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Supporting Information

Selective hydrogenation of arenes to cyclohexanes in water catalyzed by chitin-supported ruthenium nanoparticles

Yuna Morioka,^{*a*} Aki Matsuoka,^{*a*} Kellie Binder,^{*b*} Benjamin R. Knappett,^{*b*} Andrew E. H. Wheatley*^{*b*} and Hiroshi Naka*^{*a*}

^{*a*} Department of Chemistry and Research Center for Materials Science, Nagoya University, Chikusa, Nagoya 464-8602, Japan

^b Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

h_naka@nagoya-u.jp; aehw2@cam.ac.uk

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1. General Comments

GC-MS analyses were performed on Agilent 6850 series network GC system and Agilent 5975 series Mass Selective Detector (EI) for reaction mixture analysis [column: HP-5MS capillary column (l = 30 m, d = 0.25 mm, film thickness = 0.25 µm); carrier gas: He], or Agilent 6890 series network GC system and Agilent 5973 series Mass Selective Detector (EI) for chirality analysis [column: CYCLOSIL-B capillary column (l = 30 m, d = 0.25 mm, film thickness = 0.25 µm); carrier gas: He]. ¹H and ¹³C NMR spectra were recorded on a JEOL ECA-600 (600 MHz for ¹H, 150 MHz for ¹³C) or a JEOL ECA-500 (500 MHz for ¹H, 125 MHz for ¹³C) at 25 °C. Chemical shifts are reported as δ in ppm and are internally referenced to tetramethylsilane (TMS, 0.00 ppm for ¹H), HOD (4.79 ppm for ¹H), CDCl₃ (77.2 ppm for ¹³C), or dioxane (67.2 ppm in D₂O for ¹³C). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, bs = respectively.broad singlet, bd = broad doublet, bt = broad triplet, dd = double doublet, dt = double triplet, dq =double quartet, tt = triple triplet, tq = triple quartet, ddd = double double doublet, dddd = double double double double double double double triplet, and m = multiplet. High-resolution mass spectra (HRMS) were obtained from JMS (FAB or EI, JEOL) and micrOTOF-QII (ESI, Bruker). Infrared spectroscopy (IR) spectra were recorded on FT-IR6100 (JASCO). Inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) was carried out with Vista Pro (Agilent) using yttrium as an internal standard after digestion of samples (10 mg) in concd HNO₃ (2 mL) at 150 °C for 12 h. Optical rotation values were recorded on Polarimeter P-1010-GT (JASCO). Melting points were recorded on Opti-Melt automated melting point system (Stanford Research Systems). NMR, HRMS, IR, ICP-AES, optical rotation analyses were carried out at Chemical Instrumental Center, Research Center for Materials Science, Nagoya University. HRTEM and EDX analyses (see section 7) were carried out at the Department of Chemistry, University of Cambridge.

2. Materials

RuCl₃•3H₂O was purchased from Furuya Metal Co., Ltd. Chitin, sodium borohydride, ruthenium on carbon, benzyl glycidyl ether (**1a**), *n*-octane, benzhydrol (**1e**), D-(–)-mandelic acid [(*R*)-**1f**], (*S*)-1-phenylethylamine [(*S*)-**1j**], L-phenylglycine [(*S*)-**1k**], phenyl glycidyl ether (**1o**), benzamide (**1p**), 3-phenylpropionic acid (**1t**), *N*,*N*-dimethyl-4-aminopyridine (DMAP), and acetyl chloride were purchased from TCI. Dioxane, ruthenium oxide, palladium on carbon, sodium hydroxide, (*S*)-1-phenylethanol [(*S*)-**1c**], 2-phenyl-2-propanol (**1d**), *N*-benzylacetamide (**1h**), phenol (**1m**), acetanilide (**1q**), pyridine (**1v**), yttrium standard solution [Y(NO₃)₃ in HNO₃ aq, 1.00 mg Y per mL; 1000 ppm, for ICP-AES], ethyl acetate, *n*-hexane, methanol, diethyl ether, chloroform, and concd HNO₃ were purchased from Wako Chemicals. Cellulose, chitosan, activated carbon, ruthenium on alumina, rhodium on carbon, benzyl alcohol (**1b**), benzylamine (**1i**), L-phenylalanine [(*S*)-**1**], trimethylsilyldiazomethane solution, and acetic anhydride were purchased

from Sigma-Aldrich. Mesitylene, hydrochloric acid, toluene (**3a**), anisole (**1n**), benzanilide (**1r**), aniline (**1u**), triethylamine, dehydrated methanol, dehydrated *n*-hexane, dehydrated dichloromethane, dehydrated ether, sodium sulfate, and silica gel (40–100 μ m) were purchased from Kanto Chemicals. Benzoic acid (**1s**) was purchased from Nacalai Tesque. *N*-Benzylbenzamide (**1h**) and ruthenium standard solution (RuCl₃ in HCl aq, 1.00 mg Ru per mL; 1000 ppm, for ICP-AES) were purchased from Acros. γ -Al₂O₃ was purchased from Strem. Chloroform-*d* and deuterium oxide were purchased from CIL. Gases [hydrogen (99.99%), argon (99.99%), nitrogen (99.99%)] were purchased from Alphasystem. Water was purified using Demiace DX-07 (cartridge type deionizer, KURITA Water Industries LTD.). **1a**, **1b**, **1n**, and triethylamine were used after purification by known methods,¹ and other materials were used directly.

3. Preparation of Ruthenium Catalysts

A typical procedure: Ru (0.8 wt %)/chitin (0.008 mmol Ru): Ru/chitin was prepared by following the reported method.² To a 300 mL round-bottom flask, RuCl₃•3H₂O (71.6 mg, 0.30 mmol Ru), H₂O (50 mL) and chitin (2.97 g) were added. The mixture was heated at 50 °C for 30 min, and concentrated using a rotary evaporator at 50 °C (25 mmHg). The solid was dried at 50 °C in vacuo overnight to afford the catalyst precursor as dark green solids (2.95 g). To a 30 mL glass vessel with a magnetic bar equipped with a rubber septum, the catalyst precursor (101 mg) and deaerated H₂O (5.0 mL) were added under a N₂ atmosphere. Under vigorous stirring, a solution [500 µL; a mixture of NaBH₄ (30.6 mg, 0.80 mmol) and deaerated H₂O (4.0 mL)] was introduced dropwise to the vessel. The mixture was stirred at 30 °C for 3.5 h. The liquid phase was separated by centrifugation (3500 rpm, 5 min) and replaced with H₂O (5.0 mL) via syringe. After the mixture was stirred at 30 °C overnight, the solid was washed with water (2 times) and dried in vacuo at rt for 3 h to afford Ru/chitin as a grey solid (100 mg). This was directly used for arene hydrogenation. The ruthenium content was 0.0083 ± 0.0001 mmol (0.83 ± 0.01 wt %) [determined by ICP-AES, after digestion of Ru (0.8 wt %)/chitin (10.02 mg) using conced HNO₃ aq (2 mL) at 150 °C for 12 h].

¹ Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th edition, Elsevier: Sydney, 2003.

² Matsuoka, A.; Isogawa, T.; Morioka, Y.; Knappett, B. R.; Wheatley, A. E. H.; Saito, S.; Naka, H. *RSC Adv.* **2015**, *5*, 12152–12160.

Table S1. Preparation of Ruthenium Catalysts

Catalyst	Reagents and amounts	Ru content			
Ru (0.9 wt %)/cellulose	Immobilization: RuCl ₃ •3H ₂ O (11.9 mg, 0.05 mmol Ru),	0.86 ± 0.01 wt %			
	cellulose (495 mg); Reduction: Precursor (101 mg), NaBH ₄				
	aq [500 μL; NaBH ₄ (7.6 mg, 0.2 mmol) in 1.0 mL H ₂ O]				
Ru (0.8 wt %)/chitosan	Immobilization: RuCl ₃ •3H ₂ O (11.9 mg, 0.05 mmol Ru),	0.78 ± 0.02 wt %			
	chitosan (495 mg); Reduction: Precursor (101 mg), NaBH ₄				
	aq [500 $\mu L;$ NaBH4 (7.6 mg, 0.2 mmol) in 1.0 mL H2O]				
Ru (1.0 wt %)/γ-Al ₂ O ₃	Immobilization: RuCl ₃ •3H ₂ O (11.9 mg, 0.05 mmol Ru),	0.98 ± 0.02 wt %			
	γ -Al ₂ O ₃ (495 mg); Reduction: Precursor (101 mg), NaBH ₄				
	aq [500 $\mu L;$ NaBH4 (7.6 mg, 0.2 mmol) in 1.0 mL H2O]				
Ru (0.9 wt %)/C	Immobilization: RuCl ₃ •3H ₂ O (11.9 mg, 0.05 mmol Ru),	0.92 ± 0.02 wt %			
	carbon (495 mg); Reduction: Precursor (101 mg), NaBH ₄ aq				
	[500 µL; NaBH ₄ (7.6 mg, 0.2 mmol) in 1.0 mL H ₂ O]				

4. Hydrogenation of Arenes 1 to Cyclohexanes 2

A representative procedure: hydrogenation of 1a (Table 1, entry 1; Table 2, entry 1)



As per the above-mentioned typical procedure, Ru/chitin (0.008 mmol Ru) was prepared in a 30 mL glass vessel equipped with a rubber septum and a magnetic stirring bar. To the vessel were added 1a (164 mg, 1.0 mmol) and deaerated H₂O (5.0 mL). After the septum was removed, the glass vessel was placed into a pre-dried stainless autoclave under Ar flow, and the internal atmosphere was replaced with H₂ for three times. The mixture was stirred at 50 °C for 1.5 h under H₂ (2 MPa). After the autoclave was cooled down in an ice bath and the pressure was carefully released, ethyl acetate (2 mL) was mixed with the reaction mixture. The organic layer was separated after centrifugation (3500 rpm, 10 min). The product was extracted from the residual mixture of aqueous layer and Ru/chitin by repeating these processes (ethyl acetate, 3×2 mL). The combined organic layer was analyzed by GC-MS using *n*-octane as an internal standard (chromatographic elution: isothermal at 70 °C for 2 min, 70–230 °C at a rate of 20 °C min⁻¹), dried with Na₂SO₄, and concentrated in vacuo. ¹H NMR analysis of this crude mixture using mesitylene as an internal standard indicated the formation of 2a in 98% yield. The yield was determined based on the signal at δ 3.38 ppm. This result was reproducible (¹H NMR yields of **2a** in separate runs: 97, 95 and 97%). The product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 5:1) to afford **2a** as a colorless oil (143 mg, 84% yield). Analytical data for 2a: ¹H NMR (600 MHz, CDCl₃) δ 0.93 (dddd, J = 3.4,

11.7, 11.7, 11.7 Hz, 2H), 1.12–1.28 (m, 3H), 1.56–1.63 (m, 1H), 1.66–1.77 (m, 5H), 2.61 (dd, J = 2.8, 5.5 Hz, 1H), 2.79 (dd, J = 4.5, 4.8 Hz, 1H), 3.12–3.15 (m, 1H), 3.27 (dd, J = 6.9, 8.9 Hz, 1H), 3.32 (dd, J = 6.5, 8.9 Hz, 1H), 3.38 (dd, J = 5.8, 11.7 Hz, 1H), 3.69 (dd, J = 3.4, 11.7 Hz, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 26.0, 26.7, 30.1, 38.2, 44.4, 51.1, 71.7, 77.6; HRMS (EI) calcd for [C₁₀H₁₈O₂](M) 170.1307, found 170.1302. The identity was checked by comparing with the literature data.³ Ru levels in the aqueous phase of the reaction mixture (4.2 ppm) and in purified **2a** [lower than the detection limit of the instrument (< 1 ppb)] were determined by ICP-AES.

Changes in conditions and the yields of other entries in Table 1

Entry 2: without catalyst; < 1% yield.

Entry 3: chitin (101 mg) was used as a catalyst; < 1% yield.

Entry 4: RuCl₃•3H₂O (2.1 mg, 0.008 mmol) was used as a catalyst; 75% yield.

Entry 5: RuO₂ (1.1 mg, 0.008 mmol) was used as a catalyst; < 1% yield.

Entry 6: Ru (0.9 wt %)/cellulose (98 mg, 0.008 mmol Ru) was used as a catalyst; 97% yield.

Entry 7: Ru (0.8 wt %)/chitosan (100 mg, 0.008 mmol Ru) was used as a catalyst; 41% yield.

Entry 8: Ru (1.0 wt %)/γ-Al₂O₃ (96 mg, 0.009 mmol Ru) was used as a catalyst; 36% yield.

Entry 9: Ru (0.9 wt %)/C (91 mg, 0.009 mmol Ru) was used as a catalyst; 43% yield.

Entry 10: Ru (5 wt %)/Al₂O₃ (16 mg, 0.008 mmol Ru) was used as a catalyst; 15% yield.

Entry 11: Rh (5 wt %)/Al₂O₃ (16 mg, 0.008 mmol Rh) was used as a catalyst; 92% yield.

Entry 12: Ru (5 wt %)/C (16 mg, 0.008 mmol Ru) was used as a catalyst; 87% yield.

Entry 13: Rh (5 wt %)/C (16 mg, 0.008 mmol Rh) was used as a catalyst; 24% yield.

Entry 14: Pd (10 wt %)/C (8.0 mg, 0.008 mmol Pd) was used as a catalyst; < 1% yield.

Enter	Catalvat	Additive ^b	Conv. of	Yield of	Combined yield of	Combined yield of
Entry	Catalyst		$1a(\%)^{c}$	2a (%) ^c	3a and 4a $(\%)^d$	5a and 6a (%) ^c
1	Rh/Al ₂ O ₃	HOCH ₂ CH ₂ OH	83	71	10	< 1
2	Ru/C	HOCH ₂ CH ₂ OH	98	85	7	5
3	Rh/C	HOCH ₂ CH ₂ OH	97	30	46	22
4	Rh/C	HOCH ₂ CH ₂ NH ₂	61	20	8	32
5	Rh/C	HOCH ₂ CH ₂ NHCOCH ₃	> 99	72	23	< 1

Table S2. Hydrogenation of 1a in the Presence of Additives^a

^{*a*}Conditions are identical to those in Table 1, entries 11, 12, and 13 unless otherwise noted. ^{*b*}0.50 mmol was added. ^{*c*}Determined by ¹H NMR using mesitylene as an internal standard. ^{*d*}Determined by GC-MS using *n*-octane as an internal standard.

³ Motoyama, Y.; Takasaki, M.; Yoon, S.-H.; Mochida, I.; Nagashima, H. Org. Lett. **2009**, *11*, 5042–5045.

Cyclohexylmethanol (2b, Table 2, entry 1)⁴



Substrate: benzyl alcohol (**1b**, 108 mg, 1.0 mmol). GC-MS analysis of the crude mixture using *n*-octane as an internal standard showed the formation of **2b** in 78% yield. The product was purified by Kugelrohr distillation (110 °C, 85 mmHg) to afford **2b** as a colorless oil (75.4 mg, 66% yield). Analytical data for **2b**: ¹H NMR (500 MHz, CDCl₃) δ 0.91 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 2H), 1.10–1.30 (m, 3H), 1.41–1.50 (m, 1H), 1.67 (bd, *J* = 10.9 Hz, 1H), 1.69–1.78 (m, 4H), 3.36–3.41 (m, 2H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 25.9, 26.6, 29.6, 40.4, 68.3; HRMS (FAB) calcd for [C₇H₁₅O⁺](MH⁺) 115.1117, found 115.1125.

(S)-1-Cyclohexylethanol [(S)-2c, Table 2, entry 2]⁴



Substrate: (*S*)-1-phenylethanol [(*S*)-1c, 112 mg, 1.0 mmol]. The product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 5:1) to afford (*S*)-2c as a colorless oil (118 mg, 92%). Analytical data for (*S*)-2c: ¹H NMR (500 MHz, CDCl₃) δ 0.96 (dddd, *J* = 3.4, 12.0, 12.0, 12.6 Hz, 1H), 1.01 (dddd, *J* = 3.4, 12.0, 12.0, 12.6 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.17–1.31 (m, 3H), 1.39 (bs, 1H), 1.67 (bd, *J* = 12.6 Hz, 2H), 1.73–1.79 (m, 2H), 1.85 (bd, *J* = 12.6 Hz, 1H), 3.55 (quin, *J* = 6.3 Hz, 1H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 20.5, 26.3, 26.4, 26.6, 28.5, 28.9, 45.3, 72.4; HRMS (FAB) calcd for [C₈H₁₇O⁺](MH⁺) 129.1274, found 129.1288; [α]²¹_D +2.52 (c 1.1, CHCl₃) [lit.⁵ [α]²¹_D +2.07 (c 1.11, CHCl₃, 87% *ee*)]. The absolute configuration *S* was deduced from the optical rotation of the product. The *S:R* ratio of 94:6 was determined by the chiral GC analysis (section 5).

2-Cyclohexylpropan-2-ol (2d, Table 2, entry 3)



Substrate: 2-phenyl-2-propanol (1d, 136 mg, 1.0 mmol). The product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 5:1) to afford 2d as a colorless oil (125 mg, 88% yield). Analytical data for 2d: ¹H NMR (500 MHz, CDCl₃) δ 0.99 (dddd, *J* = 3.4, 12.6, 12.6, 12.6, 12.6 Hz, 2H), 1.16 (s, 6H), 1.18–1.30 (m, 3H), 1.59 (bs, 1H), 1.67 (bd, *J* = 12.6 Hz, 1H), 1.76–1.84 (m, 4H);

⁴ Kobayashi, S.; Kawamoto, T.; Uehara, S.; Fukuyama, T.; Ryu, I. Org. Lett. **2010**, *12*, 1548–1551.

⁵ Matharu, D. S.; Morris, A. J.; Clarkson, G. J.; Wills, M. Chem. Commun. 2006, 3232–3234.

¹³C{¹H} NMR (125 MHz, CDCl₃) δ 26.6, 26.9, 27.1, 27.7, 49.4, 73.1; HRMS (FAB) calcd for [C₉H₁₉O⁺](MH⁺) 143.1430, found 143.1424.

Dicyclohexylmethanol (2e, Table 2, entry 4)



Substrate: benzhydrol (**1e**, 184 mg, 1.0 mmol). The product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 20:1) to afford **2e** as a white powder (147 mg, 75%). Analytical data for **2e**: Mp 64–65 °C (lit.⁶ 63 °C); ¹H NMR (500 MHz, CDCl₃) δ 1.01 (dddd, *J* = 3.4, 12.0, 12.0, 12.0 Hz, 2H), 1.08–1.31 (m, 8H), 1.39–1.47 (m, 2H), 1.56 (bd, *J* = 12.6 Hz, 2H), 1.66 (bd, *J* = 13.8 Hz, 2H), 1.73–1.78 (m, 4H), 1.82 (bd, *J* = 13.2 Hz, 2H), 3.05 (q, *J* = 5.7 Hz, 1H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 26.3, 26.6, 26.7, 27.5, 30.1, 40.0, 80.6; HRMS (FAB) calcd for [C₁₃H₂₅O⁺](MH⁺) 197.1900, found 197.1916.

(R)-Hexahydromandelic acid [(R)-2f, Table 2, entry 5]



In a 10 mL flask with a magnetic stirring bar equipped with a rubber septum, D-(-)-mandelic acid sodium salt $[(R)-1f_{Na}]$ was prepared by mixing the corresponding D-(-)-mandelic acid [(R)-1f, 183]mg, 1.2 mmol] and NaOH aq (0.20 M, 6.0 mL, 1.2 mmol) at rt for 1 h under a N₂ atmosphere. As per the above-mentioned representative procedure, hydrogenation was conducted using (R)-1 f_{Na} (0.20 M aq, 5.0 mL, 1.0 mmol) at 100 °C for 3 h to give (R)-2f_{Na}. The catalyst was removed by filtration and washed with H₂O. To the filtrate was added HCl aq (0.5 M, 10 mL). The mixture was stirred at rt for 1 h and diluted by ether (10 mL). The product was extracted with ether (3×10 mL). The combined organic layer was dried with Na₂SO₄ and concentrated in vacuo. The product was purified by silica gel column chromatography (n-hexane/ethyl acetate/acetic acid 20:10:1) to afford (*R*)-2f as a white powder (130 mg, 82%). Analytical data for (*R*)-2f: Mp 121–122 °C (lit.⁷ 129 °C); ¹H NMR (600 MHz, CDCl₃) δ 1.15 (dddd, J = 3.4, 12.4, 12.4, 12.4 Hz, 1H), 1.22–1.36 (m, 4H), 1.53 (bd, J = 5.5 Hz, 1H), 1.68 (bd, J = 11.7 Hz, 1H), 1.73 (bd, J = 10.3 Hz, 1H), 1.77–1.85 (m, 3H), 4.12 (d, J = 3.4 Hz, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 26.1, 26.4, 29.3, 74.8, 179.3; HRMS (FAB) calcd for $[C_8H_{15}O_3^+](MH^+)$ 159.1016, found 159.0981; $[\alpha]^{21}_D$ –19.9 (c 1.0, AcOH) [lit.⁷] $[\alpha]^{23}_{D}$ +23.5 (c 1.0, AcOH, for S isomer)]. The absolute configuration R was deduced from the optical rotation of the product. The S:R ratio of 1:99 was determined by the chiral GC analysis

⁶ Brown, H. C.; Imai, T.; Perumal, P. T.; Singaram, B. J. Org. Chem. 1985, 50, 4032-4036.

⁷ Riley, D. P.; Shumate, R. E. J. Org. Chem. **1980**, 45, 5187–5193.

(section 5).

N-(Cyclohexylmethyl)acetamide (2g, Table 2, entry 6)



Substrate: *N*-benzylacetamide (**1g**, 149 mg, 1.0 mmol). The product was extracted with chloroform (5 × 2 mL) and recrystallized from chloroform/*n*-hexane to afford **2g** as colorless clear needles (144 mg, 93%). Analytical data for **2g**: Mp 46 °C (lit.⁸ 44.5–46 °C); ¹H NMR (600 MHz, CDCl₃) δ 0.92 (dddd, *J* = 2.8, 11.3, 11.3, 11.7 Hz, 2H), 1.11–1.26 (m, 3H), 1.41–1.49 (m, 1H), 1.66 (bd, *J* = 11.7 Hz, 1H), 1.72 (bd, *J* = 11.7 Hz, 4H), 1.98 (s, 3H), 3.08 (dd, *J* = 6.8, 6.9 Hz, 2H), 5.81 (bs, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 23.2, 25.7, 25.8, 26.4, 30.6, 30.9, 37.9, 45.9, 170.3; HRMS (FAB) calcd for [C₉H₁₇NO](M) 155.1310, found 155.1326.

N-(Cyclohexylmethyl)cyclohexylamide (2h, Table 2, entry 7)



Substrate: *N*-benzylbenzamide (**1h**, 211 mg, 1.0 mmol). The product was extracted with chloroform (5 × 2 mL) and recrystallized from chloroform/*n*-hexane to afford **2h** as white needles (220 mg, 98%). Analytical data for **2h**: Mp 129 °C (lit.⁹ 131–132 °C); ¹H NMR (600 MHz, CDCl₃) δ 0.92 (dddd, *J* = 2.8, 11.7, 11.7, 11.7 Hz, 2H), 1.10–1.30 (m, 6H), 1.39–1.48 (m, 3H), 1.63–1.74 (m, 6H), 1.79 (bd, *J* = 12.5 Hz, 2H), 1.86 (bd, *J* = 13.2 Hz, 2H), 2.03–2.09 (m, 1H), 3.08 (dd, *J* = 5.9, 6.6 Hz, 2H), 5.46 (bs, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 25.9, 26.0, 26.6, 30.0, 38.2, 45.6, 45.9, 176.1; HRMS (FAB) calcd for [C₁₄H₂₅NO](M) 223.1936, found 223.1941.

Cyclohexylmethylamine hydrochloride (2i•HCl, Table 2, entry 8)



In a 10 mL flask with a magnetic stirring bar equipped with rubber septum, benzylamine hydrochloride (1i•HCl) was prepared by mixing benzylamine (1i, 127 mg, 1.2 mmol) and HCl aq (0.20 M, 6.0 mL, 1.2 mmol) at rt for 1 h under a N_2 atmosphere. As per the above-mentioned representative procedure, hydrogenation was conducted using 1i•HCl (0.20 M aq, 5.0 mL, 1.0

⁸ Baumgarten, H. E.; Bower, F. A.; Setterquist, R. A.; Allen, R. E. J. Am. Chem. Soc. **1958**, 80, 4588–4593.

⁹ Striegler, A.; Weber, J. J. Fuer Praktische Chemie (Leipzig), 1965, 29, 281–295.

mmol) at 100 °C for 3 h. The catalyst was removed by filtration and washed with H₂O. The filtrate was concentrated in vacuo to afford afford **2i**•HCl as white powders (138 mg, 92%). Analytical data for **2i**•HCl: Mp 236–246 °C (lit.¹⁰ 254–257 °C); ¹H NMR (500 MHz, CDCl₃) δ 1.01 (dddd, J = 3.7, 11.9, 11.9, 11.9 Hz, 2H), 1.17 (dddt, J = 3.7, 12.8, 12.8, 12.8 Hz, 1H), 1.29 (dddt, J = 3.7, 12.8, 12.8 Hz, 2H), 1.68 (dt, J = 3.7, 12.8 Hz, 1H), 1.72–1.79 (m, 3H), 1.86 (bd, J = 12.2 Hz, 2H), 2.83 (d, J = 7.3 Hz, 2H), 8.30 (bs, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 25.5, 26.1, 30.1, 36.1, 45.8; HRMS (FAB) calcd for [C₇H₁₆N⁺](M–Cl⁻) 114.1277, found 114.1290.

(S)-1-Cyclohexylethylamine hydrochloride [(S)-2j•HCl, Table 2, entry 9]



The procedure for **2i**•HCl was applied. After (*S*)-1-phenylethylamine hydrochloride [(*S*)-**1j**•HCl] was prepared using (*S*)-1-phenylethylamine [(*S*)-**1j**, 128 mg, 1.2 mmol] and HCl aq (0.2 M, 6.0 mL), (*S*)-**1j**•HCl (0.20 M aq, 5.0 mL, 1.0 mmol) was hydrogenated to afford (*S*)-**2j**•HCl as white powders (150 mg, 92%). Analytical data for (*S*)-**2j**•HCl: Mp 232–234 °C (lit.¹¹ 239–240 °C); ¹H NMR (500 MHz, CDCl₃) δ 1.09 (dddd, *J* = 3.1, 12.5, 12.5, 12.5 Hz, 2H), 1.16 (dddt, *J* = 3.1, 12.8, 12.8, 12.8 Hz, 1H), 1.21–1.32 (m, 2H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.58–1.65 (m, 1H), 1.67 (bd, *J* = 12.8 Hz, 1H), 1.75–1.83 (m, 3H), 1.89 (bd, *J* = 12.8 Hz, 1H), 3.13 (quin, *J* = 6.7 Hz, 1H), 8.32 (bs, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 16.2, 25.9, 26.1, 28.4, 29.2, 41.5, 53.2; HRMS (FAB) calcd for [C₈H₁₈N⁺](M–CΓ) 128.1434, found 128.1444; [α]²¹_D +5.9 (c 1.0, CH₂Cl₂) [lit.¹² [α]²⁰_D –5.1 (c 1.0, CH₂Cl₂, 73% *ee* for *R* isomer)]. The absolute configuration *S* was deduced from the optical rotation of the product. The *S:R* ratio of 96:4 was determined by the chiral GC analysis of the product (section 5).

Cyclohexylglycine hydrochloride [2k•HCl, Table 2, entry 10]



In a 10 mL flask with a magnetic stirring bar equipped with rubber septum, L-phenylglycine sodium salt $[(S)-1\mathbf{k}_{Na}]$ was prepared by mixing L-phenylglycine $[(S)-1\mathbf{k}, 152 \text{ mg}, 1.00 \text{ mmol}]$ and NaOH (0.10 M aq, 10 mL, 1.0 mmol) under a N₂ atmosphere. As per the above-mentioned representative procedure, hydrogenation was conducted with $(S)-1\mathbf{k}_{Na}$ (0.10 M aq, 5.0 mL, 0.50 mmol) and Ru (0.8 wt %)/chitin (50 mg, 0.8 mol % Ru) at 100 °C for 3 h to give $2\mathbf{k}_{Na}$. The catalyst was removed by

¹⁰ Katritzky, A. R.; Jiang, J.; Urogdi, L. *Tetrahedron Lett.* **1989**, *30*, 3303–3306.

¹¹ Freifelder, M.; Stone, G. J. Am. Chem. Soc. **1958**, 80, 5270–5272.

¹² Hou, G.; Gosselin, F.; Li, W.; McWilliams, J. C.; Sun, Y.; Weisel, M.; O'Shea, P. D.; Chen, C.-y.; Davies, I. W.; Zhang, X. J. Am. Chem. Soc. 2009, 131, 9882–9883.

filtration and washed with H₂O and THF. To the filtrate was added HCl (0.5 M aq, 10 mL). The mixture was stirred at rt for 1 h and concentrated in vacuo to afford **2k**•HCl as off-white powders (87.2 mg, 90%). Analytical data for **2k**•HCl: Mp 234–240 °C (lit.¹³ 255 °C); ¹H NMR (600 MHz, D₂O) δ 1.08–1.23 (m, 3H), 1.28 (ttt, *J* = 3.4, 13.1, 13.1 Hz, 2H), 1.65 (bt, *J* = 15.1 Hz, 2H), 1.72–1.82 (m, 3H), 1.97 (tq, *J* = 3.4, 11.7 Hz, 1H), 3.80 (d, *J* = 4.8 Hz, 1H); ¹³C{¹H} NMR (150 MHz, D₂O) δ 25.9, 26.1, 28.1, 29.1, 39.3, 59.3, 173.3; HRMS (FAB) calcd for [C₈H₁₆NO₂⁺](M–Cl⁻) 158.1176, found 158.1203; [α]²¹_D+1.43 (c 0.5, 0.1 M HCl aq) [lit.¹³ [α]²³_D+23.5 (c 0.5, 0.1 M HCl aq)].

Cyclohexylalanine hydrochloride (21•HCl, Table 2, entry 11)



The procedure for **21**•HCl was applied. After L-phenylalanine sodium salt [(*S*)-**11**_{Na}] was prepared using L-phenylalanine [(*S*)-**11**, 165 mg, 1.00 mmol] and NaOH (0.10 M aq, 10 mL, 1.0 mmol), (*S*)-**11**_{Na} (0.10 M aq, 0.50 mmol) was hydrogenated and treated with HCl (0.5 M aq, 10 mL) to afford **21**•HCl as off-white powders (94.5 mg, 91%). Analytical data for **21**•HCl: Mp 255–257 °C (lit.¹⁴ 298–300 °C); ¹H NMR (600 MHz, D₂O) δ 0.92–1.02 (m, 2H), 1.14–1.29 (m, 3H), 1.38–1.45 (m, 1H), 1.63 (d, *J* = 12.4 Hz, 1H), 1.68–1.74 (m, 5H), 1.84 (ddd, *J* = 5.8, 8.3, 14.3 Hz, 1H), 3.99 (dd, *J* = 6.2, 8.3 Hz, 1H); ¹³C{¹H} NMR (150 MHz, D₂O) δ 26.0, 26.2, 26.4, 32.4, 33.4, 33.8, 38.3, 52.1, 174.4; HRMS (FAB) calcd for [C₉H₁₈NO₂⁺](M–Cl⁻) 172.1332, found 172.1335; [α]²¹_D+0.02 (c 0.5, 0.1 M HCl aq) [lit.¹⁴ [α]²³_D+10 (c 0.5, 0.1 M HCl aq)].

¹³ Wang, M.-X.; Lin, S.-J. J. Org. Chem. 2002, 67, 6542–6545.

¹⁴ Ager, D. J.; Prakash, I. Org. Process Res. Dev. 2003, 7, 164–167.

Ent	Substrate (3)		1000000000000000000000000000000000000	t	$\frac{\text{Conv.}}{\text{Conv.}}$	Product (4)		Yield
<u>ry</u> 1		3a	<u>(°C)</u> 50	(h) 1.5	<u>(%)</u> ⁶ > 99		4a	(%) ^{0,c} > 99
2	ОН	1m	50	2	> 99	ОН	2m	$[72^{a}]$ 95 $[74^{d}]$
3	OCH3	1n	50	3	98	OCH3	2n	94 [75 ^d]
4		10	50	3	> 99		20	92 [88]
5	NH ₂	1p	100	3	98	NH ₂	2p	98 [96]
6	H N O	1q	100	3	> 99		2q	> 99 [96]
7	N N N N N N N N N N N N N N N N N N N	1r	100	5	97	NH NH	2r	86 [80]
	Ŷ					N H H	2ra	12
8	ONa	1s _{Na}	100	3	> 99	ONa	2s _{Na}	99 [90 ^e]
9	ONa	1t _{Na}	100	3	71	ONa	$2t_{Na}$	68 [65 ^e]
10	NH2+HCI	1u•HCl	100	3	86	NH ₂ •HCI	2u•HCl	81 [80]
11	N•HCI	1v•HCl	100	3	> 99	NH•HCI	2v•HCl	98 [95]

 Table S3. Hydrogenation of Aromatic Compounds^a

^{*a*}Conditions: see Table 2. ^{*b*}Determined by ¹H NMR using mesitylene as an internal standard. ^{*c*}Isolated yield in parentheses. ^{*d*}Low yield due to volatile nature of product. ^{*e*}Yield of carboxylic acid **2s** or **2t** after the addition of HCl aq.



Methylcyclohexane (4a, Table S3, entry 1)



Substrate: toluene (**3a**, 92.1 mg, 1.0 mmol). GC-MS analysis of this crude mixture using *n*-octane as an internal standard showed the formation of **4a** in 95% yield. The product was purified by Kugelrohr distillation (105 °C, 760 mmHg) to afford **4a** as a colorless oil (70.6 mg, 72% yield). The spectroscopic data were identical to that of a commercial sample purchased from Kanto Chemicals.

Cyclohexanol (2m, Table S3, entry 2)¹⁵



Substrate: phenol (1m, 94.2 mg, 1.0 mmol). GC-MS analysis of this crude mixture using *n*-octane as an internal standard showed the formation of 2m in 95% yield. The product was purified by Kugelrohr distillation (95 °C, 85 mmHg) to afford 2m as a colorless oil (74.1 mg, 74% yield).

Cyclohexyl methyl ether (2n, Table S3, entry 3)¹⁶



Substrate: anisole (1n, 108 mg, 1.0 mmol). GC-MS analysis of this crude mixture using *n*-octane as an internal standard showed the formation of 2n in 94% yield. The product was purified by Kugelrohr distillation (95 °C, 85 mmHg) to afford 2n as a colorless oil (85 mg, 75% yield).

Cyclohexyl glycidyl ether (20, Table S3, entry 4)³



Substrate: phenyl glycidyl ether (**10**, 150 mg, 1.0 mmol). The product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 4:1) to afford **20** as a colorless oil (138 mg, 95% yield).

¹⁵ Maegawa, T.; Akashi, A.; Yaguchi, K.; Iwasaki, Y.; Shigetsura, M.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2009**, *15*, 6953–6963.

¹⁶ Jedlinski, Z.; Misiolek, A.; Glowkowski, W.; Janeczev, H.; Wolinska, A. *Tetrahedron* **1990**, *46*, 3547–3558.

Cyclohexane carboxyamide (2p, Table S3, entry 5)¹⁷



Substrate: benzamide (1p, 121 mg, 1.0 mmol). The product was extracted with chloroform and recrystallized from chloroform/*n*-hexane to afford 2p as colorless plates (122 mg, 96%).

Cyclohexyl acetamide (2q, Table S3, entry 6)³



Substrate: acetanilide (1q, 135 mg, 1.0 mmol). The product was extracted with chloroform and recrystallized from chloroform/*n*-hexane to afford 2q as colorless needles (135 mg, 96%).

Cyclohexyl acetamide (2r, Table S3, entry 7)



Substrate: *N*-phenylbenzamide (**1r**, 197 mg, 1.0 mmol). The product was extracted with chloroform and recrystallized from chloroform/*n*-hexane to afford **2r** as colorless needles (168 mg, 80%). Analytical data for **2r**: ¹H NMR (600 MHz, CDCl₃) δ 1.06–1.29 (m, 6H), 1.32–1.44 (m, 4H), 1.61 (dt, *J* = 4.1, 13.1 Hz, 1H), 1.66–1.71 (m, 3H), 1.77–1.80 (m, 2H), 1.84 (dd, *J* = 2.1, 13.1 Hz, 2H), 1.90 (dd, *J* = 3.4, 12.4 Hz, 2H), 2.01 (tt, *J* = 3.4, 11.7 Hz, 1H), 3.72–3.79 (m, 1H), 5.30 (bs, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 25.0, 25.7, 25.9, 29.9, 33.4, 45.9, 47.8, 175.2; HRMS (FAB) calcd for [C₁₃H₂₃NO](M) 209.1780, found 209.1795.

Cyclohexane carboxylic acid (2s, Table S3, entry 8)²



The procedure for **2s** was applied. Substrate: sodium benzoate ($1s_{Na}$, 144 mg, 1.0 mmol). After the neutralization with HCl aq, the product was extracted with diethyl ether (3 × 10 mL). The combined organic layer was dried with Na₂SO₄ and concentrated in vacuo to give **2s** as a colorless oil (115 mg, 90%).

¹⁷ Gowda, R. R.; Chakraborty, D.; *Eur. J. Org. Chem.* **2011**, 2226–2229.

3-Cyclohexylpropanoic acid (2t, Table S3, entry 9)



The procedure for **2t** was applied. Substrate: sodium 3-phenylpropanoate (**1t**_{Na}, 172 mg, 1.0 mmol). The product was extracted with chloroform and recrystallized from chloroform/*n*-hexane to afford **2t** (115 mg, 90%). Analytical data for **2t**: ¹H NMR (600 MHz, CDCl₃) δ 0.90 (dddd, *J* = 2.0, 12.1, 12.1, 12.1 Hz, 2H), 1.10–1.29 (m, 4H), 1.54 (ddd, *J* = 7.1, 8.1, 8.1 Hz, 2H), 1.64 (bd, *J* = 12.1 Hz, 1H), 1.69–1.72 (m, 4H), 2.36 (dd, *J* = 7.6, 8.1 Hz, 2H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 26.3, 26.7, 31.8, 32.2, 33.1, 37.3, 180.9; HRMS (FAB) calcd for [C₉H₁₇O₂⁺](MH⁺) 157.1223, found 157.1222.

Cyclohexylamine hydrochloride (2u•HCl, Table S3, entry 10)¹⁸



The procedure for **2u**•HCl was applied. Substrate: aniline hydrochloride (**1u**•HCl, 130 mg, 1.0 mmol). **2u**•HCl was obtained as pale yellow-brown solids (109 mg, 80%).

Cyclohexylamine hydrochloride (2v•HCl, Table S3, entry 11)¹⁹



The procedure for **2v**•HCl was applied. Substrate: pyridine hydrochloride (**1v**•HCl, 115 mg, 1.0 mmol). **2v**•HCl was obtained as pale yellow powders (116 mg, 95%).

Measurement of TON and TOF: Hydrogenation of 3a (eq 1)



As per the above-mentioned representative procedure, hydrogenation of **3a** (92.1 mg, 1.0 mmol) was conducted using Ru/chitin (0.0001 mmol Ru, prepared from 1.25 mg of the catalyst precursor) and deaerated H₂O (5.0 mL) at 120 °C for 0.5 h under H₂ (4 MPa). After the autoclave was cooled down in an ice bath and the pressure was carefully released, diethyl ether (2 mL) was added to the reaction mixture. The organic layer was separated after centrifugation (3500 rpm, 7 min). The product was

¹⁸ Kitamura, M.; Suga, T.; Chiba, S.; Narasaka, K. Org. Lett. 2004, 6, 4619–4621.

¹⁹ Cheng, C.; Sun, J.; Xing, L.; Xu, J.; Wang, X.; Hu, Y. J. Org. Chem. 2009, 74, 5671–5674.

extracted from the residual mixture of aqueous layer and Ru/chitin by repeating these processes (diethyl ether, 3×2 mL). The combined organic layer was analyzed by GC-MS using *n*-octane as an internal standard [chromatographic elution: isothermal at 70 °C for 2 min, 70–150 °C at a rate of 20 °C min⁻¹, $t_{\rm R} = 2.5$ min (**4a**), 2.8 min (*n*-octane), 3.0 min (**3a**). 10% yield, TON 3000, TOF 6000 h⁻¹.

5. Chiral GC Analysis

Derivatization of (S)-2c to (S)-cyclohexylethyl acetate [(S)-2ca]



According to a literature procedure²⁰, (*S*)-**2ca** was prepared from (*S*)-**2c** (85.2 mg, 0.50 mmol), triethylamine (140 µL, 1.0 mmol), DMAP (6.1 mg, 0.05 mmol), and acetic anhydride (94.5 µL, 1.0 mmol) in dichloromethane to afford (*S*)-**2ca** as a yellowish oil (133 mg, 78%). Analytical data for (*S*)-**2ca**: ¹H NMR (500 MHz, CDCl₃) δ 0.92–1.04 (m, 2H), 1.09–1.28 (m, 6H), 1.39–1.46 (m, 1H), 1.65–1.68 (m, 2H), 1.73–1.78 (m, 3H), 2.03 (s, 3H), 4.72 (quin, *J* = 6.3 Hz, 1H); ¹³C{¹H} NMR (125 MHz, CDCl₃) δ 17.2, 21.5, 26.1, 26.2, 26.5, 28.6, 28.7, 42.7, 74.6, 171.0; chiral GC (chromatographic elution: isothermal at 50 °C for 3 min, 50–100 °C at a rate of 25 °C min⁻¹, isothermal at 100 °C for 2 min, 100–150 °C at a rate of 10 °C min⁻¹, isothermal at 150 °C for 2 min, 150–230 °C at a rate of 25 °C min⁻¹, isothermal at 230 °C for 1 min): *t*_R = 12.3 min (*S*), 12.6 min (*R*), *S:R* ratio = 94:6. (*rac*)-**2ca** was prepared similarly using (*rac*)-**2c** and analyzed by chiral GC [*t*_R = 12.2 min (*S*), 12.5 min (*R*)].



²⁰ Fernández-Mateos, E.; Maciá, B.; Yus, M. Adv. Synth. Catal. **2013**, 355, 1249–1254.

Derivatization of (R)-2f to methyl (R)-2-acetoxy-2-cyclohexylacetate [(R)-2fa]



To a dried 30 mL J-Young tube containing a stirring bar, (*R*)-**2f** (31.6 mg, 0.20 mmol) was dissolved in a mixed solvent of benzene (500 µL) and CH₃OH (120 µL). Trimethylsilyldiazomethane (2.0 M in diethyl ether, 100 µL, 0.20 mmol) was added to the tube under N₂ flow and the reaction mixture was stirred at rt for 40 min. After concentration, the product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate 8:1–5:1) to afford the methyl ester as a yellowish oil (34.2 mg, 99%). The methyl ester was treated with triethylamine (56 µL, 0.40 mmol), DMAP (2.41 mg, 0.020 mmol), and acetic anhydride (37.8 µL, 0.40 mmol) in dichloromethane²⁰ to afford (*R*)-**2fa** as a yellowish oil (34.7 mg, 81%). Analytical data for (*R*)-**2fa**: ¹H NMR (600 MHz, CDCl₃) δ 1.11–1.31 (m, 5H), 1.63–1.68 (m, 3H), 1.75–1.78 (m, 2H), 1.84–1.91 (m, 1H), 2.14 (s, 3H), 3.75 (d, *J* = 6.8 Hz, 3H), 4.82 (d, *J* = 5.5 Hz, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃) δ 20.7, 26.0, 26.0, 26.1, 27.8, 29.0, 39.6, 52.1, 76.3, 170.4, 170.9; chiral GC (chromatographic elution: isothermal at 50 °C for 3 min, 50–170 °C at a rate of 25 °C min⁻¹, isothermal at 170 °C for 5 min, 170–180 °C at a rate of 1.0 °C min⁻¹, isothermal at 180 °C for 2 min, 180–230 °C at a rate of 25 °C min⁻¹, isothermal at 230 °C for 1 min): *t*_R = 10.5 min (*S*), 10.9 min (*R*), *S:R* ratio = 1:99. (*rac*)-**2fa** was prepared similarly using (*rac*)-**2f** and analyzed by chiral GC [*t*_R = 10.6 min (*S*), 10.9 min (*R*)].



Derivatization of (S)-2j•HCl to N-(S)-cyclohexylethylacetamide [(S)-2ja]



A mixture of (S)-2j•HCl (100.1 mg, 0.61 mmol) and anhydrous CH₃OH (4.0 mL) in a 10 mL vial was stirred at rt for 30 min with a stirring bar. CH₃ONa (0.5 M in CH₃OH, 1.2 mL, 0.60 mmol) was added by dropwise and stirred at rt for 1 h. The mixture was concentrated, diluted with diethyl ether (10 mL) and water (10 mL) and extracted with diethyl ether (10 mL \times 5). The combined organic layers were dried with Na₂SO₄ and concentrated under reduced pressure to give the corresponding amine (S)-2j as an yellow oil. The product was used directly in the next step. By following a literature procedure²¹, (S)-2ja was prepared from (S)-2j (73 µL, 0.5 mmol), triethylamine (84 µL, 0.6 mmol), and acetyl chloride (38 µL, 0.55 mmol) in ether to afford (S)-2ja as white powders (133.0 mg, 79%). Analytical data for (S)-2ia: Mp 115 °C (lit.²² 119 °C); ¹H NMR (500 MHz, CDCl₃) δ 0.96 (dddd, *J* = 3.4, 12.0, 12.0, 12.6 Hz, 1H), 1.00 (dddd, *J* = 3.4, 12.0, 12.0, 12.6 Hz, 1H), 1.07 (d, J = 6.3 Hz, 3H), 1.11–1.35 (m, 4H), 1.64–1.68 (m, 2H), 1.73–1.79 (m, 3H), 1.97 (s, 3H), 3.85 (m, 1H), 5.26 (bs, 1H); ¹³C NMR (125 MHz, CDCl₃) & 18.1, 23.8, 26.3, 26.5, 29.1, 29.2, 43.2, 49.5, 169.4; chiral GC (chromatographic elution: isothermal at 50 °C for 3 min, 50-150 °C at a rate of 30 °C min⁻¹, isothermal at 150 °C for 5 min, 150–155 °C at a rate of 1.0 °C min⁻¹, isothermal at 155 °C for 10 min, 155–230 °C at a rate of 30 °C min⁻¹, isothermal at 230 °C for 2 min): $t_{\rm R} = 19.6$ min (S), 19.8 min (R), S:R ratio = 96:4. (rac)-2ja was prepared similarly using (rac)-2j•HCl and analyzed by chiral GC [$t_R = 19.6 \min(S)$, 19.9 min (R)].



²¹ Chalard, P.; Bertrand, M.; Canet, I.; Théry, V.; Remuson, R.; Jeminet, G. *Org. Lett.* **2000**, *2*, 2431–2434.

²² Devant, R.; Braun, M. Chem. Ber. 1986, 119, 2191–2207.

6. Catalyst Reuse Experiment

As per the typical procedure shown in Section 3, Ru/chitin (0.8 mol % Ru) was prepared in a 30 mL glass vessel equipped with a rubber septum and a magnetic stirring bar. To this tube were added benzyl glycidyl ether (**1a**, 152.5 μ L, 1.0 mmol) and deaerated H₂O (5.0 mL) under an Ar atmosphere. The vessel was put into a pre-dried stainless steel autoclave under an Ar flow, and the internal atmosphere was exchanged with H₂ three times. The mixture was stirred at 50 °C for 2 h under H₂ (2 MPa). After the autoclave was cooled down in an ice bath and the pressure was carefully released, ethyl acetate (2 mL) was mixed with the reaction mixture. The liquid phase was separated by centrifugation (3500 rpm, 10 min). The product was extracted by repeating these processes (ethyl acetate, 3 × 2 mL). The combined organic layer was analyzed by GC-MS using *n*-octane as an internal standard (yield of **2a**: 98%). Residual Ru/chitin in the vessel was directly reused for the next run (50 °C, 2 h).

Run	Conv. of 1a (%)	Yield of 2a (%)	Combined yield of 3a and 4a (%)	Selectivity for 2a (%)
1	> 99	98	< 1	99
2	98	96	1	98
3	97	94	3	97
4	97	90	6	93
5	98	89	5	92
6	97	87	8	90
7	99	87	9	88

 Table S4. Catalyst Reuse Experiment^a

^aConditions: 1a (1.0 mmol), Ru/chitin (0.8 mol % Ru) and H₂O (5 mL) at 50 °C for 2 h under H₂ (2 MPa).

7. Characterization of Ruthenium Catalysts

(High-resolution) transmission electron microscopy [(HR)TEM] analysis was performed on a JEOL JEM-3011 microscope. Sample preparation required droplet coating of particle dispersions obtained by sonicating in ethanol on carbon-coated Cu grids (Agar Scientific, 300 mesh). Electron optical parameters: $C_S = 0.6$ mm, $C_C = 1.2$ mm, electron energy spread = 1.5 eV, beam divergence semi-angle = 1 mrad. Elemental analysis was by energy dispersive X-ray spectroscopy (EDX) using a PGT prism Si/Li detector and an Avalon 2000 analytical system. Spectra were analysed using the PGT eXcalibur 4.03.00 software. Observed Cu Ka and KB emission lines were attributed to scattered electrons impinging on the copper grid. Any minor Fe Ka and Co Ka emission lines of similar intensity were due to parasitic scattering from the lens polepiece. Detailed analysis of particle morphology was performed using Digital Micrograph 3.6.5 by counting the diameters of 100 particles (N), defining intervals of 0.25 nm between $d_{\min} \le d \le d_{\max}$ and counting the number of particles falling into these intervals. Particle size distributions were constructed using DataGraph 3.0. Values of average *d*-spacing were obtained from Fourier transforms of high magnification images (×800k, ×1m) using d = 20/D where D is the diameter (nm) of rings obtained. Average d-spacing was further verified using the profile tool in Digital Micrograph by averaging over 10 d-spacings. To determine the error in the value of d-spacing thus obtained, detailed TEM examination of CeO₂ and Au nanoparticles was undertaken. The relationship between FT ring diameter and DV value was established for DV values between -6 and +6 and the standard deviation in *d*-spacing was established to be 10% when compared to the literature. X-ray diffraction (XRD) data were recorded using Ni-filtered CuK α radiation from a highly stabilized and automated PAN-analytical X-ray generator operated at 40 kV and 40 mA. The generator was connected to a PW3071/60 Bracket goniometer for sample mounting. The data were recorded for $2\theta = 5-80^{\circ}$ with 2θ step size = 0.02°. Each sample was completely dried in vacuo and the obtained powder was used directly for analysis.

Ru (0.9 wt %)/cellulose



Fig. S1. (HR)TEM and EDX analysis of Ru (0.9 wt %)/cellulose: a) TEM image; b) particle size distribution of ruthenium nanoparticles; c) magnified TEM image; d) fringe plot of Ru(002); e) a representative TEM image the white-circled region of which was used to generate f) an EDX chart (Cu attributable to grid material).

Ru (0.8 wt %)/chitosan



Fig. S2. (HR)TEM and EDX analysis of Ru (0.8 wt %)/chitosan: a) TEM image; b) particle size distribution of ruthenium nanoparticles; c) magnified TEM image; d) fringe plot of Ru(100); e) a representative TEM image the white-circled region of which was used to generate f) an EDX chart (Cu attributable to grid material).





Fig. S4. XRD analysis of γ -Al₂O₃ and Ru (1.0 wt %)/ γ -Al₂O₃.



Ru (5.0 wt %)/Al₂O₃ (purchased from Sigma-Aldrich)





Fig. S7. XRD analysis of Ru (5.0 wt %)/Al₂O₃ (purchased from Sigma-Aldrich).

Ru (5.0 wt %)/C (purchased from TCI)





Fig. S9. XRD analysis of Ru (5.0 wt %)/C (purchased from TCI).

	\sim O + 3H ₂ $\frac{\text{cata}}{\text{H}_{0}}$	alyst	γ°	$<_0$			
1a , 1.0 mmol 50 °C, 1.5 h 2a							
Catalyst (wt % Ru)	Mean size of Ru nanoparticles (nm)	Conv. of $1a$ (%) ^b	Yield of 2a $(\%)^b$	Selectivity of 2a (%, yield/conv.)			
Ru/chitin (0.8)	2.3 ± 0.3	> 99	98	98			
Ru/chitin after 1 run (0.8)	2.7 ± 0.6	98	96	98			
Ru/chitin after 6 runs (0.8)	3.5 ± 0.8	99	87	88			
Ru/cellulose (0.9)	2.5 ± 0.5	> 99	97	97			
Ru/chitosan (0.8)	1.2 ± 0.3	47	41	87			
Ru/γ - $Al_2O_3(1)$	4.8 ± 1.0	40	36	90			
Ru/C (0.9)	4.2 ± 1.0	51	43	84			
Ru/Al_2O_3	79 1 7 2	10	15	70			
(5, Sigma-Aldrich)	7.8 ± 2.3	19	15	19			
Ru/C (5, TCI)	2.6 ± 0.6	> 99	87	88			
^{<i>a</i>} Conditions: see Tables 1 and S3. ^{<i>b</i>} Determined by ¹ H NMR using mesitylene as an internal standard.							

Table S5. Correlations between Particle Size and Reactivity for Hydrogenation of 1a.^a



Fig. S10. Correlation of particle size with selectivity. See Table S5 for details.

8. NMR Charts

























S33



S34

























175.215

X : parts per Million : 13C







