

Biocatalytic Reduction of Activated Cinnamic Acid Derivatives: SUPPLEMENTARY INFORMATION

Asymmetric reduction of C=C double bonds using Johnson Matthey enzymes

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NMR Results

1a: ¹H NMR (400 MHz, CDCl₃) 7.81 (d, *J* = 15.93 Hz, 1H), 7.6-7.4 (m, 3H), 7.4-7.3 (m, 2H), 6.46 (d, *J* = 16.12 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) 172.8, 147.1, 134.1, 130.7, 129.0, 128.4, 117.4 ppm. HPLC *t*_R = 2.47 min. GC *t*_R = 10.26 min.

1b: ¹H NMR (400 MHz, CDCl₃) 7.3 – 7.1 (m, 5H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H) ppm. HPLC *t*_R = 2.31 min.

2a: ¹H NMR (400 MHz, CDCl₃) 7.70 (d, *J* = 16.0 Hz, 1H), 7.6-7.5 (m, 2H), 7.4-7.3 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H) ppm. GC *t*_R = 8.08 min.

2b: ¹H NMR (400 MHz, CDCl₃) 7.4-7.3 (m, 2H), 7.3-7.2 (m, 3H), 3.68 (s, 3H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.53 (t, *J* = 7.8 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm. GC *t*_R = 6.00 min.

3a: ¹H NMR (400 MHz, CDCl₃) 7.79 (d, *J* = 16.05 Hz, 1H), 7.6-7.5 (m, 2H), 7.4-7.3 (m, 3H), 6.49 (d, *J* = 16.01 Hz, 1H), 4.60 (q, *J* = 8.48 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) 165.2, 147.2, 133.9, 130.9, 129.0, 128.3, 123.1 (q, *J* = 277 Hz), 115.9, 60.4 (q, *J* = 36.6) ppm. ¹⁹F NMR (376 MHz, CDCl₃) -73.7 ppm. GC *t*_R = 7.32 min.

3b: ¹H NMR (400 MHz, CDCl₃) 7.3-7.2 (m, 5H), 4.47 (q, *J* = 8.5 Hz, 2H), 3.1-2.9 (m, 2H), 2.76 (t, *J* = 7.8 Hz, 2H) ppm. GC *t*_R = 6.37 min.

4a: ¹H NMR (400 MHz, CDCl₃) 7.69 (d, *J* = 16.0 Hz, 1H), 7.6-7.5 (m, 2H), 7.4-7.3 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H) ppm. GC *t*_R = 9.07 min.

4b: ¹H NMR (400 MHz, CDCl₃) 7.3-7.2 (m, 2H), 7.2-7.1 (m, 3H), 4.11 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm. GC *t*_R = 7.48 min.

5a: ¹H NMR (400 MHz) 7.88 (d, *J* = 16.01 Hz, 1H), 7.59-7.53 (m, 2H), 7.5-7.3 (m, 3H), 6.52 (d, *J* = 16.01 Hz, 1H), 5.92 (hept, *J* = 6.12 Hz, 1H) ppm. ¹³C NMR (100 MHz) 163.4, 149.4, 133.4, 131.4, 129.1, 128.6, 120.6 (q, *J* = 284.8 Hz), 114.2, 66.5 (hept. *J* = 34.7 Hz) ppm. ¹⁹F NMR (376 MHz, CDCl₃) -73.3 ppm. GC *t*_R = 6.12 min.

5b: GC *t*_R = 5.21 min.

6a: ¹H NMR (400 MHz) 7.79 (d, *J* = 15.9, 1 H), 7.6-7.5 (m, 2 H), 7.5-7.4 (m, 3 H), 6.48 (d, *J* = 15.9 Hz, 1 H) 4.70, (t, *J* = 13.4 Hz, 2 H) ppm. ¹⁹F NMR (376 MHz, CDCl₃) -0.86 (t, *J* = 9.8 Hz), -120.4 (m), -127.6 (m) ppm.

6b: ^1H NMR (400 MHz) 7.4-7.3 (m, 5 H), 4.50 (t, $J = 14.4$ Hz, 2 H), 2.91 (t, $J = 7.9$ Hz, 2 H), 2.68 (t, $J = 7.9$ Hz, 2 H) ppm.

7a: ^1H NMR (400 MHz) 7.72 (d, $J = 15.9$ Hz, 1 H), 7.6-7.5 (m, 2 H), 7.3-7.4 (m, 3 H), 6.42 (d, $J = 15.9$ Hz, 1 H), 5.33 (s, 2 H) ppm. ^{19}F NMR (376 MHz, CDCl_3) -141.7 (m), -152.5 (t, $J = 20.4$ Hz), -161.5 (m) ppm.

7b: ^1H NMR (400 MHz) 7.3-7.2 (m, 5 H), 5.23 (s, 2 H), 2.90 (t, $J = 8.5$ Hz, 2 H), 2.62 (t, $J = 8.5$ Hz, 2 H) ppm.

8a: ^1H NMR (400 MHz) 7.89 (d, $J = 15.8$ Hz, 1 H), 7.83 (d, $J = 15.8$ Hz, 1 H), 7.6-7.5 (m, 2 H), 7.4-7.3 (m, 3 H), 4.43 (t, $J = 8.0$ Hz, 2 H), 4.11 (t, $J = 8.0$ Hz, 2 H) ppm. ^{13}C NMR (400 MHz) 165.4, 153.6, 146.2, 134.5, 130.7, 129.6, 128.6, 116.7, 62.1, 42.8 ppm. HPLC (chiral method A) $t_R = 18.32$ min.

8b: ^1H NMR (400 MHz) 7.25-7.10 (m, 5 H), 4.32 (t, $J = 7.8$ Hz, 2 H), 3.93 (t, $J = 7.8$ Hz, 2 H), 3.12 (t, $J = 7.8$ Hz, 2 H), 2.92 (t, $J = 7.8$ Hz, 2 H) ppm. HPLC (chiral method) $t_R = 19.52$ min.

9a: ^1H NMR (400 MHz) 7.92 (d, $J = 15.8$ Hz, 1 H), 7.84 (d, $J = 15.8$ Hz, 1 H), 7.62-7.55 (m, 2 H), 7.39-7.31 (m, 3 H), 3.89 (t, $J = 7.0$ Hz, 2 H), 2.60 (t, $J = 8.0$ Hz, 2 H), 2.02 (m, 2 H) ppm. ^{13}C NMR (100 MHz) 175.7, 166.3, 145.4, 134.9, 130.3, 128.8, 128.5, 119.0, 45.9, 34.0, 17.2 ppm.

9b: ^1H NMR (400 MHz) 7.2-7.1 (m, 5 H), 3.74 (t, $J = 7.3$, 2 H), 3.16 (t, $J = 7.3$, 2 H), 2.90 (t, $J = 7.3$, 2 H), 2.51 (t, $J = 8.1$ Hz, 2 H), 1.95 (pent, $J = 7.6$, 2 H) ppm.

10a: ^1H NMR (400 MHz) 7.4-7.3 (m, 4 H), 7.3-7.2 (m, 1 H), 6.85 (s, 1 H), 3.85 (t, $J = 7.0$ Hz, 2 H), 2.58 (t, $J = 8.0$ Hz, 2 H), 2.13 (s, 3 H), 2.1-2.0 (m, 2 H) ppm. ^{13}C NMR (100 MHz) 174.5, 172.9, 135.9, 134.2, 133.4, 129.5, 128.3, 127.9, 46.0, 33.2, 17.7, 15.5 ppm.

10b: ^1H NMR (400 MHz) 7.2-7.1 (m, 5 H), 3.98 (m, 1 H), 3.68 (m, 2 H), 2.98 (H_A of ABX, $J = 12.0$, 8.0 Hz, 1 H), 2.53 (H_B of ABX, $J = 12.0$, 8.0 Hz, 1 H), 2.5-2.4 (m, 2 H), 2.0-1.8 (m, 2 H), 1.06 (d, $J = 6.8$ Hz, 3 H) ppm. HPLC (chiral method B) rac $t_R = 17.5$ min and 19.5 min.

11a: ^1H NMR (400 MHz) 7.4-7.2 (m, 5 H), 7.2-7.1 (m, 5 H), 6.89 (s, 1 H), 3.89 (t, $J = 7.0$ Hz, 2 H), (t, $J = 8.0$ Hz, 2 H), 2.1-2.0 (m, 2 H) ppm. ^{13}C NMR (100 MHz) 173.9, 171.2, 137.3, 135.1, 134.9, 133.4, 129.8, 129.7, 128.3, 128.1, 128.1, 128.0, 45.9, 32.9, 17.5 ppm.

11b: ^1H NMR (400 MHz) 7.41 (m, 2 H), 7.33-7.14 (m, 8 H), 5.40 (dd, $J = 8.8$ Hz, $J = 6.7$ Hz, 1 H), 3.80-3.69 (m, 2 H), 3.46 (H_A of ABX, $J = 12$, 8 Hz, 1H), 3.03 (H_B of ABX, $J = 12$, 8 Hz, 1H), 2.55-2.41 (m, 2 H), 1.95-1.87 (m, 2 H) ppm.