Shape-Persistent Arylenevinylene Macrocycles (AVMs) Prepared via Acyclic Diene Metathesis Macrocyclization (ADMAC)

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SUPPORTING INFORMATION

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1. Materials and general methods

Reagents and solvents were purchased from commercial suppliers and used without further purification, unless otherwise indicated. Ether, tetrahydrofuran, toluene, CH_2Cl_2 and DMF are purified by MBRAUN solvent purification systems.

All reactions, except those performed in aqueous solvent, were conducted under dry nitrogen in oven dried glassware. Unless otherwise specified, solvents were evaporated using a rotary evaporator after workup. Unless otherwise specified, the purity of the compounds was ≥ 95 % based on ^{1}H NMR spectral integration.

Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 32-63 μm from Dynamic Absorbants Inc. Fractions were analyzed by TLC using TLC silica gel F254 250 μm precoated-plates from Dynamic Absorbants Inc.

Analytical gel permeation chromatography (GPC) was performed using a Viscotek GPCmaxTM, a Viscotek Model 3580 Differential Refractive Index (RI) Detector, a Viscotek Model 3210 UV/VIS Detector and a set of two Viscotek Viscogel columns (7.8 × 30 cm, l-MBLMW-3078, and l-MBMMW-3078 columns) with THF as the eluent at 30 °C. The analytical GPC was calibrated using monodisperse polystyrene standards.

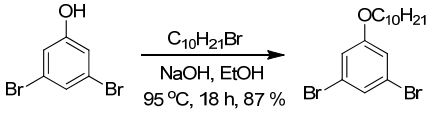
UV-vis absorption measurements were carried out with Agilent 8453 spectrophotometer and the emission measurements were obtained on a F-2500 Hitachi fluorescence spectrophotometer.

SEM images were recorded using a JSM-6480LV (LVSEM) at 5.0 kV. Sample was sputter-coated with gold prior to analysis.

Mass spectra were obtained on the Voyager-DE™ STR Biospectrometry Workstation using sinapic acid as the matrix.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. $CHCl_3$ (7.26 ppm) was used as internal references in ^{1}H NMR, and $CHCl_3$ (77.23 ppm) for ^{13}C NMR. ^{1}H NMR data were reported in order: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), number of protons, coupling constants (*J*, Hz).

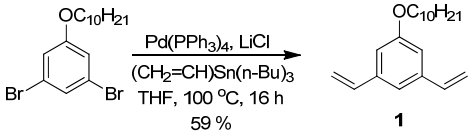
2. Experimental procedures



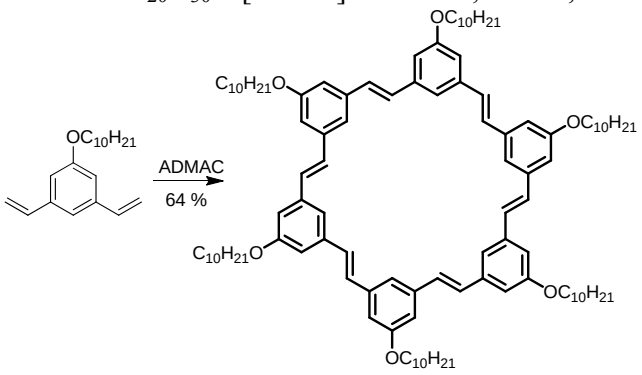
1,3-Dibromo-5-decyloxy-benzene: The procedure reported by Kandre *et. al* was followed.[1] A mixture of 3,5-dibromophenol (1.0 g, 3.97 mmol) and 1-bromodecane (922 mg, 4.17 mmol), and NaOH (167 mg, 4.17 mmol) in EtOH (25 mL) was heated in a schlenk tube at 95 °C for 18 h. It was then allowed to cool to room temperature. Water (50 mL) was added and the product was extracted with diethyl ether (4 x 40 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography using hexane as the eluent to provide the product as a colorless oil (1.35 g, 87 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.23 (1 H, t, *J* = 1.6 Hz), 6.99 (2 H, d, *J* = 1.6 Hz), 3.92 (2 H, t, *J* = 6.5 Hz), 1.92 – 1.70 (2 H,

[1] R. Kandre, K. Feldman, E. Meijer, E. H. Han, P. Smith and A. D. Schlüter, *Angew. Chem. Int. Ed.* 2007, **46**, 4956 –4959

m), 1.51 – 1.39 (2 H, m), 1.38-1.27 (12H, m), 0.89 (3 H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 160.56, 126.34, 123.26, 117.12, 68.83, 32.11, 29.76, 29.54, 29.51, 29.20, 26.13, 22.91, 14.36; HR-MS (ESI): Calcd for $C_{16}H_{24}Br_2O$ [M+Na$^+$] 415.0066; Found, 415.0069.



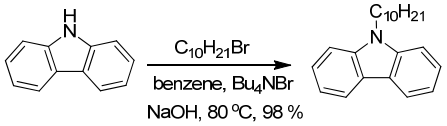
1,3-Divinyl-5-decyloxy-benzene: The procedure reported by Gauler was followed.[2] To a schlenk tube were added $Pd(PPh_3)_4$ (196 mg, 0.17 mmol), lithium chloride (73 mg, 1.72 mmol), and vinyltributylstannane (2.40 g, 7.58 mmol), followed by a solution of 1,3-dibromo-5-decyloxy-benzene (1.35 g, 3.44 mmol) in THF (35 mL). The mixture was stirred at 100 °C for 16 h, then allowed to cool to rt. Water (60 mL) was added and the mixture was extracted with diethyl ether (4 x 40 mL). The combined organic extracts were dried over Na_2SO_4, concentrated, and purified by flash column chromatography using hexane as eluent to yield pure product as a colorless oil (580 mg, 59 %): ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.02 (1 H, s), 6.86 (2 H, d, J=1.4 Hz), 6.67 (2 H, dd, J = 17.6, 10.9 Hz), 5.75 (2 H, dd, J = 17.6, 0.7 Hz), 5.32 – 5.21 (2 H, m), 3.98 (2 H, t, J = 6.6 Hz), 1.81-1.62 (2 H, m), 1.47-1.43 (2 H, m), 1.36 – 1.24 (12 H, m), 0.88 (3 H, t, J = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 159.75, 139.18, 136.90, 117.42, 114.46, 111.78, 68.23, 32.12, 29.81, 29.79, 29.62, 29.55, 29.52, 26.28, 22.91, 14.36; HR-MS (ESI): Calcd for $C_{20}H_{30}O$ [M+Li$^+$] 293.2451; Found, 293.2455.



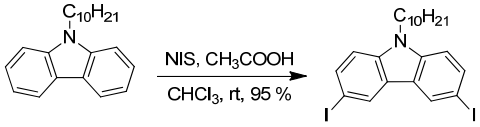
AVM 2: To a schlenk tube were added 1,3-divinyl-5-decyloxy-benzene (**1**, 217 mg, 0.76 mmol) and a solution of Grubb's 2nd generation catalyst (48 mg, 0.076 mmol) in 1,2,4-trichlorobenzene (14 mL). The reaction apparatus was evacuated and refilled with nitrogen, and this process was repeated three times. The red solution was heated at 35 °C under nitrogen for 18 h. All the solvent was removed and diethyl ether (100 mL) was added. The ethereal solution was washed with water (3 x 50 mL), dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography using CH_2Cl_2 and hexane (1:1, v/v) as the eluent afforded AVM **2** as a white solid (109 mg, 64 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.29 (1 H, s), 7.06 (2 H, s), 6.90 (2 H, d, J = 0.9 Hz), 3.99 (2 H, t, J = 6.6 Hz), 1.87 – 1.78 (2 H, m), 1.54 – 1.46 (3 H, m), 1.42-1.28 (15 H, dd, J = 27.1, 5.6), 0.91 (3 H, t, J = 6.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 159.91, 138.61, 128.55, 117.87, 112.01, 68.23, 32.16, 29.90, 29.86, 29.75, 29.66,

[2] R. Gauler and N. Risch, Eur. *J. Org. Chem.* **1998**, *63*, 1193-1200.

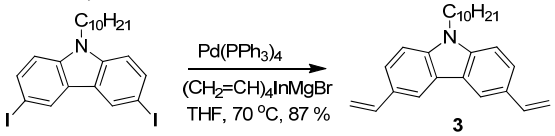
29.61, 26.38, 22.94, 14.38; MS (MALDI) calc'd for $C_{108}H_{156}O_6$ ($[M+H]^+$) 1551.19, found 1551.90.



9-Decylcarbazole: The procedure described by Zhao *et al*. was followed.[3] To a solution of carbazole (2.00 g, 12.0 mmol) in benzene (8 mL) were added phase-transfer catalyst $^{n}Bu_4NBr$ (1.5 g), 1-bromodecane (3.30 g, 15.0 mmol), and 50 % aqueous NaOH solution (16.0 mL). The mixture was heated at 80 °C for 2.5 h and allowed to cool to room temperature. The reaction mixture was extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography using hexane as the eluent provided 9-decylcarbazole as a colorless oil (3.60 g, 98 %): ^{1}H NMR(500 MHz, $CDCl_3$) δ_H 8.12 (2 H, d, J = 7.7 Hz), 7.48 (2 H, ddd, J = 8.2, 7.0, 1.2 Hz), 7.42 (2 H, d, J = 8.2 Hz), 7.26 – 7.21 (2 H, m), 4.31 (2 H, t, J = 7.3 Hz), 1.96 – 1.80 (2 H, m), 1.47 – 1.16 (14 H, m), 0.94 – 0.80 (3 H, m). The NMR spectral data are consistent with that reported in the literature.[4]



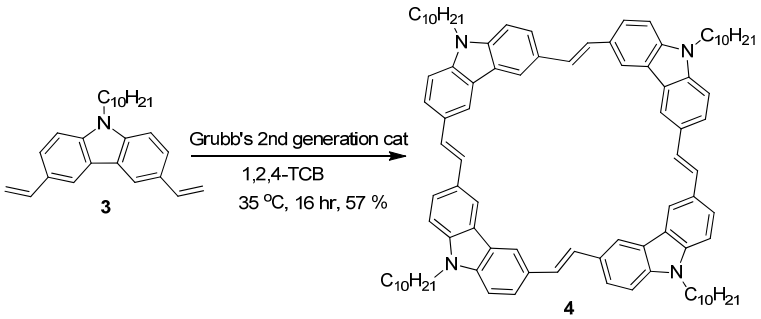
3,6-Diiodo-9-decylcarbazole: The procedure described by Zhao *et al*. was followed.[3] To a solution of 9-decylcarbazole (3.60 g, 11.7 mmol) and N-iodosuccinimide (5.53 g, 24.6 mmol) in $CHCl_3$ (78 mL) was added CH_3COOH (27 mL). The reaction mixture was stirred at room temperature for 10 h. The volatiles were removed and water (100 mL) was added. The mixture was extracted with $CHCl_3$ (3 x 100 mL). The combined organic extracts were dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography using hexane as the eluent afforded 3,6-diiodo-9-decylcarbazole as a white solid (6.40 g, 98 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.34 (2 H, d, J = 1.6 Hz), 7.72 (2 H, dd, J = 8.6, 1.7 Hz), 7.19 (2 H, d, J = 8.6 Hz), 4.24 (2 H, t, J = 7.2 Hz), 1.89 – 1.74 (2 H, m), 1.40 – 1.15 (14 H, m), 0.88 (3 H, t, J = 7.0).



3,6-Divinyl-9-decylcarbazole (3): The procedure described by Lee *et al.* was followed.[5] A solution of $InCl_3$ (114 mg, 0.52 mmol) in THF (4 mL) was stirred and cooled to -78 °C, as vinylmagnesium bromide (2.07 mL, 2.07 mmol, 1M solution in THF) was added dropwise. After

[3] T. Zhao, Z. liu, Y. Song, W. Xu, D. Zhang and Zhu, D. *J. Org. Chem.* 2006, **71**, 7422-7432.
[4] a) D. Bogdal, J. Pielichowski and K. Jaskot, *Heterocycles* 1997, **45**, 715-722.
[5] P. H. Lee, S. W. Lee, and D. Seomoon, *Org. Lett.* 2003, **5**, 4963-4966.

stirring at -78 °C for 35 min, the solution was stirred at room temperature for another 30 min. To another schlenk tube were added 3,6-diiodo-9-decylcarbazole (290 mg, 0.52 mmol), $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) and THF (4 mL). The pregenerated indate solution was added to the above schlenk tube by cannula transfer, and the mixture was heated at 70 °C for 1.5 hr. After cooling to room temperature saturated $NaHCO_3$ solution (30 mL) was added. The mixture was filtered and the filtrate was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography using hexane and EtOAc (20:1, v/v) as the eluent provided the pure product as a white solid (130 mg, 87 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.13 (2 H, s), 7.58 (2 H, d, J = 8.4 Hz), 7.37 (2 H, t, J = 18.8 Hz), 6.92 (2 H, dd, J = 17.5, 10.9 Hz), 5.79 (2 H, d, J = 17.5 Hz), 5.21 (2 H, d, J = 10.9 Hz), 4.28 (2 H, t, J = 7.2 Hz), 1.92 – 1.80 (2 H, m), 1.38 – 1.19 (27 H, m), 0.88 (3 H, t, J = 6.9 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.86, 137.64, 129.15, 124.29, 123.24, 118.64, 111.26, 109.03, 43.47, 32.06, 29.70, 29.61, 29.48, 29.21, 27.47, 22.88, 14.35. The NMR spectral data are consistent with that reported by Du *et. al*.[6]



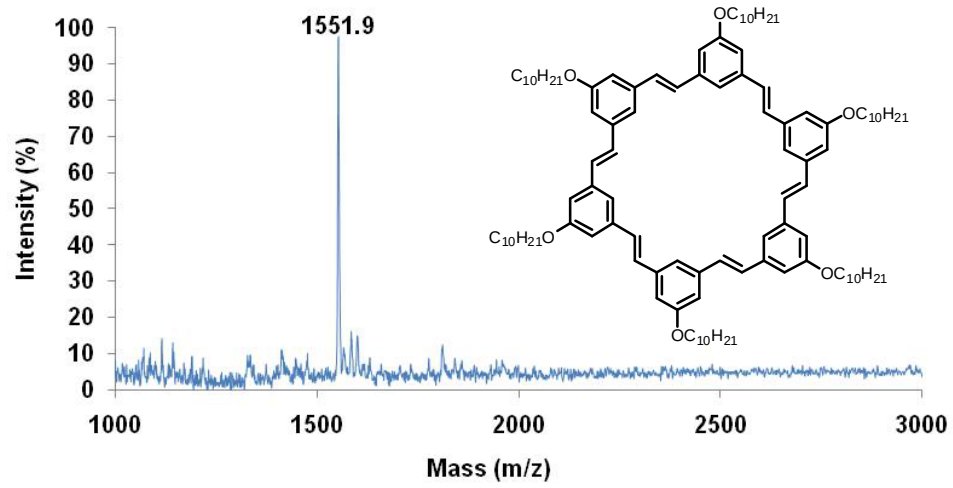
AVM 4: To a schlenk tube were added 3,6-divinyl-9-decylcarbazole (**3**, 120 mg, 0.33 mmol) and a solution of Grubb's 2nd generation catalyst (28 mg, 0.033 mmol) in 1,2,4-trichlorobenzene (6.6 mL). The reaction apparatus was evacuated and refilled with nitrogen, and this process was repeated three times. The red solution was heated at 35 °C under nitrogen for 16 h. The mixture was cooled to room temperature and diethyl ether (50 mL) was added. Light yellow solid immediately precipitated from the solution. The mixture was washed with water (3 x 50 mL) and centrifuged. The superanant was removed and the solid was washed with Et_2O (3 x 5 mL), and dried to provide AVM **4** as a light yellow solid (63 mg, 57 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.43 (2 H, s), 7.72 (2 H, dd, J = 8.5, 1.6 Hz), 7.45 (2 H, s), 7.39 (2 H, d, J = 8.5 Hz), 4.31 (2 H, t, J = 7.1 Hz), 2.00 – 1.88 (2 H, m), 1.41 – 1.36 (2 H, m), 1.33 – 1.27 (12 H, m), 0.90 (3 H, t, J = 7.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.73, 129.50, 126.66, 124.82, 123.85, 118.19, 109.18, 43.55, 32.13, 29.78, 29.67, 29.52, 29.32, 27.60, 22.89, 14.26. MS (MALDI) calc'd for $C_{96}H_{116}N_4$ ([M+]) 1325.92, found 1326.60.

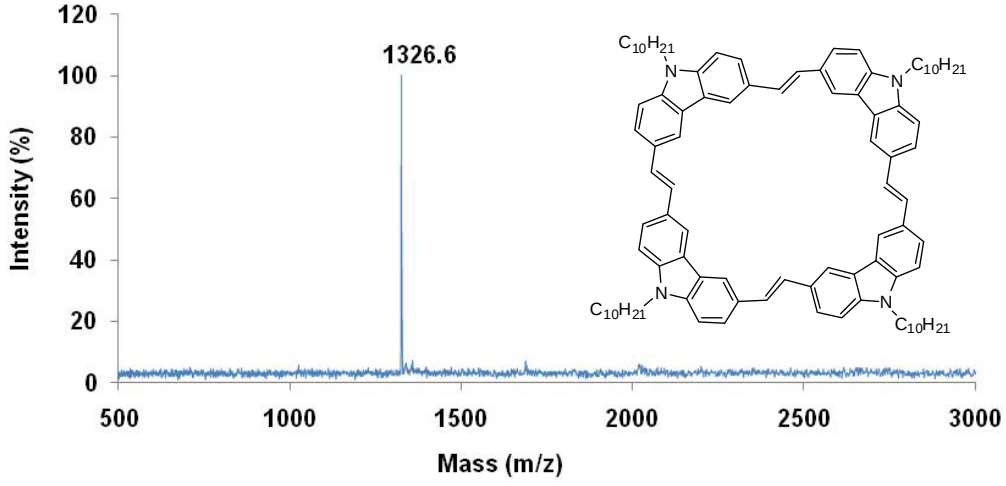
[6] J. Du, Q. Fang, X. Chen, S. Ren, A. Cao and B. Xu, *Polymer* 2005, **46**, 11927-11933.

Self Assembly Processing:

A solution injection method described by Balakrishnan *et. al* was followed.[7] Concentrated solution of AVM **2** (20 µL, 1mM) or **4** (50 µL, 0.5 mM) in $CHCl_3$ was injected to CH_3CN (5 mL), followed by rapid mixing. White (AVM **2**) or Light yellow (AVM **4**) precipitates formed slowly, which were observed as nanofibrils by SEM.

3. MALDI mass spectra of AVMs 2 & 4

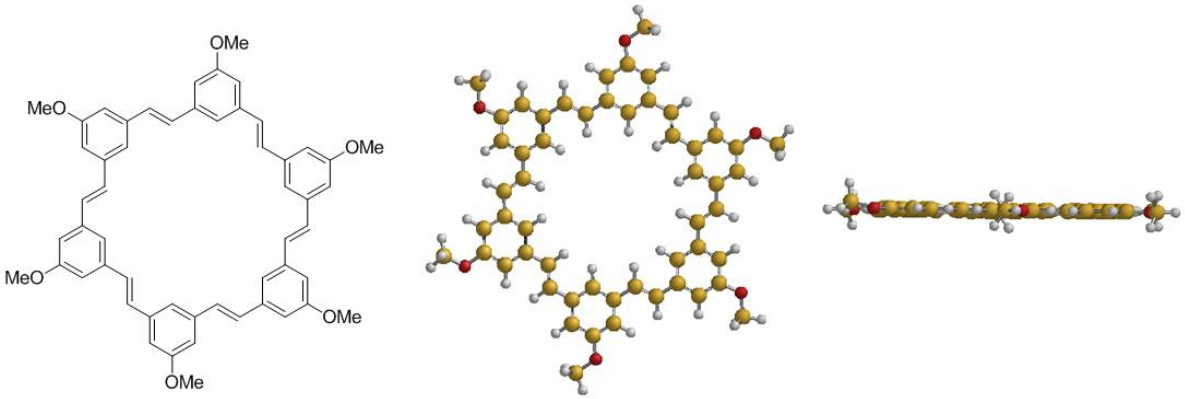




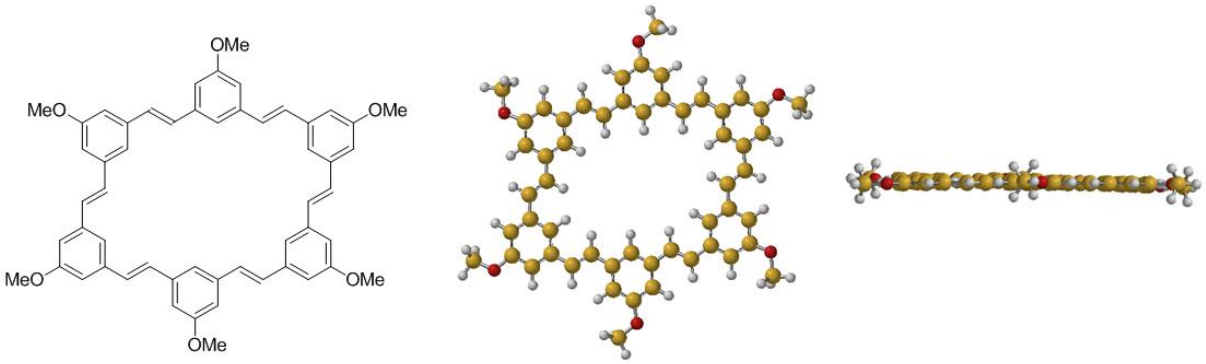
[7] K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo and L. Zang, *J. Am. Chem. Soc.* 2005, **127**, 10496-10497.

4. Computer Modeling and calculation

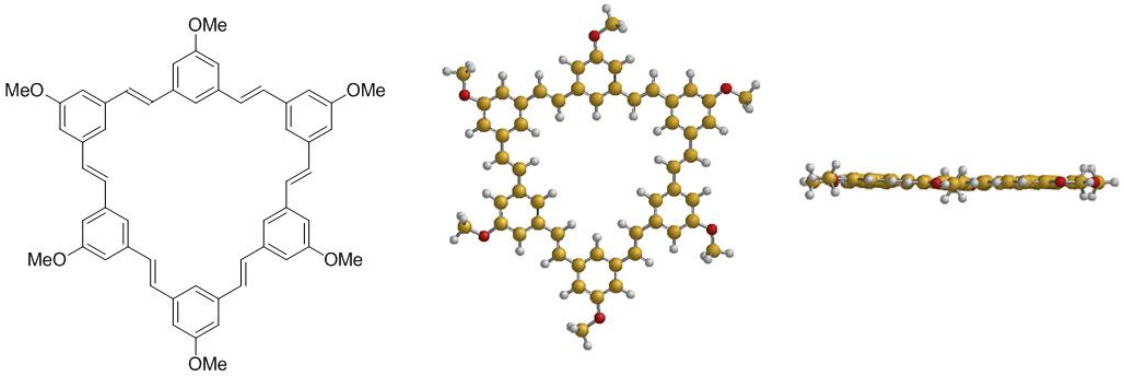
The cyclic structures of AVM **2** and AVM **4** preclude the *cis* conformation of the -C=C- bond. The concerted rotation of the -C=C- bond around phenylene-vinylene-phenylene linkage results in 8 conformers for AVM **2** and 4 conformers for AVM **4**. Energy minimized configurations of these conformers and their heat of formation were obtained using Spartan 04 at semi-empirical (PM3) level. Methyl group was used in calculation instead of decyl for simplification. AVM **2**' and AVM **4**' are used for the methyl substituted analogues of AVM **2** and AVM **4**. AVM-2'-conformer-1 and AVM-4'-conformer-1 are the most favored conformers of AVM **2**' and AVM **4**'.



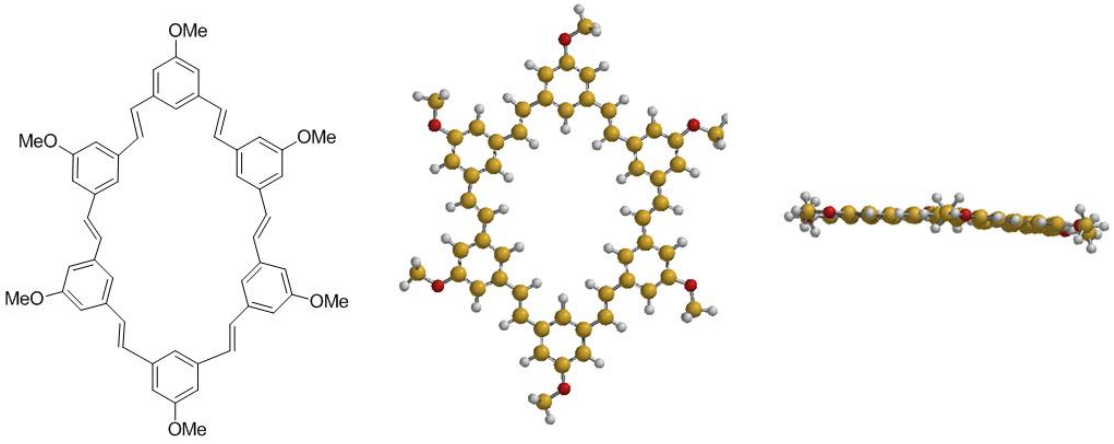
AVM-2'-Conformer-1: Heat of formation (0.082 kcal/mol)



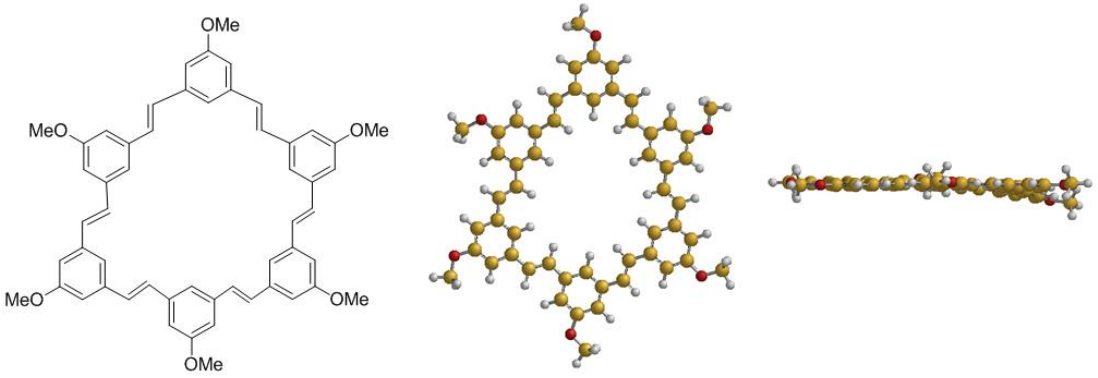
AVM-2'-Conformer-2: Heat of formation (0.151 kcal/mol)



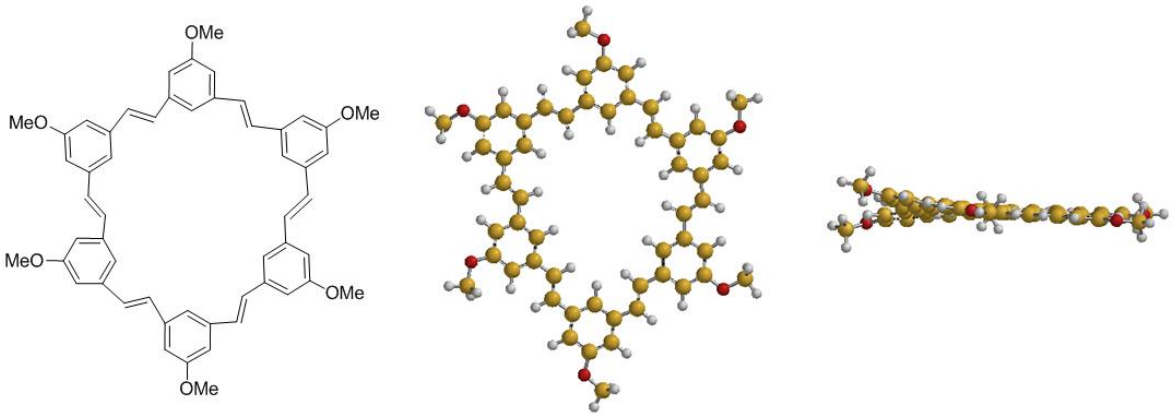
AVM-2'-Conformer-3: Heat of formation (0.213 kcal/mol)



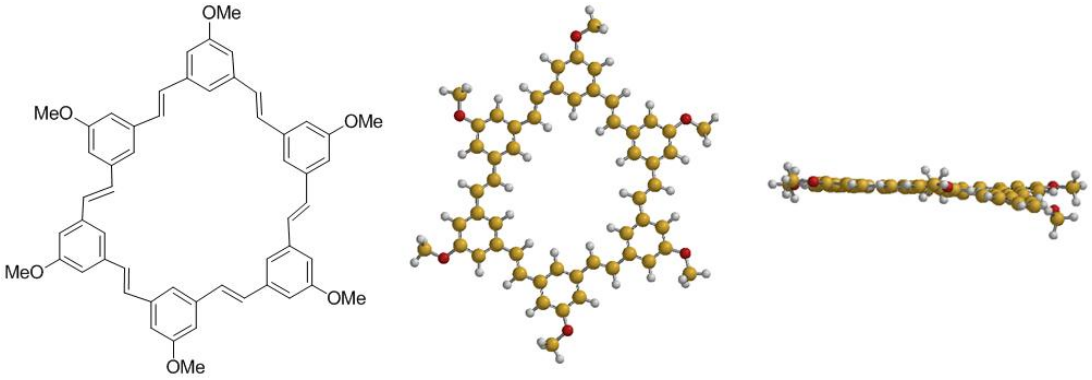
AVM-2'-Conformer-4: Heat of formation (1.798 kcal/mol)



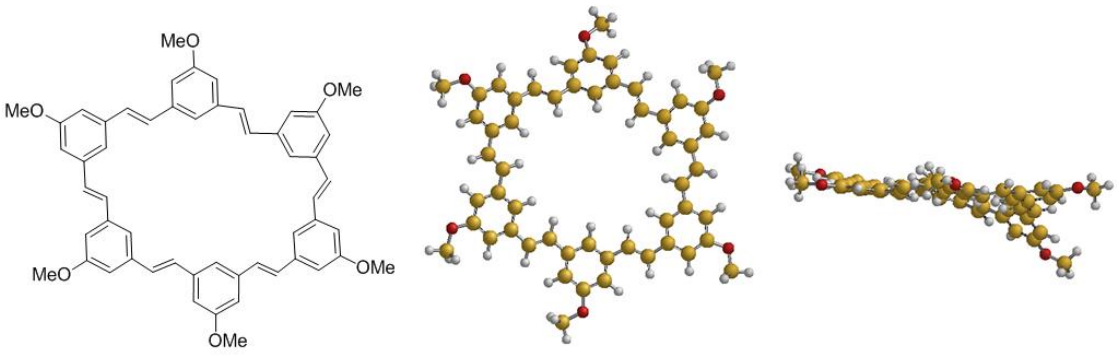
AVM-2'-Conformer-5: Heat of formation (2.077 kcal/mol)



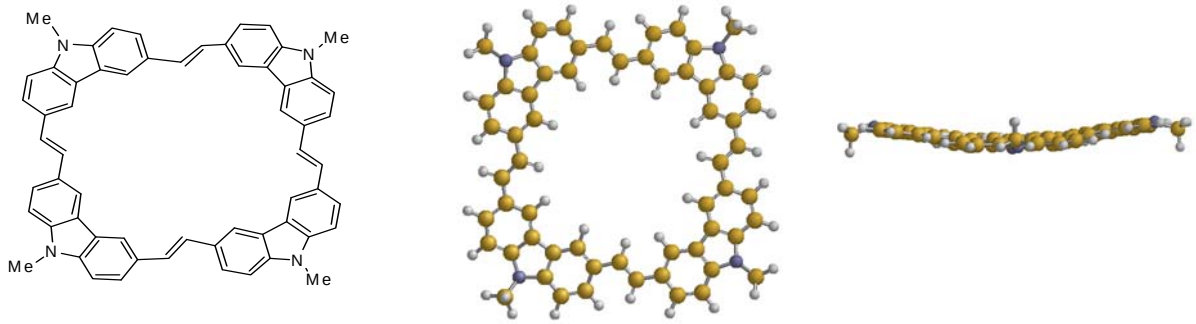
AVM-2'-Conformer-6: Heat of formation (2.101 kcal/mol)



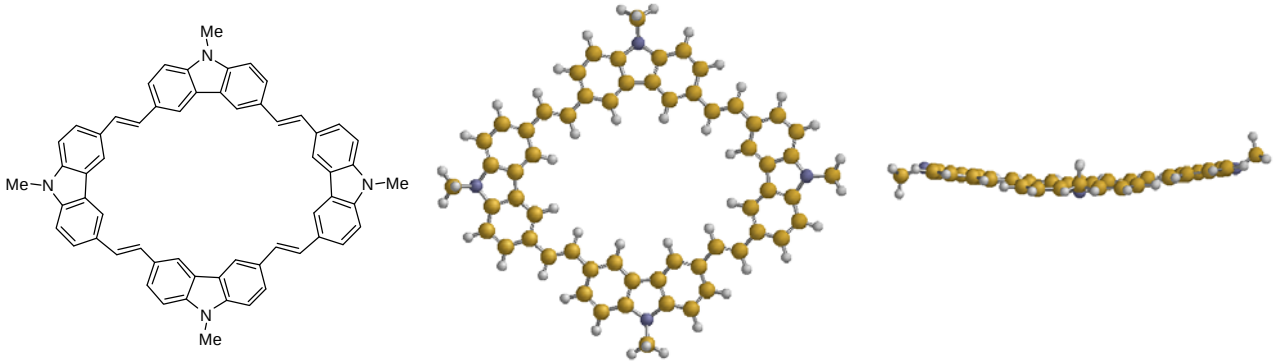
AVM-2'-Conformer-7: Heat of formation (2.122 kcal/mol)



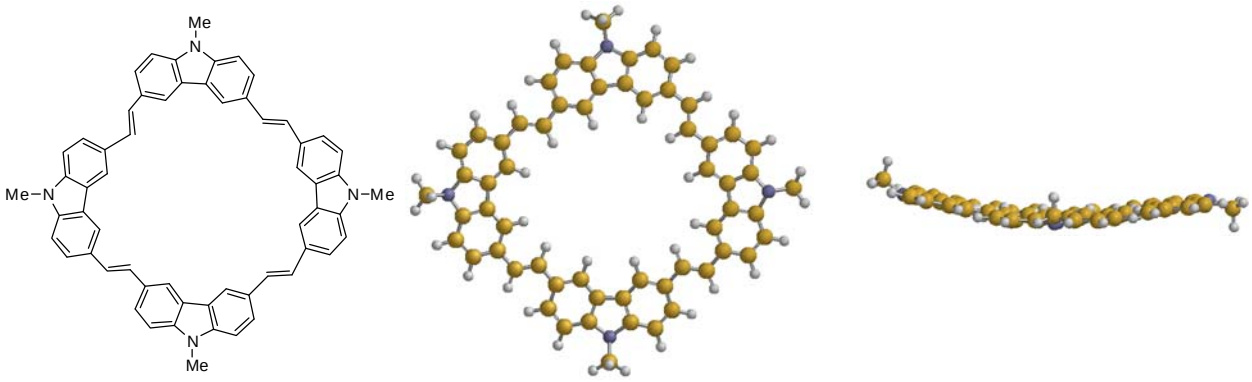
AVM-2'-Conformer-8: Heat of formation (4.570 kcal/mol)



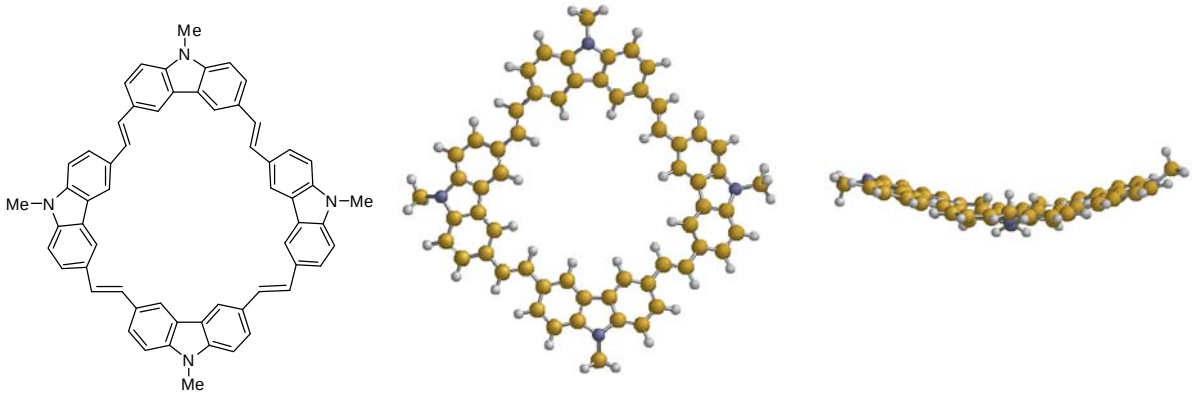
AVM-4'-Conformer-1: Heat of formation (268.824 kcal/mol)



AVM-4'-Conformer-2: Heat of formation (268.860 kcal/mol)

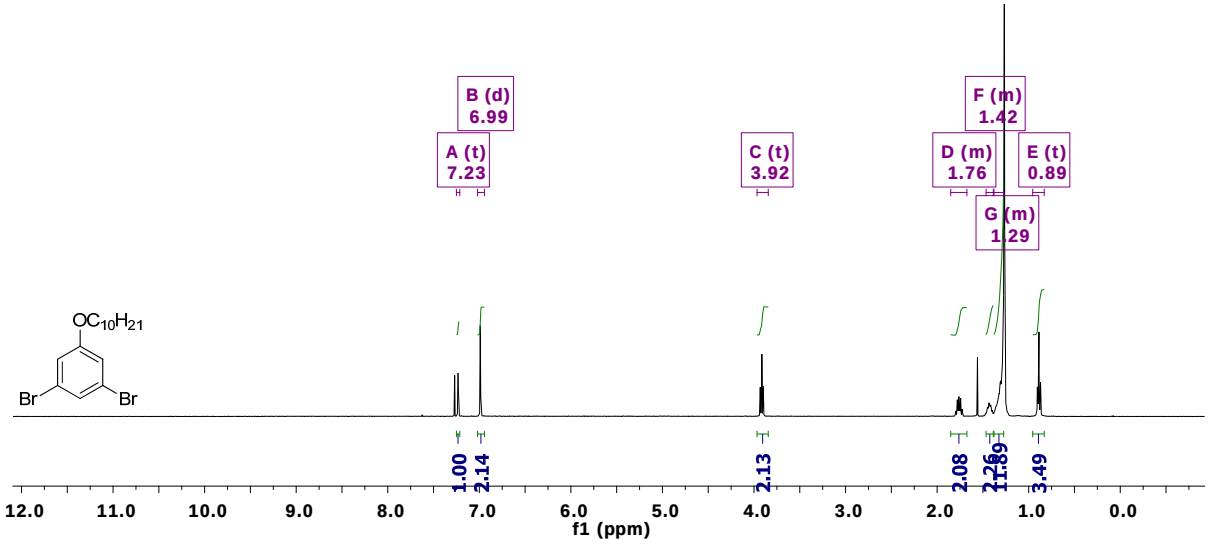


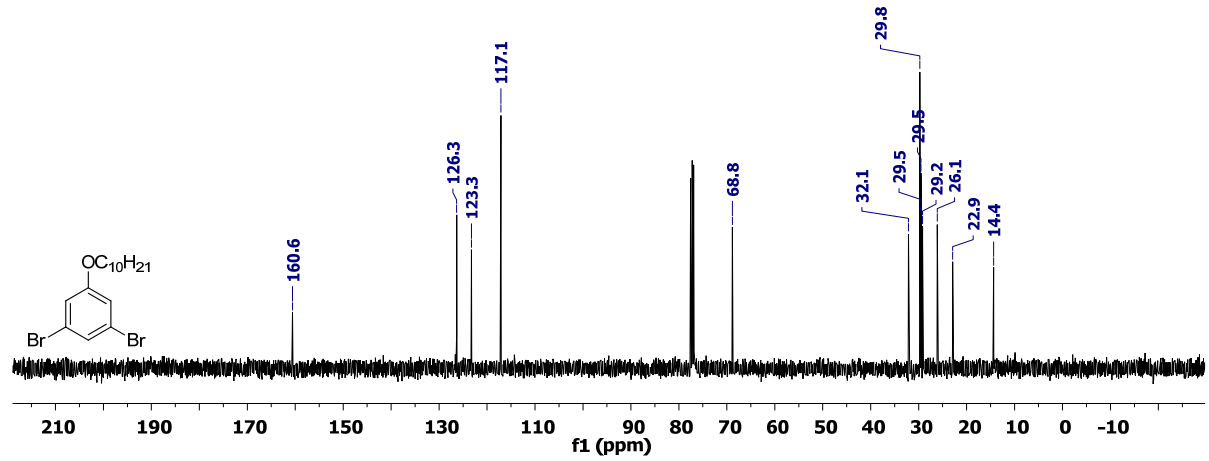
AVM-4'-Conformer-3: Heat of formati on (270.412 kcal/mol)

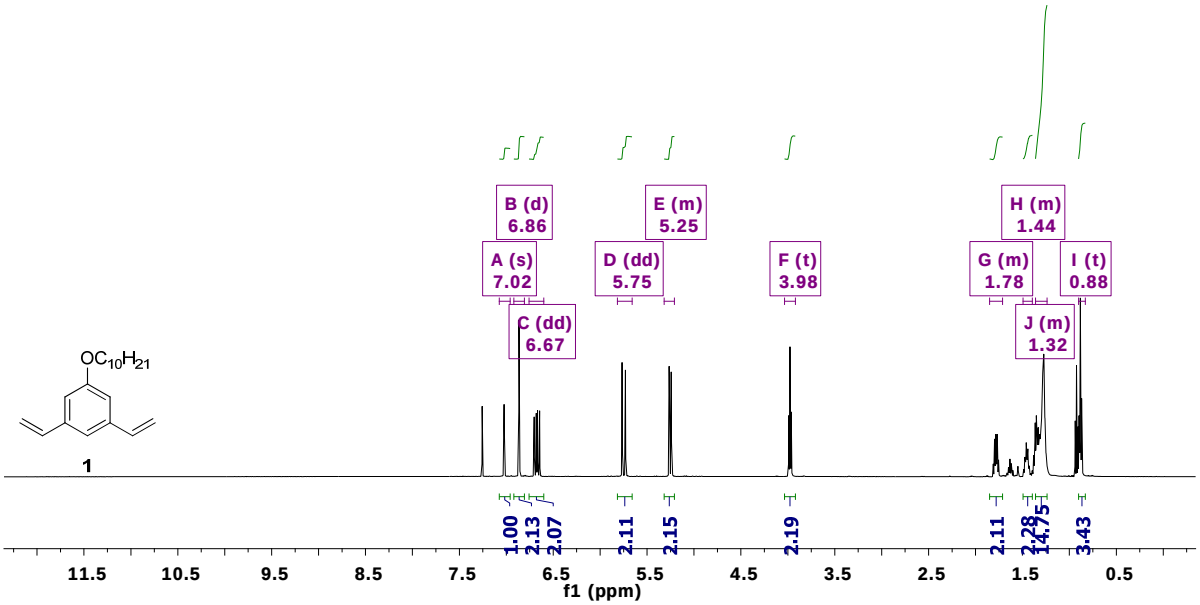


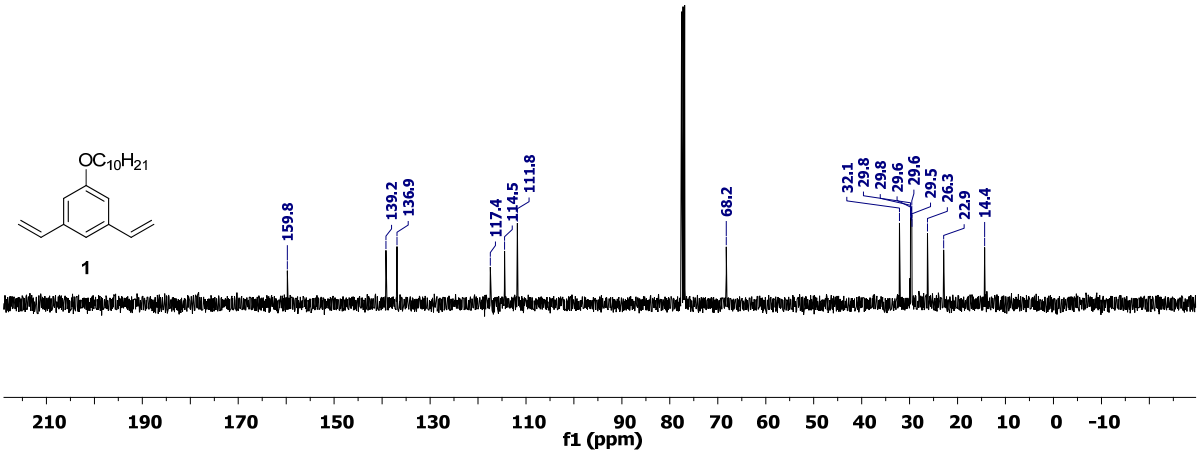
AVM-4'-Conformer-4: Heat of formation (271.472 kcal/mol)

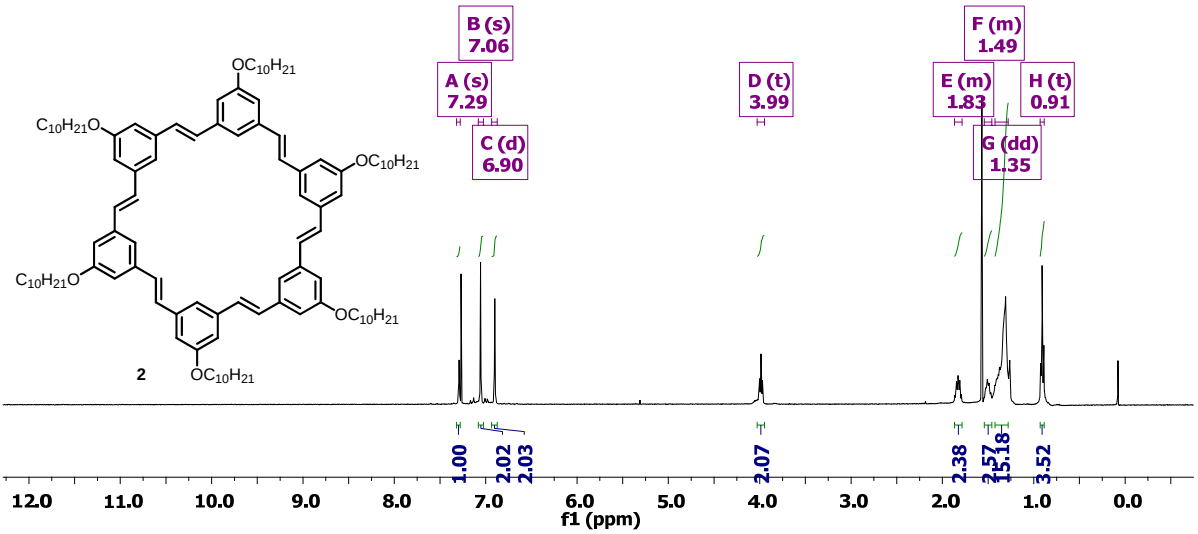
5. NMR spectra of selected compounds

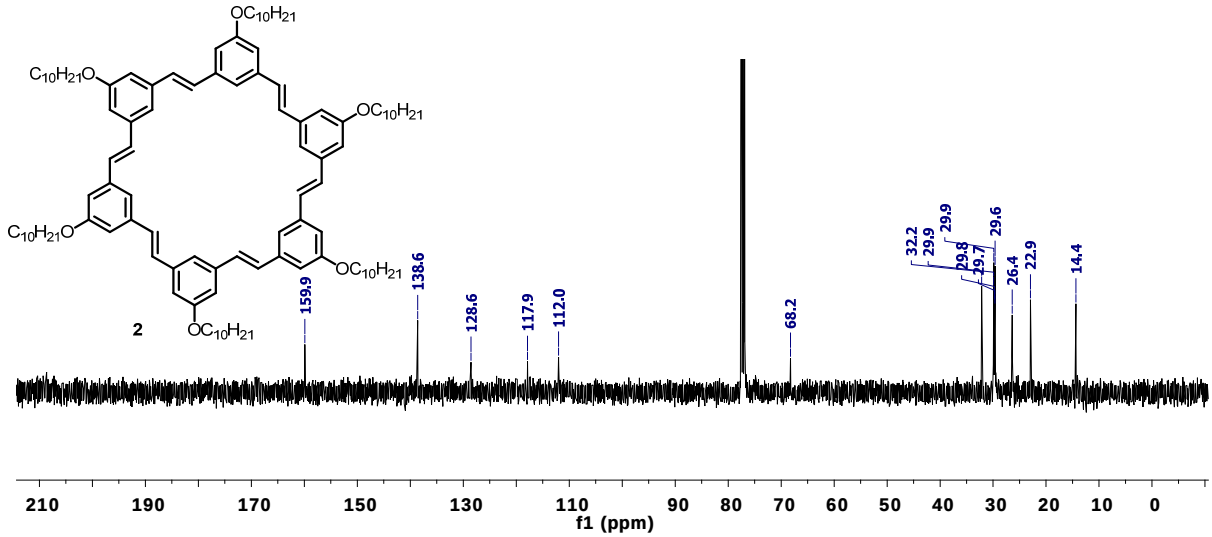


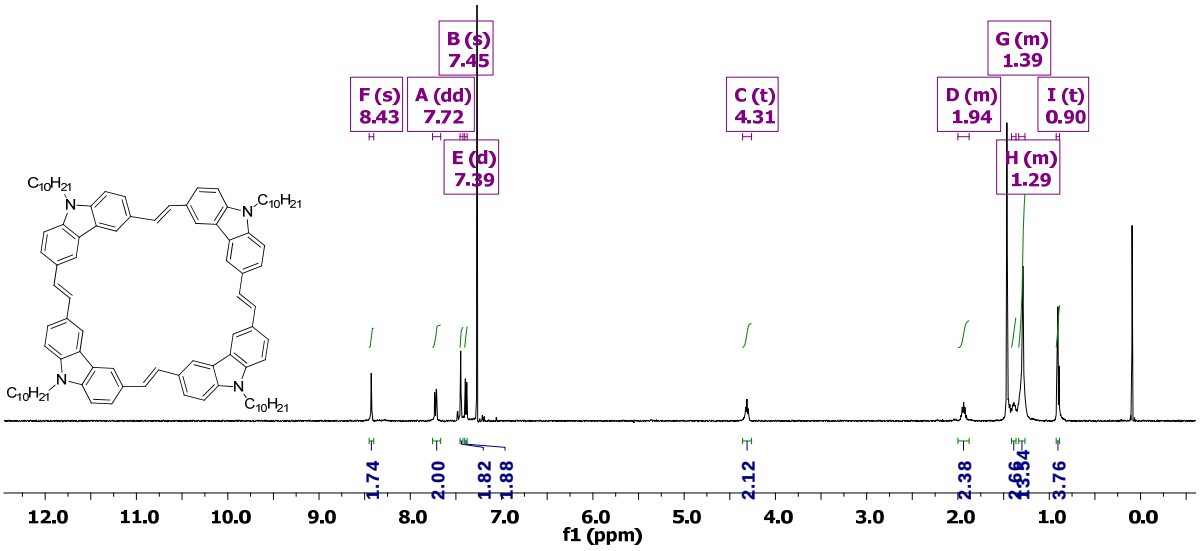


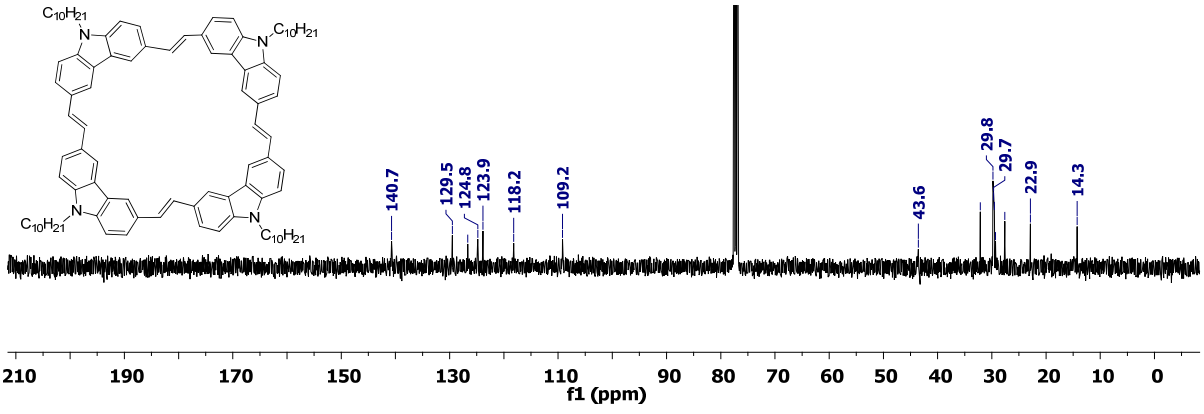

B (d)
6.86
A (s)
7.02
C (dd)
6.67
D (dd)
5.75
E (m)
5.25
F (t)
3.98
H (m)
1.44
G (m)
1.78
I (t)
0.88
J (m)
1.32
OC10H21
1
1.00
2.13
2.07
2.11
2.15
2.19
2.11
2.28
14.75
3.43
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


OC10H21
1
159.8
139.2
136.9
117.4
114.5
111.8
68.2
32.1
29.8
29.8
29.6
29.6
29.5
26.3
22.9
14.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


B (s)
7.06
A (s)
7.29
C (d)
6.90
D (t)
3.99
F (m)
1.49
E (m)
1.83
H (t)
0.91
G (dd)
1.35
OC10H21
C10H21O
2
1.00
2.02
2.03
2.07
2.38
2.57
15.18
3.52
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


OC10H21
C10H21O
2
159.9
138.6
128.6
117.9
112.0
68.2
32.2
29.9
29.9
29.8
29.7
29.6
26.4
22.9
14.4
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


B (s)
7.45
F (s)
8.43
A (dd)
7.72
E (d)
7.39
C (t)
4.31
G (m)
1.39
D (m)
1.94
I (t)
0.90
H (m)
1.29
1.74
2.00
1.82
1.88
2.12
2.38
3.76
f1 (ppm)


140.7
129.5
124.8
123.9
118.2
109.2
43.6
29.8
29.7
22.9
14.3
f1 (ppm)