Template Synthesis of Gold Nanoparticles with an Organic Molecular Cage

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Supplementary Information

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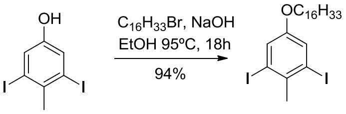
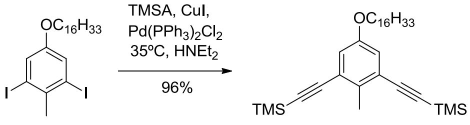
1. Materials and General Methods

All commercially available reagents and solvents were use as received, unless noted otherwise. CH_2Cl_2 and tetrahydrofuran (THF) were purified by MBBRAUN solvent purification system. 3,5-Iodo-*p*-cresol were prepared as described in the literature.[1] All reactions were carried out under dry nitrogen in flame dried glassware, unless noted otherwise. After workup, all solvents were removed by rotary evaporator. Unless other indicated, the purity of the compounds was ≥ 95 % based on ^1H NMR spectral integration. Flash column chromatography was performed using 100-150 times weight excess of 32-63 µm silica gel from Dynamic Absorbants Inc. Fractions were analyzed by TLC using TLC silica gel F254 250 µm precoated-plates from Dynamic Absorbants Inc. Gel permeation chromatorgraphy (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 x 30cm, 1- MBLMW-3078, and 1-MBMMW-3078). GPC calibration was done using monodisperse polystyrene standards and THF was used as the eluent at 30ºC. UV-vis absorption measurements were recorded with an Agilent 8453 spectrophotometer. Matrix Assisted Laser Desorption Ionisation (MALDI) mass spectra were performed on the Voyager-DE™ STR Biospectrometry Workstation in linear mode using a sinapic acid matrix. High resolution mass spectra were performed on a Waters SYNAPT G2 high definition mass spectrometry system. ^1H and ^{13}C NMR spectra were obtained from either an Inova 500 or Bruker 300 spectrometer. $CHCl_3$ (7.27 ppm) was used as an internal reference in ^1H NMR, and $CHCl_3$ (77.23 ppm) for ^{13}C NMR. NMR data is reported in the following order: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants (J, Hz), number of protons.

2. Experimental Procedures

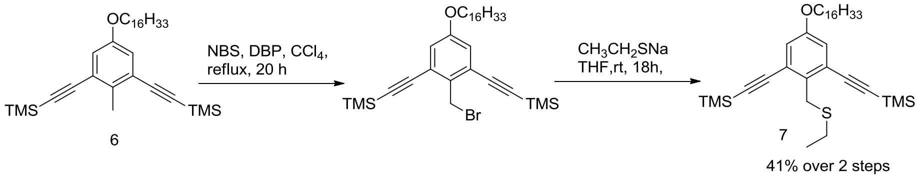


5-(hexadecyloxy)-1,3-diiodo-2-methylbenzene: To a Schlenk tube were added 3,5-iodo-p-cresol (1.0 g, 2.78 mmol), 1-bromohexadecane (0.93 g, 3.06 mmol), NaOH (120 mg, 3.06 mmol), and ethanol (35 mL) under N_2. After refluxing for 18 h, the reaction mixture was cooled to room temperature and poured into water (50 mL). The product was extracted with diethyl ether (3 x 75 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography using hexanes to afford the product as a white solid (1.5 g, 94 %): ^{1}H NMR (500 MHz, $CHCl_3$): δ 7.58 (s, 2H), δ 3.93 (t, *J* = 6.6 Hz, 2H), δ 2.24 (s, 3H), δ 1.94-1.86 (m, 2H), δ 1.59-1.49 (m, 2H), 1.27 (m, 24H), δ 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.79, 140.24, 137.46, 90.56, 73.43, 31.94, 30.04, 29.73, 29.70, 29.68, 29.66, 29.62, 29.55, 29.38, 25.99, 22.71, 19.63, 14.15; HR-MS (ESI): Cal'd for $C_{23}H_{38}I_2O$ [2M+Li$^+$] 1175.2180; Found 1175.2173.



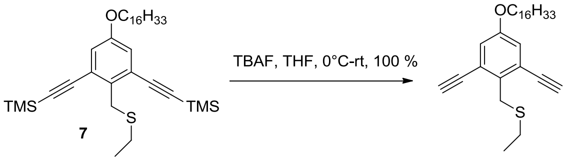
6

Compound 6: The general procedure for Sonogashira cross coupling was followed.[2] Using 5-(hexadecyloxy)-1,3-diiodo-2-methylbenzene (625 mg, 1.07 mmol), trimethylsilyacetylene (1.8 mL, 12.84 mmol), $Pd(PPh_3)_2Cl_2$ (45 mg, 0.064 mmol), CuI (4 mg, 0.021 mmol), and diethylamine (35 mL), the product was obtained as a light yellow oil (542 mg, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (s, 2H), 4.15 (t, *J* = 6.6 Hz, 2H), 2.22 (s, 3H), 1.84 – 1.76 (m, 2H), 1.55 – 1.47 (m, 2H), 1.39 – 1.21 (m, 24H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.25 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.09, 134.47, 132.52, 117.21, 101.02, 98.43, 74.27, 31.94, 30.46, 29.71, 29.69, 29.67, 29.63, 29.37, 26.17, 22.70, 20.26, 14.13, -0.08; HR-MS (ESI): Cal'd for $C_{33}H_{56}OSi_2$ [M+Li$^+$] 531.4025; Found 531.4027.

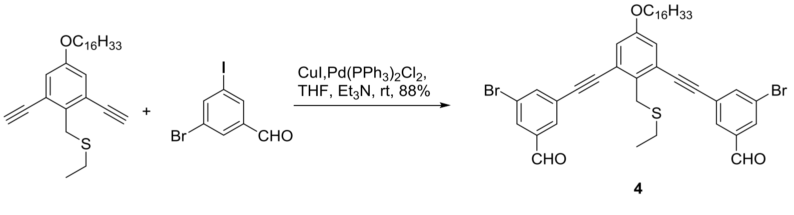


Compound 7, **Step 1:** To a Schlenk tube were added compound **6** (513 mg, 0.98 mmol), N-Bromosuccinimide (452 mg, 2.54 mmol), dibenzoyl peroxide (43 mg, 0.18 mmol) and CCl_4 (15 mL) under nitrogen atmosphere and the solution was refluxed for 20 h. The dark red solution was cooled to rt, filtered and rinsed with CCl_4. Due to the instability of the benzylic bromide the crude material was used in the following step without further purification. The physical data for the product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 2H), 4.36 (s, 2H), 4.21 (t, *J* = 6.6 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.59 – 1.45 (m, 2H), 1.26 (s, 24H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.25 (s, 18H).

Step 2: To a schlenk tube were added sodium ethanethiolate (984 mg, 1.17 mmol) and a solution of the above crude product (304 mg) in DMA (10 mL). The solution was stirred at rt for 18 h and poured into H_2O (50 mL). After extraction with CH_2Cl_2 (3 x 25 mL), the combined organic solution was dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography using 5 % ethyl acetate/hexane to afford the product as an orange oil (233 mg, 41 % over 2 steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 2H), 4.19 (t, *J* = 6.5 Hz, 2H), 3.58 (s, 2H), 2.41 (q, *J* = 7.4 Hz, 2H), 1.82 (dt, *J* = 6.6 Hz, 2H), 1.52 (m, 2H), 1.29 (m, 29H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.26 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.15, 134.16, 133.43, 128.52, 127.12, 117.51, 100.75, 98.90, 74.24, 70.79, 66.02, 34.77, 31.94, 30.46, 29.71, 29.69, 29.67, 29.64, 29.62, 29.38, 26.15, 25.18, 22.70, 14.30, 14.13, -0.12; HR-MS (ESI): Cal'd for $C_{35}H_{60}OSSi_2$ [M+H$^+$] 586.0942; Found 586.2675.

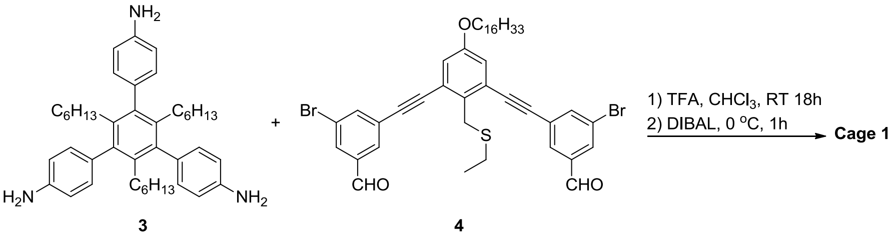


(2,6-Diethynyl-4-(hexadecyloxy)benzyl)(ethyl)sulfane: To a schlenk tube were added compound **7** (525 mg, 0.9 mmol) and THF (15 mL) under nitrogen atmosphere. The solution was cooled to 0 ºC using an ice bath. A solution of TBAF (1 M in THF, 1.8 mL, 1.8 mmol) was added dropwise at 0 ºC. The darkened solution was warmed to rt and stirred for 10 min. The solvent was removed by rotary evaporation, and the crude product was passed through a short column of silica gel using 25 % ethyl acetate/hexane to yield the product as a slightly yellow oil (395 mg, 100 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.61 (s, 2H), 3.26 (s, 2H), 2.43 (q, *J* = 7.4 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.49 (dq, *J* = 14.5, 7.0 Hz, 2H), 1.38 - 1.25 (m, 24H), 1.24 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.42, 134.88, 133.70, 116.67, 81.69, 79.45, 74.58, 34.69, 31.93, 30.25, 29.70, 29.66, 29.64, 29.46, 29.37, 25.89, 25.28, 22.70, 14.30, 14.13; HR-MS (ESI): Cal'd for $C_{29}H_{44}OS$ [2M+H$^+$] 881.6299; Found 881.6292.



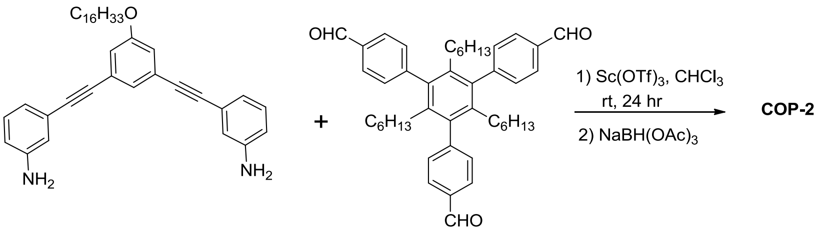
Compound 4: The general procedure for Sonogashira cross coupling was followed. Using (2,6-diethynyl-4-(hexadecyloxy)benzyl)(ethyl)sulfane (200 mg, 0.45 mmol), 3-bromo-5-iodo-benzaldyhyde (310 mg, 1.00 mmol), $Pd(PPh_3)_2Cl_2$ (19 mg, 0.027 mmol), CuI (2.0 mg, 0.009

mmol), triethylamine (5 mL), and THF (5 ml), the compound **4** was obtained as a pale yellow solid (320 mg, 88 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 2H), 8.03-7.86 (m, 6H), 7.49 (s, 2H), 4.32 (t, *J* = 6.3, 2H), 3.69 (s, 2H), 2.50 (q, *J* = 7.4 Hz, 2H), 1.95-1.82 (m, 2H), 1.64-1.54 (m, 2H), 1.41-1.14 (m, *29*H), 0.89 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.83, 160.57, 139.35, 137.84, 134.60, 134.19, 131.82, 131.34, 126.18, 123.23, 116.84, 90.88, 88.24, 75.02, 34.80, 31.93, 30.61, 29.69, 29.66, 29.37, 26.46, 25.43, 22.70, 14.36, 14.14; HR-MS (ESI): Cal'd for $C_{43}H_{50}Br_2O_3S$ [M+H$^+$] 807.7459; Found 807.6611.



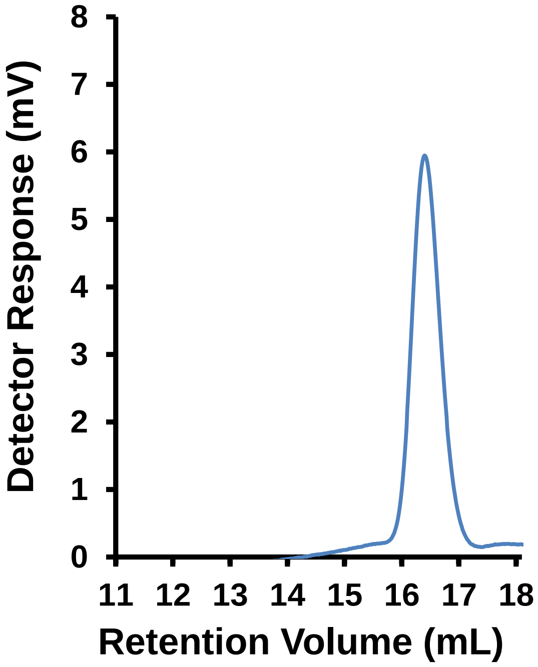
Cage 1: To a schlenk tube was added compound **3** (30 mg, 50 µmol) and compound **4** (60 mg, 74 µmol) in $CHCl_3$ (17 mL) under nitrogen atmosphere. TFA (0.57 µL, 7.43 µmol) was then added drop wise and the reaction was stirred at rt for 18 h. The reaction mixture was cooled at 0 °C, and DIBAL (1.50 mL, 1.0 M solution in CH_2Cl_2, 1.50 mmol) was added. The clear solution was stirred at 0 °C for 1 h. Saturated $NaHCO_3$ was added and the mixture was stirred at rt for 30 min. The product was extracted with $CHCl_3$ (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography using dichloromethane as the eluent to afford the product as a white solid (20 mg, 23 %): ^{1}H NMR (500 MHz, C_6D_6) δ 7.60 (s, 6H), 7.46 (s, 6H), 7.36-7.17 (m, 24H), (d, J = 8.5 Hz, 12H), 4.40 (t, J = 6.0 Hz, 6H), 3.70 (d, J = 5.3 Hz, 12H), 3.29 (m, 12H), 2.52 (s, 12H), 2.14 (q, J = 7.4 Hz, 6H), 1.93 (m, 6H), 1.65 (m, 8H), 1.51 (m, 16H), 1.31 (m, 74H), 1.11-0.86 (m, 80H), 0.79 (t, J = 7.1 Hz, 18H); ^{13}C NMR (101 MHz, C_6D_6) δ 161.03, 145.75, 142.72,

140.00, 139.48, 134.32, 134.08, 132.62, 131.33, 131.10, 130.08, 128.67, 125.33, 122.69, 117.61, 113.10, 111.54, 92.50, 87.15, 74.63, 46.89, 34.56, 32.04, 31.05, 30.77, 29.93, 29.85, 29.66, 29.54, 26.57, 24.96, 22.83, 22.31, 14.12, 14.07; MS (MALDI) calc'd for $C_{213}H_{264}Br_6N_6O_3S_3$ ([M$^+$]) 3531.50, found 3530.78.



Cage 2: For synthesis of Cage 2, refer our previous publication.[3] The physical data for Cage **2**: ^{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. GPC Graph of Cage 1



4. Gold Nanoparticle Assembly

All reactions were carried out on a 5-10 mg scale with respect to cage **1**. A solution of $HAuCl_4$ (6 mg, 0.014 mmol) in deionized H_2O (0.5 mL) was stirred and TOAB (39 mg, 0.071 mmol) in CH_2Cl_2 (0.5 mL) was added and stirred until Au(III) was transferred into organic phase (~25 min). A solution of cage **1** (5 mg, 0.0014 mmol) in CH_2Cl_2 (0.5 mL) and subsequently reduced with an aqueous solution of $NaBH_4$ (10 mg, 0.26 mmol) in deionized H_2O (0.5 mL). The resulting organic layer was dark in color and contained no precipitate. After separation, the aqueous layer was washed with CH_2Cl_2 (2 x 1 mL), the organic fractions were combined and concentrated to ca. 0.2 mL without the application of heat. Ethanol (1.5 mL) was then added and the solution was centrifuged to precipitate the AuNP@**1** complexes. This centrifugation procedure was repeated until the supernatant was no longer colored (~3 times). The resulting complexes are soluble in all organic solvents and stable in solutions, even over periods of several months.

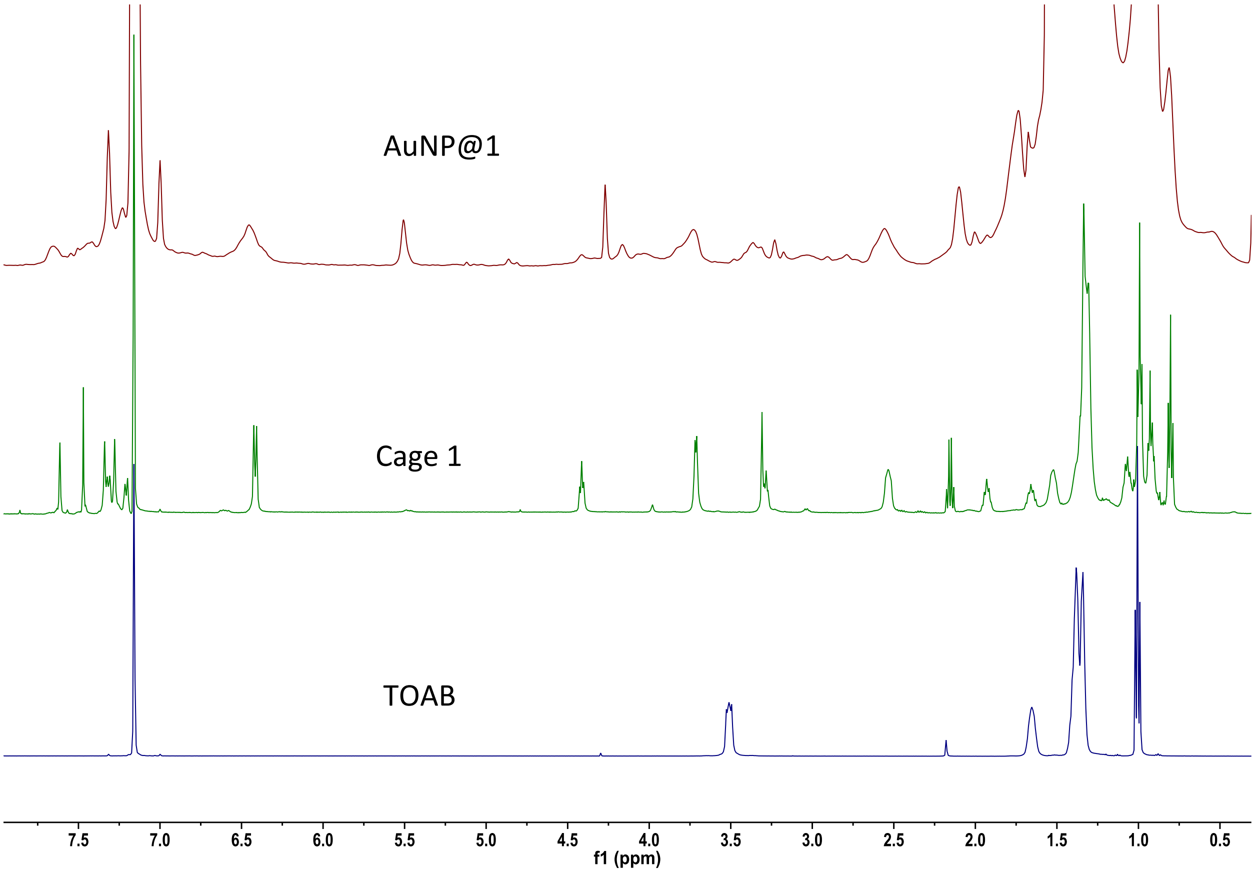


Figure S1. ^{1}H NMR spectra of TOAB, cage **1**, and AuNP@**1**.

5. Computational Methods

The Amber 11.0 molecular dynamics program package[4] was used to optimize the structures of the cage/nanoparticle complexes. The force field used for the cage was the general Amber force field (GAFF field)[5] with the charge parameters computed by AM1-BCC method.[6] The force field parameters for gold atoms were taken from the literature report.[7] For each optimization run, the atoms on gold nanoparticle were frozen and the structure of the cage was optimized. The cage was first minimized for 5000 steps using the conjugate gradient method, and then it was further optimized by simulated annealing method for 150 picosecond with a time-step of 1 femtosecond. During the simulated annealing, the system temperature was first raised up to 1000 K for 50 picosecond and then gradually cooled to 0 K for another 100 picosecond. Finally, the annealed structure was minimized again for another 5000 conjugate gradient steps. The total energy of cage-cage and cage-gold interactions was calculated based on the minimized structure.

6. Transmission Electron Microscopy (TEM)

Imaging was performed using a JEOL ARM 200F, Schottky Field Emission TEM, Bright Field only. The sample was drop cast on a Ultrathin Carbon / Holey Support on 400 Cu mesh (part number 1824) from Ted Pella (Images 45 and greater). Particle size data were obtained by analyzing TEM images using software ImageJ. Imaging conditions for figure S2 (a), and (b): 120kV, 50um aperture, TEM-L (large convergence angle). Carbon film was very apparent in images. Imaging conditions figure S2 (c): 200kV, 50um CL aperture, objective aperture (High Contrast) 60um. Carbon film was slightly less apparent in images

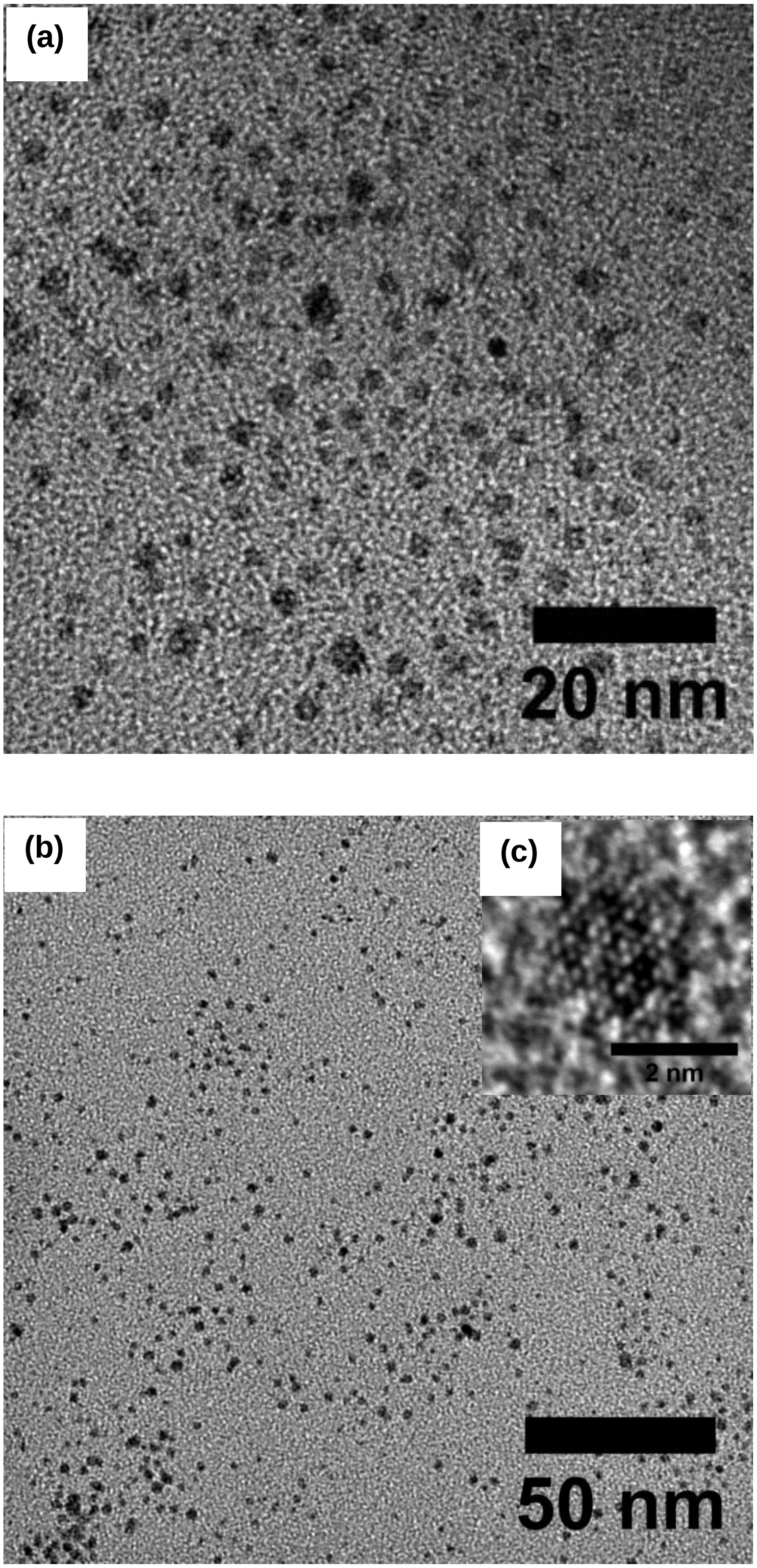


Figure S2. Representative TEM images

7. Diffusion NMR experiment

Diffusion ordered spectroscopy (DOSY) NMR was performed on a Varian Inova 500 MHz NMR spectrometer. Both samples of cage **1** and AuNP@**1** were measured using C_6D_6 as the solvent at concentrations of 6 mM. The effective hydrodynamic radius R was calculated using the Strokes-Einstein equation: $D = (k_BT)/(6\pi\eta r)$, where D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature (23 °C), and η is the viscosity of C_6D_6 (0.65 mPa·s). The measured diffusion coefficient for cage **1** was $2.5 \pm 0.4 x 10^{-10} m^2 s^{-1}$ and for AuNP@**1** $2.4 \pm 0.4 x 10^{-10} m^2 s^{-1}$ thus giving hydrodynamic radii of 13Å±1.0 Å and *14 Å±1.0 Å*, respectively.

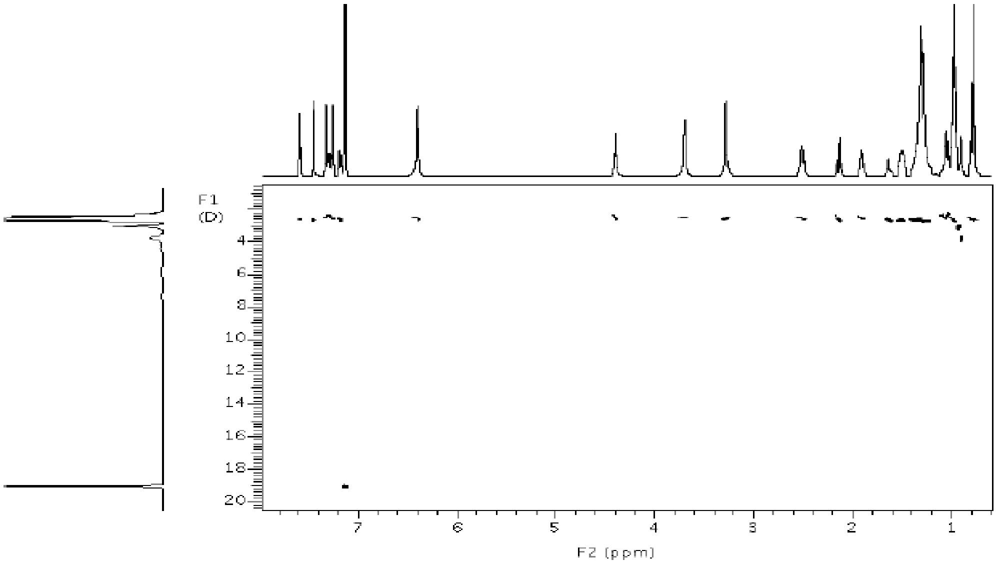


Figure S3. ^{1}H 2D-DOSY NMR spectrum of cage **1** in C_6D_6. A Diffusion cross-peak for the solvent (7.15 ppm) is also present.

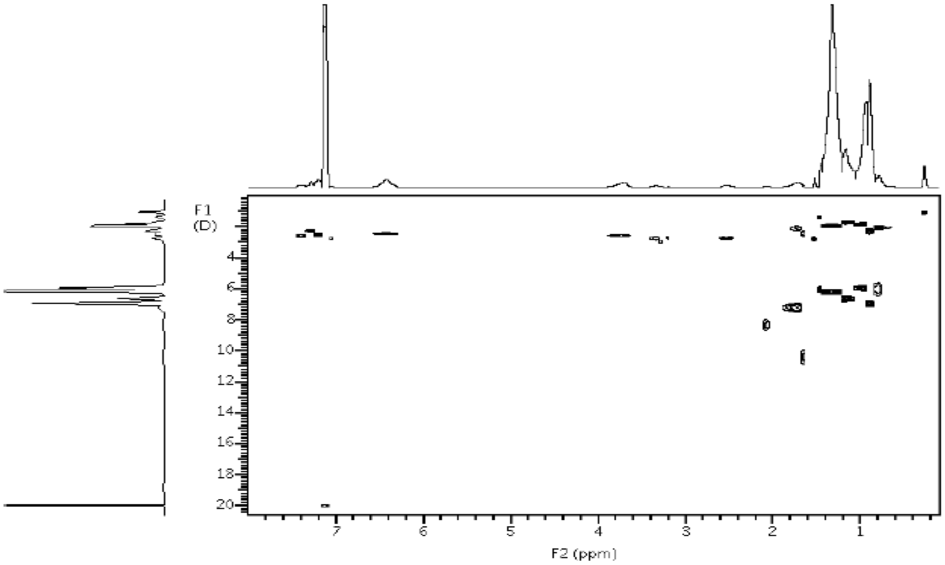


Figure S4. ^{1}H 2D-DOSY NMR spectrum of AuNP@**1** in C_6D_6. The appearance of multiple diffusion cross-peaks in the 1-2 ppm region is presumably due to a change in diffusion of the lengthy alkyl chains as they are restricted solely to the exterior of AuNP@**1** complex once the nanoparticle is formed within the cage cavity.

8. Thermal gravimetric analyses

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.

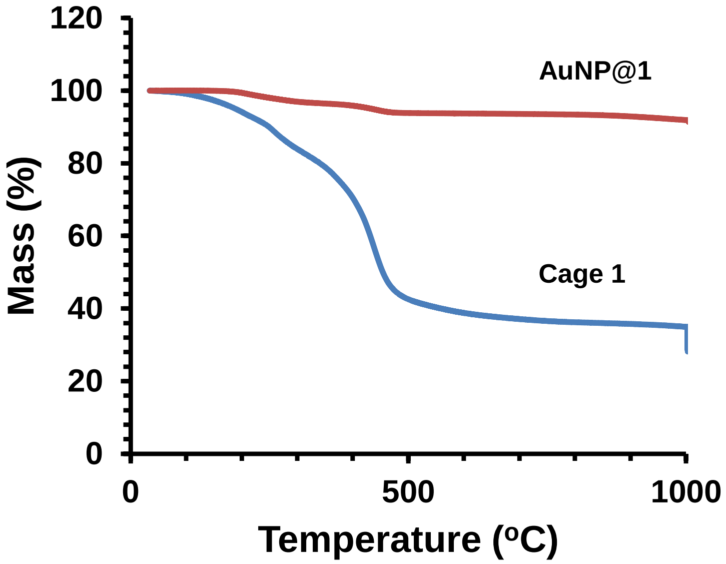
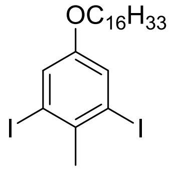
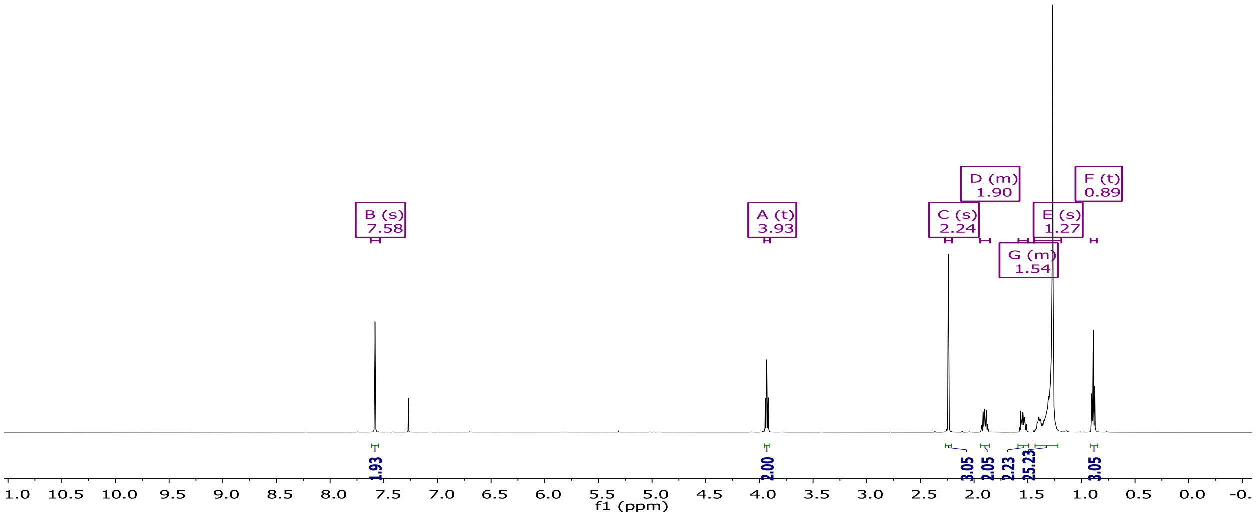
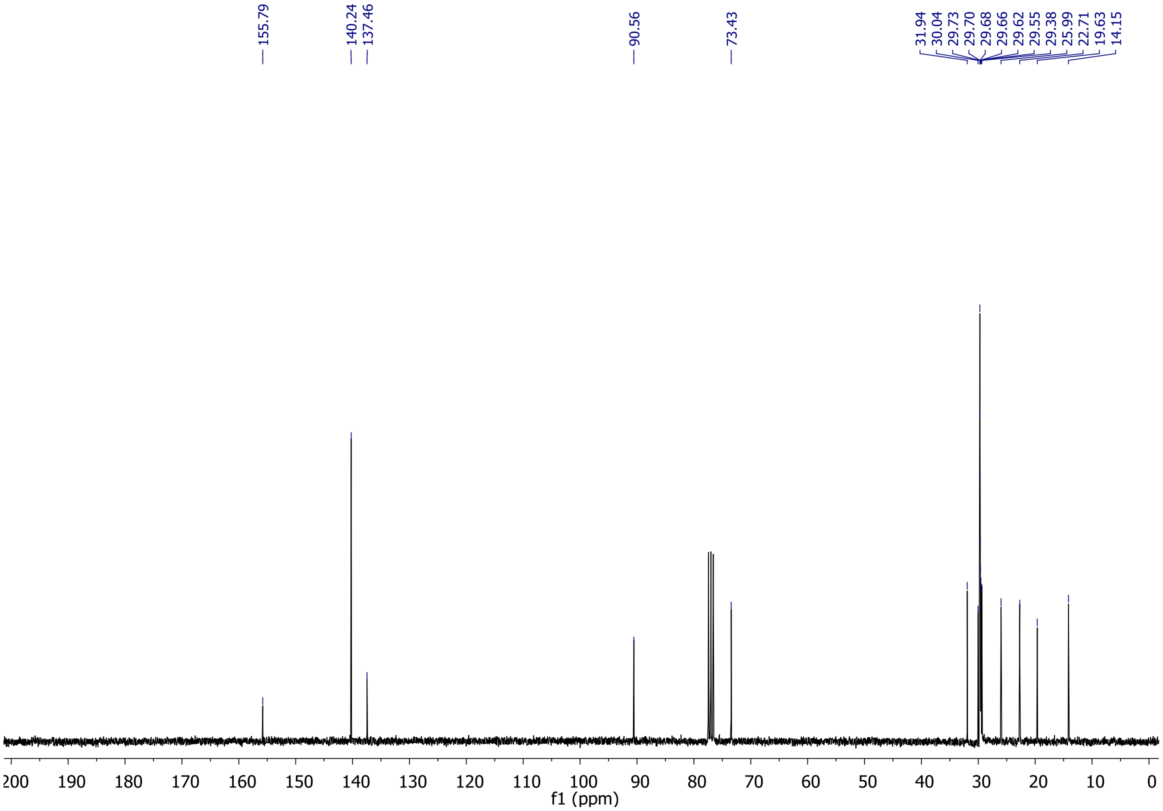


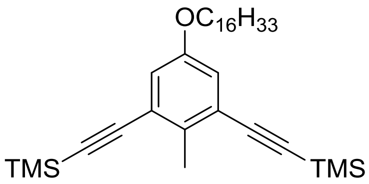
Figure S5: TGA graphs of cage **1** and AuNP@**1**.

9. NMR Spectra of Selected Compounds





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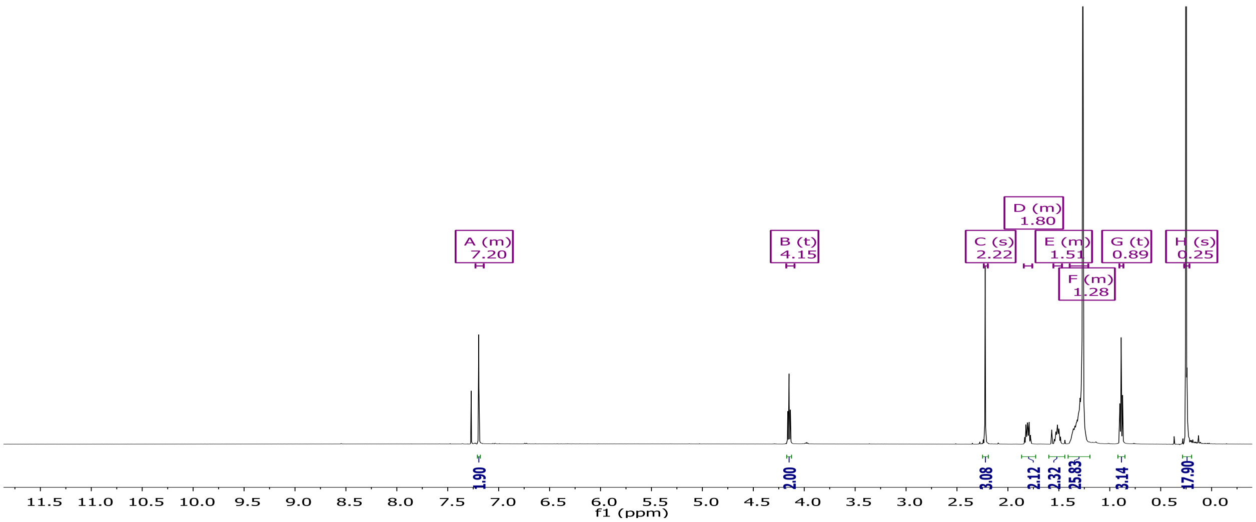
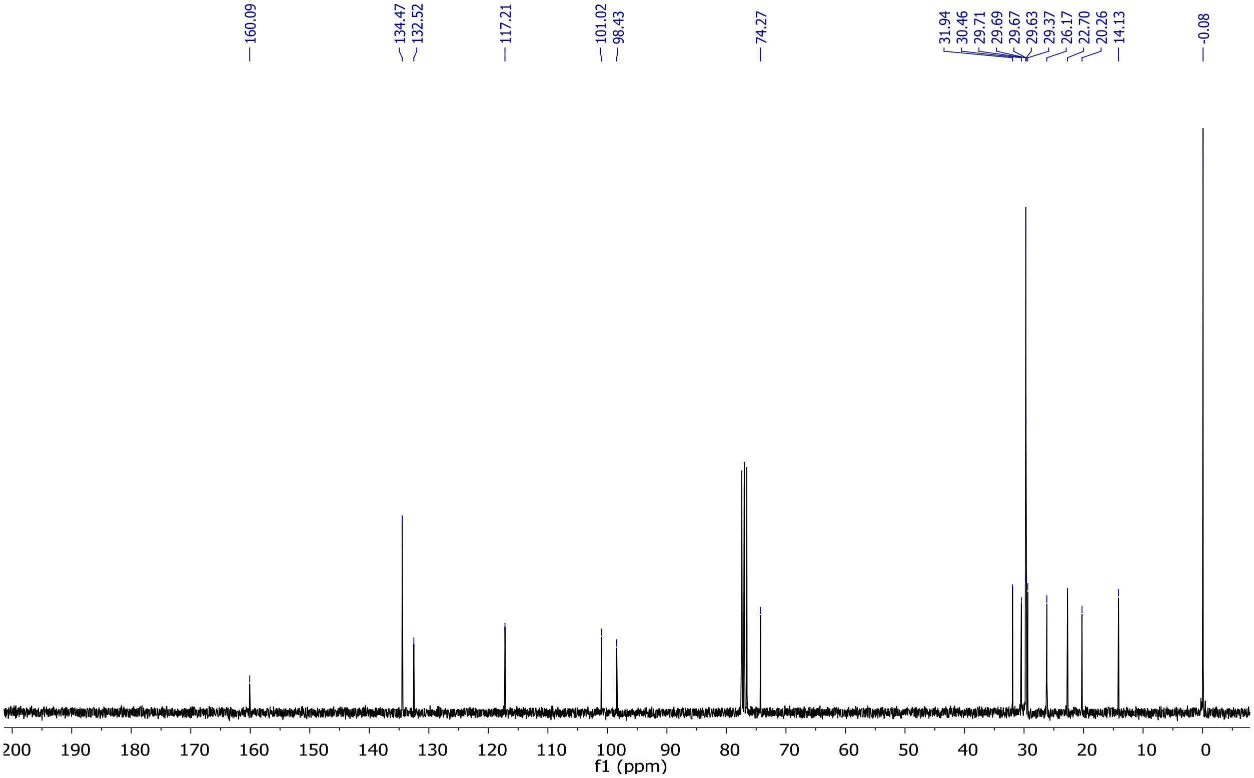
TMS
TMS


A (m) 7.20
B (t) 4.15
C (s) 2.22
D (m) 1.80
E (m) 1.51
F (m) 1.28
G (t) 0.89
H (s) 0.25
1.90
2.00
3.08
2.12
2.32
25.83
3.14
17.90
11.5 11.0 10.5 10.0 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
f1 (ppm)


160.09
134.47
132.52
117.21
101.02
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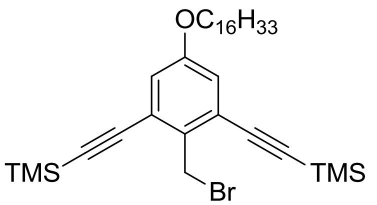
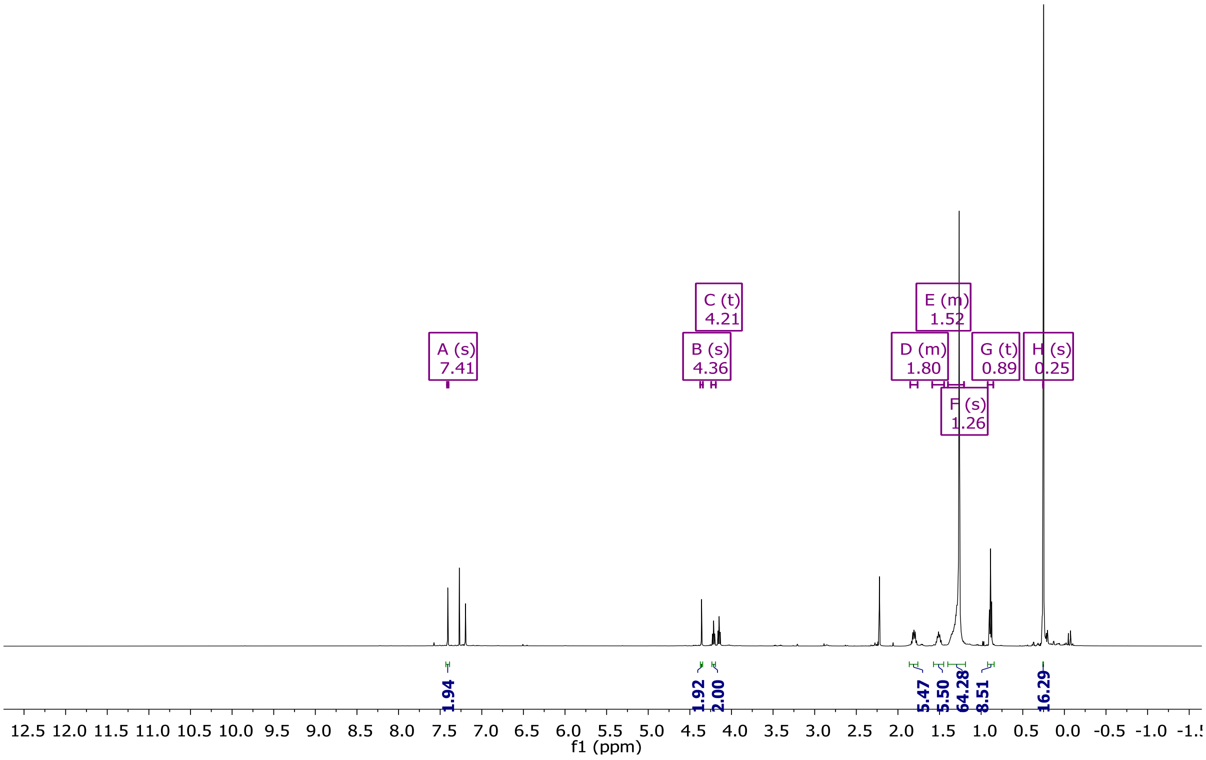
74.27
31.94
30.46
29.71
29.69
29.67
29.63
29.37
26.17
22.70
20.26
14.13
-0.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OC$_{16}$H$_{33}$
TMS
TMS
Br


A (s)
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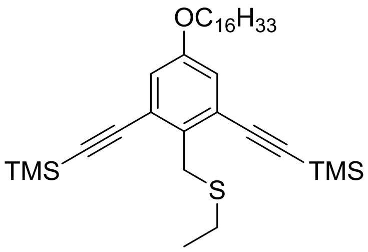
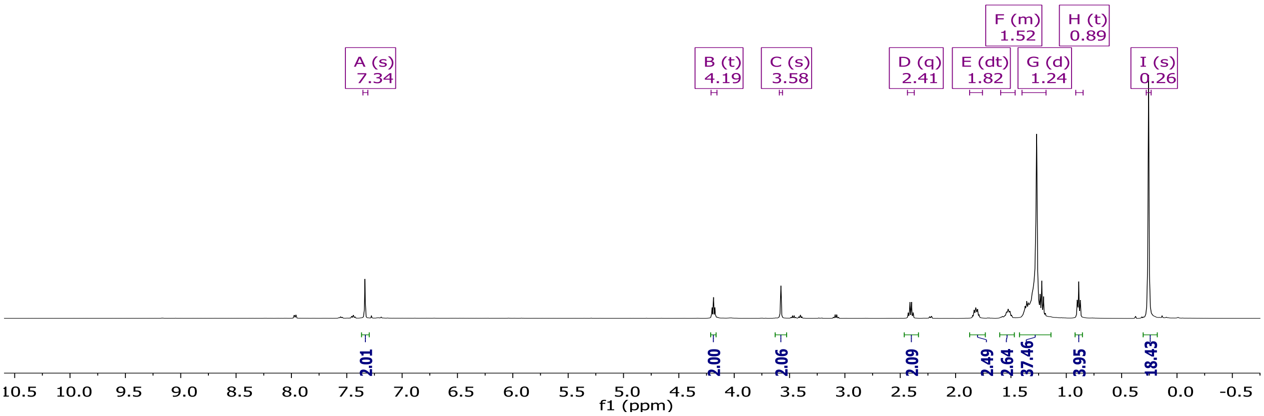
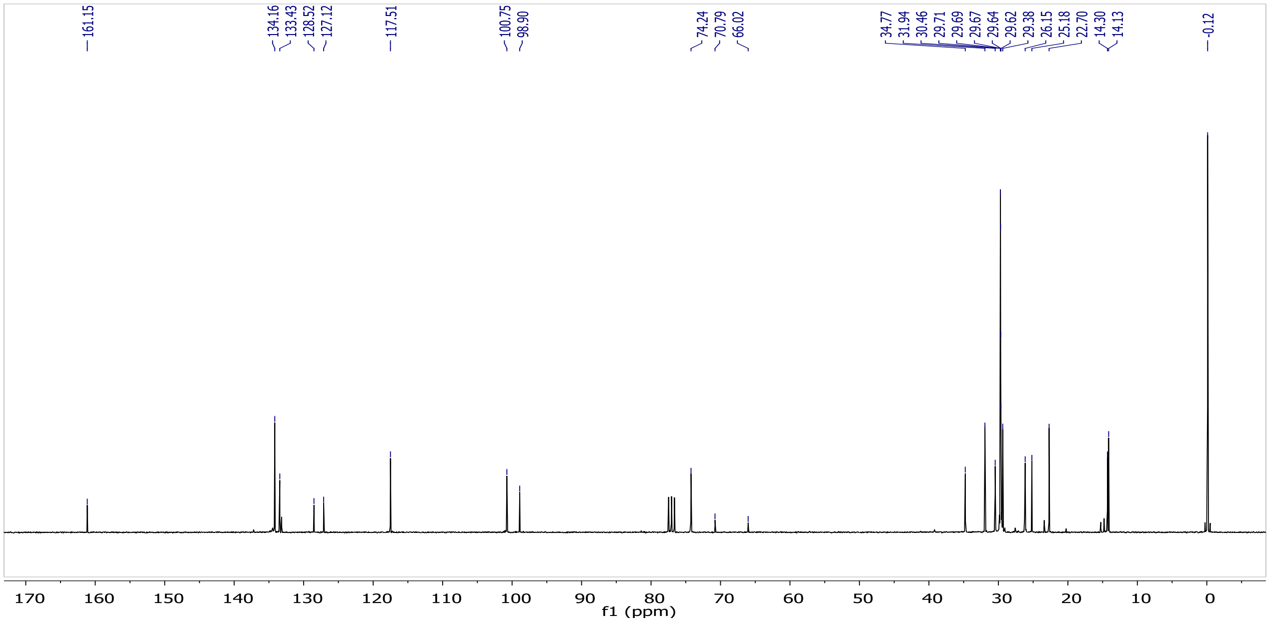
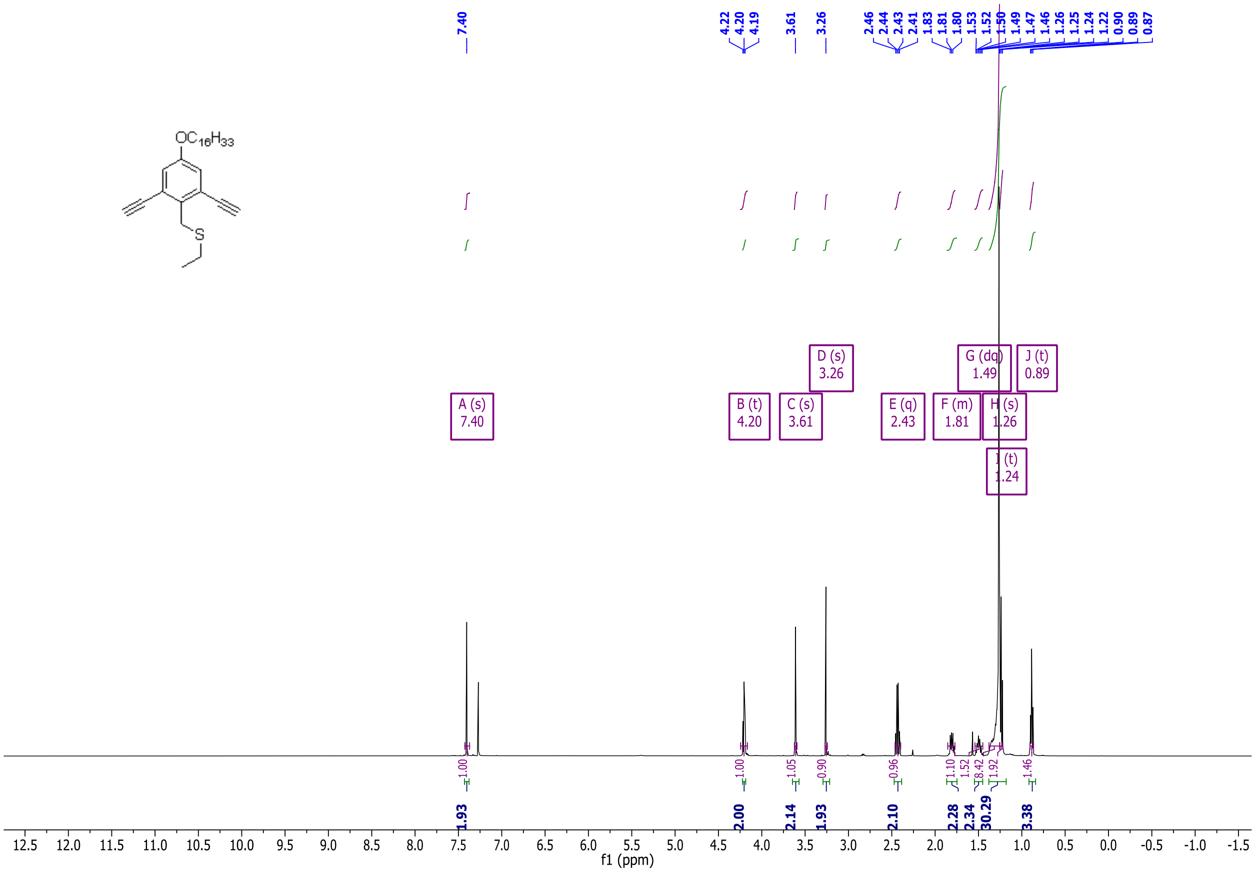
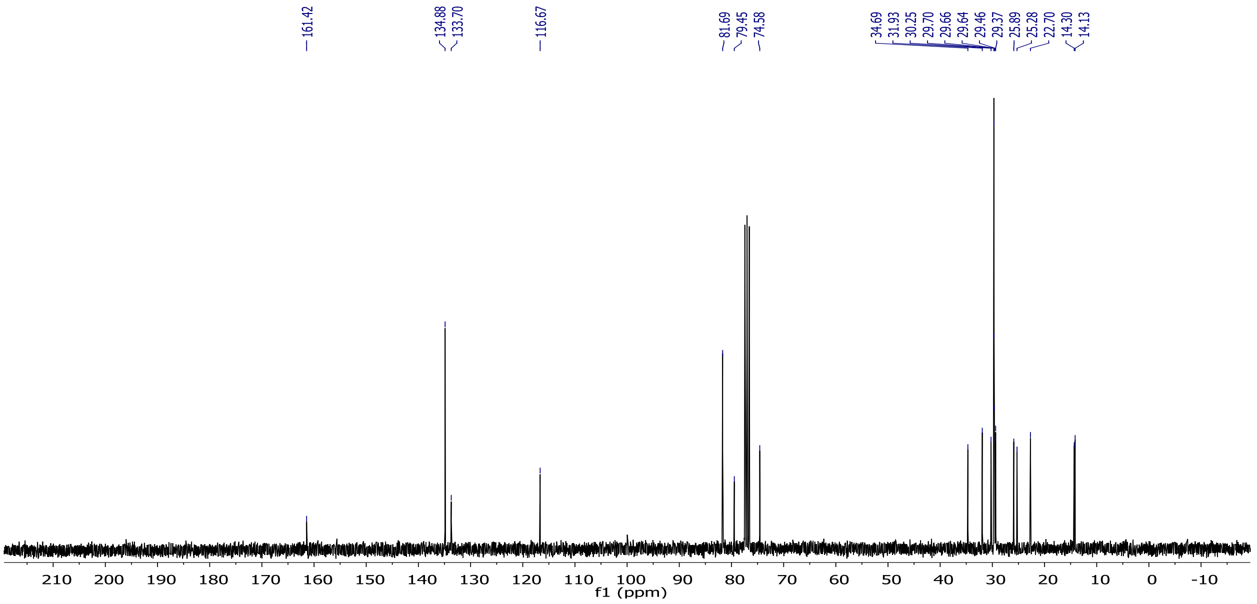
B (s)
4.36
C (t)
4.21
D (m)
1.80
E (m)
1.52
F (s)
1.26
G (t)
0.89
H (s)
0.25
1.94
1.92
2.00
5.47
5.50
64.28
8.51
16.29
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

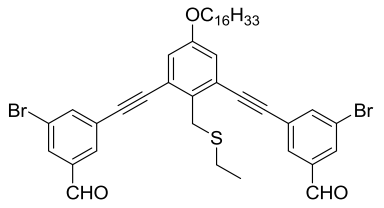

OC16H33
TMS
TMS
S

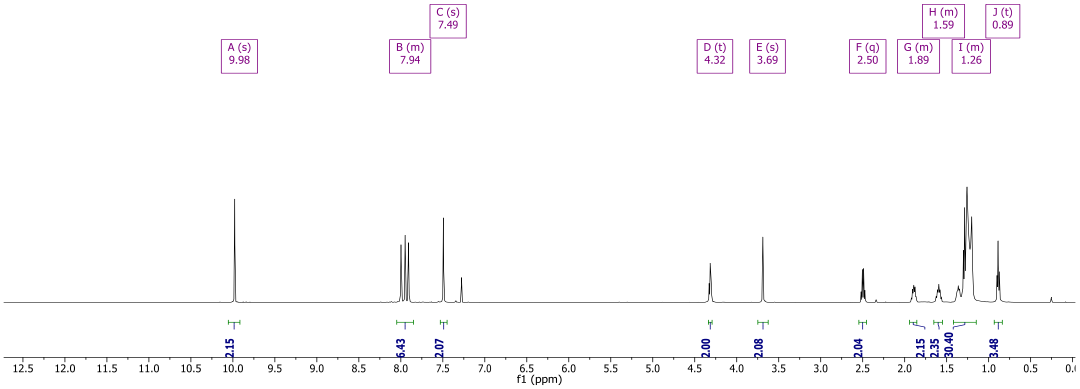

A (s)
7.34
B (t)
4.19
C (s)
3.58
D (q)
2.41
E (dt)
1.82
F (m)
1.52
G (d)
1.24
H (t)
0.89
I (s)
0.26
2.01
2.00
2.06
2.09
2.49
2.64
37.46
3.95
18.43
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

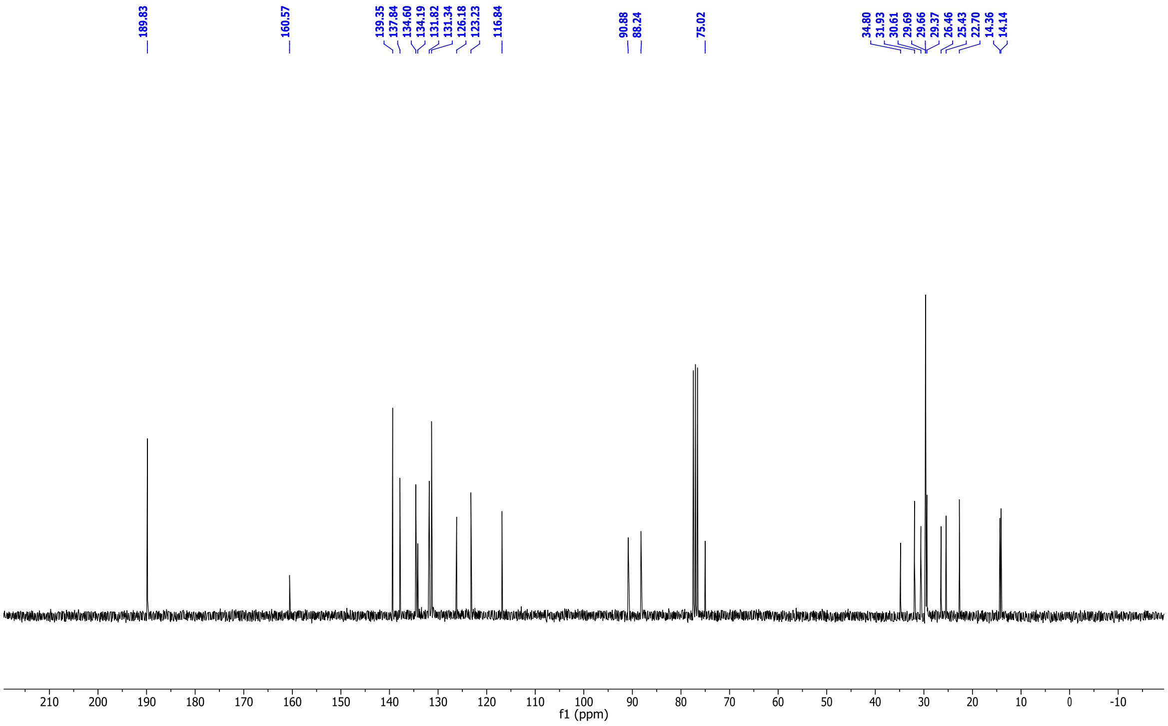

161.15
134.16
133.43
128.52
127.12
117.51
100.75
98.90
74.24
70.79
66.02
34.77
31.94
30.46
29.71
29.69
29.67
29.64
29.62
29.38
26.15
25.18
22.70
14.30
14.13
-0.12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OC16H33
S
7.40
4.22
4.20
4.19
3.61
3.26
2.46
2.44
2.43
2.41
1.83
1.81
1.80
1.53
1.52
1.50
1.49
1.47
1.46
1.26
1.25
1.24
1.22
0.90
0.89
0.87
A (s) 7.40
B (t) 4.20
C (s) 3.61
D (s) 3.26
E (q) 2.43
F (m) 1.81
G (dq) 1.49
H (s) 1.26
I (t) 1.24
J (t) 0.89
1.00
1.00
1.05
0.90
0.96
1.10
1.52
18.42
1.92
1.46
1.93
2.00
2.14
1.93
2.10
2.28
2.34
30.29
3.38
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)

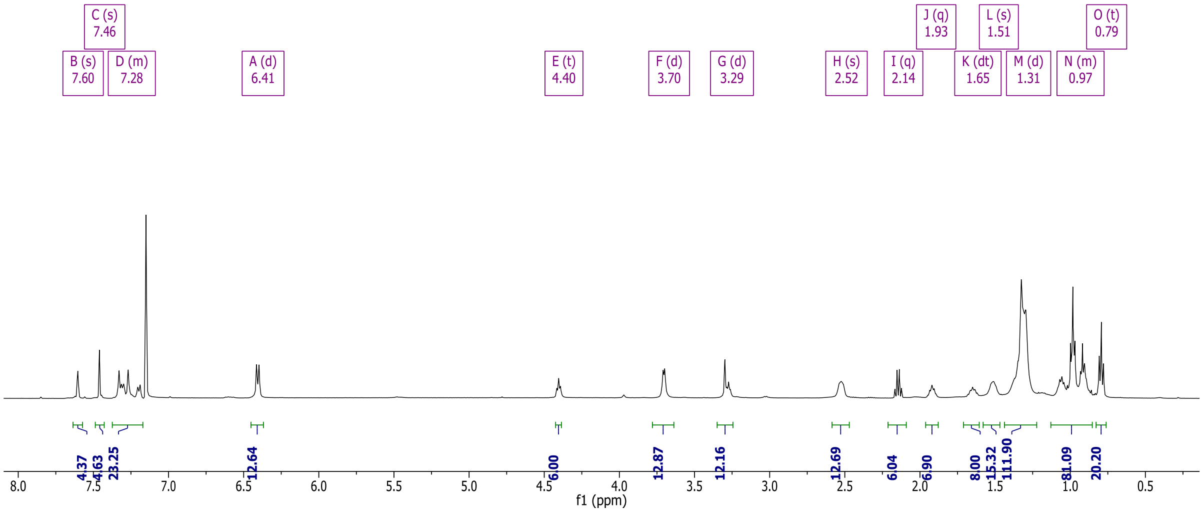

161.42
134.88
133.70
116.67
81.69
79.45
74.58
34.69
31.93
30.25
29.70
29.66
29.64
29.46
29.37
25.89
25.28
22.70
14.30
14.13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

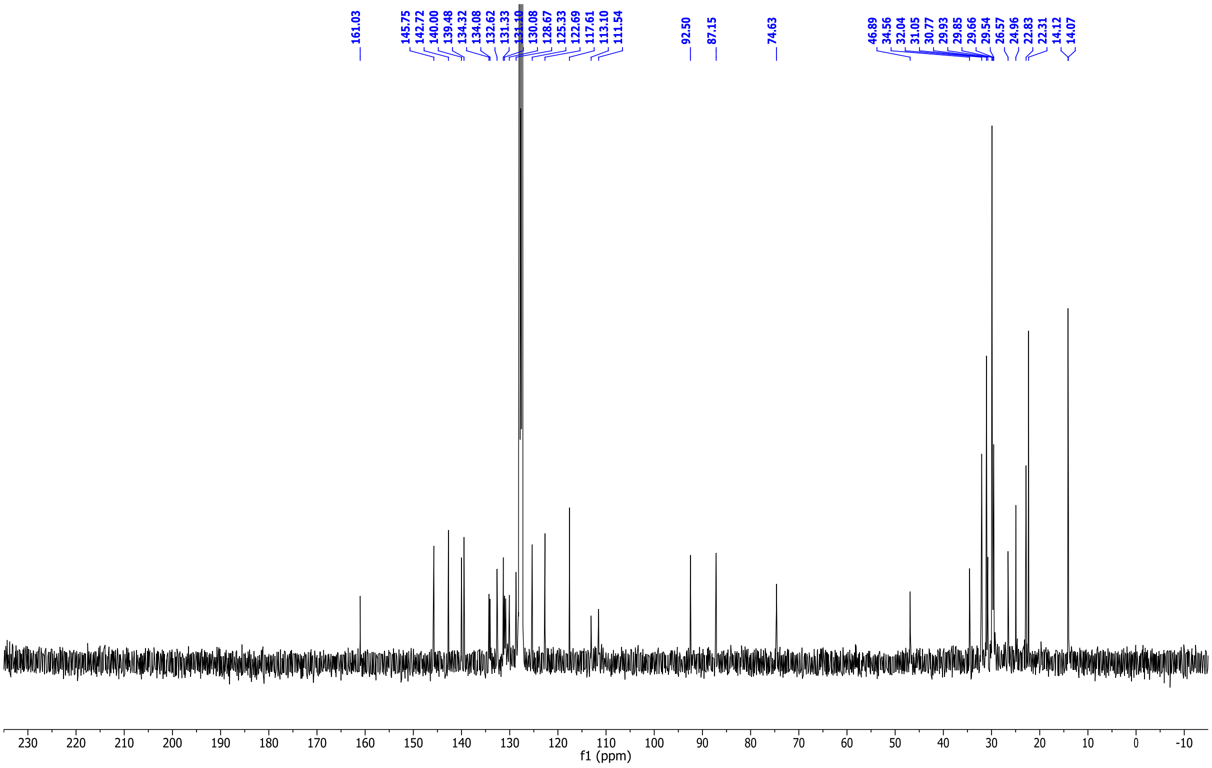

OC16H33
Br
Br
S
CHO
CHO


A (s)
9.98
B (m)
7.94
C (s)
7.49
D (t)
4.32
E (s)
3.69
F (q)
2.50
G (m)
1.89
H (m)
1.59
I (m)
1.26
J (t)
0.89
2.15
6.43
2.07
2.00
2.08
2.04
2.15
2.35
30.40
3.48
12.5
12.0
11.5
11.0
10.5
10.0
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
f1 (ppm)


189.83
160.57
139.35
137.84
134.60
134.19
131.82
131.34
126.18
123.23
116.84
90.88
88.24
75.02
34.80
31.93
30.61
29.69
29.66
29.37
26.46
25.43
22.70
14.36
14.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Cage **1**


C (s) 7.46
J (q) 1.93
L (s) 1.51
O (t) 0.79
B (s) 7.60
D (m) 7.28
A (d) 6.41
E (t) 4.40
F (d) 3.70
G (d) 3.29
H (s) 2.52
I (q) 2.14
K (dt) 1.65
M (d) 1.31
N (m) 0.97
4.37
4.63
23.25
12.64
6.00
12.87
12.16
12.69
6.04
6.90
8.00
15.32
111.90
81.09
20.20
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
f1 (ppm)


161.03
145.75
142.72
140.00
139.48
134.32
134.08
132.62
131.33
131.10
130.08
128.67
125.33
122.69
117.61
113.10
111.54
92.50
87.15
74.63
46.89
34.56
32.04
31.05
30.77
29.93
29.85
29.66
29.54
26.57
24.96
22.83
22.31
14.12
14.07
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

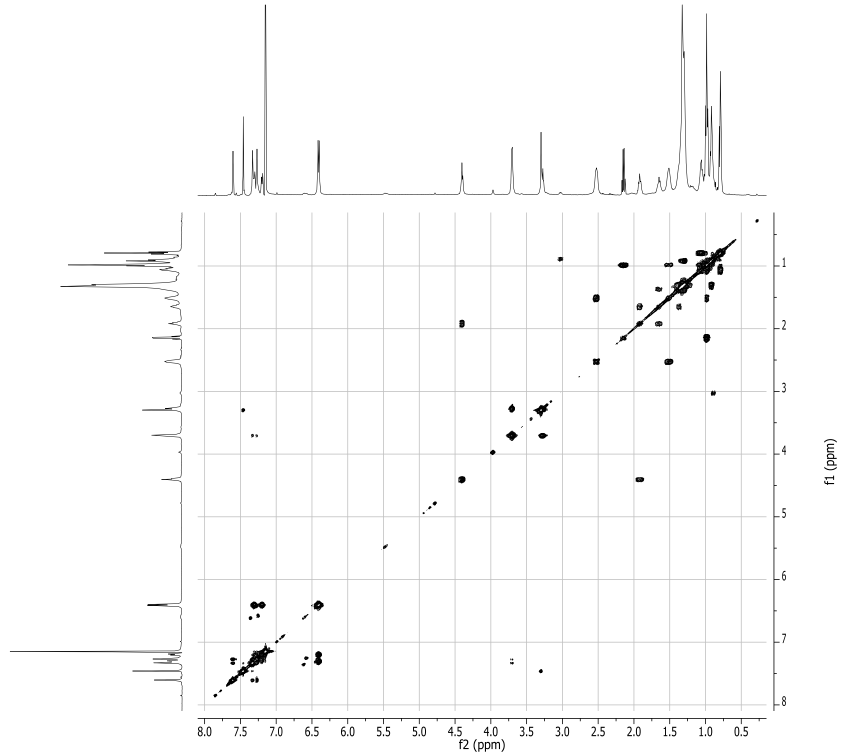


Figure S6. COSY spectrum of **1**.

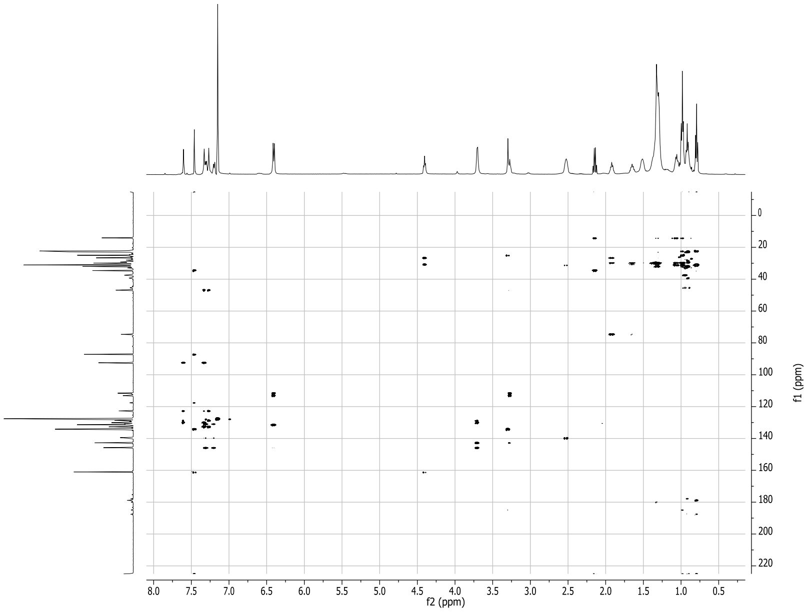


Figure S7. HMBC of **1**.

10. **References**

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