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A Facile Diastereoselective Synthesis of Functionalized 1,2,3-Trisubstituted Benzocyclopentenes through the Cycloaddition of Bis(phenylsulfonyl)iodonium Ylides to Cyclic Alkenes

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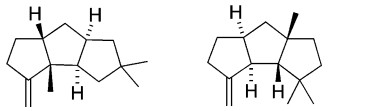
Abstract: The thermal cycloaddition of β-disulfonyl iodonium ylides to cyclic alkenes affords exclusively 1,2,3-trisubstituted *cis*(1,2)/*cis*(2,3)-configured benzocyclopentenes by an electrophilic attack of the ylide on the olefinic double bond. This unsual transformation provides a convenient and direct method for the diastereoselective synthesis of functionalized bicyclo[3.3.0]octanes (characteristic structural units contained in polyquinane natural products), when cyclopentenes are used as cycloalkene partner.

The photochemical and thermal $Cu(acac)_2$-catalyzed reaction of bis(sulfonyl)iodonium ylides with olefins affords cyclopropanes in moderate yields.[1] Exceptions are the reaction of these ylides with *trans*-stilbene and norbornene, which lead to trisubstituted indanes.[2] Evidently, an unusual cycloaddition process operates, in which an elaborate 1,2,3-trisubstituted indan is produced in a single step from readily available alkenic starting materials. The three substituents at the C-1, C-2, and C-3 positions of the 1,2,3-trisubstituted indan **4** may assume four possible configurations, namely *cis*(1,2)/*cis*(2,3), *cis*(1,2)/*trans*(2,3), *trans*(1,2)/*cis*(2,3), and *trans*(1,2)/*trans*(2,3), in which the numbers in parentheses specify the substituents at the respective positions. Thus, various phenylated alkenes, either cis- or *trans*-configured, lead to the *trans*(1,2)/*trans*(2,3) indan ring system,[3] whereas norbornene derivatives yield the *trans*(1,2)/*cis*(2,3)-product.[4] In contrast, triphenylethylene and tetraphenylethylene result in alkenyl and aryl C−H insertion products.[5] It should be realized that the sulfonyl substituent may be reductively cleaved[6] or appropriately modified through established carbanion methodology; thus, a potentially valuable synthetic method has become accessible for the stereoselective construction of the multicyclic ring systems.

The incentive of the present study was to assess whether cyclopentenes as olefinic partner would lead to the trisubstituted diquinane skeleton contained in hirsutene and $\Delta^{9(12)}$-capnellene.[7] The latter are well-known isomeric members of the hirsutane and capnellene natural products, which possess a linearly fused tricyclopentanoid framework with four sequential stereogenic centers, one of which is quaternary.



We now disclose that the reaction of phenyliodonium bis(phenylsulfonyl)methylide (**2a**) with the cyclopentenes **3a**,**b** and cyclooctene **3c** gives exclusively the *cis*(1,2)/*cis*(2,3)-indans **4** (Scheme 1). Unusual and hardly predictable is the fact that the *cis*/*cis* geometry about the ring junction is preferred, whereas previously either the *trans*/*cis* configuration was favored as in the case of norbornenes or the *trans*/*trans* arrangement as with the stilbenes.[3,4] Evidently, the choice of the alkene substrate dictates the stereochemical outcome which of the four possible configurations [*cis*(1,2)/*cis*(2,3), *cis*(1,2)/*trans*(2,3), *trans*(1,2)/*cis*(2,3), or *trans*(1,2)/*trans*(2,3)] is generated in the resulting trisubstituted cycloadduct.

The disulfonyl iodonium ylide **2a** was readily prepared from the corresponding β-disulfone **1** by treatment with iodobenzene diacetate and KOH as base at −10 °C (Scheme 1). All reactions of the cycloalkenes **3** were run with an excess of olefin until complete consumption of the ylide. The cycloadducts **4** (Table 1) were isolated by flash chromatography on silica gel in up to 46% yield, at 100% consumption of the ylide. It should be emphasized that a clean process operates, except that substantial amounts (up to 70%) of the ylide are diverted back to the β-disulfone **1** through decomposition.

As for the specific cycloalkenes examined herein, the reaction of ylide **2a** with cyclopentene **3a** and catalytic amounts of $Rh_2(OAc)_4$ was not completed even after 528 h at ca. 20 °C; however, when heated at 40 °C for 3.5 h, exclusively the *cis*(1,2)/*cis*(2,3)-indan **4a** was obtained in 31% yield (Table 1, entry 1). The cycloadduct **4a** was isolated in 27% yield in the absence of the catalyst (Table 1, entry 2). The use of the catalyst had no effect on the product composition. The reaction of the ylide **2a** with 1-methylcyclopentene (**3b**) at 70 °C gave the *cis*(1,2)/*cis*(2,3)-product **4b** in 31% yield (Table 1, entry 3); thus, the replacement of one of the olefinic hydrogen atoms by a methyl group has no effect on the reactivity of the

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SCHEME 1

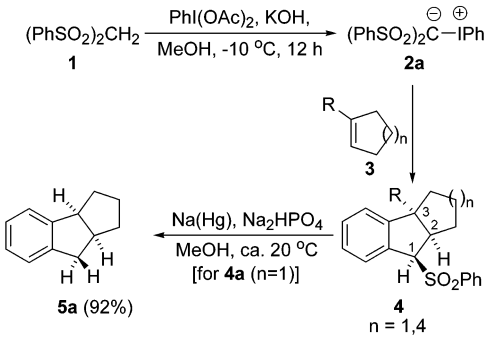


TABLE 1. Cycloaddition[a] of the Ylide 2a with the Cyclic Alkenes 3

				conditions[b]			
entry	R	*n*	alkene	*T* (°C)	*t*[c] (h)	product[d]	yield[e] (%)
1	H	1	**3a**	40	3.5	**4a**	31
2	H	1	**3a**	40	4.0	**4a**	27
3	Me	1	**3b**	70	2.0	**4b**	31
4	H	4	*trans*-**3c**	20	128	**4c**	46
5	H	4	*cis*-**3c**	20	144	**4c**	42
6	H	4	*cis*-**3c**	90	0.5	**4c**	39[f]
7	H	4	*cis*-**3c**	90	0.2	**4c**	40[f]

[a] All reactions were carried out by stirring a suspension of the ylide **2a** (1 equiv) and the alkene **3** (excess) in CH_3CN for the required time. [b] The reaction was carried out in the presence of catalytic amounts of $Rh_2(OAc)_4$, except entries 2 and 6. [c] Time required for complete consumption of the ylide. [d] The configuration of the cycloadduct is *cis*(1,2)/*cis*(2,3). [e] Yield of isolated product after silica gel chromatography. [f] The yield was estimated from the ^{1}H NMR spectrum (±5% error).

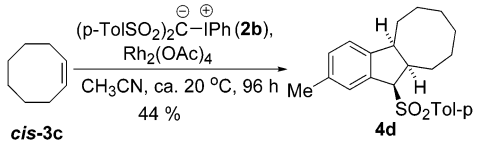
substrate toward the ylide **2a**. The cycloaddition of the ylide **2a** with either *trans*- or *cis*-cyclooctene (**3c**) afforded in both cases excusively the *cis*(1,2)/*cis*(2,3)-cycloadduct **4c** in 46% and 42% yields (Table 1, entries 4 and 5); consequently, the configuration of the olefinic double bond is not preserved in the cyclooctene cycloadduct.

The structural assignment of the products is exemplified for the **4a** derivative. The ^{1}H NMR spectrum of **4a** displays a multiplet at $\delta = 3.11$ for the proton at C-3, a multiplet at $\delta = 3.17$ for the proton at C-2, and a singlet at $\delta = 4.46$ for the proton at C-1. The existence of NOESY signals between the proton at C-1 and the C-2 or C-3 positions indicates the *cis*(1,2)/*cis*(2,3) configuration of the three substituents in the newly formed five-membered ring. In the case of the **4b**, the existence of HMBC signals between the methyl group at $\delta = 0.93$ and the carbon atoms at $\delta = 51.4$ (C-2) and $\delta = 55.6$ (C-3), but the absence of such signals with the carbon atom at $\delta = 77.8$ (C-1), indicate that the methyl group is at the C-3 position of the newly formed five-membered ring.

The arylsulfonyl functionality may be readily removed reductively by treatment with sodium amalgam.[6] This is exemplarily illustrated for the cycloadduct **4a**, which affords the bicyclo[3.3.0]octane **5** (Scheme 1). The synthetic utility of this sequence of reactions should be evident.

The mechanism of this complex reaction is still poorly understood, and we may only speculate on the detailed role played by the hypervalent iodine partner. A carbene mechanism is ruled out since under the employed reaction conditions, it is unlikely that ylide **2** decomposes into

SCHEME 2



iodobenzene and bis(phenylsulfonyl)methylene, as in the case of the thermal $Cu(acac)_2$-catalyzed decomposition[1] or in the photolysis.[8] Were this so, then phenyl benzenethiosulfonate ($PhSO_2SPh$) and CO_2, the typical products of bis(phenylsulfonyl)methylene, should have been observed. For example, when a suspension of the ylide **2a** in acetonitrile was heated at reflux for 2 h, only the β-disulfone **1** was isolated. Under similar reaction conditions, but in the presence of catalytic amounts of $Cu(acac)_2$, the β-disulfone **1** (22% yield) and $PhSO_2SPh$ (54% yield) were obtained, whereas in the presence of $Rh_2(OAc)_4$ only the β-disulfone **1** was produced in 58% yield. A metal carbenoid is also unlikely to be involved, since the ylide **2a** reacts with the cyclic alkenes in the absence of $Rh_2(OAc)_4$ to afford the same cycloadduct.

When the iodonium ylide **2b** was employed, whose *p*-methyl substituent of the arylsulfonyl moiety permitted us to determine the regioselectivity of the cycloaddition process in regard to the location of the methyl substituent in the benzo ring of the product, with cyclooctene *cis*-**3c** only cycloadduct **4d** was obtained in 44% yield (Scheme 2). The spectral data reveal that the methyl group of the benzo ring and the sulfonyl-bearing C-1 position of the newly formed five-membered ring are located *meta* to one another in the product. Originally, this methyl substituent occupied the *para* position in the toluenesulfonyl group of the iodonium ylide. This mechanistically perplexing regiochemical result is the same as reported previously for the cycloaddition between ylide **2b** and stilbenes[3] and implies a complex rearrangement process for this reaction.

In accord with our previous proposal[3] and the current results, we offer the mechanism in Scheme 3 to rationalize this unusual cycloaddition, with cyclopentene (**3a**) as illustrative substrate. What needs to be articulated is the unprecedented finding that the cyclopentene substrate affords the *cis*(1,2)/*cis*(2,3) configuration for the three substituents of the newly formed benzocyclopentene ring in the cycloadduct **4a**. This is in contrast to the *trans*-(1,2)/*cis*(2,3) configuration observed for the norbornene substrate or the *trans*(1,2)/*trans*(2,3) cycloadduct obtained with the stilbenes.[3,4] The cycloaddition process is presumably initiated either by electron transfer between the two reactants to afford the radical-ion pair (not shown) that couples to produce the dipolar intermediate **A**, or alternatively the dipolar species **A** may be generated directly by electrophilic attack of the iodonium ylide. Such an intermediate is expected to have a T-shaped structure for the trivalent iodine functionality,[9] a fact that forces the carbanionic site away from the cyclopentyl positive center. Thereby, ring closure to a four-membered-ring cyclic iodinane species is prevented, which on

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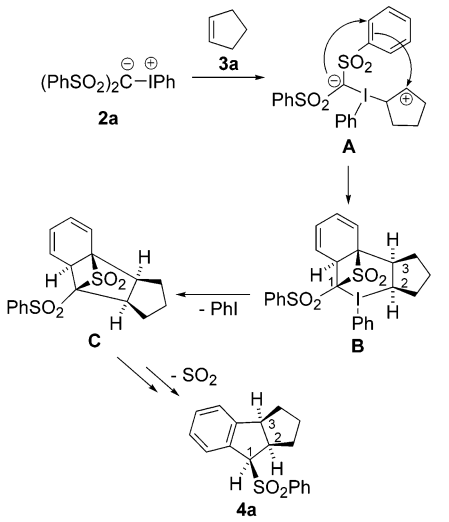
SCHEME 3



subsequent iodobenzene extrusion would afford a cyclopropane product. Instead, nucleophilic attack by the bis(sulfonyl)-centered carbanion on the *ortho* position of the phenylsulfonyl ring and closure of the resulting dipole leads to the iodinane **B**. Such a nucleophilic attack constitutes the initial step of the Truce−Smiles rearrangement,[10] observed in carbanions of diaryl sulfones with an *o*-methyl group. The novel *cis*(1,2)/*cis*(2,3) configuration of the resulting iodinane **B** species may be accounted for in terms of the 1,3-*syn-axial* interaction between the hydrogen atom at the C-3 and the cyclopentyl methylene group at the C-5 positions, as illustrated by the structures for the *cis,cis*-**B** and *trans,cis*-**B** iodinanes in Figure 1. Clearly, in the preferred *cis,cis*-**B** configuration, such steric repulsion is minimized (H/H interaction), whereas in the *trans,cis*-**B** configuration it is large (H/CH_2 interaction). This is in contrast to the cycloaddition of ylides **2** with norbornene, for which the *trans*(1,2)/*cis*(2,3)-relationship is favored. Severe steric repulsion between the sulfone functionality and the methylene bridge of the norbornene skeleton operates, as displayed in the *cis,cis*-**B′** structure. This transannular steric repulsion dominates the 1,3-*syn-axial* interaction such that the *trans,cis*-**B′** cycloadduct is favored over *cis,cis*-**B′** (Figure 1).

Elimination[11] of iodobenzene from the iodinane **B** leads to the intermediate **C**, which on sulfur dioxide extrusion and subsequent aromatization by a diastereoselective hydrogen shift[12] affords the observed **4a** product (Scheme 3). Although the mechanistic details of the SO_2/PhI extrusion are not known, evidently the configuration fixed in the **B** intermediate is preserved in the final cycloadduct.

In summary, the work described herein offers a convenient and efficient method for the direct diastereoselective synthesis of functionalized 1,2,3-trisubstituted indanes **4**, through the unusual cycloaddition of bis(phenylsulfonyl)iodonium ylides to cycloalkenes. Irrespective of the puzzling mechanistic features, complex multicyclic ring skeletons of well-defined configuration become conveniently available through this novel methodology.

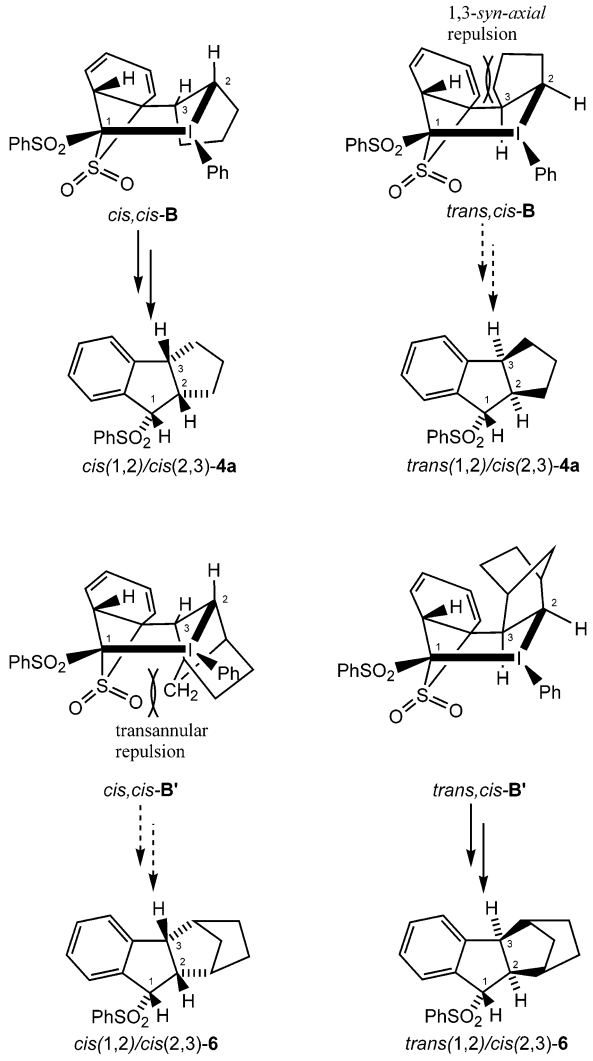


FIGURE 1. Proposed *cis,cis*-**B** and *trans,cis*-**B** iodinane structures for the cyclopentene cycloadduct to illustrate the 1,3-*syn-axial* steric interaction; for comparison, the respective *cis,cis*-**B′** and *trans,cis*-**B′** structures of the norbonene substrate are shown to illustrate the transannular interaction.

Experimental Section

Synthesis of 4a. A suspension of the iodonium ylide **2a** (1.00 g, 2.00 mmol), cyclopentene (**3a**; 2 mL, 22.7 mmol), and $Rh_2(OAc)_4$ (0.1−0.2 mol %) in acetonitrile (5 mL) was heated at 40 °C for 3.5 h. The solvent and excess cyclopentene were removed (40 °C, 10 Torr), and the residue was flash-chromatographed (silica gel, CH_2Cl_2) to afford benzo-2-phenylsulfonylbicyclo[3.3.0]oct-3-ene (**4a**) as a colorless oil (187 mg, 31%). IR (neat): 3130 cm^{-1}, 3005, 2905, 1505, 1470, 1315, 1230, 1155, 1140, 1095, 1035, 1010, 930, 835. ^1H NMR (400 MHz, $CDCl_3$): δ 1.26−1.40 (m, 2H), 1.46−1.64 (m, 2H), 1.87−2.03 (m, 2H), 3.08−3.13 (m, 1H), 3.14−3.20 (m, 1H), 4.46 (s, 1H), 7.02 (d, J = 7.6 Hz, 1H), 7.17−7.31 (m, 2H), 7.35−7.40 (m, 3H), 7.51−7.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6 (t), 33.1 (t), 33.7 (t),

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44.9 (d), 48.4 (d), 77.2 (d), 124.5 (d), 126.7 (d), 126.8 (d), 128.5 (d), 129.3 (d), 129.8 (d), 133.5 (d), 134.2 (s), 136.8 (s), 150.0 (s). HRMS [CI (NH_3)]: calcd for $C_{18}H_{18}O_2S\ NH_4^+$ $[M + NH_4]^+$, 316.1371, found 316.1370.

Synthesis of 4b. A suspension of the iodonium ylide **2a** (0.50 g, 1.00 mmol), 1-methylcyclopentene (**3b**; 328 mg, 4.00 mmol), and $Rh_2(OAc)_4$ (0.1−0.2 mol %) in acetonitrile (3 mL) was heated at 70 °C for 2 h. The solvent and excess 1-methylcyclopentene were removed (50 °C, 10 Torr), and the residue was flash-chromatographed (silica gel, CH_2Cl_2) to afford benzo-2-phenylsulfonyl-5-methylbicyclo[3.3.0]oct-3-ene (**4b**) as a colorless oil (98 mg, 31%). IR (neat): 3130 cm^{-1}, 3000, 2910, 1505, 1470, 1325, 1235, 1160, 1145, 1100, 1035, 835. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (s, 3H), 1.16−1.32 (m, 1H), 1.47−1.64 (m, 3H), 1.67−1.73 (m, 1H), 1.96−2.05 (m, 1H), 2.68−2.72 (m, 1H), 4.40 (d, J = 3.0 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 7.19−7.23 (m, 1H), 7.31−7.35 (m, 1H), 7.40−7.44 (m, 3H), 7.54−7.58 (m, 1H), 7.64 (dd, J = 1.2, 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7 (t), 27.6 (q), 35.7 (t), 42.9 (t), 51.4 (d), 55.6 (s), 77.8 (d), 123.4 (d), 126.2 (d), 126.9 (d), 128.7 (d), 129.5 (d), 129.9 (d), 133.5 (d), 133.7 (s), 136.9 (s), 153.8 (s). HRMS [CI (NH_3)]: calcd for $C_{19}H_{20}O_2S\ NH_4^+$ $[M + NH_4]^+$ 330.1528, found 330.1533.

Synthesis of 4c. A suspension of the iodonium ylide **2a** (0.50 g, 1.00 mmol), *trans*-cyclooctene (**3b**; 0.50 g, 4.50 mmol), and $Rh_2(OAc)_4$ (0.1−0.2 mol %) in acetonitrile (10 mL) was stirred at 20 °C for 128 h. The solvent and excess cyclooctene were removed (30 °C, 10 Torr), and the reaction residue was flash-chromatographed (silica gel, CH_2Cl_2) to afford benzo-2-phenylsulfonylbicyclo[6.3.0]undec-3-ene (**4c**) as colorless needles (157 mg, 46%). Mp:152−153 °C ($CHCl_3$−petroleum ether). IR (KBr): 2950 cm^{-1}, 2910, 2890, 2860, 2840, 1590, 1575, 1560, 1575, 1560, 1325, 1170, 1105, 1090, 1050, 1035, 1005, 980, 950, 930, 885, 850. ^1H NMR (400 MHz, $CDCl_3$): δ 0.54−0.60 (m, 1H), 1.37−1.78 (m, 9H), 1.82−1.95 (m, 2H), 2.56−2.63 (m, 1H), 2.97−3.03 (m, 1H), 4.37 (d, J = 5.7 Hz, 1H), 7.05 (d, J = 7.3 Hz, 1H), 7.24−7.31 (m, 2H), 7.39−7.43 (m, 2H), 7.53−7.57 (m, 1H), 7.63−7.66 (m, 2H), 7.73 (d, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.7 (t), 24.2 (t), 26.8 (t), 26.9 (t), 35.4 (t), 35.9 (t), 44.0 (d), 47.6 (d), 77.7 (d), 124.0 (d), 126.5 (d), 127.0 (d), 128.6 (d), 129.3 (d), 129.6 (d), 133.1 (d), 133.5 (s), 136.5 (s), 149.6 (s). Anal. Calcd for $C_{21}H_{24}O_2S$ (340.5): C, 74.08; H, 7.10; S, 9.42. Found: C,74.26; H, 6.91; S, 9.34.

Synthesis of 4d. A suspension of the iodonium ylide **2b** (0.526 g, 1.00 mmol), *cis*-cyclooctene (**3b**; 0.50 g, 4.50 mmol) and $Rh_2(OAc)_4$ (0.1−0.2 mol %) in acetonitrile (10 mL) was stirred at 20 °C for 96 h. The solvent and excess cyclooctene were removed (30 °C, 10 Torr), and the reaction residue was flash-chromatographed (silica gel, CH_2Cl_2) to afford **4d** as colorless needles (142 mg, 42%). Mp: 135−136 °C ($CHCl_3$−petroleum ether). IR (KBr): 2960 cm^{-1}, 2880, 1615, 1510, 1460, 1320, 1310, 1300, 1290, 1225, 1205, 1190, 1140, 1120, 1090, 1045, 1020, 830. ^1H NMR (200 MHz, $CDCl_3$): δ 0.53−0.70 (m, 1H), 1.34−1.95 (m, 11H), 2.37 (s, 3H), 2.39 (s, 3H), 2.51−2.64 (m, 1H), 2.90−3.00 (m, 1H), 4.30 (d, J = 5.8 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.22 $\kappa\alpha\iota$ 7.54 (AA′BB′ system, 4H), 7.53 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.9 (+), 21.2 (+), 23.3 (−), 23.8 (−), 26.4 (−), 26.5 (−), 35.4 (−), 35.6 (−), 44.1 (+), 47.1 (+), 77.6 (+), 124.0 (+), 127.2 (+), 129.5 (+), 129.9 (+), 130.5 (+), 133.6, 134.1, 137.1, 144.9, 147.1. HRMS [CI (NH_3)]: calcd for $C_{23}H_{28}O_2S\ NH_4^+$ $[M + NH_4]^+$ 386.2154, found 386.2151.

Synthesis of 5. Na_2HPO_4 (0.36 g) and sodium amalgam (2.50 g) were added to a solution of the cycloadduct **4a** (152 mg, 0.51 mmol) in methanol (10 mL). The reaction mixture was stirred at 20 °C for 40 h, the solvent was removed (40 °C, 10 Torr), and the residue was dissolved in dichloromethane (30 mL) and washed with brine (2 × 50 mL). After drying ($MgSO_4$), the solvent was removed (20 °C, 10 Torr) to afford benzobicyclo[3.3.0]-oct-3-ene (**5a**) as a colorless oil (74 mg, 92%). IR (neat): 3130 cm^{-1}, 3080, 2980, 2910, 1505, 1470, 1230, 1180, 1035. ^1H NMR (400 MHz, $CDCl_3$): δ 1.35−1.63 (m, 3H), 1.73−1.80 (m, 1H), 1.84−1.92 (m, 1H), 1.99−2.11 (m, 1H), 2.71 (dd, J = 3.3, 16.5 Hz, 1H), 2.85−2.94 (m, 1H), 3.24 (dd, J = 8.8, 16.5 Hz, 1H), 3.66 (ddd, J = 3.3, 8.8, 12.5 Hz, 1H), 7.11−7.19 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$): δ 26.1 (t), 34.1 (t), 34.9 (t), 39.6 (t), 42.0 (d), 50.3 (d), 124.4 (d), 124.5 (d), 126.1 (d), 126.4 (d), 143.5 (s), 148.0 (s). HRMS (EI): calcd for $C_{12}H_{14}$ $[M^+]$ 158.1095, found 158.109.

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Supporting Information Available: ^1H and ^{13}C spectra of **4a**−**d** and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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