Synthesis of Tricyclo[5.4.0.0^{2,8}]undeca-3,5,9-triene

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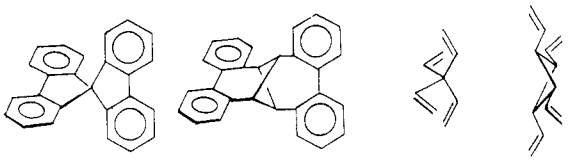
The two key reactions in the synthesis of the title compound **12** were the addition of NBS and a nucleophile (e.g., methanol or acetate) to bicyclo[5.4.0]undec-2-en-9-one (**20**), which occurs with a high degree of regio- and stereoselectivity, and the intramolecular elimination to the tricycloundecane system (**23**). The introduction of the π-bonds was achieved in nine steps. First tricyclo[5.4.0.0^{2,8}]undec-3-en-9-one (**26**) was obtained by ether cleavage and elimination from 3-bromotricyclo[5.4.0.0^{2,8}]undecan-9-one (**24**). Subsequent allylic oxidation of the protected ketone **35** yielded **36**, which was transferred in three steps to tricyclo[5.4.0.0^{2,8}]undeca-3,5-dien-9-one (**39**). The elimination to the title compound **12** was achieved via its tosylhydrazone **40** and subsequent Shapiro reaction.

Introduction

Spectroscopic investigations on conjugated spiro compounds **1** have revealed a rather strong through-space interaction between the two mutually perpendicular π-systems.[1] Some time ago it was postulated that the replacement of the sp^3 center in **1** by a four-membered ring, as in **2**, should yield a comparable strong through-bond interaction of the two π-systems via the four-membered relay.[2] Experimental evidence for the validity of this

1 2

hypothesis was found by comparing the electronic absorption spectra of 9,9′-spirobifluorene (**3**) and tetrabenzotricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene (**4**),[3] the photoelectron (PE) spectra of tetravinylmethane (**5**) and *trans,trans,trans*-1,2,3,4-tetravinylcyclobutane (**6**),[4] and the PE spectra of spiro[[4.4]nonatetraene (**7**)[1] and tricyclo[5.5.0.0^{2,8}]dodeca-3,5,9,11-tetraene (**8**).[5]



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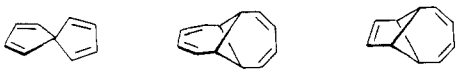
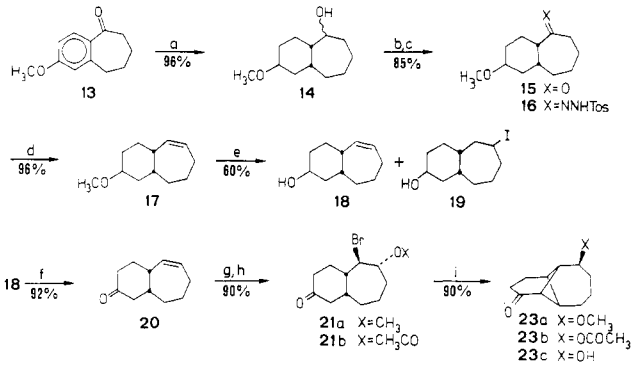


7 8 9

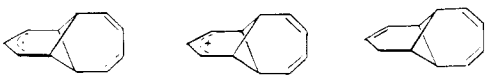
The investigations carried out so far have revealed that the interaction of the two π-fragments via the four-membered ring is at a maximum when both π-systems are identical. This is best demonstrated by comparing the PE results of **8**[5] and tricyclo[5.3.0.0^{2,8}]deca-3,5,9-triene (**9**).[5] In the latter compound, essentially no interaction can be detected between the ethylene and the butadiene fragment.

Scheme I[a]



[a] (a) 5% Ru on Al_2O_3, H_2, 120 atm, 80 °C; (b) aluminum isopropoxide, acetone, toluene, 90 °C; (c) *p*-Tos-NHNH$_2$, EtOH; (d) THF, BuLi, 0–5 °C; (e) Me_3SiCl, NaI, pyridine, CH_3CN; (f) DMSO, $(COCl)_2$, NEt_3, −70 °C; (g) NBS, MeOH; (h) NBS, NaOAc, HOAc; (i) NaH, DMSO, 70 °C.

Tricyclic systems in which two different π-systems may still interact considerably are present in the radical **10** and the cation **11**. Both compounds can be derived from tricyclo[5.4.0.0^{2,8}]undeca-3,5,9-triene (**12**) or its precursors.

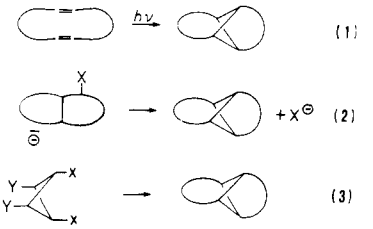


10 11 12

In Figure 1 a schematic drawing of $3a_2$ and $2a_2$ of **10** and **11** is shown. It points toward a strong spin delocalization in **10** and a delocalization of the positive charge in **11** involving both π-systems and the four-membered ring. Since **12** has not been synthesized previously, we will document in the following our approach to this system.

Synthesis

(a) Strategies. There are three known ways to prepare tricyclic systems with a central four-membered ring moiety, in which both π-systems are oriented perpendicular to each other. All three approaches are summarized in eq 1–3.



(1)

(2)

(3)

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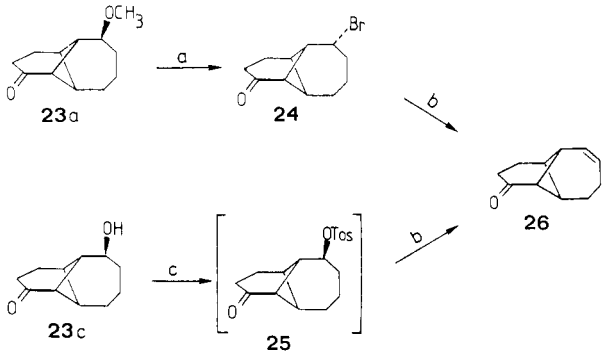
Figure 1. Qualitative drawing of $3a_2$ and $2a_2$ of **10** and **11**.

Scheme II[a]

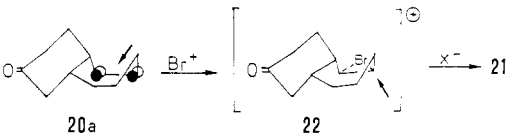


[a] (a) BBr_3/CH_2Cl_2, −78 °C; (b) DBU/CH_3CN; (c) Tos-Cl, pyridine.

The light-induced ring closure (eq 1) of a monocyclic diene has been used to synthesize the tricyclo[3.3.0.0^{2,6}]octane skeleton,[6] the tricyclo[4.4.0.0^{2,8}]decane[7] system, and the tricyclo[5.3.0.0^{2,8}]decane framework.[8,9] The intramolecular elimination (eq 2) starting from a bicyclic system was first proposed by Heathcock and has been applied to synthesize the tricyclo[4.4.0.0^{2,8}]decane system.[10] The third approach (eq 3) with a properly substituted four-membered ring system has been used successfully by Paquette et al. to synthesize **8**, **9**, and related species[11,12] and by Snider to synthesize copaene.[13] So far the tricyclo[5.4.0.0^{2,8}]undecane skeleton has been synthesized by a light-induced ring closure of cyclodeca-1,5-diene derivatives to yield the tricyclo[5.3.0.0^{2,8}]decane system (eq 1) and subsequent ring enlargement.[8]

(b) Approach. Our approach to synthesize the skeleton of the tricyclo[5.4.0.0^{2,8}]undecane system uses eq 2 and is summarized in Scheme I.[14] From the readily available 7-methoxysuberone **13**,[15] the bicyclo[5.4.0]undecane system functionalized in positions 2 and 9 can be obtained by reduction of the aromatic ring.[16] This procedure yields two isomeric alcohols **14**, which were oxidized without separation according to Oppenauer[17] to yield the ketone **15**. The conversion of **15** to the tosylhydrazone **16** and subsequent treatment with excess butyllithium (BuLi)[18] gave the olefin **17** in good yield. The ether cleavage of **17** to **18** could be achieved with trimethylchlorosilane/NaI/pyridine[19] in only 50% yield. The other products isolated were 10–20% **17** and 10–20% of the HI addition product **19**. The alcohol **18** was readily oxidized to **20** in excellent yields according to Swern.[20] The pivot point of the synthesis is the highly stereo- and regioselective formation of **21a** and **21b** when treating **20** with NBS and a nucleophile (e.g., methanol or sodium acetate).[10,21]

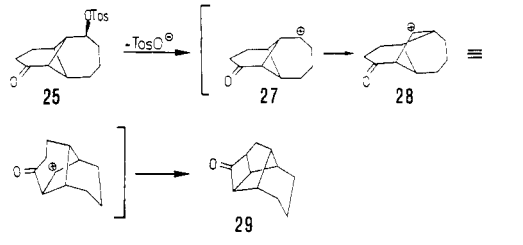
The high degree of regio- and stereoselectivity exhibited during the reaction of **20** with NBS and a nucleophile may be ascribed to the conformation of **20**. Molecular models and force-field calculations on **20**[22] suggest that conformation **20a** represents a local minimum. The attack of



an electrophile (e.g., Br^+) at the double bond takes place preferentially from the exo side since the endo side is protected by the alkyl chain. The attack by a nucleophile on the bromonium ion intermediate (**22**) must occur from the endo side, again for steric reasons, at the position α to the CH_2 group (see drawing).

The stereochemistry of **21a** and **21b** has been proven by comparing their ^1H NMR spectra with analogous systems.[10] A further proof of the stereochemistry of **21** is given by the cyclization reaction to the tricyclo[5.4.0.0^{2,8}]undecane systems **23a** and **23b** (Scheme I). To elucidate the configuration of these systems, we analyzed the 500-MHz 2D COSY ^1H NMR spectra of both compounds, which gave us a complete assignment of all protons. To rule out other possible tricyclic isomers, we carried out an X-ray investigation on the alcohol **23c** derived from **23b**.[14]

Synthesis of Tricyclo[5.4.0.0^{2,8}]undec-3-en-9-one (26). The starting point of our next step was **23a**. The ether cleavage could be achieved by treating **23a** with BBr_3 at −78 °C.[23] Two isomeric bromides were obtained in the ratio 5:3 with the main product as the desired one (**24**) (Scheme II). Both bromides were separated and treated with DBU.[24] While **24** yielded **26** in good yields, the other



isomer gave only polymeric material under the same conditions. It turned out that the separation of both bromides was not necessary to prepare **26**. In a second approach to **26**, we treated the alcohol **23c** with tosyl chloride and pyridine and subsequently with DBU. Two products were isolated in the ratio 1:1. One of them turned out to be **26**,

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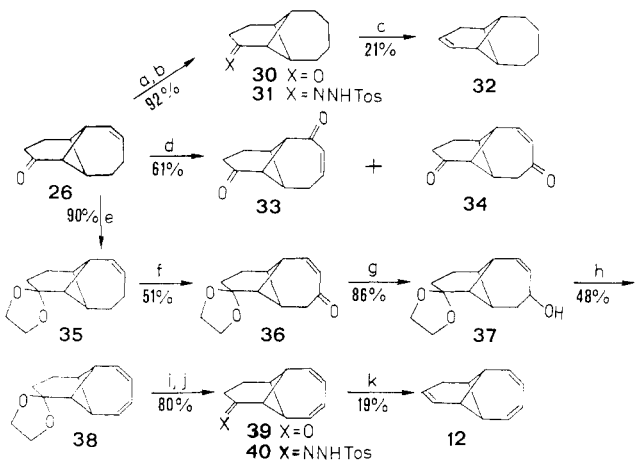
Scheme III[a]



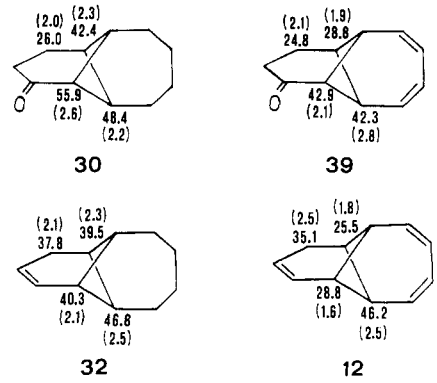
[a] (a) H_2/PtO_2, EtOH; (b) Tos-$NHNH_2$, EtOH; (c) BuLi, THF, −10 °C; (d) CrO_3/DMP/CH_2Cl_2, −20 °C; (e) $HO(CH_2)_2OH$, pyridinium tosylate, C_6H_6; (f) $C_6H_5IO_2$, dipyridyl diselenide, benzene, 80 °C; (g) $LiAlH_4$/ether; (h) $Et_3N^+SO_2N^-COOCH_3$/benzene, 50 °C; (i) $(COOH)_2/H_2O$, SiO_2, CH_2Cl_2; (j) Tos-$NHNH_2$, EtOH; (k) BuLi, THF, −10 °C.

and the second one showed no olefinic protons in the ^1H NMR spectrum. Its structure could be assigned to **29** on the basis of its spectral properties. Its formation can be rationalized by assuming that the tosylate **25** is formed when **23c** is treated with tosyl chloride and pyridine (see Scheme II). From this compound the generation of **27** and its rearrangement to **28** is assumed. The latter is trapped intramolecular in the presence of base to give **29**.

Reactions of Tricyclo[5.4.0.0^{2,8}]undec-3-en-9-one. Reduction of **26** yields the saturated ketone **30**. Its tosylhydrazone **31** can be transferred by the Shapiro reaction[18] to the monoene **32** (Scheme III). Our strategy to prepare **12** from **26** was first to functionalize the allylic position of the latter compound. Our efforts with NBS failed, and the allylic oxidation with CrO_3/dimethylpyrazole (DMP)[25] in CH_2Cl_2 yielded **33** and **34** in the ratio 9:1. We also did not obtain a bis(tosylhydrazone) from **33** or from **34**.

The second path we followed to synthesize **12** from **26** started with the acetal **35** (Scheme III). The latter was oxidized at the allylic position with dipyridyl diselenide/iodoxybenzene[26] to yield **36**. The course of this reaction has to be monitored carefully since the reaction time varied from 4 to 30 h. The diene ketal **38** can be prepared from **36** via the allylic alcohol **37** and subsequent elimination with Burgess's reagent.[27] The deketalization of **38** with oxalic acid on silica gel[28] and the transformation of the resulting ketone **39** to **12** via its tosylhydrazone worked without problems. The overall yield from **26** to **12** was 3.5%.

NMR Effects. The synthesized dienes **12** and **39** contain a rigid 1,3-cycloheptadiene unit for which relatively strong shielding is anticipated.[12a,29] Below we compare the ^{13}C and in parentheses the ^1H NMR shifts that were recorded for **12**, **32**, **39**, and **30**.



Experimental Section

General. Melting points are uncorrected. High-resolution mass spectra (HRMS) were recorded at an ionization energy of 70 eV. The IR spectra were measured with a Beckman IR 4200 spectrometer; relative intensities are indicated as follows: strong (s), medium (m), weak (w), broad (br). Electronic absorption spectra were recorded on a Cary 17D (Varian) spectrometer. Elemental analyses were performed by Microanalytical Laboratory, University of Heidelberg.

9-Methoxy-*cis*-bicyclo[5.4.0]undecan-2-ol (14). 7-Methoxybenzosuberone **13**[15] (20 g, 105 mmol) dissolved in ethyl acetate (100 mL) was hydrogenated[16] in the presence of ruthenium (3 g) on alumina (5%) at an initial pressure of 120 atm at 80 °C. After 1 day, the initial pressure had fallen to 70 atm; it was raised to 120 atm again. Three to 4 days later no hydrogen absorption could be detected. After removal of the catalyst by filtration and the solvent by distillation, the two isomeric alcohols were isolated by flash chromatography on silica gel (ether/petroleum ether, 1:1). Oily liquids, 19.5 g (96%), were obtained. **14a**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.92 (d, br, 1 H), 3.38 (m, 1 H), 3.29 (s, 3 H), 2.02–1.4 (m, 17 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 77.0 (d), 74.8 (d), 55.5 (q), 45.7 (d), 37.9 (d), 36.1 (t), 32.4 (t), 31.8 (t), 29.7 (t), 25.7 (t), 23.5 (t), 19.4 (t); IR (CCl_4) 3620 (m), 2930 (s), 2860 (s), 1090 (s) cm^{-1}. **14b**: ^1H NMR (300 MHz, $CDCl_3$) δ 3.59 (dt, 1 H), 3.33 (s, 3 H), 3.23 (m, 1 H), 2.36 (s, br, 1 H), 2.06–1.4 (m, 16 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 78.6 (d), 72.7 (d), 55.4 (q), 45.3 (d), 36.2 (t), 36.1 (d), 35.0 (t), 31.6 (t), 29.4 (t), 27.9 (t), 25.0 (t), 24.3 (t), 24.0 (t); IR (CCl_4) 3620 (m), 2920 (s), 2860 (s), 1100 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.85; H, 11.27.

9-Methoxybicyclo[5.4.0]undecan-2-one (15). To a solution of the isomeric alcohols **14** (20 g, 102 mmol) in dry acetone (260 mL) was added a solution of aluminum isopropoxide (34.1 g, 166 mmol) in dry toluene[17] (260 mL). The mixture was refluxed for 24 h. Water (300 mL) was added to the solution, the precipitate was dissolved with 1 N H_2SO_4, and the product was extracted with ether (800 mL). The combined extracts were washed with saturated $NaHCO_3$ solution and with a saturated sodium chloride solution. Removal of the solvent and subsequent flash chromatography on silica gel (ether/petroleum ether, 1:4) gave an oily liquid (16.9 g, 85%). **15**: ^1H NMR (90 MHz, $CDCl_3$) δ 3.3 (s, br, 4 H), 2.5 (m, 3 H), 2.2–1.4 (m, 15 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 214.8 (s), 77.7 (d), 55.5 (q), 50.5 (d), 43.4 (t), 35.6 (signal with double intensity, d and t), 33.9 (t), 28.5 (t), 26.8 (t), 24.6 (t), 23.0 (t); IR (film) 2870 (s), 2830 (s), 1700 (s), 1095 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.18; H, 10.36.

9-Methoxybicyclo[5.4.0]undecan-2-one (*p*-Tolylsulfonyl)hydrazone (16). To a solution of **15** (15 g, 76 mmol) in ethanol (200 mL) was added tosylhydrazine (14.25 g, 76 mmol). The mixture was refluxed for 1 h and then stirred overnight at room temperature. A white precipitate formed, which was filtered and identified as pure **16**. The solvent was removed to the half, and the mother liquor was cooled. An additional precipitate of **16** could be isolated. A total of 22.6 g (81%) of white crystalline tosylhydrazone **16** was obtained: mp 135–137 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 7.9 (d and covered s, 3 H), 7.3 (d, 2 H), 3.3 (s, 3 H), 3.15 (m, 1 H), 2.7–2.2 (m and s, total 6 H), 2.1–1.0 (m, 13 H); IR (KBr) 3200 (s), 2910 (s), 1590 (w), 1160 (s), 1100 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{28}N_2O_3S$: C, 62.61; H, 7.74; N, 7.69; S, 8.80. Found:

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C, 62.62; H, 7.89; N, 7.64; S, 9.01.

9-Methoxybicyclo[5.4.0]undec-2-ene (17). To a stirred solution of **16** (15 g, 41.2 mmol) in dry THF (250 mL) (ice cooling) was added under an argon atmosphere 1.6 N butyllithium solution (65 mL) in hexane (104 mmol) during 30 min.[18] Stirring was continued for 1 h at 0–5 °C and for 30 min at room temperature. Water was carefully added and the mixture extracted with ether (600 mL). The combined organic layers were washed with saturated sodium chloride solution and dried. The solvent was removed, and the raw product, a light yellow liquid (7.3 g, 96%), was used without further purification in the next reaction. For analytical purposes the material was purified with flash chromatography on silica gel (ether/petroleum ether, 1:9). **17**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (m, 1 H), 5.30 (td, 1 H), 3.35 (s, 3 H), 3.15 (m, 1 H), 2.64 (s, br, 1 H), 2.15 (m, 2 H), 2.0–1.3 (m, 11 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 133.8 (d), 130.8 (d), 80.0 (d), 55.1 (q), 37.7 (d), 37.2 (d), 36.4 (t), 33.2(t), 30.9 (t), 29.9 (t), 27.2 (t), 21.3 (t); IR (CCl_4) 3000 (w), 2910 (s), 2840 (s), 1090 (s) cm^{-1}.

Bicyclo[5.4.0]undec-2-en-9-ol (18). To a solution of the crude methyl ether **17** (7 g, 38.5 mmol) in dry acetonitrile (120 mL) were added dry pyridine (2.1 mL, 24.8 mmol) and dried NaI (11.5 g, 77 mmol) under argon. To the mixture was added dropwise with stirring trimethylchlorosilane (9.68 mL, 77 mmol).[19] The solution was then stirred overnight. Water was added and the mixture extracted with ether (500 mL), washed with 1 N sodium thiosulfate solution and saturated sodium chloride solution, and dried. The solvent was removed to give a yellow oily liquid. The products were isolated with flash chromatography on silica gel (ether/petroleum ether gradient 4:1 to 1:1) to give 10–20% educt **17**, 40–60% desired product **18**, and 10–20% the HI addition product **19**. Properties of **18**: mp 70–71 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.8 (m, 1 H), 5.3 (m, 1 H), 3.65 (m, 1 H), 2.65 (s, br, 1 H), 2.2 (m, 2 H), 1.9–1.3 (m, 12 H); IR (KBr) 3300 (br), 2920 (s), 2850 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.51; H, 10.75. Properties of **19**: mp 113 °C; ^{1}H NMR (90 MHz, acetone-d_6) δ 4.4 (m, 1 H), 3.4 (m, 1 H and H_2O), 2.8–1.0 (m, 17 H); IR (KBr) 3280 (br), 2900 (s), 2830 (m), 1020 (m), 630 (m) cm^{-1}. Anal. Calcd for $C_{11}H_{19}IO$: C, 44.91; H, 6.31; I, 43.14. Found: C, 44.65; H, 6.49; I, 42.87.

Bicyclo[5.4.0]undec-2-en-9-one (20). To a stirred solution of oxalyl chloride[20] (2.8 mL, 32.7 mmol) in dry CH_2Cl_2 (70 mL) was added dropwise under an argon atmosphere DMSO (5.2 mL, 73.4 mmol) in dry CH_2Cl_2 (20 mL) at −75 to −65 °C. Stirring was continued for 10 min at −75 °C followed by the addition of **18** (5 g, 32.6 mmol) in CH_2Cl_2 (70 mL) in ca. 10 min. The reaction mixture was stirred for 15 min, and dry triethylamine (19 mL) was added. The cooling bath was removed, and water was added at room temperature. Stirring was continued for 10 min, and the organic layer was separated. The aqueous phase was reextracted with CH_2Cl_2 (200 mL), the organic layers were combined, and the solvent was removed. Subsequent flash chromatography on silica gel (ether/petroleum ether, 1:4) gave, as a clear liquid, **20** (4.6 g, 92%): ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.9 (m, 1 H), 5.6 (m, 1 H), 2.9 (s, br, 1 H), 2.7–1.4 (m, 13 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 211.2 (s), 132.6 (d), 131.8 (d), 48.7 (t), 45.0 (d), 40.1 (d), 39.5 (t), 39.3 (t), 38.5 (t), 38.0 (t), 34.5 (t), 30.6 (t), 29.1 (t), 28.7 (t), 22.4 (t); IR (film) 3000 (w), 2910 (s), 1705 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.21; H, 9.97.

2-Bromo-3-methoxybicyclo[5.4.0]undecan-9-one (21a). To a solution of the ketone **20** (4 g, 24.4 mmol) in dry methanol (100 mL) was added NBS (4.3 g, 24.44 mmol).[10] The mixture was stirred at room temperature under argon for 24 h. To this solution were added ether (100 mL) and water (100 mL), and the organic layer was separated. The aqueous phase was again extracted with ether, and the organic phases were combined, washed with 5% aqueous sodium hydroxide solution and with water, and dried. Evaporation of the solvent and subsequent flash chromatography on silica gel (ether/petroleum ether, 1:4) gave an oily, light yellow liquid (5.4 g, 81%), which crystallized in the refrigerator, but melted again at room temperature. **21a**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.35 (t, 1 H), 4.75 (m, 1 H), 3.4 (s, 3 H), 2.7 (m, 2 H), 2.5–2.0 (m, 7 H), 1.9–1.4 (m, 5 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 210.3 (s), 85.1 (d), 60.0 (d), 57.2 (q), 48.6 (t), 46.9 (d), 40.5 (t), 36.3 (d), 30.1 (t), 29.2 (t), 28.8 (t), 20.9 (t); IR (film) 2920 (s), 2820 (m), 1705 (s), 1080 (s), 700 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{19}BrO_2$: C, 52.37; H, 6.96; Br, 29.04. Found: C, 52.08; H, 6.81; Br, 28.77.

2-Bromo-3-acetoxybicyclo[5.4.0]undecan-9-one (21b). To a solution of the ketone **20** (2 g, 12.2 mmol) in acetic acid (50 mL) and acetic anhydride (1 mL) were added dry NaOAc (1.98 g, 24.4 mmol) and NBS (2.17 g, 12.2 mmol).[21] The mixture was stirred under argon for 24 h. Water was added (200 mL), and the solution was extracted with ether (400 mL). The organic layer was washed with 1 N NaOH solution, water, and saturated sodium chloride solution and then dried. The solvent was removed by distillation, and the product was purified by flash chromatography on silica gel (ether/petroleum ether, 1:4) to yield white crystals (3.4 g, 92%). **21b**: mp 89 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 5.25 (m, 1 H), 4.2 (dd, 1 H), 2.9–1.4 (m, 17 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 209.7 (s)8 169.3 (s), 75.7 (d), 58.8 (d), 48.3 (t), 45.9 (d), 40.3 (t), 37.0 (d), 31.9 (t), 29.6 (t), 29.1 (t), 21.9 (t), 21.0 (q); IR (KBr) 2930 (s), 2860 (m), 1730 (s), 1705 (s), 1230 (s), 1025 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{19}BrO_3$: C, 51.50; H, 6.32; Br, 26.35. Found: C, 51.49; H, 6.42; Br, 26.15.

3-Methoxytricyclo[5.4.0.0^{2,8}]undecan-9-one (23a). To a solution of **21a** (5.94 g, 21.6 mmol) in dry DMSO (300 mL) was added dropwise at 70 °C under argon a solution of freshly prepared dimethyl sulfoxide anion (23.8 mmol) in DMSO (30 mL).[10] After 30 min, the addition was completed, and the mixture was stirred for another 1.5 h at 70 °C. After cooling to room temperature, ice water (500 mL) was added and the mixture was extracted six times with ether (900 mL). The organic layers were combined, washed with saturated sodium chloride solution, and dried. The solvent was removed, and subsequent flash chromatography on silica gel (ether/petroleum ether, 1:1) yielded an oily, light yellow liquid (3.7 g, 91%). **23a**: ^{1}H NMR (500 MHz, C_6D_6) δ 3.56 (dt, 1 H), 3.28 (s, 3 H), 2.88 (d, 1 H), 2.61 (m, 2 H), 2.38 (t, 1 H), 2.28 (td, 1 H), 2.20 (q, 1 H), 2.10–1.97 (m, 2 H), 1.96–1.89 (m, 1 H), 1.86–1.74 (m, 4 H), 1.61–1.52 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 212.5 (s), 79.1 (d), 55.6 (q), 51.0 (d), 43.8 (d), 41.7 (d), 36.8 (d), 31.8 (t), 30.0 (t), 29.3 (t), 25.2 (t), 19.4 (t); IR (film) 2920 (s), 2810 (m), 1705 (s), 1080 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.98; H, 9.41.

3-Acetoxytricyclo[5.4.0.0^{2,8}]undecan-9-one (23b). The same procedure as for **23a** was used. Flash chromatography on silica gel (ether/petroleum ether, 1:1) yielded white crystals (3.1 g, 65%). **23b**: mp 58 °C; ^{1}H NMR (500 MHz, $CDCl_3/C_6D_6$, 1:3) δ 5.06 (td, 1 H), 2.87 (d, 1 H), 2.26 (m, 2 H), 2.08 (t, 1 H), 1.84–1.80 (m, 1 H), 1.77–1.67 (m, 5 H), 1.64–1.41 (m, 4 H), 1.41–1.37 (m, 2 H), 1.32–1.24 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 211.4 (s), 169.2 (s), 72.2 (d), 51.1 (d), 44.1 (d), 41.4 (d), 36.6 (d), 31.4 (t), 30.2 (t), 29.0 (t), 24.6 (t), 20.4 (t), 19.4 (t); IR (KBr) 2940 (s), 1725 (s), 1705 (sh), 1250 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.99; H, 8.02.

3-Hydroxytricyclo[5.4.0.0^{2,8}]undecan-9-one (23c). To a solution of **23b** (1 g, 4.95 mmol) in dry methanol (50 mL) was added freshly prepared sodium methanolate (267 mg, 4.95 mmol). This mixture was stirred for 18 h at room temperature. The solvent was removed by distillation, and the residue was dissolved in CH_2Cl_2, washed with water and saturated sodium chloride solution, and dried. The product was purified with flash chromatography to yield white crystals (641 mg, 72%). **23c**: mp 108–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.10 (m, 1 H), 2.90 (d, 1 H), 2.61 (m, 2 H), 2.32 (m, 1 H), 2.26 (t, 1 H), 2.21 (q, 1 H), 2.1–1.9 (m, 2 H), 1.87 (s, 3 H), 1.84–1.5 (m, 4 H); IR (KBr) 3440 (s), 2960 (s), 2920 (s), 1690 (s), 1060 (s), 1020 (s) cm^{-1}.

3-Bromotricyclo[5.4.0.0^{2,8}]undecan-9-one (24). To a stirred solution of **23a** (4.4 g, 22.6 mmol) in dry CH_2Cl_2 was added dropwise at −78 °C under an argon atmosphere a 1 M BBr_3 solution (90.4 mL, 90.4 mmol) in CH_2Cl_2.[23] After 30 min, the addition was complete, and the mixture was stirred for an additional hour at −78 °C. The solution was then poured into 500 mL of cold, aqueous NaOH solution (280 mmol) with stirring. The phases then were separated, the aqueous layer was extracted with CH_2Cl_2 (400 mL), and the organic phases were combined, washed with saturated $NaHCO_3$ solution, and then dried. The crude mixture was usually used for the next reaction. For analytical purposes, the crude mixture was purified with flash chromatography on silica gel (ether/petroleum ether, 4:1). This gave a yield for the desired bromide **24** of 55%. The rearranged bromide yielded 31%. **24**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (m, 1 H), 2.97 (d, 1 H), 2.62 (m, 3 H), 2.4–1.6 (m, 10 H); HRMS

(M^+) calcd for $C_{11}H_{15}O^{81}Br$ 244.0286, obsd 244.0179; calcd for $C_{11}H_{15}O^{79}Br$ 242.0306, obsd 242.0284.

Tricyclo[5.4.0.0^{2,8}]undec-3-en-9-one (26). To a solution of the crude mixture of the bromide **24** (5.5 g) in dry acetonitrile was added DBU (13.7 g, 90.0 mmol).[24] The mixture was heated to reflux and stirred for 36 h. The solution was poured into ice water (300 mL) and extracted with ether (400 mL). The organic layers were combined, washed with dilute HCl and water, and dried. Removal of the solvent and subsequent flash chromatography on silica gel (ether/petroleum ether, 4:1) gave a clear liquid (2.1 g, 55% in relation to **23a**). **26**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (m, 2 H), 2.82 (d, 1 H), 2.6–2.3 (m, 7 H), 2.1–1.9 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 211.8 (s), 129.9 (signal with double intensity, 2 d), 57.7 (d), 41.7 (d), 41.5 (d), 40.4 (d), 31.4 (t), 28.7 (t), 25.3 (t), 24.5 (t); IR (CCl_4) 3000 (w), 2905 (s), 1710 (s) cm^{-1}.

Tetracyclo[7.1.1.0^{3,8}.0^{4,10}]undecan-11-one (29). To a stirred solution of tosyl chloride (210 mg, 1.1 mmol) in pyridine (5 mL) was added dropwise a solution of the alcohol **23c** (180 mg, 1 mmol) in pyridine (10 mL) at 0–5 °C. The mixture was then stirred for 24 h at room temperature. The solution was poured into ice water (100 mL) and extracted with ether (150 mL). The organic layers were combined, washed with dilute HCl and with saturated $NaHCO_3$ solution, and dried, and the solvent was removed. The crude mixture (ca. 350 mg) was dissolved in acetonitrile (20 mL), and DBU (0.75 g, 5 mmol) was added with stirring in an argon atmosphere. The mixture was refluxed for 24 h. The solution was poured into ice water (100 mL) and extracted with ether (150 mL). The organic layers were combined, washed with dilute HCl and saturated $NaHCO_3$, and dried, and the solvent was removed. Subsequent flash chromatography on silica gel (ether/petroleum ether, 1:4) yielded two isomeric products in a ratio of 1:1: the desired olefin **26** and **29** (altogether 68 mg, 42%) as oily clear liquids. **29**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.97–2.77 (m, 2 H), 2.43–2.38 (m, 2 H), 2.16 (s, br, 1 H), 2.01–1.95 (m, 1 H), 1.91–1.84 (m, 1 H), 1.76–1.66 (m, 3 H), 1.53–1.32 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 207.9 (s), 61.8 (d), 57.0 (d), 47.7 (d), 46.4 (d), 43.5 (d), 38.1 (t), 34.1 (d), 29.6 (t), 25.5 (t), 17.49 (t); GC/IR 2947 (s), 1790 (s) cm^{-1}.

Tricyclo[5.4.0.0^{2,8}]undecan-9-one (30). A solution of **26** (300 mg, 1.85 mmol) in dry ethanol (10 mL) was hydrogenated at atmospheric pressure and room temperature over platinum oxide (30 mg). After the theoretical amount of hydrogen had been absorbed (45 min), the reaction mixture was filtered and the solvent removed. The remaining liquid was purified with flash chromatography on silica gel (ether/petroleum ether, 1:4), which gave a clear liquid (280 mg, 92%). **30**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.64–2.53 (m, 3 H), 2.32–2.28 (m, 1 H), 2.27–2.19 (s, br, 2 H), 2.02–1.93 (m, 2 H), 1.79–1.59 (m, 8 H); ^{13}C NMR (75.4 MHz, acetone-d_6) δ 212.3 (s), 55.9 (d), 42.4 (d, double intensity), 39.7 (d), 32.6 (t), 30.7 (t, double intensity), 26.2 (t, double intensity), 26.0 (t); IR (film) 2920 (s), 1705 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.31; H, 9.56.

Tricyclo[5.4.0.0^{2,8}]undecan-9-one (*p*-Tolylsulfonyl)-hydrazone (31). A mixture of **30** (280 mg, 1.7 mmol) and tosylhydrazine (316 mg, 1.7 mmol) in dry ethanol (15 mL) was stirred for 24 h at room temperature. A white precipitate was formed, which was filtered and identified as pure product **31** (485 mg, 86%): mp 202 °C dec; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.9 (d, 2 H), 7.3 (m, 3 H), 2.75 (d, 1 H), 2.6–1.5 (m, 18 H); IR (KBr) 3430 (br), 3220 (s), 2929 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_2S$: C, 65.03; H, 7.28; N, 8.43. Found: C, 65.02; H, 7.38; N, 8.54.

Tricyclo[5.4.0.0^{2,8}]undec-9-ene (32). To a stirred solution of **31** (450 mg, 1.35 mmol) in dry THF (40 mL) at −10 °C was added dropwise a 1.6 M solution of BuLi (3.4 mL, 5.4 mmol) in hexane during 15 min.[18] The mixture was allowed to warm up to room temperature (1 h) and then stirred for another 30 min. Ice water (100 mL) was carefully added, the mixture was extracted with ether (100 mL), and the organic layers were dried. The solvent was carefully removed, and the residue was purified by flash chromatography on silica gel (pentane) to give a colorless, volatile liquid (41 mg, 24%). **32**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.52–6.38 (m, 1 H), 5.49–5.38 (m, 1 H), 2.48 (dd, 2 H), 2.28 (m, 1 H), 2.18–2.05 (m, 3 H), 1.8–1.5 (m, 8 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 141.5 (d), 123.0 (d), 46.8 (d, double intensity), 40.3 (d), 39.5 (d), 37.8 (t), 30.9 (t, double intensity), 25.9 (t, double intensity); GC/IR 3047 (w), 2923 (s), 1629 (w) cm^{-1}; HRMS (M^+) calcd 148.1270, obsd 148.1266.

Tricyclo[5.4.0.0^{2,8}]undec-4-ene-3,9-dione (33). Chromium trioxide (1.2 g, 12 mmol) was suspended in dry CH_2Cl_2 (30 mL) at −20 °C, and the DMP (1.15 g, 12 mmol) was added in one portion.[25] After the mixture was stirred at −20 °C for 15 min, the olefin **26** (162 mg, 1 mmol) dissolved in 10 mL of dry CH_2Cl_2 was added and the mixture was stirred for 4 h while the temperature was maintained between −10 and −20 °C. Sodium hydroxide solution (5 mL, 5 N) was then added, and the mixture was stirred for 1 h at 0 °C. The phases were separated, the aqueous phase was extracted with CH_2Cl_2 (100 mL), and the organic layers were combined and washed with dilute HCl to remove the DMP and with water. The solvent was removed, and subsequent flash chromatography on silica gel (ether) gave the two isomeric diketones (altogether 105 mg, 61%) in a ratio of 9:1 related to the rearranged, undesired product. **33**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61–6.4 (ddd, 1 H), 6.12–6.06 (dd, 1 H), 2.93 (d, 1 H), 2.89–2.83 (m, 3 H), 2.73–2.64 (m and t, 3 H), 2.46 (q, 1 H), 2.22–2.11 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 209.6 (s), 200.0 (s), 142.9 (d), 128.5 (d), 53.3 (d), 51.0 (d), 40.5 (d), 36.6 (d), 34.4 (t), 31.1 (t), 24.9 (t); GC/IR 3039 (w), 2943 (m), 1743 (s), 1685 (s) cm^{-1}. **34**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (dd, 1 H), 6.11 (d, 1 H), 2.92 (dd, 2 H), 2.84 (d, 1 H), 2.72 (dd, 1 H), 2.68–2.63 (m, 2 H), 2.62–2.58 (m, 1 H), 2.41–2.36 (q, 1 H), 2.26–2.08 (m, 2 H); GC/IR 3044 (w), 2939 (m), 1744 (s), 1686 (s) cm^{-1}; HRMS (M^+) calcd 176.0837, obsd 176.0841.

Tricyclo[5.4.0.0^{2,8}]undec-3-en-9-one Ethylene Acetal (35). A solution of **26** (3 g, 18.5 mmol), ethanediol (5.73 g, 92.5 mmol), and pyridinium tosylate (1.38 g) in dry benzene (100 mL)[30] was placed in a round-bottom flask fitted with a Dean–Stark trap and refluxed for 7 h. Water was added, the phases were separated, and the organic layer was dried. The solvent was removed by distillation, and subsequent flash chromatography on silica gel (ether/petroleum ether, 1:4) gave a colorless, clear liquid (3.4 g, 90%). **35**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (m, 1 H), 5.85 (m, 1 H), 3.97–3.87 (m, 4 H), 2.45–2.24 (m, 6 H), 2.08–2.02 (m, 2 H), 1.97–1.63 (m, 4 H); IR (film) 3010 (m), 2920 (s), 1645 (w), 1110 (s), 1090 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.66; H, 9.00.

Tricyclo[5.4.0.0^{2,8}]undec-3-ene-5,9-dione 9-Ethylene Acetal (36). Iodoxybenzene (10.6 g, 45 mmol) and then dipyridyl diselenide[28] (471 mg, 1.5 mmol) were added to a solution of **35** (3.1 g, 15 mmol) in dry benzene (150 mL), and the solution was refluxed for 4–30 h with stirring under argon. At the end of the reaction (TLC control, because if the reaction ran too long, no product could be isolated), the mixture was cooled to room temperature, filtered on Celite, and evaporated to dryness. The product was isolated by flash chromatography on silica gel (ether/petroleum ether, 1:1) as a light yellow, oily liquid (1.7 g, 51%). **36**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–7.05 (dd, 1 H), 6.02 (d, 1 H), 3.97–3.86 (m, 4 H), 2.92–2.85 (dd, 2 H), 2.68–2.63 (dd, 1 H), 2.34–2.22 (m, 2 H), 2.15–1.90 (m, 5 H); IR (film) 3040 (w), 2940 (s), 1660 (s), 1120 (s), 1100 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.86; H, 7.32. Found: C, 70.92; H, 7.59.

5-Hydroxytricyclo[5.4.0.0^{2,8}]undec-3-en-9-one Ethylene Acetal (37). A solution of **36** (1.5 g, 6.8 mmol) in 80 mL of dry ether was added dropwise to a stirred suspension of lithium aluminum hydride (119 mg, 3.4 mmol) in dry ether (30 mL) at −10 °C under argon. The reaction mixture was stirred for another 8 h at room temperature after the addition was complete. Aqueous NaOH solution (15%) (10 mL) was carefully added with cooling. The solution was extracted with ether (150 mL), and the organic layers were combined and dried. The solvent was removed, and subsequent flash chromatography yielded a white, crystalline solid (1.3 g, 86%). **37**: mp 96–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00–5.93 (m, 1 H), 5.77–5.58 (d, br, 1 H), 4.85–4.77 (m, 1 H), 3.98–3.55 (m, 4 H), 2.49–1.64 (m, 10 H); IR (film) 3420 (br), 3020 (w), 2930 (s), 1645 (w), 1120 (m), 1100 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.15; H, 8.41.

Tricyclo[5.4.0.0^{2,8}]undeca-3,5-dien-9-one Ethylene Acetal (38). A solution of **37** (1.2 g, 5.4 mmol) in dry benzene (15 mL) was added dropwise to a stirred solution of Burgess reagent[29] (1.1

(30) Sterzycki, R. *Synthesis* **1979**, *724*.

g, 10.8 mmol) in dry benzene (20 mL) under an argon atmosphere. The mixture was then refluxed for 1 h. Water was added, and the mixture was extracted with CH_2Cl_2 (150 mL). The organic layers were combined, washed with saturated $NaHCO_3$ solution, dried, and evaporated to dryness. Subsequent flash chromatography gave an oily liquid, which solidified on standing (528 mg, 48%). **38**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.19–6.11 (m, 2 H), 5.93–5.86 (m, 2 H), 3.97–3.84 (m, 4 H), 2.71–2.61 (m, 2 H), 2.07–1.92 (m, 4 H), 1.66–1.57 (m, 2 H); GC/IR 3036 (m), 2954 (s), 1114 (s) cm^{-1}; UV (pentane) λ_{max} 276 nm (ϵ 4834); HRMS (M^+) calcd 204.1188, obsd 204.1169.

Tricyclo[5.4.0.0^{2,8}]undeca-3,5-dien-9-one (39). An aqueous solution of 10% oxalic acid[28] (0.3 g, 11 drops) was added with continuous magnetic stirring to a suspension of 3 g of silica gel (Merck, silica 60, 70–230 mesh) in dry CH_2Cl_2 (4 mL). After 2–3 min, the water phase disappeared due to absorption on the silica gel surface. **38** (500 mg, 2.45 mmol) dissolved in CH_2Cl_2 (5 mL) was added, and the mixture was stirred until no more ketal **38** could be detected (TLC control) (ca. 2 h). The reaction mixture was filtered and the solid washed several times with the solvent. The solvent was removed, and subsequent flash chromatography on silica gel (ether/petroleum ether, 1:1) gave a colorless, oily liquid (341 mg, 87%). **39**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.20–6.11 (m, 2 H), 6.05–5.99 (m, 2 H), 2.79–2.75 (m, 2 H), 2.59–2.54 (m, 2 H), 2.16–2.09 (m, 3 H), 1.92–1.88 (m, 1 H); ^{13}C NMR (75.4 MHz, acetone-d_6) δ 212.6 (s), 134.6 (d, double intensity), 126.2 (d, double intensity), 42.9 (d), 42.3 (d, double intensity), 31.2 (t), 28.8 (d), 24.8 t); UV (pentane) λ_{max} 276 nm (ϵ 4879); HRMS (m^+) calcd 160.0868, obsd 160.0878.

Tricyclo[5.4.0.0^{2,8}]undeca-3,5-dien-9-one (*p*-Tolylsulfonyl)hydrazone (40). A mixture of **39** (300 mg, 1.87 mmol) and tosylhydrazine (348 mg, 1.87 mmol) in dry ethanol (20 mL) was stirred for 24 h at room temperature. A white precipitate was formed, which was filtered and identified as pure product **40** (500 mg, 81%): mp 186 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, 2 H), 7.30 (d, 2 H), 7.19 (s, br, 1 H), 6.1–6.04 (m, 2 H), 5.99–5.90 (m, 2 H), 2.49–2.37 (m, 7 H), 2.24 (d, 1 H), 2.13–2.07 (m, 2 H), 1.78–1.74 (m, 1 H); IR (KBr) 3215 (s), 2988 (s), 1333 (s), 1165 (s) cm^{-1}. Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.40; H, 6.24; N, 8.54.

Tricyclo[5.4.0.0^{2,8}]undeca-3,5,9-triene (12). To a stirred solution of **40** (500 mg, 1.65 mmol) in dry THF (40 mL) at −10 °C was added dropwise a 1.6 M solution of BuLi (4.1 mL, 6.6 mmol) in hexane during 15 min.[18] The mixture was allowed to warm up to room temperature (1 h) and then stirred for another 30 min. Ice water (100 mL) was carefully added, the mixture was extracted with ether (100 mL), and the organic layers were dried. The solvent was carefully removed, and the residue was purified by flash chromatography on silica gel (pentane) to give a colorless, volatile liquid (45 mg, 19%). **12**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.45–6.36 (m, 1 H), 6.14–6.03 (m, 2 H), 5.87–5.78 (m, 2 H), 5.49–5.41 (m, 1 H), 2.57–2.50 (m, 4 H), 1.94–1.89 (m, 1 H), 1.65–1.58 (m, 1 H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 138.5 (d), 136.0 (d, double intensity), 123.9 (d, double intensity), 122.1 (d), 46.2 (d, double intensity), 35.1 (t), 28.8 (d), 25.5 (d); GC/IR 3032 (s), 2966 (s), 694 (m); UV ($CDCl_3$) λ_{max} 293 nm; HRMS (M^+) calcd 144.0977, obsd 144.0958.

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Pouosides A–E, Novel Triterpene Galactosides from a Marine Sponge, *Asteropus* sp.

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Five new triterpene galactosides, pouosides A–E (**1–5**), have been isolated from a Pacific marine sponge, *Asteropus* sp. The carbon skeleton of the pouoside aglycons is new for naturally occurring triterpenes and parallels that of the C_{40} carotenoids. Structures were determined from spectroscopic data, especially extensive ^1H and ^{13}C NMR data and 2D NMR experiments. A novel saponin in which amino sugars are incorporated was isolated from the same sponge. Pouoside A, **1**, is cytotoxic.

Despite the great diversity that already exists among the carbon skeletons of known triterpenes, new variants continue to emerge.[1] Some of the most novel skeletal modifications occur among the less common metabolites and arise from partial cyclization of squalene. Interestingly, to date no naturally occurring triterpenes have been found that have a carbon skeleton patterned after that of the C_{40} carotenoids, i.e., terminal cyclohexane rings linked by a symmetrical, acyclic chain.[2] We report here the isolation, from an *Asteropus* sp. of sponge,[3] of five triterpene galactosides whose aglycons do have a carotenoid-type carbon skeleton. In addition to the pouosides, a novel, cytotoxic saponin (sarasinoside A_1) that contains amino sugars, was also been isolated from this sponge.[4,5]

(1) Connolly, J. D.; Hill, R. A. *Nat. Prod. Rep.* **1986**, *3*, 421 and earlier reviews cited. Devon, T. K.; Scott, A. I. *Handbook of Naturally Occurring Compounds*; Academic: New York, 1972; Vol. II, p 281.

(2) Although there are no reports of such naturally occurring compounds, synthetic carotenoid-like diterpene compounds have been synthesized before; cf. the following: Sopher, D. W.; Utley, J. H. P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1361. Foote, C. S.; Chang, Y. C.; Denny, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 5216. Feichtmayr, F.; Heilbronner, E.; Nuerrenbach, A.; Pommer, H.; Schlag, J. *Tetrahedron* **1969**, *25*, 5383.

(3) Tentative sponge identification was made by Dr. Jane Fromont, Sir George Fisher Centre for Tropical Marine Studies, James Cook University, Townsville, Australia. Voucher specimens (79-GS-61; BB3) are on hand in the principal author's collection. The galactosides are named after the small bay, Pou Bay, near where the sponge was collected since the sponge genus name could not be determined from the specimen available.

(4) Schmitz, F. J.; Ksebati, M. B.; Gunasekera, S. P.; Agarwal, S. *J. Org. Chem.*, in press. Interestingly, the pouosides were not found in specimens of *Asteropus* collected at Guam Is., although sarasinoside A_1 was.

(5) Kitagawa, I.; Kobayashi, M.; Yoshihiro, O.; Yoshikawa, M.; Hamamoto, Y. *Chem. Pharm. Bull.* **1987**, *35*, 5036.

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