SHORT PAPER

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Studies on BF_3·Et_2O-catalysed cyclisation of 2-aryl-1-(2,4,4- trimethyl-1-cyclohexen-3-yl)-ethanone†

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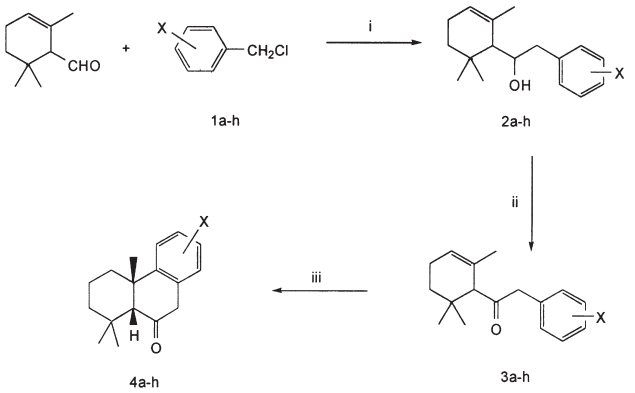
Cis-fused products were obtained in high yield from the cyclisations of a series of 2-aryl-1-(2,4,4-trimethyl-1-cyclohexen-3-yl)-ethanones bearing electron donating groups with BF_3·Et_2O as catalyst.

Keywords: cyclisation, Lewis acid, *cis*-fused, diterpenoid

In the previous study of our team on the total synthesis of (±)-celaphanol A, [1] a natural diterpenoid isolated from *Celastrus stehanotifolius*, [2] we obtained a *cis*-A/B fused key intermediate **4a** for the preparation of abietane-type or podocarpane-type tricylic diterpenoids *via* Lewis acid BF_3·Et_2O promoted cyclisations of 2-(3,4-dimethoxy phenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **3a** in very high yield. This aroused our great interest because acid-catalysed *cis*-cyclisation of A/B fused tricyclic diterpenoids in high stereoselectivity had rarely been reported.

As shown in Scheme 1, we have synthesised a series of different substituted 2-aryl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanones **3a–h** starting from (±)-α-cyclocitral[3] and different available substituted benzyl chlorides, and explored the cyclisations of **3a–h** with BF_3·Et_2O as catalyst. The results are shown in Table 1.



Scheme 1 Reagents and conditions: (i) Mg, Et_2O, reflux, 2 h; (ii) PCC, CH_2Cl_2, r. t., 2.5 h; (iii) BF_3·Et_2O, CH_2Cl_2, r.t.

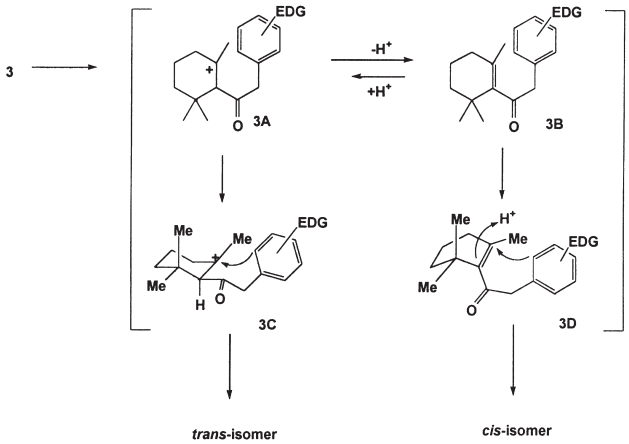
The *cis*-configuration of A/B ring junction in **4a–e** was characterised specifically by the upfield signal of the $C_{4\alpha}$ methyl group at 0.37–0.45 ppm in their ^{1}H NMR spectra. According to the literature,[4] when the A/B ring junction is *cis*, the $C_{4\alpha}$ methyl group remains within the sphere of magnetic influence of the aromatic ring C and the chemical shift of the $C_{4\alpha}$ methyl group appears at about 0.40 ppm. When A/B ring junction is *trans*, the $C_{4\alpha}$ methyl group is deshielded by the aromatic ring C and the chemical shift of the $C_{4\alpha}$ methyl group will appear at about 1.00 ppm.

Table 1 Cyclisation of 2-aryl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanones **3a–h**

Entry	Substrate	*cis*-product[a] (Yield/%)[b]	Time of reaction/h
1	**3a**, X=3,4-dimethoxy	**4a** (>95)	16
2	**3b**, X=3,4-methylenedioxy	**4b** (>95)	14
3	**3c**, X=3-methoxy	**4c** (93)	20
4	**3d**, X=4-methoxy	**4d** (92)	20
5	**3e**, X=3-*iso*propyl-4-methoxy	**4e** (94)	20
6	**3f**, X=5-*iso*propyl-2-methoxy	No reaction	36
7	**3g**, X=3,4,5-trimethoxy	No reaction	36
8	**3h**, X=H	No reaction	36

[a]Characterised by ^{1}H-NMR, ^{13}C-NMR, MS, IR. [b]Isolated yields.

The facile formation of the all-*cis* products **4a–e** in the Lewis acid-catalysed cyclisation of 2-aryl-1-(2,6,6-trimethyl-cyclohex-2-enyl)ethanone possibly proceeds through the concerted protonation cyclisation pathway (Scheme 2) which is consistent with mechanisms reported earlier on the cyclisations of cyclohexanols or cyclohexenes.[5]



Scheme 2

As shown in Table 1, due to the existence and stabilisation effect of the carbonyl group, the substrates **3a–e** with the aromatic ring bearing electron-donating groups (EDG) are sufficiently nucleophilic to react through the concerted protonation cyclisation pathway with intermediate **3B** picking up a proton from the least hindered face, *i.e. cis* to the existing methyl to give the A/B *cis*-fused product rather than by the pathway of complete protonation to carbocation **3A** via ring closure to give the least sterically hindered *trans*-product.[6] Substrates without any electron-donating groups (EDG) such

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as **3h** did not give any A/B *cis*-fused products and substrates **3f** and **3g** did not afford the cyclisation product because of the hindrance between the C-10 methyl group and the C-11 *iso*propyl or methoxy group.

Most of natural diterpenoids possess a *trans* A/B ring junction and all the *cis*-isomer obtained above may be easily converted into the *trans*-isomer in the manner reported in the literature.[7]

In conclusion, a stereoselective and high-yield method of formation of *cis*-A/B ring fused key intermediates for the preparation of tricylic diterpenoid has been developed, which will be of use for the synthesis of natural diterpenoids in high stereoselectivity.

Experimental

All the compounds here are racemates. Melting points were measured on a Kofler apparatus and are not corrected. IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrometer. Mass spectra were recorded on a ZAB-HS spectrometer. Elemental analyses were performed on a Carlo-Erba 1106 instruments. The ^{1}H NMR and ^{13}C NMR data were recorded in $CDCl_3$ with Bruker AM-200 and AM-400 MHz spectrometers. The chemical shifts are reported in ppm and are referred to $CHCl_3$ and with TMS as internal standard. The substituted benzyl chlorides were prepared from corresponding aldehydes by reduction and chlorination.

Representative procedure: *Preparation of 2-(3,4-methylenedioxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol* **(2b):** To the Grignard reagent prepared from 3,4-methylenedioxy-benzyl chloride (8.5 g, 50 mmol) and magnesium powder (1.32 g, 55 mmol) in dry ether (30 ml) under an argon atmosphere, α-cyclocitral (7.0g, 46 mmol) in ether (20 ml) was added. After refluxing for 2 h, the reaction mixture was stirred at room temperature for 4 h and then quenched with saturated NH_4Cl aqueous solution. The mixture was extracted with ether and washed with brine and dried over Na_2SO_4 and then evaporated in *vacuo*. The residue was purified by column chromatography using hexane–ethyl acetate (8:1) as the eluent, to afford **2b**(10.5 g: 79%) as an oil. IR: ν (film) 2925, 3580cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.78 (s, 3H), 0.85 (s, 3H), 1.23–2.90 (m, 8H), 1.84 (s, 3H), 4.05–4.15 (m, 1H), 5.65 (brs, 1H), 5.93 (s, 2H), 6.70–6.89 (m, 3H). MS (EI): 288, 270, 164, 135, 77. (Found: C, 75.13; H, 8.28. $C_{18}H_{24}O_3$ requires C, 75.03; H, 8.33%). Separation of diastereoisomers was not attempted.

2-(3,4-dimethoxyphenyl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2a):** Oil, yield: 78%. IR: 2930, 3579cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.79 (s, 3H), 0.85 (s, 3H), 1.83 (s, 3H), 3.78 (s, 3H), 3.82 (s, 3H), 4.05–4.14 (m, 1H), 5.65 (brs, 1H), 6.70–6.79 (m, 3H). MS (EI): 304, 180, 151, 41. (Found: C, 74.97; H, 9.18. $C_{19}H_{28}O_3$ requires C, 75.01; H, 9.21%).

2-(3-methoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2c):** Oil, yield: 75%. IR: 2935, 3587cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.80 (s, 3H), 0.86 (s, 3H), 1.33–2.99 (m, 8H), 1.88 (s, 3H), 3.81 (s, 3H), 4.05–4.16 (m, 1H), 5.67 (brs, 1H), 6.83–7.25 (m, 4H). MS (EI): 274, 256, 151, 121, 91. (Found: C, 78.75; H, 9.51. $C_{18}H_{26}O_2$ requires C, 78.83; H, 9.49%).

2-(4-methoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2d):** Oil, yield: 73%. IR: 2930, 3577cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.82 (s, 3H), 0.87 (s, 3H), 1.38–2.88 (m, 8H), 1.88 (s, 3H), 3.82 (s, 3H), 4.05–4.15 (m, 1H), 5.69 (brs, 1H), 6.85–7.55 (m, 4H). MS (EI): 274, 256, 151, 121, 109. (Found: C, 78.79; H, 9.53. $C_{18}H_{26}O_2$ requires C, 78.83; H, 9.49%).

2-(4-methoxy-3-isopropylphenyl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2e):** Oil, yield: 73%. IR: 2925, 3584cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.82 (s, 3H), 0.89 (s, 3H), 1.15(d, 6H, *J*=7Hz), 1.25–3.02 (m, 8H), 1.88 (s, 3H), 2.79 (sept, 1H, *J*=7Hz), 3.82 (s, 3H), 4.07–4.17 (m, 1H), 5.69 (brs, 1H), 6.95–7.25 (m, 3H). MS (EI): 316, 298, 193, 151, 109. (Found: C, 79.67; H, 10.18. $C_{21}H_{32}O_2$ requires C, 79.74; H, 10.13%).

2-(2-methoxy-5-isopropylphenyl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2f):** Oil, yield: 80%. IR: 2918, 3570cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.81 (s, 3H), 0.87 (s, 3H), 1.17(d, 6H, *J*=7Hz), 1.33–2.99 (m, 8H), 1.85 (s, 3H), 2.75 (sept, 1H, *J*=7Hz), 3.80 (s, 3H), 4.05–4.15 (m, 1H), 5.69 (brs, 1H), 6.95–7.25 (m, 3H). MS (EI): 316, 298, 193, 151, 130. (Found: C, 79.64; H, 10.02. $C_{21}H_{32}O_2$ requires C, 79.74; H, 10.13%).

2-(3,4,5-trimethoxyphenyl)-1-α-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2g):** Oil, yield: 85%. IR: 2915, 3565cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.81 (s, 3H), 0.87 (s, 3H), 1.23–3.01 (m, 8H), 1.89 (s, 3H), 3.82 (m, 9H), 4.07–4.15 (m, 1H), 5.70 (brs, 1H), 6.54 (s, 2H). MS (EI): 334, 316, 260, 167, 109. (Found: C, 71.94; H, 8.91. $C_{20}H_{30}O_4$ requires C, 71.86; H, 8.98%).

2-phenyl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanol **(2h):** Oil, yield: 70%. IR: 2912, 3550cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.81 (s, 3H), 0.87 (s, 3H), 1.23–2.99 (m, 8H), 1.87 (s, 3H), 4.05–4.16 (m, 1H), 5.69 (brs, 1H), 7.12–7.34 (m, 5H). MS (EI): 244, 226, 153, 135, 109. (Found: C, 83.53; H, 9.88. $C_{17}H_{24}O$ requires C, 83.61; H, 9.83%).

Representative procedure: Preparation of 2-(3,4-methylenedioxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3b):** Pyridinium chlorochromate (PCC) (3.23 g, 15 mmol) was added at 0–5°C to a stirred solution of compound **2b** (2.88 g, 10 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at room temperature for an additional 2.5h and then diluted with ether. After the addition of water, the mixture was extracted with ether and washed with brine and dried over Na_2SO_4 and then evaporated in *vacuo*. The residue was purified by column chromatography using hexane-ethyl acetate (15:1) as the eluent, to afford **3b** (2.43 g: 85%) as an oil. IR: ν (film) 1688, 2956cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.96 (s, 6H), 1.39 (s, 3H), 1.28–2.06 (m, 4H), 2.91 (s, 1H), 3.70 (d, 2H), 5.60 (brs, 1H), 5.93 (s, 2H), 6.60–6.84 (m, 3H). MS (EI): 286, 271, 135, 123, 77. (Found: C, 75.43; H, 7.78. $C_{18}H_{22}O_3$ requires C, 75.52; H, 7.69%).

2-(3,4-dimethoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone (**3a**): IR: 1680 cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.95 (s, 6H), 1.38 (s, 3H), 2.92 (s, 1H), 3.70 (d, 2H), 3.84 (s, 3H), 3.86 (s, 3H), 5.57 (brs, 1H), 6.73–6.85 (m, 3H). MS (EI): 302, 151, 123, 81. (Found: C, 75.54; H, 8.51. $C_{19}H_{26}O_3$ requires C, 75.49; H, 8.61%).

2-(3-methoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3c):** Oil, yield: 89%. IR: 1678cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.94 (s, 3H), 0.98 (s, 3H), 1.50 (s, 3H), 1.28–2.06 (m, 4H), 2.91 (s, 1H), 3.80 (d, 2H), 5.55 (brs, 1H), 7.22–7.29 (m, 4H). MS (EI): 272, 257, 149, 121. (Found: C, 79.39; H, 8.91. $C_{18}H_{24}O_2$ requires C, 79.41; H, 8.82%).

2-(4-methoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3d):** Oil, yield: 90%. IR: 1670cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.93 (s, 3H), 0.99 (s, 3H), 1.52 (s, 3H), 1.28–2.11 (m, 4H), 2.92 (s, 1H), 3.84 (d, 2H), 5.59 (brs, 1H), 7.22–7.40 (m, 4H). MS (EI): 272, 257, 149, 121, 91. (Found: C, 79.50; H, 8.79. $C_{18}H_{24}O_2$ requires C, 79.41; H, 8.82%).

2-(3-isopropyl-4-methoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3e):** Oil, yield: 87%. IR: 1676, 2940cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.93 (s, 3H), 0.97 (s, 3H), 1.18 (d, 6H, *J*=7Hz), 1.47 (s, 3H), 1.28–2.19 (m, 4H), 2.80 (sept, 1H, *J*=7Hz), 2.92 (s, 1H), 3.78 (s, 3H), 3.84 (d, 2H), 5.55 (brs, 1H), 6.77–7.25 (m, 3H). MS (EI): 314, 299, 191, 163. (Found: C, 80.17; H, 9.54. $C_{21}H_{30}O_2$ requires C, 80.21; H, 9.62%).

2-(2-methoxy-5-isopropylphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3f):** Oil, yield: 86%. IR: 1680cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.92 (s, 3H), 0.96 (s, 3H), 1.17 (d, 6H, *J*=7Hz), 1.47 (s, 3H), 1.28–2.11 (m, 4H), 2.82 (sept, 1H, *J*=7Hz), 2.91 (s, 1H), 3.75 (s, 3H), 3.88 (d, 2H), 5.55 (brs, 1H), 6.77–7.25 (m, 3H). MS (EI): 314, 299, 191, 163, 123. (Found: C, 80.11; H, 9.57. $C_{21}H_{30}O_2$ requires C, 80.21; H, 9.62%).

2-(3,4,5-trimethoxyphenyl)-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3g):** Oil, yield: 83%. IR: 1667cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.98 (s, 6H), 1.45 (s, 3H), 1.28–2.21 (m, 4H), 2.95 (s, 1H), 3.85 (m, 9H), 3.88 (d, 2H), 5.60 (brs, 1H), 6.43 (s, 2H). MS (EI): 332, 317, 181, 123. (Found: C, 72.31; H, 8.40. $C_{20}H_{28}O_4$ requires C, 72.29; H, 8.43%).

2-phenyl-1-(2,6,6-trimethylcyclohex-2-enyl)ethanone **(3h):** Oil, yield: 87%. IR: 1672cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.93 (s, 3H), 0.97 (s, 3H), 1.45 (s, 3H), 1.28–2.06 (m, 4H), 2.95 (s, 1H), 3.82 (d, 2H), 5.61 (brs, 1H), 7.22–7.29 (m, 5H). MS (EI): 242, 227, 151, 123, 91. (Found: C, 84.35; H, 9.03. $C_{17}H_{22}O$ requires C, 84.30; H, 9.09%).

Representative procedure: Preparation of (cis)-4b,6,7,8,8a,10-hexahydro-2,3-methylenedioxy-4b,8,8-trimethyl-9(5H)-phenanthrenone (**4b**): To a solution of ketone **3b** (286 mg, 1 mmol) in CH_2Cl_2 (20 ml) was added $BF_3{\cdot}Et_2O$ (0.6 ml) dropwise at room temperature. The mixture was allowed to stand for 14 h at this temperature and then quenched with aqueous sodium bicarbonate. After the usual work-up, the product was purified by column chromatography on silica gel using hexane-ethyl acetate (14:1) as the eluent, to give **4b** (272 mg: 95%) as white needles, m.p.: 144–145°C. IR: ν (film) 1275, 1688cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.40 (s, 3H), 0.96 (s, 3H), 1.04 (s, 3H), 1.26~2.42 (m, 6H), 2.08 (s, 1H),

3.52 (dd, 2H), 5.95 (d, 2H) , 6.55 (s, 1H), 6.64 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 18.7, 22.5, 32.0, 33.1, 34.2, 36.5, 38.5, 42.0, 43.9, 66.1, 100.9, 104.5, 108.6, 126.9, 134.8, 145.8, 146.8, 212.1. MS (EI): 286, 271, 201, 69. (Found: C, 75.47; H, 7.73. $C_{18}H_{22}O_3$ requires C, 75.52; H, 7.69%).

(cis)-4b,6,7,8,8a,10-hexahydro-2,3-dimethoxy-4b,8,8-trimethyl-9(5H)-phenanthrenone (**4a**)**:** White solid, yield: 95%. mp: 128–130°C. IR: 1690, 2924cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.37 (s, 3H), 0.95 (s, 3H), 1.06 (s, 3H), 1.26–2.49 (m, 6H), 2.09 (s, 1H), 3.55 (dd, 2H), 3.86 (s, 3H), 3.91 (s, 3H), 6.57 (s, 1H), 6.85 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 18.8, 22.4, 32.1, 33.3, 34.1, 36.3, 38.3, 42.0, 43.6, 55.8, 56.1, 66.4, 107.5, 111.3, 126.0, 133.4, 147.4, 147.8, 212.3. MS (EI): 302, 287, 217, 69. (Found: C, 75.54; H, 8.51. $C_{19}H_{26}O_3$ requires C, 75.49; H, 8.61%).

(cis)-4b,6,7,8,8a,10-hexahydro-2-methoxy-4b,8,8-trimethyl-9(5H)-phenanthrenone (**4c**): Oil, yield: 93%. IR: ν (film) 1684cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.37 (s, 3H), 0.95 (s, 3H), 1.04 (s, 3H), 1.26–2.42 (m, 6H), 2.06 (s, 1H), 3.46 (dd, 2H), 3.78 (s, 3H), 6.24–7.34 (m, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 18.8, 22.4, 32.1, 33.3, 34.1, 36.3, 38.3, 42.0, 43.6, 55.8, 66.1, 108.6, 111.5, 126.9, 134.8, 145.8, 147.8, 212.4. MS (EI): 272, 257, 149, 121. (Found: C, 79.59; H, 8.89. $C_{18}H_{24}O_2$ requires C, 79.41; H, 8.82%).

(cis)-4b,6,7,8,8a,10-hexahydro-3-methoxy-4b,8,8-trimethyl-9(5H)-phenanthrenone **(4d):** Oil, yield: 92%. IR: ν(film) 1680cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.35 (s, 3H), 0.94 (s, 3H), 1.04 (s, 3H), 1.26–2.42 (m, 6H), 2.09 (s, 1H), 3.42 (dd, 2H), 3.74 (s, 3H), 6.70–7.35 (m, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 18.9, 22.4, 32.3, 33.4, 34.2, 36.3, 38.3, 42.1, 43.9, 55.9, 65.9, 107.7, 110.9, 129.6, 133.8, 144.6, 146.7, 212.3. MS (EI): 272, 257, 149, 121. (Found: C, 79.57; H, 8.91. $C_{18}H_{24}O_2$ requires C, 79.41; H, 8.82%).

(cis)-4b,6,7,8,8a,10-hexahydro-2-isopropyl-3-methoxy-4b,8,8-trimethyl-9(5H)-phenanthrenone (**4e**): White solid, yield: 94%. mp: 94–96°C. IR: ν (film) 1688cm^{-1}. ^{1}H NMR (200MHz, $CDCl_3$): δ ppm 0.33 (s, 3H), 0.92 (s, 3H), 1.06 (s, 3H), 1.18 (d, 6H, *J*=7Hz), 1.26–2.42 (m, 6H), 2.00 (s, 1H), 3.10 (sept, 1H, *J*=7Hz), 3.41 (dd, 2H), 3.84 (s, 3H), 6.70 (s, 1H), 6.79 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): 18.9, 22.4, 23.8, 32.1, 33.4, 33.6, 34.2, 36.3, 38.3, 42.1, 43.6, 55.8, 66.1, 100.9, 104.5, 107.6, 129.6, 134.8, 146.8, 212.1. MS (EI): 314, 299, 191, 163. (Found: C, 80.09; H, 9.53. $C_{21}H_{30}O_2$ requires C, 80.21; H, 9.62%).

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