Pergamon

Tetrahedron 58 (2002) 9413–9422

TETRAHEDRON

5,6-Bis(trimethylsilyl)benzo[*c*]furan: an isolable versatile building block for linear polycyclic aromatic compounds☆

Siu-Hin Chan, Chung-Yan Yick and Henry N. C. Wong*

Department of Chemistry and Central Laboratory of the Institute of Molecular Technology for Drug Discovery and Synthesis,† *The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China*

Dedicated to Professor Yao-Zeng Huang on the occasion of his 90th birthday

Received 10 June 2002; revised 3 September 2002; accepted 26 September 2002

Abstract—Benzo[*c*]furans are a class of interesting and highly reactive compounds that readily undergo Diels–Alder cycloaddition with dienophiles to restore their aromaticity. Initially, the *s*-tetrazine approach established by Warrener was chosen for the synthesis of the title molecule. However, it was discovered that the rate of production of isobenzofuran from this approach was too slow to react with the fugitive arynes. Consequently, an alternative route was employed to realize the title molecule in a neat state. In this way, the reactions between the title molecule and arynes were successfully achieved. Herein, two synthetic approaches towards the title molecule and its further manipulation for the preparation of silylated linear polycyclic aromatic hydrocarbons (PAH) were reported. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Benzo[*c*]furan (**1**), also known as isobenzofuran (IBF) was postulated[2] and detected[3] as a reactive dienophile that readily undergoes Diels–Alder reaction with alkynes and other dienophiles to form the corresponding endoxide adducts. It was isolated[4] in the early seventies as a crystalline solid, stable only at low temperature but readily decomposed at room temperature. Noteworthy is that isobenzofurans, with very few exceptions,[5] are too unstable to be isolated in the conventional sense. As part of our continuing program concerning the use of silylated furans in the regiospecific synthesis of polysubstituted furans,[6,7] we sought to extend the chemistry to include a silylated benzo[*c*]furan, namely 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**), which is expected to react with various dienophiles to provide Diels–Alder adducts.

The syntheses of several benzo[*c*]furans containing trimethylsilyl groups on the furan ring were reported by Rickborn.[8–11] However, in these endeavors, all silyl groups in the isobenzofurans were used only as protecting groups rather than functional groups. Due to the β-effect of silicon,[12] aromatic rings substituted with trimethylsilyl groups have been shown to be very useful precursors in many organic transformations.[6,7] Furthermore, it is likely that the silyl group can also increase the solubility of polycyclic aromatic compounds obtained from Diels–Alder reactions. It is therefore believed that the combined use of the trimethylsilyl groups and the deoxygenation protocol depicted in Scheme 1 can lead to the realization of silylated linear polycylcic aromatic skeletons.

2. Result and discussion

5,6-Bis(trimethylsilyl)benzo[*c*]furan (**2**) was chosen as our target molecule. For the generation of **2**, we chose the *s*-tetracene approach[4,13] established by Warrener as the key step. The starting material, 1,4-endoxy-1,4-dihydro-6,7-bis-(trimethylsilyl)naphthalene (**5**), was synthesized through three steps from commercially available 1,2,4,5-tetrachlorobenzene[14,15] as illustrated in Scheme 2. Thus, the reactions of tetrachlorobenzene with magnesium and trimethylsilyl chloride, gave 1,2,4,5-tetrakis(trimethylsilyl)benzene (**3**). This was then transformed into the iodonium triflate **4** by addition of triflic acid and iodobenzenediactetate.[16] Upon treatment of **4** with TBAF, a silylated benzyne was presumably generated and was trapped by furan to afford **5**.

The generation of 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**) was successfully accomplished by treating **5** with 3,6-di(pyridin-2′-yl)-*s*-tetrazine (**6**) in a $CHCl_3$ solution. In the presence of various dienophiles, benzo[*c*]furan (**2**) produced the expected Diels–Alder adducts **7**–**10** in yields from good

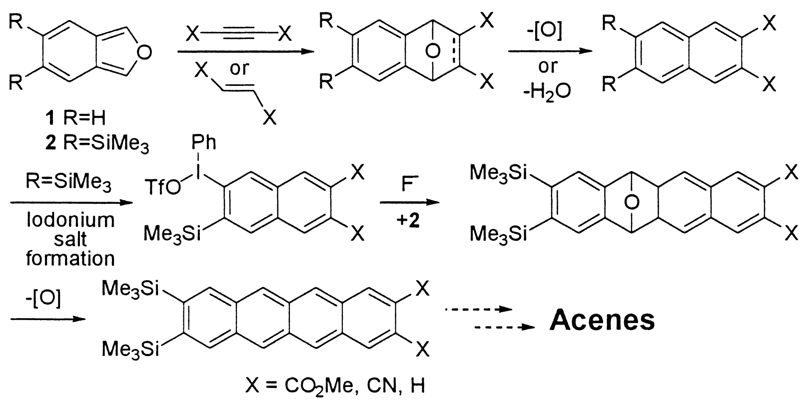
☆ See Ref. 1.

Keywords: isobenzofuran; Diels–Alder reaction; polycyclic aromatic hydrocarbon.

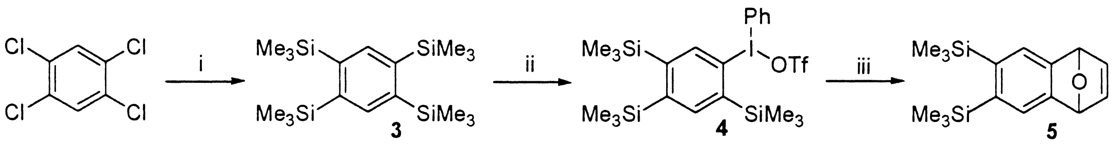
* Corresponding author. Tel.: +852-2609-6329; fax: +852-2603-5057; e-mail: hncwong@cuhk.edu.hk

† An Area of Excellence of the University Grants Committee (Hong Kong).

0040–4020/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(02)01219-X



Scheme 1.



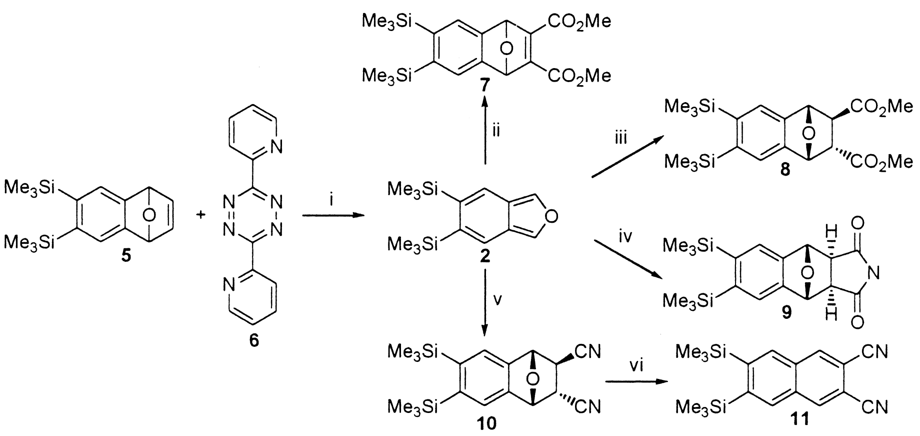
Scheme 2. *Reagents and conditions*: (i) Mg, Me_3SiCl, HMPT, THF, reflux, 48%; (ii) $PhI(OAc)_2$, CF_3SO_3H, *i*-Pr_2NH, CH_2Cl_2, 61%; (iii) furan, *n*-Bu_4NF, THF, 61%.

to excellent, as depicted in Scheme 3. Nitrile **10** could in principle be dehydrated by treatment with a strong base like bis(trimethylsilyl)amide, affording in fair yields the corresponding naphthalenenitrile, a method commonly employed in the preparation of naphthalocyanines.[17] In our hands, however, dehydration of compound **10** was smoothly accomplished in an acceptable yield by reaction with a mixture of lithium iodide and 1,8-diazabicyclo[5,4,0]undec-1-ene in refluxing THF, leading to the naphthalenenitrile **11**.

Benzo[*c*]furan **2** also reacted readily with quinones and the results are summarized in Table 1. For naphthoquinone and anthraoquinone,[18] only the *endo* adducts **13** and **14** were observed. This was confirmed by ^1H NMR spectroscopy which showed two sets of doublet of doublets for the two groups of aliphatic protons in the ring systems. While for benzoquinone an *exo*–*endo* adduct **12** was obtained. Adducts **12**–**14** were subjected to dehydration in refluxing 90% acetic acid, leading to aromatic compounds **15**–**17** as bright yellow crystals.

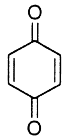
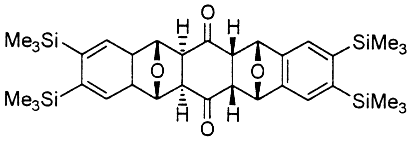
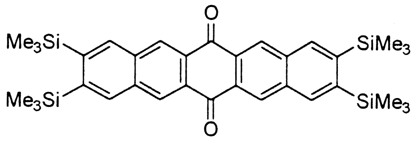
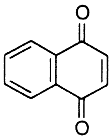
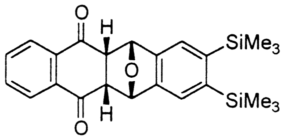
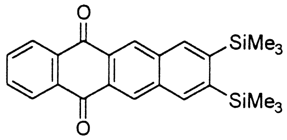
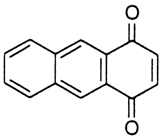
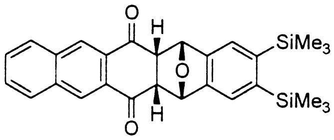
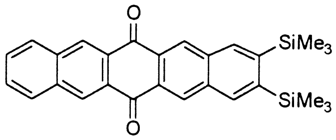
The most notable feature of our program is the manipulation of trimethylsilyl substituents to realize linear polycyclic aromatic hydrocarbon skeletons. In order to elongate the benzo framework, **11** was allowed to react with iodobenzenediacetate in triflic acid, affording the iodonium triflate **18**. The iodonium salt **18** was then allowed to undergo an elimination reaction with TBAF to presumably generate a benzyne intermediate,[16] which provided endoxide **19** upon trapping with 3,4-bis(trimethylsilyl)furan.[6] The final deoxygenating step was accomplished by employing $TiCl_4$–$LiAlH_4$–Et_3N in THF, furnishing anthracene **20** in a good yield (Scheme 4).[19]

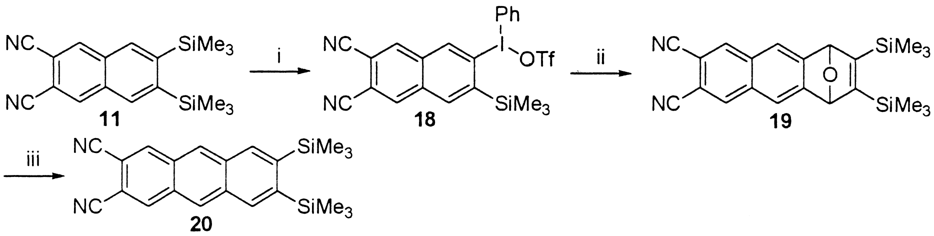
A potential application of **11** is its transformation into naphthalocyanine metal complexes. Due to their strong absorption property in the near-IR region, naphthalocyanines have been studied extensively in the field of materials science.[20] However, their strong tendency to aggregate has given rise to severe solubility problems. It is thus anticipated that by introducing appropriate bulky and



Scheme 3. *Reagents and conditions*: (i) $CHCl_3$; (ii) DMAD, 82%; (iii) dimethyl fumarate, 86%; (iv) *N*-phenyl-malemide, 76%; (v) fumaronitrile, 98%; (vi) LiI, DBU, THF, reflux, 88%.

Table 1. Diels–Alder adducts of **2** and their corresponding dehydration products

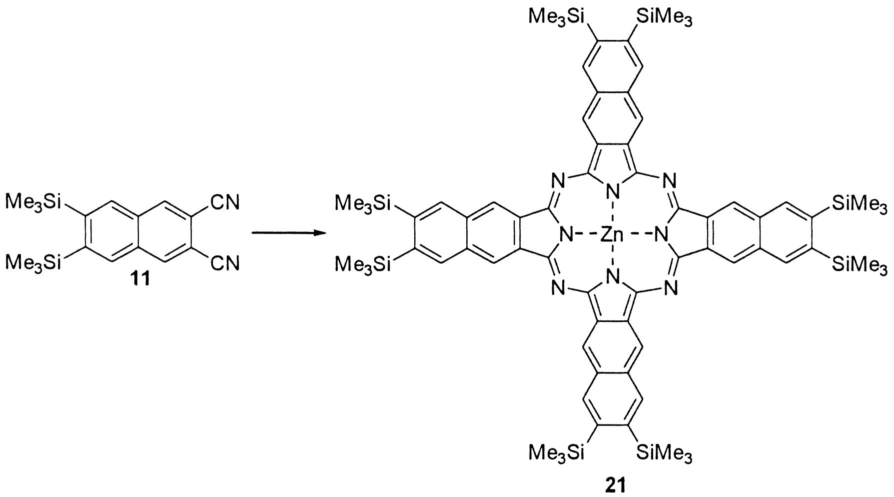
Entry	Dienophile	Diels–Alder adduct	Yield(%)	Dehydration Product	Yield(%)
1		 **12**	54	 **15**	38
2		 **13**	58	 **16**	75
3		 **14**	72	 **17**	75



Scheme 4. *Reagents and conditions*: (i) Phl(OAc)$_2$, CF$_3$SO$_3$H, CH$_2$Cl$_2$, 50%; (ii) 3,4-bis(trimethylsilyl) furan, *n*-Bu$_4$NF, CH$_2$Cl$_2$, 62%; TiCl$_4$, LiAlH$_4$, Et$_3$N, THF, 78%.

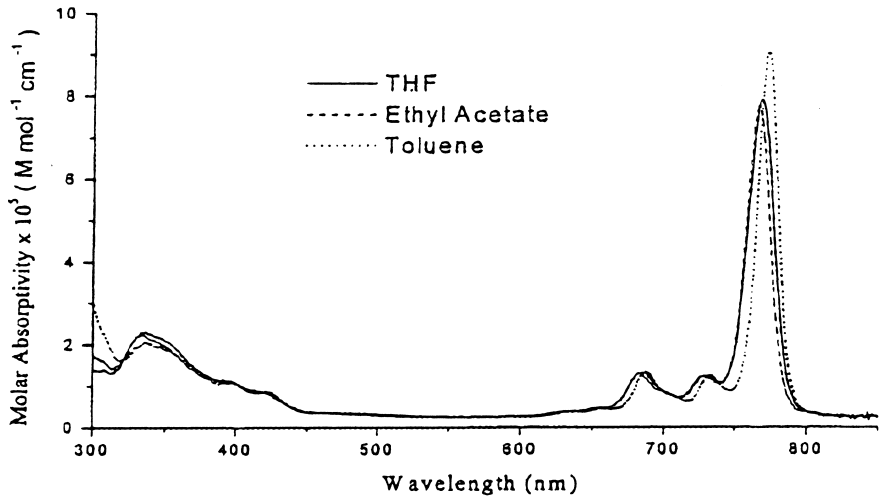
lipophilic groups at the periphery of the ring, the molecule would no longer aggregate as well as show better solubility in organic solvents. Moreover, the silyl substituents can be easily transformed into other functional groups. Thus, with a sufficient amount of **11** in hand, the realization of a naphthalocyaninozinc complex was accomplished in an acceptable yield as a deep green powder (Scheme 5). The UV–Vis absorption spectroscopy was studied, which showed a typical absorption band pattern of naphthalocyanines (Fig. 1). Furthermore, the molar absorption was found to be concentration independent over the range of 4.2×10^{-6}–1.1×10^{-4} in THF, a phenomenon that could be ascribed to the existence of monomeric forms.

As mentioned before, the most challenging goal of the project is the utilization of 5,6-bis(trimethylsilyl)benzo[*c*]-furan (**2**) for the preparation of acenes. Our original idea, as depicted in Scheme 1, required the reaction between two reactive intermediates, namely isobenzofuran and an aryne. As a preliminary study, we had attempted to carry out the



Scheme 5. *Reagents and conditions*: DBU, Zn(OAc)$_2$, C$_6$H$_{13}$OH, reflux, 40%.

Solvent Effects on UV-Vis Spectra of Nc Sample



Solvent	Wavelength (nm) (log ε)
THF	767 (5.90), 731 (5.10), 684 (5.12), 337 (5.36)
Ethyl Acetate	765 (5.89), 730 (5.09), 682 (5.11), 337 (5.35)
Toluene	771 (5.96), 733 (5.10), 687 (5.13), 336 (5.32)

Concentration Effect UV-Vis Spectra of Nc Sample

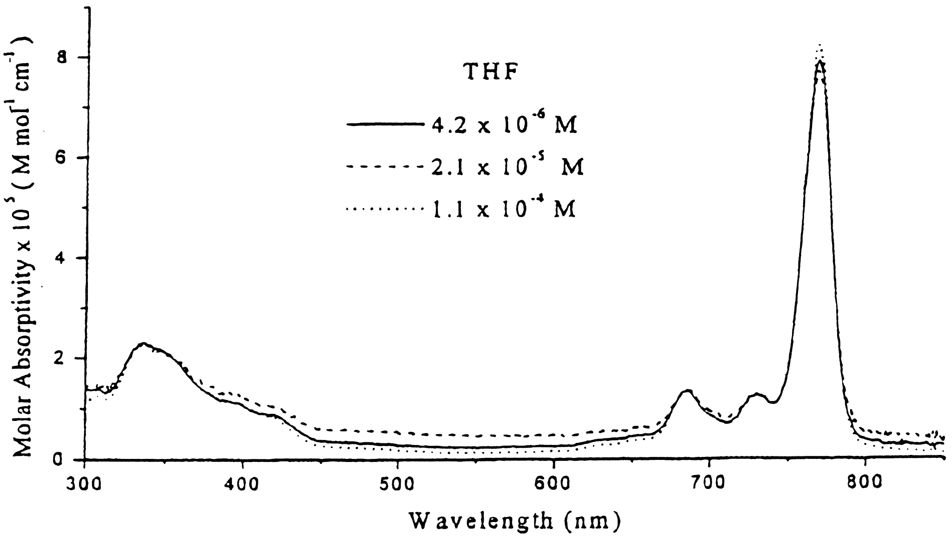
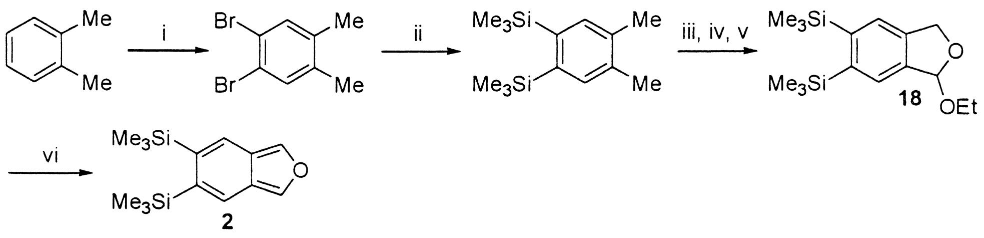


Figure 1. UV–Vis spectra of Nc sample.

reaction as usual employing isobenzofuran **2**, generated as before, and an aryne generated from phenyl[2-(trimethylsilyl)-1-phenyl]iodonium triflate[16] and a solution of TBAF. However, despite tremendous efforts, we failed to isolate any cycloadduct from the aforementioned reaction mixture. We believed that this was due to the slow generation of **2** from **5**, and the unlikely reaction between two reactive species under this condition. In view of this, we switched to an alternative method for the generation of a pure solution of isobenzofuran **2**. 4,5-Bis(trimethylsilyl)-*o*-xylene (**24**)[21] was the presursor of this new program. Starting from *o*-xylene (**22**), bromination afforded dibromide **23**[21] which was then transformed into **24** under a standard Grignard condition. The whole process can be carried out in gram



Scheme 6. *Reagents and conditions*: (i) I_2, Br_2, 0°C, 80%; (ii) Mg, Me_3SiCl, HMPA, THF, 50%; (iii) NBS, AIBN, CCl_4, reflux; (iv) $CaCO_3$, Dioxane–H_2O, reflux; (v) *p*-TsOH, EtOH, 38% ((iii)–(v) 3-steps); (vi) LDA, THF, 0°C.

scale without difficulties. Compound **24** was then brominated with 3 equiv. of NBS to afford the corresponding tribromide. Hydrolysis with calcium carbonate furnished the hemiacetal which was then transformed into **25** immediately in absolute ethanol with *p*-toluenesulfonic acid as a catalyst (Scheme 6). Compound **25** was smoothly converted to isolable **2** by reaction with lithium diisopropylamide (LDA) in THF.[22]

Before we proceeded to attempt the reaction between isobenzofuran **2** and an aryne, it was necessary to assess the stability of **2** by ^{1}H NMR spectroscopic studies. Lithium

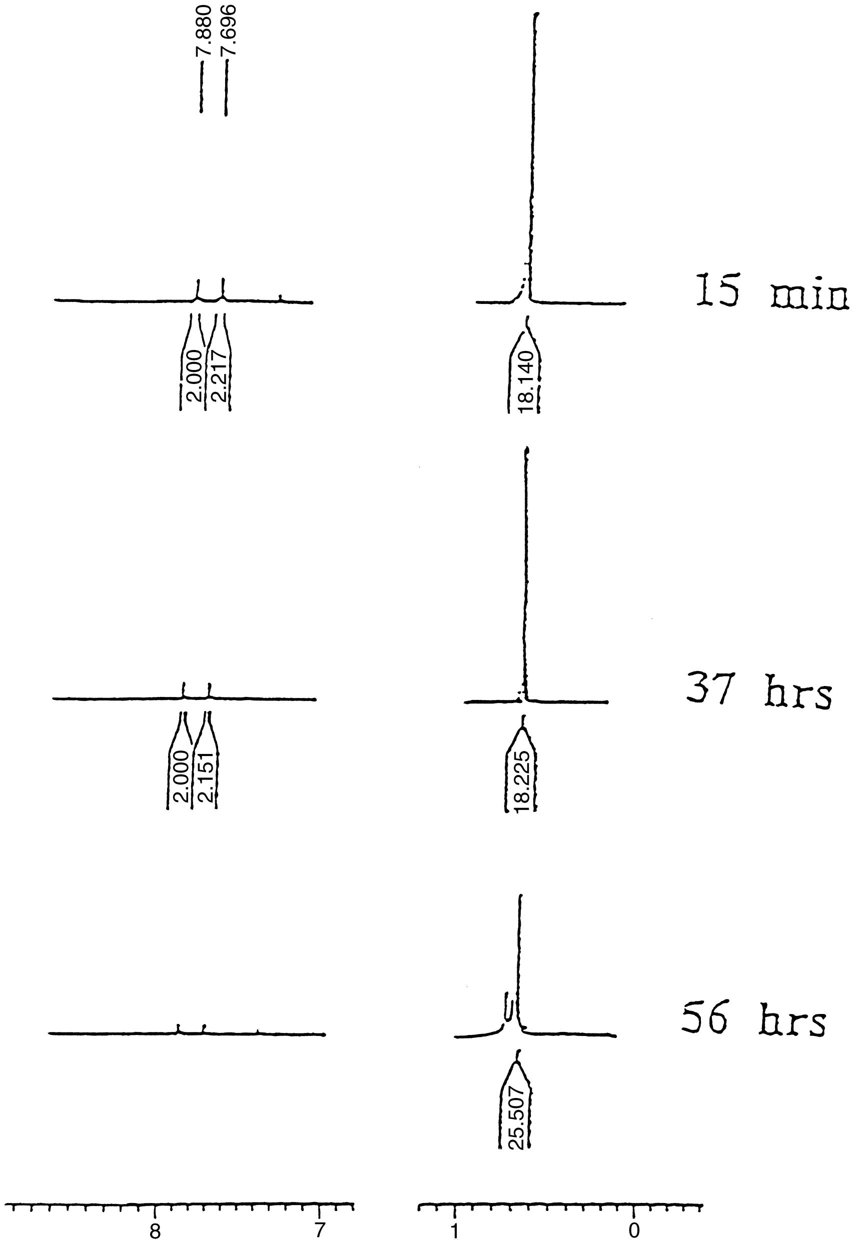
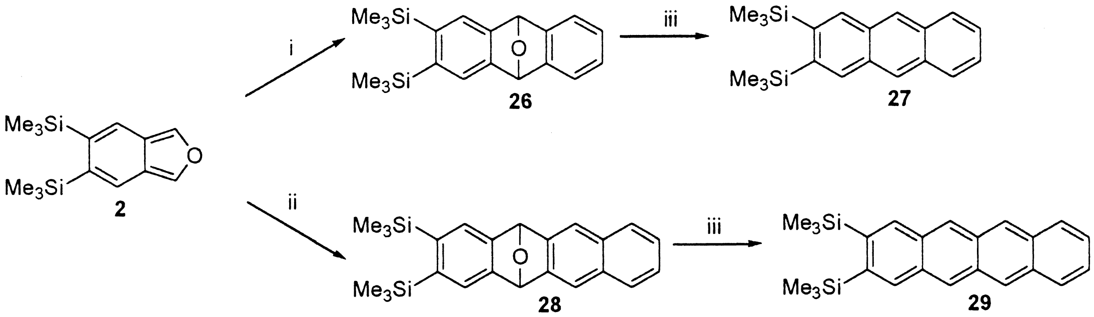


Figure 2. ^{1}H NMR spectrum of **2** in $CDCl_3$ recorded at room temperature at different times.



Scheme 7. *Reagents and conditions*: (i) Phenyl[2-(trimethylsilyl)-1-phenyl]iodonium triflate, TBAF, CH_2Cl_2, 80%; (ii) Phenyl[3-(trimethylsilyl)-2-naphthyl]iodonium triflate, TBAF, CH_2Cl_2, 75%; (iii) $TiCl_4$, $LiAlH_4$, Et_3N, THF, 88%.

diisopropylamide in THF was added to a solution of **25** in THF at 0°C under a nitrogen atmosphere (Scheme 6). The generation of isobenzofuran **2** was monitored by TLC and the reaction was eventually quenched by 1N HCl to remove all the ammonium salts. The aqueous layer was removed and the organic layer was washed with cold brine. After that the organic solution was concentrated and then diluted with deuterated chloroform to provide a neat solution of **2**. The ^{1}H NMR spectrum of **2** in $CDCl_3$ was first recorded at room temperature. From Fig. 1, absorptions at δ 7.70 and 7.88 represented the benzo protons and the furan protons, respectively. The spectrum clearly showed that the absorptions at the aromatic region were still visible after 37 h, and they only faded out after 56 h. It could therefore be concluded that a $CDCl_3$ solution of isobenzofuran **2** should be stable at room temperature for up to at least 37 h (Fig. 2).

After assessing the stability of **2**, we then carried out the reaction between **2** and an aryne. When **2** was allowed to react with benzyne generated from (phenyl)[2-(trimethylsilyl)-1-phenyl]iodonium triflate[16] and TBAF, cycloadduct **26** was obtained in a good yield. Further deoxygenation under standard conditions was also accomplished to afford anthracene **27**. Furthermore, when **2** was allowed to react with naphthalyne generated from (phenyl)[3-(trimethylsilyl)-2-naphthyl] iodonium triflate[23] and TBAF, cycloadduct **28** was obtained in excellent yield. Tetracene **29** was synthesized through a standard reduction of **28** (Scheme 7).

Besides reactions between **2** and the arynes, the cycloadditions between isobenzofuran **2** in a neat state and dienophiles can also be accomplished to afford the corresponding adducts **7** (75%), **8** (78%), **9** (70%) **10** (80%), **12** (54%), **13** (58%) and **14** (72%) with acceptable yields compared with the yields obtained from the *s*-tetrazine approach mentioned before.

In conclusion, we have successfully synthesized and trapped 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**) by two approaches. With the *s*-tetrazine approach, we have synthesized cycloadducts such as simple substituted endoxide, silylated quinones to naphthalocyanine. On the other hand, a neat solution of 5,6-bis(trimethylsilyl)benzo[*c*]furan (**2**) was also obtained in a neat state by employing the acetal approach. This method can allow the reaction between isobenzofuran **2** and elusive arynes to proceed. The latter approach will be applied to the preparation of higher acene members.

3. Experimental

3.1. General information

All reagents and solvents were reagent grade. Further purification and drying by standard methods were employed when necessary. All organic solvents were evaporated under reduced pressure with a rotary evaporator. The plates used for thin-layer chromatography (TLC) were E. Merck silica gel $60F_{254}$ (0.25 mm thickness) precoated on aluminum plates, and they were visualized under both long (365 nm) and short (254 nm) UV light. Compounds on TLC plates were visualized with a spry of 5% dodecamolybdophosphoric acid in ethanol and with subsequent heating. Column chromatography was performed using E. Merck silica gel (230–400 mesh).

Melting points were measured on a Reichert Microscope apparatus and were uncorrected. NMR spectra were recorded on a Bruker DPX-300 spectrometer (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C). All NMR measurements were carried out at 300 K in deuterated chloroform solution unless otherwise stated. Chemical shifts are reported as parts per million (ppm) in δ unit in the scale relative to the resonance of $CDCl_3$ (7.26 ppm in the ^{1}H, 77.00 ppm for the central line of the triplet in the ^{13}C modes, respectively). Coupling constants (J) are reported in Hz. Splitting patterns are described by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^{1}H NMR data is reported in this order: chemical shift; multiplicity; coupling constant(s), number of proton. Mass spectra (ERMS and HRMS) were obtained with a Thermofinnigan MAT95XL spectrometer and determined at an ionized voltage of 70 eV unless otherwise stated. Relevant data were tabulated as *m*/*z*. Elemental analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, China.

3.1.1. 1,4-Epoxy-6,7-bis(trimethylsilyl)-1,4-dihydronaphthalene (5). A suspension of $PhI(OAc)_2$ (1.1 g, 3.4 mmol) in CH_2Cl_2 (10 mL) was cooled at 0°C and treated dropwise with TfOH (0.6 mL, 7.0 mmol). After 1 h at rt, the reaction was cooled to 0°C again. Compound **3** (830 mg, 3.4 mmol) and diisopropylamine (1 mL, 7.0 mmol) in CH_2Cl_2 (10 mL) were added slowly. After 10 min, the solution was allowed to warm to rt. Furan (0.8 mL, 12 mmol), followed by TBAF (1 M in THF, 5 mL, 5 mmol) were added. After a further 10 min, the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried over $MgSO_4$. Following evaporation of solvent under reduced pressure, the residue was chromatographed on silica gel (200 g, hexanes–ethyl acetate 30:1) to afford 5 (600 mg, 2.07 mmol, 61%) as a colorless solid: mp 90–91°C; ^1H NMR ($CDCl_3$) δ 0.37 (s, 18H), 5.73 (s, 2H), 7.03 (s, 2H), 7.61 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.1, 82.3, 126.6, 142.8, 143.4, 148.3; MS *m/z* 288 (M^+). Anal. Calcd for $C_{16}H_{24}OSi_2$: C, 66.60; H, 8.38. Found: C, 66.16; H, 8.31.

3.2. General procedure for the preparation of Diels–Alder adducts 7–10, 12–14 by *s*-tetrazine approach

3.2.1. 2,3-Dicarbomethoxy-1,4-epoxy-1,4-dihydro-6,7-bis(trimethylsilyl)naphthalene (7). To a rapidly stirring solution of **5** (150 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (0.07 mL, 0.6 mmol) in chloroform (5 mL) was added **6** (140 mg, 0.06 mmol) in portions over 30 min. The mixture was allowed to stir for a further 2 h. After evaporation of solvent under reduced pressure, the residue was subjected to chromatography on silica gel (20 g, hexanes–ethyl acetate 10:1) to afford **7** (165 mg, 0.41 mmol, 82%) as a colorless solid: mp 99–100°C; ^1H NMR ($CDCl_3$) δ 0.36 (s, 18H), 3.81 (s, 6H), 5.96 (s, 2H), 7.74 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.0, 52.3, 84.8, 127.6, 144.9, 154.4, 150.9, 162.8; MS *m/z* 404 (M^+). Anal. calcd for $C_{20}H_{28}O_5Si_2$: C, 59.37; H, 6.98. Found: C, 59.18; H, 7.25.

3.2.2. *trans*-2,3-Dicarbomethoxy-1,4-epoxy-1,2,3,4,-tetrahydro-6,7-bis(trimethylsilyl) naphthalene (8). This was prepared from **5** (150 mg, 0.5 mmol), dimethyl fumarate (46 mg, 0.6 mmol) and **6** (140 mg, 0.6 mmol) in chloroform (5 mL) in the same manner as described above, yielding **8** (175 mg, 0.43 mmol, 86%) as a colorless solid: mp 103–104°C; ^1H NMR ($CDCl_3$) δ 0.32 (s, 9H), 0.35 (s, 9H), 3.05 (d, J=4.2 Hz, 1H), 3.55 (s, 3H), 3.81 (s, 3H), 3.92 (dd, J=5.4 Hz, 1H), 5.61 (d, J=5.4 Hz, 1H), 5.67 (s, 1H), 7.52 (s, 1H), 7.63 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 2.0, 2.1, 49.1, 49.4, 51.9, 52.6, 80.3, 82.9, 125.6, 126.9, 141.6, 143.3, 145.7, 146.0, 170.2, 172.4; MS *m/z* 406 (M^+). Anal. calcd for $C_{20}H_{30}O_5Si_2$: C, 59.08; H, 7.44. Found: C, 58.99; H, 7.52.

3.2.3. 3a,4,9,9a-Tetrahydro-2-phenyl-6,7-bis(trimethylsilyl)-1*H*-benz[*f*]isoindole-1,3-(2*H*)-dione (9). This was prepared from **5** (150 mg, 0.5 mmol), *N*-phenylmaleimide (100 mg, 0.6 mmol) and **6** (140 mg, 0.6 mmol) in chloroform (5 mL) in the same manner as described above, yielding **9** (165 mg, 0.38 mmol, 76%) as a colorless solid: mp 284°C (decomp.); ^1H NMR ($CDCl_3$) δ 0.39 (s, 18H), 3.15 (s, 2H), 6.00 (s, 2H), 7.33 (d, J=7.2 Hz, 2H), 7.42–7.52 (m, 3H), 7.71 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.0, 49.3, 82.0, 126.2, 126.6, 128.9, 129.2, 131.7, 142.8, 146.8, 175.5; MS *m/z* 435 (M^+). Anal. calcd for $C_{24}H_{29}NO_3Si_2$: C, 66.17; H, 6.71; N, 3.21. Found: C, 65.91; H, 6.62; N, 3.13.

3.2.4. *trans*-2,3-Dicyano-1,4-epoxy-6,7-1,2,3,4,-tetrahydro-bis(trimethylsilyl) naphthalene (10). This was prepared from **5** (150 mg, 0.5 mmol), fumaronitrile (46 mg, 0.6 mmol) and **6** (140 mg, 0.6 mmol) in chloroform (5 mL) in the same manner as described above, yielding **10** (167 mg, 0.49 mmol, 98%) as colorless crystals: mp 197–198°C; ^1H NMR ($CDCl_3$) δ 0.37 (s, 9H), 0.38 (s, 9H), 2.83 (d, J=4.5 Hz, 1H), 3.54 (dd, J=4.5, 4.5 Hz, 1H), 5.74 (d, J=4.5 Hz, 1H), 5.75 (s, 1H), 7.68 (s, 1H), 7.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 1.9, 36.1, 37.1, 80.6, 83.0, 116.1, 118.3, 125.7, 127.9, 138.9, 140.6, 148.2, 148.3; MS *m/z* 340 (M^+). Anal. calcd for $C_{18}H_{24}N_2OSi_2$: C, 63.48; H, 7.10; N, 38.23. Found: C, 63.59; H, 7.22; N, 8.20.

3.2.5. *exo/endo*-[5,14],[7,12]-Diendoxy-5,5a,6a,7,12,12a,13a,14-octahydro-2,3,9,10-tetrakis(trimethylsilyl)-pentacene-6,13-dione (12). This was prepared from **5** (170 mg, 0.5 mmol), *p*-benzoquinone (32 mg, 0.3 mmol) and **6** (170 mg, 0.7 mmol) in chloroform (10 mL) in the same manner as described above, yielding **12** (102 mg, 0.16 mmol, 54%) as colorless crystals: mp 110–111°C; ^1H NMR ($CDCl_3$) δ 0.20 (s, 18H), 0.31 (s, 18H), 1.75 (s, 2H), 3.76 (dd, J=3.0, 2.1 Hz, 2H), 5.61 (s, 2H), 5.68 (dd, J=3.0, 2.1 Hz, 2H), 7.51 (s, 2H), 7.55 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.0, 53.2, 55.0, 82.0, 83.7, 125.3, 128.0, 142.2, 142.8, 146.2, 206.4; MS *m/z* 262 ($C_{14}H_{22}OSi^+$). Anal. calcd for $C_{34}H_{48}O_4Si_4$: C, 64.50; H, 7.64. Found: C, 64.90; H, 7.46.

3.2.6. *endo*-6,11-Endoxy-5a,6,11,11a-tetrahydro-8,9-bis(trimethylsilyl)tetracene-5,12- dione (13). This was prepared from **5** (150 mg, 0.5 mmol), 1,4-naphthoquinone (110 mg, 0.7 mmol) and **6** (140 mg, 0.6 mmol) in chloroform (10 mL) in the same manner as described above, yielding **13** (120 mg, 0.29 mmol, 58%) as colorless crystals: mp 128–129°C; ^1H NMR ($CDCl_3$) δ 0.14 (s, 18H), 3.78 (dd, J=3.6, 1.8 Hz, 2H), 5.84 (dd, J=3.6, 1.8 Hz, 2H), 7.26 (s, 2H), 7.42 (dd, J=4.2, 3.3 Hz, 2H), 7.62 (dd, J=5.7, 3.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.8, 50.1, 83.3, 126.2, 127.1, 133.7, 134.0, 140.5, 146.1, 194.3; MS *m/z* 262 ($C_{14}H_{22}OSi^+$). Anal. calcd for $C_{24}H_{28}O_3Si_2$: C, 68.53; H, 6.71. Found: C, 68.16; H, 6.79.

3.2.7. *endo*-5,14-Endoxy-5,5a,13a,14-tetrahydro-2,3-bis(trimethylsilyl)pentacene-6,13-dione (14). This was prepared from **5** (150 mg, 0.5 mmol), 1,4-anthroquinone (145 mg, 0.7 mmol) and **6** (140 mg, 0.6 mmol) in chloroform (10 mL) in the same manner as described above, yielding **14** (169 mg, 0.36 mmol, 72%) as colorless crystals: mp 195–196°C; ^1H NMR ($CDCl_3$) δ −0.07 (s, 18H), 3.87 (dd, J=3.6, 2.1 Hz, 2H), 5.87 (dd, J=3.6, 2.1 Hz, 2H), 7.24 (s, 2H), 7.57 (dd, J=6.3, 3.3 Hz, 2H), 7.84 (dd, J=6.3, 3.3 Hz, 2H), 8.12 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.6, 50.7, 83.6, 127.2, 128.2, 129.2, 129.7, 130.3, 134.6, 140.7, 145.8, 194.5; MS *m/z* 262 ($C_{14}H_{22}OSi^+$). HRMS (FAB) Calcd for $C_{28}H_{31}O_3Si_2$ (MH^+): 471.1806. Found: 471.1816.

3.2.8. 2,3-Dicyano-6,7-bis(trinethylsilyl)naphthalene (11). A mixture of **10** (100 mg, 0.3 mmol), lithium iodide (53 mg, 0.5 mmol) and DBU (0.1 mL, 5 mmol) in anhydrous THF (3 mL) was heated at reflux for 3 h under a nitrogen atmosphere. The mixture was poured into brine (5 mL) and extracted with ether (3×5 mL). The combined organic extracts were dried over $MgSO_4$. After evaporation of solvent under reduced pressure, the residue was chromatographed on silica gel (20 g, hexanes–ethyl acetate 30:1) to afford **11** (85 mg, 0.26 mmol, 88%) as a colorless solid: 209–210°C; ^1H NMR ($CDCl_3$) δ 0.47 (s, 18H), 8.22 (s, 2H), 8.32 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.7, 110.2, 115.9, 131.7, 135.2, 135.7, 149.8; MS *m/z* 323 (MH^+). HRMS (FAB) Calcd for $C_{18}H_{23}N_2Si_2$ (MH^+): 323.1394. Found: 323.1403.

3.3. General procedure for the preparation of quinones 15–17

3.3.1. 2,3,9,10-Tetrakis(trimethylsilyl)pentacene-6,13-dione (15). A suspension of **12** (60 mg, 0.09 mmol) in 90% acetic acid (3 mL) was heated at 100°C for 3 h under a nitrogen atmosphere. After being cooled to rt, most of the solvent was evaporated under vacuum. The residue was then subjected to chromatography on silica gel (20 g, hexanes–ethyl acetate 30:1) to afford **15** (21 mg, 0.034 mmol, 38%) as a bright yellow solid: mp 210–211°C; ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 36H), 8.40 (s, 4H), 8.90 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 1.8, 129.5,131.1, 133.8, 137.1, 147.4, 182.8; MS *m/z* 597 (MH^+). HRMS (FAB) Calcd for $C_{34}H_{45}O_2Si_4$ (MH^+): 597.2497. Found: 597.2467.

3.3.2. 8,9-Bis(trimethylsilyl)tetracene-5,12-dione (16). This was prepared from 13 (42 mg, 0.1 mmol) in the same manner as described above, yielding **16** (30 mg, 0.08 mmol, 75%) as a bright yellow solid: mp 172–173°C; ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 18H), 7.82 (dd, *J*=6.3, 3.3 Hz, 2H), 8.37 (s, 2H), 8.39 (dd, *J*=6.3, 3.3 Hz, 2H), 8.80 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.8, 127.5, 129.4, 130.2, 133.8, 134.1, 134.5, 137.2, 147.6, 183.0; MS *m/z* 402 (M^+). Anal. Calcd for $C_{24}H_{26}O_2Si_2$: C, 71.59; H, 6.51. Found: C, 71.11; H, 6.29.

3.3.3. 2,3-Bis(trimethylsilyl)pentacene-6,13-dione (17). This was prepared from **14** (47 mg, 0.1 mmol) in the same manner as described above, yielding **17** (34 mg, 0.08 mmol, 75%) as a bright yellow solid: mp 305–306°C; ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 18H), 7.70 (dd, *J*=6.3, 3.3 Hz, 2H), 8.11 (dd, *J*=6.3, 3.3 Hz, 2H), 8.39 (s, 2H), 8.88 (s, 2H), 8.93 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.8, 129.4, 129.6, 129.8, 130.1, 130.6, 131.1, 133.9, 135.2, 137.2, 147.5, 183.0; MS *m/z* 452 (M^+). HRMS (FAB) calcd for $C_{28}H_{29}O_2Si_2$ (MH^+): 453.1700. Found: 453.1706.

3.3.4. 7,8-Dicyano-1,4-epoxy-2,3-bis(trimethylsilyl)-1,4-dihydroanthracene (19). TfOH acid (0.14 mL, 1.6 mmol) was added dropwise to a suspension of iodobenzene diacetate (250 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) at 0°C. The resulting clear yellow solution was stirred at rt for 1 h. It was then cooled again to 0°C and a solution of **11** (250 mg, 0.8 mmol) in CH_2Cl_2 was added. After stirring for a further 1 h, the solvent was evaporated under reduced pressure and the crude residue was triturated with Et_2O (10 mL). The iodonium salt **18** was collected by filtration as a white powder and was used without further purification.

The white powder **18** obtained above was suspended in CH_2Cl_2 (3 mL) followed by addition of 3,4-bis(trimethylsilyl)furan **7** (200 mg, 0.9 mmol). TBAF in THF (1 M, 0.8 mL) was added slowly to the above mixture at 0°C. After stirring for 0.5 h, the mixture was diluted with CH_2Cl_2 (5 mL) and wash with water (3 mL), and brine (3 mL) successively. After drying over $MgSO_4$ and concentrating under reduced pressure, the crude product was chromatographed on silica gel (20 g, hexanes–ethyl acetate 8:1) to afford **19** (185 mg, 0.48 mmol, 60%) as a colorless solid: mp 190°C (decomp.); ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 18H), 6.00 (s, 2H), 7.61 (s, 2H), 8.19 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −0.1. 86.9, 110.3, 116.0, 117.9, 132.8, 135.1, 150.3, 162.9; MS *m/z* 387 ($M-1^+$). HRMS (FAB) calcd for $C_{22}H_{25}N_2OSi_2$ (MH^+): 389.1500. Found: 389.1502.

3.3.5. 2,3-Dicyano-7,8-bis(trimethylsilyl)anthrancene (20). THF (0.3 mL) was added with stirring to titanium (IV) chloride (0.13 mL, 1.2 mmol) at 0°C. A solution of $LiAlH_4$ in THF (1 M, 0.5 mL) followed by Et_3N (0.01 mL, 0.1 mmol) in THF (0.1 mL) was carefully introduced into the above suspension. The mixture was refluxed at 65°C for 0.5 h. After cooling to rt, **19** (15 mg, 0.04 mmol) was added. The mixture was stirred at rt for 12 h and then poured into 20% aqueous $NaHCO_3$ (5 mL). The resulting mixture was extracted with CH_2Cl_2 (5×5 mL). The combined organic solvent was dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel (5 g, hexanes–ethyl acetate 15:1) afforded **20** (11 mg, 0.03 mmol, 78%) as a yellow solid: mp 250°C (decomp.); ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 18H), 8.38 (s, 2H), 8.52 (s, 2H), 8.53 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.5, 108.2, 116.2, 128.3, 129.9, 132.7, 135.9, 137.6, 145.9; MS *m/z* 372 (M^+). HRMS (ESI) Calcd for $C_{22}H_{24}N_2Si_2Na$: 395.1370. Found: 395.1366.

3.3.6. [3,4,12,13,21,22,30,31-Octakis(trimethylsilyl)-2,3-naphthalocyaninato]zinc (21). To a solution of **11** (200 mg, 0.6 mmol) in hexanol (6 mL) heated at 90°C was added $Zn(OAc)_2 \cdot 2H_2O$ (66 mg, 0.3 mmol) followed by DBU (0.01 mL, 0.06 mmol). The mixture was then stirred at 90°C under nitrogn for 3 h. After cooling to rt, the mixture was poured into methanol–acetone (v/v 1:1, 30 mL). The precipitate was collected by suction filtration and subsequently washed with methanol (10 mL) and then dried in vacuo. The green solid obtained was further purified with a Soxhlet extractor using methanol–acetone (v/v 1:1, 60 mL). After complete removal of the brown colored impurities, the resulting green powder left was collected by extracting with THF (50 mL). Evaporation of solvent under reduced pressure provided 21 (80 mg, 0.24 mmol, 40%) as a green powder: ^{1}H NMR (THF-d_8) δ 0.66 (s, 72H), 8.85 (s, 8H), 9.54 (br. s, 8H); UV–Vis [THF, 4.2×10^{-6} M, λ_{max} nm (log ϵ)]: 767 (5.90), 7.31 (5.10), 684 (5.12), 337 (5.36); MS (LSI): an isotope cluster peaking at *m/z* 1353.46 (calcd for $C_{72}H_{88}N_8Si_8$ (M^+) 1353.45).

3.3.7. Ethoxy-5,6-bis(trimethylsilyl)-1,3-dihydroisobenzofuran (25). A mixture of **24** (250 mg, 1 mmol), NBS (550 mg, 3.1 mmol) and AIBN (2 mg, 0.01 mmol) in CCl_4 (5 mL) was refluxed for 3 h. After cooling to rt, the white solid was filtered off and the filtrate was washed with sat. $NaHCO_3$. After drying over $MgSO_4$ and concentrated under reduced pressure, the colorless oil obtained was taken up with dioxane–water (v/v 3:1 10 mL). $CaCO_3$ (900 mg, 9.0 mmol) was added to the solution and the mixture was refluxed for 24 h. The mixture was allowed to cool to rt and the $CaCO_3$ was removed by filtration. Dioxane was evaporated under vacuum. The residue left was extracted with Et_2O (4×5 mL). The combined organic extract was dried over $MgSO_4$ and concentrating under reduced pressure. Chromatography on silica gel (20 g, hexanes–ethyl acetate 5:1) provided a light yellow oil with R_f of 0.2 which was dissolved in absolute ethanol (2 mL). *p*-TsOH (2 mg, 0.01 mmol) was added and the solution was stirred for 6 h. After addition of $NaHCO_3$, the excess base was filtered off and the filtrate was concentrated. Chromatography on silica gel with 2% of triethylamine (10 g, hexanes–ethylacetate 10:1) provided **25** (115 mg, 0.38 mmol, 38%) as a colorless oil; ^{1}H NMR (actone-d_6) δ 0.39 (s, 18H), 1.17 (t, J=4.8 Hz, 3H), 3.59–3.75 (m, 2H), 4.97 (d, J=13.2 Hz, 1H), 5.11 (dd, J=13.2, 1.8 Hz, 1H), 6.20 (d, J=1.8 Hz, 1H), 7.71 (s, 2H); ^{13}C NMR (acetone-d_6) δ 2.2, 15.7, 63.2, 72.4, 107.4, 128.8, 130.3, 138.8, 140.9, 145.5, 147.5; MS *m/z* 306 (M^+). HRMS (ESI) Calcd for $C_{16}H_{28}O_2Si_2Na$: 331.1521. Found: 331.1519.

3.3.8. 5,10-Epoxy-5,10-dihydro-2,3-bis(trimethylsilyl)-anthracene (26). A solution of **25** (56 mg, 0.18 mmol) in anhydrous THF (3 mL) was cooled at 0°C. LDA (0.18 mmol, 1 M in THF) was added dropwise under nitrogen. After stirring for 10 min, the reaction was quenched with 1N HCl (0.1 mL, 0.55 mmol). Then phenyl [2-(trimethylsilyl)-1-phenyl]iodonium triflate (90 mg, 0.2 mmol) was added. To this suspension was added TBAF (1 M in THF, 0.2 mL) dropwise. After stirring for a further 0.5 h, the mixture was poured into water. The organic layer was collected and the aqueous residue was extracted with Et_2O (3×5 mL). The combined organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel (20 g, hexanes–ethyl acetate 30:1) afforded **26** (48 mg, 0.14 mmol, 80%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 18H), 6.07 (s, 2H), 7.04 (dd, J=5.1, 3.0 Hz, 2H), 7.37 (dd, J=5.1, 3.0 Hz, 2H), 7.67 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.1, 82.6, 120.5, 125.9, 126.6, 144.5, 147.3, 148.0; MS *m/z* 338 (M^+). HRMS (FAB) Calcd for $C_{20}H_{26}OSi_2$: 338.1517. Found: 338.1531.

3.3.9. 2,3-Bis(trimethylsilyl)anthracene (27).[24] THF (0.2 mL) was introduced to stirred titanium (IV) Chloride (0.08 mL, 0.7 mmol) at 0°C under nirogen. A suspension of $LiAlH_4$ (1 M in THF, 0.25 mL) was added carefully to the above suspension. Et_3N (10 mg, 0.1 mmol) in THF (0.2 mL) was added. The mixture was stirred and refluxed at 65°C for 0.5 h. It was allowed to cooled to rt. Compound **26** (35 mg, 0.1 mmol) in THF (0.2 mL) was added dropwise. The mixture was refluxed under nitrogen for 24 h. After cooling to rt, it was then poured into 20% $NaHCO_3$ solution (5 mL) and filtered. The filtration cake was washed with ether thoroughly. The filtrate was collected and the organic layer was separated. The aqueous residue was extracted with Et_2O (3×5 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel (15 g, hexanes) afforded **27** (28 mg, 0.88 mmol, 88%) as a colorless solid: ^{1}H NMR ($CDCl_3$) δ −0.8 (s, 18H), 6.83 (s, 2H), 7.38 (dd, J=5.1, 3.0 Hz, 2H), 7.77 (dd, J=5.1, 3.0 Hz, 2H), 7.84 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.1, 125.4, 126.1, 128.3, 130.6, 132.3, 136.2, 140.9; MS *m/z* 322 (M^+). Anal. calcd for $C_{20}H_{26}Si_2$: C, 74.46; H, 8.12. Found: C, 74.41; H, 8.15.

3.3.10. 5,12-Epoxy-5,12-Dihydro-2,3-bis(trimethylsilyl)-naphthacene (28). A solution of 25 (110 mg, 0.36 mmol) in anhydrous THF (5 mL) was cooled at 0°C. LDA (1 M in THF, 0.36 mL) was added dropwise under nitrogen. After stirring for 10 min, the reaction was quenched with 1N HCl (0.1 mL, 0.55 mmol). Then phenyl [2-(trimethylsilyl)-1-naphthyl]iodonium triflate (100 mg, 0.18 mmol) was added. To this suspension was then added TBAF (1 M in THF, 0.18 mL) dropwise. After stirring for a further 0.5 h, the mixture was poured into water. The organic layer was collected and the aqueous residue was extracted with Et_2O (3×5 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Chromatography on silica gel (20 g, hexanes–ethyl acetate 30:1) afforded **28** (56 mg, 0.29 mmol, 80%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 18H), 6.20 (s, 2H), 7.43 (dd, J=6.0, 3.3 Hz, 2H), 7.71–7.76 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 2.2, 82.4, 118.9, 126.2, 126.7, 128.2, 132.4, 143.9, 145.1, 146.6; MS *m/z* 389 (MH^+). HRMS (FAB) Calcd for $C_{24}H_{29}OSi_2$ (MH^+): 389.1751. Found: 389.1740.

3.3.11. 2,3-Bis(trimethylsilyl)naphthacene (29). THF (0.7 mL) was introduced to stirred $TiCl_4$ (0.18 mL, 1.67 mmol) at 0°C under nitrogen. A suspension of $LiAlH_4$ (1 M in THF, 0.65 mL) was added carefully to the above suspension. Et_3N (0.04 mL, 0.38 mmol) in THF (0.7 mL) was added. The mixture was stirred and refluxed at 65°C for 0.5 h. It was allowed to cool to rt. Compound **28** (100 mg, 0.26 mmol) in THF (0.7 mL) was added dropwise. The mixture was refluxed under nitrogen for 24 h. After cooling to rt, it was then poured into 20% $NaHCO_3$ solution (5 mL) and filtered. The filtration cake was washed with ether thoroughly. The filtrate was collected and the organic layer was separated. The aqueous residue was extracted with Et_2O (3×5 mL). After drying over $MgSO_4$ and concentrated under reduced pressure, **29** was obtained (85 mg, 0.23 mmol, 90%) with high purity as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 18H), 7.42 (dd, J=6.9, 3.3 Hz, 2H), 8.05 (dd, J=6.6, 3.3 Hz, 2H), 8.37 (s, 2H), 8.72 (s, 2H), 8.76 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 2.0, 125.2, 126.2, 126.5, 128.3, 130.4, 130.8, 131.5, 136.5, 140.6; MS *m/z* 372 (M^+). HRMS (EI) Calcd for $C_{24}H_{28}Si_2$: 372.1724. Found: 372.1719.

3.4. General procedure for the preparation of Diels–Alder adducts 7–10, 12–14 from isobenzofuran 2

3.4.1. 2,3-Dicarbomethoxy-1,4-epoxy-1,4-dihydro-6,7-bis(trimethylsilyl)naphthalene (7). A solution of **25** (150 mg, 0.5 mmol) in anhydrous THF (5 mL) was cooled at 0°C. LDA (1 M in THF, 0.5 mL) was added dropwise under nitrogen. After stirring for 10 min at rt, the reaction was quenched with 1N HCl (0.1 mL, 0.55 mmol). Then dimethyl acetylenedicarboxylate (0.07 mL, 0.6 mmol) was added. The solution was then allowed to stir for 2 h. After evaporation of solvent under reduced pressure, the residue was subjected to chromatography on silica gel (20 g, hexanes–ethyl acetate 10:1) to afford **7** (151 mg, 0.38 mmol, 75%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

3.4.2. *trans*-2,3-Dicarbomethoxy-1,4-epoxy-1,2,3,4,-tetrahydro-6,7-bis(trimethylsilyl) naphthalene (8). This was prepared from **25** (150 mg, 0.5 mmol), dimethyl fumarate (46 mg, 0.6 mmol) and LDA (1 M in THF, 0.5 mL) in THF (5 mL) in the same manner as described above, yielding **8** (158 mg, 0.39 mmol, 78%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

3.4.3. 3a,4,9,9a-Tetrahydro-2-phenyl-6,7-bis(trimethylsilyl)-1*H*-benz[*f*]isoindole-1,3-(2*H*)-dione (9). This was prepared from 25 (150 mg, 0.5 mmol), *N*-phenylmaleimide (100 mg, 0.6 mmol) and LDA (1 M in THF, 0.5 mL) in THF (5 mL) in the same manner as described above, yielding **9** (152 mg, 0.35 mmol, 70%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

3.4.4. *trans*-2,3-Dicyano-1,4-epoxy-6,7-1,2,3,4,-tetrahydro-bis(trimethylsilyl) naphthalene (10). This was prepared from **25** (150 mg, 0.5 mmol), fumaronitrile (46 mg, 0.6 mmol) and LDA (1 M in THF, 0.5 mL) in THF (5 mL) in the same manner as described above, yielding **10** (136 mg, 0.4 mmol, 80%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

3.4.5. *exo/endo*-[5,14],[7,12]-Diendoxy-5,5a,6a,7,12,12a,13a,14-octahydro-2,3,9,10-tetrakis(trimethylsilyl)-pentacene-6,13-dione (12). This was prepared from **25** (170 mg, 0.5 mmol), *p*-benzoquinone (32 mg, 0.3 mmol) and LDA (1 M in THF, 0.5 mL) in THF (5 mL) in the same manner as described above, yielding **12** (102 mg, 0.16 mmol, 54%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

3.4.6. *endo*-6,11-Endoxy-5a,6,11,11a-tetrahydro-8,9-bis(trimethylsilyl)tetracene-5,12-dione (13). This was prepared from **25** (150 mg, 0.5 mmol), 1,4-naphthoquinone (110 mg, 0.7 mmol) and LDA (1 M in THF, 0.5 mL) in THF (5 mL) in the same manner as described above, yielding **13** (120 mg, 0.29 mmol, 58%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

3.4.7. *endo*-5,14-Endoxy-5,5a,13a,14-tetrahydro-2,3-bis(trimethylsilyl)pentacene-6,13-dione (14). This was prepared from **25** (150 mg, 0.5 mmol), 1,4-anthraoquinone (145 mg, 0.7 mmol) and LDA (1 M in THF, 0.5 mL) in THF (5 mL) in the same manner as described above, yielding **14** (169 mg, 0.36 mmol, 72%) as a colorless solid: the spectroscopic data were identical to an authentic sample prepared previously.

Acknowledgements

The work described in this project is fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (project CUHK 4014/98P).

References

1. A preliminary communications has appeared: Yick, C. Y.; Chan, S. H.; Wong, H. N. C *Tetrahedron Lett.* **2000**, *41*, 5957.
2. Wittig, G.; Pohmer, L. *Chem. Ber.* **1956**, *89*, 1334.
3. Feiser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1956**, *43*, 1599. Paquette, L. A. *J. Org. Chem.* **1965**, *30*, 629. McCullogh, R.; Rye, A. R.; Wege, D. *Tetrahedron Lett.* **1969**, 5231. Wilson, W. S.; Warrener, R. N. *Tetrahedron Lett.* **1970**, 5203.
4. Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346.
5. Shang, M.; Butler, D. N.; Warrener, R. N. *Chem Commun.* **2001**, 1550.
6. Song, Z. Z.; Ho, M. S.; Wong, H. N. C. *J. Org. Chem.* **1994**, *59*, 3917. For a review, see Ye, X.-S.; Yu, P.; Wong, H. N. C. *Liebigs Ann. Chem.* **1997**, 459.
7. Wong, M. K.; Leung, C. Y.; Wong, H. N. C. *Tetraheron* **1997**, *53*, 3497.
8. Mirsadeghi, S.; Rickborn, B. J. *J. Org. Chem.* **1986**, *51*, 986.
9. Crump, S. L.; Netka, J.; Rickborn, B. J. *J. Org. Chem.* **1985**, *50*, 2746.
10. Tobia, D.; Rickborn, B. J. *J. Org. Chem.* **1986**, *51*, 3849.
11. Pollart, D. J.; Rickborn, B. J. *J. Org. Chem.* **1986**, *51*, 3155.
12. Ushakov, S. N.; Itenberg, A. M. *Zh. Obshch. Khim.* **1937**, *7*, 2495. *Chem. Abstr.* **1938**, *32*, 2083. White, J. M. *Aust. J. Chem.* **1995**, *48*, 1227. Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.-Y.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.
13. Butte, W. A.; Case, F. H. *J. Org. Chem.* **1961**, *26*, 4690.
14. Bock, H.; Ansari, M.; Nagel, N.; Havlas, Z. *J. Organomet. Chem.* **1995**, *499*, 63.
15. Winling, A.; Russell, R. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3921.
16. Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674.
17. Polley, R.; Hanack, M. *J. Org. Chem.* **1995**, *60*, 8278.
18. Gupta, D. N.; Hodge, P.; Khan, N. *J. Chem. Soc., Perkin Trans. 1* **1981**, 689.
19. Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140.
20. Kaplan, M. L.; Lovinger, W. D.; Reents, Jr., W. D.; Schmidt, P. H. *Mol. Cryst. Liq. Cryst.* **1984**, *112*, 345.
21. Asthon, P. R.; Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Raymo, F. M.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J.; J, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 5422. Asthon, P. R.; Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Raymo, F. M.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. Eur. Pat. Appl. EP 229754, CH Appl. 16 January 1986.
22. Crump, S. L.; Rickborn, B. J. *J. Org. Chem.* **1984**, *49*, 304.
23. Fukatsu, N.; Fujiwara, Y.; Kitamura, T. *J. Org. Chem.* **1998**, *63*, 8579.
24. Wu, Y. M.; Wong, H. N. C. Unpublished results.