Electronic Supplementary Information

Alkylation of active methylene compounds with alcohols catalysed by iridium complex

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General procedures and materials.

All manipulations were performed under an argon atmosphere using standard Schlenk-type glasswares on a Schlenk line. All starting materials were commercially available and used without any purification. Iridium catalysts, [IrCl(cod)]\textsubscript{2},\textsuperscript{1} [IrCl(coe)\textsubscript{2}],\textsuperscript{1} and [Cp*IrCl\textsubscript{2}]\textsuperscript{2} were prepared according to the literature methods. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were measured with a JEOL EX-270 or a JEOL AL-400 spectrometers. GC analysis was carried out using a Shimadzu GC-2010 equipped with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). Mass spectra (EI, GCMS) were measured with an Agilent 5973 Network Mass Selective Detector. High resolution mass spectra were measured on a Micromass GCT instrument.

Compounds 3ba,\textsuperscript{3} 3ea,\textsuperscript{4} and 3fa\textsuperscript{5} were reported previously.

Compound 3ab. δ\textsubscript{H} (270 MHz; CDCl\textsubscript{3}, Me\textsubscript{4}Si) 0.92-0.98 (m, 3H), 1.10-1.16 (m, 3H), 1.33-1.48 (m, 2H), 1.62-1.73 (m, 2H), 1.95-2.06 (m, 2H), 3.45-3.50 (m, 1H) and 4.19-4.26 (m, 2H); δ\textsubscript{C} (67.5 MHz; CDCl\textsubscript{3}, Me\textsubscript{4}Si) 11.15 (CH\textsubscript{3}), 13.53 (CH\textsubscript{3}), 18.89 (CH\textsubscript{2}), 23.56(CH\textsubscript{2}), 30.31 (CH\textsubscript{2}), 38.93 (CH), 66.44 (CH\textsubscript{2}), 116.38 (C) and 166.09 (C).
\[ \nu_{\text{max}}/\text{cm}^{-1} \] 2963, 2938, 2877, 1746, 1460, 1250 and 1188; \( m/z \) (EI) 154.0872 (M\(^+\)-CH\(_3\)). C\(_8\)H\(_{12}\)NO\(_2\) requires 154.0868), 114 (18%), 96 (34), 69 (47), 57 (100) and 41 (83).

**Compound 3ac:** \( \delta_H \) (270 MHz; CDCl\(_3\), Me\(_4\)Si) 0.86-0.98 (m, 6H), 1.28-1.50 (m, 12H), 1.62-1.73 (m, 2H), 1.90-1.98 (m, 2H), 3.49 (t, \( J = 7 \) Hz, 1H) and 4.21 (t, \( J = 7 \) Hz, 2H); \( \delta_C \) (67.5 MHz; CDCl\(_3\), Me\(_4\)Si) 13.53 (CH\(_3\)), 13.96 (CH\(_3\)), 18.91 (CH\(_2\)), 22.49 (CH\(_2\)), 26.71 (CH\(_2\)), 28.67 (CH\(_2\)), 28.78 (CH\(_2\)), 29.83 (CH\(_2\)), 30.32 (CH\(_2\)), 31.55 (CH\(_2\)), 37.56 (CH), 66.44 (CH\(_2\)), 116.53 (C) and 166.27 (C); \( \nu_{\text{max}}/\text{cm}^{-1} \) 2959, 2930, 2859, 1747, 1257 and 1190; \( m/z \) (EI) 239.1886 (M\(^+\). C\(_{14}\)H\(_{25}\)NO\(_2\) requires 239.1885), 210 (4%), 196 (9), 183 (11), 166 (7), 154 (7), 141 (16), 123 (11), 110 (19), 97 (19), 57 (100) and 41 (60).

**Compound 3ad:** \( \delta_H \) (270 MHz; CDCl\(_3\), Me\(_4\)Si) 0.91-0.98 (m, 9H), 1.34-1.48 (m, 4H), 1.56-1.73 (m, 3H), 1.90-2.00 (m, 2H), 3.48 (t, \( J = 7 \) Hz, 1H) and 4.21 (t, \( J = 7 \) Hz, 2H); \( \delta_C \) (67.5 MHz; CDCl\(_3\), Me\(_4\)Si) 13.53 (CH\(_3\)), 18.90 (CH\(_3\)), 22.08 (CH\(_3\)), 22.29 (CH\(_2\)), 27.50 (CH\(_2\)), 27.86 (CH\(_2\)), 30.30 (CH\(_2\)), 35.62 (CH), 37.73 (CH), 66.44 (CH\(_2\)), 116.54 (C) and 166.24 (C); \( \nu_{\text{max}}/\text{cm}^{-1} \) 2960, 2873, 1746, 1467, 1256, 1211 and 1183; \( m/z \) (EI) \( m/z \) 211.1586 (M\(^+\). C\(_{12}\)H\(_{21}\)NO\(_2\) requires 211.1572) 137 (16%), 122 (13), 112 (15), 96 (50), 86 (22), 69 (31), 57 (100) and 41 (64%).

**Compound 3ae:** \( \delta_H \) (270 MHz; CDCl\(_3\), Me\(_4\)Si) 0.94 (t, \( J = 7 \) Hz, 3H), 1.35 (m, 2H), 1.60-1.71 (m, 2H), 2.21-2.30 (m, 2H), 2.74-2.92 (m, 2H), 3.44 (t, \( J = 7 \) Hz, 1H), 4.18 (t, \( J = 7 \) Hz, 2H) and 7.19-7.34 (m, 5H); \( \delta_C \) (67.5 MHz; CDCl\(_3\), Me\(_4\)Si) 13.55 (CH\(_3\)), 18.90 (CH\(_2\)), 30.29 (CH\(_2\)), 31.26 (CH\(_2\)), 32.59 (CH\(_2\)), 36.67 (CH), 66.58 (CH\(_2\)), 116.28 (C), 126.67 (CH), 128.46 (CH), 128.70 (CH), 138.97 (C) and 165.97 (C); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3019, 2961, 2932, 2873, 2244, 1744, 1600, 1497, 1455, 1252, 1200, 748 and 700; \( m/z \) (EI) 245.1416 (M\(^+\). C\(_{15}\)H\(_{19}\)NO\(_2\) requires 245.1416), 144 (6%), 104 (100) and 91 (29).

**Compound 3af:** \( \delta_H \) (270 MHz; CDCl\(_3\), Me\(_4\)Si) 0.88-0.94 (m, 3H), 1.29-1.34 (m, 2H),
1.55-1.63 (m, 2H), 3.19-3.26 (m, 2H), 3.69-3.75 (m, 1H), 4.14-4.19 (m, 2H) and 7.25-7.36 (m, 5H); $\delta_C$ (67.5 MHz; CDCl$_3$, Me$_4$Si) 13.52 (CH$_3$), 18.83 (CH$_2$), 30.24 (CH$_2$), 35.72 (CH$_2$), 39.59 (CH), 66.65 (CH$_2$), 116.07 (C), 127.70 (CH), 128.80 (CH), 128.95 (CH), 135.25 (C) and 165.52 (C); $\nu_{max}$/cm$^{-1}$ 2961, 2244, 1744, 1455, 1266, 1196, 1081, 1061, 1029, 748 and 699; $m/z$ (EI) 231.1247 (M+. C$_{14}$H$_{17}$NO$_2$ requires 231.1259), 186 (9), 148 (93), 130.0657 (M+-C$_5$H$_9$O$_2$, C$_9$H$_8$N requires 130.0656) and 91 (100).

**Compound 3ag:** $\delta_H$ (270 MHz; CDCl$_3$, Me$_4$Si) 0.89-0.98 (m, 3H), 1.32 (sex, $J = 7$ Hz, 2H), 1.56-1.66 (m, 2H), 2.24 (s, 6H), 3.10-3.25 (m, 2H), 3.68 (t, $J = 6$ Hz, 1H), 4.17 (t, $J = 7$ Hz, 2H) and 6.98-7.26 (m, 3H); $\delta_C$ (67.5 MHz; CDCl$_3$, Me$_4$Si) 13.57 (CH$_3$), 18.90 (CH$_3$), 19.36 (CH$_3$), 19.70 (CH$_2$), 30.33 (CH$_2$), 35.46 (CH$_2$), 39.83 (CH), 66.63 (CH$_2$), 116.28 (C), 126.29 (CH), 130.05 (CH), 130.18 (CH), 132.66 (C), 136.06 (C), 137.03 (C) and 165.72 (C); $\nu_{max}$/cm$^{-1}$ 2961, 2935, 2873, 1746, 1506, 1456, 1265, 1197, 1156 and 1023; $m/z$ (EI) 259.1577 (M+. C$_{16}$H$_{21}$NO$_2$ requires 259.1572), 158 (7%) and 119 (100).

**Compound 3ah:** $\delta_H$ (400 MHz; CDCl$_3$, Me$_4$Si) 0.90-0.94 (m, 3H), 1.30-1.39 (m, 2H), 1.58-1.65 (m, 2H), 3.04-3.20 (m, 2 H), 3.67-3.71 (m, 3H), 4.16-4.22 (m, 2H), 6.58-6.64 (m, 3H) and 7.08-7.12 (m, 1 H); $\delta_C$ (100 MHz; CDCl$_3$, Me$_4$Si) 13.56 (CH$_3$), 18.86 (CH$_2$), 30.27 (CH$_2$), 35.75 (CH$_2$), 39.57 (CH), 66.64 (CH$_2$), 114.37 (CH), 115.41 (CH), 116.25 (C), 118.87 (CH), 129.75 (CH), 136.45 (C), 146.82 (C) and 165.66 (C); $\nu_{max}$/cm$^{-1}$ 3460, 3375, 2960, 2933, 2873, 2359, 1739, 1623, 1604, 1494, 1463, 1265, 1200 and 1168; $m/z$ (EI) 246.1364 (M+. C$_{14}$H$_{18}$N$_2$O$_2$ requires 246.1368), 190 (12%), 163 (10), 145 (89), 128 (14), 106 (100) and 77 (9).

**Compound 3ai:** $\delta_H$ (270 MHz; CDCl$_3$, Me$_4$Si) 0.88 (t, $J = 7$ Hz, 6H), 1.27-1.45 (m, 12 H), 1.55-1.66 (m, 4H), 1.86 (q, $J = 7$ Hz, 4H), 3.43 (t, $J = 7$ Hz, 2H) and 4.14 (t, $J = 7$ Hz, 2H).
Hz, 4H); δC (67.5 MHz; CDCl₃, Me₄Si) 13.56 (CH₃), 18.91 (CH₂), 26.57 (CH₂), 28.39 (CH₂), 29.65 (CH₂), 30.31 (CH₂), 37.48 (CH), 66.56 (CH₂), 116.43 (C) and 166.13 (C); νmax/cm⁻¹ 2959, 2919, 2854, 1731, 1470, 1320, 1284 and 1261; m/z (EI) 291 (8%), 253 (24), 235 (64), 217 (51), 183 (59), 168 (37), 162.1147 (M⁺-C₁₀H₁₈O₄, C₁₀H₁₄N₂ requires 162.1156), 127 (79), 57 (100) and 41 (84%) Found: C, 65.89; H, 8.90; N, 7.65. C₂₀H₃₂N₂O₄ requires C, 65.91; H, 8.85; N, 7.69%.

**Compound 3aj:** δH (270 MHz; CDCl₃, Me₄Si) 0.93 (t, J = 7 Hz, 3H), 1.34 (sex, J = 7 Hz, 2H), 1.62-1.72 (m, 2H), 2.04-2.32 (m, 2H), 3.35 (s, 3H), 3.54-3.58 (m, 2H), 3.72-3.78 (m, 1H) and 4.21 (t, J = 7 Hz, 2H); δC (67.5 MHz; CDCl₃, Me₄Si) 13.55 (CH₃), 18.91 (CH₂), 29.89 (CH₂), 30.30 (CH₂), 34.44 (CH), 58.82 (CH₃), 66.52 (CH₂), 68.24 (CH₂), 116.23 (C) and 166.15 (C); νmax/cm⁻¹ 2962, 2935, 2876, 1747, 1463, 1252, 1193, 1122 and 1014; m/z (EI) 199.1210 (M⁺. C₁₀H₁₇NO₃ requires 199.1208), 126 (35%), 112 (18), 94 (27), 59 (100) and 45 (85).

**Compound 3ak:** δH (270 MHz; CDCl₃, Me₄Si) 0.93 (t, J = 7 Hz, 3H), 1.33-1.42 (m, 2H), 1.58-1.65 (m, 2H), 2.04-2.34 (m, 2H), 3.64-3.82 (m, 3H), 4.15 (t, J = 7 Hz, 2H), 4.51 (s, 2H), 7.29-7.38 (m, 5H); δC (67.5 MHz; CDCl₃, Me₄Si) 13.56 (CH₃), 18.90 (CH₂), 29.97 (CH₂), 30.27 (CH₂), 34.54 (CH), 65.96 (CH₂), 66.52 (CH₂), 73.28 (CH₂), 116.24 (C), 127.71 (CH), 127.80 (CH), 128.40 (CH), 137.63 (C) and 166.12 (C); νmax/cm⁻¹ 2960, 2873, 1745, 1454, 1252, 1208, 1113, 738 and 698; m/z (EI) 275.1519 (M⁺. C₁₆H₂₁NO₃ requires 275.1521), 107 (90%) and 91 (100).

**Compound 3ca:** δH (270 MHz; CDCl₃, Me₄Si) 0.94 (t, J = 7 Hz, 3H), 1.29-1.52 (m, 10H), 1.90-1.92 (m, 2H), 3.45 (t, J = 7 Hz, 1H) and 5.04-5.13 (m, 1H); δC (67.5 MHz; CDCl₃, Me₄Si) 13.64 (CH₃), 21.51 (CH₃), 21.89 (CH₂), 28.87 (CH₂), 29.55 (CH₂), 37.81 (CH), 70.69 (CH), 116.66 (C) and 165.74 (C); νmax/cm⁻¹ 2962, 2936, 2874, 1743, 1468,
1376, 1258, 1214, 1183 and 1105; m/z (EI) 168.1039 (M^+CH₃, C₆H₁₄NO₂ requires 168.1024), 154.0876 (M^+C₂H₅, C₈H₁₂NO₂ requires 154.0867), 124 (53%), 96 (27), 82 (12), 69 (25), 54 (34) and 43 (100).

References


5 H. Goldhahn, *Pharmazie* 1953, **8**, 324.
Supplementary Material (ESI) for Chemical Communications
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CO$_2$Bu

NH$_2$

3ah

PPM