

Efficient non-catalytic synthesis of substituted 2,3,4,9-tetrahydro-1*H*-xanthen-1-ones from salicylaldehydes and dimedone

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9-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (1a)

White solid; yield 1.65 g (90%); mp 209–211 °C (lit.¹ mp 210–212 °C); ¹H NMR (300 MHz, CDCl₃): δ 1.00 (s, 6H, 2CH₃), 1.04 (s, 3H, CH₃), 1.14 (s, 3H, CH₃), 1.94 (d, *J* = 16.5 Hz, 1H, CH₂), 2.01 (d, *J* = 16.5 Hz, 1H, CH₂), 2.34 (s, 2H, CH₂), 2.38 (s, 2H, CH₂), 2.49 (d, *J* = 17.7 Hz, 1H, CH₂), 2.61 (d, *J* = 17.7 Hz, 1H, CH₂), 4.68 (s, 1H, CH), 7.01-7.04 (m, 3H, Ar), 7.14-7.20 (m, 1H, Ar), 10.46 ppm (br s, 1H, OH).

9-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3,7-trimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (1b)

White solid; yield 1.73 g (91%); mp 213–214 °C (lit. mp² 218–219 °C); δ_H (300 MHz) 1.00 (s, 3H, CH₃), 1.01 (s, 3H, CH₃), 1.03 (s, 3H, CH₃), 1.12 (s, 3H, CH₃), 1.92-2.04 (m, 2H, CH₂), 2.33-2.38 (m, 3H, CH₂+CH₂), 2.24 (s, 3H, CH₃), 2.42 (d, *J* = 18.0 Hz, 1H, CH₂), 2.47 (d, *J* = 17.6 Hz, 1H, CH₂), 2.60 (d, *J* = 17.6 Hz, 1H, CH₂), 4.63 (s, 1H, CH), 6.81 (s, 1H, Ar), 6.90-6.97 (m, 2H, Ar), 10.49 (br s, 1H, OH).

7-Bromo-9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (1c)

Light orange solid; 2.07 g (93%); mp 250–252 °C (lit.¹ mp 251–253 °C); ¹H NMR (300 MHz, CDCl₃): δ 1.00 (s, 3H, CH₃), 1.03 (s, 6H, 2CH₃), 1.14 (s, 3H, CH₃), 1.99 (s, 2H, CH₂), 2.34 (s, 2H, CH₂), 2.36 (d, *J* = 18.1 Hz, 1H, CH₂), 2.44 (d, *J* = 18.1 Hz, 1H, CH₂), 2.48 (d, *J* = 17.7 Hz, 1H, CH₂), 2.59 (d, *J* = 17.7 Hz, 1H, CH₂), 4.62 (s, 1H, CH), 6.92 (d, *J* = 8.6 Hz, 1H, Ar), 7.14 (d, *J* = 1.9 Hz, 1H, Ar), 7.26 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.9 Hz, 1H, Ar), 10.38 ppm (br s, 1H, OH).

9-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-3,3-dimethyl-7-nitro-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (1d)

Light yellow solid; yield 1.83 g (89%) ; mp 203–205 °C (lit.¹ mp 203–205 °C °C); ¹H NMR (300 MHz, CDCl₃): δ 1.00 (s, 6H, 2CH₃), 1.04 (s, 3H, CH₃), 1.15 (s, 3H, CH₃), 1.95 (d, *J* = 16.5 Hz, 1H, CH₂), 2.02 (d, *J* = 16.5 Hz, 1H, CH₂), 2.34-2.40 (m, 3H, CH₂+CH₂), 2.47 (d, *J* = 18.0 Hz, 1H, CH₂), 2.52 (d, *J* = 17.8 Hz, 1H, CH₂), 2.62 (d, *J* = 17.8 Hz, 1H, CH₂), 4.71 (s, 1H, CH), 7.13 (d, *J* = 8.9 Hz, 1H, Ar), 7.95 (d, *J* = 2.5 Hz, 1H, Ar), 8.05 (dd, *J*₁ = 2.5 Hz, *J*₂ = 8.9 Hz, 1H, Ar), 10.32 ppm (br s, 1H, OH).

9-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-5-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1H-xanthen-1-one (1e)

White solid; yield 1.88 g (95%); mp 233–235 °C (lit.¹ mp 229–231 °C); ¹H NMR (300 MHz, CDCl₃): δ 1.00 (s, 6H, 2CH₃), 1.04 (s, 3H, CH₃), 1.13 (s, 3H, CH₃), 1.95 (d, *J* = 16.6 Hz, 1H, CH₂), 2.01 (d, *J* = 16.6 Hz, 1H, CH₂), 2.34 (s, 2H, CH₂), 2.38 (s, 2H, CH₂), 2.56 (d, *J* = 17.7 Hz, 1H, CH₂), 2.69 (d, *J* = 17.7 Hz, 1H, CH₂), 3.90 (s, 3H, OCH₃), 4.67 (s, 1H, CH), 6.60 (d, *J* = 7.6 Hz, 1H, Ar), 6.77 (d, *J* = 7.9 Hz, 1H, Ar), 6.95 (t, *J* = 7.9 Hz, 1H, Ar), 10.42 ppm (br s, 1H, OH).

7-Bromo-9-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-5-methoxy-3,3-dimethyl-2,3,4,9-tetrahydro-1H-xanthen-1-one (1f)

White solid; yield 2.09 g (88%); mp 256–257 °C; HRMS (ESI) 475.1107 [M+H]⁺, calcd for C₂₄H₂₈BrO₅: 475.1115; IR (KBr): ν = 3423, 3188, 2954, 1627, 1606, 1577, 1377, 1266, 1229, 1107 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.00 (s, 3H, CH₃), 1.03 (s, 6H, CH₃), 1.13 (s, 3H, CH₃), 2.00 (s, 2H, CH₂), 2.33 (s, 2H, CH₂), 2.36 (d, *J* = 18.1 Hz, 1H, CH₂), 2.43 (d, *J* = 18.1 Hz, 1H, CH₂), 2.54 (d, *J* = 17.7 Hz, 1H, CH₂), 2.66 (d, *J* = 17.7 Hz, 1H, CH₂), 3.88 (s, 3H, OCH₃), 4.60 (s, 1H, CH), 6.75 (s, 1H, Ar), 6.87 (s, 1H, Ar), 10.34 ppm (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃): δ 26.7, 27.1, 27.8, 29.2, 29.8, 31.1, 32.4, 41.5, 43.3, 50.0, 50.8, 56.4, 110.8, 113.9, 116.6, 117.8, 122.5, 126.9, 140.0, 147.9, 168.5, 171.2, 196.7, 200.8 ppm.

12-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (1g)

Light yellow solid; yield 1.78 g (85%); mp 239–241 °C (lit. mp² 240–242 °C); δ_H (300 MHz) 0.72 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 1.07 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 1.82 (d, *J* = 16.5 Hz, 1H, CH₂), 1.96 (d, *J* = 16.5 Hz, 1H, CH₂), 2.40 (s, 4H, CH₂), 2.56 (d, *J* = 17.6 Hz, 1H, CH₂), 2.68 (d, *J* = 17.6 Hz, 1H, CH₂), 5.27 (s, 1H, CH), 7.27 (d, *J* = 8.8 Hz, 1H, Ar), 7.38 (t, *J* = 7.4 Hz, 1H, Ar), 7.44–7.49 (m, 1H, Ar), 7.72 (d, *J* = 8.7 Hz, 2H, Ar), 7.78 (d, *J* = 8.1 Hz, 1H, Ar), 10.66 (s, 1H, OH).

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2. X.-S. Wang, D.-Q. Shi, Y.-L. Li, H. Chen, X.-Y. Wei and Z.-M. Zong, *Synth. Commun.*, 2005, **35**, 97.