Supporting Information

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

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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 EI-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 Kα radiation ($\lambda$=1.5406 Å), with a step size of 0.01995° (2θ). 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.\(^1\)

![Chemical structure of 2a](image)

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.\(^2\)

![Chemical structures of 2b-2p](image)

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 CH\(_2\)Cl\(_2\) (5 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous Na\(_2\)S\(_2\)O\(_3\), and the organic materials were extracted two times with Et\(_2\)O. The combined extracts were washed with brine and dried over MgSO\(_4\). 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 Et\(_2\)O (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 NH\(_4\)HCO\(_3\) saturated solution, and the organic materials were extracted with ethyl acetate. The organic layer was washed with brine and dried over Na\(_2\)SO\(_4\). 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 conditions\(^3\). A 100 mL round-bottom flask was charged with CuSO\(_4\) (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 NaBH\(_4\) (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](image1.png)

![Figure 2. XRD spectrum of the Cu NPs](image2.png)

4. General Procedures for CuNPs-Catalyzed Synthesize of Pyrroles

**General Procedure A:**
(1) 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, 132 mg) 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

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<th>[Cu] (mol %)</th>
<th>Solvent (mL)</th>
<th>temp. (°C)</th>
<th>yield of 3a (%)</th>
<th>yield of 3a' (%)</th>
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$^a$Alkyne (0.1 mmol), vinyl azides (0.18 mmol) were stirred for 3 h under a nitrogen atmosphere. Yields were determined by $^1$HNMR using CH$_2$ClBr as internal standard. $^b$Isolated yields. $^c$Under air atmosphere. $^d$1 equiv H$_2$O was added. $^e$Alkyne (0.2 mmol), vinyl azides (0.36 mmol), DCE (5 mL).

6. Recycling of Cu nanoparticles
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): R\text{f} = 0.43; \textsuperscript{1}H NMR (400 MHz, DMSO) \( \delta \) 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). \textsuperscript{13}C NMR (100 MHz, DMSO) \( \delta \) 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, 759, 682, 503; HRMS (ESI) m/z: calcld for C\textsubscript{17}H\textsubscript{15}NO \([\text{M}^+\text{]}\) 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): R\text{f} = 0.75; \textsuperscript{1}H NMR (400 MHz, DMSO) \( \delta \) 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). \textsuperscript{13}C NMR (100 MHz, DMSO) \( \delta \) 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, 684, 505; HRMS (ESI) m/z: calcld for C\textsubscript{17}H\textsubscript{16}N \([\text{M+H}^+\text{]}\) 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): Rf = 0.05; 1H NMR (400 MHz, DMSO) δ 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). 13C NMR (100 MHz, DMSO) δ 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 C₁₆H₁₅N₂ [M+H]+ 235.1230; found: 235.1233.

N, N-dimethyl-4-(5-phenyl-1H-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): Rf = 0.33; 1H NMR (400 MHz, DMSO) δ 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). 13C NMR (100 MHz, DMSO) δ 148.8, 134.0, 132.9, 131.5, 128.5, 125.1, 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 C₁₈H₁₉N₂ [M+H]+ 263.1543; found: 263.1545.

2-(4-Fluorophenyl)-5-phenyl-1H-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): Rf = 0.58; 1H NMR (400 MHz, DMSO) δ 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). 13C NMR (100 MHz, DMSO) δ 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 C₁₆H₁₅FN [M+H]+ 238.1027; found: 238.1023.

2-(4-Chlorophenyl)-5-phenyl-1H-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): Rf = 0.58; 1H NMR (400 MHz, DMSO) δ 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). 13C NMR (100 MHz, DMSO) δ 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 C₁₆H₁₃ClN [M+H]+ 254.0731; found: 254.0726.

2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1H-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), 7.29-7.15 (m, 4H), 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]⁺ 234.1277; 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 C₁₆H₁₃FN [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): Rᵣ = 0.68; ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (100 MHz, DMSO) δ 133.6, 133.5, 133.0, 132.5, 131.5, 130.1, 128.6, 128.0, 127.6, 127.5, 126.5, 125.9, 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 C₂₀H₁₆N [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): Rᵣ = 0.65; ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (100 MHz, DMSO) δ 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 C₁₄H₁₂NS [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): Rᵣ = 0.50; ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (100 MHz, DMSO) δ 138.2, 133.1, 129.6, 128.5, 124.8, 122.9, 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 C₁₃H₁₄N [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): Rᵣ = 0.63; ¹H NMR (400 MHz, DMSO) δ 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). ¹³C NMR (100 MHz, DMSO) δ 138.2, 133.3,
2-Cyclohexyl-5-phenyl-1\textsubscript{H}-pyrrole (3o)

Yield: 63\% (28.4 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R\_f = 0.73;
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 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).
\textsuperscript{13}C NMR (100 MHz, DMSO) \(\delta\) 139.8, 133.3, 129.5, 128.5, 124.7, 123.0, 105.2, 104.6, 38.3, 33.0, 24.6 ppm; IR (KBr)/cm\textsuperscript{-1} 3780, 3412, 1607, 1396, 1059, 751, 680, 474; HRMS (ESI) m/z: calcd for C\textsubscript{15}H\textsubscript{18}N \([M+H]^+\) 212.1434; found: 212.1431.

2-(\textsuperscript{t}ert-butyl)-5-phenyl-1\textsubscript{H}-pyrrole (3p)

Yield: 58\% (23.1 mg) as a colorless oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R\_f = 0.44;
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 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).
\textsuperscript{13}C NMR (100 MHz, DMSO) \(\delta\) 143.4, 133.3, 130.3, 128.4, 124.9, 123.4, 104.9, 103.69, 31.39, 30.29 ppm; IR (KBr)/cm\textsuperscript{-1} 3782, 3676, 2924, 1622, 1401, 659, 571, 476; HRMS (ESI) m/z: calcd for C\textsubscript{14}H\textsubscript{17}N \([M+\text{H}]^+\) 199.1356; found: 199.1354.

2-Isopentyl-5-phenyl-1\textsubscript{H}-pyrrole (3q)

Yield: 65\% (27.7 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R\_f = 0.53;
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 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).
\textsuperscript{13}C NMR (100 MHz, DMSO) \(\delta\) 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\textsuperscript{-1} 3789, 3411, 2936, 1605, 1512, 1455, 1046, 754, 681, 468; HRMS (ESI) m/z: calcd for C\textsubscript{15}H\textsubscript{20}N \([M+\text{H}]^+\) 214.1590; found: 214.1587.

2-Hexyl-5-phenyl-1\textsubscript{H}-pyrrole (3r)

Yield: 50\% (22.7 mg) as a yellow oil; TLC (petroleum ether/ethyl acetate = 20/1, v/v): R\_f = 0.44;
\textsuperscript{1}H NMR (400 MHz, DMSO) \(\delta\) 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 C\(_{16}\)H\(_{22}\)N [M+H]\(^+\) 228.1747; found: 228.1743.

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

Yield: 48% (25.1 mg) as a colorless oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): R\(_f\) = 0.65; ¹H NMR (400 MHz, DMSO) \(\delta\) 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) \(\delta\) 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 C\(_{19}\)H\(_{20}\)N [M+H]\(^+\) 262.1590; found: 262.1585.

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

Yield: 61% (25.6 mg) as a brown oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): R\(_f\) = 0.13; ¹H NMR (400 MHz, DMSO) \(\delta\) 10.99 (s, 1H), 7.60 (d, \(J\) = 8.0 Hz, 2H), 7.33 (t, \(J\) = 7.6 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) \(\delta\) 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 C\(_{14}\)H\(_{15}\)N\(_2\) [M+H]\(^+\) 211.1230; found: 211.1226.

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

Yield: 72% (33.6 mg) as an orange oil; TLC (petroleum ether/ethyl acetate = 10/1, v/v): R\(_f\) = 0.44; ¹H NMR (400 MHz, DMSO) \(\delta\) 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) \(\delta\) 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 C\(_{14}\)H\(_{17}\)ClN [M+H]\(^+\) 234.1044; found: 234.1040.

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

Yield: 75% (39.5 mg) as a yellow solid (m.p. = 192-193 °C); TLC (petroleum ether/ethyl acetate = 10/1, v/v): R\(_f\) = 0.55; ¹H NMR (400 MHz, DMSO) \(\delta\) 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) \(\delta\) 157.6, 134.6, 132.7, 132.4, 130.1, 129.1, 128.3, 127.6, 126.5, 125.6, 119.8, 114.9, 114.7, 106.8, 105.7, 105.3, 31.7, 26.7, 26.5 ppm; IR (KBr)/cm\(^{-1}\): 3788, 3415, 2924, 2856, 1604, 1395, 1060, 753, 677, 472; HRMS (ESI) m/z: calcd for C\(_{16}\)H\(_{22}\)N [M+H]\(^+\) 228.1747; found: 228.1743.
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 C₁₈H₁₇NO [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; ¹H NMR (400 MHz, DMSO) δ 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); ¹³C NMR (100 MHz, DMSO) δ 157.6, 147.9, 132.7, 132.3, 130.1, 125.7, 125.3, 125.2, 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, 834, 775, 513; HRMS (ESI) m/z: calcd for C₂₁H₂₄NO [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; ¹H NMR (400 MHz, DMSO) δ 11.14 (s, 1H), 7.78 (t, J = 6.8 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 8.6 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.52 (s, 1H), 6.45 (s, 1H), 3.77 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 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 C₁₇H₁₄FNO [M⁺] 267.1054; found: 267.1052.

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; ¹H NMR (400 MHz, DMSO) δ 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); ¹³C NMR (100 MHz, DMSO) δ 157.8, 133.6, 131.6, 130.9, 129.6, 128.5, 125.4, 125.3, 125.2, 114.1, 108.1, 106.6, 55.1 ppm; IR (KBr)/cm⁻¹ 3531, 3453, 2928, 1641, 1111, 1034, 833, 772, 517; HRMS (ESI) m/z: calcd for C₁₇H₁₄ClNO [M⁺]⁺ 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, 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 C₁₉H₁₅NO₃ [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 C18H17NO [M+][1] 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, 5H), 7.58 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.08 (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.
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); 13C 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)

![Chemical Structure](image)

Yield: 68% (42.8 mg) as a yellow crystal (m.p. = 111-112 °C); 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).

13C 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)

![Chemical Structure](image)

Yield: 71% (50.7 mg) as a yellow crystal (m.p. = 114-115 °C); 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 (t, J = 7.6 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H).

13C 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)

![Chemical Structure](image)

Yield: 75% (59.9 mg) as a Green crystal (m.p. =150-151 °C); 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), 7.31 (q, J = 7.31 Hz, 3H), 7.25-7.19 (m, 2H), 1.08 (s, 21H).

13C NMR (100 MHz, DMSO) δ 136.3, 135.3, 132.2, 128.8, 128.6, 127.4, 126.9, 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)

![Chemical Structure](image)

Yield: 75% (59.9 mg) as a Green crystal (m.p. =150-151 °C); 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).

13C NMR (100 MHz, DMSO) δ 136.3, 135.3, 132.2, 128.8, 128.6, 127.4, 126.9, 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-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), 7.22-7.18 (m, 3H), 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; IR (KBr)/cm⁻¹: 3829, 3672, 3616, 3533, 3359, 2930, 2856, 2136, 1655, 1465, 1257, 1035, 532; HRMS (ESI) m/z: calcd for C_{27}H_{32}F_{2}NSi [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 C_{35}H_{50}NSi [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): Rf = 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, 4.4 Hz), 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 C₂₉H₃₂F₆N Si [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): Rf = 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, 127.5, 127.3, 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 C₃₅H₃₈NSi [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): Rf = 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, 131.2, 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: 3409, 2931, 2858, 2138, 1664, 1607, 1395, 1267, 1108, 999, 764, 673; HRMS (ESI) m/z: calcd for C₂₈H₂₆NSi [M+H]⁺ 414.2612; found: 414.2615.

**8. Mechanistic Studies**

Radical control experiments
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;
10. NMR Spectra of Quinoline Products

2-(4-Methoxyphenyl)-5-phenyl-1H-pyrrole (3a)
2-Phenyl-5-(p-tolyl)-1\textit{H}-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-pyrrrole (3e)
2-(4-Chlorophenyl)-5-phenyl-1\textit{H}-pyrrole (3f)
2-Phenyl-5-(4-(trifluoromethyl)phenyl)-1\textsubscript{H}-pyrrole (3g)
2-Phenyl-5-(α-tolyl)-1H-pyrrole (3h)

[Chemical structure and spectra images]
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)
2-(Tert-butyl)-5-phenyl-1H-pyrrole (3p)
2-Isopentyl-5-phenyl-1H-pyrrole (3q)
2-Hexyl-5-phenyl-1H-pyrrole (3r)

\[ \text{Me} \]

\[ \text{I} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{N} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{Me} \]

\[ \text{I} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{N} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{Me} \]

\[ \text{I} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{N} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{Me} \]

\[ \text{I} \]

\[ \text{H} \]

\[ \text{Ph} \]

\[ \text{N} \]

\[ \text{H} \]

\[ \text{Ph} \]
2-Phenyl-5-(3-phenylpropyl)-1H-pyrrole (3s)

\[
\text{Pr} \begin{array}{c}
\text{Ph} \\
\end{array}
\]

\[
\text{Pr} \begin{array}{c}
\text{Ph} \\
\end{array}
\]

\[
\text{Pr} \begin{array}{c}
\text{Ph} \\
\end{array}
\]
4-(5-Phenyl-1H-pyrrol-2-yl)butanenitrile (3t)

\[
\text{NC} \quad \text{Ph}
\]

\[
\text{NC} \quad \text{Ph}
\]
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)-1H-pyrrole (4d)

![Chemical Structure Image]

![NMR Spectrum Image]
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-pyrrolyl)phenyl acetate (4h)
2-(4-Methoxyphenyl)-5-(m-tolyl)-1H-pyrrole (4i)

MeC-\(\text{phenyl}\)-\(\text{Pyrrrole}\)-\(\text{Me}\)

1H NMR spectrum

\(\delta = \text{ppm}\)

13C NMR spectrum

\(\delta = \text{ppm}\)
2-(3-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4j)

\[ \text{MeC} \quad \text{F} \]

\[ \text{H (ppm)} \quad 12.0 \quad 11.0 \quad 10.0 \quad 9.0 \quad 8.0 \quad 7.0 \quad 6.0 \quad 5.0 \quad 4.0 \quad 3.0 \quad 2.0 \quad 1.0 \quad 0.0 \]

\[ 164.034 \quad 161.822 \quad 157.887 \quad 133.383 \quad 130.912 \quad 130.357 \quad 129.369 \quad 125.290 \quad 119.866 \quad 114.886 \quad 111.580 \quad 110.983 \quad 109.854 \quad 108.673 \quad 106.827 \quad 55.070 \]

\[ 40.127 \quad 39.918 \quad 39.799 \quad 39.580 \quad 39.082 \quad 38.874 \]

\[ \text{MeC} \quad \text{F} \]

\[ \text{H (ppm)} \quad 190 \quad 170 \quad 150 \quad 130 \quad 110 \quad 90 \quad 80 \quad 70 \quad 60 \quad 50 \quad 40 \quad 30 \quad 20 \quad 10 \quad 0 \]
2-(2-Fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrrole (4k)

**Chemical Structure:**

- ![Chemical Structure](image)

**NMR Data:**

- δ (ppm) values for various signals are listed below:
  - 13C: 125.836, 126.865, 133.489, 157.093
  - 1H: 2.75, 3.28, 7.43, 7.53, 7.70, 7.99, 8.01, 8.04, 8.06, 8.07

**Additional Information:**

- Mass spectra and other analytical data are also included, providing comprehensive details for the compound.
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)
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 ($\lambda = 0.71073$ 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

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<th>Compound</th>
<th>5c</th>
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</tr>
<tr>
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<tr>
<td>Temperature (K)</td>
<td>100.01(10)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
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<tr>
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<td>15.8494(5) Å $\alpha = 90$</td>
</tr>
<tr>
<td>$b$</td>
<td>16.5920(5)Å $\beta = 90$</td>
</tr>
<tr>
<td>$c$</td>
<td>17.8554(8)Å $\gamma = 90$</td>
</tr>
</tbody>
</table>
12. GC-MS Analysis of NH Imine Generated from Copper Intermediate VI