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Cycloadditions of Vinylindoles with Chiral Carbodienophiles: The First Asymmetric Diels-Alder Reactions in the Vinylhetarene Series

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Abstract: The first asymmetric Diels-Alder reactions of some 3- and 2-vinylindoles with (*N*-propenoyl)bornane-10,2-sultam are described. With one exception, the experimental results are indicative of a high π-facial diastereoselectivity. Following a related procedure, 3-vinylindoles were also allowed to react with a racemic bis(naphthylsulfonyl)-dienophile to furnish tetrahydrocarbazoles with *endo*-diastereoselectivity

The strict demands for biologically selective and degradable drugs have prompted much research work directed at the development of stereoselective syntheses. Because of the inherent diastereoselectivity of concerted cycloaddition reactions, the Diels-Alder reaction provides a valuable method for highly stereoselective syntheses of cyclic and polycyclic compounds. A number of such routes for the diastereo-[1] and enantioselective[2] formation of chiral products have been developed. In the vinylhetarene series, 2- and 3-vinylindoles have been used as versatile diene components in various highly regio- and stereoselective HOMO(diene)-LUMO(dienophile)-controlled [4 + 2] cycloaddition reactions for the construction of (racemic) annellated indoles and alkaloids of pharmacological interest.[3-5] However, there are no reports of asymmetric Diels-Alder reactions of vinylheterocycles for the construction of enantiomerically pure annellated polycyclic systems containing hetarene skeletons. Thus, in continuation of our investigations on pericyclic 6-electron processes with vinylhetarenes,[4-6] we now describe the first π-facial diastereoselective [4 + 2] cycloadditions of 3- and 2-vinylindoles while taking into consideration two different elements of chirality. In the first part of this work, we studied cycloaddition reactions with "Oppolzer's acryloylsultam" – a dienophile with C_1 symmetry – and in the second part we employed a C_2-symmetrical binaphthyl derivative as the dienophile.

RESULTS AND DISCUSSION

The camphor-derived bornane-10,2-sultams have proved to be versatile chiral auxiliaries for a wide range of chemical transformations.[18] For asymmetric Diels-Alder reactions in particular, a high π-face selectivity has previously been reported.[7] This prompted us to investigate the [4 + 2] cycloaddition reactions of the 3- and 2-vinylindoles **1-6**[4,14,19] with the 1*R*,2*S*,4*S*-(*N*-propenoyl)bornane-10,2-sultam (**7**) and its enantiomer.

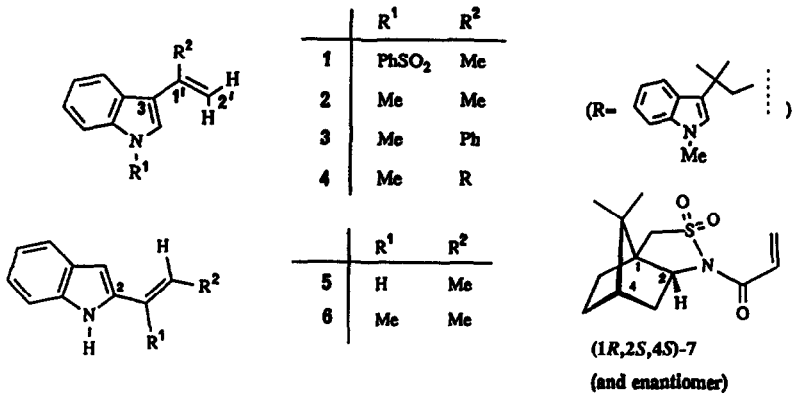
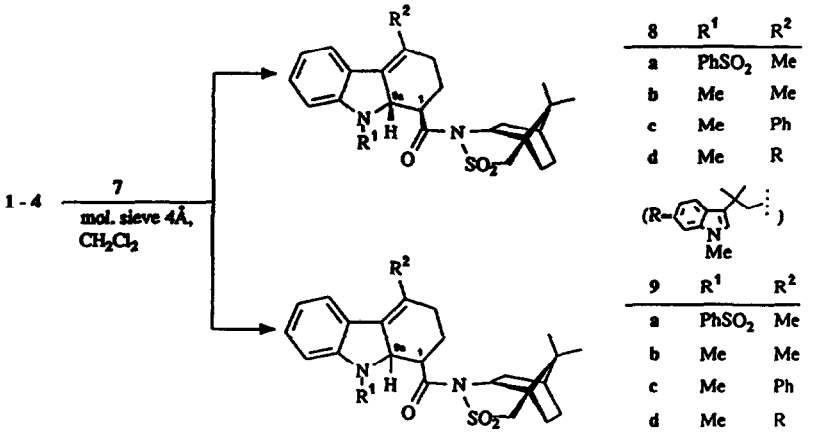


Fig. 1.

As has been reported previously,[5,20] molecular sieves are appropriate, mild catalysts for cycloaddition reactions of the 3-vinylindoles **1-4** with **7** at temperatures between 25 and 40 °C. The results were not improved by use of higher or lower temperatures. Except for the reaction with **2** where an additional diastereoisomer occurred as a minor product, these cycloaddition reactions proceeded with π-diastereoselectivity to furnish the enantiomerically pure tetrahydrocarbazoles **8a-d** (Table 1). Throughout this work, the chemical yields of the analytically pure products were unsatisfactory because of the losses of material experienced during the work-up procedures.

The ratios of the diastereoisomers were determined by HPLC and NMR analyses. The relative configurations were deduced by 400 MHz ^{1}H-NMR spectrometry including H,H-COSY and NOE techniques. The absolute configuration of **8c** was elucidated by a single crystal X-ray analysis (Fig. 2b).[8a] The absolute configurations given for **8a, b**, and **d** (and thus also of the enantiomers **8a*** and **8c***) could be deduced consistently from the CD spectra of **8a**, **8c** and their enantiomers **8a***, **8c***.



Scheme 1

In order to confirm these results, the [4 + 2] cycloaddition reactions of the 3-vinylindoles **1** and **3** with the 1*S*,2*R*,4*R*-enantiomer of **7** were also examined. The enantiomers of **8a** and **c** were formed with more than 99% d.e. (by HPLC, NMR, and CD; yields: 14 and 27%, respectively). The 2-vinylindoles **5** and **6** were also allowed to react with **7**. However, the product carbazoles were obtained as inseparable mixtures of diastereomers. Furthermore, the regio- and stereochemistries could not be analyzed satisfactorily in these mixtures as a result of overlapping of the diagnostically relevant NMR signals.

Thus, in the [4 + 2] cycloadditions of 3-vinylindoles with **7**, an *exo*-orientation in the transition state should be preferred under the given reaction conditions (Table 1). On the basis of Dreiding models, MMX molecular mechanics calculations,[9] and ^{1}H-NOE measurements, the dienophile should adopt a preferred conformation (Fig. 2a) in which the C(α)-*Re*-face is shielded efficiently. The transition state model indicates that this powerful shielding effect is due to the sulfonyl group; the function of the rigid and bulky bornane hydrocarbon skeleton in this case is to constrain its conformational freedom.

Surprisingly, the addition of $EtAlCl_2$ to the reaction mixture did not improve the yield or change the selectivity of the cycloaddition process.

Table 1. Reactions of **1-4** with the acrylamide (1*R*,2*S*,4*S*)-**7**[a]

Diene	Temp. (°C)	Time	Product	Chemical yield (%)[b]	Ratio of diastereomers (*exo*:*endo*)[c]
1	40	5 d	**8a,9a**[d]	8	>99:1
2	20	3 d	**8b,9b**	11	74:26[e]
3	20	18 h	**8c,9c**[d]	24	>99:1
4	20	3 d	**8d,9d**[d]	2	>99:1

a) Solvent CH_2Cl_2 in the presence of 4 Å molecular sieves.

b) Total yield of products isolated by flash chromatography. The crude yields (by TLC) were significantly larger but substantial losses occurred during chromatographic work-up.

c) By HPLC and ^{1}H-NMR analyses.

d) Compounds **9a**, **c**, and **d** were not detected within the limits of the HPLC analysis.

e) Ratio of *exo*·*endo* or *endo*·*exo* stereochemistry.

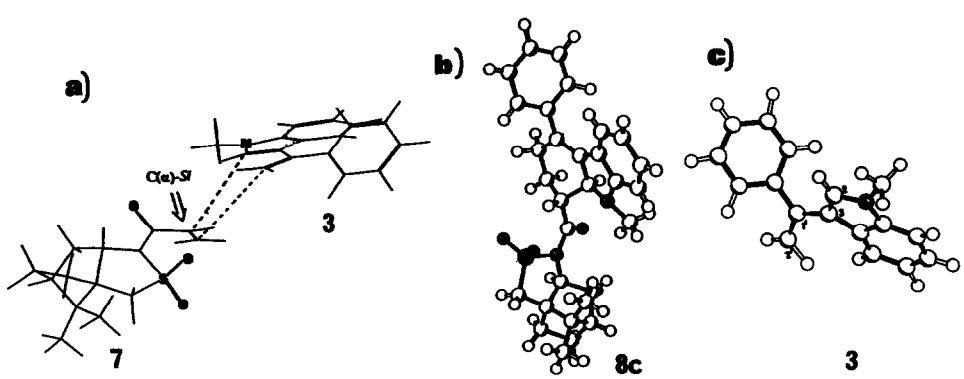


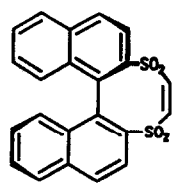
Fig. 2. (**a**) Orientation of MMX-calculated ground state conformations of **7** and **3** for the creation of the transition state to give **8c**. (**b**) X-ray crystal structure of **8c** (SCHAKAL plot)[8a]. (**c**) X-ray crystal structure of **3** (SCHAKAL plot).[8b]

In this context, an X-ray crystallographic analysis of the 3-vinylindole **3** was also carried out[8b] (Fig. 2c) and provided further information allowing an increased reliability for the calculation of the s-*Z*- (or *gauche*)/s-*E*-conformational equilibrium of the diene unit by a molecular mechanics method.[10] However, in agreement with previous X-ray crystallographic structural analyses of other 3-vinylindoles,[5,11] the vinylindole **3** adopts the s-*E*-conformation within the diene moiety in the solid state. The deviation from the full coplanarity of the entire molecule [torsional angle C2-C3-C1'-C2' is –153.9(4)°] is, first of all, induced by the bulky phenyl group on the vinyl moiety. Conformational analysis by MMX molecular mechanics calculations[10], simulating vacuum conditions, revealed that an s-*E*-conformation with a torsional angle C2-C3-C1'-C2' = –143.90° is energetically favored by about 0.64 kcal·mol^{-1} over an s-*Z*-conformation with a torsional angle C2-C3-C1'-C2' = –40.95°. Moreover, observations of Dreiding models of **3** showed that the barrier to rotation about the C3-C1' σ-bond is low enough to permit a sufficient population of the "reactive" s-*Z*-conformation for the build-up of the π-diastereofacial transition state formulated schematically in Figure 2a and to allow a fast conformational equilibrium within the reaction mixture.

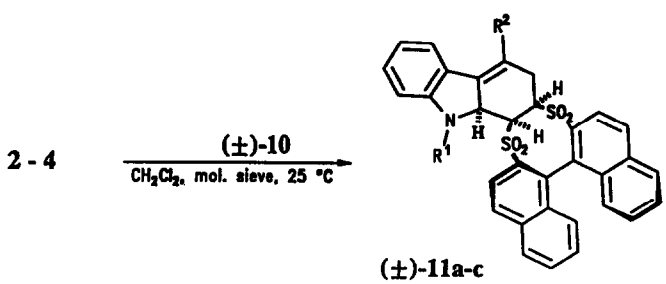
The loss of selectivity in the reaction of **2** with **7** is probably the result of the comparatively high reactivity of the diene combined with the lower steric requirements of the C1' substituent.

Applications of binaphthyl species either as mere catalysts or as reactants have enriched the field of asymmetric synthesis.[12] In both cases, stereoselection arises from the axial chirality of the atropisomeric binaphthyl moiety. Intrigued by this different source of chirality in comparison to **7**, we have investigated – among other chiral dienophiles – the behavior of (±)-7,10-dithiadinaphtho[2,1-*d*:1',2'-*f*]cyclooctene 7,7,10,10-tetraoxide in cycloaddition reactions with 3-vinylindoles. This conformationally fixed dienophile was easily prepared from (±)-1,1'-binaphthyl-2,2'-diol according to known procedures.[13,15,16,17]

The Diels-Alder reactions of (±)-**10** were performed under the same mild conditions as those with **7**. The 3-vinylindole **1** did not react with (±)-**10** to furnish stable products while the Diels-Alder reactions of **2-4** took place smoothly with high diastereoselectivity (d.e. >98% by ^{1}H-NMR) to furnish the racemic tetrahydrocarbazoles **11a-c** (Scheme 2). In these cases, the relative configurations within the cyclohexene units of the products were easily established by routine ^{1}H-NMR analysis (NOE and proton-decoupling experiments). An analysis of the coupling constants according to the Karplus equation indicates a twisted boat conformation for the cyclohexene ring.[4] The NMR spectroscopic data revealed that the cycloadducts **11** are all



(±)-**10**



(±)-**11a-c**

Scheme 2

exclusively by way of an *endo*-Diels-Alder transition state. The clear product pattern and considerations of Dreiding models revealed that the reactions of both (+)- and (–)-**10** with **2-4** also proceeded with π-diastereoselectivity.

In summary, the first Diels-Alder reactions of vinylindoles with chiral carbodienophiles have been realized. The π-facial diastereoselectivity was high in all but one case. Reactions with the enantiomerically pure acrylamide **7** proceed via an *exo*-transition state, whereas in those with the racemic binaphthyl derivative **10** *endo*-adducts were observed exclusively. Further asymmetric Diels-Alder reactions with enantiomerically pure binaphthyl carbodienophiles as well as reactions with achiral dienophiles in the presence of chiral Lewis acids are now under investigation in our laboratory.

EXPERIMENTAL SECTION

Melting points were determined on a Büchi SMP-20 apparatus and are not corrected. EI-mass spectra were recorded on a Varian MAT CH7 spectrometer at an ionizing voltage of 70 eV; FD-mass spectra were recorded on a Finnigan MAT 90 spectrometer. ^{1}H- and ^{13}C-NMR (400 and 100.6 MHz) were obtained on a Bruker WM 400 spectrometer and 200 MHz ^{1}H-NMR spectra on a Bruker AC 200 instrument (δ ppm scale, using the respective solvent as internal standard; abbreviations: C_p = primary, C_s = secondary, C_t = tertiary, and C_q = quaternary carbon atom). C,H,N-Analyses were performed with a Carlo Erba Stumentazione 1164 apparatus. For flash chromatography (FC), Merck silica gel 60 (grain size 0.040-0.063 mm) and for column chromatography (CC) Merck silica gel 60 (grain size 0.063-0.200 mm) were used. Molecular sieves were activated prior to use at 400 °C/500-600 torr. All reactions were performed in highly pure, anhydrous solvents under a nitrogen atmosphere. In those reactions in which racemic products are formed, the nomenclature and structures of only one of the enantiomers are given; these compounds are identified by a (±)-prefix. The enantiomers of **7**, **8a**, and **8c** are marked with an asterisk.

The crude yields in all cases were significantly higher than the given yields of FC-purified and crystallized products.

Asymmetric Diels-Alder Reactions, General Procedure. The respective vinylindole[4,19] was added to a suspension of 2-3 g 4 Å molecular sieves[20] in about 15 ml of dry CH_2Cl_2 under an N_2 atmosphere. The solution was brought to the temperature given in the individual descriptions below; after 30 min, a solution of the dienophile in dry CH_2Cl_2 was added dropwise. Work-up is achieved by simple filtration from molecular sieves, washing of the latter with 50 ml CH_2Cl_2 in small portions, removal of the solvent from the combined organic liquids, and FC of the residue.

{(1S,5R,7R)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-yl}-[(1S,9aR)-4-methyl-9-phenylsulfonyl-2,3,9,9a-tetrahydro-1H-carbazol-1-yl]methanone (**8a***). From vinylindole **1** (750 mg, 2.5 mmol) and **7***[18] (140 mg, 0.5 mmol). Reaction conditions: 4 h at 20 °C, then 1 h at 40 °C. Work-up: isolation by FC [petroleum ether/ethyl acetate (5/1)] and crystallization from petroleum ether/ethyl acetate. Yield: 40 mg (14%), m.p. 252 °C. CD (methanol, c = 0.351 mMol/l, d = 0.02 cm) λ_{max} [nm] (Δε): 280.2 (–40.793), 228.4 (71.852), 212.2 (–6.798), 199.8 (5.081), 190.0 (–60.479). Anal. calcd. for $C_{30}H_{34}N_2O_5S_2$ (566.74): C 63.58, H 6.05, N 4.94. Found: C 63.52, H 6.13, N 4.79. FD-MS: *m/z* (rel. intensity %) = 589.2 (M + Na$^+$, 100), 568.1 (isotope peak, 13.5), 567.1 (isotope peak, 5.8), 566.1 (M$^{+\cdot}$, 80.8), 426.1 (M – $C_6H_4O_2S$; onium reaction). ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ = 7.83 (d, 1H, ^3J = 8.2 Hz, 5-H or 8-H), 7.78 (d, 2H, ^3J = 7.62 Hz, 2"-H, 6"-H), 7.55 [d (pseudo-t), 1H, J = 6.85 Hz, 7.48 Hz, ^4J = 1.2 Hz, 4"-H], 7.39-7.45 (m, 3H, 8-H or 5-H, 3"-H, 5"-H), 7.2 (pseudo-t, 1H, J = 7.9 Hz, 7.6 Hz, 6-H or 7-H), 7.04 [d (pseudo-t), 1H, J = 7.16 Hz, 7.25 Hz, ^4J = 0.6 Hz, 7-H or 6-H)], 4.75 (m, 1H, homoallylic coupling = 2.2 Hz, ^3J = 3.60 Hz, 9a-H), 4.0 (broad m, 1H, 2'-H), 3.55 (d, 1H, ^2J = 13.84 Hz, 4'-H_a), 3.48 (d, 1H, ^2J = 13.84 Hz, 4'-H_b), 3.41 (broad m, 1H, 1-H), 2.55 (broad m, 1H, 7'-H), 2.19 (broad m, 1H, 3-H_a), 2.13-2.05 (m, 2H, 6'-H), 2.0 (d, 3H, J = 2-2.5 Hz, 4-CH_3), 1.94-1.81 (m, 5H, 3-H_b, 2-H_a, 2-H_b, 8'-H), 1.48-1.34 (m, 2H, 9'-H), 1.30 (s, 3H, 10'-CH_3), 0.98 (s, 3H, 10'-CH_3). ^{13}C-NMR

(CD_2Cl_2, spin-echo experiment, 100.6 MHz): δ = 143.62 (C_q), 136.2 (C_q), 133.80 (C_t), 132.28 (C_q, $2C_{aromatic}$), 130 (C_q), 129.24 (C_t, 2C, *o*- or *m*-phenyl-C), 128.55 (C_t, 2C, *m*- or *o*-phenyl-C), 128.14 (C_t), 127.0 (C_q), 124.45 (C_t), 124.02 (C_t), 116.2 (C_t), the signals of the two C_t at 66.5 and 64.5 are not discernable within the noise, 53.3 (C_s), 49.0 (C_q), 48.12 (C_q), 45.89 (C_t), 45.43 (C_t), 38.42 (C_s), 37.0 (C_q), 36.4 (C_t), 33.55 (C_s), 31.62 (C_s), 26.91 (C_s), 26.48 (C_s), 20.96 (C_p), 20.34 (C_p), 20.25 (C_p).

*{(1R,5S,7S)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-yl}-[(1R,9a*S*)-4-methyl-9-phenylsulfonyl-2,3,9,9a-tetrahydro-1*H*-carbazol-1-yl]methanone* (**8a**). From vinylindole **1** (900 mg, 3 mmol) and **7** (400 mg, 1.5 mmol). Reaction conditions: 6 days under reflux; after 1, 2, and 5 days, 100 mg portions of **7** (0.37 mmol) were added. After evaporation of the solvent, the product crystallized directly from ethyl acetate from the filtrate; the remaining product was isolated by FC [petroleum ether/ethyl acetate (5/1)]. Yield: 122 mg (8%), m.p. 253 °C (petroleum ether/ethyl acetate). CD (methanol, *c* = 0.373 mMol/l, d = 0.02 cm) λ_{max} [nm] (Δε): 323.6 (–5.520), 280.0 (41.623), 228.4 (–83.485), 211.8 (4.968), 199.4 (–10.622), 191.4 (54.889). EI-MS: *m/z* (rel. intensity %) = 655 ($M^{+\cdot}$, 3), 426 (M – $C_6H_4O_2S$, onium reaction, 100), 367 (M – $C_{10}H_{15}$, onium reaction, 10), 327 ($C_{18}H_{17}NO_3S$, 18), 213 ($C_{10}H_{15}NO_2S$, 28), 186 (237 – $C_6H_4O_2S$, 100). ^{1}H-NMR (CD_2Cl_2, 400 MHz): the spectrum is identical to that of **8a*** and will not be repeated. ^{13}C-NMR (CD_2Cl_2, spin-echo experiment, 100.6 MHz): δ = 174 (C_q, carbonyl-C), 143.67 (C_q), 136.19 (C_q), 133.80 (C_t), 132.27 (C_q, $2C_{aromatic}$), 130.09 (C_q), 129.25 (C_t, $2C_{aromatic}$), 128.56 (C_t, $2C_{aromatic}$), 128.15 (C_t, $2C_{aromatic}$), 126.77 (C_q), 124.47 (C_t), 124.03 (C_t), 116.17 (C_t), 66.47 (C_t, $R^1R^2\underline{C}NSO_2R^3$), 64.54 ($C_t$, $R^1R^2\underline{C}NSO_2R^3$), 53.3 ($C_s$), 48.80 ($C_q$), 48.14 ($C_q$), 45.93 ($C_t$), 45.46 ($C_t$), 38.43 ($C_s$), 33.57 ($C_s$), 31.63 ($C_s$), 26.93 ($C_s$), 26.48 ($C_s$), 20.99 ($C_p$), 20.34 ($C_p$), 20.27 ($C_p$); ($Cl_2DC$-$CDCl_2$, spin-echo experiment): δ = 174.2 (C_q, carbonyl-C), 143.33 (C_q), 135.88 (C_q), 133.74 (C_t), 132.03 (C_q, 2C), 129.63 (C_q), 129.25 (C_t, $2C_{aromatic}$), 128.48 (C_t, $2C_{aromatic}$), 128.23 (C_t, $2C_{aromatic}$), 126.52 (C_q), 124.41 (C_t), 123.98 (C_t), 116.2 (C_t), 66.2 (C_t, $R^1R^2\underline{C}NSO_2R^3$), 64.2 ($C_t$, $R^1R^2\underline{C}NSO_2R^3$), 53.33 ($C_s$), 48.72 ($C_q$), 48.00 ($C_q$), 45.62 ($C_t$), 45.17 ($C_t$), 38.29 ($C_s$), 33.44 ($C_s$), 31.50 ($C_s$), 26.91 ($C_s$), 26.50 ($C_s$), 21.02 ($C_p$), 20.53 ($C_p$), 20.39 ($C_p$).

*{(1S,5R,7R)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1 0^{1,5}]decan-4-yl}-[(4,9-dimethyl-2,3,9,9a-tetrahydro-1*H*-carbazol-1-yl]methanone* (**8b*/9b***). From vinylindole **2** (320 g, 1.9 mmol) and **7*** (270 mg, 1.0 mmol). Reaction conditions: 5 days at 20 °C. Work-up: isolation by FC [petroleum ether/ethyl acetate (5/1)] to furnish white **8b*/9b***. Yield: 49 mg (11%), m.p. 211 °C (petroleum ether/ethyl acetate). The diastereoisomers could not be separated by FC or MPLC. A direct analysis of the HPLC separation shows an isomer ratio of 71:29 (assuming that both diastereoisomers have the same adsorption coefficient at 240 nm, an assumption for which, of course, no evidence can be presented) whereas the ^{1}H-NMR spectrum reveals the presence of a 5:1 mixture. The NMR absorptions of the major component are referred to as H_H or C_H and those of the minor component as H_N or C_N, respectively. EI-MS: *m/z* (rel. intensity %) = 441.2 (isotope peak and M + H, 12.6), 440.1 ($M^{+\cdot}$, 39.0), 425.2 (M – CH_3, 10.6), 376.2 (M – SO_2, 6.3), 287.1 ($C_{14}H_{11}N_2O_3S$, 2.6), 267.2 (retro-Diels-Alder reaction, $C_{13}H_{19}NO_3S$ – H_2, 2.4), 241.1 (376 – $C_{10}H_{15}$, 3.1), 226.1 (M – $C_{10}H_{16}NO_2S$, 8.6), 225.1 (226 – H, 3.2), 224.1 (226 – H_2, 7.5), 223.2 (225 – H_2, 2.1), 210.1 ($C_{15}H_{16}NO$, 4.6), 199.1 (isotope peak, 14.0), 198.2 ($C_{14}H_{16}N$, 89.7), 197.2 ($C_{14}H_{15}N$, onium reaction, 100), 196.2 (197 – H, 86.1), 184.1 (183 + H, 4.6), 183 (198 – CH_3, 18.7), 182 (183 – H, 43.9), 181 (183 – H_2, 22.0), 180 (182 – H_2, 3.8), 172 (isotope peak and 171 + H, 10.5), 171.1 (retro-Diels-Alder reaction, $C_{12}H_{13}N$, 64.8), 170 (171 – H, 3.9), 169 (171 – H_2, 3.7), 168 (170 – H_2, 7.3), 167 (168 – H, 9.3). ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ = 7.32 (d, $1H_H$, ^3J = 7.42 Hz, 5-H_H), 7.31 (d, $1H_N$, ^3J = 6.97 Hz, 5-H_N), 7.09-7.05 (m, 1H, 7-H), 6.73-6.67 (m, 1H, 6-H), 6.55-6.52 (m, 1H, 8-H), 4.23-4.17 (m, $1H_N$, 9a-H_N), 4.14-4.10 (m, $1H_H$, 9a-H_H), 3.99-3.94 (m, 1H, 5'-H), 3.56 (d, $1H_H$, ^2J = 13.90 Hz, 2'-H_H), 3.54 (d, $1H_N$, ^2J = 13.90 Hz, 2'-H_N), 3.51 (d, $1H_N$, ^2J = 13.90 Hz, 2'-H_N), 3.49 (d, $1H_H$, ^2J = 13.89 Hz, 2'-H_H), 3.2-3.12 (broad m, $1H_N$, 1-H_N), 3.08-3.03 (broad m, $1H_H$, 1-H_H), 2.66 (s, $3H_H$, 9_H-CH_3), 2.64 (s, $3H_N$, 9_N-CH_3), 2.32-2.24 (m, $2H_{aliphatic}$, including 2-H and/or 3-H), 2.17-2.00 (m, $3H_{aliphatic}$, including 3-H and 6'-H), 1.98-1.89 (m, $3H_{aliphatic}$), 1.79-1.69 (m, 1H, 2-H), 1.48-1.23 (m, $2H_{aliphatic}$), 1.20 (s, $3H_H$, $10'_H$-CH_3), 1.17 (s, $3H_N$, $10'_N$-CH_3), 0.994 (s, $3H_H$, $10'_H$-CH_3), 0.987 (s, $3H_N$,

$10'_N$-CH_3). ^{13}C-NMR ($CDCl_3$, spin echo experiment, 100.6 MHz): δ = 175.26 (C_q, carbonyl-C_H), 174.94 (C_q, carbonyl-C_N), 154.82 (C_q), 129.80 (C_q), 128.07 (C_q), 127.98 (C_t, C_N), 127.91 (C_t, C_H), 126.00 (C_q), 123.4 (C_t, C_N), 123.34 (C_t, C_H), 118.07 (C_t, C_H), 117.75 (C_t, C_N), 107.87 (C_t, C_H), 107.63 (C_t, C_N), 70.51 (C_t, C-9a), 68.10 (C_t, C_N), 65.62 (C_t, C_H), 65.20 (C_t, C_H), 53.21 (C_s, C_N), 53.12 (C_s, C_H), 48.35 (C_q), 47.76 (C_q), 45.95 (C_t or C_p, C_H), 45.54 (C_t or C_p, C_N), 44.82 (C_t or C_p, C_H), 44.63 (C_t or C_p, C_N), 38.54 (C_s), 36.00 (C_t or C_p, C_H), 35.49 (C_p, C9-$\underline{C}H_3$), 33.12 (C_s, C_H), 32.84 (C_s, C_N), 32.25 (C_s, C_N), 32.16 (C_s, C_H), 27.33 (C_s), 26.06 (C_s), 20.91 (C_p, C_H), 20.8 (C_p, C_N), 19.92 (C_p), 19.05 (C_p, C_H), 18.97 (C_p, C_N).

{(1S,5R,7R)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-yl}-[(9-methyl-4-phenyl-2,3,9,9a-tetrahydro-1H-carbazol-1-yl]methanone (**8c***). From vinylindole **3** (470 g, 2.03 mmol) and **7*** (100 mg, 0.37 mmol). Reaction conditions: 24 h at 20 °C, then change of solvent to dry toluene, addition of 0.1 ml $EtAlCl_2$ (1.8 M solution, 0.18 mmol) at –60 °C, 18 h at 20 °C. Work-up: after addition of 10 ml of distilled water and filtration, the organic layer was washed with saturated $NaHCO_3$ solution and then with brine. The organic layer was dried with $MgSO_4$ and concentrated. The product was easily separated by column chromatography [petroleum ether/ethyl acetate (5/1)] and can be crystallized from petroleum ether/ethyl acetate to furnish a yellow, fluorescent powder. Yield: 50 mg (27%), m.p. 208 °C. CD (methanol, *c* = 0.376 mMol/l, d = 0.02 cm) λ_{max} [nm] (Δε): 351.6 (–5.022), 344.4 (–5.045), 280.0 (–10.490), 244.0 (31.984), 198.8 (–55.556), 190.0 (–32.024). EI-MS *m/z* (rel. intensity %) = 503.2 (isotope peak, 4.7), 502.2 ($M^{+\cdot}$, 14.2), 438.3 (M – SO_2, 3.3), 288.4 (M – $C_{10}H_{16}NO_2S$, 5.0), 262.4 (isotope peak, 2.7), 261.4 (isotope peak, 25.2), 260.4 (288 – CO, 100), 259.5 (260 – H, 91.1), 258.5 (260 – H_2, 85.1), 257.4 (259 – H_2, 20.2), 256.4 (257 – H, 2.9), 244.4 (259 – CH_3, 9.1), 243.4 (258 – CH_3, 10.9), 234.4 (233 + H, 15.3), 233.5 (retro-Diels-Alder reaction, $C_{17}H_{15}N$, 71.8), 232.5 (233 – H, 16.2), 218.4 (233 – CH_3, 16.9), 182.5 (259 – C_6H_5, 17.7). ^{1}H-NMR (CD_2Cl_2, 200 MHz): δ = 7.44-7.32 (m, 3H, 3"-H, 4"-H, 5"-H), 7.29-7.22 (m, 2H, 2"-H, 6"-H), 6.99 [d (pseudo-t), 1H, ^4J = 1.7 Hz, *J* = 7.45 Hz, 7.36 Hz, 6-H or 7-H], 6.53 (d, 1H, ^3J = 7.91 Hz, 5-H or 8-H), 6.39-6.27 (m, 2H, 7-H or 6-H, 8-H or 5-H), 4.32-4.23 (m, 1H, $^3J_{9aH,1H}$ = 9.6 Hz, 9a-H), 4.01 (pseudo-t, 1H, *J* = 6.4 Hz, 6.3 Hz, 5'-H), 3.59 (d, 1H, ^2J = 13.9 Hz, 4'-H_a), 3.52 (d, 1H, ^2J = 13.9 Hz, 4'-H_b), 3.29-3.18 (m, 1H, 1-H), 2.72 (s, 3H, 9-CH_3), 2.58-2.50 (m, 2H, 3-H_a, 7'-H), 2.31-2.21 (m, 1H, 2-H_a), 2.17-2.13 (m, 2H, 6'-H_a, 6'-H_b), 2.03-1.82 (m, 4H, 2-H_b, 3-H_b, 8'-H_a, 8'-H_b), 1.51-1.26 (m, 2H, 9'-H_a, 9'-H_b), 1.23 (s, 3H, 10'-CH_3), 1.01 (s, 3H, 10'-CH_3). ^{13}C-NMR (CD_2Cl_2, spin echo and DEPT experiment, 100.6 MHz): δ = 175.24 (C_q, carbonyl-C), 155.45 (C_q), 142.23 (C_q), 132.34 (C_q), 130.48 (C_q), 129.09 (C_t, $2C_{aromatic}$), 129.02 (C_t), 128.53 (C_t, presumably $2C_{aromatic}$), 127.51 (C_t), 127.05 (C_q), 123.28 (C_t), 118.37 (C_t), 108.65 (C_t), 70.91 (C_t, C-9a), 66.14 (C_t, $R^1R^2\underline{C}NSO_2R^3$), 53.4 ($C_s$), 48.85 ($C_q$), 48.16 ($C_q$), 46.15 ($C_t$), 45.45 ($C_t$), 38.97 ($C_s$), 36.60 ($C_p$, N9-$CH_3$), 33.47 ($C_s$), 32.88 ($C_s$), 26.74 ($C_s$), 26.64 ($C_s$), 21.25 ($C_p$, 10'-$CH_3$), 20.09 ($C_p$, 10'-$CH_3$).

{(1R,5S,7S)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-yl}-[(9-methyl-4-phenyl-2,3,9,9a-tetrahydro-1H-carbazol-1-yl]methanone (**8c**). From vinylindole **3** (470 g, 2.03 mmol) and **7** (110 mg, 0.4 mmol). Reaction conditions: 18 h at 20 °C. Work-up: isolation by column chromatography [petroleum ether/ethyl acetate (5/1)] and crystallization from petroleum ether/ethyl acetate furnished yellow fluorescent crystals suitable for X-ray crystallography. Yield: 50 mg (24%), m.p. 232 °C (the differing melting points of the enantiomers could be due either to different crystal modifications or to solvates). CD (methanol, *c* = 0.471 mMol/l, d = 0.02 cm) λ_{max} [nm] (Δε): 350.4 (5.033), 279.8 (10.508), 246.2 (–31.456), 242.0 (–31.311), 199.2 (58.475). Anal. calcd. for $C_{30}H_{34}N_2O_3S$ (502.68): C 71.68, H 6.82, N 5.57. Found: C 71.50, H 6.81, N 5.51. EI-MS *m/z* (rel. intensity %) = 503.2 (isotope peak, 4.7), 505.2 ($M^{+\cdot}$, 14.2), 438.3 (M – SO_2, 3.3), 288.4 (M – $C_{10}H_{16}NO_2S$, 5.0), 262.4 (isotope peak, 2.7), 261.4 (isotope peak, 25.2), 260.4 (288 – CO, 100), 259.5 (260 – H, 91.1), 258.5 (260 – H_2, 85.1), 257.4 (259 – H_2, 20.2), 256.4 (257 – H, 2.9), 244.4 (259 – CH_3, 9.1), 243.4 (258 – CH_3, 10.9), 234.4 (233 + H, 15.3), 233.5 (retro-Diels-Alder reaction, $C_{17}H_{15}N$, 71.8), 232.5 (233 – H, 16.2), 218.4 (233 – CH_3, 16.9), 182.5 (259 – C_6H_5, 17.7). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.37 (pseudo-t, 2H, *J* = 7.65 Hz, 7.29 Hz, 3"-H, 5"-H), 7.30 (pseudo-t, 1H, *J* = 7.38 Hz, 7.27 Hz, 2 long-range couplings of 1.3 Hz each, 4"-H), 7.23 (d, 2H, *J* = 8 Hz, 2"-H, 6"-H), 6.97 [d (pseudo-t), 1H, *J* = 7.67 Hz, 7.36 Hz, ^4J = 1.44

Hz, 6-H or 7-H], 6.49 (d, 1H, ^3J = 7.94 Hz, 5-H or 8-H), 6.37-6.30 (m, 2H, 7-H or 6-H, 8-H or 5-H), 4.34-4.30 (m_c, 1H, 9a-H), 3.99 (pseudo-t, 1H, J = 6.44 Hz, 6.27 Hz, 5'-H), 3.55 (d, 1H, ^2J = 13.78 Hz, 4'-H_a), 3.47 (d, 1H, ^2J = 13.78 Hz, 4'-H_b), 3.32-3.27 (m, 1H, 1-H), 2.72 (s, 3H, 9-CH_3), 2.57-2.53 (m, 2H, 3-H_a, 7'-H), 2.31-2.28 (m, 1H, 2-H_a), 2.17-2.15 (m, 2H, 6'-H_a, 6'-H_b), 2.03-1.88 (m, 4H, 2-H_b, 3-H_b, 8'-H_a, 8'-H_b), 1.47-1.35 (m, 2H, 9'-H_a, 9'-H_b), 1.23 (s, 3H, 10'-CH_3), 0.99 (s, 3H, 10'-CH_3). ^{13}C-NMR ($CDCl_3$, spin echo and experiment, 100.6 MHz): δ = 175.22 (C_q, carbonyl-C), 154.91 (C_q), 141.72 (C_q), 131.97 (C_q), 129.95 (C_q), 128.68 (C_t, 2$C_{aromatic}$), 128.59 (C_t), 128.16 (C_t, presumably 2$C_{aromatic}$), 127.09 (C_t), 126.59 (C_q), 122.99 (C_t), 117.97 (C_t), 108.16 (C_t), 70.31 (C_t, C-9a), 65.58 (C_t, $R^1R^2\underline{C}NSO_2R^3$), 53.16 ($C_s$), 48.41 ($C_q$), 47.81 ($C_q$), 45.74 ($C_t$), 44.87 ($C_t$), 38.58 ($C_s$), 36.06 ($C_p$, N9-$CH_3$), 33.15 ($C_s$), 32.44 ($C_s$), 26.45 ($C_s$), 26.29 ($C_s$), 20.93 ($C_p$, 10'-$CH_3$), 19.94 ($C_p$, 10'-$CH_3$).

{(1S,5R,7R)-10,10-Dimethyl-3,3-dioxo-3-thia-4-azatricyclo[5.2.1.0^{1,5}]decan-4-yl}-[9-methyl-4-(2-methyl-1H-indol-2-yl)propyl]-2,3,9,9a-tetrahydro-1H-carbazol-1-yl]methanone (**8d***). Isolated as a second fraction from the reaction leading to **8b***/**9b*** in the form of a white crystalline powder. Yield: 12 mg (2%), m.p. 194 °C (petroleum ether/ethyl acetate). EI-MS: *m/z* (rel. intensity %) = 612.2 (isotope peak and M + H, 0.5), 611.3 ($M^{+\cdot}$, 1.0), 442.1 (440 + H_2, 1.1), 441.1 (440 + H, 2.5), 440.2 (M – $C_{12}H_{13}N$, 5.7), 439.3 (M – $C_{12}H_{14}N$, 16.9), 425 (440 – CH_3, 0.6), 342 (retro-Diels-Alder reaction, $C_{12}H_{13}N$, 0.5), 327 (342 – CH_3, 0.3), 315 (342 – CH_2 – CH, 3.3), 287 ($C_{14}H_{11}N_2O_3S$, 1.6), 223.2 ($C_{16}H_{17}N$, 5.6), 197.2 ($C_{14}H_{15}N$, 11.7), 196.2 (197 – H, 43.7), 195.2 (197 – H_2, 3.6), 182.1 ($C_{13}H_{12}N$, 4.5), 181.1 (182 – H, 7.3), 173.1 (172 + H, 16.0), 172.1 ($C_{12}H_{14}N$ and 171 + H, 100), 171.1 ($C_{12}H_{13}N$, 6.9), 170.1 (171 – H, 172 – H_2, 8.6), 157.1 (156 + H, 6.6), 156.1 (171 – CH_3, 8.6), 144.1 (172 – C_2H_4, 5.2), 132 (C_9H_8N + H, 3.7), 131 (C_9H_8N, 7.7), 128 (131 – H – H_2, 4.1), 127 (131 – H – H_2 - H, 4.6), 115 (C_8H_5N, 4.5). ^{1}H-NMR (CD_2Cl_2, 400 MHz): δ = 7.81 (d, 1H, ^3J = 8.07 Hz, 4'''-H or 7'''-H), 7.54 (d, 1H, ^3J = 7.41 Hz, 5-H), 7.30 (d, 1H, ^3J = 8.23 Hz, 7'''-H or 4'''-H), 7.18 [d (pseudo-t), 1H, J = 7.06 Hz, 8.13 Hz, ^4J = 1 Hz, 5'''-H or 6'''-H], 7.10-7.04 (m, 2H, 6'''-H or 5'''-H, 6-H or 7-H), 6.81 (s, 1H, 2'''-H), 6.68 [d (pseudo-t), 1H, J = 7.53 Hz, 7.49 Hz, ^4J = 0.8 Hz, 7-H or 6-H], 6.54 (d, 1H, ^3J = 7.84 Hz, 8-H), 4.11 (m_c, 1H, 9a-H), 3.91 (pseudo-t, J = 6.93 Hz, 5.80 Hz, 5'-H), 3.73 (s, 1H, 1'''-CH_3), 3.52 (d, 1H, ^2J = 13.90 Hz, 4'-H_a), 3.44 (d, 1H, ^2J = 13.46 Hz, 4'-H_b), 3.07 (d, 1H, ^2J = 13.46 Hz, 1''-H_a), 2.94 (d, 1H, ^2J = 13.52 Hz, 1''-H_b), 2.94-2.85 (broad m, 1H, 1-H), 2.67 (s, 3H, 9-CH_3), 2.09-2.07 (m, 2$H_{aliphatic}$), 1.92-1.87 (m, 3$H_{aliphatic}$), 1.75-1.68 (m, 2$H_{aliphatic}$), 1.65-1.60 (m 1$H_{aliphatic}$), 1.56 (s, 3H, 2''-CH_3), 1.52 (s, 3H, 3''-H), 1.47-1.31 (m, 4$H_{aliphatic}$), 1.18 (s, 3H, 10'-CH_3), 0.98 (s, 3H, 10'-CH_3). ^{13}C-NMR (CD_2Cl_2, spin echo experiment, 100.6 MHz): δ = 175.69 (C_q, carbonyl-C), 155.59 (C_q), 138.38 (C_q), 132.92 (C_q), 130.93 (C_q), 128.48 (C_t), 127.84 (C_q), 126.77 (C_q), 125.84 (C_t), 124.74 (C_q), 123.96 (C_t), 121.79 (C_t), 121.34 (C_t), 118.59 (C_t), 118.17 (C_t), 109.78 (C_t), 108.41 (C_t), 70.89 (C_t), 66.00 (C_t), 53 (C_s), 48.77 (C_q), 48.11 (C_q), 46.45 (C_t or C_p), 45.40 (C_t or C_p), 44.65 (C_s or C_q), 38.96 (C_s or C_q), 36.72 (C_s or C_q), 36.44 (C_t or C_p), 33.41 (C_s or C_q), 32.86 (C_t or C_p), 30.79 (C_s or C_q), 30.27 (C_t or C_p), 28.78 (C_t or C_p), 26.71 (C_s or C_q), 26.62 (C_s or C_q), 21.19 (C_p), 20.05 (C_p).

14-Methyl-9-phenyl-7,7a,8,14a,14b,15-hexahydro-7,15-dithiadinaphtho[2,1-d:1',2'-f]cycloocta[2,1-a]-1H-carbazole 7,7,15,15-tetraoxide [(±)-**11a**]. From vinylindole **3** (240 mg, 1.1 mmol) and (±)-**10**[15-17] (33 mg, 0.08 mmol). Reaction conditions: 2 h at 20 °C; the dienophile has been consumed quantitatively (TLC monitoring). Work-up: the product was isolated by FC [petroleum ether/ethyl acetate (3/1)]. Yield: 25 mg (49%); m.p. 210 °C (decomp., from petroleum ether/ethyl acetate). FD-MS: *m/z* (rel. intensity %) = 641 (isotope peak, 25), 640 (isotope peak, 12), 639 ($M^{+\cdot}$, 100), 605 (5), 604 (20), 603 (M – 2 H_2O), 348 ($C_{20}H_{12}O_2S_2^{+\cdot}$, 2), 337 ($C_{19}H_{13}NO_3S^{+\cdot}$, 9), 316 ($C_{20}H_{12}O_2S^{+\cdot}$, 40), 300 (316 – O, 2), 284 (316 – 2 O, 8), 257 ($C_{19}H_{15}N^{+\cdot}$, 7). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.29 (d, 1H, ^3J = 8.87 Hz, 6-H or 16-H), 8.25 (d, 1H, ^3J = 8.92 Hz, 16-H or 6-H), 8.16 (d, 1H, ^3J = 8.84 Hz, 5-H or 17-H), 8.12 (d, 1H, ^3J = 8.92 Hz, 17-H or 5-H), 8.03 (d, 1H, ^3J = 8.18 Hz, 18-H or 21-H or 4-H or 1-H), 7.98 (d, 1H, ^3J = 8.21 Hz, 1-H or 4-H or 21-H or 18-H), 7.66-7.60 (m, 2H, ^4J = 1.0 Hz, 0.8 Hz, respectively, 2-H and 20-H or 3-H and 19-H), 7.44-7.33 (m, 5H, *m*- and *p*-phenyl-H, 3-H and 19H, or 2-H and 20-H), 7.30 (dd, 2H, ^3J = 7.49 Hz, ^4J = 1.47 Hz, *o*-phenyl-H), 7.19 (d,

1H, ^3J = 8.46 Hz, 21-H or 18-H, or 1-H or 4-H), 7.09 (pseudo-t, 1H, ^4J = 1.1 Hz, J = 7.72 Hz, 7.61 Hz, 11-H or 12-H), 7.05 (d, 1H, ^3J = 8.45 Hz, 1-H or 4-H, or 21-H or 18-H), 6.66 (d, 1H, ^3J = 7.96 Hz, 10-H or 13-H), 6.60 (d, 1H, ^3J = 7.14 Hz, 13-H or 10-H), 6.47 (pseudo-t, 1H, ^4J = 0.74 Hz, J = 7.48 Hz, 7.52 Hz, 12-H or 11-H), 4.89 (d, 1H, ^3J = 3 Hz, one homoallylic coupling < 1 Hz with 8-H$_\beta$, 14a-H$_\alpha$), 4.18 (m, 1H, ^3J = 3 Hz, 6 Hz, one W-coupling with 8-H$_\alpha$, 14b-H$_\alpha$), 3.71 (ddd, 1H, ^3J = 3 Hz, 6 Hz, 12 Hz, 7a-H$_\alpha$), 2.98 (m, 1H, 8-H$_\alpha$), 2.90 (m, 1H, ^3J = 3 Hz, 12 Hz, 8-H$_\beta$). ^{13}C-NMR ($CDCl_3$, 100.6 MHz); (2 C_q and 5 C_t atoms cannot be discerned in the aromatic resonance region because of coincidental isochronism) : δ = 148.1 (C_t), 140.19 (C_q), 138.5 (C_t), 137.79 (C_q), 135.81 (C_q), 135.06 (C_q), 134.98 (C_q), 133.3 (C_q), 132.90 (C_q), 132.85 (C_q), 132.60 (C_q), 131.09 (C_t), 130.8 (C_q), 129.90 (C_t), 129.67 (C_t), 129.38 (C_t), 128.81 (C_t), 128.38 (C_t), 125.95 (C_t), 125.2 (C_q), 124.18 (C_t), 122.56 (C_t), 119.4 (C_t), 110.0 (C_t), 66.44 (C_t, $C_{aliphatic}$), 63.80 (C_t, $C_{aliphatic}$), 63.20 (C_t, $C_{aliphatic}$), 34.6 (C_p, N-CH_3), 30.97 (C_s, C8).

*9,14-Dimethyl-7,7a,8,14,14a,14b-hexahydro-7,15-dithiadinaphtho[2,1-*d*:1',2'-f]cycloocta[2,1-*a*]-1H-carbazole 7,7,15,15-tetraoxide* [(±)-**11b**)] [*together with* (±)-**11c**]. From vinylindole **2** (310 mg, 1.8 mmol) – which dimerizes in varying extents to **4** – and (±)-**10** (100 mg, 0.25 mmol). Reaction conditions: 2 h at 20 °C. Work-up: FC [petroleum ether/ethyl acetate (3/1)] furnishes not only the Diels-Alder adduct of the monomer **2** but also that of the dimeric vinylindole **4** in a ratio of approx. 1:3 (by NMR). We were not able to separate these two species by CC as a consequence of the abundant aromatic groups. Yield: 40 mg, m.p. of mixture: 202 °C (decomp., from petroleum ether/ethyl acetate).

(±)-**11b**: FD-MS: *m/z* (rel. intensity %) = 578 (isotope peak, 6), 577 ($M^{+\cdot}$, 30), 543 (isotope peak, 13), 542 (isotope peak, 26), 541 ($M^{+\cdot}$ – 2 H_2O, 100), 529 ($M^{+\cdot}$ – $SO^{\cdot}$, 2). ^{1}H-NMR ($CDCl_3$, 400 MHz; signals extracted from a spectrum of the mixture (±)-**11b**/(±)-**11c**): δ = 8.24-6.68 (m, 16$H_{aromatic}$), 4.7 (m, 1H, $^5J_{14a\text{-}H\alpha,9\text{-}Me}$ = 3 Hz, $^5J_{14a\text{-}H\alpha,8\text{-}H\beta}$ = 3 Hz, $^3J_{14a\text{-}H\alpha,14b\text{-}H\alpha}$ = 4-5 Hz, 14a-H$_\alpha$), 4.1 (d, 1H, $^4J_{14b\text{-}H\alpha,8\text{-}H\alpha}$ < 1 Hz, $^3J_{14b\text{-}H\alpha,7a\text{-}H\alpha}$ = 3 Hz, $^3J_{14b\text{-}H\alpha,14a\text{-}H\alpha}$ = 4-5 Hz, 14b-H$_\alpha$), 3.5 (ddd, $^3J_{7a\text{-}H\alpha,8\text{-}H\alpha}$ = 3 Hz, $^3J_{7a\text{-}H\alpha,14b\text{-}H\alpha}$ = 3 Hz, $^3J_{7a\text{-}H\alpha,8\text{-}H\beta}$ = 12 Hz, 7a-H$_\alpha$), 2.95 (s, 3H, N14-CH_3), 2.7 (m, 1H, $^5J_{8\text{-}H\beta,14a\text{-}H\alpha}$ = 3 Hz, $^3J_{8\text{-}H\beta,7a\text{-}H\alpha}$ = 12 Hz, $^2J_{8\text{-}H\beta,8\text{-}H\alpha}$ = 15 Hz, 8-H$_\beta$), 2.6 (dd, 1H, $^3J_{8\text{-}H\alpha,7a\text{-}H\alpha}$ = 3 Hz, $^2J_{8\text{-}H\alpha,8\text{-}H\beta}$ = 15 Hz, 8-H$_\alpha$), 2.1 (d, 3H, $^5J_{9\text{-}Me,14a\text{-}H\alpha}$ = 3 Hz, 9-CH_3).

*14-Methyl-9-[2-methyl-2-(1-methyl-1H-indol-3-yl)-propyl]-7,7a,8,14a,14b,15-hexahydro-7,15-dithiadinaphtho[2,1-*d*·1',2'-f]cycloocta[2,1-*a*]-1H-carbazole 7,7,15,15-tetraoxide* [(±)-**11c**]. EI-MS: *m/z* (rel. intensity) = 751 (isotope peak, 2.7), 750 (isotope peak, 10), 749 (isotope peak, 24), 748 ($M^{+\cdot}$, 46). ^{1}H-NMR ($CDCl_3$, 400 MHz; signals extracted from a spectrum of the mixture (±)-**11b**/(±)-**11c**): δ = 8.24-6.59 (m, 21$H_{aromatic}$), 4.65 (m, 1H, $^3J_{14a\text{-}H\alpha,14b\text{-}H\alpha} \leq 3$ Hz, $^5J_{14a\text{-}H\alpha,8\text{-}H\beta}$ = 3 Hz, 14a-H$_\alpha$), 3.9 (m, 1H, $^3J_{14b\text{-}H\alpha,14a\text{-}H\alpha} \leq 3$ Hz, $^3J_{14b\text{-}H\alpha,7a\text{-}H\alpha}$ = 4-5 Hz, 14b-H$_\alpha$), 3.45 (s, 3H, N1'''-CH_3), 3.2 (ddd, 1H, $^3J_{7a\text{-}H\alpha,8\text{-}H\alpha}$ = 3 Hz, $^3J_{7a\text{-}H\alpha,14b\text{-}H\alpha}$ = 4-5 Hz, $^3J_{7a\text{-}H\alpha,8\text{-}H\beta}$ = 12 Hz, 7a-H$_\alpha$), 3.1 (d, 1H, $^2J_{1''\text{-}H,1''\text{-}H}$ = 10 Hz, 1''-H), 3.05 (d, 1H, $^2J_{1''\text{-}H,1''\text{-}H}$ = 10 Hz, 1''-H), 2.9 (s, 3H, N14-CH_3), 1.9 (dd, 1H, $^4J_{8\text{-}H\alpha,14b\text{-}H\alpha}$ = 1-2 Hz, $^3J_{8\text{-}H\alpha,7a\text{-}H\alpha}$ = 3 Hz, $^2J_{8\text{-}H\alpha,8\text{-}H\beta}$ = 15 Hz, 8-H$_\alpha$), 1.7 (m, 1H, $^5J_{8\text{-}H\beta,14a\text{-}H\alpha}$ = 3 Hz, $^3J_{8\text{-}H\beta,7a\text{-}H\alpha}$ = 12 Hz, $^2J_{8\text{-}H\beta,8\text{-}H\alpha}$ = 15 Hz, 8-H$_\beta$), 1.55 (s, 3H, CH_3), 1.45 (s, 3H, CH_3).

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