Preparation of Secondary Amine from Nitroarenes and Alcohols

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Supporting information.

Experimental section.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on a Bruker AVANCE 400 spectrometer. Ruthenium complexes **1 ~ 3** were prepared accordingly to the method reported previously. Other chemicals and solvents were of analytical grade and were used without further purification.

Complex 1~ 3. Ruthenium complexes **1** and **2** were prepared by mixing amino-phosphine **P~N** with a stoichiometric quantity of **[**$RuCl_2(dmso)_4$] and **[**$RuCl_2(CO)_3(THF)$] in THF to yield the corresponding complexes [(**P~N**)$RuCl_2(dmso)_2$] (**1**) and [(**P~N**)$RuCl_2(CO)_2$] (**2**), whereas [(**P~N**)Ru(dmso)(ACN)Cl_2] (**3**) was obtained by treatment of **1** with acetonitrile under refluxing conditions.

Complex **1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, 2H, $J_{H\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 12.0 Hz, Ar-*H*), 7.77 (dd, 2H, $J_{H\text{-}H}$ = 8.0 Hz, $J_{H\text{-}H}$ = 12.0 Hz, Ar *H*), 7.66 (dd, 1H, $J_{H\text{-}H}$ = 4.0 Hz, $J_{H\text{-}H}$ = 8.0 Hz, Ar-*H*), 7.58~7.23 (m, 9H, Ar *H*), 6.35 (d, 1H, $J_{H\text{-}H}$ = 12 Hz, N*H*-), 5.64 (d, 1H, $J_{H\text{-}H}$ = 12 Hz, N*H*-), 3.45 (s, 3H, DMSO), 3.40 (s, 3H, DMSO), 3.01 (s, 3H, DMSO), 2.11 (s, 3H, DMSO). ^{31}P NMR (161 MHz, $CDCl_3$): δ 54.2.

Complex **2**: ^{1}H NMR (400 MHz, d_6-dmso): δ 8.11 (d, 1H, $J_{H\text{-}P}$ = 12 Hz, N*H*-), 7.88 (dd, 2H, *J* = 8.0 Hz, *J* = 12.0 Hz, Ar *H*), 7.76 (m, 1H, Ar *H*), 7.69~7.47 (m, 9H, Ar *H*), 7.30 (m, 2H, Ar *H*), 6.70 (d, 1H, $J_{H\text{-}P}$ = 12 Hz, N*H*-); ^{31}P NMR (161 MHz, d_6-dmso): δ 54.

Complex **3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (m, 2H Ar-*H*), 7.75 (m, 1H Ar-*H*), 7.59 (m, 2H), 7.28~7.47 (m, 9H, Ar-*H*), 5.94 (d, 1H, $J_{H\text{-}H}$ = 14 Hz, -N*H*), 4.71 (d, 1H, $J_{H\text{-}H}$ = 14 Hz, -N*H*), 3.37 (s, 3H, dmso), 2.99 (s, 3H, dmso), 1.66 (s, 3H, C*H*$_3$CN). ^{31}P NMR (161 MHz, $CDCl_3$): δ 63.0.

General procedure for catalysis.

A mixture of nitrobenzene (0.3 mmol), catalysts (1 mole % based on nitrobenzene), *t*BuOK in benzyl alcohol was placed in flask under the atmospheric pressure of H_2 and was heated by an oil bath at 110 ~150 ^{o}C for 24 h. After the completion of the reaction, brine (3 mL) and CH_2Cl_2(5 mL) were added. The organic layer was separated and the aqueous layer was

extracted with CH_2Cl_2. The combined organic extracts were dried over magnesium sulfate and concentrated. Products were characterized by NMR spectroscopy and the data were consistent with those reported. Product yields were obtained by the ^1H nmr integration compared to the internal standard. Some compounds were purified by chromatography and characterized by nmr spectroscopy.

General procedure for preparation of tertiary amines.

A mixture of secondary amine (0.3 mmol), catalysts **2** (3 x 10^{-3} mmol) and sodium tetrakis(3,5-trifluoromethylphenyl)borate (6 x 10^{-3} mmol) in alcohol (1.8 mmol) was placed in flask under the atmospheric pressure of H_2 and was heated by an oil bath at 150 ^oC for 24 h. The workup procedure and characterization were similar to those for the preparation of secondary amines.

Tribenzylamine[1]

^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.11 (m, 15H), 3.47 (s, 6H).

Trihexylamine[2]

^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (t, 6H, J_{H-H} = 7.1 Hz), 1.53–1.25 (m, 24H), 0.91 (t, 9H, J = 7.1 Hz).

Tris(4-methylbenzyl)amine[3]

^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 6H, J_{H-H} = 7.8 Hz), 7.13 (d, 6H, J_{H-H} = 8.3 Hz), 3.46 (s, 6H), 2.34 (s, 9H).

N-Benzylaniline[4]

^1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 5H), 7.14 (t, 2H, J_{H-H} = 7.3 Hz), 6.71 (t, 1H, J_{H-H} = 7.3 Hz), 6.59 (d, 2H, J = 7.5 Hz), 4.27 (s, 2H), 3.93 (br , 1H).

N-benzyl-4-bromoaniline[5]

^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5H), 7.24 (d, 2H , J_{H-H} = 9.3 Hz), 6.46 (d, 2H, J_{H-H} = 9.3 Hz), 4.33 (s, 2H), 4.03 (br s, 1H).

N-Benzyl-4-chloroaniline[6]

^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, 2H, J_{H-H} = 7.2 Hz), 7.08-7.03 (m, 5H), 6.36 (d, 2H, J_{H-H} = 7.2 Hz), 4.32 (s, 2H), 4.03 (br s, 1H).

N-Benzylidene-4-fluoroaniline[7]

^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.91 (m, 2H), 7.41 (m, 3H), 7.20 (m, 2H), 7.10 (m, 2H).

N-Benzylidene-4-methoxyaniline[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.00 (m, 2H), 7.43 (m, 3H), 7.22 (m, 2H), 6.91 (m, 2H), 3.79 (s, 3H).

N-Benzyl-4-methoxyaniline[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.31 (m, 5H), 7.25 (tt, 1H, J_{H-H} = 6.9, 2.1 Hz), 6.75 (dt, 2H, J_{H-H} = 9.0, 2.9 Hz), 6.57 (dt, 2H, J_{H-H} = 9.0, 2.9 Hz), 4.25 (s, 1H), 3.72 (s, 3H).

N-benzyl-3-bromoaniline[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, 2H, J_{H-H} = 7.4, 7.2 Hz), 7.03-7.05 (m, 3H), 6.94 (dd, 1H, J_{H-H} = 7.7, 8.0 Hz), 6.75 (d, 1H, J_{H-H} = 7.7 Hz), 6.62 (s, 1H), 6.35 (d, 1H, J_{H-H} = 7.7 Hz), 4.33 (s, 2H), 4.02 (br s, 1H).

N-benzyl-2-bromoaniline[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, 1H, J_{H-H} = 1.4 Hz, J_{H-H} = 8.0 Hz), 7.35-7.23 (m, 5H), 7.15-7.10 (m, 1H), 6.60-6.55 (m, 2H), 4.74 (br s, 1H), 4.40 (d, 2H, J_{H-H} = 5.4 Hz).

N-benzyl-3,5-dimethylaniline[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 6.37 (s, 1H), 6.33 (s, 2H), 4.34 (s, 2H), 2.25 (s, 6H), 1.62 (br s, 1H).

N-(4-Chlorobenzyl)aniline[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.12 (m, 6H), 6.71 (t, 1H, J_{H-H} = 7.7 Hz), 6.57 (d, 2H, J_{H-H} = 7.7 Hz), 4.28 (s, 2H), 4.02 (br s, 1H).

N-(4-Methylbenzyl)aniline[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, 2H, J_{H-H} = 7.8 Hz), 7.15-7.06 (m, 4H), 6.67 (t, 1H, J_{H-H} = 7.3 Hz), 6.56 (d, 2H, J_{H-H} = 7.4 Hz), 4.23 (s, 2H), 3.81 (br s, 1H), 2.32 (s, 3H).

N-(4-Methoxybenzyl)aniline[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 2H, J_{H-H} = 8.8 Hz), 7.13 (t, 2H, J_{H-H} = 7.6 Hz), 6.86 (d, 2H, J_{H-H} = 8.7 Hz), 6.67 (t, 1H, J_{H-H} = 7.7 Hz), 6.57 (d, 2H, J_{H-H} = 7.7 Hz), 4.24 (s, 2H), 3.95 (br s, 1H), 3.81 (s, 3H).

N-(4-methoxybenzylidene)aniline[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.83 (d, 2H, J_{H-H} = 8.1 Hz), 7.33 (m, 2H), 7.17 (m, 3H), 6.92 (d, 2H, J_{H-H} = 7.9 Hz), 3.83 (s, 3H).

N-(naphthalen-2-ylmethyl)aniline[12]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.37 (m, 3H), 7.09 (m, 2H), 6.62 (d, 1H, J_{H-H} = 9.2 Hz), 6.57 (d, 2H, J_{H-H} = 10.2 Hz), 4.40 (s, 2H), 4.22 (s, 1H).

N-Phenylfurfurylamine[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, 1H, J_{H-H} = 1.0 Hz), 7.19 (t, 2H, J_{H-H} = 7.2 Hz), 6.72 (t, 1H, J_{H-H} = 7.2 Hz), 6.67 (d, 2H, J_{H-H} = 7.2 Hz), 6.32 (m, 1H), 6.23 (m, 1H), 4.30 (s, 2H), 3.99 (br s, 1H).

N-Hexylaniline[13]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, 2H, J_{H-H} = 7.2, 8.6 Hz), 6.69 (tt, 1H, J_{H-H} = 0.9, 7.2 Hz), 6.60 (dd, 2H, J_{H-H} = 0.9, 8.6 Hz), 3.59 (br s, 1 H), 3.11 (t, 2H, J_{H-H} = 7.2 Hz), 1.61 (quintet, 2H, J_{H-H} = 7.2 Hz), 1.44-1.27 (m, 6 H), 0.90 (t, 3H, J_{H-H} = 7.2 Hz).

N,N-Dibenzyl-1-hexanamine[14]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 10H), 3.54 (s, 4H), 2.42 (t, 2H, J_{H-H} = 7.3 Hz), 1.62-1.23 (m, 8H), 0.84 (t, 3H, J_{H-H} = 7.1 Hz).

N,N-Dibenzyl-1-(4-chlorophenyl)methanamine[15]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 14H), 3.54 (s, 4H), 3.47 (s, 2H).

N,N-Dibenzyl-1-*p*-tolylmethanamine[15]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 4H), 7.28-7.13 (m, 8H), 7.08 (d, J_{H-H} = 7.6 Hz, 2H), 3.46 (s, 4H), 3.44 (s, 2H), 2.25 (s, 3H).

N,N-Dibenzyl-1-(naphthalene-2-yl)methanamine[15]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.46 (m, 5H), 7.43-7.35 (m, 6H), 7.23-7.14 (m, 6H), 3.64 (s, 2H), 3.54 (s, 4H),.

(*E*)-*N,N*-Dibenzyl-3-phenylprop-2-en-1-amine[16]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 4H), 7.34-7.25 (m, 8H), 7.23-7.17 (m, 3H), 6.54 (d, 1H, J_{H-H} = 15.5 Hz), 6.29 (dt, 1H, J_{H-H} = 15.5, 6.7 Hz), 3.62 (s, 4H), 3.21 (d, 2H, J_{H-H} = 6.4 Hz).

N,N-Dibenzyl-3-phenylpropan-1-amine[15]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 12H), 7.13-7.09 (m, 3H), 3.54 (s, 2H), 2.54 (t, 2H, J_{H-H} = 8.1 Hz), 2.46 (t, 2H, J_{H-H} = 7.1 Hz), 1.87-1.72 (m, 2H).

1-Benzylpiperidine[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 5H), 3.46 (s, 2H), 2.35 (t, 4H, J_{H-H} = 5.2 Hz), 1.62-1.52 (m, 4H), 1.45-1.43 (m, 2H).

1-Benzylmorpholine[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 3.75 (t, 4H, J_{H-H} = 4.7 Hz), 3.52 (s, 2H), 2.42 (t, 4H, J_{H-H} = 4.7Hz).

N,N-dibenzyl-4-methylaniline[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (m, 10H), 6.96 (d, 2H, J_{H-H} = 8.6 Hz), 6.64 (d, 2H, J_{H-H} = 8.6 Hz), 4.60 (s, 4H), 2.21 (s, 3H).

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