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Iridium-Catalyzed Transfer Hydrogenation of Ketones and Aldehydes Using Glucose as a Sustainable Hydrogen Donor

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Abstract: A new catalytic system for transfer hydrogenation of carbonyl compounds using glucose as a hydrogen donor was developed. Various ketones and aldehydes were efficiently converted to corresponding alcohols with two equivalents of glucose in the presence of a small amount (0.1 to 1.0 mol%) of iridium catalyst that had a functional ligand. In this catalytic system, transfer hydrogenation reactions proceeded based on the cooperativity of iridium and a functional ligand. It should be noted that environmentally benign water could have been used as a solvent in the present catalytic system for the reduction of various carbonyl substrates. Furthermore, the reaction scope could be extended by using *N*,*N*-dimethylacetamide as a reaction solvent.

Keywords: transfer hydrogenation; iridium catalyst; functional ligand; glucose; ketone; aldehyde; alcohol; water solvent

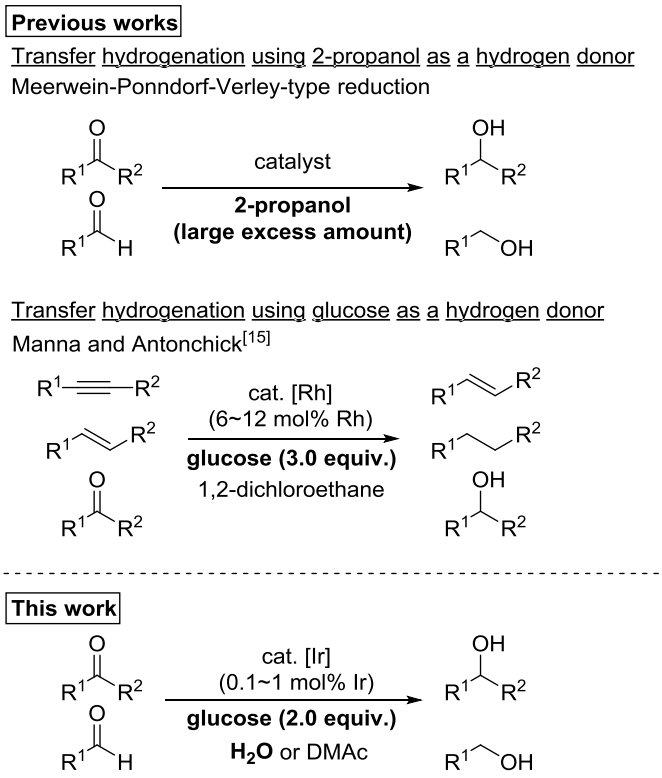
1. Introduction

Reductive conversion of carbonyl compounds to alcohols is one of the most important and fundamental reactions in the field of synthetic organic chemistry. This method has been predominantly used to prepare various alcohols. On an industrial scale and as a conventional technology, such reductive conversion has been performed via catalytic reactions using hydrogen as a reductant [1]. For small-scale laboratory experiments, reduction of carbonyl compounds to alcohols is often performed with stoichiometric amounts of metal hydride reductant, such as lithium aluminum hydride or sodium borohydride. Both the aforementioned methods are well-established; however, hydrogen poses safety issues owing to its explosive nature. Additionally, using a metal hydride reductant not only adversely affects the chemoselectivity of the reaction but also produces a stoichiometric amount of waste.

On the other hand, catalytic transfer hydrogenation reactions using a less toxic hydrogen donor are also important and widely employed in methods for converting carbonyl compounds to alcohols [2–4]. The most well-known of these would be the Meerwein–Ponndorf–Verley (MPV)-type reduction using 2-propanol as a hydrogen donor. Although an aluminum catalyst is typically used in MPV-type reductions [5,6], many highly efficient systems using transition metal catalysts have been reported [7–12]. However, MPV-type reduction depends on the equilibrium between alcohols and carbonyl compounds; therefore, a large excess of 2-propanol as a hydrogen donor must be used to obtain an alcohol in high yield. For example, Li et al. recently reported highly efficient MPV-type reduction of aldehydes using an iridium catalyst [12]; however, 65 equivalents of 2-propanol relative to the aldehyde substrates had to be used to obtain the product primary alcohols in satisfactory yields. Currently, 2-propanol is produced from propylene, which is obtained from fossil resources. Hence, it is essential to search for a low-cost hydrogen donor that is sustainably available from natural resources.

In these situations, we focused on carbohydrate as an alternative hydrogen donor for catalytic transfer hydrogenation. Thus, we studied the catalytic transfer hydrogenation of carbonyl compounds to form alcohols using glucose as a hydrogen donor. Glucose is inexpensive, easily obtained from natural renewable resources, and safe to handle [13]. Furthermore, as it is extremely soluble in water, it is expected to be an ideal hydrogen donor if the reduction can be performed in aqueous media [14]. However, few catalytic transfer hydrogenation reactions that use glucose as a hydrogen donor have been reported. Manna and Antonchick recently reported a new system for transfer hydrogenation of unsaturated organic compounds using glucose as a hydrogen donor [15]. Their system involved relatively large amounts of rhodium complex, $[Cp^*RhCl_2]_2$ (6 to 12 mol% Rh), as catalyst. The main target of this catalytic system was the reductive transformation of alkynes to alkenes, and alkenes to alkanes; therefore, only five examples of the transfer hydrogenation of carbonyl substrates have been demonstrated.

Our group developed various iridium catalysts exhibiting high catalytic performances in dehydrogenation and hydrogen transfer reactions based on the cooperativity of iridium and functional ligands [16–20]. As an expansion of our study, here, we reported the transfer hydrogenation of various ketones and aldehydes using glucose as a hydrogen donor, catalyzed by a small amount of iridium complex (0.1 to 1 mol% Ir) (Scheme 1). It should be noted that water could be used as a solvent in the present catalytic system for various carbonyl substrates, although *N*,*N*-dimethylacetamide (DMAc), was indispensable as an organic solvent for improving the reduction efficiency for some substrates.



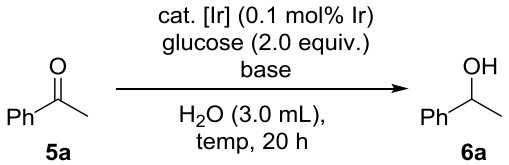
Scheme 1. Catalytic transfer hydrogenation using easily available hydrogen donors.

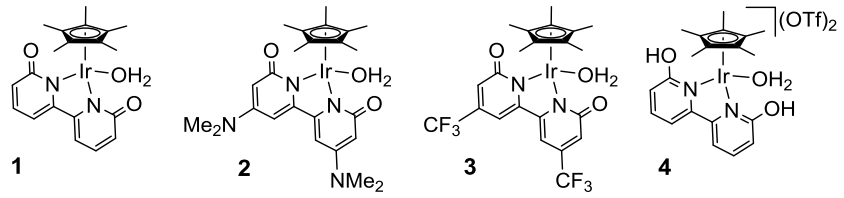
2. Results

We initially optimized the reaction conditions for the transfer hydrogenation of acetophenone (**5a**) to 1-phenylethanol (**6a**) using glucose as a hydrogen donor. The results are shown in Table 1. Reactions were conducted in a sealed stainless-steel reactor using **5a** (2.0 mmol) and glucose (4.0 mmol) in water (3.0 mL) in the presence of catalytic amounts of iridium complex and base for 20 h at 80 °C to 120 °C. As indicated in entry 1, a simple iridium complex, $[Cp^*IrCl_2]_2$, exhibited no catalytic activity, which resulted in no formation of **6a**. When the reaction of **5a** was performed in the presence of 0.1 mol%

Ir of aqua(2,2′-bipyridine-6,6′-dionato)(pentamethylcyclopentadienyl)iridium (**1**) and 5.0 mol% of Na_2CO_3 at 100 °C, transfer hydrogenation proceeded selectively to give **6a** in 85% yield (entry 2). Other iridium catalysts **2** and **3** having substituents of the functional bipyridonate ligand exhibited lower activity than **1** (entries 3 and 4). Related dicationic iridium catalyst **4** was also inferior to **1** (entry 5). Reactions at lower and higher temperatures (80 °C and 120 °C) both resulted in lower yields of **6a** (entries 6 and 7). Employing other bases such as K_2CO_3, NaO^tBu, and KO^tBu also decreased the yield of **6a** (entries 8–10). Two equivalents of glucose were indispensable in obtaining **6a** in high yield, as the reaction using just one equivalent of glucose resulted in a moderate yield of **6a** (entry 11). Finally, the highest yield of **6a** (89%) was achieved by employing 0.2 mol% Ir of the catalyst **1** (entry 12). Additionally, DMAc could be used as a solvent in place of water, maintaining a high yield of **6a** (entry 13).

Table 1. Optimization of reaction conditions for the transfer hydrogenation of acetophenone (**5a**) to 1-phenylethanol (**6a**) using glucose as a hydrogen donor.





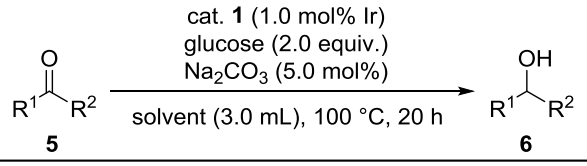
Entry	Cat.	Temp. (°C)	Base (mol%)	Conv. (%) [a]	Yield (%) [a]
1 [b]	$[Cp^*IrCl_2]_2$	100	Na_2CO_3 (5.0)	<5	0
2	**1**	100	Na_2CO_3 (5.0)	86	85
3	**2**	100	Na_2CO_3 (5.0)	62	59
4	**3**	100	Na_2CO_3 (5.0)	2	2
5	**4**	100	Na_2CO_3 (5.0)	67	67
6	**1**	80	Na_2CO_3 (5.0)	48	47
7	**1**	120	Na_2CO_3 (5.0)	92	81
8	**1**	100	K_2CO_3 (5.0)	75	72
9	**1**	100	NaO^tBu (10.0)	58	56
10	**1**	100	KO^tBu (10.0)	62	56
11 [c]	**1**	100	Na_2CO_3 (5.0)	54	53
12 [d]	**1**	100	Na_2CO_3 (5.0)	94	89
13 [b,e]	**1**	100	Na_2CO_3 (5.0)	85	80

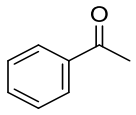
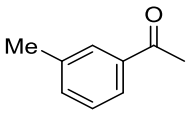
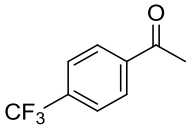
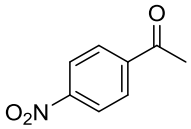
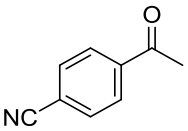
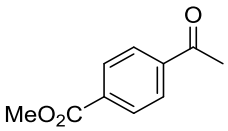
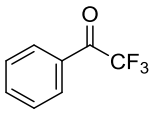
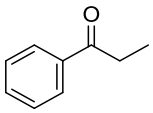
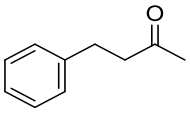
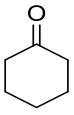
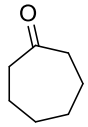
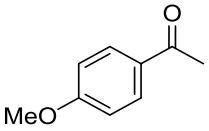
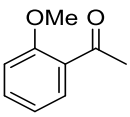
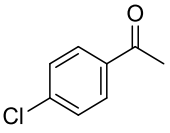
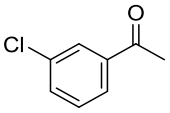
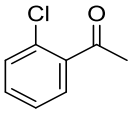
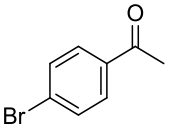
Reaction conditions: Catalyst (0.1 mol% Ir), base, **5a** (2.0 mmol), glucose (4.0 mmol), H_2O (3.0 mL) in a sealed stainless-steel reactor. [a] Determined by GC analysis. [b] Catalyst loading was 1.0 mol% Ir. [c] 1.0 equivalent of glucose was used. [d] Catalyst loading was 0.2 mol% Ir. [e] Reaction was conducted in DMAc (3.0 mL) instead of H_2O.

To explore the substrate scope for the transfer hydrogenation catalyzed by **1** using glucose as a hydrogen donor, reactions were conducted with various ketones. The results are shown in Table 2. Reactions of acetophenone derivatives bearing various substituents on the phenyl ring were initially examined in water (Conditions A). In most of these reactions, 1.0 mol% Ir of catalyst **1** was required to achieve efficient conversion of the ketone substrates. The *meta*-methyl-substituted acetophenone **5b** was converted to the corresponding secondary alcohol **6b** in 61% yield. Acetophenone derivatives **5c–f** bearing electron-withdrawing substituents such as trifluoromethyl, nitro, cyano, and methoxycarbonyl groups at the *para*-position on the phenyl ring were selectively converted to the corresponding secondary alcohols **6c–f** in moderate to good yields. The 2,2,2-trifluoroacetophenone (**5g**) was also converted to the corresponding 2,2,2-trifluoro-1-phenylethanol (**6g**) in 89% yield. Propiophenone

(**5h**) and other ketones **5i–k** were also applicable to this catalytic system. Conversely, reactions of acetophenone derivatives bearing methoxy and halogen substituents in water gave lower yields of secondary alcohols. Here, intermolecular dehydration predominantly proceeded to afford ethers [bis-(α-methylbenzyl)ether derivatives]. For these substrates, the reaction in DMAc as a solvent (Conditions B) significantly improved the yields of secondary alcohols. Starting from acetophenone derivatives **5l–q**, the desired alcohol products **6l–q** were obtained in good to excellent yields under catalytic conditions B.

Table 2. Transfer hydrogenation of various ketones catalyzed by **1** using glucose as a hydrogen donor.



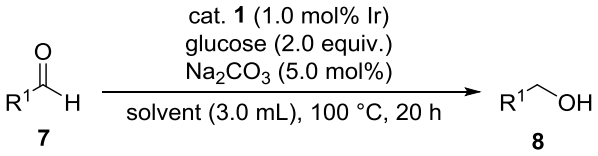
Conditions A: H_2O was used as a solvent [a]			
 **5a**, 89(79) [c, d]	 **5b**, 61(56)	 **5c**, 60(56) [e]	 **5d**, 85(84)
 **5e**, 72(67)	 **5f**, 83(81)	 **5g**, 89(79)	 **5h**, 68(58)
 **5i**, 45(45)	 **5j**, 86(77) [d]	 **5k**, 79(70)	
Conditions B: DMAc was used as a solvent [b]			
 **5l**, 63(54)	 **5m**, 90(79)	 **5n**, 88(81)	 **5o**, 96(74)
 **5p**, 84(82)	 **5q**, 92(89)		

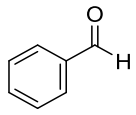
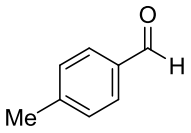
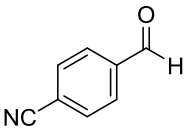
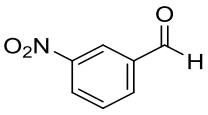
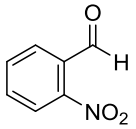
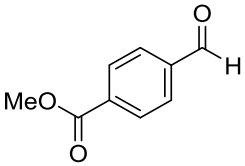
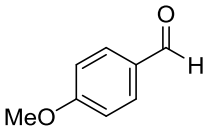
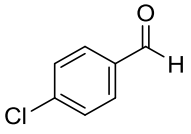
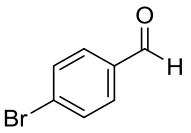
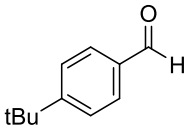
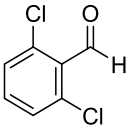
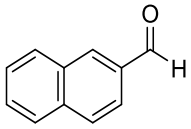
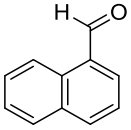
[a] Conditions A: Catalyst (1.0 mol% Ir), Na_2CO_3 (5.0 mol%), **5** (2.0 mmol), glucose (4.0 mmol), H_2O (3.0 mL). [b] Conditions B: Catalyst (1.0 mol% Ir), Na_2CO_3 (5.0 mol%), **5** (2.0 mmol), glucose (4.0 mmol), DMAc (3.0 mL). The yields were determined by ^{1}H NMR analysis. The isolated yields are indicated in parentheses. [c] The yield was determined by GC analysis. [d] Catalyst loading was 0.2 mol% Ir. [e] 6.0 mmol (3.0 equiv.) of glucose was used.

The present catalytic system was also suitable for reducing various aromatic aldehydes to primary benzyl alcohols. The results are summarized in Table 3. Reaction conditions A, which were applied for reducing ketones, as mentioned in Table 2, were also effective for reducing benzaldehyde (**7a**) and *p*-methylbenzaldehyde (**7b**) to benzyl alcohol (**8a**) and *p*-methylbenzyl alcohol (**8b**), respectively. Benzaldehyde derivatives **7c–f** bearing electron-withdrawing substituents such as cyano, nitro,

and methoxycarbonyl groups were also converted to corresponding benzylic alcohols **8c**–**f** in moderate to good yields under conditions A. Benzaldehyde derivatives **7g**–**k** bearing methoxy, *tert*-butyl, and halogen substituents were efficiently converted to benzylic alcohols **8g**–**k** under conditions B using DMAc as a solvent. Other aldehydes **7l** and **7m** with naphthyl rings were also converted to corresponding primary alcohols **8l** and **8m** in excellent yields under conditions B.

Table 3. Transfer hydrogenation of various aldehydes catalyzed by **1** using glucose as a hydrogen donor.



Conditions A: H_2O was used as a solvent [a]			
 **7a,** 87(86) [c, d]	 **7b**, 72(58)	 **7c**, 54(56)	 **7d**, 63(54)
 **7e**, 58(54)	 **7f**, 68(63)		
Conditions B: DMAc was used as a solvent [b]			
 **7g**, 73(69)	 **7h**, 88(88)	 **7i**, 95(88)	 **7j**, 81(78)
 **7k**, 94(87)	 **7l**, 97(91)	 **7m**, 88(83)	

[a] Conditions A: Catalyst (1.0 mol% Ir), Na_2CO_3 (5.0 mol%), aldehyde (2.0 mmol), glucose (4.0 mmol), H_2O (3.0 mL). [b] Conditions B: Catalyst (1.0 mol% Ir), Na_2CO_3 (5.0 mol%), aldehyde (2.0 mmol), glucose (4.0 mmol), DMAc (3.0 mL). The yields were determined by ^{1}H NMR analysis. The isolated yields are indicated in parentheses. [c] The yield was determined by GC analysis. [d] Catalyst loading was 0.5 mol% Ir.

To determine which part of glucose functioned as a hydrogen donor, two additional experiments were conducted (Figure 1). The reaction of **5a** using methyl α-glucopyranoside (**9**), in which one of the hydroxy groups of glucose at the C1 position was protected, did not proceed (Equation (1)). Conversely, 2,3,4,6-tetra-*O*-methyl α-glucopyranose (**10**), in which all four hydroxy groups except for that at the C1 position were protected, was an effective hydrogen donor for the transfer hydrogenation of **5a** to give **6a** in 97% yield (Equation (2)). These results verified that hydrogen transfer occurred from the hydroxy group at the C1 position in glucose to the carbonyl substrates during the catalytic processes.

A possible mechanism for the transfer hydrogenation of carbonyl compounds to the corresponding alcohol products catalyzed by iridium complex **1** is shown in Scheme 2. First, elimination of the aquo ligand in **1** occurred to generate coordinatively unsaturated species **I**. Then, dehydrogenation at the hydroxy moiety at the C1 position of glucose, based on the cooperativity of iridium and the functional ligand, proceeded through transition state **II**, affording gluconolactone and iridium-hydride species

III. (NMR analysis of the crude mixture obtained under optimal conditions (Table 1, entry 12) was performed. Signals due to gluconolactone were observed, indicating that catalytic hydrogen transfer from glucose to acetophenone surely occurred.) Transfer hydrogenation from species **III** to carbonyl substrates occurred through transition state **IV** to give the alcohol products along with regeneration of catalytically active species **I**.

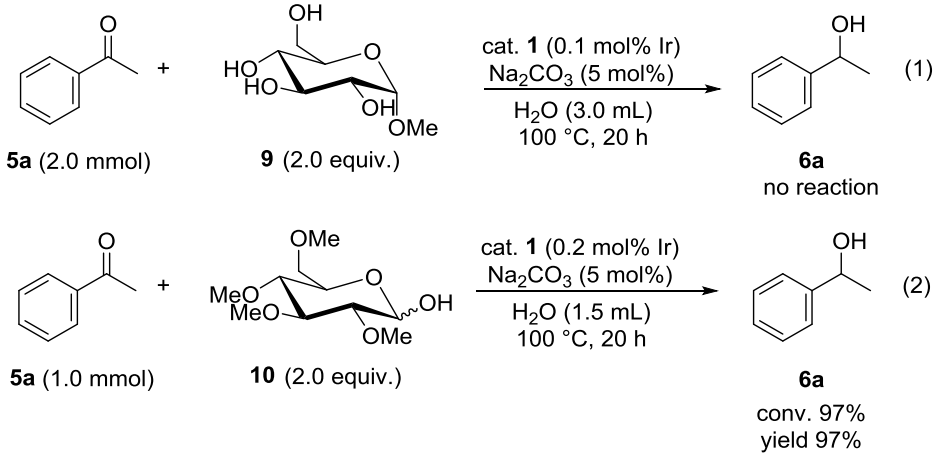
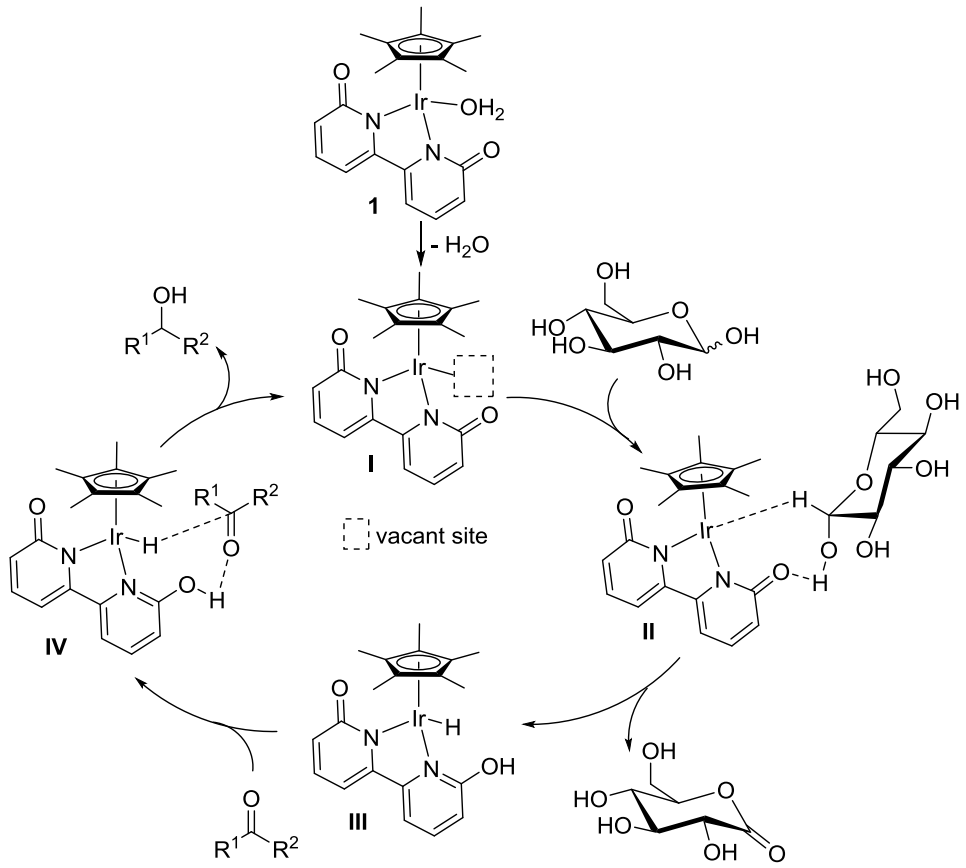


Figure 1. Additional experiments to determine which part of glucose functioned as a hydrogen donor.



Scheme 2. A possible mechanism for the transfer hydrogenation of carbonyl compounds catalyzed by **1** using glucose as a hydrogen donor.

3. Materials and Methods

3.1. General

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on JEOL ECX-500 and ECS-400 spectrometers (JEOL Ltd., Tokyo, Japan). Gas chromatography (GC) analyses were performed on a GL-Sciences GC353B gas chromatograph (GL Sciences Inc., Tokyo, Japan) with a capillary column (GL-Sciences and InertCap Pure WAX (GL Sciences Inc., Tokyo, Japan)). Silica-gel column chromatography was carried out by using Wako-gel C-200 (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan). Ketones and aldehydes were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan), Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) or nacalai tesque (Kyoto, Japan). Distilled water and *N*,*N*-dimethylacetamide(super dehydrated) were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). The compounds, $[Cp^*IrCl_2]_2$ (Cp^* = η^5-pentamethylcyclopentadienyl) [21] and iridium complexes **1–4** were prepared according to the literature methods [18,19,22,23].

3.2. General Procedure for Transfer Hydrogenation of Acetophenone to 1-phenylethanol Using Glucose (Table 1)

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst (0.1 mol% Ir), acetophenone (2.0 mmol), glucose (4.0 mmol), base (5.0 or 10.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the mixture was diluted with toluene (50 mL). The conversion of acetophenone and the yield of 1-phenylethanol were determined by GC analysis using biphenyl as an internal standard.

3.3. General Procedure for Transfer Hydrogenation of Ketones to the Corresponding Secondary Alcohols Using Glucose (Table 2)

3.3.1. Conditions A

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), ketone (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.), Na_2CO_3 (10.6 mg, 0.10 mmol, 5.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the products were extracted with dichloromethane (20 mL × 3). After evaporation of the solvent, the yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane). ^{1}H and ^{13}C{^{1}H} NMR spectra of each isolated products are shown in Supplementary Materials.

1-Phenylethanol (**6a**) [**24**]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.33 (m, 4H, aromatic), 7.31–7.25 (m, 1H, aromatic), 4.91 (qd, *J* = 6.5, 3.5 Hz, 1H, C*H*OH), 1.85 (d, 3.5 Hz, 1H, CHO*H*), 1.50 (d, *J* = 6.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 145.9, 128.6, 127.5, 125.5, 70.4, 25.2.

1-(3′-Methylphenyl)ethanol (**6b**) [25]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, *J* = 8.0 Hz, 1H, aromatic), 7.23–7.15 (m, 2H, aromatic), 7.09 (d, *J* = 7.2 Hz, 1H, aromatic), 4.87 (qd, *J* = 6.4, 2.8 Hz, 1H, C*H*(OH)CH_3), 2.36 (s, 3H, ArCH_3), 1.80 (br, 1H, O*H*), 1.49 (d, *J* = 6.4 Hz, 3H, CH(OH)CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.9, 138.3, 128.6, 128.4, 126.2, 122.6, 70.6, 25.3, 21.6.

1-(4′-Trifluoromethylphenyl)ethanol (**6c**) [25]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H, aromatic), 7.42 (d, *J* = 8.4 Hz, 2H, aromatic), 4.88 (q, *J* = 2.4 Hz, 1H, -C*H*(OH)CH_3), 2.93 (br, 1H, OH), 1.44 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.8, 129.6 (q, J_{CF3} = 31.7 Hz), 125.7, 125.4 (q, J_{CF3} = 3.9 Hz), 124.3 (q, J_{CF3} = 271.2 Hz), 69.8, 25.3.

1-(4′-Nitrophenyl)ethanol (**6d**) [24]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (dt, *J* = 9.0, 2.0 Hz, 2H, aromatic), 7.55 (ddt, *J* = 8.5, 2.0, 0.5 Hz, 2H, aromatic), 5.03 (q, *J* = 6.5 Hz, 1H, C*H*(OH)CH_3), 2.16 (br, 1H, O*H*), 1.52 (d, *J* = 6.5 Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.2, 147.3, 126.2, 123.9, 69.6, 25.6.

1-(4′-Cyanophenyl)ethanol (**6e**) [26]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.5, 1.0 Hz, 2H, aromatic), 7.49 (d, *J* = 8.0 Hz, 2H, aromatic), 4.97 (ddd, *J* = 13.0, 4.0, 2.5 Hz, C*H*(OH)CH_3), 1.92 (d, *J* = 4.0 Hz, OH), 1.50 (d, *J* = 6.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.4, 132.2, 126.1, 118.9, 110.5, 69.3, 25.2.

Methyl-4-(1-hydroxyethyl)benzoate (**6f**) [27]: ^{1}H NMR (500 MHz, $CDCl_3$) δ. 8.00 (dt, *J* = 8.0, 2.0 Hz, 2H, aromatic), 7.43 (d, *J* = 8.0 Hz, 2H, aromatic), 4.95 (q, *J* = 5.5 Hz, 1H, C*H*(OH)CH_3), 3.90 (s, 3H, C(O)OCH_3), 2.19 (br, 1H, O*H*), 1.49 (d, *J* = 6.5 Hz, 3H, CH(OH)CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.1, 151.1, 130.0, 129.3, 125.4, 70.1, 52.2, 25.4.

2,2,2-Trifluoro-1-phenylethanol (**6g**) [28]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.45 (m, 2H, aromatic), 7.45-7.37 (m, 3H, aromatic), 5.03 (m, 1H, C*H*OHCF_3), 2.60–2.58 (br, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ .134.0, 129.7, 128.8, 127.6, 124.3 (q, J_{CF3} = 280.1 Hz), 72.9 (q, J_{CF3} = 32.1 Hz).

1-Phenyl-1-propanol (**6h**) [29]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.31 (m, 4H, aromatic), 7.29–7.23 (m, 1H, aromatic), 4.58 (t, *J* = 6.5 Hz, 1H, C*H*(OH)CH_2CH_3), 1.96–1.98 (br, 1H, O*H*), 1.86-1.70 (m, 2H, CH(OH)C$H_2$$CH_3$), 0.91 (t, *J* = 7.5 Hz, CH(OH)CH_2CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ. 144.7, 128.5, 127.6, 126.1, 76.1, 32.0, 10.3.

4-Phenylbutan-2-ol (**6i**) [29]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H, aromatic), 7.23–7.17 (m, 3H, aromatic), 3.84 (sep, *J* = 6.0 Hz, 1H, C*H*(OH)), 2.80-2.64 (m, 2H, C$H_2$$CH_3$), 1.85–1.72 (m, 2H, C$H_2$), 1.34 (br, 1H, O*H*), 1.23 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 142.2, 128.5, 125.9, 67.5, 40.9, 32.2, 23.7.

Cyclohexanol (**6j**) [29]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (m, 1H, CH_2C*H*OHCH_2), 1.92–1.88 (m. 2H, CH_2), 1.78–1.68 (m, 2H, CH_2), 1.59–1.51 (m, 1H, CH_2), 1.37 (s, 1H, CH_2), 1.35–1.24 (m, 4H, CH_2), 1.22–1.12 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 70.4, 35.6, 25.5, 24.3.

Cycloheptanol (**6k**) [30]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (m, 1H, CH_2C*H*OHCH_2), 1.92 (m. 2H, CH_2), 1.65 (m, 2H, CH_2), 1.61–1.50 (m, 6H, CH_2), 1.40 (m, 2H, CH_2), 1.30 (br, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 72.9, 37.7, 28.2, 22.7.

3.3.2. Conditions B

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), ketone (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.), Na_2CO_3 (10.6 mg, 0.10 mmol, 5.0 mol%) and *N*,*N*-dimethylacetamide (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the reaction mixture was poured into water (50 mL) and the products were extracted with a mixed solvent having a volume ratio of hexane: AcOEt of 1: 1 (20 mL × 3). After evaporation of the solvent, the yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane). ^{1}H and ^{13}C{^{1}H} NMR spectra of each isolated products are shown in Supplementary Materials.

1-(4′-Methoxyphenyl)ethanol (**6l**) [24]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dt, *J* = 8.5, 2.0 Hz, 2H, aromatic), 6.89 (dt, *J* = 9.0, 2.0 Hz, 2H, aromatic), 4.86 (q, *J* = 6.0 Hz, 1H, C*H*OH), 3.81 (s, 3H, OMe), 1.78-1.75 (br, 1H, OH), 1.48 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.1, 138.1, 126.8, 113.9, 70.1, 55.4, 25.2.

1-(2′-Methoxyphenyl)ethanol (**6m**) [30]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.5, 1.5 Hz, 1H, aromatic), 7.28-7.22 (m, 1H, aromatic), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H, aromatic), 6.88 (d, *J* = 8.0 Hz, 1H, aromatic), 5.09 (quint, *J* = 6.5 Hz, C*H*(OH)CH_3), 3.87 (s, 3H, OMe), 2.69 (d, *J* = 5.0 Hz, O*H*), 1.51 (d, *J* = 7.0 Hz, CH(OH)CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.7, 133.5, 128.4, 126.2, 120.9, 110.5, 66.7, 55.4, 22.9.

1-(4′-Chlorophenyl)ethanol (**6n**) [24]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 4H, aromatic), 4.89 (m, 1H, C*H*OH), 1.91-1.84 (br, 1H, CHO*H*), 1.47 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.3, 133.2, 128.7, 126.9, 69.9, 25.4.

1-(3′-Chlorophenyl)ethanol (**6o**) [25]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 2.0 Hz, 1H, aromatic), 7.30–7.22 (m, 3H, aromatic), 4.88 (qd, *J* = 6.5, 3.5 Hz, C*H*(OH)CH_3), 1.92 (d, *J* = 3.5 Hz, 1H, O*H*), 1.48 (d, *J* = 6.5 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.0, 134.5, 129.9, 127.7, 125.8, 123.7, 70.0, 25.4.

1-(2′-Chlorophenyl)ethanol (**6p**) [31]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 2.0 Hz, 1H, aromatic), 7.33–7.27 (m, 2H, aromatic), 7.20 (td, *J* = 8.0, 2.0 Hz, 1H, aromatic), 5.28 (qd, 6.5, 3.5 Hz, 1H, C*H*(OH)CH_3), 2.13 (d, *J* = 4.0 Hz, 1H, OH), 1.48 (d, *J* = 6.5 Hz, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 143.2, 131.7, 129.5, 128.5, 127.3, 126.4, 67.1, 23.6.

1-(4′-Bromophenyl)ethanol (**6q**) [24]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (dt, *J* = 8.5, 2.5, 1.5 Hz, 2H, aromatic), 7.24 (d, *J* = 8.5 Hz, 2H, aromatic), 4.85 (q, *J* = 6.5 Hz, 1H, C*H*(OH)CH_3), 1.98 (br, 1H, O*H*), 1.46 (d, *J* = 6.5 Hz, 3H, CH(OH)CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.9, 131.7, 127.3, 121.3, 69.9, 25.4.

3.4. General Procedure for Transfer Hydrogenation of Aldehydes to the Corresponding Alcohols Using Glucose (Table 3)

3.4.1. Conditions A

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), aldehyde (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.), Na_2CO_3 (10.6 mg, 0.10 mmol, 5.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the products were extracted with dichloromethane (20 mL × 3). After evaporation of the solvent, the yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane). ^{1}H and ^{13}C{^{1}H} NMR spectra of each isolated products are shown in Supplementary Materials.

Benzyl alcohol (**8a**) [32]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.35 (m, 4H, aromatic), 7.33–7.28 (m, 1H, aromatic), 4.70 (d, *J* = 6.0 Hz, 2H, CH_2(OH)), 1.75 (t, *J* = 6.0 Hz, 1H, O*H*).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.0, 128.6, 127.7, 127.1, 65.2.

p-Methylbenzyl alcohol (**8b**) [32]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H, aromatic), 7.14 (d, *J* = 8.0 Hz, 2H, aromatic), 4.57 (d, *J* = 3.5 Hz, 2H, ArCH_2OH), 2.33 (s, 3H, Me), 2.23–2.12 (br, 1H, OH).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ138.0, 137.4, 129.3, 127.2, 65.2, 21.2.

p-Cyanobenzyl alcohol (**8c**) [30]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.57 (m, 2H, aromatic), 7.46–7.41 (m, 2H, aromatic), 4.73 (s, 2H, CH_2), 2.61 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.5, 132.3, 127.1, 119.0, 110.9, 64.1.

m-Nitrobenzyl alcohol (**8d**) [33]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H, aromatic), 8.16 (dd, *J* = 8.5, 1.0 Hz, 1H, aromatic), 7.71 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.54 (t, *J* = 8.0 Hz, 1H, aromatic), 4.84 (s, 2H, CH_2), 1.95 (br, 1H, OH). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.4, 143.0, 132.8, 129.6, 122.6, 121.6, 64.0.

o-Nitrobenzyl alcohol (**8e**) [33]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.0, 1.0 Hz, 1H, aromatic), 7.75 (d, *J* = 7.0 Hz, 1H, aromatic), 7.69 (td, *J* = 7.5, 1.0 Hz, 1H, aromatic), 7.49 (td, *J* = 8.0, 1.0 Hz, 1H, aromatic), 4.99 (d, *J* = 6.0 Hz, 2H, –C*H*(OH)–), 2.53 (t, *J* = 7.0 Hz, 1H, OH).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 147.7, 136.9, 134.3, 130.2, 128.7, 125.2, 62.7.

Methyl-4-(hydroxymethyl)benzoate (**8f**) [34]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H, aromatic), 7.37 (d, *J* = 8.0 Hz, 2H, aromatic), 4.69 (s, 2H, CH_2(OH)), 3.88 (s, 3H, OCH_3), 3.21 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 146.3, 129.8, 129.0, 126.4, 64.4, 52.2.

3.4.2. Conditions B

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (10.6 mg, 0.020 mmol, 1.0 mol%), aldehyde (2.0 mmol), glucose (720.6 mg, 4.0 mmol, 2.0 equiv.), Na_2CO_3 (10.6 mg, 0.10 mmol, 5.0 mol%) and *N*,*N*-dimethylacetamide (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the reaction mixture was poured into water (50 mL) and the products were extracted with a mixed solvent having a volume ratio of hexane: AcOEt of 1:1 (20 mL × 3). After evaporation of the solvent, the yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. The products were isolated by column chromatography (eluent = ethyl acetate/hexane). ^{1}H and ^{13}C{^{1}H} NMR spectra of each isolated products are shown in Supplementary Materials.

p-Methoxybenzyl alcohol (**8g**) [32]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dt, *J* = 9.0, 3.0, 2.0 Hz, 2H, aromatic), 6.89 (dt, *J* = 8.5, 3.0, 2.0 Hz, 2H, aromatic), 4.60 (s, 2H, CH_2), 3.80 (s, 3H, OMe), 1.87 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.2, 133.2, 128.8, 114.0, 65.1, 55.4.

p-Chlorobenzyl alcohol (**8h**) [32]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.23 (m, 4H, aromatic), 4.62 (s, 2H, ArCH_2OH), 2.21 (br, 1H, ArCH_2O*H*).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.3, 133.4, 128.8, 128.4, 64.6.

p-Bromobenzyl alcohol (**8i**) [30]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dt, *J* = 8.5, 2.0 Hz, 2H, aromatic), 7.23 (d, *J* = 8.5 Hz, 2H, aromatic), 4.65 (s, 2H, CH_2), 1.87 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.8, 131.7, 128.7, 121.6, 64.7.

p-tert-Butylbenzyl alcohol (**8j**) [35]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H, aromatic), 7.30 (d, *J* = 8.5 Hz, 2H, aromatic), 4.64 (d, *J* = 1.5 Hz, 2H, CH_2), 1.32 (d, *J* = 2.0 Hz, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 150.8, 138.0, 127.0, 125.6, 65.2, 34.6, 31.5.

2,6-Dichlorobenzyl alcohol (**8k**) [36]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H, aromatic), 7.18 (m, 1H, aromatic), 4.95 (d, *J* = 3.5 Hz, CH_2OH), 2.31 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.0, 135.7, 129.9, 128.5, 60.2.

2-Naphthalenemethanol (**8l**) [37]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.75 (m, 3H, aromatic), 7.72 (s, 1H, aromatic), 7.49–7.38 (m, 3H, aromatic), 4.76 (s, 2H, CH_2), 2.33 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 138.3, 133.4, 133.0, 128.3, 128.0, 127.8, 126.2, 126.0, 125.5, 125.3, 65.4.

1-Naphthalenemethanol (**8m**) [33]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d *J* = 8.0 Hz, 1H, aromatic), 7.88–7.74 (m, 2H, aromatic), 7.54–7.36 (m, 4H, aromatic), 5.05 (s, 2H, CH_2), 2.30–2.10 (br, 1H, O*H*). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 136.3, 133.8, 131.3, 128.7, 128.6, 126.4, 126.0, 125.5, 125.4, 123.7, 63.6.

3.5. Preparation of 2,3,4,6-tetra-O-methyl-D-glucopyranose (10). (Equation (2))

In a two-necked round-bottomed flask, aqueous NaOH (50 wt%, 4.0 mL), methyl α-D-glucopyranoside (**9**) (1.94 g, 10.0 mmol) and DMSO (35 mL) were placed. After stirring the mixture at room temperature for 5 min, iodomethane (3.3 mL, 50 mmol) was added. The mixture was stirred

at room temperature for 4 h. The reaction mixture was poured into water (100 mL) and extracted with Et_2O. An intermediate product was obtained after evaporation of the organic layer. (colorless oil, 1.64 g, 6.5 mmol, 65% yield).

In a round-bottomed flask, above intermediate product (1.64 g, 6.5 mmol) and aqueous HCl (9.6 M, 25 mL) were placed. The mixture was stirred at 60 °C for 16 h. After cooling to room temperature, the crude product was obtained by evaporation of the reaction mixture. After purifying by column chromatography (eluent = EtOH/CH_2Cl_2), the product **10** was obtained (653.5 mg, 2.8 mmol, 43% yield).

2,3,4,6-tetra-O-methyl-D-glucopyranose (**10**) [38]:^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (d, *J* = 3.5 Hz, 1H), 4.56 (d, *J* = 7.5 Hz, 0.5H), 3.91 (dt, *J* = 10.5 Hz, 2.5 Hz, 1H), 3.70 (q, *J* = 7.0 Hz, 1H), 3.66–3.60 (m, 6H), 3.59–3.5 (m, 6H), 3.53–3.50 (m, 4H), 3.42–3.30 (m, 5H,), 3.22–3.05 (m, 3H), 2.97 (dd, *J* = 9.0, 8.0 Hz, 0.5 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 96.9, 90.5, 86.4, 84.7, 83.1, 81.9, 79.7, 79.7, 74.1, 71.6, 71.4, 69.6, 60.9, 60.8, 60.5, 60.4, 59.1, 58.7.

*3.6. Reaction of Acetophenone Using α-D-glucopyranoside (**9**) (Equation (1))*

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (1.0 mg, 0.002 mmol, 0.1 mol% Ir), acetophenone (240.5 mg, 2.0 mmol), α-D-glucopyranoside (777.3 mg, 4.0 mmol), Na_2CO_3 (10.5 mg, 0.1 mmol, 5.0 mol%) and degassed distilled water (3.0 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the mixture was diluted with toluene (50 mL). The conversion of acetophenone and the yield of 1-phenylethanol were determined by GC analysis using biphenyl as an internal standard. No reaction occurred.

*3.7. Reaction of Acetophenone Using 2,3,4,6-tetra-O-methyl-D-glucopyranose (**10**) (Equation (2))*

In a 5 mL stainless-steel reactor under argon atmosphere, catalyst **1** (1.1 mg, 0.002 mmol, 0.2 mol%Ir), acetophenone (120.6 mg, 1.0 mmol), 2,3,4,6-tetra-*O*-methyl-D-glucopyranose (472.4 mg, 2.0 mmol, 2.0 equiv.), Na_2CO_3 (5.4 mg, 0.05 mmol, 5 mol%) and degassed distilled water (1.5 mL) were placed. Then, the reactor was sealed with a stainless-steel stopper, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the mixture was diluted with toluene (25 mL). The conversion of acetophenone and the yield of 1-phenylethanol were determined by GC analysis using biphenyl as an internal standard. The conversion and the yield were 97% and 97%, respectively.

4. Conclusions

In conclusion, we developed a new system for transfer hydrogenation of various ketones and aldehydes using glucose as a hydrogen donor catalyzed by a small amount of iridium complex (0.1 to 1 mol% Ir). It should be noted that environmentally benign water could be used as a solvent in the present catalytic system for various carbonyl substrates. To the best of our knowledge, the results disclosed in this paper were the first example of transfer hydrogenation in water using glucose as a hydrogen donor. Furthermore, the reaction scope could be extended by using DMAc as a reaction solvent instead of water.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/6/503/s1, detailed description of experimental procedures, ^{1}H and ^{13}C{^{1}H} NMR data of the isolated products with spectral charts.

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