Cobalt-Catalyzed Direct Carbyonylation of Aminoquinoline Benzamides

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Supporting Information

**ABSTRACT:** A method for direct carbonylation of aminoquinoline benzamides has been developed. Reactions proceed at room temperature in trifluoroethanol solvent, use oxygen from air as an oxidant, and require Mn(OAc)₃ as a cocatalyst. Benzoic and acrylic acid derivatives can be carbonylated by carbon monoxide affording imides in good yields. Halogen, nitro, ether, cyano, and ester functional groups are tolerated. The directing group can be removed under mild conditions affording phthalimides.

**Scheme 1. Aminoquinoline Amide Coupling with Alkenes and Alkynes**

- **PhHCH₃=CH₂ or Ph**
- **3 atm, CO, rt**
- **75% for styrene**
- **95% for phenylacetylene**

Gratifyingly, conditions that were successful for alkene coupling with sp² C–H bond worked also for aminoquinoline benzamide carbonylation. Reactions proceed in trifluoroethanol at room temperature with 20 mol % Co(acac)₂ catalyst, 1 equiv of Mn(OAc)₃, 2H₂O additive, and under 1 atm of CO (Table 1). Oxygen from air is the terminal oxidant, and sodium pivalate base is employed. In all cases, only one isomer of product was obtained.

**Scheme 2. Aminoquinoline Amide Coupling with Alkenes and Alkynes**

- **PhHCH₃=CH₂ or Ph**
- **3 atm, CO, rt**
- **75% for styrene**
- **95% for phenylacetylene**

directed *ortho*-carbonylation of aminoquinoline benzamides, since migratory insertion of carbon monoxide into Co(III)–C bonds is known.¹° We report here cobalt-catalyzed, aminoquinoline-directed carbonylation of sp² C–H bonds that proceeds at room temperature under 1 atm of CO, uses oxygen from air as a terminal oxidant, and affords phthalic acid derivatives.

The reaction scope is presented in Table 1. Aminoquinoline amides possessing electron-withdrawing (entries 2–5, 9–11) as well as electron-releasing substituents (entries 6–8, 12) are reactive. High functional group tolerance is observed. Bromo (entry 3), nitro (entry 4), iodo (entry 5), cyano (entry 10), and ester (entry 11) substituents are tolerated. Carbonylation of
aminoquinoline \( p \)-toluoylamide (entry 6) was carried out also on 5 mmol scale, and product was obtained in 91\% yield showing that scale-up of the reaction is feasible. The directing group can be easily removed by treatment with ammonia, affording a high yield of a phthalimide derivative (eq 1).

Two control experiments were performed to determine the source of the oxidant. First, \( p \)-toluoylamide of aminoquinoline was carbonylated under the conditions for Table 1, entry 6, but without opening of the reaction vial to air (Scheme 2). Carbon monoxide was delivered from a balloon equipped with a needle. The NMR yield of product 1 was 83\%, which is comparable to the isolated yield for entry 6, Table 1. Second, the reaction was carried out in a CO-filled Schlenk flask (25 mL) with exclusion of oxygen. The NMR yield of the product was 20\%. It can be concluded that oxygen is delivered to the reaction via slow diffusion of air through the surface of the balloon.\(^4f\)

Furthermore, aminoquinoline amides of cinnamic and methacrylic acids can be carbonylated. The products were obtained in moderate yields (Scheme 3).

### Table 1. Carbonylation of Aminoquinoline Amides\(^a\)

| entry | Ar   | product | yield, % |
|-------|------|---------|----------|
| 1     | \( \text{C}_6\text{H}_5 \) | [Structure] | 81       |
| 2     | 4-\( \text{CF}_2\text{C}_6\text{H}_4 \) | [Structure] | 83       |
| 3     | 4-\( \text{BrC}_6\text{H}_4 \) | [Structure] | 80       |
| 4     | 3-\( \text{NO}_2\text{C}_6\text{H}_4 \) | [Structure] | 69       |
| 5     | 3-\( \text{IC}_6\text{H}_4 \) | [Structure] | 84       |
| 6     | 4-\( \text{MeC}_6\text{H}_4 \) | [Structure] | 84 \(91^b\) |

\(^a\)Amide (0.5 mmol), catalyst (0.1 mmol), NaOPiv (1 mmol), Mn(OAc)$_3$·2H$_2$O (0.5 mmol), trifluoroethanol (5 mL), 1 atm of CO (balloon), 16–60 h. Yields are isolated yields. Please see Supporting Information for details.\(^b\)Scale: 5 mmol.
ASSOCIATED CONTENT

4 Supporting Information

Detailed experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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