Intramolecular Cyclization of Ene-Imine Using Dibutylzirconocene

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Contents of Supporting Information

Experimental Section S1-S17

General. All manipulations were performed under an argon atmosphere unless otherwise mentioned. Solvents were distilled under an argon atmosphere from sodium-benzophenone (THF, Et₂O, toluene, and benzene), CaH₂ (CH₂Cl₂), or sodium (EtOH, MeOH). All other solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh) using the indicated solvent.

General Procedure for the Synthesis of Imines (1a-e) from Aldehydes (3a) and Amines. A solution of ene-aldehyde **3a** (1 equiv) and amine (1 equiv) in benzene (0.1 M) was stirred in the presence of MgSO₄ (10 equiv) at room temperature overnight. The solution was filtered, and the filtrate was concentrated. The residue was used

without further purification.

***N*-(3,3-bis(benzyloxymethyl)hex-5-enylidene)(phenyl)methanamine (1a):** IR (neat) ν 3063, 3028, 2857, 1662, 1495, 1453, 1364, 1099 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.21 (d, $J = 7.6$ Hz, 2 H), 2.39 (d, $J = 5.6$ Hz, 2 H), 3.39 (d, $J = 2.8$ Hz, 4 H), 4.45 (s, 4 H), 4.49 (s, 2 H), 5.00-5.02 (m, 1 H), 5.04 (s, 1 H), 5.74-5.84 (m, 1 H), 7.83 (dt, $J = 1.6, 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.7, 39.9, 42.4, 65.3, 73.0, 73.2, 118.1, 126.7, 127.3 (x 2), 127.9 (x 4), 128.2 (x 4), 128.3 (x 2), 128.3 (x 2), 133.8 (x 2), 138.5, 164.3; LRMS (EI) m/z 428 ($\text{M}^+ + \text{H}$), 386, 350, 336, 306, 133, 91; HRMS (EI) calcd for $\text{C}_{29}\text{H}_{33}\text{NO}_2$ (M^+) 427.2511, found 427.2520.

***N*-(3,3-bis(benzyloxymethyl)hex-5-enylidene)methanamine (1b):** IR (neat) ν 3062, 3029, 2857, 1667, 1099 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.20 (d, $J = 7.6$ Hz, 2 H), 2.32 (dd, $J = 1.2, 5.4$ Hz, 2 H), 3.02 (bd, $J = 1.2$ Hz, 3 H), 3.35 (d, $J = 9.2$ Hz, 2 H), 3.41 (d, $J = 9.2$ Hz, 2 H), 4.48 (s, 2 H), 4.48 (s, 2 H), 5.02-5.06 (m, 2 H), 5.74-5.84 (m, 1 H), 7.23-7.34 (m, 10 H), 7.69 (dt, $J = 1.6, 5.2$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.6, 39.7, 42.3, 48.0, 73.0 (x 2), 73.2 (x 2), 118.0, 127.3 (x 4), 128.2 (x 2), 133.8 (x 2), 138.6, 164.3; LRMS (EI) m/z 352 ($\text{M}^+ + \text{H}$), 336, 260, 230, 107, 91, 57; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_2$ (M^+) 351.2198, found 351.2196.

***N*-(3,3-bis(benzyloxymethyl)hex-5-enylidene)propan-1-amine (1c):** IR (neat) ν 3065, 3030, 2927, 2857, 1664, 1454, 1100 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, $J = 7.2$ Hz, 3 H), 1.56 (qt, $J = 7.2, 7.2$ Hz, 2 H), 2.20 (d, $J = 7.2$ Hz, 2 H), 2.32 (d, $J = 5.6$ Hz, 1 H), 3.26 (t, $J = 7.2$ Hz, 3 H), 3.39 (dd, $J = 9.2, 10.4$ Hz, 4 H),

4.48 (s, 4 H), 5.03 (s, 1 H), 5.06 (bd, $J = 2.4$ Hz, 1 H), 5.75-5.85 (m, 1 H), 7.25-7.36 (m, 10H), 7.68 (bt, $J = 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.9, 23.9, 37.5, 39.5, 42.2, 63.3, 72.9, 73.1, 73.1, 73.2, 118.0, 127.3, 127.4, 128.2, 128.3, 133.8, 138.5, 162.8; LRMS (EI) m/z 380 ($\text{M}^+\text{+H}$), 350, 338, 288, 258, 107, 91, 85, 70, 56, 43; HRMS calcd for $\text{C}_{25}\text{H}_{33}\text{NO}_2$ (M^+) 379.2511, found 379.2504.

***N*-(3,3-bis(benzyloxymethyl)hex-5-enylidene)propan-2-amine (1d):** IR (neat) ν 3064, 3030, 2965, 2858, 1664, 1099 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (d, $J = 6.4$ Hz, 6 H), 2.20 (d, $J = 7.6$ Hz, 2 H), 2.30 (d, $J = 5.6$ Hz, 2 H), 3.20 (qq, $J = 6.4, 6.4$ Hz, 1 H), 4.42 (dd, $J = 9.2, 10.4$ Hz, 4 H), 4.48 (s, 4 H), 5.02 (s, 1 H), 5.05 (bd, $J = 2.8$ Hz, 1 H), 5.75-5.85 (m, 1 H), 7.24-7.36 (m, 10H), 7.70 (t, $J = 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 24.1, 37.6, 39.5, 42.3, 61.4, 72.7, 73.0, 73.2 (x 2), 118.0, 127.3, 127.4, 128.2, 128.3, 133.8, 138.6, 160.2; LRMS (EI) m/z 380 ($\text{M}^+\text{+H}$), 364, 338, 288, 258, 107, 91, 85, 70, 43; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{29}\text{NO}_2$ ($\text{M}^+\text{+H}$) 380.2589, found 380.2591.

***N*-(3-(benzyloxy)methyl)-3-(benzyloxymethyl)hex-5-enylidene)-2-methylpropan-2-amine (1e):** IR (neat) ν 3065, 3031, 2966, 2860, 1661, 1212, 1099 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (s, 9 H), 2.19 (d, $J = 7.6$ Hz, 2 H), 2.32 (d, $J = 5.2$ Hz, 2 H), 3.38 (s, 4 H), 4.47 (s, 1 H), 5.02 (s, 1 H), 5.05 (bd, $J = 3.2$ Hz, 1 H), 5.76-5.86 (m, 1 H), 7.25-7.36 (m, 10 H), 7.67 (t, $J = 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.6, 37.6, 40.2, 42.3, 56.8, 73.1, 73.1, 73.2, 73.2, 117.9, 127.2, 127.3, 128.1, 128.2, 133.9, 138.5, 157.2; LRMS (EI) m/z 394 ($\text{M}^+\text{+H}$), 378, 352, 302, 272, 107, 91, 84, 57,

41; HRMS (EI) calcd for $C_{26}H_{36}NO_2$ ($M^+ + H$) 394.2746, found 394.2756.

General Procedure for the zirconium-mediated cyclization of ene-imine. To a solution of Cp_2ZrCl_2 (1.3 equiv) in THF (0.1 M) was added BuLi (1.6 M solution in hexane, 2.6 equiv) at $-78\text{ }^\circ\text{C}$ and the solution was stirred at the same temperature for 1 h. To this solution was added ene-imine **1** (1 equiv) at $-78\text{ }^\circ\text{C}$ and the solution was stirred at room temperature for the appropriate hours. Saturated NH_4Cl solution was added, and the solution was stirred at room temperature for 2 h. The aqueous layer was made basic by K_2CO_3 , and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The residue was purified by flash column chromatography on silica gel to give the cyclized product.

***N*-benzyl-4,4-bis(benzyloxymethyl)-2-methylcyclopentanamine (*trans*-**2a**, *cis*-**2a**):** *trans*-**2a**: IR (neat) ν 2919, 2856, 1095 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, $J = 6.4$ Hz, 3 H), 1.10 (dd, $J = 10.6, 12.4$ Hz, 1 H), 1.27 (dd, $J = 9.6, 13.2$ Hz, 1 H), 1.40 (bs, 1 H), 1.71-1.78 (m, 1 H), 1.81 (dd, $J = 7.2, 13.2$ Hz, 1 H), 2.04 (dd, $J = 7.2, 13.2$ Hz, 1 H), 2.58 (dd, $J = 9.2, 9.6$ Hz, 1 H), 3.33 (s, 2 H), 3.38 (dd, $J = 8.8, 12.2$ Hz, 2 H), 3.67 (d, $J = 13.2$ Hz, 1 H), 3.83 (d, $J = 12.8$ Hz, 1 H), 4.51 (s, 4 H), 7.22-7.34 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 39.7, 39.8, 44.5, 52.7, 64.9, 73.1, 73.2, 75.2, 75.4, 126.7, 127.2 (x 2), 127.3 (x 4), 127.9 (x 2), 128.2 (x 4), 128.3 (x 2), 138.6 (x 2), 140.8; LRMS (FAB) m/z 430 ($M^+ + H$), 338, 91; HRMS (FAB) calcd for $C_{29}H_{36}NO_2$ ($M^+ + H$) 430.2746, found 430.2726. *cis*-**2a**: IR (neat) ν 2922, 2856, 1095 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, $J = 7.2$ Hz, 3 H), 1.39 (dd,

$J = 7.6, 13.6$ Hz, 1 H), 1.58 (dd, $J = 6.0, 13.2$ Hz, 1 H), 1.64-1.71 (m, 2 H), 2.10-2.20 (m, 1 H), 3.04 (q, $J = 6.0$ Hz, 1 H), 3.33 (s, 2 H), 3.45 (s, 2 H), 3.63 (d, $J = 13.2$ Hz, 1 H), 3.75 (d, $J = 13.2$ Hz, 1 H), 4.51 (d, $J = 2.0$ Hz, 4 H), 7.22-7.34 (m, 15 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.6, 36.5, 37.4, 38.6, 45.7, 52.2, 61.1, 73.1, 73.2, 75.2, 75.7, 126.6, 127.2 (x 2), 127.3 (x 4), 127.4 (x 2), 128.0 (x 4), 128.2 (x 2), 138.8 (x 2), 141.0; LRMS (FAB) m/z 430 ($\text{M}^+\text{+H}$), 338, 91; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{36}\text{NO}_2$ ($\text{M}^+\text{+H}$) 430.2746, found 430.2765.

4,4-bis(benzyloxymethyl)-*N*,2-dimethylcyclopentanamine (*trans*-2b, *cis*-2b):

***trans*-2b:** IR (neat) ν 3566, 2924, 2849, 1654, 1560, 1451, 1095, 1026 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.05 (d, $J = 6.4$ Hz, 3 H), 1.22 (dd, $J = 10.0, 13.4$ Hz, 1 H), 1.51 (dd, $J = 8.0, 13.6$ Hz, 1 H), 1.86-1.93 (m, 1 H) 1.99-2.08 (m, 2 H), 2.40 (s, 3 H), 2.71 (dd, $J = 8.0, 15.6$ Hz, 1 H), 3.37 (d, $J = 6.8$ Hz, 2 H), 3.39 (d, $J = 8.8$ Hz, 2 H), 3.37 (dd, $J = 8.4, 16.0$ Hz, 2H), 4.47-4.50 (m, 4 H), 7.24-7.34 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.7, 35.7, 37.4, 38.3, 45.0, 46.4, 58.2, 73.2 (x2) 75.3, 75.9, 127.3 (x 4), 127.4 (x 2), 128.2 (x 4), 138.6, 138.8; LRMS (EI) m/z 354 ($\text{M}^+\text{+H}$), 276, 262, 232, 91; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_2$ (M^+) 353.2355, found 353.2337.

***cis*-2b:** IR (neat) ν 2955, 2925, 2855, 1453, 1362, 1099, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.05 (d, $J = 6.4$ Hz, 3 H), 1.43 (dd, $J = 8.4, 13.6$ Hz, 1 H), 1.68 (dd, $J = 5.2, 14.0$ Hz, 1 H), 1.74-1.82 (m, 2 H), 2.18-2.24 (m, 1 H), 2.38 (s, 3 H), 3.07 (dd, $J = 5.6, 11.2$ Hz, 1 H), 3.28-3.47 (m, 4 H), 4.47-4.50 (m, 4 H), 7.23-7.34 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.9, 22.4, 39.5, 40.4, 44.6, 47.4, 62.7, 73.1, 73.2, 75.3,

75.5, 127.2 (x 2), 127.3 (x 2), 127.4 (x 2), 128.2 (x 4), 138.6, 138.8; LRMS (FAB) m/z 354 ($M^+ + H$), 276, 262, 232, 91; HRMS (EI) calcd for $C_{23}H_{31}NO_2$ (M^+) 353.2355, found 353.2351.

4,4-bis(benzyloxymethyl)-2-methyl-N-propylcyclopentanamine (*trans*-2c, *cis*-2c):

***trans*-2c:** IR (neat) ν 2953, 2855, 1654, 1560, 1452, 1099, 1028 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.2$ Hz, 3 H), 0.98 (d, $J = 6.4$ Hz, 3 H), 1.11 (dd, $J = 10.8$, 12.6 Hz, 1 H), 1.23 (dd, $J = 9.6$, 13.2 Hz, 1 H), 1.46 (qt, $J = 7.6$, 7.6 Hz, 2 H), 1.68-1.77 (m, 1 H), 1.81 (dd, $J = 7.6$, 12.6 Hz, 1 H), 1.99 (dd, $J = 6.4$, 13.2 Hz, 1 H), 2.04 (bs, 1 H), 2.46-2.61 (m, 3 H), 3.33 (s, 2 H), 3.36 (dd, $J = 8.4$, 12.8 Hz, 2 H), 4.50 (d, $J = 4.0$ Hz, 2 H), 7.24-7.34 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 18.0, 23.4, 39.6, 39.8, 39.8, 44.5, 50.4, 65.2, 73.1, 73.2, 75.3, 75.5, 127.2 (x 2), 127.3 (x 2), 127.4 (x 2), 128.2 (x 4), 138.7, 138.8; LRMS (EI) m/z 381 (M^+), 380, 366, 290, 91; HRMS (EI) calcd for $C_{25}H_{35}NO_2$ (M^+) 381.2668, found 381.2672. ***cis*-2c:** IR (neat) ν 2953, 2855, 1654, 1560, 1452, 1099, 1028 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.2$ Hz, 3 H), 0.98 (d, $J = 6.4$ Hz, 3 H), 1.22-1.24 (m, 1 H), 1.39 (dd, $J = 7.6$, 13.6 Hz, 1 H), 1.44-1.48 (m, 2 H), 1.68-1.77 (m, 1 H), 1.81 (dd, $J = 7.6$, 12.6 Hz, 1 H), 1.99 (dd, $J = 6.4$, 13.2 Hz, 1 H), 2.10-2.20 (m, 1 H), 2.46-2.61 (m, 3 H), 3.04 (q, $J = 6.0$ Hz, 1 H), 3.33 (s, 2 H), 3.36 (dd, $J = 8.4$, 12.8 Hz, 2 H), 4.50 (d, $J = 4.0$ Hz, 2 H), 7.24-7.34 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 37.0, 37.1, 38.5, 44.5, 50.4, 58.5, 58.7, 65.2, 73.1, 73.2, 75.3, 75.5, 127.2 (x 2), 127.3 (x 2), 127.4 (x 2), 128.2 (x 4), 138.7, 138.8; LRMS (EI) m/z 381 (M^+), 380, 366, 290, 91; HRMS (EI)

calcd for $C_{25}H_{35}NO_2$ (M^+) 381.2668, found 381.2675.

4,4-bis(benzyloxymethyl)-*N*-isopropyl-2-methylcyclopentanamine (*trans*-**2d**, *cis*-**2d**): *trans*-**2d**: IR (neat) ν 2955, 2925, 2855, 1453, 1362, 1099, 1028 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.98 (d, $J = 6.4$ Hz, 3 H), 1.01 (d, $J = 6.4$ Hz, 3 H), 1.05 (d, $J = 6.4$ Hz, 3 H), 1.11 (dd, $J = 11.2, 13.2$ Hz, 1 H), 1.21 (dd, $J = 9.6, 13.2$ Hz, 1 H), 1.65-1.73 (m, 1 H), 1.81 (dd, $J = 7.6, 13.2$ Hz, 1 H), 2.01 (dd, $J = 7.2, 13.2$ Hz, 1 H), 2.61 (dt, $J = 7.6, 9.6$ Hz, 1 H), 2.83 (qd, $J = 6.4$ Hz, 1 H), 3.33 (s, 2H), 3.36 (dd, $J = 8.8, 13.6$ Hz, 1 H), 4.50 (s, 2 H), 4.51 (s, 2 H), 7.23-7.34 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 22.4, 23.9, 39.5, 39.9, 40.4, 44.6, 47.4, 62.7, 73.1, 73.2, 75.3, 75.5, 127.2 (x 2), 127.3 (x 2), 127.4 (x 2), 128.2 (x 4), 138.6, 138.8; LRMS (EI) m/z 381(M^+), 380, 366, 290, 91; HRMS (EI) calcd for $C_{25}H_{35}NO_2$ (M^+) 381.2668, found 381.2675. *cis*-**2d**: IR (neat) ν 3566, 2924, 2849, 1654, 1560, 1451, 1095, 1026 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 0.89 (d, $J = 7.2$ Hz, 3 H), 1.02 (d, $J = 6.4$ Hz, 3 H), 1.03 (d, $J = 6.4$ Hz, 3 H), 1.38 (dd, $J = 5.6, 13.6$ Hz, 1 H), 1.44 (dd, $J = 8.2, 13.2$ Hz, 1 H), 1.68 (dd, $J = 7.6, 13.6$ Hz, 1 H), 1.76 (dd, $J = 6.4, 13.2$ Hz, 1 H), 1.84 (bs, 1 H), 2.14 (ddd, $J = 6.0, 7.2, 13.2$ Hz, 1 H), 2.81 (td, $J = 6.4, 12.4$ Hz, 1 H), 3.17 (td, $J = 6.0, 8.2$ Hz, 1 H), 3.31 (s, 2 H), 3.39 (s, 2 H), 4.50 (d, $J = 2.0$ Hz, 2 H), 4.51 (s, 2 H), 7.24-7.34 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 22.7, 23.1, 35.7, 37.4, 38.3, 45.0, 46.4, 58.2, 73.2, 73.2, 75.3, 75.9, 127.3 (x 2), 127.3 (x 2), 127.4 (x 2), 128.2 (x 4), 138.6, 138.8; LRMS (EI) m/z 381(M^+), 380, 366, 290, 91; HRMS (EI) calcd for $C_{25}H_{35}NO_2$ (M^+) 381.2668, found 381.2672.

4,4-bis(benzyloxymethyl)-*N*-tert-butyl-2-methylcyclopentanamine (*cis*-2 e): IR (neat) ν 2957, 2860, 1456, 1387, 1362, 1229, 1206, 1097, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.87 (d, J = 7.2 Hz, 3 H), 1.02 (s, 9 H), 1.33 (dd, J = 5.6, 13.6 Hz, 1 H), 1.41 (dd, J = 8.2, 13.2 Hz, 1 H), 1.48 (bs, 1 H), 1.63 (dd, J = 7.2, 13.6 Hz, 1 H), 1.75 (dd, J = 6.4, 13.2 Hz, 1 H), 1.96-2.02 (m, 1 H), 3.09 (dd, J = 10.1, 13.6 Hz, 1 H), 3.32 (s, 2 H), 4.50 (s, 2 H), 4.51 (s, 2 H), 7.23-7.31 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.1, 30.1, 37.6, 38.4, 40.9, 44.8, 50.6, 73.1, 73.2, 75.5, 76.0, 127.2 (x 2), 127.4 (x 4), 128.2 (x 4), 138.8 (x 2); LRMS (EI) m/z 395 (M^+), 380, 304, 91, 57; HRMS (EI) calcd for $\text{C}_{26}\text{H}_{37}\text{NO}_2$ (M^+) 395.2824, found 395.2811.

(2-(benzylamino)-4,4-bis(benzyloxymethyl)cyclopentyl)methanol (*trans*-6a, *cis*-6a): To a solution of azazirconacycle **5a**, which was prepared from Cp_2ZrCl_2 (95 mg, 0.325 mmol), BuLi (1.46 M in hexane, 0.44 mL, 0.65 mmol **1a** (106.9 mg, 0.25 mmol), was added $\text{NiCl}_2(\text{PPh}_3)_2$ (327 mg, 1.2 eq) at 0 °C and the whole mixture was stirred at room temperature for 6 h. The argon atmosphere in the reaction vessel changed to oxygen and the mixture was stirred for 12 h under oxygen. Sat. NH_4Cl solution was added at 0 °C and the mixture was stirred for 1 h. The aqueous layer was made basic by K_2CO_3 and was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 , and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 5/1-0/1) to give ***trans*-6a** (30.6 mg, 28%) and ***cis*-6a** (13.1 mg, 12%) as a colorless oil. ***trans*-6a**: IR (neat) ν 2919, 2856, 2360, 2342, 1095 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.08 (dd, J =

10.6, 12.4 Hz, 1 H), 1.19-1.28 (m, 1 H), 1.71-1.78 (m, 2 H), 2.01-2.06 (m, 1 H), 2.22 (dd, $J = 7.2, 13.2$ Hz, 1 H), 2.43 (bs, 1 H), 2.97 (td, $J = 10.0, 7.2$ Hz, 1 H), 3.29 (d, $J = 2.8$ Hz, 2 H), 3.36 (d, $J = 2.8$ Hz, 2 H), 3.52 (t, $J = 10.0$ Hz, 1 H), 3.72 (d, $J = 12.8$ Hz, 1 H), 3.72 (dd, $J = 4.0, 10.4$ Hz, 1 H), 3.86 (d, $J = 12.8$ Hz, 1 H), 4.49 (s, 2 H), 4.50 (s, 2 H), 7.22-7.34 (m, 15 H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.8, 32.9, 39.6, 45.2, 45.6, 52.0, 64.9, 67.9, 73.2, 73.3, 75.2, 75.4, 127.3 (x 3), 127.4 (x 3), 128.1 (x 3), 128.2 (x 2), 128.3 (x 2), 128.5 (x 2), 138.4, 138.5, 138.7; LRMS (FAB) m/z 446 (M^++1), 91; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{36}\text{NO}_3$ (M^++H) 446.2694 found 446.2684.

cis-6a: IR (neat) ν 3340, 2921, 2854, 2360, 2342, 1097 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.08 (dd, $J = 10.6, 12.4$ Hz, 1 H), 1.27 (dd, $J = 9.6, 13.2$ Hz, 1 H), 1.71-1.78 (m, 2 H), 1.81 (dd, $J = 7.2, 13.2$ Hz, 1 H), 1.90-1.97 (m, 2 H), 2.04 (dd, $J = 7.2, 13.2$ Hz, 1 H), 2.58 (dd, $J = 9.2, 9.6$ Hz, 1 H), 3.33 (s, 2 H), 3.38 (d, $J = 3.6$ Hz, 2 H), 3.42-3.50 (m, 2 H), 3.67 (d, $J = 13.2$ Hz, 1 H), 3.83 (d, $J = 12.8$ Hz, 1 H), 4.50 (s, 2 H), 4.51 (s, 2 H), 7.22-7.34 (m, 15 H); ^{13}C NMR (100 MHz, CDCl_3) δ 29.7, 32.9, 38.0, 45.1, 45.3, 51.2, 63.8, 66.5, 73.2, 73.3, 75.1, 75.2, 127.3 (x 3), 127.4 (x 2), 127.5 (x 2), 128.0 (x 2), 128.3 (x 2), 128.6 (x 2), 128.9 (x 2), 138.2, 138.3 (x 2); LRMS (FAB) m/z 446 (M^++H), 354, 154, 107, 91; HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{36}\text{NO}_3$ (M^++H) 446.2694 found 446.2694.

4,4-bis(benzyloxymethyl)-2-(but-3-enyl)-*N*-tert-butylcyclopentanamine (7e): To a solution of azazirconacycle **5e**, which was prepared from Cp_2ZrCl_2 (95 mg, 0.325 mmol) in THF (0.9 mL), BuLi (1.46 M in hexane, 0.44 mL, 0.65 mmol) and **1e**

(106.9 mg, 0.25 mmol) in THF (1.0 mL) was added CuCl (49.7 mg, 0.513 mmol) and allyl chloride (41 μ l, 0.513 mmol) in THF (0.5 mL) at 0 °C, and the solution was stirred at room temperature for 1 h. After saturated NH₄Cl solution was added at 0 °C, the mixture was stirred for 1 h. The aqueous layer was made basic by K₂CO₃. The aqueous layer was extracted with EtOAc, and the organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc=4/1-2/1) to give **7e** (61.8 mg, 57%) as a pale yellow oil. **7e**: IR (neat) ν 2957, 2860, 1456, 1387, 1362, 1229, 1206, 1097, 1028 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.98 (s, 9 H), 1.22-1.31 (m, 3 H), 1.39 (dd, J = 9.2, 13.2 Hz, 1 H), 1.47 (dd, J = 5.0, 13.6 Hz, 1 H), 1.56 (dd, J = 7.0, 13.6 Hz, 1 H), 1.69 (dd, J = 6.0, 13.2 Hz, 1 H), 1.73-1.79 (m, 1 H), 1.94-2.08 (m, 2 H), 3.06 (dd, J = 6.0, 11.0 Hz, 1 H), 3.29 (d, J = 2.8 Hz, 2 H), 3.42 (d, J = 2.8 Hz, 2 H), 4.50 (s, 2 H), 4.51 (s, 2 H), 4.90 (tdd, J = 1.2, 2.0, 10.0 Hz, 1 H), 4.97 (ddd, J = 1.6, 3.6, 16.8 Hz, 1 H), 5.79 (tdd, J = 6.8, 10.0, 16.8 Hz, 1 H), 7.24-7.35 (m, 10 H); ¹³C NMR (100 MHz, CDCl₃) δ 28.3, 30.2, 32.6, 35.7, 41.8, 43.3, 45.3, 50.4, 54.8, 73.1, 73.3, 75.7, 75.9, 113.9, 127.2, 127.3, 127.3, 127.6, 128.2, 138.7, 138.8, 139.4; LRMS (EI) m/z 435 (M⁺), 420, 394, 378, 344, 91, 57; HRMS (EI) calcd for C₂₉H₄₁NO₂ (M⁺) 435.3165, found 435.3151.

Zirconium-Mediated Diastereoselective Cyclization.

(R)-N-(3,3-bis(benzyloxymethyl)hex-5-enylidene)-1-phenylethanamine (1f): IR (neat) ν 3028, 2969, 2858, 1661, 1495, 1452, 1364, 1099, 1028 cm⁻¹; ¹H NMR (400

MHz, CDCl₃) δ 1.44 (d, J = 6.8 Hz, 3 H), 2.18 (d, J = 7.2 Hz, 2 H), 2.36 (d, J = 5.6 Hz, 3 H), 3.35 (dd, J = 9.2, 15.6 Hz, 2 H), 3.36 (s, 2 H), 4.21 (q, J = 6.8 Hz, 1 H), 4.42 (dd, J = 12.0, 14.0 Hz, 2 H), 4.44 (s, 2H), 5.78 (tdd, J = 7.2, 11.2, 16.0 Hz, 1 H), 4.99 (dd, J = 2.4, 7.2 Hz, 1 H), 5.03 (s, 1 H), 7.25-7.36 (m, 15H), 7.80 (t, J = 5.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 24.4, 37.6, 39.5, 42.0, 69.8, 72.9, 73.0, 73.2, 73.2, 118.0, 126.5 (x 3), 126.6 (x 3), 127.3 (x 3), 128.1 (x 3), 128.2 (x 3), 133.8, 138.6, 144.9, 161.9; LRMS (EI) m/z 441(M⁺), 440, 426, 400, 350, 91; HRMS (EI) calcd for C₃₀H₃₅NO₂ (M⁺+H) 442.2746, found 442.2727.

cis-4,4-bis(benzyloxymethyl)-2-methyl-N-((R)-1-phenylethyl)cyclopentanamine

(8f): IR (neat) ν 3027, 2924, 2856, 1496, 1452, 1362, 1201, 1095, 1028 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (d, J = 6.8 Hz, 3 H), 1.19 (d, J = 6.8 Hz, 3 H), 1.37 (dd, J = 8.8, 13.2 Hz, 1 H), 1.48 (bs, 1H), 1.56 (dd, J = 6.0, 13.6 Hz, 1 H), 1.60-1.64 (m, 2 H), 1.93 (q, J = 7.2, 7.2, 1 H), 2.74 (dd, J = 5.6, 10.8 Hz, 1 H), 3.25 (s, 2 H), 3.44 (s, 2 H), 3.73 (dd, J = 6.8, 13.2 Hz, 1 H), 4.46 (dd, J = 12.8, 14.0 Hz, 2 H), 4.53 (s, 2 H), 7.18-7.34 (m, 15 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.5, 24.9, 36.9, 37.4, 38.4, 45.8, 55.5, 58.7, 73.1, 73.3, 75.5, 75.9, 126.5 (x 2), 126.7 (x 2), 127.2 (x 3), 127.3 (x 2), 127.5 (x 2), 128.1 (x 2), 128.2 (x 2), 138.7, 138.8, 146.3; LRMS (EI) m/z 442 (M⁺-H), 428, 352, 105, 91; HRMS (EI) calcd for C₃₀H₃₇NO₂ (M⁺) 443.2829, found 443.2826.

trans-4,4-bis(benzyloxymethyl)-2-methyl-N-((R)-1-

phenylethyl)cyclopentanamine (8f''): IR (neat) ν 3027, 2924, 2856, 1496, 1452,

1362, 1201, 1095, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.99 (d, $J = 6.4$ Hz, 3 H), 1.02-1.11 (m, 2 H), 1.30 (d, $J = 6.8$ Hz, 3 H), 1.60-1.71 (m, 1 H), 1.75-1.81 (m, 2 H), 2.55 (dd, $J = 9.2, 16.8$, 1 H), 3.25 (s, 2 H), 3.30 (dd, $J = 8.8, 13.2$ Hz, 2 H), 3.83 (dd, $J = 6.8, 12.8$ Hz, 1 H), 4.46 (d, $J = 3.6$ Hz, 4 H), 7.19-7.32 (m, 15 H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.2, 23.9, 39.6, 40.6, 40.8, 44.4, 57.1, 63.6, 73.1 (x 2), 75.3, 75.5, 126.5 (x 3), 126.7 (x 4), 127.2 (x 4), 128.2 (x 4), 138.8, 138.9, 146.7; LRMS (EI) m/z 442 ($\text{M}^+ - \text{H}$), 428, 352, 105, 91; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{35}\text{NO}_2$ (M^+) 443.2829, found 443.2827.

***trans*-4,4-bis(benzyloxymethyl)-2-methyl-*N*-((*R*)-1-**

phenylethyl)cyclopentanamine (8f): IR (neat) ν 3028, 2923, 2855, 1496, 1452, 1362, 1201, 1099, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (d, $J = 6.4$ Hz, 3 H), 0.95 (t, $J = 12.0$ Hz, 1 H), 1.19 (dd, $J = 9.8, 12.8$ Hz, 3 H), 1.37 (dd, $J = 8.8, 13.2$ Hz, 1 H), 1.48 (bs, 1 H), 1.56 (dd, $J = 6.0, 13.6$ Hz, 1 H), 1.60-1.64 (m, 2 H), 1.93 (qd, $J = 7.2, 7.2$, 1 H), 2.74 (dd, $J = 5.6, 10.8$ Hz, 1 H), 3.25 (s, 2 H), 3.44 (s, 2 H), 3.73 (dd, $J = 6.8, 13.2$ Hz, 1 H), 4.46 (dd, $J = 12.8, 14.0$ Hz, 2 H), 4.53 (s, 2 H), 7.18-7.34 (m, 15 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.5, 25.5, 39.5, 39.9, 40.0, 44.5, 56.4, 62.3, 73.1, 73.2, 75.2, 75.4, 126.3, 126.6 (x 2), 127.2 (x 2), 127.3 (x 2), 127.4 (x 2), 128.1, 128.2 (x 2), 138.7, 138.8, 145.7; LRMS (EI) m/z 442 ($\text{M}^+ - \text{H}$), 428, 352, 105, 91; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{35}\text{NO}_2$ (M^+) 443.2829, found 443.2827.

***cis*-4,4-bis(benzyloxymethyl)-2-methyl-*N*-((*R*)-1-phenylethyl)cyclopentanamine**

(8f^o): IR (neat) ν 3027, 2924, 2858, 1458, 1362, 1095 cm^{-1} ; ^1H NMR (400 MHz,

CDCl₃) δ 0.91 (d, J = 7.2 Hz, 3 H), 1.29 (d, J = 6.4 Hz, 3 H), 1.32-1.40 (m, 2 H), 1.59 (dd, J = 7.4, 13.6 Hz, 1 H), 1.66 (dd, J = 6.4, 13.2 Hz, 1 H), 2.14 (qd, J = 5.8, 5.8, 1 H), 2.97 (td, J = 6.0, 8.4 Hz, 1 H), 3.22 (dd, J = 8.4, 11.0, 2 H), 3.36 (s, 2 H), 3.75 (q, J = 6.8 Hz, 1 H), 4.43 (dd, J = 12.4, 14.4 Hz, 2 H), 4.46 (s, 2 H), 7.20-7.34 (m, 15 H); ¹³C NMR (100 MHz, CDCl₃) δ 14.8, 24.5, 35.1, 37.9, 38.4, 44.7, 56.2, 58.5, 73.0, 73.1, 75.1, 75.9, 126.6 (x 3), 127.2 (x 4), 127.3 (x 2), 128.1 (x 2), 128.2 (x 4), 138.8 (x 2), 146.1; LRMS (EI) m/z 442 (M⁺-H), 428, 352, 105, 91; HRMS (EI) calcd for C₂₅H₃₅NO₂ (M⁺+H) 444.2903, found 444.2891.

Conversion of 11 into *trans*-12 and *trans*-12', *cis*-12 and *cis*-12'. A solution of **11** (72.8 mg, 0.25 mmol) and Pd(OH)₂ on charcoal (20% , 17.5 mg, 0.025 mmol) in EtOH (2.5 mL) was stirred at room temperature for 9 h under an atmosphere of hydrogen. After the catalyst was filtered off, the solvent was evaporated to give the crude product, which was dissolved in CH₂Cl₂ (1 mL). To this solution were added pyridine (0.69 mL, 5.0 mmol) and BzCl (0.29 mL, 2.5 mmol) and the solution was stirred at room temperature for 12 h. Ethyl acetate was added and the organic layer was washed saturated NaHCO₃ and brine and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/EtOAc, 2/1-1/2) to give *trans*-**12** (12.2 mg, 18% from **2**) and *cis*-**12** (54.8 mg, 75% from **2**). *cis*-**12**: IR (neat) ν 3362, 2955, 2926, 2854, 1663, 1540, 1107 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.97 (d, J = 6.8 Hz, 3 H), 1.46-1.67 (m, 3 H), 1.88 (dd, J = 6.0, 14.4 Hz, 1 H), 2.08-2.19 (m, 1 H), 3.18 (dd, J = 8.8, 15.2 Hz, 2 H), 3.33 (s, 3

H), 3.36 (dd, $J = 8.4, 18.0$ Hz, 2 H), 3.47 (s, 3 H), 3.45-3.50 (m, 1 H), 3.40-3.49 (m, 3 H), 7.75 (bd, $J = 8.0$ Hz, 1 H), 7.79-7.81 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.4, 26.8, 39.9, 40.5, 42.1, 44.7, 55.4 (x 2), 73.1, 73.2, 126.3, 126.8, 127.2, 127.4, 128.1, 138.7, 167.7; LRMS (EI) m/z 291 (M^+), 276, 200, 186, 105, 91; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3$ (M^+) 291.1834, found 291.1831. ***trans*-12**: IR (neat) ν 3028, 2923, 2855, 1496, 1452, 1362, 1201, 1099, 1028 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.06 (d, $J = 6.4$ Hz, 3 H), 1.22 (dd, $J = 6.8, 12.8$ Hz, 1 H), 1.19 (dd, $J = 6.8, 12.8$ Hz, 1 H), 1.47 (dd, $J = 8.8, 13.2$ Hz, 1 H), 1.93 (dd, $J = 7.6, 13.2$ Hz, 1 H), 2.00 (td, $J = 6.8, 14.0$, 1 H), 2.11 (dd, $J = 7.2, 13.6$ Hz, 1 H), 3.24 (dd, $J = 8.8, 14.4$ Hz, 2 H), 3.34 (s, 3 H), 3.40 (s, 3 H), 4.12 (dd, $J = 7.2, 14.8$ Hz, 1 H), 6.80 (bd, $J = 8.0$ Hz, 1 H), 7.40-7.52 (m, 3 H), 7.76 (bd, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.5, 25.5, 39.5, 39.9, 40.0, 44.5, 56.4 (x 2), 73.1, 73.2, 126.6, 127.2, 127.3, 127.4, 128.1, 138.8, 165.7; LRMS (EI) m/z LRMS (EI) m/z 291 (M^+), 276, 200, 186, 105, 91; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3$ (M^+) 291.1834, found 291.1831.

The enantiomeric excesses of ***cis*-12** and ***trans*-12** were determined by HPLC analysis [***trans*-12**; DAICEL CHIRALPAK AD (hexane/2-propanol 95/5), ***cis*-12**; DAICEL CHIRALPAK AS (hexane/2-propanol 9/1)].

Conversion of *cis*-11 into (S)-MTPA Ester *cis*-14 (*cis*-(S)-14): A solution of ***cis*-11** (14.6 mg, 0.035 mmol) and $\text{Pd}(\text{OH})_2$ on charcoal (20%, 2.8 mg, 0.004 mmol) in EtOH (1.5 mL) was stirred at room temperature for 2.5 h under an atmosphere of hydrogen. After the catalyst was filtered off, the solvent was evaporated to give the

crude, which was dissolved in CH_2Cl_2 . To this solution were added (*S*)-(-)- α -methoxy- α -(trifluoromethyl)phenylacetyl chloride (27 μg , 0.14 mmol), and pyridine (41 μg , 0.58 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. To the mixture was added *N, N'*-dimethyl-1,3-propanediamine (18 μl , 0.14 mmol) at 0 °C and the mixture was stirred at room temperature for 1 h. After removal of the solvent, the residue was purified by preparative TLC on silica gel (hexane/ Et_2O 5/1) to give *cis*-(*S*)-**14** (6.9 mg, 2 step 49%). *cis*-(*S*)-**14**: IR (neat) ν 3314, 2957, 2928, 2870, 1693, 1106 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.98 (d, J = 6.8 Hz, 3 H), 1.41 (d, J = 17.2 Hz, 1 H), 1.44 (d, J = 13.6 Hz, 1 H), 1.56 (dd, J = 8.0, 13.6 Hz, 1 H), 1.77 (dd, J = 6.0, 14.0 Hz, 1 H), 2.06-2.13 (m, 1 H), 3.12 (dd, J = 8.8, 18.0 Hz, 2 H), 3.21 (dd, J = 8.8, 9.6 Hz, 2 H), 3.30 (dd, J = 0.4, 1.6 Hz, 6 H), 3.52 (bd, J = 1.2 Hz, 3 H), 4.26-4.32 (m, 1 H), 7.35-7.37 (m, 3 H), 7.59-7.61 (m, 2 H), 8.06 (bd, J = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 37.7, 39.7, 40.1, 46.5, 53.8, 54.8, 58.9, 59.3, 77.9, 79.3, 116.0, 124.2, 127.5, 128.0, 129.0, 133.6, 165.3; LRMS (EI) m/z 404 ($\text{M}^+\text{+H}$), 388, 371, 356, 326, 214, 189, 171, 71; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{F}_3\text{NO}_4(\text{M}^+\text{+H})$ 404.2048, found 404.2054.

Conversion of *cis*-11 into (*R*)-MTPA Ester *cis*-14 (*cis*-(*R*)-14): IR (neat) ν 3314, 2956, 2926, 2853, 1693, 1106 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.79 (d, J = 6.8 Hz, 3 H), 1.23 (d, J = 13.6 Hz, 1 H), 1.48 (dd, J = 7.2, 13.2 Hz, 1 H), 1.58 (d, J = 14.4 Hz, 1 H), 1.83 (dd, J = 6.0, 14.0 Hz, 1 H), 2.01-2.09 (m, 1 H), 3.12 (dd, J = 8.8, 14.0 Hz, 2 H), 3.31 (d, J = 8.8 Hz, 1 H), 3.31 (d, J = 8.8 Hz, 1 H), 3.30 (s, 3 H), 3.39

(s, 1 H), 3.49 (bd, $J = 1.6$ Hz, 3 H), 4.26-4.32 (m, 1 H), 7.36-7.39 (m, 3 H), 7.64-7.66 (m, 2 H), 8.00 (bd, $J = 8.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3, 37.1, 39.6, 39.9, 46.5, 54.1, 55.1, 58.9, 59.3, 77.8, 79.3, 122.4, 125.3, 127.5, 128.1, 129.0, 133.5, 165.2; LRMS (EI) m/z 404 ($\text{M}^+ + \text{H}$), 388, 371, 356, 326, 214, 189, 171, 71; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{F}_3\text{NO}_4(\text{M}^+)$ 403.1970, found 403.1984.

Conversion of *trans*-11 into (S)-MTPA Ester *trans*-14 (*trans*-(S)-14): IR (neat) ν 3315, 2956, 2925, 1684, 1105 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.02 (d, $J = 6.4$ Hz, 3 H), 1.16 (dd, $J = 8.2, 12.9$ Hz, 1 H), 1.31 (dd, $J = 7.9, 13.6$ Hz, 1 H), 1.85 (dd, $J = 7.5, 12.6$ Hz, 1 H), 1.85-1.95 (m, 1 H), 2.01 (dd, $J = 7.5, 13.5$ Hz, 1 H), 3.18 (dd, $J = 8.8, 10.4$ Hz, 2 H), 3.21 (d, $J = 8.7$ Hz, 1 H), 3.25 (d, $J = 8.7$ Hz, 1 H), 3.32 (d, $J = 1.1$ Hz, 1 H), 3.43 (bd, $J = 1.5$ Hz, 1 H), 3.94 (td, $J = 7.5, 16.2$ Hz, 1 H), 7.11 (d, $J = 8.5$ Hz, 1 H), 7.37-7.39 (m, 3 H), 7.52-7.54 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.1, 38.4, 38.7, 41.0, 45.2, 54.9, 56.4, 59.1, 59.3, 78.1, 78.7, 115.6, 121.7, 127.6, 128.3, 129.2, 132.9, 165.6; LRMS (EI) m/z 404 ($\text{M}^+ + \text{H}$), 388, 371, 356, 326, 214, 189, 170, 71; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{F}_3\text{NO}_4(\text{M}^+)$ 403.1970, found 403.1967.

Conversion of *trans*-11 into (R)-MTPA Ester *trans*-14 (*trans*-(R)-14): IR(neat) ν 2926, 2873, 1656, 1519, 1163, 1107 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (d, $J = 6.6$ Hz, 3 H), 1.13 (dd, $J = 8.4, 13.1$ Hz, 1 H), 1.40 (dd, $J = 7.9, 13.7$ Hz, 1 H), 1.76 (dd, $J = 7.6, 12.9$ Hz, 1 H), 1.80-1.87 (m, 1 H), 2.04 (dd, $J = 7.3, 13.5$ Hz, 1 H), 3.18 (dd, $J = 8.8, 11.9$ Hz, 2 H), 3.19 (d, $J = 8.7$ Hz, 1 H), 3.27 (d, $J = 8.7$ Hz, 1 H), 3.32

(d, $J = 2.8$ Hz, 1 H), 3.44 (bd, $J = 1.3$ Hz, 1 H), 3.95 (td, $J = 7.7, 16.4$ Hz, 1 H), 7.05 (d, $J = 8.7$ Hz, 1 H), 7.37-7.39 (m, 3 H), 7.55-7.57 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.2, 38.5, 38.7, 40.9, 45.2, 54.9, 56.3, 59.1, 59.3, 78.1, 78.8, 122.3, 125.2, 127.5, 128.3, 129.2, 133.1, 165.6; LRMS (EI) m/z 404 ($\text{M}^+\text{+H}$), 388, 371, 356, 326, 214, 189, 171, 71; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{28}\text{F}_3\text{NO}_4(\text{M}^+)$ 403.1970, found 403.1974.