Supporting Information for:

Stereoselective Macrocyclization through Zirconocene-Mediated Coupling of Achiral Dialkynes

John F. Tannaci, Ian H. Kratter, Eric A. Rider, Jennifer L. McBee, Adam D. Miller, and T. Don Tilley

Dept. of Chemistry, University of California at Berkeley, Berkeley, California 94720

E-mail: tdtilley@berkeley.edu

Contents

Page S1-S2	General experimental
Page S2-S3	Experimental details and characterization data for **1a-b** and **3a**
Page S3	Description of high-temperature ^{1}H NMR experiments for **2a**
Page S4-S6	^{1}H NMR spectra of **2a-b** and **3a**
Page S7	Crystallographic data for **3a**
Page S8-S9	References

General Experimental. All reactions were performed under an inert atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Pentane, hexanes, benzene, and ether were distilled under nitrogen from sodium benzophenone ketyl. $Cp_2Zr(py)(Me_3SiC{\equiv}CSiMe_3)$ was prepared as previously reported.[1] All other materials were purchased from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to the residual peaks of the deuterated solvent.

1,4-Bis[(trimethylsilyl)ethynyl]naphthalene (1a).[2] A flask was loaded with 1,4-dibromonaphthalene (5.00 g, 17.50 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.05 g, 0.07 mmol), and copper(I) iodide (0.02 g, 0.08 mmol). Degassed triethylamine (100 mL) was transferred via cannula onto the solids, followed by addition of ethynyltrimethylsilane (4.30 g, 43.75 mmol). A condenser was attached and the dark-brown solution was stirred under reflux for 36 h. The reaction was quenched with ammonium chloride (150 mL) and the crude product was extracted with chloroform (3 × 50 mL). The organic layer was concentrated under vacuum and passed through a plug of silica gel (hexanes eluant). Recrystallization from ether gave 3.57 g (64%) of a white crystalline solid. Anal. Calcd for $C_{20}H_{24}Si_2$: C, 74.93; H, 7.55. Found: C, 74.55; H, 7.82. ^{1}H NMR, ^{13}C NMR, and GC-MS (EI) data match published values.

1,4-Bis[(trimethylsilyl)ethynyl]anthracene (1b). Butyllithium (1.60 M in hexanes, 32.42 mL, 51.87 mmol) was added slowly to a solution of ethynyltrimethylsilane (5.66 g, 57.63 mmol) in ether (80 mL). After stirring for 30 min, 1,4-anthraquinone (4.00 g, 19.21 mmol) was added and the resulting deep purple mixture was allowed to react at ambient temperature for 12 h. A saturated solution of tin(II) chloride in 10% aqueous HCl (100 mL) was added, followed by tetrahydrofuran (80 mL) to improve miscibility, and the reaction was monitored by thin-layer chromatography. Upon completion, the crude product was extracted into hexanes (250 mL), washed with water (3 × 100 mL), and passed through a plug of silica gel (hexanes eluant). Recrystallization from ethanol gave 6.46 g (91%) of bright yellow needles: mp 171 °C. Anal. Calcd for $C_{24}H_{26}Si_2$: C, 77.77; H, 7.07. Found: C, 77.47; H, 6.90. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (2 H, s), 8.06-8.11 (2 H, m), 7.65 (2 H, s), 7.52-7.57 (2 H, m), 0.40 (18 H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4, 130.7, 129.9, 128.7, 126.4, 125.9, 121.9, 103.3, 102.1, 0.3. GC-MS (EI) *m/z* 370 (M^+).

Trimeric cyclophane 3a. Starting from dialkyne **1a** (0.75 g, 2.34 mmol), macrocycle **2a** was prepared as described in the communication and suspended in THF under air. Trifluoroacetic acid (0.89 g, 7.81 mmol) was added and the resulting light-yellow solution was stirred for 24 h. The reaction mixture was concentrated under vacuum and passed through a plug of silica gel (hexanes/ethyl acetate = 10:1) to give a pale yellow solid. The crude product was washed with methanol (3 × 5 mL) to afford 0.60 g (79%) of white powder: mp (DSC) 279-281 °C. Single crystals for X-ray diffraction were obtained by slow cooling of an acetone solution. Anal. Calcd for $C_{60}H_{78}Si_6$: C, 74.46; H, 8.12. Found: C, 74.08; H, 8.48. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (2 H, m), 7.86 (2 H, m), 7.77-7.80 (2 H, m), 7.42 (2 H, m), 7.19-7.26 (4 H, m), 6.72 (2 H, s), 6.60-6.64 (6 H, m), 6.42 (2 H, d, *J* = 7 Hz), 5.84 (2 H, s), -0.21 (18 H, s), -0.33 (36 H, br s); ^{13}C NMR (100 MHz, THF-d_8): δ 163.97, 163.90, 160.9, 138.9, 138.6, 138.4, 133.7, 132.8, 132.69, 132.63, 132.4, 132.0, 129.1, 128.3, 127.4, 127.1, 126.92, 126.85, 126.1, 125.84, 125.78, 0.8, 0.6, 0.1. MS (FAB) *m/z* 966 (M^+).

High-temperature ^{1}H NMR spectra of 2a. Macrocycle **2a** (0.01 g) was dissolved in toluene-d_8 and loaded into a teflon-sealed NMR tube. The sample was heated in the NMR instrument and spectra were taken at 50 °C, 75 °C, 95 °C, 105 °C, 110 °C, and 120 °C. Minimal changes occurred in the ^{1}H NMR spectra over this temperature range, and no evidence of the “all up” stereoisomer was observed.

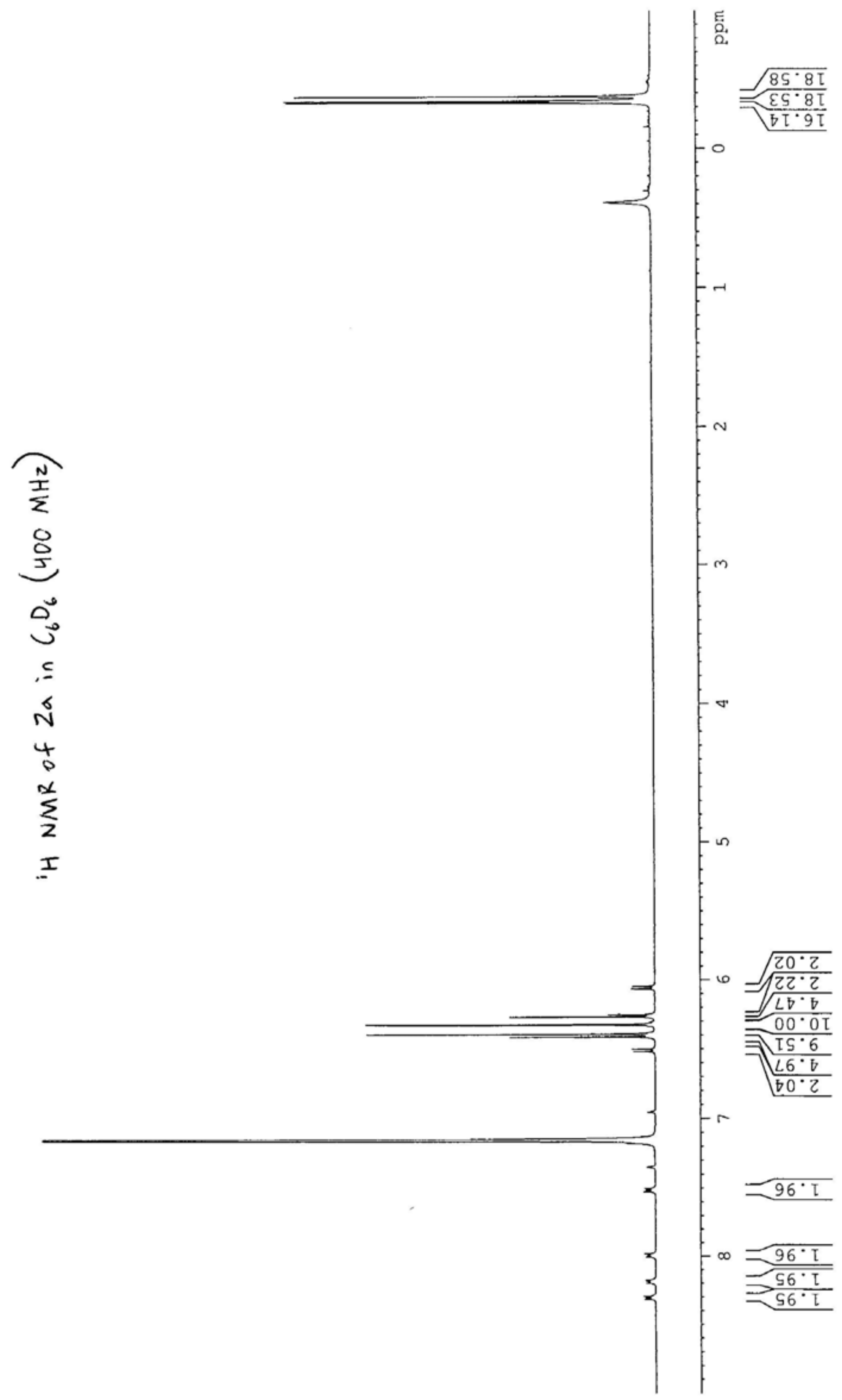

FIGURE S1. ^{1}H NMR spectrum of trimeric macrocycle **2a** in C_6D_6.

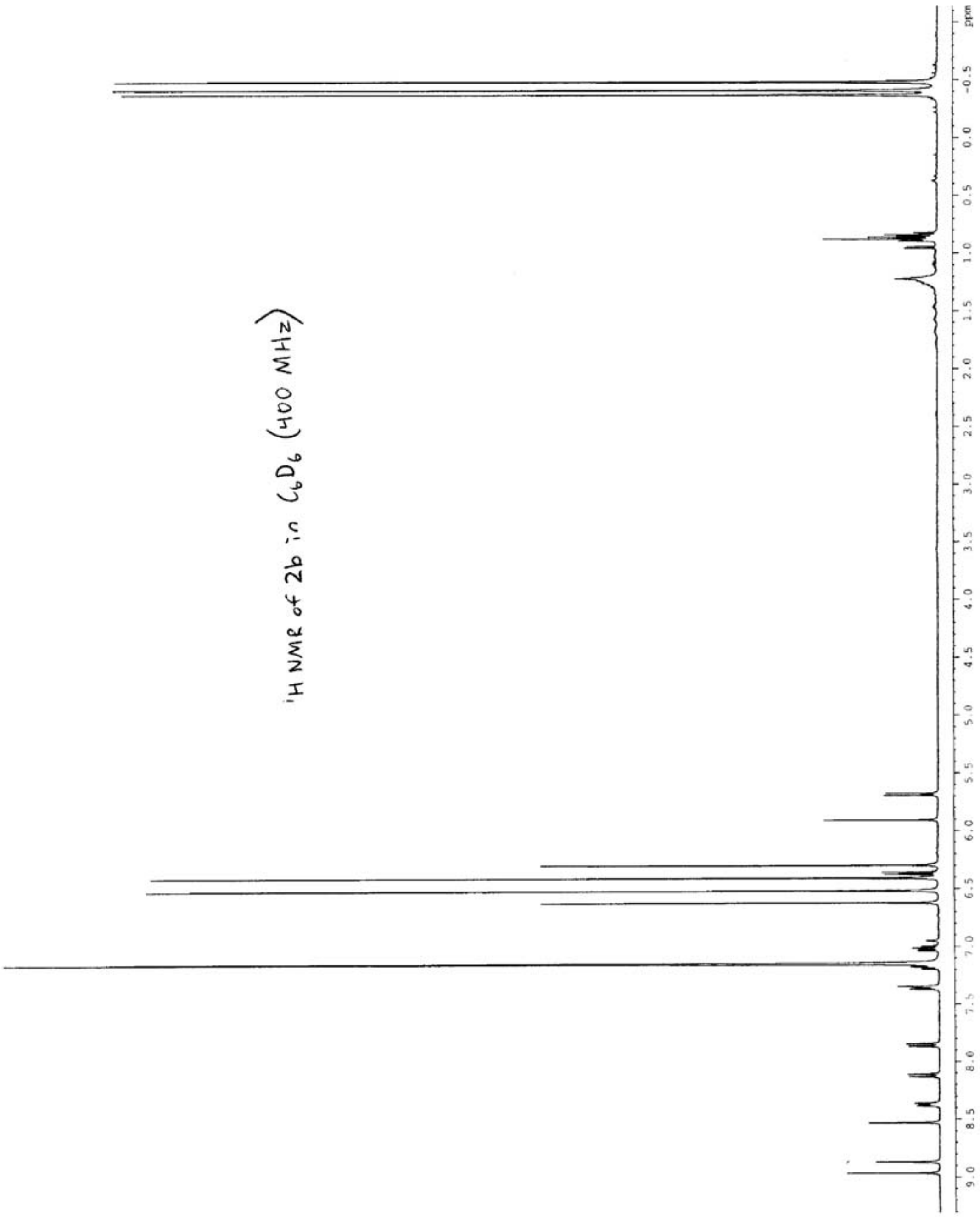

FIGURE S2. ^{1}H NMR spectrum of trimeric macrocycle **2b** in C_6D_6.

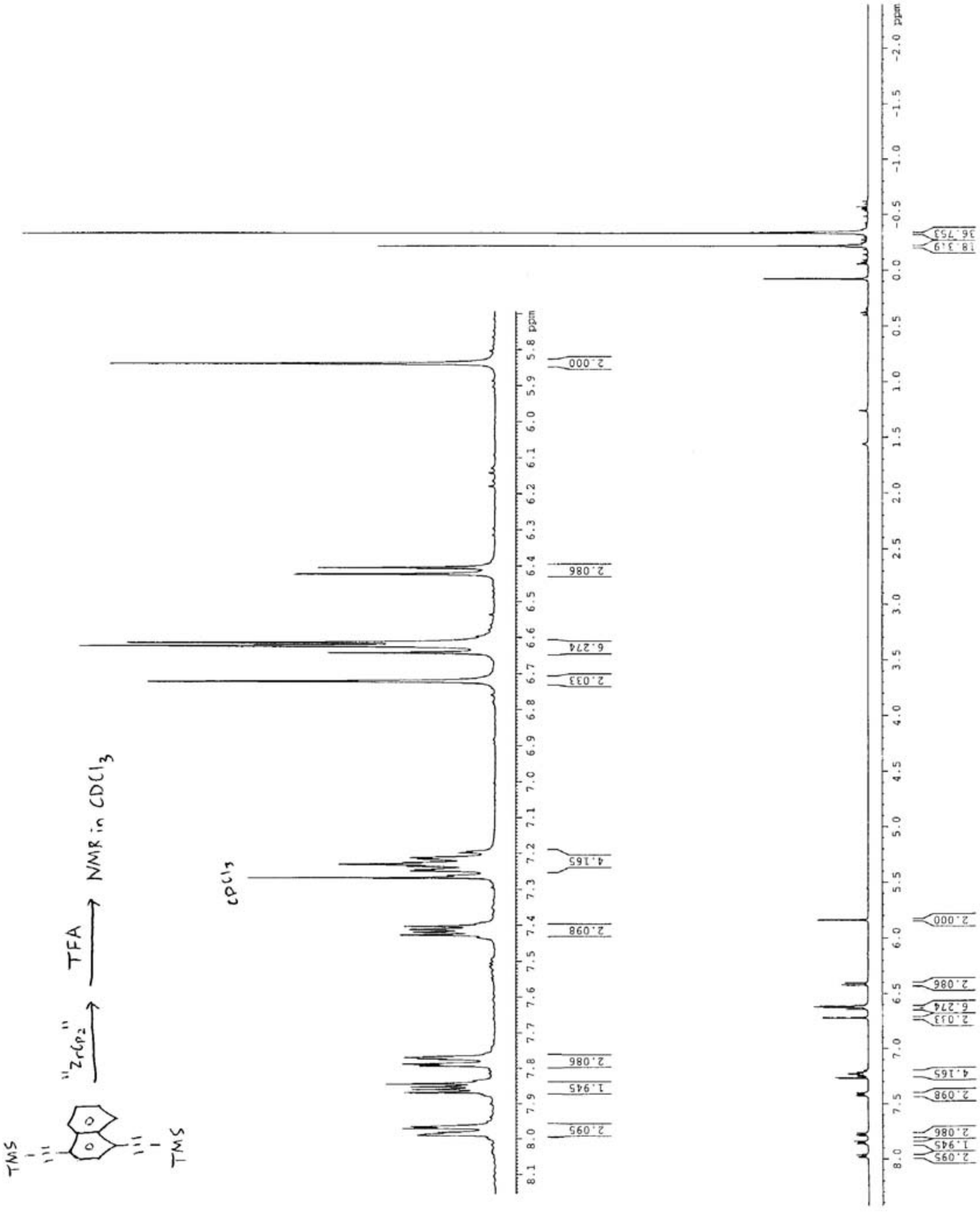

FIGURE S3. ^{1}H NMR spectrum of trimeric cyclophane **3a** in $CDCl_3$ (400 MHz).

X-ray crystallographic analysis of 3a. No data was observed beyond 0.9 Å due to low crystal quality and a cutoff was applied during integration. X-ray data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. Structure solution was complicated by disorder in certain trimethylsilyl groups, so SADI commands were employed, and the corresponding methyl positions were located and refined isotropically since they are low in electron density (20% occupancy). All calculations were performed using the SHELXTL crystallographic package.

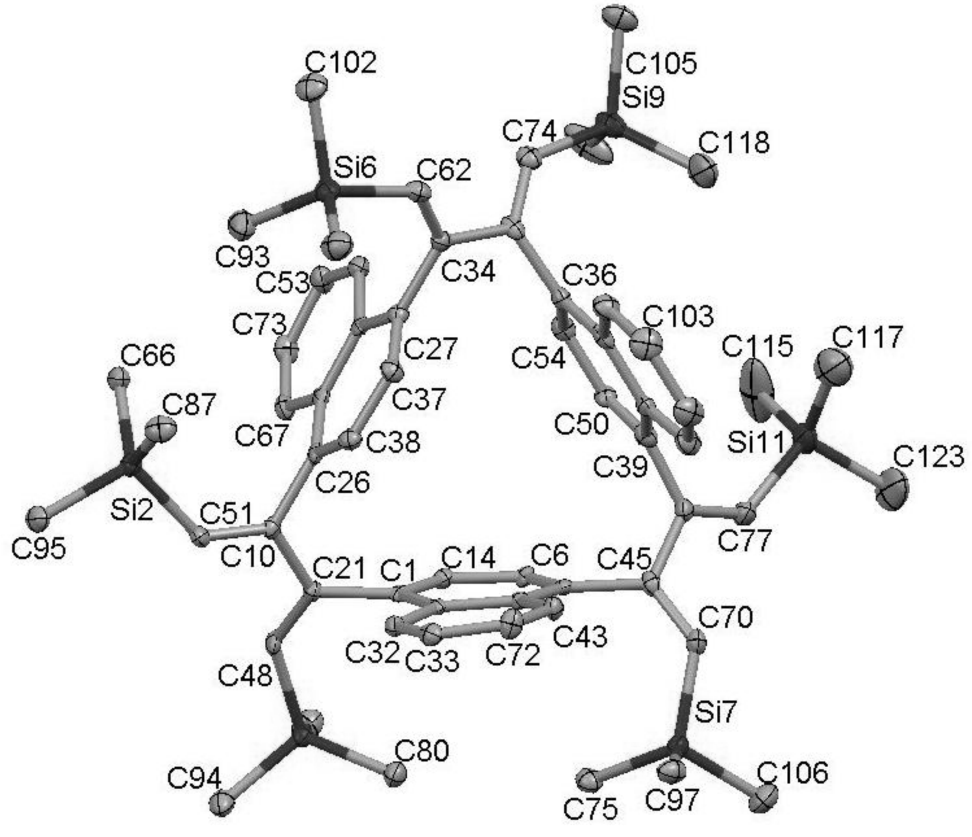

FIGURE S4. ORTEP diagram of **3a**, with thermal ellipsoids set at 30% probability; second cyclophane, solvent molecule (acetone), and hydrogen atoms removed for clarity.

References

(1) J. R. Nitschke, S. Zürcher and T. D. Tilley, *J. Am. Chem. Soc.*, 2000, **122**,10345-10352.

(2) M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, F. R. Al-Battashi, S. Al-Saadi, B. Ahrens, J. K. Bjernemose, M. F. Mahon, P. R. Raithby, M. Younus, N. Chawdhury, A. Köhler, E. A. Marseglia, E. Tedesco, N. Feeder and S. J. Teat, *Dalton Trans.*, 2004, 2377-2385.

(3) XL: Program for the Refinement of X-ray Crystal Structures, Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)

(4) Least-Squares:

Function minimized $\sum w\,(|Fo|^2 - |Fc|^2)^2$

(5) Standard deviation of an observation of unit weight:

$[\sum w\,(|Fo|^2 - |Fc|^2)^2 / (N_o - N_v)]^{1/2}$

Where N_o = number of observations, N_v = number of variables

(6) XP: Molecular Graphics Program. Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)

(7) SMART: Area-Detector Software Package, Bruker Analytical X-ray Systems Inc.: Madison, WI, (1995-99)

(8) SAINT: (V5.04) SAX Area-Detector Integration Program, Siemens Industrial Automation Inc.: Madison, WI, (1995)

(9) XPREP: (V5.03) Part of the SHELXTL Crystal Structure Determination Package, Siemens Industrial Automation Inc.: Madison, WI, (1995)

(10) SADABS: Siemens Area Detector Absorption Correction Program, George Sheldrick, (1996). Advance copy, private communication.