Supporting Information

One-Pot Copper-Catalyzed Three-Component Reaction: a Modular Approach to Functionalized 2-Quinolones

Ah Reum Kim and Hee Nam Lim*

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1. Preparation of starting materials

2-Bromobenzaldehydes 1a-b, 1e-k, 1o, 1p and 1r are purchased from Alfa-Aesar (AA) and Tokyo Chemical Industry (TCI) co., Ltd and 1e-l\textsuperscript{b}, 1l\textsuperscript{b}-m\textsuperscript{b} and 1q\textsuperscript{1} are prepared by the known methods. The ketones 1s and 1u are purchased from the AA and the TCI, respectively. The ketones 1t, 4a-4c and 1w\textsuperscript{4c} are prepared. Sodium sulfinates 2b and 2f are available from the TCI, and 2d, 2e and 2g-i are purchased from the Fluorochem. The sodium sulfinates 2c and 2j-n are prepared by the known methods.\textsuperscript{5}

2. Optimization table for the Cu-salts

![Chemical structure](image)

| Entry | Copper catalyst | Yield\textsuperscript{a} |
|-------|-----------------|------------------------|
| 1     | Cu powder (60-80nm) | 55%                    |
| 2     | Cu(dendritic)   | 42%                    |
| 3     | Cu(25nm)        | 40%                    |
| 4     | CuI             | 51%                    |
| 5     | CuBr            | 42%                    |
| 6     | CuCl            | 40%                    |
| 7     | Cu(OAc)\textsubscript{2} | 46%            |
| 8     | Cu(O\textsubscript{2})\textsubscript{2} | 32%              |
| 9     | CuO\textsubscript{2} | 12%            |

\textsuperscript{a}determined by 1H NMR using 1,3,5-trimethoxybenzene as the internal standard

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3. Optimization tables for the ketone substrate

![Chemical structures and reaction conditions]

Table S1. Additive effect

| Desiccant (1 equiv) | Yield<sup>a</sup> |
|---------------------|------------------|
| None                | 4%               |
| MgSO<sub>4</sub>    | 4%               |
| Na<sub>2</sub>SO<sub>4</sub> | trace           |
| Al<sub>2</sub>O<sub>3</sub> | 5%               |
| NaCl                | 5%               |
| CaCl<sub>2</sub>    | 2%               |
| Silica gel (100 wt%) | trace            |
| Molecular sieve 4Å (100 wt%) | 9%               |
| CaO                 | trace            |
| Ca(OH)<sub>2</sub>  | 20%              |

Table S2. Determination of Ca(OH)<sub>2</sub> equivalent

| Equivalent of Ca(OH)<sub>2</sub> | Yield<sup>a</sup> |
|---------------------------------|------------------|
| 1.0 equiv (0.50 mmol)           | 20%              |
| 1.5 equiv (0.75 mmol)           | 29%              |
| 2.0 equiv (1.00 mmol)           | 56%              |
| **2.5 equiv (1.25 mmol)**       | **59%**          |
| 3.0 equiv (1.50 mmol)           | 58%              |

<sup>a</sup>determined by 1H NMR using 1,3,5-trimethoxybenzene as the internal standard
3. $^1$H-NMR, $^{13}$C-NMR and $^{19}$F-NMR
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