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Pd(II)-Catalyzed *ortho*- or *meta*-C−H Olefination of Phenol Derivatives

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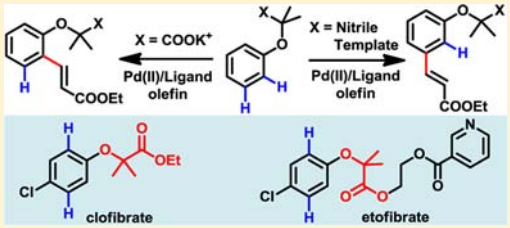
Supporting Information

ABSTRACT: A combination of weakly coordinating auxiliaries and ligand acceleration allows for the development of both *ortho*- and *meta*-selective C−H olefination of phenol derivatives. These reactions demonstrate the feasibility of directing C−H functionalizations when functional groups are distal to target C−H bonds. The *meta*-C−H functionalization of electron-rich phenol derivatives is unprecedented and orthogonal to previous electrophilic substitution of phenols in terms of regioselectivity. These methods are also applied to functionalize α-phenoxyacetic acids, a fibrate class of drug scaffolds.



INTRODUCTION

Directed C−H activation via five- or six-membered cyclopalladation has recently emerged as a versatile tool for developing synthetic transformations.[1] However, activation of C−H bonds that are more than five bonds away from the chelating atom is still rare due to the difficulty of forming larger membered palladacycles.[2] Alternative strategies relying on the proximity between remote C−H bonds and highly reactive species such as radical or *meta*-oxo species have been reported.[3] In contrast to the directed metalation processes, these strategies do not produce systematic and predictable structural patterns at this stage of development. On the other hand, directed metalation of C−H bonds at certain geometric positions that are resistant to the assembly of cyclic transition states due to ring strain has limited success, as exemplified by the lack of examples of directed *meta*-C−H activation of arenes until recently.[2b] Development of *meta*-C−H activation of a broad range of synthetically useful substrates will significantly enhance the versatility of directed C−H activation reactions in synthetic applications.

Phenol and its derivatives have attracted intensive efforts from the community studying C−H functionalizations due to their broad synthetic utility. Early studies by Rawal and Miura used phenol to direct arylation of biphenyls with ArI and Pd(0)/PPh_3 catalysts.[4] Bedford and others succeeded in using a catalytic amount of phosphites as directing groups to promote Rh(I)-catalyzed *ortho*-arylation of phenols (Figure 1).[5] Hartwig reported Ir(I)-catalyzed borylation of hydrosilyl ethers of phenols.[6] Recent emergence of C−H activation reactions with Pd(II),[7] Rh(III),[8] and Ru(II)[9] catalysts using weakly coordinating carbonyls have led to a range of *ortho*-C−H functionalization reactions of phenol derivatives (Figure 1). Due to the strong electron-donating ability of the phenoxyl group, *meta*-selective C−H activation is especially challenging and yet synthetically enabling.

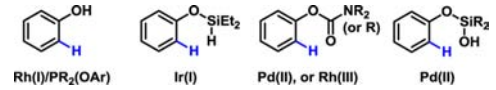


Figure 1. Previous *ortho*-C−H functionalizations of phenol.

Herein we report two approaches for achieving *ortho*- and *meta*-C−H olefination of phenol derivatives, respectively, through remote C−H activation promoted by weak coordination and ligand acceleration (Figure 2). Removal of the acetic acid auxiliaries affords synthetically valuable *ortho*- or *meta*-olefinated phenols. This protocol was successfully applied to the parent α-phenoxycarboxylic acids of drug molecules fenofibrate, clofibrate, and etofibrate (Figure 3).

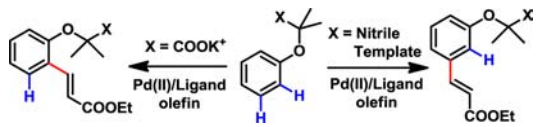


Figure 2. Remote *ortho*- and *meta*-C−H functionalizations.

RESULTS AND DISCUSSION

We initially aimed to develop *ortho*-C−H functionalization methods for late-stage diversification of α-phenoxyacetic acids, important pharmacophores found in the fibrate class of lipid-lowering agents (Figure 3).[10] Despite a number of elegant directing groups previously developed for the *ortho*-C−H functionalizations of phenols,[5−9] the distance between the C−H bonds and the functional groups in α-phenoxyacetic acids presents a challenge. Although we have developed various

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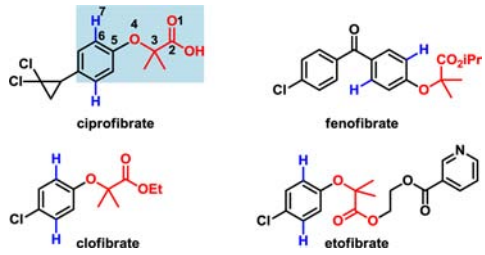


Figure 3. Drug molecules based on α-phenoxyacetic acids.

ortho-C−H functionalizations of phenylacetic acids via a relatively distal directing group, the *ortho*-C−H bonds and the chelating atom of the carboxyl group in α-phenoxyacetic acids are further apart (six bonds away), as shown in ciprofibrate (Figure 3). The presence of the α-oxygen atom in the side chain could also be problematic as Pd(II) could form a bis-chelation with this oxygen atom and the directing group, which could prevent the Pd center from aligning with C−H bonds with a relatively small dihedral angle, a requisite for facile C−H activation.

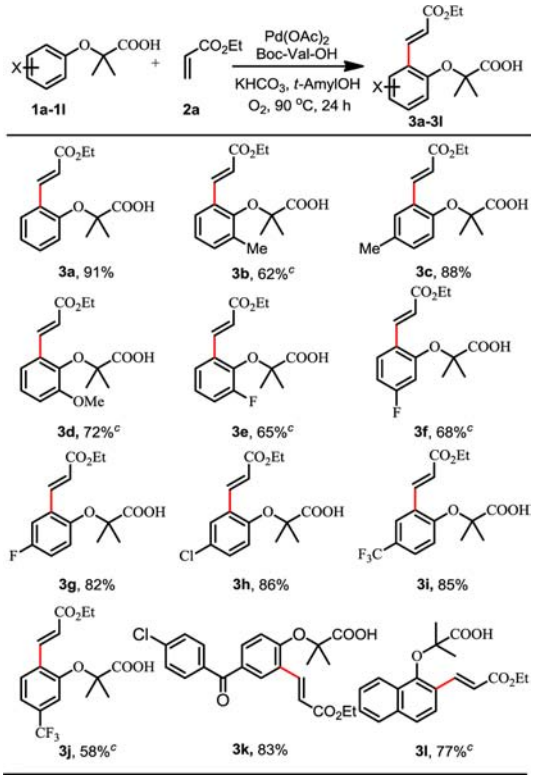
Encouraged by our recently observed ligand acceleration,[11] we began to identify ligands that can cooperate with the weak coordination of the distal carbonyl in the COOK moiety to promote the C−H activation reactivity. Guided by our previous C−H olefination of phenyl acetic acids[11] and early olefination reactions,[12] we established conditions for the *ortho*-olefination of α-phenoxyacetic acids. Thus, substrate **1a** was reacted with 2 equiv of ethyl acrylate under 1 atm of O_2 in the presence of 5 mol % of $Pd(OAc)_2$, 10 mol % of Boc-Val-OH, and 2 equiv of $KHCO_3$ in *t*-amyl alcohol at 90 °C for 24 h to give 90% of the mono-olefinated product **3a** (Table 1). The high mono-selectivity can be attributed to the steric buttress imparted by the α,α-dimethyl groups. Interestingly, the absence of the α,α-dimethyl groups resulted in a significant loss of reactivity leading to poor yields, presumably due to the loss of favorable Thorpe-Ingold effect (less than 10%; see Supporting Information). The replacement of O_2 with air dropped the yield to 34%.

This reaction tolerates electron-donating substituents such as methyl and methoxy (**3b**−**d**). The naphthalene ring in example **3l** is selectively olefinated at the 2-position. Olefination also proceeds smoothly with a wide range of electron-deficient arenes, including those with fluoro- (**3e**−**g**), chloro- (**3h**), trifluoromethyl (**3i**, **3j**), and keto functionality (**3k**). This method can be used to directly functionalize medicinally useful α-phenoxyacetic acids or prepare *ortho*-substituted phenols after removal of the acetic acid directing groups (Scheme 1). Notably, substrates **1h** and **1k** are derived from drug molecules clofibrate and fenofibrate, respectively.

Prompted by our recent development of *meta*-selective C−H olefination reactions of hydrocinnamic acids,[2b] we wondered if the end-on coordinating nitrile template can be modified to direct *meta*-C−H olefination of α-phenoxyacetic acids. We were pleased to find that olefination of **4a** proceeded with high *meta*-selectivity under our previous conditions to give the mono- and diolefinated products in 60 and 29% yields, respectively (Table 2). The *meta*-substitutions of phenol derivatives complement the *ortho*- and *para*-electrophilic substitutions, thus providing a new strategy to construct densely substituted arenes. This reaction is compatible with electron-donating groups (**5b**−**f**), as well as electron-withdrawing groups (**5g**−**m**). High mono-selectivities were obtained with *ortho*-substituted substrates (**5b**, **5e**, **5g**, **5j**, **5l**). Importantly, the template overrides the electronic influence of substituents on the arenes. The regioselectivity observed with **5l** is most striking as olefination occurs at the position that is *meta* to alkoxy and *para* to the trifluoromethyl group. The use of a directing group to govern *meta*-selectivity is fundamentally a different approach compared to previously developed *meta*-C−H functionalizations where the electronic or steric bias of arene substrates plays a decisive role.[13−17]

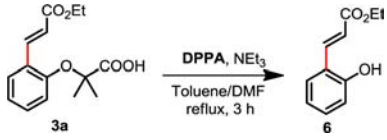
To further demonstrate the synthetic utility of this method, we performed *meta*-olefination of an *ortho*-brominated substrate **5p** (Table 3). We were pleased to find that a wide range of olefins, including disubstituted olefins, are reactive. Coupling of **4p** with *trans*-2-butenoate gave the desired product **5s** stereospecifically. It is worth noting that disubstituted olefins are generally not compatible with directed C−H olefination reactions; only rare examples have been shown to date.[2b] Additionally, the bromine functionality is a highly versatile

Table 1. Pd(II)-Catalyzed *ortho*-Olefination of Phenol Derivatives[a,b]



[a]Reaction conditions: **1a**−**1l** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), Boc-Val-OH (10 mol %), $KHCO_3$ (0.2 mmol), O_2 (1 atm), *t*-amylOH (1 mL), 90 °C, 24 h. [b]Isolated yield. [c]$Pd(OAc)_2$ (10 mol %), Boc-Val-OH (20 mol %).

Scheme 1. Removal of Directing Group[a]



[a]Reaction conditions: **3a** (0.4 mmol), DPPA (0.4 mmol), Et_3N (0.4 mmol), toluene (5 mL), DMF (0.5 mL), refluxed 3 h. DPPA: diphenylphosphoryl azide. Yield: 71%.

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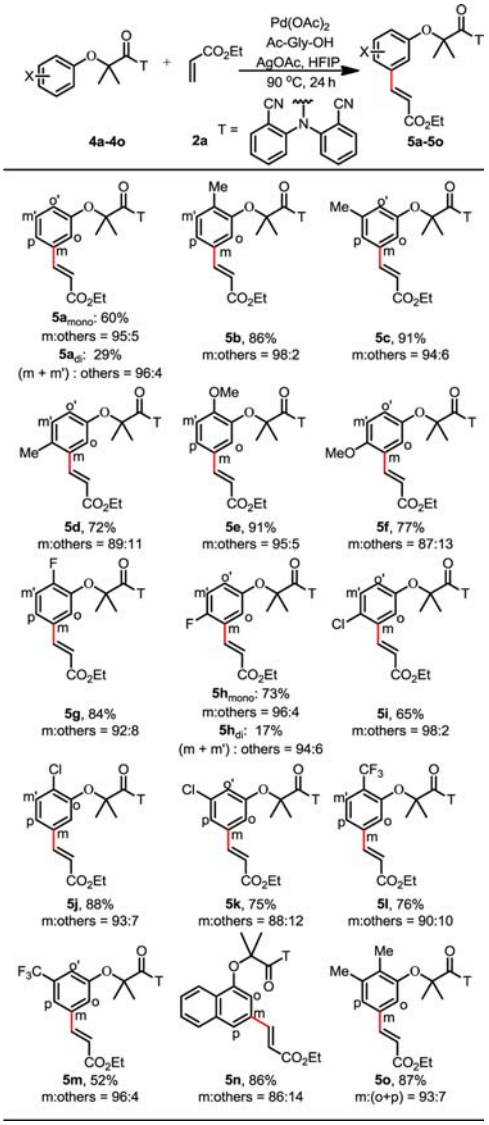
Table 2. Pd(II)-Catalyzed *meta*-Olefination of Phenol Derivatives[a,b,c]

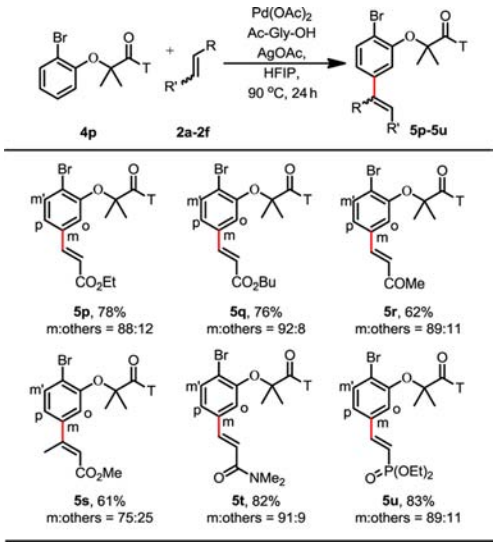


[a]Reaction conditions: **4a–4o** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), Ac-Gly-OH (20 mol %), AgOAc (0.3 mmol), HFIP (1 mL), 90 °C, 24 h. [b]Isolated yield. [c]Regioselectivity was determined by ^{1}H NMR analysis of the crude product and confirmed by one-dimensional selective NOESY experiments; the variance is estimated to be within 5%.

handle that allows for subsequent transformations. Finally, the nitrile template can be removed by hydrolysis[2b] to give the medicinally useful *meta*-substituted α-phenoxyacetic acids. The acetic acid moiety attached to the phenoxy can then be removed by treatment with DPPA to afford the *meta*-substituted phenol (Scheme 1).

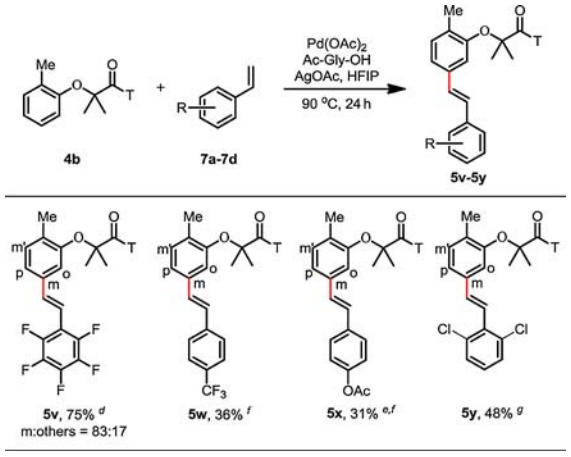
Extensive studies on C–H olefination have shown that electron-deficient olefins are, in general, more effective coupling partners, while electron-rich olefins tend to react with the Pd(II) catalyst via the Wacker oxidation pathway with rare exceptional examples.[18] To examine the scope of this *meta*-selective olefination reaction with respect to the olefins, we tested alkenes and styrenes as the coupling partners and found that only those styrenes with an electron-withdrawing group attached to the arenes reacted to some extent to give the desired product in moderate yields (Table 4). Further improvement of the C–H olefination with electron-rich olefins such as simple styrene and hexane will require the modification of the ligand.

Table 3. *meta*-Olefination of 2-Bromophenol Derivatives[a,b,c]



[a]Reaction conditions: **4p** (0.1 mmol), **2a–2f** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), Ac-Gly-OH (20 mol %), AgOAc (0.3 mmol), HFIP (1 mL), 90 °C, 24 h. [b]Isolated yield. [c]Regioselectivity was determined by ^{1}H NMR analysis of the crude product and confirmed by one-dimensional selective NOESY experiments; the variance is estimated to be within 5%.

Table 4. *meta*-Olefination with Styrenes[a,b,c]



[a]Reaction conditions: **4b** (0.1 mmol), **7a–7c** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), Ac-Gly-OH (30 mol %), AgOAc (0.3 mmol), HFIP (1 mL), 90 °C, 24 h. [b]Isolated yield. [c]Regioselectivity was determined by ^{1}H NMR analysis of the crude product and confirmed by one-dimensional selective NOESY experiments; the variance is estimated to be within 5%. [d]Ac-Gly-OH (20 mol %). [e]For 30 h. [f]Only one major regioisomer was observed. [g]NMR yield.

While the detailed mechanism and origin of the *meta*-selectivity remains to be elucidated by computational, kinetic, as well as structural studies, we have also observed a significant isotope effect (k_H/k_D = 3.8) of the nitrile-directed *meta*-selective C–H olefination with analogous substrates (see Supporting Information), suggesting that the C–H cleavage

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may be involved in the rate-determining step. A tentative catalytic cycle can also be proposed based on our previous studies (Figure 4).

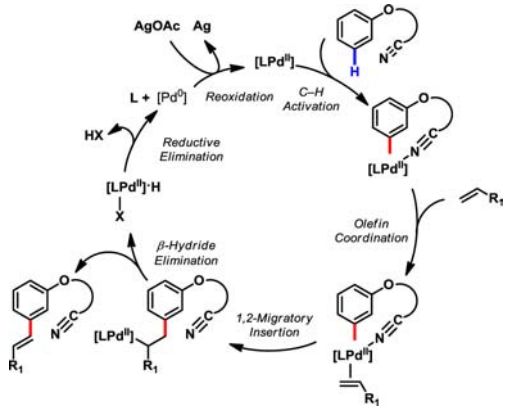

Figure 4. Catalytic cycle of *meta*-C−H olefination.

CONCLUSION

In summary, we have developed two new approaches for *ortho*- and *meta*-C−H functionalization of phenol derivatives. These C−H activation reactions feature rare cyclometalation processes of C−H bonds directed by distal chelating atoms (six bonds away). The selective functionalizations of phenol derivatives at the *meta*-positions are unprecedented and especially useful as the regioselectivity is orthogonal to the electrophilic substitution. The methods are also applied to functionalize α-phenoxyacetic acids, a fibrate class of drug scaffolds.

EXPERIMENTAL SECTION

General Information. All commercial reagents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, TCI, Oakwood, and Acros of the highest purity grade. They were used without further purification unless specified. Palladium acetate and silver acetate were purchased from Sigma-Aldrich. The amino acid ligands were bought from Novabiochem, Bachem, and Sigma-Aldrich. 2,2′-Azanediyldibenzonitrile was prepared by literature methods.[19] ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400, Varian Inova 400 (400 and 100 MHz, respectively), Bruker DRX 500 (500 and 125 MHz, respectively), and Bruker DRX 600 (600 and 150 MHz, respectively) instruments. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra were recorded at the Center for Mass Spectrometry, The Scripps Research Institute.

General Procedure for Pd(II)-Catalyzed *ortho*-C−H Olefination of α-Phenoxyacetic Acids (1a−1l). A 50 mL Schlenk-type tube (with a Teflon high-pressure valve and side arm) equipped with a magnetic stir bar was charged with acid **1** (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 5 mol %), Boc-Val-OH (4.3 mg, 0.020 mmol, 10 mol %), $KHCO_3$ (40 mg, 0.40 mmol, 2.0 equiv), ethyl acrylate **2a** (0.40 mmol, 2.0 equiv), and *t*-amylOH (2.0 mL). The reaction tube was evacuated and backfilled with O_2 (five times, balloon) and heated to 90 °C for 24 h under vigorous stirring. The reaction vessel was then cooled to 0 °C in an ice bath. A 2.0 N HCl solution (5 mL) was then added, and the mixture was extracted with EtOAc (3 × 20 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by preparative TLC using hexanes/EtOAc as the eluent to afford the product (**3a**−**3l**).

General Procedure for Pd(II)-Catalyzed *meta*-C−H Olefination of Phenol Derivatives (4a−4p). A 35 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with amide **4** (0.10 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 10 mol %), Ac-Gly-OH (2.4 mg, 0.020 mmol, 20 mol %), and AgOAc (50 mg, 0.30 mmol, 3.0 equiv). HFIP (0.60 mL) was added to the mixture, followed by ethyl acrylate **2a** (2.0 equiv) and then another 1.0 mL of HFIP. The tube was then capped and submerged into a preheated 90 °C oil bath. The reaction was stirred for 24 h and cooled to room temperature. The crude reaction mixture was diluted with EtOAc (2 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 15 mL of EtOAc. The filtrate was concentrated in vacuo, and the resulting residue was purified by preparative TLC using hexanes/EtOAc as the eluent. The positional selectivity was determined by ^{1}H NMR analysis of the unpurified reaction mixture.

Procedure for Removal of Template.[20] To a 50 mL of flask was dissolved **3a** (111.2 mg, 0.4 mmol) in anhydrous toluene (5 mL) and DMF (0.5 mL), then Et_3N (46.4 mg, 0.4 mmol) and DPPA (110 mg, 0.4 mmol) were added and the mixture was refluxed for 3 h. Thirty milliliters of water was added and continued to reflux for 2 h. After the mixture was cooled to room temperature, the solution was acidified with 2 N HCl solution (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified via column chromatography on silica with hexane and EtOAc (10:1) as eluents to afford product **A**[21] in 71% yield (54.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J = 16.2 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.26−7.21 (m, 1H), 6.93−6.85 (m, 2H), 6.80 (br, 1H), 6.65 (d, J = 16.2 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 169.3, 158.3, 141.5, 132.2, 130.1, 122.6, 121.5, 119.2, 117.3, 61.6, 15.2.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization of new compounds. 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 interest.

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