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ARTICLE

Reactions of (phenylethynyl)sulfones with tricyclo[4.1.0.0^{2,7}]heptanes

V.A. Vasin, Yu.Yu. Masterova, V.V. Razin, and N.V. Somov

Abstract: Methyl-, phenyl-, *p*-chlorophenyl-, and *p*-tolyl(phenylethynyl)sulfones under photochemical or thermal initiation add to the central bicyclobutane C1–C7 bond of 1-R(H, Me, Ph)-tricyclo[4.1.0.0^{2,7}]heptanes anti-selectively, and form norpinic adducts containing a phenylethynyl group in a geminal to substituent R position, and an *endo*-oriented sulfonyl group in position 7. The corresponding ketones were prepared by the hydration of the *anti*-adducts by the method of Kucherov. The ketone with a methylsulfonyl substituent under reflux in toluene in the presence of KOH powder and the phase-transfer catalyst (TEBA-Cl) afforded the tricyclic sulfone.

Key words: (phenylethynyl)sulfone, radical addition, sulfonyl-substituted norpinanes, tricyclo[4.1.0.0^{2,7}]heptane, cyclization.

Résumé : Sous l'influence d'une initiation photochimique ou thermique les méthyl-, phényl-, *p*-chlorophényl- et *p*-tolyl (phényléthynyl)sulfones s'additionnent sélectivement d'une façon *anti* à la liaison centrale C1-C7 du bicyclobutane des 1-R(H, Me, Ph)-tricyclo[4.1.0.0^{2,7}]heptanes, avec formation d'adduits norpiniques contenant un groupe phényléthynyle dans une position géminale par rapport au substituant R et avec une orientation *endo* par rapport au goupe sulfonyle en position 7. On a préparé les cétones correspondantes par hydratation des adduits *anti* par la méthode de Kucherov. La cétone avec un substituant méthylsulfonyle, par chauffage au reflux du toluène, en présence de KOH en poudre et d'un catalyseur de transfert de phase, le chlorure de triéthylbenzylammonium (Cl-TEBA), conduit à la formation de la sulfone tricyclique. [Traduit par la Rédaction]

Mots-clés : (phényléthynyl)sulfone, addition radicalaire, norpinanes substitués par un groupe sulfonyle, tricyclo[4.1.0.0^{2,7}]heptane, cyclisation.

Introduction

Alkynes are useful and versatile intermediates in organic synthesis.[1] The utility of the acetylenic functional group in organic chemistry has been well documented.[2] Acetylenic sulfones also have many synthetic applications.[3] Thus, for example, phenyl(arylsulfonyl)acetylenes **1a**, **1b** under thermolysis or photolysis add to bicyclic alkenes (norbornene, indene, etc.) forming 1:1-adducts as a result of the C_{sp}–S bond homolytic scission.[4] Taking into account the known similarity between the structures of a central C–C bond in bicyclo[1.1.0]butanes and a π-bond C=C, the reaction of acetylenic sulfones **1a**, **1b** with bicyclobutane compounds was expected. This assumption seemed to be quite possible inasmuch as the hydrocarbons of the tricyclo[4.1.0.0^{2,7}]heptane row **2–4** add the sulfonyl derivatives $ArSO_2X$ (X = Cl, Br, I, SPh, SMe, SePh, SCN, N_3) because of a homolytic scission of the sulfur–heteroatom bond in the latter reagents, as we have previously shown.[5–12]

Results and discussion

We investigated the interaction of (phenylethynyl)sulfones **1a–1d** and propynyl sulfone **1e** with tricycloheptanes **2–4** (Fig. 1). There is no doubt that the anticipated 1:1-adducts of these reactions are of synthetic interest, owing to the considerable transformation potential of the acetylenic moiety as well as the sulfonyl group.

After UV irradiation of equimolar amounts of tricycloheptane **2** with sulfones **1a–1c** in CH_2Cl_2 at 20 °C in quartz tubes for 15–20 h, the products of the addition to the C1–C7 bond were obtained as a mixture of *anti*- and *syn*-isomers **5a–5c** and **6a–6c** with an admixture of the sulfonylnorpinanes **7a–7c** in the ratio of 4.9:1:0.2, 3.9:1:0.2, and 4.9:1:0.3, respectively, with 40%–45% total yield (Scheme 1).

The analogous photochemical reaction between hydrocarbon **2** and acetylene **1d** resulted in the formation of the monoadducts **5d** and **6d** in the ratio of 5.5:1. After heating tricycloheptane **2** at reflux with acetylenic sulfone **1b** in equimolar amounts in toluene for 10 h, the formation of the same monoadducts as those obtained in the case of photolysis was observed. However, the content of the admixture **7b** was slightly increased. Thermolysis of sulfones **1b, 1c** carried out in sealed glass ampules at 110 °C for 6–8 h in double excess of tricycloheptane **2** afforded compounds **5b, 5c**, **6b, 6c** only, in the ratio close to that observed in the case of photolysis. Propynyl sulfone **1e**, in contrast to sulfones **1a–1d**, showed no reaction with tricycloheptane **2** under either photolysis or thermal initiation.

Photolysis of sulfones **1a–1c** in the presence of one and a half multiple excess of tricycloheptanes **3**, **4** in CH_2Cl_2 (15–20 h, 20 °C) afforded a unique addition product in each case: the corresponding *anti*-adducts **8a–8c**, **9a–9c** in the yield of 50%–55% (Scheme 2). At the same time, the presence of the respective *syn*-adducts in the reaction mixtures in trace amounts is not excluded.

The structure of compounds **5a–5d**, **6c**, **8a–8c**, **9a–9c** isolated as individual substances by column chromatography on silica gel and (or) crystallization is confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy data. We did not succeed in isolating *syn*-adducts **6a**, **6b**, **6d**, so the latter compounds were characterized in the mixtures with the respective *anti*-adducts **5a**, **5b**, **5d** by the NMR spectra. To wit, we have assigned the signals of all the non-aromatic carbon atoms and the signals of the proton at the C-atom bearing a sulfonyl group. The configuration of compounds **5** and **6** at C6 and C7 were determined on the basis of analyzing the positions and multiplicities of the signals from H6 and H7 in the ^{1}H NMR spectra taking into account the known structure–spectrum correlations

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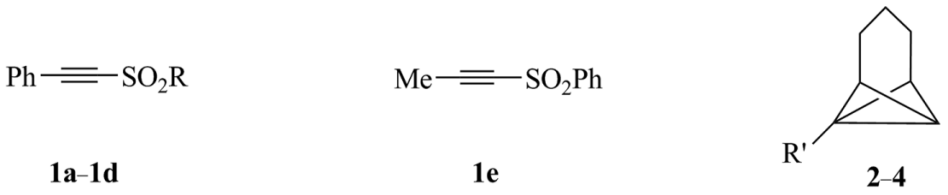
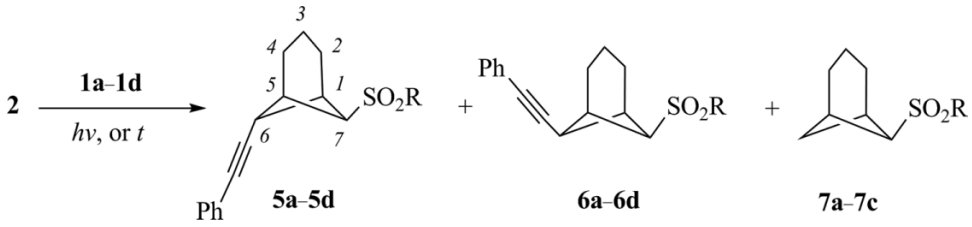
Fig. 1. Starting ethynylsulfones and tricyclo[4.1.0.0^{2,7}]heptanes.

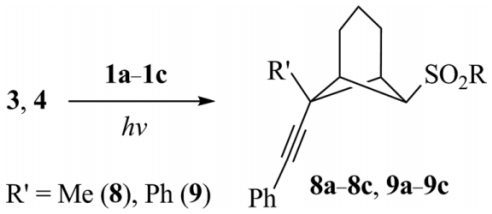


Hereinafter: R = Ph (**a**), *p*-Tol (**b**), Me (**c**), *p*-ClC$_6$H$_4$ (**d**); R' = H (**2**), Me (**3**), Ph (**4**)

Scheme 1. The reaction of compound **2** with ethynylsulfones **1a–1d**.



Scheme 2. The reaction of compounds **3**, **4** with ethynylsulfones **1a–1c**.



in the row of 6,7-disubstituted norpinanes.[13] Thus, a triplet signal of the proton at the sulfonyl-substituted C-atom indicates its *anti* (*exo*) orientation in both the norpinanes **5** and **6**. On the other hand, the observation of a singlet signal of the proton at the ethynyl-substituted C-atom attests to the *syn* (*endo*) orientation of this proton in norpinanes **5**. It was not possible to determine the multiplicity of H6 in norpinane **6** because of the signal overlap with H1,5. The *anti* (*exo*) orientation of the proton at the sulfonyl-substituted C-atom in compound **6** is based on the observed chemical shift value (~3.4 ppm). This value is ~0.6 ppm less than the chemical shift of the analogous proton in norpinane **5** because of the phenylethynyl group deshielding effect in the latter. The *anti* orientation of the geminal to a sulfonyl group proton in compounds **8a–8c** and **9a–9c** is confirmed by observing its triplet signal at ~4.35 ppm in the ^{1}H NMR spectra. The *endo* orientation of the phenyl group in compounds **9a–9c** is connected with the chemical shift value of the *endo* proton H3 (~0.60–0.75 ppm) located in the shielding field of the *endo* oriented phenyl ring.[6,8] The configuration at the tertiary C-atom of compounds **8a–8c** and **9a–9c** is accepted on the basis of the expected similarity between the chemical shifts of the geminal to a sulfonyl group protons. Compounds **7a–7c** were identified in the reaction mixtures by comparing them with authentic samples prepared according to known procedures under oxidation of the adducts of tricycloheptane **2** with thiophenol,[14] *p*-thiocresol,[11] and methanethiol,[10] respectively, using hydrogen peroxide in acetic acid.

Thus, it can be stated that in the case of the reactions between tricycloheptanes **2–4** and sulfones **1a–1d** the regio- and stereoselectivity of the addition are similar to other sulfonylation reactions of the mentioned hydrocarbons, which had been studied by us earlier.[5–12] In all the cases, 6-norpinanyl radical **A** stands as an intermediate. Reagent transfer on its reaction centre proceeds *anti*-selectively, while the extent of the selectivity depends on the substituent R type at this centre and is higher for hydrocarbons **3**, **4** than for compound **2**.[15]

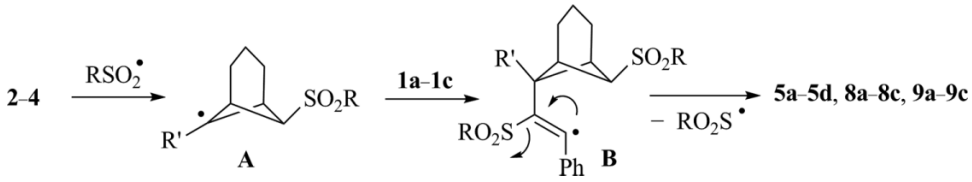
Taking into account that a sulfur–carbon bond is stronger than a sulfur–heteroatom bond, it was initially expected that (phenylethynyl)sulfones would prove to be ineffective chain transfer agents in a homolytic process. In particular, this is suggested by the fact that the latter sulfones do not react with open-chain and monocyclic olefins.[4] We suppose that in our case, on the one hand, the reaction is promoted by higher activity of the central C1–C7 bond of tricycloheptanes **2–4** in comparison with an alkene π-bond. This bond is readily opened by *endo*-directed attack of an aryl sulfonyl radical at the bridgehead C-atom with the formation of norpinanyl radical **A**[16]. On the other hand, it is also promoted by high activity of the C≡C bond in acetylenes **1a–1d** with respect to alkyl radicals, caused by the possibility of the benzyl stabilization of the intermediate, which allows us to propose Scheme 3 by way of explanation of the obtained results.

In this scheme, radical **B**, formed by the regioselective attack of radical **A** on the α-C-atom of acetylene **1a–1d**, is proposed as another key intermediate. Then, the elimination of RSO$_2^{\bullet}$ leads to the formation of an ethynyl fragment, i.e., the resulting product is formed by way of addition–elimination.[17] A similar radical substitution mechanism of a sulfo group in acetylenic sulfones and related compounds has been previously reported.[18] Apparently, the preferred formation of the *anti*-adduct is connected with a steric factor: the entrance of the reagent to the reaction centre of radical **A** from the *endo* direction is sterically hindered by the trimethylene bridge. In the case of less sterically hindered hydrocarbon **2**, this direction is partially realised, and *syn*-adduct **6a–6d** is formed in detectable amounts in the same way.

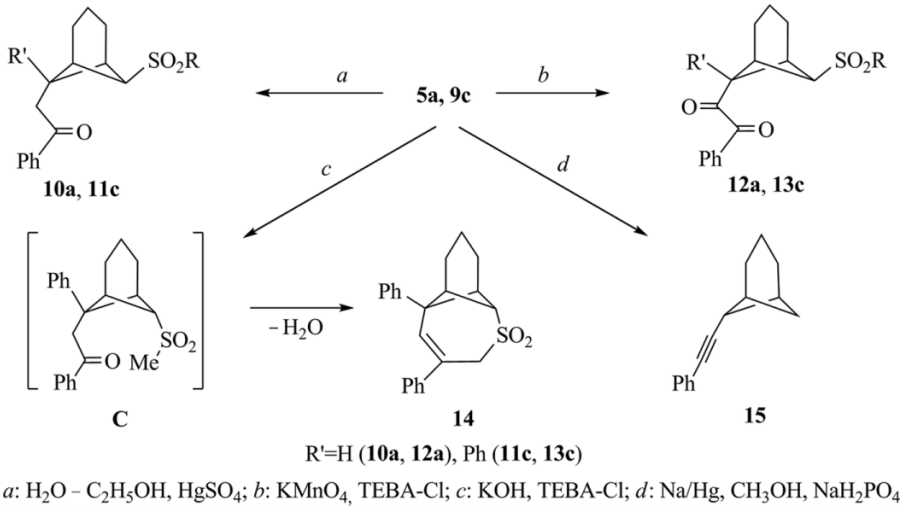
We propose that the sulfonyl radicals (RSO$_2^{\bullet}$) required for the initiation of the addition process are generated by the cleavage of the C–S bond of acetylenic sulfones **1a–1d** under thermolysis or photolysis.[19,20] Apparently, propynyl sulfone **1e** does not react with tricycloheptanes **2–4** the same way because of the less effective stabilization of the reaction centre in intermediate **B** by the methyl group, by comparison with a phenyl substituent.

We have carried out the transformations of *anti*-adducts **5a**, **9c** (Scheme 4). The hydration of the adducts by the method of Kucherov (95% aqueous ethanol, $HgSO_4$, 70 °C, 20 h)[21] proceeded strictly regioselectively and afforded the previously unknown sulfonylketones of the norpinic row **10a**, **11c**. The same *anti*-adducts **5a**, **9c** under treatment with $KMnO_4$ in the presence of the phase-transfer catalyst triethylbenzylammonium chloride

Scheme 3. The proposed mechanism for the sulfoethynylation reaction of compounds **2–4**.



Scheme 4. The transformations of *anti*-adducts **5a**, **9c**.



(TEBA-Cl),[22] were oxidized to diketones **12a**, **13c**. As was expected, these reactions proceeded on the C≡C bond only, and the configurations at C6 and C7 remained the same, as confirmed by the ^{1}H NMR spectra.

When the solution of ketone **11c** in toluene was heated at reflux in the presence of powdered KOH and a catalytical amount of TEBA-Cl for 5 h,[23] this led to the formation of the cyclic sulfone **14**. This transformation includes base-catalyzed epimerization at the C7 atom, with the formation of intermediate product **C** and cyclization of the latter by intramolecular aldol condensation proceeding with strictly regioselective dehydration.[23]

We have carried out the desulfonylation of *anti*-adduct **5a** by treatment with 6% sodium amalgam in methanol in the presence of NaH_2PO_4.[4] The structure of the resultant 6-(phenylethynyl) norpinane **15** is confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopy data and mass spectrum analysis.

The structure of the tricyclic unsaturated sulfone **14** was assigned unequivocally by X-ray crystallography (Fig. 2, Table 1) and confirmed by IR, ^{1}H, and ^{13}C NMR spectroscopy data.

Conclusions

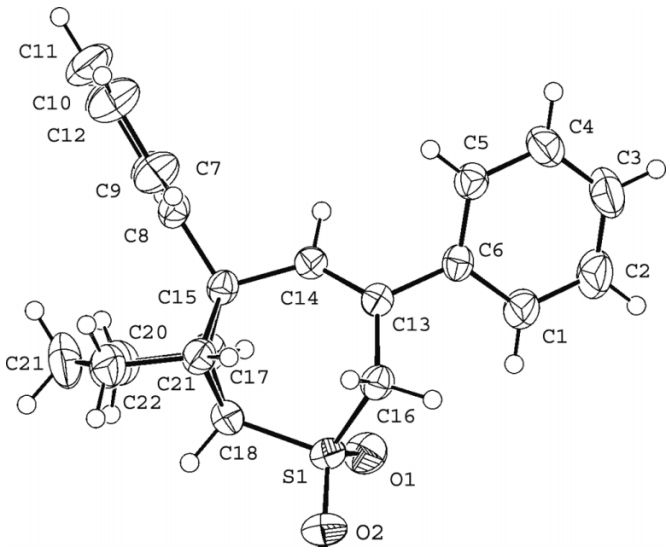
The method presented herein for acetylenyl norpinanyl sulfones, and the methods of refunctionalization and desulfonation demonstrate the considerable potentialities for further transformation of the products from reaction between quite available tricyclo[4.1.0.0^{2,7}]heptanes and (phenylethynyl)sulfones.

Experimental section

General

All melting points reported are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-400 spectrometer (400 and 100 MHz, respectively). IR spectra were measured on a Fourier Spectrometer InfraLum FT-02 (KBr pellets). Elemental analyses were carried out by a CHNS analyzer VarioMICRO. Mass spectra were recorded using a KONIK RBK-HRGC5000B-MSQ12 system (KONIXBERT HI-TECH, S.A., Spain) equipped with a column

Fig. 2. X-ray molecular structure of the tricyclic sulfone **14** with the atom numbering system used in the crystallographic analysis. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.



KAP5, 15 m × 9.25 mm × 0.25 μm; carrier gas helium, flow rate 1 mL min^{-1}; temperature was programmed from 50 to 250 °C; ionization by electronic impact, U_{ion} at 70 eV. Analytical TLC was performed by Sorbfil plates: eluent, low-boiling petroleum ether–acetone, 10–6:1; developer, iodine. Column chromatography was performed on silica gel Merck 60 (0.040–0.063 mm^{-1}); eluent, low-boiling petroleum ether –acetone, 6:1. A mercury-discharge high pressure lamp DRT-400 (400 W, λ = 240–320 nm) and halogen filament lamp KGLN-500 were used for the photochemical reactions. Suitable crystals for X-ray crystallographic study of **14** were

Table 1. Crystallographic data and selected data collection parameters for the sulfone **14**.

Parameter	Value
Empirical formula	$C_{22}H_{22}O_2S$
Formula weight	350.46
Colour, habit	Colourless, block
Crystal dimensions (mm)	0.50 × 0.31 × 0.28
Crystal system	Monoclinic
Space group	P 2_1/c
Z	4
a (Å)	8.9080 (4)
b (Å)	17.3582 (7)
c (Å)	12.1245 (6)
α (°)	90
β (°)	101.415 (5)
γ (°)	90
Collection ranges	$-7 \le h \le 8$; $-13 \le k \le 13$; $-15 \le l \le 15$
Volume (Å^3)	1837.69 (14)
D_{calcd} (Mg/m^3)	1.267
Radiation	Mo Kα (λ = 0.71073 Å)
Absorption coefficient (μ) (mm^{-1})	0.188
F(000)	744
θ range for data collection (°)	3.51–26.37
Observed reflections	8282
Independent reflections	3684
R_{int}	0.0386
Data/restraints/parameters	3684/0/227
Goodness-of-fit on F^2	1.074
Final *R* indices [$I > 2\sigma(I)$]	$R(F) = 0.0412$, $wR(F^2) = 0.104$
R indices (all data)	$R(F) = 0.0459$, $wR(F^2) = 0.107$
Largest diff. peak and hole (*e* Å^{-3})	0.293 and −0.303

obtained by crystallization from acetone – low-boiling petroleum ether (1:7). A single crystal was measured with an Oxford Diffraction Xcalibur XGemini S diffractometer equipped with a CCD-detector SAPPHIRE III at a temperature of 298(2) K. An analytical absorption correction with the program CrysAlisPro (Agilent Technologies, 2011)[24] gave a correction factor between 0.362 and 0.577. Analytical numeric absorption correction using a multifaceted crystal model was based on expressions derived by R. C. Clark and J. S. Reid.[25] The structure was determined by direct methods using the program SHELXS.[26] Refinement was performed with the program SHELXL-97.[26] Positions of hydrogen atoms were inferred from neighbouring sites and refined in the "riding model" (U_{iso}(H) = 1.2U_{equiv}(carbon) Å^2). Crystallographic data and selected data collection parameters are reported in Table 1.

Materials and reagents

Solvents (acetone, ether, benzene, methanol, low-boiling petroleum ether) were purified by known methods. Tricycloheptanes **2**,[27] **3**[28], and **4**[29,30] as well as phenyl-,[31] *p*-tolyl- and methyl (phenylethynyl)sulfones[19] were prepared according to procedures in the literature.

1-Chloro-4-(phenylethynylsulfonyl)benzene (1d)

To a solution of Na_2SO_3 (2.75 g, 21.8 mmol) and $NaHCO_3$ (3.66 g, 43.6 mmol) in water (40 mL), 4-chlorobenzenesulfonylchloride (4.60 g, 21.8 mmol) was added at 20 °C under stirring. The reaction mixture was stirred at 70 °C for 5 h and then extracted with ether (3 × 55 mL). Then I_2 (3.65 g, 14.4 mmol) in benzene (55 mL) was added to the prepared water solution. The organic layer was separated, dried with $MgSO_4$ for 1 h, and then filtered. To the filtered solution, phenylacetylene (1.76 g, 1.9 mL, 17.2 mmol) was added and the reaction mixture was irradiated by halogen lamp at 20 °C for 3.5 h. The solvent was removed under reduced pressure, and the residue was washed with ethanol – low-boiling petroleum ether (1:1) to afford 1-chloro-4-(2-iodo-2-phenylvinylsulfonyl)benzene (2.8 g, 31.8%) as a colourless solid. To a solution of the latter product (2.65 g, 6.55 mmol) in dry benzene (30 mL), NEt_3 (0.86 g, 1.2 mL, 8.52 mmol) was added. The mixture was stirred at 20 °C for 80 h. Precipitated triethylammonium iodide was filtered and washed with dry benzene (10 mL). The solvent was removed under reduced pressure, and the residue was recrystallized (ethanol – low-boiling petroleum ether, 2:1) to afford **1d** as a colourless solid. Yield: 1.50 g (82.8%); mp 103–104 °C; lit. value[32] mp 104–105 °C. ^{1}H NMR δ (ppm): 7.50 (t, *J* = 7.6 Hz, 2H, H-Ar), 7.58–7.67 (m, 3H, H-Ar), 7.69, (d, *J* = 8.8 Hz, 2H, H-Ar), 8.13 (d, *J* = 8.8 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 85.0, 94.0 (C≡C); 117.6, 128.7, 128.9, 129.7, 131.7, 132.8, 140.2, 141.0 (C-Ar). IR (KBr, cm^{-1}): 540 (m), 663 (s), 756 (s), 852 (s), 1011 (m), 1084 (s), 1157 (vs), 1331 (s), 1443 (m), 2183 (s). Anal. calcd. for $C_{14}H_9ClO_2S$ (%): C 60.76, H 3.28, S 11.58; found: C 60.69, H 3.34, S 11.48.

General procedure for photochemical reaction of tricycloheptane (2) with (phenylethynyl)sulfones (1a–1d)

A solution of tricycloheptane **2** (0.28 g, 3 mmol) and (phenylethynyl) sulfone **1** (3 mmol) in dry CH_2Cl_2 (12 mL) in a hermetically closed quartz test tube was irradiated by mercury lamp at 20 °C for 15–20 h. After evaporation of the solvent the residue was analyzed by TLC and ^{1}H NMR methods and chromatographed on silica gel.

7-syn-Benzenesulfonyl-6-exo-(phenylethynyl)bicyclo[3.1.1]heptane (5a)

Colourless solid. Yield: 0.51 g (43.6%); mp 129–130 °C; R_f = 0.38. ^{1}H NMR δ (ppm): 1.78–1.93 (m, 1H, *endo*-H3), 1.95–2.14 (m, 3H, *exo*-H3 and *endo*-H2,4), 2.62–2.75 (m, 2H, *exo*-H2,4), 2.84–2.92 (m, 2H, H1,5), 2.89 (s, 1H, H6), 4.04 (t, *J* = 5.7 Hz, 1H, H7), 7.25–7.32 (m, 3H, H-Ar), 7.33–7.40 (m, 2H, H-Ar), 7.58 (t, *J* = 7.5 Hz, 2H, H-Ar), 7.65 (t, *J* = 7.3 Hz, 1H, H-Ar), 7.92 (d, *J* = 7.6 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.9 (C3), 23.3 (C2,4), 32.0 (C7), 45.3(C1,5), 61.1 (C6); 82.6, 90.0 (C≡C); 123.0, 127.5, 128.0, 128.2, 129.3, 131.5, 133.4, 140.2 (C-Ar). IR (KBr, cm^{-1}): 621 (s), 691 (s), 729 (s), 756 (m), 1150 (vs), 1285 (s), 1316 (s), 1447 (m), 1489 (m), 2222 (w), 2951 (m). Anal. calcd. for $C_{21}H_{20}O_2S$ (%): C 74.97, H 5.99, S 9.53; found: C 74.86, H 6.12, S 9.31.

7-syn-Benzenesulfonyl-6-endo-(phenylethynyl)bicyclo[3.1.1]heptane (6a)

Fragment of ^{1}H NMR δ (ppm): 3.37 (t, *J* = 5.6 Hz, H^7). Fragment of ^{13}C NMR δ (ppm): 13.9 (C3), 21.2 (C2,4), 31.6 (C6), 43.5 (C1,5), 61.5 (C7); 84.5, 86.2 (C≡C).

6-exo-(Phenylethynyl)-7-syn-p-toluenesulfonylbicyclo[3.1.1]heptane (5b)

Colourless solid. Yield: 0.51 g (41.6%); mp 139–140 °C; R_f = 0.40. ^{1}H NMR δ (ppm): 1.79–1.92 (m, 1H, *endo*-H3),1.94–2.12 (m, 3H, *exo*-H3 and *endo*-H2,4), 2.46 (s, 3H, CH_3), 2.63–2.74 (m, 2H, *exo*-H2,4), 2.85–2.89 (m, 2H, H1,5), 2.89 (s, 1H, H6), 4.02 (t, *J* = 5.9 Hz, 1H, H7), 7.27–7.31 (m, 3H, H-Ar), 7.34–7.39 (m, 4H, H-Ar), 7.79 (d, *J* = 8.3 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.9 (C3), 21.5 (CH_3), 23.3 (C2,4), 31.9 (C6), 45.2 (C1,5), 61.1 (C7); 82.5, 90.1 (C≡C); 123.1, 127.5, 127.9, 128.2, 129.9, 131.5, 137.3, 144.3 (C-Ar). IR (KBr, cm^{-1}): 602 (m), 679 (s), 756 (m), 814 (m), 1150 (s), 1285 (vs), 1316 (s), 1489 (w), 1597 (w), 2222 (vw), 2951 (w). Anal. calcd. for $C_{22}H_{22}O_2S$ (%): C 75.40, H 6.33, S 9.15; found: C 75.35, H 6.34, S 8.82.

6-endo-(Phenylethynyl)-7-syn-p-toluenesulfonylbicyclo[3.1.1]heptane (6b)

Fragment of ^{1}H NMR δ (ppm): 3.34 (t, *J* = 5.3 Hz, H7). Fragment of ^{13}C NMR δ (ppm): 13.9 (C3), 21.2 (CH_3), 23.4 (C2,4), 31.6 (C6), 43.4 (C1,5), 61.5 (C7); 84.5, 88.2 (C≡C).

7-syn-Methylsulfonyl–6-exo-(phenylethynyl)bicyclo[3.1.1]heptane (5c)

Colourless solid. Yield: 0.39 g (40.9%); mp 125–126 °C; R_f = 0.23. ^{1}H NMR δ (ppm): 1.75–1.87 (m, 1H, *endo*-H3), 1.89–2.01 (m, 3H, *exo*-H3 and *endo*-H2,4), 2.48–2.59 (m, 2H, *exo*-H2,4), 2.86 (s, 3H, CH_3), 2.89 (s, 1H, H6), 2.98–3.04 (m, 2H, H1,5), 4.08 (t, *J* = 5.8 Hz, 1H, H7), 7.30–7.31 (m, 3H, H-Ar), 7.40–7.43 (m, 2H, H-Ar). ^{13}C NMR δ

(ppm): 13.7 (C3), 23.0 (C2,4), 32.3 (C7), 41.6 (CH_3), 45.2 (C1,5), 59.3 (C6); 82.8, 89.9 (C≡C); 123.0, 128.0, 128.3, 131.5 (C-Ar). IR (KBr, cm^{-1}): 694 (m), 764 (vs), 960 (w), 1157 (m), 1281 (vs), 1315 (m), 1489 (w), 2222 (vw), 2870 (w), 2955 (w). Anal. calcd. for $C_{16}H_{18}O_2S$ (%): C 70.04, H 6.61, S 11.68; found: C 69.91, H 6.49, S 11.69.

7-syn-*Methylsulfonyl-6*-endo-*(phenylethynyl)bicyclo[3.1.1]heptane (6c)*

Colourless solid. Yield: 75.0 mg (7.8%); mp 161–162 °C; R_f = 0.17. ^{1}H NMR δ (ppm): 1.97–2.07 (m, 2H, H3), 2.12–2.22 (m, 2H, *endo*-H2,4), 2.35–2.45 (m, 2H, *exo*-H2,4), 2.89 (s, 3H, CH_3), 3.06–3.10 (m, 3H, H1,5 and H6), 3.42 (t, *J* = 5.3 Hz, 1H, H7), 7.30–7.33 (m, 3H, H-Ar), 7.41–7.44 (m, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.6 (C3), 20.7 (C2,4), 31.6 (C6), 41.9 (CH_3), 43.1 (C1,5), 59.5 (C7); 84.5, 85.9 (C≡C); 123.1, 128.1, 128.3, 131.6 (C-Ar). IR (KBr, cm^{-1}): 544 (m), 691 (m), 756 (vs), 961 (m), 1096 (m), 1142 (s), 1254 (m), 1293 (m), 1323 (s), 1443 (m), 1489 (vs), 2218 (vw), 2959 (w). Anal. calcd. for $C_{16}H_{18}O_2S$ (%): C 70.04, H 6.61, S 11.68; found: C 69.92, H 6.70, S 11.59.

7-syn-*(*p-*Chlorobenzenesulfonyl)-6*-exo-*(phenylethynyl)bicyclo[3.1.1]heptane (5d)*

Colourless solid. Yield: 0.42 g (37.8%); mp 160–161 °C; R_f = 0.59. ^{1}H NMR δ (ppm): 1.80–1.90 (m, 1H, *endo*-H3), 1.96–2.09 (m, 3H, *exo*-H3 and *endo*-H2,4), 2.61–2.65 (m, 2H, *exo*-H2,4), 2.86–2.89 (m, 3H, H1,5 and H6), 3.99 (t, *J* = 6.0 Hz, 1H, H7), 7.27–7.29 (m, 3H, H-Ar), 7.34–7.35 (m, 2H, H-Ar), 7.54 (d, *J* = 8.9 Hz, 2H, H-Ar), 7.84 (d, *J* = 8.9 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 14.0 (C3), 23.5 (C2,4), 32.2 (C6), 45.5 (C1,5), 61.6 (C7); 82.8, 90.0 (C≡C); 123.1, 128.2, 128.4, 129.2, 129.9, 131.7, 138.8, 140.4 (C-Ar). IR (KBr, cm^{-1}): 644 (m), 756 (s), 1088 (m), 1149 (vs), 1277 (m), 1319 (m), 1473 (w), 1574 (w), 2226 (vw), 2951 (w). Anal. calcd. for $C_{21}H_{19}ClO_2S$ (%): C 68.01, H 5.16, S 8.64; found: C 68.11, H 5.26, S 8.53.

7-syn-*(*p-*Chlorobenzenesulfonyl)-6*-endo-*(phenylethynyl)bicyclo[3.1.1]heptane (6d)*

Fragment of ^{1}H NMR δ (ppm): 3.30 (t, *J* = 5.7 Hz, 1H, H7) ppm. Fragment of ^{13}C NMR δ (ppm): 13.9 (C3), 21.2 (C2,4), 31.7 (C7), 43.5 (C1,5), 61.5 (C6); 85.1, 86.1 (C≡C).

*General procedure for thermal reaction of tricycloheptane (2) with (phenylethynyl)sulfones (*1b, 1c*)*

Method A

A mixture of tricycloheptane **2** (0.564 g, 6 mmol) and (phenylethynyl)sulfone **1b, 1c** (3 mmol) in a heat-resistant glass ampule was purged with argon, fused, and heated at 110 °C for 6–8 h. Then an ampule was opened, and the content was analyzed by TLC and ^{1}H NMR methods. The products **5**, **6**, and **7** were obtained in the ratio of 5.0:1:0.2 and 5.2:1:0.2, respectively.

Method B

A solution of tricycloheptane **2** (0.282 g, 3 mmol) and (phenylethynyl)sulfone **1c** (3 mmol) in toluene (25 mL), under argon, was heated at reflux for 10 h in round-bottomed flask equipped with backflow condenser. After removing of the solvent by a water-jet air pump, the residue was analyzed by TLC and ^{1}H NMR methods. The products **5c**, **6c**, and **7c** were obtained in the ratio of 3.6:1:0.2.

*General procedure for photochemical reaction of tricycloheptanes (3, 4) with (phenylethynyl)sulfones (*1a–1c*)*

A solution of tricycloheptanes **3**, **4** (4.5 mmol) and (phenylethynyl) sulfones **2a–2c** (3 mmol) in dry CH_2Cl_2 (12 mL) in a hermetically closed quartz test tube was irradiated by mercury lamp at 20 °C for 15–20 h. Then the solvent was removed by a water-jet air pump. The products were isolated from the residue by column chromatography on silica gel and crystallization from ether.

7-syn-*Benzenesulfonyl-6*-endo-*methyl-6*-exo-*(phenylethynyl)bicyclo[3.1.1]heptane (8a)*

Colourless solid. Yield: 0.68 g (53.6%); mp 88–89 °C; R_f = 0.41. ^{1}H NMR δ (ppm): 1.41 (s, 3H, CH_3), 1.62–1.76 (m, 1H, *endo*-H3), 1.91–2.04 (m, 2H, *endo*-H2,4), 2.23–2.38 (m, 1H, *exo*-H3), 2.43–2.54 (m, 2H, *exo*-H2,4), 2.81 (br.d, 2H, H1,5), 4.23 (t, *J* = 5.7 Hz, 1H, H7), 7.25–7.31 (m, 3H, H-Ar), 7.31–7.37 (m, 2H, H-Ar), 7.58 (t, *J* = 7.3 Hz, 2H, H-Ar), 7.65 (t, *J* = 7.5 Hz, 1H, H-Ar), 7.94 (d, *J* = 7.6 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.2 (C3), 16.6 (CH_3 C6), 20.7 (C2,4), 37.1 (C6), 48.0 (C1,5), 61.9 (C7); 80.4, 95.6 (C≡C); 123.2, 127.3, 127.8, 128.2, 129.3, 131.5, 133.3, 140.7 (C-Ar). IR (KBr, cm^{-1}): 606 (vs), 691 (s), 721 (s), 764 (s), 1088 (m), 1150 (vs), 1281 (s), 1304 (s), 1485 (m), 1447 (m), 2215 (vw), 2967 (m). Anal. calcd. for $C_{22}H_{22}O_2S$ (%): C 75.40, H 6.33, S 9.15; found: C 75.40, H 6.32, S 9.36.

6-endo-*Methyl-6*-exo-*(phenylethynyl)-7*-syn-p-*toluentsulfonylbicyclo[3.1.1]heptane (8b)*

Colourless solid. Yield: 0.58 g (52.9%); mp 118–119 °C; R_f = 0.53. ^{1}H NMR δ (ppm): 1.45 (s, 3H, CH_3C6), 1.66–1.79 (m, 1H, *endo*-H3), 1.97–2.07 (m, 2H, *endo*-H2,4), 2.28–2.41 (m, 1H, *exo*-H3), 2.50 (s, 3H, $CH_3C_6H_4$), 2.47–2.58 (m, 2H, *exo*-H2,4), 2.84 (br.d, *J* = 5.6 Hz, 2H, H1,5), 4.25 (t, *J* = 5.7 Hz, 1H, H7), 7.30–7.36 (m, 3H, H-Ar), 7.37–7.44 (m, 4H, H-Ar), 7.86 (d, *J* = 8.3 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.2 (C3), 16.6 (CH_3C6), 20.7 (C2,4), 21.5 ($CH_3C_6H_4$), 37.1 (C6), 47.9 (C1,5), 62.0 (C7); 80.4, 95.8 (C≡C); 123.2, 127.4, 127.8, 128.2, 129.9, 131.5, 137.8, 144.1 (C-Ar). IR (KBr, cm^{-1}): 671 (s), 760 (s), 1088 (m), 1146 (vs), 1281 (m), 1439 (w), 1311 (m), 1489 (w), 1597 (w), 2218 (vw), 2874 (w). Anal. calcd. for $C_{23}H_{24}O_2S$ (%): C 75.79, H 6.64, S 8.80; found: C 75.71, H 6.62, S 8.97.

6-endo-Methyl-7-syn-methylsulfonyl-6-exo-(phenylethynyl)bicyclo[3.1.1]heptane (8c)

Colourless solid. Yield: 0.44 g (50.5%); mp 122–123 °C; R_f = 0.37. ^{1}H NMR δ (ppm): 1.41 (s, 3H, CH_3 C6), 1.57–1.73 (m, 1H, *endo*-H3), 1.89–2.00 (m, 2H, *endo*-H2,4), 2.05–2.19 (m, 1H, *exo*-H3), 2.30–2.42 (m, 2H, *exo*-H2,4), 2.91 (s, 3H, CH_3SO_2), 2.91–2.96 (m, 2H, H1,5), 4.22 (t, *J* = 5.6 Hz, 1H, H7), 7.29–7.34 (m, 3H, H-Ar), 7.40–7.44 (m, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.0 (C3), 16.5 (CH_3C6), 20.4 (C2,4), 37.2 (C6), 42.0 (CH_3SO_2), 47.9 (C1,5), 60.2 (C7); 80.7, 95.6 (C≡C); 123.2, 128.0, 128.3, 131.6 (C-Ar). IR (KBr, cm^{-1}): 559 (m), 694 (m), 760 (s), 1142 (s), 1284 (vs), 1304 (m), 1447 (w), 1447 (w), 1489 (w), 2230 (vw), 2948 (m). Anal. calcd. for $C_{17}H_{20}O_2S$ (%): C 70.80, H 6.99, S 11.12; found: C 70.71, H 7.07, S 11.02.

7-syn-*Benzenesulfonyl-6*-endo-*phenyl-6*-exo-*(phenylethynyl)bicyclo[3.1.1]heptane (9a)*

Colourless solid. Yield: 0.63 g (51.0%); mp 182–183 °C; R_f = 0.38. ^{1}H NMR δ (ppm): 0.66–0.80 (m, 1H, *endo*-H3), 1.61–1.74 (m, 1H, *exo*-H3), 2.04–2.16 (m, 2H, *endo*-H2,4), 2.64–2.77 (m, 2H, *exo*-H2,4), 3.36–3.42 (m, 2H, H1,5), 4.36 (t, *J* = 5.7 Hz, 1H, H7), 7.21–7.34 (m, 8H, H-Ar), 7.40 (t, *J* = 7.4 Hz, 2H, H-Ar), 7.63 (t, *J* = 7.4 Hz, 2H, H-Ar), 7.70 (t, *J* = 7.3 Hz, 1H, H-Ar), 8.00 (d, *J* = 7.2 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.0 (C3), 21.0 (C2,4), 43.5 (C6), 48.3 (C1,5), 60.4 (C7); 82.8, 94.2 (C≡C); 123.0, 125.8, 126.7, 127.5, 127.9, 128.1, 128.6, 129.4, 131.5, 133.5, 139.2, 140.4 (C-Ar). IR (KBr, cm^{-1}): 617 (s), 721 (s), 764 (s), 1088 (m), 1150 (vs), 1285 (m), 1312 (m), 1447 (m), 1489 (w), 2223 (vw), 2955 (w). Anal. calcd. for $C_{27}H_{24}O_2S$ (%): C 78.61, H 5.86, S 7.77; found: C 78.65, H 5.80, S 7.79.

6-endo-*Phenyl-6*-exo-*(phenylethynyl)-7*-syn-p-*toluenesulfonylbicyclo[3.1.1]heptane (9b)*

Colourless solid. Yield: 0.64 g (50.3%); mp 162–163 °C; R_f = 0.34. ^{1}H NMR δ (ppm): 0.63–0.77 (m, 1H, *endo*-H3), 1.59–1.70 (m, 1H, *exo*-H3), 2.01–2.13 (m, 2H, *endo*-H2,4), 2.47 (s, 3H, CH_3), 2.61–2.72 (m, 2H, *exo*-H2,4), 3.32–3.38 (m, 2H, H1,5), 4.31 (t, *J* = 5.7 Hz, 1H, H7), 7.20–7.33 (m, 8H, H-Ar), 7.35–7.43 (m, 4H, H-Ar), 7.86 (d, *J* = 8.3 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.1 (C3), 21.0 (C2,4), 21.6 (CH_3), 43.5 (C6), 48.3 (C1,5), 60.5 (C7); 82.7, 94.3 (C≡C); 123.1, 125.8, 126.7, 127.6,

127.9, 128.1, 128.6, 130.0, 131.5, 137.6, 139.3, 144.4 (C-Ar). IR (KBr, cm^{-1}): 602 (m), 671 (vs), 760 (m), 1088 (m), 1150 (vs), 1285 (s), 1312 (m), 1447 (w), 1493 (w), 1597 (m), 2222 (vw), 2955 (m). Anal. calcd. for $C_{28}H_{26}O_2S$ (%): C 78.84, H 6.14, S 7.52; found: C 78.75, H 6.19, S 7.59.

7-syn-Methylsulfonyl-6-endo-phenyl-6-exo-(phenylethynyl)bicyclo[3.1.1]heptane (9c)

Colourless solid. Yield: 0.57 g (54.2%); mp 160–161 °C; R_f = 0.22. ^{1}H NMR δ (ppm): 0.61–0.74 (m, 1H, *endo*-H3), 1.46–1.60 (m, 1H, *exo*-H3), 2.00–2.12 (m, 2H, *endo*-H2,4), 2.46–2.58 (m, 2H, *exo*-H2,4), 2.95 (s, 3H, CH_3), 3.48–3.54 (m, 2H, H1,5), 4.37 (t, *J* = 5.6 Hz, 1H, H7), 7.24–7.36 (m, 8H, H-Ar), 7.41 (t, *J* = 7.4 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 12.8 (C3), 20.6 (C2,4), 41.9 (C1,5), 43.5 (C6), 48.2 (CH_3), 58.5 (C7); 83.0, 94.1 (C≡C); 122.9, 125.7, 126.7, 128.0, 128.1, 128.6, 131.5, 138.9 (C-Ar). IR (KBr, cm^{-1}): 548 (m), 710 (m), 764 (m), 957 (m), 1142 (vs), 1285 (s), 1304 (m), 1455 (w), 1489 (w), 2226 (vw), 2948 (w). Anal. calcd. for $C_{22}H_{22}O_2S$ (%): C 75.40, H 6.33, S 9.15; found: C 75.12, H 6.27, S 8.93.

***General procedure for hydration of* anti-*adducts* (5a, 9b)**

A solution of *anti*-adducts **5a**, **9b** (3 mmol) in 95% aqueous ethanol (60 mL) in the presence of catalytic amounts of $HgSO_4$ and H_2SO_4 was heated at reflux at 70 °C for 20 h. The solvent was removed under reduced pressure, the aimed products were purified by crystallization from ethanol.

***7*-syn-*Benzenesulfonyl*-*6*-exo-*(benzoylmethyl)bicyclo[3.1.1]heptane* (10a)**

Colourless solid. Yield: 0.72 g (67.9%); mp 149–150 °C. ^{1}H NMR δ (ppm): 1.89–2.12 (m, 5H, H3 and *endo*-H2,4), 2.48 (t, *J* = 7.5 Hz, 1H, H6), 2.57 (br.d, *J* = 5.9 Hz, 2H, H1,5), 2.61–2.72 (m, 2H, *exo*-H2,4), 3.18 (d, *J* = 7.5 Hz, 2H, CH_2C=O), 3.60 (t, *J* = 5.9 Hz, 1H, H7), 7.46 (t, *J* = 7.6 Hz, 2H, H-Ar), 7.53–7.60 (m, 3H, H-Ar), 7.61–7.67 (m, 1H, H-Ar), 7.86–7.94 (m, 4H, H-Ar). ^{13}C NMR δ (ppm): 14.1 (C3), 24.3 (C2,4), 36.8 (C6), 38.9 (C1,5), 42.2 (CH_2C=O), 60.5 (C7); 127.3, 127.8, 128.6, 129.2, 133.2, 136.5, 140.5 (C-Ar), 198.4 (C = O). IR (KBr, cm^{-1}): 617 (m), 691 (m), 722 (m), 1088 (m), 1146 (vs), 1280 (m), 1316 (m), 1447 (m), 1678 (s), 2948 (m). Anal. calcd. for $C_{21}H_{22}O_3S$ (%): C 71.16, H 6.26, S 9.04; found C 71.08, H 6.20, S 9.00.

***6*-exo-*(Benzoylmethyl)*-*7*-syn-*methylsulfonyl*-*6*-endo-*phenylbicyclo[3.1.1]heptane* (11c)**

Colourless solid. Yield: 0.66 g (62.6%); mp 208–209 °C. ^{1}H NMR δ (ppm): 0.54–0.66 (m, 1H, *endo*-H3), 1.45–1.54 (m, 1H, *exo*-H3), 2.07 (t, *J* = 12.1 Hz, 2H, *endo*-H2,4), 2.45–2.53 (m, 2H, *exo*-H2,4), 2.94 (s, 3H, CH_3), 3.41 (s, 2H, CH_2C=O), 3.47 (br.d, 2H, H1,5), 3.98 (t, *J* = 5.7 Hz, 1H, H7), 7.13 (t, *J* = 6.7 Hz, 3H, H-Ar), 7.20 (t, *J* = 7.4 Hz, 2H, H-Ar), 7.27 (t, *J* = 7.8 Hz, 2H, H-Ar), 7.43 (t, *J* = 7.4 Hz, 1H, H-Ar), 7.51–7.53 (m, 2H, H-Ar). ^{13}C NMR δ (ppm): 13.3 (C3), 21.4 (C2,4), 41.8 (CH_3), 44.5 (C1,5), 46.4 (CH_2C=O), 48.0 (C6), 57.8 (C7); 126.1, 126.5, 127.8, 128.0, 128.2, 132.8, 137.4, 141.5 (C-Ar), 199.0 (C=O). IR (KBr, cm^{-1}): 706 (m), 760 (s), 1134 (vs), 1269 (m), 1289 (s), 1319 (m), 1455 (m), 1655 (vs), 2951 (m), 2971 (m). Anal. calcd. for $C_{22}H_{24}O_3S$ (%): C 71.71, H 6.57, S 8.69; found: C 71.69, H 6.37, S 8.42.

***Intramolecular cyclization reaction of* (11c)**

3,3-Dioxo-5,7-diphenyl-3-thiatricyclo[5.4.0.0^{2,8}]undec-5-ene (14)

A solution of **11c** (0.74 g, 2 mmol) in toluene (35 mL) in the presence of powdered KOH (0.79 g, 14 mmol) and TEBA-Cl (70 mg, 0.31 mmol) was heated at reflux for 25 h. The solvent was removed under reduced pressure, the residue was chromatographed on silica gel, and the tricyclic compound **14** was obtained as a colourless solid. Yield: 210 mg (27.2%); mp 213–214 °C; R_f = 0.28. ^{1}H NMR δ (ppm): 0.74–0.87 (m, 1H, *endo*-H10), 1.37–1.50 (m, 3H, *exo*-H10), 2.06–2.19 (m, 2H, *endo*-H9,11), 2.24–2.36 (m, 2H, *exo*-H9,11), 3.24 (s, 1H, H2), 3.64 (br.s, 2H, H1,8), 4.50 (s, 2H, H4), 5.95 (s, 1H, H6), 7.15 (d, *J* = 7.6 Hz, 2H, H-Ar), 7.24–7.33 (m, 6H, H-Ar), 7.40 (t, *J* = 7.5 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 12.8 (C10), 28.9 (C9,11), 46.0 (C1,8), 52.2 (C7), 53.6 (C4), 70.8 (C2), 125.1 (C-Ar), 126.1 (C=C), 126.3, 127.6 (C-Ar), 128.4 (C=C); 128.5, 128.9, 141.6, 142.6, 145.4 (C-Ar). IR (KBr, cm^{-1}): 702 (s), 756 (m), 1119 (vs), 1246 (w), 1296 (s), 1311 (w), 1446 (m), 1493 (w), 2862 (w), 2939 (w). Anal. calcd. for $C_{22}H_{22}O_2S$ (%): C 75.40, H 6.33, S 9.15. Found: C 75.38, H 6.37, S 9.11.

***General procedure for oxidation of* anti-*adducts* (5a, 9c)**

To a solution containing *anti*-adducts **5a**, **9c** (3 mmol), CH_3COOH (7.4 mL) and TEBA-Cl (0.34 g, 1.5 mmol) in CH_2Cl_2 (25 mL), a solution of $KMnO_4$ (1.90 g, 12 mmol) in H_2O (40 mL) was added. The reaction mixture was heated at reflux and stirred for 12 h, then the excess of $KMnO_4$ and formed MnO_2 were removed by the addition of small portions of Na_2SO_3. The organic layer was separated and washed with water, the water layer was extracted by CH_2Cl_2 (2 × 15 mL). The combined extract was dried with $MgSO_4$. Then the solvent was removed under reduced pressure, and the aimed products were purified by crystallization (*n*-pentane–$CHCl_3$).

***7*-syn-*Benzenesulfonyl*-*6*-exo-*(1′,2′-dioxo-2′-phenylethyl)bicyclo[3.1.1]heptane* (12a)**

Pale-yellow solid. Yield: 0.96 g (86.7%); mp 117–118 °C. ^{1}H NMR δ (ppm): 1.84–1.98 (m, 1H, *endo*-H3), 2.10–2.21 (m, 1H, *exo*-H3), 1.99–2.10 (m, 2H, *endo*-H2,4), 2.68–2.80 (m, 2H, *exo*-H2,4), 3.14 (br.s, 2H, H1,5), 3.46 (s, 1H, H6), 3.86 (t, *J* = 5.7 Hz, 1H, H7), 7.50 (t, *J* = 7.6 Hz, 2H, H-Ar), 7.58 (d, *J* = 7.5 Hz, 2H, H-Ar), 7.62–7.70 (m, 2H, H-Ar), 7.89 (d, *J* = 7.3 Hz, 2H, H-Ar), 7.95 (d, *J* = 7.3 Hz, 2H, H-Ar). ^{13}C NMR δ (ppm): 14.2 (C3), 23.9 (C2,4), 41. 7 (C1,5), 48.1 (C6), 59.5 (C7); 127.5, 128.9, 129.4, 130.2, 131.9, 133.6, 134.9, 140.1 (C-Ar), 191.3, 202.1 (C=O). IR (KBr, cm^{-1}): 610 (s), 691 (m), 725 (m), 1150 (vs), 1281 (m), 1447 (m), 1678 (s), 1694 (m), 2959 (w). Anal. calcd. for $C_{21}H_{20}O_4S$ (%): C 68.47, H 5.47, S 8.70; found: C 68.39, H 5.40, S 8.67.

***6*-exo-*(1′,2′-Dioxo-2′-phenylethyl)*-*7*-syn-*methylsulfonyl*-*6*-endo-*phenylbicyclo[3.1.1]heptane* (13c)**

Pale-yellow solid. Yield: 1.04 g (86.7%); mp 189–190 °C. ^{1}H NMR δ (ppm): 0.64–0.79 (m, 1H, *endo*-H3), 1.50–1.65 (m, 1H, *exo*-H3), 2.02–2.17 (m, 2H, *endo*-H2,4), 2.55–2.69 (m, 2H, *exo*-H2,4), 2.94 (s, 3H, CH_3), 3.70 (t, *J* = 5.7 Hz, 1H, H7), 4.08 (br.d, 2H, H1,5), 7.14–7.32 m (9H, H-Ar), 7.45 (d, *J* = 7.2 Hz, 1H, H-Ar). ^{13}C NMR δ (ppm): 13.3 (C3), 20.6 (C2,4), 41.9 (CH_3), 43.8 (C1,5), 57.1 (C7), 60.8 w (C6); 128.1, 128.15, 128.3, 129.1, 132.0, 132.2, 134.2 (C-Ar), 194.7, 200.3 (C=O). IR (KBr, cm^{-1}): 648 (m), 706 (m), 752 (m), 1142 (vs), 1285 (m), 1304 (m), 1451 (m), 1663 (s), 1694 (m), 2963 (w). Anal. calcd. for $C_{22}H_{22}O_4S$ (%): C 69.09, H 5.80, S 8.38; found: C 68.27, H 5.83, S 8.62.

***Desulfonylation of* anti-*adduct* (5a)**

6-exo-*(Phenylethynyl)bicyclo[3.1.1]heptane* (15)

A mixture of **5a** (0.84 g, 2.5 mmol) and NaH_2PO_4 (5.2 g, 43.3 mmol) in dry methanol (30 mL) was stirred under argon for 15 min. While efficiently stirred, 6% sodium amalgam (7.66 g) was added in portions. The reaction mixture was kept stirring for 10 h, and NaH_2PO_4 (5.2 g, 43.3 mmol) was added. Then 6% sodium amalgam (7.66 g) was added in portions, and the reaction mixture was kept stirring for 8 h. Then the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (15 mL), washed to neutrality with water, and dried with $MgSO_4$. The solvent was removed under reduced pressure, and distillation of the residue afforded **15** as a colourless oil. Yield: 0.38 g (77.6%); bp 117 °C (1 mm Hg). ^{1}H NMR δ (ppm): 1.48 (dd, 1H, J^4 = 5.9 and J^2 = 9.2 Hz, *syn*-H7), 1.72–1.82 (m, 1 H, *exo*-H3), 1.82–2.00 (m, 5H, *endo*-H3 and H2,4), 2.49–2.55 (m, 2H, H1,5), 2.56 (d, J^4 = 5.9 Hz, 1H, *endo*-H6), 2.66 (dt, J^3 = 6.3 and J^2 = 9.2 Hz, 1H, *anti*-H7), 7.26–7.35 (m, 3H, H-Ar), 7.42–7.49 (m, 2 H, H-Ar). ^{13}C NMR δ (ppm): 15.4 (C3), 29.2 (C2,4), 29.7 (C6), 37.9 (C7), 40.5 (C1,5); 81.3, 94.0 (C≡C); 124.2, 127.3, 128.1, 131.5 (C-Ar). MS (EI+) *m*/*z* (%): 196 (8) [M$^+$], 168 (40), 167 (58), 155 (19), 154 (30), 153 (36), 152 (18), 141 (35), 128 (72), 115 (100), 77 (18). IR (film, cm^{-1}): 536 (w), 690 (s), 756 (vs),

1443 (w), 1489 (m), 1597 (w), 2222 (w), 2858 (m), 2943 (s). Anal. calcd. for $C_{15}H_{16}$ (%): C 91.78, H 8.22; found: C 91.70, H 8.30.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2012-0159. CCDC 873094 contains the X-ray data in CIF format for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; fax: +44 1223 33603; or e-mail: deposit@ccdc.cam.ac.uk).

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