Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Functional Group-Selective Poisoning of Molecular Catalysts: Ruthenium Cluster-Catalysed Highly Amide-Selective Silane Reduction Which Does not Affect Ketones or Esters

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General Methods: All reactions were carried out under a nitrogen or argon atmosphere. Dehydrated benzene, toluene and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Ltd., and used as received. 1,4-Dioxane and tetrahydropyran (THP) were distilled under an inert atmosphere from sodium/benzophenone prior to use. Pivaloyl chloride, benzylmethylamine, and triethylamine were purchased from Kanto Chemical Co., Ltd. Thionyl chloride and dimethylamine were purchased from Kishida Chemical Co., Ltd. Decanoic acid, 6-oxo-heptanoic acid, *p*-acetylbenzoic acid, suberic acid monomethylester, terephthalic acid monomethylester chloride, and dimethylphenylsilane were purchased from Tokyo Chemical Industry Co., Ltd. Column chromatography was performed with alumina (Merck, Art 1097) or silica gel (Merck, Art 7734). ^{1}H and ^{13}C NMR spectra were measured on JEOL GSX-270 (270 MHz) and Lambda 400 (395 MHz) spectrometers. Chemical shifts for ^{1}H NMR were described in parts per million downfield from tetramethylsilane as an internal standard (δ = 0) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.1), unless otherwise noted. IR spectra were measured on a JASCO FT/IR-550 spectrometer. HRMS analysis was performed at the Analytical Center in Institute for Materials Chemistry and Engineering, Kyushu University. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with aluminum oxide (Merck, aluminum oxide 150 F_{254}, neutral) and glass plates precoated with silica gel (Merck, Kieselgel 60 F_{254}). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. (μ_3;η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**) was prepared by the method reported previously.[1]

Synthesis of Carboxamides.

***N,N*-Dimethyldecanamide:**[2] Prepared from decanoyl chloride, which was obtained by the reaction of decanoic acid and $SOCl_2$, and dimethylamine; 73% yield; bp 152 °C/12 Torr; IR (neat) ν 2929, 2854, 1650, 1494, 1396, 1266, 1146, 1105, 722 cm^{-1}; ^{1}H NMR (395 MHz, $CDCl_3$) δ 0.85 (t, *J* = 6.8 Hz, 3H), 1.17-1.38 (m, 12H), 1.62 (m, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 2.92 (s, 3H), 2.98 (s, 3H). ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 14.1, 22.7, 25.3, 29.3, 29.51, 29.52, 29.56, 31.9, 33.5, 35.4, 37.3, 173.3.

N*-Benzyl-*N*-methyl-6-oxo-heptanamide (2a):** Prepared from 6-oxo-heptanoic acid and pivaloyl chloride followed by the reaction with benzylmethylamine; 66% yield; IR (neat) ν 2939, 1713, 1651, 1453, 1359, 1264, 1119, 1076, 736, 701 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{21}NO_2$ 247.1572, found 247.1574. Spectroscopic data of this amide were obtained as a mixture of two rotational isomers (*ca*. 6:4). ***major isomer: ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.54-1.87 (m, 4H), 2.17 (s, 3H), 2.36-2.63 (m, 4H), 4.61 (s, 2H), 7.13-7.49 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.5, 24.5, 29.9, 33.2, 34.7, 43.5, 50.7, 126.2, 127.9, 128.5, 137.4, 172.6, 208.8. ***minor isomer:*** ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.54-1.87 (m, 4H), 2.14 (s, 3H), 2.36-2.63 (m, 4H), 4.55 (s, 2H), 7.13-7.49 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.4, 24.7, 29.8, 32.7, 33.9, 43.4, 53.2, 127.2, 127.5, 128.9, 136.6, 173.0, 208.7.

***N,N*-Dimethyl-7-methyl-6-oxo-octanamide (2b):** Prepared from 7-methyl-6-oxooctanoly chloride, which was obtained by the reaction of 7-methyl-6-oxooctanoic acid[3] and $SOCl_2$, and dimethylamine; 43% yield; IR (neat) ν 2944, 1713, 1644, 1469, 1397, 1265, 1140, 1090 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (d, *J* = 6.9 Hz, 6H), 1.44-1.72 (m, 4H), 2.28 (m, 2H), 2.44 (m, 2H), 2.55 (sept, *J* = 6.9 Hz, 1H), 2.89 (bs, 3H), 2.96 (bs, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.3, 23.4, 24.8, 33.2, 35.4, 37.2, 40.1, 40.8, 172.7, 214.6; HRMS (EI) calcd for $C_{11}H_{21}NO_2$ 199.1572, found 199.1571.

p*-Acetyl-*N*-benzyl-*N*-methylbenzamide (2c):** Prepared from *p*-acetylbenzoic acid and pivaloyl chloride followed by the reaction with benzylmethylamine; 37% yield; IR (KBr) ν 2928, 1684, 1633, 1507, 1453, 1402, 1359, 1265, 1080, 1016, 960, 847, 736 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{17}NO_2$ 267.1259, found 267.1261. Spectroscopic data of this amide were obtained as a mixture of two rotational isomers (*ca*. 1:1). ***isomer 1: ^{1}H NMR (395 MHz, $CDCl_3$) δ 2.60 (s, 3H), 2.82 (s, 3H), 4.74 (s, 2H), 7.29 (d, *J* = 6.8 Hz, 2H), 7.30-7.41 (m, 3H), 7.52 (m, 2H), 7.98 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.6, 36.7, 50.7, 126.9, 127.1, 127.7, 128.4, 128.7, 136.6, 137.6, 140.6, 171.1, 197.3.). ***isomer 2:*** ^{1}H NMR (395 MHz, $CDCl_3$) δ 2.57 (s, 3H), 3.04 (s, 3H), 4.45 (s, 2H), 7.13 (d, *J* = 6.8 Hz, 2H), 7.30-7.41 (m, 3H), 7.52 (m, 2H), 7.94 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.6, 33.1, 54.9, 126.5, 127.7, 128.1, 128.4, 128.9, 136.1, 137.6, 140.5, 170.4, 197.2.

***N,N*-Dimethyl-7-carbomethoxyheptanamide (3a).**[4] Prepared from suberic acid monomethyl ester chloride, which was obtained by the reaction of suberic acid monomethyl ester and $SOCl_2$, and dimethylamine; 64% yield; 123 °C/1 mmHg; IR (neat) ν 2936, 2858, 1738, 1644, 1504, 1435, 1397, 1259, 1171, 1089, 1013, 922, 880, 731 cm^{-1}; ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.26-1.38 (m, 4H), 1.53-1.67 (m, 4H), 2.23-2.33 (m, 4H), 2.91 (bs, 3H), 2.97 (bs, 3H), 3.63 (s, 3H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 24.8, 25.0, 29.0, 29.1, 33.3, 34.0, 35.4, 37.3, 51.5, 173.1, 174.2;

***N*-Benzyl-*N*-methyl-7-carbomethoxyheptanamide (3b):** Prepared from suberic acid monomethyl ester and pivaloyl chloride followed by the reaction with benzylmethylamine; 31% yield; IR (neat) ν 2938, 2857, 1738, 1644, 1494, 1454, 1402, 1358, 1257, 1201, 1118, 1078, 733, 700 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{25}NO_3$ 291.1834, found 291.1832; Spectroscopic data of this amide were obtained as a mixture of two rotational

isomers (*ca*. 3:2). ***major isomer:*** ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.23-1.50 (m, 4H), 1.53-1.81 (m, 4H), 2.21-2.47 (m, 4H), 2.90 (s, 3H), 3.66 (s, 3H), 4.59 (s, 3H), 7.11-7.41 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 24.8, 25.0, 29.0, 29.1, 33.5, 34.02, 34.04, 50.8, 51.5, 126.3, 128.0, 128.6, 137.6, 173.1, 174.3. ***minor isomer:*** ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.23-1.50 (m, 4H), 1.53-1.81 (m, 4H), 2.21-2.47 (m, 4H), 2.94 (s, 3H), 3.65 (s, 3H), 4.53 (s, 3H), 7.11-7.41 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 24.8, 25.2, 28.9, 29.1, 33.0, 33.9, 34.9, 51.5, 53.4, 127.3, 127.6, 128.9, 136.8, 173.5, 174.2.

***p*-Carbomethoxy-*N*,*N*-Dimethylbenzamide (3c):**[5] Prepared from terephthalic acid monomethylester chloride and dimethylamine; 61% yield; IR (KBr) ν 2951, 1725, 1626, 1402, 1281, 1112, 864, 729 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.95 (s, 3H), 3.13 (s, 3H), 3.93 (s, 3H), 7.48 (d, *J* = 7.9 Hz, 2H), 8.08 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 35.3, 39.4, 52.4, 127.0, 129.7, 131.0, 140.7, 166.4, 170.6.

Reaction Profiles for Individual Reactions of *N*,*N*-Dimethyldecanamide, *N*,*N*-Dimethylbenzamide, Methyl Decanoate, Methyl benzoate, 2-Undecanone, and Acetophenone in the Absence or Presence of Et_3N: Et_3N Kills the Catalytic Activity towards the Silane Reduction of Methyl Decanoate, Methyl benzoate, 2-Undecanone, and Acetophenone.

In a 5Φ NMR tube was placed (Ace)$Ru_3(CO)_7$ (**1**) (1.32 mg, 0.002 mmol), and the atmosphere was replaced by argon. In a different flask, *N*,*N*-dimethyldecanamide (43 mg, 0.2 mmol), $PhMe_2SiH$ (94 μL, 0.6 mmol), and anisole (22 mg, 0.2 mmol: internal standard) were dissolved in C_6D_6 (0.4 mL). The solution was transferred to the NMR tube containing the catalyst, which was cooled at -78 °C, by syringe. The tube was sealed by flame. After warming up to room temperature, periodical measurements of ^{1}H NMR resulted in determination of the conversion of the starting material. In similar manners, conversion of methyl decanoate, methyl benzoate (at 50 °C), 2-undecanone, and acetophenone were determined, and the results are summarized in Figure S1 and S3. Similar experiments in the presence of Et_3N (28 μL, 0.2 mmol) gave the reaction profiles shown in Figure S2 and S4.

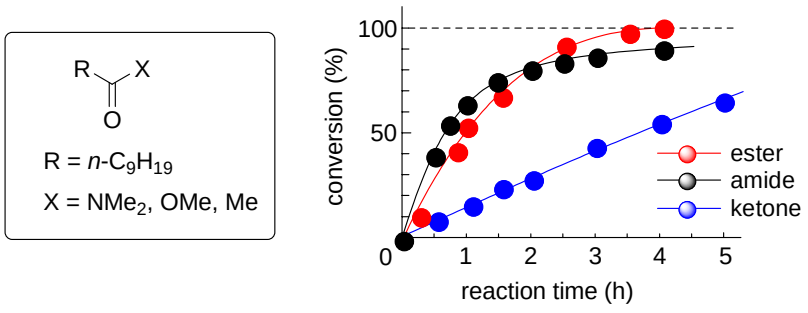


Figure S1. In the absence of Et_3N.

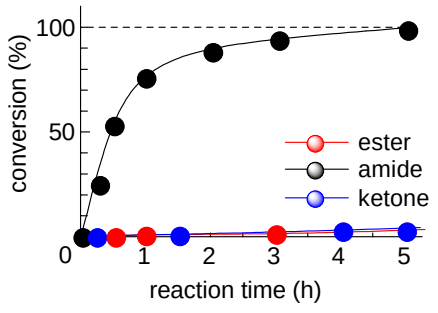
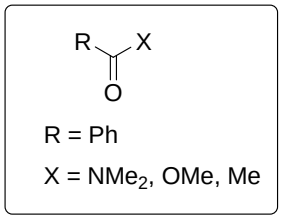


Figure S2. In the presence of Et_3N.



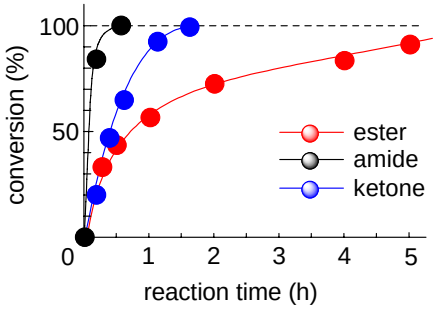


Figure S3. In the absence of Et_3N.

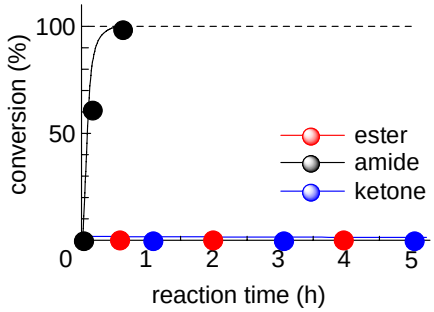


Figure S4. In the presence of Et_3N.

Reaction Profiles for Reductions of a Mixture of *N,N*-Dimethyldecanamide and Methyl Decanoate, or *N,N*-Dimethyldecanamide and 2-Undecanone in the Presence of Et_3N.

Reduction of a mixture of *N,N*-dimethyldecanamide (22 mg, 0.1 mmol) and methyl decanoate (19 mg, 0.1 mmol) was performed with the catalyst **1** (1.32mg, 0.002 mmol) and $PhMe_2SiH$ (47 μL, 0.3 mmol) in the absence of Et_3N. The conversion was determined based on the internal standard (anisole). Since the reduction of the amide produced the catalyst poison (*N,N*-dimethyldecylamine), the amide was selectively reduced as shown in Figure S5. In similar fashion, reduction of a mixture of *N,N*-dimethyldecanamide (22 mg, 0.1 mmol) and 2-undecanone (23 μL, 0.1 mmol) resulted in selective reduction of the amide as shown in Figure S6.

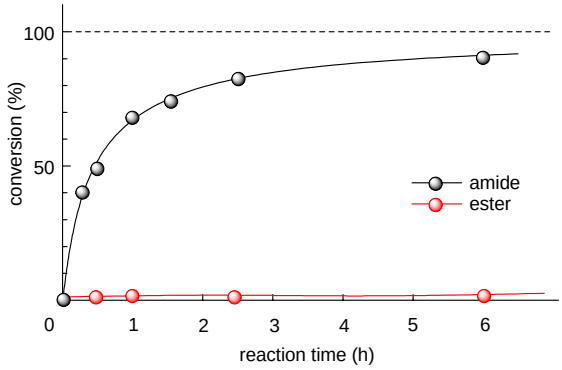


Figure S5. Reduction of amide/ester.

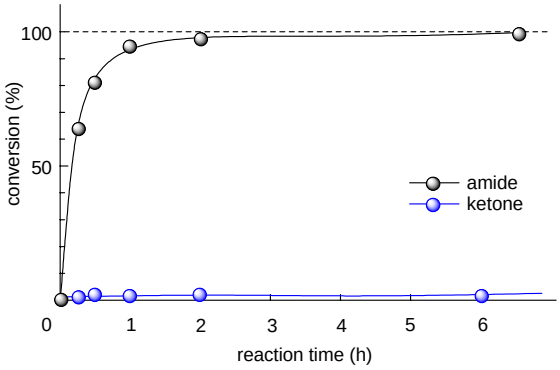


Figure S6. Reduction of amide/ketone.

General Procedure for Selective Reduction of Amide Group in Amido Ester and Amido Ketone Derivatives.

The following three procedures are applied for the selective reduction of organic molecules, in which either amide and ester groups or amide and ketone functions exist in the same molecule. The results are summarized in Table 1 in the text.

***Method A*:** In a 30 mL two-necked flask were placed a stirrer bar and (μ_3,η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ (**1**) (1.0 mol% based on the substrate), and the atmosphere was replaced by argon. A solution of the substrate (1 mmol) and Me_2PhSiH (2.5 or 3.0 mmol) dissolved in 2 mL of toluene (or benzene) was added through a

microsyringe, and the mixture was stirred at room temperature. In some cases, Et_3N (1.0 equiv. based on the substrate) was added to the solution of the substrate and $PhMe_2SiH$ in order to suppress the reduction of keto- or ester functions.

***Method B*:** In a 30 mL two-necked flask were placed a stirrer bar and **1** (1.0 mol% based on the substrate), and the atmosphere was replaced by argon. A small amount of 1,4-dioxane (180 μL) was added for dissolution of the ruthenium catalyst. Addition of Me_2PhSiH (2.5 or 3.0 mmol) resulted in color change from dark orange to yellow in 30 min at room temperature. A solution of the substrate (1 mmol) dissolved in 2 mL of toluene (or benzene) was added through a microsyringe, and the mixture was stirred at room temperature. In some cases, addition of Et_3N (1.0 equiv. based on the substrate) was preceded by addition of the substrate.

***Method C*:** In a 30 mL two-necked flask were placed a stirrer bar and **1** (1.0 mol% based on the substrate), and the atmosphere was replaced by argon. A small amount of 1,4-dioxane or THP (180 μL) was added for dissolution of the ruthenium catalyst. Addition of Me_2PhSiH (2.5 or 3.0 mmol) resulted in color change from dark orange to yellow in 30 min at room temperature. The substrate (1 mmol: neat) was added through a microsyringe, and the mixture was stirred at room temperature. In some cases, addition of Et_3N (1.0 equiv. based on the substrate) was preceded by addition of the substrate.

In all cases, the reaction was monitored by TLC, and was quenched by the addition of methanol (*ca.* 0.5 mL) as soon as the spot due to the starting material disappeared. After removal of the solvent *in vacuo*, the residue was purified by alumina column to give the desired product in good yield and high selectivity.

Selective Reduction of *N*-Benzyl-*N*-methyl -6-oxo-heptanamide 2a.

Method A (Table 1, entry 1): The following quantities of compounds were used: $(ACE)Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), toluene (2 mL), Me_2PhSiH (470 μL, 3.0 mmol), triethylamine (140 μL, 1.0 mmol), and *N*-benzyl-*N*-methyl-6-oxo-heptanamide **2a** (238 mg, 0.97 mmol). The reaction was carried out for 20 h at room temperature to give the desired amine **4a** in 81% yield (182 mg).

Method B (Table 1, entry 2): The following quantities of compounds were used: $(ACE)Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), THP (180 μL), toluene (2 mL), Me_2PhSiH (470 μL, 3.0 mmol), triethylamine (140 μL, 1.0 mmol), and *N*-benzyl-*N*-methyl-6-oxo-heptanamide **2a** (196 mg, 0.8 mmol). The reaction was carried out for 8 h at room temperature to give the desired amine **4a** in 81% yield (150 mg).

Method C (Table 1, entries 3 and 4): The following quantities of compounds were used: $(ACE)Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), THP (180 μL), Me_2PhSiH (470 μL, 3.0 mmol), triethylamine (140 μL, 1.0 mmol), and *N*,*N*-dimethyl-7-carbomethoxyheptanamide **2a** (235 mg, 0.96 mmol). The reaction was carried out for 1 h at room temperature to give the desired amine in 72% yield (160 mg). The product was available in somewhat better yields with 2.5 equiv. of $PhMe_2SiH$ based on the keto-amide: $(ACE)Ru_3(CO)_7$ (3.25 mg, 0.005 mmol), THP (90 μL), Me_2PhSiH (200 μL, 1.3 mmol), triethylamine (70 μL, 0.5 mmol), and *N*,*N*-dimethyl-7-carbomethoxyheptanamide **2a** (132 mg, 0.53 mmol). The reaction was carried out for 1 h at room temperature to give the desired amine **4a** in 91% yield (114 mg).

7-(*N*-Benzyl-*N*-methylamino)heptan-2-one (4a): ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.31 (m, 2H), 1.51 (m, 2H), 1.57 (m, 2H), 2.13 (s, 3H), 2.17 (s, 3H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 3.46 (s, 2H), 7.19-7.35 (m, 5H). ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 23.8, 27.0, 27.3, 30.0, 42.3, 43.8, 57.3, 62.4, 126.9, 128.2, 129.1, 139.3, 209.3. IR (neat) ν 2943, 2789, 1714, 1602, 1495, 1454, 1359, 1267, 1165, 1126, 1075, 1026, 909, 863, 740, 700 cm^{-1}. MS (EI) m/z = 233 (M^+), 190 (M^+-Ac), 176 (M^+-CH_2Ac), 134 (CH_2NBnMe), 120 (NBnMe), 91 (Bn). HRMS (EI) calcd for $C_{15}H_{23}NO$ 233.1780, found 233.1783.

Selective Reduction of *N,N*-Dimethyl-7-methyl-6-oxo-octanamide 2b.

Method C (Table 1, entry 5): The following quantities of compounds were used: (ACE)$Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), THP (180 μL), Me_2PhSiH (390 μL, 2.5 mmol), triethylamine (140 μL, 1.0 mmol), and *N,N*-dimethyl-7-methyl-6-oxo-pentanamide **2b** (194 mg, 0.97 mmol). The reaction was carried out for 1.5 h at room temperature to give the desired amine **4b** in 94% yield (169 mg).

8-*N,N*-Dimethylamino-2-methyloctan-3-one (4b): ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.08 (d, *J* = 6.9 Hz, 6H), 1.29 (m, 2H), 1.47 (m, 2H), 1.58 (m, 2H), 2.22 (s, 6H), 2.26 (t, *J* = 7.3 Hz, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 2.58 (sept, *J* = 6.9 Hz, 1H). ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 18.2, 23.6, 27.1, 27.5, 40.2, 40.8, 45.4, 59.6, 214.8. IR (neat) ν 2982, 2816, 2763, 1713, 1469, 1383, 1265, 1098, 1041, 834 cm^{-1}. MS (EI) m/z = 185 (M^+), 170 (M^+-Me), 142 (M^+-$CHMe_2$), 114 (M^+-Me_2CHCO), 100 (M^+-$Me_2CHCOCH_2$). HRMS (EI) calcd for $C_{11}H_{23}NO$ 185.1780, found 185.1783.

Selective Reduction of *p*-Acetyl-*N*-benzyl-*N*-methylbenzamide 2c.

Method B (Table 1, entry 6): The following quantities of compounds were used: (ACE)$Ru_3(CO)_7$ **1** (3.26 mg, 0.005 mmol), THP (90 μL), toluene (1 mL), Me_2PhSiH (240 μL, 1.75 mmol), triethylamine (70 μL, 0.5 mmol), and *p*-acetyl-*N*-benzyl-*N*-methylbenzamide **2c** (134 mg, 0.5 mmol). The reaction was carried out for 18 h at room temperature to give the desired amine **4c** in 88% yield (112 mg).

***p*-(*N*-Benzyl-*N*-methylaminomethyl)acetophenone (4c):** ^{1}H NMR (395 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.51 (s, 3H), 3.44 (s, 2H), 3.47 (s, 3H), 7.12-7.30 (m, 5H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 26.6, 42.3, 61.4, 61.9, 127.1, 128.2, 128.3, 128.8 (2C), 136.0, 139.0, 145.2, 197.8. IR (neat) ν 2945, 2788, 1682, 1573, 1495, 1454, 1411, 1359, 1267, 1176, 1132, 1074, 1016, 955, 910, 871, 814, 742, 699 cm^{-1}. MS (EI) m/z = 253 (M^+), 238 (M^+-Me), 210 (M^+-Ac), 176 (M^+-Ph), 152 (M^+-Bn), 133 (M^+-NBnMe), 119 (M^+-CH_2NBnMe), 91 (Bn). HRMS (EI) calcd for $C_{17}H_{19}NO$ 253.1467, found 253.1467.

Selective Reduction of *N,N*-Dimethyl-7-Carbomethoxyheptanamide 3a.

Method A (Table 1, entry 7): The following quantities of compounds were used: (ACE)$Ru_3(CO)_7$ (6.51 mg, 0.01 mmol), benzene (2 mL), Me_2PhSiH (470 μL, 3.0 mmol), and *N,N*-dimethyl-7-carbomethoxyheptanamide **3a** (203 mg, 0.94 mmol). The reaction was carried out in the absence of Et_3N for 6 h at room temperature to give the desired amine **5a** in 88% yield (167 mg).

Method B (Table 1, entry 8): The following quantities of compounds were used: (ACE)$Ru_3(CO)_7$ **1** (6.51 mg,

0.01 mmol), THP (180 μL), benzene (2 mL), Me_2PhSiH (470 μL, 3.0 mmol), and *N*,*N*-dimethyl-7-carbomethoxyheptanamide **3a** (203 mg, 0.94 mmol). The reaction was carried out in the absence of Et_3N for 1.5 h at room temperature to give the desired amine **5a** in 91% yield (186 mg).

Method C (Table 1, entry 9): The following quantities of compounds were used: $(ACE)Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), 1,4-dioxane (180 μL), Me_2PhSiH (470 μL, 3.0 mmol), and *N*,*N*-dimethyl-7-carbomethoxyheptanamide **3a** (233 mg, 1.08 mmol). The reaction was carried out in the absence of Et_3N for 30 min at room temperature to give the desired amine **5a** in 87% yield (206 mg).

Methyl 8-(*N*,*N*-dimethylamino)octanoate (5a): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.20-1.37 (m, 6H), 1.44 (m, 2H), 1.61 (m, 2H), 2.20 (s, 6H), 2.21 (t, *J* = 6.4 Hz, 3H), 2.29 (t, *J* = 7.6 Hz, 3H), 3.66 (s, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 24.6, 27.0, 27.4, 28.8, 28.9, 33.7, 45.2, 51.1, 59.6, 173.8. IR (neat) ν 2933, 2857, 2762, 1744, 1462, 1361, 1171, 1099, 1042, 844 cm^{-1}. MS (EI) m/z = 201 (M^+), 186 (M^+-Me), 171 (M^+-Me_2), 170 (M^+-OMe), 142 (M^+-CO_2Me), 114 (M^+-$(CH_2)_2CO_2Me$), 100 (M^+-$(CH_2)_3CO_2Me$). HRMS (EI) calcd for $C_{11}H_{23}NO_2$ 201.1729, found 201.1730.

Selective Reduction of *N*-Benzyl-*N*-methyl-7-carbomethoxyheptanamide 3b.

Method C (Table 1, entry 10): The following quantities of compounds were used: $(ACE)Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), 1,4-dioxane (180 μL), Me_2PhSiH (470 μL, 3.0 mmol), and *N*,*N*-dimethyl-7-carbomethoxyheptanamide **3b** (304 mg, 1.04 mmol). The reaction was carried out in the absence of Et_3N for 30 min at room temperature to give the desired amine **5b** in 96% yield (278 mg).

Methyl 8-(*N*-benzyl-*N*-methylamino)octanoate (5b): ^{1}H NMR (395 MHz, $CDCl_3$) δ 1.25-1.37 (m, 6H), 1.50 (m, 2H), 1.61 (m, 2H), 2.17 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 3.46 (s, 2H), 3.66 (s, 3H), 7.20-7.35 (m, 5H). ^{13}C NMR (99.4 MHz, $CDCl_3$) δ 24.8, 27.2, 27.3, 29.0, 29.1, 34.0, 42.2, 51.3, 57.4, 62.3, 126.7, 128.1, 129.0, 139.3, 174.2. IR (neat) ν 2931, 2855, 2788, 1740, 1171, 737, 699 cm^{-1}. MS (EI) m/z = 277 (M^+), 262 (M^+-Me), 246 (M^+-OMe), 218 (M^+-CO_2Me), 204 (M^+-CH_2CO_2Me), 200 (M^+-Ph), 190 (M^+-$(CH_2)_2CO_2Me$), 186 (M^+-Bn). HRMS (EI) calcd for $C_{17}H_{27}NO_2$ 277.2042, found 277.2042.

Selective Reduction of *p*-Carbomethoxy-*N*,*N*-dimethylbenzamide 3c.

Method B (Table 1, entry 11): The following quantities of compounds were used: $(ACE)Ru_3(CO)_7$ **1** (6.51 mg, 0.01 mmol), THP (180 μL), toluene (2 mL), Me_2PhSiH (470 μL, 3.0 mmol), and *p*-carbomethoxy-*N*,*N*-dimethylbenzamide **3c** (203 mg, 0.98 mmol). The reaction was carried out in the absence of Et_3N for 3.5 h at room temperature to give the desired amine **5c** in 81% yield (157 mg).

Methyl *p*-(*N*,*N*-dimethylaminomethyl)benzoate (5c):[6] ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.24 (s, 6H), 3.46 (s, 2H), 3.91 (s, 3H), 7.38 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 45.4, 51.9, 63.9, 128.8, 128.9, 129.5, 144.3, 166.9. IR (neat) ν 2948, 2816, 2769, 1726, 1611, 1435, 1414, 1361, 1280, 1173, 1146, 1110, 1019, 968, 865, 757, 700 cm^{-1}. MS (EI) m/z = 193 (M^+), 178 (M^+-Me), 162 (M^+-OMe), 149 (M^+-NMe_2), 135 (M^+-CH_2NMe_2), 134 (M^+-CO_2Me).

Application: Reduction of a Mixture of Amine and Ketone or Ester.

Reduction of a Mixture of Amide and Ketone (Amide/Ketone = 1:5): To a stirred solution of (μ_3,η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ **1** (33 mg, 0.05 mmol) in a small amount of tetrahydropyran (900 μL) was added Me_2PhSiH (2.4 mL, 15 mmol) at room temperature. After it was stirred for 30 min at that temperature, the color of the solution changed from dark orange to yellow. After addition of Et_3N (700 μL, 5.0 mmol) to the catalyst solution, a mixture of the *N*,*N*-dimethyldecanamide (1.08 g, 5.0 mmol) and 2-heptanone (2.9 g, 25 mmol) was added through a syringe, and the mixture was stirred for 2 h at room temperature. The reaction was monitored by TLC, and was quenched by the addition of methanol as soon as the spot due to the amide disappeared. After removal of the solvents under reduced pressure, the residue was dissolved in Et_2O (30 mL). The resultant solution was washed with aqueous HCl, dried over Na_2SO_4, and then concentrated under reduced pressure. Purification by vacuum distillation (68 °C/28 Torr) gave unreacted 2-heptanone in 70% yield (2.0 g). While combined aqueous layers were treated with aqueous $NaHCO_3$, then the resultant basic solution was extracted with Et_2O, and combined organic layers were dried over Na_2SO_4. The solvent was removed by evaporation to give *N*,*N*-dimethyldecanamide in 79% yield (0.80 g). ***N*,*N*-Dimethyldecylamine:**[7] ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.6 Hz, 3H), 1.11-1.39 (m, 14H), 1.43 (m, 2H), 2.19 (s, 6H), 2.21 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.2, 22.8, 27.6, 27.9, 29.4, 29.67, 29.70, 29.72, 32.0, 45.6, 60.1. IR (neat) ν 2936, 2858, 1738, 1644, 1504, 1435, 1397, 1259, 1171, 1089, 1013, 922, 731 cm^{-1}.

Reduction of a Mixture of Amide and Ketone (Amide/Ketone = 5:1): To a stirred solution of (μ_3,η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ **1** (65 mg, 0.1 mmol) in a small amount of tetrahydropyran (1.8 mL) was added Me_2PhSiH (3.4 mL, 22 mmol) at room temperature. After it was stirred for 30 min at that temperature, the color of the solution changed from dark orange to yellow. After addition of Et_3N (1.4 mL, 10 mmol) to the catalyst solution, a mixture of the *N*,*N*-dimethyldecanamide (2.16 g, 10 mmol) and 2-heptanone (230 mg, 2 mmol) was added through a syringe, and the mixture was stirred for 2 h at room temperature. The reaction was monitored by TLC, and was quenched by the addition of methanol as soon as the spot due to the amide disappeared. After removal of the solvents under reduced pressure, the residue was dissolved in Et_2O (30 mL). The resultant solution was washed with aqueous HCl, dried over Na_2SO_4, and then concentrated under reduced pressure. Purification by silica gel column chromatography (*n*-hexane, then *n*-hexane/Et_2O = 8:1) gave unreacted 2-heptanone in 75% yield (170 mg). While combined aqueous layers were treated with aqueous $NaHCO_3$, then the resultant basic solution was extracted with Et_2O, and combined organic layers were dried over Na_2SO_4. The solvent was removed by evaporation to give *N*,*N*-dimethyldecanamide in 76% yield (1.53 g).

Reduction of a Mixture of Amide and Ester (Amide/Ester = 1:5): To a stirred solution of (μ_3,η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ **1** (33 mg, 0.05 mmol) in a small amount of tetrahydropyran (900 μL) was added Me_2PhSiH (2.4 mL, 15 mmol) at room temperature. After it was stirred for 30 min at that temperature, the color of the solution changed from dark orange to yellow. After addition of Et_3N (700 μL, 5.0 mmol) to the catalyst solution, a mixture of the *N*,*N*-dimethyldecanamide (1.08 g, 5.0 mmol) and ethyl hexanoate (3.6 g, 25

mmol) was added through a syringe, and the mixture was stirred for 2 h at room temperature. The reaction was monitored by TLC, and was quenched by the addition of methanol as soon as the spot due to the amide disappeared. After removal of the solvents under reduced pressure, the residue was dissolved in Et_2O (30 mL). The resultant solution was washed with aqueous HCl, dried over Na_2SO_4, and then concentrated under reduced pressure. Purification by vacuum distillation (72 °C/25 Torr) gave unreacted ethyl hexanoate in 68% yield (2.46 g). While combined aqueous layers were treated with aqueous $NaHCO_3$, then the resultant basic solution was extracted with Et_2O, and combined organic layers were dried over Na_2SO_4. The solvent was removed by evaporation to give *N*,*N*-dimethyldecanamide in 71% yield (0.82 g).

Reduction of a Mixture of Amide and Ester (Amide/Ester = 5:1): To a stirred solution of (μ_3,η^2;η^3;η^5-acenaphthylene)$Ru_3(CO)_7$ **1** (65 mg, 0.10 mmol) in a small amount of tetrahydropyran (1.8 mL) was added Me_2PhSiH (3.4 mL, 22 mmol) at room temperature. After it was stirred for 30 min at that temperature, the color of the solution changed from dark orange to yellow. After addition of Et_3N (1.4 mL, 10 mmol) to the catalyst solution, a mixture of the *N*,*N*-dimethyldecanamide (2.16 g, 10 mmol) and ethyl hexanoate (288 mg, 2 mmol) was added through a syringe, and the mixture was stirred for 2 h at room temperature. The reaction was monitored by TLC, and was quenched by the addition of methanol as soon as the spot due to the amide disappeared. After removal of the solvents under reduced pressure, the residue was dissolved in Et_2O (30 mL). The resultant solution was washed with aqueous HCl, dried over Na_2SO_4, and then concentrated under reduced pressure. Purification by silica gel column chromatography (*n*-hexane, then *n*-hexane/Et_2O = 8:1) gave unreacted ethyl hexanoate in 66% yield (190 mg). While combined aqueous layers were treated with aqueous $NaHCO_3$, then the resultant basic solution was extracted with Et_2O, and combined organic layers were dried over Na_2SO_4. The solvent was removed by evaporation to give *N*,*N*-dimethyldecanamide in 73% yield (1.48 g).

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