

A typical cyclization procedure:

To a solution of the β -aminoallene, RX (5 equiv) and K_2CO_3 (5 equiv) in DMF (0.1 M), $Pd(PPh_3)_4$ (1 mol%) was added under an inert atmosphere. The reaction was carried out under the indicated conditions and quenched with saturated aqueous NH_4Cl . The mixture was extracted with ether (3 \times), dried with $MgSO_4$ and concentrated. The residue was purified with flash column chromatography to give the pure products.

Spectroscopic data of selected compounds:

2-Amino-4,5-hexadienoic acid amide (7): mp: 210–211 °C; IR (film) ν 3431, 3282, 3200, 2750, 1661 cm^{-1} ; 1H NMR (CD_3OD , 400 MHz) δ 2.54–2.64 (m, 2 H), 3.94 (dd, $J = 5.2, 7.4$ Hz, 1 H), 4.84–4.86 (m, 2 H), 5.13 (quintet, $J = 7.0$ Hz, 1 H); ^{13}C NMR (CD_3OD , 100 MHz) δ 32.20, 53.88, 76.38, 84.08, 171.63, 211.35; HRMS (FAB): calcd. for $C_6H_{12}N_2OCl$ (M + H): 123.0638, found: 123.0629.

(R)-2-Amino-4,5-hexadienoic acid (8): mp: 231–235 °C; $[\alpha]_D + 48$ (c 0.5, H_2O); IR (film) ν 3850–2600, 1651 cm^{-1} ; 1H NMR (CD_3OD , 400 MHz) δ 2.47–2.65 (m, 2 H), 3.58 (dd, $J = 4.2, 7.8$ Hz, 1 H), 4.79–4.82 (m, 2 H), 5.13 (q, $J = 7.0$ Hz, 1 H); ^{13}C NMR (CD_3OD , 50 MHz) δ 31.72, 56.04, 77.85, 85.50, 175.82, 211.392; HRMS (FAB): calcd. for $C_6H_{10}NO_2$ (M + H): 128.0712, found: 128.0703.

Azetidine 18a: IR (film) ν 2921, 1360, 1183 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 0.86 (s, 9 H, *t*-Bu), 1.12–1.23 (m, 1 H), 1.88–1.93 (m, 3 H), 2.06–2.09 (m, 2 H), 2.18–2.24 (m, 1 H), 2.29–2.38 (m, 2 H), 2.46 (s, 3 H), 3.70–3.74 (m, 2 H), 4.68–4.75 (m, 1 H), 5.17 (s, 1 H), 5.46 (br s, 1 H), 5.54 (d, $J = 5.6$ Hz, 1 H), 7.36 (d, $J = 8.0$ Hz, 2 H), 7.73 (d, $J = 7.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.47, 23.91, 25.26, 25.64, 27.01, 27.19, 27.24, 27.37, 32.01, 43.62, 47.32, 63.90, 109.50, 124.01, 128.34, 129.53, 132.42, 133.28, 143.70, 146.03; HRMS (EI) calcd. for $C_{22}H_{31}NO_2S$: 373.2075, found: 373.2088.

Tetrahydropyridine 20b: IR (film) ν 2836, 1529, 1349, 1169 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 2.38–2.39 (m, 2 H), 3.3–3.37 (m, 2 H), 4.04–4.05 (m, 2 H), 6.07–6.09 (m, 1 H), 7.26–7.36 (m, 5 H), 8.02 (d, $J = 8.5$ Hz, 2 H), 8.35 (d, $J = 8.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100

MHz) δ 25.23, 42.22, 46.19, 122.03, 124.24, 125.03, 127.86, 128.53, 128.56, 133.09, 138.17, 143.01, 150.02; HRMS (FAB): calcd. for $C_{17}H_{16}N_2O_4S$ (M + H): 344.0831, found: 344.0847.

Azetidine 25a: $[\alpha]_D +4.0$ (c 1, CH_2Cl_2); IR (film) ν 2967, 2923, 2852, 1734, 1260, 1092 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 2.09 (dt, $J = 7.7, 3.3$ Hz, 1 H), 2.45 (s, 3 H), 2.68 (dt, $J = 1.7, 9.0$ Hz, 1 H), 3.72 (s, 3 H), 4.70 (dd, $J = 7.7, 9.4$ Hz, 1 H), 5.00 (t, $J = 8.1$ Hz, 1 H), 5.42 (s, 1 H), 5.54 (s, 1 H), 7.27–7.31 (m, 5 H), 7.33 (d, $J = 8.1$ Hz, 2 H), 7.81 (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.50, 28.38, 52.23, 56.72, 61.62, 114.83, 126.11, 127.85, 128.13, 128.33, 129.46, 136.10, 137.68, 144.02, 146.03, 170.39; HRMS (EI): calcd. for $C_{20}H_{21}NO_4S$: 371.1191, found: 371.1195.

Pipecolic acid 25b: $[\alpha]_D -10.0$ (c 1, CH_2Cl_2); IR (film) ν 2924, 2853, 1747, 1457, 1340, 1163 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s, 3 H), 2.71–2.72 (m, 2 H), 3.49 (s, 3 H), 4.15 (dd, $J = 2.2, 16.4$ Hz, 1 H), 4.48 (dd, $J = 2.0, 16.4$ Hz, 1 H), 4.93 (dd, $J = 3.4, 5.1$ Hz, 1 H), 6.01–6.04 (m, 1 H), 7.27–7.34 (m, 5 H and d, $J = 8.3$ Hz, 2 H), 7.71 (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.41, 29.57, 43.40, 52.05, 52.13, 119.17, 125.04, 127.74, 128.39, 127.18, 129.39, 133.67, 136.11, 143.31, 138.17, 170.70; HRMS (EI): calcd. for $C_{20}H_{21}NO_4S$: 371.1191, found: 371.1169.

Azetidine 26a: IR (film) ν : 2954, 1749, 1338, 1159 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 0.86 (s, 9 H, *t*-Bu), 1.84–1.88 (m, 2 H), 1.96–1.99 (m, 2 H), 2.00–2.12 (m, 2 H), 2.25–2.28 (m, 1 H), 2.44 (s, 3 H), 2.64–2.71 (m, 1 H), 3.70 (s, 3 H), 4.63–4.68 (m, 1 H), 4.86–4.92 (m, 1 H), 5.07 (s, 1 H), 5.33 (d, $J = 10.6$ Hz, 1 H), 5.49–5.53 (m, 1 H), 7.32 (d, $J = 8.0$ Hz, 2 H), 7.79 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.49, 23.85, 27.12, 27.19, 27.26, 27.32, 29.04, 29.38, 31.99, 43.57, 52.18, 57.00, 60.70, 110.07, 124.32, 128.15, 129.40, 133.06, 133.14, 143.88, 145.42, 170.57; HRMS (FAB): calcd. for $C_{24}H_{34}NO_4S$ (M + H): 432.2209, found: 432.2207.

Azetidine 27a: $[\alpha]_D -9.2$ (c 0.9, CH_2Cl_2); IR (film) ν : 2955, 1752, 1336, 1159, 1093 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 0.85–0.92 (m, 3 H), 1.25–1.42 (m, 4 H), 1.94–2.01 (m, 1 H), 2.18 (t, $J = 7.3$ Hz, 2 H), 2.44 (s, 3 H), 2.63–2.70 (m, 1 H), 3.71 (s, 3 H), 4.65 (dd, $J = 2.0, 7.6$ Hz, 1 H), 4.73 (s, 1 H), 4.81–4.85 (m, 1 H), 4.90 (s, 1 H), 5.20 (s, 1 H), 5.49 (s, 1 H), 7.32 (d, $J = 8.1$ Hz, 2 H), 7.78 (d, $J = 8.2$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.80, 21.49, 22.38,

29.02, 30.44, 33.87, 52.21, 56.89, 60.87, 111.20, 113.17, 128.17, 129.44, 134.37, 143.99,
144.62, 144.80, 170.50; HRMS (FAB): calcd. for $C_{20}H_{28}NO_4S$ (M + H): 378.1739, found:
378.1743.