C–H Activation

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ortho-C–H Arylation of Benzoic Acids with Aryl Bromides and Chlorides Catalyzed by Ruthenium

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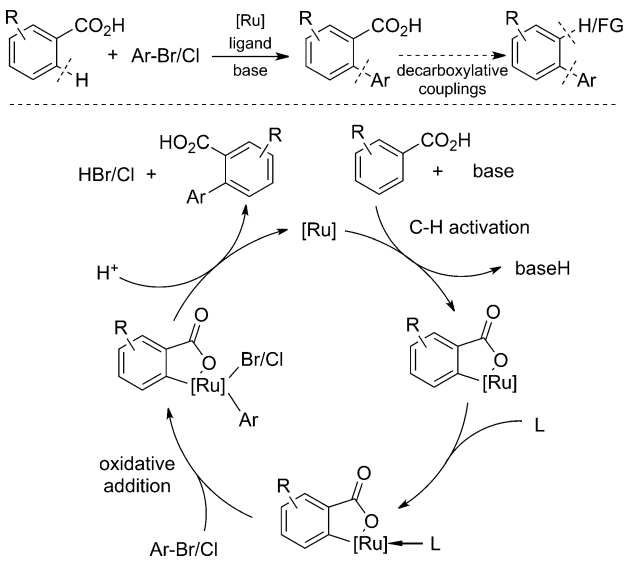
Abstract: *A system consisting of catalytic amounts of $[(p\text{-cym})RuCl_2]_2$/$PEt_3{\cdot}HBF_4$, K_2CO_3 as the base, and NMP as the solvent efficiently mediates the ortho-C–H arylation of benzoic acids with aryl bromides at 100°C. Replacing the phosphine ligand with the amino acid* DL*-pipecolinic acid enables the analogous transformation with aryl chlorides. The key advantage of this broadly applicable transformation is the use of an inexpensive ruthenium catalyst in combination with simple carboxylates as directing groups, which can either be tracelessly removed or used as anchor points for decarboxylative ipso substitutions.*

Biaryls are ubiquitous in pharmaceuticals, agrochemicals, and functional materials, and efficient methods to access these substructures are constantly sought after.[1] Traditionally, these structures are accessed by cross-coupling of preformed organometallic reagents with aryl halides[2] or by oxidative or reductive couplings of prefunctionalized substrates.[3]

The discovery of directing groups that efficiently control the regioselectivity of C–H arylations has recently revolutionized this field, enabling the regiospecific introduction of aryl groups in unfunctionalized positions.[4] However, this great conceptual advantage is often offset by the structural complexity of the required directing groups.[5] Their introduction and subsequent removal adds several steps to the overall synthetic process. Only recently, abundant functional groups with low coordinating ability, such as carboxylates, have successfully been used as directing groups for *ortho*-C–H arylations.[6] The key benefit of carboxylate groups is that they can be tracelessly removed by protodecarboxylation or utilized as leaving groups in a rapidly growing number of decarboxylative coupling reactions, with formation of C–C, C–O, C–N, C–S, C–P, and C–halogen bonds, for example.[7]

The development of transformations based on carboxylate directing groups is highly challenging. The low σ-donating ability of the carboxylate limits their ability to direct metal centers to one specific C–H bond and reduces the activity of the resulting metallacycle towards aryl electrophiles. *ortho* Arylations of benzoic acids were first reported by the groups of Daugulis,[8] Larrosa,[9] Su,[10] and Yu,[11] who employed expensive palladium catalysts.[12] With aryl iodides, these transformations proceeded smoothly even at room temperature.[10] The conversion of aryl bromides is possible only under rather harsh conditions, and the coupling of aryl chlorides has thus far required such high temperatures that selective monoarylation could not be achieved.[8] With arenediazonium salts as electrophiles, *ortho* arylation proceeds under mild conditions, but requires expensive iridium catalysts.[13] Oxidative arylations have been reported with expensive aryl boronic acids and a limited set of heteroarenes as arylating agents.[14]

Despite the remarkable progress achieved in this highly topical area, a broadly applicable carboxylate-directed C–H arylation that is based on readily available aryl bromides or chlorides and the use of a reasonably priced catalyst[15] has not yet been described. Ackermann and co-workers as well as our group have recently demonstrated that simple and affordable ruthenium catalysts efficiently promote regioselective hydroarylations of carboxylates.[16] We reasoned that the addition of electron-rich ligands might activate the intermediary ruthenacycle towards oxidative insertion into Ar–Br or Ar–Cl bonds by increasing its electron density, as outlined in Scheme 1. This hypothesis was supported by results of Dixneuf,[17] Larrosa,[18] Ackermann,[19] and others,[20] who demonstrated that ruthenium catalysts can activate aryl chlorides or bromides, and the observations by Daugulis,[8] Dixneuf,[21]



Scheme 1. Carboxylate-directed C–H arylation of arenes with aryl electrophiles assisted by electron-rich ligands.

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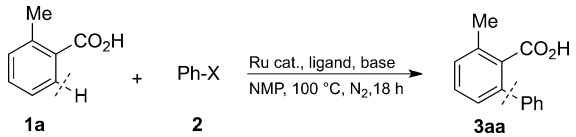
and Ackermann[22,19b] that such processes are facilitated by electron-rich phosphine and amino acid ligands.

To confirm our hypothesis, we chose the reaction of 2-methylbenzoic acid (**1a**) and bromobenzene (**2a**) as a model system and investigated various catalysts and conditions (Table 1). Encouragingly, traces of the desired product **3a** were detected when $[(p\text{-cym})RuCl_2]_2$ was used as

Table 1: Optimization of the *ortho* arylation reaction.[a]



1a **2** **3aa**

Entry	Catalyst	PhX	Base	Ligand	Yield[b] [%]
1	$[(p\text{-cym})RuCl_2]_2$	PhBr	$GuanCO_3$	–	trace
2	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	–	13
3	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	PPh_3	35
4	$[(C_6H_6)RuCl_2]_2$	PhBr	K_2CO_3	PPh_3	34
5	$[(C_6Me_6)RuCl_2]_2$	PhBr	K_2CO_3	PPh_3	0
6	$[(p\text{-cym})RuI_2]_2$	PhBr	K_2CO_3	PPh_3	35
7	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	$PPhCy_2$	59
8	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	PCy_3	76
9	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	P^iPr_3	80
10	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	$PMe_3{\cdot}HBF_4$	73
11	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	$PEt_3{\cdot}HBF_4$	90
12[c]	$[(p\text{-cym})RuCl_2]_2$	PhBr	K_2CO_3	$PEt_3{\cdot}HBF_4$	93 (**93**)
13[c]	$[(p\text{-cym})RuCl_2]_2$	PhCl	K_2CO_3	$PEt_3{\cdot}HBF_4$	12
14[d]	$[(p\text{-cym})RuCl_2]_2$	PhCl	K_2CO_3	$PEt_3{\cdot}HBF_4$	12/75[e]
15[d]	$[(p\text{-cym})RuCl_2]_2$	PhCl	K_2CO_3	L-proline	47
16[d]	$[(p\text{-cym})RuCl_2]_2$	PhCl	K_2CO_3	DL-pipecolinic acid	80 (**75**)

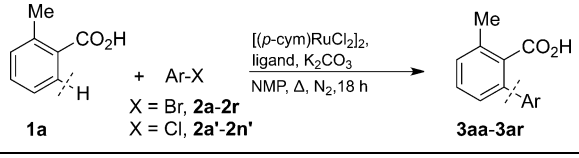
[a] Reaction conditions: **1a** (1 equiv), **2a** (4 equiv), [Ru] (4 mol%), ligand (8 mol%), base (1.1 equiv), NMP (3 mL), 100°C, 18 h, N_2 atmosphere. [b] Yields of the corresponding methyl esters determined by GC analysis after esterification with K_2CO_3 (2 equiv) and MeI (5 equiv) in NMP using *n*-tetradecane as the internal standard; yields of isolated products are given in parentheses. [c] PhX (1 equiv). [d] 120°C. [e] After 48 h. Cy = cyclohexyl, $GuanCO_3$ = guanidine carbonate, NMP = *N*-methylpyrrolidone, *p*-cym = *para*-cymene.

the catalyst in combination with guanidine carbonate at 120°C (entry 1), conditions that had been highly effective for our hydroarylation reaction.[16b] A major increase in yield was achieved upon switching to potassium carbonate as the base (entry 2). As anticipated, the yields improved substantially upon addition of a phosphine ligand (entry 3). Systematic variation of the ruthenium precursor confirmed that $[(p\text{-cym})RuCl_2]_2$ is the optimal precatalyst (entries 4–6). The nature of the ligand had a decisive influence on the reaction outcome. Among the ligands tested, electron-rich alkyl phosphines turned out to be superior. The best yields were achieved with triethylphosphine (entry 11), which can be conveniently administered in the form of its HBF_4 salt. After optimization of the reaction conditions (4 mol% $[(p\text{-cym})RuCl_2]_2$, 8 mol% $PEt_3{\cdot}HBF_4$, and 1.1 equiv K_2CO_3 in 3 mL NMP at 100°C), high yields were obtained even when using only one equivalent of the aryl bromide (entry 12). NMP is uniquely effective as the solvent (see the Supporting Information).

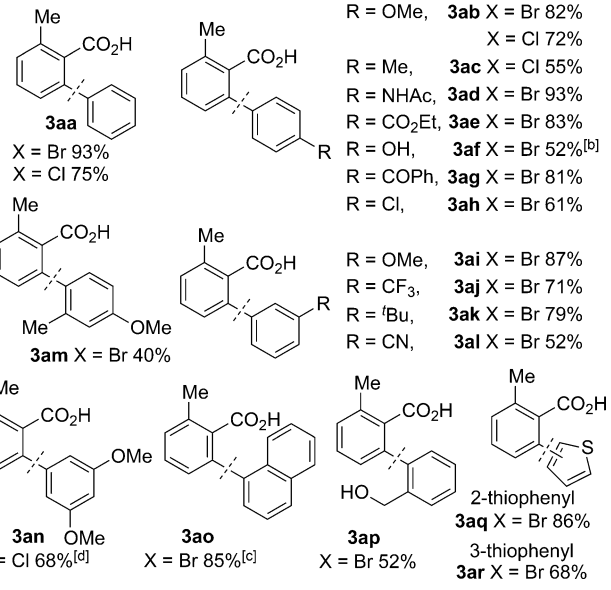
When chlorobenzene was used as the electrophile, only modest yields were observed under these conditions (entry 13), even upon increasing the temperature to 120°C (entry 14). Once again, the ligand turned out to be the decisive factor in the reaction development. Phosphine ligands were almost ineffective whereas amino acids strongly promoted the desired transformation (entry 15). After increasing the amount of aryl chloride, the monoarylated product **3a** was obtained in 80% yield. Although pipecolinic acid is a more efficient ligand than $PEt_3{\cdot}HBF_4$, the latter gave high yields when the reaction time was extended to 48 h, indicating that the reaction proceeds through a similar mechanism for aryl chlorides and bromides. Control experiments revealed that the optimal system for aryl chlorides is less effective for aryl bromides (33% yield, see the Supporting Information).

With effective methods in hand for the conversion of both aryl bromides and chlorides, we investigated the scope of the transformation. The model substrate 2-methylbenzoic acid (**1a**) was successfully coupled with various aryl bromides using method A (Table 2). Electron-rich and electron-poor substrates reacted similarly, and common functional groups, such as CF_3, CN, ester, halo, keto, alkyl, and methoxy moieties as well as unprotected phenolic and benzylic hydroxy groups,

Table 2: Substrate scope of the direct arylation with various aryl bromides and chlorides.[a]



1a **3aa-3ar**

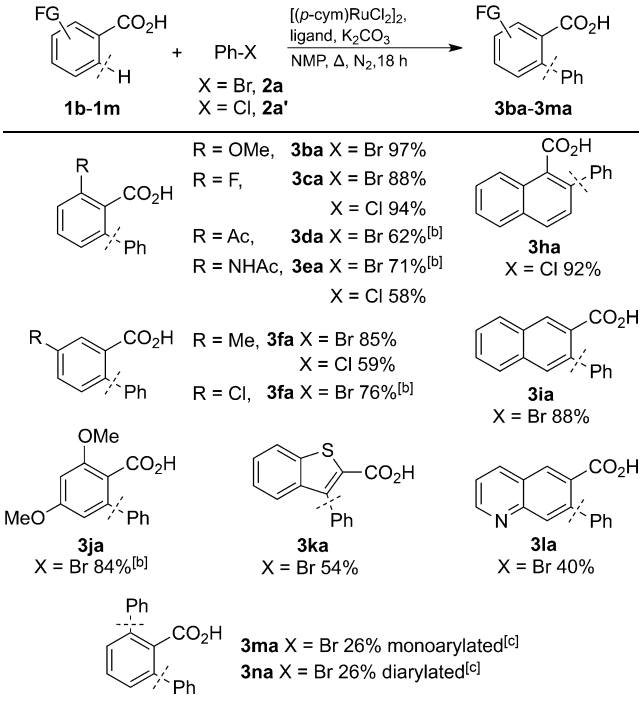


[a] Reaction conditions: Method A: **1a** (0.5 mmol), ArBr (0.5 mmol), $[(p\text{-cym})RuCl_2]_2$ (4 mol%), $PEt_3{\cdot}HBF_4$ (8 mol%), K_2CO_3 (1.1 equiv), NMP (3 mL), 100°C, 18 h, N_2 atmosphere. Method B: **1a** (0.5 mmol), ArCl (0.75 mmol), $[(p\text{-cym})RuCl_2]_2$ (4 mol%), DL-pipecolinic acid (8 mol%), K_2CO_3 (1.1 equiv), NMP (3 mL), 120°C, 18 h. Yields of the corresponding methyl esters after esterification with K_2CO_3 (2 equiv) and MeI (5 equiv) in NMP. [b] Isolated as the methyl ether. [c] ArBr (1.5 equiv). [d] Isolated as the free acid.

were tolerated in the *para* or *meta* position. *ortho* Substituents led to only moderate yields. It is noteworthy that under these conditions, aryl halides bearing functional groups that would be expected to be more efficient directing groups smoothly reacted with the *ortho* position of the carboxylates. This opens up welcome opportunities for polyfunctionalization. Products **3aa** and **3ab** demonstrate that comparable yields were achieved starting from aryl chlorides using method B (4 mol% $[(p\text{-cym})RuCl_2]_2$, 8 mol% DL-pipecolinic acid, 1.1 equiv K_2CO_3 in 3 mL NMP at 120 °C).

The scope with regard to the aromatic carboxylate was investigated with bromobenzene (**2a**) and chlorobenzene (**2a′**; Table 3). Benzoic acids bearing electron-donating or electron-withdrawing substituents, including methoxy, halo, and acyl groups, were smoothly coupled. Heterocyclic carboxylates were also successfully converted into the desired products. Unwanted double arylation could not be suppressed with unsubstituted or *para*-substituted benzoic acids. However, a substituent in the 3-position was sufficient to direct the arylation to the 6-position exclusively. This regioselectivity towards the less hindered *ortho* position was also observed with fused (hetero)aromatic quinoline 6-carboxylic acid (**1l**) and 2-naphthylcarboxylic acid (**1i**). A particularly remarkable example is the coupling of 2-acetamidobenzoic acid with **2a**. The new bond is selectively formed in the *ortho* position of the benzoic acid rather than in the *ortho* position of the amide

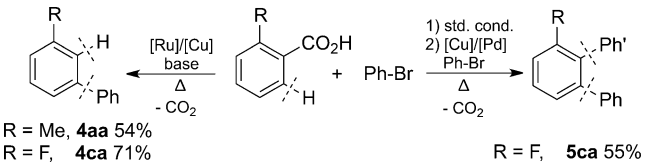
Table 3: Substrate scope of the direct arylation with various benzoic acids.[a]



[a] Reaction conditions: Method A: **1** (0.5 mmol), **2a** (0.75 mmol), $[(p\text{-cym})RuCl_2]_2$ (4 mol%), $PEt_3{\cdot}HBF_4$ (8 mol%), K_2CO_3 (1.1 equiv), NMP (3 mL), 100 °C, 18 h. Method B: **1** (0.5 mmol), **2a′** (0.75 mmol), $[(p\text{-cym})RuCl_2]_2$ (4 mol%), DL-pipecolinic acid (8 mol%), K_2CO_3 (1.1 equiv), NMP (3 mL), 120 °C, 18 h. Yields of the corresponding methyl esters after esterification with K_2CO_3 (2 equiv) and MeI (5 equiv) in NMP. [b] ArBr (1 equiv). [c] Yield determined by GC analysis.

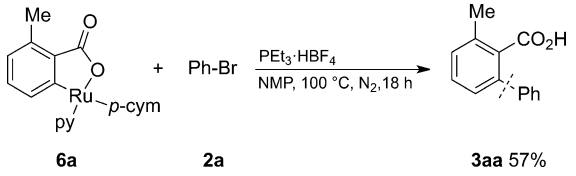
despite the C–H directing ability of the latter, which by far exceeds that of carboxylic acids in related C–H functionalizations. Four additional examples demonstrate that method B permits the coupling of aryl chlorides in comparable yields.

We next probed whether the biaryl synthesis could also be combined with concomitant protodecarboxylation.[23] The examples in Scheme 2 demonstrate that this process does not even require an additional reaction step. By simply adding a copper catalyst to the reaction medium and increasing the temperature to 190 °C, the corresponding biaryl products **4** were formed in good yields. The *ortho* arylation can also be combined with decarboxylative cross-couplings,[24] as demonstrated by the synthesis of terphenyl **5ca** in 55% non-optimized yield.



Scheme 2. *ortho* Arylations followed by decarboxylative reactions.

To shed light on the mechanism proposed in Scheme 1, we synthesized *ortho*-ruthenated toluate **6a**. The stoichiometric reaction of **6a** and $PEt_3{\cdot}HBF_4$ with bromobenzene (**2a**) yielded **3aa** in 57% yield (Scheme 3), which supports the intermediacy of an *ortho*-metalated species in the catalytic cycle. In the presence of only pyridine as the ligand, no product formation was observed, which confirmed the necessity for a suitable ligand (see the Supporting Information). In-depth mechanistic studies are underway to fully clarify the reaction pathway.



Scheme 3. Stoichiometric reaction of the *ortho*-ruthenated toluate **6a**.

In conclusion, we have shown that cost-effective ruthenium complexes are at least as effective and broadly applicable as state-of-the-art palladium systems for catalyzing the synthetically useful *ortho* arylation of benzoic acids. In combination with subsequent decarboxylative *ipso* substitutions, they promise to open up new perspectives for sustainable, regioselective arene (di)functionalization.

Experimental Section

An oven-dried 20 mL vessel was charged with $[Ru(p\text{-cym})Cl_2]_2$ (12.2 mg, 0.02 mmol, 4 mol%), triethylphosphonium tetrafluoroborate (8.3 mg, 0.04 mmol, 8 mol%, method A) or DL-pipecolinic acid (5.2 mg, 0.04 mmol, 8 mol%, method B), K_2CO_3 (76 mg, 0.55 mmol, 1.1 equiv), and benzoic acid **1** (0.50 mmol). After the vessel had been subjected to three alternating vacuum and nitrogen purge cycles, NMP (3 mL) and the aryl halide **2** (0.50 mmol, method A; 0.75 mmol, method B) were added via syringe. The resulting mixture was stirred at 100 °C for 18 h. After the reaction was complete, the mixture was

allowed to cool to room temperature. NMP (2 mL), K_2CO_3 (207 mg, 3 equiv), and MeI (156 μL, 5 equiv) were added, and the mixture was stirred at 60 °C for 2 h. The mixture was allowed to cool to room temperature, ethyl acetate (20 mL) was added, and the resulting mixture was washed with water, aqueous LiCl solution (20 %), and brine (20 mL each). The organic layer was dried over $MgSO_4$, filtered, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, ethyl acetate/hexane gradient), yielding the corresponding biaryl.

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Keywords: aryl halides · benzoic acids · biaryls · C–H arylation · ruthenium

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