Supporting Information

Transition Metal-Free Oxidative ortho-Acylation of Phenols with N-Heteroarylmethanes via Double C-H Activation

Min Liu, Tieqiao Chen,* Yongbo Zhou, Shuang-Feng Yin*

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

E-mail: chentieqiao@hnu.edu.cn; sf_yin@hnu.edu.cn

General information
All reactions were carried out under O₂ atmosphere (1 atm) using standard Schlenk technique in the parallel synthesizer. All reagent/reactant were commercial available except other noted (CF₃COOH and PhCl were purchased from Aladdin). Solvents (including r1eagent DMSO) used were purified according to the <Purification_of_Laboratory_Chemicals>. Column chromatography was performed using Silica Gel 60 (particle size 37-54 μm). The pure products were obtained by column chromatography using ethyl acetate/petroleum ether as an eluent. GC analysis was performed on GC 7820A (Shimadzu). GC-MS results were recorded on GC-MS QP2010 (Shimadzu). The ¹H NMR and ¹³C NMR data were acquired on a Brucker ADVANCE III spectrometer (400 MHz for ¹H NMR spectroscopy and 100 MHz for ¹³C NMR spectroscopy). Exact mass was conducted by the Analytical Center of State Key Laboratory of Chemo/Biosensing and Chemometrics at Hunan University, China.

Preparation of quinolin-2-ylmethanol 6a¹
To a 100 mL round bottom flask charged with 3a (1 g, 6.4 mmol) and a stir bar, 40 mL anhydrous THF was added. With stirring, NaBH₄ (0.37 g, 9.6 mmol) was added. The solution was further stirred for 15-30 min at room temperature. The mixture was quenched with 15 mL H₂O and kept stirring for 30 min, the solution was then extracted with EA (4 × 10 mL), the upper layer was dried over Na₂SO₄ and concentrated to afford 6a (light yellow solid, 0.95g, 95% yield).

Preparation of 2-(iodomethyl)quinolone 4a²
To a 100 mL glass tube charged with Cul (1.1 g, 6mmol), PhCOOH (0.73 g, 6 mmol) and a stir bar, 20 mL anhydrous THF/CH₃OH (ratio = 15:5) was added under N₂ atmosphere. With stirring, 1a (0.7 mL, 5 mmol) was added over 30 min, then a solution of 70% aqueous TBHP (2 mL, 15 mmol) was added slowly. The mixture was stirred overnight at 85 °C and then cooled to room temperature. Transfer the upper red organic layer, the mixture and the upper layer were quenched with 10-20 mL saturated Na₂S₂O₃ solution and kept stirring for 30 min. Then the solution was
extracted with CH₂Cl₂ (4×10 mL) and washed with brine (3×20 mL) together with the first partial separated. The lower layer was dried over Na₂SO₄ (10-30 min) and concentrated, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate = 20/1 as eluent) to afford analytically pure product 4a (light yellow solid, 0.54 g, 40%).

**Preparation of 2,4-dimethyl-6-(quinolin-2-ylmethyl)phenol 5a³**
To a 100 mL schlenk tube charged with 3aa (0.28 g, 1 mmol), NaBH₄ (0.23 g, 6 mmol), AlCl₃ (0.33 g, 2.5 mmol) and a stir bar, 20 mL anhydrous THF was added under N₂. The solution was stirred for 3 h at 85°C and then cooled to room temperature. The mixture was quenched with 30 mL H₂O and kept stirring for 30 min, the color of the solution turned to purple from claybank. Then the solution was extracted with DCM (3×20 mL). The lower layer was dried over Na₂SO₄ and concentrated, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 5a (white solid, 0.20 g, 75%).

**Preparation of 1-methoxy-2,4-dimethylbenzene 4a⁴**
To a 50 mL schlenk tube charged with NaH (0.19 g, 8 mmol) and a stir bar, 20 mL anhydrous DMF was added under N₂ atmosphere. With stirring, 1b (0.6 mL, 5 mmol) was added and then the solution was cooled to 0°C for 30 min, CH₃I (0.6 mL, 6 mmol) was added dropwise at 0°C. The solution was stirred for 2 h at room temperature. The mixture was quenched with 10 mL H₂O and kept stirring for 30 min. Then the solution was extracted with EA (4×10 mL), the upper layer was dried over Na₂SO₄ and concentrated to afford 4a (colorless oil, 0.65 g, 96% yield).

**Characterization and analytical data of products**

![3a](image)

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120°C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3a (Yellow solid, m.p. 111.7-112.3°C.). ¹H NMR (400 MHz, CDCl₃) δ 12.50 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.82 (dd, J = 7.2 Hz, J = 8.4 Hz, 1H), 7.73 (s, 1H), 7.67 (dd, J = 7.6 Hz, J = 7.2 Hz, 1H), 7.23 (s, 1H), 2.30 (s, 3H), 2.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.10, 160.19, 155.31, 146.45, 139.01, 137.39, 131.55, 130.41, 130.20, 128.65, 128.37, 127.71, 127.24, 127.11, 120.61, 118.18, 20.54, 15.67. HRMS (EI) m/z: [M] Calcd for C₁₈H₁₅NO₂ 277.1103, Found 277.1099.
An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 2,4-di-tert-butylphenol (0.6 mmol, 123.6 mg), degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF$_3$COOH (0.2 mmol, 15 uL) was charged into the tube under O$_2$ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3b (Yellow solid, m.p.104.9-105.7 °C.).

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.83 (s, 1H), 8.26 (d, $J = 8.8$ Hz, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 8.03 (d, $J = 2.4$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.68-7.72 (m, 1H), 7.54-7.58 (m, 2H), 1.39 (s, 9H), 1.16 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.73, 161.84, 155.53, 146.58, 139.90, 137.80, 137.29, 131.96, 130.42, 130.24, 128.89, 128.60, 128.36, 127.72, 120.84, 117.85, 35.26, 34.33, 31.32, 29.49. HRMS (EI) m/z: [M] Calcd for C$_{24}$H$_{27}$NO$_2$ 361.2042, Found 361.2027.

An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 2-(tert-butyl)-4-methylphenol (0.6 mmol, 98.4 mg), degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF$_3$COOH (0.2 mmol, 15 uL) were charged into the tube under O$_2$ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3c (Yellow oil.).

$^1$H NMR (400 MHz, CDCl$_3$) δ 12.76 (s, 1H), 8.29 (d, $J = 8.4$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.74 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H), 7.60 (dd, $J = 7.6$ Hz, $J = 7.2$ Hz, 1H), 7.55 (s, 1H), 7.28 (s, 1H), 2.15 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.19, 160.84, 154.61, 145.59, 137.33, 136.28, 134.57, 130.84, 129.34, 129.26, 127.50, 127.21, 126.68, 125.74, 119.49, 117.22, 33.91, 28.37, 19.88. HRMS (EI) m/z: [M] Calcd for C$_{21}$H$_{21}$NO$_2$ 319.1572, Found 319.1563.

An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 4-methoxy-2-methylphenol (0.6 mmol, 82.8 mg), the tube was degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol,
42 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3d (Yellow solid, m.p. 132.4-133.8 °C.). ¹H NMR (400 MHz, CDCl₃) δ 12.51 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.83 (dd, J = 7.2 Hz, J = 8.0 Hz, 1H), 7.67-7.70 (m, 2H), 7.09 (s, 1H), 3.72 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.94, 157.22, 155.10, 154.83, 150.91, 146.31, 137.54, 130.52, 130.14, 128.74, 128.57, 127.74, 126.57, 120.84, 117.90, 113.35, 55.72, 16.04. HRMS (EI) m/z: [M] Calcd for C₁₈H₁₅NO₃ 293.1052, Found 293.1051.

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), 2,5-dimethylphenol (0.6 mmol, 73.3 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3e (Yellow oil.). ¹H NMR (400 MHz, CDCl₃) δ 11.65 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.80 (dd, J = 7.6 Hz, J = 8.0 Hz, 1H), 7.67 (dd, J = 7.6 Hz, J = 7.2 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 6.67 (d, J = 7.2 Hz, 1H), 2.32 (s, 3H), 2.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 199.70, 157.13, 156.48, 146.02, 138.32, 137.29, 134.74, 130.78, 129.69, 129.13, 128.72, 127.79, 125.13, 124.26, 122.38, 119.61, 22.05, 16.14. HRMS (EI) m/z: [M] Calcd for C₁₈H₁₅NO₂ 277.1103, Found 277.1112.

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), 3,5-dimethylphenol (0.6 mmol, 73.2 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3f (Yellow oil.). ¹H NMR (400 MHz, CDCl₃) δ 11.86 (s, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.83-7.89 (m, 2H), 7.73 (dd, J = 7.2 Hz, J = 8.0 Hz, 1H), 7.60 (dd, J = 7.2 Hz, J = 7.6 Hz, 1H), 6.71 (s, 1H), 6.52 (s, 1H), 2.25 (s, 3H), 1.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.74, 159.61, 156.56, 154.92, 145.11, 140.25, 138.31, 130.80, 129.57, 129.07, 128.67, 127.79, 124.38, 121.94, 119.69, 116.91, 22.42, 21.63. HRMS (EI) m/z: [M] Calcd for C₁₈H₁₅NO₂ 277.1103, Found 277.1112.
An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), and phenol (0.6 mmol, 56.4 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3h (Yellow solid, m.p. 116.8-117.7 °C.). ¹H NMR (400 MHz, CDCl₃) δ 12.66 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.22-8.27 (m, 2H), 8.01 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.83 (dd, J = 7.2 Hz, J = 8.0 Hz, 1H), 7.69 (dd, J = 7.2 Hz, J = 7.6 Hz, 1H), 7.54 (dd, J = 7.6 Hz, J = 8.0 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 197.18, 163.42, 154.72, 146.19, 137.68, 136.78, 134.62, 130.58, 128.82, 128.66, 127.75, 120.76, 119.57, 118.95, 118.60. HRMS (EI) m/z: [M] Calcd for C₁₆H₁₁NO₂ 249.0790, Found 249.0787.

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), and p-cresol (0.6 mmol, 64.9 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3i (Yellow solid, m.p. 78.5-79 °C.). ¹H NMR (400 MHz, CDCl₃) δ 12.50 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.92-7.99 (m, 2H), 7.83 (dd, J = 7.2 Hz, J = 804 Hz, 1H), 7.69 (dd, J = 7.2 Hz, J = 7.6 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.19, 161.32, 154.91, 146.20, 137.95, 137.66, 134.00, 130.56, 130.05, 128.60, 128.58, 128.04, 127.76, 120.73, 119.28, 118.42, 20.56. HRMS (EI) m/z: [M] Calcd for C₁₇H₁₃NO₂ 263.0946, Found 263.0952.

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), o-cresol (0.6 mmol, 64.9 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF₃COOH
(0.2 mmol, 15 uL) were charged into the tube under O\textsubscript{2} atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3j (Yellow solid. m.p. 82.3-82.6 °C). ^{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 12.67 (s, 1H), 8.36 (d, \( J = 8.4 \) Hz, 1H), 8.22 (d, \( J = 8.4 \) Hz, 1H), 8.03 (d, \( J = 8.0 \) Hz, 1H), 7.90-7.96 (m, 2H), 7.81 (dd, \( J = 7.2 \) Hz, \( J = 8.4 \) Hz, 1H), 7.67 (dd, \( J = 7.6 \) Hz, \( J = 7.2 \) Hz, 1H), 7.40 (d, \( J = 6.8 \) Hz, 1H), 6.81 (t, \( J = 7.6 \) Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 198.11, 162.25, 155.12, 146.44, 137.62, 137.43, 132.27, 130.43, 130.25, 128.68, 128.46, 127.71, 127.39, 120.66, 118.44, 118.27, 15.76. HRMS (EI) m/z: [M] Calcd for C\textsubscript{17}H\textsubscript{13}NO\textsubscript{2} 263.0946, Found 263.0939.

An oven-dried Schlenk tube containing a stir bar was charged with I\textsubscript{2} (0.06 mmol, 15.3 mg), the tube was degassed and refilled with O\textsubscript{2} for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), 4-butylphenol (0.6 mmol, 92 uL), CF\textsubscript{3}COOH (0.2 mmol, 15 uL) were charged into the tube under O\textsubscript{2} atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3ag (Yellow oil). ^{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 12.48 (s, 1H), 8.39 (d, \( J = 8.4 \) Hz, 1H), 8.21 (d, \( J = 8.4 \) Hz, 1H), 8.00 (m, 2H), 7.93 (d, \( J = 8.0 \) Hz, 1H), 7.83 (dd, \( J = 7.6 \) Hz, \( J = 8.0 \) Hz, 1H), 7.69 (dd, \( J = 7.6 \) Hz, \( J = 7.6 \) Hz, 1H), 7.37 (d, \( J = 8.4 \) Hz, 1H), 7.01 (d, \( J = 8.4 \) Hz, 1H), 2.54 (t, \( J = 7.6 \) Hz, 2H), 1.52-1.59 (m, 2H), 1.31-1.37 (m, 2H), 0.90 (t, \( J = 7.6 \) Hz, 3H); ^{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 197.15, 161.47, 154.88, 146.20, 137.63, 133.64, 133.09, 130.56, 130.05, 128.82, 128.60, 127.76, 120.80, 119.23, 118.35, 34.65, 33.58, 22.14, 13.97. HRMS (EI) m/z: [M] Calcd for C\textsubscript{20}H\textsubscript{19}NO\textsubscript{2} 305.1416, Found 305.1414.

An oven-dried Schlenk tube containing a stir bar was charged with I\textsubscript{2} (0.06 mmol, 15.3 mg), 4-isopropylphenol (0.6 mmol, 81.7 mg), the tube was degassed and refilled with O\textsubscript{2} for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), 4-butylphenol (0.6 mmol, 92 uL), CF\textsubscript{3}COOH (0.2 mmol, 15 uL) were charged into the tube under O\textsubscript{2} atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3l (Yellow oil). ^{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 12.43 (s, 1H), 8.29 (d, \( J = 8.8 \) Hz, 1H), 8.13 (d, \( J = 8.8 \) Hz, 1H), 8.08 (s, 1H), 7.94 (d, \( J = 8.8 \) Hz, 1H), 7.84 (d, \( J = 8.0 \) Hz, 1H), 7.74 (dd, \( J = 7.6 \) Hz, \( J = 7.6 \) Hz, 1H), 7.60 (dd, \( J = 7.6 \) Hz, \( J = 7.2 \) Hz, 1H),
7.34 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 2.73-2.80 (m, 1H), 1.13 (d, J = 6.8 Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 196.94, 161.57, 154.83, 146.18, 139.07, 137.65, 135.49, 131.79, 130.60, 130.03, 128.83, 128.65, 127.77, 120.86, 119.24, 118.39, 33.24, 23.99. HRMS (EI) m/z: [M] Calcd for C\(_{19}\)H\(_{17}\)NO\(_2\) 291.1259, Found 291.1254.

An oven-dried Schlenk tube containing a stir bar was charged with I\(_2\) (0.06 mmol, 15.3 mg), 4-(tert-butyl)phenol (0.6 mmol, 90 mg), the tube was degassed and refilled with O\(_2\) for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF\(_3\)COOH (0.2 mmol, 15 uL) were charged into the tube under O\(_2\) atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3m (Yellow solid, m.p. 126.3-126.7 °C.). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 12.52 (s, 1H), 8.47 (b, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.82 (dd, J = 7.2 Hz, J = 8.0 Hz, 1H), 7.67 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.60 (dd, J = 2.4 Hz, J = 8.8 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 1.29 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 196.77, 161.37, 154.83, 146.19, 141.36, 137.60, 134.47, 130.99, 130.60, 130.02, 128.83, 128.68, 127.77, 120.95, 118.85, 118.09, 34.21, 31.31. HRMS (EI) m/z: [M] Calcd for C\(_{20}\)H\(_{19}\)NO\(_2\) 305.1416, Found 305.1416.

An oven-dried Schlenk tube containing a stir bar was charged with I\(_2\) (0.06 mmol, 15.3 mg), 4-(tert-pentyl)phenol (0.6 mmol, 98.5 mg), the tube was degassed and refilled with O\(_2\) for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF\(_3\)COOH (0.2 mmol, 15 uL) were charged into the tube under O\(_2\) atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3n (Yellow solid, m.p. 82.6-83.5 °C.). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 12.47 (s, 1H), 8.39 (d, J = 7.6 Hz, 2H), 8.20 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.83 (dd, J = 7.2 Hz, J = 7.4 Hz, 1H), 7.69 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 1.57-1.63 (m, 2H), 1.25 (s, 6H), 0.70-0.74 (t, J = 7.2 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 196.89, 161.29, 154.85, 146.22, 139.60, 137.57, 134.96, 131.87, 130.58, 130.06, 128.83, 128.66, 127.76, 120.98, 118.81, 118.00, 37.41, 36.67, 28.46, 9.17. HRMS (EI) m/z: [M] Calcd for C\(_{21}\)H\(_{21}\)NO\(_2\) 319.1572, Found 319.1572.
An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 1,1'-biphenyl]-4-ol (0.6 mmol, 102 mg), the tube was degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylquinoline (0.2 mmol, 27 uL), DMSO (0.6 mmol, 42 uL), CF$_3$COOH (0.2 mmol, 15 uL) was charged into the tube under O$_2$ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3o (Yellow solid, m.p. 142.6-144.3 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.81 (s, 1H), 8.59 (s, 1H), 8.41 (d, $J$ = 8.4 Hz, 1H), 8.24 (d, $J$ = 8.8 Hz, 1H), 8.08 (d, $J$ = 8.8 Hz, 1H), 7.94 (d, $J$ = 8.4 Hz, 1H), 7.78-7.86 (m, 2H), 7.70 (dd, $J$ = 7.6 Hz, $J$ = 7.2 Hz, 1H), 7.54 (d, $J$ = 7.6 Hz, 2H), 7.39 (t, $J$ = 7.4 Hz, 2H), 7.29 (dd, $J$ = 7.2 Hz, $J$ = 7.2 Hz, 1H), 7.18 (d, $J$ = 8.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 196.69, 162.64, 154.58, 146.11, 140.13, 137.84, 135.48, 132.88, 132.09, 130.72, 130.02, 128.94, 128.84, 128.81, 127.78, 126.96, 126.64, 120.89, 119.89, 119.16. HRMS (EI) m/z: [M] Calcd for C$_{22}$H$_{15}$NO$_2$ 325.1103, Found 325.1097.

An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 2,6-dimethylquinoline (0.2 mmol, 31.4 mg), the tube was degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF$_3$COOH (0.2 mmol, 15 uL) were charged into the tube under O$_2$ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3q (Yellow oil). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.60 (s, 1H), 8.25 (d, $J$ = 8.8 Hz, 1H), 8.11 (d, $J$ = 8.4 Hz, 1H), 7.90 (d, $J$ = 8.4 Hz, 1H), 7.75 (s, 1H), 7.63-7.66 (m, 2H), 7.22 (s, 1H), 2.59 (s, 3H), 2.30 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.01, 160.05, 154.42, 144.98, 138.87, 138.74, 136.64, 132.78, 131.59, 129.83, 128.77, 127.18, 127.08, 126.52, 120.72, 118.38, 21.80, 20.57, 15.74. HRMS (EI) m/z: [M] Calcd for C$_{19}$H$_{17}$NO$_2$ 291.1259, Found 291.1257.

An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 6-methoxy-2-methylquinoline (0.2 mmol, 34.6 mg), the tube was degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2a 2,4-dimethylphenol (0.6 mmol, 72 uL), CF$_3$COOH (0.2 mmol, 15 uL) were charged into the tube under O$_2$ atmosphere
successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3r (Yellow solid, m.p. 145.2-146.0 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.55 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 9.2 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 7.37 (d, J = 10.4 Hz, 1H), 7.14 (s, 1H), 7.07 (s, 1H), 3.90 (s, 3H), 2.22 (s, 3H), 2.15 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.72, 159.98, 159.38, 152.89, 142.42, 138.76, 135.85, 131.66, 130.14, 127.13, 127.04, 123.49, 121.23, 118.45, 104.90, 55.72, 20.58, 15.76. HRMS (EI) m/z: [M] Calcd for C$_{19}$H$_{17}$NO$_3$ 307.1208, Found 307.1208.

An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 6-fluoro-2-methylquinoline (0.2 mmol, 32.2 mg), the tube was degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF$_3$COOH (0.2 mmol, 15 uL) were charged into the tube under O$_2$ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3s (Yellow solid, m.p. 116.8-117.7 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.38 (s, 1H), 8.31 (d, J = 8.8 Hz, 1H), 8.21-8.25 (m, 1H), 7.94 (d, J = 8.8 Hz, 1H), 7.73 (s, 1H), 7.52-7.59 (m, 2H), 7.25 (s, 1H), 2.31 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.82, 161.60 (J$_{F-C}$ = 250.0 Hz), 160.37, 154.79, 143.59, 139.12, 136.70 (J$_{F-C}$ = 5.6 Hz), 132.90 (J$_{F-C}$ = 9.4 Hz), 131.46, 129.50 (J$_{F-C}$ = 10.3 Hz), 127.20 (J$_{F-C}$ = 9.7 Hz), 121.44, 120.98, 120.72, 117.87, 110.80 (J$_{F-C}$ = 21.8 Hz), 20.58, 15.66. HRMS (EI) m/z: [M] Calcd for C$_{18}$H$_{14}$FNO$_2$ 295.1009, Found 295.1003.

An oven-dried Schlenk tube containing a stir bar was charged with I$_2$ (0.06 mmol, 15.3 mg), 6-chloro-2-methylquinoline (0.2 mmol, 35.4 mg), the tube was degassed and refilled with O$_2$ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF$_3$COOH (0.2 mmol, 15 uL) were charged into the tube under O$_2$ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3t (Yellow solid, m.p. 159.7-160.3 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 12.35 (s, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 9.2 Hz, 1H), 7.90-7.93 (m, 2H), 7.70-7.75 (m, 2H), 7.24 (s, 1H), 2.30 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.76, 160.40, 155.51, 144.87, 139.20, 136.42, 134.33, 131.83, 131.43, 129.16, 127.28, 127.16, 126.38, 121.56, 117.79, 20.58, 15.65. HRMS (EI) m/z: [M] Calcd for C$_{18}$H$_{14}$ClNO$_2$ 311.0709, Found 311.0709.
An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), 6-bromo-2-methylquinoline (0.2 mmol, 44.2 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3u (Yellow solid, m.p. 170.4-171.1 °C). ¹H NMR (400 MHz, CDCl₃) δ 12.26 (s, 1H), 8.19 (d, J = 8.8 Hz, 1H), 8.00-8.02 (m, 2H), 7.79-7.86 (m, 2H), 7.61 (s, 1H), 7.17 (s, 1H), 2.23 (s, 3H), 2.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.79, 160.42, 155.62, 145.09, 139.21, 136.33, 133.98, 131.89, 131.41, 129.77, 129.60, 127.29, 127.18, 122.60, 121.54, 117.54, 20.58, 15.64. HRMS (EI) m/z: [M] Calcd for C₁₈H₁₄BrNO₂ 355.0208, Found 355.0722.

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), methyl 2-methylquinoline-6-carboxylate (0.2 mmol, 40.2 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3v (yellow solid, m.p. 144.5-145.6 °C). ¹H NMR (400 MHz, CDCl₃) δ 12.24 (s, 1H), 8.58 (s, 1H), 8.03 (d, J = 9.2 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.29 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.16 (s, 1H), 3.94 (s, 3H), 2.21 (s, 3H), 2.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.88, 166.33, 160.47, 157.18, 148.30, 139.21, 136.33, 133.98, 131.41, 129.77, 129.60, 127.38, 127.19, 121.32, 117.67, 52.68, 20.58, 15.64. HRMS (EI) m/z: [M] Calcd for C₂₀H₁₇NO₄ 335.1158, Found 335.1149.

An oven-dried Schlenk tube containing a stir bar was charged with I₂ (0.06 mmol, 15.3 mg), 2-methylquinoloxaline (0.2 mmol, 28.8 mg), the tube was degassed and refilled with O₂ for 3 times. Then 1.5 mL of anhydrous PhCl, DMSO (0.6 mmol, 42 uL), 2,4-dimethylphenol (0.6 mmol, 72 uL), CF₃COOH (0.2 mmol, 15 uL) were charged into the tube under O₂ atmosphere successively.
Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3z (Yellow solid, m.p. 118.6-119.1 °C). 1H NMR (400 MHz, CDCl3) δ 12.17 (s, 1H), 9.32 (s, 1H), 8.23 (dd, J = 8.0 Hz, J = 7.6 Hz, 2H), 7.88-7.95 (m, 2H), 7.75 (s, 1H), 7.28 (s, 1H), 2.32 (s, 3H), 2.25 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 196.49, 160.72, 149.66, 144.83, 142.97, 140.38, 139.71, 131.95, 131.11, 131.03, 130.34, 129.47, 127.56, 127.34, 117.59, 20.59, 15.58. HRMS (EI) m/z: [M] Calcd for C17H14N2O2 278.1055, Found 278.1054.

An oven-dried Schlenk tube containing a stir bar was charged with I2 (0.06 mmol, 15.3 mg), the tube was degassed and refilled with O2 for 3 times. Then 1.5 mL of anhydrous PhCl, 2-methylbenzo[d]thiazole (0.2 mmol, 25 μL), DMSO (0.6 mmol, 42 μL), 2,4-dimethylphenol (0.6 mmol, 72 μL), CF3COOH (0.2 mmol, 15 μL) were charged into the tube under O2 atmosphere successively. Then the mixture was stirred at 120 °C for 20 h. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure product 3z (yellow solid, m.p. 129.8-131.3 °C.). 1H NMR (400 MHz, CDCl3) δ 12.22 (s, 1H), 8.81 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.54-7.63 (m, 2H), 7.29 (s, 1H), 2.36 (s, 3H), 2.30 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 188.04, 167.34, 160.91, 153.72, 139.87, 136.68, 130.81, 127.97, 127.69, 127.02, 125.70, 122.10, 117.10, 20.74, 15.73. HRMS (EI) m/z: [M] Calcd for C16H13NO2S 283.0667, Found 283.0664.

Reference
Copies of $^1$H NMR and $^{13}$C NMR spectroscopies