Supporting Information - I: *Experimental Procedures and Characterization*

The Direct Reductive Amination of Electron-deficient Amines with Aldehydes: the Unique Reactivity of Re_2O_7 Catalyst

Braja Gopal Das and Prasanta Ghorai*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal-462023, India. *E-mail*: pghorai@iiserb.ac.in

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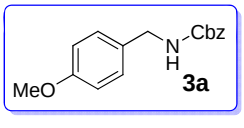
General Experimental Procedures:
All reagents and solvents were used as supplied commercially. Commercial Re_2O_7, (99.995% trace metal basis: purchased from both Alfa-Aesar and Sigma-Aldrich; 99.9% trace metal basis: purchased from Sigma-Aldrich) ranging in color from yellow to brown-black, were stored in a desiccator over $CaCl_2$. The Re_2O_7 containing 99.995% trace metal basis (purchased from Alfa-Aesar) were used for catalysis except for couple of screening reaction as mentioned in Table 1 where other source of Re_2O_7 were used. 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. ^{1}H NMR spectra were acquired on a 400 MHz spectrometer and chemical shifts are reported relative to the residual solvent peak. ^{13}C NMR spectra were acquired on a 100 MHz spectrometer 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 (quadrupole) Mass Spectrometer using CH_3CN/H_2O as solvent. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was conducted using Thermo-iCAP 6500 Series model at SID, IISc Bangalore.

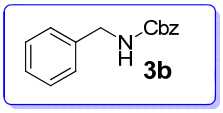
Standard procedure for direct reductive aminations: To a stirred solution of aldehyde (1.00 mmol) and carbamate (1.20 mmol) in CH_2Cl_2 (3.0 ML) at rt, triethylsilane (1.20 mmol) was added followed by the addition of Re_2O_7 (1.5 mol %). After stirring for given time on *Table 2*, *3*, or 4, the reaction was quenched with the addition of brine solution (2 mL), followed by extraction with EtOAc (3 × 15 mL). The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash column chromatography (EtOAc/Hexane) on silica gel.

Benzyl 4-methoxybenzylcarbamate (3a):[1] **96**% yield; R_f = 0.24 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 73-75°C; IR (neat): 3328, 2953, 1690, 1612, 1537, 1514, 1283, 1141, 1034, 978, 808, 696, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.44-7.31 (5H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.16 (s, 2H), 5.01 (s, 1H), 4.34 (d, *J* = 6.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100

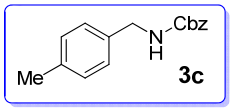


MHz, $CDCl_3$): 159.0, 156.3, 136.5, 130.4, 128.9, 128.5, 128.1, 114.0, 66.8, 55.3, 44.6; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{16}H_{17}NNaO_3$: 294.1106; found: 294.1105.

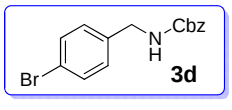
Benzyl benzylcarbamate (3b):[1] **90**% yield; R_f = 0.26 (10:90= EtOAc/n-Hexane); colourless solid; mp. 36-38°C; IR (neat): 3390, 3033, 1689, 1533, 1455, 1267, 1246, 1140, 1045, 969, 748, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.39-7.28 (10H), 5.17 (s, 3H), 4.24 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 138.4, 136.5, 128.7, 128.5, 128.1, 127.5, 66.8, 45.1; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{16}NO_2$: 242.1181; found: 242.1192.



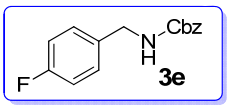
Benzyl 4-methylbenzylcarbamate (3c): 87% yield; R_f = 0.25 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 83-85°C; IR (neat): 3313, 3014, 1688, 1597, 1520, 1456, 1253, 1134, 1051, 967, 8.5, 749, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.48-7.32 (5H), 7.26-7.12 (4H), 5.17 (s, 3H), 4.37 (d, *J* = 5.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 137.1, 136.6, 135.4, 129.3, 128.5, 128.1, 127.5, 66.8, 44.9, 21.1; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{16}H_{17}NNaO_2$: 278.1157; found: 278.1159.



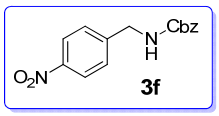
Benzyl 4-bromobenzylcarbamate (3d): 88% yield; R_f = 0.24(10:90 = EtOAc/n-Hexane); Colourless solid; mp. 83-85°C; IR (neat): 3316, 3095, 1683, 1651, 1599, 1256, 1360, 1256, 1195, 1055, 970, 809, 740, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.54-7.42 (d, *J* = 8.4 Hz, 2H), 7.41-7.32 (5H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 3H), 4.35 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 137.5, 136.3, 131.7, 128.2, 128.1, 121.3, 67.0, 44.5; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{15}H_{15}BrNO_2$: 320.0286; found: 320.0263.



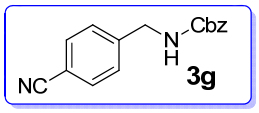
Benzyl 4-fluorobenzylcarbamate (3e): 88% yield; R_f = 0.25 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 61-63°C; IR (neat): 3321, 3066, 1689, 1665, 1541, 1510, 1272, 1221, 1139, 823, 754, 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.38-7.26 (7H), 7.03 (t, *J* = 8.8 Hz, 2H), 5.16 (s, 3H), 4.37 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.1 (d, ^{C-F}J = 244 Hz), 156.3, 136.4, 134.29, 134.22, 129.2, 129.1, 128.5, 128.2, 128.1, 115.6, 115.4, 66.9, 44.4; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{15}H_{14}NFNaO_2$: 282.0906; found: 282.0912.



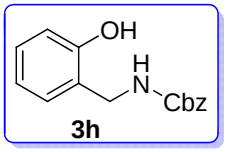
Benzyl 4-nitrobenzylcarbamate (3f):[1] **79**% yield; R_f = 0.30 (20:80 = EtOAc/n-Hexane); Colourless solid; mp. 94-96°C; IR (neat): 3294, 3099, 1688, 1607, 1537, 1513, 1452, 1354, 1273, 1146, 1061, 952, 846, 740, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.16 (d, *J* = 8.4 Hz, 2H), 7.44-7.36 (7H), 5.57 (s, 1H), 5.14 (s, 2H), 4.47 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.6, 147.2, 146.2, 136.2, 128.3, 127.9, 123.8, 67.1, 44.3; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{15}H_{15}N_2O_4$: 287.1032; found: 287.1048.



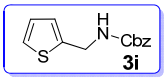
B**enzyl 4-cyanobenzylcarbamate (3g): 64**% yield; R_f = 0.29 (20:80 = EtOAc/n-Hexane); Colourless solid; mp. 82-84°C; IR (neat): 3337, 1715, 1699, 1521, 1247, 1136, 1044, 980, 814, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.63 (d, *J* = 8.4 Hz, 2H), 7.50-7.30 (7H), 5.29 (s, 1H), 5.16 (s, 2H), 4.46 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.5, 144.0, 136.1, 132.4, 128.6, 128.1, 127.8, 118.7, 111.3, 67.2, 67.9, 44.6; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{16}H_{14}N_2NaO_2$: 289.0953; found: 289.0947.



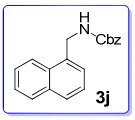
Benzyl 2-hydroxybenzylcarbamate (3h): 18% yield; R_f = 0.28 (20:80 = EtOAc/n-Hexane); Colorless liquid; IR (neat): 3329, 2953, 1686, 1523, 1357, 1256, 1127, 1044, 976, 847, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.49 (s, 1H), 7.37 (m, 5H), 7.24 (t, *J* = 7.9, 1H), 7.12 (dd, *J* = 1.52 Hz, 7.61 Hz, 1H), 6.97 (d, *J* = 7.95 Hz, 1H), 6.88 (dt, *J* = 1.09 Hz, 7.43 Hz, 1H), 5.58 (s, 1H), 5.18 (s, 2H), 4.33 (d, *J* = 6.68 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.6, 155.3, 135.7, 130.6, 129.9, 128.6, 128.4, 128.2, 124.5, 120.2, 117.6, 67.5, 41.4; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{15}H_{15}NNaO_3$: 280.0950; found: 280.0944.



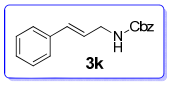
Benzyl (thiophen-2-ylmethyl)carbamate (3i): 99% yield; R_f = 0.21 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 52-54°C; IR (neat): 3415, 3332, 1723, 1698, 1591, 1455, 1253, 1128, 1048, 979, 832, 777, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.50-7.25 (6H), 7.16 (1H), 7.04 (d, *J* = 4.4 Hz, 1H), 5.22 (s, 1H), 5.16 (s, 2H), 4.14 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.3, 139.4, 136.5, 128.5, 127.1, 126.4, 122.0, 66.8, 40.3; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{13}H_{13}NNaSO_2$: 270.0565; found: 270.0568.



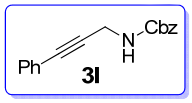
Benzyl (naphthalen-1-ylmethyl)carbamate (3j): 95% yield; R_f = 0.26 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 89-91°C; IR (neat): 3326, 3046, 1696, 1659, 1521, 1456, 1251, 1134, 1052, 770, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.02 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 5.6 Hz, 1H), 7.60-7.20 (9H), 5.20 (s, 1H), 5.15 (s, 2H), 4.83 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.2, 136.5, 133.9, 133.7, 131.3, 128.8, 128.5, 128.1, 128.1, 126.6, 126.2, 125.9, 125.4, 123.4, 66.9, 43.2; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{19}H_{18}NO_2$: 292.1338; found: 292.1332.



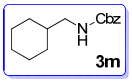
Benzyl cinnamylcarbamate (3k): 97% yield; R_f = 0.20 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 49-51°C; IR (neat): 3419, 3334, 1715, 1699, 1520, 1458, 1246, 1135, 966, 744, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.50-7.15 (10H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.30-6.10 (1H), 5.17 (s, 2H), 4.96 (s, 1H), 4.02 (t, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.2, 136.5, 131.8, 128.6, 128.5, 128.1, 127.7, 126.4, 125.8, 66.8, 43.1; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{17}H_{18}NO_2$: 268.1338; found: 268.1342.



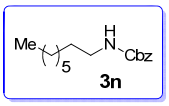
Benzyl (3-phenylprop-2-yn-1-yl)carbamate (3l): 73% yield; R_f = 0.23 (10:90 = EtOAc/n-Hexane); Light yellow solid; mp. 37-39°C; IR (neat): 3324, 3034, 1704, 1519, 1490, 1455, 1248, 1135, 1040, 986, 756, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.28 (10H), 5.18 (s, 2H), 5.12 (s, 1H), 4.26 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.9, 136.3, 131.7, 128.2, 122.5, 84.9, 83.4, 67.1, 31.7; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{17}H_{16}NO_2$: 266.1181; found: 266.1189.



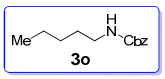
Benzyl (cyclohexylmethyl)carbamate (3m):[1] 98% yield; R_f = 0.28 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 64-66°C; IR (neat): 3315, 2924, 1691, 1546, 1446, 1249, 1138, 1094, 790, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.20 (5H), 5.08 (s, 2H), 4.88 (s, 1H), 3.02 (t, *J* = 6.4 Hz, 2H), 1.69 (5H), 1.42 (m, 1H), 1.18 (m, 3H), 0.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.5, 136.7, 128.5, 128.1, 128.0, 66.5, 47.3, 38.2, 30.6, 26.4, 25.8; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{22}NO_2$: 248.3407; found: 248.1657.



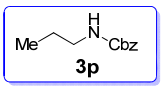
Benzyl octylcarbamate (3n): 98% yield; R_f = 0.32 (10:90 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 3336, 2927, 1726, 1704, 1531, 1455, 1250, 1137, 1027, 776, 735, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.40-7.24 (5H), 5.08 (s, 2H), 4.76 (s, 1H), 3.16 (q, *J* = 6.8 Hz, 2H), 1.46 (m, 2H), 1.26 (m, 10H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 136.7, 128.5, 128.1, 128.0, 66.5, 41.1, 31.7, 29.2, 29.2, 26.7, 22.6, 14.0; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{16}H_{26}NO_2$: 264.1964; found: 264.1973.



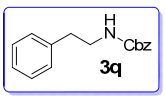
Benzyl pentylcarbamate (3o): 94% yield; R_f = 0.31 (10:90 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 3335, 2956, 2992, 2871, 1704, 1532, 1455, 1255, 1138, 1028, 735, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.42-7.28 (5H), 5.12 (s, 2H), 4.78 (s, 1H), 3.20 (q, *J* = 6.4 Hz, 2H), 1.51 (m, 2H), 1.32 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 136.7, 128.5, 128.1, 128.0, 66.5, 41.1, 29.6, 28.8, 22.3, 13.9; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{20}NO_2$: 222.1494; found: 222.1481.



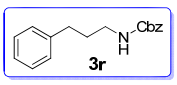
Benzyl propylcarbamate (3p): 94% yield; R_f = 0.30 (10:90 = EtOAc/n-Hexane); Colourless oil; IR (neat): 3338, 2964, 1726, 1700, 1534, 1455, 1262, 1138, 1044, 973, 749, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.28 (5H), 5.12 (s, 2H), 4.82 (s, 1H), 3.19 (q, *J* = 6.8 Hz, 2H), 1.55 (m, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 136.6, 128.5, 128.1, 128.0, 66.5, 42.8, 23.2, 11.2; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{11}H_{16}NO_2$: 194.1181; found: 194.1185.



Benzyl phenethylcarbamate (3q):[1] **97**% yield; R_f = 0.24 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 62-64°C; IR (neat): 3328, 3029, 1684, 1651, 1541, 1454, 1297, 1262, 1090, 906, 746, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.45-7.21 (10H), 5.13 (s, 2H), 4.85 (s, 1H), 3.50 (q, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.3, 138.7, 136.6, 128.8, 128.6, 128.5, 128.1, 126.5, 66.6, 42.2, 36.1; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{16}H_{18}NO_2$: 256.1338; found: 256.1343.

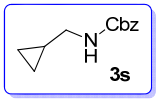


Benzyl (3-phenylpropyl)carbamate (3r): 99% yield; R_f = 0.23 (10:90 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 3419, 3336, 3029, 2939, 1726, 1698, 1520, 1454, 1246, 1134, 1027, 744, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):

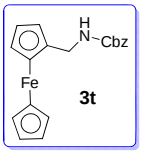


7.50-7.10 (10H), 5.15 (s, 2H), 4.90 (s, 1H), 3.26 (q, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.88 (m, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 141.4, 136.6, 128.5, 128.4, 128.4, 128.1, 126.0, 66.6, 40.7, 33.0, 31.6; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{17}H_{19}NNaO_2$: 292.1313; found: 292.1300.

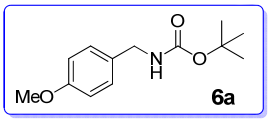
Benzyl (cyclopropylmethyl)carbamate (3s): 98% yield; R_f = 0.32 (10:90 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 3397, 3006, 1713, 1693, 1519, 1455, 1247, 1132, 1020, 993, 736, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.20 (5H), 5.12 (s, 3H), 3.07 (t, *J* = 6.0 Hz, 2H), 0.97 (m, 1H), 0.49 (d, *J* = 7.6 Hz, 2H), 0.20 (d, *J* = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.4, 136.7, 128.5, 128.3, 128.0, 128.0, 66.5, 45.9, 11.0, 3.2; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{12}H_{16}NO_2$: 206.1181; found: 206.1186.



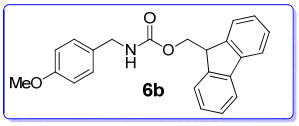
Benzyl ferrocenyl carbamate (3t): 69% yield; R_f = 0.31 (10:90 = EtOAc/n-Hexane); Light yellow solid; mp. 90°C; IR (neat): 3415, 3338, 1706, 1515, 1244, 1105, 1039, 920, 821, 737, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.28 (5H), 5.15 (s, 2H), 4.94 (s, 1H), 4.31-4.11 (12H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.0, 136.5, 128.5, 128.1, 99.9, 68.6, 68.1, 68.0, 66.7, 40.4; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{19}H_{19}NFeO_2$: 349.0765; found: 349.0762.



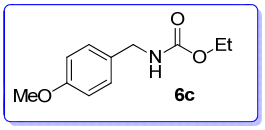
tert-Butyl 4-methoxybenzylcarbamate (6a): 76% yield; R_f = 0.30 (20:80 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 3358, 2977, 1712, 1699, 1513, 1366, 1095, 864, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.22 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.88 (s, 1H), 4.26 (d, *J* = 5.2 Hz, 2H), 3.80 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.8, 155.8, 131.0, 128.8, 113.9, 79.3, 55.2, 44.1, 28.4; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{13}H_{19}NNaO_3$: 260.1263; found: 260.1273.



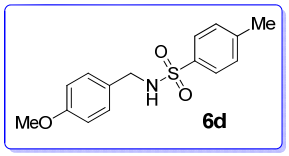
(9H-fluoren-9-yl)methyl 4-methoxybenzylcarbamate (6b): 92% yield; R_f = 0.29 (20:80 = EtOAc/n-Hexane); Colourless solid; mp. 127^{o}C; IR (neat): 3328, 1694, 1612, 1540, 1514, 1450, 1514, 1450, 1248, 1143, 1034, 988, 813, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz,



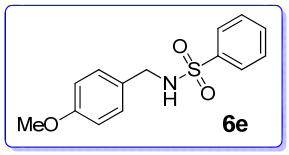
2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.98 (s, 1H), 4.43 (d, *J* = 6.8 Hz, 2H), 4.30 (d, *J* = 5.6 Hz, 2H), 4.21 (t, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), ; ^{13}C NMR (100 MHz, $CDCl_3$): 159.0, 156.3, 143.9, 141.3, 128.9, 127.6, 127.0, 125.0, 119.9, 114.0, 66.6, 55.3, 47.3, 44.6; HRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{23}H_{21}NNaO_3$: 382.1319; found: 382.1419.



Ethyl 4-methoxybenzylcarbamate (6c): 95% yield; R_f = 0.22 (10:90 = EtOAc/n-Hexane); Colourless solid; mp. 38-40°C; IR (neat): 3502, 2917, 1747, 1719, 1610, 1513, 1435, 1246, 1031, 823, 763, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.21 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.97 (s, 1H), 4.28 (d, *J* = 5.6 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.24 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 156.6, 130.7, 128.8, 114.0, 60.8, 55.2, 44.4, 14.6; HRMS (ESI, *m/z*): [M + H]$^+$ calculated for $C_{11}H_{16}NO_3$: 210.1130; found: 210.1138.

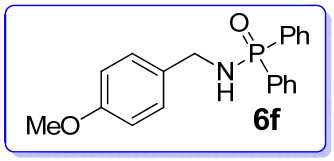


N-(4-Methoxybenzyl)-4-methylbenzenesulfonamide (6d): 74% yield; R_f = 0.23 (15:85= EtOAc/n-Hexane); Colourless solid; mp.100-102°C; IR (neat): 3681, 3248, 1595, 1558, 1322, 1258, 1157, 1091, 1032, 815, 763, 665cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.73 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 1H), 4.03 (d, *J* = 6.4 Hz, 2H), 3.75 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 143.4, 136.9, 129.73, 129.70, 129.2, 128.3, 128.2, 127.2, 126.4, 114.0, 55.3, 46.8, 21.5; HRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{15}H_{17}NNaO_3S$: 314.0827; found: 314.0839.

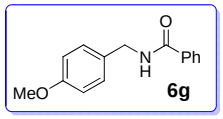


N-(4-Methoxybenzyl)benzenesulfonamide (6e): 50% yield; R_f = 0.20 (20:80= EtOAc/n-Hexane); Colourless solid; mp. 72-74°C; IR (neat): 3283, 2967, 1609, 1585, 1512, 1445, 1418, 1319, 1248, 1149, 1094, 1036, 900, 821, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.95-7.85 (2H), 7.65-7.58 (1H), 7.55-7.45 (2H), 7.11 (dt, *J* = 2.0 & 8.4 Hz, 2H), 6.8 (d, *J* = 2.0 & 8.8 Hz, 2H), 4.93 (t, *J* = 6.0 Hz, 1H), 4.08 (d, *J* = 6.0 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 139.9, 132.6, 129.2, 129.1, 128.2, 127.1, 114.0, 55.2, 46.7; HRMS (ESI, *m/z*): [M + Na]$^+$ calculated for $C_{14}H_{15}NNaO_3S$: 300.0670; found: 300.0670.

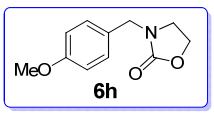
N-(4-Methoxybenzyl)-P,P-diphenylphosphinic amide (6f): 68% yield; R_f = 0.24 (50:50= EtOAc/n-Hexane); Colourless oil; IR (neat): 3360, 3005, 2995, 1612, 1586, 1514, 1464, 1302, 1248, 1139, 1035, 847, 741, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.01-7.81 (4H), 7.58-7.38 (6H), 7.30-7.20 (2H), 4.05 (t, *J* = 7.6 Hz, 2H), 3.77 (s, 3H), 3.08 (q, *J* = 5.6 Hz, 1H), 1.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 132.9, 132.2, 132.1, 131.96, 131.93, 131.7, 131.6, 129.0, 128.6, 128.5, 114.0, 55.3, 44.1; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{20}H_{21}NO_2P$: 338.1310; found: 338.1304.



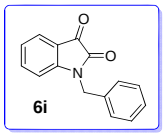
N-(4-Methoxybenzyl)benzamide (6g): 71% yield; R_f = 0.21 (20:80 = EtOAc/n-Hexane); Colourless solid; mp. 102-104°C; IR (neat): 3318, 2932, 1638, 1539, 1513, 1490, 1301, 1249, 1176, 1033, 830, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.75 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.57 (1H), 4.54 (d, *J* = 5.6 Hz, 2H), 3.77 (3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.3, 159.0, 134.4, 131.4, 130.3, 129.2, 128.5, 126.9, 114.1, 55.3, 43.6; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{16}NO_2$: 242.1181; found: 242.1192.



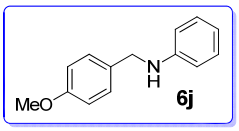
3-(4-Methoxybenzyl)oxazolidin-2-one (6h): 60% yield; R_f = 0.26 (50:50= EtOAc/n-Hexane); Colourless liquid; IR (neat): cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.14 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 4.29 (s, 2H), 4.21 (dd, *J* = 8.0 & 8.2 Hz, 2H), 3.73 (s, 3H), 3.33 (dd, *J* = 9.0 & 9.2 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 158.5, 129.5, 127.8, 114.1, 61.7, 55.3, 47.8, 43.8; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{11}H_{13}NNaO_3$: 230.0793; found: 230.0797.



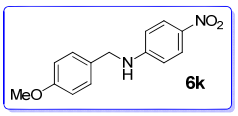
1-benzylindoline-2,3-dione (6i): 65% yield; R_f = 0.31 (20:80 = EtOAc/n-Hexane); Radish yellow solid; mp. 130°C; IR (neat): 1733, 1612, 1470, 1348, 1176, 1078, 753, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.63 (dd, *J* = 0.8 & 7.2 Hz, 1H), 7.50 (dt, *J* = Hz, 1.2 & 7.6 Hz, 1H), 7.44-7.28 (5H), 7.10 (dt, *J* = 0.8 & 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.95 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 183.2, 158.2, 150.7, 138.3, 134.5, 129.0, 128.1, 127.4, 125.4, 123.8, 117.6, 111.0, 44.0; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{15}H_{11}NNaO_2$: 260.0687; found: 260.0688.



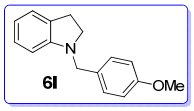
N-(4-Methoxybenzyl)aniline (6j): 81% yield; R_f = 0.26 (5:95 = EtOAc/n-Hexane); Light brown oil; IR (neat): 3417, 3050, 2933, 2895, 1609, 1585, 1506, 1495, 1302, 1245, 1177, 1033, 823, 749, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.36 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H) 4.30 (s, 2H), 3.92 (br s, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.9, 148.2, 131.4, 130.5, 129.2, 129.1, 128.8, 120.9, 117.5112.8, 55.4, 47.8; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{14}H_{16}NO$: 214.1232, ; found: 214.1232.



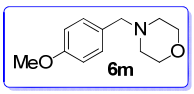
N-(4-Methoxybenzyl)-4-nitroaniline (6k): 67% yield; R_f = 0.29 (20:80 = EtOAc/n-Hexane); Yellow solid; mp. 145°C; IR (neat): 3357, 1997, 1599, 1541, 1511, 1277, 1173, 1109, 995, 815, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.10 (dt, *J* = 3.2 & 9.2 Hz, 2H), 7.29 (dt, *J* = 3.2 & 8.8 Hz, 2H), 6.90 (dt, *J* = 2.8 & 8.8 Hz, 2H), 6.58 (dt, *J* = 3.1 & 9.2 Hz, 2H), 4.88 (s, 1H), 4.38 (d, *J* = 5.2 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 153.1, 138.2, 129.3, 128.7, 126.4, 114.3, 111.3, 55.3, 47.1; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{14}H_{15}N_2O_3$: 259.2805; found: 259.2811.

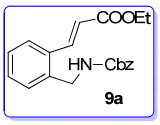


1-(4-methoxybenzyl)indoline (6l): 93% yield; R_f = 0.32 (5:95 = EtOAc/n-Hexane); Colourless oil; IR (neat): 3380, 1608, 1510, 1247, 1176, 1091, 1028, 970, 840, 770, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.33 (d, *J* = 8.4 Hz, 2H), 7.20-7.05 (2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 4.24 (s, 2H), 3.85 (s, 3H), 2.32 (t, *J* = 8.0 Hz, 2H), 3.00 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.8, 152.6, 130.5, 130.1, 129.2, 127.3, 124.5, 117.7, 113.9, 107.1, 55.3, 53.5, 53.0, 28.5; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{16}H_{18}NO$: 240.1388; found: 240.1375.



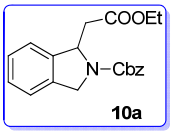
4-(4-methoxybenzyl)morpholine (6m): 83% yield; R_f = 0.23 (50:50 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 2955, 2853, 2805, 1612, 1513, 1455, 1350, 1246, 1116, 1034, 1006, 914, 866, 833, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.21 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 3H), 3.77 (t, *J* = 4.4 Hz, 4H), 3.41 (s, 2H), 2.40 (t, *J* = 4.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.8, 130.4, 129.7, 113.6, 67.0, 62.8, 55.2, 53.5; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{12}H_{18}NO_2$: 208.1338; found: 208.1344.



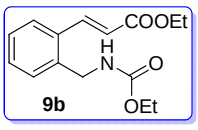
(E)-Ethyl 3-(2-((((benzyloxy)carbonyl)amino)methyl)phenyl)acrylate (9a): 

92% yield; R_f = 0.28 (20 : 80 = EtOAc/n-Hexane); Colourless solid; mp. 70-75 ^oC; IR (neat): 3341, 2924, 1699, 1635, 1521, 1367, 1253, 1178, 1040, 977, 765, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.98 (d, *J* = 16.32 Hz, 1H), 7.60 (d, *J* = 7.58 Hz, 1H), 7.36 (m, 8H), 6.39 (d, *J* = 15.73 Hz, 1H), 5.15 (s, 2H), 5.05 (s, 1H), 4.55 (d, *J* = 5.59 Hz, 2H), 4.29(dd, *J* = 7.13 Hz & 15.17 Hz, 2H), 1.36(t, *J* = 7.09Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 156.1, 140.8, 137.1, 136.3, 133.2, 130.2, 128.2, 128.0, 126.9, 120.9, 66.9, 60.6, 42.7, 14.3; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{20}H_{21}NNaO_4$: 362.1368; found: 362.1369.

Standard procedure for cyclization of 9a and 9b: To a stirred solution of **9a** or **9b** (0.50 mmol) in dry THF (2.0 mL) at rt, LiHMDS (20 mol %, 1M in toluene) was added. After stirring for given time on Scheme 3, the reaction was quenched with the addition of brine solution (1 mL), followed by extraction with EtOAc (3 × 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the crude was purified by flash column chromatography (EtOAc/Hexane) on silica gel.

Benzyl 1-(2-ethoxy-2-oxoethyl)isoindoline-2-carboxylate (10a): 

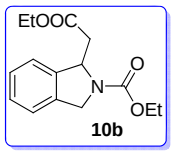
99% yield; R_f = 0.32 (20 : 80 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 2980, 2920, 1734, 1699, 1417, 1362, 1285, 1156, 1104, 1020, 751, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.35 (m, 9H), 5.50 (m ,1H), 5.23 (m, 2H), 4.77 (m, 2H), 4.08 (m, 2H), 2.99 (m, 2H), 1.18 (td, J = 2.26 Hz & 7.49, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.7, 154.5, 139.5, 136.7, 136.5, 136.2, 129.0, 128.5, 128.0, 127.9, 127.6, 125.3, 122.8, 125.6, 125.4, 67.2, 66.9, 60.3, 52.3, 52.0, 40.7, 39.2, 14.0; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{20}H_{22}NO_4$: 340.1549; found: 340.1549.

(E)-Ethyl 3-(2-(((ethoxycarbonyl)amino)methyl)phenyl)acrylate (9b): 

93% yield; R_f = 0.22 (20 : 80 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 3353, 2962, 1705, 1617, 1529, 1315, 1270, 1041, 980, 866, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.97 (d, *J* = 16.05 Hz, 1H), 7.59 (d, *J* = 7.61 Hz, 1H), 7.39-7.31 (m, 3H), 6.39 (d, *J* = 15.82 Hz, 1H), 4.94 (s, 1H), 4.52 (d, *J* = 5.67 Hz, 2H), 4.29 (dd, *J* = 7.08 Hz & 7.12 Hz, 2H), 4.16 (m, 2H), 1.36 (t, *J* = 7.16 Hz, 3H), 1.26 (m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 166.6, 156.3, 140.8, 137.3, 133.2, 126.9, 120.9, 161.0, 160.4,

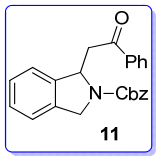
42.6, 14.6, 14.3; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{20}NO_4$: 278.1392; found: 278.1403.

Ethyl 1-(2-ethoxy-2-oxoethyl)isoindoline-2-carboxylate (10b): 97% yield; R_f = 0.29 (20 : 80 = EtOAc/n-Hexane); Colourless liquid; IR (neat): 2901, 2872, 1732, 1698, 1464, 1417, 1380, 1284, 1174, 1023, 899, 772, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.28 (m, 4H), 5.45 (m, 1H), 4.84-4.65 (m, 2H), 4.23 (m, 2H), 4.09 (m, 2H), 3.12-2.67 (m, 2H), 1.33 (t, J = 7.09 Hz, 3H), 1.19 (m, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 170.8, 170.6, 154.8, 140.0, 139.6, 136.7, 136.3, 127.9, 127.5, 122.7, 122.5, 122.4, 61.2, 60.4, 60.3, 60.2, 52.1, 51.9, 40.7, 39.3, 14.7, 14.0; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{20}NO_4$: 278.1392; found: 278.1398.



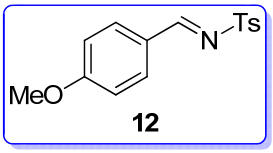
10b

Benzyl 1-(2-oxo-2-phenylethyl)isoindoline-2-carboxylate (11): 88% yield; R_f = 0.26 (30 : 70 = EtOAc/n-Hexane); Colourless solid; mp. 101 ^oC IR (neat): 3033, 2859, 1700, 1597, 1448, 1415, 1362, 1285, 1217, 1106, 970, 750, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):): 8.00 (d, *J* = 7.61, 1H), 7.87 (d, *J* = 7.61, 1H), 7.57 (m, 1H), 7.38 (m, 11H), 5.75 (m, 1H), 5.22 (m, 2H), 4.80 (m, 2H), 3.96 (dd, *J* = 3.10 Hz & 16.57 Hz, 0.6H), 3.73 (dd, *J* = 3.55 Hz & 16.89 Hz, 0.4H), 3.46 (q, *J* = 8.69 Hz, 0.6H), 3.31 (q, *J* = 8.08 Hz, 0.4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 198.0, 197.7, 154.5, 137.0, 136.3, 133.2, 133.1, 127.6, 123.4, 123.2, 122.5, 122.3, 67.1, 66.9, 59.5, 52.2, 51.9, 45.6, 43.8; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{24}H_{22}NO$: 372.1600; found: 972.1594.



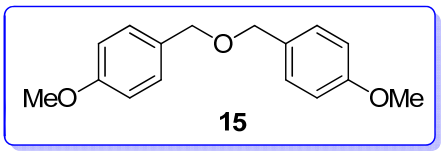
11

(E)-N-(4-methoxybenzylidene)-4-methylbenzenesulfonamide (13): 58% yield; R_f = 0.24 (20:80 = EtOAc/n-Hexane); Colorless Solid; IR (neat): 2919, 1595, 1564, 1513, 1426, 1318, 1263, 1156, 1089, 1023, 806, 762, 670, 593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 8.96 (s, 1H), 7.90 (m, 4H), 7.35 (d, *J* = 8.20 Hz, 2H), 6.99 (d, *J* = 8.88 Hz, 2H), 3.90 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 169.2, 165.2, 144.2, 135.7, 133.7, 129.7, 127.9, 125.2, 114.6, 55.6, 21.6; HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{15}H_{16}NSO_3$: 290.0851; found: 290.0845.



12

4,4'-(oxybis(methylene))bis(methoxybenzene) (15):[2] **xx**% yield; R_f = 0.30 (10:90 = EtOAc/n-Hexane); Colorless oil; IR (neat): 3002, 2931, 2836, 1614, 1506,



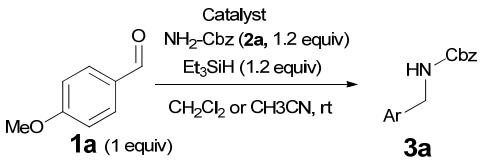
15

1364, 1244, 1171, 1032, 818 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.33 (d, *J* = 8.4 Hz, 4H), 6.93 (d, *J* = 8.4 Hz, 4H), 4.51 (s, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 130.5, 129.4, 113.8, 71.5, 55.2.

The trace analysis of Re_2O_7 99.995% (from Alfa-Aesar) using ICP-OES, the major contaminants detected [ppm]: Co (0.14), Cu (0.72), Fe (3.7).

Therefore, the following DRA were screened using different source of Re_2O_7 as well as ppm solution of catalysts (such as $CoCl_2$, $CuBr_2$, and $FeCl_3$) in absence of Re_2O_7.

Table 5 DRA using Different Source of Re_2O_7 and ppm level of major contaminants



1a (1 equiv) **3a**

	Catalyst (%)	Purity/Source	t/h	**3a**[a]
1	Re_2O_7 (1.5 mol %)	99.995% / Alfa-Aesar	0.5	100%
2	Re_2O_7 (1.5 mol %)	99.995% / Sigma-Aldrich	0.5	100%
3	Re_2O_7 (1.5 mol %)	99.9 / Sigma-Aldrich	0.5	100%
4	$CoCl_2$ (1 ppm solution in CH_3CN)		2h	0%
5	$CuBr_2$ (1 ppm solution in CH_3CN)		2h	0%
6	$FeCl_3$ (4 ppm solution in CH_3CN)		2h	0%

[a] The % was determined by TLC as well as ^1H NMR of the reaction mixture.

References:

[1] B.-L Yang, Z.-T. Weng, S.-J. Yang and S.-K. Tian, *Chem. Eur. J.*, 2010, **16**, 718.

[2] H. A. Kalviri, C. F. Petten and F. M. Kerton, *Chem. Commun.,* 2009, 5171.