Revised 10/17/03

REVISED
10/21/03

Efficient One-Step Aldol-Type Reaction of Ketones with Acetals and Ketals Mediated by Dibutylboron triflate/Diisopropylethyl amine.

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Supporting Information

Typical procedure for the aldol-type condensation: The typical experimental procedure for inter-molecular aldol-type condensation follows. To a solution of ketone (1 mmol) in dry CH_2Cl_2 (5 mL) at -78°C under argon, was added *i*-Pr₂NEt (0.2 mL, 1.15 mmol), followed by addition of Bu₂BOTf (1.0 M, 1.3 mL, 1.3 mmol) dropwise. The resulting mixture was stirred for 30 min, and then a solution of acetal (1mmol) in dry CH_2Cl_2 (3 mL) was added slowly. Stirring was continued for 30 min, and then the reaction was quenched by addition of PBS buffer (1.3 mL), methanol (1.3 mL) and H₂O₂ (0.5 mL). The resulting mixture was warmed to room temperature and stirred for 1 hour, extracted with ether, washed with brine and dried over MgSO₄. The crude product was purified by chromatography on silica gel column.

Compound **3a**: ^1H NMR (500 MHz, CDCl_3): δ 7.4-7.2 (5H, m), 4.51 (1H, dd, $J = 10.3, 1.9$ Hz), 3.78 (2H, m), 3.46 (2H, m), 2.43 (1H, dd, $J = 15.4, 10.3$ Hz), 1.88 (1H, dd, $J = 15.4, 2.2$ Hz), 1.85-1.76 (2H, m), 1.54 (3H, s); ^{13}C NMR (125 MHz, CDCl_3) δ 141.4, 128.6, 127.9, 126.2, 110.5, 78.9, 67.7, 61.5, 41.7, 31.6, 18.7; MS (ESI): 223 (MH^+), 245 (MNa^+), 221 [M-H].

Compound **3b** (*syn*): ^1H NMR (500 MHz, CDCl_3): δ 7.32 (2H, m), 7.36 (3H, m), 4.90 (1H, d, $J = 3.6$ Hz), 3.74 (2H, dt, $J = 5.9, 2.6$ Hz), 3.59-3.54 (2H, m), 2.62 (1H, broad), 2.49-2.41 (2H, m), 2.83-2.81 (1H, m), 2.03-1.98 (2H, m), 1.88 (1H, m), 1.80-1.76 (2H, m), 1.74-1.66 (2H, m), 1.54-1.44 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 211.0, 140.8, 128.2, 127.3, 126.6, 78.8, 68.1, 61.3, 57.2, 42.2, 32.0, 27.0, 26.3, 24.6; MS (ESI): 263 (MH^+), 285 (MNa^+), 297 [M+Cl].

Compound **3b** (*anti*): ^1H NMR (500 MHz, CDCl_3): δ 7.40-7.26 (5H, m), 4.57 (1H, d, $J = 8.8$ Hz), 3.71 (2H, t, $J = 5.5$ Hz), 3.52-3.42 (2H, m), 2.73-2.69 (1H, m), 2.67 (1H, broad), 2.48-2.36 (2H, m), 2.03-1.98 (1H, m), 1.77-1.67 (4H, m), 1.56 (1H, m), 1.46 (1H, m), 1.22-1.14 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 212.0, 139.5, 128.4, 127.9, 127.5, 81.0, 67.6, 61.2, 57.0, 42.4, 31.9, 30.9, 28.5, 24.5; MS (ESI): 263 (MH^+), 285 (MNa^+), 261 [M-H], 297 [M+Cl].

Compound **3c**: ^1H NMR (500 MHz, CDCl_3): δ 7.95 (2H, m), 7.55 (1H, m), 7.45 (2H, m), 7.41-7.37 (4H, m), 7.32 (1H, m), 3.79-3.73 (1H, m), 3.67 (1H, m), 3.60 (1H, dd, $J = 17.3, 9.5$ Hz), 3.58 (1H, ddd, $J = 11.0, 5.5, 3.3$ Hz), 3.42 (1H, ddd, $J = 11.0, 6.6, 2.6$ Hz), 3.11 (1H, dd, $J = 17.3, 3.0$ Hz), 3.07 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 198.2, 141.4, 136.8, 133.4, 128.7,

128.6, 128.2, 127.9, 126.4, 77.2, 70.0, 61.6, 47.1; MS (ESI): 271 (MH⁺), 293 (MNa⁺), 305 [M+Cl]⁻.

Compound **3d**: ¹H NMR (400 MHz, CDCl₃): δ 7.95 (2H, m), 7.56 (1H, m), 7.45 (4H, m), 7.37 (2H, m), 7.30 (1H, m), 5.15 (1H, dd, *J* = 9.1, 4.1 Hz), 3.61 (1H, dd, *J* = 16.4, 9.1 Hz), 3.55-3.41 (3H, m), 3.12 (1H, dd, *J* = 16.4, 3.8 Hz), 2.56 (1H, broad), 1.06 (3H, d, *J* = 6.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 198.5, 141.4, 137.0, 133.3, 128.8, 128.5, 128.2, 128.1, 126.6, 74.9, 72.9, 66.5, 47.2, 15.0; MS (ESI): 285 (MH⁺), 307 (MNa⁺), 283 [M-H]⁻, 319 [M+Cl]⁻.

Compound **3e**: ¹H NMR (500 MHz, CDCl₃): δ 7.94 (2H, m), 7.56 (1H, m), 7.39 (2H, m), 7.38 (4H, m), 7.30 (1H, m), 4.96 (1H, dd, *J* = 9.2, 3.7 Hz), 3.70 (2H, broad), 3.59 (1H, dd, *J* = 16.9, 9.2 Hz), 3.52 (2H, m), 3.10 (1H, dd, *J* = 16.9, 4.0 Hz), 2.48 (1H, broad), 1.74 (2H, m); ¹³C NMR (125 MHz, CDCl₃) δ 198.0, 141.4, 136.9, 133.3, 128.7, 128.6, 128.2, 127.9, 126.4, 78.4, 67.8, 61.4, 47.1, 31.9; MS (MALDI-FTMS): Calcd. For (M+Na⁺) C₁₈H₂₀O₃Na 307.1305, Found 307.1301.

Compound **3f**: ¹H NMR (500 MHz, CDCl₃): δ 8.02 (2H, m), 7.52 (1H, m), 7.45-7.40 (4H, m), 7.36 (2H, m), 7.28 (1H, m), 4.98 (1H, dd, *J* = 8.8 Hz), 3.60 (1H, dd, *J* = 16.5, 8.4 Hz), 3.56 (2H, m), 3.37 (2H, m), 3.07 (1H, dd, *J* = 16.5, 4.4 Hz), 2.20 (1H, broad), 1.75-1.55 (4H, m); ¹³C NMR (125 MHz, CDCl₃) δ 197.7, 141.7, 137.1, 133.0, 128.5, 128.4, 128.2, 127.8, 126.5, 78.0, 68.8, 62.5, 47.1, 29.6, 26.3; MS (ESI): 299 (MH⁺), 321 (MNa⁺), 297 [M-H]⁻, 333 [M+Cl]⁻.

Compound **3g**: ^1H NMR (500 MHz, CDCl_3): δ 7.94 (2H, m), 7.54 (1H, m), 7.45-7.35 (6H, m), 7.30 (1H, m), 4.89 (1H, dd, $J = 8.4, 4.4$ Hz), 3.59 (1H, dd, $J = 16.5, 8.5$ Hz), 3.24 (3H, s), 3.08 (1H, dd, $J = 16.5, 4.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 141.9, 137.6, 133.5, 129.0, 128.9, 128.7, 128.3, 127.1, 80.0, 57.3, 47.6; MS (MALDI-FTMS): Calcd. For $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Na}$ 263.1042, Found 263.1044.

Compound **3h**: ^1H NMR (500 MHz, CDCl_3): δ 7.96 (2H, m), 7.54 (1H, m), 7.46 (2H, m), 3.90 (1H, m), 3.54-3.47 (2H, m), 3.28 (1H, dd, $J = 15.8, 6.6$ Hz), 2.94 (1H, dd, $J = 15.8, 5.2$ Hz), 1.61 (2H, m), 1.12 (3H, t, $J = 7.0$ Hz), 0.97 (3H, t, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 199.2, 137.4, 132.9, 128.4, 128.2, 77.1, 64.9, 43.4, 27.6, 15.4, 9.6; MS (ESI): 207 (MH^+), 229 (MNa^+).

Compound **3i**: ^1H NMR (500 MHz, CDCl_3): δ 7.96 (2H, m), 7.56 (1H, m), 7.46 (2H, m), 4.68 (1H, m), 3.81 (1H, ddd, $J = 16.2, 9.2, 7.0$ Hz), 3.51-3.44 (2H, m), 3.23 (1H, dd, $J = 16.5, 5.9$ Hz), 1.83 (3H, d, $J = 2.2$ Hz), 1.18 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 136.9, 133.1, 128.5, 128.2, 81.7, 77.9, 65.4, 64.5; MS (ESI): 217 (MH^+), 239 (MNa^+).

Compound **3j** (*syn*): ^1H NMR (400 MHz, CDCl_3): δ 7.75 (2H, m), 7.48 (1H, m), 7.38 (2H, m), 7.32-7.24 (4H, m), 7.19 (1H, m), 4.60 (1H, d, $J = 7.6$ Hz), 3.83 (1H, m), 3.77

(2H, t, $J = 5.6$ Hz), 3.51 (1H, dt, $J = 9.4, 5.6$ Hz), 3.41 (1H, ddd, $J = 9.4, 6.4, 5.6$ Hz), 2.40 (1H, broad), 1.80 (2H, q, $J = 5.6$ Hz), 1.33 (3H, d, $J = 7.04$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 202.4, 140.3, 136.6, 132.9, 128.5, 128.3, 128.1, 127.7, 127.1, 83.2, 68.1, 61.8, 48.3, 32.1, 14.1; MS (ESI): 299 (MH^+), 321 (MNa^+), 333 [$\text{M}+\text{Cl}$].

Compound **3j** (*anti*): ^1H NMR (400 MHz, CDCl_3): δ 8.15 (2H, m), 7.68 (1H, m), 7.55 (2H, m), 7.5-7.3 (5H, m), 4.56 (1H, d, $J = 7.9$ Hz), 3.80 (1H, m), 3.50 (2H, m), 3.38 (2H, m), 1.98 (1H, broad), 1.68 (2H, m), 0.89 (3H, d, $J = 7.0$ Hz).

Compound **3k** (*syn:anti* = 6:1): ^1H NMR (500 MHz, CDCl_3) for *syn*-isomer: δ 7.73 (2H, m), 7.46 (1H, m), 7.37-7.29 (4H, m), 7.23 (2H, m), 7.17 (1H, m), 4.47 (1H, d, $J = 8.2$ Hz), 3.83 (1H, dd, $J = 7.9, 6.7$ Hz), 3.20 (3H, s), 1.35 (3H, d, $J = 6.8$ Hz); for *anti*-isomer: δ 8.05 (2H, m), 7.56 (1H, m), 7.48-7.24 (7H, m), 4.48 (1H, d, $J = 9.7$ Hz), 3.79 (1H, M), 3.08 (3H, s), 0.85 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) for *syn*-isomer: δ 202.5, 140.2, 136.8, 132.6, 128.4, 128.2, 128.0, 127.6, 127.3, 84.5, 56.9, 48.5, 14.5.

Compound **3i** (*syn:anti* = 3:1): ^1H NMR (500 MHz, CDCl_3) for *syn*-isomer: δ 7.31-7.23 (5H, m), 4.22 (1H, d, $J = 8.8$ Hz), 3.20 (3H, s), 3.03 (1H, m), 2.19 (1H, m), 1.24 (3H, d, $J = 7.0$ Hz), 0.90 (3H, d, $J = 7.0$ Hz), 0.59 (3H, d, $J = 6.6$ Hz); for *anti*-isomer: 7.40 (2H, m), 7.29 (3H, m), 4.18 (1H, d, $J = 9.9$ Hz), 3.06 (3H, s), 3.03 (1H, m), 2.79 (1H, m), 1.14 (6H, t, $J = 6.3$ Hz), 0.72 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3) for *syn*-isomer: δ 216.2, 140.3, 128.3, 127.8, 127.3, 84.7, 56.8, 52.4, 41.1, 17.8, 16.9, 14.5; MS (ESI): 221 (MH^+), 243 (MNa^+).

Compound **3m** (*syn*): ^1H NMR (500 MHz, CDCl_3): δ 7.35-7.27 (5H, m), 4.86 (1H, d, J = 3.0 Hz), 3.72 (2H, t, J = 5.9 Hz), 3.59-3.55 (1H, m), 3.47-3.43 (1H, m), 2.38-2.28 (2H, m), 2.20-2.03 (5H, m), 1.83-1.76 (3H, m), 1.75-1.63 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 219.0, 140.6, 128.5, 127.4, 126.1, 79.8, 68.2, 61.3, 56.1, 39.2, 32.1, 22.9, 20.6.

Compound **3m** (*anti*): ^1H NMR (500 MHz, CDCl_3): δ 7.27-7.24 (5H, m), 4.60 (1H, d, J = 5.3 Hz), 3.81 (2H, m), 3.57-3.54 (1H, m), 3.51-3.46 (1H, m), 2.85 (1H, broad), 2.71-2.66 (1H, m), 2.28-2.22 (1H, m), 1.94-1.66 (6H, m), 1.53-1.49 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 218.6, 139.1, 128.3, 127.8, 127.2, 81.2, 68.4, 62.0, 54.8, 38.7, 32.0, 25.5, 20.4; MS (ESI): 249 (MH^+), 271 (MNa^+).

Compound **3n** (*syn*): ^1H NMR (500 MHz, CDCl_3): δ 7.33 (2H, m), 7.26 (3H, m), 5.12 (1H, d, J = 2.6 Hz), 3.77-3.73 (1H, m), 3.68-3.65 (2H, m), 3.51 (1H, dd, J = 7.4, 5.2 Hz), 3.38 (1H, m), 2.49-2.43 (2H, m), 2.28 (1H, m), 2.04 (1H, m), 1.93-1.84 (2H, m), 1.80 (1H, dd, J = 13.2, 3.7 Hz), 1.70 (1H, m), 1.47 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 212.2, 140.4, 128.3, 127.3, 126.7, 77.6, 70.4, 61.6, 57.1, 42.3, 27.1, 25.7, 24.8; MS (ESI): 249 (MH^+), 271 (MNa^+), 283 [$\text{M}+\text{Cl}$].

Compound **3n** (*anti*): ^1H NMR (500 MHz, CDCl_3): δ 7.36-7.26 (5H, m), 4.65 (1H, d, J = 9.6 Hz), 3.74 (1H, m), 3.67-3.60 (2H, m), 3.50 (1H, ddd, J = 11.4, 5.5, 3.0 Hz), 3.32 (1H, ddd, J = 11.4, 7.0, 2.9 Hz), 2.72 (1H, m), 2.50-2.39 (2H, m), 2.08 (1H, m), 1.74 (1H, m), 1.67 (1H, m), 1.56 (1H, m), 1.42 (1H, m), 1.18 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 213.3, 139.4, 128.5, 128.1, 127.5, 79.9, 69.6, 61.2, 56.9, 42.8, 31.4, 28.8, 24.9.

Compound **3o** (*syn*): ^1H NMR (500 MHz, CDCl_3): δ 7.33-7.26 (5H, m), 4.90 (1H, d, J = 4.4 Hz), 3.64 (2H, m), 3.40 (2H, m), 2.49-2.40 (2H, m), 2.24 (1H, m), 2.05 (2H, m), 1.90 (1H, m), 1.80-1.55 (7H, m), 1.45 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 210.6, 141.2, 128.2, 127.2, 126.8, 78.5, 69.3, 62.8, 57.3, 42.2, 30.0, 26.9, 26.5, 26.4, 24.6; MS (ESI): 277 (MH^+), 299 (MNa^+), 311 [$\text{M}+\text{Cl}$].

Compound **3o** (*anti*): ^1H NMR (500 MHz, CDCl_3): δ 7.30-7.27 (5H, m), 4.64 (1H, d, J = 8.8 Hz), 3.61 (2H, m), 3.38 (1H, m), 3.31 (1H, m), 2.73 (1H, m), 2.48-2.39 (2H, m), 2.30 (1H, broad), 1.98 (1H, m), 1.76-1.70 (2H, m), 1.62-1.56 (5H, m), 1.54 (1H, m), 1.18 (1H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 211.5, 139.8, 128.3, 127.8, 127.6, 80.4, 68.8, 62.7, 57.1, 42.2, 30.7, 29.8, 28.4, 26.5, 24.3.

Compound **5a**: ^1H NMR (400 MHz, CDCl_3): δ 7.95 (2H, m), 7.55 (1H, m), 7.45 (2H, m), 3.24 (3H, s), 3.09 (2H, s), 1.80 (2H, m), 1.57-1.44 (7H, m), 1.21 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 199.4, 138.6, 132.8, 128.5, 128.3, 75.8, 48.8, 44.9, 34.3, 25.3, 21.7; MS (ESI): 233 (MH^+), 255 (MNa^+).

Compound **5b**: ^1H NMR (500 MHz, CDCl_3): δ 7.95 (2H, m), 7.56 (1H, m), 7.46 (2H, m), 3.72 (2H, m), 3.56 (2H, m), 3.40 (1H, t, J = 5.9 Hz), 3.10 (2H, s), 1.79 (2H, m), 1.59-1.51 (3H, m), 1.48-1.43 (4H, m), 1.23 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 200.0, 138.5,

133.1, 128.6, 128.4, 76.0, 62.3, 62.2, 43.8, 35.1, 25.3, 21.8; MS (ESI): 263 (MH⁺), 285 (MNa⁺), 261[M-H]⁻, 297 [M+Cl]⁻.

Compound **5c**: ¹H NMR (500 MHz, CDCl₃): δ 7.95 (2H, m), 7.60 (1H, m), 7.45 (2H, m), 3.90 (1H, m), 3.50 (1H, broad), 3.42 (1H, dd, *J* = 11.4, 3.7 Hz), 3.22 (1H, t, *J* = 11.0 Hz), 3.14 (1H, d, *J* = 17.3 Hz), 3.03 (1H, d, *J* = 17.3 Hz), 1.77 (2H, m), 1.57-1.42 (7H, m), 1.25 (1H, m), 1.43 (3H, d, *J* = 8.1 Hz); MS (ESI): 277 (MH⁺), 299 (MNa⁺), 311 [M+Cl]⁻.

Compound **5d**: ¹H NMR (500 MHz, CDCl₃): δ 7.95 (2H, d, *J* = 8.1 Hz), 7.57-7.44 (3H, m), 3.99 (1H, q, *J* = 6.9 Hz), 3.74-3.71 (2H, m), 3.60-3.52 (2H, m), 3.01 (1H, m), 1.92-1.40 (12H, m), 1.20 (3H, d, *J* = 7.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 203.5, 138.6, 132.8, 128.6, 128.1, 77.5, 61.9, 59.4, 44.4, 32.9, 32.1, 30.6, 25.4, 21.6, 21.4, 12.4; MS (ESI): 313 (MNa⁺), 325 [M+Cl]⁻.

Compound **5e**: ¹H NMR (500 MHz, CDCl₃): δ 7.98 (2H, m), 7.53 (1H, m), 7.45 (2H, m), 3.81 (1H, q, *J* = 7.0 Hz), 3.16 (3H, s), 1.30 (3H, s), 1.19 (3H, dd, *J* = 7.0, 0.9 Hz), 1.18 (3H, s); ¹³C NMR (125 MHz, CDCl₃): δ 203.9, 138.0, 132.5, 128.4, 77.2, 48.9, 47.8, 22.3, 21.6, 13.4; MS (ESI): 207 (MH⁺), 205 [M-H]⁻.

5f

Compound **5f**: ^1H NMR (600 MHz, CDCl_3): δ 7.96 (2H, m), 7.56 (1H, m), 7.46 (2H, m), 3.95 (1H, q, $J = 7.0$ Hz), 3.20 (3H, s), 1.89 (1H, m), 1.78 (1H, m), 1.62-1.52 (4H, m), 1.39 (2H, m), 1.18 (3H, d, $J = 7.0$ Hz), 1.07 (2H, m); ^{13}C NMR (150 MHz, CDCl_3): δ 203.6, 138.8, 132.7, 128.6, 128.1, 77.1, 48.2, 44.1, 31.9, 30.4, 25.5, 21.5, 21.3, 12.3; MS (ESI): 247 (MH^+), 269 (MNa^+).

5g

Compound **5g**: ^1H NMR (500 MHz, CDCl_3): δ 7.93 (2m, m), 7.54 (1H, m), 7.46 (2H, m), 3.94 (1H, q, $J = 6.3$ Hz), 3.66 (2H, m), 3.52-3.47 (2H, m), 2.37 (1H, t, $J = 6.3$ Hz), 1.90 (1H, m), 1.78 (1H, m), 1.64-1.51 (4H, m), 1.42 (2H, m), 1.20 (3H, d, $J = 7.0$ Hz), 1.16 (1H, m), 1.08 (1H, m); ^{13}C NMR (125 MHz, CDCl_3): δ 203.5, 138.6, 132.9, 128.6, 128.1, 77.1, 62.2, 61.2, 44.8, 32.3, 30.9, 25.4, 21.6, 21.3, 12.4.

5h

Compound **5h**: ^1H NMR (500 MHz, CDCl_3): δ 3.19 (3H, s), 2.67 (1H, h, $J = 7.0$ Hz), 2.56 (2H, s), 1.71-1.19 (10H, m), 1.04 (6H, d, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 213.5, 75.4, 48.5, 46.9, 42.0, 33.0, 25.3, 21.6, 17.9; MS (ESI): 199 (MH^+), 221 (MNa^+).

5i

Compound **5i**: ^1H NMR (500 MHz, CDCl_3): δ 7.98 (2H, m), 7.54 (2H, m), 7.45 (2H, m), 3.94 (1H, q, $J = 7.0$ Hz), 3.60 (2H, t, $J = 6.3$ Hz), 3.40 (1H, m), 3.35-3.30 (3H, m), 1.96 (2H, m), 1.82 (1H, m), 1.72 (1H, m), 1.21 (3H, s), 1.14 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 203.6, 139.3, 132.7, 128.4, 128.2, 79.5, 62.0, 45.3, 44.7, 32.9, 26.1, 19.2, 12.8.

5j

Compound **5j**: ^1H NMR (500 MHz, CDCl_3): δ 7.96 (2H, d, $J = 7.8$ Hz), 7.56-7.44 (3H, m), 4.11 (2H, q, $J = 7.0$ Hz), 3.24 (1H, d, $J = 15.0$ Hz), 3.19 (3H, s), 3.04 (1H, d, $J = 15.4$ Hz), 2.38 (2H, ddd, $J = 9.9, 8.6, 1.2$ Hz), 2.08-1.97 (2H, m), 1.32 (3H, s), 1.24 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 198.2, 173.6, 137.9, 132.9, 128.4, 128.1, 77.3, 75.7, 60.2, 48.9, 45.4, 31.8, 28.7, 22.6, 14.1; MS (ESI): 279 (MH^+), 301 (MNa^+), 313 [$\text{M}+\text{Cl}$] $^-$.

5k

Compound **5k**: ^1H NMR (500 MHz, CDCl_3): δ 3.15 (3H, s), 3.08 (1H, q, $J = 7.0$ Hz), 2.70 (1H, h, $J = 7.0$ Hz), 1.76-1.37 (10H, m), 1.06 (3H, d, $J = 7.2$ Hz), 1.00 (3H, d, $J = 6.6$ Hz), 0.97 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 217.2, 76.7, 48.2, 47.9, 42.3, 31.3, 30.0, 25.5, 21.4, 21.2, 18.8, 17.2, 11.9. MS (ESI): 213 (MH^+); 235 (MNa^+), 211 [$\text{M}-\text{H}$] $^-$.

8a

Compound **8a**: ^1H NMR (400 MHz, CDCl_3): δ 7.96 (2H, m), 7.57 (1H, m), 7.46 (2H, m), 3.94 (2H, m), 3.66 (2H, m), 3.44 (2H, t, $J = 6.8$ Hz), 3.31 (1H, dd, $J = 15.8, 6.5$ Hz), 2.95 (1H, dd, $J = 6.8$ Hz), 1.60-1.45 (8H, m), 1.28 (2H, m), 0.86 (3H, t, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 199.3, 137.3, 133.1, 128.5, 128.2, 76.1, 69.5, 62.8, 43.6, 34.7, 32.6, 32.1, 21.5, 19.2, 13.9; MS (ESI): 279 (MH^+), 301 (MNa^+).

Compound **8b**: ^1H NMR (400 MHz, CDCl_3): δ 7.97 (2H, m), 7.56 (1H, m), 7.46 (2H, m), 3.94 (2H, m), 3.48 (1H, m), 3.28 (1H, dd, $J = 16.1, 6.7$ Hz), 2.92 (1H, dd, $J = 16.1, 5.9$ Hz), 1.84 (1H, m), 1.74 (1H, m), 1.58-1.54 (3H, m), 1.38 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 198.4, 137.2, 133.1, 128.5, 128.2, 74.3, 68.6, 45.3, 32.0, 25.8, 23.3; MS (ESI): 205 (MH^+), 227 (MNa^+).

Compound **9a**: ^1H NMR (500 MHz, CDCl_3): δ 3.78 (1H, m), 3.65 (2H, t, $J = 6.3$ Hz), 3.41 (2H, m), 2.75 (1H, dd, $J = 16.2, 7.0$ Hz), 2.61 (1H, m), 2.44 (1H, dd, $J = 16.2, 5.5$ Hz), 1.59 (2H, m), 1.55-1.46 (6H, m), 1.33 (2H, m), 1.08 (6H, d, d, $J = 7.0$ Hz), 0.89 (3H, t, $J = 7.4$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 213.7, 75.7, 69.4, 62.7, 45.4, 41.7, 34.3, 32.6, 32.2, 21.5, 19.3, 17.9, 13.9; MS (ESI): 245 (MH^+), 267 (MNa^+), 279 [$\text{M}+\text{Cl}$].

Compound **11a**: ^1H NMR (400 MHz, CDCl_3): δ 7.95 (2H, m), 7.54 (1H, m), 7.44 (2H, m), 4.72 (1H, d, $J = 7.9$ Hz), 3.80 (1H, m), 3.72 (1H, m), 3.64 (2H, m), 3.44 (1H, m), 1.24 (3H, t, $J = 7.0$ Hz), 1.20 (3H, d, $J = 7.0$ Hz), 0.99 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (100

MHz, CDCl_3): δ 202.4, 137.3, 132.8, 128.4, 105.2, 64.2, 62.2, 44.9, 15.3, 15.0, 14.0; MS (ESI): 237 (MH^+), 259 (MNa^+).

Compound **12a**: ^1H NMR (400 MHz, CDCl_3): δ 7.28 (5H, m), 4.33 (1H, d, $J = 10.0$ Hz), 3.76 (3H, s), 3.71 (2H, t, $J = 5.3$ Hz), 3.42 (2H, m), 2.79 (1H, m), 2.64 (1H, broad), 1.76 (2H, m), 0.88 (3H, d, $J = 8.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 176.3, 138.7, 128.6, 128.4, 126.8, 84.9, 68.0, 61.7, 52.0, 47.0, 31.7, 14.0; MS (ESI): 275 (MNa^+).

Compound **12b**: ^1H NMR (400 MHz, CDCl_3): δ 3.68 (3H, s), 3.18 (3H, s), 2.80 (1H, q, $J = 7.0$ Hz), 1.87 (1H, m), 1.72 (1H, m), 1.63 (1H, m), 1.49 (5H, m), 1.28 (1H, m), 1.13 (1H, m), 1.11 (3H, d, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 175.2, 76.2, 51.4, 48.1, 45.0, 31.0, 30.2, 25.6, 21.4, 21.3, 11.8; MS (ESI): 201 (MH^+), 223 (MNa^+).

Compound **3p** (1.6 : 1 mixture of both diastereoisomers): ^1H NMR (500 MHz, CDCl_3): δ 7.97 and 7.95 (2H together, m; m), 7.55 (1H, m), 7.46-7.27 (5H, m), 7.16 (7H, m), 5.08 and 4.78 (1H together, dd, $J = 8.5, 3.7$ Hz; m), 4.76 and 4.30 (1H together, m; dd, $J = 9.2, 4.0$ Hz), 3.73-3.64 (2H, m), 3.71 and 3.60 (1H together, dd, $J = 16.9, 8.8$ Hz; dd, $J = 15.8, 8.1$ Hz), 3.17 and 3.13 (1H together, dd, $J = 15.8, 5.5$ Hz; dd, $J = 16.9, 3.7$ Hz), 2.70 and 2.32 (1H together, broad; broad), 1.97 and 1.76 (1H together, m; m), 1.92 (1H, m).

3q (1.7 : 1)

Compound **3q** (1.6 : 1 mixture of both diastereoisomers): ^1H NMR (500 MHz, CDCl_3): δ 7.94 (2H, m), 7.55 (1H, m), 7.46-7.26 (7H, m), 5.14 and 5.10 (1H together, dd, $J = 8.4$, 4.8 Hz; dd, $J = 9.2$, 2.9 Hz), 3.89 and 3.58 (1H together, m; m), 3.70 and 3.66 (1H together, m; m), 3.63-3.55 (2H, m), 2.63 and 2.25 (1H together, broad; broad), 3.10 and 3.05 (1H together, dd, $J = 16.2$, 4.8 Hz; dd, $J = 16.2$, 3.3 Hz), 1.76 and 1.64 (1H together, m; m), 1.61 (1H, m), 1.16 and 0.94 (3H together, d, $J = 6.3$ Hz, d, $J = 6.3$ Hz).

3r (1.3 : 1)

Compound **3r** (1.3 : 1 mixture of both diastereoisomers): ^1H NMR (500 MHz, CDCl_3): δ 7.98 and 7.78 (2H together, m; m), 7.55 (2H, m), 7.30 (6H, m), 5.88 and 5.67 (1H together, m; m), 5.16 and 5.14 (1H together, m; m), 5.01 and 4.97 (1H together, m; m), 4.68 (1H, dd, $J = 9.6$, 3.7 Hz), 4.12 and 4.01 (1H together, m; m), 3.76 (2H, m), 3.68 and 3.61 (1H together, m; m), 3.34 and 3.13 (1H together, dd, $J = 16.9$, 7.4 Hz; dd, $J = 15.8$, 6.2 Hz), 3.07 and 2.96 (1H together, dd, $J = 16.9$, 4.8 Hz; dd, $J = 15.8$, 6.6 Hz), 2.52 and 2.39 (1H together, m; m), 2.13 (1H, m), 1.98 and 1.91 (1H together, m; m), 1.81 (1H, m).