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**Authors:** Matthew H. Gieuw, Zhihai Ke, and Ying-Yeung Yeung



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# Lewis Base-Promoted Ring-Opening 1,3-Dioxygenation of Unactivated Cyclopropanes using Hypervalent Iodine Reagent

Matthew H. Gieuw, Zhihai Ke* and Ying-Yeung Yeung*

*Dedicated to Professor Elias J. Corey on the occasion of his 90th birthday*

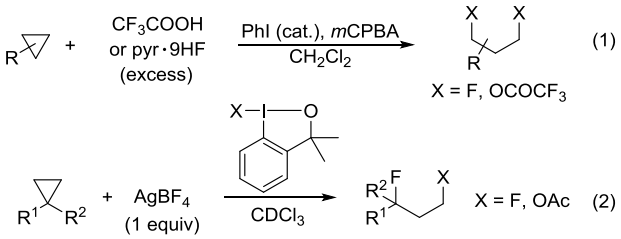
**Abstract:** A facile and effective system has been developed for the regio- and chemoselective ring-opening/electrophilic functionalization of cyclopropanes via C–C bond activation by [bis(trifluoroacetoxy)iodo]benzene with the aid of the Lewis basic promoter *p*-toluenesulfonamide. Notably, the *p*-toluenesulfonamide-promoted system works well for a wide range of cyclopropanes, resulting in the formation of 1,3-diol products in good yields and regioselectivity.

Cyclopropane is known to have a high ring strain. The inefficient orbital overlap in cyclopropane results in three bent carbon-carbon σ-bonds that each has a significant degree of π-character.[1] Thus, the reaction chemistry of cyclopropanes resembles that of olefins in many circumstances.[2] The ring-opening reactions of cyclopropanes have been an on-going attractive research area as these reactions afford synthetically useful 1,3-difunctionalized molecules that are not readily accessible by other conventional methods. Most of the existing cyclopropane ring-opening approaches rely on either radical-initiated processes or the use of activated donor–acceptor cyclopropanes, which are substrate-specific.[3] In stark contrast, the ring-opening reactions of unactivated cyclopropanes with electrophiles remain scarce, which is attributable to the formidable challenge in controlling the reactivity and regioselectivity.[4]

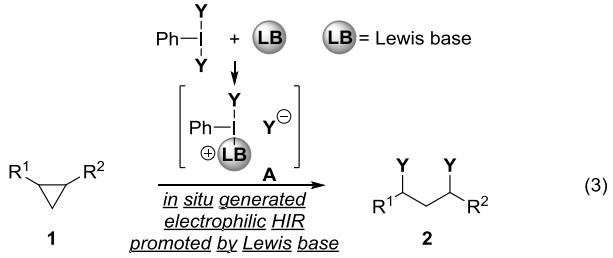
Our group has developed several methodologies for the electrophilic halogenation of olefins using Lewis bases as catalysts.[5] It is believed that the Lewis base-activated halonium species could react with olefinic substrate to give the key intermediate haliranium ion followed by the ring-opening of the haliranium ion by a nucleophile to give desired halogenated product.[6] In a continuation of this endeavor, very recently we applied the Lewis base catalytic protocol to the electrophilic halocyclization of cyclopropyl substrate and the haliranium ion-like intermediate is believed to be involved in the reaction to give the ring-opening/1,3-difunctionalization product.[4b,4c] Hypervalent iodine reagents (HIRs), for example phenyliodine bis(trifluoroacetate) (PIFA), are known to readily react with olefins to give the corresponding 1,2-dioxygenated products and the reaction mechanism is similar to that of electrophilic halogenation.[7] However, the electrophilic reaction of unactivated cyclopropane with $PhI(OCOCF_3)_2$ was sluggish in the absence of external activator, potentially because of the low reactivity of the cyclopropane system (*vide infra*, Table 1).[4e] Very recently, two elegant research works demonstrated that HIR-promoted ring-opening/functionalization of unactivated cyclopropanes could be achieved by conducting the reactions using either catalytic amount of iodobenzene and stoichiometric amount of *m*-chloroperbenzoic acid (*m*CPBA) in the presence of excess amount of Brønsted acid (Scheme 1, eq 1)[8] or iodoxole reagent in the presence of a strong Lewis acid (Scheme 1, eq 2).[9] Herein, we are pleased to report our recent success in using sulfonamides as Lewis bases to activate HIRs for the ring-opening/1,3-dioxygenation of unactivated cyclopropanes. The transformation is metal-free, the reaction conditions are mild (neutral and at room temperature), and no strong oxidant is involved. To the best of our knowledge, this case represents the first report of Lewis base activation of HIRs for electrophilic functionalization reactions. While strongly acidic reagents such as TMSOTf and $Ms_2NH$ can activate HIRs for electrophilic functionalizations of olefins, the use of Lewis bases for the activation of HIRs offers a complementary platform for relevant transformations.[10]

In alignment with our research interest on Lewis base-catalyzed reactions with olefinic and cyclopropyl substrates,[4b,4c] we hypothesized that a Lewis base promoter could react with HIR to *in situ* generate the positively charged species **A**, which could be a more active electrophile for the electrophilic ring-opening/1,3-difunctionalization of unactivated cyclopropanes **1** (Scheme 1, eq 3).[11]

a) Literature reports: Brønsted or Lewis acid-activated Hypervalent Iodine Compounds for The Ring-opening/Functionalization of Cyclopropanes




**b) This work: Lewis Base-Promoted Electrophilic Functionalization of Cyclopropanes Using Hypervalent Iodine Reagent**




**Scheme 1.** Reactions of π-character C-C bonds with activated HIR.

[*] Mr. Matthew H. Gieuw, Dr. Zhihai Ke, Prof. Dr. Ying-Yeung Yeung
Department of Chemistry, The Chinese University of Hong Kong
Shatin, NT, Hong Kong (China)
E-mail: chmkz@cuhk.edu.hk; yyyeung@cuhk.edu.hk

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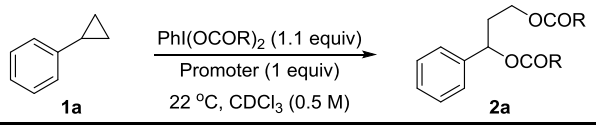
To test our hypothesis, cyclopropylbenzene (**1a**) and PIFA were used as the substrate and the electrophilic reagent, respectively. The reaction was monitored by $^1$H NMR using $CDCl_3$ as the solvent. The background reaction was sluggish with low conversion (Table 1, entry 1). Although the addition

**Table 1.** Reaction of cyclopropylbenzene (**1a**) using various HIRs and promoters.[a]



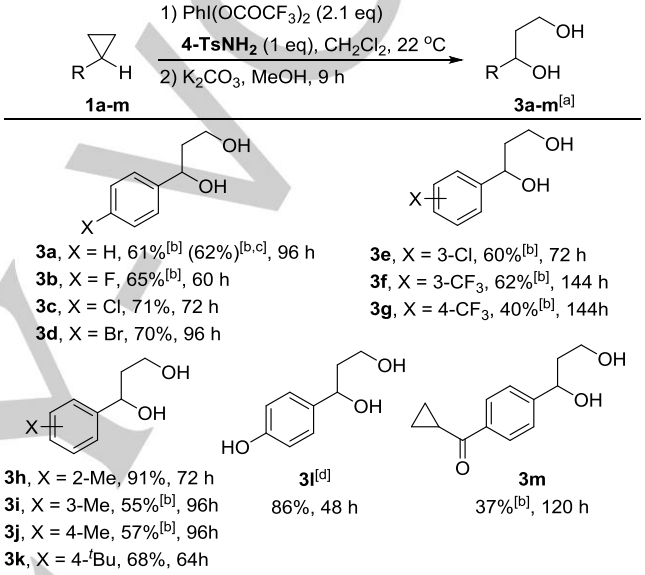

**1a** **2a**

| Entry | R | Time (d) | Promoter | Conversion (%)[b] |
|---|---|---|---|---|
| 1 | $CF_3$ | 3 | - | 28 |
| 2 | $CF_3$ | 3 | TFA | ~60[c] |
| 3 | $CF_3$ | 3 | 4-$TsNH_2$ | 74[d] |
| 4 | $CF_3$ | 3 | 4-$TsNMe_2$ | 38[e] |
| 5 | Me | 5 | 4-$TsNH_2$ | 0 |
| 6 | $C(CH_3)_3$ | 5 | 4-$TsNH_2$ | 0 |
| 7 | $CHCl_2$ | 10 | 4-$TsNH_2$ | 0 |
| 8 | $CCl_3$ | 10 | 4-$TsNH_2$ | 50 |
| 9 | $CF_3$ | 3 | 2-$NsNH_2$ | 27 |
| 10 | $CF_3$ | 3 | 4-$NsNH_2$ | 39 |
| 11 | $CF_3$ | 3 | 2-$TsNH_2$ | 43 |
| 12 | $CF_3$ | 3 | $PhCONH_2$ | 12 |
| 13 | $CF_3$ | 3 | *n*-$BuNH_2$ | 10 |
| 14 | $CF_3$ | 3 | $PhNH_2$ | 0 |
| 15[f] | $CF_3$ | 3 | 4-$TsNH_2$ | 94 |

[a] Reaction conditions: cyclopropylbenzene (**1a**) (0.2 mmol), HIR (1.1 eq), $CDCl_3$ (0.4 mL) at 22 °C in the absence of light. [b] Based on $^1$H NMR. [c] 24% of **1a** was converted into 4-iodophenylcyclopropane detected by $^1$H NMR. [d] 26% of starting material remained. [e] 62% of starting material remained. [f] 2.1 equivalents of PIFA was used. 2-$NsNH_2$ = 2-nitrobenzenesulfonamide, 4-$NsNH_2$ = 4-nitrobenzenesulfonamide.

of 1 equivalent of trifluoroacetic acid (TFA) greatly accelerated the reaction, $^1$H NMR study on the crude sample showed that 24% of **1a** was converted into 4-iodophenylcyclopropane as the side product (Table 1, entry 2).[12] To our delight, the use of Lewis basic 4-toluenesulfonamide (4-$TsNH_2$) or *N*,*N*-dimethyl 4-toluenesulfonamide (4-$TsNMe_2$) could promote the reaction of **1a** and at the same time effectively suppressed the formation of side products (Table 1, entries 3 and 4), suggesting that the Lewis basic nitrogen center might play a crucial role in the reaction. Other less electron-deficient HIRs did not work well when compared with PIFA (Table 1, entries 5–8 vs 3).[13] Next, various amines were examined. It was found that the relatively electron-deficient amides 2-$NsNH_2$ and 4-$NsNH_2$ returned diminished reactivity (Table 1, entry 9–10). Surprisingly, the relatively electron-rich amine systems including benzamide, *n*-butylamine and aniline gave sluggish reaction (Table 1, entry 12–14). In particular, aniline completely shut down the reaction and the starting material was recovered quantitatively. These results suggest that an amine with suitable Lewis basicity might be crucial for the high reaction efficiency (vide infra).[14] Finally, the conversion was further improved by employing 2.1 equivalents of PIFA (Table 1, entry 15).[15] A brief survey on some solvents revealed the superior performance of $CH_2Cl_2$ as the reaction media.

With the optimized conditions in hand, the scope of the dioxygenation reaction was examined (Scheme 2). As a result of

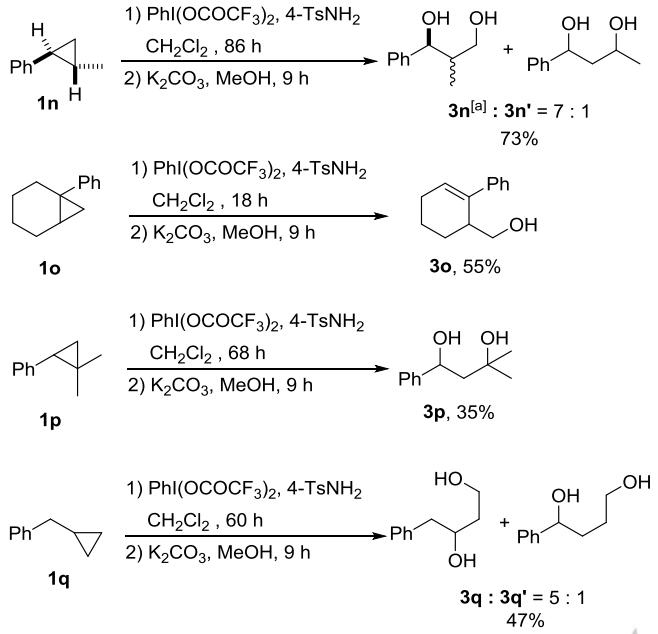



**Scheme 2.** One-pot preparation of 1,3-diols **3a-m.** [a] Isolated yield of **3** for 2 steps. The reaction time of the first step is indicated. [b] Some starting material was recovered. [c] 2 mmol scale. [d] Substrate **1l** with R = 4-AcO-$C_6H_4$ was used.

the instability of product **2** upon treatment of silica gel chromatography, **2** was hydrolyzed in an one-pot fashion to its corresponding diol **3** with the use of $K_2CO_3$ and MeOH. In general, aryl cyclopropanes bearing electron-withdrawing (**1b–1g**) and electron-rich (**1h–1l**) substituents worked well in this protocol and gave the corresponding products **3b–3l** with good yields and excellent regioselectivity. Particularly, the sterically hindered 2-methylphenylcyclopropane (**1h**) could be converted to the corresponding 1,3-diol (**3h**) in 91% isolated yield. This reaction protocol also showed good chemoselectivity, where electron-deficient carbonyl cyclopropane moiety was left intact when using **1m** as the substrate. In addition, it was found that the ring-opening and diol formation too place exclusively at the C–C bond adjacent to the aryl substituent.

Apart from monosubstituted arylcyclopropane, we also extended the substrate scope to disubstituted and trisubstituted cyclopropanes (Scheme 3). 1,2-Disubstituted cyclopropane (**1n**) and trisubstituted cyclopropane (**1p**) were converted into **3n** and **3p** in good regioselectivity. Trisubstituted cyclopropane (**1o**) was

converted into the homoallylic alcohol (**3o**), presumably obtained from the elimination of the tertiary alcohol intermediate. Surprisingly, alkyl cyclopropane (**1q**) was transformed into both 1,3- and 1,4-diol (**3q** and **3q'**).

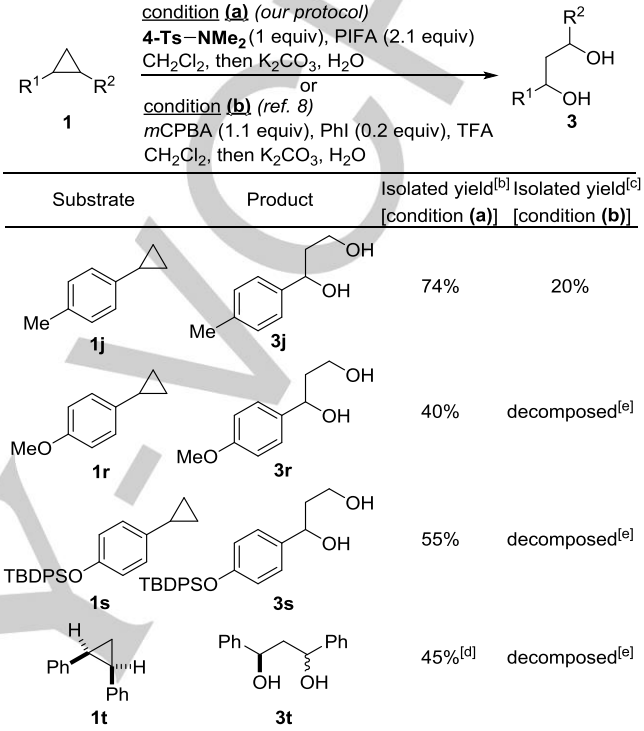



**Scheme 3.** Ring-opening and 1,3-difunctionalization of di-, tri-substituted and alkyl cyclopropanes using Lewis base-activated HIR. [a] *anti:syn* of **3n** = 3:1.

Further evaluation on the reaction protocol revealed that 4-TsNMe$_2$ could also be a potent promoter to activate HIR. Some examples are shown in Table 2 in which appreciable conversions were obtained for the electron-rich (**1j**, **1r**), silyl ether (**1s**), and 1,2-disubstituted (**1t**) substrates. In parallel, we have compared our protocol [condition **(a)**] with a recently reported literature procedure [condition **(b)**][8] involving the use of substoichiometric amount of iodobenzene and stoichiometric amount of co-oxidant *m*-chloroperbenzoic acid (*m*CPBA) in an excess amount of TFA, which can *in situ* generate PIFA for the 1,3-dioxygenation of a few electron-deficient cyclopropanes. However, under condition **(b)** the substrates were consumed but no desired products were detected (Table 2). These results highlight the significance in utilizing a Lewis base to promote the 1,3-dioxygenation of cyclopropanes in the absence of strong co-oxidant and acidic media.

In order to obtain a better understanding on the reaction mechanism, a careful $^1$H NMR study was carried out to probe the interaction between PIFA and 4-TsNH$_2$. $^1$H NMR study on pure PIFA alone gave a group of broad signals corresponding to the aromatic protons. Upon the addition of 4-TsNH$_2$, the signals of PIFA became sharpened.[16] PIFA is known to exist as a centrosymmetrical dimer with the secondary intra- and intermolecular interaction occupies the vacancy of the C-I antibonding orbital (the electron-deficient σ* orbital), which could give rise to broadened proton signals.[17] We speculate that 4-TsNH$_2$ might coordinate with PIFA through a n→σ* interaction between the lone pair of the sulfonamide N and the C-I electron-deficient σ* orbital of PIFA[18] to give species **A1**, and this interaction might disrupt the dimerization of PIFA (Scheme 4). We also suspect that species **A1** might exist in equilibrium with the charged species **A2**; the existence of species **A2** was evidenced by the mass spectrometric analysis in both mixtures

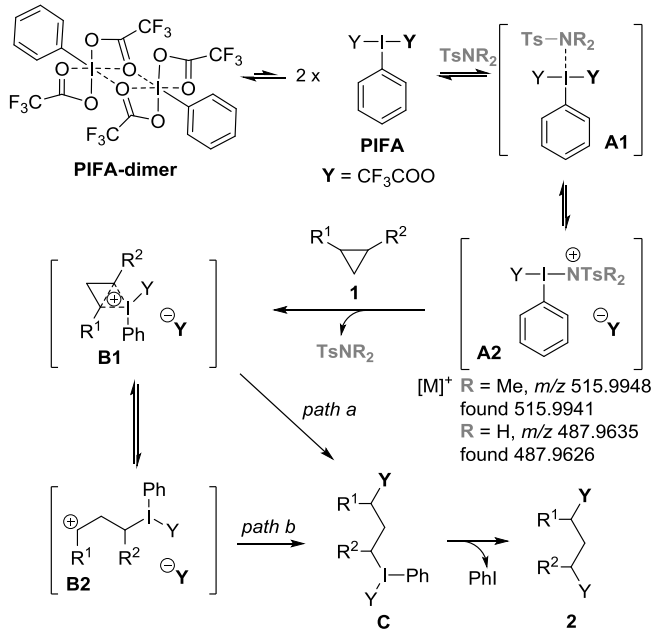
**Table 2.** Reaction of cyclopropanes using different conditions.[a]




[a] The reactions were conducted using cyclopropane **1** (0.2 mmol) under condition **(a)** or **(b)**. [b] Condition **(a)**: PIFA (2.1 equiv), 4-TsNMe$_2$ (1 equiv) in $CH_2Cl_2$ (0.4 mL) at 22 °C in the absence of light. [c] Condition **(b)**: iodobenzene (0.2 equiv), *m*CPBA (1.1 equiv) in TFA/$CH_2Cl_2$ (0.4 mL, 1:1 v/v) at 22 °C in the absence of light. [d] *anti*:*syn* = 3:1. [e] All starting material was consumed but no desired product was detected.

of 4-TsNMe$_2$ and PIFA as well as 4-TsNH$_2$ and PIFA.[19] $^{19}$F NMR study on PIFA was also conducted and two signals were observed. The major signal at –76.6 ppm and the minor signal at –78.3 ppm should correspond to the dimer and the monomer of PIFA, respectively.[20] The ratio of dimeric and monomeric PIFA reached equilibrium at approximately 72 h.[21] However, the addition of 4-TsNMe$_2$ to PIFA triggered the consumption of the dimer as indicated by the diminishment of the signal at –76.6 ppm. Concurrently, the intensity of the signal at –78.3 ppm increased dramatically in proportion to the decrement of dimeric PIFA over 72 h.[21] Upon the addition of phenylcyclopropane (**1a**) to the mixture, **1a** was consumed gradually and the diester product **2a** was formed.[14]

Although a more detailed study is needed in order to elucidate a clear mechanistic picture, a plausible explanation on the reaction mechanism that is in alignment with the spectroscopic evidences is shown in Scheme 4. We suspect that the dimeric PIFA might be inactive towards the electrophilic functionalization of cyclopropane as a result of the occupied C-I antibonding orbital of PIFA.[17] Sulfonamide might coordinate with PIFA and the resulting complex **A1** might exist in




**Scheme 4.** A plausible reaction mechanism.

equilibrium with the more electrophilic HIR species **A2**.[22] The π-character σ-bond of cyclopropane **1** might then interact with species **A2** to give the iranium-like species **B1**. Substitution of **B1** by the trifluoroacetate anion in a Markovnikov fashion could give **C** (Scheme 4, path a) and subsequent degradation of species **C** could give the product **2**. Alternatively, intermediate **C** could be formed from the carbocation species **B2** (Scheme 4, path b), which could be generated through the ring-opening of species **B1**. At this stage, we believe that both paths (a) and (b) could lead to the desired 1,3-difunctionalized product **2** while path (a) could possibly be the predominant one because *anti*-products were preferentially formed with substrate **1n** and **1t**. In another set of NMR study, it was found that other stronger Lewis bases could also form similar Lewis base-PIFA adducts. For instance, aniline could readily react with PIFA to give the corresponding aniline-PIFA adduct. However, the adduct was found to be intact upon the addition of **1a** and the ring-opening reaction was sluggish.[14] It appears that a stronger Lewis base (e.g. aniline) could coordinate tightly with PIFA, but the resulting adduct seems to be too stable for subsequent reaction as indicated by its inertness towards the ring-opening of cyclopropane substrate. On the other hand, tosylamide with proper Lewis basicity appears to be matching with HIR to form the amide-PIFA adduct **A** that has suitable reactivity; this could explain why amines that have stronger Lewis basicity could not efficiently promote the reaction (Table 1, entries 12–14). We had suspected that sulfonamide might react with PIFA to *in situ* generate TFA (e.g. collapse of **A2**) which could promote the reaction. However, this possibility was ruled out by two findings: (1) in the $^{19}F$ NMR study on a mixture of tosylamide ($TsNH_2$ or $TsNMe_2$) and PIFA, no TFA was detected; (2) $TsNMe_2$, which has no acidic proton and cannot trigger the formation of TFA, could still readily promote the formation of diol **3** (Table 2).

In summary, we devised a reaction protocol to oxidize cyclopropanes into their respective 1,3-diols from moderate to excellent yields in a regioselective manner using PIFA as the oxidant and tosylamides as the promoters. This report highlights examples of a facile, electrophilic approach to using cyclopropyl compounds in place of olefins to generate a new class of structurally diverse 1,3-diol products. This work also opens a new avenue of utilizing a Lewis base instead of a Brønsted acid in the activation of hypervalent iodine reagents for electrophilic functionalization reactions. Effort is now underway to apply the organocatalysis to other mild and regiocontrollable ring-opening reactions of cyclopropanes.

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**Keywords:** Cyclopropanes • Diols • Hypervalent iodine • Organocatalysis • Oxygenation • Sulfonamide

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[12] The yield of 4-iodophenylcyclopropane increased when increasing the amount of TFA. For detail, see Supporting Information, Tables S1 and S2.

[13] The 1,3-bis(trichloroacetic)ester product (Table 1, entry 8) readily decomposed during the purification process. The structure was confirmed by HRMS (ESI) analysis (Calc'd for $C_{13}H_{10}Cl_6O_4$ $[M+Na]^+$: 464.85737; found 464.85728).

[14] The details are shown in the Supporting Information Figure S1 and S2.

[15] >95% conversion could still be achieved with 1 equivalent of PIFA after 9 days.

[16] The details are shown in the Supporting Information Figure S3.

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[19] The details are shown in the Supporting Information Figure S4 and S5.

[20] The details are shown in the Supporting Information Figure S6.

[21] The details are shown in the Supporting Information Figure S7.

[22] It was reported that $TsNH_2$ could accelerate electrophilic cyclization of olefinic urea using HIR, although the role of $TsNH_2$ was not studied. For reference, see: 10a.

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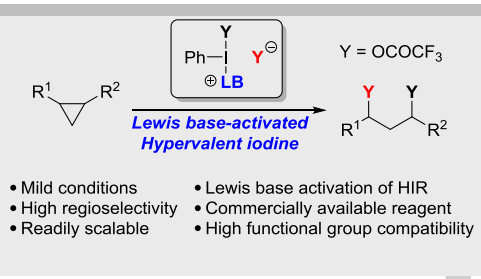
# COMMUNICATION

**Lewis base works**. A facile and effective system has been developed for the regio- and chemoselective ring-opening/electrophilic functionalization of cyclopropanes via C–C bond activation by [bis(trifluoroacetoxy)iodo]benzene with the aid of the Lewis base promoter *p*-toluenesulfonamide. Notably, the *p*-toluenesulfonamide-promoted system works well for a wide range of cyclopropanes, resulting in the formation of 1,3-diol products in good yields and regioselectivity.




*Matthew H. Gieuw, Zhihai Ke,* Ying-Yeung Yeung**

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***Lewis Base-Promoted Ring-Opening 1,3-Dioxygenation of Unactivated Cyclopropanes using Hypervalent Iodine Reagent***