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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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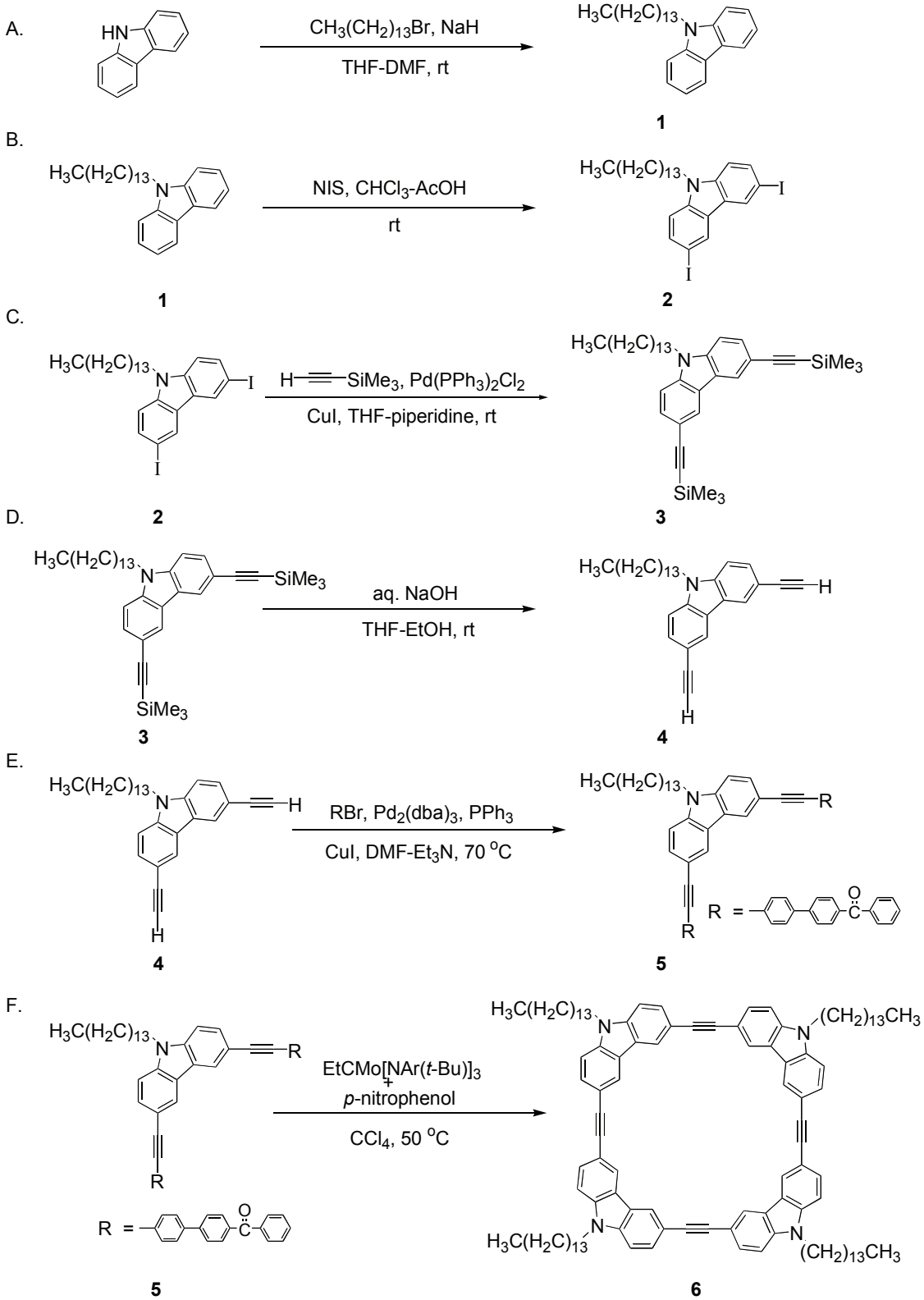
PREPARATION OF A CARBAZOLE-BASED MACROCYCLE VIA PRECIPITATION-DRIVEN ALKYNE METATHESIS



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Discussion Addendum *Org. Synth.* **2018**, *95*, 231

1. Procedure

*A. 9-Tetradecylcarbazole (**1**).* A single-necked 500-mL, round-bottomed, side-armed flask (Note 1) equipped with a glass stopper and a magnetic stirring bar is connected to a nitrogen-vacuum manifold. After evacuating and backfilling with nitrogen three times, the flask (with stopper removed), in which a positive flow of nitrogen is maintained throughout the entire procedure, is sequentially charged with carbazole (12.5 g, 0.072 mol) (Note 2), 1-bromotetradecane (24.3 mL, 0.079 mol) (Note 3), THF (60 mL) and DMF (20 mL) (Note 4). To the stirred solution, NaH (60% in oil, 4.32 g, 0.11 mol) (Note 3) is added to the solution in small portions within 20 min, avoiding vigorous bubbling and heating. The flask is capped with a glass stopper and the resulting suspension is stirred for 2 h at room temperature under nitrogen. Methanol (30 mL) is slowly added to the reaction mixture within 5 min to quench the remaining NaH. The solution is transferred to a 1-L, round-bottomed flask and then is concentrated by rotary evaporation (15–20 mmHg, water bath temperature 50–55 °C) to afford a solid residue, which is extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers are sequentially washed with 2 N aq HCl (2 x 100 mL), H_2O (2 x 100 mL), then are dried (Na_2SO_4) and concentrated by rotary evaporation. The crude product is purified by column chromatography [silica gel, 80 x 250 mm, hexanes] to afford carbazole **1** as a white solid (25.8 g, 98%) (Note 5).

*B. 3,6-Diiodo-9-tetradecylcarbazole (**2**).* A 500-mL, one-necked, round-bottomed flask equipped with a magnetic stirring bar is sequentially charged with carbazole **1** (14.5 g, 0.040 mol), *N*-iodosuccinimide (19.1 g, 0.081 mol) (Note 6), $CHCl_3$ (280 mL) and acetic acid (100 mL). The flask is capped with a nitrogen inlet adapter and wrapped in aluminum foil. The reaction mixture is stirred under nitrogen for 16 h at room temperature. Chloroform and acetic acid are removed by rotary evaporation. A pink precipitate forms upon pouring water (450 mL) into the residue and then transferring the slurry into a 1-L Erlenmeyer flask containing more water (200 mL). The solids are collected by filtration, air dried and dissolved in $CHCl_3$ (300 mL). The organic solution is sequentially washed with saturated $Na_2S_2O_3$ (3 x 70 mL), brine (2 x 100 mL), dried (Na_2SO_4), filtered and concentrated by rotary evaporation (15–20 mmHg, water bath temperature 30–35 °C). Iodinated carbazole **2** is obtained as a white solid (23.8 g, 97%) and used without further purification (Note 7).

*C. 3,6-Bis[(trimethylsilyl)ethynyl]-9-tetradecylcarbazole (**3**).* A 500-mL single-necked round-bottomed, side-arm flask equipped with a glass stopper and a magnetic stirring bar is connected to a nitrogen-vacuum manifold. After evacuating and backfilling with nitrogen three times, the flask, in which a positive flow of nitrogen is maintained throughout the procedure, is sequentially charged with iodinated carbazole **2** (23.7 g, 0.038 mol), CuI (0.147 g, 0.77 mmol) (Note 3), $Pd(PPh_3)_2Cl_2$ (1.35 g, 1.9 mmol) (Note 3), THF (90 mL), and piperidine (55 mL) (Note 3). The flask is cooled in an ambient temperature water bath before 1-trimethylsilylacetylene (45.7 mL, 0.38 mol) (Note 8) is added in two portions over 5 min (Note 9). The reaction mixture is then stirred for 23 h at room temperature. The solution changes from green to yellow with the formation of a white precipitate, and then the suspension changes to green and then black. The reaction mixture is then filtered through a coarse fritted funnel into a 1-L, one-necked, round-bottomed flask and is concentrated by rotary evaporation (15–20 mmHg, water bath temperature 40–45 °C). The crude product is purified by column chromatography [silica gel, 80 x 250 mm, hexanes 1 L, then hexanes/EtOAc 50/1 (2 L), then hexanes/EtOAc, 20/1 (1 L)] to afford diyne-substituted carbazole **3** as a yellow oil (19.9 g, 93%) (Note 10).

*D. 3,6-Diethynyl-9-tetradecylcarbazole (**4**).* A 1-L, one-necked, round-bottomed flask equipped with a magnetic stirring bar is sequentially charged with diyne substituted carbazole **3** (19.5 g, 0.035 mol), THF (100 mL) and ethanol (400 mL). As the resulting solution is stirred, a solution of NaOH (4.21 g, 0.11 mol) in H_2O (30 mL) is added slowly over 5 min. The solution is stirred under nitrogen at room temperature for an additional 2 h during which time the solution changes from orange to red. The solvent is removed by rotary evaporation (water bath temperature 45–50 °C) to afford a residue, which is partitioned between CH_2Cl_2 (450 mL) and H_2O (100 mL) in a 1-L separatory funnel. The separated organic layer is washed with H_2O (2 x 100 mL) and brine (2 x 100 mL), and then is dried (Na_2SO_4), filtered and concentrated by rotary evaporation (20–25 mmHg, water bath temperature 30–35 °C). Diyne-substituted carbazole **4** is obtained as a yellow-red oil that becomes a tan solid upon standing (14.0 g, 97%) and is used without further purification (Notes 11, 12).

*E. 3,6-Bis(benzoylbiphenyl)ethynyl-9-tetradecylcarbazole (**5**).* A 500-mL, single-necked round-bottomed, side-arm flask equipped with a Teflon thermometer adapter and a magnetic stirring bar is connected to a nitrogen-vacuum manifold. The flask is flame-dried under vacuum, then filled with

nitrogen. After evacuating and backfilling with nitrogen three times, the flask, in which a positive flow of nitrogen is maintained throughout the entire procedure, is sequentially charged with CuI (0.058 g, 0.31 mmol) (Note 3), $Pd_2(dba)_3$ (1.68 g, 1.8 mmol) (Note 13), PPh_3 (3.21 g, 12 mmol) (Note 13) and 4-benzoyl-4'-bromobiphenyl (21.7 g, 0.064 mol) (Note 14). The flask containing the solid mixture is evacuated and backfilled with nitrogen three times. Under a nitrogen purge, triethylamine (70 mL) (Note 3, Note 4) and a solution of diyne-substituted carbazole **4** (12.6 g, 0.031 mol) in DMF (150 mL) (Note 4) are sequentially added. Oxygen is removed from the mixture by three freeze-pump-thaw cycles. The reaction mixture is then stirred for 16 h at 70 °C (internal temperature). The solution changes from yellow to a dark purple. When the reaction mixture cools to room temperature, yellow precipitates are observed. The mixture is transferred to a 1-L, single-necked, round-bottomed flask with the aid of dichloromethane washes (2 x 250 mL). Dichloromethane and Et_3N are removed by rotary evaporation (15–20 mmHg, water bath temperature 40–45 °C) and DMF is removed under high vacuum by using a short-path distillation apparatus (0.50–1.0 mmHg, air bath temperature 45–55 °C) (Note 15). Dichloromethane (400 mL) is added and the organic layer is washed with saturated aq. NH_4Cl solution (2 x 200 mL), brine (2 x 200 mL) and then was dried (Na_2SO_4) and filtered. Dichloromethane is removed by rotary evaporation and the residual solid is treated with methanol (200 mL), resulting in the formation of a yellow solid. The solid bisarylethynyl-substituted carbazole **5** is collected by filtration, then is washed with methanol (3 x 50 mL), dried in vacuo (26.9 g, 95%) and used without further purification (Notes 16, 17).

*F. Carbazole-based tetrakismacrocycle (**6**)*. A 400-mL Schlenk tube equipped with a magnetic stirring bar and a glass stopper is introduced to a glove box. The flask is sequentially charged with 4-nitrophenol (0.680 g, 4.89 mmol) (Note 3), trisamidomolybdenum(VI) propylidyne (1.09 g, 1.63 mmol) (Note 18) and CCl_4 (150 mL) (Note 4). The resulting solution is stirred for 4 min and the solution changes from light yellow to orange (Note 19). A solution of monomer **5** (15.1 g, 16.3 mmol) in CCl_4 (200 mL) (Notes 20, 21) is added to the stirred catalyst solution. The flask is sealed with grease and electrical tape and is removed from the glove box. The resulting mixture is stirred at 50 °C (Note 22) for 24 h during which time a light-yellow precipitate forms and the color of the reaction mixture changes from yellow to brown. The mixture is transferred to a 1-L Erlenmeyer flask, along

with CH_2Cl_2 (200 mL). The solids are removed by suction filtration through a medium-porosity fritted-glass funnel and are washed with CH_2Cl_2 (2 x 50 mL). The filtrate is concentrated by rotary evaporation (20–25 mmHg, water bath temperature 40–45 °C). Methanol (200 mL) is added to the residue and the resulting suspension is filtered, washed with methanol (3 x 75 mL) and dried in vacuo. The crude product is further purified by silica gel column chromatography (Note 3) [silica gel, 44 x 572 mm, $CHCl_3/CH_2Cl_2$, 3/1 to 1/1] to afford macrocyclic product **6** as a pale-yellow solid (3.80 g, 61%) (Notes 23, 24).

2. Notes

1. All glassware was oven-dried at 140 °C overnight.

2. Carbazole (96%) was purchased from Acros and used as received.

3. 1-Bromotetradecane (97%), sodium hydride (60% dispersion in mineral oil), CuI (99.999%), $Pd(PPh_3)_2Cl_2$ (98%), piperidine (redistilled, 99.5+%), triethylamine (99.5%), *p*-nitrophenol (≥ 99%) and grade 62 silica gel with pore size of 150 Å were purchased from the Aldrich Chemical Company, Inc. and used as received unless further purification is indicated.

4. THF and DMF were dried by standing over 4 Å molecular sieves over night before use. Carbon tetrachloride was distilled over P_2O_5 and stored over 3 Å molecular sieves.

5. A small portion of compound **1** was further purified by recrystallization from ethanol to afford analytically pure material. The analytical data from compound **1** were as follows: mp 42–44 °C; TLC: R_f = 0.22 (hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.87 (t, *J* = 7.4 Hz, 3 H), 1.23–1.40 (m, 22 H), 1.87 (tt, *J* = 7.3 and 7.3 Hz, 2 H), 4.30 (t, *J* = 7.3 Hz, 2 H), 7.22 (dt, *J* = 7.8 and 0.9 Hz, 2 H), 7.40–7.48 (m, 4 H), 8.10 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1, 22.7, 27.3, 28.9, 29.3, 29.4, 29.47, 29.54, 29.57, 29.62, 29.64, 31.9, 43.0, 108.6, 118.6, 120.3, 122.8, 125.5, 140.4. IR (KBr): 3048, 2947, 2919, 2869, 2848, 2341, 2360, 1628, 1600, 1485, 1465, 1453, 1371, 1351, 1328, 1235, 1153, 1122 cm^{-1}; LRMS (EI): *m*/*z* 363.3, 180.1. Anal. Calcd for $C_{26}H_{37}NO$: C, 85.89; H, 10.26; N, 3.85. Found: C, 86.12; H, 10.66; N, 4.03. The spectroscopic data were in agreement with those previously reported.[2]

6. *N*-Iodosuccinimide (95%) was purchased from the Aldrich Chemical Company, Inc. and used as received.

7. The analytical data from compound **2** were as follows: mp 79–80 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, J = 7.1 Hz, 3 H), 1.22–1.30 (m, 22 H), 1.81 (tt, J = 7.1 and 7.1 Hz, 2 H), 4.21 (t, J = 7.4 Hz, 2 H), 7.16 (d, J = 8.6 Hz, 2 H), 7.70 (dd, J = 8.6 and 1.7 Hz, 2 H), 8.32 (d, J = 1.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1, 22.7, 27.2, 28.8, 29.31, 29.35, 29.35, 29.42, 29.51, 29.56, 29.61, 29.63, 29.65, 31.9, 43.2, 81.6, 110.9, 124.0, 129.3, 134.5, 139.5; IR (KBr): 3062, 2921, 2847 1585, 1466, 1428, 1374, 1348, 1312, 1290, 1236, 1216, 1152, 1047, 1014 cm^{-1}; LRMS (EI): *m*/*z* 615.1, 431.9, 208.1. These spectroscopic data were in agreement with those previously reported.[2]

8. 1-Trimethylsilylacetylene (98+%) was purchased from GFS Chemicals and used as received.

9. Upon addition of 1-trimethylsilylacetylene, a significant exotherm (15 °C) was observed, and stirring became difficult as the piperidine hydroiodide was formed.

10. The analytical data from compound **3** were as follows: TLC R_f = 0.32 (*n*-hexane/EtOAc, 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.28 (s, 18 H), 0.87 (t, J = 7.1 Hz, 3 H), 1.22–1.31 (m, 22 H), 1.83 (p, J = 7.1 Hz, 2 H), 4.25 (t, J = 7.2 Hz, 2 H), 7.29 (d, J = 8.1 Hz, 2 H), 7.56 (dd, J = 8.5 and 1.6 Hz, 2 H), 8.19 (d, J = 1.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 0.15, 14.1, 22.7, 27.2, 28.9, 29.32, 29.34, 29.45, 29.51, 29.57, 29.61, 29.63, 29.65, 31.9, 43.3, 92.0, 106.3, 108.8, 113.7, 122.3, 124.7, 130.0, 140.5; IR (film): 2926, 2854, 2153, 1869, 1629, 1598, 1483, 1406, 1382, 1350, 1318, 1287, 1248, 1202, 1149, 1133, 1059 cm^{-1}; MS (EI): *m*/*z* 555.4, 372.1, 73.1. These spectroscopic data were in agreement with those previously reported.[2]

11. A small portion of compound **4** was further purified by column chromatography (*n*-hexanes/EtOAc, 100/1 to 20/1) to afford analytically pure material. The analytical data from compound **4** were as follows: TLC R_f = 0.29 (*n*-hexanes/EtOAc, 20/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, J = 7.3 Hz, 3 H), 1.22–1.35 (m, 22 H), 1.84 (tt, J = 7.1 and 7.1 Hz, 2 H), 3.00 (s, 2 H), 4.25 (t, J = 7.3 Hz, 2 H), 7.32 (d, J = 8.6 Hz, 2 H), 7.60 (dd, J = 8.3, 1.5 Hz, 2 H), 8.21 (d, J = 1.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1, 22.7, 27.2, 28.9, 29.30, 29.33, 29.43, 29.50, 29.56, 29.60, 29.62, 29.64, 31.9, 43.3, 75.4, 84.7, 108.9, 112.7, 122.2, 124.7, 130.1, 140.6; IR (film): 3279 (s), 2924 (s), 2849 (s), 2103 (s), 1630 (m), 1598 (s), 1483 (s), 1381 (m), 1349 (s), 1321 (w), 1290 (s), 1234 (m), 1153 (s), 1134 (m), 882 (s), 812 (s), 728 (w), 681 (m), 653 (s), 614 (s) cm^{-1}; LRMS (EI): *m*/*z* 411.3, 228.1, 75.0. Anal. Calcd for $C_{30}H_{37}N$: C, 87.54; H, 9.06; N, 3.40. Found: C, 87.38; H,

8.78; N, 3.63. These spectroscopic data were in agreement with those previously reported.[2]

12. The appearance of more than one ^{1}H NMR singlet around δ 3.1 ppm (terminal acetylene) indicated the presence of mono-desilylation side product. In this case, **4** was further purified by column chromatography [*n*-hexanes/EtOAc, 100/1 to 20/1, TLC R_f = 0.29 (*n*-hexanes/EtOAc, 20/1].

13. $Pd_2(dba)_3$ and PPh_3 (99%) were purchased from Strem Chemicals, Inc. and used as received.

14. 4-Benzoyl-4'-bromobiphenyl (99%) was purchased from Lancaster and used as received.

15. The submitters reported the use of a Kugelrohr short-path distillation apparatus (Cat. No. Z401137-1SET), which was purchased from Aldrich Chemical Company, Inc.

16. A small portion (500 mg) of compound **5** was further purified by recrystallization from hot isopropyl acetate (ca. 20 mL) to provide analytically pure material. The analytical data from compound **5** were as follows: mp 162–167 °C; TLC R_f = 0.26 (CH_2Cl_2/*n*-hexanes, 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J* = 7.1 Hz, 3 H, C*H*$_3$), 1.19–1.41 (m, 22 H, C*H*$_2$), 1.89 (tt, *J* = 7.1, 7.1 Hz, 2 H), 4.31 (t, *J* = 7.3 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 7.52 (m, 4 H), 7.61 (tt, *J* = 7.5, 1.4 Hz, 2 H), 7.66–7.71 (m, 10H), 7.74 (d, *J* = 8.6 Hz, 4 H), 7.85 (m, 4 H), 7.92 (d, *J* = 8.4 Hz, 4 H), 8.32 (d, *J* = 1.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1, 22.7, 27.2, 28.9, 29.3, 29.46, 29.51, 29.57, 29.61, 29.62, 29.64, 31.9, 43.4, 87.6, 92.0, 109.1, 113.7, 122.5, 123.8, 124.2, 126.8, 127.2, 128.3, 129.8, 130.0, 130.8, 132.1, 132.4, 136.4, 137.7, 139.2, 140.6, 144.4, 196.3; IR (KBr): 2924, 2851, 2201, 1648, 1600, 1522, 1481, 1384, 1317, 1277, 1150 cm^{-1}. LRMS (MALDI): *m*/*z* 923.94, 825.5, 809.5, 755.9, 740.8, 567.4, 551.4, 545.4. Anal. Calcd for $C_{68}H_{61}NO_2$: C, 88.38; H, 6.65; N, 1.52. Found: C, 88.06; H, 6.41; N, 1.70. These spectroscopic data were in agreement with those previously reported.[2]

17. The submitters found that the appearance of more than one ^{1}H NMR triplet around δ 4.3 ppm (α-methylene protons on the tetradecyl side chain) indicated the presence of unreacted starting material and/or mono-alkynylated product. In this case, **5** could be further purified by column chromatography [*n*-hexanes/CH_2Cl_2, 1/1 v/v, TLC R_f = 0.26 (CH_2Cl_2/*n*-hexane, 1/1)].

18. Gram-scale preparation of trisamidomolybdenum(VI) propylidyne is reported in the preceding *Organic Syntheses* report.

19. A red precipitate was observed during mixing, and was presumably due to the low solubility of the species generated in CCl_4. In the case of chloroform, ethyl acetate or THF as solvent, no precipitate was observed.

20. Only a portion of monomer **5** dissolved in CCl_4 at the start of the reaction. However, the poor solubility of **5** did not affect the macrocycle synthesis. As the metathesis reaction proceeded, monomer **5** dissolved and was transformed into soluble macrocycles.

21. In addition to CCl_4, 1,2,4-trichlorobenzene and toluene are alternative solvents for the macrocycle synthesis. The amount of aromatic impurities observed in the reaction (based on ^{1}H NMR analysis) conducted in CCl_4 was less than that observed in toluene.

22. In a previous report on the small-scale synthesis of macrocycle **6** via precipitation-driven alkyne metathesis,[2] the reaction was conducted at 30 °C. However, for gram-scale preparation, the low solubility of oligomeric intermediates dramatically increased the solution viscosity and made stirring difficult. Raising the reaction temperature from 30 °C to 50 °C greatly improved the intermediate solubility and allowed efficient stirring.

23. The crude product **6** (after methanol wash, before column separation) was obtained in 98% yield (6.13 g) and contained a small amount of aromatic impurities (mainly 4-benzoyl-4'-bromobiphenyl). Macrocycles of high purity were obtained after column chromatography. The analytical data from compound **6** were as follows: mp 222–224 °C; TLC; R_f = 0.89 ($CHCl_3$/CH_2Cl_2, 3/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J* = 7.1 Hz, 12 H), 1.20–1.45 (m, 88 H), 1.90 (tt, *J* = 7.1, 7.1, 8 H), 4.31 (t, *J* = 7.1 Hz, 8 H), 7.39 (d, *J* = 8.5 Hz, 8 H), 7.71 (dd, *J* = 8.3, 1.3 Hz, 8 H), 8.42 (d, *J* = 0.7 Hz, 8 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1, 22.7, 27.3, 29.0, 29.35, 29.50, 29.55, 29.60, 29.64, 29.67, 31.9, 43.3, 89.0, 108.9, 114.4, 122.6, 123.9, 129.3, 140.1; IR (KBr): 2922, 2848, 1628, 1599, 1570, 1490, 1382, 1352, 1307, 1283, 1214, 1148, 1131 cm^{-1}; MS (MALDI): *m*/*z* 1542.7, 1370.1. Anal. Calcd for $C_{112}H_{140}N_4$: C, 87.22; H, 9.15; N, 3.63; Found: C, 86.84; H, 9.19; N, 3.26. These spectroscopic data were in agreement with those previously reported.[2]

24. The checkers found that accurate analytical data could be obtained from **6** only after thorough drying at 0.3 mm Hg in an Abderhalden apparatus heated with refluxing xylenes.

Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Shape-persistent arylene ethynylene macrocycles have attracted attention in the fields of supramolecular chemistry and materials science over the past decade due to their novel properties and potential applications.[3] However, the study and application of shape-persistent macrocycles are impeded by inefficient macrocycle syntheses. The usual preparation involves a large number of synthetic steps, requires dilute conditions (< 1 mM), and affords low overall yields.[4] Considerable efforts have been devoted to the development of methodologies allowing selectively functionalized structures to be obtained in high yields.

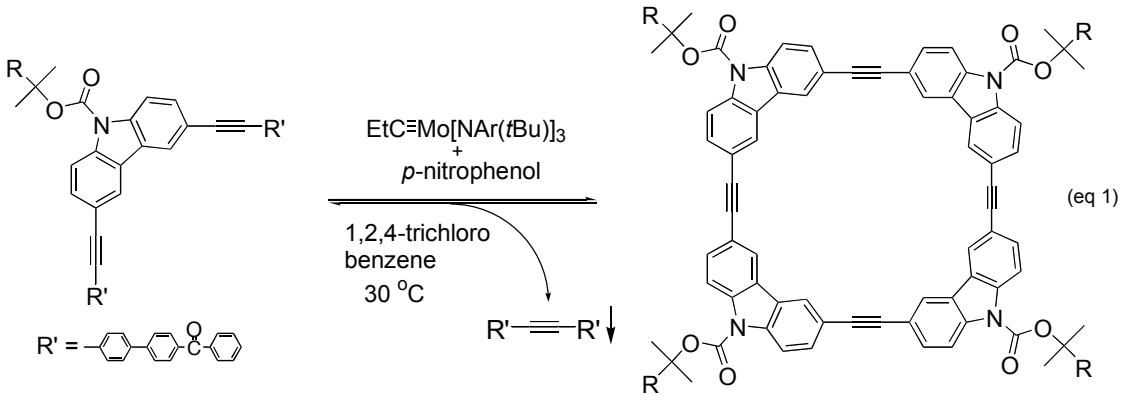
Conventional synthetic routes for arylene ethynylene macrocycles are dominated by Sonogashira coupling[5] between aryl iodides and terminal acetylenes and Glaser-type couplings[6] between terminal acetylenes. These cross-coupling approaches have advantages such as high tolerance of functional groups, with generally high yields in the individual steps. However, to obtain high yields of macrocycles, precursor oligomers must be pre-synthesized in a stepwise fashion and subsequently subjected to cross-coupling reactions under pseudo-high dilution condition (< 1 mM) to form macrocycles via intramolecular cyclization. Such tedious and time-consuming synthesis of the precursors impedes the efficient large-scale preparation of macrocycles via this route. Random cyclization of three or more monomer units has also been applied to preparing target macrocycles, but usually only low yields (1–18% on cyclization step) were obtained.[7]

Inspired by the successful applications of thermodynamically controlled reversible reactions in preparing unique molecular architectures[8] such as macrocyclic compounds, molecular capsules and interlocked structures, we envisioned that a convenient synthesis of arylene ethynylene macrocycles could be accomplished by using dynamic covalent chemistry.[9] In the past two decades, there has been rapid progress in alkyne metathesis catalyzed by either defined carbyne complexes[10] or catalysts generated in situ.[11] The ready availability of highly active Mo(VI) alkylidyne catalysts

synthesized by a reductive recycle strategy[12] and successful examples of using dynamic covalent chemistry in organic syntheses prompted us to develop a synthetic approach to macrocycle preparation directly from a monomer.

We reported a successful approach involving precipitation-driven alkyne metathesis for convenient, multi-gram synthesis of arylene ethynylene macrocycles near room temperature.[2] Driven by the precipitation of a diarylacetylene byproduct, the desired macrocycles were obtained in one step from monomers in high yields. Macrocycle formation is a thermodynamically favored process under equilibrium control.[13]

We have utilized precipitation-driven alkyne metathesis to prepare other carbazole-based tetrameric macrocycles, such as **10c**. The four side chains are easily removed via thermolysis.[14] The resulting macrocycles may exhibit interesting electronic properties such as mixed-valence (MV) states.[15]



9a: R = Methyl
9b: R = Heptyl
9c: R = dodecyl

10a: R = Methyl < 5%
10b: R = Heptyl < 5%
10c: R = dodecyl 81%

Three dialkyne monomers **9a-c**, which are functionalized with *t*-butyl carboxylate, 1,1-dimethyloctyl carboxylate and 1,1-dimethyltridecyl carboxylate, respectively, were prepared and subjected to standard metathesis conditions (eq 1). In the case of **9a-b**, at the end of the reaction nearly quantitative conversion of starting monomers into insoluble materials was observed. Based on elemental analysis, the insoluble materials are believed to be a mixture of intermediate oligomers and diarylacetylene byproduct. In great contrast, metathesis of monomer **9c** proceeded well in 1,2,4-trichlorobenzene at 30 °C, and tetrameric macrocycle **10c** was obtained in 81% isolated yield.[16]

The successful generation of tetrameric macrocycle **6** and **10c**, as well as those failed cases when using monomer **9a-b**, illustrate the importance of balancing the solubility through the course of macrocycle formation.[13] In the case of metathesis of **9a-b**, the generated oligomeric species, either open-chain or cyclic versions, presumably precipitate out of solution due to their insufficient solubility. In great contrast, carbazole oligomers with 1,1-dimethyltridecyl carboxylate side chains (from metathesis of **9c**) have better solubility and intermediate species remain in solution, thus allowing for high yield formation of tetracycles via alkyne metathesis—a dynamic covalent approach.

This finding has important practical significance in that it demonstrates that the solubility of longer arylene ethynylene oligomers, especially those overshooting the target macrocycle length, must be taken into consideration to accomplish high-yield macrocycle syntheses. All the intermediate compounds should be sufficiently soluble along the reaction pathway to allow the thermodynamically stable product to be obtained through reversible alkyne metathesis.

It is envisioned that the successful preparation of macrocycles using the precipitation-driven, reversible alkyne-metathesis may open the way to other two-dimensional or three-dimensional arylene ethynylene structures, as well as alkyne-bridged oligomers and polymers.

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16. The characterization data for macrocycle **10c** were as follows: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.87 (t, J = 6.6 Hz, 12 H, $OC(CH_3)_2CH_2(CH_2)_{10}CH_3$], 1.23–1.54 (m, 80 H, $OC(CH_3)_2CH_2(CH_2)_{10}CH_3$], 1.80 [s, 24 H, $OC(CH_3)_2CH_2(CH_2)_{10}CH_3$], 2.11 [m, 8 H, $OC(CH_3)_2CH_2(CH_2)_{10}CH_3$], 7.44 (d, J = 8.6 Hz, 8 H), 8.00 (s, 8 H), 8.10 (d, J = 8.6 Hz, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 14.1, 22.7, 24.2, 26.4, 29.4, 29.5, 29.6, 29.7 (br, signal overlap), 30.0, 31.9, 40.8, 87.0 [$OC(CH_3)_3$], 89.1 [Ar*CC*Ar], 116.0, 118.2, 122.4, 125.1, 130.7, 138.0, 150.5 (N*C*OO); MS (FD): m/z (%): 1773.3 (21), 887.0 (100), 525.3 (66); Anal. Calcd for $C_{120}H_{148}N_4O_8$ (1773.1): C, 81.22; H, 8.41; N, 3.16; Found: C, 80.93; H, 8.05; N, 3.24; GPC 2030 (M_n), 1.02 (M_w/M_n).

Appendix
Chemical Abstracts Nomenclature; (Registry Number)

Carbazole: 9H-Carbazole; (86-74-8)
1-Bromotetradecane; (112-71-0)
Sodium hydride; (7646-69-7)
N-Iodosuccinimide: 1-Iodo-2,5-Pyrrolidinedione; (516-12-1)
Copper(I) iodide; (7681-65-4)
Dichlorobis(triphenylphosphine)palladium(II); (13965-03-2)
Piperidine; (110-89-4)
1-Trimethylsilylacetylene: Silane, ethynyltrimethyl-; (1066-54-2)
Tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$]; (52409-22-0)
Triphenylphosphine; (603-35-0)
4-Benzoyl-4'-bromobiphenyl: ethanone, (4'-bromo[1,1'-biphenyl]-4-yl)phenyl-; (63242-14-8)
Trisamidomolybdenum(VI) propylidyne: Molybdenum, tris[*N*-(1,1-

dimethylethyl)-3,5-dimethylbenzenaminato]propylidyne-, (T-4)-; (616886-28-3)

p-Nitrophenol: 4-Nitrophenol; (100-02-7)

9-Tetradecylcarbazole: 9-Tetradecyl-9*H*-carbazole; (20863-25-6)

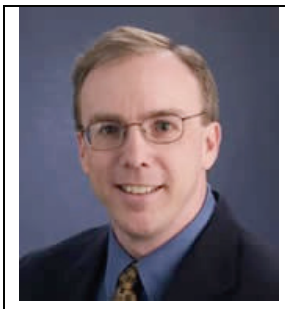
3,6-Diiodo-9-tetradecylcarbazole: 3,6-Diiodo-9-tetradecyl-9H-carbazole: (197860-64-3)

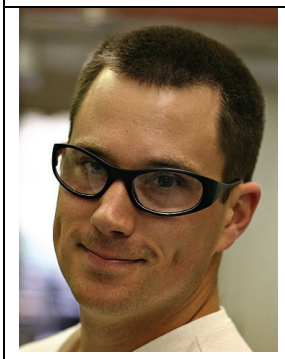
3,6-Bis[(trimethylsilyl)ethynyl]-9-tetradecylcarbazole: 9H-Carbazole, 9-tetradecyl-3,6-bis[(trimethylsilyl)ethynyl]- ; (197860-65-4)

3,6-Diethynyl-9-tetradecylcarbazole; (188740-71-8)

3,6-Bis(benzoylbiphenyl)ethynyl-9-tetradecylcarbazole: Methanone, [(9-tetradecyl-9H-carbazole-3,6-diyl)bis(2,1-ethynediyl[1,1'-biphenyl]-4',4-diyl)]bis[phenyl-; (791090-33-0)

Carbazole-based tetrakismacrocycle; (245648-36-6)

	Jeffrey Moore was born near Joliet, IL in 1962. He received his BS in chemistry (1984) from the University of Illinois, and his PhD in Materials Science and Engineering with Samuel Stupp (1989). Following a NSF postdoctoral fellowship at Caltech with Robert Grubbs and an Assistant Professor appointment at the University of Michigan in Ann Arbor, he returned in 1993 to the University of Illinois, where he is currently the William H. and Janet G. Lycan Professor of Chemistry and Materials Science and Engineering. His research focuses on molecular self-assembly, structure-controlled macromolecules and foldamers, stimuli-responsive materials, and self-healing polymers.
	Wei Zhang was born in China in 1977. After completing his BS in chemistry in 2000 at Peking University and one year of graduate study at the University of Utah, he transferred to the University of Illinois at Urbana-Champaign in 2001, where he completed his PhD in chemistry with Prof. Jeffrey Moore, working on the development of molybdenum-based alkyne metathesis catalysts and their application to the synthesis of shape-persistent macrocycles and conjugated polymers (2005). In March 2006 he began a postdoctoral position at MIT with Prof. Timothy M. Swager.

	Hyeon Mo Cho was born in South Korea in 1971. After receiving his BS in chemistry from Yonsei University (Seoul, 1994), he completed his MS (1997) and PhD (2002) in chemistry, also at Yonsei University, working on organosilicon compounds with Chang Hwan Kim and Myong Euy Lee. In 2002, he studied silica nanotube and siloxanes as a postdoctoral fellow at Natural Science Research Institute of Yonsei University. He then went to the University of Illinois as a postdoctoral fellow to study with Jeffrey Moore (2004). Currently he is a senior researcher at Electronic Chemical Materials R&D Center of Samsung Cheil Industries Inc.
	Christopher Butler received a bachelor's degree in Chemistry from Illinois Wesleyan University in 2000. He then worked for three years in drug discovery at Johnson & Johnson Pharmaceutical Research & Development in San Diego, CA, before beginning graduate school at the University of Illinois working with Professor Scott E. Denmark in 2003. His thesis work focuses on the development of palladium-catalyzed vinylation of aryl and heteroaryl bromides using inexpensive polyvinylsiloxanes.