Supplementary Material (ESI) for Chemical Communications

Supporting Information for the Paper

Direct Organocatalytic Synthesis of Enantiopure Succinimides from β-Lactam Aldehydes through Ring Expansion Promoted by Azolium Salt Precatalysts

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General methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-300, Varian VRX-300S or Bruker AC-200. NMR spectra were recorded in $CDCl_3$ solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{13}C, 76.9 ppm). Low and high resolution mass spectra were taken on a HP5989A spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. Specific rotation $[\alpha]_D$ is given in 10^{-1} deg cm^2 g^{-1} at 20 °C, and the concentration (*c*) is expressed in g per 100 mL. All commercially available compounds were used without further purification.

Succinimide (+)-4a. From 100 mg (0.426 mmol) of aldehyde (+)-**1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 88 mg (88%) of compound (+)-**4a** were obtained as a colorless solid; mp = 100–102 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +48.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21 (m, 2H), 6.99 (m, 2H), 4.36 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 3.18 (dd, *J* = 18.2, 8.2 Hz, 1H), 2.80 (dd, *J* = 18.3, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 173.4, 159.6, 127.5, 123.8, 114.5, 74.7, 59.0, 55.4,

36.0; IR (KBr, cm^{-1}) ν 1719; MS (EI), *m/z* 235 (M^+, 49), 149 (100). Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.39; H, 5.50; N, 5.99.

Succinimide (+)-4b. From 100 mg (0.323 mmol) of aldehyde (+)-**1b**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 62 mg (62%) of compound (+)-**4b** were obtained as a colorless solid; mp = 108–110 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +50.0 (*c* 0.7, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (m, 5H), 7.21 (m, 2H), 6.99 (m, 2H), 5.07 and 4.85 (d, *J* = 11.6 Hz, each 1H), 4.52 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.83 (s, 3H), 3.13 (dd, *J* = 18.3, 8.3 Hz, 1H), 2.84 (dd, *J* = 18.3, 4.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.1, 173.4, 159.6, 136.6, 128.6, 128.3, 128.3, 127.6, 123.9, 114.5, 73.1, 72.1, 55.5, 36.4; IR (KBr, cm^{-1}) ν 1716; MS (EI), *m/z* 311 (M^+, 5), 205 (100). Anal. Calcd. for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.31; H, 5.44; N, 4.53.

Succinimide (+)-4c. From 100 mg (0.286 mmol) of aldehyde (+)-**1c**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, 87 mg (87%) of compound (+)-**4c** were obtained as a colorless solid; mp = 179–180 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +8.1 (*c* 0.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.91 (m, 2H), 7.80 (m, 2H), 7.30 (m, 2H), 7.02 (m, 2H), 5.38 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.85 (s, 3H), 3.34 (dd, *J* = 18.1, 9.8 Hz, 1H), 3.10 (dd, *J* = 18.1, 6.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.0, 172.6, 166.9, 159.8, 134.6, 131.6, 127.8, 124.2, 123.9, 114.6, 55.5, 46.9, 34.2; IR (KBr, cm^{-1}) ν 1703; MS (EI), *m/z* 350 (M^+, 100). Anal. Calcd. for $C_{19}H_{14}N_2O_5$: C, 65.14; H, 4.03; N, 8.00. Found: C, 65.28; H, 4.07; N, 8.06.

Succinimide (+)-4d. From 100 mg (0.426 mmol) of aldehyde (+)-**1d**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 78 mg (78%) of compound (+)-**4d** were obtained as a colorless solid; mp = 98–100 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +48.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.17 (m, 2H), 4.36 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.68 (s, 3H), 3.18 (dd, *J* = 18.2, 8.2 Hz, 1H), 2.80 (dd, *J* = 18.3, 4.4 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.6, 173.2, 138.9, 128.6, 129.8, 126.1, 74.8, 59.0, 36.1, 21.2; IR (KBr, cm^{-1}) ν 1715; MS (EI), *m/z* 219 (M^+, 41), 133 (100). Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.61; H, 6.03; N, 6.34.

Succinimide (+)-4e. From 100 mg (0.418 mmol) of aldehyde (+)-**1e**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 76 mg (76%) of

compound (+)-**4e** were obtained as a colorless solid; mp = 119–120 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +40.0 (*c* 0.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.26 (m, 2H), 4.36 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.68 (s, 3H), 3.19 (dd, *J* = 18.3, 8.3 Hz, 1H), 2.81 (dd, *J* = 18.3, 4.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.2 , 172.8, 134.6, 129.8, 129.4, 127.5, 74.7, 59.1, 36.1; IR (KBr, cm^{-1}) ν 1707; MS (EI), *m/z* 241 (M^+, 32), 239 (M^+, 100). Anal. Calcd. for $C_{11}H_{10}ClNO_3$: C, 55.13; H, 4.21; N, 5.84. Found: C, 55.25; H, 4.37; N, 5.80.

Preparation of Succinimide (+)-4f and Maleimide 5. From 88 mg (0.29 mmol) of aldehyde (+)-**1f**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, 16 mg (20%) of the less polar compound **5** and 43 mg (49%) of the more polar compound (+)-**4f** were obtained.

Succinimide (+)-4f. Colorless solid; mp = 86–87 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +55.1 (*c* 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17 (m, 2H), 6.98 (m, 2H), 5.95 (dd, *J* = 17.9, 10.4 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 5.16 (d, *J* = 16.4 Hz, 1H), 3.83 (s, 3H), 3.34 (s, 3H), 2.90 (d, *J* = 18.9 Hz, 2H), 1.23 and 1.21 (s, each 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.4, 173.6, 159.6, 141.9, 127.5, 124.1, 115.0, 114.5, 84.9, 55.5, 52.5, 44.4, 34.3, 21.6, 21.0; IR (KBr, cm^{-1}) ν 1712; MS (EI), *m/z* 303 (M^+, 21), 235 (100). Anal. Calcd. for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.43; H, 6.93; N, 4.58.

Maleimide 5. Colorless solid; mp = 70–72 ºC (hexanes/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24 (m, 2H), 6.97 (m, 2H), 6.39 (s, 1H), 6.14 (dd, *J* = 17.6, 10.3 Hz, 1H), 5.15 (d, *J* = 11.0 Hz, 1H), 5.15 (d, *J* = 17.1 Hz, 1H), 3.83 (s, 3H), 1.47 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.3, 159.0, 155.5, 143.2, 127.5, 125.7, 124.1, 114.3, 113.6, 55.5, 38.7, 25.8; IR ($CHCl_3$, cm^{-1}) ν 1703; MS (EI), *m/z* 271 (M^+, 100). Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.92; H, 6.29; N, 5.12.

Succinimide (+)-4g. From 50 mg (0.183 mmol) of aldehyde (+)-**1g**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 41 mg (82%) of compound (+)-**4g** were obtained as a colorless solid; ; mp = 145–147 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = +1.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.98 (m, 2H), 5.88 (m, 2H), 4.49 and 4.28 (m, each 1H), 3.82 (s, 3H), 3.04 and 2.78 (d, *J* = 17.8 Hz, each 1H), 2.76 and 2.21 (m, each 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.6, 173.2, 159.6, 127.5, 125.5, 124.0, 120.8,

114.4, 74.0, 62.9, 55.4, 41.0, 31.0; IR (KBr, cm^{-1}) ν 1711; MS (EI), *m/z* 273 (M^+, 54), 149 (100). Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.04; H, 5.49; N, 5.10.

Succinimide (–)-4a. From 50 mg (0.213 mmol) of aldehyde (+)-*epim*-**1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, 40 mg (80%) of compound (–)-**4a** were obtained as a colorless solid; mp = 73–75 ºC (hexanes/ethyl acetate); $[\alpha]_D$ = –49.6 (*c* 0.7, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.21 (m, 2H), 6.99 (m, 2H), 4.36 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 3.18 (dd, *J* = 18.2, 8.2 Hz, 1H), 2.80 (dd, *J* = 18.3, 4.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.7, 173.4, 159.6, 127.6, 123.9, 114.5, 74.7, 59.0, 55.5, 36.1; IR (KBr, cm^{-1}) ν 1719; MS (EI), *m/z* 235 (M^+, 45), 149 (100). Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.40; H, 5.61; N, 6.04.