Synthesis of spiro-indanes by cycloaddition strategy

Sambasivarao Kotha * and Ethirajan Manivannan

Department of Chemistry, Indian Institute of Technology, Mumbai-400 076, India.
E-mail: srk@chem.iitb.ac.in; Fax: +91 22 576 7152; Tel: +91 22 576 7160

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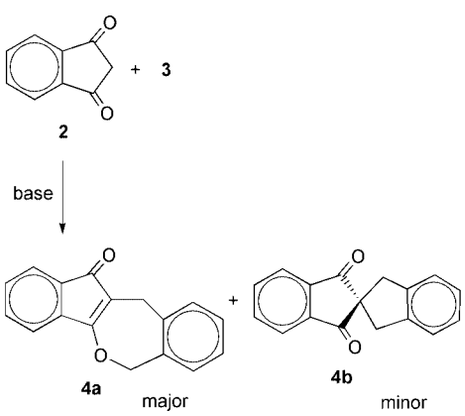
Various 2,2′-spirobiindane-1,3-dione derivatives which are useful precursors for the synthesis of unsymmetrical benzoannelated fenestranes are reported *via* [2+2+2] and [4+2] cycloaddition reactions as key steps.

Introduction

The spiro unit[1] is an important structural element in several natural products (*e.g.*, terpenoids[2] and alkaloids) and non-natural products such as fenestranes (*e.g.* **1**, Fig. 1)[3] and spiranes.[4] Some of the spiro compounds have been utilized as building blocks in thermotropic liquid crystalline materials which in turn are used in optical devices.[5] In connection with the synthesis of unsymmetrical benzoannelated fenestranes such as **1**, we need a viable route to spirobiindanediones **6**.

In this regard, a perusal of the literature indicated that the alkylation of indane-1,3-dione **2** with α,α′-dibromo-*o*-xylene **3** in the presence of a base gave *o*-alkylated product **4a**, and the required 2,2′-spirobiindane-1,3-dione **4b** was formed as a minor product (Scheme 1).[6]



Scheme 1

As part of a programme directed towards the synthesis of spirocyclic systems[7] we envisaged compound **6** as a useful precursor for the synthesis of unsymmetrical benzoannelated fenestranes. Two possible retrosynthetic routes for the preparation of compound **6** involving cycloaddition reactions are shown in Scheme 2. Path **a** identified a bis-propargylated compound **5**, which upon [2+2+2] cycloaddition reaction with various monoynes may deliver novel derivatives of **6**. Alternatively, [4+2] cycloaddition reaction of the diene **7** with a suitable dienophile followed by oxidation may give spiro analogues related to **6** (path **b**). These routes are strategically unique from the other possible methods involving preformed benzene derivatives as starting materials. The current methodologies involve the generation of a benzonoid ring system by cycloaddition reaction and consequently one can create considerable functionality in the final target by suitable selection of the reacting partners.[8] Herein, we report a detailed account of our results towards the realization of the strategies shown in Scheme 2.

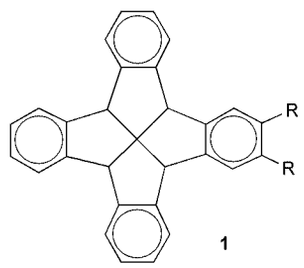
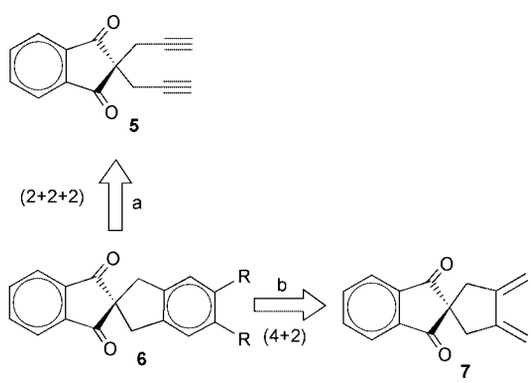


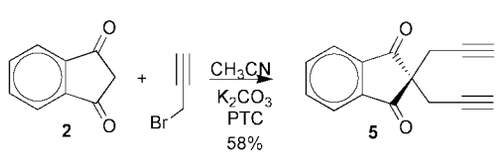
Fig. 1 Benzoannelated fenestrane.



Scheme 2

Results and discussion

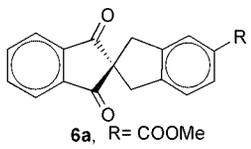
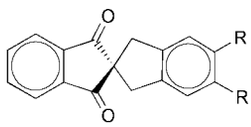
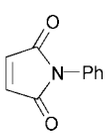
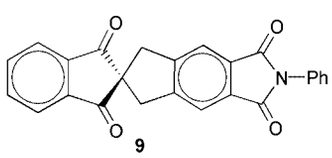
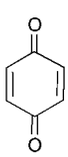
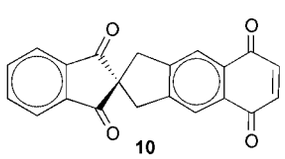
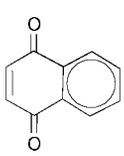
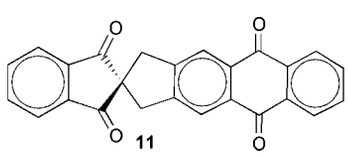
To prepare the key intermediate **5**, indanedione **2** was treated with propargyl bromide (3-bromoprop-l-yne) under phase-transfer catalysis (PTC) conditions [K_2CO_3, dry CH_3CN, tetrabutylammonium hydrogen sulfate (TBAHS) at RT] established in our laboratory[9] to deliver the expected bis-propargylated compound **5** (Scheme 3). Conventional alkylation conditions gave very low yields (less than 10%) of the required product. The symmetrical nature of compound **5** was established by its 8-line ^{13}C NMR spectral data (δ_C 22.8, 55.1, 71.9, 77.6, 123.3, 136.0, 142.3 and 200.5). The molecular-ion peak at *m*/*z* 222 further confirmed the structure of product **5**.



Scheme 3

DOI: 10.1039/b106280h

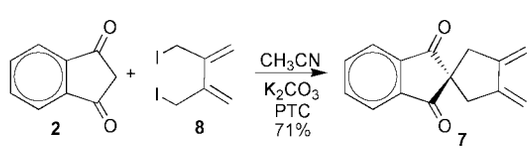
Table 1 Various spiro-indanes prepared by cycloaddition strategy

Entry	Dienophile/Monoyne	Spiro product	DA[a]/2+2+2	Yield (%)
1		 **6a**, R= COOMe	DA 2+2+2 DA 2+2+2 DA	53 18 54 25 87
		6b, R= Ts **6c**, R= TMS		
2		 **6d**, R= COOMe	DA 2+2+2 2+2+2 2+2+2	87 22 26 26
		6e, R= Ph **6f**, R= TMS		
3		 **9**	DA	65
4		 **10**	DA	45
5		 **11**	DA	75

[a] DA = Diels–Alder.

Availability of the bis-propargyl compound **5** readily, and in quantity, has encouraged us to explore the [2+2+2] cycloaddition strategy. Under Wilkinson's catalyst conditions the [2+2+2] cycloaddition strategy was not successful. However, when η^5-cyclopentadienylcobalt complex $CpCo(CO)_2$ was used as a co-trimerization catalyst the [2+2+2] cycloaddition strategy was realized.[10] Thus, the slow addition of diyne **5** in dry toluene to a refluxing solution of monoyne in *n*-octane under inert conditions gave the required spiro derivatives. Various monoynes that underwent the co-trimerization reaction are shown in Table 1. In the case of methyl propiolate as the monoyne, the reaction was complete after 26 h (syringe pump). Then, the reaction mixture was evaporated at reduced pressure to give the crude product which was further purified by silica gel column chromatography (5 : 95, ethyl acetate and petroleum ether) to give compound **6a** (mp 179–180 °C) in 18% yield. The product was characterized by its complementary spectral data (^{13}C and ^1H NMR). The molecular-ion peak at *m*/*z* 306 and the elemental analysis further confirmed the structure of product **6a**.

Having demonstrated the [2+2+2] cycloaddition strategy, the next task was the preparation of the key diene building block **7**. In this regard, alkylation of the indanedione **2** with highly sensitive 2,3-bis(iodomethyl)buta-1,3-diene[11] **8** under PTC conditions gave the diene **7** (Scheme 4).[12] The presence of the diene **7** was confirmed by GC-MS and it was stored in diethyl ether solution and used immediately (compound **7** in the solid state polymerizes even at 0 °C). Reaction of the diene **7** with various dienophiles such as methyl propiolate in dry



2 **8** **7**

Scheme 4

toluene under reflux conditions for 18 h gave the aromatized product **6a** directly (53% isolated yield). Compound **6a** obtained by this route was found to be identical with the compound prepared from the [2+2+2] cycloaddition route. The driving force for the dehydrogenation reaction of the Diels–Alder adduct under thermal conditions is the aromatization. To expand the scope of this methodology, the diene **7** was treated with other readily available dienophiles under similar reaction conditions and the results are summarized in Table 1.

Conclusions

In conclusion, we have shown that [2+2+2] and [4+2] cycloaddition strategies are useful to prepare various 2,2′-spirobiindane-1,3-dione derivatives. The methodologies reported here are likely to foster the progress of fenestrane synthesis. In addition, several indane derivatives themselves are biologically active molecules[13] and some of the quinones prepared here are useful as artificial photosynthetic probes.[14] The building blocks **5** and **7** prepared here may be useful for combinatorial synthesis of various indane-based biologically important target molecules.

Experimental

General details

Dry diethyl ether, tetrahydrofuran, benzene and toluene were obtained by distillation over sodium benzophenone ketyl. Chloroform, dichloromethane, tetrachloromethane and acetonitrile were distilled over P_2O_5. Dry toluene and *n*-octane were obtained by distillation over sodium. Phenylacetylene (trimethylsilyl)acetylene and 2,3-dimethylbuta-1,3-diene were purchased from Aldrich Chemical Co., Milwaukee, WI, USA. Cobalt catalyst $CpCo(CO)_2$ was purchased from Strem Chemical Co., Newburyport, MA, USA. Methyl propiolate and bis(trimethylsilyl)acetylene were obtained from Lancaster Synthesis, Lancashire, UK. A Razel A-99 syringe pump was used in all high-dilution reactions. Melting points are uncorrected. Petroleum ether refers to the fraction with distillation range 60–80 °C. Infrared spectra were recorded on a Nicolet 400 FT IR spectrometer in KBr–CCl_4 with absorptions in cm^{-1}. UV–visible spectra were recorded on a Shimadzu UV 2100 or UV 260 instrument. NMR spectra were recorded on a Bruker 300 MHz spectrometer for samples as $CDCl_3$ solutions. *J*-Values are in Hz. Chemical shifts δ are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a GCD 1800A Hewlett-Packard GC-MS spectrometer. Microanalyses were carried out on a Carlo-Erba Struentazione MOD 1106 instrument.

Preparation of dipropargyl compound 5

To a solution of indane-1,3-dione **2** (450 mg, 3 mmol) in dry CH_3CN (15 ml) were added powdered K_2CO_3 (300 mg, 2.17 mmol), TBAHS (99 mg, 0.29 mmol) and propargyl bromide (0.53 ml, 6 mmol). The resulting mixture was stirred at RT for 48 h. Then, the reaction mixture was filtered and the filtrate was evaporated at reduced pressure to give a crude product, which was purified on a silica gel column. Elution of the column with petroleum ether–ethyl acetate mixture (97 : 3) gave the dipropargyl product **5** (400 mg, 58%); R_f 0.50 (20% ethyl acetate–petroleum ether), mp 79–80 °C; ν_{max} (KBr)/cm^{-1} 1703 (C=O); λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 248 (10.166 × 10^3), 227 (42.138 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 1.79 (t, *J* 2.5, H-10, -10′), 2.69 (d, *J* 2.5, H-8, -8′), 7.89 (dd, *J* 2.9, 5.7, ArH), 8.04 (dd, *J* 2.9, 5.7, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 22.8 (C-8, -8′), 55.1 (C-2), 71.9 (C-10, -10′), 76.6 (C-9, -9′), 128.3 (C-4, -7), 136.0 (C-3a, -7a), 142.3 (C-5, -6), 200.5 (C=O); *m*/*z* 222 (M^+) (Found: C, 81.39; H, 4.55. $C_{15}H_{10}O_2$ requires C, 81.07; H, 4.53%).

General procedure for the synthesis of spiro-biindanes by a [2+2+2] cyclotrimerization reaction

A 5 ml two-neck round-bottom flask fitted with a reflux condenser was charged with methyl propiolate (120 mg, 1.4 mmol) in *n*-octane (3 ml), and the solution was heated at 140 °C under argon for 3 h. A solution of diyne **5** (60 mg, 0.270 mmol) and $CpCo(CO)_2$ (4 μl) in dry toluene (1 ml) was added (syringe pump) over a period of 16 h. Then, the reaction mixture was stirred at 140 °C for an additional 6 h, cooled, and the solvent was evaporated off under reduced pressure to give the crude product, which was purified on a silica gel column. Elution of the column with 5% ethyl acetate–petroleum ether gave the starting diyne (25 mg recovery). Continued elution of the column with the same solvent system gave the trimerized product **6a** (9 mg, 18%); R_f 0.47 (20% ethyl acetate–petroleum ether); mp 179–180 °C; ν_{max} (KBr)/cm^{-1}1690, 1716; λ_{max}(CH_3CN)/ε M^{-1} cm^{-1} 225 (47.586 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 3.38 (s, 4H, H-5, -12), 3.91 (s, 3H, OCH_3), 7.28 (d, *J* 7.5, 1H), 7.87–7.95 (m, 4H, ArH), 8.04 (dd, *J* 3.0, 5.7, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 40.5 (C-5, -12), 52.0 (ester OCH_3), 58.8 (C-13), 123.8 (C-7, -10), 124.1 (C-1), 125.7 (C-3), 129.2 (C-4), 129.6 (C-2), 135.9 (C-8, -9), 140.8 (C-4a), 141.6 (C-6a, -10a), 145.9 (C-12a), 166.8 (ester C=O), 202.1 (C=O); *m*/*z* 306 (M^+) (Found: C, 74.71; H, 4.95. $C_{19}H_{14}O_4$ requires C, 74.50; H, 4.61%).

Preparation of spiro-biindane 6d. By adaptation of the general procedure, dimethyl acetylenedicarboxylate (DMAD) (64 mg, 0.450 mmol) in *n*-octane (3 ml) was heated at 140 °C under argon for 3 h. A solution of diyne **5** (50 mg, 0.255 mmol) and $CpCo(CO)_2$ (4 μl) in dry toluene (1 ml) was added (syringe pump) over a period of 10 h. Then, the reaction mixture was stirred at 140 °C for an additional 8 h, cooled, and the solvent was evaporated off under reduced pressure to give the crude product, which was purified by silica gel column chromatography. Elution of the column with 10% ethyl acetate–petroleum ether gave the trimerized product **6d** (18 mg, 22%); R_f 0.15 (40% ethyl acetate–petroleum ether); mp 136–137 °C; ν_{max} (CCl_4)/cm^{-1} 1703, 1722 (C=O); λ_{max}(CH_3CN)/ε M^{-1} cm^{-1} 226 (37.926 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 3.38 (s, 4H, H-5, -12), 3.90 (s, 6H, H-14, -14′), 7.58 (s, 2H, H-1, -4), 7.90 (dd, *J* 3.2, 5.8, 2H, ArH), 8.03 (dd, *J* 3.2, 5.8, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 40.3 (C-5, -12), 52.5 (ester OCH_3), 58.6 (C-13), 123.8 (C-7, -10), 124.8 (C-1, -4), 131.5 (C-2, -3), 136.1 (C-8, -9), 141.3 (C-6a, -10a), 144.0 (C-4a, -12a), 168.0 (ester C=O), 201.9 (C=O); *m*/*z* 364 (M^+); HRMS: *m*/*z* for $C_{21}H_{16}O_6$ Calc: *M*, 364.0946. Found: M^+, 364.0920.

Preparation of spiro-biindane 6c. According to the general procedure, a solution of (trimethylsilyl)acetylene (45 mg, 0.459 mmol) in *n*-octane (3 ml) was heated at 140 °C under argon for 3 h. A solution of diyne **5** (50 mg, 0.225 mmol) and $CpCo(CO)_2$ (4 μl) in dry toluene (1 ml) was added (syringe pump) over a period of 14 h. Then, the reaction mixture was stirred at 140 °C for an additional 8 h, cooled, and the solvent was evaporated off under reduced pressure to give the crude product, which was purified by silica gel column chromatography. Elution of the column with 2% ethyl acetate–petroleum ether gave trimerized product **6c** (18 mg, 25%); R_f 0.40 (20% ethyl acetate–petroleum ether); ν_{max} (CCl_4)/cm^{-1} 1712 (C=O); λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 226 (18.00 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 0.26 (s, 9H, $SiMe_3$), 3.35 (d, *J* 2.2, 4H), 7.21 (1/2ABq, *J* 7.6, 1H, ArH), 7.37 (s, 1H), 7.38 (1/2ABq, *J* 7.6, 1H, ArH), 7.88 (dd, *J* 3.0, 5.8, 2H, ArH), 8.03 (dd, *J* 3.0, 5.7, 2H, ArH); *m*/*z* 320 (M^+); HRMS: *m*/*z* for $C_{20}H_{20}O_2Si$ Calc: *M*, 320.1232. Found: M^+, 320.1231.

Preparation of spiro-biindane 6f. As per the general procedure, a solution of bis(trimethylsilyl)acetylene (76 mg, 0.45 mmol) in *n*-octane (3 ml), was heated at 140 °C under argon for 3 h. A solution of diyne **5** (50 mg, 0.23 mmol) and $CpCo(CO)_2$ (4 μl) in dry toluene (1 ml) was added (syringe pump) over a period of 11 h. Then, the reaction mixture was stirred at 140 °C for an additional 12 h, cooled, and the solvent was evaporated off under reduced pressure to give the crude product, which was purified by silica gel column chromatography. The column was eluted with 3% ethyl acetate–petroleum ether to give trimerized product **6f** (16 mg, 28%); R_f 0.57 (20% ethyl acetate–petroleum ether); ν_{max} (CCl_4)/cm^{-1} 1709 (C=O); λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 226 (30.065 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 0.36 (s, 18H, $SiMe_3$), 3.36 (s, 4H, H-5, -12), 7.54 (s, 2H, H-1, -4), 7.88 (dd, *J* 3.0, 5.7, 2H, ArH), 8.03 (dd, *J* 3.0, 5.7, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 2.1 ($SiMe_3$), 41.0 (C-5, -12), 58.3 (C-13), 123.7 (C-7, -10), 131.2 (C-1, -4), 135.9 (C-8, -9), 140.0 (C-2, -3), 141.6 (C-4a, -12a), 144.7 (C-6a, -10a), 203.1 (C=O); *m*/*z* 392 (M^+); HRMS: *m*/*z* for $C_{23}H_{28}O_2Si_2$ Calc: *M*, 392.1627. Found: M^+, 392.1620.

Preparation of spiro-biindane 6e. A solution of diphenylacetylene (80 mg, 0.45 mmol) in *n*-octane (3 ml) was heated at 140 °C under argon for 3 h according to the general procedure. A solution of the diyne **5** (50 mg, 0.225 mmol) and $CpCo(CO)_2$

(4 μl) in dry toluene (1 ml) was added (syringe pump) over a period of 12 h. The reaction mixture was stirred at 140 °C for an additional 10 h, cooled, and the solvent was evaporated off under reduced pressure to give the crude product, crystallization of which from ethyl acetate–petroleum ether (50 : 50) gave colorless crystals of trimerized product **6e** (24 mg, 26%); R_f 0.45 (15% ethyl acetate–petroleum ether); mp 222–223 °C; ν_{max} (KBr)/cm^{-1} 1705 (C=O); λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 226 (41.04 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 3.44 (s, 4H, H-5, -12), 7.11–7.23 (m, 10H, ArH), 7.27 (s, 2H, H-1, -4), 7.90 (dd, *J* 3.2, 5.8, 2H, ArH), 8.05 (dd, *J* 3.2, 5.8, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 40.6 (C-5, -12), 58.9 (C-13), 123.7, 126.3, 127.8, 129.9, 135.9, 139.7, 139.9, 141.5, 141.7, 203.0 (C=O); *m*/*z* 400 (M$^+$) (Found: C, 86.38; H, 4.79. $C_{29}H_{20}O_2$ requires C, 86.97; H, 5.03%).

Preparation of spiro-diene 7

To a solution of indane-1,3-dione **2** (325 mg, 2.22 mmol) in dry CH_3CN (12 ml) were added diiododiene **8** (250 mg, 0.75 mmol), powdered K_2CO_3 (290 mg, 2.1 mmol) and TBAHS (90 mg, 0.26 mmol) and the reaction mixture was stirred for 24 h. Then, the reaction mixture was filtered and the filtrate was dried under reduced pressure to give a gummy solid. The crude product was purified on a silica gel column. Elution of the column with ethyl acetate–petroleum ether (3 : 97) gave the spiro-diene **7** [12] (120 mg, 71%). The diene was found to be highly sensitive in the solid state and readily polymerizes in solution, but is relatively stable when dissolved in solvents such as toluene and diethyl ether (it should be kept at sub-zero temperature and used within a week); R_f 0.44 (15% ethyl acetate–petroleum ether); *m*/*z* 224 (M$^+$).

General procedure for the synthesis of spiro-biindane derivative by the Diels–Alder approach

The diene **7** (20 mg, 0.089 mmol) was dissolved in a mixture of dry toluene (2 ml) and methyl propiolate (40 mg, 0.476 mmol) and the solution was heated at 110 °C for 48 h. The solvent was removed at reduced pressure and the resulting crude mixture was charged on a silica gel column. Elution of the column with 5% ethyl acetate–petroleum ether solvent gave the starting diene **7** (9 mg recovery). Continued elution of the column with the same solvent system gave aromatized spiro-biindane **6a** (8 mg, 53%). The spectral data of this compound matched those of the compound obtained by the [2+2+2] cycloaddition route.

Preparation of spiro-biindane 6d. By adaptation of the general procedure, the diene **7** (11 mg, 0.049 mmol) was dissolved in dry toluene (3 ml), and together with DMAD (21 mg, 0.148 mmol) the mixture was refluxed at 110 °C for 24 h. The solvent was removed at reduced pressure and the resulting crude mixture was charged on a silica gel column. Elution of the column with 5% ethyl acetate–petroleum ether gave the aromatized spiro-biindane **6d** (13 mg, 87%). The spectral data of this compound matched those of the compound obtained by the [2+2+2] cycloaddition route.

Preparation of spiro-biindane 6b. According to the general procedure, the diene **7** (30 mg, 0.134 mmol) was dissolved in dry toluene (4 ml) and treated with ethynyl *p*-tolyl sulfone (22 mg, 0.133 mmol) at 110 °C for 29 h. Then, the solvent was removed at reduced pressure and the resulting crude product was charged on a silica gel column. Elution of the column with 5% ethyl acetate–petroleum ether gave the aromatized spiro-biindane **6b** (27 mg, 54%); R_f 0.27 (30% ethyl acetate–petroleum ether); ν_{max} (CCl_4)/cm^{-1} 1705 (C=O), 1645, 1600 (SO_2Ar); λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 246 (25.175 × 10^3), 227 (49.346 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 2.41 (s, 3H, Me), 3.36 (s, 4H, H-5, -12), 7.29–7.36 (m, 3H, ArH), 7.76–7.84 (m, 4H, ArH), 7.90 (dd, *J* 3.2, 5.8, 2H, ArH), 8.00 (dd, *J* 3.2, 5.8, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 21.5 (Me), 40.2, 40.4, 58.5 (C-13), 104.9, 123.4, 123.8, 125.0, 127.0, 127.6, 130.0, 136.2, 138.8, 141.3, 141.8, 144.1, 146.3, 202.1 (C=O); *m*/*z* 402 (M$^+$); HRMS: *m*/*z* for $C_{24}H_{18}O_4S$ Calc: *M*, 402.0957. Found: M$^+$, 402.0927.

Preparation of spiro-biindane 9. To a solution of diene **7** (24 mg, 0.107 mmol) in dry toluene (3 ml) was added *N*-phenylmaleimide (40 mg, 0.231 mmol) and the reaction mixture was refluxed at 110 °C for 18 h according to the general procedure. The solvent was removed at reduced pressure and the resulting crude product was charged on a silica gel column. Elution of the column with 5% ethyl acetate–petroleum ether gave the starting diene **7** (3 mg recovery). Continued elution of the column with the same solvent system gave the aromatized spiro-biindane **9** (24 mg, 65%); R_f 0.44 (20% ethyl acetate–petroleum ether); ν_{max} (CCl_4)/cm^{-1} 1710 (C=O); NMR (300 MHz; $CDCl_3$) δ_H 3.48 (s, 4H, H-6, -13), 7.40–7.54 (m, 5H, ArH), 7.79 (s, 2H, H-1, -5), 7.94 (dd, *J* 2.9, 5.7, 2H, ArH), 8.06 (dd, *J* 2.9, 5.7, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 40.3 (C-6, -3), 58.8 (C-14), 119.8 (C-3b, -3b′), 124.0 (C-8, -11), 126.6 (C-1, -5), 128.0, 128.9 (C-3c, -3c′), 129.1, 131.7 (C-3a), 136.4 (C-9, -10), 141.3 (C-7a, -11a), 147.9 (C-5a, -13a), 167.2 (C-2, -4), 201.8 (C=O); *m*/*z* 393 (M$^+$); HRMS: *m*/*z* for $C_{25}H_{15}NO_4$ Calc: *M*, 393.1000. Found: M$^+$, 393.1003.

Preparation of spiro-biindane 10. By following the general procedure, the diene **7** (15 mg, 0.0669 mmol) was dissolved in dry toluene (3 ml) and treated with *p*-benzoquinone (30 mg, 0.278 mmol) at 110 °C for 14 h. The solvent was removed at reduced pressure and the resulting crude product was charged on a silica gel column. Elution of the column with 10% ethyl acetate–petroleum ether gave the aromatized spiro-biindane **10** (8 mg, 45%); R_f 0.31 (20% ethyl acetate–petroleum ether); mp greater than 240 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1722 (C=O), 1665; λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 226 (22.626 × 10^3), 248 (12.527 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 3.46 (s, 4H, H-7, -14), 6.96 (s, 2H, H-3, -4), 7.93 (dd, *J* 3.2, 5.8, 2H, ArH), 7.95 (s, 2H, H-1, -6), 8.05 (dd, *J* 3.2, 5.8, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 40.6 (C-7, -14), 58.0 (C-15), 122.4 (C-1, -6), 123.9 (C-9, -12), 131.8 (C-1a, -5a), 136.2 (C-10, -11), 138.5 (C-3, -4), 141.4 (C-8a, -12a), 147.2 (C-6a, -14a), 184.8 (C-2, -5), 201.8 (C=O); *m*/*z* 328 (M$^+$); HRMS: *m*/*z* for $C_{21}H_{12}O_4$ Calc: *M*, 328.0735. Found: M$^+$, 328.0710.

Preparation of spiro-biindane 11. A solution of the diene **7** (21 mg, 0.0804 mmol) in dry toluene (2 ml) was allowed to react with 1,4-naphthoquinone (40 mg, 0.253 mmol) at 110 °C for 30 h by following the general procedure. The solvent was removed at reduced pressure and the resulting crude product was charged on a silica gel column. Elution of the column with 5% ethyl acetate–petroleum ether gave the starting diene **7** (3 mg recovery). Continuous elution of the column with the same solvent system gave the aromatized spiro-biindane **11** (23 mg, 75%); R_f 0.15 (20% ethyl acetate–petroleum ether); mp 283–284 °C; ν_{max} (KBr)/cm^{-1} 1702 (C=O), 1664; λ_{max} (CH_3CN)/ε M^{-1} cm^{-1} 226 (21.429 × 10^3), 261 (12.381 × 10^3); NMR (300 MHz; $CDCl_3$) δ_H 3.50 (s, 4H, H-9, -16), 7.80 (dd, *J* 3.2, 5.8, 2H, ArH), 7.92 (dd, *J* 2.9, 5.8, 2H, ArH), 8.05 (dd, *J* 3.2, 5.8, 2H, ArH), 8.18 (s, 2H, ArH), 8.32 (dd, *J* 3.2, 5.8, 2H, ArH); NMR (75.43 MHz; $CDCl_3$) δ_C 40.5 (C-9, -16), 58.5 (C-17), 123.1 (C-11, -14), 123.8 (C-1, -8), 127.2 (C-3, -6), 133.4 (C-2a, -6a), 133.5 (C-1a, -7a), 133.9 (C-4, -5), 136.1 (C-12, -13), 141.3 (C-10a, -14a), 147.4 (C-8a, -16a), 182.8 (C-2, -7), 201.7 (C=O); *m*/*z* 378 (M$^+$); HRMS: *m*/*z* for $C_{25}H_{14}O_4$ Calc: *M*, 378.0892. Found: M$^+$, 378.0858.

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