Aryl C-H bond Functionalization with iodide(III) Reagents

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Introduction

Structural Types of Polyvalent Iodine Species

One Carbon Ligand Iodine(III) compound

Two Carbon Ligand Iodine(III) compound

Iron(II)-Catalyzed Direct Cyanation of Arenes with Aryl(cyano)-iodonium Triflates**

Zhibin Shu, Wenzhi Ji, Xi Wang, Yujing Zhou, Yan Zhang, and Jianbo Wang*

Direct facile cyanation today! A direct cyanation of aryl C–H bonds with 3,5-di(trifluoromethyl)phenyl(cyano)iodonium triflate (DFCT) under Fe^{II} catalysis was successfully applied to a wide range of aromatic substrates, including polycyclic structures and heteroaromatic compounds (see scheme). The reaction proceeded efficiently under mild conditions.

Synthesis of Aromatic Nitriles

R-C-CN

functional group transformation

Acid, aldehydes, amines, amides and heterocycles

R-CN

Cu(I)CN

aryldiazonium halide

Sandmeyer reaction

toxic copper(I) cyanide as CN- source
hash reaction conditions

R-CN

Metal catalyst

KCN, NaCN, Zn(CN)₂, acetone cyanohydrin,
TMSCN, K₄[Fe(CN)₆]

aryl halides

Nucleophilic cyanation
deactivation of the catalyst
notorious toxicity

R-CN

Metal catalyst

C-H bond functionalization
Aryl(cyano)iodonium Triflates

\[
\begin{align*}
\text{C1} & \quad \text{TfO} \quad \text{CN} \\
\text{C2} & \quad \text{TfO} \quad \text{CN} \\
\text{C3} & \quad \text{TfO} \quad \text{CN} \\
\text{C4} & \quad \text{TfO} \quad \text{CN} \\
\end{align*}
\]

Versatile iodonium transfer reagents

\[
R-\text{SnBu}_3 + \text{Arl(CN)OTf} \xrightarrow{\text{DCM, -78° to RT}} \text{Arl(OF)}_2, \text{TMSOTf, TMSCN} \xrightarrow{\text{DCM, rt, 1-4h}} \text{Arl(CN)OTf}
\]

R=alkynl, aryl,
Cyanation Reaction of \( p \)-xylene

\[
\begin{align*}
1 \xrightarrow{\text{catalyst, cyano source}} \text{DCE, 70 °C} \xrightarrow{} \text{2}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Cyanating agent (equiv)</th>
<th>Yield [%][b]</th>
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<tbody>
<tr>
<td>1</td>
<td>CuBr (10)</td>
<td>Cl (2)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>CuCl (10)</td>
<td>Cl (2)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>CoCl(_2) (10)</td>
<td>Cl (2)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>SnCl(_2) (10)</td>
<td>Cl (2)</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>FeCl(_2) (5)</td>
<td>Cl (2)</td>
<td>trace[^{[c]}]</td>
</tr>
<tr>
<td>6</td>
<td>FeBr(_2) (5)</td>
<td>Cl (2)</td>
<td>trace[^{[c]}]</td>
</tr>
<tr>
<td>7</td>
<td>FeF(_2) (5)</td>
<td>Cl (2)</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>Fe(O(\text{OTf}))(_2) (5)</td>
<td>Cl (2)</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>Fe(OAc)(_2) (5)</td>
<td>Cl (2)</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>Fe(OAc)(_2) (5)</td>
<td>C(_2) (2)</td>
<td>20</td>
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<tr>
<td>11</td>
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<td>C(_3) (2)</td>
<td>trace</td>
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<tr>
<td>12</td>
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<td>C(_4) (2)</td>
<td>47</td>
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<tr>
<td>13</td>
<td>Fe(OAc)(_2) (10)</td>
<td>C(_4) (4)</td>
<td><strong>73</strong></td>
</tr>
<tr>
<td>14</td>
<td>none</td>
<td>C(_4) (4)</td>
<td>N.R.[^{[d]}]</td>
</tr>
</tbody>
</table>

\[^{[a]}\] Reaction conditions: DCE, 70 °C

\[^{[b]}\] Yield determined by gas chromatography.

\[^{[c]}\] Trace yields are determined by NMR spectroscopy.

\[^{[d]}\] N.R. indicates not reported.
Substrate Scope

4a, 48% (p/o/m, 50:36:14)\textsuperscript{[a]}
4b, 76% (p/o, 78:22)\textsuperscript{[b]}
4c, 82%
4d, 72%
4m, 99%
4n, 70%\textsuperscript{[b]}
4o, 82%
4p, 85%
4e, 84%
4f, 80%
4g, 87%
4h, 52% (p/o, 75.25)\textsuperscript{[a]}
4q, 82%
4r, 78%
4s, 82%
4i, 76% (p/o, 85:15)\textsuperscript{[a]}
4j, 81%
4k, 38%
4l, 57%
4t, 80%
4u, 54%
4v, 57%
6a, 99%
6b, 98%
6c, 98% (C5/C3, 48:52)\textsuperscript{[a]}
6d, 67% (C3/C2, 62:38)\textsuperscript{[a]}
6h, 70%
6i, 73%
6j, 86% (C2/C3, 75:25)\textsuperscript{[a]}
6e, 78%
6f, 72%
6g, 85%
6k, 77% (C2/C3, 79:21)\textsuperscript{[a]}
6l, 90% (C2/C3, <1:30)\textsuperscript{[b]}
6m, 97%
Proposed Reaction Mechanism

Ar-OTf $\xrightarrow{\text{SET}}$ Ar$^\bullet$ $\xrightarrow{\text{SET, arene}}$ X

CN $\xrightarrow{\text{Fe}^{II} \rightarrow \text{Fe}^{III}}$ 

CN $\xrightarrow{\text{Fe}^{II} \rightarrow \text{Fe}^{III}}$ X

CN $\xrightarrow{-\text{H}^{+}}$ C

CN $\xrightarrow{\text{Fe}^{II} \rightarrow \text{Fe}^{III}}$ D
Cross-coupling

Rhodium-Catalyzed C–H Alkynylation of Arenes at Room Temperature**

Chao Feng and Teck-Peng Loh*

Mechanistic Studies

Competition experiments for amides

Electronically-deficient arenes are more favored electrophilic aromatic substitution pathway was ruled out

C-H bond activation
Rate-determining step

Precluded the silyl migration step in the catalytic cycle
Proposed Reaction Mechanism

Scheme 6. Proposed reaction mechanism.
Photoredox-Induced Three-Component Oxy-, Amino-, and Carbotrifluoromethylation of Enecarbamates

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Supporting Information

ABSTRACT: A photoredox-catalyzed trifluoromethylation of enecarbamates process is reported. This pathway uses Togni’s reagent as the CF₃ source and follows a radical/cationic pathway. Under the optimized conditions using [Ru(bpy)₃(PF₆)₂] as the photocatalyst, a wide range of substituted enecarbamates can readily be difunctionalized by means of various O, N, and C nucleophiles.
Proposed Mechanism

Selected examples

- NHCbz MeO-CH₂CF₃: 76% yield, dr=55:45
- NHCbz N₃-CH₂CF₃: 65% yield, dr=50:50
- NHCbz NC-CH₂CF₃: 60% yield, dr=78:22

Togni’s reagent