Letter

Room-Temperature meta-Functionalization: Pd(II)-Catalyzed Synthesis of 1,3,5-trialkenyl Arene and meta-Hydroxylated Olefin

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Room-Temperature *meta*-Functionalization: Pd(II)-Catalyzed Synthesis of 1,3,5-trialkenyl Arene and *meta*-Hydroxylated Olefin

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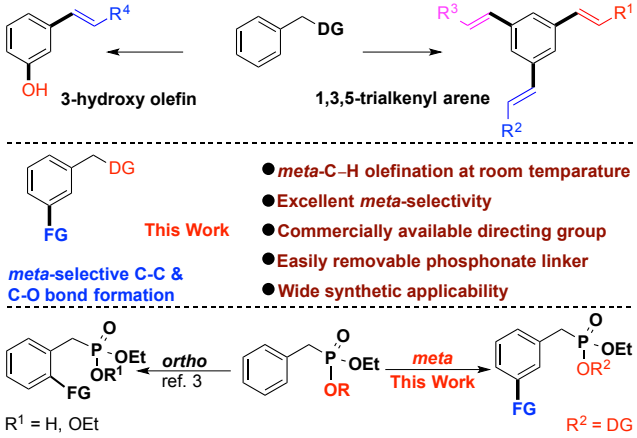
Supporting Information Placeholder

ABSTRACT: Development of *meta*-C–H functionalization reactions at room temperature continues to be a tough challenge. Use of phosphonate linkage allowed a Pd (II)-catalyzed *meta*-C–H functionalization at room temperature while incorporating a cyanophenol based directing moiety. Successful implementation of sequential di-*meta*-olefination led to the synthesis of trialkenyl arene having applications in organic electronics and optoelectronics. Under robust conditions, C–O bond formation has been discovered for the *meta*-hydroxylation and *meta*-acetoxylation.

Keywords: *Meta*-olefination, hydroxylation, acetoxylation, room-temperature, 1,3,5-trialkenyl arene, *meta*-hydroxy olefin, Palladium.

Organophosphonates have played important role in bioorganic chemistry and pharmaceuticals.[1] These are powerful synthons for a number of useful synthetic transformations including the preparation of alkenyl derivatives *via* Horner-Wadsworth-Emmons reactions.[2] Recently, directed C–H functionalizations of phosphonates have also been studied.[3]

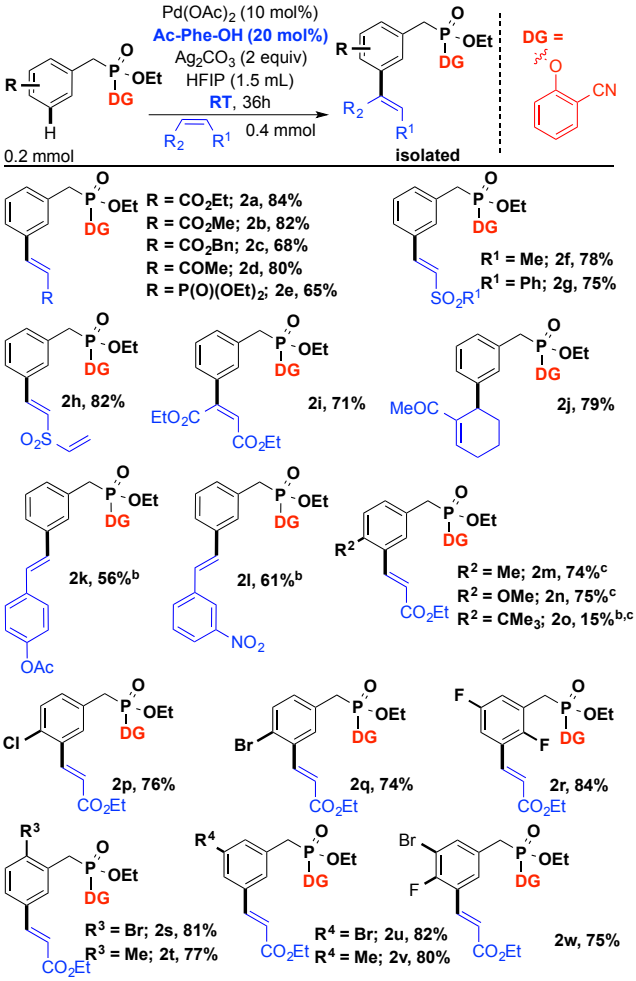
Although transition metal catalyzed *ortho*-C–H functionalization reactions are well explored,[4] related *meta*-C–H activation poses a significant challenge.[5] Regardless of the functionalization, a successful *meta*-C–H bond activation relies on the perfect design of the directing group (DG) linkage, coordinating site and the choice of metals. Overcoming these significant difficulties, DG assisted oxidative *meta*-selective functionalization of arene has been pioneered by Yu.[6] In this context, we have demonstrated the potential of commercially available, simple 2-cyanophenol moiety as the directing scaffold for *meta*-C–H functionalization reactions.[7]



Scheme 1. Overview of the present work

Despite these recent developments, *meta*-C–H activation methods still require elevated temperature. Further, the lack of selectivity for mono-*meta*- *vs.* bis-*meta*-functionalization encouraged us to ponder for a mild reaction condition that would allow a complete mono-selective *meta*-functionalization of arenes.[8]

We report herein the first example of Pd(II)-catalyzed *meta*-C–H olefination of arene at *room temperature* (Scheme 1). Using a benzylic phosphonate ester, complete mono-selectivity was achieved for the *meta*-olefination reaction. Furthermore, *meta*-selective C–O bond formation reactions can be promoted by using this scaffold. Direct hydroxylation has been achieved under mild oxidizing condition using $PhI(TFA)_2$ as the hydroxylating agent followed by its *in-situ* hydrolysis.



meta-selectivity>20:1; [b]reaction performed at 80s °C, [c]reaction performed upto 48 h. Ac-Phe-OH, *N*-acetyl phenylalanine.

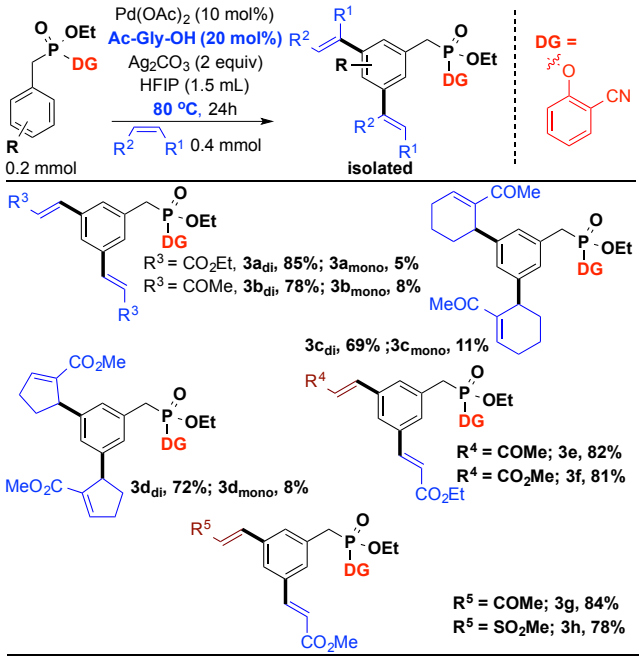
Scheme 2. *Meta*-selective mono-olefination

While changing $PhI(TFA)_2$ with $PhI(OAc)_2$, the *meta*-acetoxylated product was generated. Removal of phosphonate linker can generate di- or tri-alkenyl arene, a distinct π–conjugated organic materials, which have been spurred on by an interest in their applications in organic electronics and optoelectronics.[9]

Present studies towards developing a mild *meta*-C–H functionalization began by investigating olefination reaction. The *meta*-functionalization of benzylicphosphonates is expected to be challenging due to the presence of both *ortho*-directing [P(O)(OEt)] and *meta*-directing cyanophenol motifs in the present scaffold (Scheme 1). Reaction conditions were optimized with 2-cyanophenyl ethylbenzylphosphonate (**1a**) and ethyl acrylate as the model substrates. After extensive experimentation,[10] the desired olefinated product (**2a**) was obtained in 84% isolated yield with excellent *meta*-selectivity(≥20:1) in presence of $Pd(OAc)_2$ (10%), *N*-acetyl phenylalanine (Ac-Phe-OH, 20%) in HFIP solvent at room temperature.

Subsequently, we examined scope of the protocol with variousolefins as well as benzylicphosphonates. Most importantly, this protocol allows mono-olefination without formation of any di-olefinated product. Different acrylates and methyl vinyl ketone (MVK) produced desired mono-olefinated products in good yields (**2a-2d**, Scheme 2). Olefins with phosphonate and sulfone moiety resulted *meta*-selective products as well (**2e-2h**, Scheme 2). Interestingly, di-substituted olefin and cyclic tri-substituted olefin were successfully employed (**2i** and **2j**).

Styrene derivatives such as 4-acetoxy and 3-nitro styrene were effective with this protocol (**2k** and **2l**). Different *para*-substituted benzylic phosphonate esters promoted olefination in synthetically useful yields (**2m-2q**). However, *para*-tertbutyl phosphonate ester gave only 15% olefinated product **20**. Similarly, 2,5-difluoro arene can be incorporated under the optimized reaction condition (**2r**).



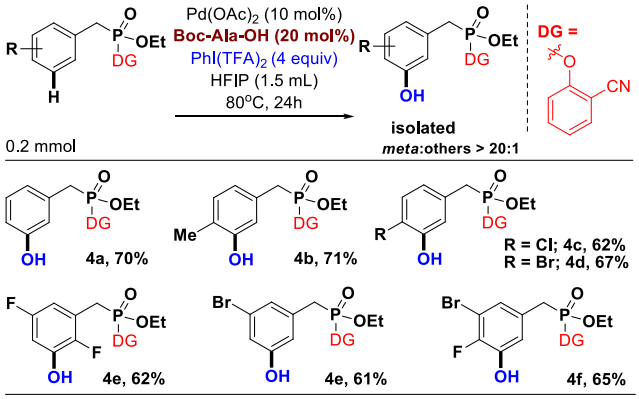
Ac-Gly-OH, *N*-acetyl glycene

Scheme 3. *Meta*-selective homo and hetero di-olefination

As expected, *ortho*- and *meta*- substituted (bromo and methyl) esters also underwent alkenylation at *meta* position (**2s-2v**). Finally, 3-bromo-4-fluoro substituted esters afforded the desired products in good yields (**2w**).[11]

We subsequently explored homo di-olefination and hetero di-olefination at the *meta* position by using $Pd(OAc)_2$ (10 %), *N*-acetyl glycene (Ac-Gly-OH, 20%) in HFIP solvent at 80 °C. A range of acrylates, MVK and cyclic olefins produced di-alkenylated products in high yield (**3a-3d**, Scheme 3). Furthermore, hetero diolefinated products (**3e-3h**) were obtained *via* incorporation of another olefin into the mono-olefinated product **2a**.[10]

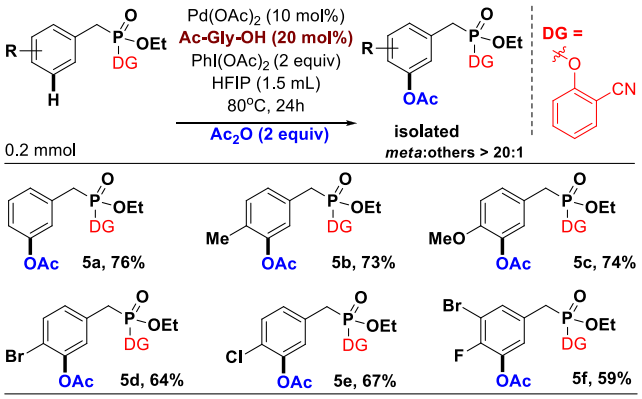
The versatility of this template based approach was extended to carbon-heteroatom bond formation by performing *meta*-hydroxylation and acetoxylation. Initial attempts of hydroxylation was unsuccessful under strong oxidizing conditions.[10] Thereafter, the *meta*-hydroxylated compound (**4a**) was obtained in 70% isolated yield with excellent *meta*-selectivity (>20:1) by using mild oxidizing condition such as $PhI(TFA)_2$ (4 *equiv.)* as the hydroxylating agent,[12] followed by its in-situ hydrolysis.[13] The optimized reaction condition involved *N*-*tert*-butyloxycarbonyl-alanine (Boc-Ala-OH, 20%) as the ligand for $Pd(OAc)_2$ (10 mol%) in HFIP.[10] With the optimized condition, the scope of the reaction was explored with benzylphosphonates (**4a-4g**, Scheme 4; *meta*-selectivity >20:1).



Boc-Ala-OH, *N*-*tert*-butyloxycarbonyl-alanine.

Scheme 4. *Meta*-selective hydroxylation

Interestingly, changing the acylating agent from $PhI(TFA)_2$ to $PhI(OAc)_2$ led to the formation of *meta*-acetoxylated compound as the sole product. This is likely due to the reduced electrophilicity of the acetate compared to trifluoroacetate. For *meta*-acetoxylation, *N*-acetyl-glycene (Ac-Gly-OH) was found to be the ligand of choice.[10] Several substrates with different substitution patterns underwent *meta*-acetoxylation successfully to give acetoxylated compounds in moderate to good yields and often with excellent *meta* selectivity (Scheme 5, **5a-5f**; *meta*-selectivity >20:1).



Scheme 5. ***Meta*-selective acetoxylation**

In consideration of the unique catalytic activity of the Pd(II)-MPAA metal-ligand system, we studied some preliminary mechanistic experiments of *meta*-selective C–C and C–O bond formation reactions. In both these cases, nitrile group of the substrate linearly coordinated with the ligated palladium species. The palladium-nitrile coordination was supported by downfield shift of *ortho* and *para* proton of 2-cyano phenol core in ^{1}H spectra (Figure 1). We have performed ESI-MS studies of stoichiometric combination of $Pd(OAc)_2$, Ac-Phe-OH, and substrate. Interestingly, a metal-substrate adduct [(Ac-Phe-OH)-H^+)Pd^{II}(1a)] was appeared withdesired isotopic pattern (Figure 2).

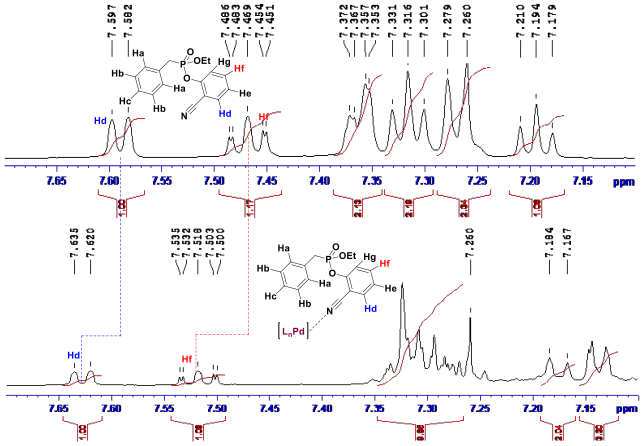


Figure 1. ^{1}H NMR study of $Pd(OAc)_2$, Ac-Phe-OH, and **1a**

The C–H palladation step likely involves the formation of a 11-membered palladacycle. ESI-MS studies of stoichiometric combination of $Pd(OAc)_2$, Ac-Phe-OH, and 4-methyl substituted phosphonic ester **1b**, suggesteda ligand free intermediate [Pd^{II}(**1b**-H^+)] (Figure 2). Efforts to isolate this species remained unsuccessful till date.

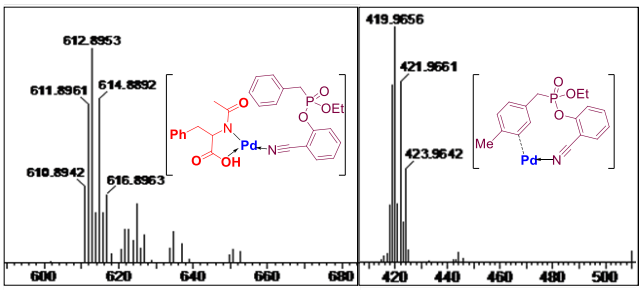
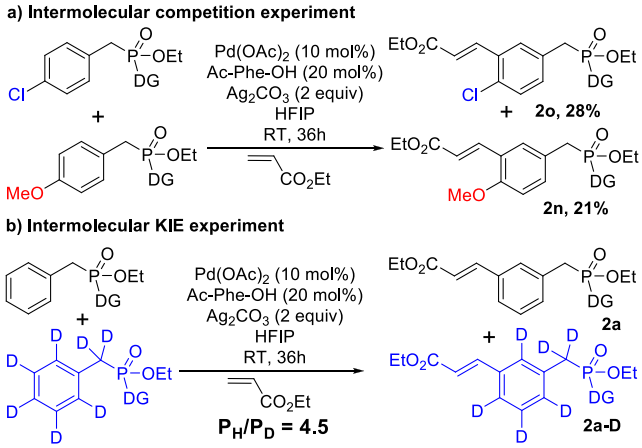


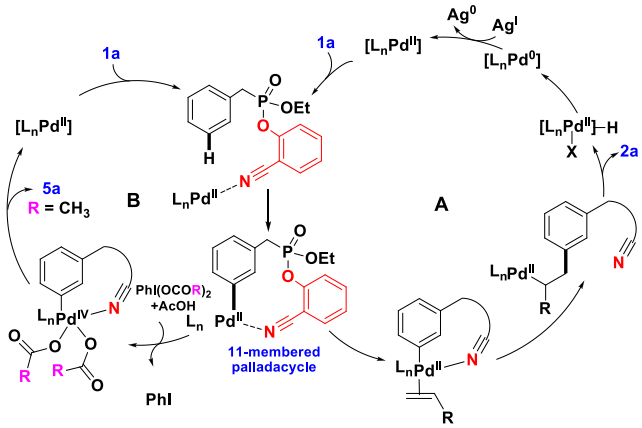
Figure 2. ESI-MS study with **1a** and **1b.**

We then performed intermolecular competition experiment between differently *para*-substituted (chloro and methoxy) benzylphosphonate esters, a (1.3:1) yield ratio was obtained for both electron-deficient and rich counterparts. This phenomenon indicates a simple electrophilic substitution type mechanism unlikely to be involved. In addition intermolecular competition between [D_7] and simple undeuterated benzylphosphonate esters **1a** gave the product distribution values of **4.5** [P_H/P_D], such a high value of [P_H/P_D] likely establishes C–H activation as the rate determining step (Scheme 6).



Scheme 6. Intermolecular competition experiments

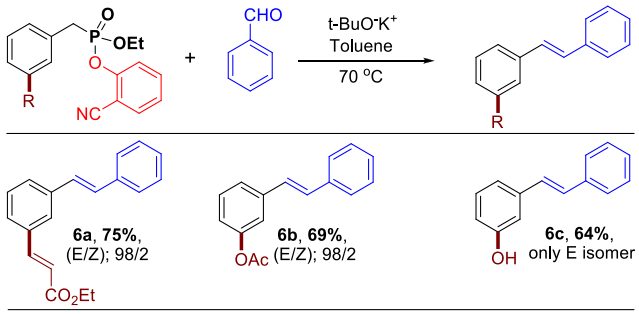
Olefination likely followed a path (depicted as **A** in Scheme 7) involving C–H activation, olefin binding, 1,2-migratory insertion, and β-hydride elimination to generate the product **2a**. The C–O bond formation reaction might proceed *via* a Pd^{II}/Pd^{IV} cycle (path **B**). The palladacycle intermediate is oxidized by $PhI(OCOR)_2$ to afford a Pd^{IV} intermediate, which undergoes a reductive elimination process to furnish the acetoxylated product **5a** and liberates the Pd^{II} catalyst. Subsequent hydrolysis of trifluoroacetoxy, $OCOCF_3$, group provides compound **4a.**



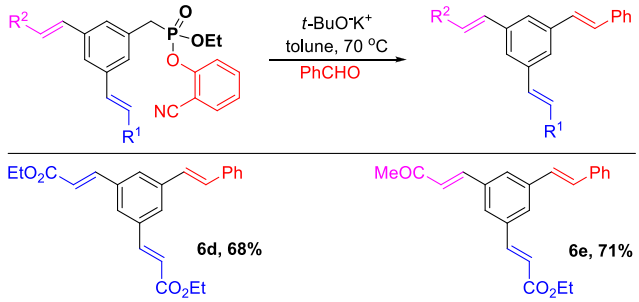
Scheme 7. Plausible pathway for *meta*-functionalization

Furthermore, the -P(O)$(OR)_2$ tether linkage can be easily cleaved by modified Horner-Wadsworth-Emmons reaction.[2] *Meta*-functionalized products were reacted with benzaldehyde in the presence of potassium *tert*-butoxide to afford corresponding alkenes in good yields (Scheme 8). In addition, ester moiety of *meta* di-olefinated compounds can

be removed to produce 1,3,5-trialkenylated arenes in good yields (Scheme 9, **6d** and **6e**).

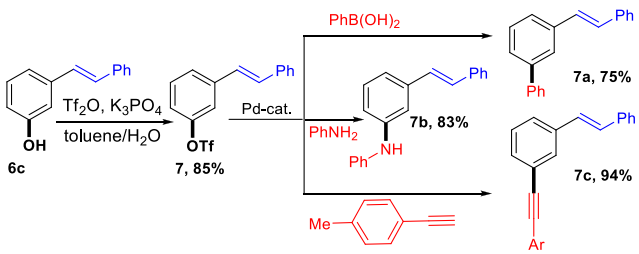


Scheme 8. Removal of phosphonates linker



Scheme 9. Synthesis of 1,3,5-trialkenyl arene

The utility of *meta*-C–H functionalization was demonstrated by attempting further extension of the hydroxylated product (Scheme 10). Triflate **7** was easily prepared from compound **6c** and then transformed to synthetically useful molecules *via* arylation **7a**, amination **7b** and alkynylation **7c**.



Scheme 10. Further functionalization of 6c

In summary, we have developed first template assisted Pd (II)-catalyzed direct *meta*-olefination at room-temperature. The *meta*-functionalizationcan be further extended to carbon-oxygen bond formation such as *meta*-hydroxylation and *meta*-acetoxylation reactions by varying the acetoxylating agent $PhI(OCOR)_2$. Different di- and tri-*meta*-substituted alkenes were synthesized by removing the tether phosphonates.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and data. This material is available free of charge via the Internet at http: //pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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(10) *see supporting information for detailed description*.

(11) This reaction is not compatible with electron neutral or unactivated alkenes such as 1-hexene.

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TOC Graphic: