Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Heterogeneous Double-Activation Catalysis: Rh Complex and Tertiary Amine on Same Solid Surface for the 1,4-Addition Reaction of Aryl- and Alkylboronic Acids

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Experimental Section

NMR measurements

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with an AVANCE 400 spectrometer (Bruker) operating at 400 and 100.6 MHz, respectively. Solid-state ^{13}C and ^{29}Si MAS NMR spectra (MAS rate = 5 kHz) were recorded with an AVANCE III spectrometer (Bruker) operating at 100.6 and 79.5 MHz, respectively. The cross-polarization (CP) contact time in the ^{13}C CP/MAS NMR measurements was 1.0 ms. The accumulation number and delay time were about 20000 and 20 s (^{13}C), and 10000 and 15 s (^{29}Si), respectively. Adamantane (δ 38.52 and 29.47 ppm) and hexamethylcyclotrisiloxane (δ -9.66 ppm) were used as external standards for the calibration of chemical shifts.

Both ^{11}B MAS NMR spectroscopy and MQ MAS experiments were performed using a Bruker Avance III spectrometer (9.4 T) operating at 128.3 MHz for boron using a 4.0 mm MAS probe. MAS was performed at a rotation speed of 14 kHz. $\pi/3$ pulses with an rf field strength of 111 kHz was used. Chemical shifts were referenced relative to an aqueous solution of $B(OH)_3$. The relaxation delays were 10 s. The ^{11}B 2D3Q MAS NMR spectra were recorded by three-pulse z-filtering with rotor synchronization at a spinning rate of 12 kHz. The excitation pulse was a π pulse, and the conversion pulse was a $\pi/3$ pulse. The conversion delay was 10 s. For each t_1 increment, 1000 scans were used to accumulate signals. Fourier transform with respect to $t1$ and $t2$ led to pure adsorption 2D spectra. The spectra were sheared, so that the orthogonal projection of the 2D spectrum on the isotropic axis gave a high-resolution 1D spectrum free of any anisotropic broadening.

XAFS data acquisition

XAFS was measured in transmission mode at the BL7 of the Kyusyu Synchrotron Light Research Center (Proposal number: 1404015F, SAGA-LS, Saga, Japan). The electron storage ring was operated at 1.4 GeV-137 mA. Synchrotron radiation from the storage ring was monochromatized with a Si (220) channel-cut crystals. Ionization chambers filled with Ar gas and Kr were used as detectors monitoring incident X-rays (I_0) and transmitted one (I), respectively. The angle of the monochromator was calibrated by using Rh foil, the inflection point of which at the edge was set at 23220 eV.

XAFS spectra were analyzed by using Athena and Altemis.[1] The backscattering amplitude and phase shift of Rh-C, Rh-O, Rh-Rh were calculated using FEFF8.4 code[2] with the crystallographic data of a bulk Rh and $[Rh(COD)OH]_2$ complex.

A goodness of curve fit was estimated using the following equation.

$$R_{factor} = \sqrt{\frac{k^n \chi_{exp}(k) - k^n \chi_{cf}(k)}{k^n \chi_{experimental}(k)}}$$

where $\chi_{exp}(k), \chi_{cf}(k)$ are the experimental data, curve-fitted data (theoretical) , respectively.

Materials

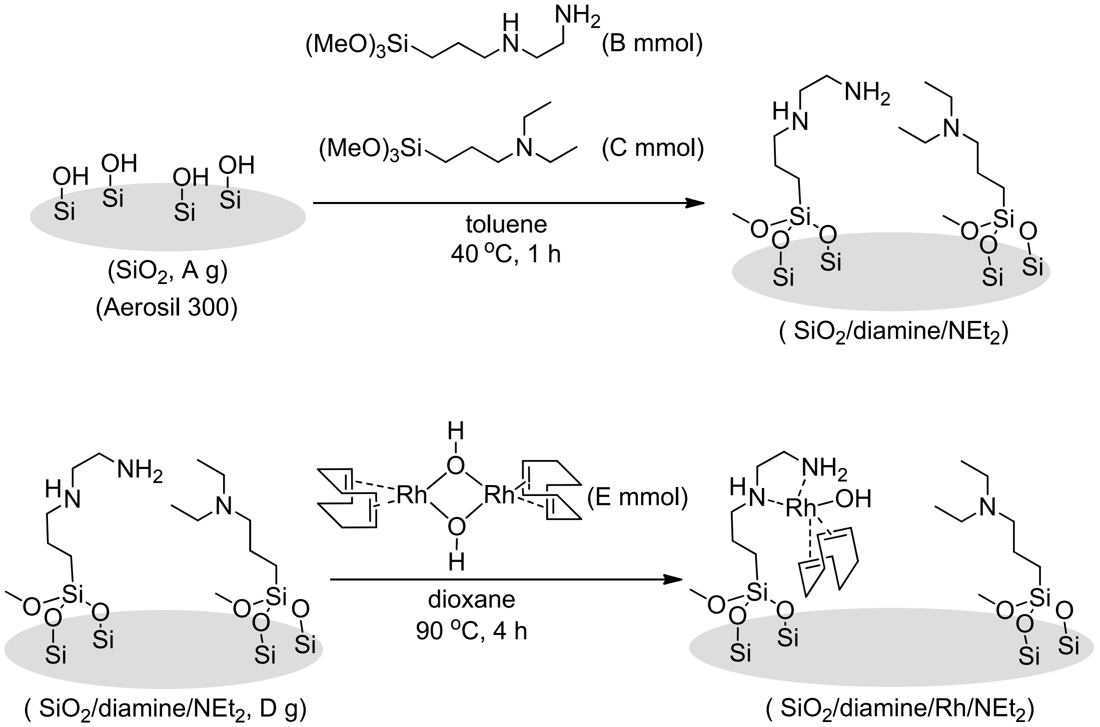
Aerosil® 300 (NIPPON AEROSIL Co.) was used as the SiO_2. SiO_2 was treated at 120 °C under vacuum before use. Unless otherwise noted, all other materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Kanto Kagaku Co., and Aldrich Inc. and were used without further purification. 1,3,5-Triisopropylbenzene was used as an internal standard in catalytic reactions.

Preparation of Catalyst

Preparation of SiO_2/diamine/NEt_2 and SiO_2/diamine/Rh/NEt_2

The SiO_2 (Aerosil® 300, 300 m^2g^{-1}, SiO_2 content: >99.9%) was pretreated at 120 °C for 3 h under vacuum. Dried SiO_2 (0.64 g) was placed in a round-bottom flask and treated with 15.0 mL of a toluene solution containing 3-(2-Aminoethylamino)propyltrimethoxysilane (0.40 mmol, 9.0×10^{-2} g) and 3-diethylaminopropyltrimethoxysilane (0.40 mmol, 9.5×10^{-2} g) at 40 °C for 1 h. Toluene was removed by vacuum evaporation, affording SiO_2/diamine/NEt_2. Then, 0.21 g of SiO_2/diamine/NEt_2 was treated with 3.0 mL of dioxane containing $[Rh(cod)OH]_2$ (5.0×10^{-2} mmol, Rh: 0.10 mmol) at 90 °C for 4 h. The resulting mixture was evaporated and dry under vacuum, affording SiO_2/diamine/Rh/NEt_2-a. For the detailed reaction conditions used in the preparation of the other SiO_2-supported Rh catalysts, see Table S1.

Table S1. Detailed conditions for preparation of catalysts



Catalyst	A: SiO_2 (g)	B: Diamine (mmol)	C: Tertiary amine (mmol)	D: SiO_2/diamine /NEt_2 (g)	E: $[Rh(cod)OH]_2$ (mmol)
SiO_2/diamine/Rh-a	0.64	0.40	-	0.18	0.050
SiO_2/diamine/Rh-b	0.89	0.070	-	0.60	0.025
SiO_2/diamine/Rh/NEt_2-a	0.64	0.40	0.40	0.21	0.050
SiO_2/diamine/Rh/NEt_2-b	0.64	0.050	0.050	0.41	0.013
SiO_2/diamine/Rh/NEt_2-c	1.30	0.10	0.70	0.60	0.021
SiO_2/diamine/Rh/NEt_2-d	1.30	0.10	1.50	1.40	0.045
SiO_2/diamine/Rh/NEt_2-e	0.64	0.30	0.30	0.21	0.038
SiO_2/diamine/Rh/NEt_2-f	0.64	0.20	0.20	0.21	0.025
SiO_2/diamine/Rh/NEt_2-g	0.64	0.10	0.10	0.41	0.025

Catalytic Reaction Procedures

1,4-Addition reaction using silica-supported Rh catalyst

The silica-supported Rh catalyst (6.0 μmol), dioxane/H_2O (10/1, 2.0 mL), cyclohexenone (**1**) (1.0 mmol) and phenylboronic acid (**2**) (1.5 mmol) were placed in a Pyrex glass reactor. The resulting mixture was stirred vigorously for 1 h at 60 °C under Ar. The product was confirmed by GC-MS and NMR. Yields and conversion were determined by ^1H NMR using a $CDCl_3$ solution of the reaction mixture.

Treatment of SiO_2/NEt_2 with phenylboronic acid for NMR analysis of the reaction intermediate

SiO_2/NEt_2 (0.10 g, N: 0.083 mmol), dioxane/H_2O (10/1, 1.0 mL), and phenylboronic acid (**2**) (0.083 mmol) were placed in a Pyrex glass reactor. The resulting mixture was vigorously stirred for 5 min at 40 °C under Ar. Then, the solvent was evaporated under vacuum, and the resulting solid was transferred to NMR sample rotor.

Treatment of SiO_2/diamine/Rh/NEt_2 with phenylboronic acid for ^{11}B NMR analysis of the reaction intermediate

SiO_2/diamine/Rh/NEt_2 (0.19 g, tertiary amine: 0.085 mmol), dioxane/H_2O (10/1, 1.0 mL), and phenylboronic acid (**2**) (0.085 mmol) were placed in a Pyrex glass reactor. The resulting mixture was vigorously stirred for 5 min at 40 °C under Ar. Then, the solvent was evaporated under vacuum, and the resulting solid was transferred to NMR sample rotor.

Solid-State ^{29}Si MAS NMR Spectra

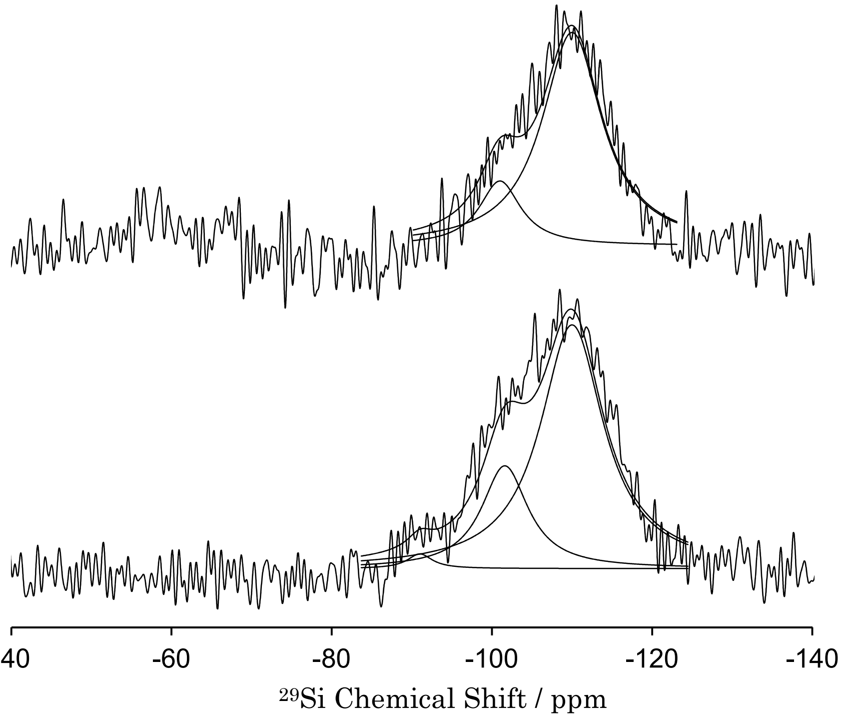


Figure S1. Solid-state ^{29}Si MAS NMR spectra of (A) SiO_2 and (B) SiO_2/diamine/Rh/NEt_2-a.

$Q^3/(Q^2 + Q^3 + Q^4)$: 0.23 → 0.17
$Q^2/(Q^2 + Q^3 + Q^4)$: 0.02 → <0.01

The total silanol content in the parent SiO_2 (4.2 mmol/g) was calculated from the Q^3/Q_{total} and Q^2/Q_{total} values and the molecular weight of SiO_2. This value was close to the amount of silanol calculated on the basis of the weight loss of the SiO_2 via thermogravimetric (TG) analysis (4.6 mmol/g). The amount of silanol decrease (1.5 mmol/g) was calculated from the silanol content of the parent SiO_2 determined by ^{29}Si NMR and the Q^3/Q_{total} and Q^2/Q_{total} values after the silane-coupling reaction.

XPS Analysis

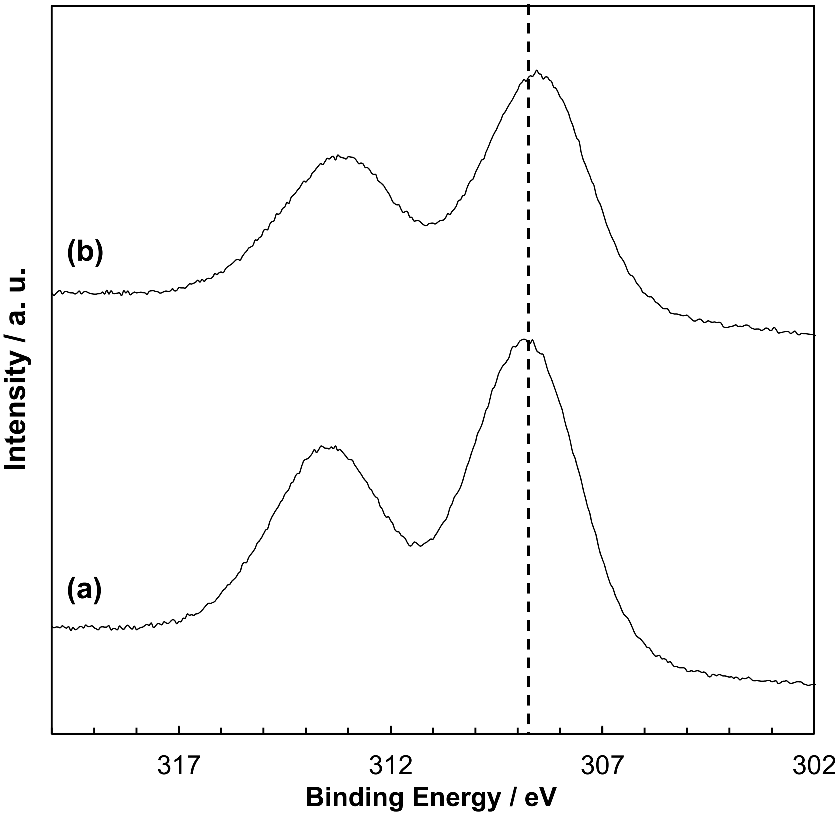


Figure S2. XPS spectra for Rh 3$d_{5/2}$ from (a) SiO_2/diamine/Rh/NEt_2-a and (b) SiO_2/diamine/Rh-a.

XANES Analysis

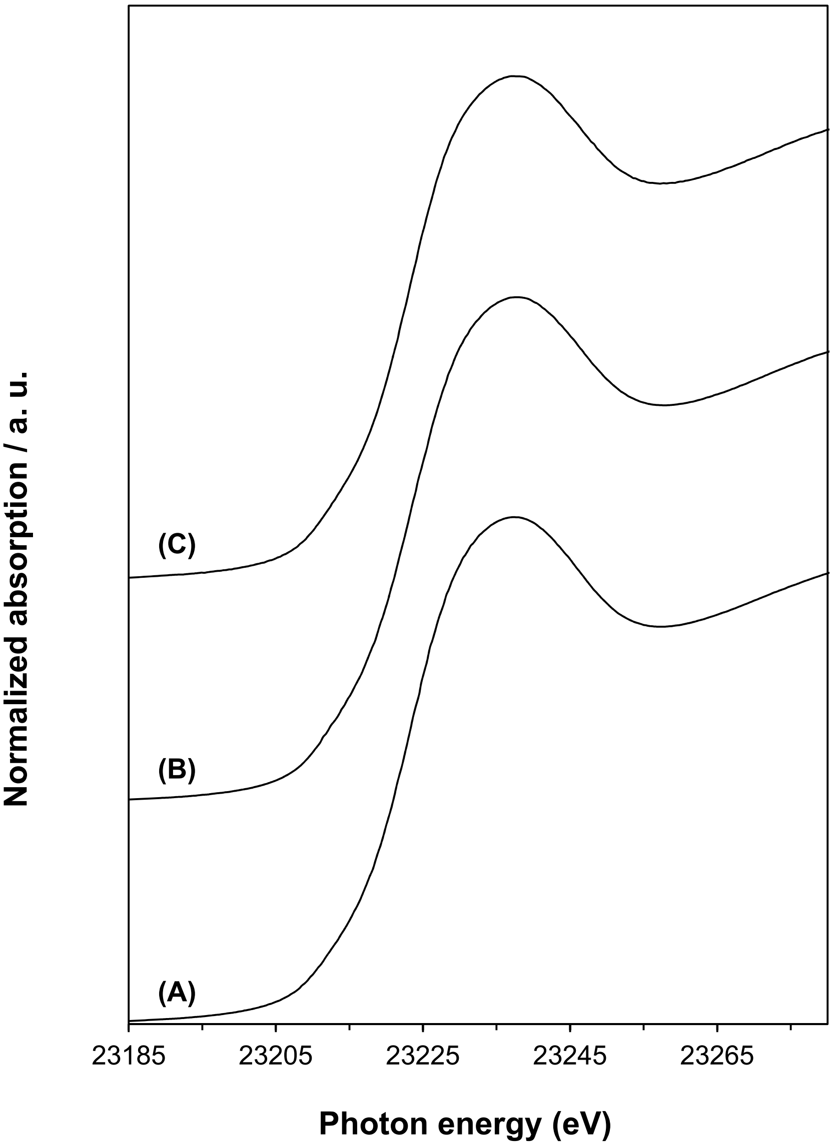


Figure S3. Rh K-edge XANES spectra of (**A**) SiO_2/diamine/Rh/NEt_2-a, (**B**) SiO_2/diamine/Rh/NEt_2-b, and (**C**) SiO_2/diamine/Rh/NEt_2-f.

EXAFS Analysis

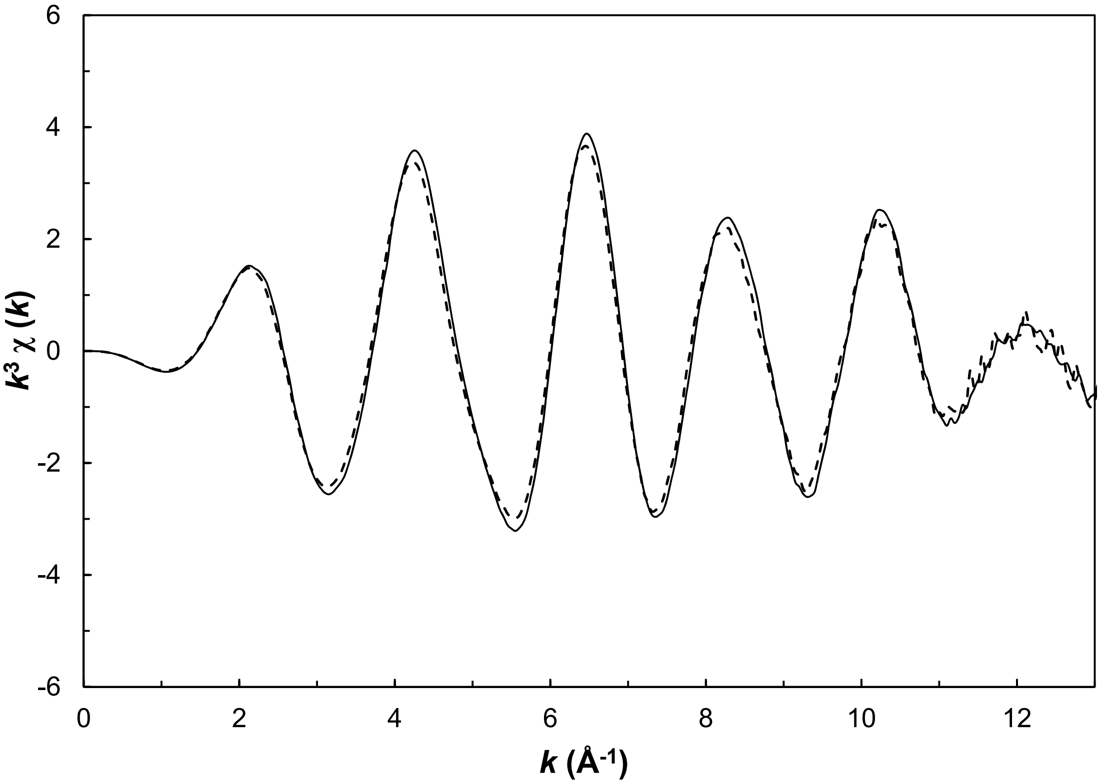


Figure S4. EXAFS spectra of (a) SiO_2/diamine/Rh/NEt_2-a (solid line) and (b) recovered SiO_2/diamine/Rh/NEt_2-a after the 1,4-addition between **1** and **2** (dashed line).

Results of Curve-Fitting Analysis of EXAFS

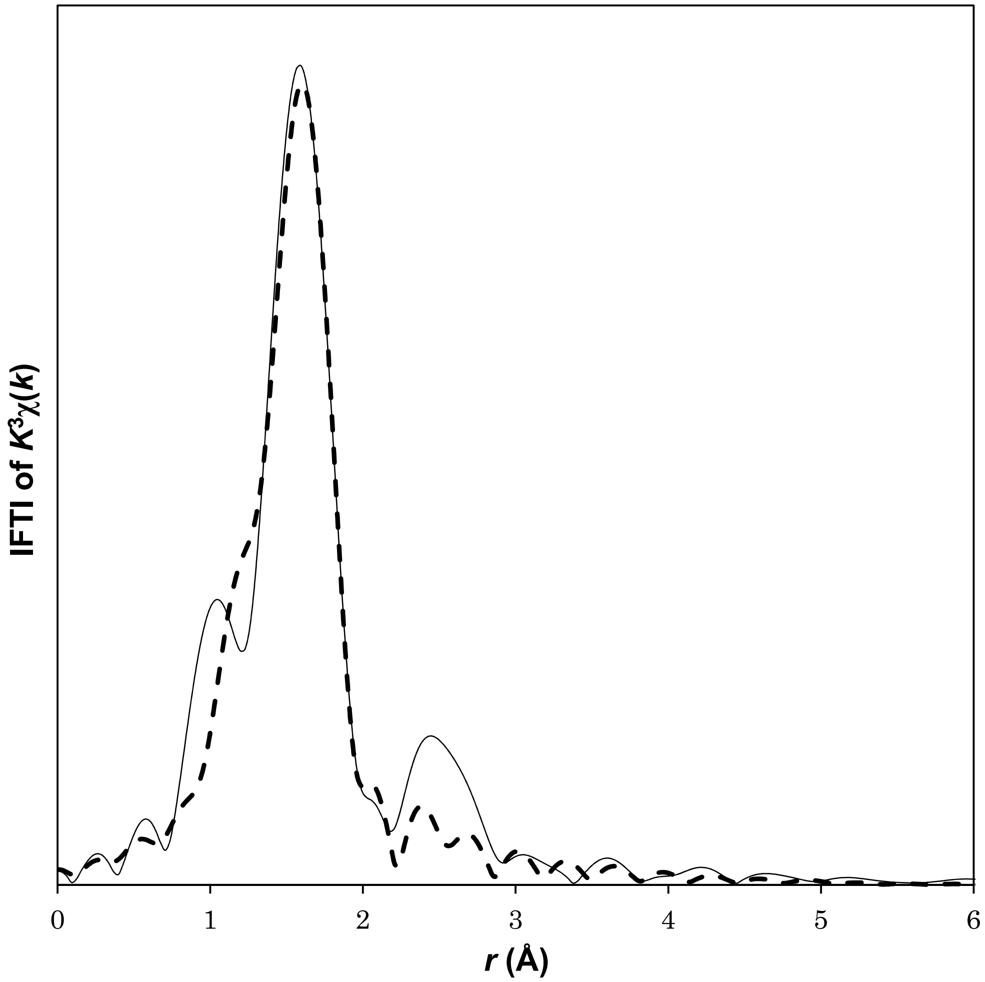


Figure S5. FT of k^3-weighted Rh K-edge EXAFS spectra for SiO_2/diamine/Rh/NEt_2-a (solid line), and fitted spectra for SiO_2/diamine/Rh/NEt_2-a (dashed line). (FT: 3–13 Å, FF: 1.2–2.0 Å)

Effect of Additional Free Amine on 1,4-addition Reaction

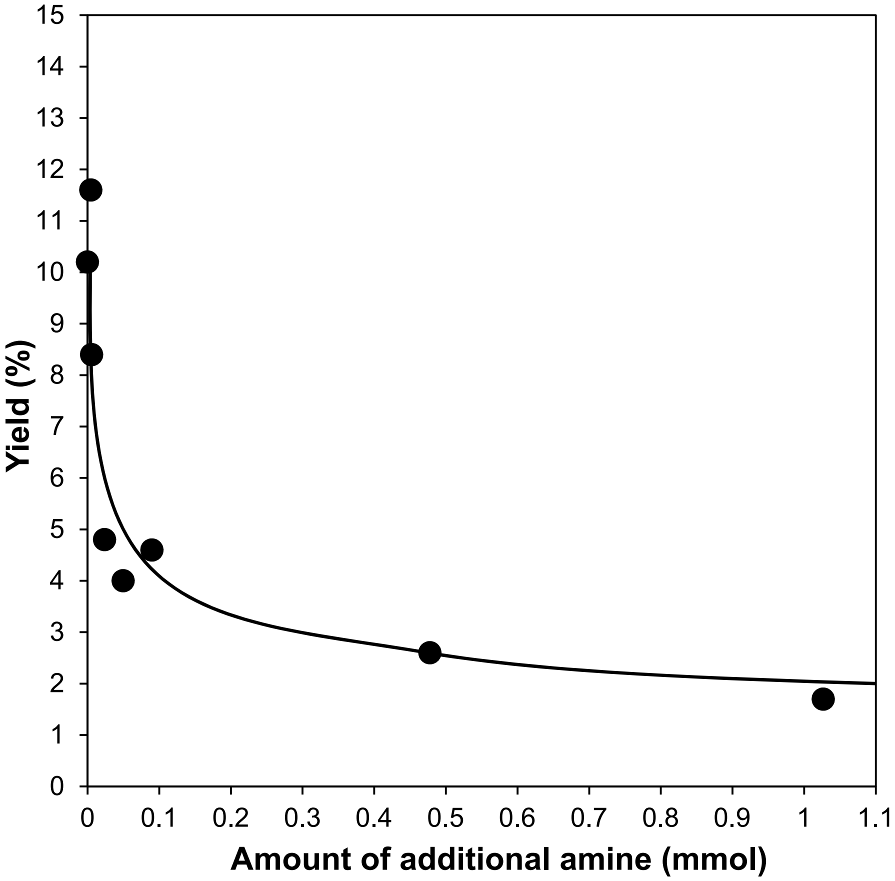


Figure S6. Effect of additional free amine with the SiO_2/diamine/Rh-a catalyst on the product yield of the 1,4-addition of phenylboronic acid to cyclohexenone. Reaction conditions: cyclohexenone (**1**) (1.0 mmol), phenylboronic acid (**2**) (1.5 mmol), SiO_2/diamine/Rh (Rh: 6.0 μmol), 1,4-dioxane/H_2O (10/1, 2.0 mL), 60 °C, 1h, free tertiary amine (diethylbutylamine: 0–1.027 mmol).

Hot Filtration

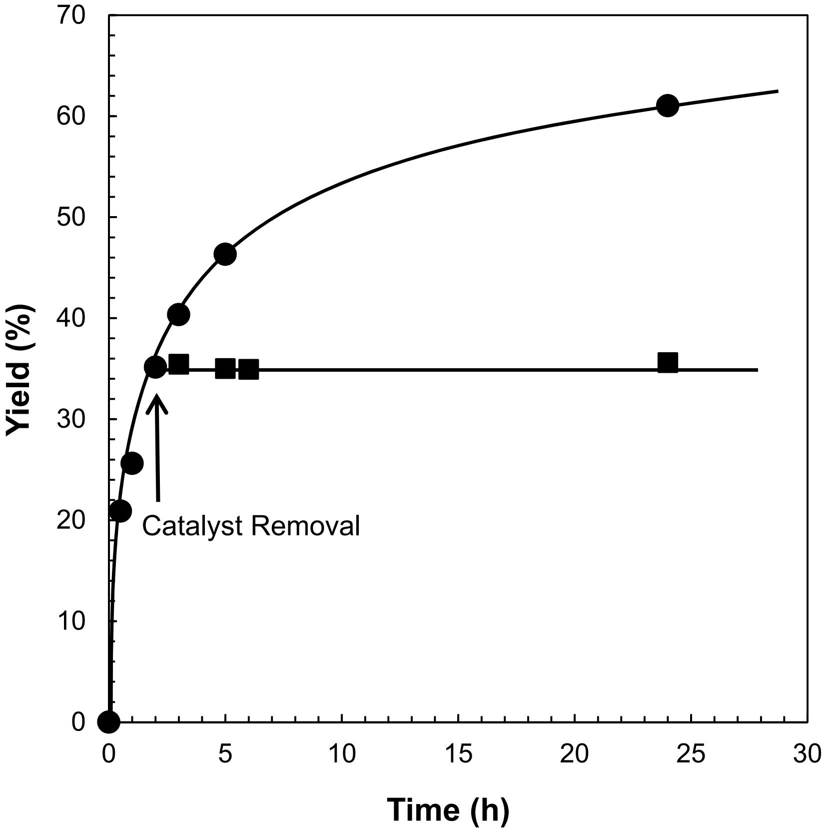
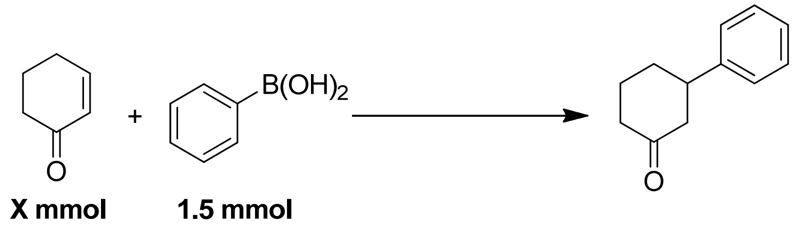


Figure S7. Effect of removal of SiO_2/diamine/Rh/NEt_2 (Rh: 0.388mmol/g, tertiary amine: 1.19 mmol/g) catalyst on product yield of 1,4-addition between **1** and **2**. Without removal of SiO_2/diamine/Rh/NEt_2-a (●); an arrow indicates the removal of SiO_2/diamine/Rh/NEt_2-a (■). Reaction conditions: phenylboronic acid (**1**) (1.0 mmol), cyclohexenone (**2**) (1.5 mmol), SiO_2/diamine/Rh/NEt_2-a (Rh: 6.0 μmol), 1,4-dioxane/H_2O (10/1, 2.0 mL), 60 °C.

Kinetic Study



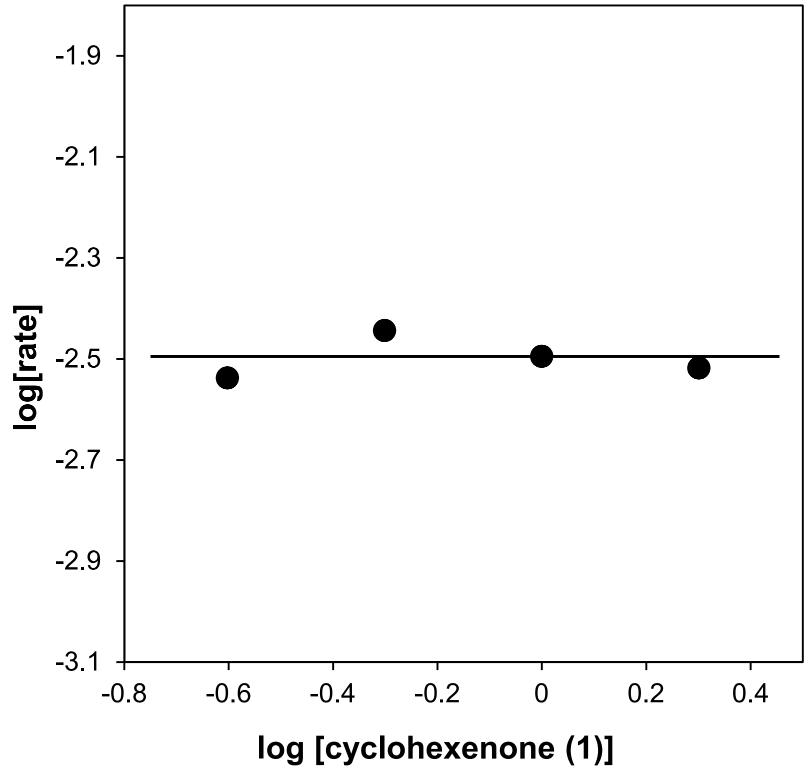


Figure S8. Plot of log[rate] vs. log[cyclohexenone] for the reaction of **1** with **2**. Reaction conditions: cyclohexenone (**1**), phenylboronic acid (**2**) (1.5 mmol), SiO_2/diamine/Rh-a (Rh: 6.0 μmol), 1,4-dioxane/H_2O (10/1, 2.0 mL), 60 °C.

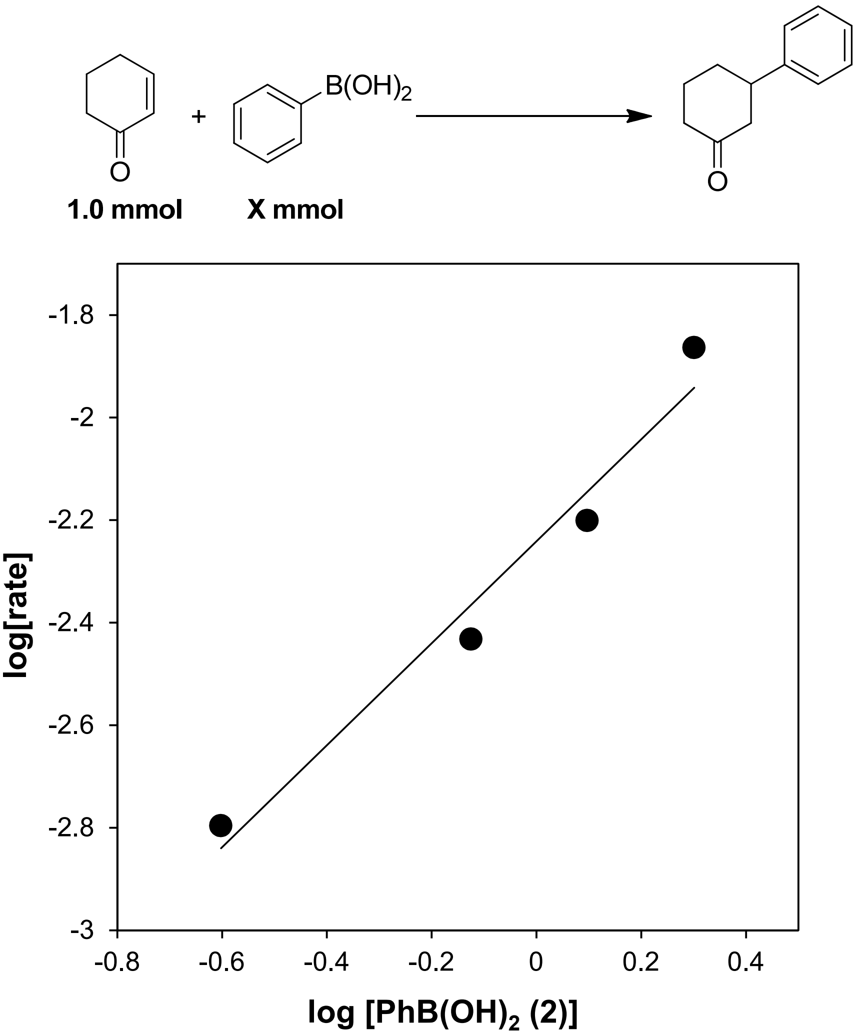


Figure S9. Plot of log[rate] vs. log[PhB(OH)$_2$] for the reaction of **1** with **2**. Reaction conditions: cyclohexenone (**1**) (1.0 mmol), phenylboronic acid (**2**), SiO$_2$/diamine/Rh-a (Rh: 6.0 μmol), 1,4-dioxane/H$_2$O (10/1, 2.0 mL), 60 °C. Slope (log[rate]/log[PhB(OH)$_2$]) = 0.995 (r^2 = 0.97).

^{13}C CP/MAS NMR of SiO_2/diamine/Rh/Me

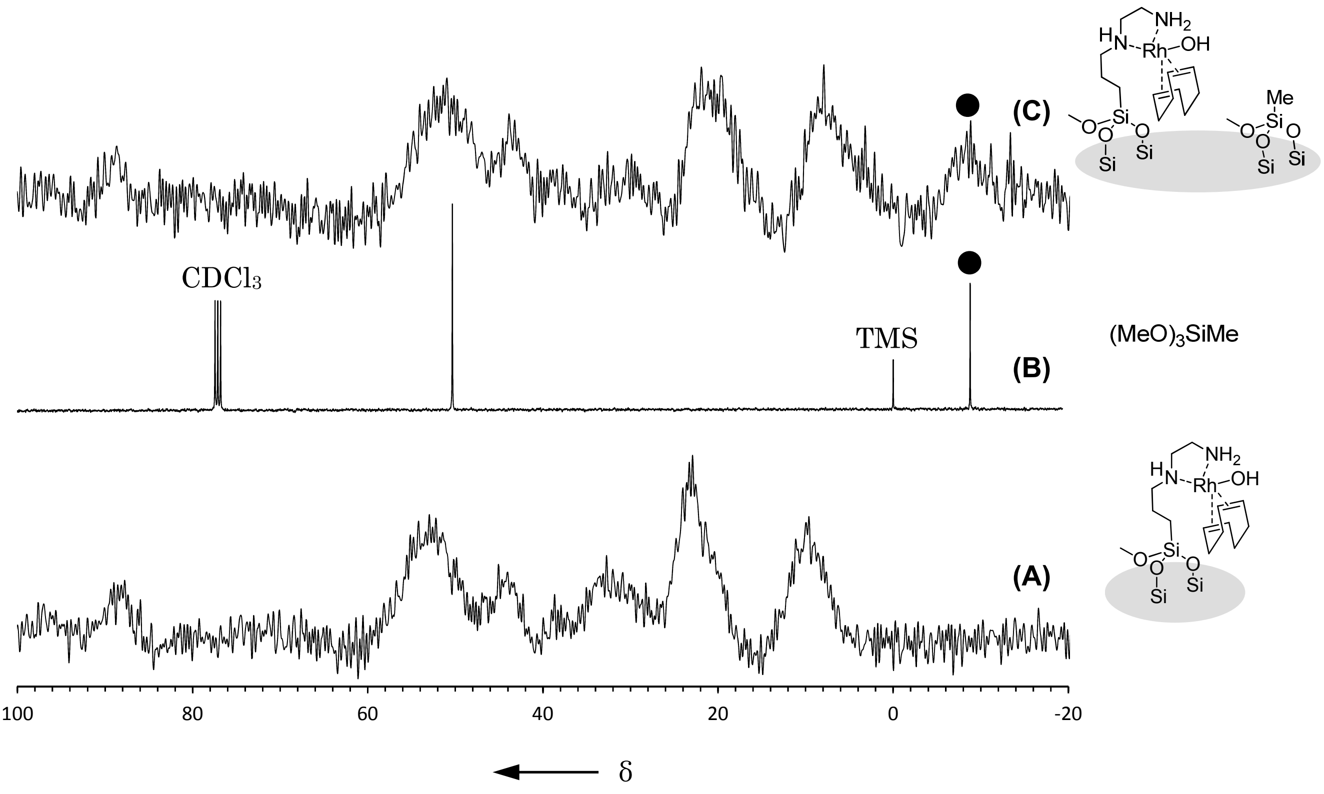


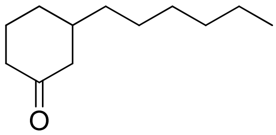
Figure S10. (A) Solid-state ^{13}C CP/MAS NMR spectrum of SiO_2/diamine/Rh-a, (B) liquid-state ^{13}C NMR spectrum of trimethoxymethylsilane, and (C) solid-state ^{13}C CP/MAS NMR spectrum of SiO_2/diamine/Rh/Me.

^{1}H and ^{13}C NMR spectra of products

Table 7

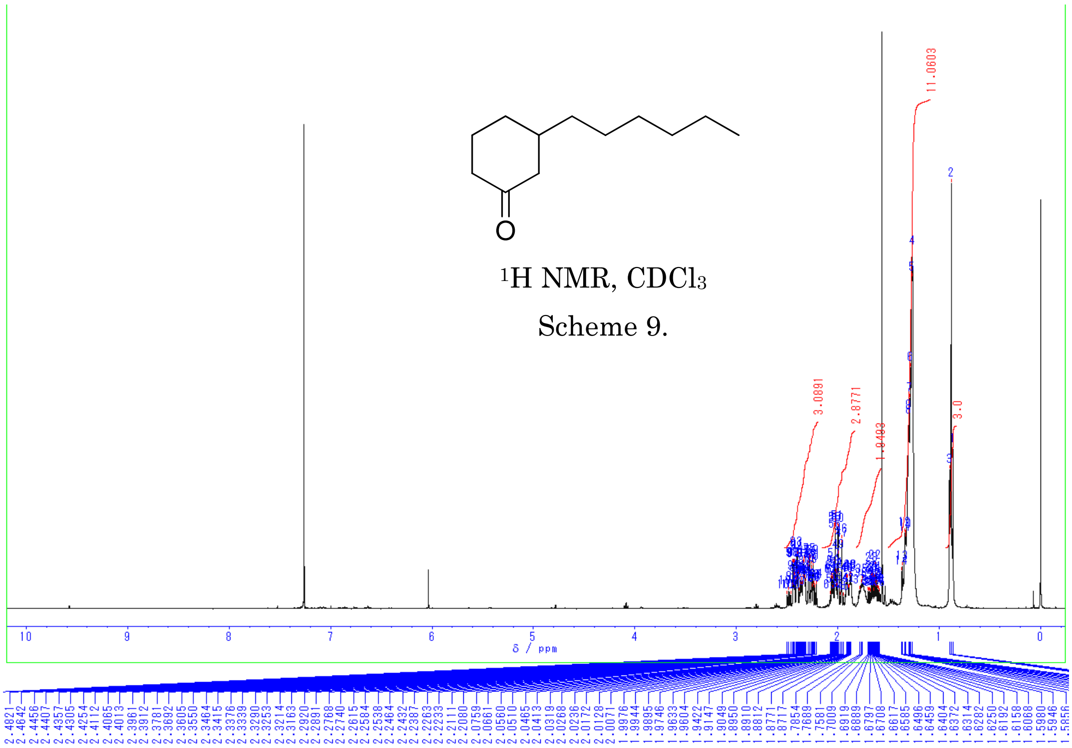
The ^{1}H NMR chemical shifts of the products (Table 7, entries 1–3, 5 and 6) corresponded with the literature values.[3] ^{1}H NMR chemical shift of products (Table 7, entry 4) corresponded with the literature.[4]

Scheme 9



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.93 (t, 3H), 1.19-1.50 (m, 11H), 1.58-1.71 (m, 1H), 1.71-1.82 (m, 1H), 1.85-1.93 (m, 1H), 1.94-2.12 (m, 2H), 2.19-2.30 (m, 1H), 2.30-2.39 (m, 1H), 2.39-2.51 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 25.5, 26.8, 29.6, 31.6, 32.0, 36.8, 39.3, 41.7, 48.5, 212.2. These spectra were in agreement with the literature.[5]


1H NMR, CDCl3
Scheme 9.
O
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2.8771
1.8493
11.0603
3.0
10
9
8
7
6
5
4
3
2
1
0
δ / ppm
2.4821
2.4642
2.4456
2.4407
2.4357
2.4305
2.4254
2.4112
2.4065
2.4013
2.3961
2.3912
2.3781
2.3692
2.3605
2.3550
2.3464
2.3415
2.3376
2.3339
2.3290
2.3253
2.3214
2.3163
2.2920
2.2891
2.2768
2.2740
2.2615
2.2584
2.2538
2.2464
2.2432
2.2387
2.2263
2.2233
2.2111
2.2080
2.0759
2.0661
2.0560
2.0510
2.0465
2.0413
2.0319
2.0268
2.0236
2.0172
2.0128
2.0071
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1.9746
1.9633
1.9604
1.9422
1.9147
1.9049
1.8950
1.8910
1.8812
1.8771
1.8717
1.7854
1.7689
1.7581
1.7009
1.6919
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1.6797
1.6708
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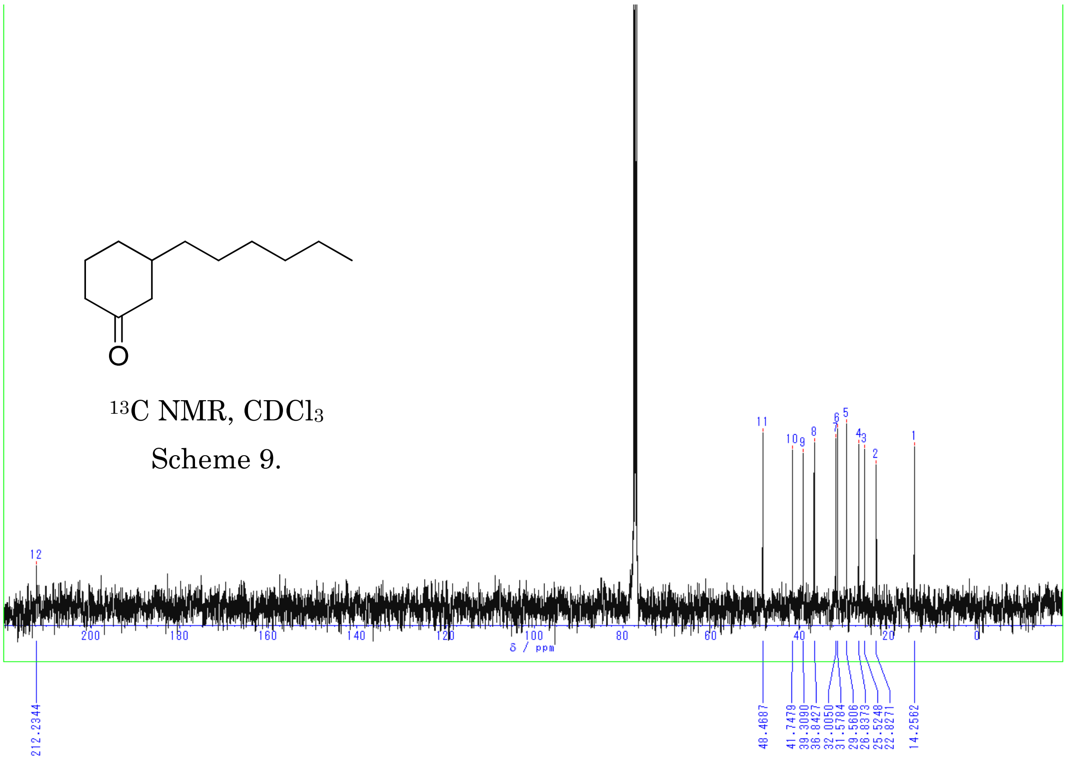
O
13C NMR, CDCl3
Scheme 9.
12
11
10
9
8
7
6
5
4
3
2
1
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
212.2344
48.4687
41.7479
39.3090
36.8427
32.0050
31.5784
29.5606
26.8373
25.5248
22.8271
14.2562

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