Supporting information

Light-Promoted N,N-dimethylation of Amine and Nitro Compound with Methanol Catalyzed by Pd/TiO$_2$ at Room Temperature

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1. Experimental

Typical procedure for catalyst preparation$^{43}$: TiO$_2$ (0.5 g, P25, J&K Scientific, anatase/rutile =80/20, BET surface, 35-65 m$^2$/g) was dispersed in deionized water (35 mL) and H$_2$PdCl$_4$ aqueous solution (0.27 mL, 0.25 g/10 mL) were added into the solution under vigorous stirring. The pH value was adjusted to about 10 using 1 M NaOH and the solution was stirred for another 3 h at room temperature. Then NaBH$_4$ (20 mg) was added to the solution in ice water bath and stirred for 2 h. The solid sample was recovered by centrifugation and washed with water. The obtained solid was dried at 80 °C.

Typical reaction procedure for the N,N-dimethylaltion of amines: amine (0.2 mmol), catalyst (20 mg) and methanol (5 mL) were added into a glass tube (35 mL). Argon was bubbled through the solution for 5 min. Then the tube was sealed with a rubber cap and photoirradiated by a LED light ($\lambda$=365 nm) with magnetic stirring at room temperature for 15 h. Subsequently, 10 mg biphenyl and 5 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

2. Characterization data of isolated products

- N-cyclohexyl-N-methylcyclohexanamine$^{41}$, colorless liquid (93% yield, Entry 7, Table 2). The product was separated by vacuum distillation after remove the catalyst by filtration. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$=1.10-1.24(m, 2H), 1.27-1.33(m, 8H), 1.61(d, 2H), 1.80-1.84(m, 8H), 2.28(s, 3H), 2.50-2.55(m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 61.8, 34.6, 32.2, 25.3, 24.9; MS (E.I., 70 eV) m/z (rel. int.): 196(3), 195(19), 153(13), 152(100), 124(7), 114(10), 112(3), 96(6), 70(21), 55(9), 42(7).

- N,N-Dimethyldodecylamine$^{15}$, colorless liquid (97% yield, Entry 13, Table 3).
The product was separated by vacuum distillation after remove the catalyst by filtration. $^1$H NMR (400 MHz, CDCl$_3$): δ=0.87(t, 3H), 1.25-1.29(m, 20H), 2.27(t, 2H), 2.22(s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 65.6, 52.2, 46.8, 31.9, 30.6, 29.6, 29.3, 27.3, 22.7, 19.2, 14.1, 13.7, 10.2; MS (E.I., 70 eV) m/z (rel. int.): 213(6), 212(1), 198(0.5), 184(0.2), 170(0.2), 156(0.2), 142(0.2), 128(0.4), 114(0.6), 100(0.4), 84(1.4), 72(5.2), 69(9.5), 58(100), 59(4.2), 41(4.4), 29(1.8).

3-((dimethylamino)methyl)-N,N,3,5,5-pentamethyl cyclohexanamine, colorless liquid (98% yield, Entry 15, Table 3). The product was separated by vacuum distillation after remove the catalyst by filtration. $^1$H NMR (400 MHz, CDCl$_3$): δ=0.92(t, 3H), 1.01(t, 6H), 1.04-1.07(m, 1H), 1.11-1.14(m, 1H), 1.45-1.48(m, 1H), 1.52-1.55(m, 1H), 1.99(s, 2H), 2.27(s, 6H), 2.28(s, 6H), 2.29(s, 2H), 2.56-2.62(m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): 74.3, 73.4, 49.2, 47.3, 40.0, 37.8, 35.3, 33.1, 31.9, 27.8, 27.7, 24.1; MS (E.I., 70 eV) m/z (rel. int.): 226 (3), 182 (4), 166 (6), 112 (11), 96 (5), 58 (100), 55 (5), 42 (4); HRMS (ESI) calculated for C$_{14}$H$_{31}$N$_2$ [M+1]: 227.2482, found: 227.2475.

4,4'-methylenebis(N,N-dimethylaniline)$^{42}$, white solid(69%yield, Entry 16, Table3). Mp 86-89°C. The product was separated by column chromatography (petroleum ether (b.p. 60-90°C)/EtOAc = 24/1). $^1$H NMR (400 MHz, CDCl$_3$): δ=2.93(s, 12H), 3.84(s, 2H), 6.72(d, 4H), 7.08(d, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): 149.1, 130.4, 129.4, 113.1, 40.9, 39.9; MS (E.I., 70 eV) m/z (rel. int.): 254(100), 253(78), 255(17), 237(15), 210(29), 134(24), 126(17), 118(14).
3. $^1$H and $^{13}$C NMR spectra of isolated products