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Stereospecific Decarboxylative Benzylation of Enolates: Development and Mechanistic Insight

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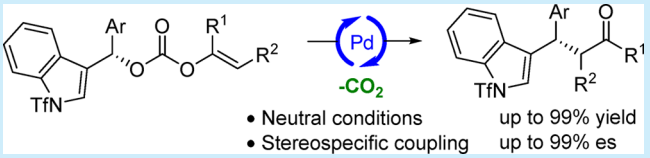
Supporting Information

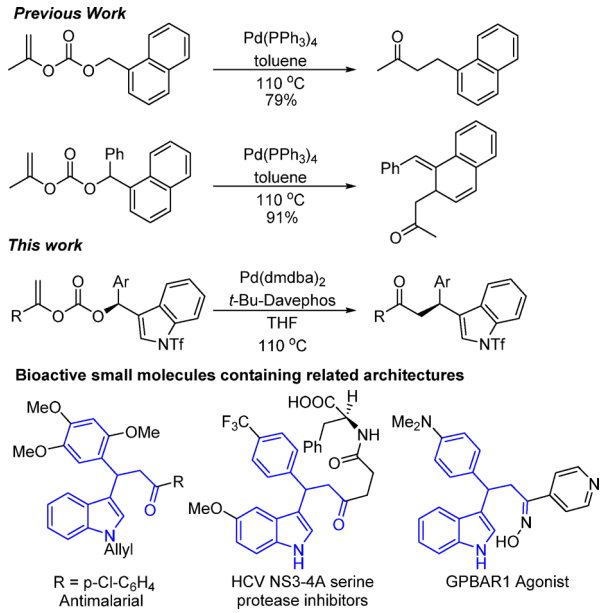
ABSTRACT: A palladium-catalyzed decarboxylative coupling of enol carbonates with diarylmethyl electrophiles that are derived from secondary benzylic alcohols has been developed. This method allows the generation of a variety of β-diaryl ketones through an efficient and highly stereospecific coupling. In addition, detailed mechanistic insight into the coupling suggests that the reaction is a rare example of an intramolecular decarboxylative coupling that proceeds without crossover between reactants.



The formation of C−C bonds via palladium-catalyzed decarboxylative coupling reactions has been proven to be a powerful tool in organic synthesis.[1] Compared to traditional coupling reactions, the avoidance of toxic organic halides and sensitive preformed organometallics, in addition to the neutral coupling conditions, make decarboxylative coupling reactions increasingly attractive. In the 30 years since Saegusa and Tsuji's pioneering work on decarboxylative allylation,[2] a large number of contributions have furthered the utility and scope of such couplings.[3] Among them, α-allylation of enolates has received significant attention in the past several years due to the synthetic flexibility of the product ketones.[4] A number of research groups, including ours as well as those of Stoltz and Trost, have been dedicated to the understanding of the mechanisms of decarboxylative allylation as well as the application of these methods toward catalytic asymmetric reactions and total synthesis.[5,6]

While there have been significant advances in the development and understanding of decarboxylative allylations, the analogous decarboxylative benzylations have seen much less progress.[7] Although decarboxylative benzylations using primary benzyl alcohol derivatives have had some success, few examples using secondary benzyl esters have been reported.[8] Moreover, the development of decarboxylative benzylations that give rise to enantioenriched products lags far behind related allylation chemistry.[9] Thus, we aimed to develop a decarboxylative coupling of diarylmethyl electrophiles that would be applicable to the stereospecific synthesis of enantioenriched tertiary diarylmethanes (Scheme 1).[10] This is particularly challenging due to the propensity of diarylmethyl electrophiles to homocouple to form benzyl dimers[11] or racemize via formation of achiral cationic intermediates.[9a,12c] Nonetheless, such a stereospecific coupling could address the difficulty of construction of tertiary stereogenic centers with two aryl substituents. Although excellent progress has been made in nickel-catalyzed cross-coupling reactions of secondary benzylic alcohol derivatives,[11b,12] those reactions inevitably require

Scheme 1. Decarboxylative Benzylation of Enolates



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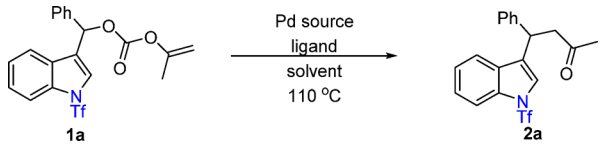
stoichiometric organometallic reagents and they are rarely used to couple diarylmethyl electrophiles that bear important heteroaromatics like indole.[12c] Herein we report the development and mechanistic study of a decarboxylative coupling of secondary benzyl esters with enolates, with a particular focus on coupling difficult indole-based diarylmethyl electrophiles.

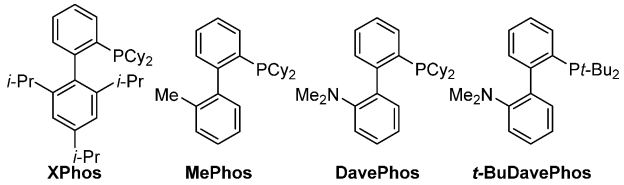
Considering the utility of the products,[13] we initially chose the secondary 3-indolylcarbinol-derived enol carbonate **1a** as a model substrate to test the feasibility of our decarboxylative coupling, and to optimize reaction conditions (Table 1). Unlike

Table 1. Optimization of Decarboxylative Coupling[a]



entry	Pd source	ligand	solvent	concn (M)	yield (%)[b]
1	$Pd(PPh_3)_4$	none	toluene	0.1	trace
2	$Pd_2dba_3CHCl_3$	$P(furyl)_3$	toluene	0.1	trace
3	$Pd_2dba_3CHCl_3$	dppe	toluene	0.1	N.R.
4	$Pd_2dba_3CHCl_3$	Xantphos	toluene	0.1	trace
5	$Pd_2dba_3CHCl_3$	MePhos	toluene	0.1	47
6	$Pd_2dba_3CHCl_3$	MePhos	dioxane	0.1	32
7	$Pd_2dba_3CHCl_3$	MePhos	DME	0.1	55
8	$Pd_2dba_3CHCl_3$	XPhos	DME	0.1	60
9	$Pd_2dba_3CHCl_3$	DavePhos	DME	0.1	73
10	$Pd(dba)_2$	DavePhos	DME	0.1	66
11	$Pd(dmdba)_2$[c]	DavePhos	DME	0.1	74
12	$Pd(dmdba)_2$	DavePhos	THF	0.1	75
13	$Pd(dmdba)_2$	DavePhos	THF	0.04	76
14	$Pd(dmdba)_2$	*t*Bu-DavePhos	THF	0.04	86 (86)

[a]Reactions of enol carbonate (0.1 mmol), Pd/ligand (10/12 mol %), 24−48 h. [b]NMR yield using 1,3,5-trimethoxybenzene internal standard (isolated yield in parentheses). [c]dmdba = 3,5,3′,5′-(dimethoxydibenzylidene)acetone.

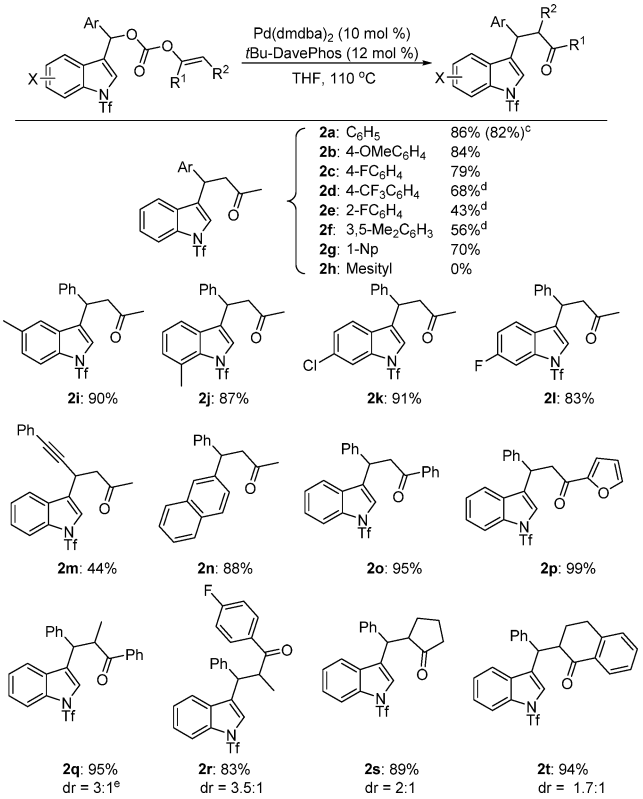


our previous experience with primary benzyl electrophiles,[8b] $Pd(PPh_3)_4$ was not an effective catalyst for coupling secondary benzylic carbonates (entry 1). Other common ligands used in palladium-catalyzed benzylic coupling reactions, including tri(2-furyl)phosphine, dppe, and xantphos, were also not suitable for this decarboxylative coupling (entries 2−4). To our delight, Buchwald's bulky monophosphorus ligand MePhos provided the desired product in moderate yield (entry 5).[14] Using DME as solvent further improved the yield to 55% (entry 7).

Testing other classes of Buchwald ligands showed that XPhos increased the yield to 60%, and DavePhos further improved the reaction to give the desired product in a good yield (entry 9, 73%). The use of $Pd(dmdba)_2$ precatalyst in THF under more dilute conditions also led to a cleaner reaction and slightly better yields (entry 13). Finally, increasing the steric hindrance of the ligand by using tBu-DavePhos led to the optimal yield (entry 14).

With the optimized conditions in hand, we first tested the generality of this method for coupling enolates with indole-derived diarylmethyl electrophiles.[15] These studies showed that various substituted secondary 3-indolylcarbinols served as suitable coupling partners (Scheme 2). Substitution with an

Scheme 2. Decarboxylative Functionalization of Different Enolates[a,b,c]



[a]Reactions of enol carbonate (0.2 mmol, 0.04 M), Pd/ligand (10/12 mol %) in 25 mL microwave vial. [b]Isolated yields. [c]1.5 mmol scale reaction. [d]140 °C in butyl ether. [e]dr values determined by ^1H NMR spectroscopy of the crude reaction mixture.

electron-donating group, such as a methoxy group (**2b**), provided somewhat higher yields than analogous reactants that were *p*-substituted with electron-withdrawing groups, such as F or CF_3 (**2c**, **2d**). The electron-donating methoxy likely stabilizes the intermediate π-benzyl palladium complex, allowing more facile oxidative addition. Sterics may also play a role in the reaction, with the *o*-F substrate giving a low yield (**2e**), and the mesityl substrate failing to undergo any reaction (**2h**) (Figure 1).

Substitution at the 4-position of the indole also completely inhibited the reaction. Presumably these substrates fail due to steric destabilization of the intermediate π-benzyl complexes,

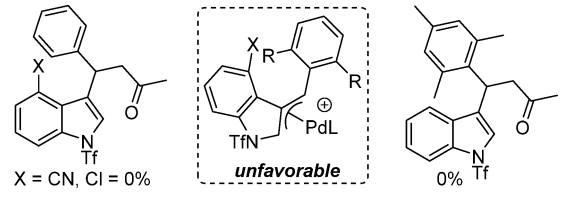


Figure 1. Reaction limitations.

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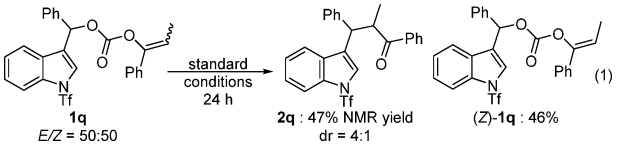
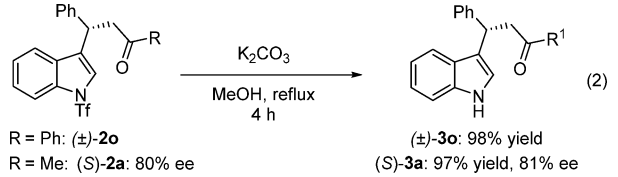
preventing oxidative addition (Figure 1). Finally, the coupling does not require both the indole and the phenyl group; replacing the phenyl group with an alkynyl group also produced a corresponding homopropargylic ketone (**2m**), and a secondary benzylic enol carbonate that lacks the indole motif was also a good substrate for decarboxylative coupling (**2n**) (Scheme 2).

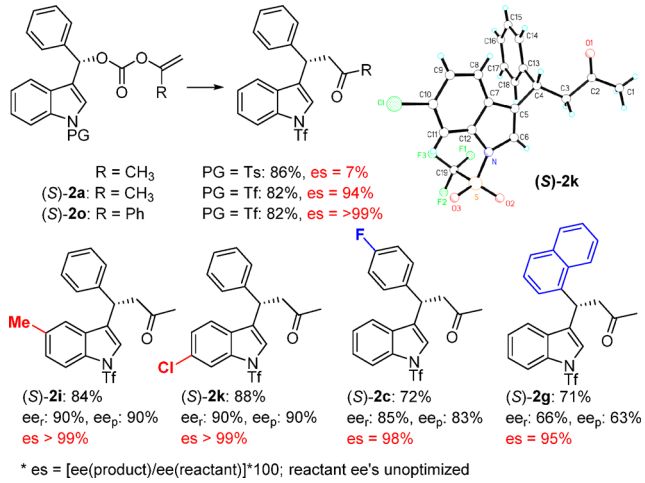
Enol carbonates derived from a variety of ketones were also compatible reaction partners, giving the corresponding α-functionalized ketones in good to excellent yields (Scheme 2). The acetophenone enolate provided the coupling product (**2o**) in even higher yield than was achieved with the acetone enolate. Similarly, other enol carbonates derived from aromatic ketones underwent decarboxylative coupling in good to high yield (**2p,q,r,t**). In addition, secondary nucleophilic coupling partners, including cyclic enolates, were also suitable for the process; the reaction efficiency was not affected, even if the newly formed bond had two tertiary stereogenic centers (**2q−t**, 83−95%). However, the diastereoselectivities of the coupling were not high. Interestingly, the geometry of the substituted enolate is critical for successful reaction. When a 50:50 *E*/*Z* mixture of enol carbonates was subjected to the reaction conditions, only the *E* isomer underwent reaction, while the majority of the *Z* isomer was isolated unchanged (eq 1). Thus, attainment of high yields with substituted enolates necessitates use of the *E*-enol carbonates.



Stereospecific cross-coupling reactions of readily available secondary alcohols, or their derivatives, has the potential to be a significant tool for asymmetric synthesis. Thus, developing an enantiospecific decarboxylative coupling under neutral conditions was highly desired. Since indole-based electrophiles form relatively stable carbocations, they have an inherent tendency toward racemization.[12c] In keeping with this observation, the *N*-protecting group proved critical for highly enantiospecific coupling. For example, an enantioenriched *N*-tosyl protected enol carbonate produced a nearly racemic product, proceeding with only 7% stereochemical fidelity, or enantiospecificity. However, we were excited to find that the analogous *N*-triflyl reactant produced **2a**, with high stereospecificity (94%, Scheme 3). Several other enol carbonates that varied the enolate, indole fragment, or aryl group all underwent similar decarboxylative coupling with high enantiospecificity to produce products in good yield, which makes this transformation a potentially practical method for asymmetric synthesis.[16,17] Importantly, the use of a triflyl protecting group destabilizes the free carbocation enough to allow stereospecific coupling and also allows straightforward deprotection to form free indoles using mild conditions that did not racemize the product (eq 2).

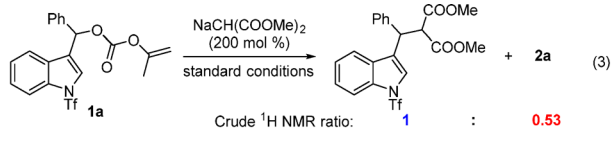


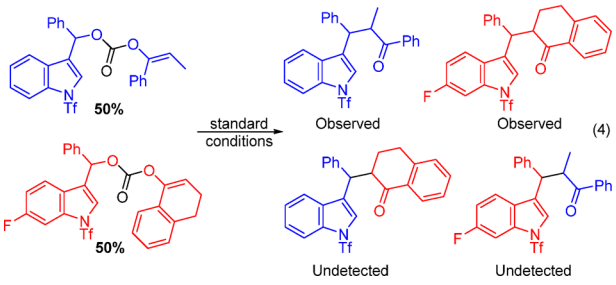
Scheme 3. Stereospecific Coupling



Next, the constitution and absolute configuration of the product were definitively determined by X-ray crystallography ((*S*)-**2k**, CCDC 1532316). The observed stereochemistry shows that the decarboxylative benzylation of enolates occurs with stereochemical retention. Since oxidative addition generally occurs with inversion of configuration,[9c,18] this critical observation suggests that the C−C bond forming step also occurs with inversion of stereochemistry.[7c,19] Thus, the coupling is an outer-sphere process, requiring dissociated enolates; both inner-sphere and outer-sphere reactions are known for related allylation chemistry,[1a,5e,g] but this is the first determination of the mechanism of decarboxylative benzylation.

To further investigate the mechanistic details of this transformation, we attempted to divert the π-benzyl palladium complex by reaction with an external nucleophile (eq 3).





Interestingly, adding 2 equiv of sodium dimethyl malonate produced a ca. 2:1 mixture of the malonate substitution product and decarboxylative coupling product. The fact that both products are formed at similar rates suggests that oxidative addition is rate-limiting, which is commonly the case for catalytic benzylic coupling.[7c] Furthermore, although the decarboxylative coupling product is the minor product, the coupling with the acetone enolate must be quite facile given that the malonate concentration is at least 20 times larger than that of the enolate.

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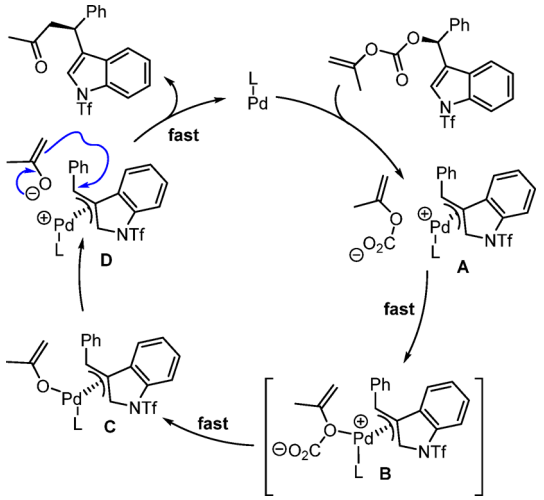
A crossover experiment performed between two different enol carbonates proved to be even more informative (eq 4). Treatment of a 50:50 mixture of two equally reactive substrates under the conditions of catalysis failed to produce either crossover product when analyzed by mass spectrometry or NMR spectroscopy.[20] This is a very rare example of an intramolecular decarboxylative coupling; most decarboxylative allylations give extensive crossover.[1a,5g,6a] The lack of crossover suggests that enolate dissociation occurs to form short-lived solvent-caged ion pairs that undergo C−C bond formation faster than escape from the solvent cage. Moreover, it is unlikely that the ion pair **A** is long-lived, as ion pairs can easily crossover by ion exchange.

Analysis of all of the data suggest that the mechanism occurs by ionization of the benzyl enol carbonate with inversion of configuration to form **A** (Scheme 4). Coordination and

Scheme 4. Hypothetical Mechanism



decarboxylation of the enol carbonate is suggested by the lack of reactivity of (*Z*)-enol carbonates,[1a] which cannot easily coordinate to Pd. The resulting palladium enolate (**C**) ionizes and rapidly collapses through an outer-sphere attack, resulting in the second inversion of stereochemistry. Intermediates **A**−**D** in this cycle can potentially all be diverted toward reaction with malonate as observed (eq 3). That said, the lack of crossover and the fact that the enolate effectively competes with excess malonate for reaction are most easily explained if malonate attack on **A** competes with a fast decarboxylation and coupling of the enolate.

To conclude, we have developed the first highly stereospecific decarboxylative coupling of secondary benzylic enol carbonates. The reaction proceeds through a somewhat standard mechanism for benzylic alkylation, with the caveat that the reaction is intramolecular and no crossover is observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00169.

Experimental procedures and complete compound characterization data (PDF)

Accession Codes

CCDC 1532316 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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