Highly CO_2-Selective Organic Molecular Cages: What Determines the CO_2 Selectivity

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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. Reagent-grade $CHCl_3$ was purchased from Mallinckrodt Chemicals, and anhydrous CH_3CN was purchased from Sigma-Aldrich. 1,3,5-trihexyl-2,4,6-tris(4-aminophenyl)benzene **11**, cage **2**, and analog **13** were synthesized as previously reported.[1] 1,8-Diformylanthracene **4** was prepared from 1,8-dicyanoanthracene as reported in the literature. [2]

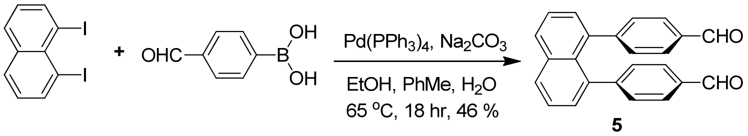
All reactions, except those performed in aqueous solvent, were conducted under dry nitrogen in oven-dried glassware. Unless otherwise specified, solvents were evaporated using a rotary evaporator after workup.

Unless otherwise specified, the purity of the compounds was ≥ 95 % based on ^1H 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.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. $CHCl_3$ (7.26 ppm) was used as internal references in ^1H NMR, and $CHCl_3$ (77.23 ppm) for ^{13}C NMR. ^1H 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), and assignments.

2. Procedures



1,8-bis(4-formylphenyl)naphthalene (5): The procedure reported by Feldman[3] et. al was followed. In a Schlenk tube, 1,8-diiodonaphthalene (1.43 g, 3.76 mmol), 4-formylphenylboronic acid (1.69 g, 11.3 mmol), $Pd(PPh_3)_4$ (434 mg, 0.38 mmol) and Na_2CO_3 (1.19 g, 11.3 mmol) were added. The reaction apparatus was then evacuated and refilled with nitrogen. Toluene (10 mL), EtOH (10 mL) and H_2O (5 mL) were added and the mixture was degassed three times before heating at 65 °C for 18 h. Water (50 mL) was added, and the mixture was extracted with ethyl acetate (3 x 50 mL). The organic extracts were washed with water (2 x 50 mL), and brine (50

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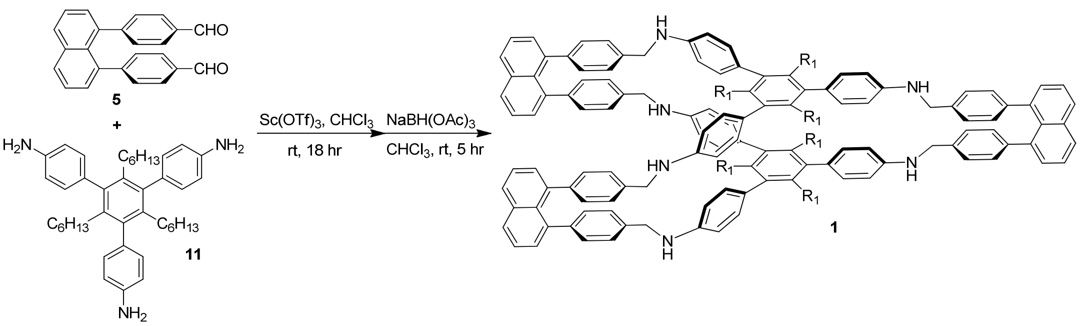
[1] Jin, Y.; Voss, B. A.; Noble, R. D.; Zhang, W. *Angew. Chem. Int. Ed.* **2010**, *49*, 6348-6351.

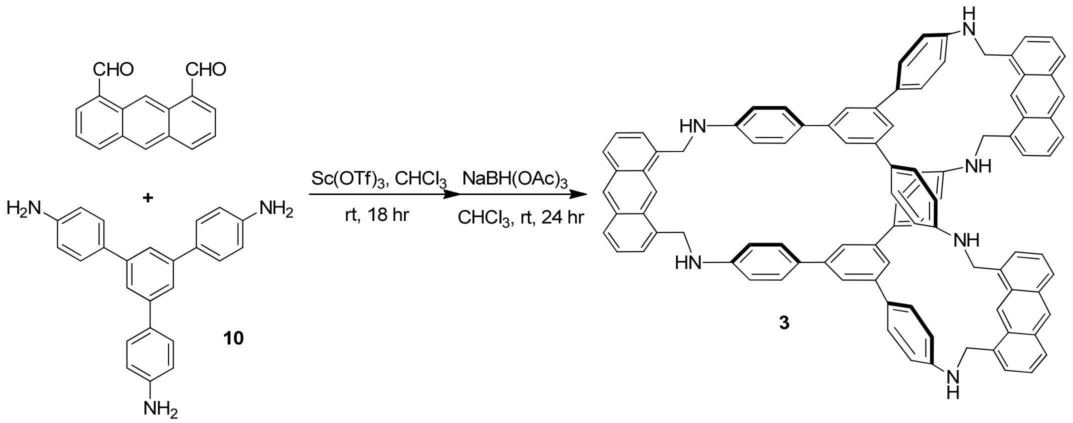
[2] Guilard, R.; Lopez, M. A.; Tabard, A.; Richard, P.; Lecomte, C.; Brands, S.; Hutchison, J. E.; Collman, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 9877.

[3] Feldman, K. S.; Campbell, R. F. *J. Org. Chem.* **1995**, *60*, 1924-1925.

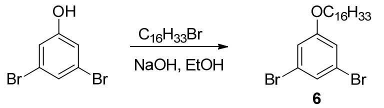
mL), dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography (gradient elution, 8 % EtOAc in hexane → 30 % EtOAc in hexane) yielded 1-iodo-8-(4-formylphenyl)naphthalene (480 mg, 52 % corrected for recovered) and the recovered 1,8-diiodonaphthalene (450 mg, 69 % conversion). The Suzuki coupling procedure described above was followed. 1-Iodo-8-(4-formylphenyl)naphthalene (480 mg, 1.34 mmol) was converted to 1,8-bis(4-formylphenyl)naphthalene (401 mg, 89 %) using 4-formylphenylboronic acid (402 mg, 2.68 mmol), $Pd(PPh_3)_4$ (77 mg, 0.067 mmol), Na_2CO_3 (284 g, 2.69 mmol), Toluene (10 mL), THF (10 mL), and H_2O (5 mL). The physical data for compound **5**: ^1H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 2H), 8.04 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.63 (dd, *J* = 8.2, 7.0 Hz, 2H), 7.48 – 7.44 (m, 6H), 7.19 – 7.15 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.79, 149.49, 138.77, 135.59, 134.21, 131.50, 130.60, 129.85, 129.02, 128.89, 125.72; HR-MS (ESI): Calcd for $C_{24}H_{16}O_2$ $[M+H^+]$ 337.1223; Found, 337.1220.



Cage 1: To a solution of 1,3,5-trihexyl-2,4,6-tris(4-aminophenyl)benzene **11** (362 mg, 0.60 mmol) and 1,8-bis(4-formylphenyl)naphthalene (**5**) (304 mg, 0.90 mmol) in chloroform (200 mL) was added $Sc(OTf)_3$ (44 mg, 0.090 mmol) in CH_3CN (10 mL) dropwise. The yellow solution was stirred at rt for 24 hr. $NaBH(OAc)_3$ (3.81 g, 18.0 mmol) was added, and the yellow suspension was stirred at rt for 5 hr. The mixture was quenched by the addition of saturated $NaHCO_3$ (50 mL), and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (3 x 50 mL). The combined organics were dried over Na_2SO_4 and concentrated to give crude product. Purification by flash column chromatography (20 % EtOAc in hexane as eluent) yielded the molecular cage **1** (570 mg, 90 %) as a light yellow solid: ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 6H), 7.58 (t, *J* = 7.6 Hz, 6H), 7.44 (d, *J* = 7.0 Hz, 6H), 7.14 (d, *J* = 8.1 Hz, 6H), 7.10 – 7.00 (m, 24H), 6.82 (d, *J* = 8.2 Hz, 6H), 6.68 (dd, *J* = 8.1, 2.1 Hz, 6H), 6.52 (dd, *J* = 8.2, 2.1 Hz, 6H), 4.23 (s, 12H), 3.61 (s, 6H), 2.23 – 1.99 (m, 12H), 1.24 – 1.16 (m, 12H), 1.09 – 1.02 (m, 12H), 0.92 – 0.83 (m, 24H), 0.77 (t, *J* = 7.3 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.70, 142.71, 140.34, 139.77, 139.23, 137.10, 135.67, 131.86, 131.60, 131.27, 130.71, 130.40, 129.63, 128.81, 126.69, 125.43, 112.74, 112.31, 49.25, 32.05, 31.24, 31.16, 29.81, 22.64, 14.48; MS (MALDI) calc'd for $C_{156}H_{162}N_6$ ([M+]) 2120.29, found 2120.52.



Cage 3: The same imine metathesis and reduction procedure described above were followed. 1,3,5-Tris(4-aminophenyl)benzene (250 mg, 0.71 mmol), 1,8-diformylanthracene (250 mg, 1.07 mmol), Sc(OTf)$_3$ (52 mg, 0.11 mmol), $CHCl_3$ (237 mL), CH_3CN (12 mL) and NaBH(OAc)$_3$ (451 mg, 21.3 mmol) were used to prepare cage **3** (348 mg, 75 %). The physical data for compound **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (s, 3H), 8.50 (s, 3H), 8.00 (d, J = 12.5 Hz, 6H), 7.51 (d, J = 6.5 Hz, 6H), 7.48 – 7.42 (m, 6H), 7.37 – 7.32 (m, 6H), 7.30 – 7.23 (m, 12H), 6.56 (d, 12H), 4.71 (s, 12H), 3.78 (br s, J = 17.1, 10.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.27, 141.71, 134.89, 132.16, 131.49, 130.59, 129.05, 128.07, 127.24, 125.41, 122.42, 112.80, 48.04; MS (MALDI) calc'd for $C_{96}H_{72}N_6$ ([M+]) 1309.64, found 1309.22.



1,3-Dibromo-5-hexadecyloxy-benzene (6): The procedure reported by Kandre *et. al* was followed.[4] A mixture of 3,5-dibromophenol (1.5 g, 5.95 mmol) and 1-bromohexadecane (1.91 g, 6.25 mmol), and NaOH (250 mg, 6.25 mmol) in EtOH (30 mL) was heated in a schlenk tube at 100 °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 (3 x 70 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 (2.50 g, 88 %):^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, J = 1.6 Hz, 1H), 6.99 (d, J = 1.6 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.49 – 1.39 (m, 2H), 1.38 – 1.20 (m, 24H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.55, 126.33, 123.26, 117.12, 68.83, 32.16, 29.92, 29.80, 29.76, 29.60, 29.51, 29.20, 26.12, 22.93, 14.37.

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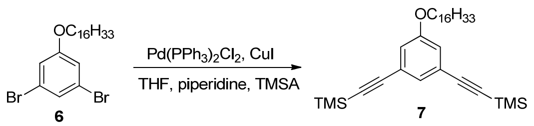
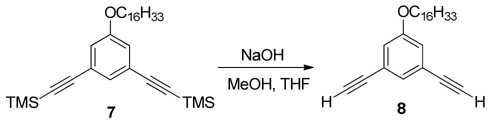
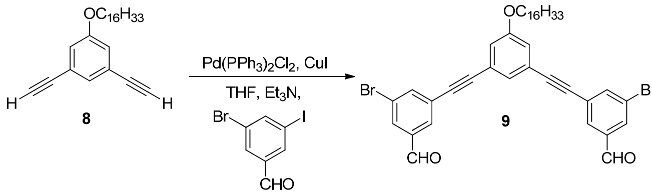
[4] R. Kandre, K. Feldman, E. Meijer, E. H. Han, P. Smith and A. D. Schlüter, *Angew. Chem. Int. Ed.* 2007, **46**, 4956 –4959



1-Hexadecyloxy-3,5-bis[2-(1,1,1-trimethylsilyl)-1-ethynyl]benzene (7): The general Sonogashira coupling procedure was followed.[5] To a Schlenk tube were added Pd(PPh$_3$)$_2$Cl$_2$ (221 mg, 0.32 mmol), CuI (20 mg, 0.11 mmol), a solution of compound **6** (2.50 g, 5.25 mmol) in THF (20 mL), and piperidine (15 mL). The mixture was degassed by evacuating and refilling with nitrogen three times. Trimethylsilylacetylene (2.08 g, 26.3 mmol) was added and heated at 65 ^{o}C for 4 h. The mixture was cooled to room temperature and filtered to remove the precipitates. The filtrate was concentrated and the residue was purified by flash column chromatography (gradient elution, hexane → 2 % EtOAc in hexane) to yield compound **7** as a yellow solid (2.60 g, 97 %): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 (t, *J* = 1.3 Hz, 1H), 6.94 (d, *J* = 1.4 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 1.81 – 1.68 (m, 2H), 1.49 – 1.38 (m, 2H), 1.33 – 1.24 (m, 24H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.24 (s, 18H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.78, 128.19, 124.33, 118.49, 104.33, 94.69, 68.41, 32.16, 29.93, 29.89, 29.82, 29.60, 29.56, 29.33, 26.18, 22.93, 14.37, 0.12; HR-MS (ESI): Calcd for $C_{32}H_{54}OSi_2$ [M+H$^+$] 511.3786; Found, 511.3787.



1-Hexadecyloxy-3,5-biethynylbenzene (8): To a solution of compound **7** (2.60 g, 5.09 mmol) in THF (40 mL) and MeOH (150 mL) was added a solution of NaOH (2.03 g, 50.9 mmol) in H$_2$O (3 mL) dropwise. The solution was stirred at room temperature for 1 h, and the volatiles were removed in vacuo. Diethyl ether (150 mL) was added and the mixture was washed with H$_2$O (2 x 50 mL) and brine (50 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated. The residue was purified by flash column chromatography (gradient elution, hexane → 2 % EtOAc in hexane) to provide product **8** as a white solid (1.78 g, 96 %): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 (t, *J* = 1.3 Hz, 1H), 7.01 (d, *J* = 1.3 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 3.06 (s, 2H), 1.82 – 1.72 (m, 2H), 1.47 – 1.38 (m, 2H), 1.35 – 1.24 (m, 24H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.88, 128.23, 123.48, 119.04, 82.85, 77.75, 68.49, 32.16, 29.92, 29.89, 29.81, 29.78, 29.60, 29.55, 29.29, 26.17, 22.93, 14.37; HR-MS (ESI): Calcd for $C_{26}H_{38}O$ [M+H$^+$] 367.2995; Found, 367.2981.



1-Hexadecyloxy-3,5-bis(3-bromo-5-formylphenylethynyl)benzene (9): The Sonogashira coupling procedure described above was followed. Coupling of 1-hexadecyloxy-3,5-

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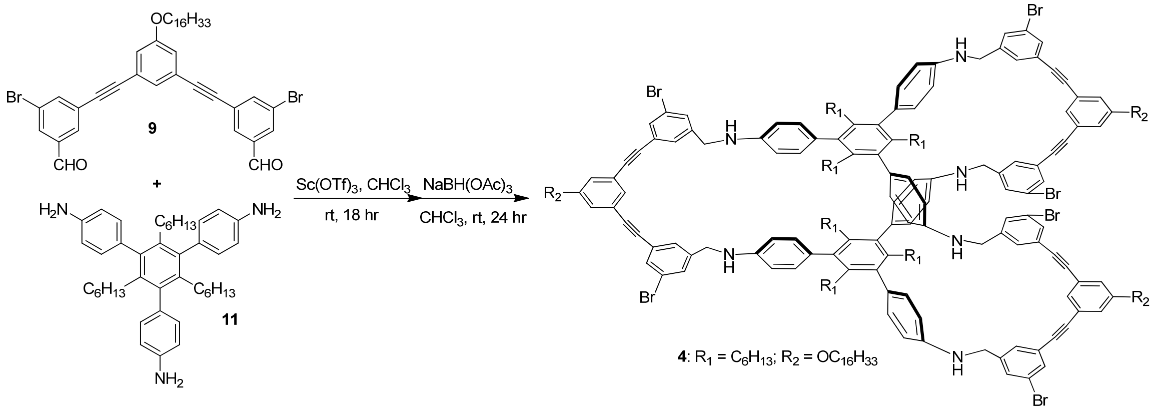
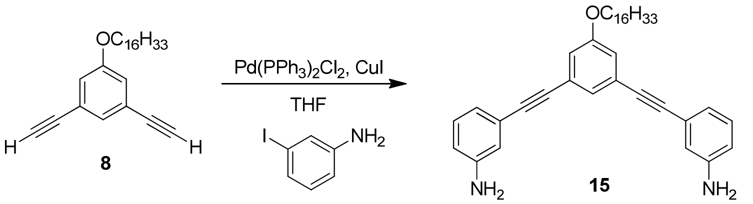
[5] Sonogashira, K.; Tohda, Y,; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467 – 4470.

biethynylbenzene (**8**, 1.24 g, 3.38 mmol) and 3-bromo-5-iodo-benzaldehyde (2.42 g, 7.78 mmol) in THF (40 mL) using $Pd(PPh_3)_2Cl_2$ (142 mg, 0.20 mmol), CuI (13 mg, 0.07 mmol) and piperidine (720 mg, 8.45 mmol) provided the product **9** (2.05 g, 83 %) as a light yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 2H), 8.03 – 7.98 (m, 2H), 7.98 – 7.94 (m, 2H), 7.94 – 7.90 (m, 2H), 7.31 (t, *J* = 1.3 Hz, 1H), 7.08 (d, *J* = 1.3 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.99 – 1.76 (m, 2H), 1.55 – 1.43 (m, 2H), 1.43 – 1.22 (m, 24H), 0.88 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 190.17, 159.17, 139.75, 137.99, 132.06, 131.76, 127.49, 126.18, 123.75, 123.41, 118.76, 91.42, 87.08, 68.64, 32.15, 29.92, 29.83, 29.80, 29.59, 29.31, 26.19, 22.92, 14.36; HR-MS (ESI): Calcd for $C_{40}H_{44}Br_2O_3[M+H^+]$ 733.1714; Found, 733.1696.

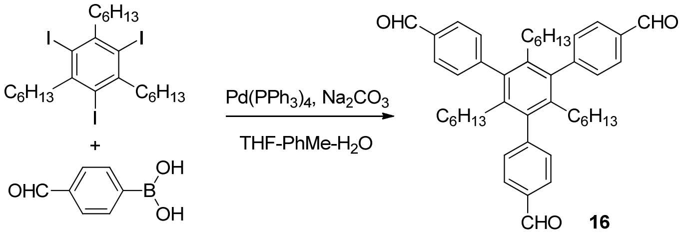


Cage 4: The cage formation procedure described above was followed. 1-Hexadecyloxy-3,5-bis(3-bromo-5-formylphenylethynyl)benzene **9** (329 mg, 0.45 mmol), 1,3,5-trihexyl-2,4,6-tris(4-aminophenyl)benzene **11** (181 mg, 0.30 mmol), $Sc(OTf)_3$ (22 mg, 0.045 mmol), $CHCl_3$ (100 mL), CH_3CN (5 mL), and $NaBH(OAc)_3$ (191 mg, 0.90 mmol) were used to prepare cage **4** (230 mg, 46 %) as a light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (br s, 6H), 7.52 (br s, 6H), 7.48 (br s, 6H), 7.23 (t, *J* = 1.3 Hz, 3H), 6.59 (br s, 12H), 4.36 (s, 12H), 4.13 (br s, 6H), 3.98 (t, *J* = 6.5 Hz, 6H), 2.09 – 1.98 (m, 12H), 1.84 – 1.74 (m, 6H), 1.52 – 1.43 (m, 6H), 1.39 – 1.19 (m, 72H), 1.16 – 1.02 (m, 12H), 1.01 – 0.93 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 9H), 0.85 – 0.73 (m, 24H), 0.69 (t, *J* = 6.6 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.02, 145.71, 142.68, 139.97, 139.02, 132.97, 131.52, 131.12, 130.39, 129.12, 127.84, 125.19, 124.13, 122.66, 118.01, 112.63, 89.90, 88.35, 68.52, 47.73, 32.14, 31.96, 30.98, 30.70, 29.92, 29.89, 29.83, 29.80, 29.59, 29.54, 29.33, 26.19, 22.92, 22.29, 14.37, 14.34; MS (MALDI) calc'd for $C_{204}H_{246}Br_6N_6O_3$ ([M+]) 3308.44, found 3308.13.

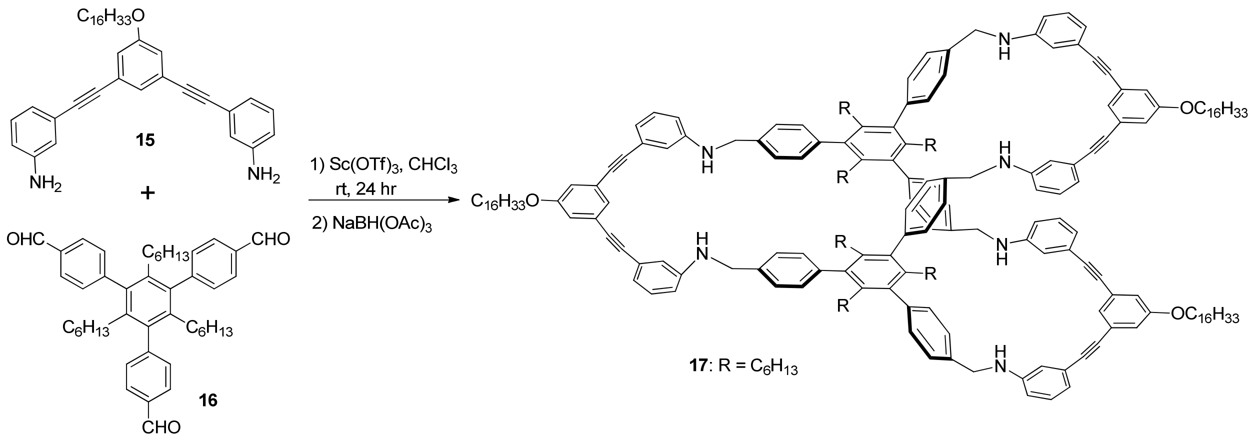
Cage framework 14: To a Schlenk tube were added $Pd(PPh_3)_2Cl_2$ (4 mg, 0.006 mmol), CuI (1 mg, 0.002 mmol), a solution of cage **4** (110 mg, 0.033 mmol) and 1,4-diethynylbenzene (5 mg, 0.037 mmol) in THF (2 mL), and piperidine (1 mL). The mixture was degassed by evacuating and refilling with nitrogen three times. The yellow solution was then heated at 85 ^{o}C for 24 h. The mixture was cooled to room temperature and the red gel-like material was washed with THF (5 x 20 mL) until the solution phase became colorless. The solid was dried to get red crispy material (113 mg).



1-Hexadecyloxy-3,5-bis(3-aminophenyl)benzene (15): The Sonagashira coupling procedure described above was followed. Coupling of 1-hexadecyloxy-3,5-biethynylbenzene (128 mg, 0.35 mmol) and 3-iodo-phenylamine (176 mg, 0.80 mmol) in THF (10 mL) using $Pd(PPh_3)_2Cl_2$ (15 mg, 0.02 mmol), CuI (1 mg, 0.006 mmol) and piperidine (2 mL) provided the product (116 mg, 61 %) as a brown solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 1.3 Hz, 2H), 6.96 – 6.92 (m, 2H), 6.88 – 6.84 (m, 2H), 6.68 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.71 (s, 4H), 1.84 – 1.74 (m, 2H), 1.59 (s, 2H), 1.50 – 1.41 (m, 2H), 1.39 – 1.22 (m, 22H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.77, 146.27, 129.30, 127.17, 124.47, 123.69, 122.13, 117.83, 117.68, 115.49, 89.80, 88.07, 68.27, 31.93, 29.71, 29.61, 29.59, 29.37, 29.17, 26.00, 22.70, 14.14; HR-MS (ESI): Calcd for $C_{38}H_{42}N_2O[M+H^+]$ 549.3839; Found, 549.3821.



1,3,5-Trihexyl-2,4,6-tris(4-formylphenyl)benzene: In a Schlenk tube, 1,3,5-trihexyl-2,4,6-triiodobenzene (881 mg, 1.24 mmol), 4-formylboronic acid (1.12 g, 7.44 mmol), $Pd(PPh_3)_4$ (215 mg, 0.19 mmol) and Na_2CO_3 (789 mg, 7.44 mmol) were added. The reaction apparatus was then evacuated and refilled with nitrogen. Toluene (15 mL), THF (15 mL) and H_2O (7 mL) were added and the mixture was degassed three times before heating at 80 °C for 48 h. Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 x 80 mL). The organic extracts were washed with water (80 mL), and brine (80 mL), dried over Na_2SO_4, and concentrated to give the crude product. Purification by flash column chromatography using 8% EtOAc, 8 % CH_2Cl_2 in hexane (v/v) yielded the product as a light yellow solid (535 mg, 67 %): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 3H), 7.95 (d, *J* = 8.0 Hz, 6H), 7.49 (d, *J* = 8.6 Hz, 6H), 2.01 – 1.89 (m, 6H), 1.13 – 1.02 (m, 6H), 0.98 – 0.87 (m, 6H), 0.77 – 0.60 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.23, 147.72, 138.49, 138.44, 135.20, 131.11, 129.56, 31.76, 30.82, 30.56, 29.40, 22.30, 14.13; HR-MS (ESI): Calcd for $C_{45}H_{54}O_3[M+Cl^-]$ 677.3767; Found, 677.3734.



Cage 17: The same imine metathesis and reduction procedure described above were followed. The trialdehyde **16** (20 mg, 0.031 mmol), the diamine **15** (26 mg, 0.047 mmol), $CHCl_3$ (10 mL), $Sc(OTf)_3$ (2 mg, 0.0047 mmol), CH_3CN (0.52 mL), and $NaBH(OAc)_3$ (594 mg, 2.80 mmol) were used to prepare cage **17** (20 mg, 45 %) as light yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 12H), 7.24 (d, *J* = 7.6 Hz, 12H), 7.19 (t, *J* = 5.7 Hz, 3H), 7.13 (t, *J* = 7.9 Hz, 6H), 6.99 (d, *J* = 1.2 Hz, 6H), 6.86 (t, *J* = 9.6 Hz, 6H), 6.80 (d, *J* = 11.0 Hz, 6H), 6.63 (dd, *J* = 8.1, 2.1 Hz, 6H), 4.39 (s, 12H), 4.24 – 4.10 (m, 6H), 3.97 (t, *J* = 6.5 Hz, 6H), 2.04 – 1.93 (m, 12H), 1.82 – 1.76 (m, 6H), 1.49 – 1.42 (m, 6H), 1.40 – 1.20 (m, 84H), 1.13 – 1.05 (m, 12H), 0.95 – 0.87 (m, 21H), 0.76 – 0.65 (m, 42H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.96, 148.13, 140.33, 139.03, 138.97, 137.16, 130.64, 129.32, 127.78, 126.67, 124.69, 123.84, 121.10, 117.53, 115.58, 113.98, 90.41, 88.04, 68.45, 48.05, 32.15, 31.81, 30.80, 30.59, 29.93, 29.84, 29.81, 29.59, 29.42, 29.38, 26.22, 22.92, 22.26, 14.37, 14.29; MS (MALDI) calc'd for $C_{204}H_{252}N_6O_3$ ([M+H$^+$]) 2836.98, found 2837.01.

3. Gas adsorption analyses of compound 1-4, 2', and 13-14

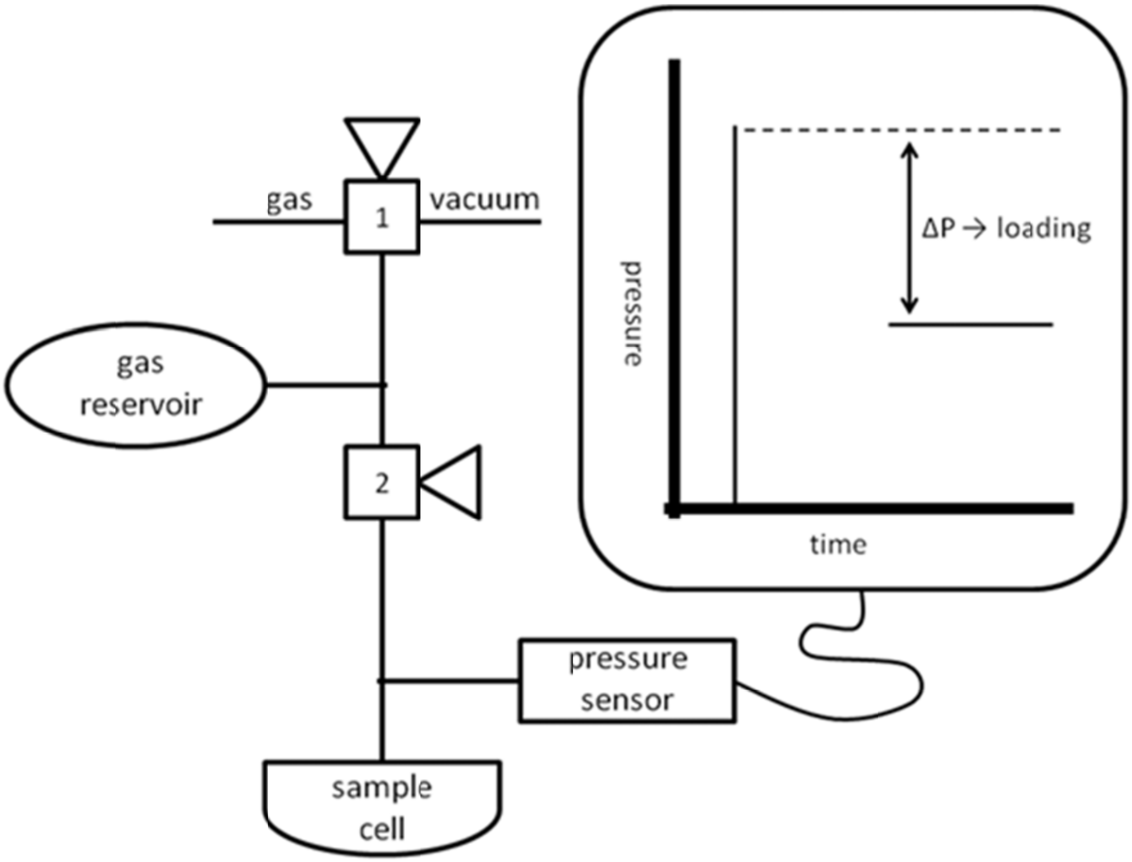


Figure S1. Low-pressure gas sorption apparatus. The amount of gas adsorbed on the sample was measured for single component pure gas. The sample was loaded into a fine mesh envelope that was placed in the sample cell. The entire system was placed under vacuum overnight. Next, valve 2 was closed and valve 1 was opened to the gas line and closed once the gas reservoir was equilibrated. Then valve 2 was opened for 1 second and closed again. As the sample adsorbed the gas in the lower volume the pressure would drop until it reached equilibrium. The pressure drop was measured and recorded from the pressure sensor. The molar amount of gas adsorbed can be determined from the total change in pressure and the ideal gas equation. The gas adsorption was measured as a function of pressure. The ideal adsorption selectivity between CO_2 and N_2 was calculated by interpolating the adsorption of the sample at 1 bar and taking the ratio.

4. Thermal gravimetric analysis of compounds 1-4 and 14

Samples were run on a TA Instruments Q-500 series thermal gravimetric analyzer with samples held in a platinum pan under nitrogen atmosphere. A 10 K min^{-1} ramp rate was used.

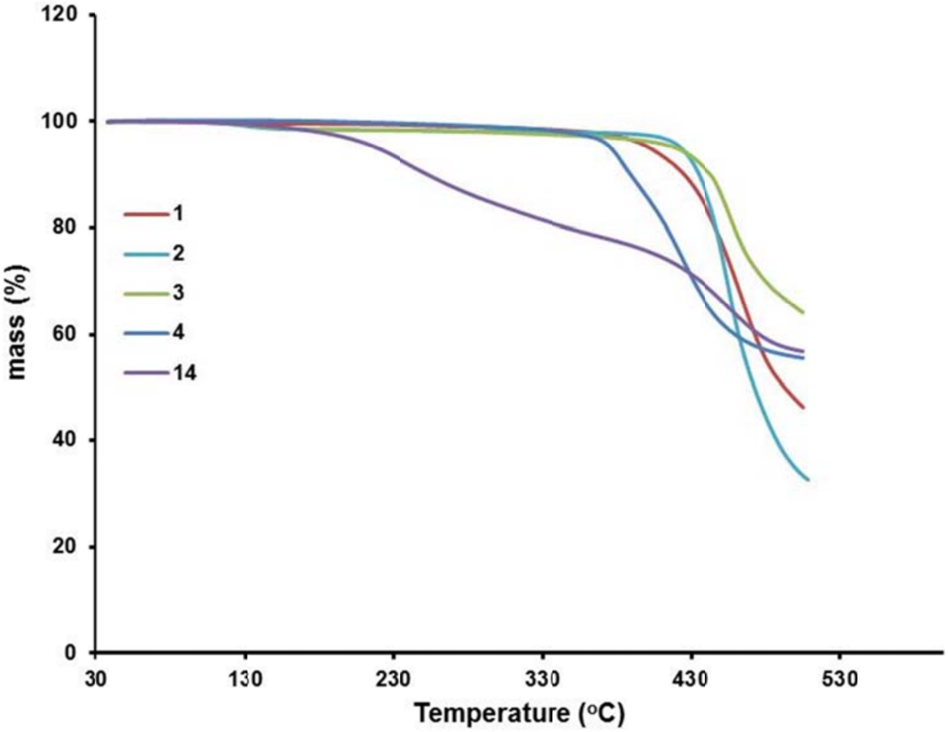


***Figure S2*:** TGA data of cage **1**-**4**, and framework **14**: Cage **1** shows about 0.7 % mass loss before it starts to decompose at 694 K; Cage **2** shows about 1.5 % mass loss before it starts to decompose at 706 K; Cage **3** shows about 1.8 % mass loss before it starts to decompose at 710 K; Cage **4** starts to decompose at 645 K; Cage framework **14** shows about 24 % mass loss between 474 K and its decomposition temperature 694 K.

5. Powder X-ray diffraction analysis of compound 1-4 and 14

Powder X-ray-diffraction (XRD) profiles were obtained with an Inel CPS 120 diffraction system, using monochromated Cu K(alpha) radiation. All XRD spectra were calibrated against silver behenate as a diffraction standard (d100 = 58 Å), so the accuracy is within 1 Å up to the value of the d-spacings. XRD measurements were all performed at ambient temperature (21 ± 1 °C).

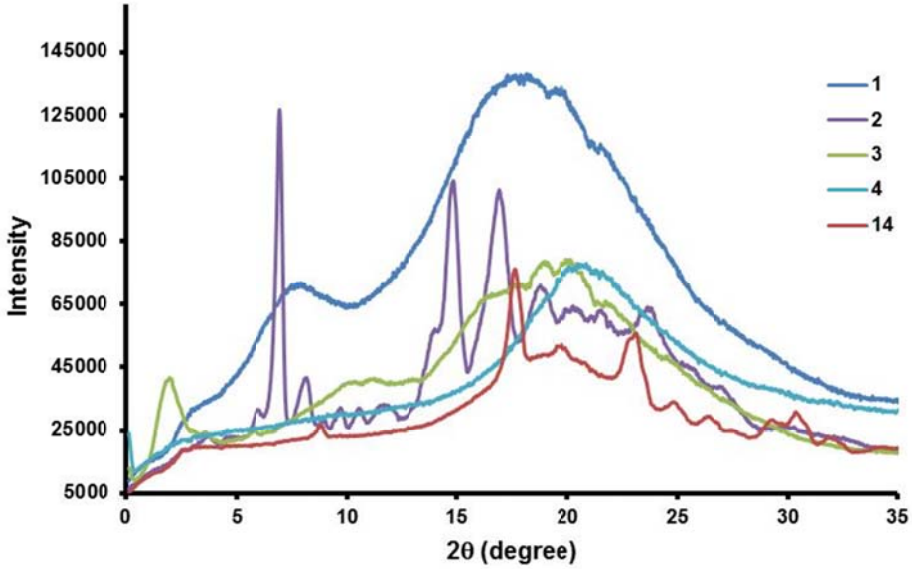


Figure S3. PXRD patterns of cage **1**-**4** and cage framework **14**. Cage **1** and **3**-**4** are amorphous and cage **2** and cage framework **14** show minor crystallinity.

6. DFT calculations on N2 adsorption and CO2 adsorption energies

Amber 10.0 program suit[6] were used to optimize cage molecular structures with semi-empirical quantum mechanics method. For each cage, it was optimized in vacuum for 2500 steps using SCC-DFTB[7] and the conjugate gradient method. A dielectric constant of 1.0 was used during the minimization. To obtain the N_2-cage interaction energy, for each cage, one N_2 molecule was put in the cage's pore and the overall structure was optimized using the same method.

Table S1. N_2 adsorption energy *vs* pore size

Compound	2'	3	2	1	4
Pore Size (Å)	7.32	6.72	6.27	6.03	5.27
N_2 interaction energy (kcal/mol)	4.5	-1.0	-0.3	-2.3	-0.2

---

[6] Case, D. A. D. *et. al.* University of California: San Francisco, 2008.

[7] Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7260-7268.

DFT Calculations for CO_2 adsorption on *N*-benzylaniline and *N*-benzyl-*N*-phenylimine.

We used Gaussian 09 program suit[8] to study the CO_2 adsorption on *N*-benzylaniline and *N*-benzyl-*N*-phenylimine. To calculate the CO_2 adsorption energy on *N*-benzylaniline, the structures of individual *N*-benzylaniline, individual CO_2, as well as the *N*-benzylaniline/CO_2 adsorption complex are optimized by B3LYP/6-31G* level of theory and their energies for the optimized structures, E_1, E_2, and E_3, are obtained. Then the adsorption energy $E_{ad} = E_3 - E_2 - E_1$. The CO_2 adsorption energy on *N*-benzyl-*N*-phenylimine can be calculated using a similar protocol.

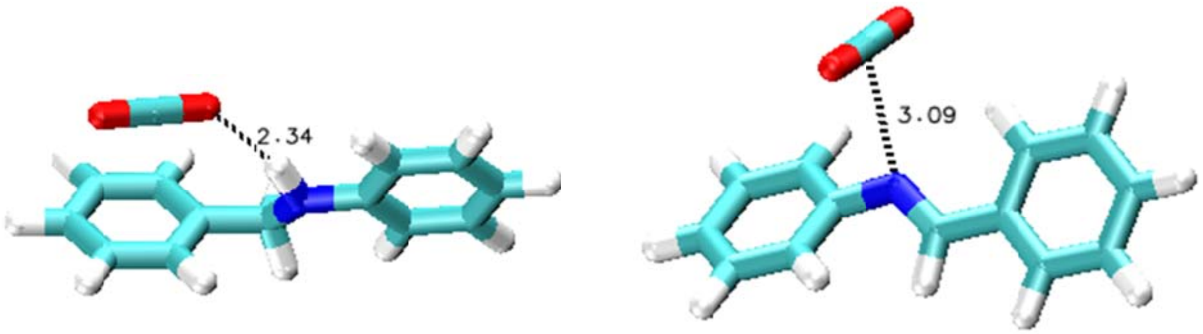


Figure S4. The optimized structures for CO_2 adsorption on *N*-benzylaniline (left) and *N*-benzyl-*N*-phenylimine (right). Color scheme: C in cyan, O in red, H in white, and N in blue.

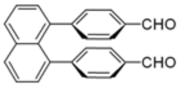
Table S2. DFT calculation for CO_2 adsorption in kcal/mol.

	E_1	E_2	E_3	E_{ad}
N-benzylaniline	-350125.85	-118336.24	-468464.39	-2.30
N-benzyl-*N*-phenylimine	-349367.08	-118336.24	-467705.55	-2.23

---

[8] Gaussian 09, Revision A.2, Frisch, M. J. *et. al.* Gaussian, Inc., Wallingford CT, 2009.

7. ^{1}H and ^{13}C NMR Spectra for selected compounds



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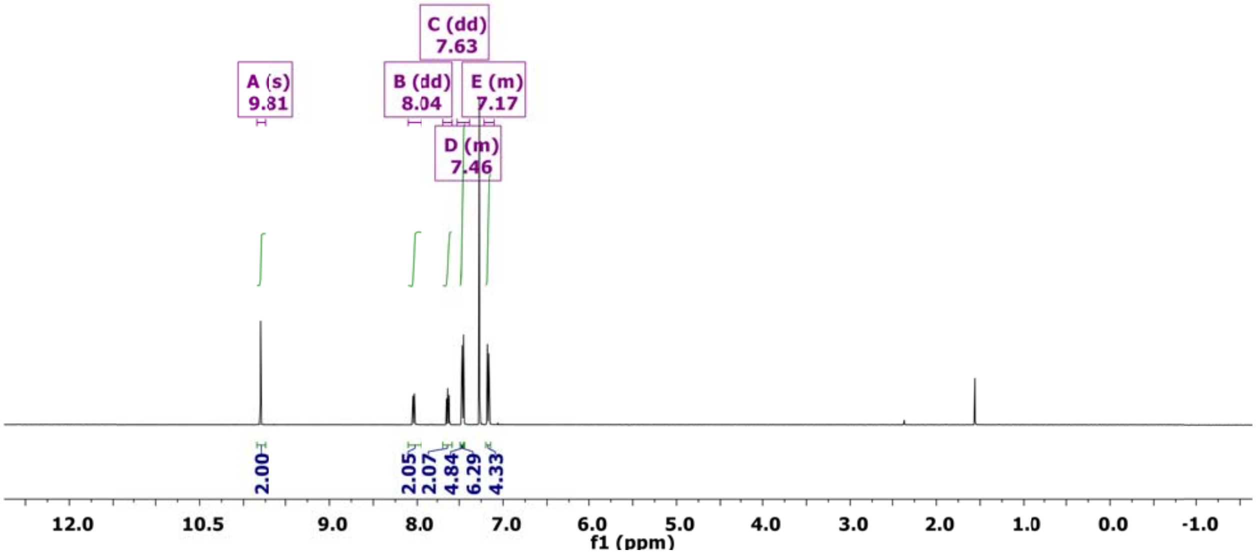

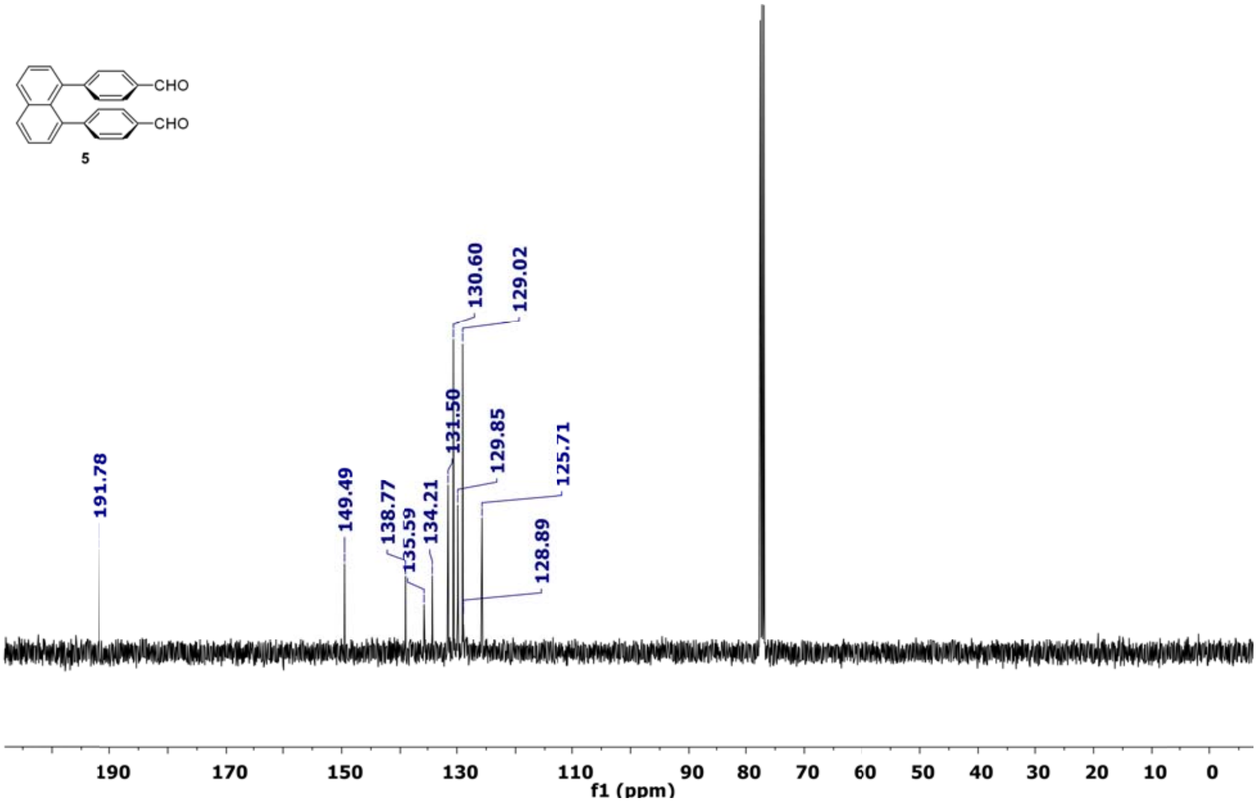

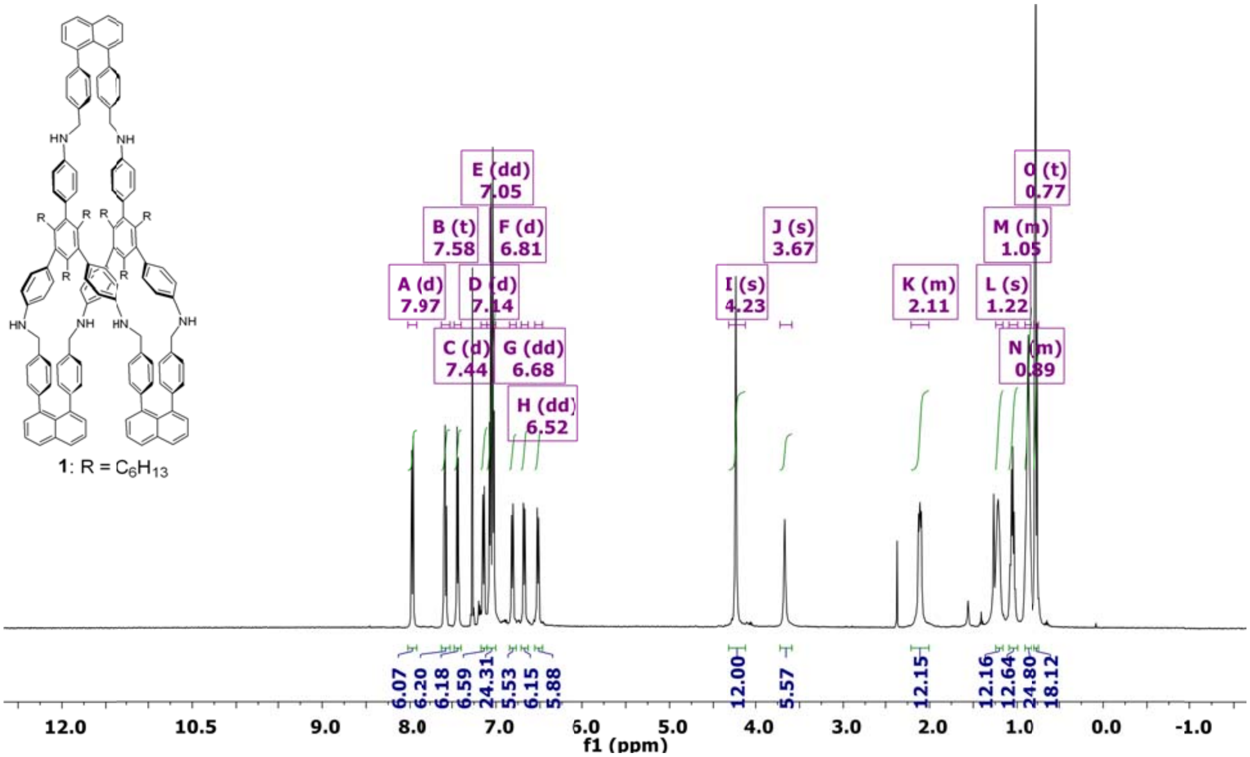
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D (d) 7.14
E (dd) 7.05
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G (dd) 6.68
H (dd) 6.52
I (s) 4.23
J (s) 3.67
K (m) 2.11
L (s) 1.22
M (m) 1.05
N (m) 0.89
O (t) 0.77
6.07
6.20
6.18
6.59
24.31
5.53
6.15
5.88
12.00
5.57
12.15
12.16
12.64
24.80
18.12
12.0
10.5
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5.0
4.0
3.0
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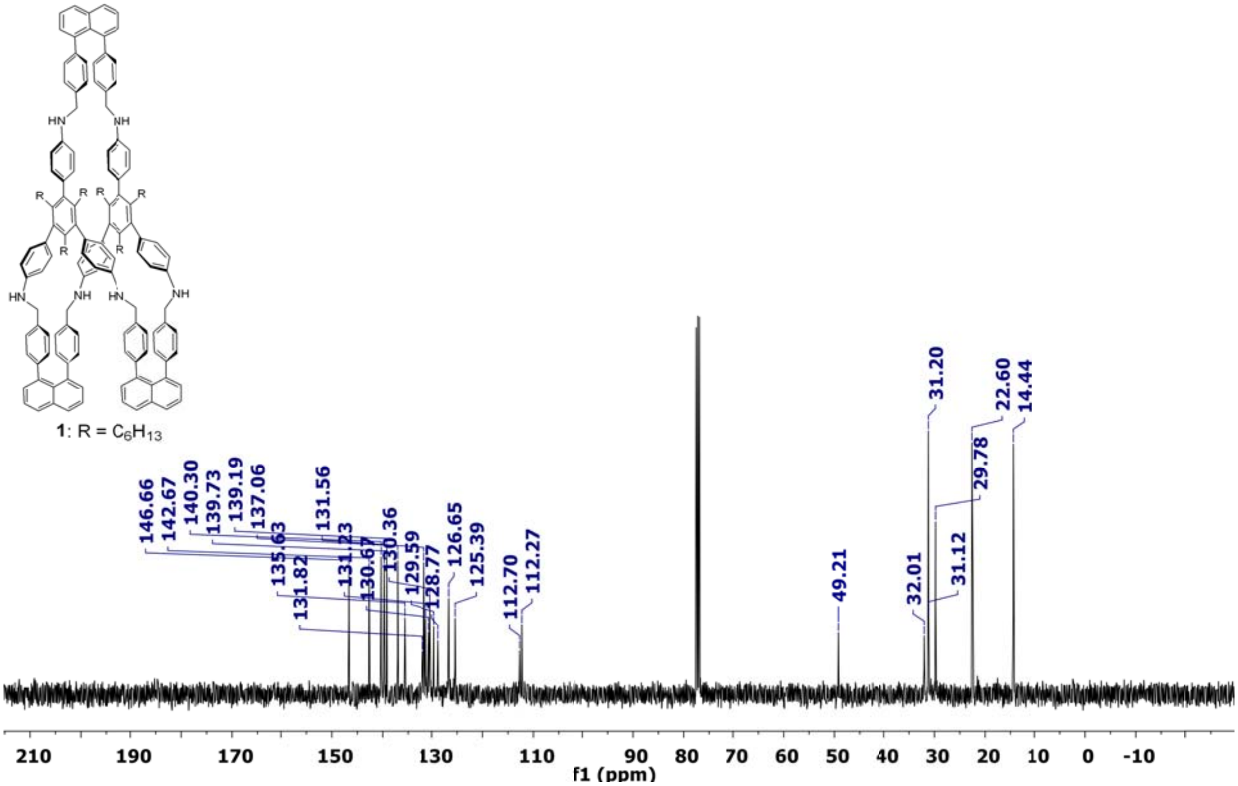
1.0
0.0
-1.0
f1 (ppm)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129.59
128.77
126.65
125.39
112.70
112.27
49.21
32.01
31.20
31.12
29.78
22.60
14.44
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150
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110
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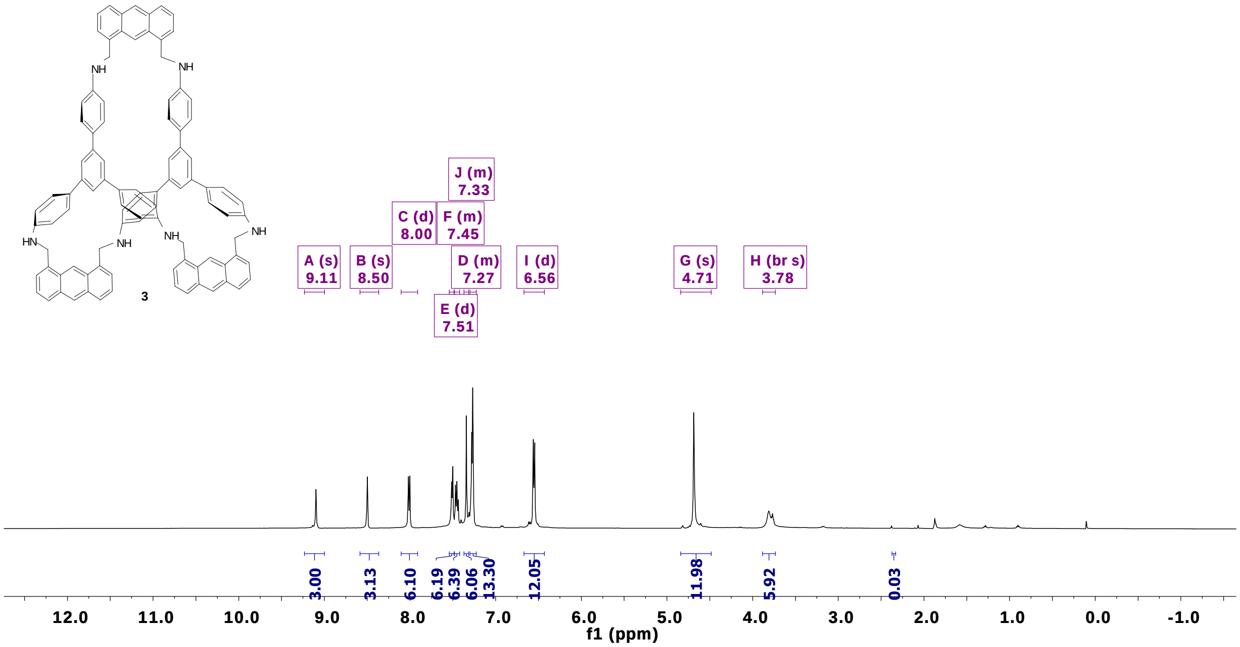
f1 (ppm)



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HN
NH
NH
NH
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F (m) 7.45
A (s) 9.11
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D (m) 7.27
I (d) 6.56
G (s) 4.71
H (br s) 3.78
E (d) 7.51
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3.13
6.10
6.19
6.39
6.06
13.30
12.05
11.98
5.92
0.03
12.0
11.0
10.0
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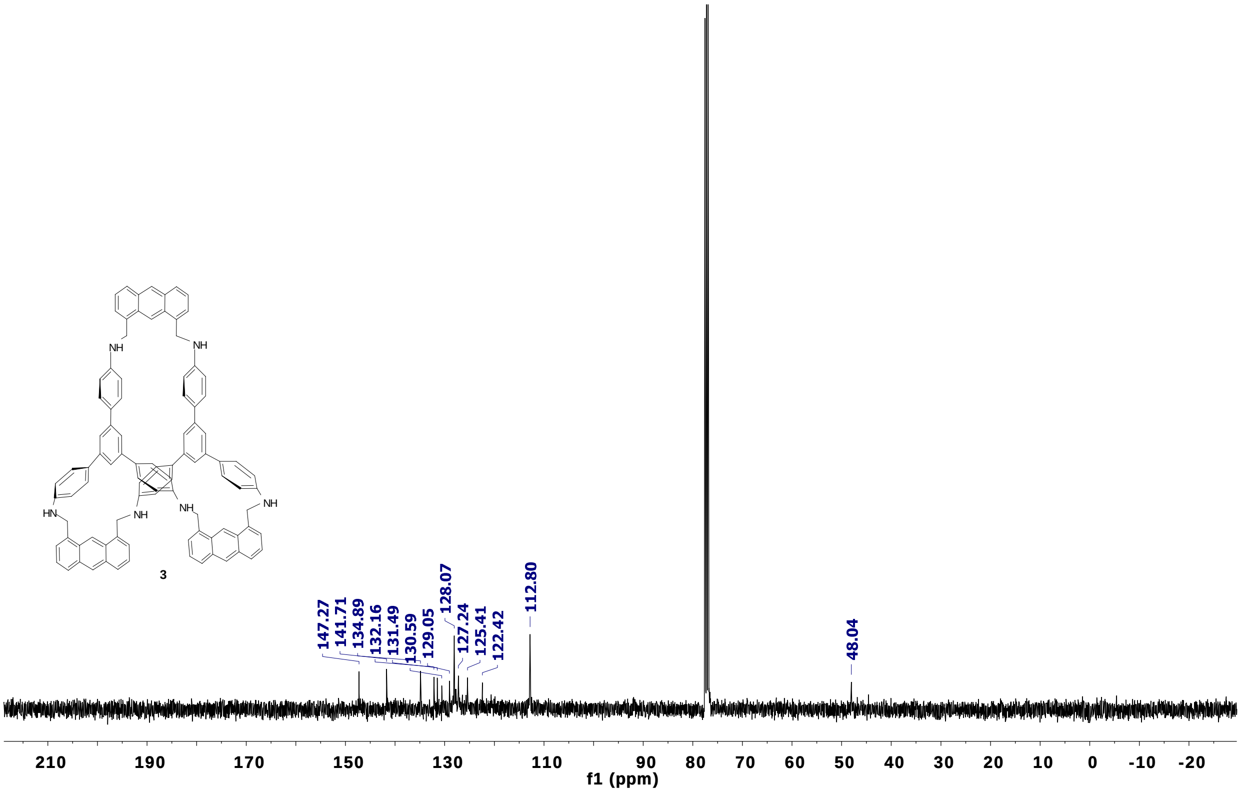

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HN
NH
NH
NH
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122.42
112.80
48.04
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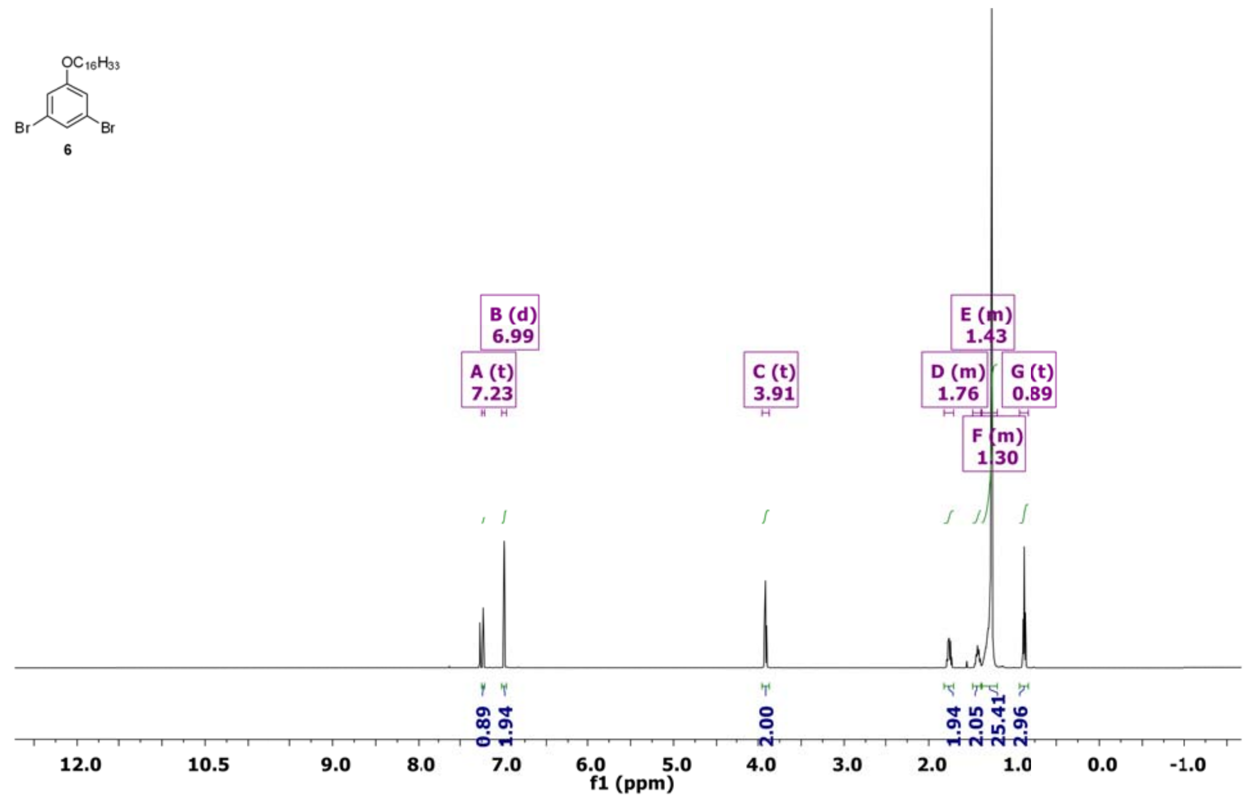
f1 (ppm)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G (t)
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F (m)
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0.89
1.94
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1.94
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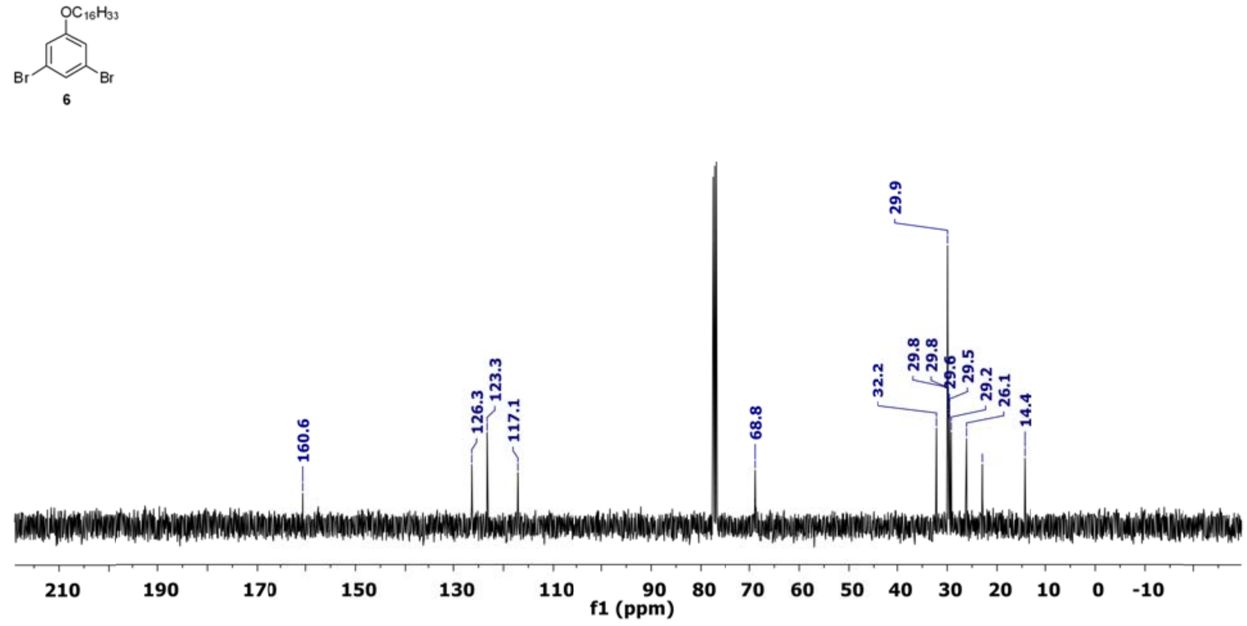
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29.2
26.1
14.4
210
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170
150
130
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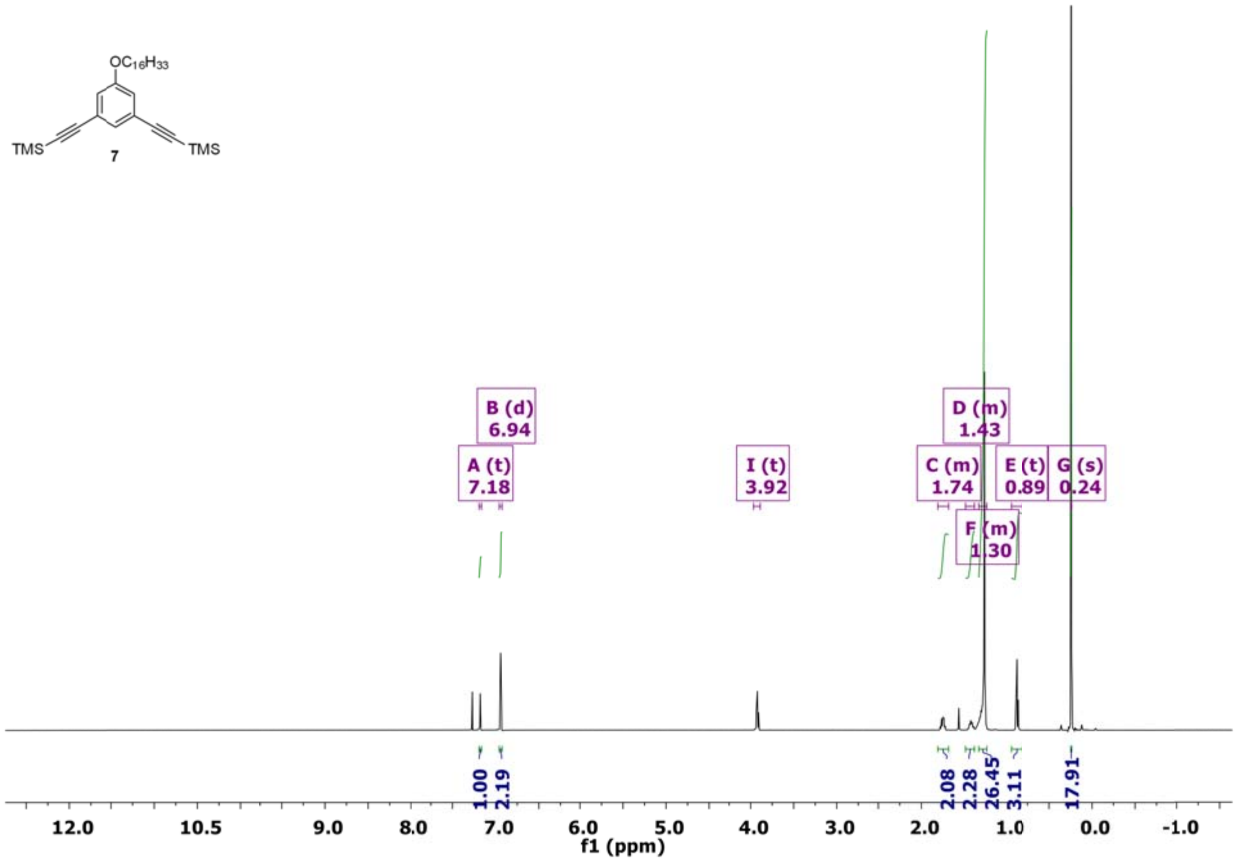
f1 (ppm)

OC16H33
TMS
TMS

7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G (s)
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F (m)
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1.00
2.19
2.08
2.28
26.45
3.11
17.91
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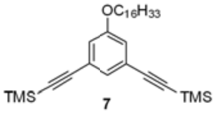
f1 (ppm)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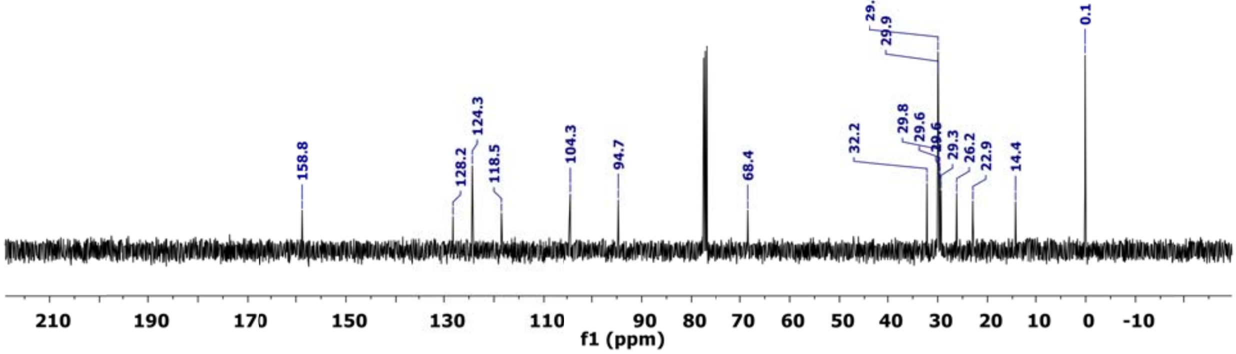
TMS
TMS

7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22.9
14.4
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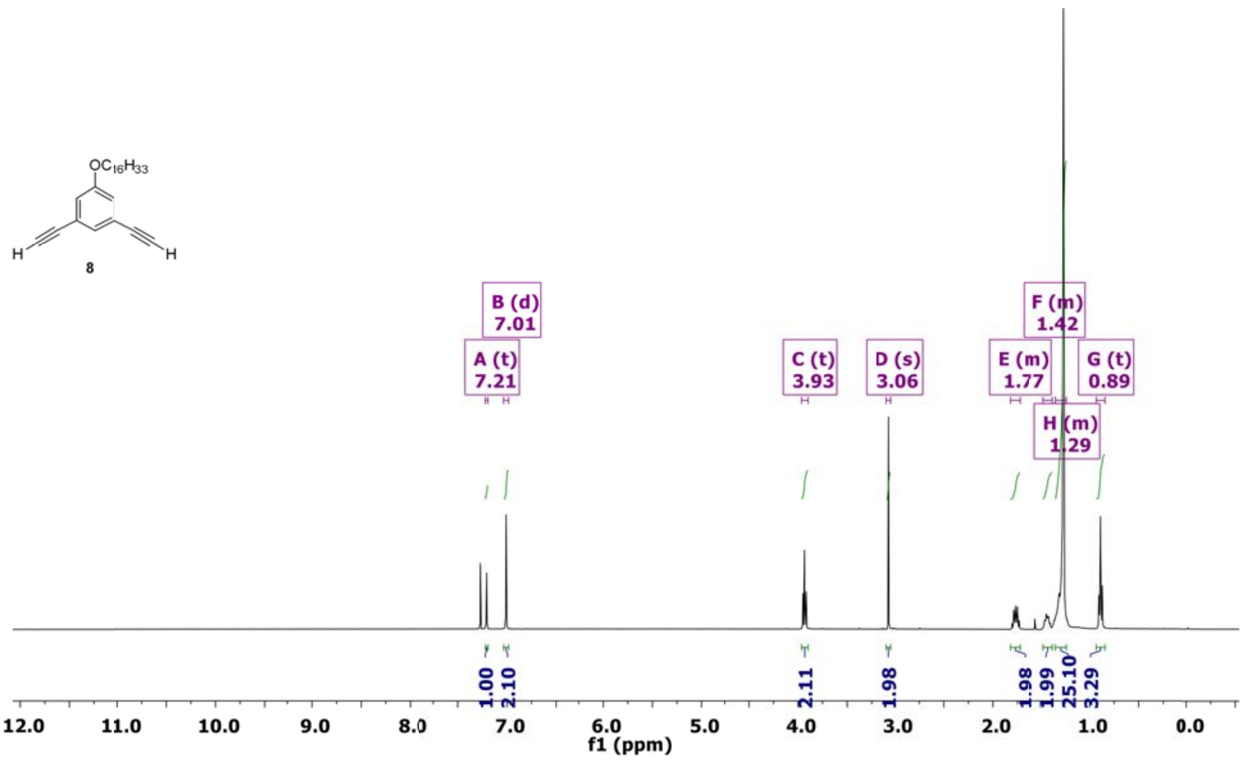
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C (t)
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E (m)
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G (t)
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H (m)
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1.98
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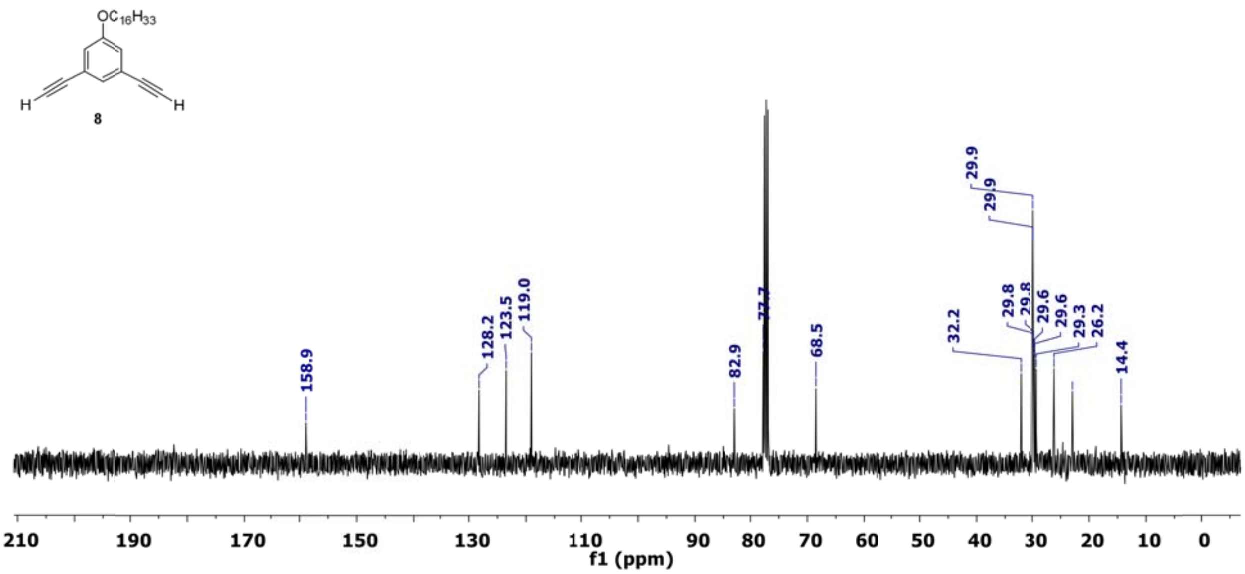
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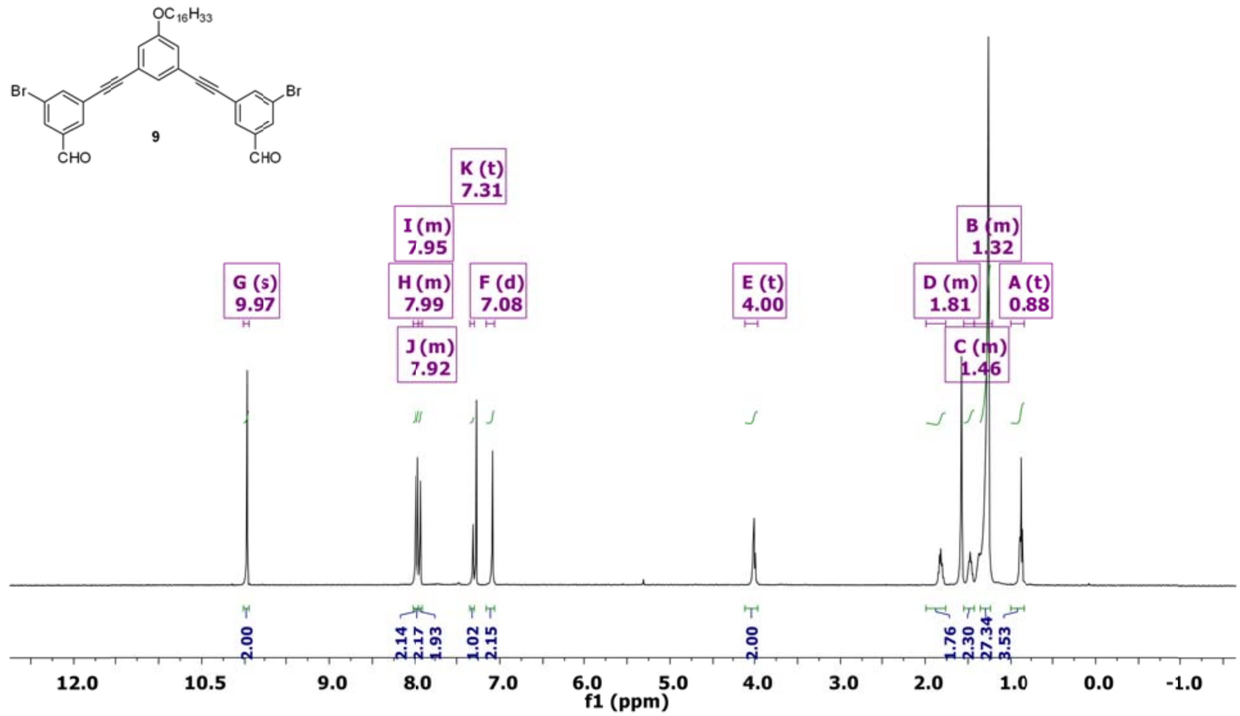
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D (m) 1.81
A (t) 0.88
J (m) 7.92
C (m) 1.46
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2.17
1.93
1.02
2.15
2.00
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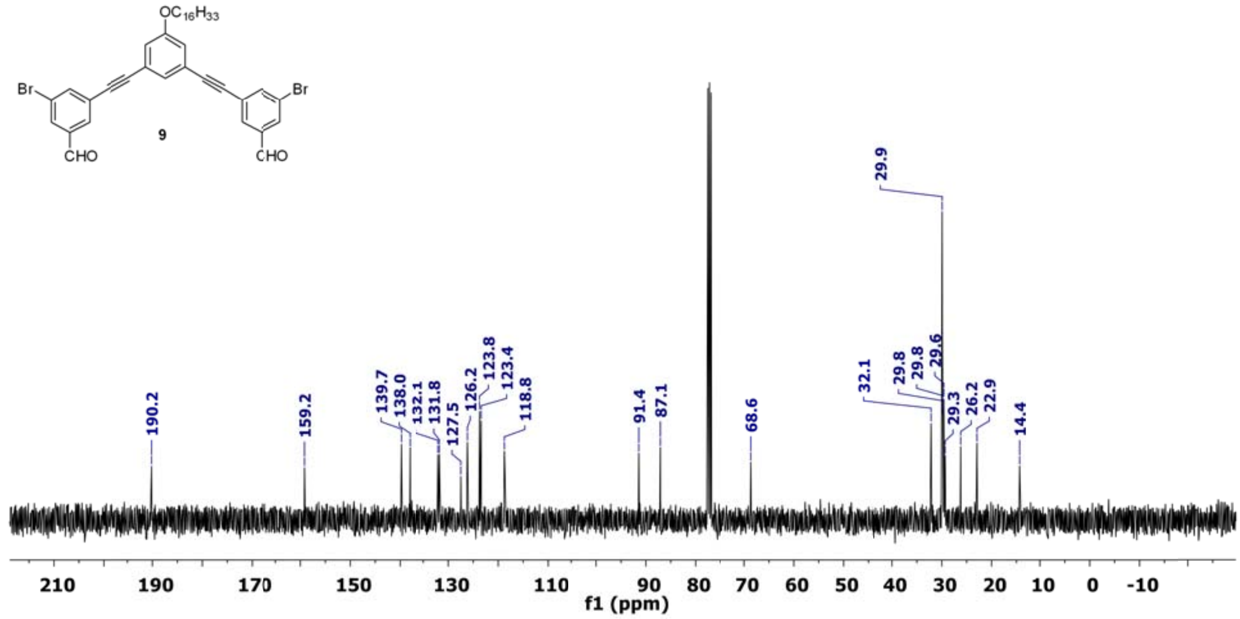
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87.1
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29.8
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22.9
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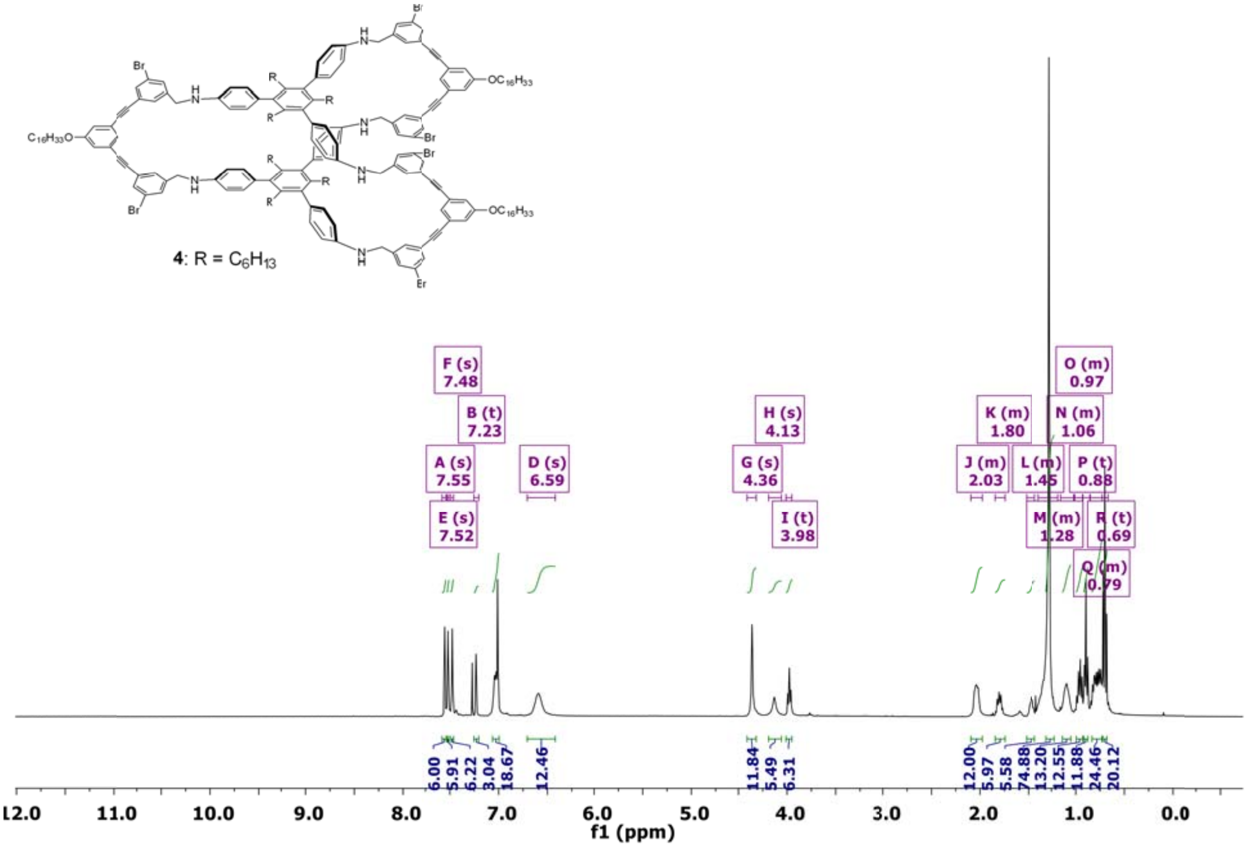
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C16H33O
R
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G (s) 4.36
I (t) 3.98
K (m) 1.80
J (m) 2.03
L (m) 1.45
M (m) 1.28
O (m) 0.97
N (m) 1.06
P (t) 0.88
R (t) 0.69
Q (m) 0.79
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5.91
6.22
3.04
18.67
12.46
11.84
5.49
6.31
12.00
5.97
5.58
74.88
13.20
12.55
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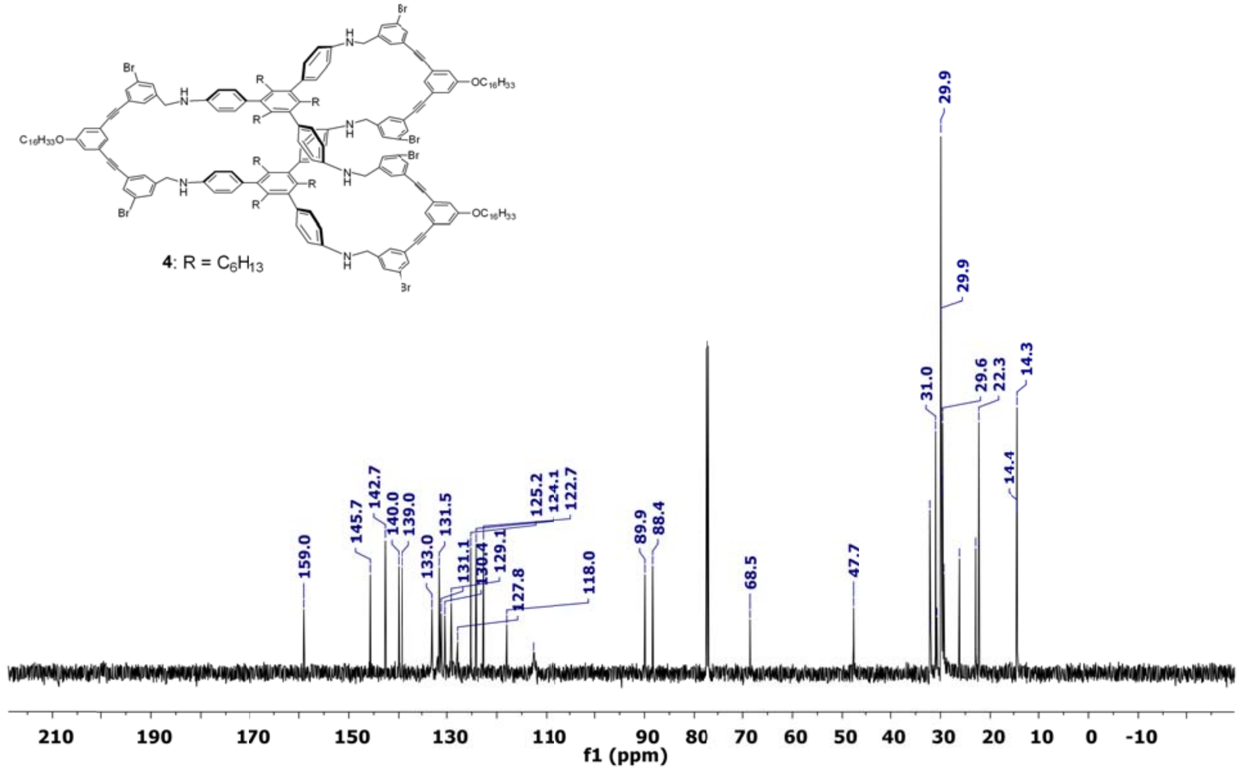
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C16H33O
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88.4
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47.7
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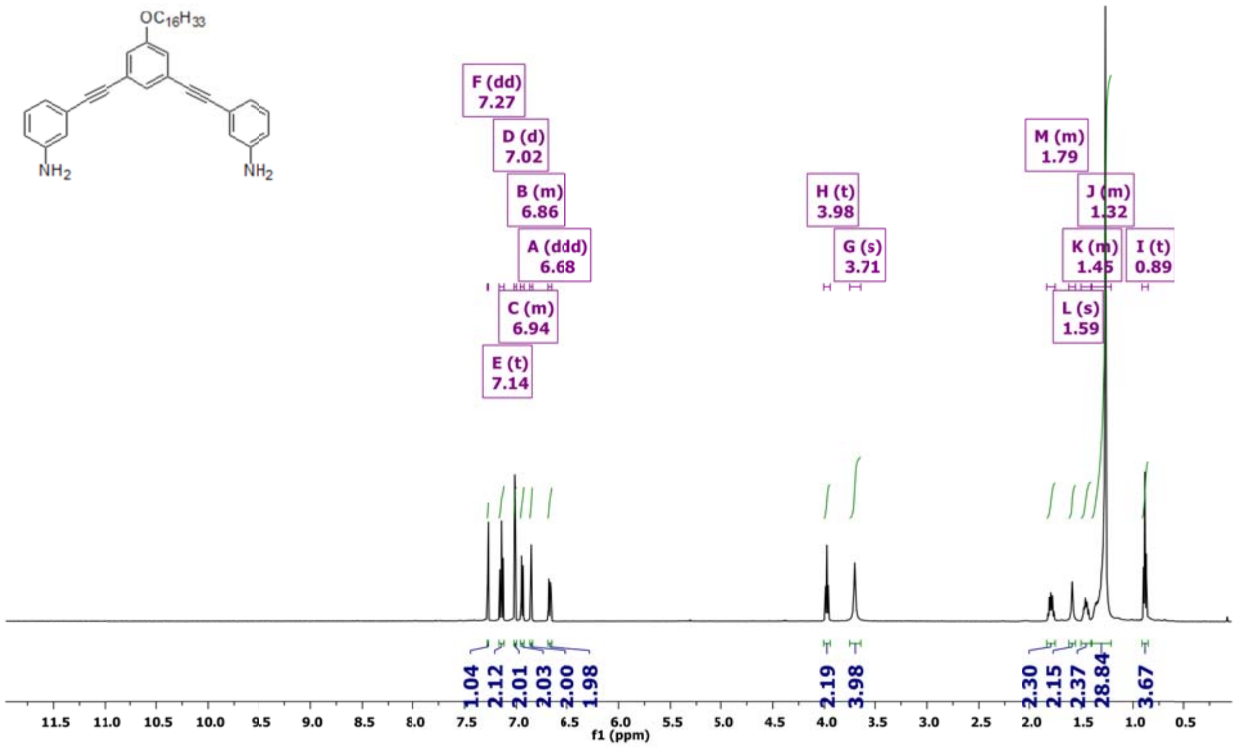
f1 (ppm)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G (s) 3.71
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J (m) 1.32
K (m) 1.45
I (t) 0.89
L (s) 1.59
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2.12
2.01
2.03
2.00
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2.19
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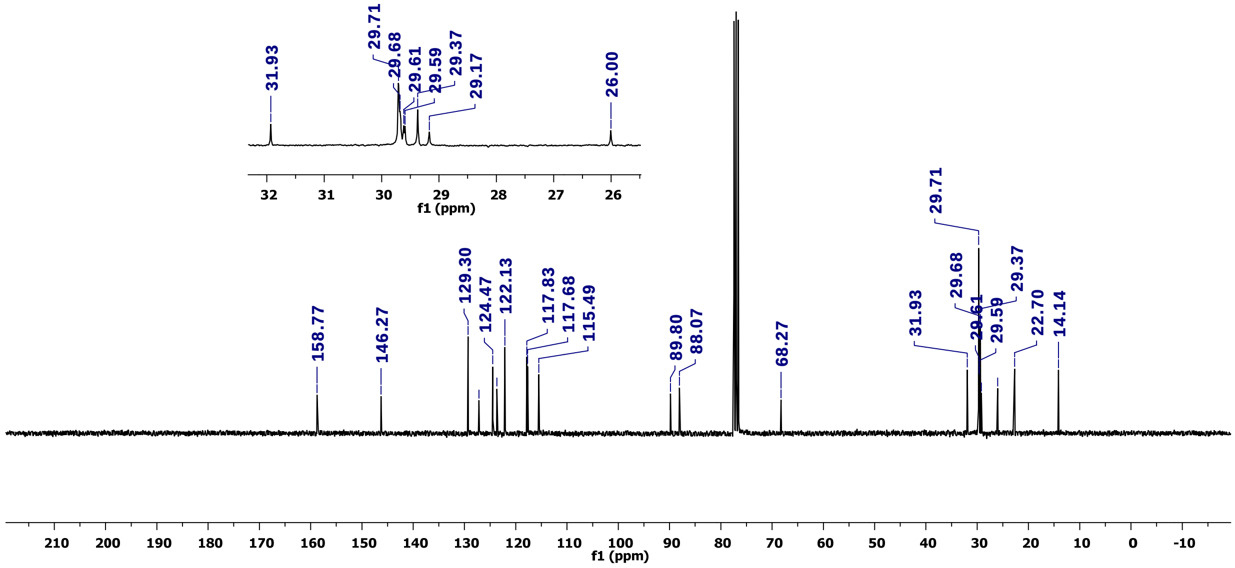
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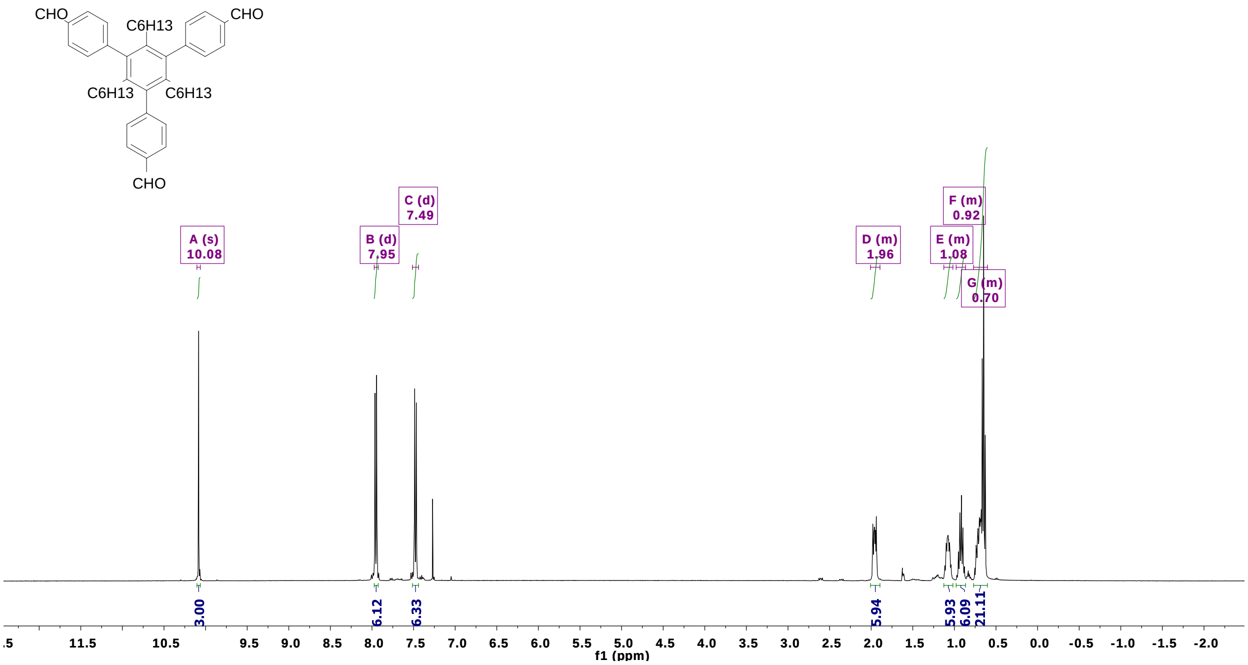
f1 (ppm)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C6H13
C6H13
CHO
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1.96
E (m)
1.08
F (m)
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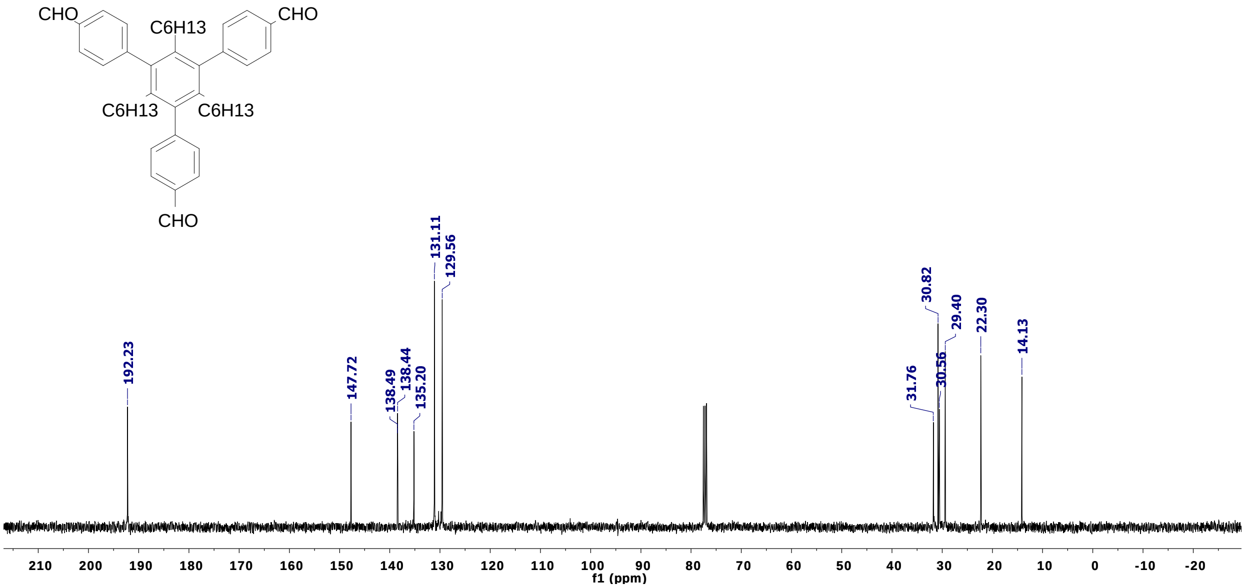
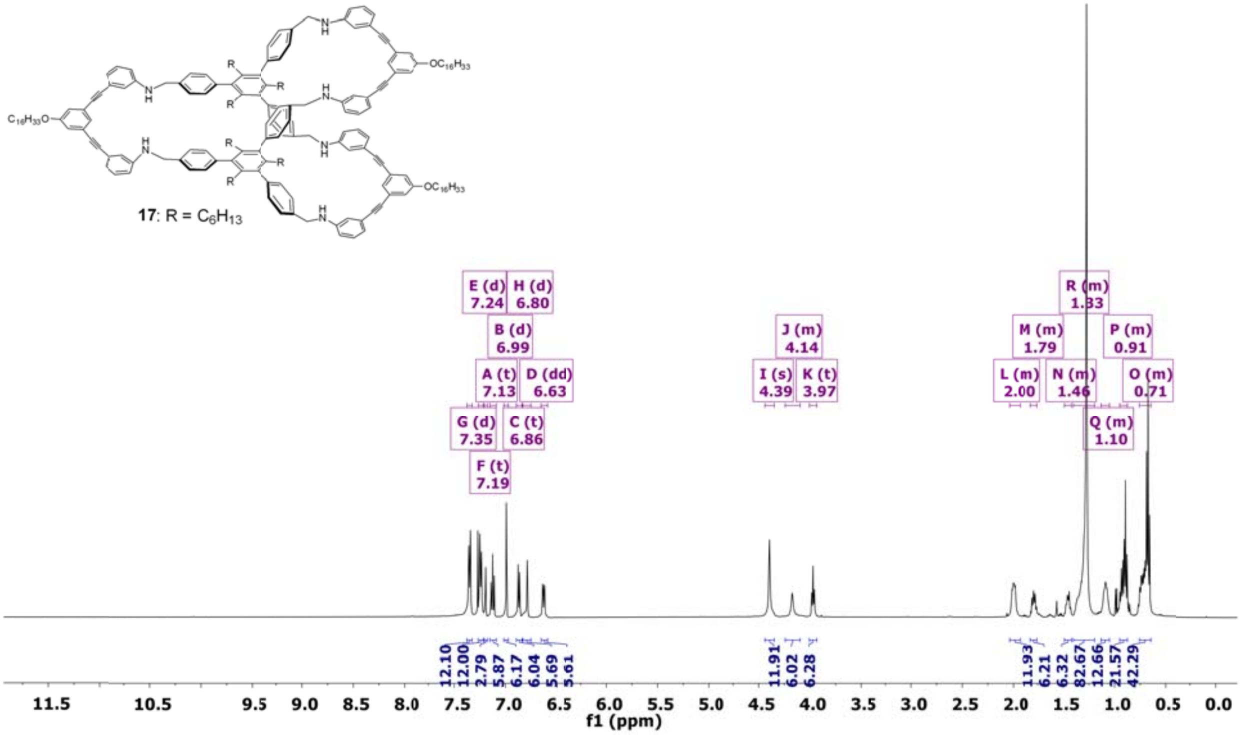
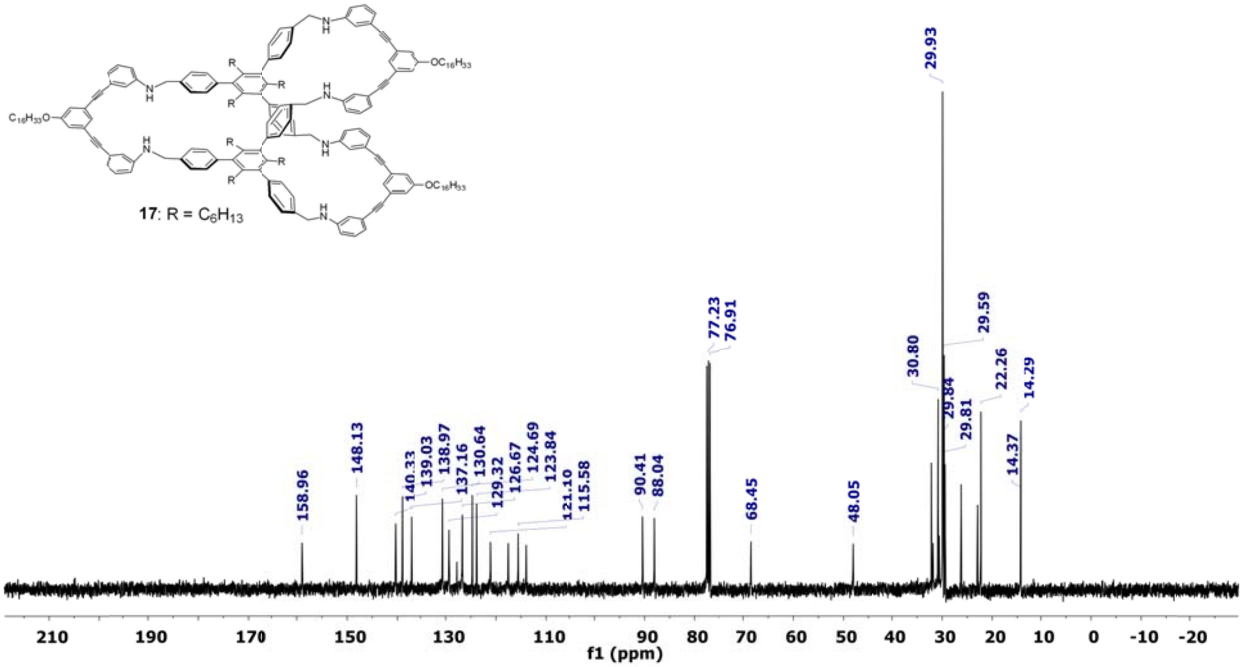
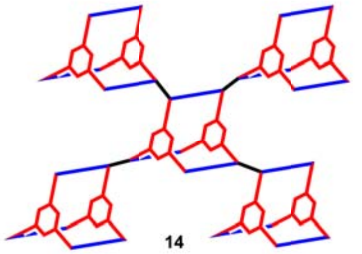
G (m)
0.70
3.00
6.12
6.33
5.94
5.93
6.09
21.11
.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)


CHO
C6H13
CHO
C6H13
C6H13
CHO
192.23
147.72
138.49
138.44
135.20
131.11
129.56
31.76
30.82
30.56
29.40
22.30
14.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

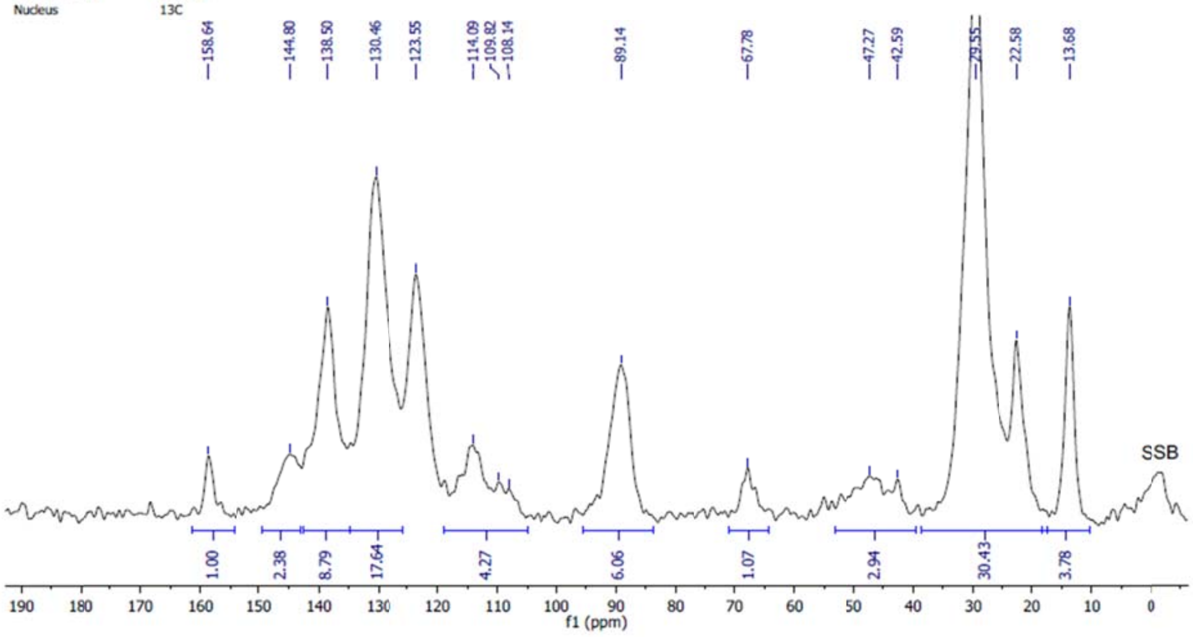

17: R = C_6H_{13}


17: R = C_6H_{13}

Parameter	Value
Data File Name	Alice-III-14-cyst_SSCPMAS-C13-ovnt.fid
Title	Alice III-14, crystallized, solid-state 13C-CPMAS, MAS=12.8KHz
Pulse Sequence	xpolvt1rho1
Acquisition Date	2010-11-30T17:10:28
Temperature	20.0
Number of Scans	1240
Pulse Width	3.0
Contact Time	5000.00
Relaxation Delay	5.0
Spinning Speed	12830
Spectrometer Frequency	100.63
Spectral Width	33085.2
Nucleus	13C



14



8. Complete citations

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