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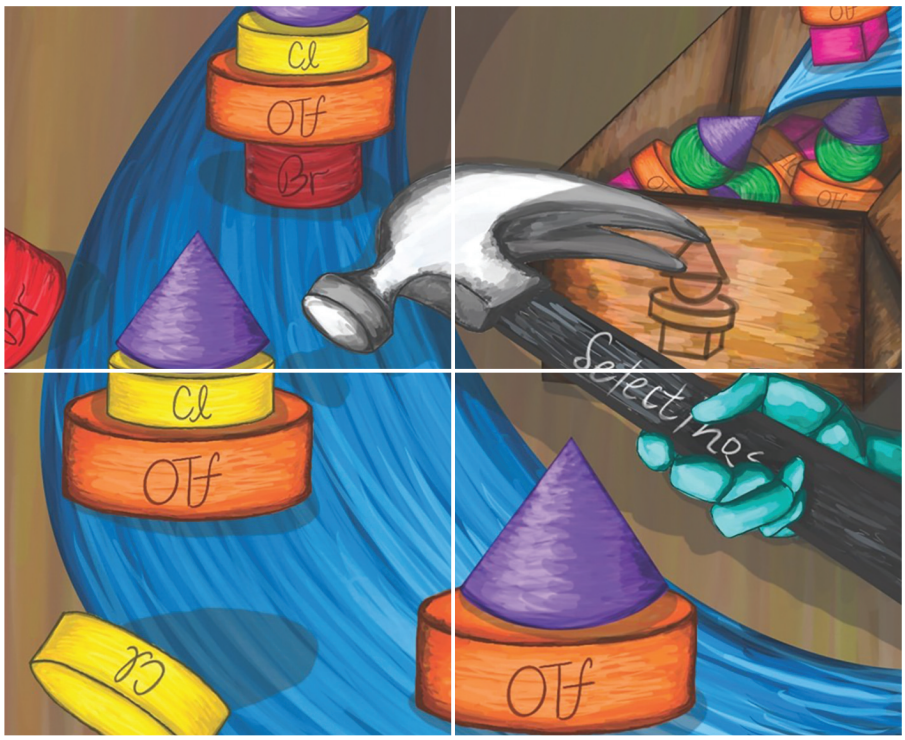

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Palladium-catalyzed chemoselective decarboxylative coupling of alkynyl carboxylic acids with halogenated aryl triflates†

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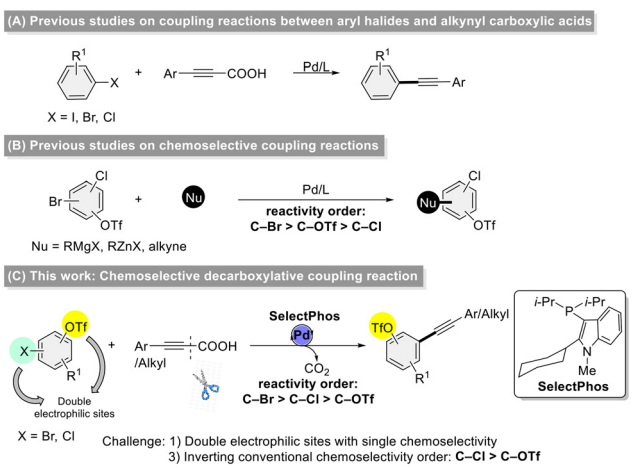
A palladium-catalyzed chemoselective decarboxylative coupling of alkynyl carboxylic acids with halogenated aryl triflates has been developed for the efficient synthesis of OTf-arylalkyne scaffolds. Notably, this transformation exhibits an inversion of the conventional chemoselectivity order, favoring C–Br > C–Cl > C–OTf. In addition, a one-pot sequential strategy was established by integrating the decarboxylative coupling with a Suzuki–Miyaura reaction, offering a versatile platform for the synthesis of difunctionalized aromatic compounds. Density functional theory (DFT) calculations indicate that the oxidative addition step governs the chemoselectivity, while the decarboxylation step is proposed to be rate-determining.

Introduction

Decarboxylative coupling is a powerful tool-type strategy for the formation of C–C and C–heteroatom bonds, allowing for the construction of useful heterocyclic skeletons and pharmaceutically active molecules.[1] Moreover, this strategy features the utilization of facilely prepared and stable carboxylic acids and low toxicity carbon dioxide as a by-product which has therefore received extensive attention.[2] Since Lee and co-workers reported the first example of decarboxylative coupling reaction[3] of alkynyl carboxylic acids with aryl halides to synthesize unsymmetric diarylalkynes in 2008, this efficient strategy has drawn wide attention, and has been explored for the construction of C–C,[4] C–N,[5] C–Br,[6] C–P,[7] C–S,[8] C–Se,[9] C–B,[10] and C–Si[11] bonds. The employment of alkynyl carboxylic acids as surrogates for terminal alkynes offers an advantageous strategy for managing low-boiling-point alkynes, enhancing both the practicality and safety of their manipulation. Although the decarboxylative coupling of alkynyl carboxylic acids has advanced significantly, most studies have focused on substrates with a single electrophilic site (Scheme 1A).[3,4] In contrast, chemoselective reactions involving dual electrophilic sites remain underexplored.[12] Aryl halides and triflates are among the most commonly used electrophiles, with a generally accepted reactivity order of I > Br ≈ OTf > Cl (Scheme 1B).[13] However, cross-coupling reactions involving more than one electrophilic sites continue to face several key challenges, including: (1) a limited substrate scope, (2) difficulty in achieving clean chemoselectivity when two electrophilic sites are present, and (3) the challenge of reversing the conventional reactivity order—such as favoring C–Cl over C–OTf bonds.

In recent years, we developed a new type of alkyl–heteroaryl-based phosphorus ligand (SelectPhos) and successfully applied it to chemoselective coupling reactions, achieving an inversion of the conventional chemoselectivity order of C–Br >



Scheme 1 From conventional to chemoselective: coupling strategies using alkynyl carboxylic acids.

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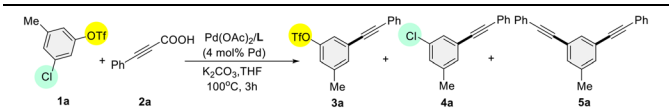
C–Cl > C–OTf.[14] In conjunction with our ongoing work on the development of new ligands and chemoselective reactions, we now present our latest research on the application of SelectPhos in the chemoselective decarboxylative coupling of alkynyl carboxylic acids with halogenated aryl triflates, demonstrating a chemoselectivity order of C–Br > C–Cl > C–OTf (Scheme 1C). To the best of our knowledge, this is the first decarboxylative coupling of alkynyl carboxylic acids with chloroaryl triflates at the C–Cl bond over the C–OTf bond.

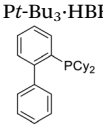
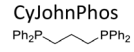
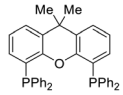
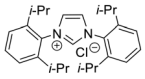
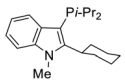
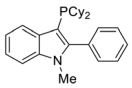
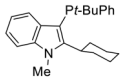
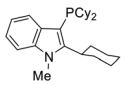
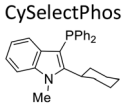
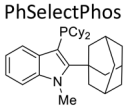
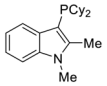
Results and discussion

We set out to investigate the chemoselective decarboxylative coupling reaction using 3-chloro-5-methylphenyl triflate **1a** and 3-phenylpropiolic acid **2a** as model substrates, with the systematic screenings of a range of ligands (Table 1). Initially, a series of classical phosphine ligands were screened (**L1–L3**). PPh_3 showed the general reactivity order: OTf > Cl with excellent yield; PCy_3 resulted in poor activity, and P*t*-Bu_3·HBF_4 show a certain extent at C–Cl bond over C–OTf bond (C–Cl : C–OTf = 10 : 1), but with low yield. Moreover, Buchwald-type biaryl ligand was also tested (**L4**), and it showed C–OTf chemoselectivity. Bidentate ligands (**L5–L7**) were evaluated, and the results indicated that most bidentate ligands provide C–OTf selectivity with excellent activity. Since NHC ligand was reported to show good C–Cl chemoselectivity over C–OTf in the Suzuki–Miyaura coupling,[15] we tested the corresponding NHC ligand in this chemoselective decarboxylative coupling reaction, but the result showed poor chemoselectivity and reactivity (**L8**). To our delight, SelectPhos (**L9**) gave the result of excellent C–Cl chemoselectivity (C–Cl : C–OTf > 70 : 1) in 71% yield. Other SelectPhos derivatives (**L11–L13**) were also tested, both substituents attached to the C2 position on the indole ring and phosphorus atom could directly affect the selectivity and activity, and replacing an aryl group at either position will show the opposite selectivity. The steric hindrance size of substituents attached to the C2 position on the indole ring could affect the selectivity, an adamantly substituent showed roughly C–Cl selectivity but the methyl group showed C–OTf selectivity (**L14–L15**).

Next, we were focused on the investigations of the optimal conditions for this chemoselective decarboxylative coupling reaction with SelectPhos (**L9**). Initially, we evaluated several palladium source (Table S1,† entries 1–3), and dichloro-(1-methylallyl)-dipalladium showed the optimal reactivity, affording the corresponding product in excellent yield (95%). The molar ratio of Pd and **L9** were also evaluated (Table S1,† entries 4–6), and 1 : 4 of Pd and **L9** was the best choice. Subsequently, we investigated several bases, including K_3PO_4, KOAc, KF, and Cs_2CO_3 (Table S1,† entries 7–10), but these did not lead to a higher yield. Regarding solvent evaluation (Table S1,† entries 11–13), we tested 1,4-dioxane, PhMe, and CPMe, but THF provided the best activity. We tried to reduce the dosage of 3-phenylpropiolic acid, but the yield dropped significantly (Table S1,† entry 14). Finally, the temperature for

Table 1 Ligand screening of chemoselective C–Cl (over C–OTf) decarboxylative coupling reaction[a]



Entry	Ligand code	Ligand	Yields[b] (%) 3a	4a	5a
1	**L1**	PPh_3	0	84	0
2	**L2**	PCy_3	0	5	0
3	**L3**	P*t*-Bu_3·HBF_4	20	2	0
4	**L4**	 CyJohnPhos	0	35	50
5	**L5**	 dppp	0	73	0
6	**L6**	 dppf	0	99	0
7	**L7**	 XantPhos	0	98	0
8	**L8**	 IPr·HCl	19	3	0
9	**L9**	 SelectPhos	71	1	2
10	**L10**	 PhendolePhos	0	63	Trace
11	**L11**	 *t*-BuPhSelectPhos	16	1	0
12	**L12**	 CySelectPhos	50	2	0
13	**L13**	 PhSelectPhos	0	77	8
14	**L14**		20	7	Trace
15	**L15**		0	27	0

[a] Reaction condition: 3-chloro-5-methylphenyl triflate **1a** (0.20 mmol), 3-phenylpropiolic acid **2a** (0.36 mmol), $Pd(OAc)_2$ (4 mol%), **L** (16 mol%), K_2CO_3 (0.40 mmol) and THF (1.0 mL) were stirred at 100 °C or 3 h. [b] Calibrated GC yields were reported by using dodecane as an internal standard.

this reaction were also evaluated, and 100 °C was the best choice (Table S1,† entries 15 and 16).

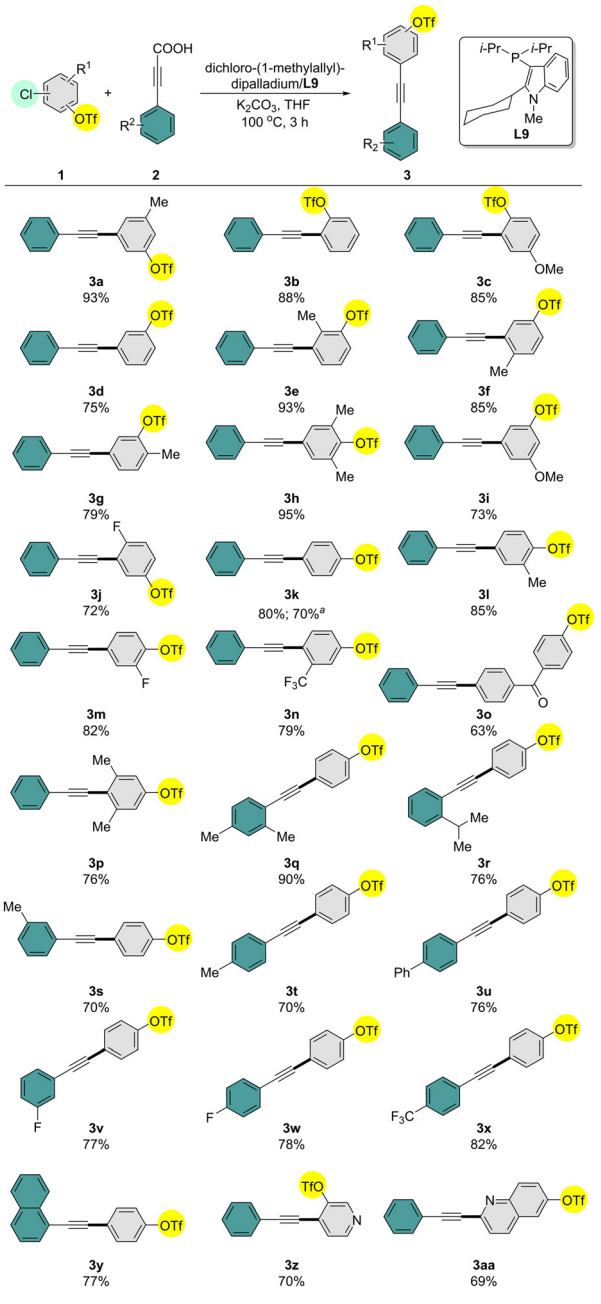
After obtaining the optimal reaction conditions, we proceeded to investigate the substrate scope of this chemoselective decarboxylative coupling reaction (Scheme 2). Initially, we examined a range of chloroaryl triflates, and the results showed the reaction has good substrate adaptability, no matter whether the C–Cl bond was at positions *ortho* (**3b–3c**), *meta* (**3a**, **3d–3g**, **3i–3j**), and *para* (**3h** and **3k–p**) to the C–OTf bond, affording the corresponding products in moderate to excellent yields (63–95%) with excellent C–Cl chemoselectivity. Broad functional group substituents were tolerated in this reaction, such as methyl (**3a**, **3e–3h**, **3l**, **3p**), methoxy (**3c**, and **3i**), fluoro (**3j** and **3m**), trifluoromethyl (**3n**), and ketone (**3o**).

Furthermore, this reaction accommodated a wide range of alkynyl carboxylic acids, regardless of the electronically neutral (2,4-di-Me, 3-Me and 4-Me), electron-donating (2-*i*-Pr), and electron-withdrawing (4-Ph, 3-F, 4-F and 4-CF_3) substituents attached to the alkynyl carboxylic acids all reacted smoothly, providing the corresponding OTf-arylalkynes in good to excellent yields with good C–Cl chemoselectivity (**3q–3x**). Moreover, the naphthyl propargylic acid also adapted to this reaction, affording the corresponding product **3y** in 77% yield. Chloroheteroaryl triflates were also applicable as substrates (**3z** and **3aa**).

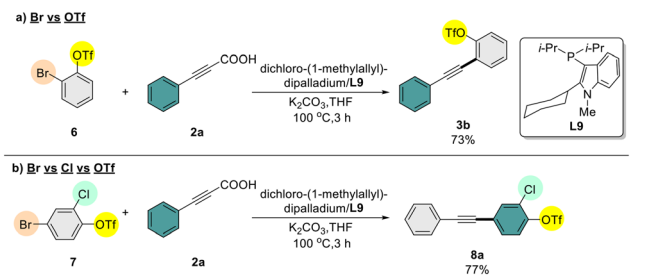
Encouraged by the positive results mentioned above, we then studied this chemoselective decarboxylative coupling reaction of bromoaryl triflate and bromochloroaryl triflate (Scheme 3). To our delight, when we used 2-bromophenyl triflate (**6**) as the substrate, the chemoselective decarboxylative coupling reaction proceeded successfully, yielding the corresponding product in 73% with excellent C–Br chemoselectivity over C–OTf (C–Br : C–OTf ≥ 99 : 1). When using 4-bromo-2-chlorophenyl triflate (**7**) as the substrate, the reaction also progressed well, providing the corresponding product in 77% yield with excellent C–Br chemoselectivity over C–Cl and C–OTf (C–Br : C–Cl : C–OTf ≥ 99 : 1 : 0).

To further expand the substrate scope, we next investigated alkyl–alkynyl carboxylic acids as cross-coupling partners (Scheme 4). 2-Pentynoic acid, 2-hexynoic acid, and 2-octynoic acid were found to be effective substrates, affording the desired products in good yields and with excellent C–Cl chemoselectivity.

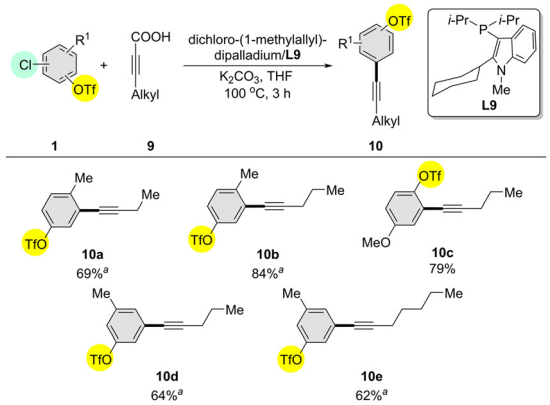
To further explore the utility of this chemoselective decarboxylative reaction, we investigated its applicability in a sequential synthetic protocol (Scheme 5). As shown, the chlor-



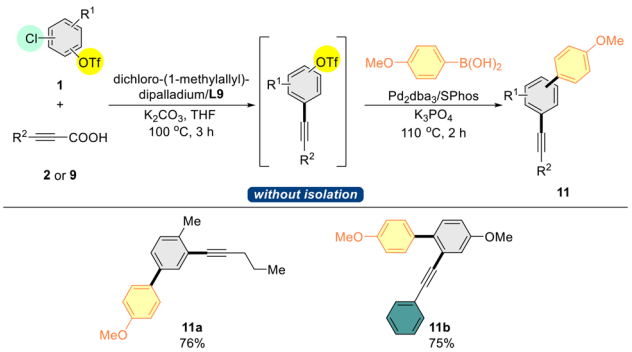
Scheme 2 Substrate scope for the chemoselective C–Cl (over C–OTf) decarboxylative coupling reaction. (Reaction condition: chloroaryl triflates **1** (0.20 mmol), alkynyl carboxylic acids **2** (0.36 mmol), dichloro-(1-methylallyl)-dipalladium (2 mol%), **L9** (16 mol%), K_2CO_3 (0.40 mmol) and THF (1.0 mL) were stirred at 100 °C for 3 h. Isolated yields based on chloroaryl triflates **1** are reported. [a] The reaction was performed on a 1.0 mmol scale.)



Scheme 3 Pd-Catalyzed chemoselective C–Br (over C–Cl and C–OTf) decarboxylative coupling reaction. (Reaction condition: halogenated aryl triflate **6** or **7** (0.20 mmol), 3-phenylpropiolic acid **2a** (0.36 mmol), dichloro-(1-methylallyl)-dipalladium (2 mol%), **L9** (16 mol%), K_2CO_3 (0.40 mmol) and THF (1.0 mL) were stirred at 100 °C for 3 h. Isolated yields based on polyhalogenated aryl triflate are reported.).



Scheme 4 Substrate scope for the chemoselective C–Cl (over C–OTf) decarboxylative coupling reaction. (Reaction condition: chloroaryl triflates **1** (0.20 mmol), alkyl–alkynyl carboxylic acids **9** (0.36 mmol), dichloro-(1-methylallyl)-dipalladium (2 mol%), **L9** (16 mol%), K_2CO_3 (0.40 mmol) and THF (1.0 mL) were stirred at 100 °C for 3 h. Isolated yields based on chloroaryl triflates **1** are reported. [a] Toluene was used.).

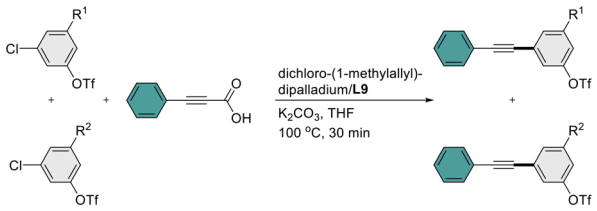


Scheme 5 One-pot sequential utilization of chemoselective decarboxylative coupling. (1st step reaction conditions: chloroaryl triflates **1** (0.20 mmol), alkyl or aryl–alkynyl carboxylic acids **2** or **9** (0.36 mmol), dichloro(1-methylallyl)dipalladium (2 mol%), **L9** (16 mol%), K_2CO_3 (0.40 mmol), and THF (1.0 mL) were stirred at 100 °C for 3 h. 2nd step reaction conditions: 4-methoxyphenylboronic acid (0.40 mmol), $Pd_2(dba)_3$ (1.5 mol%), SPhos (4.5 mol%), and K_3PO_4 (0.3 mmol) were added, and the reaction mixture was stirred at 110 °C for 2 h. Isolated yields are reported based on chloroaryl triflates **1**.).

oaryl triflates initially underwent chemoselective decarboxylation to afford the corresponding intermediates. Without isolating these intermediates, aryl boronic acids were subsequently added to the same reaction mixture, enabling a Suzuki–Miyaura coupling at the C–OTf bonds. This one-pot, two-step sequence furnished the corresponding difunctionalized products **11a** and **11b** in good yields.

To gain deeper mechanistic insight into this chemoselective decarboxylative reaction, a series of competition experiments were conducted (Table 2). The results revealed that the electron-deficient 3-chloro-5-(trifluoromethyl)phenyl triflate afforded the corresponding product in higher yield compared to the electron-rich 3-chloro-5-methylphenyl triflate and the electron-neutral 3-chlorophenyl triflate. These observations

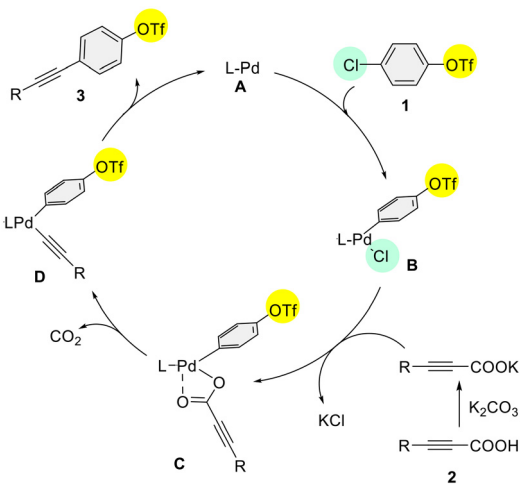
Table 2 Competitive experiment of different chloroaryl triflates[a]



Entry	Substrate 1	% yield[b]	Substrate 2	% yield[b]
1	$R^1 = CF_3$	32	R^2 = Me	18
2	$R^1 = CF_3$	31	R^2 = H	20

[a] Reaction condition: substrate 1 (0.1 mmol), substrate 2 (0.1 mmol), 3-phenylpropiolic acid **2a** (0.20 mmol), dichloro-(1-methylallyl)-dipalladium (2 mol%), **L9** (16 mol%), K_2CO_3 (0.40 mmol) and THF (1.0 mL) were stirred at 100 °C for 30 min. [b] Calibrated GC yields were reported using dodecane as the internal standard. Maximum yield for each substrate in the reaction mixture is 50%.

suggest that reductive elimination is unlikely to be the rate-limiting step. To further elucidate the reaction mechanism, a series of density functional theory (DFT) calculations were subsequently performed (see the ESI for details, Fig. S1†). The calculations involved monoligated Pd–**L9** reacting with 4-chlorophenyl triflate and 3-phenylpropiolic acid. For the reaction proceeding through the C–Cl pathway, consistent with the experimental kinetic studies, the computational results indicated that the reductive elimination step (**12K-TS**, 7.9 kcal mol^{-1}) was not rate-determining, given its notably lower activation barrier compared to the oxidative addition and decarboxylation steps. Critically, the oxidative addition step determines the chemoselectivity in this reaction. The higher activation barrier for oxidative addition of the C–OTf bond (**12N-TS**, 22.4 kcal mol^{-1}), compared to that of the C–Cl bond (**12D-TS**, 11.2 kcal mol^{-1}), strongly disfavors the C–OTf pathway. Indeed, the oxidative addition step for the C–OTf bond exhibits the highest overall energy barrier among all reaction path-



Scheme 6 Proposed mechanism.

ways examined, explaining the observed chemoselectivity towards activation of the C–Cl bond. Within the preferred C–Cl reaction pathway, the decarboxylation step (**12H-TS**, 21.3 kcal mol^{-1}) is proposed as the rate-determining step.

Based on the results discussed herein and supporting literature ref. 4*c*, a plausible mechanism for the chemoselective decarboxylative coupling reaction is proposed in Scheme 6. This mechanism initiates with the oxidative addition of chloroaryl triflate (**1**) to the Pd(0)L (**A**), forming intermediate **B**. This intermediate then undergoes a ligand-exchange reaction with the alkynyl carboxylic acid anion, produced by the reaction of alkynyl carboxylic acid (**2**) with K_2CO_3, yielding intermediate **C**. Subsequent decarboxylation of intermediate **C** releases CO_2, resulting in the formation of intermediate **D**. Finally, reductive elimination of intermediate **D** leads to the formation of the desired products (**3**), simultaneously regenerating the catalytically active species Pd(0)L, thus completing the catalytic cycle.

Conclusions

In summary, we have developed a palladium-catalyzed, chemoselective decarboxylative coupling of alkynyl carboxylic acids with halogenated aryl triflates, enabling the synthesis of OTf-arylalkyne scaffolds for the first time. Notably, this reaction inverts the conventional chemoselectivity order, favoring C–OTf over C–Cl. It also demonstrates remarkable C–Br selectivity over both C–OTf and C–Cl bonds when employing bromoaryl and bromochloroaryl triflates as substrates. Moreover, we introduce a one-pot sequential strategy that integrates decarboxylation with Suzuki–Miyaura coupling, offering a versatile platform for the efficient synthesis of difunctionalized compounds. DFT calculations suggest that chemoselectivity is governed by the oxidative addition step, while the decarboxylation step is rate-determining. We anticipate that this methodology will provide a new approach for the synthesis of alkynyl compounds bearing diverse functional groups, enabling selective modification of alkynyl scaffolds.

Data availability

All graphs and chemical structures in this article were created using ChemDraw 22. The data supporting this study have been included in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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