Pergamon

Tetrahedron: *Asymmetry* 14 (2003) 2775–2779

TETRAHEDRON:
ASYMMETRY

Synthesis of enantiopure helical cyclophanes containing five-membered heterocyclic rings

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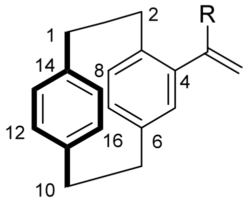
Received 30 June 2003; accepted 14 July 2003

Abstract—The preparation of optically active (*S*)-(+)-4-(2-propenyl)[2.2]paracyclophane **1b** is described. Cycloaddition reactions of this diene with *N*-phenylmaleimide **2** and maleic anhydride **5** were carried out under high pressure conditions. The cycloadducts were converted into optically active heterohelicenophanes. A systematic ^{1}H and ^{13}C NMR spectroscopic analysis of the reaction products is also presented.

1. Introduction

We have previously described[1] the development of a convergent strategy for the regiospecific construction of [2.2]paracyclophanes containing condensed aromatic subunits. This is an interesting class of compounds from the point of view of their optical and electronic properties and their potential applications as new materials and chiral ligands for asymmetric catalysis[2]. Our two-step approach was based on the Diels–Alder cycloaddition of (*S*)-(+)-4-ethenyl[2.2]paracyclophane **1a** (Fig. 1), a diene that is easily accessible from the precursor (*S*)-(+)-4-acetyl[2.2]paracyclophane.[3]

Herein we present the synthesis of two optically active heterohelicenophanes containing a heterocyclic aromatic subunit and a methyl group in the A ring of the subunit. The presence of the methyl group in a *peri*-like position with the methylene of the ethane bridge is interesting; it exerts steric hindrance and should increase the distortion of the subunit thus affecting the electronic and optical properties. We report the preparation of (*S*)-(+)-4-(2-propenyl)[2.2]paracyclophane **1b** (Fig. 1) and its use for synthesizing heterohelicenophanes. We also present a systematic ^{1}H and ^{13}C NMR spectroscopic investigation of the cycloadducts and of the heterohelicenophanes from the point of view of structural and stereochemical assignments.



1 **a**, R=H
b, R=Me

Figure 1.

2. Results and discussion

(*S*)-(+)-4-(2-Propenyl)[2.2]paracyclophane **1b** was prepared according to a previously reported procedure for the racemic form;[4] however, the dehydration of the carbinol was carried out by treating it with PBr_3 in CH_2Cl_2 and then with LiBr and Li_2CO_3 instead of with HCl.[3] The diene was also characterized by extensive NMR and GC–MS analyses.

The preferred conformation for diene **1b** is depicted in Figure 2 and is supported by NOE measurements. Indeed the largest NOE (3.6%) was observed between the C(2′) olefinic protons (5.14 and 5.19 ppm) and H(5) (6.41 ppm), while the NOE between CH_3 and H(5) was only 1.6%. The 2-propenyl side chain and the benzene ring are not coplanar because of the repulsive non-

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doi:10.1016/S0957-4166(03)00549-4

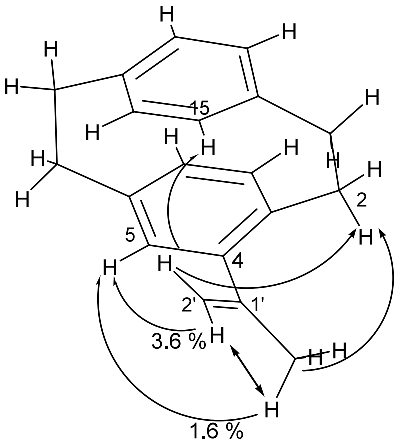


Figure 2. Minimised energy conformation of diene **1b**; the arrows indicate the relevant NOEs observed.

bonded steric interaction between the methyl group and the ethane bridge methylene of the cyclophane moiety.[4] This deviation tends to decrease the resonance between the olefinic and the aromatic π electrons thereby decreasing the activating effect of the electron-donating methyl group in a normal demand Diels–Alder reaction.[5] This deviation from planarity has already been shown to affect the [2+2] cycloaddition reaction with TCNE.[4]

When diene **1b** interacted with *N*-phenylmaleimide **2** at atmospheric pressure, no reaction occurred, although a variety of conditions were tested. The Diels–Alder reaction occurred only under high pressure conditions[6] (7 kbar) and gave *anti*- (with respect to the unsubstituted arene ring) *endo* diastereoselectively to cycloadduct (+)-**3** in high yield (80%) (Table 1). This was then converted in 78% yield into the corresponding aromatic compound (*R*)-(+)-**4** (Fig. 3) by DDQ treatment in toluene.

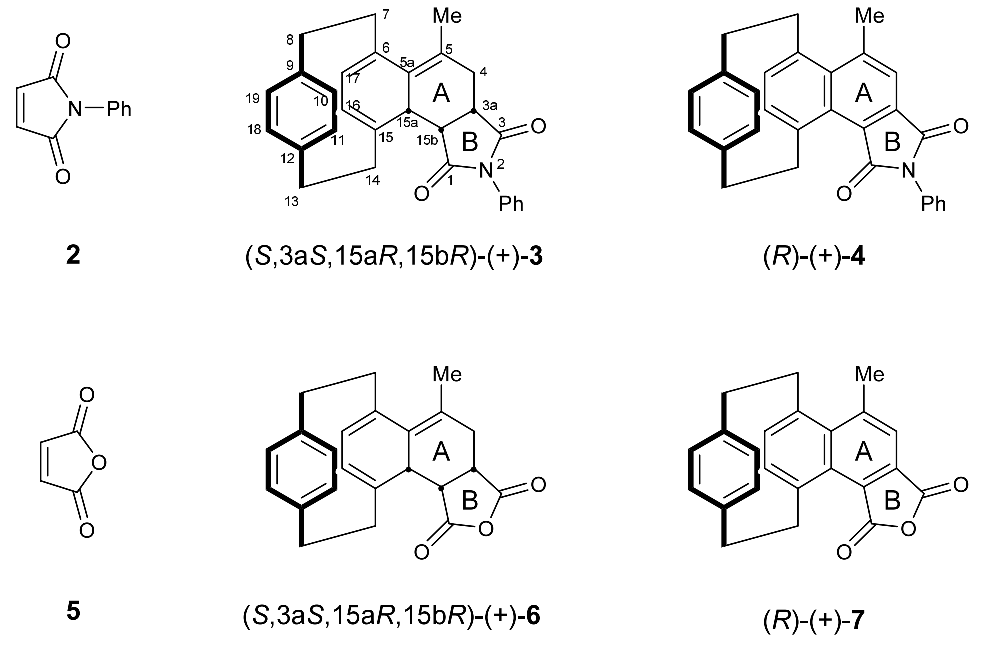
Table 1. Reaction conditions for the Diels–Alder cycloaddition of (*S*)-(+)-4-(2-propenyl)[2.2]paracyclophane **1b** with dienophiles **2** and **5**

Reactants (ratio)	Conditions	Product	Yield[a] (%)
1b-**2** (1:2)	Toluene, rfx, 24 h	–	–
1b-**2** (1:2)	7 kbar, CH_2Cl_2, rt, 24 h	**3**	80
1b-**5** (1:1.2)	Toluene, rfx, 24 h	–	–
1b-**5** (1:1.2)	7 kbar, CH_2Cl_2, 50°C, 24 h	**6**	67

[a] Isolated yield.

The Diels–Alder cycloaddition between **1b** and maleic anhydride **5** also occurred only under high pressure conditions (Table 1) and afforded *anti*-*endo* diastereoselectively cycloadduct (+)-**6** in good yield (67%). DDQ oxidation of (+)-**6** gave the aromatic compound (*R*)-(+)-**7** in 55% yield.

The strong preference for *anti* diastereoselectivity in the cycloadditions of dienophiles **2** and **5** may be ascribed to the steric hindrance of the unsubstituted arene ring. The severe non-bonded interactions between the arene ring and the dienophile strongly destabilize the transition state for *syn*-addition, thus favouring that of *anti*-addition.[5,7] The preferred *endo*-diastereoselectivity may be due to secondary orbital interactions[5,8] and high pressure.[6]



2 (*S*,3a*S*,15a*R*,15b*R*)-(+)-**3** (*R*)-(+)-**4**

5 (*S*,3a*S*,15a*R*,15b*R*)-(+)-**6** (*R*)-(+)-**7**

Figure 3.

3. Structural analysis

The structures of the reaction products were assigned by analysis of ^{1}H and ^{13}C NMR spectra. Proton and carbon shift assignments follow from the examination of ^{1}H–^{1}H and ^{1}H–^{13}C connectivities (COSY spectra) and from the observed ^{1}H–{^{1}H} NOEs; quaternary carbons were assigned by 2D long-range hetero-correlated experiments.[9] Prefixes α- and β- have arbitrarily been used to distinguish methylene hydrogen atoms; the β-prefix indicates a hydrogen atom facing the unsubstituted arene ring.

3.1. Cycloadducts 3 and 6

The stereochemical relationships of H(3a), H(15a) and H(15b) of cycloadducts **3** and **6**, were inferred from a series of selective NOE experiments (Fig. 4). Irradiation of the resonance due to H(4_β) in compounds **3** and **6** resulted in signal enhancements of the resonances attributed to H(3a), H(15a), H(4_α) and H(10) signals, suggesting a boat conformation of ring A and then a *cis* spatial relationship between H(3a), H(15a) and H(15b).

This stereochemical assignment is confirmed by the interproton coupling constant value ($^{3}J_{3a,15b}=9.4$ Hz) measured for **6**. Furthermore, the NOEs observed between H(4_β) and H(10), H(10) and H(15a) indicated that H(15a), H(3a) and H(15b) point toward the unsubstituted arene ring of the paracyclophane unit (Fig. 4), confirming a totally *anti*-*endo* diastereoselectivity in the cycloaddition reactions.

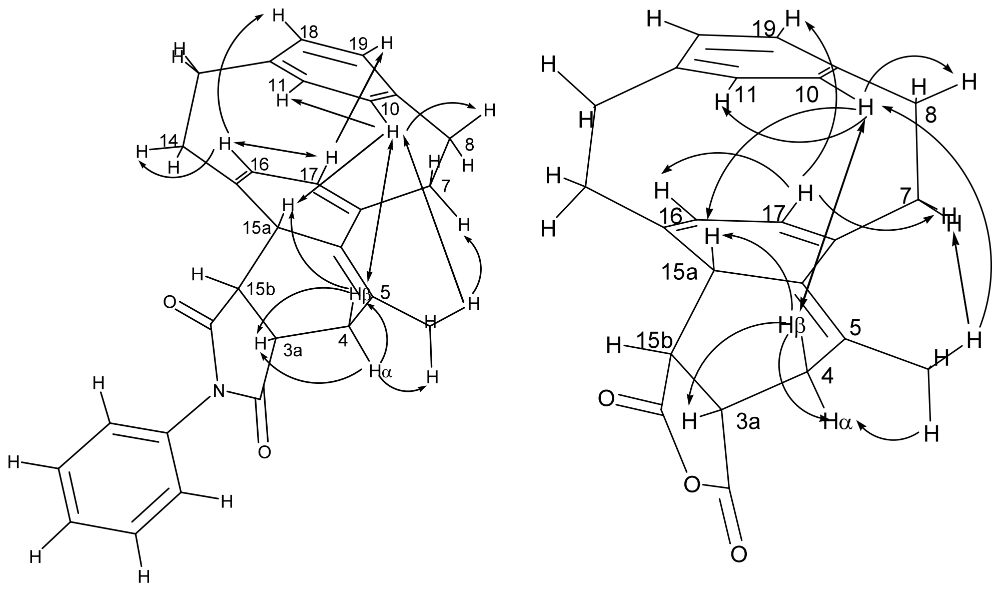
Further support for the structure assignment was also given by the NOEs observed on H(4_α), H$_s$(7), and H(10) upon selective irradiation of C(5) methyl protons, as well as by the NOEs observed between H(16) and H(17), H(17) and H(19), H(10) and H(11), H(8) and H(10) for compounds **3** and **6**. Furthermore NOEs were observed between H(14) and H(16), H(16) and H(18) for **3**.

3.2. Compounds 4 and 7

The structural determination was based on the outcome of the reaction used to prepare them and on extensive NMR investigations. Support for the structure assignment was also given by the NOE observed between C(5) methyl protons and H$_s$(7) for both compounds, as well as the NOEs observed on the resonances of H$_s$(8) and H(11) upon irradiation of the resonance attributed to H(10) for **7**. Confirmation of the structure assignment to **4** and **7** was also given by the deshielding of H(4) (7.78 and 7.75 ppm for **4** and **7**, respectively) and H(14) (4.56 and 4.45 ppm for **4** and **7**, respectively) due to the anisotropy effect of the C(3) and C(1) carbonyl functions in both compounds.

4. Conclusions

Diene **1b** has been prepared in enantiopure form and has been characterized. It has been used to synthesize two optically active helical cyclophanes containing heterocyclic five-membered rings in the aromatic condensed subunit by a two-step approach based on the Diels–Alder reaction. Due to the low reactivity of the diene **1b** the cycloadditions had to be promoted by high pressure. The comparison of the specific rotation values between **3** and **4** and the corresponding unmethylated compounds previously prepared,[1c] points out an effect of the methyl group on this property.



(*S*,3a*S*,15a*R*,15b*R*)-(+)-**3**　(*S*,3a*S*,15a*R*,15b*R*)-(+)-**6**

Figure 4. Minimised energy conformations of compounds **3** and **6**; the arrows indicate observed NOEs.

5. Experimental

5.1. General

Melting points (uncorrected): Büchi melting point apparatus. IR: Perkin–Elmer Paragon 500 FT-IR in $CHCl_3$. NMR: Varian Associates VXR-400 in $CDCl_3$, TMS as int. reference. ^1H and ^{13}C shift assignments are based on COSY, ^1H–{^1H}NOE and HETCOR experiments; quaternary carbon atoms were assigned by 2D long-range hetero-correlated experiments. Superscript 'a' indicates that the carbon shifts may be interchanged. MS: Hewlett-Packard 5970 at 70 eV. GC: Hewlett–Packard 6890 chromatograph. Optical rotations: Jasco DIP-360 polarimeter at 25°C. Absorption chromatography was carried out on Riedel-de Haën silica gel (32–63 μm; 230–400 mesh ASTM). 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).

5.2. (*S*)-(+)-4-(2-Propenyl)[2.2]paracyclophane 1b

This diene was prepared according to a previous procedure reported for the racemic compound,[4] but the dehydration of the precursor carbinol was carried out according to the procedure[3] described for diene **1a**; mp 85–86°C (EtOAc); $[\alpha]_D = +167$ (*c* 0.88, $CHCl_3$). ^1H NMR δ 2.07 (br s, 3H, CH_3), 2.94–3.06 (m, 7H, H_s-1, H_s-2, H_s-9, H_s-10), 3.37 (m, 1H, H-9), 5.14 (d, 1H, $J = 2.3$ Hz, H-2′), 5.19 (d, 1H, $J = 2.3$ Hz, H-2′), 6.36 (dd, 1H, $J = 7.8$, 1.8 Hz, H-16), 6.37 (dd, 1H, $J = 7.6$, 1.7 Hz, H-7), 6.41 (d, 1H, $J = 1.7$ Hz, H-5), 6.42 (d, 1H, $J = 7.6$ Hz, H-8), 6.55 (dd, 1H, $J = 7.8$, 1.8 Hz, H-13), 6.59 (dd, 1H, $J = 7.8$, 1.8 Hz, H-12), 6.64 (d, 1H, $J = 7.8$, 1.8 Hz, H-15); ^{13}C NMR δ 23.9 (CH_3), 34.4, 35.2, 35.3, 35.4 (C-1, C-2, C-9, C-10), 115.3 (C-2′), 130.1 (C-15), 130.6 (C-5), 132.1 (C-7), 132.2 (C-16), 132.3 (C-13), 132.9 (C-12), 135.4 (C-8), 136.8, 139.2, 139.3, 139.7 (C-14, C-3, C-6, C-11), 143.0 (C-4), 145.4 (C-1′). MS *m*/*e* (rel. int.) 51 (3), 63 (2), 78 (7), 91 (3), 105 (18), 115 (9), 129 (62), 143 (100, base), 189 (2), 202 (2), 215 (2), 248 (M^+, 26).

5.3. Diels–Alder reaction of (*S*)-(+)-4-(2-propenyl)[2.2]-paracyclophane 1b with *N*-phenylmaleimide 2

A solution of *N*-phenylmaleimide **2** (0.536 g, 3.1 mmol) in CH_2Cl_2 (6 mL) was added to a solution of diene (*S*)-(+)-**1b** (0.385 g, 1.55 mmol) in CH_2Cl_2 (4 mL). The whole mixture was placed into a 15 mL Teflon ampoule and CH_2Cl_2 was added until the ampoule was completely filled. The ampoule was closed and kept under 7 kbar pressure for 24 h at room temperature. After depressurizing, the solvent was removed in vacuo and the crude residue was purified by column chromatography on silica gel. Elution with 4:1 hexane–ethylacetate afforded (+)-**3** as white crystals (0.522 g, 80%); mp 182°C (dec.) (EtOAc); $[\alpha]_D = +367$ (*c* 1.22, $CHCl_3$); IR: 1709 (s, C=O) cm^{-1}; ^1H NMR δ 1.79 (dd, 1H, $J = 13.7$, 5.6 Hz, H-4_β), 2.01 (s, 3H, CH_3), 2.32 (m, 1H, H-15a), 2.49 (m, 1H, H-7), 2.62 (m, 1H, H-14), 2.64 (m, 1H, H-8), 2.68 (m, 1H, H-14), 2.78 (dd, 1H, $J = 13.7$, 2.0 Hz, H-4_α), 3.0 (m, 1H, H-13), 3.09 (m, 1H, H-13), 3.10 (m, 1H, H-8), 3.16 (dd, 1H, $J = 2.0$, 5.6 Hz, H-3a), 3.17 (m, 1H, H-7), 3.18 (m, 1H, H-15b), 5.29 (d, 1H, $J = 6.7$ Hz, H-17), 5.51 (d, 1H, $J = 6.7$ Hz, H-16), 6.47 (dd, 1H, $J = 7.8$, 1.8 Hz, H-10), 6.83 (dd, 1H, $J = 7.8$, 1.9 Hz, H-11), 6.85 (dd, 1H, $J = 7.9$, 1.9 Hz, H-18), 6.91 (dd, 1H, $J = 7.9$, 1.8 Hz, H-19) 6.97 (m, 2H, H-2′, H-6′), 7.27 (m, 1H, H-4′), 7.34 (m, 2H, H-3′, H-5′); ^{13}C NMR δ 21.9 (CH_3), 33.4 (C-14), 34.2 (C-13), 34.9 (C-8), 35.1 (C-4), 37.3 (C-15b), 37.9 (C-7), 42.9 (C-3a), 50.9 (C-15a), 125.4 (C-5), 126.6 (C-2′, C-6′), 128.1 (C-11), 128.4 (C-4′), 129.1 (C-3′, C-5′), 130.2 (C-16), 130.5 (C-19), 130.8 (C-10), 131.2 (C-17), 131.7 (C-6), 132.1 (C-1′), 132.4 (C-18), 135.0 (C-5a), 138.4 (C-12), 139.5 (C-9), 140.7 (C-15), 174.9 (C-1), 177.9 (C-3). Anal. calcd for: $C_{29}H_{27}NO_2$: C, 82.63; H, 6.46; N, 3.32. Found: C, 82.41; H, 6.48; N, 3.32%.

5.4. Preparation of (*R*)-(+)-4

A toluene (6 mL) solution of cycloadduct (+)-**3** (0.25 g, 0.59 mmol) was treated with DDQ (0.978 g, 4.31 mmol) under reflux for 4 h. After usual work up the crude residue was chromatographed on column and elution with 9:1 hexane–ethylacetate gave 0.195 g (78%) of compound (+)-**4** as yellow crystals; mp 191–192°C (EtOAc); $[\alpha]_D = +536$ (*c* 1.05, $CHCl_3$); IR: 1712 (s, C=O) cm^{-1}; ^1H NMR δ 2.72 (m, 1H, H-8), 2.90 (m, 1H, H-13), 2.94 (br s, 3H, CH_3), 3.02 (m, 1H, H-13), 3.10 (m, 1H, H-7), 3.20 (m, 1H, H-8), 3.28 (m, 1H, H-14), 4.05 (m, 1H, H-7), 4.56 (m, 1H, H-14), 5.63 (dd, 1H, $J = 7.8$, 1.3 Hz, H-10), 5.78 (dd, 1H, $J = 7.8$, 1.3 Hz, H-11), 6.65 (dd, 1H, $J = 7.8$, 1.3 Hz, H-18), 6.70 (dd, 1H, $J = 7.8$, 1.3 Hz, H-19), 6.91 (d, 1H, $J = 7.4$ Hz, H-17), 6.95 (d, 1H, $J = 7.4$ Hz, H-16), 7.44 (m, 1H, H-4′), 7.54 (m, 2H, H-2′, H-6′), 7.56 (m, 2H, H-3′, H-5′), 7.78 (br s, 1H, H-4); ^{13}C NMR δ 25.3 (CH_3), 35.3 (C-13), 35.7 (C-8), 38.0 (C-14), 39.6 (C-7), 122.4 (C-4), 125.2 (C-15b), 127.0 (C-2′, C-6′), 128.0 (C-4′), 129.3 (C-3′, C-5′), 129.5 (C-11), 129.9 (C-10), 131.0 (C-19), 131.3 (C-3a), 132.0 (C-15a), 132.1 (C-18), 132.4 (C-1′), 135.9 (C-16), 137.0 (C-6), 137.4 (C-17), 138.4 (C-9), 139.0 (C-15), 139.8 (C-12), 139.9, 143.0 (C-5a, C-5), 168.0, 168.2 (C-1, C-3). Anal. calcd for: $C_{29}H_{23}NO_2$: C, 83.43; H, 5.55; N, 3.55. Found: C, 83.52; H, 5.54; N, 3.32%.

5.5. Diels–Alder reaction of (*S*)-(+)-4-(2-propenyl)[2.2]-paracyclophane 1b with maleic anhydride 5

The reaction was carried out by following the procedure reported above (see Table 1 for the ratio of the reagents). After usual work up the crude product was chromatographed on column (elution: 7:3 hexane–ethylacetate) to afford 0.36 g (67%) of (+)-**6** as white crystals; mp 176–177°C (CH_2Cl_2/hexane); $[\alpha]_D = +109$ (*c* 0.37, $CHCl_3$); IR: 1779 (s, C=O) cm^{-1}; ^1H NMR δ 1.79 (dd, 1H, $J = 14.0$, 6.0 Hz, H-4), 2.02 (br d, 3H, $J = 2.7$ Hz, CH_3), 2.27 (m, 1H, H-15a), 2.46 (m, 1H, H-7), 2.52–2.70 (m, 2H, H_s-14), 2.63 (m, 1H, H-8), 2.72 (dd, 1H, $J = 14.0$, 2.1 Hz, H-4), 3.02–3.09 (m, 2H, H_s-13), 3.10 (m, 1H, H-8), 3.17 (m, 1H, H-7), 3.21 (dd, 1H,

J=9.4–5.5 Hz, H-15b), 3.31 (ddd, 1H, J=9.4, 6.0, 2.1 Hz, H-3a), 5.32 (d, 1H, J=6.5 Hz, H-17), 5.54 (d, 1H, J=6.5 Hz, H-16), 6.43 (dd, 1H, J=7.8, 1.9 Hz, H-10), 6.79 (dd, 1H, J=7.8, 1.9 Hz, H-11), 6.85 (dd, 1H, J=7.9, 1.9 Hz, H-18), 6.92 (dd, 1H, J=7.9, 1.9 Hz, H-19); ^{13}C NMR δ 21.8 (CH_3), 33.1 (C-14), 34.1 (C-13), 34.7, 34.9 (C-4, C-8), 37.6 (C-3a), 37.8 (C-7), 43.1 (C-15b), 50.1 (C-15a), 125.6 (C-5), 128.1 (C-11), 130.6, 130.7, 130.8 (C-10, C-16, C-19), 131.4 (C-17), 132.0 (C-6), 132.5 (C-18), 135.4 (C-5a), 138.3 (C-12), 139.3, 139.6 (C-9, C-15), 169.5 (C-1), 173.4 (C-3). Anal. calcd for: $C_{23}H_{22}O_3$: C, 79.74; H, 6.40. Found: C, 80.05; H, 6.36%.

5.6. Preparation of (*R*)-(+)-**7**

Compound (+)-**6** was treated with DDQ according to the above reported procedure (see Table 1 for the ratio of the reagents). Usual work up afforded compound (+)-**7** (55%) purified by column chromatography (elution with 4:1 hexane/ethylacetate); mp 254–255°C (CH_2Cl_2/hexane); $[\alpha]_D$=+364 (*c* 0.57, $CHCl_3$); IR: 1769 (s, C=O) cm^{-1}; ^{1}H NMR δ 2.71 (m, 1H, H-8), 2.89 (m, 1H, H-13), 2.95 (br s, 3H, CH_3), 3.06 (m, 1H, H-13), 3.13 (m, 1H, H-7), 3.24 (m, 1H, H-8), 3.28 (m, 1H, H-14), 4.05 (m, 1H, H-7), 4.54 (m, 1H, H-14), 5.57 (dd, 1H, J=7.9, 1.3 Hz, H-10), 5.66 (dd, 1H, J=7.9, 1.3 Hz, H-11), 6.62 (br s, 2H, H-18, H-19), 7.01 (br s, 2H, H-16, H-17), 7.75 (br s, 1H, H-4); ^{13}C NMR δ 25.5 (CH_3), 35.1, 35.6 (C-8, C-13), 37.5 (C-14), 39.4 (C-7), 123.0 (C-4), 125.1 (C-15b), 129.6 (C-11), 129.8 (C-10), 130.8[a] (C-3a), 131.3 (C-19), 132.1 (C-18), 132.2[a] (C-15a), 136.6 (C-16), 137.7 (C-6), 138.3 (C-17), 138.4 (C-9), 139.0 (C-15), 139.6 (C-12), 140.3 (C-5a), 145.3 (C-5), 163.0, 164.1 (C-1, C-3). Anal. calcd for: $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.60; H, 5.31%.

Acknowledgements

L.M., A.T, D.L., A.M. thank the MIUR and Fondazione Cassa di Risparmio di Perugia for the financial support of the work in Perugia. E.G.-B. thanks the Hungarian Academy of Sciences.

References

1. (a) Minuti, L.; Taticchi, A.; Marrocchi, A.; Lanari, D.; Broggi, A.; Gacs-Baitz, E. *Tetrahedron: Asymmetry* **2003**, *14*, 481–487; (b) Minuti, L.; Taticchi, A.; Marrocchi, A.; Lanari, D.; Gacs-Baitz, E. *Tetrahedron: Asymmetry* **2002**, *13*, 1331–1335; (c) Minuti, L.; Taticchi, A.; Marrocchi, A.; Costantini, L.; Gacs-Baitz, E. *Tetrahedron: Asymmetry* **2001**, *12*, 1179–1183; (d) Minuti, L.; Taticchi, A.; Marrocchi, A.; Dix, I.; Hopf, H.; Gacs-Baitz, E.; Jones, P. G. *Eur. J. Org. Chem.* **2001**, 4259–4268.
2. (a) Vögtle, F. *Cyclophane Chemistry*; Wiley-Sons: New York, 1993; (b) Reiss, J. A. In *Cyclophanes*; Keehn, P. M.; Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; (c) Hopf, H.; Mlynek, C.; El Tamany, S.; Ernst, L. *J. Am. Chem. Soc.* **1985**, *107*, 6620–6627; (d) Aly, A. A.; Hopf, H.; Ernst, L. *Eur. J. Org. Chem.* **2000**, 3021–3029.
3. Minuti, L.; Taticchi, A.; Marrocchi, A. *Tetrahedron: Asymmetry* **2000**, *11*, 4221–4225.
4. Aly, A. A.; Aboul-Fetouh, E. M. *Tetrahedron* **1993**, *49*, 7325–7336.
5. Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*; J. Wiley-Sons: New York, 1990.
6. (a) Fringuelli, F.; Taticchi, A. *Diels–Alder Reaction. Selected Practical Methods*; J. Wiley-Sons: New York, 2002; (b) Organic Synthesis At High Pressures; Matsumoto, K.; Achenson, R. M., Eds.; J. Wiley-Sons, New York, 1990; (c) Ciobanu, M.; Matsumoto, K. *Liebigs Ann./Recueil* **1997**, 623–635; (d) Pindur, U.; Otto, C. *Chem. Rev.* **1993**, *93*, 741–761.
7. Vogel, P. In *Stereochemistry and reactivity of system containing π electrons*, Watson, W. H., Ed. of the series Methods in Stereochemical Analysis, Verlag Chemie: Weinheim, Germany, 1983.
8. (a) Ginsburg, D. *Tetrahedron* **1983**, *39*, 2095–2135; (b) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807; (c) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537–562; (d) Stephenson, L. M.; Smith, D. E.; Current, S. P. *J. Org. Chem.* **1982**, *47*, 4170–4171.
9. Ernst, L. *Progr. Nuclear Magnetic Resonance Spectrosc.* **2000**, *37*, 47–190.