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Supporting Information

for

Metal catalyst-free N-allylation/alkylation of imidazole and benzimidazole with Morita–Baylis–Hillman (MBH) alcohols and acetates

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Full experimental details and characterization data of all new compounds

Experimental section

All cyclic MBH alcohols **4** [1-3], acetates **5** [4], and acyclic MBH alcohols **1a**,**f** [5-7] were obtained as previously described. IR spectra were recorded on a Bruker (IFS 66v/S) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded either on a Bruker AC-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) or an AC-300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$, using TMS as an internal standard (chemical shifts in δ values, *J* in Hz). High resolution mass spectra (HRMS) were recorded as EI-HRMS on an Autospec Ultima/micromass mass spectrometer. Analytical thin layer chromatography (TLC) was performed using Fluka Kieselgel 60 F254 pre-coated silica gel plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using Merck silica gel 60 and a gradient solvent system ether/acetone as eluent.

Typical procedure for the α-substitution of cyclic MBH adducts with imidazoles

A mixture of allyl acetate **5a** (2 mmol, 0.33 g) or allyl alcohol **4a** (2 mmol, 0.25 g) and imidazole (**2a**, 4 mmol, 0.27 g) in toluene (25 mL) was heated under reflux (for **5a**) or in a Dean stark apparatus (for **4a**). After completion (TLC), the reaction mixture was cooled, washed with brine, and dried. The toluene was removed and the residue was purified by column chromatography on silica gel (acetone/ether 8:2) to give the pure N-substituted imidazole **6a**.

2-((1*H*-Imidazol-1-yl)methyl)cyclohex-2-enone (6a) [8]

Yield: 82%; yellow oil; ν ($CHCl_3$) 2932, 1666, 1503, 1380, 1227, 1074 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.47 (s, 1H), 7.01 (s, 1H), 6.89 (s, 1H), 6.64 (t, *J* = 4.0 Hz, 1H), 4.70 (s, 2H), 2.47–2.35 (m, 4H), 2.04–1.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 197.6, 147.7, 137.6, 135.2, 129.3, 119.4, 45.5, 37.9, 25.8, 22.6; HRMS (EI): MH^+, found 177.1022. $C_{10}H_{13}N_2O$ requires 177.1028.

2-((1*H*-Imidazol-1-yl)methyl)cyclopent-2-enone (6b)

Yield: 65%; yellow oil; ν ($CHCl_3$) 2924, 1693, 1504, 1388, 1227, 1073 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.39 (s, 1H), 7.34 (t, *J* = 4.0 Hz, 1H), 7.02 (s, 1H), 6.94 (s, 1H), 4.71 (s, 2H), 2.64–2.60 (m, 2H), 2.46–2.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 207.2, 160.2, 142.1, 137.4, 129.5, 119.3, 41.7, 34.6, 26.7; HRMS (EI): MH^+, found 163.0866. $C_9H_{11}N_2O$ requires 163.0871.

2-((1*H*-Imidazol-1-yl)ethyl)cyclohex-2-enone (6c)

Yield: 75%; yellow oil; ν ($CHCl_3$) 2935, 1665, 1497, 1381, 1226, 1077 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.55 (s, 1H), 7.03 (s, 1H), 6.93 (s, 1H), 6.57 (t, *J* = 4.0 Hz, 1H), 5.34 (q, *J* = 6.2 Hz, 1H), 2.47–2.36 (m, 4H), 2.02–1.96 (m, 2H), 1.62 (d, *J* = 6.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 197.3, 145.4, 140.4, 136.2, 128.9, 117.8, 50.4, 38.4, 25.7, 22.4, 19.8; MS (m/z): 191 (13), 190 (M+, 100), 189 (8), 175 (15), 162 (16), 149 (7), 134 (7), 123 (62), 107 (10), 95 (48), 81 (27), 79 (38), 69 (50), 67 (75), 55 (50); HRMS (EI): MH^+, found 191.1188. $C_{11}H_{15}N_2O$ requires 191.1184.

2-((1*H*-Imidazol-1-yl)ethyl)cyclopent-2-enone (6d)

Yield: 69%; yellow oil; ν ($CHCl_3$) 2926, 1695, 1496, 1395, 1227, 1077 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.59 (s, 1H), 7.28 (t, *J* = 4.0 Hz, 1H), 7.03 (s, 1H), 7.01 (s, 1H), 5.11 (q, *J* = 6.0 Hz, 1H), 2.62–2.60 (m, 2H), 2.46–2.43 (m, 2H), 1.71 (d, *J* = 6.0 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 207.2, 159.1, 146.6, 136.0, 129.0, 117.8, 49.1, 35.2, 26.6, 19.5; MS (m/z): 177 (12), 176 (M+, 100), 175 (7), 161 (1), 147 (9), 109 (43), 81 (54), 79 (74), 69 (33), 67 (13), 53 (31); HRMS (EI): MH^+, found 177.1031. $C_{10}H_{13}N_2O$ requires 177.1028.

2-((1*H*-Benzimidazol-1-yl)ethyl)cyclohex-2-enone (7a)

Yield: 87%; yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 8.03 (s, 1H), 7.73–7.71 (m, 1H), 7.21–7.15 (m, 3H), 6.49 (t, *J* = 4.0 Hz, 1H), 5.52 (q, *J* = 6.0 Hz, 1H), 2.38–2.34 (m, 2H), 2.25–2.19 (m, 2H), 1.89–1.83 (m, 2H), 1.70 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 197.5, 146.0, 143.7, 141.3, 133.9, 133.2, 122.8, 122.1, 120.1, 110.4, 49.1, 38.1, 25.6, 22.3, 19.4 ; MS (m/z): 241 (17), 240 (M+, 100), 239 (10), 226 (15), 225 (100), 211 (10), 197 (7), 183 (5), 169 (5), 145 (14), 119 (15), 118 (55), 91 (8), 77 (7), 67 (9), 55 (5); HRMS (EI): MH^+, found 241.1347. $C_{15}H_{17}N_2O$ requires 241.1341.

2-((1*H*-Benzimidazol-1-yl)methyl)cyclohex-2-enone (7b)

Yield: 80%; yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.85 (s, 1H), 7.68–7.62 (m, 1H), 7.22–7.08 (m, 3H), 6.49 (t, *J* = 4.0 Hz, 1H), 4.78 (s, 2H), 2.30–2.25 (m, 2H), 2.15–2.10 (m, 2H), 1.82–1.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 197.7, 147.8, 143.6, 143.3, 133.8, 133.3, 122.6, 121.7, 119.9, 109.6, 43.2, 37.6, 25.3, 22.2; MS (m/z): 227 (16), 226 (M+, 100), 225 (33), 211 (5), 198 (28), 197 (19), 183 (7), 170 (30), 169 (24), 157 (7), 131 (22), 118 (15), 104 (4), 90 (5), 77 (7), 63 (3), 53 (6); HRMS (EI): MH^+, found 227.1189. $C_{14}H_{15}N_2O$ requires 227.1184.

2-((1*H*-Benzimidazol-1-yl)methyl)cyclopent-2-enone (7c)

Yield: 72%; yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 7.92 (s, 1H), 7.75–7.74 (m, 1H), 7.29–7.18 (m, 4H), 4.87 (s, 2H), 2.51–2.49 (m, 2H), 2.39–2.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 207.6, 160.6, 143.6, 143.4, 140.9, 133.4, 123.1, 122.2, 120.3, 109.6, 39.7, 34.5, 26.7; MS (m/z): 213 (14), 212 (M+, 100), 211 (46), 197 (2), 184 (11), 183 (39), 169 (17), 156 (21), 131 (10), 118 (14), 104 (5), 90 (4), 77 (5), 63 (3), 53 (3); HRMS (EI): MH^+, found 213.1033. $C_{13}H_{13}N_2O$ requires 213.1028.

2-((1*H*-Benzimidazol-1-yl)ethyl)cyclopent-2-enone (7d)

Yield: 85%; yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 8.01 (s, 1H), 7.72–7.69 (m, 1H), 7.25–7.12 (m, 4H), 5.25 (q, *J* = 6.0 Hz, 1H), 2.46–2.42 (m, 2H), 2.31–2.30 (m, 2H), 1.74 (d, *J* = 6.0 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 207.1, 159.3, 145.1, 143.4, 141.1, 132.9, 122.7, 122.1, 120.02, 110.2, 47.4, 34.8, 26.2, 18.6; MS (m/z): 227 (16), 226 (M+, 100), 225 (8), 211 (38), 197 (14), 183 (13), 169 (4), 156 (1), 119 (12), 118 (74), 109 (8), 91 (9), 79 (14),77 (7), 63 (5), 53 (7); HRMS (EI): MH^+, found 227.1190. $C_{14}H_{15}N_2O$ requires 227.1184.

Typical procedure for the preparation of imidazole derivatives 8

A mixture of acyclic MBH alcohol **1** (1 mmol), imidazole (**2a**, 2 mmol) and DABCO (1 mmol), was stirred at reflux temperature of methanol or toluene. After completion of the reaction, the solvent was removed by rotary evaporation and CH_2Cl_2 (10 mL) was added. The mixture was washed with brine and dried. Finally, the solvent was removed and the residue was purified by a column chromatography on silica gel, using acetone/ether as eluent, to give the pure imidazole derivative **8**.

Ethyl 2-((1*H*-imidazol-1-yl)methyl)-3-hydroxypropanoate (8a)

Yield: 84%; yellow oil; ν ($CHCl_3$) 3118, 2982, 2934, 1723, 1509, 1451, 1376, 1282, 1225, 1181, 1071 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.52 (s, 1H), 6.99 (s, 1H), 6.95 (s, 1H), 4.77 (s, 1H, O$\underline{H}$), 4.35 (d, *J* = 6.6 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.81–3.73 (m, 2H), 2.97–2.91 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 171.8, 137.8, 128.7, 119.6, 61.2, 59.3, 49.2, 44.6, 14.0; HRMS (EI): MH^+, found 199.1085. $C_9H_{15}N_2O_3$ requires 199.1083.

Ethyl 2-((1*H*-imidazol-1-yl)methyl)-3-hydroxy-3-phenylpropanoate (8b)

Overall yield: 75%; yellow oil; dr = 55:45. Major diastereomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.41–7.22 (m, 6H), 6.83–6.76 (m, 2H), 4.85 (d, *J* = 6.7 Hz, 1H), 4.46–3.81 (m, 4H), 3.19–3.12 (m, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 172.0, 141.1, 137.3, 129.0, 128.2, 128.2, 126.1, 119.1, 72.6, 61.2, 55.0, 45.6, 13.9. Minor diastereomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.41–7.22 (m, 6H), 6.83–6.76 (m, 2H), 4.92 (d, *J* = 7.3 Hz, 1H), 4.46–3.81 (m, 4H), 3.07–3.01 (m, 1H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 171.8, 141.7, 137.4, 129.0, 128.4, 128.0, 126.3, 119.3, 72.6, 61.., 55.8, 45.3, 13.7; HRMS (EI): MH^+, found 275.1402. $C_{15}H_{19}N_2O_3$ requires 275.1396.

Methyl 2-((1*H*-imidazol-1-yl)methyl)-3-hydroxybutanoate (8c)

Overall yield: 70%; yellow oil; dr = 59:41. Major diastereomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H δ_H 7.46 (s, 1H), 6.98 (s, 1H), 6.89 (s, 1H), 5.17 (s, 1H, O<u>H</u>), 4.43–4.30 (m, 2H), 4.05–3.99 (m, 1H), 3.62 (s, 3H), 2.84–2.77 (m, 1H), 1.27 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 172.8, 137.4, 128.8, 119.4, 66.1, 55.5, 52.0, 45.9, 21.9. Minor diastereomer ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.49 (s, 1H), 6.99 (s, 1H), 6.93 (s, 1H), 5.17 (s, 1H, O<u>H</u>), 4.43–4.30 (m, 2H), 4.05–3.99 (m, 1H), 3.67 (s, 3H), 2.92–2.87 (m, 1H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 172.3, 137.5, 128.9, 119.4, 65.8, 54.3, 52.0, 45.0, 20.7; HRMS (EI): MH^+, found 199.1085. $C_9H_{15}N_2O_3$ requires 199.1083.

3-Hydroxy-2-((1*H*-imidazol-1-yl)methyl)-1-phenylpropan-1-one (8d)

Yield: 70%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.85–7.82 (m, 2H), 7.56–7.36 (m, 4H), 6.90 (s, 1H), 6.87 (s, 1H), 6.41 (s, 1H, O<u>H</u>), 4.52–4.34 (m, 2H), 4.02–3.94 (m, 1H), 3.88–3.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 199.8, 137.6, 136.1, 133.6, 128.8, 128.7, 128.2, 119.7, 60.7, 51.5, 45.1; HRMS (EI): MH^+, found 231.1132. $C_{13}H_{15}N_2O_2$ requires 231.1134.

1-Hydroxy-2-((1*H*-imidazol-1-yl)methyl)hexan-3-one (8e)

Yield: 76%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.45 (s, 1H), 6.97 (s, 1H), 6.89 (s, 1H), 4.63 (s, 1H, O<u>H</u>), 4.36–4.17 (m, 2H), 3.80–3.69 (m, 2H), 3.11–3.05 (m, 1H), 2.56–2.26 (m, 2H), 1.56–1.49 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 210.6, 137.7, 128.9, 119.5, 59.8, 55.7, 44.9, 44.5, 16.7, 13.5; HRMS (EI): MH^+, found 197.1293. $C_{10}H_{17}N_2O_2$ requires 197.1290.

1-Cyclohexyl-3-hydroxy-2-((1*H*-imidazol-1-yl)methyl)propan-1-one (8f)

Yield: 73%; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.43 (s, 1H), 6.96 (s, 1H), 6.88 (s, 1H), 4.71 (s, 1H, O<u>H</u>), 4.36–4.16 (m, 2H), 3.74–3.41 (m, 2H), 3.31–3.24 (m, 1H), 2.42–2.34 (m, 1H), 1.72–1.54 (m, 5H), 1.43–1.15 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 213.6, 137.6, 128.8, 119.5, 60.3, 54.4, 50.8, 45.0, 29.6, 28.0, 27.2, 25.7, 25.2; HRMS (EI): MH^+, found 237.1607. $C_{13}H_{21}N_2O_2$ requires 237.1603.

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