New Short Step Synthesis of A,B-Aromatic Oxasteroids by Intra- and Inter-molecular Diels–Alder Reactions of 1,2-Naphthoquinone Dimethides generated from Substituted 1,2-Cyclobutanaphthalenes[1]

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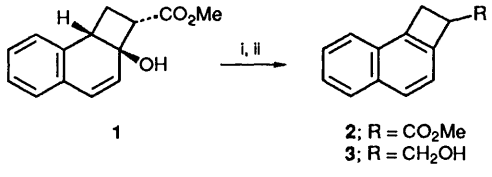
A simple, highly efficient synthesis of A/B aromatic 16-oxasteroids by either an intra- or inter-molecular Diels–Alder reaction of 1,2-naphthoquinone dimethides, generated by the thermolysis of methyl cyclobuta[*a*]naphthalene-2-carboxylate or cyclobuta[*a*]naphthalen-2-ylmethanol, is described.

O-Quinone dimethides[2] generated *in situ* from a variety of benzocyclobutene derivatives and other sources have been very successfully used as dienes in constructing polycyclic compounds.[3,4] When we initiated the present study, however, there were few reports[5,†] concerning the utilization of 1,2-naphthoquinone dimethides for the synthesis of polycyclic compounds, although a paper by Cava and colleagues in 1962 described the generation of a 1,2-naphthoquinone dimethide.[6]

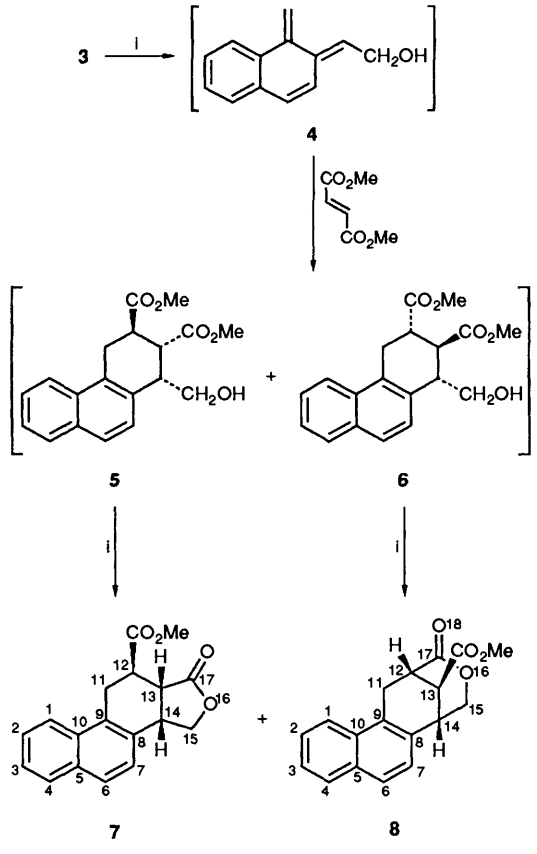
We report here the generation of new 1,2-naphthoquinone dimethide intermediates and their use for a simple, highly efficient synthesis of A/B aromatic 16-oxasteroids.‡ This study was undertaken as part of our program concerning the synthesis of heterosteroids.[8]

We have reported[9] an efficient synthesis of an undescribed and inaccessible tricyclic alcohol **1** by the photocycloaddition of 2-naphthyl trimethylsilyl ether and methyl acrylate, followed by the acidic hydrolysis of the photoadduct. Treatment of **1** with mesyl chloride and triethylamine in diethyl ether at 0 °C gave methyl 1,2-dihydrocyclobuta[*a*]naphthalene-2-carboxylate **2** (81%). Reduction of ester **2** with lithium aluminium hydride in diethyl ether at 0 °C gave 1,2-dihydrocyclobuta[*a*]-naphthalen-2-ylmethanol **3** in 74% yield (Scheme 1).



Scheme 1 *Reagents:* i, MsCl–Et_3N; ii, $LiAlH_4$–EtOEt

Substituted cyclobuta[*a*]naphthalenes **2**, **3**, and their derivatives were used for generating the corresponding 1,2-naphthoquinone dimethides. Thus, the alcohol **3** when heated with 2 equiv. of dimethyl fumarate in *o*-dichlorobenzene under reflux for 1 h gave two products, **7** and **8**, in 40 and 29% isolated yields. The IR spectra indicated that product **7** is a γ-lactone, while product **8** is a δ-lactone. It was then apparent that the structures of these products were methyl *rac*-17-oxo-16-oxa-14β-gona-1,3,5,7,9-pentaene-12β-carboxylate **7** and methyl *rac*-17(13→12) *abeo*-17-oxo-16-oxa-12β(H),13α(H),14β-estra-1,3,5,7,9-pentaene-18-oate **8**, which are formed from two Diels–Alder adducts **5** and **6**, with two *trans*-oriented methoxycarbonyl



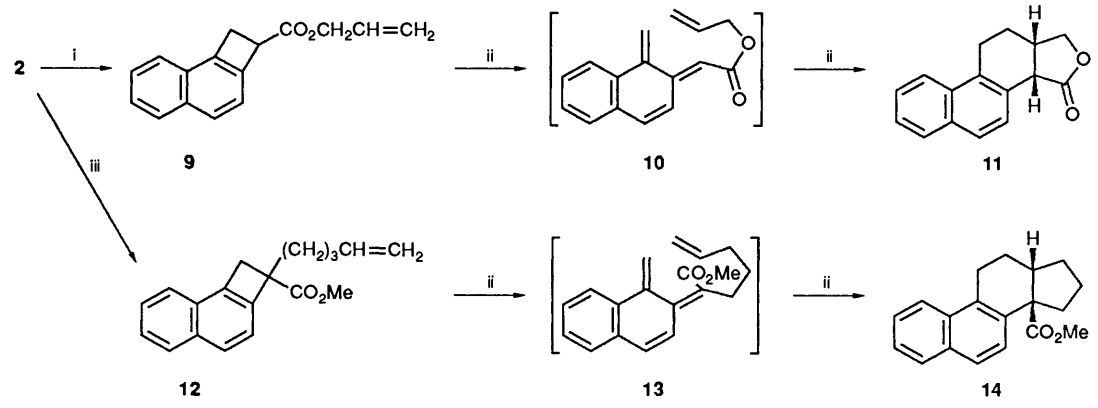
Scheme 2 *Reagent:* i, *o*-dichlorobenzene–reflux

groups (see Scheme 2). The structures of the adducts **7** and **8** including their stereochemistry were assigned on the basis of their ^1H NMR spectra and the consideration of the path leading to the adducts in the Diels–Alder reaction. Examination of the molecular model of adduct **7** indicated that the configuration of the carboxy group attached to the C-12 should be β since the initially formed β-oriented carboxy group adopts a more stable *pseudo* equatorial position. The observed coupling constant ($J_{12\text{-H}-13\text{-H}}$ 6.2 Hz) of the signal due to a hydrogen attached to the C-12 is in agreement with the β-configuration.

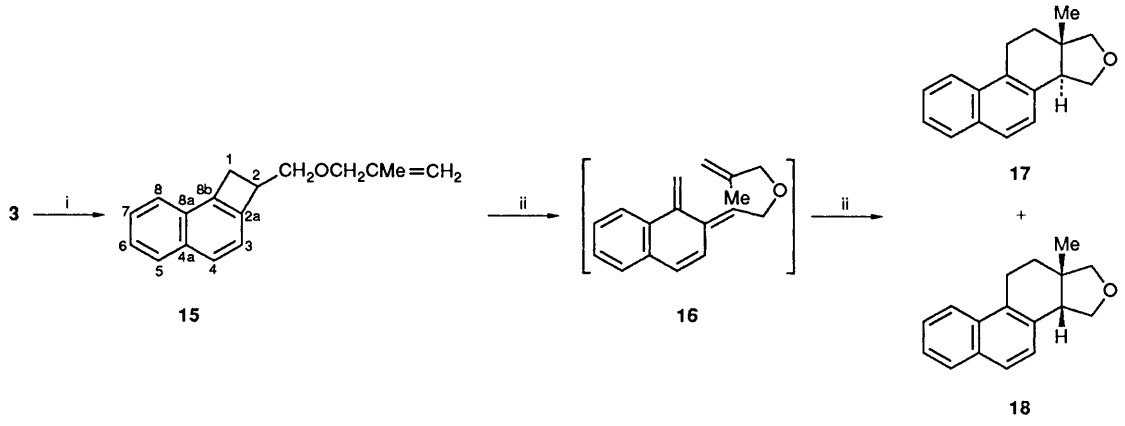
A more directed two-step synthesis of oxasteroids and steroids can be achieved by intramolecular Diels–Alder reactions. Thus, the allyl ester **9** prepared by the treatment of the methyl ester **2** with allyl alcohol in the presence of toluene-*p*-sulphonic acid at room temperature in *o*-dichlorobenzene, when heated under reflux for 19 h gave *rac*-16-oxa-14β-gona-1,3,5,7,9-

† After the completion of the present work[1] we became aware of a publication by Kessar and colleagues who report a synthesis of an azasteroid through thermolysis of *N*-cyclobutanaphthalenylpropenamides.[5]

‡ A paper[7] on the synthesis of steroidal skeletons by an approach similar to ours has appeared, when we orally reported the present work.[1]



Scheme 3 *Reagents:* i, *p*-TsOH-CH_2=$CHCH_2OH$; ii, *o*-dichlorobenzene–reflux; iii, LDA–CH_2=$CH(CH_2)_3Br$



Scheme 4 *Reagents:* i, NaH–CH_2=$C(Me)CH_2Cl$; ii, *o*-dichlorobenzene–reflux

pentaen-15-one **11** through an intermediate **10** as an exclusive product (47%) (see Scheme 3). A less stable 14α-epimer of the oxasteroid **11**, probably formed in this reaction, was isomerized to the more stable *cis*-isomer **11** under the reaction conditions. The IR and ^{1}H NMR spectra were fully consistent with the assigned structure. The *cis* junction of the C/D rings was confirmed by the coupling constant (*J* 7.69 Hz) of the doublet due to the 14-H.

The disubstituted cyclobuta[*a*]naphthalene **12**, prepared in 48% yield by the reaction of the cyclobuta[*a*]naphthalene **2** with pent-1-enyl bromide and LDA in *o*-dichlorobenzene, when heated under reflux gave methyl *rac*-gona-1,3,5,7,9-pentaene-14β-carboxylate **14**[7] in 94% yield.

A final example of the synthesis of 16-oxasteroids is shown in Scheme 4; the methacryl ether **15** (prepared in 78% yield by the treatment of cyclobutanaphthalenylmethanol **3** with methacryl chloride and sodium hydride) when heated gave *rac*-16-oxa-estra-1,3,5,7,9-pentaene **17** and its C/D *cis*-isomer **18** through a 1,2-naphthoquinone dimethide **16** in 43 and 37% yields. The stereochemistry of the C/D ring junctions of oxasteroids **17** and **18** were assigned as *trans* and *cis*, respectively, through comparisons of the chemical shifts of their 18-H (δ 0.87 and 1.16) with those of C/D *trans*- and *cis*- A, B-aromatic steroids.[10]

Experimental

M.p.s were recorded with a Yanagimoto melting point apparatus and are uncorrected. IR spectra were determined for Nujol mulls with a Hitachi 285 infrared spectrometer unless stated otherwise. The ^{1}H NMR spectra were determined with a JNM-FX 270 spectrometer (270 MHz, Faculty of Pharmaceutical Sciences of this University). $CDCl_3$ was used as the solvent with $SiMe_4$ as an internal standard, *J* values are given in Hz. PLC was carried out with Merck Kiesel gel 60-PF_{254}. The high- and low-resolution mass spectra were determined with a JEOL JMS-300 spectrometer (70 eV, Faculty of Pharmaceutical Sciences of this University). Elemental analyses were performed by the staff of the analytical laboratory of the Faculty of Pharmaceutical Sciences.

Methyl 1,2-*Dihydrocyclobuta*[a]*naphthalene-2-carboxylate* **2**.—To a stirred solution of methyl (2aα,8bα)-(±)-1,2,2a,8b-tetrahydro-2a-hydroxycyclobuta[*a*]naphthalene-2-carboxylate **1** (2.82 g, 12.3 mmol) in benzene (100 cm^3) at 0 °C was added methanesulphonyl chloride (1.69 g, 14.7 mmol) and the mixture was stirred for 30 min at that temperature. Water was added to the resulting mixture and the product was extracted with diethyl ether. The extract was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on silica gel (1:3 ethyl acetate–hexane, R_f 0.61) to give **2** (2.10 g, 81%); m.p. 48–51 °C (hexane) (lit.,[7] 47–49 °C).

1,2-*Dihydro*-2-*hydroxymethylcyclobuta*[a]*naphthalene* **3**.—To a stirred suspension of lithium aluminium hydride (400 mg, 10.5 mmol) in diethyl ether (10 cm^3) at 0 °C was added a solution of **2** (1.00 g, 4.71 mmol) in diethyl ether (5 cm^3). The mixture was stirred for 30 min after which several drops of saturated aqueous sodium sulphate were added to it. The resulting mixture was dried ($MgSO_4$), filtered through a Celite pad and the filtrate evaporated. The residue was separated by preparative TLC on silica gel to give **3** (R_f 0.42, 1:1 ethyl acetate–hexane; 641 mg, 74%) as an oil: ν_{max}(neat)/cm^{-1} 3320, 1622 and 1585; δ_H(270 MHz) 1.54 (1 H, s, OH), 3.13 (1 H, dd, *J* 14.29 and 1.83, 1-H), 3.52 (1 H, dd, *J* 14.29 and 4.76, 1-H), 3.75–3.9 (1 H, m, 2-H), 3.96 and 4.01 (2 H, each dd, *J* 10.62, 5.86 and

10.62, 6.96, CH_2OH), 7.30 (1 H, dd, *J* 8.06, 3-H), 7.35–7.55 (2 H, m, aromatic H) and 7.7–7.9 (3 H, m, aromatic H); *m/z* 184 (M^+) and 155 (51 and 100%) (Found: M^+, 184.0868. $C_{13}H_{12}O$ requires *M*, 184.0887).

Methyl rac-17-*Oxo*-16-*oxa*-14β-*gona*-1,3,5,7,9-*pentaene*-12β-*carboxylate* **7** *and Methyl* rac-17(13→12)abeo-17-*Oxo*-16-*oxa*-12β(H),13α(H),14β-*estra*-1,3,5,7,9-*pentaen*-18-*oate* **8**.—A solution of compound **3** (70 mg, 0.38 mmol) and dimethyl fumarate (65 mg, 0.76 mmol) in *o*-dichlorobenzene (5 cm^3) was heated under reflux for 1 h. Removal of the solvent under reduced pressure and separation of the residue by preparative TLC on silica gel (1:3 ethyl acetate–hexane) gave the lactones **7** (43 mg, 40%) and **8** (33 mg, 29%). **7**: M.p. 154–155 °C (hexane–diethyl ether); ν_{max}/cm^{-1} 1761 and 1727; δ_H(270 MHz) 3.21 (1 H, dd, *J* 16.85 and 6.23, 11-H), 3.5–3.6 (2 H, m, 12-H and 14-H), 3.62 (3 H, s, CO_2Me), 3.75 (1 H, br d, *J* 16.5, 11-H), 4.10 (1 H, br t, *J* 6.2, 13-H), 4.38 (1 H, dd, *J* 9.16 and 2.56, 15-H), 4.77 (1 H, dd, *J* 9.16 and 6.96, 15-H), 7.20 (1 H, d, *J* 8.43, 7-H), 7.45–7.6 (2 H, m, 2- and 3-H), 7.74 (1 H, d, *J* 8.43, 6-H), 7.82 (1 H, dd, *J* 8.43 and 1.46, 1- or 4-H), and 7.99 (1 H, α, *J* 8.43, 4- or 1-H); *m/z* 296 (M^+) and 166 (95 and 100%) (Found: C, 72.9; H, 5.35. $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%).

8: M.p. 75–77 °C (hexane–diethyl ether); ν_{max}/cm^{-1} 1734 and 1718; δ_H(270 MHz) 3.31 (1 H, dd, *J* 3.29 and 2.19, 13-H), 3.5–3.6 (2 H, m), 3.62 (3 H, S, CO_2Me), 3.7–3.8 (2 H, m), 4.48 (1 H, dd, *J* 10.99 and 0.74, 15-H), 4.71 (1 H, dd, *J* 10.99 and 3.67, 15-H) and 7.25–7.9 (6 H, m, aromatic H); *m/z* 296 (M^+) and 179 (86 and 100%) (Found: C, 73.0; H, 5.4. $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%).

Allyl 1,2-*Dihydrocyclobuta*[a]*naphthalene*-2-*carboxylate* **9**.—Compound **2** (100 mg, 0.47 mmol) and toluene-*p*-sulphonic acid monohydrate (40 mg, 0.21 mmol) were dissolved in allyl alcohol (3 cm^3). This solution was stirred for 2 d at room temperature. To the resulting mixture was added diethyl ether and aqueous sodium hydrogen carbonate. The aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was separated by preparative TLC on silica gel to give the ester **9** (75 mg, 67%); an oil R_f 0.72 (1:3 ethyl acetate–hexane); ν_{max}(neat)/cm^{-1} 1736; δ_H(270 MHz) 3.70 (2 H, br d, *J* 4.0, 1-H), 4.52 (1 H, br t, *J* 4.0, 2-H), 4.66 (2 H, dt, *J* 5.50 and 1.47, allylic H), 5.2–5.4 (2 H, m, CH=CH_2), 5.85–6.05 (1 H, m, C*H*=CH$_2$), 7.34 (1 H, d, *J* 8.06, 3-H), 7.4–7.55 (2 H, m, aromatic H) and 7.7–7.9 (3 H, m, aromatic H); *m/z* 238 (M^+) and 169 (59 and 100%) (Found: M^+, 238.0992. $C_{16}H_{14}O_2$ requires *M*, 238.0993).

rac-16-*Oxa*-14β-*gona*-1,3,5,7,9-*pentaen*-15-*one* **11**.—A solution of the ester **9** (51 mg, 0.21 mmol) in *o*-dichlorobenzene (3 cm^3) was heated under reflux for 19 h. The solvent was removed under reduced pressure, and the residue was separated by preparative TLC on silica gel to give the steroid **11** (24 mg, 47%); R_f 0.28 (1:3 ethyl acetate–hexane); m.p. 148–150 °C (hexane–diethyl ether); ν_{max}(neat)/cm^{-1} 1761; δ_H(270 MHz) 1.80 (1 H, dt, *J* 13.19, 5.13 and 1.47, 12-H), 2.18 (1 H, dq, *J* 13.19 and 4.39, 12-H), 2.85–3.05 (2 H, m, 11- and 13-H), 3.35 (1 H, dt, *J* 17.22 and 4.39, 11-H), 3.83 (1 H, d, *J* 7.69, 14-H), 4.21 (1 H, dd, *J* 9.16 and 1.84, 17-H), 4.49 (1 H, dd, *J* 9.16 and 5.86, 17-H) and 7.45–8.0 (6 H, m, aromatic H); *m/z* 238 (M^+) and 179 (79 and 100%) (Found: M^+, 238.0983. $C_{16}H_{14}O_2$ requires *M*, 238.0973).

Methyl 1,2-*Dihydro*-2-*pent*-4-*enylcyclobuta*[a]*naphthalene*-2-*carboxylate* **12**.—To a stirred solution of LDA (0.61 mmol) in THF (3 cm^3) containing hexamethylphosphoric triamide (300 mg, 1.65 mmol), which was prepared *in situ* by the standard method, was added a solution of the cyclobutene **2** (100 mg, 0.47 mmol) in THF (2 cm^3) and the mixture was stirred for 15 min. 5-Bromopent-1-ene (90 mg, 0.61) was added, and the resulting mixture was stirred for 15 min at the same temperature. The reaction was quenched by addition of aqueous ammonium chloride and the mixture extracted with diethyl ether. The extract was dried ($MgSO_4$) and evaporated to give a residue, which was separated by preparative TLC on silica gel (1:3 ethyl acetate–hexane) to give the ester **12** (63 mg, 48%). An oil; R_f 0.61; ν_{max}(neat)/cm^{-1} 1735; δ_H(270 MHz) 1.45–1.65 (2 H, m), 1.95–2.2 (4 H, m), 3.31 (1 H, d, *J* 13.92, 1-H), 3.71 (3 H, s, CO_2Me), 3.83 (1 H, d, *J* 13.92, 1-H), 4.9–5.05 (2 H, m, CH=CH_2), 5.7–5.9 (1 H, m, C*H*=CH$_2$), 7.36 (1 H, d, *J* 8.06, 3-H), 7.4–7.55 (2 H, m, aromatic H) and 7.65–7.9 (3 H, m, aromatic H); *m/z* 280 (M^+) and 165 (47 and 100%) (Found: M^+, 280.1449. $C_{19}H_{20}O_2$ requires *M*, 280.1463).

Methyl rac-*Gona*-1,3,5,7,9-*pentaene*-14β-*carboxylate* **14**.—A solution of the ester **12** (47 mg, 0.17 mmol) in *o*-dichlorobenzene (3 cm^3) was heated under reflux for 23 h. After removal of the solvent under reduced pressure the residue was subjected to preparative TLC on silica gel to afford the steroid **14** (43 mg, 92%). An oil; R_f 0.67 (1:5 ethyl acetate–hexane); ν_{max}(neat)/cm^{-1} 1727; δ_H(270 MHz) 1.55–2.15 (7 H, m, 12, 13, 16 and 17-H), 2.65–2.85 (2 H, m, 15-H), 3.11 (1 H, ddd, *J* 16.85, 11.35 and 6.96, 11-H), 3.20 (1 H, ddd, *J* 16.85, 9.89 and 5.96, 11-H), 3.62 (3 H, s, COOMe) and 7.25–8.05 (6 H, m, aromatic H); *m/z* 280 (M^+) and 221 [$(M - CO_2Me)^+$] (22 and 100%) (Found: M^+, 280.1456. $C_{19}H_{20}O_2$ requires *M*, 280.1464).

1,2-*Dihydro*-2-(2-*methylprop*-2-*enoxy*)*methylcyclobuta*[a]-*naphthalene* **15**.—To a stirred suspension of sodium hydride (50%; 75 mg, 1.56 mmol) in DMF (*N*,*N*′-dimethylformamide) (3 cm^3) at 0 °C was added dropwise a solution of the cyclobutene **3** (288 mg, 1.56 mmol) in DMF (1 cm^3). After 5 min, 3-chloro-2-methylpropene (141 mg, 1.56 mmol) was added and the resulting mixture was stirred at room temperature for 19 h. Aqueous ammonium chloride was added to the reaction mixture, and organic materials were extracted with diethyl ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated. The residue was separated by preparative TLC on silica gel to give the ether **15** (289 mg, 78%). An oil; R_f 0.67 (1:3 ethyl acetate–hexane); ν_{max}(neat)/cm^{-1} 1656, 1633 and 1090; δ_H(270 MHz) 1.76 (3 H, s, Me), 3.07 (1 H, dd, *J* 13.92 and 1.83, 1 H), 3.54 (1 H, dd, *J* 13.92 and 4.77, 1-H), (1 H, dd, *J* 9.16 and 8.06, methallyloxy CH_2), 3.73 (1 H, dd, *J* 9.16 and 6.59, methallyloxy CH_2), 3.8–3.9 (1 H, m, 2-H), 3.97 (2 H, s, methylallyl CH_2), 4.90 (1 H, s, one of olefinic protons), 4.98 (1 H, dd, *J* 1.10, one of olefinic protons) and 7.3–7.85 (6 H, m, aromatic H); *m/z* 238 (M^+) and 168 (32 and 100%) (Found: M^+, 238.1359. $C_{17}H_{18}O$ requires *M*, 238.1358).

rac-16-*Oxaestra*-1,3,5,7,9-*pentaene* **17** *and* rac-16-*Oxa*-14β-*estra*-1,3,5,7,9-*pentaene* **18**.—A solution of the adduct **15** (200 mg, 0.84 mmol) in *o*-dichlorobenzene was heated under reflux for 21 h. Removal of the solvent under reduced pressure followed by separation by PLC on silica gel (1:3 ethyl acetate–hexane) gave the oxasteroids **17** (85 mg, 43%) and **18** (73 mg, 37%). **17**: M.p. 150–151.5 °C (hexane–diethyl ether); ν_{max}/cm^{-1} 1021; δ_H(270 MHz) 0.87 (3 H, s, 18-H), 1.92 (1 H, dt, *J* 12.46 and 9.16, 12-H), 2.14 (1 H, ddd, *J* 12.46, 6.96 and 2.57, 12-H), 3.25–3.40 (3 H, m, 11- and 14-H), 3.61 (1 H, d, *J* 7.32, 17-H), 3.87 (1 H, d, *J* 7.32, 17-H), 3.92 (1 H, dd, *J* 11.72 and 7.33, 15-H), 4.48 (1 H, dd, *J* 7.67 and 7.33, 15-H) and 7.0–8.0 (m, 6 H, aromatic H); *m/z* 238 (M^+, 100%) (Found: M^+, 238.1346. $C_{17}H_{18}O$ requires *M*, 238.1357).

18: An oil; ν_{max}(neat)/cm^{-1} 1060; δ_H(270 MHz) 1.16 (3 H, s, 18-H), 1.77 (1 H, dddd, *J* 13.56, 6.87, 4.03 and 1.10, 12-H), 2.04 (ddd, *J* 13.56, 6.87 and 5.87, 12-H), 3.0–3.3 (3 H, m, 11- and

14-H), 3.70 (1 H, dd, *J* 9.16 and 8.43, 15-H), 3.76 (1 H, d, *J* 8.33, 17-H), 3.84 (1 H, d, *J* 8.33, 17-H), 4.40 (1 H, dd, *J* 8.79 and 8.43, 15-H) and 7.15–8.0 (6 H, m, aromatic H); *m/z* 238 (M^+, 100%) (Found: M^+, 238.1366. $C_{17}H_{18}O$ requires *M*, 238.1357).

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