

# Synthesis and Structure of *m*-Terphenyl-Based Cyclophanes with Nitrogen Intra-Annular Functional Groups

## Supplementary Material

Drexel H. Camacho, Eric V. Salo, Zhibin Guan\*

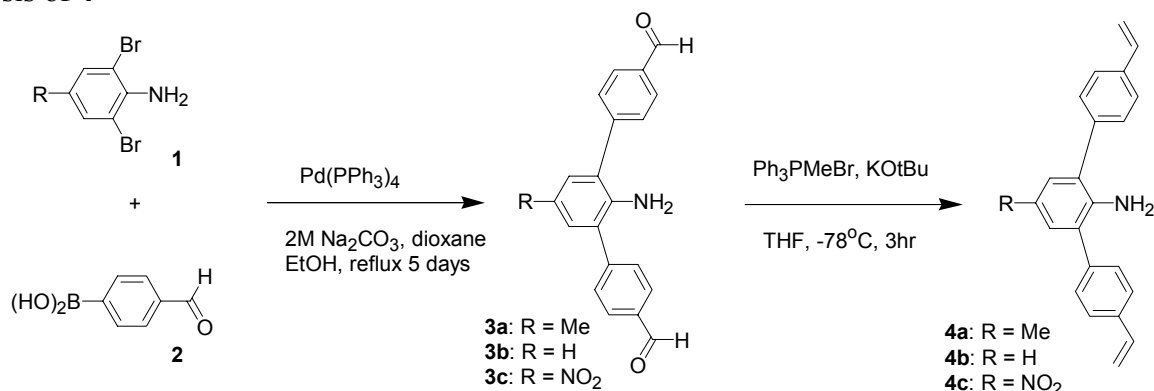
Chemistry Department, University of California – Irvine,  
Irvine, California 92697-2025

### Experimental Section

**General Considerations.** All manipulations of air and/or water sensitive compounds were performed using the standard Schlenk techniques. High resolution mass spectra were recorded on Micromass LCT or Micromass Autospec. Elemental analyses were performed by Atlantic Microlab of Norcross, GA.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance-500 or 400 spectrometers. Chemical shifts are reported relative to TMS.

**Materials.** Toluene, dichloromethane and diethyl ether were purified using the procedure described by Pangborn et. al.<sup>1</sup> Acenaphtenequinone, 4-formylphenylboronic acid, 2,6-dibromo-4-methyl aniline, and methyltriphenylphosphonium bromide were purchased from Aldrich Chemical Co.

### Synthesis of 4



A mixture of 2,6-dibromo-4-methyl aniline (R = Me) **1a** (15.9 g; 60 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (8.32 g; 12 mol%) in dioxane, was stirred at 70 °C for 20 minutes. A solution 4-formylphenylboronic acid **2** (25 g; 3 eq), dissolved in small amount of ethanol and dioxane, was added to the mixture followed by addition of 2M Na<sub>2</sub>CO<sub>3</sub> (6 eq).<sup>2</sup> The mixture was refluxed for 3-5 days. The organic layer was separated from the aqueous layer. The latter was extracted with ethyl acetate 3x and the organic layers were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. After solvent evaporation, a yellowish solid was formed which was subjected to column chromatography (silica, 2:1 hexane/EtOAc) to give the product **3a** in 85% yield.

**3a:**  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  10.06 (s, 2H, -CHO); 8.0 (d,  $J$  = 8.1 Hz, 4H, arom. H); 7.70 (d,  $J$  = 8.1 Hz, 4H, arom. H); 6.96 (s, 2H, arom. H); 4.30 (s, 2H, -NH<sub>2</sub>); 2.25 (s, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR: 192.7, 145.9, 138.9, 134.8, 130.8, 130.0, 129.8, 126.3, 126.2, 19.9 ppm.

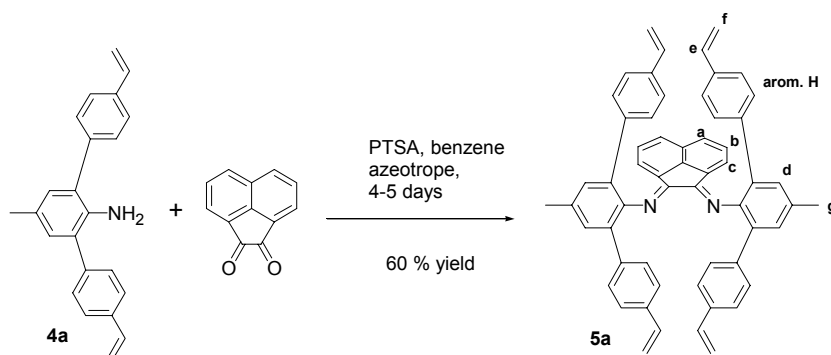
**3b:** Same procedure as **3a** using 2,6-dibromo aniline, 60% yield.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  10.07 (s, 2H, -CHO); 8.0 (d,  $J$  = 6.4 Hz, 4H, arom. H); 7.70 (d,  $J$  = 6.4 Hz, 4H, arom. H); 7.17 (d,  $J$  = 6.2 Hz, 2H, arom. H); 6.94 (s, 1H, arom. H); 3.86 (s, 2H, -NH<sub>2</sub>).  $^{13}\text{C}$  NMR: 191.7, 145.8, 140.4, 135.2, 130.3, 130.2, 129.9, 126.7, 118.6 ppm. HRMS calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}_2$ : 301.1103; found: 301.1096. Anal. calcd for  $\text{C}_{20}\text{H}_{15}\text{NO}_2$ : C 79.72%, H 5.02%, N 4.65%; found C 79.02%, H 4.81%, N 4.58%.

To a solution of methyltriphenylphosphonium bromide (162 mmol; 58 g) in THF was added potassium *tert*-butoxide (178 mmol; 21 g) in three proportions with 15-minute interval between additions. The mixture was stirred for 1 hour at room temperature under argon. The solution was then cooled to  $-78^\circ\text{C}$ . Slow addition of a solution of **3a** (54 mmol) in THF was made via a dropping funnel. The mixture was then stirred for 3 hours at  $-78^\circ\text{C}$  and warmed to room temperature. Quenching with water, extraction with ether, washing with brine, and drying over  $\text{MgSO}_4$  gave a crude product, which was then chromatographed (silica 100:1 hexane/ethyl acetate) to give **4a** as a yellow solid in 75% yield.

**4a:**  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  7.49 (s, 8H, arom. H); 6.95 (s, 2H, arom. H); 6.75 (dd,  $J$  = 17.6, 10.9 Hz, 2H, -CH=C); 5.79 (d,  $J$  = 17.6, 0.7 Hz, 2H, trans terminal vinylic H); 5.27 (d,  $J$  = 10.9, 0.7 Hz, 2H, cis terminal vinylic H); 3.74 (s, br, 2H, -NH<sub>2</sub>); 2.30 (s, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR: 139.8, 138.8, 137.0, 136.9, 130.7, 129.9, 128.2, 127.8, 127.1, 114.4, 20.8 ppm. HRMS calcd for  $\text{C}_{23}\text{H}_{21}\text{N}$ : 311.1674; found: 311.1674.

**4b:** Same procedure as **4a** using **3b**, 73% yield.  $^1\text{H}$  NMR( $\text{CDCl}_3$ ):  $\delta$  7.60 (s, 8H, arom. H); 7.23 (dd,  $J$  = 2.6, 9.4 Hz, 2H, arom. H); 6.99 (dt,  $J$  = 2.8, 2.3, 9.4 Hz, 1H, arom. H); 6.87 (dd,  $J$  = 13.6, 21.9 Hz, 2H, -CH=C); 5.91 (d,  $J$  = 1.6, 21.9 Hz, 2H, trans terminal vinylic H); 5.40 (d,  $J$  = 1.6, 13.6 Hz, 2H, cis terminal vinylic H); 3.96 (s, br, 2H, -NH<sub>2</sub>).  $^{13}\text{C}$  NMR: 140.9, 139.2, 136.5, 136.4, 129.8, 129.5, 127.6, 126.7, 118.3, 114.2 ppm. HRMS calcd for  $\text{C}_{22}\text{H}_{19}\text{N}$ : 297.1517; found: 297.1511. Anal. calcd for  $\text{C}_{22}\text{H}_{19}\text{N}$ : C 88.85%, H 6.44%, N 4.71%; found C 88.58%, H 6.41%, N 4.62%.

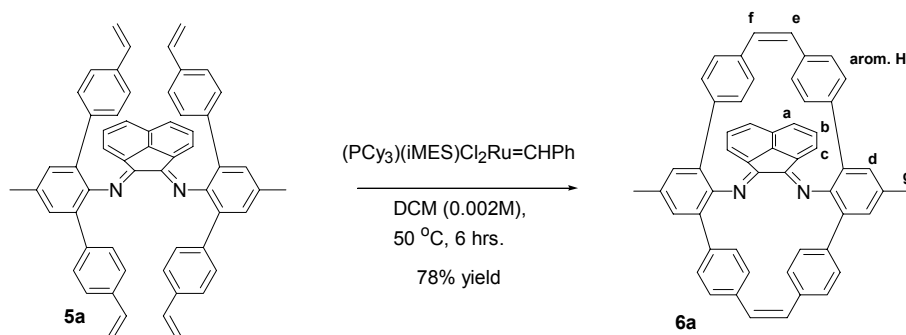
## Synthesis of diimine 5:



In a three-neck flask fitted with a Dean-Stark apparatus and a condenser, a mixture of acenaphthenequinone (15 mmol) and *para*-toluene sulfonic acid (0.25 mol%) in benzene (50 mL) was stirred under argon.<sup>3</sup> A solution of **4a** (2.5 equiv) in benzene was then added (a small amount of 1,4 hydroquinone may be added to prevent polymerization of the styrene). The mixture was stirred at reflux for 5 days. The reaction was monitored by TLC and ESMS. The volume of the solvent was then reduced under vacuum and the product was chromatographed (silica, Hexane) to give the **5a** as an orange solid in 60% yield along with some mono-condensed product.

**5a:**  $^1\text{H}$  NMR:  $\delta$  7.51 (d,  $J = 8.3$  Hz, 2H, a); 7.40 (d,  $J = 8.3$  Hz, 8H, arom. H); 7.20 (s, 4H, d); 7.15 (pseudo t, 2H, b); 7.00 (d,  $J = 8.3$  Hz, 8H, arom. H); 6.76 (d,  $J = 7.2$  Hz, 2H, c); 6.53 (dd,  $J = 10.9, 17.6$  Hz, 4H, e); 5.58 (d,  $J = 17.6$  Hz, 4H, f); 5.10 (d,  $J = 10.9$  Hz, 4H, f); 2.47 (s, 6H, g).  $^{13}\text{C}$  NMR: 161.0, 144.9, 140.6, 140.0, 137.1, 136.1, 134.6, 131.6, 131.4, 130.7, 130.1, 130.0, 128.5, 127.6, 126.1, 122.8, 113.8, 21.43 ppm. HRMS calcd for  $[\text{C}_{58}\text{H}_{44}\text{N}_2 + \text{H}]^+$ : 769.3583; found: 769.3599.

## Synthesis of 6:



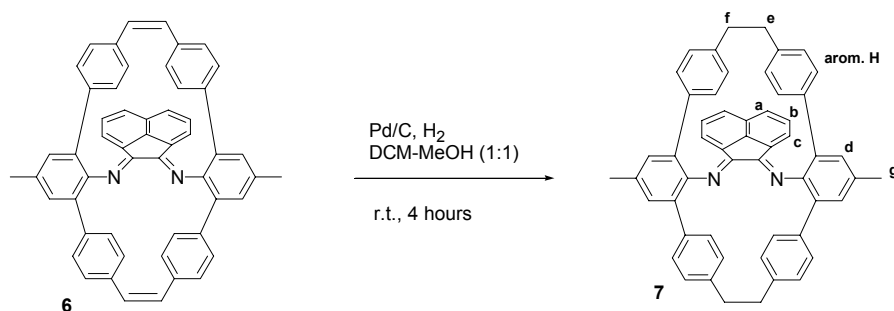
A mixture of **5a** (0.046g; 0.06 mmol) and the second generation Grubbs catalyst (6 mol%) in  $\text{CH}_2\text{Cl}_2$  was stirred at 50-60 °C under nitrogen atmosphere.<sup>4</sup> The reaction was monitored by ESMS. After

cooling, the solution was filtered thru celite. Evaporation of the solvent gave the yellow solid, which was chromatographed (silica, hexane/DCM = 1:1) to give the product **6a** in 78% yield.

**6a**:  $^1\text{H}$  NMR  $\delta$  7.86 (d,  $J = 7.9$  Hz, 2H, a); 7.42 (pseudo t, 2H, b); 7.33 (d,  $J = 7.7$  Hz, 4H, arom. H); 7.23 (s, 4H, d); 6.82-6.80 (overlapping, 10H: 4H for e/f, 4H for arom. H and 2H for c); 6.68 (d,  $J = 7.7$  Hz, 4H, arom. H); 6.48 (d,  $J = 7.7$  Hz, 4H, arom. H); 2.49 (s, 6H, g).  $^{13}\text{C}$  NMR: 162.2, 146.0, 140.5, 138.0, 137.3, 133.9, 133.4, 131.5, 131.3, 131.2, 130.6, 130.0, 129.8, 129.2, 129.1, 128.7, 128.0, 123.9, 21.4 ppm. HRMS calcd for  $[\text{C}_{54}\text{H}_{36}\text{N}_2 + \text{H}]^+$ : 713.2957; found: 713.2933.

Crystals for x-ray crystallography was obtained by slow evaporation of the compound in  $\text{CHCl}_3$ .<sup>5</sup>

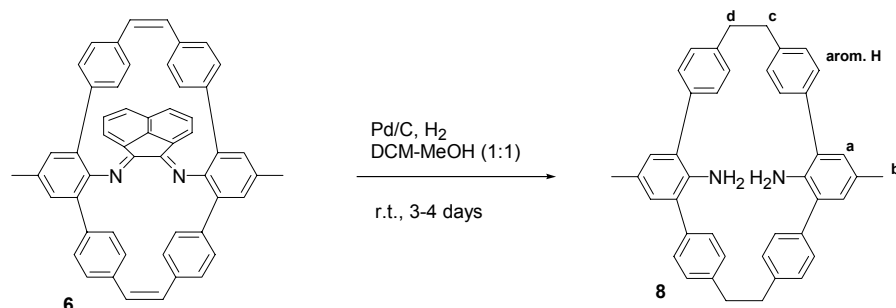
### Synthesis of 7:



A mixture of **6** (0.35 mmol) and Pd/C (10 mol%) in DCM/MeOH (1:1) was stirred for 4 hours under hydrogen atmosphere. The mixture was then filtered thru celite and the solvent was evaporated to give a yellow solid. The solid was subjected to column chromatography (silica, hexane/ethyl acetate/acetone: 7/3/0.5) to give the product **7** as a yellow powder in 77% yield.

**7**:  $^1\text{H}$  NMR:  $\delta$  7.86 (d,  $J = 8.3$  Hz, 2H, a); 7.44 (pseudo t, b); 7.28 (m; 4H, arom. H); 7.13 (s, 4H, d); 6.78 (d,  $J = 7.9$  Hz, 4H, arom. H); 6.72 (d,  $J = 7.2$  Hz, 2H, c); 6.54 (d,  $J = 7.7$  Hz, 4H, arom. H); 6.35 (d,  $J = 7.7$  Hz, 4H, arom. H); 2.94 (m, 4H, e or f); 2.79 (m, 4H, e or f); 2.45 (s, 6H, g).  $^{13}\text{C}$  NMR: 138.8; 138.0; 137.3; 137.3; 133.4; 131.6; 131.3; 130.6; 130.3; 129.8; 128.7; 127.9; 123.9; 123.8; 36.2; 21.5 ppm. UV ( $\text{DCM}$ )  $\lambda$  max (nm) 262, 302, 412. HRMS calcd for  $[\text{C}_{54}\text{H}_{40}\text{N}_2 + \text{H}]^+$ : 717.3270; found: 717.3295. Anal. calcd for  $\text{C}_{54}\text{H}_{40}\text{N}_2$ : C 90.47%, H 5.62%, N 3.91%; found C 90.12%, H 5.77%, N 3.67%.

## Synthesis of 8:



A mixture of **6** (0.35 mmol) and Pd/C (10 mol%) in DCM/MeOH (1:1) was stirred for 3-4 days under hydrogen atmosphere. The mixture was then filtered thru celite and the solvent was evaporated to give a solid. The solid was washed several times with pentane to give the product **8** as a white solid in 75% yield.

**8:**  $^1\text{H}$  NMR:  $\delta$  7.12 (d,  $J = 8.1$  Hz, 8H, arom. H); 6.97 (d,  $J = 8.1$  Hz, 8H, arom. H); 6.89 (s; 4H, a); 3.08 (s, 8H, c/d); 2.96 (s, 4H, 2NH<sub>2</sub>); 2.63 (s, 6H, b);  $^{13}\text{C}$  NMR: 139.6; 138.9; 137.2; 129.9; 129.4; 129.1; 128.6; 127.6; 36.6; 20.9 ppm. HRMS calcd for  $[\text{C}_{42}\text{H}_{38}\text{N}_2]^+$ : 570.3035; found: 570.3032.

Crystals for x-ray crystallography was obtained by slow evaporation of the compound in  $\text{CHCl}_3$ .<sup>6</sup>

## References:

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, H. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- (2) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513)
- (3) (a) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Pays Bas* **1994**, *113*, 88; (b) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskela, M.; Rieger, B. *Organometallics* **2001**, *20*, 2321.)
- (4) Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tet. Lett.* **1999**, *40*, 2247.)
- (5) CCDC **223518** contains the supplementary crystallographic data. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).
- (6) CCDC **223519** contains the supplementary crystallographic data. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).