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First Enantioselective Total Synthesis of Angucyclinone-Type Antibiotics Rubiginones A_2 and C_2

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Experimental Section

General: Melting points were obtained in open capillary tubes and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. Diastereoisomeric ratios were established by integration of well-separated signals of both diastereomers in the crude reactions mixtures. All reactions were monitored by thin-layer chromatography that was performed on precoated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was flame-dried under a stream of dry argon. CH_2Cl_2 was dried over P_2O_5. Dry THF was distilled from sodium/benzophenone ketyl. Diisopropylamine was distilled from KOH. All other reagent quality solvents were used without purification. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2, and solvent drying with $MgSO_4$.

[(S)*S*]-4-Hydroxy-4-[(*p*-tolylsulfinyl)methyl]-cyclohexa-2,5-dienone (3). To a solution of freshly distilled diisopropylamine (20.7 mL, 147.8 mmol) in THF (250 mL), *n*-butyllythium 2.4 M (56 mL, 135.5 mmol) was added under argon at –78 ºC. After stirring for 30 min, a solution of (S*S*)-methyl-*p*-tolylsulfoxide (19.0 g, 123.2 mmol) in

THF (200 mL) was added at –78ºC. After 30 min, a solution of 4,4-dimethoxy-2,5-cyclohexadienone (19.9 g, 129.4 mmol) in THF (430 mL) was slowly added and the mixture was stirred for two hours at –78 ºC. Then, the mixture was hydrolyzed with an aqueous saturated solution of ammonium chloride (40 mL) and the organic layer was extracted with EtOAc. After workup, the crude product was dissolved in THF (80 mL) and a solution of oxalic acid (1.16 g, 12.9 mmol) in water (20 mL) was added. After stirring for 2 h, hydrolysis with saturated solution of $NaHCO_3$, extraction with EtOAc and workup, the residue was crystallized from EtOAc/hexane isolating compound **3** as a white solid in 76% yield: M.p. 142-144 ºC; $[\alpha]_D^{20}$ = -177 (*c* = 1 in $CHCl_3$); ^{1}H NMR: δ = 7.54 and 7.36 (AA'BB' system, 4H), 7.25 (dd, *J* = 10.2 and 3.2 Hz, 1H), 7.00 (dd, *J* = 10.2 and 3.2 Hz, 1H), 6.30 (dd, *J* = 10.2 and 1.8 Hz, 1H), 6.18 (dd, *J* = 10.1 and 1.9 Hz, 1H), 4.93 (s, 1H), 3.16 and 2.85 (AB system, *J* = 13.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR: δ = 184.9, 149.2, 149.1, 142.2, 139.6, 130.1 (2C), 128.1, 127.6, 123.9 (2C), 68.0, 67.1, 21.3; elemental analysis calcd (%) for $C_{14}H_{14}O_3S$ (262.3): C 64.10, H 5.38, S 12.22; found C 63.91, H 5.48, S 12.47.

[4*R*,5*R*,(S)*S*]-4-Hydroxy-5-methyl-4-[(*p*-tolylsulfinyl)methyl]-2-cyclohexen-1-one (4). To a solution of Me_3Al 2M in heptane (3.8 mL, 7.6 mmol) in CH_2Cl_2 (10 mL) was added a solution of **3** (500 mg, 1.9 mmol) in CH_2Cl_2 (10 mL) under argon at –78 ºC. After 4 h at the same temperature, the excess organoaluminum reagent was destroyed with methanol, and the mixture was poured into an Erlenmeyer containing EtOAc and a saturated solution of sodium potassium tartrate and stirred vigorously for 30 min. The organic layer was

washed with brine and dried over $MgSO_4$. After workup and flash chromatography (eluent EtOAc/hexane 1:1), compound **4** was obtained as a white solid in 65% yield: M.p. 120-121 ºC (EtOAc/hexane); $[\alpha]_D^{20}$ = -245 (*c* = 1 in $CHCl_3$); ^{1}H NMR: δ = 7.56 and 7.37 (AA'BB' system, 4H), 7.25 (d, *J* = 10.2 Hz, 1H) 6.10 (dd, *J* = 10.2 Hz, 1H), 4.85 (s, 1H), 3.22 and 2.92 (AB system, *J* = 12.2 Hz, 2H), 2.62-2.22 (m, 3H), 2.44 (s, 3H), 1.10 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR: δ = 198.3, 149.7, 142.4, 139.7, 130.3 (2C), 129.0, 123.8 (2C), 71.6, 64.9, 41.7, 38.8, 21.3, 14.2; elemental analysis calcd (%) for $C_{15}H_{18}O_3S$ (278.4): C 64.72, H 6.52, S 11.52; found C 64.69, H 6.85, S 11.89.

(4*R*,5*R*)-4-Hydroxy-5-methyl-4-[(*p*-tolylsulfonyl)methyl]-2-cyclohexen-1-one (5). To a solution of **4** (3.8 g, 13.8 mmol) in CH_2Cl_2 (45 mL) at 0 ºC, a solution of *m*-CPBA (6.2 g, 17.9 mmol) in CH_2Cl_2 (60 mL) was added dropwise. After stirring at 0 ºC for 30 min, the mixture was hydrolyzed with an aqueous saturated solution of Na_2SO_3, extracted with CH_2Cl_2, and the organic layer washed with an aqueous saturated solution of $NaHCO_3$. After workup and crystallization (EtOAc/hexane) compound **5** was obtained as a white solid in 96% yield: M.p. 145-146 ºC; $[\alpha]_D^{20}$ = -65 (*c* = 1 in acetone); ^{1}H NMR: δ = 7.80 and 7.39 (AA'BB' system, 4H), 7.05 (dd, *J* = 10.2 and 0.9 Hz, 1H), 5.95 (d, *J* = 10.2 Hz, 1H), 4.08 (br s, 1H), 3.50 and 3.45 (AB system, *J* = 14.2 Hz, 2H), 2.62-2.37 (m, 3H), 2.47 (s, 3H), 1.09 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR: δ = 198.3, 149.7, 142.4, 139.9, 130.2 (2C), 129.1, 123.8 (2C), 71.7, 64.9,

41.7, 38.9, 21.4, 14.3; elemental analysis calcd (%) for $C_{15}H_{18}O_4S$ (294.4): C 61.20, H 6.16, S 10.89; found C 61.12, H 6.19, S 11.24.

(1*R*,4*S*,6*R*)-6-Methyl-1-[(*p*-tolylsulfonyl)methyl]-2-cyclohexen-1,4-diol (6). To a solution of DIBALH 1 M in hexanes (39.8 mL 39.8 mmol) in THF (130 mL), a solution of **5** (3.9 g, 13.3 mmol) in THF (45 mL) was added dropwise under argon at –78 ºC. After 30 min at the same temperature, the excess organoaluminum reagent was destroyed with methanol, and the mixture was poured into an Erlenmeyer containing ethyl acetate and a saturated solution of sodium potassium tartrate and stirred vigorously for 30 min. The organic layer was washed with brine and dried over $MgSO_4$. After workup, compound **6** was obtained in 99% yield as a white solid, which could be used without further purification: M.p. 96-97 ºC (EtOAc/hexane); $[\alpha]_D^{20}$ = -56 (*c* = 1 in acetone); ^{1}H NMR: δ = 7.79 and 7.36 (AA'BB' system, 4H), 6.17 (dd, *J* = 10.1 and 2.0 Hz, 1H), 5.85 (dt, *J* = 10.1 and 1.8 Hz, 1H), 4.5 (s, 1H), 4.23 (m, 1H), 3.46 and 3.25 (AB system, *J* = 14.3 Hz, 2H), 2.46 (s, 3H), 1.85 (m, 2H), 1.68-1.51 (m, 2H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR: δ = 144.9, 138.2, 134.6, 130.0, 129.9 (2C), 127.7 (2C), 70.3, 67.2, 63.3, 36.1 (2C), 21.6, 14.9; elemental analysis calcd (%) for $C_{15}H_{20}O_4S$ (296.1): C 60.79, H 6.80, S 10.82; found C 60.46, H 7.14, S 10.56.

(1*R*,4*S*,6*R*)-4-[(*tert*-Butyldimethylsilyl)oxy)]-6-methyl-1-[(*p*-tolylsulfonyl)methyl]-2-cyclohexen-1-ol (7). To a solution of **6** (1.8 g, 6.0 mmol) in dry CH_2Cl_2 (20 mL) at 0 ºC, 2,6-lutidine (1.8 mL, 14.9 mmol) and TBDMSOTf (1.8 mL, 25.3 mmol) were added under

argon. After 2 h, the mixture was hydrolyzed with 10% HCl, extracted with CH_2Cl_2 and the organic layer washed with brine. After workup, compound **7** was obtained as a yellowish oil, which could be use without further purification in the next step. An analytical sample was obtained after purification by flash chromatography (EtOAc/hexane 1:3) and crystallization in ethyl ether/hexane, to afford **7** as a white solid: M.p. 107-108 ºC; $[\alpha]_D^{20}$ = +41 (*c* = 1 in acetone); ^{1}H NMR: δ = 7.78 and 7.36 (AA'BB' system, 4H), 6.04 (dd, *J* = 10.1 and 2.0 Hz, 1H), 5.76 (dt, *J* = 10.1 and 2.0 Hz, 1H), 4.23 (m, 1H), 3.44 and 3.29 (AB system, *J* = 14.2 Hz, 2H), 2.59 (s, 1H), 2.45 (s, 3H), 1.91 (m, 1H), 1.74-1.53 (m, 2H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.89 (s, 9H), 0.08 and 0.07 (2s, 6H) ; ^{13}C NMR: δ = 144.8, 138.1, 135.9, 129.9 (2C), 129.8, 127.7 (2C), 70.3, 67.7, 63.2, 36.4, 35.7, 25.8 (3C), 21.6, 18.1, 15.0, -3.6, -3.7; MS (FAB): calcd. for $C_{21}H_{34}OSSi$: 411.1947, found 411.2026 $[M+H]^+$; *m/z* (%): 411 (7) $[M+H]^+$, 393 (100), 371 (46).

(4*S*,6*R*)-4-[(*tert*–Butyldimethylsilyl)oxy]-6-methyl-2-cyclohexen-1-one (8). To a solution of **7** in CH_3CN (60 mL), Cs_2CO_3 (3.9 g, 12 mmol) was added at room temperature. After stirring for 17 h, the reaction mixture was hydrolyzed with water and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After workup and purification by flash chromatography (EtOAc/hexane 1:12), compound **8** was obtained as a colorless oil in 87% yield for the two last steps: $[\alpha]_D^{20}$ = -76 (*c* = 1 in acetone); ^{1}H NMR: δ = 6.77 (dt, *J* = 10.1 and 2.0 Hz, 1H), 5.91 (dd, *J* = 10.1 and 2.4 Hz, 1H), 4.59 (m, 1H), 2.38 (m, 1H), 2.20 (m, 1H), 1.77

(ddd, *J* = 13.9, 12.5 and 10.3 Hz, 1H), 1.14 (d, *J* = 6.5 Hz, 3H), 0.91 (s, 9H), 0.12 (s, 6H); ^{13}C NMR: δ = 201.0, 154.0, 128.2, 68.0, 41.9, 40.1, 25.7 (3C), 18.0, 15.0, -3.5, -3.7; MS (EI): calcd for $C_9H_{15}O_2Si$: 183.0841; found: 183.0846 $[M\text{-}C_4H_9]^+$; *m/z* (%): 183 (100) $[M\text{-}C_4H_9]^+$, 139 (10), 113 (15).

(4*S*,6*R*)-2-Bromo-4-[(*tert*–butyldimethylsilyl)oxy]-6-methyl-2-cyclohexen-1-one (9). To a solution of **8** (72 mg, 0.30 mmol) in CCl_4 (3 mL), a solution of bromine (15 μL, 0.30 mmol) in CCl_4 (3 mL) was added dropwise at 0 °C. When no starting material was observed, tryethylamine (0.15 mL, 1.1 mmol) was added and the mixture was stirred at room temperature for 32 h. The reaction mixture was quenched with aqueous saturated solution of Na_2SO_3 and extracted with CH_2Cl_2. After workup and flash chromatography (EtOAc/hexane 1:120), compound **9** was obtained as a white solid in 80% yield: M.p. 40-41 °C; $[\alpha]_D^{20}$ = -38 (*c* = 1 in acetone); ^{1}H NMR: δ = 7.22 (m, 1H), 4.59 (m, 1H), 2.46 (m, 1H), 2.25 (m, 1H), 1.87 (m, 1H), 1.21 (d, *J* = 6.7 Hz, 3H), 0.91 (s, 9H), 0.13 and 0.12 (2s, 6H); ^{13}C NMR: δ = 193.1, 154.3, 123.4, 69.0, 41.6, 40.0, 25.7 (3C), 18.0, 15.6, -3.4, -3.6; elemental analysis calcd (%) for $C_{13}H_{23}BrO_2Si$ (319.3): C 48.90, H 7.26; found C 48.88, H 7.56.

(1*S*,4*S*,6*R*)-2-Bromo-4-[(*tert*–Butyldimethylsilyl)oxy]-6-methyl-2-cyclohexen-1-ol (10). To a solution of **7** (163 mg, 0.51 mmol) in THF (17 mL) at –100 °C, a solution of $LiAlH_4$ (31 mg, 0.76 mmol) in THF (25 mL) was added under argon. After 30 min at same temperature, the reaction was hydrolyzed with methanol, and the

mixture was poured into an erlenmeyer containing ethyl acetate and a saturated solution of sodium potassium tartrate and stirred vigorously for 30 min. The organic layer was washed with brine and dried over $MgSO_4$. After workup, compound **10** was isolated as a 93:7 diastereoisomeric ratio which could be used without further purification. An analytical sample of the major diastereoisomer could be isolated by HPTLC as a white solid: M.p. 88-89 °C; $[\alpha]_D^{20}$ = -67 (*c* = 1 in $CHCl_3$); ^{1}H NMR: δ = 6.05 (d, *J* = 1.6 Hz, 1H), 4.29 (m, 1H), 3.82 (m, 1H), 2.24 (d, *J* = 3.6 Hz, 1H), 1.90 (m, 1H), 1.78 (m, 1H), 1.45 (m, 1H), 1.15 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 9H), 0.08 and 0.07 (2s, 6H); ^{13}C NMR: δ = 136.4, 128.4, 75.8, 68.9, 39.9, 36.3, 25.8 (3C), 19.0, 18.1, -3.5, -3.6; elemental analysis calcd (%) for $C_{13}H_{25}BrO_2Si$ (321.33): C 48.59, H 7.84; found C 48.33, H 7.54.

(1*S*,4*S*,6*R*)-2-Bromo-4-[(*tert*–butyldimethylsilyl)oxy]-6-methyl-2-cyclohexen-1-yl isobutyrate (11). To a solution of the above obtained mixture containing **10** in CH_2Cl_2 (1 mL), isobutyryl chloride (76 μL, 0.71 mmol) and 4-dimethylaminopyridine (135 mg, 1.1 mmol) were added. The reaction mixture was stirred for 1 h, hydrolyzed with water and extracted with CH_2Cl_2. After workup and flash chromatography (EtOAc/hexane 1:50), compound **11** was obtained as a colorless oil in 79% yield for the two last steps: ^{1}H NMR: δ = 6.14 (dd, *J* = 3.6 and 1.6 Hz, 1H), 5.32 (m, 1H), 4.32 (m, 1H), 2.61 (sept, *J* = 7.1 Hz, 1H), 1.92 (m, 2H), 1.52 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 9H), 0.07 and 0.06 (2s, 6H); ^{13}C NMR: δ = 176.4,

138.1, 122.9, 75.6, 68.5, 39.5, 34.9, 34.2, 25.7 (3C), 19.1, 19.0, 18.5, 18.0, -3.5, -3.6; MS (EI): calcd for $C_9H_{13}BrO_3Si$: 333.0522; found: 333.0519 [*M*-C_4H_9]$^+$; *m/z* (%): 333 (35) [*M*-C_4H_9]$^+$, 311 (71), 289 (14), 259 (9), 241 (100), 223 (15).

(1*S*,4*S*,6*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]-6-methyl-2-vinyl-2-cyclohexen-1-yl isobutyrate (2). A mixture of **11** (583 mg, 1.5 mmol), tetrakistriphenylphosphine palladium (0) (207 mg, 0.18 mmol) and tributylvinylstannane (0.58 mL, 0.18 mmol) in toluene (7.5 mL) was heated at 90 ºC for 24 h. The reaction was hydrolyzed with water and extracted with CH_2Cl_2. After workup and flash chromatography (EtOAc/hexane 1:60), compound **2** was obtained as colorless oil in 78% yield: ^{1}H NMR: δ = 6.13 (dd, *J* = 17.8 and 10.9 Hz, 1H), 5.84 (m, 1H), 5.46 (m, 1H), 5.13 (d, *J* = 17.8 Hz, 1H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.45 (m, 1H), 2.51 (sept, *J* = 6.9 Hz, 1H), 1.90 (m, 2H), 1.45 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.89 (s, 9H), 0.08 and 0.07 (s, 3H); ^{13}C NMR: δ = 177.0, 135.8, 135.7, 135.0, 114.2, 72.7, 66.9, 38.3, 34.2, 33.7, 25.8, 19.0, 18.9, 18.4, 18.1, -3.5, -3.6; MS (FAB): calcd for $C_{15}H_{27}OSi$: 251.1831; found: 251.1829 [*M*-$C_4H_7O_2$]$^+$; *m/z* (%): 265 (9) [*M*-$C_3H_5O_2$]$^+$, 251 (100) [*M*-$C_4H_7O_2$]$^+$, 235 (52), 227 (10), 219 (37), 207 (22).

(1*S*,3*R*,4*S*,12b*R*)-1-[(*tert*-Butyldimethylsilyl)oxy)]-8-methoxy-3-methyl-7,12-dioxo-1,2,3,4,6,12b-hexahydrobenz[*a*]anthracen-4-yl isobutyrate (12). A solution of 2-(*p*-tolylsulfiny)-5-methoxy-1,4-naphthoquinone **1** (37 mg, 0.12 mmol) and diene **2** (16 mg, 0.048

mmol) in dry CH_2Cl_2 (1 mL) was refluxed under argon for 24 h. After elimination of the solvent and flash chromatography (eluent EtOAc/hexane 1:9), compound **12** was obtained as a yellowish solid in 52% yield): M.p. 88-89 °C; $[\alpha]_D^{20}$ = -85 (*c* = 0.25 in $CHCl_3$); ^{1}H NMR: δ = 7.71 (dd, *J* = 7.7 and 1.4 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.25 (dd, *J* = 8.3 and 1.4 Hz, 1H), 5.60 (m, 1H), 4.88 (m, 1H), 4.01 (s, 3H), 3.81 (m, 1H), 3.49 (ddt, *J* = 24.7, 4.0 and 2.2 Hz, 1H), 3.38 (m, 1H), 3.05 (ddt, *J* = 24.5, 4.6, and 2.2 Hz, 1H), 2.68 (sept, *J* = 6.9 Hz, 1H), 1.97 (dd, *J* = 8.9 and 3.8 Hz, 1H) 1.69 (m, 2H), 1.26 (d, *J* = 1.2 Hz, 3H), 1.23 (d, *J* = 1.2 Hz, 3H), 1.01 (d, *J* = 5.9 Hz, 3H) 0.73 (s, 9H), -0.12 and -0.37 (2s, 6H); ^{13}C NMR: δ = 183.7, 183.6, 176.1, 159.3, 142.9, 141.6, 135.2, 135.1, 134.5, 119.5, 116.9, 113.2, 77.3, 76.4, 56.4, 43.0, 42.9, 37.5, 34.3, 25.6 (3C), 25.1, 19.2, 19.1, 18.5, 17.8, -3.2, -3.3; MS (EI): calcd for $C_{30}H_{40}O_6Si$: 524.2594; found: 524.2573 $[M]^+$; *m/z* (%): 526 (62) $[M+2]^+$, 524 (54) $[M]^+$, 509 (57), 499 (41), 483 (100), 483 (100), 481 (71).

(3*R*,4*S*)-8-Methoxy-3-methyl-1,7,12(2*H*)-trioxo-3,4-dihydrobenz[*a*]anthracen-4-yl isobutyrate (13), Rubiginone C_2. Compound **12** (42 mg, 0.08 mmol) was exposed under solvent-free conditions to the sun light for 16 h. After flash chromatography (eluent EtOAc/hexane 1:3) and crystallization (EtOAc), compound **13** (Rubiginone C_2) was obtained as a yellowish solid in 35% yield: M.p. 218-219 °C; $[\alpha]_D^{20}$ = -57 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR: δ = 8.35 (d, *J* = 8.3 Hz, 1H), 7.78 (dd, *J* = 7.7 and 1.4 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H) 7.59 (d, *J* = 8.3 Hz, 1H), 7.31 (dd, *J* = 8.1 and 1.2

Hz, 1H), 5.84 (d, *J* = 7.1 Hz, 1H), 4.04, (s, 3H), 3.17 (m, 1H), 2.75-2.56 (m, 3H), 1.24 (d, *J* = 5.5 Hz, 3H), 1.22 (d, *J* = 5.5 Hz, 3H), 1.12 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR: δ = 196.6, 184.0, 181.2, 176.4, 159.9, 145.9, 137.5, 136.1, 135.5, 134.8, 134.6, 131.5, 130.1, 120.6, 119.7, 117.3, 73.3, 56.5, 43.8, 35.1, 34.1, 19.0, 18.9, 18.0; MS (EI): calcd for $C_{24}H_{22}O_6$: 406.1416; found: 406.1421 [*M*]$^+$; *m/z* (%): 406 (61) [*M*]$^+$, 336 (68), 318 (100), 294 (90), 151 (25), 71 (92).

[3*R*,4*S*]-4-Hydroxy-8-methoxy-3-methyl-3,4-dihydrobenz[*a*]antracene-1,7,12(2*H*)-trione (14), Rubiginone A$_2$. To a solution of **13** (4 mg, 9.8 μmol) in methanol (0.5 mL) and THF (0.5 mL), K_2CO_3 (10 mg, 72 μmol) was added. After stirring for 90 min, the mixture was filtered through silica gel, and the solvent evaporated to give **14** (Rubiginone A_2) as a yellowish solid in 91% yield: M.p. (dec) >215 ºC (EtOAc); $[\alpha]_D^{20}$ = +78 (*c* = 0.2 in $CHCl_3$); ^{1}H NMR: δ = 8.39, (d, *J* = 8.3 Hz, 1H), 8.02 (dd, *J* = 8.3 and 1.0 Hz, 1H), 7.78 (dd, *J* = 7.7 and 1.4 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 8.3 and 1.4 Hz, 1H), 4.52 (m, 1H), 4.05 (s, 3H), 3.11 (dd, *J* = 16.6 and 5.7 Hz, 1H), 2.58 (dd, *J* = 16.6 and 10.7 Hz, 1H), 2.38 (m, 1H), 2.19 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR: δ = 197.2, 184.3, 181.5, 159.9, 150.4, 137.5, 135.6, 135.5, 134.4, 134.0, 130.4, 130.2, 120.6, 119.7, 117.3, 73.5, 56.5, 44.8, 38.3, 18.2; MS (FAB): calcd for 337.1076: found 337.1069 [*M*+1]$^+$; *m/z* (%): 337 (13) [*M*+1]$^+$, 307 (10).