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Iron(III)-Catalyzed Domino Claisen Rearrangement/Regio- and Chemoselective Aerobic Dehydrogenative Cyclization of β -Naphthyl-Substituted-Allenylmethyl Ether

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Supporting Information

ABSTRACT: An FeCl₃-catalyzed allenic Claisen rearrangement/regio- and chemoselective aerobic dehydrogenative cyclization domino reaction is developed, providing a wide range of 2-aryl/alkyl, 3-(substituted-vinyl)naphtho[2,1-b]furans in high yields at 95-130 °C in an atom- and stepeconomic fashion. Mechanistic studies suggest that the FeCl₃



catalyst is responsible for the high regio- and chemoselectivity in reaction. A blue-emitting product shows quantum yield of 0.95. The reaction proceeds readily on the gram scale, and synthetic applications of the products are also demonstrated.

 \mathbf{T} he development of novel domino, tandem, or cascade¹ processes catalyzed by cheap and abundant first-row transition metals, especially involving unstable intermediates, has the potential to provide practical, atom- and step-economic access to complex structures. In sharp contrast to large amounts of reports on the Claisen rearrangements of noncumulated double bonds,² examples of Claisen rearrangements of allenes are very limited and underdeveloped.³ Hightemperature thermal Claisen rearrangements of aryl unsubstituted-allenylmethyl ethers followed by intramolecular oxocyclization have been shown to provide 4-methyl-2H-1benzo(naphtho)pyrans (Scheme 1, previous work).^{3a,c} The mechanism of this reaction involves formation of a 2-(ohydroxyaryl)buta-1,3-diene intermediate (I) via allenic Claisen rearrangement. Aryl substituted-allenylmethyl ethers have never been reported in Claisen rearrangement. The reason might be the lack of stability of their Claisen rearrangement products and their in situ rapid and efficient transformation to stable products might develop a new avenue for unprecedented complex structures.

We questioned whether the use of a β -naphthyl substitutedallenylmethyl ether 1⁴ under suitable reaction conditions could reverse the regioselectivity of intramolecular addition of naphthol to the diene in the intermediate I, leading to the 5membered naphthofuran rather than the 6-membered naphthopyran (Scheme 1, this work). The naphthofuran⁵ skeleton was found in natural products and biological active compounds⁶ which show a wide range of biological activity.⁷ Atom- and step-economic methods for functionalized novel naphthofuran derivatives are still highly demanded. Intramolecular oxidative coupling of 2-vinylphenols is a straightforward way to build benzo(naphtho)furans.⁸ However, this approach to benzofurans often requires nonideal reaction conditions, including superstoichiometric amounts of $I_{2\nu}^{8a}$ or stoichiometric $PhI(OAc)_2^{8b}$ or $Ag_2O.^{8c}$ Other approaches include the use of noble metal catalysts^{8d} or expensive

Scheme 1. Regio- and Chemoselective Allenic Claisen Rearrangement/Cyclization for Naphthopyran Derivatives or Naphthofuran Derivatives



specialized first-row catalysts $(Cp*CoI_2(CO))^{8e}$ as well as $Cu(OAc)_2/1,10$ -phenanthroline requiring 10 equiv of NaOH.^{8f} In this report, we demonstrate that the first use of β -naphthyl substituted-allenylmethyl ethers under cheap FeCl₃ catalyst and O2 conditions reverses the regio- and chemoselectivity to provide a wide range of 2-aryl/alkyl, 3-(substituted-vinyl)naphtho[2,1-b]furans in high yields at 95-130 °C without naphthopyran products. This atom- and step-

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Table 1. Optimization of the Reaction Conditions^a



entry	1	catalyst	oxidant	solvent	$T (^{\circ}C)/t (h)$	2	yield ^b (%)
1	1a		$PhI(OAc)_2^c$	CH ₃ CN ^d	82/48	2a	4
2	1a		DDQ ^c	CH_3CN^d	82/48	2a	33
3	1a		FeCl ₃ ^c	CH_3CN^d	82/48	2a	34
4	1a		FeCl ₃ ^c	CH ₃ CN and DMF ^d	reflux/36	2a	65
5	1a	FeCl ₃	air	CH ₃ CN and DMF ^d	reflux/36	2a	50
6	1a	FeCl ₃	O ₂	CH ₃ CN and DMF ^d	reflux/36	2a	59
7	1a	FeCl ₃	O ₂	CH ₃ CN and DMF	reflux/36	2a	67
8	1a	FeCl ₃	O ₂	toluene and DMF	95/20	2a	72
9	1a		O ₂	toluene and DMF	95/20	2a	<5
10	1b	FeCl ₃	O ₂	toluene and DMF	95/36	2b	0
11	1b	FeCl ₃	O ₂	xylene and DMF	130/36	2b	78
12	1b	Cu(OAc) ₂ /1,10 phenanthroline ^e	O ₂	xylene and DMF	130/36	2b	7
13	1b	InCl ₃	O ₂	xylene and DMF	130/36	2b	48
14	1a	FeCl ₃	O ₂	xylene and DMF	120/5	2a	77
¹ Condition	ns: 0.15 m	mol of 1a/1b 0.045 mmol of FeCl.	and $40 \text{ mg of } 4 \text{ Å}$	MS in 4.2 mL of solvent	(mixing solvent rati	$i_0 = 2.5 \cdot 1^3$) reacted under

"Conditions: 0.15 mmol of 1a/1b, 0.045 mmol of FeCl₃, and 40 mg of 4 A M.S. in 4.2 mL of solvent (mixing solvent ratio = 2.5:1) reacted under O_2 . ^bIsolated yield. ^c2.0 equiv of oxidant. ^dWithout 4 Å M.S. ^c20 mol %.

economic process was proposed to proceed through a trisubstituted allenic Claisen rearrangement followed by a domino aerobic iron-catalyzed oxidative cyclization to form new C–C and C–O bonds (Scheme 1, this work). To the best of our knowledge, this is the first example of an iron-catalyzed intramolecular aerobic oxidative coupling of O–H with $C(sp^2)$ –H to form benzofuran-like structures. Mechanistic study suggests that FeCl₃ plays the crucial role on the high regio- and chemoselectivity and the reactivity of the domino reaction.

We started our studies with trisubstituted allene 1a as model substrate. Selected results are shown in Table 1 [details in the Supporting Information (SI)]. Initially, a series of stoichiometric oxidants were screened in refluxing CH₃CN. PhI-(OAc)₂, Ag₂O, K₂S₂O₈, t-butyl hydroperoxide (TBHP), and di-t-butyl-peroxide (DTBP) gave poor results (entry 1 and the SI). However, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and FeCl₃ indeed afforded the desired product 2a in 33% and 34% yields, respectively (entries 2 and 3). The structure of 2a was unambiguously confirmed by single-crystal X-ray analysis (shown in Table 1). Then, solvents were extensively screened at 82 °C under 2.0 equiv of FeCl₃ (SI), and the mixing solvent of CH₃CN and DMF (2.5:1) was found to be the best (entry 4). Next, the use of 30 mol % of FeCl₃ under air was examined; 50% yield of **2a** was obtained (entry 5). Replacing air with O_2 and further adding 4 Å molecular sieves (M.S.) improved the yield to 67% (entries 6 and 7). Then, the use of the mixing solvent of toluene and DMF (2.5:1) instead of CH₃CN and DMF (2.5:1) was examined at 90, 95, and 100 °C (SI), and 95 °C afforded the best yield of 2a up to 72% (entry 8). The control reaction of O_2 and 4 Å M.S. in the absence of 30 mol % FeCl₃ gave almost no 2a, and other complex products were observed, demonstrating the crucial role of FeCl₃ on the success of the desired reaction (entry 9). When we applied the optimized conditions (entry 8) to 1b with donating substitution at R², no reaction occurred (entry 10). After further screening (SI), the use of xylene and DMF (2.5:1) as

solvent at 130 °C under 30 mol % of FeCl₃ and O₂ afforded **2b** in 78% yield (entry 11). Decreasing the amount of FeCl₃ (SI) or replacing FeCl₃ with Pd(OAc)₂, Cu(OAc)₂/1,10-phenan-throline (entry 12), or other iron salts including FeBr₃, Fe(acac)₃, Fe(OTf)₃, FeF₃, Fe(ClO₄)₃·9H₂O, FeCl₃·6H₂O, as well as InCl₃ (entry 13) all led to the decreased yield of **2b** (SI). **1a** under the later optimized conditions (entry 11) but at 120 °C afforded **2a** in 77% yield after only 5 h (entry 14).

With the optimized conditions in hand, we first investigated the scope of the substitution R^1 at the 3-position of trisubstituted allenes 1 (Scheme 2, 2c-2y). 1 bearing ortho, meta, or para electro-withdrawing (1c-1g, 1i-1k), electroneutral (1h, 1l, 1o), or electro-donating (2m, 2n, 2p, 2q) substituted aryls at the 3-position (R^1) with R^2 as alkyl gave good yields of the desired naphthofuran derivatives 2c-2q. It is important to note that chloro, bromo, fluoro, trifluoromethyl, and ester are compatible in the present transformation. Chloro, bromo, and fluoro could be further elaborated for functionalization. Heterocycles such as 3-thienyl (1r) and 2-thienyl (1s) are also tolerated. Next, 1 bearing alkyl substitution at the 3-position was examined and consistently gave good results (2t-2y). It is noteworthy that cyclopropyl as R^1 was preserved and delivered 2x in 73% yield. When R^1 was bulky tert-butyl (1w) or bulky cyclohexyl (1y), the product 2w and 2y were also smoothly produced in 78% and 76% yields, respectively.

Next, we turned our attention to the substitution R^2 at the 1position of 1 (Scheme 2, 2z-2aj). In addition to alkyl (Scheme 2, 2c-2y), R^2 as aryls and bromo are also tolerated (Scheme 2, 2z-2ac). Moreover, when R^2 was thiocyanate, a series of 2-aryl, 3-(1-thiocyanate-substituted-vinyl) naphthofurans 2ad-2ai were obtained in moderate to good yields at 120 or 95 °C. Trifluoromethylthio, a "privileged" group in medicinal chemistry, served as R^2 and performed well, delivering 2aj in 77% yield. Notably, the double allenic Claisen rearrangement/intramolecular oxidative cyclization of 1ak, 1al, and 1am also proceeded smoothly to give the corresponding Scheme 2. Scope of Substitutions R^1 and R^2 of Naphthyl-1,3-Disubstituted Allenylmethyl Ethers 1^a



^{*a*}Reaction conditions: 0.15 mmol of 1, 0.045 mmol of FeCl₃, and 40 mg of 4 Å M.S. in 3 mL of xylene and 1.2 mL of DMF reacted under O_2 at 130 °C for 36 h (2c-2y, 2ak-2am) or 120 °C for 5-24 h (2z-2aj). Isolated yield. ^{*b*}60 h. ^{*c*}95 °C in 3 mL of toluene and 1.2 mL of DMF for 20-26 or 40 h (2ag, 2ai). ^{*d*}60 mol % of FeCl₃.

2ak, **2al**, and **2am** in moderate to good yields. In particular, blue-emitting **2ak** shows an excellent quantum yield of as high as 0.95 in CHCl₃ solution and could be employed in the organic light-emitting material field. **2an** bearing 6-ester on the naphthofuran was obtained in 70% yield (Scheme 3). Interestingly, when \mathbb{R}^4 and/or \mathbb{R}^5 are methyl, the corresponding products **2ao** (E:Z = 1:1) and **2ap** were smoothly furnished (Scheme 3). Moreover, phenyl allenylmethyl ether (**1aq**) was very inert, and 11% yield of **2aq** was obtained at 145 °C in DMF (Schemed 3). α -Naphthyl 1-ethyl-3-phenyl-allenylmethyl ether (**1ar**) was also examined, and it reacted sooner than **1b**, and naphthopyran **3a** (E:Z = 1.6:1) as the main product was obtained in 64% yield along with 22% yield of the naphtho[1,2-b]furan **2ar** (Scheme 3).

Gram-scale (1.1 g) **2b** was produced under the optimized conditions in 72% yield (SI). **2b** reacted with methyl





^{*a*}Reaction conditions: 0.15 mmol of **1**, 0.045 mmol of FeCl₃, and 40 mg of 4 Å M.S. in 3 mL of xylene and 1.2 mL of DMF reacted under O_2 at 130 °C for 36 h. Isolated yield. ^{*b*}45 h. ^{*c*}145 °C in DMF for 48 h. ^{*d*}120 °C for 9 h.

phenyldiazoacetate under $AgSbF_6^9$ gave 4a in 48% yield as a single diastereoisomer (Scheme 4a). When 2b was oxidized

Scheme 4. Gram-Scale Experiment and Synthetic Applications of the Products



with *m*-CPBA, the ring-opening and dearomatized product **5a** was produced, and the structure of **5a** was unambiguously confirmed by single-crystal X-ray analysis (Scheme 4b). In addition, **2k** undergoes a Heck reaction or Heck addition/ Miyaura borylation, furnishing **6a** in 72% yield and **7a** in 47% yield, respectively (Scheme 4c). **7a** contains both Bpin functionality and a dihydro-dibenzofuran skeleton which widely exists in biological compounds.¹⁰

For insight into the mechanism, a series of other control reactions were conducted. **1b** under O_2 and 4 Å M.S. in the absence of FeCl₃ gave 23% yield of **b-I** derived from Claisen rearrangement of **1b** in addition to the 27% yield of **2b** (Scheme 5A1). **b-I** (unstable for preservation) was immediately subjected to the optimized conditions (Table 1, entry 11), affording 77% yield of **2b** after only 35 min (Scheme 5A2). To know the state of iron, the solid of the model reaction (solvent was distillation) after the reaction was studied by X-ray photoelectron spectroscopy (XPS). XPS analysis has shown that the iron salt existed as FeCl₃ and FeOOH (see details in the SI). Moreover, **1b** in the presence of 3.0 equiv of 2,6-di-*tert*-butyl-4-methylphenol (BHT) under the optimized conditions leads to the dramatically decreased

Scheme 5. Mechanism Study



25% yield of **2b** (Scheme 5A3). This supports the idea that the domino process might involve a radical mechanism. In addition, **1b** under O_2 and 4 Å M.S. in the absence of FeCl₃ with saturated hydrogen chloride xylene and DMF (4:1) solution as solvent at 130 °C for 36 h gave **2b** in 32% yield (SI), ruling out the possibility of HCl to facilitate/catalyze the transformation.

On the basis of the control reactions and XPS study, a plausible reaction mechanism was proposed (Scheme 5B). $FeCl_3$ might coordinate with the oxygen of 1 to give A, or when R² was SCN/SCF₃ R² might facilitate/direct FeCl₃ to coordinate with the oxygen of 1 to give A'.¹¹ Then, A or A' undergoes Claisen rearrangement to form B. B converts to C through keto-enol tautomerization along with the loss of HCl. C transformed to radical intermediate D and FeCl₂. Subsequently, intramolecular radical cyclization of D gives E. E is further oxidized by FeCl₃ to afford cationic intermediate F with FeCl₂. Then, F loses hydrogen to generate the desired product 2. FeCl₂ in the presence of O_2 and HCl is oxidized to regenerate FeCl₃. Part of FeCl₂ in the presence of O₂ and H₂O is oxidized to FeOOH. Adding molecular sieves could facilitate the removal of water. Thus, accordingly the less FeOOH was then formed, and the more effective catalyst FeCl₃ could be regenerated; the yield was increased. Thus, 1 only loses two hydrogens to transform to 2 through this domino process (Scheme 5B).

In summary, we have developed an FeCl₃-catalyzed trisubstituted allenic Claisen rearrangement/chemo-, and regioselective aerobic dehydrogenative cyclization domino reaction, affording a wide range of 2-aryl/alkyl, 3-(substituted-vinyl)naphtho[2,1-*b*]furans in moderate to good yields at 95-130 °C. The domino reaction highlights a cheap and green catalytic system, high regio- and chemoselectivity, very broad substrate scope, good functional group tolerance, and high atom- and step-economy. Naphthyl substituted-allenylmethyl ethers were first used in Claisen rearrangement. Mechanistic study suggests that FeCl₃ serves as catalyst which plays the key role on the high regio- and chemoselectivity and the reactivity of this reaction. This represents the first example of ironcatalyzed intramolecular aerobic oxidative coupling of 2vinylphenols to form benzofuran-like structures. This also represents the first method for synthesizing naphthofuran derivatives in which electro-withdrawing, electro-neutral, and electro-donating substituted aryls and various alkyls are all tolerated at the 2-position. The substituted vinyl at the 3position of the products has rich chemistry for elaboration. Gram-scale and various applications of the products have also been demonstrated. As high as 0.95 quantum yield of one product also demonstrates these products' potential utility in material fields. Developing other new reactions/strategies catalyzed by cheap and abundant first-row transition metals as well as developing coupling reactions involving the cleavage of C–O bonds of ethers containing allenes are under way in our laboratory.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b03941.

Experimental procedures, XPS spectra, and compound characterization data (PDF)

Accession Codes

CCDC 1865807–1865808 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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