

Reduction of Carboxylic Acid Derivatives Using Diphenylsilane in the Presence of a Rh–PPh_3 Complex

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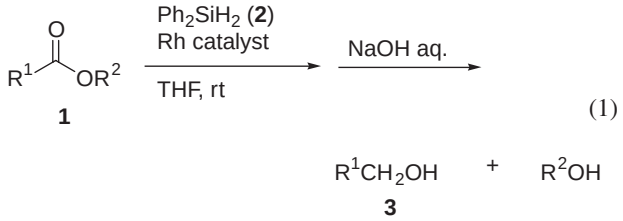
Reductions of carboxylic acid derivatives by silanes in the presence of rhodium complexes were studied. Carboxylic esters were reduced to alcohols by diphenylsilane catalyzed by $[RhCl(cod)]_2/4PPh_3$ or $[RhCl(PPh_3)_3]$ at room temperature in up to 99% yields. For example, ethyl decanoate and ethyl phenylacetate were converted to decanol and 2-phenylethanol in 98 and 92% yields, respectively. Carboxylic acids were also reduced by this reducing system to the corresponding alcohols in high yields. Furthermore, *N*-monosubstituted amides were reduced to secondary amines in moderate to good yields. For sterically hindered amides, the yields were moderate, and imines were produced in competitive yields.

Catalytic reduction[1] of carbonyl compounds is the most typical method of producing alcohols. Aldehydes and ketones are reduced to the corresponding alcohols by hydrogenation,[2] transfer hydrogenation,[3] and reduction using silane in the presence of transition metal catalysts.[4] On the other hand, carboxylic acid derivatives are not easily reduced catalytically to alcohols or amines, and only a few examples have been reported so far.[5–7] Silane reduction catalyzed by metal halides, such as $ZnCl_2$, CsF, and KF, has been applied for the reduction of esters to alcohols, but the reaction conditions are severe or a stoichiometric amount of metal halides is used.[8] Using silane in the presence of a titanium complex has been developed for the reduction of esters to alcohols by Buchwald,[9] but an alkylmetal reagent, such as *n*-BuLi and EtMgBr or heating is needed in order to produce an active catalyst. Nagashima et al. reported the unique ruthenium catalyst for silane-reduction of carboxylic acid derivatives.[10] On the other hand, esters were converted to ethers by Mn–silane system.[11] Amides were reduced by combinations of transition-metals and silanes.[12,13] We have preliminarily reported that esters were reduced to alcohols in excellent yields using silane in the presence of a rhodium complex. Now we wish to describe the details of this reaction and their application to the reduction of carboxylic acids and amides to alcohols and amines.[14]

Results and Discussion

Reduction of Carboxylic Esters. Ethyl decanoate (**1a**, $R^1 = C_9H_{19}$, $R^2 = C_2H_5$) was selected as the substrate. It was reduced to decanol (**3a**) in 98% yield using 3 equiv of diphenylsilane (**2**) as a reducing agent in the presence of $[RhCl(cod)]_2/4PPh_3$ at room temperature in THF (Table 1, Entry 3). Wilkinson's complex $[RhCl(PPh_3)_3]$ also showed good catalytic activity enough to give the product in 96% yield by the reaction for 6 h, while carbonyl complex $[RhCl(CO)(PPh_3)_3]$ showed lower catalytic activity (Entry 8). $[RhCl(cod)]_2$–BINAP[15] was effective for this reduction giving **3a** in 95% yield for 120 h; employing 1,10-phenanthroline[16] as a ligand, however, resulted in 53% yield of the alcohol **3a** (Entry 14). The ratio of catalyst strongly affected the reaction. That is, employing 2.5 mol % catalyst (Rh atom to substrate) resulted in good yields of **3a**, while using 1.0 mol % of catalyst showed unsatisfactory yields of **3a** (Entries 2 and 7). Using other silanes decreased the yields of the alcohol **3a** (Entries 10–13). For example, using trichlorosilane yielded a complex mixture, while an employment of triethylsilane resulted in trace amounts of alcohol. Interestingly, reduction using octylsilane proceeded well to give decanol in 98% yield, while using phenylsilane, decanol was obtained in 42% yield accompanied with desyl ethyl ether in 41% yield. Silane **2** was needed in more than 3 equiv to the ester for obtaining the highest yield of the reduction, whereas the yield was lower using 2 equiv of **2** (Entry 5).



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This reduction was applied to a variety of esters **1b–h**; representative results are listed in Table 2. Linear and aliphatic esters **1a**, **1b**, and **1d** were reduced smoothly to the corresponding alcohols in good yields (Entries 1, 2, and 4). From isobutyl decanoate (**1b**), ethyl phenylacetate (**1e**), and ethyl benzoate (**1f**), the corresponding alcohols were obtained in moderate yields by standard workup using 1 M NaOH aq, while workup using 6 M NaOH aq gave better yields. That is, the yields of the products from the reaction of **1b**, **1e**, and **1f** by $[RhCl(cod)]_2/4PPh_3$ increased from 70, 73, and 47 to 92, 92, and 70%, respectively. This apparently is due to the hydrolysis

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Table 1. Reduction of Ethyl Decanoate (**1a**) by Silane in the Presence of Rh Complexes[a)]

Entry	Ratio of Rh/**1a**/mol %[b)]	Silane/equiv	Reaction time/h	Yield[c)]/% of **3a**
1	$[RhCl(cod)]_2$/4PPh_3 (2.5)	Ph_2SiH_2 (4)	72	92
2	$[RhCl(cod)]_2$/4PPh_3 (1.0)	Ph_2SiH_2 (4)	72	40
3	$[RhCl(cod)]_2$/4PPh_3 (2.5)	Ph_2SiH_2 (3)	72	98
4	$[RhCl(cod)]_2$/4PPh_3 (2.5)	Ph_2SiH_2 (3)	6	90
5	$[RhCl(cod)]_2$/4PPh_3 (2.5)	Ph_2SiH_2 (2)	72	72
6	$[RhCl(PPh_3)_3]$ (2.5)	Ph_2SiH_2 (3)	6	96
7	$[RhCl(PPh_3)_3]$ (1.0)	Ph_2SiH_2 (3)	6	51
8	$[RhH(CO)(PPh_3)_3]$ (2.5)	Ph_2SiH_2 (3)	48	30
9	$[RhCl(cod)]_2$/2(*S*)-BINAP (2.5)	Ph_2SiH_2 (3.75)	120	95
10	$[RhCl(cod)]_2$/2(*S*)-BINAP (2.5)	$PhSiH_3$ (3.75)	120	42[d)]
11	$[RhCl(cod)]_2$/2(*S*)-BINAP (2.5)	Cl_3SiH (3.75)	120	0
12	$[RhCl(cod)]_2$/2(*S*)-BINAP (2.5)	Et_3SiH (3.75)	90	trace
13	$[RhCl(cod)]_2$/2(*S*)-BINAP (2.5)	$C_8H_{17}SiH_3$ (4)	144	98
14	$[RhCl(cod)]_2$/2(1,10-phenanthroline) (5)	Ph_2SiH_2 (4)	72	53

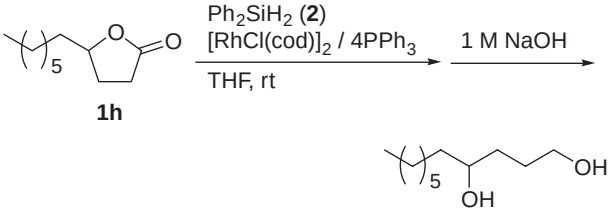
a) Reaction conditions: substrate **1a** (2.0 mmol), Ph_2SiH_2, $[RhCl(cod)]_2$, PPh_3 (2 equiv to Rh atom), THF (2 mL), and room temperature. Workup: 1 M NaOH aq. b) Rh atom/**1a**. c) Determined by ^{1}H NMR spectroscopic analysis by an internal standard (bibenzyl) method. d) Decyl ethyl ether was obtained in 41% yield.

Table 2. Reduction of Esters **1** by Diphenylsilane (**2**) in the Presence of Rhodium Complexes[a)]

Entry	Substrate **1**			Yield[b)]/% of **3**		
		R^1	R^2		$[RhCl(cod)]_2$/4PPh_3	$[RhCl(PPh_3)_3]$
1	**1a**	C_9H_{19}	C_2H_5	**3a**	98	96 (91)[c)]
2	**1b**	C_9H_{19}	*i*-C_4H_9	**3a**	92[d)]	97[d)]
3	**1c**	$C_{13}H_{27}$	*i*-C_3H_7	**3b**	66[d)]	90[d)]
4	**1d**	CH_3	$C_{10}H_{21}$	**3a**	94[d)]	97
5	**1e**	$C_6H_5CH_2$	C_2H_5	**3c**	92[d)]	86[d)]
6	**1f**	C_6H_5	C_2H_5	**3d**	70[d),e)]	56[d)]
7	**1g**	$Br(CH_2)_6$	C_2H_5	**3e**	92	92[d)]

a) Reaction conditions for $[RhCl(cod)]_2$/4PPh_3: $[RhCl(cod)]_2$ (0.025 mmol), PPh_3 (0.10 mmol), Ph_2SiH_2 (6.0 mmol), an ester (2.0 mmol), THF (2.0 mL), 72 h, and rt. For $[RhCl(PPh_3)_3]$: $[RhCl(PPh_3)_3]$ (0.05 mmol), Ph_2SiH_2 (6.0 mmol), an ester (2.0 mmol), THF (2.0 mL), 24 h, and 50 °C. Work up with 1 M NaOH aq. b) Determined by ^{1}H NMR spectroscopic analysis by an internal standard (bibenzyl) method. c) Isolated yield. d) Workup: 6 M NaOH aq. e) $[RhCl(cod)]_2$ (0.05 mmol), PPh_3 (0.20 mmol), and 144 h.

of the silicone–oxygen bond in alkoxysilane, in which the sterically bulky alkoxy group prevents smooth hydrolysis. The bromo substituent on the substrate did not suffer in the course of this reaction (**1g**, Entry 7). When the ester substrates have a carbon–carbon double bond, such as 2-ethylbutyl propenoate and 2-pentenyl acetate, the reduction of ester function was competing to the reduction of carbon–carbon double bond. Lactone **1h** was reduced by diphenylsilane in the presence of this catalyst to the corresponding diol **3f** in 63% yield.



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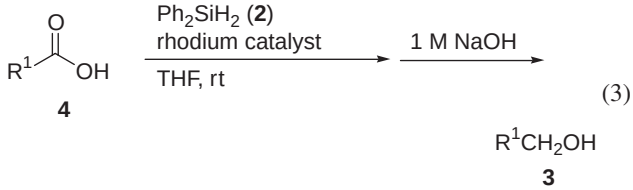
Reduction of Carboxylic Acids. Reduction of carboxylic



(3)

acids to the corresponding alcohols proceeded in good yields as well. Results of the reaction under various conditions are listed in Table 3. The use of a smaller amount of catalyst (Entries 5 and 6) and less amount of silanes than 2 equiv to the acid (Entries 3 and 4) decreased the yield of the alcohol. In the case of decanoic acid, employment of phenylsilane was as effective as the use of diphenylsilane, unlike the case of ethyl decanoate (vide infra), while triphenylsilane and triethylsilane showed no reduction ability (Entries 7–9).

Under the selecting reaction condition (2 mmol of substrate, 4 equiv of **2** to acid and 5 mol % of catalyst at room temper-

Table 3. Reduction of Decanoic Acid (**4a**) by Hydrosilanes[a)]

Entry	Catalyst/mol %[b)]	Silane/equiv	Yield[c)]/% of **3a**
1	$[RhCl(cod)]_2/4PPh_3$ (5)	Ph_2SiH_2 (4)	95
2	$[RhCl(cod)]_2/4PPh_3$ (5)	Ph_2SiH_2 (3)	90
3	$[RhCl(cod)]_2/4PPh_3$ (5)	Ph_2SiH_2 (2)	52
4	$[RhCl(cod)]_2/4PPh_3$ (5)	Ph_2SiH_2 (1)	20
5	$[RhCl(cod)]_2/4PPh_3$ (2.5)	Ph_2SiH_2 (4)	73
6	$[RhCl(cod)]_2/4PPh_3$ (1)	Ph_2SiH_2 (4)	50
7	$[RhCl(cod)]_2/4PPh_3$ (5)	$PhSiH_3$ (4)	92
8	$[RhCl(cod)]_2/4PPh_3$ (5)	Ph_3SiH (4)	0
9	$[RhCl(cod)]_2/4PPh_3$ (5)	Et_3SiH (4)	0
10	$[RhCl(cod)]_2$/2BINAP (5)	Ph_2SiH_2 (4)	97

a) Reaction conditions: decanoic acid **4a** (2.0 mmol), silane, catalyst, THF (2 mL), room temperature, and 48 h. Workup: 1 M NaOH aq. b) mol % of Rh atom to **4a**. c) Determined by ^{1}H NMR spectroscopic analysis by an internal standard (bibenzyl) method.

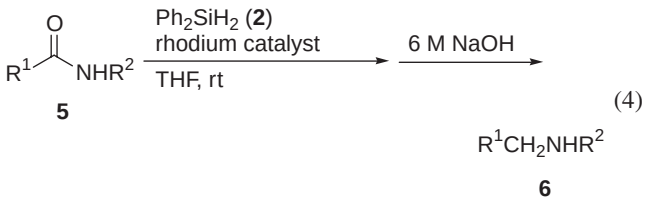
Table 4. Reduction of Carboxylic Acids **4** by Diphenylsilane (**2**) in the Presence of $[RhCl(cod)]_2/4PPh_3$ or $[RhCl(PPh_3)_3]$[a)]

Entry	Carboxylic acid		Yield[b)]/% of **3**		
		R =		$[RhCl(cod)]_2/4PPh_3$	$[RhCl(PPh_3)_3]$
1	**4a**	C_9H_{19}	**3a**	95	90
2	**4b**	C_7H_{15}	**3g**	85	
3	**4c**	$C_{15}H_{31}$	**3h**	87[c)]	
4	**4d**	$C_4H_9CH(C_2H_5)$	**3i**	75[c)]	76[c)]
5	**4f**	$Br(CH_2)_4$	**3j**	63	47[c)]
6	**4g**	$C_8H_{17}CH{=}CH(CH_2)_7$	**3k** and **3l**	90[c),d)]	99[c),e)]
7	**4h**	cyclohexyl-CH_2	**3m**	79	80[c)]
8	**4i**	C_6H_5	**3d**	62[c)]	
9	**4j**	$C_6H_5(CH_2)_2$	**3n**	86[c)]	93[c)]
10	**4k**	$C_6H_5OCH(CH_3)$	**3o**	70[c)]	
11	**4l**	4-$BrC_6H_4CH_2$	**3p**	67	77[c)]

a) Reaction conditions for $[RhCl(cod)]_2/4PPh_3$: $[RhCl(cod)]_2$ (0.025 mmol), PPh_3 (0.10 mmol), Ph_2SiH_2 (8.0 mmol), carboxylic acid (2.0 mmol), THF (2.0 mL), 48 h, and rt. For $[RhCl(PPh_3)_3]$: $[RhCl(PPh_3)_3]$ (0.05 mmol), Ph_2SiH_2 (6.0 mmol), carboxylic acid (2.0 mmol), THF (2.0 mL), 24 h, and 50 °C. b) Determined by ^{1}H NMR spectroscopic analysis by an internal standard (bibenzyl) method. c) Workup: 6 M NaOH aq. d) Oleyl alcohol (**3k**, 63%) and octadecanol (**3l**, 27%) were formed. e) Oleyl alcohol (**3k**, 70%) and octadecanol (**3l**, 29%) were formed.

ature for 48 h in THF (2 mL)), various carboxylic acids were allowed to be reduced (Table 4). Long chain carboxylic acids were reduced efficiently to give the corresponding alcohols in good yields, while sterically hindered carboxylic acids and benzoic acids were reduced in lower yields. Bromo substituents on alkyl and aryl survived in this reduction (Entries 5 and 11). Substrate **4g** with olefinic part (C=C) was reduced to a mixture of unsaturated alcohol (**3k**) and saturated alcohol (**3l**) (Entry 6).

Reduction of Amide to Amine. Carboxylic amides are



(4)

one of the carboxylic acid derivatives and can usually be reduced to amines by the reduction with $LiAlH_4$. Ito et al. reported that tertiary amide was reduced to tertiary amine by hydrosilylation using Rh complex.[13] In their reaction, primary and secondary amides and esters were not reduced.

In our reduction, secondary amides **5** were reduced to secondary amines **6** in up to 97% yields (Table 5). When substrates have bulky substituents, yields of amines **6** were moderate, and some imines **7** were produced. $[RhCl(cod)]_2/4PPh_3$ showed better catalytic activity than $[RhCl(PPh_3)_3]$ for this reduction of amides.

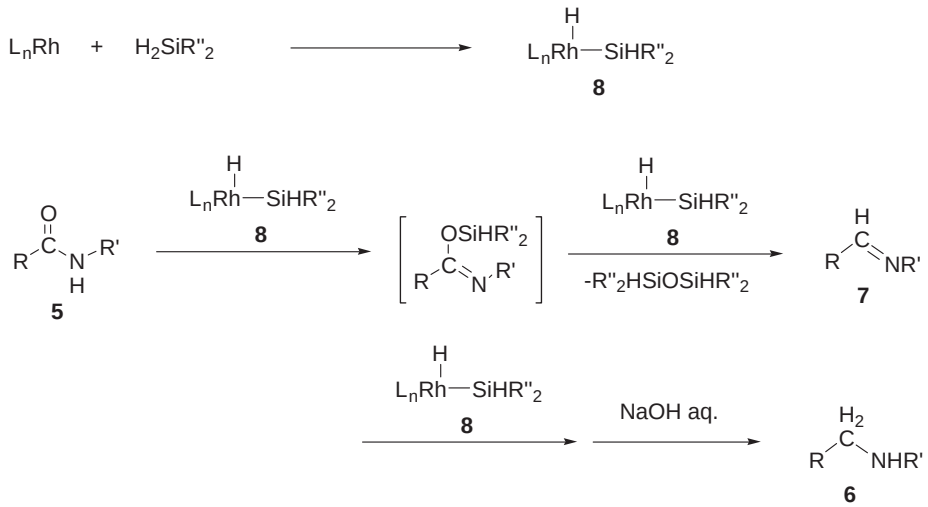
Reaction of primary amides, such as benzamide and octylamide, gave a complex mixture. In the case of benzonitrile, no reaction proceeded at all. This reduction system can be applied to esters, carboxylic acids, and secondary amide at room temperature and acetals and orthoesters[14b] at 50–60 °C. At room temperature, halide, alkoxy, acetal, hydroxyl, amine, and nitrile may survive during the reduction using diphenylsilane in the presence of rhodium complex.

Reaction Mechanism. The reaction mechanism is not clear yet. Trichlorosilane under radiation of γ-waves was known to reduce esters to the corresponding ethers via a radi-

Table 5. Reduction of Amides **5** in the Presence of Rh Complexes[a)]

Entry	Amide **5**			Yield[b)]/% of **6**	
		R^1	R^2	$[RhCl(cod)]_2/4PPh_3$	$[RhCl(PPh_3)_3]$
1	**5a**	C_6H_5	$(CH_3)_2CH$	**6a** 80	52[c),d)]
2	**5b**	C_6H_5	$(CH_3)_3C$	**6b** 52[e)]	57[c),f)]
3	**5c**	C_6H_5	$C_{10}H_{21}$	**6c** 86	30[c)]
4	**5d**	C_6H_5	$C_6H_5CH_2$	**6d** 87	97[c)]
5	**5e**	C_6H_5	2,6-$(CH_3)_2C_6H_3$	**6e** 79	45[c),g)]
6	**5f**	C_9H_{19}	$(CH_3)_2CH$	**6f** 88	86[c)]
7	**5g**	C_9H_{19}	$(CH_3)_3C$	**6g** 59	48[c),h)]

a) Reaction conditions for $[RhCl(cod)]_2/4PPh_3$: $[RhCl(cod)]_2$ (0.025 mmol), PPh_3 (0.10 mmol), Ph_2SiH_2 (8.0 mmol), amide (2.0 mmol), THF (2.0 mL), 48 h, and rt. For $[RhCl(PPh_3)_3]$: $[RhCl(PPh_3)_3]$ (0.05 mmol), Ph_2SiH_2 (6.0 mmol), amide (2.0 mmol), THF (2.0 mL), 6 h, and 50 °C. b) Determined by ^1H NMR. c) Work up: 6 M NaOH aq. d) Imine **7a** was formed in 5% yield. e) Imine **7b** was formed in 15% yield. f) Imine **7b** was formed in 20% yield. g) Imine **7e** was formed in 40% yield. h) Imine **7g** was formed in 10% yield.



Scheme 1.

cal mechanism.[17] Even though the formation of a trace amount of ethers was observed in our catalysis, high alcohol selectivities (more than 95% selectivities of alcohols in each case) may rule out such a radical mechanism. Furthermore, the reactions under light or under dark showed no difference in yields of the products. In deoxylation of esters to ethers[11] or of amides to amines[13] by hydrosilylation using Mn or Rh complexes and in reduction of esters to alcohols by Ti complex,[9] oxidative addition of silane to a metal complex was suggested. It is considered that our reaction also proceeds through oxidative addition of silane to a Rh complex producing hydrido(silyl)rhodium, followed by reduction of the ester with this rhodium hydride species to give the aldehyde. Then, the aldehyde was reduced by hydrido(silyl)rhodium species again.

In the case of the reduction of carboxylic acid, the same mechanism described above was again considered. That is, the carboxylic acid reacts with silane to give silyl ester, and then this silyl ester is reduced to the alcohol by hydrido(silyl)-rhodium species.

Reduction of tertiary amide was reported by Ito et al. using a similar rhodium phosphine complex as a catalyst.[13] In their report, hydrido(silyl)rhodium species reduced amide by a similar mechanism as $LiAlH_4$. On the other hand, our system can reduce the secondary amide to a secondary amine. Furthermore, amides with sterically bulky substituents were often converted to imines. This indicates that the mechanism is different for the reductions of tertiary amide and for those of secondary amide.[18] Basically, secondary amide may be reduced to give the imine first, and then the imine is reduced to the amine (Scheme 1). Although the reduction of imine may need the coordination of the imine to catalyst center, the bulky group substituted on the nitrogen atom of the imine makes the imine difficult to coordinate to catalyst center. Therefore, reduction of imine becomes slow, and such amides gave a mixture of the amine and the imine.

Conclusion

Rh-catalyzed reduction of carboxylic acid derivatives, such as ester, carboxylic acid, and amide, using diphenylsilane proceeded smoothly. Esters and carboxylic acids were reduced to corresponding alcohols in up to 99% yields, while secondary amides were converted to secondary amine in up to 97% yield. For esters and carboxylic acids, reduction of sterically bulky substrates was sluggish. Amides with a bulky substituent on ni-

trogen gave a mixture of corresponding amines and imines. Applicability of this reduction system to other functionalities is now underway.

Experimental

General. All solvents were dried by standard methods and were distilled under argon.[19] Commercially available compounds were used without purification. Substrates without amides were purchased from Wako Pure Chemical Industries, Ltd. or Tokyo Kasei Kogyo Co., Ltd. $[RhCl(cod)]_2$,[20] $[RhCl(PPh_3)_3]$,[21] $[RhH(CO)(PPh_3)_3]$,[22] and amide substrates[23] were prepared by the literature method. All products were known and identified by mp, bp, IR, and/or ^{1}H NMR analyses by comparison with that of authentic samples as purchased from Aldrich or Tokyo Kasei Kogyo Co. ^{1}H nuclear magnetic resonance spectra were measured on a JEOL JNM A-400 (400 MHz) spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Shimadzu IR-408 spectrometer. Analyses by gas chromatography were performed on a Shimadzu GC-14A (Column packing: 5% Silicone SE-30 on Chromosorb W AW DMCS (80–100 mesh)). Melting points were measured on a Yanako Model MP and were not corrected.

Reduction of Esters by Diphenylsilane in the Presence of $[RhCl(cod)]_2$ and PPh_3. This is a typical procedure for reduction of esters, carboxylic acids, and amides. In a 20-mL Schlenk tube were placed $[RhCl(cod)]_2$ (12.3 mg, 0.025 mmol), PPh_3 (26.2 mg, 0.10 mmol), and THF (2 mL). To the resulting clear solution were added ethyl decanoate (**1a**) (0.46 mL, 2.0 mmol) and Ph_2SiH_2 (**2**) (1.11 mL, 6.0 mmol), and the solution was stirred at room temperature for 3 d. Bibenzyl (0.342 g, 2 mmol, as an internal standard), THF (10 mL), and 1 M NaOH aq (10 mL) were added, and the mixture was stirred for 3 h. A mixture of the products and bibenzyl was obtained by extraction with diethyl ether, followed by concentration. The yield was determined by ^{1}H NMR spectroscopic analysis using an internal standard method. Otherwise, 6 M NaOH aq was used for hydrolysis, when 1 M NaOH aq did not work well. Furthermore, 8.0 mmol of diphenylsilane was used for the reduction of carboxylic acids and amides, and the reaction mixture was stirred for 48 h.

Decanol (3a): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.18–1.38 (br, 14H, $-CH_2(C\underline{H}_2)_7CH_3$), 1.54–1.68 (m, 2H, $-C\underline{H}_2CH_2OH$), 3.63 (t, $J = 6.8$ Hz, 2H, $-C\underline{H}_2OH$).

Tetradecanol (3b): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.14–1.32 (br, 24H, $-CH_2(C\underline{H}_2)_{12}CH_3$), 1.44–1.57 (m, 2H, $-C\underline{H}_2CH_2OH$), 3.64 (t, $J = 6.8$ Hz, 2H, $-C\underline{H}_2OH$).

2-Phenylethanol (3c): ^{1}H NMR ($CDCl_3$) δ 2.87 (t, $J = 6.6$ Hz, 2H, $-C\underline{H}_2CH_2O-$), 3.86 (q, $J = 6.6$ Hz, 2H, $-CH_2C\underline{H}_2O-$), 7.18–7.32 (m, 5H, $-C_6\underline{H}_5$).

Benzyl Alcohol (3d): ^{1}H NMR ($CDCl_3$) δ 4.51 (s, 2H, $-C\underline{H}_2OH$), 7.17–7.35 (m, 5H, $C_6\underline{H}_5$).

7-Bromoheptanol (3e): ^{1}H NMR ($CDCl_3$) δ 1.23–1.48 (m, 8H, $-(C\underline{H}_2)_4$), 1.78–1.82 (m, 2H, $-C\underline{H}_2CH_2Br$ or $-C\underline{H}_2CH_2OH$), 3.36 (t, $J = 6.8$ Hz, 2H, $-C\underline{H}_2OH$ or $-C\underline{H}_2Br$), 3.45 (t, $J = 6.8$ Hz, 2H, $-C\underline{H}_2OH$ or $-C\underline{H}_2Br$).

1,4-Undecanediol (3f): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.29–1.70 (m, 16H, $-(C\underline{H}_2)_6CH_3$ and $-(C\underline{H}_2)_2CH_2OH$), 3.59–3.80 (m, 3H, $-C\underline{H}(CH_2)_6CH_3$ and $-C\underline{H}_2OH$).

Octanol (3g): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.20–1.40 (m, 10H, $-(C\underline{H}_2)_5CH_3$), 1.52–1.60 (m, 2H, $-C\underline{H}_2CH_2OH$), 3.62 (t, $J = 6.8$ Hz, 2H, $-C\underline{H}_2OH$).

Hexadecanol (3h): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.20–1.40 (m, 26H, $-CH_2(C\underline{H}_2)_{13}CH_3$), 1.52–1.61 (m, 2H, $-C\underline{H}_2CH_2OH$), 3.61 (t, $J = 6.4$ Hz, 2H, $-C\underline{H}_2OH$).

2-Ethylhexanol (3i): ^{1}H NMR ($CDCl_3$) δ 0.85–0.93 (m, 6H, $-(CH_2)_3C\underline{H}_3$ and $-CHCH_2C\underline{H}_3$), 1.2–1.4 (m, 8H, $-(C\underline{H}_2)_3CH_3$ and $-CHC\underline{H}_2CH_3$), 1.64 (m, 1H, $-C\underline{H}(CH_2)_3CH_3$), 3.54 (d, $J = 6.8$ Hz, 2H, $-OC\underline{H}_2-$).

5-Bromopentanol (3j): ^{1}H NMR ($CDCl_3$) δ 1.45–1.60 (m, 4H, $-(C\underline{H}_2)_2-$), 1.86–1.90 (m, 2H, $-C\underline{H}_2CH_2Br$ or $-C\underline{H}_2CH_2OH$), 3.41 (t, $J = 7.2$ Hz, 2H, $-C\underline{H}_2OH$ or $-C\underline{H}_2Br$), 3.64 (t, $J = 7.2$ Hz, 2H, $-C\underline{H}_2OH$ or $-C\underline{H}_2Br$).

Oleyl Alcohol (3k): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.2$ Hz, 3H, $-C\underline{H}_3$), 1.20–1.40 and 1.54–1.62 (m, 24H, methylene), 1.95–2.10 (m, 4H, $-C\underline{H}_2CH{=}CHC\underline{H}_2-$), 3.63 (t, $J = 6.4$ Hz, 2H, $-C\underline{H}_2OH$), 5.37–5.40 (m, 2H, $-C\underline{H}{=}C\underline{H}-$).

Octadecanol (3l): ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 7.2$ Hz, 3H, $-C\underline{H}_3$), 1.20–1.40 (m, 30H, $-CH_2(C\underline{H}_2)_{15}CH_2-$), 1.54–1.62 (m, 2H, $-C\underline{H}_2CH_2OH$), 3.63 (t, $J = 6.4$ Hz, 2H, $-C\underline{H}_2OH$).

2-Cyclohexylethanol (3m): ^{1}H NMR ($CDCl_3$) δ 0.88–1.00 (m, 2H), 1.10–1.72 (m, 11H), 3.67 (t, $J = 6.8$ Hz, 2H, $-C\underline{H}_2OH$).

3-Phenylpropanol (3n): ^{1}H NMR ($CDCl_3$) δ 1.82–1.92 (m, 2H, $-C\underline{H}_2CH_2OH$), 2.72 (t, $J = 7.2$ Hz, 2H, $-C\underline{H}_2(CH_2)_2OH$), 3.67 (t, $J = 7.2$ Hz, 2H, $-C\underline{H}_2OH$), 7.20–7.35 (m, 5H, $-C_6\underline{H}_5$).

2-Phenoxypropanol (3o): ^{1}H NMR ($CDCl_3$) δ 1.27 (d, $J = 6.4$ Hz, 3H, $-C\underline{H}_3$), 3.70 (d, $J = 7.2$ Hz, 2H, $-C\underline{H}_2OH$), 4.46–4.54 (m, 1H, $-OC\underline{H}-$), 7.2–7.36 (m, 5H, $-C_6\underline{H}_5$).

2-(4-Bromophenyl)ethanol (3p): ^{1}H NMR ($CDCl_3$) δ 2.82 (t, $J = 6.4$ Hz, 2H, $-C\underline{H}_2CH_2OH$), 3.83 (m, 2H, $-C\underline{H}_2OH$), 7.20–7.40 (m, 4H, $-C_6\underline{H}_4Br$).

***N*-Benzylisopropylamine (6a):** ^{1}H NMR ($CDCl_3$) δ 1.06 (d, $J = 6.0$ Hz, 6H, $-CH(C\underline{H}_3)_2$), 2.79–2.91 (m, 1H, $-C\underline{H}(CH_3)_2$), 3.72 (s, 2H, $-C\underline{H}_2Ph$), 7.26–7.81 (m, 5H, $-C_6\underline{H}_5$).

***N*-Bezyl-*t*-butylamine (6b):** ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9H, $-C(C\underline{H}_3)_3$), 3.72 (s, 2H, $-NHC\underline{H}_2-$), 7.26–7.74 (m, 5H, $-C_6\underline{H}_5$).

***N*-Benzyldecylamine (6c):** ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.26–1.38 (m, 14H, $-(C\underline{H}_2)_7CH_3$), 1.59–1.67 (m, 2H, $-C\underline{H}_2(CH_2)_7CH_3$), 2.32 (t, $J = 8.0$ Hz, 2H, $-C\underline{H}_2(CH_2)_8CH_3$), 3.76 (s, 2H, $-C\underline{H}_2Ph$), 7.27–7.77 (m, 5H, $-C_6\underline{H}_5$).

Dibenzylamine (6d): ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 4H, $(-C\underline{H}_2Ph)_2$), 7.26–7.81 (m, 10H, $(-C_6\underline{H}_5)_2$).

***N*-(2,6-Dimethylphenyl)benzylamine (6e):** ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6H, $-C_6H_3(C\underline{H}_3)_2$), 4.10 (s, 2H, $-C\underline{H}_2Ph$), 7.11–7.93 (m, 8H, $-C_6\underline{H}_5$ and $-C_6\underline{H}_3(CH_3)_2$).

***N*-Isopropyldecylamine (6f):** ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 0.99 (d, $J = 6.8$ Hz, 6H, $-CH(C\underline{H}_3)_2$), 1.18–1.29 (m, 14H, $-(C\underline{H}_2)_7CH_3$), 1.57–1.65 (m, 2H, $-C\underline{H}_2-(CH_2)_7CH_3$), 2.46 (t, $J = 8.0$ Hz, 2H, $-NHC\underline{H}_2-$), 2.60–2.75 (m, 2H, $-N\underline{H}C\underline{H}(CH_3)_2$).

***N*-*t*-Butyldecylamine (6g):** ^{1}H NMR ($CDCl_3$) δ 0.88 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$), 1.09 (s, 9H, $-C(C\underline{H}_3)_3$), 1.19–1.31 (m, 14H, $-(C\underline{H}_2)_7CH_3$), 1.57–1.70 (m, 2H, $-C\underline{H}_2(CH_2)_7CH_3$), 2.52 (t, $J = 7.2$ Hz, 2H, $-NHC\underline{H}_2-$).

***N*-Isopropylbenzaldimine (7a):** ^{1}H NMR ($CDCl_3$) δ 1.25 (d, $J = 6.0$ Hz, 6H, $-CH(C\underline{H}_3)_2$), 3.48–3.60 (m, 1H, $-C\underline{H}(CH_3)_2$), 7.26–7.81 (m, 5H, $-C_6\underline{H}_5$), 8.29 (s, 1H, $-N{=}C\underline{H}-$).

***N*-*t*-Butylbenzaldimine (7b):** ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9H, $-C(C\underline{H}_3)_3$), 7.26–7.74 (m, 5H, $-C_6\underline{H}_5$), 8.28 (s, 1H, $-N{=}C\underline{H}-$).

***N*-(2,6-Dimethylphenyl)benzaldimine (7e):** ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 6H, $-C_6H_3(C\underline{H}_3)_2$), 7.11–7.93 (m, 8H, $-C_6\underline{H}_5$ and $-C_6\underline{H}_3(CH_3)_2$), 8.22 (s, 1H, $-C\underline{H}{=}N-$).

***N*-*t*-Butyldecylaldimine (7g):** ^{1}H NMR ($CDCl_3$) δ 0.88 (t,

J = 6.8 Hz, 3H, –C$\underline{H}_3$), 1.05 (s, 9H, –C(C$\underline{H}_3$)$_3$), 1.19–1.31 (m, 14H, –CH$_2$(C$\underline{H}_2$)$_7$CH$_3$), 1.57–1.70 (m, 2H, –C$\underline{H}_2$(CH$_2$)$_7$CH$_3$), 8.28 (s, 1H, –C$\underline{H}$=N–).

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References

1 Reviews, see: a) I. Ojima, M. Iguchi, and M. Tzamarioudaki, "Comprehensive Organometallic Chemistry II," ed by E. W. Abel, F. G. A. Stone, G. Wilkinson, and L. S. Hegedous, Pergamon, Oxford (1995), Vol. 12, pp. 9–39. b) A. J. Birch and D. H. Williamson, *Org. React.*, **24**, 1 (1976). c) H. Takaya and R. Noyori, "Comprehensive Organic Synthesis," ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 8, Chap. 3.2, p. 443.

2 a) R. R. Schrock and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, **1970**, 567. b) T. Ikariya, T. Ohkuma, H. Ooka, S. Hashiguchi, N. Seido, and R. Noyori, Eur. Pat. Appl. EP 718265 A2 19960626; *Chem. Abstr.*, **125**, 113927 (1996). c) T. Ohkuma, M. Koizumi, H. Doucet, T. Pham, M. Kozawa, K. Murata, E. Katayama, T. Yokozawa, T. Ikariya, and R. Noyori, *J. Am. Chem. Soc.*, **120**, 13529 (1998).

3 a) G. Brieger and T. J. Nestrick, *Chem. Rev.*, **74**, 567 (1974). b) R. A. W. Johnstone and A. H. Wilby, *Chem. Rev.*, **85**, 129 (1985). c) G. Zassinovich, G. Mestroni, and S. Gladiali, *Chem. Rev.*, **92**, 1051 (1992). d) S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, and R. Noyori, *J. Am. Chem. Soc.*, **117**, 7562 (1995).

4 I. Ojima, "The Chemistry of Organic Silicon Compounds, Part 2," ed by S. Patai and Z. Rappoport, Wiley, New York (1989), pp. 1479–1526.

5 Homogeneous hydrogenation of carboxylic esters, see: a) K. Nomura, Jpn. Kokai Tokkyo Koho, JP2001247499 (2001); *Chem. Abstr.*, **135**, 212600 (2001). b) R. A. Grey, G. P. Pez, A. Wallo, and J. Corsi, *J. Chem. Soc., Chem. Commun.*, **1980**, 783. c) R. A. Grey, G. P. Pez, and A. Wallo, *J. Am. Chem. Soc.*, **103**, 7536 (1981).

6 Hydrogenation of carboxylic acids and lactones, see: A. Behr and V. A. Brehme, *Adv. Synth. Catal.*, **344**, 525 (2002).

7 Heterogeneous hydrogenation, see: H. Adkins, *Org. React.*, **8**, 1 (1954).

8 a) R. Calas, *Pure Appl. Chem.*, **13**, 61 (1966). b) J. Boyer, R. J. P. Corriu, R. Perz, M. Poirier, and C. Reye, *Synthesis*, **1981**, 558. c) C. Chuit, R. J. P. Corriu, R. Perz, and C. Reye, *Synthesis*, **1982**, 981.

9 a) S. C. Berk, K. A. Kreutzer, and S. L. Buchwald, *J. Am. Chem. Soc.*, **113**, 5093 (1991). b) S. C. Berk and S. L. Buchwald, *J. Org. Chem.*, **57**, 3751 (1992). c) X. Verdaguer, S. C. Berk, and S. L. Buchwald, *J. Am. Chem. Soc.*, **117**, 12641 (1995). d) X. Verdaguer, M. C. Hansen, S. C. Berk, and S. L. Buchwald, *J. Org. Chem.*, **62**, 8522 (1997), and references cited therein.

10 a) K. Matsubara and H. Nagashima, *J. Synth. Org. Chem. Jpn.*, **63**, 122 (2005). b) H. Nagashima and K. Matsubara, Jpn. Kokai Tokkyo Koho, JP2003261578 (2003); *Chem. Abstr.*, **139**, 261039 (2003). c) K. Matsubara, T. Iura, T. Maki, and H. Nagashima, *J. Org. Chem.*, **67**, 4985 (2002).

11 Z. Mao, B. T. Gregg, and A. R. Cutler, *J. Am. Chem. Soc.*, **117**, 10139 (1995).

12 M. Igarashi and T. Fuchikami, *Tetrahedron Lett.*, **42**, 1945 (2001).

13 R. Kuwano, M. Takahashi, and Y. Ito, *Tetrahedron Lett.*, **39**, 1017 (1998).

14 a) T. Ohta, M. Kamiya, K. Kusui, T. Michibata, M. Nobutomo, and I. Furukawa, *Tetrahedron Lett.*, **40**, 6963 (1999). b) T. Ohta, T. Michibata, K. Yamada, R. Omori, and I. Furukawa, *Chem. Commun.*, **2003**, 1192.

15 T. Ohta, M. Ito, A. Tuneto, and H. Takaya, *J. Chem. Soc., Chem. Commun.*, **1994**, 2525.

16 a) G. Mestroni, G. Zassinovich, and A. Camus, *J. Organomet. Chem.*, **140**, 63 (1977). b) G. Mestroni, R. Spogliarich, A. Camus, F. Martinelli, and G. Zassinovich, *J. Organomet. Chem.*, **157**, 345 (1978).

17 a) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Am. Chem. Soc.*, **91**, 4587 (1969). b) R. Nakao, T. Fukumoto, and J. Tsurugi, *J. Org. Chem.*, **37**, 76 (1972). c) Y. Nagata, T. Dohmaru, and J. Tsurugi, *J. Org. Chem.*, **38**, 795 (1973). d) R. Nakao, T. Fukumoto, and J. Tsurugi, *Bull. Chem. Soc. Jpn.*, **47**, 932 (1974).

18 Reviews for asymmetric hydrosilylation of imines, see: a) H. Nishiyama, "Comprehensive Asymmetric Catalysis," ed by E. N. Jacobsen, A. Pfalts, and H. Yamamoto, Springer (1999), Chap. 6.3. b) H. Nishiyama and K. Ito, "Asymmetric Catalytic Synthesis," 2nd ed, ed by I. Ojima, VCH, New York (2000), Chap. 2.

19 W. L. F. Armarego and C. L. L. Chai, "Purification of Laboratory Chemicals," Elsevier, Amsterdam (2003).

20 J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, **1957**, 4735.

21 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, **10**, 67 (1967).

22 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1966**, 1437.

23 R. E. Kent and S. M. McElvain, *Org. Synth.*, Coll. Vol. **III**, 490 (1955).