

**SUPPORTING INFORMATION**

**Title:** Cascade Reactions of  $\beta$ -Amino-Substituted  $\alpha,\beta$ -Unsaturated Fischer Carbene Complexes with 1,5-Dien-3-yne as a Convenient Access to Ring-Annulated Benzene Derivatives

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**Ref. No.:** O200500130

**Trifluoromethanesulfonic Acid (4a*R*)-4a-Methyl-3,4,4a,5,6,7,8,8a-octahydro-naphthalen-2-yl ester (5g).** To dry ammonia (200 mL) at  $-78\text{ }^{\circ}\text{C}$  was added lithium (322 mg) within 10 min. A solution of (-)-4a-methyl-4,4a,5,6,7,8-octahydro-3*H*-naphthalen-2-one (3.28 g, 19.7 mmol) and *tert*-butyl alcohol (1.46 g, 19.7 mmol) in  $\text{Et}_2\text{O}$  (100 mL) was transferred to the above blue solution, and the mixture stirred at the same temperature for another 2 h. The reaction was quenched with isoprene (2 mL), and ammonia was allowed to evaporate at ambient temperature under a light flow of Ar. Then, the residue was dried under reduced pressure, diluted with anhydrous THF (100 mL), and the mixture cooled to  $-78\text{ }^{\circ}\text{C}$ . To this solution was added a solution of *N,N*-bis(trifluoromethanesulfonyl)aniline (19.1 g, 53.4 mmol) in anhydrous THF (100 mL) at the same temperature, and the reaction mixture was allowed to warm up to room temperature and stirred for another 24 h. After evaporation of the solvents under reduced pressure, the residue was subjected to chromatography on silica gel (300 g). Elution with pentane gave 5.24 g (88%) of **5g** [ $R_f = 0.50$  (pentane)] as a colorless oil. – IR (film):  $\tilde{\nu} = 2927\text{ cm}^{-1}$  (C–H), 2859, 1690 (C=C), 1447, 1418, 1247, 1208, 1142, 1053, 1031, 1000, 872, 847, 765. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.85$  (s, 3 H,  $\text{CH}_3$ ), 1.01–1.60 (9 H), 1.71–1.81 (1 H), 2.00–2.09 (1 H), 2.22–2.50 (2 H) [m, total 13 H,

3,4,5,6,7,8,8a-H], 5.41 (s, 1 H, 1-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta = 14.9$  (+,  $\text{CH}_3$ ), 21.4, 25.6, 26.5, 27.0, 37.6, 38.8 (–, C-3,4,5,6,7,8), 32.4 ( $\text{C}_{\text{quat}}$ , C-4a), 43.5 (+, C-8a), 122.4 (+, C-1), 118.5 ( $\text{C}_{\text{quat}}$ , q,  $^1J_{\text{C-F}} = 320$  Hz,  $\text{CF}_3$ ), 148.1 ( $\text{C}_{\text{quat}}$ , C-2). – MS (70 eV),  $m/z$  (%): 298 (16) [ $\text{M}^+$ ], 165 (64), 148 (66), 133 (15), 121 (24), 109 (100), 107 (40), 95 (30), 81 (58), 69 (100) [ $\text{CF}_3^+$ ], 55 (65), 41 (51).

**Di(1'-cyclopentenyl)ethyne (2aa).** Following GP1, to a solution of 5.84 g (39.7 mmol) of 1-bromo-1-cyclopentene (**5a**) in 40 mL of diisopropylamine was added 4.05 g (44.0 mmol) of 1-ethynyl-1-cyclopentene (**6a**),  $\text{PdCl}_2(\text{PPh}_3)_2$  (100 mg),  $\text{PPh}_3$  (100 mg),  $\text{CuI}$  (75.0 mg) and  $\text{LiCl}$  (100 mg), and the mixture was heated at 40 °C for 2 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 4.48 g (71%) of **2aa** [ $R_f = 0.63$  (pentane)] as a colorless solid which became a brown oil after exposure to air at ambient temperature for a short time. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.90$  ("qui",  $^3J = 7.6$ ,  $^3J = 7.6$  Hz, 4 H, 4'-H), 2.35–2.52 (m, 8 H, 3',5'-H), 6.01–6.05 (m, 2 H, 2'-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta = 23.3$ , 33.3, 36.4 (–, cyclopentyl  $\text{CH}_2$ ), 87.7 ( $\text{C}_{\text{quat}}$ , C-1,2), 124.6 ( $\text{C}_{\text{quat}}$ , C-1'), 137.4 (+, C-2'). – MS (70 eV),  $m/z$  (%): 158 (100) [ $\text{M}^+$ ], 129 (35), 115 (21), 91 (16).

**1'-Cyclohexenyl-3-methylbut-3-en-1-yne (2bh).** Following GP1, to a solution of 8.32 g (40.0 mmol) of 1-iodo-1-cyclohexene (**5b**) in 40 mL of diisopropylamine was added  $\text{PPh}_3$  (100 mg),  $\text{CuI}$  (75.0 mg),  $\text{LiCl}$  (100 mg), and  $\text{PdCl}_2(\text{PPh}_3)_2$  (100 mg) and finally 5.00 mL (53.6 mmol) of 2-methylbut-1-en-3-yne (**6h**), and the mixture was heated at 40 °C for 2 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 4.91 g (84%) of **2bh** [ $R_f = 0.61$  (pentane)] as a colorless oil. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.45$ –1.70 (br m, 4 H, 4',5'-H), 1.90 ("t",  $^4J = 1.3$ ,  $^4J = 1.3$  Hz, 3 H,  $\text{CH}_3$ ), 2.06–2.17 (br m, 4 H, 3',6'-H),

5.12–5.18 and 5.23–5.60 (m, 2 H, 4-H), 6.08–6.11 (m, 1 H, 2'-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 21.5, 22.3 (–, C-4',5'), 23.0, (+,  $\text{CH}_3$ ), 25.7, 29.2 (–, C-3',6'), 87.9, 90.2 ( $\text{C}_{\text{quat}}$ , C-1,2), 120.8 (–, C-4), 120.6, 127.0 ( $\text{C}_{\text{quat}}$ , C-3,1'), 134.8 (+, C-2').

**5-(Cyclohex-1'-enylethynyl)-3,4-dihydro-2H-pyran (2cb):** Following GP1, to a solution of 8.15 g (50.0 mmol) of 5-bromo-3,4-dihydro-2H-pyran (**5c**) in 40 mL of diethylamine was added 5.30 g (50.0 mmol) of 1-ethynyl-1-cyclohexene (**6b**),  $\text{PdCl}_2(\text{PPh}_3)_2$  (100 mg),  $\text{PPh}_3$  (150 mg),  $\text{CuI}$  (100 mg) and  $\text{LiCl}$  (100 mg), and the mixture was heated at 70 °C for 8 h. After filtration and evaporation of the solvent under reduced pressure, the  $^1\text{H}$ -NMR spectrum of the crude product showed that 80% of **5c** had been converted to **2cb**. The residue was subjected to chromatography on silica gel (100 g). Elution with pentane/ $\text{Et}_2\text{O}$  (from 20:1 to 10:1) gave 7.02 g (75%) of **2cb** [ $R_f$  = 0.73 (pentane/ $\text{Et}_2\text{O}$  9:1)] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 3055  $\text{cm}^{-1}$  (C–H), 2939, 2183 ( $\text{C}\equiv\text{C}$ ), 1724, 1669, 1436, 1266, 1168, 1133, 921, 737. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.47–1.67 (4 H), 1.78–1.88 (2 H), 2.06–2.12 (6 H) [m, total 12 H, 3,4,3',4',5',6'-H), 3.93 (t,  $^3J$  = 5.3 Hz, 2 H, 2-H), 5.97–6.00 (m, 1 H, 2'-H), 6.73 (s, 1 H, 6-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 21.5, 21.7, 22.3, 24.2, 25.6, 29.4 (–, C-3,4,3',4',5',6'), 65.6 (–, C-2), 85.8, 89.1 ( $\text{C}_{\text{quat}}$ ,  $\text{C}\equiv\text{C}$ ), 97.0 ( $\text{C}_{\text{quat}}$ , C-5), 120.9 ( $\text{C}_{\text{quat}}$ , C-1'), 133.2 (+, C-2'), 149.4 (+, C-6). – MS (70 eV),  $m/z$  (%): 188 (100) [ $\text{M}^+$ ], 160 (19), 131 (20), 117 (29), 115 (15), 104 (13), 91 (23), 77 (18), 51 (10), 41 (11).

**1'-Cyclooctenyl-3-methylbut-3-en-1-yne (2dh).** Following GP1, to a solution of 11.3 g (59.8 mmol) of 1-bromo-1-cyclooctene (**5d**) in 40 mL of diisopropylamine was added  $\text{PPh}_3$  (100 mg),  $\text{CuI}$  (75.0 mg),  $\text{LiCl}$  (100 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (120 mg), and 7.50 mL (80.4 mmol) of 2-methylbut-1-en-3-yne (**6h**), and the mixture was heated at 70 °C for 3.5 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 6.89 g (66%) of **2dh** [ $R_f$  =

0.69 (pentane)] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 3095  $\text{cm}^{-1}$  (C–H), 3021, 2930, 2849, 2192 (C $\equiv$ C), 1606, 1467, 1448, 1373, 1331, 889, 846. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.40–1.70 (br m, 8 H, 4',5',6',7'-H), 1.90 (dd,  $^4J$  = 1.1,  $^4J$  = 1.0 Hz, 3 H,  $\text{CH}_3$ ), 2.13–2.20 (m, 2 H, 3'-H), 2.30 (t,  $^3J$  = 6.1 Hz, 2 H, 8'-H), 5.15–5.19 and 5.22–5.25 (m, 2 H, 4-H), 6.08 (t,  $^3J$  = 8.4 Hz, 1 H, 2'-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 23.6 (+,  $\text{CH}_3$ ), 25.7, 26.3, 27.0, 28.4, 29.7, 29.9 (–, cyclooctenyl  $\text{CH}_2$ ), 87.5, 91.0 ( $\text{C}_{\text{quat}}$ , C-1,2), 120.6 (–, C-4), 123.7, 127.1 ( $\text{C}_{\text{quat}}$ , C-3,1'), 137.6 (+, C-2'). – MS (70 eV),  $m/z$  (%): 174 (72) [ $\text{M}^+$ ], 159 (19) [ $\text{M}^+$  –  $\text{CH}_3$ ], 146 (52), 131 (67), 117 (42), 105 (38), 91 (100), 79 (29), 77 (42), 67 (24), 65 (22), 53 (24), 41 (44).

**3-(3'-Buten-1'-ynyl)-7-methoxy-1,2-dihydronaphthalene (2fi) and 3-(3'-Hydroxy-1'-butynyl)-7-methoxy-1,2-dihydronaphthalene.** Following GP1, to a solution of 3.26 g (13.6 mmol) of 3-bromo-7-methoxy-1,2-dihydronaphthalene (**5f**) in 30 mL of diisopropylamine was added  $\text{PPh}_3$  (50 mg),  $\text{CuI}$  (100 mg),  $\text{LiCl}$  (50 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (100 mg), and 2.00 g (38.4 mmol) of 1-buten-3-yne (**6i**), and the mixture was heated at 70 °C for 4 h. After filtration and evaporation of the solvent under reduced pressure, the residue was obtained as an inseparable mixture (ca. 2.80 g) of **5f** and **2fi**. The residual starting material **5f** [by treatment of the mixture with 30 mL of diisopropylamine,  $\text{PPh}_3$  (50 mg),  $\text{CuI}$  (50 mg),  $\text{LiCl}$  (50 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (50 mg) and 2-hydroxy-3-butyne (1.05 g, 15.0 mmol)] was transformed to the more polar 3-(3'-hydroxy-1'-butynyl)-7-methoxy-1,2-dihydronaphthalene according to GP1. The crude product was subjected to chromatography on silica gel (100 g). Elution with pentane/ $\text{Et}_2\text{O}$  (from 1:0 to 0:1) gave 320 mg (11%) of **2fi** [ $R_f$  = 0.70 (pentane/ $\text{Et}_2\text{O}$  9:1)] as a colorless oil, which contained traces of **5f**, and 2.23 g (72%) of 3-(3'-hydroxy-1'-butynyl)-7-methoxy-1,2-dihydronaphthalene [ $R_f$  = 0.82 ( $\text{Et}_2\text{O}$ )] as a pale-yellow semi-solid. – **2fi**: IR (film):  $\tilde{\nu}$  = 2937  $\text{cm}^{-1}$  (C–H), 2834, 2166 (C $\equiv$ C), 1605 (C=C), 1449,

1270, 1249, 1153, 1124, 1037. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.50 (t,  $^3J$  = 8.3 Hz, 2 H, 2-H), 2.83 (t,  $^3J$  = 8.3 Hz, 2 H, 1-H), 3.82 (s, 3 H,  $\text{OCH}_3$ ), 5.54 (dd,  $^3J$  = 11.0,  $^2J$  = 2.2 Hz, 1 H, 4'-H), 5.73 (dd,  $^3J$  = 17.7,  $^2J$  = 2.2 Hz, 1 H, 4'-H), 6.07 (dd,  $^3J$  = 17.7,  $^3J$  = 11.0 Hz, 1 H, 3'-H), 6.73 and 6.82 (s, each 1 H, 4,8-H), 6.75 (d,  $^3J$  = 9.2 Hz, 1 H, 6-H), 7.02 (d,  $^3J$  = 9.2 Hz, 1 H, 5-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 27.2, 27.8 (–, C-1,2), 54.9 (+,  $\text{OCH}_3$ ), 89.5, 91.8 ( $\text{C}_{\text{quat}}$ ,  $\text{C}\equiv\text{C}$ ), 110.1, 113.5, 117.2, 127.5, 132.9 (+, C-4,5,6,8,3'), 117.8, 126.5, 136.4, 159.1 ( $\text{C}_{\text{quat}}$ , C-3,7,9,10), 124.5 (–, C-4'). – MS (70 eV),  $m/z$  (%): 210 (100) [ $\text{M}^+$ ], 194 (28), 165 (18), 159 (13), 115 (18). – 3-(3'-Hydroxy-1'-butynyl)-7-methoxy-1,2-dihydronaphthalene:  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.52 (d,  $^3J$  = 6.8 Hz, 3 H,  $\text{CH}_3$ ), 2.38 (t,  $^3J$  = 7.8 Hz, 2 H, 2-H), 2.79 (t,  $^3J$  = 7.8 Hz, 2 H, 1-H), 2.72–2.80 (m, 1 H, OH), 3.78 (s, 3 H,  $\text{OCH}_3$ ), 4.70–4.77 (m, 1 H, 3'-H), 6.62–6.72 (m, 3 H, Ar-H), 6.93 (d,  $^3J$  = 8.8 Hz, 1 H, Ar-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 24.3 (+, C-4'), 27.3, 27.9 (–, C-1,2), 55.1, 58.6 (+,  $\text{OCH}_3$ , C-3'), 85.3, 92.2 ( $\text{C}_{\text{quat}}$ ,  $\text{C}\equiv\text{C}$ ), 111.2, 113.6, 127.4, 132.9 (+, C-4,5,6,8), 117.4, 126.6, 136.5, 159.0 ( $\text{C}_{\text{quat}}$ , C-3,7,9,10).

**7-Methoxy-3-(3'-methylbut-3'-en-1'-ynyl)-1,2-dihydronaphthalene (2fh).** Following GP1, to a solution of 4.50 g (18.8 mmol) of 3-bromo-7-methoxy-1,2-dihydronaphthalene (**5f**) in 30 mL of diisopropylamine was added  $\text{PPh}_3$  (50 mg),  $\text{CuI}$  (50 mg),  $\text{LiCl}$  (50 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (60 mg), and 4.00 mL (42.9 mmol) of 2-methylbut-1-en-3-yne (**6h**), and the mixture was heated at 70 °C for 2 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane/ $\text{Et}_2\text{O}$ / $\text{CH}_2\text{Cl}_2$  (18:1:1) gave an inseparable mixture (3.98 g; **5f:2fh** = 14:86) as a colorless oil. – IR (film):  $\tilde{\nu}$  = 2940  $\text{cm}^{-1}$  (C–H), 2834, 2126 ( $\text{C}\equiv\text{C}$ ), 1606 (C=C), 1564, 1499, 1432, 1333, 1297, 1268, 1250, 1152, 1038, 880, 739. **2fh**:  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.98 (s, 3 H,  $\text{CH}_3$ ), 2.46 (t,  $^3J$  = 8.1 Hz, 2 H, 2-H), 2.91 (t,  $^3J$  = 8.1 Hz, 2 H, 1-H), 3.81 (s, 3 H,

OCH<sub>3</sub>), 5.26–5.28 and 5.33–5.35 (m, 2 H, 4'-H), 6.66–6.77 (m, 3 H, 4,6,8-H), 6.99 (d, <sup>3</sup>J = 8.8 Hz, 1 H, 5-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT): δ = 23.5 (+, CH<sub>3</sub>), 27.5, 28.0 (–, C-1,2), 55.1 (+, OCH<sub>3</sub>), 90.2, 91.9 (C<sub>quat</sub>, C≡C), 111.3, 113.6, 127.5, 132.7 (+, C-4,5,6,8), 118.1, 126.91, 126.95, 136.6, 159.1 (C<sub>quat</sub>, C-3,7,9,10,3'), 121.3 (–, C-4'). – MS (70 eV), *m/z* (%): 224 (100) [M<sup>+</sup>], 209 (10) [M<sup>+</sup> – CH<sub>3</sub>], 165 (16).

**7-Methoxy-3-(4',4'-dimethyl-3'-methylenepent-1'-ynyl)-1,2-dihydronaphthalene (2fj).**

Following GP1, to a solution of 4.50 g (18.8 mmol) of 3-bromo-7-methoxy-1,2-dihydronaphthalene (**5f**) in 30 mL of diisopropylamine was added PPh<sub>3</sub> (50 mg), CuI (50.0 mg), LiCl (50 mg), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (100 mg) and 2.24 g (20.7 mmol) of 2,2-dimethyl-3-methylene-4-pentyne (**6j**), and the mixture was heated at 70 °C for 4 h. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane/Et<sub>2</sub>O (20:1) gave 4.63 g (92%) of **2fj** [*R<sub>f</sub>* = 0.60 (pentane/Et<sub>2</sub>O 20:1)] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 2964 cm<sup>-1</sup> (C–H), 2834, 2177 (C≡C), 1605 (C=C), 1564, 1499, 1297, 1269, 1253, 1159, 1039, 897, 877. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 1.19 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>], 2.46 (t, <sup>3</sup>J = 8.1 Hz, 2 H, 2-H), 2.84 (t, <sup>3</sup>J = 8.1 Hz, 2 H, 1-H), 3.80 (s, 3 H, OCH<sub>3</sub>), 5.29 and 5.33 (br. s, 2 H, 4'-H), 6.68–6.75 (m, 3 H, 4,6,8-H), 6.98 (d, <sup>3</sup>J = 8.9 Hz, 1 H, 5-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT): δ = 27.6, 28.1 (–, C-1,2), 29.1 [+ , C(CH<sub>3</sub>)<sub>3</sub>], 36.1 [C<sub>quat</sub>, C(CH<sub>3</sub>)<sub>3</sub>], 55.2 (+, OCH<sub>3</sub>), 90.9, 91.8 (C<sub>quat</sub>, C≡C), 111.3, 113.7, 127.5, 132.3 (+, C-4,5,6,8), 117.2 (–, C-4'), 118.5, 127.1, 136.6, 141.8, 159.1 (C<sub>quat</sub>, C-3,7,9,10,3'). – MS (70 eV), *m/z* (%): 266 (100) [M<sup>+</sup>], 251 (5) [M<sup>+</sup> – CH<sub>3</sub>], 209 (38) [M<sup>+</sup> – C<sub>4</sub>H<sub>9</sub>], 165 (14), 115 (6), 57 (6) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>]. – Elemental analysis calcd (%) for C<sub>19</sub>H<sub>22</sub>O (266.4): C 85.67, H 8.32; found: C 85.36, H 8.06.

**(4aR)-4a-Methyl-7-(4',4'-dimethyl-3'-methylenepent-1'-ynyl)-1,2,3,4,4a,5,6,8a-octahydronaphthalene (2gj).** Like GP1, to a solution of 2.01 g (6.74 mmol) of trifluoromethanesulfonic acid (4aR)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2-yl ester (**5g**) in 40 mL of DMF was added PPh<sub>3</sub> (50 mg), CuI (50 mg), LiCl (50 mg), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (60 mg), NEt<sub>3</sub> (818 mg, 8.08 mmol) and 802 mg (7.41 mmol) of 2,2-dimethyl-3-methylene-4-pentyne (**6j**), and the mixture was heated at 50 °C for 12 h. The reaction mixture was diluted with 50 mL of pentane/Et<sub>2</sub>O (1:1) and washed with water (200 mL). The aqueous phase was extracted with pentane/Et<sub>2</sub>O (1:1; 4 × 50 mL). The combined organic phases were washed with water (30 mL) and hydrochloric acid (1 N, 30 mL). The solution was dried over MgSO<sub>4</sub>. After filtration and evaporation of the solvent under reduced pressure, the residue was subjected to chromatography on silica gel (100 g). Elution with pentane gave 1.32 g (76%) of **2gj** [*R*<sub>f</sub> = 0.85 (pentane)] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 2928 cm<sup>-1</sup> (C–H), 2864, 2186 (C≡C), 1661 (C=C), 1596, 1451, 1362, 1265, 898, 740. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 0.82 (s, 3 H, CH<sub>3</sub>), 1.14 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>], 1.10–1.62 (9 H), 1.74–1.78 (1 H), 1.89–1.95 (1 H) and 2.20–2.29 (2 H) [m, 13 H, 1,2,3,4,5,6,8a-H], 5.21–5.23 and 5.25–5.26 (m, 2 H, 4'-H), 5.75–5.77 (m, 1 H, 8-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT): δ = 15.3 (+, CH<sub>3</sub>), 21.7, 26.9, 27.1, 27.4, 37.7, 39.7 (–, C-1,2,3,4,5,6), 29.0 [+ , C(CH<sub>3</sub>)<sub>3</sub>], 32.2, 36.0 [C<sub>quat</sub>, C(CH<sub>3</sub>)<sub>3</sub>, C-4a], 45.0 (+, C-8a), 86.9, 91.5 (C<sub>quat</sub>, C≡C), 116.7 (–, C-4'), 119.5, 141.8 (C<sub>quat</sub>, C-7,3'), 138.7 (+, C-8). – MS (70 eV), *m/z* (%): 256 (81) [M<sup>+</sup>], 241 (100) [M<sup>+</sup> – CH<sub>3</sub>], 213 (17), 199 (37), 185 (16), 173 (32), 157 (14), 143 (16), 128 (16), 115 (20), 109 (18), 91 (23), 77 (14), 67 (20), 57 (47) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>], 41 (42).

**3-Cyclopropyl-4,7-dimethylindan-1-one (8hh-cPr).** Following GP2, to a solution of complex **1-cPr** (719 mg, 2.00 mmol) in pyridine (40 mL) was added 531 mg (5.00 mmol) of 2,5-dimethylhexa-1,5-dien-3-yne (**2hh**), and the mixture stirred at 80 °C for 3 d.

Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1) gave 87 mg (22%) of **8hh-cPr** [*R<sub>f</sub>* = 0.59 (pentane/Et<sub>2</sub>O 3:1)] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 3000 cm<sup>-1</sup> (C–H), 2923 (C–H), 1705 (C=O), 1494, 1248, 820. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.11–0.20 (m, 1 H, *cPr*-H), 0.38–0.51 (m, 2 H, *cPr*-H), 0.60–0.69 (m, 1 H, *cPr*-H), 0.81–0.93 (m, 1 H, *cPr*-H), 2.44 (s, 3 H, CH<sub>3</sub>), 2.49 (AB, dd, <sup>2</sup>*J* = 18.5, <sup>3</sup>*J* = 1.6 Hz, 1 H, 2-H), 2.58 (s, 3 H, CH<sub>3</sub>), 2.79 (AB, dd, <sup>2</sup>*J* = 18.5, <sup>3</sup>*J* = 7.9 Hz, 1 H, 2-H), 2.97 ("t"d, <sup>3</sup>*J* = 7.9, <sup>3</sup>*J* = 7.9, <sup>3</sup>*J* = 1.6 Hz, 1 H, 3-H), 7.02 (d, <sup>3</sup>*J* = 7.5 Hz, 1 H, 5-H), 7.25 (d, <sup>3</sup>*J* = 7.5 Hz, 1 H, 6-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 2.9, 6.8 (–, *cPr*-C), 16.4 (+, *cPr*-C), 18.1, 19.0 (+, CH<sub>3</sub>), 40.5 (+, C-3), 44.5 (–, C-2), 129.5, 135.4 (+, C-5,6), 133.3, 133.9, 135.7, 156.8 (C<sub>quat</sub>, C-3a,4,7,7a), 207.8 (C<sub>quat</sub>, C-1). – MS (70 eV), *m/z* (%): 200 (100) [M<sup>+</sup>], 172 (54) [M<sup>+</sup> – CO], 159 (88) [M<sup>+</sup> – C<sub>3</sub>H<sub>5</sub>], 157 (34), 141 (18), 129 (36), 128 (41), 115 (41), 91 (17). – Elemental analysis calcd (%) for C<sub>14</sub>H<sub>16</sub>O (200.3): C 83.95, H 8.05; found: C 83.43, H 8.72.

**3-Cyclopropyl-4-methyl-3,6,7,8-tetrahydro-2H-as-indacen-1-one (8ah-cPr) and 1-Cyclopropyl-4-methyl-1,6,7,8-tetrahydro-2H-as-indacen-3-one (9ah-cPr):** Following GP2, to a solution of complex **1-cPr** (719 mg, 2.00 mmol) in pyridine (40 mL) was added 651 mg (4.43 mmol; purity 90%) of 4-(1'-cyclopentenyl)-2-methylbut-1-en-3-yne (**2ah**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1) gave 72 mg (16%) of **8ah-cPr** and **9ah-cPr** [*R<sub>f</sub>* = 0.47 (pentane/Et<sub>2</sub>O 3:1); ratio 1:1.1] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 2955 cm<sup>-1</sup> (C–H), 1696 (C=O), 1559, 1243. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): 0.09–0.25 (m, 1 H, *cPr*-H), 0.38–0.53 (m, 2 H, *cPr*-H), 0.57–0.76 (m, 1 H, *cPr*-H), 0.79–0.95 (m, 1 H, *cPr*-H), 1.95–2.24 (m, 3 H, 2,7-H), 2.44, 2.59 (s, 3 H, CH<sub>3</sub>), 2.45–2.57 (m, 1 H, 2-H), 2.63–3.20 (m, 5 H, 6,8-H, 3-H of **8ah-cPr**, 1-H of **9ah-cPr**), 7.00, 7.26 (s, 1 H, 5-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 2.7, 2.9, 6.8 × 2 (–, *cPr*-C), 16.0, 16.5 (+, *cPr*-C), 18.4, 19.3 (+, CH<sub>3</sub>), 25.2, 25.4 (

–, C-7), 30.7, 31.5, 31.6, 33.1 (–, C-6,8), 41.2, 41.8 (+, C-3 of **8ah-cPr**, C-1 of **9ah-cPr**), 44.2, 44.4 (–, C-2), 125.7, 131.7 (+, C-5), 132.4, 132.6, 133.6, 136.7, 138.8, 140.0, 144.8, 151.8, 154.5 × 2 (C<sub>quat</sub>, Ar-C), 207.0, 207.5 (C<sub>quat</sub>, CO). – MS (70 eV), *m/z* (%): 226 (100) [M<sup>+</sup>], 198 (42) [M<sup>+</sup> – CO], 185 (53) [M<sup>+</sup> – C<sub>3</sub>H<sub>5</sub>], 183 (48), 169 (14), 155 (14), 141 (12), 115 (12). – Elemental analysis calcd (%) for C<sub>16</sub>H<sub>18</sub>O (226.3): C 84.92, H 8.02; found: C 84.78, H 7.70.

**3-tert-Butyl-4-methyl-3,6,7,8-tetrahydro-2H-as-indacen-1-one (8ah-*t*Bu) and 1-tert-Butyl-4-methyl-1,6,7,8-tetrahydro-2H-as-indacen-3-one (9ah-*t*Bu).** Following GP, to a solution of 751 mg (2.00 mmol) of complex **1-*t*Bu** in 40 mL of pyridine was added 651 mg (4.43 mmol; purity 90%) of 4-(1'-cyclopentenyl)-2-methylbut-1-en-3-yne (**2ah**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide [II, 40 g; elution with pentane/Et<sub>2</sub>O (from 1:0 to 3:1)] and later on silica gel [50 g, elution with pentane/Et<sub>2</sub>O (5:1)] gave 178 mg (37%) of **8ah-*t*Bu** and **9ah-*t*Bu** [*R<sub>f</sub>* = 0.73 (pentane/Et<sub>2</sub>O 3:1); ratio 1:1.1] as a colorless oil. Two yellow fractions of chromium complexes were also isolated [78 mg; *R<sub>f</sub>* = 0.59 (pentane/Et<sub>2</sub>O 3:1) and 148 mg; *R<sub>f</sub>* = 0.32 (pentane/Et<sub>2</sub>O 3:1)]; both of them show a signal between 10–11 ppm in their <sup>1</sup>H-NMR spectra, and they were not stable enough to be fully identified. – IR (film):  $\tilde{\nu}$  = 2954 cm<sup>-1</sup> (C–H), 1706 (C=O), 1658, 1467, 1366, 1241, 1100. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): 0.85, 0.87 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>], 1.19–2.16 (m, 2 H, 7-H), 2.36, 2.58 (s, 3 H, CH<sub>3</sub>), 2.59–2.62 (m, 1 H, 2-H), 2.82–3.28 (m, 6 H, 2,6,8-H, 3-H of **8ah-*t*Bu**, 1-H of **8ah-*t*Bu**), 7.23, 7.26 (s, 1 H, 5-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 18.4, 20.1 (+, CH<sub>3</sub>), 25.4, 26.1 (–, C-7), 28.0, 28.1 [+ , C(CH<sub>3</sub>)<sub>3</sub>], 30.7, 31.6, 32.8, 33.4 (–, C-6,8), 37.0, 37.2 [C<sub>quat</sub>, C(CH<sub>3</sub>)<sub>3</sub>], 44.1, 44.2 (–, C-2), 48.0, 48.4 (+, C-3 of **8ah-*t*Bu**, C-1 of **9ah-*t*Bu**), 125.8, 131.3 (+, C-5), 133.4, 133.6, 133.9, 136.2, 139.7, 139.8, 144.8, 151.2, 152.7, 153.1 (C<sub>quat</sub>, Ar-C), 207.3, 207.6 (C<sub>quat</sub>, C=O). – MS (70 eV), *m/z* (%): 242 (20) [M<sup>+</sup>], 186

(100), 57 (10) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>]. – Elemental analysis calcd (%) for C<sub>17</sub>H<sub>22</sub>O (242.4): C 84.25, H 9.15; found: C 84.04, H 8.97.

**3-Cyclopropyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (8aa-cPr).** Following GP2, to a solution of 719 mg (2.00 mmol) of complex **1-cPr** in 40 mL of pyridine was added 633 mg (4.00 mmol) of di(1-cyclopentenyl)ethyne (**2aa**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1) gave 98 mg (19%) of **8aa-cPr** [*R*<sub>f</sub> = 0.45 (pentane/Et<sub>2</sub>O 3:1)] as a colorless solid, m. p. 97–98 °C. – IR (KBr):  $\tilde{\nu}$  = 2839 cm<sup>-1</sup> (C–H), 1701 (C=C), 1594, 1276, 1237, 1120, 1021. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.15–0.25 (m, 1 H, *cPr*-H), 0.43–0.55 (m, 2 H, *cPr*-H), 0.61–0.73 (m, 1 H, *cPr*-H), 0.75–0.90 (m, 1 H, *cPr*-H), 2.03–2.39 (m, 4 H, 5,8-H), 2.47 (AB, dd, <sup>2</sup>*J* = 18.1, <sup>3</sup>*J* = 2.2 Hz, 1 H, 2-H), 2.60–2.98 (m, 7 H) and 3.04–3.23 (m, 3 H) [total 10 H, 2,3,4,6,7,8-H]. – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 2.7, 6.8 (–, *cPr*-C), 16.0 (+, *cPr*-C), 25.1, 25.3 (–, C-5,8), 30.3, 30.9, 31.6, 31.7 (–, C-4,6,7,9), 42.5 (+, C-3), 44.0 (–, C-2), 131.6, 139.2, 140.2, 141.0, 147.5, 152.1 (C<sub>quat</sub>, Ar-C), 206.7 (C<sub>quat</sub>, C-1). – MS (70 eV), *m/z* (%): 252 (100) [M<sup>+</sup>], 224 (56) [M<sup>+</sup> – CO], 211 (34) [M<sup>+</sup> – C<sub>3</sub>H<sub>5</sub>], 195 (14), 181 (12), 165 (22), 153 (16). – Elemental analysis calcd (%) for C<sub>18</sub>H<sub>20</sub>O (252.4): C 85.67, H 7.99; found: C 85.32, H 7.51.

**3-Methyl-2,3,4,5,6,7,8,9-octahydrotrinden-1-one (8aa-Me).** Following GP2, to a solution of 667 mg (2.00 mmol) of complex **1-Me** in 40 mL of pyridine was added 633 mg (4.00 mmol) of di(1-cyclopentenyl)ethyne (**2aa**), and the mixture stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1) gave 54 mg (12%) of **8aa-Me** [*R*<sub>f</sub> = 0.49 (pentane/Et<sub>2</sub>O 3:1)] as a colorless solid, m. p. 84–85 °C. – IR (KBr):  $\tilde{\nu}$  = 2955 cm<sup>-1</sup> (C–H), 1700 (C=O), 1596. – <sup>1</sup>H NMR (250 MHz,

CDCl<sub>3</sub>):  $\delta$  = 1.34 (d,  $^3J$  = 7.1 Hz, 3 H, CH<sub>3</sub>), 2.04–2.31 (m, 5 H, 2,5,8-H), 2.75–3.07 (m, 7 H) and 3.20 (t,  $^3J$  = 7.5 Hz, 2 H) [total 9 H, 2,4,6,7,9-H], 3.37–3.43 (m, 1 H, 3-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 20.5 (+, CH<sub>3</sub>), 25.3, 25.4 (–, C-5,8), 30.3 × 2, 30.9, 31.6 (–, C-4,6,7,9), 32.2 (+, C-3), 46.1 (–, C-2), 130.8, 138.6, 140.1, 141.2, 147.5, 153.9 (C<sub>quat</sub>, Ar-C), 207.1 (C<sub>quat</sub>, C-1). – MS (70 eV),  $m/z$  (%): 226 (100) [M<sup>+</sup>], 211 (30) [M<sup>+</sup> – CH<sub>3</sub>], 198 (8) [M<sup>+</sup> – CO], 183 (14), 115 (12). – Elemental analysis calcd (%) for C<sub>16</sub>H<sub>18</sub>O (226.3): C 84.91, H 8.02; found: C 84.71, H 7.87.

**3-Isopropyl-4-methyl-2,3,6,7,8,9-hexahydrocyclopenta[*a*]naphthalen-1-one (8bh-*i*Pr) and 1-Isopropyl-4-methyl-1,2,6,7,8,9-hexahydrocyclopenta[*a*]naphthalen-3-one (9bh-*i*Pr).** Following GP2, to a solution of 989 mg (2.74 mmol) of complex **1-*i*Pr** in 55 mL of pyridine was added 536 mg (3.68 mmol) of 4-(1'-cyclohexenyl)-2-methylbut-1-en-3-yne (**2bh**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1) gave 302 mg (46%) of **8bh-*i*Pr** and **9bh-*i*Pr** [ $R_f$  = 0.74 (pentane/Et<sub>2</sub>O 3:1); ratio 1.1:1] as a colorless oil. – IR (film):  $\tilde{\nu}$  = 2929 cm<sup>-1</sup> (C–H), 1701 (C=O), 1576, 1464, 1248, 1116. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.37, 0.38 (d,  $^3J$  = 6.8 Hz, 3 H, *i*Pr-H), 1.00 (d,  $^3J$  = 6.8 Hz, 3 H, *i*Pr-H), 1.50–2.00 (m, 4 H, 7,8-H), 2.26, 2.48 (s, 3 H, CH<sub>3</sub>), 2.40–2.50 (m, 3 H), 2.60–2.89 (m, 3 H), 3.05–3.15 (m, 1 H) and 3.25–3.33 (m, 1 H) [total 8 H, 2,6,9-H, *i*Pr-H, 3-H of **8bh-*i*Pr** and 1-H of **9bh-*i*Pr**], 6.74, 6.99 (s, 1 H, 5-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 14.5, 14.6, 17.6, 17.7 (+, *i*Pr-C), 21.8, 21.9 (+, CH<sub>3</sub>), 22.3, 22.36, 22.38, 22.6 (–, C-7,8), 28.5, 28.9 (+, *i*Pr-C), 25.2, 25.4, 29.0, 29.6 (–, C-6,9), 38.2, 38.3 (–, C-2), 42.1, 42.2 (+, C-3 of **8bh-*i*Pr** and 1-H of **9bh-*i*Pr**), 130.4, 136.5 (+, C-5), 131.4, 131.6, 132.2, 133.9, 134.3 × 2, 136.1, 143.4, 154.8, 157.2 (C<sub>quat</sub>, Ar-C), 207.2, 207.7 (C<sub>quat</sub>, CO). – MS (70 eV),  $m/z$  (%): 242 (42) [M<sup>+</sup>], 199 (100) [M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>], 43 (16) [C<sub>3</sub>H<sub>3</sub><sup>+</sup>]. – HRMS (EI) calcd for C<sub>17</sub>H<sub>22</sub>O: 242.1671 (correct HRMS).

**3-tert-Butyl-4-methyl-2,3,6,7,8,9-hexahydrocyclopenta[*a*]naphthalen-1-one (8bh-*t*Bu)**  
**and 1-tert-Butyl-4-methyl-1,2,6,7,8,9-hexahydrocyclopenta[*a*]naphthalen-3-one (9bh-*t*Bu).** Following GP2, to a solution of 751 mg (2.00 mmol) of complex **1-*t*Bu** in 40 mL of pyridine was added 438 mg (3.00 mmol) of 4-(1'-cyclohexenyl)-2-methylbut-1-en-3-yne (**2bh**), and the mixture was stirred at 80 °C for 3 d. Chromatography on aluminum oxide [II, 40 g; elution with pentane/Et<sub>2</sub>O (from 1:0 to 3:1)] and later on silica gel [50 g, elution with pentane/Et<sub>2</sub>O (5:1)] gave 106 mg (21%) of **8bh-*t*Bu** and **9bh-*t*Bu** [*R*<sub>f</sub> = 0.64 and 0.54 (pentane/Et<sub>2</sub>O 3:1); ratio 1.1:1] as a pale-yellow oil. – IR (film):  $\tilde{\nu}$  = 2937 cm<sup>-1</sup> (C–H), 1706 (C=O), 1573, 1480, 1277, 1113, 738. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): 0.84, 0.85 [s, 9 H, (CH<sub>3</sub>)<sub>3</sub>], 1.41–2.10 (m, 4 H, 7,8-H), 2.31, 2.54 (s, 3 H, CH<sub>3</sub>), 2.50–2.60 (m, 2 H), 2.70–2.90 (m, 3 H) and 3.10–3.22 (m, 2 H) [total 7 H, 2,6,9-H, 3-H of **8bh-*t*Bu**, 1-H of **9bh-*t*Bu**], 6.84, 7.06 (s, 1 H, 5-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 17.9, 19.7 (+, CH<sub>3</sub>), 22.47, 22.54, 22.6, 22.7 (–, C-7,8), 28.0, 28.2 [+ , C(CH<sub>3</sub>)<sub>3</sub>], 25.4, 27.5, 29.2, 29.7 (–, C-6,9), 37.1, 37.2 [C<sub>quat</sub>, C(CH<sub>3</sub>)<sub>3</sub>], 44.7, 44.8 (–, C-2), 47.0, 47.1 (+, C-3 of **8bh-*t*Bu**, C-1 of **9bh-*t*Bu**), 130.7, 136.3 (+, C-5), 132.8, 133.0, 133.8, 134.4, 134.5, 134.7, 136.5, 143.5, 153.5, 155.9 (C<sub>quat</sub>, Ar-C), 207.3, 207.9 (C<sub>quat</sub>, C=O). – MS (70 eV), *m/z* (%): 256 (28) [M<sup>+</sup>], 200 (100), 57 (10) [C<sub>4</sub>H<sub>9</sub><sup>+</sup>]. – HRMS (EI) calcd for C<sub>18</sub>H<sub>24</sub>O: 256.1827 (correct HRMS).

**3-tert-Butyl-2,3,4,5,6,7,8,9,10,11-decahydrocyclopenta[*l*]phenanthren-1-one (8bb-*t*Bu).** Following GP2, to a solution of 751 mg (2.00 mmol) of complex **1-*t*Bu** in 40 mL of pyridine was added 745 mg (4.00 mmol) of di(1-cyclohexenyl)ethyne (**2bb**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide [II, 40 g; elution with pentane/Et<sub>2</sub>O (from 1:0 to 3:1)] and later on silica gel [50 g, elution with pentane/Et<sub>2</sub>O (5:1)] gave 110 mg (19%) of **8bb-*t*Bu** [*R*<sub>f</sub> = 0.69 (pentane/Et<sub>2</sub>O 5:1)] as a colorless solid, m. p.

115 °C. – IR (KBr):  $\tilde{\nu}$  = 2930  $\text{cm}^{-1}$  (C–H), 1700 (C=O), 1567, 1448, 1364, 1291, 1253, 1120. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.86 [s, 9 H,  $(\text{CH}_3)_3$ ], 1.38–2.10 (m, 8 H, 5,6,9,10-H), 2.45–2.90 (m, 8 H, 4,7,8,11-H), 3.02–3.30 (m, 3 H, 2,3-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 22.0, 22.4, 22.8, 23.0, 26.1, 26.7, 27.3, 28.4 (–, C-5,6,9,10), 28.2 [+ ,  $\text{C}(\text{CH}_3)_3$ ], 37.2 [ $\text{C}_{\text{quat}}$ ,  $\text{C}(\text{CH}_3)_3$ ], 45.1 (–, C-2), 46.7 (+, C-3), 132.0, 133.3, 134.1, 135.1, 141.9, 153.5 ( $\text{C}_{\text{quat}}$ , Ar-C), 207.6 ( $\text{C}_{\text{quat}}$ , C-1). – MS (70 eV),  $m/z$  (%): 296 (22) [ $\text{M}^+$ ], 240 (100). – Elemental analysis calcd (%) for  $\text{C}_{21}\text{H}_{28}\text{O}$  (296.5): C 85.08, H 9.52; found: C 84.88, H 9.36.

**1-Isopropyl-1,2,5,6,8,9,10,11-octahydro-4H-7-oxacyclopenta[1]phenanthren-3-one (8cb-*i*Pr)** and **3-Isopropyl-3,4,5,6,8,9,10,11-octahydro-2H-7-oxacyclopenta[1]phenanthren-1-one (9cb-*i*Pr)**. Following GP2, to a solution of 723 mg (2.00 mmol) of complex **1-*i*Pr** in 40 mL of pyridine was added 565 mg (3.00 mmol) of 5-(cyclohex-1'-enylethynyl)-3,4-dihydro-2H-pyran (**2cb**), and the mixture was stirred at 80 °C for 4 d. Chromatography on aluminum oxide (II, 40 g) eluting with pentane/ $\text{Et}_2\text{O}$  (from 1:0 to 1:1) gave 378 mg (67%) of a mixture of **8cb-*i*Pr** and **9cb-*i*Pr** (1.1:1) as a colorless oil. Two isomers could be separated by chromatography on silica gel (60 g) eluting with pentane/ $\text{Et}_2\text{O}$  (5:1).

**8cb-*i*Pr** [ $R_f$  = 0.53 (pentane/ $\text{Et}_2\text{O}$  3:1)]: a colorless solid, m. p. 129 °C. – IR (KBr):  $\tilde{\nu}$  = 2956  $\text{cm}^{-1}$  (C–H), 2936, 1696 (C=O), 1576, 1465, 1431, 1320, 1292, 1277, 1107, 1062, 985. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.43 (d,  $^3J$  = 6.6 Hz, 3 H, *i*Pr-H), 1.03 (d,  $^3J$  = 6.6 Hz, 3 H, *i*Pr-H), 2.26–2.39 (m, 1 H, *i*Pr-H), 1.53–1.74 (2 H), 1.86–2.02 (4 H), 2.44–2.81 (6 H), and 3.14 (t,  $^3J$  = 6.5 Hz, 2 H) [m, total 14 H, 2,4,5,8,9,10,11], 3.29–3.33 (m, 1 H, 1-H), 4.12–4.24 (m, 2 H, 6-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta$  = 14.8, 22.2 (+, *i*Pr-C), 21.4  $\times$  2, 21.7, 22.4, 24.2, 26.2 (–, C-4,5,8,9,10,11), 28.9 (+, *i*Pr-C), 38.7 (–, C-2), 42.1 (+, C-1), 66.4 (–, C-6), 116.7, 132.0, 132.92, 132.96, 149.5, 151.9 ( $\text{C}_{\text{quat}}$ , Ar-C), 208.1 ( $\text{C}_{\text{quat}}$ , C-3).

– MS (70 eV),  $m/z$  (%): 284 (18) [ $M^+$ ], 241 (100) [ $M^+ - C_3H_7$ ]. – Elemental analysis calcd (%) for  $C_{19}H_{24}O_2$  (284.4): C 80.24, H 8.51; found: C 80.48, H 8.38.

**9cb-*i*Pr** [ $R_f = 0.43$  (pentane/Et<sub>2</sub>O 3:1)]: a colorless solid, m. p. 136 °C. – IR (KBr):  $\tilde{\nu} = 2939\text{ cm}^{-1}$  (C–H), 1685 (C=O), 1576, 1291, 1260, 1134, 1111, 1081. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 0.48$  (d, <sup>3</sup> $J = 6.5$  Hz, 3 H, *i*Pr-H), 1.05 (d, <sup>3</sup> $J = 6.5$  Hz, 3 H, *i*Pr-H), 2.25–2.38 (m, 1 H, *i*Pr-H), 1.70–1.79 (4 H), 1.85–2.11 (2 H), 2.43–2.56 (4 H), 2.74–2.81 (2 H), 3.10–3.16 (2 H) [m, total 14 H, 2,4,5,8,9,10,11], 3.12–3.31 (m, 1 H, 3-H), 3.14 (dt, <sup>3</sup> $J = 10.7$  Hz, <sup>4</sup> $J = 2.8$  Hz, 1 H, 6-H), 4.40–4.48 (m, 1 H, 6-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta = 14.8, 22.1$  (+, *i*Pr-C), 21.8, 22.1, 22.2 × 2, 23.4, 25.9 (–, C-4,5,8,9,10,11), 28.9 (+, *i*Pr-C), 38.4 (–, C-2), 42.3 (+, C-3), 66.7 (–, C-6), 115.2, 125.3, 126.8, 136.9, 156.9, 157.6 (C<sub>quat</sub>, Ar-C), 206.6 (C<sub>quat</sub>, C-1). – MS (70 eV),  $m/z$  (%): 284 (67) [ $M^+$ ], 241 (100) [ $M^+ - C_3H_7$ ]. – Elemental analysis calcd (%) for  $C_{19}H_{24}O_2$  (284.4): C 80.24, H 8.51; found: C 80.50, H 8.24.

### 1,2-Di(1'-cyclohexenyl)-5-dimethylamino-3-ethoxy-5-isopropyl-1,3-cyclopentadiene

**(11)**. Applying the same reaction conditions as used for the preparation of **8bb-*i*Pr**, but with a reaction time of only 40 h, work-up and chromatography on aluminum oxide (II, 40 g) eluting with pentane to remove alkyne **2bb** and Cr(CO)<sub>5</sub>Py, and then washing with pentane/Et<sub>2</sub>O (3:1) gave 211 mg of a mixture, which contained **11** (major product), **8bb-*i*Pr** (first minor product) and some impurities. – MS (70 eV),  $m/z$  (%): 361 (1%), 355 (30) [ $M^+(\mathbf{11})$ ], 326 (65) [ $M^+(\mathbf{11}) - C_2H_5$ ], 312 (100) [ $M^+(\mathbf{11}) - C_3H_7$ ], 310 (46), 282 (21) [ $M^+(\mathbf{8bb-}i\text{Pr})$ ], 239 (36) [ $M^+(\mathbf{8bb-}i\text{Pr}) - C_3H_7$ ], 202 (18), 200 (90), 173 (33), 129 (30), 83 (41), 74 (46), 59 (100), 45 (47), 41 (28). – Selected signals of **11**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 0.39$  (d, <sup>3</sup> $J = 6.8$  Hz, 3 H, *i*Pr-H), 1.00 (d, <sup>3</sup> $J = 6.8$  Hz, 3 H, *i*Pr-H), 1.28 (t, <sup>3</sup> $J = 6.8$  Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.28 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], 3.80 (q, <sup>3</sup> $J = 6.8$  Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 4.57 (s, 1 H, 4-H), 5.57, 5.65 (s, 2 H, 1'-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta = 14.2, 14.6, 16.6$  (+, *i*Pr-C, OCH<sub>2</sub>CH<sub>3</sub>),

42.0 [+ , N(CH<sub>3</sub>)<sub>2</sub>], 64.1 (–, OCH<sub>2</sub>CH<sub>3</sub>), 78.5 (C<sub>quat</sub>, C-5), 97.6 (+, C-4), 125.8, 126.3 (+, C-1'), 154.7, 158.8 (C<sub>quat</sub>, C-1,3).

**17-Isopropyl-3-methoxy-6,7,16,17-tetrahydrocyclopenta[*a*]phenanthren-15-one (14fi-*i*Pr) and 15-Isopropyl-3-methoxy-6,7,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (15fi-*i*Pr):** According to GP2, to a solution of 470 mg (1.31 mmol) of complex **1-cPr** in 26 mL of pyridine was added 310 mg (1.48 mmol) of 3-(but-3'-en-1'-ynyl)-1,2-dihydronaphthalene (**2fi**), and the mixture was stirred at 80 °C for 6 d. After dilution with Et<sub>2</sub>O, conc. hydrochloric acid was added to the reaction mixture (< pH 2). Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (+ 10% CH<sub>2</sub>Cl<sub>2</sub>; from 20:0 to 2:1) gave 146 mg (37%) of **14fi-*i*Pr** [*R*<sub>f</sub> = 0.55 (pentane/Et<sub>2</sub>O 3:1)] as a colorless solid, m. p. 115 °C and 114 mg (29%) of **15fi-*i*Pr** [*R*<sub>f</sub> = 0.31 (pentane/Et<sub>2</sub>O 3:1)] as a colorless solid, m. p. 100 °C. – **14fi-*i*Pr**: IR (KBr):  $\tilde{\nu}$  = 2963 cm<sup>-1</sup> (C–H), 2937, 1706 (C=O), 1604, 1506, 1461, 1310, 1273, 1244, 1165, 1129, 1050, 1032, 1018, 840, 822. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.69 (d, <sup>3</sup>*J* = 6.7 Hz, 3 H, *i*Pr-H), 1.02 (d, <sup>3</sup>*J* = 6.7 Hz, 3 H, *i*Pr-H), 2.18–2.29 (m, 1 H, *i*Pr-H), 2.46 (dd, <sup>2</sup>*J* = 18.9, <sup>3</sup>*J* = 3.3 Hz, 1 H, 16-H), 2.66 (dd, <sup>2</sup>*J* = 18.9, <sup>3</sup>*J* = 7.7 Hz, 1 H, 16-H), 2.81 (t, <sup>3</sup>*J* = 7.3 Hz, 2 H) and 3.28–3.52 (3 H) [m, total 5 H, 6,7,17-H], 3.82 (s, 3 H, OCH<sub>3</sub>), 6.79–6.86 (m, 2 H, Ar-H), 7.35 (d, <sup>3</sup>*J* = 6.9 Hz, 1 H, Ar-H), 7.62 (d, <sup>3</sup>*J* = 8.3 Hz, 1 H, Ar-H), 7.86 (d, <sup>3</sup>*J* = 8.3 Hz, 1 H, Ar-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 16.5, 21.1 (+, *i*Pr-C), 22.4, 28.4 (–, C-6,7), 31.4 (+, *i*Pr-C), 39.4 (–, C-16), 43.1 (+, C-17), 55.2 (+, OCH<sub>3</sub>), 112.4, 113.3, 123.7, 125.0, 129.0 (+, Ar-C), 126.4, 133.8, 134.1, 136.3, 139.0, 156.9, 159.2 (C<sub>quat</sub>, Ar-C), 208.0 (C<sub>quat</sub>, CO). – MS (70 eV), *m/z* (%): 306 (56) [M<sup>+</sup>], 263 (100) [M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>], 245 (12), 191 (11), 55 (11). – Elemental analysis calcd (%) for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub> (306.4): C 82.32, H 7.24; found: C 82.51, H 6.35. – **15fi-*i*Pr**: IR (film):  $\tilde{\nu}$  = 2967 cm<sup>-1</sup> (C–H), 2932, 1705 (C=O), 1592, 1568, 1436, 1276, 1249, 1077, 1033, 796. – <sup>1</sup>H NMR (250 MHz,

CDCl<sub>3</sub>):  $\delta$  = 0.42 (d,  $^3J$  = 6.7 Hz, 3 H, *i*Pr-H), 1.08 (d,  $^3J$  = 6.7 Hz, 3 H, *i*Pr-H), 2.21–2.34 (m, 1 H, *i*Pr-H), 2.50–3.02 (m, 6 H, 6,7,16-H), 3.52–3.58 (m, 1 H, 15-H), 3.84 (s, 3 H, OCH<sub>3</sub>), 6.81 (d,  $^4J$  = 2.5 Hz, 1 H, Ar-H), 6.86 (dd,  $^3J$  = 8.6,  $^4J$  = 2.5 Hz, 1 H, Ar-H), 7.62–7.73 (m, 3 H, Ar-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 14.8, 22.2 (+, *i*Pr-C), 24.5, 28.8 (–, C-6,7), 30.0 (+, *i*Pr-C), 38.0 (–, C-16), 43.0 (+, C-15), 55.2 (+, OCH<sub>3</sub>), 112.5, 113.4, 121.6, 123.2, 126.2 (+, Ar-C), 126.6, 133.3, 135.3, 139.4, 140.6, 155.6, 159.9 (C<sub>quat</sub>, Ar-C), 206.6 (C<sub>quat</sub>, CO). – MS (70 eV), *m/z* (%): 306 (100) [M<sup>+</sup>], 263 (72) [M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>], 235 (10). – Elemental analysis calcd (%) for C<sub>21</sub>H<sub>22</sub>O<sub>2</sub> (306.4): C 82.32, H 7.24; found: C 82.05, H 6.99.

**17-Isopropyl-3-methoxy-12-methyl-6,7,16,17-tetrahydrocyclopenta[*a*]phenanthren-15-one (14fh-*i*Pr) and 15-Isopropyl-3-methoxy-12-methyl-6,7,15,16-tetrahydrocyclopenta[*a*]phenanthren-17-one (15fh-*i*Pr):** According to GP2, to a solution of 723 mg (2.00 mmol) of complex **1-*i*Pr** in 40 mL of pyridine was added 781 mg (86% pure; 3.00 mmol) of 7-methoxy-3-(3'-methylbut-3'-en-1'-ynyl)-1,2-dihydronaphthalene (**2fh**), and the mixture was stirred at 80 °C for 6 d. After dilution with Et<sub>2</sub>O, conc. hydrochloric acid was added to the reaction mixture (< pH 2). Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1) gave 472 mg (74%) of **14fh-*i*Pr** and **15fh-*i*Pr** [ratio 1.1:1] as a semi-solid. The two isomers could be separated by chromatography on silica gel (80 g) eluting with pentane/Et<sub>2</sub>O (6:1). **14fh-*i*Pr** [*R*<sub>f</sub> = 0.55 (pentane/Et<sub>2</sub>O 3:1)]: a colorless solid, m. p. 140 °C. – IR (KBr):  $\tilde{\nu}$  = 2957 cm<sup>-1</sup> (C–H), 1696 (C=O), 1608, 1507, 1473, 1318, 1243, 1231, 1170, 1033, 847, 822. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.49 (d,  $^3J$  = 7.1 Hz, 3 H, *i*Pr-H), 1.09 (d,  $^3J$  = 7.1 Hz, 3 H, *i*Pr-H), 2.31–2.40 (m, 1 H, *i*Pr-H), 2.43 (s, 3 H, CH<sub>3</sub>), 2.55–2.68 (2 H), 2.76–2.86 (2 H) and 3.23–3.56 (3 H) [m, total 7 H, 6,7,16,17-H], 3.83 (s, 3 H, OCH<sub>3</sub>), 6.80 (s, 1 H, Ar-H), 6.84 (dd,  $^3J$  = 8.6,  $^4J$  = 2.4 Hz, 1 H, Ar-H), 7.63 (d,  $^3J$  = 8.6 Hz, 1 H, Ar-H), 7.68 (s, 1 H, Ar-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 15.0, 22.1 (+, *i*Pr-

C), 18.3 (+, CH<sub>3</sub>), 21.9, 28.5 (–, C-6,7), 29.3 (+, *i*Pr-C), 38.9 (–, C-16), 42.3 (+, C-17), 55.1 (+, OCH<sub>3</sub>), 112.3, 113.2, 124.8, 130.5 (+, Ar-C), 126.3, 133.0, 133.51, 133.56, 134.1, 139.0, 155.3, 159.0 (C<sub>quat</sub>, Ar-C), 208.5 (C<sub>quat</sub>, CO). – MS (70 eV), *m/z* (%): 320 (52) [M<sup>+</sup>], 277 (100) [M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>], 55 (12). – Elemental analysis calcd (%) for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub> (320.4): C 82.46, H 7.55; found: C 82.27, H 7.39. – **15fh-*i*Pr** [*R*<sub>f</sub> = 0.55 (pentane/Et<sub>2</sub>O 3:1)]: a semi-solid, m. p. 118 °C. – IR (film):  $\tilde{\nu}$  = 2957 cm<sup>–1</sup> (C–H), 2834, 1700 (C=O), 1598, 1560, 1279, 1248, 1119, 1037, 801. – <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.43 (d, <sup>3</sup>*J* = 6.7 Hz, 3 H, *i*Pr-H), 1.07 (d, <sup>3</sup>*J* = 6.8 Hz, 3 H, *i*Pr-H), 2.17–2.27 (m, 1 H, *i*Pr-H), 2.66 (s, 3 H, CH<sub>3</sub>), 2.54–2.60 (2 H), 2.73–2.99 (4 H) [m, total 6 H, 6,7,16-H], 3.45–3.51 (m, 1 H, 15-H), 3.85 (s, 3 H, OCH<sub>3</sub>), 6.81 (d, <sup>4</sup>*J* = 2.5 Hz, 1 H, Ar-H), 6.87 (dd, <sup>3</sup>*J* = 8.5, <sup>4</sup>*J* = 2.4 Hz, 1 H, Ar-H), 7.44 (s, 1 H, Ar-H), 7.73 (d, <sup>3</sup>*J* = 8.2 Hz, 1 H, Ar-H). – <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, plus DEPT):  $\delta$  = 14.9, 22.2 (+, *i*Pr-C), 18.5 (+, CH<sub>3</sub>), 24.1, 29.1 (–, C-6,7), 30.1 (+, *i*Pr-C), 38.7 (–, C-16), 42.4 (+, C-15), 55.3 (+, OCH<sub>3</sub>), 112.5, 113.4, 124.9, 126.5 (+, Ar-C), 126.7, 130.6, 132.9, 136.3, 139.71, 139.74, 156.4, 159.8 (C<sub>quat</sub>, Ar-C), 207.6 (C<sub>quat</sub>, CO). – MS (70 eV), *m/z* (%): 320 (100) [M<sup>+</sup>], 277 (78) [M<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>], 249 (10), 43 (10) [C<sub>3</sub>H<sub>7</sub><sup>+</sup>]. – Elemental analysis calcd (%) for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub> (320.4): C 82.46, H 7.55; found: C 82.70, H 7.33.

**(5*R*,17*R/S*)-17-Isopropyl-5,12-dimethyl-1,2,3,4,5,6,7,10,16,17-decahydrocyclopenta-*[a]*phenanthren-15-one (14gh-*i*Pr) and (5*R*,15*R/S*)-15-Isopropyl-5,12-dimethyl-1,2,3,4,5,6,7,10,15,16-decahydrocyclopenta-*[a]*phenanthren-17-one (15gh-*i*Pr):** According to GP2, to a solution of 900 mg (2.49 mmol) of complex **1-*i*Pr** in 50 mL of pyridine was added 801 mg (3.74 mmol) of (4*aR*)-4*a*-methyl-7-(3'-methylbut-3'-en-1'-ynyl)-1,2,3,4,4*a*,5,6,8*a*-octahydronaphthalene (**2gh**), and the mixture was stirred at 80 °C for 5 d. After dilution with Et<sub>2</sub>O, conc. hydrochloric acid was added to the reaction mixture (< pH 2). Chromatography on aluminum oxide (II, 40 g) eluting with pentane/Et<sub>2</sub>O (from 1:0 to 3:1)

gave 557 mg (72%) of **14gh-*i*Pr** and **15gh-*i*Pr** [ratio 1.3:1, d. r. of each isomer 1.2:1] as a semi-solid. – IR (KBr):  $\tilde{\nu} = 2924 \text{ cm}^{-1}$  (C–H), 1701 (C=O), 1576, 1482, 1464, 1446, 1378, 1282, 1121, 988, 737. –  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.38, 0.40$  (d,  $^3J = 6.8 \text{ Hz}$ , 3 H, *i*Pr-H), 0.68, 0.69, 0.71, 0.78 (s, 3 H,  $\text{CH}_3$ ), 1.00, 1.02 (d,  $^3J = 6.8 \text{ Hz}$ , 3 H, *i*Pr-H), 1.08–1.78 (10 H) and 2.15–2.55 (6 H) [m, total 16 H, *i*Pr-H, 1,2,3,4,6,7,10,16), 2.24, 2.49 (s, 3 H,  $\text{CH}_3$ ), 3.22–3.38 (m, 1 H, 17-H of **14gh-*i*Pr** and 15-H of **15gh-*i*Pr**), 6.68, 6.71, 6.94 (s, 1 H, 11-H). –  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ , plus DEPT):  $\delta = 14.5, 14.7 \times 2, 14.9$  (+, *i*Pr-C), 15.6, 15.7  $\times 2$ , 15.9 (+,  $\text{CH}_3$ ), 17.6, 17.72, 17.76, 17.80 (+,  $\text{CH}_3$ ), 21.8, 21.9  $\times 2$ , 22.2 (+, *i*Pr-C), 21.8  $\times 2$ , 21.9  $\times 2$ , 26.4  $\times 2$ , 26.5  $\times 2$ , 28.6  $\times 2$ , 28.75, 28.80, 29.1, 29.8, 29.9, 30.1 (–, C-1,2,3,4), 28.0, 29.0  $\times 3$  (+, *i*Pr-C), 31.7, 31.8  $\times 2$ , 32.1 ( $\text{C}_{\text{quat}}$ , C-5), 38.1, 38.3, 38.5, 38.9, 40.6, 40.8, 40.9  $\times 2$ , 45.7, 46.0, 46.7, 47.0 (–, C-6,7,16), 39.89, 39.94, 40.0, 40.2 (+, C-10), 42.2  $\times 2$ , 42.32, 42.35 (+, C-17 of **14gh-*i*Pr** and C-15 of **15gh-*i*Pr**), 130.7, 130.9, 136.8, 136.9 (+, C-11), 130.6, 131.62, 131.64  $\times 2$ , 132.35, 132.37, 133.64  $\times 4$ , 134.4, 134.6, 135.47, 135.54, 142.9, 143.0, 154.6, 154.8, 156.7, 157.0 ( $\text{C}_{\text{quat}}$ , Ar-C), 207.2, 207.3, 207.9  $\times 2$  ( $\text{C}_{\text{quat}}$ , CO). – MS (70 eV),  $m/z$  (%): 310 (84) [ $\text{M}^+$ ], 267 (100) [ $\text{M}^+ - \text{C}_3\text{H}_7$ ]. – HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{30}\text{O}$ : 310.2297 (correct HRMS).