Supporting Information - I: ***Experimental Procedures and Characterization***

Stereoselective Direct Reductive Amination of Ketones with Electron-Deficient Amines using $Re_2O_7/NaPF_6$ Catalyst

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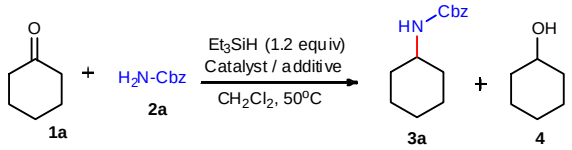
General Experimental Procedures:

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 desiccators 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 $KMnO_4$, $CeSO_4$ + ammonium phosphomolybdate + 10% H_2SO_4, ninhydrine solution followed by heating. Melting points are uncorrected. ^1H NMR spectra were acquired on a Bruker AVANCE (at 400 MHz or 500 MHz) and chemical shifts are reported relative to the residual solvent peak. ^{13}C NMR spectra were acquired on either a Bruker AVANCE (at 100 MHz or 125 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 2000 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, Indian Institute of Science Education and Research Bhopal on a Bruker Daltonics MicroTOF-Q-II Mass Spectrometer using CH_3CN/H_2O as solvent.

Optimization of the reaction conditions:



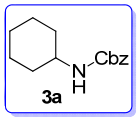
1a **2a** **3a** **4**

	Catalysts (1.5 mol %)	Additives (mol %)	Solvent	t/min	**3** [%][a]
1	Re_2O_7		CH_2Cl_2	rt, 3 d	0
2	Re_2O_7		CH_2Cl_2	reflux, 9h	0
3	$ReCl_3O(PPh_3)_2$		CH_2Cl_2	20h	0
4	$ReIO_2(PPh_3)_2$		CH_2Cl_2	20h	0
5	$ReCl_3O(SMe_2)OPPh_3$		CH_2Cl_2	20h	0
6	Re_2O_7	$NaBF_4$ (20)	CH_2Cl_2	15h	100
7	Re_2O_7	NH_4PF_6 (20)	CH_2Cl_2	15h	46
8	Re_2O_7	KPF_6 (20)	CH_2Cl_2	15h	7
9	Re_2O_7	$NaSbF_6$ (20)	CH_2Cl_2	15h	5
10	$ReCl_3O(SMe_2)PPh_3$	$NaPF_6$ (20)	CH_2Cl_2	20h	7
11	$ReIO_2(PPh_3)_2$	$NaPF_6$ (20)	CH_2Cl_2	20h	11
12	**Re_2O_7**	**$NaPF_6$ (20)**	CH_2Cl_2	**15h**	**100**
13	Re_2O_7	$NaPF_6$ (20)	THF	15h	2.5
14	Re_2O_7	$NaPF_6$ (20)	Et_2O	15h	55
15	Re_2O_7	$NaPF_6$ (20)	Tolune	15h	36
16	Re_2O_7	$NaPF_6$ (20)	MeOH	15h	0
17	Re_2O_7	$NaPF_6$ (20)	CH_3CN	15h	4
18	**Re_2O_7**	**$NaPF_6$ (20)**	CH_2Cl_2	**20h**	**(79)**[b]
19	Re_2O_7	$NaPF_6$ (5)	CH_2Cl_2	20h	(48)[b]

20	Re_2O_7	$NaPF_6$ (10)	CH_2Cl_2	20h	(60)[b]
21		$NaPF_6$ (20)	CH_2Cl_2	20h	0
22	NH_4OReO_3	$NaPF_6$ (20)	CH_2Cl_2	20h	0

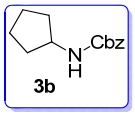
[a]The % was determined by ^{1}H NMR spectroscopy of the reaction mixture using *p*-anisaldehyde. [b]In parentheses the yield of the isolated product after column chromatography.

Standard procedure for reductive amination of ketone: To a stirred solution of carbonyl (1.00 mmol) and amine (1.20 mmol, 1.2 equiv) in CH_2Cl_2 (3.0 ml) was taken in a round bottom flask fitted with reflux condenser, sodium hexafluorophosphate (20 mol %) and triethylsilane (1.20 mmol, 1.2 equiv) was added followed by the addition of Re_2O_7 (1.5 mol %). After stirring at 50^{o}C on an oil-bath for a given time on *Table 2*, *3*, or 4, the reaction mixture was passed through a small silica bed & washed properly with dichloromethane. The solvent was removed under vacuum and the crude was purified by flash column chromatography (EtOAc/n-Hexane) on silica gel.



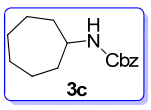
3a

Benzyl cyclohexylcarbamate (3a):[1] 79% yield; R_f = 0.25 (5:95 = EtOAc/n-Hexane); Colorless solid; mp. 81-84°C; IR (neat): 3320, 2931, 2855, 1699, 1684, 1540, 1456, 1313, 1276, 1143, 1050, 965, 825, 724, 693, 614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.39-7.29 (m, 5H), 5.11 (s, 2H), 4.69 (s, 2H), 3.53 (m, 1H), 1.98-1.94 (m, 2H), 1.75-1.70 (m, 2H), 1.64-1.60 (m, 1H), 1.37 (m, 2H), 1.23-1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.5, 136.7, 128.5, 128.1, 128.0, 66.4, 49.9, 49.8, 33.4, 25.4, 24.7; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{14}H_{20}NO_2$: 234.1494; found: 234.1411.



3b

Benzyl cyclopentylcarbamate (3b):[1] 67% yield; R_f = 0.20 (5:95 = EtOAc/n-Hexane); Colorless solid; mp. 51-53°C; IR (neat): 3325, 2953, 2870, 1695, 1683, 1539, 1256, 1048, 875, 825, 750, 728, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.39-7.28 (m, 5H), 5.12 (s, 2H), 4.74 (s, 1H), 4.02 (m, 1H), 1.98 (m, 2H), 1.64 (m, 4H), 1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.9, 136.6, 128.5, 128.1, 128.0, 66.5, 52.8, 33.2, 23.5; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{18}NO_2$: 220.1338; found: 220.1332.

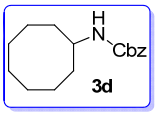


3c

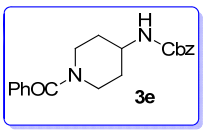
Benzyl cycloheptylcarbamate (3c): 83% yield; R_f = 0.27 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 54-57°C; IR (neat): 3331, 2928, 2857, 1715, 1694, 1531, 1455, 1315, 1239, 1104, 1040, 1020, 824, 776, 737, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.34-7.28 (m, 5H), 5.06 (s, 2H), 4.74 (s, 1H), 3.69 (s, 1H), 1.91 (m, 2H), 1.64-

1.35 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.4, 136.7, 128.5, 128.1, 128.0, 66.4, 52.1, 35.3, 28.0, 23.9 ; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{22}NO_2$: 248.1651; found: 248.1645.

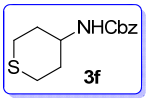
Benzyl cyclooctylcarbamate (3d):[2] 59% yield; R_f = 0.3 (10:90 = EtOAc/n-Hexane); Colorless liquid; IR (neat): 3331, 2923, 2855, 1712, 1694, 1520, 1455, 1312, 1245, 1093, 1045, 989, 776, 737, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.35-7.29 (m, 5H), 5.06 (s, 2H), 4.69 (s, 1H), 3.73 (s, 1H), 1.82 (m, 2H), 1.72-1.22 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.4, 136.7, 128.5, 128.0, 66.4, 51.1, 32.3, 27.2, 25.4, 23.5; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{16}H_{24}NO_2$: 262.1807; found: 262.1802.



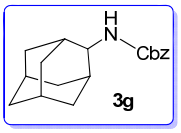
Benzyl (1-benzoylpiperidin-4-yl)carbamate (3e): 92% yield; R_f = 0.23 (30:70 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3306, 3061, 2947, 2862, 1713, 1614, 1531, 1446, 1370, 1318, 1275, 1233, 1109, 1041, 920, 848, 781, 733, 709, 629, 570cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.48-7.28 (m, 10 H), 5.11 (s, 2H), 4.85 (m, 1H), 4.61 (s, 1H), 3.78 (m, 2H), 3.04 (m, 2H), 2.51 (s, 1H), 1.99 (m, 2H), 1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 206.7, 170.4, 155.5, 136.3, 135.8, 129.7, 128.5, 128.2, 126.8, 66.7, 48.4, 41.0, 33.0, 32.1; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{20}H_{23}N_2O_3$: 339.1709; found: 339.1707.



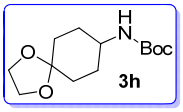
Benzyl (tetrahydro-2H-thiopyran-4-yl)carbamate (3f): 89% yield; R_f = 0.32 (20:80 = EtOAc/n-Hexane); Colorless solid; mp. 126-131°C; IR (neat): 3314, 2942, 1682, 1542, 1310, 1266, 1229, 1141, 1066, 1029, 968, 845, 757, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.31 (m, 5H), 5.07 (s, 2H), 4.73 (s, 1H), 3.52 (m, 1H), 2.62 (m, 4H), 2.20 (d, *J* = 12.66 Hz, 2H), 1.53 (dd, *J* = 17.25 Hz & 3.24 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 155.4, 136.4, 128.5, 128.1, 66.7, 49.3, 34.4, 27.7; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{18}NO_2S$: 252.1058; found: 252.1053



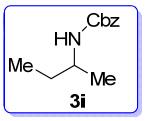
Benzyl-adamantan-2-ylcarbamate (3g): 91% yield; R_f = 0.33 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 66°C; IR (neat): 3340, 2907, 2857, 1717, 1700, 1522, 1507, 1456, 1431, 1090, 1013, 875, 824, 676 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.28 (m, 5H), 5.12 (s, 3H), 3.85 (d, *J* = 6.77 Hz, 1H), 1.96 (m, 2H), 1.82 (m, 10H), 1.63 (d, *J* = 12.63 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 155.6,



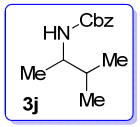
136.6, 128.5, 128.2, 128.1, 66.5, 55.0, 37.5, 37.1, 36.5, 31.7, 27.1, 27.0; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{24}NO_2$: 286.1807; found: 286.1807.



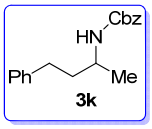
***tert*-Butyl 1,4-dioxaspiro[4.5]decan-8-ylcarbamate (3h):**[3] 72% yield; R_f = 0.28 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 115-120°C; IR (neat): 3371, 2952, 2872, 1681, 1519, 1456, 1366, 1274, 1159, 1103, 929, 877, 831, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 4.46 (s, 1H), 3.94 (s, 4H), 3.53(s, 1H), 1.93 (m, 2H), 1.73 (m, 3H), 1.63 (dt, *J* = 12.25 & 3.82 Hz, 2H), 1.49 (dd, *J* = 12.16 & 3.94 Hz, 1H), 1.45 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 155.2, 107.9, 79.2, 64.3, 64.2, 48.1, 38.1, 33.8, 33.0, 30.1, 28.4, 28.2; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{24}NO_4$: 258.1705; found: 258.1706.



Benzyl sec-butylcarbamate (3i):[4] 81% yield; R_f = 0.29 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 47°C; IR (neat): 3327, 2968, 1717, 1699, 1521, 1456, 1240, 1099, 1026, 737, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.38-7.28 (m, 5H), 5.11 (s, 2H), 4.63 (s, 1H), 3.68 (m, 1H), 4.18 (m, 2H), 1.15 (d, *J* = 6.60 Hz, 3H), 0.93 (t, *J* = 7.42 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.8, 136.7, 128.5, 128.0, 66.4, 48.5, 29.8, 20.6, 10.2; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{12}H_{18}NO_2$: 208.1338; found: 208.1359.

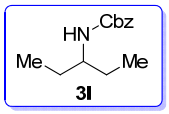


Benzyl (3-methylbutan-2-yl)carbamate (3j):[5] 95% yield; R_f = 0.31 (10:90 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3331, 3034, 2962, 2875, 1713, 1537, 1454, 1374, 1343, 1241, 101, 1028, 932, 775, 737, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.38-7.31 (m, 5H), 5.11 (s, 2H), 4.70 (s, 1H), 3.63 (m, 1H), 1.72 (m, 1H), 1.11 (d, *J* = 6.74 Hz, 3H), 0.92 (d, *J* = 6.74 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.9, 136.7, 128.5, 128.1, 128.0, 66.5, 51.9, 33.1, 28.3, 18.3, 17.7; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{20}NO_2$: 222.1494; found: 222.1492.

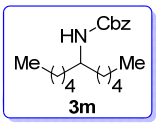


Benzyl (4-phenylbutan-2-yl)carbamate (3k): 66% yield; R_f = 0.37 (10:90 = EtOAc/n-Hexane); Off white solid; mp. 48°C; IR (neat): 3326, 3029, 2930, 1717, 1521, 1455, 1338, 1245, 1053, 1024, 748, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.40-7.19 (m, 10H), 5.31 (s, 2H), 4.63 (m, 1H), 3.83 (m, 1H), 2.29 (dt, *J* = 8.15 Hz & 2.79 Hz, 2H), 1.78 (m, 2H), 1.22 (d, *J* = 6.54 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):

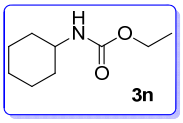
155.7, 141.7, 136.6, 128.5, 128.4, 128.3, 128.1, 125.9, 66.5, 47.0, 38.9, 32.4, 21.3; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{22}NO_2$: 284.1651; found: 284.1645.



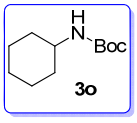
Benzyl pentan-3-ylcarbamate (3l):[6] 91% yield; R_f = 0.33 (10:90 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3314, 3035, 2960, 2875, 1693, 1537, 1454, 1298, 1249, 1159, 1101, 1044, 967, 777, 727, 694, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.38-7.31 (m, 5H), 5.12 (s, 2H), 4.57 (s, 1H), 3.52 (s, 1H), 1.45 (m, 2H), 1.36 (m, 3H), 0.93 (t, *J* = 7.39 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.3, 136.7, 128.5, 128.0, 66.4, 54.0, 27.6, 10.1; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{20}NO_2$: 222.1494; found: 222.1486.



Benzyl undecan-6-ylcarbamate (3m): 60% yield; R_f = 0.25 (03:97 = EtOAc/n-Hexane); Colorless solid; mp. 66°C; IR (neat): 3321, 2934, 2857, 1697, 1688, 1540, 1458, 1276, 1252, 1112, 1040, 825, 726, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.38-7.33 (m, 5H), 5.12 (s, 2H), 4.50 (d, *J* = 8.77 Hz, 1H), 3.63 (m, 1H), 1.49 (m, 2H), 1.32 (m, 15H), 0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.1, 136.8, 128.5, 128.0, 66.4, 51.3, 37.4, 35.4, 31.9, 31.7, 25.3, 22.5, 14.0; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{19}H_{32}NO_2$: 306.2433; found: 306.2435.

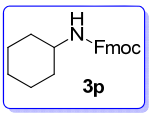


Ethyl cyclohexylcarbamate (3n):[7] 91% yield; R_f = 0.22 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 52-55°C; IR (neat): 3323, 2974, 2932, 2856, 1685, 1540, 1447, 1371, 1314, 1280, 1251, 1235, 1146, 1056, 968, 892, 779, 667, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 4.59 (s, 1H), 4.09 (d, *J* = 6.91 Hz, 2H), 3.47 (s, 1H), 1.91 (m, 2H), 1.70 (m ,2H), 1.59 (m, 1H), 1.34 (m, 2H), 1.23 (t, *J* = 7.10 Hz, 3H), 1.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.8, 60.4, 49.6, 33.4, 25.4, 24.7, 14.6; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_9H_{18}NO_2$: 172.1338; found: 172.1388.

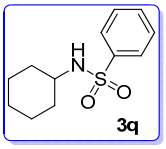


tert-butyl cyclohexylcarbamate (3o): 61% yield; R_f = 0.29 (05:95 = EtOAc/n-Hexane); Colorless solid; mp. 72-74°C; IR (neat): 3364, 2933, 2853, 1681, 1523, 1447, 1365, 1315, 1279, 1251, 1232, 1167, 1048, 902, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 4.44 (s, 1H), 3.43 (s, 1H), 1.93 (m, 2H), 1.70 (m, 2H), 1.60 (m, 1H), 1.45 (s, 9H), 1.34 (m, 2H), 1.13 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.2, 78.9, 49.3, 33.5, 28.4, 25.5, 24.8; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{11}H_{21}NaNO_2$: 222.1470; found: 222.1478.

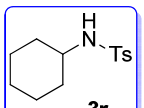
(9H-Fluoren-9-yl)methyl cyclohexylcarbamate (3p): 84% yield; R_f = 0.29 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 161-163°C; IR (neat): 3324, 2933, 2852, 1683, 1534, 1445, 1311, 1276, 1140, 1041, 757, 734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.79 (d, *J* = 7.52 Hz, 2H), 7.62 (d, *J* = 7.52 Hz, 2H), 7.43 (t, *J* = 7.44 Hz, 2H), 7.34 (td, *J* = 7.49 Hz, 0.92 Hz, 2H), 4.67 (s, 1H), 4.32 (d, *J* = 6.58 Hz, 2H), 4.25 (t, *J* = 6.63 Hz, 1H), 3.52 (s, 1H), 1.97 (m, 2H), 1.74 (m, 2H), 1.63 (m, 1H), 1.38 (m, 2H), 1.16 (m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 155.6, 144.0, 141.3, 127.6, 127.0, 125.0, 119.9, 66.3, 49.9, 47.3, 33.4, 25.5, 24.8; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{21}H_{24}NO_2$: 322.1807; found: 322.1814.



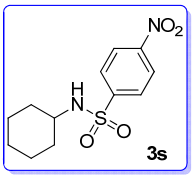
N-Cyclohexylbenzenesulfonamide (3q): 55% yield; R_f = 0.19 (10:90 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3281, 2934, 2856, 1484, 1448, 1324, 1160, 1094, 993, 914, 884, 840, 756, 720, 690, 593, 561 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.90 (m, 2H), 7.55 (m, 3H), 4.59 (d, *J* = 7.30 Hz, 1H), 3.17 (m, 1H), 1.77 (m ,2H), 1.64 (m, 3H), 1.53 (m, 1H), 1.20 (m, 5H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 141.4, 132.4, 129.0, 126.8, 52.6, 33.9, 25.1, 24.6; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{12}H_{18}NO_2S$: 240.1058; found: 240.1091.



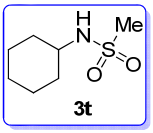
N-Cyclohexyl-4-methylbenzenesulfonamide (3r):[8] 86% yield; R_f = 0.21 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 81-83°C; IR (neat): 3278, 2933, 2856, 1599, 1451, 1324, 1160, 1094, 994, 914, 883, 815, 666, 572 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.79(d, *J* = 8.24 Hz, 2H), 7.31 (d, *J* = 8.09), 4.77 (d, J = 6.38 Hz, 1H), 3.12 (m, 1H), 2.44 (s, 3H), 1.75 (m, 2H), 1.63 (m, 2H), 1.51(m, 1H), 1.18 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.0, 138.5, 129.6, 126.9, 52.5, 33.8, 25.1, 24.6, 21.5; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{13}H_{19}NaNO_2S$: 276.1034; found: 276.1068.



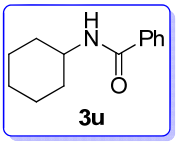
N-Cyclohexyl-4-nitrobenzenesulfonamide (3s): 42% yield; R_f = 0.32 (20:80 = EtOAc/n-Hexane); Colorless solid; mp. 129-131°C; IR (neat): 3287, 2933, 2856, 1530, 1451, 1350, 1164, 1093, 854, 736, 685, 615, 560, 466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.39 (d, *J* = 8.17 Hz, 2H), 8.09 (s, *J* = 8.17 Hz, 2H), 4.55 (m, 1H), 3.26 (m, 1H), 1.80 (m, 1H), 1.68 (m, 1H), 1.59 (m, 3H, having residual water peak), 1.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 149.9, 147.5, 128.1, 124.3, 53.1, 34.0, 29.7, 24.9, 24.6; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{12}H_{16}NaN_2O_4S$: 307.0728; found: 307.0724.



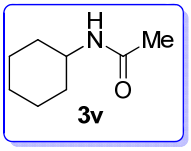
N-Cyclohexylmethanesulfonamide (3t): 66% yield; R_f = 0.22 (20:80 = EtOAc/n-Hexane); Colorless solid; mp. 100-104°C; IR (neat): 3254, 2934, 2854, 1452, 1423, 1307, 1155, 1080, 999, 884, 738, 525 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 4.37 (d, *J* = 6.38 Hz, 1H), 3.31 (m, 1H), 2.99 (s, 3H), 2.01 (m, 2H), 1.75 (m, 2H), 1.63 (m, 1H), 1.29 (m, 5H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 52.8, 42.1, 44.4, 25.1, 24.7; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_7H_{15}NaNO_2S$: 200.0721; found: 200.0767.



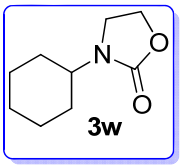
N-Cyclohexylbenzamide (3u): 85% yield; R_f = 0.25 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 149-151°C; IR (neat): 3314, 2929, 2852, 1627, 1535, 1330, 1256, 1149, 1081, 849, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.76 (d, *J* = 7.22 Hz, 2H), 7.44 (tt, *J* = 7.35 Hz & 2.14 Hz, 1H), 7.36 (t, *J* = 7.68 Hz, 2H), 6.43 (d, *J* = 6.80 Hz, 1H), 3.94 (m, 1H), 1.98 (m, 2H), 1.72 (m, 2H), 1.62 (m, 1H), 1.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 135.0, 131.1, 128.3, 126.9, 48.7, 33.1, 25.5, 24.9 ; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{17}NO$: 204.1388; found: 204.1401.



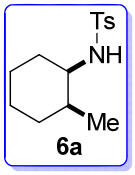
N-Cyclohexylacetamide (3v): 63% yield; R_f = 0.28 (50:50 = EtOAc/n-Hexane); Colorless solid; mp. 107-109°C; IR (neat): 3299, 2932, 2852, 1640, 1557, 1445, 1374, 1314, 1155, 1117, 981, 893, 737, 607, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 5.45 (s, 1H), 3.76 (m, 1H), 1.96 (s, 3H), 1.92 (m, 2H), 1.71 (m, 2H), 1.62 (m, 1H), 1.37 (m, 2H), 1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 169.1, 48.2, 33.2, 25.5, 24.8, 23.5; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_8H_{15}NO$: 142.1232; found: 142.1237.



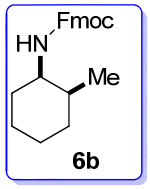
3-Cyclohexyloxazolidin-2-one (3w):[9] 65% yield; R_f = 0.27 (30:70 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3494, 2932, 2856, 1713, 1484, 1422, 1422, 1252, 1148, 1062, 999, 973, 893, 823, 763, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 4.27 (t, *J* = 8.07 Hz, 2H), 3.62 (m, 1H), 3.49 (t, *J* = 8.03 Hz, 2H), 1.77 (m, 4H), 1.63 (m, 1H), 1.33 (m, 4H), 1.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.8, 62.0, 52.4, 40.5, 30.2, 25.3, 25.2; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_9H_{16}NO_2$: 170.1181; found: 170.1199.



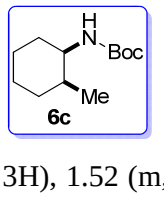
4-Methyl-N-(2-methylcyclohexyl)benzenesulfonamide (6a): 50% yield; *dr* = *19:81*; R_f = 0.21 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 95°-97°C; IR (neat): 3290, 22, 2858, 1599, 1453, 1326, 1162, 1093, 1022, 1007, 918, 882, 814, 666, 574, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.79 (d, *J* = 8.44 Hz, 2H), 7.30 (d, *J* = 7.99 Hz, 2H), 4.76 (m, 1H), 3.34 (m, 1H), 2.44 (s, 3H), 1.68 (m, 2H), 1.53 (m, 2H), 1.40 (m, 3H), 1.20 (m, 2H), 0.77 (d, *J* = 7.00 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.0, 138.3, 129.5, 127.0, 59.1, 54.4, 38.4, 34.3, 2.8, 25.4, 25.3, 23.4, 21.5, 19.0, 16.3; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{14}H_{22}NO_2S$: 268.1371; found: 268.1418.



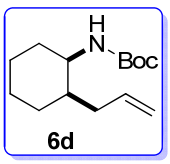
(9H-fluoren-9-yl)methyl (2-methylcyclohexyl)carbamate (6b) 88% yield; *dr* = *17:83*; R_f = 0.25 (10:90 = EtOAc/n-Hexane); Colorless solid; mp. 156-159°C; IR (neat): 3339, 2929, 2856, 1697, 1531, 1449, 1327, 1237, 1107, 1078, 991, 758, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.80 (d, *J* = 7.57 Hz, 2H), 7.63 (d, *J* = 7.45 Hz, 2H), 7.43 (t, *J* = 7.37 Hz, 2H), 7.35 (td, *J* = 7.49 Hz, 0.98 Hz, 2H), 4.83 (d, J = 8.36 Hz, 1H), 4.44 (m, 2H), 4.27 (t, *J* = 6.81 Hz, 1H), 3.83 (m, 1H), 1.17 (m, 1H), 1.76-1.16 (m, 9H), 0.91 (d, *J* = 7.02 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.0, 144.0, 141.3, 127.6, 127.0, 125.0, 119.9, 66.3, 51.3, 47.4, 33.7, 30.0, 22.0, 16.4 ; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{22}H_{26}NO_2$: 336.1964; found: 336.1958.



tert-Butyl (2-methylcyclohexyl)carbamate (6c):[10] 54% yield; *dr* = *9:91*; R_f = 0.31 (05:95 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3344, 2930, 2857, 1698, 1503, 1455, 1390, 1365, 1245, 1174, 1101, 1068, 1052, 967 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 4.59 (m, 1H), 3.74 (m, 1H), 1.85 (m, 1H), 1.68 (m, 3H), 1.52 (m, 2H), 1.46 (s, 9H), 1.32 (m, 2H), 1.20 (m, 2H), 0.87 (d, *J* = 6.95 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.6, 78.8, 50.6, 38.9, 33.8, 28.4, 25.5, 22.2, 16.2; HRMS (ESI, *m/z*): $[M - H]^+$ calculated for $C_{12}H_{22}NO_2$: 212.1651; found: 212.1677.

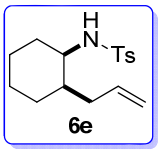


tert-Butyl (2-allylcyclohexyl)carbamate (6d): 75% yield; *dr* = *19:81*; R_f = 0.31 (10:90 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3347, 2977, 2930, 2857, 1697, 1505, 1454, 1391, 1365, 1247, 1172, 1062, 971, 910, 873, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 5.76 (m, 1H), 4.98 (m, 2H), 4.61 (m, 1H), 3.81 (m, 1H), 2.07 (m, 1H), 1.88 (m, 2H), 1.69 (m, 1H), 1.51 (m, 2H), 1.43 (s, 9H), 1.35 (m, 1H), 1.25 (m, 2H), 1.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.4, 137.1, 115.8, 78.9,



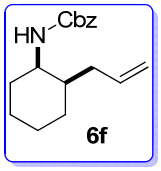
;53.5, 49.2, 43.4, 37.2, 34.3, 30.9, 30.7, 29.7, 28.4, 27.3, 25.5, 25.4, 24.3, 21.6; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{14}H_{26}NO_2$: 240.1964; found: 240.1945.

N-(2-Allylcyclohexyl)-4-methylbenzenesulfonamide (6e):[11] 74% yield; *dr* = *3:97*; R_f = 0.3 (15:85 = EtOAc/n-Hexane); White solid; mp. 145°-148°C; IR (neat): 3288, 2930, 2858, 1452, 1425, 1327, 1161, 1093, 1001, 910, 813, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.78 (d, *J* = 8.22 Hz, 2H), 7.31 (d, *J* = 8.03 Hz, 2H), 5.62 (m, 1H), 4.95 (m, 2H), 4.63 (d, *J* = 8.52 Hz, 1H), 3.48 (m, 1H), 2.44 (s, 3H), 2.00 (m, 1H), 1.89 (m, 1H), 1.54 (m, 3H), 1.42-1.04 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.1, 136.6, 129.6, 127.0, 116.0, 53.2, 40.1, 35.6, 30.5, 26.9, 23.8, 21.5, 21.2; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{16}H_{24}NO_2S$: 294.1528; found: 294.1541



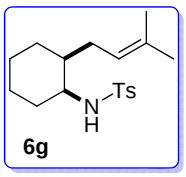
6e

Benzyl (2-allylcyclohexyl)carbamate (6f): 91% yield; *dr* = *>1:99*; R_f = 0.31 (5:95 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3342, 2930, 2856, 1713, 1695, 1519, 1455, 1335, 1237, 1105, 1064, 978, 911, 737, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.40-7.26 (m, 5H), 5.79 (m, 1H), 5.12 (s, 2H), 5.01 (d, *J* = 14.08 Hz, 2H), 4.89 (d, *J* = 7.73 Hz, 1H), 3.95 (m, 1H), 2.10 (m, 1H), 1.93 (m, 1H), 1.77 (m, 1H), 1.67 (m, 2H), 1.52 (m, 3H),1.34 (m, 2H), 1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.8, 136.9, 136.6, 128.5, 128.1, 116.0, 66.6, 49.9, 39.6, 36.2, 30.7, 27.2, 24.3, 21.5; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{17}H_{24}NO_2$: 274.1807; found: 274.1818.



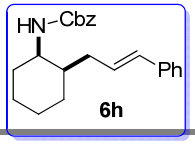
6f

4-Methyl-N-(2-(3-methylbut-2-en-1-yl)cyclohexyl)benzenesulfonamide (6g): 68% yield; *dr* = *>1:99*; R_f = 0.22 (10:90 = EtOAc/n-Hexane); Colorless solid, mp. 117°-123°C; IR (neat): 3291, 2928, 2856, 1599, 1451, 1328, 1158, 1093, 1021, 1001, 918, 814, 707, 670, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.76 (d, *J* = 8.25 Hz, 2H), 7.26 (d, *J* = 8.03 Hz, 2H), 4.82 (m, 2H), 3.41 (m, 1H), 2.39 (s, 3H), 1.77 (m, 2H), 1.60 (s, 3H), 1.54 (m, 2H), 1.48 (s, 3H), 1.37 (m, 4H), 1.26 (m, 1H), 1.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.0, 138.3, 129.5, 127.0, 122.3, 53.4, 40.8, 30.8, 27.1, 25.7, 21.5, 21.2, 17.7; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{18}H_{28}NO_2S$: 322.1841; found: 322.1837.



6g

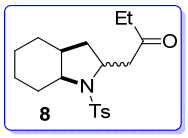
(E)-Benzyl (2-cinnamylcyclohexyl)carbamate (6h): 75% yield; *dr* = *12:88*; R_f = 0.21 (5:95 = EtOAc/n-Hexane); Colorless solid; mp. 81-85°C;



6h

IR (neat): 3432, 3346, 2930, 1704, 1505, 1455, 1335, 1232, 1094, 1059, 969, 743, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.33 (m, 9H), 7.21 (m, 1H), 6.40 (q, *J* = 16.03 Hz, 1H), 6.24 (m, 1H), 5.13 (s, 2H), 4.93 (d, *J* = 8.58 Hz, 1H), 3.98 (m, 1H), 2.26 (m, 1H), 2.08 (m, 1H), 1.78 (m, 2H), 1.58 (m, 4H), 1.32 (m, 2H), 1.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.8, 137.7, 137.6, 136.6, 128.5, 128.4, 128.2, 128.1, 126.9, 126.0, 125.9, 69.1, 66.6, 50.0, 41.8, 40.2, 33.1, 30.7, 25.1, 21.5, 20.4; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{23}H_{28}NO_2$: 350.2120; found: 350.2143.

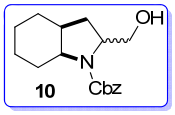
Synthesis of (1-(1-Tosyloctahydro-1H-indol-2-yl)butan-2-one (8):[12] To an oven dried round bottom flask, N-(2-allylcyclohexyl)-4-methylbenzenesulfonamide **6e** (0.5 mmol, 1 equiv), ethyl vinyl ketone (1.25 mmol, 2.5 equiv) were taken. After adding dry DCM (3 ml) to the flask, the solution was degassed for 0.5h with nitrogen gas. Next, 5 mol % of Grubbs-II catalyst was added into the reaction flask and continued to stirred for 18h at 40°C. The reaction mixture was passed through a plug of silica, concentrated, and the mixture was purified by column chromatography.



8

95% yield; R_f = 0.25 (30:70 = EtOAc/n-Hexane); colorless oil; IR (neat): 2933, 2859, 1713, 1599, 1455, 1415, 1337, 1158, 1094, 1009, 890, 816, 709, 665, 591 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.15-8.03 (2H), 7.55-7.15 (10H), 6.70-6.55 (3H), 6.41 (dd, *J* = 6, 16 Hz, 1H), 5.23 (d, *J* = 6 Hz, 1H), 4.93 (b s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.1, 140.3, 138.5, 136.0, 132.3, 129.2, 128.7, 128.6, 128.2, 128.1, 127.1, 126.6, 126.2, 112.1, 60.0; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{19}H_{28}NO_3S$: 350.1790; found: 350.1790.

Synthesis of Benzyl 2-(hydroxymethyl)octahydro-1H-indole-1-carboxylate (10): mCPBA (0.6 mmol, 1.2 equiv) was added to a cooled solution (ice bath) of Benzyl (2-allylcyclohexyl)-carbamate **6f** (0.5 mmol, 1 equiv) dissolved in 3 mL of CH_2Cl_2. After 10 minutes, the ice bath was removed and continued to stir at room temperature for additional 3h. The reaction mixture was diluted by adding 30 ml CH_2Cl_2 and then washed twice with 1N NaOH. The organic layer was evaporated after drying over anhydrous sodium sulfate. After dissolving the residue in *tert*-butanol (3 ml), ^{t}BuOK (0.6 mmol) was added followed by stirring for 12h at room temperature. The excess ^{t}BuOK was quenched (at 0°C) with 1N HCl and extract twice with 20 ml EtOAc. The organic layer was dried, concentrated and finally purified by column chromatography on silica-gel.



10

89% yield; R_f = 0.26 (20:80 = EtOAc/n-Hexane); colorless oil; IR (neat): 3430, 2931, 2861, 1682, 1416, 1337, 1298, 1122, 1094, 1046, 773, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.15-8.03 (2H), 7.55-7.15 (10H), 6.70-6.55 (3H), 6.41 (dd, *J* = 6, 16 Hz, 1H), 5.23 (d, *J* = 6 Hz, 1H), 4.93 (b s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.1, 140.3, 138.5, 136.0, 132.3, 129.2, 128.7, 128.6, 128.2, 128.1, 127.1, 126.6, 126.2, 112.1, 60.0; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{17}H_{24}NO_3$: 290.1756; found: 290.1751.

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