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Supporting Information

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Gold(I)-Catalyzed Intramolecular Hydroamination of Alkenyl Carbamates

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Experimental procedures and analytical and spectroscopic data for selected compounds (14 pages).

Experimental

General Methods. Catalytic reactions were performed in sealed glass tubes under an atmosphere of dry nitrogen. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR in $CDCl_3$ at room temperature unless noted otherwise. IR spectra were obtained on a Bomen MB-100 FT IR spectrometer. Gas chromatography was performed on a Hewlett-Parkard 5890 gas chromatograph equipped with a 25 m polydimethylsiloxane capillary column. Flash column chromatography was performed employing 200-400 mesh silica gel (EM). Thin layer chromatography (TLC) was performed on silica gel 60 F254 eluting with 5:1 mixtures of hexanes/EtOAc unless noted otherwise. Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ).

Sodium tetrachloroaurate(III) dihydrate, anhydrous toluene, anhydrous acetonitrile (Aldrich), $AuPPh_3Cl$, tertiary phosphines (Strem), 2,5-dimethylpyrrolidine (mixture of cis and trans isomers), anhydrous 1,4-dioxane, AgOTf, and TfOH (Acros) were used as received. Diethyl ether and THF were freshly distilled over sodium benzoquinone ketyl under nitrogen. Dichloromethane and 1,2-dichloroethane (DCE) were freshly distilled over CaH_2 under nitrogen. Au[P(*t*-Bu)$_2$*o*-biphenyl]Cl (**6**) was synthesized employing a literature procedure.[1]

Au(I) complexes:

Au[P(CH$_3$)$_2$Ph]Cl. Au[P(CH$_3$)$_2$Ph]Cl was synthesized in 56 % yield as a white solid employing a procedure similar to that reported for the synthesis of **6**. ^{1}H NMR: δ 7.75-7.79 (dd, *J* = 8.8, 13.6 Hz, 2 H), 7.54-7.47 (m, 3 H), 1.86 (d, *J* = 10.8 Hz, 6 H). ^{13}C{^{1}H} NMR: δ 132.4 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 13.3 Hz), 131.4 (d, *J* = 62.2 Hz), 129.6 (d, *J* = 11.8 Hz), 16.4, (d, *J* = 39.4 Hz). ^{31}P NMR: δ 4.0. Anal. Calcd (found) for $C_8H_{11}AuClP$: C, 25.93 (26.09); H, 2.99 (2.96).

Au[P(4-MeOPh)$_3$]Cl. Au[P(4-MeOPh)$_3$]Cl was isolated in 68 % yield as a white solid employing a procedure similar to that reported for **6**. ^{1}H NMR: δ 7.43 (dd, *J* = 8.8, 12.4 Hz, 6 H),

7.43 (dd, J = 1.6, 8.8 Hz, 6 H), 3.84 (s, 9 H). $^{13}C\{^{1}H\}$ NMR: δ 162.7, 135.9 (d, J = 15.5 Hz), 120.7, (d, J = 67.9 Hz), 151.1 (d, J = 12.9 Hz), 55.8. ^{31}P NMR: δ 29.8. Anal. Calcd (found) for $C_{21}H_{21}AuClO_3P$: C, 43.13 (43.49); H, 3.62 (3.57).

Au[P(4-CF$_3$Ph)$_3$]Cl. Au[P(4-CF_3Ph)$_3$]Cl was isolated in 45 % yield as a white solid employing a procedure similar to that reported for **6**. ^{1}H NMR: δ 7.80 (d, J = 6.8 Hz, 6 H), 7.43 (dd, J = 8.4, 13.2 Hz, 6 H). ^{31}P NMR: δ 33.6. Anal. Calcd (found) for $C_{21}H_{12}AuClF_9P$: C, 36.10 (35.70); H, 1.73 (1.71).

Alkenyl carbamates

Benzyl 2,2-diphenyl-4-pentenylcarbamate (4). Benzyl chloroformate (0.70 mL, 4.9 mmol) was added slowly to a mixture of 2,2-diphenyl-4-pentenylamine (**S1**)[2] (1.16 g, 4.89 mmol) and $NaHCO_3$ (0.63 g, 7.3 mmol) in ethanol/water (3:2, 25 mL) at room temperature. The resulting suspension was stirred for 1 h and treated with water (40 mL). The resulting mixture was extracted with ether (2 × 50 mL) and the combined ether extracts were dried ($MgSO_4$) and concentrated. The resulting oily residue was chromatographed (hexanes–EtOAc = 20:1) to give **4** (1.68 g, 92%) as a white solid. mp 56-58 ºC. TLC: R_f = 0.41. ^{1}H NMR (50 ºC): δ 7.37-7.29 (m, 9 H), 7.25-7.18 (m, 6 H), 5.54-5.42 (m, 1 H), 5.08 (s, 2 H), 5.02-4.97 (m, 2 H), 4.37 (br s, 1 H), 3.96 (d, J = 6.0 Hz, 2 H), 2.90 (d, J = 7.2 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR (50 ºC): δ 156.6, 145.6, 137.0, 134.1, 128.8, 128.6, 128.44, 128.40, 128.35, 126.8, 118.8, 67.1, 50.7, 48.3, 42.2. IR (neat, cm^{-1}): 3434, 3348, 3060, 2935, 1724, 1511, 1445, 1222, 1143. Anal. Calcd (found) for $C_{25}H_{25}NO_2$: C, 80.83 (81.03); H, 6.78 (6.73); N, 3.77 (3.79).

***tert*-Butyl 2,2-diphenyl-4-pentenylcarbamate (Table 2, entry 3)**. A solution of BOC_2O (0.81 g, 3.7 mmol), **S1** (0.73 g, 3.1 mmol), and Et_3N (0.60 g, 4.3 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature overnight, treated with water (30 mL), and extracted with CH_2Cl_2 (30 mL). The organic extract was dried ($MgSO_4$) and concentrated under vacuum. The resulting oily

residue was chromatographed (hexanes–EtOAc = 20:1) to give *tert*-butyl 2,2-diphenyl-4-pentylcarbamate (0.88 g, 85%) as a white solid. mp 65-67 ºC. TLC: R_f = 0.44. ^{1}H NMR (50 ºC): δ 7.32-7.27 (m, 4 H), 7.23-7.17 (m, 6 H), 5.50-5.40 (m, 1 H), 5.00-4.96 (m, 2 H), 4.13 (br s, 1 H), 3.86 (d, *J* = 6.0 Hz, 2 H), 2.88 (d, *J* = 6.8 Hz, 2 H), 1.39 (s, 9 H). ^{13}C{^{1}H} NMR (50 ºC): δ 156.1, 145.9, 134.3, 128.6, 128.4, 126.7, 118.7, 79.6, 50.8, 47.4, 42.3, 28.7. IR (neat, cm^{-1}): 3442, 2975, 2929, 1718, 1507, 1364, 1232, 1168. Anal. Calcd (found) for $C_{22}H_{27}NO_2$: C, 78.30 (78.50); H, 8.06 (8.25); N, 4.15 (4.18).

4-Methoxybenzyl 2,2-diphenyl-4-pentenylcarbamate (Table 2, entry 4). 4-Methoxybenzyl 2,2-diphenyl-4-pentenylcarbamate was isolated in 45% yield as a white solid from reaction of **S1** and 4-methoxybenzyloxycarbonyl azide employing a procedure similar to that used to synthesize **4**. mp 69-71 ºC. TLC (hexanes–EtOAc = 2:1): R_f = 0.66. ^{1}H NMR (60 ºC): δ 7.28-7.14 (m, 13 H), 6.85 (br d, *J* = 8.8 Hz, 2 H), 5.45-5.40 (m, 1 H), [4.97 (s), 4.94 (s), 4 H], 4.28 (br s, 1 H), 3.92 (d, *J* = 6.0 Hz, 2 H), 3.77 (s, 3 H), 2.86 (d, *J* = 6.8 Hz, 2 H). ^{13}C{^{1}H} NMR (60 ºC): δ 160.1, 156.7, 145.6, 134.1, 130.2, 129.2, 128.6, 128.4, 126.8, 118.8, 114.4, 66.9, 55.6, 50.7, 48.3, 42.2. IR (neat, cm^{-1}): 3435, 2934, 1722, 1514, 1246, 1223, 1033. Anal. Calcd (found) for $C_{26}H_{27}NO_3$: C, 77.78 (77.80); H, 6.78 (6.84); N, 3.49 (3.74).

9-Fluorenylmethyl 2,2-diphenyl-4-pentenylcarbamate (Table 2, entry 5). A solution of 9-fluorenylmethyl chloroformate (0.62 g, 2.4 mmol), **S1** (0.57 g, 2.41 mmol), and Et_3N (0.51 g, 3.62 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h at room temperature, treated with water (30 mL), and extracted with ether (2 × 30 mL). The combined ether extracts were washed (brine), dried ($MgSO_4$), and concentrated under vacuum. The resulting oily residue was chromatographed (hexanes–EtOAc = 20:1) to give 9-fluorenylmethyl 2,2-diphenyl-4-pentenylcarbamate (0.82 g, 73%) as a white solid. mp: 90-91 ºC. TLC: R_f = 0.31. ^{1}H NMR (75 ºC, C_6D_6): δ 7.56 (d, *J* = 7.6 Hz, 2 H), 7.38 (d, *J* = 7.2, Hz, 2 H), 7.22-6.97 (m, 14 H), 5.56-5.46 (m, 1 H), 4.95-4.87 (m, 2 H), 4.35 (d, *J* = 6.4 Hz, 2 H), 4.12 (br s, 1 H), 4.01 (t, *J* = 6.4 Hz, 1 H), 3.85 (br d, *J* = 5.6 Hz, 2 H), 2.71 (d, *J* = 7.2 Hz, 2 H).

$^{13}C\{^{1}H\}$ NMR (75 ºC, C_6D_6): δ 156.6, 146.2, 145.1, 142.3, 134.7, 128.83, 128.81, 127.7, 127.6, 127.0, 125.7, 120.5, 118.8, 67.1, 51.4, 48.8, 48.4, 42.6. IR (neat, cm^{-1}): 3343, 3059, 2974, 1708, 1521, 1492, 1447, 1235. Anal. Calcd (found) for $C_{32}H_{29}NO_2$: C, 83.63 (83.86); H, 6.36 (6.20); N, 3.05 (2.99).

Benzyl (1-allylcyclohexyl)methylcarbamate (Table 2, entry 6). Benzyl (1-allyl-cyclohexyl)methylcarbamate was isolated in 87% yield as a colorless oil from the reaction of (1-allylcyclohexyl)methylamine[2] and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. TLC: R_f = 0.41. ^{1}H NMR (60 ºC): δ 7.37-7.29 (m, 5 H), 5.83 (tdd, *J* = 8.0, 10.8, 17.6 Hz 1 H), 5.16-5.03 (m, 4 H), 4.72 (br s, 1 H), 3.13 (d, *J* = 6.4 Hz, 2 H), 2.06 (td, *J* = 1.2, 7.2 Hz, 2 H), 1.56-1.24 (m, 10 H). $^{13}C\{^{1}H\}$ NMR (60 ºC): δ 157.1, 137.3, 134.9, 128.8, 128.43, 128.37, 117.7, 67.1, 48.1, 41.2, 37.3, 33.7, 26.5, 21.8. IR (neat, cm^{-1}): 3436, 3343, 2925, 2855, 1712, 1537, 1518, 1242, 1130, 1002. Anal. Calcd (found) for $C_{18}H_{25}NO_2$: C, 75.22 (74.93); H, 8.77 (8.81); N, 4.87 (4.78).

Benzyl [1-(2-methylallyl)cyclohexyl]methylcarbamate (Table 2, entry 7). Benzyl [1-(2-methylallyl)cyclohexyl]methylcarbamate was isolated in 96% yield as a colorless oil from the reaction of [1-(2-methyl-2-propenyl)cyclohexyl]methylamine[2] and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. TLC: R_f = 0.53. ^{1}H NMR (60 ºC): δ 7.37-7.28 (m, 5 H), 5.12 (s, 2 H), 4.91-4.88 (m, 1 H), 4.80 (br s, 1 H), 4.71-4.70 (m, 1 H), 3.20 (d, *J* = 6.4 Hz, 2 H), 2.04 (s, 2 H), 1.80 (s, 3 H), 1.56-1.34 (m, 10 H). $^{13}C\{^{1}H\}$ NMR (60 ºC): δ 157.0, 143.5, 137.3, 128.8, 128.4, 128.3, 115.2, 67.0, 47.8, 45.5, 38.0, 34.3, 26.5, 25.6, 22.0. IR (neat, cm^{-1}): 3341, 2926, 2859, 1706, 1516, 1454, 1237. Anal. Calcd (found) for $C_{19}H_{27}NO_2$: C, 75.71 (75.51); H, 9.03 (9.23); N, 4.65 (4.77).

Benzyl [1-(1-hydroxyallyl)cyclohexyl]methylcarbamate (Table 2, entry 8). Benzyl [1-(1-hydroxyallyl)cyclohexyl]methylcarbamate was isolated in 77% as a white solid from the reaction of 1-(1-aminomethylcyclohexyl)-2-propen-1-ol[2] and benzyl chloroformate employing a procedure

similar to that used to synthesize **4**. mp 61-62 ºC. TLC (hexanes–EtOAc = 2:1): R_f = 0.58. ^{1}H NMR: δ 7.36-7.28 (m, 5 H), 5.95 (ddd, *J* = 6.4, 10.4, 17.2 Hz, 1 H), 5.16 (br s, 1 H), 5.28-5.19 (m, 2 H), 5.09 (s, 2 H), 3.96-3.92 (m, 1 H), 3.38 (dd, *J* = 6.8, 14.0 Hz, 1 H), 3.20 (dd, *J* = 4.8, 14.0 Hz, 1 H), 2.49 (d, *J* = 3.6 Hz, 1 H), 1.64-1.18 (m, 10 H). ^{13}C{^{1}H} NMR: δ 157.5, 137.3, 137.0, 128.8, 128.41, 128.36, 117.2, 79.6, 67.0, 44.0, 40.4, 30.4, 30.2, 26.4, 21.6, 21.5. IR (neat, cm^{-1}): 3400, 2928, 2861, 1694, 1519, 1454, 1253. Anal. Calcd (found) for $C_{18}H_{25}NO_3$: C, 71.26 (71.37); H, 8.31 (8.39); N, 4.62 (4.43).

Benzyl [1-(1-acetoxyallyl)cyclohexyl]methylcarbamate (Table 2, entry 9). A solution of acetic anhydride (0.45 mL, 4.7 mmol), benzyl [1-(1-hydroxyallyl)cyclohexyl]methylcarbamate (0.95 g, 3.1 mmol), DMAP (0.38 g, 3.1 mmol), and Et_3N (0.44 mL, 3.1 mmol) in CH_2Cl_2 (15 mL) was stirred for 1 h at room temperature and quenched with water (30 mL). The resulting mixture was extracted with ether (2 × 30 mL) and the combined ether extracts were dried ($MgSO_4$) and concentrated to give an oily residue that was chromatographed (hexanes–EtOAc = 20:1) to give benzyl [1-(1-acetoxy-allyl)cyclohexyl]methylcarbamate (0.99 g, 90%) as a viscous colorless oil. TLC: R_f = 0.20. ^{1}H NMR (50 ºC): δ 7.35-7.27 (m, 5 H), 5.86 (ddd, *J* = 6.4, 10.8, 16.8 Hz, 1 H), 5.29-5.22 (m, 3 H), 5.11 (s, 2 H), 5.08 (br s, 1 H), 3.48 (br dd, *J* = 8.4 13.2, 1 H), 3.11 (dd, *J* = 4.8, 14.4 Hz, 1 H), 2.06 (s, 3 H), 1.56-1.28 (m, 10 H). ^{13}C{^{1}H} NMR (50 ºC): δ 170.1, 156.9, 137.2, 133.0, 128.8, 128.34, 128.32, 118.8, 79.2, 67.0, 43.8, 40.6, 30.5, 29.8, 26.2, 21.43, 21.38, 21.2. IR (neat, cm^{-1}): 3354, 2931, 2863, 1725, 1521, 1237, 1021. Anal. Calcd (found) for $C_{20}H_{27}NO_4$: C, 69.54 (69.66); H, 7.88 (7.96); N, 4.05 (4.11).

Benzyl 2-(4-methoxy)phenyl-4-pentenylcarbamate (Table 2, entry 10). Benzyl 2-(4-methoxy)-phenyl-4-pentenylcarbamate was isolated in 75 % as a white solid from the reaction of 2-(4-methoxyphenyl)-4-pentenylamine[2] and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. mp 57-59 ºC. TLC: R_f = 0.26. ^{1}H NMR (50 ºC): δ 7.37-7.28 (m, 4 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 5.69 (tdd, *J* = 7.2, 10.4, 16.8 Hz 1 H), 5.08-4.95

(m, 4 H), 4.60 (br s, 1 H), 3.79 (s, 3 H), 3.66-3.54 (m, 1 H), 3.23 (ddd, J = 5.2, 8.8, 13.6 Hz 1 H), 2.88-2.80 (m, 1 H), 2.44-2.30 (m, 2 H). $^{13}C\{^1H\}$ NMR (50 ºC): δ 158.9, 156.6, 137.1, 136.3, 134.3, 129.0, 128.8, 128.3, 116.8, 114.5, 67.0, 55.6, 46.6, 45.3, 38.6. IR (neat, cm^{-1}): 3339, 2928, 1702, 1511, 1247, 1034. Anal. Calcd (found) for $C_{20}H_{23}NO_3$: C, 73.82 (73.66); H, 7.12 (6.89); N, 4.30 (4.09).

Benzyl 1-methyl-4-pentenylcarbamate (Table 2, entry 11).[3] Benzyl 1-methyl-4-pentenylcarbamate was isolated in 60 % yield as a colorless oil from the reaction of 1-methyl-4-pentenylamine[3] and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. TLC: R_f = 0.42. ^1H NMR (60 ºC): δ 7.36-7.28 (m, 5 H), 5.81 (tdd, J = 6.4, 10.4, 17.6 Hz, 1 H), 5.11 (s, 2 H), 5.05-4.95 (m, 2 H), 4.56 (br s, 1 H), 3.80-3.67 (m, 1 H), 2.13-2.07 (m, 2 H), 1.61-1.48 (m, 2 H), 1.16 (d, J = 6.4 Hz, 3 H). $^{13}C\{^1H\}$ NMR (60 ºC): δ 156.1, 138.3, 137.2, 128.8, 128.3, 115.2, 66.8, 47.3, 36.8, 30.5, 21.5.

Benzyl 4-pentenylcarbamate (Table 2, entry 12). Benzyl 4-pentenylcarbamate was isolated in 43% yield as a colorless oil from the reaction of 4-pentenylamine and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. TLC (hexanes–EtOAc = 2:1): R_f = 0.71. ^1H NMR (60 ºC): δ 7.36-7.27 (m, 5 H), 5.80 (tdd, J = 6.8, 10.4, 17.2 Hz, 1 H), 5.11 (s, 2 H), 5.06-4.97 (m, 2 H), 4.73 (br s, 1 H), 3.21 (q, J = 6.8 Hz, 2 H), 2.10 (q, J = 7.2 Hz, 2 H), 1.62 (quintet, J = 7.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (60 ºC): δ 156.8, 138.0, 137.2, 128.8, 128.4, 115.5, 67.0, 41.1, 31.2, 29.6. IR (neat, cm^{-1}): 3334, 2934, 1697, 1536, 1454, 1255, 1137, 1002, 912. Anal. Calcd (found) for $C_{13}H_{17}NO_2$: C, 71.21 (71.20); H, 7.81 (7.93); N, 6.39 (6.51).

Benzyl (2-allylphenyl)carbamate (Table 2, entry 13).[4] Benzyl (2-allylphenyl)carbamate was isolated in 77% as a pale yellow solid from the reaction of 2-allyl-phenylamine[5] and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. ^1H NMR (60 ºC): δ 7.80 (d, J = 8.0 Hz, 1 H), 7.42-7.23 (m, 6 H), 7.17 (dd, J = 2.0, 7.6 Hz, 1 H), 7.09 (td, J = 1.2, 7.6 Hz, 1 H), 6.61 (br s, 1 H), 5.96 (tdd, J = 6.4, 10.0, 16.8 Hz, 1 H), 5.22 (s, 2 H), 5.15 (qd, J = 1.6, 10.0 Hz, 1

H), 5.07 (qd, *J* = 2.0, 17.2 Hz, 1 H), 3.37 (td, *J* = 1.2, 6.0 Hz, 2 H). $^{13}C\{^{1}H\}$ NMR (60 ºC): δ 154.3, 136.8, 136.5, 136.1, 130.5, 130.0, 128.9, 128.6, 128.5, 127.8, 125.0, 122.9, 117.0, 67.4, 36.8.

***cis*-Benzyl (2-allylcyclohexyl)carbamate (Table 2, entry 14)**. *cis*-Benzyl (2-allylcyclohexyl)carbamate was isolated in 77 % as a colorless oil from the reaction of *cis*-2-allyl-cyclohexylamine[6] and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. TLC: R_f = 0.44. ^{1}H NMR (60 ºC): δ 7.38-7.28 (m, 5 H), 5.84-5.73 (m, 1 H), 5.12 (s, 2 H), 5.03-4.97 (m, 2 H), 4.84 (br s, 1 H), 3.96-3.91 (m, 1 H), 2.15-2.03 (m, 1 H), 1.96-1.89 (m, 1 H), 1.78-1.25 (m, 8 H), 1.19-1.10 (m, 1 H). $^{13}C\{^{1}H\}$ NMR (60 ºC): δ 156.3, 137.3, 137.2, 128.8, 128.4, 128.3, 116.2, 66.9, 50.5, 40.1, 36.4, 31.2, 27.7, 24.7, 22.0. IR (neat, cm^{-1}): 3337, 2929, 2855, 1697, 1530, 1453, 1334, 1239. Anal. Calcd (found) for $C_{17}H_{23}NO_2$: C, 74.69 (74.38); H, 8.48 (8.25); N, 5.12 (5.21).

Benzyl [1-(3-butenyl)cyclohexyl]methylcarbamate (Table 2, entry 15). Benzyl [1-(3-butenyl)cyclohexyl]methylcarbamate was isolated in 79 % as a colorless oil from the reaction of 1-(3-butenyl)cyclohexylmethylamine and benzyl chloroformate employing a procedure similar to that used to synthesize **4**. TLC: R_f = 0.38. ^{1}H NMR (60 ºC): δ 7.34-7.25 (m, 5 H), 5.77 (tdd, *J* = 6.4, 10.8, 17.0 Hz, 1 H), 5.08 (s, 2 H), 5.00-4.88 (m, 2 H), 4.65 (br s, 1 H), 3.11 (d, *J* = 6.4 Hz, 2 H), 1.99-1.93 (m, 2 H), 1.45-1.21 (m, 12 H). $^{13}C\{^{1}H\}$ NMR (60 ºC): δ 157.0, 139.5, 137.2, 128.8, 128.4, 128.3, 114.5, 67.0, 47.7, 36.7, 35.3, 33.8, 27.7, 26.5, 21.8. IR (neat, cm^{-1}): 3343, 2925, 2852, 1712, 1537, 1519, 1244, 1130. Anal. Calcd (found) for $C_{19}H_{27}NO_2$: C, 75.71 (75.52); H, 9.03 (8.92); N, 4.65 (4.67).

Cyclic Carbamates

Benzyl 2-methyl-4,4-diphenylpyrrolidinylcarbamate (5). A mixture of **4** (165 mg, 0.445 mmol), **6** (12 mg, 0.022 mmol), and AgOTf (6 mg, 0.02 mmol) in 1,4-dioxane (0.45 mL) was degassed via one freeze-pump-thaw cycle, pressurized with nitrogen, and stirred for 18 hours at 60

ºC. The crude mixture was chromatographed without evaporation of solvent (hexanes–EtOAc = 20:1) to give benzyl 2-methyl-4,4-diphenylpyrrolidinylcarbamate (**5**, 160 mg, 97%) as a viscous colorless oil. TLC: R_f = 0.41. ^{1}H NMR (1:1 ratio of rotamers): δ 7.40-7.11 (m, 5 H), [5.31 (d, *J* = 12.4 Hz), 5.09 (d, *J* = 12.4 Hz), 1:1, 1 H], [5.18 (abq, *J* = 12.4 Hz)], 1:1, 1 H], [4.74 (dd, *J* = 2.0, 11.6 Hz), 4.58 (dd, *J* = 1.6, 11.6 Hz), 1:1, 1 H], 3.81-3.65 (m, 2 H), 2.86-2.80 (m, 1 H), [2.31 (dd, *J* = 9.6, 12.4 Hz), 2.26 (dd, *J* = 9.6, 12.8 Hz), 1:1, 1 H], [1.36 (d, *J* = 6.0 Hz), 1.29 (d, *J* = 6.0 Hz), 1:1, 3 H]. ^{13}C{^{1}H} NMR: δ [155.7, 154.9, (1:1)], [146.00, 145.96, (1:1)], [145.4, 145.3, (1:1)], [137.4, 137.3, (1:1)], 128.84, 128.82, 128.76, 128.73, 128.32, 128.28, 128.1, 127.8, 127.1, 126.79, 126.76, 126.68, 126.60, 126.57, [67.1, 66.9, (1:1)], 56.2, [53.13, 53.09, (1:1)], [52.9, 52.5, (1:1)], [47.2, 46.3, (1:1)], [21.5, 20.4, (1:1)]. IR (neat, cm^{-1}): 3031, 2963, 1700, 1447, 1410, 1357, 1216, 1095. Anal. Calcd (found) for $C_{25}H_{25}NO_2$: C, 80.83 (80.83); H, 6.78 (6.59); N, 3.77 (3.80).

All remaining cyclic carbamates were synthesized from the corresponding alkenyl carbamates employing a procedure analogous to that used to synthesize **5** unless noted otherwise.

***tert*-Butyl 2-methyl-4,4-diphenylpyrrolidinylcarbamate (Table 2, entry 3).** Viscous colorless oil. TLC: R_f = 0.44. ^{1}H NMR (1.3:1 ratio of rotamers): δ 7.29-7.11 (m, 10 H), [4.71 (d, *J* = 11.6 Hz), 4.49 (d, *J* = 11.6 Hz), 1.3:1, 1 H], [3.75-3.69 (m), 3.60-3.50 (m), 3.59 (d *J* = 12.0 Hz), 3.52 (d, *J* = 11.6 Hz), 2 H], 2.81-2.73 (m, 1 H), [2.29 (dd, *J* = 9.6, 12.0 Hz), 2.22 (dd, *J* = 9.6, 12.0 Hz), 1.3:1, 1 H], [1.50 (s), 1.45 (s), 1:1.3, 9 H], [1.30 (d, *J* = 6.0 Hz), 1.26 (d, *J* = 6.0 Hz), 1:1.3, 3 H]. ^{13}C{^{1}H} NMR: δ [155.4, 154.7, (1.3:1)], [146.1, 146.0, (1:1.3)], [145.63:145.56, (1:1.3)], 128.73, 128.69, 127.1, 126.9, 126.8, 126.7, 126.5, 126.4, 79.6, [56.5, 55.6, (1:1.3)], [53.2, 52.8, (1:1.3)], [52.55, 52.50, (1:1.3)], [47.3, 46.5, (1.3:1)], [28.9, 28.7, (1:1.3)], [21.3, 20.6, (1.3:1)]. IR (neat, cm^{-1}): 2970, 2930, 1690, 1392, 1160, 1135. Anal. Calcd (found) for $C_{22}H_{27}NO_2$: C, 78.30 (78.06); H, 8.06 (8.20); N, 4.15 (4.24).

4-Methoxybenzyl 2-methyl-4,4-diphenylpyrrolidinylcarbamate (Table 2, entry 4). Viscous colorless oil. TLC (hexanes–EtOAc = 2:1): R_f = 0.66. ^{1}H NMR (1:1 ratio of rotamers): δ

[7.35, (d, *J* = 8.4 Hz), 7.29-7.11 (m), 12 H], [6.92 (d, *J* = 8.4 Hz), 6.85 (d, *J* = 8.8 Hz), 1:1, 2 H], [5.24 (d, *J* = 12.0 Hz), 5.09 (s), 5.02 (d, *J* = 11.6 Hz), 1:2:1, 2 H], [4.72, (dd, *J* = 2.0, 11.6 Hz), 4.54 (dd, *J* = 2.0, 11.6 Hz), 1:1, 1 H], [3.82-3.63 (m), 3.82 (s), 3.79 (s), 3.65 (dd, *J* = 2.0, 11.6 Hz), 5 H], 2.86-2.78 (m, 1 H), [2.29 (dd, *J* = 9.6, 12.4 Hz), 2.24 (dd, *J* = 9.6, 12.4 Hz), 1:1, 1 H], [1.34 (d, *J* = 6.0 Hz), 1.25 (d, *J* = 6.0 Hz), 1:1, 3 H]. $^{13}C\{^{1}H\}$ NMR: δ [159.8, 159.6, (1:1)], [155.8, 155.0, (1:1)], 146.0, [145.4, 145.3, (1:1)], [130.2, 129.7, (1:1)], [129.6, 129.4, (1:1)], 128.83, 128.78, 128.7, [128.6, 128.3, (1:1)], [127.1, 126.8, (1:1)], 126.7, [126.6, 126.5, (1:1)], [114.2, 114.1, (1:1)], [66.9, 66.7, (1:1)], 55.2, [55.6, 55.5, (1:1)], 53.1, [52.9, 52.5, (1:1)], [47.1, 46.3, (1:1)], [21.4, 20.4, (1:1)]. IR (neat, cm^{-1}): 2959, 1698, 1513, 1407, 1354, 1247, 1093, 1033. Anal. Calcd (found) for $C_{26}H_{27}NO_3$: C, 77.78 (77.62); H, 6.78 (6.57); N, 3.49 (3.60).

9-Fluorenylmethyl 2-methyl-4,4-diphenyl-pyrrolidinyl-carbamate (Table 2, entry 5). White solid. mp 57-60 ºC. TLC: R_f = 0.27. ^{1}H NMR (1:1 ratio of rotamers): δ 7.79 (d, *J* = 6.8 Hz, 1 H), 7.74 (dd, *J* = 2.8, 7.6 Hz, 1 H), [7.64 (d, *J* = 7.6 Hz), 7.61 (d, *J* = 7.2 Hz), 1:1, 1 H], [7.55 (d, *J* = 7.2 Hz) 7.43-7.14 (m), 15 H], [4.71 (d, *J* = 11.6 Hz), 4.59 (dd, *J* = 6.4, 10.8 Hz), 1:1, 1 H], 4.49 (d, *J* = 6.4 Hz, 1 H), 4.45-4.37 (m, 1 H), [4.31 (t, *J* = 6.8 Hz), 4.26 (t, *J* = 6.4 Hz), 1:1, 1 H], [3.83-3.77 (m), 3.71-3.60 (m), 3.69 (t, *J* = 11.6 Hz), 2 H], 2.84 (dd, *J* = 6.0, 12.4 Hz, 1 H), [2.29 (dd, *J* = 9.2, 12.4 Hz), 2.24 (dd, *J* = 9.2, 12.8 Hz), 1:1, 1 H], [1.35 (d, *J* = 6.0 Hz), 1.14 (d, *J* = 6.0 Hz), 1:1, 3 H]. $^{13}C\{^{1}H\}$ NMR: δ [155.7, 154.8, (1:1)], [146.1, 146.0, (1:1)], [145.5, 145.3, (1:1)], [144.6, 144.5, (1:1)], [144.41, 144.40, (1:1)], [141.73, 141.69, (1:1)], [141.66, 141.64, (1:1)], [128.92, 128.90, (1:1)], 128.8, [127.99, 127.95, (1:1)], [127.89, 127.83, (1:1)], 127.42, 127.37, 127.27, 127.1, [126.83, 126.80, (1:1)], [126.73, 126.70, (1:1)], [126.67, 126.64, (1:1)], 125.32, 125.24, 125.17, 120.3, [120.19, 120.18, (1:1)], [67.3, 67.2, (1:1)], [56.25, 56.22, (1:1)], [53.1, 53.0, (1:1)], [52.9, 52.5, (1:1)], [47.8, 47.7, (1:1)], [47.1, 46.3, (1:1)], [21.2, 20.4, (1:1)]. IR (neat, cm^{-1}): 3061, 2963, 1696, 1449, 1415, 1352, 1200, 1097. HRMS Calcd (found) for $C_{32}H_{29}NO_2$ (M^+): 459.2198 (459.2197).

Benzyl 2-methyl-4-cyclohexylpyrrolidinylcarbamate (Table 2, entry 6). Colorless oil.

TLC: R_f = 0.41. ^{1}H NMR (60 ºC): δ 7.34-7.23 (m, 5 H), 5.11 (ABq, *J* = 12.4, 2 H), 3.93-3.84 (m, 1 H), 3.56 (br d, *J* = 10.0, 1 H), 2.99 (d, *J* = 11.2, 1 H), 1.99 (ddd, *J* = 2.0, 7.6, 13.2, 1 H), 1.44-1.22 (m, 14 H). ^{13}C{^{1}H} NMR (60 ºC): δ 155.5, 137.6, 128.7, 127.99, 127.96, 66.8, 57.2, 52.7, 46.4 (br), 41.5, 37.0, 35.2, 26.4, 24.1, 23.2, 21.5 (br). IR (neat, cm^{-1}): 2924, 2854, 1702, 1449, 1411, 1357, 1212, 1124, 1086. Anal. Calcd (found) for $C_{18}H_{25}NO_2$: C, 75.22 (75.03); H, 8.77 (8.85); N, 4.87 (4.99).

Benzyl 2,2-dimethyl-4-cyclohexylpyrrolidinylcarbamate (Table 2, entry 7). Colorless oil. TLC: R_f = 0.61. ^{1}H NMR (1.5:1 ratio of rotamers): δ 7.38-7.27 (m, 5 H), [5.15 (s), 5.10 (s), 1:1.5, 2 H], [3.41(s), 3.34 (s), 1:1.5, 2 H], [1.79 (s), 1.76 (s), 1:1.5, 2 H], 1.54-1.36 (m, 16 H). ^{13}C{^{1}H} NMR: δ [155.6, 154.3, (1:1.5)], [137.7, 137.2, (1.5:1)], 128.7, 128.3, 128.1, 128.0, 127.9, [67.1, 66.2, (1:1.5)], [61.0, 60.2, (1.5:1)], [60.0, 58.3, (1:1.5)], [55.4, 53.9, (1:1.5)], [39.8, 39.2, (1.5:1)], 37.4, [29.6, 28.3, (1:1.5)], 26.2, 23.7. IR (neat, cm^{-1}): 2925, 2852, 1703, 1450, 1403, 1348, 1066. Anal. Calcd (found) for $C_{19}H_{27}NO_2$: C, 75.71 (75.80); H, 9.03 (8.98); N, 4.65 (4.81).

Benzyl 2-methyl-3-hydroxy-4-cyclohexylpyrrolidinylcarbamate (Table 2, entry 8). Viscous colorless oil. TLC (hexanes–EtOAc = 2:1): R_f = 0.40. ^{1}H NMR (60 ºC, 3.6:1 mixture of diastereomers): δ 7.35-7.26 (m, 5 H), 5.13 (ABq, *J* = 12.4 Hz, 2 H), [3.98 (q, *J* = 6.4 Hz), 3.41 (br s), 3.6:1, 1 H], 3.78 (br s, 1 H), 3.58-3.50 (m, 1 H), [3.23 (d, *J* = 10.8 Hz), 2.99 (d, *J* = 11.6 Hz), 1 H, 3.6:1], [2.19 (br s), 1.89 (br s), 1 H, 1:3.6], [1.68-1.22 (m), 1.31 (d, *J* = 6.0 Hz), 13 H]. ^{13}C{^{1}H} NMR (60 ºC): δ 156.0, 137.5, 128.7, 128.1, 128.0, [85.7, 78.9, (1:3.6)], 67.0, [58.8, 56.9, (1:3.6)], [54.4, 53.8, (1.3:1)], [45.4, 43.7, (3.6:1)], [34.7, 33.9, (1:3.6)], 29.9, [26.9, 26.4, (1:3.6)], [24.0, 23.4, (1:3.6)], [22.9, 22.7, (3.6:1)], [19.5 (br s), 14.3 (br s), 1:3.6]. IR (neat, cm^{-1}): 3437, 2926, 2853, 1684, 1449, 1419, 1356, 1121, 1022. Anal. Calcd (found) for $C_{18}H_{25}NO_3$: C, 71.26 (70.95); H, 8.31 (8.57); N, 4.62 (4.42).

Benzyl 2-methyl-3-acetyl-4-cyclohexylpyrrolidinylcarbamate (Table 2, entry 9). Viscous colorless oil. TLC: R_f = 0.22. ^{1}H NMR (60 ºC, 3.0:1 mixture of diastereomers): δ 7.34-7.27 (m, 5 H), [5.14, (abq, *J* = 12.4 Hz), 5.14 (d, *J* = 5.2 Hz), 4.78 (d, *J* = 4.0 Hz), 3 H], [4.14-4.07 (m), 3.75-3.56 (m), 2 H], [3.31 (d, *J* = 10.8 Hz), 3.18 (d, *J* = 10.8 Hz), 1:3.0, 1 H], [2.08 (s), 2.06 (s), 3.0:1, 3 H], 1.57-1.19 (m, 13 H). ^{13}C{^{1}H} NMR (60 ºC): δ [170.5, 170.4, (1:3.0)], [155.6, 155.4, (3.0:1)], 137.3, 128.6, 128.1, 128.0, [85.0, 80.2, (1:3.0)], 67.0, [59.3, 55.9, (1:3.0)], [54.8, 54.7, (1:3.0)], [44.7, 44.0, (3.0:1)], [34.7, 33.4, (1:3.0)], [29.9, 29.4, (3.0:1)], [26.1, 26.0, (3.0:1)], 23.2, [23.0, 22.5, (1:3.0)], [21.0, 20.6, (1:3.0)], [19.2 (br), 14.27 (br), (1:3.0)]. IR (neat, cm^{-1}): 2930, 2855, 1735, 1701, 1409, 1355, 1229, 1120, 1023. Anal. Calcd (found) for $C_{20}H_{27}NO_4$: C, 69.54 (69.65); H, 7.88 (7.82); N, 4.05 (4.23).

Benzyl 2-methyl-4-(4-methoxyphenyl)pyrrolidinylcarbamate (Table 2, entry 10). Colorless oil. TLC: R_f = 0.28. ^{1}H NMR (60 ºC, 3.5:1 mixture of diastereomers): δ 7.41-7.29 (m, 5 H), 7.16-7.14 (m, 2 H), 6.89-6.85 (m, 2 H), 5.19 (abq, *J* = 12.4 Hz, 2 H), [4.24-3.97 (m), 3.90-3.84 (m), 2 H], 3.79 (s, 3 H), [3.51-3.16 (m), 3.30 (t, *J* = 12.4 Hz), 2 H], [2.51 (quintet, *J* = 6.4 Hz), 2.16 (dt, *J* = 8.0, 12.4 Hz), 3.5:1, 1 H], [1.94 (dd, *J* = 6.0, 12.0 Hz), 1.74-1.64 (m), 1:3.5, 1 H], [1.40 (br d, *J* = 3.6 Hz), 1.32 (br d, *J* = 5.6 Hz), 3.5:1, 3 H]. ^{13}C{^{1}H} NMR (60 ºC): δ [158.92, 158.90, (3.5:1)], [155.2 (br s), 155.0 (br s), (3.5:1)], [137.51, 137.46, (1:3.5)], [133.6, 132.9, (1:3.5)], 128.7, 128.3, 128.2, 128.12, 128.10, 128.07, [114.45, 114.42, (1:3.5)], [66.91, 66.86, (3.5:1)], 55.5, 54.3 (br s), 53.4, 42.6, 40.8 (br s), 21.1 (br s). IR (neat, cm^{-1}): 2960, 1697, 1515, 1411, 1355, 1269, 1179, 1034. Anal. Calcd (found) for $C_{20}H_{23}NO_3$: C, 73.82 (73.86); H, 7.12 (6.92); N, 4.30 (4.45).

The cis stereochemistry of the major diastereomer was determined by combined ^{1}H-^{1}H COSY and NOESY analysis of a pure sample of the major diastereomer.

Benzyl 2,5-dimethyl-pyrrolidinylcarbamate (Table 2, entry 11).[3,7] ^{1}H NMR (1.5:1 mixture of diastereomers): δ 7.38-7.27 (m, 5 H), [5.17 (d, *J* = 12.4 Hz), 5.09 (d, *J* = 12.0 Hz)], 5.13 (s), 1:1.5, 2 H], 4.06-3.90 (m, 2 H), [2.16-2.04 (m), 2.04-1.92 (m), 1:1.5, 2 H], 1.64-1.50 (m, 2 H),

[1.25 (br s), 1.18 (d, J = 6.4 Hz), 1.11 (d, J = 6.4 Hz), 3 H]. An authentic sample was prepared in 84% yield by reaction of 2,5-dimethylpyrrolidine and benzyl chloroformate employing a procedure similar to that used to synthesize **4**.

Benzyl 2-methyl-pyrrolidinylcarbamate (Table 2, entry 12).[8] ^{1}H NMR (60 ºC): δ 7.38-7.25 (m, 5 H), 5.14 (ABq, J = 12.8 Hz, 2 H), 4.02-3.95 (m, 1 H), 3.44 (dd, J =6.4, 7.2 Hz, 2 H), 2.05-1.75 (m, 3 H), 1.60-1.54 (m, 1 H), 1.20 (d, J = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR (60 ºC): δ 155.1, 137.7, 128.7, 128.1, 128.0, 66.8, 53.5, 46.7, 33.4, 23.7, 20.6 (br).

Benzyl 2-methyl-2,3-dihydroindolylcarbamate (Table 2, entry 13). Viscous colorless oil. TLC: R_f = 0.48. ^{1}H NMR (60 ºC): δ 7.75 (br s, 1 H), 7.45-7.32 (m, 6 H), 7.20-7.14 (m, 2 H), 6.97 (dd, J = 1.2, 7.6 Hz, 1 H), 5.31 (s, 2 H), 4.65-4.56 (dtd, J = 2.4, 6.4, 15.6 Hz 1 H), 3.38 (dd, J = 9.6, 16.0 Hz, 1 H), 2.66 (dd, J = 2.4, 16.0 Hz, 1 H), 1.33 (d, J = 6.4 Hz, 3 H). ^{13}C{^{1}H} NMR (60 ºC): δ 153.3, 141.8, 136.9, 130.4, 128.9, 128.45, 128.41, 127.8, 125.3, 123.1, 115.9, 67.5, 55.8, 36.3, 21.5. IR (neat, cm^{-1}): 2968, 1698, 1484, 1404, 1281, 1137, 1045. Anal. Calcd (found) for $C_{17}H_{17}NO_2$: C, 76.38 (76.56); H, 6.41 (6.48); N, 5.24 (5.26).

Benzyl 2-methyl-octahydroindolylcarbamate (Table 2, entry 14). Colorless oil. TLC: R_f = 0.44. ^{1}H NMR (60 ºC, 2.5:1 mixture of rotamers): δ 7.37-7.25 (m, 5 H), [5.134 (s), 5.126 (ABq, J = 12.4 Hz), 2 H, 2.5:1], 4.4-3.72 (m, 2 H), 2.44-1.91 (m, 3 H), 1.74-1.57 (m, 4 H), [1.50-1.08 (m), 1.36 (d, J = 6.0 Hz), 7 H]. ^{13}C{^{1}H} NMR (60 ºC, major isomer): δ 155.2, 137.8, 128.7, 128.1, 128.0, 66.6, 58.4, 54.0, 36.7, 36.4, 29.9, 26.4, 24.4, 22.7 (br), 20.9. IR (neat, cm^{-1}): 2926, 2855, 1698, 1407, 1355, 1087. Anal. Calcd (found) for $C_{17}H_{23}NO_2$: C, 74.69 (74.57); H, 8.48 (8.34); N, 5.12 (5.34).

Benzyl 2-methyl-5-cyclohexylcarbamate (Table 2, entry 15). Colorless oil. TLC: R_f = 0.44. ^{1}H NMR: δ 7.36-7.27 (m, 5 H), 5.14 (ABq, J = 12.4 Hz, 2 H), 4.45 (br s, 1 H), 3.95 (br d, J = 10.4 Hz, 1 H), 2.56 (d, J = 13.6 Hz, 1 H), 1.91-1.82 (m, 1 H), 1.45-1.17 (m, 13 H), 1.13 (d, J = 7.2 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 156.0, 137.5, 128.7, 128.1, 128.0, 67.1, 47.3, 46.7, 38.4, 33.4, 31.3,

30.8, 26.9, 25.6, 21.9, 21.8, 16.3. IR (neat, cm^{-1}): 2927, 1696, 1423, 1337, 1223, 1145. Anal. Calcd (found) for $C_{19}H_{27}NO_2$: C, 75.71 (75.45); H, 9.03 (9.12); N, 4.65 (4.66).

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