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Vicarious Nucleophilic Substitution of Hydrogen in Nitro-1,6-methano[10]annulenes [1]

S. Ostrowski*,[1], **R. J. Moritz**[2], and **B. Mudryk**[1]

[1] Institute of Organic Chemistry, Polish Academy of Sciences, PL-01224 Warszawa, Poland
[2] Institut für Organische Chemie, Universität Köln, D-50939 Köln, Federal Republic of Germany

Summary. The 2- and 3-nitro-1,6-methano[10]annulenes and their 11,11-difluoro derivatives react with carbanions bearing leaving groups at the carbanionic center according to the Vicarious Nucleophilic Substitution of Hydrogen (VNS) scheme. The analogy between corresponding annulenes and naphthalenes with respect to reactivity is discussed.

Keywords. Carbanions; 2-Nitro- and 3-nitroannulenes; 1-Nitro and 2-nitronaphthalenes; Vicarious Nucleophilic Substitution.

Vicarielle nucleophile Substitution von Wasserstoff in Nitro-1,6-methano[10]annulenen

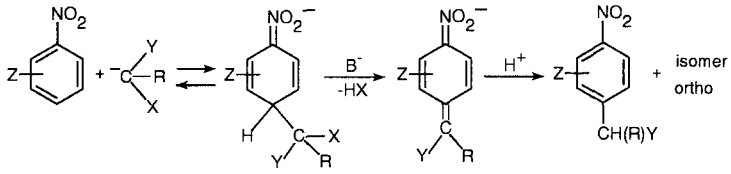
Zusammenfassung. 2- und 3-Nitro-1,6-methano[10]annulene und ihre 11,11-Difluoroderivate reagieren mit Carbanionen, die am carbanionischen Zentrum Abgangsgruppen aufweisen, nach dem Schema der vicariellen nucleophilen Substitution (VNS). Die Analogie zwischen entsprechenden Annulenen und Naphthalinen bezüglich ihrer Reaktivität wird diskutiert.

Introduction

1,6-Methano[10]annulenes (bicyclo[4.4.1]undeca-1,3,5,7,9-pentaenes), a large class of nonbenzenoid aromatic compounds [2], are isoelectronic with naphthalenes and in many types of organic reactions behave similarly to the latter. Thus, they undergo electrophilic aromatic substitution [3–5], such as nitration [3, 4] or sulfonylation [5], metalation with lithium alkyls [6–8], copper catalyzed substitution of halogen [9], nucleophilic aromatic substitution [10–12], *etc.*

The recently discovered Vicarious Nucleophilic Substitution of Hydrogen (VNS) in highly electrophilic arenes, particularly nitroarenes, with carbanions bearing a leaving group X at the carbanionic center [13–17], hydroperoxide [18] or nitrogen [19] anions, is a new general type of aromatic nucleophilic substitution. It consists of addition of these nucleophiles to carbon atoms bearing hydrogen (*ortho*-or *para*- to the nitro group), followed by base induced β-elimination of HX, and finally protonation.

VNS is a general process between nitroarenes and nucleophiles and can be used to introduce a variety of substituents into aromatic rings. Many highly electrophilic



Scheme 1

aromatic and heteroaromatic compounds without a nitro group [20–26] can also undergo this reaction.

Amongst the great variety of nitroarenes, nitronaphthalenes are particularly active substrates in VNS reactions [27]. Depending upon the kind of nucleophile and reaction conditions, VNS in 1-nitronaphthalene can occur at positions 2 and 4 (*ortho-* or *para-*). Although C-2 is strongly preferred as the substitution site, the ratio of the isomeric VNS products can often be controlled [18, 21]. On the other hand, VNS in 2-nitronaphthalene takes place exclusively at C-1. Therefore, bulky carbanions usually do not undergo the VNS reaction with 2-nitronaphthalene due to steric hindrance.

A benzene ring should contain a nitro group in order to enter the VNS reaction. The naphthalene ring is more reactive in this respect; hence, 1-cyanonaphthalene reacts with the carbanion of chloromethyl aryl sulfone to give a *bis*-annulated product, whereas with dicyanonaphthalenes *bis*-annulation and VNS occur [20, 21]. Both of these reactions proceed *via* a common intermediate – an anionic σ-adduct to the electrophilic naphthalene ring. These adducts undergo an intramolecular substitution of the halogen, which leads to *bis*-annulation or base induced β-elimination giving the VNS products.

Taking into account the behaviour of the electrophilic naphthalene ring in the VNS reaction it was of great interest to compare naphthalenes with 1,6-methano[10]annulenes in this respect. Therefore, we have undertaken studies of the VNS reactions with 2- and 3-nitro-1,6-methano[10]annulenes and their 11,11-difluoro derivatives with a variety of carbanions [28, 29].

In the meantime, *Neidlein* has reported [30] that 2- and 3-nitro-1,6-methano-[10]annulenes enter the VNS reaction with chloromethyl *p*-tolyl sulfone, methyl chloroacetate, *etc.*

Results and Discussion

We have found that nitro-1,6-methano[10]annulenes (**3**–**7**) react with chloromethyl *para*-tolyl sulfone (**8**), bromomethyl *para*-tolyl sulfone (**9**), bromomethyl phenyl sulfone (**10**), α-chloroethyl phenyl sulfone (**11**), α-chlorobenzyl phenyl sulfone (**12**), chloroacetonitrile (**13**), (phenyl)phenoxyacetonitrile (**14**), *tert*-butyl chloroacetate (**16**), chloroform (**17**), and *tert*-butyl hydroperoxide (**18**) according to the VNS scheme giving in many cases high yields of products (*e.g.* **22**, 92%; **37**, 90%).

The reaction of 2-nitro-1,6-methano[10]annulene (**3**) with bromomethyl *para*-tolyl sulfone (**9**) proceeds readily giving only one product of VNS at position 3 (**21**)

Table 1. Carbanion and O-anion precursors

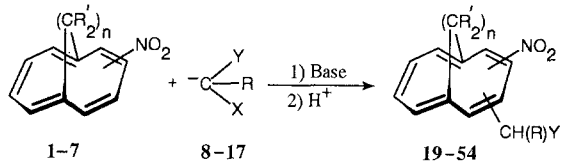
			*X*CH(R)*Y*		
8	$ClCH_2SO_2Tol$	**12**	$ClCH(Ph)SO_2Ph$	**16**	$ClCH_2CO_2{}^tBu$
9	$BrCH_2SO_2Tol$	**13**	$ClCH_2CN$	**17**	$CHCl_3$
10	$BrCH_2SO_2Ph$	**14**	PhCH(OPh)CN	**18**	^tBuOOH
11	$ClCH(Me)SO_2Ph$	**15**	$ClCH_2CO_2Et$		

as was observed by *Neidlein* [30] with chloromethyl *para*-tolyl solfone (**8**). The reactions of bromomethyl phenyl sulfone (**10**) with annulene **3** and with its 7-iododerivative (**7**) also proceed exclusively at position 3, giving the products in high yields. These results show close analogy to the behaviour of 1-nitronaphthalene in the VNS reaction. The reaction of 1-nitronaphthalene with α-bromosulfone (**9**) gave mainly the 2-substituted product (ratio of isomers C-2:C-4 ≈ 7:1). Surprisingly, the reaction of 11,11-difluoro-2-nitro-1,6-methano[10]annulene (**5**) with bromosulfone **10** gave two isomeric products of VNS at positions 3 and 5 which were formed in almost equal amounts – 49% and 44%, respectively. Similar results were obtained in the reaction of **5** with *tert*-butyl chloroacetate (**16**). Such a substantial deviation from the usual orientation pattern imposed by the difluoromethylene bridge is difficult to explain. Some suggestions are discussed elsewhere [31].

The orientation of the VNS reaction of 1-nitronaphthalene (**1**) and 2-nitro-1,6-methano[10]annulene (**3**) with other secondary carbanions such as chloroacetonitrile (**13**) and alkyl chloroacetates (**15**, **16**) was analogous. In these cases, the latter exhibited a higher tendency for *ortho* substitution with respect to the nitro group.

Similar observations were made in the reactions of these nitroaromatics with the tertiary carbanions of α-chloroethyl phenyl sulfone (**11**), α-chlorobenzyl phenyl sulfone (**12**), and (phenyl)phenoxyacetonitrile (**14**). The reaction of 2-nitro-1,6-methano[10]annulene (**3**) with **11** afforded the products of substitution at C-3 and C-5 in a similar ratio to that observed for 1-nitronaphthalene (**1**). In both cases the yields were not high, rendering the results not useful for a discussion of regioselectivity. On the other hand, **12** and **14** gave excellent yields of the VNS products in the reaction with **3**. **14** reacted only at position 5, whereas **12** gave two isomeric products at C-3 (28%) and C-5 (54%); hence, in this case also a higher tendency for **3** to react in the *ortho*-position is observed. 1-Nitronaphthalene (**1**) reacted exclusively at the *para*-position with both of these carbanions.

Of particular interest was the VNS hydroxylation with hydroperoxide anions because the regiochemistry of the reaction with **1** can be efficiently controlled by the reaction conditions [18]. The reaction of 2-nitro-1,6-methano[10]annulene (**3**) with *t*-butyl hydroperoxide produced two isomeric 3- and 5-hydroxy-2-nitro-1,6-methano[10]annulenes, which exist in the corresponding 2,3- and 2,5-dihydro keto forms **46** and **47**. The ratio of these products could not be so easily controlled by the conditions. When the soluble base *t*-BuOK was used in excess, **46** and **47** were formed in a ratio of ~9:2, whilst in the presence of an insoluble base such as KOH the corresponding ratio was 2:3. The hydroxylation of 1-nitronaphthalene (**1**) under



1–7 8–17 19–54

Scheme 2

	1	**2**	**3**	**4**	**5**	**6**	**7**
n	0	0	1	1	1	1	1
R'	–	–	H	H	F	F	H
Position of $-NO_2$	1-	2-	2-	3-	2-	3-	2- 7-iodo

					Position of	
Products	n	R'	R	*Y*	$-NO_2$	$-CH(R)Y$
19	0	–	H	*p*-Ts[a]	1-	2-
20	0	–	H	*p*-Ts	1-	4-
21	1	H	H	*p*-Ts	2-	3-
22	1	H	H	SO_2Ph	2-	3-
23	1	H	H	SO_2Ph	2-	3-,7-iodo
24	1	F	H	SO_2Ph	2-	3-
25	1	F	H	SO_2Ph	2-	5-
26	0	–	Me	SO_2Ph	1-	2-
27	0	–	Me	SO_2Ph	1-	4-
28	1	H	Me	SO_2Ph	2-	3-
29	1	H	Me	SO_2Ph	2-	5-
30	0	–	Ph	SO_2Ph	1-	4-
31	1	H	Ph	SO_2Ph	2-	3-
32	1	H	Ph	SO_2Ph	2-	5-
33	0	–	H	CN	1-	2-
34	0	–	H	CN	1-	4-
35	1	H	H	CN	2-	3-
36	0	–	Ph	CN	1-	4-
37	1	H	Ph	CN	2-	5-
38	0	–	H	CO_2Et	1-	2-
39	1	H	H	$CO_2{}^tBu$	2-	3-
40	1	F	H	$CO_2{}^tBu$	2-	3-
41	1	F	H	$CO_2{}^tBu$	2-	5-
42	0	–	Cl	Cl	1-	2-
43'	1	H	Cl	Cl	2-	3-
44	0	–	–	–	1-	2-OH
45	0	–	–	–	1-	4-OH
46	1	H	–	–	2-	2,3-dihydro-3-one
47	1	H	–	–	2-	2,5-dihydro-5-one
48	0	–	H	*p*-Ts	2-	1-
49	1	H	H	*p*-Ts	3-	2-
50	1	H	H	SO_2Ph	3-	2-
51	1	F	H	*p*-Ts	3-	2-
52	0	–	H	CN	2-	1-
53	1	H	H	CN	3-	2-
54	0	–	H	$CO_2{}^tBu$	2-	1-

[a] cf. Fig. 1

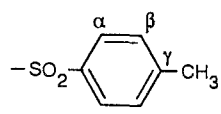


Fig. 1

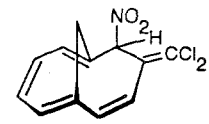


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Fig. 2.

Table 2. Reactions of nitronaphthalenes and nitro-1,6-methanol[10]annulenes with the carbanions of **8**–**17** and O-anion **18**

Starting materials	Procedure[a]	Product, Yield (%)
1, 9	*A*	**19**, 50
		20, 7
3, 9	*A*	**21**, 88[b]
3, 10	*A*	**22**, 92
7, 10	*A*	**23**, 83
5, 10	*A*	**24**, 49
		25, 44
1, 11	*A*	**26**, 40[c]
		27, 5
3, 11	*A*	**28**, 23
		29, 5
1, 12	*B*	**30**, 70
3, 12	*B*	**31**, 28
		32, 54
1, 13	*C*	**33**, 58[d]
		34, 4.5
3, 13	*C*	**35**, 35[c]
1, 14	*B*	**36**, 77[d]
3, 14	*B*	**37**, 90
1, 15	*C*	**38**, 86[f]
3, 16	*C*	**39**, 73[g]
5, 16	*C*	**40**, 32
		41, 24
1, 17	*D*	**42**, 68[h]
3, 17	*D*	**43'**, 30
1, 18	*E*	**44**, 87[i]
	F	**45**, 89[i]
3, 18	*E*	**46**, 70[j]
		47, 16[j]
	F	**46**, 16[k]
		47, 24[k]
2, 8	*A*	**48**, 90[l]
4, 9	*A*	**49**, 90
4, 10	*A*	**50**, 67
6, 8	*A*	**51**, 43
2, 13	*C*	**52**, 52
4, 13	*C*	**53**, 32[m]
2, 16	*C*	**54**, 95[f]
4, 16	*C*	no reaction

[a] for procedures *A*–*F*, see experimental; [b] product reported by Neidlein [30]; from $ClCH_2SO_2Tol$ and **3**, 40% yield; [c] data from Ref. [32]; [d] data from Ref. [33]; [e] reported earlier in MeONa/*DME* under argon; 72% yield [30]; [f] data from Ref. [34]; [g] with $ClCH_2CO_2Me$ in MeONa/*DME*, the corresponding product of substitution at position C-3 was obtained in 75% yield [30]; [h] data from Ref. [35]; [i] data from Ref. [18], other isomers (2- and 4- respectively) are produced in amounts below 1%; [j] calculated for consumed **3**; 40% of **3** was recovered; [k] calculated for consumed **3**; 21% of **3** was recovered; [l] data from Ref. [27]; [m] obtained earlier as a one of the products of a mixture of **3** and **4** with **13** [30]

such conditions produced 2-hydroxy-1-nitro- and 4-hydroxy-1-nitronaphthalenes in ratios of *ca.* 90:1 and 1:90, respectively [18].

From these results one can conclude that there is a close analogy between 1-nitronaphthalene and 2-nitro-1,6-methano[10]annulene as far as the VNS reaction is concerned. There is also a close analogy between 2-nitronaphthalene (**2**) and 3-nitro-1,6-methano[10]annulene (**4**). Both compounds undergo the VNS reaction exclusively at positions C-1 and C-2, respectively. These positions are sterically hindered; therefore only secondary, but not bulky tertiary carbanions are able to react with **2** and **4**. The steric hindrance in **4** is undoubtedly greater because it does not react even with some bulky secondary carbanions, *e.g.* that generated from *t*-butyl chloroacetate (**16**), which reacts satisfactorily with **2**.

The results of the reactions of nitronaphthalenes and nitro-1,6-methano-[10]annulenes with carbanions and with the *t*-butyl hydroperoxide anion are given in Table 2.

Experimental

^{1}H NMR spectra were recorded with Varian EM-360 (60 MHz), Varian GEMINI (200 MHz), Bruker AM-300 (300 MHz) and Bruker AF-300 (300 MHz) spectrometers. ^{13}C NMR spectra were recorded with a Bruker AM-300 (75.5 MHz) spectrometer. Chemical shift values are given in δ [ppm] units relative to *TMS*; coupling constants are expressed in Hertz [Hz]. The assigments of the chemical shifts of protons and carbons accompanied by an asterisk or by a double cross may be interchanged. IR spectra were recorded with a Perkin-Elmer IR 283 spectrometer. UV/Vis spectra were recorded with a Perkin-Elmer 559 spectrometer. MS spectra were measured with a Finnigan 3200, Finnigan MAT 731 and AMD-604. Melting points are uncorrected. TLC analyses were made on foil plates coated with Merck 60F 254. For column chromatography, silica gel 100–200 and 230–400 mesh (Merck) was used. Starting materials were either commercially available or prepared by known methods: 11,11-difluoro-2-nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (11,11-difluoro-2-nitro-1,6-methano[10]annulene, **5**), 11,11-difluoro-3-nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (11,11-difluoro-3-nitro-1,6-methano[10]annulene, **6**) [4, 39], chloromethyl *p*-tolyl sulfone (**8**) [27], bromomethyl *p*-tolyl sulfone (**9**) and bromomethyl phenyl sulfone (**10**) [36], 1-chloroethyl phenyl sulfone (**11**) [32], 1-chlorobenzyl phenyl sulfone (**12**) [37], (phenyl)phenoxyacetonitrile (**14**) [38].

2-Nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**3**) and *7-iodo-2-nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene* (**7**)

To a solution of 1,6-methano[10]annulene (9.94 g, 70 mmol) and tetrabutylammonium iodide (25.83 g, 70 mmol) in dry CH_3CN (500 ml) warmed to 60 °C, a solution of cerium ammonium nitrate (*CAN*, $(NH_4)_2[Ce(NO_3)_6]$; 76.72 g, 140 mmol; dried 15 h at 90°/0.05 Torr) in dry CH_3CN (600 ml) was added dropwise over a period of 1.5 h. The reaction was continued for additional 0.5 h (60 °C). After concentration to half of the initial volume, a saturated solution of sodium thiosulfate (500 ml) was added. The mixture was extracted with CH_2Cl_2 (4 × 250 ml); the combined organic layers were washed with water (2 × 200 ml) and dried over $MgSO_4$. After concentration, chromatography the crude oil with CCl_4 (150 cm, ϕ 11 cm) afforded 1.69 g 2-iodobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (9%; m.p.: 36–37 °C (ethanol), 0.22 g **7** (1%), and 7.07 g **3** (54%; m.p.: 29–30 °C (ethanol); Ref. [40], m.p.: 29–30 °C).

3: UV/Vis (acetonitrile): λ_{max} (lgε) = 235 (4.51), 270 (4.16), and 360 nm (3.85); IR (neat): ν_{max} = 3050, 2959, 2880, 2810, 1500, 1320, and 750 cm^{-1}; ^{1}H NMR (300 MHz; acetone-d_6): δ = 8.25 (1H, d, J = 10.0 Hz, 3-H), 8.21 (1H, d, J = 9.0 Hz, 10-H), 7.87 (1H, d, J = 8.8 Hz, 5-H), 7.61 (1H, dd, ^3J = 8.6 Hz, $^4J_{7,11b}$ = 1.2 Hz, 7-H),7.44 (1H, t(dd), J = 9.5, 9.0 Hz, 9-H), 7.32 (1H, dd, J = 9.5, 8.6 Hz, 8-H), 7.31 (1H,

dd, $J = 10.0$, 8.8 Hz, 4-H), −0.49 (1H, dd, $^2J = 9.8$ Hz, $^4J_{5,11a} = 0.8$ Hz, 11a-H), −0.55 (1H, dt, $^2J = 9.8$ Hz, $^4J_{7/10,11b} \approx 1.2$ Hz, 11b-H); ^{13}C NMR (75.5 MHz; acetone-d_6): $\delta = 145.4$ (s, C-2), 138.1 (dm, $^1J = 161.2$ Hz, C-5), 132.4 (dd, $^1J = 157.1$ Hz, C-9), 131.2 (dm, $^1J = 165.9$ Hz, C-10), 130.5 (dm, $^1J = 165.5$ Hz, C-7), 129.3 (dd, $^1J \approx 157.1$ Hz, C-8), 126.8 (d, $J = 161.1$ Hz, C-4), 125.6 (dd, $^1J = 160.7$ Hz, C-3), 121.1 (s, C-6), 107.1 (s, C-1), 34.4 (t, $J = 142.9$ Hz, C-11); MS: $m/z = 187$ ($M^{+\cdot}$, 19%), 170 (39), 157 (2), 141 (38), 140 (60), 139 (60), 128 (30), 127 (20), 115 (100), 89 (12), 63 (25), 51 (7), 39 (9).

7: m.p.: 117–118 °C (CH_2Cl_2); $C_{11}H_8INO_2$ (313.10); found: C, 42.40; H, 2.60; I, 40.50; N, 4.30; calcd.: C, 42.20; H, 2.58; I, 40.53; N, 4.47%; UV/Vis (acetonitrile): λ_{max} (lgε) = 237 (4.28), 257 (4.31), 280 (4.23), 310 (3.92), 380 (3.90), and 405 nm (3.77); IR (KBr): $\nu_{max} = 1500$, 1310, and 767 cm^{-1}; ^{1}H NMR (300 MHz; acetone-d_6): $\delta = 8.43$ (1H, d, $J = 10.2$ Hz, 3-H), 8.23 (1H, d, $J = 9.1$ Hz, 10-H), 8.07 (1H, d, $J = 9.0$ Hz, 5-H), 7.83 (1H, d, $J = 9.9$ Hz, 8-H), 7.54 (1H, dd, $J = 10.2$,9.0 Hz, 4-H), 7.30 (1H, t(dd), $J = 9.9$, 9.1 Hz, 9-H), −0.15 (1H, dd, $^2J = 10.4$ Hz, $^4J_{10,11b} = 1.25$ Hz, 11b-H), −0.35 (1H, dd, $^2J = 10.4$ Hz, $^4J_{5,11a} = 1.1$ Hz, 11a-H); ^{13}C NMR (75.5 MHz; acetone-d_6): $\delta = 145.6$ (s, C-2), 141.5 (dm, $^1J = 141.5$ Hz, C-5), 139.3 (dd, $^1J = 163.2$ Hz, C-8), 133.4 (d, $J = 159.6$ Hz, C-9), 131.3 (dm, $^1J = 166.7$ Hz, C-10), 128.8 (d, $J = 162.2$ Hz, C-4), 126.8 (dd, $^1J = 161.2$ Hz, C-3), 121.0 (s, C-6), 110.0 (s, C-1), 94.9 (s, C-7), 34.7 (t, $J = 144.1$ Hz, C-11); MS: $m/z = 313$ ($M^{+\cdot}$, 2%), 296 (1), 267 (3), 266 (2), 186 (7), 157 (6), 140 (39), 139 (100), 128 (21), 113 (6), 89 (4), 63 (10).

3-Nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**4**)

1,3,5-Cycloheptatriene-1,6-dicarbaldehyde (29.63 g, 0.20 mol) and chloromethyltriphenylphosphonium chloride (76.39 g, 0.22 mol) were dissolved in dry *THF* (500 ml) and heated to reflux. To this mixture, a solution of NaOMe (13.6 g, 0.20 mol) in dry *THF*-EtOH (1:1, 400 ml) was added over 1.5 h. Water (50 ml) was added and the solution concentrated to half of its volume under reduced pressure. To the residue, water (200 ml) and CH_2Cl_2 (300 ml) were added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 200 ml). The combined organic layers were dried over $MgSO_4$, concentrated and chromatographed with a CH_2Cl_2/*n*-pentane (1:1) mixture. The third fraction (yellow oil) was distilled (40 °C/0.02 Torr) to give a mixture of *E*/*Z* isomers of 6-(2-chlorovinyl)-1,3,5-cycloheptatriene-1-carbaldehyde (20.23 g, 56%). To this mixture, dissolved in *THF* (600 ml), iodine (0.1 g, 0.4 mmol) was added and stirred for 24 h. The solution was concentrated to 200 ml, 10% aqueous $Na_2S_2O_3$ (100 ml) was added and the mixture was extracted with CH_2Cl_2 (3 × 150 ml). The combined organic layers were dried over $MgSO_4$ and concentrated to give 6-[(*E*)-2-chlorovinyl]-1,3,5-cycloheptatriene-1-carbaldehyde (19.63 g, 54%).

6-[(*E*)-2-Chlorovinyl)]-1,3,5-cycloheptatriene-1-carbaldehyde (18.06 g, 0.10 mol) was dissolved in a propionic acid/*o*-xylene mixture (5:1, 600 ml). Piperidine (43 g, 0.5 mol) was added, the reaction mixture was warmed, and to the refluxing solution CH_3NO_2 (305 g, 5 mol) was added dropwise over 3 h. After an additional 1.5 h, the refluxed mixture was cooled, poured into water (500 ml), and extracted with Et_2O (5 × 400 ml). The combined organic layers were washed with aqueous 10% NaOH until the aqueous phase indicated alkaline reaction and dried over $MgSO_4$. After concentration, the remaining oil was chromatographed (100 cm, ϕ 8 cm) with $CHCl_3$ as eluent. The second fraction was recrystallized to give **4** as yellow needles (8.6 g, 46%). M.p.: 48–49 °C (acetone); (Ref [40], m.p.: 46–47 °C; UV/Vis (acetonitrile): λ_{max} (lgε) = 240 (4.48), 285 (4.43), 345 (3.98), and 405 nm (3.22); IR (neat): $\nu_{max} = 3053$, 2962, 1551, 1325, and 747 cm^{-1}; ^{1}H NMR (300 MHz; acetone-d_6): $\delta = 8.56$ (1H, d, $J_{2,4} = 1.2$ Hz, 2-H), 8.10 (1H, dd, $J = 9.6$, 1.2 Hz, 4-H), 7.76, 7.72, and 7.59 (3H, 3 × m, 10-, 5-, and 7-H, respectively), 7.24 and 7.22 (2H, 2 × m, 8-, 9-H), −0.15 (1H, dt, $^2J = 9.3$ Hz, $^4J_{7,11b} = 1.2$ Hz, $^4J_{10,11b} = 1.1$ Hz, 11b-H), −0.35 (1H, dt, $^2J = 9.3$ Hz, $^4J_{2,11a} = 1.1$ Hz, $^4J_{5,11a} = 1.1$ Hz, 11a-H); ^{13}C NMR (75.5 MHz; acetone-d_6): $\delta = 146.7$ (s, C-3), 132.4 (d, $J = 164.9$ Hz, C-10), 131.6 (d, $J = 162.6$ Hz, C-5), 130.1 (d, $J = 159.6$ Hz, C-7), 129.5 (dd, $^1J = 157.8$, C-8), 128.5 (dd, $^1J = 158.4$ Hz, C-9), 127.8 (d, $J = 165.6$ Hz, C-2), 121.7 (s, C-6), 121.7 (dd, $^1J = 161.4$ Hz, C-4), 112.4 (s, C-1), 35.4 (t, $J = 144.5$ Hz, C-11); MS: $m/z = 187$ ($M^{+\cdot}$, 32%), 170 (8), 141 (57), 140 (29), 139 (38), 129 (12), 128 (13), 127 (10), 115 (100), 89 (13), 63 (19), 51 (9), 39 (11).

General Reaction Procedures

A. $ArSO_2CH_2Cl$, $ArSO_2CH_2Br$ and $PhSO_2CH(Me)Cl$

To a solution of ^{t}BuOK (560 mg, 5 mmol) in dry *DMF* (10 ml) cooled to −40 °C, a solution of the carbanion precursor (2 mmol) and a nitroannulene (2 mmol) in *DMF* (1–4 ml) was added dropwise during 10 min. The mixture was stirred at −30° to −40 °C for 1–1.5 h, then poured into dilute HCl (200 ml) and the products were extracted with CH_2Cl_2 or with ethyl acetate (2 × 20 ml). The combined organic layers were washed twice with water, dried over $MgSO_4$, and the solvent was evaporated. The pure products were isolated by column chromatography (eluents: **21**, **22**, CH_2Cl_2; **23**, CCl_4/CH_2Cl_2 = 3:1; **24** and **25**, $CCl_4/CHCl_3$ = 4:1; **28** and **29**, *n*-hexane/$CHCl_3$ = 1:1; **49**, **50**, ether/*n*-pentane = 3:1; **51**, from *n*-hexane/$CHCl_3$ = 1:1 to $CHCl_3$) and recrystallization.

B. $PhSO_2CH(Ph)Cl$ and $PhCH(OPh)CN$

The reactions were conducted at room temperature for 15–20 min in the way described above. The carbanion precursor and nitroannulene were added in one portion to the solution of ^{t}BuOK (an exothermic effect of 8–12 °C was observed). The work-up and isolation of the products were as in procedure *A* (eluent for chromatography: $CHCl_3$).

C. $ClCH_2CN$ and $ClCH_2CO_2{}^tBu$

To a solution of ^{t}BuOK (670 mg, 6 mmol) in dry *DMF* (10 ml) cooled to −10 °C, a solution of the carbanion precursor (2.4 mmol) and the nitroannulene (2 mmol) in *DMF* (2 ml) was added dropwise over a period of 2–3 min, the temperature being kept at −10 to −5 °C. After additional stirring for 2–3 min, the reaction mixture was worked up and the products were isolated as in procedure *A* (eluent for chromatography: $CHCl_3$/*n*-hexane from 1:1 to 2:1).

D. $CHCl_3$

To a solution of ^{t}BuOK (780 mg, 7 mmol) in a mixture of dry *DMF*/*THF* (5:4, 10 ml) cooled to −73 °C, a solution of chloroform (260 mg, 2.2 mmol) and the nitroannulene (2 mmol) in *DMF* (1 ml) was added dropwise at such a rate that the temperature did not exceed −68 °C (2–3 min). After additional stirring for 1 min at this temperature, the mixture was quenched with acetic acid/methanol (1:3, 3 ml), poured into water (200 ml), and worked up as in procedure *A*. The product was isolated by column chromatography with *n*-hexane/$CHCl_3$ 3:1 mixture as an eluent and recrystallized from *n*-hexane.

E. ^{t}BuOOH; ^{t}Bu OK/NH_3 system

To a solution of Bu^{t}OK (840 mg, 7.5 mmol) in liquid ammonia (10 ml), a solution of the nitroannulene (560 mg, 3 mmol) and ^{t}BuOOH (300 mg, 0.42 ml 80% solution in $(^tBuO)_2$, 3.3 mmol) in *THF* (3 ml) was added dropwise. After 15 min, ammonium chloride was added, the ammonia was evaporated, and diluted HCl (50 ml) and $CHCl_3$ (50 ml) were added to the residue. The organic layer was separated and the water phase was extracted with $CHCl_3$ (2 × 20 ml). The combined organic layers were dried over $MgSO_4$, the solvent was evaporated, and the products were isolated by column chromatography (eluent: from *n*-hexane/$CHCl_3$ = 6:1 to $CHCl_3$).

F. ^{t}BuOOH; NaOH/NH_3 system

As above, but with NaOH (2 g, 50 mmol) being used instead of ^{t}BuOK; reaction time: 1 h.

All VNS products with 1- and 2-nitronaphthalenes (except **30** and **52**) were reported earlier (cf. Table 2).

2-Nitro-3-(p-tolylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**21**): m.p.: 94–95 °C (CH_3CN); $C_{19}H_{17}NO_4S$ (355.41); found: C, 64.30; H, 4.90; N, 3.70; S, 9.20; calcd: C, 64.21; H, 4.82; N, 3.94; S, 9.02%; UV/Vis (acetonitrile): λ_{max} (lgε) = 255 (4.52), 285 (4.16), and 375 nm (3.51); IR (CsI): ν_{max} = 3048,

1597, 1517, 1450, 1414, 1320, and 1152 cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3): $\delta = 7.66$ (1H, m, 10-H), 7.63 (2H, m, 2 × H_α-Tol), 7.56 (1H, d, $J = 9.2$ Hz, 7-H), 7.44 (1H, d, $J = 8.3$ Hz, 5-H), 7.32 (2H, m, 2 × H_β-Tol), 7.22 (1H, m, 9-H), 7.20 (1H, d, $J = 8.3$ Hz, 4-H), 7.15 (1H, m, 8-H), 4.97 and 4.66 (2H, 2 × d, $J = 14.5$ Hz, CH_2), 2.36 (3H, s, CH_3), −0.19 (1H, dd, $^2J = 9.7$ Hz, 11a-H), −0.76 (1H, dt, $^2J = 9.7$ Hz, 11b-H); ^{13}C NMR (acetonitrile-d_3): $\delta = 146.5$ (s, C-2), 146.4* (s, C(Tol)-SO_2), 136.0* (s, C_γ-Tol), 134.1 (dt, $^1J = 162.8$ Hz, C-4), 133.2 (d, $^1J = 163.0$ Hz, C-5), 132.1 (dd, $^1J = 158.8$ Hz, C-9), 131.8 (d, $^1J = 158$ Hz, C-7), 130.8 (d, $^1J = 162.0$ Hz, 2 × C_β-Tol), 129.7 (d, $^1J = 160$ Hz, C-10), 129.3 (d, $^1J = 162.1$ Hz, 2 × C_α-Tol), 123.9# (s, C-6), 122.5# (s, C-1), 63.1 (td, $^1J = 141.0$ Hz, CH_2), 33.5 (tq, $^1J = 144.2$ Hz, C-11), 21.6 (qt, $^1J = 127.4$ Hz, CH_3); MS: $m/z = 355$ ($M^{+\cdot}$, <0.1%), 309 (0.4), 245 (1), 230 (2), 229 (2), 215 (2), 200 (47), 183 (16), 169 (20), 154 (43), 153 (37), 152 (62), 146 (100), 139 (94), 127 (43), 115 (72), 91 (50), 89 (15), 77 (16), 65 (27), 63 (14), 51 (9), 41 (12).

2-Nitro-3-(phenylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**22**): m.p.: 96–97 °C (MeOH); $C_{18}H_{15}NO_4S$ (341.38); found: C, 63.13; H, 4.39; N, 3.89; S, 9.28; calcd.: C, 63.33; H, 4.43; N, 4.10; S, 9.39%; UV/Vis (acetonitrile); λ_{max} (lgε) = 255 (4.54), 285 (4.15), and 375 nm (3.49); IR (KBr): $\nu_{max} = 3054$, 1502, 1308, and 1150 cm^{-1}; ^1H NMR (300 MHz; acetonitrile-d_3): $\delta = 7.77$ (2H, m, 2 × H_α-Ph), 7.66 (1H, tt, overlapped, H_γ-Ph), 7.65 (1H, m, 10-H), 7.56 (1H, dd, $^3J = 8.7$ Hz, 7-H), 7.52 (2H, m, 2 × H_β-Ph), 7.44 (1H, d, $J = 8.3$ Hz, 5-H), 7.22 (1H, m, 9-H), 7.20 (1H, d, overlapped, 4-H), 7.15 (1H, m, 8-H), 5.00 and 4.70 (2H, 2 × d, $J = 14.6$ Hz, CH_2), −0.20 (1H, dd, $^2J = 9.7$ Hz, 11a-H), −0.78 (1H, dt, $^2J = 9.7$ Hz, 11b-H); ^{13}C NMR (75.5 MHz; acetonitrile-d_3): $\delta = 146.5$ (s, C-2), 138.8 (s, C(Ph)-SO_2), 135.2 (dt, $^1J = 163.5$ Hz, C_γ-Ph), 134.1 (dt, $^1J = 162.4$ Hz, C-4), 133.2 (d, $^1J = 163.8$ Hz, C-5), 132.1 (dd, $^1J = 158.8$ Hz, C-9), 131.8 (d, $^1J = 157.0$ Hz, C-7), 130.3 (dd, $^1J = 166.7$ Hz, 2 × C_β-Ph), 129.7 (d, $^1J = 159.0$ Hz, C-10), 129.6 (dd, $^1J = 159.0$ Hz, C-8), 129.3 (d, $^1J = 168.4$ Hz, 2 × C_α-Ph), 124.0 (s, C-6), 122.3 (s, C-3), 108.8 (s, C-1), 63.0 (td, $^1J = 141.1$ Hz, CH_2), 33.5 (tq, $^1J = 144.1$ Hz, C-11); MS (FAB): $m/z = 342$ ([M + H], 6%), 295 (2), 212 (5), 200 (17), 170 (9), 120 (14), 69 (12), 65 (15), 63 (15), 59 (41), 51 (15).

7-Iodo-2-nitro-3-(phenylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**23**): m.p.: 164–165 °C (MeOH); $C_{18}H_{14}INO_4S$ (467.28); found: C, 45.64; H, 2.87; I, 28.03; N, 2.91; calcd.: C, 46.27; H, 3.02; I, 27.16; N, 3.00%; UV/Vis (acetonitrile): λ_{max} (lgε) = 255 (4.40), 267 (4.57), 290 (4.28), 330 (3.91), and 380 nm (3.62); IR (KBr): $\nu_{max} = 1507$, 1442, 1412, 1338, 1302, and 1142 cm^{-1}; ^1H NMR (300 MHz; acetone-d_6): $\delta = 7.84$ (2H, m, 2 × H_α-Ph), 7.74 (1H, m, H_γ-Ph), 7.72 (1H, d, $J = 8.4$ Hz, 5-H), 7.70 (1H, d, $J = 9.4$ Hz, 8-H), 7.68 (1H, d, $J = 9.8$ Hz, 10-H), 7.61 (2H, m, 2 × H_β-Ph), 7.51 (1H, d, $J = 8.4$ Hz, 4-H), 7.06 (1H, dd, $J = 9.8$, 9.4 Hz, 9-H), 4.98 and 4.95 (2H, AB, $J = 14.5$ Hz, CH_2), 0.19 (1H, dd, $^2J = 10.3$ Hz, $^4J_{5,11a} = 1.3$ Hz, 11a-H), −0.53 (1H, dd, $^2J = 10.3$ Hz, $^4J_{10,11b} = 1.2$ Hz, 11b-H); ^{13}C NMR (75.5 MHz; acetone-d_6): $\delta = 146.3$ (s, C-2), 139.3 (d, C-8), 139.2 (s, C(Ph)-SO_2), 136.2 (d, $^1J = 163.9$ Hz, C-5), 135.7 (d, $^1J = 163.5$ Hz, C-4), 135.1 (dt, $^1J = 161.2$ Hz, C_γ-Ph), 132.9 (d, $^1J = 160.3$ Hz, C-9), 130.3 (dd, $^1J = 166.0$ Hz, 2 × C_β-Ph), 129.8 (d, $^1J = 165.8$ Hz, C-10), 129.4 (d, $^1J = 167.2$ Hz, 2 × C_α-Ph), 124.4 (s, C-3), 123.9 (s, C-6), 110.9 (s, C-1), 95.7 (s, C-7), 63.0 (td, $^1J = 141.1$ Hz, CH_2), 33.6 (tt, $^1J = 144.8$ Hz, C-11); MS: $m/z = 467$ ($M^{+\cdot}$, 1%), 421 (1), 326 (4), 296 (2), 295 (4), 280 (1), 267 (3), 254 (1), 169 (19), 152 (45), 141 (53), 125 (100), 115 (48), 77 (30), 63 (6), 51 (8).

11,11-Difluoro-2-nitro-3-(phenylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**24**) in a mixture with **25**, purity 85%: ^1H NMR (300 MHz; acetonitrile-d_3): $\delta = 7.79$ (2H, dd, $^3J = 8.5$ Hz, 2 × H_α-Ph), 7.74 (1H, tt, $^3J = 7.4$ Hz, H_γ-Ph), 7.59 (1H, d, $J = 8.5$ Hz, 4-H), 7.58 (2H, dd, $J = 8.5$, 7.4 Hz, 2 × H_β-Ph), 7.53 (1H, m, 10-H), 7.50 (1H, m, 7-H), 7.36 (1H, m, $J_{8,9} = 9.7$ Hz, 9-H), 7.33 (1H, m, 8-H), 7.18 (1H, d, $J = 8.5$ Hz, 5-H), 4.86 and 4.64 (2H, 2 × d, $J = 14.7$ Hz, CH_2); ^{13}C NMR (75.5 MHz; acetonitrile-d_3): $\delta = 145.3$ (s, C-2), 138.9 (s, C(Ph)-SO_2), 135.4 (dt, $^1J = 163.6$ Hz, C_γ-Ph), 134.7 (dm, $^1J = 162.7$ Hz, $J_{C,F} = 4.8$ Hz, C-9), 132.4 (dm, $^1J = 162.1$ Hz, $J_{C,F} = 5.0$ Hz, C-8), 131.1 (dm, $^1J = 162.5$ Hz, $J_{C,F} = 4.2$ Hz, C-4), 130.4 (dd, $^1J = 165.8$ Hz, 2 × C_β-Ph), 130.3 (dm, $^1J = 165.2$ Hz, $J_{C,F} = 3.6$ Hz, C-5), 129.5 (d, $^1J = 162.0$ Hz, 2 × C_α-Ph), 126.4 (dt, $^1J = 169.9$ Hz, $J_{C,F} = 2.6$ Hz, C-10), 125.2 (m, $J_{C,F} = 33.9$ Hz, C-6), 124.6 (dt, $^1J = 167.7$ Hz, $J_{C,F} = 2.2$ Hz, C-7), 123.5 (s, C-3), 111.6 (t, $J_{C,F} = 237.7$ Hz, C-11), 108.9 (m, $J_{C,F} = 30.6$ Hz, C-1), 62.2 (t, $^1J = 141.6$ Hz, CH_2).

11,11-Difluoro-2-nitro-5-(phenylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**25**) in a mixture with **24**, purity 95%: ^{1}H NMR (300 MHz; acetonitrile-d_3): $\delta = 8.14$ (1H, d, $J = 9.8$ Hz, 3-H), 8.09 (1H, m, 10-H), 7.66 (2H, dd, $^3J = 8.0$ Hz, 2 × H_α-Ph), 7.64 (1H, tt, $^3J = 6.8$ Hz, H_γ-Ph), 7.51 (1H, d, $J = 11.9$ Hz, 7-H), 7.50 (1H, dd, $J = 9.6$,9.3 Hz, 9-H), 7.48 (2H, dd, overlapped, 2 × H_β-Ph), 7.39 (1H, dd, $J = 11.9$, 9.3 Hz, 8-H), 7.05 (1H, d, $J = 9.8$ Hz, 4-H), 4.87 and 4.80 (2H, AB, $J = 14.3$ Hz, CH_2); ^{13}C NMR (75.5 MHz; acetonitrile-d_3): $\delta = 142.6$ (s, C-2), 138.5 (s, C(Ph)-SO_2), 135.4 (d, $^1J = 155.6$ Hz, C_γ-Ph), 134.3 (t, $J_{C,F} = 3.2$ Hz, C-5), 133.4 (dm, $^1J = 144.6$ Hz, $J_{C,F} = 5.2$ Hz, C-9), 131,8 (dm, $^1J = 166.8$ Hz, $J_{C,F} = 5.3$ Hz, C-8), 131.2 (dm, $^1J = 159.9$ Hz, $J_{C,F} = 4.3$ Hz, C-4), 130.3 (d, $^1J = 166.0$ Hz, 2 × C_β-Ph), 129.5 (d, $^1J = 166.7$ Hz, 2 × C_α-Ph), 128.2 (dt, $^1J = 168.4$ Hz, $J_{C,F} = 2.7$ Hz, C-10), 126.8 (dm, $^1J = 167.9$ Hz, $J_{C,F} = 4.6$ Hz, C-3), 125.4 (dt, $^1J = 166.7$ Hz, $J_{C,F} = 2.5$ Hz, C-7), 122.4 (t, $J_{C,F} = 31.5$ Hz, C-6), 112.2 (t, $J_{C,F} = 239.6$ Hz, C-11), 110.9 (t, $J_{C,F} = 31.5$ Hz, C-1), 60.8 (t, $^1J = 140.5$ Hz, CH_2).

2-Nitro-3-[1-(phenylsulfonyl)ethyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**28**): m.p.: 167 °C (acetone); $C_{19}H_{17}NO_4S$ (355.41); found: C, 64.48; H, 5.31; N, 4.47; calcd.: C, 64.21; H, 4.82; N, 3.94%; ^{1}H NMR (200 MHz; acetone-d_6): $\delta = 7.85$–7.57 and 7.40–7.24 (10H, 2 × m, 4-, 7-, 8-, 9-, 10-H and H-Ph), 7.64 (1H, dd, $J = 8.0$, 0.8 Hz, 5-H), 5.23 (1H, q, $J = 6.9$ Hz, CH), 1.77 (3H, d, $J = 6.9$ Hz, CH_3), −0.22 (1H, dd, $^2J = 9.6$ Hz, $^4J_{5,11a} = 0.8$ Hz, 11a-H), −0.52 (1H, dt, $^2J = 9.6$ Hz, $^4J_{7/10,11b} = 1.2$ Hz, 11b-H).

2-Nitro-5-[1-(phenylsulfonyl)ethyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**29**) in a mixture with **28**, purity 75%: ^{1}H NMR (200 MHz; acetone-d_6): $\delta = 8.25$ (1H, d, $J = 10.4$ Hz, 3-H), 8.05–6.80 (10H, m, 4-, 7-, 8-, 9-, 10-H and H-Ph), 5.29 (1H, q, $J = 7.1$ Hz, CH), 1.73 (3H, d, $J = 7.1$ Hz, CH_3), −0.68 (1H, dt, $^2J = 10.1$ Hz, $^4J_{7/10,11b} = 1.4$ Hz, 11b-H), −0.85 (1H, d, $J = 10.1$ Hz, 11a-H).

1-Nitro-4-[(phenyl)phenylsulfonylmethyl]naphthalene (**30**): m.p.: 197–198 °C (MeOH); $C_{23}H_{17}NO_4S$ (403.45); found: C, 68.11; 3.97; N, 3.71; calcd.: C, 68.47; H, 4.25; N, 3.47%; ^{1}H NMR (60 MHz; $CDCl_3$): $\delta = 8.57$ and 8.17 (2H, AB, $J = 8.0$ Hz, 2-, 3-H), 8.50–7.10 (14H, m, 5-, 6-, 7-, 8-H and 2 × H-Ph), 6.18 (1H, s, CH).

2-Nitro-3-[(phenyl)phenylsulfonylmethyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**31**) in a mixture with **32**: ^{1}H NMR (300 MHz; $CDCl_3$): $\delta = 8.36$ and 8.11 (2H, 2 × d, $J = 10.5$ Hz, 4-, 5-H), 8.30* (1H, d, $J = 8.8$ Hz, 10-H), 7.82* (1H, d, $J = 8.0$ Hz, 7-H), 7.70–7.12 (12H, m, 8-, 9-H and 2 × H-Ph), 6.09 (1H, s, CH), −0.55 and −0.64 (2H, AB, $J = 10.0$ Hz, 11-CH_2).

2-Nitro-5-[(phenyl)phenylsulfonylmethyl]bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**32**): m.p.: 198–199 °C (MeOH); $C_{24}H_{19}NO_4S$ (417.48); found: C, 68.85; H, 4.41; N, 3.51; calcd.: C, 69.05; H, 4.59; N, 3.36%; ^{1}H NMR (300 MHz; $CDCl_3$): $\delta = 8.48$ (1H, d, $J = 10.6$ Hz, 3-H), 8.28* (1H, d, $J = 9.2$ Hz, 10-H), 8.09 (1H, d, $J = 10.6$ Hz, 4-H), 7.94–7.90*,# (2H, m, 7-, 9-H), 7.50–6.90# (11H, m, 8-H and 2 × H-Ph), 5.95 (1H, s, CH), −0.57 and −0.70 (2H, AB, $J = 10.1$ Hz, 11-CH_2).

2-Nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-3-ylacetonitrile (**35**): see Ref. [30]

2-Nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-5-yl(phenyl)acetonitrile (**37**): m.p.; 125–127 °C (MeOH); $C_{19}H_{14}N_2O_2$ (302.33); found: C, 75.16; H, 4.50; N, 9.14; calcd.: C, 75.48; H, 4.67; N, 9.27%; ^{1}H NMR (300 MHz; CD_2Cl_2): $\delta = 8.39$ (1H, d, $J = 9.8$ Hz, 3-H), 8.36* (1H, d, $J = 10.5$ Hz, 10-H), 7.71* (1H, d, $J = 8.5$ Hz, 7-H), 7.62–7.28 (8H, m, 4-, 8-, 9-H and H-Ph), 5.67 (1H, s, CH), −0.39 (2H, s, 11-CH_2).

tert-Butyl-2-nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-3-yl-acetate (**39**): m.p.: 66–67 °C (MeOH); $C_{17}H_{19}NO_4$ (301.34); found: C, 67.60; H, 6.37; N, 4.94; calcd.: C, 67.76; H, 6.36; N, 4.65%; ^{1}H NMR (300 MHz; $CDCl_3$): $\delta = 7.79$* (1H, d, $J = 9.2$ Hz, 10-H), 7.50 (2H, d, $J = 8.6$ Hz) and 7.27–7.12* (3H, m) [H-Ar], 3.92 and 3.77 (2H, AB, $J = 16.7$ Hz, CH_2), 1.44 (9H, s, $C(CH_3)_3$), −0.21 and −0.45 (2H, 2 × d, $J = 9.4$ Hz, 11-CH_2).

tert-Butyl-11,11-difluoro-2-nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-3-yl-acetate (**40**) and *tert-Butyl-11,11-difluoro-2-nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-5-yl-acetate* (**41**): mixture (**40**: 57%; **41**: 43%); ^{1}H NMR (200 MHz; acetone-d_6): $\delta = 8.25$ (d, $J = 9.7$ Hz, 3-H of isomer **41**), 8.16 (dm, $J_{9,10} = 7.9$ Hz, 10-H of isomer **41**), 7.85–7.34 (m, 4-, 5-, 7-, 8-, 9- and 10-H of isomer **40** and 7-, 8-, 9-H of isomer **41**), 7.24 (d, $J = 9.7$ Hz, 4-H of isomer **41**), 4.10 and 4.06 (AB, $J = 17.1$ Hz, CH_2 of isomer **41**), 3.94 and 3.80 (AB, $J = 16.5$ Hz, CH_2 of isomer **40**), 1.42 (s, $C(CH_3)_3$ of isomer **40**), 1.39 (s, $C(CH_3)_3$ of isomer **41**).

3-Dichloromethylidene-2-nitrobicyclo[4.4.1]undeca-4,6,8,10-tetraene (**43'**): m.p.: 98–100 °C (*n*-hexane); $C_{12}H_9Cl_2NO_2$ (270.12); found: C, 52.91; H, 3.27; Cl, 26.33; N, 5.10; calcd.: C, 53.36; H, 3.36; Cl, 26.25; N, 5.19%; IR ($CHCl_3$): $\nu_{max} = 1507$ and 1328 cm^{-1}; ^{1}H NMR (300 MHz; $CDCl_3$): $\delta = 6.56$ and 6.16 (2H, 2 × d, $J = 10.3$ Hz, 4-, 5-H), 6.42 (1H, s, >$CHNO_2$), 6.32–5.98 (4H, m, 7-, 8-, 9-, and 10-H), 1.70 (1H, d, $J = 4.3$ Hz, 11b-H), 0.42 (1H, d, $J = 4.3$ Hz, 11a-H).

2-Nitrobicyclo[4.4.1]undeca-4,6,8,10-tetraen-3-one (**46**): oil; $C_{11}H_9NO_3$ (203.20); found: C, 64.91; H, 4.39; N, 7.05; calcd.: C, 65.02; H, 4.46; N, 6.89%; IR ($CHCl_3$); $\nu_{max} = 3003$, 2938, 2895, 1690, 1303, and 990 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$); $\delta = 8.20$ (1H, dt, $J = 8.0$, 1.3 Hz, 10-H), 7.68 (1H, d, $J = 10.2$ Hz, 5-H), 7.55–7.22 (3H, m, 7-, 8-, and 9-H), 6.89 (1H, d, $J = 10.2$ Hz, 4-H), 0.60 (1H, dt, $^2J = 10.1$ Hz, $^4J_{7/10,11b} = 1.3$ Hz, 11b-H), −0.31 (1H, dd, $^2J = 10.1$ Hz, $^4J_{5,11a} = 1.1$ Hz, 11a-H), 2-H–undetected; MS: $m/z = 203$ ($M^{+\cdot}$, 23%), 171 (10), 170 (10), 158 (25), 156 (27), 141 (22), 128 (100), 115 (63), 102 (27), 91 (11), 89 (17), 77 (33), 63 (24), 51 (28), 43 (17), 38 (20).

2-Nitrobicyclo[4.4.1]undeca-3,6,8,10-tetraen-5-one (**47**): oil; IR ($CHCl_3$): $\nu_{max} = 3025$, 2954, 1685, 1525, 1255, 1080, and 1014 cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$): $\delta = 13.21$ (1H, s, 2-H), 7.84 (1H, d, $J = 7.6$ Hz, 10-H), 7.62* (1H, d, $J = 10.8$ Hz, 3-H), 7.42–7.16* (3H, m, 4-, 8-, and 9-H), 7.07 (1H, d, $J = 10.6$ Hz, 7-H), 0.97 (1H, dt, $^2J = 10.1$ Hz, $^4J_{7(10),11b} = 1.1$, 1.0 Hz, 11b-H), −0.31 (1H, dd, $^2J = 10.1$ Hz, $^4J_{2,11a} = 1.3$ Hz, 11a-H); MS: $m/z = 203$ ($M^{+\cdot}$, 14%), 186 (5), 171 (3), 156 (4), 155 (5), 149 (7), 129 (26), 128 (20), 115 (16), 102 (12), 94 (58), 79 (100), 71 (14), 57 (30), 55 (16), 51 (13), 43 (24), 40 (19); HR-MS: calcd. for $C_{11}H_9NO_3$ 203.0582, found 203.0598.

3-Nitro-2-(p-tolylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**49**): m.p.: 138–139 °C (MeOH); $C_{19}H_{17}NO_4S$ (355.41); found: C, 64.34; H, 5.03; N, 3.75; S, 8.97; calcd.: 64.21; H, 4.82; N, 3.94; S, 9.02%; UV/Vis (acetonitrile): $\lambda_{max}(\lg\varepsilon) = 250$ (4.37), 290 (4.27), 350 (3.74), and 410 nm (3.20); IR (KBr): $\nu_{max} = 3034$, 1543, 1504, 1446, 1323, 1299, 1159, and 1132 cm^{-1}; ^{1}H NMR (300 MHz; acetonitrile-d_3): $\delta = 8.41$ (1H, d, $J = 8.6$ Hz, 4-H), 7.61 (1H, d, $J = 8.6$ Hz, 5-H), 7.50 (1H, dd, $^3J = 9.6$ Hz, 7-H), 7.09 (1H, d, $J = 9.9$ Hz, 10-H), 6.93 (1H, dd, $J = 9.9$, 8.9 Hz, 9-H), 6.76 (2H, d, $J = 8.6$ Hz, 2 × H_α-Tol), 6.65 (1H, dd, $J = 9.6$, 8.9 Hz, 8-H), 6.49 (2H, d, $J = 8.6$ Hz, 2 × H_β-Tol), 5.37 and 4.90 (2H, 2 × d, $J = 15.3$ Hz, CH_2), −0.10 (1H, dd, $^2J = 9.6$ Hz, 11a-H), −0.64 (1H, dt, $^2J = 9.6$ Hz, 11b-H); ^{13}C NMR (75.5 MHz; acetonitrile-d_3): $\delta = 151.2$ (s, C-3), 145.9 (s, C_γ-Tol), 134.1 (s, C(Tol)-SO_2), 132.0 (d, $J = 163.0$ Hz, C-10), 131.9 (d, $J = 163.0$ Hz, C-7), 130.5 (d, $J = 161.4$ Hz, 2 × C_β-Tol), 129.6 (d, $J = 158.0$ Hz, C-5), 129.5 (dd, $^1J = 159.1$ Hz, C-8), 129.1 (dd, $^1J = 158.4$ Hz, C-9), 128.1 (dd, $^1J = 162.3$ Hz, 2 × C_α-Tol), 127.8 (s, C-2), 125.6 (d, $J = 161.9$ Hz, C-4), 121.5 (s, C-6), 115.4 (s, C-1), 56.9 (t, $J = 141.4$ Hz, CH_2), 35.7 (tq, $^1J = 143.8$ Hz, C-11), 21.4 (qt, $^1J = 127.2$ Hz, CH_3); MS: $m/z = 355$ ($M^{+\cdot}$, 0.2%), 338 (<0.1), 325 (0.2), 309 (<0.1), 279 (1), 229 (1), 215 (1), 200 (33), 186 (45), 182 (10), 169 (19), 152 (45), 141 (100), 128 (39), 115 (43), 91 (23), 77 (7), 65 (9), 63 (3).

3-Nitro-2-(phenylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**50**): m.p.: 147–148 °C (MeOH); $C_{18}H_{15}NO_4S$ (341.38); found: C, 63.30; H, 4.20; N, 3.90; S, 9.40; calcd.: C, 63.33; H, 4.43; N, 4.10; S, 9.39%; UV/Vis (acetonitrile): λ_{max} ($\lg\varepsilon$) = 250 (4.37), 285 (4.29), 350 (3.76), 410 (3.19), and 465 nm (2.35); IR (CsI): $\nu_{max} = 3082$, 3055, 2999, 1544, 1486, 1449, 1316, 1177, and 1163 cm^{-1}; ^{1}H NMR (300 MHz; acetonitrile-d_3): $\delta = 8.39$ (1H, d, $J = 8.6$ Hz, 4-H), 7.62 (1H, d, $J = 8.6$ Hz, 5-H), 7.51 (1H, d,

$J = 9.6$ Hz, 7-H), 7.34 (1H, t, $J = 8.2$ Hz, H_γ-Ph), 7.18 (1H, d, $J = 10.9$ Hz, 10-H), 7.04 (2H, td, $^3J = 8.2$ Hz, $2 \times H_\beta$-Ph), 6.92 (1H, m, $J_{8,9} = 9.4$ Hz, 9-H), 6.71 (2H, d, $J = 8.3$ Hz, $2 \times H_\alpha$-Ph), 6.70 (1H, m, 8-H), 5.40 and 4.97 (2H, $2 \times$ d, $J = 15.3$ Hz, CH_2), −0.09 (1H, dd, $^2J = 9.6$ Hz, 11a-H), −0.62 (1H, dt, $^2J = 9.6$ Hz, 11b-H); ^{13}C NMR (75.5 MHz; acetonitrile-d_3): $\delta = 151.2$ (s, C-3), 137.4 (s, C(Ph)-SO_2), 134.7 (d, $J = 159.5$ Hz, C_γ-Ph), 131.9 (d, overlapped, C-10), 131.8 (d, overlapped, C-7), 130.0 (d, $J = 161.7$ Hz, $2 \times C_\beta$-Ph), 129.8 (d, overlapped, C-5), 129.6 (dd, $^1J = 159.9$ Hz, C-8), 129.6 (dd, $^1J = 159.9$ Hz, C-9), 128.2 (d, $J = 164.8$ Hz, $2 \times C_\alpha$-Ph), 127.7* (s, C-1), 125.5 (d, $J = 162.0$ Hz, C-4), 121.3* (s, C-6), 115.4* (s, C-2), 56.8 (t, $J = 141.6$ Hz, CH_2), 35.8 (tq, $^1J = 143.6$ Hz, C-11); MS: $m/z = 341$ ($M^{+\cdot}$, 0.2%), 324 (0.2), 311 (0.1), 295 (<0.1), 265 (0.2), 229 (0.5), 215 (1), 200 (26), 186 (25), 169 (9), 152 (33), 141 (100), 128 (20), 115 (23), 102 (2), 77 (19), 51 (2).

11,11-Difluoro-3-nitro-2-(p-tolylsulfonylmethyl)bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene (**51**): m.p.: 172–173 °C (MeOH); $C_{19}H_{15}F_2NO_4S$ (391.39); found: C, 58.31; H, 3.85; N, 3.55; calcd.: C, 58.31; H, 3.86; N, 3.58%; IR ($CHCl_3$): $\nu_{max} = 3039$, 1612, 1545, 1341, 1161, and 1097 cm^{-1}; ^{1}H NMR (200 MHz; acetone-d_6): $\delta = 8.26$ (1H, d, $J = 9.7$ Hz, 4-H), 7.83 (1H, d, $J = 10.2$ Hz, 10-H), 7.61 (1H, d, $J = 9.7$ Hz, 5-H), 7.77–7.68 and 7.56–6.89 (7H, $2 \times$ m, 7-, 8-, 9-H and H-Tol), 5.46 and 5.16 (2H, $2 \times$ d, $J = 15.2$ Hz, CH_2), 2.34 (3H, s, CH_3); MS: $m/z = 391$ ($M^{+\cdot}$, 4%), 345 (2), 341 (4), 295 (5), 236 (37), 217 (12), 186 (100), 170 (21), 155 (15), 139 (44), 128 (97), 115 (18), 91 (49), 77 (11), 65 (25), 39 (13).

2-Nitro-1-naphthylacetonitrile (**52**): m.p.: 154–155 °C (MeOH); $C_{12}H_8N_2O_2$ (212.21); found: C, 67.78; H, 3.69; N, 12.91; calcd.: C, 67.92; H, 3.80; N, 13.20%; ^{1}H NMR (60 MHz; acetone-d_6): $\delta = 8.60$–7.70 (6H, m, H-Ar), 4.56 (2H, s, CH_2).

3-Nitrobicyclo[4.4.1]undeca-1,3,5,7,9-pentaen-2-yl-acetonitrile (**53**): m.p.: 126–128 °C (MeOH); $C_{13}H_{10}N_2O_2$ (226.24); found: C, 69.12; H, 4.19; N, 12.27; calcd.: C, 69.02; H, 4.46; N, 12.38%; ^{1}H NMR (300 MHz; $CDCl_3$): $\delta = 8.16$ (1H, d, $J = 8.9$ Hz, 4-H), 7.87* (1H, d, $J = 9.2$ Hz, 7-H), 7.61 (1H, d, $J = 8.9$ Hz, 5-H), 7.58* (1H, d, $J = 9.1$ Hz, 10-H), 7.40–7.20 (2H, m, 8-, 9-H), 4.09 and 4.01 (2H, AB, $J = 17.8$ Hz, CH_2CN), 0.03 (11a-H) and −0.38 (11b-H) (2H, $2 \times$ d, $J = 9.8$ Hz, 11-CH_2).

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