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SUBSTITUENT EFFECTS ON THE EFFICIENCIES AND REGIOSELECTIVITIES OF THE DI-Π-METHANE REARRANGEMENT OF VINYL-SUBSTITUTED BICYCLIC SYSTEMS

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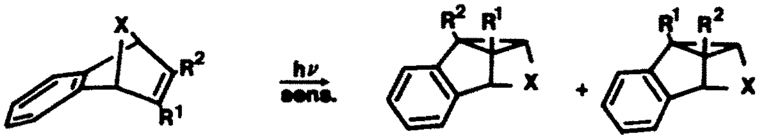
Abstract - Dihydrobenzobarrelenes 4a-4j and 7,7-dimethylbenzonorbornadienes 7a-7q which were mono- or disubstituted at the vinyl moiety were synthesized. The substituent effects on the efficiencies and regioselectivities of the di-π-methane rearrangement were studied with the results: 1) The dihydrobenzobarrelene system rearranges less efficiently than the 7,7-benzonorbornadiene system. 2) The effect of the substituents on the efficiencies is more pronounced in the less efficient dihydrobenzobarrelene systems. 3) The efficiency is higher, if the radical stabilizing effect of the substituent is greater. But the effect of the substituent to enhance the rate of intersystem crossing to the ground state of the starting materials reduces the efficiencies. 4) The radical stabilization by the substituents controls the regioselectivity. 5) In disubstituted systems the second substituent contributes to the efficiency. Electron-donating substituents increase the efficiencies slightly, whereas with electron-withdrawing substituents as cyano or carbomethoxy groups the photoisomerization becomes completely inefficiently.

The effect of substituents on the regiospecifity of the di-π-methane rearrangement of bicyclic compounds was investigated by a few research groups, lately. Particularly, vinyl-substituted systems were studied by Bender[1-4] and Paquette[5-13], and it was found that a cyano group controls the regiospecifity of the photorearrangement of the benzonorbornadiene[7] 1 and the dihydrobenzobarrelene[3] 3a, and the photoreactions proceeded exclusively in one direction yielding 2 and 5a, respectively. Contrary, the controlling effect of a methyl group bonded to the vinyl moiety is less pronounced. In order to get information on the regiospecifity and efficiency of the di-π-methane rearrangement of vinyl-substituted bicyclic systems, the photorearrangements of appropriate substituted dihydrobenzobarrelenes 4a - 4j and 7,7-dimethylbenzonorbornadienes 7a - 7q were investigated.

SYNTHESIS OF PHOTOCHEMICAL REACTANTS

Compounds 4a - 4e and 4j were synthesized from 5,6-benzobicyclo[2.2.2]octen-2-one obtained from 5,6-benzobicyclo[2.2.2]5,7-octadien-2-one[14] by conventional methods. The derivatives 4f and 4g were synthesized by cycloaddition of dicyano-



1: X=CH_2 2: X=CH_2 3: X=CH_2

4: X=$(CH_2)_2$ 5: X=$(CH_2)_2$ 6: X=$(CH_2)_2$

a: R^1=CN, R^2=H; b: R^1=CH_3, R^2=H; c: R^1=OCH_3, R^2=H; d: R^1=CO_2CH_3, R^2=H;
e: R^1=Cl; R^2=H; f: R^1=R^2=CN; g: R^1=R^2=CO_2CH_3; h: R^1=CF_3, R^2=H;
i: R^1=R^2=CH_3; j: R^1=CN, R^2=CH_3

7: X=$C(CH_3)_2$ 8: X=$C(CH_3)_2$ 9: X=$C(CH_3)_2$

a: R^1=CN, R^2=H; b: R^1=CH_3, R^2=H; c: R^1=OCH_3, R^2=H; d: R^1=CO_2CH_3, R^2=H;
e: R^1=Cl, R^2=H; f: R^1=R^2=CN; g: R^1=R^2=CO_2CH_3

and dicarbomethoxyacetylene, respectively, to naphthalene and subsequent selective reduction of the unsubstituted double bond. 4h was prepared by aryne addition to trifluorotoluene. 4i was obtained by Diels-Alder reaction of benzoquinone with 2,3-dimethyl-1,3-cyclohexadiene followed by reduction, tosylation and elimination.

The monosubstituted dimethylbenzonorbornadienes 7a -7c and 7e were prepared from 7,7-dimethylbenzonorbornen-2-one[15] by conventional methods. The synthesis of the disubstituted compounds 7f - 7g and the monosubstituted compound 7e were performed by Diels-Alder addition of dicyano- and dicarbomethoxyacetylene, respectively, to 3,3-dimethylisoindene[16].

PHOTOREARRANGEMENTS AND QUANTUM YIELDS

Acetone sensitized irradiation at 300 nm or direct irradiations in n-hexane at could be detected. The photoproducts could be isolated and, in the cases isomers were formed, could be separated by high performance liquid chromatography with the exception of 5h and 6h. The results are listed in Table 1 and 2. Acetophenone (E_T 310 kJ/mole)[17] as sensitizer was effective in all cases as well, but benzophenone (E_T 289 kJ/mole)[17] yielded only photoproducts in irradiations of 7a and 7d. No system could be sensitized by Michler's ketone (E_T 260 kJ/mole)[17]. The quantum yields were measured by irradiation with a HBO 200 lamp at 304 nm using a Bausch & Lomb high intensity monochromator. Details are given in the experimental section.

STRUCTURAL ASSIGNMENTS

The structure of the photoproducts could be elucidated on the basis of spectral data obtained by ^1H NMR (400 MHz), ^{13}C NMR and differential nuclear Overhauser experiments.

The ^1H NMR spectrum of 5i in which the resonance signals were well separated could be used as a guide for the interpretation of the spectra of the monosubsti-

Table 1: Regiospecifities and quantum yields of photoproducts of the irradiations of substituted dihydrobenzobarrelenes 4a-4j

	R^1	R^2	regiospecifity 5	 6	quantum yields[b] ϕ_5	 ϕ_6	 $\phi_{tot.}$
4a[a]	CN	H	100	-	0.51	-	0.51[3]
4b	CH_3	H	73	27	0.062	0.023	0.085±0.002
4c	OCH_3	H	-	-	-	-	-
4d	CO_2CH_3	H	-	-	-	-	-
4e	Cl	H	-	-	-	-	-
4f	CN	CN	-	-	-	-	-
4g	CO_2CH_3	CO_2CH_3	-	-	-	-	-
4h[a]	CF_3	H	86	14	0.082	0.014	0.096±0.003
4i	CH_3	CH_3	50	50	0.093	0.093	0.186±0.009
4j[a]	CN	CH_3	100	-	0.496	-	0.496±0.09
4[c]	H	H	50	50	0.019	0.019	0.038±0.002

a: product formation could be observed by direct irradiations
b: quantum yields were measured from irradiations in acetone
c: lit. ref. 18

Table 2: Regiospecifities and quantum yields of photoproducts of the irradiations of substituted 7,7-dimethylbenzonorbornadienes 7a-7g

	R^1	R^2	regiospecifity 8	 9	quantum yields[c] ϕ_8	 ϕ_9	 $\phi_{tot.}$
7a	CN	H	100	-	0.653	-	0.653±0.01
7b	CH_3	H	70	30	0.425	0.181	0.606±0.005
7c[a]	OCH_3	H	100	-	0.289	-	0.289±0.006
7d[a,b]	CO_2CH_3	H	100	-	0.313	-	0.313±0.005
7e	Cl	H	-	-	-	-	-
7f	CN	CN	-	-	-	-	-
7g	CO_2CH_3	CO_2CH_3	-	-	-	-	-
7[d]	H	H	50	50	0.29	0.29	0.58±0.09

a: product formation could be observed by direct irradiations
b: secondary photoproducts were formed in direct irradiations which were not isolated
c: quantum yields from irradiations in acetone
d: lit. ref. 18

tuted dihydrobenzosemibullvalenes. The signal of H(5) appears downfield as a broad doublet. As was shown by Paquette[20] and Bender[3] for some dihydrobenzosemibullvalenes H(5) does not couple with endo-H(6), since the dihedral angle is supposed to be 90°. The only significant coupling occurs with exo-C6-H with $J_{5,exo-6}=5.5$ Hz. The broadening of the signal may be attributed to a long range coupling with exo-H(7). In addition, from molecular models[20] it could be derived that the dihedral angle between endo-H(6) and exo-H(7) is close to 90° as well, and the coupling constant is expected to be zero. The signal of the endo-H(6) appears as a doublet of doublets with the coupling constants $J_{6gem}=11.5$ Hz and $J_{endo-6,endo-7}=6$ Hz. The signal of exo-H(6) is split into twelve lines. The following coupling constants could be extracted: J_{6gem}, $J_{exo-6,exo-7}=8.8$, $J_{exo-6,endo-7}=11.5$ Hz and $J_{exo-6,5}$. The resonance signal of exo-H(7) is split into sixteen lines, and again four coupling constants were derived: $J_{7gem}=13.5$, $J_{exo-7,8}=6.9$, $J_{exo-7,exo-6}$ and $J_{exo-7,8}=2$ Hz. The signals of endo-H(6) and endo-H(7) are shifted upfield. From the splitting of the signal of endo-H(7) the following coupling constants were obtained: J_{7gem}, $J_{endo-7,exo-6}$, $J_{endo-7,endo-6}$ and $J_{endo-7,8}=2$ Hz. The signal of H(8) appears as a doublet of doublets with $J_{exo-7,8}$ and $J_{endo-7,8}$. The chemical shift

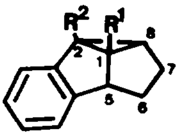


Table 3. ^1H NMR chemical shift values of the hydrogen atoms of the dihydrosemibenzobullvalenes 5 and 6 (ppm) in the aliphatic region

	R^1	R^2	C1-H	C2-H	C5-H	C6-H_e[a]	C6-H_x[a]	C7-H_e[a]	C7-H_x[a]	C8-H
5a[15]	CN	H	-	3.15	3.87	1.76	2.45	1.20	2. 01	2.60
5b	CH_3	H	-	2.21	3.28	1.61	2.25	1.14	1.85	1.64
6b	H	CH_3	2.51	-	3.53	1.59	2.11	1.03	1.80	1.74
5h	CF_3	H	-	2.89	3.81	1.70	2.35	1.15	1.89	2.31
6h	H	CF_3	3.05	-	3.68	1.60	2.19	1.15	1.89	2.41
5i	CH_3	CH_3	-	-	3.22	1.57	2.15	1.01	1.79	1.35
5j	CN	CH_3	-	-	3.76	1.56	2.33	1.03	1.90	2.31
5k	H	H	2.69	2.29	3.48	1.54	2.11	1.14	1.75	1.80

a: e signifies endo-H, x signifies exo-H

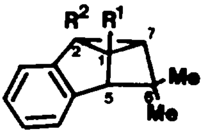


Table 4. ^1H NMR chemical shift values of the hydrogen atoms of 8 and 9 (ppm) in the aliphatic region

	R^1	R^2	C1-H	C2-H	C5-H	CH_{3x}[a]	CH_{3e}[a]	C7-H
8a	CN	H	-	3.20	3.23	1.67	0.10	2.53
8b	CH_3	H	-	2.21	2.67	1.48	0.02	1.70
9b	H	CH_3	3.00	-	2.77	1.38	-0.02	1.60
8c	OCH_3	H	-	2.70	3.15	1.54	-0.08	1.85
8d	CO_2CH_3	H	-	3.28	3.25	1.52	0.05	2.51
8h	H	H	3.25	2.50	2.85	1.55	0.05	1.85

a: x signifies exo-, e signifies endo-

values of the substituted dihydrobenzosemibullvalenes are collected in Table 3. In addition, the values of the unsubstituted compound 4 are given for comparison.[18] The coupling constants are given in the experimental section.

Since from ^1H NMR data the positions of the substituents in 5j could not be deduced without doubt, a differential nuclear Overhauser experiment was performed. Irradiation at 1.53 ppm i. e. the position of the signal of the methyl group solely produced signals at 2.31 ppm (C8-H) and 7.1 ppm (aromatic ortho-hydrogen).

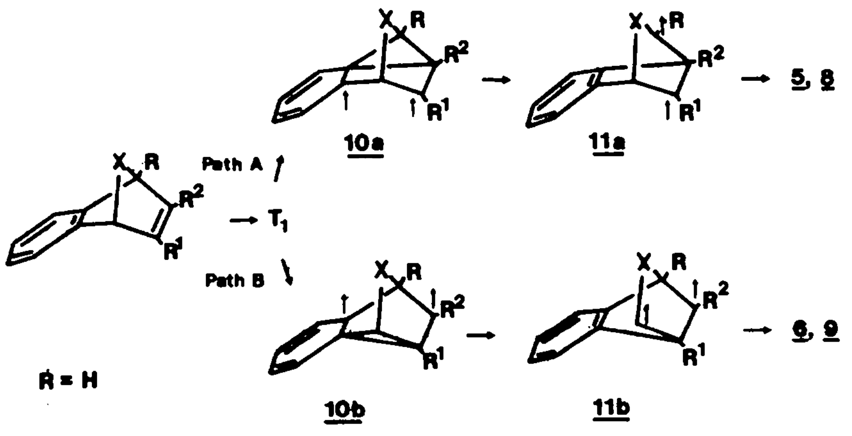
The position of the substituents in the photoproducts of the irradiations of the 7,7-dimethylbenzonorbornadienes 7a - 7q could be derived from ^{1}H NMR spectra. In the 1-substituted products the lowfield signal of C5-H is found as a doublet with a coupling constant $J_{5,7}$ equal 2.5 to 3.0 Hz, whereas in the 2-substituted ones the signal appears as a triplet with $J_{1,5}=J_{5,7}=2.8$ Hz. ^{1}H NMR chemical shift values of the hydrogen atoms bonded to the tricyclus of the photoproducts are presented in Table 4. For comparison, the values for the unsubstituted compound 8h[19] are given, too.

Additional proof for the structural assignment was obtained by hydrogenation of 8c. It was shown by Bender[4] that catalytic hydrogenation leads to opening of the cyclopropane ring at the least substituted bond. The hydrogenation of 8c produced 6,6-dimethyl-1-methoxy-3,4-benzobicyclo[3.2.0]heptene (19). The ^{1}H NMR spectrum of 19 showed two AB systems with geminal couplings $J_{2gem}=17$ Hz and $J_{7gem}=13$ Hz. In addition, long range couplings of the W-type of 2 Hz were found for the hydrogen atoms exo-H(2), H(5) and exo-H(7). Further, the signals of H(5) at 3.32 ppm, exo-H(2) at 3.26 ppm and endo-H(2) at 2.90 ppm are found in the benzylic region.

INTERPRETATIVE DISCUSSION

Bicyclic di-π-methane systems prefer to rearrange via the excited triplet states[22]. Since all systems investigated in this work rearrange substantially more efficiently in acetone sensitized irradiations than in direct ones, the excited triplet state will be the photoreactive one in these cases as well. Acetophenone sensitization yielded photoproducts in all cases, whereas benzophenone sensitization was only successful in the irradiations of 7a and 7d. But attempts to sensitize the rearrangement with Michler's ketone were ineffective even in these cases. Consequently, the triplet energies are in the range of 305-313 kJ/mole for the dihydrobenzobarrelenes and 290-300 kJ/mole for the dimethylbenzonorbornadienes.

Only in a few cases the sensitized irradiations of the mono- and disubstituted dihydrobenzobarrelenes and dimethylbenzonorbornadienes produced rearrangement products, and the efficiencies vary over a large range. The reason for these results may be discussed on the basis of the basic mechanism describing the skeletal change in the di-π-methane rearrangement.[23] (Scheme 1)



SCHEME 1

It was noted by Zimmerman that biradicals like 10 and 11 are approximations of species along the reaction coordinate and are not necessarily intermediates i. e. energy minima, but simply points on the energy surface, and each case must be considered separately. The participation of biradicals 10 and 11 as intermediates in the course of the di-π-methane rearrangement was discussed in special cases by Zimmerman[24]. Similar observations were made by Adam who generated photochemically unsubstituted 11 from an azoalkane and found that only 1-4% of the benzonorbornadiene 1 was formed[25]. Despite the small quantities of 1 formed it was concluded that 11 reacts irreversibly to photoproducts. In one particular case direct proof for the existence of triplet biradicals was presented by Schaffner et al.[26] in an investigation of a naphthobarrelene system at 77 K. It was found that the first triplet biradical reacts irreversibly to the second more stable biradical implying a small energy barrier.

Generally, the fully bonded biradicals 10a and 10b were considered as the regiochemistry controlling points on the reaction coordinate. In contrast, Paquette et al. claimed that on the basis of their results on the di-π-methane rearrangements of a large number of substituted benzonorbornadienes and an appreciable number of observations in other laboratories the biradicals 10 can be rationalized more succintly in terms of "a fleeting transition-state entity", with direct 1,2-aryl-shift being product determining.[10,13] Their interpretation rests predominately upon the strong directive effects exerted by bridgehead substituents (R ≠H) "at the intramolecular competition level" provided that there is no reversibility. This is likely, since the efficiencies of the rearrangements of the benzonorbornadienes are very high. If the substituent R can stabilize a radical center, biradical 11a is thermodynamically more stabilized than any other biradical and path A should be strongly favored. In some cases an entity similar to the biradicals 10, probably partially bonded, could not be ruled out entirely and a "gradient mechanism" seemed possible.[13]

Considering the results of this work, the first point to be noticed is that all monosubstituted dimethylbenzonorbornadienes isomerize more efficiently than the corresponding dihydrobenzobarrelenes. (Table 1 and 2) The unsubstituted systems 7 and 4 rearrange with quantum yields of 0.58 and 0.038. Further extension of the bridge in the di-π-methane systems is accompanied with a further decrease of the efficiencies. The benzobicyclo[3.2.2]nonadiene rearranges with a quantum efficiency of 0.020, and the benzobicyclo[4.2.2]decadiene is completely photochemically unreactive.[27] The reason may be seen in the higher flexibility of the dihydrobenzobarrelenes. The effect of ring size on triplet decay rates was demonstrated by Zimmerman for monocyclic systems.[28] This signifies that the ratio of the rates of triplet energy dissipation to the rates of rearrangement is higher for the dihydrobenzobarrelenes than for the benzonorbornadienes. Dihydrodibenzobarrelene triplets will therefore utilize chemical deactivation for energy dissipation i. e. nuclear motion toward a geometry where the excited state and the ground state hypersurfaces come close to reach a funnel.[29] In addition, in substituted systems spin-orbit coupling will enhance the rate of intersystem crossing.[29] The critical geometry of the systems at that funnel is not known, but it must be assumed that an interaction exists between the aryl and the vinyl moiety by some "bridging". The structures as written for the biradicals 10 are by no means a definite picture of the critical geometry.

All reactive monosubstituted systems with R^2=H react along path A pointing to the fact that radical stabilization of the substituents is controlling the regioselectivity. In addition, the efficiencies are higher compared to the unsubstituted systems 4 and 7. (Table 1 and 2) The radical stabilizing effect is most pronounced with the cyano groups, for 4a, 4j and 7a used route A exclusively. The stabilizing effect is less accentuated with the methyl and trifluoromethyl groups, since 4b, 4h and 7b used route B to some extent. Similar observations were reported by Paquette.[13]

Notable are the findings that the irradiations of the monosubstituted systems 4c, 4d, 4e and 7e are totally inefficient, whereas 7c and 7d isomerize. Recently, Paquette reported that 2-bromonorbornadiene did not exhibit any tendency to rearrange. The inefficiency of this compound to rearrange was interpreted in terms of 10a. In the beginning of the rearrangement as soon as spin density builds up on the vinyl carbon which is substituted with bromine spin-orbit coupling is maximized, and the rate of intersystem crossing to the surface of the starting material be becomes fast.[12] This explanation can be brought forward as well for the lack to rearrange of 4e and 7e, since chloro atoms are known to accelerate intersystem crossing.[30] Hahn reported too that a chloro-substituted benzobicyclo[4.2.1]nonatriene did not give a di-π-methane rearrangement.[31]

The lack to rearrange of the carbomethoxy-substituted system 4d was not expected, since 7d and carbomethoxydibenzobarrelene[32] could be isomerized. It is to be noted however that the quantum yield of the rearrangement of 7d is only half of 7a (R^1=CN, R^2=H) and of the parent compound 7. Probably the same effects will operate as for the chloro-substituted compounds 4e and 7e and, spin-orbit coupling enhances the rate of intersystem crossing to starting material. The same effect might even drive a system photochemically unreactive, if the basic efficiency of the bicyclic system is lower as it is the case with 4d. Similar arguments can be brought forward for the alkoxy-substituted systems 4c and 7c.

The photorearrangement of disubstituted 4j (R^1=CN, R^2=CH_3) uses only path A pointing to the fact that the radical stabilization by the cyano group is much greater than by the methyl group. The quantum yields of 4j (R^1=CN, R^2=CH_3) and 4a (R^1=CN, R^2=H) are comparable. The effect of the methyl group on the chemical deactivation is minor, although 4i (R^1=R^2=CH_3) rearranges twice as efficiently as 4b (R^1=CH_3, R^2=H).

In remarkable contrast, the dicyano-substituted 4f and 7f (R^1=R^2=CN) do not rearrange at all, although the monocyano-substituted compounds belong to the most efficient rearranging systems. Although one cyano group can provide stabilization for the biradical 11, 4f and 7f fail to rearrange. The second cyano group enhances the rate of radiationless decay to an extent that no photoproducts can be observed. The effect of the second cyano group is not entirely clear. The group is not placed on a carbon atom where odd electron density is built up during the course of the rearrangement and spin-orbit coupling is hardly the reason. It is more likely that the second cyano group influences either the energy and/or the shape of the triplet hypersurface in the region of the funnel that the probability for the system to advance to 11 is zero. If it is assumed that the critical nuclear geometry of the funnel has acquired the structure of a partially bonded cyclopropane the cyano group could exert effects on these bonds and therefore on the geometry of the funnel. The cyano group on the cyclopropyl ring might destabilize the adjacent bond which is formed in the early stage of the rearrangement so that intersystem crossing and return to the surface of the starting material become the dominating path, or the cyano group might strengthen the opposite bond which could increase the energy barrier on the way to 11. In a theoretical investigation on the equilibrium position of the cycloheptatriene-norcaradiene rearrangement Günther derived that electron-withdrawing substituents strengthen the opposite cyclopropane bond which shifts the equilibrium toward the norcaradiene, whereas electron-donating substituents increase the strength of the adjacent bond.[33] Apparently, ground state reasoning is applicable to the substituent effects on the critical geometry of the funnel.

The effect of the carbomethoxy group in the dicarbomethoxy-substituted systems 4g and 7g must be comparable to the effect of the cyano group, although the enhanced rate of intersystem crossing might cooperate and drive the photoisomerization completely inefficiently.

EXPERIMENTAL

^1H NMR spectra were recorded on a BRUKER WP 80 (80 MHz), BRUKER WH 250 (250 MHz) and BRUKER AM 400 (400 MHz). The ^{13}C NMR spectra were recorded with a BRUKER WH 90 (22.63 MHz), BRUKER WH 250 (62.86 MHz) and BRUKER AM 400 (100.61 MHz); $CDCl_3$ was used as solvent in all cases. In most cases the coupling constants could be directly derived from 400 MHz NMR spectra. If necessary decoupling experiments were performed. Differential nuclear Overhauser effects were measured on a BRUKER WP 80 using solutions of the 0.015 mmol samples in 0.5 ml $CDCl_3$ after degassing with nitrogen for 15 min in an ultrasonic bath. Mass spectra were obtained using a Varian MAT CH-5. High resolution mass spectra were recorded using a Varian MAT 731 (70 eV) spectrometer. The following values were used for calculation of the theoretical values : H=1.0078, C=12.0000, N=14.0031, O=15.9949, F=18.9984 and Cl=34.9689. Analytical and semipreparative separations were performed with a HPLC apparatus consisting of a Waters M 6000 pump, Waters UK 6 injector and LDC UV 254 nm detector.

Synthesis of compounds:

2-Cyano-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4a)[34,35]: A sample of 0.850 g (5.00 mmol) 5,6-benzobicyclo[2.2.2]octen-2-one[36] was dissolved in 2 ml benzene, and 0.640 g (6.50 mmol) trimethylsilylcyanide and 0.04 g ZnI_2 were added. The mixture was stirred at room temperature for 24 h. Pyridine (8 ml) and 2.30 g $POCl_3$ were added, and the mixture was refluxed for 6 h. After addition of 20 ml benzene the solution was filtered through a 1.5 cm layer of silica. The solvents were removed in vacuo, and the product was purified by column chromatography on silica (Kieselgel 60, Merck, 0.063-02 mm, 280 x 24 mm Ø) with hexane/ether (80/20). The first fraction yielded 0.36 g (40%) 1-cyano-6,7-benzobicyclo[3.2.1]octa-2,6-diene (12) as an oil and the second fraction 0.32 g (35%) 4a as colorless crystals. 4a: m.p. 66° C (hexane); ^1H NMR (80 MHz): 7.30 ppm (dd, 1H, C3-H), 7.1-7.3 (m, 4H, H-arom.), 4.05-4.25 (m, 2H, C1-H and C4-H), 1.40-1.80 (m, 4H, CH_2). 12: ^1H NMR (400 MHz): 7.05-7.25 ppm (m, 4H, H-arom.), 6.0 (dddd, 1H, C2-H), 5.25 (dddd, 1H, C3-H), 3.3 (br.dd, 1H, C5-H), 2.56 (dd, 1H, exo-C8-H), 2.46 (dddd, 1H, exo-C4-H), 2.30 (d, 1H, endo-C8-H), 1.90 (m, 1H, endo-C4-H); $J_{2,3}$=9.5 Hz, $J_{8,gem}$=10 Hz, $J_{4,gem}$=18.5 Hz, $J_{5,8(exo)}$=5 Hz, $J_{4(exo),5}$=5 Hz; ^{13}C NMR (400 MHz): 30.47 ppm (t, C4), 38.49 (d, C5), 41.94 (s, C1), 45.28 (t, C8), 121.21 (s, CN), 118.99, 123.54, 124.82, 126.56, 127.64, 130.29 (six doublets, C-arom. and C2, C3), 143.20, 147.23 (two s, C-arom.); MS: 181 (M^+, 100%). Analysis: found C, 85.96; H, 6.11; $C_{13}H_{11}N$ requires C, 86.15; H, 6.11.

2-Methoxy-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4c): A sample of 516 mg (3.00 mmol) 5,6-benzobicyclo[2.2.2]octen-2-one[36] was dissolved in 13.5 ml dry THF and 1.5 ml dry HMPTA, cooled to -78° C and purged with N_2. 662 mg (3.60 mmol) sodium bistrimethylsilylamide were added, and the reaction mixture was stirred at this temperature. After 30 min 590 mg (3.6 mmol) methyl trifluorosulfonate dissolved in 4 ml ether were added, and the reaction mixture was allowed to warm up to room temperature. After dilution with water the products were extracted with ether, washed with water and dried over Na_2SO_4. The solvent was removed in vacuo and the O- and C-alkylated products were separated by chromatography using silica deactivated with triethylamine and hexane/triethylamine (99:1) as mobile phase (Kieselgel 60, Merck, 230 mesh, 300 x 15 mm Ø). The first fraction yielded 4c and the second a mixture of exo/endo-3-methyl-5,6-benzobicyclo[2.2.2]octen-2-one (13) and starting material. This mixture was separated by chromatography using silica (Kieselgel 60, Merck, 0.063 mm, 250 x 15 mm Ø) with hexane/ether (80:20). The first fraction yielded 181 mg exo/endo-13, which could not be separated, and 30 mg of starting material. 4c: yield 273 mg (49%); m.p. 46° C (pentane); ^1H NMR (60 MHz): 7.0 ppm (m, 4H, H-arom), 5.10 (dd, 1H, C3-H), 3.80 (m, 1H, C4-H), 3.70 (m, 1H, C1-H), 3.46 (s, 3H, CH_3), 1.4-1.8 (m, 4H, CH_2); $J_{3,4}$=6 Hz, $J_{1,3}$=2 Hz; ^{13}C NMR (400 MHz): 25.97 ppm (t, C7), 27.51 (t, C8), 39.15 (d, C1), 43.82 (d, C4), 55.11 (q, CH_3), 96.73 (d, C3), 121.68, 122.68, 124.78, 125.21 (four doublets, C-arom.), 143.11 and 146.27 (two s, C-arom.), 165.48 (s, C2); MS: 186 (M^+,10%), 130 (100); MS-high resolution: found 186.1050; $C_{13}H_{14}O$ requires 186.1045. exo/endo-13: yield 181 mg (31%); ^1H NMR (60 MHz): 7.2 ppm (br.s, 4H, H-arom), 3.6 (m, 1H, C1-H), 3.2 (m, 1H, C4-H), 2.5-1.5 (m, 5H, C3-H and CH_2), 1.23 (d, 3H, exo-CH_3), 0.9 (d, 3H, endo-CH_3); ratio of exo/endo=1:2; MS: 186 (M^+, 12%), 130 (100).

2-Carbomethoxy-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4d): A sample of 0.340 g (2.00 mmol) 4a was dissolved in 20 ml glycol containing 5% KOH and refluxed for 30 min. After cooling to room temperature 100 ml H$_2$O were added and acidified with HCl. The acid was extracted with ether, and after washing the organic phase with water, was reacted directly without purification with diazomethane. Yield: 0.30 g (95%) 4d; m.p. 87° (CH$_3$OH); ^{1}H NMR: 7.50 ppm (dd, 1H, C3-H), 7.0-7.4 (m, 4H, H-arom.), 4.6 (m, 1H, C1-H), 4.16 (m, 1H, C4-H), 3.75 (s, 3H, CH$_3$), 1.6-1.8 (m, 4H, CH$_2$); $J_{3,4}$=6 Hz, $J_{1,3}$=2 Hz; MS: 214 (M$^+$,10%), 186 (100); MS-high resolution: found 214.0993; C$_{14}$H$_{14}$O$_2$ requires 214.0994.

2-Chloro-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4e): A sample of 1.00 g (5.80 mmol) 5,6-benzobicyclo[2.2.2]octen-2-one^{36} was dissolved in 2 ml POCl$_3$ and cooled to 0° C. 1.3 g (6.2 mmol) PCl$_5$ were added, and the reaction mixture was stirred for 24 h at room temperature. The mixture was poured on 50 g ice, and the product was extracted with pentane. The combined extracts were washed, neutralized and dried. The solution was concentrated to 10% of the volume by distillation and filtered through a 1 cm layer of silica. After removal of the pentane in vacuo 30 ml t-butanol and 2 g (18 mmol) KO-t-C$_4$H$_9$ were added, and the reaction mixture was stirred under reflux for 1 h. The solution was added to ice/water and extracted with pentane. The solvent was removed in vacuo, and 720 mg (3.8 mmol, 65%) 4e were obtained as a colorless oil. ^{1}H NMR (60 MHz): 7.1 ppm (m, 4H, H-arom.), 6.30 (dd, 1H, C3-H), 3.96 (m, 2H, C1-H, C4-H), 1.4-1.9 (m, 4H, CH$_2$); $J_{1,3}$=2 Hz, $J_{3,4}$=7 Hz; MS: 192 (M$^+$+2,3%), 190 (M$^+$,8%), 162 (100). Analysis: found C, 75.54; H, 5.84; C$_{12}$H$_{11}$Cl requires C, 75.59; H, 5.81.

2,3-Dicyano-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4f): A sample of 1.00 g (4.90 mmol) 2,3-dicyano-5,6-benzobicyclo[2.2.2]octa-2,5,7-triene^{41} and 4 g (20.6 mmol) potassium azodicarboxylate were dissolved in 50 ml CH$_3$OH and cooled to -30° C. 4 ml acetic acid were added, and the temperature was raised within 2 h to room temperature. 100 ml methylene chloride were was and the solution was washed with 100 ml NaOH (5%) and water. After drying of the organic phase the solvents were removed in vacuo and the residue chromatographed on silica (Kieselgel 60, Merck, 0.063 mm, 250 x 15 mm Ø) with hexane/ether (80:20). The first fraction yielded 570 mg (2.7 mmol, 56%) 4f and the second 415 mg starting material. 4f: m.p. 143° C (CH$_3$OH); ^{1}H NMR (60 MHz): 7.25 ppm (m, 4H, H-arom.), 4.40 (dd, 2H, C1-H, C4-H), 1.8 (m, 4H, CH$_2$); MS: 206 (M$^+$,10%), 178 (100). Analysis: found C, 81.64; H, 5.03; C$_{14}$H$_{10}$N$_2$ requires C, 81.53; H, 4.88.

2,3-Dicarbomethoxy-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4g): A sample of 5.40 g (0.020 mol) 2,3-dicarbomethoxy-5,6-benzobicyclo[2.2.2]octa-2,5,7-triene^{40} was dissolved in 100 ml ethyl acetate and was hydrogenated in the presence of 0.2 g Pd/C at atmospheric pressure. The catalyst was filtered and the solvent removed in vacuo. 5.4 g (0.02 mol, 100%) 4g were obtained. m.p. 67° C; ^{1}H NMR (60 MHz): 7.1 ppm (dd, 4H, H-arom.), 4.40 (dd, 2H, C1-H, C4-H), 3.8 (s, 6H, CH$_3$O), 1.6-1.8 (m, 4H, CH$_2$); MS: 272 (M$^+$,12%), 213 (100). Analysis: found C, 70.32; H, 5.96; C$_{16}$H$_{16}$O$_4$ requires C, 70.58; H, 5.88.

2-Trifluoromethyl-5,6-benzobicyclo[2.2.2]octa-2,5,7-triene (15): The procedure of Yoshida^{37} for the preparation of 15 was modified. A sample of 6.00 g (40.2 mmol) benzenediazonium-2-carboxylate^{38} was suspended in 500 ml trifluoromethylbenzene and was stirred at 45° C for 36 h until the gas evolution had ceased. The solution was treated with an aqueous solution of NaHCO$_3$ and water and was dried with MgSO$_4$. The solvent was removed in vacuo and the residue dissolved in 50 ml benzene. This solution was filtered through a 1.5 cm layer of silica, and the benzene was removed in vacuo. The product was purified by chromatography on silica (Kieselgel 60, Merck, 0.063-0.2 mm, 350x40 mm Ø) with hexane/THF (99.8:0.2). The second fraction contained 347 mg (1.56 mmol, 4%) 15 as a colorless oil. ^{1}H NMR (60 MHz): 6.6-7.5 ppm (m, 7H, H-arom. and H-vinyl), 5.0 (m, 2H, C1-H, C4-H).

2-Trifluoromethyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4h): 333 mg (1.50 mmol) 15 were dissolved in 15 ml CH$_3$OH, cooled to -30° C, and 600 mg (3.09 mmol) potassium azodicarboxylate was added with vigorous stirring. 1 ml acetic acid was added and the reaction mixture allowed to warm up to room temperature within 2 h. 50 ml hexane was added, and the solution was washed with water and sodiumhydrogencarbonate and was dried over MgSO$_4$. The solvent was removed in vacuo and the residue chromatographed on silica (Kieselgel 60, Merck, 0.063 mm, 250x15 mm Ø) with hexane/THF (99.8:0.2). The first fraction yielded 213 mg (0.94 mmol,63%) 4h as a colorless oil and the second 100 mg starting material. ^{1}H NMR (80 MHz): 7.16 ppm (m, 4H, H-arom.), 7.00 (m, 1H, C3-H), 4.00-4.30 (m, 2H, C1-H, C4-H), 1.4-1.8 (m, 4H, CH$_2$); MS: 224 (M$^+$, 6%), 196 (100); MS-high resolution: found 224.0812; C$_{13}$H$_{11}$F$_3$ requires 224.0813.

9,10-Dimethyltricyclo[6.2.2.0^{2,7}]dodeca-4,9-dien-3,6-diol (16): A sample of 100 mg (0.460 mmol) 9,10-dimethyltricyclo[6.2.2.0^{2,7}]dodeca-4,9-dien-3,6-dione^{39} was dissolved in 10 ml toluene, and 2 ml (1 M) solution of diisobutylaluminum hydride in hexane was added at 40° C under N$_2$. After stirring the reaction mixture at room temperature for 30 min, 2 ml cold aqueous KOH (30%) was added, and stirring was continued for another 30 min. The organic layer was separated, and the aqueous layer was extracted with three portions of10 ml ether. The combined organic phases were dried with $MgSO_4$ and the solvents removed in vacuo. The residue was suspended in pentane, filtered and washed with pentane to yield 66 mg (0.3 mmol,65%) 16. m.p. 126° C; ^1H NMR (60 MHz): 6.16 ppm (dd, 2H, C4-H, C5-H), 4.1 (m, 2H, C3-H, C6-H), 2.0-2.3 (m, 6H, C1-H, C2-H, C7-H, C8-H, OH), 1.75 (s, 6H, CH_3), 1.2-1.6 (m, 4H, CH_2); MS: 220 (M^+, 24%), 93 (100).

2,3-Dimethyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4i): A sample of 165 mg (0.75 mmol) 16 and 1.425 g (7.50 mmol) p-toluenesulfonyl chloride was dissolved in 5 ml $CHCl_3$, and 0.5 ml dry pyridine was added at 0° C. The mixture was stirred for 24 h at room temperature and was poured onto 20 g ice, 15 ml conc. HCl and 20 ml $CHCl_3$. The organic layer was separated, washed and dried. After removal of the solvents in vacuo the residue was dissolved in 20 ml benzene, and 1.5 g KO-t-C_4H_9 were added and the mixture was stirred at 50° C for 2 h. 50 ml H_2O and 50 ml pentane were added, and the organic layer was separated, washed and dried. After removal of the solvents in vacuo 93 mg (0.51 mmol,67%) 4i were obtained as colorless oil, which solidified on cooling. m.p. 48° C; ^1H NMR (80 MHz): 6.90-7.15 ppm (m, 4H, H-arom.), 3.45-3.65 (m, 2H, C1-H, C4-H), 1.75 (s, 6H, CH_3), 1.25-1.75 (m, 4H, CH_2); MS: 184 (M^+, 16%), 156 (100). Analysis: found C, 91.13; H, 8.72; $C_{14}H_{16}$ requires C, 91.24; H, 8.75.

2-Cyano-3-methyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4j): A sample of 740 mg (7.30 mmol) trimethylsilylcyanide and 100 mg ZnI_2 were added to 1.07 g (5.75 mmol) exo/endo-13 in 5 ml benzene, and the reaction mixture was stirred for 18 h at room temperature. 20 ml benzene was added, and the mixture was filtered through a 1 cm layer of silica. The solvent was removed in vacuo, and the residue was dissolved in 10 ml pyridine. After addition of 2.65 g (17.25 mmol) $POCl_3$ the mixture was stirred under reflux for 18 h. 20 ml benzene was added, the solution was filtered through a 1.5 cm layer of silica and the solvent removed in vacuo. The residue was purified by column chromatography (Kieselgel 60, Merck, 0.063-0.2 mm, 280x24 mm Ø) using hexane/ether (80:20) for elution. The first fraction contained a mixture of exo/endo-1-cyano-8-methyl-6,7-benzobicyclo[3.2.1]octa-2,6-diene (14), and the second fraction yielded 150 mg (0.77 mmol,13%) 4j. 4j: m.p. 53° C (pentane); ^1H NMR (60 MHz): 7.25 ppm (br.s, 4H, H-arom.), 4.20 (m, 1H, C1-H), 4.00 (m, 1H, C4-H), 2.3 (s, 3H, CH_3), 1.75 (m, 4H, CH_2); MS: 195 (M^+,14%), 167 (10); MS-high resolution: found 195.1044; $C_{14}H_{13}N$ requires 195.1048. exo/endo-14: oil; ^1H NMR (80 MHz): multiplets were found at 6.15 and 5.36 ppm for the vinylprotons and doublets at 0.95 and 1.00 ppm for the methyl groups. Further interpretation of the spectrum of the mixture was not attempted; MS: 195 (M^+, 82%), 166 (100).

7,7-Dimethyl-5,6-benzonorbornen-2-hydrazone (17): A sample of 3.20 g (17.2 mmol) 7,7-dimethyl-6-benzonorbornen-2-one[15] was mixed with 9.00 g (0.36 mol) hydrazine hydrate and 27.1 g (0.27 mol) triethylamine in 30 ml dry ethanol and was refluxed for 3 h. After cooling 100 ml water was added, and the aqueous phase was extracted with ether three times. After washing and drying the organic phase the solvent was removed in vacuo to yield 3.4 g (17 mmol,99%) 17 as a colorless oil. ^1H NMR (60 MHz): 7.20 ppm (m, 4H, H-arom.), 4.81 (m, 2H, -NH_2), 3.40 (br.s, 1H, C1-H), 3.10 (dd, 1H, C4-H), 2.71 (dd, 1H, exo-C3-H), 1.93 (d, 1H, endo-C3-H), 1.30 (s, 3H, exo-CH_3), 0.92 (s, 3H, endo-CH_3).

2-Iodo-7,7-dimethyl-5,6-benzonorbornadiene (18): A sample of 1.70 g (8.50 mmol) 17 was dissolved in 20 ml benzene and 9 ml triethylamine, and a solution of 4.323 g iodine in 12.5 ml benzene was added in a nitrogen atmosphere at room temperature. After stirring for 1 h 100 ml water was added, and the phase was extracted three times with 50 ml ether. The ether solution was washed with HCl, water and aqueous sodiumbisulfite. After drying the solvent was removed in vacuo, and the residue was dissolved in 50 ml dry ether, and 2.24 g (22 mmol) KO-t-C_4H_9 was added in five portions at 0° C. After 24 h at room temperature 50 ml water were added, and the ether phase was separated. The solvent was removed in vacuo, the residue dissolved in pentane and the solution filtered through a layer of 1.5 cm silica. The pentane was removed in vacuo to yield 1.7 g (5.75 mmol,67%) 18 as a faintly yellow oil. ^1H NMR (60 MHz): 6.9-7.4 ppm (m, 5H, C3-H, H-arom.), 3.3-3.5 (m, 2H, C1-H, C4-H), 1.42 (s, 3H, exo-CH_3), 0.92 (s, 3H, endo-CH_3); MS: 296 (M^+,30%), 169 (100) Analysis: found C, 52.59; H, 4.24; $C_{13}H_{13}I$ requires C, 52.7; H, 4.39.

2-Cyano-7,7-dimethyl-5,6-benzonorbornadiene (7a): A sample of 1.30 g (4.40 mmol) 18 in 20 ml dry HMPTA and 1 g (11 mmol) CuCN was heated to 90-95° C in a nitrogen atmosphere for 4 h. The reaction mixture was added to an aqueous solution of $FeCl_3$, filtered and extracted with 3 portions of 50 ml ether. After drying and removing the solvent in vacuo the residue was chromatographed (Kieselgel 60, Merck, 0.063 mm, 250x15 mm Ø) with hexane/ether (80:20) to yield 386 mg (1.98 mmol,45%) 7a as a colorless oil which solidified on cooling. m.p. 45° C (pentane); ^1H NMR (60 MHz): 7.35 ppm (dd, 1H, C3-H), 6.73-7.25 (m, 4H, H-arom.), 3.53 (s, 1H, C1-H), 3.50 (d, 1H, C4-H), 1.18 (s, 3H, exo-CH_3), 0.71 (s, 3H, endo-CH_3); MS: 195 (M^+, 23%), 180 (100). Analysis: found C, 86.18; H, 6.76; $C_{14}H_{13}N$ requires C, 86.11; H, 6.71.

2,7,7-Trimethyl-5,6-benzonorbornadiene (7b): A sample of 2.96 g (0.01 mol) 18 was reacted with a fivefold excess of dimethyllithiumcuprate prepared from 9.63 g (0.05 mol) CuI and 2.22 g (0.1 mol) CH_3Li in ether in analogy to the procedure reported by Paquette et al.[42] The isolation was performed by semipreparative HPLC (LiChrosorb RP-18, 250x4.6 mm Ø) with CH_3OH/H_2O (80:20). Yield 309 g (1.67 mmol,16.7%) 7b as a colorless oil; ^1H NMR (400 MHz): 6.9-7.2 ppm (m, 4H, H-arom.), 6.15 (m, 1H, C3-H), 3.30 (dd, 1H, C4-H), 3.05 (br.s, 1H, C1-H), 1.85 (s, 3H, C3-CH_3), 1.30 (s, 3H, exo-C7-CH_3), 0.81 (s, 3H, endo-C7-CH_3); ^{13}C NMR (400 MHz): 16.97 ppm (q, CH_3), 22.51 (q, CH_3), 23.34 (q, CH_3), 60.27 (d, C4), 64.76 (d, C1), 77.06 (s, C7), 121.4, 121.75, 123.61, 124.08 (four d, C-arom.), 133.49 (d, C3), 151.24, 152.02, 152.49 (three s, C2, C5, C6); MS: 184 (M^+,30%), 169 (100). Analysis: found C, 90.95; H, 8.79; $C_{14}H_{16}$ requires C, 91.24; H, 8.75.

2-Methoxy-7,7-dimethyl-5,6-benzonorbornadiene (7c): 7c was synthesized in the same way as 4c. A sample of 1.02 g (5.50 mmol) 7,7-dimethyl-6-benzonorbornen-2-one[15] was treated to yield 550 mg (2.75 mmol,50%) 7c as a colorless oil. C-Alkylation was not observed. ^{1}H NMR (400 MHz): 6.85-7.3 ppm (m, 4H, H-arom.), 5.13 (dd, 1H, C3-H), 3.60 (s, 3H, $-OCH_3$), 3.35 (m, 1H, C4-H), 3.16 (m, 1H, C1-H), 1.50 (s, 3H, exo-C7-CH_3), 0.86 (s, 3H, endo-C7-CH_3); ^{13}C NMR (400 MHz): 22.68 ppm (q, endo-CH_3), 23.38 (q, exo-CH_3), 56.51 (q, O-CH_3), 57.68 (d, C4), 61.56 (d, C1), 75.51 (s, C7), 100.57 (d, C3), 120.81, 122.28, 123.70, 124.47 (four d, C-arom.), 144.85, 149.50 (two s, C-arom.), 153.86 (s, C2); MS: 200 (M^+, 6%), 144 (100); MS-high resolution: found 200.1197; $C_{14}H_{16}O$ requires 200.1197.

2-Carbomethoxy-7,7-dimethyl-5,6-benzonorbornadiene (7d): A sample of 5.60 g (66.0 mmol) methyl acetylenecarboxylate[43] was added to 2,2-dimethylisoindene prepared from 1.44 g (0.01 mol) 1,1-dimethylindene by photoisomerization at -10° C in pentane[16]. The solution was allowed to warm to room temperature and kept stirring under nitrogen for 24 h. The solvent was removed and the residue purified by preparative chromatography on silica (Kieselgel S, Riedel de Haen, 0.063-0.2 mm, 300x10 mm Ø) with hexane/ether (99.5:05). The first fraction contained unreacted 1,1-dimethylindene. Elution with hexane/ether (95:5) yielded 377 mg (1.6 mmol,16%) 7d as a pale yellow oil. ^{1}H NMR (80 MHz): 7.50 ppm (dd, 1H, C3-H), 6.85-7.30 (m, 4H, H-arom.), 3.73 (s, 1H, C1-H), 3.70 (s, 3H, $-OCH_3$), 3.51 (dd, 1H, C4-H), 1.25 (s, 3H, exo-C7-CH_3), 0.81 (s, 3H, endo-C7-CH_3); $J_{1,3}$=1 Hz, $J_{3,4}$=3.5 Hz; MS: 228 (M^+,54%), 73 (100). Analysis: found C, 78.91; H, 7.11; $C_{15}H_{16}O_2$ requires C, 78.91; H, 7.06.

2-Chloro-7,7-dimethyl-5,6-benzonorbornadiene (7e): A sample of 1.00 g (5.37 mmol) 7,7-dimethyl-6-benzonorbornen-2-one[15] was dissolved in 2 ml $POCl_3$. 1.3 g (6.25 mmol) PCl_5 was added, and the reaction mixture was stirred at room temperature overnight . Isolation was performed analogous to 37. 900 mg (4.4 mmol,81%) 7e was obtained as a colorless oil. ^{1}H NMR (80 MHz): 7.10-7.61 (m, 4H, H-arom.), 6.62 (d, 1H, C3-H), 3.60 (br.d, 1H, C4-H), 3.45 (br.s, 1H, C1-H), 1.60 (s, 3H, exo-CH_3), 1.05 (s, 3H, endo-CH_3); MS: 206 (M^++2, 6%), 204 (M^+, 18), 169 (100). Analysis: found C, 76.16; H, 6.53; $C_{13}H_{13}Cl$ requires C, 76.27; H, 6.40.

2,3-Dicyano-7,7-dimethyl-5,6-benzonorbornadiene (7f): A solution of 2,2-dimethylisoindene was prepared as described for 7d, and a solution of 230 mg (3 mmol) acetylenedicarbonitrile was added. The temperature was raised to room temperature, and stirring was continued for 6 h. The solvent was removed in vacuo and the residue chromatographed on silica (conditions as for 7d) with hexane/ether (80:20). The second fraction yielded 240 mg (1.8 mmol,18%) 7f; m.p. 101-102° C (pentane/ether); ^{1}H NMR (80 MHz): 7.23 ppm (m, 4H, H-arom.), 3.84 (s, 2H, C1-H, C4-H), 1.32 (s, 3H, exo-C7-CH_3), 0.88 (s, 3H, endo-C7-CH_3); MS: 220 (M^+,30%), 205 (100). Analysis: found C, 81.83; H, 5.59; $C_{15}H_{12}N_2$ requires C, 81.79; H, 5.49.

2,3-Dicarbomethoxy-7,7-dimethyl-5,6-benzonorbornadiene (7g): A solution of 2,2-dimethylisoindene was prepared as described for 7d, and a solution of 230 mg (3 mmol) dimethyl acetylenedicarboxylate in 20 ml methylene chloride was added. The temperature was raised to room temperature and the reaction mixture stirred for 2 h. The solvents were removed in vacuo, and the residue was chromatographed on silica (conditions as for 7d) with hexane/ether (80:20). The second fraction yielded 230 mg (0.8 mmol,8%) 7g; m.p. 124° C (CH_3OH); ^{1}H NMR (80 MHz): 7.05 ppm (m, 4H, H-arom.), 3.93 (s, 2H, C1-H, C4-H), 3.90 (s, 6H, $-OCH_3$), 1.25 (s, 3H, exo-C7-CH_3), 0.75 (s, 3H, endo-C7-CH_3); MS: 286 (M^+, 10%), 213 (100); MS-high resolution: found 286.1196; $C_{17}H_{18}O_4$ requires 286.1200.

Preparative photoisomerizations:

The starting materials were dissolved in dry acetone and the solutions stirred and irradiated in a quartz vessel, which was purged with N_2 prior and during the reaction and was cooled with tap water in a Rayonet-Photochemical Reactor with 16 Sunlight Phosphor lamps. The irradiations were run until all starting materials were consumed, which was monitored by HPLC.

Irradiation of 2-methyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4b):[9] A solution of 170 mg (1 mmol) 4b in 800 ml acetone was irradiated for 4 h. The solvent was removed in vacuo, and the residue was separated into two fractions by reversed phase HPLC (LiChrosorb 100, C-18, 250 x 4.6 mm Ø) with methanol/water (75:25) to yield as the first fraction 112 mg 1-methyl-3,4-benzotricyclo[$3.3.0.0^{2,8}$]octene 5b and as the second fraction 42 mg 2-methyl-3,4-benzotricyclo $3.3.0.0^{2,8}$ octene 6b. 5b: oil; ^{1}H NMR (400 MHz): 7.05-7.25 ppm (m, 4H, H-arom.), 3.28 (d, 1H, C5-H), 2.25 (dddd, 1H, exo-C6-H), 2.21 (d, 1H, C2-H), 1.85 (dddd, 1H, exo-C7-H), 1.64 (ddd, 1H, C8-H), 1.61 (dd, 1H, endo-C6-H), 1.49 (s, 3H, CH_3), 1.14 (dddd, 1H, endo-C7-H); $J_{5,exo-6}$=5.5, $J_{6,gem}$=11.5, $J_{endo-6,endo-7}$=6, $J_{7,gem}$=13.5, $J_{endo-7,8}$=1.6, $J_{2,8}$=7.5, $J_{exo-6,exo-7}$=8.5, $J_{exo-6,endo-7}$=11.5, $J_{exo-7,5}$=1.3, $J_{5,endo-6}$=0, $J_{endo-6,exo-7}$=0, $J_{exo-7,8}$=7 Hz; ^{13}C NMR (400 MHz): 18.61 ppm (q, CH_3, J_{C-H}=129 Hz), 23.60 (t, C7, 133), 35.02 (d, C8, 167), 39.25 (d, C2, 166), 42.71 (d, C6, 129), 47.17 (s, C1), 54.10 (d, C5, 139), 122.85, 123.50, 125.17, 126.09 (four d, C-arom.), 143.21, 148.55 (two s, C-arom.); MS: 170 (M^+, 5%), 142 (100); MS-high resolution: found 170.1095; $C_{13}H_{14}$ requires 170.1095. 6b: oil, ^{1}H NMR (400 MHz): 6.95-7.2 ppm (m, 4H, H-arom.), 3.53 (dd, 1H, C5-H), 2.51 (dd, 1H, C1-H), 2.11 (dddd, 1H, exo-C6-H), 1.80

(dddd, 1H, exo-C7-H), 1.74 (ddd, 1H, C8-H), 1.59 (dd, 1H, endo-C6-H), 1.44 (s, 3H, CH_3), 1.03 (dddd, 1H, endo-C7-H); $J_{5,exo-6}$=5, $J_{6,gem}$=11.3, $J_{endo-6,endo-7}$=6, $J_{7,gem}$=12.2, $J_{endo-7,8}$=1.4, $J_{exo-6,exo-7}$=8.8, $J_{exo-6,endo-7}$=11.3, $J_{exo-7,5}$=1.3, $J_{5,endo-6}$=0, $J_{endo-6,exo-7}$=0, $J_{exo-7,8}$=7; $J_{1,8}$=7, $J_{1,5}$=5.5 Hz; ^{13}C NMR (400 MHz): 18.60 ppm (q, CH_3, J_{C-H}=129 Hz), 23.25 (t, C7, 130), 36.08 (d, C8, 160), 38.31 (s, C2), 43,68 (t, C6, 129), 45.41 (d, C1, 160), 48.49 (d, C5, 132), 122.50, 123.48, 125.40, 126.12 (d, C-arom.), 145.81, 148.67 (s, C-arom); MS: 170 (M^{+}, 22%), 142 (100); MS-high resolution: found 170.1097; $C_{13}H_{14}$ requires 170.1095.

Irradiation of 2-trifluoromethyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4h): A solution of 112 mg (0.50 mmol) 4h in 750 ml acetone was irradiated for 3 h. The solvent was removed in vacuo and the residue separated in two fractions by reversed phase chromatography (LiChrosorb 100, RP-C18, 250 x 4.6 mm Ø) with water/methanol (80:20). The first fraction contained starting material and the second fraction of 92 mg of a mixture of 1- (5h) and 2-trifluoromethyl-3,4-benzotricyclo[3.3.0.0^{2,8}]octene (6h) in the ratio 86/14 (determined by ^{1}H NMR), which could not be separated. 5f: ^{1}H NMR (400 MHz): 7.00-7.25 ppm (m, 4H, H-arom.), 3.81 (d, 1H, C5-H), 2.89 (d, 1H, C2-H), 2.35 (dddd, 1H, exo-C6-H), 2.31 (dd, 1H, C8-H), 1.89 (dddd, 1H, exo-C7-H), 1.70 (dd, 1H, endo-C6-H), 1.15 (dddd, 1H, endo-C7-H); $J_{5,exo-6}$=5.5, $J_{2,8}$=8.5, $J_{6,gem}$=11.5, $J_{exo-6,endo-7}$=11.5, $J_{endo-6,endo-7}$=6, $J_{7,gem}$=13.5, $J_{endo-7,8}$=0, $J_{exo-6,exo-7}$=9, $J_{5,endo-6}$=0, $J_{endo-6,exo-7}$=0, $J_{exo-7,8}$=7 Hz; 6f: ^{1}H NMR (400 MHz): 7.00-7.40 ppm (m, 4H, H-arom.), 3.68 (dd, 1H, C5-H), 3.05 (dd, 1H, C1-H), 2.41 (ddd, 1H, C8-H), 2.19 (dddd, 1H, exo-C6-H), 1.89 (dddd, 1H, exo-C7-H), 1.60 (dd, 1H, endo-C6-H), 1.15 (dddd, 1H, endo-C7-H); $J_{1,5}$=5.2, $J_{5,exo-6}$=5, $J_{1,8}$=7.9, $J_{exo-7,8}$=6.9, $J_{endo-7,8}$=1.9, $J_{6,gem}$=11.5, $J_{exo-6,endo-7}$=11.5, $J_{exo-6,exo-7}$=9, $J_{endo-6,endo-7}$=6, $J_{7,gem}$=13.5, $J_{5,exo-7}$=1.1, $J_{5,endo-6}$=0, $J_{endo-6,exo-7}$=0 Hz.

For MS and MS-high resolution the isomer mixture was analyzed. MS: 224 (M^{+},20%), 196 (100); MS-high resolution: found 224.0812; $C_{13}H_{11}F_3$ requires 224.0813.

Irradiation of 2,3-dimethyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4i): A solution of 100 mg (0.5 mmol) 4i in 750 ml acetone was irradiated for 4 h. The solvent was removed in vacuo and the residue purified by chromatography (Kieselgel 60, Merck, 0.063 mm, 250 x 15 mm Ø) with hexane/THF (99.8:0.2). The first fraction yielded 95 mg 1,2-dimethyl-3,4-benzotricyclo[3.3.0.0^{2,8}]octene (5i) as an oil, which solidified on cooling; m.p. 47° C; ^{1}H NMR (400 MHz): 6.94 ppm (m, 4H, H-arom.), 3.22 (d, 1H, C5-H), 2.15 (dddd, 1H, exo-C6-H), 1.79 (dddd, 1H, exo-C7-H), 1.57 (dd, 1H, endo-C6-H), 1.41 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35 (dd, 1H, C8-H), 1.01 (dddd, 1H, endo-C7-H); $J_{5,-exo-6}$=5.5, $J_{7,gem}$=13.5, $J_{6,gem}$=11.5, $J_{exo-6,exo-7}$=8.8, $J_{exo-6,endo-7}$=11.5, $J_{endo-6,endo-7}$=6, $J_{endo-7,8}$=2, $J_{exo-7,8}$=6.9, $J_{5,exo-7}$=1.3, $J_{5,endo-6}$=$J_{endo-6,exo-7}$=0 Hz; ^{13}C NMR (400 MHz): 14.82 ppm (q, CH_3, J_{CH}=130 Hz), 15.12 (q, CH_3, 131), 24.24 (t, C7, 129), 40.18 (d, C8, 165), 41.13 (s, C2), 42.06 (t, C6, 131), 50.53 (s, C1), 54,66 (d, C5, 135), 122.46, 122.57, 125.33, 126.15 (four d, C-arom.), 146.63, 147.72 (two s, C-arom); MS: 184 (M^{+}, 4%), 156 (100); MS-high resolution: found 184.1252; $C_{14}H_{16}$ requires 184.1252.

Irradiation of 2-cyano-3-methyl-5,6-benzobicyclo[2.2.2]octa-2,5-diene (4j): A solution of 97.0 mg (0.50 mmol) 4j in 750 ml acetone was irradiated for 2 h. The solvent was removed in vacuo and the residue purified by chromatography (Kieselgel 60, Merck, 0.063 mm, 250 x 15 mm Ø) with hexane/ether (80:20). Yield 80 mg (82%) 1-cyano-2-methyl-3,4-benzotricyclo[3.3.0.0^{2,8}]octene (5j); m.p. 47° C (pentane); ^{1}H NMR (400 MHz): 6.9-7.1 ppm (m, 4H, H-arom.), 3.76 (d, 1H, C5-H), 2.33 (dddd, 1H, exo-C6-H), 2.31 (dd, 1H, C8-H), 1.90 (dddd, 1H, exo-C7-H), 1.65 (dd, 1H, endo-C6-H), 1.58 (s, 3H, CH_3), 1.03 (dddd, 1H, endo-C7-H); $J_{5,exo-6}$=5, $J_{6,gem}$=11.5, $J_{exo-6,endo-7}$=11.5, $J_{exo-6,exo-7}$=8.5, $J_{endo-6,endo-7}$=6, $J_{7,gem}$=13.5, $J_{endo-7,8}$=2, $J_{endo-6,5}$=0, $J_{exo7,8}$=7, $J_{5,exo-7}$=1, $J_{endo-6,exo-7}$=0 Hz; differential NOE: irradiation at 1.58 ppm (CH_3) led to an increase in intensity of the signals at 2.32 (C8-H) and 7.11 ppm (ortho-H); ^{13}C NMR (400 MHz): 16.77 (q, CH_3, J_{CH}=129 Hz), 23.18 (t, C7, 131), 40,30 (s, C2), 43.82 (t, C6, 130), 44.58 (d, C8, 167), 47.47 (s, C1), 51.90 (d, C5, 134), 120.06 (s, CN), 122.69, 122.94, two signals at 127.21 (four d, C-arom.), 141.21, 145.62 (two s, C-arom.); MS: 195 (M^{+}, 15%), 167 (100); MS-high resolution: found 195.1047; $C_{14}H_{13}N$ requires 195.1048.

Irradiation of 2-cyano-7,7-dimethyl-5,6-benzonorbornadiene (7a): A solution of 97 mg (0.5 mmol) 7a in 750 ml acetone was irradiated for 25 min. The solvent was removed in vacuo and the residue purified by chromatography (Kieselgel 60, Merck, 0.063 mm, 250 x 15 mm Ø) with hexane/ether (80:20). Yield 86 mg (89%) of 1-cyano-6,6-dimethyl-3,4-benzotricyclo[3.2.0.0^{2,7}]-heptene (8a); m.p. 51° C (pentane); ^{1}H NMR (400 MHz): 6.9-7.45 ppm (m, 4H, H-arom.), 3.23 (d, 1H, C5-H), 3,20 (d, 1H, C2-H), 2.53 (dd, 1H, C7-H), 1.67 (s, 3H, exo-CH_3), 0.10 (s, 3H, endo-CH_3); $J_{2,5}$=0, $J_{5,7}$=3, $J_{2,7}$=6 Hz; ^{13}C NMR (400 MHz): 20.54 ppm (q, endo-CH_3, J_{CH}=126 Hz), 28.41

(q, exo-CH_3, 128), 36.31 (s, C6), 38.25 (s, C1), 39.77 (d, C2, 169), 40.22 (d, C7, 180), 57.66 (d, C5, 158), 118.45 (s, CN), 122.24, 123.09, 126.23, 126.90 (four d, C-arom.), 139.39, 142.78 (two s, C-arom.); MS: 195 (M^+,40%), 180 (100); MS-high resolution: found 195.1047; $C_{14}H_{13}N$ requires 195.1048.

Irradiation of 2-carbomethoxy-7,7-dimethyl-5,6-benzonorbornadiene (<u>7d</u>): A solution of 60 mg (0.263 mmol) <u>7d</u> in 200 ml acetone was irradiated for 30 min. The solvent was removed in vacuo, and the residue purified as described for <u>7a</u>. Yield 48 mg (80%) of 1-carbomethoxy-6,6-dimethyl-3,4-benzotricyclo[3.2.0.0^{2,7}]heptene (<u>8d</u>) as pale yellow oil; ^1H NMR (400 MHz): 6.95-7.35 ppm (m, 4H, H-arom.), 3.67 (s, 3H, OCH_3), 3.28 (d, 1H, C2-H), 3.25 (d, 1H, C5-H), 2.51 (dd, 1H, C7-H), 1.52 (s, 3H, exo-CH_3), 0.05 (s, 3H, endo-CH_3); $J_{2,7}$=5.5, $J_{5,7}$=2.5, $J_{2,5}$=0 Hz; ^{13}C NMR (400 MHz): 20.72 ppm (q, endo-CH_3, J_{CH}=126 Hz), 28.74 (q, exo-CH_3, 129), 37.02 (s, C6), 41.38 (d, C2, 168), 42.66 (d, C7, 178), 51.63 (q, OCH_3, 134), 53.74 (s, C1), 54.30 (d, C5, 153), 122.18, 122.51, 125.53, 126.13 (four d, C-arom.), 141.04, 144.31 (two s, C-arom.), 172.17 (s, CO_2CH_3); MS: 228 (M^+, 30%), 169 (100); MS-high resolution: found 228.1149; $C_{15}H_{16}O_2$ requires 228.1150.

Irradiation of 2,7,7-trimethyl-5,6-benzonorbornadiene (<u>7b</u>): A solution of 184 mg (1.00 mmol) <u>7b</u> in 750 ml acetone was irradiated for 1 h. The solvent was removed in vacuo, and the mixture of photoproducts was separated by reversed phase chromatography (LiChrosorb 100, C18, 250 x 4.6 mm Ø) with CH_3OH/H_2O (75:25). The first fraction yielded 115 mg 1,6,6-trimethyl-3,4-benzo tricyclo[3.2.0.0^{2,7}]heptene (<u>8b</u>) and the second fraction 50 mg 2,6,6-trimethyl-3,4-benzotricyclo 3.2.0.0^{2,7} heptene (<u>9b</u>). <u>8b</u>: ^1H NMR (400 MHz): 6.90-7.30 ppm (m, 4H, H-arom.), 2.67 (d, 1H, C5-H), 2.21 (d, 1H, C2-H), 1.70 (dd, 1H, C7-H), 1.51 (s, 3H, C1-CH_3), 1.48 (s, 3H, exo-CH_3), 0.02 (s, 3H, endo-CH_3); $J_{2,7}$=5.1, $J_{5,7}$=2.8, $J_{2,5}$=0 Hz; ^{13}C NMR (400 MHz): 16.44 ppm (q, CH_3, J_{CH}=127 Hz), 21.22 (q, endo-CH_3, 125), 29.14 (q, exo-CH_3, 126), 35.11 (d, C7, 173), 35.61 (s, C6), 36.50 (d, C2, 163), 52.87 (s, C1), 57.89 (d, C5, 149), 122.07, 122.39, 124.20, 125.61 (four d, C-arom.), 144.55, 145.46 (two s, C-arom.); MS: 184 (M^+, 62%), 169 (100); MS-high resolution: found: 184.1252; $C_{14}H_{16}$ requires 184.1252; <u>9b</u>: ^1H NMR (400 MHz): 6.9-7.35 ppm (m, 4H, H-arom.), 3.00 (dd, 1H, C1-H), 2.77 (dd, 1H, C5-H), 1,60 (dd, 1H, C7-H), 1.48 (s, 3H, C2-CH_3), 1.38 (s, 3H, exo-CH_3), -0.02 (s, 3H, endo-CH_3); $J_{1.5}$=2.8, $J_{1,7}$=4.6, $J_{5,7}$=2.8 Hz; ^{13}C NMR (400 MHz): 15.41 ppm (q, CH_3, J_{CH}=127 Hz), 21.83 (q, endo-CH_3, 126), 29.48 (s, exo-CH_3, 127), 36.99 (s, C6), 38.63 (d, C7), 39.33 (s, C2), 49.94 (d, C1, 165), 54.18 (d, C5, 148), 121,40, 121.60, 124.39, 125.65 (four d, C-arom.), 146.22, 147.46 (two s, C-arom.); MS: 184 (M^+, 54%), 169 (100); MS-high resolution: found 184.1252; $C_{14}H_{16}$ 184.1252.

Irradiation of 2-methoxy-7,7-dimethyl-5,6-benzonorbornadiene (<u>7c</u>): A solution of 100 mg (0.500 mmol) <u>7c</u> in 750 ml acetone was irradiated for 90 min. The solvent was removed in vacuo, and the residue was purified by chromatography (Kieselgel 60, Merck, 0.063 mm, 280 x 15 mm Ø) with hexane/ether (95:5) to yield 85 mg (85%) 1-methoxy-6,6-dimethyl-3,4-benzotricyclo[3.2.0.0^{2,7}]heptene (<u>8c</u>) as a colorless oil. ^1H NMR (400 MHz): 7.00-7.35 ppm (m, 4H, H-arom.), 3.30 (s, 3H, OCH_3), 3.15 (br.d, 1H, C5-H), 2.70 (dd, 1H, C2-H), 2.34 (dd, 1H, C7-H), 1.54 (s, 3H, exo-CH_3), -0.08 (s, 3H, exo-CH_3); $J_{2,7}$=5.6, $J_{5,7}$=2.8, $J_{2,5}$=0.8 Hz; ^{13}C NMR (400 MHz): 19.55 (q, endo-CH_3, J_{CH}=128 Hz), 28.38 (q, exo-CH_3, 127), 34.53 (d, C7, 175), 34.79 (s, C6), 39.69 (d, C2, 169), 57.01 (q, OCH_3, 128), 57.69 (d, C5, 150), 93.40 (s, C1), 122.00, 122.41, 124.39, 125.67 (four d, C-arom.), 143.07, 144.15 (two s, C-arom.); MS: 200 (M^+, 16%), 185 (100); MS-high resolution: found 200.1201; $C_{14}H_{16}O$ requires 200.1201.

1-Methoxy-6,6-dimethyl-3,4-benzobicyclo[3.2.0]heptene (<u>19</u>): A sample of 20 mg <u>8c</u> was dissolved in 10 ml methanol, and 50 mg Pd/C was added. After hydrogenation for 2 h, the solution was filtered through a 1 cm layer of silica. The solvent was removed in vacuo. The residue was chromatographed on silica (Kieselgel 60, Merck, 0.063, 250 x 15 mm Ø) with hexane/ether (95:5) to yield four fractions. The largest fraction contained 15 mg (0.074 mmol) <u>19</u> as a colorless oil. ^1H NMR (80 MHz): 7.00-7.30 ppm (m, 4H, H-arom.), 3.32 (dd, 1H, C5-H), 3.26 (ddd, 1H, exo-C2-H), 3.20 (s, 3H, OCH_3), 2.90 (d, 1H, endo-C2-H), 2.15 (ddd, 1H, exo-C7-H), 1.74 (d, 1H, endo-C7-H), 1.37 (s, 3H, exo-CH_3), 0.62 (s, 3H, endo-CH_3); $J_{2,gem}$=17, $J_{7,gem}$=13, $J_{exo-2,exo-7}$=$J_{exo-2,5}$=$J_{5,exo-7}$=2 Hz; ^{13}C NMR (400 MHz): 25.42 ppm (q, endo-CH_3), 31.82 (q, exo-CH_3), 33.76 (s, C6), 43.42 (t, C7), 44.72 (t, C2), 50.64 (q, OCH_3), 57.57 (d, C5), 82.02 (s, C1), 124.97, 125.83, 126.27, 126.54 (four d, C-arom.), 142.69 (br. s, C-arom.); MS: 202 (M^+, 24), 146 (100); MS-high resolution: found 202.1357; $C_{14}H_{18}O$ requires 202.1358.

Quantum yields: Light from an Osram HBO 200 W high pressure mercury lamp was passed through a Bausch and Lomb high intensity monochromator,[44] entrance slit 5.4 and exit slit 3.0 mm, giving a band pass of 20 nm at half peak height. Samples were irradiated in 1 cm quartz cells in an electronic actinometer[45] calibrated by ferrioxalate actinometry.[46] Solutions used acetone as solvent and were degassed 15-30 min prior to and during photolysis using deoxygenated nitrogen. The values given below result from the average of at least three measurments. Analysis was performed with HPLC (A: Nucleosil 50/5 C18, Macherey-Nagel, 250 x 4.6 mm Ø; B: Polygosil 60/, Macherey-Nagel, 150 x 4.6 mm Ø; C: Hypersil, Shandon, 3 μm, 1256 x 4.6 mm Ø). All runs were conducted to a conversion of less than 6% and may be taken to be kinetic.

The results are listed in the order: starting material; concentration (mmol/l); amount of quanta absorbed (-Einstein); chromatographic conditions; quantum yields of formation.

4b: 10.00; 14.00; A, MeOH/H_2O (80:20); ϕ_{5b}=0.063, ϕ_{6b}=0.023, $\phi_{tot.}$=0.085±0.002. 4h: 9.83; 11.19; A, MeOH/H_2O (80:20); ϕ_{5h}=0.083, ϕ_{6h}=0.014, $\phi_{tot.}$=0.097±0.003. 4i: 9.90, 11.14, A, MeOH/H_2O (80:20); ϕ_{5i}=0.186±0.009. 4j: 10.00; 7.00; C, hexane/THF (99:1); ϕ_{5j}=0.496±0.009. 7a: 10.00; 7.34; C, hexane/THF (99:1); ϕ_{8a}=0.653±0.013. 7b: 10.16; 5.60; A, MeOH/H_2O (80:20); ϕ_{8b}=0.424, ϕ_{9b}=0.182, $\phi_{tot.}$=0.606±0.005. 7c: 10.06; 7.44; B, hexane/THF (99.8:0.2); ϕ_{8c}=0.289±0.013. 7d: 10.26; 7.32; C, hexane/THF (99:1); ϕ_{8d}=0.313±0.006.

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