Supplementary Information

Copper-catalyzed oxidative dehydrogenative [3 + 2] annulation of oximes with *α*-amino ketones: Entry to 3-aminopyrroles

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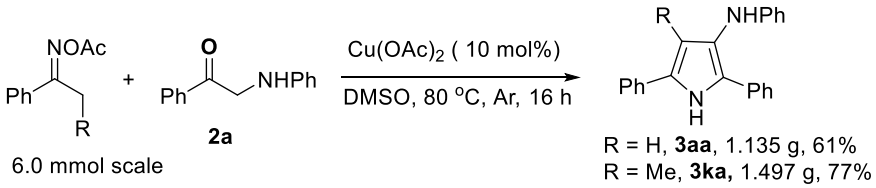
(A) General Information

All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Agilent 400 MHz at room temperature using $CDCl_3$ as solvent with tetramethylsilane as internal standard or DMSO-d_6. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Column chromatography was generally performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA), and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. Melting points were measured on a YRT-3 and uncorrected. Unless otherwise noted, all reagents were purchased from commercial sources and were used as received. Oximes **1a-1r** were prepared according to literature procedures.[1] α-Amino carbonyls **2a**-**2r** were prepared according to the reported methods.[2]

(a) General experimental procedure

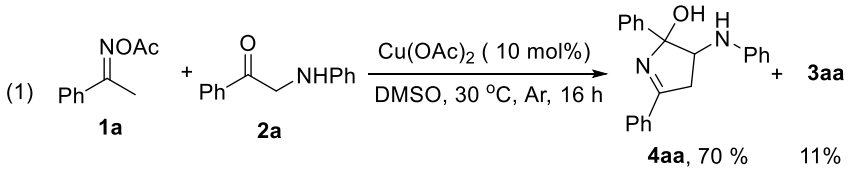
To a Schlenk tube were added $Cu(OAc)_2$ (10 mol%), Oxime **1** (0.3 mmol), α-amino carbonyl compound **2** (0.45 mmol) and DMSO (2 mL). Then the tube was recharged with argon, and the mixture was stirred at 80 ºC for 16 hours. After cooling to room temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (petroleum ether: ethyl acetate = 30 : 1) to afford the desired products **3**.

(b) Gram-scale synthesis of 3aa and 3ka



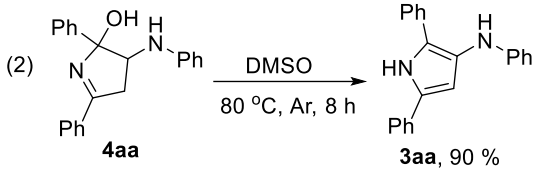
To a Schlenk tube were added $Cu(OAc)_2$ (109.0 mg, 10 mol%), oxime **1a** (1.062 g, 6 mmol, 1.0 equiv) or **1k** (1.146 g, 6 mmol, 1.0 equiv), α-amino carbonyl compound **2a** (1.899 g, 9 mmol, 1.5 equiv.) and DMSO (40 mL). Then the tube was recharged with argon, and the mixture was stirred at 80 °C for 16 hours. After cooling to room temperature, the resulting mixture was extracted with EtOAc (3×30 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane: ethyl acetate = 30 : 1) to afford the desired product **3aa** (1.135 g, 61%) or **3ka**(1.497 g, 77%).

(c) Control experiments

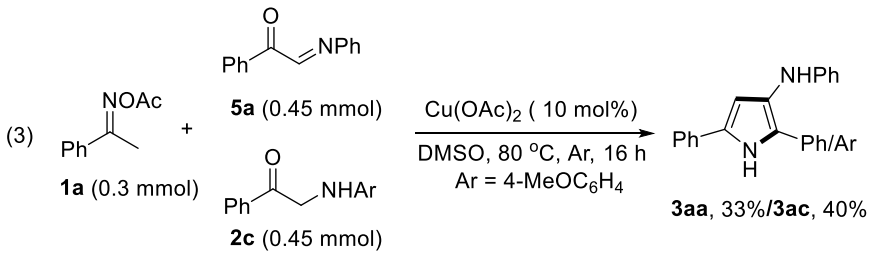


To a Schlenk tube were added **1a** (0.3 mmol, 53.1 mg), **2a** (0.45 mmol, 95.0 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), and DMSO (2 mL) under an argon atmosphere was stirred at 30 °C for 16 h. The resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column

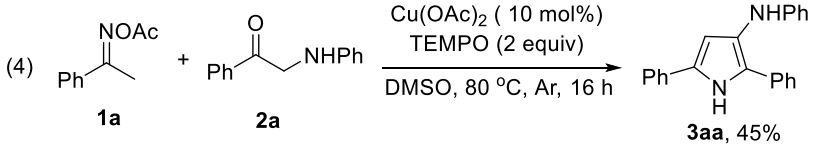
chromatography (hexane: ethyl acetate = 30 : 1 to 5 :1) to afford **4aa** (68.9 mg, 70% yield), **3aa** (10.2 mg, 11% yield).



To a Schlenk tube were added **4aa** (0.2 mmol, 65.6 mg), and DMSO (2 mL) under an argon atmosphere was stirred at 80 °C for 8 h. After cooling to room temperature, the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane: ethyl acetate = 30 : 1) to afford the desired product **3aa** (55.8 mg, 90% yield).

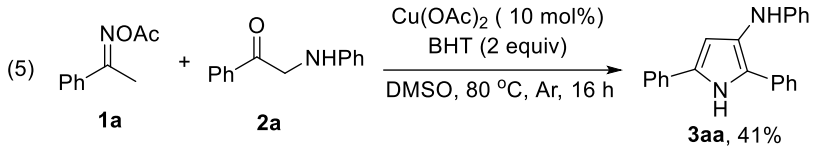


According to the general procedure, **1a** (0.3 mmol, 53.1 mg), **5a** (0.45 mmol, 94.1 mg), **2c** (0.45 mmol, 108.5 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), and DMSO (2 mL) under an argon atmosphere was stirred at 80 °C for 16 h to afford **3aa** (30.7 mg, 33% yield), **3ac** (40.8 mg, 40% yield).

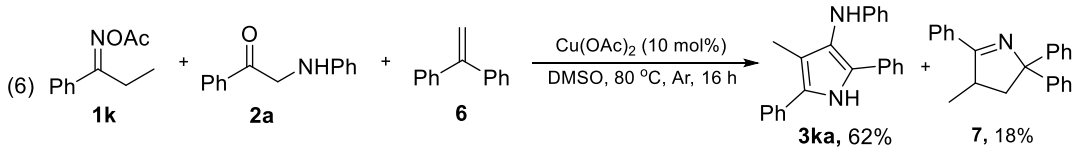


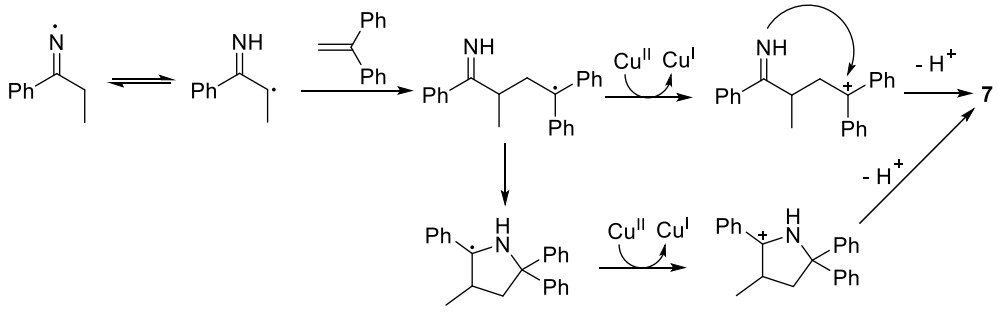
According to the general procedure, **1a** (0.3 mmol, 53.1 mg), **2a** (0.45 mmol, 95.0 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), TEMPO (0.6 mmol, 93.8 mg) and DMSO (2

mL) under an argon atmosphere was stirred at 80 °C for 16 h to afford **3aa** (42.0 mg, 45% yield).



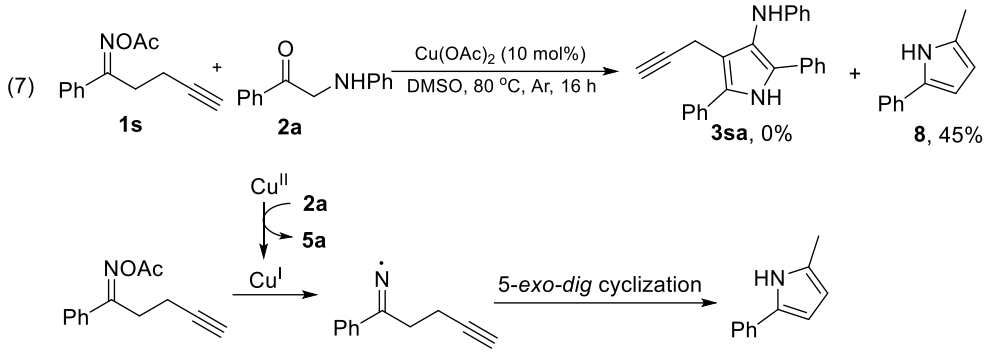
According to the general procedure, **1a** (0.3 mmol, 53.1 mg), **2a** (0.45 mmol, 95.0 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), BHT (0.6 mmol, 132.0 mg) and DMSO (2 mL) under an argon atmosphere was stirred at 80 °C for 16 h to afford **3aa** (38.1 mg, 41% yield).





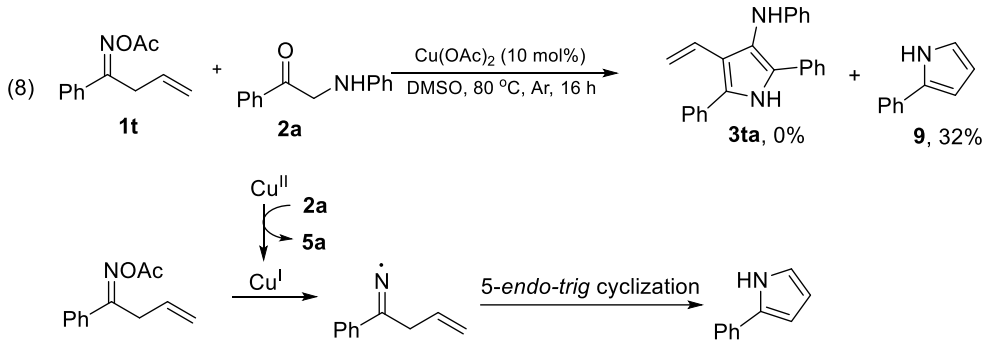
Supplementary Scheme 1. Proposed mechanistic pathways for the formation of pyrroline **7**

According to the general procedure, **1k** (0.3 mmol, 57.3 mg), **2a** (0.45 mmol, 95.0 mg), **6** (0.6 mmol, 108 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), and DMSO (2 mL) under an argon atmosphere was stirred at 80 °C for 16 h to afford **3ka** (60.3 mg, 62% yield), pyrroline **7** (16.8 mg, 18% yield).



Supplementary Scheme 2. Proposed mechanistic pathways for the formation of pyrrole **8**

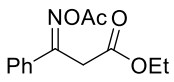
According to the general procedure, **1s** (0.3 mmol, 64.5 mg), **2a** (0.45 mmol, 95.0 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), and DMSO (2 mL) under an argon atmosphere was stirred at 80 °C for 16 h to afford pyrrole **8** (21.2 mg, 45% yield), which could form via an iminyl radical 5-*exo-dig* cyclization. No desired product **3sa** was detected by GC-MS.



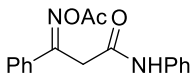
Supplementary Scheme 3. Proposed mechanistic pathways for the formation of pyrrole **9**

According to the general procedure, **1t** (0.3 mmol, 64.5 mg), **2a** (0.45 mmol, 95.0 mg), $Cu(OAc)_2$ (0.03 mmol, 5.4 mg), and DMSO (2 mL) under an argon atmosphere was stirred at 80 °C for 16 h to afford pyrrole **9** (13.7 mg, 32% yield), which could form via an iminyl radical 5-*endo-trig* cyclization.[1d] No desired product **3ta** was detected by GC-MS.

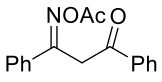
(d) Some other unsuccessful substrates



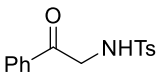
1u



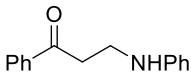
1v



1w

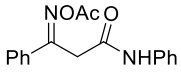


2s

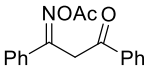


2t

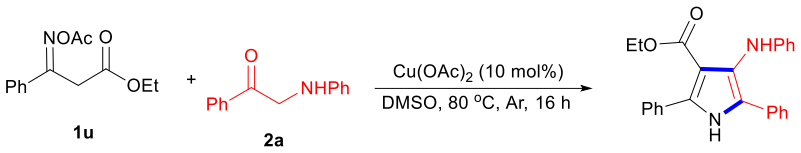
Substrates **1u**,[1c] **2s**,[3] **2t**[4] were prepared according to the reported methods. **1v** and **1w** were unreported substrates, and were synthesized from corresponding 1,3-diphenylpropane-1,3-dione/3-oxo-*N*,3-diphenylpropanamide according to literature procedures.[1c]



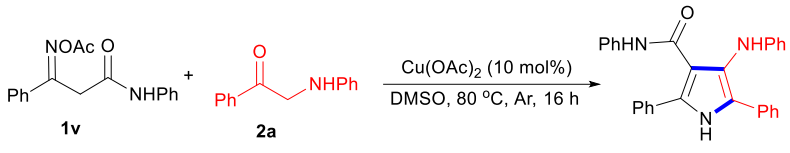
3-(Acetoxyimino)-*N*,3-diphenylpropanamide (1v): White solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.36 (s, 1H), 7.81 (d, J = 6.0 Hz, 2H), 7.57 (d, J = 6.4 Hz, 2H), 7.53-7.47 (m, 3H), 7.31 (t, J = 6.4 Hz, 2H), 7.05 (t, J = 6.0 Hz, 1H), 4.06 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.5, 165.9, 160.9, 139.4, 134.6, 131.2, 129.3, 129.1, 127.6, 123.9, 119.6, 36.8, 20.0; HRMS *m/z* (ESI) calcd for $C_{17}H_{17}N_2O_3$ $(M+H)^+$ 297.1234, found 297.1238.



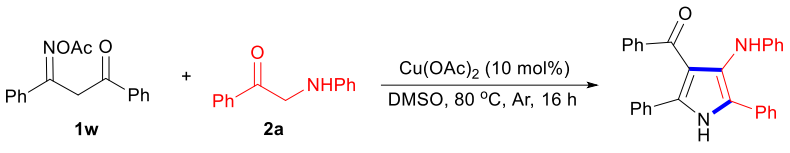
3-(Acetoxyimino)-1,3-diphenylpropan-1-one (1w): White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J = 6.4 Hz, 2H), 7.12 (d, J = 6.4 Hz, 2H), 7.62 (t, J = 6.0 Hz, 1H), 7.50 (t, J = 6.0 Hz, 2H), 7.45-7.37 (m, 3H), 4.54 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.0, 168.4, 159.9, 135.8, 134.0, 133.7, 130.6, 128.8, 128.6, 128.2, 127.1, 39.0, 19.5; HRMS *m/z* (ESI) calcd for $C_{17}H_{16}NO_3$ $(M+H)^+$ 282.1125, found 282.1123.



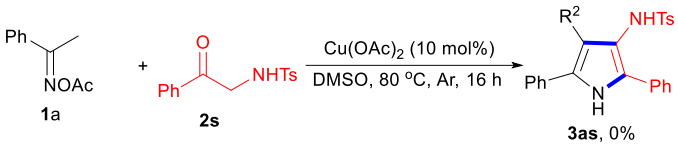
3ua, 0%



3va, 0%

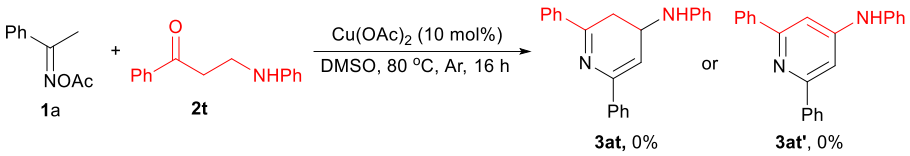


3wa, 0%



3as, 0%

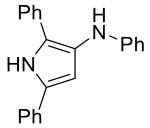
Nearly 100% of **2s** was recovered



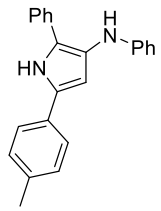
3at, 0% **3at'**, 0%

97% of **2t** was recovered

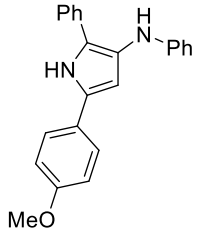
(B) Analytical Data



***N*,2,5-Triphenyl-1*H*-pyrrol-3-amine (3aa):** Light yellow oil; 66.0 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.57-7.55 (m, 2H), 7.51-7.49 (m, 2H), 7.40-7.34 (m, 4H), 7.23-7.18 (m, 4H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 3.2 Hz, 1H), 5.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 132.1, 131.8, 130.9, 129.2, 129.0, 126.5, 126.4, 125.5, 125.2, 124.8, 123.6, 118.1, 113.9, 105.7; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}N_2$ $(M+H)^+$ 311.1543, found 311.1548.

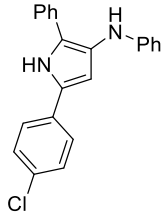


***N*,2-Diphenyl-5-*p*-tolyl-1*H*-pyrrol-3-amine (3ba):** Light yellow oil, 71.9 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.39-7.32 (m, 4H), 7.21-7.17 (m, 5H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 5.18 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 136.4, 131.9, 131.1, 129.6, 129.4, 129.2, 128.9, 126.2, 125.2, 125.0, 124.8, 123.6, 118.1, 113.9, 105.2, 21.1; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2$ $(M+H)^+$ 325.1699, found 325.1705.

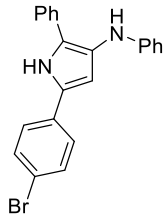


5-(4-Methoxyphenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ca): Light yellow oil, 78.5 mg, 77% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.40-7.36 (m, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.19-7.14 (m, 3H), 6.90-6.87 (m, 2H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 2.8 Hz, 1H), 5.14 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 147.2, 131.9, 130.9, 129.2, 128.9, 126.1, 125.2, 125.1, 125.0,

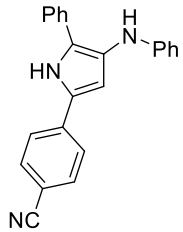
124.7 (2C), 118.0, 114.4, 113.9, 104.7, 55.3; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2O$ $(M+H)^+$ 341.1648, found 341.1654.



5-(4-Chlorophenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3da): Light yellow oil, 72.2 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (s, 1H), 7.55-7.53 (m, 2H), 7.40-7.31 (m, 6H), 7.23-7.17 (m, 3H), 6.83-6.75 (m, 3H), 6.53 (d, *J* = 2.8 Hz, 1H), 5.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 132.0, 131.6, 130.6, 129.7, 129.2, 129.0, 128.9, 126.5, 125.8, 125.3, 125.0, 124.7, 118.2, 113.9, 106.0; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}ClN_2$ $(M+H)^+$ 345.1153, found 345.1155.

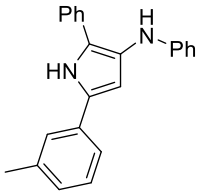


5-(4-Bromophenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ea): Light yellow oil, 83.8 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.50-7.46 (m, 2H), 7.37-7.32 (m, 4H), 7.23-7.17 (m, 3H), 6.83-6.75 (m, 3H), 6.54 (d, *J* = 2.8 Hz, 1H), 5.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 132.0, 131.6, 131.1, 129.7, 129.3, 129.0, 126.6, 125.9, 125.3, 125.1, 125.0, 120.0, 118.3, 114.0, 106.1; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}BrN_2$ $(M+H)^+$ 389.0648, found 389.0657.

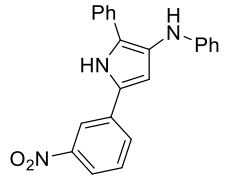


4-(5-Phenyl-4-(phenylamino)-1*H*-pyrrol-2-yl)benzonitrile (3fa): Light-yellow solid; 60.3 mg, 60% yield; mp 198-199 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.4 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 6.8 Hz, 4H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.32 (s, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 2.8 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.57 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 148.6, 137.0, 133.1, 132.1, 129.5,

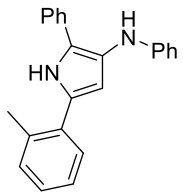
129.2, 128.9, 126.8, 126.5, 125.8, 124.5, 119.9, 117.1, 113.6, 109.4, 107.7; HRMS *m/z* (ESI) calcd for $C_{23}H_{18}N_3$ $(M+H)^+$ 336.1495, found 336.1491.



***N*,2-diphenyl-5-(*m*-tolyl)-1*H*-pyrrol-3-amine (3ga):** Light yellow oil, 71.0 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.35-7.16 (m, 8H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 2.8 Hz, 1H), 5.16 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 138.5, 132.0, 131.8, 131.0, 129.2, 128.9, 128.8, 128.4, 127.4, 126.3, 125.3, 125.2, 124.8, 124.3, 120.7, 118.1, 113.9, 21.5; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}N_3O_2$ $(M+H)^+$ 325.1699, found 325.1705.

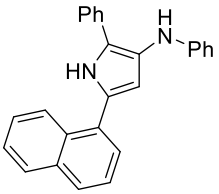


5-(3-Nitrophenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ha): Red solid, 66.0 mg, 62% yield; mp 145-146 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (s, 1H), 8.27 (t, *J* = 1.6 Hz, 1H), 7.98 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.25-7.18 (m, 3H), 6.83-6.76 (m, 3H), 6.65 (d, *J* = 2.8 Hz, 1H), 5.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 146.8, 133.7, 131.2, 129.8, 129.3, 129.2, 129.0, 128.2, 127.0, 126.9, 125.5, 125.3, 120.6, 118.5, 117.7, 114.0, 107.2; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}N_3O_2$ $(M+H)^+$ 356.1394, found 356.1392.

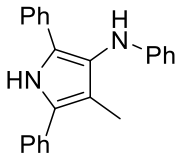


***N*,2-diphenyl-5-(*o*-tolyl)-1*H*-pyrrol-3-amine (3ia):** Light yellow oil, 69.0 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (s, 1H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz,

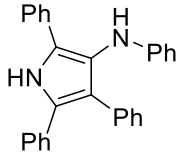
2H), 7.26-7.17 (m, 6H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 2.8 Hz, 1H), 5.19 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 135.0, 132.2, 131.9, 131.2, 130.2, 129.2, 128.9, 127.4, 127.0, 126.21, 126.15, 125.1, 124.7, 123.9, 118.0, 113.8, 108.8, 21.3; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}N_3O_2$ $(M+H)^+$ 325.1699, found 325.1703.



5-(Naphthalen-1-yl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ja): Light yellow oil, 71.3 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38-8.36 (m, 1H), 8.28 (s, 1H), 7.89-7.85 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.56-7.46 (m, 6H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.22-7.16 (m, 3H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 5.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 134.0, 131.9, 131.1, 131.0, 129.6, 129.3, 129.0, 128.5, 127.8, 126.5, 126.3, 126.0, 125.8, 125.5, 125.4, 125.2, 124.2, 118.1, 113.9, 109.3; HRMS *m/z* (ESI) calcd for $C_{26}H_{21}N_2$ $(M+H)^+$ 361.1699, found 361.1703.

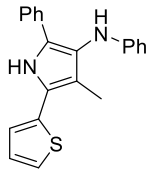


4-Methyl-*N*,2,5-triphenyl-1*H*-pyrrol-3-amine (3ka): Light yellow oil, 83.6 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 4H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31-7.23 (m, 3H), 7.19-7.15 (m, 3H), 6.74-6.67 (m, 3H), 5.06 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 133.4, 131.8, 129.2, 128.9, 128.8, 127.7, 126.6, 126.3 (2C), 126.0, 125.1, 123.3, 117.7, 116.8, 113.3, 9.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2$ $(M+H)^+$ 325.1699, found 325.1705.

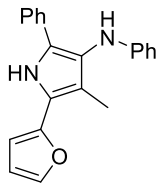


***N*,2,4,5-Tetraphenyl-1*H*-pyrrol-3-amine (3la):** Light yellow solid, 103.1 mg, 89% yield; mp 170-171 °C (uncorrected); ^{1}H NMR (400

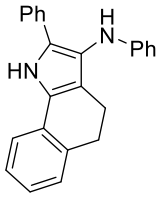
MHz, $CDCl_3$) δ: 8.36 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.30-7.08 (m, 15H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 5.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 134.0, 132.6, 131.5, 130.2, 129.1, 128.8, 128.6, 128.3, 128.0, 126.9, 126.7 (2C), 126.4, 126.3, 124.9, 122.5, 121.9, 117.9, 113.8; HRMS *m/z* (ESI) calcd for $C_{28}H_{23}N_2$ $(M+H)^+$ 387.1856, found 387.1851.



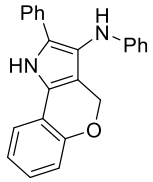
4-Methyl-*N*,2-diphenyl-5-(thiophen-2-yl)-1*H*-pyrrol-3-amine (3ma): Brown oil, 76.2 mg, 77% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.09 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.22-7.15 (m, 4H), 7.08-7.06 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 135.7, 131.5, 129.3, 128.9, 127.6, 126.6, 126.5, 125.1, 123.2, 123.0, 122.5, 121.9, 117.7, 117.3, 113.2, 9.7; HRMS *m/z* (ESI) calcd for $C_{21}H_{19}N_2S$ $(M+H)^+$ 331.1263, found 331.1275.



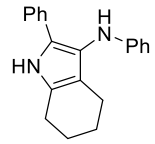
5-(Furan-2-yl)-4-methyl-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3na): Brown oil, 67.8 mg, 72% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 (s, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 3H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.48-6.47 (m, 1H), 6.33 (d, *J* = 3.6 Hz, 1H), 5.00 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 147.8, 140.0, 131.5, 129.2, 128.8, 126.4, 126.2, 125.0, 122.9, 119.9, 117.7, 116.4, 113.2, 111.7, 103.4, 9.5; HRMS *m/z* (ESI) calcd for $C_{21}H_{19}N_2O$ $(M+H)^+$ 315.1492, found 315.1502.



***N*,2-Diphenyl-4,5-dihydro-1*H*-benzo[*g*]indol-3-amine (3oa):** Light yellow oil, 79.6 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27-7.15 (m, 6H), 7.10-7.06 (m, 1H), 6.75-6.69 (m, 3H), 5.08 (s, 1H), 2.88 (t, *J* = 8.0 Hz, 2H), 2.54 (t, *J* = 8.0 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 135.1, 132.0, 129.2, 128.9, 128.8, 128.5, 126.9, 126.7, 126.6, 126.3, 125.5, 125.2, 121.2, 119.9, 118.1, 117.8, 113.4, 29.5, 19.9; HRMS *m/z* (ESI) calcd for $C_{24}H_{21}N_2$ $(M+H)^+$ 337.1699, found 337.1702.

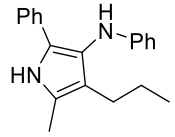


***N*,2-Diphenyl-1,4-dihydrochromeno[4,3-*b*]pyrrol-3-amine (3pa):** Light yellow oil, 71.0 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24-7.16 (m, 4H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.94-6.88 (m, 2H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 2H), 5.00 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7, 147.1, 131.5, 129.4, 129.0, 127.4 (2C), 126.7, 125.3, 122.7, 121.4, 119.2, 118.5, 118.3, 117.7, 116.8, 113.9, 113.3, 64.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{19}N_2O$ $(M+H)^+$ 339.1492, found 339.1490.

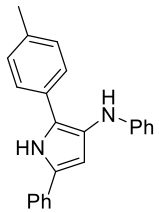


***N*,2-Diphenyl-4,5,6,7-tetrahydro-1*H*-indol-3-amine (3qa):** Light yellow oil, 36.3 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.17-7.10 (m, 3H), 6.73-6.67 (m, 3H), 5.02 (s, 1H), 2.61 (t, *J* = 6.0 Hz, 2H), 2.29 (t, *J* = 6.0 Hz, 2H), 1.85-1.80 (m, 2H), 1.72-1.67 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 132.5, 129.1, 128.7, 126.8, 125.6, 124.7, 124.0, 120.5, 117.4, 117.3, 113.4, 23.2, 22.9, 21.0; LRMS (EI, 70

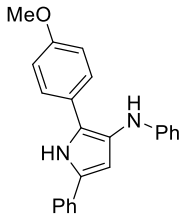
eV) *m/z* (%): 288 (M^+, 100), 259 (43), 207 (14), 129 (14); HRMS *m/z* (ESI) calcd for $C_{20}H_{21}N_2$ $(M+H)^+$ 289.1699, found 289.1701.



***N*,2-Diphenyl-4,5,6,7-tetrahydro-1*H*-indol-3-amine (3ra):** Light yellow oil, 33.1 mg, 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.15-7.07 (m, 3H), 6.71-6.62 (m, 3H), 4.98 (s, 1H), 2.25 (t, *J* = 7.6 Hz, 2H), 2.24 (s, 3H), 1.46-1.37 (m, 2H), 0.83 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 132.2, 129.1, 128.7, 125.4, 124.4, 124.1, 123.6, 121.5, 119.6, 117.3, 113.2, 25.7, 23.9, 14.0, 11.8; HRMS *m/z* (ESI) calcd for $C_{20}H_{21}N_2$ $(M+H)^+$ 291.1856, found 291.1854.

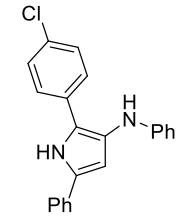


***N*,5-Diphenyl-2-*p*-tolyl-1*H*-pyrrol-3-amine (3ab):** Light yellow oil, 70.0 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 1H), 7.48-7.42 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.23-7.14 (m, 5H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 5.15 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 136.2, 132.2, 130.5, 129.6, 129.2, 129.0, 128.9, 126.4, 125.7, 125.2, 124.4, 123.5, 118.0, 113.9, 105.7, 21.1; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2$ $(M+H)^+$ 325.1699, found 325.1703.

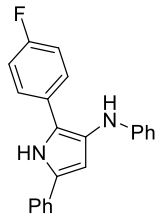


2-(4-Methoxyphenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ac): Light yellow oil, 75.5 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (s, 1H), 7.49-7.46 (m, 4H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.23-7.17 (m, 3H), 6.91-6.87 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 2.8 Hz, 1H), 5.14 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 147.5, 132.3, 130.2, 129.2, 128.9, 126.8, 126.3, 125.9, 124.6, 123.7, 123.5, 118.0,

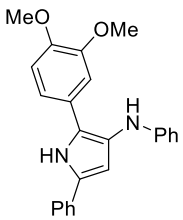
114.4, 113.8, 105.8, 55.3; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2O$ $(M+H)^+$ 341.1648, found 341.1652.



2-(4-Chlorophenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ad): Light yellow oil, 72.2 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 4H), 7.39-7.36 (m, 2H), 7.31-7.28 (m, 2H), 7.25-7.17 (m, 3H), 6.81-6.75 (m, 3H), 6.53 (d, *J* = 2.8 Hz, 1H), 5.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 131.9 (2C), 131.3, 130.2, 129.3, 129.1, 129.0, 126.8, 126.3, 125.3, 124.6, 123.7, 118.4, 114.0, 106.0; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}ClN_2$ $(M+H)^+$ 345.1153, found 345.1153.

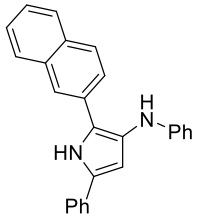


2-(4-Fluorophenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ae): Light yellow oil, 67.9 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.52-7.47 (m, 4H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.25-7.17 (m, 3H), 7.06-7.00 (m, 2H), 6.81-6.74 (m, 3H), 6.53 (d, *J* = 3.2 Hz, 1H), 5.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4 (d, *J* = 245.2 Hz), 147.2, 132.0, 130.9, 129.3, 129.0, 128.0 (d, *J* = 3.3 Hz), 127.0 (d, *J* = 7.8 Hz), 126.6, 125.1, 124.5, 123.6, 118.2, 115.9 (d, *J* = 21.4 Hz), 113.9, 105.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ: -115.2 (s, 1F); HRMS *m/z* (ESI) calcd for $C_{22}H_{18}FN_2$ $(M+H)^+$ 329.1449, found 329.1452.

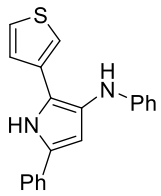


2-(3,4-Dimethoxyphenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3af): Light yellow oil, 81.0 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.22-7.14 (m, 3H), 7.09 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.83-6.71 (m, 4H), 6.52 (d, *J* = 3.2 Hz, 1H), 5.15 (s, 1H), 3.82 (s, 3H), 3.59 (s, 3H); ^{13}C NMR

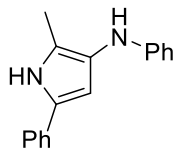
(100 MHz, $CDCl_3$) δ: 149.0, 147.7, 147.6, 132.2, 130.2, 129.2, 128.9, 126.3, 126.2, 124.8, 123.6, 123.5, 118.0, 117.3, 113.6, 111.4, 109.4, 106.3, 55.8, 55.4; HRMS *m/z* (ESI) calcd for $C_{24}H_{23}N_2O_2$ $(M+H)^+$ 371.1754, found 371.1766.



2-(Naphthalen-2-yl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ag): Light yellow oil, 71.3 mg, 66% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 7.90 (s, 1H), 7.79-7.72 (m, 4H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.46-7.36 (m, 4H), 7.25-7.18 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 5.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 133.7, 132.1, 131.9, 131.2, 129.3 (2C), 129.0, 128.6, 127.8, 127.7, 126.6, 126.4, 125.6, 125.5, 125.3, 124.0, 123.7, 123.0, 118.3, 114.1, 105.7; HRMS *m/z* (ESI) calcd for $C_{26}H_{21}N_2$ $(M+H)^+$ 361.1699, found 361.1702.

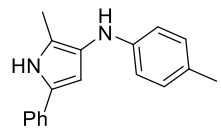


***N*,5-Diphenyl-2-(thiophen-3-yl)-1*H*-pyrrol-3-amine (3ah):** Light yellow solid, 68.3 mg, 72% yield; mp 48-49 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31-7.27 (m, 3H), 7.23-7.16 (m, 3H), 6.79-6.73 (m, 3H), 6.49 (d, *J* = 2.8 Hz, 1H), 5.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 132.3, 132.1, 130.2, 129.2, 128.9, 126.5, 126.2, 125.1, 124.2, 123.5, 123.1, 118.4, 118.1, 113.8, 105.8; HRMS *m/z* (ESI) calcd for $C_{20}H_{17}N_2S$ $(M+H)^+$ 317.1107, found 317.1105.

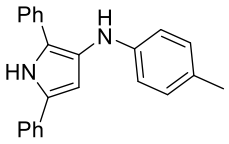


2-Methyl-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ai): Light yellow solid, 50.6 mg, 68% yield; mp 147-148 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H),

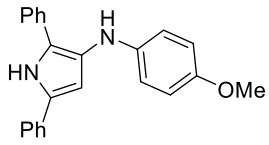
7.19-7.14 (m, 3H), 6.70 (d, J = 8.4 Hz, 3H), 6.37 (d, J = 3.2 Hz, 1H), 4.97 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.1, 132.6, 129.1, 128.9, 128.6, 125.8, 123.9, 123.3, 123.1, 117.5, 113.2, 104.8, 10.5; HRMS *m/z* (ESI) calcd for $C_{17}H_{17}N_2$ $(M+H)^+$ 249.1386, found 249.1381.



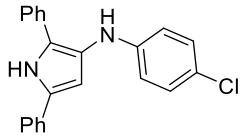
2-Methyl-5-phenyl-*N*-*p*-tolyl-1*H*-pyrrol-3-amine (3aj): Light yellow solid, 51.9 mg, 66% yield; mp 176-177 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (s, 1H), 7.40 (d, J = 7.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 6.36 (d, J = 2.8 Hz, 1H), 4.86 (s, 1H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.8, 132.7, 129.6, 128.8, 128.5, 126.7, 125.8, 123.9, 123.7, 123.1, 113.3, 104.7, 20.4, 10.5; HRMS *m/z* (ESI) calcd for $C_{18}H_{19}N_2$ $(M+H)^+$ 263.1543, found 263.1549.



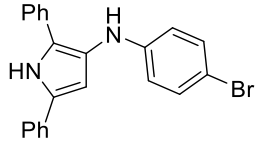
2,5-Diphenyl-*N*-*p*-tolyl-1*H*-pyrrol-3-amine (3ak): Light yellow oil, 73.9 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.57-7.54 (m, 2H), 7.49-7.47 (m, 2H), 7.39-7.33 (m, 4H), 7.23-7.18 (m, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 3.2 Hz, 1H), 5.10 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.8, 132.2, 131.9, 130.8, 129.7, 129.0, 128.9, 127.4, 126.5, 126.3, 125.5, 125.2, 125.1, 123.6, 114.2, 105.5, 20.4; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2$ $(M+H)^+$ 325.1699, found 325.1702.



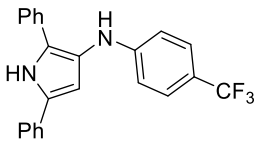
***N*-(4-Methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3al):** Light yellow oil, 73.4 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.39-7.34 (m, 4H), 7.24-7.18 (m, 2H), 6.82-6.78 (m, 4H), 6.51 (d, *J* = 2.8 Hz, 1H), 5.03 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7, 141.0, 132.2, 132.0, 130.9, 129.0, 128.9, 126.5, 126.4, 126.2, 125.1, 124.6, 123.6, 115.6, 114.8, 105.0, 55.8; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2O$ $(M+H)^+$ 341.1648, found 341.1654.



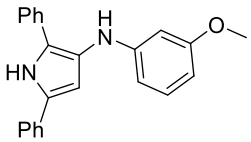
***N*-(4-Chlorophenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3am):** Light yellow oil, 86.7 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 7.52-7.47 (m, 4H), 7.40-7.33 (m, 4H), 7.25-7.20 (m, 2H), 7.14-7.10 (m, 2H), 6.74-6.70 (m, 2H), 6.50 (d, *J* = 2.8 Hz, 1H), 5.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.9, 132.0, 131.6, 131.0, 129.1, 129.0 (2C), 126.7, 126.6, 125.8, 125.2, 124.3, 123.6, 122.6, 115.0, 105.7; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}ClN_2$ $(M+H)^+$ 345.1153, found 345.1156.



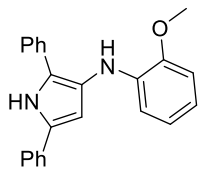
***N*-(4-Bromophenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3an):** Light yellow oil, 93.1 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (s, 1H), 7.51-7.47 (m, 4H), 7.39-7.33 (m, 4H), 7.26-7.19 (m, 4H), 6.69-6.65 (m, 2H), 6.49 (d, *J* = 2.8 Hz, 1H), 5.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4, 132.0, 131.9, 131.6, 131.0, 129.0, 126.7, 126.6, 125.9, 125.2, 124.1, 123.6, 115.4, 109.7, 105.7; HRMS *m/z* (ESI) calcd for $C_{22}H_{18}BrN_2$ $(M+H)^+$ 389.0648, found 389.0654.



2,5-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-amine (3ao): Light yellow solid, 99.8 mg, 88% yield; mp 139-140 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.50-7.47 (m, 4H), 7.41-7.33 (m, 6H), 7.26-7.21 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 2.8 Hz, 1H), 5.38 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.0, 131.9, 131.4, 131.1, 129.0, 126.8 (2C), 126.6 (q, *J* = 3.7 Hz), 126.4, 126.3, 125.3, 123.6, 123.0, 119.6 (q, *J* = 32.4 Hz), 113.0, 105.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ: -60.9 (m, 3F); HRMS *m/z* (ESI) calcd for $C_{23}H_{18}F_3N_2$ $(M+H)^+$ 379.1417, found 379.1423.

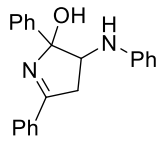


***N*-(3-Methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3ap):** Light yellow oil, 72.4 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 7.56-7.46 (m, 4H), 7.38-7.32 (m, 4H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.13-7.07 (m, 1H), 6.56-6.54 (m, 1H), 6.46-6.32 (m, 3H), 5.18 (s, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.8, 148.7, 132.1, 131.8, 130.9, 130.0, 128.9, 126.5, 126.4, 125.6, 125.3, 124.5, 123.6, 106..9, 105.9, 103.4, 99.8, 55.1; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2O$ $(M+H)^+$ 341.1648, found 341.1656.

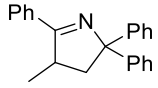


***N*-(2-Methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3aq):** Light yellow oil, 70.4 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39-7.32 (m, 4H), 7.23-7.17 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.86-6.79 (m, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 2.8 Hz, 1H), 5.81 (s, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 136.9, 132.2, 132.0, 130.8, 128.9 (2C), 126.5, 126.2,

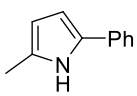
125.4, 125.0, 124.8, 123.6, 121.2, 117.3, 112.1, 109.9, 105.7, 55.5; HRMS *m/z* (ESI) calcd for $C_{23}H_{21}N_2O$ $(M+H)^+$ 341.1648, found 341.1654.



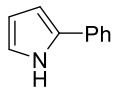
2,5-Diphenyl-3-(phenylamino)-3,4-dihydro-2*H*-pyrrol-2-ol (4aa): Light yellow oil, 68.9 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.2 Hz, 2H), 7.54-7.41 (m, 5H), 7.22-7.13 (m, 5H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 5.96 (s, 1H), 4.83 (d, *J* = 6.4 Hz, 1H), 4.06 (q, *J* = 6.4 Hz, 1H), 3.42 (dd, *J* = 16.8, 6.8 Hz, 1H), 2.98 (dd, *J* = 17.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 147.2, 144.3, 133.4, 131.7, 129.2, 128.6, 128.24, 128.17, 127.7, 125.2, 117.5, 113.3, 100.7, 61.2, 42.1. HRMS *m/z* (ESI) calcd for $C_{22}H_{21}N_2O$ $(M+H)^+$ 329.1648, found 329.1652.



4-Methyl-2,2,5-triphenyl-3,4-dihydro-2*H*-pyrrole (7):[5] Light yellow oil, 16.8 mg, 18% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (t, *J* = 2.8 Hz, 2H), 7.56 (d, *J* = 6.4 Hz, 2H), 7.45-7.44 (m, 5H), 7.30 (t, *J* = 6.0 Hz, 2H), 7.25 (t, *J* = 6.0 Hz, 2H), 7.20-7.13 (m, 2H), 3.60-3.53 (m, 1H), 3.04 (dd, *J* = 10.4, 6.8 Hz, 1H), 2.49 (dd, *J* = 10.4, 4.0 Hz, 1H), 1.11 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 149.0, 148.3, 134.2, 130.1, 128.4, 128.3, 128.12, 128.09, 126.6, 126.5, 126.22, 126.20, 82.0, 46.4, 42.8, 18.5.



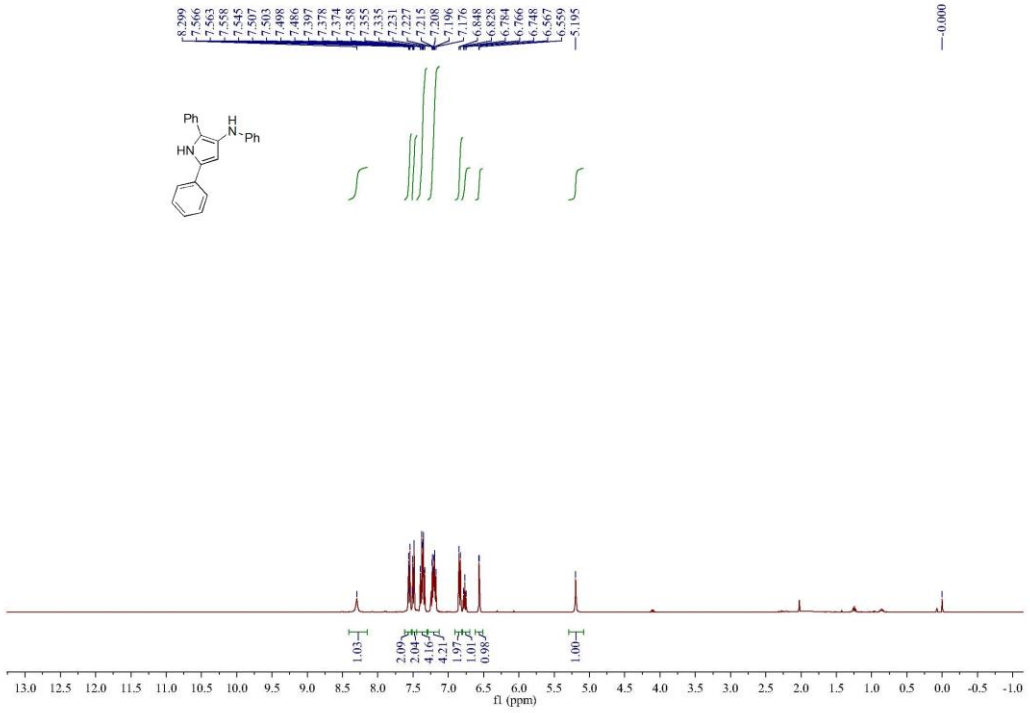
2-Methyl-5-phenyl-1*H*-pyrrole (8):[6] White solid, 21.2 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (s, 1H), 7.40 (d, *J* = 6.0 Hz, 2H), 7.31 (t, *J* = 6.0 Hz, 2H), 7.14 (t, *J* = 6.0 Hz, 1H), 6.39 (t, *J* = 2.4 Hz, 1H), 5.94 (brs, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.9, 130.7, 129.0, 128.8, 125.6, 123.3, 107.9, 106.1, 13.1.



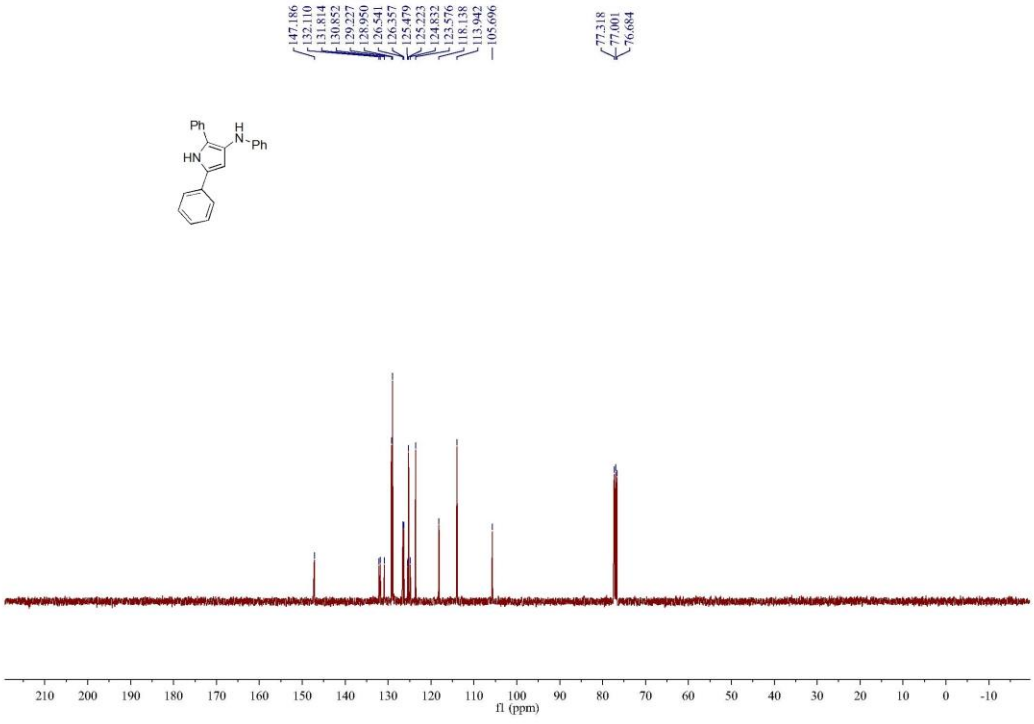
2-Phenyl-1*H*-pyrrole (9):[1c] White solid, 13.7 mg, 32% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (s, 1H), 7.43 (d, *J* = 6.4 Hz, 2H), 7.33 (t, *J* = 6.4 Hz, 2H), 7.19 (t, *J* = 6.4 Hz, 1H), 6.80 (brs, 1H), 6.52 (brs, 1H), 6.29 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.7, 132.0, 128.8, 126.1, 123.8, 118.8, 110.0, 105.9.

(C) NMR Spectra

N,2,5-Triphenyl-1*H*-pyrrol-3-amine (3aa)

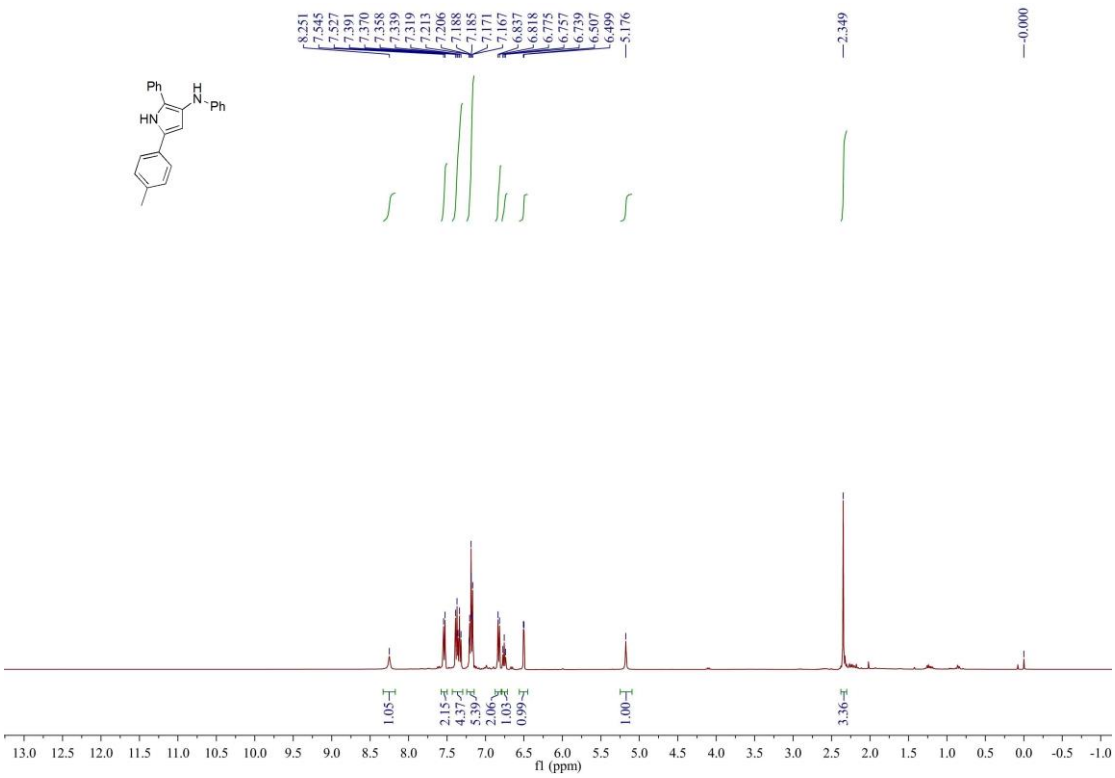


^{1}H NMR spectra of compound 3aa in $CDCl_3$ (400 MHz)

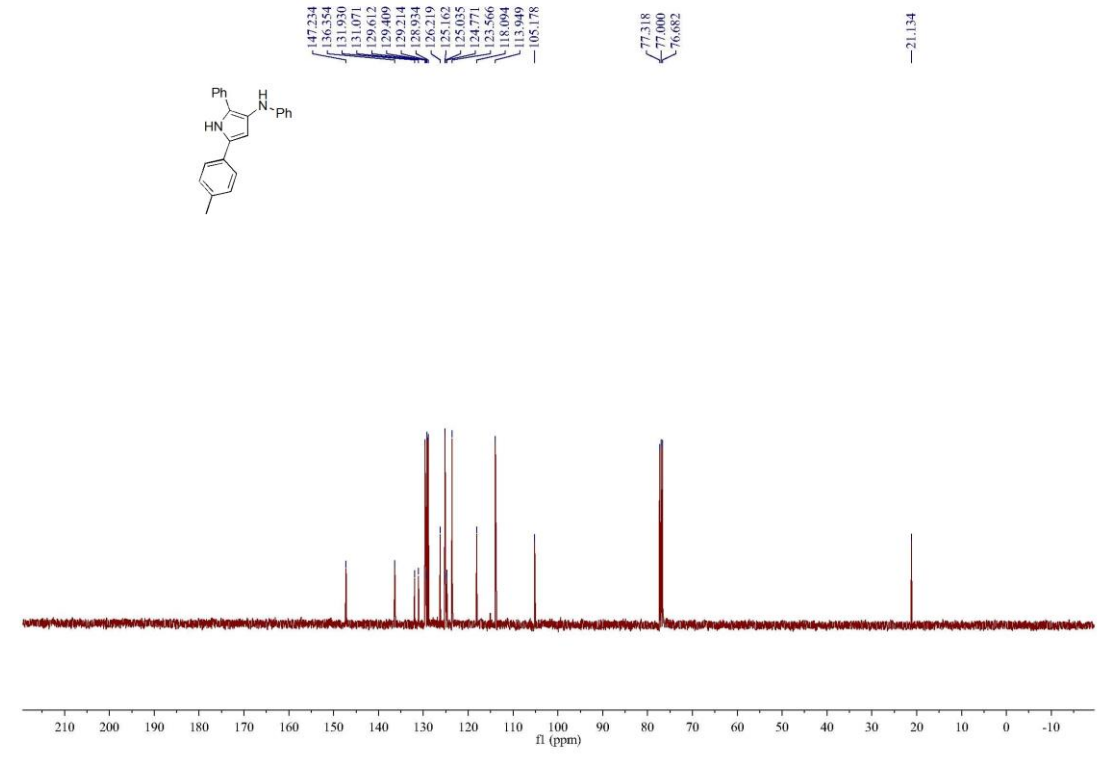


^{13}C NMR spectra of compound 3aa in $CDCl_3$ (400 MHz)

_N_,2-Diphenyl-5-_p_-tolyl-1_H_-pyrrol-3-amine (3ba)

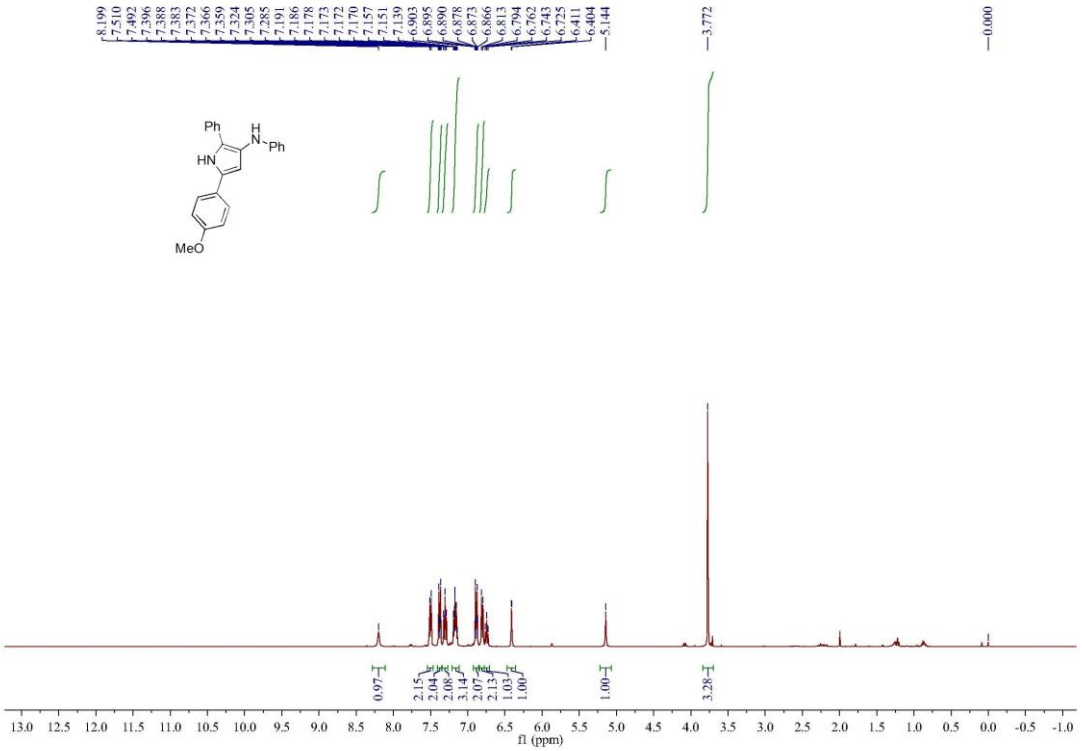


^{1}H spectra of compound 3ba in $CDCl_3$ (400 MHz)

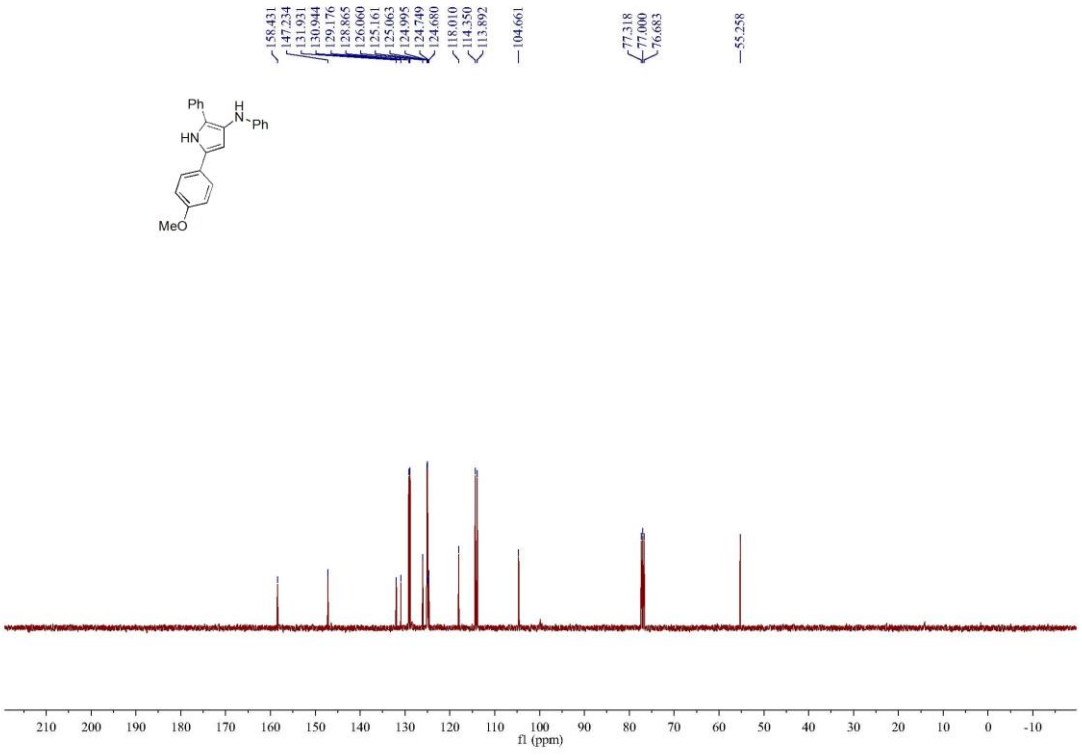


^{13}C NMR spectra of compound 3ba in $CDCl_3$ (400 MHz)

5-(4-Methoxyphenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ca)

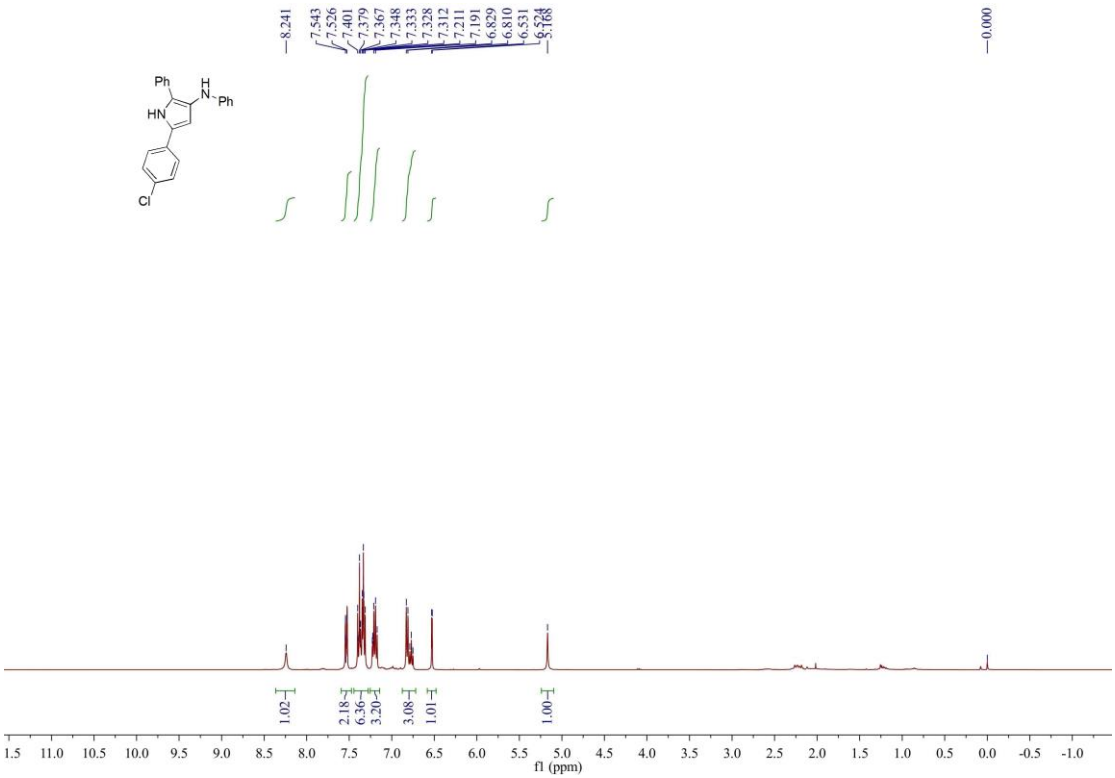


^{1}H NMR spectra of compound 3ca in $CDCl_3$ (400 MHz)

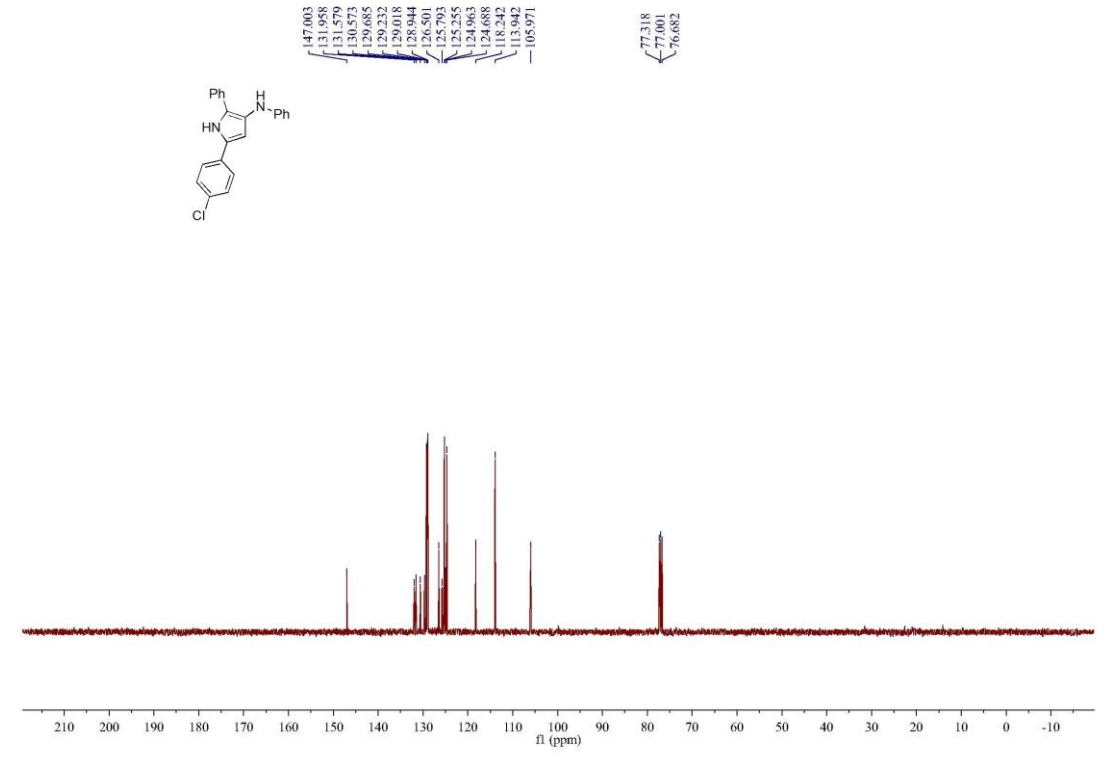


^{13}C NMR spectra of compound 3ca in $CDCl_3$ (400 MHz)

5-(4-Chlorophenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3da)

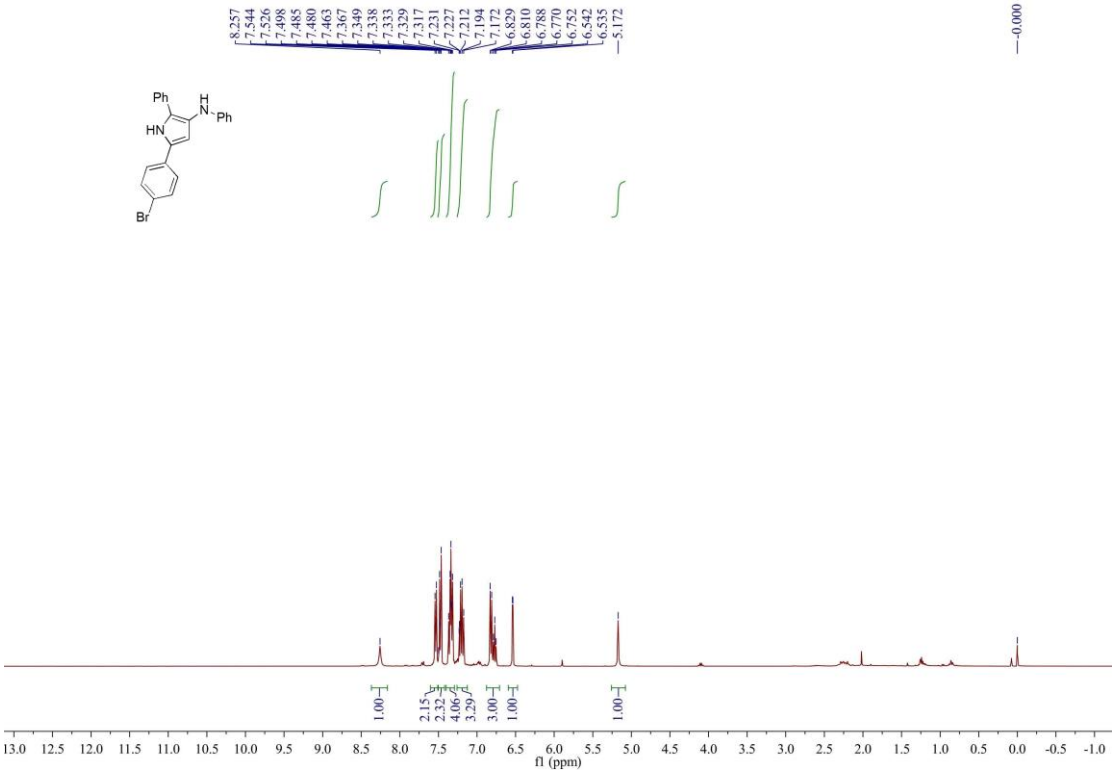


^{1}H NMR spectra of compound 3da in $CDCl_3$ (400 MHz)

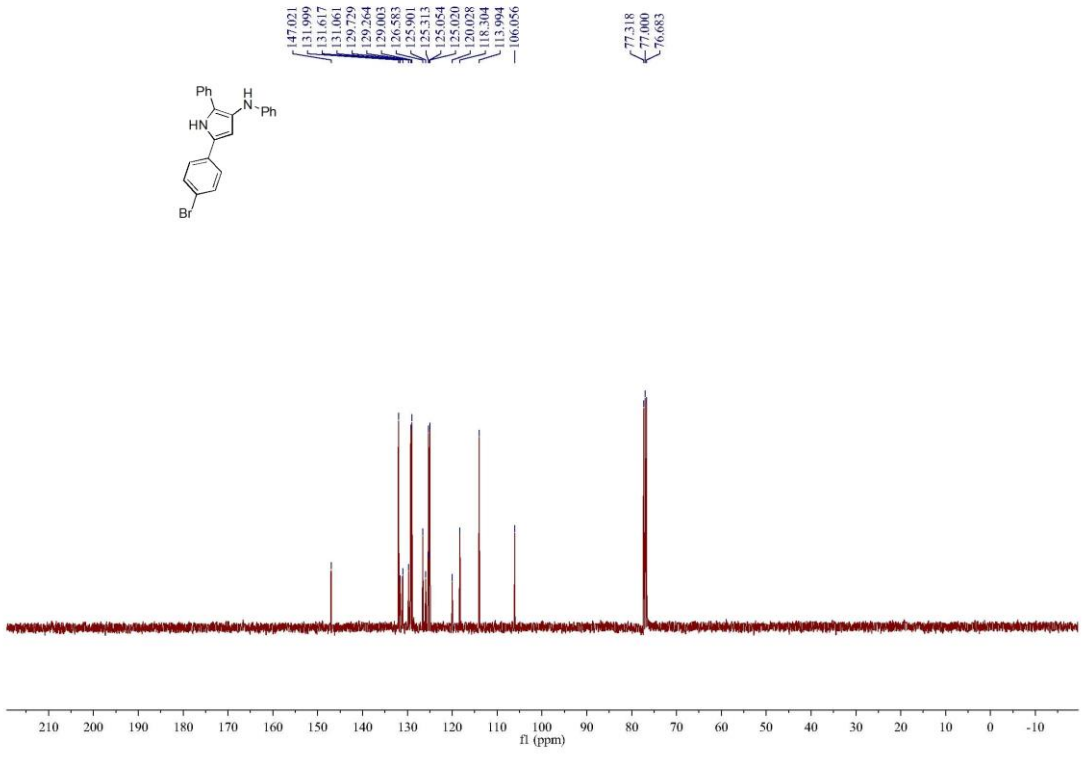


^{13}C NMR spectra of compound 3da in $CDCl_3$ (400 MHz)

5-(4-Bromophenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ea)

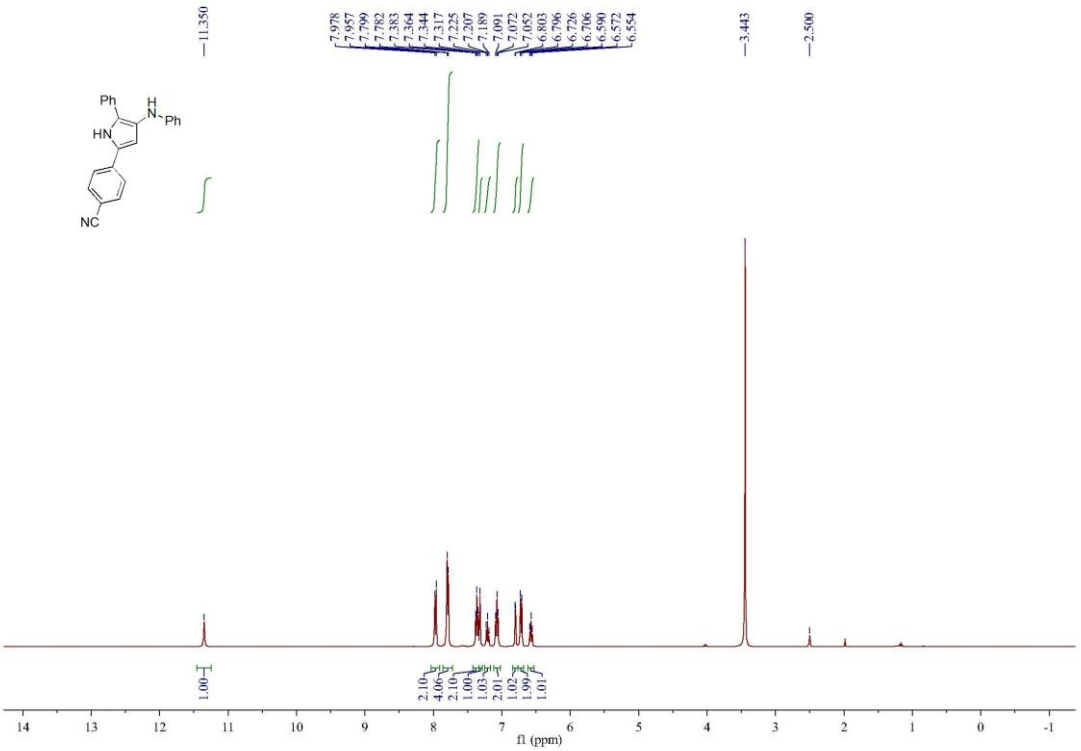


^{1}H NMR spectra of compound 3ea in $CDCl_3$ (400 MHz)

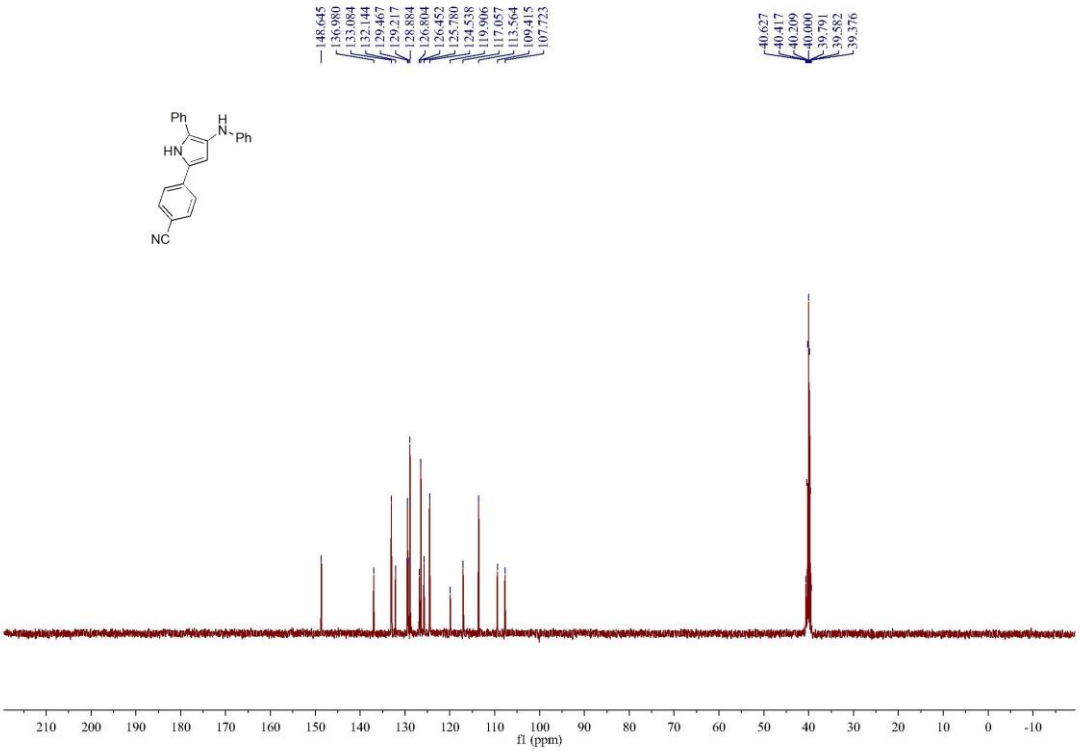


^{13}C NMR spectra of compound 3ea in $CDCl_3$ (400 MHz)

4-(5-Phenyl-4-(phenylamino)-1*H*-pyrrol-2-yl)benzonitrile (3fa)

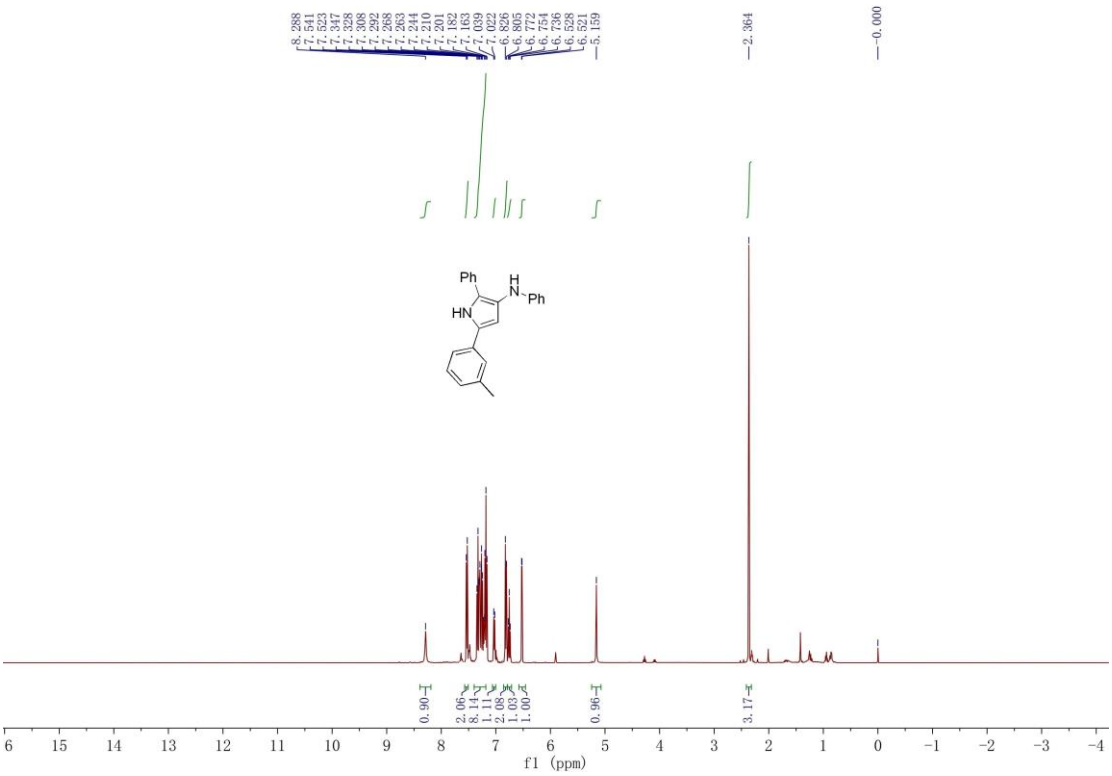


^{1}H NMR spectra of compound 3fa in DMSO-d6 (400 MHz)

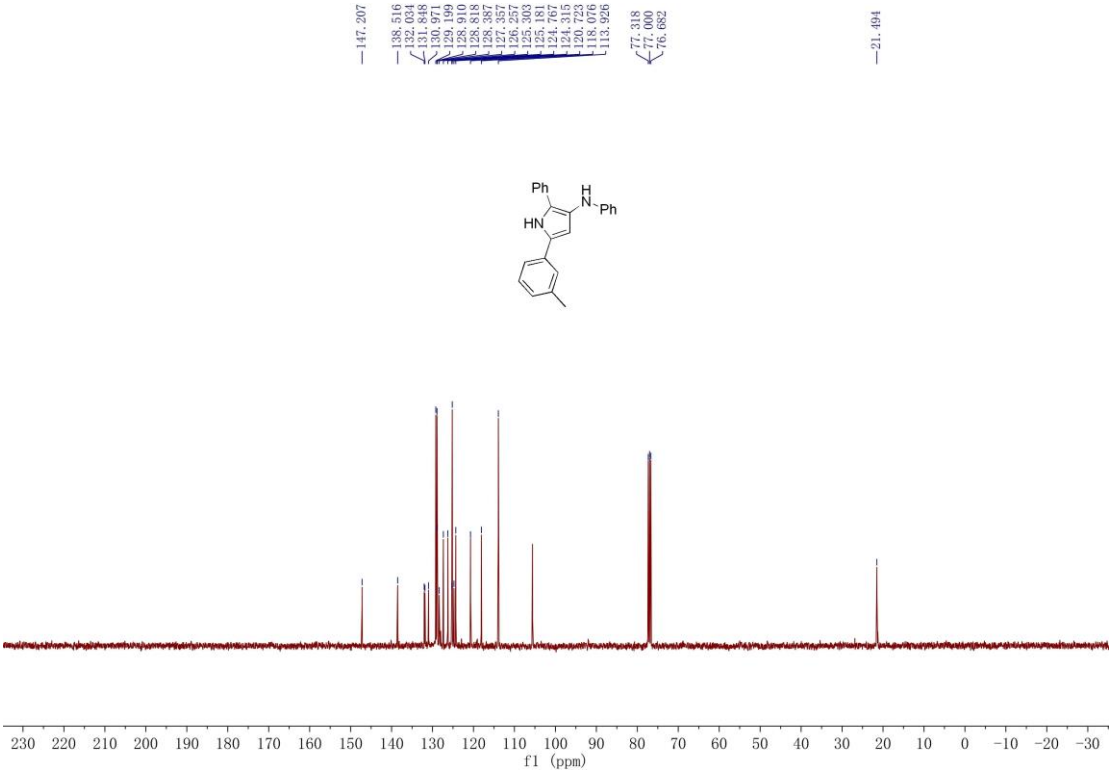


^{13}C NMR spectra of compound 3fa in DMSO-d6 (400 MHz)

N,2-diphenyl-5-(*m*-tolyl)-1*H*-pyrrol-3-amine (3ga)

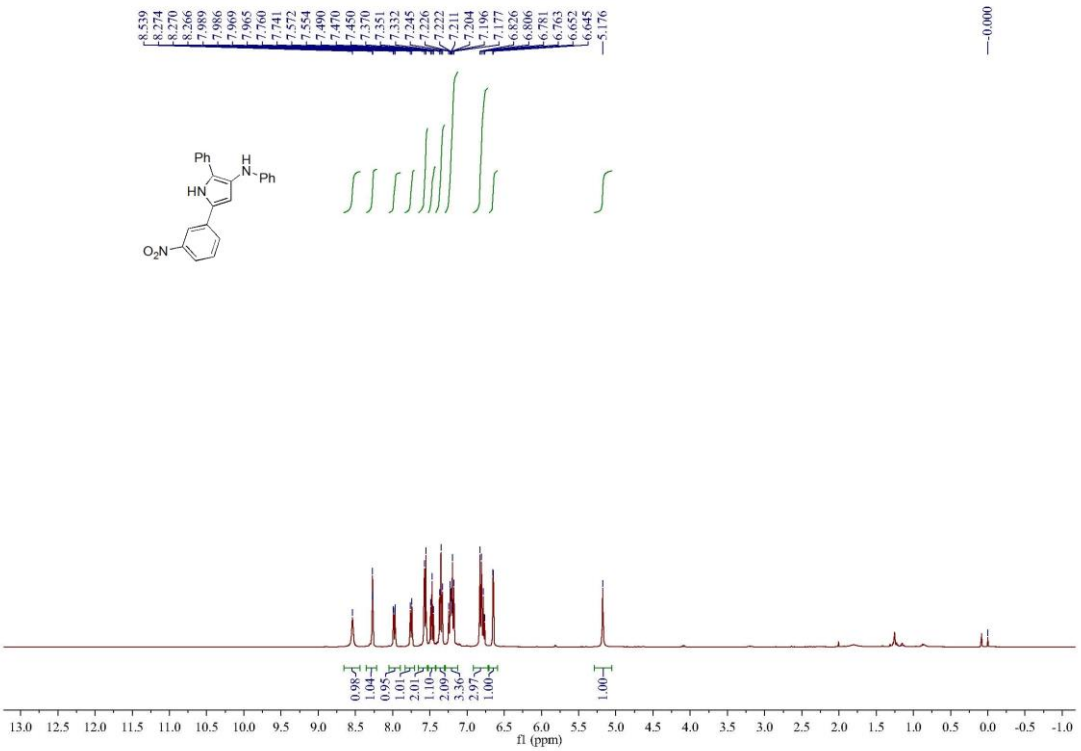


^{1}H NMR spectra of compound 3ga in $CDCl_3$ (400 MHz)

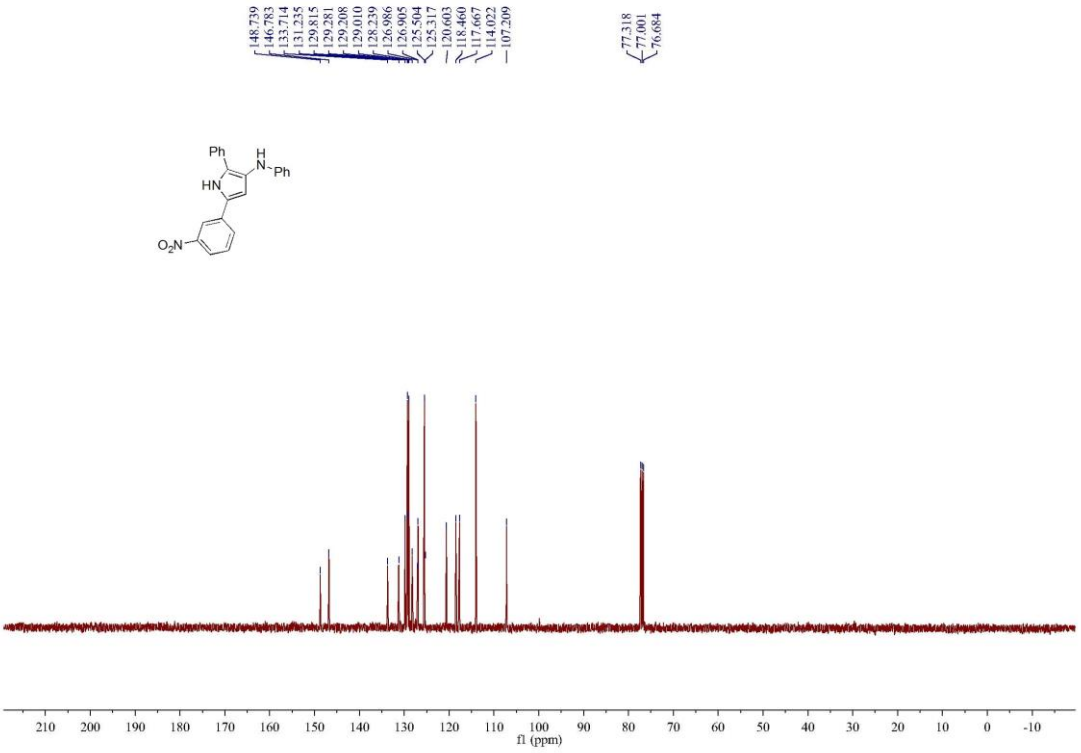


^{13}C NMR spectra of compound 3ga in $CDCl_3$ (400 MHz)

5-(3-Nitrophenyl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ha)

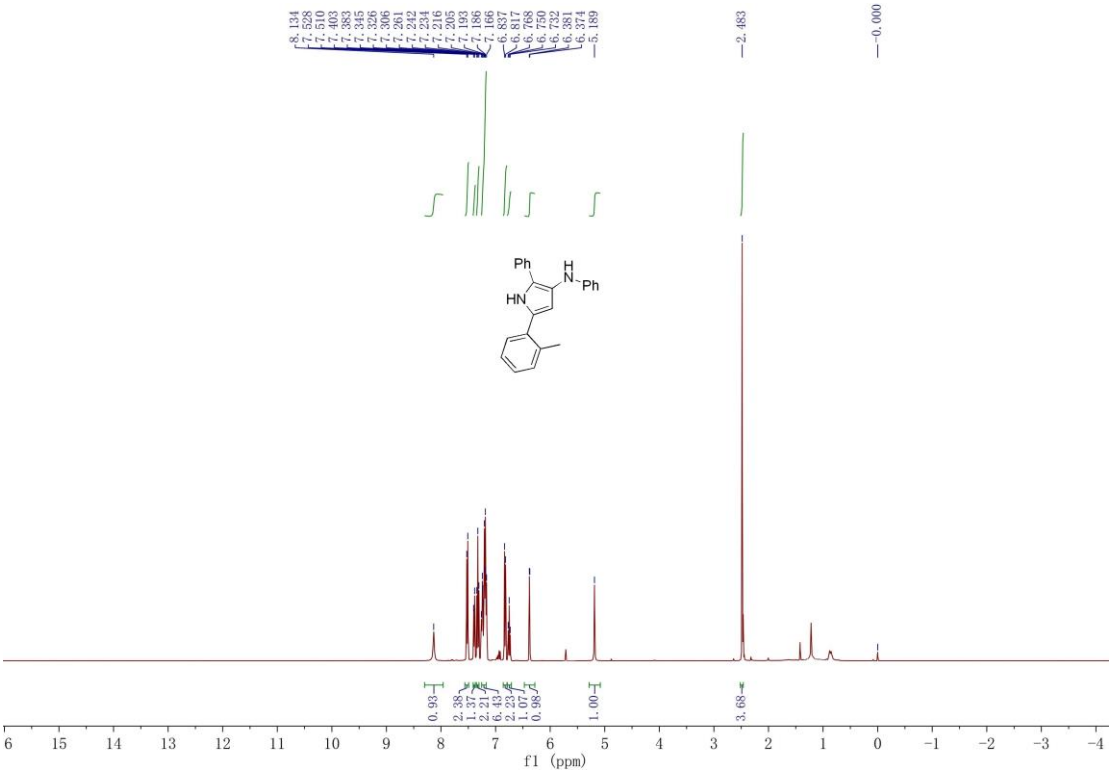


^{1}H NMR spectra of compound 3ha in $CDCl_3$ (400 MHz)

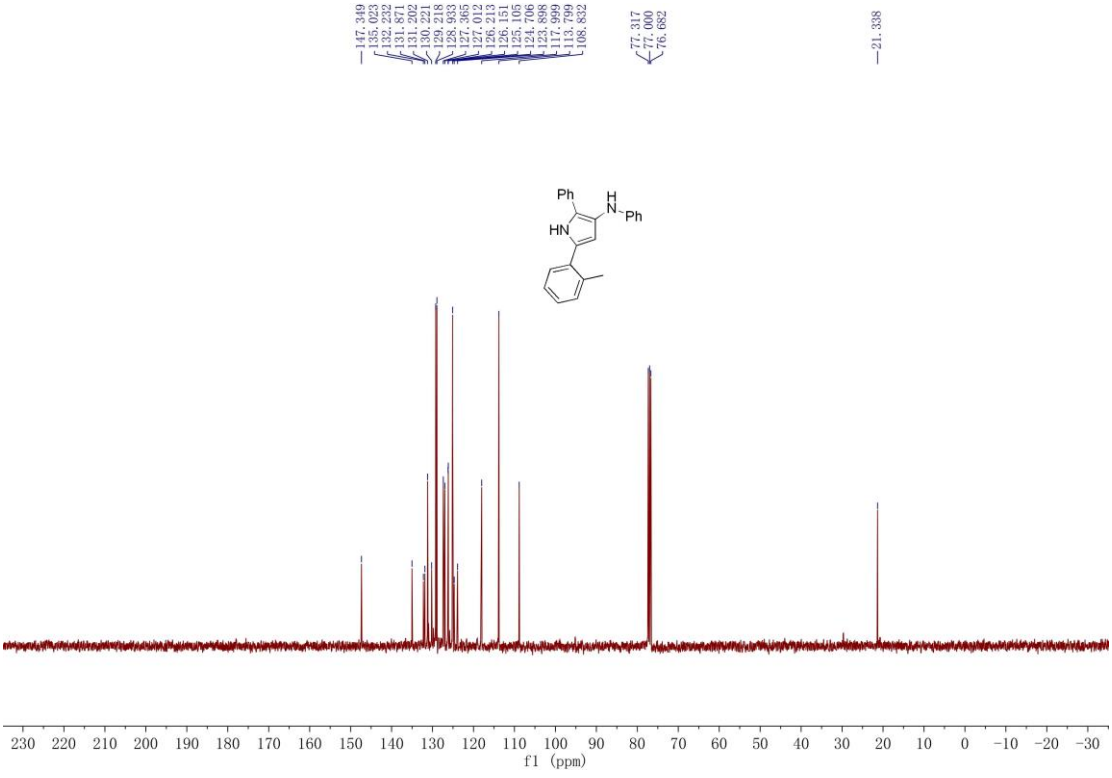


^{13}C NMR spectra of compound 3ha in $CDCl_3$ (400 MHz)

***N*,2-diphenyl-5-(*o*-tolyl)-1*H*-pyrrol-3-amine (3ia)**

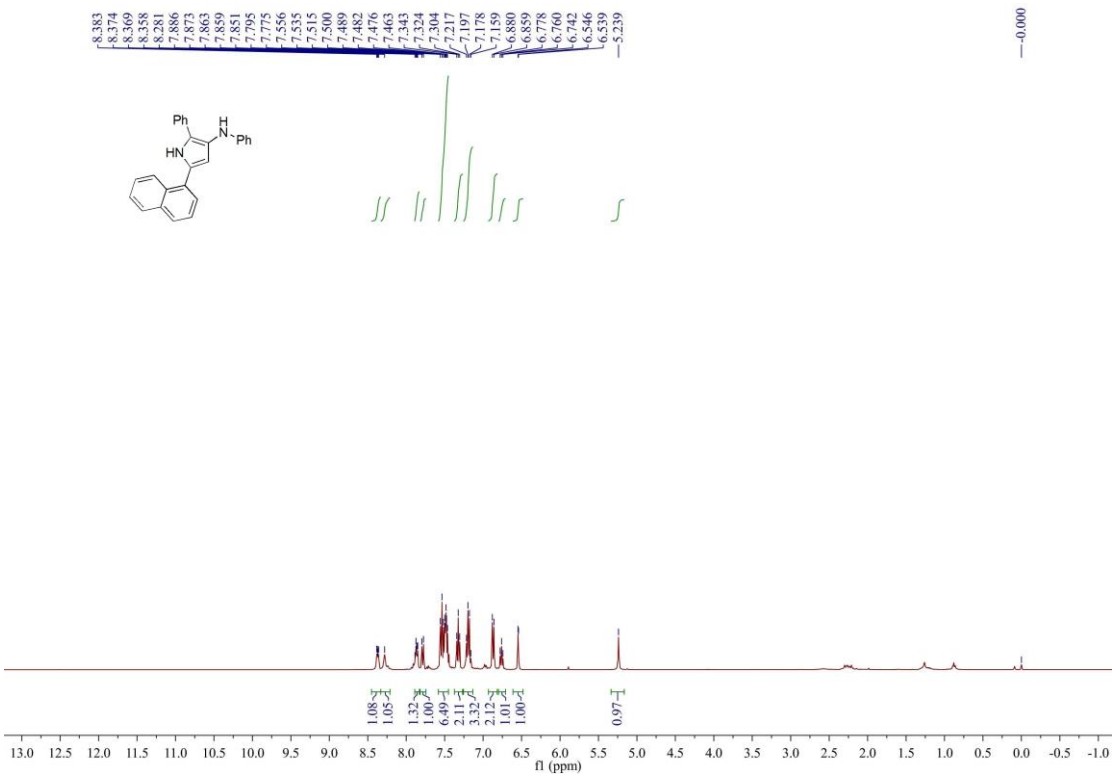


^{1}H NMR spectra of compound 3ia in $CDCl_3$ (400 MHz)

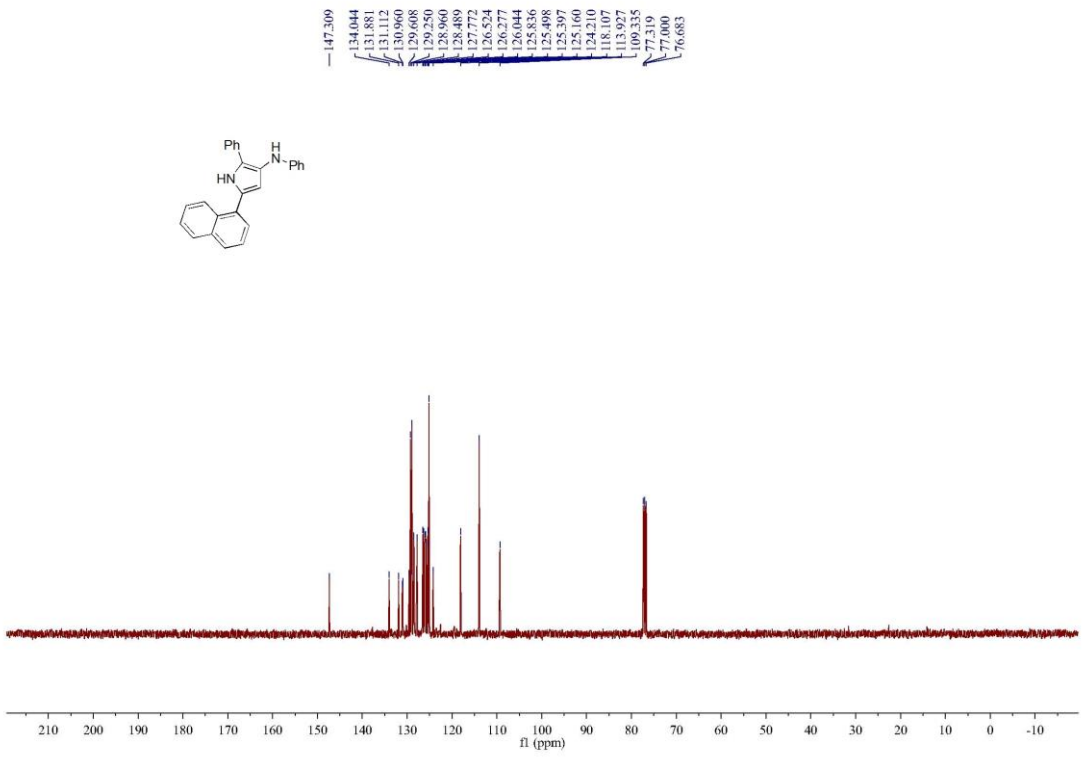


^{13}C NMR spectra of compound 3ia in $CDCl_3$ (400 MHz)

5-(Naphthalen-1-yl)-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3ja)

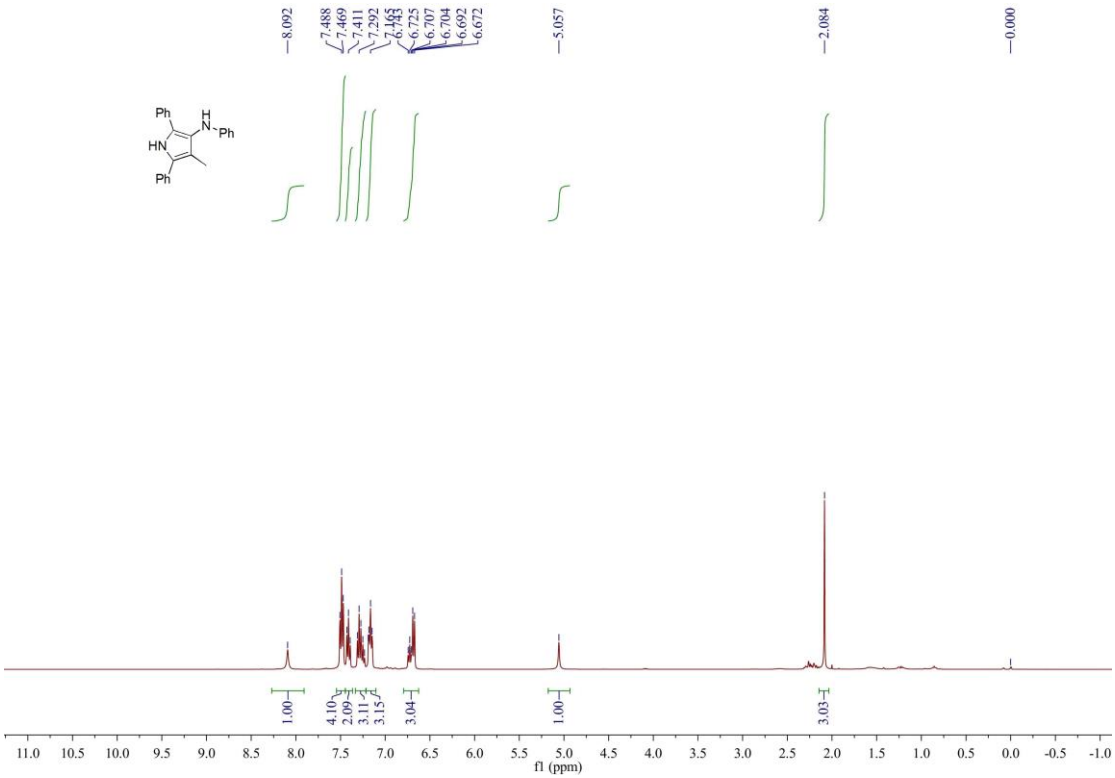


^{1}H NMR spectra of compound 3ja in $CDCl_3$ (400 MHz)

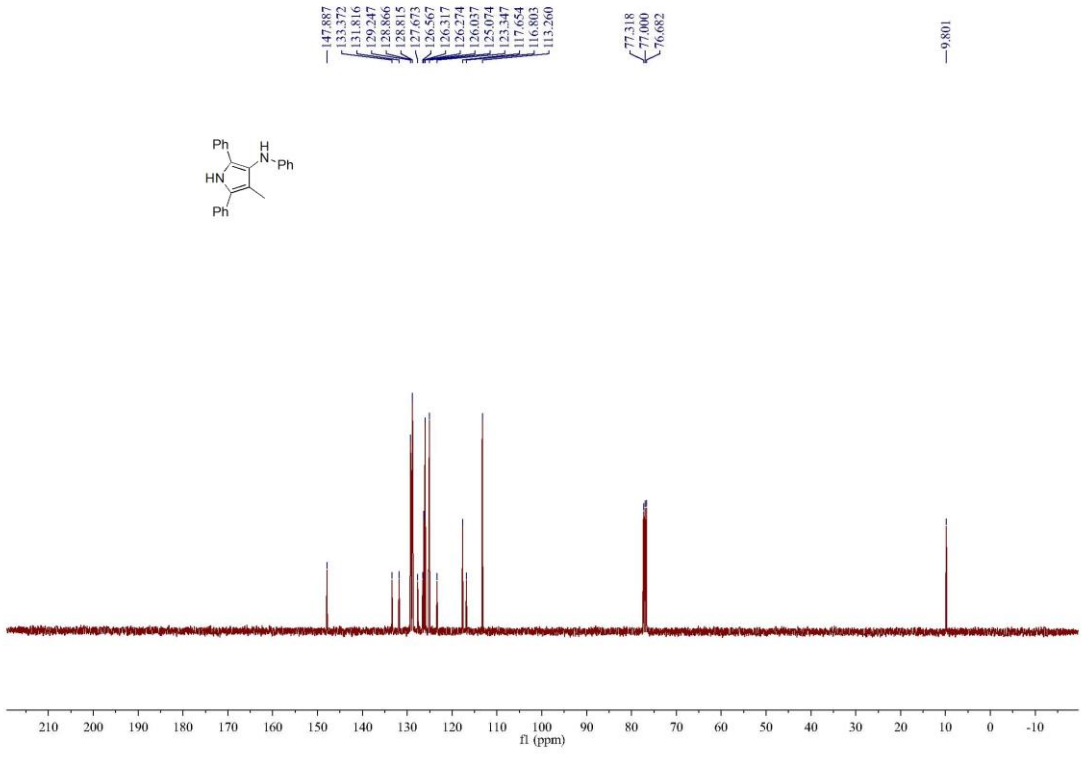


^{13}C NMR spectra of compound 3ja in $CDCl_3$ (400 MHz)

4-Methyl-*N*,2,5-triphenyl-1*H*-pyrrol-3-amine (3ka)

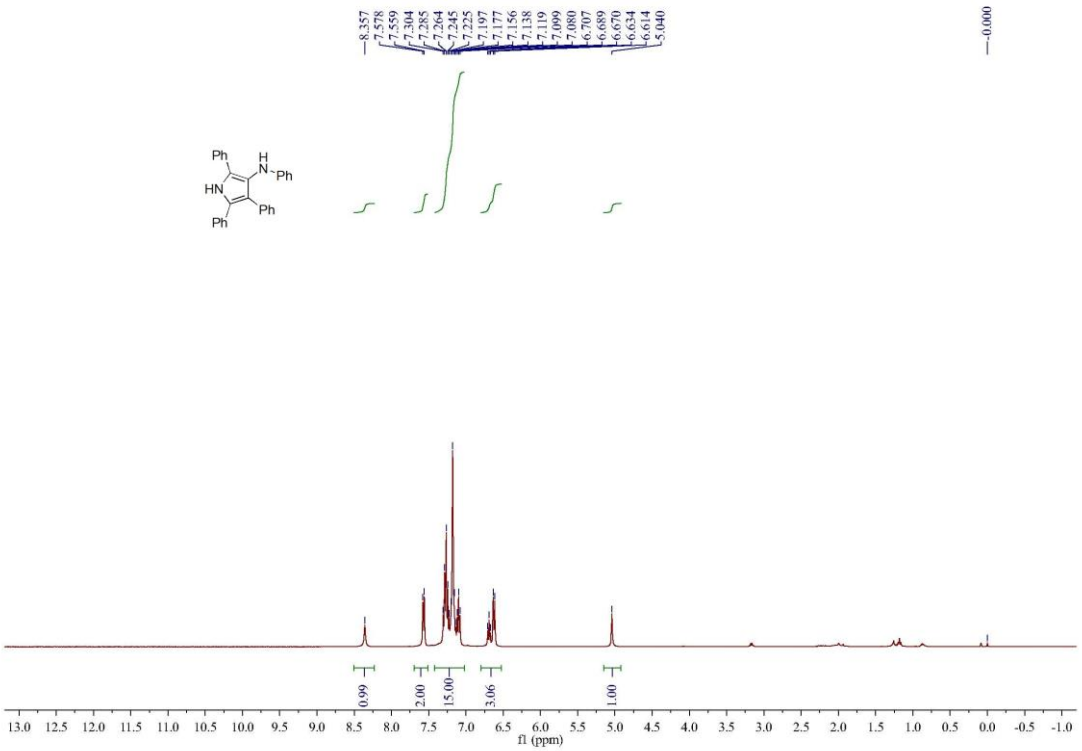


^{1}H NMR spectra of compound 3ka in $CDCl_3$ (400 MHz)

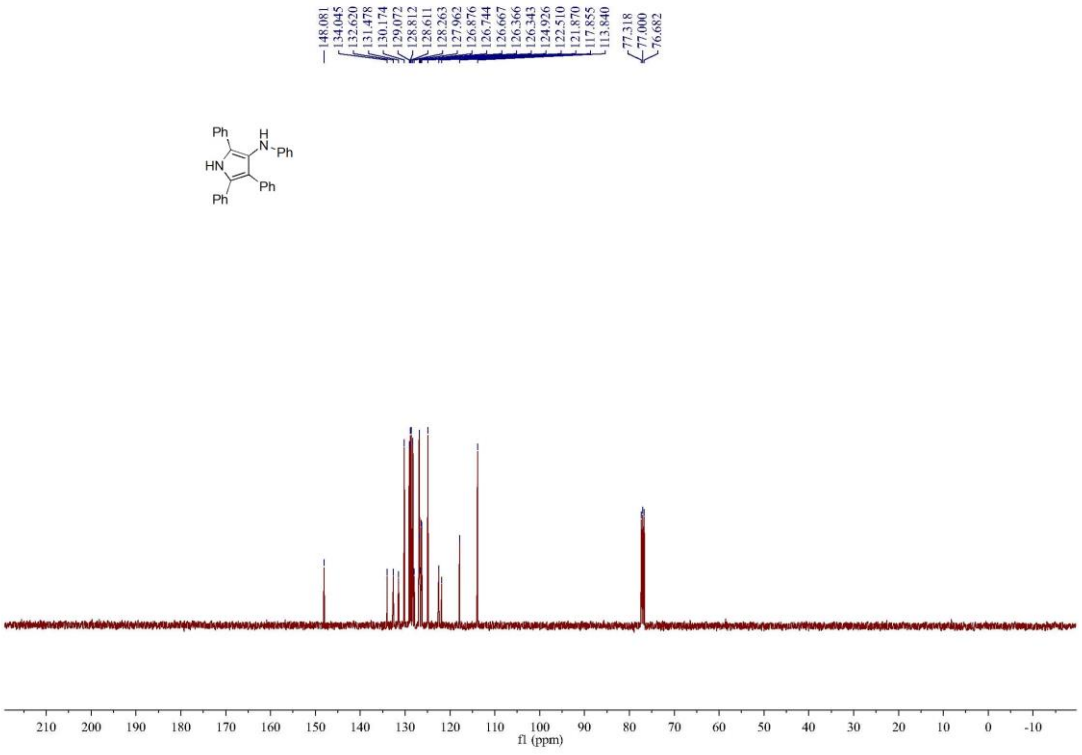


^{13}C NMR spectra of compound 3ka in $CDCl_3$ (400 MHz)

N,2,4,5-Tetraphenyl-1*H*-pyrrol-3-amine (3la)

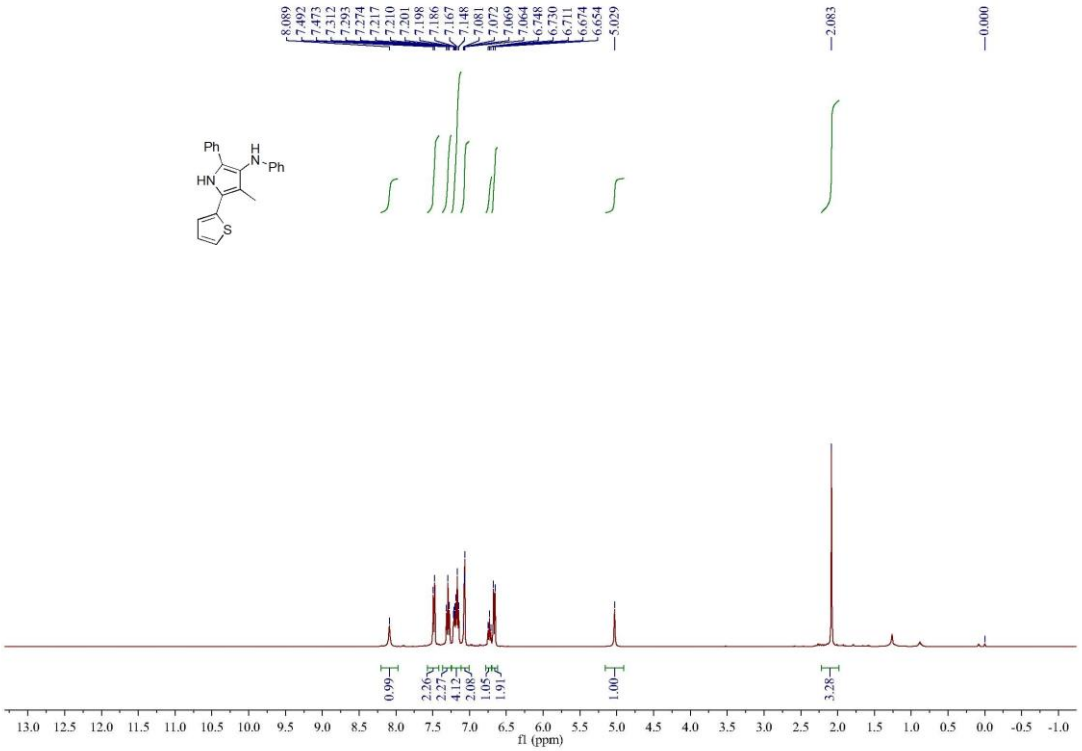


^{1}H NMR spectra of compound 3la in $CDCl_3$ (400 MHz)

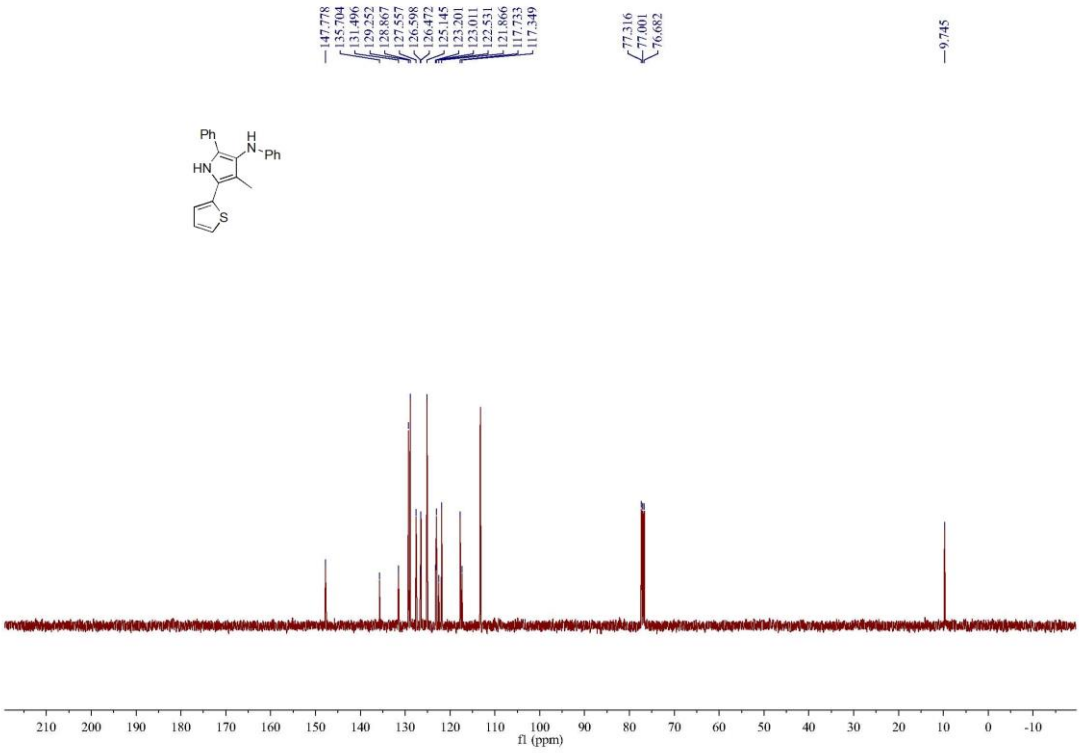


^{13}C NMR spectra of compound 3la in $CDCl_3$ (400 MHz)

4-Methyl-*N*,2-diphenyl-5-(thiophen-2-yl)-1*H*-pyrrol-3-amine (3ma)

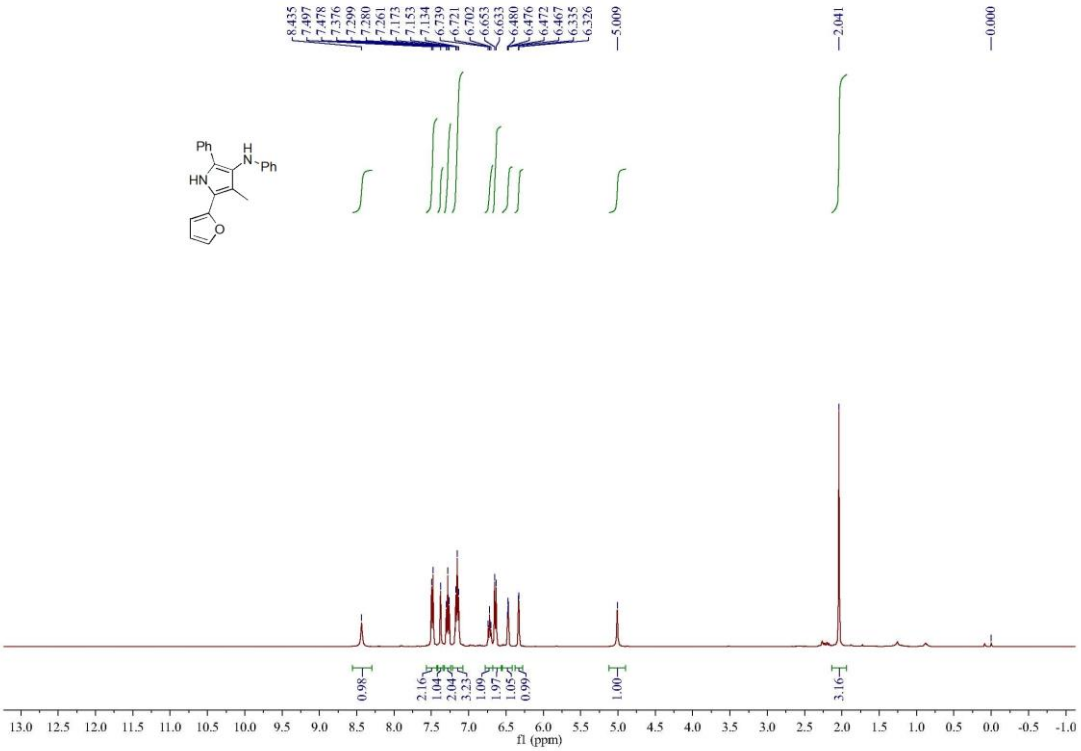


^{1}H NMR spectra of compound 3ma in $CDCl_3$ (400 MHz)

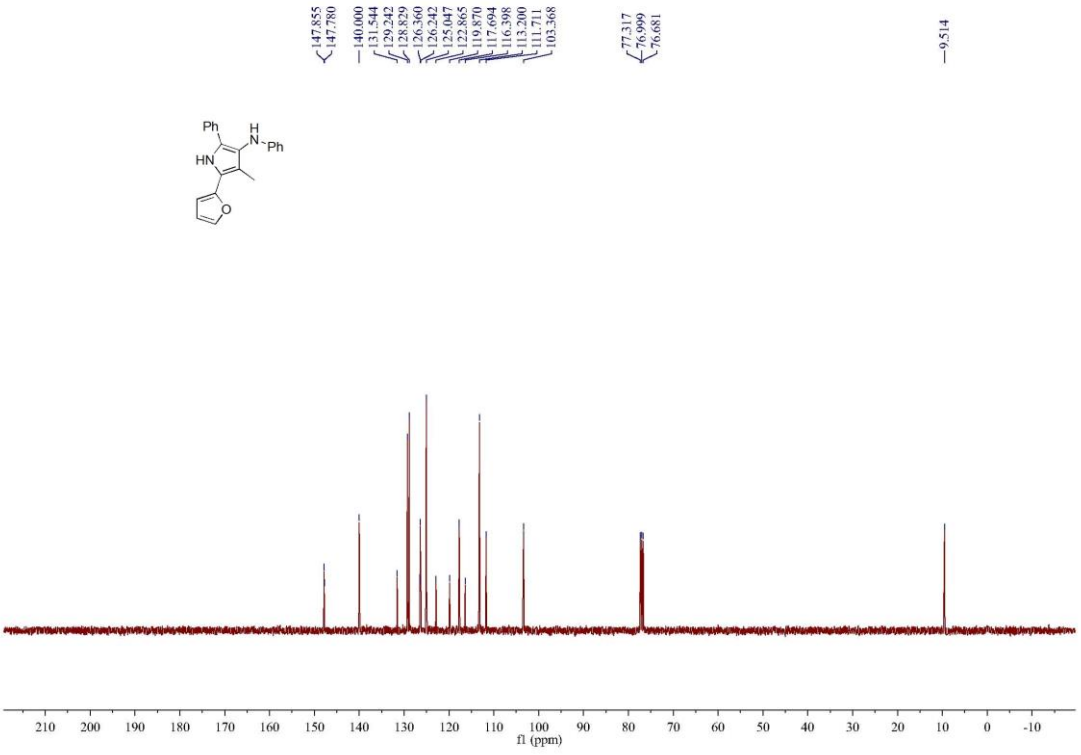


^{13}C NMR spectra of compound 3ma in $CDCl_3$ (400 MHz)

5-(Furan-2-yl)-4-methyl-*N*,2-diphenyl-1*H*-pyrrol-3-amine (3na)

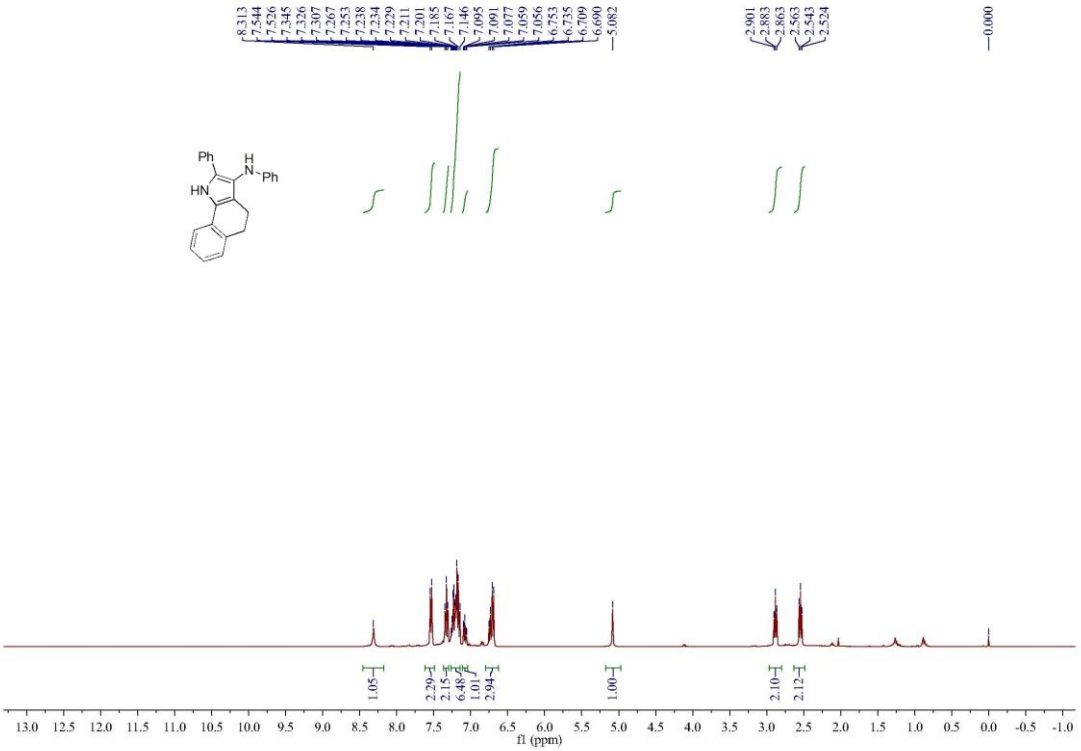


^{1}H NMR spectra of compound 3na in $CDCl_3$ (400 MHz)

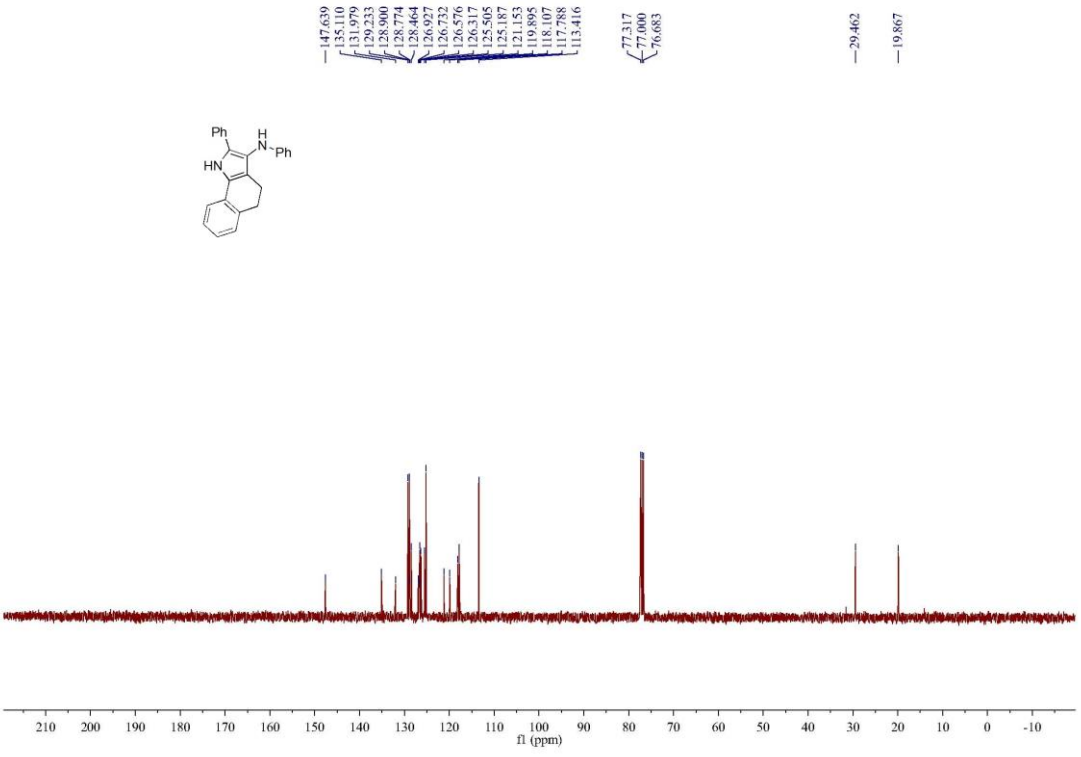


^{13}C NMR spectra of compound 3na in $CDCl_3$ (400 MHz)

_N_,2-Diphenyl-4,5-dihydro-1_H_-benzo[_g_]indol-3-amine (3oa)

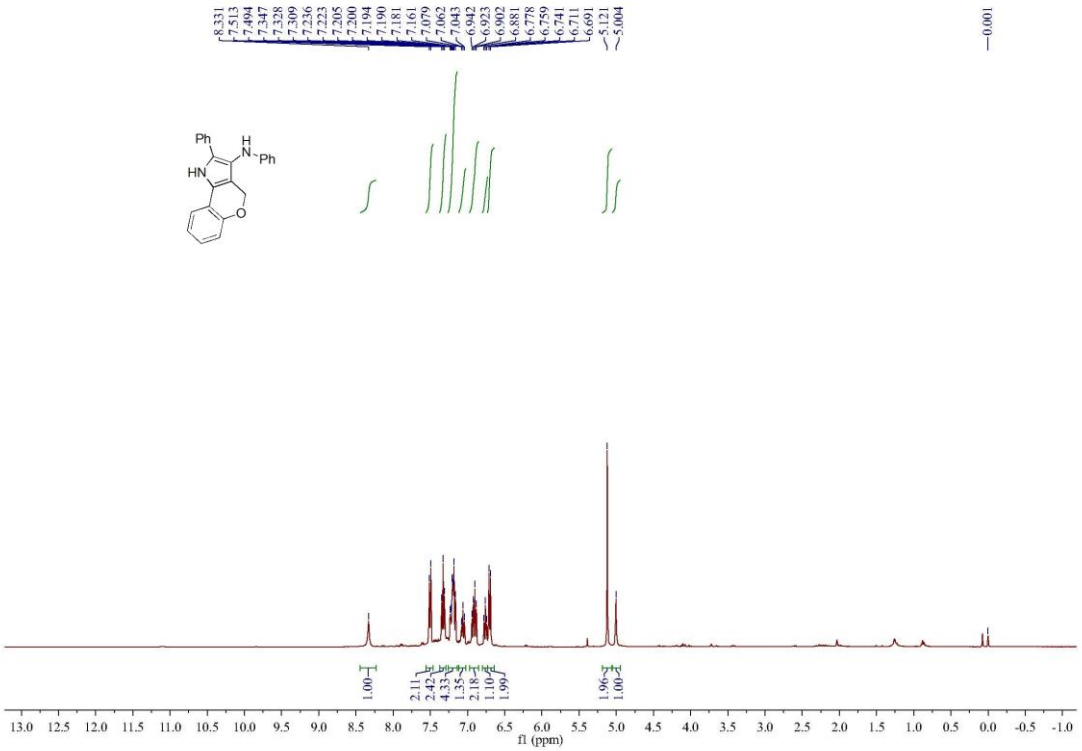


^{1}H NMR spectra of compound 3oa in $CDCl_3$ (400 MHz)

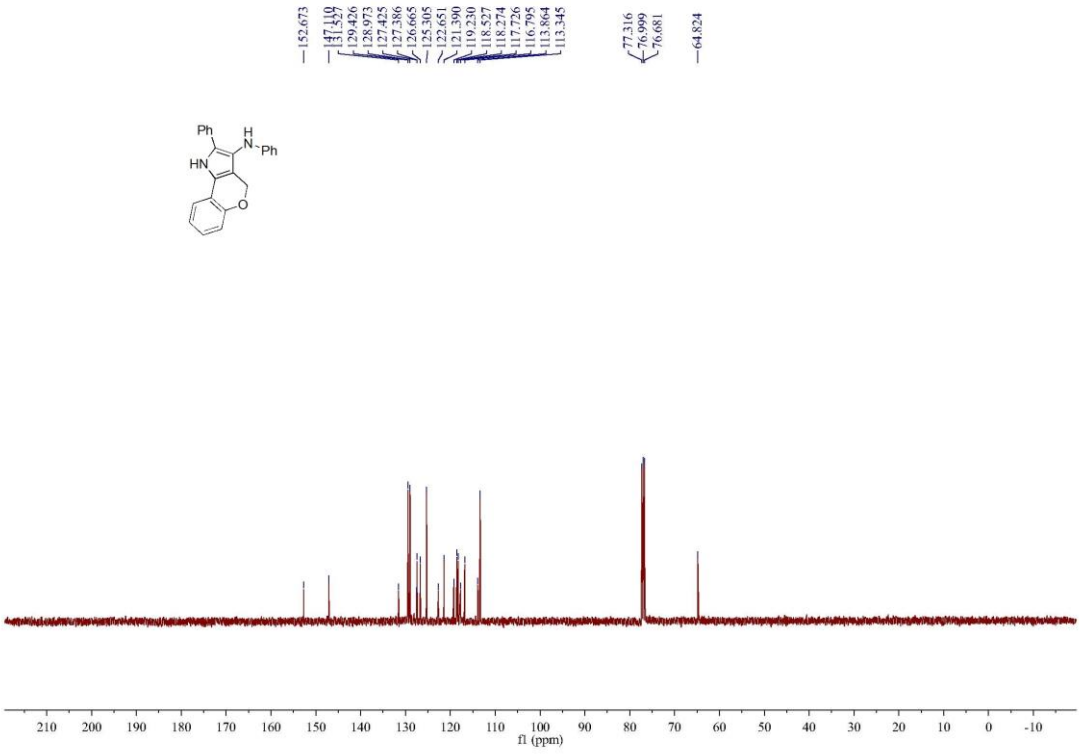


^{13}C NMR spectra of compound 3oa in $CDCl_3$ (400 MHz)

_N_,2-Diphenyl-1,4-dihydrochromeno[4,3-_b_]pyrrol-3-amine (3pa)

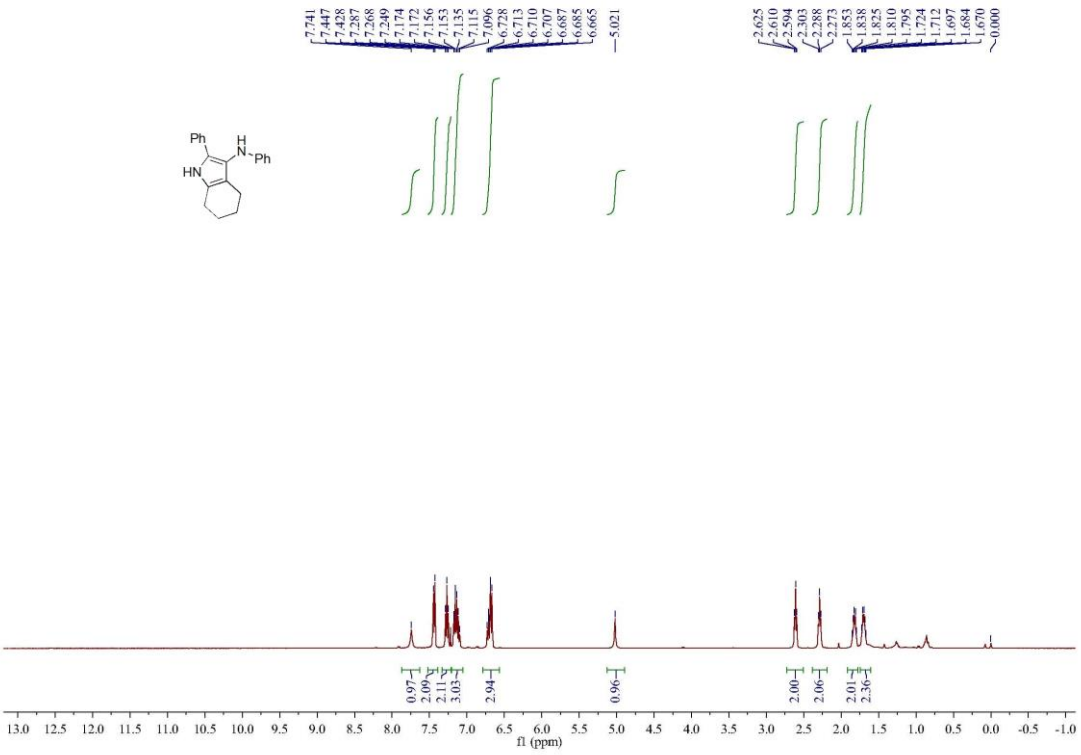


^{1}H NMR spectra of compound 3pa in $CDCl_3$ (400 MHz)

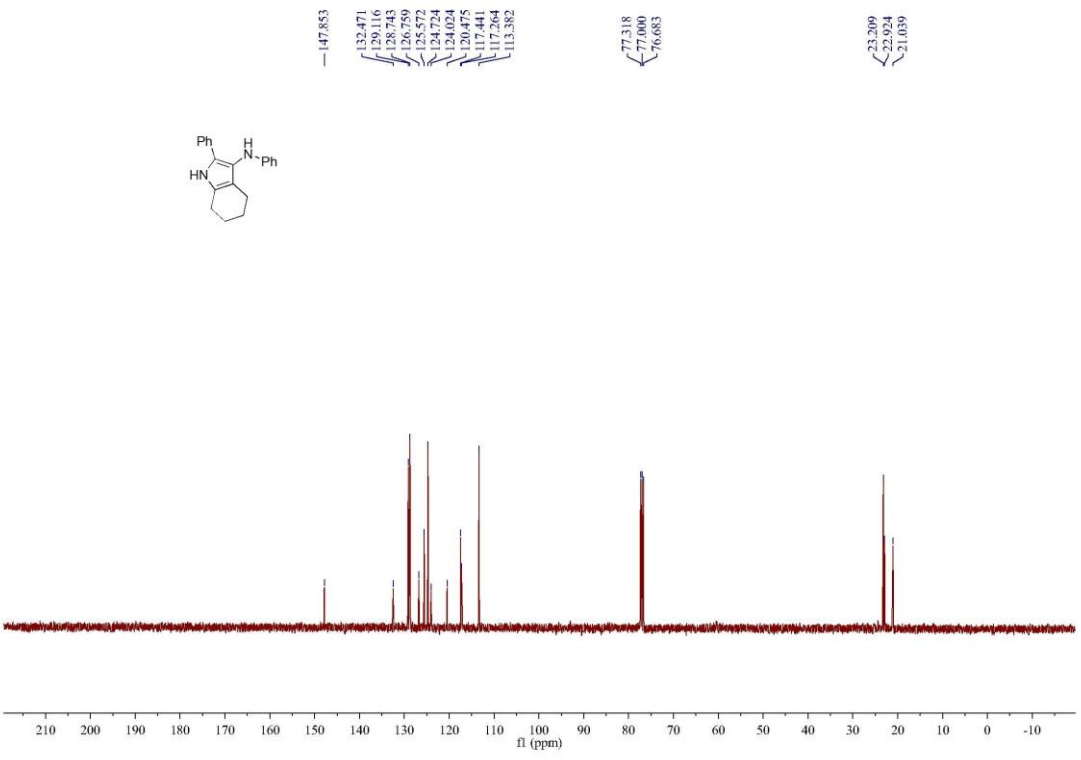


^{13}C NMR spectra of compound 3pa in $CDCl_3$ (400 MHz)

N,2-Diphenyl-4,5,6,7-tetrahydro-1*H*-indol-3-amine (3qa)

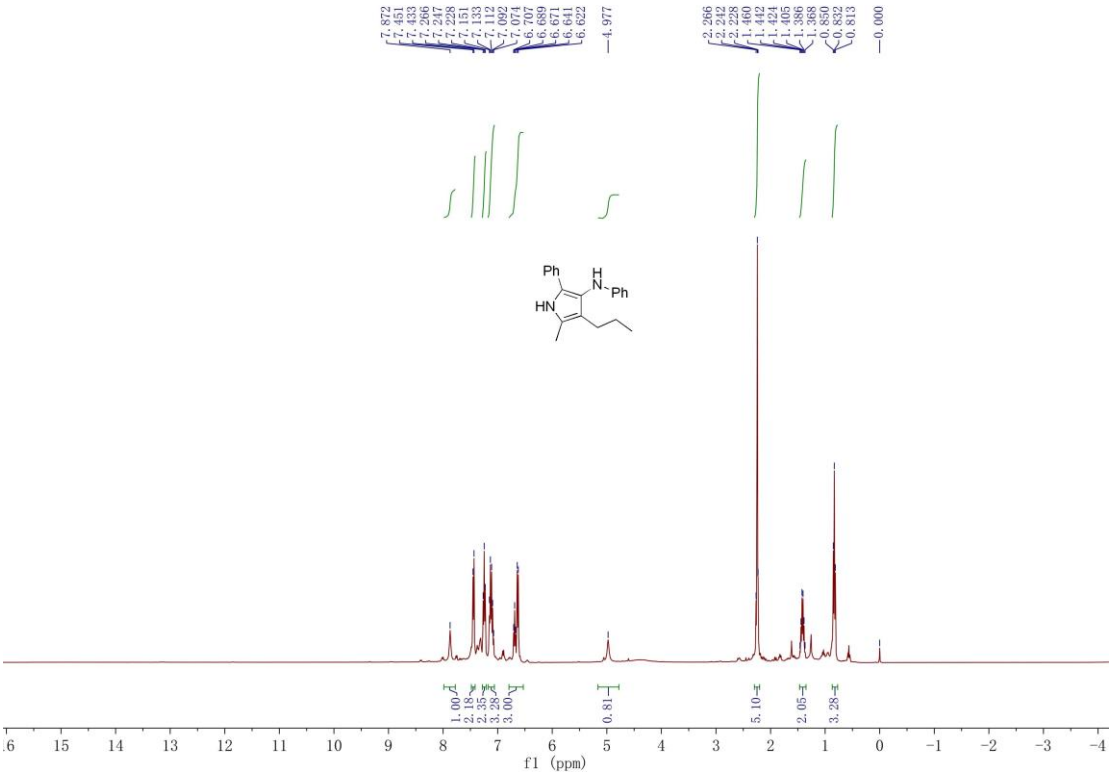


^{1}H NMR spectra of compound 3qa in $CDCl_3$ (400 MHz)

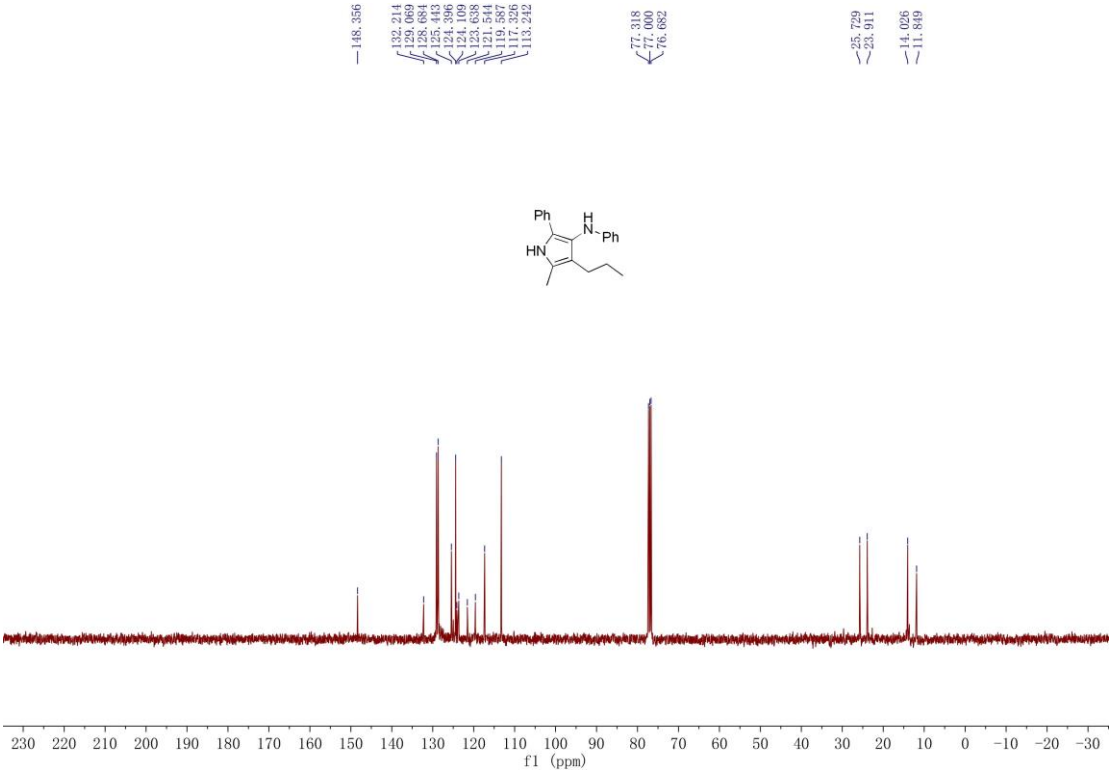


^{13}C NMR spectra of compound 3qa in $CDCl_3$ (400 MHz)

_N_,2-Diphenyl-4,5,6,7-tetrahydro-1_H_-indol-3-amine (3ra)

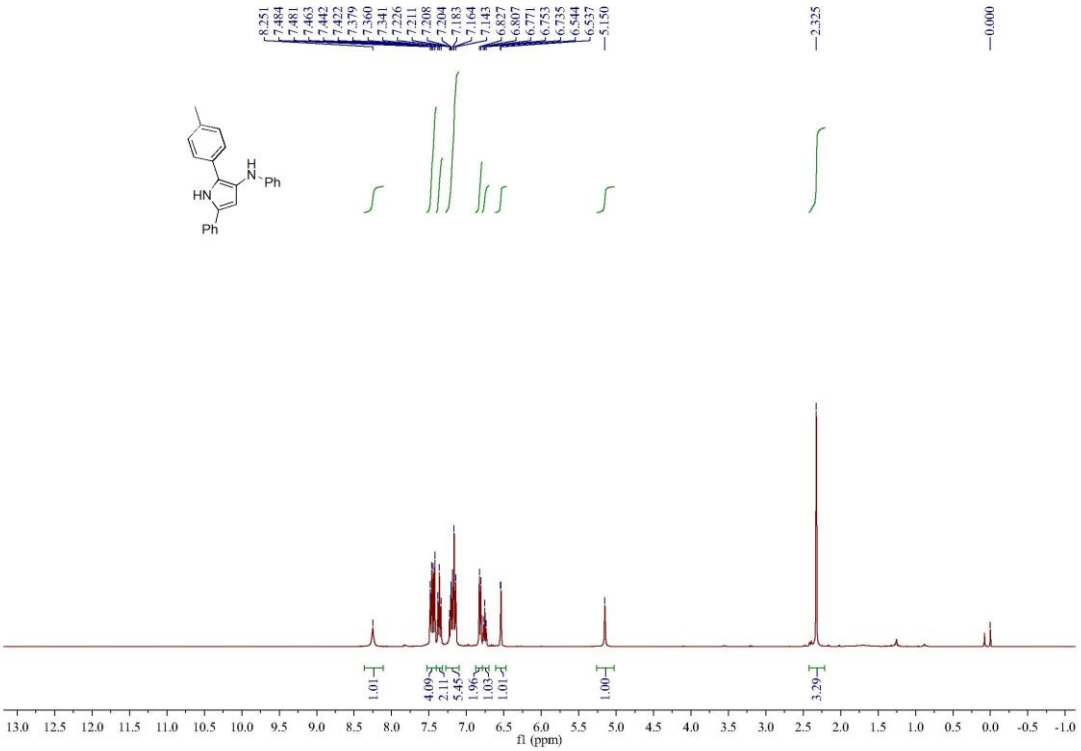


^{1}H NMR spectra of compound 3ra in $CDCl_3$ (400 MHz)

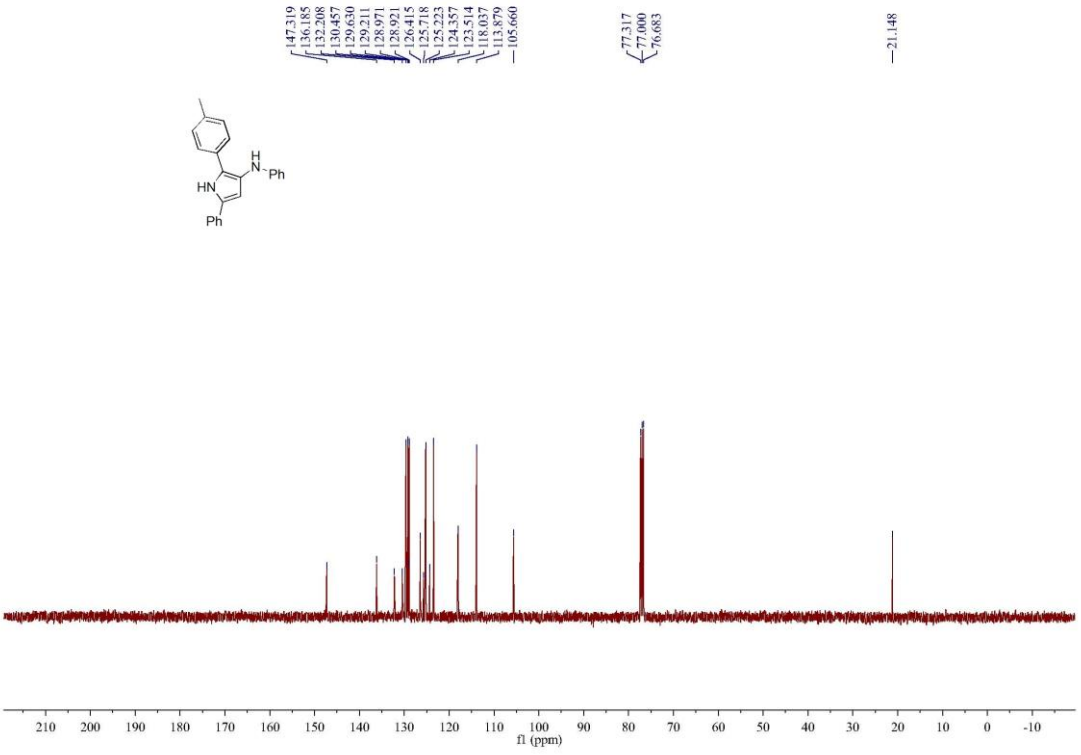


^{13}C NMR spectra of compound 3ra in $CDCl_3$ (400 MHz)

_N_,5-Diphenyl-2-_p_-tolyl-1_H_-pyrrol-3-amine (3ab)

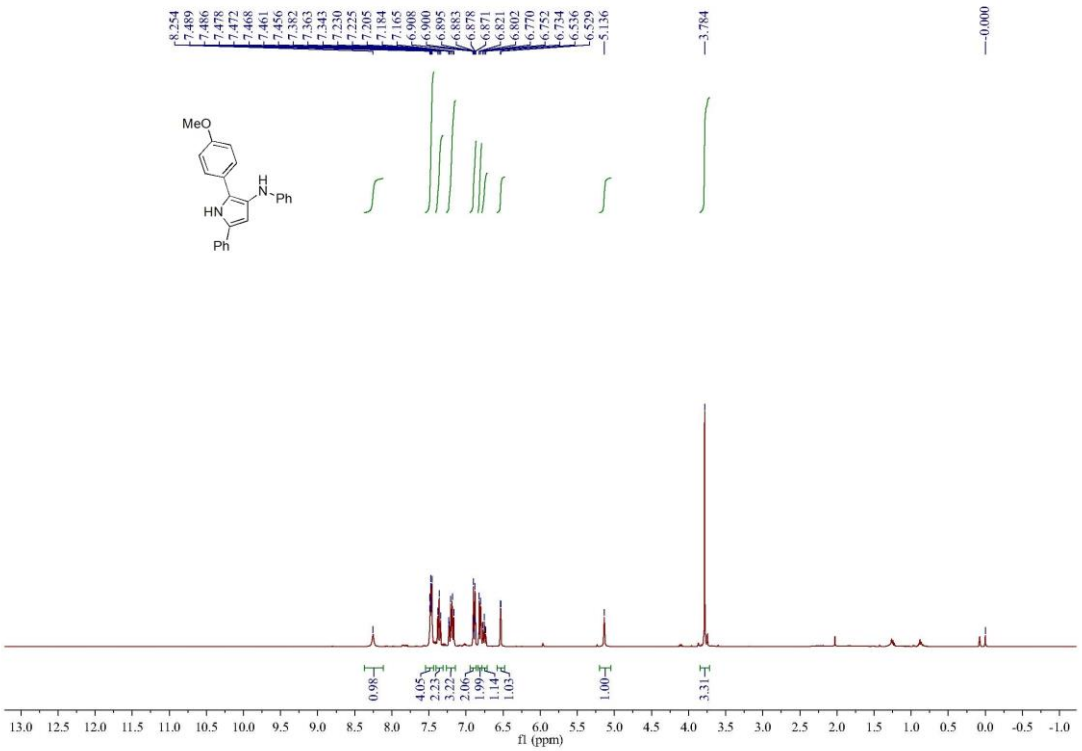


^{1}H NMR spectra of compound 3ab in $CDCl_3$ (400 MHz)

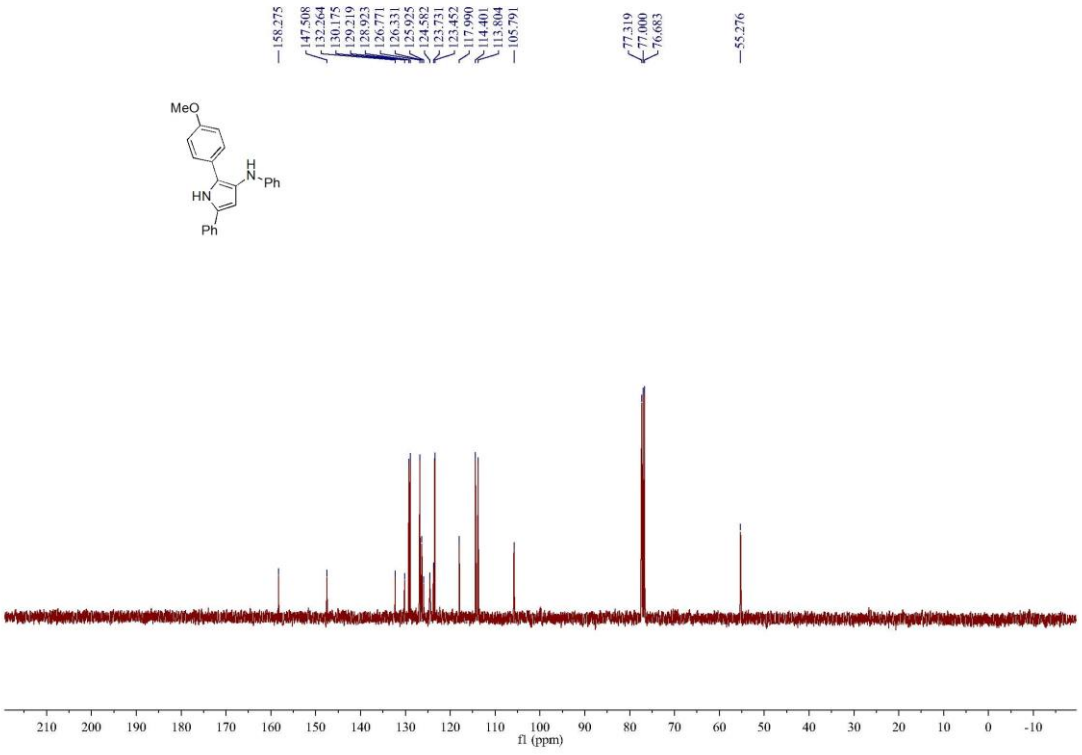


^{13}C NMR spectra of compound 3ab in $CDCl_3$ (400 MHz)

2-(4-Methoxyphenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ac)

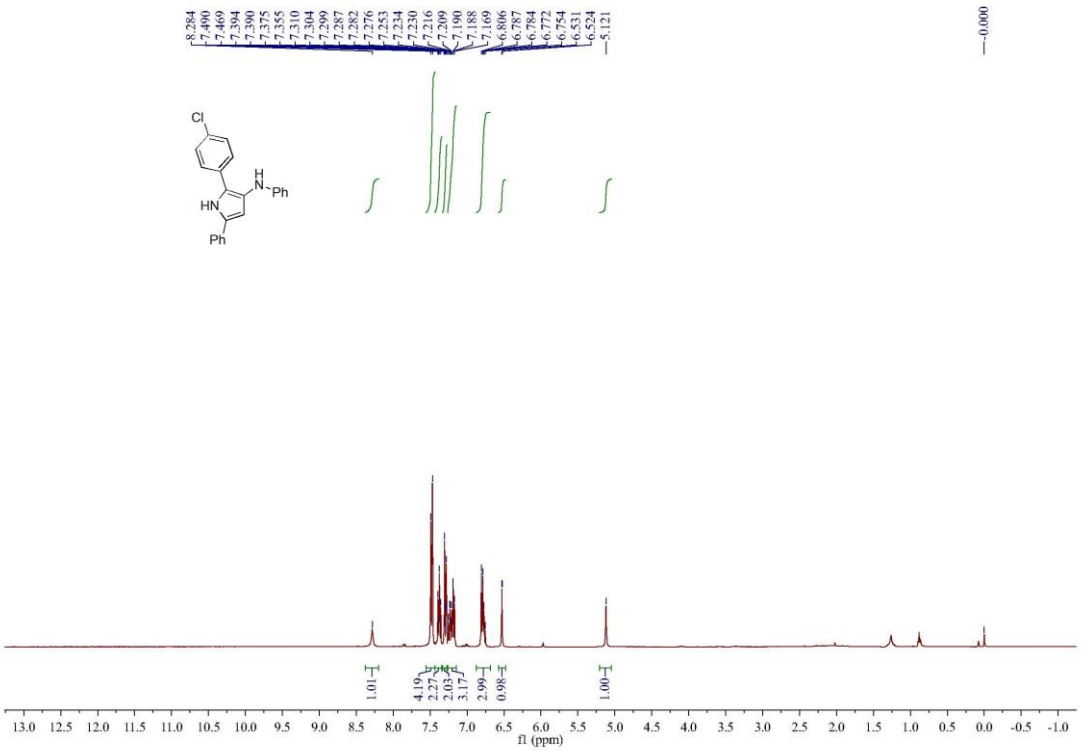


^{1}H NMR spectra of compound 3ac in $CDCl_3$ (400 MHz)

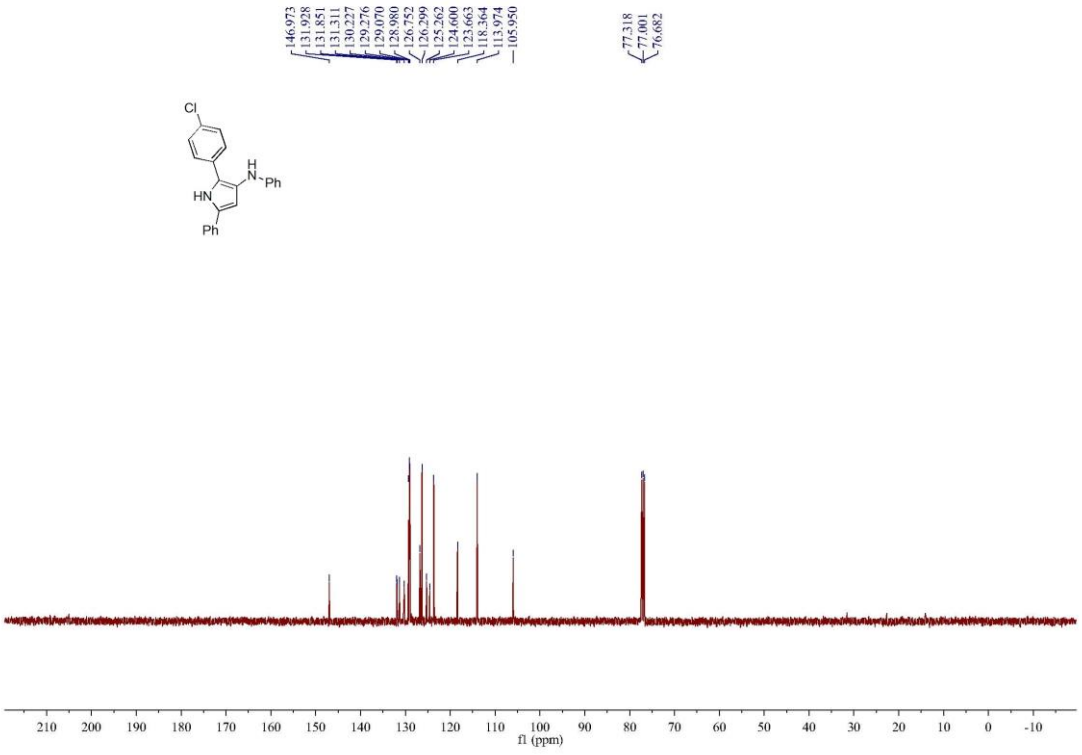


^{13}C NMR spectra of compound 3ac in $CDCl_3$ (400 MHz)

2-(4-Chlorophenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ad)

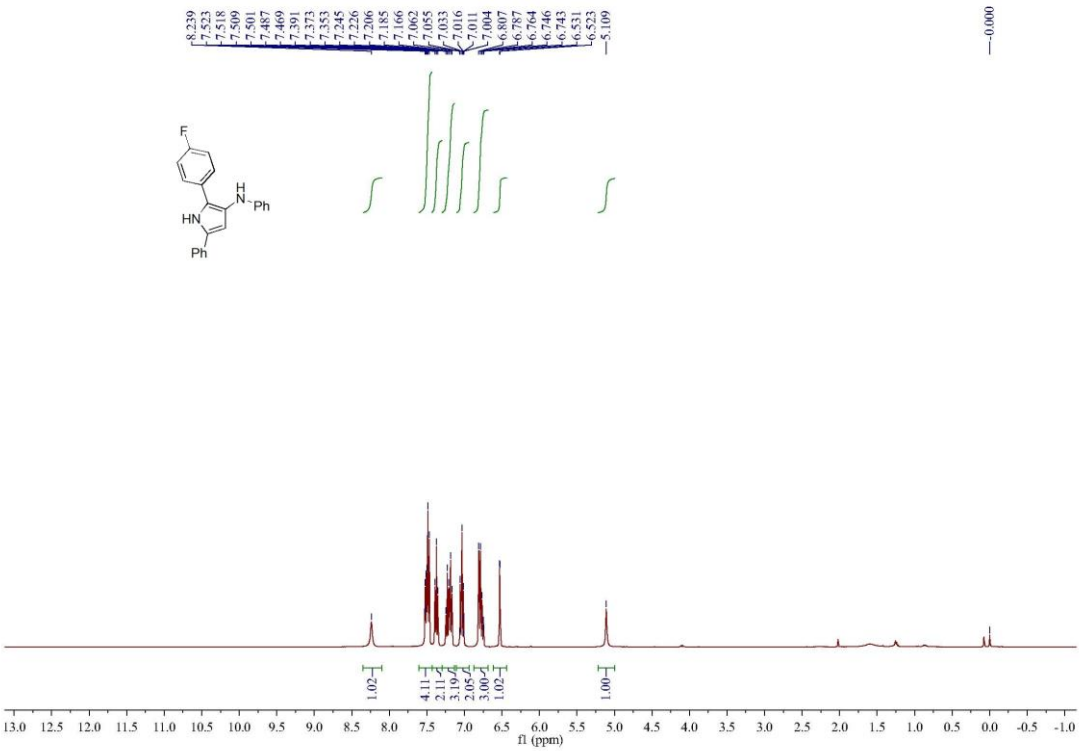


^{1}H NMR spectra of compound 3ad in $CDCl_3$ (400 MHz)

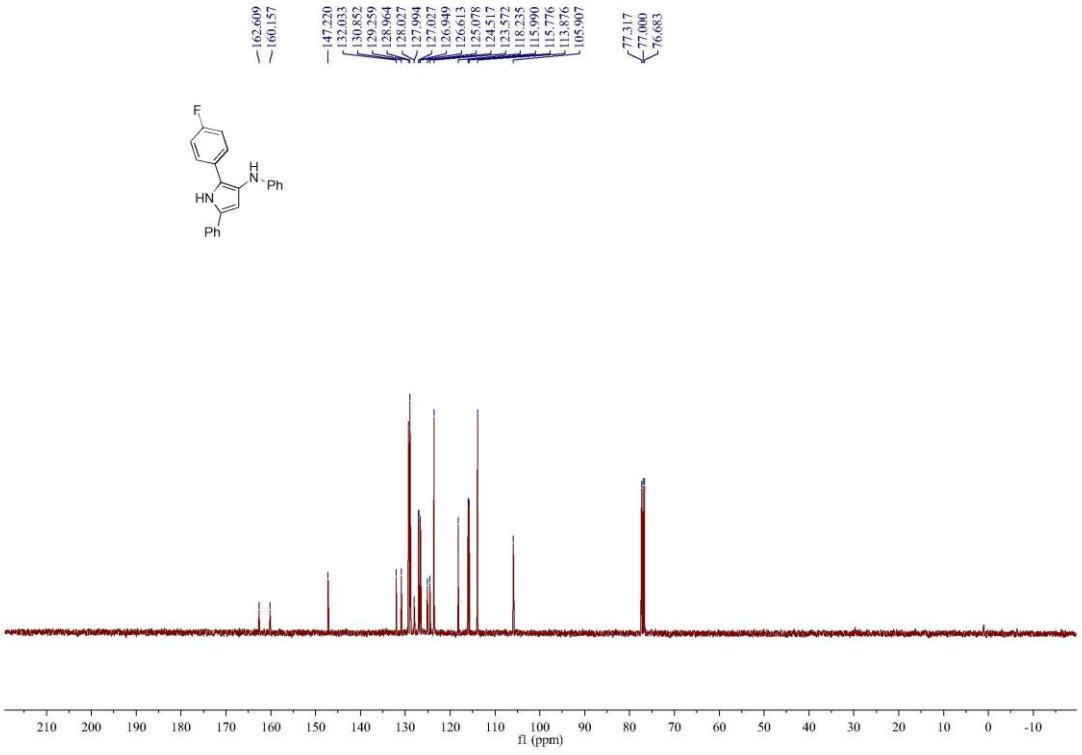


^{13}C NMR spectra of compound 3ad in $CDCl_3$ (400 MHz)

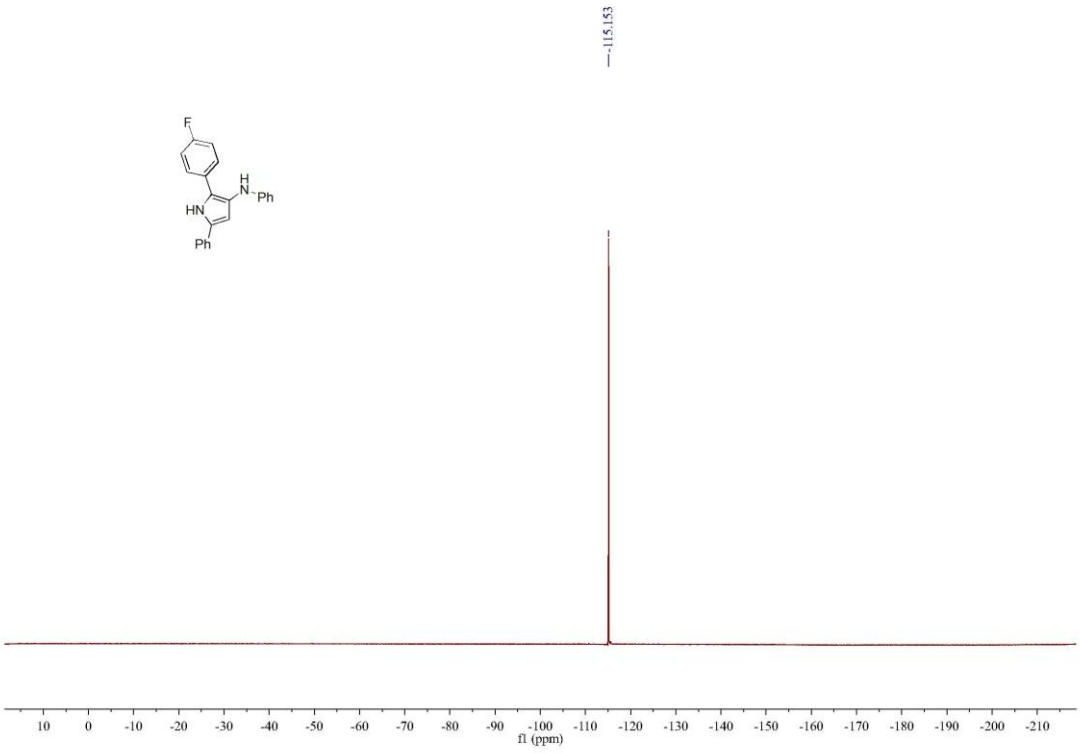
2-(4-Fluorophenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ae)



^{1}H NMR spectra of compound 3ae in $CDCl_3$ (400 MHz)

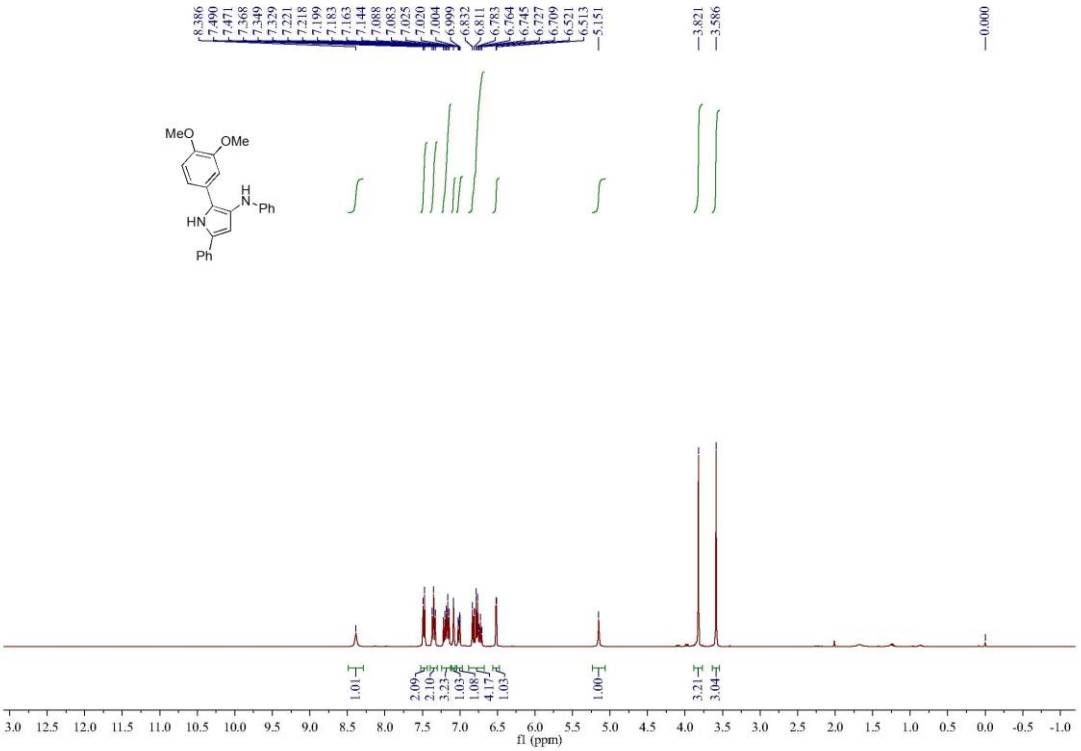


^{13}C NMR spectra of compound 3ae in $CDCl_3$ (400 MHz)

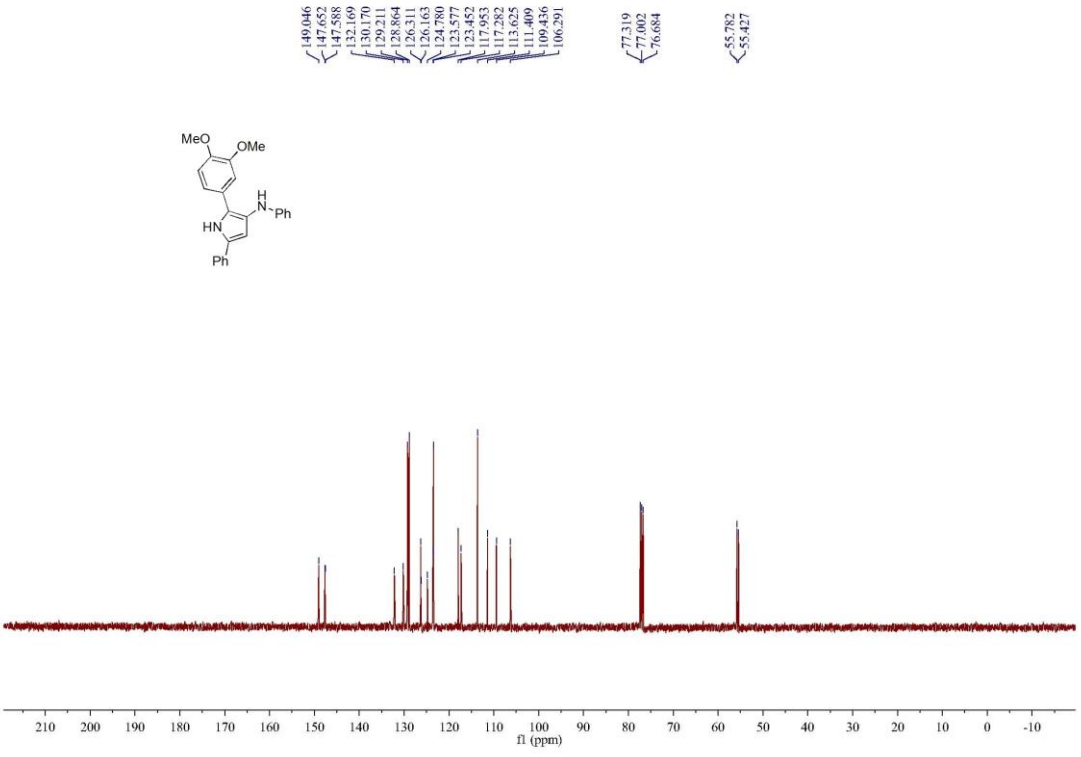


^{19}F NMR spectra of compound 3ae in $CDCl_3$ (400 MHz)

2-(3,4-Dimethoxyphenyl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3af)

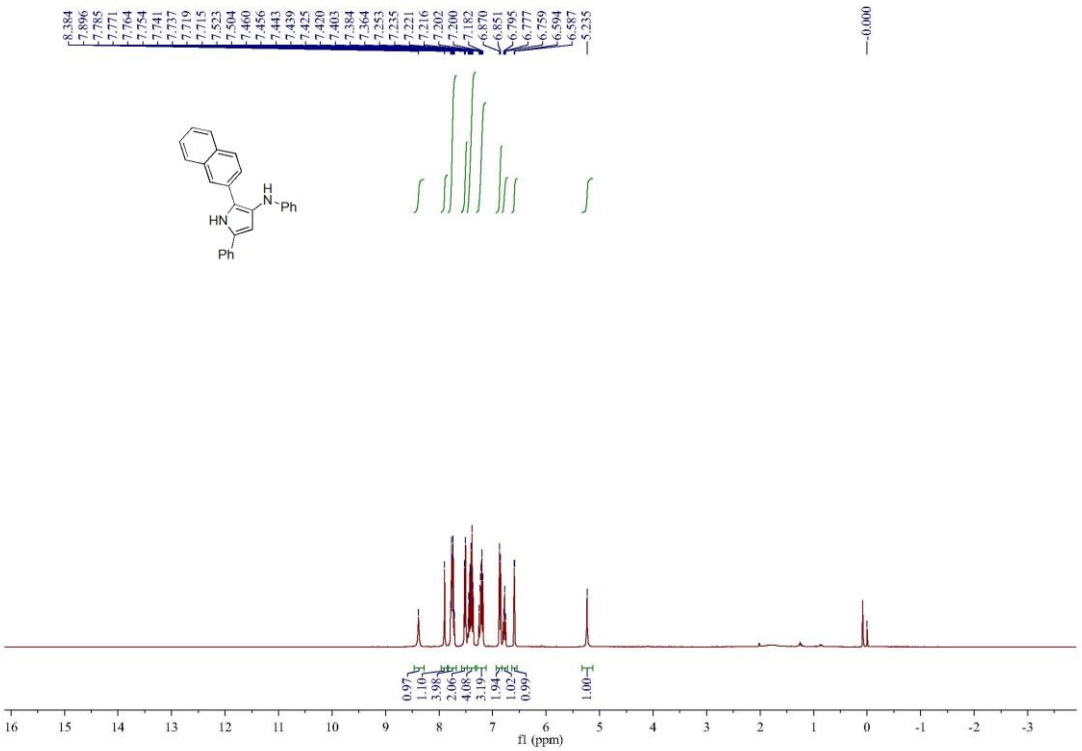


^{1}H NMR spectra of compound 3af in $CDCl_3$ (400 MHz)

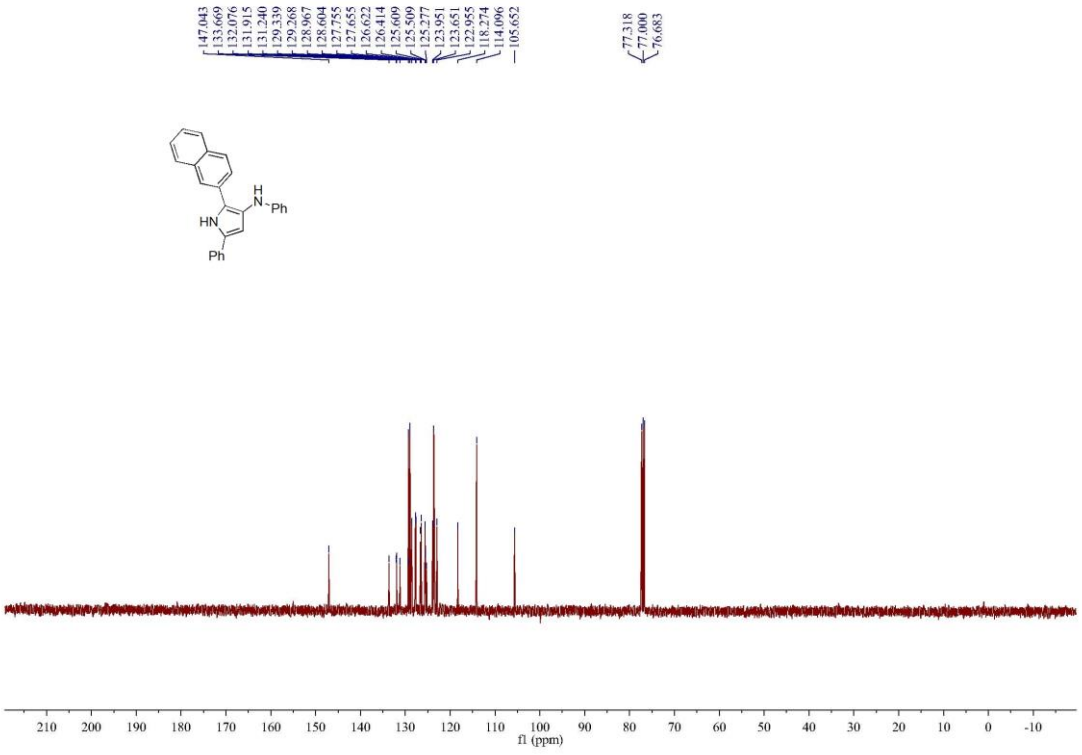


^{13}C NMR spectra of compound 3af in $CDCl_3$ (400 MHz)

2-(Naphthalen-2-yl)-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ag)

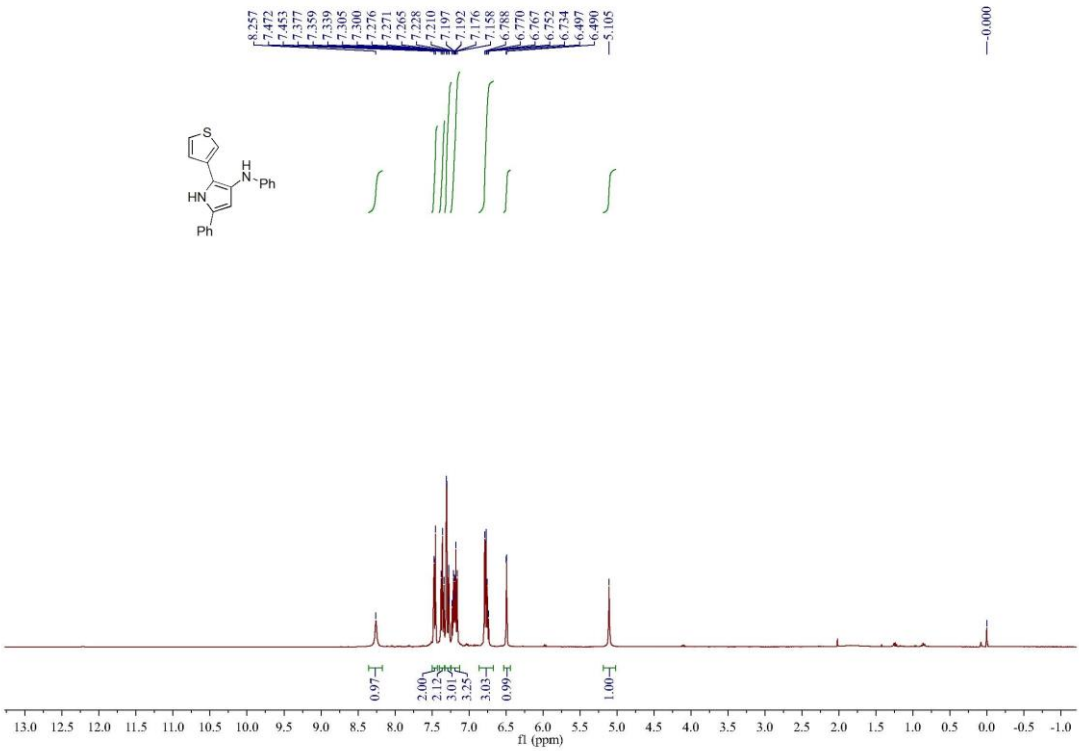


^{1}H NMR spectra of compound 3ag in $CDCl_3$ (400 MHz)

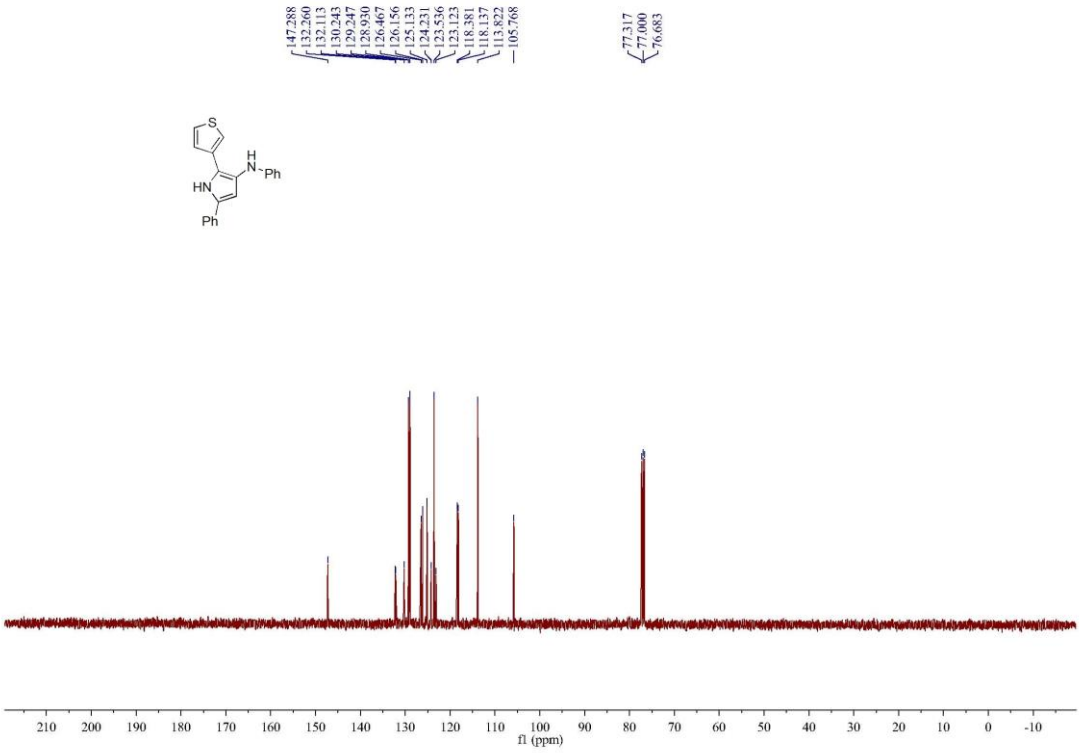


^{13}C NMR spectra of compound 3ag in $CDCl_3$ (400 MHz)

N,5-Diphenyl-2-(thiophen-3-yl)-1*H*-pyrrol-3-amine (3ah)

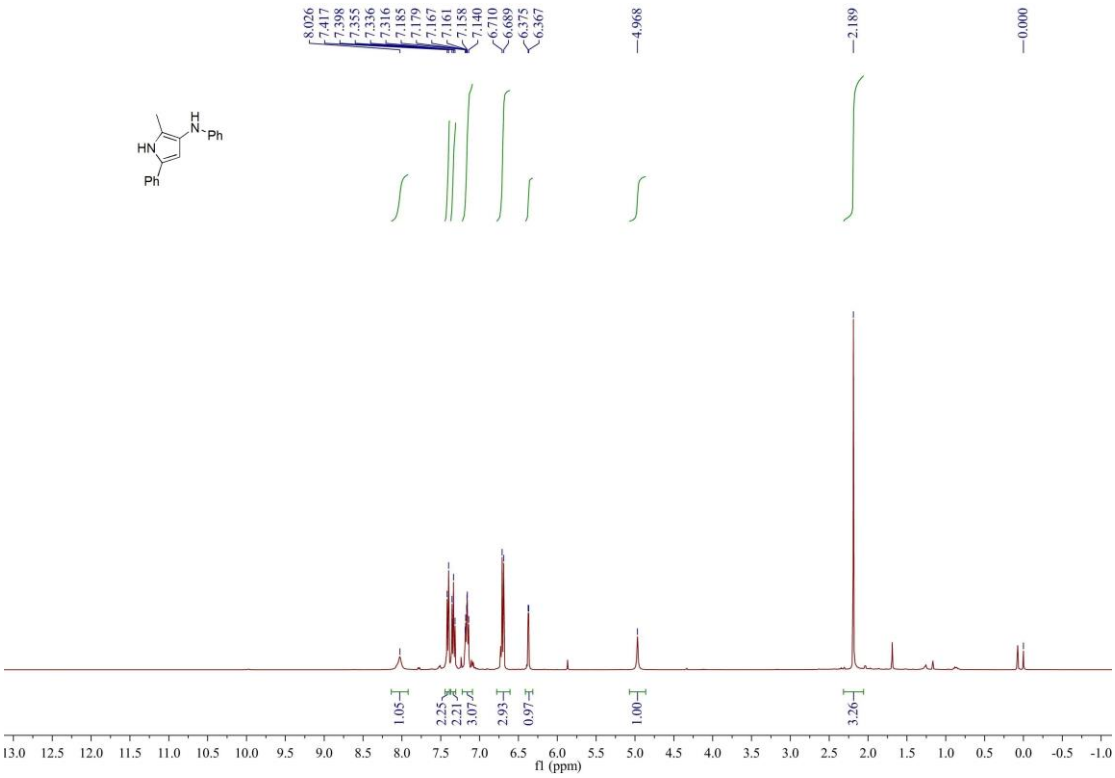


^{1}H NMR spectra of compound 3ah in $CDCl_3$ (400 MHz)

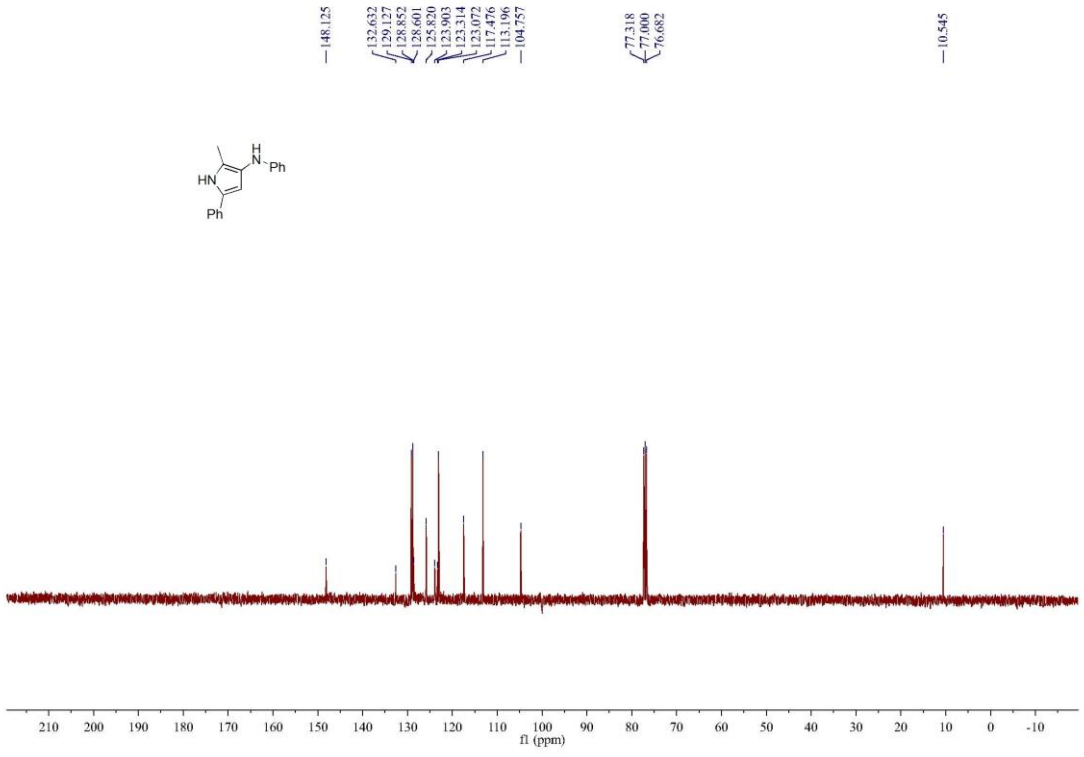


^{13}C NMR spectra of compound 3ah in $CDCl_3$ (400 MHz)

2-Methyl-*N*,5-diphenyl-1*H*-pyrrol-3-amine (3ai)

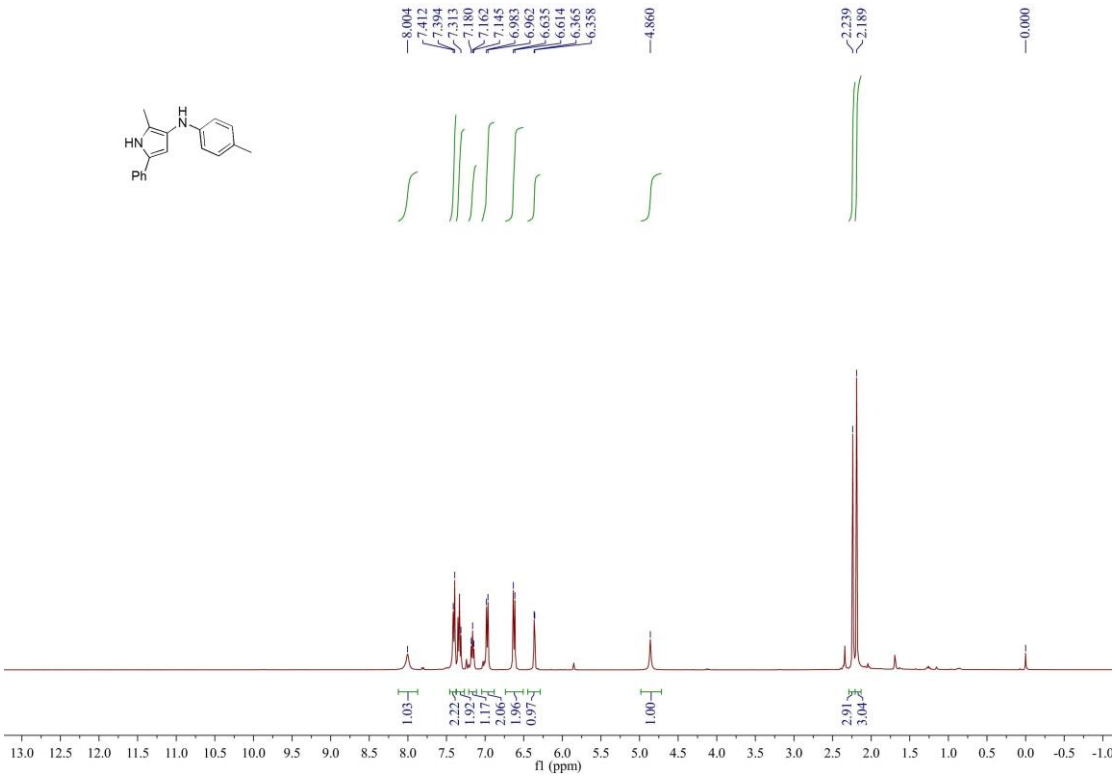


^{1}H NMR spectra of compound 3ai in $CDCl_3$ (400 MHz)

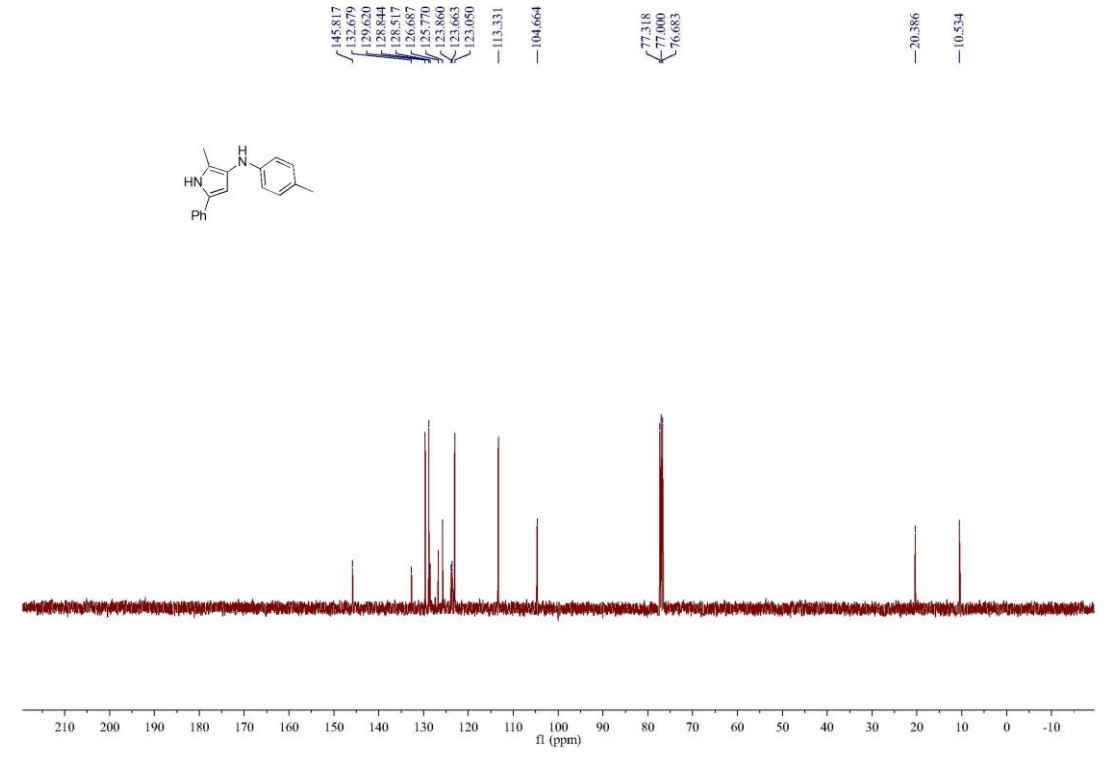


^{13}C NMR spectra of compound 3ai in $CDCl_3$ (400 MHz)

2-Methyl-5-phenyl-*N*-*p*-tolyl-1*H*-pyrrol-3-amine (3aj)

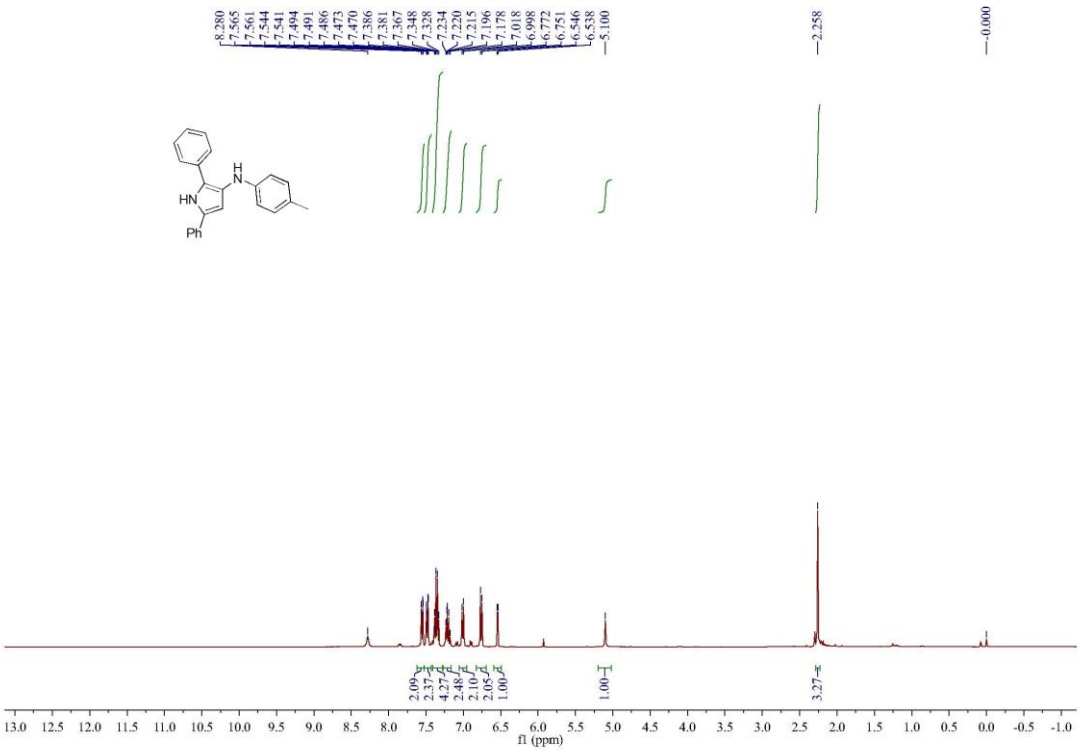


^{1}H NMR spectra of compound 3aj in $CDCl_3$ (400 MHz)

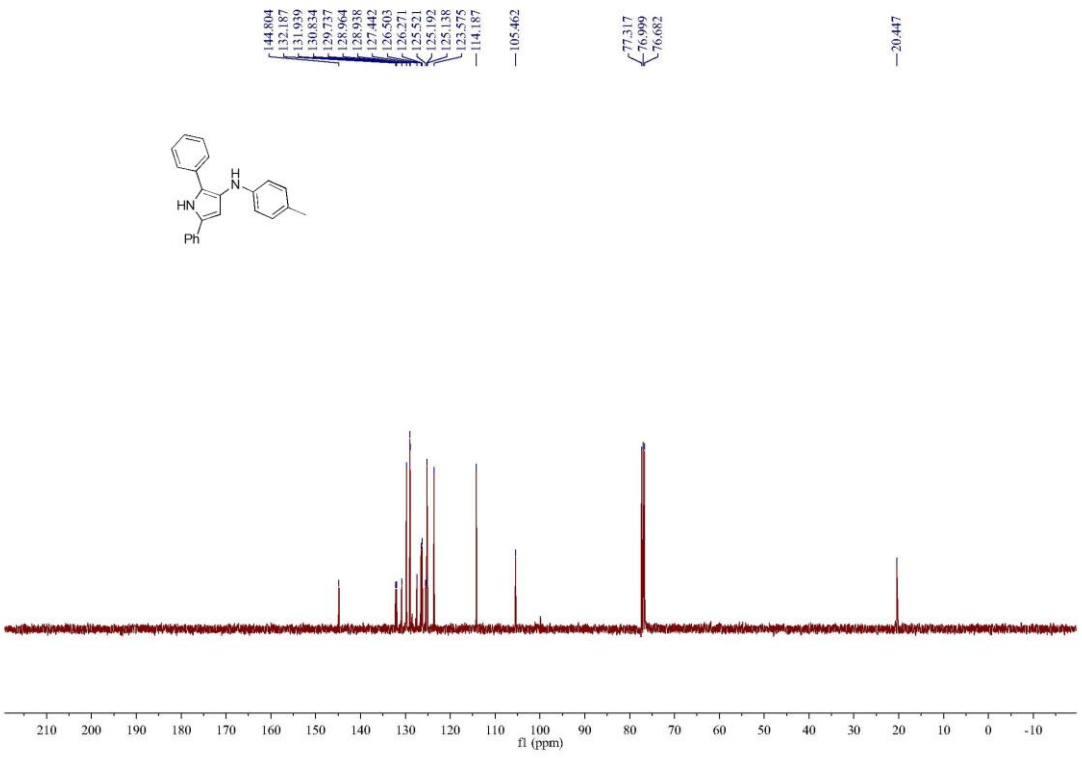


^{13}C NMR spectra of compound 3aj in $CDCl_3$ (400 MHz)

2,5-Diphenyl-*N*-*p*-tolyl-1*H*-pyrrol-3-amine (3ak)

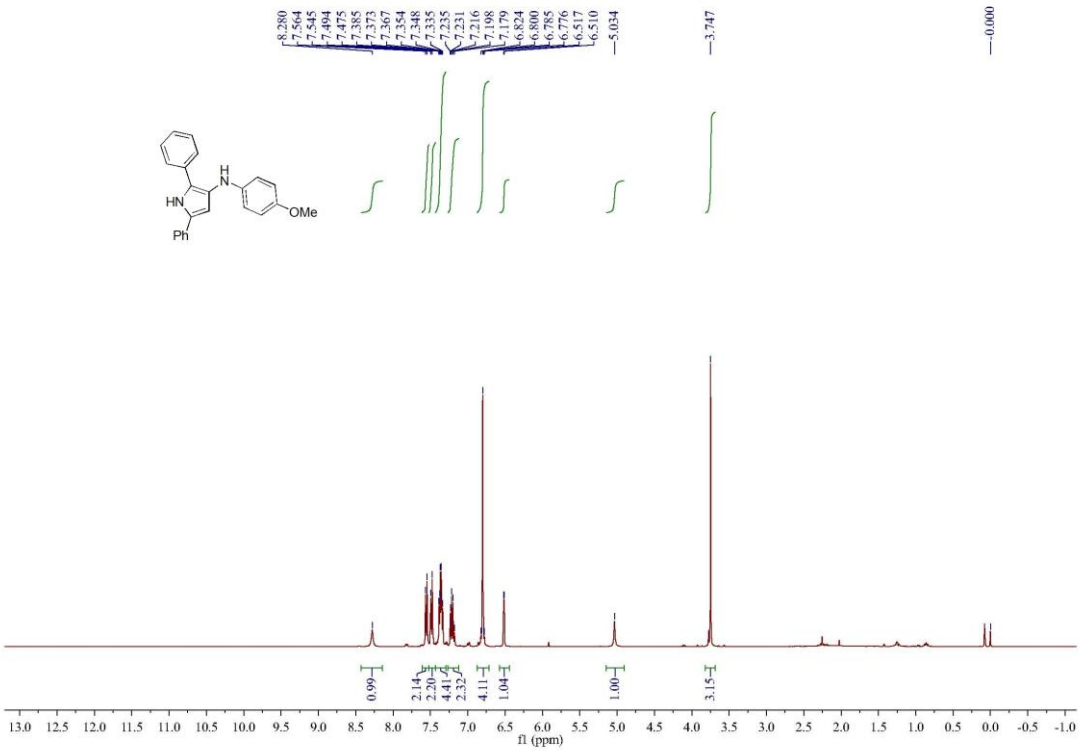


^{1}H NMR spectra of compound 3ak in $CDCl_3$ (400 MHz)

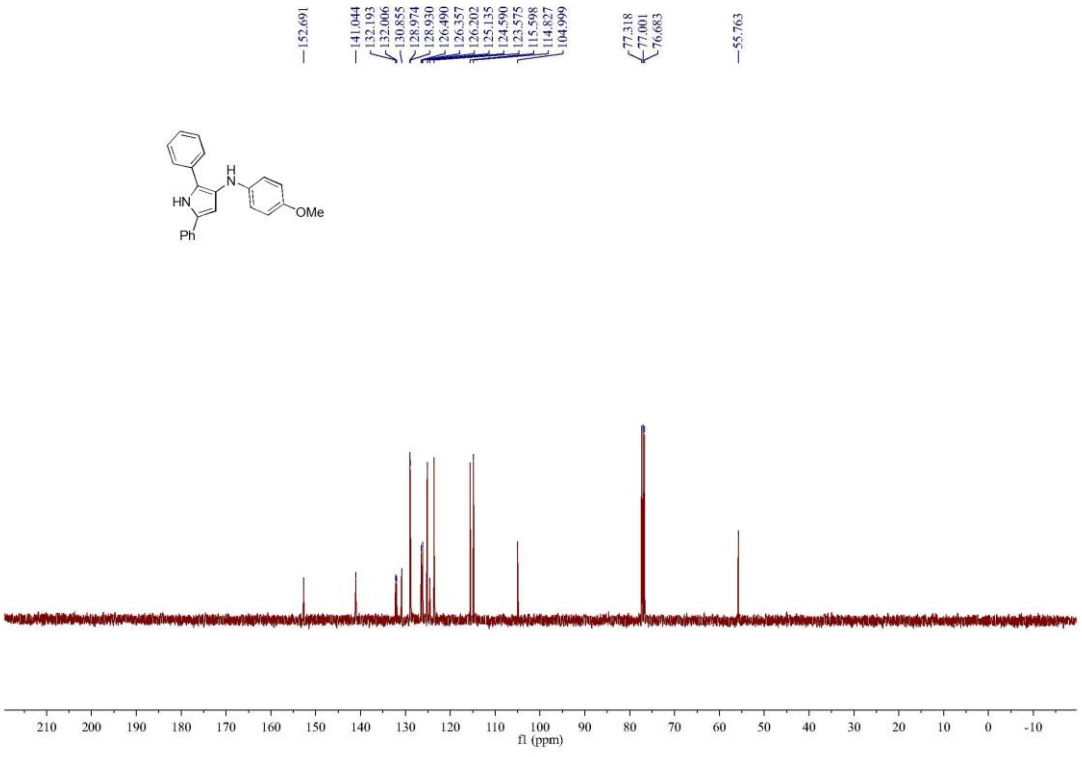


^{13}C NMR spectra of compound 3ak in $CDCl_3$ (400 MHz)

N-(4-Methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3al)

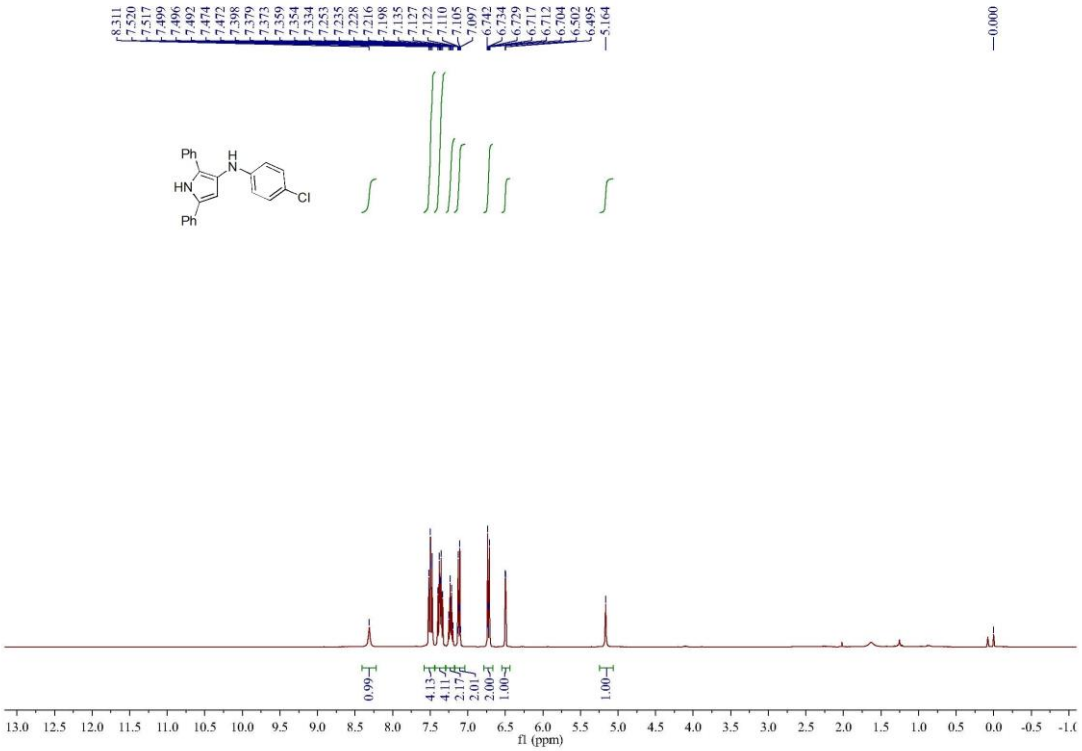


^{1}H NMR spectra of compound 3al in $CDCl_3$ (400 MHz)

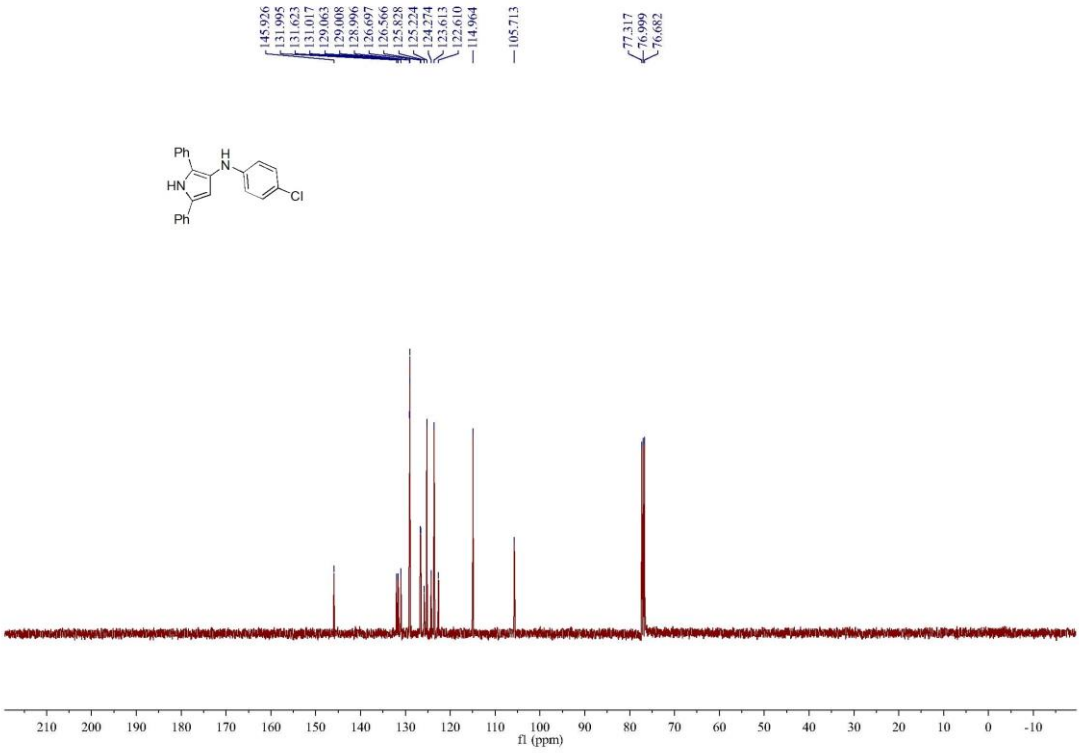


^{13}C NMR spectra of compound 3al in $CDCl_3$ (400 MHz)

N-(4-Chlorophenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3am)

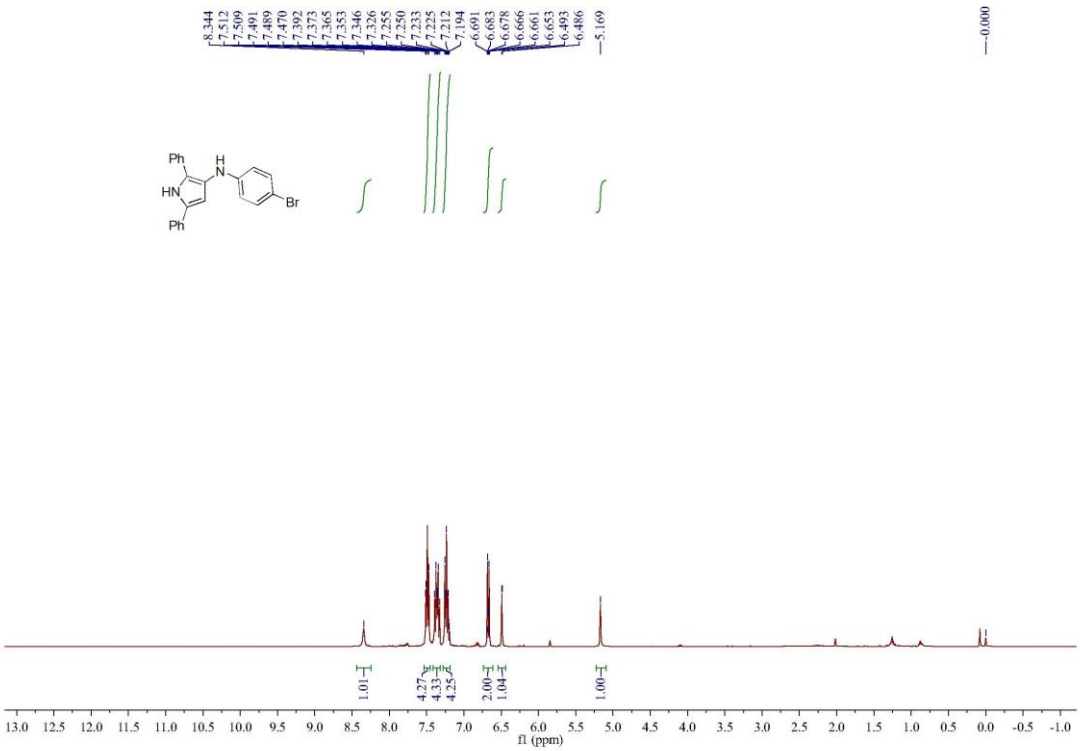


^{1}H NMR spectra of compound 3am in $CDCl_3$ (400 MHz)

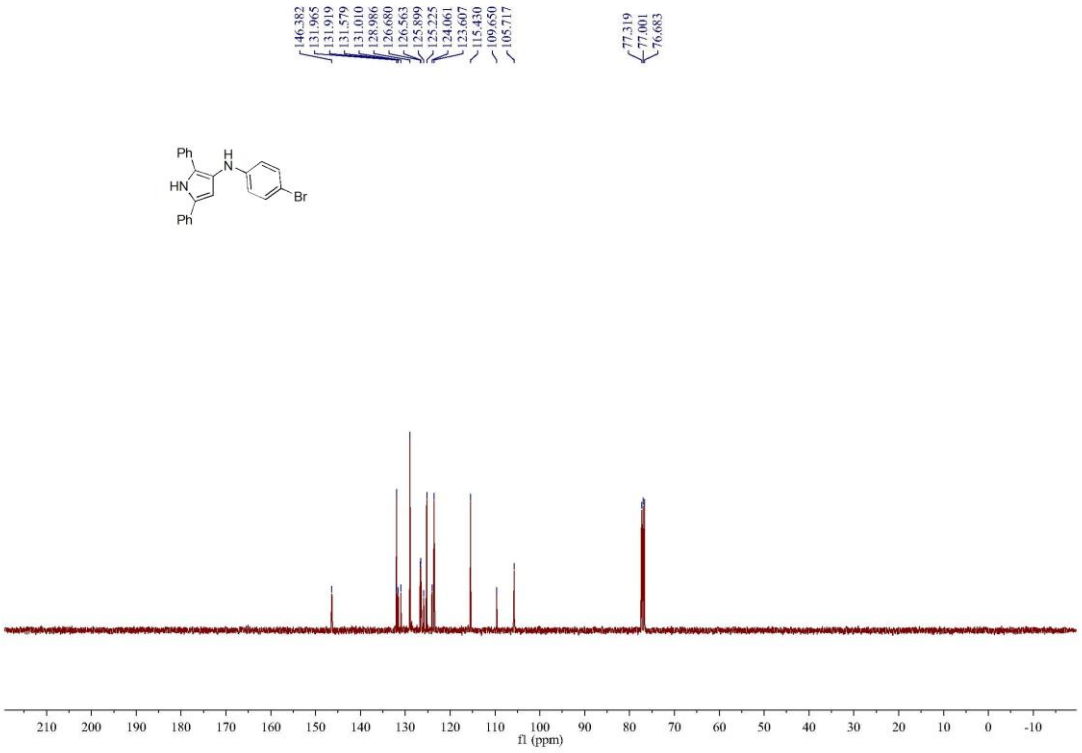


^{13}C NMR spectra of compound 3am in $CDCl_3$ (400 MHz)

N-(4-Bromophenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3an)

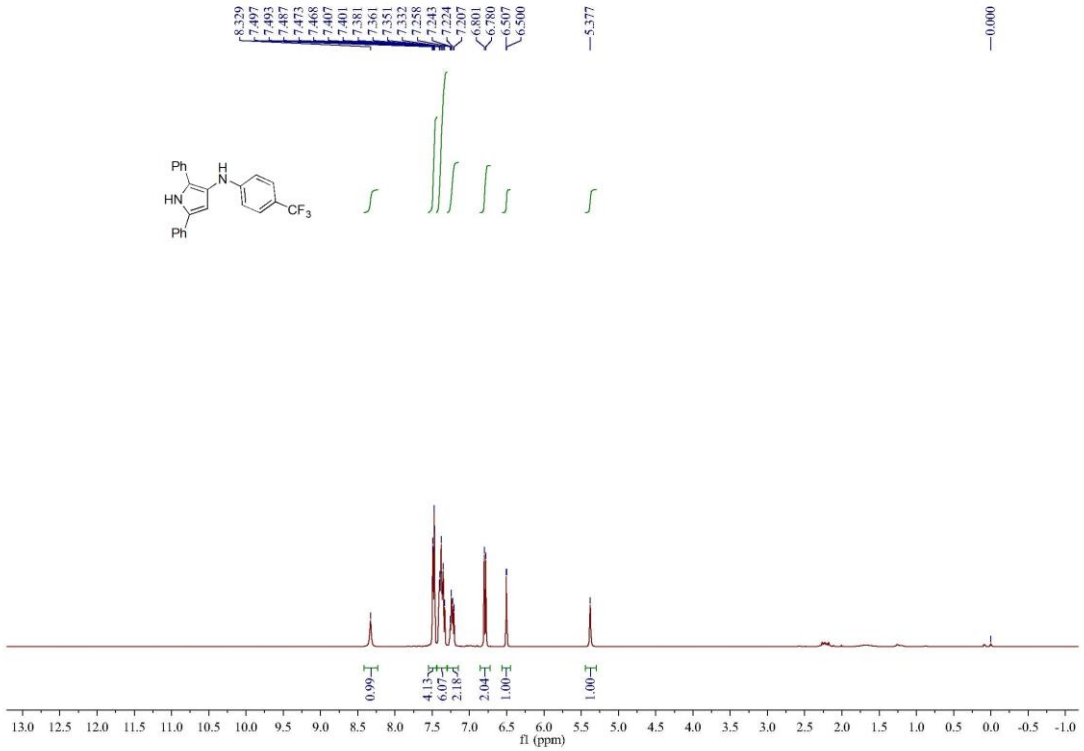


^{1}H NMR spectra of compound 3an in $CDCl_3$ (400 MHz)

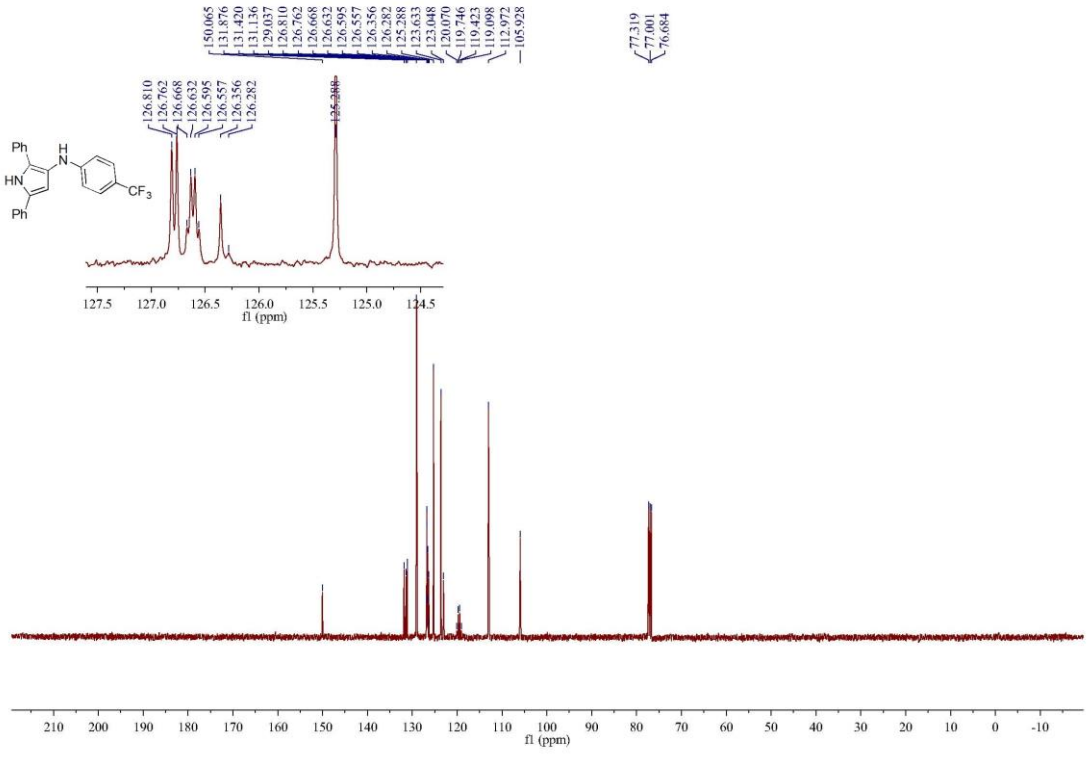


^{1}H NMR spectra of compound 3an in $CDCl_3$ (400 MHz)

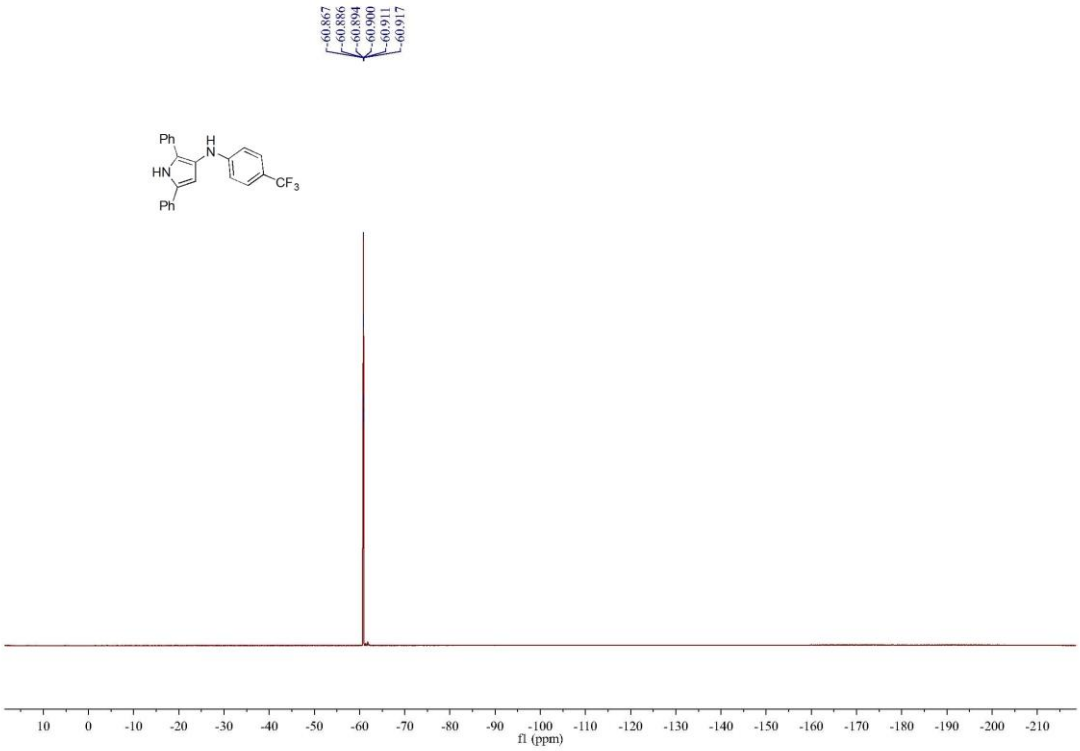
2,5-Diphenyl-*N*-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-amine (3ao)



^{1}H NMR spectra of compound 3ao in $CDCl_3$ (400 MHz)

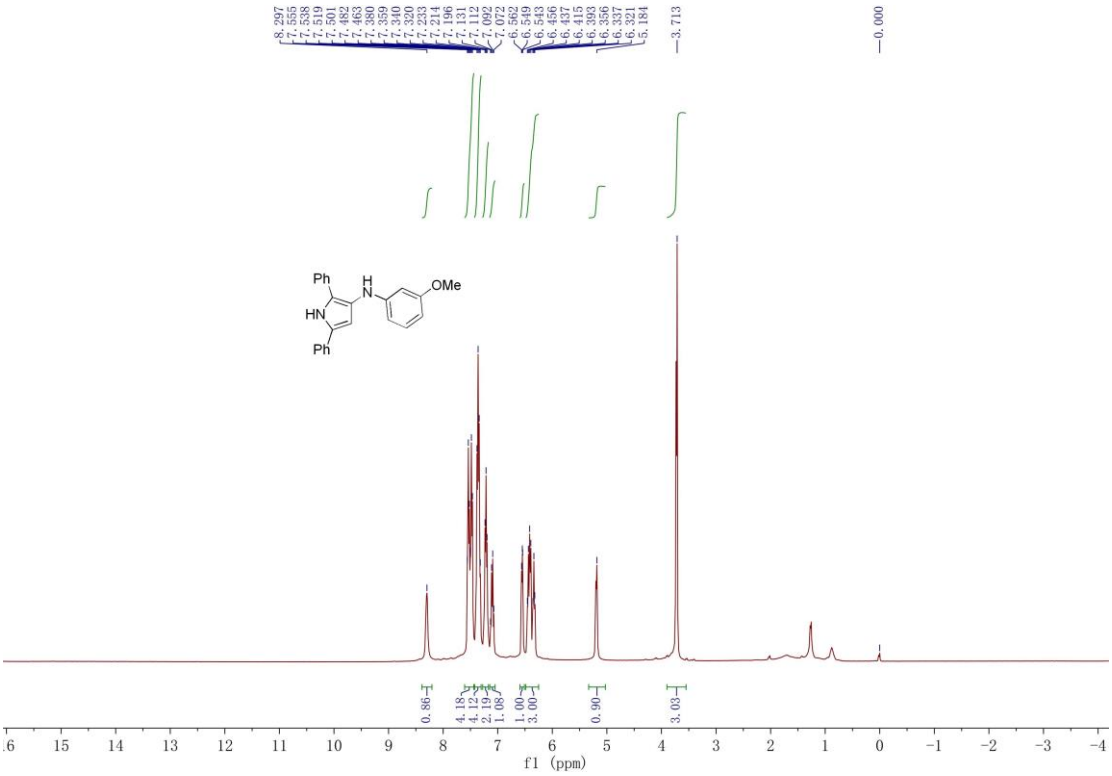


^{13}C NMR spectra of compound 3ao in $CDCl_3$ (400 MHz)

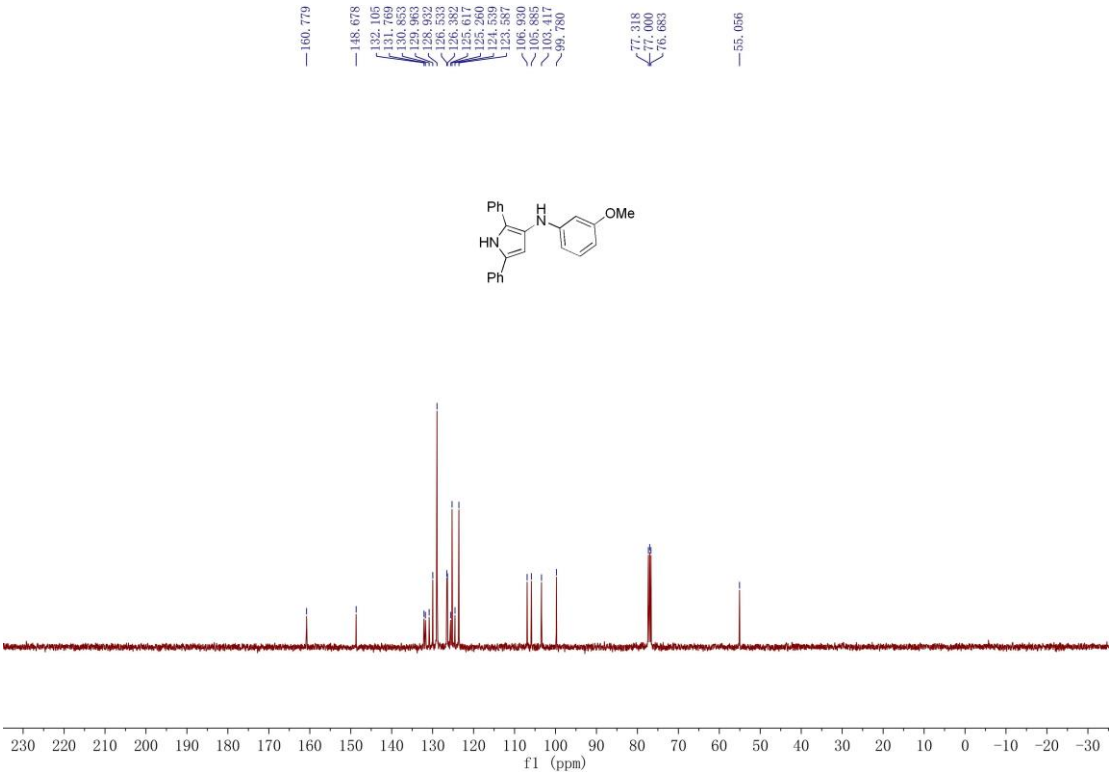


^{19}F NMR spectra of compound 3ao in $CDCl_3$ (400 MHz)

N-(3-Methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3ap)

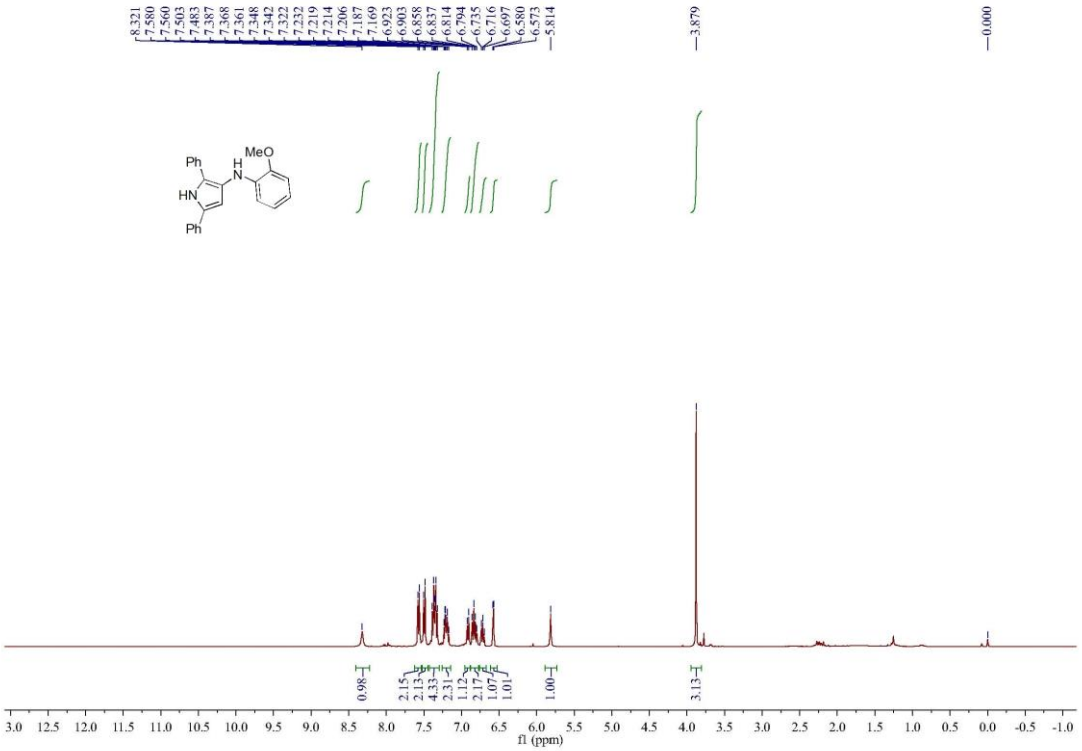


^{1}H NMR spectra of compound 3ap in $CDCl_3$ (400 MHz)

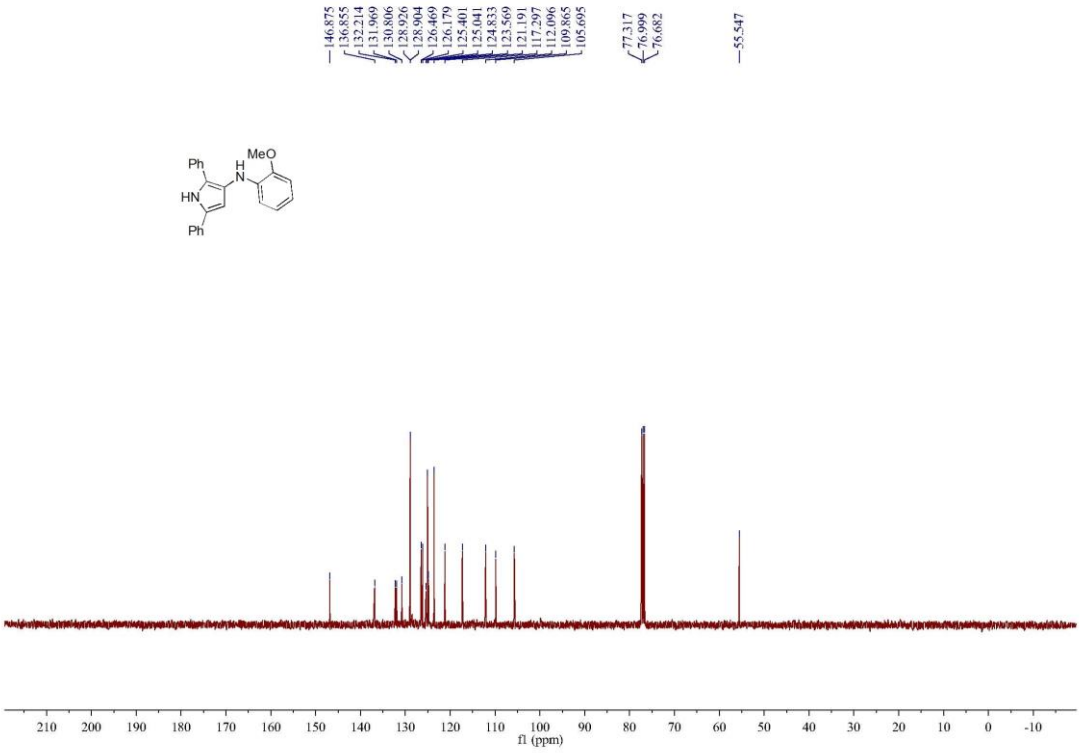


^{13}C NMR spectra of compound 3ap in $CDCl_3$ (400 MHz)

N-(2-Methoxyphenyl)-2,5-diphenyl-1*H*-pyrrol-3-amine (3aq)

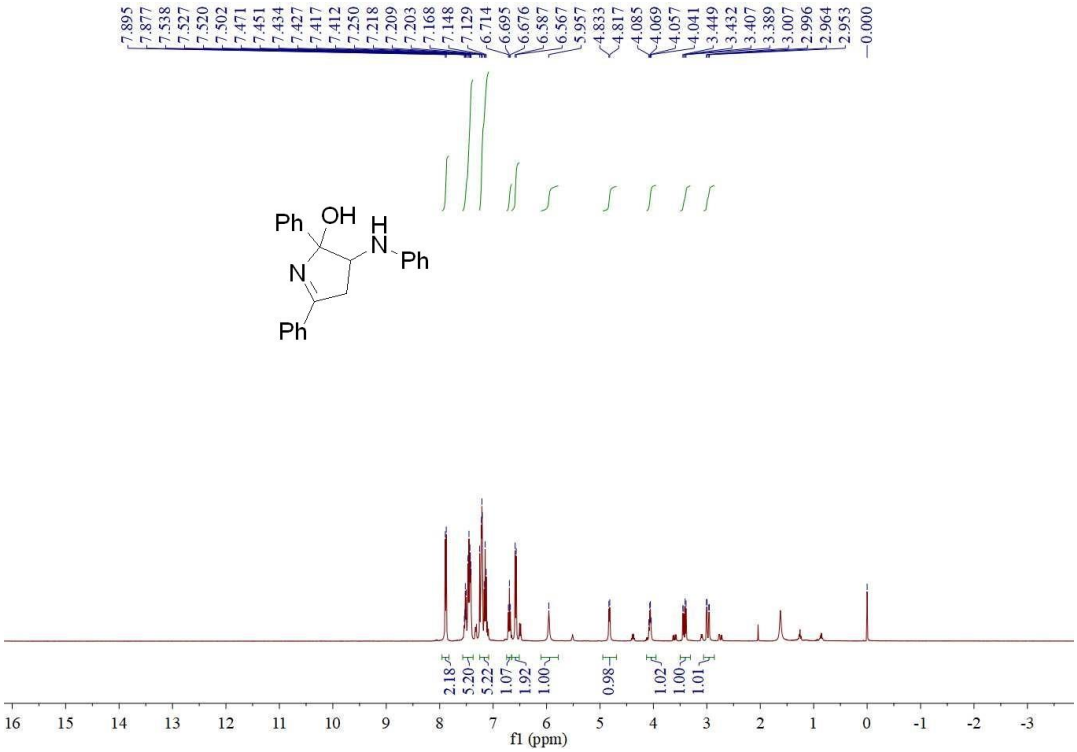


^{1}H NMR spectra of compound 3aq in $CDCl_3$ (400 MHz)

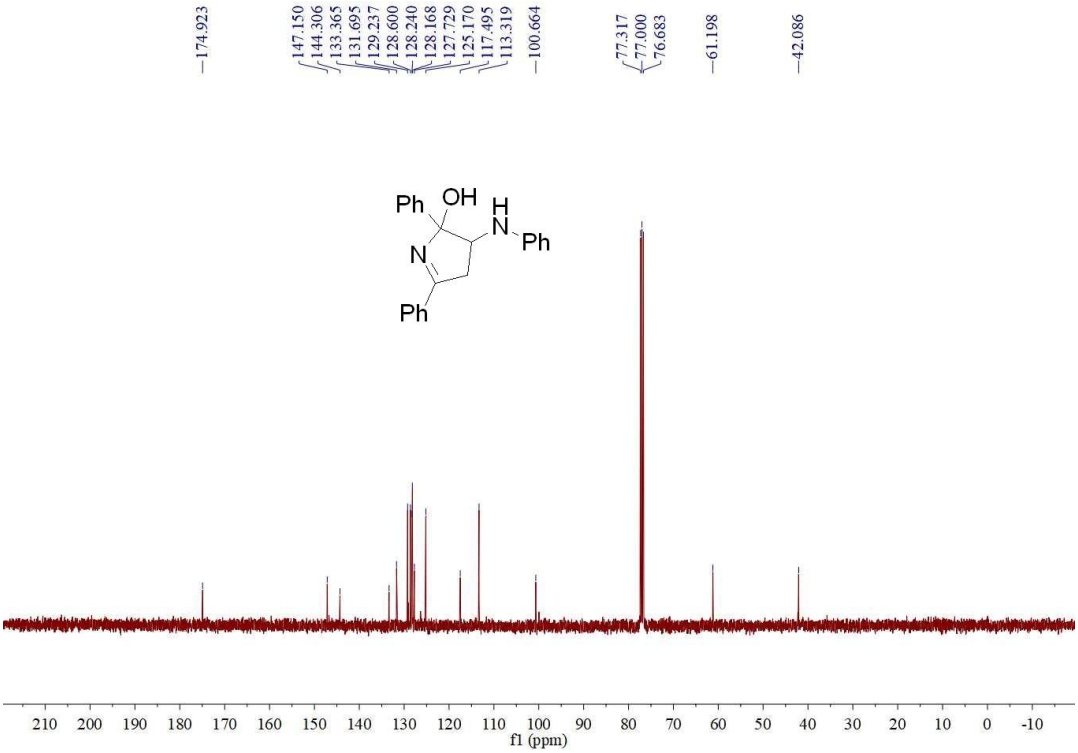


^{13}C NMR spectra of compound 3aq in $CDCl_3$ (400 MHz)

2,5-diphenyl-3-(phenylamino)-3,4-dihydro-2*H*-pyrrol-2-ol (4aa)

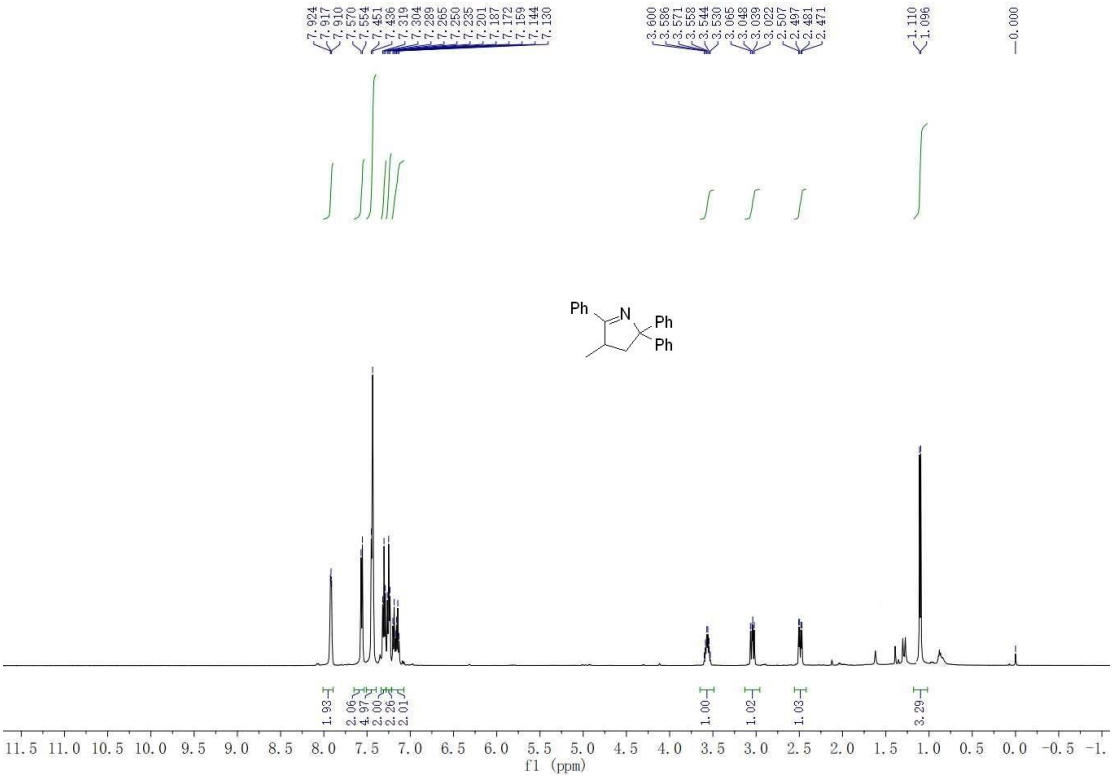


^{1}H NMR spectra of compound 4aa in $CDCl_3$ (400 MHz)

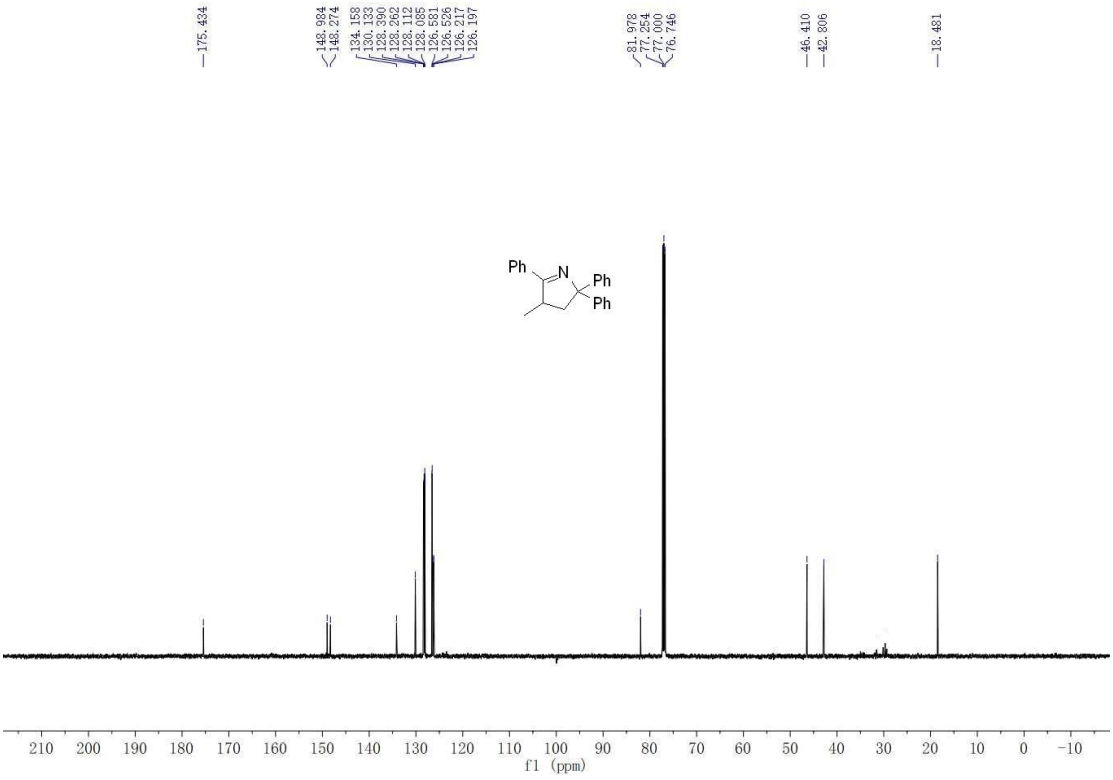


^{13}C NMR spectra of compound 4aa in $CDCl_3$ (400 MHz)

4-Methyl-2,2,5-triphenyl-3,4-dihydro-2*H*-pyrrole (7)

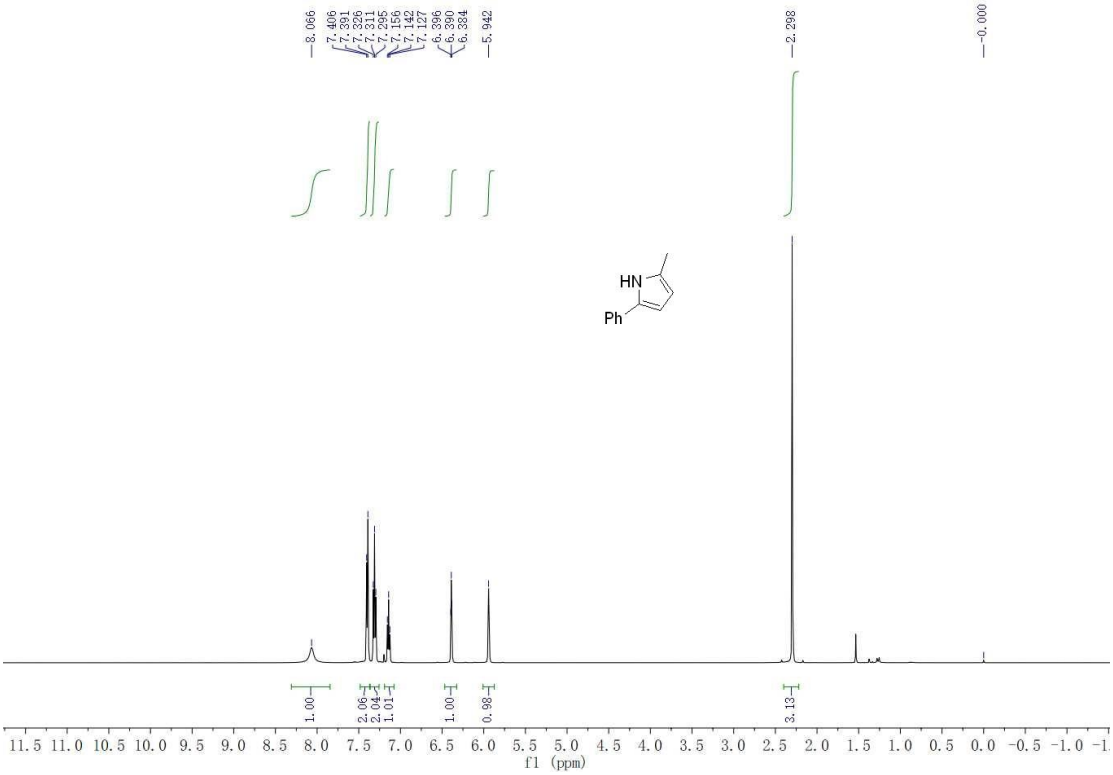


^{1}H NMR spectra of compound 7 in $CDCl_3$ (400 MHz)

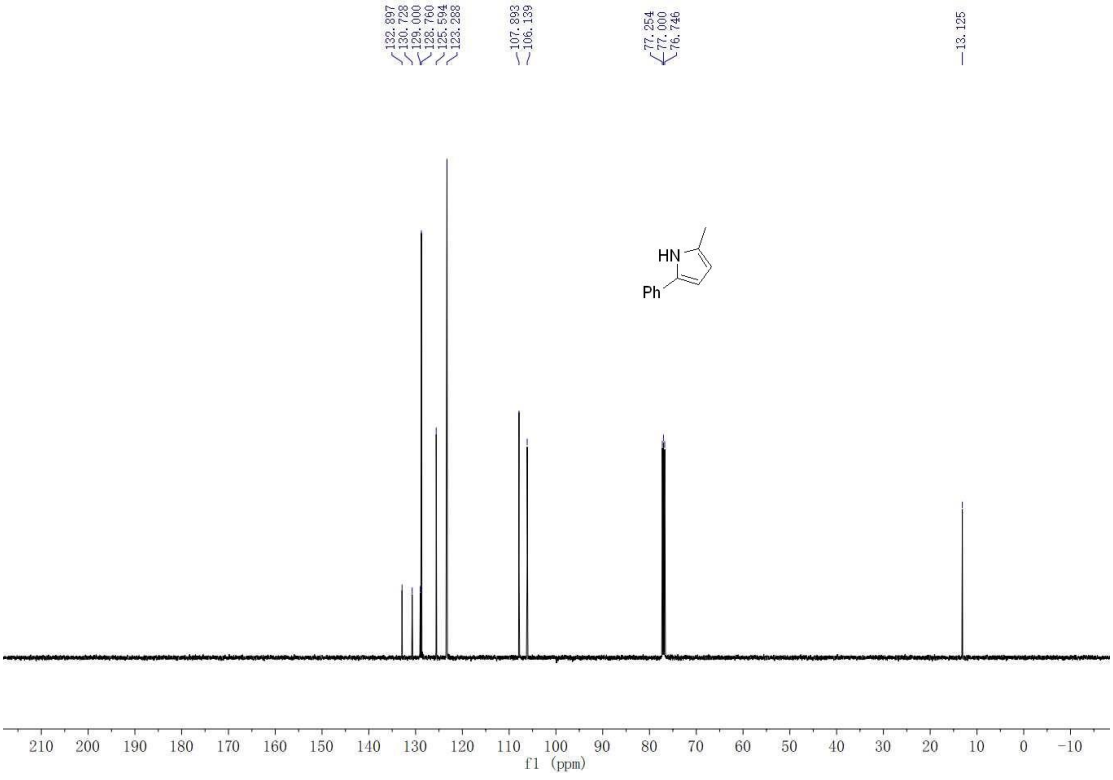


^{13}C NMR spectra of compound 7 in $CDCl_3$ (400 MHz)

2-Methyl-5-phenyl-1*H*-pyrrole (8)

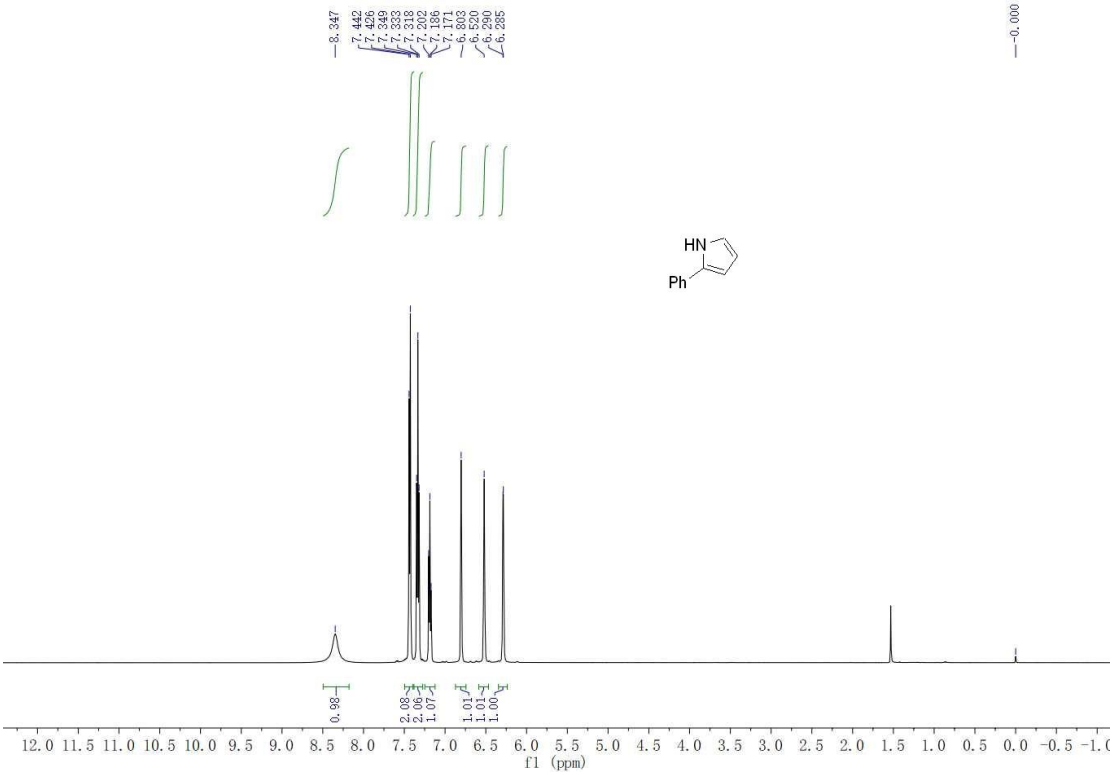


^{1}H NMR spectra of compound 8 in $CDCl_3$ (400 MHz)

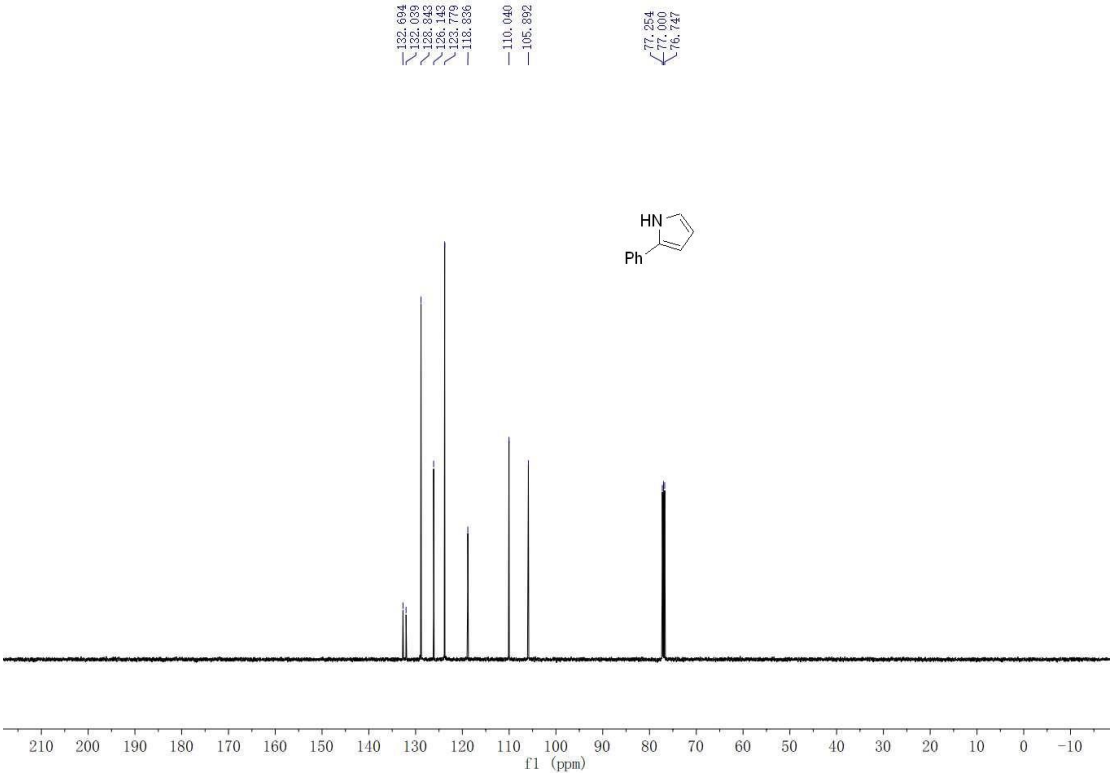


^{13}C NMR spectra of compound 8 in $CDCl_3$ (400 MHz)

2-Phenyl-1*H*-pyrrole (9)

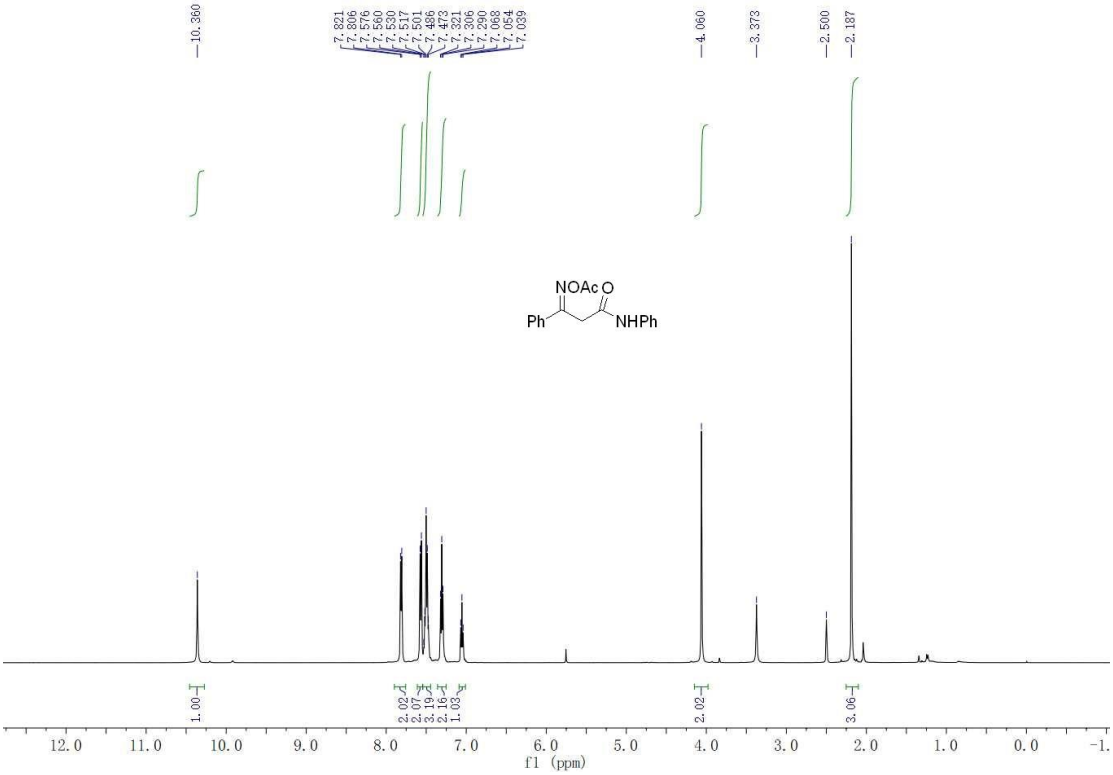


^{1}H NMR spectra of compound 9 in $CDCl_3$ (400 MHz)

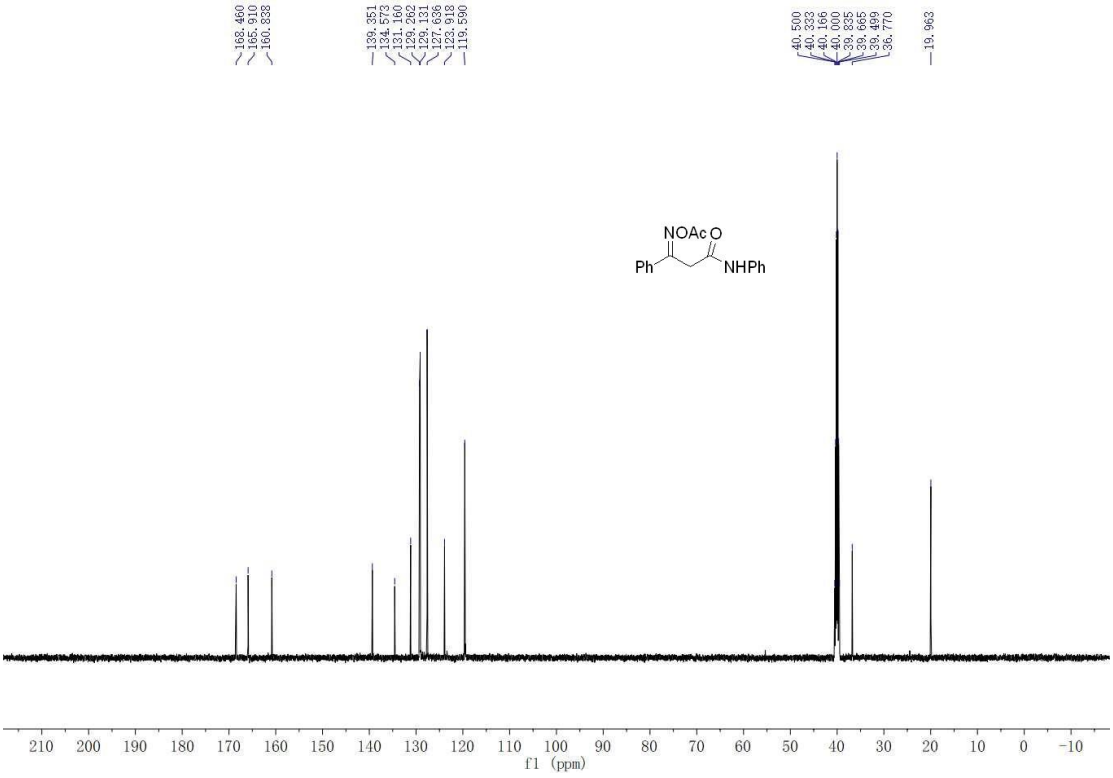


^{13}C NMR spectra of compound 9 in $CDCl_3$ (400 MHz)

3-(acetoxyimino)-1,3-diphenylpropan-1-one (1v)

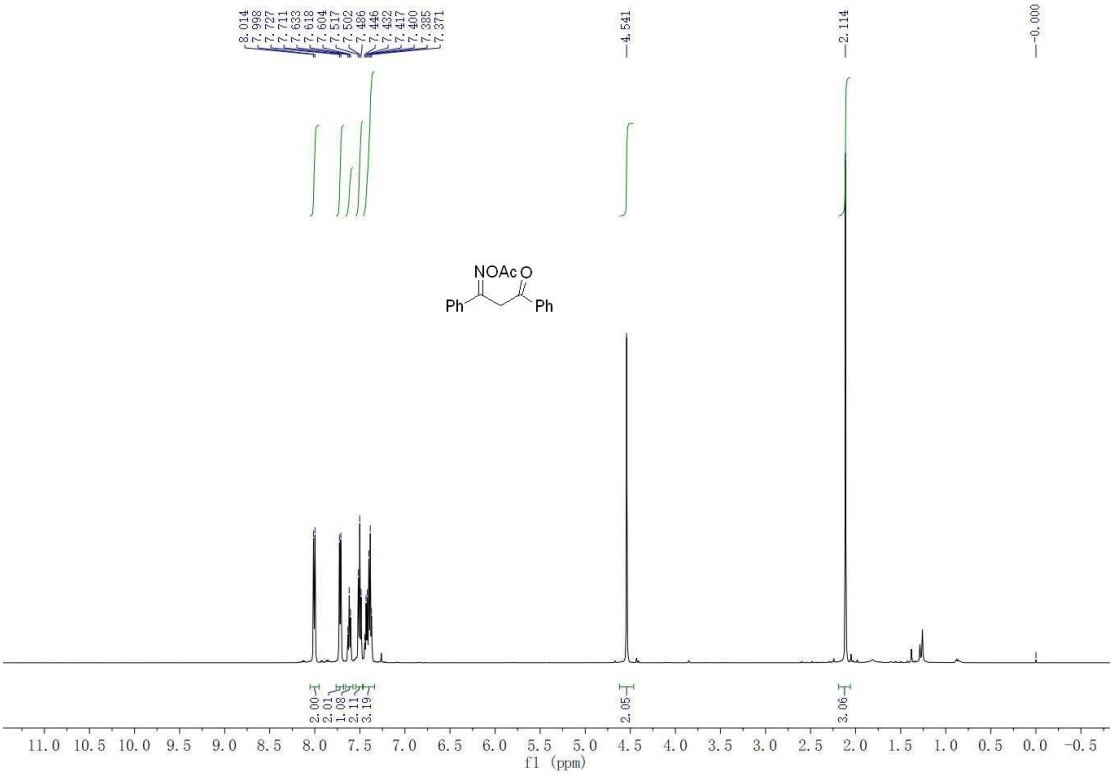


^{1}H NMR spectra of compound 1v in DMSO-*d6* (400 MHz)

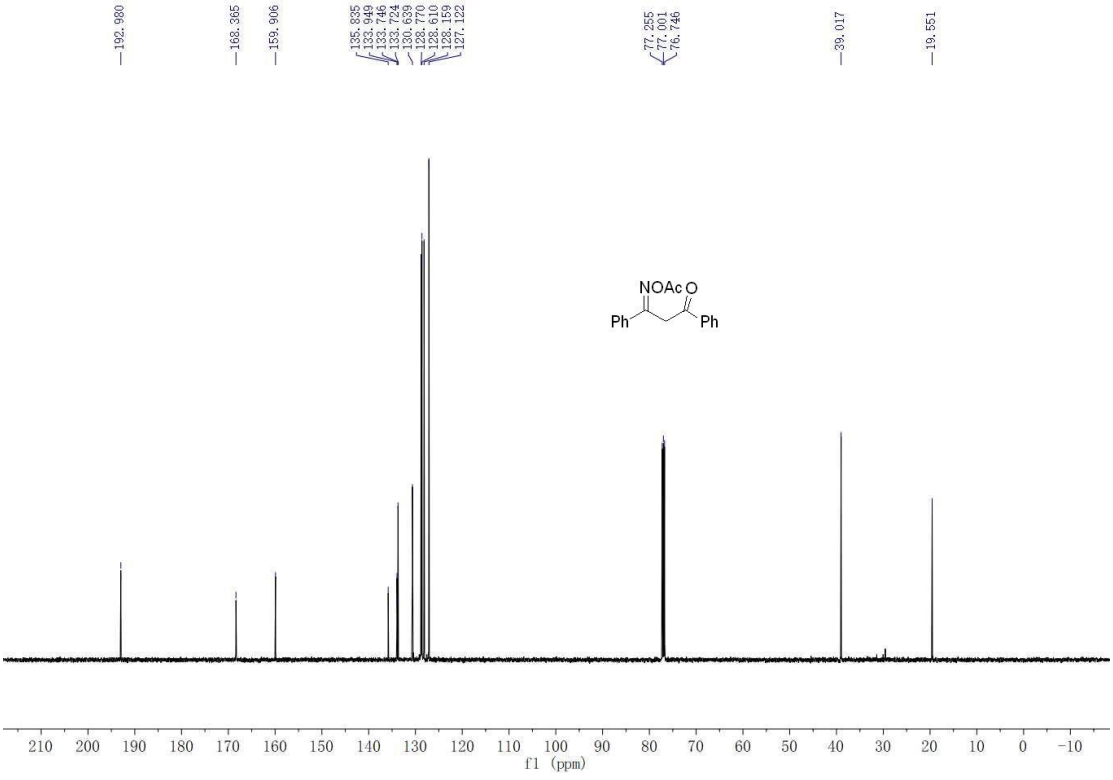


^{13}C NMR spectra of compound 1v in DMSO-*d6* (400 MHz)

3-(acetoxyimino)-1,3-diphenylpropan-1-one (1w)

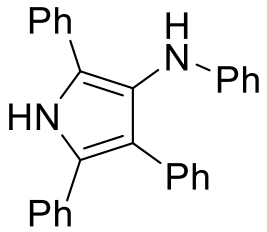


^{1}H NMR spectra of compound 1w in $CDCl_3$ (400 MHz)



^{13}C NMR spectra of compound 1w in $CDCl_3$ (400 MHz)

(D) The X-Ray Single-Crystal Diffraction Analysis of 3la (CCDC: 2060673)



3la

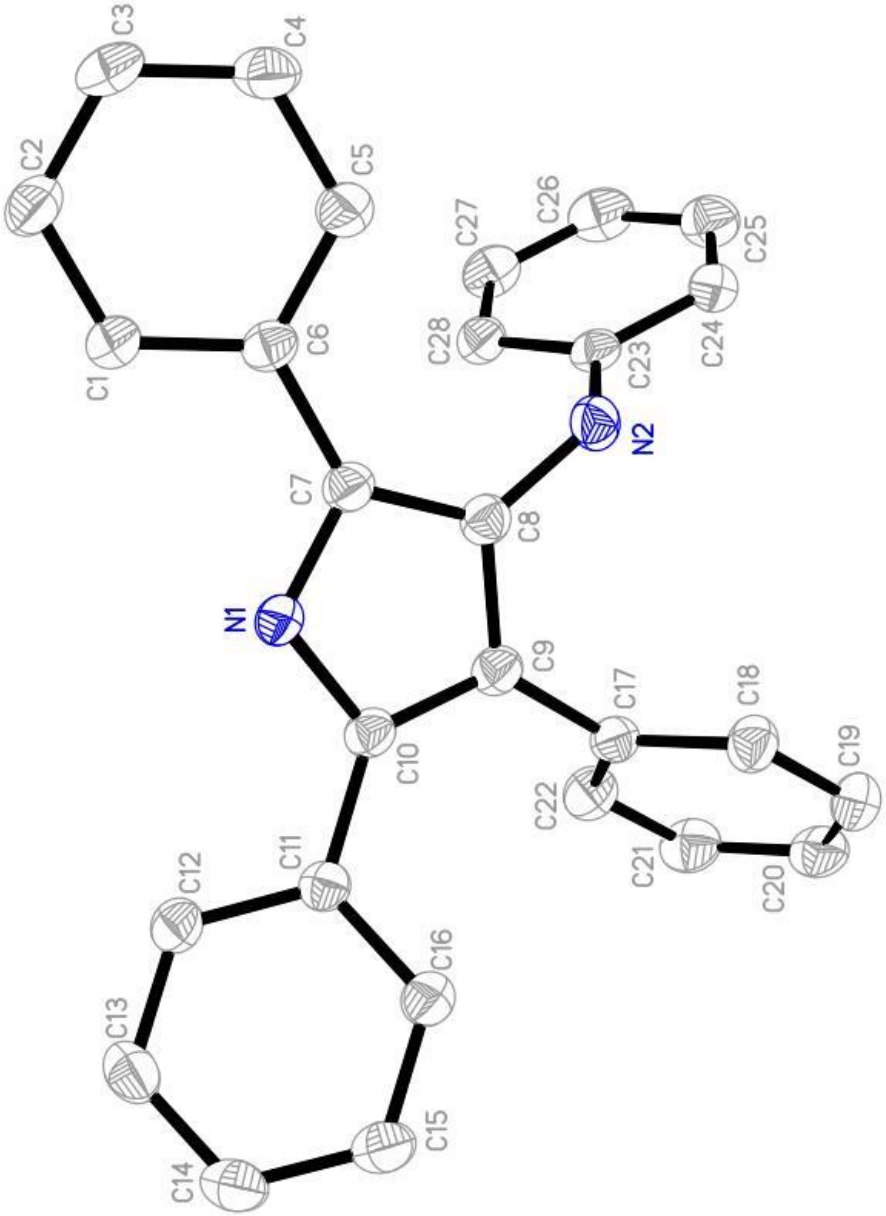


Table S1. Crystal data and structure refinement for mo_20141115A_0m.

Identification code	mo_20141115a_0m
Empirical formula	C28 H22 N2
Formula weight	386.48
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 37.838(9) A alpha = 90 deg. b = 5.7784(14) A beta = 108.615(4) deg. c = 19.980(5) A gamma = 90 deg.
Volume	4140.0(18) A^3
Z, Calculated density	8, 1.240 Mg/m^3
Absorption coefficient	0.072 mm^-1
F(000)	1632
Crystal size	0.25 x 0.19 x 0.15 mm
Theta range for data collection	2.09 to 26.00 deg.
Limiting indices	-46<=h<=46, -6<=k<=7, -24<=l<=24
Reflections collected / unique	16356 / 4063 [R(int) = 0.0233]
Completeness to theta = 26.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9892 and 0.9821
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4063 / 0 / 271
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1260
R indices (all data)	R1 = 0.0566, wR2 = 0.1316
Largest diff. peak and hole	0.337 and -0.321 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for mo_20141115A_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	1730(1)	2662(2)	1216(1)	40(1)
N(2)	1142(1)	7348(2)	1388(1)	45(1)
C(1)	2178(1)	3256(3)	2686(1)	46(1)
C(2)	2407(1)	3631(4)	3373(1)	52(1)
C(3)	2376(1)	5631(4)	3724(1)	52(1)
C(4)	2117(1)	7279(4)	3381(1)	54(1)
C(5)	1887(1)	6921(3)	2694(1)	49(1)
C(6)	1911(1)	4889(3)	2334(1)	40(1)
C(7)	1659(1)	4432(3)	1617(1)	40(1)
C(8)	1321(1)	5394(3)	1215(1)	40(1)
C(9)	1184(1)	4131(3)	571(1)	40(1)
C(10)	1450(1)	2466(3)	577(1)	38(1)
C(11)	1487(1)	852(3)	36(1)	37(1)
C(12)	1693(1)	-1192(3)	224(1)	44(1)
C(13)	1739(1)	-2670(3)	-286(1)	53(1)
C(14)	1575(1)	-2173(3)	-994(1)	54(1)
C(15)	1367(1)	-176(3)	-1187(1)	51(1)
C(16)	1325(1)	1337(3)	-683(1)	44(1)
C(17)	811(1)	4487(3)	33(1)	40(1)
C(18)	721(1)	6509(3)	-358(1)	48(1)
C(19)	367(1)	6859(4)	-838(1)	60(1)
C(20)	94(1)	5155(4)	-934(1)	60(1)
C(21)	184(1)	3156(4)	-547(1)	57(1)
C(22)	538(1)	2812(3)	-72(1)	52(1)
C(23)	928(1)	7288(3)	1839(1)	39(1)
C(24)	699(1)	9169(3)	1856(1)	46(1)
C(25)	492(1)	9163(4)	2313(1)	59(1)
C(26)	504(1)	7333(4)	2759(1)	63(1)
C(27)	729(1)	5492(4)	2743(1)	54(1)
C(28)	942(1)	5414(3)	2294(1)	44(1)

Table S3. Bond lengths [A] and angles [deg] for mo_20141115A_0m.

N(1)-C(7)	1.376(2)
N(1)-C(10)	1.3787(19)
N(1)-H(1A)	0.8600
N(2)-C(23)	1.393(2)
N(2)-C(8)	1.415(2)
N(2)-H(2A)	0.8600
C(1)-C(2)	1.387(2)
C(1)-C(6)	1.398(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.377(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.381(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.386(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.395(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.470(2)
C(7)-C(8)	1.391(2)
C(8)-C(9)	1.426(2)
C(9)-C(10)	1.389(2)
C(9)-C(17)	1.492(2)
C(10)-C(11)	1.469(2)
C(11)-C(16)	1.397(2)
C(11)-C(12)	1.399(2)
C(12)-C(13)	1.381(2)
C(12)-H(12)	0.9300
C(13)-C(14)	1.381(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.381(3)
C(14)-H(14)	0.9300
C(15)-C(16)	1.381(2)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-C(22)	1.382(2)
C(17)-C(18)	1.386(2)
C(18)-C(19)	1.389(2)
C(18)-H(18)	0.9300
C(19)-C(20)	1.395(3)
C(19)-H(19)	0.9300
C(20)-C(21)	1.371(3)
C(20)-H(20)	0.9300

C(21)-C(22)	1.385(3)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-C(24)	1.395(2)
C(23)-C(28)	1.404(2)
C(24)-C(25)	1.382(2)
C(24)-H(24)	0.9300
C(25)-C(26)	1.374(3)
C(25)-H(25)	0.9300
C(26)-C(27)	1.370(3)
C(26)-H(26)	0.9300
C(27)-C(28)	1.384(2)
C(27)-H(27)	0.9300
C(28)-H(28)	0.9300
C(7)-N(1)-C(10)	111.44(13)
C(7)-N(1)-H(1A)	124.3
C(10)-N(1)-H(1A)	124.3
C(23)-N(2)-C(8)	124.18(13)
C(23)-N(2)-H(2A)	117.9
C(8)-N(2)-H(2A)	117.9
C(2)-C(1)-C(6)	121.03(16)
C(2)-C(1)-H(1)	119.5
C(6)-C(1)-H(1)	119.5
C(3)-C(2)-C(1)	120.44(17)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(2)-C(3)-C(4)	119.29(16)
C(2)-C(3)-H(3)	120.4
C(4)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	120.68(17)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.80(17)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	117.75(15)
C(5)-C(6)-C(7)	121.70(15)
C(1)-C(6)-C(7)	120.54(15)
N(1)-C(7)-C(8)	105.95(13)
N(1)-C(7)-C(6)	121.04(14)
C(8)-C(7)-C(6)	132.92(15)
C(7)-C(8)-N(2)	127.04(14)
C(7)-C(8)-C(9)	108.60(14)
N(2)-C(8)-C(9)	124.33(14)

C(10)-C(9)-C(8)	107.00(13)
C(10)-C(9)-C(17)	128.24(14)
C(8)-C(9)-C(17)	124.61(14)
N(1)-C(10)-C(9)	106.95(13)
N(1)-C(10)-C(11)	120.57(13)
C(9)-C(10)-C(11)	132.24(14)
C(16)-C(11)-C(12)	118.04(14)
C(16)-C(11)-C(10)	121.01(14)
C(12)-C(11)-C(10)	120.94(14)
C(13)-C(12)-C(11)	120.91(16)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	120.35(17)
C(12)-C(13)-H(13)	119.8
C(14)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	119.34(16)
C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3
C(14)-C(15)-C(16)	120.84(16)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-C(11)	120.50(16)
C(15)-C(16)-H(16)	119.7
C(11)-C(16)-H(16)	119.7
C(22)-C(17)-C(18)	117.85(15)
C(22)-C(17)-C(9)	120.22(15)
C(18)-C(17)-C(9)	121.89(15)
C(17)-C(18)-C(19)	121.40(17)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(18)-C(19)-C(20)	119.94(19)
C(18)-C(19)-H(19)	120.0
C(20)-C(19)-H(19)	120.0
C(21)-C(20)-C(19)	118.56(17)
C(21)-C(20)-H(20)	120.7
C(19)-C(20)-H(20)	120.7
C(20)-C(21)-C(22)	121.23(18)
C(20)-C(21)-H(21)	119.4
C(22)-C(21)-H(21)	119.4
C(17)-C(22)-C(21)	121.01(18)
C(17)-C(22)-H(22)	119.5
C(21)-C(22)-H(22)	119.5
N(2)-C(23)-C(28)	121.91(14)
C(24)-C(23)-C(28)	118.74(15)

C(25)-C(24)-C(23)	120.07(17)
C(25)-C(24)-H(24)	120.0
C(23)-C(24)-H(24)	120.0
C(26)-C(25)-C(24)	121.45(18)
C(26)-C(25)-H(25)	119.3
C(24)-C(25)-H(25)	119.3
C(27)-C(26)-C(25)	118.39(17)
C(27)-C(26)-H(26)	120.8
C(25)-C(26)-H(26)	120.8
C(26)-C(27)-C(28)	122.30(18)
C(26)-C(27)-H(27)	118.8
C(28)-C(27)-H(27)	118.8
C(27)-C(28)-C(23)	119.05(16)
C(27)-C(28)-H(28)	120.5
C(23)-C(28)-H(28)	120.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for mo_20141115A_0m.
The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	34(1)	46(1)	36(1)	-2(1)	5(1)	7(1)
N(2)	53(1)	41(1)	43(1)	6(1)	19(1)	6(1)
C(1)	45(1)	46(1)	41(1)	-3(1)	4(1)	1(1)
C(2)	44(1)	59(1)	45(1)	3(1)	1(1)	-1(1)
C(3)	40(1)	71(1)	39(1)	-7(1)	4(1)	-11(1)
C(4)	47(1)	60(1)	53(1)	-19(1)	12(1)	-7(1)
C(5)	43(1)	51(1)	48(1)	-6(1)	8(1)	1(1)
C(6)	34(1)	47(1)	37(1)	-3(1)	10(1)	-5(1)
C(7)	37(1)	44(1)	36(1)	-3(1)	9(1)	1(1)
C(8)	39(1)	44(1)	37(1)	2(1)	12(1)	2(1)
C(9)	36(1)	46(1)	36(1)	0(1)	9(1)	1(1)
C(10)	33(1)	44(1)	35(1)	-2(1)	7(1)	-1(1)
C(11)	30(1)	41(1)	38(1)	-3(1)	8(1)	-3(1)
C(12)	36(1)	48(1)	42(1)	-1(1)	5(1)	0(1)
C(13)	43(1)	46(1)	66(1)	-9(1)	14(1)	5(1)
C(14)	51(1)	60(1)	52(1)	-18(1)	19(1)	-2(1)
C(15)	51(1)	64(1)	38(1)	-6(1)	13(1)	-2(1)
C(16)	43(1)	47(1)	40(1)	1(1)	10(1)	2(1)
C(17)	38(1)	45(1)	34(1)	-2(1)	11(1)	4(1)
C(18)	43(1)	47(1)	47(1)	3(1)	7(1)	1(1)
C(19)	61(1)	61(1)	48(1)	4(1)	3(1)	19(1)
C(20)	40(1)	80(1)	50(1)	-14(1)	2(1)	10(1)
C(21)	39(1)	73(1)	55(1)	-10(1)	7(1)	-8(1)
C(22)	47(1)	58(1)	48(1)	0(1)	11(1)	-2(1)
C(23)	34(1)	46(1)	33(1)	-6(1)	5(1)	-4(1)
C(24)	47(1)	45(1)	43(1)	-2(1)	9(1)	5(1)
C(25)	49(1)	71(1)	57(1)	-12(1)	18(1)	6(1)
C(26)	54(1)	87(2)	54(1)	-9(1)	25(1)	-7(1)
C(27)	53(1)	65(1)	46(1)	2(1)	18(1)	-10(1)
C(28)	43(1)	47(1)	40(1)	0(1)	9(1)	0(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for mo_20141115A_0m.

	x	y	z	U(eq)
H(1A)	1924	1788	1348	48
H(2A)	1167	8655	1202	54
H(1)	2203	1896	2455	56
H(2)	2584	2523	3598	63
H(3)	2527	5870	4187	62
H(4)	2097	8644	3613	65
H(5)	1714	8048	2471	58
H(12)	1801	-1560	699	52
H(13)	1880	-4008	-151	63
H(14)	1604	-3173	-1337	65
H(15)	1253	155	-1663	61
H(16)	1188	2688	-822	53
H(18)	901	7656	-298	57
H(19)	313	8227	-1096	72
H(20)	-144	5371	-1252	72
H(21)	4	2008	-605	69
H(22)	592	1433	180	62
H(24)	687	10427	1559	56
H(25)	340	10425	2319	71
H(26)	364	7346	3065	76
H(27)	740	4249	3045	65
H(28)	1092	4139	2293	53

Table S6. Torsion angles [deg] for mo_20141115A_0m.

C(6)-C(1)-C(2)-C(3)	0.0(3)
C(1)-C(2)-C(3)-C(4)	-1.0(3)
C(2)-C(3)-C(4)-C(5)	0.9(3)
C(3)-C(4)-C(5)-C(6)	0.0(3)
C(4)-C(5)-C(6)-C(1)	-0.9(2)
C(4)-C(5)-C(6)-C(7)	177.50(16)
C(2)-C(1)-C(6)-C(5)	0.9(2)
C(2)-C(1)-C(6)-C(7)	-177.53(15)
C(10)-N(1)-C(7)-C(8)	0.03(18)
C(10)-N(1)-C(7)-C(6)	176.95(14)
C(5)-C(6)-C(7)-N(1)	167.34(15)
C(1)-C(6)-C(7)-N(1)	-14.3(2)
C(5)-C(6)-C(7)-C(8)	-16.7(3)
C(1)-C(6)-C(7)-C(8)	161.67(17)
N(1)-C(7)-C(8)-N(2)	-176.40(14)
C(6)-C(7)-C(8)-N(2)	7.2(3)
N(1)-C(7)-C(8)-C(9)	1.44(18)
C(6)-C(7)-C(8)-C(9)	-174.94(16)
C(23)-N(2)-C(8)-C(7)	-81.0(2)
C(23)-N(2)-C(8)-C(9)	101.46(19)
C(7)-C(8)-C(9)-C(10)	-2.38(18)
N(2)-C(8)-C(9)-C(10)	175.54(14)
C(7)-C(8)-C(9)-C(17)	173.54(15)
N(2)-C(8)-C(9)-C(17)	-8.5(2)
C(7)-N(1)-C(10)-C(9)	-1.52(18)
C(7)-N(1)-C(10)-C(11)	173.49(14)
C(8)-C(9)-C(10)-N(1)	2.34(17)
C(17)-C(9)-C(10)-N(1)	-173.38(15)
C(8)-C(9)-C(10)-C(11)	-171.86(16)
C(17)-C(9)-C(10)-C(11)	12.4(3)
N(1)-C(10)-C(11)-C(16)	-148.39(15)
C(9)-C(10)-C(11)-C(16)	25.2(3)
N(1)-C(10)-C(11)-C(12)	30.1(2)
C(9)-C(10)-C(11)-C(12)	-156.33(17)
C(16)-C(11)-C(12)-C(13)	0.8(2)
C(10)-C(11)-C(12)-C(13)	-177.76(15)
C(11)-C(12)-C(13)-C(14)	-1.2(3)
C(12)-C(13)-C(14)-C(15)	0.4(3)
C(13)-C(14)-C(15)-C(16)	0.8(3)
C(14)-C(15)-C(16)-C(11)	-1.2(3)
C(12)-C(11)-C(16)-C(15)	0.4(2)
C(10)-C(11)-C(16)-C(15)	178.92(15)

C(10)-C(9)-C(17)-C(22)	64.6(2)
C(8)-C(9)-C(17)-C(22)	-110.44(19)
C(10)-C(9)-C(17)-C(18)	-117.64(19)
C(8)-C(9)-C(17)-C(18)	67.3(2)
C(22)-C(17)-C(18)-C(19)	0.4(3)
C(9)-C(17)-C(18)-C(19)	-177.46(16)
C(17)-C(18)-C(19)-C(20)	0.1(3)
C(18)-C(19)-C(20)-C(21)	-0.2(3)
C(19)-C(20)-C(21)-C(22)	-0.2(3)
C(18)-C(17)-C(22)-C(21)	-0.7(3)
C(9)-C(17)-C(22)-C(21)	177.16(16)
C(20)-C(21)-C(22)-C(17)	0.6(3)
C(8)-N(2)-C(23)-C(24)	-166.24(15)
C(8)-N(2)-C(23)-C(28)	15.6(2)
N(2)-C(23)-C(24)-C(25)	-178.38(15)
C(28)-C(23)-C(24)-C(25)	-0.1(2)
C(23)-C(24)-C(25)-C(26)	0.1(3)
C(24)-C(25)-C(26)-C(27)	0.0(3)
C(25)-C(26)-C(27)-C(28)	-0.2(3)
C(26)-C(27)-C(28)-C(23)	0.2(3)
N(2)-C(23)-C(28)-C(27)	178.19(15)
C(24)-C(23)-C(28)-C(27)	0.0(2)

Symmetry transformations used to generate equivalent atoms:

(E) References

1 (*a*) P. C. Too, Y.-F. Wang and S. Chiba, Rhodium(III)-Catalyzed Synthesis of Isoquinolines from Aryl Ketone *O*-Acyloxime Derivatives and Internal Alkynes, *Org. Lett.*, 2010, **12**, 5688-5691; (*b*) Y. Wei and N. Yoshikai, Modular Pyridine Synthesis from Oximes and Enals through Synergistic Copper/Iminium Catalysis, *J. Am. Chem. Soc.*, 2013, **135**, 3756-3759; (c) H.-B. Yang and N. Selander, Divergent Iron-Catalyzed Couplings of *O*-Acyloximes with Silyl Enol Ethers, *Chem. Eur. J.*, 2017, 23, 1779-1783; (d) W. Du, M.-N. Zhao, Z.-H. Ren, Y.-Y. Wang and Z.-H, Guan, Copper-catalyzed 5-*endo*-*trig* cyclization of ketoxime carboxylates: a facile synthesis of 2-arylpyrroles, *Chem. Commun*., 2014, **50**, 7437-7439.

2 (*a*) F. J. Lakner, M. A. Parker, B. Rogovoy, A. Khvat and A. Ivachtchenko, Synthesis of Novel Trisubstituted Imidazolines, *Synthesis*, 2009, **12**, 1987-1990; (*b*) M. Pal, N. K. Swamy, P. S. Hameed, S. Padakanti and K. R. Yeleswarapu, A rapid and direct access to symmetrical/unsymmetrical 3,4-diarylmaleimides and pyrrolin-2-ones, *Tetrahedron*, 2004, **60**, 3987-3997; (*c*) J.-C. Wu, R.-J. Song, Z.-Q. Wang, X.-C. Huang, Y.-X. Xie and J.-H. Li, Copper-Catalyzed C-H Oxidation/Cross-Coupling of *α*-Amino Carbonyl Compounds, *Angew. Chem., Int. Ed*., 2012, **51**, 3453-3457.

3 S. Mahato, S. Santra, G. V. Zyryanov and A. Majee, Metal-Free Amidation Reactions of Terminal Alkynes with Benzenesulfonamide, *J. Org. Chem*., 2019, **84**, 3176-3183.

4 X.-J. Tang, Z.-L. Yan, W.-L. Chen, Y.-R. Gao, S. Mao, Y.-L. Zhang and Y.-Q. Wang, Aza-Michael reaction promoted by aqueous sodium carbonate solution, *Tetrahedron Lett.*, 2013, **54**, 2669-2673.

5 W. E. Almaraz-Ortiz, A. R. Orea, O. Casadiego-Díaz, A. Reyes-Salgado, A. Mejía-Galindo and R. O. Torres-Ochoa, Divergent copper-catalyzed syntheses of 3-carboxylpyrroles and 3-cyanofurans from *O*-acetyl oximes and *β*-ketoesters/nitriles, *RSC Adv*., 2022, **12**, 26673-26679.

6 G. E. Veitch, K. L. Bridgwood, K. Rands-Trevor and S. V. Ley, Magnesium Nitride as a Convenient Source of Ammonia: Preparation of Pyrroles, *Synlett*, 2008, 2597-2600.