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Carboxylation of Aromatic and Aliphatic Bromides and Triflates with CO_2 by Dual Visible Light - Nickel Catalysis

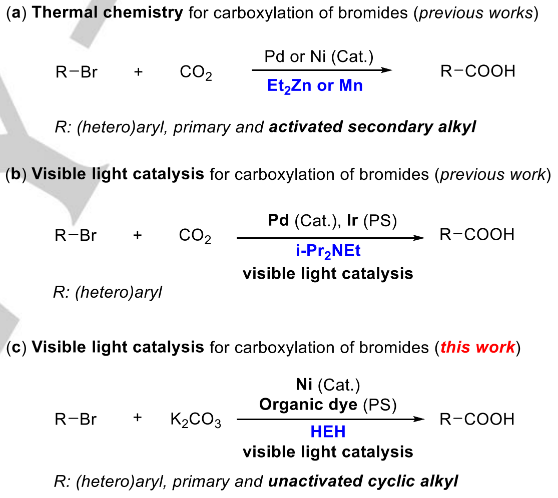
Qing-Yuan Meng, Shun Wang, and Burkhard König*

Dedicated to Prof. Chen-Ho Tung on the occasion of his 80th birthday

Abstract: We report the efficient carboxylation of bromides and triflates with K_2CO_3 as the source of CO_2 using an organic photocatalyst in combination with a nickel complex under visible light irradiation at room temperature. The reaction is compatible with a variety of functional groups and has been successfully applied to the synthesis and derivatization of biologically active molecules. Particularly, the carboxylation of unactivated cyclic alkyl bromides proceeds well under our protocol extending the scope of this transformation. Spectroscopic and spectroelectrochemical investigations indicate the generation of a Ni(0) species as catalytic reactive intermediate.

Carbon dioxide (CO_2), due to its abundance, low cost and nontoxicity, has been regarded as an ideal and green one-carbon (C1) building block for organic synthesis.[1] As one of the most important conversions of CO_2, carboxylation of carbon nucleophiles provides a straightforward approach for accessing carboxylic acid functional groups,[2] some of which have been proved to be necessary to maintain their biological properties.[3] Among these nucleophiles, organic (pseudo)halides have been employed widely as coupling partners, thus avoiding the application of traditionally used organometallic chemicals based on organolithium or Grignard reagents. Martín and Correa developed the catalytic carboxylation of readily available aryl bromides with CO_2 in the presence of $Pd(OAc)_2$ as catalyst.[4] Tsuji and co-workers applied $NiCl_2(PPh_3)_2$ to accomplish the carboxylation of more inert aryl and vinyl chlorides under a CO_2 pressure of 1 atm at room temperature.[5] Later, a variety of surrogates including sulfonates,[6] ester derivatives,[7] allylic alcohols,[8] as well as ammonium salts[9] were devised to complement the reaction scope. Notably, all of these systems require stoichiometric metal reagents based on Et_2Zn, Mn or Zn powder as reducing agents (Scheme 1a, previous works). Therefore, it is highly desirable to search for a new system that utilizes non-metallic and mild reductants to realize carboxylation of (pseudo)halides with CO_2.

The rapid development of photocatalysis[10] has also brought new impetus to carboxylation with CO_2.[11] In 2015, Murakami and co-workers disclosed the first example of a novel and direct carboxylation of benzylic C_{sp3}-H bonds under UV irradiation.[11a] In contrast, Jamison and co-workers reported a photoredox activation of CO_2 and amines to synthesize α-amino acid derivatives in moderate to excellent yields under UV light irradiation.[11c] And very recently, Iwasawa and Martín employed $Pd(OAc)_2$ and an Ir complex as catalyst and photosensitizer (PS), respectively, to accomplish visible light-driven carboxylation of aryl halides using i-Pr_2NEt as the non-metallic reductant (Scheme 1b, previous work).[12] However, only aromatic and heteroaromatic halides were reacted. Herein, we presented a cheap and mild method to realize carboxylation of bromides and triflates with CO_2 under visible light catalysis, *i.e.* $NiBr_2$·glyme as the catalyst, an organic photosensitizer and Hantzsch ester (HEH) as the reductant. In addition to (hetero)aryl and primary alkyl bromides, unactivated cyclic alkyl bromides react well under our conditions (Scheme 1c, this work) overcoming previous limitations.



Scheme 1. Carboxylation of bromides.

The donor-acceptor dye 4CzIPN[13] and HEH were chosen as photosensitizer and stoichiometric reductant (Table S1); $NiBr_2$·glyme combined with neocuproine was employed as co-catalyst. When a solution of bromobenzene with the above components in MeCN was irradiated with blue LEDs in the presence of K_2CO_3 as the source of CO_2, the desired product benzoic acid was formed after work up with aqueous HCl, albeit in low yield (Table S1, entry 1). Then solvent screening indicated that DMF was much more effective than CH_3CN, DMSO and DMA (Table S1, entries 2-4). Considering that the source of CO_2 may have an influence on the formation of benzoic acid, we investigated other carbonates, but inferior results were obtained to K_2CO_3 (Table S2, entries 1-5). Optimization of the amount of K_2CO_3 had a negligible effect on the reactivity (Table S2, entries 6-8). Obviously, CO_2 generated *in situ* from K_2CO_3 partially escapes from the solution into the gas phase, thus reducing the CO_2 concentration in solution. Therefore, a balloon filled with CO_2 was used, which increased the product yield to 45% (Table

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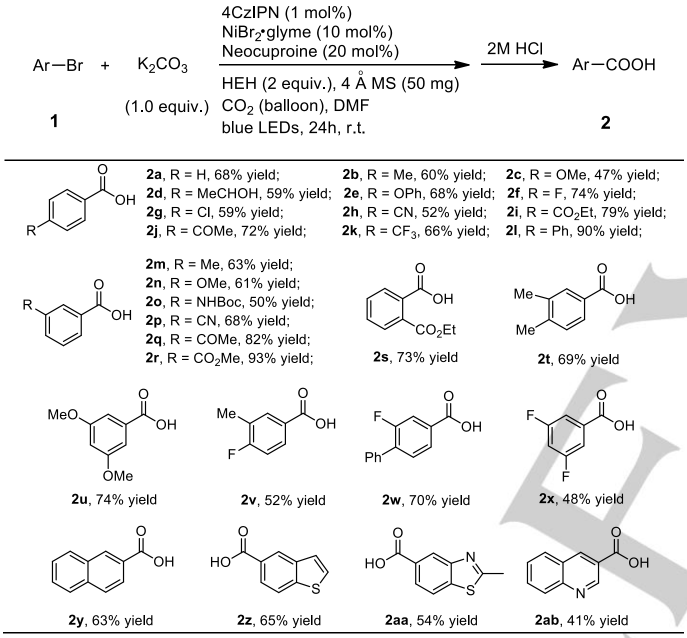
S1, entry 5). Then a variety of photosensitizers including organic dyes, Ru(II)- and Ir(III)-based metal complexes were screened for this transformation, but only [Ir(dF-CF_3-ppy)$_2$(t-Bu-bpy)]PF_6 gave a comparable result (Figure S1). Other investigated ligands and catalysts provided inferior efficiencies than neocuproine and $NiBr_2$·glyme (Table S2, entries 9-13). Further increasing the amount of HEH showed better performance (Table S1, entry 6, Table S2, entries 14 and 15). H_2O had a deleterious effect on this reaction (Table S1, entry 7) and we anticipated that the addition of molecular sieves (MS) facilitates the transformation (Table S1, entry 8). Gratifyingly, 71% yield of benzoic acid was obtained by subtle change of the concentration (Table S1, entry 9, Table S2, entries 16 and 17). Control experiments revealed that all reaction components were essential to promote this transformation (Table S2, entries 18-21).

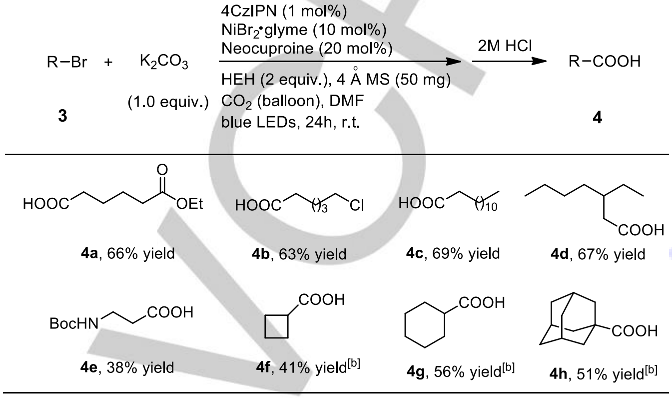
Table 1. Scope of aryl bromides for carboxylation[a]



[a] All reactions were carried out with aryl bromides (0.2 mmol), K_2CO_3 (0.2mmol), 4CzIPN (0.002 mmol), $NiBr_2$·glyme (0.02 mmol), neocuproine (0.04 mmol), HEH (0.4 mmol) and 50 mg 4Å MS in anhydrous DMF (4 mL), irradiation with blue LEDs at room temperature with a CO_2 balloon for 24 h.

With the optimum reaction conditions established, we investigated the scope of this protocol (Table 1). A broad range of *para*-(**2b**-**2l**) or *meta*-substituted (**2m**-**2r**) arenes reacted with CO_2 smoothly to afford carboxylic acids in moderate to excellent yields (47-93%). It is noteworthy that many reactive groups including ether (**2c**, **2e** and **2n**), alcohol (**2d**), fluoro (**2f**), chloro (**2g**), cyano (**2h** and **2p**), ester (**2i** and **2r**), ketone (**2j** and **2q**), trifluoromethyl (**2k**) and Boc-protected amine (**2o**) are tolerated under the reaction conditions. Intriguingly, *ortho*-substituted aryl bromides with an ester group could be used as substrate to give the desired product with good efficiency (**2s**), which was difficult in previous reported systems.[5] Next, di-substituted aryl rings were investigated, affording carboxylic acids in moderate to good yields (48-74%). Particularly, the obtained 3,5-difluorobenzoic acid has been regarded as an important precursor for the synthesis of liquid crystalline materials.[14] This carboxylation method was also compatible with naphthalene and hetero-aromatic rings including benzothiophene, benzothiazole, as well as quinoline (**2y**, **2z**, **2aa** and **2ab**). Only hydrogenation adducts have been detected as the by-products and no dimerization adducts were observed (Table S3).

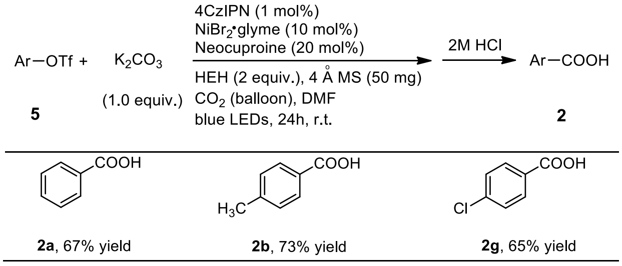
Table 2. Scope of alkyl bromides for carboxylation[a]



[a] All reactions were carried out with alkyl bromides (0.2 mmol), K_2CO_3 (0.2mmol), 4CzIPN (0.002 mmol), $NiBr_2$·glyme (0.02 mmol), neocuproine (0.04 mmol), HEH (0.4 mmol) and 50 mg 4Å MS in anhydrous DMF (4 mL), irradiation with blue LEDs at room temperature with a CO_2 balloon for 24 h. [b] 1 equiv. CsF was added.

Next, we explored the substrate scope of alkyl bromides for this protocol. As shown in Table 2, all primary alkyl bromides react well to give the corresponding products with yields ranging from 38% to 69% (**4a**-**4e**). Compounds **4a** and **4b** are suitable for a subsequent synthesis of unsymmetric dicarboxylates and cross-coupling reactions. Tridecanoic acid **4c** is an important starting material for the production of surfactants and spices. BocNH is tolerated, but the product **4e** is only obtained in low yield. Remarkably, non-activated cyclic alkyl bromides can be converted into the corresponding products in moderate yields (**4f**-**4h**).[15] Furthermore, the reaction scope was extended to aryl triflates. It is noteworthy that electron-rich aryl triflates showed better efficiencies than electron-deficient substrates (Table 3, **2a** **2b** and **2g**), which is an inverse trend compared to aryl bromides (Table 1, **2a**, **2b** and **2g**). For chlorides, only substrates bearing electron-withdrawing substituents on the aryl ring gave moderate to good yields of the desired products (Table S4).

Table 3. Scope of aryl triflates for carboxylation[a]



[a] All reactions were carried out with aryl triflates (0.2 mmol), K_2CO_3 (0.2mmol), 4CzIPN (0.002 mmol), $NiBr_2$·glyme (0.02 mmol), neocuproine (0.04 mmol), HEH (0.4 mmol) and 50 mg 4Å MS in anhydrous DMF (4 mL), irradiation with blue LEDs at room temperature with a CO_2 balloon for 24 h.

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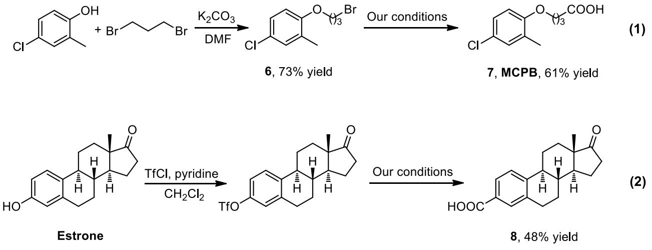
Finally, some synthetic applications of this Ni-based photocatalytic transformation are demonstrated by the concise synthesis of MCPB, which exhibits potent biological activity (Scheme 2, equation 1).[16] Moreover, estrone could be derivatized into the desired carboxylic acid **7** directly in a moderate yield without column separation (Scheme 2, equation 2).



Scheme 2. Photocatalytic carboxylation in multistep synthesis.

Preliminary mechanistic studies were performed. When radical inhibitors such as butylated hydroxytoluene (BHT), 9,10-dihydroanthracene (DHA) or 1,1-diphenylethylene (DPE) were added to the system, the reactions proceeded well. The use of TEMPO as an additive reduced the reactivity, presumably acting as an interfering oxidant (Scheme S1, equation 1). The amount of the ligand neocuproine could be decreased to equimolar amounts to $NiBr_2$·glyme, maintaining still 61% yield of the final product (Scheme S1, equation 2). Accordingly, we suggest that $NiBr_2$·glyme and neocuproine form the initial catalyst in a ratio of 1:1, which was confirmed by Job's method (Figure S2). On the other hand, when we mixed neocuproine with $NiBr_2$·glyme in DMF solution, characteristic absorptions of $LNiBr_2$ (L = neocuproine) were observed, which also supported the generation of $LNiBr_2$ (L = neocuproine) *in situ* during the initial process (Figure 1a). Moreover, 77% yield of benzoic acid was produced when $LNiBr_2$ (L = neocuproine) was used as the catalyst instead of $NiBr_2$·glyme and neocuproine (Scheme S1, equation 3).

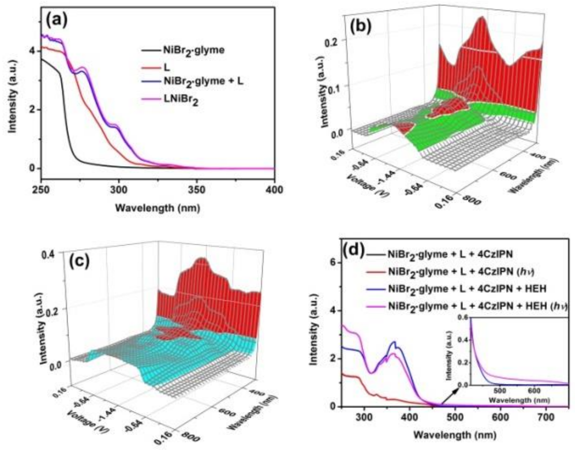
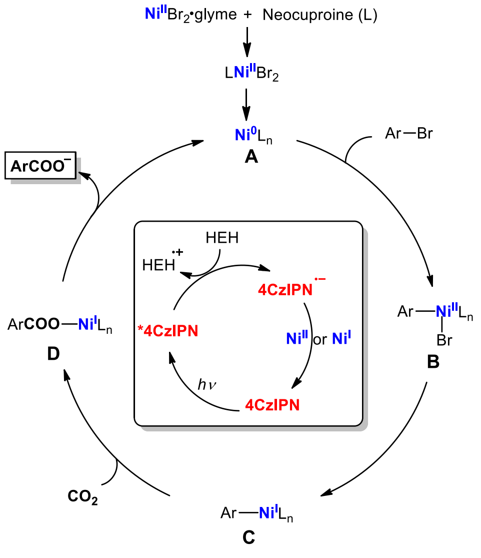


Figure 1. Spectroscopic investigations. (a) UV-vis spectrum of $NiBr_2$·glyme (1.0×10^{-4} M), L (1.0×10^{-4} M), $LNiBr_2$ (1.0×10^{-4} M), mixture of $NiBr_2$·glyme (1.0×10^{-4} M) and L (1.0×10^{-4} M) in DMF. (b) Spectroelectrochemical absorption spectrum of the mixture of $NiBr_2$·glyme (2.5×10^{-3} M) and L (2.5×10^{-3} M) in DMF as a function of the change of voltage. (c) Spectroelectrochemical absorption spectrum of $LNiBr_2$ (2.5×10^{-3} M) in DMF as a function of the change of voltage. (d) UV-vis spectrum of the catalytic system before and after illumination. (**L**: neocuproine).

We next investigated the initial electron transfer during the process by fluorescence quenching and electrochemical experiments. The luminescence of 4CzIPN [$E_{1/2}$(*P/P$^-$) = +1.35 V vs SCE][13b] at λ_{max} = 537 nm in degassed DMF solution was readily quenched by HEH ($E_{1/2}{}^{red}$ = +0.887 V vs SCE),[17] showing a Stern-Volmer kinetic with a rate of 0.61 M^{-1} (Figure S3a). In addition, $NiBr_2$·glyme ($E_{1/2}{}^{Ox}$ = -1.70 V vs Fc/Fc$^+$, Figure S4b) can also quench the luminescence of 4CzIPN [$E_{1/2}$($^+$P/*P) = -1.04 V vs SCE][13b] with a rate of 0.18 M^{-1} (Figure S3b). Introduction of neocuproine as the ligand increased the rate slightly (0.20 M^{-1}, Figure S3c) due to the *in situ* generation of $LNiBr_2$ (L = neocuproine) with a relatively positive reduction potential ($E_{1/2}{}^{Ox}$ = -1.27 V vs Fc/Fc$^+$ for $LNiBr_2$, Figure S4a and 4c). No quenching was observed with bromobenzene as the estimated potential difference is unfeasible ($E_{1/2}{}^{Ox}$ < -2.0 V vs SCE).[18] Therefore, both reductive and oxidative quenching of the excited state of 4CzIPN may occur, while the former is faster than the latter. Furthermore, spectroelectrochemistry was employed to investigate a solution containing $NiBr_2$·glyme and neocuproine. At the beginning, a new absorption between 600-800 nm assigned to the one electron reduced species was observed with decreasing potential. Subsequently, another new absorption between 450-600 nm appeared, which can be ascribed to the two electron reduced species (Figure 1b). Using $LNiBr_2$ (L = neocuproine) instead, the same phenomenon was obtained, showing absorptions between 600-800 nm and 450-600 nm, which might correspond to LNi(I)Br and $L_nNi(0)$ (L = neocuproine), respectively (Figure 1c). Indeed, monitoring the UV-vis spectrum also showed the generation of these characteristic absorptions upon irradiation with blue LEDs in the presence of HEH, whereas the absence of HEH led to no change of the absorption (Figure 1d).



Scheme 3. Plausible reaction mechanism

Accordingly, a plausible catalytic cycle is proposed (Scheme 3). First, ligand exchange occurs between $NiBr_2$·glyme and neocuproine, giving rise to a complex $LNiBr_2$ (L = neocuproine), which can be reduced to intermediate **A** by $4CzIPN^{\bullet-}$ [$E_{1/2}(P/P^-)$ = -1.21 V vs SCE][13b] generated from reductive quenching by HEH. Then oxidative addition of aryl bromide yields an Ni(II) species **B**. Although attempts to synthesize intermediate **B** were unsuccessful, the fact that reduction potentials of its analogues locate around -1.20 V (vs SCE),[19] thus SET from $4CzIPN^{\bullet-}$ to **B** might be thermodynamically feasible, suggest a transformation pathway to the Ni(I) species **C**. However, the formation of species **C** by energy transfer and reduction cannot be excluded at this time. Subsequently, the intermediate **C** inserts CO_2 to give the nickel carboxylate intermediate **D**, followed by further reduction leading to the generation of the carboxylate and **A** to complete the cycle.

In conclusion, we have developed a new, efficient and mild strategy to realize carboxylation of bromides and triflates with CO_2 generated *in situ* from K_2CO_3 at room temperature by combining visible light catalysis with Ni catalysis. A broad scope of functional groups is tolerated, affording the desired products in moderate to excellent yields. As supported by spectroscopic investigations, $LNiBr_2$ (L = neocuproine) was produced from $NiBr_2$·glyme and neocuproine during the initial step, and reduced to $Ni(0)L_n$ promoting the catalytic cycle. Further mechanistic studies are under way in our laboratory.

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Keywords: visible light • Ni catalysis • CO_2 • carboxylation• photocatalysis

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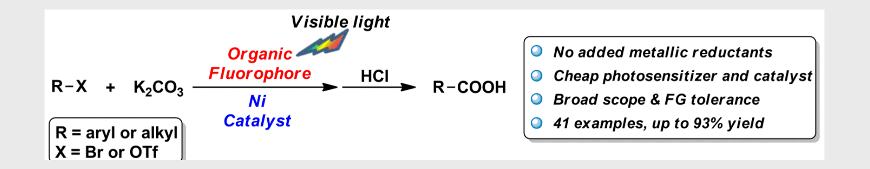

An efficient and mild carboxylation of bromides and triflates with K_2CO_3 as the source of CO_2 using an organic fluorophore in combination with a nickel complex under visible light irradiation is reported. The present protocol can tolerate a variety of functional groups. Non-activated cyclic alkyl bromides react well. The synthesis and derivatization of biologically active molecules demonstrate the applications of the method in multistep synthesis.

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