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Fe-Catalyzed Acceptorless Dehydrogenation of Secondary Benzylic Alcohols

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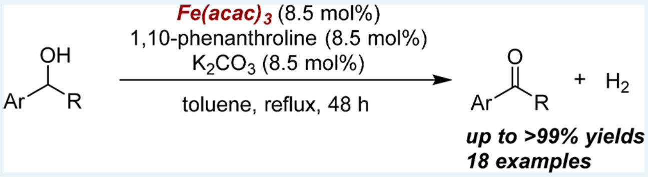
Supporting Information



ABSTRACT: Oxidation of alcohols is an essential organic reaction, affording versatile carbonyl groups. To provide a sustainable solution for environmentally harmful traditional oxidation methods, the transition-metal catalyzed acceptor-free dehydrogenation of alcohols has attracted much attention. The widely used catalysts for the dehydrogenation reaction are based on precious metals, which are not economical and environmentally benign. We developed an operationally simple, economical, and environmentally benign acceptorless Fe-catalyzed dehydrogenation of various secondary benzylic alcohols to afford the corresponding ketones and H_2. A simple in situ mixture of readily available Fe(III) acetylacetonate, 1,10-phenanthroline, and K_2CO_3 was identified as an active catalyst for this transformation.

KEYWORDS: *iron catalysis, dehydrogenation, oxidation, alcohol, ketone, H_2 production*

INTRODUCTION

Oxidation of alcohols is a fundamental and important organic transformation. Readily available alcohols have been widely used as the precursors for synthetically useful carbonyl compounds.[1] Traditional methods for the oxidation of alcohols require stoichiometric amounts of oxidants such as hypochlorite,[2] Cr salts,[3] Mn salts,[4] oxalyl chloride,[5] hypervalent iodine,[6] oxygen with transition-metal catalysts,[7] and H_2O_2.[8] The traditional methods have several drawbacks in terms of atom economy, economics, and environmental effects as most of the methods generate a huge amount of wastes or undesirable byproducts.

The catalytic acceptorless dehydrogenation of alcohols has been considered as an important transformation to overcome these problems. Many catalytic systems have been developed, based on precious metals such as Rh,[9] Ru,[10] Ir,[11] and Os.[12] Although the oxidation method itself is simple and clean, the precious metals used for the catalytic dehydrogenation of alcohols have disadvantages in terms of toxicity and high cost. Therefore, significant recent efforts have been made to develop dehydrogenation catalysts based on earth-abundant metals such as Co[13] and Fe.[26−28]

Fe is the most abundant, economical, and nontoxic transition metal.[14] Fe has been developed as a catalyst for many organic reactions: (i) chemical reduction processes such as the hydrogenation of C−C multiple bonds or polar multiple bonds,[15] transfer hydrogenation,[16] and hydrosilylation,[17] and (ii) bond-forming processes such as C−H bond oxidation,[18] and C−N,[19] C−O,[20] and C−C bond formation.[21] The hydrogenation reactions using Fe as the catalyst have been well-developed. Chirik and co-workers developed Fe(II) and Fe(0) complexes **1** (Figure 1), which can catalyze alkene hydrogenation and hydrosilylation.[22] Casey and co-workers demonstrated that Knölker's Fe complex **2**[23] is an efficient and selective catalyst for the hydrogenation of the polar multiple bonds of carbonyl compounds and imines.[24] Milstein and co-workers reported PNP pincer-type ligand-based Fe complexes **3**, which were active for the hydrogenation of ketones and CO_2, and the dehydrogenation of formic acids.[25]

Compared to the actively ongoing development of Fe catalysts for hydrogenation reactions, the development of Fe catalysts for the dehydrogenation process has been limited. Recently, Jones and co-workers reported a well-defined Fe complex **5** supported by a bis(phosphino)amine pincer ligand for acceptorless dehydrogenation of N-heterocycles.[26] For dehydrogenation of alcohols, Beller and co-workers used the dehydrogenation of MeOH for the generation of H_2 catalyzed by Fe-hydride complex **4**.[27] Nakazawa and co-workers just reported the $CpFe(CO)_2Cl$-catalyzed dehydrogenation of alcohols; however, the catalytic reaction only worked for 2-pyridylmethanol derivative because of the crucial chelating role of pyridine for the catalytic activity.[28] Because some Fe complexes can mediate hydrogen-transfer reactions,[29] we envisioned that an operationally simple Fe-based catalytic system is possible for the environmentally benign and atom-economical acceptorless dehydrogenation of alcohols. Herein, we report the Fe-catalyzed dehydrogenation of

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secondary benzylic alcohols using a simple in situ Fe-catalyst system based on readily available sources.

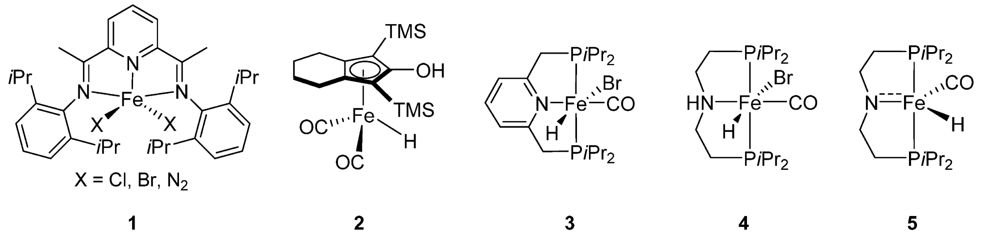
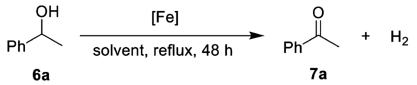


Figure 1. Previously reported Fe complexes.

Table 1. Optimization of Reaction Conditions



entry[a]	Fe complex (mol %)	ligand[b]	base[b]	solvent	yield[c] (%)
1	$Fe(acac)_2$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	>99
2	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	>99
3	$Fe(acac)_3$ (5.0)	1,10-phenanthroline	K_2CO_3	toluene	80
4	$Fe(acac)_3$ (7.5)	1,10-phenanthroline	K_2CO_3	toluene	93
5[d]	$Fe(acac)_3$ (5.0)	1,10-phenanthroline	K_2CO_3	toluene	48
6	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	1,4-dioxane	28
7	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	acetonitrile	10
8	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	1,2-dichloroethane	5
9	$Fe(acac)_3$ (8.5)	1,10-phenanthroline		toluene	58
10	$Fe(acac)_3$ (8.5)		K_2CO_3	toluene	54
11		1,10-phenanthroline	K_2CO_3	toluene	N.R.
12	$Fe(acac)_3$ (8.5)			toluene	29
13		1,10-phenanthroline		toluene	N.R.
14[e]	$Fe(acac)_2$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	80
15[e]	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	80
16[f]	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	trace
17	$Fe_2(CO)_9$ (4.3)	1,10-phenanthroline	K_2CO_3	toluene	38
18	$Fe_3(CO)_{11}$ (2.8)	1,10-phenanthroline	K_2CO_3	toluene	60
19	FeI_2 (8.5)	1,10-phenanthroline	K_2CO_3	toluene	36
20	$FeBr_2$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	5
21	FeF_2 (8.5)	1,10-phenanthroline	K_2CO_3	toluene	5
22	$FeCl_2$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	73
23	$Fe(OAc)_2$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	13
24	$Fe(TMHD)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	59
25	$Fe(Hfac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	72
26	$Fe(Tfac)_3$ (8.5)	1,10-phenanthroline	K_2CO_3	toluene	50
27	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	KO^tBu	toluene	69
28	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	NaOAc	toluene	60
29	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	NaOH	toluene	83
30	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	$NaCO_3$	toluene	71
31	$Fe(acac)_3$ (8.5)	1,10-phenanthroline	$NaHCO_3$	toluene	77
32	$Fe(acac)_3$ (8.5)	2,2′-bypyridyl	K_2CO_3	toluene	43
33	$Fe(acac)_3$ (8.5)	4,4′-dinonyl-2,2′-dipyridyl	K_2CO_3	toluene	42
34	$Fe(acac)_3$ (8.5)	(*E*)-2,6-diisopropyl-*N*-(pyridin-2-ylmethylene)aniline	K_2CO_3	toluene	29
35	$Fe(acac)_3$ (8.5)	TMEDA	K_2CO_3	toluene	34
36	$Fe(acac)_3$ (5.0)	1,10-phenanthroline (10)	K_2CO_3 (10)	toluene	78
37	$Fe(acac)_3$ (5.0)	1,10-phenanthroline (20)	K_2CO_3 (40)	toluene	73

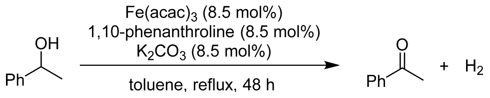
[a] 1-Phenylethanol (0.4 mmol). [b] The same loading (mol %) with Fe complex used unless otherwise described. [c] HPLC yield using anisole as the internal standard. [d] 18-crown-6 (5 mol %) was added as an additive. [e] 24 h reaction time. [f] Room temperature.

RESULTS AND DISCUSSION

The dehydrogenation of 1-phenylethanol (**6a**) was selected as the model reaction to achieve our goal. We investigated various combinations of Fe sources, ligands, and bases (Table 1). To our delight, the use of $Fe(acac)_2$ or $Fe(acac)_3$ afforded acetophenone (**7a**) in quantitative yields using 1,10-phenanthroline as the ligand and K_2CO_3 as the base (entries 1 and 2). Lower catalyst loadings than 8.5 mol % were not as effective (entries 3 and 4). To increase the solubility of precatalyst mixtures, polar solvents and 18-crown-6 were used, but those trials were unsuccessful (entries 5−8). Without Fe, the reaction did not occur (entries 11 and 13). Fe(acac)$_2$ and Fe(acac)$_3$ exhibited identical activity under the reaction conditions investigated (entries 1, 2, 14, and 15), and we selected more economical Fe(acac)$_3$ as the Fe source for further studies. When the base was not used, the product was obtained in 58% yield (entry 9). When 1,10-phenanthroline was not used, the product was obtained in 54% yield (entry 10). A shorter reaction time of 24 h decreased the conversion of alcohol to ketone than 48 h (entries 14 and 15). Other Fe sources were investigated; however, Fe(acac)$_3$ was the best catalyst for this transformation (entries 17−26). The reactions of Fe(0) carbonyl compounds afforded the corresponding ketones in moderate yields (entries 17 and 18). The use of Fe(II) sources such as Fe(II) halides and Fe(OAc)$_2$ usually afforded low yields (entries 19−23), except FeCl$_2$ (73%, entry 22) and Fe(acac)$_2$ (>99%, entry 1). Other Fe(III) species with ligands such as 2,2,6,6-tetramethyl-3,5-heptanedionate (TMHD), hexafluoroacetylacetonate (Hfac), and trifluoroacetylacetonate (Tfac) afforded **7a** in moderate yields (entries 24−26). Other bases instead of K$_2$CO$_3$ exhibited reduced activity (entries 27−31). Several *N*,*N*-bidentate ligands were also investigated. The use of bipyridyl ligands afforded the products in moderate yields (entries 32 and 33). The diimine-type ligand, reported by Ritter to facilitate the Fe-catalyzed 1,4-hydroboration of 1,3-dienes,[30] was not effective. Tetramethylethylenediamine (TMEDA) was also investigated; however, it showed a low reactivity (entry 35). Varying the ratios of Fe to ligand or base was not as effective (entries 36−37).

The reaction conditions were investigated to evaluate the stability of the catalytic system in air and the effect of open and closed systems (Table 2). The dehydrogenation reaction in air atmosphere afforded the product in an excellent yield, demonstrating that the in situ Fe catalyst system is quite stable to air (entry 2). When the reaction was conducted in a closed system, the reaction efficiency significantly decreased, indicating that the removal of H$_2$ from the reaction mixture is essential for reaction progress, as reported in other dehydrogenative transformations (entry 3).[31]

Table 2. Reactions in Open/Closed Systems



entry[a]	open/closed	atmosphere	yield[b] (%)
1	open	Ar	>99
2	open	air	92
3	closed	Ar	36

[a] 1-Phenylethanol (0.4 mmol) in a 25 mL Schlenk tube. [b] HPLC yield using anisole as the internal standard.

The substrate scope and selectivity of alcohols with various electronic properties and functional groups were investigated using the developed method (Table 3). The reactions of *para*-substituted aryl alcohols afforded the corresponding ketones in excellent yields regardless of the presence of electron-donating or -withdrawing functional groups (entries 2−7). The reactions of *meta*-substituted benzyl alcohols afforded the corresponding products in good yields (entries 8 and 9). Various functional groups including aryl halides, ethers, amines, olefins, and trifluoromethyl groups were tolerant under the catalytic reaction conditions. The reactions of 2-methoxyphenyl-1-ethanol (**6j**) and diphenylmethanol (**6k**) afforded the corresponding ketones in excellent yields (entries 10 and 11). 1,2,3,4-Tetrahydro-1-naphthalenol (**6l**) was oxidized in a moderate yield, and 1-indanol (**6m**) afforded the corresponding product in 22% yield (entries 12 and 13). The acetylnaphthalene products were obtained in high yields (entries 14 and 15). The reaction of 1-phenylbutanol (**6p**) afforded the corresponding ketone in a moderate yield (entry 16). Amino group was tolerated, even though the yield was slightly reduced (entry 17). The reaction of a secondary alcohol with an intramolecular olefin moiety, 1-(4-(pent-4-en-1-yloxy)phenyl)ethanol (**6r**), was investigated. Unlike in the reported Ru-catalyzed dehydrogenation of olefin-containing alcohols,[10b] where the hydrogenation of olefins occurred, the olefin functional group was not reduced (entry 18); thus, this reaction can be beneficial for the selective dehydrogenation of olefin-containing alcohols.

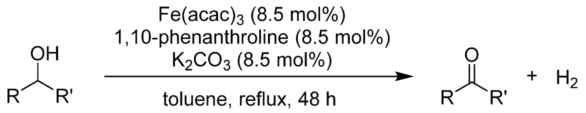
Unfortunately, primary and aliphatic alcohols were not dehydrogenated under our catalytic reaction conditions. When benzyl alcohol (**6s**) and 1-phenyl-2-propanol (**6t**) were used as the substrates, trace amounts of corresponding carbonyl products were obtained with mostly remaining unreacted starting materials (entries 19 and 20). An allyl secondary alcohol (**6u**) also did not react (entry 21).

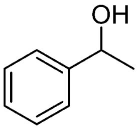
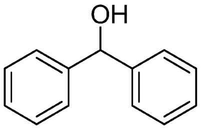
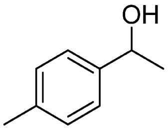
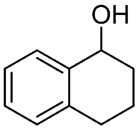
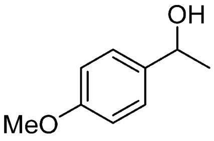
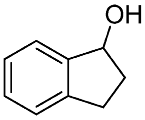
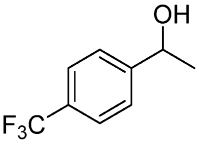
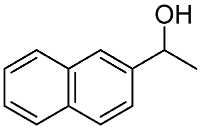
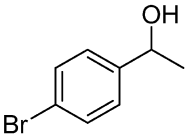
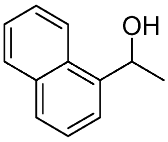
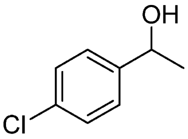
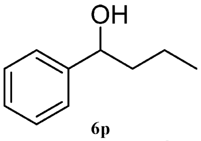
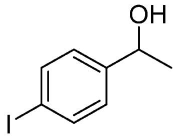
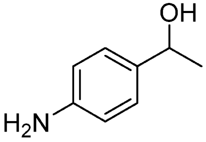
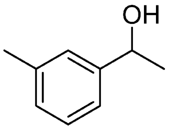
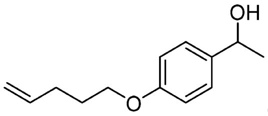
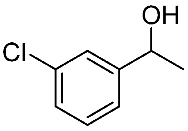
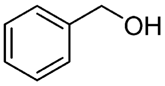
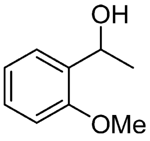
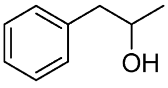
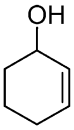
To confirm H$_2$ evolution in the reactions, intermolecular hydrogen transfer experiments were conducted (Scheme 1). When the dehydrogenation of **6a** was conducted in the presence of 4-methoxybenzaldehyde (**7**) in a closed system, 1-phenylethanol was dehydrogenated to acetophenone (**7a**) in 40% yield, and **8** was hydrogenated to (4-methoxyphenyl)methanol (**9**) in 31% yield (Scheme 1a). In an open system and Ar atmosphere, the dehydrogenation and hydrogen transfer reactions were relatively retarded (Scheme 1b). The hydrogen transfer efficiency was calculated using a simple equation: [yield of **9**]/[yield of **7a**]; 77% of hydrogen transfer occurred in a closed system (Scheme 1a). In contrast, in an open system, the transfer efficiency significantly decreased to 41% (Scheme 1b). In addition, we detected H$_2$ gas evolved during dehydrogenation of **6a** by gas chromatography (GC) analysis (Figure S1). The results conclusively indicate that the catalytic reaction system works in a dehydrogenative manner, producing H$_2$ similar to other reported precious metal-based catalytic systems. A deuterium-labeled study was conducted using **6a-*d*$_2$** to confirm the source of hydrogen of hydrogenated compounds. Only deuterium exchange was observed in **9**, which conclusively proved that the source of H$_2$ was exclusively from the dehydrogenation of **6a** (Scheme 1c).

With the concern that the reaction could be mediated by precious-metal contamination, the reaction was screened with eight different Fe(acac)$_3$ samples from various sources: two different chemical manufacturers, three different laboratories, and different purity grades (>97%, >99%, and >99.9%). In all the cases, the products of the dehydrogenation of **6a** were obtained in quantitative yields in a consistent manner under the standard catalytic reaction conditions (entry 1, Table 2).

Kinetic isotope effect (KIE) was measured to gain insight into the rate-limiting step of the developed Fe-catalyzed dehydrogenation reactions. The initial reaction rates of the three reactions were measured with nondeuterated (**6a**) and deuterated (**6a-*d*$_2$** and **6a-*d*$_1$**) substrates (Scheme 2 and Figure 2). The KIEs showed a primary isotope effect of ∼2.5. Compounds **6a-*d*$_2$** and **6a-*d*$_1$** exhibited essentially the same reaction rates. From these results, we concluded that $C_{(\alpha\text{ position of alcohol})}$-H cleavage is the rate-limiting step similar to those in the reported precious transition-metal-based catalytic dehydrogenation reactions.[32]

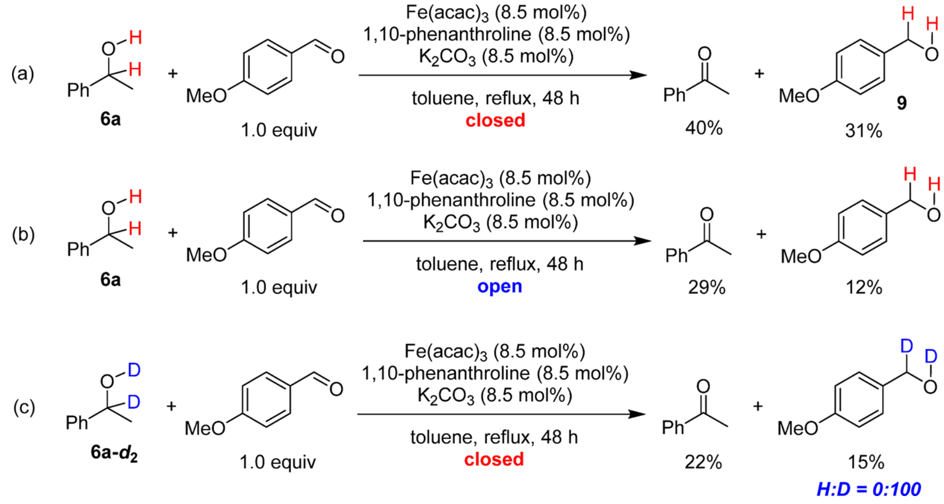
Table 3. Substrate Scope



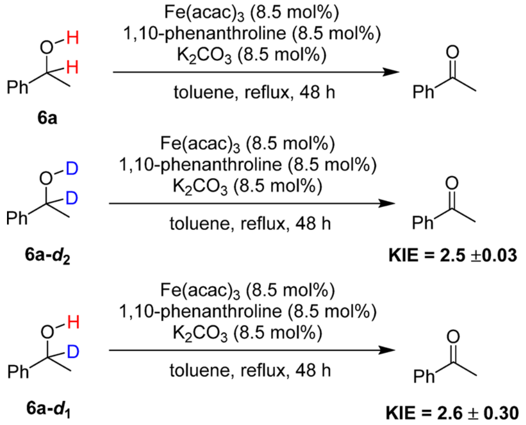
entry[a]	substrates	yield[b] (%)	entry[a]	substrates	yield[b] (%)
1	 **6a**	>97[c]	11	 **6k**	94
2	 **6b**	>97	12[e]	 **6l**	60
3	 **6c**	>97	13	 **6m**	22
4	 **6d**	>97	14[d]	 **6n**	87
5[d]	 **6e**	>97	15[e]	 **6o**	93
6	 **6f**	>97	16[e]	 **6p**	61
7	 **6g**	94	17	 **6q**	54
8[e]	 **6h**	70	18[e]	 **6r**	80
9	 **6i**	87	19	 **6s**	trace
10[d]	 **6j**	97	20	 **6t**	trace
			21	 **6u**	N.R.

[a] Substrate 0.4 mmol. [b] Isolated yield. Unreacted starting material was observed when dehydrogenation reaction was not quantitative. [c] HPLC yield using anisole as the internal standard. [d] 15 mol % catalyst loading. [e] 10 mol % catalyst loading.

Scheme 1. Intermolecular Hydrogen Transfer Process



Scheme 2. Isotope-Labeling Reactions for Measuring Kinetic Isotope Effect



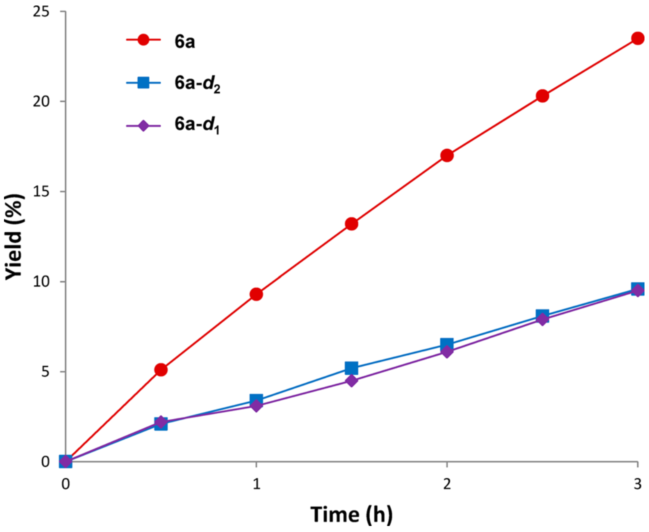


Figure 2. Reaction profile with deuterated 1-phenylethanol for KIE study.

CONCLUSION

An operationally simple, economical, and environmentally benign acceptorless Fe-catalyzed dehydrogenation of alcohols was developed based on readily available starting materials such as Fe(acac)$_3$, 1,10-phenanthroline, and K_2CO_3. Various types of secondary benzylic alcohols, which were inaccessible to the dehydrogenation reaction with the recently reported Fe-based catalytic systems, could be converted to the corresponding ketones with good functional group tolerance. Based on this catalytic system, further studies are underway to develop well-defined Fe complexes in order to expand the substrate scope of the reaction and understand the precise role of Fe and ligands.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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