Ir(III)-Catalyzed Room-Temperature Synthesis of Multisubstituted Benzofurans Initiated by C–H Activation of α-Aryloxy Ketones

Takanori Shibata,*[a] Yu-ki Hashimoto,[a] Maiko Otsuka,[a] Kyoji Tsuchikama,[a] Kohei Endo[b]

[a] Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, Okubo, Shinjuku, Tokyo, 169-8555, Japan
Fax +81(3)52868098; E-mail: tshibata@waseda.jp

[b] Waseda Institute for Advanced Study, Shinjuku, Tokyo, 169-8050, Japan

Received 9 May 2011

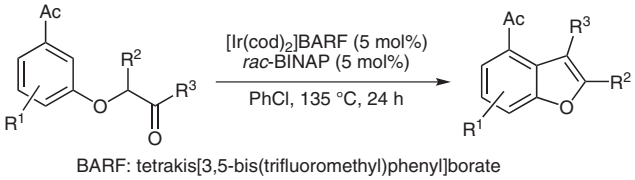
Abstract: Cyclodehydration of various α-aryloxy ketones proceeded to give various multisubstituted benzofurans by using an Ir(III) catalyst, which was prepared from $[Cp^*IrCl_2]_2$, $AgSbF_6$, and $Cu(OAc)_2$. The use of the cationic iridium complex with a carboxylate salt realized the efficient transformation at ambient temperature.

Key words: C–H activation, benzofurans, cyclodehydration, iridium, room temperature

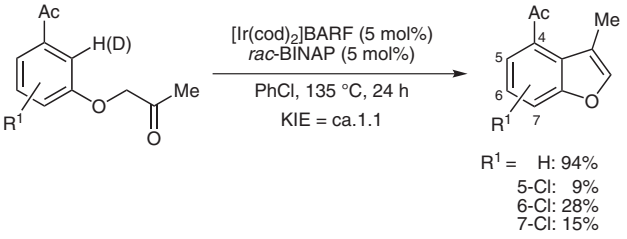
Direct C–H bond functionalization is an atom-economical transformation, because it can omit the pre-activation step of the substrate and, as a result, the formation of byproduct(s) derived from the activating group. In the last decade, various fascinating transformations initiated by transition-metal-catalyzed C–H bond activation have been reported.[1] But the bond energy of the C–H bond is intrinsically large, and high reaction temperature is generally required, which sometimes limits the scope of synthetic application. Therefore, the development of efficient catalysts for the C–H bond activation, which can operate under milder reaction conditions, is strongly desired.[2]

In these years, we have focused on the development of cationic iridium(I) catalyzed synthesis initiated by C–H bond activation and realized carbonyl- or amide-directed C–H bond cleavage for the reaction with alkynes and alkenes, respectively.[3] We further reported the synthesis of benzofurans initiated by C–H bond activation of α-3-acetylphenyloxy ketones along with intramolecular 1,2-additon and dehydration (Scheme 1).[4,5] This regioselective transformation provided various 4-acetyl benzofurans without the formation of 6-acetyl benzofurans, but the high reaction temperature of 135 °C was required. We herein report an iridium(III)-catalyzed synthesis, which realized a reaction at room temperature and widened the substrate scope.

In the course of mechanistic study of the above transformation,[4] we found that the value of the KIE (kinetic isotope effect) was approximately 1.1, and that introduction of the electron-withdrawing chloro group on the benzene ring apparently decreased the reactivity, and most of substrates remained (Scheme 2).

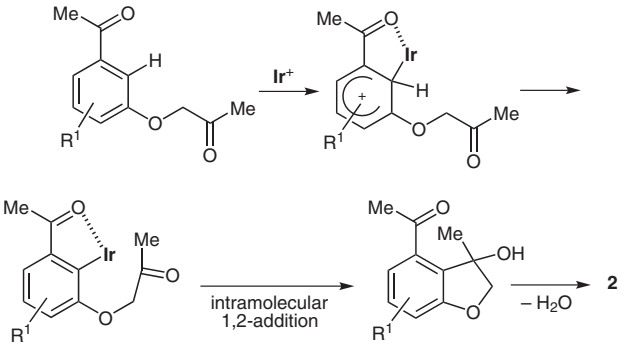


Scheme 1 Ir(I)-catalyzed cyclodehydration of α-aryloxy ketones



Scheme 2 Effect of substituents (R^1) on the benzene ring in the previous catalysis

Judging from these results, we assumed that C–H bond cleavage by electrophilic metalation is more probable than oxidative addition (Scheme 3)[6] and anticipated that a more electrophilic complex could accelerate the reaction.[7]



Scheme 3 Possible mechanism including electrophilic metalation

We chose α-aryloxy ketone **1a** as a model substrate and submitted it to the reaction using the dicationic iridium species Cp^*Ir^{2+} (Cp^*: pentamethylcyclopentadienyl), which was in situ prepared from $[Cp^*IrCl_2]_2$ (10 mol% Ir) and $AgSbF_6$ (20 mol%),[8] as a catalyst in 1,2-dichloroethane (DCE, Table 1, entry 1). We were pleased to find

SYNLETT 2011, No. 14, pp 2075–2079
Advanced online publication: 03.08.2011
DOI: 10.1055/s-0030-1260981; Art ID: U04111ST

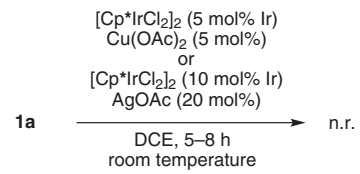
that the cyclodehydration proceeded even at room temperature to give benzofuran **2a** yet in low yield due to low conversion. In order to improve the yield, we screened a catalytic amount of additives: when sodium acetate was added, the yield dramatically increased to 66%, which includes benzofuranol **3a** (Table 1, entry 2).[9] More bulky sodium pivalate achieved the yield of 85% without the formation of benzofuranol **3a** (Table 1, entry 3). When potassium pivalate was used, the yield was further improved (Table 1, entry 4), and, in the case of cesium pivalate, benzofuranol **3a** was a major product (Table 1, entry 5).[10] The heavy metal acetates were also efficient additives to give benzofuran **2a** as a sole product, and copper acetate realized the excellent yield of 96% (Table 1, entries 6 and 7).[11] Between potassium pivalate and copper acetate, the latter gave better results under the conditions of lower catalyst loading (Table 1, entries 8 and 9). When $[Cp^*RhCl_2]_2$ was used in place of $[Cp^*IrCl_2]_2$, the reaction sluggishly proceeded to give product **2a** in much lower yield (Table 1, entry 10).

Table 1 Screening of Various Carboxylates in the Ir(III)-Catalyzed Cyclodehydration at Room Temperature

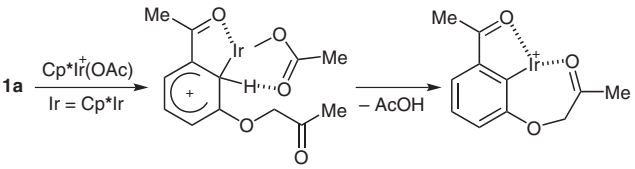
Entry	Additive	Time (h)	Yield of **2a** (%)	Yield of **3a** (%)
1	none	8	7	n.d.[a]
2	NaOAc	8	45	21
3	NaOPiv	8	85	n.d.[a]
4	KOPiv	8	93	3
5	CsOPiv	8	28	51
6	AgOAc	8	87	n.d.[a]
7	$Cu(OAc)_2$	8	96	n.d.[a]
8[b]	KOPiv	24	85	n.d.[a]
9[b]	$Cu(OAc)_2$	20	93	n.d.[a]
10[b,c]	$Cu(OAc)_2$	20	7	n.d.[a]

[a] Not detected.
[b] The amount of catalyst was halved: $[Cp^*IrCl_2]_2$ (5 mol% Ir), $AgSbF_6$ (10 mol%), additive (5 mol%).
[c] $[Cp^*RhCl_2]_2$ was used in place of $[Cp^*IrCl_2]_2$.

The combination of $[Cp^*IrCl_2]_2$ and $Cu(OAc)_2$ without $AgSbF_6$ showed almost no catalytic activity. Moreover, when AgOAc was used in place of $AgSbF_6$ for the formation of cationic Ir species, almost no reaction proceeded (Scheme 4). These results mean that the existence of naked cationic species along with stable counteranion (SbF_6) was important,[12] therefore, we now assume that monocationic iridium acetate is an efficient catalyst[13] and that acetate facilitates hydrogen abstraction,[14] which realized the reaction even at room temperature (Scheme 5).



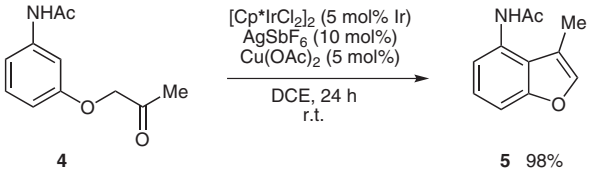
Scheme 4 Preparation of Ir(III) catalyst without $AgSbF_6$



Scheme 5 Proposed mechanism of hydrogen abstraction by acetate

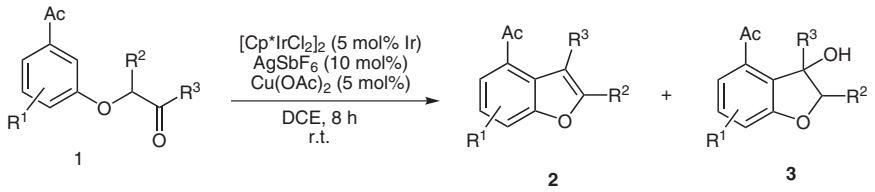
We next investigated the substrate scope under the reaction conditions of entry 9 in Table 1 (Table 2). All reactions proceeded with perfect regioselectivity to give 4-acetylbenzofurans or -furanols.[15] When bulky ketones such as phenyl and *tert*-butyl ketones were submitted, the reaction smoothly proceeded to give benzofurans **2b** and **2c** along with the formation of benzofuranols **3b** and **3c** (Table 2, entries 1 and 2). 2,3,4-Trisubstituted benzofurans **2d** and **2e** were also obtained in high yields as sole products, respectively (Table 2, entries 3 and 4). Cyclic ketone **1f** was converted into tricyclic compound **2f** in quantitative yield (Table 2, entry 5). When a methoxy group was installed on the benzene ring, the corresponding regioisomers were obtained in high to excellent yields (Table 2, entries 6–8). Notably, the regioselective reaction of ketone **1h**, which has acetyl and methoxy groups at the *meta* position, proceeded to give 4-acetylbenzofuran **2h** as a sole product, without the formation of 6-acetylbenzofuran. These results mean that the C–H bond adjacent to the acetyl group, not the methoxy group, was selectively cleaved, which supports the directing effect of the acetyl group. Elevated temperature of 60 °C was required, but it is noteworthy that chloro-substituted aryloxy ketones **1j**, **1k**, and **1l** were also transformed into benzofurans **2j**, **2k**, and **2l** in high yield (Table 2, entries 9–11). A more electron-withdrawing fluoro group could be also introduced into the benzene ring of benzofurans (Table 2, entry 12).

Other than the acetyl group, the acetylamino group could also operate as an efficient directing group, and 4-aminobenzofuran **5** was obtained in excellent yield at room temperature (Scheme 6).



Scheme 6 Amide-directed synthesis of benzofuran **5**

Table 2 Substrate Scope of Ir(III)-Catalyzed Cyclodehydration



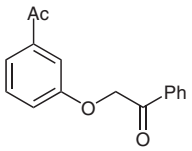
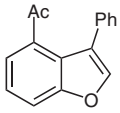
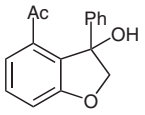
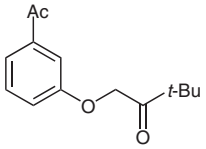
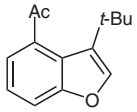
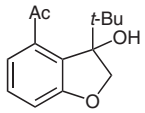
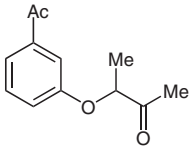
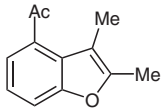
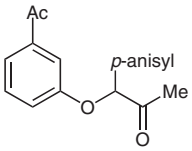
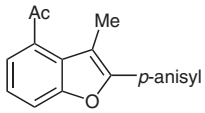
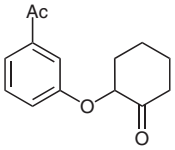
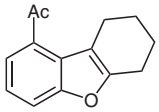
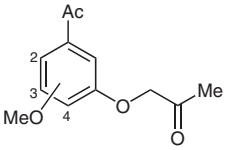
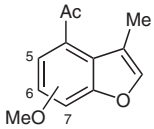
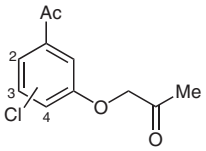
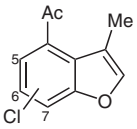
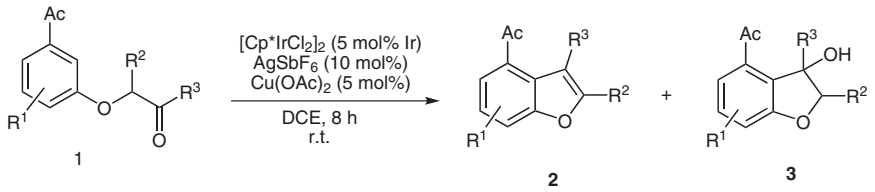
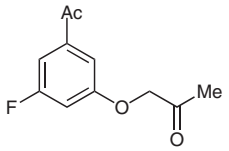
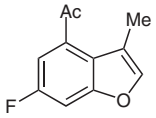
Entry	Substrate **1**	Yield of **2** and **3** (%)	
1	 **1b**	 **2b** 65	 **3b** 18
2	 **1c**	 **2c** 51	 **3c** 33
3	 **1d**	 **2d** 97	
4	 **1e**	 **2e** 87	
5	 **1f**	 **2f** >99	
			
6	**1g** 2-OMe	**2g** 5-OMe, 91	
7	**1h** 3-OMe	**2h** 6-OMe, >99	
8	**1i** 4-OMe	**2i** 7-OMe, 91	
			
9	**1j** 2-Cl	**2j** 5-Cl, 87	
10[a]	**1k** 3-Cl	**2k** 6-Cl, 89	
11[a]	**1l** 4-Cl	**2l** 7-C,l 89	

Table 2 Substrate Scope of Ir(III)-Catalyzed Cyclodehydration (continued)



Entry	Substrate **1**	Yield of **2** and **3** (%)
12[a]	 **1m**	 **2m** 77

[a] The reaction was examined at 60 °C.

In conclusion, we developed Ir(III)-catalyzed cyclodehydration of α-aryloxy ketones at room temperature. The catalyst prepared from $[Cp^*IrCl_2]_2$, $AgSbF_6$, and $Cu(OAc)_2$ realized the mild reaction conditions, and various multisubstituted benzofurans were obtained in high to excellent yield with perfect regioselectivity. The precise mechanistic study of the present catalysis and its application for other reactions are under way in our laboratory.

In a Schlenk tube, $[Cp^*IrCl_2]_2$ (2.1 mg, 2.5 μmol) and $AgSbF_6$ (3.6 mg, 11 μmol) were placed under an atmosphere of argon and acetone (0.5 mL) was added. Silver salt was precipitated, and the acetone solution was transferred into another Schlenk tube via a syringe filter for the removal of the precipitate. After acetone was excluded under reduced pressure, and the Schlenk tube was backfilled with argon (×3), a DCE solution (0.3 mL) of substrate **1** (0.1 mmol) and $Cu(OAc)_2$ (1.0 mg, 6 μmol) was added. The reaction mixture was stirred at r.t. for 8 h, then the crude products were purified by preparative TLC to give analytically pure benzofuran **2**.

1-(3-Acetyl-4-chlorophenoxy)propan-2-one (1j)
Pale yellow solid (mp 29–30 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 2.66 (s, 3 H), 4.58 (s, 2 H), 6.94 (dd, *J* = 3.2, 8.8 Hz, 1 H), 7.05 (d, *J* = 3.2 Hz, 1 H), 7.34 (d, *J* = 8.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 30.7, 73.1, 115.0, 118.6, 123.8, 131.8, 139.9, 156.4, 199.9, 204.0. IR (KBr disk): 1718, 1668, 1178, 889 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_{12}ClO_3$: 227.0475 [M + H]; found: 227.0468.

4-Acetyl-5-chloro-3-methylbenzofuran (2j)
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 3 H), 2.68 (s, 3 H), 7.25 (d, *J* = 8.8 Hz, 1 H), 7.40 (d, *J* = 8.8 Hz, 1 H), 7.45 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.1, 32.3, 113.2, 115.0, 122.9, 125.1, 125.9, 133.7, 144.0, 154.2, 202.2. IR (neat): 1707, 1234, 797 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_{10}ClO_2$: 209.0369 [M + H]; found: 209.0405.

1-(3-Acetyl-5-chlorophenoxy)propan-2-one (1k)
White solid; mp 92–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 2.57 (s, 3 H), 4.62 (s, 2 H), 7.11 (s, 1 H), 7.34 (s, 1 H), 7.55 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 26.6, 72.9, 111.9, 119.8, 122.1, 135.5, 139.4, 158.5, 196.2, 203.5. IR (KBr disk): 1716, 1683, 1068, 750 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_{11}ClO_3$: 226.0397 [M]; found: 226.0393.

4-Acetyl-6-chloro-3-methylbenzofuran (2k)
White solid; mp 50–51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 2.66 (s, 3 H), 7.48 (s, 1 H), 7.57 (s, 1 H), 7.61 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3, 28.8, 115.4, 117.0, 124.1, 125.0, 128.9, 134.1, 144.8, 156.7, 198.5. IR (KBr disk): 1691, 1107, 721 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_{10}ClO_2$: 209.0369 [M + H]; found: 209.0369.

1-(5-Acetyl-2-chlorophenoxy)propan-2-one (1l)
White solid; mp 74–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 2.58 (s, 3 H), 4.66 (s, 2 H), 7.41 (d, *J* = 2.3 Hz, 1 H), 7.51 (s, 1 H), 7.52 (d, *J* = 2.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 26.8, 73.4, 111.8, 122.8, 128.7, 130.6, 136.8, 153.6, 196.5, 204.0. IR (KBr disk): 1720, 1670, 1219, 827 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_{12}ClO_3$: 227.0475 [M + H]; found: 227.0468.

4-Acetyl-7-chloro-3-methylbenzofuran (2l)
White solid; mp 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 2.67 (s, 3 H), 7.33 (d, *J* = 12.2 Hz, 1 H), 7.56 (d, *J* = 12.2 Hz, 1 H), 7.56 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 28.7, 118.1, 121.2, 123.4, 124.7, 127.9, 132.4, 144.9, 152.3, 198.7. IR (KBr disk): 1684, 1099, 804 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_9ClO_2$: 208.0291 [M]; found: 208.0277.

1-(3-Acetyl-5-fluorophenoxy)propan-2-one (1m)
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.58 (s, 3 H), 4.62 (s, 2 H), 6.81–6.85 (m, 1 H), 7.26–7.29 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 26.6, 73.1, 107.2 (d, *J* = 25.6 Hz, 1 C), 108.8 (d, *J* = 22.3 Hz, 1 C), 109.6 (d, *J* = 3.3 Hz, 1 C), 139.7 (d, *J* = 8.2 Hz, 1 C), 159.1 (d, *J* = 9.1 Hz, 1 C), 163.4 (d, *J* = 247.9 Hz, 1 C), 196.2 (d, *J* = 2.5 Hz, 1 C), 203.5. IR (neat): 1689, 1593, 1144, 858 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_{11}FO_3$: 211.0770 [M]; found: 211.0731.

4-Acetyl-6-fluorobenzofuran (2m)
White solid; mp 43–44 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.56 (s, 3 H), 2.65 (s, 3 H), 7.32 (d, J_H = 2.3 Hz, J_F = 7.9 Hz, 1 H), 7.34 (d, J_H = 2.3 Hz, J_F = 9.9 Hz, 1 H), 7.48 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3, 28.8, 98.3, 102.8 (d, *J* = 20.9 Hz, 1 C), 111.7 (d, *J* = 24.8 Hz, 1 C), 116.8, 122.7, 133.8 (d, *J* = 7.1 Hz, 1 C), 144.7 (d, *J* = 4.1 Hz, 1 C), 159.3 (d, *J* = 243.0 Hz, 1 C), 198.6. IR (KBr disk): 1712, 1274, 764 cm^{-1}. HRMS (FAB$^+$): *m/z* calcd for $C_{11}H_9FO_2$: 192.0587 [M]; found: 192.0607.

Acknowledgment

This research was supported by Grant-in-Aid for Scientific Research on Innovative Areas, 'Molecular Activation Directed toward Straightforward Synthesis', MEXT, Japan, and by a Waseda University Grant for Special Research Projects.

Reference and Notes

(1) For recent reviews, see: (a) *Handbook of C–H Transformations*; Dyker, G., Ed.; Wiley-VCH: Weinheim, **2005**. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) Davies, H. M. L.; Manning, J. R. *Nature (London)* **2008**, *451*, 417. (d) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (e) Kitamura, T. *Eur. J. Org. Chem.* **2009**, 1111. (f) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (g) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (h) Lyons, T. M.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (i) *C–H Activation*; Yu, J.-Q.; Shi, Z., Eds.; Springer: Berlin, **2010**.

(2) Rare examples of transition-metal-catalyzed C–H activation at or below room temperature: (a) Fujii, N.; Kakiuchi, F.; Yamada, A.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 285. (b) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem. Int. Ed.* **2002**, *41*, 3056. (c) Boele, M. D. K.; van Strijdonck, G. P. F.; de Vries, A. H. M.; Kamer, P. C. J.; de Vries, J. G.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2002**, *124*, 1586. (d) Zhang, H.-B.; Liu, L.; Chen, Y.-J.; Wang, D.; Li, C.-J. *Adv. Synth. Catal.* **2006**, *348*, 229. (e) Norinder, J.; Matsumoto, A.; Yoshikai, N.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 5858. (f) Nishikata, T.; Abela, A. R.; Lipshutz, B. H. *Angew. Chem. Int. Ed.* **2010**, *49*, 781. (g) Xiao, B.; Fu, Y.; Xu, J.; Gong, T.-J.; Dai, J.-J.; Yi, J.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 468. (h) Fumitoshi, K.; Kochi, T.; Mizushima, E.; Murai, S. *J. Am. Chem. Soc.* **2010**, *132*, 17741.

(3) (a) Tsuchikama, K.; Kasagawa, M.; Hashimoto, Y.; Endo, K.; Shibata, T. *J. Organomet. Chem.* **2008**, *693*, 3939. (b) Tsuchikama, K.; Kasagawa, M.; Endo, K.; Shibata, T. *Org. Lett.* **2009**, *11*, 1821. (c) Tsuchikama, K.; Kasagawa, M.; Endo, K.; Shibata, T. *Synlett* **2010**, 97.

(4) Tsuchikama, K.; Hashimoto, Y.; Endo, K.; Shibata, T. *Adv. Synth. Catal.* **2009**, *351*, 2850.

(5) C–H bond activation along with 1,2-addition to imines: (a) Kuninobu, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2005**, *127*, 13498. (b) Kuninobu, Y.; Tokunaga, Y.; Kawata, A.; Takai, K. *J. Am. Chem. Soc.* **2006**, *128*, 202.

(6) We already excluded a Friedel–Crafts mechanism by competitive experiment of 4-(3-acetylphenyl)butan-2-one (**1a**) and 4-(3-methoxyphenyl)butan-2-one, see Supporting Information of ref. 4 in detail.

(7) Dicationic Pd complex as an efficient catalyst for C–H bond activation: Nishikata, T.; Abela, A. R.; Huang, S.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 4978.

(8) Preparation and characterization of dicationic Cp*Ir complex: (a) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *127*, 415. (b) Amouri, H.; Guyard-Duhayon, C.; Vaissermann, J.; Rager, M. N. *Inorg. Chem.* **2002**, *41*, 1397.

(9) Base suppressed dehydration from benzofuranols to benzofurans: (a) Liu, G.; Lu, X. *J. Am. Chem. Soc.* **2006**, *128*, 16504. (b) Liu, G.; Lu, X. *Tetrahedron* **2008**, *64*, 7324.

(10) The effect of inorganic salts for the ratio of benzofuran **2a** and benzofuranol **3a** is unclear.

(11) In recent years, a stoichiometric or more amounts of $Cu(OAc)_2$ was often used as an oxidant in C–H activation using Rh catalyst prepared from $[Cp^*RhCl_2]_2$ and $AgSbF_6$: (a) Stuart, D. R.; Bertrand-Laperle, M.; Burgess, K. M. N.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 16474. (b) Guinond, N.; Fagnou, K. *J. Am. Chem. Soc.* **2009**, *131*, 12050. (c) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585. (d) Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9982. (e) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 18326. (f) Patureau, F. W.; Besset, T.; Glorius, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 1064. (g) Tsai, A. S.; Brasse, M.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2011**, *13*, 540.

(12) Other silver salts, such as AgOTf and $AgBF_4$, gave poorer results than $AgSbF_6$.

(13) Iridium dicarboxylate complex, which was prepared from $[Cp^*IrCl_2]_2$ (5 mol% Ir), $AgSbF_6$ (10 mol%), and KOPiv (10 mol%), had almost no catalytic activity.

(14) (a) Davies, D. L.; Al-Duaji, O.; Fawcett, J.; Giardiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132. (b) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Polleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (c) Li, L.; Brennessel, W. W.; Jones, W. D. *J. Am. Chem. Soc.* **2008**, *130*, 12414. (d) Li, L.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2009**, *28*, 3492. (e) Boutadla, Y.; Davies, D. L.; Macgregor, S. A.; Poblador-Bahamonde, A. I. *Dalton Trans.* **2009**, 5887.

(15) The reaction of 4-(3-acetylphenyl)butan-2-one or 1-(3-acetylphenylamino)propan-2-one did not proceed under the same reaction conditions.