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Generation of Synthetic Equivalents of Benzdiynes from Benzobisoxadisiloles

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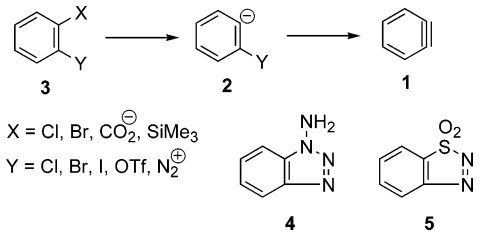
Linear and angular benzobisoxadisiloles **14** and **16** can serve as the precursors for stepwise generations of the syntetic equivalents of 1,4- and 1,3-benzdiynes. Benzynes generated were trapped as [4+2] cycloaddition products. Two identical or different rings can be fused to the benzdiyne equivalents. Highly substituted arenes were obtained by removing the oxygen bridges from the furan adducts. The synthesis of naphthoxadisilole **28**, which can serve as the precursor of 2,3-naphthyne, is also described.

Introduction

Benzyne **1** is one of the most important reactive intermediates and synthons in organic chemistry. Since its discovery,[1] benzyne has been subjected to theoretical studies as well as many practical applications.[2] For example, it has been widely used as the building block of many aromatic based molecular architectures. Benzyne is also a versatile intermediate in natural product synthesis.[3]

There are many known methods for benzyne generation.[4] Basically, these methods can be divided into two main categories. The first set of methods involves β-elimination of β-carbanion **2** or its equivalent generated from various precursors (**3**) (Scheme 1). The second set of approaches relies on *retro*-cycloaddition processes of benzo-fused heterocycles such as **4** and **5**. A recent addition to the first category reported by Kitamura involves the use of (phenyl)[*o*-(trimethylsilyl)phenyl]-iodonium triflate (**7**).[4a,5] The iodonium compound **7** is synthesized through phenyliodination of bis(trimethylsilyl)benzene **6**, which is prepared from 1,2-dichlorobenzene via Grignard type reaction in HMPA (Scheme 2). Upon treatment with fluoride ion, benzyne can be generated in good yield under very mild conditions. Since its publication, this highly attractive and efficient hypervalent iodine approach to benzyne generation has caught the attention of many research groups. Various applications, particularly in the syntheses of theoretically interesting molecules and functional materials, were reported.[6] To avoid the uses of carcinogenic HMPA, the same research team also introduced (phenyl)[2-(hydroxydimethylsilyl)phenyliodonium triflate (**9**) as an alternate benzyne procursor.[7] Iodonium triflate **9** is prepared from 1,3-dihydro-1,1,3,3-tetramethyl-2,1,3-benzoxadisilole (**8**) which can be synthesized from 1,2-bromobenzene without the use of HMPA (Scheme 2).

SCHEME 1



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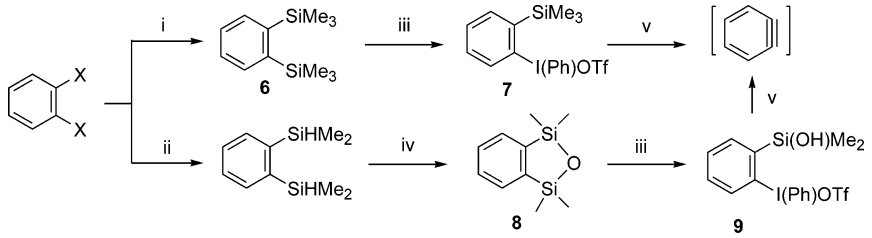
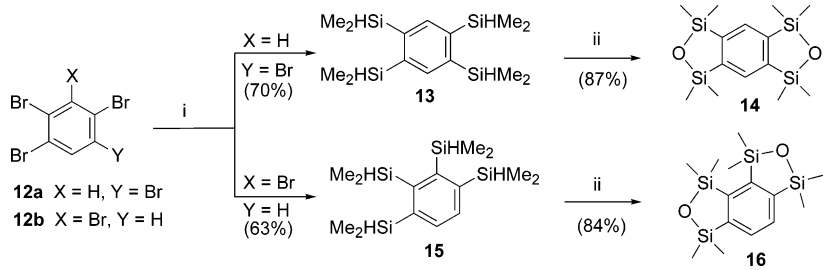
SCHEME 2[a]



[a] Reagents and conditions: (i) X = Cl, Mg/HMPA, Me_3SiCl; (ii) X = Br, Mg/THF, Me_2HSiCl; (iii) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0 °C to room temperature; (iv) (a) NaOMe/MeOH, rt, (b) H_2O, 50 °C;(v) *n*-Bu_4NF/THF.

SCHEME 3[a]



[a] Reagents and conditions: (i) Mg/Me_2HSiCl, THF, reflux; (ii) (a) NaOMe/MeOH, rt, (b) H_2O, 50 °C.

1,3- and 1,4-benzdiynes (tetradehydrobenzenes, **10** and **11**) are extraordinary labile owing to the high ring strain that arises from the two triple bonds in a benzene ring. They have been subjected to theoretical calculations[8] and have been detected in gas phase or by means of matrix isolation techniques.[9] However, they have not been established as intermediates in solution chemistry. Synthetic equivalents leading to the stepwise generation of these benzdiynes as well as the metal complexes of **11** have been reported in the literature.[2b,10] Herein, we describe our results of the generation of benzynes from linear and angular benzobisoxadisiloles (**14** and **16**) via the corresponding iodonium triflate intermediates, which can be viewed as the synthetic equivalents of benzdiynes **10** and **11**.

10 **11**

Results and Discussion

Preparation of Linear and Angular Benzobisoxadisiloles, 1,3,5,7-Tetradihydro-1,1,3,3,5,5,7,7-octamethylbenzo[1,2-*c*:4,5-*c*′]bis[1,2,5]oxadisilole (14) and 1,3,6,8-Tetradihydro-1,1,3,3,6,6,8,8-octamethyl-benzo-[1,2-*c*:3,4-*c*′]bis[1,2,5]oxadisilole (16). The preparation of linear and angular benzobisoxadisiloles **14** and **16** based on modified literature procedures is outlined in Scheme 3.[11,12] The tetrasilylated compounds **13** and **15** can be readily prepared from the tetrabromobenzenes **12a** and **12b**, respectively, via Grignard-type reactions with chlorodimethylsilane. 1,2,4,5-Tetrabromobenzene (**12a**) is commercially available. The isomeric 1,2,3,4-tetrabromobenzene (**12b)** was prepared by regioselective debromination of hexabromobenzene with excess hydrazine hydrate.[13] Upon treatment with sodium methoxide and warming in water, the tetra(dimethylsilyl)benzenes (**13** and **15**) cyclized into the corresponding linear and angular benzobisoxadisiloles **14** and **16** as crystalline solids in 87% and 84% yields, respectively. The structure of **14**[14] is also confirmed by X-ray analyses.

Stepwise Generation of Benzyne from Linear Benzobisoxadisilole 14 and the Trapping Experiments. With the linear benzobisoxadisilole **14** in hand, we were ready to explore its benzyne generation chemistry. In situ phenyliodination of **14** with a 1.5:3 mixture of phenyliodium diacetate ($PhI(OAc)_2$) and trifluoromethanesulfonic acid (TfOH) took place readily at room temperature in CH_2Cl_2 (Scheme 4). Without isolation of the ring-opened iodination intermediate **17**, benzyne **18** could be generated in situ upon treatment with a 1.0 M

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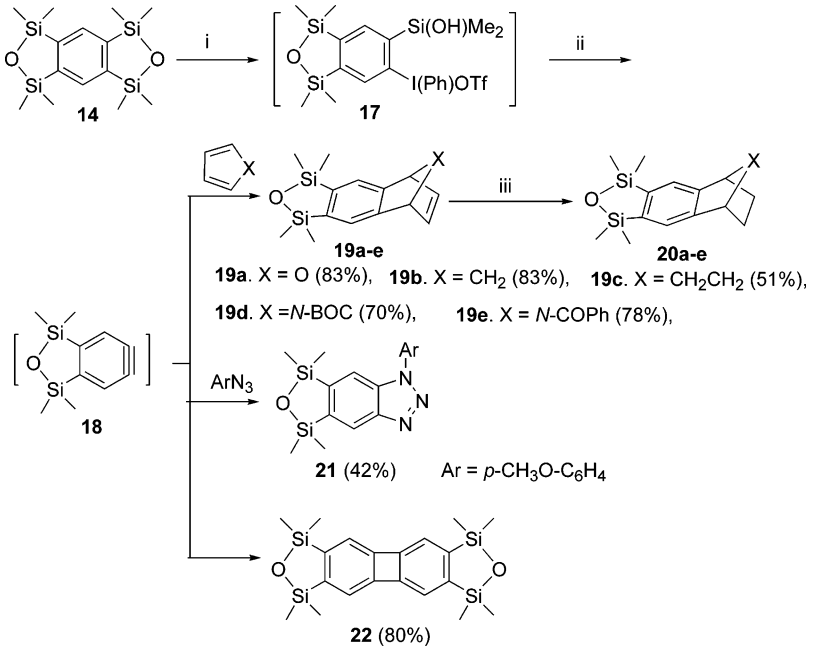
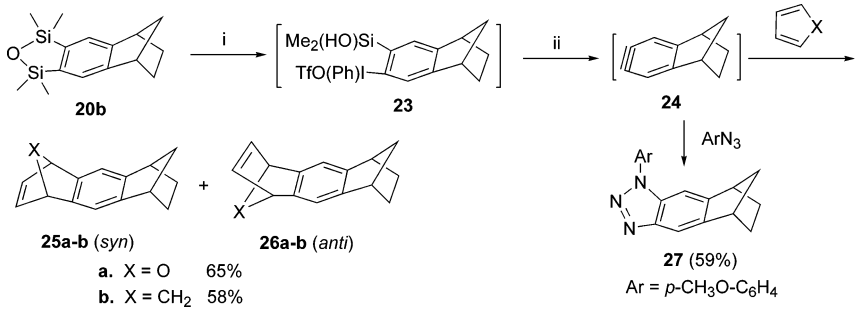
SCHEME 4[a]



[a] Reagents and conditions: (i) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0 °C to room temperature; (ii) *n*-Bu_4NF/THF, *i*-Pr_2NH, rt; (iii) H_2, Pd/C, rt.

SCHEME 5[a]



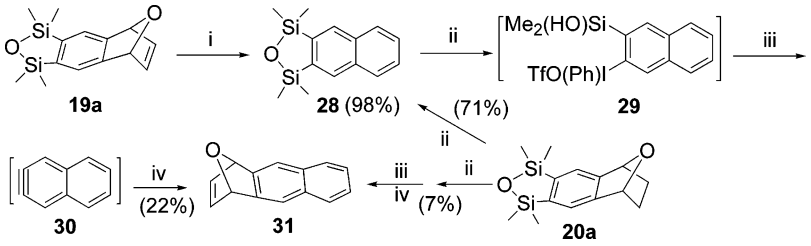
[a] Reagents and conditions: (i) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0 °C to room temperature; (ii) *n*-Bu_4NF/THF, *i*-Pr_2NH, rt.

THF solution of tetrabutylammonium fluoride (*n*-Bu_4NF). It is worth mentioning that despite the use of excess phenyliodination reagents ($PhI(OAc)_2$/TfOH), only one of the oxadisilole rings of **14** could be opened. There was no sign for the formation of the bis-hypervalent iodine intermediate from **14**. Trapping experiments were carried out with various carbocyclic and heterocyclic dienes (furan, cyclopentadiene, 1,3-cyclohexadiene, *N*-*tert*-butoxycarbonylpyrrole, and *N*-benzoylpyrrole) as well as aryl azide with good isolated yields of the cycloadducts from **14**. The cycloadducts could be easily hydrogenated to **20a**−**e** in 85% to 95% yields. We also observed that addition of 2 equiv of diisopropylamine to the reaction mixture improved the overall transformation yields. In the furan trapping experiment, a trace amount of dimer **22** was detected. Therefore, we ran a control experiment without the trapping agents. In the absence of the trapping agents, dimer **22** was isolated in 80% yield. In addition to the spectroscopic evidence, structures of selected compounds (**19a**, **19d**, **20b**, **20c**, and **22**) were also confirmed by X-ray analyses.

Hydrogenated product **20b** was further treated with excess $PhI(OAc)_2$/TfOH (1.5:3) in CH_2Cl_2 at room temperature (Scheme 5). Without isolation of the intermediate, the homogeneous reaction mixture was treated with *n*-Bu_4NF to generate benzyne **24**. In the presence of excess trapping diene (furan or cyclopentadiene), cycloadducts **25a/26a** and **25b/26b** were obtained as mixtures of syn and anti isomers in 65% and 58% yields (three steps from **20b**), respectively. From the ^1H NMR spectrum, the ratio of **25a** and **26a** was estimated to be 1:1. The syn isomer of the furan cycloadduct **25a** could be purified by recrystallization. Its structure is confirmed by X-ray analyses. Benzyne **24** could also be trapped with *p*-methoxylphenyl azide as adduct **27** in 59% yield. The overall transformation of **14** to **25/26** and **27** demonstrated that the linear benzobisoxadisilole **14** can be viewed as a synthetic equivalent for the stepwise generation of 1,4-benzdiyne (**11**). Two different rings can be selectively fused to the benzene ring in a stepwise manner.

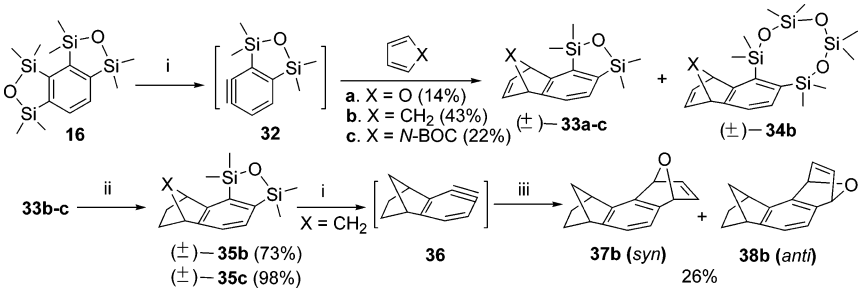
Further Manipulation of 19a and Synthesis of a 2,3-Naphthyne Precursor. A previously unknown 2,3-naphthoxadisilole **28** can be prepared by deoxygenation

SCHEME 6[a]



[a] Reagents and conditions: (i) $TiCl_4$, $LiAlH_4$, Et_3N-THF, reflux; (ii) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0 °C to room temperature; (iii) *n*-Bu_4NF/THF, i-Pr_2NH, rt; (iv) furan.

SCHEME 7[a]



[a] Reagents and conditions: (i) (a) $PhI(OAc)_2$, TfOH, CH_2Cl_2, 0 °C to room temperature, (b) *n*-Bu_4NF/THF, *i*-Pr_2NH, rt; (iii) furan.

of **19a** with $TiCl_4-LiAlH_4-Et_3N$ in THF[15] in almost quantitative yield. Obviously, naphthoxadisilole **28** can be used as a 2,3-naphthyne (**30**) precursor. Compound **28** reacted readily under the phenyliodination conditions and opened up to **29** at room temperature. Without isolation of **29**, treatment of **29** with *n*-Bu_4NF in the presence of excess furan afforded the cycloadduct **31** in 22% yield.

The hydrogenated compound **20a** (obtained from **19a** in 90% yield) was also subjected to the phenyliodination followed by fluoride-induced benzyne generation and furan trapping. A complicated mixture resulted with only a trace amount (7%) of **31**. It is possible that under these conditions **20a** was first transformed to **28**, which then served as the naphthyne precursor leading to **31**. To support this speculation, phenyliodination of **20a** was worked up after 1 h, and a good yield (71%) of naphthoxadisilole **28** was obtained.

Stepwise Generation of Benzyne from Angular Benzobisoxadisilole 16 and the Trapping Experiments. The ring-opening phenyliodination of the angular benzobisoxadisilole **16** was found to be slower than its linear counterpart **14**. Without isolation of the intermediate, the homogeneous reaction mixture was treated with *n*-Bu_4NF and *i*-Pr_2NH to afford benzyne **32**, which was trapped with furan, cyclopentadiene, and *N*-*t*-BOC-pyrrole (Scheme 7) to afford the racemic cycloadducts (**33a**−**c**). The yields of the racemic cycloadducts were relatively lower as compared with similar reactions of the linear series. In addition to **33**, a trace amount of a less polar byproduct was also detected from the reaction mixtures of the trapping experiments. However, no dimeric product similar to **22** was detected. This less polar byproduct **34b** was isolated by column chromatography. Compound **34b** whose structure is confirmed by X-ray analysis contains a macrocyclic siloxy ring. Cycloadducts **33b** and **33c** were saturated via hydrogenation reactions. To further demonstrate that **16** can serve as a 1,3-benzdiyne equivalent, the saturated cyclopentadiene adduct **35b** was subjected to another cycle of phenyliodination ($PhI(OAc)_2$/TfOH, 1.5:3) and *n*-Bu_4NF treatment followed by furan trapping. Benzyne **36** generated was successfully trapped with furan as an inseparable mixture of syn and anti adducts (**37b/38b**). It is worth nothing that without any plane of symmetry, benzyne **36** can exist in two chiral forms. Of course, under the present reaction conditions, the angular bis-annulated benzo-fused cycloadducts obtained are in racemic forms.

In summary, we have demonstrated that benzynes **18**, **24**, **32**, and **36** could be generated from the linear benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]oxadisilole (**14**) and angular benzo[1,2-*c*:3,4-*c*′]bis[1,2,5]oxadisilole (**16**), respectively. They were trapped as the [4+2] cycloadducts. In the case of **18**, cyclodimerization was also observed. These linear and angular benzobisoxadisiloles (**14** and **16**) can also be viewed as the synthetic equivalents for the stepwise generations of 1,3- and 1,4-benzdiynes. The synthesis of naphthoxadisilole **28**, which can serve as the precursor of 2,3-naphthyne **30**, is also reported.

Experimental Section

1,2,3,4-Tetrabromobenzene (12b). Hexabromobenzene (5.00 g, 9.07 mmol), hydrazine hydrate (100 mL), and ethanol (100 mL) were heated under reflux for 24 h. The cooled reaction mixture was poured into water. Filtered crude product was dissolved in *n*-hexane. The *n*-hexane solution was washed with water, then dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with *n*-hexane as eluent. Compound **12b** (2.00 g, 5.08 mmol) was obtained in 56% yield

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as white powder. Mp 62−63 °C (lit.[13] mp 62−63 °C); ^{1}H NMR (400 MHz) δ 7.45 (s, 2H); ^{13}C NMR (101 MHz) δ 124.8, 129.1, 132.7.

1,2,4,5-Tetrakis(dimethylsilyl)benzene (13). 1,2,4,5-Tetrabromobenzene (3.93 g, 10.00 mol) and chlorodimethylsilane (8.90 mL, 0.08 mol) were added to magnesium (1.94 g, 0.08 mol) in 20 mL of THF. The mixture was refluxed at 85−90 °C for 5 h. After the tetrabromobenzene disappeared (monitored by TLC), the solvent was evaporated. The mixture was extracted with Soxhlet extractor by *n*-hexane at 95−100 °C. The extract was concentrated under reduced pressure, then purified by column chromatography on silica gel with *n*-hexane as eluent. Compound **13** (2.18 g, 7.01 mmol) was obtained in 70% yield as white powder. Mp 64 °C (lit.[11] mp 66 °C); ^{1}H NMR (400 MHz) δ 0.37 (d, J = 3.6 Hz, 24H), 4.63−4.67 (m, 4H), 7.75 (s, 2H); ^{13}C NMR (101 MHz) δ −2.7, 139.5, 144.0; IR (KBr, cm^{-1}) 2958, 2146, 2105, 1251, 1093; MS m/z 311 (M$^+$).

1,3,5,7-Tetradihydro-1,1,3,3,5,5,7,7-octamethylbenzo-[1,2-*c*:4,5-*c*′]bis[1,2,5]oxadisilole (14). A solution of sodium methoxide in methanol (1.84 g of sodium, 0.08 mol; 30 mL of methanol) was added to 1,2,4,5-tetrakis(dimethylsilyl)benzene **13** (3.11 g, 10.00 mol). The mixture was stirred under N_2 for 1 h at room temperature. The reaction mixture was added to 1 mL of H_2O and the sooution was warmed to 45−50 °C. After **13** disappeared (monitored by TLC), the crude product was filtered and redissolved in EtOAc. After being washed with H_2O and dried over $MgSO_4$, the EtOAc solution was concentrated under reduced pressure. Recrystallization from CH_2Cl_2/*n*-hexane mixture afforded **14** (2.94 g, 8.70 mmol) in 87% yield. Mp 243−245 °C (lit.[11] mp 244 °C); ^{1}H NMR (400 MHz) δ 0.38 (s, 12H), 7.80 (s, 2H); ^{13}C NMR (101 MHz) δ 1.1, 133.5, 148.5; IR (KBr, cm^{-1}) 2959, 1248, 1105; MS m/z 338 (M$^+$); HRMS for $C_{14}H_{26}O_2Si_4$ [M + Na]$^+$ calcd 361.0907, found 361.0896. Recrystallization from CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

1,2,3,4-Tetrakis(dimethylsilyl)benzene (15). 1,2,3,4-Tetrabromobenzene (3.93 g, 10.0 mol) and chlorodimethylsilane (8.90 mL, 0.08 mol) were added to magnesium (1.94 g, 0.08 mol) in 20 mL of THF. The mixture was refluxed at 85−90 °C for 5 h. After tetrabromobenzene disappeared (monitored by TLC), the solvent was evaporated. The mixture was extracted with Soxhlet extractor by *n*-hexane at 95−100 °C. The extract was concentrated under reduced pressure and then purified by column chromatography on silica gel with *n*-hexane as eluent. Compound **15** (1.96 g, 6.30 mmol) was obtained in 63% yield as a colorless oil. ^{1}H NMR (400 MHz) δ 0.37 (d, J = 4.0 Hz, 12H), 0.48 (d, J = 4.0 Hz, 12H), 4.68−4.72 (m, 2H), 4.80−4.84 (m, 2H), 7.58 (s, 2H); ^{13}C NMR (101 MHz) δ −1.9, −0.6, 134.2, 146.3, 152.1.

1,3,6,8-Tetradihydro-1,1,3,3,6,6,8,8-octamethylbenzo-[1,2-*c*:3,4-*c*′]bis[1,2,5]oxadisilole (16). A solution of sodium methoxide in methanol (1.84 g of sodium, 0.08 mol; 30 mL of methanol) was added to 1,2,3,4-tetrakis(dimethylsilyl)benzene (**15**) (3.11 g, 10.00 mol). The mixture was stirred under N_2 for 1 h at room temperature. The reaction mixture was added to 1 mL of H_2O and the solution was warmed to 45−50 °C. After **15** disappeared (monitored by TLC), the crude product was filtered and redissolved in EtOAc. After being washed with H_2O and dried over $MgSO_4$, the EtOAc solution was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with 2% EtOAc in petroleum ether (60−80 °C) as eluent. Compound **16** (2.84 g, 8.40 mmol) was obtained in 84% yield. Mp 90−92 °C (lit.[11] mp 89−91 °C); ^{1}H NMR (400 MHz) δ 0.38 (s, 12H), 0.43 (s, 12H), 7.62 (s, 2H); ^{13}C NMR (101 MHz) δ 1.0, 2.2, 131.1, 149.3, 151.9; MS m/z 338 (M$^+$); HRMS for $C_{14}H_{26}O_2Si_4$ [M + H]$^+$ calcd 339.1088, found 339.1104.

Adducts 19a−c from Benzyne Generated from Benzobisoxadisilole 14. Trifluoromethanesulfonic acid (0.27 mL, 3.0 mmol) was added with a syringe to a stirred solution of phenyliodium diacetate (493 mg, 1.5 mmol in 10 mL of CH_2Cl_2) at 0 °C. The mixture was stirred under N_2 for 1 h at 0 °C and for 2 h at room temperature. The clear yellow solution was cooled again to 0 °C followed by dropwise addition of a cold (0 °C) solution of the benzobisoxadisilole **14** (338 mg, 1.0 mmol in 5 mL of CH_2Cl_2). The mixture was stirred for 0.5 h at 0 °C and warmed to room temperature. After the benzobisoxadisilole **14** disappeared (monitored by TLC), diisopropylamine (0.35 mL, 2.5 mmol) and the diene (furan, cyclopentadiene, 1,3-cyclohexadiene, *N*-*tert*-butoxycarbonylpyrrole, or *N*-benzoylpyrrole, 10 mmol) were added followed by a solution of tetrabutylammonium fluoride (2.5 mL, 2.5 mmol, 1.0 M solution in THF). After a further 10 min, water was added and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent.

1,3,5,8-Tetrahydro-1,1,3,3-tetramethyl-5,8-epoxynaphth-[2,3-*c*][1,2,5]oxadisilole (19a): 79% yield (216 mg, 0.79 mmol), mp 121−123 °C; ^{1}H NMR (400 MHz) δ 0.32 (s, 6H), 0.33 (s, 6H), 5.70 (s, 2H), 7.03 (s, 2H), 7.42 (s, 2H); ^{13}C NMR (101 MHz) δ 1.0, 1.1, 82.2, 122.2, 142.7, 145.9, 150.1; IR (KBr, cm^{-1}) 3038, 2957, 1277, 1252, 1098; MS m/z 274 (M$^+$); HRMS for $C_{14}H_{18}O_2Si_2$:[M]$^+$ calcd 274.0835, found 274.0845. Anal. Calcd for $C_{14}H_{18}O_2Si_2$: C, 61.25; H, 6.62. Found: C, 61.17; H, 6.75. Recrystallization from CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

1,3,5,8-Tetrahydro-1,1,3,3-tetramethyl-5,8-methanonaphth[2,3-*c*][1,2,5]oxadisilole (19b): 83% yield (226 mg, 0.83 mmol), mp 64−65 °C; ^{1}H NMR (400 MHz) δ 0.31 (s, 6H), 0.33 (s, 6H), 2.25−2.27 (m, 1H), 2.33−2.35 (m, 1H), 3.88−3.89 (m, 2H), 6.80 (t, J = 2.0 Hz, 2H), 7.40 (s, 2H); ^{13}C NMR (101 MHz) δ 1.1, 1.2, 50.2, 69.7, 123.7, 142.9, 144.6, 153.2; IR (KBr, cm^{-1}) 3065, 2962, 1565, 1250, 1100; MS m/z 272 (M$^+$); HRMS for $C_{15}H_{20}OSi_2$ [M + H]$^+$ calcd 273.113, found 273.1144. Anal. Calcd for $C_{15}H_{20}OSi_2$: C, 66.10; H, 7.41. Found: C, 65.94; H, 7.31.

1,3,5,8-Tetrahydro-1,1,3,3-tetramethyl-5,8-ethanonaphth[2,3-*c*][1,2,5]oxadisilole (19c): 51% yield (146 mg, 0.51 mmol), mp 122−124 °C; ^{1}H NMR (400 MHz) δ 0.31 (s, 6H), 0.36 (s, 6H), 1.48−1.50 (m, 2H), 1.57−1.60 (m, 2H), 3.96−3.97 (m, 2H), 6.51−6.53 (m, 2H), 7.36 (s, 2H); ^{13}C NMR (101 MHz) δ 1.1, 1.2, 25.6, 40.5, 125.0, 135.1, 144.6, 145.5; IR (KBr, cm^{-1}) 2962, 1653, 1249, 1112; MS m/z 286 (M$^+$); HRMS for $C_{16}H_{22}OSi_2$ [M + H]$^+$ calcd 287.1287, found 287.1292.

***N*-*tert*-Butoxycarbonyl-1,3,5,8-tetrahydro-1,1,3,3-tetramethyl-5,8-iminenaphth[2,3-*c*][1,2,5]oxadisilole (19d):** 70% yield (261 mg, 0.70 mmol), mp 156−157 °C; ^{1}H NMR (400 MHz) δ 0.30 (s, 6H), 0.32 (s, 6H), 1.38 (s, 9H), 5.47−5.53 (m, 2H), 6.95−7.02 (m, 2H), 7.42 (s, 2H); ^{13}C NMR (101 MHz) δ 0.96, 1.04, 28.1, 66.7, 80.7, 122.4, 123.0, 142.1, 143.5, 145.7, 149.2, 155.0; IR (KBr, cm^{-1}) 3000, 2978, 1713, 1367, 1254, 1163, 1102; HRMS for $C_{19}H_{27}NO_3Si_2$ [M + Na]$^+$ calcd 396.1427, found 396.1445. Anal. Calcd for $C_{19}H_{27}NO_3Si_2$: C, 61.08; H, 7.28. Found: C, 61.14; H, 7.23. Recrystallization from CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

***N*-Benzoyl-1,3,5,8-tetrahydro-1,1,3,3-tetramethyl-5,8-iminenaphth[2,3-*c*][1,2,5]oxadisilole (19e):** 78% yield (294 mg, 0.78 mmol), mp 160−162 °C; ^{1}H NMR (400 MHz) δ 0.31−0.36 (m, 12H), 5.56 (s 1H), 6.02 (s, 1H), 6.89−6.91 (m, 1H), 7.18−7.20 (m, 1H), 7.36 (s, 1H), 7.41−7.56 (m, 6H); ^{13}C NMR (101 MHz) δ 1.0, 63.7, 68.1, 122.2, 123.4, 128.0, 128.5, 131.0, 134.4, 142.1, 144.8, 146.0, 146.3, 148.9, 149.0, 167.5; IR (KBr, cm^{-1}) 2957, 1646, 1365, 1252, 1184, 1104; HRMS for $C_{21}H_{23}NO_2Si_2$ [M + Na]$^+$ calcd 400.1165, found 400.1155. Anal. Calcd for $C_{21}H_{23}NO_2Si_2$: C, 66.80; H, 6.14. Found: C, 66.62; H, 6.21.

Hydrogenated Products (20a−e). Palladium on activated carbon (Pd/C, 10%) was added to a stirred solution of **19a−e** (1.0 mmol) in 10 mL of ethanol. The mixture was stirred under H_2 at room temperature for 2 h. After filtering off the palladium catalyst, the organic solvent was concentrated under

reduced pressure. The residue was purified by column chromatography on silica gel by using a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent.

1,3,5,6,7,8-Hexahydro-1,1,3,3-tetramethyl-5,8-epoxynaphth[2,3-*c*][1,2,5]oxadisilole (20a): 90% yield (248 mg, 0.9 mmol), mp 122−124 °C; ^{1}H NMR (400 MHz) δ 0.32 (s, 6H), 0.36 (s, 6H), 1.43−1.44 (m, 2H), 2.07−2.10 (m, 2H), 5.39−5.40 (m, 2H), 7.41 (s, 2H); ^{13}C NMR (101 MHz) δ 1.0, 1.2, 26.4, 78.8, 120.9, 146.7, 146.9; IR (KBr, cm^{-1}) 3011, 2952, 1275, 1249, 1097; MS *m*/*z* 276 (M^+). Anal. Calcd for $C_{14}H_{20}O_2Si_2$: C, 60.82; H, 7.29. Found: C, 60.84; H, 7.34; HRMS for $C_{14}H_{20}O_2Si_2$ [M + Na]$^+$ calcd 299.0899, found 299.0889.

1,3,5,6,7,8-Hexahydro-1,1,3,3-tetramethyl-5,8-methanonaphth[2,3-*c*][1,2,5]oxadisilole (20b): 90% yield (247 mg, 0.90 mmol), mp 71−72 °C; ^{1}H NMR (400 MHz) δ 0.33 (s, 6H), 0.34 (s, 6H), 1.20−1.22 (m, 2H), 1.52−1.54 (m, 1H), 1.75−1.77 (m, 1H), 1.91−1.93 (m, 2H), 3.34 (s, 2H), 7.34 (s, 2H); ^{13}C NMR (101 MHz) δ 1.1, 1.3, 26.9, 43.6, 49.1, 122.8, 145.2, 149.5; IR (KBr, cm^{-1}) 3053, 2965, 1253, 1099; MS *m*/*z* 274 (M^+); HRMS for $C_{15}H_{22}OSi_2$ [M + H]$^+$ calcd 275.1287, found 275.1293. Anal. Calcd for $C_{15}H_{22}OSi_2$: C, 65.63; H, 8.08. Found: C, 65.43; H, 8.08. Recrystallization from a CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

1,3,5,6,7,8-Hexahydro-1,1,3,3-tetramethyl-5,8-ethanonaphth[2,3-*c*][1,2,5]oxadisilole (20c): 96% yield (276 mg, 0.96 mmol), mp 148−150 °C; ^{1}H NMR (400 MHz) δ 0.36 (s, 12H), 1.42 (d, J = 8.0 Hz, 4H), 1.80 (d, J = 8.0 Hz, 4H), 2.99 (S, 2H), 7.33 (s, 2H); ^{13}C NMR (101 MHz) δ 1.2, 26.2, 34.3, 126.1, 145.1, 145.4; IR (KBr, cm^{-1}) 2942, 1248, 1110; MS *m*/*z* 288 (M^+); HRMS for $C_{16}H_{24}OSi_2$ [M + H]$^+$ calcd 289.1443, found 289.1448. Recrystallization from a CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

***N*-*tert*-Butoxycarbonyl-1,3,5,6,7,8-hexahydro-1,1,3,3-tetramethyl-5,8-iminenaphth[2,3-*c*][1,2,5]-oxadisilole (20d):** 98% yield (368 mg, 0.98 mmol), mp 180−182 °C; ^{1}H NMR (400 MHz) δ 0.31 (s, 6H), 0.35 (s, 6H), 1.34−1.36 (m, 2H), 1.41 (s, 9H), 2.11 (b, 2H), 5.11 (s, 2H), 7.41 (s, 2H); ^{13}C NMR (101 MHz) δ 1.0, 1.2, 26.6, 28.2, 60.9, 80.0, 121.5, 145.9, 146.4, 154.9; IR (KBr, cm^{-1}) 2958, 1695, 1366, 1250, 1161, 1100; HRMS for $C_{19}H_{29}NO_3Si_2$ [M + Na]$^+$ calcd 398.1583, found 398.1578.

***N*-Benzoyl-1,3,5,6,7,8-hexahydro-1,1,3,3-tetramethyl-5,8-iminenaphth[2,3-*c*][1,2,5]oxadisilole (20e):** 85% yield (322 mg, 0.85 mmol), mp 173−175 °C; ^{1}H NMR (400 MHz) δ 0.34 (s, 6H), 0.35 (s, 6H), 1.41−1.43 (m, 2H), 2.11 (s, 1H), 2.30 (s, 1H), 5.11 (s 1H), 5.66 (s, 1H), 7.34 (s, 1H), 7.40−7.56 (m, 6H); ^{13}C NMR (101 MHz) δ 1.0, 1.1, 25.6, 28.1, 58.6, 63.2, 121.1, 122.0, 128.0, 128.4, 130.8, 135.1, 145.2, 145.8, 146.8, 147.1, 168.1; IR (KBr, cm^{-1}) 2954, 1635, 1387, 1251, 1111, 1097; HRMS for $C_{21}H_{25}NO_2Si_2$ [M + Na]$^+$ calcd 402.1321, found 402.1303.

Adducts 21 with Benzyne Generated from Benzobisoxadisilole 14. The trapping experiment of benzobisoxadisilole **14** described above was repeated with *p*-methoxyphenyl azide as the trapping agent. The crude product was purified by column chromatography on silica gel with 2% EtOAc in petroleum ether (60−80 °C) as eluent to afford adduct **21** (149 mg, 0.42 mmol) in 42% yield. Mp 113−115 °C; ^{1}H NMR (270 MHz) δ 0.41 (s, 6H), 0.44 (s, 6H), 3.90 (s, 3H), 7.11−7.14 (m, 2H), 7.64−7.68 (m, 2H), 7.82 (d, J = 1.1 Hz, 1H), 8.30 (d, J = 1.1 Hz, 1H); ^{13}C NMR (68 MHz) δ 1.27, 1.30, 55.6, 112.6, 114.9, 123.0, 124.7, 129.7, 133.7, 142.5, 147.37, 147.42, 159.7; IR (KBr, cm^{-1}) 2953, 1515, 1462, 1254, 1083; HRMS for $C_{17}H_{21}N_3O_2Si_2$ [M + H]$^+$ calcd 356.1250, found 356.1241. Anal. Calcd for $C_{17}H_{21}N_3O_2Si_2$: C, 57.43; H, 5.95. Found: C, 57.28; H, 5.99.

Dimer 22. The trapping experiment of benzobisoxadisilole **14** described above was repeated without the trapping agent. The crude product was purified by column chromatography on silica gel with 2% EtOAc in petroleum ether (60−80 °C) as eluent to afford adduct **22** (165 mg 0.40 mmol) in 80% yield. Mp 255−257 °C; ^{1}H NMR (400 MHz) δ 0.32 (s, 24H), 6.83 (s, 4H); ^{13}C NMR (101 MHz) δ 0.8, 118.8, 149.7, 152.6; IR (KBr, cm^{-1}) 2955, 1256, 1075; MS *m*/*z* 412 (M^+); HRMS for $C_{20}H_{28}O_2Si_4$ [M]$^+$ calcd 412.1166, found 412.1164. Recrystallization from a CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

Adducts 25a,b/26a,b (Syn and Anti) from Compound 20b. The trapping experiment of arene **20b** described above was repeated with the diene (furan or cyclopentadiene) as the trapping agents. The crude product was purified by column chromatography on silica gel by using a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford the mixture **25a**,**b** and **26a**,**b**.

1,4,5,6,7,8-Hexahydro-1,4-epoxy-5,8-methanoanthracene (25a/26a) (syn and anti): 65% yield (137 mg, 0.65 mmol); ^{1}H NMR (400 MHz) δ 1.05−1.12 (m, 2H), 1.45−1.48 (m, 1H), 1.69−1.73 (m, 1H), 1.83−1.86 (m, 2H), 3.24−3.25 (m, 2H), 5.62 (s, 1H), 5.65 (s, 1H), 7.0 (s, 2H), 7.07 (s, 1H), 7.09 (s, 1H); ^{13}C NMR (101 MHz) δ 26.8 (26.9), 43.5 (43.6), 49.5 (50.0), 82.4 (82.6), 113.9 (114.1), 143.3 (145.1), 145.2, 146.7 (146.8); IR (KBr, cm^{-1}) 3005, 2974, 2961, 1562, 1278; MS *m*/*z* 210 (M^+); HRMS for $C_{15}H_{14}O$ [M + Na]$^+$ calcd 233.0942, found 233.0942. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.56; H, 6.70. The syn isomer was recrystallized from *n*-hexane. Mp 125−127 °C. The X-ray structure was determined.

1,4,5,6,7,8-Hexahydro-1,4,5,8-dimethanoanthracene (25b/26b) (syn and anti): 58% yield (121 mg, 0.58 mmol); ^{1}H NMR (400 MHz) δ 1.09−1.14 (m, 2H), 1.43−1.48 (m, 1H), 1.69−1.74 (m, 1H), 1.81−1.86 (m, 2H), 2.20−2.31 (m, 2H), 3.22−3.23 (m, 2H), 3.80−3.82 (m, 2H), 6.78−6.79 (m, 2H), 7.04 (s, 1H), 7.05 (s, 1H); ^{13}C NMR (101 MHz) δ 27.1 (27.2), 43.6, 49.5, 50.0 (50.3), 70.4 (70.9), 114.9 (115.0), 143.2 (143.4), 144.1, 149.1; IR (KBr, cm^{-1}) 2961, 1559; MS *m*/*z* 208 (M^+); HRMS for $C_{16}H_{16}$ [M + Na]$^+$ calcd 231.1149, found 231.1155.

Adducts 27 from Compound 20b. The trapping experiment of **20b** described above was repeated with *p*-methoxyphenyl azide as the trapping agent. The crude product was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford **27** (172 mg, 0.59 mmol) in 59% yield as colorless oil. ^{1}H NMR (400 MHz) δ 1.21−1.27 (m, 2H), 1.62−1.65 (m, 1H), 1.80−1.83 (m, 1H), 1.96−1.98 (m, 2H), 3.42 (s, 1H), 3.49 (s, 1H), 3.88 (s 3H), 7.06−7.09 (m, 2H), 7.37 (s, 1H), 7.61−7.63 (m, 2H), 7.76 (s, 1H); ^{13}C NMR (101 MHz) δ 27.3, 27.4, 43.2, 43.8, 48.6, 55.6, 101.6, 110.6, 114.7, 124.6, 130.2, 131.9, 145.4, 146.0, 150.4, 159.5; IR (KBr, cm^{-1}) 2964, 1518, 1456, 1253; HRMS for $C_{18}H_{17}N_3O$ [M + H]$^+$ calcd 292.1449, found 292.1452. Anal. Calcd for $C_{18}H_{17}N_3O$: C, 74.20; H, 5.88. Found: C, 74.30; H, 5.86.

1,3-Dihydro-1,1,3,3-tetramethylnaphth[2,3-*c*][1,2,5]-oxadisilole (28). To a suspension of $LiAlH_4$ (0.38 g, 10 mmol) in 10 mL of anhydrous THF was carefully added $TiCl_4$ (3.1 mL, 28 mmol) followed by Et_3N (5.0 mL, 36 mmol) at 0 °C under N_2. The mixture was stirred and refluxed for 30 min and then allowed to warm to room temperature. A solution of **19a** (0.22 g, 0.8 mmol) in 10 mL of anhydrous THF was added. The mixture was refluxed for 24 h and then was poured into crushed ice (20 g) containing 20 mL of 1 N HCl. The resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as the eluent to afford product **28** (202 mg, 0.78 mmol) in 98% yield. Mp 110−112 °C; ^{1}H NMR (400 MHz) δ 0.43 (s, 6H), 7.50−7.52 (AA′BB′, m, 2H), 7.85−7.87 (AA′BB′, m, 2H), 8.07 (s, 2H); ^{13}C NMR (101 MHz) δ 1.0, 1.2, 126.5, 128.2, 131.2, 133.6, 143.7; IR (KBr, cm^{-1}) 3024, 2955, 1251, 1093; MS *m*/*z* 258 (M^+); HRMS for $C_{14}H_{18}OSi_2$ [M]$^+$ calcd 258.0896, found 258.0897. Anal. Calcd for $C_{14}H_{18}OSi_2$: C, 65.04; H, 7.03. Found: C, 64.69; H, 6.88.

1,4-Dihydro-1,4-epoxyanthracene (31). Trifluoromethanesulfonic acid (0.05 mL, 0.6 mmol) was added with a syringe to a stirred solution of phenyliodium diacetate (98.6 mg, 0.3 mmol in 3 mL of CH_2Cl_2) at 0 °C. The mixture was stirred under N_2

for 1 h at 0 °C and for 2 h at room temperature. The clear yellow solution was cooled again to 0 °C followed by dropwise addition of a cold (0 °C) solution of the naphthoxadisilole **28** (51.6 mg, 0.2 mmol in 3 mL of CH_2Cl_2). The mixture was stirred for 0.5 h at 0 °C and warmed to room temperature. After the naphthoxadisilole **28** disappeared (monitored by TLC), diisopropylamine (0.07 mL, 0.5 mmol) and furan (0.15 mL, 2.0 mmol) were added followed by a solution of tetrabutylammonium fluoride (0.5 mL, 0.5 mmol, 1.0 M solution in THF). After a further 10 min, water was added and the resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford product **31** (8.54 mg, 0.044 mmol) in 22% yield. Mp 152−154 °C (lit.[16] mp 163−164 °C); ^{1}H NMR (400 MHz) δ 5.82 (m, 2H), 6.98 (m, 2H), 7.45−7.46 (m, 2H), 7.60 (m, 2H), 7.72−7.74 (m, 2H); ^{13}C NMR (101 MHz) δ 81.7, 118.6, 126.1, 128.1, 131.9, 141.6, 144.1; IR (KBr, cm^{-1}) 3032, 2957, 1605, 1284; MS *m*/*z* 194 (M^+); HRMS for $C_{14}H_{10}O$ $[M + Na]^+$ calcd 217.0629, found 217.0628.

Adducts 33a−c (Racemic) from Benzyne Generated from Benzobisoxadisilole 16. Trifluoromethanesulfonic acid (0.27 mL, 3.0 mmol) was added with a syringe to a stirred solution of (diacetoxyiodo)benzene (493 mg, 1.5 mmol in 10 mL of CH_2Cl_2) at 0 °C. The mixture was stirred under N_2 for 1 h at 0 °C and for 2 h at room temperature. The clear yellow solution was cooled again to 0 °C and then treated dropwise with a cold (0 °C) solution of arene **16** (338 mg, 1.0 mmol in 5 mL of CH_2Cl_2). The mixture was stirred for 0.5 h at 0 °C and warmed to room temperature. After benzobisoxadisilole **16** disappeared (monitored by TLC), the mixture was cooled to −50 °C. Diisopropylamine (0.35 mL, 2.5 mmol) and the diene (furan, cyclopentadiene, or *N*-*tert*-butoxycarbonylpyrrole, 10 mmol) were added followed by a solution of tetrabutylammonium fluoride (2.5 mL, 2.5 mmol, 1.0 M solution in THF). The reaction mixture was kept at −50 °C for 1 h, then gradually warmed to room temperature and stirred for 2 h. Water was added and the resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford the adducts **33a−c**.

1,3,6,9-Tetrahydro-1,1,3,3-tetramethyl-6,9-epoxynaphth-[2,3-*c*][1,2,5]oxadisilole (33a): 14% yield (38.4 mg, 0.14 mmol), mp 88−90 °C; ^{1}H NMR (270 MHz) δ 0.33−0.34 (m, 9H), 0.46 (s, 3H), 5.63−5.64 (m, 1H), 5.74−5.75 (m, 1H), 6.98−7.01 (m, 1H), 7.04−7.06 (m, 1H), 7.19 (d, J = 7.0 Hz, 1H), 7.33 (d, J = 7.0 Hz, 1H); ^{13}C NMR (101 MHz) δ 1.2, 1.3, 1.8, 82.2, 82.4, 121.3, 124.9, 128.0, 142.6, 143.2, 144.1, 149.1, 152.5; IR (KBr, cm^{-1}) 2958, 1274, 1254, 1099; MS *m*/*z* 274 (M^+); HRMS for $C_{14}H_{18}O_2Si_2$ $[M + Na]^+$ calcd 297.0743, found 297.0732.

1,3,6,9-Tetrahydro-1,1,3,3-tetramethyl-6,9-methano-naphth[2,3-*c*][1,2,5]oxadisilole (33b): 43% yield (117 mg, 0.43 mmol), mp 68−70 °C; ^{1}H NMR (400 MHz) δ 0.33 (s, 3H), 0.36 (s, 3H), 0.37 (s, 3H), 0.45 (s, 3H), 2.29−2.31 (m, 1H), 2.36−2.39 (m, 1H), 3.84−3.93 (m, 2H), 6.77−6.84 (m, 2H), 7.18 (d, J = 7.2 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz) δ 1.2, 1.3, 1.40, 1.43, 50.1, 50.6, 70.2, 122.9, 127.3, 139.5, 142.7, 143.1, 143.3, 152.2, 155.5; IR (KBr, cm^{-1}) 2959, 1563, 1258, 1092; MS *m*/*z* 272 (M^+); HRMS for $C_{15}H_{20}OSi_2$ $[M + Na]^+$ calcd 295.095, found 295.0946.

***N*-*tert*-Butoxycarbonyl-1,3,6,9-tetrahydro-1,1,3,3-tetramethyl-6,9-iminenaphth[2,3-*c*][1,2,5]oxadisilole (33c):** 22% yield (82.1 mg, 0.22 mmol), oil; ^{1}H NMR (400 MHz) δ 0.31 (s, 3H), 0.32 (m, 3H), 0.35 (m, 3H), 0.48 (s, 3H), 1.37 (s, 9H), 5.35−5.52 (m, 2H), 6.91−7.00 (m, 2H), 7.17 (d, J = 7.2 Hz, 1H), 7.30−7.35 (m, 1H); ^{13}C NMR (101 MHz) δ 1.1, 1.2, 1.5, 28.1, 66.7, 80.7, 122.4, 124.9, 128.0, 142.1, 142.7, 143.4, 144.1, 148.3; IR (neat, cm^{-1}) 2965, 1711, 1368, 1253, 1167, 1085; HRMS for $C_{19}H_{27}NO_3Si_2$ $[M + Na]^+$ calcd 396.1427, found 396.1441.

Compound 34b: mp 70−72 °C, ^{1}H NMR (400 MHz) δ 0.09 (s, 3H), 0.12 (s, 3H), 0.19 (s, 3H), 0.22 (s, 3H), 0.42 (s, 3H), 0.45 (s, 3H), 0.47 (s, 3H), 0.50 (s, 3H), 2.15−2.17 (m, 1H), 2.28−2.31 (m, 1H), 3.86−3.87 (m, 1H), 4.09−4.10 (m, 1H), 6.76−6.77 (m, 1H), 6.79−6.81 (m, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz) δ 1.5, 1.6, 3.4, 3.5, 4.0, 4.1, 49.8, 51.4, 68.1, 121.6, 131.6, 137.9, 139.6, 142.4, 143.2, 151.8, 157.2; IR (KBr, cm^{-1}) 2959, 1571, 1259, 1092; MS *m*/*z* 420 (M^+); HRMS for $C_{19}H_{32}O_3Si_4$ $[M + Na]^+$ calcd 443.1326, found 443.1323. Recrystallization from CH_2Cl_2/*n*-hexane mixture afforded the crystal sample for X-ray structure determination.

Hydrogenated Products 35b,c. Palladium on activated carbon (Pd/C, 10%) was added to a stirred solution of **33b**,**c** (1.0 mmol) in 10 mL of ethanol. The mixture was stirred under H_2 at room temperature for 2 h. The palladium catalyst was filtered and the organic solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford the adducts **35b**,**c**.

1,3,6,7,8,9-Hexahydro-1,1,3,3-tetramethyl-6,9-methanonaphth[2,3-*c*][1,2,5]oxadisilole (35b): 73% yield (200 mg, 0.73 mmol), oil; ^{1}H NMR (400 MHz) δ 0.33 (s, 3H), 0.34 (s, 3H), 0.36 (s, 3H), 0.43 (s, 3H), 1.13−1.18 (m, 2H), 1.52−1.55 (m, 1H), 1.77−1.80 (m, 1H), 1.91−1.95 (m, 2H), 3.29−3.38 (m, 2H), 7.22−7.24 (m, 1H), 7.29−7.30 (m, 1H); ^{13}C NMR (101 MHz) δ 1.2, 1.32, 1.34, 26.67, 26.68, 43.4, 43.9, 49.2, 121.7, 128.5, 138.8, 144.7, 148.3, 151.4; IR (neat, cm^{-1}) 2960, 1258, 1094; MS *m*/*z* 274 (M^+); HRMS for $C_{15}H_{22}OSi_2$ $[M + Na]^+$ calcd 297.1106, found 297.1099.

***N*-*tert*-Butoxycarbonyl-1,3,6,7,8,9-hexahydro-1,1,3,3-tetramethyl-6,9-iminenaphth[2,3-*c*][1,2,5]oxadisilole (35c):** 98% yield (368 mg, 0.98 mmol), oil; ^{1}H NMR (270 MHz) δ 0.33 (s, 3H), 0.35 (s, 3H), 0.37 (s, 3H), 0.47 (s, 3H), 1.24−1.30 (m, 2H), 1.40 (s, 9H), 2.12−2.15 (m, 2H), 5.02 (s, 1H), 5.14 (s, 1H), 7.28−7.36 (m, 2H); ^{13}C NMR (68 MHz) δ 1.2, 1.3, 1.4, 1.5, 26.6, 28.3, 60.8, 80.0, 120.5, 129.2, 145.0, 145.9, 147.7, 155.1; IR (neat, cm^{-1}) 2981, 2951, 1703, 1366, 1248, 1158, 1103; HRMS for $C_{19}H_{29}NO_3Si_2$ $[M + Na]^+$ calcd 398.1583, found 398.1586.

1,4,7,8,9,10-Hexahydro-1,4-epoxy-7,10-methanophenanthrene (37b/38b) (Syn and Anti). Trifluoromethanesulfonic acid (0.05 mL, 0.6 mmol) was added with a syringe to a stirred solution of phenyliodium diacetate (98.6 mg, 0.3 mmol in 2 mL of CH_2Cl_2) at 0 °C. The mixture was stirred under N_2 for 1 h at 0 °C and for 2 h at room temperature. The clear yellow solution was cooled again to 0 °C and followed by dropwise addition of a cold (0 °C) solution of **35b** (54.8 mg, 0.2 mmol in 2 mL of CH_2Cl_2). The mixture was stirred for 0.5 h at 0 °C and warmed to room temperature. After **35b** disappeared (monitored by TLC), diisopropylamine (0.07 mL, 0.5 mmol) and furan (0.15 mL, 2.0 mmol) were added followed by a solution of tetrabutylammonium fluoride (0.50 mL, 0.5 mmol, 1.0 M solution in THF). After a further 2 h, water was added and the resulting mixture was extracted with CH_2Cl_2. The organic extract was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with a gradient of 2−5% EtOAc in petroleum ether (60−80 °C) as eluent to afford the mixture **37b**/**38b** (syn and anti) (10.9 mg, 0.052 mmol) in 26% yield as a colorless oil. ^{1}H NMR (400 MHz) δ 1.07−1.18 (m, 2H), 1.50−1.54 (m, 1H), 1.66−1.77 (m, 1H), 1.86−1.90 (m, 2H), 3.30 (s, 1H), 3.41(d, J = 13.2 Hz, 1H), 5.65−5.67 (m, 1H), 5.75−5.79 (m, 1H), 6.71−6.74 (m, 1H), 6.94−7.02 (m, 3H); ^{13}C NMR (101 MHz) δ 26.9 (27.0), 29.7 41.2 (41.4), 43.2, 48.3 (48.9), 80.7, 82.2 (82.5), 115.6 (115.8), 117.0 (117.3), 139.4, 140.1 (142.1), 142.1 (142.3), 142.9 (143.2), 145.5 (145.7), 145.97

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(146.00); IR (neat, cm^{-1}) 2963, 1559, 1280; MS *m*/*z* 210 (M^+); HRMS for $C_{15}H_{14}O$ $[M + H]^+$ calcd 211.1122, found 211.1123.

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Supporting Information Available: Carbon and proton spectra for reaction products, and X-ray crystallographic structures and data for **14**, **19a**, **19d**, **20b**, **20c**, **22**, **25a**, and **34b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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