JOC The Journal of Organic Chemistry

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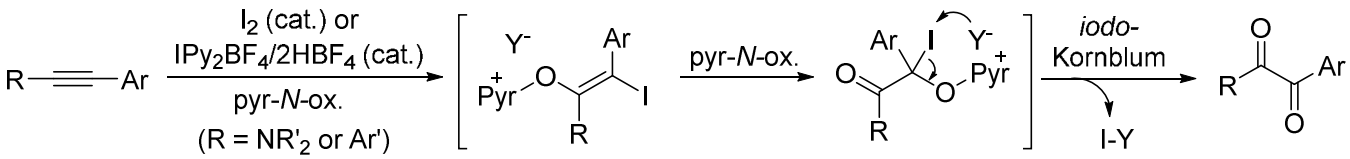
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b00484 • Publication Date (Web): 01 Apr 2018

Metal-Free Iodine-Catalyzed Oxidation of Ynamides and Diaryl Acetylenes into 1,2-Diketo Compounds

*Seung Woo Kim, Tae-Woong Um, and Seunghoon Shin**

Department of Chemistry, Center for New Directions in Organic Synthesis (CNOS) and Research Institute for Natural Sciences, Hanyang University, 222-Wangsimni-ro, Seongdong-gu, Seoul 04763, Korea, sshin@hanyang.ac.kr



ABSTRACT Metal-free oxidation of ynamides is described, employing pyridine-*N*-oxides as oxidants under molecular iodine catalysis. In stark contrast to Brønsted acid catalysis, iodophilic activation of ynamides diverts the reaction manifold into a dioxygenation pathway. This oxidation is very rapid at room temperature with only 2.5 mol% of I_2. Furthermore, this protocol could be extended to non-activated alkynes, such as diarylacetylenes, to deliver various benzil derivatives.

KEYWORDS iodine catalysis; 1,2-diketo compound; pyridine-*N*-oxide; alkyne oxidation; halogen bonding.

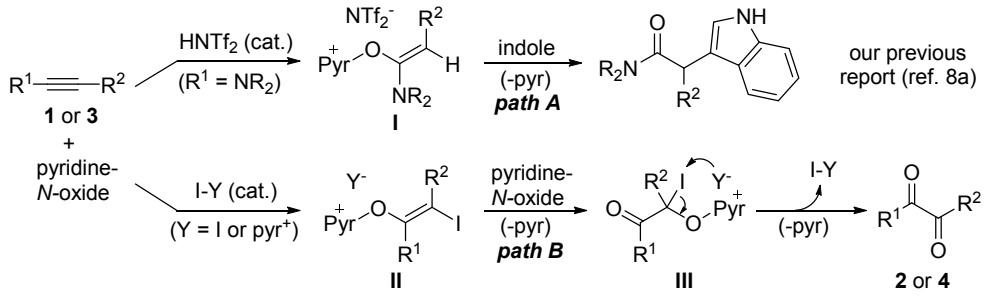
INTRODUCTION

Molecular iodine, being inexpensive and easy to handle, has been widely used in organic synthesis.[1] Besides stoichiometric iodofunctionalizations that incorporate an iodine atom in the product, a wide variety of iodine-catalyzed transformations have been developed as promising alternatives to the metal catalysis, including dehydration, condensation, conjugate addition, esterification, acetalization and glycosylation.[2] However, some of these transformations are suspected to involve trace amount of HI formed in-situ as the true catalyst.[3] In principle, I_2 interacts with Lewis basic heteroatoms through halogen bonding induced by the positive polarization (σ-hole).[4] Considering the softness of such bonding, the activation by I_2 could be extended to C-C π-bonds in an analogous fashion to electrophilic metal catalysis[5] and indeed iodofunctionalizations of alkynes have provided versatile synthetic methods.[6] However, alkyne activation that is catalytic in I_2 is surprisingly rare,[7] presumably due to the highly endergonic I-Y (Y= Lewis base) bond formation during the catalyst turnover (for example, BDE (I-I) = 36 kcal/mol). In the course of our recent investigation on the Brønsted acid-catalyzed oxidation of ynamides (Scheme 1A),[8] we thus initiated a study directed toward I_2-catalyzed activation of alkynes.

Catalytic oxidation by iodous species have typically employed super-stoichiometric end oxidants, such as H_2O_2,[9a] TBHP,[9b] *m*CPBA,[9c] DMSO,[9d] chloramines,[9e] and hypochlorite.[9f] These oxidants generate catalytically active iodine species with higher oxidation states, such as hypoiodites (IO^-) and iodites (IO_2^-), reminiscent of inner-sphere oxidation in transition metal catalysis. However, use of less reactive oxidants, such as pyridine-*N*-oxides or DMSO, have required transition metal[10,11] or Brønsted acid catalysis.[12] Furthermore, the mechanism of molecular iodine catalysis is not understood well and some of the iodonium-mediated reactions were proposed to involve radical mechanisms.[13] Herein, we report an I_2- or IPy_2BF_4/$2HBF_4$-catalyzed oxidation of ynamides and diaryl alkynes into α-ketoamides and benzil derivatives, respectively. This metal-free protocol obviates the use of toxic or expensive transition metal catalysts, and provides an efficient route to 1,2-diketo compounds.[14]

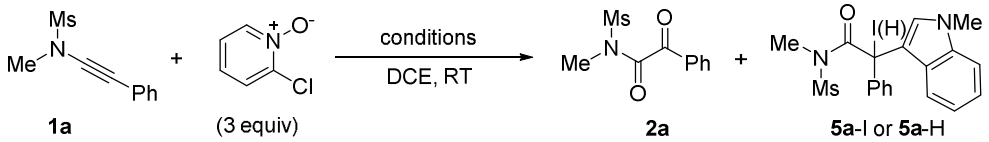
RESULTS AND DISCUSSION

Comparison of Brønsted acid *vs.* Iodophilic Activation.



Scheme 1. Iodine-catalyzed oxidation of alkynes with pyridine-*N*-oxides

Table 1. Pyridine-*N*-oxide-mediated oxidation of ynamide **1a**[a]



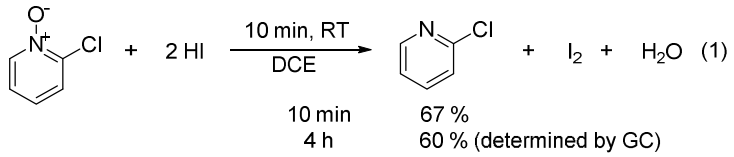
entry	conditions	**2a** (%)[b]	**5a** (%)[b]
1	$HNTf_2$ (10 mol%), *N*-Me-indole (3 equiv), 2 h	0	**5a**-H, 70
2	I_2 (100 mol%), *N*-Me-indole (3 equiv), 30min	14	**5a**-H, 22
3	I_2 (2.5 mol%), 10 min	86	-
4	HI (10 mol%),[c] *N*-Me-indole (3 equiv), 80 °C, 3 h	0	**5a**-H, 34
5	HI (10 mol%),[c] 1 h	83	-
6	$HNTf_2$ (10 mol%), 6 h	0[d]	-

[a][**1a**] = 0.5 M in DCE (1,2-dichloroethane). [b]Yields after chromatography. [c]Hydriodic acid was generated *in situ* from nBu$_4$NI and TfOH. [d]Unreacted **1a** was recovered.

Initially, we set out to examine the feasibility of I_2 to activate ynamide **1a** in a similar manner to our previous $HNTf_2$-catalyzed oxidative coupling protocol (path A, Scheme 1). While the oxidative coupling of **1a** with *N*-Me-indole in the presence of 10 mol% of $HNTf_2$ delivered indole adduct **5a**-H uneventfully as in our previous report (entry 1, Table 1),[8a] a similar reaction with I_2 (1.0 equiv.) gave a messy mixture from which the desired adduct **5a-**I could not be observed and instead **5a**-H (22 %) and unexpected ketoamide **2a** (14 %) were identified (entry 2). Presumably, the formation of **5a**-H could be due to action of HI generated from the reaction of I_2 and *N*-Me-indole. Surprisingly, use of a catalytic

amount of I_2 (2.5 mol%) gave ketoamide **2a** in 86 % yield with remarkable efficiency (entry 3). Considering the similarity of the postulated intermediates **I** and **II** (Scheme 1) except the presence of iodine at C2 and the counter-anion, this sharp change of chemoselectivity (path A vs. B) depending on the activator was remarkable. We interpreted that iodo-adduct **II**, formed from **1a** and I_2, was preferentially attacked by another molecule of 2-Cl-pyridine-*N*-oxide instead of indole nucleophile into **III**. Subsequent attack of I^- would deliver α-ketoamide **2a** via a Kornblum-type oxidation, liberating I_2 for the next catalytic cycle.[15]

We next checked whether the formation of **2a** can be catalyzed by Brønsted acid. The reaction with HI as a catalyst in the presence of *N*-Me-indole did not proceed at RT, but upon heating, only indole adduct **5a**-H could be isolated, albeit with much less efficiency than $HNTf_2$ (entries 4 vs. 1). Surprisingly, with HI as a catalyst in the absence of an indole nucleophile, a highly efficient formation of ketoamide **2a** was still observed (entry 5). In this case, a facile oxidation of HI by 2-Cl-pyridine-*N*-oxide generated I_2 which then catalyzed oxidation into **2a**, because we confirmed that treating 2-Cl-pyridine-*N*-oxide with 2 equiv. of HI immediately generated 2-Cl-pyridine, presumably in a reversible manner (Eq. 1).[16] Therefore, the formation of **2a** is most likely from the action of I_2, not HI. This was corroborated by the observation that redox-inactive Brønsted acid, $HNTf_2$, failed to produce **2a** (entry 6). These experiments suggested that protio-intermediate **I** formed reversibly in the mixture in entries 1, 2, 4 and 6, but could not be oxidized into **2a**, in contrast to the iodo-intermediate **II**.

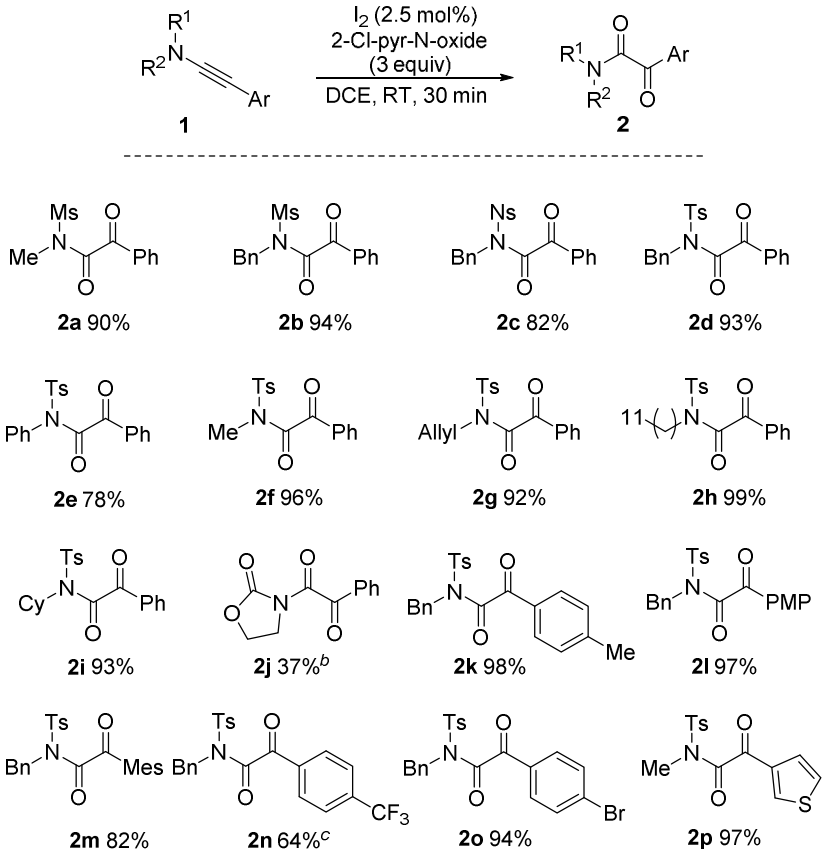


The Scope of Ynamide Oxidation.

Encouraged by the efficiency of this *N*-oxide mediated oxidation of ynamides, we examined the scope of this iodine catalysis (Scheme 2). Ynamides having various *N*-sulfonyl groups (Ms, *p*-Ts, and *o*-Ns) were excellent substrates in the current conditions (**2a-d**). *N*-Alkyl, allyl, aryl as well as benzyl groups were well accommodated with excellent chemoselectivity. Generally, electron-rich Ar group led to a

faster and more selective oxidation than electron-poor Ar substrates (**2k-m** vs. **2n**). Sterically hindered aryl group (**2m**) or heteroaryl group (**2p**) did not have any deleterious effect. However, the reaction of a carbamate substrate led to a poorer result even with higher I_2 loading (40 mol%) and at 80 ^oC (**2j**). Unfortunately, replacing Ar group with alkyl (*n*-hexyl) or CO_2Et or terminal ynamides led to no conversion, even under harsher conditions.

Scheme 2. Scope of iodine catalyzed oxidation of ynamides **1**[a]



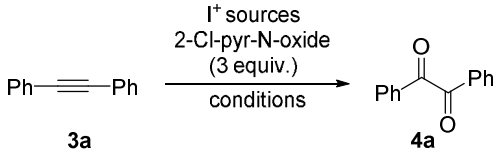
[a]**1** (0.2 mmol) in DCE (0.5 M); Yields after chromatography; abbreviations: PMP (*p*-MeO-C_6H_4), Ns (2-nitrobenzenesulfonyl). [b]The reaction was conducted at 80 ^oC for 19 h in the presence of 40 mol% of I_2. [c]20 mol% of I_2 was used (RT, 4 h).

Examination of Conditions for Diaryl Acetylenes.

Next, we turned our attention to extending the ynamide oxidation into unactivated alkynes such as diphenylacetylene. However, the reaction **3a** with 5 mol% of I_2 did not proceed at RT and the conversion of **3a** required heating (80 ^oC) and extended reaction time (72 h) (entries 1-2, Table 2). In

terms of solvent, the reaction was substantially accelerated in CH_3CN, with a complete conversion being observed in 24 h (entries 3-6). Increasing the amount of I_2 (20 mol%) led to 95 % of **3a** in 13 h at 80 ^oC (entry 7). Notably, the iodonium sources had a profound effect on the reaction (entries 8-11). Among them, ICl (5 mol%) and Barluenga reagent IPy_2BF_4 (5 mol%) stood out in promoting this oxidation. Gratifyingly, the catalytic activity of IPy_2BF_4 was further boosted with 10 mol% of HBF_4 as a co-catalyst,[7c] delivering **4a** even at RT in 4 hours (entries 12-13). Most likely, HBF_4 help dissociate the pyridinium from IPy_2^+, generating coordinatively unsaturated IPy^+ which activates alkynes as a true catalyst. Other oxidants were also examined along with I_2 (20 mol%): the reaction with *m*CPBA and *t*BuOOH as oxidants gave the product in 90 % and 16 % yield, respectively, although the reaction took a longer time and was slightly messier (entries 14-15). However, all other oxidants, including H_2O_2, oxone, $Ph_3P{=}O$, trimethylamine-*N*-oxide, DMSO and O_2, did not produce **4a**.

Table 2. 2-Cl-Pyridine-*N*-oxide-mediated oxidation of diphenylacetylene **3a**



3a **4a**

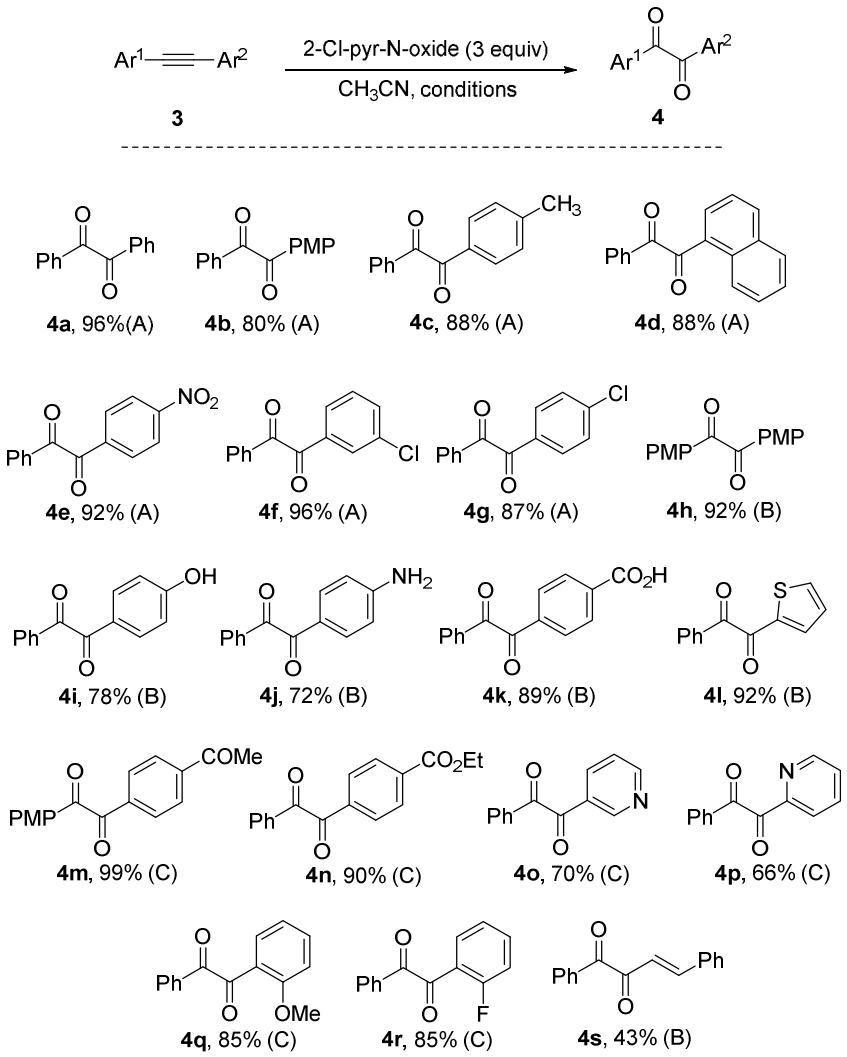
entry	Catalyst (mol %)	conditions	Solvent	**4a** (%)[a,b]
1	I_2 (5)	RT, 72 h	DCE	trace
2	I_2 (5)	80 °C, 60 h	DCE	83 %
3	I_2 (5)	80 °C, 72 h	DMSO	15 %
4	I_2 (5)	80 °C, 72 h	Dioxane	80 %
5	I_2 (5)	80 °C, 72 h	DMF	81 %
6	I_2 (5)	80 °C, 24 h	CH_3CN	84 %
7	I_2 (20)	80 °C, 13 h	CH_3CN	(95 %)
8	IBr (5)	80 °C, 7 h	CH_3CN	(70 %)
9	ICl (5)	80 °C, 6 h	CH_3CN	(86 %)
10	ICl (10)	80 °C, 4 h	CH_3CN	(97 %)
11	IPy_2BF_4 (5)	80 °C, 6 h	CH_3CN	(76 %)
12	IPy_2BF_4 (5)+HBF_4 (10)	80 °C, 10 min	CH_3CN	(96 %)
13	IPy_2BF_4 (5)+HBF_4 (10)	RT, 4 h	CH_3CN	(95 %)
14[c]	I_2 (20)	80 °C, 13 h	CH_3CN	90 %
15[d]	I_2 (20)	80 °C, 48 h	CH_3CN	16 %

[a]Determined by GC with 1,2-diethyl phthalate as an internal reference; isolated yields in parenthesis. [b]The remaining mass balance was unreacted starting **3a**. [c]*m*CPBA was used instead of 2-Cl-pyr-*N*-oxide. [d]*t*-BuOOH (5.5 M in n-decane) was used instead of 2-Cl-pyr-*N*-oxide.

The Scope of Diaryl Acetylene Oxidation.

We set out to examine the scope of unactivated alkynes employing three different catalytic systems, *i.e.* condition A: 5 mol% of $IPy_2BF_4/2HBF_4$ at RT; condition B: 10 mol% of ICl at 80 ^oC; condition C: 20 mol% of I_2 at 80 ^oC (Scheme 3). $IPy_2BF_4/2HBF_4$ (5 mol%, condition A) performed well with **3a-d** and those bearing electron-withdrawing groups, such as **3e-g**, delivering respective products (**4a-g**) at room temperature in good yields. However, substrates bearing electron-rich aryl ring (**3h** and **3l**) and Lewis basic atoms, such as free phenol, aniline and acid (**3i-k**), failed with $IPy_2BF_4/2HBF_4$, presumably because of facile deactivation of the catalyst. In these cases, ICl (10 mol%, condition B) produced respective products smoothly (**4h-l**). Presence of Lewis basic atoms in ketone (**3m**), ester (**3n**) and pyridyl rings (**3o-p**) as well as ortho-substituents (**3q-r**) seemed to interfere with both $IPy_2BF_4/2HBF_4$ or ICl catalyst systems. In these cases (**3m-r**), I_2 (20 mol%, condition C) was found to be the most robust and resistant to deactivation, although it took higher catalyst loading and longer time than conditions A and B. Surprisingly, substrate **3s** bearing styryl group also delivered **4s** with ICl, albeit lower yield. Unfortunately, however, phenylacetylene readily decomposed and 1-phenyl-1-heptyne as well as 1,4-diphenyl-1,3-diynes was unreactive under conditions A~C.

Scheme 3. Scope of 2-Cl-pyridine-*N*-oxide-mediated oxidation of diarylacetylenes[a]



[a]**3** (0.2 mmol) in CH_3CN (0.5 M); Condition A: IPy_2BF_4 (5 mol%)/HBF_4 (10 mol%), RT, 2~5 h; Condition B: ICl (10 %), 80 ^oC, 6~12 h; Condition C: I_2 (20 %), 80 ^oC, 12~36 h; Yields after chromatography.

Mechanistic Discussion

In order to shed light on the mechanism of this iodonium catalysis, we obtained time profile for the conversions of **1a** and **3a** using different iodonium sources (Figure 1). The reaction of **1a** was followed by GC with 1 mol% of iodonium loadings. Typically, the reaction proceeded very fast initially (<5 min), and this is followed by a mild plateau in the conversion. The observed conversion was in the order of I_2 >> IPy_2BF_4 > ICl > IBr (Figure 1a). The order of reactivity was significantly changed in non-polarized alkyne **3a**: ICl > IPy_2BF_4 > IBr >> I_2 (10 mol% loading, Figure 1b). For ynamide **1a**, use of IPy_2BF_4 (1

mol%) along with HBF_4 co-catalyst (2 mol%) did not make any difference in the conversion. In sharp contrast, the reaction of diphenylacetylene **3a** was dramatically improved with the use of co-catalyst HBF_4, allowing a fast reaction *even at RT*: with 5 mol% of IPy_2BF_4 and 10 mol% of HBF_4 at RT, >90 % conversion into **4a** was achieved in 2 h.[17]

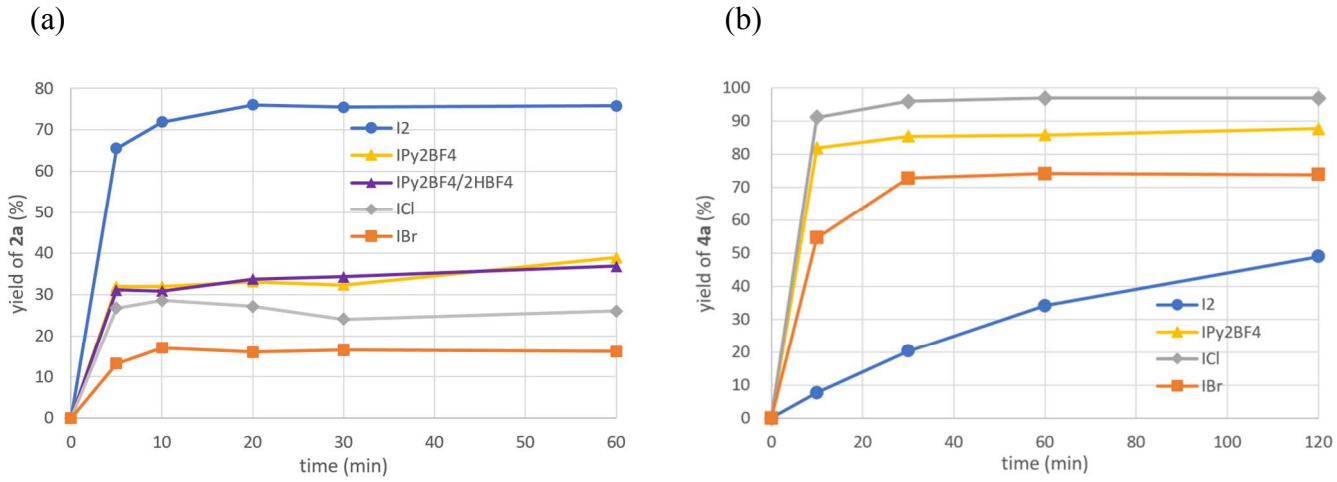
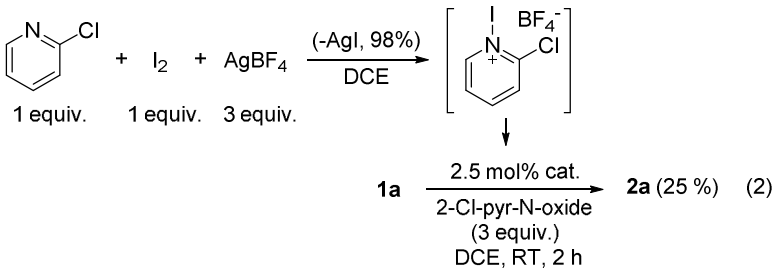


Figure 1. Time course for the oxidation of **1a** and **3a** by using gas chromatography: (a) Conversion of **1a** in the presence of 1 mol% of iodonium sources in DCE (RT); (b) Conversion of **3a** in the presence of 10 mol% of iodonium sources in CH_3CN (80°C).

Evaluation of various iodonium salts in Figure 1(a) indicated I_2 had the fastest conversion among I_2, IBr and ICl, which suggested the strongest nucleophile I^- (as Y^- in **III**, Scheme 1) presumably led to the fastest conversion. Therefore, in the reaction of electron-rich alkynes such as ynamide **1a**, our data are consistent with a rate-limiting catalyst turnover step (**III** to **2a**). We also considered the possible involvement of 2-Cl-pyridine, liberated from 2-Cl-pyridine-*N*-oxide, acting in the catalyst turnover step as nucleophile Y^- (in **III**) to generate I(2-Cl-Py)$^+$ as an active catalyst. However, as in Figure 1(a), the conversion with IPy_2BF_4 (with or without HBF_4 co-catalyst) was much slower than that with I_2 and furthermore, less basic 2-Cl-pyridine would be less likely to participate as a nucleophile than pyridine in the catalyst turnover.[18] In addition, we attempted to generate putative I(2-Cl-Py)$^+$ by mixing I_2, 2-Cl-pyridine and $AgBF_4$ in 1:1:3 ratio[19] in an effort to quantify the conversion due to I(2-Cl-Py)$^+$. The

filtrate of this mixture was tested as a potential catalyst (2.5 mol% loading, Eq. 2): in this experiment, only 25 % of **2a** was obtained after a longer time (2 h), suggesting that 1 mol% of I_2 is a superior catalyst to 2.5 mol% of "I(2-Cl-Py)$^+$". This suggest that involvement of 2-Cl-pyridine in the catalyst turnover step is much less likely.



In the case of non-activated alkynes, such as diphenylacetylene **3a**, a more polarized ICl performs the best overall oxidation among I_2, ICl and IBr at 80 ^oC (Figure 1(b)). In addition, the observed rate-enhancement with the co-catalytic system (*i.e.* $IPy_2BF_4/2HBF_4$ vs. IPy_2BF_4 alone) was much more dramatic than ynamide **1a**. This suggests that polarization of iodonium species is critical with **3a** and is consistent with rate-determining activation of the alkyne **3a** to form **II** (Scheme 1). Based on the different overall efficiency depending on the iodonium sources (Figure 1(b)), catalyst turnover in the reaction **3a** may also be achieved through the attack of Y^- on **III** (Y^- = Cl^-, Pyr, Br^- or I^-, respectively for ICl, $IPyr_2BF_4$, IBr and I_2).[20] Finally, the oxidation of **1a** was not affected when run in the presence of radical inhibitors (2,6-di-^{t}Bu-phenol) and the oxidation of **1a** performed inside Ar-atmosphere glove box proceeded in an essentially the same manner. These experiments excluded the possible involvement of radical species or oxygen-dependent pathways.[13]

CONCLUSION

In conclusion, we presented herein a novel molecular iodine-catalyzed oxidation of alkynes, using pyridine-*N*-oxides as terminal oxidants. Ynamides can be efficiently oxidized into α-ketoamides with only 2.5 mol% of I_2 and diaryl alkynes can also be oxidized into benzil derivatives with $IPy_2BF_4/2HBF_4$, ICl, or I_2. This non-metal oxidation by pyridine-*N*-oxides was proposed to follow a closed shell

mechanism, with iodonium species function as π-activators[5] and the catalyst turnover is achieved through I-Y (Y = respective Lewis bases in I-Y reagents) bond formation.

Experimental Section

General Information: All materials were obtained from commercial suppliers and were used without further purification. ^{1}H, proton-decoupled $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra were recorded on a Bruker (400 MHz) spectrometer with TMS as an internal standard. Gas chromatographic analysis was conducted on Agilent Technology 7890B GC system with *n*-dodecane or *o*-diethyl phthalate as internal standards. LCMS analysis was conducted on Agilent 6150 Quadrupole LC/MS with ESI or APCI ionization sources. High resolution mass spectra (HRMS) were obtained from Korea Basic Science Institute (KBSI, Daegu) on a magnetic sector-electric sector double focusing mass analyzer.

Representative formation of ketoamides **2a** from ynamides **1a**: Ynamide **1a** (41.9 mg, 0.2 mmol) and 2-chloro-pyridine *N*-oxide (77.7 mg, 0.6 mmol) was dissolved in 1,2-dichloroethane (0.4 ml) in a 4 ml screw-capped vial. Iodine (1.3 mg, 2.5 mol%) as a stock solution was added and the reaction mixture was stirred at RT for 30 min. The residue was directed loaded onto SiO_2 column and was purified by flash chromatography (EtOAc:*n*Hex = 1:10~1:4).

Representative formation of benzil **4a** from diarylacetylene **3a**: Diphenylacetylene (35.6 mg, 0.2 mmol) and 2-chloro-pyridine *N*-oxide (77.7mg, 0.6mmol) was dissolved in CH_3CN (0.4 ml) in a 4 ml screw-capped vial. To this was added IPy_2BF_4 (3.7 mg, 5 mol%) and HBF_4·etherate (4.7mg, 10 mol%) in a freshly made, premixed stock solution and the mixture was stirred at RT for the indicated time. The residue was directed loaded onto SiO_2 column and was purified by flash chromatography (EtOAc:*n*Hex = 1:10~1:4).

*N-Methyl-N-(methanesulfonyl)-2-oxo-2-phenylacetamide (**2a**)*.[10b] yellow solid (91%, 44.0 mg); mp 76-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* =

7.5 Hz, 2H), 3.38 (s, 3H), 3.28 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 188.5, 167.2, 134.8, 132.3, 130.0, 128.9, 40.8, 31.3; HRMS (FAB) Calcd for $C_{10}H_{12}NO_4S^+$ $[M+H]^+$ 242.0482; found 242.0484.

*N-Benzyl-N-(methanesulfonyl)-2-oxo-2-phenylacetamide (**2b**).*[10d] yellow sticky oil (94%, 59.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.45-7.35 (m, 5H), 5.16 (s, 2H), 2.90 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 188.5, 167.2, 134.80, 134.78, 132.3, 130.0, 129.1, 128.9, 128.7, 128.6, 47.5, 43.1; HRMS (FAB) Calcd for $C_{16}H_{16}NO_4S^+$ $[M+H]^+$ 318.0795; found 318.0798.

*N-Benzyl-N-((2-nitrophenyl)sulfonyl)-2-oxo-2-phenylacetamide (**2c**).* yellow solid (85%, 72.0 mg); mp 90-92 ^{o}C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31-8.14 (m, 1H), 7.79-7.66 (m, 5H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 2H), 7.23-7.17 (m, 3H), 5.16 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 187.3, 166.9, 148.3, 135.1, 134.9, 134.8, 132.3, 132.1, 131.7, 129.8, 128.8, 128.7, 128.6, 128.2, 124.7, 49.9; HRMS (FAB) Calcd for $C_{21}H_{17}N_2O_6S^+$ $[M+H]^+$ 425.0802; found 425.0804.

*N-Benzyl-2-oxo-2-phenyl-N-tosylacetamide (**2d**).*[13b] white solid (95%, 75.7 mg); mp 89-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.26-7.22 (m, 7H), 4.98 (s, 2H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 187.8, 167.6, 145.6, 134.7, 134.5, 134.4, 132.9, 129.8, 129.7, 129.3, 128.7, 128.5, 128.1, 127.8, 48.3, 21.7; HRMS (FAB) Calcd for $C_{22}H_{20}NO_4S^+$ $[M+H]^+$ 394.1108; found 394.1109.

*2-Oxo-N,2-diphenyl-N-tosylacetamide (**2e**).*[10f] yellow solid (78%, 58.9 mg); mp 152-154 ^{o}C; 1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, H), 7.52 (t, *J* = 7.9 Hz, 2H), 7.33-7.45 (m, 5H), 7.13 (d, *J* = 7.3 Hz, 2H), 2.48 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 187.6, 166.7, 146.0, 134.7, 134.1, 133.5, 132.7, 130.6, 130.2, 129.8, 129.6, 129.5, 129.1, 129.0, 21.8; HRMS (FAB) Calcd for $C_{21}H_{18}NO_4S^+$ $[M+H]^+$ 380.0951; found 380.0952.

*N-Methyl-2-oxo-2-phenyl-N-tosylacetamide (**2f**).*[10f] white solid (96%, 61.0 mg); mp 113-114 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 3.24 (s, 3H), 2.46 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz,

$CDCl_3$): δ 188.1, 167.3, 145.9, 134.5, 133.5, 132.8, 130.2, 129.7, 128.9, 128.4, 30.7, 21.7; HRMS (FAB) Calcd for $C_{16}H_{16}NO_4S^+$ $[M+H]^+$ 318.0795; found 318.0797.

*N-Allyl-2-oxo-2-phenyl-N-tosylacetamide (**2g**).*[10f] pale yellow oil (92%, 63.1 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.94-7.89 (m, 4H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 5.75 (ddt, *J* = 17.1, 10.2, 6.0 Hz, 1H), 5.25 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.16 (dd, *J* = 10.2, 1.1 Hz, 1H), 4.35 (d, *J* = 5.9 Hz, 2H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.8, 167.0, 145.8, 134.5, 134.4, 132.8, 130.7, 130.0, 129.7, 128.9, 128.6, 119.5, 47.3, 21.8; HRMS (FAB) Calcd for $C_{18}H_{18}NO_4S^+$ $[M+H]^+$ 344.0951; found 344.0953.

*N-Dodecyl-2-oxo-2-phenyl-N-tosylacetamide (**2h**).* white sticky oil (99%, 62.6 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.94-7.90 (m, 4H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 3.64 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 1.66-1.61 (m, 2H), 1.32-1.26 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.9, 167.3, 145.7, 134.5, 134.4, 133.0, 130.1, 129.7, 128.9, 128.4, 45.8, 31.9, 29.6, 29.5, 29.45, 29.37, 29.0, 28.2, 26.8, 22.7, 21.7, 14.1; HRMS (FAB) Calcd for $C_{27}H_{38}NO_4S^+$ $[M+H]^+$ 472.2516; found 472.2518.

*N-Cyclohexyl-2-oxo-2-phenyl-N-tosylacetamide (**2i**).* white solid (93%, 71.61 mg); mp 124-126 ^oC ; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.2 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 3.78 (tt, *J* = 12.2, 3.6 Hz, 1H), 2.46 (s, 3H), 2.38-2.21 (m, 2H), 1.87-1.72 (m, 2H), 1.72-1.50 (m, 2H), 1.26-1.17 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.8, 167.9, 145.5, 134.9, 134.1, 133.0, 130.1, 129.7, 128.8, 128.3, 61.0, 29.1, 26.4, 24.9, 21.8; HRMS (FAB) Calcd for $C_{21}H_{24}NO_4S^+$ $[M+H]^+$ 386.1421, found 386.1423.

*1-(2-Oxooxazolidin-3-yl)-2-phenylethane-1,2-dione (**2j**).*[10f] brown oil (37%, 16.2 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.0 Hz, 2H), 7.65 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), 4.60 (t, *J* = 7.7 Hz, 2H), 4.17 (t, *J* = 8.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.8, 166.5, 153.1, 134.8, 132.4, 129.4, 129.1, 64.0, 41.0; HRMS (FAB) Calcd for $C_{11}H_{10}NO_4^+$ $[M+H]^+$ 220.0604, found 220.0607.

*N-Benzyl-2-oxo-2-(p-tolyl)-N-tosylacetamide (**2k**).* yellow solid (96%, 78.8 mg); mp 120-122 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 8.7 Hz, 4H), 7.21-7.30 (m, 9H), 4.97 (s, 2H), 2.41 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.5, 167.7, 145.7, 145.6, 134.8, 134.6, 130.5, 129.8, 129.6, 129.1, 128.52, 128.49, 128.1, 127.8, 48.3, 21.9, 21.7; HRMS (FAB) Calcd for $C_{23}H_{22}NO_4S^+$ $[M+H]^+$ 408.1264, found 408.1265.

*N-Benzyl-2-(4-methoxyphenyl)-2-oxo-N-tosylacetamide (**2l**).* yellow solid (97%, 76.0 mg); mp 152-155 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 6.1 Hz, 2H), 7.26-7.21 (m, 7H), 6.95 (d, *J* = 8.7 Hz, 2H), 4.97 (s, 2H), 3.85 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.6, 167.7, 164.7, 145.5, 134.9, 134.6, 132.1, 129.8, 128.54, 128.49, 128.0, 127.8, 125.9, 114.3, 55.6, 48.3, 21.7; HRMS (FAB) Calcd for $C_{23}H_{22}NO_5S^+$ $[M+H]^+$ 424.1213, found 424.1216.

*N-Benzyl-2-mesityl-2-oxo-N-tosylacetamide (**2m**).* white solid (82%, 72.2 mg); mp 59-60 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.26-7.18 (m, 7H), 6.88 (s, 2H), 4.99 (s, 2H), 2.44 (s, 6H), 2.39 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.9, 167.6, 145.4, 143.3, 140.1, 135.1, 134.7, 130.8, 129.6, 129.5, 128.9, 128.34, 128.32, 127.7, 48.9, 22.0, 21.7, 21.3; HRMS (FAB) Calcd for $C_{25}H_{26}NO_4S^+$ $[M+H]^+$ 436.1577, found 436.1579.

*N-Benzyl-2-oxo-N-tosyl-2-(4-(trifluoromethyl)phenyl)acetamide (**2n**).* white solid (64%, 59.0 mg); mp 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.78-7.72 (m, 4H), 7.27-7.24 (m, 7H), 4.99 (s, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.5, 167.0, 145.9, 135.9, 135.4 (q, *J* = 32.7, 65.4 Hz), 134.4, 134.2, 129.92, 129.90, 128.6, 128.5, 128.1, 128.0, 125.9 (q, *J* = 3.7, 3.5 Hz), 123.4 (q, *J* = 271.5, 271.5 Hz), 48.3, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.3 HRMS (FAB) Calcd for $C_{23}H_{19}F_3NO_4S^+$ $[M+H]^+$ 462.0981, found 462.0984.

*N-Benzyl-2-(4-bromophenyl)-2-oxo-N-tosylacetamide (**2o**).* yellow solid (93%, 88.0 mg); mp 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.72 (m, 4H), 7.63 (d, J = 8.7 Hz, 2H), 7.25-7.22 (m, 7H), 4.97 (s, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.8, 167.2, 145.8, 134.5, 134.4, 132.3, 131.7, 131.0, 129.9, 128.55, 128.48, 128.1, 127.9, 48.3, 21.7; HRMS (FAB) Calcd for $C_{22}H_{19}BrNO_4S^+$ $[M+H]^+$ 472.0213, found 472.0216.

*N-Methyl-2-oxo-2-(thiophen-3-yl)-N-tosylacetamide (**2p**).* pale yellow solid (97%, 62.7 mg); mp 96-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 2.8, 1.0 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 5.1, 1.0 Hz, 2H), 7.42-7.39 (m, 3H), 3.23 (s, 3H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ181.6, 167.0, 146.0, 137.8, 135.7, 133.6, 130.1, 128.4, 127.2, 127.0, 30.9, 21.7; HRMS (FAB) Calcd for $C_{14}H_{14}NO_4S_2^+$ $[M+H]^+$ 324.0359; found 324.0356.

*Benzil (**4a**).*[11b] pale yellow solid (96%, 40.3 mg); mp 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 8.1, 1.0 Hz, 4H), 7.66 (tt, *J* = 7.4, 1.2 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 4H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.6, 134.9, 133.0, 129.9, 129.0; HRMS (FAB) Calcd for $C_{14}H_{11}O_2^+$ $[M+H]^+$ 211.0754, found 211.0756.

*1-(4-Methoxyphenyl)-2-phenylethane-1,2-dione (**4b**).*[11b] yellow sticky oil (80%, 38.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.92 (m, 4H), 7.64 (tt, *J* = 7.4, 1.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.9, 193.2, 165.0, 134.8, 133.2, 132.4, 129.9, 129.0, 126.1, 114.4, 55.7; HRMS (FAB) Calcd for $C_{15}H_{13}O_3^+$ $[M+H]^+$ 241.0859, found 241.0862.

*1-Phenyl-2-(p-tolyl)ethane-1,2-dione (**4c**).*[11b] yellow sticky oil (88%, 39.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.86(d, *J* = 8.3 Hz, 2H), 7.63 (tt, *J* = 1.2, 7.4 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 194.8, 194.4, 146.3, 134.8, 133.1, 130.6, 130.0, 129.9, 129.8, 129.0, 22.0; HRMS (FAB) Calcd for $C_{15}H_{13}O_2^+$ $[M+H]^+$ 225.0910, found 225.0912.

*1-(Naphthalen-1-yl)-2-phenylethane-1,2-dione (**4d**).* yellow solid (88%, 45.8 mg); mp 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (d, *J* = 8.6 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 7.1 Hz, 2H), 7.91 (t, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.65-7.58 (m, 2H), 7.51-7.44 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.2, 194.6, 136.0, 135.1, 134.8, 134.1, 133.4, 131.0, 130.0, 129.5, 129.1, 128.9, 128.6, 127.2, 126.0, 124.5; HRMS (FAB) Calcd for $C_{18}H_{13}O_2^+$ $[M+H]^+$ 261.0910, found 261.0912.

*1-(4-Nitrophenyl)-2-phenylethane-1,2-dione (**4e**).*[11c] yellow solid (92%, 46.9 mg); mp 140-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 9.0 Hz, 2H), 8.17 (d, *J* = 9.0 Hz, 2H), 8.00-7.98 (m, 2H), 7.71

(tt, *J* = 7.5, 1.3 Hz, 1H), 7.55 (t, *J* = 8.2 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 192.9, 192.1, 151.2, 137.3, 135.5, 132.4, 131.0, 130.1, 129.3, 124.1; HRMS (FAB) Calcd for $C_{14}H_{10}NO_4^+$ $[M+H]^+$ 256.0604, found 256.0606.

*1-(3-chlorophenyl)-2-phenylethane-1,2-dione (**4f**)*.[11c] pale yellow solid (96%, 47.0 mg); mp 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (m, 3H), 7.84 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.71-7.65 (m, 1H), 7.63 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.53 (t, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 193.6, 193.0, 135.5, 135.2, 134.8, 134.5, 132.7, 130.4, 130.0, 129.6, 129.1, 128.1; HRMS (FAB) Calcd for $C_{14}H_{10}ClO_2^+$ $[M+H]^+$ 245.0364, found 245.0366.

*1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (**4g**)*.[11b] yellow solid (87%, 42.6 mg); mp 76-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.70-7.63 (m, 2H), 7.51 (t, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 194.0, 193.2, 141.7, 135.2, 132.9, 131.5, 131.3, 130.0, 129.6, 129.2; HRMS (FAB) Calcd for $C_{14}H_{10}ClO_2^+$ $[M+H]^+$ 245.0364, found 245.0367.

*1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (**4h**)*.[11b] yellow solid (92 %, 49.7 mg); mp 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 9.0 Hz, 4H), 6.96 (d, *J* = 9.0 Hz, 4H), 3.87 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 193.5, 164.9, 132.4, 126.3, 114.3, 55.6; HRMS (FAB) Calcd for $C_{16}H_{15}O_4^+$ $[M+H]^+$ 271.0965, found 271.0967.

*1-(4-Hydroxyphenyl)-2-phenylethane-1,2-dione (**4i**)*.[11c] pale yellow solid (78%, 35.3 mg); mp 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (m, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.65 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 195.3, 193.5, 162.2, 135.0, 133.0, 132.8, 130.0, 129.1, 125.9, 116.1; HRMS (FAB) Calcd for $C_{14}H_{11}O_3^+$ $[M+H]^+$ 227.0703, found 227.0706.

*1-(4-Aminophenyl)-2-phenylethane-1,2-dione (**4j**)*. yellow solid (72%, 32.4 mg); mp 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.76 (3, *J* = 8.5 Hz, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 195.6, 192.8,

153.1, 134.6, 133.4, 132.7, 129.9, 128.9, 123.1, 114.0; HRMS (FAB) Calcd for $C_{14}H_{12}NO_2^+$ $[M+H]^+$ 226.0863, found 226.0865.

*4-(2-Oxo-2-phenylacetyl)benzoic acid (**4k**).* pale yellow solid (89%, 45.2 mg); mp 219-221 ^oC; ^1H NMR (400 MHz, acetone-d_6): δ 8.24 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H), 8.01(dd, J = 8.4, 1.2 Hz, 2H), 7.80 (tt, J = 7.4, 1.3 Hz, 1H), 7.64 (t, J = 8.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 195.01, 194.97, 166.6, 137.0, 136.8, 133.6, 131.1, 130.59, 130.58, 130.2; HRMS (FAB) Calcd for $C_{15}H_{11}O_4^+$ $[M+H]^+$ 255.0652, found 255.0655.

*1-Phenyl-2-(thiophen-2-yl)ethane-1,2-dione (**4l**).*[11c] yellow sticky oil (92%, 39.7 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H), 7.83 (dd, J = 4.9, 1.1 Hz, 1H), 7.79 (dd, J = 3.9, 1.1 Hz, 1H), 7.64 (tt, J = 7.4, 1.2 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.17 (dd, J = 4.9, 3.9 Hz, 1H), 7.53-7.48 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.1, 185.7, 139.9, 137.0, 136.8, 134.9, 132.6, 130.2, 129.0, 128.9; HRMS (FAB) Calcd for $C_{12}H_9O_2S^+$ $[M+H]^+$ 217.0318, found 217.0320.

*1-(4-Acetylphenyl)-2-(4-methoxyphenyl)ethane-1,2-dione (**4m**).*[11b] yellow solid (99 %, 55.9 mg); mp 128-131^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10-8.02 (m, 4H), 7.95 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 3.90 (s, 3H), 2.65 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.3, 193.9, 192.3, 165.2, 141.2, 136.2, 132.5, 130.1, 128.7, 125.8, 114.5, 55.7, 27.0; HRMS (FAB) Calcd for $C_{17}H_{15}O_4^+$ $[M+H]^+$ 283.0965, found 283.0968.

*Ethyl 4-(2-oxo-2-phenylacetyl)benzoate (**4n**).* yellow sticky oil (90 %, 50.7 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.8, 193.7, 165.4, 136.0, 135.7, 135.1, 132.7, 130.1, 130.0, 129.8, 129.1, 61.7, 14.3; HRMS (FAB) Calcd for $C_{17}H_{15}O_4^+$ $[M+H]^+$ 283.0965, found 283.0968.

*1-Phenyl-2-(pyridin-3-yl)ethane-1,2-dione (**4o**).* dark purple sticky oil (70%, 29.6mg); ^1H NMR (400 MHz, $CDCl_3$): δ 9.18 (dd, J = 2.1, 0.6 Hz, 1H), 8.88 (dd, J = 4.9, 1.7 Hz, 1H), 8.33 (dt, J = 8.0, 2.1 Hz, 1H), 8.02-7.99 (m, 2H), 7.70 (tt, J = 5.9, 1.6 Hz, 1H), 7.57-7.49 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$): δ 192.8, 192.5, 154.5, 151.1, 137.2, 135.3, 132.5, 130.1, 129.2, 128.8, 124.0; HRMS (FAB) Calcd for $C_{13}H_{10}NO_2$ $[M+H]^+$ 212.0706, found 212.0708.

*1-Phenyl-2-(pyridin-2-yl)ethane-1,2-dione (**4p**).* yellow solid (72%, 30.4 mg); mp 72-73 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.7 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.96-7.91 (m, 3H), 7.63 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.53-7.48 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 196.2, 195.2 151.7 149.9, 137.3, 134.7, 133.2, 129.6, 128.9, 128.2, 123.2; HRMS (FAB) Calcd for $C_{13}H_{10}NO_2^+$ $[M+H]^+$ 212.0706, found 212.0708.

*1-(2-Methoxyphenyl)-2-phenylethane-1,2-dione (**4q**).*[11b] yellow sticky oil (85%, 40.8 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.62-7.56 (m, 2H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.54 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 194.7, 193.6, 160.5, 136.6, 133.8, 132.9, 130.5, 129.3, 128.8, 123.8, 121.6, 112.4, 55.7; HRMS (FAB) Calcd for $C_{15}H_{13}O_3^+$ $[M+H]^+$ 241.0859, found 241.0862.

*1-(2-Fluorophenyl)-2-phenylethane-1,2-dione (**4r**).* pale yellow solid (85%, 38.8 mg); mp 57-59 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (td, *J* = 7.4, 1.8 Hz, 1H), 7.99-7.96 (m, 2H), 7.68-7.61 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.34 (td, *J* = 7.6, 1.0 Hz, 1H), 7.12 (ddd, *J* = 10.5, 8.4, 0.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.1, 191.9, 162.9 (d, *J* = 256.9 Hz), 136.9 (d, *J* = 9.0 Hz), 134.7, 132.1 (d, *J* = 2.0 Hz), 130.8 (d, *J* = 1.7 Hz), 129.9, 129.0, 125.0 (d, *J* = 3.3 Hz), 122.4 (d, *J* = 11.0 Hz), 116.7 (d, *J* = 21.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -107.3; HRMS (FAB) Calcd for $C_{14}H_{10}FO_2^+$ $[M+H]^+$ 229.0659, found 229.0661.

*(E)-1,4-Diphenylbut-3-ene-1,2-dione (**4s**).* yellow sticky oil (43%, 19.8 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 16.4 Hz, 1H), 7.67-7.59 (m, 3H), 7.52 (t, *J* = 6.4 Hz, 2H), 7.47-7.39 (m, 3H), 7.14 (dd, *J* = 16.4, 1.1 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 193.3, 192.8, 148.9, 134.7, 134.0, 132.8, 131.6, 130.2, 131.6, 130.2, 129.1, 128.92, 128.89, 122.4; HRMS (FAB) Calcd for $C_{16}H_{13}O_2^+$ $[M+H]^+$ 237.0910, found 237.0913.

ACKNOWLEDGMENT

The authors thank the National Research Foundation of Korea (NRF-2012M3A7B4049653, NRF-2014-011165 and NRF-2017R1A2B4010888) for generous financial support.

SUPPORTING INFORMATION

Reaction conditions optimization; reaction summary (conditions A~C) for Table 3; details of mechanistic experiments; copies of ^{1}H and ^{13}C NMR spectra of all new compounds.

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16. Experimental details can be found in Supporting Informations.

17. In contrast, the reaction of **3a** with ICl (10 mol%) at RT, under otherwise the standard condition, led to **4a** only in ~30 % after 6 h.

18. In addition, the oxidation of **1a** under the standard condition was significantly inhibited by 2,2'-bipyridyl or 1,10-phenanthroline, but not by 2-Cl-pyridine at all (Figure S4 in Supporting Informations). Therefore, liberated 2-Cl-pyridine do not deactivate I_2 catalyst and the formation of $I(2\text{-Cl-Py})^+$ from I_2 and 2-Cl-pyridine as an active catalyst is not likely.

19. For a related synthesis of IPy_2BF_4: Chalker, J. M.; Thompson, A. L.; Davis, B. G. *Org. Synth.* **2010**, *87*, 288-298. We found that the formation of $I(2\text{-Cl-pyridine})^+$ from this mixture is nearly quantitative as judged from the gravimetric analysis of AgI (98%) formed (Eq. 2). In a control experiment, we observed no reaction of **1a** with 2-Cl-pyridine-*N*-oxide (3 equiv.) and $AgBF_4$ (5 %) as a catalyst (see Supporting Information), supporting that presence of excess $AgBF_4$ is not responsible for the conversion of **1a**.

20. If 2-Cl-pyridine participates in the catalyst turnover, identical conversions should have been observed after 10 % conversion in Figure 1(b).