Supporting information

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Title : The C-H and C-C Bond Activation of Primary Amine Through Dehydrogenation and Transimination

Genaeral procedure for the experiments of 1a, 1b and 1c with 1-alkene.

Typical experiment of **1a** with **2a** to produce **6a**: A screw-capped pressure vial (1mL) was charged with freshly purified phenethylamine (**1a**) (0.43mmol), 2-amino-3-picoline (**4**) (0.21mmol), 3,3-dimethyl-but-1-ene (**2a**) (2.15mmol), $Rh(PPh_3)_3Cl$ (**3**) (0.02mmol) and toluene (20mg). The mixture was stirred at 170 ^{o}C for 24 h. After cooling the reaction mixture to room temperature, it was hydrolyzed with 1 N HCl for 6 h. And then, ketone **6a** was isolated with 96 % yield after extraction with CH_2Cl_2 and purifying by column Chromatography (*n*-hexane:ethyl acetate = 5:1).

7f : ^{1}H NMR(250MHz, $CDCl_3$)_(ppm) 7.9 (d, *J*=7.6Hz, 1H in phenyl group), 7.3 (m,3H), 2,9 (t, =7.2Hz, 2H, _-CH_2 to C=O), 2.8 (t, *J*=7.6Hz, 2H, ArCH_2), 1.7 (m, 2H, -CH_2-), 1.5(m, 2H, _-CH_2 to CO), 1.3 (m, 8H, -CH_2-), 0.9(m, 6H, -CH_3); ^{13}C NMR (62.9MHz, $CDCl_3$)_(ppm) 205.9(C=O), 142-125(Cs in phenyl group), 42.4 (_-CH_2 to C=O), 32.0 (ArCH_2), 33.9, 31.8, 31.7, 24.3, 22.7 (-CH_2-), 14.2,14.1 (-CH_3); IR(neat): 1689(CO) cm^{-1}; MS: *m/z* (%); 246 (2) [M^+], 91(24), 175(100); HRMS calcd for $C_{17}H_{26}O$ (M^+) 246.1984 found 246.1985.

7g: ^{1}H NMR(250MHz, $CDCl_3$)_(ppm) 7.6 (d, *J*=7.8Hz, 1H in phenyl group), 7.3 (m,3H), 2,9 (t, *J*=7.3Hz, 2H, _-CH_2 to C=O), 2.8 (t, *J*=7.7Hz, 2H, ArCH_2), 1.7 (m, 2H, -CH_2-), 1.5(m, 2H, _-CH_2 to CO), 1.3 (m, 20H, -CH_2-), 0.9(m, 6H, -CH_3); ^{13}C NMR (62.9MHz, $CDCl_3$)_(ppm)

205.8(C=O), 142-126(Cs in phenyl group), 42.4 (_-CH_2 to C=O), 29.3 ($ArCH_2$), 24.6 (_-CH_2 to C=O), 33.9, 32.1, 32.1, 32.0, 29.9, 29.7, 29.6, 29.5, 27.8, 22.9, 22.8 (-CH_2-), 14.3 (-CH_3); IR(neat): 1689(CO) cm^{-1}; MS: *m/z* (%); 330 (1) [M^+], 91(29), 217(100); HRMS calcd for $C_{23}H_{38}O$ (M^+) 330.2923 found 330.2939.

Typical experiment of **1a** with **2a** under H_2O to produce **6a**: A screw-capped pressure vial (1mL) was charged with freshly purified phenethylamine (**1a**) (0.43mmol), 2-amino-3-picoline (**4**) (0.21mmol), 3,3-dimethyl-but-1-ene (**2a**) (2.15mmol), $Rh(PPh_3)_3Cl$ (**3**) (0.02mmol), toluene (20mg) and H_2O. The mixture was stirred at 170 ^oC for 24 h. After cooling the reaction mixture to room temperature, it was hydrolyzed with 1 N HCl for 6 h. Then, ketone **6a** and **14a** were isolated with 78 % and 8% yields, respectively, after extraction with CH_2Cl_2 and purifying by column Chromatography (*n*-hexane:ethyl acetate = 5:1).

Typical experiment of **1c** with **2a** under H_2O : A screw-capped pressure vial (1mL) was charged with freshly purified 3-phenyl-propylamine (**1c**) (0.21mmol), 2-amino-3-picoline (**4**) (0.21mmol), 3,3-dimethyl-but-1-ene (**2a**) (1.08mmol), $Rh(PPh_3)_3Cl$ (**3**) (0.02mmol), toluene (0.86mmol) and H_2O (0.21mmol). The mixture was stirred at 170 ^oC for 48 h. After cooling the reaction mixture to room temperature, it was hydrolyzed with 1 N HCl for 6 h. Then, ketone **6i** and **14a** were isolated with 49% and 48 % yields, respectively, after extraction with CH_2Cl_2 and purifying by column Chromatography (*n*-hexane:ethyl acetate = 5:1).

6j: ^{1}H NMR(250MHz, $CDCl_3$)_(ppm) 7.3 (d, *J*=7.8Hz, 1H in phenyl group), 7.2 (m,3H), 2.4 (t, *J*=7.5Hz, 2H, _-CH_2 to C=O), 2.7 (t, *J*=7.5Hz, 2H, $ArCH_2\mathit{CH_2}$), 2.9 (t, *J*=7.5Hz, 2H, $ArCH_2$), 1.5(qt, *J*=7.4Hz, 2H, _-CH_2 to CO), 1.3 (m, 4H, -CH_2-), 0.9(t, *J*=6.7Hz, 3H, -CH_3); ^{13}C NMR

(62.9MHz, $CDCl_3$)_(ppm) 210(C=O), 141-126(Cs in phenyl group), 43.2 (_-CH_2 to C=O), 44.4 ($ArCH_2\mathit{CH_2}$), 29.9 ($ArCH_2$), 23.6 (_-CH_2 to C=O), 31.5, 22.5 (-CH_2-), 14.0 (-CH_3); IR(neat): 1720.9 (CO) cm^{-1}; MS: *m/z* (%); 204 (7) [M^+], 91(100), 105(75), 133(31), 148(15); HRMS calcd for $C_{14}H_{20}O$ (M^+) 204.1514 found 204.1515.