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Oxadisilole Fused Triptycene and Extended Triptycene: Precursors of Triptycyne and Extended Triptycyne

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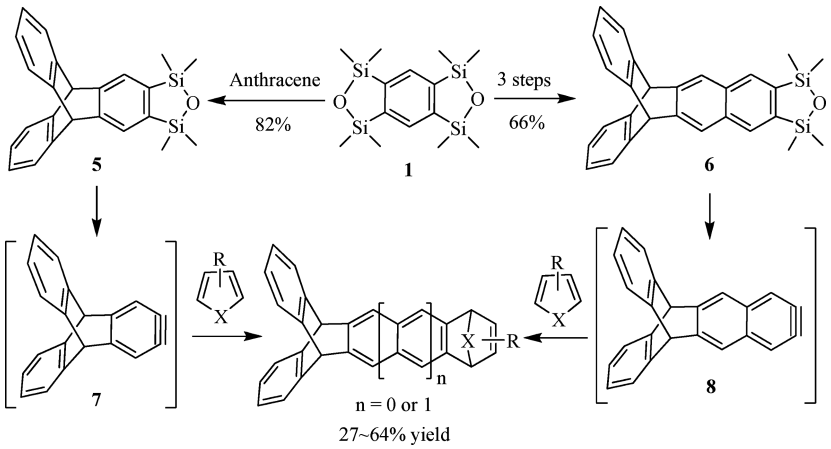
Received August 16, 2010



With benzobisoxadisilole **1** as a 1,4-benzdiyne equivalent, oxadisilole fused triptycene **5** and extended triptycene **6** were synthesized. Triptycenes **5** and **6** are new precursors of triptycyne **7** and extended triptycyne **8** respectively via the phenyliodination/fluoride induced elimination protocol. Using these two arynes, a series of triptycene derivatives were synthesized.

Introduction

Iptycenes refer to a large family of compounds with unique [2.2.2] bicyclic bridgehead ring systems built up by a number of arene units. A prefix is used to further describe the number of independent arenes.[1] Triptycene, 9,10-dihydro-9,10[1′,2′]-benzenoanthracene, is the most basic structure of the iptycene family. It is named after "the triptych of antiquity" which was a book with three leaves hinged on a common axis.[2] Because of its unique geometrical, structural and electronic characters such as rigidity, bulkiness, nonplanarity, and π-electron richness, triptycene has been used as key building block of molecules and polymers of both fundamental and practical importance.[3] A wide range of research fields including intramolecular charge transfer,[4] atropisomerism studies,[5] ligands design,[6] host−guest chemistry,[7] supramolecular chemistry,[8] molecular gear devices,[9] and pharmaceutical

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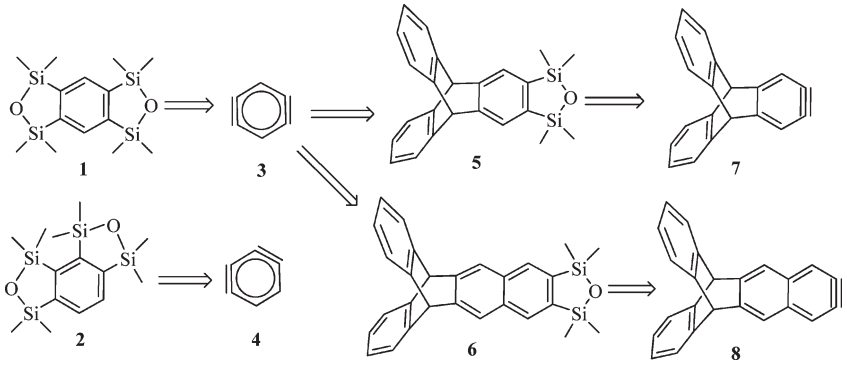
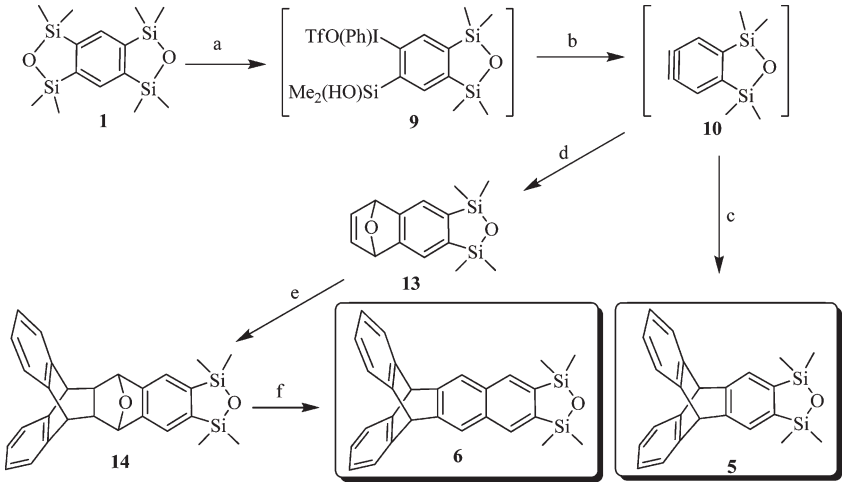
Published on Web 10/14/2010 DOI: 10.1021/jo1016025

SCHEME 1. Linear and Angular Benzobisoxadisilole as Synthetic Equivalents of 1,4- and 1,3-Benzdiyne



SCHEME 2. Synthesis of Oxadisilole Fused Triptycene 5 and Extended Triptycene 6



Reagents and conditions: (a) $PhI(OAc)_2$/TfOH, CH_2Cl_2. 0 °C-rt, 3 h; (b) KF/TBAF, rt; (c) anthracene, 10 h, 82% from **1**; (d) furan, 1 h, 88% from **1**; (e) anthracene, H_2O, microwave, 135 °C, 40 min, 93%; (f) $AcOH/Ac_2O$, 130 °C, 12 h, 81%.

designs[10] have incorporated various triptycene structures into their studies.

Recently, we demonstrated that linear and angular benzobisoxadisilole **1** and **2** can serve as the precursors for stepwise generation of 1,4- and 1,3-benzdiyne **3** and **4** (Scheme 1).[11] This chemistry has been applied to the synthesis of acenes,[12] acenequinones,[13]and benzo[*b*]triphenylenes[14] with interesting photophysical properties. Isolatable oxadisilole fused isobenzofuran[12] and isoindole[15] were also prepared and used as building blocks for functional materials. Among the known methods to prepare triptycenes, Diels−Alder cycloaddition is the most widely used approach.[3a] In this paper, we would like to report our efforts in using linear benzobisoxadisilole **1** as a synthon for the preparation of oxadisilole fused triptycene **5** and extended triptycene **6**. Subsequently, these oxadisilole fused triptycenes serve as new precursors of triptycyne **7** and extended triptycyne **8** (Scheme 1).

Results and Discussion

Preparation of Oxadisilole Fused Triptycene and Extended Triptycene. The opening of one oxadisilole ring of **1** to benzyne **10** via intermediate **9** proceeded smoothly under the phenyliodination/fluoride induced elimination protocol.[11,16] Trapping of oxadisilole fused benzyne **10** with anthracene should afford one of the target molecules, oxadisilole fused triptycene **5** (Scheme 2). However, with 4 equiv of anthracene and tetrabutylammonium fluoride (TBAF, 2 equiv) as the fluoride source, the desired product **5** could only be isolated in 52% yield (Table 1, entry 1). Two major side products, dimer **11**[11b] and amine addition product **12**, were obtained with total yield of 30%. In our previous studies of trapping benzyne **10** with other dienes, we observed that addition of a

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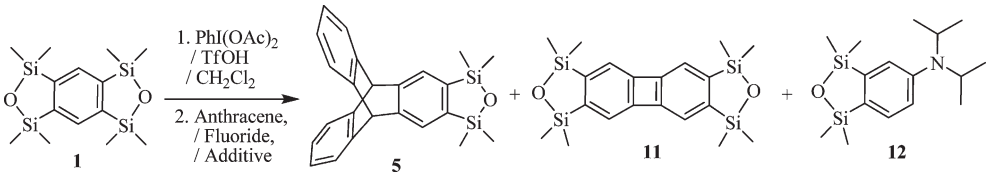
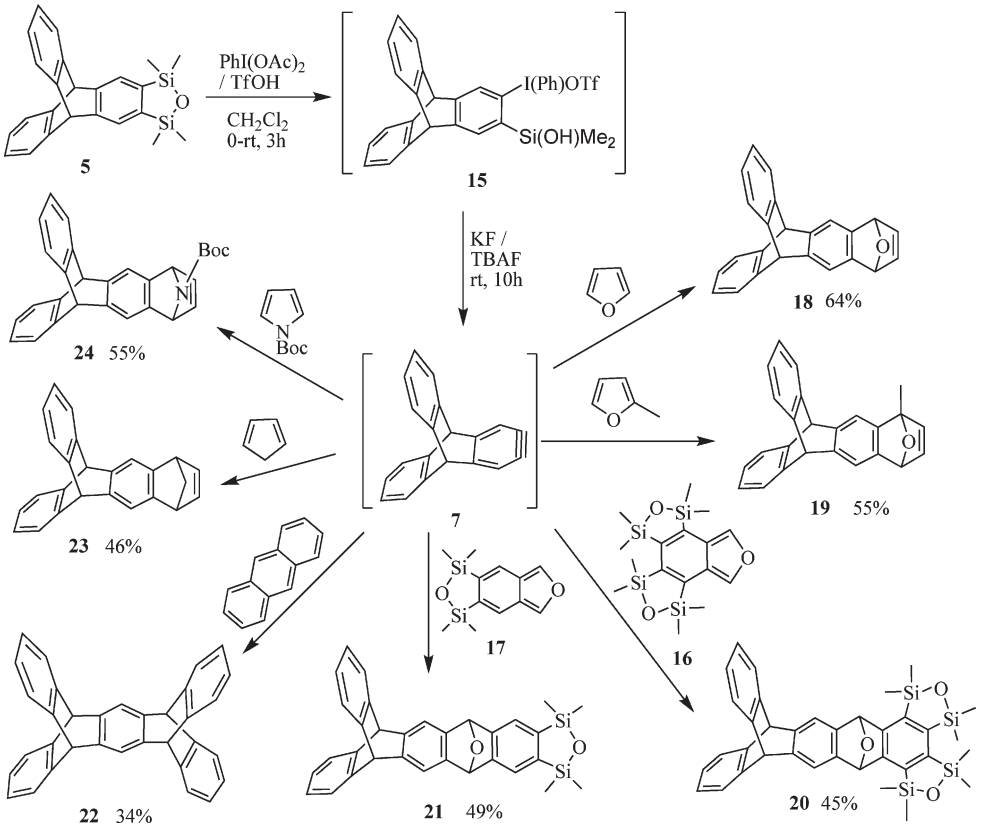
TABLE 1. Effect of Different Fluoride Sources in the Preparation of 5



			yields of products		
entry	fluoride source	additive	**5** (%)	**11** (%)	**12** (%)
1	TBAF (2 equiv)	$NH(i\text{-}Pr)_2$ (3 equiv)	52	19	11
2	TBAF (2 equiv)	–	56	22	–
3	KF (4 equiv)	–	71	< 5	–
4	CsF (4 equiv)	–	73	< 5	–
5	KF (4 equiv)/TBAF (0.3 equiv)	–	82	< 5	–

SCHEME 3. Triptycyne 7 Generation and Trapping Experiments



bulky amine such as diisopropylamine was beneficial to the reactions.[11,17] However, in the present case, omission of the amine did not affect the yield of **5** but dimer **11** was still the major side product (entry 2). Since anthracene is not a very reactive diene as compared to those we used previously, we believed that the rate of the formation of benzyne **10** should be slowed down so that the chance of the dimerization could be reduced. The use of KF as the fluoride source, which is only slightly soluble in CH_2Cl_2, solved the problem. The yield of oxadisilole fused triptycene **5** jumped to 71% with less than 5% of the dimer **11** (entry 3). Using CsF afforded a similar result with 73% yield of **5** (entry 4). Finally, we found that combination of KF and a catalytic amount of TBAF gave the best result. Oxadisilole fused triptycene **5** could be obtained in 82% isolated yield in a three-step reaction from **1** (entry 5).

For the extended triptycene series, furan was used to provide the extra four carbons (Scheme 2).[18] Reacting benzyne **10** with furan afforded oxadisilole fused endoxide **13** in 88% overall yield

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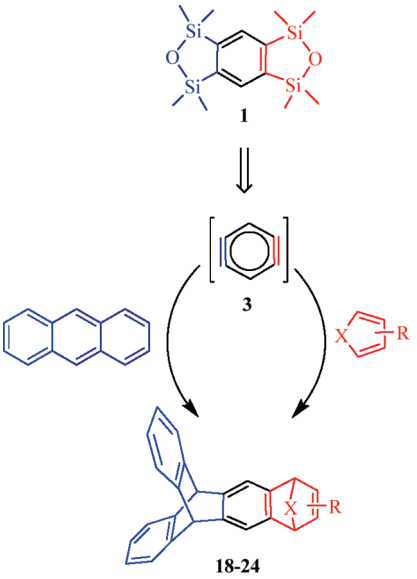
from **1**.[11] Diels−Alder reaction between **13** and anthracene was first carried out in refluxing *p*-xylene for 2 days. Cycloadduct **14** was obtained in 55% yield. Finally, the yield of **14** could be improved to 93% when the Diels−Alder reaction was carried out in water under microwave irradiation for 40 min.[19] To complete the synthesis of oxadisilole fused extended triptycene **6**, cycloadduct **14** was dehydrated. Typical acidic dehydrated conditions found in the literature (TsOH, HCl and H_3PO_4)[18] gave poor results. In most case, the unexpected *retro*-Diels−Alder and desilylated products were obtained. Eventually, we found that the use of AcOH/Ac_2O (2: 1) mixture at reflux for 12 h could afford the target compound **6** in 81% yield.

Triptycyne 7 and Extended Triptycyne 8 from 5 and 6. Oxadisilole fused triptycene **5** and oxadisilole fused extended triptycene **6** are set up as the precursors of the corresponding triptycynes **7** and **8**. These triptycynes are versatile building blocks for a series of triptycene derivatives via Diels−Alder reactions (Schemes 3 and 5).

Phenyliodination of **5** with phenyliodonium diacetate (PhI(OAc)$_2$) and trifluoromethanesulfonic acid (TfOH) to intermediate **15** took place readily in CH_2Cl_2 at room temperature.

SCHEME 4. Benzobisoxadisilole 1 as 1,4-Benzdiyne Synthetic Equivalent for the Preparation of Triptycene Derivatives 18−24



Without isolation, **15** was treated with KF and a catalytic amount of TBAF to generate triptycyne **7**. Trapping experiments of **7** with furan, 2-methylfuran, oxadisilole fused isobenzofurans (**16** and **17**),[12] cyclopentadiene, anthracene, and *N*-*tert*-butoxycarbonylpyrrole are depicted in Scheme 3. Cycloadducts **18**−**24** were obtained in moderate to good yields from triptycyne precursor **5**.

With the generation of triptycyne **7** from oxadisilole fused triptycene **5**, we have once again demonstrated that benzobisoxadisilole **1** is a synthetic equivalent of 1,4-benzdiyne **3**. As depicted in Scheme 4, the stepwise generated 1,4-benzdiyne was first reacted with anthracene and then with another diene to build up a series of triptycene derivatives **18**−**24**.

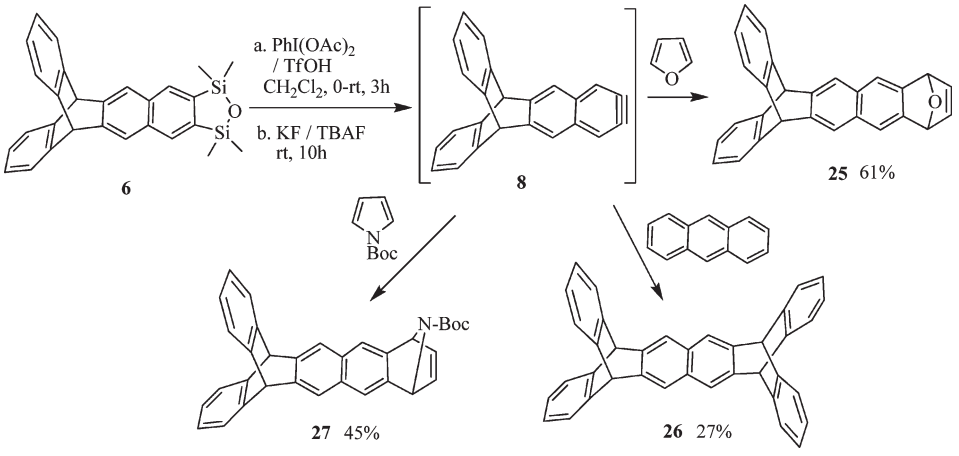
We then moved onto the chemistry of extended triptycyne **8**. Under the standard protocol of phenyliodination/fluoride induced elimination, extended triptycyne **8** was generated from oxadisilole fused extended triptycene **6**. Cycloaddition reactions of **8** with furan, anthracene, and *N*-*tert*-butoxycarbonylpyrrole to cycloadducts **25**−**27** are summarized in Scheme 5.

In summary, starting from benzobisoxadisilole **1**, oxadisilole fused triptycene **5** and extended triptycene **6** were synthesized with good overall yields. Triptycenes **5** and **6** are new precursors of triptycyne **7** and extended triptycyne **8** respectively via the phenyliodination/fluoride induced elimination protocol. Cycloaddition of **7** and **8** with various dienes afforded a series of triptycene derivatives **18**−**27**. In the overall transformations, benzobisoxadisilole **1** served as a synthetic equivalent of 1,4-benzdiyne **3**.

Experimental Section

Oxadisilole Fused Triptycene 5. Trifluoromethanesulfonic acid (0.21 mL, 2.4 mmol) was added with a syringe to a stirred solution of phenyliodonium diacetate (392 mg, 1.2 mmol) in 10 mL of CH_2Cl_2 at 0 °C under N_2. The mixture was stirred for 0.5 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 solution of benzobisoxadisilole **1** (338 mg, 1.0 mmol) in 4 mL of CH_2Cl_2. The mixture was warmed to room temperature and stirred for 0.5 h. Anthracene (632 mg, 4.0 mmol) was added followed by KF (232 mg, 4.0 mmol) and TBAF (1.0 M in THF, 0.3 mL, 0.3 mmol). After 10 h, water was added and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under

SCHEME 5. Generation of Extended Triptycyne 8 and Trapping Experiments



reduced pressure. A mixture of CH_2Cl_2 (3 mL) and petroleum ether (20 mL) was added to the residue and then filtered. The filtrate was concentrated and purified by flash chromatography on silica gel with 2% EtOAc in petroleum ether as eluent to afford product **5** as white solid in 82% yield (315 mg). Mp 264−266 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 0.29 (s, 12H), 5.44 (s, 2H), 7.00 (m, 4H), 7.40 (m, 4H), 7.57 (s, 2H). ^{13}CNMR ($CDCl_3$, ppm): δ 1.1, 54.2, 123.7, 125.2, 125.9, 145.0, 145.3, 146.1; IR (KBr, cm^{-1}): 3039, 2953, 1457, 1251, 1106, 936; MS *m*/*z* 385.1 (MH^+). HRMS (MALDI-TOF) for $C_{24}H_{25}OSi_2$ $[M + H]^+$ calcd 385.1443, found 385.1452.

Compound 12. As a side product, compound **12** is more polar than compoud **5**. White solid; mp 38−40 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 0.34 (s, 6H), 0.37(s, 6H), 1.29 (d, J = 6.8 Hz, 12H), 3.90 (m, 2H), 6.93 (dd, J = 2.4, 8.4 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H). ^{13}CNMR ($CDCl_3$, ppm): δ 1.0, 1.5, 21.2, 47.2, 117.9, 118.0, 131.3, 133.1, 148.6, 148.7. IR (KBr, cm^{-1}): 2985, 1252, 1124, 928. HRMS (MALDI-TOF) for $C_{10}H_{29}NOSi_2$ $[M + H]^+$ calcd 308.1860, found 308.1873.

Cycloadduct 14. Anthracene (106 mg, 0.6 mmol), endoxide **13** (137 mg, 0.5 mmol) and H_2O (4 mL) were added into a 10 mL glass vessel which was then sealed with rubber septa and put into the Microwave Reactor (750W). The highest power (750 W) was set at the beginning so the targeted temperature can be reached within 4 min. During the reaction, the temperature (135 °C) and the pressure (1.0−1.2 MPa) in the vessel were steady. The mixture was stirred for 40 min at 135 °C and then cooled to room temperature. The resulting mixture was extracted by CH_2Cl_2 (2 × 10 mL). The organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 25% CH_2Cl_2 in petroleum ether as eluent to afford product **14** as white solid in 93% yield (210 mg). Mp 205−206 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.27 (s, 6H), 0.29 (s, 6H), 2.29 (s, 2H), 4.44(s, 2H), 4.95 (s, 2H), 7.00 (m, 2H), 7.16 (m, 2H), 7.22 (m, 2H), 7.31 (m, 4H). ^{13}CNMR (100 MHz, $CDCl_3$): δ 0.9, 1.0, 47.4, 48.9, 81.2, 120.8, 123.5, 123.8, 125.7, 126.0, 141.4, 144.2, 146.6, 148.0. IR (KBr, cm^{-1}): 3062, 2951, 2927, 1464, 1456, 1251, 1101, 926. HRMS (MALDI-TOF) for $C_{28}H_{28}O_2Si_2Na$ $[M + Na]^+$: calcd 475.1520, found 475.1522.

Oxadisilole Fused Extended Triptycene 6. Compound **14** (181 mg, 0.4 mmol) was dissolved in a mixture of AcOH (4.0 mL) and Ac_2O (2.0 mL). The reaction mixture was stirred at 130 °C for 12 h and then poured into 10 mL ice−water. The mixture was extracted by CH_2Cl_2 (3 × 10 mL) and the organics were dried over anhydrous Na_2SO_4. After being filtered and concentrated, the residue was purified by column chromatography on silica gel with 20% CH_2Cl_2 in petroleum ether as eluent to afford product **6** as white solid in 81% yield (140 mg). Mp 296−297 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ 0.38 (s, 12H), 5.51 (s, 2H), 7.02 (m, 4H), 7.42 (m, 4H), 7.78 (s, 2H), 7.92 (s, 2H). ^{13}CNMR (100 MHz, $CDCl_3$): δ 1.2, 53.7, 121.9, 123.7, 125.5, 130.7, 132.1, 142.7, 143.5, 144.4. IR (KBr, cm^{-1}): 3065, 2960, 1456, 1251, 1096, 931. HRMS (MALDI-TOF) for $C_{28}H_{26}OSi_2$ $[M]^+$: calcd. 434.1517, found 434.1496.

Cycloadducts 18−24 from Triptycyne 7 Generated from Oxadisilole Fused Triptycene 5. Trifluoromethanesulfonic acid (0.088 mL, 1.0 mmol) was added with a syringe to a stirred solution of phenyliodonium diacetate (164 mg, 0.5 mmol) in 6 mL of CH_2Cl_2 at 0 °C under N_2. The mixture was stirred for 0.5 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 solution of **5** (135 mg, 0.4 mmol in 3 mL of CH_2Cl_2). The mixture was warmed to room temperature and stirred for 1 h. After cooled to 0 °C, the diene (furan (4.0 mmol), 2-methylfuran (4.0 mmol), isobenzofuran **16** (1.0 mmol), isobenzofuran **17** (1.0 mmol), cyclopentadiene (4.0 mmol), anthracene (1.6 mmol) or *N*-*tert*-butoxycarbonylpyrrole (4.0 mmol)) was added followed by KF (93 mg, 1.6 mmol) and TBAF (1.0 M in THF, 0.12 mL, 0.12 mmol). The reaction mixture was stirred at 0 °C for 0.5 h then warmed to room temperature and stirred overnight. Water was added and the resulting mixture was extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with 2 to 10% EtOAc in petroleum ether as eluent to afford products **18**−**24**.

Cycloadduct 18. Sixty-four percent yield; white solid; mp 183−185 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 5.34 (s, 2H), 5.60 (s,2H), 6.96 (m, 6H), 7.32 (s, 2H), 7.35 (m, 4H). ^{13}CNMR ($CDCl_3$, ppm): δ 54.2, 82.2, 116.9, 123.4, 123.4, 125.0, 125.0, 143.1, 143.2, 145.3, 145.4, 146.6. IR (KBr, cm^{-1}): 3014, 2954, 1457, 1279, 1191, 980. HRMS (MALDI-TOF) for $C_{24}H_{17}O$ $[M + H]^+$: calcd 321.1274, found 321.1292.

Cycloadduct 19. Fifty-five percent yield; white solid; mp 128−130 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 1.89 (s, 3H), 5.38 (s, 1H), 5.39 (s, 1H), 5.54 (d, J = 2.0 Hz, 1H), 6.71 (d, J = 5.2 Hz, 1H), 7.00 (m, 5H), 7.27 (s, 1H), 7.31 (s, 1H), 7.38 (m, 4H). ^{13}CNMR ($CDCl_3$, ppm): δ 15.2, 54.2, 54.3, 81.7, 89.3, 115.5, 116.6, 123.4, 123.4, 125.0, 125.0, 142.8, 143.0, 144.5, 145.4, 145.4, 145.5, 145.7, 148.2, 149.0. IR (KBr, cm^{-1}): 3016, 2955, 1457, 1384, 1198, 1108. HRMS (MALDI-TOF) for $C_{25}H_{19}O$ $[M + H]^+$: calcd 335.1430, found 335.1446.

Cycloadduct 20. Forty-five percent yield; white solid; mp 248−250 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 0.33 (s, 6H), 0.38 (s, 6H), 0.39 (s, 6H), 0.51 (s, 6H), 5.36 (s, 2H), 5.89 (s, 2H), 6.97 (m, 4H), 7.33 (s, 2H), 7.36 (m, 4H). ^{13}CNMR ($CDCl_3$, ppm): δ 1.42, 1.57, 2.24, 2.32, 54.2, 82.5, 116.9, 123.4, 123.5, 123.6, 125.1, 125.2, 139.9, 143.9, 145.2, 145.5, 149.7, 151.3. IR (KBr, cm^{-1}): 2959, 1458, 1254, 942. HRMS (MALDI-TOF) for $C_{36}H_{38}O_3Si_4$ $[M]^+$: calcd 630.1892, found 630.1905.

Cycloadduct 21. Forty-nine percent yield; white solid; mp 225−227 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 0.29 (s, 6H), 0.34 (s, 6H), 5.38 (s, 2H), 5.95 (s, 2H), 6.99 (m, 4H), 7.37 (m, 4H), 7.42 (s, 2H), 7.44 (s, 2H). ^{13}CNMR ($CDCl_3$, ppm): δ 0.8, 1.0, 54.2, 82.3, 116.9, 122.1, 123.4, 123.5, 125.1, 125.1, 143.8, 145.1, 145.2, 145.4, 146.6, 149.2. IR (KBr, cm^{-1}): 2954, 1458, 1252, 1096, 935. HRMS (MALDI-TOF) for $C_{32}H_{29}O_2Si_2$ $[M + H]^+$: calcd 501.1700, found 501.1712.

Cycloadduct 22. Thirty-four percent yield; white solid; mp > 350 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 5.33 (s, 4H), 6.93 (m, 8H), 7.31 (m, 8H), 7.46 (s, 2H). ^{13}CNMR ($CDCl_3$, ppm): δ 53.9, 119.7, 123.4, 125.0, 142.4, 145.3. HRMS for $C_{34}H_{22}$ $[M]^+$: calcd 430.1716, found 430.1732.

Cycloadduct 23. Forty-six percent yield; white solid; mp 220−222 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 2.15 (d, J = 6.8 Hz, 1H), 2.25 (d, J = 6.8 Hz, 1H), 3.75 (s, 2H), 5.31 (s, 2H), 6.68 (s, 2H), 7.00 (m, 4H), 7.31 (s, 2H), 7.34 (m, 4H). ^{13}CNMR ($CDCl_3$, ppm): δ 50.1, 54.3, 70.6, 118.0, 123.3, 123.3, 124.8, 124.8, 141.8, 143.1, 145.9, 146.0, 149.0. IR (KBr, cm^{-1}): 3001, 2947, 1638, 1458, 1300, 1192, 935. HRMS (MALDI-TOF) for $C_{25}H_{18}$ $[M]^+$: calcd 318.1403, found 318.1401.

Cycloadduct 24. Fifty-five percent yield; white solid; mp 135−137 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 1.35 (s, 9H), 5.35 (s, 2H), 5.41 (m, 2H), 6.87 (br, 1H), 6.97 (m, 5H), 7.35 (m, 6H). ^{13}CNMR ($CDCl_3$, ppm): δ 28.1, 54.1, 65.9, 66,7, 80.5, 117.1, 117.6, 123.4, 124.9, 125.0, 142.5, 143.0, 144.0, 145.3, 145.4, 154.6. IR (KBr, cm^{-1}): 2973, 1705, 1458, 1367, 1324, 1252, 1164. HRMS (MALDI-TOF) for $C_{29}H_{25}NO_2Na$ $[M + Na]^+$: calcd 442.1777, found 442.1784.

Cycloadducts 25−27 from Extended Triptycyne 8 Generated from Oxadisilole Fused Extended Triptycene 6. The extended triptycyne **8** was generated from **6** under the similar procedure for triptycyne **5** generation. Triptycyne **8** was reacted with furan,

(19) Pei, B. J.; Lee, A. W. M. *Tetrahedron Lett.* **2010**, *51*, 4519.

anthracene and *N*-*tert*-butoxycarbonylpyrrole to afford the cycloadducts **25**−**27**.

Cycloadduct 25. Sixty-one percent yield; light yellow solid; mp 191−193 °C. ^{1}HNMR ($CDCl_3$, ppm): δ 5.52 (s, 2H), 5.76 (s, 2H), 6.90 (s, 2H), 7.03 (m, 4H), 7.41(m, 4H), 7.47 (s, 2H), 7.68 (s, 2H). ^{13}CNMR ($CDCl_3$, ppm): δ 53.7, 81.8, 118.4, 122.2, 123.6, 123.7, 125.3, 125.4, 129.9, 141.7, 142.7, 144.3, 144.6, 144.8. HRMS (MALDI-TOF) for $C_{28}H_{18}O$ $[M]^+$: calcd 370.1352, found 370.1352.

Cycloadduct 26. Twenty-seven percent yield; white solid; mp >350 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ 5.44 (s, 4H), 6.96 (m, 8H), 7.35 (m, 8H), 7.62 (s, 4H). ^{13}CNMR (100 MHz, $CDCl_3$): δ 53.7, 121.4, 123.6, 125.3, 129.7, 142.1, 144.6. HRMS for $C_{38}H_{24}$ $[M]^+$: calcd 480.1872, found 480.1870.

Cycloadduct 27. Forty-five percent yield; light yellow solid; mp 180−182 °C. ^{1}HNMR (400 MHz, $CDCl_3$): δ 1.34 (s, 9H), 5.50 (s, 2H), 5.54 (m, 2H), 6.85 (br, 1H), 7.02 (m, 5H), 7.42 (m, 6H), 7.66 (s, 2H). ^{13}CNMR (100 MHz, $CDCl_3$): δ 28.1, 53.7, 65.4, 66.1, 80.6, 122.1, 123.6, 123.7, 123.8, 125.3, 125.4, 125.7, 142.5, 143.9, 144.6, 144.7, 155.1. IR (KBr, cm^{-1}): 2955, 1705, 1458, 1367, 1337, 1252, 1161. HRMS (MALDI-TOF) for $C_{33}H_{27}NO_2Na$ $[M + Na]^+$: calcd 492.1934, found 492.1928.

Acknowledgment. Financial support from the Hong Kong Research Grants Council (HKBU 201307) is gratefully acknowledged.

Supporting Information Available: General Methods section and ^{1}H and ^{13}C NMR spectra of compounds **5**, **6**, **12**, **14**, and **18**−**27**. This material is available free of charge via the Internet at http://pubs.acs.org.