

Preparation of Cyclophanes by Room-Temperature Ring-Closing Alkyne Metathesis with Imidazolin-2-iminato Tungsten Alkylidyne Complexes

Stephan Beer, Kai Brandhorst, Jörg Grunenberg, Cristian Hrib, Peter G. Jones and Matthias Tamm*

*Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30,
D-38106 Braunschweig, Germany*

Supporting Information

Index

- I. General
- II. Preparation of starting materials
- III. Ring-closing alkyne metathesis
- IV. Crystal Structure Determinations
- V. Mathematical details for the calculation of the monomer-/dimer- ratio from computed Gibbs free energy changes
- VI. Electronic Structure Calculations
- VII. Cartesian coordinates of the minimum energy structures of the *ortho*-, *meta*- and *para*-monomers and dimers (B3LYP/6-311G(d,p)
- VIII. Spectra

I. General

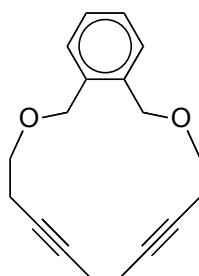
All operations with air and moisture-sensitive compounds were performed in a glove box under a dry argon atmosphere (MBraun 200B) or on a high vacuum line using Schlenk techniques. All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. The ¹H and ¹³C spectra were recorded on Bruker DPX 200 (200 MHz), Bruker DRX 400 (400 MHz), and Bruker DPX 600 (600 MHz), devices. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard. Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Elemental analysis (C, H, N) succeeded by combustion and gas chromatographical analysis with an Elementar varioMICRO. GC analysis was performed on a SHIMADZU GC-2010, GC-MS were accomplished on a JEOL AccuTOF, MS on a Finnigan MAT 95 (EI), Finnigan MAT 95 XL (ESI), respectively and HR-MS from Bruker-Demo QTOF micro. Unless otherwise indicated, all starting materials were obtained from Aldrich and were used without further purification. Flash chromatography was performed using Merck silica gel (230-400 mesh).

II. Preparation of starting materials

Catalyst **1**¹ was prepared following literature procedures.

General synthesis of the diynes (Williamson etherification):

In a 250 ml Schlenk flask 0.060 mol of 3-pentyn-1-ol were dissolved in 30 ml THF and degassed several times. 0.040 mol sodium were added and stirred for 2 h at room temperature. A solution of 0.015 mol of the dihalide in 25 ml THF were added to the resulting sodium salt and refluxed over night. After cooling the suspension to room temperature the reaction was quenched by adding 100 ml H₂O. The product was extracted with 60 ml Et₂O and washed several times with 25 ml H₂O. Evaporation of the solvent afforded the pure product in yields > 68% as light yellow oils or white solids, respectively.



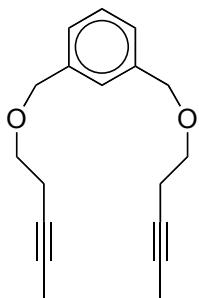
2a

o-Xylylenedi(oxapent-3-yne)

¹ Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M. *Angew. Chem.* **2007**, *119*, 9047; *Angew. Chem.; Int. Ed.* **2007**, *46*, 8890.

Isolated yield: 89% as colorless oil

¹H NMR (200.1 MHz, CDCl₃, 25 °C): δ 1.78 (6 H, t, CH₃), 2.43 (4 H, tq, CCH₂), 3.56 (4 H, t, CH₂), 4.63 (4 H, s, OCH₂), 7.31 (4 H, m, ArH); ¹³C NMR (50.3 MHz, CDCl₃, 25 °C): δ 3.5 (s, CH₃), 20.1 (s, CCH₂), 69.0 (s, OCH₂), 70.6 (s, OCH₂), 75.9 (s, C≡C), 76.8 (s, C≡C), 127.8 (s, Ar-C), 128.7 (s, Ar-C), 136.4 (s, Ar-C); elemental analysis: calculated for C₁₈H₂₂O₂: C 79.96 %, H 8.20 %; found: C 79.97 %, H 8.03 %.

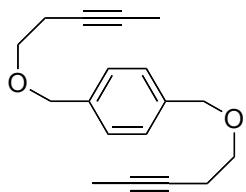


2b

m-Xylylenedi(oxapent-3-yne)

Isolated yield: 91% as yellow oil

¹H NMR (200.1 MHz, CDCl₃, 25 °C): δ 1.77 (6 H, t, ⁵J_{HH} = 2.6 Hz, CH₃), 2.44 (4 H, tq, CCH₂), 3.54 (4 H, t, ³J_{HH} = 7.1 Hz CH₂), 4.54 (4 H, s, OCH₂), 7.28 (4 H, m, ArH); ¹³C NMR (50.3 MHz, CDCl₃, 25 °C): δ 4.6 (s, CH₃), 21.3 (s, CCH₂), 70.0 (s, OCH₂), 73.9 (s, OCH₂), 77.0 (s, C≡C), 77.8 (s, C≡C), 128.1 (s, Ar-C), 129.6 (s, Ar-C), 139.6 (s, Ar-C); elemental analysis: calculated for C₁₈H₂₂O₂: C 79.96 %, H 8.20 %; found: C 79.57 %, H 8.26 %.



2c

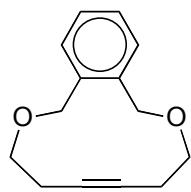
p-Xylylenedi(oxapent-3-yne)

Isolated yield: 68% as white solid

¹H NMR (200.1 MHz, CDCl₃, 25 °C): δ 1.78 (6 H, t, CH₃), 2.43 (4 H, tq, CCH₂), 3.54 (4 H, t, CH₂), 4.54 (4 H, s, OCH₂), 7.32 (4 H, s, ArH); ¹³C NMR (50.3 MHz, CDCl₃, 25 °C): δ 3.5 (s, CH₃), 20.1 (s, CCH₂), 68.7 (s, OCH₂), 72.6 (s, OCH₂), 75.8 (s, C≡C), 77.4 (s, C≡C), 127.8 (s, Ar-C), 137.6 (s, Ar-C); elemental analysis: calculated for C₁₈H₂₂O₂: C 79.96 %, H 8.20 %; found: C 79.94 %, H 8.40 %.

III. Ring closing alkyne metathesis (RCAM)

A 4.5 mM hexane solution of the diynes **2** (150.0 mg, 0.055 mmol) and catalyst **1** (9.0 mg, $1.11 \cdot 10^{-5}$ mol, 2 mol %) was stirred at room temperature under reduced pressure (350 mbar). After 2 h the solution was filtered through alumina in order to remove the catalyst **1** and elution with Et₂O afforded the cyclization products after evaporation of the solvent. In the case of **3b** and **4c** colorless crystals could be obtained from a cooled (4 °C) hexane or CHCl₃ solution, respectively. Employing **2a** afforded a mixture of monomeric cycloalkyne **3a** and dimeric cycloalkyne **4a** in a 24:76 ratio according to a ¹H NMR spectrum, which was taken from the crude product after evaporation of the solvent. Isolation of **3a** and **4a** could be achieved by fractional crystallization from hexane, whereby the dimeric product precipitated. After removal of **4a** colorless crystals of **3a** could be obtained from the supernatant hexane solution.

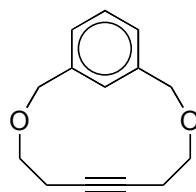


3a

2,9-Dioxa[10]orthocyclophane-5-yne

Isolated yield: 18% as colorless crystals

¹H NMR (200.1 MHz, CDCl₃, 25 °C): δ 2.41 (4 H, tt, C≡CCH₂), 3.73 (4 H, t, OCH₂), 4.87 (4 H, s, OCH₂), 7.33 (4 H, m, ArH). ¹³C NMR (50.3 MHz, CDCl₃, 25 °C): δ 21.2 (s, CH₂), 68.4 (s, OCH₂), 71.7 (s, OCH₂), 80.9 (s, C≡C), 128.1 (s, Ar-C), 130.1 (s, Ar-C), 138.5 (s, ipso-C). elemental analysis: calculated for C₁₄H₁₆O₂: C 77.75 %, H 7.46 %; found: C 77.54 %, H 7.66 %. MS (ESI), m/z (% relative intensity): 239.1 (M⁺ + Na, 100). GC-MS (EI), m/z (relative intensity): 215 (M⁺, 10); 197 (15); 171 (100); 155 (18); 141 (20); 119 (19); 104 (19); 91 (21); 77 (24); 65 (8).



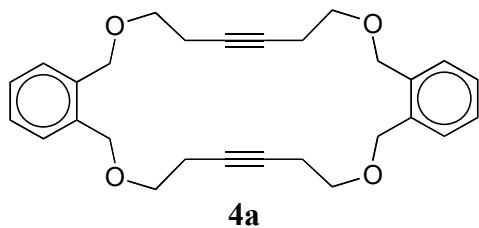
3b

2,9-Dioxa[10]metacyclophane-5-yne

Isolated yield: 93% as colorless crystals

¹H NMR (200.1 MHz, CDCl₃, 25 °C): δ 2.45 (4 H, tt, ³J_{HH} = 5.2 Hz, C≡CCH₂), 3.65 (4 H, t, ³J_{HH} = 4.8 Hz, OCH₂), 4.65 (4 H, s, OCH₂), 7.03 (2 H, d(q), ArH), 7.27 (1 H, m, ArH), 8.30 (1 H, s(q),

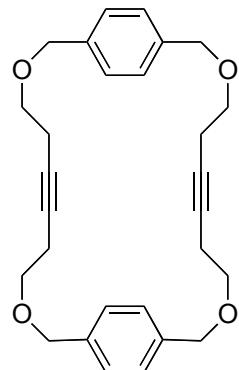
ArH). ^{13}C NMR (50.3 MHz, CDCl_3 , 25 °C): δ 20.9 (s, CH_2), 68.9 (s, OCH_2), 71.1 (s, OCH_2), 79.5 (s, $\text{C}\equiv\text{C}$), 124.5 (s, Ar-C), 125.0 (s, Ar-C), 127.6 (s, Ar-C), 139.7 (s, ipso-C). elemental analysis: calculated for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C 77.75 %, H 7.46 %; found: C 77.66 %, H 7.70 %.



2,9,2',9'-Tetraoxa[10.10]orthocyclophane-5,5'-diyne

Isolated yield: 65% as white solid

^1H NMR (200.1 MHz, CDCl_3 , 25 °C): δ 2.50 (4 H, tt, $\text{C}\equiv\text{CCH}_2$), 3.62 (4 H, t, OCH_2), 4.68 (4 H, s, OCH_2), 7.33 (4 H, m, ArH). ^{13}C NMR (50.3 MHz, CDCl_3 , 25 °C): δ 19.6 (s, CH_2), 68.5 (s, OCH_2), 70.3 (s, OCH_2), 77.7 (s, $\text{C}\equiv\text{C}$), 127.3 (s, Ar-C), 128.5 (s, Ar-C), 135.9 (s, ipso-C). elemental analysis: calculated for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C 77.75 %, H 7.46 %; found: C 77.12 %, H 7.30 %. MS (ESI), m/z (% relative intensity): 456.2 ($\text{M}^+ + \text{Na}$, 100).



4c

2,9,2',9'-Tetraoxa[10.10]metacyclophane-5,5'-diyne

Isolated yield: 68% as colorless crystals

^1H NMR (200.1 MHz, CDCl_3 , 25 °C): δ 2.45 (8 H, tt, $\text{C}\equiv\text{CCH}_2$), 3.51 (8 H, t, OCH_2), 4.55 (8 H, s, OCH_2), 7.28 (8 H, s, ArH); ^{13}C NMR (50.3 MHz, CDCl_3 , 25 °C): δ 20.3 (s, CH_2), 68.3 (s, OCH_2), 72.6 (s, OCH_2), 78.2 (s, $\text{C}\equiv\text{C}$), 127.7 (s, Ar-C), 137.7 (s, ipso-C); elemental analysis: calculated for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C 77.75 %, H 7.46 %; found: C 77.75 %, H 8.10 %.

IV. Crystal Structure Determinations

The hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Diffractometer: Bruker APEX2. Program system: SHELXL-97 (G. M. Sheldrick, University of Göttingen).

Crystal data of **3b**: C₁₄H₁₆O₂, M_r = 216.27 g/mol, crystal dimensions 0.10 x 0.05 x 0.03 mm³, monoclinic, P2₁/c, *a* = 8.292(4), *b* = 16.943(9), *c* = 8.169(4) Å, β = 93.057(14)°, V = 1146.1(10) Å³, Z = 4, ρ_{calc} = 1.253 Mg/m³, μ = 0.082 mm⁻¹, MoK_α (λ = 0.71073 nm⁻¹), T = 100 K, 2θ_{max} = 50, 17243 reflections, 2027 independent (*R*_{int} = 0.1899), *R*₁(*I* > 2σ(*I*)) = 0.0583, *wR*₂ (all data) = 0.1597, Δρ = 0.27/-0.31 e.Å⁻³.

Crystal data of **4c**: C₂₈H₃₂O₄, M_r = 432.54 g/mol, crystal dimensions 0.18 x 0.10 x 0.04 mm³, monoclinic, P2₁/c, *a* = 12.9818(8), *b* = 9.8352(7), *c* = 8.9683(6) Å, β = 90.586(4)°, V = 1145.00(13) Å³, Z = 2, ρ_{calc} = 1.255 Mg/m³, μ = 0.082 mm⁻¹, MoK_α (λ = 0.71073 nm⁻¹), T = 100 K, 2θ_{max} = 56, 15577 reflections, 2813 independent (*R*_{int} = 0.0707), *R*₁(*I* > 2σ(*I*)) = 0.0843, *wR*₂ (all data) = 0.2488, Δρ = 0.37/-0.37 e.Å⁻³.

V. Mathematical details for the calculation of the monomer/dimer-ratio from computed Gibbs free energies

The underlying mathematics for the given ratios of the concentrations at the thermodynamic equilibrium of the *ortho*-, *meta*-, *para*- monomer and dimer are as following:

All Δ*G* values have been obtained by statistical thermodynamics as implemented in the Gaussian03 set of programs². The equilibrium constants *K* have been calculated via the van't Hoff relationship between standard free energy change and equilibrium constant *K*

² M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Revision D.02, Gaussian, Inc., Wallingford CT, 2004.

$$\Delta G = -RT \ln K \quad (1)$$

where R is the gas constant and T is the temperature in Kelvin. Solving for K results in

$$K = \exp\left(-\frac{\Delta G}{RT}\right). \quad (2)$$

As K_c is defined as the ratio between the concentrations at equilibrium of the product and the educt, for the equation



we obtain

$$K_c = \frac{c(d)}{c(m)^2}. \quad (4)$$

If all concentrations have the dimension $\text{mol} \cdot \text{l}^{-1}$, $K_c = K$ and thus

$$\exp\left(-\frac{\Delta G}{RT}\right) = \frac{c(d)}{c(m)^2}. \quad (5)$$

To obtain a ratio of m and d in dependence of the initial concentration of the monomer $c_0(m)$ we need the relation

$$c_0(m) = 2 \cdot c(d) + c(m). \quad (6)$$

Solving the above equation (6) for $c(d)$, substitution of that expression into eq. (5) and solving the latter for $c(m)$ finally leads to the expression

$$c(m) = \frac{\sqrt{1 + 8 \exp\left(-\frac{\Delta G}{RT}\right) c_0(m)} - 1}{4 \exp\left(-\frac{\Delta G}{RT}\right)} \quad (7)$$

By applying eq. (6) again, the concentration of d is given by

$$c(d) = \frac{c_0(m)}{2} - \frac{\sqrt{1 + 8 \exp\left(-\frac{\Delta G}{RT}\right) c_0(m)} - 1}{8 \exp\left(-\frac{\Delta G}{RT}\right)} \quad (8)$$

The last step is the calculation of the fraction r_m of $c(m)$ according to

$$r_m = \frac{c(m)}{c(m) + c(d)} \quad (9)$$

which for given ΔG , R and T can then be plotted as a function of $c_0(m)$.

VI. Electronic Structure Calculations

The gas phase global minima of the relevant molecules **3a – 4b** were obtained by first applying an extended conformational analysis using the MMFF94 force field³ together with a Monte Carlo torsional sampling as implemented in the Macromodel 9.5 program⁴. Each lowest energy conformation of **3a – 4b**, respectively, has then been optimized by applying density functional theory. The B3LYP hybrid functional⁵ was employed, and all atoms were described by a standard triple zeta all electron basis set augmented with one set of polarization functions (6-311G(d,p)). After the relevant stationary points were localized on the energy surface, they were further characterized as minima states by normal mode analysis based on the analytical energy second derivatives. Enthalpic and entropic contributions were calculated by statistical thermodynamics as implemented in the Gaussian03 set of programs.²

VII. Cartesian coordinates of the minimum energy structures of the *ortho*-, *meta*- and *para*-monomers and dimers (B3LYP/6-311G(d,p))

³ Halgren, T. A. *J. Comp. Chem.* **1996**, *17*, 490-519.

⁴ MacroModel version 9.5, Schrödinger, LLC, New York, NY, 2007.

⁵ Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

3a (*ortho*-monomer)

E = -435277,0732771 a.u.

C	-1,46608	0,60990	-0,35109
C	-1,46608	-0,60990	0,35109
C	-2,68539	-1,20380	0,67995
C	-3,89712	-0,60625	0,34041
C	-3,89712	0,60623	-0,34043
C	-2,68539	1,20379	-0,67995
H	-2,68331	-2,14902	1,21307
H	-4,83254	-1,08528	0,60721
H	-4,83254	1,08525	-0,60724
H	-2,68332	2,14901	-1,21308
C	-0,18004	-1,28675	0,75780
H	0,53568	-0,54724	1,12535
H	-0,38580	-2,00048	1,56662
C	-0,18004	1,28676	-0,75779
H	0,53568	0,54725	-1,12533
H	-0,38579	2,00048	-1,56660
O	0,36898	1,99092	0,36765
O	0,36899	-1,99091	-0,36763
C	1,59400	2,65936	0,09938
H	1,73998	2,78388	-0,98029
H	1,52618	3,65610	0,54784
C	2,80661	1,92867	0,70847
H	2,68765	1,90492	1,79728
H	3,70854	2,51829	0,50258
C	1,59401	-2,65935	-0,09935
H	1,74001	-2,78382	0,98032
H	1,52619	-3,65610	-0,54776
C	2,80661	-1,92868	-0,70848
H	2,68764	-1,90497	-1,79729
H	3,70855	-2,51829	-0,50258
C	2,95329	0,56575	0,20554
C	2,95330	-0,56575	-0,20560

4a (*ortho*-dimer)

E = -870566,7232050

C	6,54659	-0,55896	0,78017
C	5,41599	-0,63933	-0,03449
C	4,23174	-1,19727	0,48818
C	4,21759	-1,65300	1,80592
C	5,35563	-1,56565	2,60645
C	6,52699	-1,01968	2,09501
H	7,45771	-0,12946	0,37473
H	3,30483	-2,08210	2,19613
H	5,32228	-1,92642	3,62863

H	7,41662	-0,94824	2,71054
C	-5,41599	0,63933	-0,03448
C	-6,54659	0,55896	0,78017
C	-4,23174	1,19726	0,48818
C	-6,52698	1,01969	2,09501
H	-7,45771	0,12947	0,37473
C	-4,21758	1,65299	1,80592
C	-5,35563	1,56565	2,60645
H	-7,41662	0,94825	2,71054
H	-3,30482	2,08209	2,19613
H	-5,32227	1,92643	3,62863
C	5,48271	-0,13307	-1,46156
H	6,51469	0,16212	-1,69741
H	5,19728	-0,91939	-2,16590
C	2,99482	-1,30391	-0,37554
H	2,69087	-0,30606	-0,71447
H	3,22891	-1,88937	-1,28059
C	-5,48272	0,13307	-1,46156
H	-6,51469	-0,16212	-1,69741
H	-5,19729	0,91939	-2,16590
C	-2,99482	1,30388	-0,37554
H	-2,69085	0,30603	-0,71445
H	-3,22891	1,88932	-1,28060
O	4,59116	0,94556	-1,74309
O	1,94159	-1,92863	0,33753
O	-4,59117	-0,94557	-1,74309
O	-1,94159	1,92863	0,33752
C	4,96969	2,17694	-1,14925
H	5,94062	2,50187	-1,55429
H	5,06875	2,07745	-0,06166
C	3,90675	3,22446	-1,48809
H	4,30182	4,21161	-1,22059
H	3,76157	3,22610	-2,57380
C	0,76941	-2,08807	-0,43995
H	0,95342	-2,76765	-1,28460
H	0,44576	-1,12304	-0,85363
C	-0,31986	-2,65971	0,47037
H	-0,46108	-1,97533	1,31342
H	0,03715	-3,60648	0,88945
C	-4,96969	-2,17695	-1,14925
H	-5,06876	-2,07745	-0,06167
H	-5,94062	-2,50188	-1,55429
C	-3,90674	-3,22446	-1,48809
H	-3,76156	-3,22610	-2,57381
H	-4,30181	-4,21161	-1,22059
C	-0,76940	2,08805	-0,43995

H	-0,44574	1,12300	-0,85359
H	-0,95341	2,76760	-1,28463
C	0,31984	2,65974	0,47035
H	0,46107	1,97541	1,31343
H	-0,03718	3,60653	0,88939
C	2,62777	3,01580	-0,81235
C	1,58637	2,86019	-0,22844
C	-1,58638	-2,86017	-0,22842
C	-2,62777	-3,01579	-0,81236

3b (*meta*-monomer)

E	= -435281,1961681	a.u.	
C	1,52501	1,21497	0,24096
C	0,94959	-0,00002	0,61496
C	1,52496	-1,21504	0,24096
C	2,69860	-1,20746	-0,51658
C	3,28557	-0,00007	-0,88904
C	2,69866	1,20734	-0,51658
H	3,15123	-2,14558	-0,82342
H	4,19140	-0,00010	-1,48548
H	3,15132	2,14544	-0,82342
C	0,89487	-2,51845	0,70150
C	0,89499	2,51841	0,70150
H	1,23445	2,75340	1,71502
H	1,21640	3,34504	0,05147
O	-0,52074	2,46144	0,78798
O	-0,52085	-2,46141	0,78799
C	-1,18642	2,60339	-0,45843
H	-1,22289	3,66683	-0,73797
H	-0,65973	2,05667	-1,24965
C	-2,61303	2,06155	-0,31745
H	-3,20565	2,42329	-1,16603
H	-3,05564	2,49519	0,58568
C	-1,18654	-2,60334	-0,45842
C	-2,61313	-2,06143	-0,31745
H	-3,20577	-2,42317	-1,16603
H	-3,05575	-2,49504	0,58569
C	-2,66998	0,60188	-0,26739
C	-2,67001	-0,60176	-0,26741
H	1,21624	-3,34509	0,05147
H	1,23433	-2,75346	1,71502
H	-1,22306	-3,66678	-0,73795
H	-0,65983	-2,05665	-1,24965
H	0,02690	0,00000	1,18080

4b (*meta*-dimer)

E	= -870567,3161822	a.u.	
C	-5,59212	0,92840	0,35778
C	-4,24043	0,88637	0,71030
C	-3,36872	1,91188	0,34779
C	-3,85800	2,99606	-0,38746
C	-5,19982	3,04238	-0,74999
C	-6,06486	2,01263	-0,38120
H	-3,17822	3,78394	-0,68703
H	-5,57321	3,87872	-1,33087
H	-7,10861	2,05009	-0,67814
C	5,28927	-0,97012	0,64048
C	6,12408	-2,05133	0,34757
C	3,99063	-0,95994	0,12952
C	5,66147	-3,10993	-0,42919
H	7,14177	-2,06373	0,72593
C	3,51895	-2,01013	-0,66099
C	4,36239	-3,09005	-0,92995
H	6,31580	-3,94568	-0,65103
H	4,00223	-3,91408	-1,53693
C	-6,52470	-0,18396	0,80177
H	-6,84277	-0,01250	1,83450
H	-7,42953	-0,18551	0,17607
C	-1,92395	1,86178	0,78127
H	-1,78736	2,45368	1,70138
H	-1,64093	0,82634	1,01832
C	5,77352	0,15816	1,53428
H	5,46266	-0,03008	2,56628
H	6,87330	0,19317	1,52439
C	2,10681	-1,98808	-1,18680
H	1,86232	-0,99355	-1,58888
H	1,99622	-2,71396	-2,00494
O	-5,92073	-1,46867	0,81263
O	-1,08944	2,38184	-0,24234
O	5,23222	1,42952	1,21518
O	1,21000	-2,31186	-0,12775
C	-5,73717	-2,02813	-0,47836
H	-5,20078	-1,33303	-1,13560
H	-6,71630	-2,24463	-0,93207
C	-4,94824	-3,33119	-0,33366
H	-5,45311	-3,95515	0,41184
H	-5,00127	-3,87153	-1,28613
C	0,27574	2,44236	0,13139
H	0,66040	1,43668	0,35371
H	0,40518	3,05676	1,03379
C	1,04954	3,05662	-1,03784
H	0,62916	4,04497	-1,25193

H	0,87799	2,44455	-1,92951
C	5,76316	2,00582	0,03292
H	6,84624	2,16465	0,14785
H	5,60354	1,34908	-0,83101
C	5,07625	3,35396	-0,19315
H	5,59089	3,86857	-1,01306
H	5,21823	3,96599	0,70416
C	-0,14016	-2,39250	-0,55023
H	-0,49022	-1,42219	-0,93214
H	-0,24862	-3,12890	-1,35969
C	-0,97620	-2,82109	0,65863
H	-0,85706	-2,07428	1,45071
H	-0,56048	-3,75614	1,04849
C	-3,54757	-3,14411	0,04012
C	-2,38826	-2,99554	0,32923
C	2,47877	3,16559	-0,75974
C	3,65103	3,24893	-0,49914
H	-3,87160	0,02391	1,25521
H	3,34921	-0,11180	0,34237

3c (*para*-monomer)

E = -435272, 9492007 a.u.

C	1,40292	-1,55101	0,07476
C	0,75703	-1,61133	-1,16292
C	-0,63050	-1,60044	-1,23711
C	-1,40291	-1,55102	-0,07474
C	-0,75703	-1,61128	1,16294
C	0,63051	-1,60038	1,23713
H	-1,34466	-1,61763	2,07567
H	1,12026	-1,57074	2,20466
C	-2,87266	-1,22861	-0,17735
C	2,87267	-1,22860	0,17735
H	3,34596	-1,77848	0,99327
H	3,40063	-1,47647	-0,75286
O	3,04917	0,15323	0,51141
O	-3,04916	0,15322	-0,51143
C	2,83762	1,07759	-0,55138
C	2,06297	2,30680	-0,04845
H	2,31242	3,15062	-0,70383
H	2,45332	2,56008	0,94310
C	-2,83765	1,07759	0,55135
C	-2,06297	2,30680	0,04843
H	-2,31243	3,15062	0,70380
H	-2,45329	2,56007	-0,94313
C	0,60279	2,18746	-0,00064
C	-0,60279	2,18745	0,00065

H	-3,34595	-1,77850	-0,99326
H	-3,40063	-1,47647	0,75287
H	-2,29385	0,61738	1,38113
H	-3,81675	1,40654	0,92478
H	1,34466	-1,61772	-2,07565
H	-1,12025	-1,57084	-2,20464
H	2,29380	0,61736	-1,38113
H	3,81672	1,40652	-0,92483

4c (*para*-dimer)

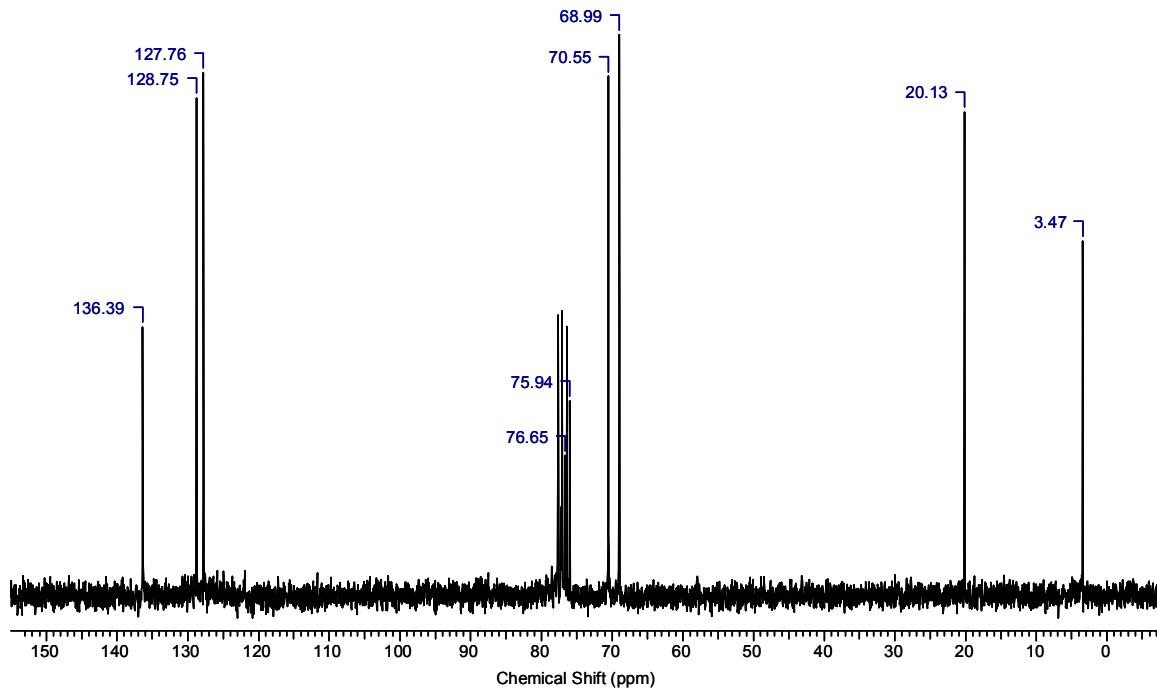
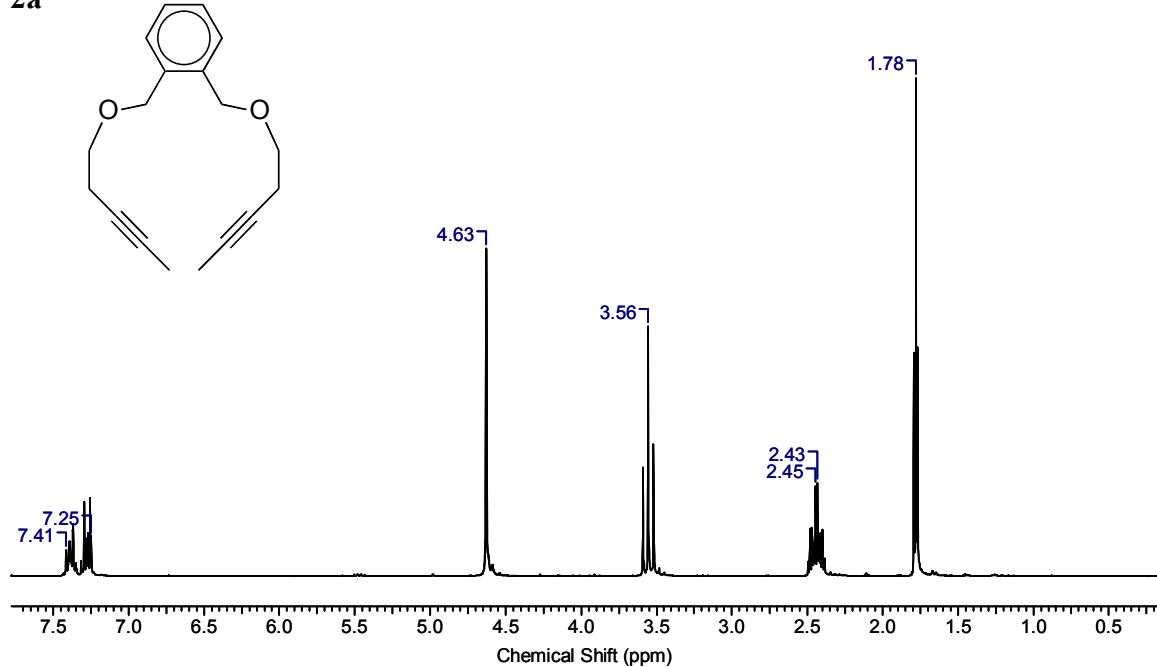
E = -870565, 1207541 a.u.

C	0,57622	-3,08689	0,76255
C	-0,63096	-3,19093	1,45368
C	-1,59948	-2,19184	1,36590
C	-1,34330	-1,08092	0,55410
C	-0,14331	-0,97876	-0,13878
C	0,83222	-1,97761	-0,04128
H	-2,09386	-0,30594	0,44796
H	0,03345	-0,10803	-0,76207
C	-1,16136	3,08264	0,33212
C	-0,81808	2,78888	1,65121
C	-0,14384	3,13881	-0,62572
C	0,50952	2,56403	2,00791
H	-1,59569	2,71774	2,40448
C	1,18221	2,91903	-0,27211
C	1,52354	2,63170	1,05292
H	0,75304	2,31982	3,03718
C	2,12821	-1,82647	-0,80508
H	1,90505	-1,58567	-1,85534
H	2,70996	-0,98943	-0,39897
C	-2,88919	-2,28552	2,15749
H	-3,03186	-3,31707	2,51423
H	-2,83772	-1,63928	3,03890
C	-2,59385	3,31882	-0,06776
H	-3,24230	3,32833	0,81928
H	-2,69177	4,30008	-0,55937
C	2,96303	2,44218	1,46463
H	3,38287	3,40929	1,78879
H	3,02166	1,76021	2,32512
O	2,87192	-3,03847	-0,74185
O	-4,04014	-1,84047	1,45271
O	-3,00888	2,29806	-0,96938
O	3,72756	1,93717	0,38229
C	3,95863	-3,15286	-1,63884
H	3,75872	-2,60042	-2,56617
H	4,03412	-4,21574	-1,88718

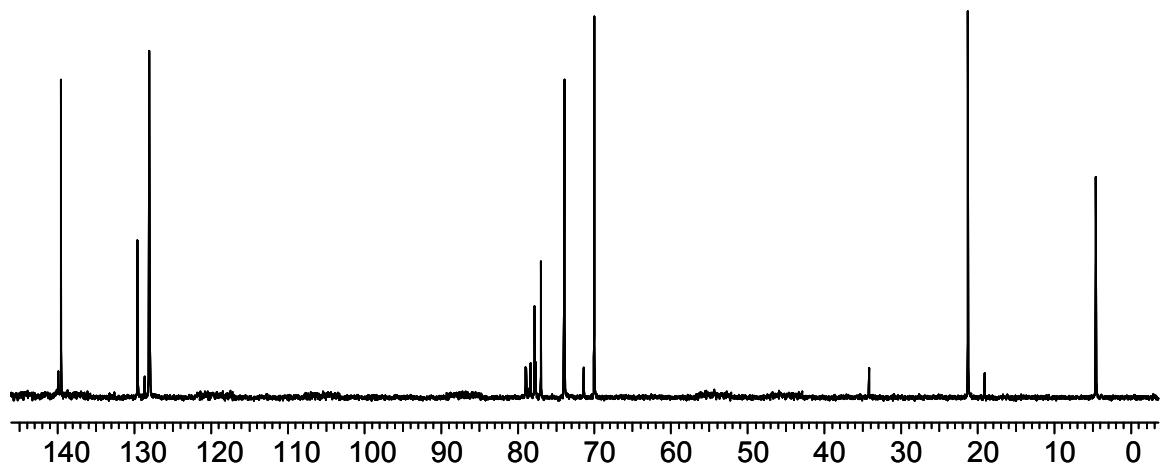
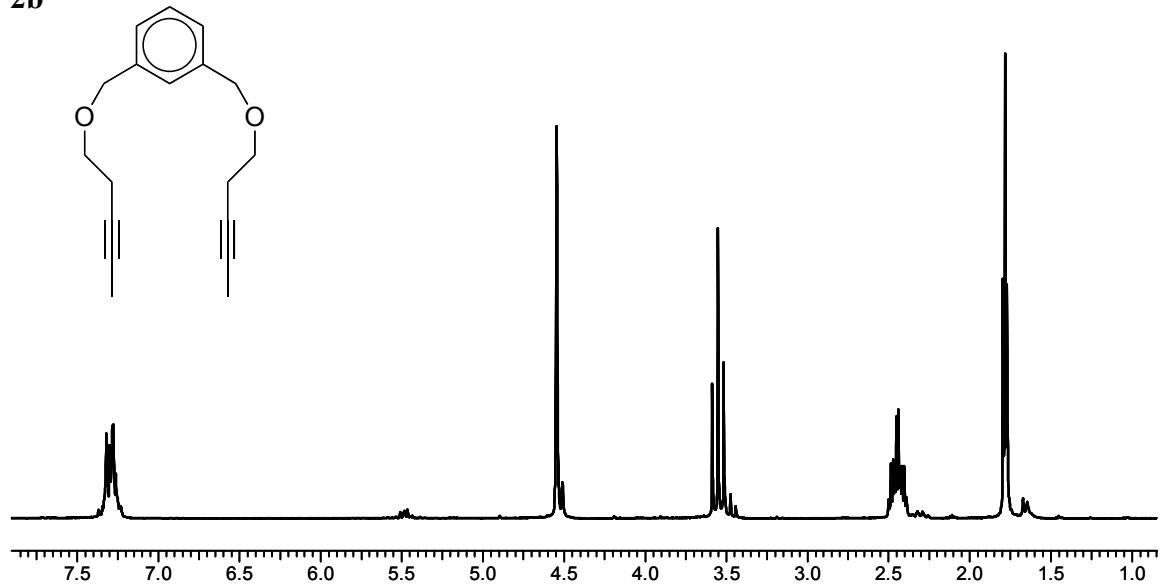
C	5,30708	-2,71178	-1,03753
H	5,42483	-3,21765	-0,07302
H	6,10462	-3,09157	-1,68913
C	-4,44216	-2,70570	0,40521
H	-4,74370	-3,68094	0,81877
H	-3,62219	-2,87380	-0,30333
C	-5,63594	-2,07027	-0,31061
H	-6,40882	-1,85578	0,43571
H	-6,05816	-2,81115	-0,99991
C	-4,29307	2,54141	-1,51591
H	-5,03481	2,68065	-0,71684
H	-4,27187	3,45990	-2,12334
C	-4,69268	1,35891	-2,40064
H	-3,87440	1,16822	-3,10368
H	-5,55883	1,66184	-3,00121
C	5,11913	1,94212	0,64334
H	5,46566	2,97395	0,80809
H	5,34517	1,35930	1,54734
C	5,85313	1,34869	-0,55983
H	6,92463	1,54470	-0,43430
H	5,53789	1,89297	-1,45677
C	5,47974	-1,27151	-0,86615
C	5,64009	-0,08505	-0,73942
C	-5,30385	-0,85221	-1,04638
C	-5,01569	0,14070	-1,66218
H	-0,81899	-4,06793	2,06668
H	-0,39799	3,34992	-1,65901
H	1,96359	2,95701	-1,02049
H	1,31809	-3,87136	0,83041

VIII. Spectra

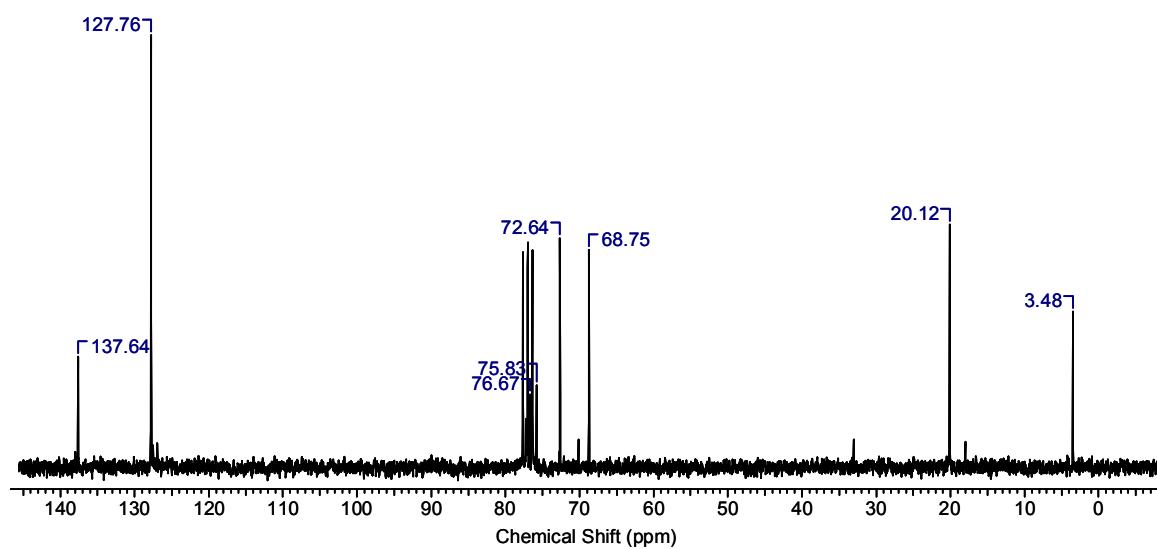
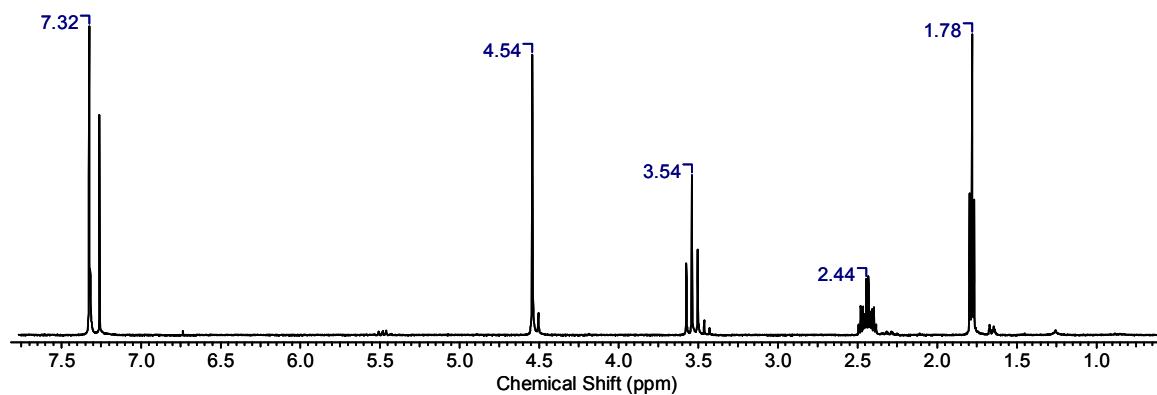
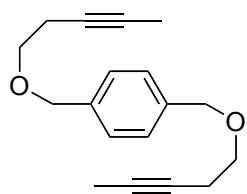
2a



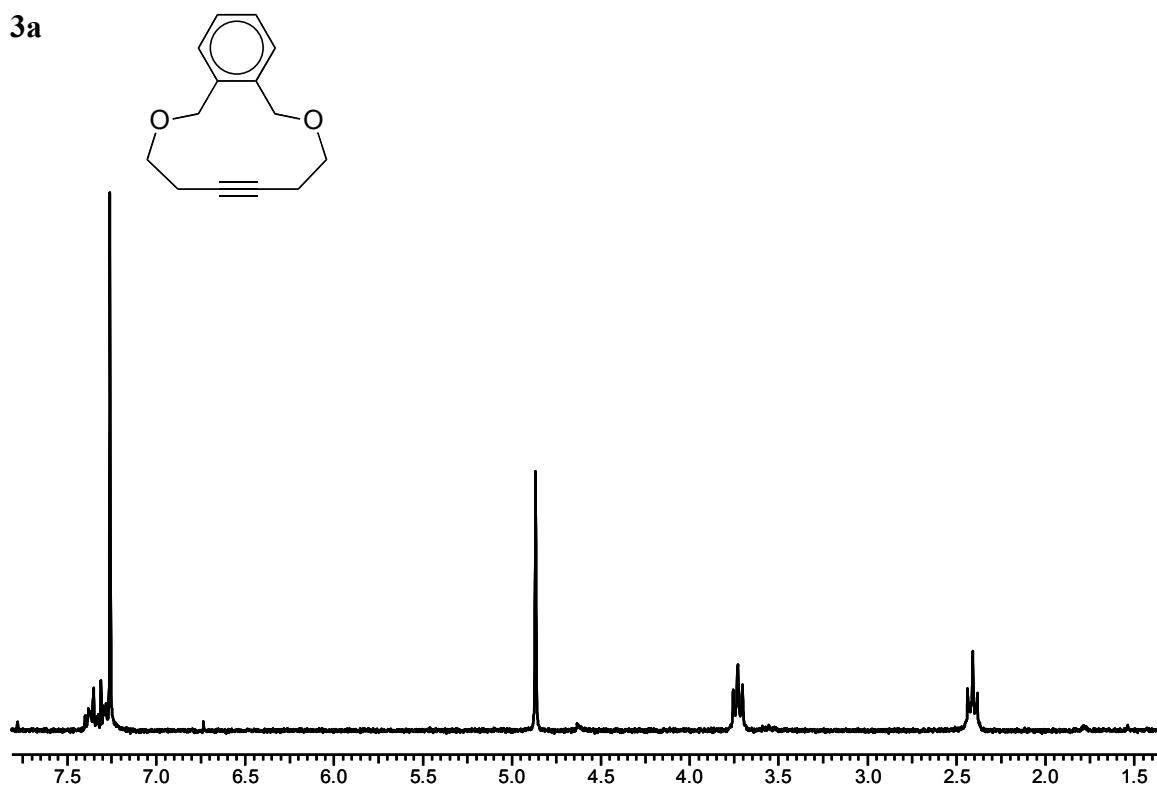
2b



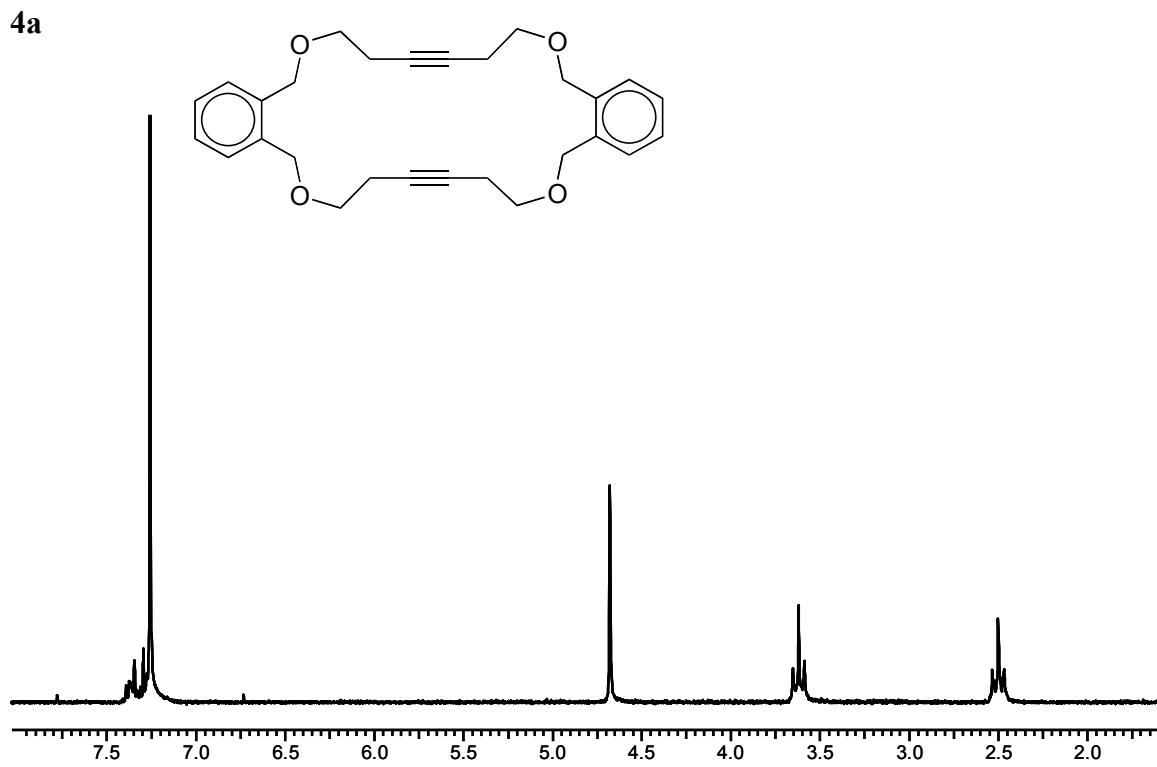
2c



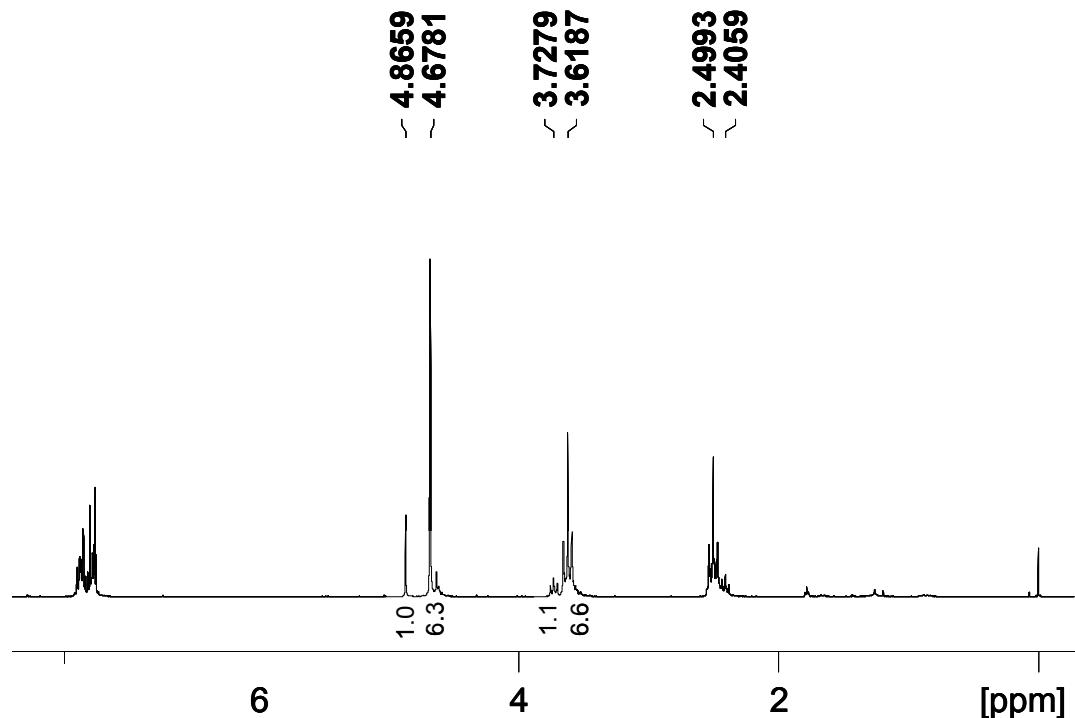
3a



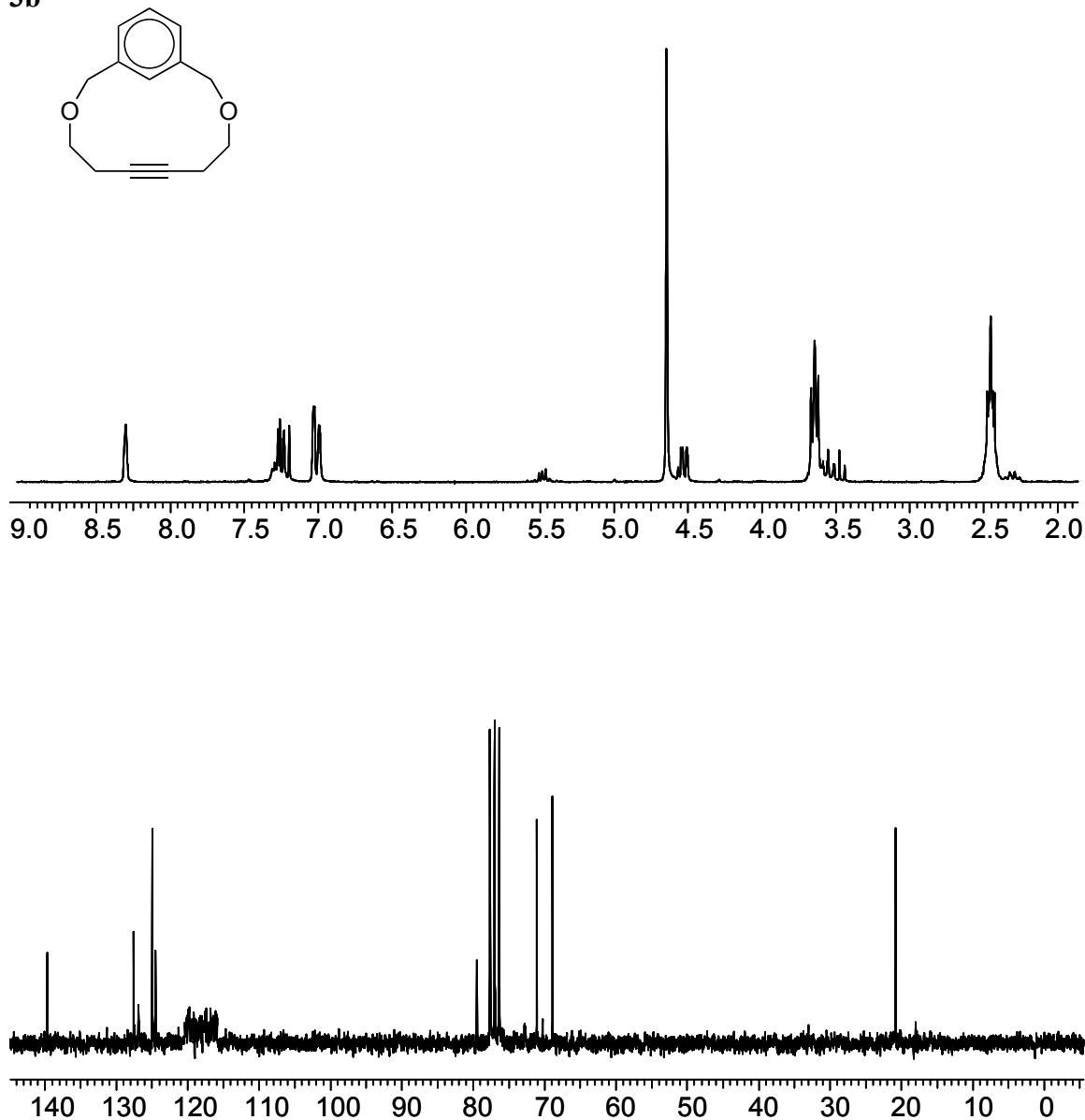
4a



Crude ^1H NMR from mixture of **3a** and **4a**



3b



4c

