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Mild Copper-Catalyzed Addition of Arylboronic Esters to Di-*tert*-butyl Dicarbonate: An Easy Access to Methyl Arylcarboxylates

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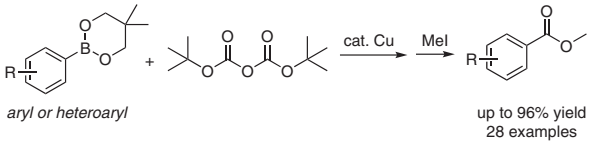

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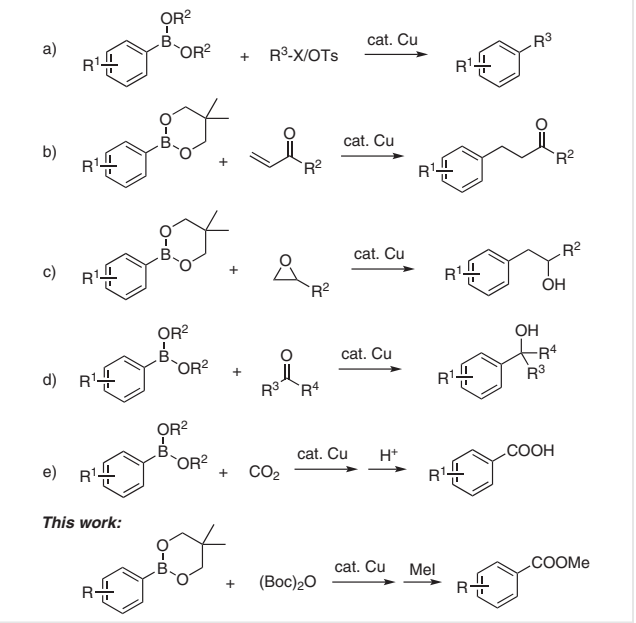
Abstract An efficient copper-catalyzed addition of arylboronic esters to $(Boc)_2O$ was developed. The reaction can be conducted under exceedingly mild conditions and is compatible with a variety of synthetically relevant functional groups. It therefore represents a useful alternative route for the synthesis of methyl arylcarboxylates. A preliminary mechanistic study indicated the involvement of an addition–elimination mechanism.

Key words copper catalysis, arylboronic esters, addition, carboxylation, methyl arylcarboxylates

Organocopper reagents are commonly used to deliver carbon-containing nucleophiles in modern C–C bond-forming reactions.[1] Conventional transformations involve the use of an excess of an organocopper reagent (R_2CuLi) to achieve high reaction efficiency,[2] which entails unnecessary waste of valuable organometallic species. It is not surprising that alternative catalytic procedures have been developed to generate active organocopper reagents in situ from a combination of a copper catalyst and a stoichiometric strongly nucleophilic organometallic reagent, such as a Grignard reagent.[3] However, owing to the robust reactivity and limited commercial availability of these reagents, such procedures usually suffer from harsh reaction conditions and poor functional-group tolerance. In contrast, organoboron derivatives exhibits a high stability and controllable reactivity, are readily available from commercial sources, and are well known to serve as excellent reaction partners for introducing desirable functionalities into organic scaffolds.[4,5] Consequently, recent researches on copper catalysis have paid increasing attention to the use of organoboron reagent as substitutes for organometallic compounds in C–C bond-forming reactions. Several successful examples have been reported, mainly involving transformations of arylboronic acid derivatives (Scheme 1), including (a) Suzuki-type coupling reactions with organic halides or pseudohalides,[6–8] (b) 1,4-additions to α,β-unsaturated compounds,[9] (c) ring-opening reactions with epoxides to afford β-substituted alcohols,[10] (d) inter- or intramolecular additions to aldehydes or ketones,[11] and (e) carboxylation reactions with CO_2 to afford aromatic carboxylic acids.[12] These elegant works not only provide ready access to specific synthetically important structural motifs, but also show intriguing promise in the exploration of novel organoboron-based copper-catalyzed procedures.

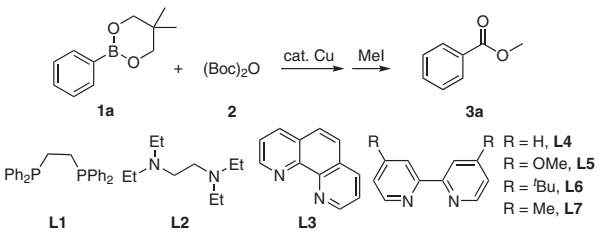


Scheme 1 Copper-catalyzed arylboron-based C–C bond-forming reactions

In this context, we report our finding that copper can promote the addition of arylboronic esters to di-*tert*-butyl carbonate [$(Boc)_2O$] under mild conditions to give moderate to high yields of methyl arylcarboxylates after simple post-processing. Preliminary mechanistic studies revealed that an unusual addition–elimination mechanism might be involved in this transformation. Our method therefore provides a powerful additional route for the synthesis of arylcarboxylic acid derivatives and expands the scope of organoboron-based copper catalysis.

Our initial study focused on examining the feasibility of copper-catalyzed addition of arylboronic ester **1a** to various carboxylic anhydrides, in the hope that this might provide a useful complement to conventional synthetic procedures involving Grignard reagents. After numerous unsuccessful attempts, we serendipitously obtained a 23% yield of methyl benzoate (**3a**) from a reaction system with $(Boc)_2O$ (**2**) as a coupling partner, CuCl as a catalyst, LiOMe as a base, and 1,2-bis(diphenylphosphino)ethane (**L1**) as a ligand in *N*,*N*-dimethylacetamide (DMA) at 50 ℃. It appeared that LiOMe can further attack the intermediate addition product of **1a** to **3a** to afford a methylated product. Subsequent analysis of the reaction residue also showed the presence of a 10% yield of benzoic acid together with a tiny amount of *tert*-butyl benzoate, which might have resulted from the decomposition of the addition intermediate under the alkaline conditions. On quenching the reaction with MeI, the total yield of **3a** reached 33% (Table 1, entry 1). Excitingly, lowering the reaction temperature to 30 ℃ had no significant effect on the reaction (entry 2). The choice of ligand played a crucial role in this reaction. Without a ligand, the yield of **3a** was only 8% (entry 3). Replacing **L1** with *N*,*N*,*N*′,*N*′-tetraethylethane-1,2-diamine (**L2**) improved the yield to 54% (entry 4), whereas the use of 1,10-phenanthroline (**L3**) dramatically inhibited the reaction (entry 5). When 2,2′-bipyridine (**L4**) was used as the ligand, an excellent catalytic performance was observed, with a yield of 71% (entry 6). This encouraged us to test a series of bipyridine ligands (entries 6–9). As a result, the electron-rich bipyridine ligand bearing two methyl groups **L7** gave the optimal result (80% HPLC yield; 78% isolated yield). Replacing LiOMe base with KOMe or NaOMe led to lower yields (entries 10 and 11). Replacement of CuCl with other copper catalyst also failed to improve the yield (entries 12–15). A screening of DMF, NMP, or DMSO as solvent also negatively affected the reaction (entries 16–18). After further optimization of the reaction time, a period of six hours was selected as optimal (entries 19 and 20). Exposing the reaction system to air led to a sharp decrease in the reaction efficiency (entry 21). Finally, in a control experiment without CuCl, the cross-coupling failed to occur, indicating that the copper catalyst was necessary for the transformation (entry 22).

Table 1 Copper-Catalyzed Cross-Coupling under Various Conditions[a]



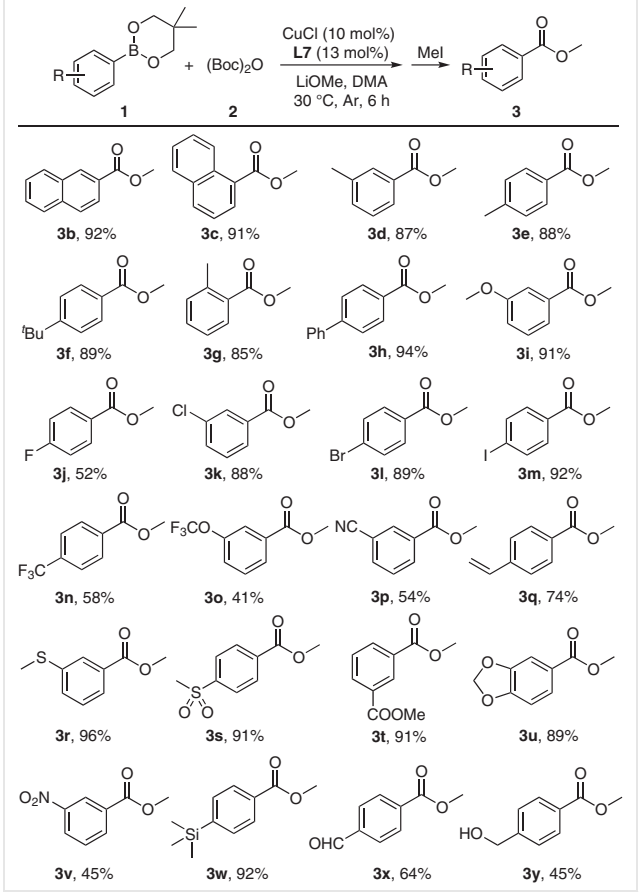
Entry	Catalyst	Ligand	Base	Solvent	Temp (℃)	Time (h)	Yield[b](%)
1	CuCl	**L1**	LiOMe	DMA	50	6	33
2	CuCl	**L1**	LiOMe	DMA	30	6	34
3	CuCl	–	LiOMe	DMA	30	6	8
4	CuCl	**L2**	LiOMe	DMA	30	6	54
5	CuCl	**L3**	LiOMe	DMA	30	6	11
6	CuCl	**L4**	LiOMe	DMA	30	6	71
7	CuCl	**L5**	LiOMe	DMA	30	6	74
8	CuCl	**L6**	LiOMe	DMA	30	6	75
9	**CuCl**	**L7**	**LiOMe**	**DMA**	**30**	**6**	**80 (78)[c]**
10	CuCl	**L7**	KOMe	DMA	30	6	68
11	CuCl	**L7**	NaOMe	DMA	30	6	17
12	CuI	**L7**	LiOMe	DMA	30	6	36
13	CuBr	**L7**	LiOMe	DMA	30	6	69
14	$Cu(OTf)_2$	**L7**	LiOMe	DMA	30	6	25
15	$Cu(OAc)_2$	**L7**	LiOMe	DMA	30	6	50
16	CuCl	**L7**	LiOMe	DMF	30	6	45
17	CuCl	**L7**	LiOMe	NMP	30	6	61
18	CuCl	**L7**	LiOMe	DMSO	30	6	50
19	CuCl	**L7**	LiOMe	DMA	30	4	51
20	CuCl	**L7**	LiOMe	DMA	30	8	79
21[d]	CuCl	**L7**	LiOMe	DMA	30	6	5
22	–	**L7**	LiOMe	DMA	30	6	trace

[a] Reaction conditions: **1a** (0.375 mmol), **2** (0.25 mmol), catalyst (10 mol%), ligand (13 mol%), LiOMe (2.5 equiv), solvent (0.5 mL) under Ar, then MeI (5 equiv), stirring, 2 h.
[b] Yields (average of two runs) were determined by HPLC with benzophenone as the internal standard.
[c] Isolated yield.
[d] The reaction was conducted under air.

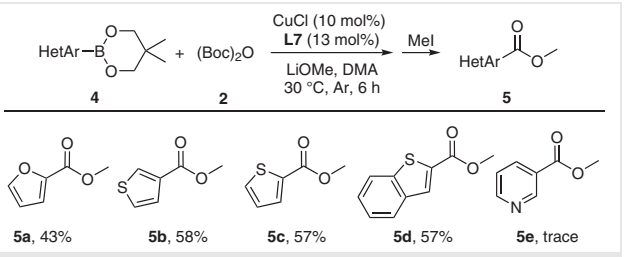
With the optimized conditions in hand, we then examined the scope of the reaction with respect to the arylboronic ester. As shown in Scheme 2, a wide range of arylboronic esters with electron-donating or electron-withdrawing substituents smoothly participated in the reaction to afford the desired products **3** in moderate to good yields. Besides phenylboronic esters, naphthylboronic esters were also suitable coupling partners (**3b** and **3c**). Substituents in the *meta*- (**3d**) or *para*-positions (**3e**) of the phenyl rings had no significant effect on the reaction efficiency. A more sterically hindered *ortho*-substituted arylboronic ester

could also be successfully converted into the corresponding methyl arylcarboxylate **3g**. A variety of synthetically important functional groups such as alkyl (**3d–g**), phenyl (**3h**), methoxy (**3i**), fluoro (**3j**), chloro (**3k**), bromo (**3l**), iodo (**3m**), trifluoromethyl (**3n**), trifluoromethoxy (**3o**), cyano (**3p**), terminal olefin (**3q**), methylsulfanyl (**3r**), sulfone (**3s**), ester (**3t**), and piperonyl (**3u**) were tolerated. A nitro-substituted arylboronic ester gave ester **3v** in a moderate yield of 45%. This protocol showed good compatibility with a trimethylsilyl group (**3w**), thereby offering additional opportunities for downstream structural modification. Notably, an arylboronic ester with an aldehyde substituent (**3x**) was also compatible, and no carbonyl-addition product was observed under our optimized reaction conditions. Finally, our catalytic procedure could be applied to the coupling of active hydrogen-containing arylboronic esters. A substrate with an unprotected hydroxy group reacted with $(Boc)_2O$ to provide the desired product **3y** in a relatively low yield of 45%.

Next, several hetarylboronic esters were synthesized and subjected to the reaction system to test the generality of this transformation (Scheme 3). Both oxygen- and sulfur-containing hetarylboronic esters including furyl (**5a**), thienyl (**5b** and **5c**), and benzothienyl (**5d**) esters were effectively converted into the corresponding products in moderate yields. Unfortunately, with a pyridine-based boronic ester as a substrate, none of the desired product **5e** was observed, and most of substrate remained unreacted.

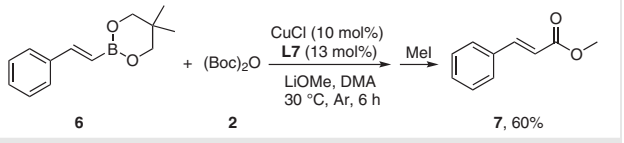


Scheme 2 Copper-catalyzed cross-coupling reactions of arylboronic esters. *Reagents and conditions*: **1** (0.375 mmol), **2** (0.25 mmol), CuCl (10 mol%), **L7** (13 mol%), LiOMe (2.5 equiv), DMA (0.5 mL), 30 °C, 6 h, under Ar, then MeI (5 equiv), stirring, 2 h. Isolated yields are reported.



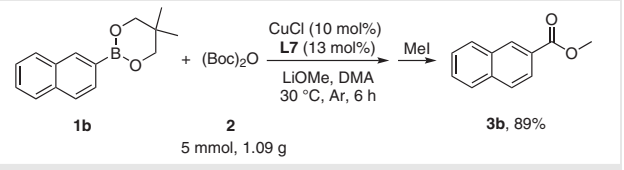
Scheme 3 Copper-catalyzed cross-coupling with hetarylboronic esters. *Reagents and conditions*: **4** (0.375 mmol), **2** (0.25 mmol), CuCl (10 mol%), **L7** (13 mol%), LiOMe (2.5 equiv), DMA (0.5 mL), 30 °C, 6 h, under Ar, then MeI (5 equiv), stirring, 2 h. Isolated yields are reported.

Our catalytic protocol could also be applied to the coupling of alkenylboronic esters. The β-styrylboronic ester **6** reacted smoothly with $(Boc)_2O$ to give α,β-unsaturated methyl cinnamate (**7**) in 60% yield (Scheme 4).



Scheme 4 Copper-catalyzed cross-coupling of an alkenylboronic ester

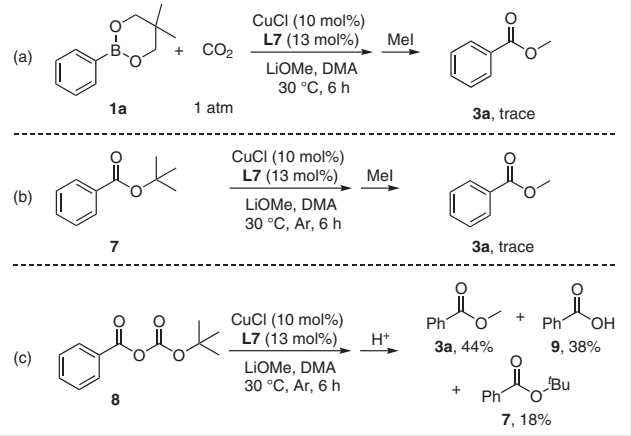
To further explore the synthetic practicability of our new reaction, we conducted a gram-scale (5 mmol) experiment with the 2-naphthylboronic ester **1b** as a reaction partner (Scheme 5). This copper-catalyzed coupling also worked well, and afforded product **3b** with a negligible change in yield compared with that of the smaller-scale experiment.



Scheme 5 A copper-catalyzed gram-scale cross-coupling

Next, several control experiments were performed to probe the mechanism of this reaction (Scheme 6). When $(Boc)_2O$ was replaced with CO_2, no carboxylation product was observed under the standard reaction conditions. This suggested that a mechanism involving the reaction of **1a** with CO_2 generated in situ by decomposition of $(Boc)_2O$ can

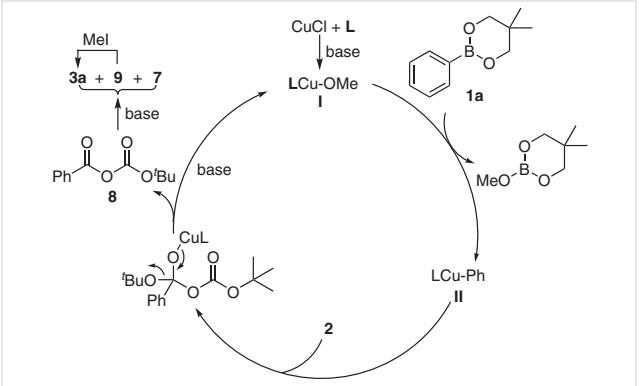
be excluded. An addition–elimination mechanism, unlike those of previously reported carboxylation reactions of arylboronic acid derivatives,[12] is more likely to be involved in this transformation. To further identify the actual active intermediate we synthesized two possible elimination products **7** and **8**[13] and we subjected these to the reaction conditions. Substrate **7** remained unchanged under the current reaction conditions, indicating that it is not the key product of the addition–elimination step. However, carbonate **8** decomposed quickly under basic conditions and afforded a 44% yield of **3a**, a 38% yield of benzoic acid (**9**) and a small amount of *tert*-butyl benzoate (**7**) after quenching with HCl; this result was consistent with the analysis of reaction residue from Table 1, entry 1.



Scheme 6 Control experiments for mechanistic studies

On the basis of these results and previous reports,[11,12,14] we proposed a plausible reaction mechanism for this copper-catalyzed protocol (Scheme 7). First, CuCl reacts with ligand **L** to afford the **L**Cu–OMe complex **I**, which undergoes transmetalation with the arylboronic ester **1a** to give intermediate **II**. Addition of intermediate **II** to the carbonyl group of $(Boc)_2O$ (**2**) is followed by elimination to afford intermediate **8**, along with the regeneration of the copper catalyst. Finally, base-promoted decomposition of **8** gives rise to a mixture of arylcarboxylic acid derivatives. A high yield of **3a** is obtained after quenching the reaction system with MeI.

In conclusion, we found that addition of arylboronic esters to $(Boc)_2O$ could be achieved under mild conditions with a copper catalyst.[15] Further explorations showed that this reaction might proceed through an addition–elimination pathway and that it was compatible with a range of aryl, hetaryl, and alkenylboronic esters. It therefore presents a conceptually new approach to the synthesis of arylcarboxylic acid derivatives. We hope the findings reported above will inspire future research aimed at exploring the synthetic versatility of organoboron-based copper catalysis.



Scheme 7 Plausible reaction mechanism

Funding Information

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/a-1377-7369.

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(15) **Methyl (Het)arylcarboxylates 3a–y, 5a–e; General Procedure**
A 15 mL Schlenk tube equipped with a stirrer bar was charged with CuCl (10 mol%), **L7** (13 mol%), LiOMe (2.5 equiv), and the appropriate boronic ester **1** or **4** (0.375 mmol). The vessel was then evacuated and filled with Ar (three cycles). DMA (0.5 mL) and $(Boc)_2O$ (0.25 mmol) were added sequentially under Ar, and the mixture was stirred at 30 ℃ for 6 h. MeI (5 equiv) was then added in air, and the mixture was stirred at 30 ℃ for additional 2 h. The mixture was finally diluted with EtOAc and washed with sat. aq NaCl (20 mL). The aqueous phase was further extracted with EtOAc (3 × 20 mL), and the combined organic phases were dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography [silica gel EtOAc–hexane (1:100 to 1:50)].
Methyl 2-Naphthoate (3b)
Prepared by following the general procedure as a white solid; yield: 91% (by HPLC). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 8.08–8.05 (m, 1 H), 7.96 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.7 Hz, 2 H), 7.63–7.49 (m, 2 H), 3.98 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.29, 135.53, 132.51, 131.09, 129.37, 128.25, 128.17, 127.78, 127.41, 126.66, 125.24, 52.26. The NMR spectral data agreed with the reported values.[16]

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