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Synthetic Methods

Morita–Baylis–Hillman-Type [3,3]-Rearrangement: Switching from *Z*- to *E*-Selective α-Arylation by New Rearrangement Partners

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Abstract: *α-aryl α,β-unsaturated carbonyls represent an important class of derivatizable synthetic intermediates, however, the synthesis of such compounds still remains a challenge. Recently, we showcased a novel Z-selective α-arylation of α,β-unsaturated nitriles with aryl sulfoxides via [3,3]-rearrangement involving an Morita–Baylis–Hillman (MBH) process. Herein, we demonstrate the feasibility of reversing the stereoselectivity of such MBH-type [3,3]-rearrangement by switching to a new pair of rearrangement partners consisting of aryl iodanes and α,β-unsaturated oxazolines. As a result, the two protocols complement each other in approaching E- or Z-α-aryl α,β-unsaturated carbonyl derivatives. Mechanistic studies reveal a possible reaction pathway and provide an explanation for the opposite stereoselectivities.*

Introduction

α-Aryl α,β-unsaturated carbonyls are valuable synthetic building blocks.[1] Traditional methods to synthesize these molecules rely on the cross coupling of α-halogenated or metalated α,β-unsaturated carbonyls with a proper arene moiety source.[2] However, the use of prefunctionalized α,β-unsaturated carbonyls decreases the step efficiency of such protocols. Direct α-C–H arylation of α,β-unsaturated carbonyls is a straightforward approach, but it has rarely been developed.[3] In 2004, Krische and co-workers accomplished α-arylation of enones and enals with triarylbismuth reagents via nucleophilic catalysis.[3a] Despite the impressive step efficiency, the difficulty in synthesizing unconventional bismuth reagents limits the adoption of the protocol.[4] Therefore, the development of efficient stereoselective α-C–H arylation of α,β-unsaturated carbonyls is highly desirable.

In the past few years, the iodonium- and sulfonium-Claisen rearrangements have attracted great attention from synthetic community.[5,6] This type of rearrangement can be conducted by directly mixing readily available activated aryl iodanes and aryl sulfoxides with certain nucleophiles,[7–11] which allows in situ construction of a highly reactive transient rearrangement precursor. In this context, we were interested in constructing the rearrangement precursor in a stepwise fashion which, we conceived, not only enhances the reaction efficiency but also render the reaction capable of adopting new intriguing functions.[12,13] For examples, with the stepwise strategy, we were able to implement [3,3]- and [5,5]-rearrangement of aryl sulfoxides with alkyl nitriles and allyl nitriles, respectively, via an assembly/deprotonation sequence.[12] The same protocol also allows us to develop asymmetric [3,3]-rearrangement of aryl iodanes with chiral oxazolines.[13]

Recently, the stepwise strategy continued to illuminate us to merge Morita–Baylis–Hillman (MBH) reaction with the rearrangement chemistry.[14,15] As depicted in Scheme 1, the addition/elimination of MBH process could be merged with the rearrangement of aryl sulfoxides and aryl iodanes. As a result, the MBH-type rearrangement of aryl sulfoxides enables Z-selective α-C–H arylation of α,β-unsaturated nitriles as we disclosed recently (Scheme 1B).[15] In contrast with the established *Z*-selectivity, we herein describe an *E*-selective MBH-type rearrangement by employing a new pair of rearrangement partners consisting of aryl iodanes and α,β-unsaturated oxazolines (Scheme 1C). Henceforth, with these two MBH-type rearrangements in hand, both *E*- and *Z*-α-aryl α,β-unsaturated carbonyl derivatives can now be accessed on demand by switching to a proper rearrangement partners. In this Article, we also describe mechanistic studies towards understanding the intriguing opposite stereoselectivities associated with such two MBH-type rearrangement reactions.

Notably, while our study was underway, Wengryniuk reported an elegant iodine(III)-Claisen rearrangement of β-pyridinium silyl enol ethers that allows for α-arylation of α,β-unsaturated ketones (Scheme 2).[16] Unlike our method, the reagents and substrates of Wengryniuk's protocol were employed in a different order. As a result, the reported reaction is mechanistically different with our protocol. In their reaction, TMSOTf and base were added to enones for forming silyl enol ethers which then undergo a metathesis with aryl iodanes to construct enolate-iodonium rearrangement precursors. However, the generation of such unconventional silyl enol ethers, called β-pyridinium silyl enol ethers, suffers from limited substrate scope[17] that generally restricts the reaction scope to structurally defined cyclic enones.

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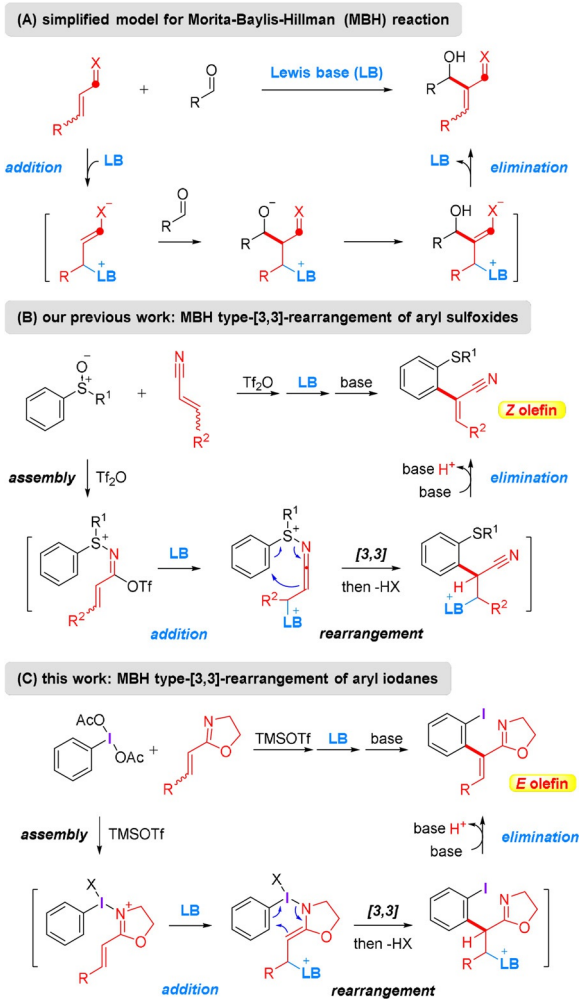
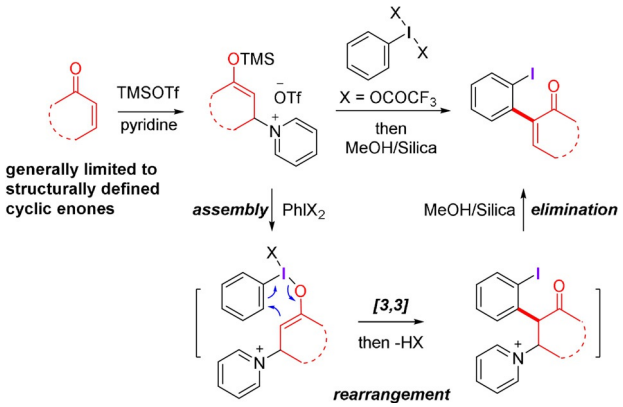


Scheme 1. Background and the Morita–Baylis–Hillman (MBH) type [3,3]-rearrangement of aryl iodanes. Tf_2O = triflic anhydride.



Scheme 2. [3,3]-rearrangement of β-pyridinium silyl enol ethers developed by Wengryniuk (ref. [16]).

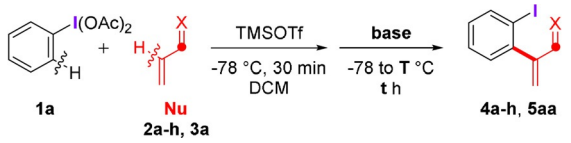
Results and Discussion

With the MBH-type [3,3]-rearrangement hypothesis in mind, we commenced the study by investigating the reaction of $PhI(OAc)_2$ **1a** with α,β-unsaturated carbonyl derivatives including α,β-unsaturated nitrile **2a**, aldehyde **2b**, ketone **2c**, ester **2d**, amide **2e**, imidate **2f**, imine **2g**, oxime **2h** and 2-oxazoline **3a**, as shown by entries 1–9 in Table 1. DABCO, which is often used as Lewis base for the MBH reaction, was employed for our initial exploration. Although no desired products **4a–4h** could be determined from the reactions of **2a–2h**, α,β-unsaturated oxazoline **3a** was found to be promising for the transformation albeit giving desired product **5aa** in low yield (19%) (entry 9). The feasibility of oxazoline **3a** could be attributed to its higher nucleophilicity than other unsaturated carbonyls, which enhanced its interaction with aryl iodanes. Probably, due to the same factor, we could successfully achieve asymmetric rearrangement of aryl iodanes with chiral oxazolines.[13] Further studies revealed that the choice of bases was also critical to the reaction. Pyridine derivatives were more effective than aliphatic tertiary amines (entries 10–13). Further optimization of the reaction temperatures and reaction times identified the best conditions giving **5aa** in 71% yield (entry 16).[18]

With the optimized conditions in hand, we investigated the reaction scope with respect to α,β-unsaturated oxazolines **3** and aryl iodanes (Scheme 3). Impressively, the reaction demonstrated excellent *E*-selectivity when facing with a wide variety of α,β-unsaturated oxazolines **3**. Regardless of the length of the terminal alkyl chains, oxazolines **3b–3d** smoothly afforded **5ab–5ad** in similar yields (69–72%). The method was also applicable to bulky oxazolines **3g–3k** bearing β-cyclopropyl, cyclopentyl, cyclohexyl, cyclohexenyl, and piperidine groups that afforded stereohindered alkenes **5ag–5ak** in synthetically useful yields (47–57%). Remarkably, β,β′-dimethyl substituted oxazoline **3l** could even furnish tetrasubstituted alkene **5al**, albeit in a low yield (25%). In addition to β-alkyl oxazolines, β-aryl oxazoline **3m** and **3n** also proved suitable for the process giving **5am** and **5an** in modest yields. Further studies demonstrated that the reaction possessed excellent functional group (FG) compatibility. An array of FGs including alkene groups (**5aj**, **5ay** and **5aa′**), protected amines (**5ak** and **5ab′**), alkyl/aryl halides (**5ao**, **5au**, **5av** and **5az**), ethers (**5ap–5ar**, **5aw** and **5ax**), esters (**5as–5av** and **5ay–5aa′**), propargyl groups (**5aw**), and nitrile groups (**5ax**) were all well tolerated in the reaction. Notably, alkene, alkynyl and heteroaryl groups that could be readily oxidized by hypervalent iodines were also tolerated here. This unconventional FG compatibility could be attributed to the relatively high affinity of oxazolines with iodine (III) species, which inhibited the undesired oxidation of electron-rich FGs. In addition, the highly electrophilic α,β-unsaturated esters (**5ay** and **5aa′**) that can be challenging substrates for conventional cross-coupling reactions were also compatible with the current reaction conditions. The broad scope of FGs adopted in the reaction provided a versatile platform for further elaboration of the products and demonstrated the practicability of the protocol.

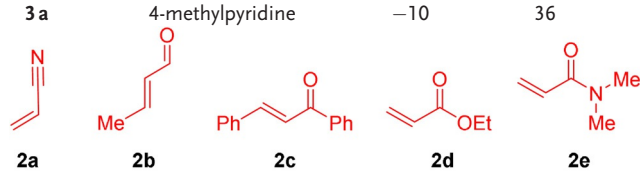
Next, the scope of aryl iodanes **1** was explored under the optimum conditions (Scheme 3). *para*-Alkylated aryl iodanes (**5bb** and **5cb**) were slightly more productive than those bearing *para*-halide substituents (**5db–5gb**). Impressively, aryl iodanes **1** bearing functional groups including alkyl/aryl halides (**5db–5gb**, **5hb**, **5rb** and **5vb**), *N*-protected amines

Table 1: Development of the reaction.

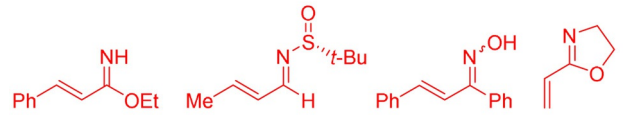


1a **Nu** **2a-h, 3a** **4a-h, 5aa**

Entry[a]	Nu	Base	*T* [°C]	*t* [h]	Yield [%][b]
1	**2a**	DABCO	0	12	**4a**, 0[c]
2	**2b**	DABCO	0	12	**4b**, 0[c]
3	**2c**	DABCO	0	12	**4c**, 0[c]
4	**2d**	DABCO	0	12	**4d**, 0[c]
5	**2e**	DABCO	0	12	**4e**, 0[c]
6	**2f**	DABCO	0	12	**4f**, 0[c]
7	**2g**	DABCO	0	12	**4g**, 0[c]
8	**2h**	DABCO	0	12	**4h**, 0[c]
9	**3a**	DABCO	0	12	**5aa**, 19
10	**3a**	DBU	0	12	**5aa**, 16
11	**3a**	*i*-Pr$_2$EtN	0	12	**5aa**, 32
12	**3a**	pyridine	0	12	**5aa**, 39
13	**3a**	4-methylpyridine	0	12	**5aa**, 42
14	**3a**	4-methylpyridine	−10	12	**5aa**, 58
15	**3a**	4-methylpyridine	−20	12	**5aa**, 53
16	**3a**	4-methylpyridine	−10	24	**5aa**, 71
17	**3a**	4-methylpyridine	−10	36	**5aa**, 69



2a **2b** **2c** **2d** **2e**



2f **2g** **2h** **3a**

[a] Reactions were performed on 0.5 mmol scale; **2a**–**2e** and **3a** (2.0 equiv), TMSOTf (2.0 equiv) and bases (2.0 equiv) were used. [b] Isolated yield. [c] Volatile **2a** (19%), **2b** (55%) and **2d** (85%) were detected by crude ^{1}H NMR spectroscopy whereas **2c** (83%), **2e** (47%), **2f** (63%), **2g** (77%), and **2h** (51%) were recovered after the reaction.

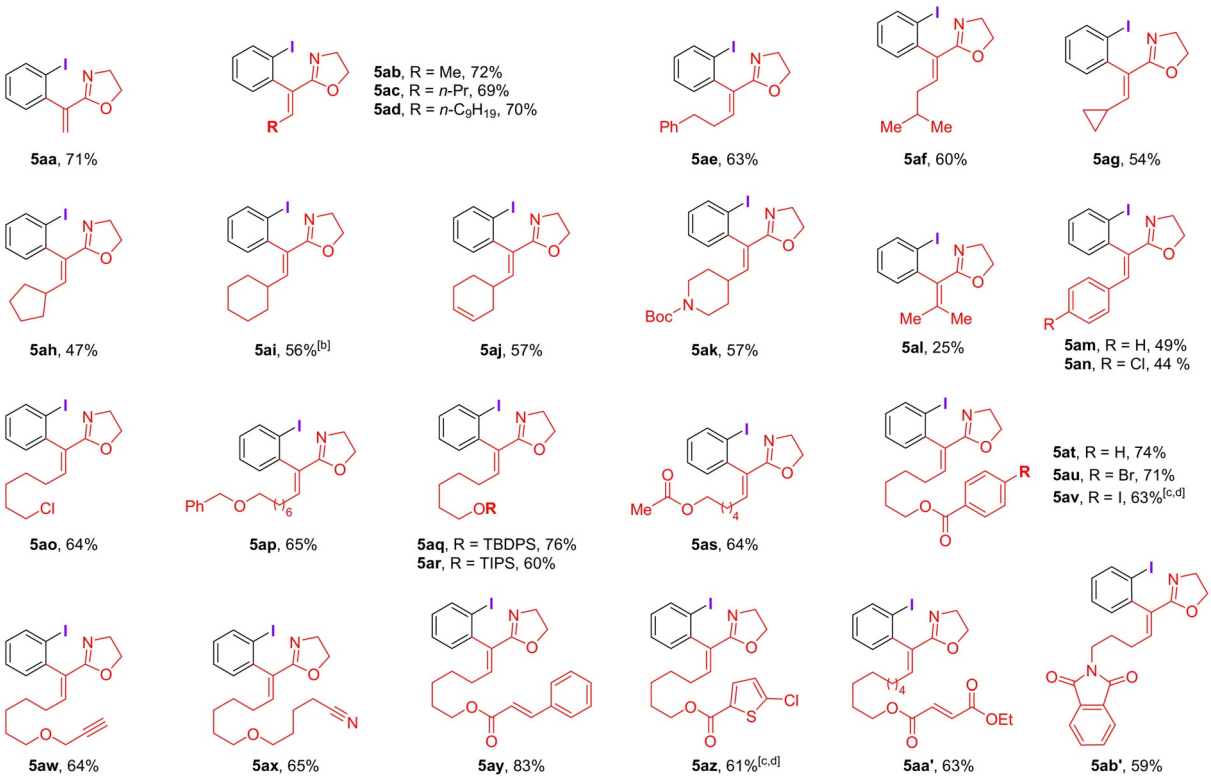
(**5ib** and **5sb**–**5ub**), esters (**5ib** and **5pb**–**5rb**), ethers (**5lb**–**5ob**), and nitriles (**5ob**) were all suitable for the reaction. Even highly reactive benzylic chlorides (**5hb**) and α,β-unsaturated esters (**5qb**) that can be problematic FGs for conventional arylation reactions could be tolerated in the reaction. Aryl iodane **1j** with electron withdrawing groups (benzoyl group) failed to furnish any desired products **5jb** under optimum conditions. This was probably due to the relatively low nucleophilicity of this electron-poor substrate, which made the electrophilic activation of **1j** with TMSOTf more difficult. However, raising the activation temperature from −78 °C to rt, **1j** still afforded **5jb** albeit in a low yield (33%). Remarkably, *meta*-substituted aryl iodanes exclusively produced less hindered products (**5kb**–**5wb**) demonstrating an excellent regioselectivity. It is also impressive that sterically hindered substrates furnished intriguing polysubstituted arenes (**5xb**–**5zb**) without loss of efficiency. In addition to phenyl iodanes, the method could also be applicable to naphthalene and thiophene iodanes (**1a′** and **1b′**) albeit giving relatively low yields (**5a′b** and **5b′b**). It should be noted that in the synthesis of **5a′b**, trace amount of ipso substituted deiodinated coupling product **7** was determined from the reaction. In contrast with reactions of other aryl iodanes wherein *Z*-products could not be obtained, the reaction of thiophene iodane (**1b′**) afforded an *E*/*Z* (96/4) mixture of **5b′b**.

To deeply understand the reaction mechanism and the *E*-selectivity of the reaction, we combined DFT calculations (see SI8 for computational details) and control experiments to study the reactions of **1a** with *E*-**3c** and *Z*-**3c** (Figure 2A).

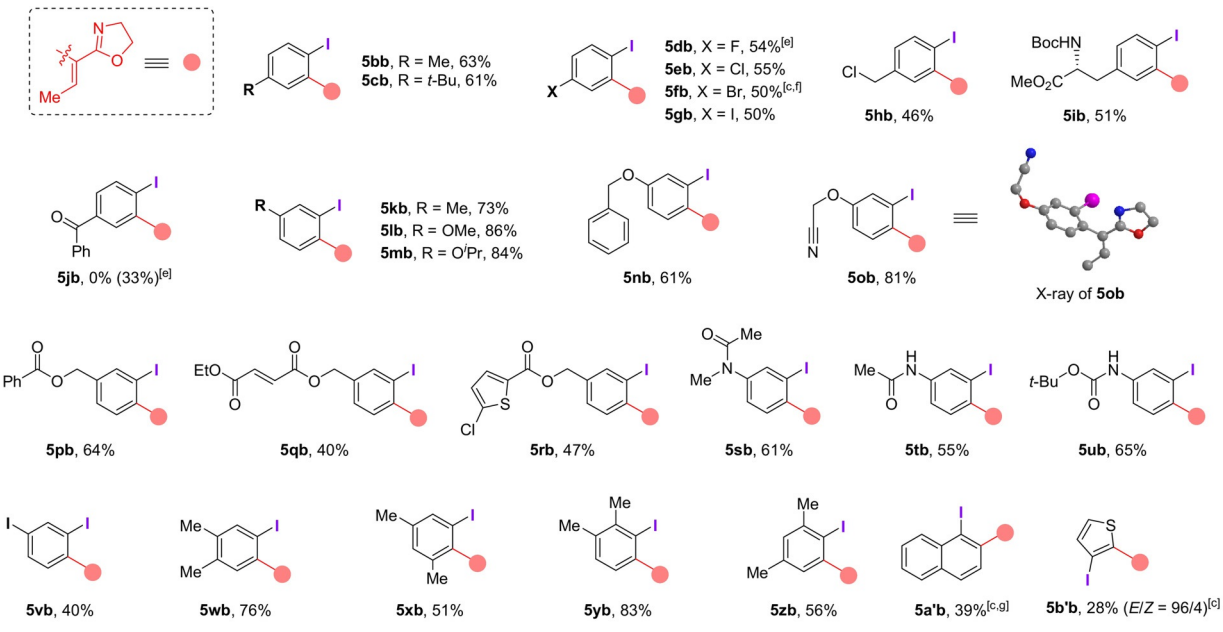
The overall mechanism of the reaction

Figure 1 shows the energy profile for the reaction with *E*-**3c** as a substrate to afford *E*-**5ac**. The reaction proceeds via sequential four stages. Stage I undergoes electrophilic assembly to generate the precursors (**EIM1** and **EIM1′**) for subsequent MBH-like addition. To start stage I, TMSOTf first activates PhI(OAc)$_2$ to give PhI(OTf)OAc[19] via a S_N2 transition state **TS1**. Further activation of PhI(OTf)OAc via **TS2** gives PhI(OTf)$_2$. The activation to give PhI(OTf)OAc is exergonic by 4.3 kcal mol^{-1} and that to give PhI(OTf)$_2$ is endergonic by 2.2 kcal mol^{-1}. The energetic results agree with the observation of PhI(OTf)OAc instead of PhI(OTf)$_2$ reported by Dutton and Shafir and our NMR studies.[19,20] After the activation, *E*-**3c** undergoes substitutions with PhI(OTf)OAc or PhI(OTf)$_2$. Substitution with PhI(OTf)OAc can take place via either **TS3** or **TS4**, leading to **EIM1′** or **EIM1**, respectively and that with PhI(OTf)$_2$ via **TS5**, giving **EIM1**.[21] Because OTf$^-$ is a much greater leaving group than OAc$^-$, **TS4** is much higher than **TS3** and **TS5**. The formation of **EIM1** is kinetically less favorable but thermodynamically more favorable than that of **EIM1′**. Both **EIM1** and **EIM1′** are accessible. We first consider more stable **EIM1** to start stage II. As illustrated by (*R*)**ETS6** or (*S*)**ETS6**, the base 4-methylpyridine (denoted as **Py**) can attack **EIM1** from either side of the alkene plane to undergo MBH-like nucleophilic addition, giving (*R*)**IM2** and (*S*)**IM2**, respectively. Stage III from **IM2** to **IM4** forms a C–C bond via dearomative [3,3]-sigmatropic rearrangement through **TS7**, followed by rearomatization via a negligible barrier (**TS8**, not shown in Figure 1A, see Figure S1). After forming the C–C bond, a stepwise E1cb elimination (stage IV) takes place through deprotonation via **TS9**, followed by **Py** elimination via **TS10**, affording the final product *E*-**5ac**. Compared to

α,β-unsaturated oxazolines



aryl iodanes



Scheme 3. Reaction scope. [a] Reactions were performed with **1** (0.5 mmol), (*E*)-α,β-unsaturated oxazolines **3** (2.0 equiv), TMSOTf (2.0 equiv) and 4-methylpyridine (2.0 equiv). For all cases except **5b'b**, *Z*-isomeric products were not observed. [b] 4-Methylpyridine (2.5 equiv), −78 to 10 °C, 36 h. [c] 1.0 mmol scale reaction. [d] Products (**5av** and **5az**) were contaminated by trace amount of inseparable unknown compounds. [e] TMSOTf was added at 0 °C (**5db**) or rt (**5jb**). [f] α-OTf-substituted α,β-unsaturated oxazoline **6** was obtained in 3% yield. [g] Inseparable *ipso*-coupling product **7** was obtained in 3% NMR yield as a mixture with **5a'b**.

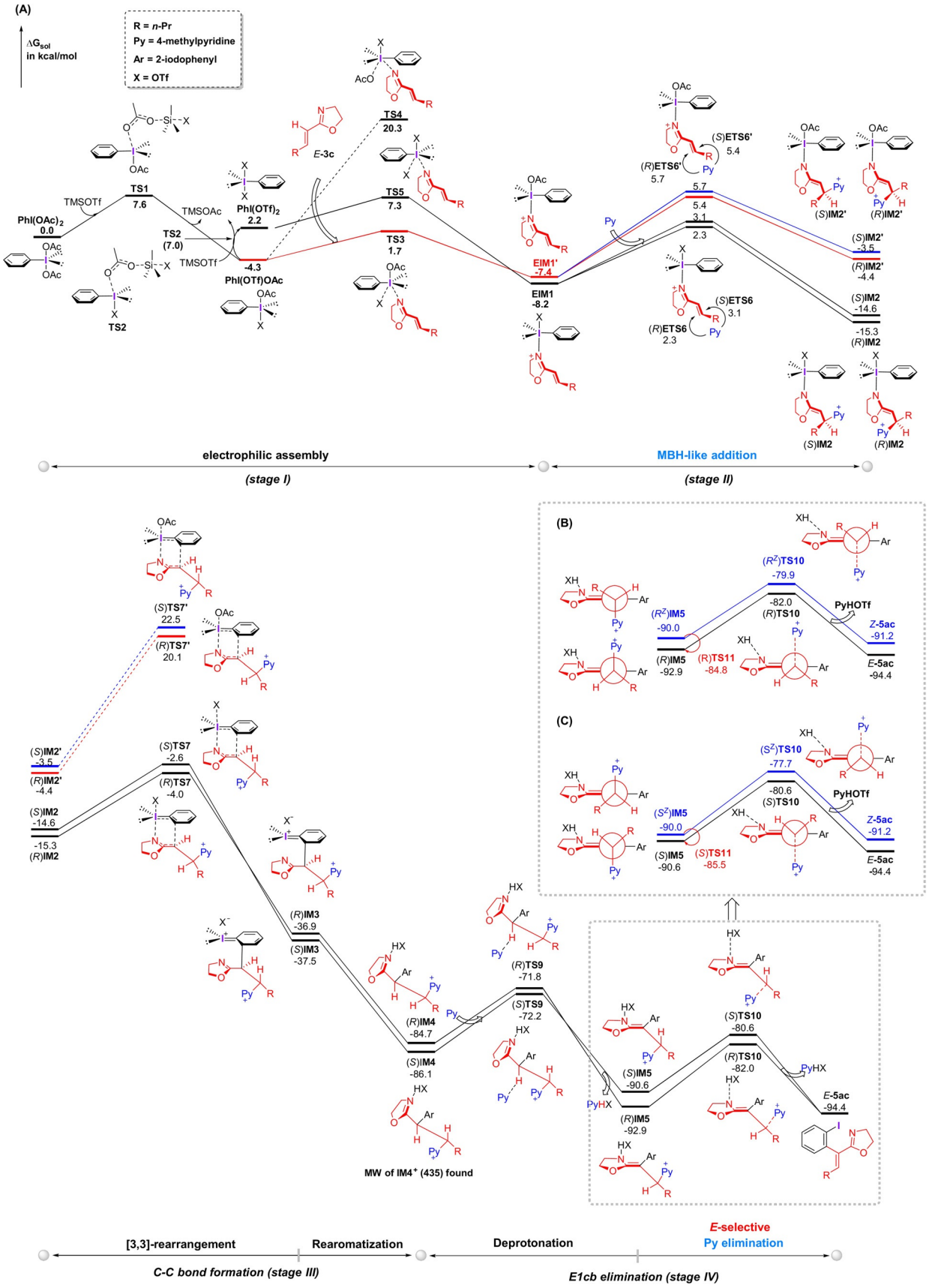


Figure 1. (A) Free energy profile of the reaction with *E*-**3c** as a substrate. B) (*R*)-Pathway to form *E*-**5ac**. C) (*S*)-Pathway to form *E*-**5ac**.

EIM1, **EIM1′** is less favorable to undergo MBH-like addition. Furthermore, the addition products (*R*)/(*S*)**IM2′** cannot undergo rearrangements because of the much higher barriers than those of **IM2**. Thus, the kinetically accessible **EIM1′** would convert back to **EIM1** for rearrangement. The much higher **TS7′** than **TS7** can be attributed to the poorer leaving group OAc^- than OTf^-, because the rearrangement forms a formal I^+=C double bond, which dissociates the axial OTf^-/OAc^- group, as shown by the I···C and O···I distances (see Figure S2).

Examining the energy profile, as the reaction proceeds, the system becomes more and more stable with an overall exergonicity of 94.4 kcal mol^{-1}. The rate determining step lies at the deprotonation of **IM4**, with a barrier of 12.9 and 13.9 kcal mol^{-1} for (*R*)- and (*S*)-pathway, respectively. The favorable energetics rationalizes why the reaction could proceed smoothly, thus corroborating our strategy using MBH-like addition to generate a reactive rearrangement precursor (i.e. **IM2**). Supporting the mechanism, we were able to observe the cationic **IM4** (435) by mass spectrometry. Unfortunately, we were not able to further confirm **IM4** with NMR spectrum even after great efforts.[22]

It should be noted that we used OTf group throughout the calculations of the free energy profile. However, it is possible that **EIM1** and **IM2** first substitute the axial OTf group with **3c** or **Py** and the resultant intermediates then undergo MBH-like additions or [3,3]-rearrangements. Using **EIM1** as an example, we considered the possibility. As detailed in Figure S1E in the supporting information (S54), it was found that the substitutions are kinetically accessible, but the resultant intermediates are less favourable to undergo MBH-like addition than **EIM1**. On the other hand, no matter whether these substitutions take place or not, stage III can only give **IM4** which we observed. As such, the *E*-selectivity of the reaction, which is determined by stage IV, would not change.

Understanding the E*-selectivity of the reaction*

After grasping the reaction mechanism, we further understand the *E*-selectivity of the reaction. Along the (*R*)-pathway, all structures from (*R*)**IM2** to (*R*)**IM5** were optimized with the conformations in which *n*-Pr and oxazoline groups are in *trans* arrangement, thus giving *E*-**5ac**. To gain insight to the *E*-selectivity, we further considered the *cis*-isomer of *trans*-(*R*)**IM5**. As illustrated in Figure 1B, the *cis* conformation (i.e. (R^Z)**IM5**) of **IM5** can lead to *Z*-**5ac** by crossing (R^Z)**TS10**. However, because (*R*)**IM5** and (R^Z)**IM5** can convert each other easily with a barrier (*R*)**TS11** lower than (*R*)**TS10**, *E*-**5ac** is lower than *Z*-**5ac**, and the barrier for the reverse conversion of *Z*-**5ac** to (R^Z)**IM5**) is not high (11.3 kcal mol^{-1}), the formation of *E*-**5ac** is preferred in terms of both kinetics and thermodynamics, explaining the *E*-selectivity of the reaction. Due to the conformation convergence of **IM5** to (*R*)**IM5**, the conformations of the intermediates and transition states from **IM2** to **IM4** cannot affect the *E*-selectivity of the reaction, although they may have multiple conformations, respectively. Similar discussion can be applied to the (*S*)-pathway (see Figure 1C), which shows that *E*-**5ac** is a preferred product.

Understanding the reaction of Z-3c

Figure 2B considers the stage II of the reaction with *Z*-**3c** as a substrate. Because the MBH-like addition of **Py** converts the sp^2 hybridized carbon to the sp^3 hybridized carbon, the stage II of *Z*-**3c** merges to that of *E*-**3c** at (*R*)**IM2** and (*S*)**IM2**, respectively. Therefore, the configuration of **3c** cannot affect the selectivity of the reaction. Indeed, under the standard experimental conditions, no matter which configuration **3c** adopts, the reactions afforded *E*-**5ac** with comparable yields [see Eq. (1) and Eq. (2) in Figure 2A]. Taking the results of both *E*-**3c** and *Z*-**3c** together, the reaction prefers *E*-product (*E*-**5ac**).

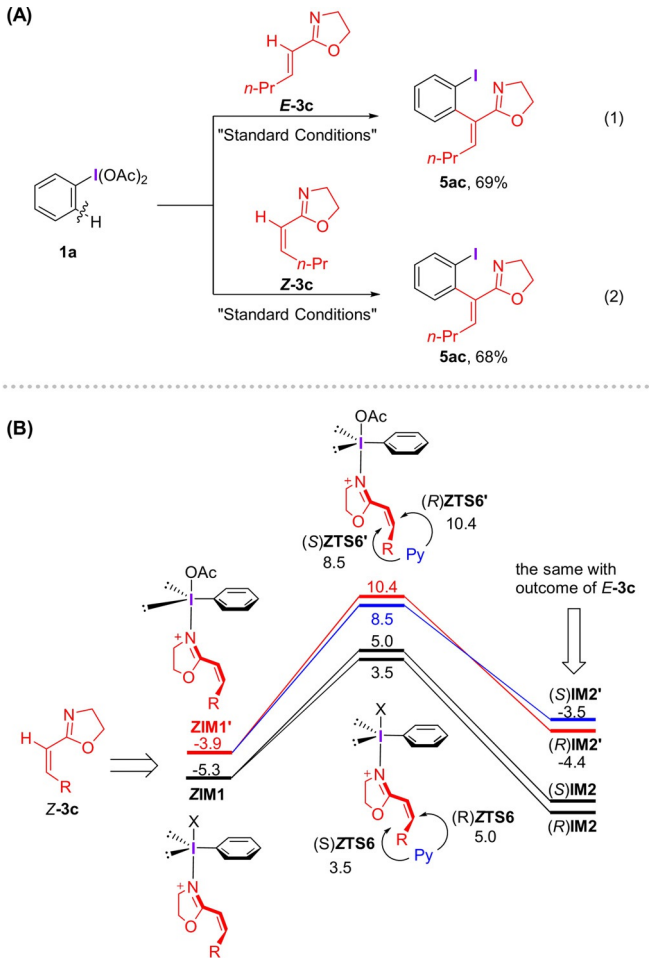


Figure 2. A) Control experiments and B) profile for stage II of *Z*-**3c**.

Comparison of the Z*-selective sulfonium and* E*-selective iodonium MBH-type [3,3]-rearrangements*

Intriguingly, as the present reaction of aryl iodanes prefers *E*-product, the reaction of aryl sulfoxide (Scheme 1B) favours the *Z*-product. Comparing the two reactions (Figure 3), they

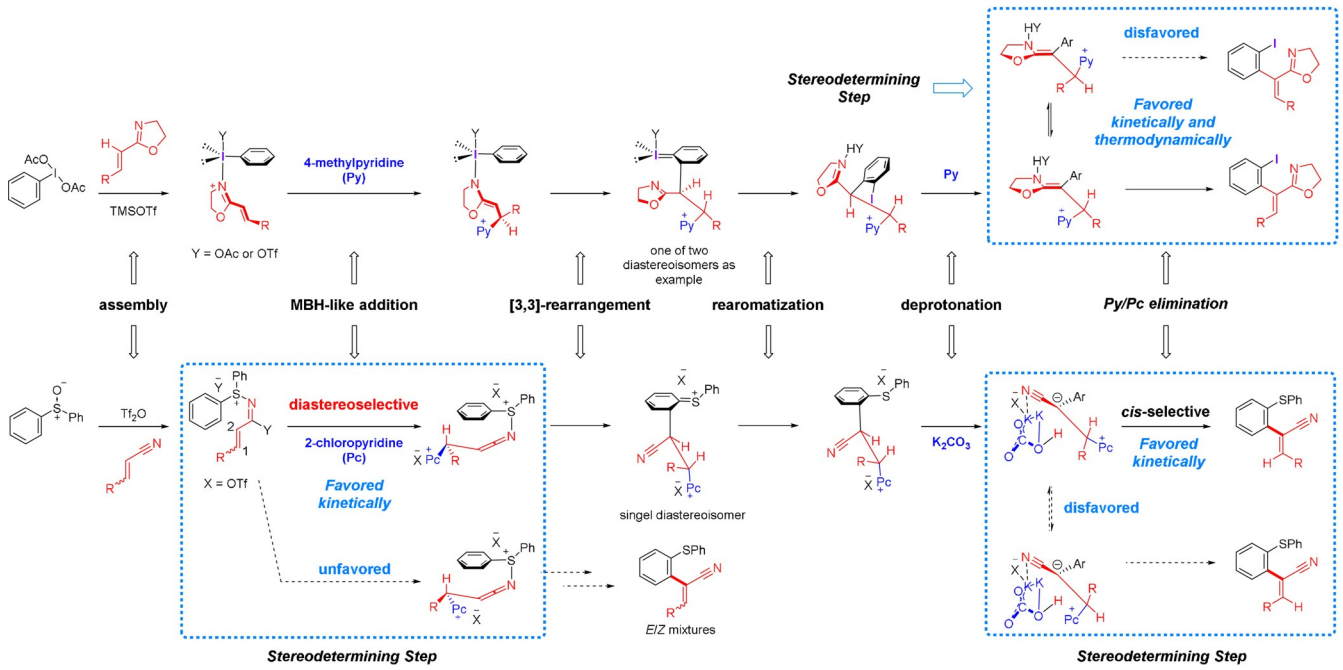


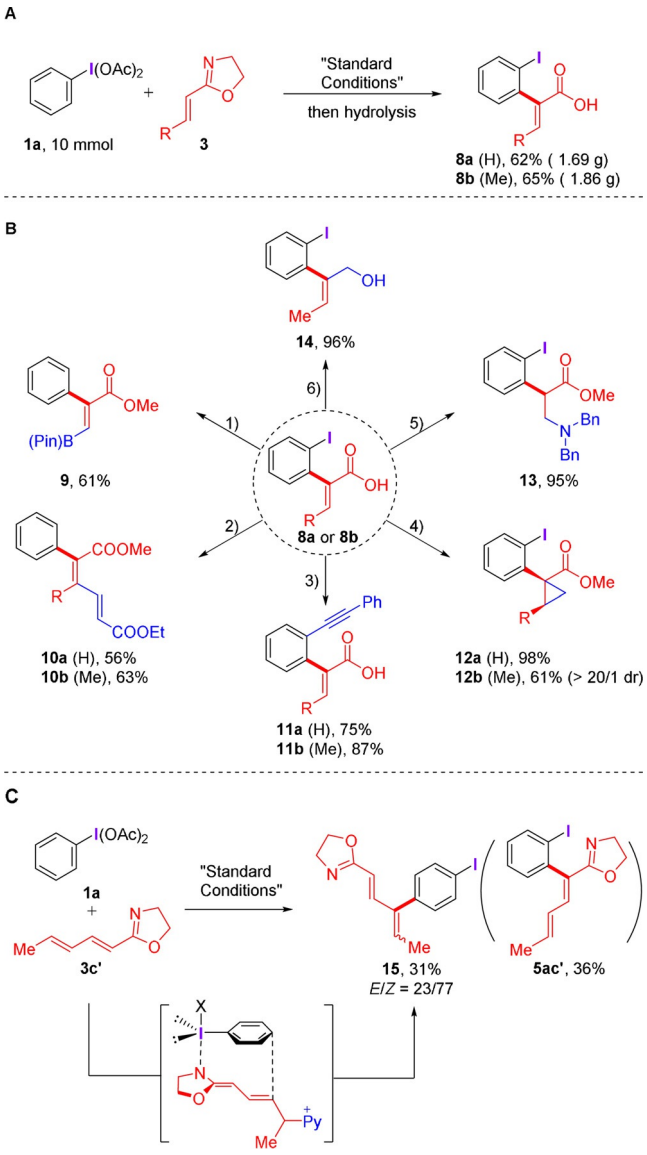
Figure 3. A comparison between *Z*-selective sulfonium and *E*-selective iodonium MBH-type [3,3]-rearrangement reactions.

proceed similarly, but their E1cb-elimination stages differ significantly; the reaction of aryl sulfoxide requires an external (i.e. K_2CO_3) to enable the E1cb elimination, while the present reaction can take place without an external base. The external base-free E1cb elimination can be attributed to the N-protonation of **IM4** with HOTf at oxazoline moiety. Supportively, in the absence of the N-protonation, the deprotonation of (*S*)**IM4** has a barrier of 27.0 kcal mol^{-1}, which is much higher than the 13.9 kcal mol^{-1} from (*S*)**IM4** to (*S*)**TS9**. The significantly decreased deprotonation barrier is due to the electron-buffering effect of the N-protonated oxazoline. The effect enables the formation of the (oxazoline)C=C$^{\alpha}$ double bond to stabilize the electrons resulted from the deprotonation, as indicated by the shortened (oxazoline)C-C$^{\alpha}$ bond length from 1.50 to 1.43 to 1.36 Å in (*S*)**IM4**, (*S*)**TS9**, and (*S*)**IM5**, respectively (for more detailed structural evolutions see Figure S3). More importantly, the electron-buffering effect through deprotonation/protonation of oxazoline also makes Py-elimination reversible. As such, the *E*-selectivity of the reaction is controlled kinetically and thermodynamically at the Py-elimination and the kinetics (selectivity) of other processes does not affect the *E*-selectivity of the reaction. In contrast, the E1cb-elimination in the reaction of aryl sulfoxides is prompted by K_2CO_3 and is irreversible. The *Z*-selectivity of the reaction is jointly controlled by the kinetics of the diastereoselective MBH addition and cis-selective Pc-elimination elimination.[15]

To our delight, the method followed by hydrolysis of oxazolines could be used for gram-scale synthesis of α-aryl α,β-unsaturated carboxylic acids **8a** and **8b** with synthetically useful yields (Scheme 4A). The remaining iodide atom allowed for elaborating alkenes with a boryl group (**9**) or vinyl ester moieties (**10a** and **10b**), and incorporating an alkynyl group into phenyl ring (**11a** and **11b**) (Scheme 4B). The product **8** could also be readily converted to intriguing arylcyclopropanes (**12a** and **12b**) and α-aryl-β-amine ester (**13**) via conventional cyclopropanation and Michael addition, respectively. In addition, the reduction of **8b** afforded valuable 2-aryl allylic alcohol **14**. Encouraged by the success of the MBH-type [3,3]-rearrangement, we attempted to examine the possibility of corresponding [5,5]-rearrangement by employing 1,3-diene-1-oxazoline **3c′** (Scheme 4C). Excitingly, the reaction indeed afforded *para*-C–H functionalized product **15** (31% yield) with *ortho*-functionalized product **5ac′** (36% yield).[23] Although suffering from a poor selectivity, this preliminary result demonstrated the feasibility of applying the current protocol for developing MBH-type [5,5]-rearrangement reactions.

Conclusion

In summary, the incorporation of MBH reaction into the rearrangement process forged [3,3]-rearrangement of aryl iodanes with α,β-unsaturated oxazolines. Experimental and computational mechanistic studies revealed that the transformation involves the assembly of both coupling partners, MBH-like addition triggered [3,3]-rearrangement, and E1cb elimination to give the final products. The reaction allows for the mild synthesis of a wide variety of valuable α-aryl α,β-unsaturated oxazolines in a redox-neutral manner. In addition to the excellent chemo- and regioselectivity, the reaction showed a remarkable *E*-selectivity. The formation of *E*-product is both kinetically and thermodynamically favoured and is probably due to the final *trans*-β-H-elimination. The stereocontrol of the reaction is different with MBH-type sulfur(IV)-rearrangement, previously developed in our laboratory, wherein the diastereoselective MBH-like addition and



Scheme 4. A) Gram-scale reactions. B) Synthetic utility. (1) K_2CO_3, MeI, DMF; then $Pd(OAc)_2$ (5 mol%)/ligand (7.5 mol%), $B_2(Pin)_2$, CsOAc, THF. (2) K_2CO_3, MeI, DMF; then $Pd(OAc)_2$ (5 mol%)/ligand (10 mol%), ethyl acrylate, CsOAc, THF. (3) $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%), phenylacetylene, toluene/Et_3N. (4) $(CH_3)_3SOI$, NaH, DMSO. (5) N,N-dibenzylamine, DBU, THF. (6) K_2CO_3, MeI, DMF; then DIBAL-H, THF. C) Attempts of MBH-type [5,5]-rearrangement.

final cis-selective elimination determines the Z-selectivity of the reaction. As a result, these two MBH type rearrangement reactions complement each other allowing for the synthesis of *Z*- or *E*-α-aryl α,β-unsaturated carbonyls on demand. Further exploration of MBH-type rearrangement reactions is currently under way in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

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