

## RESEARCH ARTICLE

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Chemo-orthogonal biaryl formation *via* Pd/Cu-catalyzed decar-boxylative coupling of arylthianthrenium saltsDuo Zhang,<sup>†a</sup> Xiaowen Teng,<sup>†b</sup> Shixin Zhuang,<sup>b</sup> Lukas J. Gooßen \*<sup>c</sup> and Guodong Zhang \*<sup>b</sup>

Thianthrenium groups are versatile synthetic handles that can be selectively installed into complex arenes *via* C–H functionalization. We disclose a bimetallic Pd/Cu system that enables their substitution by functionalized (hetero)arenes through a cooperatively catalyzed decarboxylative coupling with aromatic carboxylates. The reaction makes use of widely available substrates and is broadly applicable, even to drug-like substrates. By exploiting a reactivity mode that is orthogonal to classical cross-couplings, this method allows the introduction of (hetero)arenes bearing typical anchor groups for subsequent derivatization—namely bromide, triflate, nitro, and even iodide groups. This streamlines diversification of the (hetero)biaryl products, significantly expanding the utility of thianthrenium salts as synthetic lynchpins.

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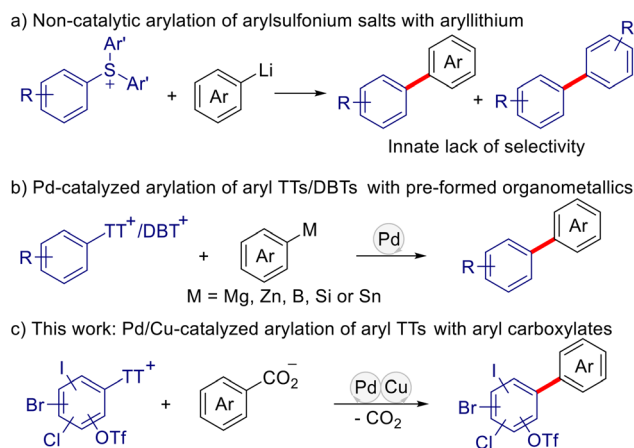
## Introduction

The synthesis of aryl sulfonium salts was reported by Calvin, Lucken, and Shine already in 1950s.<sup>1</sup> Their relevance for selective aromatic functionalization was established by Ritter and co-workers, who demonstrated that thianthrenium (TT) moieties can be regioselectively installed onto arenes *via* electrophilic C–H functionalization and subsequently serve as controlled leaving groups in C–C and C–heteroatom bond-forming reactions.<sup>2</sup> The resulting arylthianthrenium salts combine facile, site-selective installation with bench stability and controlled reactivity, allowing their activation in nucleophilic substitutions,<sup>3</sup> transition-metal-catalyzed cross-coupling reactions,<sup>4</sup> and photoredox processes.<sup>5</sup> Their utility in the formation of C–C, C–N, C–O, C–S, and C–halogen bonds has been demonstrated by the groups of Ritter,<sup>6</sup> Alcarazo,<sup>7</sup> Procter,<sup>8</sup> Ackermann,<sup>9</sup> ourselves,<sup>10</sup> and others.<sup>11</sup>

Arylation reactions employing aryl sulfonium salts were already explored in the 1960s, when their reactions with aryllithium reagents were shown to proceed *via* tetra-arylsulfurane intermediates that fragment to give biaryls along with diaryl sulfide byproducts (Scheme 1a).<sup>12</sup> However, these transformations suffered from limited selectivity and a strong dependence

on the electronic properties of the aryl substituents bound to sulfur.<sup>13</sup> Later refinements by Kano and co-workers using arylphenothiazinium salts improved regiocontrol,<sup>14</sup> but the reliance on highly reactive aryllithium nucleophiles substantially restricted the scope and functional-group tolerance.

Recently, efficient transition-metal-catalyzed arylations of aryl thianthrenium salts have been developed. However, these rely on pre-formed organometallic reagents such as boron-,<sup>2,15</sup> magnesium-,<sup>16</sup> zinc-,<sup>17</sup> silicon-,<sup>18</sup> or tin-derived reagents<sup>19</sup> (Scheme 1b). To overcome structural limitations of thianthrenium salt arylations that arise from the preparation and hand-



**Scheme 1** Biaryl synthesis from arylsulfonium salts with aryl nucleophiles.

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ling of such reagents, it is highly desirable to utilize widely available, stable compounds as coupling partners.

The use of carboxylic acids as alternative coupling partners in transition-metal catalysis leverages their abundance and atom economy to enable diverse synthetic pathways.<sup>20</sup> This is exemplified by the advancement of decarboxylative cross-coupling reactions, which marks a pivotal development in biaryl synthesis.<sup>21</sup> In these transformations, abundantly available aromatic carboxylate salts are transformed into organometallic reagents by the extrusion of carbon dioxide, and are then coupled with aryl halides or pseudo-halides within the coordination sphere of transition metals. The synthetic utility of decarboxylative arylations was demonstrated *e.g.* by Nilsson,<sup>22</sup> Forgiione,<sup>23</sup> Su,<sup>24</sup> our groups<sup>25</sup> and others.<sup>26</sup>

Conceptually, enabling carboxylic acids to engage directly with aryl thianthrenium salts would combine two central advantages of modern arylation chemistry: the use of abundant carboxylates in place of pre-formed organometallic reagents and of leaving groups that are readily installed by C–H activation. Ideally, the couplings would proceed chemo-orthogonal to that of aryl halides. Realizing this reaction concept posed a fundamental challenge, as the elevated temperatures required for CO<sub>2</sub> extrusion were likely to cause uncontrolled thianthrenium decomposition or unselective aryl transfer. Addressing this challenge, we herein disclose a bimetallic catalyst system that enables the chemoselective coupling of aromatic carboxylates with aryl thianthrenium salts in the presence of aryl halides and pseudohalides. This strategy establishes carboxylic acids as viable aryl sources in thianthrenium-based coupling chemistry while allowing to introduce versatile anchor points for downstream functionalization (Scheme 1c).

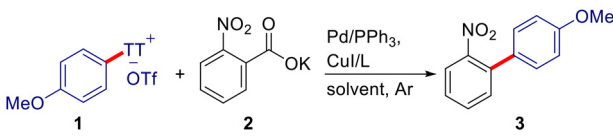
The mechanistic blueprint for the targeted transformation is outlined in Scheme 2. The aryl thianthrenium activation is accomplished *via* oxidative addition to a palladium catalyst yielding aryl–Pd(II) intermediate **A** along with recyclable thianthrene (TT), while copper promotes the selective decarboxylation of aromatic carboxylates yielding aryl–Cu(I) species **C**. The ligand system of the Pd must be tuned in a way that it selectively activates aryl thianthrenium salts over aryl (pseudo) halides and does not get blocked by the coordinating TT leaving group. The copper catalyst must operate at tempera-

tures low enough to ensure the stability of the thianthrenium salts. Subsequent transmetalation between **A** and **C** would then form a diaryl–Pd(II) intermediate **D**, which undergoes reductive elimination to furnish the biaryl product while regenerating the Pd(0) catalyst and closing the catalytic cycle.

## Results and discussion

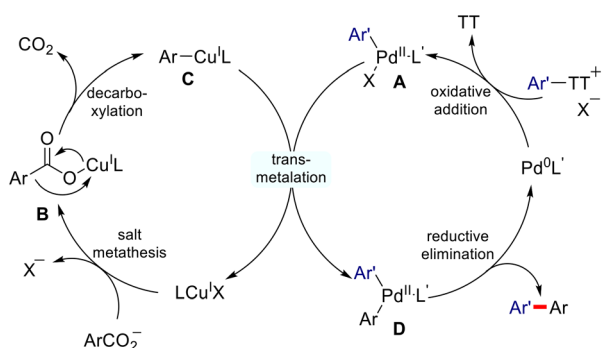
In search for a catalyst system that efficiently promotes this reaction, we chose the reaction of potassium 2-nitrobenzoate (**1**) and *p*-methoxyphenylthianthrenium salt as the model (**2**). We systematically evaluated catalysts and reaction parameters starting from established conditions for decarboxylative couplings of aryl halides,<sup>21</sup> but reducing the reaction temperature by 160 °C to only 110 °C (Table 1 and Table S1). The choice of solvent was found to play a key role. Under standard conditions, Pd(OAc)<sub>2</sub> and CuI as the catalysts, PPh<sub>3</sub> and 1,10-phenanthroline as the ligands, NMP/pyridine as the solvent, unsatisfactory yield and selectivity was observed (entry 1, 28% yield of the target product, and diaryl ether as side product for **1**). Both yield and selectivity were markedly increased when switching to DMSO as solvent (Table 1, entry 2), significantly outperforming other polar aprotic (*e.g.*, DMF, DMAc, NMP) and nonpolar solvents (*e.g.*, *p*-xylene, anisole) (Table 1, entries 3–7). When increasing the temperature to 120%, an encouraging 79% yield was obtained (Table 1, entry 8). A copper co-catalyst was found to be essential, with best yields obtained with CuI ligated by the diamine ligand bpy (Table 1, entry 10, see also Table S1, entries 9–16). The choice of the palladium

**Table 1** Optimisation of the reaction conditions<sup>a</sup>



Entry	Pd	L	Solvent	T	Yield <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	Phen	NMP/Py	110	28
2	Pd(OAc) <sub>2</sub>	Phen	DMSO	110	43
3	Pd(OAc) <sub>2</sub>	Phen	DMAc	110	35
4	Pd(OAc) <sub>2</sub>	Phen	NMP	110	36
5	Pd(OAc) <sub>2</sub>	Phen	DMF	110	30
6	Pd(OAc) <sub>2</sub>	Phen	<i>p</i> -Xylene	110	2
7	Pd(OAc) <sub>2</sub>	Phen	Anisole	110	0
8	Pd(OAc) <sub>2</sub>	Phen	DMSO	120	79
9	Pd(OAc) <sub>2</sub>	None	DMSO	120	40
10	Pd(OAc) <sub>2</sub>	bpy	DMSO	120	91
11	PdCl <sub>2</sub>	bpy	DMSO	120	85
12	Pd(acac) <sub>2</sub>	bpy	DMSO	120	88
13	Pd(TFA) <sub>2</sub>	bpy	DMSO	120	88
14	Pd(OAc) <sub>2</sub>	bpy	DMSO	120	78
15 <sup>c</sup>	Pd(OAc) <sub>2</sub>	bpy	DMSO	120	99
16 <sup>d</sup>	None	bpy	DMSO	120	0

<sup>a</sup> Conditions: 0.2 mmol **1**, 0.24 mmol **2**, 2.5 mol% Pd catalyst, 5 mol% of PPh<sub>3</sub>, 5 mol% CuI, 5 mol% L, in 1 mL solvent, under an argon atmosphere for 16 h. <sup>b</sup> Yields determined by GC using *n*-tetradecane as the internal standard. <sup>c</sup> 2 mol% Pd(OAc)<sub>2</sub>. <sup>d</sup> Without PPh<sub>3</sub>.



**Scheme 2** Mechanistic blueprint of the envisioned transformation.



precursor had only a negligible effect, with similar yields obtained with Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>, Pd(acac)<sub>2</sub>, and Pd(TFA)<sub>2</sub> at a minimal loading of 2.5 mol% (Table 1, entries 11–14). Remarkably, a decisive step-up in the yield to 99% was observed, when omitting the phosphine ligand (Table 1, entry 15). We rationalize this with the coordination ability of thianthrene, which seems to sufficiently stabilize the Pd-catalyst, with additional phosphine unnecessarily blocking the access to the already ligated metal center. Control experiments confirmed the necessity of palladium loading (Table 1, entry 16) and of air- and water-free conditions (Table S1, entries 28 and 29). The thianthrene generated *in situ* does not seem to interfere with the coupling, as the addition of exogenous thianthrene did not alter the reaction yield (Table S1, entry 30). Attempts to use carboxylic acids with K<sub>2</sub>CO<sub>3</sub> as the external base instead of pre-formed carboxylates resulted in predominant protodecarboxylation and only 5% yield of the desired biaryl (Table S1, entry 31).

We next probed whether this catalyst system would also allow to convert (pseudo)halides and found that they displayed much lower reactivity (Scheme 3). Aryl chlorides and triflates gave no conversion at all, while aryl bromides and iodides afforded the products in moderate yields (35% and 56%). In direct competition, *p*-methoxyphenylthianthrenium salt gave near quantitative coupling with potassium 2-nitrobenzoate in the presence of *p*-chlorotoluene and *p*-tolyl trifluoromethanesulfonate, while only 9% and 21% of 4'-methyl-2-nitro-1,1'-biphenyl was observed in the presence of *p*-bromotoluene and *p*-iodotoluene. This demonstrates the high preference of the

catalyst for couplings of aryl thianthrenium salts over aryl halides and pseudohalides. Interestingly, the addition of thianthrene further enhanced this selectivity in favor of the thianthrenium salt over the aryl halides. Control experiments indicate that this effect does not arise from inhibition of competing aryl halide couplings by thianthrene, but rather from its promotion of oxidative addition of the TT salt.

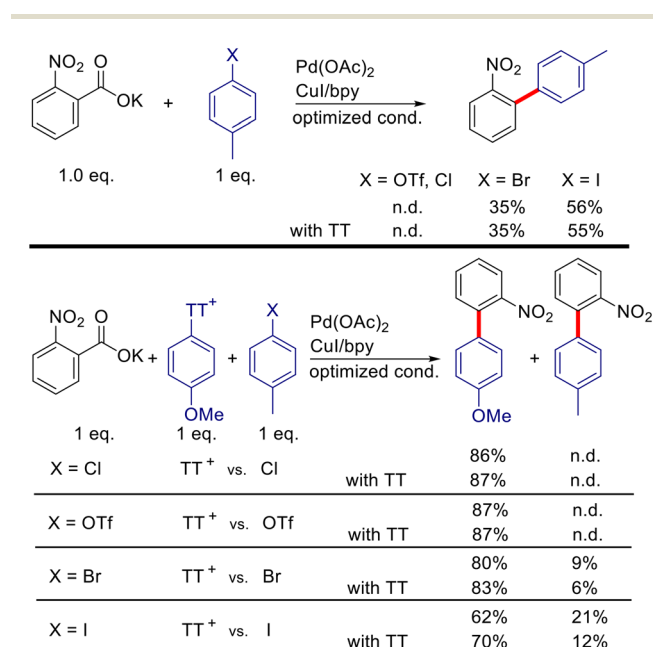
Our investigation into the substrate scope demonstrates the high efficiency and broad applicability of the final protocol (Table 2). The coupling is particularly effective for *o*-nitrobenzoate derivatives. Various functional groups including methyl, fluoro, amide, sulfonyl, methoxy, and trifluoromethyl were all well tolerated (3–13), furnishing the desired biaryls in good to excellent yields. Beyond *o*-nitrobenzoates, other *ortho*-substituted benzoates bearing fluoro, ester, keto, trifluoromethyl, or sulfonyl groups remained viable substrates (14–19). Interestingly, the addition of thianthrene significantly improved the yields for substrates bearing *ortho*-fluoro, ester, or keto functional groups, that gave only moderate yields using the standard conditions.

The reaction is also applicable to heteroaromatic carboxylates, as evidenced by the successful coupling of indole-2-carboxylate (20) and thiophene-2-carboxylate (21). It should be noted that this method is most effective for *ortho*-electron-withdrawing group-substituted benzoates; *meta*- or *para*-substituted benzoates lacking such activation give substantially lower yields under the standard conditions. For example, *meta*- and *para*-nitrobenzoates afforded <30% yield even at elevated reaction temperatures (22–23).<sup>25f</sup>

The scope with regard to the arylthianthrenium salt is rather broad (24–53), and covers the electron-rich derivatives accessible *via* Ritter's regioselective C–H functionalizations. These substrates typically feature the thianthrenium moiety *para* to electron-donating groups. Remarkably, even oxidation- and reduction-sensitive aldehydes were well tolerated under the redox-neutral conditions (32). For xanthone, dibenzofuran, and carbazol, selective thianthrenolysis was achieved with high efficiency (40–42). *ortho*-Substituted arylthianthrenium salts were successfully converted (43) despite their steric hindrance, albeit with moderate yields. The moderate yields observed for some other derivatives can be attributed to competitive side reactions (46), with hydrolysis of the arylthianthrenium salt to form phenolic byproducts and aryl esters being the most prominent.

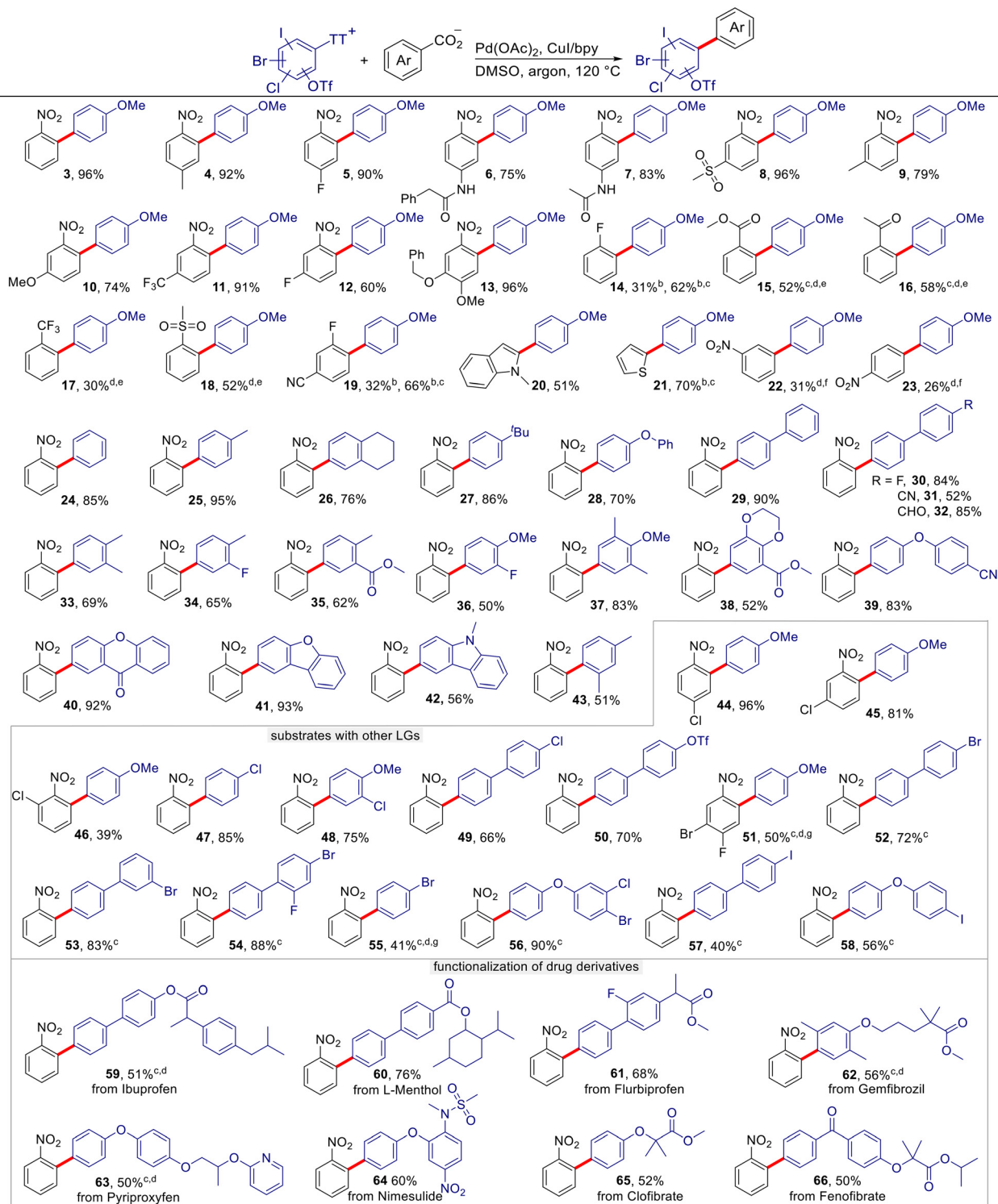
A key feature of our system is its orthogonality to conventional decarboxylative couplings that utilize aryl (pseudo) halide electrophiles. This is critically demonstrated with substrates containing triflate, chloride, bromide, or iodide leaving groups; the reaction selectively cleaves the C–S bond of the thianthrenium salt, leaving the other potential coupling sites completely intact (44–58). This chemoselectivity provides valuable opportunities for subsequent functionalization, as these groups remain available to participate in diverse cross-coupling reactions as competent electrophilic handles.<sup>27</sup>

The application of this protocol to the late-stage functionalization of natural products and drug molecules is



**Scheme 3** Selectivity on arylthianthrenium salts vs arylhalides and aryl triflates. Conditions: 0.2 mmol 2-nitrobenzoate, 0.2 mmol aryl electrophiles, with or without 0.1 mol thianthrene, 2.5 mol% Pd(OAc)<sub>2</sub>, 5 mol% Cul, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 16 h; isolated yields.



Table 2 Substrate scope<sup>a,b</sup>

<sup>a</sup> Reaction conditions: 0.2 mmol arylthianthrenium salt, 0.24 mmol potassium carboxylate, 2.5 mol% Pd(OAc)<sub>2</sub>, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 16 h; isolated yields. <sup>b</sup> 10 mol% CuI and 10 mol% bpy at 160 °C. <sup>c</sup> With 0.1 mmol thianthrene. <sup>d</sup> 5 mol% Pd(OAc)<sub>2</sub>. <sup>e</sup> 0.10 mmol CuCl, 10 mol% bpy at 160 °C. <sup>f</sup> 5 mol% Cu<sub>2</sub>O, and 10 mol% Me<sub>4</sub>Phen, and 10 mol% XPhos in NMP/quinoline (1 : 1) at 180 °C. <sup>g</sup> 0.3 mmol arylthianthrenium salt, 0.2 mmol potassium carboxylate.



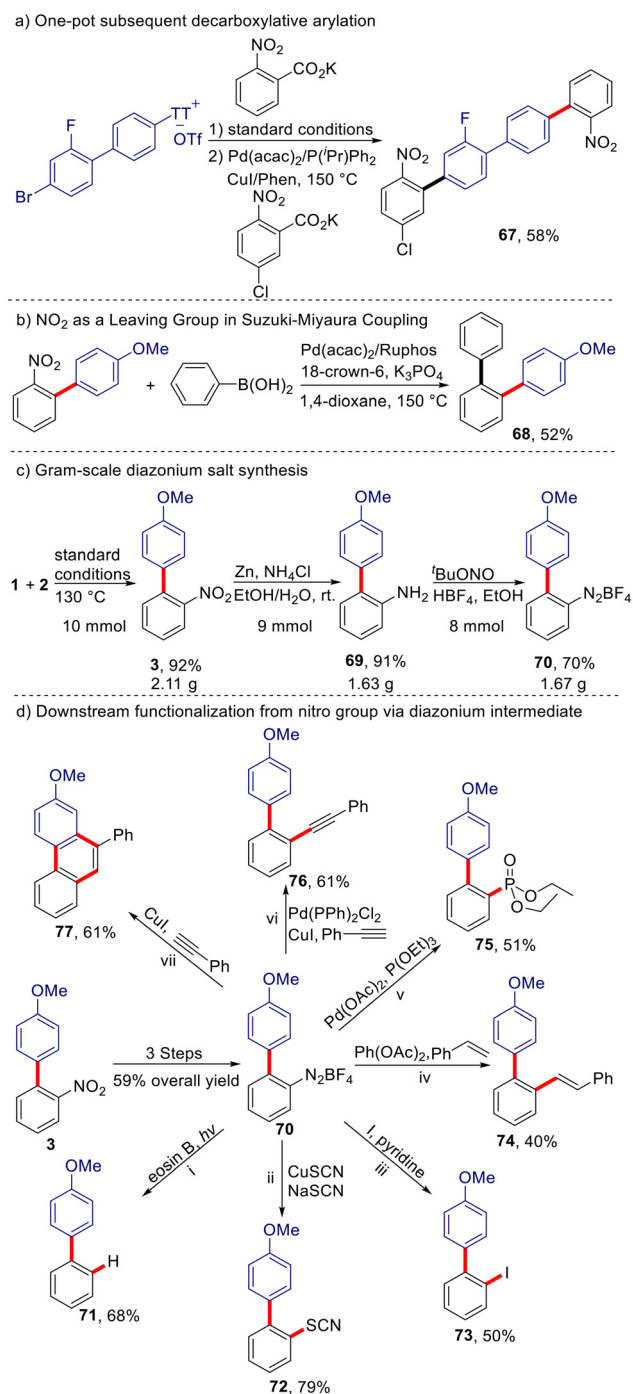
exemplified by its successful transformation of substructures derived from ibuprofen, flurbiprofen, gemfibrozil, pyriproxyfen, nimesulide, clofibrate and fenofibrate (59–66).

The orthogonal reactivity of arylthianthrenium salts *versus* aryl halides was demonstrated in a one-pot process using a substrate bearing both a thianthrenium group and a halide. First, selective decarboxylative coupling occurred at the thianthrenium site with a benzoate. The resulting halogenated

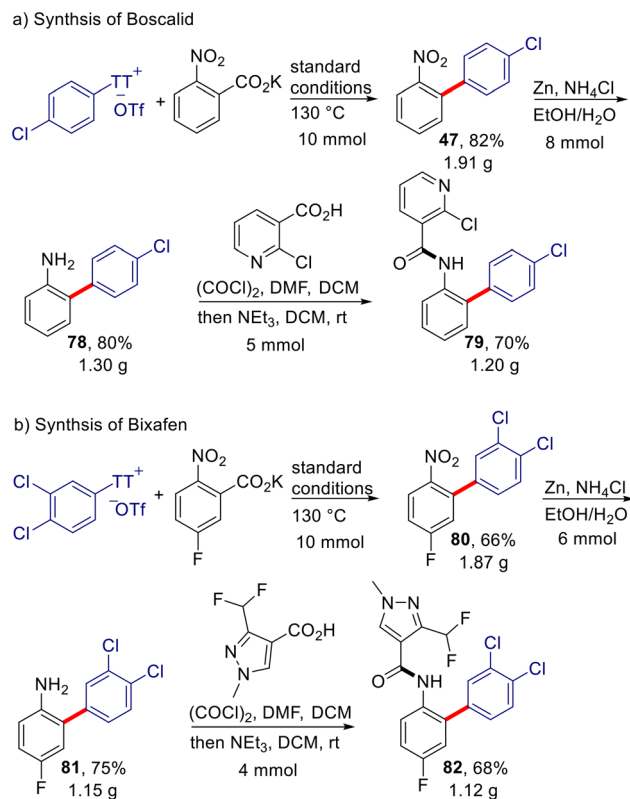
biaryl intermediate then underwent another decarboxylative coupling at the halide site with a second benzoate (Scheme 4a). Furthermore, Scheme 4b shows that the nitro group can also function as a leaving group in Suzuki–Miyaura cross-couplings. The orthogonal reactivity of arylthianthrenium salts and aryl halides was demonstrated in a one-pot process, in which a decarboxylative arylation of a halogenated benzoic acid is combined with a Suzuki–Miyaura arylation of the halogenated biaryl intermediate (Scheme 4a). In a second reaction sequence, performed on gram scale, the decarboxylative coupling of nitrobenzoic acid was followed by reduction of the nitro group and subsequent diazotization (Scheme 4c). The resulting diazonium salt is a versatile intermediate, since diazonium groups (71) can be tracelessly removed, transformed into a range of functional groups, including SCN (72), iodine (73), alkenyl (74), phosphoryl (75), and alkynyl (76) substituents, or engaged in cyclizations with acetylenes to furnish fused polycyclic compounds (77).

A practical route for the multigram-scale synthesis of *ortho*-nitro-substituted fungicides is provided through simple reduction and condensation with carboxylic acids (Scheme 5). This method is particularly valuable for accessing valuable products such as the fungicide Bixafen.

A series of control experiments were conducted to shed light on the reaction mechanism. The addition of thianthrene was found to significantly enhance the reaction rate, leading to higher yields within shorter time (Scheme 6a). In the pres-

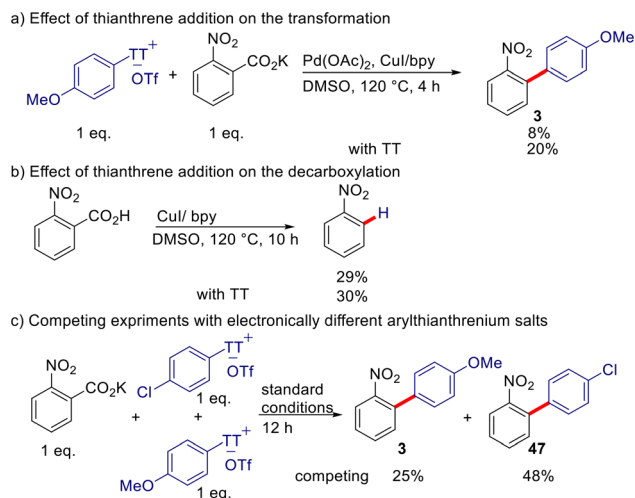


Scheme 4 Further transformation and gram scale reaction.



Scheme 5 Synthesis of fungicides.





**Scheme 6** Mechanistic investigations.

ence of thianthrene, even iodine-containing arylthianthrenium salts could selectively be converted at the thianthrenium group (40% yield of **57** vs. 56% yield of **58**), which provides further evidence that thianthrene specifically facilitates the oxidative insertion of the palladium into the Ar–S bond. Further experiments revealed that the addition of thianthrene does not affect the decarboxylation process (Scheme 6b). Electron-deficient arylthianthrenium salts were found to react faster than electron-rich ones (Scheme 6c). These results suggest that oxidative addition is rate-limiting for the coupling of *ortho*-nitrobenzoates at 120 °C. However, for less reactive carboxylates, decarboxylation becomes rate-limiting, requiring elevated temperatures ( $\geq 160$  °C) for efficient conversion. Thus, the rate-determining step is substrate-dependent.

## Conclusions

In summary, we have utilized palladium/copper dual catalysis to enable decarboxylative arylations of aryl thi-anthrenium salts with abundant aromatic carboxylates. The reaction proceeds under redox-neutral conditions, tolerates aryl (pseudo) halides, and is accelerated rather than slowed by the thianthrene byproduct. This strategy provides a scalable entry to functionally diverse biaryls and enables downstream diversification in pharmaceutical or agrochemical syntheses.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary infor-

mation is available. Experimental procedures, characterization data for compounds, and NMR spectra of products. See DOI: <https://doi.org/10.1039/d6qo00448b>.

## Acknowledgements

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