Supporting Information - I: *Experimental Procedures and Characterization*

Re_2O_7-Catalyzed Three-Component Synthesis of Protected Secondary and Tertiary Homoallylic Amines

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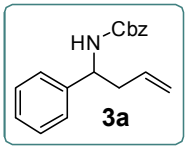
Contents: **Page:**

General Experimental Procedures:

All reagents and solvents were used as supplied commercially. Commercial Re_2O_7, ranging in color from yellow to brown-black, were stored in a desiccator over $CaCl_2$. Reactions were conducted in open atmosphere. Analytical thin-layer chromatography (TLC) were performed on 0.2 mm coated Science silica gel (EM 60-F254) plates purchased from Merck, Germany. Visualization was accomplished with UV light (254 nm) and exposure to either ethanolic phosphomolybdic acid (PMA), anisaldehyde or $KMnO_4$ solution followed by heating. Melting points are uncorrected. ^{1}H NMR spectra were acquired on a Bruker AVANCE (at 400 MHz) and chemical shifts are reported relative to the residual solvent peak. ^{13}C NMR spectra were acquired on a Bruker AVANCE (at 100 MHz) and chemical shifts are reported in ppm relative to the residual solvent peak. Unless noted, NMR spectra were acquired in $CDCl_3$; individual peaks are reported as: multiplicity, integration, coupling constant in Hz. All IR spectra were obtained as neat films with a Perkin-Elmer Model Spectrum BX FT-IR and selected absorbances are reported in cm^{-1}. Low resolution (LR) and High-resolution (HR) mass spectrometry data were acquired by the Central Instrumentation Facility (CIF), Indian Institute of Science Education and Research Bhopal on a Bruker Daltonics MicroTOF-Q-II Mass Spectrometer using CH_3CN/H_2O as solvent.

Standard procedure for one-pot homoallylic amine synthesis: To a stirred solution of carbonyl (1.00 mmol) and carbamate (1.20 or 1.50 mmol) in acetonitrile (4.0 ml) at rt allyl trimethyl silane (1.50 or 2.00 mmol) was added followed by the addition of Re_2O_7 (1.5 or 2.5 mol%). After stirring for given time on *Table 2, 3*, or 4, the reaction mixture was passed through a plug of silica. The solvent was removed under vacuum and the crude was purified by flash column chromatography (EtOAc/Hexane) on silica gel.

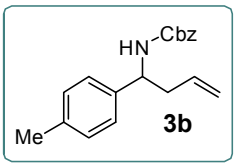


3a

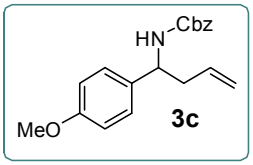
Benzyl-(1-phenylbut-3-en-1-yl)carbamate (3a):[1-3] 90% yield; R_f = 0.32 (10:90 = EtOAc/Hexane); Colorless solid; mp. 62-64°C; IR (neat): 3325, 3065, 3032, 1715, 1519, 1250, 1027, 917, 752, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50–7.17 (10H), 5.80-5.62 (m, 1H), 5.25-5.05 (5H), 4.85 (s br, 1H), 2.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7 (***C***=O), 141.9 (***C***), 136.5 (***C***), 133.7 (***C***H=CH_2), 128.6, 128.5,

128.2, 127.3, 126.3 (***C***H^{Ar}), 118.5 (CH=***C***H$_2$), 66.8 (O***C***H$_2$), 54.5 (allyl-***C***H), 41.0 (vinyl-***C***H$_2$); LRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{18}H_{19}NNaO_2$: 304.1; found; 304.1.

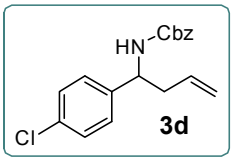
Benzyl-(1-(p-tolyl)but-3-en-1-yl)carbamate (3b):[4] 90% yield; R_f = 0.31 (10:90 = EtOAc/Hexane); Colorless solid; mp. 66-67°C; IR (neat): 3335, 3032, 2922, 1697, 1515, 1250, 1042, 917, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.45-7.20 (5H), 7.19-7.05 (4H), 5.75-5.55 (1H), 5.20-4.95 (5H), 4.80-4.60 (1H), 2.49 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.6 (q ***C***=O), 138.9, 136.9, 136.5 (***C***), 133.9 (***C***H=CH$_2$), 129.2, 128.5, 128.1, 126.2 (***C***H^{Ar}), 118.3 (CH=***C***H$_2$), 66.7 (O***C***H$_2$), 54.3 (allyl-***C***H), 41.0 (vinyl-***C***H$_2$), 21.0 (***C***H$_3$); LRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{19}H_{21}NNaO_2$, 318.1; found, 318.1.



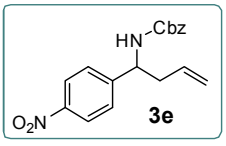
Benzyl-(1-(4-methoxyphenyl)but-3-en-1-yl)carbamate (3c):[1-3] 82% yield; R_f = 0.22 (10:90 = EtOAc/Hexane); Colorless solid; mp. 68-69°C; IR (neat): 3317, 2953, 1694, 1513, 1245, 1033, 919 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55-7.30 (5H), 7.20 (d, *J* = 8 Hz, 2H), 6.90 (d, *J* = 8 Hz, 2H), 5.70 (m, *J* = 8 Hz, 1H), 5.24-5.02 (5H), 4.78 (br, 1H), 3.82 (s, 3H), 2.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.8 (***C***-OMe), 155.7 (***C***=O), 136.5 (***C***), 133.9 (***C***H=CH$_2$), 128.5, 128.1, 127.4 (***C***H^{Ar}), 118.3 (CH=***C***H$_2$), 114 (***C***H), 66.7 (O***C***H$_2$), 55.3 (***C***H$_3$O), 54.0 (allyl-***C***H), 41.0 (vinyl-***C***H$_2$); LRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{19}H_{21}NNaO_3$, 334.1; found: 334.1.



Benzyl-(1-(4-chlorophenyl)but-3-en-1-yl)carbamate (3d):[2,3] 81% yield; R_f = 0.32 (10:90 = EtOAc/Hexane); Colorless solid; mp. 65-66°C; IR (neat): 3343, 3034, 1693, 1520, 1250, 1038, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55-7.05 (9H), 5.66 (m, *J* = 8 Hz, 1H), 5.25-4.95 (5H), 4.90-4.60 (s, 1H), 2.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.5 (***C***=O), 140.5 (***C***), 136.2 (***C***), 133.2 (***C***H=CH$_2$), 132.9 (q ***C***), 128.5, 128.1, 127.5 (***C***H), 118.8 (***C***H$_2$), 66.8 (O***C***H$_2$), 53.9 (allyl-***C***H), 40.8 (vinyl-***C***H$_2$); LRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{18}H_{18}ClNNaO_2$, 338.0; found: 338.0.

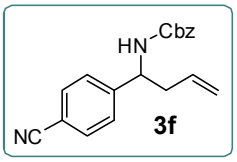


Benzyl (1-(4-nitrophenyl)but-3-en-1-yl)carbamate (3e):[1,2] 63% yield; R_f = 0.16 (10:90 = EtOAc/Hexane); Colorless solid; mp. 87-88°C; IR (neat):

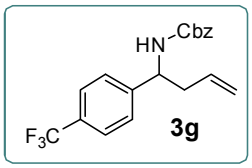


3324, 3032, 1693, 1519, 1347, 1257, 1041, 854 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.21 (d, J = 8 Hz, 2H), 7.55-7.15 (7H), 5.75-5.55 (1H), 5.27 (s, 1H), 5.26- 5.01 (4H), 4.89 (br s, 1H) 2.56 (2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.6 (***C***=O), 149.7 (***C***), 147.2 (NO_2-***C***), 136.1 (***C***), 132.5 (***C***H=CH_2), 128.6, 128.3, 128.2, 127.1, 123.9 (***C***H^{Ar}), 119.7 (CH=***C***H_2), 67.1 (O***C***H_2), 54.1 (allyl-***C***H), 40.7 (vinyl-***C***H_2); LRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{18}H_{18}N_2NaO_4$, 349.1; found; 349.1.

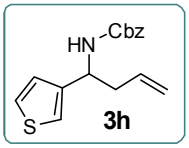
Benzyl (1-(4-cyanophenyl)but-3-en-1-yl)carbamate (3f):[3] 64% yield; R_f = 0.34 (20:80 = EtOAc/Hexane); Colorless oil; IR (neat): 3343, 3067, 2228, 1713, 1519, 1250, 1042, 921, 836, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.64 (d, J = 8 Hz, 2H), 7.50-7.21 (7H), 5.73-5.53 (1H), 5.33-5.00 (5H), 4.85 (br s, 1H), 2.56 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.6 (***C***=O), 147.7 (***C***), 136.1 (***C***), 132.6 (***C***H=CH_2), 132.4, 128.5, 128.3, 127.0 (***C***H^{Ar}), 119.5 (***C***N), 118.7 (CH=***C***H_2), 111.2 (NC-***C***), 67.1 (O***C***H_2), 54.3 (ally-***C***H), 40.7 (vinyl-***C***H_2); LRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{19}H_{18}N_2NaO_2$, 329.1; found: 329.1.



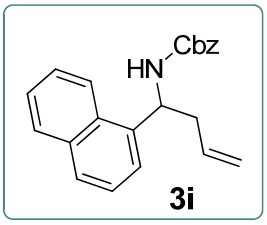
Benzyl (1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)carbamate (3g):[3] 87% yield; R_f = 0.37 (10:90 = EtOAc/Hexane); Colorless solid; mp. 69-70°C; IR (neat): 3334, 2945, 1681, 1530, 1331, 1260, 1116, 921, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.61 (d, J = 8 Hz, 2H), 7.48-6.80 (7H), 5.80-5.56 (1H), 5.34-5.02 (5H), 4.88 (s br, 1H), 2.55 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.6 (***C***=O), 146.2 (***C***), 136.2 (***C***), 132.9 (***C***H=CH_2), 130.0, 129.7, 129.4, 129.0, (quartet, ***C***F_3) 128.5, 128.4, 128.3, 126.5 (***C***H^{Ar}), 125.63, 125.59, 125.55, 125.51, 125.4 (CF_3-***C***), 122.7 (***C***H^{Ar}), 119.2 (CH=***C***H_2), 67.0 (O***C***H_2), 54.1 (allyl-***C***H), 40.9 (vinyl-***C***H_2); LRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{19}H_{18}F_3NNaO_2$, 372.1; found: 372.1.



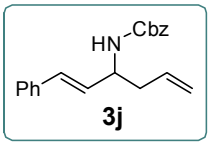
Benzyl (1-(thiophen-3-yl)but-3-en-1-yl)carbamate (3h): 92% yield; R_f = 0.25 (10:90 = EtOAc/Hexane); Colorless solid; mp. 45-46°C; IR (neat): 3324, 3068, 1702, 1527, 1328, 1250, 1042, 917, 785 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.50-7.25 (6H), 7.13 (s, 1H), 7.03 (d, J = 4 Hz, 1H), 5.84-5.64 (m,1H), 5.28-4.72 (6H), 2.61 (2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7 (***C***=O), 143.0 (***C***), 136.5 (***C***), 133.7 (***C***H=CH_2), 128.5,



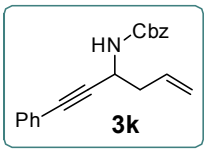
128.2, 126.2, 126.1, 120.9 (***C***H^{Ar}), 118.5 (CH=***C***H$_2$), 66.8 (O***C***H$_2$), 50.5 (ally-***C***H), 40.3 (vinyl-***C***H$_2$); HRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{16}H_{17}NNaO_2S$, 310.0872; found: 310.0879.



Benzyl (1-(naphthalen-1-yl)but-3-en-1-yl)carbamate (3i): 93% yield; R_f = 0.30 (10:90 = EtOAc/Hexane); Colorless solid; mp. 111-113°C; IR (neat): 3328, 3065, 1702, 1510, 1250, 1027, 917, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 8.17 (s, 1H), 7.91 (d, *J* = 8 Hz, 1H), 7.82 (1H), 7.65-7.25 (9H), 5.90-5.55 (2H), 5.40-5.85 (5H), 2.90-2.55 (2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7 (***C***=O), 137.4 (***C***), 136.5 (***C***), 134.0 (***C***H=CH$_2$), 130.8 (***C***), 128.9, 128.5, 128.1, 126.4, 125.7, 125.2 (***C***H^{Ar}), 123.0 (***C***), 122.7 (***C***H^{Ar}), 118.4 (CH=***C***H$_2$), 66.8 (O***C***H$_2$), 50.4 (allyl-***C***H), 40.2 (vinyl-***C***H$_2$); HRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{22}H_{21}NNaO_2$, 354.1470; found: 354.1495.

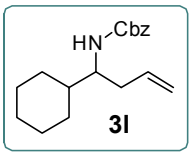


(E)-Benzyl (1-phenylhexa-1,5-dien-3-yl)carbamate (3j):[2] 85% yield; R_f = 0.33 (10:90 = EtOAc/Hexane); Colorless solid; mp. 73-75°C; IR (neat): 3326, 3063, 1713, 1519, 1236, 1027, 966, 917, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55-7.10 (10H), 6.56 (d, *J* = 16 Hz, 1H), 6.17 (dd, *J* = 8 Hz, 16 Hz, 1H), 5.91-5.75 (1H), 5.26-5.08 (4H), 4.92 (s, 1H), 4.51 (s, 1H), 2.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7 (***C***=O), 136.6 (C), 136.5 (C), 133.5 (***C***H=CH$_2$), 130.5 (***C***H), 129.5, 128.6, 128.5, 128.2, 127.7, 126.5 (***C***H^{Ar}), 118.6 (***C***H=CH$_2$), 66.8 (O***C***H$_2$), 52.2 (allyl-***C***H), 39.8 (vinyl-***C***H$_2$); LRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{20}H_{21}NNaO_2$, 346.1; found: 346.1.



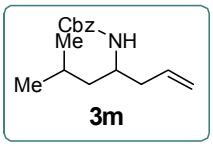
Benzyl (1-phenylhex-5-en-1-yn-3-yl)carbamate (3k):[2] 98% yield; R_f = 0.21 (05:95 = EtOAc/Hexane); Colorless solid; mp. 54-55°C; IR (neat): 3318, 3065, 1713, 1505, 1337, 1237, 1027, 918, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.54-7.22 (10H), 6.10-6.85 (1H), 5.40-5.00 (5H), 4.84 (s, 1H), 2.80-2.40 (2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.3 (***C***=O), 136.3 (***C***), 132.8 (***C***H=CH$_2$), 131.7, 128.5, 128.4, 128.3, 128.2 (***C***H^{Ar}), 122.5 (***C***), 119.1 (CH=***C***H$_2$), 87.8 (Ph-***C***≡C), 83.7 (Ph-C≡***C***), 67.0 (O***C***H$_2$), 43.4 (allyl-***C***H), 40.4 (vinyl-***C***H$_2$); LRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{20}H_{19}NNaO_2$: (M + Na): 328.1; found; 328.1.

Benzyl (1-cyclohexylbut-3-en-1-yl)carbamate (3l):[2,3] 96% yield; R_f = 0.48 (10:90 = EtOAc/Hexane); Colorless solid; mp. 59-60°C; IR (neat): 3329, 2926, 1694, 1537, 1255, 1026, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.30 (5H), 5.78 (m, *J* = 4, 8 Hz,1H), 5.20-5.00 (4H), 4.61 (d, *J* = 8 Hz, 1H), 3.61 (1H), 2.40-2.05 (2H), 1.85-1.60 (5H), 1.50-0.85 (6H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.3 (***C***=O), 136.7 (C), 134.7 (***C***H=CH_2), 128.5, 128.0 (***C***H^{Ar}), 117.5 (CH=***C***H_2), 66.5 (O***C***H_2), 55.2 (allyl-***C***H), 41.4 (***C***H), 36.7 (vinyl-***C***H_2), 29.7, 28.3, 26.4, 26.2, 26.1 (***C***H_2); LRMS (ESI, *m/z*): $[M + K]^+$ calculated for $C_{18}H_{25}NKO_2$, 326.1; found: 326.1.



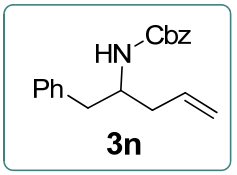
3l

Benzyl (6-methylhept-1-en-4-yl)carbamate (3m): 90% yield; R_f = 0.43 (10:90 = EtOAc/Hexane); Colorless liquid; IR (neat): 3329, 2956, 1694, 1531, 1263, 1232, 1025, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.42-7.30 (5H), 5.79 (m, *J* = 8 Hz, 1H), 5.25-4.95 (4H), 4.55 (1H), 3.82 (1H), 2.25 (dq, *J* = 8, 16 Hz, 2H), 1.69 (ht, *J* = 8 Hz, 1H), 1.32 (t, *J* = 8 Hz, 2H), 0.94 (t, *J* = 4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.9 (***C***=O), 136.7 (C), 134.2 (***C***H=CH_2), 128.5, 128.04, 128.01 (***C***H^{Ar}), 117.9 (CH=***C***H_2), 66.5 (O***C***H_2), 48.8 (allyl-***C***H), 43.9 (***C***H_2), 40.0 (***C***H_2), 24.8 (***C***HMe_2), 23.0, 22.2 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{16}H_{23}NNaO_2$: 284.1621; found: 284.1627.



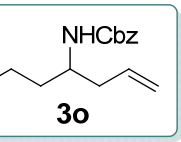
3m

Benzyl (1-phenylpent-4-en-2-yl)carbamate (3n):[1,3] 76% yield; R_f = 0.40 (10:90 = EtOAc/Hexane); Colorless solid; mp. 46-48°C; IR (neat): 3351, 2933, 1726, 1505, 1455, 1237, 1086, 916, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.10 (10H), 5.95-5.70 (1H), 5.25-5.00 (4H), 4.68 (s, 1H), 4.01 (s, 1H), 2.98-2.70 (2H), 2.45-2.05 (2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7 (***C***=O), 137.8 (***C***), 136.6 (***C***), 134.1 (***C***H=CH_2), 129.4, 128.5, 128.4, 128.1, 128.0, 126.4, 118.2 (CH=***C***H_2), 66.5 (O***C***H_3), 51.6 (allyl-***C***H), 40.4 (***C***H_2), 38.1 (***C***H_2); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{19}H_{21}NNaO_2$, 318.1470; found: 318.1462.



3n

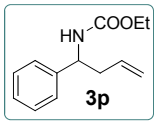
Benzyl (1-phenylhex-5-en-3-yl)carbamate (3o):[2] 88% yield; R_f = 0.17 (5:95 = EtOAc/Hexane); Colorless solid; mp. 49-50°C; IR (neat): 3328, 3029, 2944, 1698, 1531, 1454, 1242, 1046, 915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.50-7.08 (10H), 5.92-5.65 (1H), 5.25-5.00 (4H), 4.81- 4.40 (1H), 4.00 – 3.60



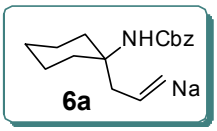
3o

(1H), 2.80-2.60 (2H), 2.40-2.15 (2H), 1.95-1.65 (2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.0 (***C***=O), 141.1 (***C***), 136.6 (***C***), 133.9 (***C***H=CH_2), 128.5, 128.4, 128.3, 128.1, 128.0, 125.9 (***C***H^{Ar}), 118.1 (CH=***C***H_2), 66.6 (O***C***H_2), 50.5 (allyl-***C***), 39.5 (vinyl-***C***H_2), 36.5, 32.4 (***C***H_2); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{20}H_{23}NNaO_2$, 332.1626; found: 332.1617.

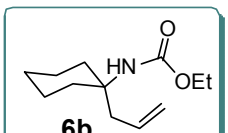
Ethyl (1-phenylbut-3-en-1-yl)carbamate (3p): [2,3] 95% yield; R_f = 0.27 (10:90 = EtOAc/Hexane); Colorless liquid; IR (neat): 3324, 2980, 1694, 1531, 1252, 1047, 917 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.42-7.21 (5H), 5.80-5.60 (1H), 5.20-5.00 (3H), 4.81 (s, 1H), 4.10 (q, J = 8 Hz, 2H), 2.56 (t, J = 8 Hz, 2H), 1.24 (bs, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.9 (***C***=O), 142.1 (***C***), 133.8 (***C***H=CH_2), 128.5, 127.2, 126.2 (***C***H^{Ar}), 118.3 (CH=***C***H_2), 60.9 (O***C***H_2), 54.3 (allyl-***C***H), 41.1 (vinyl-***C***H_2), 14.6 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{13}H_{17}NNaO_2$: 242.1157; found: 242.1161.



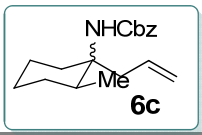
Benzyl (1-allylcyclohexyl)carbamate (6a): [2] 70% yield; R_f = 0.43 (05:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3352, 2931, 1730, 1505, 1248, 1092, 973, 917 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.42-7.30 (5H), 5.86-5.70 (1H), 5.15-4.95 (4H), 4.56 (s, 1H), 2.50 (d, *J* = 8 Hz, 2H), 2.99 (bs, 2H), 1.65-1.11 (8H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.5 (***C***=O), 136.8 (***C***), 133.7 (***C***H=CH_2), 128.5, 128.0 (***C***H^{Ar}), 118.0 (CH=***C***H_2), 65.9 (O***C***H_2), 54.7 (allyl-***C***), 42.5 (vinyl-***C***H_2), 34.7, 25.6, 21.6 (***C***H_2); LRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{17}H_{23}NNaO_2$, 296.1; found: 296.1.



Ethyl (1-allylcyclohexyl)carbamate (6b): 75% yield; R_f = 0.42 (05:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3352, 2932, 1713, 1505, 1228, 1103, 914 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 5.86-5.66 (1H), 5.16-5.00 (2H), 4.43 (s, 1H), 4.07 (s, 2H), 2.47 (d, J = 8Hz, 2H), 2.08- 1.85 (2H), 1.65-1.05 (11H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.8 (***C***=O), 133.8 (***C***H=CH_2), 117.9 (CH=***C***H_2), 60.0 (O***C***H_2), 54.5 (allyl-***C***), 42.6 (vinyl-***C***H_2), 34.7, 25.6, 21.6 (***C***H_2), 14.6 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{12}H_{21}NNaO_2$: (M + Na): 234.1465; found: 234.1467.

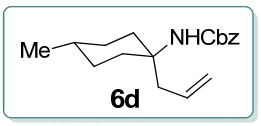


Benzyl (1-allyl-2-methylcyclohexyl)carbamate (6c): 61% yield; R_f = 0.50 (5:95 = EtOAc/Hexane); *dr* = 20:80; Colorless liquid; IR (neat): 3358, 2931,

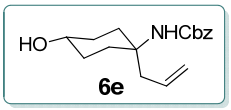


1714, 1513, 1213, 1075, 913 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.30 (5H), 5.79 (m, J = 8 Hz, 1H), 5.25-4.95 (4H), 4.76-4.48 (1H), 2.96 (s, 1H), 2.65-1.95 (2H), 1.90-1.10 (8H), 1.01-0.86 (3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.8 (***C***=O), 154.7 (***C***=O of second diastereomer), 136.8 (C), 134.1, 133.4, 128.54, 128.51, 128.1, 128.06, 128.02, 128.00, 118.6 (CH=***C***H_2), 117.9 (CH=***C***H_2 of second diastereomer), 66.1 (O***C***H_2), 57.9 (allyl-***C***), 57.3 , 40.7, 36.8, 35.4, 31.5, 29.8, 24.6, 22.1, 21.5, 15.0 (CH_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{18}H_{25}NNaO_2$, 310.1778; found: 310.1777.

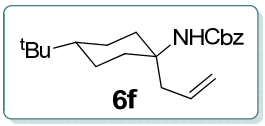
Benzyl ((1r,4r)-1-allyl-4-methylcyclohexyl)carbamate (6d): 82% yield; R_f = 0.15 (2:98 = EtOAc/Hexane); *dr* = 10:90; Colorless liquid; IR (neat): 3351, 2924, 1713, 1505, 1455, 1226, 1094, 988, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.45-7.30 (5H), 5.90-5.70 (1H), 5.30-4.90 (4H), 4.70-4.30 (two s, 1H), 2.56 & 2.48 (two d for two diatereomers, *J* = 7.2 Hz, 2H), 2.11 (d, *J* = 13.2 Hz, 2H), 1.67-1.45 (2H), 1.43-1.20 (3H), 1.18-1.01 (2H), 0.97-0.85 (3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.58 & 154.53 (***C***=O of two diastereomers), 136.9 (***C***), 133.8 & 133.6 (***C***H=CH_2), 128.5, 128.02, 128.01 (***C***H^{Ar}), 118.1 & 118.0 (CH=***C***H_2), 66.0 (O***C***H_2), 54.2 (allyl-***C***), 43.9 (vinyl-***C***H_2), 34.5, 32.2 (***C***H), 30.2 (***C***H_2), 22.2 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{18}H_{25}NNaO_2$, 310.1783; found: 310.1788.



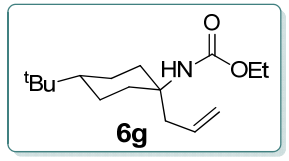
Benzyl ((1r,4r)-1-allyl-4-hydroxycyclohexyl)carbamate (6e): 76% yield; R_f = 0.33 (40:60 = EtOAc/Hexane); *dr* = 23:77; Colorless liquid; IR (neat): 3410, 3342, 2935, 1702, 1508, 1455, 1247, 1073, 989, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.20 (5H), 5.87-5.66 (1H), 5.25-4.95 (4H), 4.75-4.55 (two s, 1H), 3.98 - 3.54 (two m for two diatereomers, 1H), 2.52 & 2.46 (two d, *J* = 7.2 Hz, 2H), 1.96 (b s, 1H), 1.86-1.65 (5H), 1.64-1.25 (3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.7 & 154.6 (***C***=O of two diastereomers), 136.7 (***C***), 133.4 133.2 (***C***H=CH_2), 128.5, 128.08, 128.04, 128.01 (***C***H^{Ar}), 118.5 & 118.4 (CH=***C***H_2), 69.7, 66.9 (HO-***C***H), 66.1 (O***C***H_2), 54.4, 53.7 (allyl-***C***), 41.1 (vinyl-***C***H_2), 30.4, 29.2 (***C***H_2); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{17}H_{23}NNaO_3$, 312.1570; found: 312.1554.



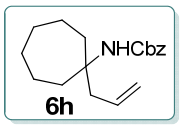
Benzyl ((1r,4r)-1-allyl-4-(tert-butyl)cyclohexyl)carbamate (6f): 90% yield; R_f = 0.45 (5:95 = EtOAc/Hexane); *dr* = 6:94; Colorless solid; mp. 80-81°C; IR (neat): 3353, 2948, 1694, 1523, 1256, 1234, 1098, 911 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.25 (5H), 5.88-5.70 (1H), 5.30-4.90 (4H), 4.48 (s, 1H), 2.46 (d, *J* = 8 Hz, 2H), 2.17 (d, *J* = 12 Hz, 2H), 1.72-1.52 (2H), 1.40-1.06 (4H), 1.05-0.75 (10H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.6 (***C***=O), 154.5 (***C***=O), 136.9 (***C***), 133.8 (***C***H=CH_2), 128.0, 127.9 (***C***H^{Ar}), 118.0 (CH=***C***H_2), 65.9 (O***C***H_2), 54.3 (allyl-***C***), 47.7, 44.0, 35.0, 32.3, 27.5, 22.3 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{21}H_{31}NNaO_2$, 352.2247; found: 352.2247.



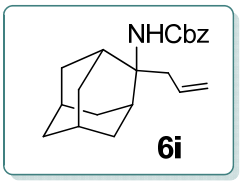
Ethyl ((1r,4r)-1-allyl-4-(tert-butyl)cyclohexyl)carbamate (6g): 86% yield; R_f = 0.42 (5:95 = EtOAc/Hexane); *dr* = 6:94; Colorless liquid; IR (neat): 3346, 2943, 1713, 1505, 1257, 1234,1103, 913 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 5.90-5.70 (1H), 5.18-4.98 (2H), 4.35 (s, 1H), 4.08 (q, *J* = 8 Hz, 2H), 2.44 (d, *J* = 8Hz, 2H), 2.26-1.98 (2H), 1.68-1.52 (2H), 1.35-0.75 (17H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.9 (***C***=O), 134.0 (***C***H=CH_2), 117.8 (CH=***C***H_2), 60.0 (O***C***H_2), 54.1 (allyl-***C***), 47.8, 44.0, 35.1, 32.3, 27.5, 22.9, 22.3 (***C***H_2), 14.6 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{16}H_{29}NNaO_2$: (M + Na): 290.2096; found: 290.2096.



Benzyl (1-allylcycloheptyl)carbamate (6h):[2] 77% yield; R_f = 0.41 (5:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3351, 2926, 2856, 1715, 1505, 1461, 1227, 1099, 1024, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.44-7.29 (5H), 5.86-5.70 (1H), 5.20-4.95 (4H), 4.61 (s, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 2.00-1.80 (2H), 1.78-1.40 (10H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.5 (***C***=O), 136.8 (***C***), 134.1 (***C***H=CH_2), 128.5, 128.03, 128.01 (***C***H^{Ar}), 118.1 (CH=***C***H_2), 66.0 (O***C***H_2), 58.5 (allyl-***C***), 43.0 (vinyl-***C***H_2), 38.4, 29.4, 22.2 (***C***H_2); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{18}H_{25}NNaO_2$, 310.1778; found: 310.1776.

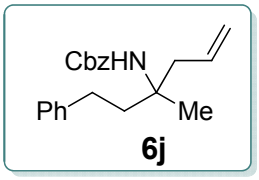


Benzyl ((1r,3r,5r,7r)-2-allyladamantan-2-yl)carbamate (6i): 68% yield; R_f = 0.41 (5:95 = EtOAc/Hexane); Colorless solid; mp. 52-53°C; IR (neat): 3352, 2910, 1738, 1505, 1230, 1089, 991, 913 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.41-7.30 (5H), 7.85-7.65 (1H), 5.20-4.95 (4H), 4.63 (s,

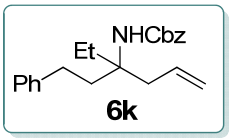


1H), 2.80 (d, J = 8 Hz, 2H), 2.15 (s, 2H), 2.10-1.93 (4H), 1.94-1.78 (2H), 1.77-1.53 (6H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.2 (***C***=O), 136.9 (***C***), 133.7 (***C***H=CH_2), 128.5, 128.0, 127.9 (***C***H^{Ar}), 117.8 (CH=***C***H_2), 65.9 (O***C***H_2), 59.5 (allyl-***C***), 38.5 (vinyl-CH_2), 37.0 (CH), 33.3 (*C*H_2), 32.9, 32.8, 27.2 (***C***H), 27.0 (***C***H_2); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{21}H_{27}NNaO_2$: (M + Na): 348.1934; found: 348.1936.

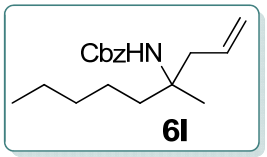
Benzyl (3-methyl-1-phenylhex-5-en-3-yl)carbamate (6j): 62% yield; R_f = 0.32 (5:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3351, 2933, 1713, 1505, 1237, 1074, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.10 (10H), 5.92-5.76 (1H), 5.25-5.03 (4H), 4.71 (s, 1H), 2.70-2.54 (3H), 2.50-2.32 (1H), 2.22-1.82 (2H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 153.6 (***C***=O), 141.2 (***C***), 135.9 (***C***), 132.5 (***C***H=CH_2), 127.6, 127.5, 127.24, 127.21, 124.9 (***C***H^{Ar}), 117.9 (CH=***C***H_2), 65.2 (O***C***H_2), 54.1 (allyl-***C***), 42.4 (vinyl-***C***H_2), 39.6, 29.3 (***C***H_2), 23.6 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{21}H_{25}NNaO_2$, 346.1778; found: 346.1778.



Benzyl (3-ethyl-1-phenylhex-5-en-3-yl)carbamate (6k): 40% yield; R_f = 0.39 (5:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3353, 2962, 2937, 1715, 1505, 1455, 1231, 1088, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.10 (10H), 5.95-5.67 (1H), 5.25-5.00 (4H), 4.54 (s, 1H), 2.66-2.38 (4H), 2.10-1.85 (2H), 1.75 (q, J = 7.6 Hz, 2H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.3 (***C***=O), 142.2 (***C***), 136.8 (***C***), 133.2 (***C***H=CH_2), 128.5, 128.3, 128.0, 125.8 (***C***H^{Ar}), 118.5 (CH=***C***H_2), 66.1 (O***C***H_2), 57.8 (allyl-***C***), 39.2, 37.1, 29.8, 27.9 (***C***H_2), 7.8 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{22}H_{27}NNaO_2$, 360.1939; found: 360.1937.

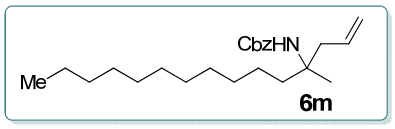


Benzyl (4-methylnone-1-en-4-yl)carbamate (6l): 54% yield; R_f = 0.45 (5:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3352, 2931, 1714, 1505, 1235, 1089, 914 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.45-7.25 (5H), 5.88-5.72 (1H), 5.16-5.00 (4H), 4.63 (s, 1H), 2.60-2.25 (2H), 1.85-1.45 (2H), 1.40-1.10 (9H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.5 (***C***=O), 136.8 (***C***), 133.7 (***C***H=CH_2), 128.5, 128.0, 128.01 (***C***H^{Ar}), 118.4 (CH=***C***H_2), 66.0 (O***C***H_2), 55.0

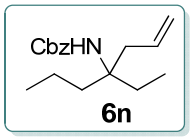


(allyl-***C***), 43.0 (vinyl-***C***H_2), 38.6, 32.1, 29.7, 24.3 (***C***H_2), 23.2 (***C***H_3), 22.6 (***C***H_2), 14.0 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{18}H_{27}NNaO_2$: 312.1934; found: 312.1931.

Benzyl (4-methylpentadec-1-en-4-yl)carbamate (6m): 49% yield; R_f = 0.41 (5:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3356, 2925, 1730, 1505, 1235, 1088, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.44-7.29 (5H), 5.88-5.68 (1H), 5.20-5.00 (4H), 4.62 (s, 1H), 2.60-2.22 (2H), 1.90-1.10 (23H), 0.90 (t, *J* = 8Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.5 (***C***=O), 136.8 (***C***), 133.8 (***C***H=CH_2), 128.5, 128.05, 128.02 (***C***H^{Ar}), 118.4 (CH=***C***H_2), 55.0 (O***C***H_2), 31.9, 29.9, 29.6, 29.3 (***C***H_2), 23.6 (***C***H_3), 22.7 (***C***H_2), 14.1 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{24}H_{39}NNaO_2$, 396.2873; found: 396.2863.



Benzyl (4-ethylhept-1-en-4-yl)carbamate (6n): 78% yield; R_f = 0.33 (5:95 = EtOAc/Hexane); Colorless liquid; IR (neat): 3351, 2961, 1715, 1506, 1455, 1233, 1097, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.25 (5H), 5.88-5.72 (1H), 5.20-5.00 (4H), 4.48 (s, 1H), 2.42 (d, J = 7.2 Hz, 2H), 1.80-1.50 (4H), 1.40-1.20 (2H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.3 (***C***=O), 136.8 (***C***), 133.5 (***C***H=CH_2), 128.5, 128.0 (***C***H^{Ar}), 118.2 (CH=***C***H_2), 65.9 (O***C***H_2), 57.8 (allyl-***C***), 39.3, 37.4, 27.9, 16.3 (***C***H_2), 14.4, 7.5 (***C***H_3); HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{17}H_{25}NNaO_2$: 298.1783; found: 298.1784.



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