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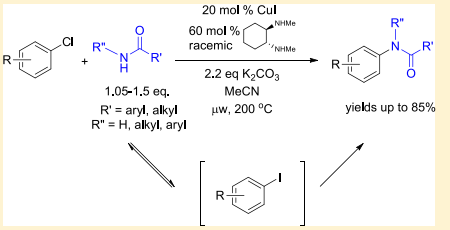
Amidation of Aryl Chlorides Using a Microwave-Assisted, Copper-Catalyzed Concurrent Tandem Catalytic Methodology

Raymond K. Chang, Brice P. Clairmont, Shirley Lin,* and Amy H. Roy MacArthur*

Department of Chemistry, United States Naval Academy, 572 Holloway Road, Annapolis, Maryland 21402, United States

Supporting Information

ABSTRACT: A concurrent tandem catalytic (CTC) methodology has been developed for the amidation of aryl chlorides where the aryl chloride is first converted to an aryl iodide via halogen exchange and the aryl iodide is subsequently transformed into the aryl amide. A variety of aryl chlorides were converted to aryl amides in up to 85% isolated yield using 20 mol % CuI, 60 mol % *N*,*N*′-cyclohexane-1,2-diamine, 2.2 equiv of K_2CO_3, and 1.05−1.5 equiv of amide in acetonitrile at 200 °C after 0.75−1 h. The same copper/ligand system served as multifunctional catalyst for both steps of the concurrent catalytic process with iodide present in substoichiometric amounts. Mechanistic studies were consistent with CTC amidation occurring via a nonradical mechanism. Kinetic modeling was conducted to investigate the effect of competitive direct amidation of an aryl chloride or aryl bromide on the formation of product over time during a CTC amidation reaction.

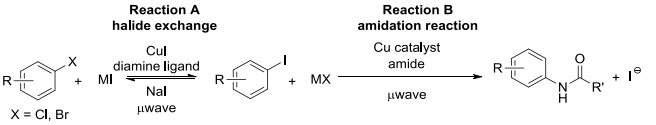


INTRODUCTION

The prevalence of aryl−N bonds in important biomolecules, pharmaceuticals, and polymers has rendered the catalytic amidation of aryl halides an extremely attractive synthetic methodology.[1] Initial development of such transformations using copper were first reported by Ullmann and Goldberg.[2,3] However, these reactions often required long reaction times, high temperatures, and, in some examples, the presence of copper in stoichiometric amounts. The development of nickel[4,5] and palladium[6−19] catalysts has led to the cross-coupling of aryl halides and amides under milder conditions. In addition to these methodologies, Buchwald[20,21] has developed effective copper-catalyzed amidations of aryl iodides and bromides using simple 1,2-diamines as ligands. In this case the copper-catalyzed amidation of less reactive aryl chlorides has proved to be challenging. Buchwald reported a more successful amidation of four aryl chloride substrates in the presence of 5 mol % CuI, 11 mol % *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine, and 2 equiv of K_2CO_3 in neat aryl chloride for 23 h at 110−130 °C to produce the corresponding aryl amides in 51−95% yield.[21] Functionalized substrates did not tolerate the reaction conditions particularly well and resulted in the lower yields of the range reported above.

Our research group has recently been engaged in developing a strategy for improving metal-catalyzed cross-couplings of aryl chlorides. The methodology employs concurrent tandem catalysis (CTC) (Scheme 1) to transform a relatively unreactive aryl chloride into a more reactive aryl iodide (Reaction A) that can subsequently undergo a variety of coupling reactions (Reaction B). In our previous work, we reported CTC hydrodehalogenation[22] and CTC cyanation.[23] To accompany these C−H and C−C bond forming reactions, we present in this study an example of C−N bond formation with the CTC amidation of aryl chlorides. This report complements the examples of the intramolecular amidation of aryl chlorides found in the syntheses of alkaloids employed by Koutentis[24,25] and the work of Ma on the Cu_2O-catalyzed coupling of heteroaryl chlorides with amides.[26]

Scheme 1. CTC Methodology for the Amidation of Aryl Chlorides



RESULTS AND DISCUSSION

Optimizing Reaction Conditions. Reaction conditions were screened to optimize the microwave-assisted CTC amidation method using 4-chlorotoluene and either benzamide (**A1**), a primary amide, or 2-pyrrolidinone (**A2**), a secondary amide, as the coupling partners. The initial conditions examined were predicated upon both Buchwald's reported conditions for CTC amidation of aryl bromides and aryl chlorides[20,21] (vide supra) and our experiences with CTC hydrodehalogenation of aryl chlorides and aryl bromides[22] and the CTC cyanation of aryl chlorides.[23] In both of these CTC methodologies, a multifunctional copper/diamine species served as the catalyst for both catalytic cycles. The thorough mechanistic studies performed by Buchwald[27,28] and Hartwig[29] on copper-catalyzed amidation of aryl iodides identify a

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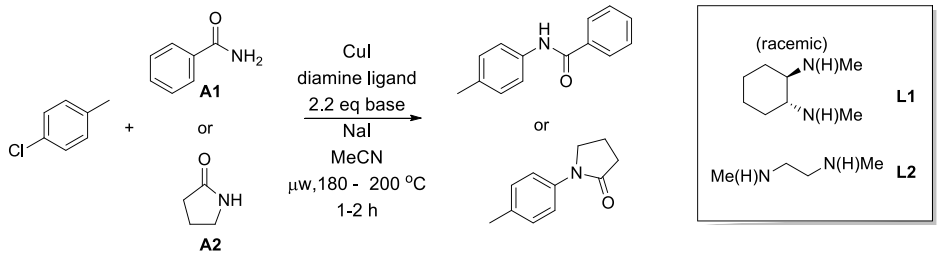
Table 1. Screening Conditions for Amidation of 4-Chlorotoluene with Primary and Secondary Amides



entry	mol % CuI	ligand	mol % ligand	amide (equiv)	time (h)	base (2.2 equiv)	equiv NaI	T (°C)	% yield Ar amide[a]
1	20	**L1**	60	**A1** (1.05)	1	K_2CO_3	0	200	92
2	20	**L1**	60	**A1** (1.05)	2	K_2CO_3	0	200	95
3	20	**L1**	60	**A1** (2.0)	1	K_2CO_3	0	200	90
4	20	**L1**	40	**A1** (1.1)	1	K_2CO_3	0	200	90
5	20	**L1**	80	**A1** (1.05)	1	K_2CO_3	0	200	94
6	10	**L1**	20	**A1** (1.05)	1	K_2CO_3	0	200	63
7	10	**L1**	60	**A1** (1.05)	1	K_2CO_3	0	200	77
8	20	**L1**	60	**A1** (1.05)	1	K_2CO_3	0	180	86
9	20	**L2**	60	**A1** (1.05)	1	K_2CO_3	0	200	50
10	20	**L1**	60	**A1** (1.05)	1	K_3PO_4	0	200	3
11	20	**L1**	40	**A1** (1.1)	1	K_2CO_3	0.5	200	65
12	20	**L1**	60	**A2** (1.5)	1	K_2CO_3	0	200	87
13	20	**L1**	60	**A2** (1.2)	1	K_2CO_3	0	200	81
14	20	**L1**	60	**A2** (2.0)	1	K_2CO_3	0	200	82
15	20	**L1**	60	**A2** (1.2)	1	K_3PO_4[b]	0	200	0
16	0	**L1**	60	**A1** (1.05)	1	K_2CO_3	0	200	<1
17	20[c]	**L1**	60	**A1** (1.05)	1	K_2CO_3	0	200	6
18	20[c]	**L1**	60	**A1** (1.05)	1	K_2CO_3	0.2	200	21

[a]Uncorrected GC yield. [b]Using 2.0 equiv of base. [c]CuCl instead of CuI.

neutral, monodiamine, Cu(I)-amidate complex as the active catalyst. According to Buchwald's work, this species is in equilibrium with two inactive species, an anionic diamide species that was observed at low concentrations of diamine and a neutral diamine−Cu(I)−X compound (X = I^- or PO_4^{3-}, the latter derived from the base in the reaction) at high concentrations of diamine. Therefore, we anticipated that the yield of desired aryl amide product would be sensitive to small changes in the amount of ligand and base used.

The optimized reaction conditions as determined by GC analysis employed 20 mol % CuI, 60 mol % *N*,*N*′-dimethylcyclohexane-1,2-diamine (ligand **L1**), 1.05 equiv of benzamide **A1**, and 2.2 equiv of K_2CO_3 in acetonitrile at 200 °C for 1 h, resulting in a yield of 92% of the desired product, *N*-(4-methylphenyl)-benzamide (Table 1, entry 1). Similar yields of aryl amide were obtained when the reaction time was increased to 2 h (Table 1, entry 2), when the amount of benzamide was increased to 2.0 equiv (Table 1, entry 3), or when the amount of ligand **L1** was decreased to 40 mol % or increased to 80 mol % (Table 1, entries 4 and 5, respectively). Given our observations that ligand **L1** sometimes reacted with aryl chloride substrates to give the aryl amination product, 60 mol % ligand was considered to be optimal.

Lower yields of product were observed in the presence of only 10 mol % CuI with 30 or 60 mol % of **L1** (Table 1, entries 6−7) or when the reaction temperature was decreased from 200 to 180 °C (Table 1, entry 8). Substituting *N*,*N*′-dimethylethylenediamine **L2** as the ligand (Table 1, entry 9) substantially decreased the yield. Replacing K_2CO_3 with K_3PO_4 (Table 1, entry 10) resulted in the formation of product in only 3% yield. Addition of 0.5 eq. of NaI (Table 1, entry 11) also decreased the yield of aryl amide due to competing formation of the hydrodehalogenation product, toluene.

The optimized reaction conditions for the coupling between 4-chlorotoluene and 2-pyrrolidinone (**A2**), a secondary amide, were identical to the optimized conditions for the primary amide **A1** with the exception of the equivalents of amide required. A slightly higher yield of 1-(4-methylphenyl)-2-pyrrolidinone was observed in the presence of 1.5 equiv of **A2** (Table 1, entry 12) than when 1.2 or 2.0 equiv were employed (Table 1, entries 13−14, respectively). Substituting K_3PO_4 for K_2CO_3 resulted in no product formation (Table 1, entry 15).

Table 1, entries 16−18 show the results of experiments conducted to further elucidate the role of the metal in the reaction. As expected, removal of CuI from the reaction (Table 1, entry 16) resulted in only trace amounts of aryl amide being formed. Substitution of CuCl for CuI produced only 6% yield of the product (Table 1, entry 17) with the remainder of the crude reaction mixture consisting of unreacted aryl chloride and a small amount of toluene derived from hydrodehalogenation. The addition of 20 mol % iodide (with respect to substrate), in the form of NaI, to the CuCl-catalyzed reaction (Table 1, entry 18) increased the yield of aryl amide to 21%. Further mechanistic implications of these results are discussed later in this article (vide infra).

Substrate Scope. The optimized reaction conditions in Table 1, entries 1 (for primary amides) and 12 (for secondary amides), were applied to a variety of aryl chloride substrates and amides (Table 2 and Table 3) to establish the substrate scope of CTC amidation. Aryl amides were synthesized in isolated yields up to 85% from the coupling of benzamide with substituted chlorobenzenes containing various substituents,

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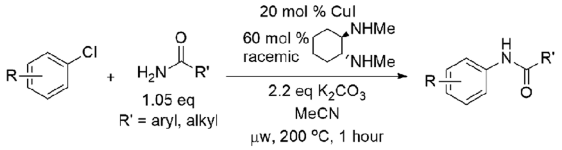
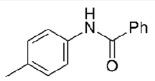
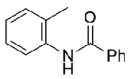
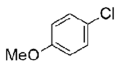
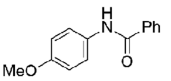
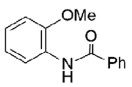
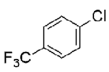
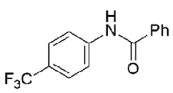
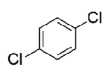
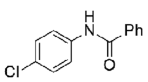
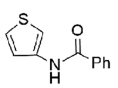
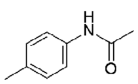
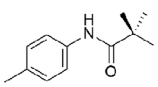
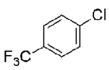
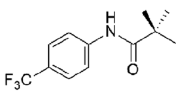
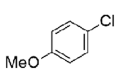
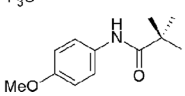
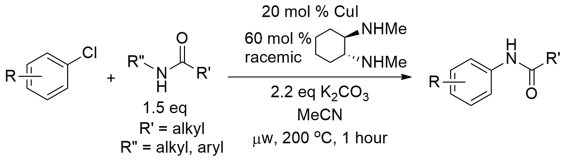
Table 2. Results of Substrate Scope Study of Microwave-Assisted Copper-Catalyzed Amidation of Aryl Chlorides with Primary Amides To Form Aryl Amides via Concurrent Tandem Catalysis

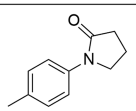
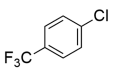


Entry	ArCl	amide	Ar amide	Yield, %[a]
1				85
2				38[b]
3				83
4				50 (72[b])[c]
5				62
6				4[b]
7				75
8				75
9				77
10				74[d]
11				79

[a]Isolated yields (average of two runs). [b]Uncorrected GC yield, average of 2 runs. [c]Difference between GC and isolated yield was due to difficulties isolating the product, a volatile oil. [d]Reaction time = 0.75 h.

Table 3. Results of Substrate Scope Study of Microwave-Assisted Copper-Catalyzed Amidation fo Aryl Chlorides with Secondary Amides to Form Aryl Amides via Concurrent Tandem Catalysis



Entry	ArCl	amide	Ar amide	Yield, %[a]
1				83
2				77
3				75
4				40
5				trace
6				48[b]

[a]Isolated yields (average of two runs). [b]Uncorrected GC yield, average of 2 runs.

including $-CH_3$, $-CF_3$, and $-OCH_3$, and with one heteroaromatic ring, 3-chlorothiophene (Table 2, entries 1–7); lower yields were observed with 1,4-dichlorobenzene as substrate (Table 2, entry 6) due to increased formation of chlorobenzene through hydrodehalogenation, a reaction previous studied by our research group.[22] A reduced yield of product was also observed when there was steric hindrance near the C–Cl bond of the substrate (Table 2, entries 2 and 4), a result previously seen with CTC cyanation.[23]

Good yields of aryl amide (74–79%) were also obtained with two other primary amides, acetamide (Table 2, entry 8) and 2,2-dimethylpropanamide (Table 2, entries 9–11). Only one example of coupling between an aryl chloride and acetamide is presented (Table 2, entry 8); in contrast to benzamide and 2,2-dimethylpropanamide, reactions involving acetamide were prone to the formation of side-products arising from deacetylation of the aryl amide. The GC-MS chromatogram of the crude reaction mixture also revealed the presence of the compound that would result from the deacetylation product undergoing an amination reaction with another equivalent of the aryl chloride substrate.

CTC amidation between various 4-substituted aryl chlorides and a secondary amide, 2-pyrrolidinone, occurred with yields similar to those observed for primary amides (Table 3, entries 1–3). A lower yield of product, 40%, was observed in the coupling reaction starting with 4-chlorobenzylalcohol and 2-pyrrolidinone (Table 3, entry 4). With 1,4-dichlorobenzene as substrate (Table 3, entry 5), only trace amounts of the desired coupling product was observed, along with similar amounts of side-products from hydrodehalogenation, chlorobenzene and benzene, and 1,1′-(1,4-phenylene)bis-2-pyrrolidinone, the result of C–N coupling at both C–Cl bonds. Attempts to perform CTC amidation with acyclic secondary amides, including *N*-methylformamide, *N*-methylbenzamide, and *N*-phenylacetamide (acetanilide) resulted in small to moderate amounts of desired aryl amide product being formed along with numerous side-products derived from loss of methyl or phenyl from the amide. For example, the reaction between 4-

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chlorotoluene and acetanilide resulted in 48% yield of the corresponding aryl amide (Table 3, entry 6). Careful analysis of the GC-MS chromatogram of the crude product mixtures resulting from these reactions revealed the presence of a compound with m/z = 232, consistent with the species *N*-(4-methylphenyl)-*N*,*N*′-dimethylcyclohexane-1,2-diamine, the product of an amination reaction between the aryl chloride substrate and diamine ligand **L1**. Formation of this compound likely indicates that the increased steric crowding around the nitrogen of the acyclic secondary amide decreased the rate of amidation enough that amination of the ligand became competitive.

Mechanistic Studies. Further investigation of the amidation reactions shown in Tables 1, 2 and 3 yielded results consistent with the proposed CTC mechanism in Scheme 1. The relevant studies were conducted using 4-chlorotoluene and benzamide as representative reactants. The importance of iodide in the coupling reaction was demonstrated by replacing the iodide source, 20 mol % CuI, with 20 mol % CuCl, resulting in a decrease in GC yield of aryl amide from 92 to 6% (Table 1, entries 1 and 17, respectively). Interestingly, adding 20 mol % iodide in the form of NaI to the reaction with CuCl (Table 1, entry 18) increased the yield only slightly to 21%, suggesting that formation of a Cu−I species is important to the reaction and was not achieved under these conditions.

As with CTC hydrodehalogenation[22] and CTC cyanation,[23] the progress of the reaction over time was also monitored; the results are shown in Figure 1. At early reaction times (10 min),

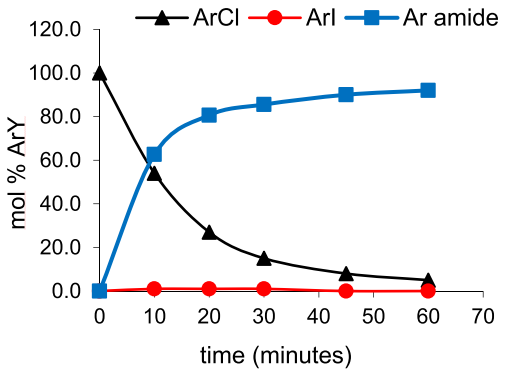
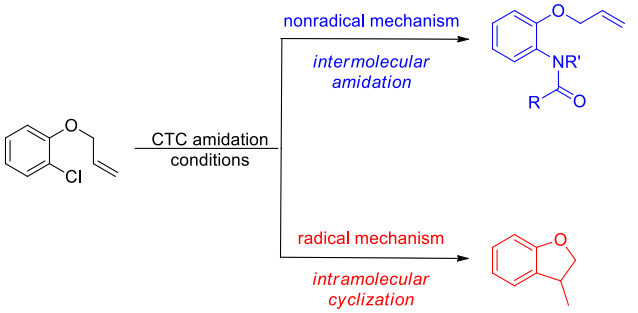


Figure 1. Copper-catalyzed amidation of 4-chlorotoluene, performed using 20 mol % CuI, 60 mol % diamine ligand **L1**, 2.2 equiv of K_2CO_3, and 1.05 equiv of benzamide (**A1**) at 200 °C in acetonitrile. Yields of ArCl, ArI, and Ar amide (ArY) were determined by GC.

only a trace amount of 4-iodotoluene was observed, similar to CTC cyanation. In contrast, approximately 40 mol % aryl iodide was formed at short reaction times during CTC hydrodehalogenation which utilized 1.5 equiv of NaI. Kinetic modeling demonstrated that when the rate of halogen exchange is 2 orders of magnitude slower than the subsequent coupling reaction of the intermediate aryl iodide only small amounts of aryl iodide will be observed in the reaction mixture.[23] Similar to CTC cyanation, CTC amidation occurs in the presence of only 0.2 equiv of iodide, which is expected to result in slow halogen exchange relative to the rate of coupling of the aryl iodide.

In addition to addressing the viability of a CTC mechanism for this transformation, studies were conducted to determine whether the amidation reaction was taking place via radical or nonradical pathways. Following the elegant design of experiments by Hartwig and co-workers,[29] 1-allyloxy-2-chlorobenzene was subjected to CTC amidation conditions in the presence of 2-pyrrolidinone. As shown in Scheme 2, formation

Scheme 2. Comparison of Products Formed from Radical and Nonradical Mechanisms in the Amidation of 1-Allyloxy-2-chlorobenzene



of a radical at the carbon bonded to chlorine would be expected to result in rapid intramolecular cyclization to yield 2,3-dihydro-2-methylbenzofuran rather than the amidation coupling product.

The results of this experiment are shown in Figure 2. The reaction time was limited to 15 min to mitigate the formation

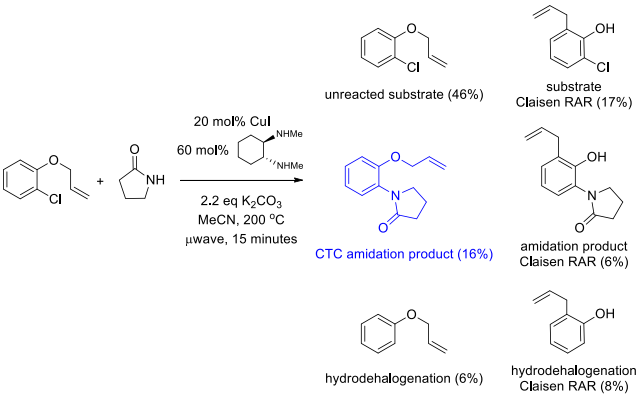


Figure 2. Products formed in CTC amidation of 1-allyloxy-2-chlorobenzene.

of multiple side products at such a high reaction temperature (200 °C). Nevertheless, a complex reaction mixture was observed by GC-MS. The major species observed were unreacted aryl chloride (46%) and 2-allyl-6-chlorophenol (17%), the Claisen rearrangement product derived from the aryl chloride; Claisen rearrangement of allyloxybenzenes under microwave heating has been reported.[30,31] We also observed the expected CTC coupling product, 1-[2-(2-propen-1-yloxy)-phenyl]-2-pyrrolidinone, in 16% yield, along with its Claisen rearrangement product (6%). The remaining identifiable species in the reaction were 1-allyloxybenzene (6%), the hydrodehalogenation product of the aryl chloride, and its Claisen rearrangement product. Significantly, 2,3-dihydro-2-methylbenzofuran, the compound expected if a carbon radical were formed during the course of the reaction, was not observed, consistent with CTC amidation occurring via a nonradical mechanism.

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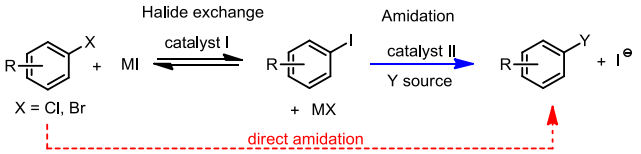
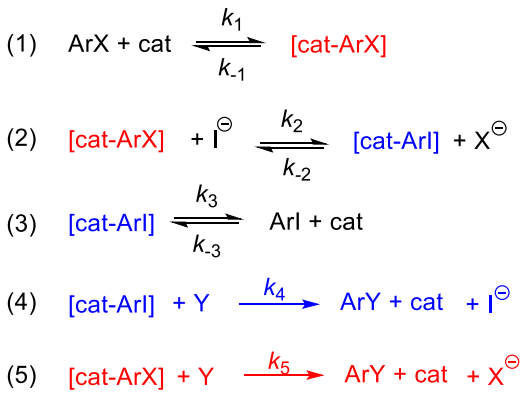
Kinetic Modeling. Although we were able to develop reaction conditions for CTC amidation of aryl chlorides, our attempts to do the same for aryl bromides were unsuccessful. Initially we were encouraged when reaction of 4-bromotoluene and benzamide in the presence of 20 mol % CuI, 40 mol % *N*,*N*′-dimethylcyclohexane-1,2-diamine, and 2 equiv of K_3PO_4 in 1,4-dioxane at 80 °C for 1 h produced *N*-(4-methylphenyl)-benzamide in 84% yield according to GC-MS. However, the reaction also proceeded in the presence of 20 mol % CuBr to form 68% yield of product, suggesting that halide exchange (left reaction, Scheme 3) is unnecessary for amidation to occur and that direct amidation of the substrate (red arrow, Scheme 3) is competitive with halide exchange.

Scheme 3. CTC versus Direct Amidation Pathways



To investigate this hypothesis, the kinetic model shown in Scheme 4 was constructed in GEPASI.[32] The first 3 steps

Scheme 4. Five-Step Kinetic Model To Investigate the Effect of Competitive Direct Amidation of ArX on CTC Amidation Yield



create aryl iodide from ArX (X = Cl and Br). Step 4 achieves the formation of aryl amide from aryl iodide while step 5 is the direct reaction between ArCl or ArBr and amide Y. During the kinetic simulation, "observed" rate constants[33] k_1, k_{-1}, k_2, k_3, and k_{-3} were set equal to 1.0 M/s, k_{-2} was equal to 0.10 M/s, k_4 was 10 M/s, and k_5 was allowed to vary from 0.01 to 1.0 M/s. The yield of product formed over time was compared between reactions where 0.2 equiv of iodide was present and CTC amidation could occur versus situations where the concentration of iodide was zero, ensuring that product could only be formed through direct amidation of aryl chloride or aryl bromide.

The two key results from the kinetic modeling are shown in Figure 3. As revealed in Figure 3a, when the rate constant for amidation of the intermediate aryl iodide, k_4 = 10 M/s, is 1000 times larger than the rate constant for direct amidation of ArX (k_5 = 0.01 M/s), CTC conditions allow for more product to be formed in a given period of time in the presence of 0.2 equiv of iodide (blue curve) than in the absence of iodide (red curve),

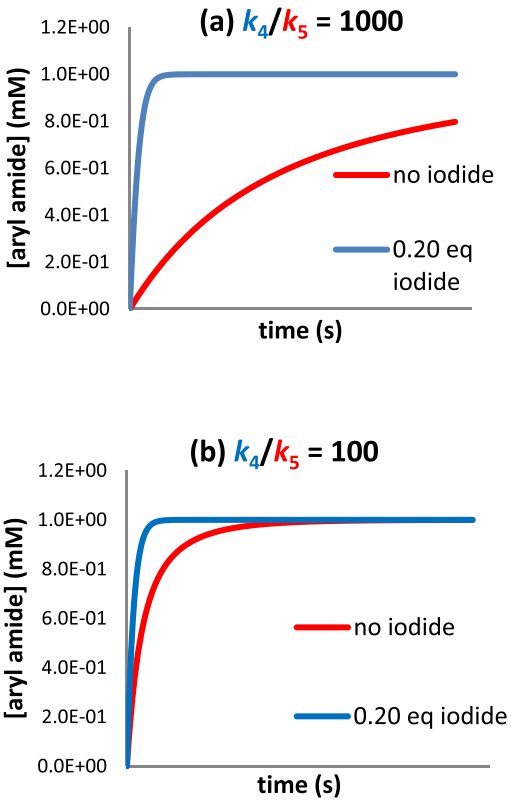


Figure 3. Formation of aryl amide product in the absence of iodide versus in the presence of 0.20 equiv of iodide over time using the kinetic model in Scheme 4. (a) The rate constant of step 4 (k_4 = 10 M/s), the amidation of aryl iodide, is 1000 times larger than the rate constant of step 5 (k_5 = 0.01 M/s), the direct amidation of aryl chloride. (b) The rate constant of step 4 (k_4 = 10 M/s) is 100 times larger than the rate constant of step 5 (k_5 = 0.1 M/s).

particularly at short reaction times. In contrast, Figure 3b shows that when the ratio of k_4/k_5 = 100, the amount of aryl amide that is produced is similar regardless of the presence or absence of iodide, negating the advantage of a CTC methodology. These results are consistent with the observation that for many transition-metal-catalyzed cross-coupling reactions, the order of reactivity of aryl halides is ArCl < ArBr < ArI.[34,35] Therefore a CTC methodology is most likely to improve the yield of products derived from aryl chlorides more than aryl bromides.

In conclusion, a concurrent tandem methodology for the amidation of aryl chlorides has been developed, expanding the repertoire of CTC methodologies studied by our group to include C−N bond formation reactions. Aryl amides were formed and isolated in good to excellent yields in the presence of a variety of functional groups; lower yields of product were observed when there was steric crowding near the site of C−Cl bond cleavage. The reaction behaved in a manner consistent with a nonradical mechanism where the formation of an intermediate aryl iodide is expected to be advantageous in increasing the yield of aryl amide product, particularly at short reaction times. Further opportunities exist to expand CTC methodologies to include other important cross-coupling reactions such as trifluoromethylation, amination, and etherification. We hope to report on such studies in the near future.

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EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard nitrogen drybox techniques. Anhydrous acetonitrile, copper(I) iodide, copper(I) chloride, potassium phosphate, most aryl chlorides (except 1,4-dichlorobenzene from TCI), most amides (except trimethylacetamide from Aldrich), and *n*-decane were purchased from Acros and used as received. *trans-N,N′*-Dimethylcyclohexane-1,2-diamine was purchased from Acros and Aldrich and was used as received. Potassium carbonate was purchased from Aldrich and oven-dried before use. Microwave reactions were performed in a CEM Discover SP microwave reactor with IR temperature monitoring and Activent technology to prevent unsafe overpressurization of the reaction tube. GC-MS analysis was performed on a Shimadzu GCMS-QP5050A with a Restek Rxi-5 ms capillary column (30 m, 0.25 mm ID, 0.25 μm film thickness, 5% diphenyl/95% dimethylpolysiloxane). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-400 spectrometer and were referenced to residual protio solvent peaks. Melting points were measured on an Electrothermal Mel-temp device.

General Procedure for the Cu-Catalyzed Amidation of Aryl Chlorides. In a nitrogen-filled glovebox, copper(I) iodide (38 mg, 0.20 mmol, 20 mol %), *trans-N,N′*-dimethylcyclohexane-1,2-diamine (85 mg, 0.60 mmol, 60 mol %), amide (1.05 mmol), potassium carbonate (304 mg, 2.2 mmol), and aryl chloride (1.00 mmol) were weighed into an oven-dried microwave tube containing a small stir bar. Acetonitrile (0.5 mL) was added by syringe and the sample was stirred for approximately 10 s. The initial reaction mixture appeared to be a transparent, colorless or pale yellow liquid over a white, granular solid. The tube was then capped and removed from the nitrogen glovebox and immediately placed in a CEM Discover microwave reactor for 60 min at 200 °C and 150 W (with power adjustments to maintain temperature) following a 2−3 min ramp time. After cooling, the reaction mixture contained a dark brown liquid over a solid, but the color of the solid was difficult to determine due to the dark color of the liquid. The reaction was quenched with 2 mL of 30% aqueous ammonia solution and transferred to a separatory funnel, and the product was extracted with 3 × 20 mL of ethyl acetate. The product was then washed with 2 × 20 mL of distilled water and dried over magnesium sulfate. The organic solvent was evaporated under vacuum and the resulting product was purified by column chromatography on silica. The reaction conditions and average yields for each reaction are shown in Table 2 and Table 3.

General Procedure for the Cu-Catalyzed Amidation of 4-Bromotoluene. In a nitrogen-filled glovebox, either copper(I) iodide (38 mg, 0.20 mmol, 20 mol %) or copper(I) bromide (30 mg, 0.21 mmol, 20 mol %) was mixed with *trans-N,N′*-dimethylcyclohexane-1,2-diamine (57 mg, 0.40 mmol, 40 mol %), benzamide (126 mg, 1.04 mmol), potassium phosphate (423 mg, 1.99 mmol), and 4-bromotoluene (171 mg, 1.00 mmol) in an oven-dried microwave tube containing a small stir bar. Solvent (1,4-dioxane, 0.5 mL) was added by syringe. The tube was then capped and removed from the nitrogen glovebox and immediately placed in a CEM Discover microwave reactor for 60 min at 80 °C and 50 W (with power adjustments to maintain temperature) following a 1 min ramp time. After cooling, an equimolar amount (versus ArCl) of *n*-decane (141.7 mg, 0.996 mmol) was added. The reaction was quenched with 2 mL of 30% aqueous ammonia solution, and the product was extracted with 2 mL of ethyl acetate. The solids in the mixture were dispersed using the pre-existing stir bar and a stir plate. Then, 10 μL of the top (organic) layer was taken from the sample and placed in a small vial containing 2 mL of ethyl acetate. This sample was then analyzed by GC-MS.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00561.

Experimental data (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: lin@usna.edu (S.L.).
*E-mail: macarthu@usna.edu (A.H.R.M.).

ORCID

Shirley Lin: 0000-0001-8085-5006
Amy H. Roy MacArthur: 0000-0002-5828-4208

Notes

The authors declare no competing financial interest.

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