Supporting information

Direct synthesis of quinazolinones by acceptorless dehydrogenative coupling of *o*-aminobenzamide and alcohols by heterogeneous Pt catalysts

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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 purifications. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA⁺-5 (Frontier Laboratories Ltd.) using nitrogen as the carrier gas.

Catalyst: HBEA (JRC-Z-HB25, SiO₂/Al₂O₃ = 25±5), CeO₂ (JRC-CEO-1, 157 m² g⁻¹), MgO (JRC-MGO-3), TiO₂ (JRC-TIO-4) and SiO₂-Al₂O₃ (JRC-SAL-2) were supplied by Catalysis Society of Japan. H⁺-type MFI zeolite (HMFI) with a SiO₂/Al₂O₃ ratio of 22.3 was kindly supplied by Tosoh Co. γ -Al₂O₃ was prepared by calcination of γ -AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. Hydroxides of Zr and Y were prepared by hydrolysis of zirconium oxynitrate 2-hydrate and yttrium nitrate in distilled water by gradually adding an aqueous NH₄OH solution (1.0 mol dm⁻³), followed by filtration of precipitate, washing with distilled water three times, drying at 100 °C for 12 h. Nb₂O₅·nH₂O was kindly supplied by CBMM. Y₂O₃, ZrO₂, and Nb₂O₅ were prepared by calcination of these hydroxides at 500 °C for 3 h. Active carbon (296 m² g⁻¹) was purchased from Kishida Chemical. SiO₂ (Q-10, 300 m² g⁻¹) was kindly supplied by Fuji Silysia Chemical Ltd.

Precursor of 5 wt% Pt/HBEA catalyst was prepared by an impregnation method; a mixture of HBEA and an aqueous HNO₃ solution of Pt(NH₃)₂(NO₃)₂ was evaporated at 50 °C, followed by drying at 90 °C for 12 h. The pre-reduced catalyst (Pt/HBEA) was prepared by pre-reduction of the precursor in a pyrex tube under a flow of H₂ (20 cm³ min⁻¹) at 300 °C for 0.5 h. Platinum oxides-loaded HBEA (PtOx/HBEA), as a comparative catalyst, was prepared 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/HBEA. TiO₂–supported metal catalysts, M/TiO₂ (M = Ir, Re, Ru, Pd, Rh, Ni, Cu) with metal loading of 5 wt% were prepared by impregnation method in the similar manner as Pt/HBEA using aqueous solution of metal nitrates (for Ni, Cu), RuCl₃, IrCl₃ *n*H₂O, NH₄ReO₄ or aqueous HNO₃ solution of Rh(NO₃)₃ or Pd(NO₃)₂.

The number of surface metal atoms in Pt/HBEA, in situ reduced under H₂ at 300 °C, was estimated by the CO pulse-adsorption experiment at room temperature in a flow of He using BELCAT (BELL Japan Inc.). The average Pt particle size was calculated from the CO uptake assuming that CO was adsorbed on the surface of spherical Pt particles at CO/(surface Pt atom) = 1/1 stoichiometry.

Typical procedures of catalytic test: Pt/HBEA was used as a standard catalyst. After the pre-reduction at 300 °C, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air as follows. Typically, the mixture *o*-aminobenzamide (1.0 mmol) and benzylalcohol (1.0 mmol) in mesitylene (1.5 g) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube) through a septum inlet, followed by filling N₂. Then, the resulting mixture was magnetically stirred for 24 h under reflux condition; the bath temperature was 180 °C and reaction temperature was *ca* 165 °C. After cooling the mixture, followed by removal of the catalyst, the volatile compound was removed under vacuum. Then, compounds **3** in Table 2 were isolated by column chromatography using silica gel 60 (spherical, 63-210 μ m, Kanto Chemical Co. Ltd.) and the eluting solvent of hexane/ethylacetate (7:3) and analyzed by ¹H NMR, ¹³C NMR and GCMS. For the standard reaction of *o*-aminobenzamide and benzylalcohol in Table 1, entry 2 of Table 2, and control reactions in eq. 1 and 2, conversion and yields of products were determined by GC using *n*-dodecane as an internal standard adopting the GC-sensitivity estimated using the isolated product.

NMR and GC/MS analysis

¹H and ¹³C NMR spectra for quinazolinones of Table-2 were assigned and reproduced to the corresponding literature. ¹H and ¹³C 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, 40.45 ppm dimethylsulfoxide, respectively. Abbreviations used in the NMR experiments: s, singlet d, doublet; t, triplet; q, quartet; m, multiplet. GC-MS spectra was taken by SHIMADZU QP2010.

2-Phenyl-3#-quinazolin-4-one:¹ ¹H NMR (600.17 MHz, DMSO-D₆), TMS: δ 12.59 (br s, 1H, NH), 8.23-8.19 (m, 2H), 7.89-7.86 (m, 1H), 7.78 (d, *J* = 7.56 Hz, 1H), 7.63-7.55 (m, 4H); ¹³C NMR (150.92 MHz, DMSO-D₆) δ 163.19, 153.25, 149.69, 135.57, 133.66, 132.34, 129.56 (C×2), 128.71 (C×2), 128.47, 127.55, 126.80; GC-MS

m/e 222.105

2-*p***-Tolyl-3***H***-quinazolin-4-one:¹ ¹H NMR (600.17 MHz, CDCl₃, TMS): \delta 11.81 (br s, 1H, NH), 8.33 (d,** *J* **= 7.50 Hz, 1H), 8.17 (d,** *J* **= 7.26 Hz, 2H), 7.82-7.78 (m, 2H), 7.49 (t,** *J* **= 6.84 Hz, 1H), 7.37 (d,** *J* **= 8.28 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (150.92 MHz, CDCl₃) \delta 164.01, 151.82, 149.63, 142.11, 134.78, 129.96, 129.69 (C×2),**

127.86, 127.36 (C×2), 126.84, 126.31, 120.75, 20.98; GC-MS m/e 236.105.

2-(4-tert-Butyl-phenyl)-3*H***-quinazolin-4-one:**² ¹H NMR (600.17 MHz, CDCl₃, TMS): δ 11.69 (br s, 1H, NH), 8.35 (dd, *J* = 8.28, 1.38 Hz, 1H), 8.20 (d, *J* = 8.28 Hz, 2H), 7.84-7.80 (m, 2H), 7.60-7.59 (m, 2H), 7.50 (t, *J* = 6.90 Hz, 1H), 1.40 (s, 9H); ¹³C NMR (150.92 MHz, CDCl₃) δ 163.92, 155.20, 151.74, 149.65, 134.78, 129.93, 127.93, 127.15 (C×2), 126.52, 126.34, 126.01(C×2), 120.78, 35.01,

31.16 (C×3); GC-MS m/e 278.150.

154.50, 150.34, 148.96, 135.43, 132.72, 129.79, 127.80, 127.12, 126.64, 121.39, 117.52, 115.91, 113.26; GC-MS m/e 240.075.

2-(4-Chloro-phenyl)-3*H*-quinazolin-4-one:² GC-MS m/e 256.050



2-Thiophen-2-yl-3*H***-quinazolin-4-one:**² ¹H NMR (600.17 MHz, CDCl₃, TMS): δ 12.25 (br s, 1H, NH), 8.33 (d, J = 7.56 1H), 8.24 (d, J = 3.18 Hz, 1H), 7.76 (d, J = 4.14 Hz, 2H), 7.57 (d, J = 4.80 Hz, 1H), 7.47-7.46 (m, 1H), 7.23-7.22 (m, 1H); ¹³C NMR (150.92 MHz, CDCl₃) δ 164.12, 149.60, 147.28, 137.68, 134.89, 131.19, 128.51, 128.32, 127.73, 126.47, 126.44, 120.71; GC-MS m/e 228.045.

2-(2-Hydroxy-phenyl)-3H-quinazolin-4-one: GC-MS m/e 238.080.



2-Pyridin-2-yl-3*H***-quinazolin-4-one:** ¹H NMR (600.17 MHz, CDCl₃, TMS): δ 10.92 (br s, 1H, NH), 8.61 (d, J = 4.80 1H), 8.52 (d, J = 7.56 Hz, 1H), 8.32-8.30 (m, 1H), 7.88-7.85 (m, 1H), 7.78-7.74 (m, 2H), 7.49-7.42 (m, 1H), 7.45-7.42 (m, 1H); ¹³C NMR (150.92 MHz, CDCl₃) δ 161.26, 149.01, 148.92, 148.60, 148.28, 137.38, 134.43, 127.94, 127.61, 126.63, 126.11, 122.38, 121.87; GC-MS m/e 223.085.

2-Furan-2-yl-3*H*-quinazolin-4-one:² GC-MS m/e 212.075.

2-Benzyl-3*H***-quinazolin-4-one:**¹ ¹H NMR (600.17 MHz, DMSO-D₆, TMS): δ 12.45 (br s, 1H, NH), 8.10 (d, J = 8.22 Hz, 1H), 7.81 (t, J = 7.56 Hz, 1H), 7.64 (d, J = 8.28 Hz, 1H), 7.50 (t, J = 8.28 Hz, 1H), 7.41 (d, J = 7.56 Hz, 2H), 7.37-7.32 (m, 2H), 7.30-7.27 (m, 1H), 3.97 (s, 2H); ¹³C NMR (150.92 MHz, DMSO-D₆) δ 162.79, 156.90, 149.75, 137.49, 135.32, 129.80 (C×2), 129.43 (C×2), 127.86, 127.73, 127.14, 126.63, 121.67, 41.32; GC-MS m/e 236.105.

2-Cyclohexyl-3*H*-quinazolin-4-one:² ¹H NMR (600.17 MHz, CDCl₃, TMS): 11.85 (br s, 1H, NH), 8.28 (dd, J = 8.68, 1.38 Hz, 1H), 7.77-7.74 (m, 1H), 7.70 (d, J = 8.22 Hz, 1H), 7.47-7.45 (m, 1H), 2.75-2.72 (m, 1H), 2.05-2.04 (m, 2H), 1.93-1.91 (m, 2H), 1.81-1.76 (m, 3H), 1.47-1.38 (m, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 164.29,

160.24, 149.55, 134.63, 127.34, 126.21, 126.15, 120.74, 44.85, 30.45 (C×2), 26.01 (C×2), 25.69; GC-MS m/e 207.150.

2-Pentyl-3*H***-quinazolin-4-one:**³ ¹H NMR (600.17 MHz, CDCl₃, TMS: δ 12.28 (br s, 1H, NH), NH 8.27 (d, J = 6.84 Hz, 1H), 7.77-7.75 (m, 1H), 7.69 (d, J = 7.44 Hz, 1H), 7.46 (t, J = 7.53 Hz, 1H), 2.80 (t, J = 7.89 Hz, 2H), 1.91-1.87 (m, 2H), 1.45-1.39 (m, 4H), 0.92 (t, J = 7.53 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 164.51, 157.10, 149.52, 134.72, 127.17, 126.24, 126.15, 120.44, 35.89, 31.38, 27.24, 22.29, 13.91; GC-MS m/e 216.135

2-Hexyl-3*H*-**quinazolin-4-one:**² ¹H NMR (600.17 MHz, CDCl₃, TMS: δ 12.15 (br s, 1H, NH), 8.28 (d, J = 8.22 Hz, 1H), 7.77-7.75 (m, 1H), 7.70 (d, J = 8.28 Hz, 1H), 7.47-7.45 (m, 1H), 2.80 (t, J = 7.56 Hz, 2H), 1.90-1.86 (m, 2H), 1.47-1.44 (m, 2H), 1.37-1.31 (m, 4), 0.88 (t, J = 6.90 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 164.43, 157.06, 149.51, 134.72, 127.18, 126.25, 126.16, 120.45, 35.96, 31.42, 28.89, 27.52, 22.45,

14.01; GC-MS m/e 230.150

2-Heptyl-3*H*-quinazolin-4-one:¹ ¹H NMR (600.17 MHz, DMSO-D₆, TMS): δ 12.20 (br s, 1H, NH), 8.10 (dd, J = 7.56, 1.38 Hz, 1H), 7.81-7.78 (m, 1H), 7.61 (d, J = 8.28 Hz, 1H), 7.48 (t, J = 7.53 Hz, 1H), 2.61 (t, J = 7.92 Hz, 2H), 1.75-1.73 (m, 2H), 1.33-1.27 (m, 8H), 0.87 (t, J = 6.87 Hz, 3H); ¹³C NMR (150.92 MHz, DMSO-D₆)

δ 162.77. 158.45, 149.91, 135.20, 127.73, 126.83, 126.61, 121.71, 35.44, 32.06, 29.43, 29.32, 27.72, 22.99, 14.87; GC-MS m/e 201.100.

2-Nonyl-3*H***-quinazolin-4-one:** ¹H NMR (600.17 MHz, CDCl₃, TMS: δ 11.95 (br, s, 1H, NH), 8.28 (dd, *J* = 8.91, 1.38 Hz, 1H), 7.78-7.76 (m, 1H), 7.70 (d, *J* = 8.28 Hz, 1H), 7.46 (t, *J* = 7.56 Hz, 1H), 2.79 (t, *J* = 7.56 Hz, 2H), 1.90-1.87 (m, 2H), 1.47-1.44 (m, 2H), 1.38-1.36 (m, 4H), 1.29-1.24 (m, 6H), 0.86 (t, *J* = 6.84 Hz, 3H); ¹³C

NMR (150.92 MHz, CDCl₃) δ 164.31, 157.00, 149.50, 134.73, 127.19, 126.26, 126.19, 120.49, 35.98, 31.83, 29.41, 29.26 (C×2), 29.23, 27.58, 22.64, 14.08; GC-MS m/e 272.195.

2-(1-Methyl-butyl)-3*H***-quinazolin-4-one:** ¹H NMR (600.17 MHz, CDCl₃, TMS: δ 11.29 (br s, 1H, NH), 8.28 (dd, *J* = 8.78, 1.38 Hz, 1H), 7.77-7.73 (m, 1H), 7.70 (d, *J* = 7.56 Hz, 1H), 7.47-7.44 (m, 1H), 2.90-2.87 (m, 1H), 1.92-1.85 (m, 1H), 1.72-1.64 (m, 1H), 1.48-1.41 (m, 4H), 1.38-1.34 (m, 1H), 0.93 (t, *J* = 7.56 Hz, 3H); ¹³C

NMR (150.92 MHz, CDCl₃) δ 163.90, 160.32, 149.44, 134.64, 127.37, 126.25, 126.23, 120.77, 40.39, 37.20, 20.57, 18.52, 13.96; GC-MS m/e 216.135.

2-(1-Ethyl-pentyl)-3*H***-quinazolin-4-one:**⁴ ¹H NMR (600.17 MHz, CDCl₃, TMS: δ 11.99 (br s, 1H, NH), 8.30 (d, *J* = 7.56 Hz, 1H), 7.76-7.73 (m, 1H), 7.46 (t, *J* = 6.84 Hz, 1H), 2.69-2.67 (m, 1H), 1.94-1.88 (m, 2H), 1.83-1.76 (m, 2H), 1.33-1.22 (m, 4H), 0.93 (t, *J* = 7.56 Hz, 3H), 0.82 (t, *J*

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= 6.18 Hz, 3H); ¹³C NMR (150.92 MHz, CDCl₃) δ 164.32, 159.84, 149.50, 134.54, 127.36, 126.17, 126.10, 120.69, 48.34, 33.03, 29.63, 26.71, 22.59, 13.86, 12.01; GC-MS m/e 244.175.

2-Isopropyl-3*H*-**quinazolin-4-one:**⁵ ¹H NMR (600.17 MHz, CDCl₃, TMS): δ 11.21 (br s, 1H, NH), 8.28 (dd, J = 8.78, 1.38 Hz, 1H), 7.76-7.71 (m, 2H), 7.46-7.44 (m, 1H), 3.04-3.02 (m, 1H), 1.44 (d, J = 6.90 Hz, 6H); ¹³C NMR (150.92 MHz, CDCl₃) δ 174.63, 171.36, 160.20, 145.42, 138.17, 137.07, 137.04, 131.56, 34.93, 20.40 (C×2);

GC-MS m/e 188.105

2-Butyl-3H-quinazolin-4-one:⁶ GC-MS m/e 202.115.



2-Phenyl-2,3-dihydro-1//-quinazolin-4-one:⁷ ¹H NMR (600.17 MHz, DMSO-D₆, TMS): δ 8.34 (br s, 1H, NH), 7.65 (d, J = 8.28 Hz, 1H), 7.53 (d, J = 7.56 Hz, 2H), 7.43 (t, J = 7.56 Hz, 2H), 7.40-7.37 (m, 1H), 7.29-7.27 (m, 1H), 7.16 (br s, 1H, NH), 6.79 (d, J = 8.28 Hz, 1H), 6.71 (t, J = 7.56 Hz, 1H), 5.79 (s, 1H); ¹³C NMR (150.92 MHz, DMSO-D₆) δ 164.54, 148.81, 142.56, 134.26, 129.40, 129.27 (C×2), 128.29, 145.04 (7.50 DK) (6, 2) 110.06 115.00 115.24 (7.50 DK) (7.50 DK)

127.81 (C×2), 118.06, 115.88, 115.34, 67.50; GC-MS m/e 224.105.

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0 9.0 $\|$ NH = Exp-hakim-135-6b-carb = delta = digla_pulse_dec = Exp-hakim-135-6b-carb DMSO-D6 = 11-DEC-2013 06:05:11 = 11-DEC-2013 10:09:08 = 11-DEC-2013 10:09:12 Filename Author Experiment Sample_id Solvent Creation_time Revision_time Current_time N 8.0 F = Exp-hakim-135-6b-carb = 1D COMPLEX = 32768 = 13C = [ppm] = X Content Data_format Dim_size Dim_title Dim_units Dimensions Site Spectrometer 2.0 ECA 600 DELTA2_NMR Spectrometer Field_strength X_acq_duration X_south X_offset X_present X_present X_resolution X_resolution X_sweep Irr_freq Irr_freq Irr_freq Irr_freq Konset Clipped Mod_return Scans Total_scans Y a g.with > 14.09636928[T] (600[M = 0.868352[s] = 13C = 150.91343039[MHz] = 100[ppm] = 32768 = 4 6.0 = 32768 = 4 = 1.15160672[Hz] = 37.73584906[KHz] = 1H = 500.1723046[MHz] = 5[Dpn] = 7KUE = 1 = 8000 = 8000 5.0 4 = 8000 = 11.4[us] = 0.468352[s] = 7.5[d0] = 3.8[us] = 19.331[d3] = 19.331[d3] = WALTZ = TRUE = 19.331[d3] = TRUE = TRUE = 2.5[s] = 76 = 2.5[s] = 3.368352[s] = 25.1[dC] X_90_width X_acq_time X_angle X_atn X_pulse Irr_atn_ace Irr_atn_ace Irr_noise Decoupling Initial_wait Noe 3.0 Initial_wait Noe_time Recvr_gain Relaxation_delay Repetition_time Temp_get 50 2 abundance 111111111 h 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0 X : parts per Million : 13C















































