Supporting Information

Switchable Reactivity between Vinyl Azides and Terminal Alkyne by Nano Copper Catalysis

Jinghe Cen, Yaodan Wu, Jianxiao Li, Liangbin Huang, Wanqing Wu, Zhongzhi Zhu, Shaorong Yang* and Huanfeng Jiang*

Key Laboratory of Functional Molecular Engineering of Guangdong Province,

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

jianghf@scut.edu.cn

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1. General Information

$^1$H and $^{13}$C NMR spectra were recorded using a 400 MHz NMR spectrometer. Chemical shifts were reported in ppm from the solvent resonance as the internal reference (DMSO$_{d6}$ $\delta_H = 2.50$ ppm, downfield from TMS, $\delta_C = 39.50$ ppm. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were obtained as potassium bromide pellets between two potassium bromide pellets with a spectrometer. GC-MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer or recorded on an El-ion trap High Resolution mass spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 powder diffractometer at 40kV, 40mA with Cu Ka radiation ($\lambda=1.5406$ Å), with a step size of 0.01995 (20). TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. X-ray structural analyses were conducted on an x-ray analysis instrument.

Materials Acetonitrile was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was conducted using silica gel (200–300 mesh) with the indicated solvent system. All the reaction temperatures reported are oil bath temperatures.

2. General Procedures for the Synthesis of Substrates

Vinyl azides 2a was prepared according to the previously reported procedure with slight modification on the conditions.$^1$

$$\text{Ar} = \begin{matrix} & N_3 \end{matrix}$$

To a solution of (1,2-dibromoethyl)benzene (2.62g, 10 mmol, 1 equiv ) in dry DMF (30 mL) was added NaN$_3$ (1.95g, 30 mmol, 3 equiv). The mixture was stirred for 24 h at room temperature, then diluted with water and extracted with petroleum ether. The combined organic layers were washed three times with brine, dried with Na$_2$SO$_4$. After evaporation of solvents, the crude residue was purified by flash column chromatography (silica gel; pure petroleum ether) to give vinyl azides 2a (1.31g, 9 mmol) in 90% yield.

Vinyl azides 2b-2p was prepared according to the previously reported procedure with slight modification on the conditions.$^2$

$$\text{Ar} = \begin{matrix} & N_3 \end{matrix}$$

To a suspension of NaN$_3$ (812.5 mg, 12.5 mmol, 2.5 equiv) in acetonitrile (3 mL) was added dropwise a solution of iodine monochloride (1214.0 mg, 7.5 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (5 mL) at
-20 °C, and the mixture was stirred at the same temperature. After 30 min, a solution of 1-fluoro-2-vinylbenzene (610.3 mg, 5 mmol, 1 equiv) in CH₂Cl₂ (5 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous Na₂S₂O₃, and the organic materials were extracted two times with Et₂O. The combined extracts were washed with brine and dried over MgSO₄. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification. To a solution of the obtained compounds above in Et₂O (10 mL) was added t-BuOK (672.0 mg, 6 mmol, 1.2 equiv) at 0 °C, and the mixture was stirred for 1.5 h at the same temperature. The reaction was quenched by adding NH₄HCO₃ saturated solution, and the organic materials were extracted with ethyl acetate. The organic layer was washed with brine and dried over Na₂SO₄. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography (silica gel; pure petroleum ether) to give 1-(1-azidovinyl)-2-fluorobenzene (2b) (619.4 mg, 76% yield) as a yellow liquid.

3. Preparation and Characterization of Cu NPs Catalysts

Preparation of Catalysts. The Cu NPs catalyst was prepared by the reductive method according to the reported literature with slight modification on the conditions³. A 100 mL round-bottom flask was charged with CuSO₄ (399 mg, 2.5 mmol) and distilled water (5 mL). The resulting solution was stirred at room temperature, and then excess ammonium hydroxide was added until the precipitate dissolve and the mixture turn out to be a deep blue transparent solution. During continuous stirring, PEG600 (35 mL) was added. To this suspension a freshly prepared aqueous NaBH₄ (1 M, 20 mL) was added dropwise while it was vigorously stirred at 65 °C. Then the mixture was stirred at 65 °C for 30 min. This process was accompanied by a change in color from blue to dark which indicated the formation of the Cu NPs. The crude products were then centrifuged and the obtained precipitates were washed several times with absolute ethanol and distilled water. Finally, the Cu NPs was dried under vacuum for 24 hours at 60 °C. Pure Cu NPs (149.8 mg, 2.34 mmol) was obtained as an atropurpureus solid.

Characterization.

Figure 1. SEM image of the Cu NPs

Figure 2. XRD spectrum of the Cu NPs

4. General Procedures for CuNPs-Catalyzed Synthesize of Pyrroles

General Procedure A:
In a 25 mL sealed test tube, CuNPs (30 mol %), 5 mL of DCE, alkyne 1 (0.2 mmol) and vinyl azides 2 (0.36 mmol, 1.8 equiv) was added in sequence. The reaction mixture was sealed under a nitrogen atmosphere and vigorously stirred together at 135 °C for 3 h. After completion of the reaction, the resulting mixture was cooled to room temperature and then was filtered. The filtrate was then concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product 3.

(2) Large-scale synthesis of 3a. In a 100 mL sealed test tube, CuNPs (30 mol %, 19 mg), 20 mL of DCE, 1-ethynyl-4-methoxybenzene 1a (1 mmol, 132mg) and (1-azidovinyl)benzene 2a (1.8 mmol, 261 mg, 1.8 equiv) was added in sequence. The reaction mixture was sealed under a nitrogen atmosphere and vigorously stirred together at 135 °C for 6 h. After completion of the reaction, the resulting mixture was cooled to room temperature and then was filtered. The filtrate was then concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluent: PET: EA = 20: 1) to afford the corresponding 2-(4-methoxyphenyl)-5-phenyl-1H-pyrrole 3a (174.4 mg, 0.7 mmol) in 70% yield.

General Procedure B:

(1) In a 25 mL sealed test tube, Cu NPs (30 mol %), 5 mL of DCE, alkyne 1 (0.2 mmol) and vinyl azides 2 (0.5 mmol, 2.5 equiv) was added in sequence. The reaction mixture was sealed under a nitrogen atmosphere and vigorously stirred together at 135 °C for 3 h. After completion of the reaction, the resulting mixture was cooled to room temperature and then was filtered. The filtrate was then concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) afforded the pure product 5.

(2) In a 100 mL sealed test tube, Cu NPs (30 mol %, 19 mg), 20 mL of DCE, ethynyltrisopropylsilane 1w (1 mmol, 182 mg) and (1-azidovinyl)benzene 2a (2.5 mmol, 362.5 mg, 2.5 equiv) was added in sequence. The reaction mixture was sealed under a nitrogen atmosphere and vigorously stirred together at 135 °C for 6 h. After completion of the reaction, the resulting mixture was cooled to room temperature and then was filtered. The filtrate was then concentrated in vacuum. Further purification by flash column chromatography on silica gel (eluent: PET: EA = 10: 1) to afford the corresponding 2,4-diphenyl-3-((triisopropylsilyl) ethynyl)-1H-pyrrole 5c (251.4 mg, 0.63 mmol) in 63 % yield.
5. Optimization of the Reaction Conditions

| entry | [Cu] (mol %) | Solvent (mL) | temp. (°C) | yield of 3a (%) | yield of 3a' (%) |
|-------|-------------|--------------|------------|----------------|-----------------|
| 1     | CuI (30)    | CH\textsubscript{3}CN (4) | 135        | 5              | 40              |
| 2     | CuI (30)    | DCE (4)      | 135        | 18             | n.d.            |
| 3     | CuTC (30)   | DCE (4)      | 135        | n.d.           | 76              |
| 4     | CuCl (30)   | DCE (4)      | 135        | 45             | n.d.            |
| 5     | CuSCN (30)  | DCE (4)      | 135        | 60             | n.d.            |
| 6     | CuBr (30)   | DCE (4)      | 135        | 37             | n.d.            |
| 7     | CuCN (30)   | DCE (4)      | 135        | 48             | n.d.            |
| 8     | CuNPs (30)  | DCE (4)      | 135        | 81 (77)        | n.d.            |
| 9     | Cu dust (30)| DCE (4)      | 135        | 23             | n.d.            |
| 10    | -           | DCE (4)      | 135        | n.d.           | n.d.            |
| 11    | FeCl\textsubscript{2} (30) | DCE (4) | 135 | n.d. | n.d. |
| 12    | Pd(OAc)\textsubscript{2} (30) | DCE (4) | 135 | n.d. | n.d. |
| 13    | CuNPs (30)  | DCM (4)      | 135        | 63             | n.d.            |
| 14    | CuNPs (30)  | CH\textsubscript{3}CN (4) | 135 | n.d. | n.d. |
| 15    | CuNPs (15)  | DCE (4)      | 135        | 74             | n.d.            |
| 16    | CuNPs (50)  | DCE (4)      | 135        | 60             | n.d.            |
| 17    | CuNPs (30)  | DCE (4)      | 145        | 81             | n.d.            |
| 18    | CuNPs (30)  | DCE (4)      | 125        | 78             | n.d.            |
| 19    | CuNPs (30)  | DCE (4)      | 135        | 67             | n.d.            |
|       | CuNPs (30)  | DCE (4)      | 135        | 80             | n.d.            |
|       | CuNPs (30)  | DCE (4)      | 135        | 80             | n.d.            |

Entries 1-7: Alkyne (0.1 mmol), vinyl azides (0.18 mmol) were stirred for 3 h under a nitrogen atmosphere. Yields were determined by \textsuperscript{1}HNMR using CH\textsubscript{3}ClBr as internal standard. \textsuperscript{b}Isolated yields. \textsuperscript{c}Under air atmosphere. \textsuperscript{d}1 equiv H\textsubscript{2}O was added. \textsuperscript{e}Alkyne (0.2 mmol), vinyl azides (0.36 mmol), DCE (5 mL).

6. Recycling of Cu nanoparticles

- CuNPs (30) in DCE (4 mL) were recycled.
- CuNPs (30) in DCE (4 mL) were used in a subsequent run.
7. Analysis Data of Pyrrole Products

2-(4-Methoxyphenyl)-5-phenyl-1H-pyrrole (3a)

Yield: 77% (38.4 mg) as a yellow solid (m.p. = 162-163 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.43; $^1$H NMR (400 MHz, DMSO) δ 11.15 (s, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.71 (d, J = 8.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 2.0 Hz, 1H), 6.46 (s, 1H), 3.77 (s, 3H). $^{13}$C NMR (100 MHz, DMSO) δ 157.7, 133.2, 132.8, 132.2, 128.6, 125.6, 125.5, 125.4, 123.7, 114.1, 107.5, 106.5, 55.1 ppm; IR (KBr)/cm⁻¹ 3860, 3448, 2922, 1629, 1464, 1393, 1253, 1028, 832, 759, 682, 503; HRMS (ESI) m/z: calcd for C₁₇H₁₅NO [M+] 249.1148; found: 249.1147.

2-Phenyl-5-(p-tolyl)-1H-pyrrole (3b)

Yield: 70% (32.6 mg) as a yellow solid (m.p. = 142-143 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.75; $^1$H NMR (400 MHz, DMSO) δ 11.17 (s, 1H), 7.76 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 8.8 Hz, 3H), 6.57 (t, J = 3.0 Hz, 1H), 6.53 (t, J = 2.8 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, DMSO) δ 134.9 133.2, 132.6, 132.6, 129.9, 129.1, 128.6, 125.6, 123.9, 123.8, 107.5, 107.1, 20.7 ppm; IR (KBr)/cm⁻¹ 3781, 3455, 2920, 1621, 1456, 1396, 1056, 761, 648, 505; HRMS (ESI) m/z: calcd for C₁₇H₁₆N [M+H]⁺ 234.1277; found: 234.1274.

4-(5-Phenyl-1H-pyrrol-2-yl) aniline (3c)

Yield: 73% (34.2 mg) as a yellow solid (m.p. = 160-161 °C); TLC (petroleum ether/ethyl acetate =
10/1, v/v): \( R_f = 0.05 \); \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 10.93 (s, 1H), 7.72 (d, \( J = 8.0 \) Hz, 2H), 7.46 (d, \( J = 8.0 \) Hz, 2H), 7.34 (t, \( J = 7.6 \) Hz, 2H), 7.12 (t, \( J = 7.4 \) Hz, 1H), 6.62 (d, \( J = 8.4 \) Hz, 2H), 6.52 (s, 1H), 6.31 (s, 1H), 5.17 (s, 2H). \(^{13}\)C NMR (100 MHz, DMSO) \( \delta \) 146.9, 134.5, 132.9, 131.2, 128.5, 125.2, 125.1, 123.5, 121.1, 114.1, 107.3, 104.9 ppm; IR (KBr)/cm\(^{-1}\) 3788, 2922, 1607, 1482, 1399, 1275, 1054, 758, 675, 481; HRMS (ESI) m/z: calcd for C\(_{16}\)H\(_{15}\)N\(_2\) [M+H]\(^+\) 235.1230; found: 235.1233.

\( N, N\)-dimethyl-4-(5-phenyl-1\( H\)-pyrrol-2-yl) aniline (3d)

Yield: 82% (43.0 mg) as a brown solid (m.p. = 148-149°C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): \( R_f = 0.33 \); \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 11.06 (s, 1H), 7.77 (d, \( J = 7.6 \) Hz, 2H), 7.64 (d, \( J = 7.6 \) Hz, 2H), 7.36 (t, \( J = 7.6 \) Hz, 2H), 7.15 (t, \( J = 7.4 \) Hz, 1H), 6.77 (d, \( J = 8.4 \) Hz, 2H), 6.57 (d, \( J = 2.4 \) Hz, 1H), 6.40 (s, 1H), 2.91 (s, 6H). \(^{13}\)C NMR (100 MHz, DMSO) \( \delta \) 148.8, 134.0, 132.9, 131.5, 128.5, 125.1, 123.6, 121.3, 112.5, 107.4, 105.4, 40.1 ppm; IR (KBr)/cm\(^{-1}\) 3787, 3422, 1603, 1479, 1049, 820, 755, 685, 535; HRMS (ESI) m/z: calcd for C\(_{18}\)H\(_{19}\)N\(_2\) [M+H]\(^+\) 263.1543; found: 263.1545.

2-(4-Fluorophenyl)-5-phenyl-1\( H\)-pyrrole (3e)

Yield: 60% (28.5 mg) as a yellow crystal (m.p. = 148-149°C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): \( R_f = 0.58 \); \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 11.26 (s, 1H), 7.82-7.75 (m, 4H), 7.37 (t, \( J = 7.6 \) Hz, 2H), 7.24-7.16 (m, 3H), 6.59 (t, \( J = 2.8 \) Hz, 1H), 6.56 (t, \( J = 2.6 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO) \( \delta \) 160.6 (d, \( J = 242.7 \) Hz), 133.0, 132.5, 132.1, 129.3 (d, \( J = 3.0 \) Hz), 128.6, 125.9, 125.8 (d, \( J = 2.1 \) Hz), 123.9, 115.5, 115.3, 107.6 (d, \( J = 3.0 \) Hz) ppm; IR (KBr)/cm\(^{-1}\) 3864, 3793, 3455, 2925, 1606, 1460, 1394, 834, 760, 510; HRMS (ESI) m/z: calcd for C\(_{16}\)H\(_{13}\)F\(_{2}\)N [M+H]\(^+\) 238.1027; found: 238.1023.

2-(4-Chlorophenyl)-5-phenyl-1\( H\)-pyrrole (3f)

Yield: 57% (28.9 mg) as a yellow solid (m.p. = 153-154°C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): \( R_f = 0.58 \); \(^1\)H NMR (400 MHz, DMSO) \( \delta \) 11.32 (s, 1H), 7.79 (dd, \( J = 8.8, 8.0 \) Hz, 4H), 7.46-7.34 (m, 4H), 7.19 (t, \( J = 7.4 \) Hz, 1H), 6.63 (t, \( J = 3.0 \) Hz, 1H), 6.61 (t, \( J = 3.0 \) Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO) \( \delta \) 133.5, 132.4, 131.8, 131.4, 130.0, 128.6, 128.5, 125.9, 125.5, 124.0, 108.3, 107.8 ppm; IR (KBr)/cm\(^{-1}\) 3789, 3455, 2920, 1633, 1462, 1400, 1102, 829, 760, 683, 503; HRMS (ESI) m/z: calcd for C\(_{16}\)H\(_{13}\)ClN [M+H]\(^+\) 254.0731; found: 254.0726.

2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1\( H\)-pyrrole (3g)
Yield: 56% (32.2 mg) as a yellow solid (m.p. = 168-169 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.58; 1H NMR (400 MHz, DMSO) δ 11.48 (s, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.65 (t, J = 2.6 Hz, 1H). 13C NMR (100 MHz, DMSO) δ 136.3, 134.5, 132.2, 131.4, 128.6, 126.3, 125.7, 125.5 (dd, J = 7.6, 3.7 Hz), 125.4, 124.3, 124.0, 109.8, 108.1 ppm; IR (KBr)/cm⁻¹: 3455, 2920, 1625, 1330, 1116, 840, 762, 686, 503; HRMS (ESI) m/z: calcd for C17H13F3N [M+H]⁺ 288.0995; found: 288.0993.

2-Phenyl-5-(o-tolyl)-1H-pyrrole (3h)

Yield: 69% (32.2 mg) as a yellow crystal (m.p. = 63-64 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.80; 1H NMR (400 MHz, DMSO) δ 11.21 (s, 1H), 7.75 (d, J = 6.8 Hz, 2H), 7.50 (d, J = 7.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 6.62 (s, 1H), 6.29 (d, J = 1.6 Hz, 1H), 2.44 (s, 3H). 13C NMR (100 MHz, DMSO) δ 134.8, 132.8, 132.8, 132.3, 132.0, 130.6, 128.6, 126.5, 125.7, 125.5, 110.3, 106.8, 21.0 ppm; IR (KBr)/cm⁻¹: 3794, 3424, 1596, 1467, 1255, 1046, 750, 683, 470; HRMS (ESI) m/z: calcd for C17H16N [M+H]⁺ 234.1277; found: 234.1275.

2-Phenyl-5-(m-tolyl)-1H-pyrrole (3i)

Yield: 68% (31.7 mg) as a yellow solid (m.p. = 132-133 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.67; 1H NMR (400 MHz, DMSO) δ 11.22 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.62 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.59 (s, 2H), 2.35 (s, 3H). 13C NMR (101 MHz, DMSO) δ 137.6, 133.1, 132.9, 132.6, 128.5, 128.4, 126.5, 125.7, 124.5, 123.9, 121.2, 107.6, 107.5, 21.1 ppm; IR (KBr)/cm⁻¹: 3841, 3652, 3443, 2921, 1599, 1397, 1276, 1050, 758, 686, 499; HRMS (ESI) m/z: calcd for C17H16N [M+H]⁺ 234.1272; found: 234.1272.

2-(3-Fluorophenyl)-5-phenyl-1H-pyrrole (3j)

Yield: 63% (29.9 mg) as a yellow solid (m.p. = 116-117 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.73; 1H NMR (400 MHz, DMSO) δ 11.31 (s, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.67 (d, J = 11.2 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.2 Hz, 3H), 7.20 (t, J = 7.2 Hz, 1H), 6.98 (t, J = 8.4 Hz, 1H), 6.70 (s, 1H), 6.61 (s, 1H). 13C NMR (100 MHz, DMSO) δ 162.8 (d, J = 241.8 Hz), 134.9 (d, J = 8.6 Hz), 133.7, 132.3, 131.7 (d, J = 2.6 Hz), 130.4 (d, J = 8.8 Hz), 128.6,
126.0, 124.1, 119.9 (d, J = 2.4 Hz), 112.0 (d, J = 21.2 Hz), 110.2 (d, J = 23.0 Hz), 108.8, 107.8 ppm; IR (KBr/cm\(^{-1}\)) 3781, 3434, 2920, 1596, 1471, 1275, 1180, 1052, 846, 761, 682, 532; HRMS (ESI) m/z: calcd for C\(_{16}\)H\(_{13}\)FN [M+H]\(^+\) 238.1027; found: 238.1024.

**2-(Naphthalen-2-yl)-5-phenyl-1H-pyrrole (3k)**

Yield: 78% (42.0 mg) as a brown solid (m.p. = 162-163 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R\(_f\) = 0.68; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.46 (s, 1H), 8.34 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.91-7.83 (m, 5H), 7.51 (t, J = 7.4 Hz, 1H), 7.45-7.38 (m, 3H), 7.21 (t, J = 7.2 Hz, 1H), 6.77 (t, J = 2.8 Hz, 1H), 6.67 (t, J = 2.8 Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 133.6, 133.5, 133.0, 132.5, 131.5, 130.1, 128.6, 128.0, 127.6, 127.5, 126.5, 125.9, 125.2, 124.1, 123.5, 120.9, 108.6, 107.9 ppm; IR (KBr)/cm\(^{-1}\) 3868, 3783, 3658, 3553, 3455, 2921, 2856, 2789, 1624, 1391, 758, 685, 479; HRMS (ESI) m/z: calcd for C\(_{20}\)H\(_{16}\)N [M+H]\(^+\) 270.1277; found: 270.1272.

**2-Phenyl-5-(thiophen-2-yl)-1H-pyrrole (3l)**

Yield: 76% (34.2 mg) as a red solid (m.p. = 108-109 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R\(_f\) = 0.65; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 11.41 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 3.6 Hz, 1H), 7.39-7.33 (m, 3H), 7.19 (t, J = 7.2 Hz, 1H), 7.07 (t, J = 4.4 Hz, 1H), 6.56 (t, J = 3.0 Hz, 1H), 6.38 (t, J = 2.8 Hz, 1H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 136.0, 132.6, 132.3, 128.6, 127.8, 127.7, 125.8, 123.9, 122.8, 121.5, 108.0, 107.4 ppm; IR (KBr)/cm\(^{-1}\) 3780, 3443, 2926, 2849, 1607, 1403, 1058, 762, 681, 489; HRMS (ESI) m/z: calcd for C\(_{14}\)H\(_{12}\)NS [M+H]\(^+\) 226.0685; found: 226.0680.

**2-Cyclopropyl-5-phenyl-1H-pyrrole (3m)**

Yield: 60% (22.0 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R\(_f\) = 0.50; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 10.93 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.2 Hz, 1H), 6.34 (d, J = 2.4 Hz, 1H), 5.71 (s, 1H), 1.95-1.78 (m, 1H), 0.91-0.74 (m, 2H), 0.63 (q, J = 5.2 Hz, 2H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 138.2, 133.3, 129.6, 105.5, 104.1, 8.5, 7.3 ppm; IR (KBr)/cm\(^{-1}\) 3788, 3454, 2921, 2850, 1602, 1397, 748, 670, 472; HRMS (ESI) m/z: calcd for C\(_{13}\)H\(_{14}\)N [M+H]\(^+\) 184.1121; found: 184.1116.

**2-Cyclopentyl-5-phenyl-1H-pyrrole (3n)**

Yield: 61% (25.8 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R\(_f\) = 0.63; \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 10.81 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 6.35 (t, J = 2.8 Hz, 1H), 5.84 (t, J = 2.8 Hz, 1H), 3.10-2.95 (m, 1H), 1.99 (d, J = 3.6 Hz, 2H), 1.71 (m, 2H), 1.67-1.52 (m, 4H). \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 138.2, 133.3,
129.8, 128.5, 124.7, 123.0, 105.2, 104.6, 38.3, 33.0, 24.6 ppm; IR (KBr)/cm⁻¹ 3780, 3412, 1607, 1396, 1059, 751, 680, 474; HRMS (ESI) m/z: calcd for C₁₅H₁₈N [M+H]⁺ 212.1434; found: 212.1431.

2-Cyclohexyl-5-phenyl-1H-pyrrole (3o)

Yield: 63% (28.4 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.73; ¹H NMR (400 MHz, DMSO) δ 10.78 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.34 (t, J = 2.8 Hz, 1H), 5.79 (t, J = 2.4 Hz, 1H), 2.59-2.54 (m, 1H), 1.96 (d, J = 9.6 Hz, 2H), 1.77 (dd, J = 6.8, 2.8 Hz, 2H), 1.68 (d, J = 12.4 Hz, 1H), 1.43-1.33 (m, 4H), 1.22 (dd, J = 15.7, 6.7 Hz, 1H).

³¹C NMR (100 MHz, DMSO) δ 139.8, 133.3, 129.5, 128.5, 124.7, 123.0, 105.2, 104.0, 36.5, 32.9, 26.0, 25.7 ppm; IR (KBr)/cm⁻¹ 3793, 2920, 2850, 1601, 1395, 1051, 751, 678, 475; HRMS (ESI) m/z: calcd for C₁₆H₂₀N [M+H]⁺ 226.1590; found: 226.1588.

2-(Tert-butyl)-5-phenyl-1H-pyrrole (3p)

Yield: 58% (23.1 mg) as a colorless oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.44; ¹H NMR (400 MHz, DMSO) δ 10.55 (s, 1H), 7.64 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.31 (t, J = 2.8 Hz, 1H), 5.81 (t, J = 2.8 Hz, 1H), 1.31 (s, 9H).

¹³C NMR (100 MHz, DMSO) δ 143.4, 133.3, 130.3, 128.4, 124.9, 123.4, 104.9, 103.69, 31.39, 30.29 ppm; IR (KBr)/cm⁻¹ 3782, 3676, 2924, 1622, 1401, 659, 571, 476; HRMS (ESI) m/z: calcd for C₁₄H₁₇N [M⁺] 199.1356; found: 199.1354.

2-Isopentyl-5-phenyl-1H-pyrrole (3q)

Yield: 65% (27.7 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.53; ¹H NMR (400 MHz, DMSO) δ 10.86 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.36 (s, 1H), 5.81 (s, 1H), 2.59 (t, J = 8.0 Hz, 2H), 1.61-1.57 (m, 1H), 1.56-1.49 (m, 2H), 0.92 (d, J = 6.4 Hz, 6H).

¹³C NMR (100 MHz, DMSO) δ 134.3, 133.2, 129.5, 128.5, 124.7, 122.8, 106.0, 105.5, 38.6, 27.1, 25.1, 22.3 ppm; IR (KBr)/cm⁻¹ 3789, 3411, 2936, 1605, 1512, 1455, 1046, 754, 681, 468; HRMS (ESI) m/z: calcd for C₁₅H₂₀N [M+H]⁺ 214.1590; found: 214.1587.

2-Hexyl-5-phenyl-1H-pyrrole (3r)

Yield: 50% (22.7 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R_f = 0.44; ¹H NMR (400 MHz, DMSO) δ 10.86 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.36 (t, J = 2.8 Hz, 1H), 5.81 (t, J = 2.4 Hz, 1H), 2.57 (t, J = 7.6 Hz, 2H), 1.64-1.57 (m, 2H), 1.35-1.27 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H).
134.3, 133.3, 129.6, 128.5, 124.7, 122.9, 106.2, 105.5, 31.1, 29.4, 28.4, 27.3, 22.1, 13.9 ppm; IR (KBr/cm⁻¹) 3788, 3415, 2924, 2856, 1604, 1395, 1060, 753, 677, 472; HRMS (ESI) m/z: calcd for C₁₆H₂₂N [M+H]⁺ 228.1747; found: 228.1743.

2-Phenyl-5-(3-phenylpropyl)-1H-pyrrole (3s)

![Structure](image)

Yield: 48% (25.1 mg) as a colorless oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rₚ = 0.65; ¹H NMR (400 MHz, DMSO) δ 10.92 (s, 1H), 7.60 (d, J = 7.9 Hz, 2H), 7.30 (q, J = 7.30 Hz, 4H), 7.25-7.15 (m, 3H), 7.09 (t, J = 7.2 Hz, 1H), 6.40 (s, 1H), 5.87 (s, 1H), 2.67-2.60 (m, 4H), 1.99-1.90 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ 142.0, 133.8, 133.2, 129.7, 128.5, 128.3, 128.2, 125.6, 124.8, 122.9, 106.4, 105.5, 34.9, 31.0, 26.9 ppm; IR (KBr)/cm⁻¹ 3782, 3413, 2921, 1601, 1397, 749, 679, 471; HRMS (ESI) m/z: calcd for C₁₉H₂₀N [M+H]⁺ 262.1590; found: 262.1585.

4-(5-Phenyl-1H-pyrrol-2-yl)butanenitrile (3t)

![Structure](image)

Yield: 61% (25.6 mg) as a brown oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rₚ = 0.13; ¹H NMR (400 MHz, DMSO) δ 10.99 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.40 (t, J = 2.8 Hz, 1H), 5.89 (t, J = 2.6 Hz, 1H), 2.70 (t, J = 7.6 Hz, 2H), 2.51 (t, J = 6.8 Hz, 2H), 1.97-1.88 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ 133.1, 132.1, 130.2, 128.6, 125.0, 123.0, 120.4, 106.8, 105.6, 26.2, 25.1, 15.8 ppm; IR (KBr)/cm⁻¹ 3787, 3699, 3354, 1603, 1399, 1055, 758, 678, 470; HRMS (ESI) m/z: calcd for C₁₄H₁₅N₂ [M+H]⁺ 211.1230; found: 211.1226.

2-(4-Chlorobutyl)-5-phenyl-1H-pyrrole (3u)

![Structure](image)

Yield: 72% (33.6 mg) as an orange oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rₚ = 0.44; ¹H NMR (400 MHz, DMSO) δ 10.91 (s, 1H), 7.57 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 6.37 (t, J = 2.8 Hz, 1H), 5.83 (t, J = 2.6 Hz, 1H), 5.64 (t, J = 6.0 Hz, 2H), 2.60 (t, J = 7.2 Hz, 2H), 1.80-1.71 (m, 4H). ¹³C NMR (100 MHz, DMSO) δ 133.7, 133.2, 129.8, 128.6, 124.9, 123.0, 106.5, 105.6, 45.3, 31.7, 26.7, 26.5 ppm; IR (KBr)/cm⁻¹ 3794, 3429, 2930, 1598, 1509, 1449, 1044, 756, 685, 509; HRMS (ESI) m/z: calcd for C₁₄H₁₃ClN [M+H]⁺ 234.1044; found: 234.1040.

2-(4-Methoxyphenyl)-5-(p-tolyl)-1H-pyrrole (4a)

![Structure](image)

Yield: 75% (39.5 mg) as a yellow solid (m.p. = 192-193 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rₚ = 0.55; ¹H NMR (400 MHz, DMSO) δ 11.06 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.49 (s, 1H), 6.43 (s, 1H), 3.77 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 157.6, 134.6, 132.7, 132.4, 130.1, 129.1,
125.6, 125.3, 123.7, 114.0, 106.9, 106.3, 55.1, 20.7 ppm; IR (KBr)/cm$^{-1}$ 3893, 3457, 2930, 1641, 1254, 1034, 830, 770, 516; HRMS (ESI) m/z: calcd for C$_{18}$H$_{17}$NO [M$^+$] 263.1305; found: 263.1303.

2-(4-(Tert-butyl)phenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4b)

Yield: 77% (47.0 mg) as a white solid (m.p. = 177-178 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R$_f$ = 0.62; $^1$H NMR (400 MHz, DMSO) $\delta$ 11.09 (s, 1H), 7.68 (t, $J = 9.2$ Hz, 4H), 7.38 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.49 (t, $J = 3.0$ Hz, 1H), 6.44 (t, $J = 2.8$ Hz, 1H), 3.77 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 157.6, 147.9, 132.7, 132.3, 130.1, 125.7, 125.3, 123.6, 114.0, 106.9, 106.3, 55.1, 34.1, 31.1 ppm; IR (KBr)/cm$^{-1}$ 3626, 3455, 2960, 1641, 1529, 1462, 1260, 1034, 775, 513; HRMS (ESI) m/z: calcd for C$_{21}$H$_{24}$NO [M+H]$^+$ 306.1852; found: 306.1847.

2-(4-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4c)

Yield: 73% (39.0 mg) as a yellow solid (m.p. = 160-161 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R$_f$ = 0.55; $^1$H NMR (400 MHz, DMSO) $\delta$ 11.14 (s, 1H), 7.78 (t, $J = 6.8$ Hz, 2H), 7.20 (t, $J = 8.0$ Hz, 2H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.52 (s, 1H), 6.45 (s, 1H), 3.77 (s, 3H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 160.5 (d, $J = 242.3$ Hz), 157.7, 133.1, 131.3, 129.5 (d, $J = 3.0$ Hz), 125.6, 125.5 (d, $J = 2.1$ Hz), 125.3, 115.4 (d, $J = 21.4$ Hz), 114.1, 107.4, 106.4, 55.1 ppm; IR (KBr)/cm$^{-1}$ 3456, 2925, 1645, 1518, 1252, 1032, 835, 770, 522; HRMS (ESI) m/z: calcd for C$_{17}$H$_{14}$FNO [M+H]$^+$ 267.0544; found: 267.052.

2-(4-Chlorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4d)

Yield: 70% (39.6 mg) as a yellow solid (m.p. = 204-205 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R$_f$ = 0.38; $^1$H NMR (400 MHz, DMSO) $\delta$ 11.19 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.59 (s, 1H), 6.46 (s, 1H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 157.8, 133.6, 131.6, 130.9, 129.6, 128.5, 125.4, 125.3, 125.2, 114.1, 108.1, 106.5, 55.1 ppm; IR (KBr)/cm$^{-1}$ 3531, 3453, 2928, 1641, 1111, 1034, 833, 772, 517; HRMS (ESI) m/z: calcd for C$_{17}$H$_{14}$ClNO [M+H]$^+$ 283.0758; found: 283.0755.

2-(4-Bromophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4e)
Yield: 52% (34.0 mg) as a yellow solid (m.p. = 225-226 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.38; 1H NMR (400 MHz, DMSO) δ 11.18 (s, 1H), 7.69 (t, J = 7.6 Hz, 4H), 7.53 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.60 (t, J = 2.8 Hz, 1H), 6.46 (t, J = 2.8 Hz, 1H), 3.78 (s, 3H); 13C NMR (100 MHz, DMSO) δ 157.8, 133.7, 131.9, 131.4, 130.9, 125.6, 125.4, 125.3, 118.0, 114.1, 108.2, 106.6, 55.1 ppm; IR (KBr)/cm⁻¹ 3900, 3777, 3544, 3448, 2922, 1624, 1397, 1043, 831, 774, 495; HRMS (ESI) m/z: calcd for C17H14BrNO [M⁺] 327.0253; found: 327.0252.

2-(4-Methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (4f)

Yield: 81% (51.4 mg) as a white solid (m.p. = 196-197 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.45; 1H NMR (400 MHz, DMSO) δ 11.37 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.75 (t, J = 2.8 Hz, 1H), 6.51 (t, J = 2.8 Hz, 1H), 3.78 (s, 3H); 13C NMR (100 MHz, DMSO) δ 158.1, 136.5, 134.7, 130.6, 126.0, 125.7, 125.5 (dd, J = 7.7, 3.9 Hz, 3H), 125.1, 123.7, 123.3, 114.1, 109.7, 107.0, 55.1 ppm; IR (KBr)/cm⁻¹ 3457, 2930, 1609, 1437, 1324, 1120, 1041, 837, 773, 518; HRMS (ESI) m/z: calcd for C18H15F3NO [M+H⁺] 318.1100; found: 318.1098.

4-(5-(4-Methoxyphenyl)-1H-pyrrol-2-yl)benzonitrile (4g)

Yield: 80% (43.8 mg) as a yellow solid (m.p. = 147-148 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.11; 1H NMR (400 MHz, DMSO) δ 11.37 (s, 1H), 7.92 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.81 (s, 1H), 6.53 (s, 1H), 3.78 (s, 3H). 13C NMR (100 MHz, DMSO) δ 158.2, 136.8, 135.3, 132.5, 130.4, 125.8, 124.9, 123.7, 119.4, 114.1, 110.7, 106.7, 55.1 ppm; IR (KBr)/cm⁻¹ 3769, 3567, 3354, 2924, 2217, 1599, 1488, 1258, 1173, 1031, 829, 773; HRMS (ESI) m/z: calcd for C18H14N2O [M+H⁺] 274.1101; found: 274.1099.

4-(5-(4-Methoxyphenyl)-1H-pyrrol-2-yl)phenyl acetate (4h)

Yield: 54% (33.2 mg) as a white solid (m.p. = 153-154 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.13; 1H NMR (400 MHz, DMSO) δ 11.18 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.56 (s, 1H), 6.47 (s, 1H), 3.78 (s, 3H), 2.28 (s, 3H); 13C NMR (100 MHz, DMSO) δ 169.4, 157.7, 148.4, 133.3, 131.6, 130.6, 125.5, 125.4, 124.7, 122.0, 114.1, 107.7, 106.5, 55.1, 20.8 ppm; IR (KBr)/cm⁻¹ 3415, 2927, 1741, 1501, 1217, 1033, 914, 837, 779, 557; HRMS (ESI) m/z: calcd for C19H14NO3 [M+H⁺] 308.1281; found: 308.1285.
2-(4-Methoxyphenyl)-5-(m-tolyl)-1H-pyrrole (4i)

Yield: 77% (40.5 mg) as a yellow solid (m.p. = 170-171 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.43; 1H NMR (400 MHz, DMSO) δ 11.11 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.60 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 3H), 6.55 (s, 1H), 6.45 (s, 1H), 3.78 (s, 3H), 2.35 (s, 3H); 13C NMR (100 MHz, DMSO) δ 157.7, 137.8, 133.0, 132.7, 132.3, 128.4, 126.2, 125.6, 125.4, 124.3, 121.0, 114.0, 107.4, 106.4, 55.1, 21.2 ppm; IR (KBr)/cm⁻¹: 3787, 3436, 2915, 1590, 1473, 1241, 1021, 828, 759, 523; HRMS (ESI) m/z: calcd for C₁₅H₁₇NO [M⁺] 263.1305; found: 263.1306.

2-(3-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4j)

Yield: 74% (39.5 mg) as a yellow solid (m.p. = 130-131 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.53; 1H NMR (400 MHz, DMSO) δ 11.21 (s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 11.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.37 (dd, J = 7.6, 7.6 Hz, 1H), 6.96 (t, J = 11.2 Hz, 3H), 6.67 (s, 1H), 6.48 (s, 1H), 3.78 (s, 3H); 13C NMR (100 MHz, DMSO) δ 162.8 (d, J = 241.6 Hz), 157.9, 135.1 (d, J = 8.7 Hz), 133.8, 130.9 (d, J = 2.6 Hz), 130.4 (d, J = 8.8 Hz), 125.5, 125.3, 119.7 (d, J = 2.2 Hz), 114.1, 111.7 (d, J = 21.2 Hz), 110.0 (d, J = 23.0 Hz), 108.7, 106.6, 55.1 ppm; IR (KBr)/cm⁻¹: 3460, 2941, 1589, 1468, 1257, 1182, 1031, 840, 768, 494; HRMS (ESI) m/z: calcd for C₁₇H₁₄FNO [M⁺] 267.1054; found: 267.1051.

2-(2-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4k)

Yield: 83% (44.3 mg) as a yellow solid (m.p. = 113-114 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.48; 1H NMR (400 MHz, DMSO) δ 11.20 (s, 1H), 7.93 (t, J = 7.8 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.26-7.22 (m, 3H), 6.97 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 1.2 Hz, 1H), 6.52 (s, 1H), 3.77 (s, 3H); 13C NMR (100 MHz, DMSO) δ 158.3 (d, J = 245.4 Hz), 158.0, 133.5, 127.0 (d, J = 8.4 Hz), 126.9 (d, J = 3.7 Hz), 125.9 (d, J = 2.2 Hz), 125.7, 125.4, 124.5 (d, J = 3.1 Hz), 120.8 (d, J = 12.1 Hz), 116.1 (d, J = 22.1 Hz), 114.2, 111.5 (d, J = 10.0 Hz), 106.6, 55.1 ppm; IR (KBr)/cm⁻¹: 3804, 3456, 1643, 1467, 1233, 1024, 753, 541; HRMS (ESI) m/z: calcd for C₁₇H₁₄FNO [M⁺] 267.1054; found: 267.1054.

2-(4-Methoxyphenyl)-5-(naphthalen-2-yl)-1H-pyrrole (4m)

Yield: 71% (42.5 mg) as a brown solid (m.p. = 193-194 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.35; 1H NMR (400 MHz, DMSO) δ 11.32 (s, 1H), 8.28 (s, 1H), 7.93-7.83 (m, 3H), 7.83-7.73 (m, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 2H), 6.87 (s, 1H), 6.40 (s, 1H), 6.28 (s, 1H), 3.76 (s, 3H); 13C NMR (100 MHz, DMSO) δ 159.3, 158.8, 134.9, 132.1, 130.8, 129.8, 129.5, 129.2, 125.7, 125.5, 125.0, 124.8, 124.6, 121.4, 121.3, 119.7, 119.6, 114.2, 114.0, 111.6, 111.5 (d, J = 10.0 Hz), 106.6, 55.1 ppm; IR (KBr)/cm⁻¹: 3787, 3436, 2915, 1590, 1473, 1241, 1024, 753, 541; HRMS (ESI) m/z: calcd for C₁₉H₁₄NO [M⁺] 271.1325; found: 271.1325.
4H), 7.75 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.73 (s, 1H), 6.52 (s, 1H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, DMSO) δ 157.8, 133.7, 133.6, 132.2, 131.4, 130.3, 128.1, 127.6, 127.5, 126.5, 125.5, 125.1, 123.5, 120.6, 114.2, 108.5, 106.8, 55.2 ppm; IR (KBr)/cm$^{-1}$ 3904, 3785, 3557, 3457, 2921, 1608, 1486, 1250, 1033, 830, 774, 478; HRMS (ESI) m/z: calcd for C$_{21}$H$_{18}$NO [M+H]$^+$ 300.1383; found: 300.1378.

2,4-diphenyl-3-((trimethylsilyl)ethynyl)-1H-pyrrole (5a)

Yield: 68% (42.8 mg) as a yellow crystal (m.p. = 111-112 ºC); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R$_f$ = 0.63; $^1$H NMR (400 MHz, DMSO) δ 11.74 (s, 1H), 7.97 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.37-7.29 (m, 3H), 7.26-7.20 (m, 2H), 0.22 (s, 9H). $^{13}$C NMR (100 MHz, DMSO) δ 135.7, 134.8, 131.7, 128.4, 128.2, 127.0, 126.3, 126.2, 125.9, 125.4, 117.2, 103.2, 98.7, 97.3, -0.07 ppm; HRMS (ESI) m/z: calcd for C$_{21}$H$_{22}$NSi [M+H]$^+$ 316.1516; found: 316.1521.

2,4-diphenyl-3-((triethylsilyl)ethynyl)-1H-pyrrole (5b)

Yield: 71% (50.7 mg) as a yellow crystal (m.p. = 114-115 ºC); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R$_f$ = 0.65; $^1$H NMR (400 MHz, DMSO) δ 11.75 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.87 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (q, J = 7.31 Hz, 3H), 7.25-7.19 (m, 2H), 1.01 (s, J = 7.6 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H). $^{13}$C NMR (100 MHz, DMSO) δ 135.8, 134.8, 131.7, 128.3, 128.1, 127.0, 126.3, 126.2, 125.8, 125.4, 117.2, 104.1, 98.9, 94.8, 7.4, 4.1 ppm; HRMS (ESI) m/z: calcd for C$_{24}$H$_{28}$NSi [M+H]$^+$ 358.1986; found: 358.1990.

2,4-diphenyl-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5c)

Yield: 75% (59.9 mg) as a Green crystal (m.p. = 150-151 ºC); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R$_f$ = 0.70; $^1$H NMR (400 MHz, DMSO) δ 11.74 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.30 (dd, J = 7.6, 1.6 Hz, 3H), 7.24 (d, J = 2.8 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 1.08 (s, 21H). $^{13}$C NMR (100 MHz, DMSO) δ 136.3, 135.3, 132.2, 128.8, 128.6, 127.4, 126.9, 126.8, 126.3, 125.9, 117.7, 104.9, 99.5, 93.9, 19.0, 11.5 ppm; HRMS (ESI) m/z: calcd for C$_{27}$H$_{34}$NSi [M+H]$^+$ 400.2455; found: 400.2456.

2,4-bis(4-methoxyphenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5d)
Yield: 70% (64.3 mg) as a yellow crystal (m.p. = 133-134 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.33; 1H NMR (400 MHz, DMSO) δ 11.50 (s, 1H), 7.94 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 1.08 (s, 21H). 13C NMR (100 MHz, DMSO) δ 158.3, 157.5, 135.8, 127.5, 127.4, 126.8, 126.0, 124.6, 115.6, 113.7, 113.5, 104.9, 97.8, 92.7, 55.2, 55.0, 18.5, 11.0 ppm; HRMS (ESI) m/z: calcd for C29H38NO2Si [M+H]+ 460.2666; found: 460.2662.

2,4-bis(4-fluorophenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5e)

Yield: 78% (67.9 mg) as a yellow crystal (m.p. =122-123 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.50; 1H NMR (400 MHz, DMSO) δ 11.76 (s, 1H), 8.07-8.03 (m, 2H), 7.89-7.86 (m, 2H), 7.10 (t, J = 8.6 Hz, 2H), 1.05 (s, 21H). 13C NMR (100 MHz, DMSO) δ 162.1 (d, J = 42.0 Hz), 159.7 (d, J = 39.9 Hz), 134.9, 131.2 (d, J = 2.9 Hz), 128.3 (d, J = 3.0 Hz), 128.1 (d, J = 7.6 Hz), 127.5 (d, J = 10.8 Hz), 125.4, 117.0, 115.1 (d, J = 21.2 Hz), 114.7 (d, J = 20.9 Hz), 104.0, 98.9, 93.4, 18.4, 10.9 ppm; HRMS (ESI) m/z: calcd for C27H32F2NSi [M+H]+ 436.2267; found: 436.2269.

2,4-bis(4-(tert-butyl)phenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5f)

Yield: 50% (51.1 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): Rf = 0.28; 1H NMR (400 MHz, DMSO) δ 11.60 (s, 1H), 7.93 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.13 (s, 1H), 1.28 (d, J = 5.3 Hz, 19H), 1.07 (s, 20H). 13C NMR (101 MHz, DMSO) δ 149.3, 148.0, 135.8, 132.0, 129.0, 126.4, 126.2, 125.3, 125.0, 124.7, 116.4, 104.7, 98.9, 92.9, 34.2, 34.0, 31.1, 31.0, 18.5, 11.0 ppm; IR (KBr)/cm\(^{-1}\) 3829, 3672, 3616, 3533, 3359, 2930, 2856, 2136, 1655, 1465, 1257, 1035, 532; HRMS (ESI) m/z: calcd for C35H50NSi [M+H]+ 512.3707; found: 512.3708.

2,4-bis(4-(trifluoromethyl)phenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5g)
Yield: 82% (87.8 mg) as a colorless crystal (m.p. = 185-186 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.14; ^1H NMR (400 MHz, DMSO) δ 12.16 (s, 1H), 8.21 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 2.0 Hz, 1H), 1.05 (d, J = 4.4 Hz, 21H). ^13C NMR (100 MHz, DMSO) δ 138.7, 135.3, 134.4, 127.3, 127.0, 126.7, 126.5, 126.2, 125.8, 125.6, 125.3 (q, 4.4Hz), 125.0 (q, J = 3.6 Hz), 123.1, 122.9, 119.8,103.2, 100.7, 95.2, 18.4, 10.9 ppm; IR (KBr)/cm⁻¹ 3406, 2943, 2867, 2139, 1614, 1326, 1125, 844, 771, 668, 581; HRMS (ESI) m/z: calcd for C_{29}H_{32}F_{6}NSi [M+H]^+ 536.2203; found: 536.2208.

2,4-di(naphthalen-2-yl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5h)

Yield: 70% (69.9 mg) as a yellow crystal (m.p. = 153-154 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.50; ^1H NMR (400 MHz, DMSO) δ 11.99 (s, 1H), 8.50 (s, 1H), 8.44 (s, 1H), 8.25 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.93 (t, J = 9.0 Hz, 2H), 7.88-7.80 (m, 4H), 7.56-7.41 (m, 5H), 1.15-1.08 (m, 21H). ^13C NMR (100 MHz, DMSO) δ 136.1, 133.2, 133.0, 132.4, 131.9, 131.6, 129.3, 127.8, 127.7, 127.6, 127.6, 127.5, 127.3, 126.5, 126.5, 126.0, 125.9, 125.7, 125.2, 124.1, 123.7, 123.7, 118.4, 104.4, 99.5, 93.6, 18.6, 11.0 ppm; HRMS (ESI) m/z: calcd for C_{35}H_{38}NSi [M+H]^+ 500.2768; found: 500.2773.

2-methyl-3,5-diphenyl-4-((triisopropylsilyl)ethynyl)-1H-pyrrole (5i)

Yield: 53% (43.8 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): R_f = 0.31; ^1H NMR (400 MHz, DMSO) δ 11.40 (s, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.37-7.31 (m, 4H), 7.22 (q, J = 7.22 Hz, 2H), 2.30 (s, 3H), 1.02 (s, 21H). ^13C NMR (100 MHz, DMSO) δ 134.7, 132.9, 131.8, 128.8, 128.2, 127.7, 126.4, 125.8, 125.5, 125.0, 123.7, 104.5, 100.3, 92.3, 18.4, 11.8, 10.9 ppm; IR (KBr)/cm⁻¹ 3849, 2931, 2858, 2138, 1664, 1607, 1395, 1267, 1108, 999, 764, 673; HRMS (ESI) m/z: calcd for C_{28}H_{38}NSi [M+H]^+ 414.2612; found: 414.2615.

8. Mechanistic Studies
Radical control experiments

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For (eq1), in a 25 mL sealed test tube, Cu NPs (30 mol %), TEMPO (0.25 mmol, 2.5 equiv), 4 mL of DCE, 1-ethynyl-4-methoxybenzene 1a (0.1 mmol) and (1-azidovinyl)benzene 2a (0.18 mmol, 1.8 equiv) was added in sequence. The reaction mixture was sealed under a nitrogen atmosphere and vigorously stirred together at 135 °C for 3 h. The reaction mixture was diluted with CH₂Cl₂ and monitored by GCMS after filtration.

For (eq2), in a 25 mL sealed test tube, Cu NPs (30 mol %), TEMPO (0.25 mmol, 2.5 equiv), 4 mL of DCE, 1-ethynyl-4-methoxybenzene 1w (0.1 mmol) and (1-azidovinyl)benzene 2a (0.25 mmol, 2.5 equiv) was added in sequence. The reaction mixture was sealed under a nitrogen atmosphere and vigorously stirred together at 135 °C for 3 h. The reaction mixture was diluted with CH₂Cl₂ and monitored by GCMS after filtration.

9. References
(1) Xiang, L.; Niu, Y.; Pang, X.; Yang, X.; Yan, R. *Chem. Commun.* 2015, 51, 6598-6600;
(2) Zhang, F.-L.; Wang, Y.-F.; Lonca, G. H.; Zhu, X.; Chiba, S. *Angew. Chem., Int. Ed.* 2014, 53, 4390-4394;
(3) Li, J.; He, W.; Wang, S.; Zhou, G.; Tan, Z. *Electron Compounds and Materials* 2015, 34, 27-30.
10. NMR Spectra of Quinoline Products

2-(4-Methoxyphenyl)-5-phenyl-1H-pyrrole (3a)
2-Phenyl-5-(p-tolyl)-1H-pyrrole (3b)
4-(5-Phenyl-1H-pyrrol-2-yl)aniline (3c)
N, N-dimethyl-4-(5-phenyl-1H-pyrrol-2-yl)aniline (3d)
2-(4-Fluorophenyl)-5-phenyl-1H-pyrrole (3e)
2-(4-Chlorophenyl)-5-phenyl-1H-pyrrole (3f)
2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (3g)
2-Phenyl-5-(o-tolyl)-1H-pyrrole (3h)
2-Phenyl-5-(m-tolyl)-1H-pyrrole (3i)
2-(3-Fluorophenyl)-5-phenyl-1H-pyrrole (3j)
2-(Naphthalen-2-yl)-5-phenyl-1H-pyrrole (3k)
2-Phenyl-5-(thiophen-2-yl)-1H-pyrrole (3l)
2-Cyclopropyl-5-phenyl-1H-pyrrole (3m)
2-Cyclopentyl-5-phenyl-1H-pyrrole (3n)
2-Cyclohexyl-5-phenyl-1H-pyrrole (3o)

![Chemical Structure Image]

NMR Spectra Image

Chemical Shifts and Integration Patterns
2-(Tert-butyl)-5-phenyl-1H-pyrrole (3p)
2-Isopentyl-5-phenyl-1H-pyrrole (3q)
2-Hexyl-5-phenyl-1H-pyrrole (3r)
2-Phenyl-5-(3-phenylpropyl)-1H-pyrrole (3s)
4-(5-Phenyl-1H-pyrrol-2-yl)butanenitrile (3t)
2-(4-Chlorobutyl)-5-phenyl-1H-pyrrole (3u)
2-(4-Methoxyphenyl)-5-(p-tolyl)-1H-pyrrole (4a)
2-(4-(Tert-butyl)phenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4b)
2-(4-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4c)
2-(4-Chlorophenyl)-5-(4-methoxyphenyl)-1\(H\)-pyrrole (4d)
2-(4-Bromophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4e)
2-(4-Methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)-1H-pyrrole (4f)
4-(5-(4-methoxyphenyl)-1H-pyrrol-2-yl)benzonitrile (4g)
4-(5-(4-Methoxyphenyl)-1H-pyrrol-2-yl)phenyl acetate (4h)
2-(4-Methoxyphenyl)-5-(m-tolyl)-1H-pyrrole (4i)
2-(3-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4j)

\[
\text{MeC} - \text{C-H}_{\text{F}}\text{C} - \text{C}_\text{F}\text{C} - \text{C}_\text{Me}
\]

\[
\begin{align*}
1H (\text{ppm}) & \quad 13C (\text{ppm}) \\
7.304 & \quad 161.823 \\
7.300 & \quad 153.853 \\
7.274 & \quad 133.368 \\
7.220 & \quad 125.699 \\
7.014 & \quad 114.566 \\
7.014 & \quad 111.459 \\
6.989 & \quad 110.988 \\
6.988 & \quad 109.854 \\
6.987 & \quad 108.673 \\
6.986 & \quad 106.627 \\
5.278 & \quad 141.127 \\
3.874 & \quad 39.919 \\
3.979 & \quad 39.500 \\
3.382 & \quad 39.182 \\
3.874 & \quad 39.874
\end{align*}
\]
2-(2-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4k)
2-(4-Methoxyphenyl)-5-(naphthalen-2-yl)-1H-pyrrole (4m)
2,4-diphenyl-3-((trimethylsilyl)ethynyl)-1H-pyrrole (5a)
2,4-diphenyl-3-((triethylsilyl)ethynyl)-1H-pyrrole (5b)

[Chemical structure image]

[1H-NMR spectrum image]

[13C-NMR spectrum image]
2,4-diphenyl-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5c)
2,4-bis(4-methoxyphenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5d)
2,4-bis(4-fluorophenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5e)
2,4-bis(4-(tert-butyl)phenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5f)
2,4-bis(4-(trifluoromethyl)phenyl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5g)
2,4-di(naphthalen-2-yl)-3-((triisopropylsilyl)ethynyl)-1H-pyrrole (5h)
2-methyl-3,5-diphenyl-4-((triisopropylsilyl)ethynyl)-1H-pyrrole (5i)
11. X-ray Crystallographic Data
Single-crystal X-ray diffraction data for 3ac were collected on a Rigaku Mercury CCD diffractometer operated at 90 kV and 50 mA using MoKα radiation (\(\lambda = 0.71073 \text{ Å}\)) at the temperature 100.00(10)K. All empirical absorption corrections were performed using the CrystalClear program. The structure was solved by a direct method and refined on \(F^2\) by the full-matrix least squares technique using the SHELXTL-97 program package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. Crystallographic data for compound 3ac is given in Table S1. Metrical parameters for the structures of 3ac are available free of charge from the Cambridge Crystallographic Data Centre under accession numbers CCDC-1865535, respectively.

![Figure S1. X-ray crystal structure of compound 5c](image)

**Table S1. Crystal data and structure refinements for 5c**

| Compound | 5c |
|----------|----|
| Empirical formula | C_{27}H_{33}NSi |
| Formula weight | 399.63 |
| Temperature (K) | 100.01(10) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Orthorhombic |
| Space group | Pna2_1 |
| \(a\) | 15.8494(5)Å, \(a = 90\) |
| \(b\) | 16.5920(5)Å, \(\beta = 90\) |
| \(c\) | 17.8554(8)Å, \(\gamma = 90\) |
12. GC-MS Analysis of NH Imine Generated from Copper Intermediate VI