Supporting Information

Rhodium on Carbon-Catalyzed Hydrogen Scavenger- and Oxidant-free Dehydrogenation of Alcohols in Aqueous Media

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1. General information

10% Pt/C, Pd/C, Ru/C and Rh/C were supplied by the N. E. Chemcat Corporation (Tokyo, Japan). Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX 400, AL 400 or ECA 500 spectrometer at room temperature in $CDCl_3$ as a solvent and internal standard (^{1}H NMR: δ = 7.27; ^{13}C NMR: δ = 77.0) with tetramethylsilane as an internal standard. IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high resolution mass spectra (HRMS) were measured by a Shimazu hybrid IT-TOF mass spectrometer.

2. General procedure for dehydrogenation of secondary alcohols.

A mixture of *sec*-Alcohol (0.25 mmol), 10 % Rh/C (51.2 mg, 20 μmol), Na_2CO_3 (29.1

mg, 0.28 mmol or 58.2 mg, 0.55 mmol) and H_2O (1 mL) in 15 mL-test tube was stirred at 100 ^oC under argon atmosphere using a personal organic synthesizer (Chemistation, EYELA, Tokyo). After stirring for appropriate time, the mixture was filtrated through a membrane filter (Millipore, Millex-LH, 0.45 μm) to remove Rh/C. The filtrate was extracted with AcOEt (10 mL) and H_2O (10 mL), then the aqueous layer was further extracted with AcOEt (10 mL × 4). The combined organic layers were dried over anhydrous $MgSO_4$, filtrated and concentrated in vacuo. (The residue was purified by silicagel column chromatography using hexane/EtOAc as an eluent, if necessary.)

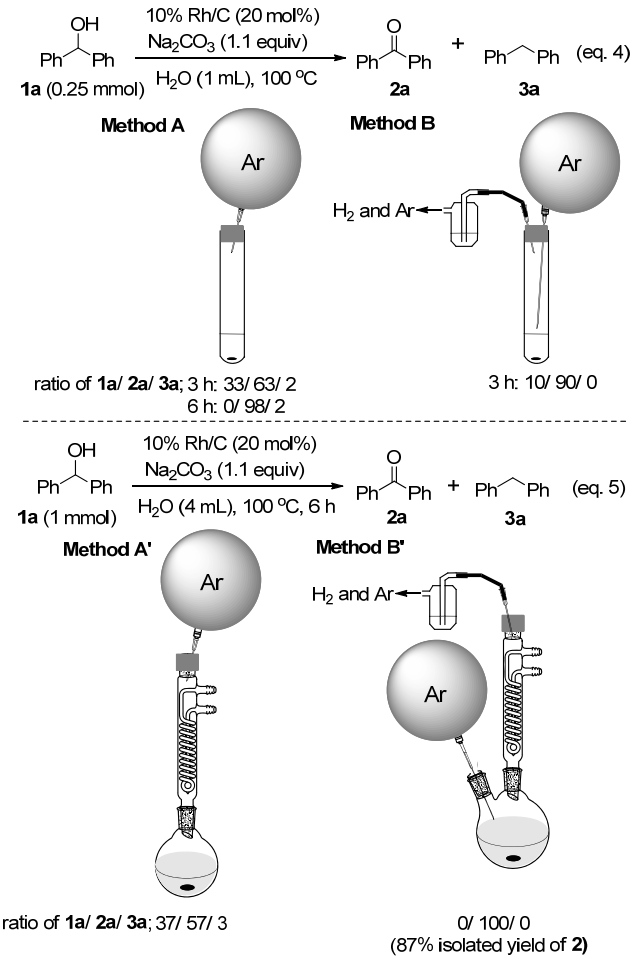
3. General procedure for dehydrogenation of primary alcohols.

A mixture of *pri*-Alcohol (0.25 mmol), 10 % Rh/C (51.2 mg, 20 μmol), NaOH (22.9 mg, 0.55mmol) and H_2O (1 mL) in 15 mL-test tube was stirred at 100 ^oC under argon atmosphere using a personal organic synthesizer (Chemistation, EYELA, Tokyo). After stirring for appropriate time, the reaction mixture was quenched with 1N H_2SO_4 aq. and passed through a membrane filter (Millipore, Millex-LH, 0.45 μm) to remove Rh/C. The filtrate was extracted with diethyl ether (10 mL) and H_2O (10 mL), then the aqueous layer was further extracted with diethyl ether (10 mL × 4). The combined organic layers were dried over anhydrous $MgSO_4$, filtrated and concentrated in vacuo. (The residue was purified by silicagel column chromatography using *n*-hexane/EtOAc as an eluent, if necessary.)

4. Reactivity difference in test-tube and flask

When the reactions shown in Tables 1-5 of the manuscript were carried out using 0.25 mmol of the substrate in 15 mL-test tube and stirred using a personal organic synthesizer (eq. 4, Method A), in situ-generated hydrogen did not so affect on the undesirable (reverse) reduction of the generated ketone into the original alcohol. In reuse test, we attempted the scale-up using 1 mmol of substrate due to the technical easiness to recover the Rh/C catalyst. Consequently, the depression of the reactivity was obviously observed when using a round-bottomed flask attached to a reflux condenser as a reaction apparatus (eq. 5, Method A'). Therefore, we revised the reaction system using the argon flow to remove the generated hydrogen gas from the inside of reaction apparatus (Methods B and B'). In comparison with Methods A and B in the dehydrogenation of **1a** (0.25 mmol) in test tube for 3 h, the argon flow system could effectively enhance the dehydrogenation efficency (eq. 4). The scale up under the argon flow using a two-necked flask could be accomplished to give only the desired ketone

for 6 h in good yield (eq. 5, Method B'). Therefore, the reuse test in Table 6 of manuscript was carried out using Method B'.



5. Reuse test

A mixture of benzhydrol (184.3 mg, 1.0 mmol), 10 % Rh/C (204.8 mg, 80 μmol), Na_2CO_3 (116.4 mg, 1.1 mmol) and H_2O (4.0 mL) in a two-necked flask was stirred for 6 h at 100 °C under argon atmosphere (Method B'). The mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 60 mm] and the catalyst was washed with H_2O (20 mL × 5) and EtOAc (20 mL × 5). The filtrate was separated into organic and aqueous layers and the aqueous layer was extracted with EtOAc (30 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silicagel (*n*-hexane/EtOAc, 20/1) to give benzophenone.

The filtered catalyst was further washed with methanol (100 mL) and water (50 mL), and dried in vacuo for 12 h, then the recovered catalyst was reused for the next run.

6. Analysis of metal-leaching

A mixture of benzhydrol (921.0 mg, 5.0 mmol), 10 % Rh/C (1024 mg, 0.4 mmol), Na_2CO_3 (582 mg, 5.5 mmol) and H_2O (20.0 mL) in a two necked flask was stirred for 12 h at 100 ^oC under argon atmosphere (Method B' described in section 4). The mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 40 mm] and the catalyst was washed with H_2O (20 mL × 5) and EtOAc (20 mL × 5). The filtrate was separated into organic and aqueous layers, and the aqueous layer was further extracted with EtOAc (30 mL × 5). The combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The organic layer was dissolved with EtOAc, and the aqueous layer was diluted with H_2O to 100 mL, respectively. The Rh leaching in each layers was investigated by ICP-OES analysis using SPS5520 (SII Nano Technology, Tokyo, Japan). Consequently, < 1 ppm of meal leaching was observed in each layers.

7. Spectroscopic data of products

Benzophenone (2a): ^{1}H NMR (500 MHz, $CDCl_3$); δ 7.81 (d, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 4H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 1.

Acetophenone (2b): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.46 (dt, *J* = 8.0, 7.8, 2H), 2.61 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 1.

1-Phenylpenten-1-one (2c): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.97—7.95 (m 2H), 7.56—7.54 (m, 1H), 7.47—7.44 (m, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 1.76—1.68 (m, 2H), 1.44—1.38 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 2.

2,2-Dimetylpropiophenone (2d): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.69—7.67 (m, 2H), 7.45—7.37 (m, 3H), 1.35 (s, 9H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 3.

Cyclopropylphenylketone (**2ea**) and *n*-propylphenylketone (**2eb**) were obtained as inseparable mixture.

Cyclopropylphenylketone (2ea): ^{1}H NMR (400MHz, $CDCl_3$); δ 8.03—8.01 (m, 2H) 7.58—7.55 (m, 1H), 7.50—7.46 (m, 2H), 2.71—2.65 (m, 1H), 1.30—1.20 (m, 2H), 1.09—1.02 (m, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 3.

***n*-Propylphenylketone (2eb)**: ^{1}H NMR (400MHz, $CDCl_3$); δ 7.97—7.95 (m, 2H), 7.57—7.53 (m,1H), 7.48—7.43 (m, 2H), 2.97 (t, *J*= 7.4 Hz, 2H), 1.82—1.73 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 4.

α-Tetrarone (2f): ^{1}H NMR (500 MHz, $CDCl_3$); δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.47 (dt, *J* = 8.0, 7.5 Hz, 1H), 7.34—7.22 (m, 2H), 2.97 (t, *J* = 6.5 Hz, 2H), 2.66 (t, *J* = 6.5 Hz, 2H), 2.17—2.12 (quintet, *J* = 6.5 Hz, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 3.

Fluorene-9-one(2g): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.54—7.47 (m, 4H), 7.32—7.24 (m, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 5.

4,4'-Dimethoxybenzophenone (2h): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.79 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4 H), 3.89 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 6.

4,4'-Dichlorobenzophenone (2i): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.73 (d, *J* = 8.8 Hz, 4H), 7.47 (d, *J* = 8.8 Hz, 4H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 7.

4,4'-Difluorobenzophenone (**2ja**) and 4-fluorobenzophenone (**2jb**) were obtained as inseparable mixture.

4,4'-Difluorobenzophenone (2ja):^{1}H NMR (400 MHz, $CDCl_3$); δ 7.82 (m, 4H), 7.17 (m, 4H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 8.

4-Fluorobenzophenone (2jb): ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.86—7.83 (m, 2H), 7.78—7.76 (m, 2H), 7.62—7.57 (m, 1H), 7.50—7.47 (m, 2H), 7.19—7.14 (m, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 4.

3-Decanone (2k): ^{1}H NMR (400MHz, $CDCl_3$); δ 2.45—2.37 (m, 4H), 1.59—1.50 (m, 2H), 1.30—1.24 (m, 8H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H). Spectroscopic data of ^{1}H NMR was identical to commercial 3-decanone (TCI).

4-Cyclohexylcyclohexanone (2l): ^{1}H NMR (400 MHz, $CDCl_3$); δ 2.40—2.25 (m, 4H), 2.03—1.99 (m, 2H), 1.77—1.61 (m, 5H), 1.57—1.41 (m, 3H), 1.28—1.07 (m, 4H), 1.07—0.95 (m, 2H) . Spectroscopic data of ^{1}H NMR was identical to that of the reference 9.

Propiophenone (2m):^{1}H NMR (500 MHz, $CDCl_3$); δ 7.98—7.94 (m, 2H), 7.57—7.52 (m, 1H), 7.48—7.43 (m, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 10.

11-Phenylmethoxy-2-undecanone (2n): Colorless oil; IR (ATR) cm^{-1}: 2926, 2852, 1714, 1453, 1359, 1160, 1099, 1027; ^{1}H NMR (500 MHz, $CDCl_3$); δ 7.36—7.27 (m, 5H), 4.50 (s, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.63—1.55 (m, 4H), 1.35—1.28 (m, 10H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 209.5, 138.6, 128.3, 127.5, 127.4, 72.8, 70.5, 43.8, 29.9, 29.8, 29.7, 29.4, 29.3, 29.1, 26.1, 23.8; ESI-HRMS m/z: 277.2158 ($[M+H]^+$); Calcd for $C_{18}H_{29}O_2$: 277.2162.

11-Phenylmethoxy-undecanophenone (2o):Yellow oil; IR (ATR) cm^{-1}: 3061, 3034, 2926, 2912, 2849, 2791, 1681, 1579, 1494, 1449, 1407, 1362, 1305, 1277, 1245, 1212, 1190, 1113, 1075, 1024, 1001; ^{1}H NMR (500MHz, $CDCl_3$); δ 7.95 (d, *J* = 7.5, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.35—7.26 (m, 5H), 4.50 (s, 2H), 3.46 (t, *J* = 6.5 Hz, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 1.75—1.70 (m, 2H), 1.64—1.58 (m, 4H), 1.35—1.30 (m, 10H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 200.6, 138.6, 137.0, 132.8, 128.5, 128.3, 128.0, 127.6, 127.4, 72.8, 70.4, 38.6, 29.7, 29.5, 29.4, 29.3, 26.1, 24.3; ESI-HRMS m/z: 339.2312 ($[M+H]^+$); Calcd for $C_{23}H_{31}O_2$: 339.2319.

Decanoicacid (8a): ^{1}H NMR (500MHz, $CDCl_3$); δ 2.35 (t, *J*= 7.8 Hz, 2H), 1.64—1.60 (m, 2H), 1.29—1.26 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 11.

6-Phenylhexanoic acid (8b): ^{1}H NMR (500 MHz, $CDCl_3$); δ 7.36—7.17 (m, 5H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.71—1.62 (m, 4H), 1.43—1.37 (m, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 12.

Benzoicacid (8c): ^{1}H NMR (400MHz, $CDCl_3$); δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 6.5 Hz, 1H), 7.49 (dd, *J* = 8.0, 6.5 Hz, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 13.

4-Butylbenzoic acid (8d):^{1}H NMR (400MHz, $CDCl_3$); δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 1.66—1.58 (m, 2H), 1.38—1.34 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 14.

4-Methoxybenzoic acid (8e): ^{1}H NMR (400MHz, $CDCl_3$); δ 7.91(d, *J* = 9.0 Hz, 2H), 7.03(d, *J* = 9.0 Hz, 2H), 3.83(s, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 14.

8. References

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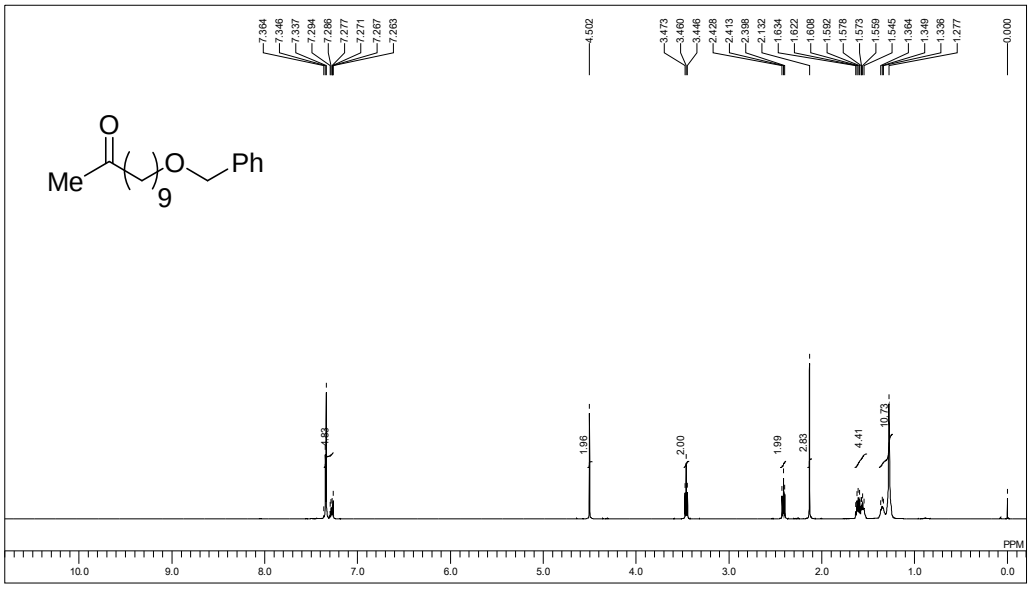
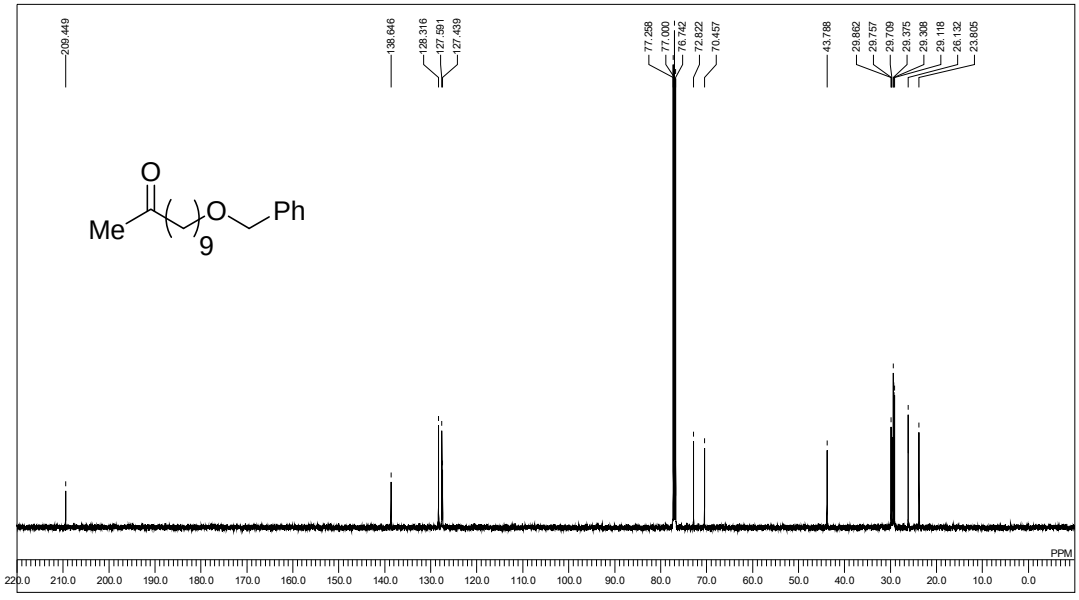
9. ^{1}H and ^{13}C NMR spectra of newly synthesized compounds

^{1}H NMR of 11-phenylmethoxy-2-undecanone (**2n**)



^{13}C NMR of 11-phenylmethoxy-2-undecanone (**2n**)



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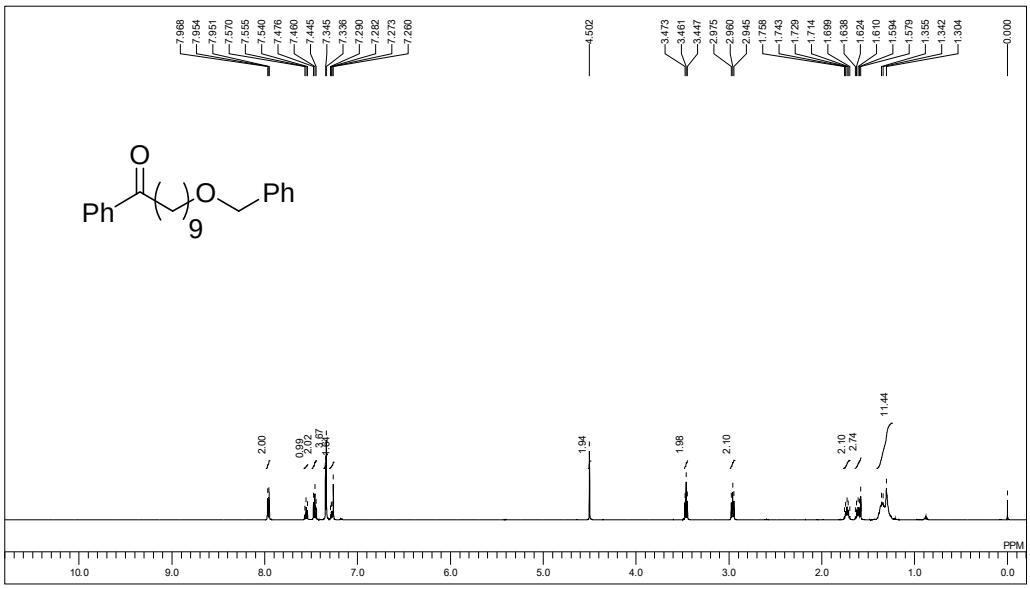

^{13}C NMR of 11-phenylmethoxy-undecanophenone (**2o**)