Synthesis of 2-Mono- and 2,3-Disubstituted Polycyclic Alkenes

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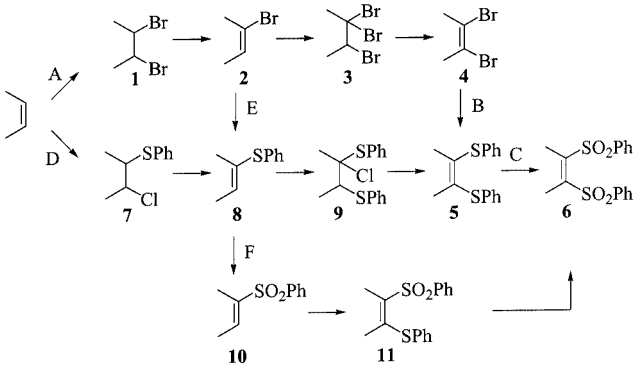
A range of mono- and disubstituted (–Br, –Cl, –SPh, –SO_2Ph) polycyclic alkenes has been prepared starting from alkenes by inexpensive and high-yielding synthetic routes.

Introduction

The synthesis of innumerable biologically active targets entails the use of a wide variety of usefully functionalised polycyclic intermediates.[1] Among several examples, some substituents, such as halogen and arylsulfonyl moieties, make polycyclic alkenes of interest because these groups can be transformed into other functions and, if necessary, eventually removed.[2] Prior to this work, the preparation of polycyclic 1,2-bis(phenylsulfonyl)alkenes had generally been achieved essentially through cycloaddition reactions between appropriately functionalised dienophiles and dienes.[3] The Diels–Alder reaction is undoubtedly of exceptional utility for the construction of certain six-membered rings, but the applicability of the method is sometimes limited by unavailability of the reagents. For the development of synthetic strategies suitable for the preparation of *meso*-1,2-bis(phenylsulfonyl) polycyclic alkenes not directly accessible by cycloaddition reactions, alternative synthetic routes via halogen- or phenylthio-substituted cycloalkenes were considered attractive. Here we report on the synthesis of a series of mono- and bis(phenylsulfonyl)-substituted polycyclic alkenes produced through simple and inexpensive transformations of readily accessible alkenes.

Results and Discussion

The envisaged direct synthetic routes to functionalised norbornene, norbornadiene, benzonorbornadiene and naphthonorbornadiene, starting from commercial or simply achievable compounds, are represented in Scheme 1.[4] They involve (path A) the preparation of the vinyl-brominated key intermediates **1**–**4**, the subsequent transformation (path B) of **4** into the corresponding bis(phenylthio) derivative **5** and the oxidation (path C) of **5** to bis(phenylsulfonyl) derivative **6**. Alternatively (path D), compound **5** can be obtained through the formation of **7**–**9**, by a double PhSCl addition and dehydrochlorination sequence. Some common intermediates also offer synthetic alternative means to reach the final bis(phenylsulfonyl) derivatives **6**, such as, for example (paths E, F), the conversion of vinyl bromide **2** into the corresponding phenylsulfone **10**, which is in turn transformed, through **11**, into the desired bis(phenylsulfonyl)alkene **6**.



Scheme 1

By path A, 2-bromonorbornadiene **2b** and 2,3-dibromonorbornadiene **4b** were prepared through a synthetic procedure modified from that originally reported by Szeimis.[5] The first bromination step for norbornene, benzonorbornadiene, naphthonorbornadiene and 5,8-(dimethoxy)benzonorbornadiene[4] was more conveniently (Scheme 2) performed under radical conditions, with 1,2-dibromotetrachloroethane serving as the source of bromine in CCl_4 solution.[6] Under these reaction conditions, the Wagner–Meerwein rearrangement of the polycyclic skeleton of the intermediate carbocation was totally suppressed,[7] and compounds **1a** and **1c**–**e** were obtained predominantly as their *anti*-dibrominated isomers. In any case, the mixtures of isomers were directly treated with base (*t*BuOK in refluxing THF) to afford the 2-bromoalkenes **2a** and **2c**–**e**.[7c] Treatment of **2a** and **2c**–**e** with bromine in

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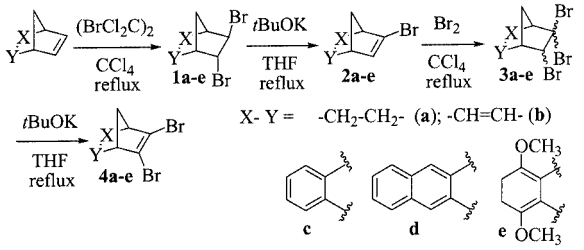
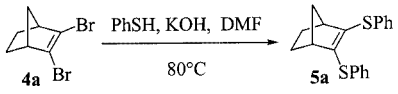
CCl_4 at reflux temperature furnished tribromo derivatives **3a** and **3c**−**e**, which were dehydrobrominated to afford the 2,3-dibromo derivatives **4a** and **4c**−**e** under the reaction conditions described above.



Scheme 2

These last compounds were fruitfully employed for the preparation of bis(phenylthio)-substituted alkenes **5a**−**e** (path B) under suitably optimised reaction conditions. 2,3-Dibromonorbornene **4a** proved to be inert towards the freshly prepared thiophenol sodium salt in THF, even after prolonged reaction times at reflux temperatures. However, the synthesis of 2,3-bis(phenylthio)norbornene **5a** was accomplished in 80% isolated yield (Scheme 3) by treatment of **4a** with equivalent amounts of PhSH in KOH/DMF at 80 °C.



Scheme 3

Under these reaction conditions, the dibrominated norbornadiene **4b**, the benzonorbornadienes **4c** and **4e** and the naphthonorbornadiene **4d** (Figure 1) also furnished the corresponding bis(phenylthio) derivatives **5b**−**e** in comparable yields.

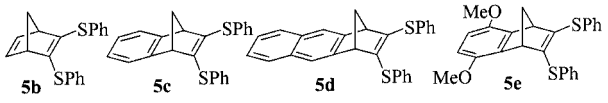
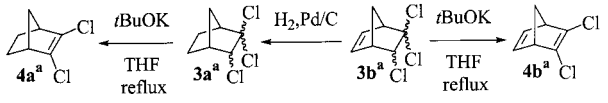


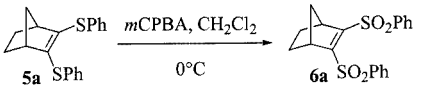
Figure 1. 2,3-Bis(phenylthio)norbornadiene derivatives

Compounds **5a** and **5b** were also prepared from 2,3-dichloronorbornene **4a**[a] and 2,3-dichloronorbornadiene **4b**[a], used in place of 2,3-dibromonorbornene **4a** and 2,3-dibromonorbornadiene **4b** as starting reagents. Compounds **4a**[a] and **4b**[a] are inexpensive reagents, readily obtained by cycloaddition reaction between trichloroethylene and cyclopentadiene.[8] In particular, **4b**[a] was obtained by dehydrochlorination of the primary cycloadduct **3b**[a], while **4a**[a] was obtained from **3b**[a] by catalytic hydrogenation and dehydrochlorination (Scheme 4).



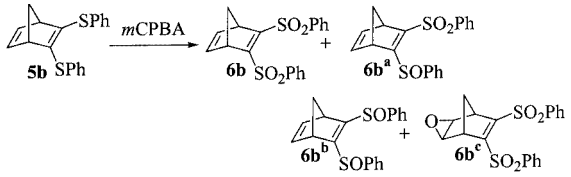
Scheme 4

(Phenylsulfonyl)-substituted polycyclic alkenes **6a**−**e** were prepared from (phenylthio)-substituted precursors through sulfur oxidation processes. The oxidation of 2,3-bis(phenylthio)norbornene **5a** (Scheme 5) with *m*CPBA in CH_2Cl_2 at 0 °C furnished 2,3-bis(phenylsulfonyl)norbornene **6a**.



Scheme 5

Under the same reaction conditions, however, compound **5b**, containing an additional C−C double bond, produced a complex mixture of compounds (Scheme 6) consisting of partially oxidised products **6b**[a,b], overoxidised epoxide **6b**[c] and the desired **6b**, the latter in 50% yield.[3d] Similar yields of **6b** were also obtained in experiments performed at lower temperature or with other classic oxidising agents such as H_2O_2 under acidic catalysis conditions or dimethyldioxirane.[9]



Scheme 6

It was found that the oxidation of **5b** could be carried out successfully by use of TBA-OXONE® in CH_2Cl_2, a sulfur-selective oxidising system,[9b] which provided **6b** in almost quantitative yield.

Oxidation of compounds **5c**−**e** was performed without inconvenience with *m*CPBA, affording bis(phenylsulfonyl) derivatives **6c**−**e** (Figure 2).

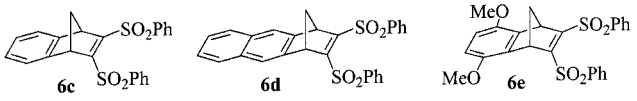
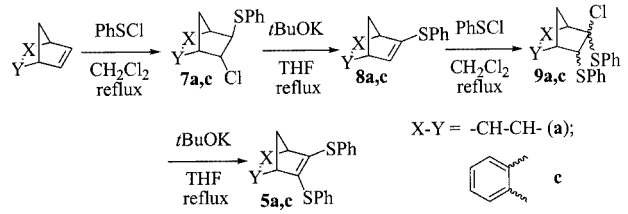


Figure 2. 2,3-Bis(phenylsulfonyl)benzonorbornadienes

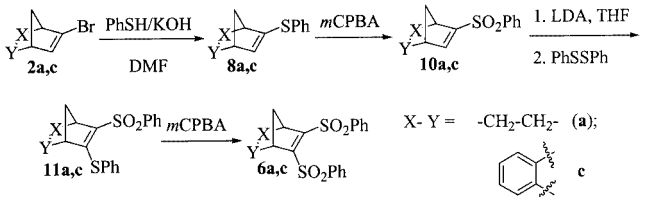
The second synthetic route (Path D, Scheme 1) to mono- and bis(phenylsulfonyl)alkenes **6** requires a double PhSCl addition/dehydrochlorination sequence, followed by a final oxidation. Although the addition of this reagent to a double bond is a widely applied methodology,[10] this reaction presents some difficulty in some instances when applied to polycyclic hydrocarbons, because of rearrangement of the hydrocarbon skeleton.[10b] The addition of freshly prepared PhSCl to the double bond of a norbornene and benzonorbornadiene occurs instantaneously in refluxing dichlorome-



Scheme 7

thane (Scheme 7) affording *exo*-(phenylthio), *endo*-chloro derivatives **7a** and **7c** as the products of a totally *anti*-selective addition, as confirmed by NMR (COSY, NOESY) experiments. On dehydrochlorination of **7a** and **7c** (*t*BuOK/THF), phenyl vinyl sulfides **8a** and **8c** were obtained, and these were again treated with PhSCl as described above. In this case an inseparable mixture of isomers of **9a** and **9c** was isolated, and this partially decomposed under silica gel chromatographic conditions. Consequently, **9a** and **9c** were used as obtained in the successive dehydrochlorination step (*t*BuOK/THF at reflux), giving 2,3-bis(phenylthio)alkenes **5a** and **5c**.

However, the electronic features of the benzo-fused ring influence the behaviour of the reagents. For example, the methoxy group has an activating effect on the aromatic ring of 5,8-dimethoxybenzonorbornadiene, and in the case of naphthonorbornadiene the external aromatic ring also activates the internal α-naphthalenic position towards electrophilic reagents. Surprisingly, treatment of these alkenes with PhSCl, of more weakly electrophilic character than bromine,[10b] resulted in the formation of a complex mixture of products. In this regard, the PhSCl and the bromine addition/elimination processes represent complementary methods, the former appearing to be more appropriate for the functionalisation of norbornene and benzonorbornadiene systems and the latter more suitable for other substrates.



Scheme 8

In addition (Scheme 8), an alternative synthetic route to bis(phenylsulfonyl)alkenes **6** starting from vinyl bromide **2** (path E) was explored, as demonstrated in the cases of **6a** and **6c**. Treatment of **2a** with PhSH in DMF/KOH indeed resulted in the formation of **8a**. After oxidation (*m*CPBA or TBA-OXONE®), (phenylsulfonyl)alkene **10a** (path F) was recovered. This compound, when treated with lithium diisopropylamide (LDA) and subsequent quenching of the derived anions with diphenyl disulfide (PhSSPh), gave phenylthio derivative **11a** in excellent yields. The bis(phenylsulfonyl)alkene **6a** was obtained by subsequent oxidation (*m*CPBA). The synthesis of **6c** from **2c** was carried out under identical reaction conditions, through the formation of intermediates **8**, **10** and **11c**.

Taking the reactivity of polycyclic alkenes into account, we considered a conceptually new role for these 2,3-bis(phenylsulfonyl)alkenes: the *meso* stereochemistry makes them key intermediates in a new stereoselective process. In fact, racemic mixtures of polycyclic ketones could be "*symmetrised*" to the corresponding symmetric *meso*-2,3-bis(phenylsulfonyl) derivative,[11] and then asymmetrically desymmetrised. The overall process comprises a total resolution process with some peculiar aspects (Figure 3): a) a racemic mixture of compounds could be totally converted into only one enantiomer of a desired configuration, thus avoiding the formation of waste products, and b) the synthesis of otherwise unavailable antipodes from available enantiomers could be achieved through the total switch of configuration of the reagents.

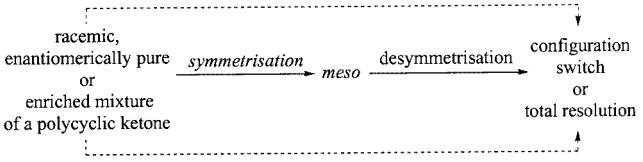


Figure 3. Double role of "symmetrisation"/"desymmetrisation" strategy

This approach constitutes an alternative synthetic method for the preparation of enantiopure polycyclic ketones, always of interest even for simple structures.[12] With the goal of confirming this hypotheses, some very simple preliminary experiments starting from racemic norcamphor, chosen as the model, were performed (Figure 4).

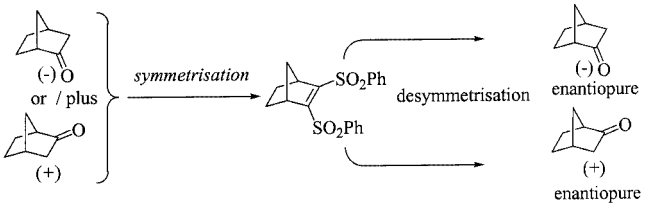
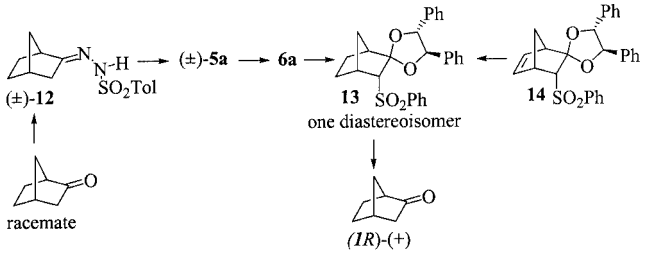


Figure 4. Total resolution of norcamphor

Commercial (±)-norcamphor was quantitatively transformed into tosylhydrazone **12**, which was in turn converted into (±)-2-bromonorbornene **1a** (15−35% unoptimised average yields) through a Shapiro reaction.[13] Racemic **1a** was transformed (this work) into 2,3-bis(phenylsulfonyl)norbornene **6a**, which was desymmetrised by use of the hydrobenzoin[2a] or hydrobenzoin monomethyl ether[2b,2e] methodology. The synthetic procedure affords either (+)-norcamphor [(*R*,*R*)-hydrobenzoin or (*S*,*S*)-hydrobenzoin monomethyl ether method] or alternatively (−)-norcamphor as the final products. The absolute configuration was established by correlation of the data for ketal **13** with the data obtained by catalytic hydrogenation of ketal **14**. This compound was also obtained by an independent pathway, while the absolute configurations both of *endo*- and *exo*-(phenyl-

sulfonyl) derivatives had been established previously (Scheme 9).[2a,2b,2f]



Scheme 9

Conclusion

Several routes for the preparation of both mono- and disubstituted polycyclic alkenes, much of these latter hitherto unknown, from symmetric alkenes have been reported. The concepts of total resolution of racemic ketones and of chiral interconversion between enantiomers are intrinsically implicit in the proposed transformations. In order to develop new approaches to biologically active compounds by asymmetric discrimination processes (ADPs) with *meso* compounds, and in view of the fact that different functionalities, of associated different properties, may play important roles in synthetic organic chemistry, numerous experiments concerning the behaviour of the structurally related molecules of C_s symmetry presented here, or their oxa and aza analogues, also in chiral versions, towards different classes of reagents are in progress.

Experimental Section

General Remarks: Melting points are not corrected and were determined with a Büchi 535 apparatus. NMR spectra were recorded with a Bruker AC 200 spectrometer operating at 200 (^{1}H) and 50 (^{13}C) MHz. IR spectra were recorded with a Nicolet Magna IR-750 spectrophotometer. Commercial high purity reagents were employed without further purification. High purity solvents were prepared by standard procedures. Known compounds were prepared according to literature procedures or purchased from standard chemical suppliers and purified to match the reported physical and spectroscopic data. Microanalyses were performed with a Perkin−Elmer 2400 CHN Elemental Analyser.

2-Bromobicyclo[2.2.1]hepta-2,5-diene (2b): A solution of bicyclo-[2.2.1]hepta-2,5-diene (25.02 g, 271.6 mmol, 27.6 mL) in THF (250 mL) was stirred under argon at −35 °C and cautiously treated (exothermic reaction) with portions of *t*BuOK (30.57 g, 272 mmol). The resulting mixture was cooled to −78 °C, and *n*BuLi (108.6 mL of a 2.5 M solution in hexanes, 271 mmol) was added by syringe over 30 min. After 10 min at −78 °C, the temperature was adjusted to −60 °C and, after a further 30 min, 1,2-dibromoethane (61.0 g, 28 mL, 324 mmol) was added by syringe over 15 min. The reaction mixture was allowed to come to room temperature (6 h), treated with H_2O (1 mL) and diluted with Et_2O (50 mL). The organic phase was washed with brine (2 × 20 mL) and with H_2O (2 × 20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue, purified by distillation (3 Torr, 50 °C) in a Kugelrohr apparatus, afforded a colourless oil (24.6 g, 54% yield). The compound exhibits spectroscopic data identical to those reported.[5]

2,3-Dibromobicyclo[2.2.1]hepta-2,5-diene (4b): A solution of bicyclo[2.2.1]hepta-2,5-diene (8.91 g, 97 mmol, 10 mL) in dry THF (40 mL), stirred under argon at −35 °C, was treated with a solution of *t*BuOK (10.9 g, 97 mmol) in the same solvent (50 mL). After 5 min, the resulting mixture was cooled to −80 °C. *n*BuLi (40 mL of a 2.5 M solution in hexanes) was cautiously added dropwise over 1 h. The temperature was adjusted to −65 °C and 2-bromobicyclo[2.2.1]hepta-2,5-diene (**2b**) (16.6 g, 97 mmol) was added by syringe over 15 min. The reaction mixture was stirred for 1 h at −35 °C, treated with 1,2-dibromoethane (10 mL, excess, added by syringe over 15 min), and finally allowed to come to room temperature. H_2O (15 mL) was added and the organics were extracted with Et_2O (4 × 30 mL). The combined organic phases were washed with H_2O (3 × 40 mL) and brine (2 × 20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was distilled (3 Torr, 70 °C), giving a colourless oil (12 g, 50% yield). The compound exhibits spectroscopic data identical to those reported.[5]

2,2,3-Tribromo-1,4-dihydro-1,4-methanonaphthalene (3c) and 2,3-Dibromo-1,4-dihydro-1,4-methanonaphthalene (4c): A solution of Br_2 (3.6 g, 22.6 mmol, 1.16 mL) in CCl_4 (5 mL) was added rapidly to a solution of 2-bromo-1,4-dihydro-1,4-methanonaphthalene (**2c**)[7c] (5.0 g, 22.6 mmol) in CCl_4 (25 mL), stirred under argon at reflux temperature. After a few minutes, the solvent was removed under reduced pressure, giving **3c** as a red oil consisting of a mixture of isomers (8.6 g, quantitative yield). **2-*endo*,2-*exo*,3-*endo* Isomer:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (dt, *J* = 10.2, 1.8 Hz, 1 H, 1/2 AB system), 2.63 (dt, *J* = 10.2, 1.5 Hz, 1 H, 1/2 AB system), 3.49−4.04 (m, 2 H, 1-H, 4-H), 5.22 (d, *J* = 3.8 Hz, 1 H, 3-H), 7.08−7.29 (m, 4 H, Ar). **2-*endo*,2-*exo*,3-*exo* Isomer:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.19 (dq, *J* = 10.0, 2.0 Hz, 1 H, 1/2 AB system), 2.73 (dt, *J* = 10.0, 1.3 Hz, 1 H, 1/2 AB system), 3.49−4.04 (m, 2 H, 1-H, 4-H), 4.35 (d, *J* = 2.5 Hz, 1 H, 3-H), 7.08−7.29 (m, 4 H, Ar). A solution of **3c** (mixture of isomers, 5.0 g, 13.1 mmol) in THF (15 mL), stirred under argon at room temperature, was treated with a solution of *t*BuOK (4.5 g, 39.3 mmol) in the same solvent (20 mL). The resulting brown mixture was then stirred at reflux temperature for an additional 3 h. After the mixture had cooled to room temperature, the solvent was removed under reduced pressure and the residue was diluted with Et_2O (60 mL). The organic phase was washed with H_2O (3 × 50 mL) and brine (2 × 30 mL), dried ($MgSO_4$) and concentrated under reduced pressure (3.8 g, 96% yield). The compound, after recrystallisation from *n*-hexane, shows spectroscopic data identical to those reported.[7b]

2,2,3-Tribromo-1,4-dihydro-1,4-methanoanthracene (3d) and 2,3-Dibromo-1,4-dihydro-1,4-methanoanthracene (4d): The procedure previously described for the preparation of **3c** and **4c** was employed. By use of a solution of 2-bromo-1,4-dihydro-1,4-methanoanthracene (**2d**)[7c] (0.92 g, 3.39 mmol) in CCl_4 (20 mL) and a solution of Br_2 (0.54 g, 3.39 mmol, 0.17 mL) in the same solvent, the reaction furnished **3d** as a pale yellow oil (1.5 g, quantitative yield). ^{1}H NMR (200 MHz, $CDCl_3$, mixture of isomers): δ = 2.22−2.48 (m, 2 H), 2.74−2.94 (m, 2 H), 3.67−3.74 (m, 2 H), 4.04 (t, *J* = 1.6 Hz, 1 H), 4.23−4.29 (m, 1 H), 4.56 (d, *J* = 2.7 Hz, 1 H), 5.42 (d, *J* = 3.6 Hz, 1 H), 7.38−7.95 (m, 12 H, Ar). A solution of **3d** (1.46 g, 3.39 mmol) in THF (20 mL) treated with a solution of *t*BuOK (0.57 g, 5.1 mmol) in the same solvent (20 mL) for 6 h at reflux, and recrystallisation from Et_2O/*n*-hexane gave red crystals. 0.9 g; 80% yield; m.p. 161 °C. IR (KBr disk): $\tilde{\nu}$ = 3063, 3040, 3002, 2948, 2871, 1574, 1513, 1275, 891, 753, 737 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (dt, *J* = 7.9, 2.4 Hz, 1 H, 1/2 AB system), 2.80

(dt, J = 7.9, 1.7 Hz, 1 H, 1/2 AB system), 4.04 (t, J = 1.7 Hz, 2 H), 7.50−7.40 (m, 2 H, Ar), 7.70 (s, 2 H, Ar), 7.72−7.79 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 57.93, 63.68, 120.40, 125.85, 127.86, 132.24, 133.00, 144.11, 206.97 ppm. $C_{15}H_{10}Br_2$ (350): calcd. C 51.47, H 2.88; found C 51.61, H 2.60.

2,2,3-Tribromo-5,8-dimethoxy-1,4-dihydro-1,4-methanonaphthalene (3e) and 2,3-Dibromo-5,8-dimethoxy-1,4-dihydro-1,4-methanonaphthalene (4e): The procedure described above for the preparation of **3c** and **4c** was employed. Through the use of a solution of 2-bromo-1,4-dihydro-1,4-methano-5,8-dimethoxynaphthalene (**2e**)[7c] (1.0 g, 3.56 mmol) in CCl_4 (20 mL) and a solution of Br_2 (0.57 g, 3.56 mmol, 0.17 mL) in the same solvent (2 mL), a yellow oil (1.57 g, quantitative yield) was obtained. **3e:** ^{1}H NMR (200 MHz, $CDCl_3$, mixture of isomers in 2:1 ratio): δ = 2.10−3.11 (series of m, 4 H, both isom.), 3.62−3.66 (m, 1 H, maj. isom), 3.78 (s, 3 H, OMe, maj. isom.), 3.80 (s, 3 H, OMe, min. isom.), 3.82 (s, 3 H, OMe, maj. isom.), 3.85 (s, 3 H, OMe, min. isom.), 4.01−4.10 (m, 1 H, maj. isom.), 4.25−4.29 (m, 1 H, maj. isom), 4.37−4.43 (m, 1 H, min. isom.), 4.47 (d, J = 2.9 Hz, 1 H, min. isom.), 5.25 (d, J = 3.4 Hz, 1 H, min. isom.), 6.70 (s, 2 H, Ar, min. isom.), 6.73 (s, 2 H, Ar, maj. isom.) ppm. Subsequent treatment of a solution of **3e** (1.57 g, 3.56 mmol) in THF (20 mL) with a solution of *t*BuOK (1.2 g, 10.68 mmol) in the same solvent (15 mL, 6 h at reflux temperature) afforded colourless crystals (0.64 g, 50% yield) after flash chromatography (eluent: *n*-hexane/CH_2Cl_2, 9:1); m.p. 87−88 °C. IR (KBr disk): $\tilde{\nu}$ = 3009, 2964, 2940, 2833, 1590, 1505, 1443, 1282, 1244, 1159, 791, 722, 638 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.33 (dt, J = 6.0, 4.0 Hz, 1 H, 1/2 AB system), 2.67 (dt, J = 6.0, 4.0 Hz, 1 H, 1/2 AB system), 3.83 (s, 6 H, OMe), 4.22 (t, J = 4.0 Hz, 2 H), 6.63 (s, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.54, 56.93, 67.37, 111.78, 133.44, 136.73, 149.27 ppm. $C_{13}H_{12}Br_2O_2$ (360): calcd. C 43.37, H 3.36, found C 43.12, H 3.21.

2,3-Bis(phenylthio)bicyclo[2.2.1]heptene (5a). Method A: A mixture of 2,3-dibromobicyclo[2.2.1]heptene (**4a**) (1.0 g, 4.0 mmol), PhSH (0.9 g, 8.0 mmol, 0.84 mL), KOH (0.7 g, 12 mmol) and DMF (15 mL) was stirred under argon at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (40 mL), washed with H_2O (3 × 20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: *n*-hexane). **Method B:** A solution of PhSCl (0.28 g, 1.94 mmol) in CH_2Cl_2 (5 mL) was added to a solution of 2-(phenylthio)bicyclo[2.2.1]heptene (**8a**) (0.4 g, 1.98 mmol) in 15 mL of the same solvent, stirred under argon at reflux temperature. After a few minutes, the solvent was removed under reduced pressure, giving **9a** as a pale yellow oil [0.68 g, ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.13−1.85 (series of m, 7 H), 2.93−3.06 (m, 2 H), 7.06−7.52 (series of m, 12 H, Ar)], which was diluted with THF (8 mL) and treated with a solution of *t*BuOK (0.442 g, 3.94 mmol) in THF (40 mL) at room temperature for 30 min, and then at reflux temperature for an additional 3 h. After the mixture had cooled to room temperature, the solvent was removed under reduced pressure and the mixture was diluted with Et_2O (60 mL). The organic phase was washed with H_2O (3 × 30 mL) and brine (3 × 30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent *n*-hexane) to give a colourless solid (0.39 g, 71% yield); m.p. 77 °C. IR (KBr disk): $\tilde{\nu}$ = 3072, 2967, 2947, 2868, 1591, 1485, 1446, 1288, 762, 696 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20−1.35, 1.54−1.74 (series of m, 6 H), 2.97 (br. s, 2 H), 7.19−7.43 (m, 10 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.24, 44.22, 48.15, 126.57, 128.57, 128.98, 129.92, 131.87 ppm. $C_{19}H_{18}S_2$ (310): calcd. C 73.50, H 5.84; found C 73.72, H 5.62.

2,3-Bis(phenylthio)bicyclo[2.2.1]hepta-2,5-diene (5b). Method A: A solution of 2,3-dibromobicyclo[2.2.1]hepta-2,5-diene (**4b**) (1.0 g, 4.0 mmol), PhSH (0.9 g, 8.0 mmol, 0.84 mL) and KOH (0.7 g, 12 mmol) in dry DMF (15 mL) was stirred under argon at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O (40 mL), washed with H_2O (3 × 20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: *n*-hexane/acetone, 9:1) affording a pale yellow oil (1.0 g, 80% yield). **Method B:** Under the same reaction conditions, starting from 2,3-dichlorobicyclo[2.2.1]hepta-2,5-diene (**4b**[a]) (1.5 g, 14.1 mmol), 3.0 g (70% yield) of product was obtained. IR (neat, NaCl): $\tilde{\nu}$ = 3072, 2979, 2940, 2868, 1591, 1486, 1446, 1301, 748, 696 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (dt, J = 6.4, 1.6 Hz, 1 H, 1/2 AB system), 2.22 (dt, J = 6.4, 1.6 Hz, 1 H, 1/2 AB system), 3.43−3.50 (m, 2 H), 6.67 (t, J = 1.8 Hz, 2 H), 7.12−7.40 (m, 10 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.86, 69.14, 126.66, 128.94, 130.22, 134.75, 141.10, 146.78 ppm. $C_{19}H_{16}S_2$ (308): calcd. C 73.98, H 5.23; found C 73.73, H 5.41.

2,3-Bis(phenylthio)-1,4-dihydro-1,4-methanonaphthalene (5c): The procedures reported above for the preparation of **5a** were employed. **Method A:** Through the use of a mixture of 2,3-dibromo-1,4-dihydro-1,4-methanonaphthalene (**4c**) (1.0 g, 3.33 mmol) in DMF (15 mL), PhSH (1.1 g, 9.99 mmol, 1.0 mL) and KOH (0.56 g, 9.99 mmol) (80 °C for 20 h), a solid residue was obtained. This was recrystallised from *n*-hexane/Et_2O as a colourless solid (0.95 g, 80% yield). **Method B:** A solution of PhSCl (1.15 g, 8.0 mmol) in *n*-hexane (20 mL) was added under argon, at reflux temperature, to a stirred solution of 2-(phenylthio)-1,4-dihydro-1,4-methanonaphthalene (**8c**) (2.0 g, 8.0 mmol) in CH_2Cl_2 (15 mL). After a few minutes, the solvent was removed under reduced pressure to give 2-chloro-2,3-bis(phenylthio)-1,4-dihydro-1,4-methanonaphthalene (**9c**) (2.2 g, 70% yield) as an oil, which was purified by flash chromatography (eluent: *n*-hexane/CH_2Cl_2, 9:1). ^{1}H NMR (200 MHz, $CDCl_3$, mixture of isomers): δ = 2.30−2.76 (series of m, 4 H), 3.13−3.15 (m, bs, 1 H), 3.17−3.21 (m, bs, 1 H), 3.49 (d, J = 4.0 Hz, 1 H), 3.61−3.69 (m, 1 H), 3.70−3.80 (m, 1 H), 3.89 (d, J = 4.0 Hz, 1 H), 7.12−7.64 (m, 14 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, mixture of isomers): δ = 47.05, 47.53, 48.17, 48.58, 52.65, 52.96, 54.14, 54.81, 56.85, 57.19, 66.92, 121.90, 122.84, 123.21, 123.65, 124.12, 124.34, 126.94, 127.08, 127.26, 127.47, 127.58, 127.75, 128.01, 128.30, 128.71, 128.92, 129.03, 129.24, 129.33, 130.60, 130.87, 130.99, 131.31, 132.81, 133.55, 134.11, 135.45, 135.64, 136.47, 138.70, 144.96 ppm. A solution of **9c** (4.0 g, 10 mmol) in THF (15 mL) was treated with a solution of *t*BuOK (1.7 g, 15 mmol) in the same solvent (30 mL), and heated at reflux temperature for 1 h. The compound was purified by flash chromatography (eluent: *n*-hexane/CH_2Cl_2, 97:3) to give colourless crystals (2.5 g, 70% yield); m.p. 116 °C. IR (KBr disk): $\tilde{\nu}$ = 3072, 2979, 2947, 2868, 1755, 1591, 1479, 1446, 1268, 755, 748, 696 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.35 (dt, J = 8.0, 1.6 Hz, 1 H, 1/2 AB system), 2.53 (dt, J = 8.0, 1.2 Hz, 1 H, 1/2 AB system), 3.80−3.85 (m, 2 H), 6.93−7.45 (m, 14 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.60, 63.85, 121.57, 124.96, 126.97, 129.06, 130.52, 134.35, 147.50, 149.28 ppm. $C_{23}H_{18}S_2$ (358): calcd. C 77.05, H 5.06; found C 76.90, H 5.24.

2,3-Bis(phenylthio)-1,4-dihydro-1,4-methanoanthracene (5d): The procedure previously described (Method A) for the preparation of **5a** was employed, with a mixture of 2,3-dibromo-1,4-dihydro-1,4-methanoanthracene (**4d**) (0.1 g, 0.28 mmol), DMF (20 mL), PhSH (0.092 g, 0.84 mmol, 0.086 mL) and KOH (0.047 g, 0.84 mmol). Workup after 30 h at 80 °C gave a residue that, when treated with

n-hexane, furnished a colourless solid (0.09 g, 79% yield); m.p. 180−181 °C. IR (KBr disk): $\tilde{\nu}$ = 3065, 3012, 1986, 2947, 1755, 1591, 1479, 1446, 755, 696 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.37 (dt, 1 H, *J* = 8.12, 1.5 Hz, 1/2 AB system), 2.57 (dt, *J* = 8.1, 1.5 Hz, 1 H, 1/2 AB system), 3.93 (br. s, 2 H), 7.31−7.46 (m, 10 H, Ar), 7.50 (s, 2 H, Ar), 7.65−7.76 (m, 4 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 54.76, 60.25, 119.65, 125.44, 127.07, 127.76, 129.13, 130.58, 132.23, 134.30, 145.95, 146.86 ppm. $C_{27}H_{20}S_2$ (408): calcd. C 79.37, H 4.93; found C 79.02, H 4.78.

5,8-Dimethoxy-2,3-bis(phenylthio)-1,4-dihydro-1,4-methanonaphthalene (5e): The procedure described above (Method A) for the preparation of **5a** was employed, with a mixture of **4e** (0.1 g, 0.28 mmol), DMF (20 mL), PhSH (0.092 g, 0.84 mmol, 0.086 mL) and KOH (0.047 g, 0.84 mmol). Workup after 24 h at 80 °C gave a solid that, after recrystallisation from Et_2O/*n*-hexane, provided colourless crystals (0.08 g, 68% yield); m.p. 134−135 °C. IR (KBr disk): $\tilde{\nu}$ = 3066, 3013, 2973, 2933, 2913, 2840, 1593, 1500, 1446, 1280, 1253, 1173, 1080, 746, 700, 653 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.28 (dt, *J* = 8.0, 2.0 Hz, 1 H, 1/2 AB system), 2.42 (dt, *J* = 8.0, 2.0 Hz, 1 H, 1/2 AB system), 3.75 (s, 6 H, OMe), 4.13 (t, *J* = 2.0 Hz, 2 H), 6.56 (s, 2 H, Ar), 7.23−7.44 (m, 12 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.57, 57.02, 63.92, 111.79, 126.95, 128.98, 130.80, 134.42, 138.27 ppm. $C_{25}H_{22}O_2S_2$ (418): calcd. C 71.74, H 5.30; found C 71.53, H 5.52.

2,3-Bis(phenylsulfonyl)bicyclo[2.2.1]heptene (6a): A stirred solution of 2,3-bis(phenylthio)bicyclo[2.2.1]heptene (**5a**, 0.1 g, 0.32 mmol) in CH_2Cl_2 (10 mL) was treated at 0 °C with a solution of *m*CPBA (0.3 g of a 70% mixture in H_2O, 1.28 mmol) in CH_2Cl_2 (15 mL) with monitoring by TLC. After 1 h, the crude reaction mixture was washed with Na_2CO_3 (3 × 40 mL of a 10% aqueous solution), H_2O (3 × 30 mL) and brine (3 × 20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by recrystallisation from Et_2O to afford a colourless solid (0.09 g, 80% yield); m.p. 153 °C. IR (KBr disk): $\tilde{\nu}$ = 3068, 3003, 2941, 2879, 1583, 1564, 1479, 1448, 1336, 1311, 1180, 1147, 1085, 866, 796, 752, 688, 636, 617, 603 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.07−1.94 (series of m, 6 H), 3.48−3.58 (br. s, 2 H), 8.04−8.15, 7.52−7.74 (m, 10 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.47, 48.90, 128.63, 129.27, 134.12, 140.17, 152.90 ppm. $C_{19}H_{18}O_4S_2$ (374): calcd. C 60.94, H 4.85 found C 61.12, H 5.02.

2,3-Bis(phenylsulfonyl)bicyclo[2.2.1]hepta-2,5-diene (6b): A mixture of 2,3-bis(phenylthio)bicyclo[2.2.1]hepta-2,5-diene (**5b**) (1.0 g, 3.2 mmol), dry CH_2Cl_2 (25 mL) and TBA-OXONE® (8.3 g, 9.7 mmol) was stirred under argon at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was percolated through a short silica gel column and recrystallised from CH_2Cl_2/Et_2O to afford colourless needles (1.16 g, 98% yield). The recorded spectroscopic data are identical to those reported in literature.[3]

2,3-Bis(phenylsulfonyl)-1,4-dihydro-1,4-methanonaphthalene (6c). Method A (from 5c): A solution of *m*CPBA (5.4 g, 70% purity mixed with H_2O, 31.6 mmol) in CH_2Cl_2 (40 mL) was cautiously added to a solution of **5c** (2.27 g, 6.33 mmol) in CH_2Cl_2 (10 mL), stirred at 0 °C and monitored by TLC (CH_2Cl_2). After 3 h, the reaction mixture was diluted with CH_2Cl_2 (40 mL) and the organic phase was washed with Na_2CO_3 (3 × 20 mL of a 10% aqueous solution) and brine (2 × 20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue, after recrystallisation from Et_2O, gave pale yellow needles (2.0 g, 75% yield). **Method B (from 11c):** The reaction was performed with **11c** (0.5 g, 1.28 mmol), *m*CPBA (0.66 g, 70% mixture in H_2O, 3.8 mmol) and CH_2Cl_2 (25 mL), under the conditions described above, to afford the compound (0.4 g, 80% yield); m.p. 163 °C. IR (KBr disk): $\tilde{\nu}$ = 3092, 3057, 3015, 2998, 2947, 2878, 1583, 1564, 1460, 1321, 1159, 1086, 1018, 771, 754, 689, 638, 602 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.26 (dt, *J* = 6.8, 1.2 Hz, 1 H, 1/2 AB system), 2.62 (dt, *J* = 8.0, 1.7 Hz, 1 H, 1/2 AB system), 4.45 (m, 2 H), 7.42−7.90, 6.85−7.09 (series of m,14 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.02, 68.40, 122.87, 127.87, 128.50, 129.17, 134.15, 139.15, 145.87, 159.96 ppm. $C_{23}H_{18}O_4S_2$ (422): calcd. C 65.38, H 4.01; found C 65.27, H 4.01.

2,3-Bis(phenylsulfonyl)-1,4-dihydro-1,4-methanoanthracene (6d): The reaction conditions described for the preparation of compound **6c** (Method A) were employed. Starting from a solution of **5d** (0.08 g, 0.196 mmol) in CH_2Cl_2 (5 mL), and a solution of *m*CPBA (0.26 g, 50% mixture in H_2O, 0.98 mmol) in CH_2Cl_2 (10 mL), the reaction was complete after 5 h. The residue was purified by recrystallisation from Et_2O, giving colourless crystals (0.09 g, quantitative yield); m.p. 165 °C. IR (KBr disk): $\tilde{\nu}$ = 3061, 2993, 2951, 1446, 1319, 1161, 1086, 879, 758, 730, 689, 647, 601 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.26 (dt, *J* = 4.0, 2.0 Hz, 1 H, 1/2 AB system), 2.68 (dt, *J* = 4.0, 2.0 Hz, 1 H, 1/2 AB system), 4.56 (t, *J* = 2.0 Hz, 2 H), 7.40−7.89 (m, 16 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.18, 65.16, 121.68, 126.20, 127.94, 128.56, 129.13, 131.91, 134.19, 139.33, 141.73, 158.67 ppm. $C_{27}H_{20}O_4S_2$ (472): calcd. C 68.62, H 4.27; found C 68.73, H 4.05.

5,8-Dimethoxy-2,3-bis(phenylsulfonyl)-1,4-dihydro-1,4-methanonaphthalene (6e): The reaction conditions described for the preparation of compound **6c** (Method A) were employed, starting from a solution of **5e** (0.07 g, 0.167 mmol) in CH_2Cl_2 (5 mL) and a solution of *m*CPBA (0.182 g, 70% mixture in H_2O, 0.83 mmol) in CH_2Cl_2 (10 mL). Workup after 6 h at 0 °C furnished a solid that was purified by crystallisation from Et_2O, giving yellow crystals (0.05 g, 66% yield); m.p. 161 °C. IR (KBr disk): $\tilde{\nu}$ = 3101, 3072, 3016, 2992, 2953, 2938, 2837, 1661, 1568, 1500, 1456, 1338, 1319, 1269, 1257, 1155, 1084, 1059, 798, 762, 729, 687 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.20 (dt, *J* = 7.9, 1.5 Hz, 1 H, 1/2 AB system), 2.52 (dt, *J* = 7.9, 1.6 Hz, 1 H, 1/2 AB system), 3.72 (s, 6 H, OMe), 4.73 (t, *J* = 1.0 Hz, 2 H), 6.44 (s, 2 H, Ar), 7.40−8.03 (m, 10 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.05, 55.76, 69.48, 110.43, 128.71, 128.87, 133.86, 134.37, 139.48, 148.93, 160.64 ppm. $C_{25}H_{22}O_4S_2$ (450): calcd. C 66.64, H 4.92; found C 66.91, H 4.74.

2-*endo*-Chloro-3-*exo*-(phenylthio)bicyclo[2.2.1]heptane (7a):[10] A solution of PhSCl (15 g, 106 mmol) in CH_2Cl_2 (100 mL) was added at reflux temperature under argon to an efficiently stirred solution of norbornene (10 g, 106 mmol) in CH_2Cl_2 (50 mL). After a few minutes, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (eluent: *n*-hexane). Colourless oil (17.7 g, 70% yield). IR (neat, NaCl): $\tilde{\nu}$ = 3078, 3050, 2967, 2874, 1591, 1485, 1446, 1308, 780, 755, 696 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.11−1.32 (m, 6 H), 2.25−2.37 (m, 1 H), 2.45−2.57 (m, 1 H), 3.11 (td, 1 H, *J* = 3.0, 1.6 Hz), 4.05 (td, 1 H, *J* = 2.4, 1.6 Hz), 7.19−7.46 (m, 5 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.75, 28.81, 35.81, 43.68, 44.21, 59.03, 67.15, 126.60, 128.90, 130.56, 135.28 ppm. $C_{13}H_{15}ClS$ (238): calcd. C 65.39, H 6.33; found C 65.51, H 6.14.

2-*endo*-Chloro-3-*exo*-(phenylthio)-1,2,3,4-tetrahydro-1,4-methanonaphthalene (7c): The reaction conditions previously described for the preparation of **7a** were adopted. From a solution of PhSCl (3.05 g, 21.1 mmol) in *n*-hexane (20 mL), and a solution of benzonorbornadiene (3.0 g, 21.1 mmol) in CH_2Cl_2 (20 mL), a col-

ourless oil (4.0 g, 70% yield) was obtained after flash chromatography (eluent: *n*-hexane/CH_2Cl_2, 9:1). IR (neat, NaCl): $\tilde{\nu}$ = 3078, 3065, 2986, 2947, 1591, 1492, 1275, 801, 769, 748, 696 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.31 (dt, *J* = 10.0, 1.1 Hz, 1 H, 1/2 AB system), 2.32 (dt, *J* = 10.0, 1.1 Hz, 1 H, 1/2 AB system), 3.20 (t, *J* = 4.0 Hz, 1 H), 3.40−3.44 (m, 1 H), 3.58−3.64 (m, 1 H), 4.46 (t, *J* = 4.0 Hz, 1 H), 7.22−7.55 (m, 9 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 46.58, 50.06, 51.55, 57.39, 64.14, 120.82, 124.59, 126.27, 126.79, 126.98, 129.03, 130.50, 135.01, 142.80, 145.70 ppm. $C_{17}H_{15}ClS$ (286): calcd. C 71.19, H 5.27; found C 70.91, H 5.04.

2-(Phenylthio)bicyclo[2.2.1]heptene (8a): A solution of *t*BuOK (16.6 g, 149 mmol) in THF (80 mL) was slowly added over 30 min to a solution of **7a** (17.7 g, 74.2 mmol) in the same solvent (25 mL), stirred under argon at room temperature. The mixture was then heated at reflux temperature for 3 h. After the mixture had cooled to room temperature, the solvent was removed under reduced pressure, H_2O (60 mL) was added, and the mixture was extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with H_2O (2 × 30 mL) and brine (2 × 30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: *n*-hexane), giving a pale yellow oil (10.5 g, 70% yield). IR (neat, NaCl): $\tilde{\nu}$ = 3072, 2973, 2881, 1591, 1564, 1492, 1453, 827, 748, 696 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.05−1.84 (m, 6 H), 2.85 (br. s, 1 H), 2.98 (br. s, 1 H), 6.02 (d, *J* = 3.6 Hz, 1 H, vin.), 7.16−7.40 (m, 5 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.73, 26.87, 43.64, 46.26, 46.82, 126.26, 128.78, 129.71, 135.77, 139.73 ppm. $C_{13}H_{14}S$ (202): calcd. C 77.18, H 6.98; found C 77.41, H 7.16.

2-(Phenylthio)-1,4-dihydro-1,4-methanonaphthalene (8c): The reaction conditions described above for the preparation of **8a** were adopted. From a solution of **7c** (6.38 g, 22.2 mmol) in THF (10 mL) and a solution of *t*BuOK (3.73 g, 33.3 mmol) in the same solvent (40 mL), a pale yellow oil (3.9 g, 70% yield) was obtained after flash chromatography (eluent: *n*-hexane/CH_2Cl_2, 97:3). IR(neat, NaCl): $\tilde{\nu}$ = 3085, 3012, 2980, 2933, 2868, 1591, 1479, 1446, 1275, 781, 768, 742, 643 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.33 (dt, *J* = 7.4, 1.5 Hz, 1 H, 1/2 AB system), 2.50 (dt, *J* = 7.4, 1.5 Hz, 1 H, 1/2 AB system), 3.73 (br. s, 1 H), 4.00 (br. s, 1 H), 6.66 (d, *J* = 3.0 Hz, 1 H, vin.), 6.90−7.46 (m, 9 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 51.23, 54.28, 67.35, 120.85, 121.69, 124.07, 124.55, 126.70, 128.75, 130.49, 131.00, 140.14, 149.51, 150.00, 150.42 ppm. $C_{17}H_{14}S$ (250): calcd. C 81.56, H 5.64; found C 81.27, H 5.50.

2-(Phenylsulfonyl)bicyclo[2.2.1]heptene (10a).[14] **A)** The reaction conditions described above for the preparation of **6b** were adopted. Through the use of a solution of **8a** (0.4 g, 2.0 mmol) in CH_2Cl_2 (10 mL) and TBA-OXONE® (5.0 g, 6.0 mmol) (1 h, room temperature) and purification by rapid percolation through a short silica gel column (eluent CH_2Cl_2) a pale yellow oil (0.45 g, 97% yield) was obtained. **B)** The reaction conditions described above for the preparation of **6a** were adopted. Through the use of a solution of **8a** (0.2 g, 1.0 mmol) in CH_2Cl_2 (10 mL) and a solution of *m*CPBA (0.3 g of a 70% mixture in H_2O, 1.28 mmol), the reaction was complete after 2 h at 0 °C (0.21 g, 90% yield); m.p. 49−50 °C (*n*-hexane/Et_2O) (ref.[14] 47.5−48.5 °C). IR (KBr disk): $\tilde{\nu}$ = 2986, 2970, 2881, 1584, 1453, 1321, 1295, 1183, 1156, 1091, 768, 735, 689 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.87−1.87 (m, 6 H), 3.09 (br. s, 1 H), 3.14 (br. s, 1 H), 6.93 (d, *J* = 3.2 Hz, 1 H, vin), 7.48−7.66 (m, 3 H, Ar), 7.85−7.94 (m, 2 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.73, 24.82, 43.05, 43.67, 49.38, 127.74, 129.14, 133.23, 146.03, 147.94, 165.96 ppm. $C_{13}H_{14}O_2S$ (234): calcd. C 66.64, H 6.02; found C 66.78, H 6.29.

2-(Phenylsulfonyl)-1,4-dihydro-1,4-methanonaphthalene (10c): The reaction conditions described above for the preparation of **6a** were adopted. With a solution of **8c** (2.0 g, 8.0 mmol) in CH_2Cl_2 (30 mL) and a solution of *m*CPBA (3.96 g, 70% mixture in H_20, 16 mmol) in the same solvent (40 mL) the reaction was complete after 1 h at 0 °C (TLC, eluent CH_2Cl_2). By recrystallisation from Et_2O/*n*-hexane, colourless crystals (1.8 g, 83% yield) were collected; m.p. 121 °C. IR (KBr disk): $\tilde{\nu}$ = 3086, 3008, 29895, 2985, 2953, 1579, 1454, 1321, 1150, 1087, 767, 728, 701, 673, cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.33 (dd, *J* = 7.5, 1.2 Hz, 1 H, 1/2 AB system), 2.56 (dt, *J* = 8.0, 1.2 Hz, 1 H, 1/2 AB system), 3.99−4.06 (m, 1 H), 4.08−4.18 (m, 1 H), 7.21 (d, *J* = 6.8 Hz, 1 H, vin.), 6.65−6.97, 7.37−7.78 (series of m, 9 H, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 50.70, 51.22, 69.54, 122.03, 122.32, 124.71, 125.08, 127.92, 129.09, 133.22, 138.87, 146.85, 148.62, 152.45, 156.33 ppm. $C_{17}H_{14}O_2S$ (282): calcd. C 72.32, H 5.00; found C 72.24, H 5.12.

2-(Phenylsulfonyl)-3-(phenylthio)bicyclo[2.2.1]heptene (11a): A well-stirred solution of LDA [freshly prepared under standard reaction conditions from a solution of diisopropylamine (0.3 mL, 2.21 mmol) in THF (10 mL) and *n*BuLi (0.9 mL of a 2.5 M solution in hexanes, 2.21 mmol)] was treated at −78 °C under argon with a solution of **10a** (0.2 g, 0.85 mmol) in THF (5 mL). After the mixture had been kept for 30 min at −78 °C, a solution of PhSSPh (0.48 g, 2.21 mmol) in THF (10 mL) was added at the same temperature and the mixture was stirred for 3 h at −78 °C and then for an additional 12 h at room temperature. The crude reaction mixture was treated with brine (1 mL), concentrated under reduced pressure and diluted with Et_2O (40 mL). The organic phase was washed with H_2O (3 × 20 mL) and brine (2 × 10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (eluent: *n*-hexane/ethyl acetate, 95:5) and recrystallised from Et_2O, to afford colourless crystals (0.2 g, 70% yield); m.p. 153 °C. IR (KBr disk): $\tilde{\nu}$ = 3085, 2999, 2947, 2881, 1538, 1453, 1301, 1150, 1077, 729, 715, 696, 623 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.05−1.75 (m, 6 H), 2.70−2.83 (m, 1 H), 3.24−3.35 (m, 1 H), 7.35−7.66, 7.99−8.09 (10 H, series of m, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.74, 27.08, 46.01, 46.19, 49.23, 127.05, 129.16, 129.04, 129.30, 131.05, 133.07, 133.98, 134.44, 141.86, 157.45 ppm. $C_{19}H_{18}O_2S_2$ (342): calcd. C 66.64, H 5.30; found C 66.81, H 5.47.

2-(Phenylsulfonyl)-3-(phenylthio)1,4-dihydro-1,4-methanonaphthalene (11c): The reaction conditions described for the preparation of **11a** were employed. With LDA [freshly prepared from a solution of diisopropylamine (0.64 mL, 4.6 mmol) in THF (7 mL) and *n*BuLi (1.84 mL of a 2.5 M solution in hexanes, 4.6 mmol)], **10c** (0.5 g, 1.77 mmol) in THF (10 mL) and diphenyl disulfide (1.0 g, 4.6 mmol) in THF (30 mL), an oil was obtained and purified by flash chromatography (eluent: *n*-hexane/CH_2Cl_2, 9:1) and recrystallised from Et_2O, to afford pale yellow crystals. 0.5 g; 74% yield; m.p. 190−192 °C. IR (KBr disk): $\tilde{\nu}$ = 3078, 3023, 2984, 2922, 1766, 1454, 1321, 1157, 759, 696, 610 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.06 (dd, *J* = 7.8, 1.3 Hz, 1 H, 1/2 AB system), 2.46 (dd, *J* = 7.8, 1.3 Hz, 1 H, 1/2 AB system), 3.65 (br. s, 1 H), 4.15 (br. s, 1 H), 6.66−6.90, 7.34−7.59, 7.73−7.80 (14 H, series of m, Ar) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.56, 56.23, 64.93, 121.13, 121.88, 124.60, 124.95, 126.86, 128.70, 129.22, 129.72, 129.96, 132.82, 135.30, 138.26, 140.14, 145.26, 148.20, 164.97 ppm. $C_{23}H_{18}O_2S_2$ (390): calcd. C 70.74, H 4.65; found C 70.63, H 4.60.

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