JOC The Journal of Organic Chemistry

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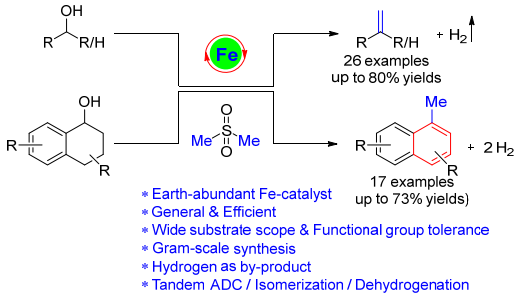
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c01173 • Publication Date (Web): 29 Jun 2020

Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Iron-Catalyzed Direct Julia-type Olefination of Alcohols

Vinod G. Landge,[†] Reshma Babu,[†] Vinita Yadav,[‡] Murugan Subaramanian,[†] Virendrakumar Gupta,[¶]* and Ekambaram Balaraman[†]*



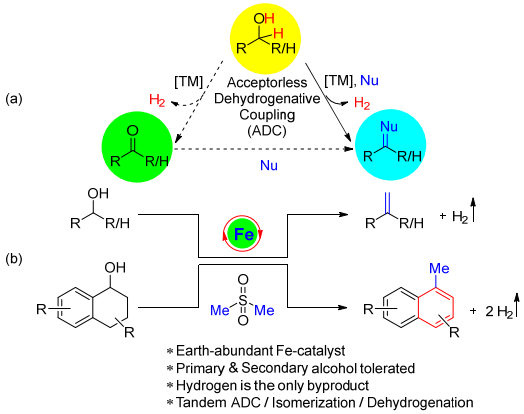
ABSTRACT: Herein we report an iron-catalyzed, convenient and expedient strategy for the synthesis of styrene and naphthalene derivatives with the liberation of dihydrogen. The use of a catalyst derived from an earth-abundant metal provides a sustainable strategy to olefins. This method exhibits wide substrate scope (primary and secondary alcohols) functional group tolerance (amino, nitro, halo, alkoxy, thiomethoxy, and S- and N-heterocyclic compounds) and can be scaled up. The unprecedented synthesis of 1-methyl naphthalenes proceeds *via* tandem methenylation / double dehydrogenation. Mechanistic study shows that the cleavage of the C-H bond of alcohol is the rate determining step.

INTRODUCTION

Olefins are important for synthetic chemistry and ubiquitous in polymer, agrochemical, pharmaceutical, and functional materials.[1] The traditional approaches for the synthesis of olefins include Wittig;[2-3] Horner–Wadsworth–Emmons,[4] Peterson olefination,[5] Julia olefination,[6] and Tebbe olefination.[7] Sulfones are widely used in the multi-step classical Julia olefination, and it operates *via* the formation of β-acyloxy alkyl sulfones from aldehydes followed by the reductive elimination with Na/Hg to furnish the olefin. In some cases, the aldehydes or ketones are not easily accessible or may undergo undesired side-reactions. Therefore, it is not surprising that despite the existing methods the development of new versatile and efficient protocols for their synthesis is of continuing interest. Recently, research progress has been made on the synthesis of olefins *via* oxidation of alcohols under oxygen in the presence of Pd, Rh, Cu, Ru, Ni and under catalyst-free conditions by using alcohol as a solvent and copious amount of base.[8] However, the requirement of precious metals, expensive ligands, and toxic additives always obstruct their practical application.

The development of a cascade process that mimics the biosynthesis in living cells significantly enhances the efficiency of organic synthesis with reduction in the intermediate recovery steps and further purification. Because of the improved step-economy, cascade reactions are highly desirable in industrial bulk process chemistry.[9] Hence, the direct catalytic Julia-type olefination of alcohols *via* an acceptorless dehydrogenative coupling (ADC) strategy[10-12] has emerged as a powerful tool for the straightforward synthesis of olefins (Scheme 1a). However, existing methods suffer from the use of expensive precious metal catalysts,[12a-b] and other competing reaction (e.g. α-methyl substituted styrenes were observed with primary alcohols in Ru-PNN system).[12a] It is noted that secondary alcohols failed to afford the desired olefins under base-metal catalyzed conditions.[12d-e]

Scheme 1. Olefination *via* ADC strategy.



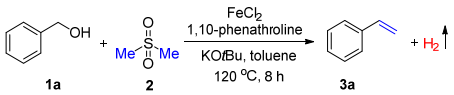
Recently, notable progress has been witnessed in the development of homogeneous catalysts based on bio-relevant, earth-abundant base-metals for dehydrogenation reactions.[11,13-15] However, to mimic their reactivity with cheap metal catalysts is always challenging. Iron is generally less-toxic, and the most abundant metal on the Earth's crust. In this regard, the development of efficient catalytic systems using abundant, inexpensive and benign iron would be highly desirable.[14,16] Herein, we report the first iron-catalyzed direct catalytic ole-

fination of alcohols with the liberation of hydrogen gas. The present olefination has a broad substrate scope with primary and secondary alcohols. Notably, an unprecedented synthesis of 1-methyl naphthalenes proceeds *via* the tandem ADC/isomerization/dehydrogenation is reported (Scheme 1b).

RESULT AND DISCUSSION

We began our initial study using benzyl alcohol (**1a**) and dimethyl sulfone (**2**) as benchmark substrates for iron-catalyzed direct Julia-type olefination reaction. The olefination reaction was performed in the presence of $Fe(OTf)_2$ (3 mol%), 1,10-phenanthroline (3 mol%), and KO*t*Bu (1.1 equiv) as a base in toluene heated at 120 °C (oil-bath temperature) for 8 h. This resulted in 58% isolated yield of styrene **3a** (Table 1, entry 1). The effect of each of the key parameters such as Fe-catalyst, ligand, base, and reaction temperature were carefully investigated (Table 1). Among the commercially available different iron sources, $FeCl_2$ gave the optimal results (Table 1, entries 1-6). The variation of ligands such as BBBPY (4,4′-di-tert-butyl-2,2′-dipyridyl), TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), and PPh_3 were found to be ineffective and gave unsatisfactory yields (Table 1, entries 4, and 7-9). By lowering the temperature, we have obtained the product **3a**, albeit in lower yield (Table 1, entry 10). The oxidative olefination was observed (~10% yield) in the absence of the Fe-catalyst (Table 1, entry 12). Other bases such as KOH and K_2CO_3 gave moderate yield of **3a** (Table 1, entries 13-14). Next, the effect of solvent was tested. It was observed that the reaction proceeds efficiently in toluene compared to other solvents (Table 1, entries 4, and 15-16). Notably, the liberated H_2 gas was detected by gas chromatography and quantified.

Table 1. Optimization of the reaction conditions[a,b]

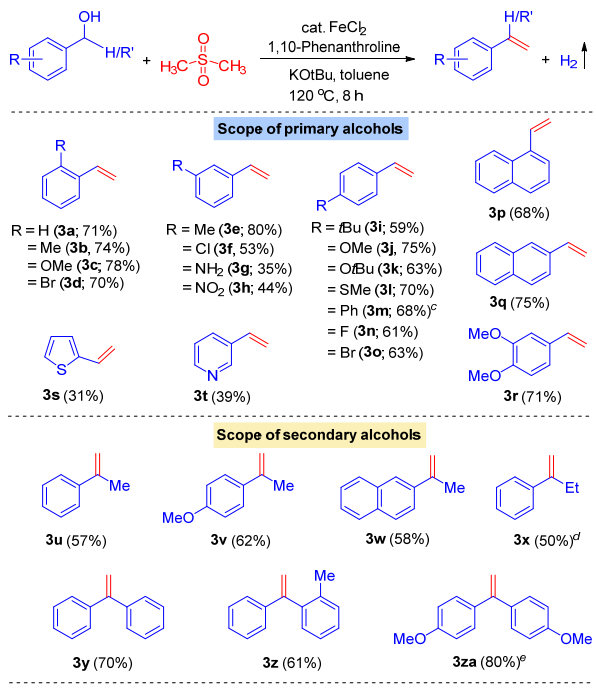


Entry	Reaction conditions	Yield (%)[b]
1	$Fe(OTf)_2$ used as [Fe] source	58
2	$Fe(BF_4)_2$•$6H_2O$	trace
3	$Cp^*Fe(CO)_2I$	54
4	standard conditions	76
5	FeC_2O_4	40
6	$FeBr_2$ used as [Fe] source	55
7	BBBPY used as Ligand	35
8	TMEDA used as Ligand	20
9	PPh_3 used as Ligand	40
10	at 80 °C	61
11	without 1,10-phenathroline	55
12	without $FeCl_2$	10
13	KOH instead of KO*t*Bu	65
14	K_2CO_3instead of KO*t*Bu	40
15	*t*-amyl alcohol used as solvent	51
16	trifluorotoluene used as solvent	73

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), $FeCl_2$ (3 mol%), 1,10-phenathroline (3 mol%), KO*t*Bu (0.55 mmol), and toluene (1 mL) heated at 120 °C (oil-bath temperature) for 8 h. [b]Isolated yields.

To demonstrate the versatility of the present iron-catalyzed direct olefination of alcohols, the substrate scope regarding various primary and secondary alcohols were investigated (Table 2). The present Fe-catalysis is compatible with various benzyl alcohols containing electron-neutral, electron-rich, and electron-deficient substituents, affording the desired olefins in excellent yields (up to 80%). The direct catalytic olefination of *ortho*-substituted benzyl alcohols bearing groups, such as 2-Me, 2-OMe and 2-Br proceeded efficiently and yielded the corresponding olefins in very good yields (products **3b** in 74%, **3c** in 78% yield, **3d** in 70% yield, respectively). The *meta-, and para*-substituted benzyl alcohols containing a range of functional groups, such as fluoro, chloro, bromo, amino, nitro, alkyl, aryl, ether, and thioether were well tolerated and gave the corresponding styrene derivatives (**3i-3o** and **3r**) in good yields (up to 80% yield).

Table 2. Styrene derivatives *via* ADC strategy: Scope of Alcohols[a,b]



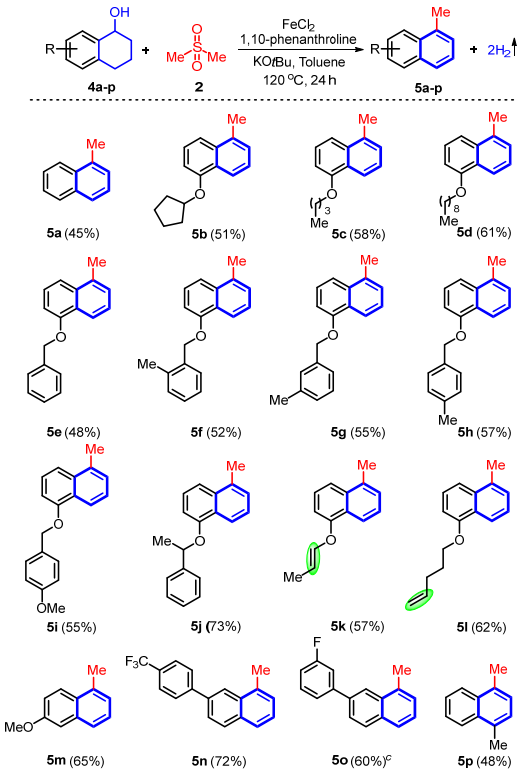
[a]Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), KO*t*Bu (0.55 mmol), and toluene (1 mL) heated at 120 °C (oil-bath temperature) for 8 h. [b]Isolated yields. [c]18% α-methyl substituted product was observed. [d]Isomerized product (but-2-en-2-ylbenzene) was also observed. [e]12% hydrogenated product was observed.

It is interesting to note that halo substituted benzyl alcohols were well tolerated and the desired halo-substituted styrenes (**3d**, **3f**, **3n** and **3o**) were obtained in good yield, which could be further used for functionalization. Pleasingly, sensitive functional groups such as unprotected amine group, nitro, alkoxy, thiomethoxy and dimethoxy groups were well tolerated and gave the desired styrene derivatives in good yields (products **3g**, **3h**, **3j**, **3k**, **3l** and **3r**). The methenylation of π–extended benzyl alcohols (1-naphthyl and 2-naphthyl) proceeded efficiently and yielded the corresponding olefins in excellent yields (products **3p** in 68%, and **3q** in 75% yields, respectively). Heteroaryl alcohols such as 2-thiophenemethanol and 2-pyridinemethanol worked under the optimized reaction conditions and afforded the expected products in low yields (**3s** in 31% and **3t** in 39% yield, respectively). To our delight, the secondary alcohols which gave lower

yield in PNN-Ru(II) catalyzed conditions underwent direct olefination smoothly under our Fe-catalyzed conditions. Thus, the secondary alcohols **1u**, **1v**, **1w** and **1x** furnished the expected α,α'-disubstituted olefins in moderate yield (up to 62% yield). Indeed, diphenyl methanol (**1y**), phenyl(*o*-tolyl)methanol (**1z**), and bis(4-methoxyphenyl)methanol (**1za**) reacted effectively, and yielded the corresponding olefins in excellent yields (up to 80% yield). To demonstrate the practical utility of the present Fe-catalyzed direct synthesis of styrene derivatives (**3c**, **3q** and **3r**) a larger scale synthesis has been performed.

The synthesis of the naphthalene scaffold has a great attention because of its use in synthetic, medicinal, and material chemistry.[17] Several natural products (e.g. Gossypol, and Rifampici) possess a naphthalene core in their structures and exhibit promising biological activities.[18] Interestingly, under our Fe-catalyzed conditions 1,2,3,4-tetrahydronaphthalene-1-ol (**4**) reacted with **2** and yielded the 1-methylnaphthalene derivatives with the liberation of hydrogen gas (Table 3). This unprecedented reaction proceeds *via* ADC of secondary alcohols with **2** to form the terminal olefins which further undergo isomerization followed by dehydrogenation under Fe-catalysis to lead to the corresponding 1-methylnaphthalene derivatives as the single product.

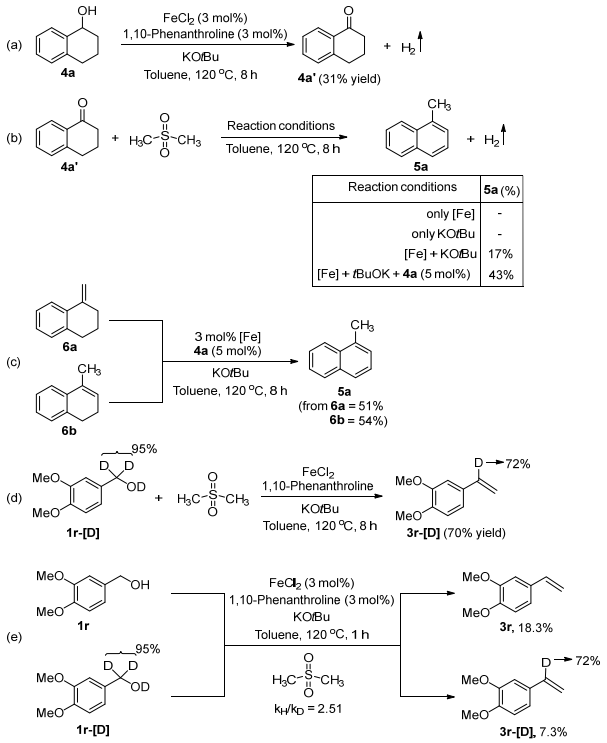
Table 3. Synthesis of 1-methyl naphthalene derivatives *via* tandem ADC/isomerization/dehydrogenation[a,b]



[a]Reaction conditions: **4a-p** (0.5 mmol), 2 (0.5 mmol), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), KO*t*Bu (0.55 mmol), and toluene (1 mL) heated at 120 °C (oil-bath temperature) for 24 h. [b]Isolated yields. [c]2:1 mixture of **5o** and the partially dehydrogenated product.

To demonstrate the generality of our iron-catalyzed unprecedented synthesis of 1-methyl naphthalene derivatives, various 1,2,3,4-tetrahydronaphthalene-1-ols were investigated (Table 3). Thus, diverse 1,2,3,4-tetrahydronaphthalene-1-ols containing substituted cyclic ether, aliphatic, and substituted benzylic groups afforded the corresponding 1-methylnaphthalene derivatives in good to moderate yields (**5a-5p**). Surprisingly, retention of the double bond was observed when performing the reactions with 5-(allyloxy)-1,2,3,4-tetrahydronaphthalen-1-ol (**4k**) and 5-(pent-4-enyloxy)-1,2,3,4-tetrahydronaphthalen-1-ol (**4l**) under optimal conditions. Interestingly, compound **4k** afforded the product **5k** in moderate yield (57%) with isomerization of the double bond. We believe that the isomerization of the double bond in **4k** occurs *via* migratory insertion followed by *β*-hydride elimination by the *in situ* generated Fe-H complex.[19] Casey and co-workers reported that the iron-catalyzed isomerization of olefins can occur by either an iron-hydride addition-elimination mechanism or by a mechanism involving a π-allyl iron-hydride intermediate.[20] Various substituted 1,2,3,4-tetrahydronaphthalene-1-ol possessing 6-OMe and 4-CF_3-Ph gave the corresponding 1-methylnaphthalene products in good yields (products **5m** in 65% and **5n** in 72% yields). In the case of **4o**, a mixture of **5o** and a partially dehydrogenated product (7-(3-fluorophenyl)-1-methylene-1,2,3,4-tetrahydronaphthalene) were obtained in 2:1 ratio. This result revealed that the formation of 1-methyl naphthalene occurs *via* initial olefination followed by isomerization and subsequent dehydrogenation reaction under Fe-catalysis. A substrate with a substituent on aliphatic ring such as 4-methyl-1,2,3,4-tetrahydronaphthalene-1-ol (**4p**) was compatible with this reaction and delivered **5p** in 48% isolated yield.

Scheme 2 Mechanistic investigations

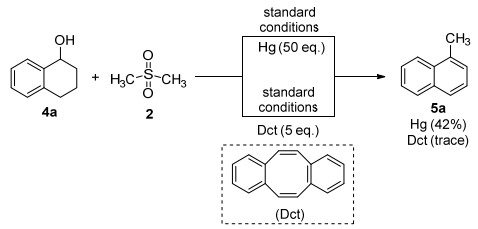


To gain insight into the reaction mechanism, several control experiments were performed (Scheme 2). Notably, a simultaneous evolution of molecular hydrogen during the Fe-catalyzed tandem ADC/isomerization/dehydrogenation of **4a** with **2** was detected using gas chromatography (GC) analysis, and the quantity of the evolution of hydrogen gas also determined.[21] Indeed, in the absence of **2**, the formation of dehydrogenated product, 1-tetralone (**4a'**) and H_2 gas were observed (Scheme 2a). Performing the reaction using 1-tetralone under our Fe-catalyzed conditions, the reaction proceeded smoothly and provided **5a** in 43% isolated yield. Recent stud-

ies on iron-catalyzed C-alkylation of carbonyl compounds using primary alcohols as alkylating agents disclosed that the intermediate iron alkoxy species undergoes base-mediated β-hydride elimination and resulted in the formation of aldehyde and iron-hydride species.[22] Hence, we envisioned that the dehydrogenation of 1,2,3,4-tetrahydronaphthalene-1-ol (**4a**) under Fe-catalysis offered the corresponding dehydrogenated product 1-tetralone (**4a'**) with the formation of transient Fe−H species (Scheme 2b). The two independent reactions using 1-methylene-1,2,3,4-tetrahydronaphthalene (**6a**), and 4-methyl-1,2-dihydronaphthalene (**6b**) under the Fe-catalyzed conditions yielded the expected 1-methylnaphthalene (**5a**) in moderate yields in the presence of catalytic amount of **4a**. These results indicated that **6a** and **6b** are the potential intermediate in the synthesis of 1-methyl naphthalene derivatives *via* Fe-catalyzed tandem reaction (Scheme 2c). Additionally, deuterium-labeling experiments were performed for the Fe-catalyzed olefination of **[D]-1r** with **2**, and **[D]-3r** was obtained in 70% yield along with 72% deuterium incorporation at the α-position (Scheme 2d). The kinetic deuterium labeled experiment indicated that the dissociation of C-H bond of alcohol might be the moderately slow step in the reaction as the k_H/k_D ratio is 2.53. Next, we have performed competitive KIE to verify the k_H/k_D. Thus, two parallel reactions using dimethyl sulfone (**2**, 0.2 mmol), alcohol (**1r**, 0.2 mmol), or deuterated alcohol (**1r-[D]**), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), KO*t*Bu (0.22 mmol), and toluene (1 mL) were performed under standard conditions. It was found that with alcohol **1r** and deuterated alcohol (**1r-[D]**), the isolated yield of the product is 18.3% and 7.3% (Scheme 2e), respectively which indicates $k_H/k_D = 2.51$. This result is in close agreement with the already mentioned k_H/k_D value (KIE = 2.53) and provide a support for the breaking of the C−H bond of alcohol is the rate determining step.

To gain preliminary insights into the active catalytic species, we have conducted two sets of experiments with selective poisoning reagents (Scheme 3). Mercury is a poison for heterogeneous catalysis due to a potential amalgam formation with heterogeneous metal species.[23] Upon addition of excess Hg (50eq per [Fe]) to the Fe-catalyzed ADC of **1a** with **2**, there is no significant change of the catalytic activity was observed in comparison with the control experiment. A similar poisoning experiments with dibenzo[a,e]cycloocta-tetraene (dct) is also conducted. Dibenzo[a,e]cycloocta-tetraene is a selective poison for homogeneous metal species.[24] The presence of an excess amount of dct poison (5eq per [Fe]) had a significant effect on the activity of the iron catalyst. These poison experiments suggest that a homogeneous species possibly serves as the active catalyst.

Scheme 3. Homogeneous nature of Fe-species



Reaction conditions: **4a** (0.5 mmol), **2** (0.5 mmol), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), KO*t*Bu (0.55 mmol), and toluene (1 mL) heated at 120 °C (oil-bath temperature).

In summary, an earth-abundant iron catalyzed convenient and efficient protocol for sustainable synthesis of styrene and naphthalene derivatives with the liberation of dihydrogen is disclosed. Mechanistic study illustrated that the cleavage of the C-H bond of alcohol is the rate determining step. The unprecedented synthesis of 1-methyl naphthalenes proceeds *via* a tandem ADC/isomerization/dehydrogenation.

ASSOCIATED CONTENT

General Information. All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenone and followed by distilled under argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (SilicycleSiliaflash F60 (230-400 mesh). ^1H NMR (400 or 500 MHz), $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.26 for ^1H (chloroform-d), δ 77.2 for $^{13}C\{^1H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer). HPLC analysis was performed on Agilent Technologies 1260 Infinity with UV detector.

1a. General procedure for the Fe-catalyzed olefination of alcohols: To an oven-dried 10 mL screw-capped vial, $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), dimethyl sulfone **2** (0.5 mmol), alcohol **1** or **4** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120 °C (oil-bath temperature). The reaction was monitored by TLC. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

1b. Procedure for Large-scale Synthesis (3c, 3q and 3r): To demonstrate the practical utility of the present Fe-catalyzed direct synthesis of styrene derivatives a larger scale synthesis has been performed.

To a 100 mL oven dried seal tube, $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), dimethyl sulfone **2** (5 mmol), alcohol **1c** or **1q** or **1r** (5.2 mmol), KOtBu (5.5 mmol), toluene (20 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120 °C (oil-bath temperature). The reaction was monitored by TLC. After 24 h, the reaction mixture was cooled to room temperature and chloroform was added to dilute the mixture. Then it was filtered through celite and filtrate was concentrated under reduced pressure. The crude residue was purified further by silica gel (230-400

mesh) column chromatography using a mixture of petroleum ether and EtOAc as eluent. Yield of **3c** is (561 mg, 81%), **3q** (642 g, 83%), and **3r** (605 mg, 74%).

2. Mechanistic Studies:

GC Conditions: GC make & Column: Agilent 7890 GC carbosphere column; Detector: Thermal Conductivity Detector (TCD); Carrier gas: Nitrogen; Make up flow of N_2: 5 mL/min; Detector Temperature: 200 degree Celsius and oven temperature 80 degree Celsius at the time of injection.

2.1 Qualitative analysis of hydrogen gas formation*:* (a) To an oven-dried 10 mL screw-capped vial, $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), alcohol **4a** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120 ºC (oil-bath temperature) for 8 h. The GC analysis of the gaseous mixture showed that the formation of dihydrogen. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

(b) Under standard conditions the ADC of benzyl alcohol (**1a**) with dimethyl sulfone (**2**) was carried out using the J. Young NMR tube. After 8 h, the gas was also collected by a gas-tight syringe and qualitatively analyzed by GC-TCD with a Carbon plot capillary column gas chromatography which showed the presence of H_2 gas at retention time 0.65 min. The retention of hydrogen gas is already calibrated.

2.2 Quantification of hydrogen gas*:* For the detection of hydrogen, the following dual reaction was performed. To schlenk tube (**A**), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), dimethyl sulfone (**2**, 0.5 mmol), benzyl alcohol (**1a**, 0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), toluene (1 mL) were added under a gentle stream of argon. The entire system was degassed and flushed with argon for 5 minutes (three times) and packed with rubber septum. To another 25 mL Schlenk tube (**B**), $RhCl(PPh_3)_3$ (10 mol%) catalyst, and cyclohexene (0.5 mmol) were dissolved in benzene (2 mL). Both the flasks (**A** & **B**) were connected through a double headed syringe and allowed to equilibrate for 5 minutes. The mixture in the flask (**A**) was heated at 120 ºC (oil-bath temperature), while the mixture in the flask (**B**) was stirred at 80 °C. After 8 hours, the organic entities present in the flask (**B**) were analyzed by GC-MS and GC which showed a clean conversion (63%) of the cyclohexene to cyclohexane (yield of **3a** = 71%).

2.3 Formation of transient Fe−H species*:* (a) To an oven-dried 10 mL screw-capped vial, 1-tetralone **4a'** (0.5 mmol), **2** (0.5 mmol), toluene (1 mL) were added under a gentle stream of argon (with various conditions, Scheme 2b). The reaction mixture was kept for stirring at 120 ºC (oil-bath temperature) for 8 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

(b) To an oven-dried 10 mL screw-capped vial, $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), 1-methylene-1,2,3,4-tetrahydronaphthalene (**6a**) or 4-methyl-1,2-dihydronaphthalene (**6b**) (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), 5 mol% of **4a**, and toluene (1 mL) were added under a gentle stream of argon (Scheme 2c). The reaction mixture was kept for stirring at 120 ºC (oil-bath temperature) for 8 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

2.4 Deuterium labelling experiment: GC Conditions: Column: Agilent HP-5 (30m x 0.320mm x 0.25µm); Carrier gas: Nitrogen; Flow: 1.0 mL/min (Split ratio: 100:1); Injection volume: 1 µL; Detector: FID, Detector Temp.: 300 degrees Celsius; Injection Temp.: 250 degrees Celsius; Temperature Program: 80 degrees Celsius (1 min hold), 20 degrees celsius/min – 280 degrees Celsius (10 min hold).

Synthesis of 1r-[D]

To an oven-dried 10 mL screw-capped vial, Ru-MACHO (3 mol%), 3,4-dimethoxy benzyl alcohol **1r** (0.1 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), deuterium oxide (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 130 ºC (oil-bath temperature) for 18 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

To an oven-dried 10 mL screw-capped vial, $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), dimethyl sulfone **2** (0.5mmol), 3,4-dimethoxy benzyl alcohol **1r-[D]** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for heating at 120 ºC (oil-bath temperature) for 8 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

2.5 KIE Experiment:

(a) Time dependent formation of product 3r using 1r and 1r-[D]*:* To an oven dried 15 mL screw cap pressure tube, dimethyl sulfone (**2**, 0.5 mmol), alcohol (**1r**, 0.5 mmol), or deuterated alcohol (**1r-[D]**), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), KO*t*Bu (0.55 mmol), and mesitylene (0.5 mmol) as an internal standard and toluene were added under a gentle stream of argon to make up the total volume of the reaction mixture to 1 mL. The reaction mixture was kept for stirring at 120 ºC (oil-bath temperature). At regular intervals (2 min, 4 min, 6 min, 8 min, 10 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (M) *vs* time (min.) plot.

(b) Competitive KIE experiment: Parallel reaction: To an oven dried 15 mL screw cap pressure tubes (two separate tubes), dimethyl sulfone (**2**, 0.2 mmol), alcohol (**1r**, 0.2

mmol), or deuterated alcohol (**1r-[D]**), $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), KO*t*Bu (0.22 mmol), and toluene (1 mL) were added under a gentle stream of argon. Both the reaction mixture was kept for stirring at 120 °C (oil-bath temperature) for 1 h. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

2.6 Homogeneous nature of Fe-species: To an oven-dried 10 mL screw-capped vial, $FeCl_2$ (3 mol%), 1,10-phenanthroline (3 mol%), dimethyl sulfone **2** (0.5mmol), **4a** (0.5 mmol), KO*t*Bu (0.55 mmol, 1.1 equivalent), Hg (50 equivalent with respect to catalyst) or Dibenzo[a,e]cycloocta-tetraene (Dct, 5 equivalent with respect to catalyst), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120 °C (oil-bath temperature) for 24 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

3. Characterization Data

Styrene (**3a**)[12a] Colorless liquid, 37 mg, 71% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.55 - 7.24 (m, 5 H), 6.79 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.82 (dd, *J* = 0.8, 17.6 Hz, 1H), 5.31 (dd, *J* = 0.8, 10.9 Hz, 1H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 137.5, 136.9, 128.5, 127.7, 126.2, 113.7.

1-methyl-2-vinylbenzene (**3b**)[25] Colorless liquid, 43 mg, 74% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.49 (brs, 1H), 7.24 - 7.10 (m, 3H), 7.05 - 6.85 (m, 1H), 5.65 (dd, *J* = 1.4, 17.4 Hz, 1H), 5.30 (dd, *J* = 1.4, 11.0 Hz, 1H), 2.37 (s, 3 H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 134.8, 130.2, 127.6, 126.1, 125.3, 115.1, 19.7.

1-methoxy-2-vinylbenzene (**3c**)[26] Colorless liquid, 54 mg, 78% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.47 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.30 - 7.16 (m, 1H), 7.14 - 6.71 (m, 3H), 5.73 (dd, *J* = 1.6, 17.7 Hz, 1H), 5.26 (dd, *J* = 1.6, 11.2 Hz, 1H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 156.6, 131.6, 128.8, 126.6, 126.4, 120.5, 114.4, 110.7, 55.3.

2-bromo styrene (**3d**) Colorless liquid, 64 mg, 70% isolated yield. R_f = 0.79 (hexane = 100), ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 7.47 (d, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 6.91 - 7.10 (m, 2H), 5.63 (d, *J* = 17.1 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, CHLOROFORM-d) δ ppm 137.5, 135.8, 132.9, 129.4, 129.1, 127.5, 126.8, 123.6, 116.7, 77.3, 77.0, 76.7.

3-methyl styrene (**3e**) Colorless liquid, 38 mg, 80% isolated yield. R_f = 0.5 (hexane = 100), ^{1}H NMR (500 MHz, CHLOROFORM-d) δ ppm 7.36 (d, *J* = 4.6 Hz, 3H), 7.12 - 7.27 (m, 1H), 6.84 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.78 - 5.97 (m, 1H), 5.37 (d, *J* = 11.1 Hz, 1H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, CHLOROFORM-d) δ ppm 138.1, 137.7, 137.1, 128.7, 128.5, 127.1, 123.5, 113.6, 77.4, 77.2, 76.9, 21.5.

1-chloro-3-vinylbenzene (**3f**)[25] Colorless liquid, 36 mg, 53% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.38 (s, 1H), 7.33 - 7.13 (m, 3H), 6.65 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 139.4, 135.6, 134.5, 129.7, 127.7, 126.1, 124.4, 115.3.

3-vinylaniline (**3g**) Yellow liquid, 21 mg, 35% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.17 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.83 - 6.43 (m, 3H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 3.61 (s, 2H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 146.4, 138.5, 136.9, 129.3, 116.7, 114.7, 113.5, 112.6.

3-nitro styrene (**3h**) Yellow liquid, 33 mg, 44% isolated yield. R_f = 0.39 (hexane: ethyl acetate = 9:1), ^{1}H NMR (200 MHz, CHLOROFORM-d) δ ppm 8.22 (s, 1H), 8.08 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.5 Hz, 1H), 5.43 (d, *J* = 10.8 Hz, 1H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ ppm 148.6, 139.2, 134.7, 132.1, 129.5, 122.4, 120.8, 117.05, 77.8, 77.1, 76.5.

1-tert-butyl-4-vinylbenzene (**3i**)[12c] Colorless liquid, 47 mg, 59% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.55 - 7.59 (m, 4H), 6.86 - 7.01 (m, 1H), 5.93 (dd, *J* = 1.0, 17.6 Hz, 1H), 5.41 (dd, *J* = 1.0, 10.9 Hz, 1H), 1.53 (s, 9H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 150.6, 136.7, 134.8, 126.0, 125.3, 112.7, 34.4, 31.2.

1-methoxy-4-vinylbenzene (**3j**)[12a] Colorless liquid, 50 mg, 75% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.52 - 7.30 (m, 2H), 7.01 - 6.84 (m, 2H), 6.73 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.67 (dd, *J* = 0.9, 17.6 Hz, 1H), 5.19 (dd, *J* = 0.9, 10.9 Hz, 1H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 159.3, 136.2, 130.4, 127.3, 113.8, 111.5, 55.2.

1-tert-butoxy-4-vinylbenzene (**3k**)[27] Colorless liquid, 55 mg, 63% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.57 - 7.30 (m, 2H), 7.18 - 6.96 (m, 2H), 6.79 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.76 (dd, *J* = 0.9, 17.6 Hz, 1H), 5.27 (dd, *J* = 0.9, 10.9 Hz, 1H), 1.46 (s, 9 H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 155.1, 136.1, 132.3, 126.4, 123.6, 111.9, 77.8, 28.5.

methyl(4-vinylphenyl)sulfane (**3l**)[28] Yellow liquid, 52 mg, 70% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.34 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 4.6, 8.4 Hz, 3H), 6.68 (dd, *J* = 11.1, 17.5 Hz, 1H), 5.72 (d, *J* = 17.5 Hz, 1H), 5.22 (d, *J* = 10.7 Hz, 1H), 2.50 (s, 4 H). ^{13}C{^{1}H} NMR (126 MHz, CHLOROFORM-d) δ = 138.0, 136.2, 134.6, 113.2, 15.8.

4-vinylbiphenyl (**3m**)[29] Colorless liquid, 61 mg, 68% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.84 - 7.30 (m, 9H), 6.78 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.81 (dd, *J* = 0.8, 17.6 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 140.7, 140.6, 136.6, 136.4, 128.8, 127.3, 127.2, 126.9, 126.6, 113.9.

1-fluoro-4-vinylbenzene (**3n**)[12a] Colorless liquid, 37 mg, 61% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.56 - 7.34 (m, 2H), 7.19 - 6.93 (m, 2H), 6.72 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.70 (d, *J* = 17.6 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H). ^{13}C{^{1}H} NMR (50 MHz, CHLOROFORM-d) δ = 162.4 (d, $J_{C\text{-}F}$ = 245 Hz),135.6, 133.6 (d, $J_{C\text{-}F}$ = 5 Hz), 127.7(d, $J_{C\text{-}F}$ = 5 Hz), 115.3(d, $J_{C\text{-}F}$ = 20 Hz), 113.3.

1-bromo-4-vinylbenzene (**3o**)[12b] Colorless liquid, 57 mg, 63% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.61 - 7.33 (m, 2H), 7.32 - 7.13 (m, 2H), 6.64 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.73 (dd, *J* = 0.7, 17.6

Hz, 1H), 5.34 - 5.16 (m, 1H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 136.4, 135.7, 131.6, 127.7, 121.5, 114.5.

1-vinylnaphthalene (**3p**)[12a] Colorless liquid, 52 mg, 68% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 8.36 - 8.08 (m, 1H), 8.08 - 7.79 (m, 2H), 7.79 - 7.36 (m, 5H), 5.86 (dd, *J* = 1.5, 17.3 Hz, 1H), 5.54 (dd, *J* = 1.5, 10.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 135.6, 134.3, 133.5, 131.1, 128.5, 128.1, 126.0, 125.7, 125.6, 123.7, 123.6, 117.1.

2-vinylnaphthalene (**3q**)[12a] Colorless liquid, 58 mg, 75% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.97 - 7.74 (m, 4H), 7.74 - 7.62 (m, 1H), 7.56 - 7.40 (m, 2H), 6.92 (dd, *J* = 10.9, 17.6 Hz, 1H), 5.90 (dd, *J* = 0.8, 17.6 Hz, 1H), 5.37 (dd, *J* = 0.6, 10.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 136.9, 135.0, 133.1, 128.1, 128.0, 127.6, 126.3, 126.2, 125.9, 123.2, 114.1.

1,2-dimethoxy-4-vinylbenzene (**3r**)[12a] Colorless liquid, 58 mg, 71% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.01 - 6.92 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 10.7, 17.5 Hz, 1H), 5.62 (d, *J* = 17.5 Hz, 1H), 5.16 (d, *J* = 10.7 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 149.0, 149.0, 136.5, 130.7, 119.4, 111.8, 111.0, 108.5, 55.9, 55.8.

2-vinyl thiophene (**3s**)[12b] Colorless liquid, 17 mg, 31% isolated yield. R_f = 0.5 (hexane = 100), ^{1}H NMR (200 MHz, CHLOROFORM-d) δ ppm 7.04 - 7.16 (m, 1H), 6.85 - 7.03 (m, 2H), 6.75 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.50 (d, *J* = 17.3 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H).

3-vinyl pyridine (**3t**)[12b] Colorless liquid, 20 mg, 39%. R_f = 0.3 (hexane: ethyl acetate = 9:1), ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 8.60 (d, *J* = 4.3 Hz, 1H), 7.60 - 7.87 (m, 1H), 7.37 (d, *J* = 7.9 Hz, 1H), 7.18 (dd, *J* = 7.0, 5.2 Hz, 1H), 6.84 (dd, *J* = 17.1, 10.9 Hz, 1H), 6.22 (d, *J* = 17.1 Hz, 1H), 5.51 (d, *J* = 10.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CHLOROFORM-d) δ ppm 155.7, 149.5, 136.9, 136.5, 122.4, 121.2, 118.2.

prop-1-en-2-ylbenzene (**3u**)[26] Colorless liquid, 34 mg, 57% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.66 - 7.54 (m, 2H), 7.50 - 7.34 (m, 3H), 5.48 (dd, *J* = 0.8, 1.5 Hz, 1H), 5.28 - 5.08 (m, 1H), 2.26 (dd, *J* = 0.8, 1.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 143.3, 141.2, 128.2, 127.4, 125.5, 112.4, 21.8.

1-methoxy-4-(prop-1-en-2-yl)benzene (**3v**) Colorless liquid, 46 mg, 62% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 7.43 (brs, 2H), 6.88 (brs, 2H), 5.29 (brs, 1H), 5.00 (brs, 1H), 3.82 (brs, 3H), 2.14 (brs, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 159.0, 142.6, 133.7, 126.6, 113.5, 110.6, 55.3, 21.9. HRMS (EI): *m/z* Calcd for $C_{10}H_{12}O$ $[M+H]^+$: 149.0961; Found: 149.0960.

2-(prop-1-en-2-yl)naphthalene (**3w**) Colorless liquid, 49 mg, 58% isolated yield. R_f = 0.9 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.92 - 7.80 (m, 4H), 7.76 - 7.65 (m, 1H), 7.53 - 7.44 (m, 2H), 5.57 (s, 1H), 5.32 - 5.15 (m, 1H), 2.31 (s, 3H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 143.0, 138.4, 133.4, 132.8, 128.2, 127.7, 127.5, 126.1, 125.8, 124.2, 123.9, 113.0, 21.8. HRMS (EI): *m/z* Calcd for $C_{13}H_{13}$ $[M+H]^+$: 169.1012; Found: 169.1011.

but-1-en-2-ylbenzene (**3x**) Colorless liquid, 34 mg, 50% isolated yield. R_f = 0.30 (hexane= 100), ^{1}H NMR (400 MHz, CHLOROFORM-d) δ ppm 7.45 - 7.50 (m, 2H), 7.23 - 7.45 (m, 6H), 5.33 (s, 1H), 5.12 (d, *J* = 1.2 Hz, 1H), 2.58 (q, *J* = 7.3 Hz, 2H), 1.16 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CHLOROFORM-d) δ ppm 150.1, 141.6, 128.3, 127.3, 126.0, 122.5, 110.9, 77.4, 77.3, 77.1, 76.7, 28.1, 12.9.

ethene-1,1-diyldibenzene (**3y**)[12a] Colorless liquid, 63 mg, 70% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 5.40 (s, 2 H), 7.27 (brs, 10H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 150.0, 141.5, 128.2, 128.1, 127.7, 114.3.

1-methyl-2-(1-phenylvinyl)benzene (**3z**) Colorless liquid, 59 mg, 61% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 7.47 - 7.17 (m, 10H), 5.85 (s, 1H), 5.27 (s, 1H), 2.13 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 149.4, 141.6, 140.6, 136.1, 130.0, 130.0, 128.3, 127.5, 127.5, 126.5, 125.6, 114.8, 77.3, 76.7, 20.1. HRMS (EI): *m/z* Calcd for $C_{15}H_{15}$ $[M+H]^+$: 195.1168; Found: 195.1169.

4,4'-(ethene-1,1-diyl)bis(methoxybenzene) (**3za**) Colorless liquid, 96 mg, 80% isolated yield. R_f = 0.3 (hexane/ethyl acetate = 10/1). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 7.23 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 5H), 5.25 (s, 2H), 3.77 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 159.3, 148.9, 134.3, 129.4, 128.4, 113.7, 113.5, 111.6, 55.3. HRMS (EI): *m/z* Calcd for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1223; Found: 241.1221.

1-methylnaphthalene (**5a**) Colorless liquid, 32 mg, 45% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 8.03 (brs, 1H), 7.88 (brs, 1H), 7.74 (brs, 1H), 7.62 - 7.46 (m, 2H), 7.46 - 7.38 (m, 1H), 7.35 (brs, 1H), 2.73 (brs, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 134.2, 133.5, 132.6, 128.5, 126.5, 126.3, 125.7, 125.5, 125.5, 124.1, 19.4. HRMS (EI): *m/z* Calcd for $C_{11}H_{11}$ $[M+H]^+$: 143.0855; Found: 143.0855.

1-(cyclopentyloxy)-5-methylnaphthalene (**5b**) Colorless liquid, 58 mg, 51% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (500 MHz, CHLOROFORM-d) δ = 8.21 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.43 - 7.35 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.08 - 4.94 (m, 1H), 2.72 (s, 3H), 2.12 - 1.99 (m, 4H), 1.98 - 1.87 (m, 2H), 1.80 - 1.67 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 154.1, 133.8, 133.8, 127.0, 126.3, 125.6, 124.6, 120.5, 115.8, 105.9, 79.5, 77.3, 76.7, 32.9, 24.2, 19.8. HRMS (EI): *m/z* Calcd for $C_{16}H_{19}O$ $[M+H]^+$: 227.1430; Found: 227.1431.

1-butoxy-5-methylnaphthalene (**5c**) Colorless liquid, 62 mg, 58% isolated yield. R_f = 0.3 (hexane = 100). ^{1}H NMR (200 MHz, CHLOROFORM-d) δ = 8.37 - 8.07 (m, 1H), 7.70 - 7.53 (m, 1H), 7.53 - 7.29 (m, 3H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.17 (t, *J* = 6.3 Hz, 2H), 2.71 (s, 3H), 2.05 - 1.86 (m, 2H), 1.80 - 1.54 (m, 2H), 1.17 - 0.93 (m, 3H). $^{13}C\{^{1}H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 155.3, 133.8, 127.1, 125.7, 124.7, 120.3, 116.2, 104.4, 67.9, 31.4, 19.8, 19.5, 13.9. HRMS (EI): *m/z* Calcd for $C_{15}H_{19}O$ $[M+H]^+$: 215.1430; Found: 215.1429.

1-methyl-5-(nonyloxy)naphthalene (**5d**) Colorless liquid, 86 mg, 61% isolated yield. R_f = 0.3 (hexane: ethyl acetate = 10:1). ^{1}H NMR (400 MHz, CHLOROFORM-d) δ = 8.21 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.51 - 7.30 (m, 3H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 2.70 (s, 3H), 2.03 - 1.84 (m, 2H), 1.58 (d, *J* = 7.3 Hz, 2H), 1.49 - 1.20 (m, 11H), 0.96 - 0.82 (m, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz,

CHLOROFORM-d) δ = 155.3, 133.8, 133.6, 127.1, 125.8, 125.7, 124.7, 120.3, 116.1, 104.4, 77.3, 76.7, 68.2, 31.9, 29.6, 29.4, 29.3, 26.3, 22.7, 19.8, 14.1. HRMS (EI): *m/z* Calcd for $C_{20}H_{29}O$ $[M+H]^+$: 285.2213; Found: 285.2212.

1-(benzyloxy)-5-methylnaphthalene (**5e**) Colorless liquid, 59 mg, 48% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (200 MHz, CHLOROFORM-d) δ = 8.50 - 8.14 (m, 1H), 7.72 - 7.12 (m, 10H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.28 (s, 2H), 2.90 - 2.48 (m, 3H). $^{13}C\{^1H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 154.9, 137.2, 133.9, 133.7, 128.6, 127.9, 127.3, 127.2, 125.9, 125.6, 124.9, 120.4, 116.7, 105.1, 70.1, 19.8. HRMS (EI): *m/z* Calcd for $C_{18}H_{17}O$ $[M+H]^+$: 249.1274; Found: 249.1272.

1-methyl-5-(2-methylbenzyloxy)naphthalene (**5f**) Colorless liquid, 68 mg, 52% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.22 (dd, *J* = 3.0, 6.6 Hz, 1H), 7.67 - 7.59 (m, 1H), 7.57 - 7.52 (m, 1H), 7.45 (dd, *J* = 7.8, 8.7 Hz, 1H), 7.39 - 7.34 (m, 2H), 7.30 - 7.25 (m, 3H), 6.97 (d, *J* = 7.3 Hz, 1H), 5.24 (s, 2H), 2.70 (s, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 155.1, 136.8, 135.1, 134.0, 133.8, 130.5, 128.6, 128.3, 127.3, 126.1, 125.9, 125.7, 125.0, 120.5, 116.8, 105.0, 68.8, 19.9, 19.0. HRMS (EI): *m/z* Calcd for $C_{19}H_{19}O$ $[M+H]^+$: 263.1430; Found: 263.1429.

1-methyl-5-(3-methylbenzyloxy)naphthalene (**5g**) Colorless liquid, 72 mg, 55% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (500 MHz, CHLOROFORM-d) δ = 8.28 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.49 - 7.28 (m, 6H), 7.19 (d, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 2H), 2.71 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 155.0, 138.2, 137.1, 133.9, 133.7, 128.6, 128.5, 128.1, 127.2, 125.8, 125.6, 124.9, 124.4, 120.4, 116.7, 105.1, 77.3, 76.7, 70.2, 21.5, 19.8. HRMS (EI): *m/z* Calcd for $C_{19}H_{19}O$ $[M+H]^+$: 263.1430; Found: 263.1428.

1-methyl-5-(4-methylbenzyloxy)naphthalene (**5h**) Colorless liquid, 74 mg, 57% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (500 MHz, CHLOROFORM-d) δ = 8.28 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.53 - 7.31 (m, 5H), 7.25 (s, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 5.25 (s, 2H), 2.72 (s, 3H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CHLOROFORM-d) δ = 155.0, 137.6, 134.2, 133.8, 133.7, 129.2, 127.5, 127.2, 125.8, 125.6, 124.8, 120.4, 116.6, 105.1, 70.1, 21.2, 19.8. HRMS (EI): *m/z* Calcd for $C_{19}H_{19}O$ $[M+H]^+$: 263.1430; Found: 263.1429.

1-(4-methoxybenzyloxy)-5-methylnaphthalene (**5i**) Colorless liquid, 76 mg, 55% isolated yield. R_f = 0.3 (hexane: ethyl acetate = 10:1). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.25 (dd, *J* = 2.1, 7.6 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.52 - 7.32 (m, 5H), 7.01 - 6.91 (m, 3H), 5.20 (s, 2H), 3.86 (s, 3H), 2.71 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 159.3, 154.9, 133.8, 133.7, 129.2, 129.0, 127.2, 125.8, 125.6, 124.8, 120.4, 116.6, 113.9, 105.0, 69.9, 55.3, 19.8. HRMS (EI): *m/z* Calcd for $C_{19}H_{19}O_2$ $[M+H]^+$: 279.1380; Found: 279.1379.

1-methyl-5-(1-phenylethoxy)naphthalene (**5j**) Colorless liquid, 95 mg, 73% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.36 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.48 - 7.38 (m, 3H), 7.38 - 7.30 (m, 3H), 7.30 - 7.20 (m, 2H), 6.69 (d, *J* = 7.6 Hz, 1H), 5.53 (d, *J* = 6.9 Hz, 1H), 2.67 (s, 3H), 1.77 (d, *J* = 6.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 153.8, 143.3, 133.9, 133.7, 128.6, 127.4, 127.0, 126.1, 125.5, 125.4, 124.8, 120.4, 116.3, 106.8, 76.1, 24.6, 19.8. HRMS (EI): *m/z* Calcd for $C_{19}H_{19}O$ $[M+H]^+$: 263.1430; Found: 263.1428.

(E)-1-methyl-5-(prop-1-enyloxy)naphthalene (**5k**) Colorless liquid, 56 mg, 57% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.22 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.51 - 7.33 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.57 (dd, *J* = 1.6, 6.2 Hz, 1H), 5.01 (dd, *J* = 6.0, 6.9 Hz, 1H), 2.71 (s, 3H), 1.84 (dd, *J* = 1.8, 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 153.7, 141.1, 134.0, 133.8, 127.3, 125.7, 125.5, 125.2, 120.1, 118.2, 108.1, 107.9, 19.8, 9.5. HRMS (EI): *m/z* Calcd for $C_{14}H_{15}$ $[M+H]^+$: 199.1117; Found: 199.1118.

1-methyl-5-(pent-4-enyloxy)naphthalene (**5l**) Colorless liquid, 70 mg, 62% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.22 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.50 - 7.33 (m, 3H), 6.85 (d, *J* = 7.3 Hz, 1H), 6.09 - 5.80 (m, 1H), 5.23 - 4.94 (m, 2H), 4.17 (t, *J* = 6.1 Hz, 2H), 2.70 (s, 3H), 2.39 (q, *J* = 7.1 Hz, 2H), 2.17 - 2.00 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 155.2, 137.9, 133.9, 133.7, 127.1, 125.8, 125.7, 124.8, 120.3, 116.3, 115.3, 104.5, 76.7, 67.3, 30.4, 28.5, 19.8. HRMS (EI): *m/z* Calcd for $C_{16}H_{19}O$ $[M+H]^+$: 227.1430; Found: 227.1430.

6-methoxy-1-methylnaphthalene (**5m**) Colorless liquid, 56 mg, 65% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 7.96 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.35 - 7.12 (m, 3H), 3.97 (s, 3H), 2.72 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 157.3, 134.8, 134.2, 128.0, 126.2, 125.7, 125.3, 124.5, 118.2, 106.5, 55.2, 19.3. HRMS (EI): *m/z* Calcd for $C_{12}H_{13}O$ $[M+H]^+$: 173.0961; Found: 173.0961.

1-methyl-7-(4-(trifluoromethyl)phenyl)naphthalene (**5n**) Colorless liquid, 102 mg, 72% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.20 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.88 - 7.82 (m, 2H), 7.80 - 7.70 (m, 4H), 7.47 - 7.35 (m, 2H), 2.77 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 145.2, 137.1, 134.8, 133.1, 132.8, 129.6 (t, J_{C-F} = 31.0 Hz), 129.5, 127.9, 127.4, 127.2, 126.3, 126.2, 125.9 (t, J_{C-F} = 2.8 Hz), 125.0, 123.1, 122.9 (t, J_{C-F} = 214.7 Hz), 19.5. HRMS (EI): *m/z* Calcd for $C_{18}H_{14}F_3$ $[M]^+$: 287.1042; Found: 287.1034.

7-(3-fluorophenyl)-1-methylnaphthalene (**5o**) Colorless liquid, 70 mg, 60% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (400 MHz, CHLOROFORM-d) δ = 8.24 - 8.12 (m, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.82 - 7.67 (m, 2H), 7.58 - 7.35 (m, 7H), 2.78 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, CHLOROFORM-d) δ = 163.2 (d, J_{C-F} = 214.7 Hz), 163.1 (d, J_{C-F} = 245.0 Hz), 143.9 (d, J_{C-F} = 7.6 Hz), 143.4, 138.3, 137.6, 137.1, 134.6, 132.9, 132.7, 130.3 (d, J_{C-F} = 7.6 Hz), 129.7, 129.4, 129.2, 128.0, 127.6, 127.3, 127.2, 126.3, 126.1, 126.0, 125.4, 125.1, 124.9, 124.5, 123.1, 122.5, 122.4, 114.3 (d, J_{C-F} = 22 Hz),114.0, (d, J_{C-F} = 21.0 Hz), 113.6, 113.5, 29.7, 29.5, 29.1, 27.6, 27.1, 23.2, 19.5. HRMS (EI): *m/z* Calcd for $C_{17}H_{13}F$ $[M]^+$: 236.0996; Found: 236.0988.

1,4-dimethylnaphthalene (**5p**) Colorless liquid, 37 mg, 48% isolated yield. R_f = 0.3 (hexane = 100). ^1H NMR (200 MHz, CHLOROFORM-d) δ = 8.06 - 7.68 (m, 2H), 7.63 - 7.33 (m, 2H), 7.11 (s, 2H), 2.56 (s, 6H). $^{13}C\{^1H\}$ NMR (50 MHz, CHLOROFORM-d) δ = 132.7, 132.3, 126.2, 125.3, 124.6, 77.6, 76.4, 19.3. HRMS (EI): *m/z* Calcd for $C_{12}H_{13}$ $[M+H]^+$: 157.1012; Found: 157.1012.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org." and includes:

Mechanistic studies and copy of ^{1}H and ^{13}C NMR spectra.

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ACKNOWLEDGMENT

This work was supported by the SERB, India (CRG/2018/002480), and IISER Tirupati. VY and MS acknowledges UGC, India for research fellowships. RB acknowledges IISER-Tirupati for research fellowship.

REFERENCES

(1) (a) Dumeunier, R.; Marko, I. E., in Modern Carbonyl Olefination, ed. T. Takeda, Wiley-VCH, Weinheim, **2004**, 104–161. (b) Kocienski, P. J. in Comprehensive Organic Synthesis, ed. Trost, B. M.; Fleming, I., **1991**, *6*, 987–1000.

(2) (a) Maryanoff, B. E.; Reitz, A. B. The Wittig Olefination Reaction and Modifications Involving Phosphoryl-Stabilized Carbanions. Stereochemistry, Mechanism, and Selected Synthetic Aspects. *Chem. Rev.* **1989**, *89*, 863-927. (b) Li, C.-Y.; Wang, X.-B.; Sun, X.-L.; Tang, Y.; Zheng, J.-C.; Xu, Z.-H.; Zhou, Y.-G.; Dai, L.-X. Iron Porphyrin-Catalyzed Olefination of Ketenes with Diazoacetate for the Enantioselective Synthesis of Allenes. *J. Am. Chem. Soc.* **2007**, *129*, 1494-1995. (c) Wang, S. R.; Zhu, C.-Y.; Sun, X.-L.; Tang, Y. Reaction of Allylic Phosphoranes with Iron Porphyrin Carbenoids: Efficient, Selective, and Catalytic Intermolecular Formal Carbenoid Insertion into Olefinic C−H Bonds. *J. Am. Chem. Soc.* **2009**, *131*, 4192-413 (d) Dong, D.-J.; Li H.-H.; Tian, S.-K. A Highly Tunable Stereoselective Olefination of Semistabilized Triphenylphosphonium Ylides with N-Sulfonyl Imines. *J. Am. Chem. Soc.* **2010**, *132*, 5018-5020.

(3) (a) Horner, L.; Hoffmann, H.; Wipel, H. C.; Klahre, G., Organophosphorus Compounds, XX. Phosphine Oxides as Olefining Agents. *Chem. Ber.* **1959**, *92*, 2499-2505. (b) van Steenis, J. H.; van Es J. J. G. S.; van der Gen, A. Stereoselective Synthesis of (E)-Vinyl Sulfoxides by the Horner−Wittig Reaction. *Eur. J. Org. Chem.* **2000**, 2787-2793.

(4) (a) Wadsworth, W. S.; Emmons, W. D. The Utility of Phosphonate Carbanions in Olefin Synthesis. *J. Am. Chem. Soc.* **1961**, *83*, 1733-1738. (b) Boutagy, J.; Thomas, R. Olefin Synthesis with Organic Phosphonate Carbanions. *Chem. Rev.* **1974**, *74*, 87-99.

(5) (a) Peterson, D. J. Carbonyl Olefination Reaction Using Silyl-Substituted Organometallic Compounds. *J. Org. Chem.* **1968**, *33*, 780-784. (b) van Staden, L. F.; Gravestock, D.; Ager, D. J. New Developments in the Peterson Olefination Reaction. *Chem. Soc. Rev.* **2002**, *31*, 195-200.

(6) (a) Zhao, Y.; Gao, B.; Hu, J. From Olefination to Alkylation: In-Situ Halogenation of Julia–Kocienski Intermediates Leading to Formal Nucleophilic Iodo- and Bromodifluoromethylation of Carbonyl Compounds. *J. Am. Chem. Soc.* **2012**, *134*, 5790-5793. (b) Blakemore, P. R. The Modified Julia Olefination: Alkene Synthesis via the Condensation of Metallated Heteroarylalkylsulfones with Carbonyl Compounds. *J. Chem. Soc. Perkin Trans.* 1, **2002**, 2563-2585.

(7) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. Olefin Homologation with Titanium Methylene Compounds. *J. Am. Chem. Soc.* **1978**, *100*, 3611-3613.

(8) (a) Lebel, H.; Paquet, V. Multicatalytic Processes Using Diverse Transition Metals for the Synthesis of Alkenes. *J. Am. Chem. Soc.* **2004**, *126*, 11152-11153. (b) Davi, M.; Lebel, H. Copper-Catalyzed Tandem Oxidation−Olefination Process. *Org. Lett.* **2009**, *11*, 41-44. (c) Lebel, H.; Paquet, V.; Proulx, C. Methylenation of Aldehydes: Transition Metal Catalyzed Formation of Salt-Free Phosphorus Ylides. *Angew. Chem., Int. Ed.* **2001**, *40*, 2887-2890. (d) Lebel, H.; Ladjel, C.; Bréthous, L. Palladium-Catalyzed Cross-Coupling Reactions in One-Pot Multicatalytic Processes. *J. Am. Chem. Soc.* **2007**, *129*, 13321-13326. (e) Lebel, H.; Ladjel, C. Iridium Complexes in Olefination Reactions. *Organometallics* **2008**, *27*, 2676-2678. (f) Alonso, F.; Riente, P.; Yus, M. Wittig-Type Olefination of Alcohols Promoted by Nickel Nanoparticles: Synthesis of Polymethoxylated and Polyhydroxylated Stilbenes. *Eur. J. Org. Chem.* **2009**, *34*, 6034-6042.

(9) Bruggink, A.; Schoevaart, R.; Kieboom, T. Concepts of Nature in Organic Synthesis: Cascade Catalysis and Multistep Conversions in Concert. *Org. Process Res. Dev.* **2003**, *7*, 622-640.

(10) For recent representative reviews on acceptorless dehydrogenation (ADH) reactions, see: (a) Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Acc. Chem. Res.* **2018**, *51*, 1558-1569. (b) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M. Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **2018**, 118, 372-433. (c) Crabtree, R. H. Homogeneous Transition Metal Catalysis of Acceptorless Dehydrogenative Alcohol Oxidation: Applications in Hydrogen Storage and to Heterocycle Synthesis. *Chem. Rev*. **2017**, *117*, 9228-9246. (d) Kumar, A.; Bhatti, T. M.; Goldman, A. S. Dehydrogenation of Alkanes and Aliphatic Groups by Pincer-Ligated Metal Complexes. *Chem. Rev.* **2017**, *117*, 12357-12384. (e) Thoi, V. S.; Sun, Y.; Long, J. R.; Chang, C. J. Complexes of Earth-Abundant Metals ffor Catalytic Electrochemical Hydrogen Generation under Aqueous Conditions. *Chem. Soc. Rev.* **2013**, *42*, 2388-2400. (f) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 1229712. (g) Dobereiner, G. E.; Crabtree, R. H. Dehydrogenation as a Substrate-Activating Strategy in Homogeneous Transition-Metal Catalysis. *Chem. Rev.* **2010**, *110*, 681-703.

(11) For selected recent reviews on non-precious 3d-transition metal catalyzed AD and HA reactions, see: (a) Guillena, G.; Ramln, D. J.; Yus, M. Hydrogen Autotransfer in the N-Alkylation of Amines and Related Compounds using Alcohols and Amines as Electrophiles. *Chem. Rev.* **2010**, *110,* 1611-1641. (b) Werkmeister, S.; Neumann, J.; Junge, K.; Beller, M. Pincer-Type Complexes for Catalytic (De)Hydrogenation and Transfer (De)Hydrogenation Reactions: Recent Progress. *Chem. Eur. J.* **2015**, *21*, 12226-12250. (c) Garbe, M.; Junge, K.; Beller, M. Homogeneous Catalysis by Manganese-Based Pincer Complexes. *Eur. J. Org. Chem.* **2017**, 4344-4362. (d) Balaraman, E.; Nandakumar, A.; Jaiswal, G.; Sahoo, M. K. Iron-Catalyzed Dehydrogenation Reactions and their Applications in Sustainable Energy and Catalysis. *Catal. Sci. Technol.* **2017**, *7*, 3177-3195. (e) Maji, B.; Barman, M. K. Recent Developments of Manganese Complexes for Catalytic Hydrogenation and Dehydrogenation Reactions. *Synthesis* **2017**, *49*, 3377-3393. (f) Kallmeier, F.; Kempe, R. Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angew. Chem. Int. Ed.* **2018**, *57*, 46-60. (g) Filonenko, G.A.; van Putten, R.; Hensena, E. J. M.; Pidko, E. A. Catalytic (De)hydrogenation Promoted by Non-precious Metals – Co, Fe and Mn: Recent Advances in an Emerging Field. *Chem. Soc. Rev.* **2018**, *47*, 1459-1483. (h) Kulkarni, N. V.; Jones, W. D., Chemistry of Mn and Co Pincer Compounds, **2018**, 491-518. (in Pincer Compounds

Chemistry and Applications, Ed. D. Morales-Morales; Elsevier, 1st ed; Amsterdam).
(12) (a) Srimani, D.; Leitus, G.; Ben-David, Y.; Milstein, M. Direct Catalytic Olefination of Alcohols with Sulfones. *Angew. Chem., Int. Ed.* **2014**, *53*, 11092-11095. (b) Siddiki, S. M. A. H.; Touchy, A. S.; Kon, K.; Shimizu, K. I. Direct Olefination of Alcohols with Sulfones by Using Heterogeneous Platinum Catalysts. *Chem. Eur. J.* **2016**, *22*, 6111-6119. (c) Yao, C. Z.; Li, Q. Q.; Wang, M. M.; Ninga, X. S.; Kang, Y. B. (E)-Specific Direct Julia-Olefination of Aryl Alcohols Without Extra Reducing Agents Promoted by Bases. *Chem. Commun*., **2015**, *51*, 7729 -7732. (d) Landge, V. G.; Yadav, V.; Subaramanian, M.; Dangarh, P.; Balaraman, E. Nickel(II)-Catalyzed Direct Olefination of Benzyl Alcohols with Sulfones with the Liberation of H_2. *Chem. Commun.* **2019**, *55*, 6130-6133. (c) Waiba, S.; Das, A.; Barman, M. K.; Maji, B. Base Metal-Catalyzed Direct Olefinations of Alcohols with Sulfones. *ACS Omega* **2019**, *4*, 7082-7087.
(13) (a) Albrecht, M.; Bedford, R.; Plietker, B. Catalytic and Organometallic Chemistry of Earth-Abundant Metals. *Organometallics* **2014**, *33*, 5619-5621. (b) Bullock, R.M.; Catalysis without Precious Metals; Wiley- VCH: Weinheim, **2010.**
(14) Representative examples of Fe-catalyzed acceptorless-dehydrogenation strategy and related reactions: (a) Yang, J.; Liu, X.; Meng, D.-L.; Chen, H.-Y.; Zong, Z.-H.; Feng, T.-T.; Sun, K. Efficient Iron-Catalyzed Direct β-Alkylation of Secondary Alcohols with Primary Alcohols. *Adv. Synth. Catal.* **2012**, *354*, 328-334. (b) Yan, T.; Feringa, B. L.; Barta, K. Iron Catalysed Direct Alkylation of Amines with Alcohols. *Nat. Commun.* **2014**, *5*, 5602-5609. (c) Bielinski, E. A.; Förster, M.; Zhang, Y.; Bernskoetter, W. H.; Hazari, N.; Holthausen, M. C. Base-Free Methanol Dehydrogenation Using a Pincer-Supported Iron Compound and Lewis Acid Co-catalyst. *ACS Catal.* **2015**, *5*, 2404-2415. (d) Rawlings, A. J.; Diorazio, L. J.; Wills, M. C–N Bond Formation between Alcohols and Amines Using an Iron Cyclopentadienone Catalyst. *Org. Lett.* **2015**, *17*, 1086-1089. (e) Elangovan, S.; Sortais, J.-B.; Beller, M.; Darcel, C. Iron-Catalyzed α-Alkylation of Ketones With Alcohols. *Angew. Chem. Int. Ed.* **2015**, *54*, 14483-14486. (f) Yan, T.; Feringa, B. L.; Barta, K. Benzylamines via Iron-Catalyzed Direct Amination of Benzyl Alcohols. *ACS Catal.* **2016**, *6*, 381-388. (g) Emayavaramban, B.; Roy, M.; Sundararaju, B. Iron-Catalyzed Allylic Amination Directly from Allylic Alcohols. *Chem. Eur. J.* **2016**, *22*, 3952-3955. (h) Mastalir, M.; Stöger, B.; Pittenauer, E.; Puchberger, M.; Allmaier, G.; Kirchner, K. Air Stable Iron(II) PNP Pincer Complexes as Efficient Catalysts for the Selective Alkylation of Amines with Alcohols. *Adv. Synth. Catal.* **2016**, *358*, 3824-3831. (i) Ma, W.; Zhang, X.; Fan, J.: Liu, Y.; Tang, W.; Xue, D.; Li, C.; Xiao, J.; Wang, C. Iron-Catalyzed Anti-Markovnikov Hydroamination and Hydroamidation of Allylic Alcohols. *J. Am. Chem. Soc.* **2019**, 141, 13506-13515. (j) Ma, W.; Cui, S.; Sun, H.; Tang, W.; Xue, D.; Li, C.; Fan, J.; Xiao, J.; Wang C. Iron-Catalyzed Alkylation of Nitriles with Alcohols. *Chem. Eur. J.* **2018**, 24, 13118 - 13123.
(15) (a) Bauer, I.; Knölker, H.-J. Iron Catalysis in Organic Synthesis. *Chem. Rev.* **2015**, *115*, 3170-3387. (b) Morris., R. H. Exploiting Metal–Ligand Bifunctional Reactions in the Design of Iron Asymmetric Hydrogenation Catalysts. *Acc. Chem. Res.* **2015**, *48*, 1494-1502. (c) Chirik, P.J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. *Acc. Chem. Res.* **2015**, *48*, 1687-1695. (d) Zell, T.; Milstein, D. Hydrogenation and Dehydrogenation Iron Pincer Catalysts Capable of Metal–Ligand Cooperation by Aromatization/Dearomatization. *Acc. Chem. Res.* **2015**, *48*, 1979-1994. (e) Chakraborty, S.; Bhattacharya, P.; Dai, H.; Guan, H. Nickel and Iron Pincer Complexes as Catalysts for the Reduction of Carbonyl Compounds. *Acc. Chem. Res.* **2015**, *48*, 1995-2003. (f) McNeil, W.; Ritter, T. 1,4-Functionalization of 1,3-Dienes with Low-Valent Iron Catalysts. *Acc. Chem. Res*. **2015**, *48*, 2330-2343. (g) Benito-Garagorri, D.; Kirchner, K. Modularly Designed Transition Metal PNP and PCP Pincer Complexes based on Aminophosphines: Synthesis and Catalytic Applications. *Acc. Chem. Res.* **2008**, *41*, 201-213.
(16) (a) Gopalaiah, K. Chiral Iron Catalysts for Asymmetric Synthesis. *Chem. Rev.* **2013**, *113*, 3248-3296. (b) Darwish, M., Wills, M. Asymmetric Catalysis using Iron Cmplexes – 'Ruthenium Lite'?. *Catal. Sci. Technol.* **2012**, *2*, 243-255. (c) Enthaler, S.; Junge, K.; Beller, M. Sustainable Metal Catalysis with Iron: From Rust to a Rising Star?. *Angew. Chem., Int. Ed*. **2008**, *47*, 3317-3321. (d) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. Iron-Catalyzed Reactions in Organic Synthesis. *Chem. Rev.* **2004**, *104*, 6217-6254.
(17) For applications of naphthalene scaffold, see: (a) Bhosale, S. V.; Janiab, C. H.; Langford, S. J. Chemistry of naphthalene diimides. *Chem. Soc. Rev.* **2008**, *37*, 331-342. (b) Gil, J. F.; Ramh, D. J.; Yus, M. Reductive Opening of 2-Phenyl-1,3-Dioxolanes by a Naphthalene-Catalysed Lihiation: Synthetic Applications. *Tetrahedron* **1993**, *49*, 9535-9546. (c) Oberwinkler, S.M.; Wetzel, M.; Ziegler, E.; Kruchten, P.; Werth, R.; Henn, C.; Hartmann, R. W.; Frotscher, M. New Drug-Like Hydroxyphenylnaphthol Steroidomimetics As Potent and Selective 17β-Hydroxysteroid Dehydrogenase Type 1 Inhibitors for the Treatment of Estrogen-Dependent Diseases. *J. Med. Chem.* **2011**, *54*, 534-547.
(18) Koning, C. B. D.; Rousseau, A. L.; Otterlo, W. A. L. V. Modern Methods for the Synthesis of Substituted Naphthalenes. *Tetrahedron* **2003**, *59*, 7-36.
(19) (a) Jennerjahn, R.; Jackstell, R.; Piras, I.; Franke, R.; Jiao, H.; Bauer, M.; Beller, M. Benign Catalysis with Iron: Unique Selectivity in Catalytic Isomerization Reactions of Olefins. *ChemSusChem* **2012**, *5*, 734-739. (b) Mayer, M.; Welther, A.; von Wangelin, A. J. Iron-Catalyzed Isomerizations of Olefins. *ChemCatChem* **2011**, *3*, 1567-1571. (c) Marcelo Vilches-Herrera, M.; Domke, L.; Börner, A. Isomerization–Hydroformylation Tandem Reactions. *ACS Catal.* **2014**, *6*, 1706-1724. (d) Hassam, M.; Taher, A.; Arnott, G. E.; Green, I. R.; van Otterlo, W. A. L. Isomerization of Allylbenzenes. *Chem. Rev.* **2015**, *115*, 5462-5569. (e) Sawyer, K. R.; Glascoe, E. A.; Cahoon, J. F.; Schlegel, J. P.; Harris, C. B. Mechanism for Iron-Catalyzed Alkene Isomerization in Solution. *Organometallics* **2008**, *27*, 4370-4379.
(20) Casey, C. P.; Cyr, C. R. Iron Carbonyl Catalyzed Isomerization Of 3-Ethyl-1-Pentene. Multiple Olefin Isomerizations via a π-Allyl Metal Hydride Intermediate. *J. Am. Chem. Soc*. **1973**, *95*, 2248-2253.
(21) See Supporting Information.
(22) (a) Elangovan, S.; Sortais, J.-B.; Beller, M.; Darcel, C. Iron-Catalyzed α-Alkylation of Ketones with Alcohols. *Angew. Chem., Int. Ed.* **2015**, *54*, 14483-14486. (b) Seck, C.; Mbaye, M. D.; Coufourier, S.; Lator, A.; Lohier, J.-F.; Poater, A.; Ward, T. R.; Gaillard, S.; Renaud, J.-L. Alkylation of Ketones Catalyzed by Bifunctional Iron Complexes: From Mechanistic Understanding to Application. *ChemCatChem* **2017**, *9*, 4410-4416. (c) Das, J.; Vellakkaran, M.; Sk, M.; Banerjee, D. Iron-Catalyzed Coupling of Methyl N-Heteroarenes with Primary Alcohols: Direct Access to E-Selective Olefins. *Org. Lett*. **2019**, *21*, 7514-7518. (d) Alanthadka, A.; Bera, S.; Debasis Banerjee, D. Iron-Catalyzed Ligand Free α-Alkylation of Methylene Ketones and β-Alkylation of Secondary Alcohols Using Primary Alcohols. *J. Org. Chem*. **2019**, *84*, 11676-11686. (e) Lapinte, C.; Astruc, D. Stepwise Reduction of Iron(II) Co-ordinated CO by NaBH4. Access to New Hydroxymethyl and Hydride Complexes. *J. Chem. Soc. Chem. Commun*. **1983**, 430-431. (f) Knölker, H.-J.; Baum, E.; Goesmann, H.; Rüdiger Klauss, R. Demetalation of Tricarbonyl(cyclopentadienone)iron Complexes Initiated by a Ligand Exchange Reaction with NaOH: X-Ray Analysis of a Complex with Nearly Square-Planar Coordinated Sodium. *Angew. Chem. Int. Ed*. **1999**, *38*, 2064–2066. (g) Weber, K.; Weyhermüller, T.; Bill, E.; Erdem, Ö, F.; Lubitz, W. Design and Characterization of Phosphine Iron Hydrides: Toward Hydrogen-Producing Catalysts. *Inorg. Chem*. **2015**, *54*, 6928-6937. (h) Kallmeier, F.; Kempe, R. Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angew. Chem. Int. Ed*. **2018**, *57*, 46-60.
(23) (a) Gieshoff, T. N.; Villa, M.; Welther, A.; Plois, M.; Chakraborty, U.; Wolf, R.; Wangelin, A. J. V. Iron-Catalyzed Olefin Hydrogenation at 1 bar H_2 with a $FeCl_3$–$LiAlH_4$ Catalyst. *Green Chem*. **2015**, *17*, 1408-1413. (b) Ren, Y.; Yan, M.; Wang, J.; Zhang, Z. C.; Yao, K. Selective Reductive Cleavage of Inert Aryl C-O Bonds by an Iron Catalyst. *Angew. Chem. Int. Ed*. **2013**, *52*, 12674-12678.
(24) (a) Franck, G.; Brill, M.; Helmchen, G. Dibenzo[a,e]cyclooctene: Multi-gram Synthesis of a Bidentate Ligand. *Org. Synth*. **2012**, *89*, 55-65. (b) Sonnenberg, J. F.; Morris, R. H. Distin-

guishing Homogeneous from Nanoparticle Asymmetric Iron Catalysis. *Catal. Sci. Technol*. **2014**, *4*, 3426-3438.
(25) Smith, C. R.; RajanBabu, Low Pressure Vinylation of Aryl and Vinyl Halides via Heck–Mizoroki Reactions Using Ethylene. T.V. *Tetrahedron* **2010**, *66*, 1102-1110.
(26) Lebel, H.; Davi, M.; Díez-González, S.; Nolan, S. P. Copper−Carbene Complexes as Catalysts in the Synthesis of Functionalized Styrenes and Aliphatic Alkenes. *J. Org. Chem.* **2007**, *72*, 144-149.
(27) Knapp, D. M.; Gillis, E. P.; Burke, M. D. A General Solution for Unstable Boronic Acids: Slow-Release Cross-Coupling from Air-Stable MIDA Boronates. *J. Am. Chem. Soc.* **2009**, *131*, 6961-6963.
(28) Seferos, D. S.; Banach, D. A.; Alcantar, N. A.; Israelachvili J. N.; Bazan, G. C. α,ω-Bis(thioacetyl)oligophenylenevinylene Chromophores from Thioanisol Precursors. *J. Org. Chem*. **2004**, *69*, 1110-1119.
(29) Udumula, V.; Tyler, J. H.; Davis, D. A.; Wang, H.; Linford, M. R.; Minson, P. S.; Michaelis, D. J. Dual Optimization Approach to Bimetallic Nanoparticle Catalysis: Impact of M1/M2 Ratio and Supporting Polymer Structure on Reactivity. *ACS Catal*. **2015**, *5*, 3457-3462.
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