Supporting Information

For

Copper-catalyzed oxidation of arene-fused cyclic amines to cyclic imides

Xiaoyu Yan\textsuperscript{a}, Kun Fang\textsuperscript{a}, Hailan Liu\textsuperscript{a}, Chanjuan Xi\textsuperscript{a,b,*}

\textsuperscript{a}Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China
\textsuperscript{b}State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China
Email: cjxi@tsinghua.edu.cn

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**General Considerations**

All manipulations were conducted in sealed tube under an atmosphere of air. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Isoindolines 1a-1k were prepared by reaction of 1,2-bis(bromomethyl)benzene with amine in the present of base. Compound 1l was prepared by reaction of 1,8-bis(bromomethyl)naphthalene with methanamine. N,N-bispropargylamine was prepared by A³ coupling. ¹H NMR and ¹³C NMR spectra were recorded on 300 MHz and 400 MHz NMR spectrometer with TMS as internal standard. Mass spectra were obtained using a Bruker Esquire ion trap mass spectrometer in positive ion mode. Flash column chromatography was performed on silica gel and Al₂O₃ (200-300 mesh).
Experimental Procedures

General procedure for copper-catalyzed oxidation of isoindoline

To a 25 mL tube with teflon-coated magnetic stir bar and a rubber septum, was added isoindoline 1 (0.4 mmol), CuCl (0.04 mmol), CH₂Cl₂ 1 mL, TBHP (0.55 mL, 4 mmol, 70% in water). The tube was sealed and stirred for 24 h at 50 ºC. The reaction mixture was quenched by water and extracted by ethyl acetate. The organic extract was dried over MgSO₄. Removing the solvent and subsequent purification by column chromatography on Al₂O₃ afforded 2.

Procedure for copper-catalyzed oxidation of isoindoline on 5 mmol scale

To a 100 mL tube with teflon-coated magnetic stir bar and a rubber septum, was added isoindoline 1 (5 mmol), CuCl (0.5 mmol), CH₂Cl₂ 13 mL, TBHP (6.9 mL, 50 mmol, 70% in water). The tube was sealed and stirred for 24 h at 50 ºC. The reaction mixture was quenched by water and extracted by ethyl acetate. The organic extract was dried over MgSO₄. Removing the solvent and subsequent purification by column chromatography on Al₂O₃ afforded 2a (589 mg).

Procedure for copper-catalyzed oxidation of isoindoline on 10 mmol scale

To a 100 mL tube with teflon-coated magnetic stir bar and a rubber septum, was added isoindoline 1e or 1g (10 mmol), CuCl (1 mmol), CH₂Cl₂ 25 mL, TBHP (13.7 mL, 100 mmol, 70% in water). The tube was sealed and stirred for 24 h at 50 ºC. The reaction mixture was quenched by water and extracted by ethyl acetate. The organic extract was dried over MgSO₄. Removing the solvent and subsequent purification by column chromatography on Al₂O₃ afforded 2e (995 mg) or 2g (825 mg).

2-Butylisoindoline-1,3-dione, 2a

68% isolated yield. ^1H NMR (400 MHz, CDCl₃) δ 7.84-7.80 (m, 2H), 7.71-7.67 (m, 2H), 3.67 (t, J = , 2H), 1.68-1.60 (m, 2H), 1.40-1.31 (m, 2H), 0.93 (t, J = , 3H); ^13C NMR (100 MHz, CDCl₃) δ 168.5, 133.9, 132.3, 123.2, 37.9, 30.7, 20.2, 13.7. GC-MS: 203.

2-Octylisoindoline-1,3-dione, 2b

73% isolated yield. ^1H NMR (300 MHz, CDCl₃) δ 7.84-7.80 (m, 2H), 7.72-7.68
(m, 2H), 3.66 (t, J = 7.2 Hz, 2H), 1.70-1.62 (m, 2H), 1.43-1.24 (m, 10H), 0.85 (t, J = 6.4 Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.5, 133.9, 132.3, 123.2, 38.2, 31.9, 29.2, 28.7, 27.0, 22.7, 14.2. GC-MS: 259.

2-(\textit{Tert}-butyl)-isoindoline-1,3-dione, 2c\(^7\)

71% isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77-7.74 (m, 2H), 7.69-7.65 (m, 2H), 1.69 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.8, 133.7, 132.2, 122,7, 57.9, 29.2. GC-MS: 203.

2-Allylisoindoline-1,3-dione, 2d\(^8\)

45% isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\))\(\delta\) 7.86-7.83 (m, 2H), 7.73-7.69 (m, 2H), 5.93-5.83 (m, 1H), 5.27-5.17 (m, 2H), 4.30-4.27 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.0, 134.0, 132.2, 131.6, 123.4, 117.8, 40.1. GC-MS: 187.

2-Benzylisoindoline-1,3-dione, 2e\(^5\)

48% isolated yield. \(^1\)H NMR (300 MHz, CDCl\(_3\))\(\delta\) 7.85-7.80 (m, 2H), 7.71-7.67 (m, 2H), 7.45-7.25 (m, 5H), 4.84 (s, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 168.1, 136.5, 134.0, 132.2, 128.8, 128.7, 127.9, 123.4, 41.7. GC-MS: 237.

Methyl 2-(1,3-dioxoisoindolin-2-yl)acetate, 2f\(^7\)

40% isolated yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.90-7.85 (m, 2H), 7.77-7.73(m, 2H), 4.45 (s, 2H), 3.76 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 167.5, 134.3, 132.1, 123.7, 52.8, 38.9. GC-MS: 219.

2-Phenylisoindoline-1,3-dione, 2g\(^5\)

42% isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98-7.94 (m, 2H), 7.81-7.77 (m, 2H), 7.53-7.39 (m, 5H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.4, 134.5, 131.9, 131.8, 129.2, 128.2, 126.7, 123.8. GC-MS: 223.

2-(4-Chlorophenyl)isoindoline-1,3-dione, 2h\(^5\)

47% isolated yield. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.98-7.93 (m, 2H), 7.83-7.78 (m, 2H), 7.52-7.46 (m, 2H), 7.44-7.38 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.1, 134.7, 133.9, 131.7, 130.3, 129.4, 127.8, 124.0. GC-MS: 257.

2-(4-Isopropylphenyl)isoindoline-1,3-dione, 2i

30% isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96-7.94(m, 2H),7.80-7.77 (m, 2H), 7.38-7.33 (m, 4H), 3.00-2.94 (m, 1H), 1.29 (d, J = 6.9 Hz, 6H); \(^{13}\)C NMR
(100 MHz, CDCl₃) δ 167.5, 149.0, 134.4, 131.9, 129.3, 127.3, 126.5, 123.9, 34.0, 24.0. GC-MS: 265.

2-(Naphthalen-2-yl)isoindoline-1,3-dione 2j

57% isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 7.99-7.94 (m, 4H), 7.90-7.88 (m, 2H), 7.82-7.79 (m, 5H), 13C NMR (100 MHz, CDCl₃) δ 167.5, 134.5, 133.4, 132.7, 129.2, 129.1, 128.3, 127.8, 126.8, 126.7, 125.6, 124.3, 123.9. GC-MS: 273.

2-Butyl-5-chloroisoindoline-1,3-dione, 2k

48% isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 7.79-7.75 (m, 2H), 7.65 (q, J = 7.8 Hz, 1.8 Hz, 1H), 3.67 (t, J = 7.3 Hz, 2H), 1.68-1.60 (m, 2H), 1.40-1.30 (m, 2H), 0.93 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 167.2, 140.6, 133.9, 130.3, 124.4, 123.7, 38.1, 30.6, 20.1, 13.6. GC-MS: 237.

2-Methyl-1H-benzo[de]isoquinoline-1,3(2H)-dione, 2l

75% isolated yield. ¹H NMR (300 MHz, CDCl₃) δ 8.50 (d, J = 7.2 Hz, 2H), 8.13 (d, J = 8.3 Hz, 2H), 7.68 (dd, J = 8.3, 7.2 Hz, 2H), 3.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 164.4, 133.9, 131.5, 131.2, 128.0, 126.9, 122.5, 27.0. GC-MS: 211.

**General procedure for preparation of TPD**

To a solution of Cp₂ZrCl₂ (702 mg, 2 mmol) in 10 mL of THF, BuLi (1.6 M in hexane, 4.8 mmol), was added at -78 °C and the mixture was stirred for 1 h at the same temperature. To this solution, N,N-bis(3-phenylprop-2-yn-1-yl)butan-1-amine (2.0 mmol) was added and stirred for 3 h at room temperature. Then, S₂Cl₂ (3 mmol) was added and stirred overnight. The reaction mixture was quenched by water and extracted by ethyl acetate. The organic extract was dried over MgSO₄. Removing the solvent and subsequent purification by column chromatography on silica gel afforded 3a in 64% isolated yield.¹¹ 3b was prepared in 57% isolated yield by using similar procedure with N,N-bis(3-(thiophen-2-yl)prop-2-yn-1-yl)butan-1-amine as starting material.

To a 25 mL tube with teflon-coated magnetic stir bar and a rubber septum, was added 3 (0.4 mmol), CuCl (0.04 mol), CH₂Cl₂ 1 mL, TBHP (4 mmol, 70% in water). The tube was sealed and stirred for 24 h at 50°C. The reaction mixture was quenched by water and extracted by ethyl acetate. The organic extract was dried over MgSO₄.
Removing the solvent and subsequent purification by column chromatography on Al₂O₃ afforded 4.

5-Butyl-1,3-diphenyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 4a.

82% isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 8.14-8.12 (m, 4H), 7.50-7.41 (m, 6H), 3.68 (t, J = 7.3 Hz, 2H), 1.71-1.63 (m, 2H), 1.42-1.36 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 145.1, 130.7, 130.5, 130.2, 129.1, 128.2, 38.4, 30.6, 20.3, 13.8. HRMS calcd for C₂₂H₁₉NO₂S 361.1136, found 361.1131.

5-Octyl-1,3-di(thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione, 4b.

55% isolated yield. ¹H NMR (300 MHz, CDCl₃) δ 8.01 (d, J = 3.8 Hz, 2H), 7.43 (d, J = 5.2 Hz, 2H), 7.14-7.10 (m, 2H), 3.66 (t, J = 7.2 Hz, 2H), 1.72-1.63 (m, 2H), 1.42-1.20 (m, 10H), 0.87 (t, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 162.7, 136.6, 132.5, 130.0, 128.7, 128.5, 38.7, 31.9, 29.3, 29.2, 28.6, 27.0, 22.7, 14.2. HRMS calcd for C₂₂H₂₃NO₂S₃ 429.0891, found 429.0893.
**Proposed mechanism**

Based on the results, a plausible mechanism was proposed as follow. Firstly, amine 1 was oxidized to radical cation 7 in the present of TBHP and CuCl. 7 was further oxidized to iminium 8. 8 reacted with water to yield compound 9, which was then oxidized to amide 10. 10 was further oxidized to form 11, which reacted with TBHP to give 12. Oxidation of 12 afforded imide 13.
References

X-ray structure of 4a

ORTEP drawing of C$_{22}$H$_{19}$NO$_2$S with 35% probability ellipsoids, showing the atomic numbering scheme.
Copies of $^1$H and $^{13}$C NMR Spectra

$^1$H NMR for compound 2a
$^{13}$C NMR for compound 2a
$^1$H NMR for compound 2b
$^{13}$C NMR for compound 2b
$^1$H NMR for compound 2c
$^{13}$C NMR for compound 2c
$^{1}$H NMR for compound 2d
$^{13}$C NMR for compound 2d
$^1$H NMR for compound 2e
$^{13}$C NMR for compound 2e
$^1$H NMR for compound 2f
$^{13}$C NMR for compound 2f
$^1$H NMR for compound 2g
$^{13}$C NMR for compound 2g
$^1$H NMR for compound 2h
$^{13}$C NMR for compound 2h
$^1$H NMR for compound 2i

S26
$^{13}$C NMR for compound 2i
$^1$H NMR for compound 2j
$^{13}$C NMR for compound 2j
$^1$H NMR for compound 2k
$^{13}$C NMR for compound 2k
$^1$H NMR for compound 21
\[ ^{13}\text{C} \text{NMR for compound 2l} \]
$^1$H NMR for compound 4a
$^{13}$C NMR for compound 4a
$^1$H NMR for compound 4b

S36
$^{13}$C NMR for compound 4b