# Electrochemical Oxidative Annulation from Amines and Aldehydes or Ketones to Syntheize Polysubstituted Pyrroles

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# Contents

General information	S2
General procedure	S3
Detail descriptions for products	S7
References	
Copies of product NMR spectra	

#### **General information**

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anodic electrode was carbon cloth (15 mm×15 mm×0.36 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). <sup>1</sup>H and <sup>13</sup>C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for <sup>1</sup>H), CDCl<sub>3</sub> (77.0 ppm for <sup>13</sup>C) and DMSO (2.50 ppm for <sup>1</sup>H, 39.52 ppm for <sup>13</sup>C), respectively. High resolution mass spectra (HRMS) were recorded on Bruker UltiMate3000 & Compact and Thermo Fisher Scientific LTQ FTICR-MS.

#### **General procedure**

General procedure for electrochemical-oxidation-induced intermolecular cyclization: The electrolysis was carried out in an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar. Aryl acetaldehyde (0.50 mmol), amine (0.75 mmol), NaOAc (0.75 mmol, 61.5 mg), <sup>*n*</sup>Bu<sub>4</sub>NBF<sub>4</sub> (1.00 mmol, 329.0 mg) and THF (10 mL) were combined and added. The bottle was equipped with carbon cloth (15 mm×15 mm×0.36 mm) as the anode and platinum plate (15 mm×15 mm×0.30 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 60 °C for 2 h. When the reaction was finished, the solution was washed with water (10 mL) and extracted with diethyl ether (3×10 mL). The combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (250:1).

General procedure for electrochemical synthesis of tetrasubstituted pyrrole from keto ester and *N*-butyl amine: The electrolysis was carried out in an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar. Methyl 2-oxo-3-phenylpropanoate (0.50 mmol), *N*-butyl amine (0.75 mmol), "Bu<sub>4</sub>NBF<sub>4</sub> (1.00 mmol, 329.0 mg) and DCE (10 mL) were combined and added. The bottle was equipped with carbon cloth (15 mm×15 mm×0.36 mm) as the anode and platinum plate (15 mm×15 mm×0.30 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 80 °C for 2 h. When the reaction was finished, the solution was washed with water (10 mL) and extracted with diethyl ether (3×10 mL). The combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (20:1).



General procedure for electrochemical synthesis of tetrasubstituted pyrrole from imine: Ketone (5.0 mmol), *N*-butyl amine (25.0 mmol, 1.83 g), molecular sieves 4Å (2.0 g) and dry MeOH (10 mL) were placed in a 100 mL round bottomed flask. The mixture was stirred at room temperature for 3 days under nitrogen atmosphere. The reaction mixture was filtered on celite and washed with  $CH_2Cl_2$ . The resulting filtrate was concentrated under reduced pressure to afford imine. Subsequently, imine synthesized in situ, "Bu<sub>4</sub>NBF<sub>4</sub> (5.00 mmol, 1.65 g) and MeCN (40 mL) were combined and added in an oven-dried undivided three-necked flask (50 mL) equipped with a stir bar. The bottle was equipped with carbon cloth (20 mm×20 mm×0.36 mm) as the anode and platinum plate (15 mm×15 mm×0.30 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under 80 °C for 11 h. When the reaction was finished, the solution was washed with water (20 mL) and extracted with diethyl ether (3×20 mL). The combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (100:1).

$$\begin{array}{c} O \\ R^{1} \\ R^{2} \\ R^$$

**General procedure for the gram-scale reaction:** In an oven-dried undivided three-necked flask (100 mL) equipped with a stir bar, phenylacetaldehyde (10.00 mmol, 1.20 g), *p*-toluidine (15.00 mmol, 1.61 g), NaOAc (15.00 mmol, 1.23 g), *n*Bu<sub>4</sub>NBF<sub>4</sub> (10.00 mmol, 3.29 g) and THF (80 mL) were combined and added. The bottle was equipped with carbon cloth (30 mm×30 mm×0.36 mm) as the anode and platinum plate (15 mm×15 mm×0.30 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under 60 °C for 20 h. When the reaction was finished, the solution was washed with water (50 mL) and extracted with diethyl ether (3×50 mL). The combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (250:1). White soild (0.93 g) was obtained in 60% isolated yield.

General procedure for later stage functionalization: In a round-bottomed flask (100 mL) equipped with a stir bar, 1,3,4-triphenyl-1*H*-pyrrole (0.50 mmol, 147.5 mg), 1-bromopyrrolidine-

2,5-dione (1.00 mmol, 178.0 mg) and DCM (15 mL) were combined and stirred under room temperature for 10 min. When the reaction was finished, the solution was washed with water (10 mL) and extracted with diethyl ether ( $3 \times 10$  mL). The combined organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent (100:1). White soild (203.8 mg) was obtained in 90% isolated yield.





**General procedure for cyclic voltammerty (CV):** Cyclic voltammerty was performed in a threeelectrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode; the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution and was seperated from reaction by a salt bridge. 10 mL of MeCN containing 0.1 M "Bu<sub>4</sub>NBF<sub>4</sub> was poured into the electrochemical cell in all experiments. The scan rate is 0.05 V/s, ranging from 0 V to 3.0 V.

**General procedure for detecting imine :** In a round-bottomed flask (100 mL) equipped with a stir bar, phenylacetaldehyde (0.50 mmol), aniline (0.50 mmol) and THF (10 mL) were combined and added. The reaction mixture was stirred under room temperature for 0.5 h. Subsequently, the reaction system was measured by mass spectrometry. HRMS (ESI) calculated for  $C_{14}H_{14}N$  [M+H]<sup>+</sup>: 196.1121; found: 196.1123.

Figure S2 Mass spectrogram of reaction mixture



Mass spectrogram of a:



Mass spectrogram of b:





Mass spectrogram of c:

## **Detail descriptions for products**



**1,3,4-Triphenyl-1***H***-pyrrole (3aa)**:<sup>1</sup> white solid was obtained in 74% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.75 – 7.70 (m, 2H), 7.62 (s, 2H), 7.52 – 7.47 (m, 2H), 7.32 – 7.26 (m, 9H), 7.23 – 7.18 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 139.42, 135.14, 129.76, 128.29, 128.08, 125.99, 125.60, 124.62, 119.22, 118.64.



**3,4-Diphenyl-1-(p-tolyl)-1***H***-pyrrole(3ab)**:<sup>2</sup> white solid was obtained in 74% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.30 (m, 6H), 7.30 – 7.26 (m, 3H), 7.26 – 7.18 (m, 5H), 7.17 – 7.15 (m, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.85, 135.61, 135.32, 130.13, 128.44, 128.20, 125.91, 125.22, 120.09, 118.59, 20.86.



**3,4-Diphenyl-1-(o-tolyl)-1***H***-pyrrole(3ac)**.<sup>2</sup> white solid was obtained in 62% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.24 (m, 8H), 7.22 – 7.16 (m, 4H), 2.33 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 139.56, 135.35, 132.63, 131.36, 128.27, 128.08, 127.57, 126.94, 126.02, 125.76, 123.05, 121.85, 17.98.



**3,4-Diphenyl-1-(m-tolyl)-1***H***-pyrrole(3ad)**:<sup>2</sup> white solid was obtained in 53% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.24 (m, 11H), 7.23 – 7.18 (m, 4H), 7.10 – 7.05 (m, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.13, 139.65, 135.29, 129.43, 128.44, 128.20, 126.62, 125.93, 125.37, 120.88, 118.57, 117.25, 21.51.



**1-(4-Chlorophenyl)-3,4-diphenyl-1***H***-pyrrole(3ae)**:<sup>1</sup> light yellow solid was obtained in 69% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (m, 4H), 7.32 – 7.25 (m, 8H), 7.24 – 7.19 (m, 2H), 7.13 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.67, 134.94, 131.17, 129.71, 128.42, 128.25, 126.14, 125.96, 121.15, 118.34.



**1-(4-Bromophenyl)-3,4-diphenyl-1***H***-pyrrole(3af)**:<sup>2</sup> light yellow solid was obtained in 68% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.74 – 7.63 (m, 6H), 7.32 – 7.25 (m, 8H), 7.24 – 7.19 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 138.66, 134.94, 132.48, 128.30, 128.07, 126.10, 124.98, 121.10, 118.64, 117.72.



**1-(4-Methoxyphenyl)-3,4-diphenyl-1***H***-pyrrole(3ag)**:<sup>1</sup> light yellow solid was obtained in 52% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 – 7.34 (m, 2H), 7.36 – 7.18 (m, 10H), 7.11 (s, 2H), 7.04 – 6.90 (m, 2H), 3.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.78, 135.35, 133.86, 128.43, 128.20, 125.87, 124.99, 121.82, 118.94, 114.70, 55.55.



**4-(3,4-Diphenyl-1***H***-pyrrol-1-yl)benzonitrile(3ah)**: white solid was obtained in 47% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 – 7.71 (m, 2H), 7.59 – 7.53 (m, 2H), 7.34 – 7.22 (m, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.07, 134.41, 133.90, 128.43, 128.33, 127.32, 126.52, 119.51, 118.45, 117.81, 108.67. HRMS (ESI) calculated for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub> M<sup>+</sup>: 320.1308; found: 320.1306.



**Ethyl 4-(3,4-diphenyl-1***H***-pyrrol-1-yl)benzoate(3ai)**: white solid was obtained in 47% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.09 – 8.00 (m, 2H), 7.94 – 7.86 (m, 2H), 7.77 (s, 2H), 7.35 – 7.19 (m, 10H), 4.32 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 165.18, 142.79, 134.76, 130.91, 128.34, 128.13, 126.37, 126.27, 125.60, 118.65, 118.54, 60.81, 14.26. HRMS (ESI) calculated for C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 368.1645; found: 368.1656.



**1-Phenyl-3,4-di**-*p*-tolyl-1*H*-pyrrole (3ba): white solid was obtained in 63% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.38 (m, 4H), 7.26 – 7.19 (m, 5H), 7.16 (s, 2H), 7.11 – 7.06 (m, 4H), 2.33 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.20, 135.48, 132.35, 129.58, 128.93, 128.30, 125.63, 125.44, 120.00, 118.16, 21.14. HRMS (ESI) calculated for C<sub>24</sub>H<sub>21</sub>N [M+H]<sup>+</sup>: 324.1747; found: 324.1737.



**3,4-Bis(4-chlorophenyl)-1-phenyl-1***H***-pyrrole(3ca)**: white solid was obtained in 62% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.42 (m, 4H), 7.31 – 7.28 (m, 1H), 7.28 – 7.18 (m, 8H), 7.16 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.90, 133.42, 131.95, 129.71, 129.61, 128.50, 126.16, 124.27, 120.24, 118.72. HRMS (ESI) calculated for C<sub>22</sub>H<sub>15</sub>Cl<sub>2</sub>N M<sup>+</sup>: 363.0576; found: 363.0577.



**3,4-Bis(4-methoxyphenyl)-1-phenyl-1***H***-pyrrole(3da)**: white solid was obtained in 58% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.39 (m, 4H), 7.26 – 7.21 (m, 5H), 7.13 (s, 2H), 6.86 – 6.81 (m, 4H), 3.79 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.96, 140.20, 129.57, 129.48, 127.79, 125.55, 125.08, 119.91, 117.73, 113.63, 55.13. HRMS (ESI) calculated for C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 356.1645; found: 356.1643.



**2,5-Dibromo-1,3,4-triphenyl-1***H***-pyrrole (3aa')**: light yellow solid was obtained in 90% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.48 (m, 3H), 7.43 – 7.38 (m, 2H), 7.30 – 7.19 (m, 10H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.13, 133.61, 130.17, 129.23, 129.14, 128.96, 127.92, 126.68, 125.20, 103.21. HRMS (ESI) calculated for C<sub>22</sub>H<sub>15</sub>Br<sub>2</sub>N M<sup>+</sup>: 450.9566; found: 450.9567. Ph Ph



**1-Methyl-3,4-diphenyl-1***H***-pyrrole(5aa)**: colorless oil was obtained in 54% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.21 (m, 8H), 7.19 – 7.13 (m, 2H), 6.71 (s, 2H), 3.68 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.77, 128.36, 128.11, 125.50, 123.33, 121.29, 36.24. HRMS (ESI) calculated for C<sub>17</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 234.1277; found: 234.1275.



**1-Butyl-3,4-diphenyl-1***H***-pyrrole(5ab)**:<sup>3</sup> colorless oil was obtained in 65% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.20 (m, 8H), 7.19 – 7.12 (m, 2H), 6.82 – 6.68 (m, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.45 – 1.33 (m, 2H), 1.00 – 0.93 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.96, 128.31, 128.08, 125.39, 122.86, 120.19, 49.51, 33.39, 19.96, 13.67.



**1-Isopropyl-3,4-diphenyl-1***H***-pyrrole(5ac)**: colorless oil was obtained in 72% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 – 7.20 (m, 8H), 7.18 – 7.12 (m, 2H), 6.86 – 6.79 (m, 2H), 4.31 – 4.16 (m, 1H), 1.50 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  136.06, 128.28, 128.08, 125.36, 122.61, 117.95, 50.94, 23.84. HRMS (ESI) calculated for C<sub>19</sub>H<sub>19</sub>N [M+Na]<sup>+</sup>: 284.1410; found: 284.1420.



**1-(Tert-butyl)-3,4-diphenyl-1***H***-pyrrole (5ad)**:<sup>1</sup> colorless solid was obtained in 66% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.21 (m, 8H), 7.20 – 7.13 (m, 2H), 6.93 (s, 2H), 1.58 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.15, 128.28, 128.08, 125.34, 122.47, 117.44, 55.03, 30.67.



**1-Cyclopropyl-3,4-diphenyl-1***H***-pyrrole (5ae)**: colorless oil was obtained in 42% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.26 – 7.20 (m, 4H), 7.19 – 7.11 (m, 6H), 7.00 (s, 2H), 3.53 – 3.45 (m, 1H), 1.02 – 0.96 (m, 2H), 0.94 – 0.88 (m, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 135.80, 128.20, 127.86, 125.45, 121.97, 120.81, 30.17, 6.23. HRMS (ESI) calculated for C<sub>19</sub>H<sub>17</sub>N [M+Na]<sup>+</sup>: 282.1253; found: 282.1262.



**1-Cyclohexyl-3,4-diphenyl-1***H***-pyrrole (5af)**:<sup>1</sup> light yellow oil was obtained in 79% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.20 (m, 8H), 7.18 – 7.12 (m, 2H), 6.83 (s, 2H), 3.87 – 3.74 (m, 1H), 2.22 – 2.11 (m, 2H), 1.94 – 1.86 (m, 2H), 1.76 – 1.61 (m, 3H), 1.47 – 1.34 (m, 2H), 1.29 – 1.23 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.10, 128.28, 128.06, 125.32, 122.41, 118.24, 58.79, 34.53, 25.62, 25.40.



**1-((3s,5s,7s)-Adamantan-1-yl)-3,4-diphenyl-1***H***-pyrrole (5ag): white solid was obtained in 61% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.19 (m, 8H), 7.18 – 7.12 (m, 2H), 7.00 – 6.94** 

(m, 2H), 2.27 - 2.19 (m, 3H), 2.18 - 2.08 (m, 6H), 1.84 - 1.70 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  136.25, 128.26, 128.05, 125.26, 122.15, 116.43, 55.24, 43.74, 36.11, 29.60. HRMS (ESI) calculated for C<sub>26</sub>H<sub>27</sub>N [M+H]<sup>+</sup>: 354.2216; found: 354.2217.



**1-(2-Methoxyethyl)-3,4-diphenyl-1***H***-pyrrole (5ah)**: colorless oil was obtained in 57% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.26 – 7.21 (m, 4H), 7.18 – 7.11 (m, 6H), 6.97 (s, 2H), 4.07 (d, *J* = 5.6 Hz, 2H), 3.66 (d, *J* = 5.6 Hz, 2H), 3.28 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  135.95, 128.21, 127.78, 125.35, 121.78, 121.11, 71.63, 58.03, 48.58. HRMS (ESI) calculated for C<sub>19</sub>H<sub>19</sub>NO [M+H]<sup>+</sup>: 278.1539; found: 278.1542.



**1-Allyl-3,4-diphenyl-1***H***-pyrrole (5ai)**: colorless oil was obtained in 58% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 – 7.21 (m, 8H), 7.20 – 7.14 (m, 2H), 6.77 (s, 2H), 6.12 – 5.97 (m, 1H), 5.32 – 5.25 (m, 1H), 5.26 – 5.24 (m, 1H), 4.51 (dt, *J* = 6.0, 1.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.80, 133.80, 128.36, 128.11, 125.52, 123.35, 120.26, 118.21, 52.33. HRMS (ESI) calculated for C<sub>19</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 260.1434; found: 260.1442.



**1-Benzyl-3,4-diphenyl-1***H***-pyrrole (5aj)**:<sup>1</sup> light yellow oil was obtained in 48% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.39 – 7.34 (m, 4H), 7.33 – 7.28 (m, 1H), 7.26 – 7.20 (m, 4H), 7.17 – 7.11 (m, 6H), 7.06 (s, 2H), 5.13 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 138.46, 135.80, 128.68, 128.23, 127.81, 127.68, 127.64, 125.45, 122.23, 121.01, 52.48.



**1-(Furan-2-ylmethyl)-3,4-diphenyl-1***H***-pyrrole (5ak)**: light yellow oil was obtained in 47% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (m, 1H), 7.27 – 7.20 (m, 8H), 7.20 – 7.13 (m, 2H), 6.81 (s, 2H), 6.45 – 6.25 (m, 2H), 5.03 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.95, 135.72, 135.42, 130.24, 128.54, 128.30, 126.01, 125.32, 120.20, 118.70, 20.97. HRMS (ESI) calculated for C<sub>21</sub>H<sub>17</sub>NO [M+H]<sup>+</sup>: 300.1383; found: 300.1372.



**3,4-Diphenyl-1-(thiophen-2-ylmethyl)-1***H***-pyrrole (5al)**: light yellow oil was obtained in 45% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.27 – 7.21 (m, 8H), 7.21 – 7.14 (m, 2H), 7.06 – 7.02 (m, 1H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.82 (s, 2H), 5.24 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.52, 135.67, 128.37, 128.11, 127.00, 126.67, 125.93, 125.59, 123.70, 120.16, 48.10. HRMS (ESI) calculated for C<sub>21</sub>H<sub>17</sub>NS [M+H]<sup>+</sup>: 316.1154; found: 316.1162.



**2-((3,4-Diphenyl-1***H***-pyrrol-1-yl)methyl)pyridine (5am)**: light yellow oil was obtained in 46% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.66 – 8.52 (m, 1H), 7.66 (td, *J* = 7.6, 1.6 Hz, 1H), 7.31 – 7.21 (m, 9H), 7.20 – 7.14 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 2H), 5.23 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.62, 149.36, 137.25, 135.62, 128.35, 128.13, 125.62, 123.92, 122.64, 121.20, 120.90, 55.36. HRMS (ESI) calculated for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 311.1543; found: 311.1546.



**Ethyl 2-(3,4-diphenyl-1***H***-pyrrol-1-yl)acetate (5an)**: colorless oil was obtained in 57% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.21 (m, 8H), 7.21 – 7.15 (m, 2H), 6.78 (s, 2H), 4.65 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.44, 135.47, 128.46, 128.08, 125.67, 124.06, 121.25, 61.79, 50.97, 14.15. HRMS (ESI) calculated for C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub> [M+Na]<sup>+</sup>: 328.1308; found: 328.1315.



Ethyl 3-(3,4-diphenyl-1*H*-pyrrol-1-yl)propanoate (5ao): colorless oil was obtained in 58% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 – 7.21 (m, 8H), 7.20 – 7.14 (m, 2H), 6.78 (s, 2H), 4.23 (t, *J* = 6.8 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.00, 135.68, 128.33, 128.12, 125.56, 123.47, 120.21, 60.98, 45.09, 36.41, 14.14. HRMS (ESI) calculated for C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 320.1645; found: 320.1648.



**Methyl 2-(3,4-diphenyl-1***H***-pyrrol-1-yl)-4-methylpentanoate (5ap)**: colorless oil was obtained in 55% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 – 7.22 (m, 8H), 7.20 – 7.14 (m, 2H), 6.86 (s, 2H), 4.66 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.75 (s, 3H), 2.08 – 1.99 (m, 1H), 1.99 – 1.90 (m, 1H), 1.59 – 1.48 (m, 1H), 1.00 – 0.93 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.31, 135.64, 128.35, 128.08, 125.59, 123.50, 119.57, 60.29, 52.59, 41.45, 24.51, 22.73, 21.69. HRMS (ESI) calculated for C<sub>23</sub>H<sub>25</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 348.1958; found: 348.1964.



**1-Butyl-3,4-bis(4-fluorophenyl)-2,5-dimethyl-1***H***-pyrrole (7ab)**: colorless oil was obtained in 53% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.02 – 6.95 (m, 4H), 6.94 – 6.86 (m, 4H), 3.89 – 3.77 (m, 2H), 2.26 (s, 6H), 1.77 – 1.65 (m, 2H), 1.50 – 1.39 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.82 (d, <sup>1</sup>*J*<sub>C-F</sub> = 242.1 Hz), 132.22 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.2 Hz), 131.68 (d, <sup>3</sup>*J*<sub>C-F</sub> = 7.7 Hz), 124.24, 119.08, 114.62 (d, <sup>2</sup>*J*<sub>C-F</sub> = 20.9 Hz), 43.96, 33.15, 20.27, 13.85, 10.63. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -118.09. HRMS (ESI) calculated for C<sub>22</sub>H<sub>23</sub>NF<sub>2</sub> [M+H]<sup>+</sup>: 340.1871; found: 340.1868.



**1-Butyl-3,4-bis(4-chlorophenyl)-2,5-dimethyl-1***H***-pyrrole (7bb)**: light yellow oil was obtained in 43% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 – 7.16 (m, 4H), 6.98 – 6.93 (m, 4H), 3.87 – 3.79 (m, 2H), 2.26 (s, 6H), 1.77 – 1.64 (m, 2H), 1.50 – 1.39 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  134.68, 131.53, 130.86, 128.00, 124.65, 118.84, 43.99, 33.10, 20.26, 13.85, 10.68. HRMS (ESI) calculated for C<sub>22</sub>H<sub>23</sub>Cl<sub>2</sub>N [M+H]<sup>+</sup>: 372.1280; found: 372.1277.



**3,4-Bis(4-bromophenyl)-1-butyl-2,5-dimethyl-1***H***-pyrrole (7cb)**: light yellow oil was obtained in 39% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.30 (m, 4H), 6.94 – 6.86 (m, 4H), 3.88 – 3.78 (m, 2H), 2.25 (s, 6H), 1.74 – 1.65 (m, 2H), 1.49 – 1.39 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C

NMR (101 MHz, CDCl<sub>3</sub>) δ 135.11, 131.90, 130.93, 124.67, 119.02, 118.77, 43.98, 33.08, 20.25, 13.85, 10.68. HRMS (ESI) calculated for C<sub>22</sub>H<sub>23</sub>Br<sub>2</sub>N [M+H]<sup>+</sup>: 460.0270; found: 460.0267.



**1-Butyl-3,4-bis(4-methoxyphenyl)-2,5-dimethyl-1***H***-pyrrole** (7db) : light yellow oil was obtained in 40% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.02 – 6.96 (m, 4H), 6.81 – 6.74 (m, 4H), 3.86 – 3.81 (m, 2H), 3.77 (s, 6H), 2.27 (s, 6H), 1.77 – 1.66 (m, 2H), 1.49 – 1.39 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.04, 131.34, 128.93, 123.80, 119.52, 113.14, 55.04, 43.93, 33.19, 20.29, 13.86, 10.72. HRMS (ESI) calculated for C<sub>24</sub>H<sub>29</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 364.2271; found: 364.2268.



**1-Butyl-2,5-dimethyl-3,4-bis(4-nitrophenyl)-1***H***-pyrrole (7eb)**: orange oil was obtained in 18% isolated yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.12 – 8.06 (m, 4H), 7.21 – 7.15 (m, 4H), 3.95 – 3.86 (m, 2H), 2.26 (s, 6H), 1.67 – 1.57 (m, 2H), 1.44 – 1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  144.74, 143.39, 130.57, 127.12, 123.43, 117.67, 43.47, 32.37, 19.66, 13.69, 10.54. HRMS (ESI) calculated for C<sub>22</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 394.1761; found: 394.1760.

**1-Butyl-2,3,4,5-tetraphenyl-1***H***-pyrrole (7fb)**: white solid was obtained in 56% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.25 (m, 10H), 7.06 – 6.97 (m, 6H), 6.96 – 6.91 (m, 4H), 3.84 – 3.76 (m, 2H), 1.40 – 1.30 (m, 2H), 1.03 – 0.92 (m, 2H), 0.60 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.61, 133.18, 131.42, 131.20, 130.83, 128.07, 127.31, 127.27, 124.91, 122.01,

44.39, 33.21, 19.68, 13.36. HRMS (ESI) calculated for C<sub>32</sub>H<sub>29</sub>N [M+Na]<sup>+</sup>: 450.2192; found: 450.2199.

**Dimethyl 1-butyl-3,4-diphenyl-1***H***-pyrrole-2,5-dicarboxylate (7gb)**: white solid was obtained in 32% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 – 7.11 (m, 6H), 7.05 – 6.96 (m, 4H), 4.77 – 4.63 (m, 2H), 3.57 (s, 6H), 1.89 – 1.78 (m, 2H), 1.47 – 1.36 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.09, 134.45, 130.69, 130.29, 127.18, 126.37, 123.96, 51.35, 46.92, 34.15, 20.00, 13.78. HRMS (ESI) calculated for C<sub>24</sub>H<sub>25</sub>NO<sub>4</sub> [M+Na]<sup>+</sup>: 414.1676; found: 414.1681.



**1,2,5-Tributyl-3,4-diphenyl-1***H***-pyrrole (7hb)**: light yellow oil was obtained in 29% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 – 7.14 (m, 4H), 7.13 – 7.04 (m, 6H), 3.90 – 3.70 (m, 2H), 2.69 – 2.52 (m, 4H), 1.79 – 1.70 (m, 2H), 1.58 – 1.40 (m, 6H), 1.36 – 1.26 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  136.96, 130.34, 128.97, 127.55, 124.79, 120.48, 43.76, 34.24, 33.37, 24.65, 22.78, 20.46, 13.84, 13.78. HRMS (ESI) calculated for C<sub>28</sub>H<sub>37</sub>N [M+H]<sup>+</sup>: 388.2999; found: 388.2996.



**1-Butyl-2,5-diisopropyl-3,4-diphenyl-1***H***-pyrrole (7ib)**: light yellow oil was obtained in 43% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 – 7.01 (m, 10H), 3.92 – 3.83 (m, 2H), 3.14 – 3.03 (m, 2H), 1.82 – 1.73 (m, 2H), 1.50 – 1.40 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 12H), 1.01 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.85, 131.95, 131.59, 126.91, 125.09, 121.23, 43.95, 34.53, 26.02, 23.28, 20.43, 13.87. HRMS (ESI) calculated for C<sub>26</sub>H<sub>33</sub>N M<sup>+</sup>: 359.2608; found: 359.2604.

**1-Butyl-3,4-dimethyl-2,5-diphenyl-1***H***-pyrrole (7jb)**: colorless oil was obtained in 29% isolated yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 – 7.35 (m, 8H), 7.34 – 7.28 (m, 2H), 3.84 – 3.76 (m, 2H), 2.02 (s, 6H), 1.12 – 1.03 (m, 2H), 0.84 – 0.74 (m, 2H), 0.49 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.58, 131.41, 130.46, 128.19, 126.67, 116.47, 44.62, 32.79, 19.39, 13.34, 9.95. HRMS (ESI) calculated for C<sub>22</sub>H<sub>25</sub>N [M+H]<sup>+</sup>: 304.2060; found: 304.2058.



**3,4-dibenzyl-1-butyl-1***H***-pyrrole (7kb)**: colorless oil was obtained in 29% isolated yield. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 4H), 7.21 – 7.11 (m, 6H), 6.29 – 6.20 (m, 2H), 3.75 – 3.62 (m, 6H), 1.70 – 1.60 (m, 2H), 1.32 – 1.22 (m, 2H), 0.94 – 0.86 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.86, 128.66, 128.10, 125.48, 121.17, 119.28, 49.17, 33.57, 31.85, 19.95, 13.67. C<sub>22</sub>H<sub>25</sub>N [M+H]<sup>+</sup>: 304.2060; found: 304.2060.

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# **Copies of product NMR Spectra**

3aa







3ac



3ad

<sup>1</sup>H NMR



3ae



3af







3ah



3ai





170 160 150 140 130 120 110 100 90 f1 (ppm)

200 190 180

31

80 70

60

50

40

30

20

10 (





33

## 3aa'





5ab



5ac

36



5ae









110 100 90 f1 (ppm) 00 190 140 130 Ċ

5af







5ah







5aj



5ak





5al



## 5am







5ap



#### <sup>19</sup>F NMR

0	-10	-20	-30	-40	-50	-60	-70	-80	-90 f	-100 1 (ppm)	-110	-120	-130	-140	-150	-160	-170	-180	-190



7bb



7cb

110 100 90 f1 (ppm) 200 190 (



7db



7eb





7gb



7hb



## 7ib

#### <sup>1</sup>H NMR





7jb

7kb





