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Rearrangements in the Scholl oxidation: implications for molecular architectures

Jason L. Ormsby, Tessa D. Black, Cameron L. Hilton, Bharat, Benjamin T. King*

Department of Chemistry, University of Nevada, Reno, NV 89557, United States

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ABSTRACT

Rearrangements readily occur in Scholl oxidations and interfere with the construction of certain molecular architectures. $3,3^{"'},4,4',4'',4''',5',5''$ -Octamethoxy-1,1',2',1'',2'',1'''-quaterphenyl and $3,3^{"'},4,4',4'',4''',5',5''$ -octamethyl-1,1',2',1'',2'',1'''-quaterphenyl, which were conceived as precursors to benzenoid strips, rearranged under Scholl conditions to the unexpected C_{2v} -substituted products 1,2,5,6,9,10,12,13-octamethoxydibenzo[fg,op]naphthacene and 1,2,5,6,9,10,12,13-octamethyldibenzo[fg,op]naphthacene. This corrects a widely propagated error in the literature in which the assignments of 1,2,5,6,9,10,12,13-octamethoxydibenzo[fg,op]naphthacene (C_{2v}) and 1,2,5,6,8,9,12,13-octamethoxydibenzo[fg,op] naphthacene (C_{2h}) are crossed. A mechanism involving the migration of an aryl ring on an arenium cation intermediate is proposed.

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1. Introduction

The architectural design of large polycyclic aromatic hydrocarbons (PAHs) is still in its infancy. Müllen, the pioneer of this field, has prepared many large PAHs by the Scholl oxidation of dendritic oligophenylenes.^{1–5} The architectural variety is mostly limited to discotic PAHs, with a few exceptions.^{6,7}

Other architectures have received less attention. PAHs with a high aspect ratio, often referred to as strips or ribbons, are appealing targets because of potential application in molecular electronics^{3,8} and carbon-based materials.³ While syntheses of short, linear graphitic ribbons⁹ and polymeric, graphitic ladder polymers¹⁰ have been reported, the synthesis of polymeric graphitic ribbons are rare.^{6,7} In many cases, including some syntheses of PAHs, the Scholl oxidation has been employed in a key condensation step.^{6,7} The utility of the Scholl oxidation arises from its ability to form multiple aryl-aryl bonds between unfunctionalized C-H vertices.¹¹

We intended to synthesize polymeric graphitic ribbons by the Scholl oxidation of poly-*ortho*-phenylenes (Scheme 1). Recent studies on the mechanism and substituent effects¹¹⁻¹⁶ provided clear guidelines for our initial strategy: use electron-donating groups to direct bond formation and blocking groups to inhibit unwanted bond formation.¹² We were thwarted by rearrangements. Our experiments and literature survey demonstrate that rearrangements are prevalent in the Scholl oxidation of oligophenyls. The propensity to rearrange effectively precludes use of the Scholl reaction to construct complex molecular architectures.

Both methoxy- and methyl-substituted quaterphenyls rearranged to give unexpected dibenzonaphthacenes. Our characterization of the rearranged, $C_{2\nu}$ -substituted product 1,2,5,6,9,10,12,13-octame-thoxydibenzo[fg,op]naphthacene corrects a widely propagated error in the literature, where Musgrave crossed the assignments of the $C_{2\nu}$ - and C_{2h} -substituted isomers of octamethoxydibenzo[fg,op]-naphthacene.^{17–19} In more than one dozen papers, most of which deal



* Corresponding author. Tel.: +1 775 784 1736; fax: +1 775 784 6804.

E-mail address: king@chem.unr.edu (B.T. King).









Scheme 3. Expected oxidation products.

with discotic liquid crystals, Musgrave's methodology was reproduced and his assignment error propagated.

Table 1X-ray crystallographic data

2. Results and discussion

Guided by known principles for the application of the Scholl reaction,¹² a family of methoxy-substituted *ortho*-oligophenylenes (**3**, Scheme 2) was conceived as precursors to graphitic strips. Methoxy substituents played the dual role of directing intra-molecular bond formation and blocking the unwanted intermolecular bond formation.

Yamamoto polymerization of 2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl (**2**), prepared from 4,5-dibromoveratrole (**1**) according to the literature,²⁰ afforded polymer **3** (Scheme 2). MALDI-TOF-MS revealed a distribution of oligomers with up to 18 phenylene units with the sexiphenyl most abundant.

Preparative HPLC afforded pure dodecamethoxysexiphenyl **4** (60 mg), which was subjected to Scholl oxidation using MoCl₅, an oxidant commonly used in aryl-aryl coupling reactions.^{12,21} Three





Figure 1. Thermal ellipsoid plot of 6. Arrows indicate hydroxy substituents.



Scheme 4. (a) *n*-BuLi (1 equiv), TMSCI, THF, -78 °C, (**7**) 70%; (b) Ni(COD)₂, COD, bipy, DMF/toluene, 80 °C, (**8**) 40%; (c) HBF₄, CH₂Cl₂, 0 °C, (**9**) 96%.



Figure 2. Thermal ellipsoid plot of 11.

products were expected, differing in the orientation of the terminal alkoxy groups arising from rotation of the terminal phenyl rings (Scheme 3). Of these, isomer **5** possesses the fewest methoxy-methoxy bay interactions and was expected to be the main product.

HPLC and MALDI-TOF-MS analysis revealed the product mixture to be dauntingly complex. A few crystals grew during storage of the product mixture in toluene at -20 °C. Single-crystal X-ray diffraction analysis (Fig. 1, Table 1) revealed the product to be **6**, which corresponds to the anticipated structure **5**, but with two hydrolyzed methoxy groups. The length of the C–OH bonds (1.374 Å) rules out a quinonoidal structure. We were unable to obtain sufficient material for full characterization.

While it is apparent that the oxidation of **4** afforded a short graphitic strip, the reaction was not synthetically useful. To understand the origin of the unexpectedly complex reaction mixture in this oxidation, we turned to a simpler substrate, octamethoxy-quaterphenyl **9**.

Stepwise synthesis of **9** was straightforward (Scheme 4). Yamamoto homocoupling of 2-bromo-2'-trimethylsilyl-4,4',5,5'tetramethoxybiphenyl (**7**) afforded quaterphenyl **8**, which bore TMS functionality at the terminus. The TMS functionality, which was easily removed with HBF₄, served two roles: prevention of oligomerization and promotion of crystallinity. ¹H and ¹³C NMR spectra were identical to the literature values for quaterphenyl (**9**),



Figure 3. NOE measurements distinguish C_{2v} and C_{2h} substitution patterns.

which had been prepared using an alternate strategy.²² The structure of **9** was confirmed by single-crystal X-ray diffraction analysis.

Scholl oxidation of methoxy-substituted *ortho*-quaterphenyl (**9**) using bis(trifluoroacetoxy)iodobenzene (PIFA) and $BF_3 \cdot Et_2O$, a mild oxidant cocktail used for the synthesis of alkoxy biaryls,^{13–16} gave a single product (HPLC and ¹H NMR) in 47% yield. Both ¹H and ¹³C NMR were in accord with the anticipated product **10**.

Single-crystal X-ray diffraction analysis (Fig. 2) revealed a surprise: the product was not **10**, but rather **11**. The carbon skeleton rearranged (Scheme 5). A series of 1-D NOE experiments (Fig. 3) established that the entire sample was **11**, not **10**. The $C_{2\nu}$ -substituted compound **11** should exhibit a single NOE between one pair of methoxy resonances, but the C_{2h} -substituted compound **10** should show two NOEs between two pairs of methoxy resonances. Only one methoxy-methoxy NOE was observed, confirming the identity of the bulk sample as **11**.

In a series of papers^{17–19} Musgrave reported the synthesis and characterization of both **10** and **11**. The ¹H NMR spectra of these two compounds were, not surprisingly, superimposable. And both NMR spectra matched our spectrum of **11**.

Musgrave's characterization^{17–19} of the compound they claimed to be **10** was indirect, as was de rigueur in the late 1960s, and relied on the tacit assumption that the aryl–aryl bond in 3,3',4,4'-tetramethoxybiphenyl was fixed. His synthesis (Scheme 6) used the Scholl oxidation of 3,3',4,4'-tetramethoxybiphenyl with chloranil and sulfuric acid. Quaterphenyl **9** was proposed as an intermediate but was not isolated or characterized. The reaction afforded an overoxidized quinone that was reduced and methylated to give an octamethoxynaphthacene. Based on the symmetry evident from the NMR



Scheme 5. The Scholl oxidation of 9. The expected product (10) and the actual product (11). PIFA, BF3·Et2O, CH2Cl2, 25 °C, 24 h, (11) 47%.



Scheme 6. Scholl oxidation of 3,3',4,4'-tetramethoxybiphenyl.

spectrum and the presumed invariability of the aryl–aryl bond in the biphenyl reactant, Musgrave assigned structure **10** to the product.

Our results were confusing. The melting point of compound **11**, which we unambiguously characterized, is 219–220 °C. Our melting point matched Musgrave's value for **10** (222.5–223.5 °C), not **11** (283–285 °C). We suspected that that Musgrave's assignments of **10** and **11** were crossed.

Repeating Musgrave's synthesis that was reported to provide **10** confirmed our suspicions. Isolation and comparison (mp, ¹H, ¹³C, and NOE spectra) of this product with an authentic sample of **11** demonstrated that Musgrave's preparation afforded **11**, not **10** as originally claimed.

A mechanism involving a single aryl migration can explain the rearrangement (Scheme 7). A 1,2-aryl migration proceeds via a bridged arenium cation (**13**), which may be an intermediate or transition state. Aryl–aryl bond formation and oxidation complete the sequence. In this mechanism, **12** and **14** are in rapid equilibrium, and **14** cyclizes faster because it has two *para* electron-donating groups.¹²

Musgrave also prepared, albeit in low yield, the other symmetrical isomer of octamethoxydibenzonaphthacene. Oxidation of veratrole with chloranil in sulfuric acid gave mostly 2,3,6,7,10,11-hexamethoxytriphenylene and a small amount (7%) of a quinone. Reduction and methylation afforded a second symmetrical octamethoxynaphthacene. Because only two symmetrical octamethoxynaphthacenes exist, Musgrave assigned this octamethoxynaphthacene to **11**. As is now evident, this product must have been **10**. The formation of **10** from veratrole can be explained by the intermediacy of 1,2,6,7,10,11-hexamethoxytriphenylene, which is presumably formed in small amounts during the Scholl oxidation of veratrole (Scheme 8). This isomer reacts again with veratrole to form **10**. As pointed out by Musgrave,¹⁷ the dominant isomer, 2,3,6,7,10,11-hexamethoxytriphenylene, does not react with veratrole.

Musgrave's mis-assignment has been propagated in the literature. A family of liquid crystals has been built on the octaalkoxynaphthacene core prepared by the Scholl oxidation of 3,3',4,4'-tetralkoxybiphenyls, often using Musgrave's exact conditions.²³ Structural assignments were based on Musgrave's erroneous results. The discotic cores of this family of liquid crystals are probably based on **11**, not **10**, and possess C_{2v} not C_{2b} , substitution patterns.

This error is also entrenched in the patent²⁴ and review^{4,5,25} literature. It may affect some assignments in recent synthetic reports²⁶ and alter the historical discussion in other reports.²⁷

Our use of methoxy groups was a poor choice as they strongly promote aryl migrations. Bachmann and Ferguson determined the migratory aptitudes for *p*-anisyl (500), *p*-tolyl (15.7), phenyl (1.0), and other arenes and concluded that electron-donating substituents in *para* or *meta* positions increase migratory aptitude.²⁸ We hypothesized that use of methyl groups instead of methoxy groups might suppress rearrangement.

Our synthetic strategy to methyl-substituted *ortho*quaterphenyl (**19**) was analogous to the methoxy strategy (Scheme 9). The structure of **19** was confirmed by single-crystal X-ray crystallography.



Scheme 7. A plausible arenium cation rearrangement mechanism of alkoxy substituted ortho-aryls.



Scheme 8. Scholl oxidation of veratrole.



Scheme 9. (a) Cat. I₂, 2.0 equiv Br₂, 0 °C, (15) 53%; (b) 0.5 equiv *n*-BuLi, THF, -78 °C, 24 h, (16) 71%; (c) 1.0 equiv *n*-BuLi, TMSCl, THF, -78 °C, (17) 86%; (d) Ni(COD)₂, COD, bipy, DMF/ toluene, 80 °C, 24 h (18) 51%; (e) HBF₄, CH₂Cl₂, 0 °C, (19) 78%.

Scholl oxidation of **19** using MoCl₅ gave a single product, as evidenced by ¹H, ¹³C, and HPLC analysis of the reaction products. Isolation by normal-phase semi-preparative HPLC afforded **20**. Measurement of NOE and single-crystal X-ray diffraction analysis²⁹ (Fig. 4) established a $C_{2\nu}$ substitution pattern. It too rearranged (Scheme 10).

We are not the first to observe rearrangements in the Scholl oxidation. Aryl migrations similar to those reported here have been noted in products from aryl oligomers without alkoxy or alkyl substituents.^{1,2,30} Müllen and co-workers reported a rearrangement involving a shift of a methoxy-substituted phenyl group and invoke a similar arenium cation mechanism.³¹ In other work, oligophenylenes designed with overlapping phenyl groups cleanly rearrange to give fully planar products.³² Nenitzescu even provided a table, 'Rearrangements in the Scholl Reaction,' in his 1964 review.³³ There were 11 entries.

Musgrave was also not the first to incorrectly assign a structure on the assumptions that aryl–aryl bonds are fixed under Scholl conditions. As pointed out by Nenitzescu,³³ even Scholl made this error.³⁴ The product of his namesake reaction between *ortho*-tolyl-1-naphthyl ketone gave 9-methylbenz[*de*]anthracen-7-one, not the expected product 8-methylbenz[*de*]anthracen-7-one. Even our teasingly suggestive oxidation of sexiphenyl **4** to give **6** may involve a double rearrangement (Scheme 11).

These rearrangements provide hints to the mechanism of the Scholl reaction. Both radical cation³⁵ and arenium cation pathways^{11,33} for the Scholl mechanism have been proposed. While the



Figure 4. Thermal ellipsoid plot of 20.

arenium cation pathway is energetically more favorable than a radical cation pathway and standard directing group effects operate¹² it is still difficult to distinguish the mechanisms. These rearrangements require an arenium cation intermediate and therefore support the arenium cation pathway.

3. Conclusions

Rearrangements are common in the Scholl reaction. PAHs prepared using Scholl oxidations should be completely characterized, as rearranged products may not be immediately identifiable by mass spectrometry or even by simple NMR experiments. In many successful Scholl reactions, the rearrangements are degenerate; this is the case for most discotic PAHs. For most other architectures, rearrangements are not degenerate, and multiple or unexpected products may be formed. This restriction effectively precludes use of the Scholl reaction to prepare interesting molecular architectures.

4. Experimental section

4.1. 2,2'-Dibromo-4,4',5,5'-tetramethoxybiphenyl (2)

The methoxy-substituted dibromo-biphenyl was prepared according to the literature.²⁰ To a stirring solution of 4,5-dibromoveratrole (29.678 g, 0.100 mol) in THF (250 mL), *n*-BuLi (18.23 mL, 0.050 mol, 2.75 M in hexane) was added dropwise at -78 °C. Five hours after the addition of *n*-BuLi, the reaction was quenched with dilute HCl. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×50 mL). The organic layers were combined and dried under vacuum. The product was recrystallized from absolute ethanol, filtered, and dried under vacuum to yield white crystals (16.644 g, 77%). Mp 149–150 °C (lit.²⁰ 154–158 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.12 (s, 2H), 6.77 (s, 2H), 3.93 (s, 6H), 3.87 (s, 6H). GC–MS: *m*/*z* 432.

4.2. Methoxy-substituted *ortho*-phenyls (3), including the sexiphenyl (4)

A solution of 2,2'-dibromo-4,4',5,5'-tetramethoxybiphenyl (1.05 g, 2.43 mmol), 2,2'-bipyridyl (540 mg, 3.6 mmol), 1,5-cyclooctadiene (0.40 mL, 3.6 mmol), dry DMF (20 mL), and dry toluene (70 mL) was degassed with bubbling N₂ (20 min) and heated to 80 °C. Bis(1,5-cyclooctadiene)nickel(0) (990 mg, 3.6 mmol) was added under positive pressure of N₂, and the reaction mixture was



Scheme 10. The Scholl oxidation of 15. The unrearranged product and the rearranged product (20), 33%.



Scheme 11. A proposed isomerization of 4, analogous to the isomerization of 9 and 19. Nascent bonds possessing two para directing groups are highlighted in gray.

stirred overnight. The solvent was removed under reduced pressure, and the remaining residue was washed first with toluene, then with CH_2Cl_2 . The solvent was again removed under reduced pressure to give 0.94 g (90% yield) of crude material. The crude product mixture was partially characterized by MALDI-TOF-MS. Fractionation into separate samples, including one enriched in the sexiphenyl was accomplished by column chromatography (hexane/ ethyl acetate 1:2). Normal-phase preparative HPLC afforded the dodecamethoxysexiphenyl **4** (60 mg, 9%) as a beige solid.

4.3. Characterization data of dodecamethoxysexiphenyl 4

¹H NMR (DMSO-*d*₆, 150 °C, 500 MHz): δ 6.78 (s, 2H), 6.69 (d, *J*=8.5 Hz, 2H), 6.46 (s, 2H), 6.36 (s, 2H), 6.16 (m, 6H), 3.78 (s, 6H), 3.75 (s, 6H), 3.58 (s, 6H), 3.56 (s, 6H), 3.54 (s, 6H), 3.49 (s, 6H). ¹³C NMR (DMSO-*d*₆, 100 °C, 126 MHz), unresolved after 12 h due to hindered rotation. UV-vis (CH₂Cl₂) λ_{max} 231 nm (-log ε 4.73), 294 (-log ε 4.46). HRMS (MADLI) *m*/*z* calcd for C₄₈H₅₀O₈ 818.3302, found 818.3341.

4.4. Graphitic ribbon (6)

A solution of the methoxy-substituted sexiphenyl (**4**) (22 mg, $\sim 0.027 \text{ mmol}$) in CH₂Cl₂ was degassed with bubbling N₂ (20 min) and cooled to 0 °C. MoCl₅ (29 mg, 0.110 mmol) was added to the solution. The reaction mixture was stirred and allowed to warm to room temperature overnight. The solution was washed with H₂O (3×10 mL). The solvent was removed under reduced pressure to leave a crude residue (25 mg), which was partially analyzed by MALDI-TOF-MS. The residue was redissolved in toluene and stored at -20 °C. A few small crystals formed, and single-crystal X-ray crystallography and MALDI-TOF-MS were performed. Insufficient material was available for full characterization.

4.5. 2-Bromo-2'-trimethylsilyl-4,4',5,5'tetramethoxybiphenyl (7)

To a stirring solution of 2 (5.54 g, 12.8 mmol) in THF (50 mL), *n*-BuLi (4.6 mL, 12.8 mmol; 2.75 M in hexane) was added dropwise at -78 °C. The reaction was immediately quenched with trimethylsilyl chloride (3.24 mL, 25.6 mmol) and allowed to warm to room temperature. The solution was diluted with water (30 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×25 mL). The organic layers were combined and dried under vacuum. The product was recrystallized from absolute ethanol, filtered, and dried under vacuum to yield white crystals (4.28 g, 70%). Mp 129-130 °C. ¹H NMR (CDCl₃, 500 MHz): δ 7.08 (s, 1H), 7.06 (s, 1H), 6.79 (s, 1H), 6.68 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 0.03 (s, 9H). ¹³C NMR (CDCl₃, 126 MHz): δ 149.0, 149.0, 147.77, 147.57, 141.1, 136.4, 130.0, 116.8, 115.1, 115.0, 114.8, 114.0, 56.4, 56.2, 56.05, 56.0, 0.551. UV-vis (CH_2Cl_2, nm) : λ_{max} 230 ($-\log \varepsilon$ 4.32), 290. EIMS: m/z 426, 331. Anal. Calcd for C₁₉H₂₅BrO₄Si: C, 53.65; H, 5.95. Found: C, 53.81; H, 5.93.

4.6. 4,4',4,",4"",5,5',5"",5""-Octamethoxy-2,2" - bistrimethylsilyl-1,1',2',1",2'',1"" -quaterphenyl (8)

A solution of **7** (3.00 g, 7.05 mmol), 2,2'-bipyridyl (2.91 g, 10.5 mmol), 1,5-cyclooctadiene (1.3 mL, 10.6 mmol), dry DMF (60 mL), and dry toluene (200 mL) was heated to 80 °C. Bis(1,5-cyclooctadiene)nickel(0) (2.91 g, 10.6 mmol) was added and the reaction mixture was stirred overnight. The reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with toluene (3×50 ml). The organic layers were combined, and the solvent was removed under vacuum. The remaining material was purified by column chromatography (hexane/ethyl acetate 80:20). The solvent was removed under vacuum to yield white crystals (0.97 g, 40%). Mp 204 °C. ¹H

NMR (CDCl₃, 500 MHz): δ 7.11 (s, 2H), 6.80 (s, 2H), 6.43 (s, 2H), 6.35 (s, 2H), 3.90 (s, 6H), 3.84 (s, 6H), 3.50 (s, 6H), 3.38 (s, 6H), 0.00 (18H). ¹³C NMR (CDCl₃, 126 MHz): δ 149.1, 147.3 (two peaks, coincidentally degenerate), 147.28, 146.6, 142.0, 135.0, 131.0, 130.6, 117.6, 115.2, 114.1, 56.3, 56.0, 55.6, 55.5, 31.1, 1.2. UV–vis (CH₂Cl₂, nm): λ_{max} 231 (–log ε 4.63), 297. MALDI-TOF-MS: *m*/*z* 690.22. Anal. Calcd for C₃₈H₅₀O₈Si₂: C, 66.05; H, 7.29. Found: C, 65.79; H, 7.19.

4.7. 3,3^{*m*},4,4′,4′′,4^{*m*},5′,5″-Octamethoxy-1,1′,2′,1′′,2″,1^{*m*}-quaterphenyl (9)

A solution of the bistrimethylsilyl ortho-quaterphenyl (8) (82 mg, 0.012 mmol) in CH₂Cl₂ (5 mL) at 0 °C was treated with tetrafluoroboric acid (HBF₄) (0.10 mL of a 54 wt % solution in diethyl ether, 0.6 mmol) and the reaction mixture was stirred for 2 h at this temperature, then guenched with saturated agueous NaHCO₃. The mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried with anhydrous Na₂SO₄, filtered, and dried under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate/hexanes (50:50). The solvent was removed to yield white crystals (62 mg, 96%). Mp 154-156 °C (lit.²² 219 °C). ¹H and ¹³C NMR match the literature.²² ¹H NMR (CDCl₃, 500 MHz): δ 6.94 (s, 2H), 6.71 (s, 2H), 6.57 (d, J=8 Hz, 2H), 6.22 (dd, J=8/2 Hz, 2H), 6.18 (d, J=2 Hz, 2H), 3.90 (s, 6H), 3.89 (s, 6H), 3.84 (s, 6H), 3.53 (s, 6H). 13 C NMR (CDCl₃, 126 MHz): δ 148.3. 148.1, 148.0, 147.4, 133.9, 133.7, 132.3, 121.5, 114.8, 112.9, 112.6, 110.6, 56.4, 56.2, 56.0, 55.6. UV–vis (CH₂Cl₂, nm): λ_{max} 230 (–log ε 4.62), 292 (-log ε 4.30). MADLI-TOF-MS: *m*/*z* 546.15.

4.8. 1,2,5,6,9,10,12,13-Octamethoxydibenzo-[*fg*,*op*]naphthacene (11)

The octamethoxy-*ortho*-quaterphenyl (**9**) (181 mg, 0.332 mmol) was dissolved in CH₂Cl₂ (10 mL). A solution of PIFA (285 mg, 0.66 mmol) and BF₃·Et₂O (0.166 mL, 1.33 mmol) was added at 25 °C. After 24 h of stirring, the reaction mixture was diluted with degassed MeOH. Aqueous NaOH (2.5 M, 5 mL) was added, and the mixture was extracted with methylene chloride (3×5 mL). The combined organic layers were combined and purified by flash chromatography on alumina (ethyl acetate/methylene chloride 10:90), and the solvent was removed under vacuum (85 mg, 47% yield). NOE and crystallography established connectivity. ¹H NMR (CD₂Cl₂, 500 MHz): δ 9.31 (s, 2H), 8.17 (s, 2H), 7.98 (s, 2H), 4.21 (s, 6H), 4.13 (s, 6H), 4.07 (s, 6H), 3.94 (s, 6H). ¹³C NMR (CD₂Cl₂, 126 MHz): δ 152.2, 150.4, 149.0, 145.9, 125.3, 125.1, 124.2, 123.1, 119.9, 110.2, 105.6, 105.1, 60.9, 56.9, 56.6, 56.1. Mp 219–220 °C.

4.9. 4,5-Dibromo-ortho-xylene (15)

Prepared according to the literature.³⁶ The material was recrystallized to give 106 g of **15** (0.402 mol, 53% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.38 (s, 2H), 2.20 (s, 6H).

4.10. 2,2'-Dibromo-4,4',5,5'-tetramethylbiphenyl (16)

Prepared according to the literature.²⁰ The product was recrystallized from absolute ethanol, filtered, and dried under vacuum to yield white crystals (15.33 g, 71% yield). ¹H NMR (CDCl₃, 500 MHz): δ 7.43 (s, 2H), 6.99 (s, 2H), 2.29 (s, 6H), 2.42 (s, 6H). GC–MS: *m/z* 368.

4.11. 2-Bromo-2'-trimethylsilyl-4,4',5,5'tetramethylbiphenyl (17)

To a stirring solution of 2,2'-dibromo-4,4',5,5'-tetramethylbiphenyl (10.338 g, 0.028 mol) in THF (100 mL), *n*-BuLi (22.9 mL, 0.031 mol, 2.50 M in hexane) was added dropwise at -78 °C. The

reaction was immediately quenched with trimethylsilyl chloride (4.10 mL, 0.032 mol) and allowed to warm to room temperature. The solution was diluted with water (60 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×50 mL). The organic layers were combined and dried under vacuum. The product was recrystallized from methanol, filtered, and dried under vacuum to yield white crystals (8.728 g, 86%). Mp 104–105 °C. ¹H NMR (CDCl₃, 500 MHz): δ 7.40 (s, 1H), 7.37 (s, 1H), 7.00 (s, 1H), 6.94 (s, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H), 0.00 (s, 9H). ¹³C NMR (CDCl₃, 126 MHz): δ 145.5, 141.8, 137.6, 137.0, 136.2, 135.6, 135.0, 135.0, 133.4, 133.1, 131.5, 121.1, 19.9, 19.8, 19.5, 19.3, 0.4. UV–vis (EtOH, nm): λ_{max} 208 (–log ε 4.86), 282, 287. GC–MS: *m/z* 347. Anal. Calcd for C₁₉H₂₅BrSi: C, 63.15; H, 6.97. Found: C, 63.21; H, 6.90.

4.12. 4,4',4,'',4''',5,5',5'',5''' -Octamethyl-2,2''' -bistrimethylsilyl-1,1',2',1'',2'',1'''-quaterphenyl (18)

A solution of 17 (7.73 g, 21.4 mmol), 2,2'-bipyridyl (4.81 g, 32.1 mmol), 1,5-cyclooctadiene (3.9 mL, 31.8 mmol), dry DMF (85 mL), and dry toluene (315 mL) was heated to 80 °C. Bis(1,5cyclooctadiene)nickel(0) (7.66 g, 32.1 mmol) was added and the reaction mixture was stirred overnight. The reaction mixture was diluted with water and the organic layer was separated. The aqueous layer was extracted with toluene (3×100 mL). The organic lavers were combined and the solvent was removed under vacuum. The solid was recrystallized from EtOH twice to yield 3.11 g(51%) of **18**. Mp 180–181 °C. ¹H NMR (CDCl₃, 500 MHz): δ 7.30 (s, 2H), 6.83 (s. 2H), 6.74 (s, 2H), 6.62 (s, 2H), 2.21 (s, 6H), 2.16 (s, 6H), 2.03 (s, 6H). 2.00 (s, 6H), 0.00 (18H). ¹³C NMR (DMSO, 126 MHz): δ 144.9, 139.3, 135.3, 135.3, 135.2, 134.7, 132.6, 132.3, 132.3, 132.2, 131.9, 130.5, 18.4, 18.1, 17.8, 17.6, 0.2. UV-vis (EtOH, nm): λ_{max} 212 (-log ε 4.27), 265 (shoulder), 287 (shoulder). GC-MS: m/z 563. Anal. Calcd for C₃₈H₅₀Si₂: C, 81.07; H, 8.95. Found: C, 80.86; H, 9.03.

4.13. 3,3^{*m*},4,4^{*i*},4^{*m*},5^{*i*},5^{*n*}-Octamethyl-1,1^{*i*},2^{*i*},1^{*n*},2^{*n*},1^{*m*}-quaterphenyl (19)

A solution of the bistrimethylsilyl ortho-quaterphenyl (18) (2.414 g, 4.296 mmol) in CH₂Cl₂ (40 mL) at 0 °C was treated with tetrafluoroboric acid (HBF₄) (7.4 mL of a 54 wt % solution in diethyl ether, 44 mmol) and the reaction mixture was stirred and allowed to slowly rise to room temperature overnight, then quenched with saturated aqueous NaHCO₃. The mixture was diluted with CH₂Cl₂ and washed with saturated NaHCO3 $(3 \times 20 \text{ mL})$ and water $(3 \times 20 \text{ mL})$. The solvent was removed under vacuum, and the remaining solid was recrystallized from EtOH. The recrystallized solid was collected and washed with hexane on a vacuum filter and dried under vacuum to yield white crystals (1.410 g, 78.5%). Mp 211 °C. ¹H NMR (CDCl₃, 500 MHz): δ 7.21 (s, 2H), 6.88 (s, 2H), 6.70 (d, *J*=7 Hz, 2H), 6.32 (dd, *J*=7/2 Hz, 2H), 6.21 (d, *J*=2 Hz, 2H), 2.33 (s, 6H), 2.28 (s, 6H), 2.18 (s, 6H), 2.02 (s, 6H). ¹³C NMR (CDCl₃, 126 MHz): § 139.0, 138.7, 137.8, 135.5, 135.3, 135.1, 133.5, 133.1, 131.2, 130.5, 128.4, 126.7, 19.7, 19.6, 19.6, 19.5. UV-vis (EtOH, nm): λ_{max} 209, 238 (-log ε 4.46), 260 (shoulder). GC-MS: m/z 419. Anal. Calcd for C₃₂H₃₄: C, 91.81; H, 8.19. Found: C, 91.71; H, 8.38.

4.14. 1,2,5,6,9,10,12,13-Octamethyldibenzo[fg,op]naphthacene (20)

The octamethyl-*ortho*-quaterphenyl (**19**) (43.5 mg, 0.104 mmol) was dissolved in CH_2Cl_2 (35 mL). $MoCl_5$ (80.0 mg, 0.208 mmol) was added to the stirring solution at 0 °C under nitrogen, and the reaction mixture was allowed to warm slowly to room temperature overnight. The reaction was quenched by filtration through silica gel in CH_2Cl_2 . The solvent was removed under vacuum, and the

product was purified by column chromatography, followed by normal-phase semi-preparative HPLC (chloroform/hexane 20:80). The solvent was removed, and the remaining material was finally recrystallized from chloroform. The product was then dried under vacuum (14.3 mg, 33% yield). Mp 255–285 °C (decomposed). ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.46 (s, 2H), 8.42 (s, 2H), 8.16 (s, 2H), 3.01 (s, 6H), 2.72 (s, 6H), 2.56 (s, 6H), 2.48 (s, 6H). ¹³C NMR (CD₂Cl₂. 126 MHz): δ 136.3, 135.8, 134.1, 130.5, 130.4, 130.0, 130.0, 127.9, 126.0, 124.3, 124.1, 122.4, 21.9, 21.4, 20.5, 20.4. UV-vis (CH₂Cl₂, nm): λ_{max} 288 (-log ε 4.64), 231, 300. HRMS (EI⁺): m/z calcd for C₃₂H₃₀ 414.2348, found 414.2348.

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Supplementary data

MALDI-TOF mass spectra of **3**, **4**, and **6**, ¹H NMR spectrum of **4**, ¹H and ¹³C NMR spectra of **7**, **8**, **17**, **18**, **19**, and **20**, 1D ¹H NMR NOESY of 11 and 20, thermal ellipsoid plots of 8, 9 and 19, and a table of crystallographic parameters for 7, 8, 9, and 19. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 697840 (6), 697841 (7), 697842 (8), 697843 (9), 697837 (11). 697838 (**19**), and 697839 (**20**). Copies of the data can be obtained. free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.105.

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