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## Abstract

In the presence of catalytic  $[\text{IrCp}^*\text{Cl}_2]_2$  and  $\text{Ag}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3$  as the base and acetone as the solvent, benzoic acids react with arenediazonium salts to give the corresponding diaryl-2-carboxylates. This C–H arylation process is generally applicable to diversely substituted substrates, ranging from extremely electron-rich to electron-poor derivatives. The carboxylate directing group can be tracelessly removed or employed for further functionalization.

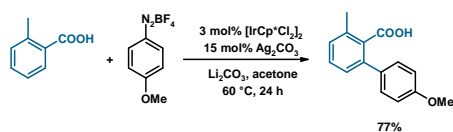
## Introduction

Transition-metal-catalyzed C–H arylations constitute modern and sustainable tools for the formation of C–C and C–heteroatom bonds. The regioselectivity of the C–H arylation can be controlled by various directing groups.<sup>[1]</sup> However, these directing groups often need to be introduced and later removed in additional reaction steps, increasing the complexity of the overall synthetic sequence.

The use of carboxylates as directing groups represents a tremendous advance in this area.<sup>[2]</sup> Benzoic acids are widely available in great structural diversity, and after *ortho*-arylation, the carboxylate group can be tracelessly removed,<sup>[2c,d,3]</sup> or utilized as a leaving group in further functionalization steps.<sup>[4]</sup> However, the low coordinating ability of this group poses substantial challenges with regard to reactivity and selectivity of the C–H activating step.

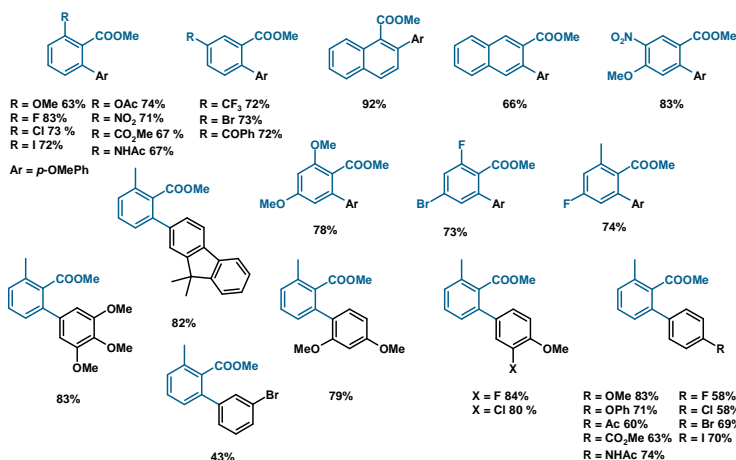
## Ir-Catalyzed *ortho*-Arylation with Arenediazonium Salts

We have disclosed a straightforward iridium-catalyzed *ortho*-arylation of benzoic acids with arenediazonium salts under mild conditions.<sup>[5]</sup> Arenediazonium salts can be easily prepared from low-cost anilines in great structural diversity in large scale, and their intrinsic reactivity is high even at low temperatures.



## Substrate Scope

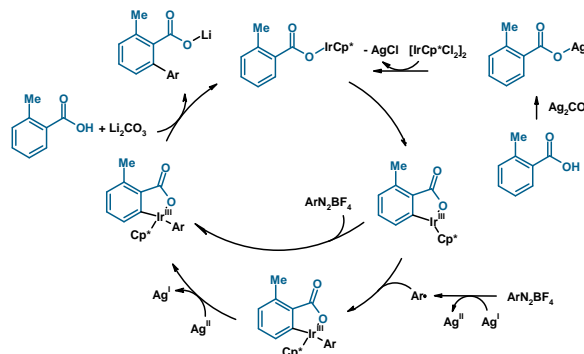
The C–H arylation process is generally applicable to diversely substituted substrates. The tolerance of bromo and iodo groups demonstrates the orthogonality of the present transformation to traditional cross-coupling processes.



## References

- [1] L. Ackermann, R. Vicente, A. R. Kapti, *Angew. Chem. Int. Ed.* **2009**, *48*, 9792. [2] a) H. A. Chiong, Q.-N. Pham, O. Daugulis, *J. Am. Chem. Soc.* **2007**, *129*, 9879; b) R. Giri, N. Mangel, J.-J. Li, D.-H. Wang, S. P. Breazzano, L. B. Saunders, J.-Q. Yu, *J. Am. Chem. Soc.* **2007**, *129*, 3510; c) J. Cornella, M. Righi, I. Larrosa, *Angew. Chem. Int. Ed.* **2011**, *50*, 9429; d) Y. Zhang, H. Zhao, M. Zhang, W. Su, *Angew. Chem. Int. Ed.* **2015**, *54*, 3817. [3] a) P. Mamone, G. Danoun, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 6704; b) S. Bhadra, W. I. Dzik, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2013**, *52*, 2959. [4] L. J. Gooßen, G. Deng, L. M. Levy, *Science* **2006**, *313*, 662. [5] L. Huang, D. Hackenberger, L. J. Gooßen, *Angew. Chem. Int. Ed.* **2015**, *54*, 12607.

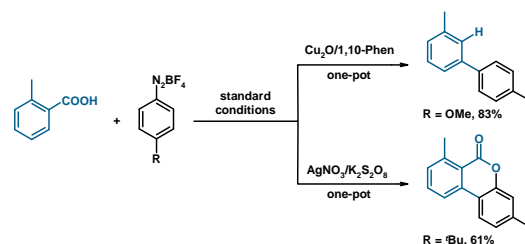
## Proposed Mechanism



Control experiments show that the silver salt not only acts as the halide abstractor but also enables one-electron transfer steps of the iridium catalyst.

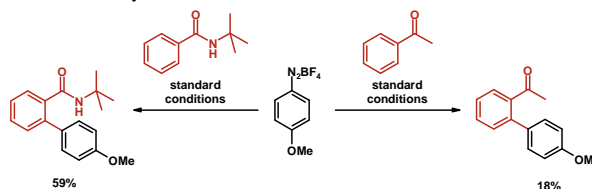
## Optional Functionalizations

*In situ* protodecarboxylation directly leads to the parent biaryl in high yield and the oxidative cyclization gives lactones in good yield.

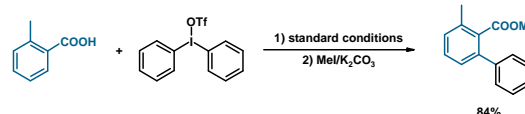


## Further Substrates

Under the optimal conditions, the free carboxylate is not only the simplest and thus most desirable, but also the most effective directing group. However, carboxamides and ketones also gave the desired product, albeit in low to moderate yields.



Furthermore, C–H arylation can alternatively be achieved with diaryliodonium salts electrophiles.



## Acknowledgement

