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Chemo-orthogonal biaryl formation *via* Pd/Cu-catalyzed decar-boxylative coupling of arylthianthrenium salts

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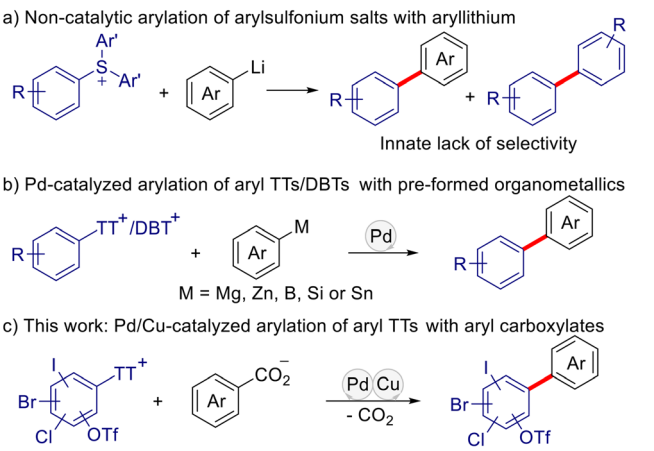
Thianthrenium groups are versatile synthetic handles that can be selectively installed into complex arenes *via* C–H functionalization. We disclose a bimetallic Pd/Cu system that enables their substitution by functionalized (hetero)arenes through a cooperatively catalyzed decarboxylative coupling with 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.

Introduction

The synthesis of aryl sulfonium salts was reported by Calvin, Lucken, and Shine already in 1950s.[1] 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.[2] The resulting arylthianthrenium salts combine facile, site-selective installation with bench stability and controlled reactivity, allowing their activation in nucleophilic substitutions,[3] transition-metal-catalyzed cross-coupling reactions,[4] and photoredox processes.[5] 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,[6] Alcarazo,[7] Procter,[8] Ackermann,[9] ourselves,[10] and others.[11]

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).[12] However, these transformations suffered from limited selectivity and a strong dependence on the electronic properties of the aryl substituents bound to sulfur.[13] Later refinements by Kano and co-workers using arylphenothiazinium salts improved regiocontrol,[14] 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-,[2,15] magnesium-,[16] zinc-,[17] silicon-,[18] or tin-derived reagents[19] (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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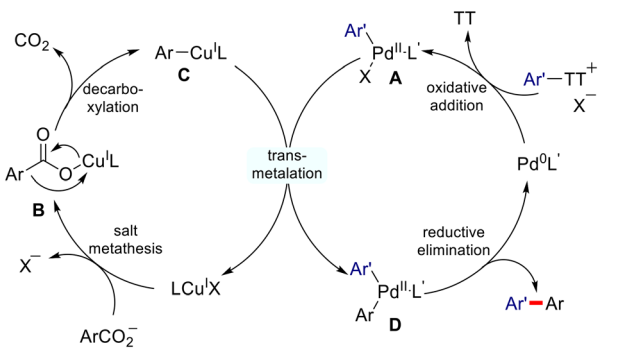
ling of such reagents, it is highly desirable to utilize widely available, stable compounds as coupling partners.

The use of carboxylic acids as alternative coupling partners in transition-metal catalysis leverages their abundance and atom economy to enable diverse synthetic pathways.[20] This is exemplified by the advancement of decarboxylative cross-coupling reactions, which marks a pivotal development in biaryl synthesis.[21] 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,[22] Forgione,[23] Su,[24] our groups[25] and others.[26]

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_2 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 temperatures 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.

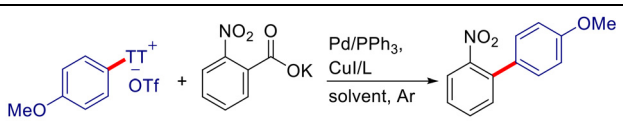


Scheme 2 Mechanistic blueprint of the envisioned transformation.

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,[21] 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, $Pd(OAc)_2$ and CuI as the catalysts, PPh_3 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[a]

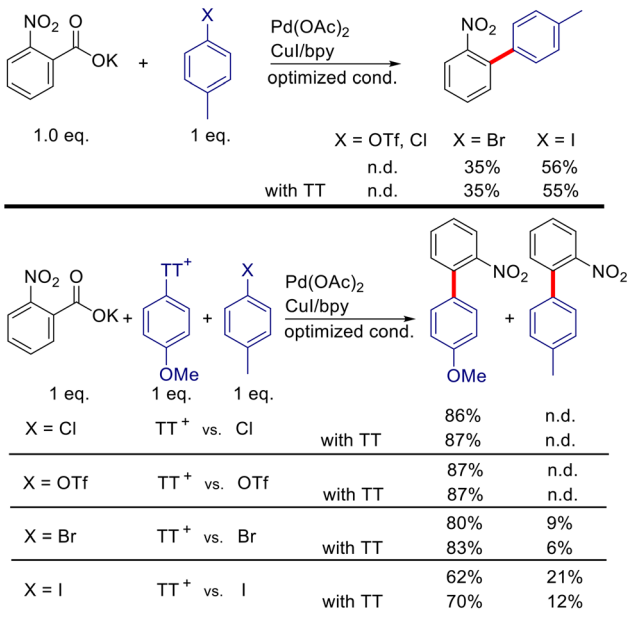


Entry	Pd	L	Solvent	*T*	Yield[b] (%)
1	$Pd(OAc)_2$	Phen	NMP/Py	110	28
2	$Pd(OAc)_2$	Phen	DMSO	110	43
3	$Pd(OAc)_2$	Phen	DMAc	110	35
4	$Pd(OAc)_2$	Phen	NMP	110	36
5	$Pd(OAc)_2$	Phen	DMF	110	30
6	$Pd(OAc)_2$	Phen	*p*-Xylene	110	2
7	$Pd(OAc)_2$	Phen	Anisole	110	0
8	$Pd(OAc)_2$	Phen	DMSO	120	79
9	$Pd(OAc)_2$	None	DMSO	120	40
10	$Pd(OAc)_2$	bpy	DMSO	120	91
11	$PdCl_2$	bpy	DMSO	120	85
12	$Pd(acac)_2$	bpy	DMSO	120	88
13	$Pd(TFA)_2$	bpy	DMSO	120	88
14	$Pd(OAc)_2$	bpy	DMSO	120	78
15[c]	$Pd(OAc)_2$	bpy	DMSO	120	99
16[d]	None	bpy	DMSO	120	0

[a] Conditions: 0.2 mmol **1**, 0.24 mmol **2**, 2.5 mol% Pd catalyst, 5 mol% of PPh_3, 5 mol% CuI, 5 mol% **L**, in 1 mL solvent, under an argon atmosphere for 16 h. [b] Yields determined by GC using *n*-tetradecane as the internal standard. [c] 2 mol% $Pd(OAc)_2$. [d] Without PPh_3.

precursor had only a negligible effect, with similar yields obtained with $Pd(OAc)_2$, $PdCl_2$, $Pd(acac)_2$, and $Pd(TFA)_2$ 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_2CO_3 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



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% $Pd(OAc)_2$, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 16 h; isolated yields.

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 benzo-ates 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.

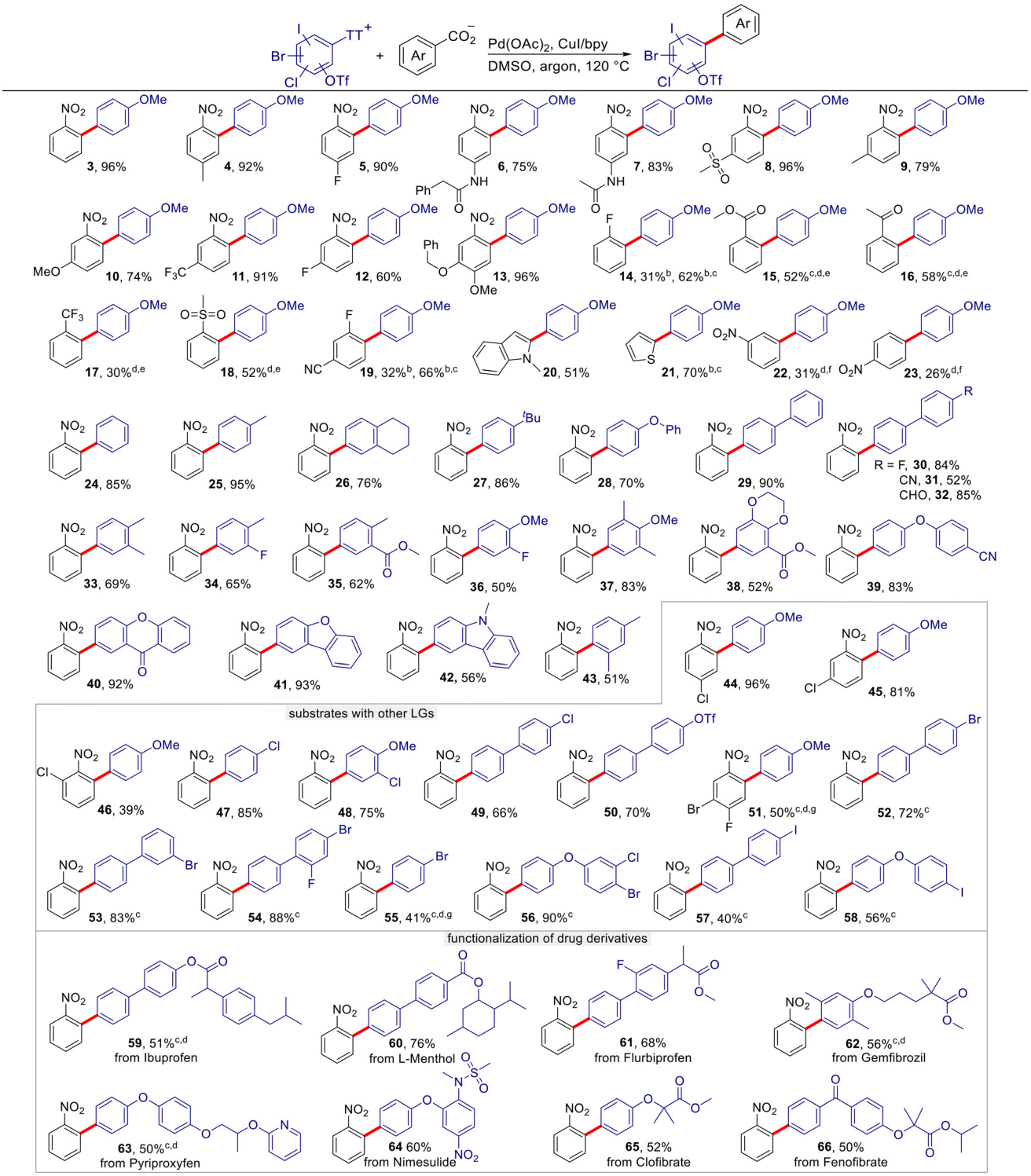
The reaction is also applicable to heteroaromatic carboxylates, as evidenced by the successful coupling of indole-2-carboxylate (**20**) and thiophene-2-carboxylate (**21**). It should be noted that this method is most effective for *ortho*-electron-withdrawing group-substituted benzoates; *meta*- or *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**).[25f]

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.[27]

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

Table 2 Substrate scope[a,b]



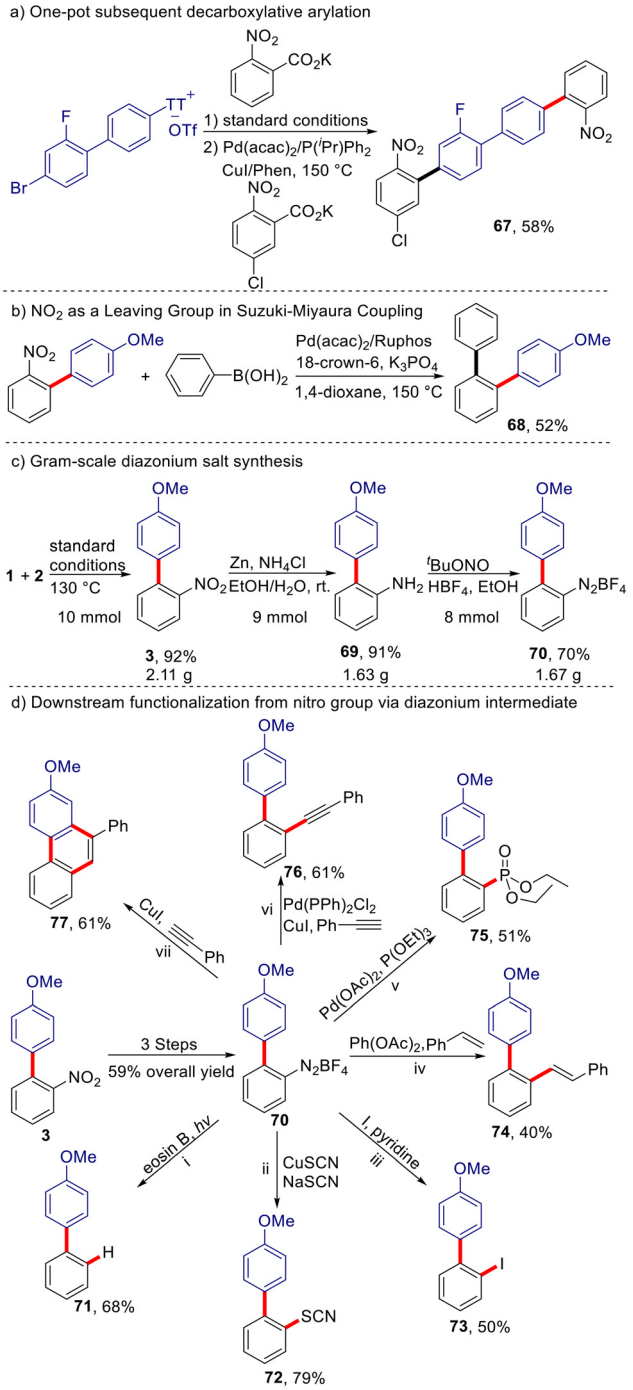
[a] Reaction conditions: 0.2 mmol arylthianthrenium salt, 0.24 mmol potassium carboxylate, 2.5 mol% $Pd(OAc)_2$, 5 mol% CuI, 5 mol% bpy, in 1 mL DMSO, at 120 °C, under an argon atmosphere for 16 h; isolated yields. [b] 10 mol% CuI and 10 mol% bpy at 160 °C. [c] With 0.1 mmol thianthrene. [d] 5 mol% $Pd(OAc)_2$. [e] 0.10 mmol CuCl, 10 mol% bpy at 160 °C. [f] 5 mol% Cu_2O, and 10 mol% Me_4Phen, and 10 mol% XPhos in NMP/quinoline (1 : 1) at 180 °C. [g] 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**).

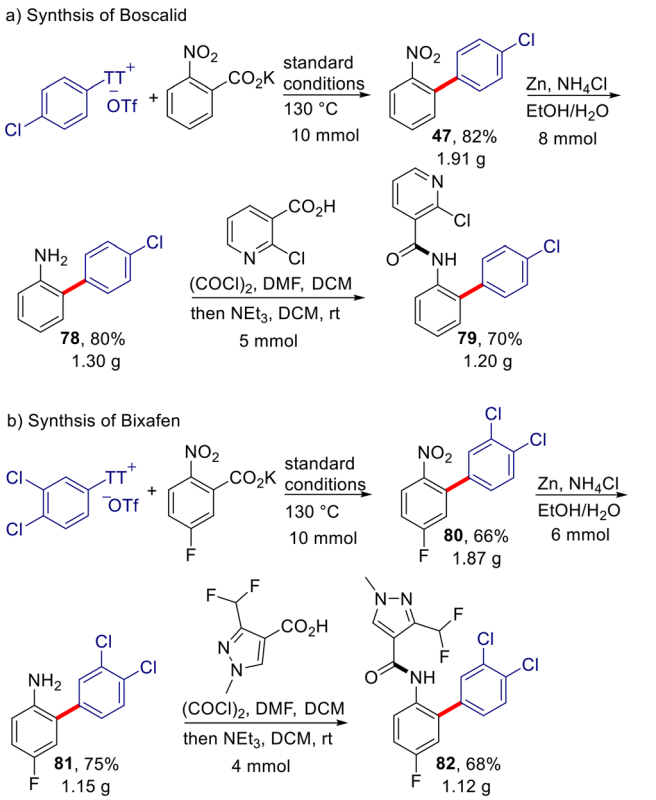
The orthogonal reactivity of arylthianthrenium salts *versus* aryl halides was demonstrated in a one-pot process using a substrate bearing both a thianthrenium group and a halide. First, selective decarboxylative coupling occurred at the thianthrenium site with a benzoate. The resulting halogenated biaryl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

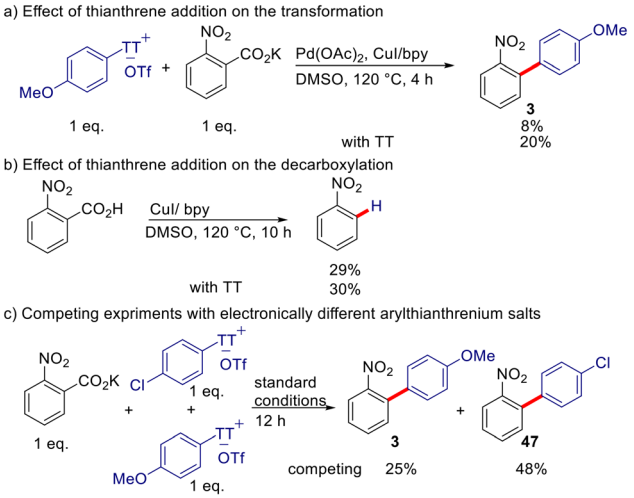
A series of control experiments were conducted to shed light on the reaction mechanism. The addition of thianthrene was found to significantly enhance the reaction rate, leading to higher yields within shorter time (Scheme 6a). In the pres-



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 (≥160 °C) for efficient conversion. Thus, the rate-determining step is substrate-dependent.

Conclusions

In summary, we have utilized palladium/copper dual ca-talysis 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 information is available. Experimental procedures, characterization data for compounds, and NMR spectra of products. See DOI: **https://doi.org/10.1039/d6qo00448b**.

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References

1 (*a*) A. Fava, P. B. Sogo and M. Calvin, Chemistry and Spin Resonance Spectroscopy of Radicals from Thioaromatic Compounds[1], *J. Am. Chem. Soc.*, 1957, **79**, 1078–1083; (*b*) E. A. C. Lucken, 1,4-Dithiinium Radical-Cations, *J. Chem. Soc.*, 1962, 4963; (*c*) Y. Murata and H. J. Shine, Ion Radicals. XVIII. Reactions of Thianthrenium Perchlorate and Thianthrenium Trichlorodiiodide, *J. Org. Chem.*, 1969, **34**, 3368–3372; (*d*) H. J. Shine and J. J. Silber, Reaction of Thianthrenium Perchlorate (C12H8S2.+ClO4-) with Aromatics, *J. Org. Chem.*, 1971, **36**, 2923–2926; (*e*) H. J. Shine and C. F. Dais, The Reactions of Thianthrene Oxide in Hydrochloric Acid[1,2], *J. Org. Chem.*, 1965, **30**, 2145–2148; (*f*) *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations Vol. 31a: Arene-X (X=Hal, O, S, Se, Te)*, ed. C. A. Ramsden, Georg Thieme Verlag, Stuttgart, 1st edn, 2007.

2 F. Berger, M. B. Plutschack, J. Riegger, W. Yu, S. Speicher, M. Ho, N. Frank and T. Ritter, Site-Selective and Versatile Aromatic C–H Functionalization by Thianthrenation, *Nature*, 2019, **567**, 223–228.

3 (*a*) M. J. Cabrera-Afonso, A. Granados and G. A. Molander, Sustainable Thioetherification via Electron Donor–Acceptor Photoactivation Using Thianthrenium Salts, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202706; (*b*) J. Corpas, H. P. Caldora, E. M. Di Tommaso, A. C. Hernandez-Perez, O. Turner, L. M. Azofra, A. Ruffoni and D. Leonori, A General Strategy for the Amination of Electron-Rich and Electron-Poor Heteroaromatics by Desaturative Catalysis, *Nat. Catal.*, 2024, **7**, 593–603; (*c*) A. Granados, M. J. Cabrera-Afonso, M. Escolano, S. O. Badir and G. A. Molander, Thianthrenium-Enabled Sulfonylation via Electron Donor-Acceptor Complex Photoactivation, *Chem Catal.*, 2022, **2**, 898–907; (*d*) L. Mu, C. R. Fischer, J. P. Holland, J. Becaud, P. A. Schubiger, R. Schibli, S. M. Ametamey, K. Graham, T. Stellfeld, L. M. Dinkelborg and L. Lehmann, [18] F–Radiolabeling of Aromatic Compounds Using Triarylsulfonium Salts, *Eur. J. Org. Chem.*, 2012, 889–892.

4 (*a*) H. Meng, M.-S. Liu and W. Shu, Organothianthrenium Salts: Synthesis and Utilization, *Chem. Sci.*, 2022, **13**, 13690–13707; (*b*) X.-Y. Chen, Y. Wu and P. Wang, Recent

Advances in Thianthrenation/Phenoxathiination Enabled Site-Selective Functionalization of Arenes, *Synthesis*, 2022, 3928–3940; (*c*) S. Timmann, Z. Feng and M. Alcarazo, Recent Applications of Sulfonium Salts in Synthesis and Catalysis, *Chem. – Eur. J.*, 2024, **30**, e202402768.

5 (*a*) Á. Péter, G. J. P. Perry and D. J. Procter, Radical C–C Bond Formation Using Sulfonium Salts and Light, *Adv. Synth. Catal.*, 2020, **362**, 2135–2142; (*b*) X. Wu, P. Gao and F. Chen, Synthetic Applications of Sulfonium Salts as Aryl Radical Precursors, *Eur. J. Org. Chem.*, 2023, e202300864.

6 (*a*) D. Ahmadli, S. Müller, Y. Xie, T. Smejkal, S. Jaeckh, A. V. Iosub, S. R. Williams and T. Ritter, Standardized Approach for Diversification of Complex Small Molecules via Aryl Thianthrenium Salts, *J. Am. Chem. Soc.*, 2025, **147**, 4268–4283; (*b*) Y. Cai, T. K. Roy, T. J. B. Zähringer, B. Lansbergen, C. Kerzig and T. Ritter, Arylthianthrenium Salts for Triplet Energy Transfer Catalysis, *J. Am. Chem. Soc.*, 2024, **146**, 30474–30482; (*c*) Y. Cai and T. Ritter, Meerwein–type Bromoarylation with Arylthianthrenium Salts, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209882; (*d*) M. Mrozowicz, S. Chatterjee, M. A. Mermigki, D. A. Pantazis and T. Ritter, *Meta* –Dimethylation of Arenes via Catellani Reaction from Aryl Thianthrenium Salts, *Angew. Chem., Int. Ed.*, 2025, **64**, e202419472.

7 (*a*) K. Kafuta, A. Korzun, M. Böhm, C. Golz and M. Alcarazo, Synthesis, Structure, and Reactivity of 5–(Aryl) Dibenzothiophenium Triflates, *Angew. Chem., Int. Ed.*, 2020, **59**, 1950–1955.

8 (*a*) M. H. Aukland, M. Šiaučiulis, A. West, G. J. P. Perry and D. J. Procter, Metal-Free Photoredox-Catalysed Formal C–H/C–H Coupling of Arenes Enabled by Interrupted Pummerer Activation, *Nat. Catal.*, 2020, **3**, 163–169; (*b*) A. Dewanji, L. Van Dalsen, J. A. Rossi-Ashton, E. Gasson, G. E. M. Crisenza and D. J. Procter, A General Arene C–H Functionalization Strategy via Electron Donor–Acceptor Complex Photoactivation, *Nat. Chem.*, 2023, **15**, 43–52; (*c*) L. Van Dalsen, R. E. Brown, A. Rossi-Ashton and D. J. Procter, Sulfonium Salts as Acceptors in Electron Donor–Acceptor Complexes, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303104.

9 (*a*) T. Michiyuki, S. L. Homölle, N. K. Pandit and L. Ackermann, Electrocatalytic Formal $C(Sp^2)$–H Alkylations via Nickel–Catalyzed Cross–Electrophile Coupling with Versatile Arylsulfonium Salts, *Angew. Chem., Int. Ed.*, 2024, **63**, e202401198; (*b*) H. Simon, A. Zangarelli, T. Bauch and L. Ackermann, Ruthenium(II)–Catalyzed Late–Stage Incorporation of *N* –Aryl Triazoles and Tetrazoles with Sulfonium Salts via C–H Activation, *Angew. Chem., Int. Ed.*, 2024, **63**, e202402060.

10 (*a*) K. Wang, X. Teng, D. Zhang, B. Xu, P. Gao, S. Wang, S. Zhang, L. J. Gooßen, F. Chen and G. Zhang, Ruthenium Catalyzed *Ortho* –Arylation Reaction of Benzoic Acids with Arylthianthrenium Salts, *Angew. Chem., Int. Ed.*, 2025, **64**, e202504888; (*b*) S. Zhuang, L. Yu, D. Zhang, X. Teng and G. Zhang, Arylative Coupling of Pyridylphosphonium Salts with Aryl Thianthrenium Salts Enabled by Palladium Catalysis, *Org. Lett.*, 2026, **28**, 1586–1591; (*c*) H. Ma, D. Zhang, B. Cheng, L. Wang, B. Xu, S. Wang, S. Zhang, J. Lv, B. König and G. Zhang, Photoredox/Copper Cooperatively Catalyzed Arylalkynylation of [1.1.1] Propellane, *Org. Lett.*, 2025, **27**, 3446–3451.

11 (*a*) K. Sun, C. Ge, X. Chen, B. Yu, L. Qu and B. Yu, Energy-Transfer-Enabled Photocatalytic Transformations of Aryl Thianthrenium Salts, *Nat. Commun.*, 2024, **15**, 9693; (*b*) S. Tang, X. Zhao, L. Yang, B. Li and B. Wang, Copper–Catalyzed Carboxylation of Aryl Thianthrenium Salts with CO_2, *Angew. Chem., Int. Ed.*, 2022, **61**, e202212975; (*c*) Y. Zhao and X. Wu, Carbonylative Transformations of Aryl Sulfonium Salts, *Chemistry Methods*, 2025, **5**, e202500089.

12 (*a*) B. Trost, R. LaRochelle and R. Atkins, Pentacoordinate Sulfur Compounds as Intermediates in Organic Reactions, *J. Am. Chem. Soc.*, 1969, **91**, 2175–2177; (*b*) R. W. LaRochelle and B. M. Trost, Reactions of Organolithiums with Arylsulfonium Salts, *J. Am. Chem. Soc.*, 1971, **93**, 6077–6086; (*c*) B. M. Trost and H. C. Arndt, Sigma.-Sulfurane Chemistry. Effect of Substituents on the Coupling Reactions, *J. Am. Chem. Soc.*, 1973, **95**, 5288–5298; (*d*) S. Oae, H. Ishihara and M. Yoshihara, Reaction of Triphenylsulfonium Salt with Organolithium Reagents, *Chem. Heterocycl. Compd.*, 1995, **31**, 917–921; (*e*) M. Hori, T. Kataoka, H. Shimizu, M. Ikemori and Y. Aoyama, Syntheses and Reactions of 9-Substituted 10-Phenylthioxanthenium Salts: Negative Evidence for Thia-Anthracene Oligomerisation, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1209; (*f*) Y. H. Khim and S. Oae, The Mechanism of the Alkaline Decomposition of Triarylsulfonium Bromide with Phenyllithium, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1968–1971.

13 (*a*) A. M. Horan, V. K. Duong and E. M. McGarrigle, Synthesis of Bis-Heteroaryls Using Grignard Reagents and Pyridylsulfonium Salts, *Org. Lett.*, 2021, **23**, 9089–9093; (*b*) V. K. Duong, A. M. Horan and E. M. McGarrigle, Synthesis of Pyridylsulfonium Salts and Their Application in the Formation of Functionalized Bipyridines, *Org. Lett.*, 2020, **22**, 8451–8457.

14 T. Morofuji, T. Yoshida, R. Tsutsumi, M. Yamanaka and N. Kano, Arylation of Aryllithiums with *S* -Arylphenothiazinium Ions for Biaryl Synthesis, *Chem. Commun.*, 2020, **56**, 13995–13998.

15 (*a*) L. Zhang, Y. Xie, Z. Bai and T. Ritter, Suzuki–Miyaura Coupling of Arylthianthrenium Tetrafluoroborate Salts under Acidic Conditions, *Nat. Synth.*, 2024, **3**, 1490–1497; (*b*) Y. Xie, L. Zhang and T. Ritter, Late–Stage Cross–Electrophile Coupling of Arylthianthrenium Salts with (Hetero)Aryl (Pseudo)Halides via Palladium Catalysis, *Angew. Chem., Int. Ed.*, 2025, **64**, e202502441; (*c*) D. Vasu, H. Yorimitsu and A. Osuka, Base-Free Palladium-Catalyzed Cross-Coupling of Arylsulfonium Salts with Sodium Tetraarylborates, *Synthesis*, 2015, 3286–3291; (*d*) Z. Mravíková, T. Peňaška, D. Horniaková and R. Šebesta, Mechanochemical Palladium–Catalyzed Cross–Coupling of

Thianthrenium Salts and Arylboronic Acids, *ChemSusChem*, 2025, **18**, e202402599.

16 Q.-Q. Fu, Y. Liang, X.-X. Sun, X.-Q. Chu, H. Xu, X. Zhou, W. Rao and Z.-L. Shen, Palladium-Catalyzed Cross-Electrophile Couplings of Aryl Thianthrenium Salts with Aryl Bromides via C–S Bond Activation, *Org. Lett.*, 2024, **26**, 8577–8582.

17 (*a*) C. Yang, L. P. Slavětínská, M. Fleuti, B. Klepetářová, M. Tichý, S. Gurská, P. Pavliš, P. Džubák, M. Hajdúch and M. Hocek, Synthesis of Polycyclic Hetero-Fused 7-Deazapurine Heterocycles and Nucleosides through C–H Dibenzothiophenation and Negishi Coupling, *J. Am. Chem. Soc.*, 2022, **144**, 19437–19446; (*b*) T. Čarný, M. Mart, M. Blauciak, B. Steinhüblová and R. Šebesta, Pd–Catalyzed Cross–Coupling of Organozinc Pivalates with Arene Thianthrenium Salts Under Ball–Milling Conditions, *ChemCatChem*, 2025, **17**, e202500373.

18 Z.-W. Cao, J.-X. Zhang, J.-T. Wang, L. Li, X.-Y. Chen, S. Jin, Z.-Y. Cao and P. Wang, Palladium-Catalyzed Hiyama-Type Coupling of Thianthrenium and Phenoxathiinium Salts, *Org. Lett.*, 2024, **26**, 6681–6686.

19 J. Jing, Y. Hu, Z. Tian, Y. Wang, L. Yao, L. Qiu, L. Ackermann, K. Karaghiosoff and J. Li, C–S–Selective Stille–Coupling Enables Stereodefined Alkene Synthesis, *Angew. Chem., Int. Ed.*, 2024, e202408211.

20 (*a*) A. G. Myers, D. Tanaka and M. R. Mannion, Development of a Decarboxylative Palladation Reaction and Its Use in a Heck-Type Olefination of Arene Carboxylates, *J. Am. Chem. Soc.*, 2002, **124**, 11250–11251; (*b*) N. Rodríguez and L. J. Goossen, Decarboxylative Coupling Reactions: A Modern Strategy for C–C-Bond Formation, *Chem. Soc. Rev.*, 2011, **40**, 5030; (*c*) Y. Wei, P. Hu, M. Zhang and W. Su, Metal-Catalyzed Decarboxylative C–H Functionalization, *Chem. Rev.*, 2017, **117**, 8864–8907; (*d*) A. Varenikov, E. Shapiro and M. Gandelman, Decarboxylative Halogenation of Organic Compounds, *Chem. Rev.*, 2021, **121**, 412–484; (*e*) S. Tamaki, T. Kusamoto and H. Tsurugi, Decarboxylative Functionalization of Carboxylic Acids with Easily Oxidizable, Unstable, and Difficult Substituents Under Visible Light Irradiation, *ChemCatChem*, 2025, **17**, e202402106; (*f*) F. Foubelo, C. Nájera, M. G. Retamosa, J. M. Sansano, A. Sirvent and M. Yus, Decarboxylative Photocatalytic Transformations, *Chem. Soc. Rev.*, 2025, **54**, 11856–12042; (*g*) W. Yan, T. Tian and Y. Nishihara, From Carboxylic Acids or Their Derivatives to Amines and Ethers: Modern Decarboxylative Approaches for Sustainable C–N and C–O Bond Formation, *Org. Biomol. Chem.*, 2025, **23**, 7367–7382.

21 L. J. Gooßen, G. Deng and L. M. Levy, Synthesis of Biaryls via Catalytic Decarboxylative Coupling, *Science*, 2006, **313**, 662–664.

22 M. Nilsson, E. Kulonen, S. Sunner, V. Frank, J. Brunvoll, E. Bunnenberg, C. Djerassi and R. Records, A New Biaryl Synthesis Illustrating a Connection between the Ullmann Biaryl Synthesis and Copper-Catalysed Decarboxylation, *Acta Chem. Scand.*, 1966, **20**, 423–426.

23 (*a*) P. Forgione, M.-C. Brochu, M. St-Onge, K. H. Thesen, M. D. Bailey and F. Bilodeau, Unexpected Intermolecular Pd-Catalyzed Cross-Coupling Reaction Employing Heteroaromatic Carboxylic Acids as Coupling Partners, *J. Am. Chem. Soc.*, 2006, **128**, 11350–11351; (*b*) F. Bilodeau, M.-C. Brochu, N. Guimond, K. H. Thesen and P. Forgione, Palladium-Catalyzed Decarboxylative Cross-Coupling Reaction Between Heteroaromatic Carboxylic Acids and Aryl Halides, *J. Org. Chem.*, 2010, **75**, 1550–1560; (*c*) C. Buonomano, M. Holtz-Mulholland, S. Sullivan and P. Forgione, Development of a Palladium-Catalyzed Decarboxylative Arene Cross-Coupling of Pyrrole Derivatives in a Flow Reactor, *J. Flow Chem.*, 2022, **12**, 275–283; (*d*) J. T. Liu, H. Hase, S. Taylor, I. Salzmann and P. Forgione, Approaching the Integer–Charge Transfer Regime in Molecularly Doped Oligothiophenes by Efficient Decarboxylative Cross–Coupling, *Angew. Chem., Int. Ed.*, 2020, **59**, 7146–7153.

24 J. Kan, S. Huang, J. Lin, M. Zhang and W. Su, Silver-Catalyzed Arylation of (Hetero)Arenes by Oxidative Decarboxylation of Aromatic Carboxylic Acids, *Angew. Chem., Int. Ed.*, 2015, **54**, 2199–2203.

25 (*a*) L. J. Goossen, N. Rodríguez, B. Melzer, C. Linder, G. Deng and L. M. Levy, Biaryl Synthesis via Pd-Catalyzed Decarboxylative Coupling of Aromatic Carboxylates with Aryl Halides, *J. Am. Chem. Soc.*, 2007, **129**, 4824–4833; (*b*) L. J. Gooßen, B. Zimmermann and T. Knauber, Palladium/Copper–Catalyzed Decarboxylative Cross–Coupling of Aryl Chlorides with Potassium Carboxylates, *Angew. Chem., Int. Ed.*, 2008, **47**, 7103–7106; (*c*) L. J. Goossen, N. Rodríguez and C. Linder, Decarboxylative Biaryl Synthesis from Aromatic Carboxylates and Aryl Triflates, *J. Am. Chem. Soc.*, 2008, **130**, 15248–15249; (*d*) L. J. Gooßen, N. Rodríguez, P. P. Lange and C. Linder, Decarboxylative Cross–Coupling of Aryl Tosylates with Aromatic Carboxylate Salts, *Angew. Chem., Int. Ed.*, 2010, **49**, 1111–1114; (*e*) A. Fromm, C. Van Wüllen, D. Hackenberger and L. J. Gooßen, Mechanism of Cu/Pd-Catalyzed Decarboxylative Cross-Couplings: A DFT Investigation, *J. Am. Chem. Soc.*, 2014, **136**, 10007–10023; (*f*) J. Tang, A. Biafora and L. J. Goossen, Catalytic Decarboxylative Cross–Coupling of Aryl Chlorides and Benzoates without Activating *Ortho* Substituents, *Angew. Chem., Int. Ed.*, 2015, **54**, 13130–13133.

26 (*a*) C. Wang, I. Piel and F. Glorius, Palladium-Catalyzed Intramolecular Direct Arylation of Benzoic Acids by Tandem Decarboxylation/C–H Activation, *J. Am. Chem. Soc.*, 2009, **131**, 4194–4195; (*b*) A. Voutchkova, A. Coplin, N. E. Leadbeater and R. H. Crabtree, Palladium-Catalyzed Decarboxylative Coupling of Aromatic Acids with Aryl Halides or Unactivated Arenes Using Microwave Heating, Palladium-Catalyzed Decarboxylative Coupling of Aromatic Acids with Aryl Halides or Unactivated Arenes Using Microwave Heating, *Chem. Commun.*, 2008, 6312; (*c*) L. Liang, Y.-H. Wang, C. Li, H.-J. Wang, Q.-L. Yang, C.-G. Li, G.-R. Qu, H.-M. Guo and H.-Y. Niu, Regioselective

and late-stage polyfluoroarylation of arenes with diverse fluoroaryl nucleophiles via Pd-catalysis, *Org. Chem. Front.*, 2022, **9**, 5832–5839; (*d*) O. Baudoin, New Approaches for Decarboxylative Biaryl Coupling, *Angew. Chem., Int. Ed.*, 2007, **46**, 1373–1375; (*e*) R. Shang, Y. Fu, Y. Wang, Q. Xu, H. Yu and L. Liu, Copper–Catalyzed Decarboxylative Cross–Coupling of Potassium Polyfluorobenzoates with Aryl Iodides and Bromides, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350–9354; (*f*) J.-M. Becht, C. Catala, C. Le Drian and A. Wagner, Synthesis of Biaryls via Decarboxylative Pd-Catalyzed Cross-Coupling Reaction, *Org. Lett.*, 2007, **9**, 1781–1783.

27 J. I. Ayogu and E. A. Onoabedje, Recent Advances in Transition Metal-Catalysed Cross-Coupling of (Hetero)Aryl Halides and Analogues under Ligand-Free Conditions, *Catal. Sci. Technol.*, 2019, **9**, 5233–5255.