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Synthesis of [60]fullerene-fused dihydroindolizines via copper-catalyzed dearomative *N*-heteroannulation†

Qian-Wen Zhang,^{‡a} Yuanyuan Liu,^{‡a} Zheng-Chun Yin,^{ID *ab} Wen-Jie Qiu,^{ID a} Xinmin Huang,^a Jian-Feng Li^a and Guan-Wu Wang^{ID *abc}

A novel copper-catalyzed approach for the construction of [60]fullerene-fused dihydroindolizine derivatives has been developed through dearomative *N*-heteroannulation of [60]fullerene with electron-withdrawing group-substituted 2-picolines. A plausible reaction mechanism has been proposed. Additionally, a representative fullerene product can be applied in organic solar cells as the third component.

Over the past three decades, [60]fullerene (C₆₀) and its derivatives have been extensively utilized in materials science, biomedicine and photoelectric materials owing to their outstanding physical and chemical properties.¹ Therefore, the functionalization of fullerenes has attracted widespread attention.² Transition metal-catalyzed/promoted reactions, including those mediated by Mn(III),^{3,4} Fe(II)/Fe(III),^{3,5} Ag(I)⁶ and Pd(0)/Pd(II)⁷ salts, have been one of the most frequently employed and efficient strategies. Notably, copper salts with economic feasibility, ready availability and reduced toxicity have been extensively used in fullerene functionalization.⁸

On the other hand, the unique molecular structure and electronic properties of C₆₀ lead to its strong electron-deficient nature. Consequently, C₆₀ tends to undergo nucleophilic and radical additions with electron-rich compounds, whereas its reaction with electron-deficient compounds remains a significant

challenge.² The Cu(I)/Cu(II) promoted/catalyzed free-radical reactions of C₆₀ with electron-deficient compounds, such as *N*-sulfonylated *o*-amino-arylmalonates^{8b} and α -bromoacetamides,^{8c} have been reported. However, these reactions require long reaction times and still result in relatively low yields. Therefore, an efficient and productive protocol that can facilitate reactions between C₆₀ and electron-deficient compounds is urgently needed.

Moreover, dearomative transformations of aromatic compounds have become a key focus in contemporary research.⁹ Extensive research in this field has concentrated on electron-rich aromatic compounds such as indoles,¹⁰ furans¹¹ and phenols.^{9a} However, the transformation of electron-deficient pyridine compounds remains a significant challenge.^{9c,10a} 2-(Pyridine-2-yl)acetates, as some of the common electron-withdrawing group-substituted 2-picolines, are versatile building blocks for constructing various heterocycles such as quinolines, bipyrimidines and indolizines.¹² In 2022, the Yan group developed a Cu-catalyzed oxidative [3+2] annulation of 2-(pyridine-2-yl)acetates with maleimides to access 1*H*-pyrrolo[3,4-*b*]indolizine-1,3-diones (Scheme 1a).¹³ The dearomatization in fullerene chemistry has garnered research interest. The divergent additions of 2,2'-diazidobiphenyls to C₆₀ and Sc₃N@I_h-C₈₀ were recently reported, disclosing an unexpected cascade dearomative process to afford unprecedented

^a Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: gwang@ustc.edu.cn

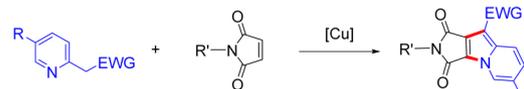
^b Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, and School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241002, P. R. China. E-mail: zcyin@ahnu.edu.cn

^c State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou, Gansu 730000, P. R. China

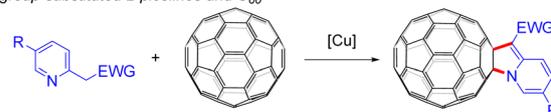
† Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization data, ¹H NMR, ¹³C NMR, HRMS, UV-vis spectra, CVs and DPVs of 2a-t; X-Ray data of 2f. CCDC 2411224. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5cc00820d>

‡ These authors contributed equally to this work.

(a) Previous work: Cu-catalyzed oxidative [3+2] annulation between electron-withdrawing group-substituted 2-picolines and maleimides



(b) This work: Cu-catalyzed oxidative [3+2] annulation between electron-withdrawing group-substituted 2-picolines and C₆₀



Scheme 1 Cu-catalyzed reactions of electron-withdrawing group-substituted 2-picolines and (a) maleimides, (b) C₆₀.

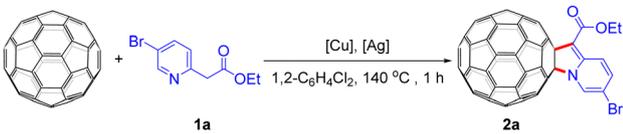


azafulleroids fused with a 7-6-5-membered ring system, which represented a new dearomative mode of benzenoid structures.¹⁴ With our continuous interest in copper salt-catalyzed reactions⁷ and dearomatization transformations¹⁴ in fullerene chemistry, herein we report a copper-catalyzed reaction of C₆₀ with electron-withdrawing group-substituted 2-picolines *via* dearomative *N*-heteroannulation to provide C₆₀-fused dihydroindolizines (Scheme 1b).

To establish the optimal reaction conditions, ethyl 2-(5-bromopyridin-2-yl)acetate (**1a**) was selected as the model substrate to react with C₆₀ (Table 1). Initially, a mixture of C₆₀ (0.05 mmol), **1a** (0.15 mmol), Cu(OAc)₂·H₂O (0.10 mmol) and AgNO₂ (0.10 mmol) in 1,2-dichlorobenzene (1,2-C₆H₄Cl₂, 6 mL) was heated under stirring in an oil bath at 140 °C for 1 h. To our delight, the C₆₀-fused dihydroindolizine (**2a**) was obtained in 5% yield (Table 1, entry 1). Replacing AgNO₂ with AgNO₃, AgOAc, AgCl or Ag₂O could increase the yield to over 20% (Table 1, entries 2–5). To our satisfaction, when Ag₂CO₃ was used, the yield of **2a** was significantly enhanced to 61% (Table 1, entry 6). Different copper salts were subsequently examined. However, the reaction yield dropped remarkably when Cu(OAc)₂ or CuCl₂ was employed (Table 1, entries 7 and 8). Hydrated copper salts, including Cu(NO₃)₂·3H₂O and Cu(TFA)₂·xH₂O, were also examined, but could not give higher yields (Table 1, entries 9 and 10). Further screening of cuprous salts CuOAc and CuCl led to lower yields (Table 1, entries 11 and 12). When the reaction was performed without Cu(OAc)₂·H₂O, only a trace amount of **2a** was formed (Table 1, entry 13), whereas the absence of Ag₂CO₃ resulted in a significantly reduced yield of **2a** (Table 1, entry 14), indicating the importance of the copper and silver salts in this transformation. Subsequently, we investigated the impact of varying the molar equivalents of silver and copper salts in this reaction. We found that either increasing or decreasing the molar equivalents could not result in a higher yield of **2a** (Table 1, entries 15–18). In addition, shortening or prolonging the reaction time and reducing or increasing the reaction temperature were also detrimental to the product yield (Table 1, entries 19–22). Moreover, when 0.3 equiv. of Cu(OAc)₂·H₂O was employed, the isolated yield remained at a respectable 41%, indicating that even a catalytic amount of the copper salt could efficiently promote the reaction (Table 1, entry 23). Based on the above results, the optimized conditions were established as follows: C₆₀ (0.05 mmol), **1a** (3 equiv.), Cu(OAc)₂·H₂O (2 equiv.) and Ag₂CO₃ (2 equiv.) in 1,2-C₆H₄Cl₂ (6 mL) at 140 °C for 1 h (Table 1, entry 6).

With the optimal reaction conditions in hand, we next explored the scope of substrates, and the results are shown in Scheme 2. Firstly, different substituent groups on the aromatic ring of 2-(pyridine-2-yl)acetates were examined in this reaction. The reactions of C₆₀ with substrates **1b–e** having the electron-withdrawing chloro, fluoro, trifluoromethyl and nitro groups at the 5-position on the aromatic ring proceeded well at 140 °C (150 °C for **1d**) for 1 h and were smoothly transformed into the corresponding products **2b–e** in 23–50% yields. For the more reactive ethyl 2-(pyridine-2-yl)acetate (**1f**), the target product **2f** could not be obtained under the above optimal conditions. However, when the reaction with C₆₀ was carried out at a catalytic amount (0.3 equiv.) of Cu(OAc)₂·H₂O and at a lower temperature of 25 °C for 4 h, product **2f** was isolated in a high yield of 71%. Substrates **1g** and **1h** containing electron-donating methyl and methoxy groups on the pyridyl ring were also very reactive and able to generate products **2g** and **2h** in 66% and 45% yields, when the Cu-catalyzed reactions with C₆₀ were conducted at 25 °C for 4 h and 0 °C for 24 h, respectively. Secondly, 2-picolines bearing other electron-withdrawing groups at the methylene moiety were investigated. The reaction of C₆₀ with substrate **1i** containing a benzyl ester at 25 °C for 4 h provided product **2i** in 64% yield. The Cu-promoted reactions of C₆₀ with 2-picolines **1j**, **1k** and **1l** bearing a cyano group instead of an ester group required a higher temperature of 140 °C for 1 h, generating products **2j**, **2k** and **2l** in 25%, 33% and 20% yields, respectively. Substrates **1m–o** having a phosphate group were also compatible with this protocol, and the Cu-promoted reactions at 140 °C for 1 h gave products **2m–o** in 41–42% yields. When 2-picolines **1p** and **1q** bearing a sulfonyl group were employed, the Cu-promoted reactions with C₆₀ at 140 °C for 1 h could provide products **2p** and **2q** in 32% and 26% yields, respectively. The Cu-promoted reactions of 2-picolines **1r** and **1s** containing a keto group with C₆₀ also performed well at 140 °C for 1 h and afforded products **2r** and **2s** in 36% and 50%

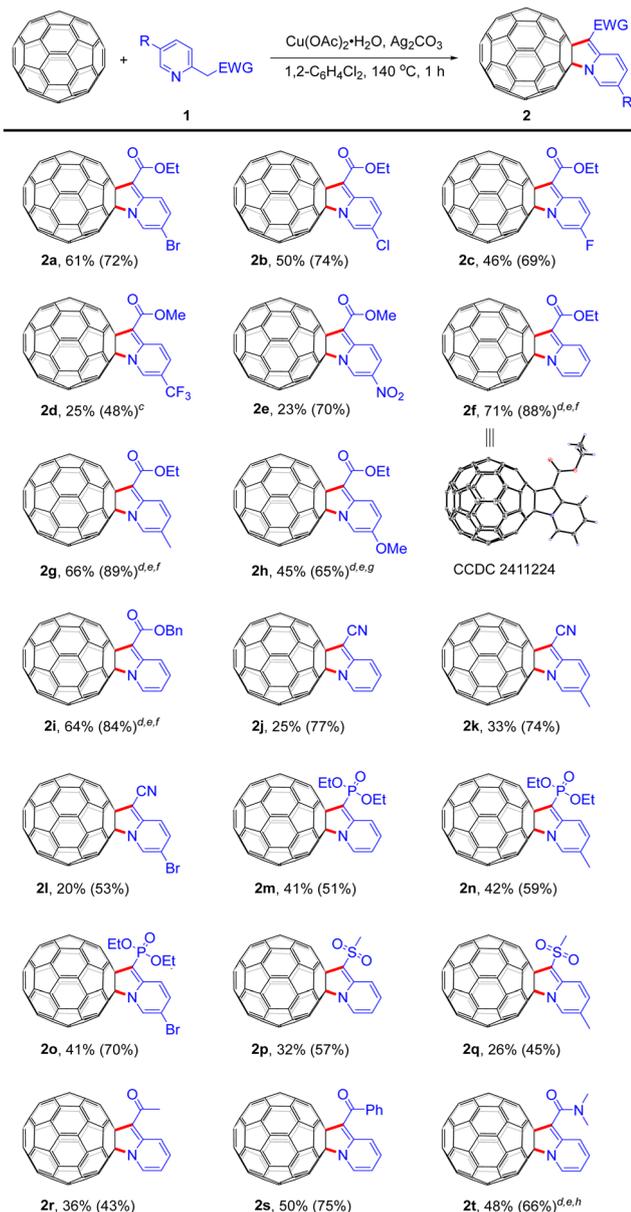
Table 1 Optimization of the reaction conditions^a



Entry	Copper salt	Silver salt	Yield ^b (%)
1	Cu(OAc) ₂ ·H ₂ O	AgNO ₂	5 (12)
2	Cu(OAc) ₂ ·H ₂ O	AgNO ₃	24 (34)
3	Cu(OAc) ₂ ·H ₂ O	AgOAc	27 (69)
4	Cu(OAc) ₂ ·H ₂ O	AgCl	28 (60)
5	Cu(OAc) ₂ ·H ₂ O	Ag ₂ O	23 (42)
6	Cu(OAc)₂·H₂O	Ag₂CO₃	61 (72)
7	Cu(OAc) ₂	Ag ₂ CO ₃	31 (62)
8	CuCl ₂	Ag ₂ CO ₃	26 (56)
9	Cu(NO ₃) ₂ ·3H ₂ O	Ag ₂ CO ₃	10 (19)
10	Cu(TFA) ₂ ·xH ₂ O	Ag ₂ CO ₃	41 (62)
11	CuOAc	Ag ₂ CO ₃	24 (50)
12	CuCl	Ag ₂ CO ₃	5 (18)
13	—	Ag ₂ CO ₃	Trace
14	Cu(OAc) ₂ ·H ₂ O	—	26 (61)
15 ^c	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	51 (72)
16 ^d	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	33 (68)
17 ^e	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	40 (70)
18 ^f	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	53 (70)
19 ^g	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	56 (78)
20 ^h	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	49 (58)
21 ⁱ	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	46 (75)
22 ^j	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	59 (85)
23 ^k	Cu(OAc) ₂ ·H ₂ O	Ag ₂ CO ₃	41 (69)

^a Unless otherwise specified, all reactions were conducted with C₆₀ (0.05 mmol), **1a** (0.15 mmol), copper salt (0.10 mmol) and silver salt (0.10 mmol) in 1,2-C₆H₄Cl₂ (6 mL) at 140 °C for 1 h. ^b Isolated yields. Values in parentheses were based on consumed C₆₀. ^c 0.075 mmol of copper salt. ^d 0.125 mmol of copper salt. ^e 0.075 mmol of silver salt. ^f 0.125 mmol of silver salt. ^g 0.5 h instead of 1 h. ^h 1.5 h instead of 1 h. ⁱ 120 °C instead of 140 °C. ^j 160 °C instead of 140 °C. ^k 0.015 mmol of Cu(OAc)₂·H₂O.



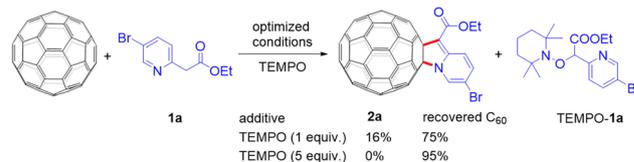


Scheme 2 Results for the reactions of C₆₀ with electron-withdrawing group-substituted 2-picolines **1a–t**. ^a Unless otherwise specified, all reactions were conducted with C₆₀ (0.05 mmol), **1** (0.15 mmol), Cu(OAc)₂·H₂O (0.10 mmol) and Ag₂CO₃ (0.10 mmol) in 1,2-C₆H₄Cl₂ (6 mL) at 140 °C for 1 h. ^b Isolated yields. Values in parentheses were based on consumed C₆₀. ^c Reaction at 150 °C for 1 h. ^d 0.3 equiv. of Cu(OAc)₂·H₂O was added. ^e PhCl as the solvent instead of 1,2-C₆H₄Cl₂. ^f Reaction at 25 °C for 4 h. ^g Reaction at 0 °C for 24 h. ^h Reaction at 40 °C for 1 h.

yields, respectively. 2-Picoline **1t** bearing an amide group was very reactive, and the Cu-catalyzed reaction with C₆₀ could take place at 40 °C for 1 h to give product **2t** in 48% yield.

A scale-up reaction of C₆₀ (0.5 mmol) with **1a** (1.5 mmol) was conducted under the optimal reaction conditions. Product **2a** was obtained in 245.1 mg (51% yield), demonstrating the practicability of the present method at a larger scale.

To better understand the reaction mechanism, control experiments were performed (Scheme 3). Under the optimal



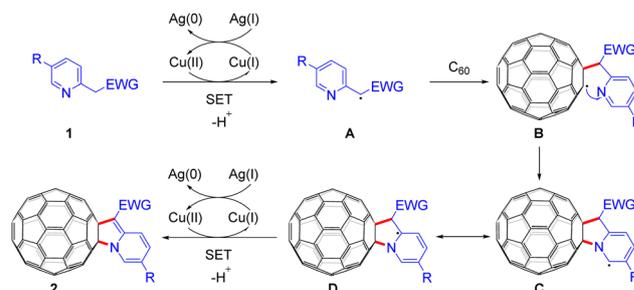
Scheme 3 Control experiments.

reaction conditions, the formation of product **2a** was significantly inhibited by adding 1 equiv. of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), resulting in a yield of only 16%. In comparison, while 5 equiv. of TEMPO were added, **2a** could not be identified. Interestingly, the radical coupling product TEMPO-**1a** between TEMPO and **1a** could be detected by ESI-MS. Similarly, the radical coupling product BHT-**1a** could also be detected by ESI-MS (for details, see ESI[†]). These results strongly indicated that a radical process was likely involved in the present reaction.

Based on the above experimental results and the previous literature,^{13,15} a plausible mechanism for this reaction is proposed in Scheme 4. First, electron-withdrawing group-substituted 2-picoline **1** proceeds through a single electron transfer (SET) reaction and is oxidized to form the methylenyl radical species **A**. Then, the intermediate **A** is captured by C₆₀ to produce the fulleranyl radical **B**. Then, the intermediate **B** undergoes intramolecular cyclization to generate the carbon radical **C**, which can then form radical **D** through resonance. Finally, compound **2** can be obtained through carbocation formation by oxidation followed by deprotonation.

The molecular structures of products **2a–t** were characterized by HRMS, ¹H NMR, ¹³C NMR, FT-IR and UV-vis spectra, and **2f** was further identified by single-crystal X-ray crystallography. All HRMS of these products presented the correct [M]⁺ or [M]⁻ peaks. Their ¹H NMR spectra displayed the expected chemical shifts for all protons. The ¹³C NMR spectra of the products showed no more than 30 peaks in the range of 132.6–150.8 ppm for the 58 sp²-carbons of the C₆₀ cage and two peaks in the 69.82–87.41 ppm range for the two sp³-carbons of the C₆₀ skeleton, consistent with the C_s symmetry of their molecular structures. The UV-vis spectra of **2a–t** displayed characteristic peaks at around 315 nm and 430 nm, which are diagnostic absorptions for 1,2-adducts of C₆₀.⁸

In addition, the half-wave reduction potentials and energy levels of C₆₀-fused dihydroindolizines **2a–t** and C₆₀ were investigated by cyclic voltammetry (CV) and differential pulse



Scheme 4 Proposed reaction mechanism.



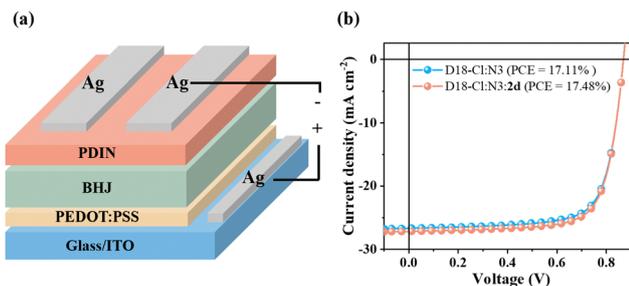


Fig. 1 (a) Schematic illustration of the OSC structure used in this work. (b) J - V curves of D18-Cl:N3 (blue line) and D18-Cl:N3:2d (red line)-based OSCs.

voltammetry (DPV) and are summarized in Table S2 (see ESI†). All of their electrochemical properties were quite similar and showed no more than three reversible redox processes.

Given that fullerene derivatives have been applied in organic solar cells (OSCs) as the third component,^{5c,14,16} preliminary results showed that **2d** could be employed in OSCs with the architectures of ITO/PEDOT:PSS/D18-Cl:N3:2d (1:1.4:0.2)/PDIN/Ag (Fig. 1). The selection of **2d** was based on its higher solubility and the beneficial effects of the fluoro atoms.¹⁷ The device with **2d** as the third component showed an improved power conversion efficiency (PCE) of 17.48% with a short circuit current density (J_{SC}) of 27.14 mA cm⁻², an open-circuit voltage (V_{OC}) of 0.87 V and a fill factor (FF) of 74.13%. The control device without a fullerene additive showed a lower PCE of 17.11% with a J_{SC} of 26.65 mA cm⁻², a V_{OC} of 0.87 V and an FF of 73.91%. Additionally, the external quantum efficiency (EQE) in the 300–1000 nm range was measured. The J_{SC} values were in good agreement with the values achieved from the J - V measurements within a 5% mismatch (25.61 and 26.48 mA cm⁻²) (for details, see ESI†). These results revealed that the C₆₀-fused dihydroindolizine **2d** was a beneficial third-component material in the active layer of OSCs.

In summary, the copper-catalyzed dearomative N -heteroannulation reaction of C₆₀ with electron-withdrawing group-substituted 2-picolines has been successfully developed for the synthesis of C₆₀-fused dihydroindolizines. This method possesses the merits of a high yield of up to 71% and a broad substrate scope compatible with different electron-withdrawing groups. A plausible mechanism for the construction of C₆₀-fused dihydroindolizines has been proposed based on control experiments. The representative product **2d** has also been utilized as the third component in OSCs and has shown an improved performance.

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Data availability

The data supporting the findings of this study are available in the ESI† of this article.

Conflicts of interest

There are no conflicts to declare.

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