Supporting information

Acceptorless dehydrogenative synthesis of 2-substituted quinazolines from 2-aminobenzylamine with primary alcohols or aldehydes 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 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 AlKα 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 C1s 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 TiO2 at 500 °C).

Catalyst preparation

CeO2 (JRC-CEO-1, 157 m2 g−1), MgO (JRC-MGO-1), TiO2 (JRC-TIO-4), SiO2Al2O3 (JRC-SAL2, Al2O3 = 13.75 wt%) and H-type BEA zeolite (HBEA, SiO2/Al2O3 = 25±5, JRC-Z-HB25) were supplied from Catalysis Society of Japan. SiO2 (Q-10, 300 m2 g−1) was supplied from Fuji Silysia Chemical Ltd. Hydroxides of Zr and La were prepared by hydrolysis of zirconium oxinitrate 2-hydrate and La(NO3)3·6H2O 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 supplied from CBMM. La2O3, ZrO2, and Nb2O5 were prepared by calcination of these hydroxides at 500 °C for 3 h. γ-Al2O3 was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. Precursor of 1 wt% Pt/CeO2 catalyst was prepared by an impregnation method; a mixture of CeO2 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. A pre-reduced catalyst (named Pt/CeO2) was prepared by pre-reduction of the precursor in a pyrex tube under a flow of H2 (20 cm3 min−1) at 500 °C for 0.5 h. Platinum oxides-loaded CeO2 (PtO/CeO2), 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/CeO2. CeO2-supported metal catalysts, M/CeO2 (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**

1 wt% 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)**

\[ \text{N} \quad \text{N} \quad \text{n-C}_7\text{H}_{15} \]

\(^1\)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)**

\[ \text{N} \quad \text{N} \quad \text{n-C}_5\text{H}_{11} \]

\(^1\)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, \(J = 7.56\) Hz, 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)

\[
\begin{align*}
^1H \text{ NMR (600 MHz, CDCl}_3) \delta & \ 9.27 (s, 1H), 7.91 (d, J = 8.94 Hz, 1H), 7.80 (t, J = 8.28 Hz, 2H), 7.50 (t, J = 7.56, 1H), 3.06 (t, J = 7.56 Hz, 2H), 1.88-1.84 (m, 2H), 1.32-1.27 (m, 2H), 1.22-1.18 (m, 8H), 0.81 (t, J = 7.56 Hz, 3H); \\
^{13}C \text{ NMR (150.92 MHz, CDCl}_3) \delta & \ 167.9, 160.3, 150.3, 133.9, 127.9, 127.0, 126.8, 123.0, 40.0, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 22.6, 14.1. \text{ GC-MS m/e 256.19.}
\end{align*}
\]

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

\[
\begin{align*}
^1H \text{ NMR (600 MHz, CDCl}_3) \delta & \ 9.34 (s, 1H), 7.96 (d, J = 8.22 Hz, 1H), 7.80 (t, J = 8.28 Hz, 2H), 7.50 (t, J = 8.22, 1H), 3.06 (t, J = 7.56 Hz, 2H), 1.46 (t, J = 7.56 Hz, 3H); \\
^{13}C \text{ NMR (150.92 MHz, CDCl}_3) \delta & \ 168.5, 160.4, 150.3, 133.9, 127.8, 127.0, 126.8, 123.0, 33.0, 12.9. \text{ GC-MS m/e 158.08.}
\end{align*}
\]

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

\[
\begin{align*}
^1H \text{ NMR (600.17 MHz, CDCl}_3) \delta & \ 9.29 (s, 1H), 7.91 (d, J = 8.94 Hz, 1H), 7.80 (t, J = 6.84 Hz, 2H), 7.49 (t, J = 6.84, 1H), 3.36-3.32 (m, 1H), 1.39 (d, J = 6.90 Hz, 6H); \\
^{13}C \text{ NMR (150.92 MHz, CDCl}_3) \delta & \ 171.7, 160.4, 150.3, 133.8, 128.0, 127.0, 126.8, 123.2, 37.9, 21.8. \text{ GC-MS m/e 172.10.}
\end{align*}
\]

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

\[
\begin{align*}
^1H \text{ NMR (600.17 MHz, CDCl}_3) \delta & \ 9.38 (s, 1H), 8.00 (d, J = 6.84 Hz, 1H), 7.89 (t, J = 6.84 Hz, 2H), 7.61 (t, J = 6.84, 1H), 3.01-2.99 (m, 1H), 1.93-1.90 (m 2H), 1.82-1.78 (m, 2H), 1.30-1.26 (m, 4H), 0.84-0.80 (m, 6H); \\
^{13}C \text{ NMR (150.92 MHz, CDCl}_3) \delta & \ 170.5, 160.4, 150.2, 133.8, 128.0, 127.0, 126.8, 123.2, 51.1, 34.5, 29.9, 28.0, 22.8, 14.0, 12.2. \text{ GC-MS m/e 228.16.}
\end{align*}
\]

2-Cyclohexyl-quinazoline: (Table 4 entry 7)

\[
\begin{align*}
^1H \text{ NMR (600.17 MHz, CDCl}_3) \delta & \ 9.35 (s, 1H), 7.97 (d, J = 8.28 Hz, 1H), 7.82-7.79 (m, 2H), 7.57 (t, J = 8.28, 1H), 3.07-3.03 (m, 1H), 2.03 (d, J = 11.08 Hz, 2H), 1.91-1.88 (m, 2H), 1.80-1.76 (m, 3H), 1.50-1.43 (m, 2H), 1.39-1.34 (m, 1H); \\
^{13}C \text{ NMR (150.92 MHz, CDCl}_3) \delta & \ 170.8, 160.3, 150.3, 133.8, 127.9, 127.0, 126.8, 123.2, 47.9, 31.9, 29.3, 26.2, 26.0. \text{ GC-MS m/e 212.13.}
\end{align*}
\]
2-Phenyl-quinazoline:¹ (Table 2 entry 5 and Table 4 entry 8)

![ Structural formula of 2-Phenyl-quinazoline ]

¹H NMR (600.17 MHz, CDCl₃) 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 ); ¹³C NMR (150.92 MHz, CDCl₃) 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)

![ Structural formula of 2-(4-Fluoro-phenyl)-quinazoline ]

¹H NMR (600.17 MHz, CDCl₃) 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 ); ¹³C NMR (150.92 MHz, CDCl₃) 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)

![ Structural formula of 2-(p-Tolyl)-quinazoline ]

¹H NMR (600.17MHz, CDCl₃) 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); ¹³C NMR (150.92 MHz, CDCl₃) 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)

![ Structural formula of 2-(4-Methoxy-phenyl)-quinazoline ]

¹H NMR (600.17MHz, CDCl₃) 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); ¹³C NMR (150.92 MHz, CDCl₃) 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:

![ Structural formula of 2-Heptyl-1,2,3,4-tetrahydro-quinazoline ]

¹H NMR (600.17 MHz, CDCl₃) 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); ¹³C NMR (150.92 MHz, CDCl₃) 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