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Stereoselective synthesis of enantiopure condensed [2.2]paracyclophanes

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Abstract—The Diels–Alder reaction of (*S*)-(+)-4-ethenyl[2.2]paracyclophane with 1,4-benzoquinone, *N*-phenylmaleimide and 3-nitrocyclohexen-1-one has been investigated under atmospheric and high pressure conditions. The synthesis of five optically active [2.2]paracyclophanes containing condensed polycyclic aromatic subunits is described. A structural analysis of the reaction products by ^{1}H and ^{13}C NMR spectroscopy is also presented. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

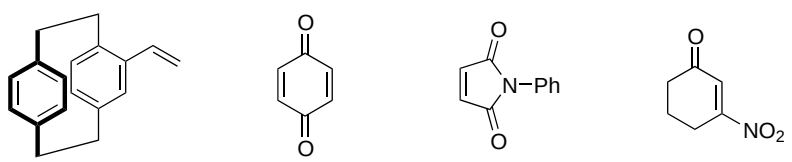
There is a great deal of interest in [2.2]paracyclophane derivatives with a view to their stereochemical properties[1] and attention has recently been directed towards developing methods for the synthesis of [2.2]paracyclophanes containing condensed polycyclic aromatic subunits. Photodehydrocyclisation of stilbene-like compounds, a valuable method for synthesising polycyclic aromatic compounds, has been used to synthesise phenanthreno[2.2]paracyclophanes. However, this methodology has severe limitations since it requires very dilute solutions and often leads to isomeric mixtures.

In the course of our work on polycyclic aromatic compounds, we developed a short, flexible approach, based on the Diels–Alder reaction of arylethenes, which allows a variety of condensed aromatic polycycles to be prepared.[2] Recently, we described the resolution of the 4-acetyl[2.2]paracyclophane by the SAMP/hydrazone method[3] and the conversion of both enantiomers to the (*S*)-(+)- and (*R*)-(−)-4-ethenyl[2.2]paracyclophane **1**.[3]

In view of the increasing interest in optically active paracyclophanes, we have undertaken a study on the synthesis of these compounds and herein report the preparation of five novel enantiomerically pure condensed [2.2]paracyclophanes based on the Diels–Alder reaction of diene (*S*)-(+)-**1** with 1,4-benzoquinone **2**, *N*-phenylmaleimide **3** and 3-nitro-2-cyclohexen-1-one **4** (Fig. 1).

2. Results and discussion

The Diels–Alder cycloadditions between (*S*)-(+)-**1** and **2** were carried out under a number of different experimental conditions both at atmospheric pressure and under high pressure (Table 1). A mixture of two products was always obtained but the best reaction yield of 38% was achieved when the cycloaddition was carried



(*S*)-(+)-**1** **2** **3** **4**

Figure 1.

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Table 1. Reaction conditions of the Diels–Alder reaction of (*S*)-(+)-4-ethenyl[2.2]paracyclophane **1** with dienophiles **2**–**4**

Reactants	Solvent	Conditions	Products (ratio)	Yield[a] (%)
1-2	Toluene	1 bar, reflux, 5 days	**5**, **6** (5:1)	13
1-2	AcOH	1 bar, 100°C, 19 h	**5**, **6** (2.3:1)	38
1-2	Neat	1 bar, 140°C, 4 h	**5**, **6** (7:1)	38
1-2	CH_2Cl_2	10 kbar, 40°C, 18 h	**5**, **6** (1:9)	20
1-3	Neat	1 bar, 130°C, 3 h	–	–
1-3	CH_2Cl_2	10 kbar, 40°C, 21 h	**7**	70
1-4	Toluene	1 bar, reflux, 36 h	–	–
1-4	Toluene	1 bar, cat.[b], reflux, 6 h	–	–
1-4	CH_2Cl_2	10 kbar, 40°C, 39 h	**10**[c]	15
1-4	CH_2Cl_2	10 kbar, 40°C, 5 days	**10**[c]	20

[a] Isolated yield.
[b] $EtAlCl_2$ (0.25 equiv.) or $Yb(Fod)_3$ (0.20 equiv.).
[c] Produced after treatment of initial adduct with DBN, followed by DDQ oxidation.

out at 140°C without a solvent, or in acetic acid solution at 100°C. Column chromatography of the reaction mixtures allowed the major product to be isolated and purified. Structural analysis based on GC–MS analysis and NMR spectroscopy showed that it was the [2]paracyclo[2](1,4)phenanthro-4,8-quinonophane **5**. Based on GC–MS analysis the structure of the dihydroderivative **6** was tentatively assigned to the minor product. Clearly, 1,4-benzoquinone also acts as an oxidant. DDQ oxidation of the crude reaction mixture afforded product (*R*)-(−)-**5** almost quantitatively (95%).

When diene (*S*)-(+)-**1** interacted with *N*-phenylmaleimide **3** at atmospheric pressure, no reaction occurred. The cycloaddition took place only under high pressure conditions[4] (10 kbar) and led to cycloadduct (*S*)-(+)-**7** (70% yield) which was then converted into aromatic compound (*R*)-(+)-**8** (Fig. 2) by DDQ treatment, in high yield (84%).

The structure of products **7** and **8** was assigned by GC–MS and NMR spectroscopy. As shown by the structure of cycloadduct **7**, as expected, the Diels–Alder reaction occurred with *anti*- (with respect to the unsubstituted benzene ring) *endo*-diastereoselectivity, *syn* addition being precluded by steric factors.

The cycloaddition between (*S*)-(+)-**1** and 3-nitro-2-cyclohexen-1-one **4**,[5] an interesting dienophile that permits tetralone-like compounds to be prepared, was also studied. The presence of the strongly electron-withdrawing nitro-group is essential for increasing the reactivity, since cycloalkenones are known to be very poor dienophiles.[6] Furthermore, the nitrocycloadduct can undergo an easy HNO_2 elimination reaction. When (*S*)-(+)-**1** and **4** were mixed under Lewis acid catalysis at atmospheric pressure, no reaction occurred. The cycloaddition required forced activation and took place only when a dichloromethane solution of the reactants was treated under high pressure (10 kbar) at 40°C. The cycloadduct could not be isolated due to its instability. Therefore, it was treated with DBN which afforded a 1:3.5 mixture of the aromatic ketone **10** and its dihydroderivative **9** as shown by GC–MS analysis. An analytically pure sample of (*R*)-(−)-**9** was obtained by column chromatography of this mixture. DDQ oxidation of the reaction mixture gave pure (*R*)-(+)-**10** in 20% overall yield. The structures of compounds **9** and **10** were assigned by NMR spectroscopy (Fig. 2). As expected the regiochemistry of the Diels–Alder reaction was controlled by the nitro-group.

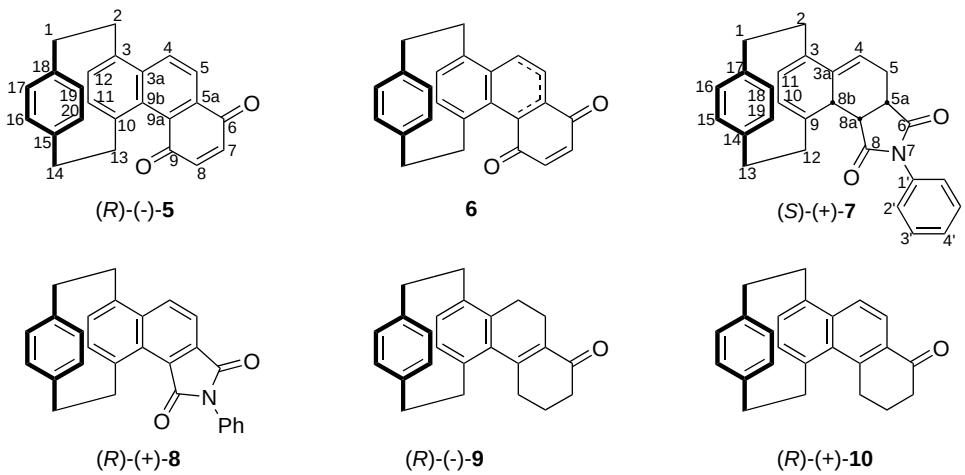


Figure 2.

2.1. Structural analysis

The structures of [2.2]paracyclophane derivatives **5** and **7**–**10** were assigned by analysis of ^{1}H and ^{13}C NMR spectra. Proton and carbon shift assignments were based on COSY, HETCOR and ^{1}H–$\{^{1}H\}$ NOE experiments. Selective pre-irradiation of the C(2)H resonance of compounds **5** and **7**–**10** resulted in signal enhancement of the resonance attributed to C(4)H. Further support to the structure assignment was also given by the NOE effects observed between C(11)H and C(16)H, C(12)H and C(17)H, C(4)H and C(19)H for compounds **5** and **10** (Fig. 3), as well as between C(10)H and C(15)H, C(11)H and C(16)H, C(18)H and C(4)H protons for **8**. Interestingly, the large chemical shift of one of the C(12)H methylene protons (4.63 ppm) in **8** is due to the anisotropy effect of C(8) carbonyl and reveals spatial proximity of C(8) and C(12).

The *cis*-relationship of C(5a)H, C(8a)H and C(8b)H for cycloadduct **7** followed from NOE effects observed on the resonances of C(5)H, C(5a)H and C(8a)H upon irradiation of the resonance attributed to the C(8b)H proton. Furthermore, selective pre-irradiation of the C(19)H resonance gave large NOE effect on the signal attributed to C(8b)H. This indicated a *cis*-relationship between C(8b)H and the unsubstituted benzene ring of the paracyclophane unit (Fig. 3), confirming a totally *anti-endo* diastereoselectivity in the cycloaddition reaction between **1** and **3**.

The regiochemistry of the carbonyl function of **9** and **10** was established by mutual dipolar contact observed between C(9)H and C(13)H protons, as well as from the long-range heterocorrelation observed between C(5)H and C(6) for both ketones.

3. Conclusion

A two-step synthetic approach to enantiomerically pure condensed [2.2]paracyclophanes based on the Diels–Alder reaction of (*S*)-(+)-4-ethenyl[2.2]paracyclophane **1**, has been described. Optically active helicenophanes containing three condensed rings have never been synthesised. The Diels–Alder reaction of diene **1** with **3** has been shown to occur with *anti-endo* diastereoselectivity. It is reasonable to hypothesise that each cycloaddition of diene **1** with dienophiles **2**–**4** was *anti-endo* diastereoselective, since the *syn* addition is hindered by the unsubstituted benzene ring of the paracyclophane moiety. The cycloadditions of the poorly reactive dienophiles **3** and **4** have been activated by high pressure.

4. Experimental

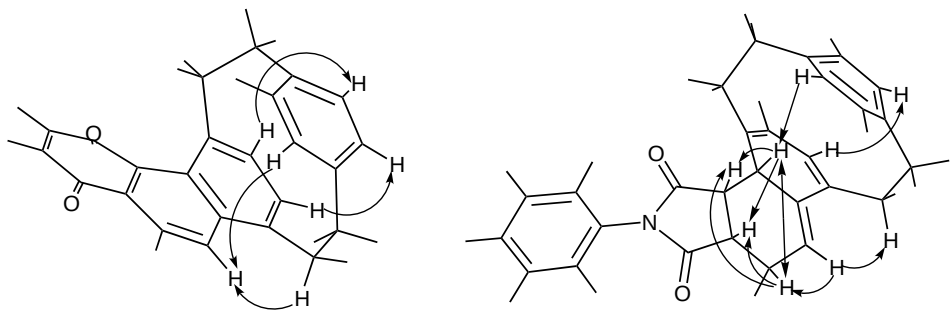
4.1. General procedures

Melting points were determined on a Büchi melting point apparatus and are uncorrected. Optical rotations were measured on a Jasco DIP-360 polarimeter in a quartz cell at 25°C. GC analyses were performed on a Hewlett–Packard 6890 chromatograph. IR spectra were recorded in $CHCl_3$ solution at rt on a Perkin–Elmer Paragon 500 FT IR. Mass spectra were observed on a Hewlett–Packard 5970 GC–MS instrument (70 eV). The NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument in $CDCl_3$ solution (internal standard Me_4Si). Proton and carbon shift assignments were based on COSY, ^{1}H–$\{^{1}H\}$ NOE and HETCOR experiments.

4.2. Diels–Alder reaction of (*S*)-(+)-4-ethenyl[2.2]paracyclophane 1 with 1,4-benzoquinone 2

Diene (*S*)-(+)-**1** (0.30 g, 1.26 mmol) and 1,4-benzoquinone **2** (1.38 g, 12.76 mmol) were heated together at 140°C for 4 h (Table 1). Excess benzoquinone was removed by steam distillation and the residue extracted with $CHCl_3$. The combined extracts were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure to afford a residue which was purified by flash chromatography (9:1 hexane/ethyl acetate), giving a 7:1 mixture (0.16 g, 38%) of compounds **5** and **6** as shown by GC–MS and ^{1}H NMR analyses. This mixture was directly submitted to DDQ oxidation.

When a mixture of (*S*)-(+)-**1** (0.10 g, 0.43 mmol) and **2** (0.50 g, 4.62 mmol) in acetic acid (3 mL) was heated at 100°C with stirring, a 2.3:1 mixture of compounds **5** and **6** was obtained in 38% yield.



(*R*)-(-)-**5** (*S*)-(+)-**7**

Figure 3. Minimised energy conformations of **5** and **7**; the arrows indicate observed NOEs.

When a solution of (*S*)-(+)-**1** (0.10 g, 0.43 mmol) and **2** (0.50 g, 4.62 mmol) in toluene (4 mL) was heated at reflux temperature, a 5:1 mixture of compounds **5** and **6** was obtained in 13% yield.

When a solution of (*S*)-(+)-**1** (0.20 g, 0.85 mmol) and **2** (0.10 g, 0.92 mmol) in CH_2Cl_2 (5 mL) was stirred under high pressure, a 1:9 mixture of compounds **5** and **6** was obtained in 20% yield.

4.3. Preparation of (*R*)-(−)-5

A toluene (9 mL) solution of the above mixture of **5** and **6** (0.16 g) was treated with DDQ (0.72 g, 3.17 mmol) and stirred under reflux under nitrogen for 20 h. After cooling, the mixture was diluted with toluene (20 mL), washed with 10% KOH aqueous solution and saturated brine, then dried (Na_2SO_4) and concentrated in vacuo. Column chromatography of the residue on silica gel eluting with 9:1 hexane/ethyl acetate afforded (*R*)-(−)-**5** as red crystals (0.15 g, 95%); mp 170–171°C (hexane/CH_2Cl_2); $[\alpha]_D^{25}=-229$ (*c* 0.027, $CHCl_3$); IR: 1659 (s, C=O) cm^{-1}; ^1H NMR: δ 2.81 (m, 2H, H-14), 2.93 (m, 1H, H-1), 3.05 (m, 1H, H-2), 3.11 (m, 1H, H-13), 3.23 (m, 1H, H-1), 3.36 (m, 1H, H-13), 3.81 (m, 1H, H-2), 5.52 (dd, 1H, $J=7.8$, 1.9 Hz, H-20), 5.63 (dd 1H, $J=7.8$, 1.9 Hz, H-19), 6.59 (dd, 1H, $J=7.8$, 1.9 Hz, H-16), 6.65 (dd, 1H, $J=7.8$, 1.9 Hz, H-17), 6.83 (d, 1H, $J=7.2$ Hz, H-12), 6.95 (dd, 1H, $J=7.2$, 0.9 Hz, H-11), 6.96 (d, 1H, $J=9.8$ Hz, H-7), 7.05 (d, 1H, $J=9.8$ Hz, H-8), 8.05 (d, 1H, $J=8.5$ Hz, H-4), 8.13 (d, 1H, $J=8.5$ Hz, H-5); ^{13}C NMR: δ 33.3 (C-2), 34.5 (C-1), 35.1 (C-14), 37.6 (C-13), 121.0 (C-5), 128.2 (C-20), 130.4 (C-4, C-19), 131.1 (C-17), 131.3 (C-9a), 131.4 (C-5a), 132.4 (C-16), 134.8 (C-12), 135.2 (C-11), 135.6 (C-10), 136.2 (C-7), 138.0 (C-18), 139.1 (C-15), 130.3, 136.3, 139.6 (C-3a, C-3, C-9b), 139.7 (C-8), 185.8 (C-6), 186.5 (C-9); MS (*m*/*z*): 104 (50), 178 (32), 207 (10), 220 (100), 338 (M^+, 77). Anal. calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.3; H, 5.4%.

4.4. Diels–Alder reaction of (*S*)-(+)-4-ethenyl[2.2]paracyclophane 1 with *N*-phenylmaleimide 3

A solution of *N*-phenylmaleimide **3** (0.24 g, 1.38 mmol) in CH_2Cl_2 (6 mL) was added to a solution of diene (*S*)-(+)-**1** (0.33 g, 1.41 mmol) in CH_2Cl_2 (4 mL) containing a small amount of hydroquinone (Table 1). 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 10 kbar pressure for 5 days at 40°C. After depressurising, the solvent was removed in vacuo and the crude residue was purified by column chromatography. Elution with 85:15 toluene/ethyl acetate afforded pure (*S*)-(+)-**7** as white crystals (0.41 g, 70%); mp 210°C (dec.) (hexane/CH_2Cl_2); $[\alpha]_D^{25}=+275$ (*c* 1, $CHCl_3$); IR: 1709 (s, C=O) cm^{-1}; ^1H NMR: δ 1.71 (m, 1H, H-5), 2.42 (m, 1H, H-2), 2.35 (dd, 1H, $J=5.8$, 4.0 Hz, H-8b), 2.62 (m, 1H, H-12), 2.72 (m, 1H, H-12), 2.81 (m, 1H, H-2), 2.85 (m, 1H, H-13), 3.00 (m, 1H, H-13), 3.04 (ddd, 1H, $J=14.5$, 8.9, 7.3 Hz, H-5), 3.05–3.11 (m, 2H, H-1), 3.20 (ddd, 1H, $J=8.8$, 5.8, 2.0 Hz, H-8a), 3.25 (ddd, 1H, $J=8.9$, 8.8, 6.0 Hz, H-5a), 5.25 (d, 1H, $J=6.8$ Hz, H-11), 5.55 (d, 1H, $J=6.8$ Hz, H-10), 5.68 (ddd, 1H, $J=7.3$, 5.0, 4.0 Hz, H-4), 6.49 (dd, 1H, $J=7.9$, 1.7 Hz, H-18), 6.77 (dd, 1H, $J=7.9$, 1.6 Hz, H-19), 6.85 (dd, 1H, $J=7.9$, 1.7 Hz, H-16), 6.89 (dd, 1H, $J=7.9$, 1.6 Hz, H-15), 6.98 (m, 2H, H-2′), 7.26 (m, 1H, H-4′), 7.30 (m, 2H, H-3′); ^{13}C NMR: δ 25.7 (C-5), 31.5 (C-2), 33.3 (C-12), 33.8 (C-13), 34.0 (C-1), 37.5 (C-8a), 42.8 (C-5a), 47.3 (C-8b), 116.1 (C-4), 126.4 (C-2′), 127.1 (C-11), 127.8 (C-19), 128.2 (C-4′), 128.8 (C-3′), 130.3 (C-10), 131.0 (C-18), 131.1 (C-9), 131.2 (C-15), 132.2 (C-16), 132.5 (C-1′), 138.2, 138.9 (C-3, C-14), 139.3 (C-17), 142.7 (C-3a), 174.5 (C-8), 178.0 (C-6); MS (*m*/*e*): 104 (41), 141 (82), 156 (59), 303 (62), 407 (M^+, 100). Anal. calcd for $C_{28}H_{25}NO_2$: C, 82.53; H, 6.18; N, 3.44. Found: C, 82.7; H, 6.2; N, 3.4%.

4.5. Preparation of (*R*)-(+)-8

A toluene (20 mL) solution of **7** (0.40 g, 0.98 mmol) was treated with DDQ (1.60 g, 7.05 mmol) under reflux for 21 h then evaporated to afford a solid residue, which was purified by column chromatography. Elution with 4:1 hexane/ethyl acetate gave pure (*R*)-(+)-**8** (0.33 g, 84%) as yellow crystals; mp 260–261°C (hexane/CH_2Cl_2); $[\alpha]_D^{25}=+418$ (*c* 0.06, $CHCl_3$); IR: 1711 (s, C=O) cm^{-1}; ^1H NMR: δ 2.83 (m, 1H, H-13), 2.98 (m, 1H, H-1), 3.02 (m, 1H, H-13), 3.17 (m, 1H, H-2), 3.20 (m, 1H, H-1), 3.25 (m, 1H, H-12), 3.86 (m, 1H, H-2), 4.63 (m, 1H, H-12), 5.64 (dd, 1H, $J=7.7$, 1.5 Hz, H-18), 5.67 (dd, 1H, $J=7.7$, 1.5 Hz, H-19), 6.57 (dd, 1H, $J=8.0$, 1.5 Hz, H-15), 6.61 (dd, 1H, $J=8.0$, 1.5 Hz, H-16), 6.90 (d, 1H, $J=7.3$ Hz, H-11), 7.01 (d, 1H, $J=7.3$ Hz, H-10), 7.42–7.53 (m, 5H, N-Ph protons), 7.95 (d, 1H, $J=8.3$ Hz, H-5), 8.16 (d, 1H, $J=8.3$ Hz, H-4); ^{13}C NMR: δ 33.7 (C-2), 34.3 (C-1), 35.1 (C-13), 37.2 (C-12), 118.1 (C-5), 126.8 (Cs-2′), 127.1 (C-8b), 128.0 (C-4′), 128.7 (C-18), 129.1 (Cs-3′), 129.8 (C-3a), 130.2 (C-19), 131.1 (C-9), 131.8 (C-4), 131.9 (C-1′), 132.0 (C-15), 132.2 (C-16), 134.0 (C-11), 136.4 (C-10), 137.5, 137.6, 137.9 (C-3, C-17, C-14), 139.4, 140.3 (C-5a, C-8a), 167.8, 167.9 (C-6, C-8); MS (*m*/*z*): 77 (25), 103 (100), 152 (22), 207 (24), 299 (83), 403 (M^+, 39). Anal. calcd for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47. Found: C, 83.2, H, 5.3; N, 3.5%.

4.6. Diels–Alder reaction of (*S*)-(+)-4-ethenyl[2.2]paracyclophane 1 with 3-nitro-2-cyclohexen-1-one 4

A solution of (*S*)-(+)-4-ethenyl[2.2]paracyclophane **1** (0.30 g, 1.39 mmol) and 3-nitro-2-cyclohexene-1-one **4** (0.26 g, 1.84 mmol) in CH_2Cl_2 (15 mL), containing a small amount of hydroquinone was stirred under 10 kbar pressure for 5 days at 40°C. After depressurising, the solvent was removed in vacuo and the crude residue diluted with dry THF (15 mL) and treated with DBN (0.42 mL) at 0°C under nitrogen for 30 min. The reaction mixture was then poured into water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried (Na_2SO_4) and evaporated in vacuo to give the crude product (0.55 g), which was shown to contain ketones **9** and **10** in a 3.5:1 ratio (GC–MS

analysis). An analytically pure sample of (*R*)-(−)-**9** was obtained by chromatography on silica gel of this mixture (elution with 85:15 hexane/ethyl acetate). (*R*)-(−)-**9**: colourless crystals; mp 179–180°C (CH_2Cl_2/hexane); $[\alpha]_D^{25} = -26.4$ (*c* 0.06, CH_2Cl_2); IR: 1644 (s, C=O) cm^{-1}; ^1H NMR: δ 1.87 (m, 1H, H-8), 2.09 (m, 1H, H-8), 2.30 (m, 1H, H-4), 2.44 (m, 1H, H-9), 2.55 (m, 2H, H-7), 2.58 (m, 1H, H-5), 2.82 (m, 1H, H-13), 2.85 (m, 1H, H-5), 2.88 (m, 1H, H-4), 2.89 (m, 1H, H-14), 3.01 (m, 1H, H-9), 3.06 (m, 2H, H-1, H-2), 3.10 (m, 1H, H-14), 3.12 (m, 1H, H-1), 3.37 (m, 1H, H-2), 3.38 (m, 1H, H-13), 6.38 (dd, 1H, $J = 8.0$, 1.2 Hz, H-19), 6.40 (d, 1H, $J = 7.2$ Hz, H-11), 6.43 (d, 1H, $J = 7.2$ Hz, H-12), 6.47 (dd, 1H, $J = 8.0$, 1.2 Hz, H-20), 6.63 (d, 2H, $J = 1.2$ Hz, H-16, H-17); ^{13}C NMR: δ 18.7 (C-5), 23.9 (C-4), 24.2 (C-8), 31.3 (C-9), 32.7 (C-13), 34.4 (C-14), 35.4 (C-1), 36.5 (C-2), 38.2 (C-7), 131.4 (C-19), 131.7 (C-9b, C-20), 132.0 (C-16), 133.1 (C-17), 134.5 (C-12), 135.5 (C-11), 136.3, 136.7, 137.4 (C-3, C-3a, C-10), 138.6, 138.9, 139.5 (C-5a, C-15, C-18), 152.4 (C-9a), 199.3 (C-6); MS (*m*/*e*): 104 (25), 165 (52), 191 (66), 223 (100), 328 (M^+, 77). Anal. calcd for $C_{24}H_{24}O$: C, 87.76; H, 7.37. Found: C, 87.9; H, 7.4%.

4.7. Preparation of (*R*)-(+)-10

A toluene solution (20 mL) of the above mixture (0.55 g) and DDQ (0.60 g, 2.64 mmol) was heated at reflux temperature for 6 h under nitrogen. The mixture was then cooled and worked-up as usual to afford a residue that was chromatographed on silica gel. Elution with 9:1 hexane/ethyl acetate afforded pure (*R*)-(+)-**10** (0.09 g, 20% overall yield) as orange crystals; mp 219–220°C (ethyl acetate); $[\alpha]_D^{25} = +201$ (*c* 0.3, $CHCl_3$); IR: 1667 (s, C=O) cm^{-1}; ^1H NMR: δ 1.87 (m, 1H, H-8), 2.31 (m, 1H, H-8), 2.68 (m, 1H, H-14), 2.78 (m, 1H, H-7), 2.82 (m, 1H, H-7), 3.00 (m, 1H, H-1), 3.05 (m, 1H, H-2), 3.11 (m, 1H, H-14), 3.15 (m, 1H, H-13), 3.18 (m, 1H, H-1), 3.35 (m, 1H, H-9), 3.42 (m, 1H, H-9), 3.80 (m, 1H, H-2), 3.90 (m, 1H, H-13), 5.46 (dd, 1H, $J = 7.8$, 1.5 Hz, H-20), 5.81 (dd, 1H, $J = 7.8$, 1.5 Hz, H-19), 6.48 (dd, 1H, $J = 8.0$, 1.5 Hz, H-16), 6.52 (dd, 1H, $J = 8.0$, 1.5 Hz, H-17), 6.78 (d, 1H, $J = 7.2$ Hz, H-12), 6.87 (d, 1H, $J = 7.2$ Hz, H-11), 7.65 (d, 1H, $J = 8.8$ Hz, H-4), 8.10 (d, 1H, $J = 8.8$ Hz, H-5); ^{13}C NMR: δ 23.7 (C-8), 30.6 (C-9), 32.9 (C-2), 34.2 (C-1), 35.3 (C-14), 38.6 (C-7), 38.8 (C-13), 122.5 (C-5), 123.9 (C-4), 128.7 (C-19), 129.4 (C-20), 129.7 (C-9b), 131.3 (C-16), 132.0 (C-17), 132.8 (C-12), 134.1 (C-10), 134.9 (C-11), 137.5, 138.0, 138.2, 138.6 (C-3a, C-3, C-5a, C-15), 138.1 (C-18), 142.4 (C-9a), 199.2 (C-6); MS (*m*/*e*): 104 (51), 179 (36), 207 (19), 222 (100), 326 (M^+, 48). Anal. calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.2; H, 6.8%.

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