Advances in Decarboxylative Oxidative Coupling Reaction

Journal:	*The Journal of Organic Chemistry*
Manuscript ID	jo-2018-01080r.R1
Manuscript Type:	JOCSynopsis
Date Submitted by the Author:	12-Jun-2018
Complete List of Authors:	Zhang, Tong; Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, Chinese Academy of Sciences Wang, Nai-Xing; Chinese Academy of Sciences, Technical Institute of Physics and Chemistry Xing, Yalan; William Paterson University, Chemistry

Advances in Decarboxylative Oxidative Coupling Reaction

Tong Zhang,[†] Nai-Xing Wang*,[†] and Yalan Xing,*,[‡]

[†]Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing, China;

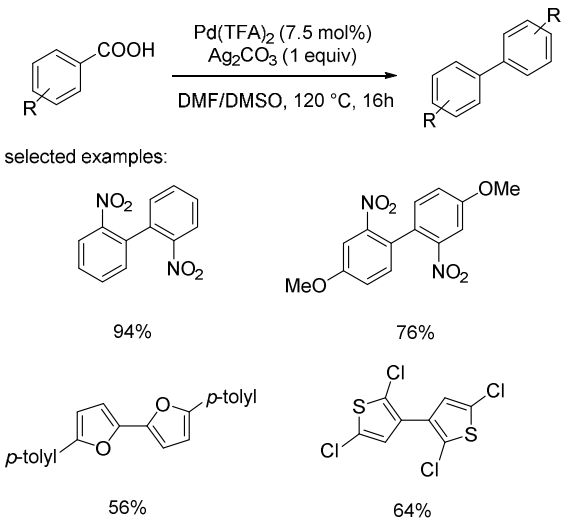
[‡]Department of Chemistry, William Paterson University of New Jersey, New Jersey, United States.

ABSTRACT: Since carboxylic acid derivatives are commercially available, non-toxic, cheap and normally stable to air and moisture, carboxylic acid derivatives are ideal reactants for synthetic strategy. In recent years, decarboxylative oxidative coupling reaction, which normally involves direct C-H bond activation, attracts more and more interests from synthetic community. Compared with conventional methods, this strategy is more environmental friendly and step-economic. This review mainly focuses on the recent advances of decarboxylative oxidative coupling reaction.

1 Introduction

Coupling reaction is one of the most important tools of organic synthesis. In recent yearrs, oxidative coupling attracts lots of attention.[1-6] Unlike traditional coupling reactions which normally involve a nucleophilic reagent and an electrophilic reagent, oxidative coupling utilizes two nucleophilic reagents as coupling components with help of oxidants. In this case, many substrates could directly participate in synthesis without pre-functionalization. This strategy could achieve C-H functionalization and C-C bond formation with atom and step economy, and oxidative coupling is in a stage of rapid development.

Since carboxylic acid derivatives are commercially available, non-toxic, cheap and normally stable to air and moisture, carboxylic acid derivatives are ideal reactants for synthetic strategy. Decarboxylative coupling reactions are very convenient synthetic strategies which could be easily operated and produce less toxic byproducts. Lots of novel methods have been reported.[7-11] This review will focus on the recent advances of decarboxylative oxidative coupling reactions.



Scheme 1. Pd/Ag-catalyzed decarboxylative homocoupling of aromatic and heteroaromatic carboxylic acids

2 Decarboxylative Homocoupling

Through decarboxylative homocoupling reactions of simple carboxylic acids, symmtrical biaryl compounds could be smoothly synthesized. Compared with other synthetic routes, this method produces much less toxic waste. Many novel reactions have been developed in this field.

In 2009, Larrosa's group reported the first decarboxylative homocoupling of carboxylic acids.[12] (Scheme 1) Aromatic and heteroaromatic carboxylic acids underwent a decarboxylative protocol and generated symmetrical biaryls. In this Pd/Ag bimetallic system, Ag catalyst was crucial for the activation of C-COOH bond.

Cai's group developed Cu-catalyzed decarboxylative homocoupling of *ortho*-nitrobenzoic acids.[13] The decarboxylative homocoupling reaction could occur without precious metal catalyst, and adding molecule sieves surprisingly enhanced the reaction and increased the yields. The 2,2'-dinitrosubstituted biaryl products could transform into bioactive amino-substituted biaryls.

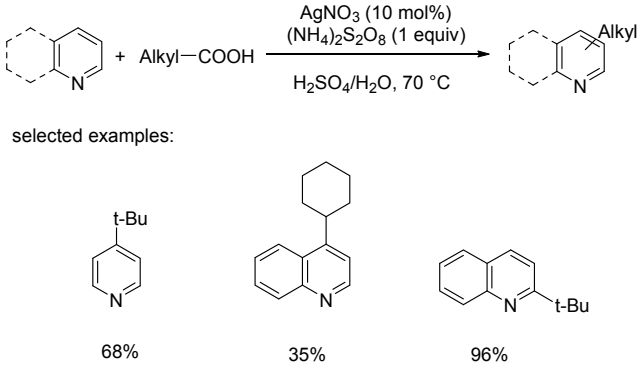
Catalytic decarboxylative coupling could be used to synthesize assymmtrical biaryls like Gooßen's work.[14] They reported Cu-catlyzed decarboxylative cross-coupling of aromatic carboxylic acids and aryl halides, which had very large scope of substrates. Cross-coupling of different aromatic carboxylic acids could be a very attractive strategy for synthesis of assymmtrical biaryls since it's much more environmentally friendly. However, due to the homocoupling pathway, it's very hard for cross-coupling of

different aromatic carboxylic acids to achieve satisfying yields. Normally this strategy requires electronically different aromatic carboxylic acids to make it work. In 2012, Su's group described a decarboxylative cross-coupling of aromatic carboxylic acids that could apply to various aromatic carboxylic acids.[15] By choosing a suitable solvent and ligand, they successfully controlled the decarboxylation rate of different aromatic carboxylic acids and promote the formation of cross-coupling products. It is noteworthy that this protocol also worked for electronically similar aromatic carboxylic acids and provided good yields.

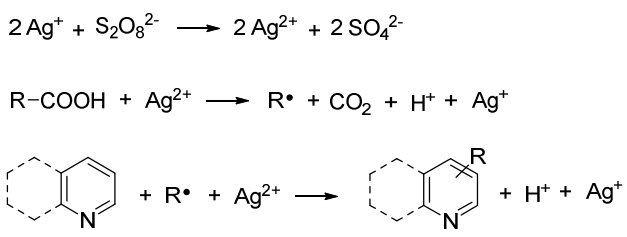
3 Decarboxylative Oxidative Cross-Coupling

3.1 Decarboxylative Oxidative Alkylation/Arylation

Decarboxylative oxidative cross-coupling with simple carboxylic acids is a convenient method for alkylation or arylation. In order to introduce alkyl group to arenes or heteroarenes, Minisci Reaction is the most general synthetic strategy. In 1971, Minisci et al. reported a novel Ag-catalyzed alkylation of heteroarenes.[16] (Scheme 2) Ammonium persulphate oxidized Ag(I) to Ag(II). With silver catalyst, alkane underwent oxidative decarboxylative protocol and generated radicals. Then the alkyl radicals attacked heteroarenes and generated desired coupling products. (Scheme 3) This method worked so well that nowadays chemists are still applying it to the synthesis of complex structure and trying to extend the substrate scope.[17-21]



Scheme 2. Ag-catalyzed alkylation of heteroarenes



Scheme 3. Proposed possible mechanism

Since it's much harder for aryl carboxylic acids to generate radical through oxidative decarboxylative protocol, Minisci reaction can't utilize aryl carboxylic acids as starting material. A lot of methods were reported to solve this problem. Glorius's group described an intramolecular oxidative decarboxylative arylation.[22] Pd and Ag catalyst helped 2-phenoxybenzoic acid to undergo oxidative decarboxylative protocol and form dibenzofuran in good yield.

Su's group reported an oxidative decarboxylative synthetic route for 2-arylthiophene in 2012.[23] Using Pd/Ag bimetallic system, a variety of benzoic acids could smoothly couple with substituted thiophenes in satisfying yields. Later in 2014, they extended the substrate scope of this reaction system and reported decarboxylative C-2 arylation of furans. And substituted pyrroles also could be utilized as starting materials.[24]

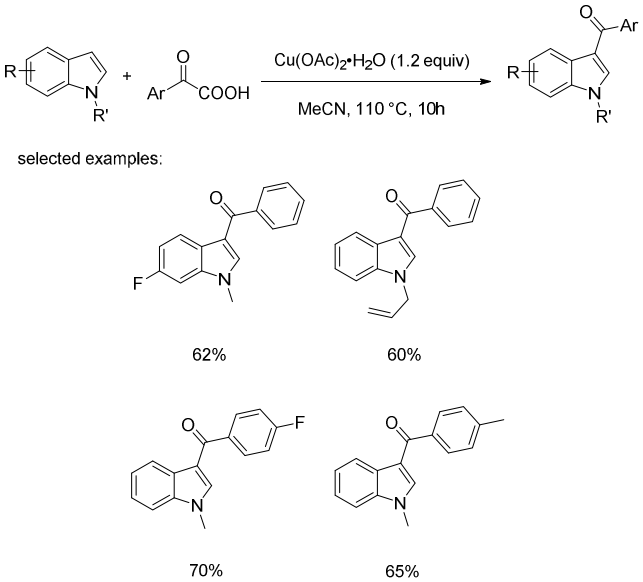
In 2016, Maiti's group described a novel Cu-catalyzed decarboxylative arylation.[25] Without precious metal catalyst, a wide range of 5-membered heteroarenes that contains one or two heteroatoms could be easily coupled with benzoic acids. With oxygen as oxidant, this protocol produced far less waste products than previous works.

3.2 Decarboxylative Oxidative Acylation

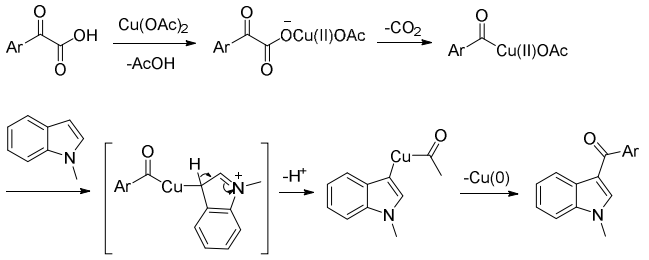
3.2.1 Decarboxylative Acylation

In 1991, Fontana et al. reported the first oxidative decarboxylative cross-coupling of heterocycles and α-keto acids.[26] In the presence of Ag salts and ammonium persulphate, α-keto acids generated acyl radicals and then attacked N-containing heterocycles. In recent years, decarboxylative coupling of α-keto acids is still a widely used approach for direct acylation.

Wang's group described a Cu-catalyzed C3-acylation of N-substituted indoles.[27] (Scheme 4) In this reaction, $Cu(OAc)_2$ worked as both catalyst and oxidant. First α-keto acid reacted with $Cu(OAc)_2$ and afforded a salt of Cu(II) carboxylate. Then the intermediate eliminated CO_2 and attacked indole. After elimination of H^+ and Cu(0), the desired coupling product was obtained. (Scheme 5) This method showed great functional group tolerance.



Scheme 4. Cu-catalyzed C3-acylation of indoles



Scheme 5. Proposed possible mechanism

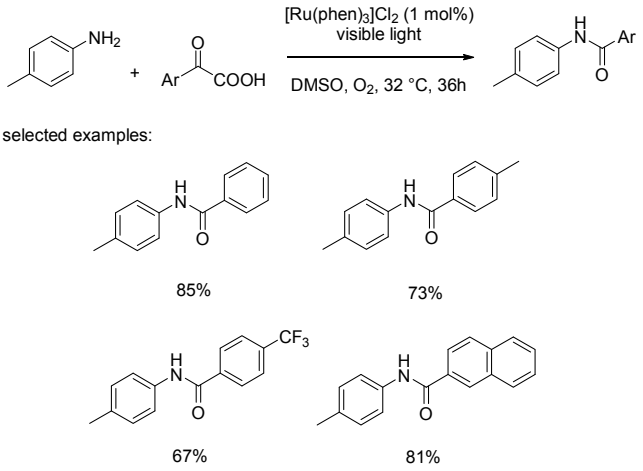
Zhang's group developed a Cu-catalyzed decarboxylative cross-coupling of free (N–H) indoles and α-keto acids.[28] After screening metal catalysts, they found $Cu(OAc)_2$ was crucial for their system and performed better than Pd catalyst. Ag_2CO_3 not only promoted the decarboxylation of α-keto acids, but also worked as terminal oxidant.

With the help of proper directing groups, aromatic compounds without active $C(sp^2)$-H bonds could also undergo the decarboxylative acylation protocol. Ge's group did a lot of work in this field. They reported a Pd-catalyzed decarboxylative cross-coupling of acetanilides and α-keto acids in 2010.[29] Pd catalyst activated C-H bond of *ortho*-position, and then the reaction underwent a decarboxylative oxidative elimination cycle at room temperature. Ge's group also described an *ortho*-acylation of 2-phenylpyridine in 2010.[30] Using $Pd(PhCN)_2Cl_2$, Ag_2O and $K_2S_2O_8$ gave the best result. Both aromatic and aliphatic α-keto acids could work well as starting materials. In 2013, They developed a Pd-catalyzed decarboxylative cross-coupling of benzoic acids and α-keto acids.[31] *Ortho*-acylation products were synthesized in good yields.

Wang's group reported a Pd-catalyzed decarboxylative cross-coupling of azobenzenes and α-keto acids in 2013.[32] This mild method afforded *ortho*-acylation products with oxidant $K_2S_2O_8$. After acylation, the products could transform into indazoles at room temperature. They also developed a decarboxylative acylation of benzamides in 2017.[33] In the presence of $Pd(OAc)_2$, $K_2S_2O_8$ and TfOH, benzamides coupled with α-keto acids and generated *ortho*-acylated products. In this reaction, bis-acylated products weren't observed.

Kim's group reported a Pd-catalyzed decarboxylative cross-coupling of phenylacetamides and α-keto acids in 2013.[34] Through a decarboxylative oxidative elimination Pd catalytic cycle, the decarboxylative *ortho*-acylation of phenylacetamides could proceed. And the products could transform into 3-isochromanone derivatives.

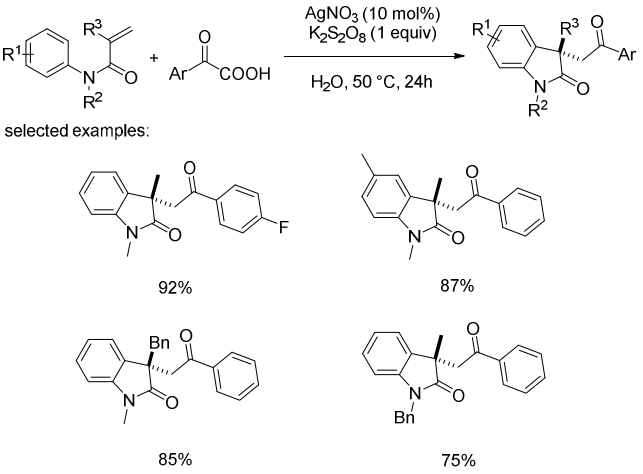
Other than C-C bond formation, decarboxylative coupling could also be route for C-heteroatom bond formation. Lei et al. reported the first photocatalyzed oxidative decarboxylative cross-coupling of amines and α-keto acids in 2014.[35] (Scheme 6) In the presence of visible light, oxygen and photocatalyst $[Ru(phen)_3]Cl_2$, amines and α-keto acids were both activated and then generated amide products. Notably, Lei's team utilized electron paramagnetic resonance (EPR) and detected $[Ru(phen)_3]^+$, which proved the single electron transfer between $[Ru(phen)_3]^{2+}$ and amine.



Scheme 6. Photocatalyzed oxidative decarboxylative acylation of amines

3.2.2 Decarboxylative Cyclization

Normally decarboxylative reaction of α-keto acids involves radical mechanism. Therefore, when α-keto acids react with molecules that have multiple reactive cites, the reaction may undergo a tandem decarboxylative cross-coupling/cyclization and generate complex products. Guo et al. described a Ag-catalyzed decarboxylative cross-coupling/cyclization of N-arylacrylamides with α-keto acids in 2013.[36] (Scheme 7) This environmentally friendly method used water as solvent, and the tandem decarboxylative cyclization could proceed under mild condition.



Scheme 7. Ag-catalyzed tandem decarboxylative cyclization of N-arylacrylamides and α-keto acids

Ding et al. reported 5-exo cyclization of alkynoates with α-keto acids in 2015.[37] With Ag catalyst, α-keto acid converted to acyl radical and attacked the alkynyl group, and then the radical intermediate underwent cyclization and migration in sequence to generate desired product. Various coumarin derivatives were obtained in good yields. Wang et al. also developed a phototatalyzed decarboxylative cross-coupling/cyclization of alkynoates and α-keto acids in 2017.[38] Unlike Ding's work, hypervalent iodine reagent BI-OH

converted α-keto acid to radical under visible light irradiation in this strategy.

Li's group developed a decarboxylative cross-coupling/cyclization of *ortho*-cyanoarylacrylamides with α-keto acids in 2016.[39] In the presence of $AgNO_3$ and $(NH_4)_2S_2O_8$, this method afforded carbonyl-containing quinoline-2,4(1H,3H)-diones. Notably, with $(NH_4)_2S_2O_8$ and benzoic acid, aldehydes could also react with *ortho*-cyanoarylacrylamides in a similar way.

Other carboxylic acids that are able to afford radicals can also participate in decarboxylative cyclization. Lei's group reported NIS-mediated oxidative coupling/annulation of malonate monoesters and 2-vinylpyridines.[40] With assist of base, NIS converted Malonate monoester to key intermediate ethyl 2,2-diiodoacetate. Then ethyl 2,2-diiodoacetate reacted with 2-vinylpyridine and generated indolizine via radical process.

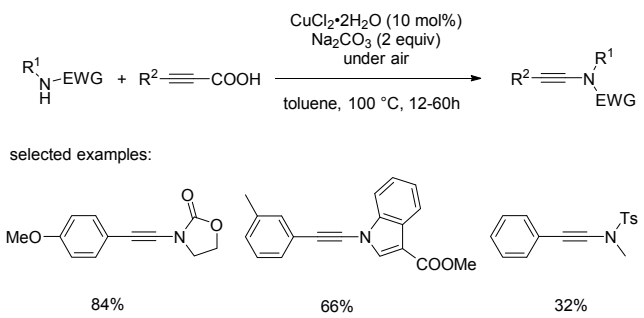
3.3 Decarboxylative Oxidative Alkynylation

Decarboxylative coupling of alkynyl carboxylic acids is an excellent strategy for introducing alkynyl group. In 2012, Zhao's group reported a Pd-catalyzed decarboxylative cross-coupling of indolizines and phenylpropiolic acids.[41] With $Pd(OAc)_2$ and Ag_2CO_3, direct C3-alkynylation of indolizines could proceed. Electron-withdrawing group at C1-position of indolizine is required.

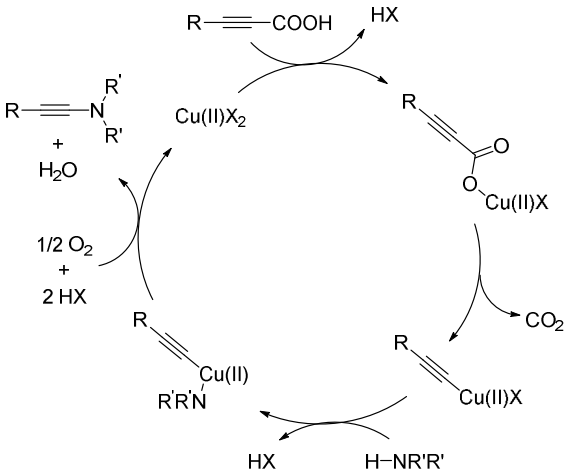
Lee's group developed a Pd-catalyzed decarboxylative cross-coupling of benzoxazoles and alkynyl carboxylic acids in 2013.[42] Ag_2O promoted decarboxylation of alkynyl carboxylic acids and also worked as oxidant. C2-Alkynylation products were obtained under air in high yields. It is noteworthy that this system works under air and doesn't require strong base.

Yu et al. reported a decarboxylative cross-coupling of alkynyl carboxylic acids and alkynes.[43] In the presence of CuI,1,10-phenanthroline and Et_3N, the coupling reaction proceeded under air and formed C(sp)-C(sp) bond without toxic waste.

Jing's group developed a novel Cu-catalyzed decarboxylative oxidative amidation of alkynyl carboxylic acids.[44] (Scheme 8) It is noteworthy that this method utilize air as oxidant, therefore the only byproducts are CO_2 and H_2O. First alkynyl carboxylic acid reacted with $CuCl_2$ and eliminated CO_2. Then the intermediate attacked amide. Finally desired product was afforded by C-N elimination. (Scheme 9)



Scheme 8. Cu-catalyzed decarboxylative cross-coupling of alkynyl carboxylic acids and amides

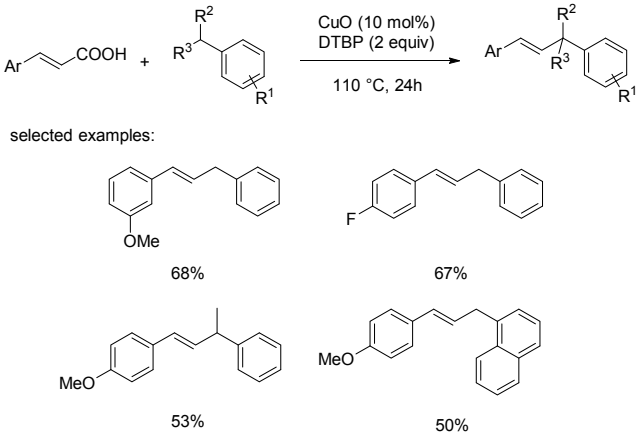


Scheme 9. Proposed possible mechanism

3.4 Decarboxylative Oxidative Olefination/Oxoalkylation

Decarboxylative coupling reaction of cinnamic acids is also a hot topic in this field. Although direct decarboxylation of cinnamic acid couldn't afford stable radical to react, the C=C bond of cinnamic acid offered extra reactive cite. Besides olefination products, decarboxylative reaction of cinnamic acid could also generate oxoalkylation products under proper condition.

Mao's group described a Cu-catalyzed decarboxylative cross-coupling of cinnamic acids and benzylic compounds in 2012.[45] (Scheme 10) DTBP activated C(sp^3)-H bond of benzylic compound. Then the benzylic radical would attack cinnamic acid and afforded olefination product. Later they reported a Fe-catalyzed olefination of benzylic compounds, which had much larger scope of substrate and higher yields.[46]



Scheme 10. Cu-catalyzed decarboxylative olefination of benzylic compounds

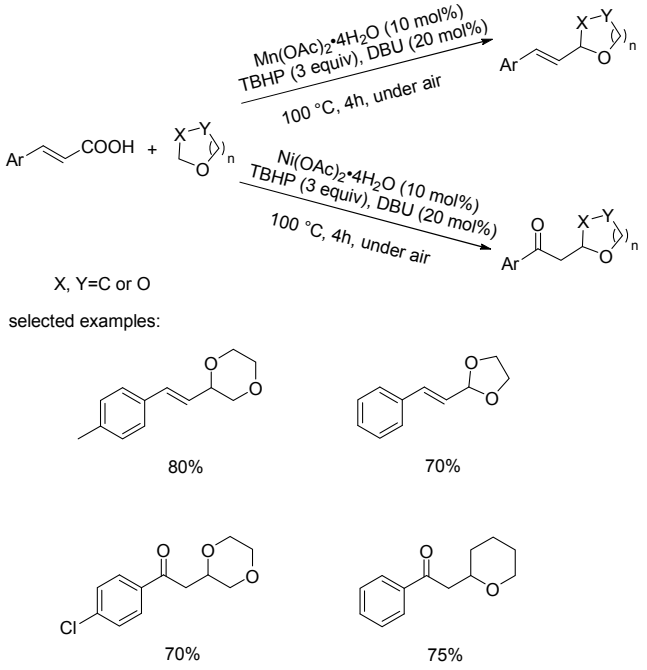
Liu's group developed a Cu-catalyzed decarboxylative cross-coupling of cinnamic acids and alcohols in 2012.[47] A variety of olefination products were obtained in up to 99% yields. Some ethers, alkanes, and toluenes could also react with cinnamic acids in moderate yields.

Our group made some progress about decarboxylative coupling reaction of cinnamic acids. We developed a

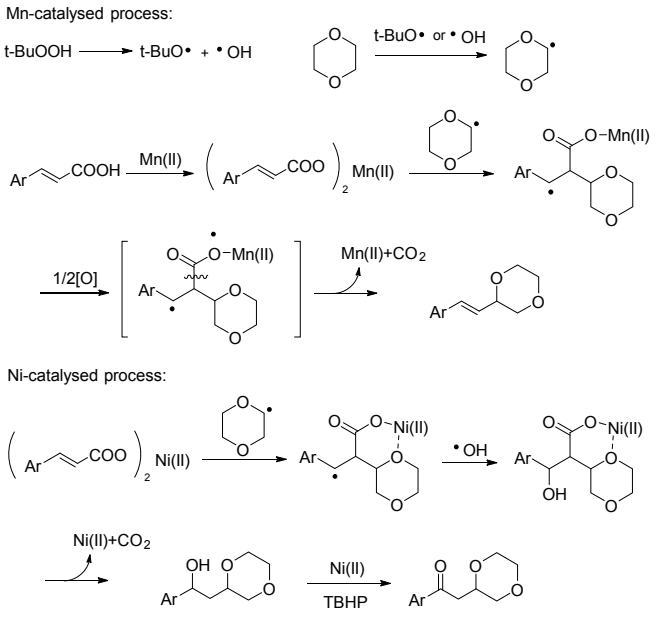
decarboxylative cross-coupling of cinnamic acids and amides in 2014.[48] With catalyst $Ni(OAc)_2$ and oxidant TBHP, this method activated the C-H bond adjacent to nitrogen atom and directly functionalized it.

Later we reported a selective Mn- and Ni-catalyzed decarboxylative coupling reaction of cinnamic acids and cyclic ethers.[49] (Scheme 11) In this system, $Mn(OAc)_2$ catalyst would promote olefination of cyclic ethers while oxoalkylation products were obtained in the presence of $Ni(OAc)_2$. TBHP generated tert-butoxy radical and hydroxyl radical, which activated cyclic ether and transformed it into radical. $Mn(OAc)_2$ reacted with cinnamic acid and afforded a salt of Mn(II) carboxylate. Ether radical attacked the salt of Mn(II) carboxylate and trace oxygen in the solution oxidized the intermediate. After elimination of Mn catalyst and CO_2, the olefination product was generated. The Ni-catalyzed process involved different mechanism. Ether radical attacked the salt of Ni(II) carboxylate, and then hydroxyl radical added to the intermediate. After elimination of Ni catalyst and CO_2, the hydroxylalkylated cyclic ether was oxidized to desired oxoalkylation product. (Scheme 12)

Recently we extended the substrate scope of this reaction system and reported decarboxylative coupling reaction of cinnamic acids and low boiling-point non-cyclic ethers.[50] The best combination for olefination was copper powder, TBHP and Na_2CO_3. When we employ $Co(OAc)_2$ as catalyst, some substrates could afford oxoalkylation products.



Scheme 11. Selective Mn- and Ni-catalyzed decarboxylative coupling of cinnamic acids and cyclic ethers



Scheme 12. Proposed possible mechanism

Sun's group developed a selective transition metal-free decarboxylative coupling of cinnamic acids and alkanes.[51] Oxoalkylation products were obtained in the presence of DTBP, TBHP and molecule sieve while olefination products with (E)-configuration were obtained with only DTBP.

4 Conclusions

Since Nilsson described the first decarboxylative coupling reaction in 1966,[52] the decarboxylative coupling reaction has become one of the most important tools for organic synthesis. In recent years, decarboxylative oxidative coupling reactions, which normally involve direct C-H bond activation, attract more and more interests. Compared with other conventional methods, this strategy is more environmental friendly and step-economic.

There are still some challenges in this method. In order to fulfill decarboxylation, high reaction temperature excess radical initiators, and oxidants are often required. These flaws keep decarboxylative oxidative coupling reaction from wide applications in synthesis of complex structures and natural products. Development of methods with milder conditions is highly desired. Although further research needs to be done to solve these problems, we believe decarboxylative oxidative coupling reaction is a promising area and more novel reactions would be reported.

AUTHOR INFORMATION

Corresponding Author

*E-Mail: nxwang@mail.ipc.ac.cn. Tel.: +86-10-82543575. Fax: +86-10-62554670.
*E-Mail: xingy@wpunj.edu. Tel.: (973)-720-3462

Tong Zhang obtained obtained his B.Sc form College of Chemistry and Molecular Engineering at Peking University and M.Sc. from College of Chemistry and Chemical Engineering at University of Chinese Academy of Sciences. He will obtain his doctorate under guidance of Professor Nai-Xing Wang at the Technical Institute of Physics and Chemistry, Chinese Academy of Science.

Nai-Xing Wang was appointed professor at the Technical Institute of Physics and Chemistry, Chinese Academy of Sciences and a "Hundred Talent Program" of the Chinese Academy of Sciences in May 2000 after completing his post-doctoral research at Rice University. At present, Professor Wang is primarily engaged in the synthesis of complex chiral compounds and research into new methodologies of organic synthesis.

Yalan Xing joined the chemistry department of the William Paterson University as an assistant professor in fall 2014 after completing her postdoctoral training in Professor Yoshito Kishi's group at Harvard University. At William Paterson University, she conducts research in developing new synthetic methodologies to provide unique access to bioactive small-molecule agents and ultimately to address the increasing needs in biomedical research.

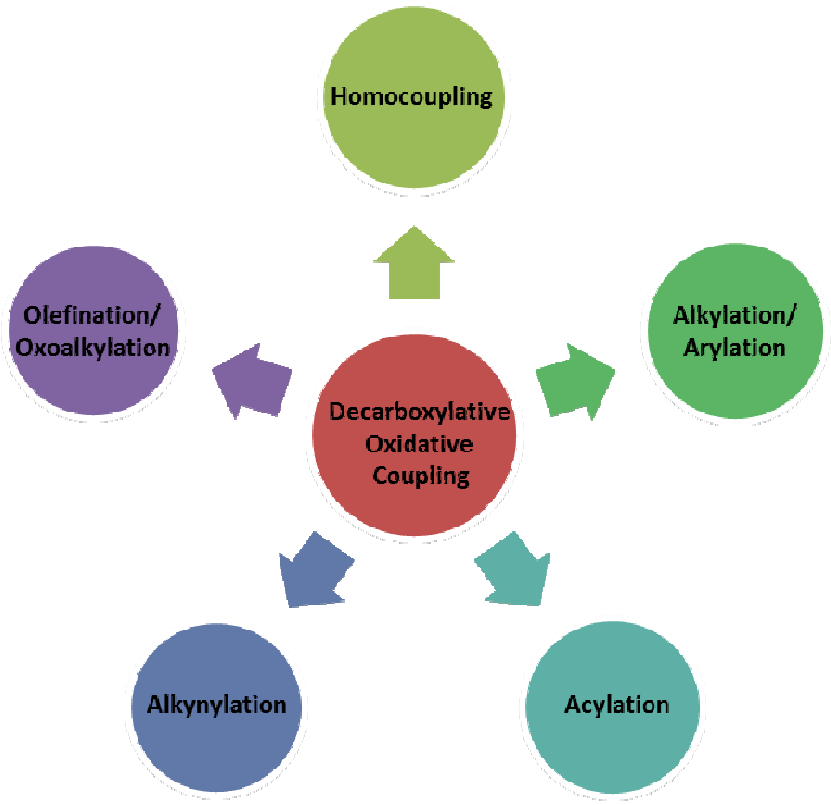
ACKNOWLEDGMENT

Support for this research was provided by the Natural Science Foundation of China (21572240).

REFERENCES

(1) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. Palladium(II)-Catalyzed C-H Activation/C-C Cross-Coupling Reactions: Versatility and Practicality. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094-5115.
(2) Liu, C.; Yuan, J.; Gao, M.; Tang, S.; Li, W.; Shi, R.; Lei, A. Oxidative Coupling between Two Hydrocarbons: An Update of Recent C–H Functionalizations. *Chem. Rev.* **2015**, *115*, 12138-12204.
(3) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. Pd-catalyzed oxidative coupling with organometallic reagents via C-H activation. *Chem. Comm.* **2010**, *46*, 677-685.
(4) Yang, Y.; Lan, J.; You, J. Oxidative C–H/C–H Coupling Reactions between Two (Hetero)arenes. *Chem. Rev.* **2017**, *117*, 8787-8863.
(5) Zi, W.; Zuo, Z.; Ma, D. Intramolecular Dearomative Oxidative Coupling of Indoles: A Unified Strategy for the Total Synthesis of Indoline Alkaloids. *Acc. Chem. Res.* **2015**, *48*, 702-711.
(6) Twilton, J.; Le, C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. The Merger of Transition Metal and Photocatalysis. *Nature Reviews Chemistry* **2017**, *1*, 0052.
(7) Borah, A. J.; Yan, G. Decarboxylative Functionalization of Cinnamic Acids. *Org. Biomol. Chem.* **2015**, *13*, 8094-8115.
(8) Guo, L.-N.; Wang, H.; Duan, X.-H. Recent Advances in Catalytic Decarboxylative Acylation Reactions via a Radical Process. *Org. Biomol. Chem.* **2016**, *14*, 7380-7391.
(9) Perry, G. J. P.; Larrosa, I. Recent Progress in Decarboxylative Oxidative Cross-Coupling for Biaryl Synthesis. *Eur. J. Org. Chem.* **2017**, *2017*, 3517-3527.
(10) Rodriguez, N.; Goossen, L. J. Decarboxylative Coupling Reactions: A Modern Strategy for C-C-Bond Formation. *Chem. Soc. Rev.* **2011**, *40*, 5030-5048.
(11) Wei, Y.; Hu, P.; Zhang, M.; Su, W. Metal-Catalyzed Decarboxylative C–H Functionalization. *Chem. Rev.* **2017**, *117*, 8864-8907.
(12) Cornella, J.; Lahlali, H.; Larrosa, I. Decarboxylative Homocoupling of (Hetero)aromatic Carboxylic Acids. *Chem. Comm.* **2010**, *46*, 8276-8278.
(13) Fu, Z.; Li, Z.; Xiong, Q.; Cai, H. Facile Synthesis of 2,2'-Dinitrosubstituted Biaryls through Cu-Catalyzed Ligand-Free Decarboxylative Homocoupling of ortho-Nitrobenzoic Acids. *RSC Adv.* **2015**, *5*, 52101-52104.
(14) Gooßen, L. J.; Deng, G.; Levy, L. M. Synthesis of Biaryls via Catalytic Decarboxylative Coupling. *Science* **2006**, *313*, 662-664.
(15) Hu, P.; Shang, Y.; Su, W. A General Pd-Catalyzed Decarboxylative Cross-Coupling Reaction between Aryl Carboxylic Acids: Synthesis of Biaryl Compounds. *Angew. Chem. Int. Ed.* **2012**, *51*, 5945-5949.
(16) Minisci, F.; Bernardi, R.; Bertini, F.; Galli, R.; Perchinummo, M. Nucleophilic Character of Alkyl Radicals—VI: A New Convenient Selective Alkylation of Heteroaromatic Bases. *Tetrahedron* **1971**, *27*, 3575-3579.
(17) Monga, V.; Meena, C. L.; Kaur, N.; Kumar, S.; Pawar, C.; Sharma, S. S.; Jain, R. Facile Synthesis of N-α-Boc-1,2-Dialkyl-L-Histidines: Utility in the Synthesis of Thyrotropin-Releasing Hormone (trh) Analogs and Evaluation of the CNS Activity. *J. Heterocycl. Chem.* **2008**, *45*, 1603-1608.
(18) Palde, P. B.; Gareiss, P. C.; Miller, B. L. Selective Recognition of Alkyl Pyranosides in Protic and Aprotic Solvents. *J. Am. Chem. Soc.* **2008**, *130*, 9566-9573.
(19) Shore, D. G. M.; Wasik, K. A.; Lyssikatos, J. P.; Estrada, A. A. Minisci Alkylations of Electron-Deficient Pyrimidines with Alkyl Carboxylic Acids. *Tetrahedron Lett.* **2015**, *56*, 4063-4066.
(20) Lipp, B.; Nauth, A. M.; Opatz, T. Transition-Metal-Free Decarboxylative Photoredox Coupling of Carboxylic Acids and Alcohols with Aromatic Nitriles. *J. Org. Chem.* **2016**, *81*, 6875-6882.
(21) Garza-Sanchez, R. A.; Tlahuext-Aca, A.; Tavakoli, G.; Glorius, F. Visible Light-Mediated Direct Decarboxylative C–H Functionalization of Heteroarenes. *ACS Catal.* **2017**, *7*, 4057-4061.
(22) Wang, C.; Piel, I.; Glorius, F. Palladium-Catalyzed Intramolecular Direct Arylation of Benzoic Acids by Tandem

Decarboxylation/C–H Activation. *J. Am. Chem. Soc.* **2009**, *131*, 4194-4195.
(23) Hu, P.; Zhang, M.; Jie, X.; Su, W. Palladium-Catalyzed Decarboxylative C-H Bond Arylation of Thiophenes. *Angew. Chem. Int. Ed.* **2012**, *51*, 227-231.
(24) Pei, K.; Jie, X.; Zhao, H.; Su, W. Palladium-Catalyzed Decarboxylative C–H Bond Arylation of Furans. *Eur. J. Org. Chem.* **2014**, *2014*, 4230-4233.
(25) Patra, T.; Nandi, S.; Sahoo, S. K.; Maiti, D. Copper Mediated Decarboxylative Direct C-H Arylation of Heteroarenes with Benzoic Acids. *Chem. Comm.* **2016**, *52*, 1432-1435.
(26) Fontana, F.; Minisci, F.; Nogueira Barbosa, M. C.; Vismara, E. Homolytic Acylation of Protonated Pyridines and Pyrazines with α-Keto Acids: The Problem of Monoacylation. *J. Org. Chem.* **1991**, *56*, 2866-2869.
(27) Yu, L.; Li, P.; Wang, L. Copper-Promoted Decarboxylative Direct C3-Acylation of N-Substituted Indoles with α-Oxocarboxylic Acids. *Chem. Comm.* **2013**, *49*, 2368-2370.
(28) Wang, C.; Wang, S.; Li, H.; Yan, J.; Chi, H.; Chen, X.; Zhang, Z. Copper-Catalyzed Decarboxylative C3-Acylation of Free (N-H) Indoles with α-Oxocarboxylic Acids. *Org. Biomol. Chem.* **2014**, *12*, 1721-1724.
(29) Fang, P.; Li, M.; Ge, H. Room Temperature Palladium-Catalyzed Decarboxylative ortho-Acylation of Acetanilides with α-Oxocarboxylic Acids. *J. Am. Chem. Soc.* **2010**, *132*, 11898-11899.
(30) Li, M.; Ge, H. Decarboxylative Acylation of Arenes with α-Oxocarboxylic Acids via Palladium-Catalyzed C–H Activation. *Org. Lett.* **2010**, *12*, 3464-3467.
(31) Miao, J.; Ge, H. Palladium-Catalyzed Chemoselective Decarboxylative Ortho Acylation of Benzoic Acids with α-Oxocarboxylic Acids. *Org. Lett.* **2013**, *15*, 2930-2933.
(32) Li, H.; Li, P.; Tan, H.; Wang, L. A Highly Efficient Palladium-Catalyzed Decarboxylative ortho-Acylation of Azobenzenes with α-Oxocarboxylic Acids: Direct Access to Acylated Azo Compounds. *Chem. Eur. J.* **2013**, *19*, 14432-14436.
(33) Jing, K.; Yao, J.-P.; Li, Z.-Y.; Li, Q.-L.; Lin, H.-S.; Wang, G.-W. Palladium-Catalyzed Decarboxylative ortho-Acylation of Benzamides with α-Oxocarboxylic Acids. *J. Org. Chem.* **2017**, *82*, 12715-12725.
(34) Park, J.; Kim, M.; Sharma, S.; Park, E.; Kim, A.; Lee, S. H.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. Pd(II)-Catalyzed Decarboxylative Acylation of Phenylacetamides with α-Oxocarboxylic Acids via C-H Bond Activation. *Chem. Comm.* **2013**, *49*, 1654-1656.
(35) Liu, J.; Liu, Q.; Yi, H.; Qin, C.; Bai, R.; Qi, X.; Lan, Y.; Lei, A. Visible-Light-Mediated Decarboxylation/Oxidative Amidation of α-Keto Acids with Amines under Mild Reaction Conditions Using O_2. *Angew. Chem. Int. Ed.* **2014**, *53*, 502-506.
(36) Wang, H.; Guo, L.-N.; Duan, X.-H. Silver-Catalyzed Decarboxylative Acylarylation of Acrylamides with α-Oxocarboxylic Acids in Aqueous Media. *Adv. Synth. Catal.* **2013**, *355*, 2222-2226.
(37) Liu, T.; Ding, Q.; Zong, Q.; Qiu, G. Radical 5-exo Cyclization of Alkynoates with 2-Oxoacetic Acids for Synthesis of 3-Acylcoumarins. *Org. Chem. Front.* **2015**, *2*, 670-673.
(38) Yang, S.; Tan, H.; Ji, W.; Zhang, X.; Li, P.; Wang, L. Visible Light-Induced Decarboxylative Acylarylation of Phenyl Propiolates with α-Oxocarboxylic Acids to Coumarins Catalyzed by Hypervalent Iodine Reagents under Transition Metal-Free Conditions. *Adv. Synth. Catal.* **2017**, *359*, 443-453.
(39) Wang, S.-S.; Fu, H.; Shen, Y.; Sun, M.; Li, Y.-M. Oxidative Radical Addition/Cyclization Cascade for the Construction of Carbonyl-Containing Quinoline-2,4(1H,3H)-Diones. *J. Org. Chem.* **2016**, *81*, 2920-2929.
(40) Tang, S.; Gao, X.; Lei, A. Decarboxylative (4+1) Oxidative Annulation of Malonate Monoesters with 2-Vinylpyridine Derivatives. *Adv. Synth. Catal.* **2016**, *358*, 2878-2882.
(41) Zhao, B. Pd-Catalyzed C-3 Functionalization of Indolizines via C-H Bond Cleavage. *Org. Biomol. Chem.* **2012**, *10*, 7108-7119.
(42) Kim, J.; Kang, D.; Yoo, E. J.; Lee, P. H. Palladium-Catalyzed Decarboxylative C–H Alkynylation of Benzoxazoles with α,β-Ynoic Acids. *Eur. J. Org. Chem.* **2013**, *2013*, 7902-7906.
(43) Yu, M.; Pan, D.; Jia, W.; Chen, W.; Jiao, N. Copper-Catalyzed Decarboxylative Cross-Coupling of Propiolic Acids and Terminal Alkynes. *Tetrahedron Lett.* **2010**, *51*, 1287-1290.
(44) Jia, W.; Jiao, N. Cu-Catalyzed Oxidative Amidation of Propiolic Acids Under Air via Decarboxylative Coupling. *Org. Lett.* **2010**, *12*, 2000-2003.
(45) Yang, H.; Sun, P.; Zhu, Y.; Yan, H.; Lu, L.; Qu, X.; Li, T.; Mao, J. Copper-Catalyzed Decarboxylative $C(sp^2)$-$C(sp^3)$ Coupling Reactions via Radical Mechanism. *Chem. Comm.* **2012**, *48*, 7847-7849.
(46) Yang, H.; Yan, H.; Sun, P.; Zhu, Y.; Lu, L.; Liu, D.; Rong, G.; Mao, J. Iron-Catalyzed Direct Alkenylation of sp^3(C-H) Bonds via Decarboxylation of Cinnamic Acids under Ligand-Free Conditions. *Green Chem.* **2013**, *15*, 976-981.
(47) Cui, Z.; Shang, X.; Shao, X.-F.; Liu, Z.-Q. Copper-Catalyzed Decarboxylative Alkenylation of sp^3 C-H Bonds with Cinnamic Acids via a Radical Process. *Chem. Sci.* **2012**, *3*, 2853-2858.
(48) Zhang, J.-X.; Wang, Y.-J.; Wang, N.-X.; Zhang, W.; Bai, C.-B.; Li, Y.-H.; Wen, J.-L. Nickel-Catalyzed sp^3 C–H Bond Activation from Decarboxylative Cross-Coupling of α,β-Unsaturated Carboxylic Acids with Amides. *Synlett* **2014**, *25*, 1621-1625.
(49) Zhang, J.-X.; Wang, Y.-J.; Zhang, W.; Wang, N.-X.; Bai, C.-B.; Xing, Y.-L.; Li, Y.-H.; Wen, J.-L. Selective Nickel- and Manganese-Catalyzed Decarboxylative Cross Coupling of Some α,β-Unsaturated Carboxylic Acids with Cyclic Ethers. *Sci. Rep.* **2014**, *4*, 7446-7450.
(50) Zhang, T.; Lan, X.-W.; Zhou, Y.-Q.; Wang, N.-X.; Wu, Y.-H.; Xing, Y.; Wen, J.-L. $C(sp^3)$–H Bond Functionalization of Non-Cyclic Ethers by Decarboxylative Oxidative Coupling with α,β-Unsaturated Carboxylic Acids. *Sci. China Chem.* **2018**, *61*, 180-183.
(51) Ji, J.; Liu, P.; Sun, P. Peroxide Promoted Tunable Decarboxylative Alkylation of Cinnamic Acids to Form Alkenes or Ketones under Metal-Free Conditions. *Chem. Comm.* **2015**, *51*, 7546-7549.
(52) Nilsson, M. A New Biaryl Synthesis Illustrating a Connection between Ullmann Biaryl Synthesis and Copper-Catalysed Decarboxylation. *Acta Chem. Scand.* **1966**, *20*, 423-426.


Homocoupling
Olefination/
Oxoalkylation
Alkylation/
Arylation
Decarboxylative
Oxidative
Coupling
Alkynylation
Acylation