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ARTICLE

Hydration of Nitriles to Amides by a Chitin-supported Ruthenium Catalyst

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Aki Matsuoka[a], Takahiro Isogawa[a], Yuna Morioka[a], Benjamin R. Knappett[b], Andrew E. H. Wheatley*[b], Susumu Saito*[ac] and Hiroshi Naka*[a],

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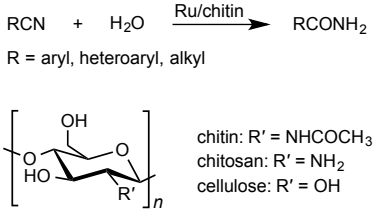
Chitin-supported ruthenium (Ru/chitin) promotes the hydration of nitriles to carboxamides under aqueous conditions. The nitrile hydration can be performed on a gram-scale and is compatible with the presence of various functional groups including olefins, aldehydes, carboxylic esters and nitro and benzyloxycarbonyl groups. The Ru/chitin catalyst is easily prepared from commercially available chitin, ruthenium(III) chloride and sodium borohydride. Analysis of Ru/chitin by high-resolution transmission electron microscopy indicates the presence of ruthenium nanoparticles on the chitin support.

Introduction

The catalytic hydration of nitriles (RCN) to carboxamides ($RCONH_2$) represents a fundamentally important pathway to these products in both laboratory and industrial contexts.[1–3] Since the discovery of alumina-supported ruthenium hydroxide catalysts [$Ru(OH)_x/Al_2O_3$] by Yamaguchi *et al.*,[4] solid-supported Ru has become an important class of catalyst for nitrile hydration, demonstrating high selectivity for carboxamide formation as well as other practical advantages.[5–8] Although $RuCl_3 \bullet nH_2O$ itself catalyzes nitrile hydration, the choice of solid support is critically important for achieving sufficient reactivity as well as for retaining Ru species on support.[4,6] Examples of supports successfully used for Ru species include inorganic γ-Al_2O_3,[4] nanoferrite[5a] and magnetic silica, [5b] as well as organic chitosan,[5c] amberlite[6] and Nafion.[7] However, these systems typically require the use of microwave irradiation[5,6] or high reaction temperatures (~175 °C).[7] Moreover, the tolerance of base-sensitive functional groups such as carboxylic esters has not been documented in these reports.[4–7] Such chemoselectivity is important in modern organic synthesis,[9] but is generally considered elusive in nitrile hydration promoted by metal-loaded heterogeneous catalysts, a single exception (Au/TiO_2[8f]) notwithstanding. In this work we establish that chitin-supported ruthenium (abbreviated as Ru/chitin) serves as a versatile catalyst for the hydration of nitriles to carboxamides (Scheme 1). Using this system, nitrile hydration can be operated under near-neutral, aqueous conditions without requiring any special apparatus. Moreover,



Scheme 1. Hydration of nitriles to carboxamides with Ru/chitin.

the morphologies of ruthenium nanoparticles on the chitin support were clarified by high-resolution transmission electron microscopy (HRTEM) analysis.

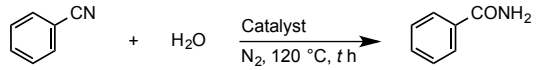
After cellulose, chitin is the second most abundant polysaccharide in nature.[10] It has a wide range of applications in materials, food, medical and environmental contexts. These include in the preparation of chitosan, affinity chromatography, wound-dressing and metal-extraction in water purification.[11] Whereas chitin has been intensively used as a catalyst support for enzymes,[12] its use as a support for metal catalysts has been less widely explored than has that of chitosan.[13,14] So far, chitin has been used as a support for Pt in asymmetric arene hydrogenation,[15] Pd in the hydrogenation of nitrobenzene and unsaturated fatty acid esters[16] and Re in the epoxidation of olefins.[14d] We expected that chitin would represent a potentially attractive support for the Ru-catalyzed hydration of nitriles because it is highly stable under aqueous conditions and effectively adsorbs Ru species using its carboxamide functionality.[17]

Results and discussion

Catalytic tests

Ru/chitin catalyst was prepared by impregnating commercially available chitin with an aqueous solution of $RuCl_3•3H_2O$ followed by reduction with $NaBH_4$,[18] and was tested for its effectiveness in the hydration of benzonitrile (**1a**, Table 1). When a mixture of **1a** (1.0 mmol), H_2O (1.0 mL) and Ru/chitin (0.016 mmol Ru, 1.6 mol % Ru) was heated at 120 °C for 3 h, the corresponding amide **2a** was obtained in 33% ^{1}H NMR yield (Table 1, entry 1). The presence of ruthenium was found to be essential, with the reaction hardly proceeding without catalyst or using only chitin (entries 2 and 3). Meanwhile, the chitin support was also found to be critical, with $RuCl_3•3H_2O$ alone catalyzing the hydration of **1a** but with significantly lower efficiency (entry 4). The optimization of reaction conditions using Ru/chitin increased the yield of **2a** from 33% to 87% (entries 5–7). Ru/chitin with a higher Ru content [2.3 mol % Ru, prepared from catalyst precursor (202 mg, 1.2 wt % Ru)] gave slightly better yield still (entry 8). This result proved to be reproducible (^{1}H NMR yields of separate runs: 97%, 91%, 89% and 89%). Analogously prepared Ru catalysts that utilized other polysaccharide supports such as chitosan and cellulose were found to be less reactive than Ru/chitin (entries 9 and 10).

Table 1. Hydration of benzonitrile (**1a**) to benzamide (**2a**).[a]



1a, 1.0 mmol **2a**

Entry	Catalyst (mol % Ru)	H_2O (mL)	*t*/h	Yield (%)[b]
1	Ru/chitin (1.6)	1	3	33
2	None	1	3	< 1
3	Chitin	1	3	< 1
4	$RuCl_3•3H_2O$ (2.0)	1	3	17
5	Ru/chitin (1.6)	1	20	77
6	Ru/chitin (1.6)	1	30	87
7	Ru/chitin (1.6)	4	20	87
8	Ru/chitin (2.3)[c]	4	20	97
9	Ru/chitosan (3.2)[d]	4	20	74
10	Ru/cellulose (3.2)[e]	4	20	17

[a] Conditions: **1a** (1.0 mmol), H_2O (1.0 mL, 56 equiv) and catalyst [1.6 mol % Ru, prepared from catalyst precursor (202 mg, 0.8 wt % Ru)] at 120 °C under a N_2 atmosphere unless otherwise stated. The mol % Ru was confirmed by ICP-AES analysis. [b] Of **2a**, determined by ^{1}H NMR using mesitylene as an internal standard. [c] Ru/chitin (2.3 mol % Ru), prepared from catalyst precursor (1.2 wt % Ru). [d] Ru/chitosan (3.2 mol % Ru), prepared from catalyst precursor (1.7 wt % Ru). [e] Ru/cellulose (3.2 mol % Ru), prepared from catalyst precursor (1.6 wt % Ru).

Scope and limitation

The scope of the Ru/chitin-catalyzed hydration of nitriles is outlined in Table 2. These reactions were run under comparable conditions to those in entry 8 of Table 1. Benzamide (**2a**) was obtained in 87% isolated yield (Table 2, entry 1) and variously substituted benzonitriles could be converted to the

Table 2. Catalytic hydration of nitriles with Ru/chitin.[a]

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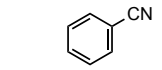
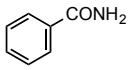
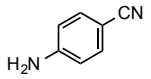
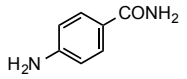
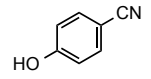
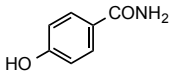
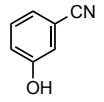
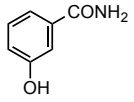
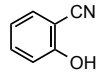
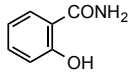
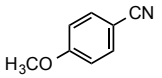
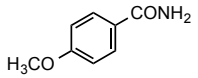
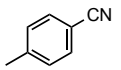
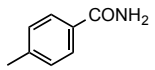
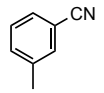
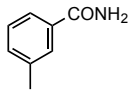
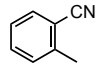
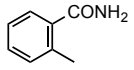
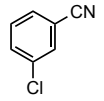
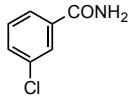
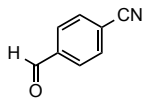
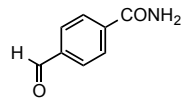
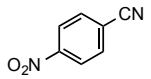
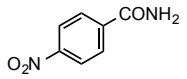
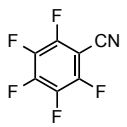
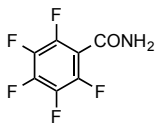
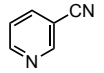
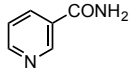
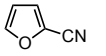
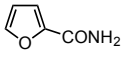
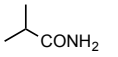
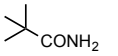
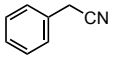
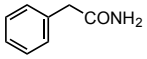
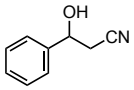
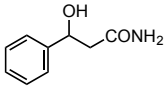
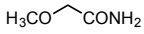
Entry	Nitrile (**1**)	*t*/h	Amide (**2**)	Isolated yield (%)
1		**1a** 20		**2a** 87
2		**1b** 60		**2b** 89
3		**1c** 40		**2c** 98
4		**1d** 32		**2d** 97
5		**1e** 32		**2e** 79
6		**1f** 40		**2f** 88
7		**1g** 50		**2g** 96
8		**1h** 60		**2h** 92
9		**1i** 60		**2i** 49
10		**1j** 24		**2j** 80
11		**1k** 40		**2k** 76
12		**1l** 18		**2l** 92
13		**1m** 50		**2m** 65
14		**1n** 24		**2n** 94

Table 2. *Continued.*[a]

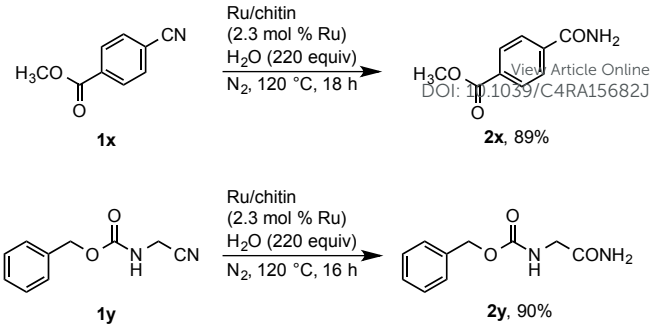
Entry	Nitrile (**1**)		*t*/h	Amide (**2**)		Isolated yield (%)
15		**1o**	20		**2o**	91
16	CH_3CN	**1p**	36	CH_3CONH_2	**2p**	65
17		**1q**	36		**2q**	55
18		**1r**	48		**2r**	65
19		**1s**	48		**2s**	23
20		**1t**	36		**2t**	85
21		**1u**	24		**2u**	66
22		**1v**	30		**2v**	46
23	H_3CO 	**1w**	24	H_3CO 	**2w**	81

[a] Conditions: **1** (1.0 mmol), H_2O (4 mL, 220 equiv) and Ru/chitin (2.3 mol % Ru) at 120 °C under a N_2 atmosphere.

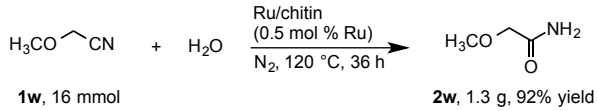
corresponding amides in good-to-excellent yield (entries 2–13). *o*-Methyl-substituted **1i** was somewhat less reactive (Table 2, entry 9) though *m*- and *p*-substituted analogues reacted in satisfying yields (entries 7 and 8). Benzonitrile **1l**, which bore an electron-withdrawing *p*-nitro group, was completely hydrated in shorter reaction times than **1b**, **1c**, **1f** and **1g**, each of which bore electron-donating groups at the *para* positions. *p*-Formylbenzonitrile (**1k**) could be converted to the corresponding amide **2k** with an intact formyl moiety in 76% yield, though formation of the hydrate of the aldehyde was also noted under aqueous conditions. Furthermore, heteroaromatic nitriles could be efficiently hydrated to the corresponding amides (entries 14 and 15).

The Ru/chitin system was also applied to the hydration of aliphatic nitriles (Table 2, entries 16–23). Although the hydration reaction proved susceptible to steric hindrance (entry 19), primary and secondary nitriles **1p–r** and **1t–w** could all be converted to amides (entries 16–18 and 20–23) with retention of olefin (entry 21), *β*-hydroxy (entry 22) and *α*-methoxy (entry 23) groups in fair-to-good yields.

Importantly, the presence of a base-sensitive carbonyl functionality in methyl ester **1x** was tolerated by virtue of the



Scheme 2. Hydration nitriles bearing carboxylic ester and carbamate functionalities.



Scheme 3. Gram-scale hydration of nitrile **1w**.

near-neutral conditions that could be used for catalyst preparation[6,18] (Scheme 2). Similarly, α-amino nitrile conjugated with a redox-sensitive benzyloxycarbonyl (Cbz) group (as in **1y**) was converted to protected α-amino amide **2y** with retention of the carbamoyl linkage. The tolerance to carboxylic ester and CbzN functionality shown in Scheme 2 illustrates the applicability of the present method to the nitrile hydration of complex molecules bearing redox- or base-sensitive functional groups.

Upscale experiment

To verify the scalability of this method, a gram-scale hydration was carried out (Scheme 3). The hydration of **1w** using a decreased loading of Ru/chitin catalyst (0.5 mol % Ru) yielded the amide **2w** in excellent yield [conditions: **1w** (16 mmol), H_2O (13 mL), Ru/chitin (0.5 mol % Ru), 120 °C, 36 h, 92% isolated yield (77% isolated yield after 24 h under otherwise identical conditions)].

HRTEM analysis

To elucidate the nature of the Ru/chitin catalyst, the catalyst was analyzed by HRTEM. The presence of nanoparticles with a mean size of 2.1 ± 0.4 nm was established (Figs. 1a–c). Energy dispersive X-ray spectroscopy (EDX) and measurement of the *d*-spacings (d = 0.23 nm) indicated the presence of both Ru(0) and RuO_2 [Figs. 1c, inset, and 1d]. EDX also revealed the presence of Ca and P in both Ru/chitin (Fig. 1d) and chitin (Figs. 1e and 1f). This was attributed to calcium phosphate on account of the crustaceous origin of the chitin and was found not to incur significant catalytic activity (Table 1, entry 3).

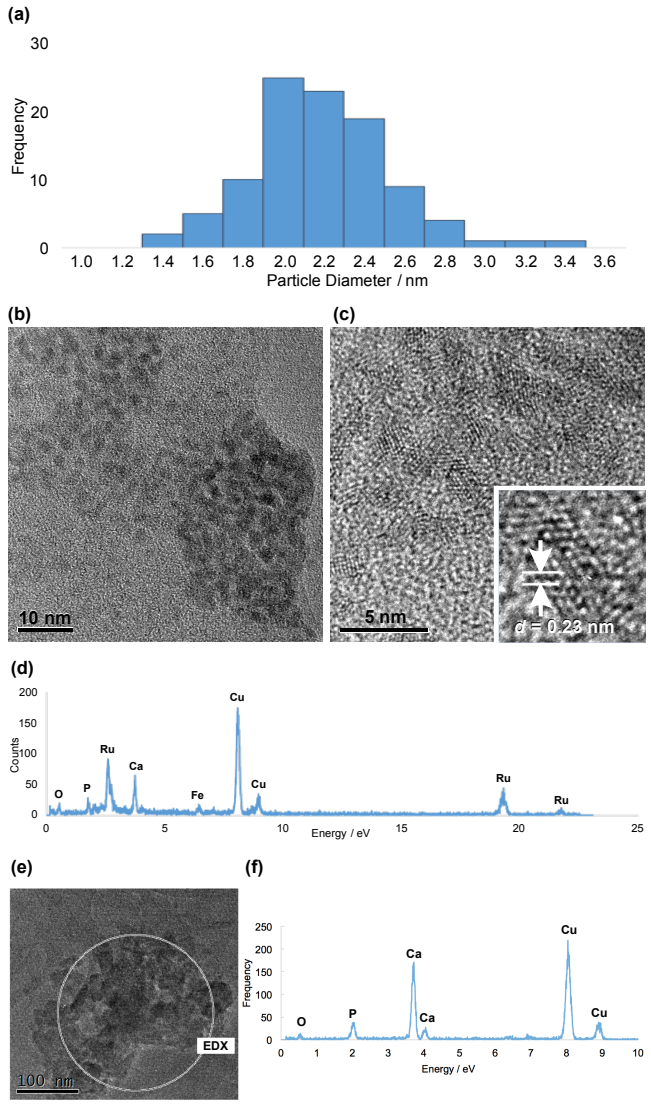


Fig. 1. (a) A histogram representing the particle size distribution of Ru nanoparticles on chitin. (b) Low-magnification and (c and inset) high resolution TEM images of chitin-supported Ru nanoparticles. (d) EDX of Ru/chitin. (e) A low-magnification TEM image of chitin. (f) EDX of chitin.

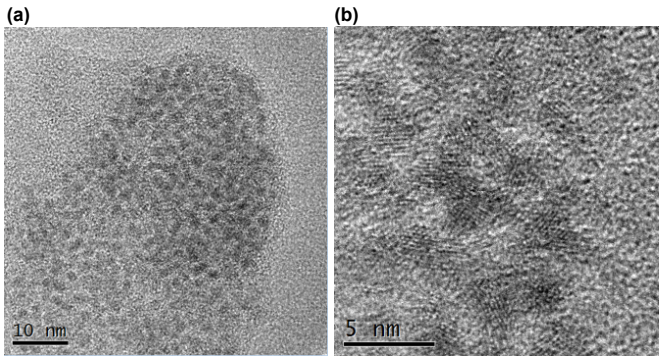


Fig. 2. (a) Low-magnification and (b) high resolution TEM images of Ru/chitin after nitrile hydration.

TEM analysis of the Ru nanoparticles after hydration of **1w** showed that they remained morphologically essentially unchanged (Fig. 2). In fact, the Ru/chitin catalyst could be reused without significant loss of catalytic activity (hydration of **1a** to **2a**, conditions: identical to Table 1, entry 8, first run, 95% yield; reuse run, 87% yield).

Conclusions

We have established that chitin-supported ruthenium displays high catalytic activity towards the hydration of nitriles to amides under aqueous conditions. The catalyst is easily prepared, and applicable to the hydration of a wide variety of nitriles with aromatic, heteroaromatic and aliphatic substituents. HRTEM analysis of Ru/chitin revealed the presence of ruthenium nanoparticles before and after hydration reactions, indicating that chitin could serve as an effective solid support for ruthenium nanoparticles.

Experimental section

General comments

^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA-600 (600 MHz for ^{1}H, 150 MHz for ^{13}C, 564 MHz for ^{19}F) or a JEOL ECA-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) at 25 °C. Chemical shifts are reported as δ in ppm and are internally referenced to tetramethylsilane (TMS, 0.00 ppm for ^{1}H), CD_2HOH (3.30 ppm for ^{1}H), CD_2HSOCD_3 (2.50 ppm for ^{1}H), HOD (4.79 ppm for ^{1}H), $CDCl_3$ (77.2 ppm for ^{13}C), CD_3OD (49.0 ppm for ^{13}C), dioxane (67.2 ppm in D_2O for ^{13}C), or dimethyl sulfoxide-d_6 (DMSO-d_6, 39.5 ppm for ^{13}C). Chemical shifts for ^{19}F NMR were externally referenced to CF_3COOH (–78.5 ppm, neat). Infrared (IR) spectra were recorded on a FT-IR6100 (JASCO). High-resolution mass spectrometry (HRMS) was recorded with a Bruker Daltonik micrOTOF-QII spectrometer. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) spectra were recorded on an Agilent VISTA-PRO. Elemental analyses were recorded on a Yanaco CHN recorder MT-6. These analytical experiments were carried out at the Chemical Instrumental Center, Research Center for Materials Science, Nagoya University. Melting points were recorded on an OptiMelt automated melting point system (Stanford Research Systems). Ruthenium content was analyzed by ICP-AES using yttrium as an internal standard after digestion of samples (10 mg) in concd HNO_3 (2 mL) at 150 °C for 12 h. Products **2a–y** were known compounds and their identities were confirmed by comparing with literature data.[6,7,8g,19–34]

TEM analysis

High-resolution transmission electron microscopy (HRTEM) analysis was performed on a JEOL JEM-3011 microscope. Samples illustrated in Figs. 1a–d and 2 were prepared as per the typical procedure for the preparation of Ru/chitin (0.016 mmol Ru, vide infra) and by the hydration of **1w** (0.5 mmol) using Ru/chitin (0.016 mmol Ru) at 120 °C for 6 h, respectively. Sample preparation required droplet coating of particle dispersions obtained by sonicating in CH_3CH_2OH 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 analyzed using the PGT eXcalibur 4.03.00 software. Observed Cu Kα and Kβ emission lines were attributed to scattered electrons impinging on the copper grid. Any minor Fe Kα and Co Kα 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 confirmed 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 CeO_2 and Au nanoparticles was undertaken. The relationship between FT ring diameter and DV value (a measure of objective lens focusing voltage) 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.

Materials

$RuCl_3$•$3H_2O$ was purchased from Furuya Metal Co., Ltd. Benzonitrile (**1a**), *m*-hydroxybenzonitrile (**1d**), *p*-methylbenzonitrile (**1g**), *m*-methylbenzonitrile (**1h**), *o*-methylbenzonitrile (**1i**), *m*-chlorobenzonitrile (**1j**), *p*-nitrobenzonitrile (**1l**), 2,3,4,5,6-pentafluorobenzonitrile (**1m**), acetonitrile (**1p**), pivalonitrile (**1s**), 2-phenylacetonitrile (**1t**), 3-hydroxy-3-phenylpropanonitrile (**1v**), α-methoxyacetonitrile (**1w**) and 4-(methoxycarbonyl)benzonitrile (**1x**), were purchased from TCI. *p*-Aminobenzonitrile (**1b**), *p*-methoxybenzonitrile (**1f**), 2-furonitrile (**1o**), yttrium standard solution [$Y(NO_3)_3$ in HNO_3, 1.00 mg Y / mL; 1000 ppm] and concd HNO_3 were purchased from Wako Chemicals. *p*-Hydroxybenzonitrile (**1c**), *p*-formylbenzonitrile (**1k**), propionitrile (**1q**), 2-methylpropanenitrile (**1r**) and acrylonitrile (**1u**) were purchased from Aldrich. *o*-Hydroxybenzonitrile (**1e**) was purchased from Merck. Nicotinonitrile (**1n**) and chitin were purchased from Kanto Chemicals. Ruthenium standard solution (1 mg Ru / mL in HCl) for ICP-AES was purchased from Acros. *α*-(Benzyloxycarbonylamino)acetonitrile (**1y**) was prepared according to the literature procedure by protecting *α*-aminoacetonitrile with CbzCl.[35]

Catalyst Preparation

A typical procedure for the preparation of Ru/chitin (0.016 mmol Ru). To a 300 mL round-bottom flask, $RuCl_3$•$3H_2O$ (71.6 mg, 0.30 mmol Ru), H_2O (50 mL) and chitin (2980.4 mg) were added. The mixture was heated at 50 °C for 30 min, and concentrated using a rotary evaporator at 50 °C for 25 min (17 mmHg). The solid was dried at 50 °C *in vacuo* overnight to afford the catalyst precursor (0.8 wt % Ru as determined by ICP-AES analysis, dark green solid, 2784.0 mg). To a 10 mL test tube with a screw cap, a magnetic stirring bar and the catalyst precursor (202 mg, 0.8 wt % Ru), deaerated H_2O (8 mL) was added under a N_2 atmosphere. Under vigorous stirring, a solution [1.0 mL; a mixture of $NaBH_4$ (39.4 mg, 1.0 mmol) and deaerated H_2O (5.2 mL)] was introduced dropwise to the test tube. The mixture was stirred at room temperature (rt) for 3.5 h. The liquid phase was separated by centrifugation (3500 rpm, 5 min) and replaced with H_2O (8 mL) via syringe. After the mixture was stirred at rt overnight, the solid was washed with water (2 times) and dried *in vacuo* at rt for 2 h to afford Ru/chitin as a grey solid, which was directly used for nitrile hydration.

Ru/chitin (0.023 mmol Ru). As per the above-mentioned typical procedure, the catalyst precursor was prepared using $RuCl_3$•$3H_2O$ (107.4 mg, 0.45 mmol Ru), H_2O (50 mL), and chitin (2957 mg). Dark green solid (1.2 wt % Ru determined by ICP-AES analysis, 2813 mg). As per the above-mentioned typical procedure, the Ru/chitin (0.023 mmol Ru) was prepared using precursor (202 mg, 1.2 wt % Ru), deaerated H_2O (7.5 mL) and a reducing solution [1.5 mL; a mixture of $NaBH_4$ (103.0 mg, 2.7 mmol) and deaerated H_2O (20 mL)].

Hydration of Nitriles to Amides

A typical procedure for hydration of nitriles: benzamide (2a, Table 1, entry 8; Table 2, entry 1).[19] As per the above-mentioned procedure, Ru/chitin (0.023 mmol Ru) was prepared in a screw-cap 10 mL test tube equipped with a rubber septum and a magnetic stirring bar. To this tube were added nitrile **1a** (0.986 mmol, 101.6 mg) and deaerated H_2O (2.2×10^2 mmol, 4 mL) under a N_2 atmosphere. After the septum inlet was replaced with a plastic screw cap and the cap was wrapped with Teflon tape, the mixture was shaken at 120 °C for 20 h [*ca.* 100 rpm, with a constant temperature oven (EYELA MG-2300, Tokyo Rikakikai Co. Ltd.)] on a rotary shaker (EYELA Multi Shaker MMS, Tokyo Rikakikai Co. Ltd.). The mixture was cooled down with ice water, and mixed with CH_3OH (4 mL) under air. The liquid phase was separated by centrifugation (3500 rpm, 10 min). Extraction of the product was carried out by repeating this process (CH_3OH, 6 × 4 mL). Liquid phases were combined and concentrated *in vacuo*. ^{1}H NMR analysis of this crude mixture using mesitylene as an internal standard indicated the formation of amide **2a** in 97% yield. The product was purified by sequential column chromatography on silica gel (acetone/dichloromethane 3:7; tetrahydrofuran/diethyl ether 1:10) to afford amide **2a** as colorless plates (103.8 mg, 87% yield). Mp 126.5–127.1 °C (lit.[19] 125–128 °C); IR (KBr) 1405, 1577, 1625, 1660, 3175, 3369 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.36 (bs, 1H), 7.42–7.47 (m, 2H), 7.51 (tt, J = 1.5, 7.3 Hz, 1H), 7.85–7.89 (m, 2H), 7.97 (bs, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 127.4, 128.2, 131.2, 134.3, 167.9; elemental analysis calcd for [C_7H_7NO•$0.1H_2O$]: C, 68.39; H, 5.90; N, 11.39, found: C, 68.64; H, 5.92; N, 11.15.

***p*-Aminobenzamide (2b).**[19] Light yellow blocks, purified by column chromatography on silica gel (methanol/chloroform 1:8); mp 176.3–180.9 °C (lit.[19] 180–183 °C); IR (KBr) 780, 1397, 1563, 1600, 3219,

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3326, 3464 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.59 (s, 2H), 6.53 (d, J = 8.6 Hz, 2H), 6.86 (bs, 1H), 7.53 (bs, 1H), 7.60 (d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 112.5, 121.0, 129.2, 151.7, 168.2; elemental analysis calcd for [$C_7H_8N_2O$]: C, 61.75; H, 5.92; N, 20.58, found: C, 61.79; H, 5.87; N, 20.30.

***p*-Hydroxybenzamide (2c).**[20] White powder, purified by column chromatography on silica gel (tetrahydrofran/diethyl ether 4:6–10:0, gradient); mp 157.1–159.2 °C (lit.[20] 148 °C); IR (KBr) 1247, 1403, 1558, 1618, 1649, 3124, 3340, 3417 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.78 (d, J = 8.6 Hz, 2H), 7.08 (bs, 1H), 7.68–7.79 (m, 3H), 9.94 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 114.7, 125.0, 129.5, 160.2, 167.7; elemental analysis calcd for [$C_7H_7NO_2$]: C, 61.31; H, 5.15; N, 10.21, found: C, 61.13; H, 5.14; N, 10.01.

***m*-Hydroxybenzamide (2d).**[21] White powder, purified by column chromatography on silica gel (2-propanol/*n*-hexane/ethyl acetate 1:20:200); mp 165.1–168.0 °C (lit.[21] 167–168 °C); IR (KBr) 1256, 1450, 1580, 1653, 3247, 3400 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.88–6.92 (m, 1H), 7.20–7.24 (m, 1H), 7.24–7.30 (m, 3H), 7.86 (s, 1H), 9.60 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 114.5, 118.0, 118.1, 129.2, 135.8, 157.3, 168.0; elemental analysis calcd for [$C_7H_7NO_2$]: C, 61.31; H, 5.15; N, 10.21, found: C, 61.23; H, 5.12; N, 10.05.

***o*-Hydroxybenzamide (2e).**[7] Colorless plates, purified by column chromatography on silica gel (chloroform only); mp 138.2–139.2 °C; IR (KBr) 1253, 1359, 1424, 1447, 1493, 1590, 1630, 1675, 3189, 3395 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.83–6.89 (m, 2H), 7.37–7.42 (m, 1H), 7.84 (dd, J = 1.6, 8.0 Hz, 1H), 7.89 (bs, 1H), 8.39 (bs, 1H), 13.0 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 114.4, 117.4, 118.3, 128.1, 134.1, 161.1, 172.1; elemental analysis calcd for [$C_7H_7NO_2$]: C, 61.31; H, 5.15; N, 10.21, found: C, 61.22; H, 5.21; N, 10.01.

***p*-Methoxybenzamide (2f).**[6] Colorless plates, purified by column chromatography on silica gel (tetrahydrofuran/diethyl ether 0:10–10:0, gradient); mp 164.3–169.3 °C; IR (KBr) 1146, 1253, 1396, 1422, 1573, 1643, 3170, 3391 cm^{-1}; ^{1}H NMR (600 MHz, CD_3OD) δ 3.82 (s, 3H), 6.93–6.97 (m, 2H), 7.81–7.85 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 55.9, 114.7, 126.9, 130.6, 164.1, 172.0; elemental analysis calcd for [$C_8H_9NO_2$]: C, 63.56; H, 6.00; N, 9.27, found: C, 63.37; H, 6.00; N, 9.23.

***p*-Methylbenzamide (2g).**[8g] Colorless plates, purified by column chromatography on silica gel (acetone/dichloromethane 2:5); mp 157.6–159.0 °C (lit.[8g] 159–160 °C); IR (KBr) 1397, 1414, 1571, 1618, 1671, 3168, 3343 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.34 (s, 3H), 7.22–7.30 (m, 3H), 7.75–7.80 (m, 2H), 7.89 (bs, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 20.9, 127.5, 128.7, 131.5, 141.0, 167.8; elemental analysis calcd for [C_8H_9NO]: C, 71.09; H, 6.71; N, 10.36, found: C, 70.99; H, 6.66; N, 10.26.

***m*-Methylbenzamide (2h).**[8g] Colorless plates, purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 2:3); mp 91.0–92.4 °C (lit.[8g] 92–93 °C); IR (KBr) 687, 1114, 1387, 1432, 1616, 1650, 3195, 3376 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.34 (s, 3H), 7.25–7.35 (m, 3H), 7.64–7.69 (m, 1H), 7.69–7.72 (m, 1H), 7.91 (bs, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 20.9, 124.6, 128.1 (2C), 131.7, 134.3, 137.4, 168.0; elemental analysis calcd for [C_8H_9NO]: C, 71.09; H, 6.71; N, 10.36, found: C, 71.04; H, 6.78; N, 9.98.

***o*-Methylbenzamide (2i).**[8g] Colorless needles, purified by column chromatography on silica gel (ethyl acetate/*n*-hexane 2:3); mp 140.1–140.5 °C (lit.[8g] 140 °C); IR (KBr) 1140, 1395, 1623, 1656, 3187, 3368 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.36 (s, 3H), 7.18–7.24 (m, 2H), 7.28–7.37 (m, 3H), 7.68 (bs, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 19.6, 125.4, 127.0, 129.1, 130.4, 135.1, 137.1, 171.0; elemental analysis calcd for [C_8H_9NO]: C, 71.09; H, 6.71; N, 10.36, found: C, 71.35; H, 6.72; N, 10.36.

***m*-Chlorobenzamide (2j).**[8g] Colorless plates, purified by sequential column chromatography on silica gel (*n*-hexane/ethyl acetate 1:1; ethyl acetate only; tetrahydrofuran only) and activated carbon treatment; mp 132.6–133.4 °C (lit.[8g] 134–136 °C); IR (KBr) 1123, 1389, 1432, 1569, 1626, 1658, 3181, 3366 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.46–7.52 (m, 1H), 7.54 (bs, 1H), 7.56–7.61 (m, 1H), 7.81–7.86 (m, 1H), 7.89–7.94 (m, 1H), 8.10 (bs, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 126.2, 127.3, 130.3, 131.1, 133.1, 136.3, 166.4; elemental analysis calcd for [C_7H_6NClO]: C, 54.04; H, 3.89; N, 9.00, found: C, 53.96; H, 3.89; N, 8.95.

***p*-Formylbenzamide (2k).**[22] White powder, purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 1:3); mp 155.4–159.2 °C; IR (KBr) 1212, 1397, 1607, 1670, 1698, 3194, 3288, 3354 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.60 (bs, 1H), 7.96–8.00 (m, 2H), 8.03–8.08 (m, 2H), 8.17 (bs, 1H), 10.08 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 128.1, 129.3, 137.8, 139.3, 167.0, 192.9; elemental analysis calcd for [$C_8H_7NO_2$]: C, 64.42; H, 4.73; N, 9.39, found: C, 64.69; H, 4.85; N, 9.16.

***p*-Nitrobenzamide (2l).**[6] Colorless needles, purified by column chromatography on silica gel (triethylamine/2-propanol/chloroform 0.05:3:7); mp 197.1–200.0 °C; IR (KBr) 1346, 1413, 1526, 1600, 1678, 3177, 3477 cm^{-1}; ^{1}H NMR (600 MHz, CD_3OD) δ 8.05–8.08 (m, 2H), 8.29–8.33 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, CD_3OD) δ 124.6, 130.0, 140.9, 151.2, 170.1; elemental analysis calcd for [$C_7H_6N_2O_3$]: C, 50.61; H, 3.64; N, 16.86, found: C, 50.67; H, 3.69; N, 16.64.

2,3,4,5,6-Pentafluorobenzamide (2m).[7] Colorless plates, purified by column chromatography on silica gel (ethyl acetate/*n*-hexane 1:2); mp 146.8–147.2 °C; IR (KBr) 1001, 1493, 1675, 3186, 3358 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.16 (bs, 1H), 8.30 (bs, 1H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 112.9 (t, J = 21.6 Hz), 135.9–137.9 (m), 139.9–141.9 (m), 141.8–143.9 (m), 158.3; ^{13}C{^{19}F} NMR (150 MHz, DMSO-d_6); δ 112.9 (d, J = 8.7 Hz), 136.9, 140.9, 142.9, 158.3; ^{19}F NMR (564 MHz, DMSO-d_6) δ –162.0—161.3 (m, 2F), –154.0—153.4 (m, 1F), –142.3—141.9 (m, 2F); elemental analysis calcd for [$C_7H_2F_5NO$]: C, 39.83; H, 0.96; N, 6.64, found: C, 40.00; H, 6.65; N, 1.09.

Nicotinamide (2n).[23] Colorless needles, purified by column chromatography on silica gel (ethyl acetate only) and recrystallization (from dichloromethane); mp 126.0–127.7 °C; IR (KBr) 1620, 1682, 3159, 3370 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 7.48–7.51 (m, 1H), 7.59 (bs, 1H), 8.15 (bs, 1H), 8.19–8.21 (m, 1H), 8.69–8.70 (m, 1H), 9.02–9.03 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 123.3, 129.6, 135.1, 148.6, 151.8, 166.4; elemental analysis calcd for [$C_6H_6N_2O$]: C, 59.01; H, 4.95; N, 22.94, found: C, 59.00; H, 4.91; N, 22.70.

2-Francarbamide (2o).[24] White powder, purified by column chromatography on silica gel (dichloromethane/acetone 1:4) and recrystallization (from water); mp 139.6–140.9 °C (lit.[24] 141–142 °C); IR (KBr) 1626, 1665, 3171, 3351 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.53 (bs, 1H), 6.26 (bs, 1H), 6.52–6.53 (m, 1H), 7.16–7.18 (m, 1H), 7.46–7.49 (m, 1H); $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$) δ 112.5, 115.3, 144.6, 147.6, 160.4; elemental analysis calcd for [$C_5H_5NO_2$]: C, 54.05; H, 4.54; N, 12.61, found: C, 53.73; H, 4.55; N, 12.49.

Acetamide (2p).[25] White powder, purified by recrystallization (from dichloromethane/*n*-hexane); mp 79.2–80.1 °C; IR (KBr) 1665, 3212, 3389 cm^{-1}; ^1H NMR (600 MHz, D_2O) δ 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, D_2O) δ 21.9, 178.0; elemental analysis calcd for [C_2H_5NO•0.001H_2O]: C, 40.66; H, 8.53; N, 23.71, found: C, 40.26; H, 8.54; N, 23.53.

Propionamide (2q).[26] Colorless plates, purified by recrystallization (from dichloromethane/*n*-hexane); mp 79.1–80.5 °C; IR (KBr) 1664, 3202, 3370 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.18 (t, J = 7.6 Hz, 3H), 2.27 (q, J = 7.6 Hz, 2H), 5.04–5.58 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 9.8, 29.1, 176.3; elemental analysis calcd for [C_3H_7NO•0.02H_2O]: C, 49.05; H, 9.66; N, 19.07, found: C, 48.70; H, 9.56; N, 18.82.

2-Methylpropanamide (2r).[27] White powder, purified by recrystallization (from dichloromethane/*n*-hexane); mp 124.7–127.3 °C; IR (KBr) 1641, 3179, 3355 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.19 (d, J = 6.9 Hz, 6H), 2.43 (sept, J = 6.9 Hz, 1H), 5.10–5.75 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 19.7, 35.2, 179.8; elemental analysis calcd for [C_4H_9NO]: C, 55.15; H, 10.41; N, 16.08, found: C, 54.95; H, 10.45; N, 15.89.

Pivalamide (2s).[28] Colorless needles, purified by recrystallization (from dichloromethane/*n*-hexane); mp 148.7–152.0 °C; IR (KBr) 1627, 1656, 3204, 3398 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.23 (s, 9H), 5.21 (bs, 1H), 5.59 (bs, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 27.8, 38.8, 181.5; elemental analysis calcd for [$C_5H_{11}NO$•0.08H_2O]: C, 58.54; H, 10.97; N, 13.65, found: C, 58.29; H, 10.85; N, 13.36.

2-Phenylacetamide (2t).[29] White powder, purified by washing with *n*-hexane; mp 157.9–158.5 °C (lit.[29] 155 °C); IR (KBr) 1637, 3178, 3355 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 3.60 (s, 2H), 5.13–5.64 (m, 2H), 7.28–7.38 (m, 5H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 43.5, 127.6, 129.2, 129.6, 135.0, 173.7; elemental analysis calcd for [C_8H_9NO]: C, 71.09; H, 6.71; N, 10.36, found: C, 71.07; H, 6.76; N, 10.28.

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Acrylamide (2u).[30] Colorless plates, purified by recrystallization (from dichloromethane/*n*-hexane); mp 78.2–80.3 °C; IR (KBr) 1613, 1675, 3193, 3357 cm^{-1}; ^1H NMR (600 MHz, D_2O) δ 5.83 (d, J = 10.3 Hz, 1H), 6.22–6.33 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, D_2O) δ 129.1, 130.1, 171.6; elemental analysis calcd for [C_3H_5NO•0.07H_2O]: C, 49.81; H, 7.16; N, 19.36, found: C, 49.52; H, 7.02; N, 18.99.

3-Hydroxy-3-phenylpropanamide (2v).[31] Colorless needles, purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 1:6–0:7, gradient); mp 121.0–121.7 °C; IR (KBr) 1624, 1658, 3194, 3386 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 2.52 (dd, J = 4.8, 14.4 Hz, 1H), 2.63 (dd, J = 8.9, 14.5 Hz, 1H), 5.05 (dd, J = 4.8, 8.9 Hz, 1H), 7.22–7.39 (m, 5H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 46.1, 71.9, 126.9, 128.5. 129.4, 145.4, 176.4; elemental analysis calcd for [$C_9H_{11}NO_2$]: C, 65.44; H, 6.71; N, 8.48, found: C, 65.41; H, 6.71; N, 8.45.

α-Methoxyacetamide (2w).[32] Colorless needles, purified by short-column chromatography on silica gel (dichloromethane only); mp 96.2–96.9 °C; IR (KBr) 1638, 3198, 3384 cm^{-1}; ^1H NMR (500 MHz, D_2O) δ 3.45 (s, 3H), 4.02 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, D_2O) δ 59.6, 71.1, 176.4; elemental analysis calcd for [$C_3H_7NO_2$]: C, 40.44; H, 7.91; N, 15.72, found: C, 40.28; H, 8.02; N, 15.78.

***p*-(Methoxycarbonyl)benzamide (2x).**[33] Off-white plates, purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 1:4); mp 205.0–206.6 °C (lit.[33] 200–201 °C); IR (KBr) 1281, 1660, 1725, 3195, 3406 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 3.87 (s, 3H), 7.57 (bs, 1H), 7.96–8.04 (m, 4H), 8.15 (bs, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 52.3, 127.8, 129.1, 131.8, 138.4, 165.7, 167.0; elemental analysis calcd for [$C_9H_9NO_3$]: C, 60.33; H, 5.06; N, 7.82, found: C, 60.32; H, 5.14; N, 7.72.

α-(Benzyloxycarbonylamino)acetamide (2y).[34] White needles, purified by column chromatography on silica gel (chloroform/methanol 95:5–92:8, gradient); mp 135.0–136.6 °C (lit.[34] 138–139 °C); IR (KBr) 1537, 1652, 1688, 3191, 3324, 3381 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 3.55 (d, J = 3.1 Hz, 2H), 5.03 (s, 2H), 7.01 (s, 1H), 7.26–7.40 (m, 7H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ 43.3, 65.4, 127.7, 127.8, 128.3, 137.1, 156.4, 171.1; HRMS (ESI-TOF) m/z calcd for $C_{10}H_{12}N_2O_3Na$ $[M + Na]^+$ 231.0740, found 231.0757.

Gram-scale hydration (Scheme 3). To a 30 mL test tube with a screw cap, a magnetic stirring bar and catalyst precursor (657 mg, 1.2 wt % Ru), deaerated H_2O (13 mL) was added under a N_2 atmosphere. Under vigorous stirring, a solution [4.9 mL; a mixture of $NaBH_4$ (82.1 mg, 2.2 mmol) and deaerated H_2O (10.9 mL)] was introduced dropwise to the test tube. The mixture was stirred at rt for 3.5 h. The liquid phase was separated by centrifugation (3500 rpm, 5 min) and replaced with H_2O (13 mL) via syringe. After the mixture was stirred at rt overnight, the solid was washed with water (2 times) and dried *in vacuo* at rt for 2 h to afford Ru/chitin as a grey solid. To

this Ru/chitin in the test tube were added **1w** (16.3 mmol, 1.16 g) and deaerated H_2O (7.2×10^2 mmol, 13 mL) under a N_2 atmosphere. After this the septum inlet was replaced with plastic screw cap and the cap was wrapped with Teflon tape. The mixture was then shaken at 120 °C for 36 h (*ca.* 100 rpm). After cooling with ice water, the catalyst was removed by filtration and washed with methanol (300 mL). The solvent was concentrated *in vacuo*. The product was purified by short-column chromatography on silica gel (ethyl acetate only) to afford **2w** as colorless needles (1.34 g, 92% yield).

Reuse experiment. As per the typical procedure, Ru/chitin (0.023 mmol Ru) was prepared in a screw-cap 10 mL test tube equipped with a rubber septum and a magnetic stirring bar. To this tube was added nitrile **1a** (1.01 mmol, 104.1 mg) and deaerated H_2O (2.2×10^2 mmol, 4.0 mL) under a N_2 atmosphere. After this septum inlet was replaced with a plastic screw cap and the cap was wrapped with Teflon tape. The mixture was shaken at 120 °C for 20 h (*ca.* 100 rpm). The mixture was cooled down with ice water, mixed with deaeraed H_2O (4 mL) under a N_2 atmosphere, and stirred at 100 °C for 1 min. The liquid phase was separated by centrifugation (3500 rpm, 3 min). Extraction of the product was carried out by repeating this process (deaerated H_2O, 7×4 mL). The combined liquid phases were concentrated *in vacuo*. ^{1}H NMR analysis of this crude mixture using mesitylene as an internal standard indicated the formation of **2a** in 95% yield. Ru/chitin in the test tube was directly reused for the next run [conditions: **1a** (1.04 mmol, 107.2 mg), deaerated H_2O (2.2×10^2 mmol, 4.0 mL) and the reused catalyst at 120 °C for 20 h under a N_2 atmosphere]. ^{1}H NMR analysis of this crude mixture showed the formation of **2a** in 87% yield.

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Notes and references

[a] Graduate School of Science 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

[c] Institute for Advanced Research, Nagoya University, Chikusa, Nagoya 464-8601, Japan

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