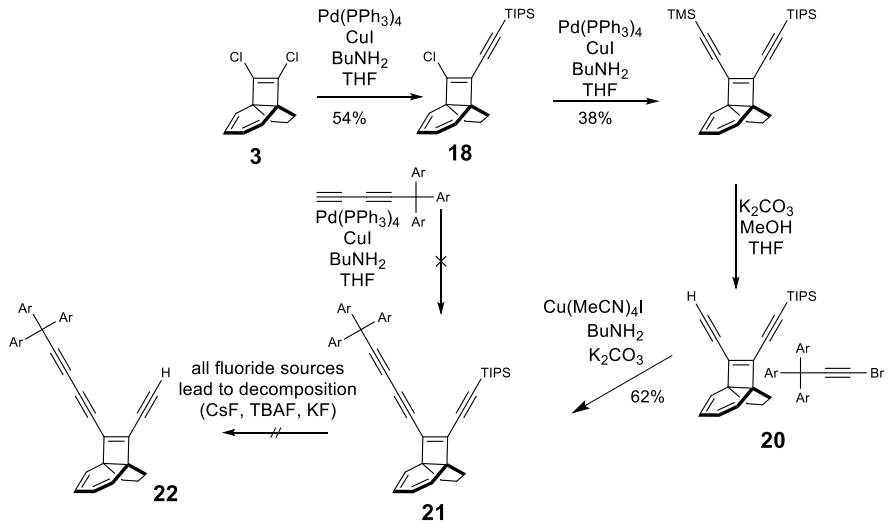
Scheme S4. Synthesis of octayne rotaxane **28** and axle **30**.



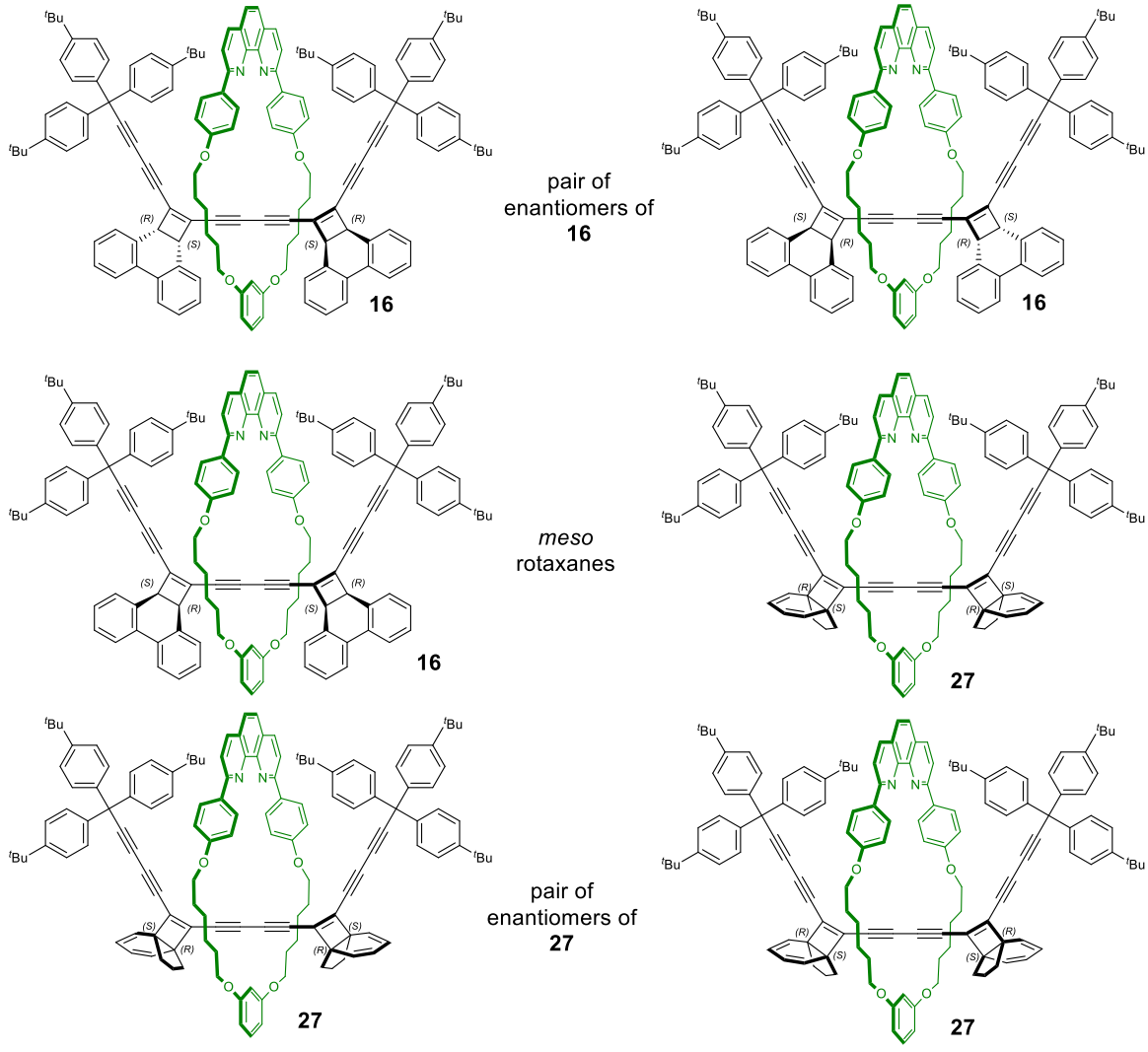
Scheme S5. Failed synthesis of a shorter analogue of **16**.



Scheme S6. Comparison of different alkyne spacer lengths.



Scheme S7. Failed deprotection of a TIPS-protected indane.



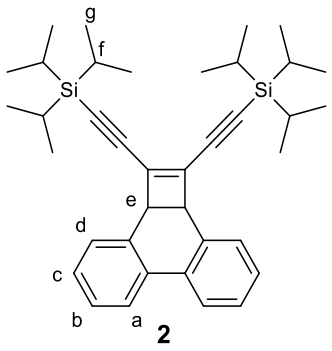
Scheme S8. Stereoisomers of **16** and **27**.

S3. Synthetic procedures

S3.1 Reported compounds

Compounds **1**[S6], **3**[S7], **11**[S9] and **15**[S10] were prepared according to literature procedures.

S3.2 Synthesis of **2**



2

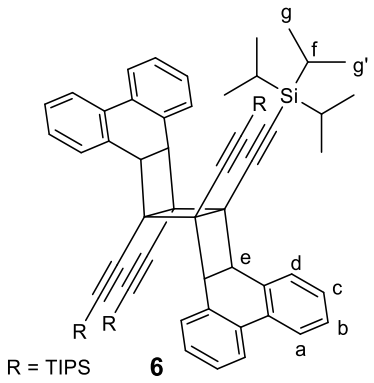
Dichloride **1** (55 mg, 0.2 mmol), $Pd(PPh_3)_4$ (14 mg, 12 µmol) and CuI (6 mg, 32 µmol) were placed in a Schlenk tube and thoroughly degassed. THF (1 mL), freshly distilled *n*-butyl amine (140 µL) and triisopropylsilylacetylene (200 µL, 0.9 mmol) were added. The resulting mixture was stirred for 4 h at ambient temperature under nitrogen.

The solvents were removed under reduced pressure and the crude product filtered through a plug of silica (PE) to yield 196 mg (89%) of **2** as a white solid.

Single crystals suitable for X-ray diffraction was obtained by slow evaporation of a solution in $MeOH/CH_2Cl_2$.

Mp: 138 °C; **HR-ESI-MS:** *m/z* = 587.34975 $[M+Na]^+$ (calc. for $C_{38}H_{52}Si_2Na$: 587.34998 $[M+Na]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.93 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 2H, H_a), 7.18-7.29 (m, 6H, H_b, H_c, H_d), 4.27 (s, 2H, H_e), 1.03-1.06 ppm (m, 42H, H_f, H_g); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 135.2 (C≡C-<u>C</u>-C_e), 133.4 (<u>C</u>-C_a), 131.2 (C_d-<u>C</u>-C_e), 129.6 (C_b), 127.9 (C_d), 127.4 (C_c), 123.3 (C_a), 99.7(<u>C</u>≡C), 99.5(C≡<u>C</u>), 45.0 (C_e), 18.7 (C_g), 11.3 ppm (C_f); **UV-Vis (CH_2Cl_2):** λ_{max} (ε) 304 (18400), 271 (44700), 261 (31100), 216 (49500), 212 nm (48400 $M^{-1}cm^{-1}$).

S3.3 Synthesis of **6**



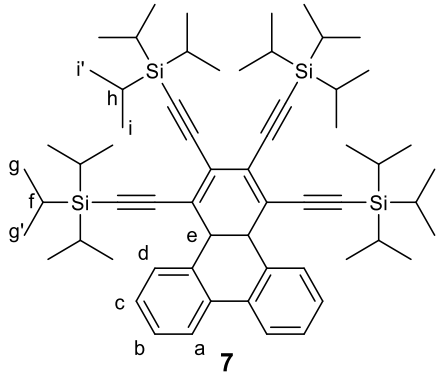
6

Cyclobutene **2** (56 mg, 0.10 mmol) was dissolved in $CDCl_3$ (0.5 mL) and the solution was transferred to an NMR tube. The solution was irradiated with UV light (λ = 350 nm) for 24 h under air. Removal of the solvent gave 56 mg (100%) of **6** as a white solid.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution in $MeOH/CH_2Cl_2$.

Mp: 245 °C; **HR-TOF-MS-ASAP:** *m/z* = 1129.7269 $[M+H]^+$ (calc. for $C_{76}H_{104}Si_4H$: 1129.7294 $[M+H]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 4H, H_a), 7.23 (appdt, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 4H, H_b), 7.17 (appdt, J_1 = 7.4 Hz, J_2 = 1.2 Hz, 4H, H_c) 7.10 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 4H, H_d), 4.66 (s, 4H, H_e), 0.86-0.95 ppm (m, 84H, H_f, H_g, $H_{g'}$); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 132.4 (C_d-$\underline{C}$-C_e), 131.9 ($\underline{C}$-C_a), 131.2 (C_d), 127.7 (C_c), 127.2 (C_b), 122.5 (C_a), 103.1 ($\underline{C}$≡C), 94.1 (C≡$\underline{C}$), 58.1 (C_e-$\underline{C}$-C≡C), 41.6 (C_e), 18.8 (C_g), 18.8 ($C_{g'}$), 11.2 ppm (C_f).

S3.4 Synthesis of **7**



7

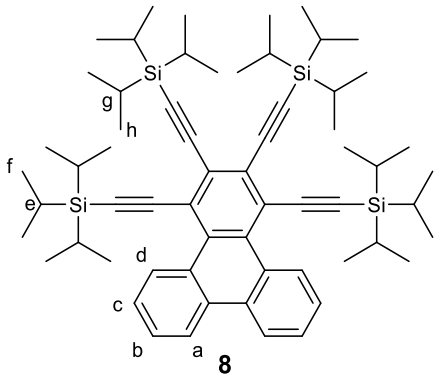
Dimer **6** (56 mg, 0.10 mmol) was dissolved in $CDCl_3$ (0.5 mL) and the solution was transferred to an NMR tube. The solution was irradiated with UV light (λ = 250 nm) for 22 h under air. Compound **8** was formed in 50% yield (determined by NMR).

For an analytical sample the solvent was evaporated and the crude product subjected to column chromatography (PE) to remove phenanthrene. The obtained mixture of **6** and **7** was dissolved in a minimal amount of hot hexane and cooled to –25 °C which led to the formation of a precipitate of dimer **6**. The solvent of the mother liquor was removed under reduced pressure and the residue purified by column chromatography (PE) to obtain a pure sample of **7**.

To obtain crystalline material, a solution in $MeOH/CH_2Cl_2$ was allowed to evaporate until an amorphous precipitate started forming. Part of the mother liquor was taken and cooled from 25 °C to –25 °C to obtain crystals suitable for X-ray diffraction.

Mp: 193 °C; **HR-TOF-MS-ASAP:** *m/z* = 951.6497 $[M+H]^+$ (calc. for $C_{62}H_{94}Si_4H$: 951.6511 $[M+H]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.20 (dd, J_1 = 7.8 Hz, J_2 = 0.8 Hz, 2H, H_d), 7.71 (dd, J_1 = 7.7 Hz, J_2 = 1.2 Hz, 2H, H_a), 7.32 (appdt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2H, H_b) 7.22 (appdt, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 2H, H_c), 3.77 (s, 2H, H_e), 1.13-1.18 (m, 42H, H_h, H_i, $H_{i'}$), 0.94-1.01 ppm (m, 42H, H_f, H_g, $H_{g'}$); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 142.0 (C_d-$\underline{C}$-C_e), 135.2 ($\underline{C}$-C_a), 127.0 (C_b), 126.9 (C_c), 125.6 (C_{diene}), 125.6 (C_{diene}), 125.2 (C_d), 124.9 (C_a), 107.1 (C_{alkyne}), 107.0 (C_{alkyne}), 104.0 (C_{alkyne}), 99.6 (C_{alkyne}), 45.4 (C_e), 19.2 (C_i), 19.2($C_{i'}$), 18.9 (C_g), 18.8 ($C_{g'}$), 12.1 (C_h), 11.7 ppm (C_f).

S3.1 Synthesis of **8**



8

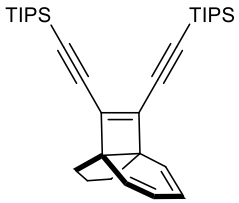
Dihydrotriphenylene **7** (25 mg, 0.03 mmol) was dissolved in CH_2Cl_2 and was stirred under O_2 atmosphere (balloon) at ambient tamperature for 5 days.

Removal of the solvent yielded 24 mg (96%) of triphenylene **8** as a white solid.

To obtain crystalline material, a solution in MeOH/CH_2Cl_2 was slowly allowed to evaporate to yield crystals suitable for X-ray diffraction.

Mp: decomposition > 200 °C without melting; **HR-ESI-MS:** *m/z* = 949.6342 $[M+H]^+$ (calc. for $C_{62}H_{93}Si_4$: 949.6349 $[M+H]^+$) **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 9.53 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H, H_d), 8.42 (dd, J_1 = 8.2 Hz, J_2 = 1.3 Hz, 2H, H_a), 7.59 (appdt, J_1 = 7.6 Hz, J_2 = 1.3 Hz, 2H, H_b), 7.43 (appdt, J_1 = 7.7 Hz, J_2 = 1.3 Hz, 2H, H_c), 1.18-1.22 (m, 42H, H_g, H_h), 1.02-1.07 ppm (m, 42H, H_e, H_f); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 133.9, 131.1, 129.0 (C_d), 129.0, 128.4 (C_b), 127.7, 126.1 (C_c), 123.0 (C_a), 121.8, 106.9 (C_{alkyne}), 104.1 (C_{alkyne}), 102.5 (C_{alkyne}), 101.5 (C_{alkyne}), 19.7 (C_h), 18.9 (C_f), 12.5 (C_g), 11.9 (C_e) ppm.

S3.2 Synthesis of **4**



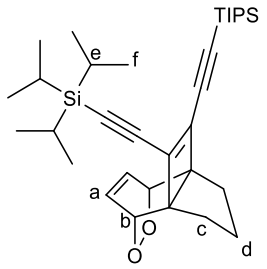
4

CuI (63 mg, 0.33 mmol) and $Pd(PPh_3)_4$ (160 mg, 0.14 mmol) were placed in a Schlenk flask and thoroughly degassed. A solution of **3** (0.50 g, 2.35 mmol) in THF (15 mL) was added followed by freshly distilled *n*-butyl amine (0.7 mL) and triisopropylsilylacetylene (1.45 mL, 6 mmol) and the mixture was stirred at ambient temperature for 18 h under nitrogen. The solvents were removed under reduced pressure and the crude product purified by column chromatography (PE) to yield 1.2 g (100%) of **4**.

Analytical data were in accordance with reported values.[S7]

S3.3

S3.4 Synthesis of **9**



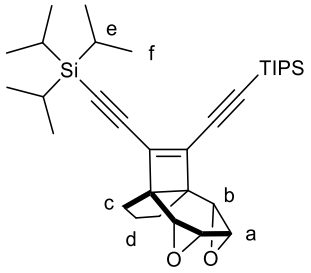
9

Indane **4** (100 mg, 0.20 mmol) was dissolved in $CDCl_3$ (7 mL) and the solution was transferred to four NMR tubes. The solution was irradiated with UV light (λ = 350 nm) for 3.5 h. Compound **9** was formed in 25% yield (determined by NMR).

The solvent was removed under reduced pressure and the crude product purified by column chromatography (PE → CH_2Cl_2) to yield 20 mg (19%) of **9** as a colorless oil as well as 30 mg (28%) of **10** as a white solid.

HR-ESI-MS: *m/z* = 537.35827 $[M+H]^+$ (calc. for $C_{33}H_{53}O_2Si_2$: 537.35786 $[M+H]^+$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45-6.50 (m, 2H, H_a), 4.57-4.62 (m, 2H, H_b), 2.00-2.07 (m, 1H, H_d) 1.87-1.96 (m, 3H, H_c, $H_{d'}$), 1.65-1.72 (m, 2H, H_c), 1.00-1.12 ppm (m, 54H, H_e, H_f); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.2 (≡C-<u>C</u>=<u>C</u>), 129.0 (C_a), 100.0 (C_{alkyne}), 99.1 (C_{alkyne}), 77.8 (C_b), 55.2 (C_b-<u>C</u>-C_c), 28.0 (C_d), 24.1 (C_c), 18.7 (C_f), 11.3 ppm (C_e).

S3.5 Synthesis of **10**



10

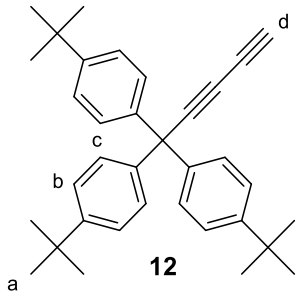
Indane **8** (5 mg, 0.01 mmol) was dissolved in $CDCl_3$ (0.5 mL) and the solution was transferred to an NMR tube. The solution was irradiated with UV light (λ = 350 nm) for 8 h. Compound **10** was formed in 55% yield (determined by NMR).

An analytical sample was obtained according to the procedure for compound **9**.

Single crystals suitable for X-ray diffraction was obtained by slow evaporation of a solution in acetone/water at –20 °C.

Mp: 109 °C; HR-ESI-MS: *m/z* = 537.35815 $[M+H]^+$ (calc. for $C_{33}H_{53}O_2Si2$: 537.35786 $[M+H]^+$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56-3.60 (m, 2H, H_a), 3.22-3.25 (m, 2H, H_b), 1.81-1.88 (m, 2H, H_c) 1.70-1.79 (m, 1H, H_d), 1.57-1.68 (m, 1H, $H_{d'}$), 1.40-1.50 (m, 2H, $H_{c'}$), 1.01-1.13 ppm (m, 54H, H_e, H_f); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 131.7 (C=C), 101.4 (C_{alkyne}), 98.2 (C_{alkyne}), 55.1 (C_b-C-C_c), 52.7 (C_b), 49.9 (C_a), 28.4 (C_c), 21.1 (C_d), 18.7 (C_f), 11.3 ppm (C_e).

S3.6 Synthesis of **12**



12

Alcohol **11** (3.0 g, 7.0 mmol) was dissolved in THF (15 mL) and oxalyl chloride (3.0 mL, 35 mmol) was added slowly. The mixture was stirred for 2 h. The solvents were removed under reduced pressure and the residue suspended in THF (20 mL).

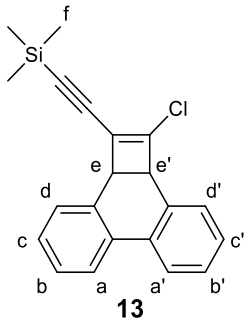
In a separate flask, 1,4-bis(trimethylsilyl)butadiyne (3.38 g, 17.4 mmol) was dissolved in THF (30 mL) and cooled to –78 °C. MeLi·LiBr complex (1.5 M, 11.6 mL, 17.4 mmol) was added, the cooling bath removed and the solution stirred for 30 min to be then cooled to 0 °C. The suspension derived from **11** was added, the resulting mixture allowed to reach ambient temperature and stirred for 3 d.

After cooling to 0 °C, sat. NH_4Cl solution (20 mL) was added. The organic layer was isolated and the aqueous layer washed with CH_2Cl_2 (2 x 15 mL). The organic layers were combined, the solvents removed under reduced pressure and the crude product suspended in THF (150 mL) and MeOH (150 mL). K_2CO_3 (3 g) was added and the resulting mixture was stirred for 45 min.

The solvents were removed under reduced pressure and the crude product filtered through a plug of silica (PE → 20% CH_2Cl_2 in PE) to give 1.85 g (58%) of **12** as a brown solid.

Mp: 247 °C; **HR-EI-GCMS:** *m/z* = 460.3130 $[M]^+$ (calc. for $C_{35}H_{40}$: 460.3125 $[M]^+$).; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.31 (d, *J* = 8.6 Hz, 6H, H_b), 7.14 (d, *J* = 8.6 Hz, 6H, H_c), 2.17 (s, 1H, H_d), 1.32 ppm (s, 27H, H_a); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 149.9 (C-C_b), 141.4 (C-C_c), 128.8 (C_c), 125.1 (C_b), 82.9 (C_{alkyne}), 68.9 (C_{alkyne}), 68.7 (C_{alkyne}), 67.5 (C_d), 55.1 (C-Ar_3), 34.6 (C-C_a), 31.5 ppm (C_a).

S3.7 Synthesis of **13**



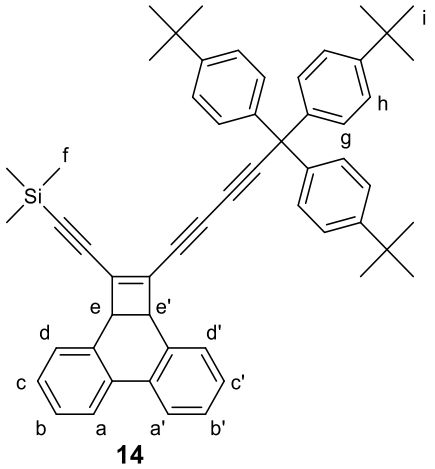
13

Dichloride **1** (820 mg, 3.0 mmol), $Pd(PPh_3)_4$ (210 mg, 0.2 mmol) and CuI (90 mg, 0.5 mmol) were placed in a Schlenk tube and thoroughly degassed. THF (15 mL), freshly distilled *n*-butyl amine (2.1 mL) and trimethylsilylacetylene (1.5 mL, 10.8 mmol) were added. The resulting mixture stirred for 4 h at ambient temperature under nitrogen.

The solvents were removed under reduced pressure and the crude product purified by column chromatography (PE → 10% CH_2Cl_2 in PE) to yield 380 mg (38%) of **13** as a white solid. It was possible to recover 220 mg (27%) of **1**.

Mp: 108 °C; **HR-EI-GCMS:** *m/z* = 334.0943 $[M]^+$ (calc. for $C_{21}H_{19}SiCl$: 334.0939 $[M]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.95-7.99 (m, 2H, H_a, $H_{a'}$), 7.24-7.36 (m, 6H, H_b, $H_{b'}$, H_c, $H_{c'}$, H_d, $H_{d'}$), 4.29-4.32 (m, 2H, H_e, $H_{e'}$), 0.22 ppm (s, 9H, H_f); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 133.5, 133.0, 131.5, 131.2, 130.7, 129.7, 129.5, 128.3, 128.1, 128.1, 127.9, 127.6, 123.6, 123.5, 103.1, 95.1, 47.8, 44.4, -0.1 ppm.

S3.8 Synthesis of **14**



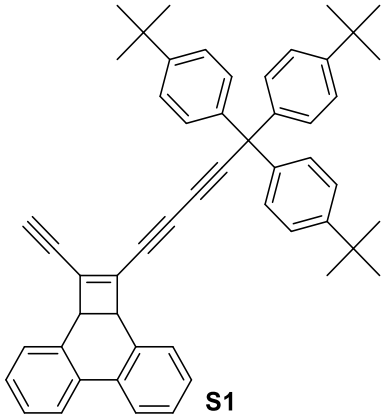
14

Chloride **13** (235 mg, 0.70 mmol), stopper **12** (1.0 g, 2.2 mmol), $Pd(PPh_3)_4$ (270 mg, 230 µmol) and CuI (9 mg, 50 µmol) were placed in a Schlenk tube and thoroughly degassed. THF (25 mL) and *n*-butyl amine (2.5 mL) were added and the solution stirred at 50 °C overnight under nitrogen.

The solvents were removed under reduced pressure and the crude product purified by column chromatography (PE → 15% CH_2Cl_2 in PE) to give 270 mg (51%) of **14** as a brown solid.

Mp: 165 °C; **HR-ESI-MS:** *m/z* = 781.42010 $[M+Na]^+$ (calc. for $C_{56}H_{58}SiNa$: 781.42000 $[M+Na]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.91-7.96 (m, 2H, H_a, $H_{a'}$), 7.25-7.32 (m, 12H, H_b, $H_{b'}$, H_c, $H_{c'}$, H_d, $H_{d'}$, H_h), 7.12 (d, *J* = 8.6 Hz, 6H, H_g) 4.25-4.31 (m, 2H, H_e, $H_{e'}$), 1.31 (s, 27H, H_i), 0.22 ppm (s, 9H, H_f); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 149.9, 141.4, 137.8, 133.2, 133.1, 133.0, 131.1, 131.1, 129.7, 129.5, 128.8, 128.4, 128.0, 127.6, 127.5, 125.1, 123.4, 123.4, 104.7, 97.9, 92.5, 81.3, 70.9, 69.4, 55.6, 45.4, 45.3, 34.6, 31.5, -0.1 ppm.

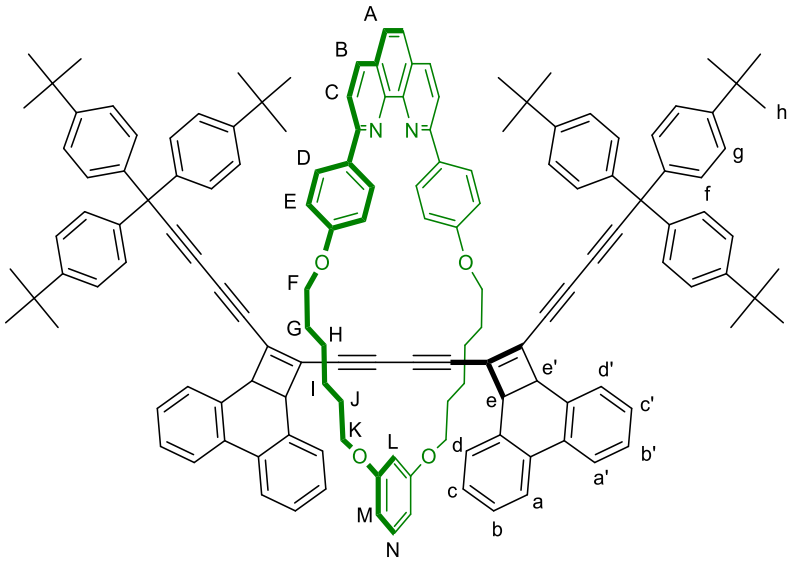
S3.9 Synthesis of **S1**



S1

Phenanthrene stopper **14** (220 mg, 0.29 mmol) was dissolved in THF (22 mL) and MeOH (22 mL) and K_2CO_3 (220 mg, 1.6 mmol) were added. The mixture was stirred for 2 h and then filtered to a plug of silica (CH_2Cl_2). The solvents were removed under reduced pressure to yield 180 mg (90%) of a crude product that was used without further purification for the next steps.

S3.10 Synthesis of **16**



16

Macrocycle **15** (21 mg, 33 µmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of CuI (4.2 mg, 22 µmol) in MeCN (2.5 mL) was added. The resulting solution was stirred for 1 h at ambient temperature. The solvents were removed under reduced pressure and the resulting solid re-dissolved in THF (3 mL).

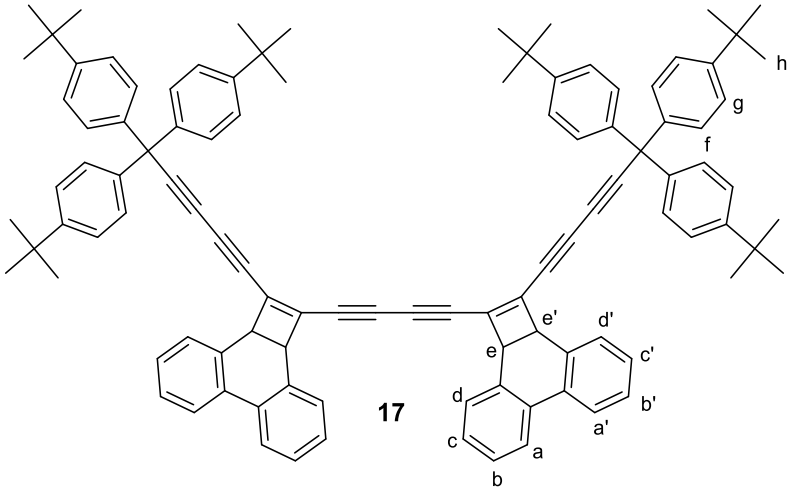
A separate flask was loaded with phenanthrene stopper **S1** (69 mg, 100 µmol), I_2 (13 mg, 50 µmol) and K_2CO_3 (22 mg, 150 µmol), thoroughly degassed and THF (4 mL) was added. The solution of the macrocycle was added and the resulting mixture stirred for three days at 60 °C under nitrogen.

The solvent was removed under reduced pressure and the residue re-dissolved in CH_2Cl_2 (50 mL). The solution was washed with saturated solution of EDTA in aq. ammonia (17% NH_3, 25 mL) and sat. aq. NaCl solution (25 mL). The solvent was removed under reduced pressure and the crude product purified by column chromatography (PE → CH_2Cl_2) to give 37 mg (56%) of phenanthrene rotaxane **16** as a yellow solid (as a mixture of stereoisomers).

Mp: partially molten sample decomposes >250 °C; **LR-ESI-MS:** *m/z* = 2010.2 $[M+H]^+$; **HR-ESI-MS:** m/z = 2010.09014 $[M+H]^+$ (calc. for $C_{148}H_{141}O_4N_2$: 2010.08859 $[M+H]^+$); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.45-8.57 (m, 4H, H_D), 8.13-8.20 (m, 2H, H_B), 7.95-8.07 (m, 2H, H_C), 7.79-7.85 (m, 4H, H_a, $H_{a'}$), 7.67-7.70 (m, 2H, H_A), 7.21 (d, *J* = 8.5 Hz, 12H, H_g), 6.86-7.18 (m, 29H, H_b, $H_{b'}$, H_c, $H_{c'}$, H_d, $H_{d'}$, H_E, H_f, H_N), 6.46-6.54 (m, 1H, H_L), 6.27-6.39 (m, 2H, H_M), 4.00-4.14 (m, 4H, H_e, $H_{e'}$), 3.84-3.98 (m, 4H, H_F), 3.72-3.79 (m, 4H, H_K), 1.66-1.77 (m, 4H, H_G), 1.51-1.64 (m, 4H, H_J), 1.34-1.39 (m, 8H, H_H, H_I), 1.21-1.23 ppm (m, 54H, H_h); **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.7, 160.7, 160.5, 160.5, 160.5, 160.5, 156.2, 156.1, 149.8, 146.3, 146.3, 141.2, 132.6, 132.6, 132.5, 130.8, 129.6, 129.6, 129.5, 129.2, 129.2, 128.8, 128.5, 128.4, 127.6, 127.6, 125.1, 123.4, 123.3, 123.3, 115.2, 115.1, 115.1, 107.8, 107.3, 100.0, 99.9, 94.0, 94.0, 82.9, 82.9, 81.6, 78.6, 71.2, 71.2, 69.5, 68.2, 68.1, 68.0, 67.7, 67.7, 63.3, 55.7,

45.8, 45.8, 45.6, 34.5, 33.0, 32.1, 31.4, 29.8, 29.8, 29.8, 29.6, 29.5, 29.4, 29.2, 29.1, 25.9, 25.8, 25.8, 25.7, 25.7, 22.9, 18.7, 14.3, 11.3 ppm.

S3.11 Synthesis of **17**



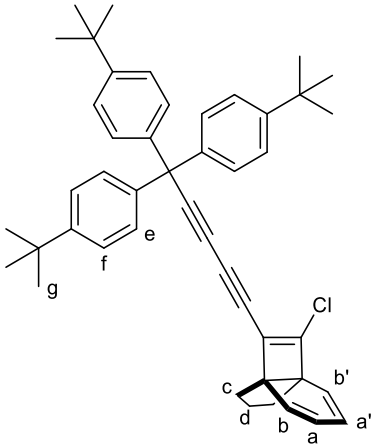
17

Phenanthrene stopper **S1** (30 mg, 44 µmol) and CuCl (4 mg, 4 µmol) were suspended in CH_2Cl_2 (10 mL). Tetramethylethylenediamine (70 µL, 46 µmol) was added and the resulting mixture stirred for 4 h at ambient temperature under air.

The solvents were removed under reduced pressure and the crude product purified by column chromatography (PE → 15% CH_2Cl_2 in PE) to give 15 mg (50%) of **17** as a yellow solid (as a mixture of stereoisomers).

Mp: solid sample decomposes >250 °C; **MALDI-MS:** *m/z* = 1409.610 $[M+K]^+$ (calc. for $C_{106}H_{98}K$: 1409.730 $[M+K]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90-7.96 (m, 4H, H_a, $H_{a'}$), 7.24-7.33 (m, 24H, H_b, $H_{b'}$, H_c, $H_{c'}$, H_d, $H_{d'}$, H_g), 7.12 (d, *J* = 8.5 Hz, 12H, H_f) 4.25-4.31 (m, 4H, H_e, $H_{e'}$), 1.31 (s, 54H, H_h), 0.22 ppm (s, 9H, H_f); **^{13}C NMR (126 MHz, $CDCl_3$):** δ = 149.9, 141.3, 137.6, 137.6, 135.8, 132.6, 132.6, 132.6, 132.5, 131.1, 131.0, 131.0, 129.7, 129.6, 129.5, 128.8, 128.5, 128.5, 127.7, 125.1, 123.5, 123.5, 93.9, 83.3, 81.6, 78.5, 77.4, 70.9, 69.3, 55.7, 45.9, 45.6, 34.6, 31.5 ppm.

S3.12 Synthesis of **25**



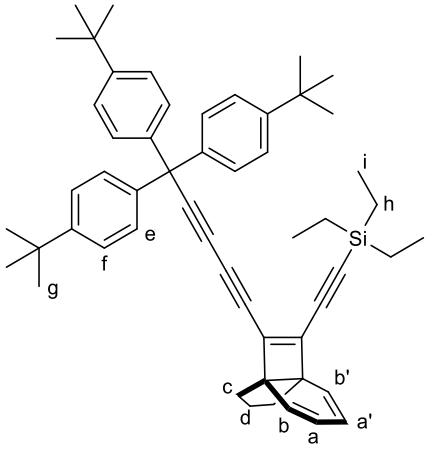
25

Stopper **12** (400 mg, 0.87 mmol), $Pd(PPh_3)_4$ (64 mg, 56 µmol) and CuI (26 mg, 136 µmol) were placed in a Schlenk tube and thoroughly degassed. A solution of dichloride **3** (200 mg, 0.94 mmol) in THF (4 mL) was added followed by freshly distilled *n*-butyl amine (560 µL). The resulting mixture was stirred for 40 h at 60 °C.

The solvents were removed under reduced pressure and the crude product purified by column chromatography (PE → 10% CH_2Cl_2 in PE) to yield 90 mg (15%) of **25** as a white solid.

Mp: 168 °C; **HR-APCI-MS:** *m/z* = 637.35891 $[M+H]^+$ (calc. for $C_{46}H_{50}Cl$: 637.35956 $[M+H]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.31 (d, *J* = 8.7 Hz, 6H, H_f), 7.14 (d, *J* = 8.7 Hz, 6H, H_e), 5.75-5.95 (m, 4H, H_a, $H_{a'}$, H_b, $H_{b'}$), 1.95-2.02 (m, 2H, H_c, $H_{c'}$), 1.58-1.66 (m, 1H, H_d), 1.36-1.48 (m, 1H, $H_{d'}$) 1.32 (s, 27H, H_g), 1.19-1.27 ppm (m, 2H, $H_{c''}$, $H_{c'''}$); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 149.9, 141.4, 133.7, 129.1, 128.8, 127.4, 125.1, 122.9, 121.8, 91.00, 79.3, 69.2, 67.4, 59.6, 56.5, 55.6, 34.6, 32.5, 31.9, 31.6, 31.5, 18.6 ppm.

S3.13 Synthesis of **24**



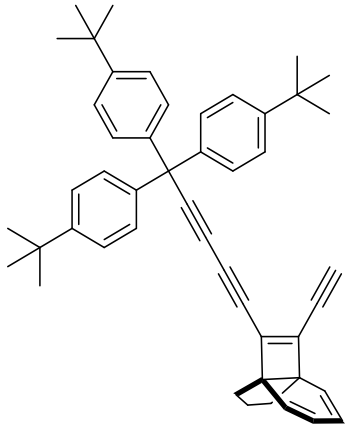
24

Indane stopper **25** (90 mg, 0.14 mmol), $Pd(PPh_3)_4$ (16 mg, 14 µmol) and CuI (5 mg, 26 µmol) were placed in a Schlenk tube and thoroughly degassed. THF (2.5 mL) was added followed by freshly distilled *n*-butyl amine (400 µL) and triethylsilylacetylene (0.5 mL, 2.8 mmol). The resulting mixture was stirred for 24 h at ambient temperature.

The solvents were removed under reduced pressure and the crude product purified by column chromatography (PE → 10% CH_2Cl_2 in PE) to yield 95 mg (91%) of **24** as a white solid.

Mp: 233 °C; **HR-APCI-MS:** *m/z* = 741.4842 $[M+H]^+$ (calc. for $C_{54}H_{64}Si$: 741.4855 $[M+H]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.30 (d, *J* = 8.6 Hz, 6H, H_f), 7.14 (d, *J* = 8.6 Hz, 6H, H_e), 5.75-5.90 (m, 4H, H_a, $H_{a'}$, H_b, $H_{b'}$), 1.92-2.02 (m, 2H, H_c, $H_{c'}$), 1.55-1.64 (m, 1H, H_d), 1.41-1.51 (m, 1H, $H_{d'}$) 1.32 (s, 27H, H_g), 1.19-1.27 (m, 2H, $H_{c''}$, $H_{c'''}$), 1.02 (t, *J* = 8.0 Hz, 9H, H_i), 0.65 ppm (t, *J* = 8.0 Hz, 6H, H_h); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 149.8, 141.6, 136.1, 131.2, 128.8, 128.7, 128.6, 125.1, 122.0, 122.0, 100.3, 98.0, 91.6, 79.6, 70.3, 69.6, 56.4, 56.3, 55.6, 34.6, 33.1, 32.9, 31.5, 18.9, 7.6, 4.5 ppm.

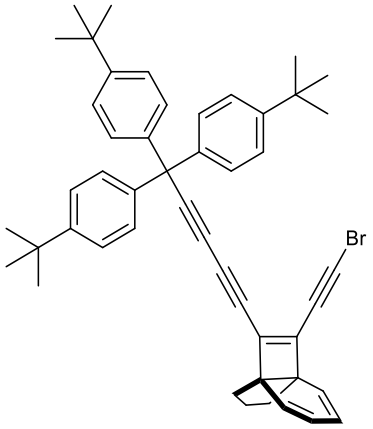
S3.14 Synthesis of **22**



22

Indane stopper **24** (50 mg, 0.07 mmol) was dissolved in THF (5 mL) and MeOH (5 mL) and K_2CO_3 (50 mg, 0.36 mmol) were added. The mixture stirred for 3 h and then filtered through a plug of silica (CH_2Cl_2). The solvents were removed under reduced pressure to yield 35 mg (83%) of a crude product that was used without further purification for the next steps.

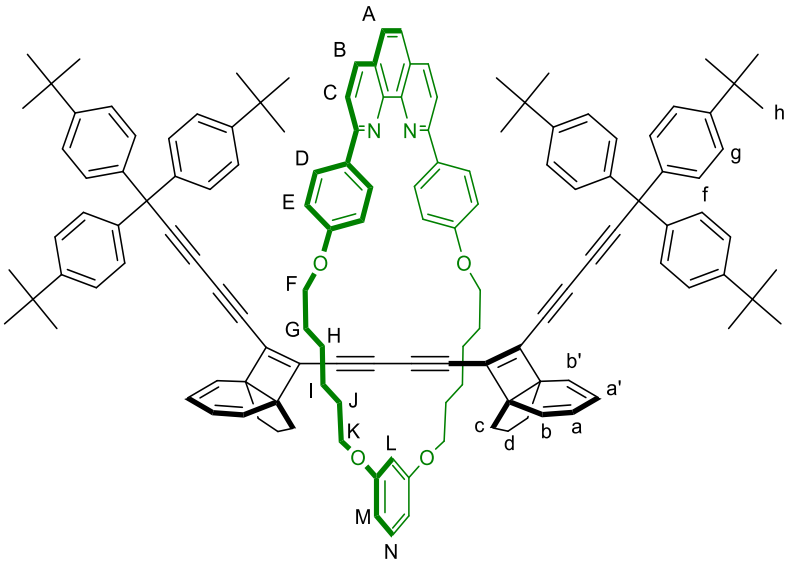
S3.15 Synthesis of **26**



26

Indane stopper **24** (35 mg, 0.06 mmol) was dissolved in acetone (5 mL) and *N*-bromo-succinimide (18 mg, 0.10 mmol) and $AgNO_3$ (18 mg, 0.11 mmol) were added. The mixture stirred for 3 h and then filtered through a plug of silica (PE → 10% CH_2Cl_2 in PE). The solvents were removed under reduced pressure to yield 22 mg (56%) of **26** as a yellow solid which can be used without further purification.

S3.16 Synthesis of **27**



27

Step one: Stopper **24** (100 mg, 135 µmol) was dissolved in THF (10 mL) and MeOH (10 mL) and K_2CO_3 (100 mg, 725 µmol) was added. The resulting mixture was stirred for 1 h. The mixture was filtered through a plug of silica (CH_2Cl_2) and the solvents were removed under reduced pressure.

Step two: Half of the crude product of step one was dissolved in acetone (25 mL) and *N*-bromosuccinimide (25 mg, 14 µmol) and $AgNO_3$ (25 mg, 15 µmol) were added and the resulting mixture was stirred for 75 min. The solution was filtered and passed through a plug of silica (50% PE in CH_2Cl_2) and the solvents removed under reduced pressure. The crude product was transferred together with the other half of the product of step one to a Schlenk tube, K_2CO_3 (50 mg, 360 µmol) was added and the Schlenk tube was thoroughly degassed.

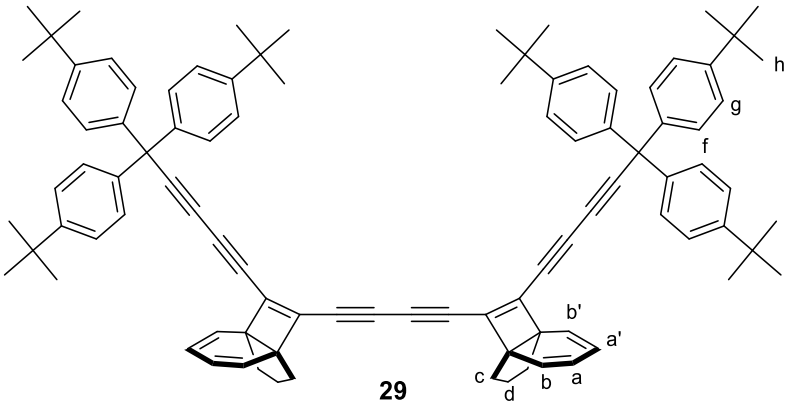
Step three: Macrocycle **15** (45 mg, 70 µmol) was dissolved in CH_2Cl_2 (5 mL) and a solution of CuI (4 mg, 21 µmol) in MeCN (1 mL) was added, the resulting solution was stirred for 1 h, the solvents were removed under reduced pressure and the product re-dissolved in degassed THF (12 mL) and added to the Schlenk tube containing the stopper. The mixture was stirred overnight at 60 °C.

The solvent was removed under reduced pressure and the crude product purified by column chromatography (PE → CH_2Cl_2) to yield 60 mg (47% over three steps) of indane rotaxane **27** as a yellow solid (as a mixture of stereoisomers).

Mp: 208 °C; **LR-ESI-MS:** *m/z* = 1890.1 $[M+H]^+$; **HR-ESI-MS:** m/z = 1890.09036 $[M+H]^+$ (calc. for $C_{138}H_{141}O_4N_2$: 1890.08859 $[M+H]^+$); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.49 (d, *J* = 8.8 Hz, 4H, H_D), 8.19-8.23 (m, 2H, H_B), 8.03-8.07 (m, 2H, H_C), 7.70-7.72 (m, 2H, H_A), 7.22 (d, *J* = 8.5 Hz, 12H, H_g), 7.12-7.16 (m, 4H, H_E), 7.11 (d, *J* = 8.5 Hz, 12H, H_f), 7.06 (t, *J* = 8.2 Hz, 1H, H_N), 6.63 (t, *J* = 2.2 Hz, 1H, H_L), 6.45 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 2H, H_M), 5.67-5.76 (m, 8H, H_a, $H_{a'}$, H_b, $H_{b'}$), 4.03-4.08 (m, 4H, H_F), 3.93-3.98 (m, 4H, H_K), 1.90-1.96 (m, 2H, H_c), 1.81-1.89 (m, 6H, $H_{c'}$, H_G),

1.73-1.79 (m, 4H, H_J), 1.47-1.59 (m, 8H, H_H, H_I), 1.39-1.46 (m, 2H, H_d), 1.27-1.33 (m, 2H, $H_{d'}$), 1.23 (s, 54H, H_h), 1.04-1.13 ppm (m, 4H, $H_{c''}$); **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.6, 160.6, 160.6, 156.3, 149.7, 146.3, 141.3, 136.5, 135.1, 135.1, 133.6, 131.9, 131.9, 129.5, 129.2, 128.7, 128.1, 128.1, 128.1, 127.4, 125.5, 125.1, 122.3, 122.2, 118.9, 115.1, 115.1, 115.1, 107.9, 107.9, 107.8, 100.0, 93.2, 81.4, 80.1, 77.4, 70.4, 69.5, 68.3, 68.3, 68.3, 67.9, 57.0, 56.9, 55.7, 34.5, 33.1, 33.1, 31.4, 29.6, 29.2, 26.0, 26.0, 25.9, 25.9, 18.8 ppm.

S3.17 Synthesis of **29**



29

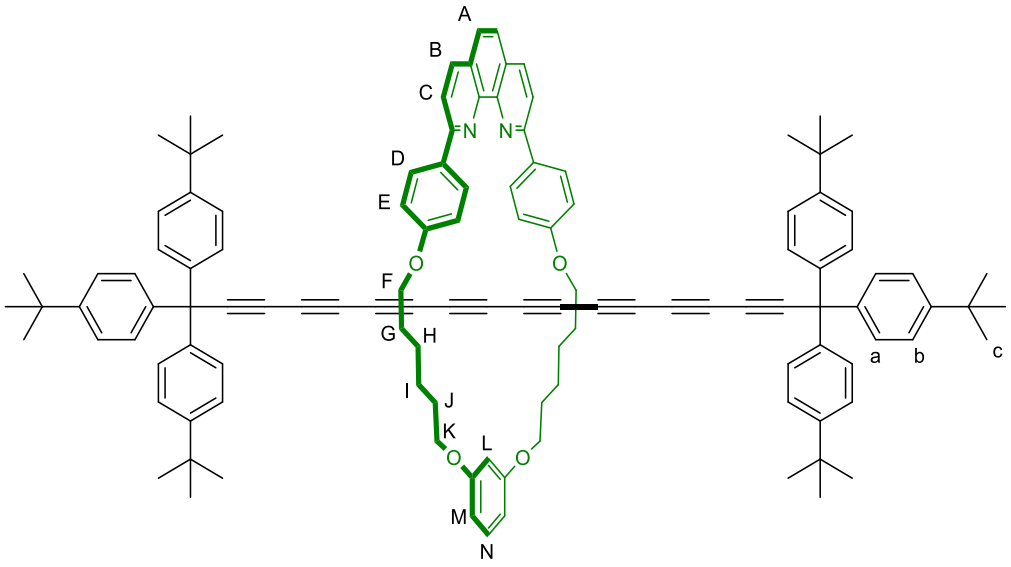
Silyl stopper **24** (20 mg, 26.7 µmol) was dissolved in THF (5 mL) and MeOH (5 mL) and K_2CO_3 (50 mg, 360 µmol) was added. The resulting mixture was stirred for 1 h. The mixture was filtered through a plug of silica (CH_2Cl_2) and the solvents were removed under reduced pressure.

The crude product was dissolved in CH_2Cl_2 (15 mL) and CuCl (20 mg, 200 µmol) was added followed by TMEDA (0.5 mL, 3.3 mmol). The mixture was stirred for 30 min.

Then, CH_2Cl_2 (100 mL) was added and the mixture was washed with water (2 x 200 mL) and the solvent removed under reduced pressure. The crude product was purified by column chromatography (PE → 10% CH_2Cl_2 in PE) to yield 12 mg (71%) of **29** as a yellow solid.

Mp: solid sample decomposes >250 °C; **HR-ESI-MS:** *m/z* = 1290.73567 $[M+K]^+$ (calc. for $C_{138}H_{141}O_4N_2$: 1290.73337 $[M+K]^+$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.29 (d, *J* = 8.6 Hz, 12H, H_g), 7.12 (d, *J* = 8.6 Hz, 12H, H_f), 5.78-5.90 (m, 8H, H_a, $H_{a'}$, H_b, $H_{b'}$), 1.92-2.02 (m, 4H, H_c), 1.56-1.64 (m, 2H, H_d), 1.39-1.49 (m, 2H, $H_{d'}$), 1.30 (s, 54H, H_h), 1.19-1.26 ppm (m, 4H, $H_{c'}$); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 149.9, 141.4, 135.4, 133.6, 128.8, 128.3, 125.1, 122.2, 93.0, 81.6, 80.0, 77.4, 77.1, 70.1, 69.4, 57.0, 56.9, 55.7, 34.6, 33.2, 31.5, 29.9, 18.9 ppm.

S3.18 Synthesis of **28**

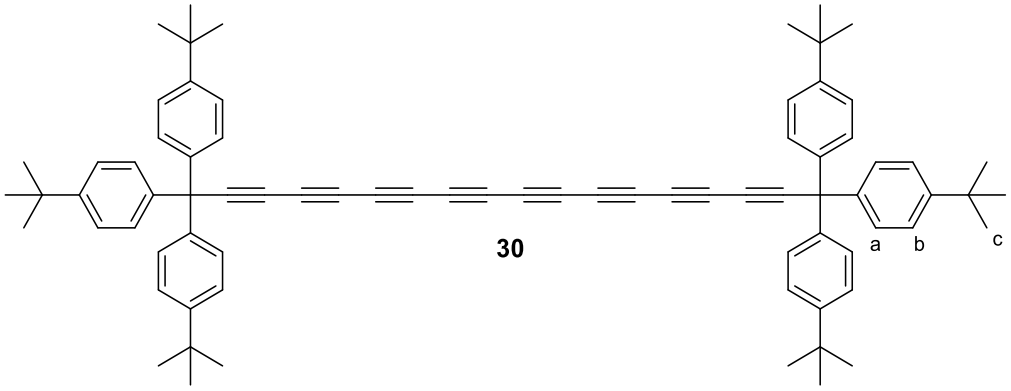


28

Indane rotaxane **27** (10 mg, 5 µmol) was dissolved in deuterated cyclohexane (1 mL). The resulting solution was transferred into a quartz NMR tube and degassed by three cycles of freeze-thawing. The solution was irradiated with UV light (λ = 250 nm) for 7 h under nitrogen. The crude product was purified by column chromatography (PE → CH_2Cl_2) to yield 3 mg (34%) of rotaxane **28** as a yellow solid.

Mp: starts decomposing >200 °C, liquefies slightly >300 °C; **LR-ESI-MS:** m/z = 1656.1 $[M+H]^+$; **HR-ESI-MS:** m/z = 1653.93351 $[M+H]^+$ (calc. for $C_{120}H_{121}O_4N_2$: 1653.93209 $[M+H]^+$); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 8.49 (d, *J* = 8.8 Hz, 4H, H_D), 8.23 (d, *J* = 8.5 Hz, 2H, H_B), 8.08 (d, *J* = 8.5 Hz, 2H, H_C), 7.71 (s, 2H, H_A), 7.23 (d, *J* = 8.5 Hz, 12H, H_b), 7.09-7.13 (m, 5H, H_E, H_N), 7.03 (d, *J* = 8.5 Hz, 12H, H_a), 6.54 (t, *J* = 2.2 Hz, 1H, H_L), 6.47 (dd, ^3J = 8.2 Hz, ^4J = 2.2 Hz, 2H, H_M), 4.08 (t, *J* = 7.1 Hz, 4H, H_F), 3.97 (t, *J* = 6.4 Hz, 4H, H_K), 1.85-1.92 (m, 4H, H_G), 1.78-1.85 (m, 4H, H_J), 1.52-1.62 (m, 8H, H_H, H_I), 1.26 ppm (s, 54H, H_c); **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 160.6 (C-O), 160.6 (C-O), 156.4 (N-C-C_C), 150.1 (C-C_b), 146.2 (N-C-C-N), 140.6 (C-C_a), 136.7 (C_B), 131.9 (C-C_D), 129.8 (C_N), 129.1 (C_D), 128.7 (C_a), 127.5 (C_A-C-C_B), 125.6 (C_A), 125.2 (C_b), 119.0 (C_C), 114.9 (C_E), 107.4 (C_M), 100.5 (C_L), 86.2 (C_{alkyne}), 69.5 (C_{alkyne}), 68.2 (C_F), 67.9 (C_K), 63.6 (C_{alkyne}), 63.5 (C_{alkyne}), 63.3 (C_{alkyne}), 63.3 (C_{alkyne}), 63.0 (C_{alkyne}), 62.7 (C_{alkyne}), 55.6 (C-Ar_3), 34.6 (C-C_c), 31.4 (C_c), 29.7 (C_J), 29.2 (C_H), 26.1 (C_H or C_I), 26.0 ppm (C_I or C_H).

S3.19 Synthesis of **30**



Indane thread **29** (8 mg, 6.4 µmol) was dissolved in deuterated cyclohexane (1 mL). The resulting solution was transferred into a quartz NMR tube and thoroughly degassed. The solution was irradiated with UV light (λ = 250 nm) for 6 h. The crude product was purified by column chromatography (PE → CH_2Cl_2) to yield 2 mg (31%) of octayne thread **30** as a yellow solid.

Mp: solid sample decomposes >250 °C; **HR-ASAP-MS:** m/z = 1015.6185 $[M+H]^+$ (calc. for $C_{78}H_{79}$: 1015.6182 $[M+H]^+$); **^{1}H NMR (500 MHz, $CDCl_3$):** δ = 7.30 (d, *J* = 8.6 Hz, 12H, H_b) 7.08 (d, *J* = 8.6 Hz, 12H, H_a), 1.30 ppm (s, 54H, H_c); **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 150.3 ($\underline{C}$-C_b), 140.7 ($\underline{C}$-C_a), 128.7 (C_a), 125.3 (C_b), 86.0 (C_{alkyne}), 69.5 (C_{alkyne}), 63.4 (C_{alkyne}), 63.4 (C_{alkyne}), 63.3 (C_{alkyne}), 63.2 (C_{alkyne}), 62.8 (C_{alkyne}), 62.6 (C_{alkyne}), 55.6 ($\underline{C}$-Ar_3), 34.6 ($\underline{C}$-C_c), 31.5 ppm (C_c).

S4. Mass Spectrometry

S4.1 Low-resolution ESI-MS of interlocked compounds

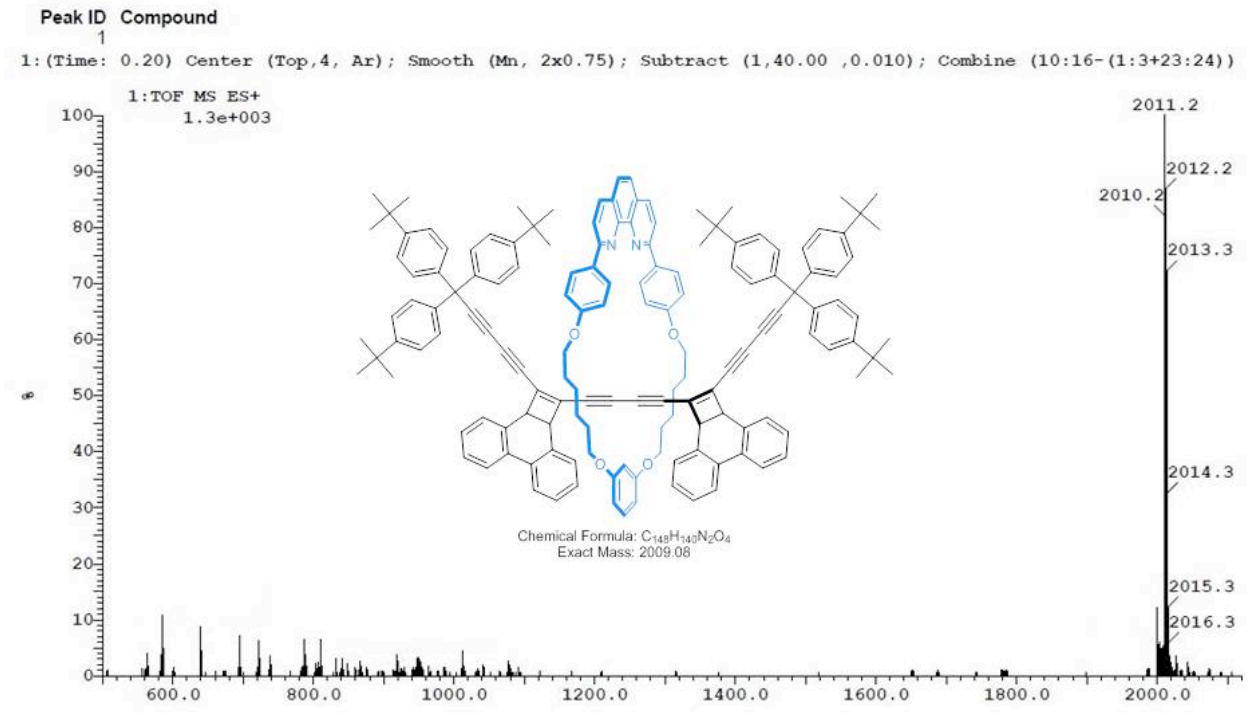


Figure S1. ESI-MS of **16**. *m/z* = 2010.2 $[M+H]^+$ (calc. for $C_{148}H_{141}O_4N_2$: 2010.09 $[M+H]^+$).

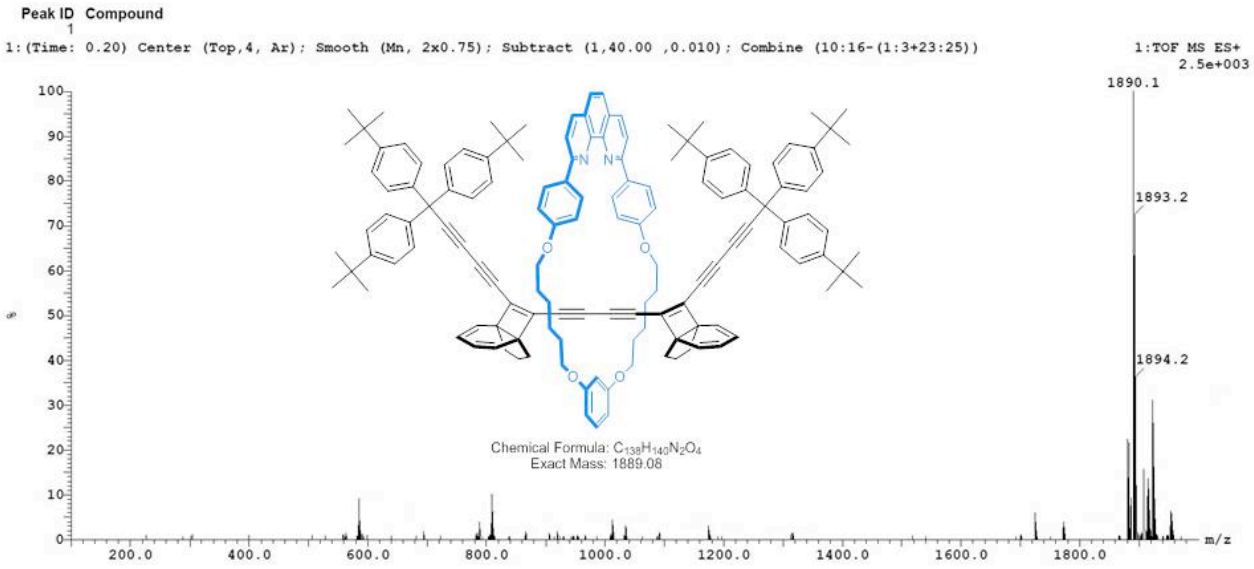


Figure S2. ESI-MS of **27**. LR-ESI-MS: *m/z* = 1890.1 $[M+H]^+$ (calc. for $C_{138}H_{141}O_4N_2$: 1890.09 $[M+H]^+$).

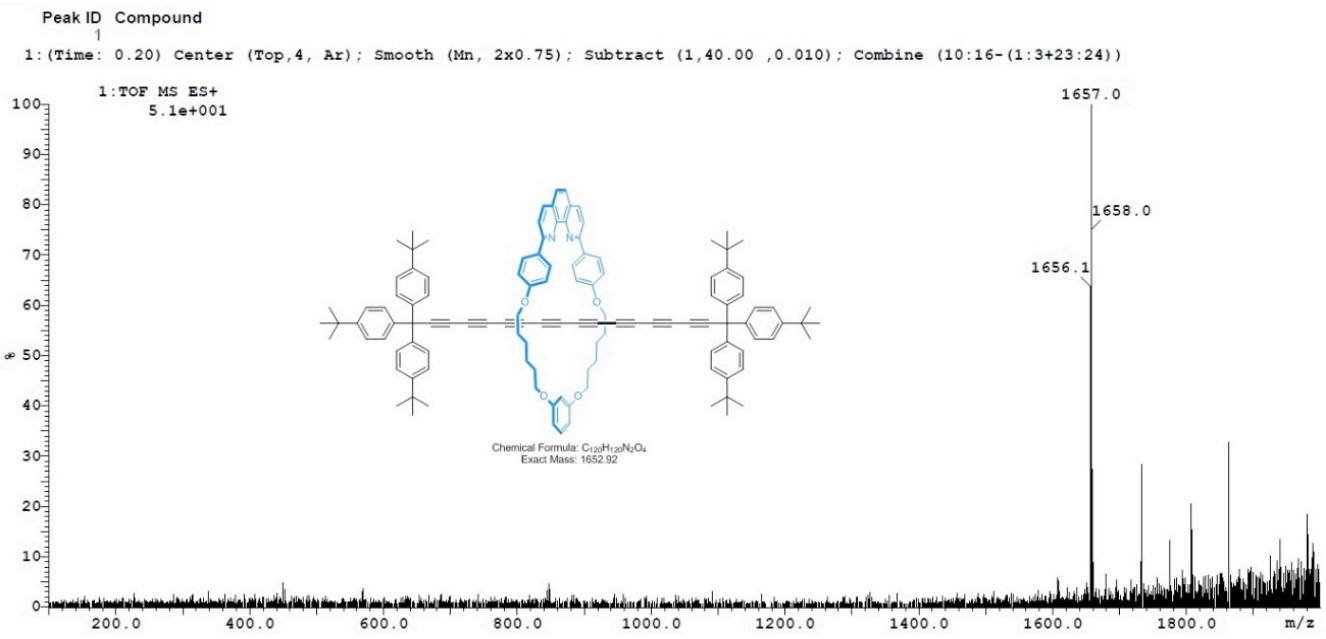
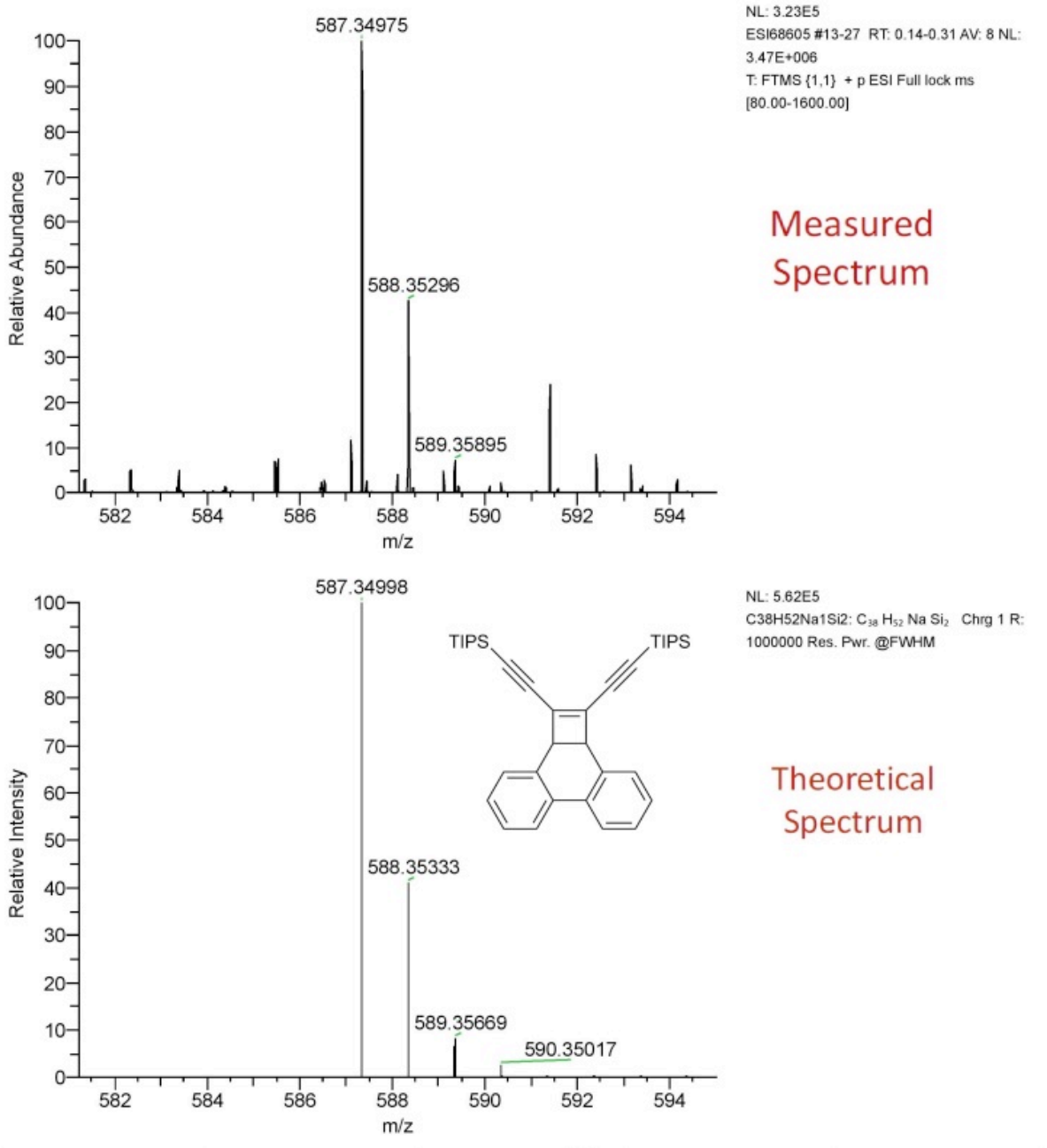


Figure S3. ESI-MS of **28**. LR-ESI-MS: m/z = 1656.1 $[M+H]^+$ (calc. for $C_{120}H_{121}O_4N_2$: 1653.93 $[M+H]^+$).

S4.2 High-resolution MS data



m/z	Formula	RDB	Delta ppm	Theo. Mass
587.34973	$C_{38}H_{52}{}^{23}Na^{28}Si_2$	14.5	-0.42	587.34998

Figure S4. HR-ESI-MS of **2.**

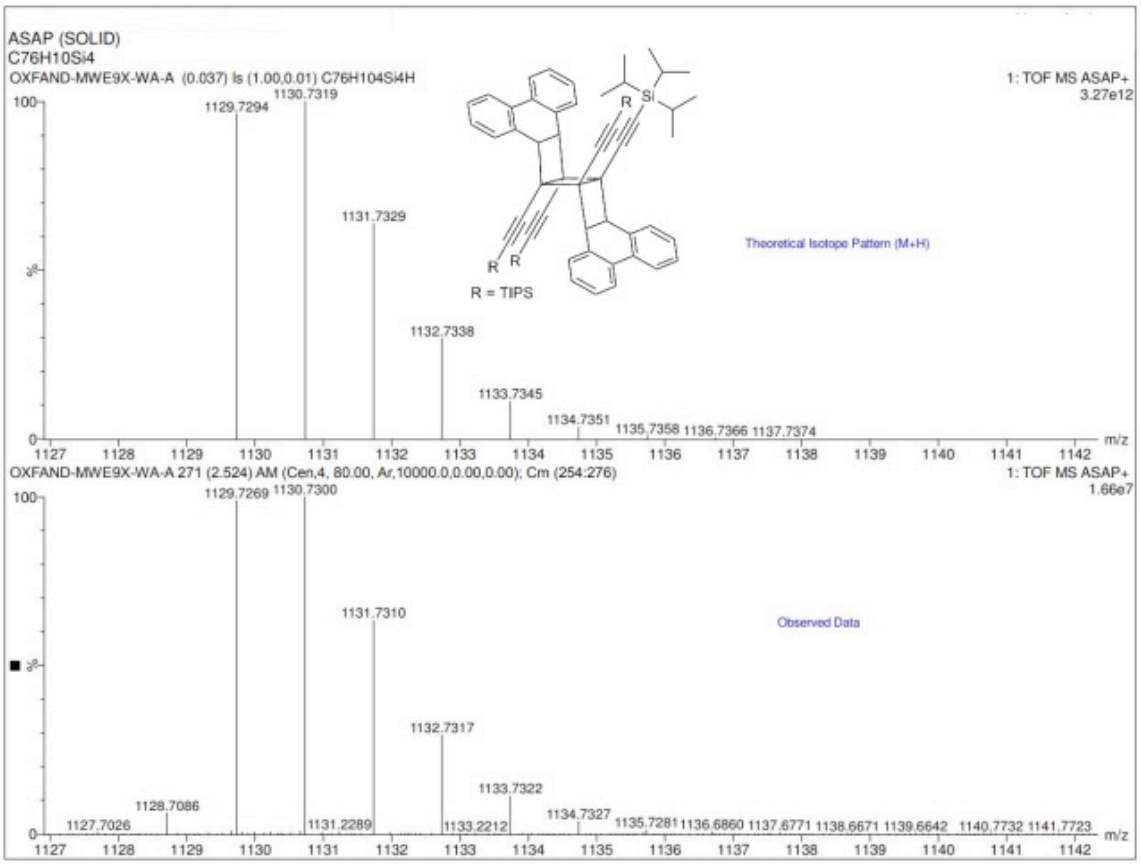


Figure S5. HR-TOF-MS-ASAP of **6**.

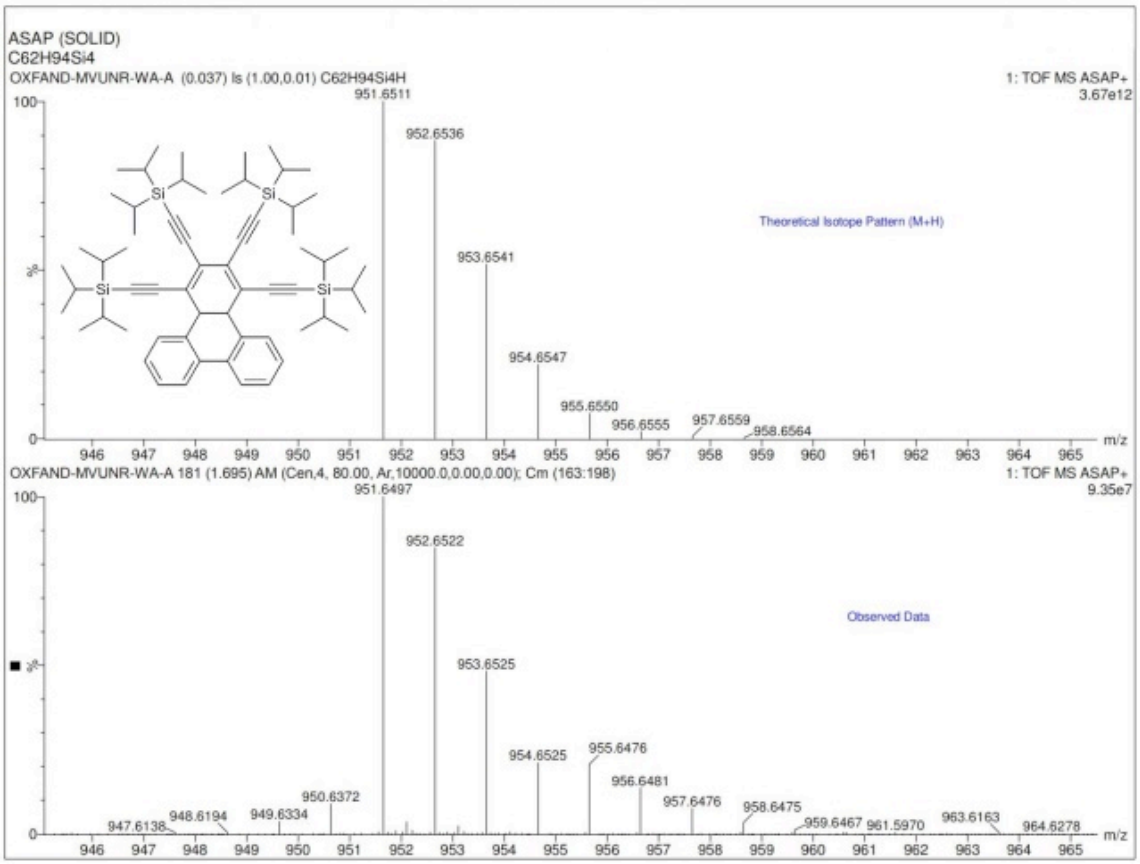
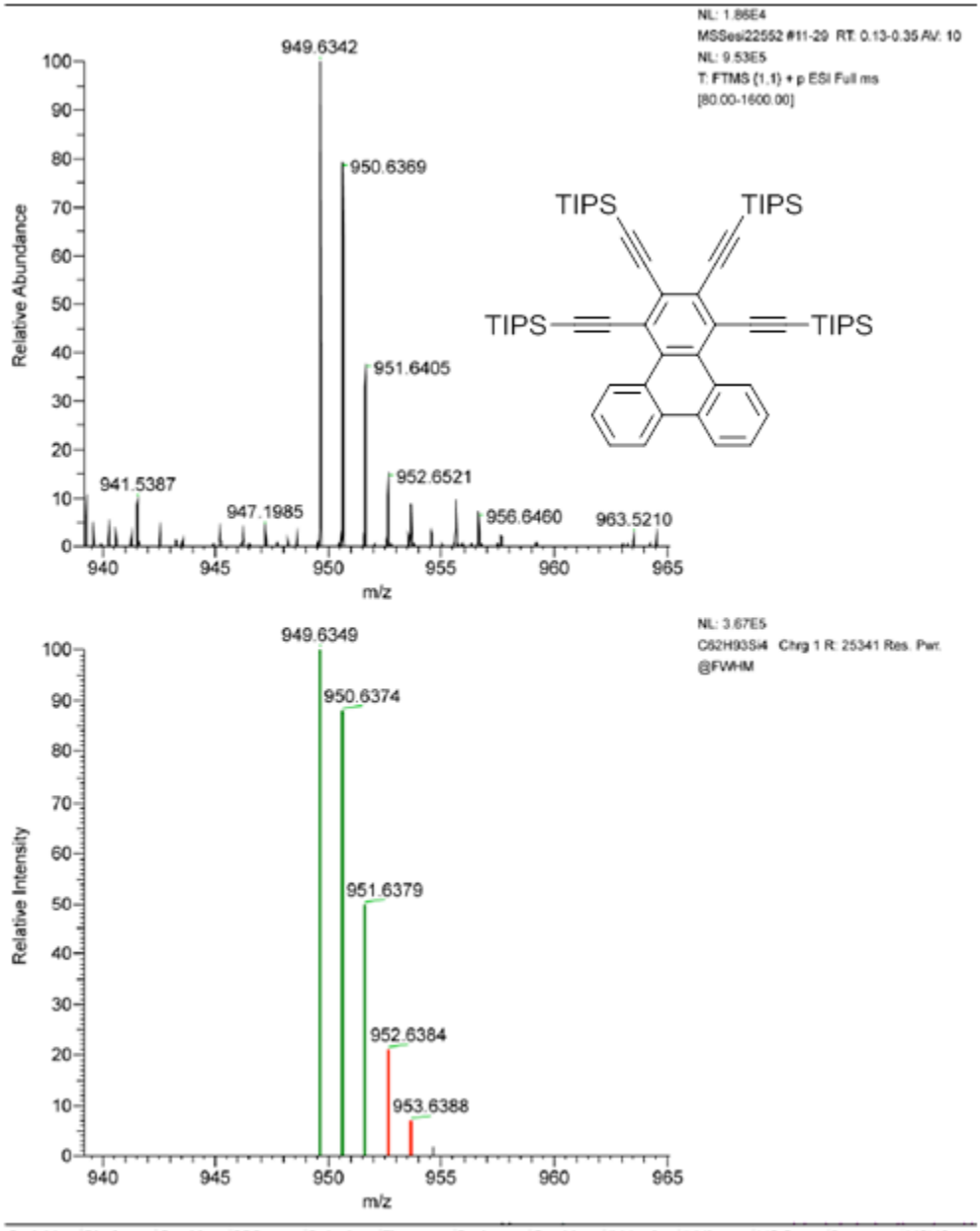
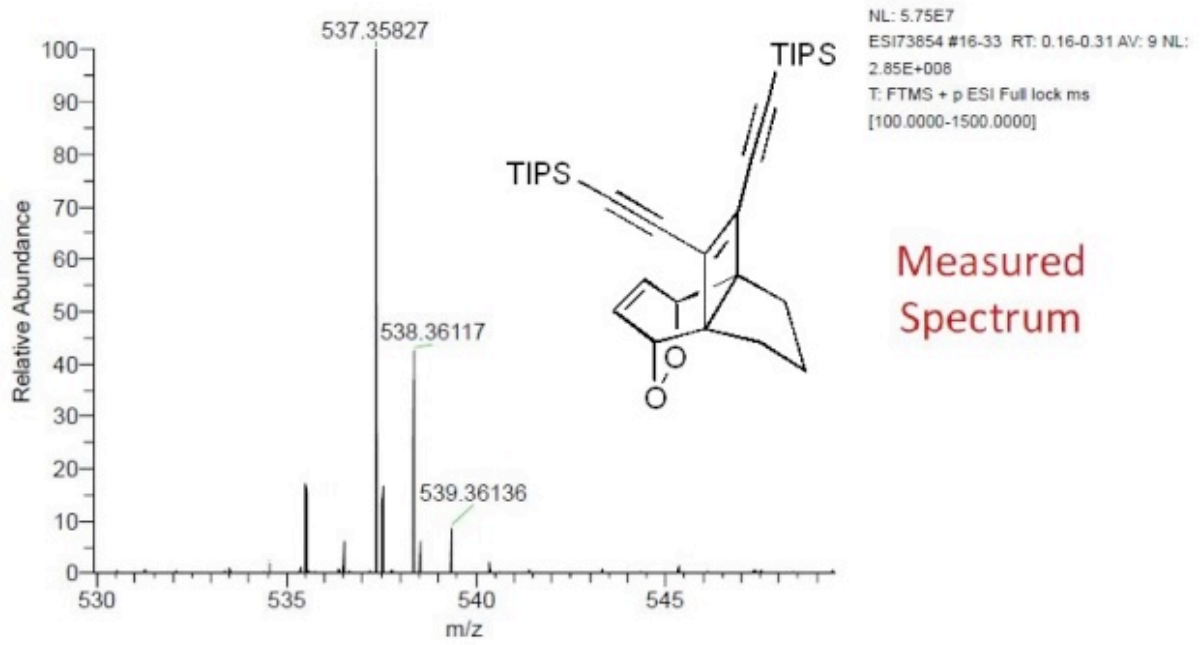


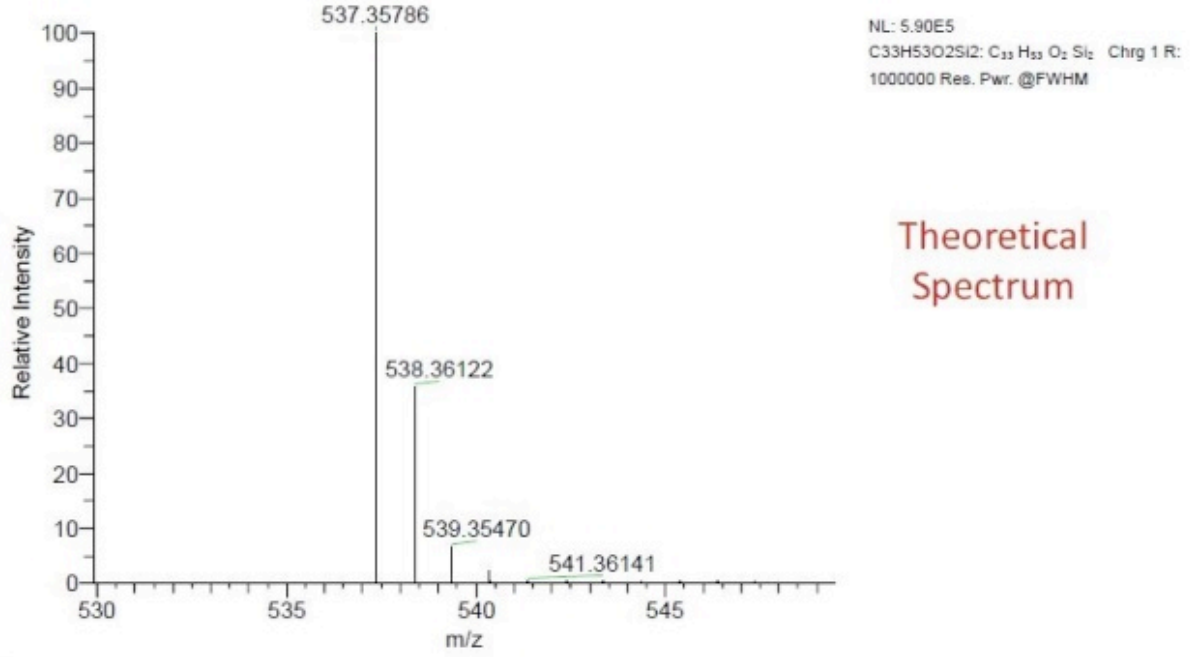
Figure S6. HR-TOF-MS-ASAP of **7**.



Peak Mass	Display...	Combin...	RDB	Delta (p...	Theo. m...	Rank	Combin...	# Match...	# Misse...	MS Cov...	Pattern...	MSMS...
949.6342	$C_{62}H_{93}^{2}$...	21.017...	20.50	-0.73	949.63...	1	71.068...	3	2	73.849...	70.841...	(Collec...

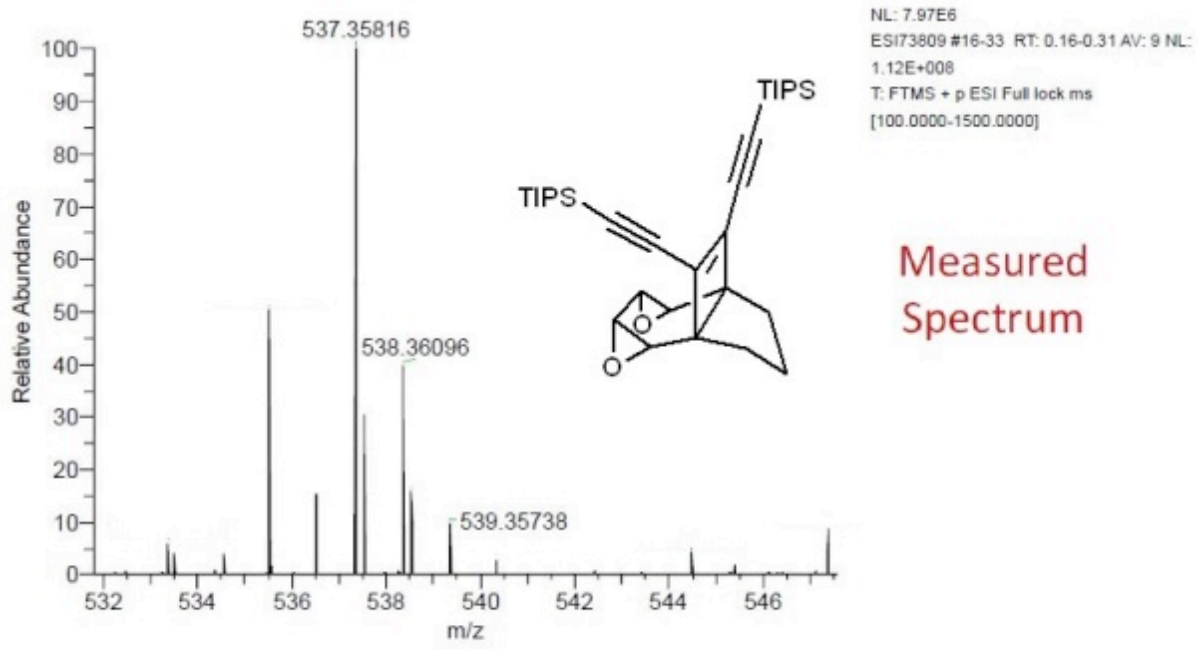
Figure S7. HR-ESI-MS of **8**.

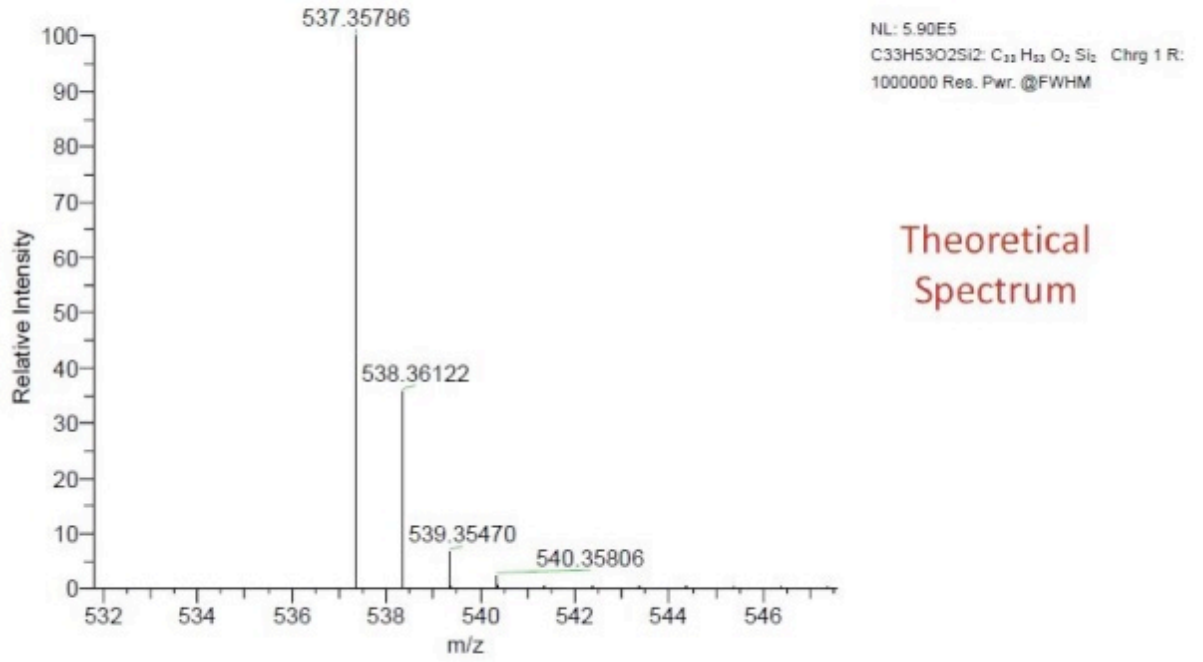




m/z	Formula	RDB	Delta ppm	Theo. Mass
537.35827	$C_{33}H_{53}O_2{}^{28}Si_2$	9.5	0.77	537.35786

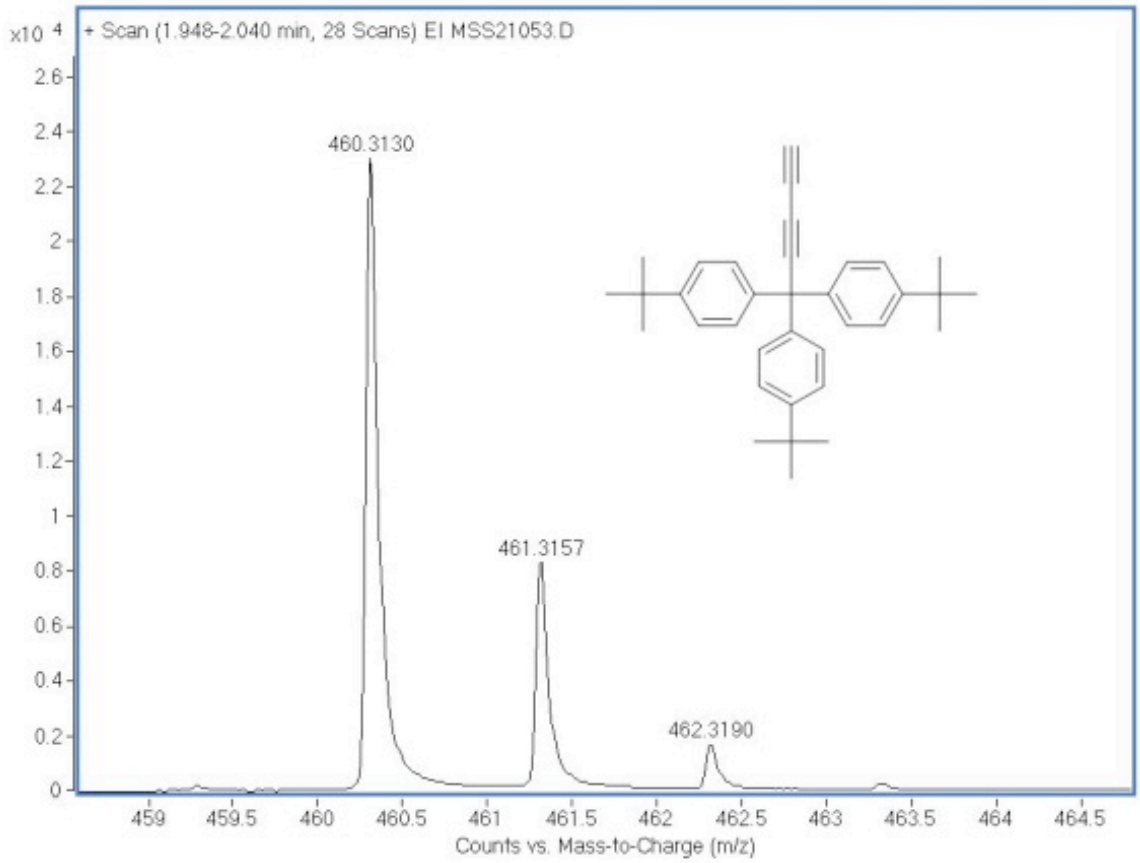
Figure S8. HR-ESI-MS of **9**.





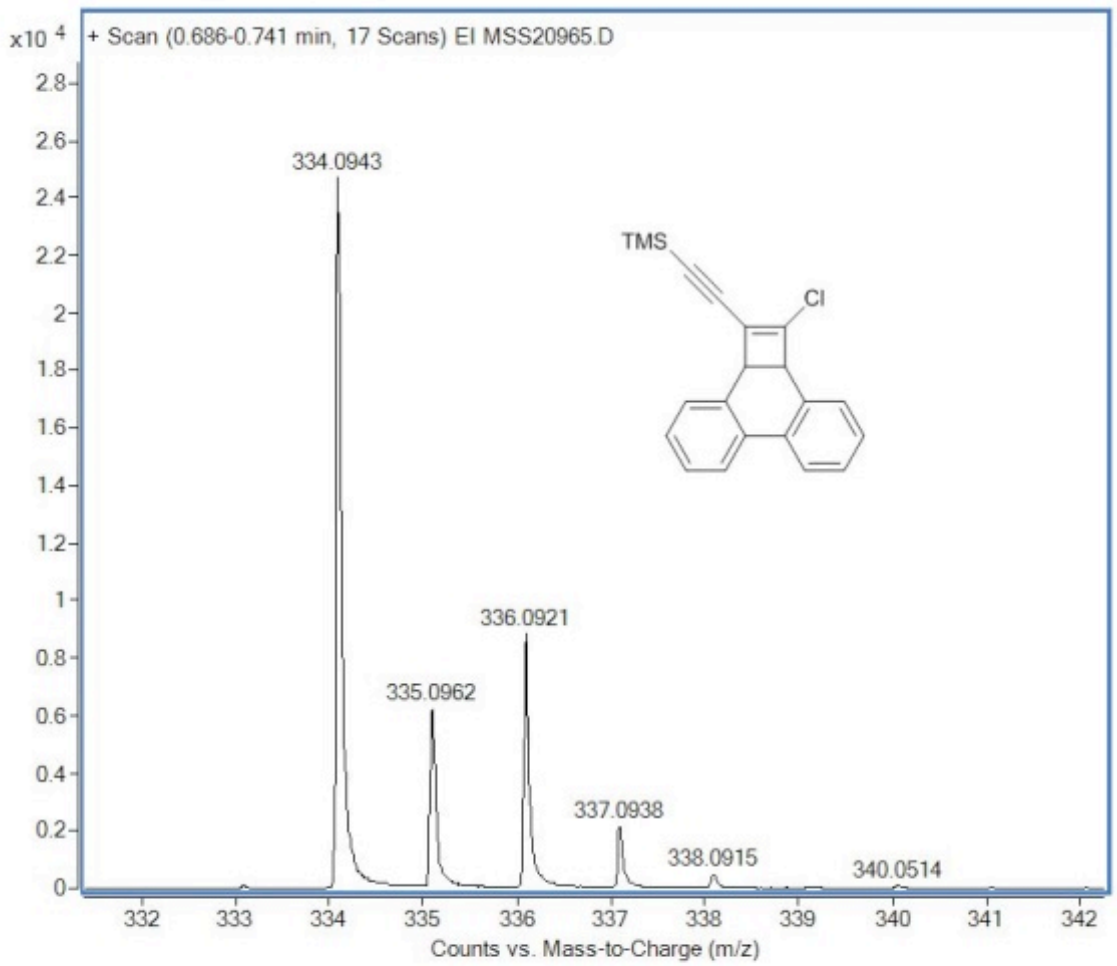
m/z	Formula	RDB	Delta ppm	Theo. Mass
537.35815	$C_{33}H_{53}O_2{}^{28}Si_2$	9.5	0.55	537.35786

Figure S9. HR-ESI-MS of **10**.



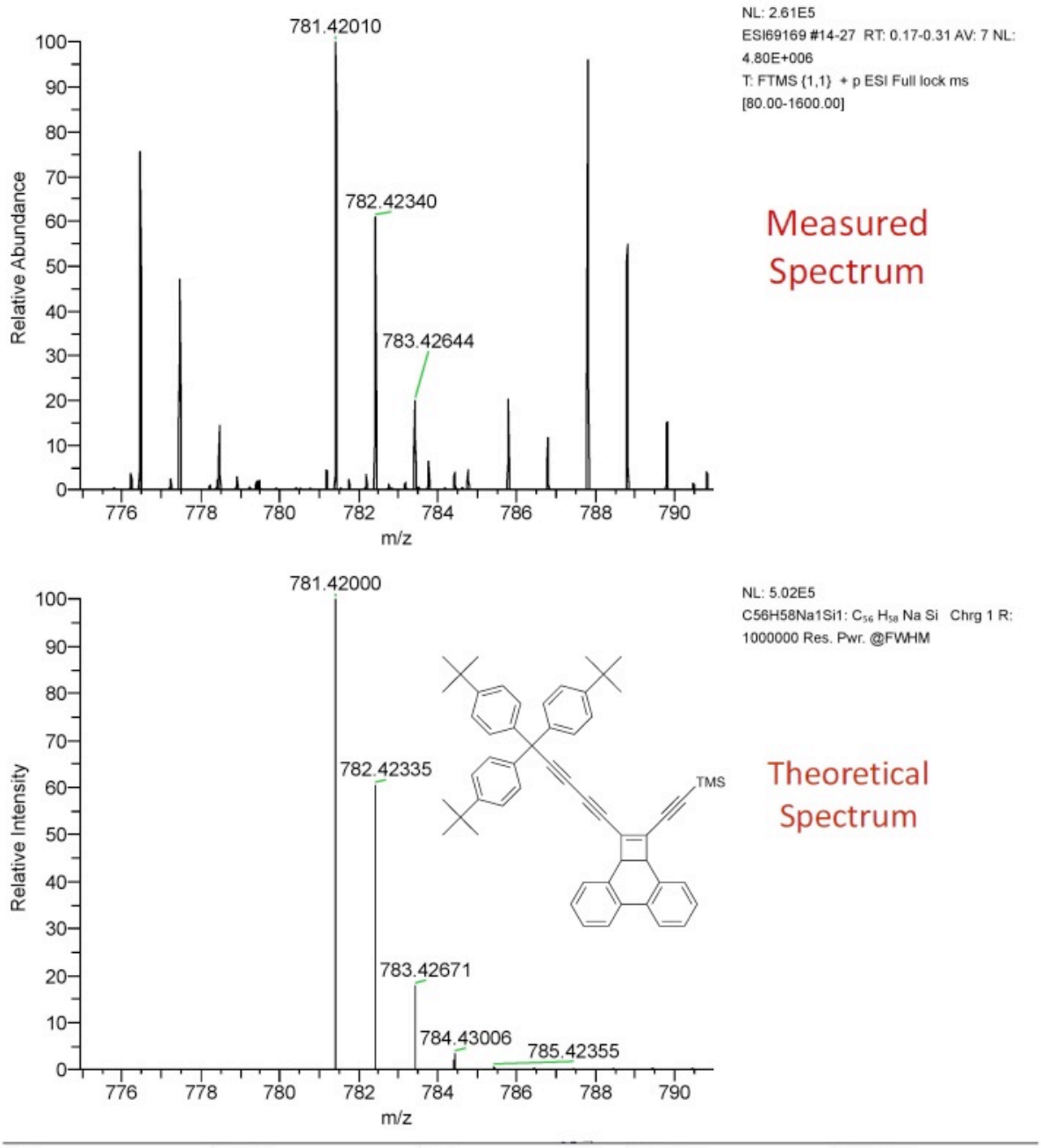
Formula (M)	Ion Formula	m/z	m/z (Calc)	Diff (ppm)	DBE
C35 H40	C35 H40	460.313	460.3125	-1.19	16

Figure S10. HR-EI-GCMS of **12**.



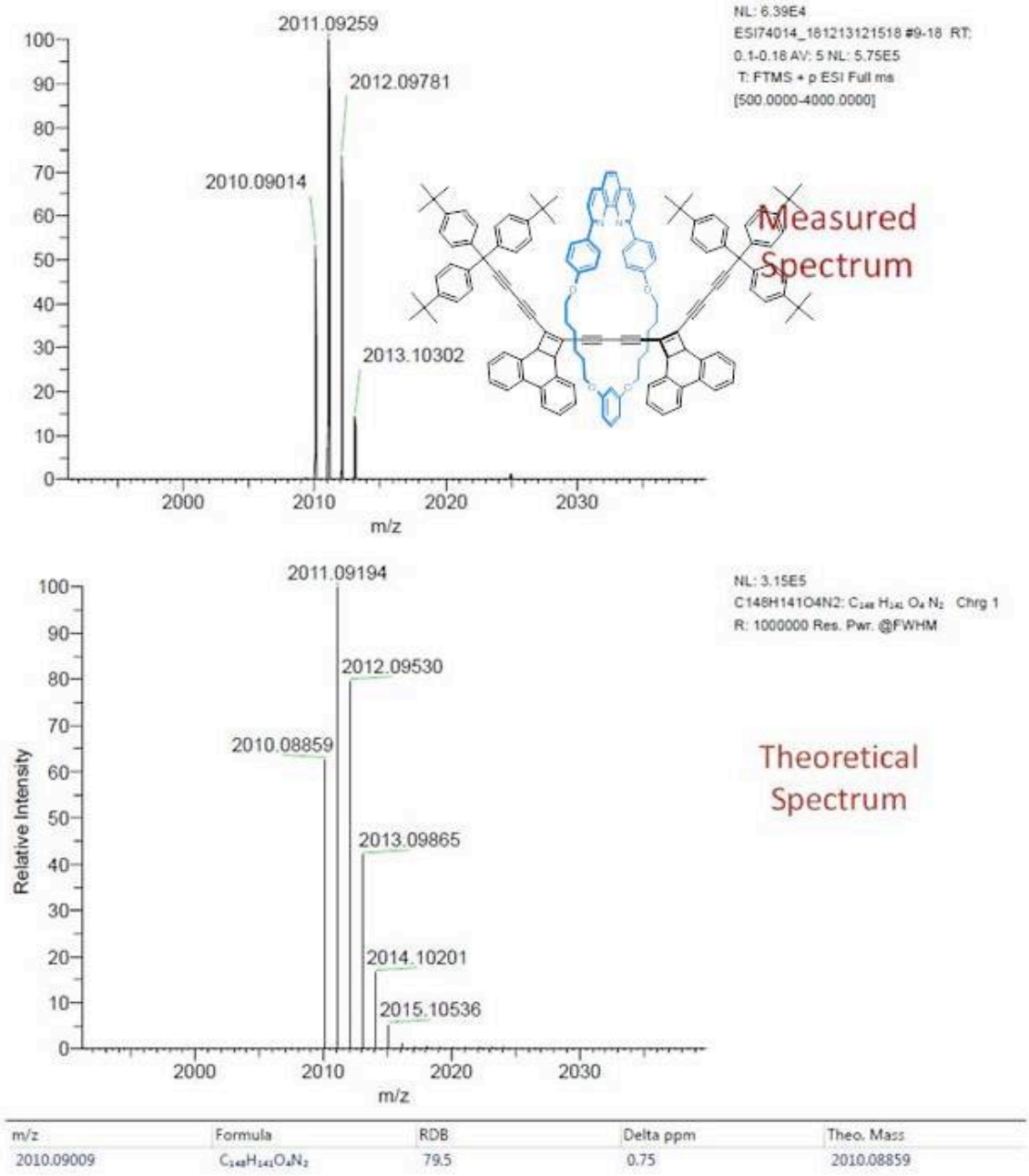
Formula (M)	Ion Formula	m/z	m/z (Calc)	Diff (ppm)	DBE
C21 H19 Cl Si	C21 H19 Cl Si	334.0943	334.0939	-1.18	13

Figure S11. HR-EI-GCMS of **13**.



m/z	Formula	RDB	Delta ppm	Theo. Mass
781.42010	$C_{56}H_{58}{}^{23}Na^{28}Si$	28.5	0.13	781.42000

Figure S12. HR-ESI-MS of **14**.



m/z	Formula	RDB	Delta ppm	Theo. Mass
2010.09009	$C_{148}H_{141}O_4N_2$	79.5	0.75	2010.08859

Figure S13. HR-ESI-MS of **16**.

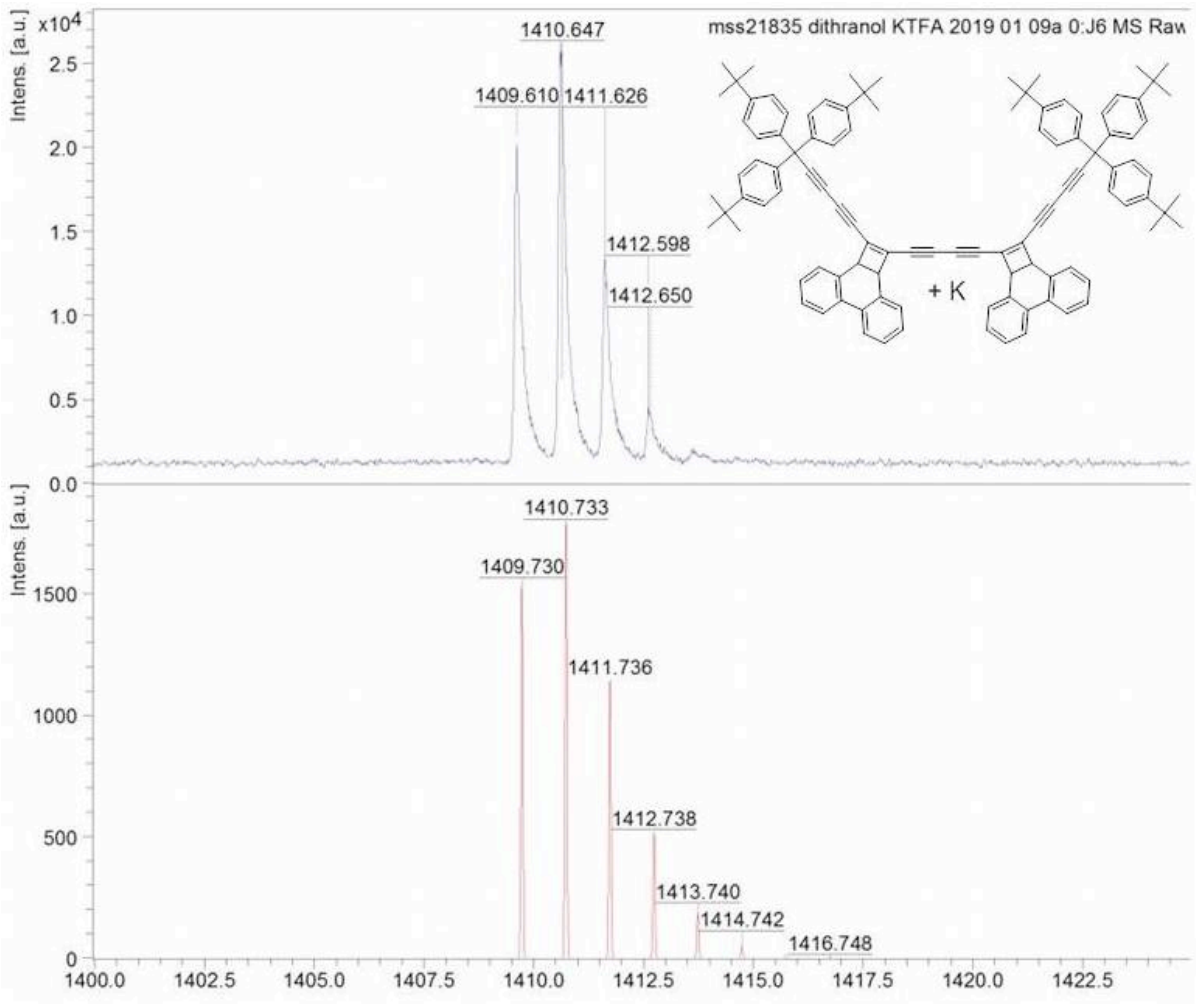
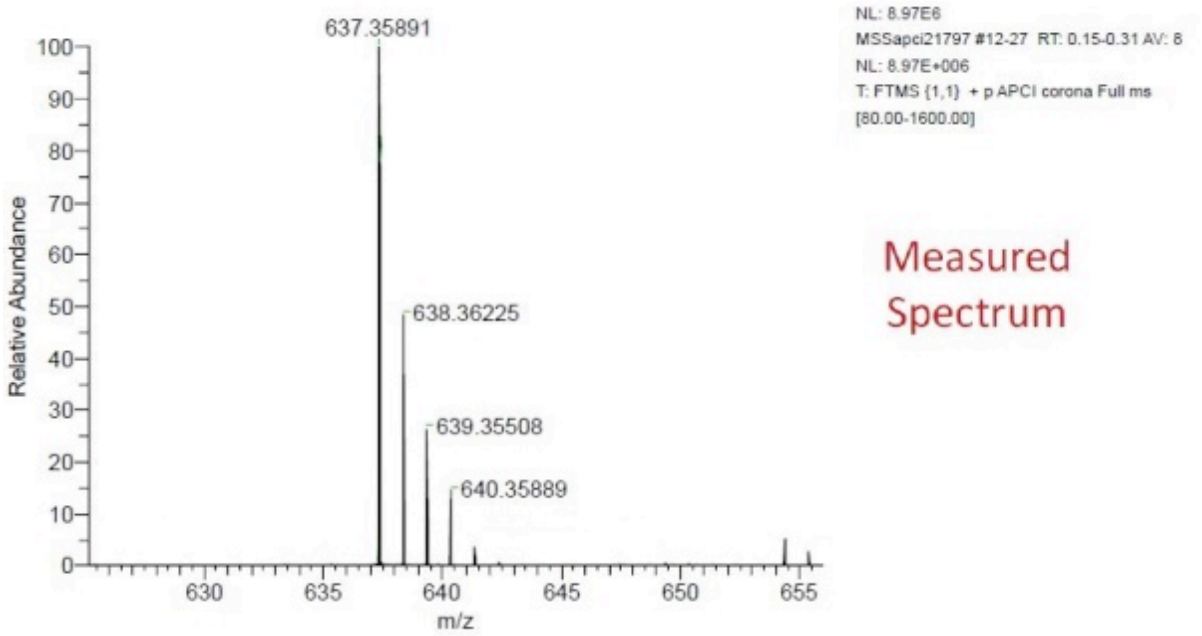
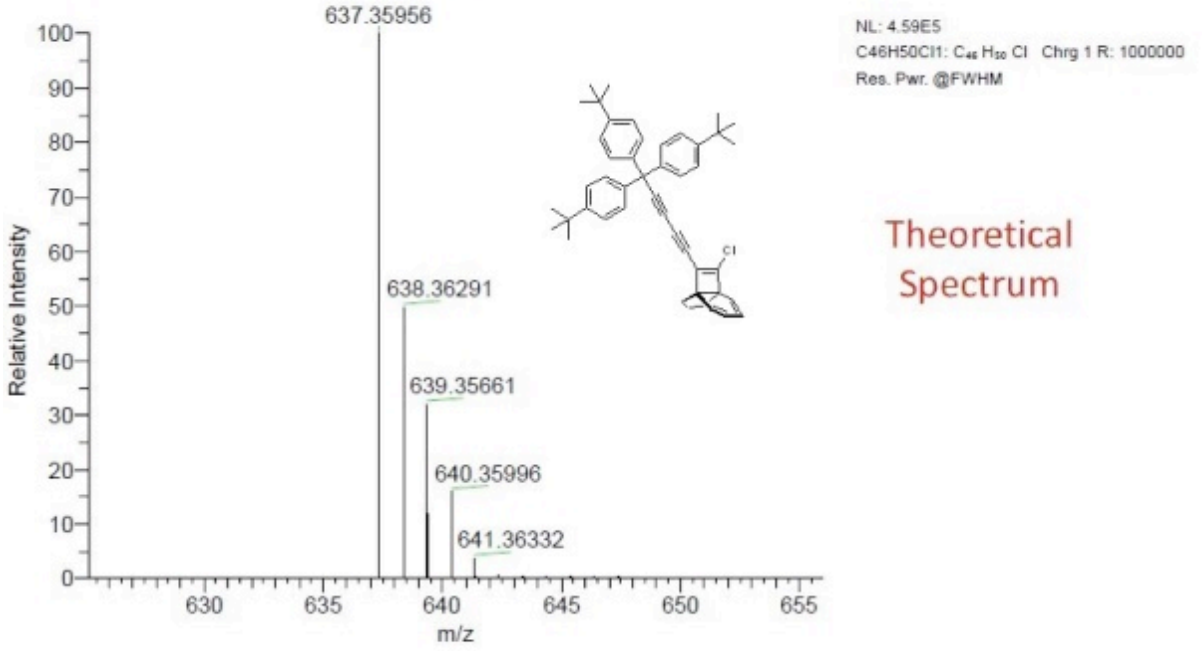


Figure S14. MALDI-MS of **17**.





m/z	Formula	RDB	Delta ppm	Theo. Mass
637.35889	$C_{46}H_{50}{}^{35}Cl$	21.5	-1.05	637.35956

Figure S15. HR-APCI-MS of **25**.

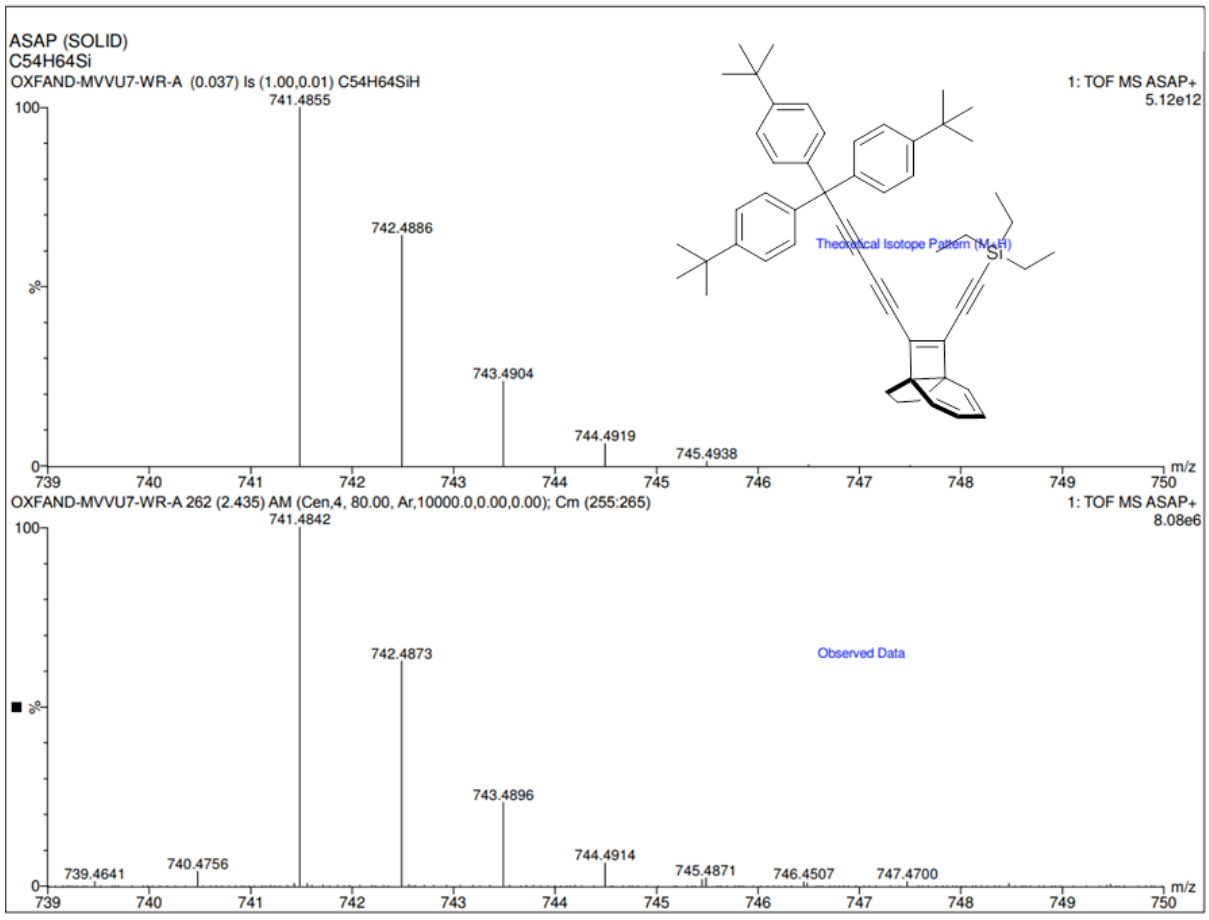
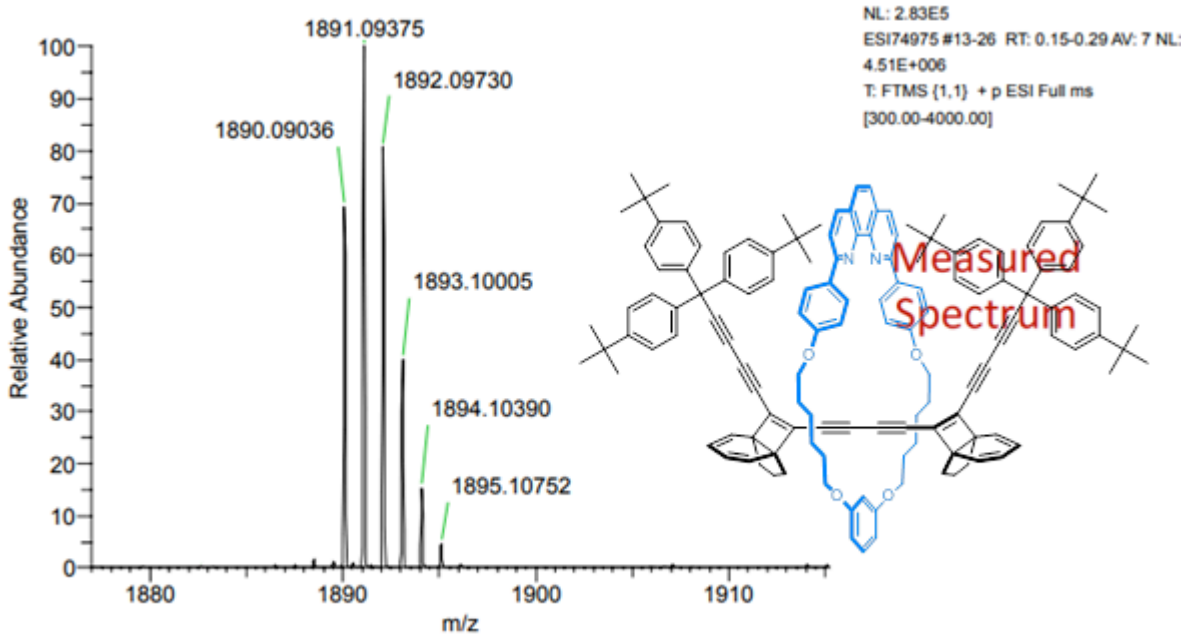
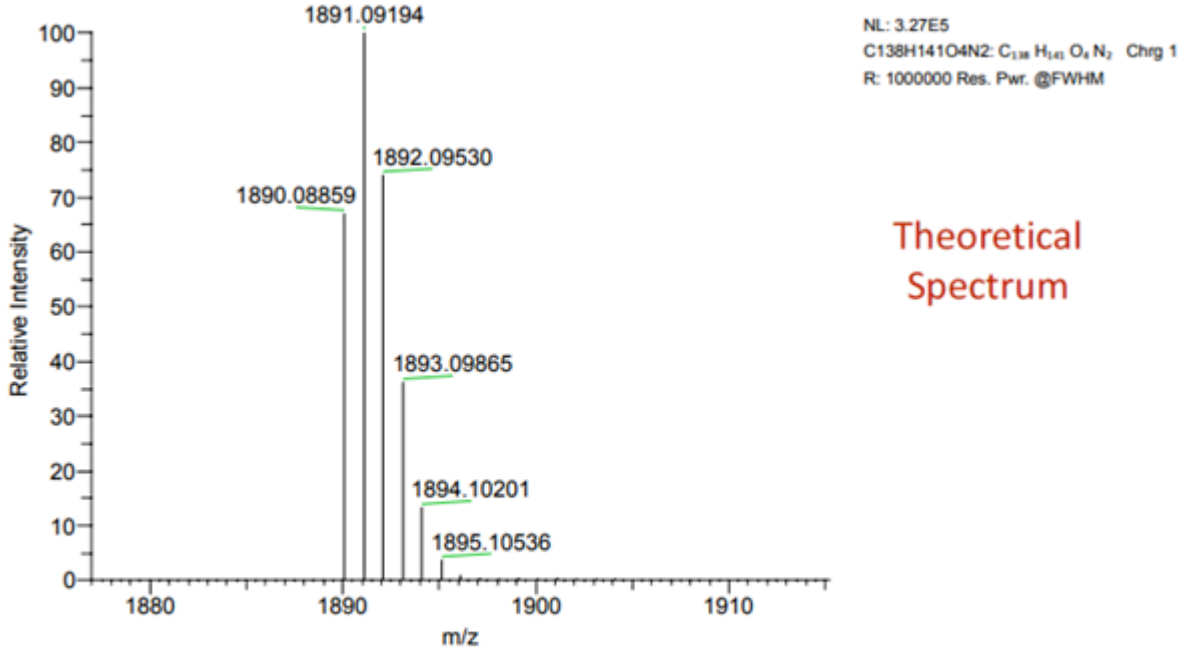


Figure S16. HR-TOF-MS-ASAP of **24**.





m/z	Formula	RDB	Delta ppm	Theo. Mass
1890.09033	$C_{138}H_{141}O_4N_2$	69.5	0.92	1890.08859

Figure S17. HR-ESI-MS of **27**.

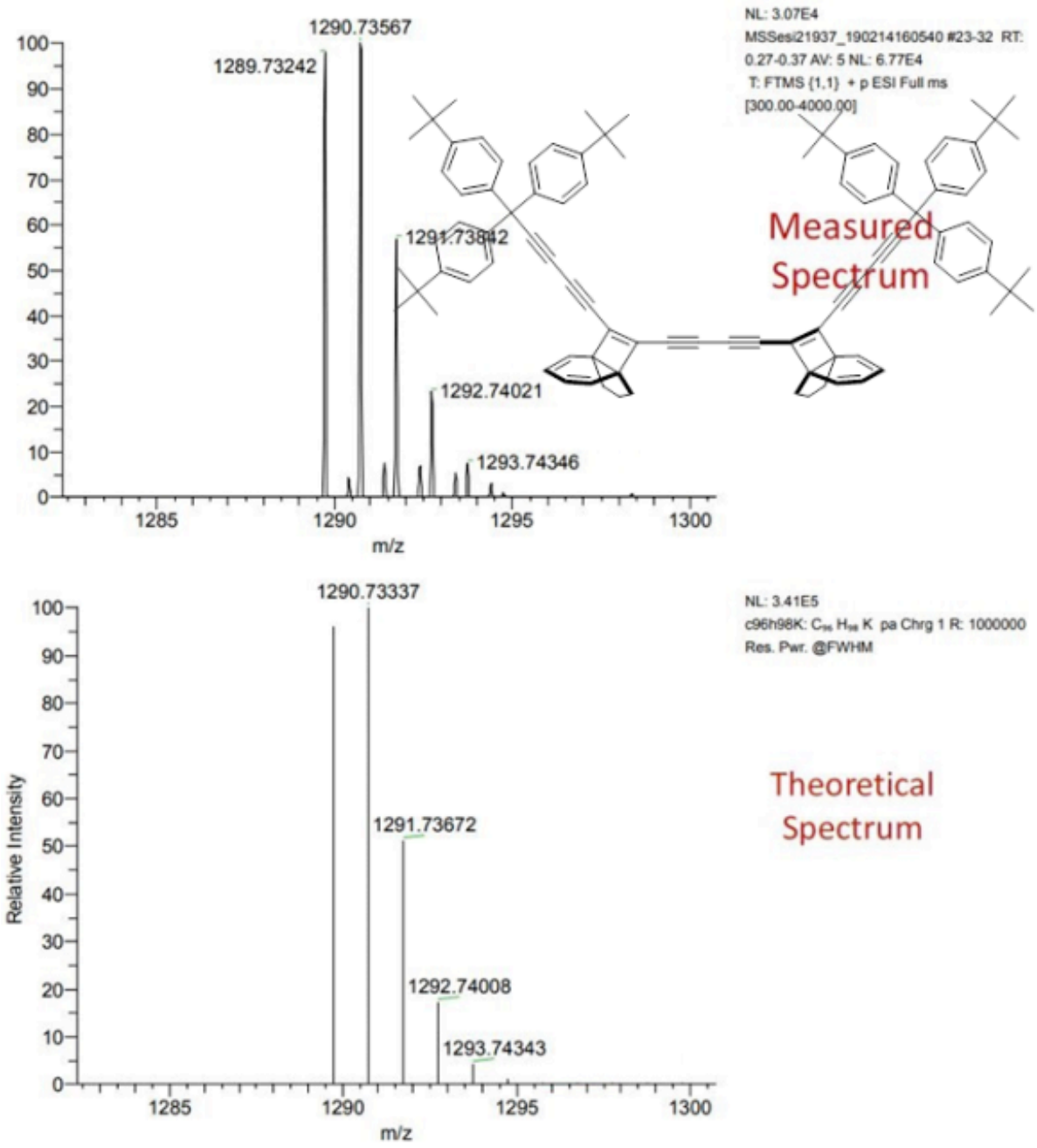
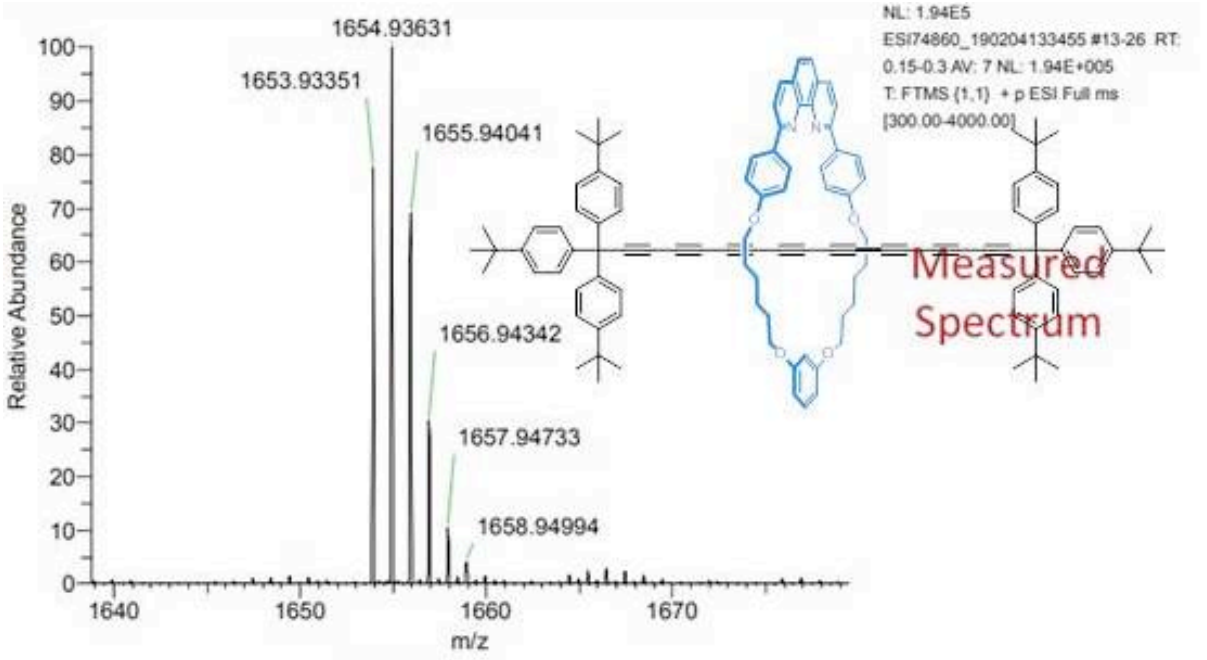
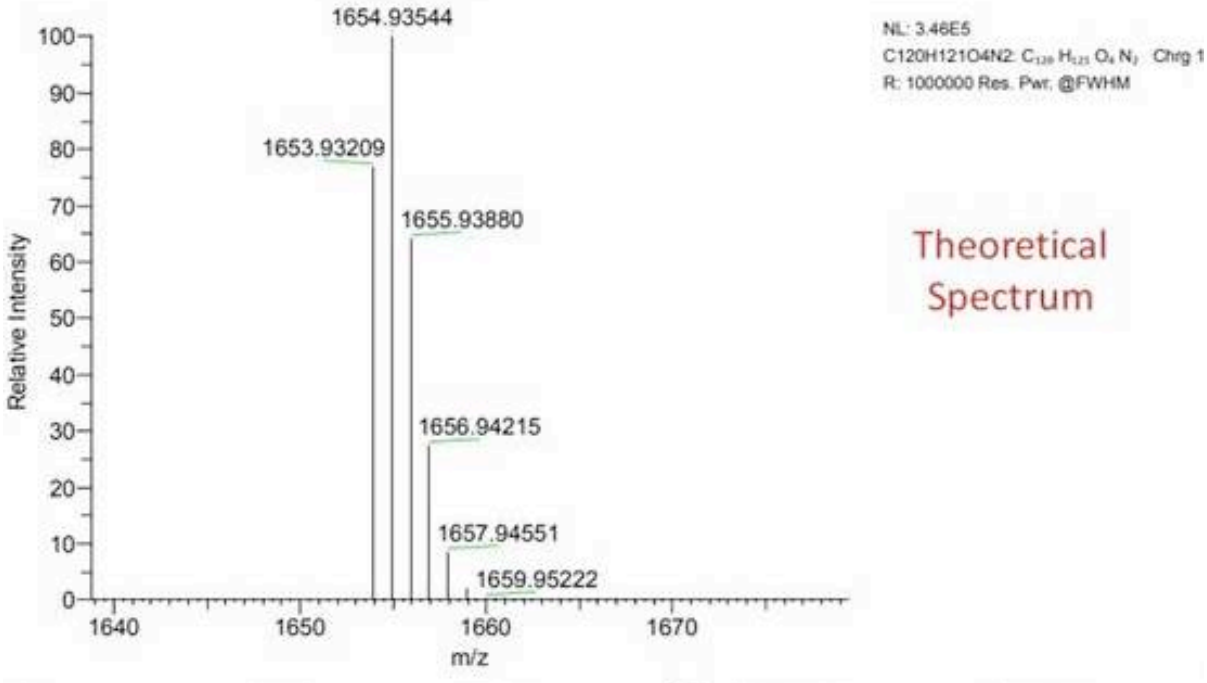


Figure S18. HR-ESI-MS of **29**.





m/z	Formula	RDB	Delta ppm	Theo. Mass
1653.93347	$C_{120}H_{121}O_4N_2$	61.5	0.84	1653.93209

Figure S19. HR-ESI-MS of **28**.

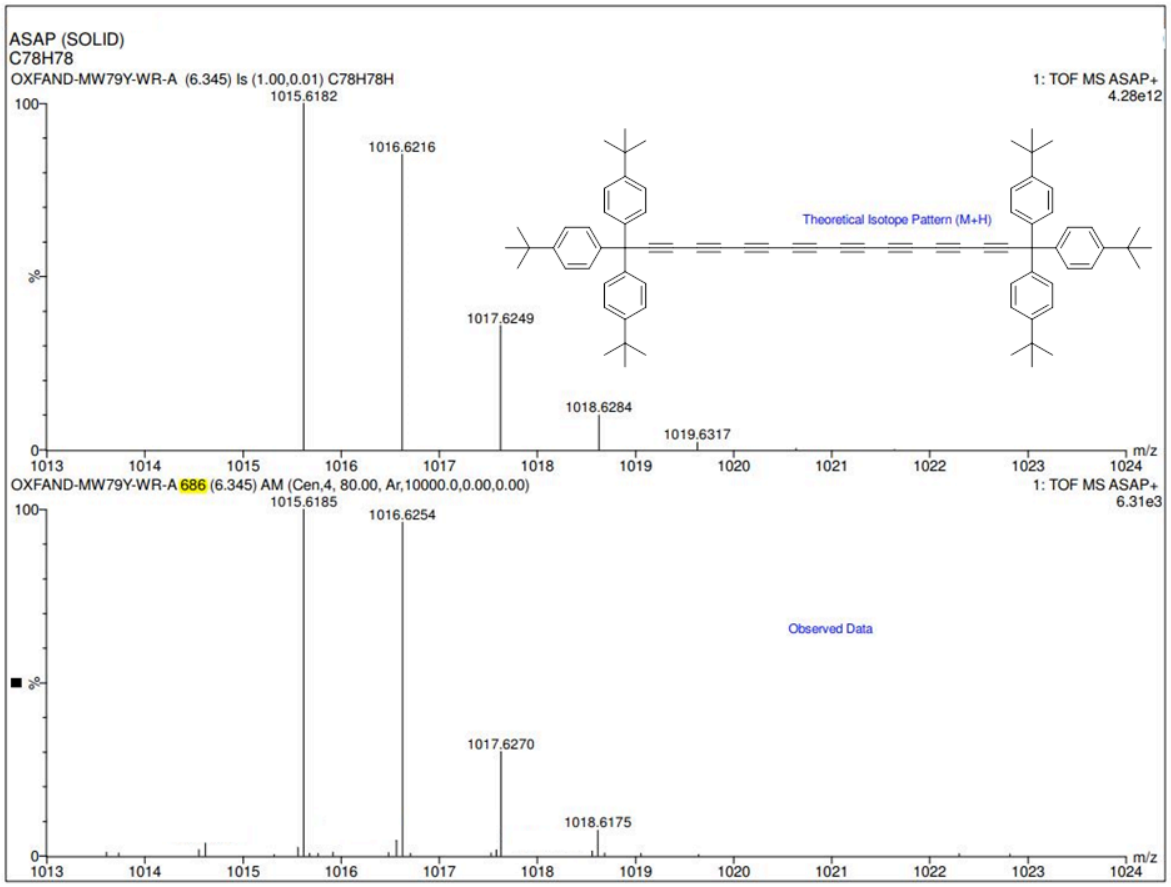


Figure S20. HR-TOF-MS-ASAP of **30**.

S5. NMR Spectra of Novel Compounds

S5.1 1D ^{1}H and ^{13}C NMR data

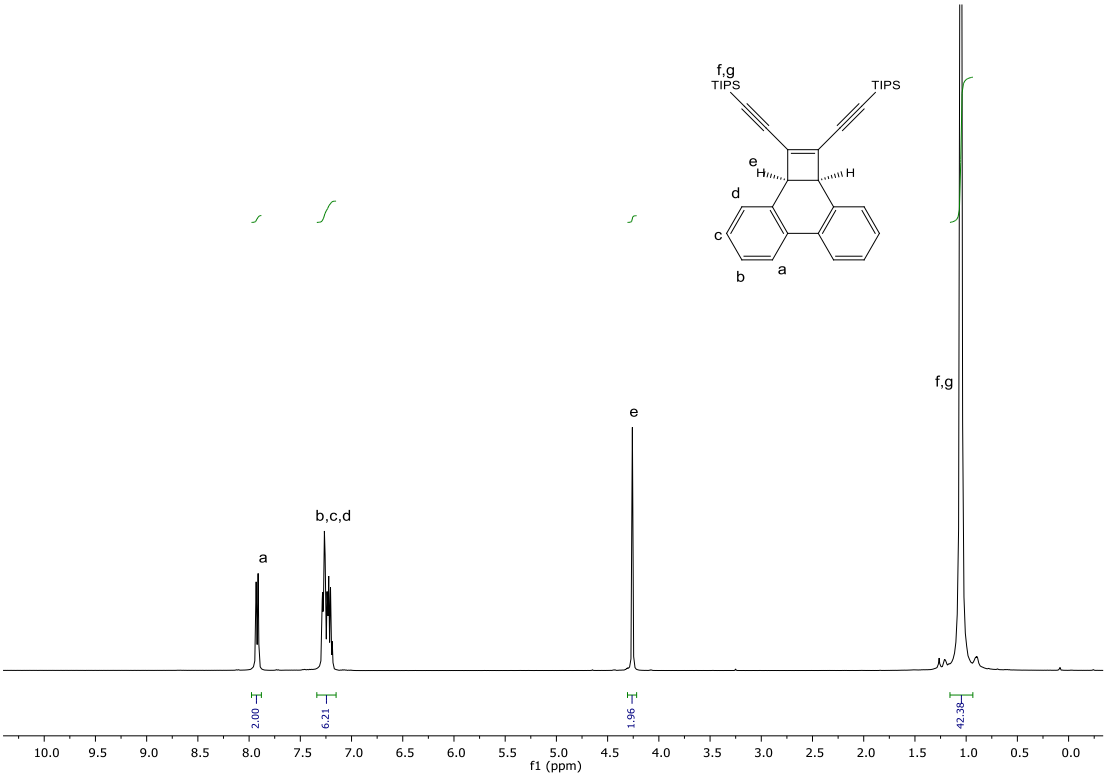


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of **2**.

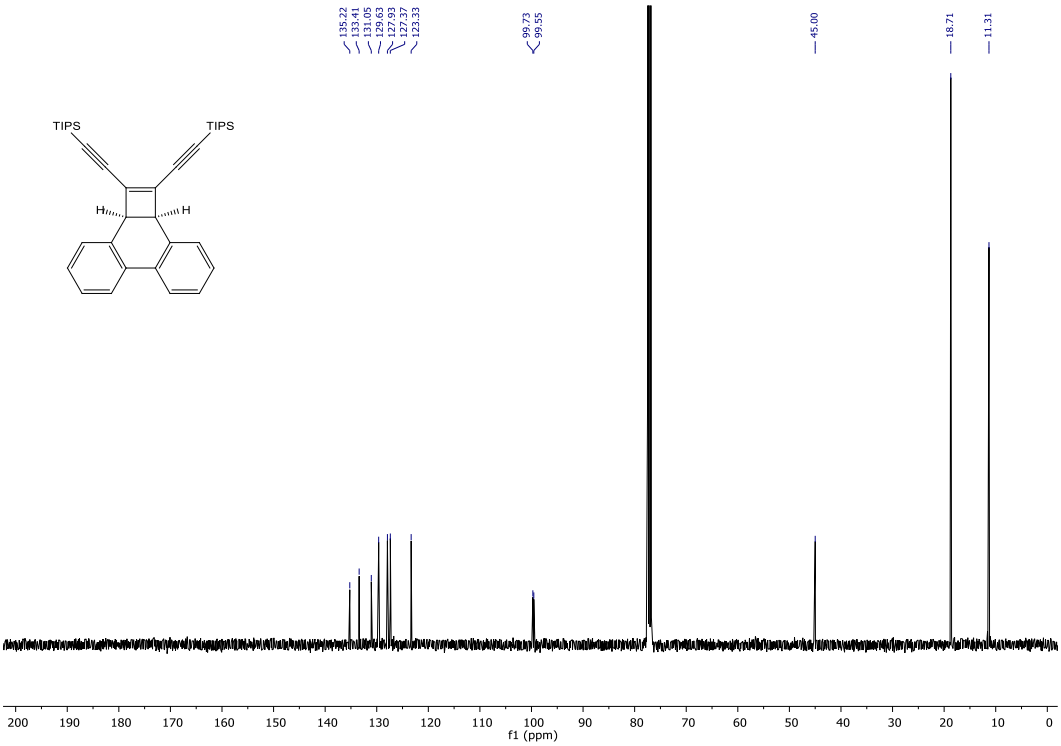


Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) of **2**.

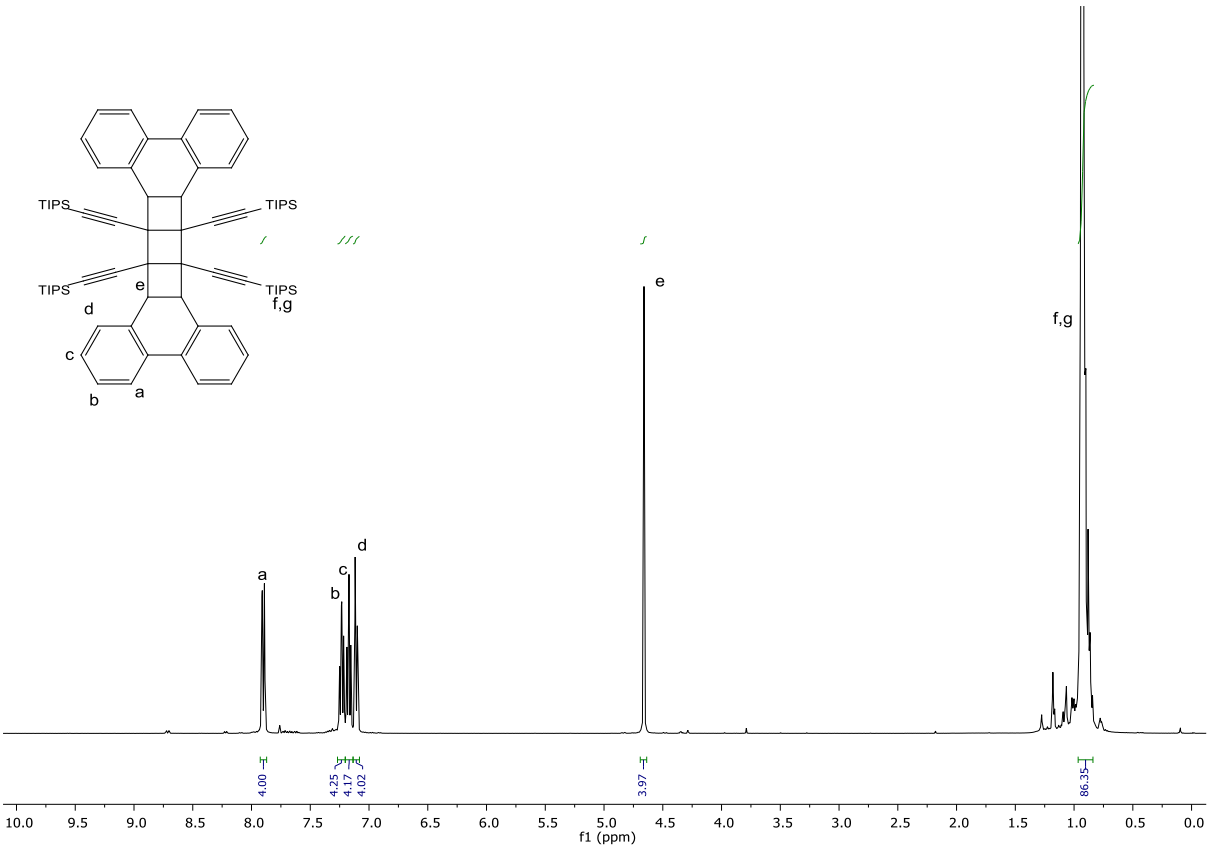


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of **6**.

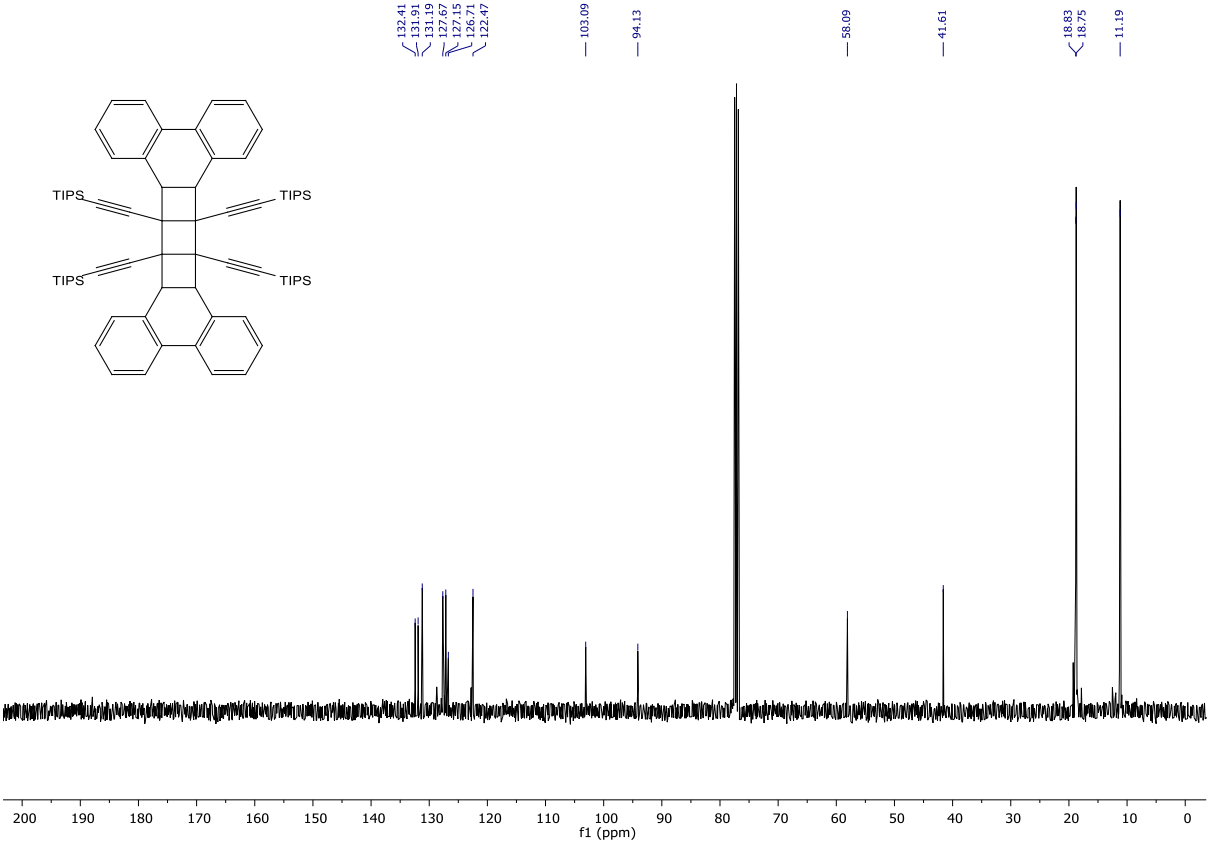


Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) of **6**.

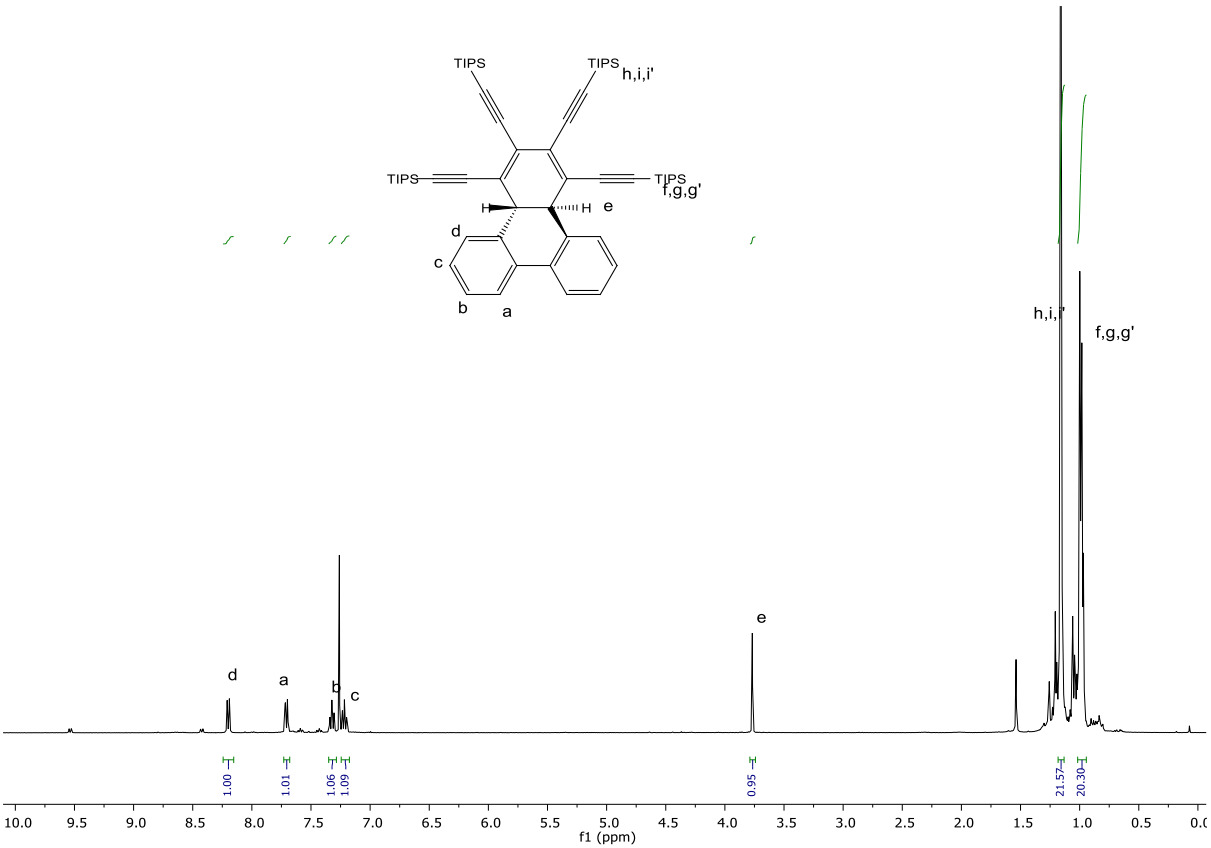


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) of **7**.

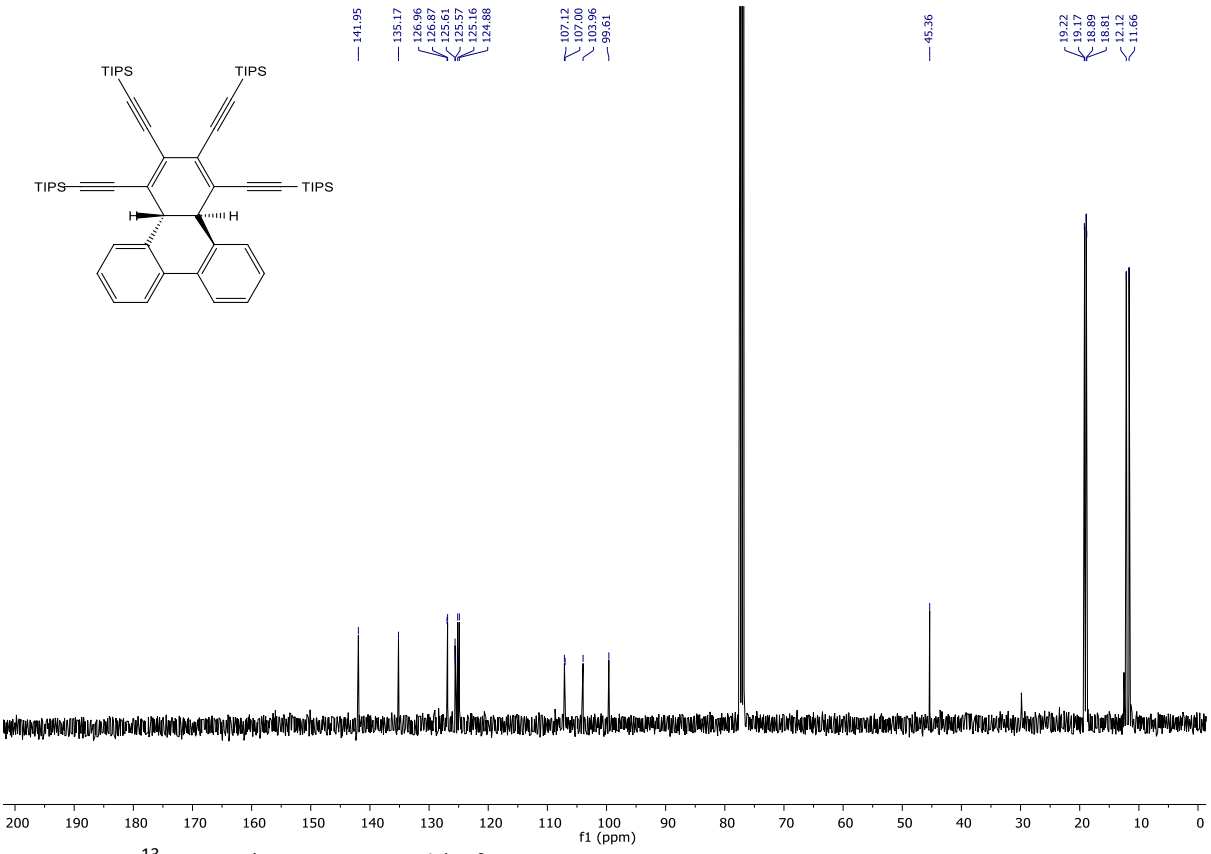


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) of **7**.

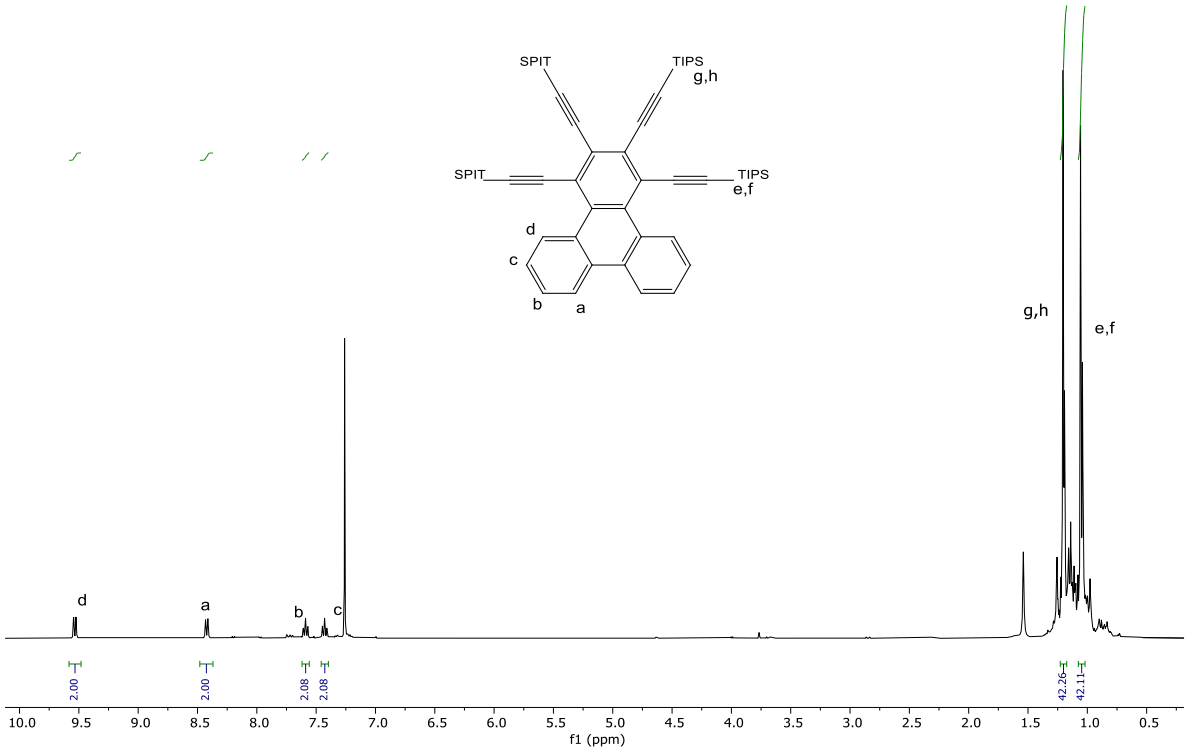


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of **8**.

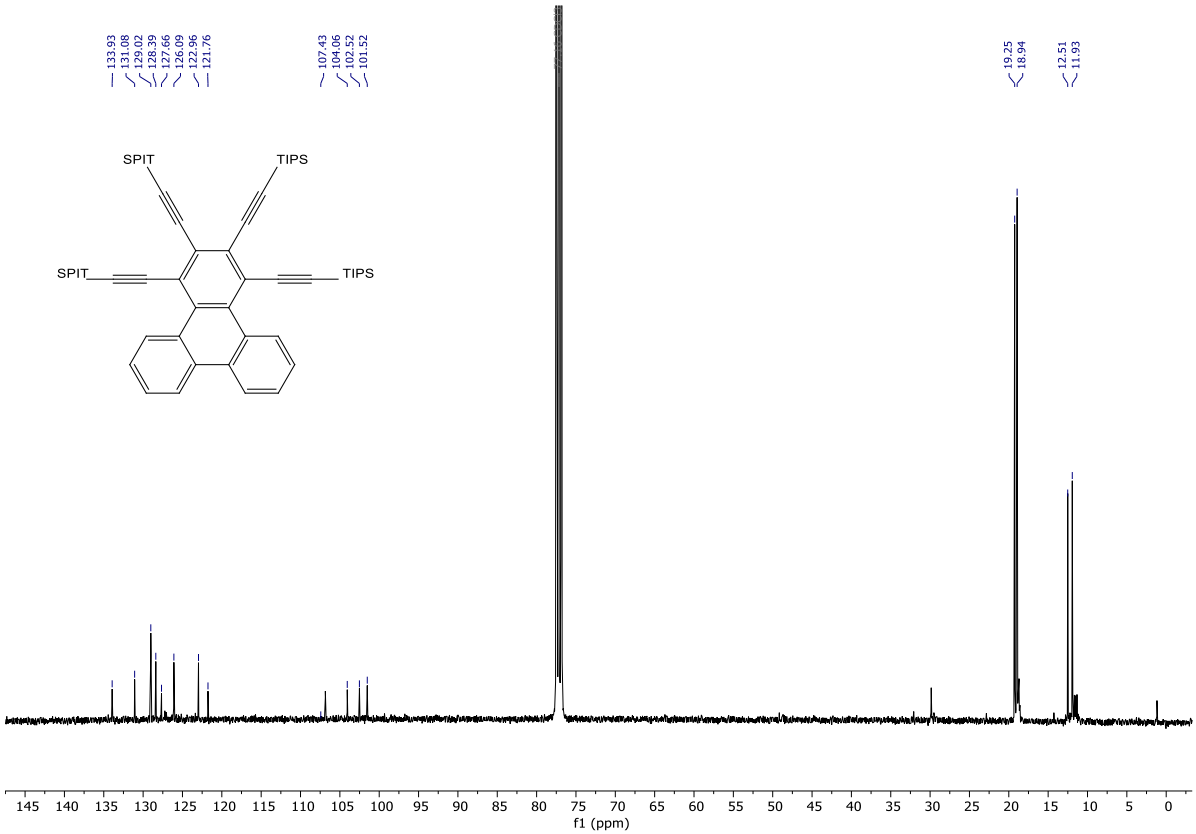


Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) of **8**.

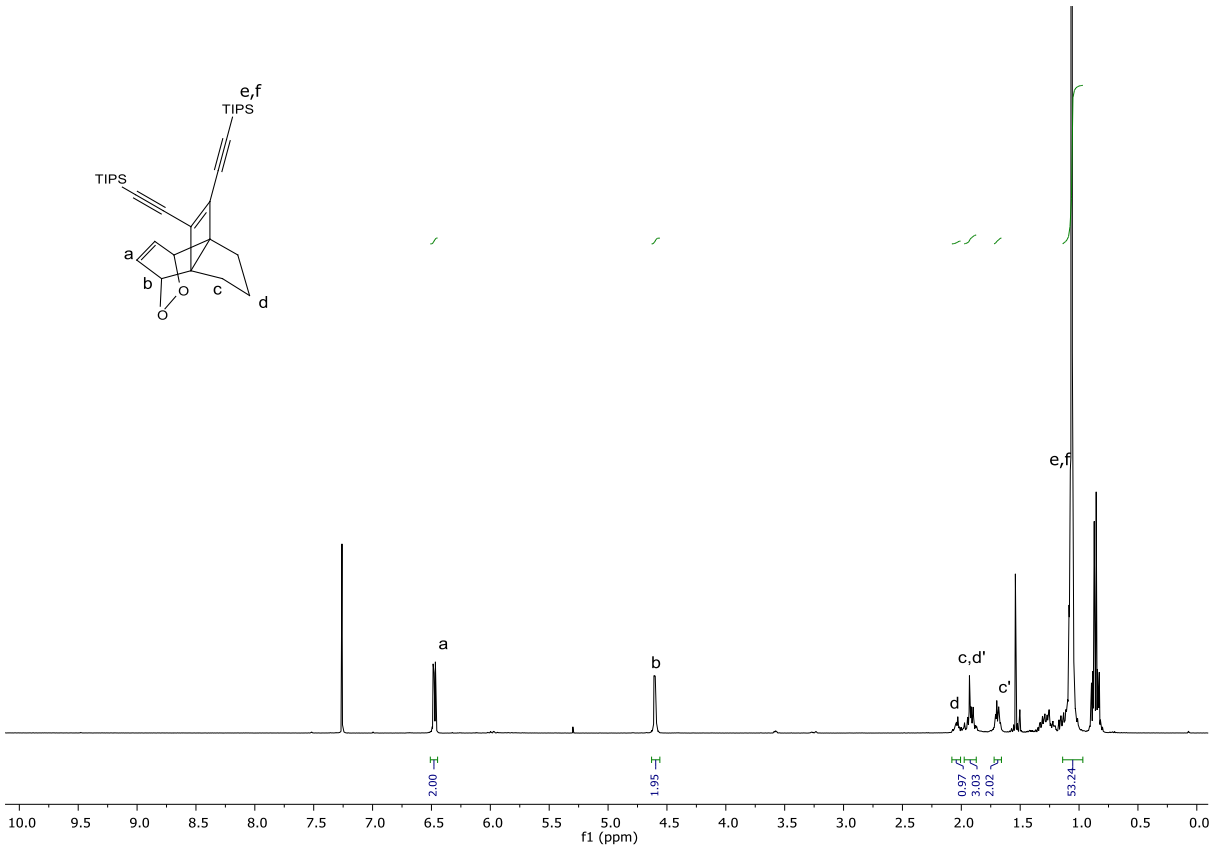


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) of **9**.

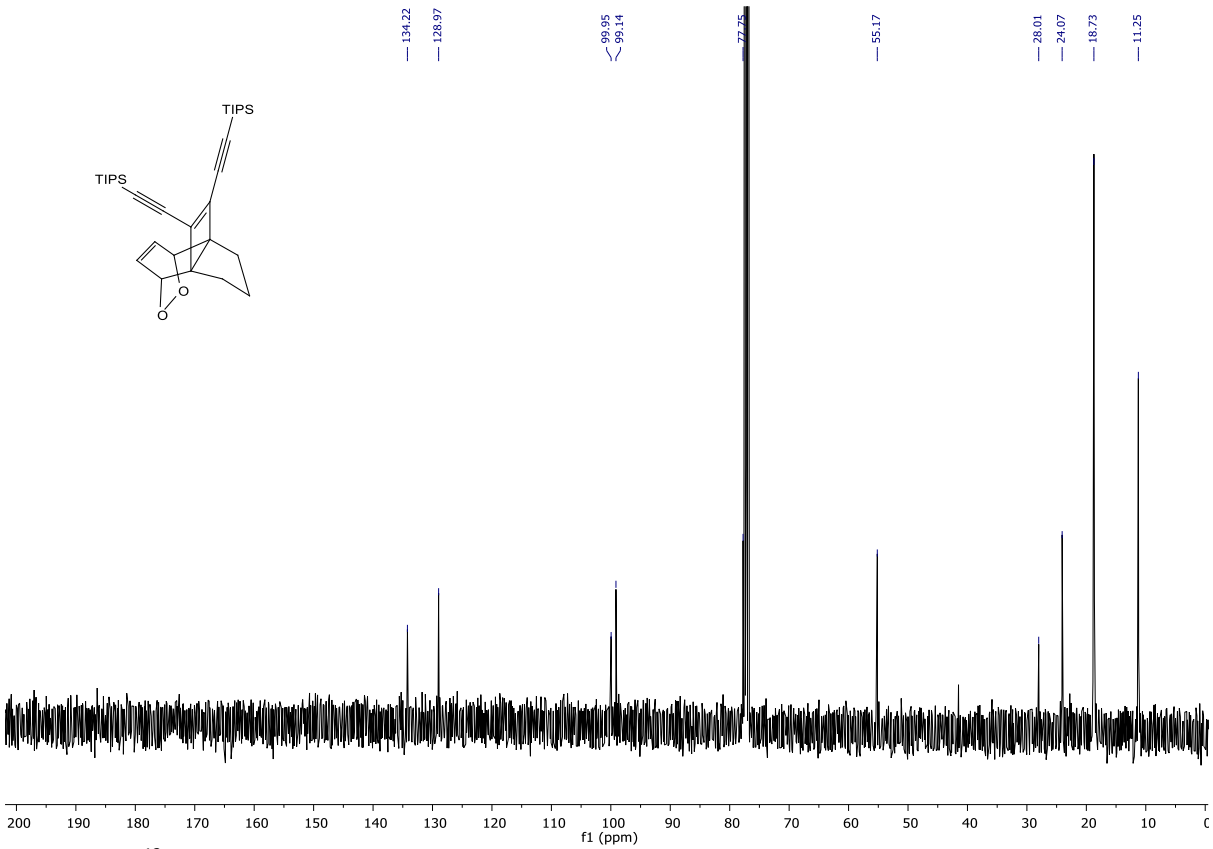


Figure S30. ^{13}C NMR (100 MHz, $CDCl_3$) of **9**.

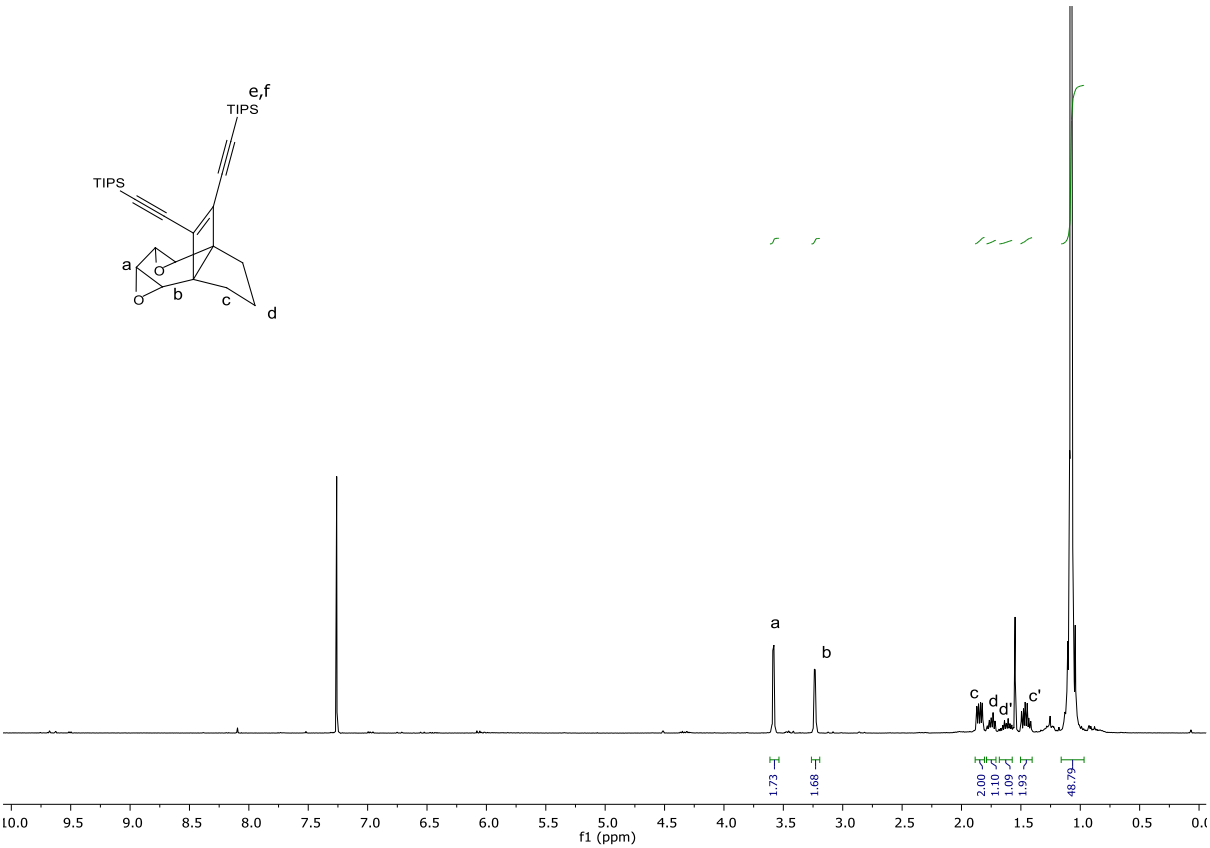


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of **10**.

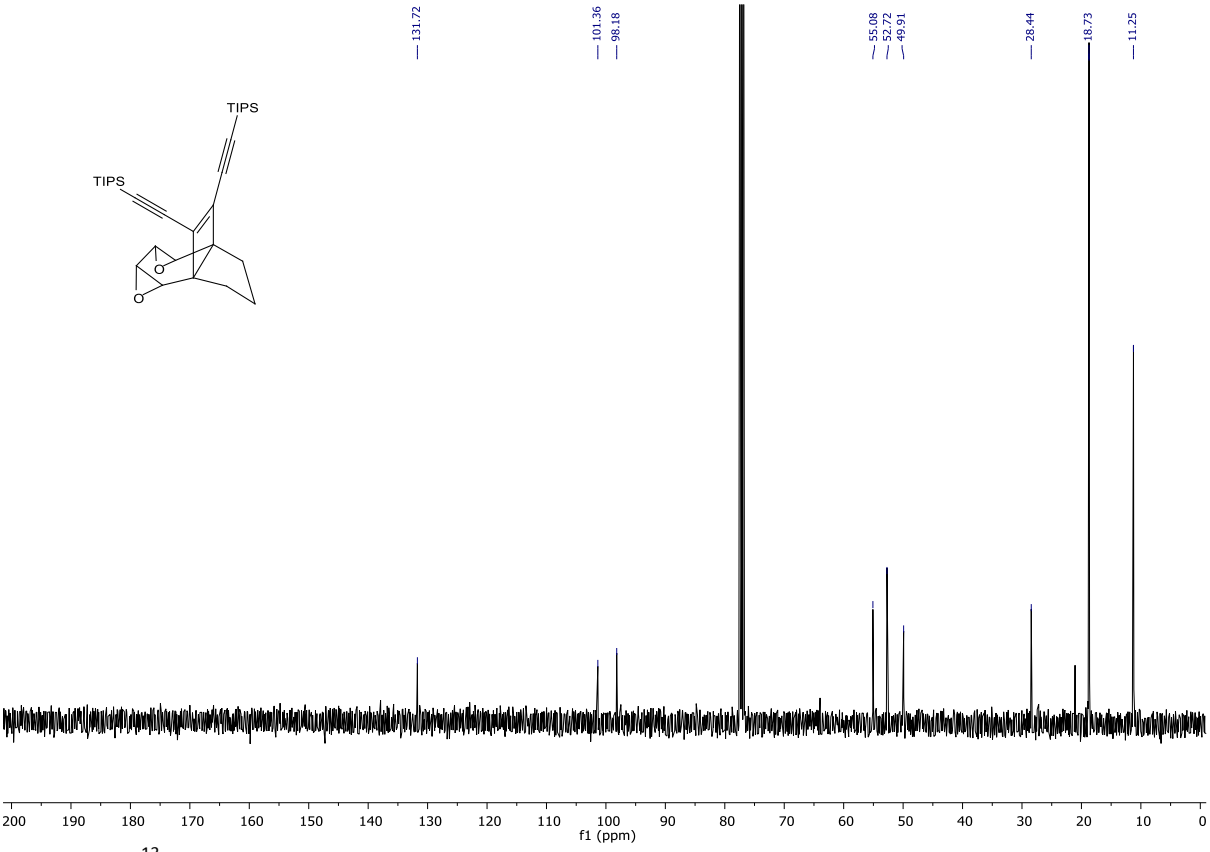


Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) of **10**.

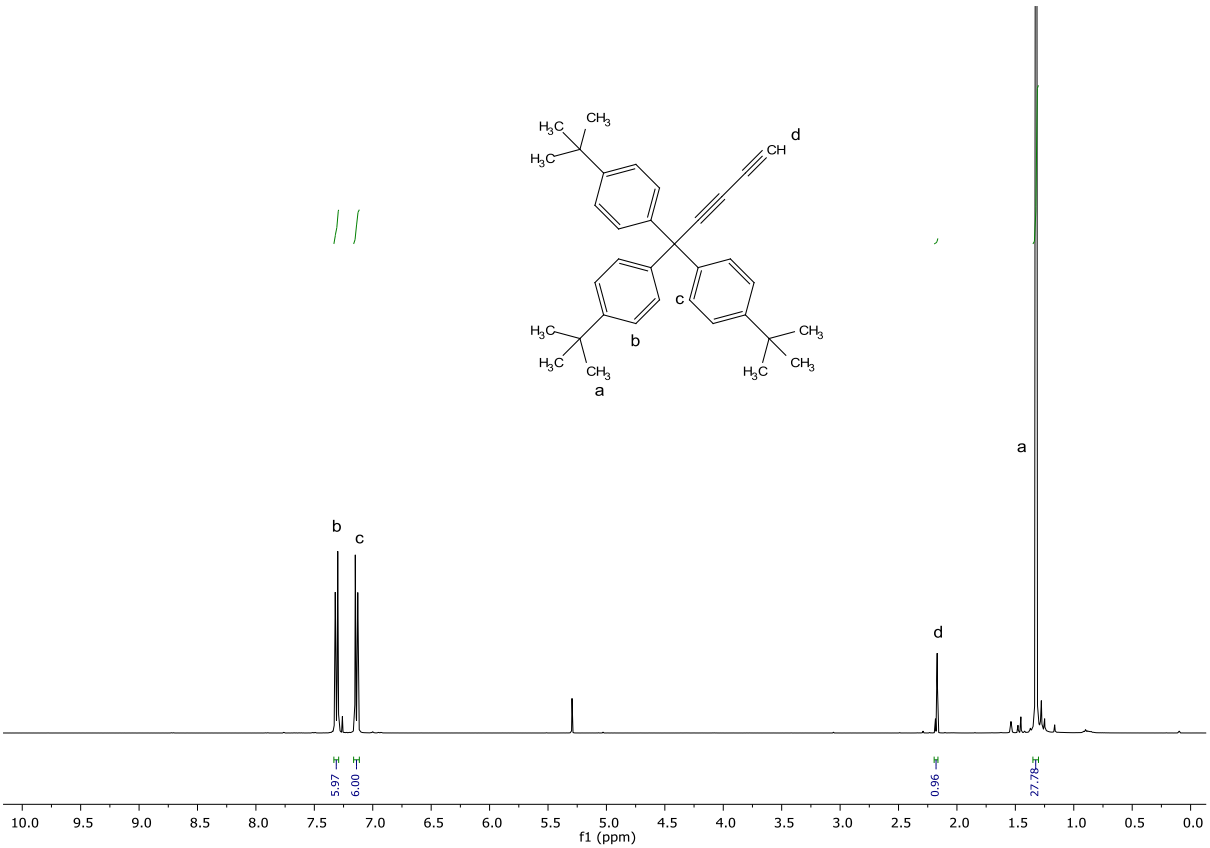


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) of **12**.

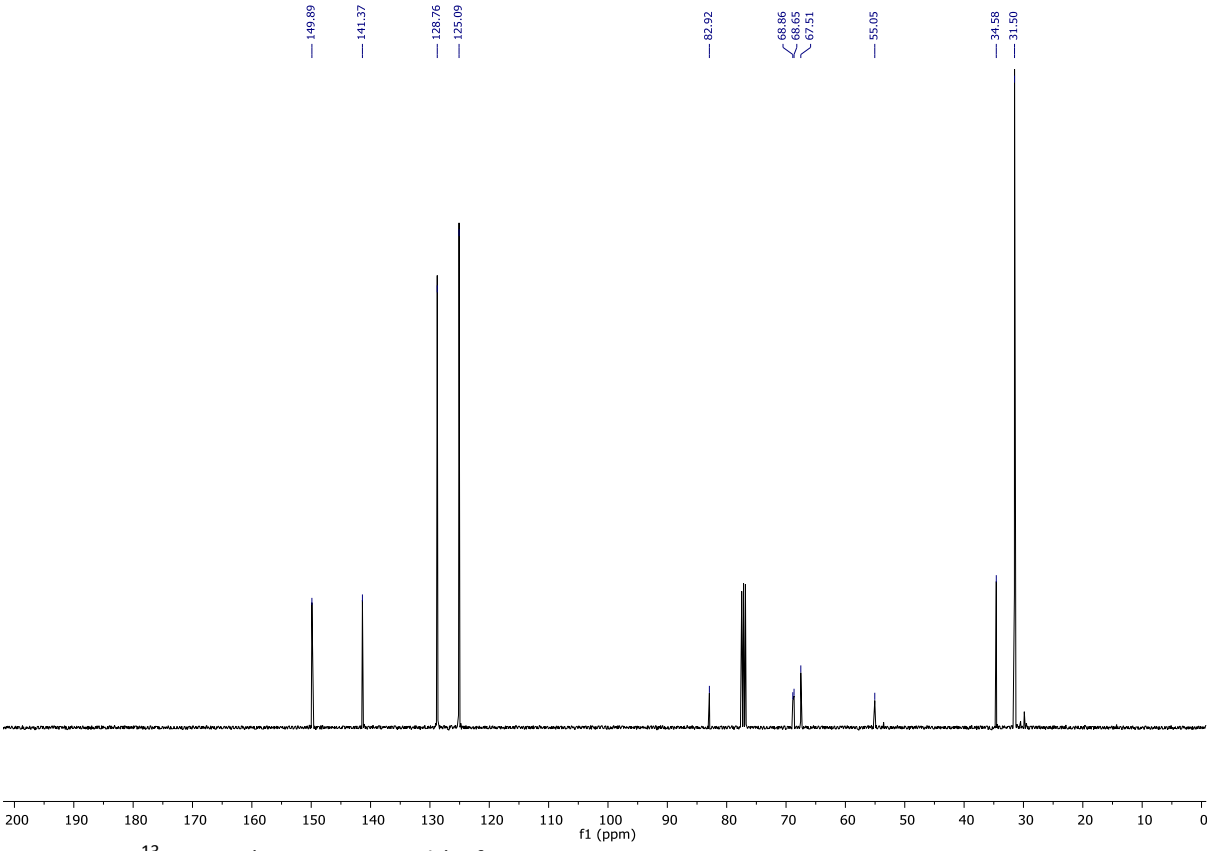


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) of **12**.

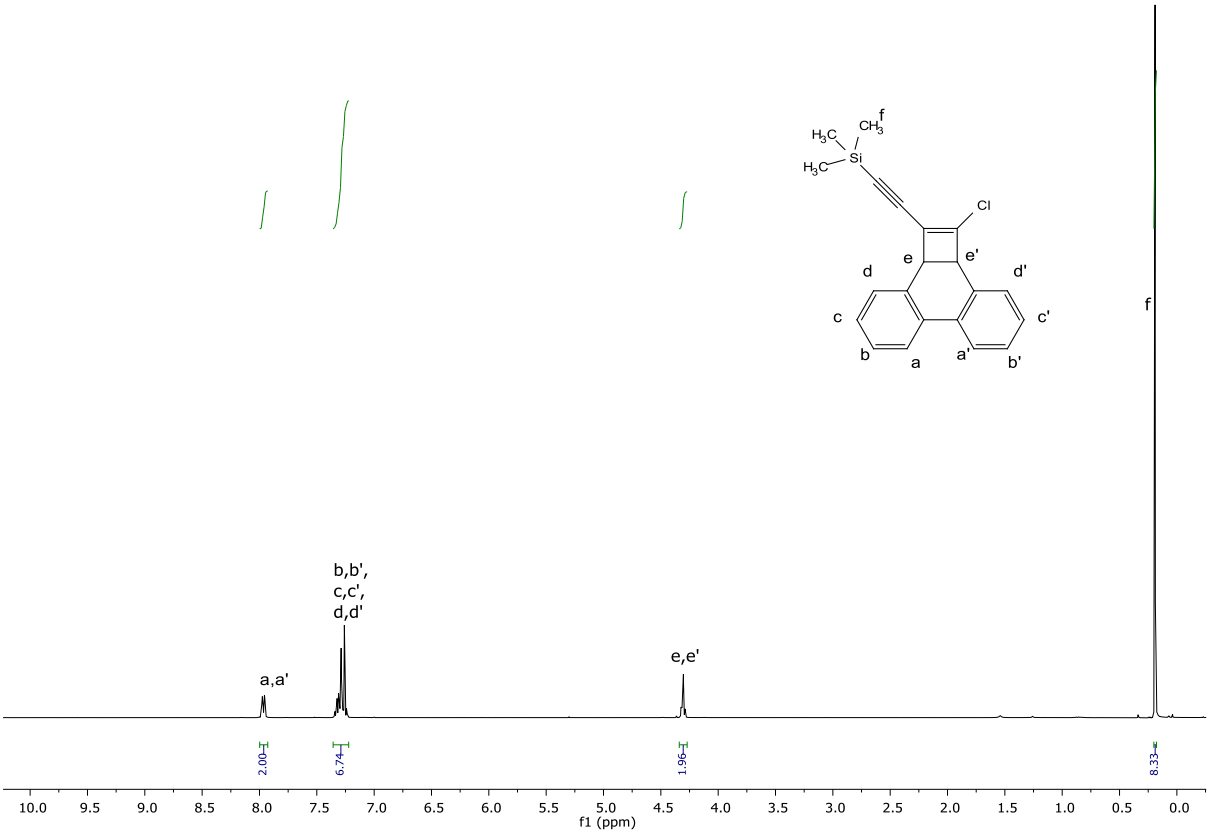


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of **13**.

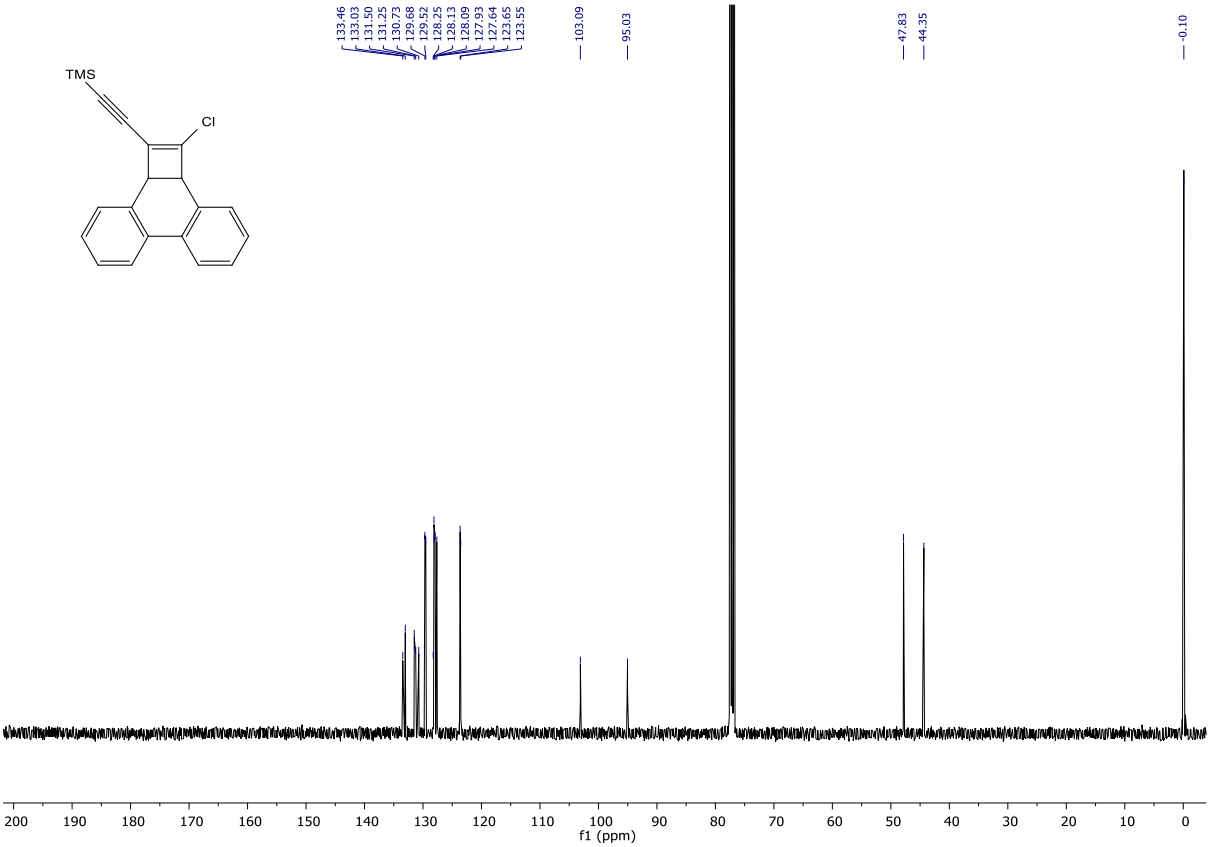


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) of **13**.

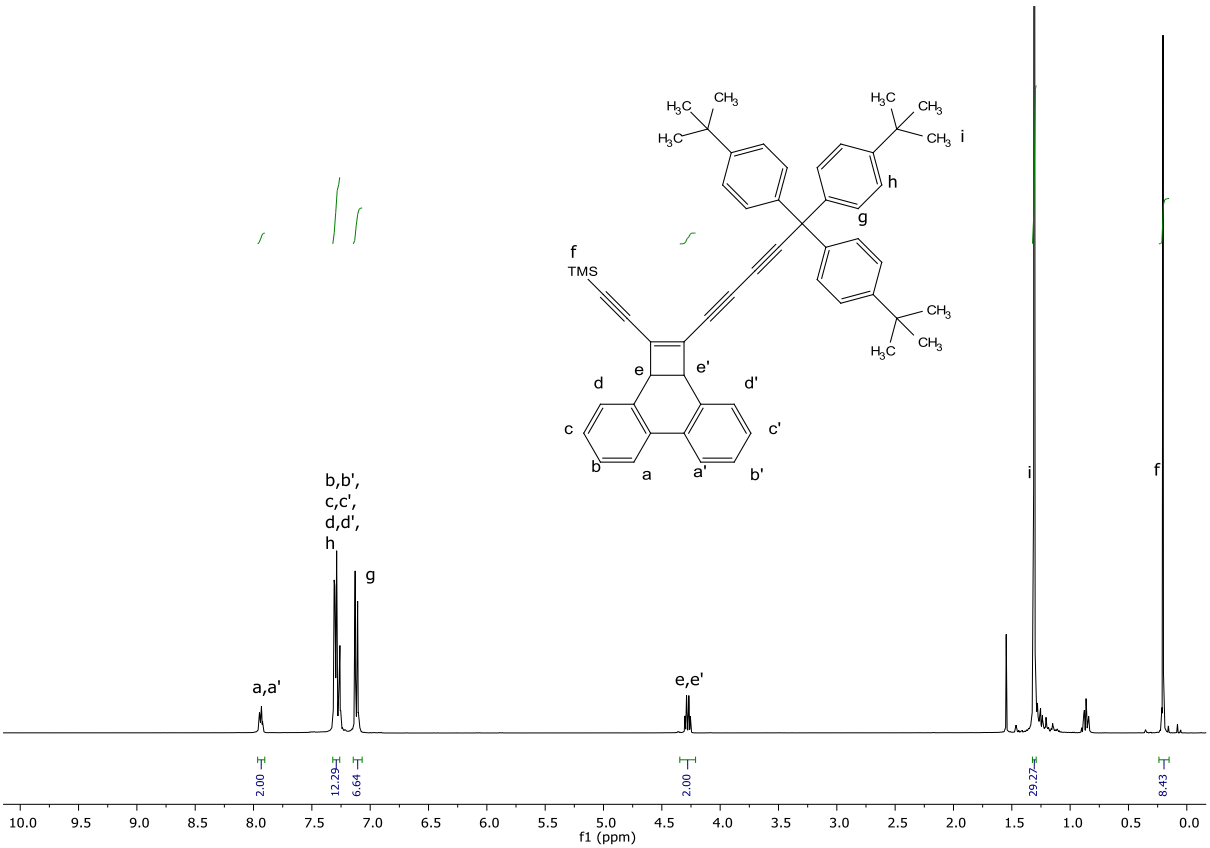


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) of **14**.

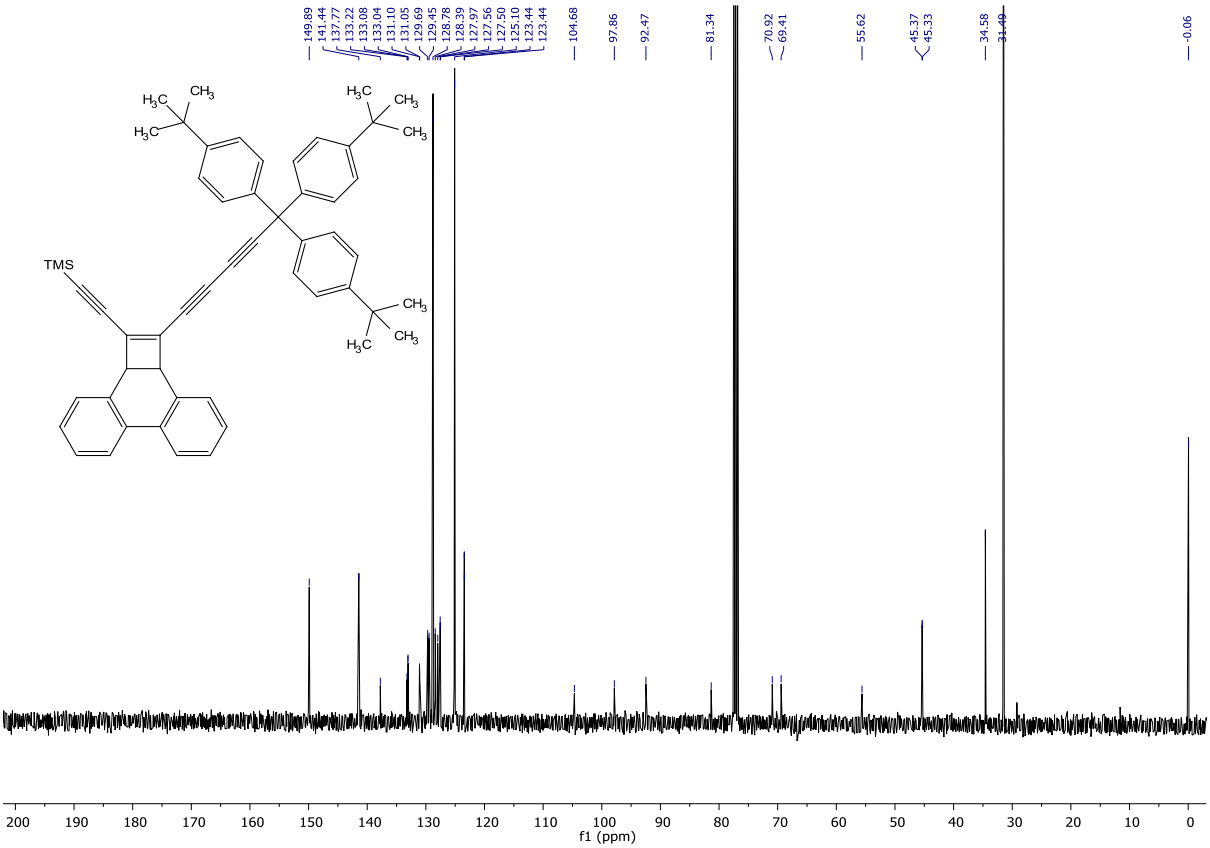


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) of **14**.

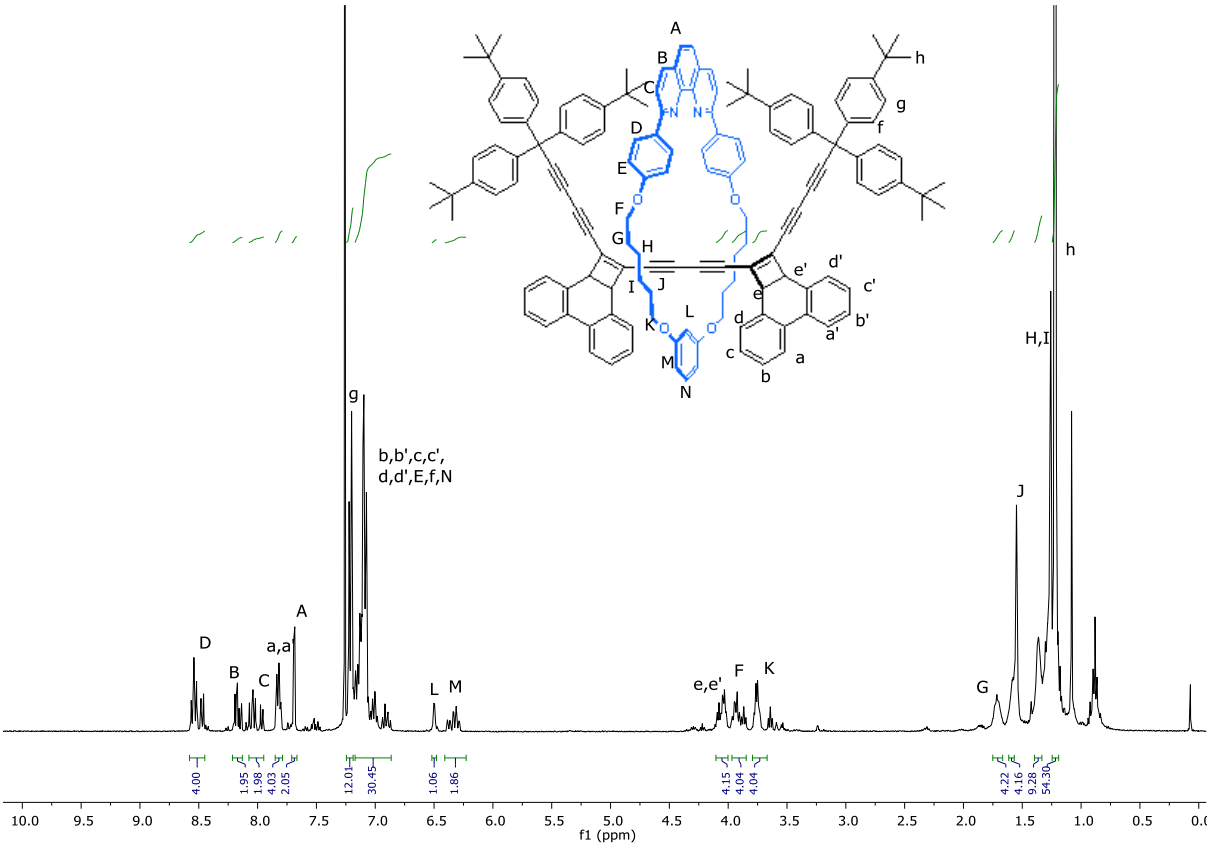


Figure S39. ^{1}H NMR (600 MHz, $CDCl_3$) of **16**.

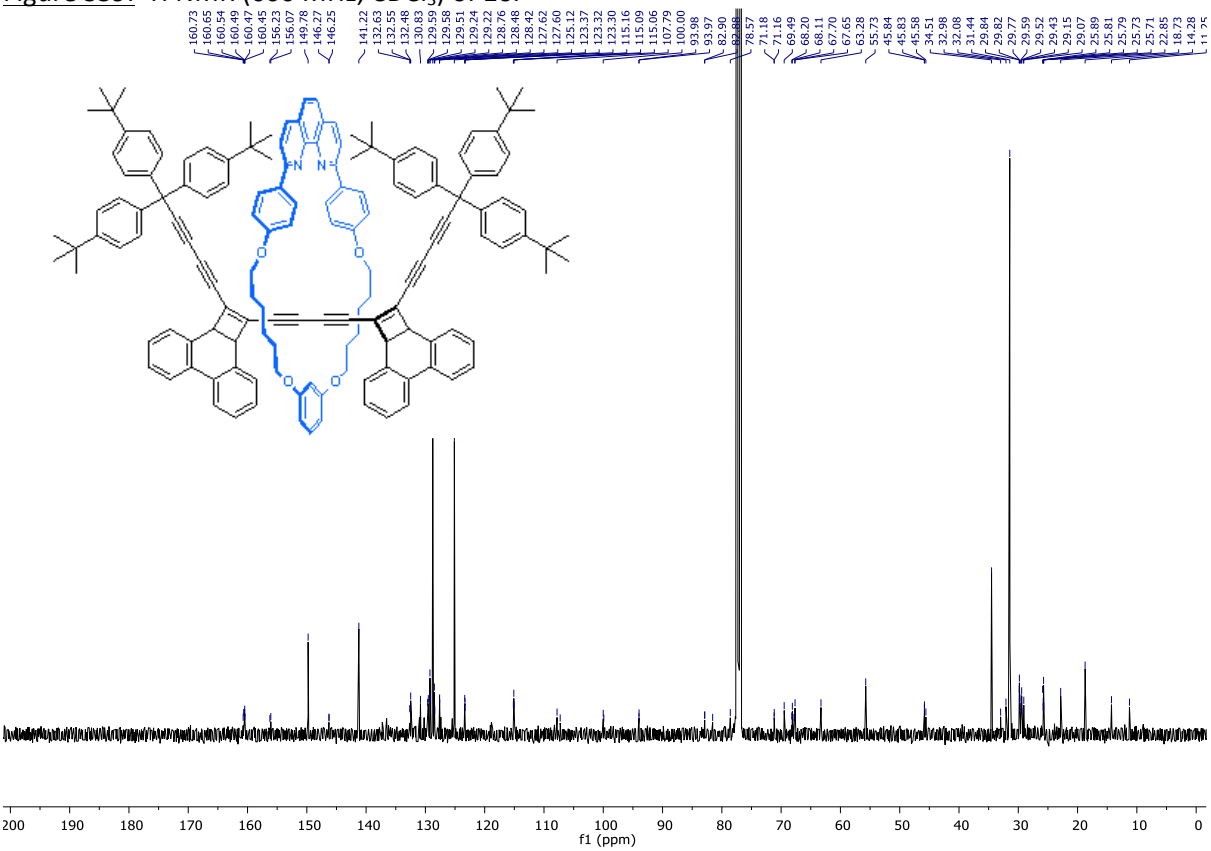


Figure S40. ^{13}C NMR (125 MHz, $CDCl_3$) of **16**.

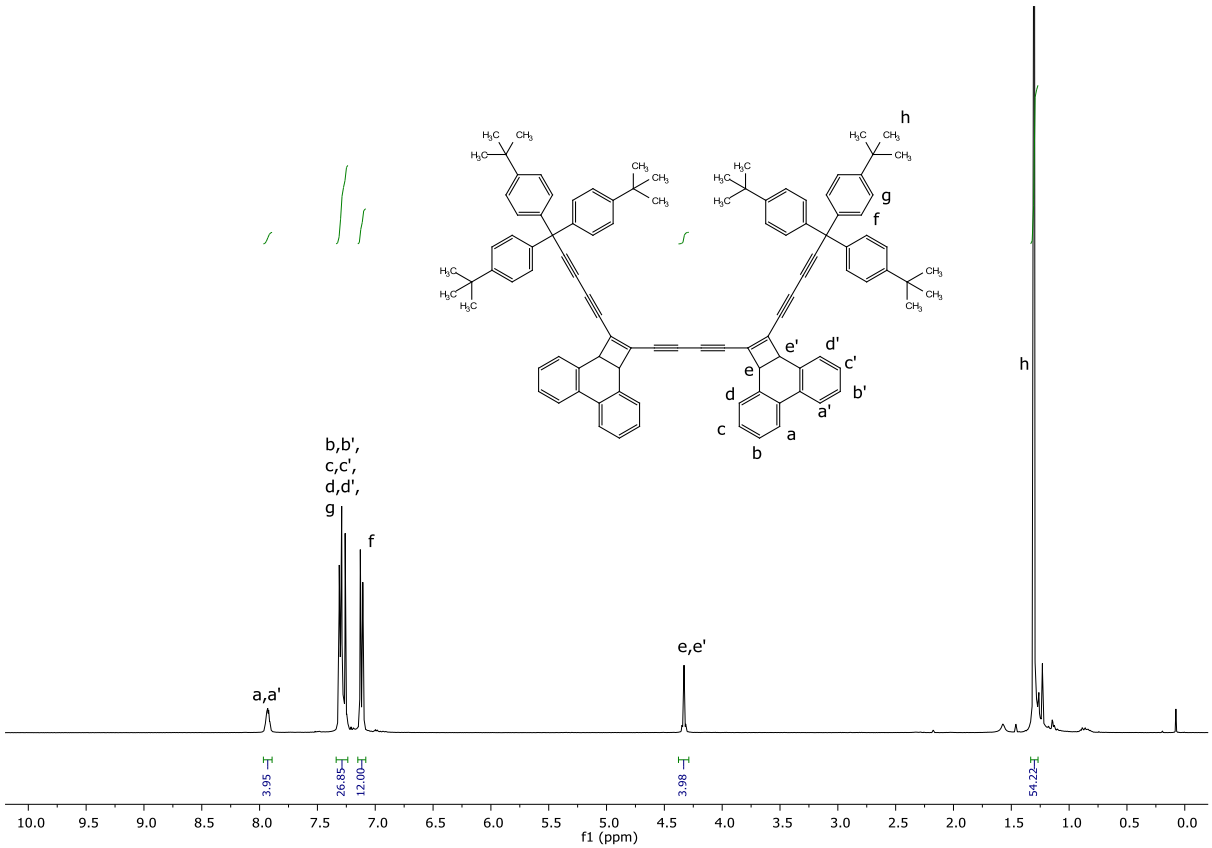


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) of **17**.

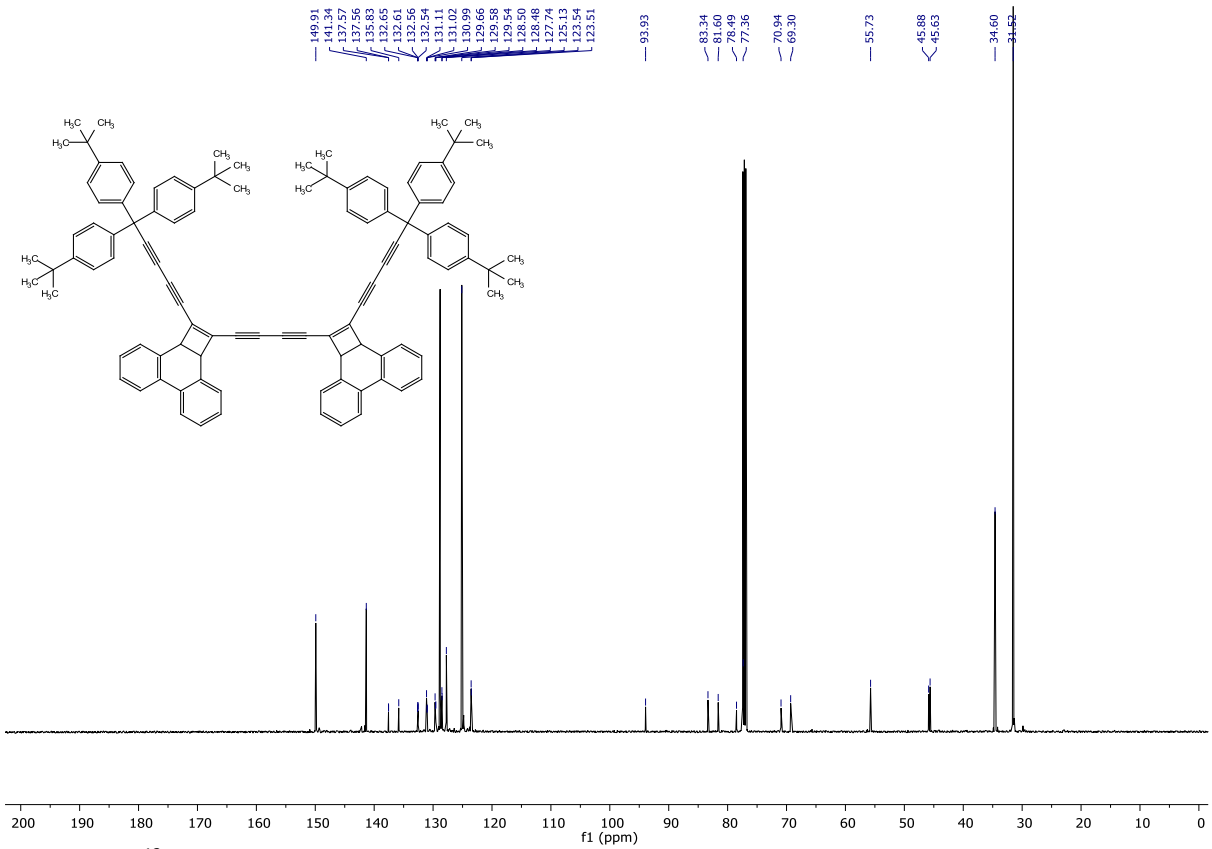


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) of **17**.

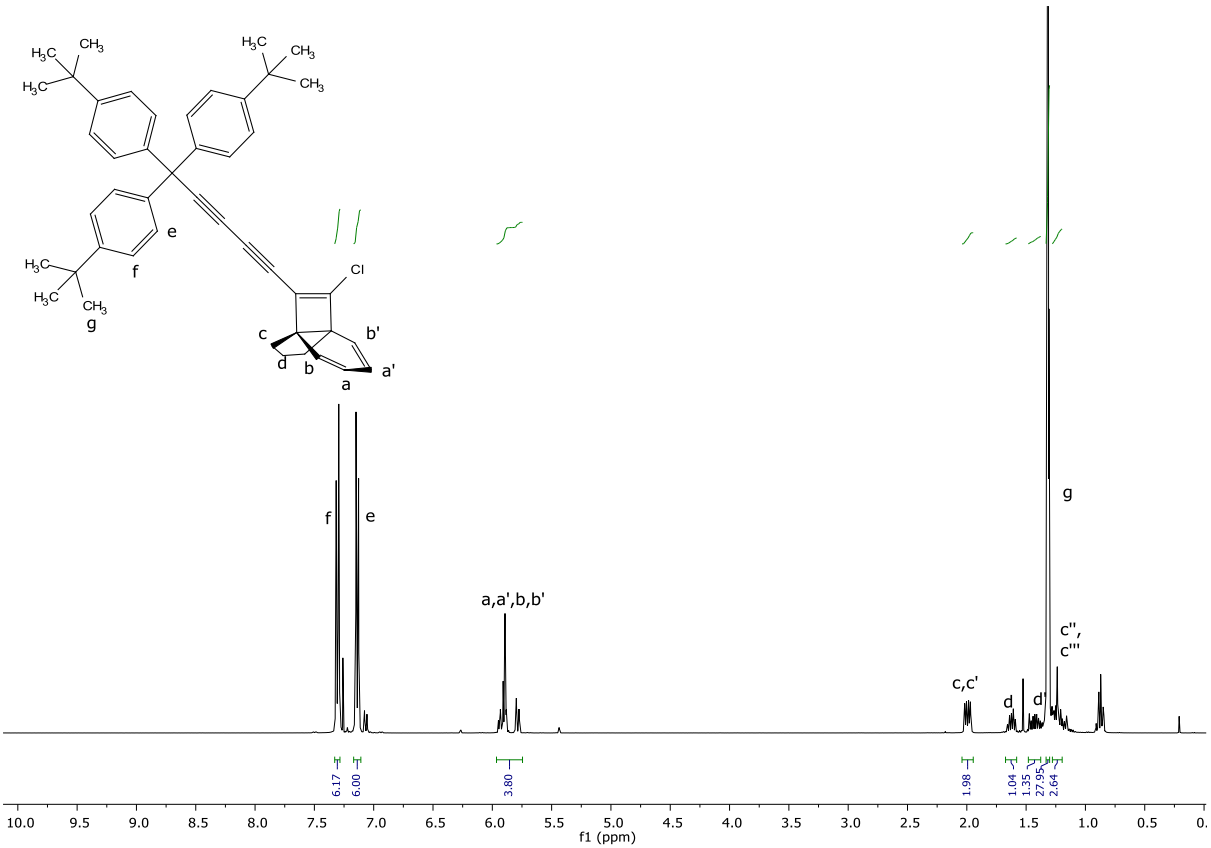


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of **25**.

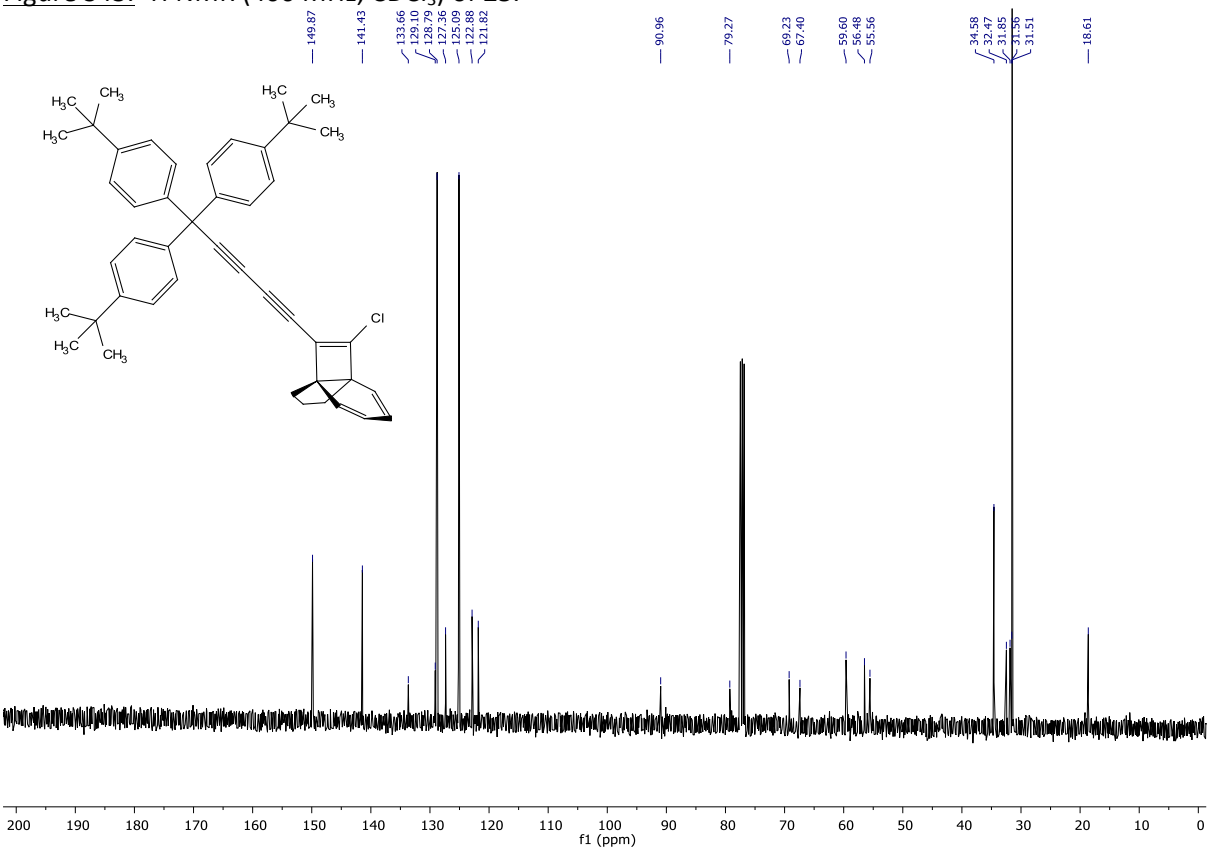


Figure S44. ^{13}C NMR (100 MHz, $CDCl_3$) of **25**.

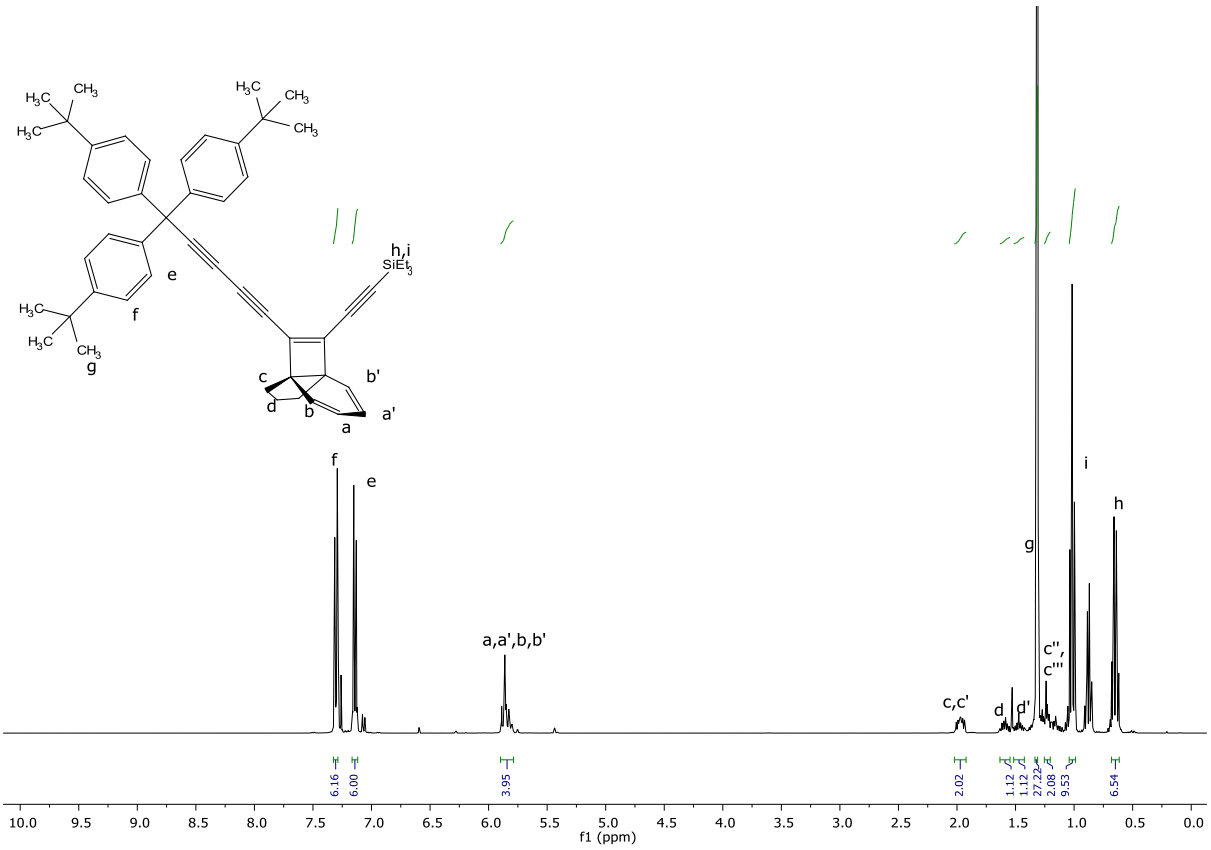


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) of **24**.

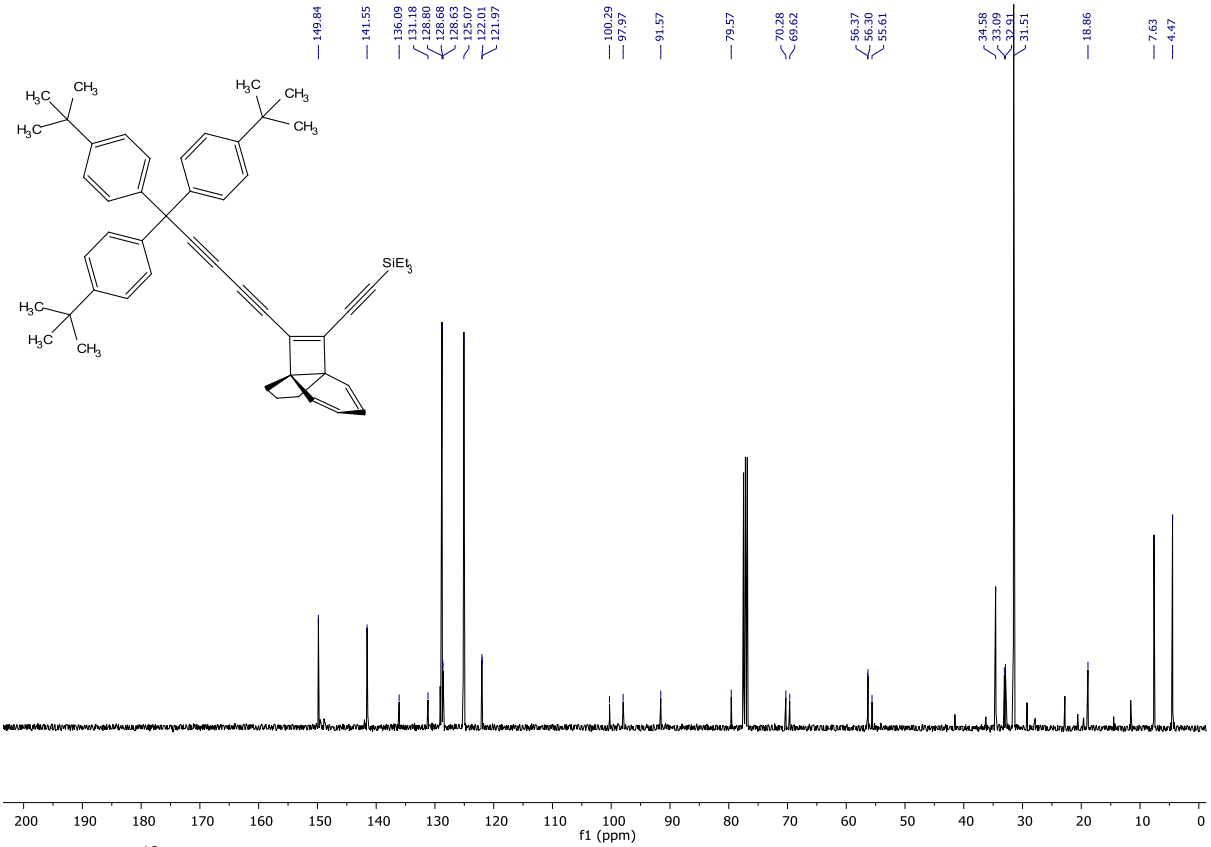


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) of **24**.

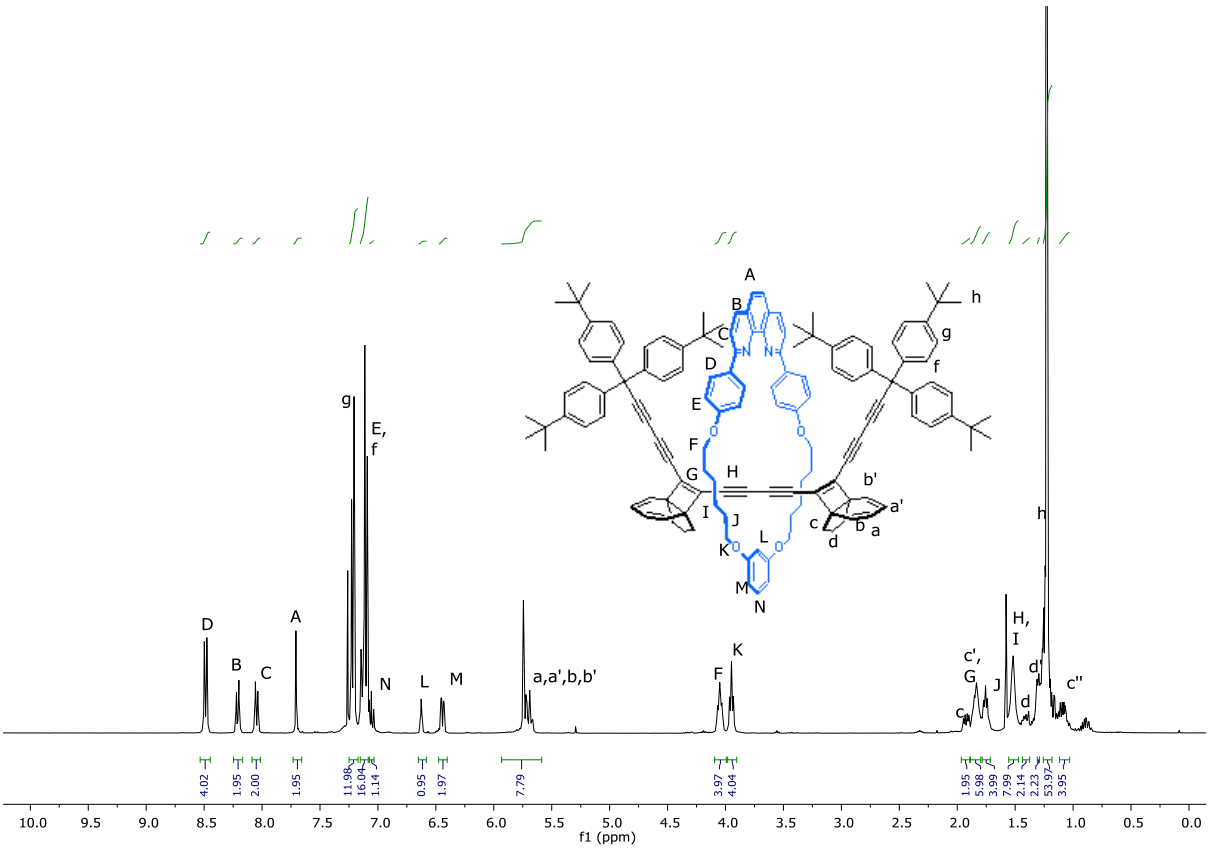


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of **27**.

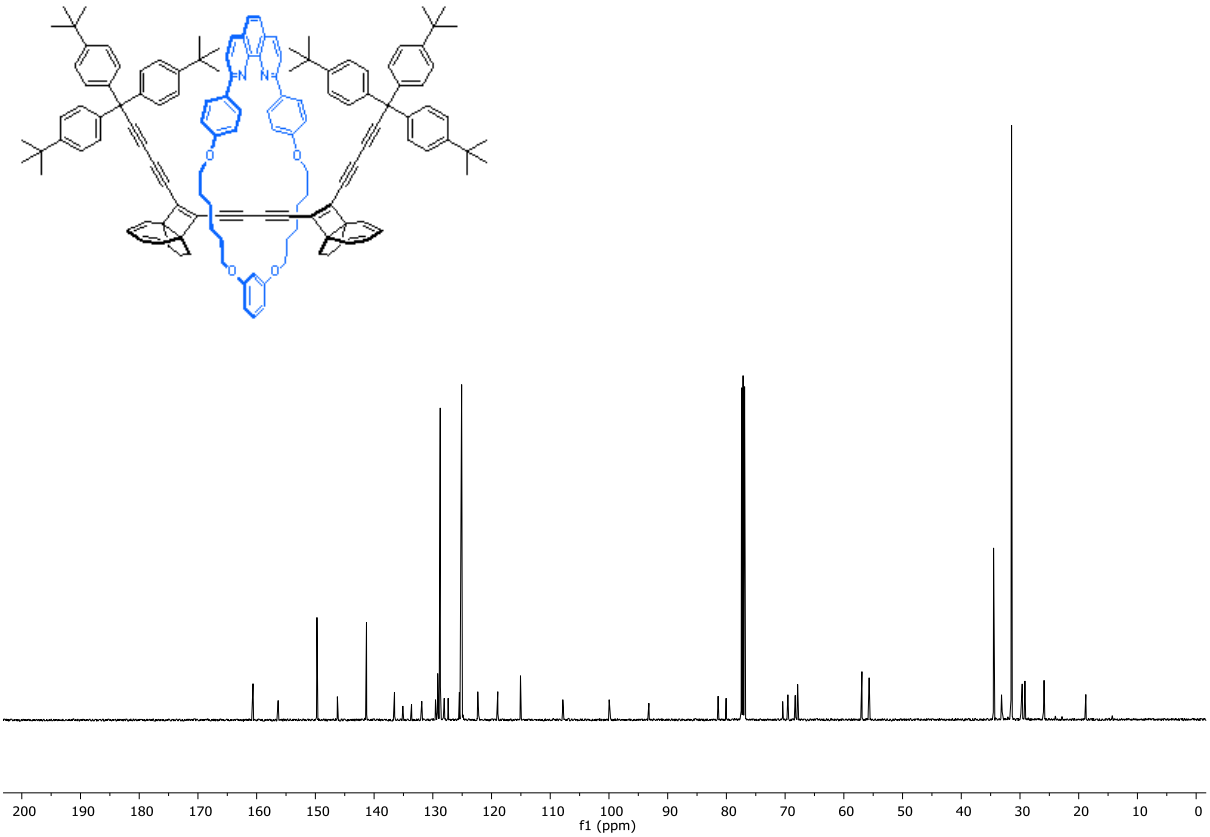


Figure S48. ^{13}C NMR (125 MHz, $CDCl_3$) of **27**.

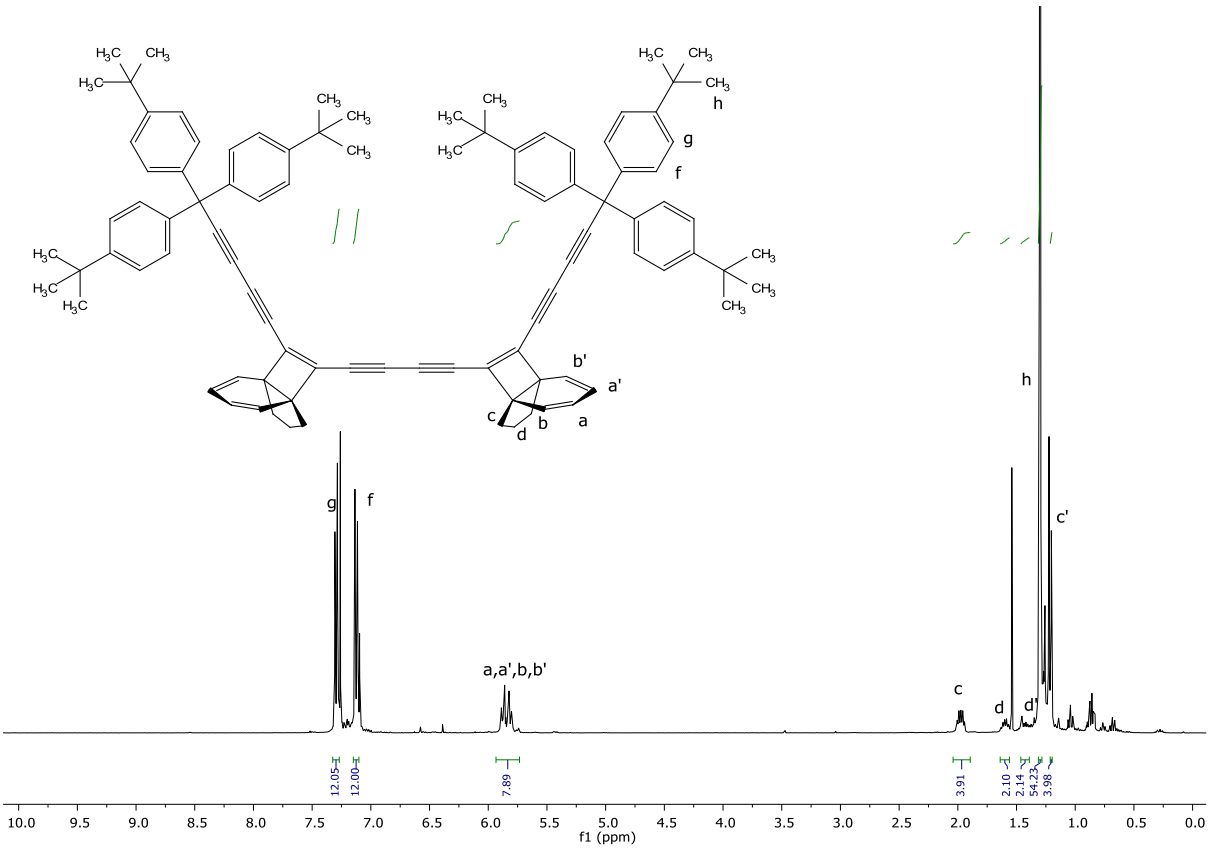


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) of **29**.

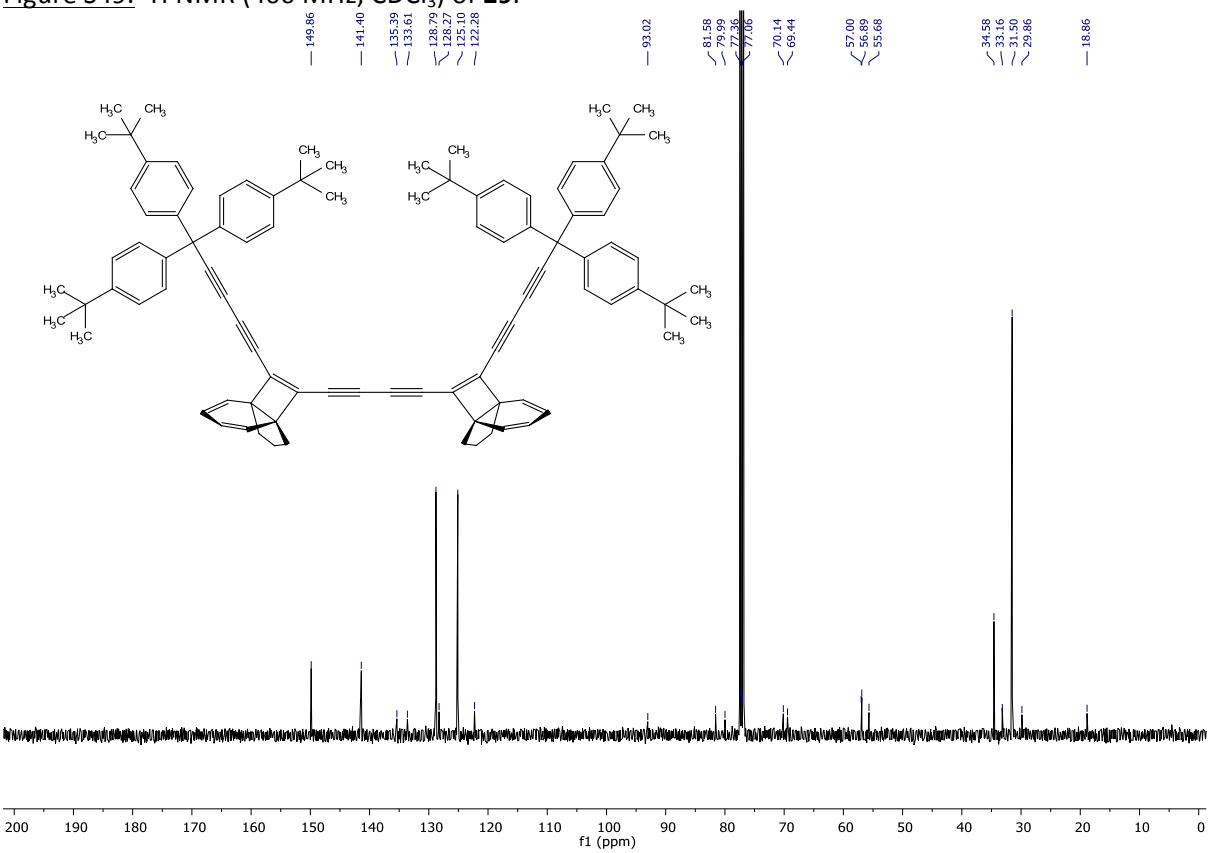


Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) of **29**.

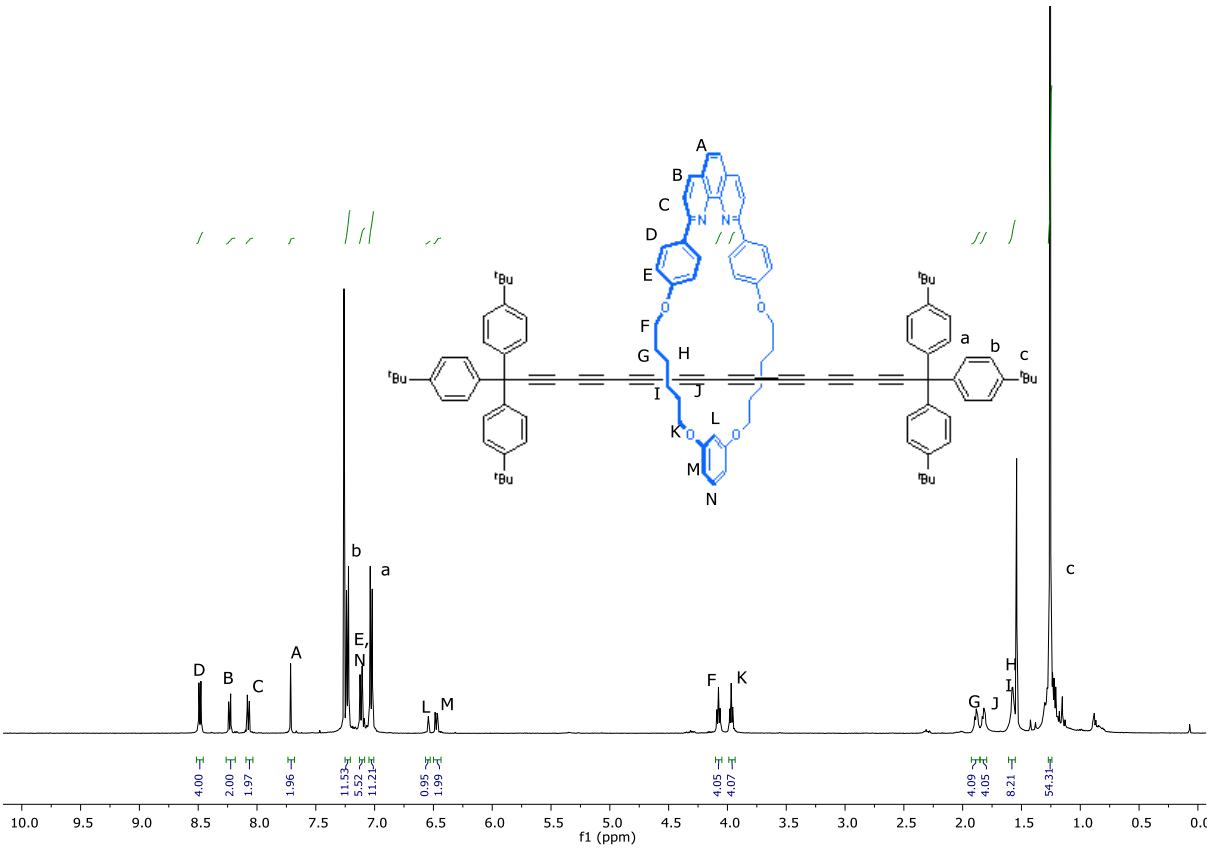


Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$) of **28**.

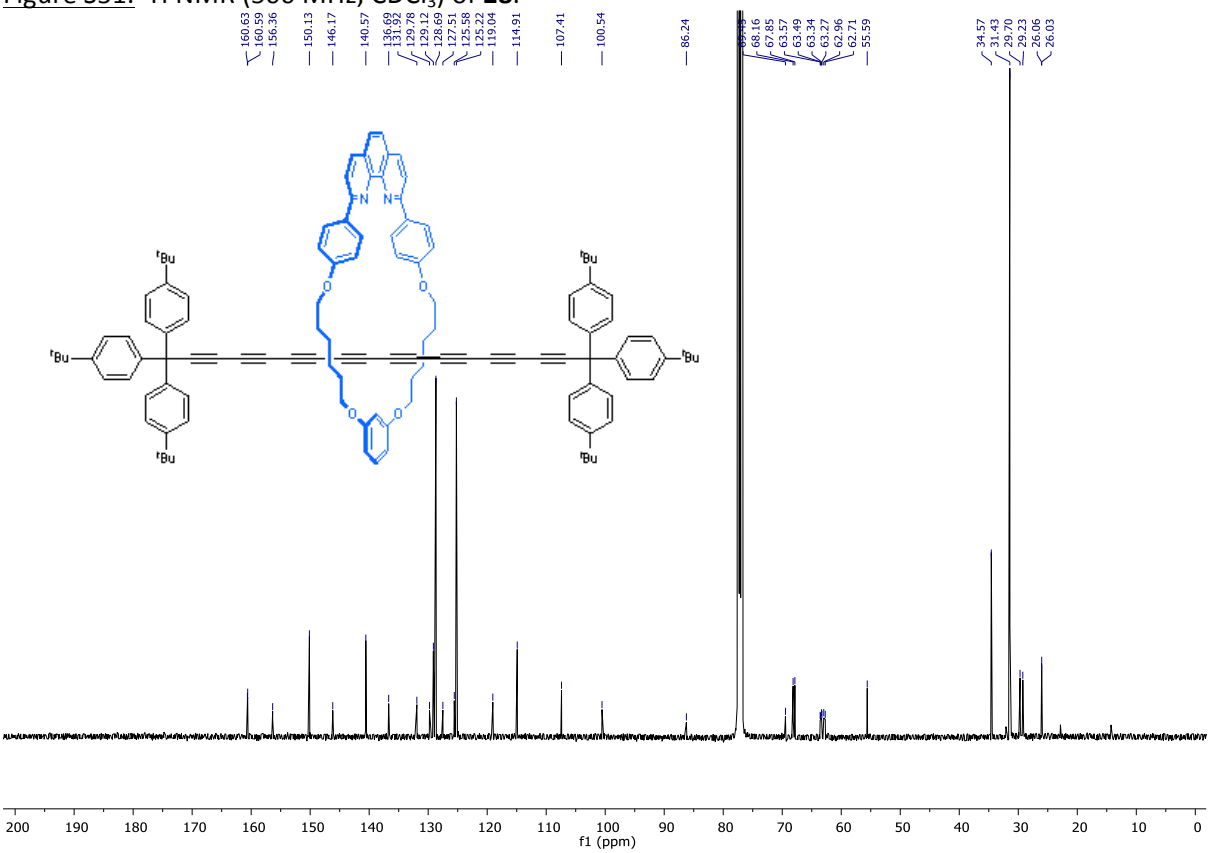


Figure S52. ^{13}C NMR (125 MHz, $CDCl_3$) of **28**.

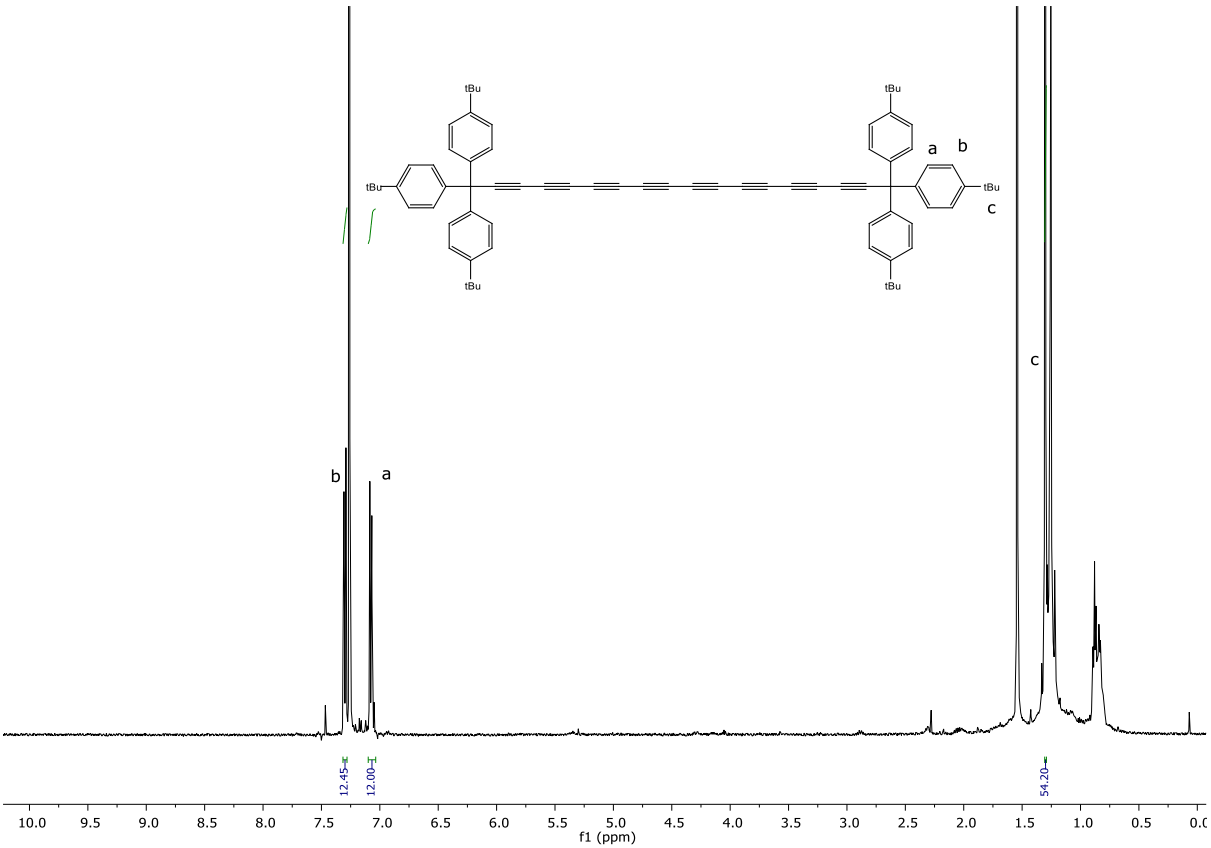


Figure S53. ^{1}H NMR (500 MHz, $CDCl_3$) of **30**.

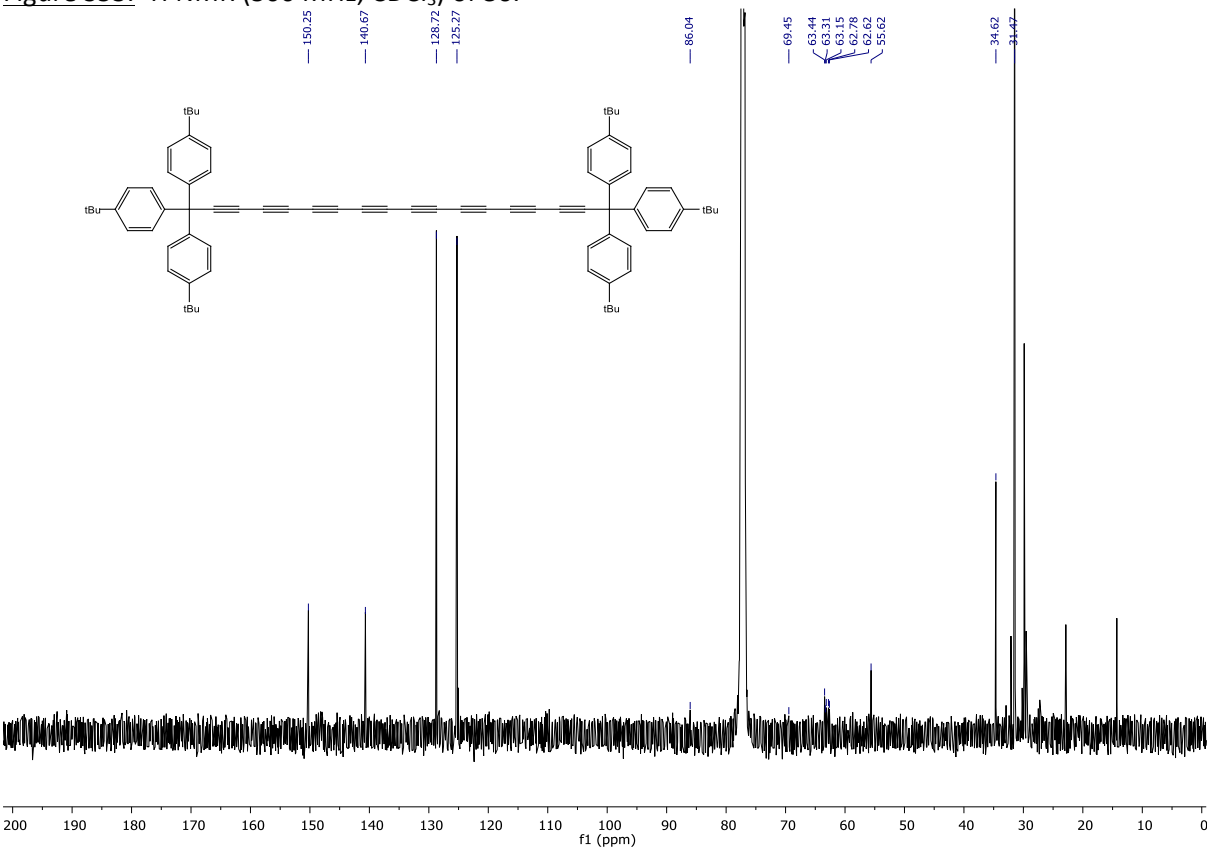


Figure S54. ^{13}C NMR (125 MHz, $CDCl_3$) of **30**.

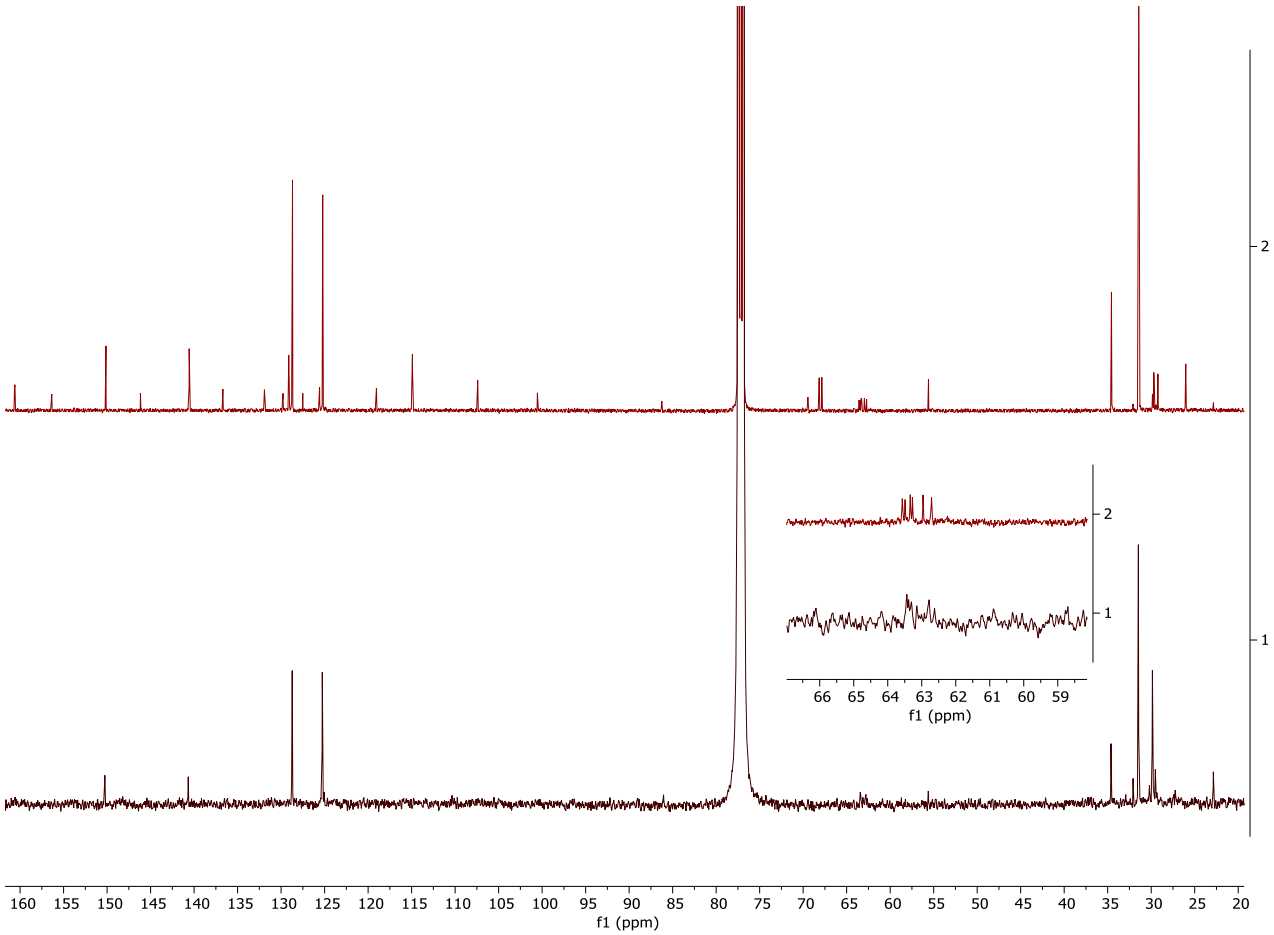


Figure S55. ^{13}C NMR (125 MHz, $CDCl_3$) of **28** (red) and **30** (black) in comparison. Carbon shifts of the axle are not affected by threading through the cavity of the macrocycle.

S5.2 2D $^{1}H/^{13}C$ NMR data and NOE data

Spectra of **2**:

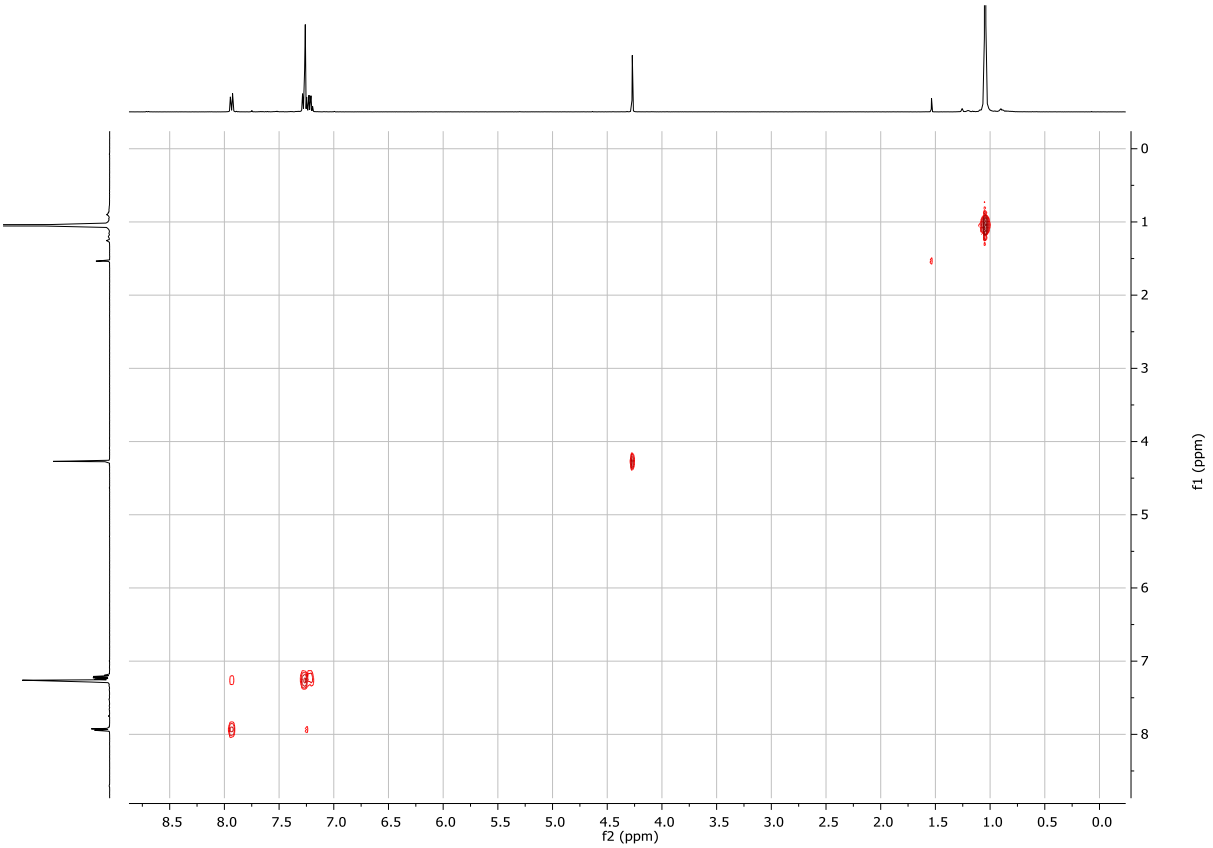


Figure S56. COSY (400 MHz, $CDCl_3$) of **2.**

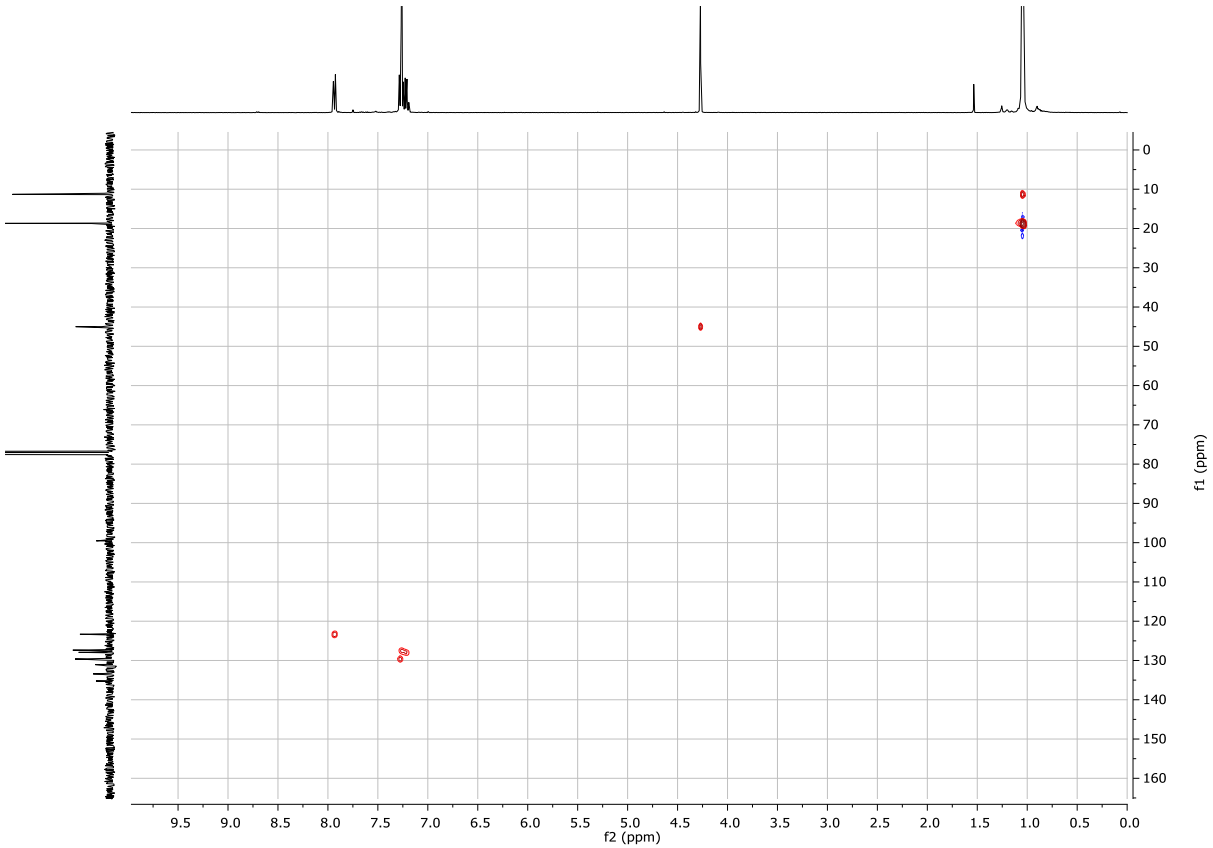


Figure S57. HSQC (400 MHz, $CDCl_3$) of **2.**

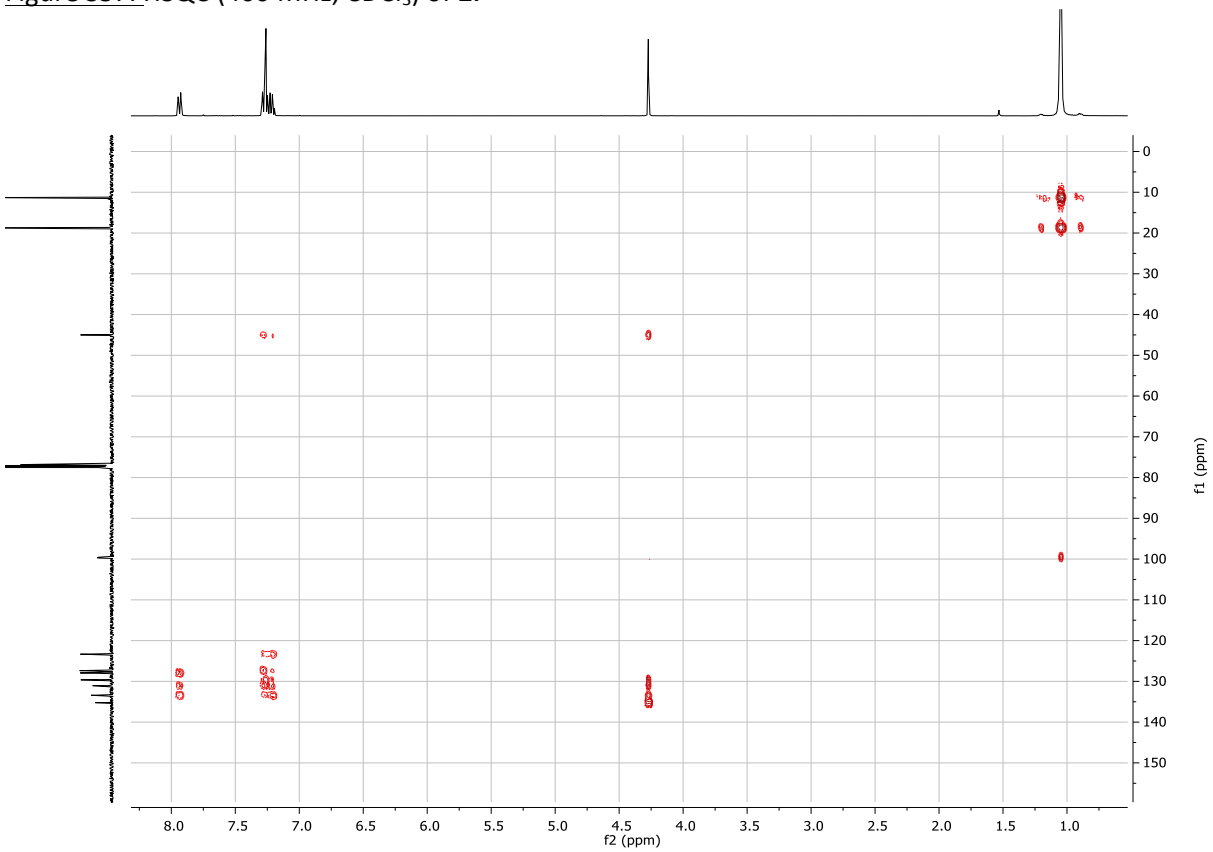


Figure S58. HMBC (400 MHz, $CDCl_3$) of **2.**

Spectra of **7**:

Figure S59. COSY (400 MHz, $CDCl_3$) of **7.**

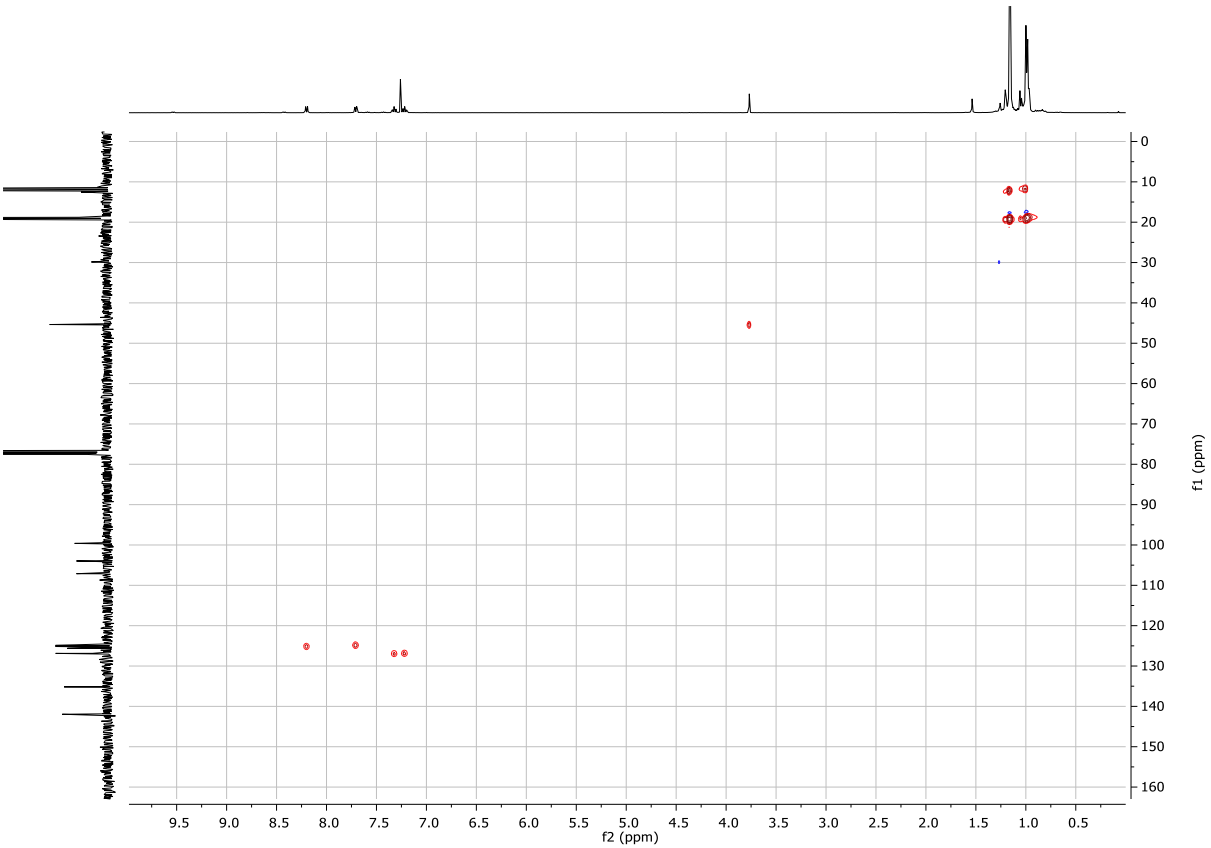


Figure S60. HSQC (400 MHz, $CDCl_3$) of **7.**

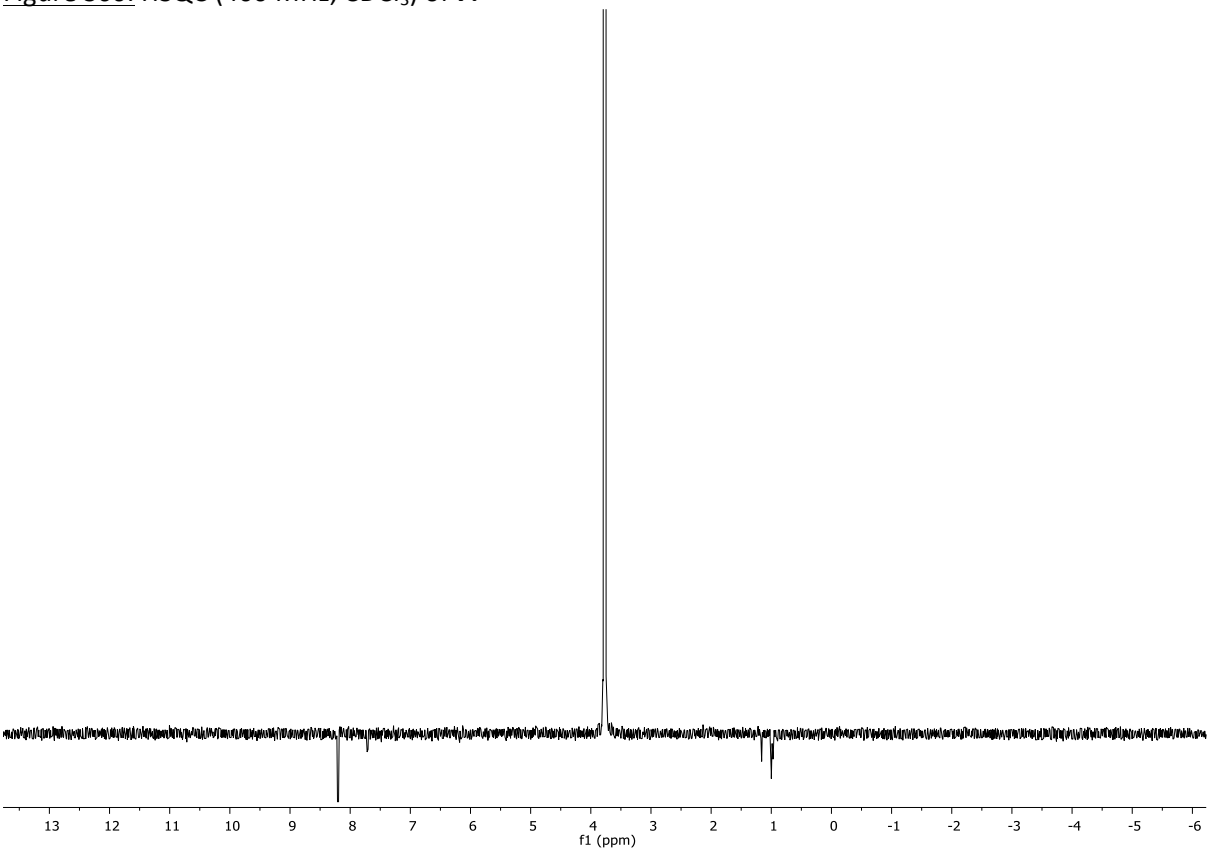


Figure S61. 1D-NOE (400 MHz, $CDCl_3$) of the peak at 3.77 ppm.

Spectra for **8**:

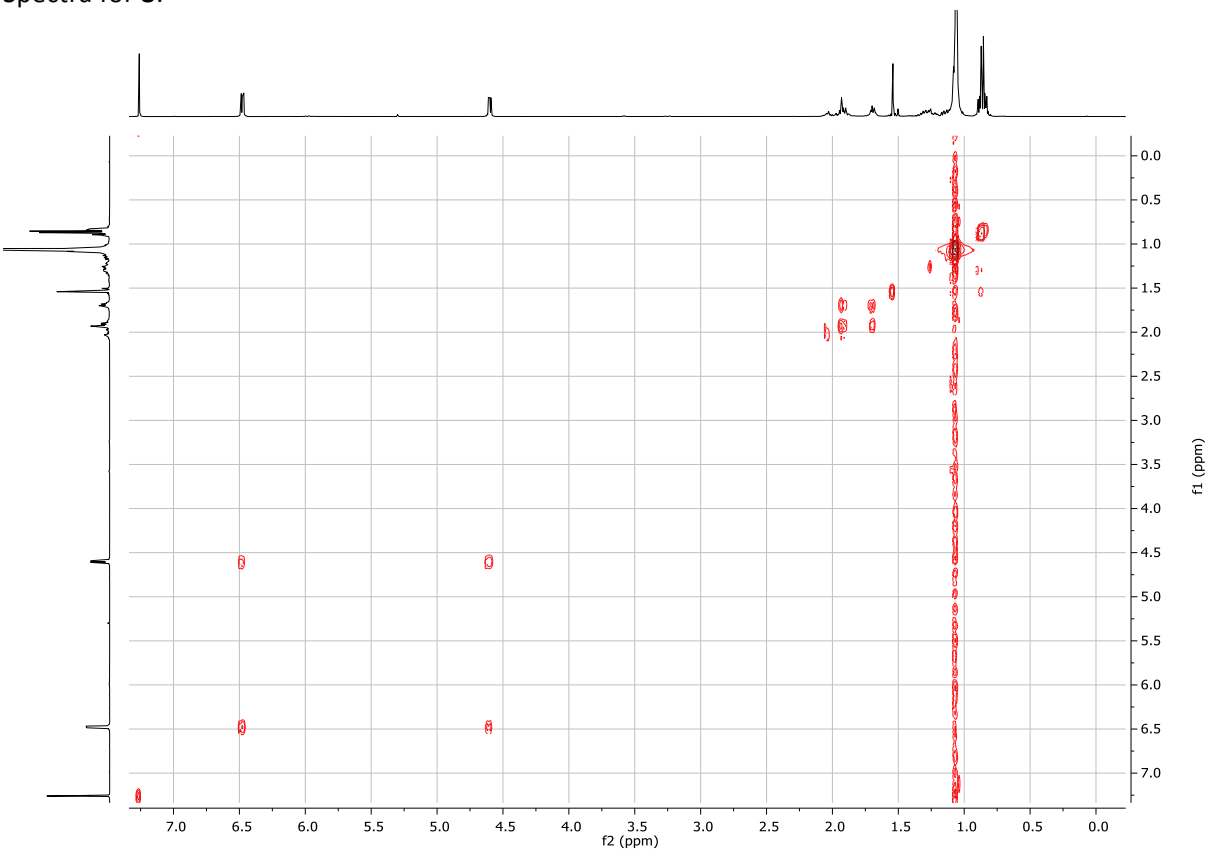


Figure S62. COSY (400 MHz, $CDCl_3$) of **8.**

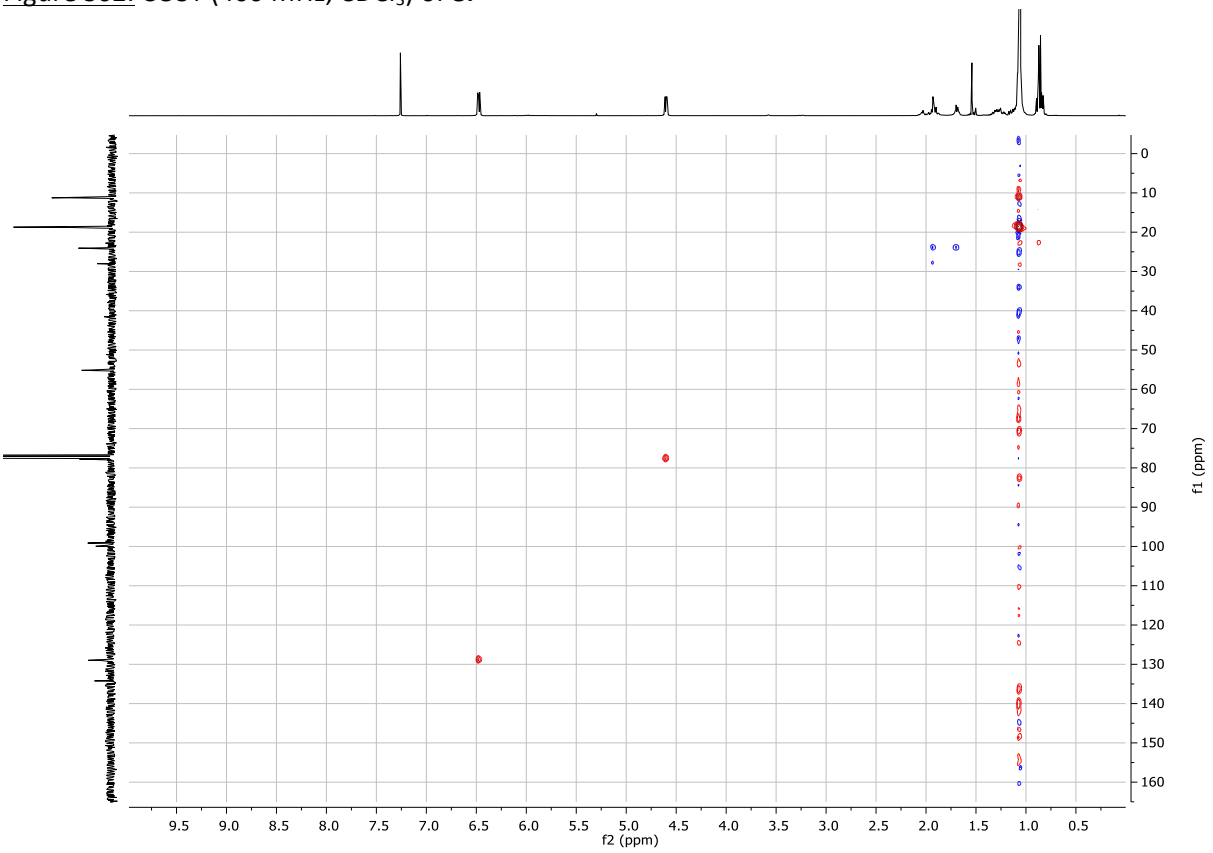


Figure S63. HSQC (400 MHz, $CDCl_3$) of **8.**

Spectra of **9**:

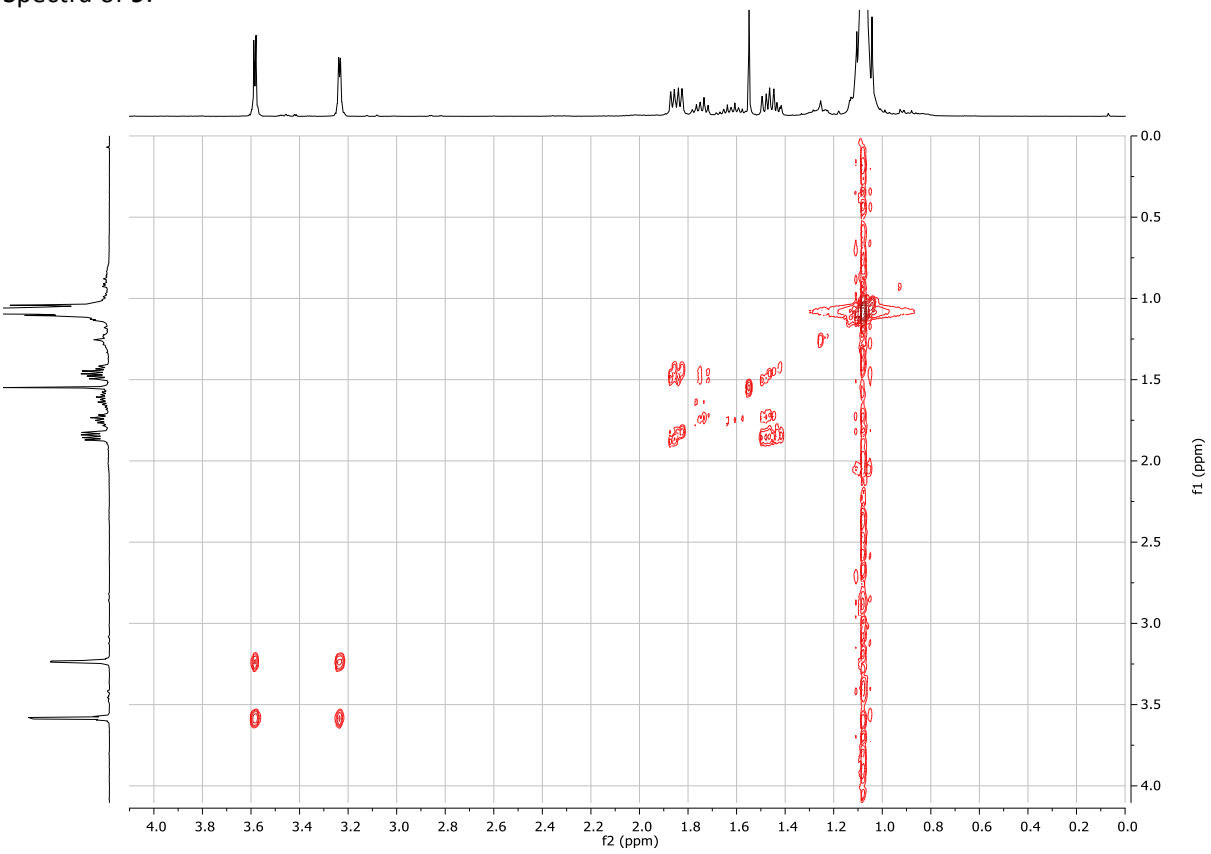


Figure S64. COSY (400 MHz, $CDCl_3$) of **9.**

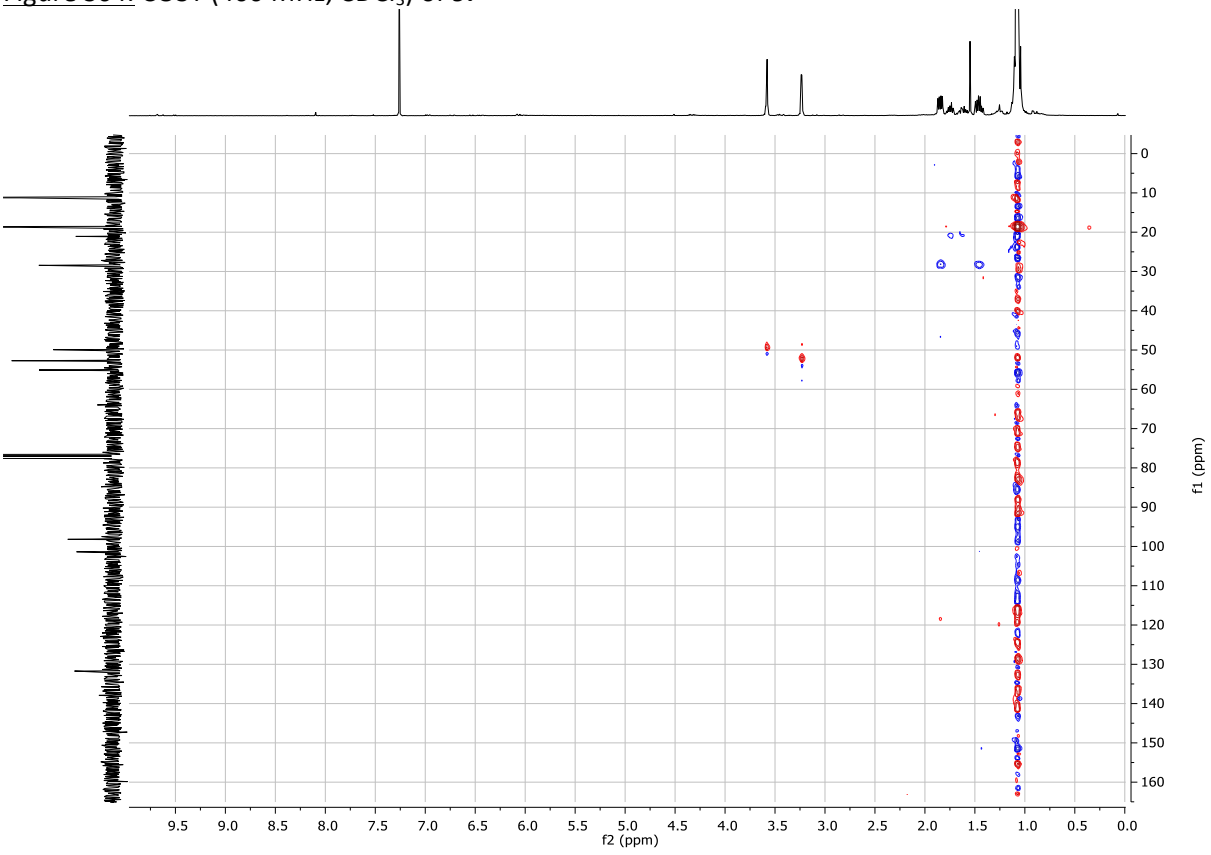


Figure S65. HSQC (400 MHz, $CDCl_3$) of **9.**

Spectra of **11**:

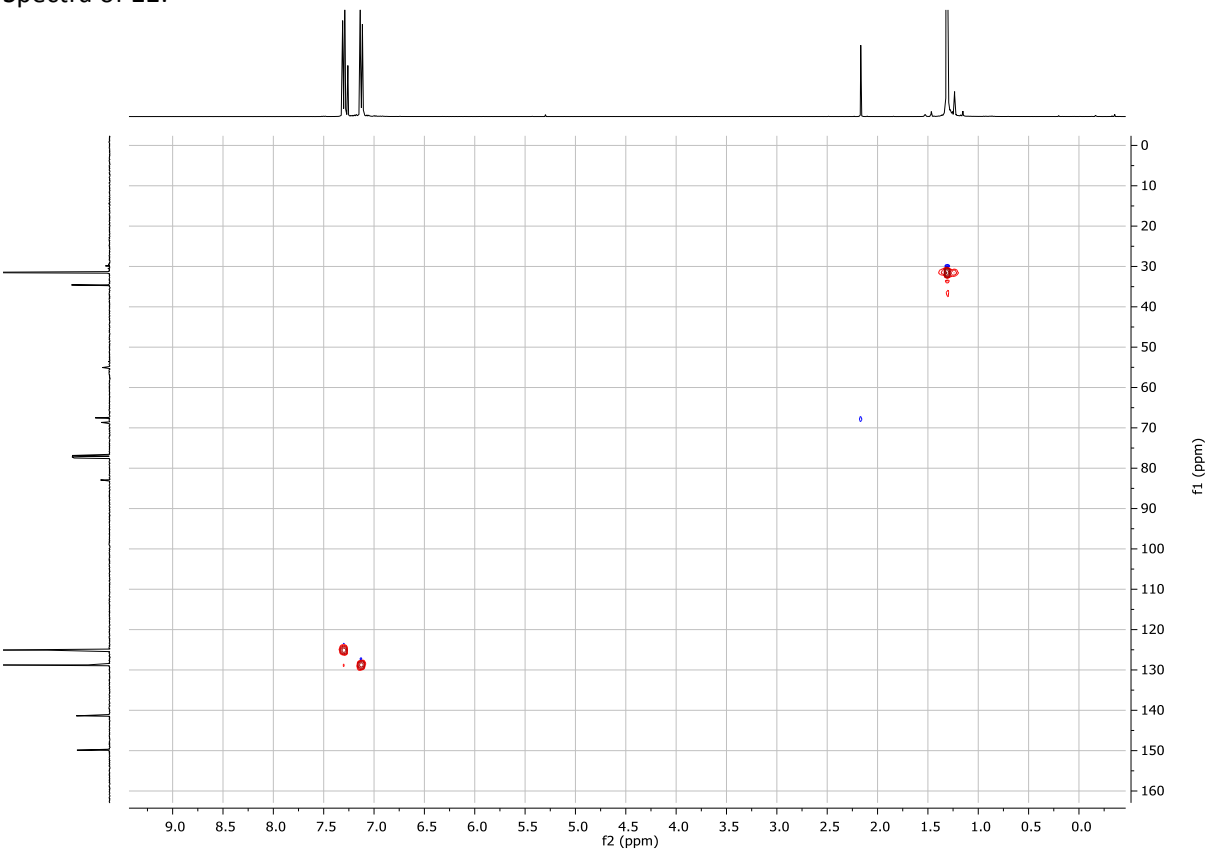


Figure S66. HSQC (400 MHz, $CDCl_3$) of **11.**

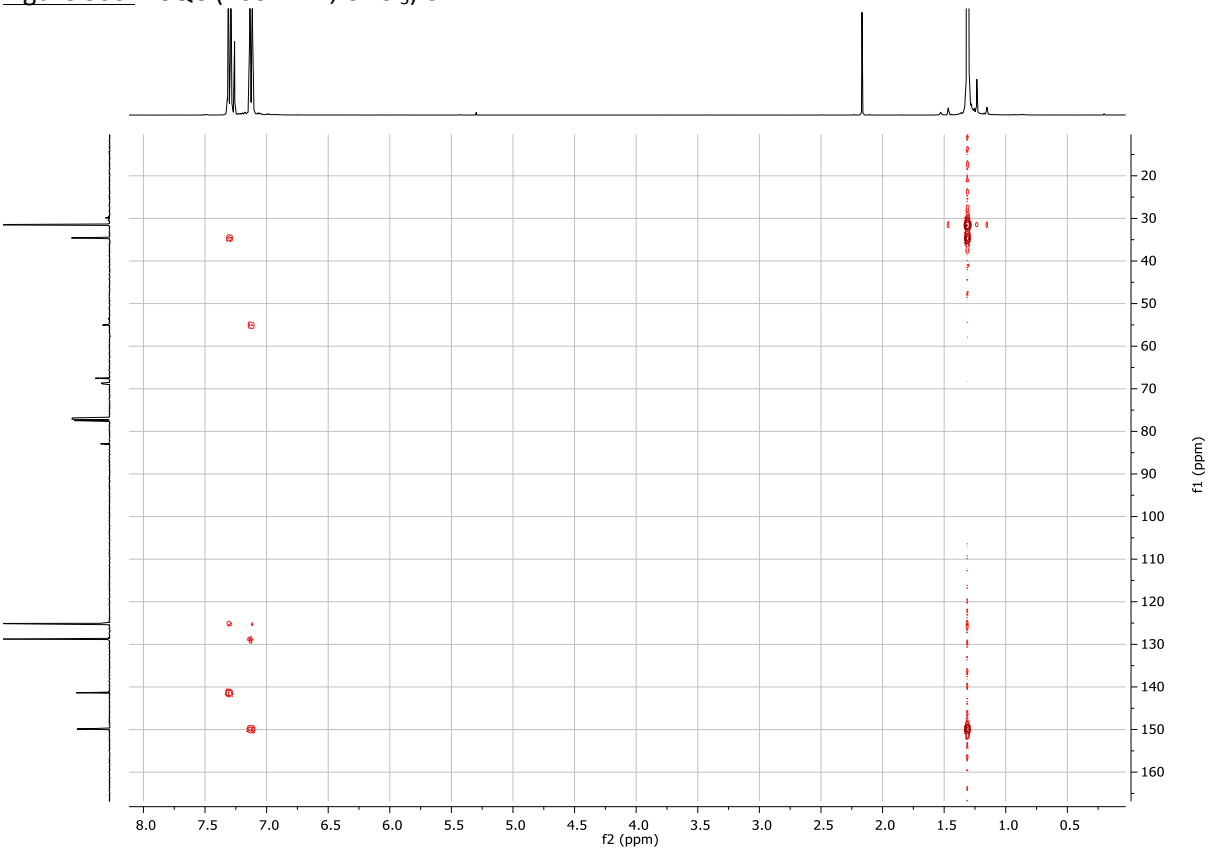


Figure S67. HMBC (400 MHz, $CDCl_3$) of **11.**

Spectra of **12**:

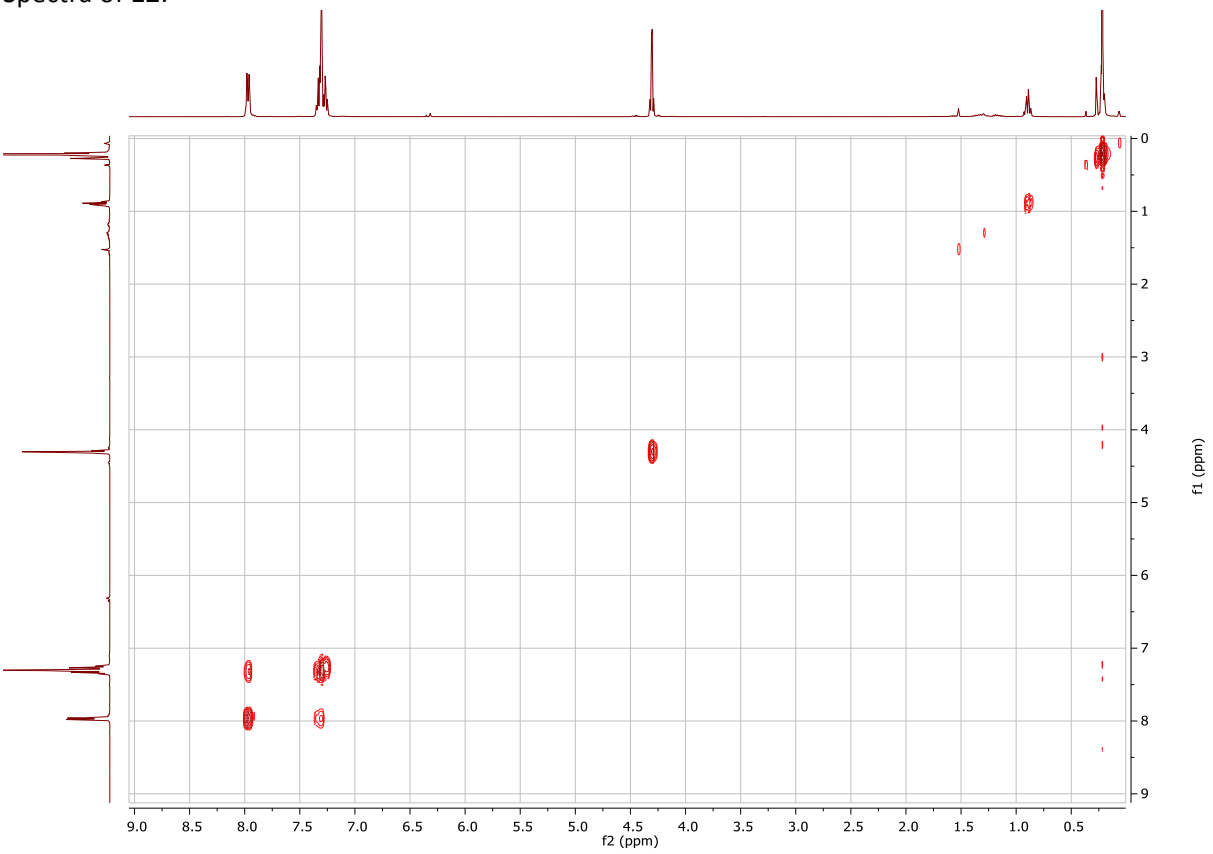


Figure S68. COSY (400 MHz, $CDCl_3$) of **12.**

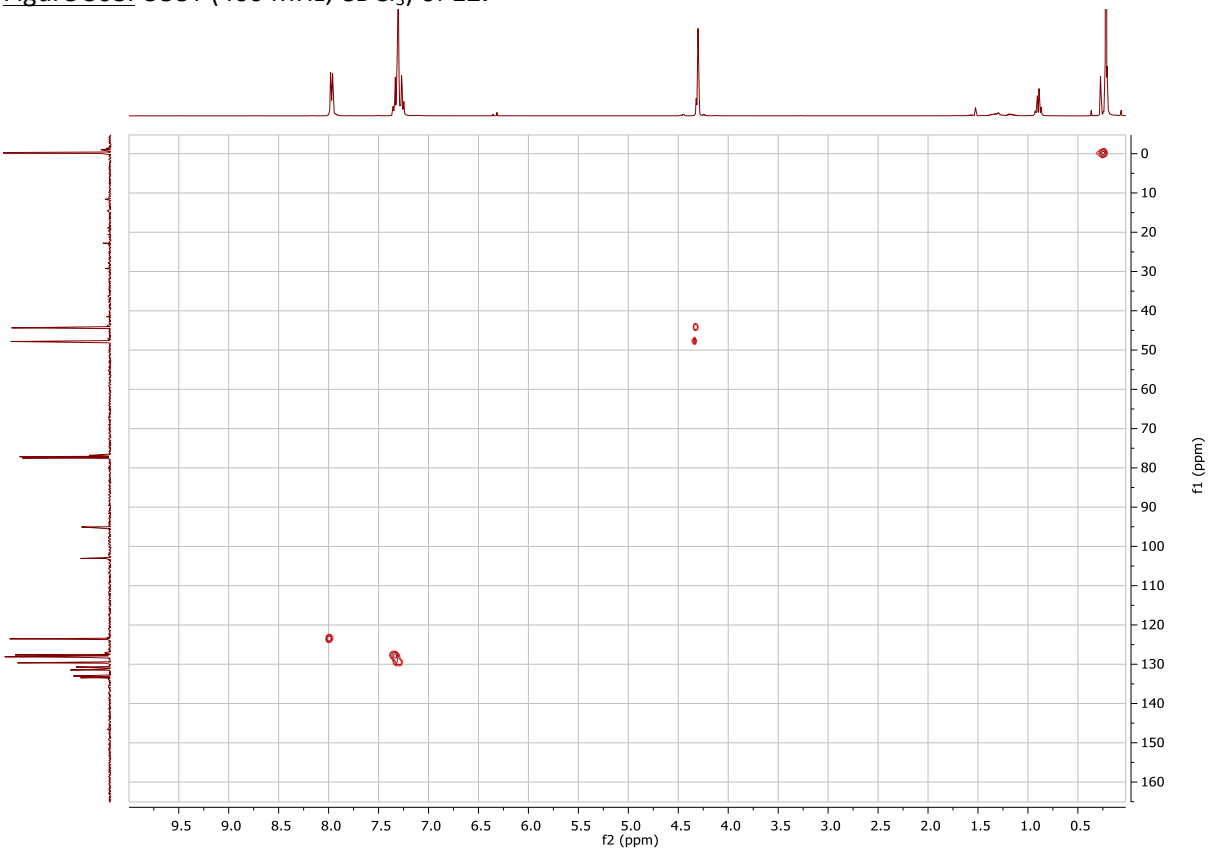


Figure S69. HSQC (400 MHz, $CDCl_3$) of **12.**

Spectra for **15**:

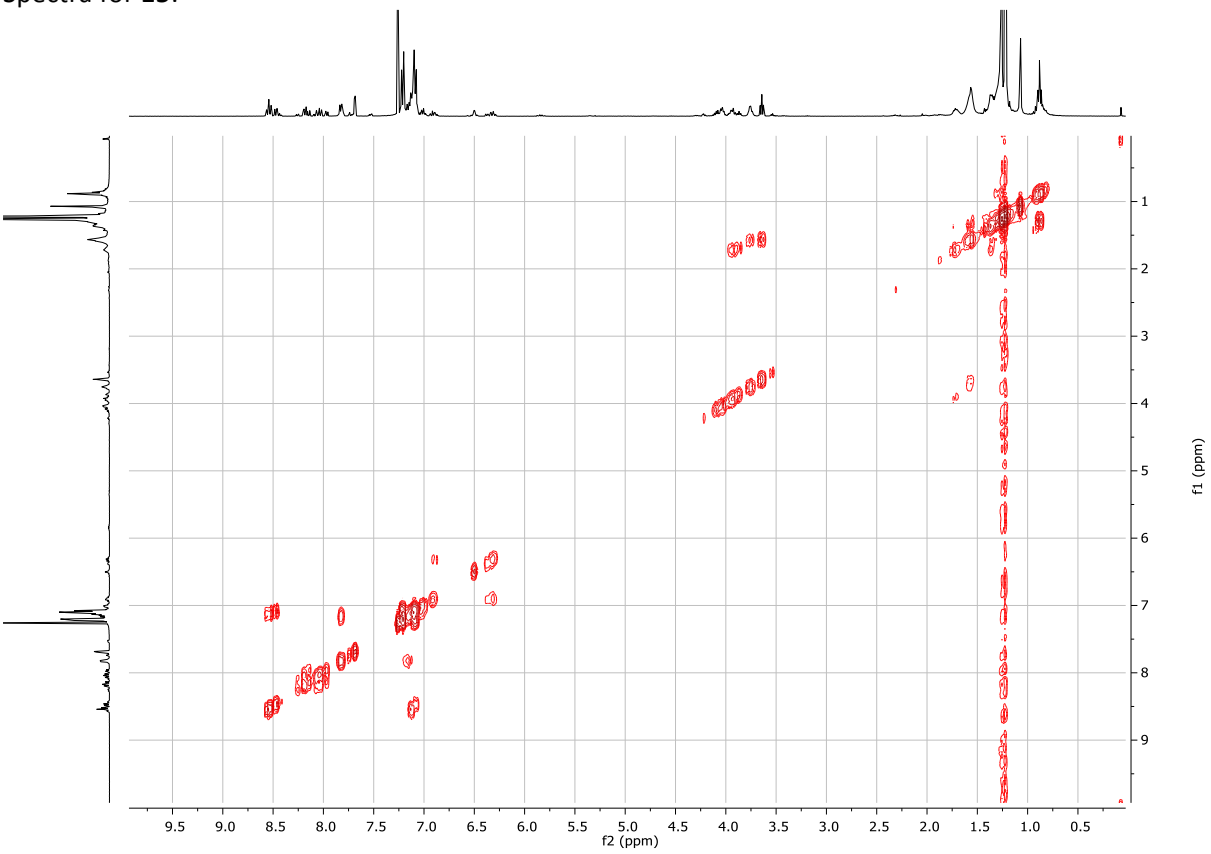


Figure S70. COSY (500 MHz, $CDCl_3$) of **15.**

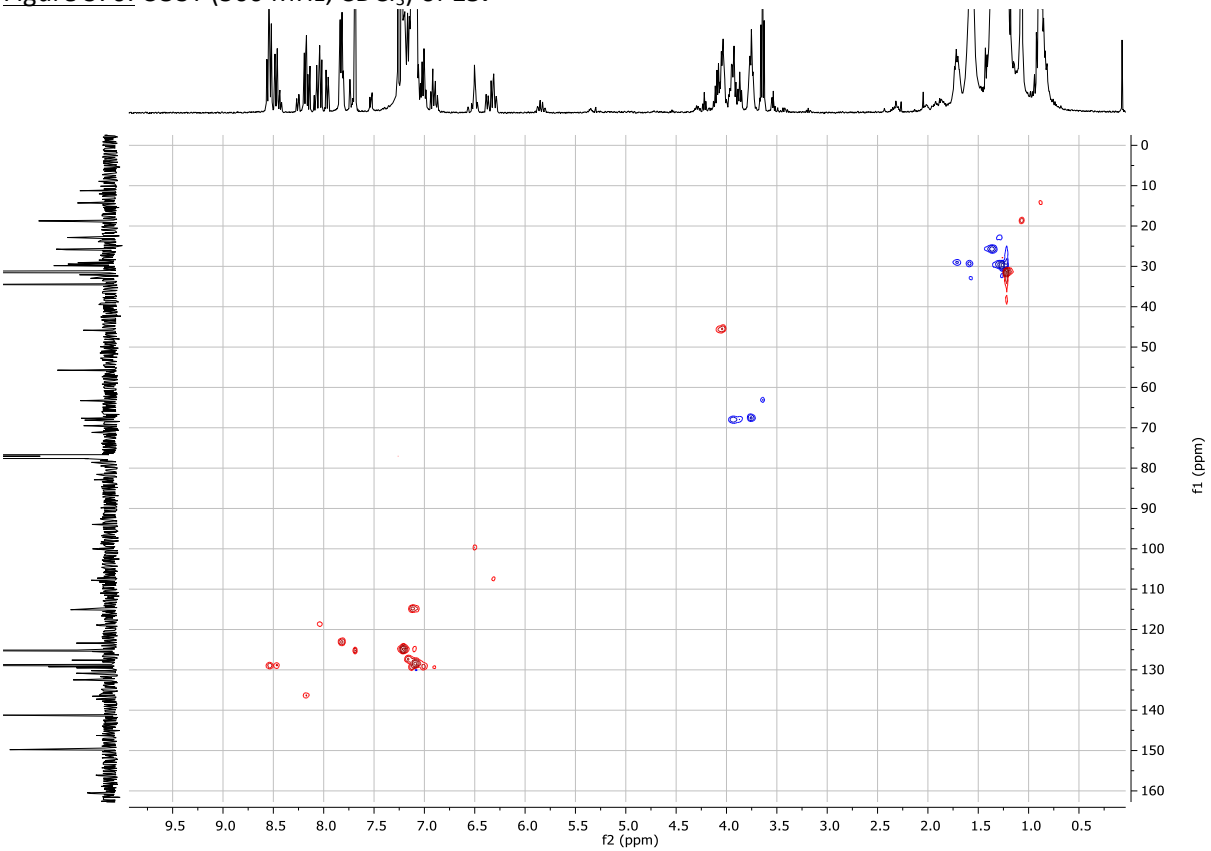


Figure S71. HSQC (500 MHz, $CDCl_3$) of **15.**

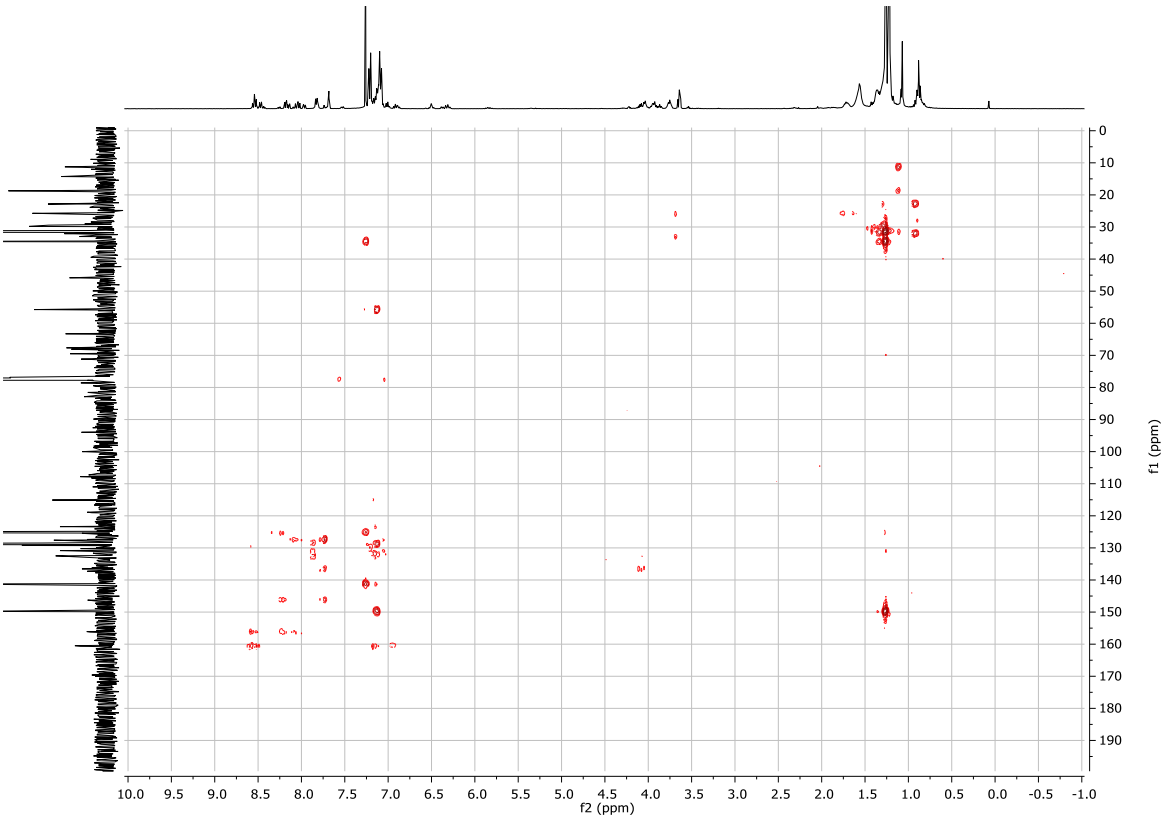


Figure S72. HMBC (500 MHz, $CDCl_3$) of **15.**

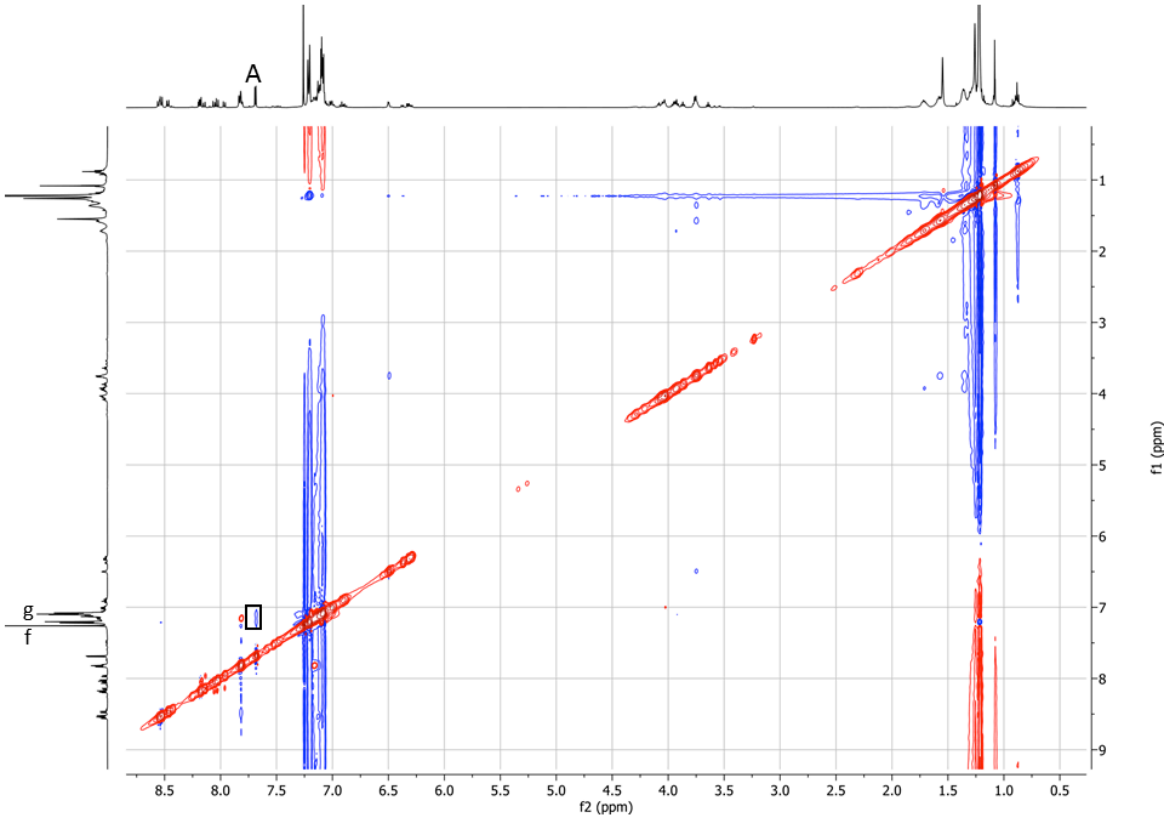


Figure S73. NOESY (500 MHz, $CDCl_3$) of **15.** Interactions between macrocycle signal A and aromatic stopper protons suggests that the macrocycle is slipping over the phenanthrene group (black box, protons A, f and g in S3.13).

Spectra for **18**:

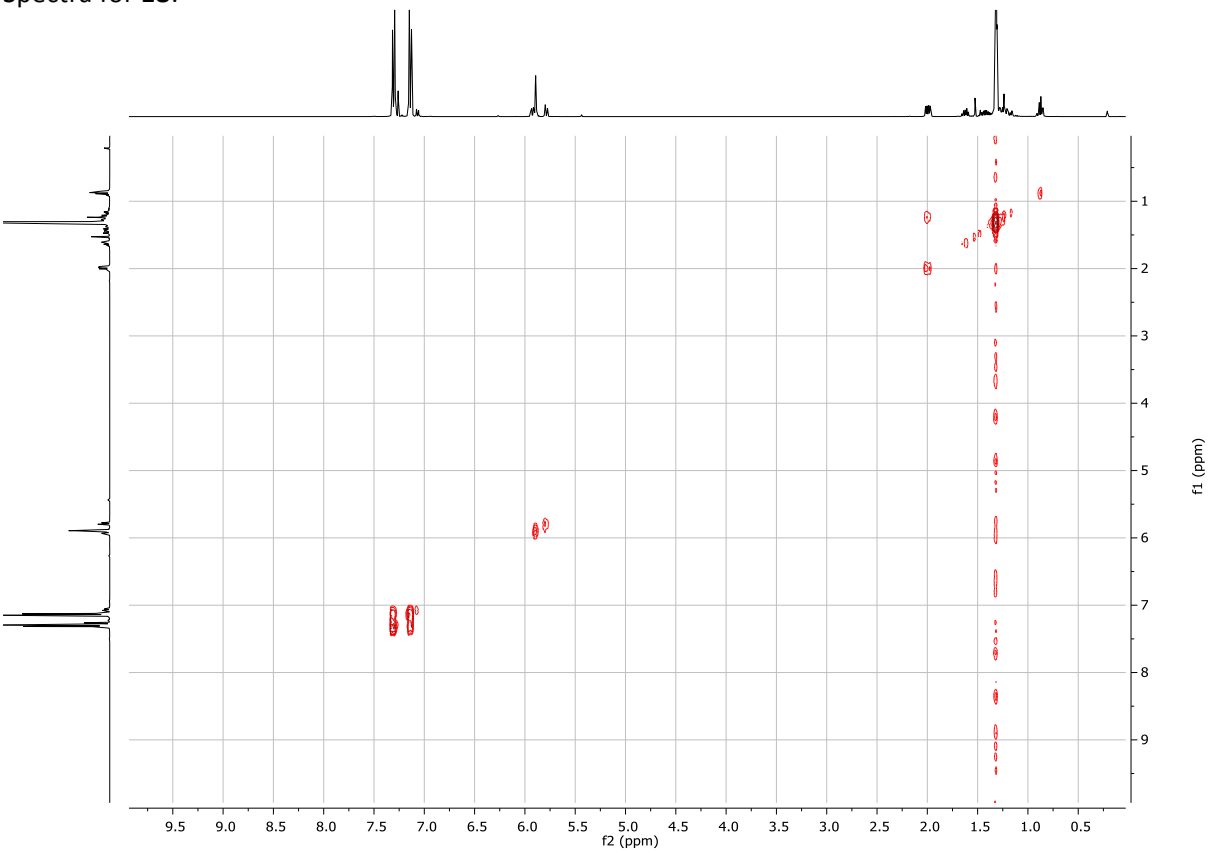


Figure S74. COSY (400 MHz, $CDCl_3$) of **18.**

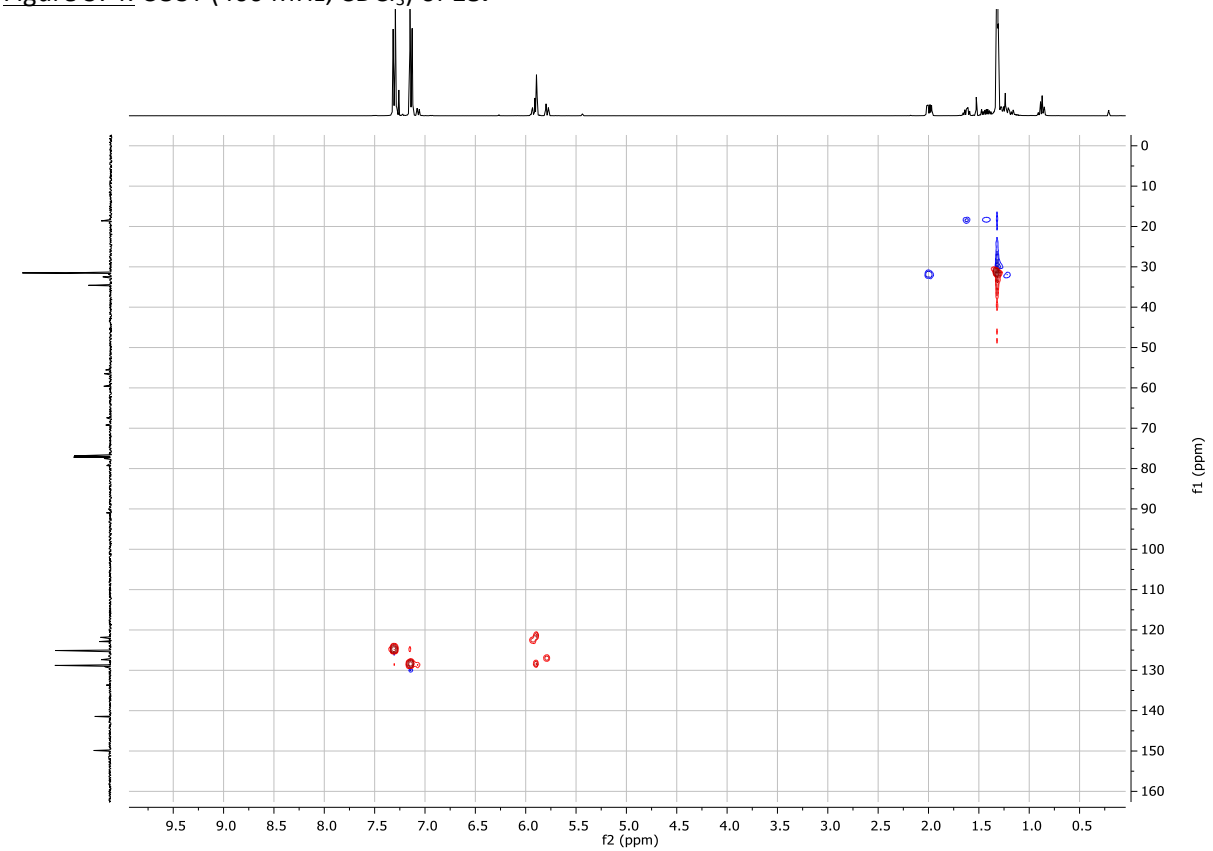


Figure S75. HSQC (400 MHz, $CDCl_3$) of **18.**

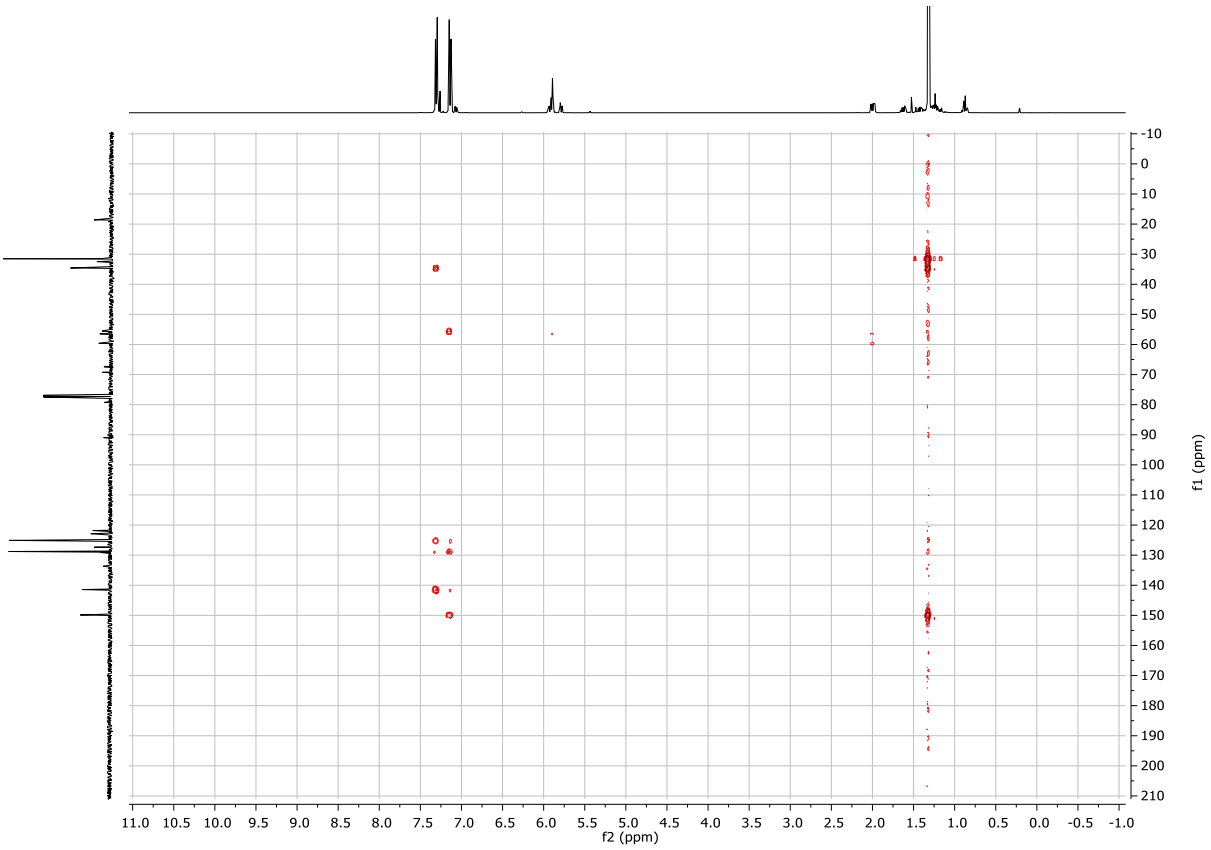


Figure S76. HMBC (400 MHz, $CDCl_3$) of **18.**

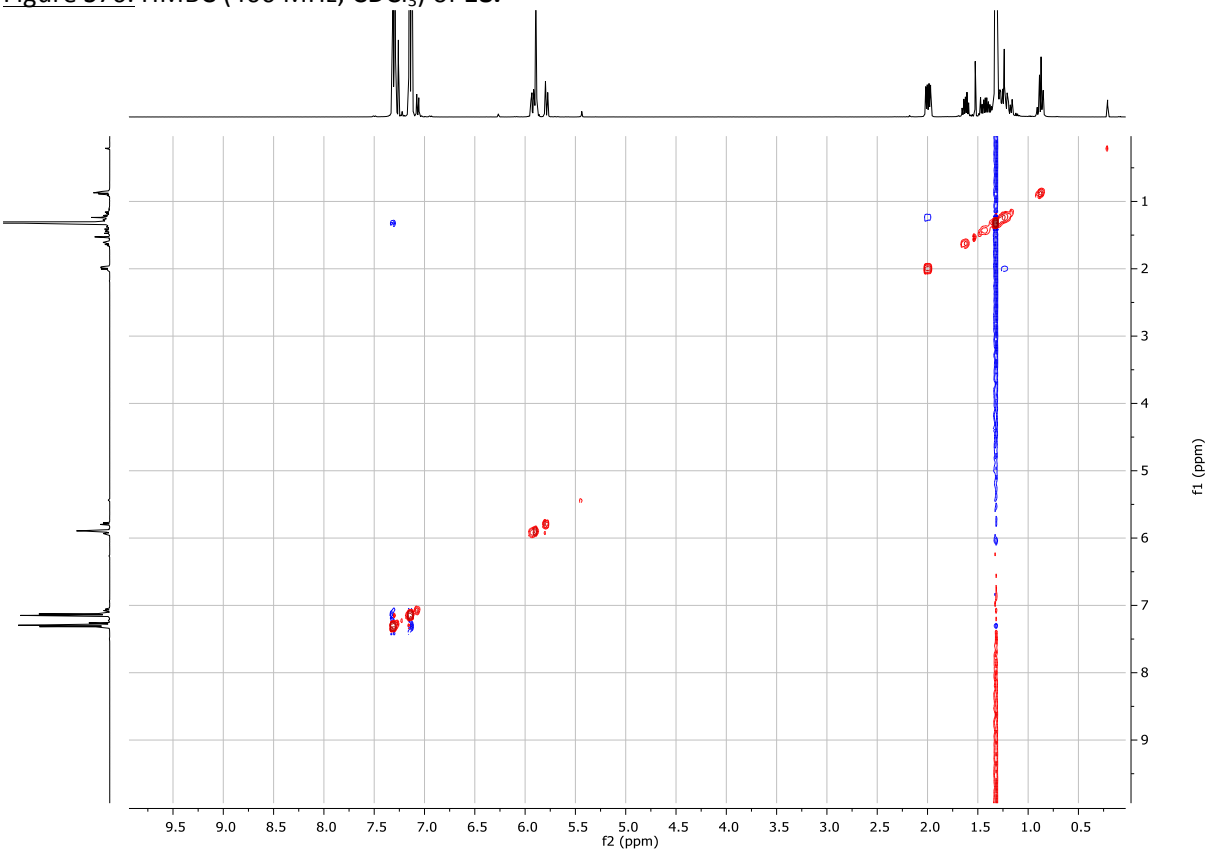


Figure S77. NOESY (400 MHz, $CDCl_3$) of **18.** No strong interactions between trityl unit and indane are observed.

Spectra for **24**:

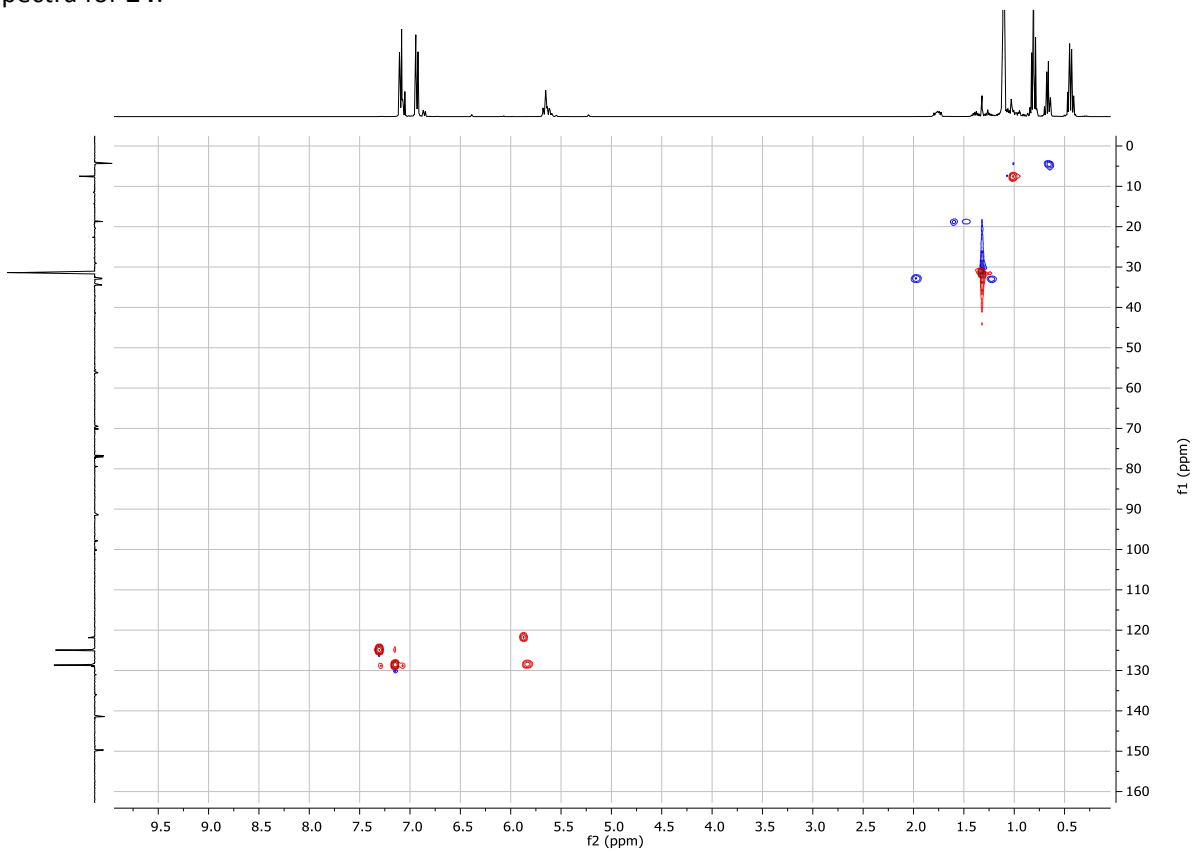


Figure S78. HSQC (400 MHz, $CDCl_3$) of **24.**

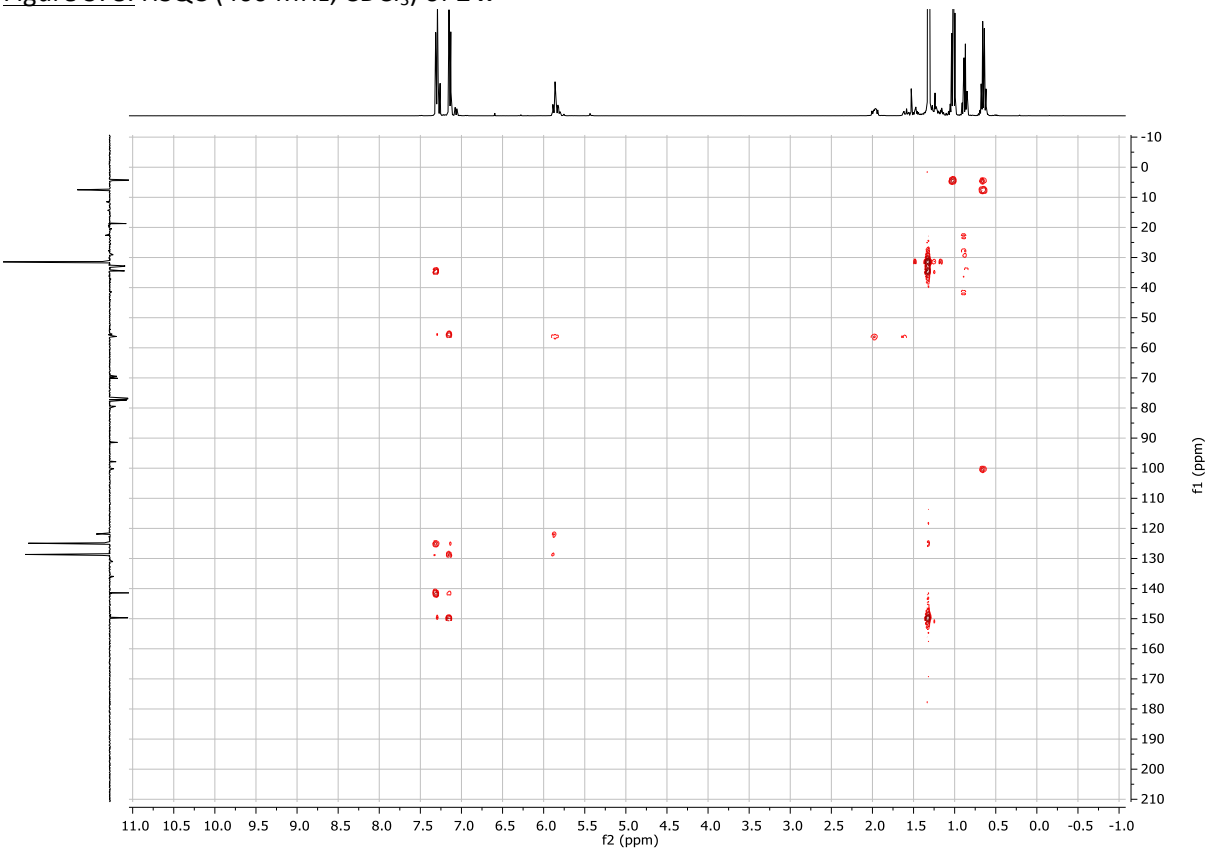


Figure S79. HMBC (400 MHz, $CDCl_3$) of **24.**

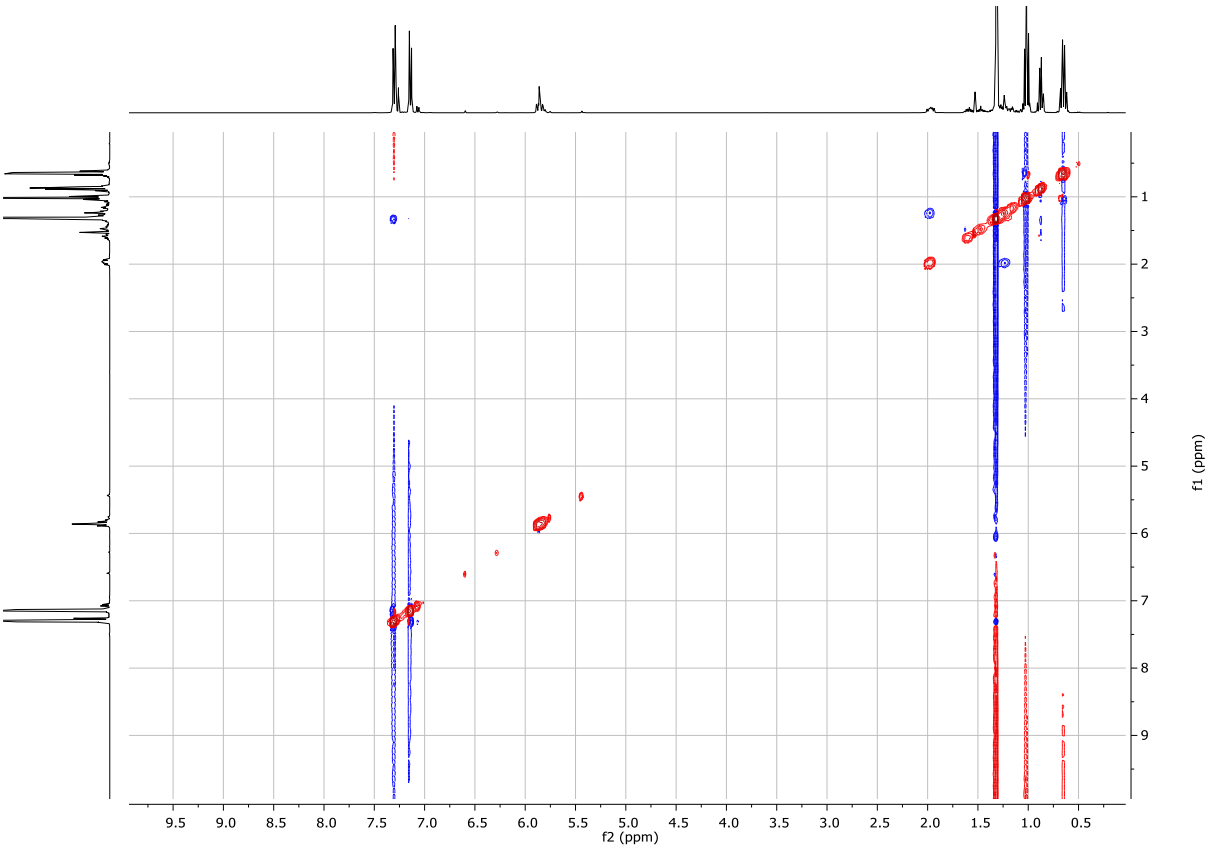


Figure S80. NOESY (400 MHz, $CDCl_3$) of **24.** No strong interactions between the indane and the trityl unit or the TES group are observed.

Spectra for **27**:

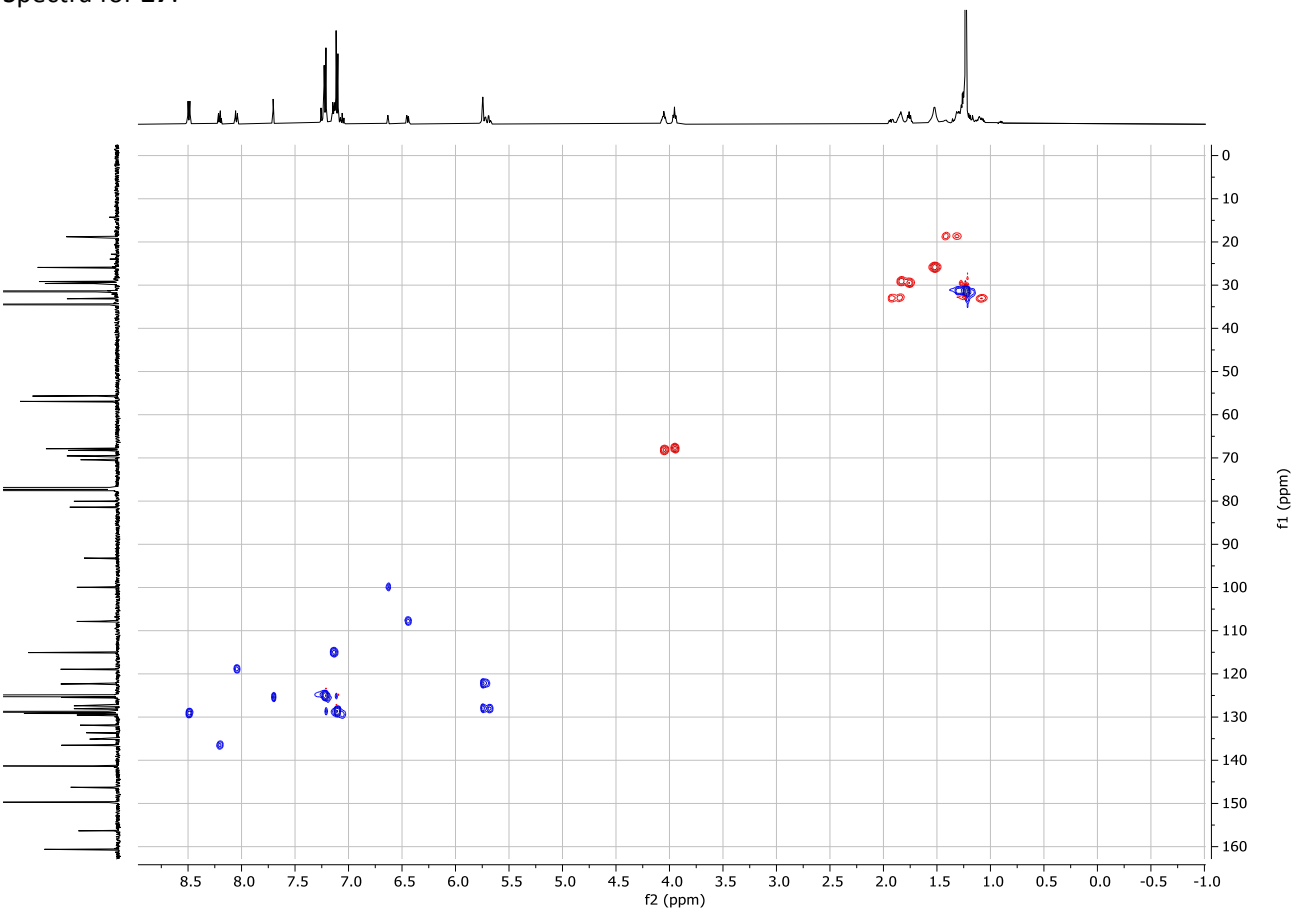


Figure S81. HSQC (500 MHz, $CDCl_3$) of **27.**

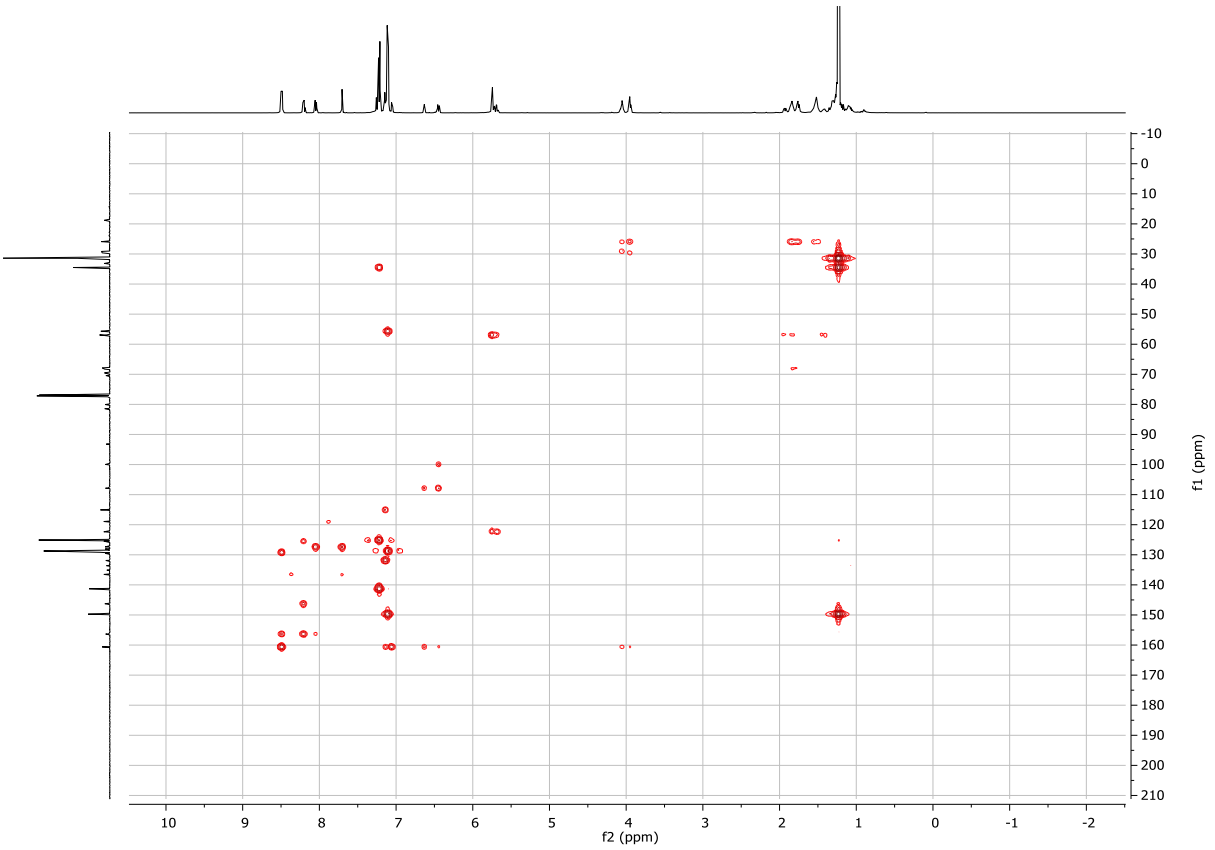


Figure S82. HMBC (500 MHz, $CDCl_3$) of **27.**

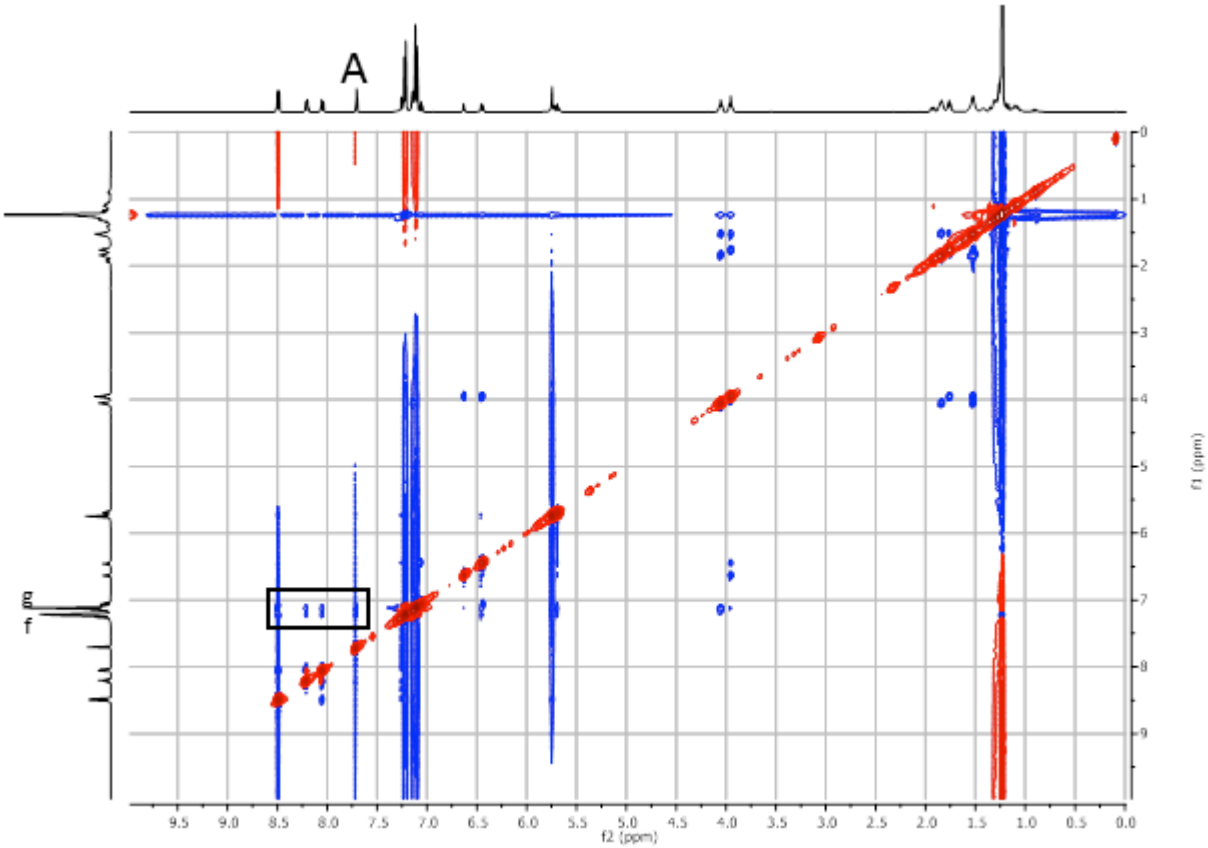


Figure S83. NOESY (500 MHz, $CDCl_3$) of **27.** Interactions between macrocycle signal A and aromatic stopper protons suggests that the macrocycle is slipping over the indane group (black box, protons A, f and g in S3.19).

Spectra for **28**:

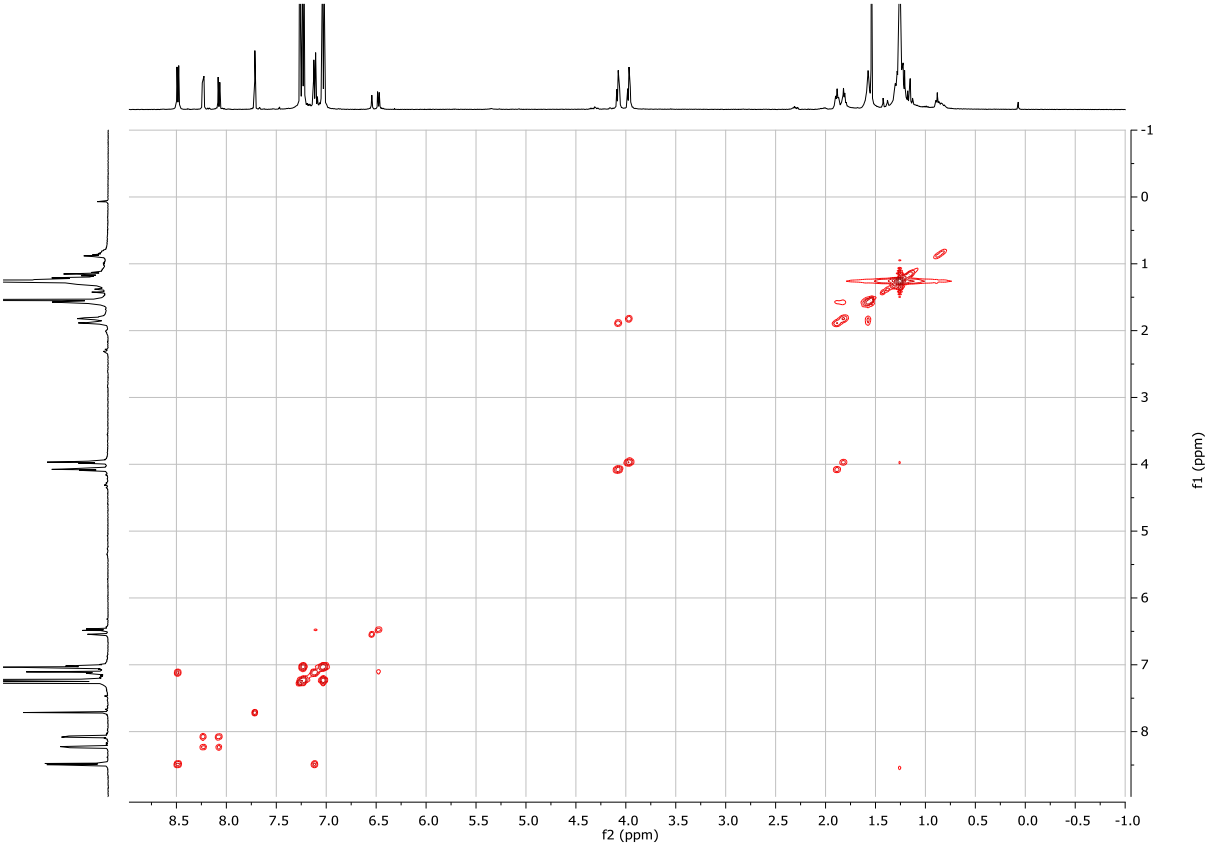


Figure S84. COSY (500 MHz, $CDCl_3$) of **28.**

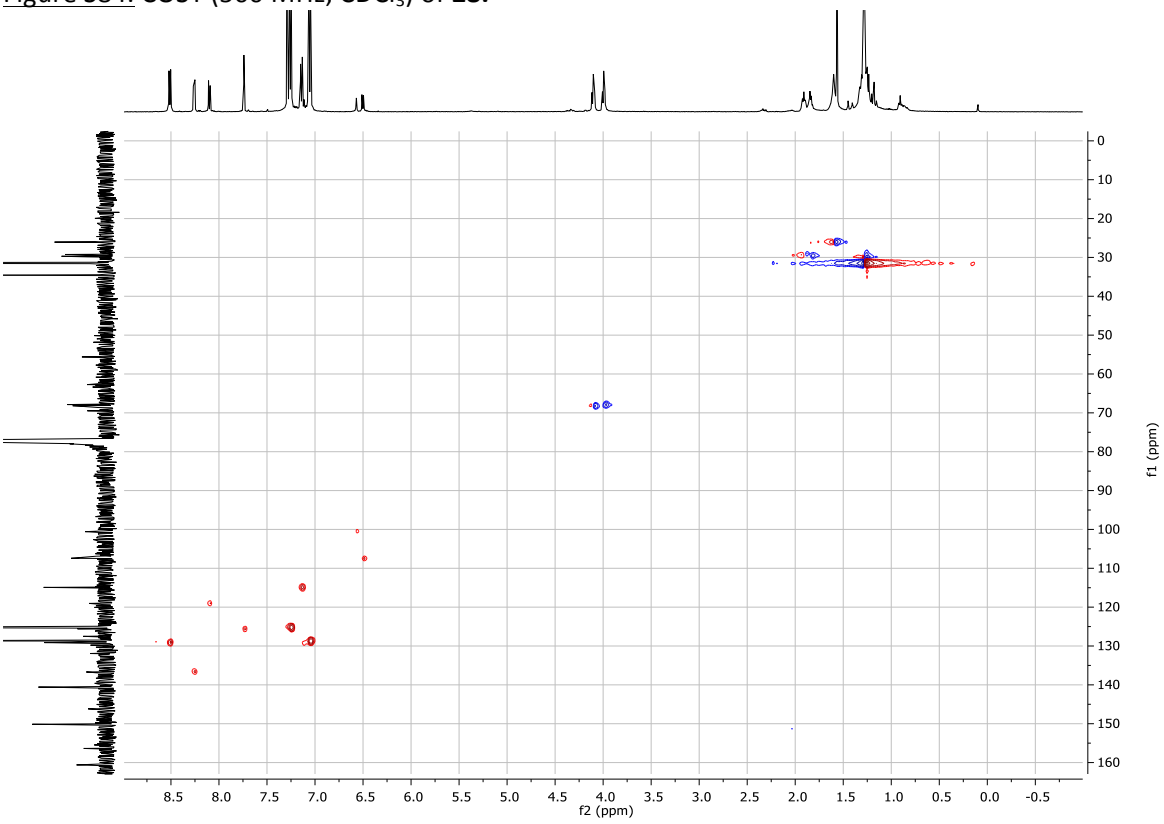


Figure S85. HSQC (500 MHz, $CDCl_3$) of **28.**

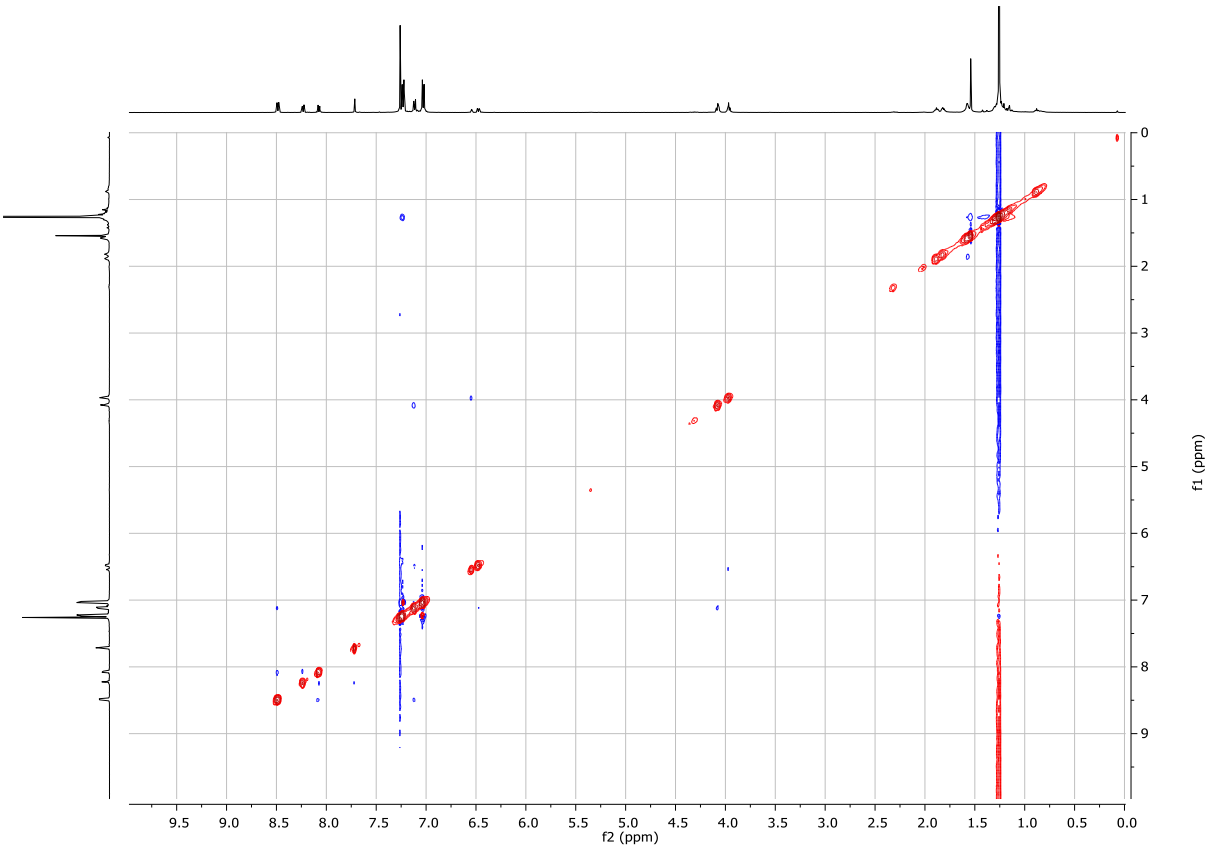


Figure S86. NOESY (500 MHz, $CDCl_3$) of **28.** No interactions are observed between the macrocycle and the axle, suggesting that the macrocycle resides near the center of the thread.

Spectra for **30**:

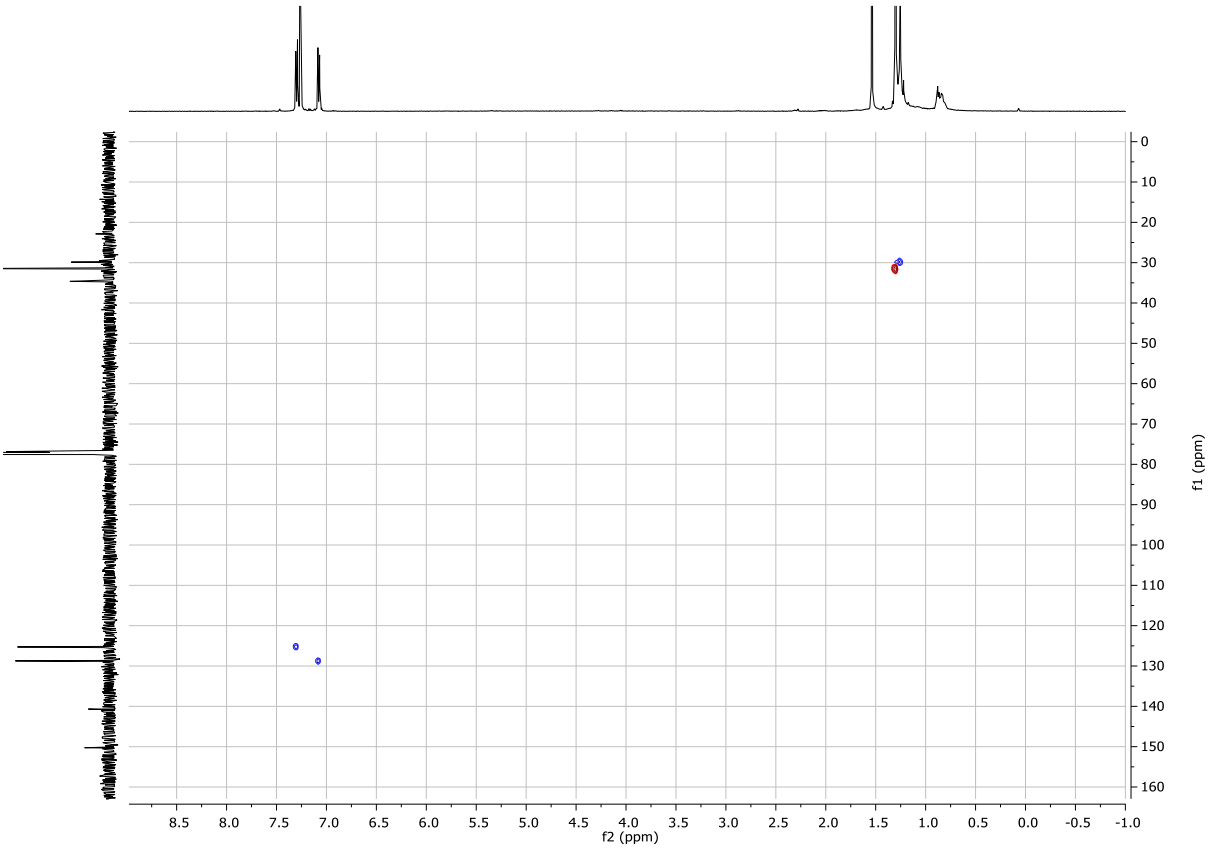
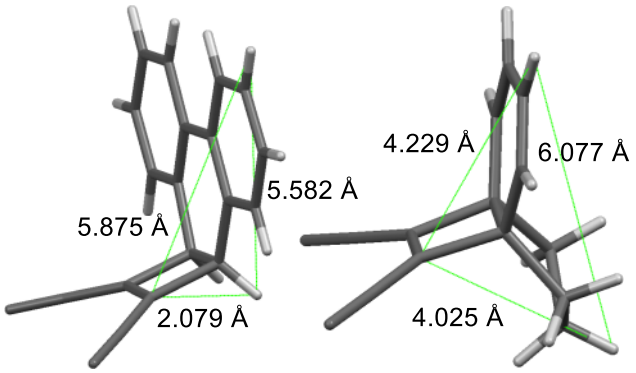


Figure S87. HSQC (500 MHz, $CDCl_3$) of **30.**

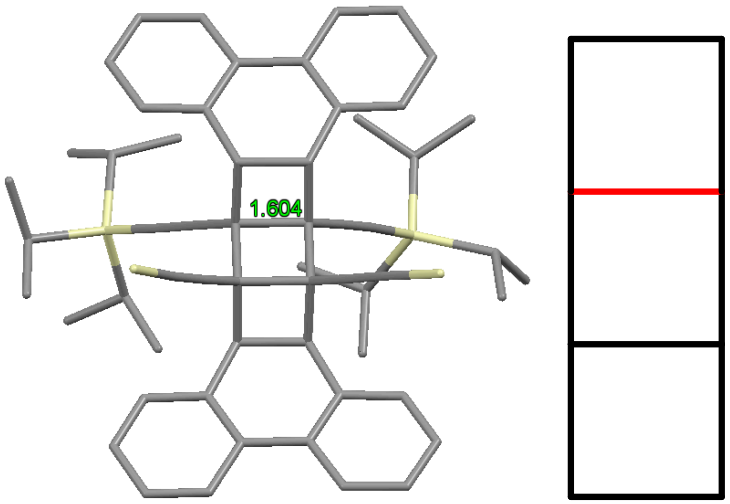
S6. X-ray Crystallography

S6.1 Size Comparison of the MAEs

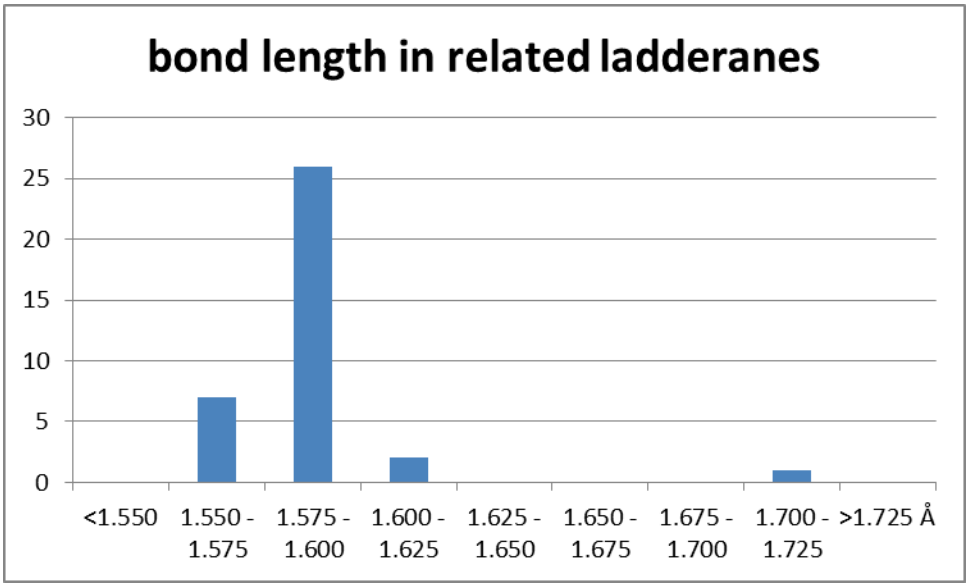
A comparison of the size of the phenanthrene MAE with a reported crystal structure of the indane MAE[S11]: shows that the steric demand of the indane group (taken from a reported structure) and of the phenanthrene group is approximately the same. The end points in the indane group are slightly further away from the masked alkyne but the effective size is reduced by the flexibility of the cyclopentane ring. This means that they should have similar properties when used as a stopper. At the same time, the anisotropy of the phenanthrene group is much larger with implications for the shape of different stereoisomers in rotaxanes (see also Scheme S8).

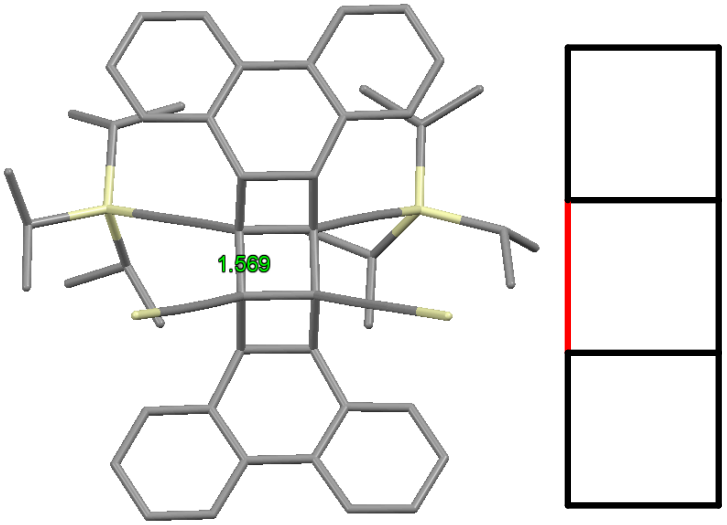


S6.2 Comparison of **6** to other ladderanes

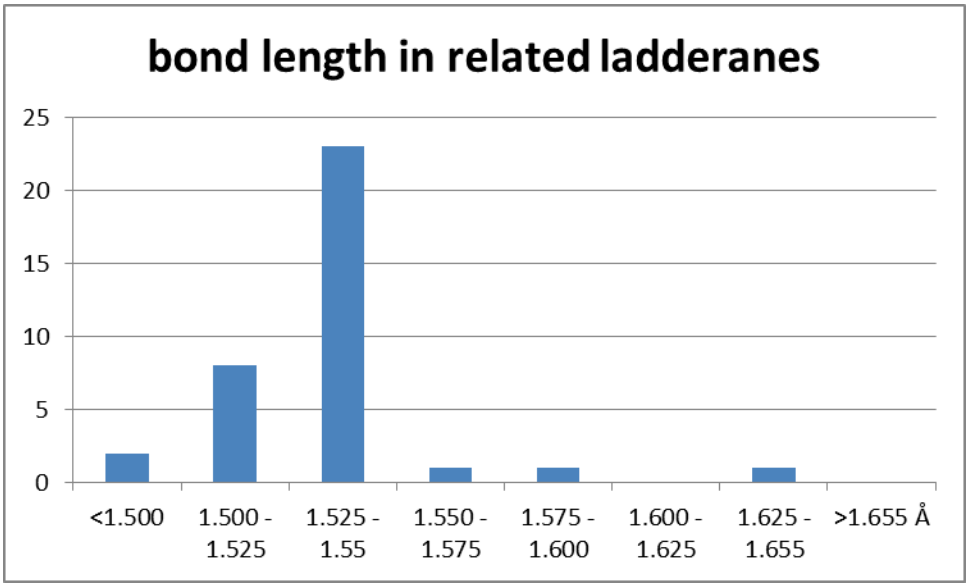


Due to repulsion of the TIPS groups, more than 94% of reported values are shorter than the present value of 1.604 Å for the bond fusing two cyclobutane units (34 of 36 entries). All structures including *anti*-fused [3]-ladderane motif were included in the search.





Due to repulsion of the TIPS groups, more than 94% of reported values are shorter than the present value of 1.569 Å for the lateral bond of the central cyclobutane ring (34 of 36 entries).



S7. Electronic Structure Calculations

The molecular structures of ladderane models **S2**, **S3**, **S4**, **S5** and **S6** were optimized in the gas phase at the B3LYP/6-31G(d)[S12,S13,S14] level of theory by using the software package Gaussian 16 Rev. A.03.[S15] All structures are confirmed ground-state minima according to the analysis of their vibrational frequencies computed at the same level, which show no imaginary frequencies. In order to explain an unusual bond lengths in a 3-ladderane unit in **6** we calculated five ladderane derivatives: unsubstituted [3]-ladderane **S2**, 1,2,5,6-tetramethyl-[3]-ladderane **S3**, 1,2,5,6-tetraethynyl-[3]-ladderane **S4**, 1,2,5,6-tetra-(trimethylsilyl)ethynyl)-[3]-ladderane **S5**, and 1,2,5,6-tetra-(triisopropylsilyl)ethynyl)-[3]-ladderane **S5** (Figure S88).

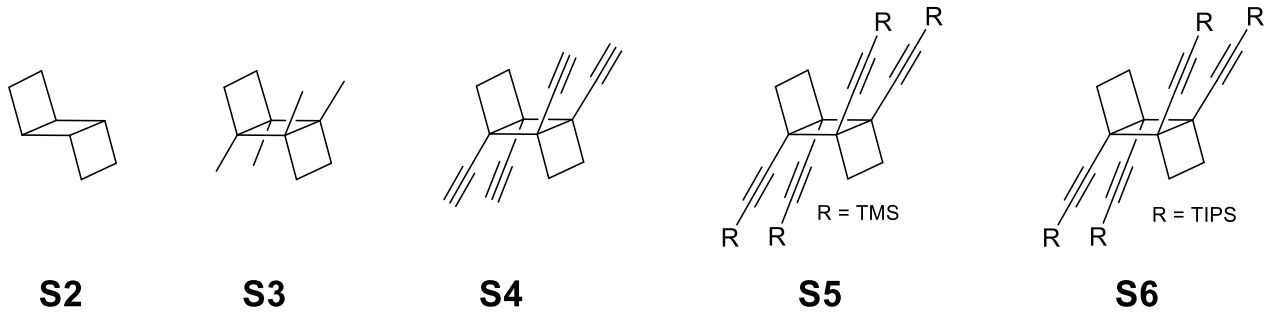


Figure S88. Studied [3]-ladderane derivatives **S2–S6** and arbitrary bond nomenclature.

The increase in the length of **B** bond in the **S2, S2, S4** series reaching a plateau for acetylene-substituted derivatives **S4, S5, S6** (Figure S89) suggests that the repulsion between adjacent alkynes is the major factor for an unusual bond lengths in **6**. However, the slight increase from **S4** to **S6** in bonds **B**, and **D**, suggests that bulky TIPS groups have slight effect as well. All calculated bond lengths are given in Table S1.

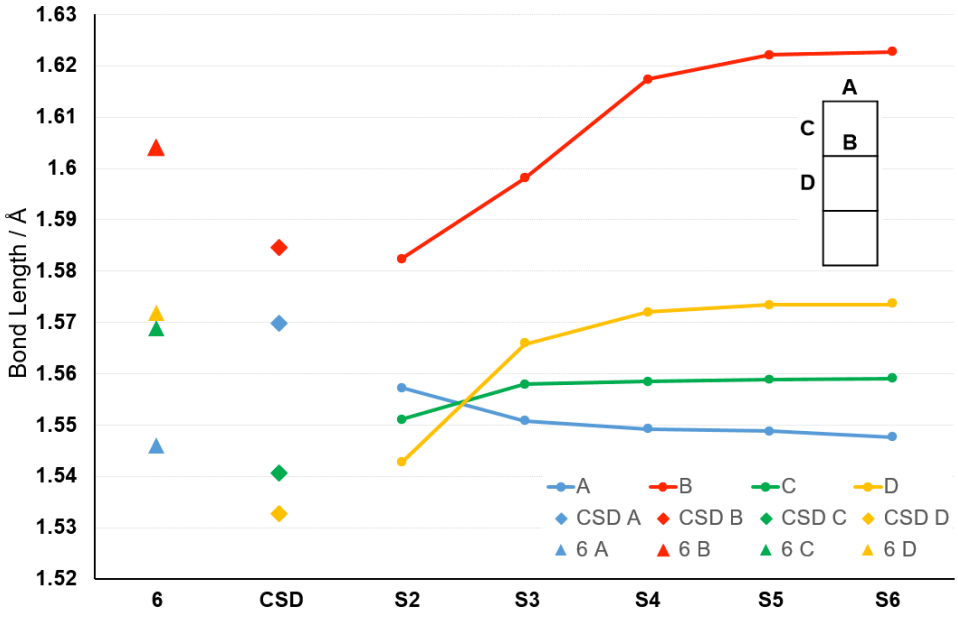
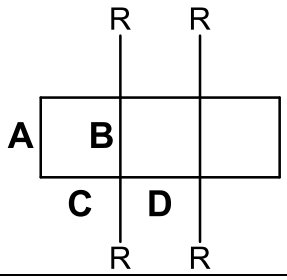


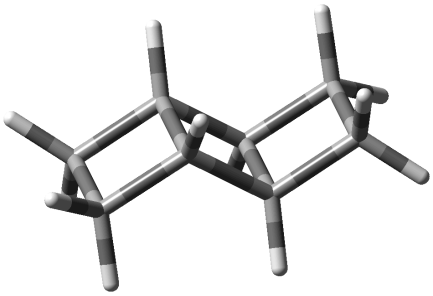
Figure S89. Comparison of the experimental values for bond lengths of **6** to average CCDC values (November 2019) and averaged calculated bond lengths in **S2**–**S6**.

Table S1. Calculated bond lengths of substituted ladderanes. Values in Å.



compound\bond	A	B	C	D
S2 3-Ladderane	1.5573	1.58234	1.55119	1.5426
R = H	1.5573	1.58234	1.5512	1.54276
			1.55108	
			1.55109	
S2 average	**1.5573**	**1.58234**	**1.55114**	**1.54268**
S3	1.55082	1.59814	1.55773	1.56604
R = Me	1.55082	1.59815	1.55775	1.5655
			1.55804	
			1.55802	
S3 average	**1.55082**	**1.598145**	**1.557885**	**1.56577**
S4	1.54924	1.61734	1.5584	1.57226
R = H-acetylene	1.54924	1.61734	1.5584	1.57193
			1.55853	
			1.55853	
S4 average	**1.54924**	**1.61734**	**1.558465**	**1.572095**
S5	1.54878	1.62215	1.55875	1.57345
R = TMS-acetylene	1.54879	1.62215	1.55882	1.57345
			1.55882	
			1.55875	
S5 average	**1.548785**	**1.62215**	**1.558785**	**1.57345**
S6	1.54786	1.62159	1.55755	1.57736
R = TIPS-acetylene	1.54743	1.62386	1.55748	1.56962
			1.5607	
			1.5606	
S6 average	**1.547645**	**1.622725**	**1.559083**	**1.57349**

Cartesian coordinates and structural parameters of cumulenes 1a, 1b, 1c, 1e

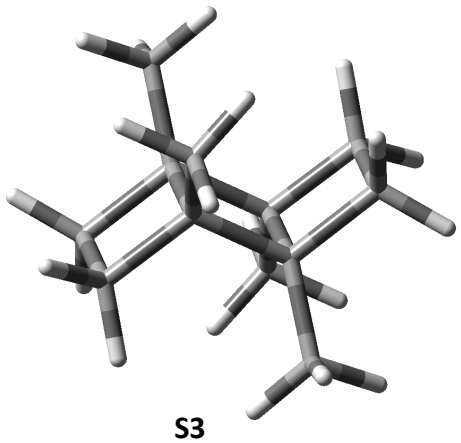


S2

B3LYP/6-31G(d,p)

Atom type, (x,y,z) coordinates:

C	-0.57785	0.79084	0.51100
C	-0.57818	-0.79149	0.51050
C	0.57818	-0.79149	-0.51050
C	0.57785	0.79084	-0.51100
C	-1.99126	-0.77836	-0.12920
H	-2.76326	-1.21267	0.51269
H	-2.06033	-1.25936	-1.11098
C	-1.99141	0.77893	-0.12740
H	-2.06208	1.26255	-1.10777
H	-2.76265	1.21118	0.51681
C	1.99126	-0.77836	0.12920
H	2.76326	-1.21267	-0.51269
H	2.06033	-1.25936	1.11098
C	1.99141	0.77893	0.12740
H	2.06208	1.26255	1.10777
H	2.76265	1.21118	-0.51680
H	0.44584	-1.40649	-1.40642
H	-0.44416	1.40528	1.40710
H	0.44416	1.40528	-1.40710
H	-0.44584	-1.40649	1.40642

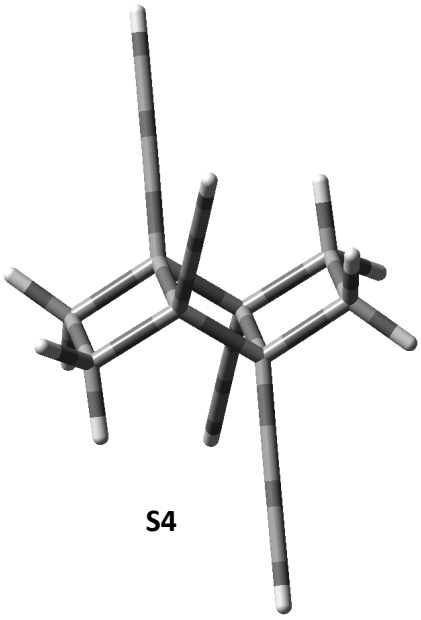


S3

B3LYP/6-31G(d,p)

Atom type, (x,y,z) coordinates:

C	-0.77622	-0.79891	-0.10297
C	-0.77631	0.79923	-0.10023
C	0.77633	0.79924	0.10004
C	0.77620	-0.79890	0.10312
C	-1.57638	0.77283	1.23644
H	-2.57565	1.20686	1.13080
H	-1.10362	1.25030	2.09837
C	-1.58115	-0.77797	1.23051
H	-1.11601	-1.26589	2.09077
H	-2.58290	-1.20409	1.11634
C	1.57654	0.77258	-1.23652
H	2.57589	1.20638	-1.13069
H	1.10411	1.25011	-2.09861
C	1.58105	-0.77822	-1.23043
H	1.11564	-1.26608	-2.09055
H	2.58272	-1.20456	-1.11641
C	1.39101	1.65815	1.19261
H	2.46818	1.47193	1.27177
H	1.26120	2.72532	0.97017
H	0.95664	1.47237	2.17937
C	1.38586	-1.65335	1.20197
H	1.25452	-2.72145	0.98498
H	2.46315	-1.46881	1.28318
H	0.94910	-1.46134	2.18649
C	-1.38579	-1.65366	-1.20165
H	-1.25484	-2.72170	-0.98412
H	-2.46299	-1.46881	-1.28331
H	-0.94863	-1.46223	-2.18611
C	-1.39114	1.65785	-1.19292
H	-2.46843	1.47202	-1.27146
H	-1.26083	2.72507	-0.97107
H	-0.95734	1.47142	-2.17980

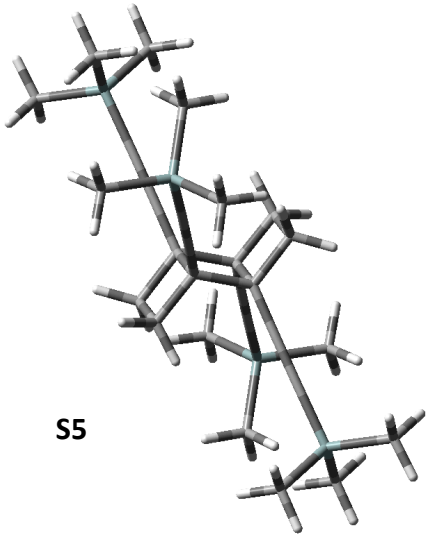


S4

B3LYP/6-31G(d,p)

Atom type, (x,y,z) coordinates:

C	0.64314	-0.80885	-0.45206
C	0.64242	0.80849	-0.45285
C	1.76333	-1.60965	-0.02553
C	2.71194	-2.27468	0.32226
C	1.76276	1.61056	-0.02908
C	2.71133	2.27674	0.31661
C	-0.64240	0.80853	0.45280
C	-0.64313	-0.80881	0.45211
C	-1.76273	1.61058	0.02898
C	-2.71138	2.27666	-0.31669
C	-1.76333	-1.60963	0.02564
C	-2.71190	-2.27472	-0.32217
H	3.54803	2.86386	0.61707
H	3.54888	-2.86053	0.62453
H	-3.54903	-2.86020	-0.62463
H	-3.54842	2.86331	-0.61711
C	0.32279	0.77342	-1.97785
H	1.12443	1.21302	-2.57379
H	-0.61992	1.25803	-2.24053
C	0.32584	-0.77581	-1.97745
H	-0.61404	-1.26476	-2.24221
H	1.13099	-1.21192	-2.57125
C	-0.32277	0.77356	1.97780
H	-1.12441	1.21320	2.57370
H	0.61995	1.25818	2.24045
C	-0.32584	-0.77568	1.97751
H	0.61403	-1.26462	2.24229
H	-1.13099	-1.21173	2.57135



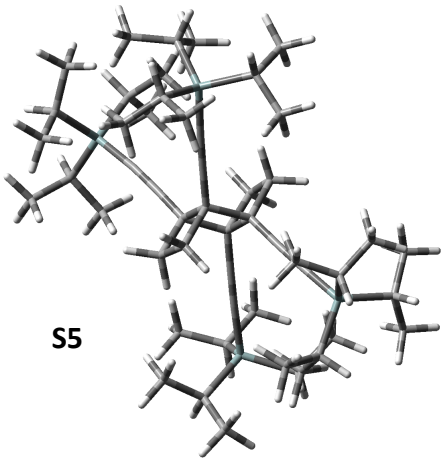
S5

B3LYP/6-31G(d,p)

Atom type, (x,y,z) coordinates:

C	0.54488	-0.81180	-0.56649
C	0.54517	0.81036	-0.56816
C	1.72552	-1.60959	-0.36405
C	2.73835	-2.27166	-0.20295
Si	4.27184	-3.26502	0.01412
C	1.72593	1.60833	-0.36716
C	2.73847	2.27106	-0.20697
Si	4.26952	3.26699	0.01317
C	-0.54493	0.81173	0.56647
C	-0.54523	-0.81042	0.56815
C	-1.72556	1.60954	0.36404
C	-2.73837	2.27165	0.20292
Si	-4.27177	3.26516	-0.01409
C	-1.72599	-1.60840	0.36715
C	-2.73852	-2.27115	0.20698
Si	-4.26955	-3.26710	-0.01318
C	3.80711	-4.96289	0.70079
H	4.70011	-5.58277	0.84033
H	3.30481	-4.87620	1.66959
H	3.13274	-5.49445	0.02182
C	5.41626	-2.36565	1.21891
H	5.68091	-1.37143	0.84480
H	4.94240	-2.23935	2.19772
H	6.34534	-2.92802	1.36648
C	5.11693	-3.45241	-1.66548
H	4.46544	-3.96097	-2.38335
H	5.38162	-2.47735	-2.08687
H	6.03786	-4.03952	-1.57404
C	4.48897	4.39042	-1.49005
H	4.57527	3.80734	-2.41254
H	3.63916	5.07113	-1.60343
H	5.39529	4.99879	-1.39184
C	5.73962	2.08944	0.16635
H	5.62043	1.41935	1.02391
H	5.84343	1.47027	-0.73056
H	6.67432	2.64558	0.30119

C	4.10254	4.30784	1.58129
H	3.96698	3.67636	2.46524
H	4.99899	4.91806	1.73990
H	3.24385	4.98398	1.51890
C	-3.80727	4.96167	-0.70424
H	-3.30618	4.87319	-1.67350
H	-4.70022	5.58164	-0.84373
H	-3.13188	5.49414	-0.02698
C	-5.41790	2.36405	-1.21595
H	-4.94522	2.23583	-2.19507
H	-5.68244	1.37059	-0.83974
H	-6.34696	2.92646	-1.36344
C	-5.11481	3.45580	1.66618
H	-5.37931	2.48158	2.08962
H	-4.46231	3.96544	2.38236
H	-6.03567	4.04304	1.57478
C	-5.74003	-2.08968	-0.16373
H	-5.84337	-1.47160	0.73399
H	-5.62157	-1.41853	-1.02057
H	-6.67468	-2.64587	-0.29861
C	-4.10375	-4.30583	-1.58283
H	-5.00027	-4.91595	-1.74148
H	-3.96913	-3.67306	-2.46601
H	-3.24491	-4.98192	-1.52221
C	-4.48744	-4.39249	1.48881
H	-3.63738	-5.07315	1.60055
H	-4.57301	-3.81058	2.41210
H	-5.39372	-5.00093	1.39067
C	0.05971	0.77635	2.00281
H	-0.61448	1.21549	2.74016
H	1.03473	1.26224	2.08013
C	-0.05946	0.77236	-2.00437
H	0.61471	1.20988	-2.74271
H	-1.03439	1.25840	-2.08233
C	-0.05978	-0.77642	-2.00282
H	-1.03480	-1.26231	-2.08012
H	0.61441	-1.21557	-2.74017
C	0.05940	-0.77243	2.00436
H	1.03433	-1.25846	2.08231
H	-0.61477	-1.20995	2.74270



S5

B3LYP/6-31G(d,p)

Atom type, (x,y,z) coordinates:

C	0.59787	0.84679	0.55142
C	0.43724	-0.76904	0.56580
C	1.81838	1.57056	0.30465
C	2.83367	2.22476	0.12042
Si	4.29809	3.32980	-0.07679
C	1.50050	-1.72189	0.37844
C	2.37303	-2.56432	0.23338
Si	3.62206	-3.90659	0.03519
C	-0.65065	-0.67288	-0.56156
C	-0.53282	0.94434	-0.54408
C	-1.87290	-1.41069	-0.37538
C	-2.90063	-2.05475	-0.23050
Si	-4.41513	-3.08830	-0.03474
C	-1.62956	1.84396	-0.29584
C	-2.55906	2.61526	-0.11280
Si	-3.93709	3.83158	0.04187
C	3.79620	5.08652	0.53461
H	4.50187	5.76505	0.02866
C	4.81398	3.39088	-1.93033
H	5.87485	3.68724	-1.90671
C	5.75065	2.65807	0.99507
H	6.33918	3.55610	1.24205
C	4.00037	-4.66006	1.76690
H	5.00411	-5.10177	1.66046
C	5.22501	-3.17093	-0.73541
H	5.70382	-4.02572	-1.23928
C	2.88651	-5.25334	-1.12955
H	3.42927	-6.17318	-0.85860
C	-3.87588	-4.86591	0.47613
H	-4.75615	-5.27871	0.99476
C	-5.52952	-2.31509	1.33147
H	-6.54088	-2.68934	1.10567
C	-5.35796	-3.14350	-1.71317
H	-5.92344	-4.08829	-1.67456
C	-5.44737	3.12413	-0.88366
H	-5.95086	2.43382	-0.19609
H	-6.15996	3.94525	-1.04739
C	-4.36096	4.13474	1.89700
H	-4.60031	5.20840	1.95033
C	-3.35881	5.49250	-0.72155

H	-4.22430	6.16526	-0.60591
C	-0.04139	-0.66148	-1.99838
H	-0.72196	-1.08074	-2.74122
H	0.91743	-1.18016	-2.06582
C	0.04322	0.87897	2.00643
H	-0.84969	1.49589	2.12709
H	0.80194	1.21112	2.71730
C	0.01702	0.88527	-2.00015
H	1.00219	1.34071	-2.12192
H	-0.67514	1.34302	-2.70916
C	1.38457	-5.50342	-0.88714
H	1.02441	-6.32716	-1.51675
H	1.16041	-5.76101	0.15104
H	0.79645	-4.61397	-1.13624
C	3.13121	-5.00891	-2.63066
H	2.61230	-4.10847	-2.97884
H	4.19225	-4.89860	-2.87387
H	2.74556	-5.84892	-3.22235
C	3.05011	-5.79357	2.19699
H	3.02027	-6.61564	1.47562
H	3.36851	-6.21437	3.15932
H	2.02580	-5.42779	2.33089
C	4.06995	-3.59556	2.87973
H	3.09458	-3.11850	3.02236
H	4.35816	-4.05337	3.83473
H	4.79146	-2.80349	2.66367
C	6.23882	-2.62326	0.28641
H	6.53807	-3.37161	1.02648
H	7.15015	-2.28471	-0.22289
H	5.83571	-1.76011	0.82796
C	4.93279	-2.09777	-1.80277
H	4.43844	-1.22827	-1.35685
H	5.86511	-1.75054	-2.26665
H	4.28570	-2.46438	-2.60408
C	4.72643	2.01643	-2.62206
H	3.68838	1.67038	-2.67210
H	5.10377	2.07653	-3.65101
H	5.30167	1.24411	-2.10554
C	4.07055	4.44250	-2.77536
H	4.17135	5.45475	-2.37265
H	4.46454	4.45727	-3.79962
H	3.00074	4.21563	-2.84734
C	6.69952	1.68404	0.27216
H	6.19093	0.75109	0.00579
H	7.12167	2.10776	-0.64415
H	7.53976	1.41491	0.92493
C	5.27357	2.03013	2.31964
H	6.13083	1.73654	2.93899
H	4.65775	2.71197	2.91220
H	4.67644	1.13164	2.13148
C	2.36904	5.48838	0.11196
H	2.15134	6.51862	0.42135
H	2.21492	5.43010	-0.96835
H	1.62597	4.83656	0.58316
C	3.96243	5.30481	2.05058
H	4.98181	5.11027	2.39708
H	3.71914	6.34145	2.31634
H	3.28519	4.66064	2.62291
C	-3.56157	-5.80659	-0.70260
H	-3.33432	-6.81554	-0.33546

H	-4.39457	-5.89572	-1.40639
H	-2.68358	-5.46541	-1.26271
C	-2.69631	-4.87439	1.46886
H	-2.47316	-5.89894	1.79320
H	-1.79187	-4.47032	1.00222
H	-2.89374	-4.28174	2.36583
C	-5.19132	-2.76158	2.76637
H	-5.90620	-2.33114	3.47921
H	-5.22273	-3.84836	2.88850
H	-4.19450	-2.41946	3.06745
C	-5.57140	-0.77526	1.26642
H	-4.58163	-0.34927	1.46188
H	-5.89766	-0.40307	0.29192
H	-6.26223	-0.37689	2.02090
C	-4.41110	-3.21163	-2.92779
H	-3.70717	-4.04577	-2.86932
H	-4.98304	-3.32612	-3.85754
H	-3.82207	-2.29232	-3.01266
C	-6.38251	-2.01232	-1.92113
H	-7.12678	-1.96477	-1.12044
H	-5.89267	-1.03394	-1.98248
H	-6.92556	-2.15797	-2.86370
C	-0.16151	-0.65484	2.00244
H	0.43912	-1.18343	2.74450
H	-1.19366	-1.00560	2.06997
C	-5.17626	2.38872	-2.20815
H	-4.47898	1.55844	-2.05983
H	-6.10184	1.97819	-2.62803
H	-4.73973	3.04607	-2.96577
C	-3.03484	5.40105	-2.22377
H	-3.90235	5.09476	-2.81594
H	-2.70273	6.37343	-2.60961
H	-2.23009	4.68189	-2.41370
C	-2.17744	6.11730	0.04483
H	-2.41351	6.29789	1.09831
H	-1.29357	5.47031	0.00711
H	-1.89520	7.08178	-0.39617
C	-3.16938	3.87844	2.83992
H	-2.27135	4.42875	2.54400
H	-3.41717	4.17367	3.86755
H	-2.90786	2.81491	2.85732
C	-5.60000	3.36561	2.39260
H	-6.49935	3.60788	1.81784
H	-5.45167	2.28091	2.33373
H	-5.80805	3.60556	3.44312

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