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ROYAL SOCIETY OF CHEMISTRY

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DOI: 10.1039/C9CC01995B

Journal Name

COMMUNICATION

Iron-catalyzed oxidative C–C(vinyl) σ-bond cleavage of allylarenes to aryl aldehydes at room temperature with ambient air

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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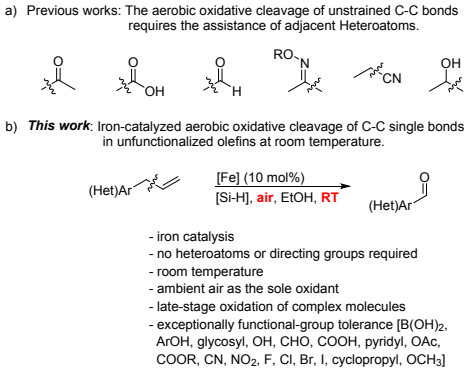
A general and selective iron-catalyzed allylic C–C(vinyl) σ-bond cleavage of allylarenes without the assistance of heteroatoms to give aryl aldehydes is reported. The unstrained carbon–carbon single bond cleavage reaction uses ambient air as the sole oxidant, proceeds efficiently at room temperature, and allows for exceptional functional-group tolerance, which addresses the long-standing challenges of current C–C bond cleavage/functionalization. Notably, the method enables rapid late-stage oxidation of complex bioactive molecules, and can be used to expedite syntheses of natural products (Vanillin and Glucovanillin) from readily available chemical feedstocks.

Catalytic unstrained carbon–carbon bond cleavage/functionalization in the absence of directing groups is highly desirable, but remains challenging.[1] The level difficulty of this transformation increases drastically when regio- and chemoselectivity issues are present. In addition, as a result of the high dissociation energies of the breaking unstrained C–C bonds, the current means to cleave such thermodynamically stable bonds suffer from the need for drastic conditions and elevated temperatures (often above 100°C) which limit their scope and functional-group compatibility.[1] Allylarene motif is extensively present in biologically active compounds[2] and the corresponding allylic C–C bond cleavage/functionalization has attracted increased interest. However, this transformation suffers from at least two big challenges: The HOMO/LUMO orbitals of the nonpolar allylic C–C σ-bonds mismatch with the frontier orbitals of catalysts, leading to an increased difficulty of allylic C–C bond activation[3]; regio- and chemoselectivity issues originates from the presence of more reactive allylic C–H bonds and a π-bond.[4] Consequently, catalytic activation of allylic C–C single bonds in unfunctionalized olefins remains unexplored to date, with the exception of specific substrates bearing strained rings,[5] chelation-assisted groups,[6] or electron-withdraw groups to polarize the allylic C–C bonds.[7]

Aryl aldehydes are versatile building blocks in organic synthesis for natural products, pharmaceuticals, pesticides, and dyes.[8] Although aerobic oxidative C–C single bond cleavage has been employed for the synthesis of acids,[9] esters,[10] amides,[11] nitriles,[12] and ketones,[13] it remains a challenging task to use this strategy for the synthesis of aldehydes, probably due to their easy overoxidation to the carboxylic acids.[14] Recently, Bi[15] and Li[16] reported two elegant examples of aerobic oxidative C(CO)–C(α) bond cleavage of ketones to aldehydes at 110-120°C. Despite the major advances achieved in aerobic oxidative C–C bond cleavage, the cleavable bonds are required to be adjacent to ketones,[9a-d,10a-d,11a-c,12a,13a] carboxylic acids,[11d-e] aldehydes,[11f,13b] oximes,[9e,12b] cyanides,[10e,11g] and alcohols[9f-g] (Scheme 1, a). A groundbreaking method reported by Jiao and co-workers used an alkyl azide reagent as the promoter to achieve allylic C–C cleavage of simple olefins to give cinnamyl aldehydes with DDQ as the oxidant.[3] While powerful, this non-catalytic metho d used a hazardous alkyl azide reagent and 10 equiv of trifluoroacetic acid, thus limiting its scope and functional group



Scheme 1. Transition metal-catalyzed aerobic oxidative cleavage of unstrained C–C single bonds.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

tolerance. Compared with allylic C–C σ-bond, allylic C–C(vinyl) is more thermodynamically stable,[4] thus leading to direct cleavage and functionalization of this σ-bond being unexplored.[3]

Here, we report a novel iron-catalyzed aerobic oxidative allylic C–C(vinyl) σ-bond cleavage of allylbenzenes without the assistance of heteroatms or directing groups to produce aryl aldehydes in high yields and selectivities (Scheme 1, b).[17] This catalytic method features exceptional functional-group tolerance and the late-stage oxidation of structurally complex molecules, which are unprecedented by other C–C bond functionalizations to date. Notably, this transformation is accomplished with ambient air as the sole oxidant at room temperature.

Olefin by an *in situ*-formed Fe hydride can be converted to alkyl radical species[18] that can be intercepted by O_2 to give the alkyl peroxide radical.[19] It is well known that alkyl peroxide radicals undergoing O–O bonds homolysis can give carbonyl compounds and/or alcohols.[19] We questioned whether the alkyl peroxide radical could form the dioxetane intermediate which readily undergoes C–C bond cleavage to provide the carbonyl product[20] when an adjacent C–H bond is prone to deprotonation. In this context, allylarenes would be ideal candidates for use as substrates because they not only possess reactive benzylic C–H bonds, but also are bench-stable, readily accessible, and widely prevalent in bioactive compounds.[2]

Details of our design principle are depicted in Figure 1. Initially, allylbenzene would abstract a hydrogen radical from Fe hydride, *in situ* generated from Fe(III) species and hydrosilane, to give reduced Fe(II) species **II** and alkyl radical **III**.[19] Deuterium labelling and radical-trapping experiments (with galvinoxyl) support the origin of the hydrogen and the presence of **III**, respectively (for details, see the ESI). Recently, Baran group reported that olefin could abstract a hydrogen radical from iron(III) hydride *in situ* generated from Fe(III) species and $PhSiH_3$, to give alkyl radical.[18] Submission of 4-allylanisole (**1a**) to the Baran's reaction conditions[18c] resulted in 85% yield of 4-methoxybenzaldehyde (**2a**), further supporting the hydrogen radical transfer process involved in our transformation. Subsequently, **II** and **III** would be trapped by O_2 to provide the Fe(III)-superoxo **IV**[21] and the alkyl peroxi ed radical **V** intermediates, respectively. At this point, **IV**-assisted **V** deprotonation would form the dioxetane **VI** which decompose readily to afford the aryl aldehyde product along with acetaldehyde,[20] and the Fe(III)-hydroperoxide **VII** which would then undergo reduction by hydrosilane to close cycle. A

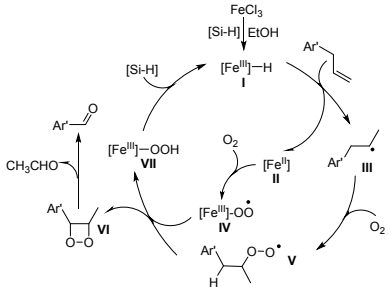
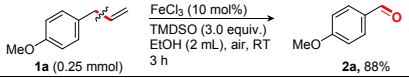


Figure 1 Mechanistic rationale for the iron-catalyzed aerobic oxidative cleavage of C–C single bonds in allylbenzenes.

primary intramolecular isotope effect (k_H/k_D =3.5) was observed, indicating that deprotonation is the overall turnover-limiting step (for details, see the ESI). Acetaldehyde was also detected by GC analysis of a reaction mixture (for details, see the ESI). Additionally, no product was formed when the reaction of **1a** was performed under nitrogen atmosphere, confirming that the incorporated oxygen atom originates from the oxygen atmosphere. It is well-known that aryl aldehydes can be obtained via tandem allylbenzenes isomerization-oxidation cleavage.[22] However, subjecting *trans*-anethole (**1a'**) to our reaction conditions failed to give the aldehyde product, excluding the possibility of tandem allylbenzene isomerization-oxidation.

Guided by the theory mentioned above, a more systematic evaluation of various parameters with exposure of **1a** to an iron species and a hydrosilane under ambient air and room temperature was carried out (Figure 2). We were pleased to find that the aerobic oxidative allylic C–C(vinyl) σ-bond cleavage of **1a** proceeded smoothly to afford aldehyde **2a** exclusively in 88% yield under ambient air and 25 °C in the presence of 10 mol % $FeCl_3$ and 3 equiv TMDSO (Tetramethyldisiloxane) in EtOH without adding additional ligands. No desired product but untouched starting material **1a** was observed when the reaction was performed in the absence of the iron catalyst or hydrosilane (Entries 1 and 2), verifying the essential nature of these components in the catalytic process. Replacing $FeCl_3$ with $FeCl_2$, $Fe(NO_3)_3{\cdot}9H_2O$, or $Fe(acac)_3$ as the catalyst gave **2a** in lower yields, respectively (Entries 3–5). TMDSO appeared to be the choice of hydrosilane after the common hydrosilanes had been tested, e.g., $(EtO)_3SiH$ (70%), $(EtO)_2MeSiH$ (58%), and $PhSiH_3$ (81%) (Entries 6–8). We have also tested the effects of other solvents on the reaction efficiency. The use of *i*PrOH as the solvent led to a moderate yield of **2a**, while DMF or DMSO resulted in poor results (Entries 9-10).

With the optimized iron-catalyzed aerobic oxidative C–C bond cleavage reaction in hand, we examined the substrate scope of allylarenes. A variety of allylarenes with different electronic properties and substitution patterns provided the corresponding oxidative C–C bond cleavage products **2** with excellent reactivity (Figure 3). For instance, *ortho*-, *meta*-, *para*-methoxyl- substituted, as well as sterically hindered allylarenes proceed successfully (**2a**-**2d**). Notably, in the case of **2c**, the highly strained cyclopropyl moiety, which generally undergoes smooth ring opening with transition-metal catalysis, remained intact in this new reaction. Additionally, aryl fluorides (**2e** and **2m**), aryl iodide (**2e**), aryl nitrile (**2f**), nitroarene (**2g**), aryl chloride (**2n**), aryl bromides (**2o-2q** and **2w**-**2x**), esters (**2s**-**2t**), and even aryl carboxylic acid (**2r**) are also compatible. Particularly noteworthy is the tolerance of oxidation-



1a (0.25 mmol) **2a**, 88%

Entry	Deviation from standard conditions	Yield (%)
1	no [Fe]	0
2	no [Si-H]	0
3	$FeCl_2$ instead of $FeCl_3$	55
4	$Fe(NO_3)_3{\cdot}9H_2O$ instead of $FeCl_3$	8
5	$Fe(acac)_3$ instead of $FeCl_3$	54
6	$(EtO)_3SiH$ instead of TMDSO	70
7	$(EtO)_2MeSiH$ instead of TMDSO	58
8	$PhSiH_3$ instead of TMDSO	81
9	*i*PrOH instead of EtOH	64
10	DMF or DMSO instead of EtOH	10-15

Yields of the isolated products are given; TMDSO: 1,1,3,3-Tetramethyldisiloxane.

Figure 2 Conditional optimization.

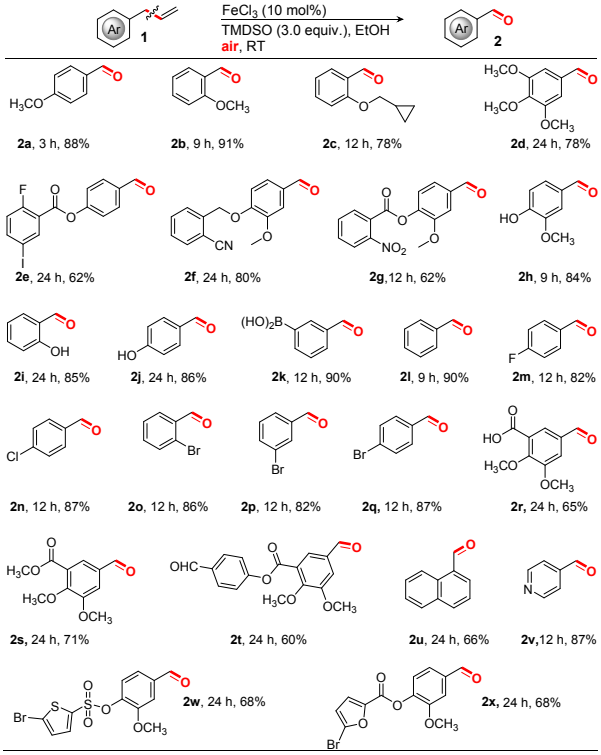


Figure 3 Substrate scope**.** Reported yields are for the isolated products.

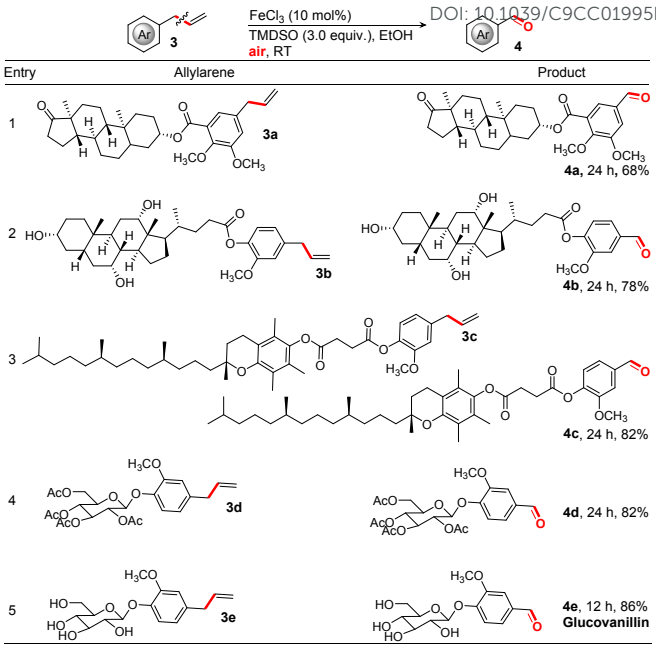
labile phenols (**2h**-**2j**), aryl boronic acid (**2k**) and aryl aldehyde (**2t**), and strong coordinating pyridyl group (**2v**), which is a formidable challenge in C–H/C–C bond functionalization and highlights again the excellent chemoselectivity of this method. Furthermore, the reaction can move beyond the simple aryl group. For example, allyl-substituted naphthalene, pyridine, thiophene, and furan are competent substrates (**2u**-**2x**).

Apart from allylbenzenes, homoallylbenzene (**1y)** is also amenable to the iron-catalyzed oxidative C–C bond cleavage by increasing the reaction temperature to 80 °C and using CH_3CN as solvent [eqn (S2) in the ESI]. To our delight, unactivated internal olefin **1z** can be conveniently converted into the aldehyde **2l** under ambient reaction conditions [eqn (S3) in the ESI]. Although 1,2-diarylethene **1aa** doesn't belong to the allylbenzene class, it is also suitable for the reaction, still consistent with our design principle [eqn (S4) in the ESI].

Vanillin is a natural product, which can be isolated from vanilla beans and pods, pine woods, and roasted coffee,[23] and a popular flavoring material widely employed in foods, beverages, and pharmaceuticals.[24] Its manufacturing from eugenol (**1h**) requires two steps (isomerization and oxidation) (Scheme S2 in the ESI) and suffers from efficiency and selectivity issues.[22] In our case, vanillin (**2h**) was synthesized in 84% isolated yield with high selectivity in one step under environmentally benign conditions (Figure 3, **2h**). Moreover, the reaction could be performed on a larger scale (5 mmol) without substantial erosion of the yield under 1 atm of O_2 (Scheme S2 in the ESI).

To further demonstrate the practicality of the process, more structurally intricate contexts were tested under the standard reaction conditions (Table 1). For instance, **3a** derived from epiandrosterone, was readily oxidized to provide the desired aldehyde **4a** in 68% yield. Notably, a cholic acid derivative **3b** bear-

Table 1 Late-stage oxidation of complex small molecules[a]



[a] Yields of the isolated products are given.

ing three oxidation-labile hydroxy groups, was proceeded well with high selectivity. A Vitamin E succinate derivative **3c** also afforded the product **4c** in 82% yield. Furthermore, biologically relevant molecules **3d**-**3e** having glycoside moieties were identified as viable substrates. Remarkably, an unprotected carbohydrate fragment in **3e** was compatible with the oxidative C–C bond cleavage reaction and gave Glucovanillin (**4e**, 86% yield) that is present in the green seed pods of Vanilla planifolia and is used extensively in pharmaceutic aid.[25] Generally, the late-stage functionalization of medicinally relevant compounds with high chemoselectivity of the iron-catalyzed oxidation is an unique advantage over the known oxidative C–C bond cleavage reactions.

In summary, we have developed a general and selective iron-catalyzed allylic C–C(vinyl) single bond cleavage of allylarenes without the assistance of heteroatoms to give aryl aldehydes by using 1 atm of air as the sole oxidant. High yield and selectivity are achieved even at room temperature. The extremely mild conditions enable exceptional functional-group tolerance, which is inaccessible using current C–C bond-cleavage reactions. Notably, the unstrained carbon–carbon cleavage/oxidation is particularly useful for late-stage oxidation of structurally complex molecules, and allows unprotected synthesis of Vanillin and Glucovanillin from readily available chemical feedstocks. Considering the wide utility of aryl aldehydes, these results will certainly pave the way for important applications in both the academic and industrial fields through the cost efficiency and shortening of synthetic sequences.

The work was sponsored by the Natural Science Foundation of China (21776139, 21302099), the Natural Science Foundation of Jiangsu Province (BK20161553), the Natural Science Foundation of Jiangsu Provincial Colleges and Universities (16KJB150019), and the Qing Lan project.

Conflicts of interest

There are no conflicts to declare.

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DOI: 10.1039/C9CC01995B

Iron-catalyzed oxidative C–C(vinyl) σ-bond cleavage of allylarenes to aryl aldehydes at room temperature with ambient air

Binbin Liu, Lu Cheng, Penghui Hu, Fangning Xu, Dan Li, Wei-Jin Gu and Wei Han*

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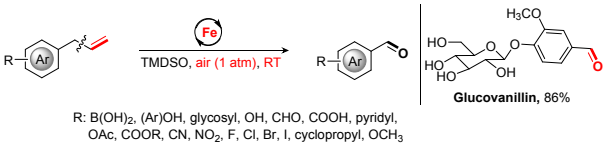

R: $B(OH)_2$, (Ar)OH, glycosyl, OH, CHO, COOH, pyridyl, OAc, COOR, CN, NO_2, F, Cl, Br, I, cyclopropyl, OCH_3

The iron-catalyzed C−C single bond cleavage and oxidation of allylarenes without the assistance of heteroatoms/directing groups to produce aryl aldehydes is disclosed.