Supporting Information

Influence of Michael Acceptor Stereochemistry on Intramolecular Morita-Baylis-Hillman Reactions

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General Methods. ¹H and ¹³C NMR spectra were recorded on a 300 MHz spectrometer in CDCl₃ with tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded using the EI method. Tetrahydrofuran and toluene were distilled from Na/benzophenone under an Ar atmosphere. Acetonitrile and 1,2-dichloroethane were distilled from CaH₂ under an Ar atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC analysis using GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

Representative reports of intermolecular MBH reactions where cycloalkenenones were used as the Michael acceptor: (a) Kataoka, T.; Iwama, T.; Tsujiyama, S.-I.; Iwamura, T.; Watanabe, S.-I. *Tetrahedron* **1998**, *54*, 11813-11824. (b) Kataoka, T.; Iwama, T.; Tsujiyama, S.-I. *Chem. Commun.* **1998**, 197-198. (c) Rezgui, F.; El Gaied, M. M. *Tetrahedron Lett.* **1998**, *39*, 5965-5966. (d) Kawamura, M.; Kobayashi, S. *Tetrahedron Lett.* **1999**, *40*, 1539-1542. (e) Aggarwal, V. K.; Mereu, A. *Chem. Commun.* **1999**, 2311-2312. (f) Li, G.; Wei, H.-X.; Gao, J. J.; Caputo, T. D. *Tetrahedron Lett.* **2000**, *41*, 1-5. (g) Yamada, Y. M. A.; Ikegami, S. *Tetrahedron Lett.* **2000**, *41*, 2165-2169. (h) Iwamura, T.; Fujita, M.; Kawakita, T.; Kinoshita, S.; Watanabe, S.-I.; Kataoka, T. *Tetrahedron* **2001**, *57*, 8455-8462. (i) Bauer, T.; Tarasuik, J. *Tetrahedron: Asymmetry* **2001**, *12*, 1741-1745. (j) Jauch, J. *J. Org. Chem.* **2001**, *66*, 609-611. (k) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295-4298. (l) Pei, W.; Wei, H.-X.; Li, G. *Chem. Commun.* **2002**, 2412-2413. (m) Patra, A.; Batra, S.; Joshi, B. S.; Roy, R.; Kundu, B.; Bhaduri, A. P. *J. Org. Chem.* **2002**, *67*, 5783-5788. (n) Franck, X.; Figadère, B. *Tetrahedron Lett.* **2002**, *43*, 1449-1451. (o) Luo, S.; Zhang, B.; He, J.; Janczuk, A.; Wang, P. G.; Cheng, J.-P. *Tetrahedron Lett.* **2002**, *43*, 7369-7371. (p) Gatri, R.; El Gaied, M. M. *Tetrahedron Lett.* **2002**, *43*, 7835-7836. (q) McDougal, N. T.; Schaus, S. E. *J. Am. Chem. Soc.* **2003**, *125*, 12094-12095. (r) McDougal, N. T.; Trevellini, W. L.; Rodgen, S. A.; Kliman, L. T.; Schaus, S. E. *Adv. Synth. Catal.* **2004**, *346*, 1231-1240.

6-Acetoxy-2-cyclohexene-1-one (5).¹ To a stirred solution of 2-cyclohexene-1-one (3.06 g, 30.00 mmol) in toluene (60 mL) was added Pb(OAc)₄ (28.00 g, 60.00 mmol). The mixture was then heated to reflux for 4 h, and cooled to room temperature. The resulting mixture was diluted with ether, washed with 1 M HCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford **5** (2.31 g, 15.00 mmol) in 50% yield.

Typical reaction procedure for nucleophilic 1,2-addition to 5: 2-ethyl-3-cyclohexene-1,2-diol (6a).¹ To a stirred solution of **5** (2.44 g, 15.84 mmol) in THF (30 mL) was added 1 M THF solution of EtMgBr (50 mL, 47.53 mmol) at 0 °C. The mixture was stirred at that temperature for 0.5 h and then stirred at room temperature for 0.5 h. It was then quenched by the addition of a saturated aq solution of NH₄Cl (40 mL). The resulting mixture was stirred for 1 h more, diluted with ethyl acetate, wash with saturated aq NaCl solution, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford diol **6a** (1.079 g, 7.60 mmol) in 48 % yield as a mixture of diastereoisomers.

Table 1. Synthesis of intramolecular MBH reaction substrates.

$\text{6a-f} \xrightarrow{\text{Pb(OAc)}_4} \text{1a-f} + \text{2a-f}$

Entry	Compounds	1:2	Combined yield (%) ^a
1	1a + 2a , R = -Et	4.1:1	53
2	1b + 2b , R = -Bu	8.8:1	40
3	1c + 2c , R = -Ph	4.8:1	57
4	1d + 2d , R = -C ₆ H ₄ -4-Cl	1.9:1	39
5	1e + 2e , R = -C ₆ H ₄ -3-Me	9.7:1	66
6	1f + 2f , R = -C ₆ H ₄ -4-Me	6.7:1	57

^a Isolated yield.

Typical reaction procedure for oxidative cleavage reactions: (*Z*)-6-oxo-4-octenal (1a**) and (*E*)-6-oxo-4-octenal (**2a**).**¹ To a stirred solution of **6a** (253 mg, 1.78 mmol) in MeCN (20 mL) was added Pb(OAc)₄ (830 mg, 1.78 mmol). The reaction mixture was stirred at room temperature for 15 min, diluted with ethyl acetate, washed with 1 M aq HCl solution, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford **1a** (106 mg, 0.76 mmol) in 42% yield and **2a** (26 mg, 0.19 mmol) in 10% yield. These dicarbonyl compounds were found to be relatively unstable and had to be used in the intramolecular MBH reactions soon after preparation.

Typical reaction procedure for the intramolecular Morita-Baylis-Hillman reactions:

1-(5-hydroxy-1-cyclopentenyl)-1-propanone (3a).¹ To a stirred solution of **1a** (105 mg, 0.75 mmol) in *t*-BuOH (7.5 mL) was added PPh₃ (197 mg, 0.75 mmol) at 40 °C. The mixture was stirred at that temperature for 60 h, diluted with ethyl acetate, washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford **3a** (76 mg, 0.54 mmol) in 72% yield.

Table 2. Intramolecular MBH reaction results using PBu₃ as the catalyst.

Entry	Substrate	Solvent	Conc.	Temp.	Time	Product	Yield (%) ^a
3	1a , R = -Et	<i>t</i> -BuOH	0.1 M	40 °C	48 h	3a	17
4	2a , R = -Et	<i>t</i> -BuOH	0.1 M	40 °C	48 h	3a	0
11	1c , R = -Ph	CH ₃ CN	0.1 M	rt	12 h	3c	27
12	2c , R = -Ph	CH ₃ CN	0.1 M	rt	12 h	3c	0

^a Isolated yield.

(Z)-6-Oxo-4-octenal (1a).¹ Yellow oil; IR (CH₂Cl₂): ν 3448, 2973, 2938, 2728, 1748, 1697, 1631, 1374, 1074, 982, 817 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.08 (3H, t, J = 7.4 Hz, CH₃), 2.51 (2H, q, J = 7.2 Hz, CH₂), 2.63 (2H, t, J = 7.2 Hz, CH₂), 2.92 (2H, q, J = 7.2 Hz, CH₂), 6.09 (1H, dt, J_d = 11.1 Hz, J_t = 7.5 Hz, CH), 6.21 (1H, t, J = 11.4 Hz, CH), 9.78 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 7.5, 22.0, 37.1, 42.8, 127.1, 145.0, 201.3, 201.8; MS (EI) m/z (%): 140 (1.2) [M⁺], 111 (14.5), 83 (25.2), 66 (100), 57 (30.2); HRMS (EI) calcd. for C₈H₁₂O₂ (M⁺) requires 140.0837, found 140.0818.

(Z)-6-Oxo-4-decenal (1b).¹ Yellow oil; IR (CH₂Cl₂): ν 3431, 2958, 2932, 2724, 1725, 1691, 1618, 1412, 1379, 1062, 980, 751 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.91 (3H, t, J = 7.2 Hz, CH₃), 1.25-1.37 (2H, m, CH₂), 1.53-1.63 (2H, m, CH₂), 2.44-2.50 (2H, m, CH₂), 2.60-2.67 (2H, m, CH₂), 2.90 (2H, q, J = 7.2 Hz, CH₂), 6.08 (1H, dt, J_d = 11.4 Hz, J_t = 7.4 Hz, CH), 6.20 (1H, t, J = 11.1 Hz, CH), 9.78 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.8, 22.1, 22.2, 25.9, 43.0, 43.8, 127.5, 145.1, 201.3, 201.7; MS (EI) m/z (%): 168 (0.9) [M⁺], 139 (9.5), 93 (13.2), 85 (20.7), 66 (100), 57 (29.6); HRMS (EI) calcd. for C₁₀H₁₆O₂ (M⁺) requires 168.1150, found: 168.1131.

1b

1b

1c

(Z)-6-Oxo-6-phenyl-4-hexenal (1c).¹ Yellow oil; IR (CH₂Cl₂): ν 3426, 3060, 2897, 2826, 2726, 1722, 1664, 1611, 1448, 1007, 739, 691 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.66 (2H, t, J = 6.9 Hz, CH₂), 2.92 (2H, q, J = 7.4 Hz, CH₂), 6.34 (1H, dt, J_d = 11.4 Hz, J_t = 7.5 Hz, CH), 6.87 (1H, dt, J_d = 11.4 Hz, J_t = 1.8 Hz, CH), 7.42-7.58 (3H, m, ArH), 7.91-7.94 (2H, m, ArH), 9.79 (1H, t, J = 1.4 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 22.4, 42.9, 125.1, 128.1, 128.4, 132.7, 138.0, 146.4, 191.4, 201.2; MS (EI) m/z (%): 188 (2.3) [M⁺], 170 (15.3), 159 (34.3), 105 (100), 77 (81.2), 66 (33.5); HRMS (EI) calcd. for C₁₂H₁₂O₂ (M⁺) requires 188.0837, found: 188.0843.

1c

1c

1d

(Z)-6-(4-Chlorophenyl)-6-oxo-4-hexenal (1d). Yellow oil; IR (CH₂Cl₂): ν 3460, 3063, 2932, 2853, 2726, 1725, 1668, 1490, 1401, 1092, 1010, 828, 530 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.69 (2H, t, J = 6.6 Hz, CH₂), 2.93 (2H, ddd, J_d = 1.2 Hz, J_d = 7.2 Hz, J_d = 13.7 Hz, CH₂), 6.38 (1H, dt, J_d = 11.4 Hz, J_t = 7.5 Hz, CH), 6.83 (1H, dt, J_d = 11.7 Hz, J_t = 1.5 Hz, CH), 7.42-7.46 (2H, m, ArH), 7.85-7.90 (2H, m, ArH), 9.81 (1H, t, J = 1.4 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 22.6, 43.0, 124.8, 128.9, 129.7, 136.5, 139.3, 147.3, 190.3, 201.2; MS (EI) m/z (%): 222 (0.7) [M⁺], 204 (3.5), 141 (26.5), 139 (100), 111 (26.9), 75 (8.3); HRMS (EI) calcd. for C₁₂H₁₁O₂Cl (M⁺) requires 222.0448, found: 222.0447.

1d

1d

1e

(Z)-6-Oxo-6-m-tolyl-4-hexenal (1e). Yellow oil; IR (CH₂Cl₂): ν 3424, 3056, 2924, 2832, 2727, 1724, 1666, 1613, 1437, 1051, 1022, 767, 613 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.39 (3H, s, CH₃), 2.65 (2H, t, $J = 6.8$ Hz, CH₂), 2.91 (2H, ddd, $J_d = 1.5$ Hz, $J_d = 7.5$ Hz, $J_d = 14.7$ Hz, CH₂), 6.32 (1H, dt, $J_d = 11.7$ Hz, $J_t = 7.5$ Hz, CH), 6.86 (1H, dt, $J_d = 11.6$ Hz, $J_t = 1.5$ Hz, CH), 7.30-7.35 (2H, m, ArH), 7.70-7.74 (2H, m, ArH), 9.78 (1H, t, $J = 1.4$ Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.1, 22.4, 42.9, **125.3**, **125.3**, 128.3, 128.6, 133.5, 138.0, 138.2, 146.1, 191.6, 201.2; MS (EI) m/z (%): 202 (1.5) [M⁺], 184 (10.1), 119 (100), 91 (80.8), 65 (27.8); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0991.

(Z)-6-Oxo-6-p-tolyl-4-hexenal (1f). Yellow oil; IR (CH₂Cl₂): ν 3428, 3031, 2923, 2827, 2727, 1723, 1662, 1608, 1422, 1181, 1010, 778 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.39 (3H, s, CH₃), 2.65 (2H, dt, J_d = 1.5 Hz, J_t = 7.1 Hz, CH₂), 2.90 (2H, ddd, J_d = 2.0 Hz, J_d = 7.1 Hz, J_d = 15.0 Hz, CH), 6.30 (1H, dt, J_d = 11.7 Hz, J_t = 7.7 Hz, CH), 6.85 (1H, dt, J_d = 11.7 Hz, J_t = 7.5 Hz, CH), 7.23-7.26 (2H, m, ArH), 7.81-7.85 (2H, m, ArH), 9.77 (1H, t, J = 1.5 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.4, 22.3, 42.9, 125.2, 128.2, 129.1, 135.4, 143.5, 145.8, 191.1, 201.3; MS (EI) m/z (%): 202 (1.2) [M⁺], 173 (12.1), 119 (100), 91 (53.1), 65 (16.1); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0997.

(E)-6-Oxo-4-octenal (2a).¹ Yellow oil; IR (CH₂Cl₂): ν 3429, 2974, 2937, 2726, 1724, 1693, 1622, 1459, 1413, 1379, 1121, 1040, 980, 816 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.09 (3H, t, J = 7.2 Hz, CH₃), 2.53-2.60 (4H, m, CH₂), 2.64-2.70 (2H, m, CH₂), 6.12 (1H, dt, J_d = 15.4 Hz, J_t = 1.5 Hz, CH), 6.82 (1H, dt, J_d = 15.9 Hz, J_t = 6.6 Hz, CH), 9.81 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 7.9, 24.5, 33.3, 41.8, 130.6, 143.9, 200.3, 200.6; MS (EI) m/z (%): 140 (2.5) [M⁺], 111 (57.3), 83 (85.2), 57 (20.5), 55 (100); HRMS (EI) calcd. for C₈H₁₂O₂ (M⁺) requires 140.0837, found: 140.0851.

2a

2a

(E)-6-Oxo-4-decenal (2b).¹ Yellow oil; IR (CH₂Cl₂): ν 3448, 2932, 2871, 2727, 1728, 1655, 1629, 1458, 1374, 1045, 748, 606 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.91 (3H, t, J = 7.4 Hz, CH₃), 1.26-1.39 (4H, m, CH₂), 1.53-1.63 (2H, m, CH₂), 2.50-2.57 (2H, m, CH₂), 2.61-2.69 (2H, m, CH₂), 6.13 (1H, d, J = 15.9 Hz, CH), 6.81 (1H, dt, J_d = 15.0 Hz, J_t = 6.9 Hz, CH), 9.80 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.8, 22.3, 24.5, 26.1, 40.0, 41.8, 130.9, 144.0, 200.3, 200.4; MS (EI) m/z (%): 168 (1.6) [M⁺], 143 (9.5), 129 (26.1), 109 (27.7), 69 (46.8), 55 (100), 41 (62.6); HRMS (EI) calcd. for C₁₀H₁₆O₂ (M⁺) requires 168.1150, found: 168.1127.

2b

2b

(E)-6-Oxo-6-phenyl-4-hexenal (2c).¹ Yellow oil; IR (CH₂Cl₂): ν 3426, 3060, 2925, 2854, 2727, 1723, 1668, 1620, 1448, 1005, 977, 742, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.60-2.74 (4H, m, CH₂), 6.93 (1H, d, J = 15.6 Hz, CH), 7.01 (1H, dt, J_d = 15.3 Hz, J_t = 5.9 Hz, CH), 7.45-7.59 (3H, m, ArH), 7.90-7.93 (2H, m, ArH), 9.82 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 24.9, 41.9, 126.7, 128.5, 128.5, 132.8, 137.6, 146.7, 190.4, 200.4; MS (EI) m/z (%): 188 (1.6) [M⁺], 159 (28.6), 105 (100), 77 (41.5), 55 (10.1); HRMS (EI) calcd. for C₁₂H₁₂O₂ (M⁺) requires 188.0837, found: 188.0839.

(E)-6-(4-Chlorophenyl)-6-oxo-4-hexenal (2d). Yellow oil; IR (CH₂Cl₂): ν 3475, 3034, 2936, 2875, 1748, 1695, 1618, 1428, 1373, 1074, 1042, 919, 816, 747 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.61-2.75 (4H, m, CH₂), 6.89 (1H, dt, $J_d = 15.3$ Hz, $J_t = 1.2$ Hz, CH), 7.03 (1H, dt, $J_d = 15.6$ Hz, $J_t = 6.5$ Hz, CH), 7.42-7.47 (2H, m, ArH), 7.84-7.89 (2H, m, ArH), 9.83 (1H, t, $J = 1.1$ Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 25.0, 41.9, 126.3, 128.8, 129.9, 135.9, 139.2, 147.2, 189.0, 200.3; MS (EI) m/z (%): 222 (16.9) [M⁺], 193 (35.3), 180 (12.1), 138 (100), 111 (25.5); HRMS (EI) calcd. for C₁₂H₁₁O₂Cl (M⁺) requires 222.0448, found: 222.0444.

2d

2d

2e

(E)-6-Oxo-6-m-tolyl-4-hexenal (2e). Yellow oil; IR (CH₂Cl₂): ν 3450, 2925, 2875, 2720, 1721, 1668, 1622, 1429, 1054, 1009, 781 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.41 (3H, s, CH₃), 2.59-2.80 (4H, m, CH₂), 6.88-7.05 (2H, m, CH), 7.25-7.36 (3H, m, ArH), 7.69-7.73 (1H, m, ArH), 9.81 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.3, 24.9, 41.9, 125.4, 125.7, 128.3, 129.0, 133.6, 137.6, 138.3, 146.5, 190.6, 200.4; MS (EI) m/z (%): 202 (2.1) [M⁺], 173 (9.0), 119 (100), 91 (36.2), 65 (8.9); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0995.

2e

2e

2f

(E)-6-Oxo-6-p-tolyl-4-hexenal (2f). Yellow oil; IR (CH₂Cl₂): ν 3428, 3031, 2922, 2828, 2726, 1724, 1669, 1621, 1571, 1410, 1181, 1042, 977, 810, 726 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.41 (3H, s, CH₃), 2.60-2.73 (4H, m, CH₂), 6.92 (1H, d, J = 15.3 Hz, CH), 6.96-7.04 (1H, m, CH), 7.21-7.28 (2H, m, ArH), 7.82-7.97 (2H, m, ArH), 9.82 (1H, t, J = 1.5 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.5, 24.9, 41.9, 126.6, 128.6, 129.2, 134.9, 143.6, 146.1, 189.9, 200.5; MS (EI) m/z (%): 202 (3.0) [M⁺], 173 (21.8), 119 (100), 91 (32.6), 65 (9.5); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.1005.

2f

2f

Year	Number of People (Millions)
1960	58.70
1961	59.50
1962	60.30
1963	61.10
1964	61.90
1965	62.70
1966	63.50
1967	64.30
1968	65.10
1969	65.90
1970	66.70
1971	67.50
1972	68.30
1973	69.10
1974	69.90
1975	70.70
1976	71.50
1977	72.30
1978	73.10
1979	73.90
1980	74.70
1981	75.50
1982	76.30
1983	77.10
1984	77.90
1985	78.70
1986	79.50
1987	80.30
1988	81.10
1989	81.90
1990	82.70

3a

3a

3b

1-(5-Hydroxy-1-cyclopentenyl)pentanone (3b).¹ Yellow oil; IR (CH₂Cl₂): ν 3487, 3055, 2933, 2871, 1659, 1619, 1455, 1380, 1055, 982, 739 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.92 (3H, t, J = 7.4 Hz, CH₃), 1.26-1.41 (2H, m, CH₂), 1.56-1.66 (2H, m, CH₂), 1.77-1.88 (1H, m, CH₂), 2.24-2.51 (2H, m, CH₂), 2.66-2.71 (3H, m, CH₂), 3.40 (1H, s, OH), 5.12 (1H, br s, CH), 6.87 (1H, t, J = 2.1 Hz, CH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.6, 22.1, 26.2, 30.8, 31.3, 38.5, 75.1, 145.4, 145.6, 200.4; MS (EI) m/z (%): 168 (0.6) [M⁺], 150 (13.0), 126 (15.7), 111 (100), 83 (48.7), 55 (30.2); HRMS (EI) calcd. for C₁₀H₁₆O₂ (M⁺) requires 168.1150, found: 168.1130.

3b

3b

3c

(5-Hydroxy-1-cyclopentenyl)-phenyl-methanone (3c).¹ Yellow oil; IR (CH₂Cl₂): ν 3441, 3059, 2937, 1641, 1598, 1446, 1352, 1053, 931, 724, 697 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.90-2.00 (1H, m, CH₂), 2.32-2.60 (2H, m, CH₂), 2.71-2.85 (1H, m, CH₂), 3.35 (1H, s, OH), 5.30 (1H, br s, CH), 6.72 (1H, t, J = 2.6 Hz, CH), 7.43-7.60 (3H, m, ArH), 7.75-7.78 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 31.3, 31.5, 76.1, 128.1, 128.7, 132.2, 137.9, 144.4, 148.9, 194.5; MS (EI) m/z (%): 188 (65.8) [M⁺], 170 (26.1), 128 (45.0), 105 (92.3), 83 (100), 77 (81.8); HRMS (EI) calcd. for C₁₂H₁₂O₂ (M⁺) requires 188.0837, found: 188.0842.

3c

3c

3d

(5-Hydroxy-1-cyclopentenyl)-4-chlorophenyl-methanone (3d).² Yellow oil; IR (CH₂Cl₂): ν 3443, 3056, 2930, 1639, 1586, 1486, 1400, 1347, 1175, 1014, 931, 839, 695 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.89-1.99 (1H, m, CH₂), 2.30-2.42 (1H, m, CH₂), 2.47-2.59 (1H, m, CH₂), 2.72-2.84 (1H, m, CH₂), 3.43 (1H, s, OH), 5.28 (1H, br s, CH), 6.68 (1H, t, J = 2.6 Hz, CH), 7.40-7.45 (2H, m, ArH), 7.70-7.74 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 31.3, 31.7, 76.3, 128.6, 130.2, 136.3, 138.7, 144.4, 149.0, 193.3; MS (EI) m/z (%): 222 (34.9) [M⁺], 204 (19.4), 187 (65.0), 139 (100), 111 (74.8), 83 (84.7); HRMS (EI) calcd. for C₁₂H₁₁O₂Cl (M⁺) requires 222.0448, found: 222.0448.

3e

(5-Hydroxy-1-cyclopentenyl)-m-tolyl-methanone (3e). Yellow oil; IR (CH₂Cl₂): ν 3430, 3056, 2934, 1730, 1644, 1584, 1427, 1347, 1189, 1053, 931, 775 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.88-1.99 (1H, m, CH₂), 2.30-2.37 (1H, m, CH₂), 2.40 (3H, s, CH₃), 2.46-2.58 (1H, m, CH₂), 2.70-2.83 (1H, m, CH₂), 3.50 (1H, s, OH), 5.28 (1H, br s, CH), 6.68 (1H, t, J = 2.7 Hz, CH), 7.28-7.37 (2H, m, ArH), 7.54-7.57 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.2, 31.3, 31.6, 76.3, 126.1, 128.0, 129.2, 133.1, 138.0, 144.5, 148.8, 194.9; MS (EI) m/z (%): 202 (70.5) [M⁺], 187 (26.4), 159 (37.4), 119 (100), 83 (58.6); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0996.

3f

(5-Hydroxy-1-cyclopentenyl)-p-tolyl-methanone (3f). Yellow oil; IR (CH₂Cl₂): ν 3485, 3055, 2925, 2854, 1723, 1633, 1605, 1457, 1351, 1180, 1052, 739 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.87-1.98 (1H, m, CH₂), 2.25-2.35 (1H, m, CH₂), 2.41 (3H, s, CH₃), 2.45-2.59 (1H, m, CH₂), 2.68-2.82 (1H, m, CH₂), 3.52 (1H, s, OH), 5.27 (1H, br s, CH), 6.66 (1H, t, J = 2.9 Hz, CH), 7.20-7.28 (2H, m, ArH), 7.66-7.70 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.5, 31.3, 31.6, 76.5, 128.9, 129.0, 135.3, 143.1, 144.4, 148.2, 194.4; MS (EI) m/z (%): 202 (44.4) [M⁺], 187 (40.7), 159 (32.9), 119 (100), 83 (35.7); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0991.

References:

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