Synthesis of Fused Oxabicyclic Systems by Metal-catalyzed Intramolecular Addition of 1,3-Cycloalkyldiones to Alkynes

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SUPPORTING INFORMATION

General: All dry solvents were freshly distilled under argon from the appropriate drying agent before use. THF and Et₂O were distilled from sodium/benzophenone. CH₂Cl₂ was distilled from CaH₂. All reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, or by treating the plates with a *p*-anisaldehyde or phosphomolybdic reagent followed by heating. Flash chromatography was performed on silica gel using mixtures of EtOAc/hexanes as eluent. Purification of products **4b**, **7a** and **7b** was best carried out by previously washing the silica gel with 1% Et₃N/hexanes.. Dryings were performed with anhydrous Na₂SO₄. Concentrations were carried out in a rotary evaporator. ¹H and ¹³C NMR spectra were recorded in CDCl₃, at 250 MHz and 62.9 MHz, respectively, and in some cases at 300 or 500 MHz (75.4 or 125.7 for ¹³C NMR). Carbon types were determined from DEPT ¹³C NMR experiments. The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

General procedure for the cyclizations with Pd(OAc)₂ or PtCl₂

A solution of Pd(OAc)₂ (11 mg, 0.05 mmol) or PtCl₂ (13 mg, 0.05 mmol) and the alkynyldiketone (1.0 mmol) in THF (10 mL) was stirred at rt under argon. The resulting solution was filtered over celite to remove the catalyst, the filtrate was concentrated under vacuum and the residue was purified by silica-gel flash chromatography to afford the cyclized compounds.

General procedures for the cyclizations with W(CO)₅-THF

A slurry of W(CO)₆ (176 mg, 0.50 mmol) in dry THF (5 mL) was irradiated for 4 h using high pressure 400 W mercury lamp. This 0.1 M W(CO)₅-THF solution (1 mL, 0.1 mmol) was added to a diketone (1.0 mmol) and the resulting solution was stirred at rt. The solution was filtered over celite to remove the catalyst, the filtrate was concentrated and the residue purified by silica-gel flash chromatography.

2-Methylene-3,3a,4,5-tetrahydro-2H-benzofuran-6-one (**5a**)

White solid [*R*_f = 0.64 (50 % EtOAc/hexanes), mp 55-56 °C]. ¹H NMR δ (CDCl₃): 5.55 (d, *J* = 2.0 Hz, 1H), 4.70 (t, *J* = 2.8 Hz, 1H), 4.35 (t, *J* = 2.7 Hz, 1H), 3.05 (m, 1H), 2.89 (dd, *J* = 15.3 Hz and 8.9 Hz, 1H), 2.6-2.2 (m, 4H), 1.71 (m, 1H); ¹³C NMR δ (CDCl₃): 198.8 (C), 179.8 (C), 159.8 (C), 102.2 (CH), 87.9 (CH₂), 38.6 (CH), 36.7 (CH₂), 32.7 (CH₂), 27.7 (CH₂); MS: *m/z*

151 ($[M+H]^+$, 100), 135 (8), 123 (3), 109 (4), 95 (2); HRMS: calcd. for $C_9H_{11}O_2$ 151.0759, found 151.0758.

2-Ethylidene-3-3a,4,5-tetrahydro-2H-benzofuran-6-one (5b)

Colorless oil [R_f = 0.69 (40 % EtOAc/hexanes)]. 1H NMR δ ($CDCl_3$): 5.51 (s, 1H), 4.65 (qd, J = 6.9 Hz and 2.2 Hz, 1H), 2.97 (m, 1H), 2.76 (dd, J = 14.6 and 8.6 Hz, 1H), 2.47 (d, J = 15.2 Hz, 1H), 2.5-2.1 (m, 3H), 1.8-1.5 (m, 4H); ^{13}C NMR δ ($CDCl_3$): 198.9 (C), 180.1 (C), 152.6 (C), 101.7 (CH), 98.2 (CH), 38.5 (CH), 36.6 (CH_2), 32.5 (CH_2), 27.6 (CH_2), 10.0 (CH_3); MS: m/z 165 ($[M+H]^+$, 61), 147 (2), 135 (3), 125 (2), 108 (3); HRMS: calcd. for $C_{10}H_{13}O_2$ 165.0916, found 165.0920.

Key data for assigning the structure are the observation of HMBC between C-3 and H-1', the coupling constant between H-1' and the vinylic CH_3 and the observation of NOE between H-1' and one of the hydrogens at C-3.

2-Methyl-4,4a,5,6-tetrahydrochromen-7-one (6b)

Colorless oil [R_f = 0.42 (40 % EtOAc/hexanes)]. 1H NMR δ ($CDCl_3$): 5.48 (s, 1H), 4.78 (d, J = 6.7 Hz, 1H), 2.52 (m, 1H), 2.33 (m, 1H), 2.25 (m, 1H), 2.13 (m, 2H), 1.75 (s, 3H), 1.73 (m, 1H), 1.55 (m, 1H); ^{13}C NMR δ ($CDCl_3$): 199.4 (C), 173.7 (C), 148.0 (C), 107.2 (CH), 98.3 (CH), 36.9 (CH_2), 31.6 (CH), 28.8 (CH_2), 24.7 (CH_2), 18.7 (CH_3); MS: m/z 165 ($[M+H]^+$), 147 (3), 137 (4), 125 (6), 108 (4), 99 (3); HRMS: calcd. for $C_{10}H_{13}O_2$ 165.0916, found 165.0918.

Key data for assigning the regiochemistry is the observation of HMBC between C-4a and H-3.

4a,5,7,7a-Tetrahydro-4H-cyclopenta[b]pyran-6-one (8a)

8a

Yellow solid [R_f = 0.45 (40 % EtOAc/hexanes), mp 52-53 °C]. ^1H NMR δ (CDCl_3): 6.55 (dd, J = 5.9 Hz and 3.2 Hz, 1H), 5.50 (s, 1H), 5.23 (ddd, J = 12.9 Hz, 5.9 Hz and 1.7 Hz, 1H), 2.92 (m, 1H), 2.75 (dd, J = 17.6 Hz and 6.9 Hz, 1H), 2.42 (dt, J = 16.6 Hz and 7.0 Hz, 1H), 2.10 (dd, J = 17.6 Hz and 2.2 Hz, 1H), 1.97 (m, 1H); ^{13}C NMR δ (CDCl_3): 203.8 (C), 184.7 (C), 140.8 (CH), 108.4 (CH), 104.9 (CH), 41.6 (CH_2), 32.8 (CH), 24.3 (CH_2); MS: m/z 137 ($[\text{M}+\text{H}]^+$, 100), 123 (1), 109 (1), 95.0 (1); HRMS: calcd. for $\text{C}_8\text{H}_9\text{O}_2$ 137.0602, found 137.0608.

2-Methyl-4a,5,dihydro-4H-cyclopenta[b]pyran-6-one (8b)

8b

White solid [R_f = 0.75 (60 % EtOAc/hexanes), mp 49-51 °C]. ^1H NMR δ (CDCl_3): 5.43 (d, J = 1.8 Hz, 1H), 4.91 (d, J = 6.3 Hz, 1H), 2.81 (m, 1H), 2.68 (dd, J = 6.6 Hz and 17.5 Hz, 1H), 2.33 (m, 1H), 2.06 (dd, J = 3.3 Hz and 17.5 Hz, 1H), 1.94 (m, 4H); ^{13}C NMR δ (CDCl_3): 204.2 (C), 185.7 (C), 148.8 (C), 107.6 (CH), 99.4 (CH), 41.4 (CH_2), 32.7 (CH), 24.8 (CH_2), 18.6 (CH_3); MS: m/z 151 ($[\text{M}+\text{H}]^+$, 100), 123 (7), 111 (24), 99 (11); HRMS: calcd. for $\text{C}_9\text{H}_{11}\text{O}_2$ 151.0759, found 151.0760.

Key data for assigning the regiochemistry is the observation of HMBC between C-4a and H-3.

3a-(tert-Butyldimethylsilyloxy)-2-methylene-2,3,3a,4,5,6-hexahydro-benzofuran-7-carbaldehyde (3)

3

Yellow solid [R_f = 0.52 (10 % EtOAc/hexanes)]. ^1H NMR δ (CDCl_3): 10.0 (s, 1H), 4.75 (t, J = 2.8 Hz, 1H), 4.30 (t, J = 2.9 Hz, 1H), 2.78 (d, J = 16.0 Hz, 1H), 2.52 (dt, J = 16.9 Hz and 2.5 Hz, 1H), 2.38 (dd, J = 17.0 Hz and 6.0 Hz, 1H), 2.16 (m, 2H), 1.80 (m, 2H), 1.41 (dt, J = 13.1 Hz and 4.1 Hz, 1H), 0.83 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H); ^{13}C NMR δ (CDCl_3): 189.7 (CH), 169.6 (C), 158.5 (C), 111.3 (C), 87.5 (CH_2), 75.9 (C), 41.9 (CH_2), 34.5 (CH_2), 25.6 (CH_3), 19.5

(CH₂), 18.2 (C), 16.7 (CH₂), -3.1 (CH₃), -3.4 (CH₃); MS: m/z 295 ([M+H]⁺, 20), 279 (4), 267 (4), 237 (10), 163 (54), 149 (28), 133 (36), 117 (34), 115 (57), 75 (100); HRMS: calcd. for C₁₆H₂₇O₃Si 295.1729, found 295.1733.

General procedures for hydrogenation

10 % Pd/C (9 mg, 0.01 mmol of Pd) was added to a solution of the dienolether (0.33 mmol) in EtOAc (10 mL) and the reaction mixture was stirred at rt for 30 min under H₂ pressure (balloon). The mixture was filtered over celite, the filtrate was concentrated and the residue was flash chromatographed (30 % EtOAc/hexanes) to afford the monohydrogenated derivatives.

(2*S**, 3*aR**)-2-Methyl-3,3*a*,4,5-tetrahydro-2*H*-benzofuran-6-one (9).

White solid [95 %, R_f = 0.31 (50 % EtOAc/hexanes), mp 65-66 °C]. ¹H NMR δ (CDCl₃): 5.33 (d, 1H), 4.61 (m, 1H), 2.97 (m, 1H), 2.4-2.1 (m, 4H), 1.66 (m, 1H), 1.40 (d, *J* = 6.3 Hz, 3H), 1.33 (m, 1H); ¹³C NMR δ (CDCl₃): 199.3 (C), 183.8 (C), 99.8 (CH), 82.4 (CH), 41.1 (CH), 38.3 (CH₂), 36.3 (CH₂), 27.6 (CH₂), 20.0 (CH₃); MS: m/z 153 ([M+H]⁺, 100), 139 (5), 124 (12), 95 (2); HRMS: calcd. for C₉H₁₃O₂ 153.0916, found 153.0916.

(2*S**, 3*aR**, 7*aS**)- 2-Methylhexahydrobenzofuran-6-one (10)

Colourless oil [71 %, R_f = 0.49 (60 % EtOAc/hexanes)]. ¹H NMR δ (CDCl₃): 4.17 (m, 1H), 3.81 (m, 1H), 2.51 (m, 3H), 2.20 (m, 2H), 2.16 (m, 1H), 1.94 (m, 1H), 1.67 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H); 1.22 (m, 1H); ¹³C NMR δ (CDCl₃): 210.9 (C), 76.7 (CH), 74.5 (CH), 42.9 (CH₂), 39.9 (CH₂), 36.0 (CH₂), 36.0 (CH), 97.3 (CH₂), 20.1 (CH₃). MS: m/z 155 ([M+H]⁺, 37), 139 (100), 137 (45), 121 (29), 111 (30), 97 (44), 95 (23); HRMS: calcd. for C₉H₁₅O₂ 155.1072, found 155.1077.

Procedure for tandem cyclization-hydrogenation

50 mg of diketone **4a** (50 mg, 0.33 mmol) was added to a solution of Pd/C (5 mg, 0.005 mmol of Pd) and Pd(OAc)₂ (2 mg, 3 mol %) in THF (10 mL) and the reaction mixture was stirred for 0.5 h under H₂ pressure (balloon). The mixture was filtered over celite, the filtrate was concentrated and the residue was flash chromatographed (20 % EtOAc/hexanes) to afford **9** in a 65 % of yield.

SYNTHESIS OF THE PRECURSOR ALKYNILCYCLOHEXANEDIONES

Formation of i-butylenoether derivatives of the cycloalkanediones

A mixture of 1,3-cyclohexanedione or 1,3-cyclopentanedione (44.6 mmol), p-toluenesulfonic acid monohydrate (425 mg, 2.2 mmol) and isobutyl alcohol (24 mL) in benzene (80 mL) was refluxed for 12 h and the mixture allowed to come to rt. Most of the solvent was removed under vacuum and the resulting residue was poured into brine and extracted with ether. The organic phase was dried, filtered and concentrated to give a crude residue which was purified by flash chromatography to afford the expected enones.

3-Isobutoxy-2-cyclohexenone

Yellow oil [93 %, R_f = 0.5 (100 % EtOAc)]. ¹H NMR δ (CDCl₃): 5.18 (s, 1H), 3.45 (d, J = 5.5 Hz, 2H), 2.27 (t, J = 6.4 Hz, 2H), 2.21 (t, J = 6.4 Hz, 2H), 1.85 (m, 3H), 0.83 (d, J = 6.7 Hz, 6H); ¹³C NMR δ (ppm): 199.2 (C), 177.7 (C), 102.3 (CH), 74.2 (CH₂), 36.4 (CH₂), 28.6 (CH₂), 27.3 (CH), 20.9 (CH₂), 18.7 (CH₃); MS: m/z 169 ([M+H]⁺, 100), 141 (54), 113 (88); calcd. for C₁₀H₁₇O₂ 169.1228, found 169.1221.

3-Isobutoxy-2-cyclopentenone

Yellow oil [91 %, R_f = 0.33 (40 % EtOAc/hexanes)]. ¹H NMR δ (CDCl₃): 5.17 (s, 1H), 3.63 (d, J = 6.2 Hz, 2H), 2.50 (d, 2H), 2.32 (m, 2H), 1.96 (m, 1H), 0.89 (d, J = 6.7 Hz, 6H); ¹³C NMRδ

(CDCl₃): 205.8 (C), 191.2 (C), 104.4(CH), 77.8 (CH₂), 33.7 (CH₂), 28.2 (CH₂), 27.5 (CH), 18.7 (CH₃); MS: m/z: 155 ([M+H]⁺, 45), 127 (28), 99 (100), 79 (14); HRMS: calcd. for C₉H₁₅O₂ 155.1072, found 155.1072.

Alkylation with propargyl bromide and 1-bromo-2-butyne, and hydrolysis with aqueous HCl

A solution of LDA (19.7 mL, 1 M in dry THF) was added dropwise to a solution of the enone (17.9 mmol) in THF (40 mL) cooled at -78°C . After stirring for 30 min alkynyl bromide (19.0 mmol) was added dropwise. The reaction mixture was allowed to reach slowly rt (in the case of 1-bromo-2-butyne it was necessary to keep the reaction under reflux for 6h). The resulting solution was poured into brine and the mixture was extracted thoroughly with ether. The combined extracts were dried over anhydrous magnesium sulphate and the solvent removed under vacuum to give a residue. The residue was dissolved in acetone (40 mL) and aqueous HCl (20 mL, 1M) was added. The resultant solution was vigorously stirred at rt for 8h. Most of the acetone was removed under reduced pressure and the residual material was diluted with 20 mL of brine and extracted with ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered and concentrated to give a residue which was purified by flash chromatography and in the cases of **4a** recrystallized (from ether-hexanes), to give the expected diones.

4-Prop-2-ynyl-cyclohexane-1,3-dione (**4a**)

White solid [77 %, $R_f = 0.30$ (50 % EtOAc/hexanes), mp $89-90^{\circ}\text{C}$]. ¹H NMR δ (CDCl₃): 9.45 (br s, 0.6H), 5.45 (br s, 0.6H), 3.45 (AB, $J = 17.1$ Hz, 0.8H), 2.8-1.3 (m, 8H); ¹³C NMR δ (CDCl₃): 203.6 (C), 202.7 (C), 195.5 (C), 187.8 (C), 104.8 (CH), 81.7 (CH), 81.0 (CH), 70.5 (C), 70.2 (C), 58.1 (CH₂), 48.1 (CH), 41.4 (CH), 39.8 (CH₂), 30.1 (CH), 25.8 (CH₂), 23.7 (CH₂), 19.6 (CH₂), 18.6 (CH₂); MS: m/z 151 ([M+H]⁺, 100), 133 (35), 123 (36), 109 (36), 95 (27); MS: calcd. for C₉H₁₁O₂ 151.07592, found 151.0759.

4-But-2-ynyl-cyclohexane-1,3-dione (**4b**)

White solid [59 %, $R_f = 0.87$ (40 % EtOAc/hexanes), mp $100-101^{\circ}\text{C}$]. ¹H NMR δ (CDCl₃): 9.05 (br s, 0.8H), 5.43 (s, 0.8H), 3.42 (AB, $J = 16.9$ Hz, 0.6H), 2.7-1.9 (m, 7H), 1.75 (t, $J = 2.3$ Hz,

3H); ^{13}C NMR δ (CDCl_3): 204.37 (C), 203.8 (C), 195.7 (CH), 188.8 (C), 104.6 (C), 78.2(C), 77.9 (C), 76.8 (C), 76.0 (C), 58.5 (CH_2), 48.9 (CH), 42.2 (CH), 40.1(CH_2), 30.6 (CH), 26.4 (CH_2), 24.3 (CH_2), 20.4 (CH_2), 19.4 (CH_2), 3.85 (CH_3); MS: m/z 165 ($[\text{M}+\text{H}]^+$, 100), 147 (19), 137 (32), 123 (27), 109 (16), 95 (14); HRMS: calcd. for $\text{C}_{10}\text{H}_{13}\text{O}_2$ 165.0916, found 165.0921.

4-Prop-2-ynylcyclopentane-1,3-dione (7a)

Yellow solid [49 %, R_f = 0.52 (20 % MeOH/ CH_2Cl_2)]. ^1H NMR δ (CD_3CN): 5.21 (s, 1H), 3.77 (br s, OH), 3.8-2.3 (m, 5H), 2.17 (t, J = 2.7 Hz, 1H); ^{13}C NMR δ (CD_3CN): 201.4 (C), 196.7 (C), 106.7 (CH), 82.0 (CH), 71.3 (C), 42.9 (CH), 37.0 (CH_2), 20.8 (CH_2); MS: m/z 137 ($[\text{M}+\text{H}]^+$, 56), 15 (3), 109 (22), 97 (19), 95 (17); HRMS calcd. for $\text{C}_8\text{H}_9\text{O}_2$ 137.0603, found 137.0604.

4-But-2-ynylcyclopentane-1,3-dione (7b)

Orange solid [42 %, R_f = 0.45 (20 % MeOH/ CH_2Cl_2), mp 135-138 $^\circ\text{C}$]. ^1H NMR δ (acetone- D_6): 6.08 (br s, OH), 5.15 (s, 0.9H), 3.89 (m, 0.2H), 2.8-2.2 (m, 5H), 1.74 (d, J = 2.5 Hz, 3H); ^{13}C NMR δ (CDCl_3): 200.9 (C), 196.4 (C), 107.3 (CH), 78.3 (C), 77.2 (C), 44.1 (CH), 38.0 (CH_2), 22.0 (CH_2), 4.2 (CH_3); MS: m/z 151 ($[\text{M}+\text{H}]^+$, 100), 135 (31), 123 (20), 109 (35), 95 (11); HRMS: calcd. for $\text{C}_9\text{H}_{11}\text{O}_2$ 151.0759, found 151.0760.

2-(*tert*-Butyldimethylsilyloxy)-2-cyclohexenone

TBSCl (1.55 g, 10.3 mmol) and imidazole (1.30 g, 19.6 mmol) were consecutively added to a solution of 1,2-cyclohexanedione (1.10 g, 9.8 mmol) in CH_2Cl_2 (35 mL). The reaction mixture was stirred overnight at rt, poured in 3% aqueous HCl solution and extracted with Et_2O . The combined extracts dried over anhydrous magnesium sulfate, and concentrated, and the crude was flash chromatographed (1-2 % EtOAc/hexanes) to afford 2.212 g [95 %, R_f = 0.65 (10 % EtOAc/hexanes), colourless oil]. ^1H -RMN δ (CDCl_3): 6.11 (t, J = 4.6 Hz, 1H), 2.43-2.19 (m, 4H), 1.9 (m, 2H), 0.88 (s, 9H), 0.08 (s, 6H); ^{13}C NMR δ (CDCl_3): 195.4 (C), 147.9 (C), 127.5 (CH), 38.6 (CH_2), 25.6 (CH_3), 24.7 (CH_2), 23.1 (CH_2), 18.3 (C), -4.8 (CH_3); MS: m/z 169 [$\text{M}^+ - \text{C}(\text{CH}_3)_3$, 100], 139 (11), 111 (6), 95 (4); HRMS: calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{Si}$ 227.1467, found 227.1467.

2-(*tert*-Butyldimethylsilyloxy)-1-prop-2'-ynyl-2-cyclohexene

A propargyl magnesium solution in ether (3.2 mL, 5 M, 16.5 mmol) was added to a solution of ketone (1.70 g, 7.52 mmol) in THF (30 mL) cooled at 0 °C. After stirring for 1 h, the mixture was poured into 3 % aqueous HCl solution and extracted with Et₂O. The combined extracts were dried over anhydrous magnesium sulfate, were concentrated and the crude was purified by flash chromatography on SiO₂ (1-2 % EtOAc/hexanes) to afford 1.560 g of alcohol [78 %, R_f = 0.6 (10 % EtOAc/hexanes), colourless oil]. ¹H NMR δ (CDCl₃): 4.84 (t, *J* = 4.0 Hz, 1H), 2.53 (m, 2H), 2.26 (s, 1H), 2.1-1.9 (m, 7H), 0.91 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ¹³C NMR δ (CDCl₃): 150.7 (C), 104.8 (CH), 80.7 (C), 71.4 (CH), 70.6 (C), 34.6 (CH₂), 29.7 (CH₂), 25.7 (CH₃), 24.2 (CH₂), 19.1 (CH₂), 18.8 (C), -4.6 (CH₃) -4.8 (CH₃); MS: *m/z* 266 (M⁺, 6), 249 (88), 227 (27), 211 (55), 209 (100), 191 (9), 169 (24), 135 (26); HRMS: calcd. for C₁₅H₂₆O₂Si 266.1702, found 266.1697.

2-(*tert*-Butyldimethylsilyloxy)-2-prop-2'-ynylcyclohexanone

K₂CO₃ (aprox. 30 mg) was added to a solution of the previous alcohol (1.10 g, 4.13 mmol) in MeOH (20 mL) and the resulting solution was stirred at rt for 12 h. Then was poured into brine, extracted with Et₂O, dried, filtered and concentrated. The crude residue was flash chromatographed on silica (1-2 % EtOAc/hexanes) to afford 1.088 g of ketone [99 %, R_f = 0.70 (5 % EtOAc/hexanes), colourless oil]. ¹H NMR δ (CDCl₃): 2.70 (m, 1H), 2.53 (m, 2H), 2.25 (m, 1H), 2.11 (m, 1H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.95-1.5 (m, 4H), 0.86 (s, 9H), 0.13 (s, 3H), -0.02 (s, 3H); ¹³C NMR δ (CDCl₃): 209.7 (C), 80.0 (C), 79.2 (C), 71.6 (CH), 39.6 (CH₂), 38.5 (CH₂), 27.6 (CH₂), 27.4 (CH₂), 25.8 (CH₃), 21.0 (CH₂), 18.4 (C), -2.5 (CH₃), -3.5 (CH₃); MS: *m/z* 266 (M⁺, 3), 249 (3), 227 (6), 211 (29), 209 (47), 169 (100), 142 (27); HRMS: calcd. for C₁₅H₂₆O₂Si 266.1702, found 266.1697.

2-(*tert*-Butyldimethylsilyloxy)-6-hydroxymethylene-2-prop-2'-ynylcyclohexanone (1)

NaH (105 mg, 2.64 mmol) was added a solution of the previous ketone (640 mg, 2.40 mmol) in Et₂O. After stirring for 1 h, ethyl formiate (0.23 mL, 2.88 mmol) and MeOH (catalytic) were successively added. The mixture was stirred for 24 h and then poured into aqueous 3 % HCl and extracted with ether. The combined extracts were dried over anhydrous magnesium sulfate, concentrated and the crude was purified by flash chromatography (2-3 % EtOAc/hexanes) to afford 364 mg of the dicarbonylic compound [51 %, R_f= 0.65 (5 % EtOAc/hexanes), colourless oil]. ¹H NMR δ (CDCl₃): 14.20 (s, OH), 8.82 (s, 1H), 2.8-1.2 (m, 9H), 0.83 (m, 9H), 0.15 (s, 3H), 0.00 (s, 3H); ¹³C NMR δ (CDCl₃): 190.4 (CH), 109.5 (C), 102.3 (C), 80.4 (C), 74.3 (C), 71.3 (CH), 40.1 (C), 35.8 (CH₂), 29.4 (CH₂), 26.0 (CH₃), 24.0 (CH₂), 18.9 (CH₂), 18.8 (C), -2.88 (CH₃), -2.93 (CH₃); MS: m/z 295 (M⁺,6), 279 (25), 255 (20), 237 (32), 191 (14), 177 (9), 163 (87), 133 (47), 117 (52), 115 (59); HRMS: calcd. for C₁₆H₂₇O₃Si 295.1729, found 295.1733.