Supporting information

Acceptorless dehydrogenative synthesis of 2-substituted quinazolines from 2-aminobenzylamine with primary alcohols or aldehydes by heterogeneous Pt catalysts

Chandan Chaudhari,[a] S. M. A. Hakim Siddiki,[b] Masazumi Tamura,[c] Ken-ichi Shimizu* [a,b]

[a] Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan
[b] Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan
[c] Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

*Corresponding author
Ken-ichi Shimizu
Catalysis Research Center, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan
E-mail: kshimizu@cat.hokudai.ac.jp, Fax: +81-11-706-9163

Experimental section

General

Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, Wako Pure Chemical Industries, Kishida Chemical, or Mitsuwa Chemicals) were used without further purification. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA$^+$-1 (Frontier Laboratories Ltd.) using nitrogen and helium as the carrier gas. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS-900MC with Al$K\alpha$ anode operated at 20 mA and 10 kV. The oxygen 1s core electron levels in support oxides were recorded. Binding energies were calibrated with respect to C_{1s} at 285.0 eV. Prior to the XPS measurement, metal oxide samples were preheated in air at 600 °C for 0.5 h (except for TiO_2 at 500 °C).

Catalyst preparation

CeO_2 (JRC-CEO-1, 157 m^2 g^{-1}), MgO (JRC-MGO-1), TiO_2 (JRC-TIO-4), $SiO_2Al_2O_3$ (JRC-SAL2, Al_2O_3 = 13.75 wt%) and H$^+$-type BEA zeolite (HBEA, SiO_2/Al_2O_3 = 25±5, JRC-Z-HB25) were supplied from Catalysis Society of Japan. SiO_2 (Q-10, 300 m^2 g^{-1}) was supplied from Fuji Silysia Chemical Ltd. Hydroxides of Zr and La were prepared by hydrolysis of zirconium oxynitrate 2-hydrate and $La(NO_3)_3{\cdot}6H_2O$ in distilled water by gradually adding an aqueous NH_4OH solution (1.0 mol dm^{-3}), followed by filtration of precipitate, washing with distilled water three times, drying at 100 °C for 12 h. $Nb_2O_5{\cdot}nH_2O$ was supplied from CBMM. La_2O_3, ZrO_2, and Nb_2O_5 were prepared by calcination of these hydroxides at 500 °C for 3 h. γ-Al_2O_3 was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. Precursor of 1 wt% Pt/CeO_2 catalyst was prepared by an impregnation method; a mixture of CeO_2 and an aqueous HNO_3 solution of $Pt(NH_3)_2(NO_3)_2$ was evaporated at 50 °C, followed by drying at 90 °C for 12 h. A pre-reduced catalyst (named Pt/CeO_2) was prepared by pre-reduction of the precursor in a pyrex tube under a flow of H_2 (20 cm^3 min^{-1}) at 500 °C for 0.5 h. Platinum oxides-loaded CeO_2 (PtO_x/CeO_2), as a comparative catalyst, was prepared by calcination of the precursor at 300 °C for 3 h. By using various supports, several pre-reduced Pt catalysts were prepared by the same method as Pt/CeO_2. CeO_2-supported metal catalysts, M/CeO_2 (M = Co, Ni, Cu, Ru, Rh,

Pd, Ag, Ir) with metal loading of 1 wt% were prepared by impregnation method in a similar manner as Pt/CeO_2 using an aqueous solution of metal nitrates (for Co, Ni, Cu, Ag), $RuCl_3$, $IrCl_3$, or an aqueous HNO_3 solution of $Rh(NO_3)_3$ or $Pd(NO_3)_2$

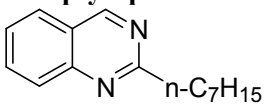
Catalytic test

1wt% Pt/CeO_2 (195 mg, 0.01 mmol of Pt) was used as a standard catalyst. After the pre-reduction at 500 °C, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air as follows. Typically, the mixture of 2-aminobenzylamine (1.0 mmol) and 1-octanol or 1-octanal (1.2 mmol) in mesitylene (1.2 mL) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube) through a septum inlet, followed by filling N_2. Then, the resulting mixture was magnetically stirred for 30-48 h under reflux condition; the bath temperature was 170 °C and reaction temperature was *ca.* 165 °C. For the scope and limitation study in Tables 2 and 4, isolated yields of products were determined as follows. After the reaction, the catalyst was removed by filtration and then the reaction mixture was concentrated under vacuum evaporator to remove the volatile compounds. Then, 2-substituted quinazolines were isolated by column chromatography using silica gel 60 (spherical, 63-210 μm, Kanto Chemical Co. Ltd.) with ethylacetate/hexane (5/95 to 15/85) as the eluting solvent, followed by analyses by ^{1}H NMR, ^{13}C NMR and GCMS. For the kinetic, catalyst screening, and catalyst recycle studies, the yields of the un-reacted 2-aminobenzylamine **1a**, 2-substituted quinazoline **3a** and 2-heptyl-1,2,3,4-tetrahydro-quinazoline **2a** were determined by GC using *n*-dodecane as an internal standard. The analysis of the gas phase product (H_2) was carried out by the mass spectrometer (BELMASS).

NMR and GCMS analysis

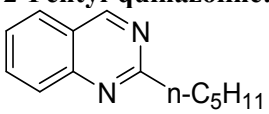
^{1}H and ^{13}C NMR spectra were recorded using at ambient temperature on JEOL-ECX 600 operating at 600.17 and 150.92 MHz, respectively with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform), respectively. Abbreviations used in the NMR experiments: s, singlet d, doublet; t, triplet; m, multiplet. GC-MS spectra were recorded by SHIMADZU QP2010.

2-Heptyl-quinazoline: (Table 2 entry 1 and Table 4 entry 1)



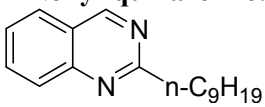
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.94 (d, *J* = 8.22 Hz, 1H), 7.85 (t, *J* = 6.84 Hz, 2H), 7.55 (t, *J* = 6.84 Hz, 1H), 3.08 (t, *J* = 7.56 Hz, 2H), 1.89-1.88 (m, 2H), 1.46-1.40 (m, 2H), 1.39-1.33 (m, 2H), 1.30-1.27 (m, 4H), 0.83 (t, *J* = 6.84 Hz, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 167.9, 160.3, 150.3, 133.9, 127.8, 127.0, 126.9, 123.0, 40.0, 31.7, 29.5, 29.1, 29.0, 22.6, 14.0. GC-MS m/e 228.16.

2-Pentyl-quinazoline: (Table 2 entry 2 and Table 4 entry 2)



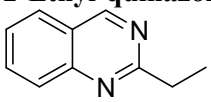
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.95 (d, *J* = 7.38 Hz, 1H), 7.85 (t, *J* = 8.28 Hz, 2H), 7.56 (t, *J* = 7.56, 1H), 3.09 (t, *J* = 7.68 Hz, 2H), 1.92-1.88 (m, 2H), 1.42-1.34 (m,4H), 0.88 (t, *J* = 6.84 Hz, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 167.9, 160.3, 150.3, 134.0, 127.8, 127.0, 126.9, 123.0, 40.0, 31.7, 28.7, 22.5, 14.0.GC-MS m/e 200.13.

2-Nonyl-quinazoline: (Table 2 entry 3 and Table 4 entry 3)



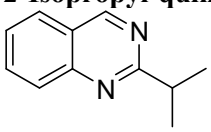
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.91 (d, *J* = 8.94 Hz, 1H), 7.80 (t, *J* = 8.28 Hz, 2H), 7.50 (t, *J* = 7.56, 1H), 3.06 (t, *J* = 7.56 Hz, 2H), 1.88-1.84 (m, 2H), 1.40-1.35 (m,2H), 1.32-1.27 (m, 2H), 1.22-1.18 (m, 8H), 0.81 (t, *J* = 7.56 Hz, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 167.9, 160.3, 150.3, 133.9, 127.9, 127.0, 126.8, 123.0, 40.0, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 22.6, 14.1.GC-MS m/e 256.19.

2-Ethyl-quinazoline: (Table 4 entry 4)



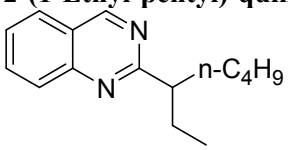
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.96 (d, *J* = 8.22 Hz, 1H), 7.80 (t, *J* = 8.28 Hz, 2H), 7.50 (t, *J* = 8.22, 1H), 3.06 (t, *J* = 7.56 Hz, 2H), 1.46 (t, *J* = 7.56 Hz, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 168.5, 160.4, 150.3, 133.9, 127.8, 127.0, 126.8, 123.0, 33.0, 12.9. GC-MS m/e 158.08.

2-Isopropyl-quinazoline: (Table 2 entry 4 and Table 4 entry 5)



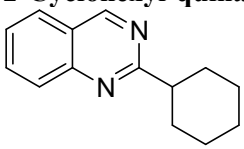
^{1}H NMR (600.17 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.91 (d, *J* = 8.94 Hz, 1H), 7.80-7.78 (t, *J* = 6.84 Hz, 2H), 7.49 (t, *J* = 6.84, 1H), 3.36-3.32 (m, 1H), 1.39 (d, *J* = 6.90Hz, 6H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 171.7, 160.4, 150.3, 133.8, 128.0, 127.0, 126.8, 123.2, 37.9, 21.8. GC-MS m/e 172.10.

2-(1-Ethyl-pentyl)-quinazoline: (Table 4 entry 6)



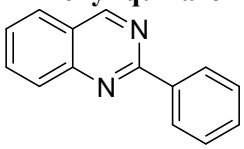
^{1}H NMR (600.17 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.00 (d, *J* = 6.84 Hz, 1H), 7.89 (t, *J* = 6.84 Hz, 2H), 7.61 (t, *J* = 6.84, 1H), 3.01-2.99 (m, 1H), 1.93-1.90 (m 2H), 1.82-1.78 (m, 2H), 1.30-1.26 (m, 4H), 0.84-0.80 (m, 6H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 170.5, 160.4, 150.2, 133.8, 128.0, 127.0, 126.8, 123.2, 51.1, 34.5, 29.9, 28.0, 22.8, 14.0, 12.2. GC-MS m/e 228.16.

2-Cyclohexyl-quinazoline:[1] (Table 4 entry 7)



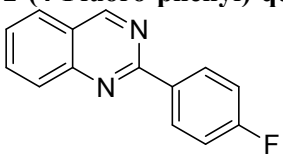
^{1}H NMR (600.17 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.97 (d, *J* = 8.28 Hz, 1H), 7.82-7.79 (m, 2H), 7.57 (t, *J* = 8.28, 1H),3.07-3.03 (m, 1H), 2.03 (d, *J* = 11.08 Hz, 2H), 1.91-1.88 (m, 2H), 1.80-1.76 (m, 3H), 1.50-1.43 (m, 2H), 1.39-1.34 (m, 1H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 170.8, 160.3, 150.3, 133.8, 127.9, 127.0, 126.8, 123.2, 47.9, 31.9, 26.2, 26.0. GC-MS m/e 212.13.

2-Phenyl-quinazoline:[1] (Table 2 entry 5 and Table 4 entry 8)



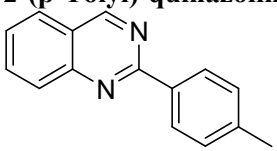
^{1}H NMR (600.17 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.64 (dd, *J* = 1.38 Hz, *J* = 1.38 Hz, 2H), 8.08 (d, *J* = 8.94 Hz, 1H), 7.88 (m, 2H), 7.60-7.51 (m, 4H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 169.9, 160.4, 150.6, 138.0, 134.0, 130.5, 128.6, 128.5, 127.2, 127.0, 123.5. GC-MS m/e 206.08.

2-(4-Fluoro-phenyl)-quinazoline:[2] (Table 2 entry 6 and Table 4 entry 9)



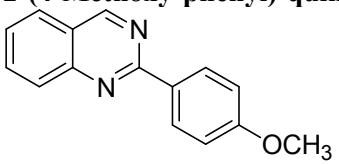
^{1}H NMR (600.17 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.64-8.61 (m, 2H), 8.05 (d, *J* = 8.94 Hz, 1H), 7.89 (t, *J* = 7.56, 2H), 7.51 (t, *J* = 7.44 Hz, 1H), 7.22-7.19 (m, 2H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 165.4 2 (d, *J* = 249.98 Hz, 4-F-C), 163.8, 160.4, 160.0, 150.6, 134.1, 130.6 (d, *J* = 8.66 Hz, meta to 4-F, C×2), 128.5 , 127.2, 127.1, 123.4, 115.6 (d, *J* = 21.67 Hz, ortho to 4-F, C×2). GC-MS m/e 224.07.

2-(p-Tolyl)-quinazoline:[1] (Table 4 entry 10)



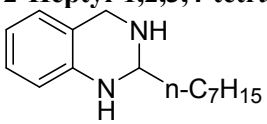
^{1}H NMR (600.17MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.53 (d, *J* = 8.22 Hz, 2H), 8.06 (d, *J* = 8.88 Hz, 1H), 7.87 (m, 2H), 7.56 (t, *J* = 7.56 Hz, 1H), 7.35 (d, *J* = 8.28 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 161.0, 160.3, 150.7, 140.8, 135.3, 133.9, 129.3, 128.5, 128.4, 127.0, 126.9, 123.4, 21.4. GC-MS m/e 220.10.

2-(4-Methoxy-phenyl)-quinazoline:[1] (Table 4 entry 11)



^{1}H NMR (600.17MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.58 (d, *J* = 6.84 Hz, 2H), 8.04 (d, *J* = 8.28 Hz, 1H), 7.88 (d, *J* = 6.84 Hz, 2H), 7.57 (t, *J* = 6.84 Hz, 1H), 7.05 (d, *J* = 6.36 Hz, 2H) 3.90 (s, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 161.8, 160.8, 160.3, 150.8, 134.0, 130.7, 130.1, 128.3, 127.1 126.7, 123.2, 113.9, 55.3. GC-MS m/e 236.09.

2-Heptyl-1,2,3,4-tetrahydro-quinazoline:



^{1}H NMR (600.17 MHz, $CDCl_3$) δ 7.01 (t, *J* = 7.56 Hz,1H), 6.89 (d, *J* = 7.56 Hz, 1H), 6.69-6.66 (m, 1H), 6.51 (d, *J* = 7.54 Hz, 1H), 4.14-4.12 (m, 2H), 3.94 (d, *J* =16.50 Hz, 1H), 1.64-1.58 (m, 2H), 1.53-1.48 (m, 1H), 1.47-1.42 (m, 1H), 1.35-1.27 (M, 10H), 0.91-0.88 (m, 3H); ^{13}C NMR (150.92 MHz, $CDCl_3$) δ 143.6, 127.1, 126.1, 121.6, 117.8, 114.8, 66.8, 46.5, 36.6 31.7, 29.5, 29.1, 24.9, 22.6, 14.0. GC-MS m/e 232.19.

References

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2 B. Han, X. L. Yang, C. Wang, Y. W. Bai, T. C. Pan, X. Chen and W. Yu, *J. Org. Chem.*, 2012, **77**, 1136.