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Various oxidative reactions with novel ion-supported (diacetoxyiodo)benzenes

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ABSTRACT

The oxidation of secondary alcohols and primary alcohols with two novel ion-supported (diacetoxyiodo) benzenes (IS-DIBs) **A** and **B** in the presence of a catalytic amount of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in dichloromethane at room temperature proceeded efficiently to provide the corresponding ketones and aldehydes, respectively, in good yields. The oxidative reaction of *N*,*N*-diisopropylbenzylamines with those IS-DIBs was also carried out to generate the corresponding aromatic aldehydes in good yields. In addition, the Hofmann rearrangement of primary amides in methanol under basic conditions and the oxidative 1,2-rearrangement of propiophenones in trimethyl orthoformate under acidic conditions with those IS-DIBs provided the corresponding methyl carbamates and methyl 2-arylpropanoates, respectively, in good yields. Moreover, treatment of acetophenones with those IS-DIBs in the presence of trifluoromethanesulfonic acid in acetonitrile generated the corresponding 5-aryl-2-methyloxazoles in good yields. In those five reactions, the desired products were obtained in good yields with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract. Moreover, ion-supported iodobenzenes, which were the co-products derived from IS-DIBs in the present oxidative reactions, were recovered in good yields and could be re-oxidized to IS-DIBs **A** and **B** for reuse in the same oxidative reactions.

1. Introduction

Organic synthesis that features high efficiency and low toxicity and produces a minimal amount of reaction waste is very important for green chemistry. Efficient organic synthesis with less toxic reagents has been studied actively.[1] The oxidation of alcohols to ketones or aldehydes is one of the most fundamental, widely used, and important reactions in both research laboratories and production plants.[2] Among the various methods for the oxidation of alcohols to ketones or aldehydes, the Swern oxidation[3] with dimethyl sulfoxide (DMSO) and oxalyl chloride or trifluoroacetic anhydride, and the Dess–Martin oxidation[4] with 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-2-one (Dess–Martin periodinane) are the most popular, efficient, and selective methods for the preparation of ketones or aldehydes from alcohols in organic synthesis, because both reactions do not require any toxic metals and proceed under mild and nearly neutral conditions. However, each reaction still has major drawbacks, i.e., dimethyl sulfide, a co-product of the Swern oxidation, is a highly malodorous volatile compound that makes handling of the reaction extremely difficult, and Dess–Martin pentavalent periodinane is explosive. In 1997, the 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO)-mediated oxidation of alcohols to ketones or aldehydes with (diacetoxyiodo)benzene (DIB) in dichloromethane at room temperature was reported[5a] and has become a very popular method for the efficient and selective oxidation of alcohols to ketones or aldehydes, due to simple experimental operation, the use of non-explosive trivalent iodine, and the lack of unpleasant odor.[5] However, the reaction produces a stoichiometric amount of iodobenzene as a co-product, which must be removed by troublesome column chromatography on silica gel. To solve this problem and simplify the isolation of the desired product, the polymer-supported DIB, poly [4-(diacetoxyiodo)styrene], was developed.[5b] However, there are still drawbacks, such as the low purity of carbonyl compounds after filtration of the reaction mixture because of containing low-molecular-weight polymer-supported iodobenzenes. Moreover, the elemental analysis of polymer-supported DIB must be carried out in each preparation of polymer-supported DIB to evaluate the loading rate of the (diacetoxy)iodo groups in the polymer-supported DIB. Recently, the oxidation of alcohols with a 1-(4′-diacetoxyiodobenzene)-3-methylimidazolium tetrafluoroborate/

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KBr/[emim]BF_4 system,[6a] a 1-(4′-diacetoxyiodobenzene)-3-methylimidazolium tetrafluoroborate/3-methylimidazolium-supported TEMPO/water system,[6b] and a bifunctional catalyst bearing ionic-liquid-supported (2,2,6,6-tetramethylpiperidin-1-yl)oxyl and iodoarene moieties/peracetic acid system[6c] was reported. However, there are still certain drawbacks, such as the addition to the carbon–carbon double bond of substrates by bromonium ion species, the solubility of substrates in water, and the reusability of reagents. Here, as part of our ongoing studies of trivalent iodines for organic synthesis,[7] we would like to report the TEMPO-mediated oxidation of alcohols to ketones or aldehydes with ion-supported (diacetoxyiodo)benzenes (IS-DIBs),[8] the oxidative reaction of *N*,*N*-diisopropylbenzylamines with IS-DIBs to generate aromatic aldehydes, the Hofmann rearrangement of primary amides with IS-DIBs in methanol to form methyl carbamates, the oxidative 1,2-rearrangement of propiophenones with IS-DIBs in trimethyl orthoformate to form methyl 2-arylpropanoates, and the formation of 5-aryl-2-methyloxazoles with acetophenones and IS-DIBs in acetonitrile. The experimental scheme is shown in Fig. 1.

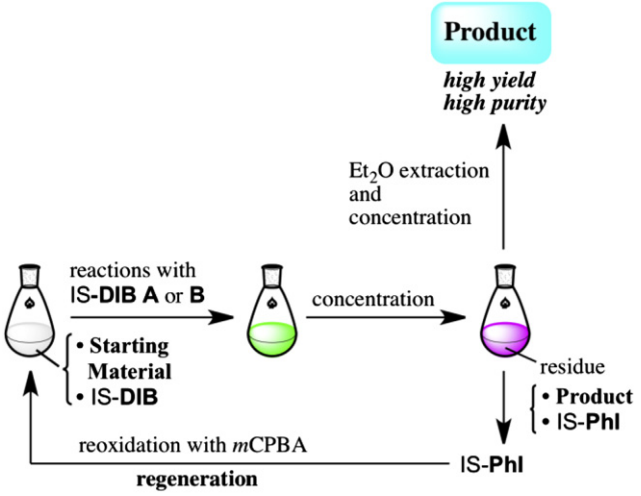
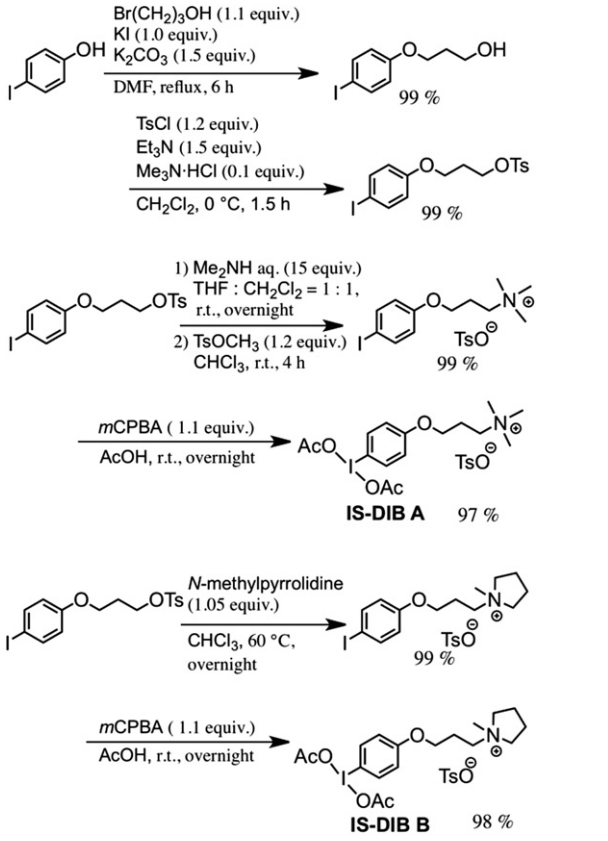


Fig. 1. Reaction, recovery, regeneration, and reuse of IS-**DIB A** and **B**.

2. Results and discussion

Two IS-DIBs **A** and **B** (IS-DIBs), i.e., *N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-*N*,*N*,*N*-trimethyl-ammonium 4″-methylbenzenesulfonate (IS-DIB **A**) and *N*-methyl-*N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]pyrrolidinium 4″-methylbenzenesulfonate (IS-DIB **B**), were prepared by the oxidation of *N*-[3-(4′-iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate and *N*-methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4″-methylbenzenesulfonate, respectively, with *m*-chloroperoxybenzoic acid (*m*CPBA) in acetic acid at room temperature, as shown in Scheme 1.[7o] *N*-[3-(4′-Iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate and *N*-methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4″-methylbenzenesulfonate were easily prepared from commercially available *p*-iodophenol and 3-bromo-1-propanol in three steps, respectively, in good yields.

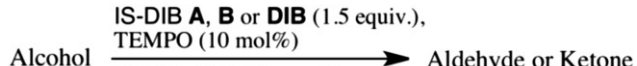
The oxidation of secondary and primary alcohols with IS-DIBs **A** and **B** (or DIB) in the presence of TEMPO in CH_2Cl_2 at room temperature was carried out by means of the same experimental procedure as that described in the literature.[5a] Thus, to a solution of IS-DIB **A** or **B** (1.5 equiv) in CH_2Cl_2 were added alcohol (1.0 equiv) and TEMPO (10 mol %, 0.1 equiv). Then, the mixture was stirred at room temperature. After the disappearance of alcohol, the solvent was removed. Addition of water and extraction with diethyl ether provided ketone or aldehyde in good yield with high purity. Thus,



Scheme 1. Preparation of ion-supported (diacetoxyiodo)benzenes **A** and **B**.

when diphenylmethanol (**1a**) was used as the substrate in the oxidation with IS-DIBs **A** and **B**, benzophenone (**2a**) was obtained in 97% and 99% yields with 98% and 99% purity, respectively, by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract, as shown in Table 1. Here, use of an excess amount of IS-DIB suppressed the contamination of TEMPO into the diethyl ether extracts from the reaction mixture. On the other hand, when DIB was used as the oxidant for the oxidation of diphenylmethanol (**1a**) under the same conditions and procedure, benzophenone (**2a**) was obtained in 99% yield; however, its purity was 48% because of containing iodobenzene. Therefore, the purification of benzophenone by column chromatography on silica gel was required. Here, when IS-DIBs **A** and **B** were used as the oxidant, the oxidation product was obtained in good yield with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract. The oxidation of 9-fluorenol (**1b**), 1-phenyl-1-propanol (**1c**), and 1-(5′-methylfuran-2′-yl)-1-pentanol (**1d**) with IS-DIBs **A** and **B** were carried out under the same conditions and procedure to give the corresponding ketones **2b**, **2c**, and **2d** in good yields with high purity, respectively, by simple extraction treatment of the reaction mixture. Moreover, the treatment of benzylic and allylic alcohols, such as *p*-chlorobenzyl alcohol (**1e**), *p*-methylbenzyl alcohol (**1f**), piperonyl alcohol (**1g**), 4-phenylbenzyl alcohol (**1h**), 2-thiophenemethanol (**1i**), geraniol (**1j**), and *trans*-cinnamyl alcohol (**1k**), with IS-DIBs **A** and **B** under the same conditions and procedure provided the corresponding aromatic aldehydes **2e**–**i** and α,β-unsaturated aldehydes **2j** and **2k** in good yields with high purity, respectively, by simple extraction treatment of the reaction mixture. The oxidation of primary alcohols, such as 1-adamantanemethanol (**1l**), β-citronellol (**1m**), and 8-(*p*-methylbenzenesulfonyloxy)-1-octanol (**1n**), with IS-DIBs **A** and **B** in the presence of TEMPO at room temperature provided the

Table 1
Oxidation of alcohols with DIB and IS-DIB **A** and **B**



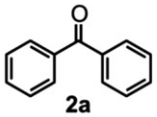
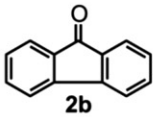
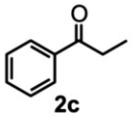
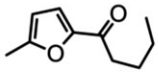
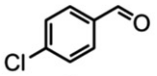
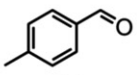
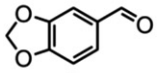
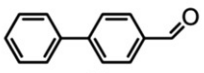
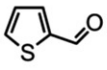
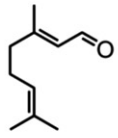
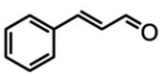
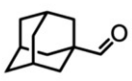
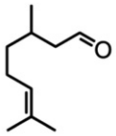
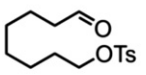
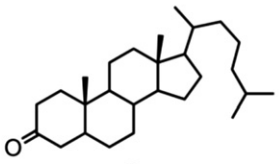
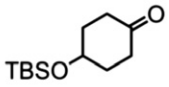
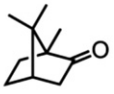
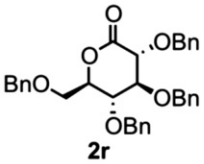
IS-DIB **A**, **B**, or **DIB**	Aldehyde or Ketone **2** time (h), yield (%)[a], [purity (%)]	
	 **2a**	 **2b**
IS-DIB **A**	9, 97, [98]	18, 99, [97]
IS-DIB **B**	10, 99, [99]	12, 99, [99]
DIB	5, 99, [48]	9, 99, [47]
	 **2c**	 **2d**
IS-DIB **A**	8, 97, [97]	9, 99, [99]
IS-DIB **B**	4.5, 99, [99]	10.5, 93, [98]
	 **2e**	 **2f**
IS-DIB **A**	6, 98, [99]	4, 98, [99]
IS-DIB **B**	2, 98, [99]	1.5, 98, [99]
	 **2g**	 **2h**
IS-DIB **A**	8, 95, [92]	6, 98, [98]
IS-DIB **B**	3.5, 97, [99]	6, 99, [99]
	 **2i**	 **2j**
IS-DIB **A**	6, 99, [99]	2, 99, [98]
IS-DIB **B**	3, 99, [99]	1.5, 94, [99]
DIB	1.5, 99, [48]	
	 **2k**	 **2l**
IS-DIB **A**	4, 98, [99]	18, 91, [88]
IS-DIB **B**	2, 98, [99]	12, 84, [83]
DIB		4, 91, [50]
IS-DIB **A**[b]	4, 99, [98]	
IS-DIB **B**[b]	2, 99, [99]	

Table 1 *(continued)*

IS-DIB **A**, **B**, or **DIB**	Aldehyde or Ketone **2** time (h), yield (%)[a], [purity (%)]	
	 **2m**	 **2n**
IS-DIB **A**	2, 99, [99]	8, 81, [81]
IS-DIB **B**	1.5, 92, [99]	6, 79, [79]
IS-DIB **A**[b]	2, 98, [99]	
IS-DIB **B**[b]	2, 98, [98]	
	 **2o**	 **2p**
IS-DIB **A**	8, 97, [97]	8, 86, [85]
IS-DIB **B**	7, 95, [99]	16, 97, [97]
DIB	6, 97, [49]	
	 **2q**	 **2r**
IS-DIB **A**	12, 99, [99]	6, 94, [94]
IS-DIB **B**	6, 95, [99]	5, 99, [99]
DIB	4.5, 99, [48]	1.5, 97, [48]

[a] Isolated yield as a purified state.
[b] Recovered and regenerated IS-DIB was used.

corresponding aldehydes **2l**–**n** in good yields with high purity, respectively, by simple extraction treatment of the reaction mixture, although the yield and purity were slightly decreased in the oxidation of 8-(*p*-methylbenzenesulfonyloxy)-1-octanol (**1n**). When DIB was used as the oxidant in the same oxidation of 1-adamantanemethanol (**1l**) under the same conditions and procedure, the corresponding aldehyde **2l** was obtained in good yield by simple extraction treatment of the reaction mixture. However, the purity was 50% again because of containing iodobenzene. The TEMPO-mediated oxidation of alcohols, such as β-cholestanol (**1o**), 4-(*tert*-butyldimethylsilyloxy)-1-cyclohexanol (**1p**), borneol (**1q**), and 2,3,4,6-tetra-*O*-benzyl-D-glucose (**1r**), with IS-DIBs **A** and **B** under the same conditions and procedure also gave the corresponding ketones **2o**–**r** in good yields with high purity, respectively. On the other hand, the purity of ketones **2o**, **2q**, and **2r** obtained from the reaction of alcohols **1o**, **1q**, and **1r** with DIB under the same conditions and procedure was 49%, 48%, and 48%, respectively, although the yields were quite good. Then, the reuse of IS-DIBs **A** and **B** in the oxidation of alcohols in the presence of TEMPO was carried out. After the extraction of the oxidation product from the reaction mixture with diethyl ether, the aqueous solution was extracted with chloroform to recover ion-supported iodobenzenes (IS-PhIs) in good yields. The recovered IS-PhIs were re-oxidized with *m*CPBA in acetic acid at room temperature to regenerate IS-DIBs **A** and **B**, respectively, in good yields. Reuse of the recovered and regenerated IS-DIBs **A** and **B** for the oxidation of

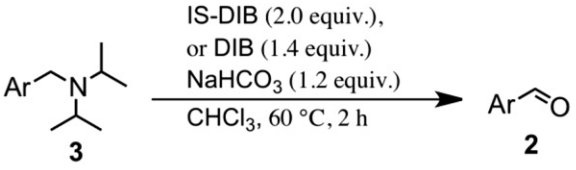
trans-cinnamyl alcohol (**1k**) and β-citronellol (**1m**) in the presence of TEMPO under the same conditions as those of the first reactions provided the corresponding aldehydes **2k** and **2m** in good yields with high purity again by simple extraction treatment of the reaction mixture, as shown in Table 1 Thus, IS-DIBs **A** and **B** could be recovered, regenerated, and reused for the same oxidation of alcohols.

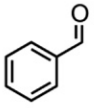
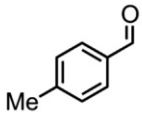
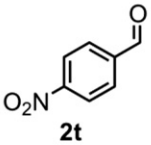
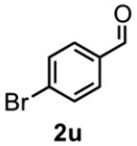
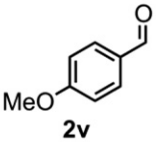
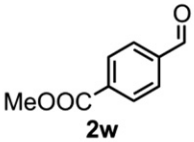
Recently, the oxidative deamination of *N*,*N*-diisopropylbenzylamines with DIB at 60 °C to produce aromatic aldehydes was reported.[9] Based on that report, the oxidative conversion of *N*,*N*-diisopropylbenzylamines bearing phenyl (**3s**), *p*-methylphenyl (**3f**), *p*-nitrophenyl (**3t**), *p*-bromophenyl (**3u**), *p*-methoxyphenyl (**3v**), and *p*-methoxycarbonylphenyl (**3w**) groups, into the corresponding aromatic aldehydes **2s**, **2f**, and **2t**–**w** with IS-DIBs **A** and **B** (or DIB) was carried out, and the yields and purity of aromatic aldehydes **2s**, **2f**, and **2t**–**w** were shown in Table 2. When IS-DIBs **A** and **B** were used as the oxidant, aromatic aldehydes were obtained in good yields with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract. On the other hand, when DIB was used as the oxidant for the same oxidative conversion of *N*,*N*-diisopropylbenzylamines **3s**, **3f**, **3t**–**w** under the same conditions and procedure, the corresponding aromatic aldehydes **2s**, **2f**, and **2t**–**w** were obtained in good yields. However, the purity was lower than 45% because of containing iodobenzene. Therefore, the purification of the aromatic aldehydes by column chromatography on silica gel was required in each reaction. After the extraction of benzaldehyde from the reaction mixture of *N*,*N*-diisopropylbenzylamine **3s** and IS-DIBs **A** and **B** with diethyl ether, the aqueous solution was extracted with chloroform to recover IS-PhIs in good yields.

The recovered IS-PhIs were re-oxidized by *m*CPBA in acetic acid at room temperature to regenerate IS-DIBs **A** and **B**, respectively, in good yields. Reuse of the recovered and regenerated IS-DIBs **A** and **B** for the same oxidative reaction of *N*,*N*-diisopropylbenzylamine **3s** under the same conditions as those of the first reactions provided benzaldehyde **2s** in good yields with high purity again, by simple extraction treatment of the reaction mixture, as shown in Table 2.

Then, the Hofmann rearrangement of primary amide[10] bearing phenyl (**4a**), *p*-methylphenyl (**4b**), *p*-chlorophenyl (**4c**), *p*-methoxyphenyl (**4d**), 1-adamantyl (**4e**), and cinnamyl (**4f**) groups, with IS-DIBs **A** and **B** (or DIB) in the presence of KOH in methanol was carried out to provide the corresponding methyl carbamates **5a**–**f** in good yields with high purity again by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract, as shown in Table 3. When DIB was used instead of IS-DIBs **A** and **B** for the same oxidative reaction with the

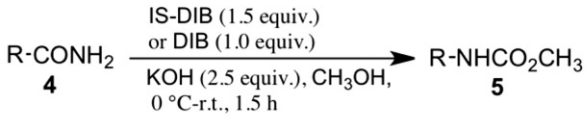
Table 2
Oxidation of *N*,*N*-diisopropylbenzylamines to aromatic aldehydes with DIB and IS-DIB **A** and **B**

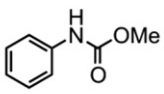
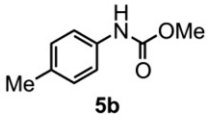
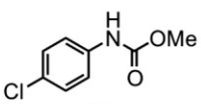
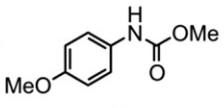
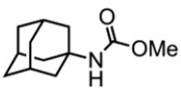
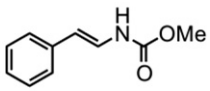


IS-DIB **A**, **B**, or **DIB**	Aldehyde **2** yield (%)[a], [purity (%)]	
	 **2s**	 **2f**
IS-DIB **A**	94, [99]	94, [99]
IS-DIB **B**	97, [98]	93, [97]
DIB	82, [33]	87, [45]
IS-DIB **A**[b)]	95, [97]	
IS-DIB **B**[b)]	96, [94]	
	 **2t**	 **2u**
IS-DIB **A**	92, [99]	91, [99]
IS-DIB **B**	93, [98]	92, [97]
DIB	88, [45]	87, [40]
	 **2v**	 **2w**
IS-DIB **A**	93, [98]	87, [86]
IS-DIB **B**	92, [98]	88, [87]
DIB	86, [42]	81, [33]

[a] Isolated yield as a purified state.
[b] Recovered and regenerated IS-DIB was used.

Table 3
Hofmann rearrangement with DIB and IS-DIB **A** and **B**



IS-DIB **A**, **B**, or **DIB**	Methylcarbamate **5** yield (%)[a], [purity (%)]	
	 **5a**	 **5b**
IS-DIB **A**	99, [99]	97, [98]
IS-DIB **B**	99, [99]	98, [99]
DIB	99, [68]	99, [70]
IS-DIB **A**[b)]	99, [99]	
IS-DIB **B**[b)]	99, [99]	
	 **5c**	 **5d**
IS-DIB **A**	99, [99]	98, [98]
IS-DIB **B**	97, [99]	97, [98]
DIB	98, [67]	98, [66]
	 **5e**	 **5f**
IS-DIB **A**	99, [99]	97, [99]
IS-DIB **B**	99, [99]	96, [97]
DIB	99, [65]	98, [66]

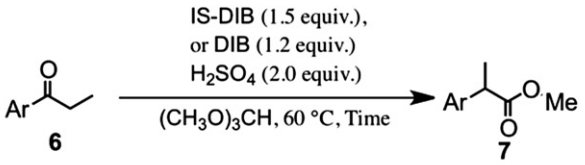
[a] Isolated yield as a purified state.
[b] Recovered and regenerated IS-DIB was used.

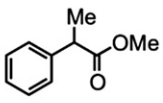
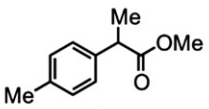
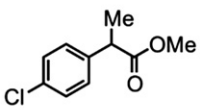
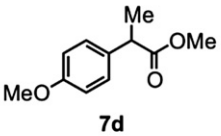
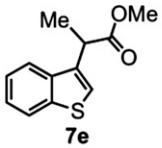
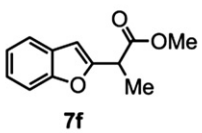
same substrates **4a**–**f** under the same conditions and procedure, the purity of the products was lower than 70% because of containing iodobenzene, although the yields were quite good. Again, reuse of the recovered and regenerated IS-DIBs **A** and **B** for the same Hofmann rearrangement of benzamide **4a** under the same conditions as those of the first reactions provided methyl *N*-phenyl carbamate **5a** in good yields with high purity again, by simple extraction treatment of the reaction mixture, as shown in Table 3.

Treatment of propiophenones, bearing phenyl (**6a**), *p*-methylphenyl (**6b**), *p*-chlorophenyl (**6c**), *p*-methoxyphenyl (**6d**), benzothiphen-3-yl (**6e**), and benzofuran-2-yl (**6f**) groups, with IS-DIBs **A** and **B** (or DIB)[11] in the presence of sulfuric acid in trimethyl orthoformate gave the corresponding methyl 2-arylpropanoates **7a**–**f** in good yields with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract, as shown in Table 4. When DIB was used instead of IS-DIBs **A** and **B**, for the same reaction with propiophenones **6a**, **6b**, **6e**, and **6f** under the same conditions and procedure, the purity of the corresponding methyl 2-arylpropanoates **7a**, **7b**, **7e**, and **7f** was lower than 52% because of containing iodobenzene, although the yields were good. Reuse of the recovered IS-PhIs and regenerated IS-DIBs **A** and **B** for the same oxidative rearrangement of propiophenones **6a** and **6b** under the same conditions as those of the first reactions gave methyl 2-phenylpropanoate **7a** and methyl 2-(4′-methylphenyl)propanoate **7b**, respectively, in good yields with high purity again, by simple extraction treatment of the reaction mixture, as shown in Table 4.

Finally, acetophenones bearing phenyl, *p*-chlorophenyl, *p*-bromophenyl, *p*-methylphenyl, and *p*-nitrophenyl groups, were treated with IS-DIBs **A** and **B** (or DIB)[7g,h] in the presence of trifluoromethanesulfonic acid in acetonitrile to provide the corresponding 4-aryl-2-methyloxazoles **8a**–**e** in good yields with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract, as shown in Table 5. When DIB was used instead of IS-DIBs **A** and **B** for the same reaction of acetophenones under the same conditions and procedure, the corresponding 5-aryl-2-methyloxazoles **8a**–**e** were obtained in good yields. However, the purity of the products was lower than 42% because of containing iodobenzene. Reuse of the

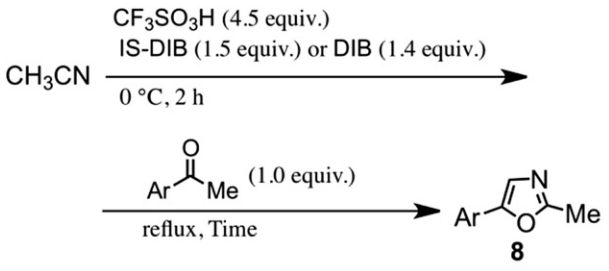
Table 4
Oxidative 1,2-aryl migration of aryl ketones with DIB and IS-DIB **A** and **B**

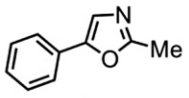
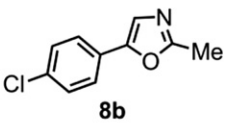
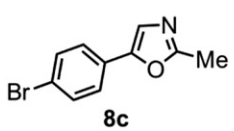
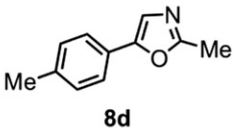
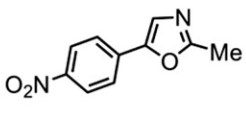


IS-DIB **A**, **B**, or **DIB**	Methyl ester **7** time (h), yield (%)[a], [purity (%)]	
	 **7a**	 **7b**
IS-DIB **A**	3, 95, [95]	3, 98, [99]
IS-DIB **B**	3, 99, [99]	3, 94, [97]
DIB	2, 94, [52]	2, 95, [47]
IS-DIB **A**[b)]	3, 97, [97]	3, 94, [96]
IS-DIB **B**[b)]	3, 96, [96]	3, 94, [97]
	 **7c**	 **7d**
IS-DIB **A**	5, 96, [99]	3, 99, [99]
IS-DIB **B**	5, 95, [98]	3, 95, [97]
	 **7e**	 **7f**
IS-DIB **A**[c)]	5, 94, [95]	5, 94, [99]
IS-DIB **B**[c)]	5, 96, [97]	5, 95, [96]
DIB[c)]	5, 94, [48]	5, 95, [48]

[a] Isolated yield as a purified state.
[b] Recovered and regenerated IS-DIB was used.
[c] H_2SO_4 (4.0 equiv.) was used.

Table 5
Preparation of 5-aryl-2 methyloxazoles from ketones with DIB and IS-DIB **A** and **B** in acetonitrile



IS-DIB **A**, **B**, or **DIB**	Oxazole **8** time (h), yield (%)[a], [purity (%)]	
	 **8a**	 **8b**
IS-DIB **A**	5, 93, [95]	5, 92, [93]
IS-DIB **B**	5, 92, [96]	5, 91, [92]
DIB	3, 91, [38]	3, 94, [40]
IS-DIB **A**[b)]	5, 92, [94]	
IS-DIB **B**[b)]	5, 92, [95]	
	 **8c**	 **8d**
IS-DIB **A**	5, 94, [94]	7, 92, [94]
IS-DIB **B**	5, 93, [93]	7, 90, [90]
DIB	3, 92, [39]	6, 92, [41]
	 **8e**	
IS-DIB **A**	5, 94, [95]	
IS-DIB **B**	5, 93, [93]	
DIB	3, 97, [42]	

[a] Isolated yield as a purified state.
[b] Recovered and regenerated IS-DIB was used.

recovered IS-PhIs and regenerated IS-DIBs **A** and **B** for the same oxidative reaction of acetophenone in acetonitrile under the same conditions as those of the first reactions provided 2-methyl-5-phenyloxazole **8a** in good yields with high purity again by simple extraction treatment of the reaction mixture, as shown in Table 5.

3. Conclusion

Two ion-supported (diacetoxyiodo)benzenes (IS-DIBs) **A** and **B**, i.e., *N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate (IS-DIB **A**) and *N*-methyl-*N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]pyrrolidinium 4″-methylbenzenesulfonate (IS-DIB **B**), were prepared for the first time. The TEMPO-mediated oxidation of secondary and primary alcohols with IS-DIBs **A** and **B** provided the corresponding ketones and aldehydes in good yields. The oxidative reaction of *N*,*N*-diisopropylbenzylamines with IS-DIBs **A** and **B** was also carried out to generate the corresponding aromatic aldehydes in good yields. In addition, the Hofmann rearrangement of primary amides in methanol under basic conditions and the oxidative 1,2-rearrangement of propiophenones in trimethyl orthoformate under acidic conditions with IS-DIBs **A** and **B** provided the corresponding methyl carbamates and methyl 2-arylpropanoates, respectively, in good yields again. Moreover, treatment of *p*-substituted acetophenones with IS-DIBs **A** and **B** in the presence of trifluoromethanesulfonic acid in acetonitrile generated the corresponding 5-aryl-2-methyloxazoles in good yields. In those five reactions, the products were obtained in good yields with high purity by simple extraction of the reaction mixture with diethyl ether and subsequent removal of the solvent from the extract. Moreover, IS-PhIs, which were co-products derived from IS-DIBs **A** and **B** in the present oxidative reactions, were recovered in good yields and could be re-oxidized to IS-DIBs **A** and **B** for reuse in the same oxidative reactions. Thus, the present IS-DIBs **A** and **B** are simple, user-friendly for easy isolation of desired products, and recyclable oxidative reagents.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in parts per million downfield from TMS in δ units. Mass spectra were recorded on JMS-T100GCV, JMS-HX110, and Thermo LTQ Orbitrap XL spectrometers. IR spectra were measured with a JASCO FT-IR4100 spectrometer. Melting points were determined on an YAMATO Melting Point electrothermal apparatus MP-21 in open capillary tubes and are uncorrected. Kieselgel 60 F_{254} (Merck) was used for TLC and Silica gel 60 (Kanto Kagaku Co.) was used for short column chromatography.

4.2. Preparation ion-supported (diacetoxy)iodo-benzenes A and B

4.2.1. Typical procedure for the preparation of N-[3-(4′-iodophenoxy)-1-propyl]-N,N,N-trimethyl-ammonium 4″-methylbenzenesulfonate. 3-(4′-Iodophenoxy)propyl 4″-methylbenzenesulfonate (5 mmol, 2.16 g) in CH_2Cl_2 (20 mL) was added to aq dimethylamine (ca. 50% in water, 5 equiv, 7.89 mL). The mixture was stirred for 24 h at room temperature. After the reaction, the reaction mixture was concentrated in vacuo. H_2O (30 mL) was added to the residue. The aqueous layer was extracted with $CHCl_3$ (3×20 mL). The organic layer was dried over Na_2SO_4, and then, removal of the solvent under reduced pressure afforded *N*,*N*-dimethyl 3-(4′-iodophenoxy)propyl-1-amine. Methyl *p*-toluenesulfonate (1.2 equiv 1.11 g) was added to a solution of *N*,*N*-dimethyl 3-(4′-iodophenoxy)propyl-1-amine (5 mmol 1.52 g) in CH_2Cl_2 (20 mL). The mixture was stirred for 4 h at room temperature. After the reaction, the reaction mixture was concentrated in vacuo. Et_2O (20 mL) was added to the residue and the mixture was filtered to afforded *N*-[3-(4′-iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethyl-ammonium 4″-methylbenzenesulfonate in 99% yield. If necessary, the solids were washed with EtOAc to afford the product in pure state. *N*-Methyl-*N*-[3-(4′-iodophenoxy)-1-propyl]pyrrolidinium 4″-methylbenzenesulfonate was prepared in 99% yield, by the same procedure.

4.2.1.1. N-[3-(4′-Iodophenoxy)-1-propyl]-N,N,N-tri-methyl-ammonium 4″-methylbenzenesulfonate. Mp 222–226 °C; IR (KBr): 1285, 1010, 816 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.12–2.19 (m, 2H), 2.29 (s, 3H), 3.08 (s, 9H), 3.46 (t, *J*=8.3 Hz, 2H), 4.02 (t, *J*=6.0 Hz, 2H), 6.80 (d, *J*=9.0 Hz, 2H), 7.12 (d, *J*=7.9 Hz, 2H), 7.47 (d, *J*=7.9 Hz, 2H), 7.61 (d, *J*=9.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO) δ=20.74, 22.42, 52.25, 62.84, 64.84, 83.53, 117.29, 125.44, 128.00, 137.51, 138.01, 145.80, 158.04; HRMS (APPI) calcd for $C_{12}H_{19}ONI$ [M+]: 320.0506; found: 320.0499.

4.2.1.2. N-Methyl-N-[3-(4′-iodophenoxy)-1-propyl]-pyrrolidinium 4″-methylbenzenesulfonate. Mp 114–116 °C; IR (Nüjol): 1195, 1010, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.08–2.23 (m, 6H), 2.30 (s, 3H), 3.15 (s, 3H), 3.54–3.72 (m, 6H), 3.92 (t, *J*=5.8 Hz, 2H), 6.60 (d, *J*=9.1 Hz, 2H), 7.09 (d, *J*=8.2 Hz, 2H), 7.50 (d, *J*=9.1 Hz, 2H), 7.71 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.23, 21.55, 23.99, 48.27, 61.16, 64.27, 64.38, 83.24, 116.90, 125.70, 128.63, 138.22, 139.22, 144.02, 158.04; HMRS (ESI) calcd for $C_{14}H_{21}ONI$ [M+]: 346.0662; found: 346.0655.

*4.2.2. Typical procedure for the preparation of N-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-N,N,N-trimethylammonium 4″-methylbenzenesulfonate (IS-DIB **A**).* To a solution of *N*-[3-(4′-iodophenoxy)-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate (5 mmol, 2.45 g) in AcOH (15 mL) was added 3-chloroperoxybenzoic acid (*m*CPBA, 5.5 mmol, 1.46 g>65% purity). The mixture was stirred for 24 h at room temperature. After the reaction, the reaction mixture was added to Et_2O (15 mL) at 0 °C and was filtered to afford *N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]-*N*,*N*,*N*-trimethylammonium 4″-methylbenzenesulfonate in 97% yield. *N*-Methyl-*N*-[3-(4′-diacetoxyiodo)phenoxy-1-propyl] pyrrolidinium 4″-methylbenzenesulfonate (IS-DIB **B**) was prepared by the same procedure. The purity of IS-DIB **A** and **B** was estimated to be over 95% by ^{1}H NMR spectroscopy, due to containing a trace amount of ion-supported iodobenzene (monovalent iodine), respectively.

*4.2.2.1. 3-[4′-(Diacetoxyiodo)phenoxy]-1-propyl]-N,N,N-trimethylammonium 4″-Methylbenzenesulfonate (IS-DIB **A**).* Viscous colorless oil; IR (neat): 1650, 1243, 1040, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.98 (s 6H), 2.30–2.35 (m, 2H), 3.28 (s, 9H), 3.67 (t, *J*=8.4 Hz, 2H), 4.13 (t, *J*=5.5 Hz, 2H), 6.96 (d, *J*=9.1 Hz, 2H), 8.00 (d, *J*=9.1 Hz, 2H); δ (anion TsO^-)=2.31 (s, 3 H), 7.12 (d, *J*=8.2 Hz, 2H), 7.71 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.24, 21.43, 23.03, 53.44, 64.12, 64.68, 111.79, 116.98, 126.35, 129.23, 137.09, 138.19, 142.44, 160.76, 176.63; ESI-HRMS: *m*/*z* calcd for $C_{16}H_{25}O_5NI$ [M+]:438.0772; found: 438.0760.

*4.2.2.2. N-Methyl-N-[3-(4′-diacetoxyiodo)phenoxy-1-propyl]pyrrolidinium 4″-Methylbenzenesulfonate (IS-DIB **B**).* Viscous colorless oil; IR (neat): 1650, 1583, 1275, 1010, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (cation)=1.98 (s, 6H), 2.18–2.29 (m, 6H), 3.17 (s, 3H), 3.59–3.74 (m, 6H), 4.13 (t, *J*=5.6 Hz, 2H), 6.93 (d, *J*=9.1 Hz, 2H), 7.97 (d, *J*=9.1 Hz, 2H); δ (anion TsO^-)=2.31 (s, 3H), 7.12 (d, *J*=8.2 Hz, 2H), 7.73 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.28, 21.58,

22.03, 23.85, 48.46, 61.51, 64.51, 64.85, 111.67, 117.03, 125.66, 128.66, 137.02, 138.20, 143.32, 160.77, 176.43; ESI-HRMS: *m*/*z* calcd for $C_{18}H_{27}O_5NI$ [M+]: 464.0928; found: 464.0919.

4.3. General procedure for oxidation of alcohols with IS-DIB A or B in the presence of TEMPO

To a solution of IS-DIB **A** or **B** (1.5 equiv, 0.75 mmol) in CH_2Cl_2 (2 mL) were added alcohol (0.5 mmol) and TEMPO (10 mol %, 0.05 mmol). Then, the reaction mixture was stirred for 2 h at room temperature under argon atmosphere. The reaction mixture was concentrated in vacuo, H_2O (20 mL) was added to the residue, and the aqueous layer was extracted with Et_2O (3×20 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the product (aldehyde or ketone), and purity of the product was estimated by ^1H NMR spectroscopy. On the other hand, the aqueous layer was extracted with $CHCl_3$ (3×20 mL). Then, the organic layer was washed with aq Na_2SO_3 and brine, and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded ion-supported iodobenzene.

*4.3.1. Benzophenone (**2a**).* Mp 49–52 °C (commercial, mp 49 °C); IR (Nüjol): 1657 cm^{-1}; ^1H NMR (400 MHz $CDCl_3$): δ=7.48 (t, *J*=7.5 Hz, 4H), 7.58 (t, *J*=7.5 Hz, 2H), 7.80 (d, *J*=7.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=128.20, 129.98, 132.35, 137.51, 196.70.

*4.3.2. 9-Fluorenone (**2b**).* Mp 79–80 °C (commercial, mp 80–83 °C); IR (Nüjol): 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.29 (td, *J*=7.5, 1.4 Hz, 2H), 7.46–7.54 (m, 4H), 7.66 (d, *J*=7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=120.28, 124.31, 129.06, 134.14, 134.66, 144.42, 193.94.

*4.3.3. Propiophenone (**2c**).* Colorless oil (commercial, oil); IR (neat): 1686 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=1.23 (t, *J*=7.3 Hz, 3H), 3.00 (q, *J*=7.3 Hz, 2H), 7.45 (t, *J*=7.7 Hz, 2H), 7.55 (t, *J*=7.7 Hz, 1H), 7.96 (d, *J*=7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$: 100 MHz): δ=7.72, 31.25, 127.44, 128.02, 132.35, 136.39, 200.28.

*4.3.4. 1-(5′-Methylfuran-2′-yl)-1-pentanone (**2d**).* Colorless oil; IR (neat): 3121, 2931, 2827, 1671, 1518, 1452, 876 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ=0.94 (t, *J*=7.5 Hz, 3H), 1.39 (sext, *J*=7.5 Hz, 2H), 1.69 (quin, *J*=7.5 Hz, 2H), 2.39 (s, 3H), 2.75 (t, *J*=7.5 Hz, 2H), 6.14 (d, *J*=3.4 Hz, 1H), 7.09 (d, *J*=3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.15, 13.33, 21.76, 26.11, 37.17, 108.10, 118.22, 150.84, 156.84, 188.40. ESI-HRMS: *m*/*z* calcd for $C_{10}H_{15}O_2$ [M+H]: 167.1067; found: 167.1065.

*4.3.5. 4-Chlorobenzaldehyde (**2e**).* Mp 48–49 °C (commercial, mp 47–50 °C); IR (Nüjol): 2727, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.52 (d, *J*=8.4 Hz, 2H), 7.83 (d, *J*=8.4 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=128.93, 130.36, 134.16, 140.39, 190.31.

*4.3.6. 4-Methylbenzaldehyde (**2f**).* Colorless oil (commercial, oil); IR (neat): 2827, 2734, 1702, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.44 (s, 3H), 7.33 (d, *J*=7.9 Hz, 2H), 7.78 (d, *J*=7.9 Hz, 2H), 9.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.50, 129.33, 129.46, 133.81, 145.15, 191.62.

*4.3.7. Piperoylaldehyde (**2g**).* Mp 37–39 °C (commercial, mp 36–38 °C); IR (Nüjol): 2725, 1685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=6.07 (s, 2H), 6.93 (d, *J*=7.9 Hz, 1H), 7.32 (d, *J*=1.6 Hz, 1H), 7.41 (dd, *J*=7.9, 1.6 Hz, 1H), 9.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=102.02, 106.77, 108.24, 128.55, 131.77, 148.60, 153.00, 190.17.

*4.3.8. 4-Phenylbenzaldehyde (**2h**).* Mp 57–58 °C (commercial, mp 58 °C); IR (Nüjol): 2726, 1708, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.40 (t, *J*=7.2 Hz, 1H), 7.47 (t, *J*=7.2 Hz, 2H), 7.62 (d, *J*=7.2 Hz, 2H), 7.73 (d, *J*=8.2 Hz, 2H), 7.93 (d, *J*=8.2 Hz, 2H), 10.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=126.94, 127.26, 128.06, 128.60, 129.85, 134.77, 139.26, 146.74, 191.49.

*4.3.9. 2-Thiophenecarboxaldehyde (**2i**).* Colorless oil (commercial, oil); IR (neat): 2820, 2761, 1671 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.22 (dd, *J*=4.8, 3.8 Hz, 1H), 7.75–7.82 (m, 2H), 9.95 (s, 1H); ^{13}C NMR ($CDCl_3$: 100 MHz): δ=128.22, 135.03, 136.21, 143.94, 182.89.

*4.3.10. Geranial (**2j**).* Colorless oil (commercial, oil); IR (neat): 2768, 1673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.61 (s, 3H), 1.69 (s, 3H), 2.17 (s, 3H) 2.17–2.27 (m, 4H), 5.03–5.14 (m, 1H), 5.88 (d, *J*=7.9 Hz, 1H), 9.99 (d, *J*=7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.87, 16.99, 24.92, 25.02, 39.89, 121.86, 126.68, 132.14, 163.07, 190.54.

*4.3.11. trans-Cinnamaldehyde (**2k**).* Colorless oil (commercial, oil); IR (neat): 2816, 2743, 1676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=6.72 (dd, *J*=7.7, 16.1 Hz, 1H), 7.41–7.46 (m, 3H), 7.48 (d, *J*=16.1 Hz, 1H), 7.54–7.60 (m, 2H), 9.71 (d, *J*=7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=128.31, 128.42, 128.93, 131.09, 133.81, 152.60, 193.52.

*4.3.12. 1-Adamantanecarboxaldehyde (**2l**).* Mp 140–142 °C (lit.[12] mp: 146–148 °C); IR (Nüjol): 2815, 2698, 1722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.68–1.80 (m, 12H), 2.03–2.09 (m, 3H), 9.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=27.31, 35.80, 36.52, 44.82, 206.09.

*4.3.13. Citronellal (**2m**).* Colorless oil (commercial, oil); IR (neat): 2855, 2716, 1726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.97 (d, *J*=6.6 Hz, 3H), 1.22–1.42 (m, 2H), 1.60 (s, 3H), 1.68 (s, 3H), 1.94–2.12 (m, 3H), 2.21–2.27 (m, 1H), 2.37–2.42 (m, 1H), 5.05–5.12 (m, 1H), 9.75 (t, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=17.58, 19.80, 25.33, 25.62, 27.71, 36.88, 50.93, 123.98, 131.68, 202.94.

*4.3.14. 8-(4′-Methylbenzenesulfonyloxy)octanal (**2n**).* Colorless oil; IR (neat): 2859, 2723, 1723, 1359, 1176 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.21–1.36 (m, 6H), 1.54–1.58 (m, 4H), 2.41 (t, *J*=7.4 Hz, 2H), 2.45 (s, 3H), 4.02 (t, *J*=6.5 Hz, 2H), 7.35 (d, *J*=8.2 Hz, 2H), 7.78 (d, *J*=8.2 Hz, 2H), 9.73–9.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.43, 21.65, 24.95, 28.45, 28.52, 28.67, 43.58, 70.38, 127.67, 129.66, 132.96, 144.54, 202.50. ESI-HRMS: *m*/*z* calcd for $C_{15}H_{23}O_4S$ [M+H]: 299.1312; found: 299.1310.

*4.3.15. 5α-Cholestan-3-one (**2o**).* Mp 123–125 °C (commercial, mp: 128–129 °C); IR (Nüjol): 1719 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=0.68 (s, 3H), 0.69–0.76 (m, 1H), 0.84–0.92 (m, 9H), 1.01 (s, 3H), 0.94–1.18 (m, 9H), 1.23–1.44 (m, 9H), 1.46–1.60 (m, 4H), 1.66–1.74 (m, 1H), 1.78–1.89 (m, 1H), 1.96–2.12 (m, 3H), 2.21–2.44 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=11.43, 12.04, 18.64, 21.42, 22.53, 22.79, 23.79, 24.19, 27.98, 28.21, 28.95, 31.69, 35.36, 35.61, 35.76, 36.11, 38.17, 38.54, 39.47, 39.88, 42.56, 44.70, 46.68, 53.78, 56.23, 212.12.

*4.3.16. 4-[(tert-Butyldimethylsilyl)oxy]cyclohexanone (**2p**).* Colorless oil; IR (neat): 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.10 (s, 6H), 0.92 (s, 9H), 1.83–2.02 (m, 4H), 2.18–2.28 (m, 2H), 2.61–2.73 (m, 2H), 4.10–4.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=−5.39, 17.53, 25.24, 33.65, 36.38, 65.39, 211.26; HRMS (APPI): *m*/*z* calcd for $C_{12}H_{25}O_2Si$ [M+H]: 229.1618; found: 229.1617.

*4.3.17. Camphor (**2q**).* Mp 170–173 °C (commercial, mp: 172–180 °C); IR (Nüjol): 1749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.84 (s, 3H), 0.91 (s, 3H), 0.96 (s, 3H), 1.30–1.45 (m, 2H), 1.68 (td, *J*=12.5, 4.0 Hz, 1H), 1.84 (d, *J*=18.4 Hz, 1H), 1.90–2.00 (m, 1H), 2.09 (t, *J*=4.0 Hz, 1H), 2.35 (dt, *J*=18.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ=9.08, 18.98, 19.61, 26.89, 29.75, 42.89, 43.14, 46.62, 57.53, 219.53.

*4.3.18. 2,3,4,6-Tetra-O-benzy-D-glucono-1,5-lactone (**2r**).* Viscous colorless oil; IR (neat): 2919, 2869, 1755, 1454, 1165, 1094, 738, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.64–3.75 (m, 2H), 3.88–3.98 (m, 2H), 4.12 (d, J=6.1 Hz, 1H), 4.43–4.76 (m, 8H), 4.98 (d, J=11.3 Hz, 1H), 7.15–7.41 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=68.21, 73.52, 73.69(2C), 73.91, 76.01, 78.12, 80.92, 127.79(3C), 127.91, 127.96(3C), 128.08, 128.37, 128.41(2C), 128.45, 136.90, 137.46(2C), 137.55, 169.31; ESI-HRMS: m/z calcd for $C_{34}H_{35}O_6$ [M+H]: 539.2428; found: 539.2423.

4.4. General procedure for oxidation of *N,N*-diisopropylbenzylamines into aromatic aldehydes with IS-DIB A or B

To a solution of tertiary amine (1.0 equiv, 1.0 mmol) in $CHCl_3$ (4 mL) was added $NaHCO_3$ (1.2 equiv, 1.2 mmol) and IS-DIB **A** or **B** (2.0 equiv, 2.0 mmol). The solution was stirred for 2 h at 60 °C under argon atmosphere. After the reaction, aq NH_4Cl (10 mL) was added. The aqueous layer was extracted with Et_2O (3×20 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded aromatic aldehyde, and purity of the product was estimated by ^1H NMR spectroscopy. On the other hand, the aqueous layer was extracted with $CHCl_3$ (3×20 mL). Then, the organic layer was washed with aq Na_2SO_3 and brine, and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded ion-supported iodobenzene.

*4.4.1. Benzaldehyde (**2s**).* Colorless oil (commercial, oil); IR (neat): 1710, 1206 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.54 (t, J=7.6 Hz, 2H), 7.64 (t, J=7.5 Hz, 1H), 7.90 (d, J=6.8 Hz, 2H), 10.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=128.04, 128.65, 133.39, 135.58, 192.38.

*4.4.2. 4-Nitrobenzaldehyde (**2t**).* Mp 101–103 °C (commercial, mp: 105 °C); IR (neat): 1702, 1536, 1343, 1194, 813, 737 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=8.10 (d, J=8.9 Hz, 2H), 8.40 (d, J=8.6 Hz, 2H), 10.19 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=124.20, 130.40, 139.99, 151.02, 190.26.

*4.4.3. 4-Bromobenzaldehyde (**2u**).* Mp 57–59 °C (commercial, mp: 55–58 °C); IR (neat): 1689, 1587, 1383, 1203, 1065, 808 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=7.68 (d, J=8.6 Hz, 2H), 7.75 (d, J=8.4 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=129.74, 130.93, 132.40, 135.04, 191.03.

*4.4.4. 4-Methoxybenzaldehyde (**2v**).* Colorless oil (commercial, oil); IR (neat): 1698, 1602, 1511, 1263, 1162 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.89 (s, 3H), 7.01 (d, J=8.7 Hz, 2H), 7.84 (d, J=8.8 Hz, 2H), 9.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.54, 114.26, 129.91, 131.94, 164.56, 190.76.

*4.4.5. Methyl 4-formylbenzoate (**2w**).* Mp 60–62 °C (commercial, mp: 60 °C); IR (neat): 2965, 1722, 1683, 1280, 1105 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=3.96 (s, 3H), 7.96 (d, J=8.1 Hz, 2H), 8.20 (d, J=8.0 Hz, 2H), 10.11 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=52.53, 129.45, 130.13, 135.03, 139.09, 165.99, 191.56.

4.5. General procedure for preparation of *N*-aryl methyl carbamates from amides with IS-DIB A or B

To a solution of potassium hydroxide (2.5 equiv, 2.5 mmol) in methanol (10 mL) was added amide (1.0 equiv, 1.0 mmol). The mixture was stirred at room temperature until a homogeneous solution was obtained followed by cooling to 5–10 °C in an ice-water bath. IS-DIB **A** or **B** (1.5 equiv, 1.5 mmol) was added. Then, the reaction mixture was stirred at 0 °C for 15 min, followed by warming to room temperature under argon atmosphere while stirring for an additional 1.5 h. After the reaction, the reaction mixture was concentrated in vacuo, H_2O (20 mL) was added to the residue, and the aqueous layer was extracted with Et_2O (3×20 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded methyl carbamate, and purity of the product was estimated by ^1H NMR spectroscopy. On the other hand, the aqueous layer was extracted with $CHCl_3$ (3×20 mL). Then, the organic layer was washed with aq Na_2SO_3 and brine, and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded ion-supported iodobenzene.

*4.5.1. Methyl N-phenyl carbamate (**5a**).* Mp 45–47 °C (lit.[10] mp: 48–49 °C); IR (KBr): 3315, 1705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.77 (s, 3H), 6.70 (br s, 1H, NH), 7.08 (t, J=7.4 Hz, 1H), 7.30 (t, J=7.9 Hz, 2H), 7.39 (d, J=7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=52.28, 118.61, 123.38, 128.97, 137.77, 153.99.

*4.5.2. Methyl N-(4-methylphenyl)carbamate (**5b**).* Mp 93–95 °C (lit.[13] mp: 97–98 °C); IR (KBr): 3328, 1704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.30 (s, 3H), 3.76 (s, 3H), 6.56 (br s, 1H, NH), 7.11 (d, J=8.3 Hz, 2H), 7.26 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.61, 52.11, 118.76, 129.36, 132.83, 135.21, 154.23.

*4.5.3. Methyl N-(4-chlorophenyl)carbamate (**5c**).* Mp 108–110 °C (lit.[13] mp: 113–116 °C); IR (KBr): 3338, 1703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=3.78 (s, 3H), 6.64 (br s, 1H, NH), 7.27 (d, J=7.6 Hz, 2H), 7.33 (d, J=7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=52.45, 119.80, 128.38, 128.99, 136.40, 153.89.

*4.5.4. Methyl N-(4-methoxyphenyl)carbamate (**5d**).* Mp 83–85 °C (lit.[13] mp: 88 °C); IR (KBr): 3343, 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.75 (s, 3H), 3.78 (s, 3H), 6.64 (br s, 1H, NH), 6.86 (d, J=8.8 Hz, 2H), 7.30 (d, J=8.8 Hz, 2H).

*4.5.5. Methyl N-(1-adamantyl)carbamate (**5e**).* Mp 114–115 °C (lit.[10] mp: 117–119 °C); IR (KBr): 3407, 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.66–1.68 (m, 6H), 1.90–1.94 (m, 6H), 2.04–2.08 (m, 3H), 3.60 (s, 3H), 4.51 (br s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ=29.35, 36.22, 41.75, 41.95, 50.54, 51.23, 154.90.

*4.5.6. Methyl N-[(E)-styryl]carbamate (**5f**).* Mp 118–120 °C (lit.[10] mp: 120–121 °C); IR (KBr): 3301, 1705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.78 (s, 3H), 6.00 (d, J=14.7 Hz, 1H), 6.58 (br s, 1H, NH), 7.20–7.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=52.64, 110.69, 124.02, 125.17, 126.20, 128.55, 136.17, 154.27.

4.6. General procedure for preparation of methyl 2-arylpropanoates from propiophenones with IS-DIB A or B

Sulfuric acid (2.0 equiv, 2.0 mmol) was added dropwise to a solution of IS-DIB **A** or **B** (1.5 equiv, 1.5 mmol) and propiophenone (1.0 equiv, 1.0 mmol) in 4 mL of trimethyl orthoformate at 0 °C. The mixture was stirred for 3 h at 60 °C under argon atmosphere. After the reaction, the reaction mixture was quenched with water (20 mL), and the aqueous layer was extracted with Et_2O (3×20 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded methyl 2-phenylpropionate, and purity of the product was estimated by ^1H NMR spectroscopy. On the other hand, the aqueous layer was extracted with $CHCl_3$ (3×20 mL). Then, the organic layer was washed with aq Na_2SO_3 and brine, and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded ion-supported iodobenzene.

*4.6.1. Methyl 2-phenylpropanoate (**7a**).* Colorless oil (lit.[11b] oil); IR (neat): 2982, 1738, 1454, 1208, 1167 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=1.50 (d, J=7.2 Hz, 2H), 3.66 (s, 3H), 3.73 (q, J=7.2 Hz, 1H), 7.24–7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=18.32, 45.11, 51.54, 126.84, 127.19, 128.36, 140.34, 174.52.

*4.6.2. Methyl 2-(4′-methylphenyl)propanoate (**7b**).* Colorless oil (lit.[11b] oil); IR (neat): 2951, 1738, 1205, 1165 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=1.49 (d, J=7.2 Hz, 3H), 2.32 (s, 3H), 3.65 (s, 3H), 3.68 (q, J=7.2 Hz, 1H), 7.13 (d, J=8.0 Hz, 2H), 7.18 (d, J=8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=18.52, 20.90, 44.88, 51.82, 127.20, 129.21, 136.62, 137.50, 175.00.

*4.6.3. Methyl 2-(4′-chlorophenyl)propanoate (**7c**).* Colorless oil (lit.[11b] oil); IR (neat): 2952, 1739, 1493, 1208, 1167, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=1.47 (d, J=7.2 Hz, 3H), 3.64 (s, 3H), 3.69 (q, J=7.2 Hz, 1H), 7.22 (d, J=8.3 Hz, 2H), 7.27 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=18.33, 44.60, 51.87, 128.57, 128.73, 132.79, 138.83, 174.31.

*4.6.4. Methyl 2-(4′-methoxyphenyl)propanoate (**7d**).* Colorless oil (lit.[11b] oil); IR (neat): 2952, 1736, 1512, 1247, 1208, 1178 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=1.47 (d, J=7.2 Hz, 3H), 3.65 (s, 3H), 3.67 (q, J=7.2 Hz, 1H), 3.78 (s, 3H), 6.85 (d, J=8.5 Hz, 2H), 7.22 (d, J=8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=18.32, 44.17, 51.47, 54.75, 113.67, 128.13, 132.34, 158.42, 174.80.

*4.6.5. Methyl 2-(benzo[b]thiophen-3-yl)propanoate (**7e**).* Colorless oil; IR (neat): 2983, 1737, 1430, 1200, 1165, 763 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.63 (d, J=7.2 Hz, 3H), 3.66 (s, 3H), 4.14 (q, J=7.2 Hz, 1H), 7.31 (s, 1H), 7.34–7.40 (m, 2H), 7.81 (d, J=7.9 Hz, 1H), 7.84 (d, J=7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=17.24, 39.01, 51.84, 121.49, 122.47, 122.66, 123.90, 124.17, 134.60, 137.74, 140.17, 174.05; ESI-HRMS: m/z calcd for $C_{12}H_{13}O_2S$ [M+H]: 221.0631; found: 221.0627.

*4.6.6. Methyl 2-(benzofuran-2-yl)propanoate (**7f**).* Colorless oil; IR (neat): 2989, 1743, 1455, 1201 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=1.62 (d, J=7.5 Hz, 3H), 3.73 (s, 3H), 3.96 (q, J=7.3 Hz, 1H), 6.57 (s, 1H), 7.20 (t, J=7.5 Hz, 1H), 7.25 (t, J=7.7 Hz, 1H), 7.44 (d, J=8.0 Hz, 1H), 7.52 (d, J=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=15.71, 39.76, 52.41, 103.08, 111.07, 120.72, 122.66, 123.88, 128.31, 154.71, 156.18, 172.52; ESI-HRMS: m/z calcd for $C_{12}H_{12}O_3Na$ [M+Na]: 227.0679; found: 227.0673.

4.7. General procedure for preparation of 5-aryl-2-methyloxazoles from acetophenones with IS-DIB A or B in acetonitrile

To a solution of IS-DIB **A** or **B** (1.5 equiv, 1.5 mmol) in CH_3CN (10 mL) was added TfOH (4.5 equiv, 4.5 mmol) at 0 °C. The obtained mixture was stirred for 2 h at 0 °C under argon atmosphere. Then, a solution of acetophenone (1.0 equiv, 1.0 mmol) in CH_3CN (2 mL) was added. The mixture was stirred for 5 h under refluxing conditions. After the reaction, aq $NaHCO_3$ (10 mL) was added. The aqueous layer was extracted with Et_2O (3×20 mL). The organic layer was dried over Na_2SO_4, and removal of the solvent under reduced pressure afforded 2-methyl-5-phenyloxazole, and purity of the product was estimated by ^1H NMR spectroscopy. On the other hand, the aqueous layer was extracted with $CHCl_3$ (3×20 mL). Then, the organic layer was washed with aq Na_2SO_3 and brine, and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded ion-supported iodobenzene.

*4.7.1. 2-Methyl-5-phenyloxazole (**8a**).* Mp 55–57 °C (lit.[7g] mp: 57–58.5 °C); IR (neat): 1578, 1560, 1485 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.52 (s, 3H), 7.20 (s, 1H), 7.29 (t, J=7.5 Hz, 1H), 7.40 (t, J=7.6 Hz, 2H), 7.60 (d, J=7.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.03, 121.83, 123.87, 128.03, 128.15, 128.78, 151.04, 160.95.

*4.7.2. 5-(4′-Chlorophenyl)-2-methyloxazole (**8b**).* Mp 68–70 °C (lit.[7g] mp: 74–75.5 °C); IR (neat): 3053, 1573, 1554, 1482, 1089, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.52 (s, 3H), 7.19 (s, 1H), 7.35 (d, J=8.5 Hz, 2H), 7.51 (d, J=8.7 Hz, 2H): ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.93, 122.18, 125.24, 126.53, 128.94, 133.64, 149.98, 161.10.

*4.7.3. 5-(4′-Bromophenyl)-2-methyloxazole (**8c**).* Mp 97–99 °C (lit.[14] mp: 98–100 °C); IR (neat): 2971, 1589, 1575, 1478, 1402, 1105, 1067, 826, 761 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.53 (s, 3H), 7.51 (d, J=8.9 Hz, 2H), 7.57 (d, J=8.9 Hz, 2H), 7.80 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=13.91, 121.64, 126.91, 130.09, 131.81, 133.33, 139.74, 161.99.

*4.7.4. 2-Methyl-5-(4′-methylphenyl)oxazole (**8d**).* Mp 51–53 °C (lit.[7g] mp: 54–55 °C); IR (neat): 1587, 1505, 1109, 1070, 821 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.35 (s, 3H), 2.49 (s, 3H), 7.19 (d, J=7.7 Hz, 2H), 7.59 (d, J=8.3 Hz, 2H), 7.74 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=13.9121.19, 125.22, 128.27, 129.32, 132.64, 137.61, 140.63, 161.61; ESI-HRMS: m/z calcd for $C_{11}H_{12}ON$ [M+H]: 174.0913; found: 174.0913.

*4.7.5. 2-Methyl-5-(4′-nitrophenyl)oxazole (**8e**).* Mp 157–159 °C (lit.[7g] mp: 161–162 °C); IR (neat): 3122, 1607, 1557, 1504, 1347, 1328, 1132, 1105, 1059, 942, 851, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=2.58 (s, 3H), 7.42 (s, 1H), 7.76 (d, J=9.1 Hz, 2H), 8.28 (d, J=8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=14.10, 124.20, 124.45, 125.46, 133.86, 146.97, 149.11, 162.90.

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