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Reactions of (*S*)-(+)-4-ethenyl[2.2]paracyclophane with heterocyclic quinones

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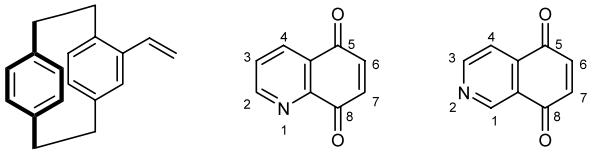
Abstract—The reactions of (*S*)-(+)-4-ethenyl[2.2]paracyclophane **1** and 1-vinylnaphthalene **11** with quinoline-5,8-dione **2** and isoquinoline-5,8-dione **3** have been studied under high pressure and Lewis acid-catalyzed conditions. In contrast to the reactivity of diene **11**, diene **1** was found to add to quinones **2** and **3** in an abnormal fashion. A structural analysis of the reaction products by ^{1}H and ^{13}C NMR spectroscopy is presented.

1. Introduction

As a continuation of our study on the synthesis of optically active helical cyclophanes bearing polycyclic aromatic units,[1–3] we have studied the Diels–Alder reaction between (*S*)-(+)-4-ethenyl[2.2]paracyclophane **1** and the heterocyclic quinones **2** and **3** in order to synthesize heterohelicenophanes using a two-step approach that was previously developed in our laboratory.[1–4]

These dienophiles are seldom used in the cycloaddition reactions presumably because of their low stability and the reactions usually involve highly reactive electron-rich dienes. Compound **1** is an inner–outer styrene-like diene and is, therefore, of low reactivity.[5]

Herein we report the results of the reactions of diene **1** with quinoline-5,8-dione **2** and isoquinoline-5,8-dione **3** (Scheme 1).



(*S*)-(+)- **1** **2** **3**

Scheme 1.

2. Results and discussion

The reactions of heterocyclic quinones **2** and **3** were examined under a variety of experimental conditions that are summarized in Table 1. When the reactions were carried out under thermal conditions in the presence of trichloroacetic acid, complex mixtures were obtained and no product was isolated. Under the same conditions, using the carbocyclic analogue, 1,4-naphthoquinone **4**, a 1.7:1 mixture of compounds **5** and **6** was obtained as previously shown[2] (Scheme 2). The heterocyclic quinones **2** and **3** behaved differently when the reactions were catalyzed by boron trifluoride at atmospheric pressure. Whereas unchanged reactants were recovered in the reaction of quinone **2**, product **7** in reasonable yield (30%) was obtained in the reaction of quinone **3** (Scheme 2). Although this compound could not be characterized because it was unstable and very sensitive to oxygen, IR and ^{1}H NMR measurements of the crude product allowed the structure to be tentatively assigned. Further support for the structure of **7** was given by the NMR spectroscopic analysis of the diacetoxy derivative **8** prepared by treating **7** with zinc in acetic anhydride.

High pressure was used[6] in an attempt to accelerate the cycloaddition reactions but both quinones **2** and **3** completely decomposed under these conditions. Surprisingly, when the reaction mixtures were treated under high pressure but in the presence of a Lewis acid ($BF_3{\cdot}Et_2O$), the quinones did not decompose. In contrast to isoquinoline-5,8-dione **3** that afforded a complex mixture from which no product could be isolated, quinoline-5,8-dione **2** regiospecifically gave the

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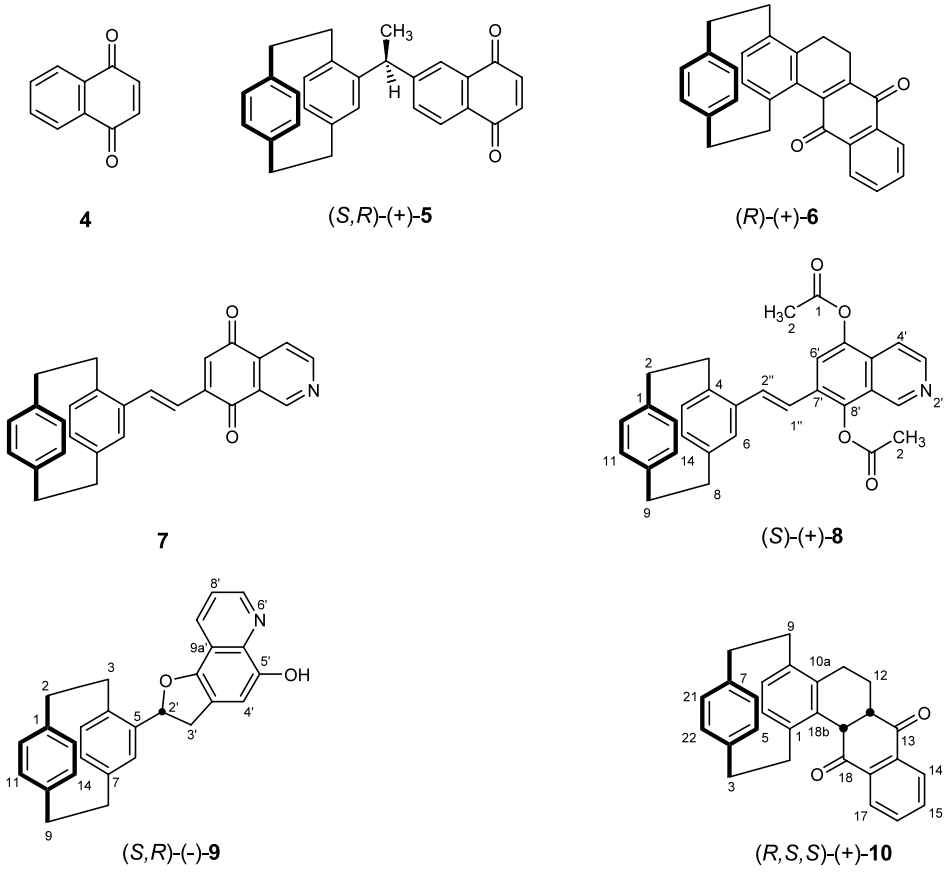
Table 1. Reaction conditions of the Diels–Alder reaction of dienes **1** and **11** with dienophiles **2**–**4**

Reactants	Conditions	Products (ratio)	Yield (%)
1–**2**	6 kbar, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 50°C, 16 h[a]	**9**	53
1–**2**	6 kbar, CH_2Cl_2, 50°C, 18 h	–	–
1–**3**	$BF_3{\cdot}Et_2O$, toluene, 120°C, 18 h[b]	**7**	30
1–**3**	6 kbar, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 50°C, 16 h[b]	–	–
1–**4**	8 kbar, CCl_3COOH, toluene, rt, 18 h[b]	**10**, **6** (7.6:1)	68
1–**4**	8 kbar, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 50°C, 16 h	–	–
1–**4**[2]	CCl_3COOH, toluene, reflux, 18 h[b]	**5**, **6** (1.7:1)	57
11–**2**	$BF_3{\cdot}Et_2O$, toluene, rt, 2 h	**12**	62
11–**3**	$BF_3{\cdot}Et_2O$, toluene, rt, 2 h	**13**	58

[a] No product was detected at atmospheric pressure.
[b] No product was detected in uncatalyzed reactions.



Scheme 2.

furoquinoline **9** in good yield (53%) as shown by NMR spectroscopy (Scheme 2).

Regiospecific formation of furoquinolines was previously observed in a reaction of quinone **2** and 1-aza-3-substituted dienes and was rationalized[7] by assuming a nucleophilic attack of the diene at the activated C-6 position of **2**, followed first by a cyclization with a carbonyl function and then by aromatization. In our case, the nucleophilic diene attack was favored by the presence of a Lewis acid.

In contrast to quinoline-5,8-dione **2**, isoquinoline-5,8-dione **3** regioselectively and stereoselectively gave the trans-stilbene-like compound **7**. To the best of our knowledge this is the first example of a reaction between heterocyclic quinones and dienes that has led to stilbenes. We cannot suggest the sequence of events that led to compound **7**; however, we can assume that the sequence first involves a nucleophilic diene attack at the C-7 position of the isoquinoline-5,8-dione **3** activated by the interaction of boron trifluoride with nitrogen and the carbonyl oxygen at C-5, thus controlling the regioselectivity. These unexpected results stimulated us to re-examine the Diels–Alder reaction of 1,4-naphthoquinone **4** with diene **1** under high pressure conditions. Pressure alone did not accelerate the reaction. However, when the reaction was carried out under high

pressure and in the presence of trichloroacetic acid, a 7.6:1 mixture of the Diels–Alder cycloadduct **10** and its dihydroderivative **6** was obtained in very good yield (68%). The reaction was *anti*- (with respect to the unsubstituted benzene ring) diastereoselective and the presence of compound **6** clearly indicated that 1,4 naphthoquinone **4** also acted as an oxidant. A comparison of these results with those previously obtained under thermal conditions[3] demonstrated that pressure markedly affects the reactions and strongly favors the Diels–Alder reaction because the pressure-induced acceleration is probably greater[5c,6] in this reaction.

To gain more information about the reactivity of heterocyclic quinones **2** and **3**, we have also examined the Diels–Alder reactions of **2** and **3** with 1-vinylnaphthalene **11**, a more reactive inner-outer ring diene.[5b,c] The reactions of diene **11** with dienophiles **2** and **3** occurred easily at room temperature and led regioselectively and in good yield to the aromatized compounds **12** and **13**, (Scheme 3) respectively, thus showing that **11** added to both **2** and **3** in a normal fashion. The cycloadducts could not be isolated because they were oxidized under the reaction conditions to the fully aromatized products.

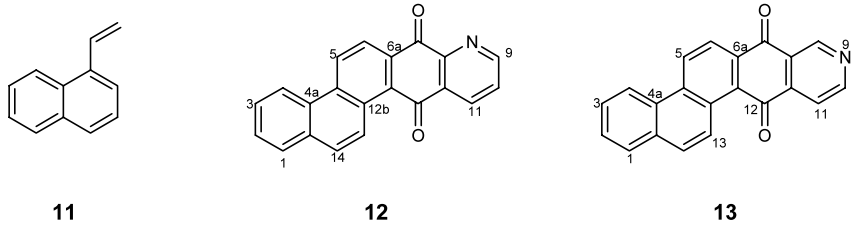
The results of this study point out that heterocyclic quinones react differently depending on the diene reactivity. This is in line with the results of previous studies[8–12] on reactions of heterocyclic quinones with reactive electron-rich dienes in which the reactants easily underwent Diels–Alder cycloaddition reactions.

3. Structural analysis

To determine the structure of compounds, extensive ^{1}H and ^{13}C NMR investigations are required, especially ^{1}H-{^{1}H}NOE experiments and long-range hetero-correlations (HMBC and INEPT-long range spectra). A common feature of the [2.2]paracyclophane units in **8–10** is that the aromatic protons have rather high-field chemical shifts (6.33–6.61 ppm). This is the consequence of the mutual magnetic anisotropy of the aromatic rings, which are in a quasi parallel position.[13] These results are summarized in Figure 1 for compounds **8–10**.

3.1. Compounds 7 and 8

Firstly, the structure of **7** was tentatively assigned on the basis of IR and ^{1}H NMR spectra. The absorption at 1673 and 1659 cm^{-1} in the IR spectrum revealed the presence of a quinoid system, while the shifts of H(1″) and H(2″), as well as the $^{3}J_{1'',2''}$ value (16.2 Hz) in the



Scheme 3.

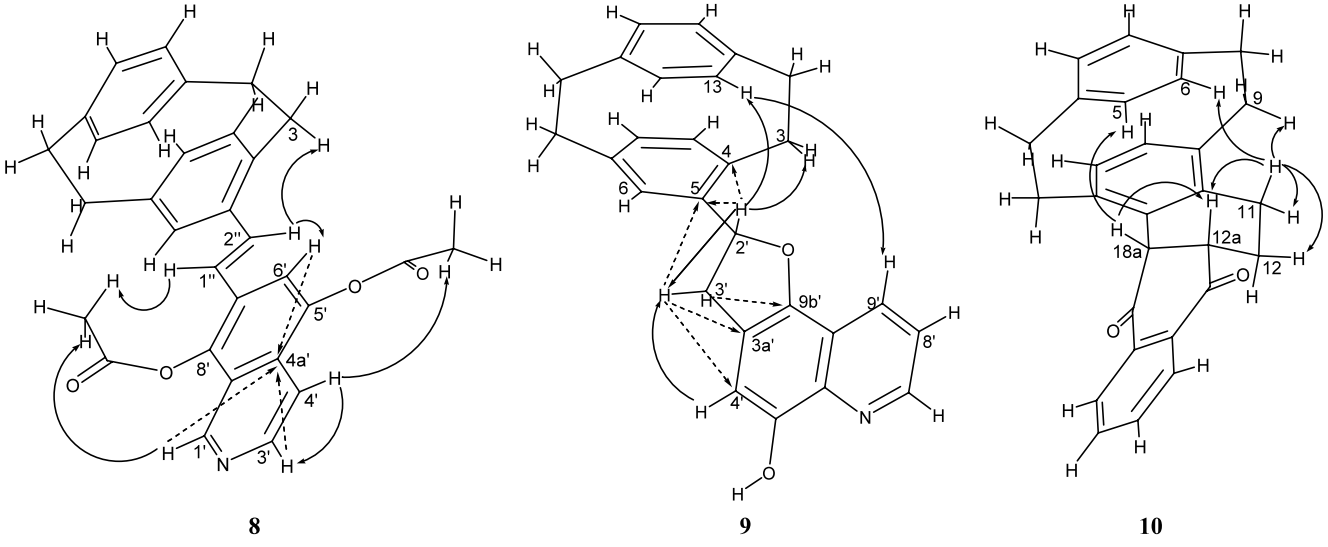


Figure 1. Minimized energy conformations of compounds **8–10**; the arrows indicate observed NOEs; dotted arrows indicate long-range hetero-correlation's.

^{1}H NMR spectrum indicated the presence of a *trans*-olefin moiety. The structure assignment of **7** was confirmed from extensive NMR analysis of compound **8** prepared from **7**. The proton spectrum of **8** revealed that it was an alkene, *trans*-disubstituted ($J_{1'',2''}=16.1$ Hz) with a [2.2]paracyclophane and an isoquinoline unit. Support for the structure assignment of **8** was also given by the long-range hetero-correlations observed on the C(4a′) upon selective irradiation of C(1′)H, C(3′)H and C(6′)H and by NOE measurements. Selective pre-irradiation of the C(2″)H resonance gave NOE on the signals attributed to C(3)H and C(6′)H, while enhancement of the C(8′) acetyl protons was observed upon selective irradiation of the resonances attributed to C(1′)H and C(1″)H, thus indicating the connection of the C(1″) with C(7′). Finally, the structure for **8** was also confirmed by the NOEs observed on C(3′)H and C(5′) acetyl protons upon selective irradiation of C(4′)H.

3.2. Compound 9

The ^{1}H and ^{13}C NMR spectra revealed the presence of [2.2]paracyclophane, dihydrofuran and quinoline units. The C(3a′)-C(9b′) junction between dihydrofuran and quinoline ring was assured by long-range hetero-correlation experiments. C(3′)H_s protons gave long-range correlations with C(3a′), C(4′), C(5) and C(9b′), while C(2′)H was correlated with C(4), C(5) and C(6) carbons. The configuration of the C(2′) carbon is supported by ^{1}H-{^{1}H}NOE experiments. Selective pre-irradiation of the C(2′)H resonance resulted in signal enhancement of the resonances attributed to C(3)H, C(3′)H and C(13)H, while saturation of C(4′)H enhanced the signal of C(3′)H. Further support for the structure assignment was also given by the NOE observed between C(13)H and C(9′)H.

3.3. Compound 10

The *cis*-relationship of C(12a)H and C(18a)H followed from the $^3J_{12a,18a}$ value (5.6 Hz) and from the NOEs observed on C(5)H and C(12a)H upon irradiation of the resonance attributed to C(18a)H.

Furthermore, selective pre-irradiation of the C(11)H resonance gave NOEs on the signals attributed to C(6)H, C(9)H, C(12)H and C(12a)H, confirming a *cis*-relationship between C(12a)H, C(18a)H and the unsubstituted benzene ring of the paracyclophane unit (Fig. 1).

3.4. Compounds 12 and 13

The position of the nitrogen in the heterocyclic ring followed from the long-range hetero-correlations observed between C(6)H and C(7) and between C(11)H and C(12) for both compounds.

Further support for the structure assignment was also given by the NOE observed between C(4)H and C(5)H and by the deshielding of the C(13)H (9.48 ppm and 9.57 ppm for **12** and **13**, respectively) due to the anisotropy effect of the C(12) carbonyl function in both compounds.

4. Conclusions

This study makes a contribution to the chemistry of the heterocyclic quinones and is remarkable in view of the limited number of investigations on the reactivity of these dienophiles.[14] The most significant indication is that these quinones react with dienes in a normal fashion (Diels–Alder reaction) or an abnormal fashion depending on diene reactivity. Furthermore, high pressure activation markedly favors the cycloaddition reactions. New optically active naphthoacrydine derivatives have been prepared.

5. Experimental

5.1. General

Melting points were determined on a Büchi melting point apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$ solution on a Jasco DIP-360 polarimeter in a quartz cell at 25°C. IR spectra were recorded in $CHCl_3$ solution at rt on a Perkin–Elmer Paragon 500 FT-IR. NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument (internal Me_4Si). GC analyses were performed on a Hewlett-Packard 6890 chromatograph. Preparative HPLC was carried out on a Waters Prep LC 40 mm Assembly module (column: DeltaPak C18, 100 Å, 40× 100 mm) using a Waters 590 Pump and a Waters Lambda-Max 481 LC spectrophotometer at 254 nm. Analytical HPLC was done on a Hewlett–Packard 1100 instrument (column: Supelcosil LC-PAH, 5 μm, 150× 4.6 mm; mobile phase CH_3CN/H_2O 6:4; flow rate: 1 mL/min; detection: UV at 254 nm). Absorption chromatography was carried out on Riedel–de Haën silica gel (32-63 μm; 230–400 mesh ASTM). Quinoline-5,8-dione **2** and isoquinoline-5,8-dione **3** were prepared according to a previously reported procedure.[15]

5.2. Reaction of diene (*S*)-(+)-1 with isoquinoline-2,5-dione 3

$BF_3{\cdot}Et_2O$ (0.066 mL, 0.52 mmol) was added to a solution of isoquinoline-5,8-dione **3** (77 mg, 0.52 mmol) and diene **1** (100 mg, 0.43 mmol) in dry toluene. The mixture was heated at 120°C in a deaerated tube sealed under vacuum for 18 h. The solid product was separated by filtration; the filtrate was treated with a saturated aqueous $NaHCO_3$ solution and extracted with chloroform. The extract was then dried (Na_2SO_4) and concentrated in vacuo and the residue was chromatographed; elution with CH_2Cl_2/MeOH 99:1 afforded compound **7** (52 mg, 30%). This product was unstable and sensitive to oxygen and, therefore, could not be purified and characterized. Only IR and ^{1}H NMR spectra of the crude product could be measured. **7**: IR 1673, 1659 (s, C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.82–3.18 (m, 1H, H_s-2, H-3, H_s-8, H_s-9), 3.55 (m, 1H,

H-3), 6.36–6.61 (m, 6H, H-6, H-11, H-12, H-13, H-14, H-15, H-16), 6.75 (bs, 1H, H-6), 7.03 (d, 1H, $J=16.3$ Hz, H-1″), 7.16 (s, 1H, H-6′), 7.68 (d, 1H, $J=16.3$ Hz, H-2″), 7.84 (d, 1H, $J=5.7$ Hz, H-4′), 9.03 (d, 1H, $J=5.7$ Hz, H-3′), 9.38 (bs, 1H, H-1′).

When diene **1** and quinoline-5,8-dione **2** were treated under the same experimental conditions, no reaction occurred and the reactants were recovered.

The reductive acetylation of **7** with zinc in acetic anhydride afforded the diacetoxy derivative **8** in 80% yield. The reaction was carried out according to a previous procedure.[16] The product was purified by column chromatography; elution with hexane/EtOAc 80:20 gave a product that was then crystallized. (*S*)-(+)-**8**: mp 142°–143°C (hexane/EtOAc); $[\alpha]_D=+212$ (*c* 0.70, $CHCl_3$); IR 1765 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3H, 5′-OCOCH_3), 2.49 (s, 3H, 8′-OCOCH_3), 2.82–3.11 (m, 8H, H_s-2, H_s-3, H_s-8, H_s-9), 6.33 (dd, 1H, $J=7.8$, 1.8 Hz, H-14), 6.41 (d, 1H, $J=7.9$ Hz, H-16), 6.44 (dd, 1H, $J=7.9$, 1.8 Hz, H-12), 6.46 (dd, 1H, $J=7.9$, 1.8 Hz, H-11), 6.47 (dd, 1H, $J=7.9$, 1.7 Hz, H-15), 6.54 (d, 1H, $J=1.7$ Hz, H-6), 6.58 (dd, 1H, $J=7.8$, 1.8 Hz, H-13), 6.87 (d, 1H, $J=16.1$ Hz, H-1″), 7.14 (d, 1H, $J=16.1$ Hz, H-2″), 7.54 (d, 1H, $J=5.9$ Hz, H-4′), 7.74 (s, 1H, H-6′), 8.51 (d, 1H, $J=5.9$ Hz, H-3′), 9.17 (bs, 1H, H-1′); ^{13}C NMR ($CDCl_3$). δ 20.7 (8′-OCO**C**H_3), 21.2 (5′-OCO**C**H_3), 34.1 (C-3), 35.1, 35.5, 35.7 (C-2, C-8, C-9), 114.5 (C-4′), 120.2 (C-6′), 121.8 (C-1″), 123.5 (C-8a′), 128.8 (C-7′), 130.1 (C-4a′), 130.2 (C-13), 130.9 (C-6), 131.7 (C-2′), 131.9 (C-14), 133.0 (C-15), 133.3 (C-12), 133.4 (C-11), 135.3 (C-16), 137.1 (C-5), 139.2, 139.4, 139.5, 140.4 (C-4, C-7, C-1, C-10), 141.8 (C-8′), 144.1 (C-5′), 144.2 (C-3′), 147.2 (C-1′), 169.1 (5′-O**C**OCH$_3$), 169.2 (8′-O**C**OCH$_3$) Anal. calcd for $C_{32}H_{29}NO_4$: C, 78.19; H, 5.95; N, 2.85. Found: C, 78.30, H, 5.93, N, 2.87.

5.3. Reaction of (*S*)-(+)-diene 1 with quinoline-5,8-dione 2

$BF_3{\cdot}Et_2O$ (0.198 mL, 1.56 mmol) was added to a solution of diene **1** (300 mg, 1.28 mmol) and quinoline-5,8-dione **2** (231 mg, 1.56 mmol) in dry CH_2Cl_2 (15 mL). The whole mixture was placed into a 15 mL Teflon ampoule. The ampoule was closed and kept under 6 kbar pressure for 16 h at 50°C. After depressurizing, the reaction mixture was treated with a saturated aqueous $NaHCO_3$ solution. The solvent was dried (Na_2SO_4), evaporated in vacuo and the residue was purified by column chromatography (elution with CH_2Cl_2) to give **9** as a pale yellow crystalline solid (264 mg, 53%); (*S*)-(−)-**9**: 199°C (dec.) (CH_2Cl_2); $[\alpha]_D=-67$ (*c* 0.33, $CHCl_3$); IR 3420 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.91 (m, 1H, H-3), 2.95–3.2(m, 6H, H_s-2, H_s-8, H_s-9), 3.46 (m, 1H, H-3), 3.52 (dd, 1H, $J=15.7$, 10.4 Hz, H-3′), 3.62 (dd, 1H, $J=15.7$, 9.4 Hz, H-3′), 5.79 (dd, 1H, $J=10.4$, 9.4 Hz, H-2′), 6.48 (dd, 1H, $J=7.8$, 1.8 Hz, H-14), 6.49 (d, 1H, $J=1.7$ Hz, H-6), 6.50 (d, 1H, $J=7.7$ Hz, H-16), 6.54 (dd, 1H, $J=7.7$, 1.7 Hz, H-15), 6.57 (dd, 1H, $J=7.8$, 2.0 Hz, H-13), 7.12 (s, 1H, H-4′), 7.39 (dd, 1H, $J=8.5$, 4.2 Hz, H-8′), 7.81 (bs, 1H, OH), 8.32 (dd, 1H, $J=8.5$, 1.6 Hz, H-9′), 8.73 (dd, 1H, $J=4.2$, 1.6 Hz, H-7′); ^{13}C NMR ($CDCl_3$). δ 34.3 (C-3), 35.4, 35.5_8, 35.6_1 (C-2, C-8, C-9), 38.7 (C-3′), 85.8 (C-2′), 106.7 (C-4′), 115.9 (C-9a′), 121.3 (C-8′), 121.6 (C-3a′), 130.7 (C-9′), 132.1 (C-13), 132.5 (C-6), 132.6, 132.9, 133.2, 133.6 (C-11, C-12, C-14, C-15), 136.5 (C-16), 137.7 (C-5a′), 137.9 (C-5), 139.3 (C-4), 139.7, 139.8, 140.4 (C-1, C-10, C-7), 146.0 (C-9b′), 146.5 (C-5′), 147.7 (C-7′). Anal. calcd for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56. Found: C, 82.31, H, 5.92, N, 3.54.

5.4. High pressure Diels–Alder reaction between diene 1 and 1,4 naphthoquinone 4

A solution of diene **1** (300 mg, 1.28 mmol) and 1,4 naphthoquinone **4** (243 mg, 1.53 mmol) in toluene (3 mL) containing trichloroacetic acid (150 mg, 0.93 mmol) was kept at 8 kbar at rt for 18 h. After depressurizing, the reaction mixture was diluted with chloroform and treated with an aqueous saturated $NaHCO_3$ solution. The solvent was dried (Na_2SO_4) and evaporated in vacuo to give a residue which was shown by analytical HPLC to be a 7.6: 1 mixture of **10** and **6**.[2] After a flash chromatography (elution with EtOAc/hexane 9:1) the products were separated by HPLC. 304 mg of **10** and 41 mg of **6** were obtained for a total yield of 68%.

(*R*)-(+)-**10**: white crystals, mp 208°–209°C (hexane/EtOAc); $[\alpha]_D=+84$ (*c* 0.36); IR 1688 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.59 (ddd, 1H, $J=13.0$, 12.5, 5.2 Hz, H-12), 2.19 (m, 1H, H-12), 2.53 (ddd, 1H, $J=16.0$, 12.1, 6.2 Hz, H-11), 2.86 (m, 1H, H-11), 2.85–3.22 (m, 6H, H_s-2, H_s-3, H_s-8), 2.88 (m, 1H, H-9), 3.18 (m, 1H, H-9), 3.36 (ddd, 1H, $J=13.0$, 5.6, 2.6 Hz, H-12a), 4.17 (d, 1H, $J=5.6$ Hz, H-18a), 6.42 (dd, 1H, $J=7.9$, 1.7 Hz, H-5), 6.48 (d, 1H, $J=7.7$ Hz, H-19),6.54 (dd, 1H, $J=7.8$, 1.8 Hz, H-21), 6.60 (d, 1H, 7.7 Hz, H-20), 6.61 (dd, 1H, $J=7.8$, 1.8 Hz, H-22), 6.84 (dd, 1H, $J=7.9$, 1.8 Hz, H-6), 7.73 (m, 1H, H-16), 7.82 (m, 1H, H-15), 8.03 (m, 1H, H-17), 8.15 (m, 1H, H-14);^{13}C NMR ($CDCl_3$) δ 26.7 (C-12), 28.0 (C-11), 32.3 (C-9), 33.0, 33.7, 34.1 (C-2, C-3, C-8), 48.8 (C-12), 50.0 (C-18), 127.1 (C-6), 127.2 (C-14), 127.4 (C-17), 129.4 (C-5), 129.5 (C-18b), 132.0 (C-20), 133.1 (C-21), 133.4 (C-22), 133.5 (C-13), 134.3 (C-19), 134.4 (C-15 or C-16), 134.5 (C-10a), 134.8 (C-15 or C-16), 135.3 (C-17a), 139.1, 139.3, 139.4 (C-4, C-7, C-10), 140.1 (C-1), 195.0 (C-18), 199.7 (C-13). Anal. calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.71, H, 6.19.

5.5. Diels–Alder reaction of 1-vinylnaphthalene 11 and quinoline-5,8-dione 2

$BF_3{\cdot}Et_2O$ (0.24 mL, 1.89 mmol) was added to a solution of diene **11** (240 mg, 1.56 mmol) and quinone **2** (300 mg, 1.89 mmol) in dry toluene (15 mL). The reaction mixture was stirred at rt for 2 h under nitrogen. The reaction mixture was then worked up as usual to afford a solid residue. Crystallization from ethanol gave **12** (279 mg, 62%) as a yellow crystalline product.

12: mp 240–241°C (EtOH); IR 1679 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$+DMSO) δ 7.64–7.74 (m, 2H, H-2, H-3), 7.78 (dd, 1H, $J=8.1$, 4.6 Hz, H-10), 7.89 (m, 1H, H-1), 7.96 (d, 1H, $J=9.6$ Hz, H-14), 8.57 (d, 1H, $J=8.8$ Hz, H-6), 8.58 (d, 1H, $J=8.1$ Hz, H-11), 8.69 (m, 1H, H-4), 9.00 (d, 1H, $J=4.6$ Hz, H-9), 9.11 (d, 1H, $J=8.8$ Hz, H-5), 9.48 (d, 1H, $J=9.6$ Hz, H-13); ^{13}C NMR ($CDCl_3$+ DMSO) δ 123.7 (C-4), 124.4 (C-6), 124.9 (C-13), 127.8 (C-1), 128.3, 128.7 (C-2, C-3), 128.8 (C-12a), 128.9 (C-10), 129.5 (C-4a), 129.7 (C-5), 130.6 (C-12b), 131.7 (C-14), 132.6 (C-11a), 132.7 (C-14a), 133.9 (C-6a), 135.4 (C-4b), 135.8 (C-11), 148.1 (C-7a), 154.8 (C-9), 182.4 (C-7), 185.6 (C-12). Anal. calcd for $C_{21}H_{11}NO_2$: C, 81.54; H, 3.58; N, 4.53. Found: C, 81.62, H, 3.60, N, 4.49.

5.6. Diels–Alder reaction of 1-vinylnaphthalene 11 and isoquinoline-5,8-dione 3

The reaction was carried out according to the procedure described for quinoline-5,8-dione **2** to afford **13** in 58% yield as a yellow crystalline product.

13: mp 247–248°C (EtOH); IR 1672 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72–7.77 (m, 2H, H-2, H-3), 7.99 (m, 1H, H-1), 8.07 (d, 1H, $J=9.7$ Hz, H-14), 8.14 (d, 1H, $J=5.1$ Hz, H-11), 8.61 (d, 1H, 8.8 Hz, H-6), 8.78 (m, 1H, H-4), 9.13 (d, 1H, $J=5.1$ Hz, H-10), 9.21 (d, 1H, $J=8.8$ Hz, H-5), 9.56 (brs, 1H, H-9), 9.57 (d, 1 H, $J=9.7$ Hz, H-13); ^{13}C NMR ($CDCl_3$) δ 119.6 (C-11), 123.6 (C-4), 124.0 (C-6), 124.8 (C-13), 125.4 (C-7a), 127.9 (C-1), 128.8, 128.9 (C-2, C-3), 129.1 (C-21), 129.7 (C-12a), 130.1 (C-5, C-12b), 132.4 (C-14), 132.7 (C-14a), 133.5 (C-6a), 135.4 (C-4b), 140.6 (C-11a), 149.3 (C-9), 155.7 (C-10), 183.3 (C-7), 185.6 (C-12). Anal. calcd for $C_{21}H_{11}NO_2$: C, 81.54; H, 3.58; N, 4.53. Found: C, 81.45, H, 3.55, N, 4.59.

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