Supporting Information

Stereospecific Synthesis of Polyfunctionalized Carbacephams Induced by Titanocene (III) Chloride

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NMR Data for Alkenes **3** and **5**, Epoxides **1** and **2**, and Carbacephams **6** and **7**.

3a: ^1H NMR (200 MHz, CDCl_3) δ 1.18 (6H, 2t, $J = 7.4$ Hz), 1.31, 1.38, 1.41, 1.58 (12H, 4s), 2.55-2.75 (4H, 2q, $J = 7.4$ Hz), 3.47 (3H, s), 3.59 (1H, t, $J = 7.8$ Hz), 3.89 (1H, dd, $J = 4.4$, 7.8 Hz), 4.02-4.15 (3H, m), 4.19 (1H, dd, $J = 5.0$, 1.6 Hz), 4.67 (1H, d, $J = 4.4$ Hz), 4.71 (1H, dd, $J = 4.4$, 2.4 Hz), 4.95 (1H, dd, $J = 1.6$, 7.8 Hz), 6.62-6.82 (2H, m), 7.28-7.48 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 14.2, 23.3, 24.5, 25.3, 26.2, 26.5, 27.5, 52.9, 54.5, 58.8, 63.3, 67.8, 77.3, 78.5, 78.6, 85.4, 109.7, 110.1, 124.7, 126.8, 128.2, 128.7, 135.6, 136.4, 167.6.

3b: ^1H NMR (200 MHz, CDCl_3) δ 1.22, 1.24 (6H, 2t, $J = 7.4$ Hz), 1.28, 1.29, 1.33 (12H, 3s), 2.60-2.90 (4H, m), 3.43 (3H, s), 3.72 (1H, t, $J = 7.4$ Hz), 3.97 (1H, dd, $J = 5.4$, 7.6 Hz), 4.00 (1H, dd, $J = 9.5$, 3.5 Hz), 4.02-4.19 (2H, m), 4.33 (1H, d, $J = 9.5$ Hz), 4.59 (1H, d, $J = 4.8$ Hz), 4.65 (1H, dd, $J = 4.8$, 7.1 Hz), 4.69 (1H, dd, $J = 3.5$, 7.4 Hz), 6.42 (1H, dd, $J = 7.1$, 15.5 Hz), 6.65 (1H, d, $J = 15.5$ Hz), 7.25-7.45 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 15.1, 15.2, 25.1, 26.1, 26.2, 27.4, 28.0, 52.6, 56.7, 59.5, 63.6, 68.7, 77.9, 79.1, 80.0, 86.2, 110.2, 110.8, 127.0, 127.7, 128.9, 129.5, 135.6, 137.4, 169.4.

5a: ^1H NMR (200 MHz, CDCl_3) δ 1.30, 1.36, 1.39, 1.45, (12H, 4s), 3.44 (3H, s), 3.53 (3H, s), 3.72 (1H, t, $J = 7.1$ Hz), 3.96 (1H, dd, $J = 5.0$, 8.0 Hz), 4.04 (2H, m), 4.15 (1H, dd, $J = 5.6$, 8.0 Hz), 4.37 (1H, t, $J = 7.1$ Hz), 4.59-4.69 (2H, m), 6.05 (1H, d, $J = 15.6$ Hz), 6.22 (1H, ddd, $J = 0.8$, 8.6, 15.7 Hz), 6.69 (1H, d, $J = 15.7$ Hz), 6.89 (1H, dd, $J = 8.0$, 15.7 Hz), 7.22-7.43 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 25.1, 26.3, 27.2, 27.5, 51.4, 54.1, 58.6, 62.2, 67.6, 77.0, 79.1, 80.0, 85.3, 110.1, 110.4, 124.4, 124.8, 126.7, 128.2, 128.6, 136.2, 142.0, 165.8, 166.9.

5b: ^1H NMR (200 MHz, CDCl_3) δ 1.29, 1.32, 1.36, 1.40 (12H, 4s), 3.44 (3H, s), 3.46 (1H, dd, $J = 1.8$, 7.9 Hz), 3.72 (1H, dd, $J = 5.2$, 8.0 Hz), 3.74 (3H, s), 3.87 (1H, dd, $J = 5.2$, 7.8 Hz), 3.98 (1H, dd, $J = 5.2$, 8.0 Hz), 4.10 (1H, dd, $J = 5.3$, 7.8 Hz), 4.26 (1H, dd, $J = 1.8$, 5.2 Hz), 4.42 (1H, dd, $J = 4.5$, 9.1 Hz), 4.60 (1H, d, $J = 4.5$ Hz), 6.05 (1H, d, $J = 15.7$ Hz), 6.35 (1H, dd, $J = 9.1$, 15.9 Hz), 6.73 (1H, d, $J = 15.9$ Hz), 7.09 (1H, ddd, $J = 2.1$, 7.9, 15.7 Hz), 7.28-7.49 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 26.1, 27.2, 28.5, 28.6, 52.5, 57.9, 59.5,

62.6, 68.6, 77.7, 80.8, 80.9, 86.3, 110.9, 111.4, 125.4, 125.9, 127.7, 129.2, 129.5, 136.7, 137.1, 141.6, 166.8, 167.4.

1aa: ^1H NMR (200 MHz, CDCl_3) δ 1.29, 1.33, 1.36, 1.41 (12H, 4s), 3.21 (1H, dd, $J = 8.4$, 2.1 Hz), 3.44 (3H, s), 3.55–4.11 (6H, m), 3.75 (3H, s), 4.14 (1H, dd, $J = 6.0$, 8.3 Hz), 4.39 (1H, dd, $J = 5.0$, 7.6 Hz), 4.65 (1H, d, $J = 4.9$ Hz), 6.19 (1H, d, $J = 15.8$ Hz), 7.08 (1H, dd, $J = 8.3$, 15.8 Hz), 7.21–7.40 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 25.3, 26.4, 27.8, 51.7, 55.7, 57.4, 59.2, 60.7, 61.4, 67.5, 76.5, 79.0, 80.0, 83.9, 110.2, 110.9, 125.4, 125.8, 128.6, 136.0, 141.2, 166.0, 166.9.

1ab: ^1H NMR (200 MHz, CDCl_3) δ 1.32, 1.39, 1.41, 1.44 (12H, 4s), 3.21 (1H, dd, $J = 8.4$, 2.1 Hz), 3.33 (3H, s), 3.62 (3H, s), 3.74 (1H, dd, $J = 4.5$, 8.4 Hz), 3.80 (1H, d, $J = 2.1$ Hz), 3.92–4.19 (5H, m), 4.32 (1H, dd, $J = 4.1$, 6.9 Hz), 4.72 (1H, d, $J = 4.5$ Hz), 5.97 (1H, d, $J = 15.8$ Hz), 6.79 (1H, dd, $J = 8.3$, 15.8 Hz), 7.20–7.41 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 25.2, 26.4, 27.1, 27.5, 51.5, 52.4, 58.1, 58.7, 59.5, 61.6, 67.8, 77.1, 78.9, 80.1, 84.7, 110.3, 110.5, 124.9, 126.0, 128.5, 135.7, 141.5, 165.3, 167.0.

1ba: ^1H NMR (200 MHz, CDCl_3) δ 0.98, 1.11, 1.38, 1.43 (12H, 4s), 3.28 (1H, dd, $J = 8.0$, 2.0 Hz), 3.52 (1H, dd, $J = 4.5$, 8.0 Hz), 3.64 (3H, s), 3.75–3.78 (1H, m), 3.76 (1H, d, $J = 2.0$ Hz), 3.79 (3H, s), 3.85–3.91 (2H, m), 4.12–4.15 (2H, m), 4.56 (1H, dd, $J = 6.9$, 7.0 Hz), 4.66 (1H, d, $J = 4.5$ Hz), 6.13 (1H, dd, $J = 15.8$, 1.2 Hz), 7.00 (1H, dd, $J = 7.5$, 15.8 Hz), 7.27–7.38 (5H, m); ^{13}C NMR (50 MHz, CDCl_3) δ 25.3, 26.3, 27.2, 27.3, 51.8, 55.7, 57.9, 59.3, 59.5, 60.0, 67.8, 77.0, 79.7, 79.9, 84.6, 110.1, 110.7, 125.7, 125.9, 128.5, 136.3, 140.2, 165.8, 166.8.

1bb: ^1H NMR (400 MHz, CDCl_3) δ 1.36, 1.41, 1.43, 1.44 (12H, 4s), 3.38 (1H, dd, $J = 7.8$, 1.6 Hz), 3.48 (3H, s), 3.51 (1H, dd, $J = 4.8$, 7.8 Hz), 3.72 (1H, d, $J = 1.6$ Hz), 3.77 (3H, s), 3.79 (1H, dd, $J = 7.4$, 5.1 Hz), 3.93 (1H, dd, $J = 4.9$, 7.8 Hz), 4.03–4.12 (2H, m), 4.16 (1H, dd, $J = 7.4$, 5.1 Hz), 4.50 (1H, dd, $J = 5.1$, 7.4 Hz), 4.65 (1H, d, $J = 4.8$ Hz), 6.14 (1H, dd, $J = 15.9$, 1.0 Hz), 7.08 (1H, dd, $J = 7.2$, 15.9 Hz), 7.25–7.45 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 25.1, 26.2, 27.6, 27.7, 51.7, 56.8, 56.9, 59.2, 60.3, 60.9, 67.5, 76.7, 79.6, 80.1, 83.8, 110.0, 110.7, 125.3, 125.7, 128.5, 135.9, 140.2, 165.9, 166.5.

2aa: ^1H NMR (200 MHz, CDCl_3) δ 1.29, 1.33, 1.38, 1.41 (12H, 4s), 3.38 (1H, dd, $J_{5,4} = 8.1$ Hz, $J = 1.0$ Hz), 3.51 (3H, s), 3.62–4.25 (5H, m), 3.77 (1H, d, $J = 1.0$ Hz), 4.69 (1H, d, $J = 3.1$ Hz), 4.65–4.72 (1H, m), 4.76 (1H, d, $J = 4.9$ Hz), 7.26–7.33 (5H, m), 9.77 (1H, s); ^{13}C NMR (50 MHz, CDCl_3) δ 25.2, 26.4, 27.0, 27.3, 57.4, 59.3, 60.4, 61.6, 62.3, 67.8, 76.8, 77.1, 78.8, 84.4, 110.4, 110.6, 125.8, 128.6, 136.0, 167.9, 195.4.

2ab: ^1H NMR (200 MHz, CDCl_3) δ 1.32, 1.41, 1.43, 1.44 (12H, 4s), 3.31 (1H, dd, $J = 8.2$, 2.1 Hz), 3.61 (1H, dd, $J = 7.8$, 8.2 Hz), 3.65 (3H, s), 3.82 (1H, d, $J = 2.1$ Hz), 3.86–4.15 (3H, m), 4.18 (1H, dd, $J = 5.9$, 7.9 Hz), 4.55 (1H, dd, $J = 2.5$, 7.8 Hz), 4.78 (1H, d, $J = 2.5$ Hz), 4.82 (1H, d, $J = 4.6$ Hz), 7.22–7.40 (5H, m), 9.47 (1H, s); ^{13}C NMR (50 MHz, CDCl_3)

δ 25.0, 26.3, 26.5, 27.1, 57.2, 58.3, 59.3, 59.6, 62.5, 67.7, 76.9, 77.1, 77.5, 85.1, 110.3, 110.4, 125.5, 128.5, 128.9, 135.7, 195.0.

2ba: ^1H NMR (200 MHz, CDCl_3) δ 0.95, 1.35, 1.36, 1.46 (12H, 4s), 3.21 (1H, dd, $J = 8.0$, 1.1 Hz), 3.63 (3H, s), 3.76 (1H, d, $J = 1.1$ Hz), 3.80–4.19 (3H, m), 4.38 (1H, dd, $J = 4.8$, 7.2 Hz), 4.66 (1H, d, $J = 4.8$ Hz), 4.73 (1H, d, $J = 5.0$ Hz), 7.21–7.40 (5H, m), 9.77 (1H, s); ^{13}C NMR (50 MHz, CDCl_3) δ 25.3, 26.6, 26.7, 57.6, 59.0, 59.6, 61.0, 62.0, 68.0, 77.1, 77.7, 78.7, 84.9, 110.3, 110.4, 125.7, 128.5, 135.5, 195.3.

2bb: ^1H NMR (200 MHz, CDCl_3) δ 1.34, 1.43, 1.47 (12H, 3s), 3.31 (1H, dd, $J = 8.0$, 2.0 Hz), 3.48 (3H, s), 3.71 (1H, d, $J = 2.0$ Hz), 3.81 (1H, dd, $J = 4.9$, 8.0 Hz), 3.91 (1H, dd, $J = 7.0$, 7.6 Hz), 3.97 (1H, dd, $J = 4.6$, 7.7 Hz), 4.06–4.17 (2H, m), 4.58 (1H, d, $J = 5.5$ Hz), 4.66 (1H, dd, $J = 5.5$, 7.0 Hz), 4.75 (1H, d, $J = 4.9$ Hz), 7.21–7.42 (5H, m), 9.81 (1H, s); ^{13}C NMR (50 MHz, CDCl_3) δ 25.2, 26.4, 27.1, 56.6, 59.3, 60.6, 62.0, 63.3, 68.0, 77.1, 77.2, 79.2, 84.3, 110.3, 110.6, 125.8, 128.7, 136.2, 195.2.

6ab: ^1H NMR (400 MHz, CDCl_3) δ 1.39, 1.41, 1.42, 1.44 (12H, 4s), 2.21–2.35 (2H, m), 2.61 (1H, q, $J = 4.4$ Hz), 3.56 (3H, s), 3.59 (1H, dd, $J = 4.1$, 11.4 Hz), 3.64 (3H, s), 3.77 (1H, dd, $J = 4.1$, 9.8 Hz), 3.87 (1H, dd, $J = 6.4$, 8.3 Hz), 3.91 (1H, dd, $J = 4.6$, 4.8 Hz), 3.98 (1H, dd, $J = 5.2$, 8.4 Hz), 4.08–4.13 (1H, m), 4.18 (1H, dd, $J = 6.2$, 8.4 Hz), 4.32 (1H, dd, $J = 4.8$, 6.4 Hz), 4.39 (1H, dd, $J = 9.8$, 11.4 Hz), 4.73 (1H, d, $J = 4.1$ Hz), 7.22–7.31 (3H, m), 7.37–7.39 (2H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 25.5, 26.3, 27.3, 27.4, 31.9, 41.3, 47.0, 51.6, 52.1, 58.6, 59.1, 62.7, 67.8, 77.3, 79.5, 81.6, 84.9, 110.0, 110.5, 127.3, 128.9, 138.0, 168.3, 172.4.

6ba: ^1H NMR (400 MHz, CDCl_3) δ 1.23, 1.33, 1.34, 1.51 (12H, 4s), 2.22 (1H, dd, $J = 3.4$, 17.3 Hz), 2.66 (1H, dd, $J = 8.0$, 17.3 Hz), 2.83–2.87 (1H, m), 3.14 (1H, dd, $J = 3.6$, 11.5 Hz), 3.38 (1H, dd, $J = 4.3$, 8.2 Hz), 3.41 (3H, s), 3.63 (3H, s), 3.78 (1H, dd, $J = 3.6$, 3.8 Hz), 3.90 (1H, dd, $J = 7.2$, 7.9 Hz), 3.96–4.06 (2H, m), 4.11 (1H, dd, $J = 5.4$, 7.9 Hz), 4.27 (1H, dd, $J = 3.8$, 7.2 Hz), 4.37 (1H, dd, $J = 8.2$, 11.5 Hz), 4.59 (1H, d, $J = 4.3$ Hz), 7.27–7.41 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 25.3, 26.5, 26.9, 27.4, 28.7, 42.0, 51.2, 53.4, 59.1, 60.2, 62.7, 67.9, 77.3, 78.2, 83.7, 109.6, 110.1, 127.4, 128.7, 129.1, 137.7, 164.0, 172.6.

7aa: ^1H NMR (400 MHz, CDCl_3) δ 1.34, 1.38, 1.41 (12H, 4s), 2.82 (1H, br s), 3.67 (3H, s), 3.76 (1H, s), 3.84 (1H, d, $J = 2.9$ Hz), 3.93 (1H, br s), 4.01–4.04 (1H, m), 4.08–4.14 (1H, m), 4.16–4.22 (3H, m), 4.25 (1H, dd, $J = 1.0$, 1.1 Hz), 4.33 (1H, dd, $J = 7.9$, 4.8 Hz), 4.66 (1H, ddd, $J = 2.9$, 3.5, 7.9 Hz), 4.78 (1H, d, $J = 4.8$ Hz), 7.30–7.41 (5H, m); ^{13}C NMR (100

MHz, CDCl₃) δ 25.3, 26.1, 26.7, 27.4, 53.8, 54.1, 56.6, 59.8, 67.9, 70.6, 70.9, 77.4, 78.9, 81.2, 84.7, 110.3, 110.5, 126.9, 128.3, 128.8, 140.8, 170.8.

7ab: ¹H NMR (400 MHz, CDCl₃) δ 1.33, 1.40, 1.45, 1.49 (12H, 4s), 3.30 (1H, dd, J = 10.8, 10.4 Hz), 3.58 (3H, s), 3.74 (1H, t, J = 8.2 Hz), 3.87 (1H, dd, J = 8.6, 4.2 Hz), 3.97 (1H, dd, J = 4.8, 8.5 Hz), 4.02 (1H, dd, J = 10.4, 8.6 Hz), 4.02–4.10 (2H, m), 4.15 (1H, dd, J = 6.2, 8.5 Hz), 4.34 (1H, dd, J = 1.2, 6.8 Hz), 4.51 (1H, dd, J = 1.2, 8.2 Hz), 4.69 (1H, d, J = 4.2 Hz), 7.36–7.47 (5H, m); ¹³C NMR (100 MHz, CDCl₃) δ 25.2, 26.4, 26.9, 27.0, 50.5, 53.4, 58.7, 59.1, 67.7, 69.2, 70.6, 77.1, 77.2, 78.1, 84.5, 109.9, 110.2, 128.1, 129.0, 129.2, 129.3, 137.0, 168.3.

7ba: ¹H NMR (400 MHz, CDCl₃) δ 0.99, 1.23, 1.42, 1.4 (12H, s), 2.73 (1H, dd, J = 0.4, 11.2 Hz), 3.25 (1H, dd, J = 8.8, 0.5 Hz), 3.53 (1H, dd, J = 8.0, 4.4 Hz), 3.62 (3H, s), 3.69 (1H, dd, J = 7.2, 8.8 Hz), 3.85 (1H, d, J = 4.8 Hz), 3.93 (1H, dd, J = 5.2, 8.8 Hz), 3.95–3.98 (1H, m), 4.08 (1H, ddd, J = 8.8, 5.2, 6.4 Hz), 4.19 (1H, dd, J = 6.4, 8.8 Hz), 4.65 (1H, d, J = 4.4 Hz), 4.68 (1H, dd, J = 11.2, 8.0 Hz), 5.12 (1H, dd, J = 8.8, 7.2 Hz), 7.31–7.50 (5H, m); ¹³C NMR (100 MHz, CDCl₃) δ 24.6, 25.2, 26.6, 26.9, 53.5, 58.8, 59.0, 63.7, 64.6, 68.5, 70.8, 77.3, 77.5, 79.2, 83.7, 110.1, 110.2, 127.4, 128.4, 129.3, 138.4, 168.0.

7bb: ¹H NMR (400 MHz, CDCl₃) δ 1.38, 1.44, 1.47 (12H, 3s), 3.60 (3H, s), 3.69 (1H, dd, J = 5.9, 3.5 Hz), 3.78 (1H, dd, J = 2.1, 4.9 Hz), 3.84 (1H, dd, J = 7.5, 8.4 Hz), 3.90 (1H, dd, J = 8.4, 9.8 Hz), 4.12 (1H, ddd, J = 8.8, 7.5, 6.0 Hz), 4.20 (1H, dd, J = 6.0, 8.4 Hz), 4.24 (1H, dd, J = 7.2, 8.8 Hz), 4.37 (1H, dd, J = 3.5, 2.1 Hz), 4.53 (1H, d, J = 4.9 Hz), 4.59 (1H, ddd, J = 0.9, 9.8, 5.9 Hz), 4.97 (1H, dd, J = 7.2, 8.4 Hz), 7.22–7.28 (1H, m), 7.33 (2H, t, J = 7.2 Hz), 7.42 (2H, d, J = 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 25.3, 26.1, 26.4, 26.9, 50.9, 51.7, 59.5, 61.7, 64.9, 68.9, 71.1, 77.7, 78.2, 79.8, 83.0, 108.7, 110.5, 126.9, 128.6, 129.9, 166.7.

HMQC 145 Hz