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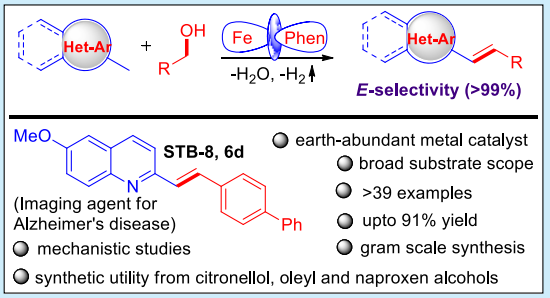
Iron-Catalyzed Coupling of Methyl *N*-Heteroarenes with Primary Alcohols: Direct Access to *E*-Selective Olefins

Jagadish Das,[†] Mari Vellakkaran,[†] Motahar Sk, and Debasis Banerjee*

Department of Chemistry, Laboratory of Catalysis and Organic Synthesis, Indian Institute of Technology Roorkee, Roorkee 247667, Uttarakhand, India

Supporting Information

ABSTRACT: An efficient Fe-catalyzed system is reported for direct α-olefination of methyl-substituted *N*-heteroarenes with primary alcohols. The catalytic dehydrogenative coupling enables a series of functionalized *E*-olefinated *N*-heteroaromatics with excellent selectivity (>99%). Initial mechanistic studies including deuterium-labeling experiments provide evidence for the participation of the benzylic C−H/D bond of alcohols.



Transition-metal-catalyzed functionalization of methylazaarenes with suitable nucleophiles provides access to valuable *E*-olefins having heteroaromatic cores. These *E*-selective conjugated heteroarenes are ubiquitous structural motifs found in many bioactive natural products, agrochemicals, and pharmaceuticals.[1,2] Notably, several classical approaches for the synthesis of regioselective alkenes are Wittig reaction, Horner−Wadsworth−Emmons reaction, Julia olefination, Peterson olefination, etc.,[3] involving a suitable leaving group. Furthermore, Heck or Suzuki couplings and olefin metathesis are well-established approaches for their synthesis (Scheme 1a).[4] Again, condensation of methylazaarenes with aldehydes using stoichiometric amounts of strong acids or bases were also used for such conjugated olefins.[5] Nevertheless, often such processes suffer from (i) generation of stoichiometric waste, (ii) harsh reaction conditions, (iii) multistep sequences, (iv) and poor *E*/*Z* selectivity.[3,4] In this direction, a recent report for the functionalization of alkylazaarenes using Fe catalyst involving activated *N*-sulfonylaldimines has been developed (Scheme 1b).[6] Applications of Lewis acids,[7] or Pd catalysts,[8] were also used for such azaarene derivatives.

In the past decades, dehydrogenative coupling of alcohols were extensively used for the synthesis of unsaturated compounds. In this context, replacement of expensive and precious metal catalysts by nonprecious earth abundant metals (Fe, Mn, Ni, and Co) would be more attractive for such key catalytic conversions.[9] In this direction, recently we developed a couple of nickel-catalyzed novel protocols for the synthesis of secondary amines, amides, including interesting *N*-heterocycles.[10] Most recently, we and others have also developed the alkylation of methyl substituted *N*-heteroarenes with alcohols.[11a−h,12] Recent studies for α-olefination of alkylazaarenes with primary alcohols has been developed using manganese pincer catalysts.[12a,b] Notably, such pincer complexes employed expensive ligands systems based on PN_5P or NNN core and required multistep synthesis (Scheme 1c).

Therefore, storing, handling, and expensive nature of these ligands are key issues in comparison to base−metal catalysts.[12a,b] More recently, we have also demonstrated the Ni-catalyzed synthesis of *E*-selective olefins involving methyl substituted *N*-heteroarenes with alcohols (Scheme 1c).[12c] We observed diminished reactivity for electron poor functionalities, halides substituted alcohols (Cl or Br) and even with alkyl alcohols.[12c] Therefore, there is still a need to develop a general and chemoselective catalytic protocol for the synthesis of functionalized *E*-olefins.

Notably, iron is the most earth-abundant metal, inexpensive and less toxic. Iron is capable of existing in variable oxidation states and is an integral part of living systems. Therefore, utilization of iron catalysts for key organic transformations is attracting increased interest.[13] However, to the best of our knowledge, to date, no iron-catalyzed olefination of methyl *N*-heteroaromatics with primary alcohols is known.

Herein, we report the first Fe-catalyzed route for *E*-olefination of a series of methylazaarenes with alcohols (Scheme 1d). The catalytic protocol is tolerant of a series of electron-poor functional groups, halides, and linear as well as cyclic alkyl alcohols that established the novelty of the present protocol.

Initially, we examined the reaction between 2-methylquinoline (**1a**) with 4-methoxybenzyl alcohol (**2a**) as the model substrates of our choice. When Fe(II) acetate (5 mol %) and 1,10-phenanthroline **L1** (6 mol %) were used with *t*-BuOK (1.0 equiv) as a base, 80% isolated yield of **3a** was obtained along with a trace amount of undesired alkylated product **3a′**

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Scheme 1. Classical approaches and metal-catalyzed olefin synthesis

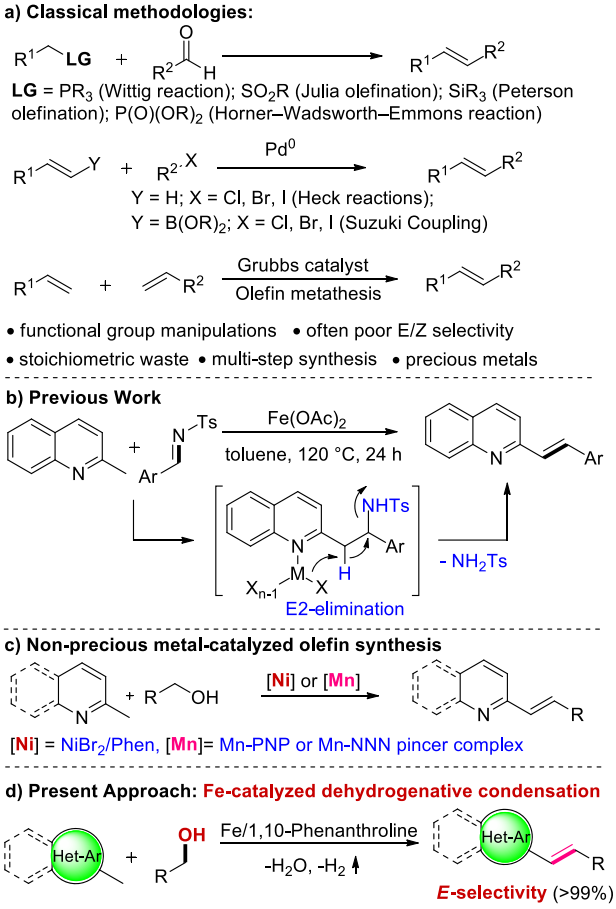
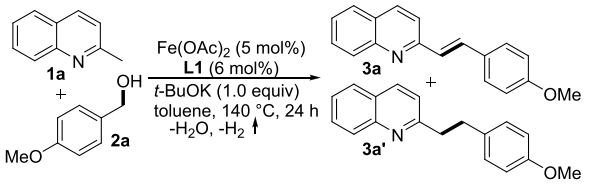


Table 1. Optimization Studies for α-Olefinations[a]



entry	deviations from the above	GC–MS conversion 3a (%)	3a′
1		**82 (80)**	**8**
2[b]	$Fe_2(CO)_9$	69	19
3	$Fe(acac)_3$	29	5
4	**L2** instead of **L1**	59	39
5	**L3** instead of **L1**	56	22
6	**L4** instead of **L1**	12	2
7	**L5** instead of **L1**	41	8
8	*t*-BuONa	47	9
9	NaOH	66	11
10	KOH	26	6
11	$Fe(OAc)_2$ (2.5 mol %), **L1** (3.0 mol %)	43	6
12	no $Fe(OAc)_2$, no **L1**, *t*-BuOK	20	
13	No *t*-BuOK	0	0
14	**L1**, *t*-BuOK	36	
15	molecular sieves (3 Å)	20	

[a]Unless specified, the reaction was carried out with **1a** (0.25 mmol), **2a** (0.50 mmol), $Fe(OAc)_2$ (5.0 mol %), **L1** (6.0 mol %), *t*-BuOK (0.25 mmol), and toluene (1.0 mL), Schlenk tube under nitrogen atmosphere, 140 °C oil bath, 24 h. [b]$Fe_2(CO)_9$ (2.5 mol %) and **L1** (3.0 mol %) were used. **L1** = 1,10-phenanthroline. **L2** = 2,9-dimethyl-1,10-phenanthroline. **L3** = 2,2′-bipyridine. **L4** = 4,4′-dimethyl-2,2′-bipyridine. **L5** = 2,2′-biquinoline.

(Table 1, entry 1, and SI Table S1). However, iron catalyst having a variable oxidation state (0 or III) further did not improve the product yields (entries 2 and 3). Thereafter, applications of different nitrogen-based ligands **L2**–**L5** resulted in up to 59% conversion to the desired *E*-selective olefin (entries 4–7 and SI Table S2). Screening of different solvents, such as *p*-xylene, 1,4-dioxane, and *tert*-amyl alcohol, were found to be less effective for the olefination process (SI Table S3). Examination of different bases, *t*-BuONa, NaOH, and KOH, resulted only 26–66% conversion to the desired product **3a** (entries 8–10 and SI Table S4). An olefination reaction at lower catalyst loading resulted moderate product yield (entry 11). Control experiments resulted in poor or no α-olefination product (entries 12 and 13, SI Table S4). However, a combination of **L1**/*t*-BuOK in the absence of Fe catalyst gave 36% yield of **3a**, and use of molecular sieves resulted in only 20% product (entries 14 and 15). Notably, NMR analysis identified the *E*-selective desired product, whereas we did not observe any *Z*-selective olefin (entries 1–12). However, in some cases we detected α-alkylated product **3a′** using GC–MS analysis of the crude reaction mixture and in the case of **3a** we detected (<3%) α-alkylated product **3a′** as an inseparable mixture in the isolated product yield (see the SI).

Having the optimized reaction conditions in hand, we then investigated the reactivity of quinaldine and pyrazines with primary alcohols (Scheme 2). For instance, 2-methylquinoline reacted with electron-rich benzyl alcohols having methoxy, methyl, ethyl, and isopropyl substituents resulted the desired olefins **3a**–**3e** in up to 80% yields. Importantly, sterically hindered 2-methylbenzyl alcohol **2f**, gave 58% yield to **3f**. Notably, electron poor *p*-nitrobenzyl alcohol **2g** and *p*-trifluoromethyl benzyl alcohol **2h** were efficiently transformed into the *E*-olefinated azaarenes **3g** and **3h** in 35–50% yields, respectively (Scheme 2).[12c] Pleasingly, *m*-bromo- as well as *p*-chloro-substituted benzyl alcohols **2i** and **2j** gave the desired *E*-olefins **3i**–**3j** in acceptable yields. 1-Naphthylmethanol **2k** and alcohol **2l** reacted smoothly with **1a**, and **3k**–**3l** were obtained in moderate yields. The catalytic protocol could be applied for more challenging alkyl alcohols, such as *n*-octanol **2m**, *n*-decanol **2n**, 1-cyclohexylmethanol **2o**, and 1-cyclopropylmethanol **2p**, and resulted the alkyl substituted *E*-olefins **3m**–**3p** in acceptable yields (Scheme 2). Again, 2-methylpyrazine **1b** reacted with alcohols having different alkyl or alkoxy groups (**2a**–**2e**), the desired vinyl pyrazines **4a**–**4e** were obtained in up to 80% yields. However, alcohol **2k** gave the desired product **4f** in 50% yield. Unfortunately, the reactions with *p*-chlorobenzyl alcohol **2j** and *n*-octanol **2m** were sluggish and resulted in moderate product yields (**4g**–**4h**). Remarkably, reaction of 2,5-dimethylpyrazine **1c** with benzyl alcohol resulted in selective bis-*E*-vinylarenes **4i** in 58% yield (Scheme 2).

Again, we extended the α-olefinations using different *N*-heteroarenes with alcohols (Scheme 3). Gratifyingly, 6-methoxyquinaldine **1d** resulted in almost quantitative yield (91%) to **5a**. However, 6-bromoquinaldine **1e** furnished the desired olefin **5b** in moderate yield (48%) along with dehalogenated product **3b** in 28% yield (Scheme 3). Under identical conditions, 8-methoxyquinaldine **1f**, as well as 8-

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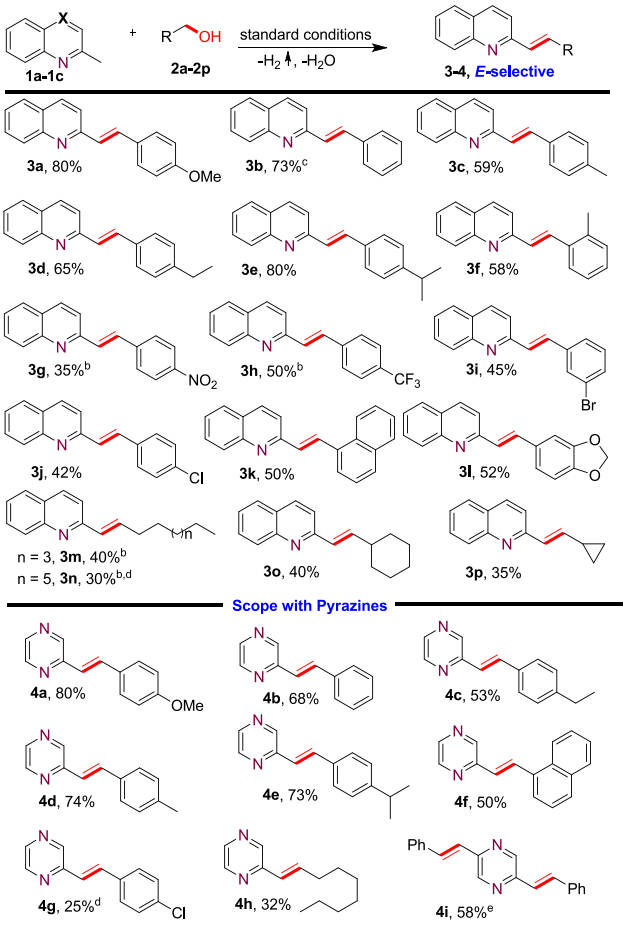
Scheme 2. Scope of Quinaldine and Pyrazines[a]

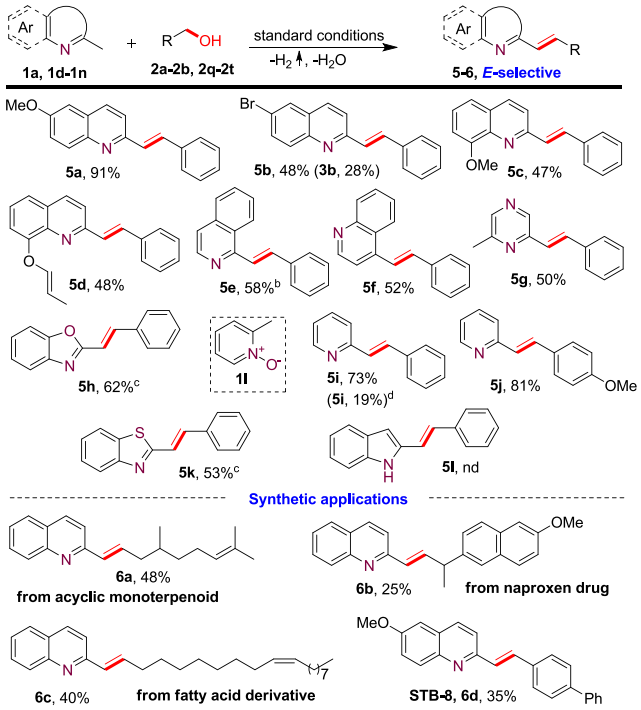


[a]Reaction conditions: (a) Standard conditions of Table 1; (b) 1,4-dioxane was used; (c) *t*-BuOK (0.125 mmol) was used; (d) GC–MS yield; (e) **2b** (1.0 mmol), $Fe(OAc)_2$ (0.025 mmol), **L1** (0.03 mmol), *t*-BuOK (0.50 mmol) were used.

alkoxyquinaldine **1g**, participated with benzyl alcohol to access *E*-vinylquinolines **5c–5d** in up to 48% yield. Notably, 1-methylisoquinoline **1h** and 4-methylquinoline **1i** could efficiently transform into the desired *E*-olefins **5e–5f** in 52–58% yield, respectively (Scheme 3). Remarkably, 2,6-dimethylpyrazine **1j** and 2-methylbenzoxazole **1k** also led to interesting *E*-olefins **5g–5h** in good isolated yields. However, the reaction of 2-methylpyridine was sluggish under the standard conditions, whereas 2-methylpyridine *N*-oxide **1l** resulted the deoxygenated *E*-vinylpyridines in excellent yields (Scheme 3, **5i–5j**). Importantly, 2-methylbenzo[d]thiazole **1m** efficiently transformed into the interesting *E*-olefins **5k** in 53% yield, whereas, in case of 2-methylindole, we did not observe any desired product (Scheme 3).

Further, we employed dihydrgeraniol **2q** (a natural acyclic monoterpenoid), as well as oleyl alcohol **2s** (an unsaturated fatty acid derived alcohol) and chemo-selectively converted to the *E*-olefinated products **6a** and **6c** in up to 48% yield (Scheme 3). Interestingly, alcohol **2r**, derived from naproxen, extensively used as nonsteroidal anti-inflammatory drug, resulted the desired *E*-olefinated quinoline **6b** in acceptable yield. Importantly, when 6-methoxyquinaldine **1d** was reacted with biphenyl-4-methanol **2t** olefin **6d** (**STB-8**), widely used as an imaging agent for Alzheimer's disease *β*-amyloid plaques, resulted. A gram-scale reaction using model substrates resulted

Scheme 3. Scope of Methylazaarenes with Alcohols[a]



[a]Reaction conditions: (a) standard conditions of Table 1; (b) 12 h reaction time; (c) 1,4-dioxane was used; (d) 2-methylpyridine was used.

the *E*-olefinated product **3a** in 72% isolated yield (Scheme S5, 1.16 g). Additionally, we attempted the straightforward synthesis of the antimalarial drug (±)-galipinine **8**; starting from **3l** followed by Ni-catalyzed hydrogenation and *N*-methylation resulted in the desired drug **8** in excellent yield (Figure 1). These examples highlight the potential applications of our established protocol.

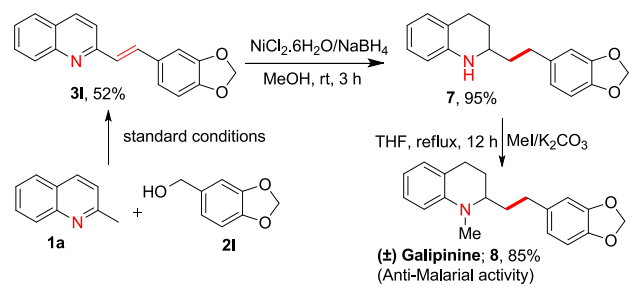


Figure 1. Synthesis of antimalarial drug (±)-galipinine.

Notably, the present protocol is tolerant to various *N*-heterocycles and alcohols having nitro, trifluoromethyl, bromo, chloro, 1,3-dioxolone, alkyl, and alkoxy substituents, including allylic ether functionalities. Remarkable chemoselective transformations in the presence of sensitive internal and terminal olefins establish the synthetic utility of the present protocol.

Thereafter, to study the mechanistic aspect, initially, a series of control experiments were performed using **1a** with 4-methoxybenzaldehyde **2a′** and **2a** in the presence and absence of iron catalyst (Scheme 4). Nevertheless, in the presence of Fe catalyst, **2a** and **2a′** resulted in 52% and 21% yield of **3a**, whereas a control experiment involving a mixture of **2a′** and **2b** with **1a** under the standard conditions gave 40% yield of **3a**

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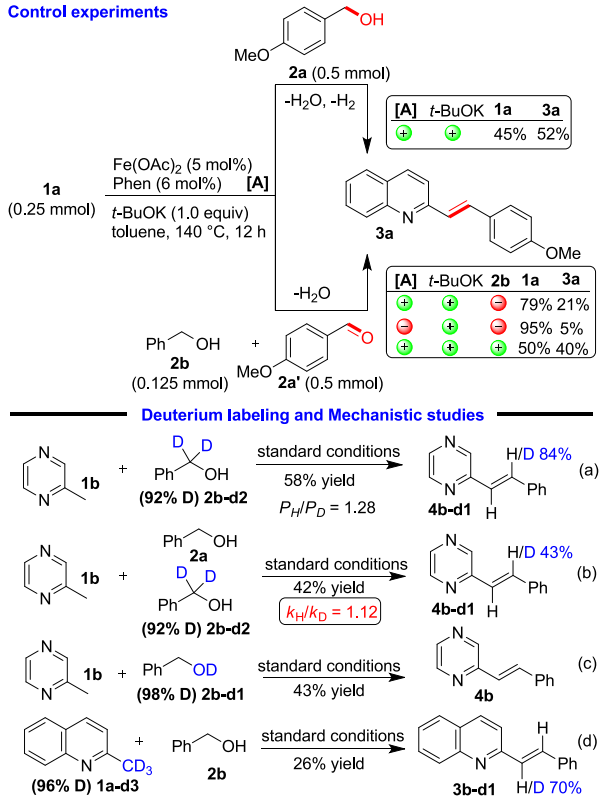
Scheme 4. Catalytic and Mechanistic Studies



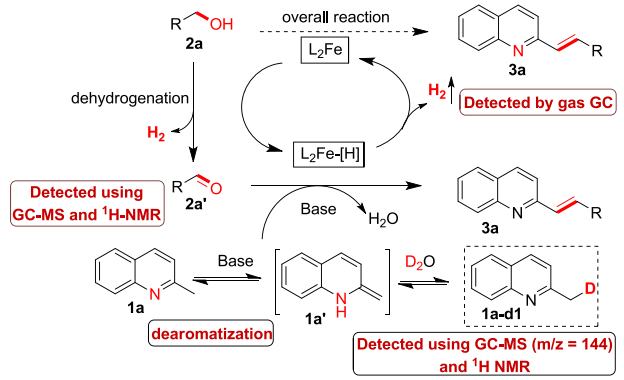
(Scheme 4). We believe that, in the presence of an aldehyde, Fe catalyst might form an adduct with the enamine **1a′**, which partially retarded the dearomatization process and resulted diminished product conversion.[12]

Additionally, deuterium-labeling experiments were performed for the α-olefination of **1b** with **2b-d2** (92% D), and **4b-d1** was obtained in 58% yield along with 84% deuterium incorporation at the β-position (Scheme 4a and Scheme S1). Further, we compared the individual α-olefination of **1b** with **2b** and **2b-d2** and found a value of P_H/P_D = 1.28 (SI, Scheme S1). This KIE value indicates that the rate of the reaction depends on the breaking of the C−H bond of alcohol and hence the oxidation of alcohol to aldehyde is the rate limiting step. Again, a competitive experiment involving 1:1 mixture of **2b** and **2b-d2** (92% D) with **1b** was performed and resulted only 42% **4b-d1** along with 43% of deuterium incorporation, which shows that breaking of C−D bond of alcohol is slower as compared to the C−H bond and we observed k_H/k_D = 1.12 (Scheme 4b and Scheme S2).

Furthermore, no deuterated olefin was observe when **1b** with **2b-d1** (Scheme 4c) were used. Importantly, when **1a-d3** (96% D) was treated with **2b**, the desired deuterated olefin **3b-d1** was obtained in 26% yield and showed 70% deuterium incorporation at the α-position (Scheme 4d and Scheme S3).[13] Additionally, α-olefination of **1a** with **2b** was monitored using gas chromatography analysis for 11 h, and the observed time-course conversion plot revealed the constant formation of benzaldehyde **2b′** following dehydrogenation of benzyl alcohol **2b** (Scheme S4). Pleasingly, simultaneous evolution of hydrogen gas during olefination process was detected using gas chromatography analysis, and we have also determined the quantity of the evolution of hydrogen gas (Scheme S7).

On the basis of the control experiments, a plausible mechanism is depicted in Scheme 5.[12] Indeed, in the absence

Scheme 5. Plausible Mechanism



of base, we did not observe any **3a** (Table 1, entry 13), emphasizing the potential role of *t*-BuOK for (de)-aromatization of quinaldine **1a** to **1a′** (Scheme 5). Furthermore, reaction of **1a** with D_2O and *t*-BuOK at 140 °C gave 20% yield to **1a-d1**, which confirmed the participation of enamine **1a′** (Scheme S8). We envisioned that Fe-catalyzed dehydrogenation of primary alcohol **2a** gave corresponding aldehyde **2a′**, and the formation of transient Fe−H species occurred. Next, base-mediated condensation of aldehyde with enamine **1a′** gave the desired *E*-vinylquinoline **3a** with the elimination of water and dihydrogen as byproducts (Scheme 5).

In conclusion, we have developed the selective synthesis of functionalized *E*-vinyl olefins (>99%) using a simple and commercially available iron catalyst involving methylheteroarenes with primary alcohols. The process is tolerant to pyridine, pyrazine, quinolines, benzoxazoles, benzothiazole, and isoquinolines, etc. and extended to a range of aryl, alkyl, and heteroaryl alcohol derivatives (>39 examples) in up to 91% yield. Primary alcohols having nitro, trifluoromethyl, halide (Cl, Br), 1,3-dioxolone, internal olefin, and allylic ether functionalities could be used. Functionalization of oleyl alcohol, naproxen derivative, and the synthesis of the antimalarial drug (±)-galipinine was demonstrated. Mechanistic studies and deuterium-labeling studies confirm the participation of an enamine intermediate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02793.

Experimental procedures, screening of the reactions conditions, and spectroscopic data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dbane.fcy@iitr.ac.in.

ORCID

Debasis Banerjee: 0000-0001-8626-8742

Author Contributions

†J.D. and M.V. contributed equally to this work.

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Notes

The authors declare no competing financial interest.

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