Supporting Information

Highly Selective Reductive Cross-amination between Aniline or Nitroarene Derivatives and Alkylamines Catalyzed by Polysilane-immobilized Rh/Pt Bimetallic Nanoparticles

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1. General remarks

- Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F254 glass plates purchased from Merck KGaA and were visualized under UV light (254 nm) and/or by staining with KMnO4.
- NMR spectra were recorded with JEOL JMN-LA 500 or 600 spectrometers operating at 500, 600 MHz (1H) and 125, 150 MHz (13C) respectively. Chemical shifts were recorded in parts per million (ppm), from relative to internal references of the CDCl3, defined at 7.24 ppm (1H NMR) and 77.0 ppm (13C NMR). The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in literatures.
- Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis was performed on Shimadzu ICPS-7510 equipment.
- Aqua regia for ICP sample preparation was made by mixing concentrated hydrochloric acid and concentrated nitric acid in a volume of 3:1.
- Energy-dispersive X-ray spectroscopy/Scanning transmission electron microscopes (STEM/EDS) images were obtained using a JEOL JEM-2100F instrument operated at 200 kV. All STEM specimens were prepared by placing a drop of the solution on carbon-coated copper grids and allowed to dry in air (without staining).
- GC analysis was performed on a Shimadzu GC-2010 apparatus (column = J & W Scientific DB-1; gas pressure: 157.5 kPa, total flow: 41.3 mL/min, column flow: 0.93 mL/min, linear velocity: 21.1 cm/s, sprit ratio: 40.1, injection temperature: 300 °C, detector temperature: 300 °C). Anisole was used as internal standard for quantitative analysis.
- NaBH4 was purchased from Wako Pure Chemical Company and recrystallized from diglyme by heating according to the literature[1] and stored in a glove box.
- Substrates were used as purchased or purified by distillation following the normal procedures, if it is needed.
- Preparative TLC (PTLC) was performed using Wakogel® B-5F from Wako Pure Chemical Industries. Column chromatography was performed on silica
gel 60 (Merck).

- Solvents were purchased from Wako Pure Chemical Industries, Tokyo Kasei CO., and Kanoto Chemical.
- Na₂PtCl₆·6H₂O was purchased from Strem Chemical Inc. Pd(OAc)₂ was purchased from Aldrich Inc.
- Polisilane (DMPSi) was purchased from NIPPON SODA CO. LTD.
- Batch reactions under atmospheric hydrogen were conducted with Carousel® system (parallel synthesizer; Radleys) and hydrogen filled plastic balloon.
- Rh-Pt/(DMPSi-Al₂O₃) was prepared following previous report.[²]
2. Characterization of the products in reductive cross-amination of alkylamines and aniline

*N*-Octylcyclohexylamine (3aa)

Rh-Pt/(DMPSi-Al2O3) (33.4 mg, 0.75 mol% as Rh), *n*-octylamine (1a) (51.7 mg, 0.4 mmol) and aniline (2a) (74.0 mg, 0.8 mmol) were placed in caroucel® tube. The atmosphere was exchanged to H2 using balloon and pump. After the reaction mixture was stirred at 50 °C for 24 h, the reaction was quenched by the addition of 5 ml of AcOEt and the reaction mixture was analyzed by GC using decane as an internal standard. Yield: 93%; GC flow rate (157.5 kPa, He), Inject (50 °C), Detect. (100 °C), Int. T. (50 °C), Int. T. (0 min), Rate (5 °C/min), Fin. T. (100 °C), Fin. T. (10 min) : tR (min) 30.068 (*N*-octylcyclohexylamine), 19.304 (internal standard (decane)).

*N*-hexylcyclohexylamine (3ba)[1]

Rh-Pt/(DMPSi-Al2O3) (81.2 mg, 0.75 mol% as Rh), *n*-hexylamine (1b) (121.4 mg, 1.2 mmol) and aniline (2a) (279.4 mg, 3.0 mmol) were placed in caroucel® tube. The atmosphere was exchanged to H2 using balloon and pump. After the reaction mixture was stirred at 50 °C for 24 h, the reaction was quenched by the addition of 5 ml of DCM. The catalyst was filtered off and the filtrate was concentrated. The desired product was isolated from the crude mixture by column chromatography (hexane:AcOEt:Et3N = 20:1:0.5). The catalyst was filtered off and the filtrate was concentrated. The desired product was isolated from the crude mixture by column chromatography (hexane:AcOEt:Et3N = 20:1:0.5). Yield: >99%; 1H NMR (600 MHz, CDCl3) δ 2.61-2.59 (m, 2H), 2.42-2.37 (m, 1H), 1.87 (d, 2H, J = 12.4 Hz), 1.72 (d, 2H, J = 13.0 Hz), 1.61 (d, 1H, J = 12.4 Hz), 1.47-1.44 (m, 2H), 1.33-1.22 (m, 8H), 1.16-1.12 (m, 1H), 1.08-1.02 (m, 2H), 0.88 (t, 3H, J = 13.7 Hz); 13C NMR (100 MHz, CDCl3) δ 56.9, 47.1, 33.7, 31.8, 30.5, 27.2, 26.2, 25.1, 22.6, 14.0.

*N*-(3-phenylpropyl)cyclohexanamine (3ca)[2]

Rh-Pt/(DMPSi-Al2O3) (81.2 mg, 0.75 mol% as Rh), 3-phenylpropylamine (1c) (162.3 mg, 1.2 mmol) and aniline (2a) (279.4 mg, 3.0 mmol) were placed in caroucel® tube. The atmosphere was exchanged to H2 using balloon and pump. After the reaction mixture was stirred at 50 °C for 3 days, the
reaction was quenched by the addition of 5 ml of DCM. The catalyst was filtered off and the filtrate was concentrated. The desired product was isolated from the crude mixture by column chromatography (hexane:AcOEt:Et₃N = 20:1:0.5). Yield: 92%; 

\[ ^1H \text{ NMR} \quad (600 \text{ MHz, CDCl}_3 \delta 7.29-7.26 \text{ (m, 2H), 7.20-7.16 (m, 3H), 2.67-2.63 (m, 4H), 2.41-2.35 (m, 1H), 1.88-1.59 (m, 7H), 1.30-1.15 (m, 3H), 1.13-0.99 (m, 2H);} \]

\[ ^13C \text{ NMR} \quad (100 \text{ MHz, CDCl}_3 \delta 142.2, 128.3, 128.3, 125.7, 56.8, 46.5, 33.8, 33.7, 32.1, 26.2, 25.1.} \]

**N-(3-methoxypropyl)cyclohexanamine (3da)**

\[ \text{Rh-Pt/(DMPSi-Al}_2\text{O}_3) \quad (81.2 \text{ mg, 0.75 mol\% as Rh), 3-methoxypropylamine (1d) (176.7 mg, 1.2 mmol) and aniline (2a) (279.4 mg, 3.0 mmol) were placed in carousel® tube. The atmosphere was exchanged to H}_2 \text{ using balloon and pump. After the reaction mixture was stirred at 50 °C for 38 h, the reaction was quenched by the addition of 5 ml of DCM. The catalyst was filtered off and the filtrate was concentrated. The desired product was isolated from the crude mixture by column chromatography (hexane:AcOEt:Et}_3\text{N = 3:2:0.1). Yield: 97%;} \]

\[ ^1H \text{ NMR} \quad (600 \text{ MHz, CDCl}_3 \delta 3.44 \text{ (t, 2H, } J = 6.2 \text{ Hz), 3.32 (s, 3H), 2.71 (t, 2H, } J = 6.9 \text{ Hz), 2.44-2.39 (m, 1H), 1.87 \text{ (d, 2H, } J = 13.0 \text{ Hz), 1.77-1.70 (m, 4H), 1.63-1.59 (m, 1H), 1.42 \text{ (br, 1H), 1.29-1.21 (m, 2H), 1.19-1.14 (m, 1H), 1.09-1.03 (m, 2H);} \]

\[ ^13C \text{ NMR} \quad (100 \text{ MHz, CDCl}_3 \delta 71.4, 58.6, 56.9, 44.3, 33.6, 30.4, 26.2, 25.1.;} \]

\[ \text{IR (neat) cm}^{-1} \quad 3579, 3312, 2928, 2853, 1672, 1454, 1375, 1304, 1255, 1195.;} \]

\[ \text{HRMS (DART) calculated for C}_{10}\text{H}_{22}\text{NO}^+ \quad [\text{M+H}^+] \quad 172.17014, \text{ found 172.16781.} \]

**Tert-butyl (6-(cyclohexylamino)hexyl)carbamate (3ea)**

\[ \text{Rh-Pt/(DMPSi-Al}_2\text{O}_3) \quad (47.1 \text{ mg, 0.75 mol\% as Rh), tert-butyl (6-aminohexyl)carbamate (1e) (130.5 mg, 0.7 mmol) and aniline (2a) (226.9 mg, 2.4 mmol) were placed in carousel® tube. The atmosphere was exchanged to H}_2 \text{ using balloon and pump. After the reaction mixture was stirred at 50 °C for 24 h, the reaction was quenched by the addition of 5 ml of DCM. The catalyst was filtered off and the filtrate was concentrated. The desired product was isolated from the crude mixture by column chromatography (AcOEt:MeOH:Et}_2\text{O:Et}_3\text{N = 2:1:7:0.1). Yield: 85%;} \]

\[ ^1H \text{ NMR} \quad (600 \text{ MHz, CDCl}_3 \delta 4.60 \text{ (bs, 1H), 3.07 (q, 2H, } J = 6.5 \text{ Hz), 2.58 \text{ (t, 2H, } J = 7.1 \text{ Hz), 2.42-2.32 (m, 1H),} \]
1.84 (m, 2H), 1.73-1.57 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.4, 79.3, 57.3, 47.3, 40.7, 34.0, 30.8, 30.4, 28.5, 27.5, 27.1, 26.6, 25.5.

$\text{N}^1$-$\text{cyclohexyl}$-$\text{N}^2$, $\text{N}^3$-$\text{dimethyl}$propane-1,3-diamine (3fa)$^{[4]}$

Rh-Pt/(DMPSi-Al$_2$O$_3$) (94.8 mg, 0.75 mol% as Rh), $\text{N}^1$, $\text{N}^1$-$\text{dimethyl}$propane-1,3-diamine (1f) (122.6 mg, 1.2 mmol) and aniline (2a) (391.1 mg, 4.2 mmol) were placed in caroucel® tube. The atmosphere was exchanged to H$_2$ using balloon and pump. After the reaction mixture was stirred at 50 °C for 24 h, the reaction was quenched by the addition of 5 ml of DCM. The catalyst was filtered off and the filtrate was concentrated. The desired product was isolated from the crude mixture by column chromatography (hexane:AcOEt = 95:5). Yield: >99%; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 2.65 (t, 2H, $J = 7.6$ Hz), 2.42-2.39 (m, 1H), 2.30 (t, 2H, $J = 7.6$ Hz), 2.21 (s, 6H), 1.88-1.85 (m, 2H), 1.73-1.60 (m, 3H), 1.29-1.14 (m, 5H), 1.09-1.02 (m, 2H), 0.90-0.87 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 58.1, 57.0, 45.6, 45.5, 33.7, 28.6, 26.2, 25.1.
3. Charts of isolated Products

$^1$H NMR chart of $N$-hexylcyclohexylamine (3ba)

$^{13}$C NMR chart of $N$-hexylcyclohexylamine (3ba)
$^1$H NMR chart of $N$-(3-phenylpropyl)cyclohexanamine (3ca)

$^{13}$C NMR chart of $N$-(3-phenylpropyl)cyclohexanamine (3ca)
$^1$H NMR chart of $N$-(3-methoxypropyl)cyclohexanamine (3da)

$^{13}$C NMR chart of $N$-(3-methoxypropyl)cyclohexanamine (3da)
\[ \text{\( ^{1} \)H NMR chart of tert-butyl (6-(cyclohexylamino)hexyl)carbamate (3ea)} \]

\[ \text{\( ^{13} \)C NMR chart of tert-butyl (6-(cyclohexylamino)hexyl)carbamate (3ea)} \]
$^1$H NMR of $N^1$-cyclohexyl-$N^3,N^3$-dimethylpropane-1,3-diamine (3fa)

$^{13}$C NMR of $N^1$-cyclohexyl-$N^3,N^3$-dimethylpropane-1,3-diamine (3fa)
4. References