Bornane with Integrated push–pull Butadienes

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Dedicated to Professor Dr. Hartmut Oehme on the Occasion of his 60th Birthday

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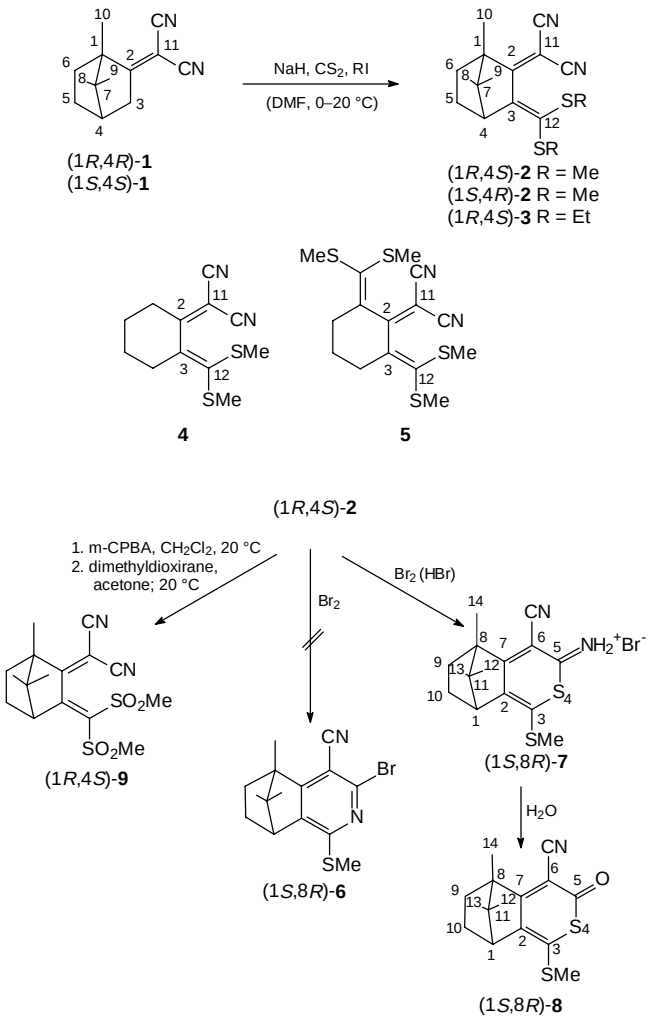
Abstract. The {3-[bis(alkylthio)methylene]-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ylidene}malononitriles ((1*R*,4*S*)-**2**, (1*S*,4*R*)-**2** and (1*R*,4*S*)-**3**) were prepared starting from 1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ylidenemalononitriles ((1*R*,4*R*)-**1** and (1*S*,4*S*)-**1**) arisen from (+)-, (–)-camphor. The reaction of (1*R*,4*S*)-**2** with bromine yielded the (1*S*,8*R*)-8,11,11-trimethyl-3-methylthio-5-oxo-4-thiatricyclo-[6.2.1.0^{2,7}]undeca-2,6-diene-6-carbonitrile (**8**) after hydrolysis of the initially formed (1*S*,8*R*)-6-cyano-8,11,11-trimethyl-3-methylthio-4-thia-tricyclo[6.2.1.0^{2,7}]undeca-2,6-diene-5-iminium bromide (**7**).

Acceptor–donor substituted alkenes and butadienes, generally known as polarized or push–pull alkenes and butadienes are versatile precursors for the synthesis of different kinds of carbocyclic and heterocyclic compounds [1]. Particularly the alkylsulfanyl substituted push-pull alkenes and butadienes were prepared by the reaction of the corresponding CH-acidic methylene compounds and carbon disulfide in presence of a base followed by alkylation with a suitable alkyl halogenide. The reaction of 3-aryl-2-cyano-5,5-bis(methylthio)-2,4-pentadienenitriles as a type of such push–pull butadienes with alkanethiols and hydrogen bromide, respectively, could be used for the synthesis of a variety of substituted pyridines with potential pharmacological importance [2].

Carbocyclic and heterocyclic anellated norbornane compounds show miscellaneous biological activities [3]. Naphtho-anellated derivatives of norbornane have been synthesized as tumor-inhibitors [4, 5]. Dibenzofurano-anellated norbornanes inhibit cell differentiation [6]. CNS stimulating activities were found for fused ring systems containing norbornane and pyrazolo(triazolo)-triazine moieties [7]. Jutz and Müller have obtained a pyrido-anellated bornane by Vilsmeier-reaction of 2-methylene-bornane followed by treatment with ammonium chloride [8]. Therefore, this paper describes the preparation of norbornane with an integrated push–pull butadiene to offer other heterocyclic anellations.

The reaction of the Knoevenagel compounds (1*R*,4*R*)-**1** [9] and (1*S*,4*S*)-**1** with carbon disulfide and methyl iodide and ethyl iodide, respectively, in DMF in the presence of sodium hydride afforded the push–pull butadienes (1*R*,4*S*)-**2**, (1*S*,4*R*)-**2**, and (1*R*,4*S*)-**3**, respectively, as deeply coloured compounds in 23 to 53% yields (Scheme 1). The yields were diminished by side reac-



Scheme 1 Synthesis and reactions of bornane with integrated push–pull butadienes

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tions to give the corresponding alkyl dithiocarboxylates and dimerization products of **1**.

The ^{13}C NMR spectra of the substances showed the typical alternating scheme of their ^{13}C chemical shifts [10]. The observed high-field shift for C-11 and the down-field shift for C-12 in **2** showed the polarized delocalization along the π-system. Due to the sterical hindrance in the bornane system a coplanar configuration of the *s-cis* butadiene was not favoured. Similar results were obtained with the push–pull butadienes **4** synthesized by Ege and Schuck [11] and **5** [12] as shown in Table 1 (Scheme 1).

Table 1 Selected ^{13}C NMR chemical shifts of the push–pull butadienes **2**–**5** (values in ppm relative to TMS; δ/ppm = 0, recorded in $CDCl_3$)

	2; R = Me	**3**; R = Et	**4** [11]	**5** [12]
C-11	75.2	75.6	82.7	84.7
C-2	181.7	181.4	181.4	176.8
C-3	145.2	146.3	138.6	138.5
C-12	149.3	147.2	140.3	139.4

Further structural analysis have been performed by single crystal diffraction experiments [13]. From the X-ray analyses of (1*R*,4*S*)-**2** the structure of the newly formed product could be determined (Figure 1). The molecular structure clearly showed a twist conformation through the C1–C2 double bond (arbitrary numbering). The dihedral angle (S2–C1)–(C2–C8) amounted to −25.9° for the dihedral angle (S1–C1)–(C2–C3) −22.5° was observed. Due to the rigid bornane system the dihedral angle (C1–C2)–(C3–C4) had a value of −40.2°. This was the main reason for the extremely hindered conjugation along the butadiene system in compound (1*R*,4*S*)-**2**. On the other hand, the effect of the polymethine structure properties in (1*R*,4*S*)-**2** could also be observed. The shorter length of the single bond C2–C3 (146.6 pm) and the longer double bonds C1–C2 and C3–C4 (135.3 pm and 135.8 pm, respectively) in contrast with the bond lengths for C–C single bonds (148 pm) and double bonds (132–134 pm) in the simple buta-1,3-diene [14, 15] showed the effect of delocalization along the push-pull butadiene. For the ethylsulfanyl substituted compound (1*R*,4*S*)-**3** similar results were obtained.

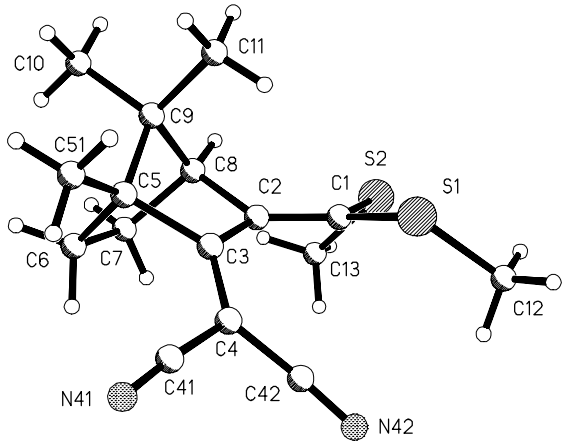

Fig. 1 Molecular structure of compound (1*R*,4*S*)-**2** (arbitrary numbering). Selected bond lenghts (Å), angles (°) and dihedral angles (°): C(1)–C(2) 1.353(4), C(2)–C(3) 1.466(3), C(3)–C(4) 1.358(3), C(4)–C(41) 1.432(4), C(4)–C(42) 1.433(4), C(1)–S(2) 1.755(2), C(1)–S(1) 1.755(3), S(1)–C(1)–C(2) 119.8(2), C(1)–C(2)–C(3) 128.5(2), C(2)–C(3)–C(4) 126.6(2), C(3)–C(4)–C(42) 122.3(2), S(2)–C(1)–C(2)–C(8) −25.9(4), S(1)–C(1)–C(2)–C(3) −22.5(3), C(1)–C(2)–C(3)–C(4) −40.2(4), C(2)–C(3)–C(4)–C(42) −172.6(2), C(5)–C(3)–C(4)–C(41) −9.1(4).

The found bond lengths in the push–pull butadiene (1*R*,4*S*)-**2** are summarized in Table 2 in relation to buta-1,3-diene [15] and {2,6-bis[bis(methylsulfanyl)methylene]cyclohexylidene}malononitrile (**5**) investigated by Stohrer and Kuhlmann [16].

Table 2 Selected bond lenghts in the push–pull butadiene (1*R*,4*S*)-**2** and **5** relative to buta-1,3-diene

	C3–C4 (pm)	C2–C3 (pm)	C1–C2 (pm)
buta-1,3-diene [15]	132.0	148.0	132.0
(1*R*,4*S*)-**2**	135.8 (3)	146.6 (3)	135.3 (4)
5 [16]	136.1 (3)	148.6 (2)	135.6 (2)

The treatment of (1*R*,4*S*)-**2** with bromine should furnish the substituted pyridine (1*S*,8*R*)-**6** which could be considered as an analogue to structures already known [2].

However, the reaction of (1*R*,4*S*)-**2** with bromine in chloroform provided the iminium bromide (1*S*,8*R*)-**7** as yellow crystals in 40% yield. The hydrolyses of (1*S*,8*R*)-**7** in aqueous ethanol provided the thiopyran (1*S*,8*R*)-**8**. The reaction to furnish (1*S*,8*R*)-**7** instead of the pyridine (1*S*,8*R*)-**6** can be explained with a nitrile cyclization by attack of a thiol on the nitrile group. This thiol group was generated through a C–S splitting of the methylsulfanyl group caused by hydrogen bromide [17] resulting from a side reaction of (1*R*,4*S*)-**2** with bromine.

The molecular structure of (1*S*,8*R*)-**8** could be confirmed through X-ray single crystal analyses [18]. The molecular structure of compound (1*S*,8*R*)-**8** is shown in Figure 2. For C2–C3 and C7–C6 of the bornane anellated thiopyrane distances of 136.2 pm and 136.5 pm, respectively, were found. The dihedral angle (C3–C2)-(C7–C6) amounted to only 1.9°.

The typical substitution pattern in push–pull butadienes should be of great value for the synthesis of the corresponding *N*-substituted derivatives. However, attempts to substitute the alkylsulfanyl groups in (1*R*,4*S*)-

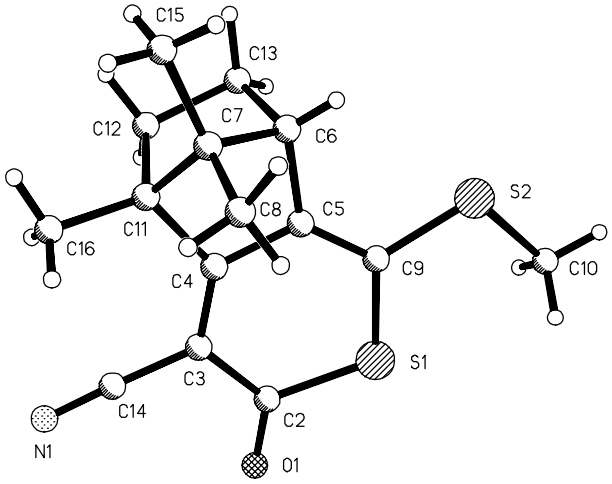

Fig. 2 Molecular structure of compound (1*S*,8*R*)-**8** (arbitrary numbering) [18].

2 or (1*R*,4*S*)-**3** with amines and hydrazine failed. Even the use of high boiling solvents like *n*-butanol or xylene instead of ethanol and prolonged reaction times furnished to full recovery of starting material. It was shown that oxidation of sulfur could lead to a better tendency for the substitution reaction with *N*-nucleophiles [19]. The reaction of (1*R*,4*S*)-**2** with *m*-chloroperbenzoic acid in dichloromethane afforded after 24 hours the corresponding sulfonyl compound (1*R*,4*S*)-**9** in 81% yield as colorless crystals. The same compound could also be prepared by the oxidation in a homogenous solution with dimethyldioxirane in acetone [20] in 84% yield (Scheme 1).

The ^{13}C NMR chemical shifts demonstrated the absence of a push–pull effect in the methylsulfonyl compounds **9**. As shown in Table 3 the signals for C-11 and C-12 were observed at lower field in comparison to (1*R*,4*S*)-**2**.

Table 3 ^{13}C NMR spectroscopic data for the butadiene carbons in (1*R*,4*S*)-**2** and (1*R*,4*S*)-**9** (values are in ppm relative to TMS, δ/ppm = 0, recorded in $CDCl_3$).

	C–11	C–2	C–3	C–12
(1*R*,4*S*)-**2**	75.2	181.7	145.2	149.3
(1*R*,4*S*)-**9**	90.1	180.7	143.4	166.3

The structure of **9** was finally assigned through X-ray single crystal analysis [21]. The already found hindered delocalization along the π-system in **9** could also be seen in the molecular structure. Similar to (1*R*,4*S*)-**2** the dihedral angle (C1–C2)–(C3–C4) amounted to –46.3° (arbitrary numbering corresponding to (1*R*,4*S*)-**2**). The conjugation is therefore disfavoured. The investigation of the bond lengths in **9** showed 150.1 pm for C2–C3 as a further proof.

First experiments to use the sulfone **9** for substitution reactions gave only poor results. Even after short reaction times only decomposed products or complex mixtures were isolated which could not be further characterized.

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Experimental

All solvents were dried according to standard procedures and freshly distilled prior to use. Reactions were monitored by TLC on silica gel F_{254} plates (MERCK) with detection by UV-light or charring with sulfuric acid. Melting points were determined with a Boëtius melting point apparatus and are corrected. Specific rotations were measured using a Polar LμP (IBZ Messtechnik), specific rotation values are given in units of 10^{-1}deg cm^2 g^{-1}. Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^1H NMR (250.133 MHz and 300.133 MHz, respectively) and ^{13}C NMR (62.896 MHz and 75.466 MHz, respectively) were obtained with Bruker instruments AC 250 and WM 300, respectively. ^1H and ^{13}C chemical shifts (δ) were given in ppm relative to the solvent signal. Mass spectra were recorded on an ADM 402/3 spectrometer. For column chromatography Merck Silica gel 60 (63–200 mesh) was used. TLC was performed on silica gel 60 GF_{254} (Merck) and visualized with UV light (λ = 254 nm) and/or by heating after alcoholic sulfuric acid treatment. Elemental analyses were carried out with a Leco CHNS-932.

*{(1R,4R)-1,7,7-Trimethyl-bicyclo[2.2.1]hept-2-ylidene}malononitrile (1R,4R-**1**)*

was prepared according to the literature procedure [9].

*{(1S,4S)-1,7,7-Trimethyl-bicyclo[2.2.1]hept-2-ylidene}malononitrile (1S,4S-**1**)*

To a solution of 3.9 g (2.0×10^{-2} mol) (1*S*,4*S*)-1,7,7-trimethyl-*N*-nitro-bicyclo[2.2.1]heptan-2-imine [22] and 1.5 g (2.5×10^{-2} mol) malononitrile in 10 ml of dry ethanol at 25 °C 0.42 g (5.0×10^{-3} mol) piperidine were added. The solution was allowed to stand at 25 °C until gas evolution had finished, heated under reflux for 10 min and cooled down to room temperature. The crystalline solid was filtered off and recrystallized from a small amount of dry ethanol. Yield 60%, colorless crystals, *m.p.* 117 °C. – $[\alpha]_D^{18}$ = + 10.3 (c = 1; $CHCl_3$). – IR (KBr): ν/cm^{-1} = 1 600 (C=C), 2 227 (CN). – ^1H NMR($CDCl_3$): δ/ppm = 0.81 (s, 3H, 9-CH_3), 0.96 (s, 3H, 8-CH_3), 1.20–1.50 (m, 2H, 6a-H, 6b-H), 1.36 (s, 3H, 10-CH_3), 1.84–1.95 (m, 2H, 5a-H, 5b-H), 2.03 (t, $^3J_{4,3a/3b}$ = $^3J_{4,5a/5b}$ = 4.1 Hz, 1H, 4-H), 2.28–2.95 (d, $^2J_{3a,3b}$ = 19.2 Hz, ddd, $^4J_{3a,5a}$ = 1.83 Hz, 2H, 3a-H, 3b-H). – ^{13}C NMR($CDCl_3$): δ/ppm = 12.2 (C-10), 18.6 (C-9), 19.8 (C-8), 26.7 (C-5), 33.9 (C-6), 41.3 (C-3), 43.6 (C-4), 51.1 (C-7), 58.1 (C-1), 79.2 (C-11), 111.5 (CN), 112.4 (CN), 194.7 (C-2). – MS (70 eV); *m/z* (%):

200 (40) [M+], 185 (30), 158 (100), 144 (97), 41 (50), 28 (61).

$C_{13}H_{16}N_2$	Calcd.:	C 77.96	H 8.05	N 13.99
(200.3)	Found:	C 77.87	H 7.98	N 13.89.

{3-[Bis(methylthio)methylene]-1,7,7-trimethyl-bicyclo-[2.2.1]hept-2-ylidene}malononitrile (**2**)

To 0.3 g (1.0×10^{-2} mol) of a suspension of sodium hydride (80% in mineral oil, activated by washing with *n*-hexane) in 5 ml of DMF under argon at 0 °C a solution of 0.8 g (4.0×10^{-3} mol) **1**, 0.6 g (8.0×10^{-3} mol) carbon disulfide and 2.84 g (2.0×10^{-2} mol) methyl iodide in 10 ml of DMF was added dropwise. The suspension was stirred for 30 min at 0 °C and further 60 min at room temperature. After the reaction had completed (t.l.c. control) the mixture was cooled down to 0 °C, treated with ice-water and extracted with $CHCl_3$ (3 × 50 ml). The combined organic phases were washed with water (50 ml), brine (50 ml) and water (50 ml), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give a red syrup which was crystallized from ethanol at room temperature. – (1*R*,4*S*)-**2**: 0.65 g red prisms (53%), *m.p.* 105.5 °C. – $[\alpha]_D^{21}$ = + 170.8 (c = 1.55; $CHCl_3$). – IR (KBr): ν/cm^{-1} = 2 222 (CN). – ^{1}H NMR($CDCl_3$): δ/ppm = 0.77 (s, 3H, 9-CH_3), 0.91 (s, 3H, 8-CH_3), 1.33–1.66 (m, 2H, 6a-H, 6b-H), 1.46 (s, 3H, 10-CH_3), 1.86–2.05 (m, 2H, 5a-H, 5b-H), 2.41 (s, 3H, SCH_3), 2.49 (s, 3H, SCH_3), 3.03 (d, $^3J_{4,5a/5b}$ = 3.9 Hz, 1H, 4-H). – ^{13}C NMR($CDCl_3$): δ/ppm = 12.7 (C-10), 16.5 (C-9), 18.4 (2 × SCH_3), 20.3 (C-8), 24.9 (C-5), 36.9 (C-6), 51.3 (C-7), 58.9 (C-4), 59.7 (C-1), 75.2 (C-11), 114.3 (CN), 115.1 (CN), 145.2 (C-3), 149.3 (C-12), 181.7 (C-2). – MS (70 eV); *m/z* (%): 304 (100) [M+], 289 (51) [M+ – CH_3], 276 (40), 261 (25), 220 (35), 199 (20), 193 (22), 91 (45), 70 (24).

$C_{16}H_{20}N_2S_2$	Calcd.:	C 63.12	H 6.62	N 9.20	S 21.06
(304.5)	Found:	C 63.00	H 6.40	N 9.30	S 21.11.

Compound (1*R*,4*S*)-**2** was subjected to X-ray analysis at 298 *K* with a Siemens P-4 diffractometer. The structure was solved by direct methods with the assistance of Siemens SHELXTL and refined with SHELXL-93. All non-hydrogen atoms were refined anisotropically, hydrogens introduced at theoretical positions and refined according to the riding model. Crystal size (mm): 0.95 × 0.67 × 0.17; space group $P2_1$; *Z* = 2; monoclinic; a = 772.4(2) pm; b = 1 358.5 (3) pm; c = 869.3 (2) pm; β = 115.70 (3)°; V = 821.9 × 10^6 pm^3; *F*(000) = 324; radiation, wavelength (Mo-K$_\alpha$) 71.073 pm, $2\Theta_{max}$ (°) = 50.0; *R* refinement against (F) = 0.0406; R_W refinement against (F^2) = 0.1038.

– (1*S*,4*R*)-**1**: 0.65 g red prisms (53%), *m.p.* 105.5 °C. – $[\alpha]_D^{21}$ = –195.5 (c = 1; $CHCl_3$). – IR (KBr): ν/cm^{-1} = 2 216 (CN). – ^{1}H NMR($CDCl_3$): δ/ppm = 0.77 (s, 3H, 9-CH_3), 0.91 (s, 3H, 8-CH_3), 1.33–1.65 (m, 2H, 6a-H, 6b-H), 1.46 (s, 3H, 10-CH_3), 1.88–2.06 (m, 2H, 5a-H, 5b-H), 2.41 (s, 3H, SCH_3), 2.49 (s, 3H, SCH_3), 3.03 (d, $^3J_{4,5a/5b}$ = 3.9 Hz, 1H, 4-H). – ^{13}C NMR($CDCl_3$): δ/ppm = 12.7 (C-10), 16.5 (C-9), 18.4 (2 × SCH_3), 20.3 (C-8), 24.9 (C-5), 36.9 (C-6), 51.3 (C-7), 58.9 (C-4), 59.7 (C-1), 75.2 (C-11), 114.3 (CN), 115.1 (CN), 145.2 (C-3), 149.3 (C-12), 181.7 (C-2). – MS (70 eV); *m/z* (%): 304 (100) [M+], 289 (51) [M+ – CH_3], 276 (40), 261 (25), 220 (35), 199 (20), 193 (22), 91 (45), 70 (24).

$C_{16}H_{20}N_2S_2$	Calcd.:	C 63.12	H 6.62	N 9.20	S 21.06
(304.5)	Found:	C 63.03	H 6.79	N 9.23	S 21.09.

*{(1R,4S)-3-[Bis(ethylthio)methylene]-1,7,7-trimethyl-bicyclo[2.2.1]hept-2-ylidene}malononitrile ((1R,4S)-**3**)*

According to the procedure above 0.3 g (1.0×10^{-2} mol) of a sodium hydride suspension, 0.8 g (4.0×10^{-3} mol) **1**, 0.6 g (8.0×10^{-3} mol) carbon disulfide, and 3.12 g (2.0×10^{-2} mol) ethyl iodide were combined. Yield 0.3 g (23%) light red prisms, *m.p.* 70–72 °C. – $[\alpha]_D^{21}$ = + 178.3 (c = 1.1; $CHCl_3$). – IR (KBr): ν/cm^{-1} = 2 213 (CN). – ^{1}H NMR($CDCl_3$): δ/ppm = 0.78 (s, 3H, 9-CH_3), 0.92 (s, 3H, 8-CH_3), 1.32 (2 t, $^3J_{SEt}$ = 7.3 Hz, 6H, 2S$CH_2C\underline{H}_3$), 1.38–1.65 (m, 2H, 6a-H, 6b-H), 1.46 (s, 3H, 10-CH_3), 1.88–2.04 (m, 2H, 5a-H, 5b-H), 2.73–3.2 (m, 4H, 2S$C\underline{H}_2CH_3$), 3.09 (d, $^3J_{4,5a/5b}$ = 4.3 Hz, 1H, 4-H). – ^{13}C NMR($CDCl_3$): δ/ppm = 12.7 (C-10), 13.8 (C-9), 15.2 (s, $SCH_2\underline{C}H_3$), 18.5 (s, $SCH_2\underline{C}H_3$), 20.4 (C-8), 24.9 (C-5), 28.9 (s, $S\underline{C}H_2CH_3$), 29.9 (s, $S\underline{C}H_2CH_3$), 36.9 (C-6), 51.5 (C-7), 58.6 (C-4), 59.9 (C-1), 76.5 (C-11), 114.4 (CN), 114.8 (CN), 146.4 (C-3), 147.2 (C-12), 181.4 (C-2). – MS (70 eV); *m/z* (%): 332 (100) [M+], 318 (28), 303 (75) [M+ – Et], 289 (24), 275 (20), 234 (33), 199 (20), 105 (25), 70 (21), 28 (26).

$C_{18}H_{24}N_2S_2$	Calcd.:	C 65.02	H 7.27	N 8.42	S 19.29
(332.5)	Found:	C 65.05	H 7.21	N 8.57	S 19.43.

*(1S,8R)-6-Cyano-8,11,11-trimethyl-3-methylthio-4-thia-tricyclo[6.2.1.0^{2,7}]undeca-2,6-diene-5-iminium bromide ((1S,8R)-**7**)*

To a solution of 0.304 g (1.0×10^{-3} mol) (1*R*,4*S*)-**2** in 5 ml $CHCl_3$ were added at room temperature 0.16 g (1.0×10^{-3} mol) bromine. The solution was stirred for further 6 h at room temperature and allowed to stand over night. The formed residue was filtered, and washed with a small amount of dry $CHCl_3$ and recrystallized form dry ethanol to furnish yellow crystals. Yield 0.15 g (40%), *m.p.* 169–175.5 °C. – $[\alpha]_D^{18}$ = + 5.6 (c = 1.25; DMSO). – IR (KBr): ν/cm^{-1} = 2 225 (CN), 3 406 (NH). – ^{1}H NMR([D$_6$]DMSO): δ/ppm = 0.69 (s, 3H, 13-CH_3), 0.98 (s, 3H, 12-CH_3), 1.08–1.55 (m, 2H, 9a-H, 9b-H), 1.46 (s, 3H, 14-CH_3), 1.90–2.16 (m, 2H, 10a-H, 10b-H), 2.81 (s, 3H, SCH_3), 3.04 (d, $^3J_{1,10a/10b}$ = 3.1 Hz, 1H, 1-H), 4.4–5.2 (b, 1H, NH_2^+). – ^{13}C NMR([D$_6$]DMSO): δ/ppm = 12.0 (C-14), 15.6 (C-13), 18.1 (s, SCH_3), 19.8 (C-12), 23.8 (C-10), 32.9 (C-9), 50.4 (C-1), 55.0 (C-11), 58.9 (C-8), 92.1 (C-6), 112.2 (CN), 137.9 (C-2), 147.3 (C-3), 173.1 (C-5), 173.8 (C-7). – MS (CI): *m/z* = 292 (100) [M + H], 278 (11), 246 (13), 89 (20) [HBr].

$C_{15}H_{19}BrN_2S_2$	Calcd.:	C 48.51	H 5.16	N 7.54	S 17.27
(371.2)	Found:	C 48.70	H 5.27	N 7.68	S 17.52.

*(1S,8R)-8,11,11-Trimethyl-3-methylthio-5-oxo-4-thia-tricyclo[6.2.1.0^{2,7}]undeca-2,6-diene-6-carbonitrile ((1S,8R)-**8**)*

A solution of 0.29 g (1.0×10^{-3} mol) 1*S*,8*R*-**7** in 5 ml of 50% aqueous ethanol was heated under reflux for 12 h. This mixture was cooled to room temperature, the formed residue was filtered off and recrystallized from ethanol. Yield 0.26 g (89%), yellow prisms, *m.p.* 171–172.5 °C. – $[\alpha]_D^{18}$ = + 7.0 (c = 1; $CHCl_3$). – IR (KBr): ν/cm^{-1} = 1 639 (CO), 2 214 (CN). – ^{1}H NMR($CDCl_3$): δ/ppm = 0.75 (s, 3H, 13-CH_3), 0.99 (s, 3H, 12-CH_3), 1.1–1.55 (2 m, 2H, 9a-H, 9b-H), 1.51 (s, 3H, 14-CH_3), 1.84–2.13 (m, 2H, 10a-H, 10b-H), 2.55 (s, 3H, SCH_3), 2.93 (d, $^3J_{1,10a/10b}$ = 3.7 Hz, 1H, 1-H). – ^{13}C NMR($CDCl_3$):

δ/ppm = 12.4 (C-14), 15.1 (C-13), 18.3 (s, SCH_3), 20.1 (C-12), 24.6 (C-10), 33.6 (C-9), 50.7 (C-1), 53.8 (C-11), 58.0 (C-8), 98.8 (C-6), 113.6 (CN), 135.1 (C-2), 145.4 (C-3), 172.9 (C-5), 182.2 (C-7). – MS (70 eV, EI);*m/z* (%): 290 (100) [M^+], 275 (48), 247 (38), 220 (32), 173 (18), 199 (10).

$C_{15}H_{17}NOS_2$	Calcd.:	C 61.82	H 5.88	N 4.81	S 22.01
(291.3)	Found:	C 61.88	H 5.78	N 5.11	S 22.23.

*{(1R,4S)-3-[Bis(methylsulfonyl)methylene]-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene}malononitrile ((1R,4S)-**9**)*

Method A: To a solution of 0.304 g (1.0×10^{-3} mol) (1*R*,4*S*)-**2** in 10 ml CH_2Cl_2 were added at room temperature with stirring 1.25 g (4.1×10^{-3} mol) *m*-chloroperbenzoic acid. The mixture was stirred for 24 h at room temperature and filtered through silica gel. To the filtrate 20 ml CH_2Cl_2 were added, and the organic phase was washed three times with cold saturated $NaHCO_3$-solution, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography. Yield 0.30 g (81%), colorless crystals.

Method B: To a solution of 0.304 g (1.0×10^{-3} mol) (1*R*,4*S*)-**2** in 10 ml acetone were added at room temperature 15 ml of a freshly prepared 0.1M solution of dimethyldioxirane in acetone. The solution was allowed to stand at room temperature for 24 h, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to yield a crude colorless product which was purified by column chromatography. Yield 0.31 g (84%). *m.p.* 196–203 °C. – $[\alpha]_D^{18}$ = + 9.8 (c = 1.45; $CHCl_3$). – IR (KBr): ν/cm^{-1} = 2 231 (CN), 1 142, 1 322 (SO_2). – ^{1}H NMR($CDCl_3$): δ/ppm = 0.93 (s, 3H, 9-CH_3), 0.98 (s, 3H, 8-CH_3), 1.47 (s, 3H, 10-CH_3), 1.60–1.72 (m, 2H, 6a-H, 6b-H), 2.00–2.12 (m, 2H, 5a-H, 5b-H), 3.28 (s, 3H, SO_2CH_3), 3.35 (t, $^3J_{4,5a/5b}$ = 2.4 Hz, 1H, 4-H), 3.59 (s, 3H, SO_2CH_3). – ^{13}C NMR($CDCl_3$): δ/ppm = 11.8 (C-10), 18.7 (C-8), 21.1 (C-9), 22.6 (C-5), 38.3 (C-6), 41.4 (SO_2CH_3), 45.2 (s, SO_2CH_3), 52.4 (C-7), 59.0 (C-1), 59.3 (C-4), 90.1 (C-11), 111.3 (CN), 113.7 (CN), 143.4 (C-3), 166.3 (C-12), 180.7 (C-2). – MS (CI); *m/z* (%): 369 (100) [M + H$^+$], 291 (75) [M – SO_2CH_3], 213 (23), 81 (39).

$C_{16}H_{20}N_2O_4S_2$	Calcd.:	C 52.15	H 5.47	N 7.60	S 17.40
(368.2)	Found:	C 51.84	H 5.47	N 7.75	S 17.19.

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