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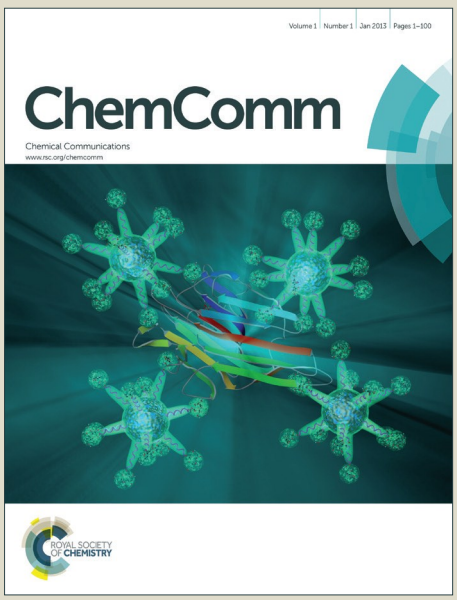

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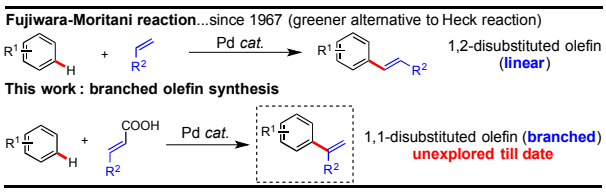
Traceless directing group mediated branched selective alkenylation of unbiased arenes

Soumitra Agasti, Aniruddha Dey and Debabrata Maiti*

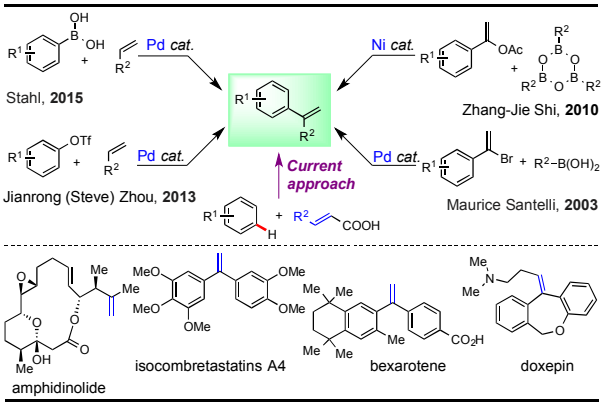
Owing to the synthetic importance of branched olefinated products, we report a palladium catalyzed formation of branched olefins facilitated by a C–H activation based protocol. This involves selective insertion of olefins and subsequent decarboxylation using completely unbiased benzene ring as the starting pre-cursor. Significance of the protocol has been further highlighted by exhibition of functionality tolerance along with a late-stage modification of the branched olefinated products leading to the formation of other functionalized molecules.

In the recent years, development of C–H activation based protocols has ensured a promising alternative for enhanced regioselectivity in a wide variety of chemical transformations.[1] Importantly, the significance of olefination reactions based on C–H activation chemistry had been long realized.[2] Literature reports highlight the application of directing groups in olefination of arene cores.[3] Amidst all, the year of 1967 claims a special mention owing to the discovery of the Fujiwara-Moritani reaction.[4] The vast majority of this protocol was executed by using activated olefin as a coupling partner.[5] A myriad of catalytic versions over the last couple of years has immensely popularized the stoichiometric coupling between arenes and olefins resulting in order to form linear 1,2-disubstituted olefins.[4a,6] Development of protocols involving oxidative alkenylation at sp^2 centres by C–H activation was supported by the use of pre-functionalized arene coupling partners like aryldiazonium salts, arylboronic acids, aryl triflates, *etc*.[7] However, a regioselective translation of the insertion mode of olefins into unactivated arenes leading to the generation of a 1,1-disubstituted analogue seemed to be challenging and had remained unexplored (Scheme 1).



Scheme 1. Linear and branched selective olefination

Olefins with 1,1-disubstitution constitute the core structures of medicinally significant molecules like bexarotene (antineoplastic), doxepin (antidepressant), *etc* (Scheme 2). Bio-active natural products like amphidonilide contain distinct α,α-disubstituted olefinic units which define its anticancer and antineoplastic characteristics.[8] A prime concern therefore revolves around exercising an effective control on the regioselectivity of the olefinic substitution pattern.



Scheme 2. Formation of branched olefinated product

An effective measure in this regard was employed through a catalyst and ligand based modification of the famous Heck reaction.[9] Intermolecular Heck reaction yielding augmented branched/linear selectivity had been executed with aryltriflates as efficient coupling partners by Zhou and co-workers.[10] Moreover, a switch of the regioselectivity was obtained by use of bulky phosphane ligands *(eg.* dnpf).[11] Even Suzuki coupling of aryl boronic acids with vinyl bromides was found to be feasible under a compatible combination of catalyst and ligand by Santelli and co-workers.[12] Nickel as a catalyst has been demonstrated to be useful in the formation of 1,1-disubstituted olefins.[13] This was shown by Z.-J. Shi and co-workers by the coupling of vinyl acetates with phenyl boroxine.[13a] A recent report by Stahl and co-workers on a Mizoroki-Heck coupling reaction emphasized the significance of a bulky bidentate dmphen ligand in preferential formation of the branched olefinic products.[14] Till date, the existing reports on branched olefination required use of pre-functionalized arenes as starting precursor.[15] Effective control over regioselectivity relied much on a choiced concoction of the catalyst, ligand, nature of reactant and terminal oxidant. Interestingly, the use of easily available non-functionalized arenes as starting materials remained unexplored.

In an attempt to use completely unbiased arene system with an aim to promote branched olefination, we used cinnamic acid derivative as the coupling partner.[16] Herein we report the formation of 1,1-disubstituted olefins by promoting C–H functionalization of arene, following selective olefin insertion and subsequent decarboxylation.

Preliminary investigation for the synthesis of branched olefin was initiated for reaction of benzene (**1**) with 4-

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: dmaiti@chem.iitb.ac.in *†Electronic supplementary information (ESI) available: Experimental procedure, spectral data, and copies of the NMR spectra of products. See DOI: 10.1039/x0xx00000x*

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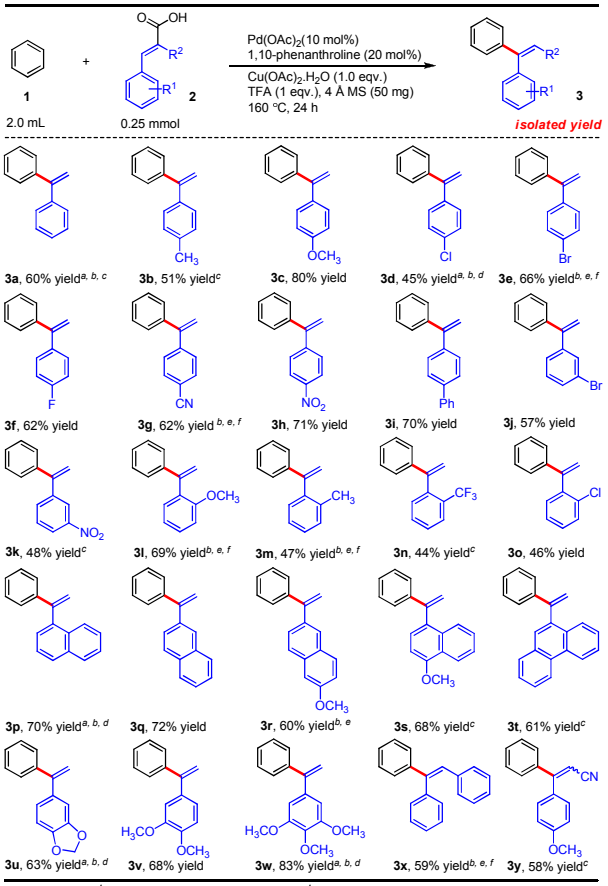
methoxycinnamic acid (**2c**). In the presence of $Pd(OAc)_2$ as the catalyst, 1,10-phenanthroline as the ligand and $Cu(OAc)_2.H_2O$ as oxidant, branched olefinated product was obtained with 23% yield.[17] Addition of stoichiometric amount of TFA increased the yield to 44%. Use of different co-solvent with the arene partner failed to show any positive impact on the reaction. A variety of palladium and ligand source were tested. Palladium catalysts such as $Pd(OAc)_2$ and $Pd(OPiv)_2$ proved to be most effective. With $Pd(OAc)_2$ and bipyridine ligand combination, the reaction between **1** and **2c** afforded 68% yield of **3c** at 130 °C. This was conducted in presence of 4 Å molecular sieves, which serves as a drying reagent. Performing the reaction at an elevated temperature shows positive impact upon the reaction. Improved yields for the branched product were observed upon using nitrogen containing bidentate ligands. Ligand optimization shows bipyridine and 1,10-phenanthroline to be the superior choices.[17]

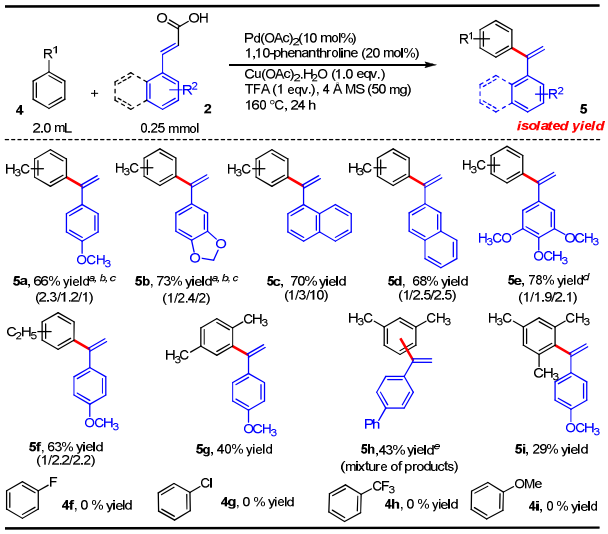


[a]$Pd(OPiv)_2$ [b]2,2'-bipyridine [c]140 °C [d]$Cu(OAc)_2.H_2O$ (1.25 eqv.) [e]Ac_2O (1 eqv.) [f]$Cu(OAc)_2.H_2O$ (0.75 eqv.) [g]minor side product[17]

Scheme 3. Branched olefination with various cinnamic acids

With the optimized conditions, we surveyed the scope of the vinyl-coupling partners (Scheme 3). Besides a successful olefination with unsubstituted benzene (**3a**), different *ortho-*, *meta-* and *para-* substituted arene containing α, β -unsaturated carboxylic acids yielded the branched olefinated product with good to excellent selectivity (**3b**-**3o**). Interestingly, electron-donating substituents in the arene ring of the olefin were well tolerated (**3c**, **3l**, **3v**, and **3w**). A severe drawback of the Fujiwara-Moritani reaction had been the reluctance of olefins with electron deficient arene substituents to act as good coupling partners. Here, cinnamic acids containing halide substituents like chloro, bromo and fluoro groups in the phenyl ring were found to proceed with favourable selectivity (**3d**-**3f**, **3j,** and **3o**). Importantly, selectivity was also maintained in case of the derivatives with cyano, nitro, and trifluoromethyl groups installed on the arene ring (**3g**, **3h**, **3k**, and **3n**). Cinnamic acids containing ether linkages remained intact under the reaction condition (**3u**). Moreover, naphthalene-containing olefins successfully produced the desired product with good selectivity by overcoming any probable steric influence (**3p**-**3s**). Coupling reactions were also performed with internal olefins flanked by electron-withdrawing groups. All of them (**3x** and **3y**) proceeded with excellent regioselectivity (Scheme 3).

A similar olefination reaction, with branched product formation was also obtained on using simple toluene as the arene coupling partner. Notably, 4-methoxycinnamic acid (**2c**) underwent olefination with greater *ortho*-selectivity. On the other hand, 2,3-methylenedioxycinnamic acid and other bulky derivatives such as naphthoic and 3,4,5-trimethoxy substituted cinnamic acids afforded *para*-olefinated product in a relatively greater ratio (**5b**-**5e**). Substrate scope was further extended to verify the suitability of other arenes for this protocol. Besides toluene, arenes like ethylbenzene, *para-* and *meta* - xylene were found to comply with the reaction condition yielding 1,1-diolefinated product in each case (**5f**-**5h**). Although ethylbenzene provided acceptable yields of the desired olefinated product, the yields decreased for both the xylene variants. Olefination was also performed in mesitylene as an arene substrate with excellent 1,1-diastereoselectivity in **5i** although steric demands led to decrease in their final yields. Olefination reaction was unfortunately found to fail in case of other electron-deficient arene systems like **4f**-**4h** and with anisole (**4i**).



[a]2,2'-bipyridine [b]Ac_2O (1.0 eqv.) [c]$Cu(OAc)_2.H_2O$ (0.75 eqv.) [d]140 °C [e]GC yield. Ratio reported as *o/m/p*

Scheme 4. Arene scope for branched olefination

In order to assess the possibility of rate determining C–H activation, isotope effects study was conducted.[17] First set of reaction was carried out in presence of benzene and second set was performed by using d_6-benzene. Labeling study for the

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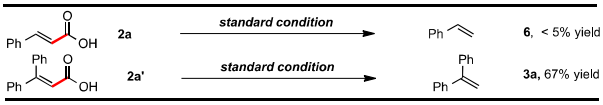
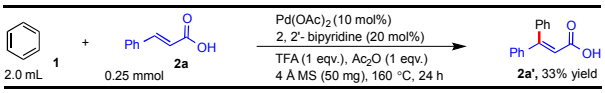
individual reaction revealed a kinetic isotope effect (KIE) of k_H/k_D = 2.5. The observed kinetic isotope value likely implies that the C–H metalation step is the rate-determining step.[18]

To get the idea about probable intermediate of the reaction, we have studied comparative decarboxylation reaction of cinnamic acid and 3,3-diphenyl acrylic acid (**2a'**).[17] Both the olefin were subjected to the standard reaction condition separately. Presence of extra aryl group in the *β*-position of –COOH group showed facile decarboxylation under the reaction condition. It produced 67% yield of the 1, 1-diphenyl styrene whereas, cinnamic acid gave <5% yield for the desired product (Scheme 5). It indicates that 3,3-diphenyl acrylic acid could be involved in the reaction as a plausible intermediate.



Scheme 5. Protodecarboxylation of cinnamic acid derivatives

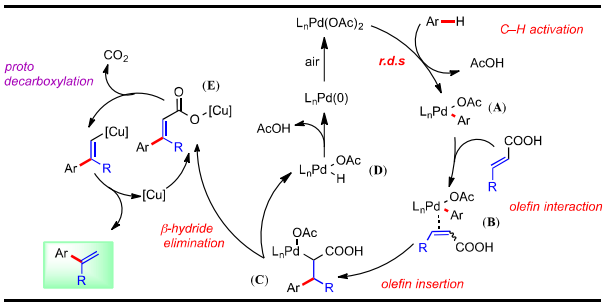
To intercept the probable intermediate we carried out the reaction in absence of Cu-salt (Scheme 6). Gratifyingly, we found that 3,3-diphenyl acrylic acid (**2a'**) was formed under the copper-free reaction condition with 33% yield.[17] This was suggestive of the fact that the mechanistic pathway consist of Heck reaction followed by Cu-catalyzed proto-decarboxylation.[19] Similar type of reactivity was previously shown by Fujiwara and co-workers to produce di-aryl acrylic acid in absence of Cu-salt.[5a] This meant that copper was responsible for proto-decarboxylation and di-aryl acrylic acid involved as an intermediate.



Scheme 6. Interception of probable intermediate

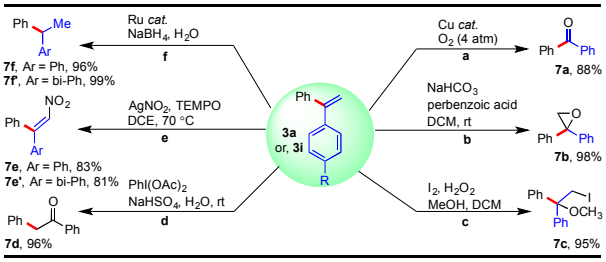
Subsequently, we have performed a series of control experiments to get more insights about the reaction mechanism. 4-Methoxy styrene reacted with benzene to give linear 1,2-olefinated product with excellent selectivity, which suggested that carboxylic acid group was responsible for altering the character of olefin double bond.[19] Cinnamic acid and cinnamate shows similar reactivity under the standard reaction condition, which indicates that –COOH group is not acting as a ligand with palladium through carboxylate exchange.[17] Moreover, it played the role of a traceless directing group for the olefination reaction.

The following mechanistic cycle can be therefore proposed based on experimental observations (Scheme 7). The C–H activation of arene generates a bidentate ligand chelated aryl-palladium(II) species A.[20] Presence of the trifluroacetic acid in the reaction medium helps in the generation of $[Pd(CF_3CO_2)_xL_y]^+$. This is a highly electrophilic complex cation that helps in the metalation of the aromatic C–H bond.[21] After that, formation of a π-complex B occurs by interaction of the palladated intermediate with the cinnamic acid.[1e] Subsequent insertion into the C=C leads to C. The regioselectivity of the insertion determines the regiochemistry of the reaction. Palladium is probably inserted at the α-position of olefin (–COOH attached carbon), which is supported by the control experiment.[16] A similar regio-preference is known for the insertion step in the Heck-coupling as well.[9a,22] *β*-hydride elimination from C generates an intermediate which follows a Cu-catalyzed protodecarboxylation pathway to give the desired product. [23] Intermediate C produces a Pd(II) species D along with E. Removal of AcOH from intermediate D leaves the metal in zero oxidation state. Presence of oxidant in the reaction medium helps in the regeneration of the catalyst by oxidation of Pd(0) back to Pd(II).



Scheme 7. Proposed catalytic cycle

After a thorough study of the substrate scope, applicative potential of the newly established protocol was demonstrated (Scheme 8). Starting from a simple benzene moiety, formation of the diarylketone (**7a**) was performed successfully through a two-step process *via* formation of the branched olefin.[24] Also, formation of diaryl substituted epoxide ring (**7b**) was executed through this pathway involving branched olefin synthesis.[25] Importance of the protocol was further emphasized by late-stage functionalization for the branched product. Iodinated compounds have been found to be important synthons for several organic transformations. Formation of **7c** was thus carried out.[26] Further, synthetic applicability of **3a** was emphasized by the synthesis of **7d** through an oxidative rearrangement pathway mediated by hypervalent iodine containing reagent.[27] A convenient route **e** for the synthesis of nitro olefin compounds was also portrayed.[28] Desired nitro product was obtained for both the substituents with very good yield (**7e** and **7e'**). Finally, Ru-catalyzed double bond reduction was carried out successfully with excellent yield (**7f** and **7f'**).[29]



Scheme 8. Applicative potential for late-stage functionalization

In summary, a novel approach for the synthesis of branched olefin products has been reported. This methodology underlines the significance of simple arene based substrates to readily undergo the transformation. In future, detailed mechanistic insights as well as extension of the strategy towards synthesis of natural products, drug molecules and other synthetically important molecule formation shall be explored in our laboratory.

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