Pd-Catalyzed [3+2] Cycloaddition of Ketoimines with Alkynes *via* Directed sp^3 C-H Bond Activations

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Supporting Information

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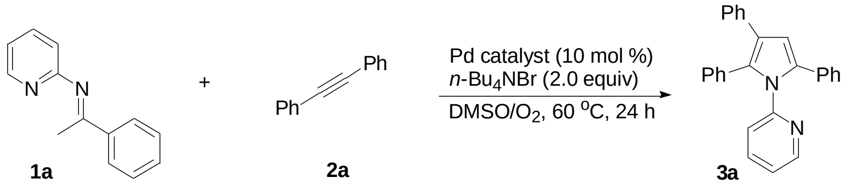
1. General experimental information

1.1. General methods

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or Strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (40-63 mm). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

1.1. Table 1. Catalyst screening for Pd(II)-catalyzed cycloaddition of ketoimine 1a with alkyne 2a [a]

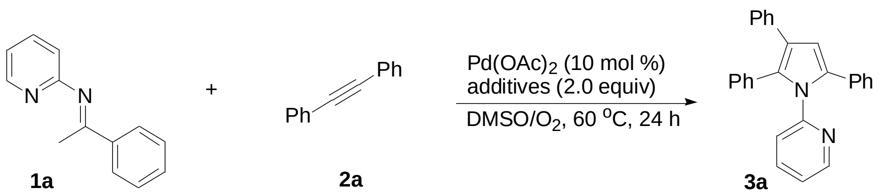


Entry	Catalyst	Yield (%) [b]
1	$PdCl_2$	N.R.
2	$PdCl_2(CH_3CN)_2$	Trace
3	$PdCl_2(PPh_3)_2$	13
4	$Pd(TFA)_2$	16

5	$Pd(OAc)_2$	59

[a] The reactions were carried out using ketoimine **1a** (0.1 mmol) and alkyne **2a** (0.1 mmol) with *n*-Bu_4NBr (0.2 mmol) in solvent DMSO (1.0 mL) in the presence of Pd catalyst (10 mol %) in a sealed pressure tube at 60 ℃ for 24 h under O_2, followed by flash chromatography on SiO_2. [b] Isolated yield.

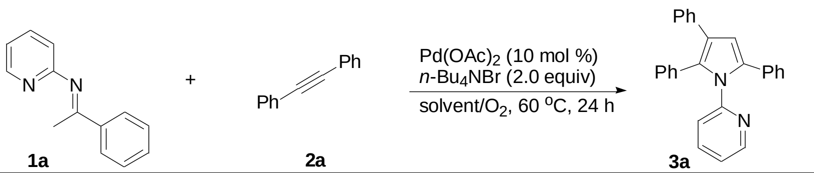
1.2. Table 2. The effect the additives on the Pd(II)-catalyzed cycloaddition of ketoimine 1a with alkyne 2a [a]



Entry	Additive	Yield (%) [b]
1	*n*-Bu_4NI	27
2	*n*-Bu_4NCl	48
3	*n*-Bu_4NBr	59

[a] The reactions were carried out using ketoimine **1a** (0.1 mmol) and alkyne **2a** (0.1 mmol) with additives (0.2 mmol) in solvent DMSO (1.0 mL) in the presence of $Pd(OAc)_2$ (10 mol %) in a sealed pressure tube at 60 ℃ for 24 h under O_2, followed by flash chromatography on SiO_2. [b] Isolated yield.

1.3. Table 3. The Effect of the solvent on the Pd(II)-catalyzed cycloaddition of ketoimine 1a with alkyne 2a [a]

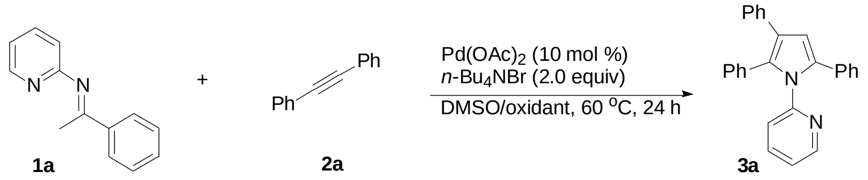


Entry	Solvent	Yield (%) [b]
1	DCE	16
2	CH_3NO_2	21
3	1,4-Dioxane	24
4	CH_3CN	32
5	Toluene	38
6	DMF	54
7	DMSO	59

[a] The reactions were carried out using ketoimine **1a** (0.1 mmol) and alkyne **2a** (0.1 mmol) with *n*-Bu_4NBr (0.2 mmol) in solvent (1.0 mL) in the presence of $Pd(OAc)_2$ (10 mol %) in a sealed pressure tube at 60 ℃ for 24 h under O_2, followed by flash chromatography on SiO_2. [b] Isolated

yield.

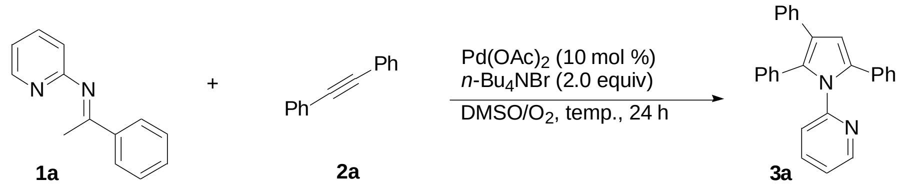
1.4. Table 4.The Effect of the oxidant on the cycloaddition of ketoimine 1a with alkyne 2a [a]



Entry	Oxidant	Yield (%) [b]
1	$Cu(OAc)_2$	10
2	AgOAc	13
3	$PhI(OAc)_2$	21
4	Air	38
5	DDQ	56
6	O_2	59

[a] The reactions were carried out using ketoimine **1a** (0.1 mmol), alkyne **2a** (0.1 mmol), oxidants (2.0 equiv.) with *n*-Bu_4NBr (0.2 mmol) in solvent DMSO (1.0 mL) in the presence of $Pd(OAc)_2$ (10 mol %) in a sealed pressure tube at 60 ℃ for 24 h, followed by flash chromatography on SiO_2. [b] Isolated yield.

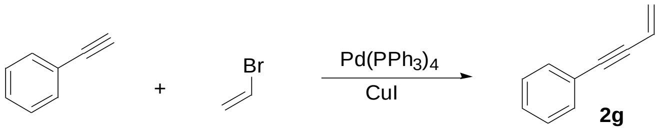
1.5. Table 5. The effect of the reaction temperature on the cycloaddition of ketoimine 1a with alkyne 2a [a]



Entry	Temp. (℃)	Yield (%) [b]
1	60	59
2	80	83
3	100	91
4	120	78

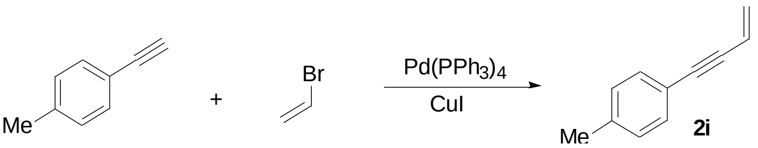
[a] The reactions were carried out using ketoimine **1a** (0.1 mmol) and alkyne **2a** (0.1 mmol) with *n*-Bu_4NBr (0.2 mmol) in solvent DMSO (1.0 mL) in the presence of $Pd(OAc)_2$ (10 mol %) in a sealed pressure tube at the given temperature for 24 h under O_2, followed by flash chromatography on SiO_2. [b] Isolated yield.

1.6. Procedures for synthesis of alkyne derivatives (2g, 2h, 2i)



But-3-en-1-ynyl-benzene (2g) [1]: To a stirred solution of vinyl bromide (1.0 M solution in THF, 15 mL, 15.0 mmol), $Pd(PPh_3)_4$ (173 mg, 0.15 mmol), CuI (76 mg, 0.4 mmol), and triethylamine (2.0 mg, 20.0 mmol) was added a solution of phenylacetylene (1.0 g, 10.0 mmol) in THF (5 mL) via a syringe pump for 1h, the reaction mixture was stirred at room temperature for 3 h and then it was filtered through celite. The filtrate was evaporated under reduced pressure and the resulting was subjected to column chromatography on silica gel with petroleum ether to yield 1.0 g of **2g** (78％ yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.44 (d, J = 2.3 Hz, 2H), 7.31 (d, J = 2.3 Hz, 2H), 6.02 (dd, J = 17.5, 11.1 Hz, 1H), 5.73 (d, J = 17.5 Hz, 1H), 5.54 (d, J = 11.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.59, 128.34, 128.32, 126.95, 123.14, 117.21, 89.99, 88.10.

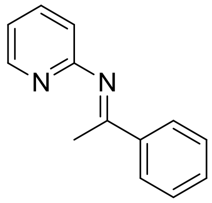
1, 4-Diphenylbuta-1, 3-diyne (2h) [2]: The mixture of ethynylbenzene (400 mg, 2 mmol), CuCl (2.0 mg, 10 mol ％) in DMSO (1 mL) was stirred at room temperature for 16 h. Then the reaction mixture was extracted with CH_2Cl_2, the corresponding combined organic layers were dried and concentrated. The resulting was subjected to column chromatography on silica gel with petroleum ether as eluent to yield 190 mg of **2h** (95％ yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.56 (d, J = 7.6 Hz, 4H), 7.39 (q, J = 6.7 Hz, 6H).



1-But-3-en-1-ynyl-4-methylbenzene (2i) [1]: The synthetic procedure of **2i** is the same as **2g**. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.33 (d, J = 8.1 Hz, 2H), 7.08 (dd, J = 20.2, 8.2 Hz, 2H), 6.00 (dd, J = 17.5, 11.1 Hz, 1H), 5.76 – 5.63 (m, 1H), 5.50 (dd, J = 11.1, 2.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.44, 131.50, 129.11, 126.47, 120.11, 117.36, 90.22, 87.52, 21.49.

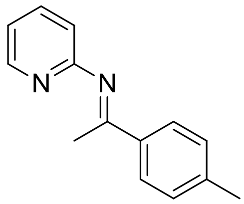
1.7. General procedure for synthesis of ketoimines (1a-1t)

The mixture of acetophenone derivatives (0.1 mmol, 1.0 equiv.) and substituted 2-aminopyridine (0.1 mmol, 1.0 equiv.) was stirred in toluene (3.0 mL) at 120 ℃ in the presence of molecular sieve (4Å) (0.40 g) and a catalytic amount of concentrated H_2SO_4 (10 mol %) for 24 h. The mixture was then filtered and the solvent was removed under reduced pressure to produce crude ketoimines, except that ketoimines **1a**, **1b**, **1c**, **1e**, **1f, 1h** and **1t** could be purified by flash chromatography to get pure starting material, the other crude ketoimines including **1d**, **1g**, **1i-1s** could be directly used for synthetic purpose without further purification because these ketoimine compounds are easily decomposed on silica gel. [3]



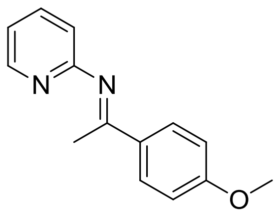
1a

(*E*)-*N*-(1-phenylethylidene)pyridin-2-amine (1a)[1]**:** oil; 15 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.5 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.03 – 6.97 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.69, 163.53, 148.86, 139.04, 137.70, 130.89, 128.33, 127.45, 118.85, 115.19, 18.15. MS (ESI): m/z = 196.09 [M^+]. IR (KBr): 2917, 2850, 1609, 1555, 987, 784 cm $^{-1}$.



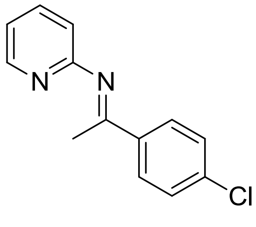
1b

(*E*)-*N*-(1-(p-tolyl)ethylidene)pyridin-2-amine (1b): white solid; 15 mg, 71% yield; m.p. 81-82.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.0 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.69 – 7.62 (m, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.04 – 6.97 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.48, 163.67, 148.84, 141.22, 137.65, 136.36, 129.04, 127.46, 118.71, 115.25, 21.41, 18.07. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{14}H_{15}N_2$: 211.1230, found: 211.1229; IR (KBr): 2920, 2850, 1639, 1555, 987, 784 cm $^{-1}$.



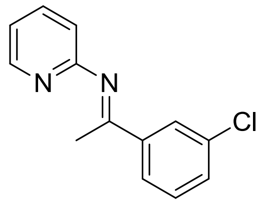
1c

(*E*)-*N*-(1-(4-methoxyphenyl)ethylidene)pyridin-2-amine (1c): oil; 14 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.1 Hz, 1H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.66 (td, *J* = 7.8, 1.8 Hz, 1H), 6.99 (dd, *J* = 6.9, 5.4 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.66, 163.73, 161.88, 148.83, 137.63, 131.70, 129.21, 118.62, 115.33, 113.57, 55.36, 17.91. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{14}H_{15}N_2O$: 227.1179, found: 227.1178; IR (KBr): 3077, 2962, 2837, 1635, 1583, 1462, 1234, 1114, 812 cm $^{-1}$.



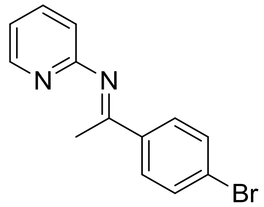
1e

(***E***)-***N*-(1-(4-chlorophenyl)ethylidene)pyridin-2-amine (1e):** oil; 18 mg, 78% yield; m.p. 91-93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.1 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.69 (td, *J* = 7.5, 1.4 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.62, 163.20, 148.90, 137.90, 137.75, 131.54, 129.06, 125.62, 119.03, 115.15, 17.98. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{13}H_{12}ClN_2$: 231.0684, found: 231.0682; IR (KBr): 3081, 3050, 1489, 1277, 1260, 799, 766 cm^{-1}.



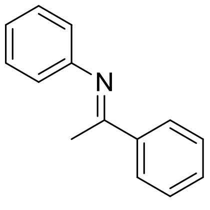
1f

(***E***)-***N*-(1-(3-chlorophenyl)ethylidene)pyridin-2-amine (1f):** oil; 15 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.7 Hz, 1H), 8.02 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.48, 163.04, 148.89, 140.78, 137.81, 134.57, 130.85, 129.60, 127.64, 125.61, 119.14, 115.16, 18.14. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{13}H_{12}ClN_2$: 231.0684, found: 231.0683; IR (KBr): 3067, 3004, 1688，1586，1425，1366，1235，815，789 cm^{-1}.



1h

(***E***)-***N*-(1-(4-bromophenyl)ethylidene)pyridin-2-amine (1h):** oil; 20 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.7 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.03 (t, *J* = 5.8 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.48, 163.22, 148.90, 137.75, 137.45, 137.10, 128.84, 128.56, 119.01, 115.17, 18.01. HR-MS (ESI) calcd for $[M]^+$: $C_{13}H_{12}BrN_2$: 275.0178, found: 275.0177; IR (KBr): 1277, 1260, 1053, 1032, 1010, 766, 748 cm^{-1}.

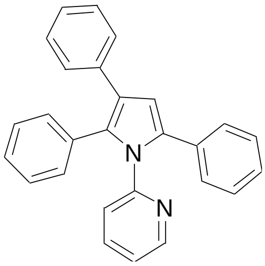


1t

(***E***)-***N*-(1-phenylethylidene)aniline (1t)**[5]**:** oil; 16 mg, 82％ yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 5.6 Hz, 3H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.47, 151.77, 139.56, 130.49, 128.99, 128.56, 128.40, 127.22, 123.25, 119.41, 17.39. MS (ESI): m/z = 195.06 [M^+].

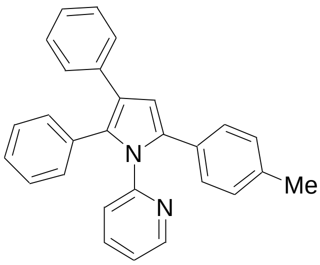
1.8 General procedure for synthesis of pyrrole derivatives **3a-3za**

To the solution of ketoimines **1** (0.1 mmol) in dry DMSO (1.0 mL) were added alkynes **2** (0.1 mmol), $Pd(OAc)_2$ (2.0 mg, 10 mol ％) and Bu_4NBr (65 mg, 0.2 mmol) under O_2 atmosphere, and then the corresponding reaction mixture was stirred in a sealed tube at 100 ℃ for 24 h. After the starting materials were disappeared, then cooled down to room temperature and added 1mL of H_2O, then extracted with CH_2Cl_2 (3×10 mL). The corresponding combined organic layers were dried over Na_2SO_4 and concentrated under vacuum, and the resulting crude products were purified by flash chromatography on silical gel using 10％ (v/v) ethyl acetate in petroleum ether as eluent to afford the desired pyrroles **3**.



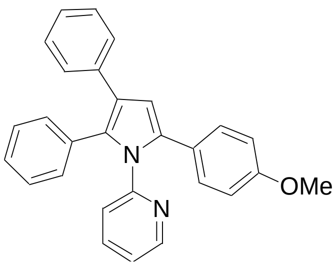
3a

2-（2, 3, 5-Triphenyl-pryyol-1-yl）-pyridine (3a): White solid; 34.0 mg, 91% yield; m.p. 211-213 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.37 (d, *J* = 4.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.27 (s, 1H), 7.23 – 7.10 (m, 15H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 152.22, 148.83, 137.42, 136.10, 135.11, 132.97, 132.61, 132.29, 131.29, 128.34, 128.33, 128.15, 128.09, 127.91, 127.03, 126.47, 125.63, 123.98, 122.53, 110.66. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{21}N_2$: 373.1699, found: 373.1719; IR (KBr): 3057, 2922, 2373, 1660, 1468, 759, 698 cm^{-1}.



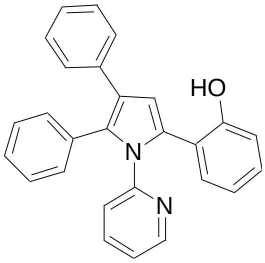
3b

2-(2, 3-Diphenyl-5-*p*-tolyl-pyrrol-1-yl)-pyridine (3b): White solid; 36 mg, 93% yield; m.p. 193-194.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.30 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.41 (td, *J* = 7.7, 1.9 Hz, 1H), 7.18 (t, *J* = 6.9 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.04 (dt, *J* = 10.3, 3.6 Hz, 7H), 6.94 (dd, *J* = 18.3, 8.2 Hz, 4H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.58 (s, 1H), 2.20 (s, 3H). HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{23}N_2$: 387.1856, found: 387.1856; IR (KBr): 3483, 3414, 2919, 2850, 2028, 1640, 1103, 617 cm^{-1}.



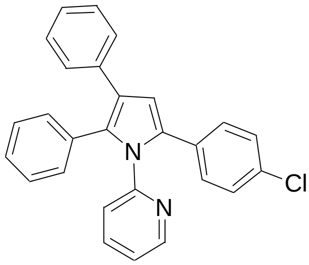
3c

2-[5-(4-Methoxyl-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine (3c): White solid; 38 mg, 93% yield; m.p. 164.5-166 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.50 (td, *J* = 7.7, 1.9 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.15 – 7.05 (m, 9H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 2H), 6.61 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.36, 152.28, 148.80, 137.37, 136.19, 134.95, 132.68, 131.67, 131.22, 129.67, 128.31, 128.11, 127.87, 126.89, 125.61, 125.54, 124.02, 123.79, 122.44, 113.57, 109.90, 55.18. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{23}N_2O$: 403.1805, found: 403.1808; IR (KBr): 3743, 3056, 2920, 2844, 1583, 1469, 1246, 765, 698 cm^{-1}.



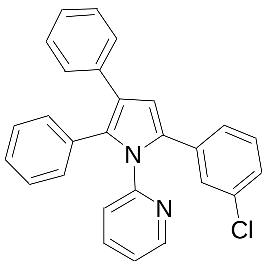
3d

2-(4, 5-Dipheynl-1-pyridin-2-yl-1*H*-pyrrol-2-yl)-phenol (3d): White solid; 17 mg, 44% yield; m.p. 201-213 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 9.54 (s, 1H), 8.39 (d, *J* = 4.5 Hz, 1H), 7.44 (td, *J* = 7.8, 1.6 Hz, 1H), 7.28 – 7.01 (m, 14H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.32, 151.81, 147.35, 138.25, 135.75, 132.56, 132.24, 132.00, 131.52, 130.83, 129.97, 128.37, 128.21, 128.18, 127.12, 125.84, 124.85, 123.59, 122.71, 122.44, 120.36, 118.85, 113.13. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{21}N_2O$: 389.1648, found: 389.1644; IR (KBr): 3667, 3644, 2986, 2918, 2849, 1767, 1594, 1258, 698 cm^{-1}.



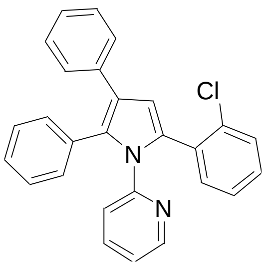
3e

2-[5-(4-Chloro-phenyl-2,3-diphenyl-2,3-diphenyl-pyrrol-1-yl)-pyridine (3e): White solid; 32 mg, 78% yield; m.p. 206.8-208 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.52 (td, *J* = 7.7, 1.9 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.26 – 7.07 (m, 11H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.96, 148.93, 137.57, 135.82, 133.87, 132.72, 132.34, 131.92, 131.23, 129.71, 128.27, 128.16, 127.94, 127.17, 125.73, 124.13, 123.89, 122.71, 120.51, 110.93. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}ClN_2$: 407.1310, found: 407.1310; IR IR (KBr): 3743, 3056, 2920, 2844, 1267, 756 cm^{-1}.



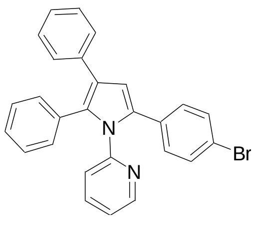
3f

2-[5-(3-Chloro-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine (3f): White solid; 24 mg, 59% yield; m.p. 199.3-210.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 4.7, 1.2 Hz, 1H), 7.53 (td, *J* = 7.7, 1.8 Hz, 1H), 7.28 – 7.06 (m, 14H), 7.00 – 6.95 (m, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.89, 148.92, 137.58, 135.78, 134.69, 133.95, 133.60, 132.88, 132.30, 131.25, 129.22, 128.26, 128.19, 128.17, 127.96, 127.22, 126.41, 126.22, 125.75, 124.13, 123.89, 122.76, 111.25. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}ClN_2$: 407.1310, found: 407.1314; IR (KBr): 3667, 3644, 2986, 2849, 2354, 2315, 1767, 1594, 1258, 764 cm^{-1}.



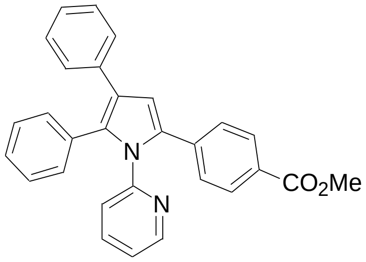
3g

2-[5-(2-Chloro-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine (3g): White solid; 22 mg, 54% yield; m.p. 188-189.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.22 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.41 (td, *J* = 7.8, 1.9 Hz, 1H), 7.31 – 7.25 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.09 (m, 8H), 7.04 – 6.96 (m, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.82, 148.39, 136.98, 136.08, 134.25, 133.00, 132.63, 132.48, 131.49, 131.15, 131.10, 129.39, 128.67, 128.41, 128.12, 127.99, 127.00, 126.15, 125.60, 123.63, 123.26, 121.94, 112.49. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}ClN_2$: 407.1310, found: 407.1310; IR (KBr): 3479, 3417, 2026, 1640, 1103, 764, 618 cm^{-1}.



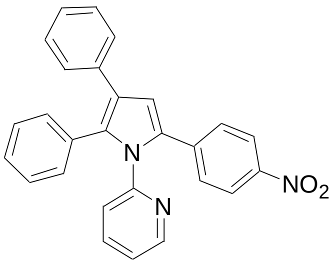
3h

2-[5-(2-Bromo-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine (3h): White solid; 38 mg, 84% yield; m.p. 187.2-189 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.39 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.51 (td, *J* = 7.7, 1.9 Hz, 1H), 7.26 – 7.05 (m, 15H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.98, 148.93, 137.56, 135.85, 133.88, 132.65, 132.36, 131.48, 131.24, 129.43, 128.30, 128.29, 128.17, 127.95, 127.17, 125.73, 124.10, 123.90, 122.70, 110.91. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}BrN_2$: 451.0804, found: 451.0805; IR (KBr): 3479, 3417, 1473, 1267, 756 cm $^{-1}$.



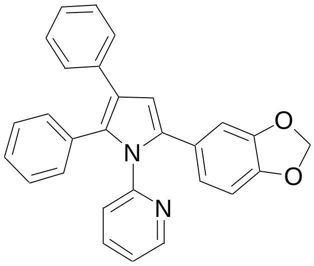
3i

4-(4, 5-Diphenyl-1-pyridin-2yl-1H-pyrrol-2-yl)-benzoic acid methyl ester (3i): White solid; 30 mg, 70% yield; m.p. 195.2-197.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.39 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.52 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29 – 7.08 (m, 13H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.81 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.97, 151.94, 148.98, 137.64, 137.37, 135.68, 133.94, 133.53, 132.19, 131.26, 129.46, 128.27, 128.19, 127.98, 127.62, 127.32, 125.82, 124.41, 123.84, 122.82, 111.92, 52.01. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{29}H_{23}N_2O_2$: 431.1754, found: 431.1750; IR (KBr): 3479, 2921, 2850, 1717, 1603, 1469, 1276, 1183, 1110, 811, 759 cm $^{-1}$.



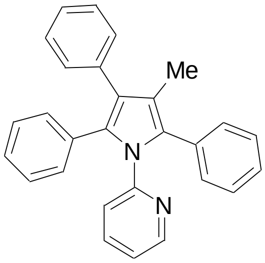
3j

2-[5-(4-Nitro-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine (3j): White solid; 28 mg, 67% yield; m.p. 187.5-189 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.43 (dd, *J* = 4.8, 1.1 Hz, 1H), 8.04 (d, *J* = 8.9 Hz, 2H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.26 – 7.08 (m, 13H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.66, 149.15, 145.72, 139.32, 137.89, 135.28, 134.70, 132.76, 131.80, 131.22, 128.27, 128.25, 128.08, 127.84, 127.63, 126.06, 124.85, 123.76, 123.60, 123.15, 113.11. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}N_3O_2$: 418.1550, found: 418.1550; IR (KBr): 1632, 1514, 1335, 1267, 756 cm $^{-1}$.



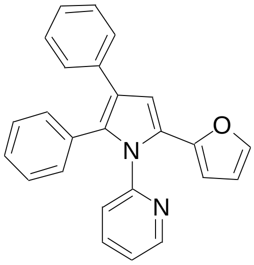
3k

2-(5-Benzo [1, 3] dioxol-5-yl-2, 3-diphenyl-pyrrol-1-yl)-pyridine (3k): White solid; 38 mg, 91% yield; m.p. 181-183 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.39 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.51 (td, *J* = 7.7, 1.9 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.20 (dd, *J* = 10.1, 4.8 Hz, 2H), 7.16 – 7.05 (m, 7H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.65 (s, 3H), 6.60 (s, 1H), 5.94 – 5.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.16, 148.84, 147.32, 146.39, 137.43, 136.07, 134.85, 132.59, 131.88, 131.24, 128.29, 128.13, 127.88, 127.04, 126.97, 125.59, 123.98, 123.77, 122.55, 122.24, 110.24, 109.06, 108.07, 100.93. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{21}N_2O_2$: 417.1598, found: 417.1597; IR (KBr): 3450, 2922, 2854, 1637, 1474, 1269, 1038, 755, 697 cm $^{-1}$.



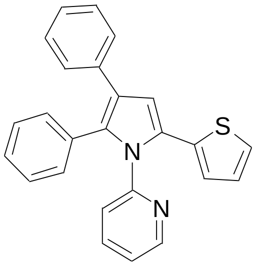
3l

2-(3-Methyl-2, 4, 5-triphenyl-pyrrol-1-yl)-pyridine (3l): White solid; 20 mg, 52% yield; m.p. 124-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.30 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.43 (tt, *J* = 5.3, 2.6 Hz, 1H), 7.27 – 7.14 (m, 10H), 7.04 – 6.97 (m, 6H), 6.88 (d, *J* = 7.9 Hz, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.45, 148.58, 137.11, 136.03, 132.85, 132.44, 131.94, 131.64, 130.91, 130.70, 130.52, 127.87, 127.75, 127.50, 126.43, 126.26, 125.76, 124.91, 123.82, 121.98, 117.41, 10.82. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{23}N_2$: 387.1856, found: 387.1866; IR (KBr): 3479, 3416, 2026, 1640, 1617, 1133, 1104, 767, 618 cm $^{-1}$.



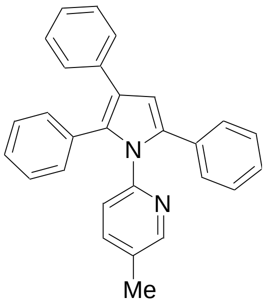
3m

2-(5-Furan-2-yl-2, 3-diphenyl-pyrrol-1-yl)-pyridine (3m): White solid; 17 mg, 47% yield; m.p. 150.5-151.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.54 – 8.50 (m, 1H), 7.58 (tt, *J* = 5.4, 2.7 Hz, 1H), 7.29 – 7.08 (m, 12H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.87 (s, 1H), 6.23 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.57 – 5.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.09, 148.91, 147.15, 141.13, 137.76, 135.83, 132.42, 132.06, 131.11, 128.29, 128.15, 127.97, 127.15, 126.21, 125.72, 124.01, 123.98, 123.29, 110.90, 109.66, 105.65. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{25}H_{19}N_2O$: 363.1492, found: 363.1498; IR (KBr): 3057, 2990, 2918, 2849, 1584, 1270, 758 cm $^{-1}$.



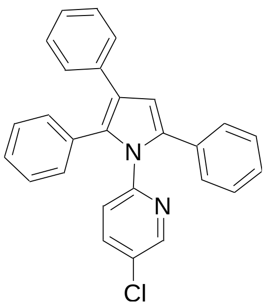
3n

2-(2, 3-Diphenyl-5-thiophen-2-yl-pyrrol-1-yl)-pyridine (3n): White solid; 21 mg, 56% yield; m.p. 171-173.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.51 – 8.47 (m, 1H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.27 (t, *J* = 1.8 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.16 – 7.09 (m, 8H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.84 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.75 (s, 1H), 6.61 (dd, *J* = 3.6, 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.83, 148.95, 137.67, 135.79, 134.72, 132.54, 132.20, 131.09, 128.52, 128.30, 128.16, 127.94, 127.10, 126.98, 125.72, 125.04, 124.42, 123.92, 123.25, 110.96. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{25}H_{19}N_2S$: 379.1264, found: 379.1264; IR (KBr): 3796, 3667, 3644, 2917, 2847, 2353, 1573, 1464, 1260, 748 cm $^{-1}$.



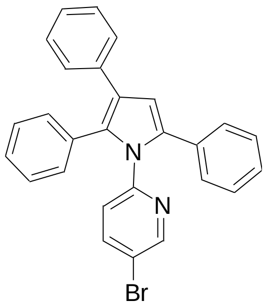
3o

5-Methyl-2-(2, 3, 5-triphenyl-pyrrol-1-yl)-pyridine (3o): White solid; 32 mg, 82% yield; m.p. 218-219.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.29 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.22 – 7.18 (m, 3H), 7.17 – 7.09 (m, 10H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.82, 149.03, 138.02, 136.19, 135.11, 133.05, 132.67, 132.33, 132.25, 131.29, 128.31, 128.12, 128.05, 127.87, 126.94, 126.37, 125.55, 123.86, 123.30, 110.49, 18.05. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{23}N_2$: 387.1856, found: 387.1851; IR (KBr): 2919, 2848, 1771, 1596, 1477, 1277, 1025, 911, 751 cm $^{-1}$.



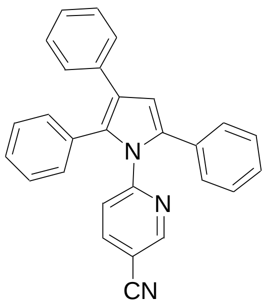
3p

5-Chloro-2-(2, 3, 5-triphenyl-pyrrol-1-yl)-pyridine (3p): White solid; 25 mg, 61% yield; m.p. 215.3-217 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.32 (d, *J* = 2.5 Hz, 1H), 7.46 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.26 – 7.13 (m, 13H), 7.10 (dd, *J* = 7.1, 2.0 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.41, 147.58, 137.17, 135.80, 135.17, 132.70, 132.31, 132.23, 131.26, 130.67, 128.39, 128.27, 128.22, 128.16, 128.07, 127.26, 126.69, 125.75, 124.47, 124.27, 110.98. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}ClN_2$: 407.1310, found: 407.1311; IR (KBr): 3796, 2917, 2847, 2353, 1770, 1464, 1260, 748 cm $^{-1}$.



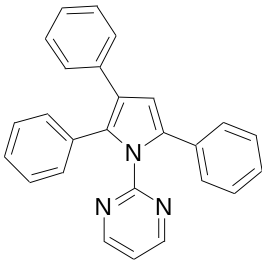
3q

5-Bromo-2-(2, 3, 5-triphenyl-pyrrol-1-yl)-pyridine (3q): White solid; 28 mg, 62% yield; m.p. 223-224.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.08 (m, 15H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.84, 149.85, 140.03, 135.80, 135.13, 132.70, 132.30, 132.18, 131.27, 128.40, 128.28, 128.24, 128.18, 128.09, 127.29, 126.71, 125.76, 124.97, 124.33, 119.17, 111.06. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{20}BrN_2$: 451.0804, found: 451.0804; IR (KBr): 3666, 3307, 2916, 2847, 1568, 1462, 1259, 1067, 747 cm $^{-1}$.



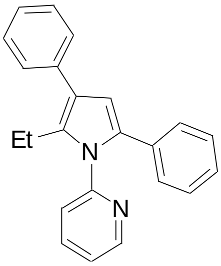
3r

6-(2, 3, 5-Triphenyl-pyrrol-1-yl)-nicotinonitrile (3r): White solid; 16 mg, 40% yield; m.p. 209-211 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.8 Hz, 1H), 7.71 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.24 – 7.15 (m, 11H), 7.12 – 7.06 (m, 4H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.71 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.75, 151.78, 140.28, 135.31, 135.12, 132.40, 132.00, 131.95, 131.23, 128.49, 128.36, 128.26, 128.23, 127.63, 127.06, 126.03, 125.03, 123.47, 116.13, 112.04, 108.02. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{20}N_3$: 398.1652, found: 398.1646; IR (KBr): 3558, 3480, 2919, 2849, 2233, 2026, 1641, 1103, 618 cm $^{-1}$.



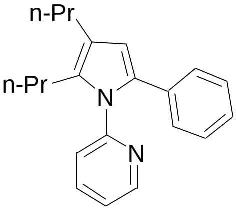
3s

2-(2, 3, 5-Triphenyl-pyrrol-1-yl)-pyrimidine (3s): White solid; 18 mg, 48% yield; m.p. 186.3-188 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.55 (d, *J* = 4.8 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.12 (m, 13H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.55, 158.16, 135.87, 135.36, 133.04, 132.56, 132.43, 130.94, 128.40, 128.18, 128.12, 127.98, 127.90, 127.08, 126.59, 125.76, 124.44, 119.23, 111.38. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{26}H_{20}N_3$: 374.1652, found: 374.1652; IR (KBr): 2958, 2920, 1766, 1563, 1446, 1261, 762, 698 cm^{-1}.



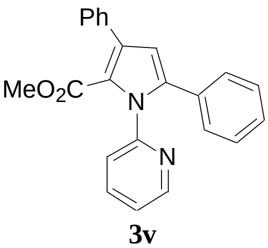
3t

2-(2-Ethyl-3, 5-diphenyl-pyrrol-1-yl)-pyridine (3t): White solid; 26 mg, 80% yield; m.p. 123-125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.33 (ddd, *J* = 4.9, 1.9, 0.7 Hz, 1H), 7.48 (td, *J* = 7.8, 1.9 Hz, 1H), 7.20 – 7.06 (m, 11H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.43, 148.77, 137.29, 134.33, 133.37, 132.82, 132.03, 130.48, 128.20, 127.95, 127.70, 126.44, 126.05, 125.49, 123.58, 122.02, 19.41, 15.68. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{23}H_{21}N_2$: 325.1699, found: 325.1699; IR (KBr): 3481, 3416, 2963, 2926, 1640, 1468, 1103, 750, 698, 617 cm^{-1}.



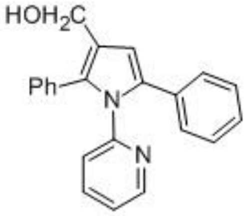
3u

2-(5-Phenyl-2, 3-dipropyl-pyrrol-1-yl)-pyridine (3u): oil; 20 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.58 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.21 (dd, *J* = 7.0, 5.3 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.06 – 7.02 (m, 2H), 7.02 – 6.96 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.26 (s, 1H), 2.61 (t, *J* = 16.5, 8.9 Hz, 2H), 2.49 – 2.40 (t, 2H), 1.65 (q, *J* = 15.1, 7.5 Hz, 2H), 1.29 – 1.20 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.07, 148.93, 137.56, 133.60, 132.75, 132.62, 127.94, 127.69, 125.52, 123.45, 122.08, 121.89, 110.60, 28.27, 26.73, 24.28, 23.51, 14.28, 13.96. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{21}H_{25}N_2$: 305.2071, found: 325.2071; IR (KBr): 3737, 2961, 2927, 1712, 1587, 1516, 1436, 1376, 758, 698 cm^{-1}.



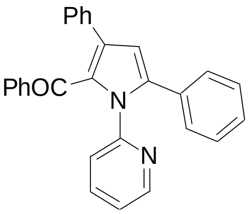
3v

3, 5-Diphenyl-1-pyridin-2-yl-1H-pyrrole-2-carboxylic acid methyl ester (3v): White solid; 25 mg, 71% yield; m.p. 155-157 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.33 (m, 1H), 7.49 (td, *J* = 7.7, 1.9 Hz, 1H), 7.25 – 7.15 (m, 8H), 7.14 – 7.07 (m, 3H), 6.93 (s, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.08, 151.25, 148.93, 139.96, 137.60, 134.90, 132.19, 131.36, 131.14, 128.41, 128.15, 127.89, 127.34, 126.96, 123.78, 123.00, 114.16, 111.10, 51.04. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{23}H_{19}N_2O_2$: 355.1441, found: 355.1449; IR (KBr): 3058, 2950, 2918, 1713, 1587, 1470, 1436, 1227, 1118, 792, 760 cm^{-1}.



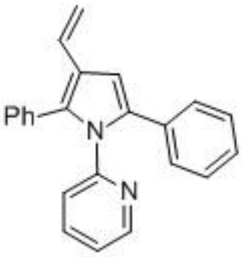
3w

(3, 5-Diphenyl-1-pyridin-2-yl-1H-pyrrol-2-yl)-methanol (3w): White solid; 20 mg, 61% yield; m.p. 181-183 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.37 (d, *J* = 3.7 Hz, 1H), 7.51 (td, *J* = 7.8, 1.7 Hz, 1H), 7.22 – 7.06 (m, 11H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.59 (s, 1H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.05, 148.89, 137.54, 135.05, 133.89, 132.92, 131.61, 130.38, 128.36, 128.05, 127.91, 127.05, 126.46, 123.69, 122.82, 122.48, 110.68, 58.00. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{22}H_{19}N_2O$: 327.1492, found: 327.1497; IR (KBr): 3703, 3668, 2960, 2849, 1711, 1598, 1468, 1262, 752, 712 cm^{-1}.



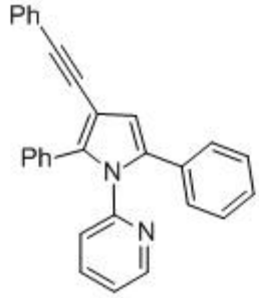
3x

(3, 5-Diphenyl-1-pyridin-2-yl-1H-pyrrol-2-yl)-Phenyl-methanone (3x): White solid; 32 mg, 80% yield; m.p. 161-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.42 (s, 1H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.20 – 7.06 (m, 11H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.25, 151.34, 148.98, 139.71, 139.39, 137.75, 134.99, 132.13, 131.57, 131.23, 131.07, 129.62, 128.52, 128.18, 127.82, 127.67, 127.51, 127.05, 123.92, 123.19, 122.76, 112.56. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{21}N_2O$: 401.1648, found: 401.1654; IR (KBr): 3701, 3670, 3058, 2358, 1766, 1590, 1467, 1276, 897, 757 cm^{-1}



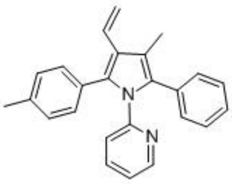
3y

2-(3, 5-Diphenyl-2-vinyl-pyrrol-1-yl)-pyridine (3y): White solid; 22 mg, 68% yield; m.p. 131-133.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.36 (d, *J* = 3.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.10 (m, 11H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.73 (s, 1H), 6.66 – 6.59 (m, 1H), 5.57 (d, *J* = 17.5 Hz, 1H), 5.05 (d, *J* = 11.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.96, 148.84, 137.45, 135.61, 134.16, 132.88, 131.71, 130.81, 129.47, 128.43, 128.02, 127.81, 127.01, 126.57, 123.63, 122.38, 122.09, 110.79, 106.81. HR-MS (ESI) calcd for [M + 1]$^+$: $C_{23}H_{19}N_2$: 323.1543, found: 323.1552; IR (KBr): 3703, 3668, 3306, 3184, 2358, 1766, 1600, 1274, 1020, 753 cm $^{-1}$.



3z

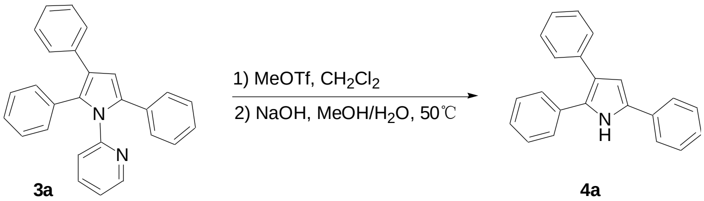
2-(3, 5-Diphenyl-2-phenylethynyl-pyrrol-1-yl)-pyridine (3z): White solid; 17 mg, 43% yield; m.p. 160.2-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.59 (d, *J* = 4.3 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.78 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.16 (m, 10H), 6.73 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.61, 149.06, 137.67, 136.61, 134.80, 132.29, 130.69, 130.64, 128.45, 128.27, 128.25, 128.05, 127.79, 127.11, 126.98, 126.65, 123.48, 122.97, 122.93, 114.55, 109.93, 96.12, 82.62. HR-MS (ESI) calcd for [M + 1]$^+$: $C_{29}H_{21}N_2$: 397.1699, found: 397.1704; IR (KBr): 3482, 3415, 2921, 2850, 2199, 2026, 1640, 1591, 1467, 1101, 758, 693 cm $^{-1}$.



3za

2-(3-Methyl-2-phenyl-4-p-tolyl-5-vinyl-pyrrol-1-yl)-pyridine (3za): White solid; 15 mg, 43% yield; m.p. 142-144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.26 (d, *J* = 4.1 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.24 – 6.98 (m, 10H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 18.0, 11.8 Hz, 1H), 5.44 (d, *J* = 17.9 Hz, 1H), 5.08 (d, *J* = 11.9 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.22, 148.55, 137.05, 136.58, 133.48, 132.50, 132.39, 130.82, 130.68, 130.58, 129.25, 128.53, 127.74, 126.51, 123.56, 121.83, 120.27, 116.61, 112.25, 21.21, 12.10. HR-MS (ESI) calcd for [M + 1]$^+$: $C_{25}H_{23}N_2$: 351.1856, found: 351.1865; IR (KBr): 3554, 3411, 2919, 2852, 2026, 1636, 1103, 618 cm $^{-1}$.

1.9 Procedure for synthesis of 2, 3, 5-triphenyl-1H-pyrrole (4a)

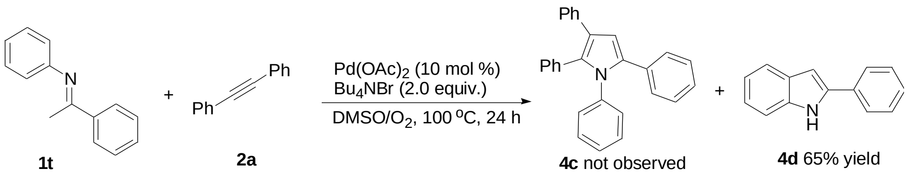


The solution of methyl trifluoromethanesulfonate (17 mg, 0.1 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise to a solution of pyrrole **3a** (37 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) at 0 ℃, and the resulting solution was stirred for 12 h at room temperature. Then the solvent was removed under vacuum, and residue was dissolved in MeOH (2.0 mL). An aqueous NaOH solution (2.0 M, 0.5

mL) was added, and the mixture was stirred at 50 ℃ for 6 h. After the solvent was removed under vacuum, and the resulting residue was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried and concentrated. The resulted residue was purified by flash column chromatography to afford **4a** [4] as a white solid (22 mg, 75%), ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.35 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.34 (m, 6H), 7.32 – 7.17 (m, 7H), 6.67 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.46, 133.17, 132.30, 129.40, 129.05, 128.79, 128.51, 128.42, 127.58, 127.05, 126.60, 126.03, 123.93, 123.88, 108.68. MS (ESI): m/z = 295.14 [M^+].

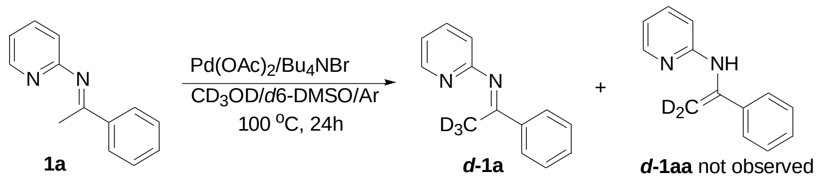
2. Controlled experiments for mechanism studies

(a) Pd(II)-catalyzed cyclization of ketoimine (1t) with alkyene (2a) under our standard reaction conditions.



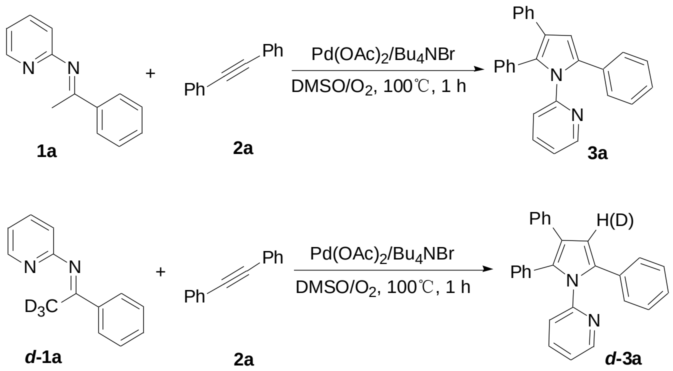
To the solution of ketoimine **1t** (0.1 mmol) in dry DMSO (1.0 mL) were added alkyne **2a** (0.1 mmol), $Pd(OAc)_2$ (2.0 mg, 10 mol%) and Bu_4NBr (65 mg, 0.2 mmol) under O_2 atmosphere. The reaction mixture was stirred at 100 ℃ for 24 h. After the reaction mixture was cooled down to room temperature, and 1.0 mL of H_2O was added, then extracted with CH_2Cl_2 (3×10 mL). The corresponding combined organic layers were dried over Na_2SO_4, and concentrated under vacuum and purified by flash chromatography on silica gel using 10% (v/v) ethyl acetate in petroleum ether as eluent to give the compound **4d**.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.28 (s, 1H), 7.63 (t, *J* = 5.8 Hz, 3H), 7.45 – 7.35 (m, 3H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.20 (dd, *J* = 14.4, 7.2 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.92, 136.85, 132.40, 129.30, 129.06, 127.75, 125.20, 122.39, 120.71, 120.32, 110.94, 100.03.

(b) H/D Exchange of *N*-(2-pyridyl) ketoimine (**1a**)



To the solution of ketoimine **1a** (0.1 mmol) in dry d_6-DMSO (1.0 mL) were added CD_3OD (0.5 mL) $Pd(OAc)_2$ (2.0 mg, 10 mol %) and Bu_4NBr (65 mg, 0.2 mmol) under Ar. The reaction mixture was stirred for 100℃ and then cooled down to room temperature. After removal of solvent the resulted crude was purified by flash column chromatography to give the desired compound ***d*-1a** (25% yield) as oil. ^{1}H NMR (400 MHz, *d*-DMSO) δ= 8.42 (d, *J* = 4.7 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.14 – 7.10 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 2.18 (s, 0.26H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.68, 163.53, 148.85, 139.02, 137.70, 130.89, 128.33, 127.44, 118.85, 115.18. HR-MS (ESI) calcd for $[M+1]^+$: $C_{13}H_{10}D_3N_2$: 200.1262, found: 200.1262.

(c): Kinetic isotope effect of this transformation



A sample experimental set-up is shown as follows: ketoimine **(1a:** 20 mg**,** 0.1 mmol; or ***d*-1a:** 20 mg, 0.1 mmol) in dry DMSO (2.0 mL) were added alkynes **2a** (0.1 mmol), $Pd(OAc)_2$ (2 mg, 10 mol ％) and Bu_4NBr (65 mg, 0.2 mmol) under O_2 atmosphere, and then the corresponding reaction mixture was stirred in a sealed tube for 100 ℃. Aliquots (0.4 mL) were removed at 10 minutes intervals for the first 50 minutes of the reaction. Each aliquot was removed under reduced pressure and analyzed by ^{1}H NMR spectrum (see **Figure 1** and **Figure 2**). A sample plot of the initial rate data for reactions of both **1a** and ***d*-1a** was shown in **Figure 3.** The reaction progress in the early stage (0-60 min) indicated a kinetic isotope effect of 1.52. Then above reaction was combined, added 1.0 mL of H_2O. Then the mixture was extracted with DCM (3×10 mL), and the corresponding crude ***d*-3a** was purified by flash chromatography on silical gel using 10％ ethyl acetate in petroleum ether as eluent. ***d*-3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 4.6 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.08 (m, 16H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.70 (s, 0.25 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.19, 148.82, 137.42, 136.06, 135.01, 132.93, 132.58, 132.24, 131.26, 128.31, 128.14, 128.08, 127.90, 127.02, 126.46, 125.62, 123.97, 122.52, 110.65.

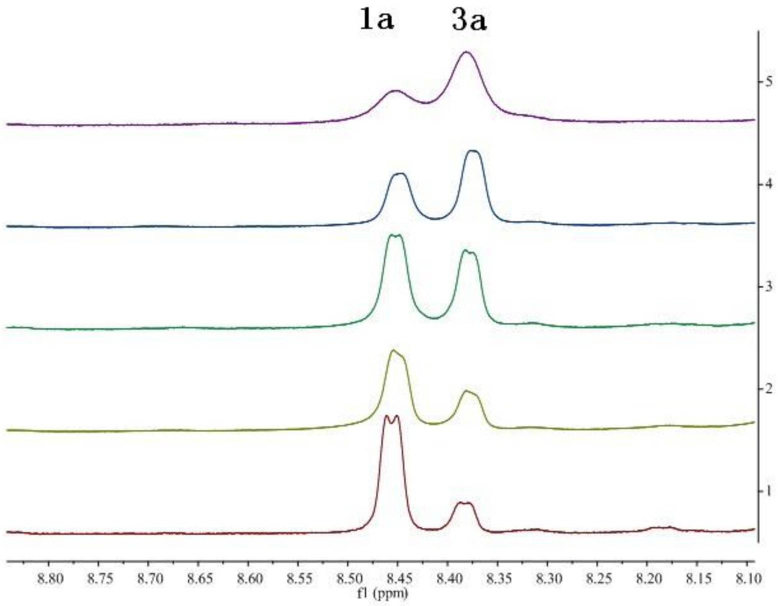


Figure 1. The conversion of **1a** was monitored by ^{1}H NMR method

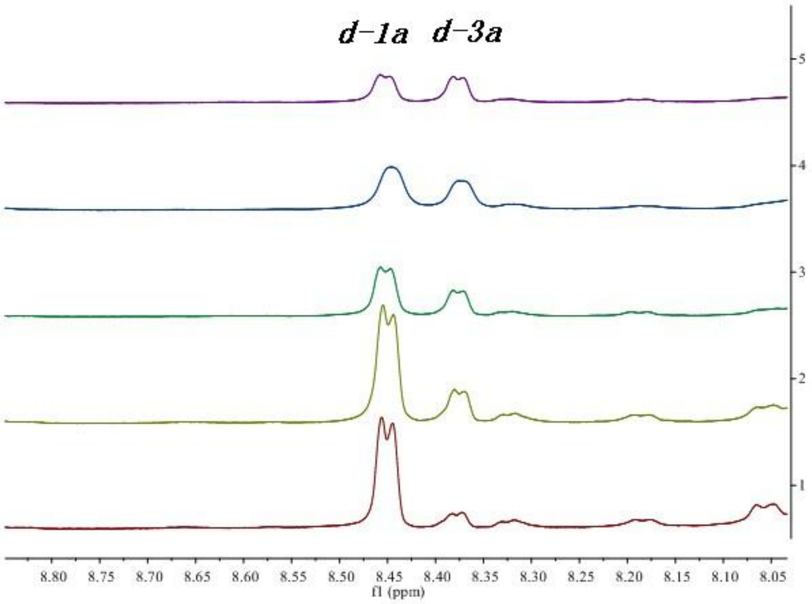


Figure 2. The conversion of ***d*-1a** was monitored by ^{1}H NMR method

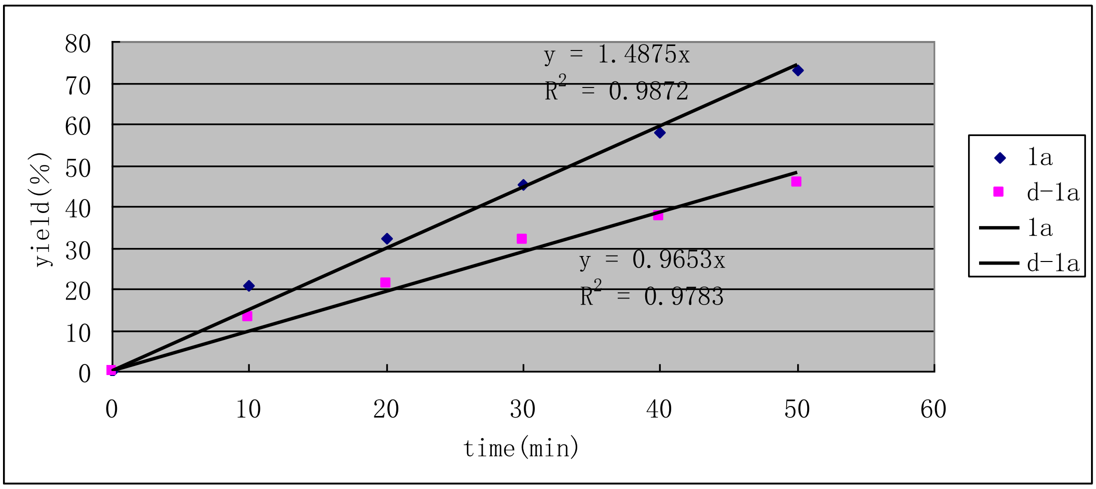
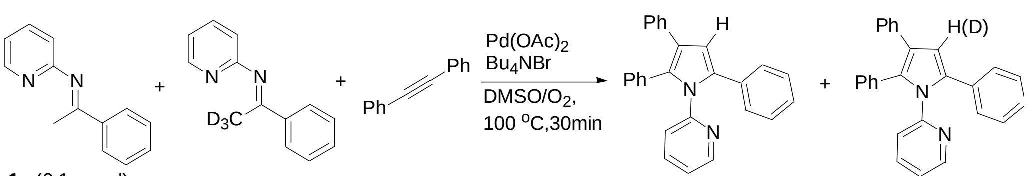


Figure 3. The plot of initial rates for KIE measurements

(d): The KIE determination via competitive experiment between 1a and *d*-1a



A sample experimental set-up is described as follows: ketoimine **(1a:** 20 mg**,** 0.1 mmol; and ***d*-1a:** 20 mg, 0.1 mmol) in dry DMSO (4.0 mL) were added alkynes **2a** (0.2 mmol), $Pd(OAc)_2$ (4 mg, 10 mol %) and Bu_4NBr (130.0 mg, 0.4 mmol) under O_2 atmosphere, and then the corresponding reaction mixture was stirred in a sealed tube for 100 ℃. Aliquots (0.4 mL) were removed at 10 minutes intervals for the first 30 minutes of the reaction. Each aliquot was removed under reduced pressure and analyzed by ^{1}H NMR. A sample plot of the initial rate data for reactions of both **1a** and ***d-1a*** was shown in **Figure 4.** The reaction progress in the early stage (0-30min) indicated a kinetic isotope effect of 3.0 (KIE = 3.0).

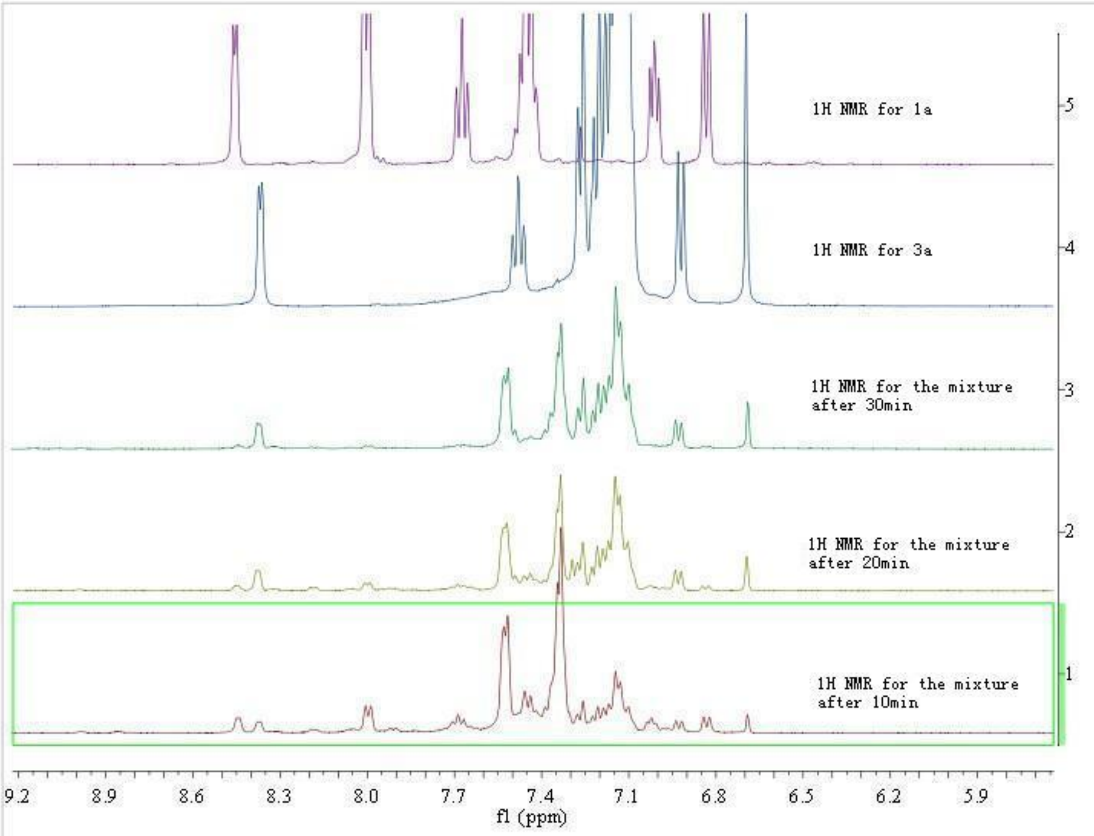


Figure 4. The conversion of **1a** and ***d*-1a** was monitored by ^{1}H NMR method

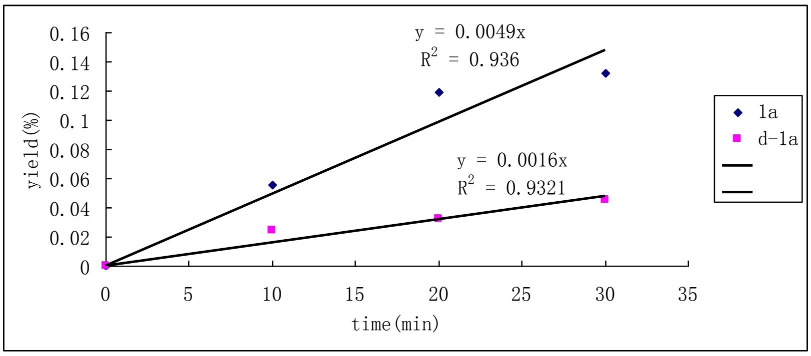
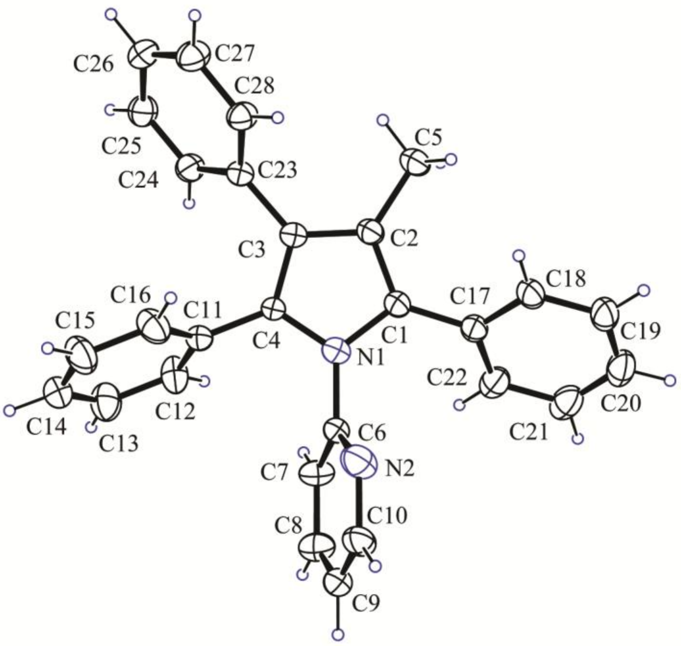


Figure 5. The plot of initial rates for KIE measurements

3. Single crystal data about 3l



Fingure 4. The single crystal structure of **3l**

Table 6. Crystal data and structure refinement for SAD

Empirical formula	$C_{28}H_{22}N_2$
Formula weight	386.48
Crystal system	Monoclinic
Temperature	293 K
Wavelength	0.71073 A
Space group	P 21/c
a (Å)	12.208(2)
b (Å)	9.4997(19)
c (Å)	19.300(7)
α (°)	90
β (°)	109.62(3)
γ (°)	90
V (Å3)	2108.3(9)
Z	4
Dc (g cm $^{-3}$)	1.218
Crystal size (mm)	0.25×0.20×0.20
F (000)	816
Range / °	3.10 to 27.48
Reflections collected / unique	4818/2506[R(int)= 0.0297]
Data / restraints / parameters	4818/0/ 273
Goodness-of-fit on F^2	1.092

Rindices (all data)	R1 = 0.0737, wR2 = 0.2221

Table 7. Atomic coordinates and equivalent isotropic displacement parameters for shelxl. U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	0.2100(2)	-0.2253(2)	-0.12453(11)	0.0678(6)
N(2)	0.3306(3)	-0.0726(3)	-0.02713(15)	0.0977(9)
C(1)	0.2518(2)	-0.2208(3)	-0.18342(13)	0.0602(6)
C(2)	0.1548(2)	-0.2155(3)	-0.24753(14)	0.0614(6)
C(3)	0.0557(2)	-0.2167(3)	-0.22724(13)	0.0589(6)
C(4)	0.0909(2)	-0.2228(2)	-0.15126(11)	0.0498(5)
C(5)	0.1548(3)	-0.2223(4)	-0.32500(14)	0.0773(8)
C(6)	0.2780(2)	-0.2008(3)	-0.04769(13)	0.0559(6)
C(7)	0.2889(3)	-0.3025(3)	0.00203(14)	0.0738(8)
C(8)	0.3519(3)	-0.2769(4)	0.07358(18)	0.0885(9)
C(9)	0.4057(3)	-0.1536(3)	0.09611(16)	0.0756(8)
C(10)	0.3959(3)	-0.0514(4)	0.04676(17)	0.0843(9)
C(11)	0.0181(2)	-0.2103(3)	-0.10621(13)	0.0611(6)
C(12)	0.0120(3)	-0.3161(3)	-0.06222(19)	0.0826(9)
C(13)	-0.0572(3)	-0.3044(4)	-0.0201(2)	0.1015(11)
C(14)	-0.1225(3)	-0.1877(4)	-0.02247(18)	0.0891(10)
C(15)	-0.1165(4)	-0.0806(4)	-0.0671(2)	0.1038(12)
C(16)	-0.0469(3)	-0.0918(4)	-0.10992(18)	0.0898(10)
C(17)	0.3744(2)	-0.2300(3)	-0.17709(14)	0.0661(7)
C(18)	0.4167(3)	-0.1490(3)	-0.22278(16)	0.0776(8)
C(19)	0.5309(3)	-0.1597(5)	-0.2195(2)	0.0993(12)
C(20)	0.6042(4)	-0.2510(5)	-0.1709(3)	0.1065(13)
C(21)	0.5659(3)	-0.3289(4)	-0.1242(2)	0.1000(11)
C(22)	0.4513(3)	-0.3188(3)	-0.12764(18)	0.0819(9)
C(23)	-0.0671(2)	-0.2152(3)	-0.27519(13)	0.0580(6)
C(24)	-0.1455(3)	-0.3164(3)	-0.27066(15)	0.0682(7)

C(25)	-0.2586(3)	-0.3135(3)	-0.31641(17)	0.0776(8)
C(26)	-0.2964(3)	-0.2109(3)	-0.36906(17)	0.0795(8)
C(27)	-0.2198(3)	-0.1110(3)	-0.37503(18)	0.0822(9)
C(28)	-0.1064(3)	-0.1123(3)	-0.32845(15)	0.0688(7)

Table 8. Bond lengths [A] for shelxl

Bond	Lengths [A]
N(1)-C(4)	1.369(3)
N(1)-C(1)	1.395(3)
N(1)-C(6)	1.455(3)
N(2)-C(6)	1.371(4)
N(2)-C(10)	1.395(4)
C(1)-C(2)	1.398(4)
C(1)-C(17)	1.462(4)
C(2)-C(3)	1.391(3)
C(2)-C(5)	1.497(3)
C(3)-C(4)	1.384(3)
C(3)-C(23)	1.474(4)
C(4)-C(11)	1.442(3)
C(6)-C(7)	1.337(3)
C(7)-C(8)	1.358(4)
C(8)-C(9)	1.342(4)
C(9)-C(10)	1.337(4)
C(11)-C(12)	1.334(4)
C(11)-C(16)	1.366(4)
C(12)-C(13)	1.360(4)
C(13)-C(14)	1.357(5)
C(14)-C(15)	1.350(5)
C(15)-C(16)	1.374(4)
C(17)-C(22)	1.379(4)
C(17)-C(18)	1.394(4)

C(18)-C(19)	1.378(5)
C(19)-C(20)	1.368(6)
C(20)-C(21)	1.363(6)
C(21)-C(22)	1.382(4)
C(23)-C(24)	1.380(4)
C(23)-C(28)	1.382(4)
C(24)-C(25)	1.366(4)
C(25)-C(26)	1.372(4)
C(26)-C(27)	1.363(4)
C(27)-C(28)	1.375(4)

Table 9. Anisotropic displacement parameters for shelxl.

	U11	U22	U33	U23	U13	U12
N(1)	0.0703(15)	0.0797(14)	0.0540(12)	-0.0037(10)	0.0215(11)	0.0029(11)
N(2)	0.117(3)	0.101(2)	0.0817(18)	-0.0126(15)	0.0420(18)	-0.0142(17)
C(1)	0.0591(16)	0.0695(14)	0.0543(13)	-0.0070(11)	0.0221(12)	-0.0019(12)
C(2)	0.0629(16)	0.0724(15)	0.0499(12)	-0.0041(11)	0.0201(12)	-0.0064(12)
C(3)	0.0583(15)	0.0674(14)	0.0492(12)	-0.0006(11)	0.0158(11)	0.0003(11)
C(4)	0.0461(13)	0.0613(12)	0.0412(11)	0.0007(9)	0.0134(10)	-0.0007(10)
C(5)	0.079(2)	0.102(2)	0.0531(14)	-0.0092(14)	0.0259(14)	-0.0116(16)
C(6)	0.0548(14)	0.0633(13)	0.0501(12)	-0.0054(10)	0.0181(11)	0.0011(11)
C(7)	0.089(2)	0.0620(14)	0.0568(15)	0.0034(12)	0.0070(15)	-0.0039(13)
C(8)	0.096(3)	0.088(2)	0.0687(18)	0.0046(16)	0.0105(18)	0.0100(18)
C(9)	0.0626(18)	0.101(2)	0.0626(16)	-0.0114(16)	-0.0114(16)	0.0045(16)
C(10)	0.094(2)	0.095(2)	0.0668(18)	-0.0242(17)	0.0310(17)	-0.0242(17)
C(11)	0.0569(15)	0.0735(15)	0.0516(13)	-0.0067(11)	0.0164(12)	-0.0041(12)
C(12)	0.082(2)	0.0722(16)	0.111(2)	0.0176(16)	0.055(2)	0.0121(14)
C(13)	0.097(3)	0.103(3)	0.118(3)	0.015(2)	0.054(2)	0.000(2)
C(14)	0.076(2)	0.119(3)	0.077(2)	-0.0098(19)	0.0323(18)	0.0033(19)
C(15)	0.119(3)	0.113(3)	0.098(2)	-0.001(2)	0.061(2)	0.030(2)
C(16)	0.111(3)	0.0861(19)	0.085(2)	0.0074(16)	0.049(2)	0.0241(18)
C(17)	0.0603(16)	0.0807(16)	0.0594(14)	-0.0205(13)	0.0231(13)	-0.0045(13)
C(18)	0.0731(19)	0.102(2)	0.0645(16)	-0.0220(15)	0.0323(15)	-0.0159(16)
C(19)	0.076(2)	0.146(3)	0.086(2)	-0.046(2)	0.041(2)	-0.029(2)
C(20)	0.067(2)	0.146(3)	0.114(3)	-0.057(3)	0.039(2)	-0.014(2)
C(21)	0.068(2)	0.109(2)	0.113(3)	-0.031(2)	0.019(2)	0.0109(18)
C(22)	0.0651(19)	0.0856(19)	0.090(2)	-0.0146(16)	0.0188(17)	0.0010(15)

C(23)	0.0587(15)	0.0656(14)	0.0486(12)	-0.0034(11)	0.0168(11)	0.0168(11)
C(24)	0.0661(18)	0.0691(15)	0.0675(16)	0.0080(12)	0.0201(14)	-0.0063(13)
C(25)	0.0674(19)	0.0820(18)	0.083(2)	0.0014(15)	0.0243(17)	-0.0145(14)
C(26)	0.0594(17)	0.096(2)	0.0736(18)	0.0004(16)	0.0097(15)	-0.0028(15)
C(27)	0.076(2)	0.0828(18)	0.0786(19)	0.0141(16)	0.0144(17)	0.0054(16)
C(28)	0.0647(17)	0.0697(15)	0.0657(15)	0.0079(13)	0.0135(14)	-0.0049(13)

Table 10. Hydrogen coordinates and isotropic displacement parameters for shelxl.

	x	y	z	U(eq)
H(5A)	0.0813	-0.2576	-0.3565	0.116
H(5B)	0.2159	-0.2838	-0.3273	0.116
H(5C)	0.1674	-0.1297	-0.3409	0.116
H(7A)	0.2538	-0.3896	-0.0122	0.089
H(8A)	0.3579	-0.3473	0.1082	0.106
H(9A)	0.4492	-0.1395	0.1454	0.091
H(10A)	0.4329	0.0345	0.0618	0.101
H(12A)	0.0550	-0.3976	-0.0604	0.099
H(13A)	-0.0599	-0.3780	0.0111	0.122
H(14A)	-0.1704	-0.1816	0.0061	0.107
H(15A)	-0.1596	0.0009	-0.0688	0.125
H(16A)	-0.0441	-0.0188	-0.1414	0.108
H(18A)	0.3672	-0.0867	-0.2559	0.093
H(19A)	0.5580	-0.1050	-0.2503	0.119
H(20A)	0.6807	-0.2600	-0.1696	0.128
H(21A)	0.6168	-0.3886	-0.0902	0.120
H(22A)	0.4255	-0.3730	-0.0960	0.098
H(24A)	-0.1210	-0.3877	-0.2359	0.082
H(25A)	-0.3104	-0.3817	-0.3118	0.093
H(26A)	-0.3733	-0.2094	-0.4003	0.095

H(27A)	-0.2445	-0.0415	-0.4109	0.099
H(28A)	-0.0554	-0.0430	-0.3328	0.083

Table 11. Bond angles [deg] for shelxl.

Bond	Bond angles [deg]
C(4)-N(1)-C(1)	109.0(2)
C(4)-N(1)-C(6)	123.47(19)
C(1)-N(1)-C(6)	125.9(2)
C(6)-N(2)-C(10)	118.4(3)
N(1)-C(1)-C(2)	106.8(2)
N(1)-C(1)-C(17)	125.1(2)
C(2)-C(1)-C(17)	128.0(2)
C(3)-C(2)-C(1)	108.0(2)
C(3)-C(2)-C(5)	125.0(3)
C(1)-C(2)-C(5)	126.7(3)
C(4)-C(3)-C(2)	107.9(2)
C(4)-C(3)-C(23)	123.7(2)
C(2)-C(3)-C(23)	128.3(2)
N(1)-C(4)-C(3)	108.3(2)
N(1)-C(4)-C(11)	124.4(2)
C(3)-C(4)-C(11)	126.9(2)
C(7)-C(6)-N(2)	120.7(3)
C(7)-C(6)-N(1)	120.1(2)
N(2)-C(6)-N(1)	119.3(2)
C(6)-C(7)-C(8)	119.1(3)
C(9)-C(8)-C(7)	122.3(3)
C(10)-C(9)-C(8)	119.1(3)
C(9)-C(10)-N(2)	120.4(3)
C(12)-C(11)-C(16)	119.9(2)
C(12)-C(11)-C(4)	120.0(2)
C(16)-C(11)-C(4)	120.1(2)

C(11)-C(12)-C(13)	119.9(3)
C(14)-C(13)-C(12)	121.4(3)
C(15)-C(14)-C(13)	118.7(3)
C(14)-C(15)-C(16)	120.1(3)
C(11)-C(16)-C(15)	119.9(3)
C(22)-C(17)-C(18)	117.7(3)
C(22)-C(17)-C(1)	122.3(3)
C(18)-C(17)-C(1)	120.0(3)
C(19)-C(18)-C(17)	121.0(4)
C(20)-C(19)-C(18)	119.8(4)
C(21)-C(20)-C(19)	120.5(4)
C(20)-C(21)-C(22)	119.8(4)
C(17)-C(22)-C(21)	121.2(3)
C(24)-C(23)-C(28)	117.7(3)
C(24)-C(23)-C(3)	122.3(2)
C(28)-C(23)-C(3)	120.0(2)
C(25)-C(24)-C(23)	121.1(3)
C(24)-C(25)-C(26)	120.6(3)
C(27)-C(26)-C(25)	119.2(3)
C(26)-C(27)-C(28)	120.5(3)
C(27)-C(28)-C(23)	121.0(3)

4. References

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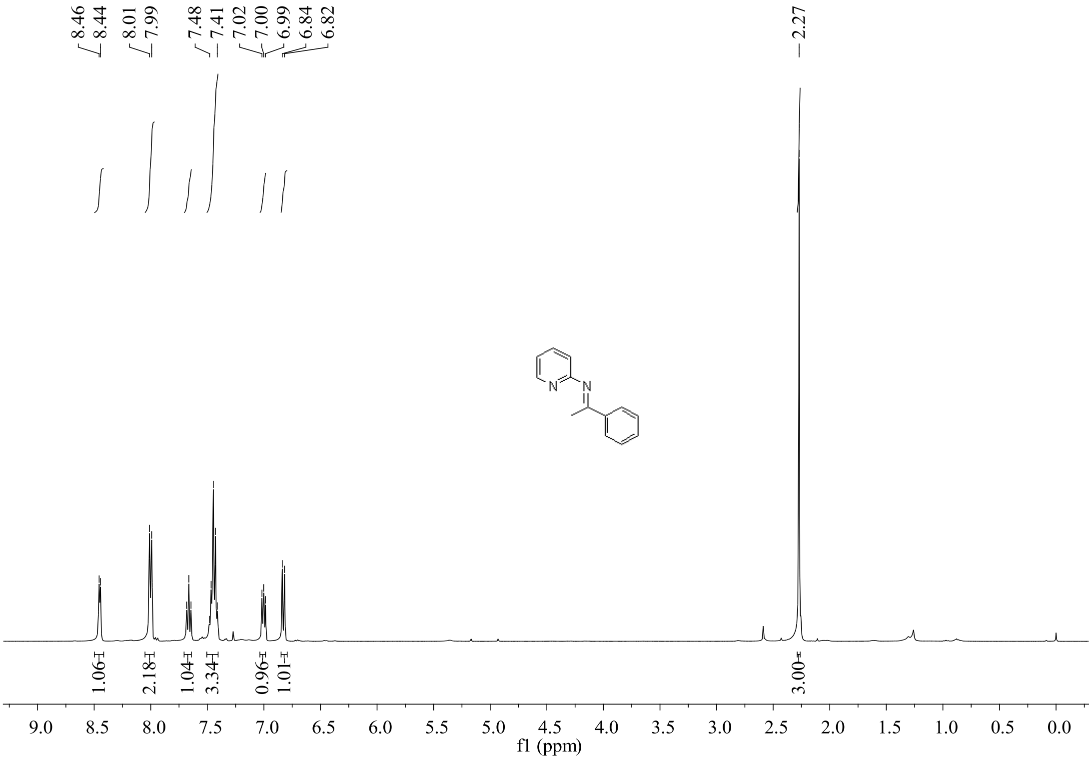
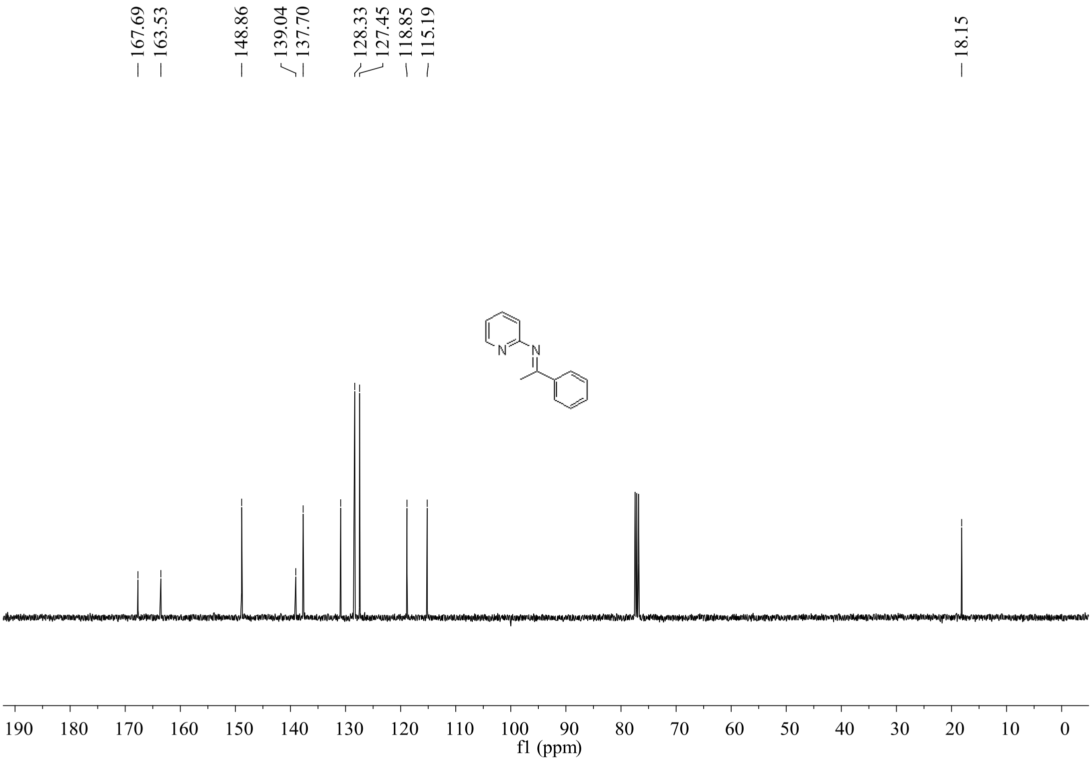
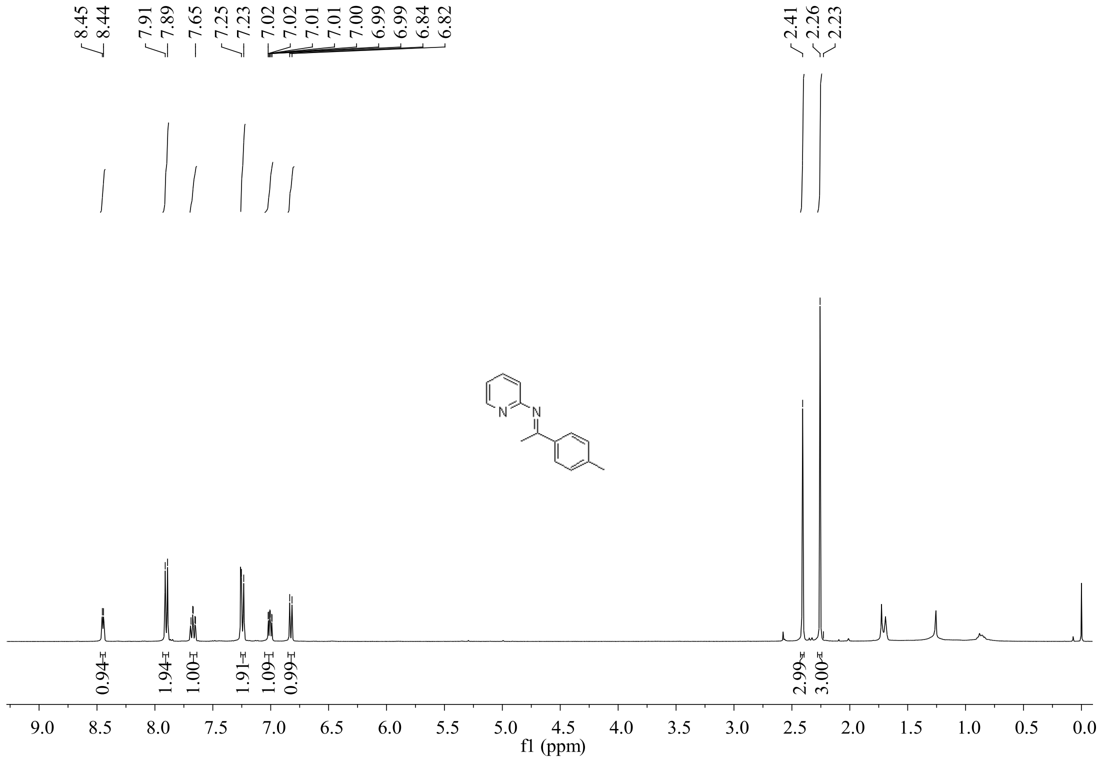
5. ^{1}H NMR and ^{13}C NMR spectrum for all isolated products.

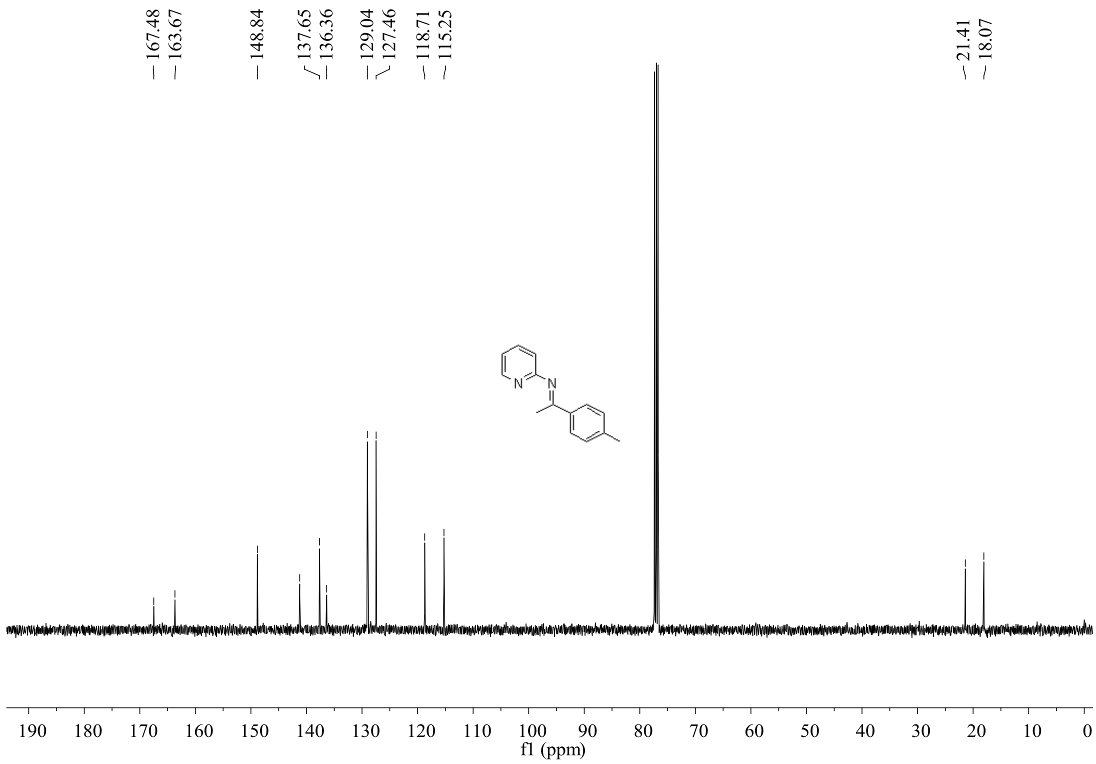
1) (*E*)-*N*-(1-phenylethylidene)pyridin-2-amine (**1a**) (Using $CDCl_3$ as solvent)



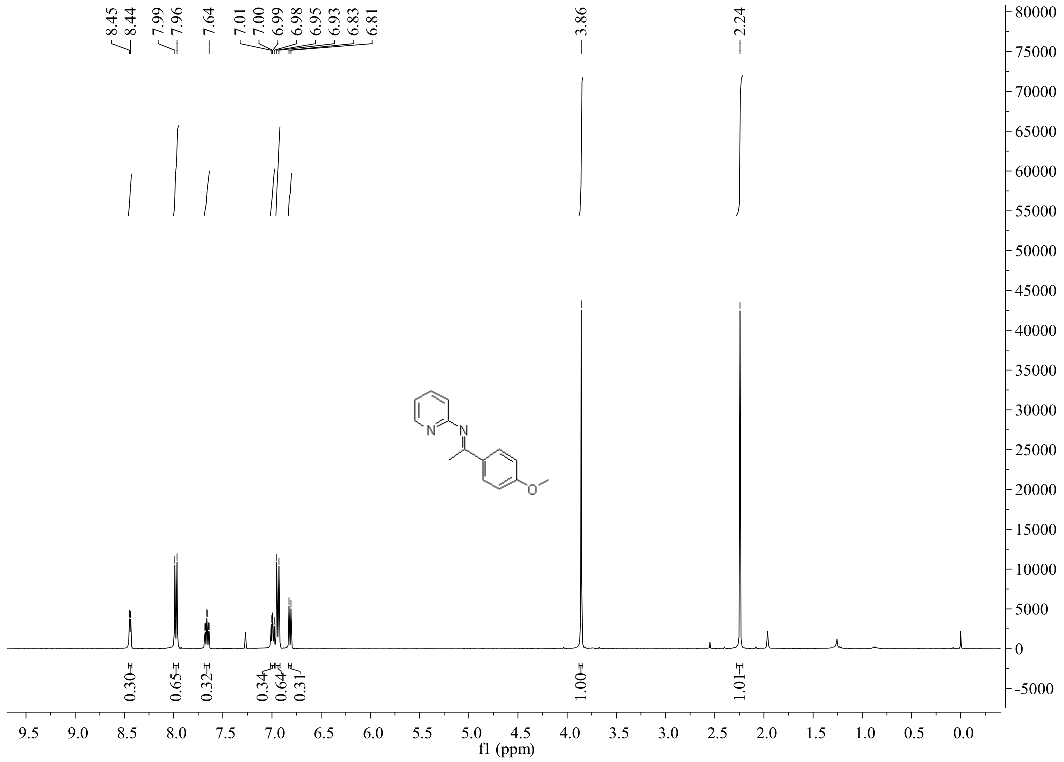


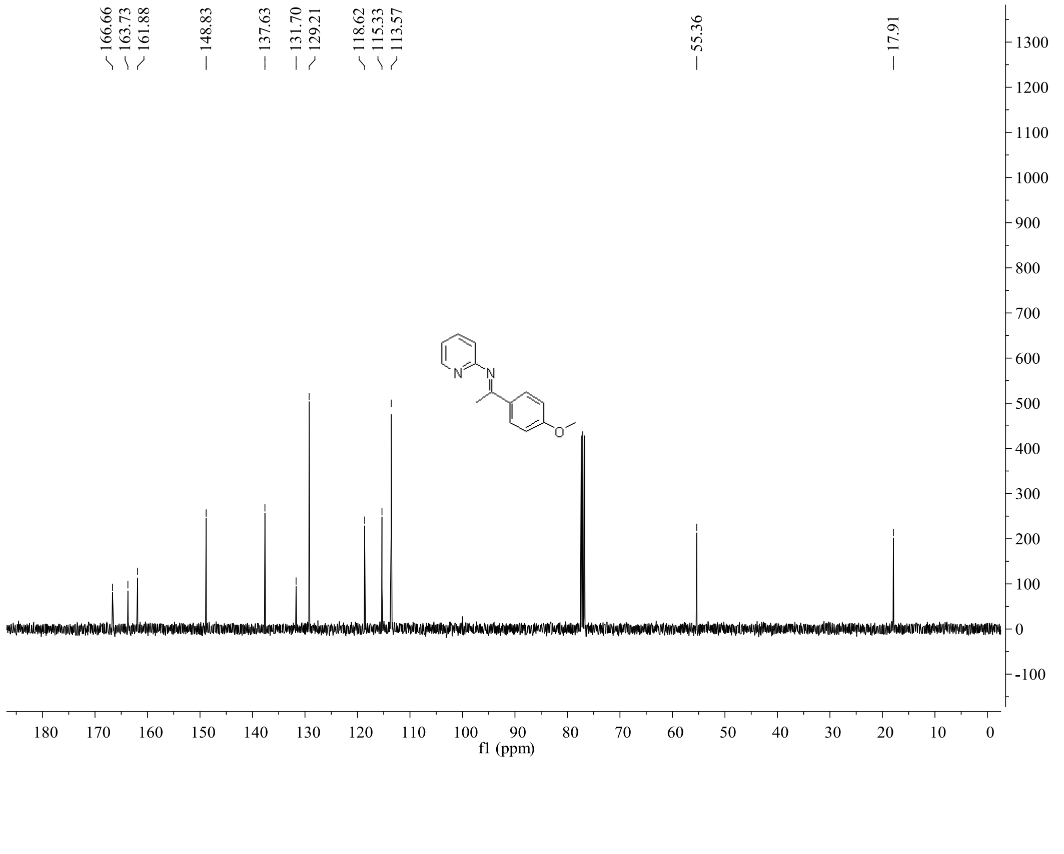
2) (*E*)-*N*-(1-(p-tolyl)ethylidene)pyridin-2-amine (**1b**): (Using $CDCl_3$ as solvent)



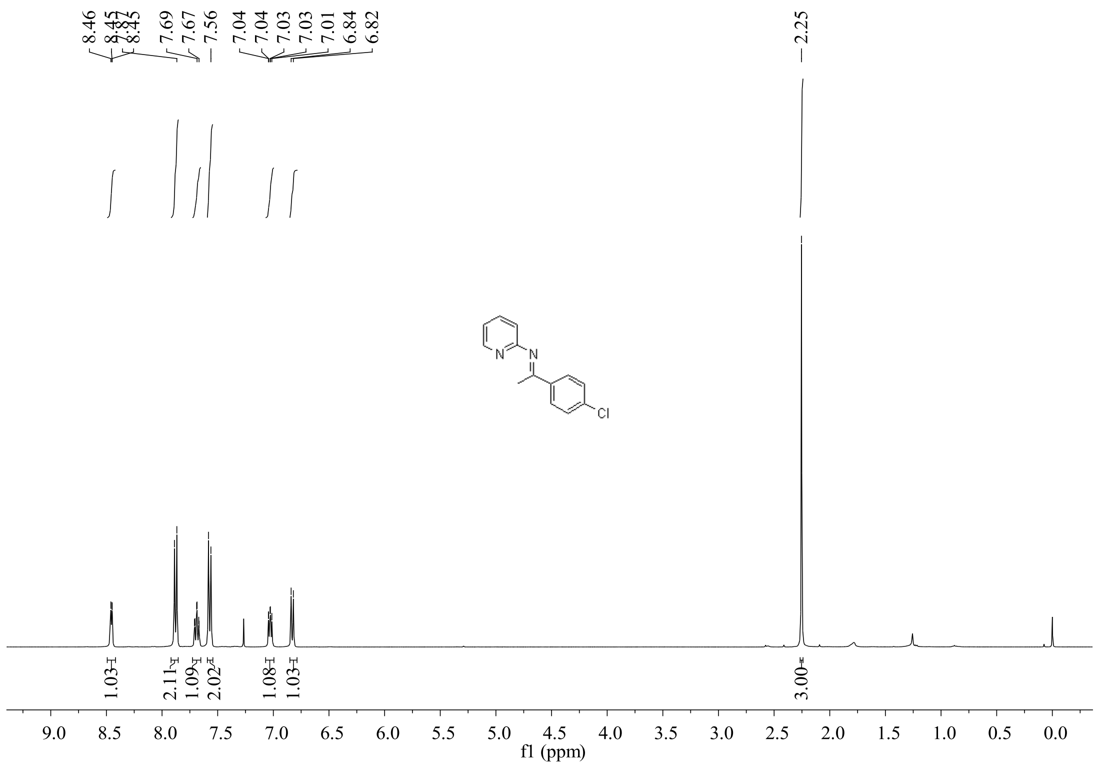


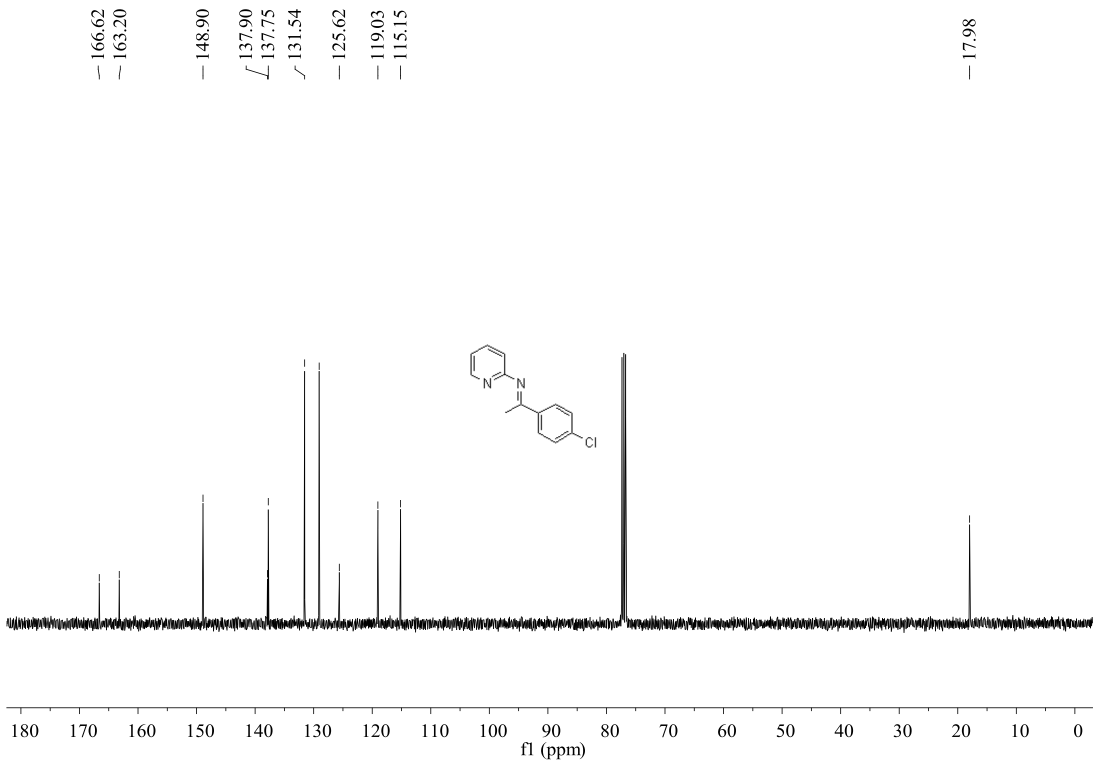
3) (*E*)-*N*-(1-(4-methoxyphenyl)ethylidene)pyridin-2-amine (**1c**): (Using $CDCl_3$ as solvent)



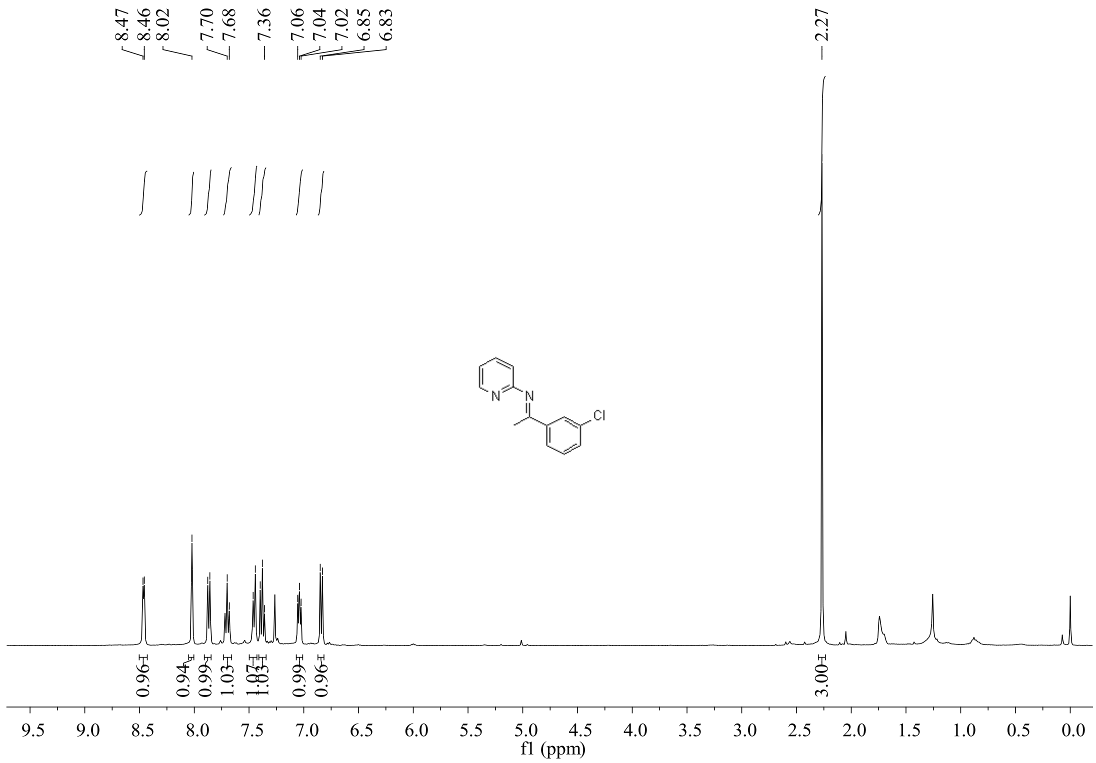


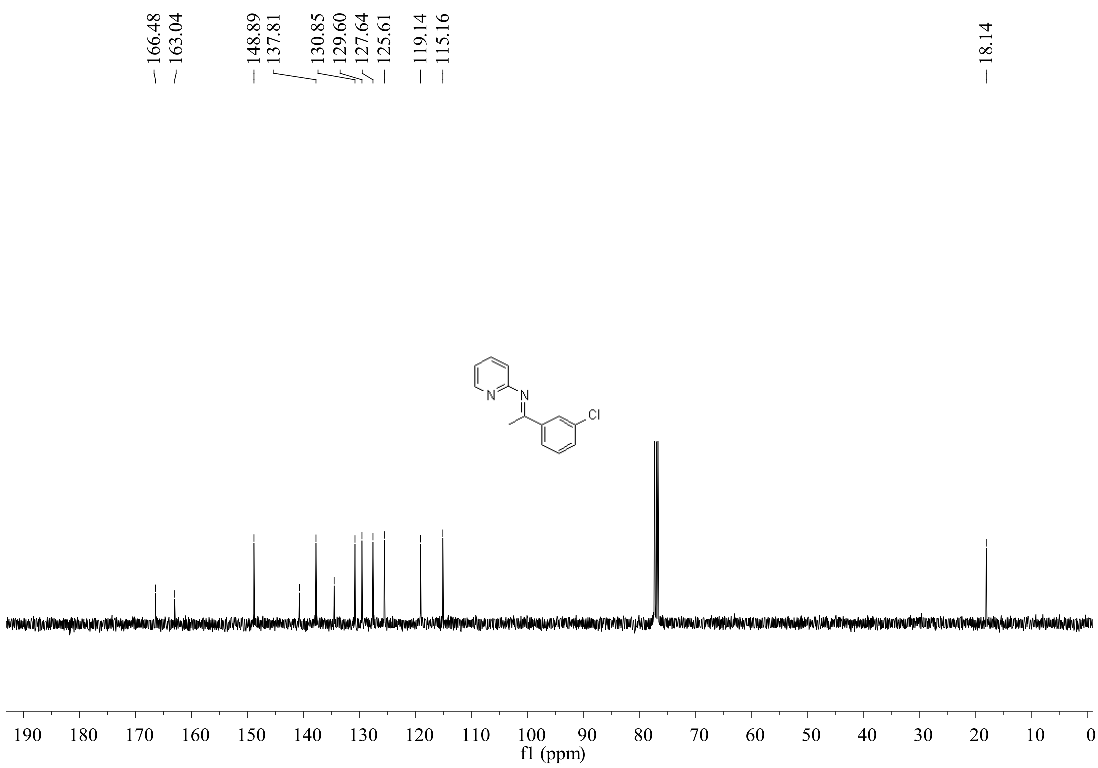
4) (*E*)-*N*-(1-(4-chlorophenyl)ethylidene)pyridin-2-amine (**1e**): (Using $CDCl_3$ as solvent)



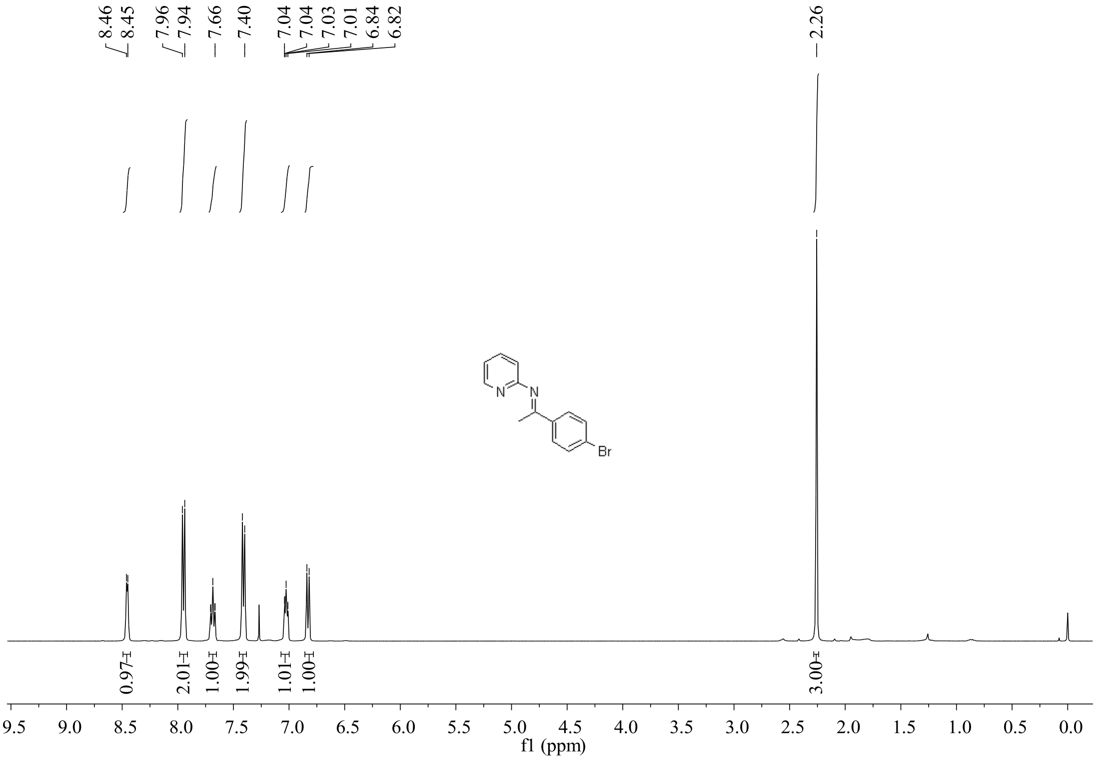


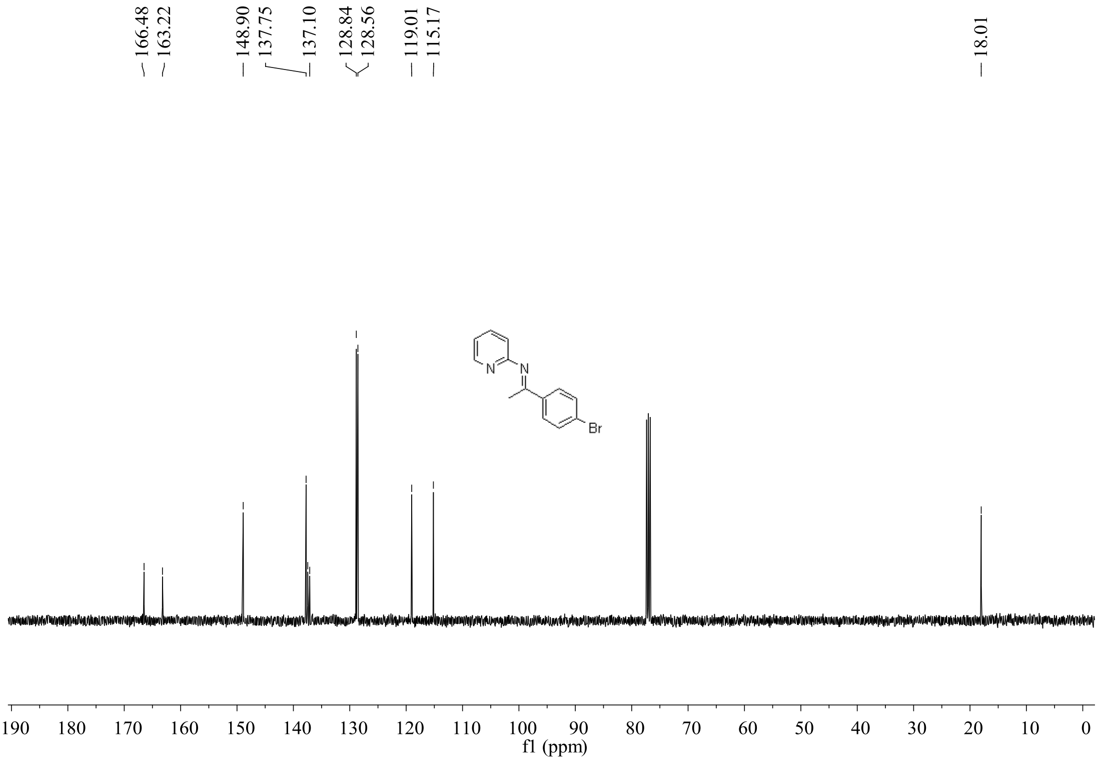
5) (*E*)-*N*-(1-(3-chlorophenyl)ethylidene)pyridin-2-amine (**1f**): (Using $CDCl_3$ as solvent)



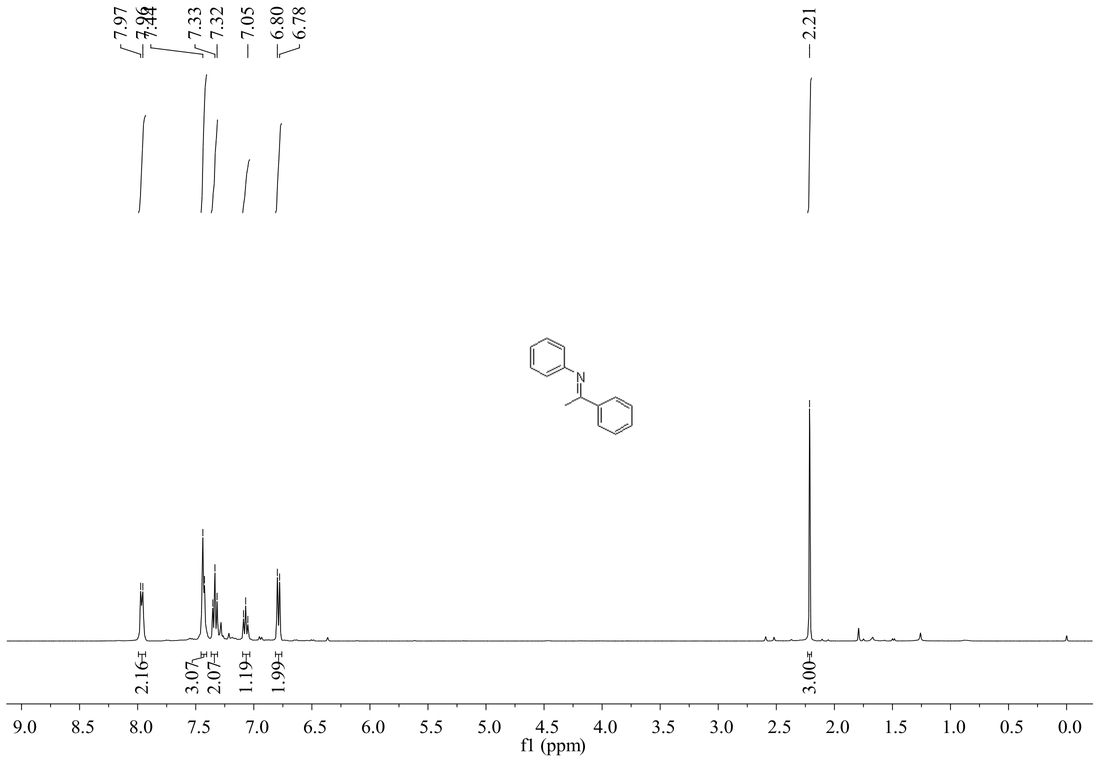


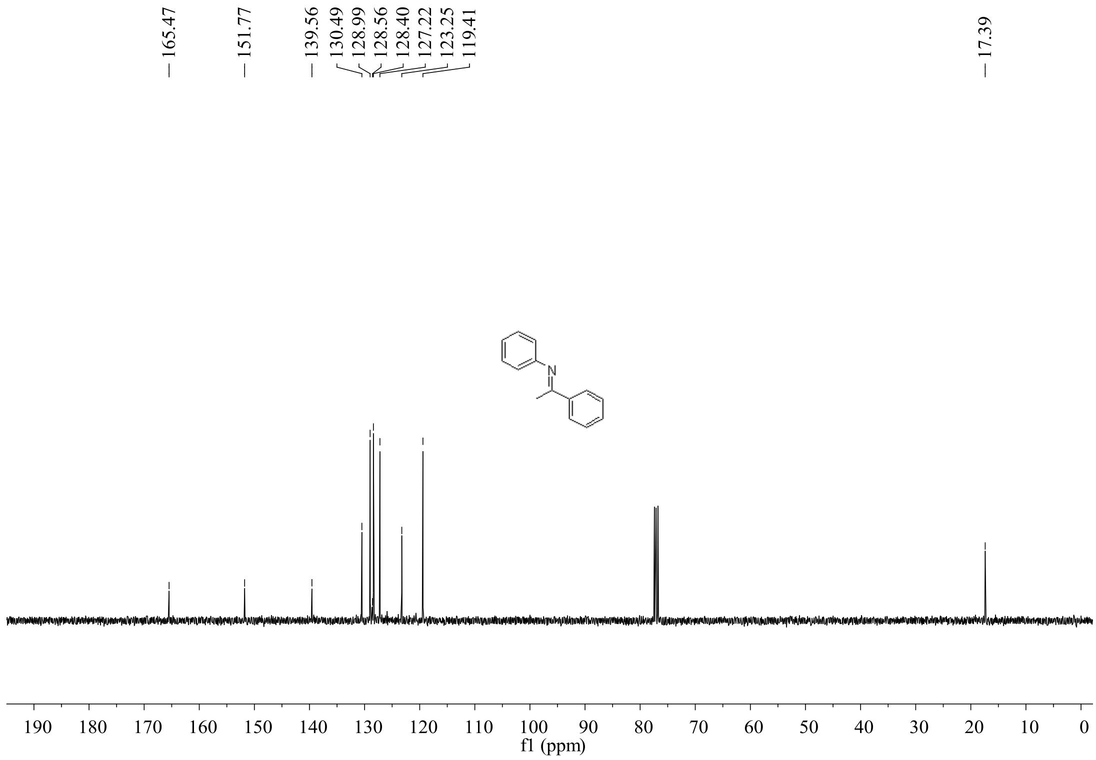
6) (*E*)-*N*-(1-(4-bromophenyl)ethylidene)pyridin-2-amine (**1h**): (Using $CDCl_3$ as solvent)



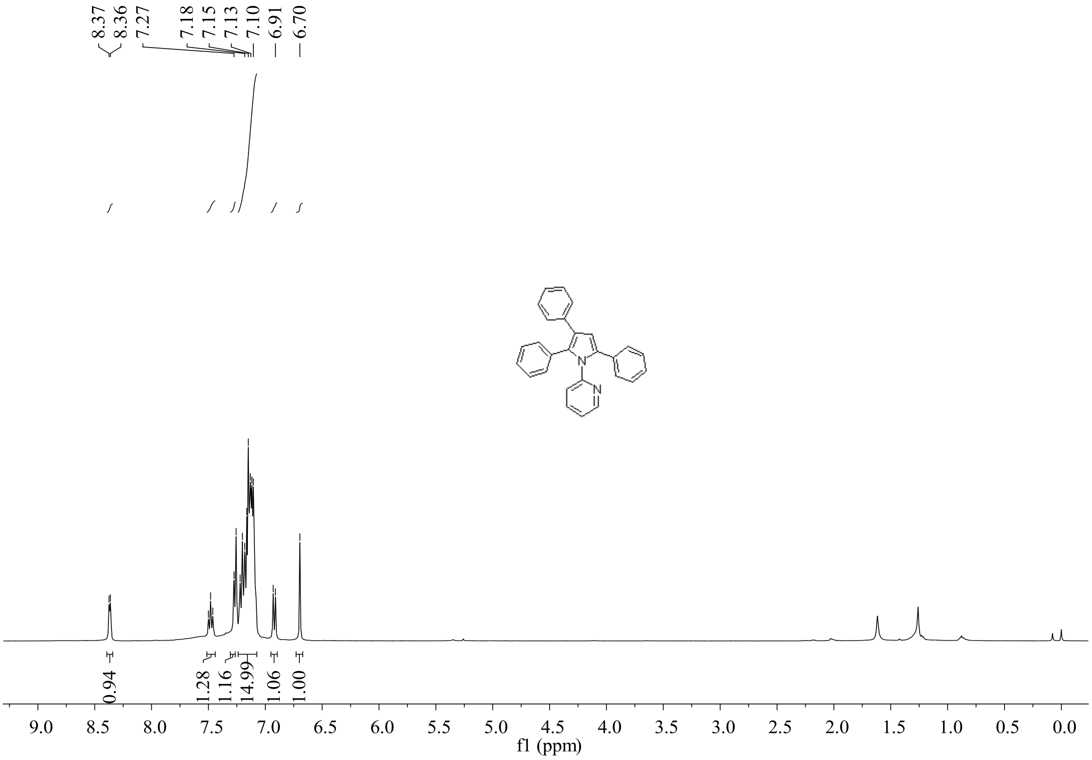


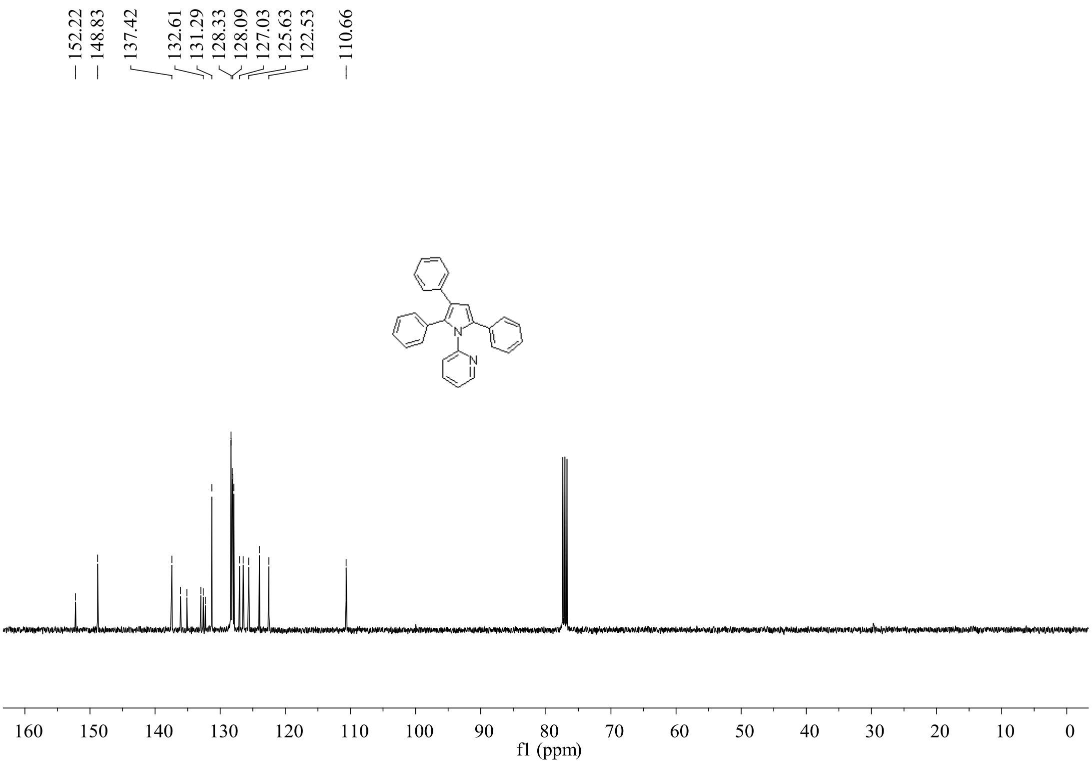
7) (*E*)-*N*-(1-phenylethylidene)aniline (**1t**) (Using $CDCl_3$ as solvent)



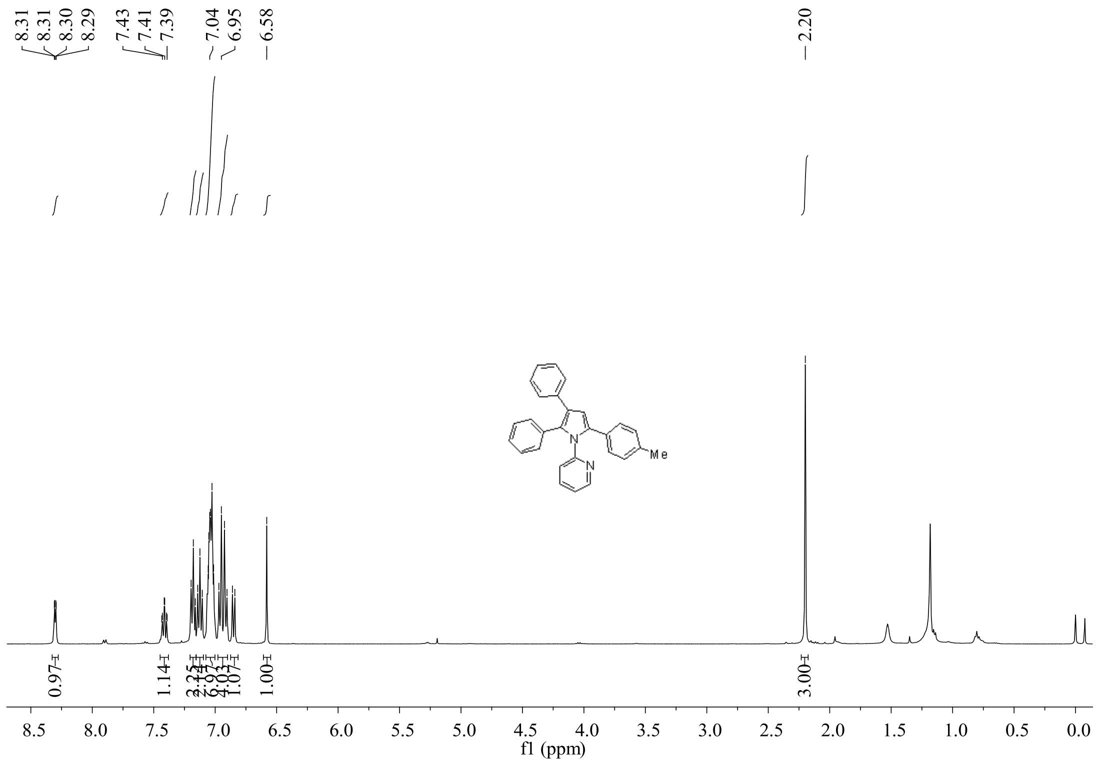


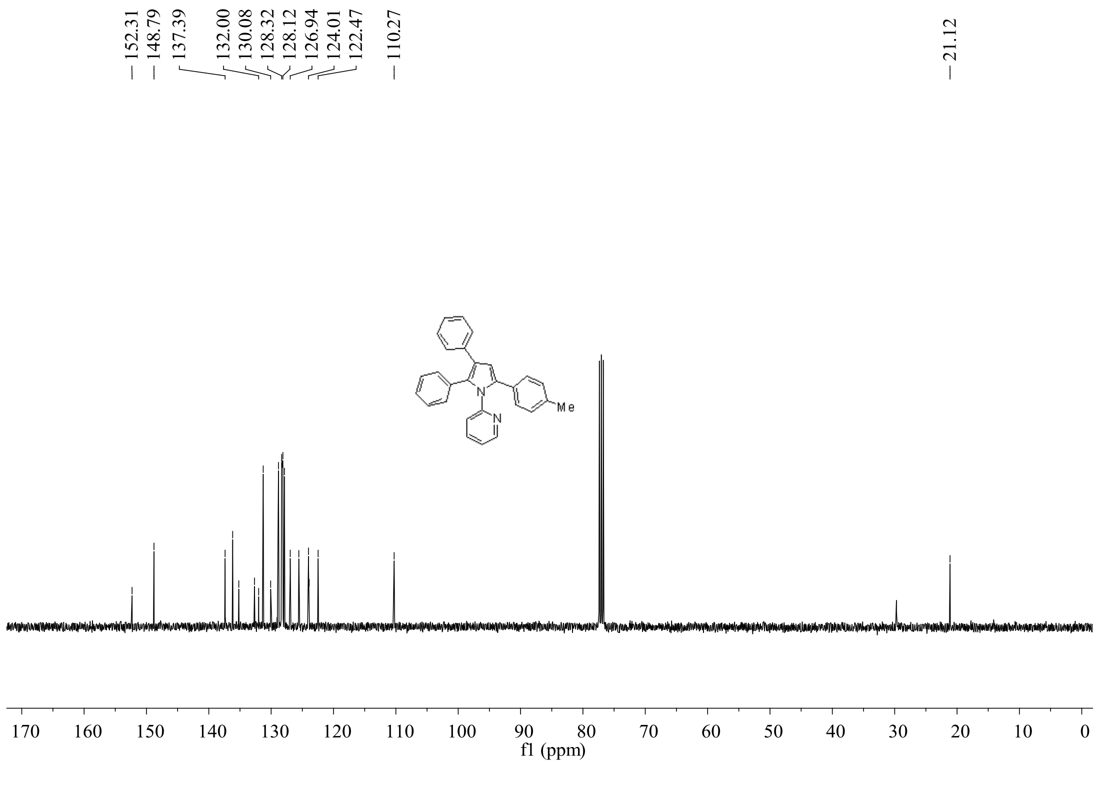
8) 2-（2, 3, 5-Triphenyl-pryyol-1-yl）-pyridine (**3a**) (Using $CDCl_3$ as solvent)



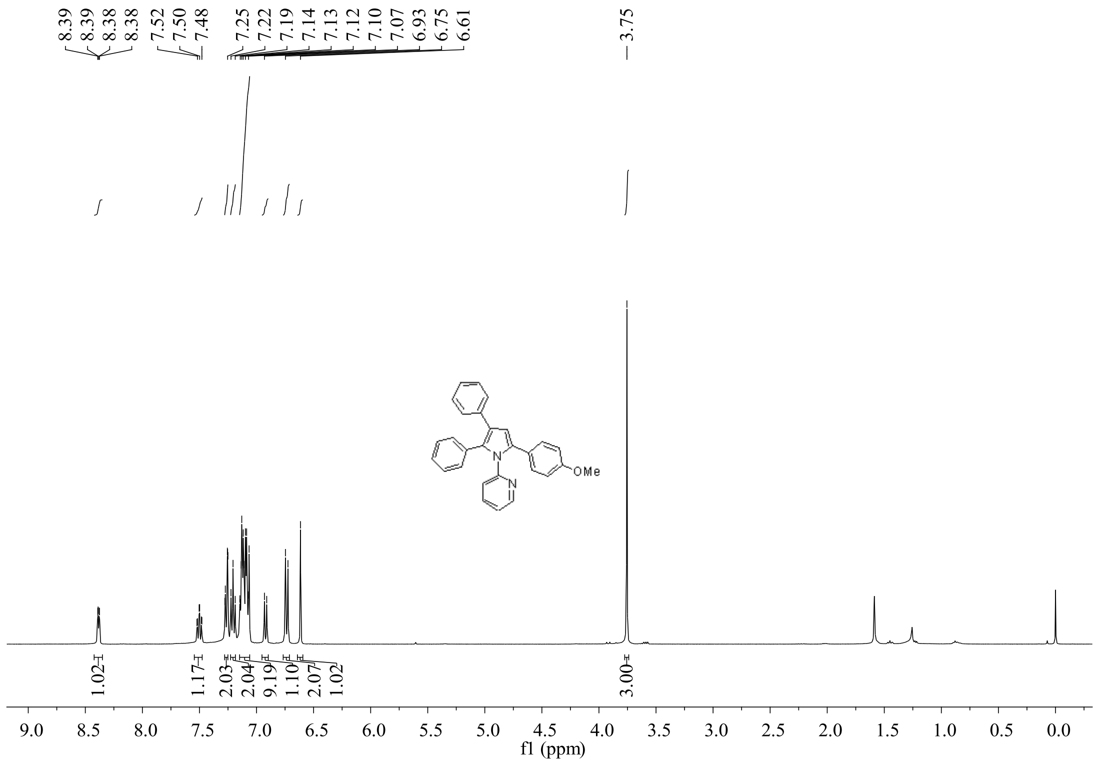


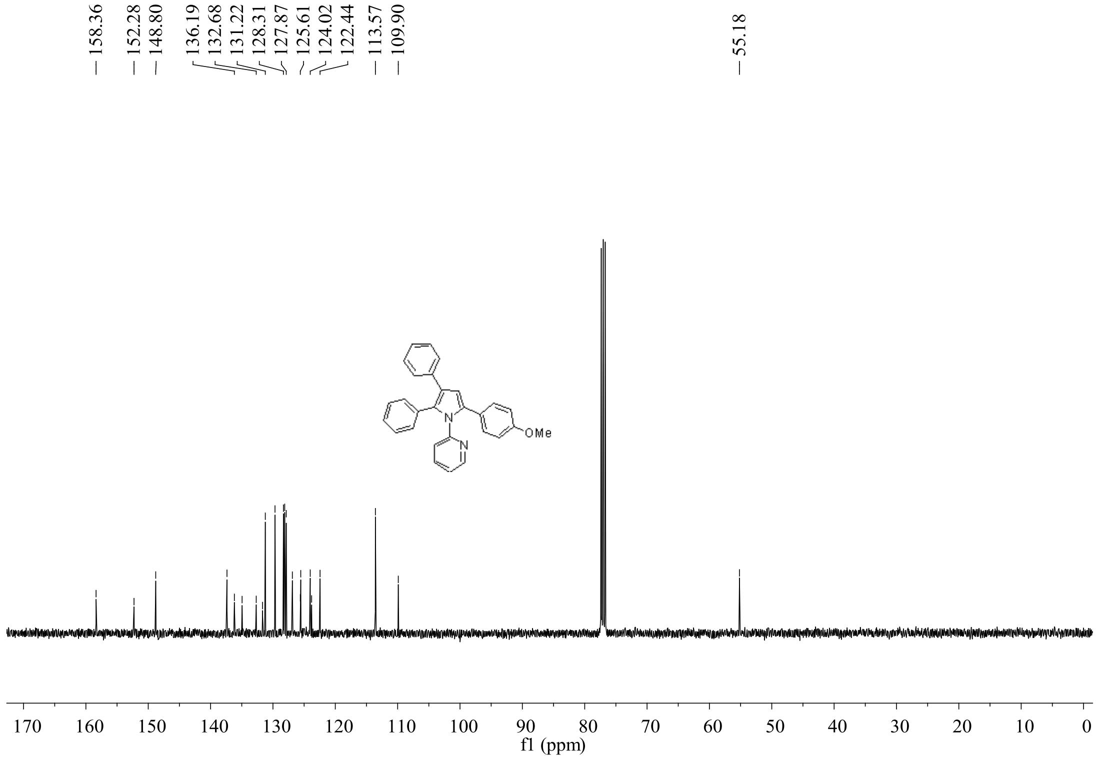
9) 2-（2, 3-Diphenyl-5-p-tolyl-pyrrol-1-yl）-pyridine **(3b)** (Using $CDCl_3$ as solvent)



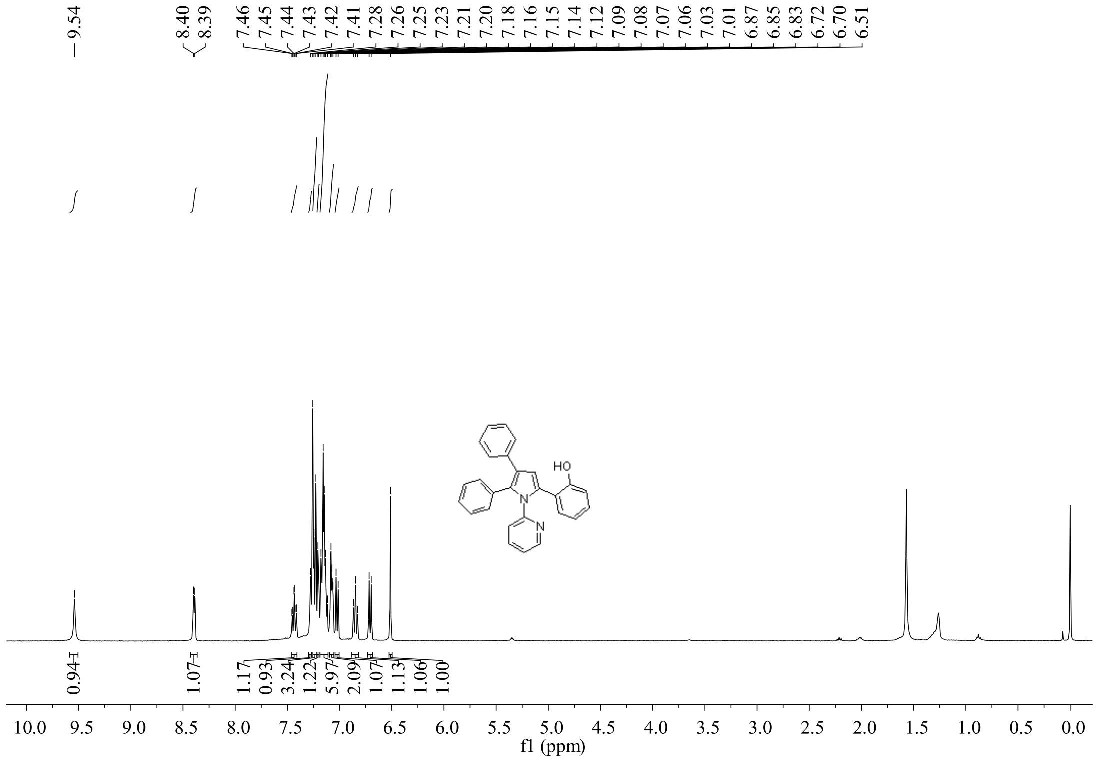


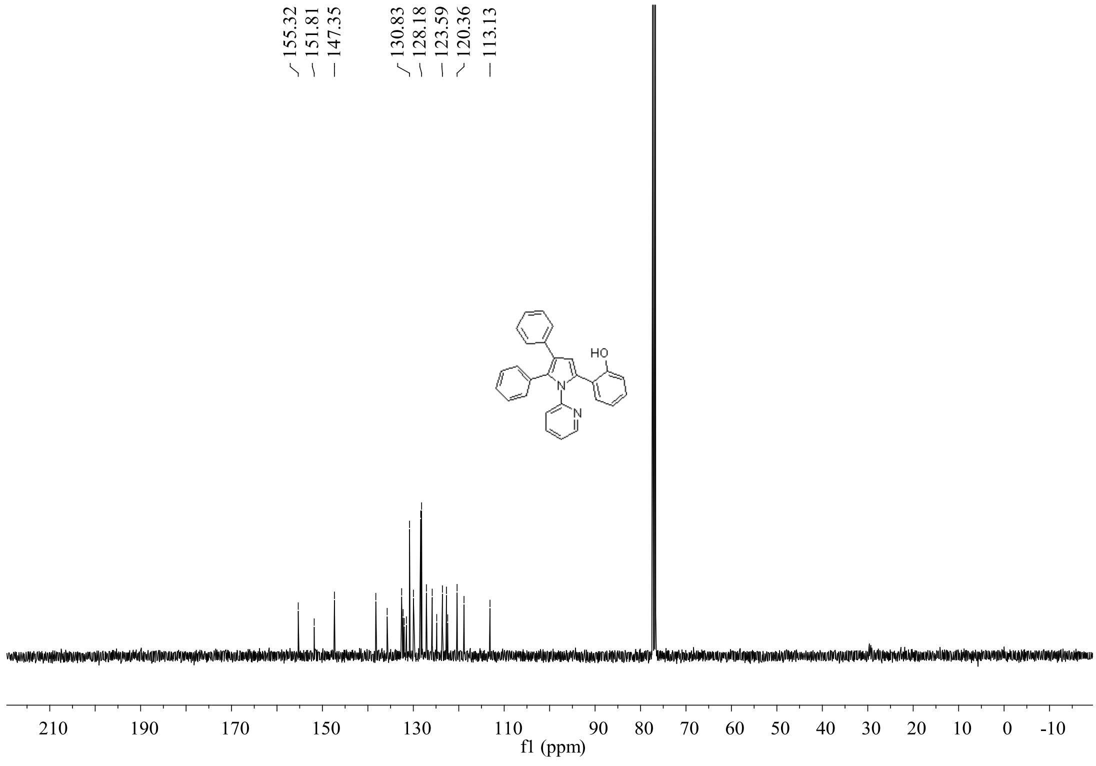
10) 2-[5-(4-Methoxyl-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine **(3c)** (Using $CDCl_3$ as solvent)



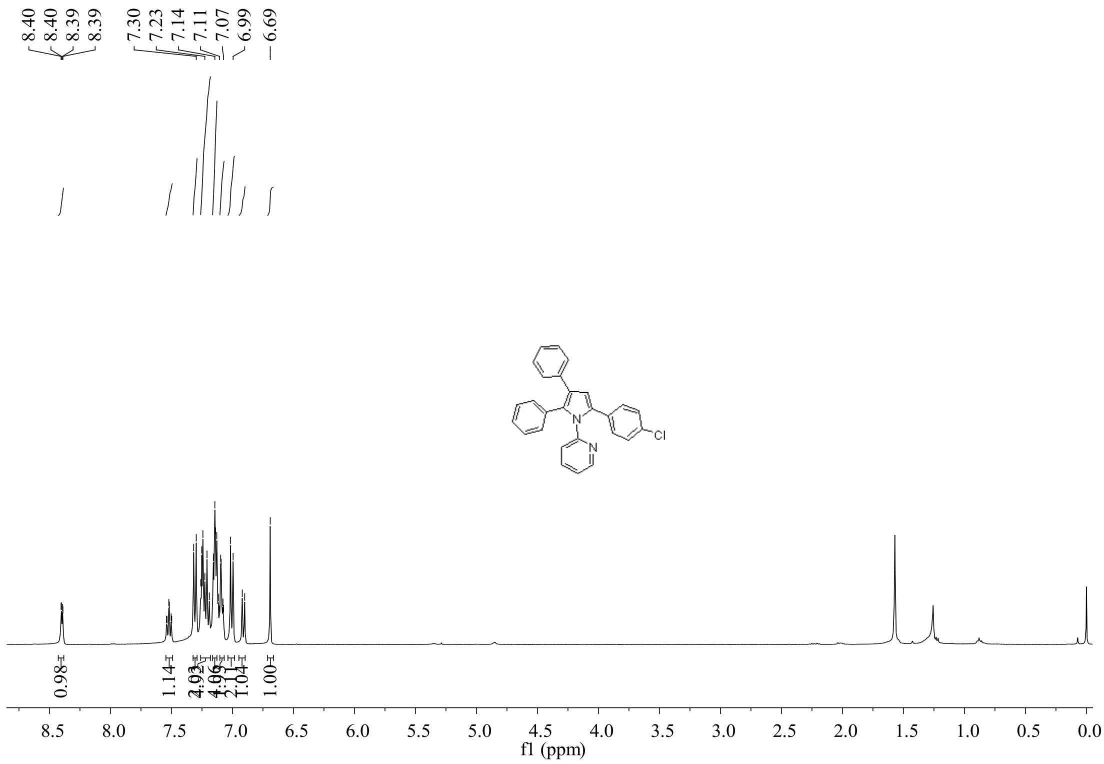


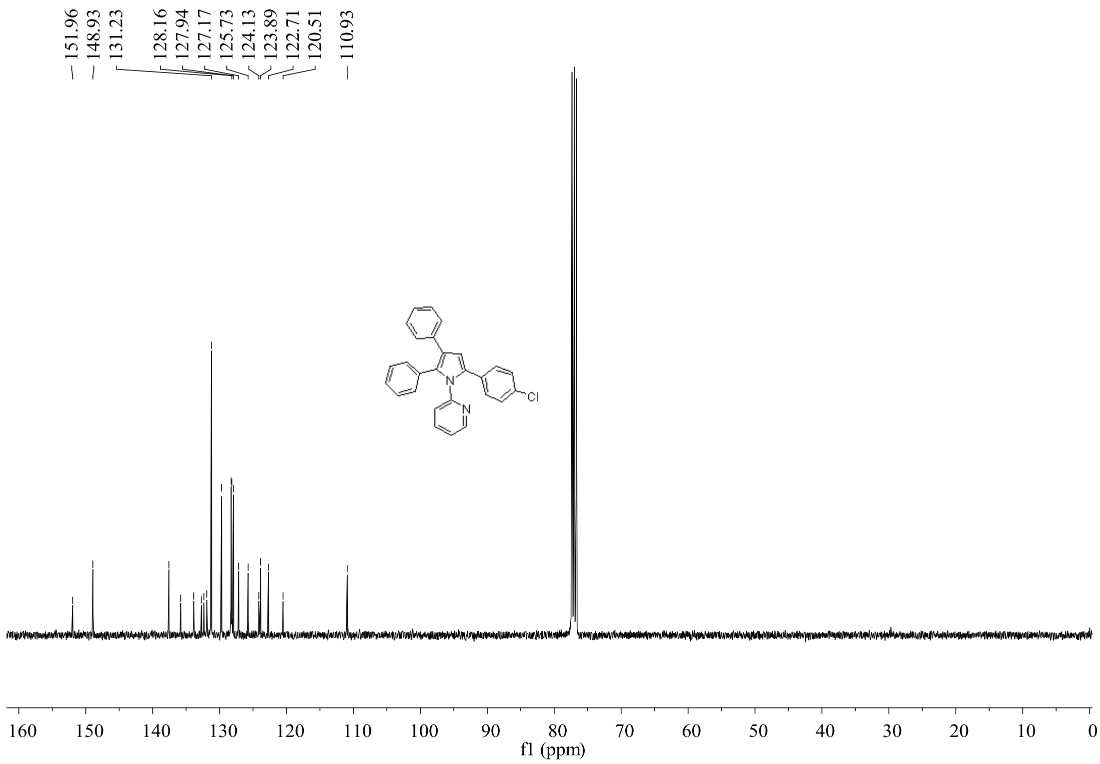
11) 2-(4, 5-Dipheynl-1-pyridin-2-yl-1*H*-pyrrol-2-yl)-phenol **(3d)** (Using $CDCl_3$ as solvent)



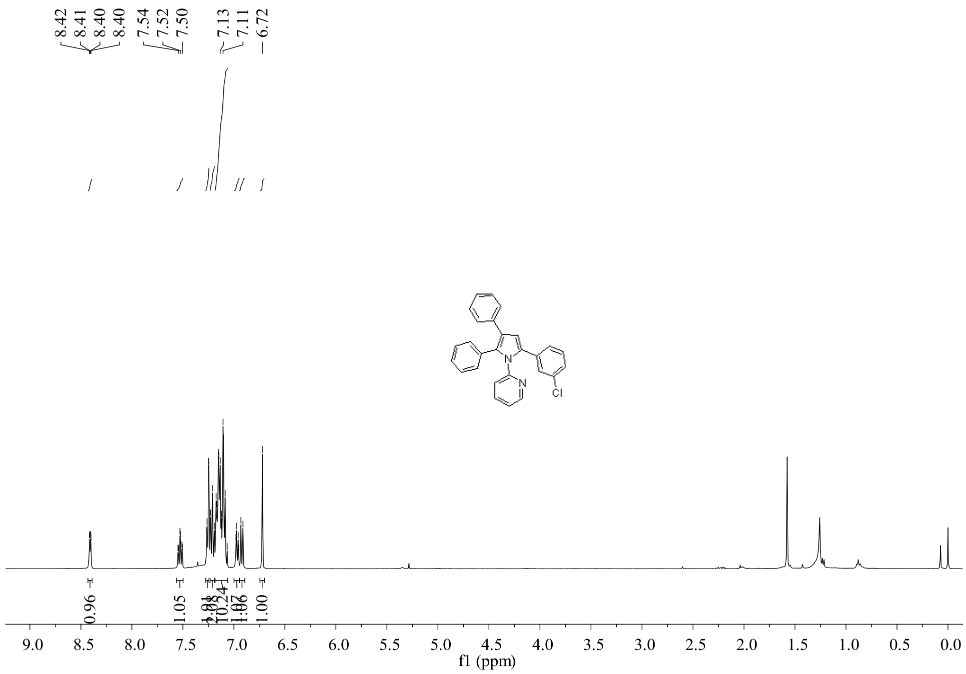


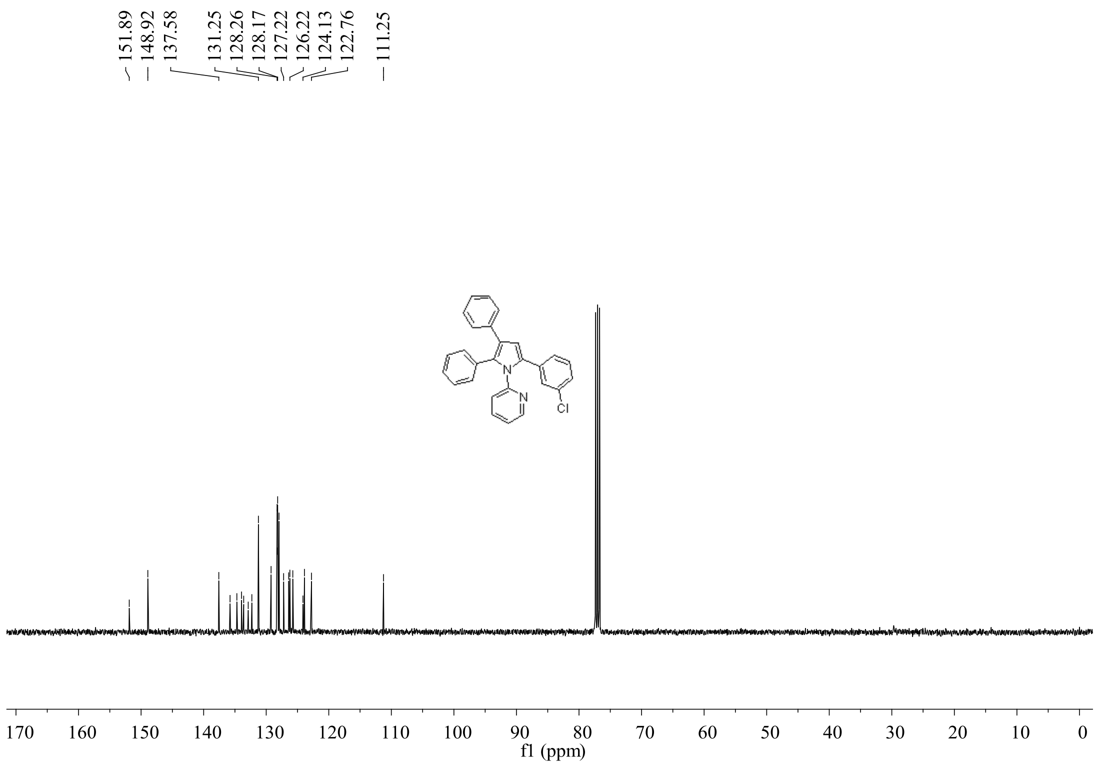
12) 2-[5-(4-Chloro-phenyl-2, 3-diphenyl-2,3-diphenyl-pyrrol-1-yl)-pyridine **(3e)** (Using $CDCl_3$ as solvent)



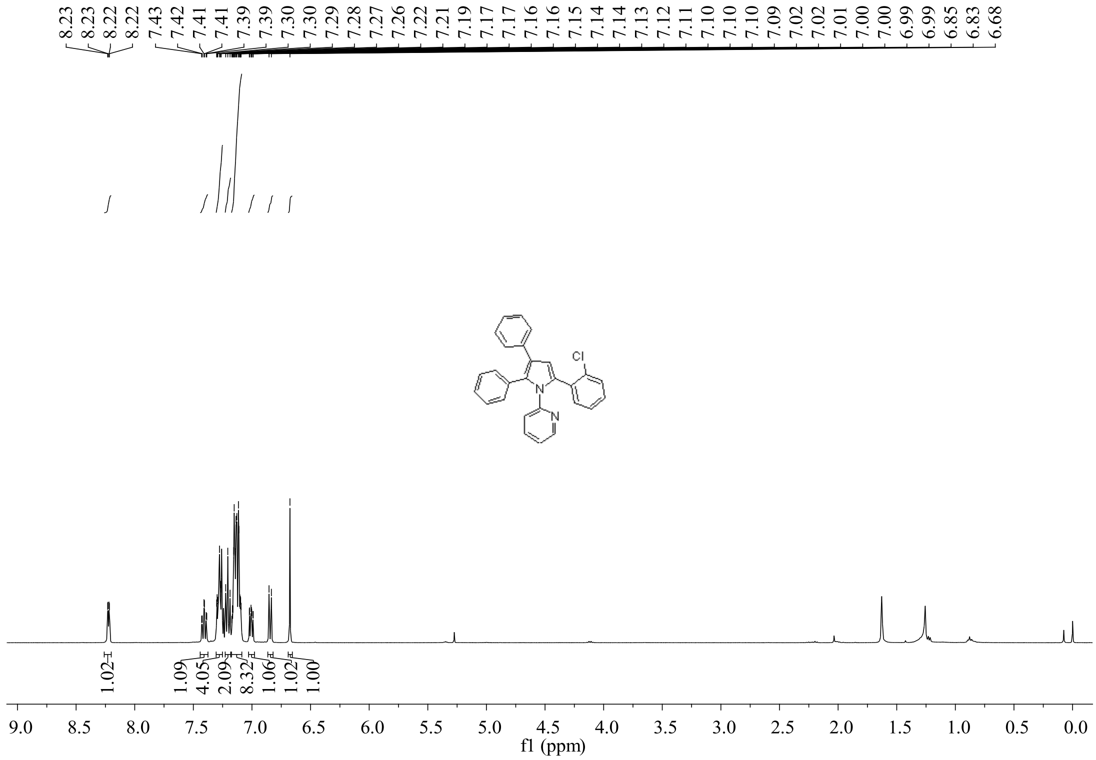


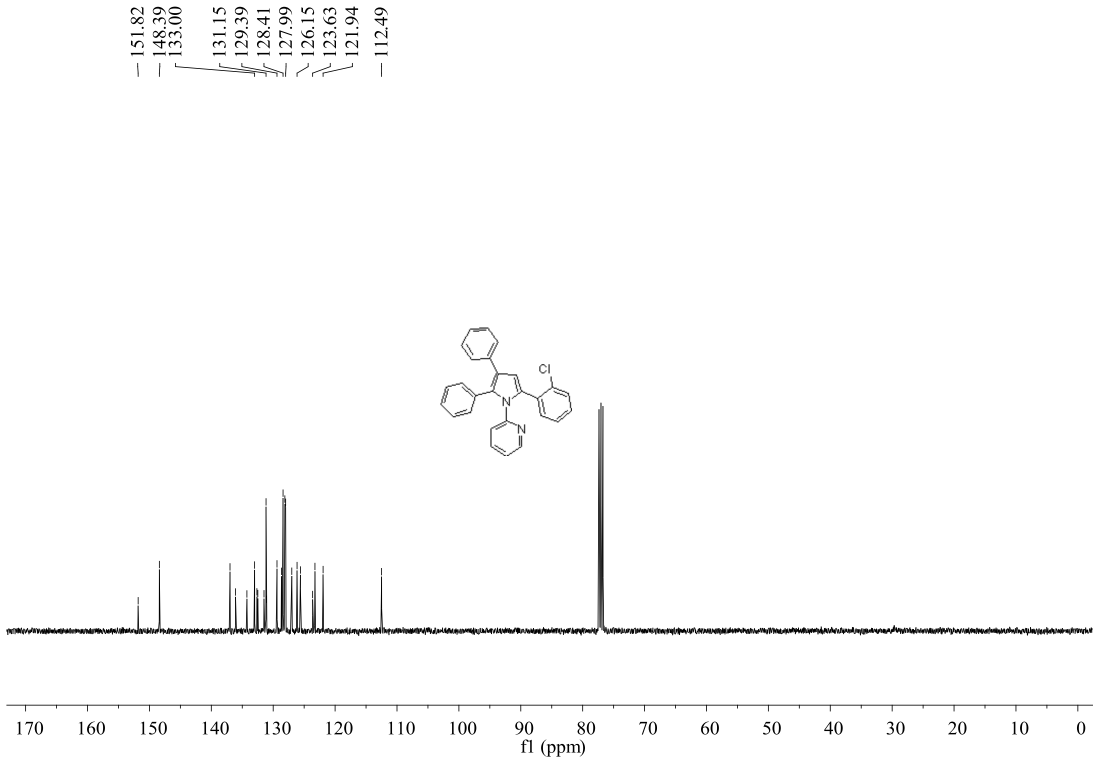
13) 2-[5-(3-Chloro-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine **(3f)** (Using $CDCl_3$ as solvent)



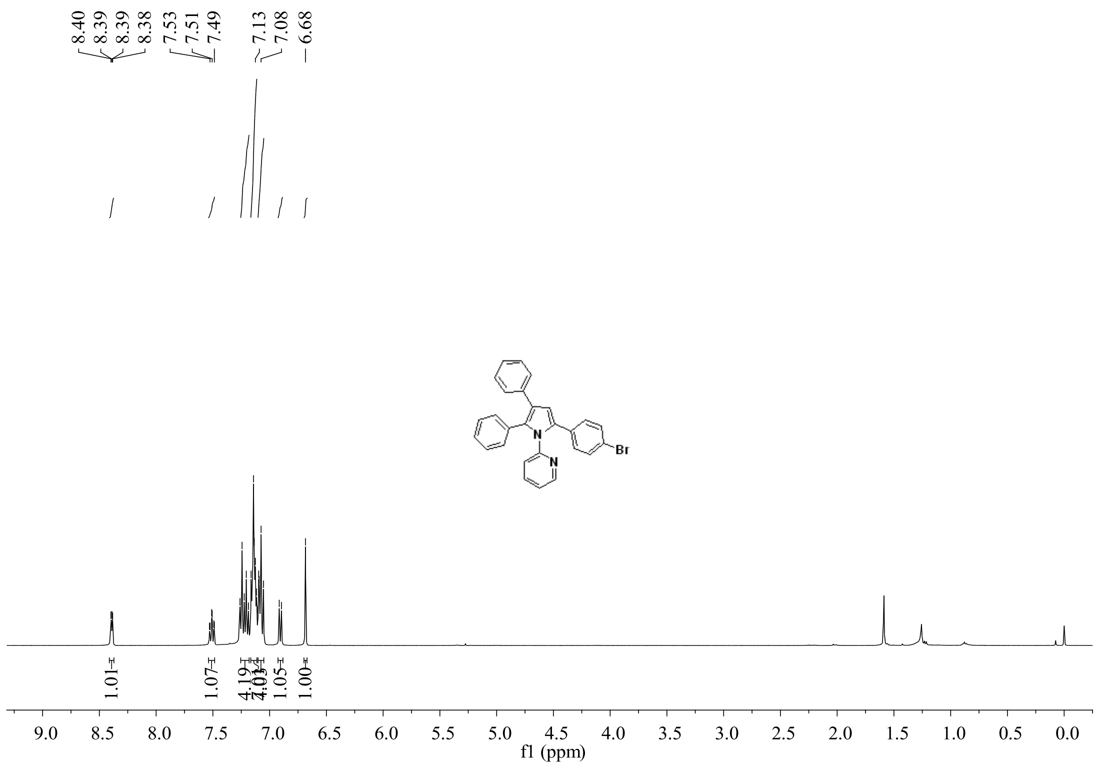


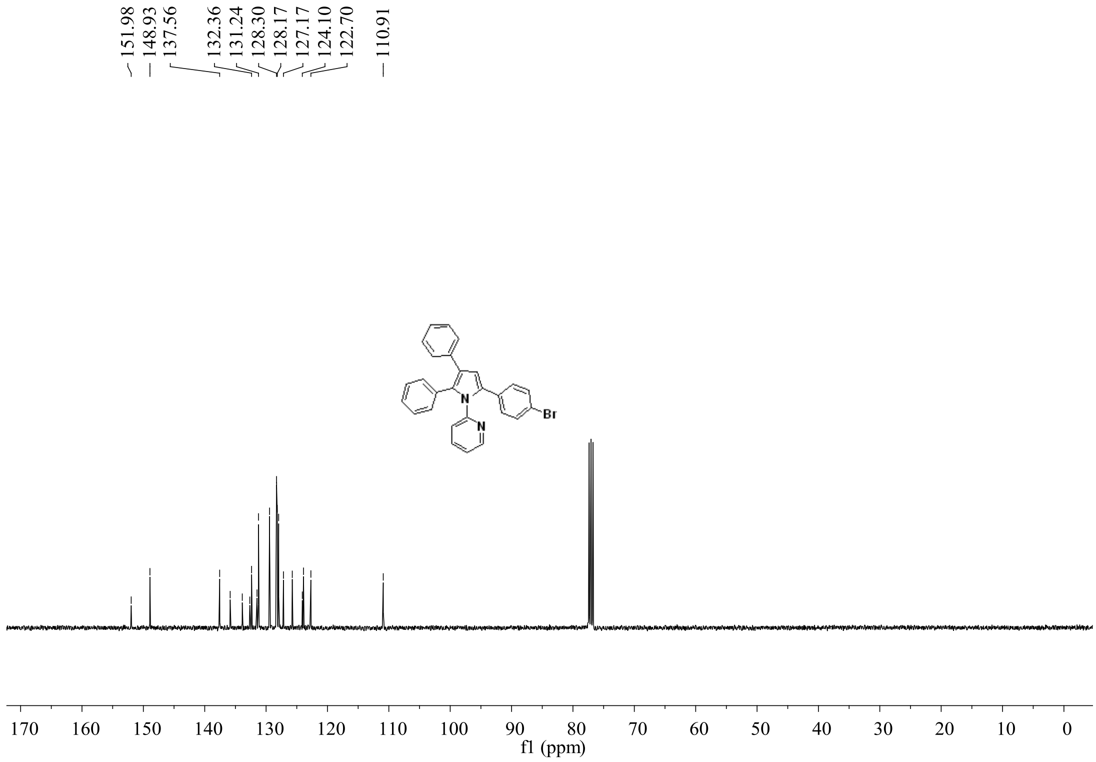
14) 2-[5-(2-Chloro-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine **(3g)** (Using $CDCl_3$ as solvent)



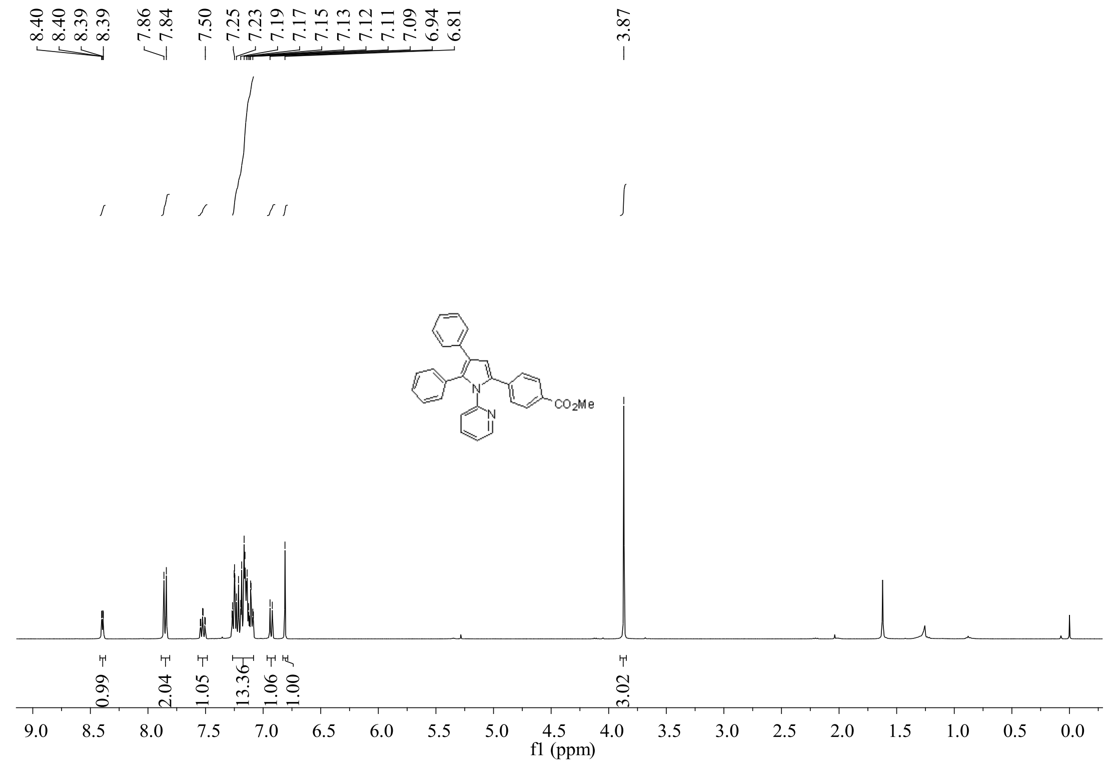


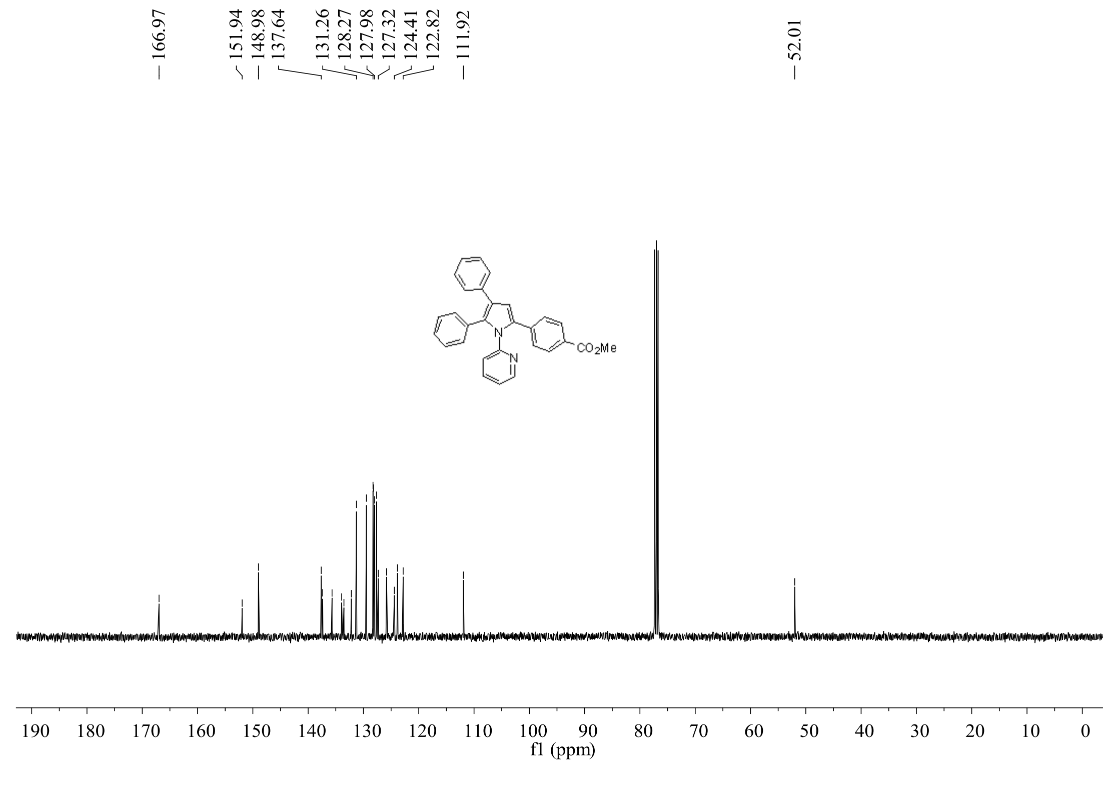
15) 2-[5-(2-Bromo-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine **(3h)** (Using $CDCl_3$ as solvent)



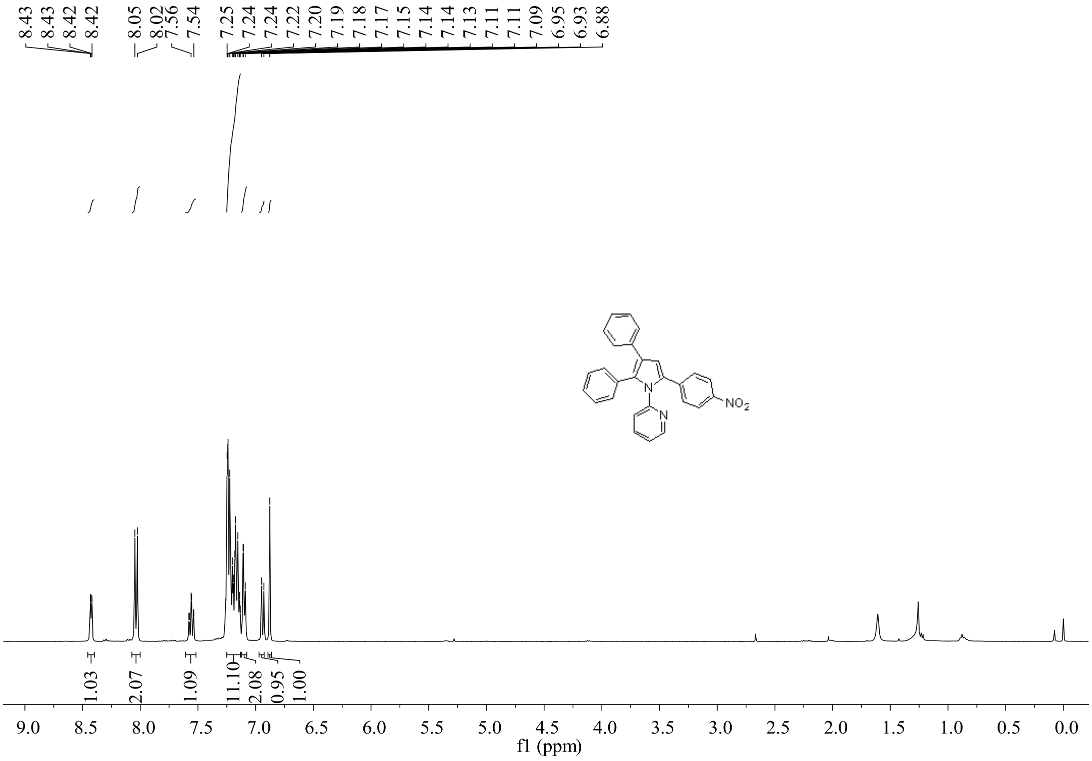


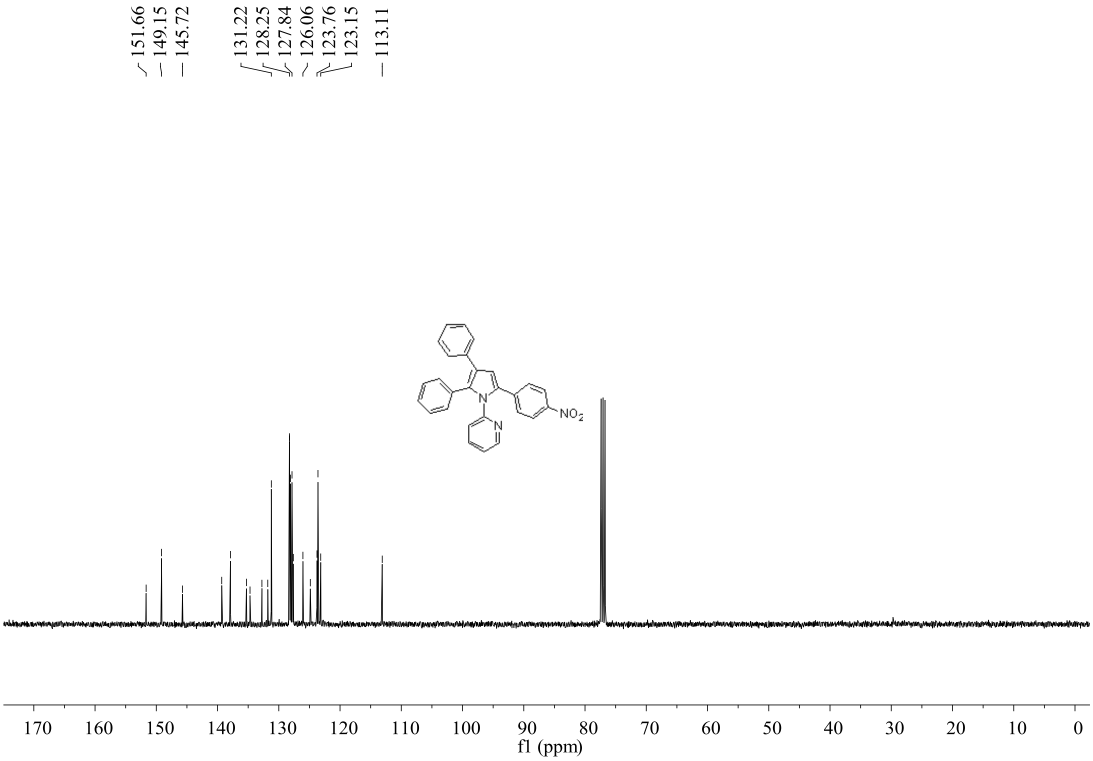
16) 4-(4, 5-Diphenyl-1-pyridin-2yl-1H-pyrrol-2-yl)-benzoic acid methyl ester **(3i)** (Using $CDCl_3$ as solvent)



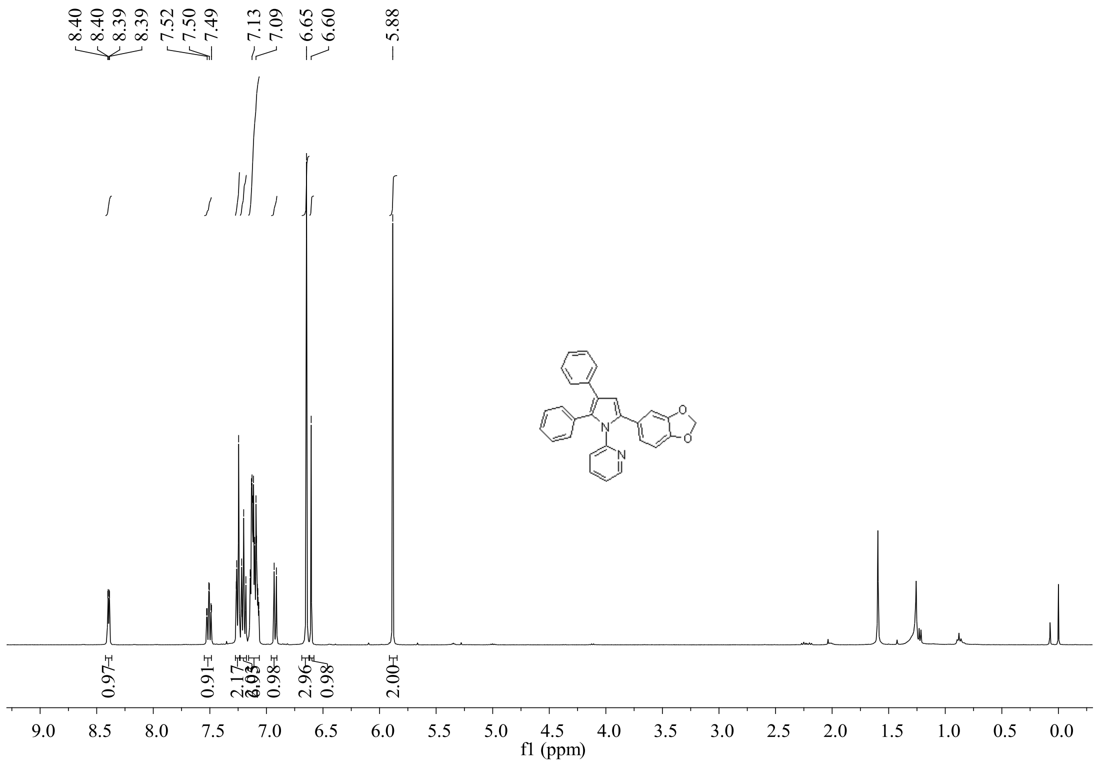


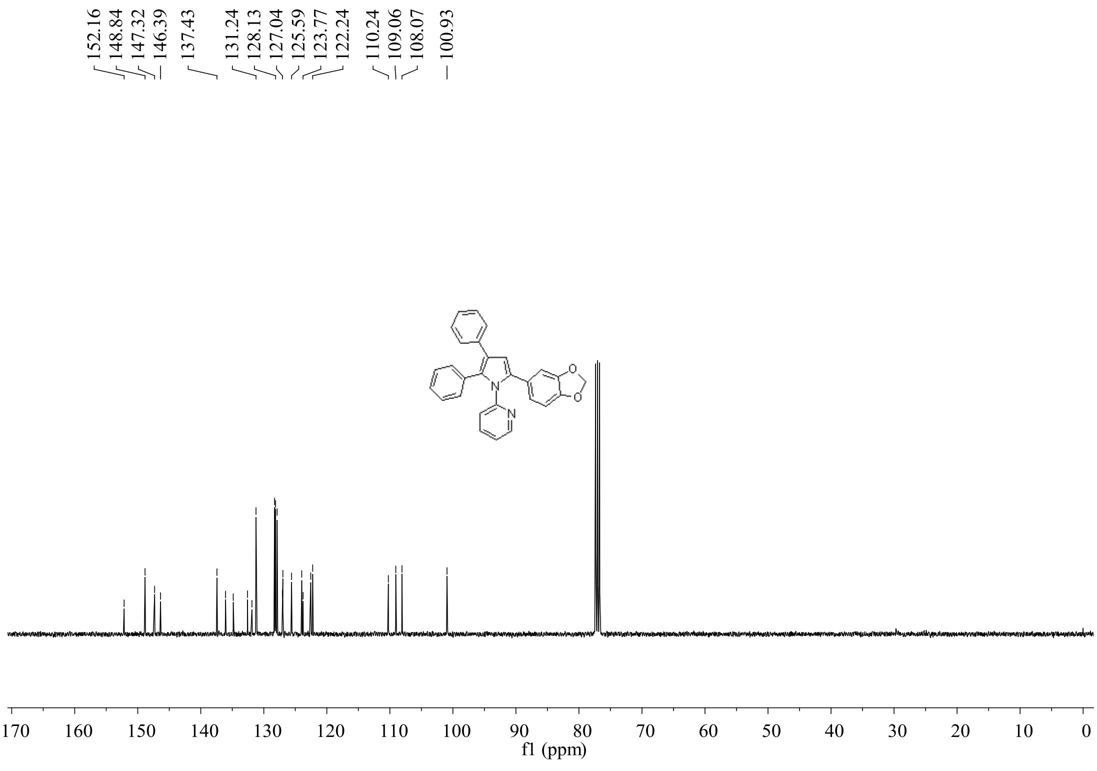
17) 2-[5-(4-Nitro-phenyl)-2, 3-diphenyl-pyrrol-1-yl]-pyridine **(3j)** (Using $CDCl_3$ as solvent)



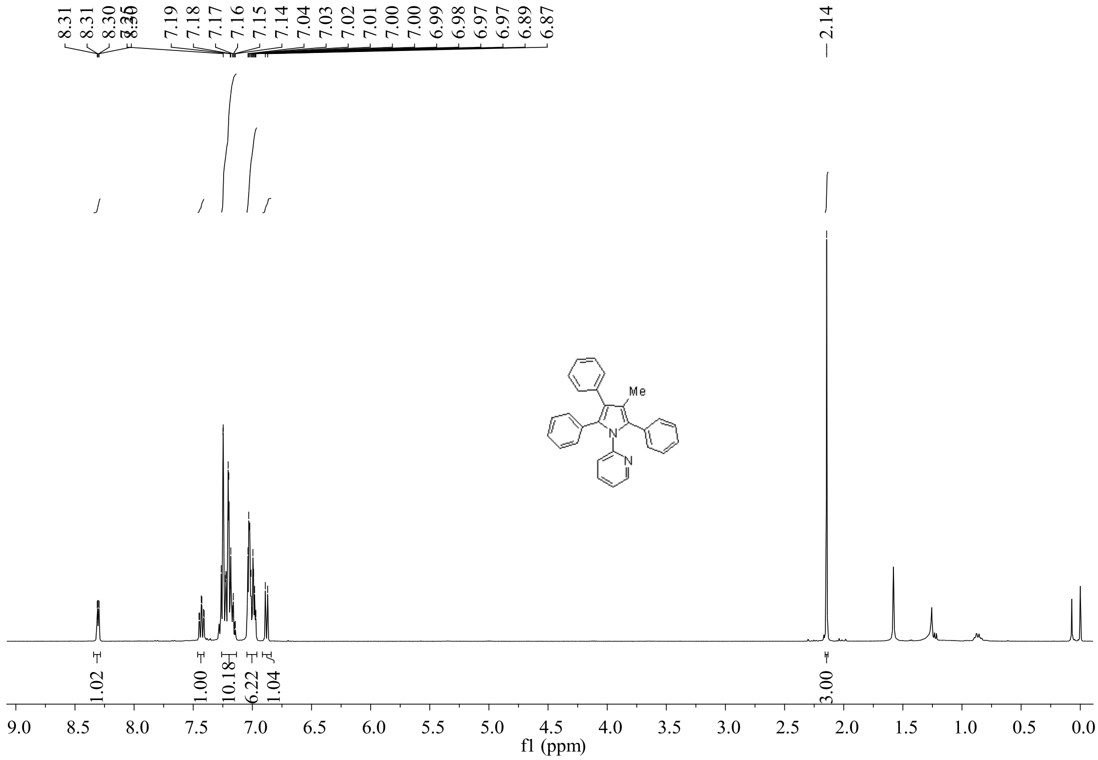


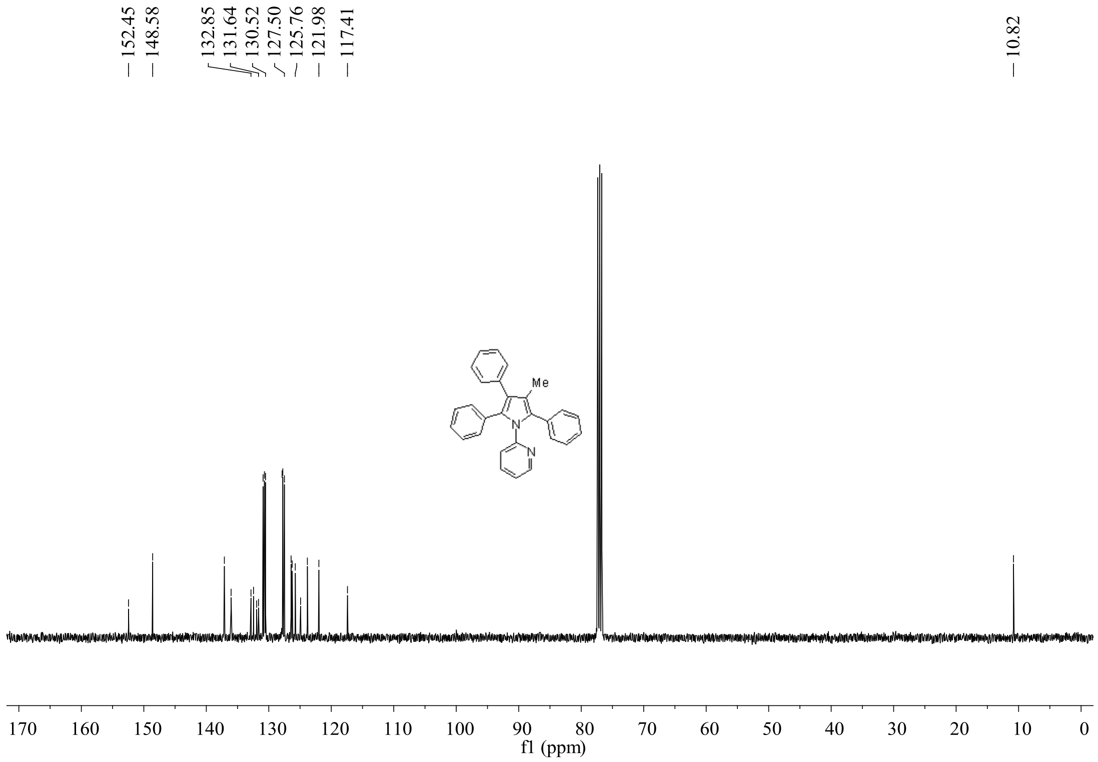
18) 2-(5-Benzo [1, 3] dioxol-5-yl-2,3-diphenyl-pyrrol-1-yl)-pyridine **(3k)** (Using $CDCl_3$ as solvent)



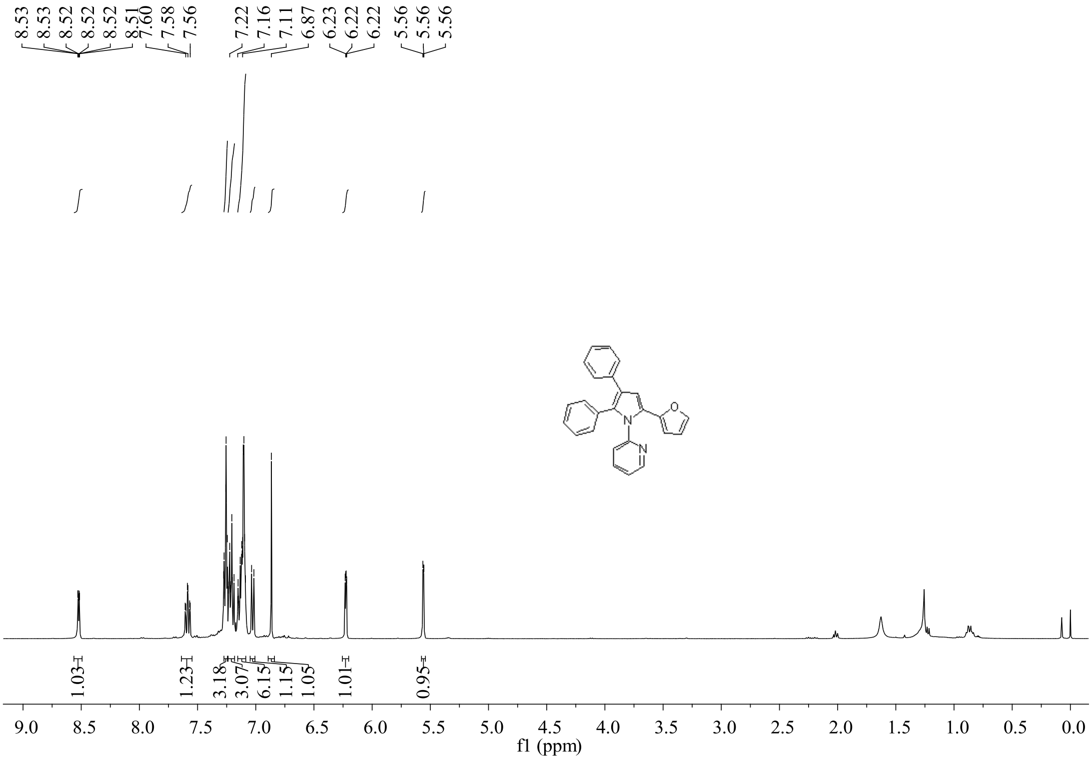


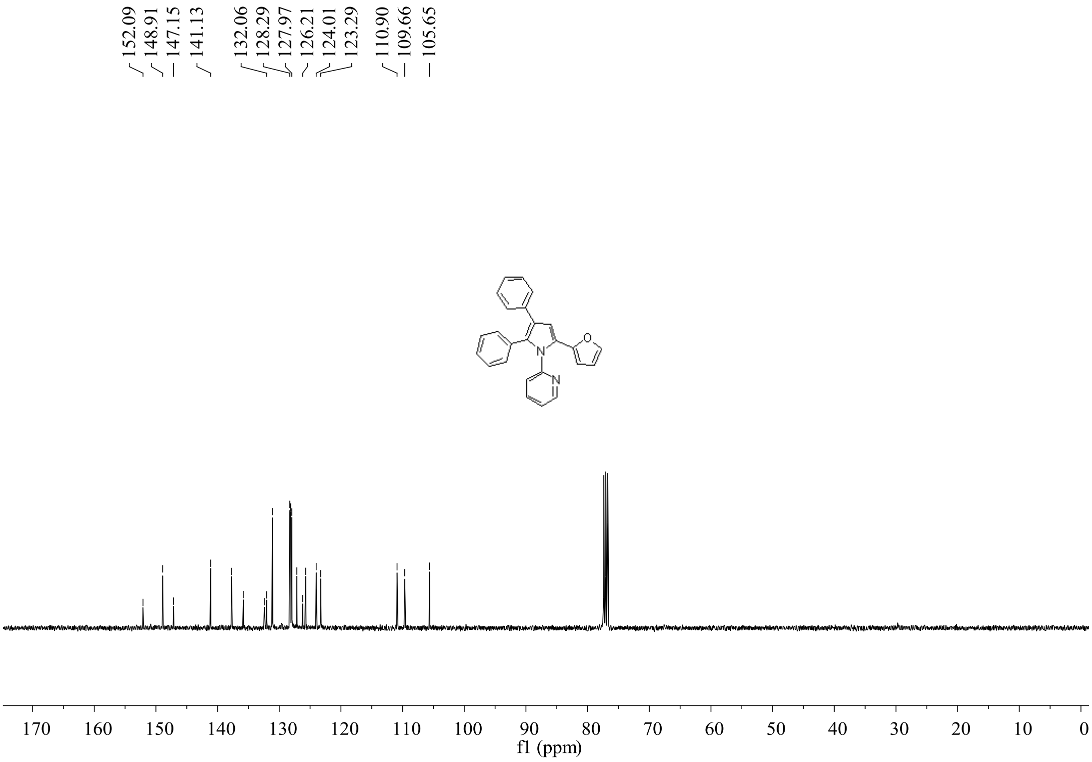
19) 2-(3-Methyl-2, 4, 5-triphenyl-pyrrol-1-yl)-pyridine **(3l)** (Using $CDCl_3$ as solvent)



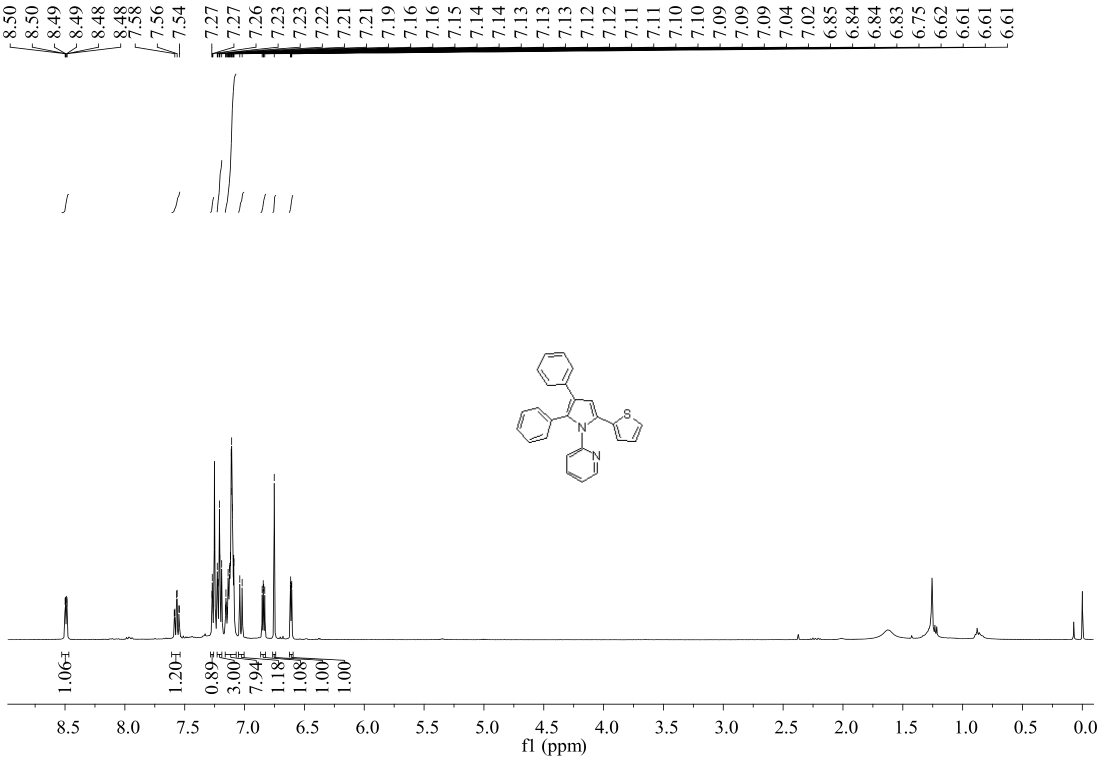


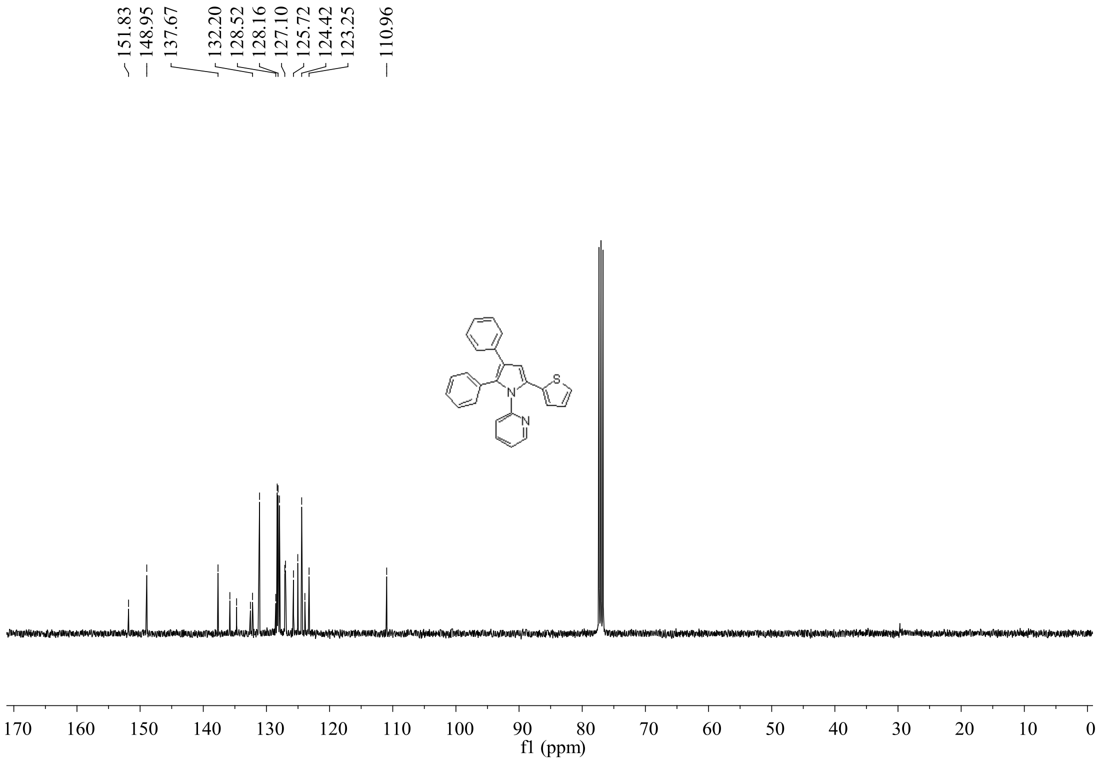
20) 2-(5-Furan-2-yl-2, 3-diphenyl-pyrrol-1-yl)-pyridine **(3m)** (Using $CDCl_3$ as solvent)



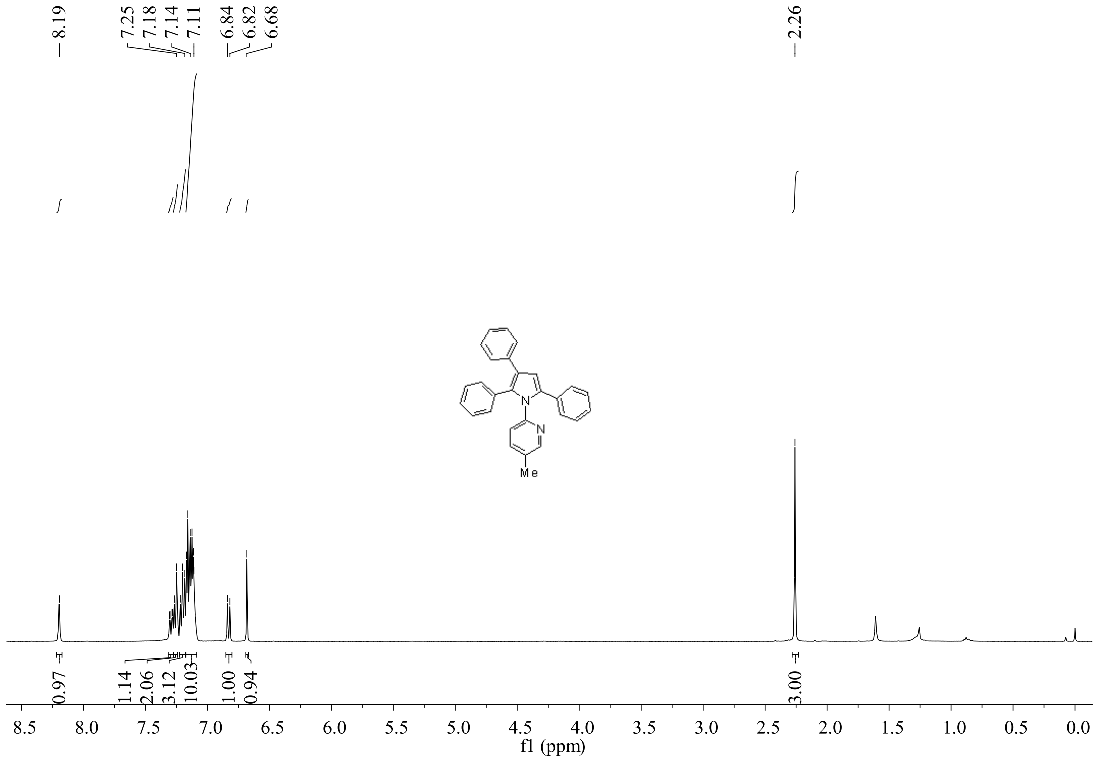


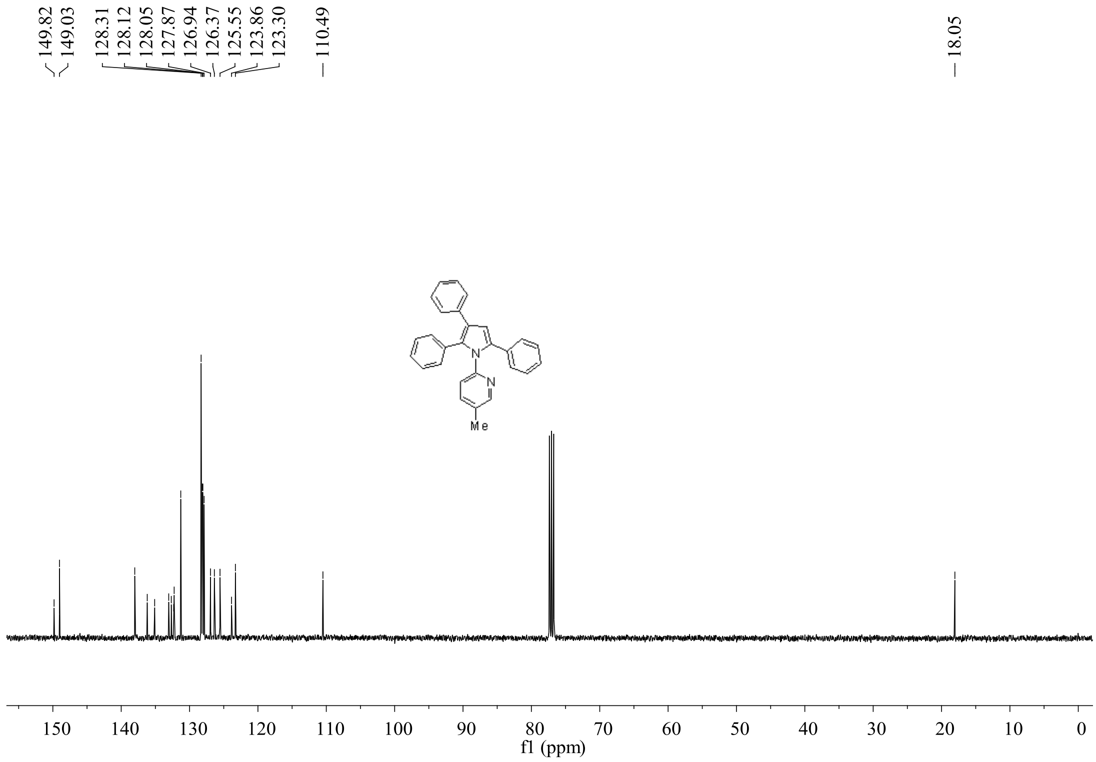
21) 2-(2, 3-Diphenyl-5-thiophen-2-yl-pyrrol-1-yl)-pyridine **(3n)** (Using $CDCl_3$ as solvent)



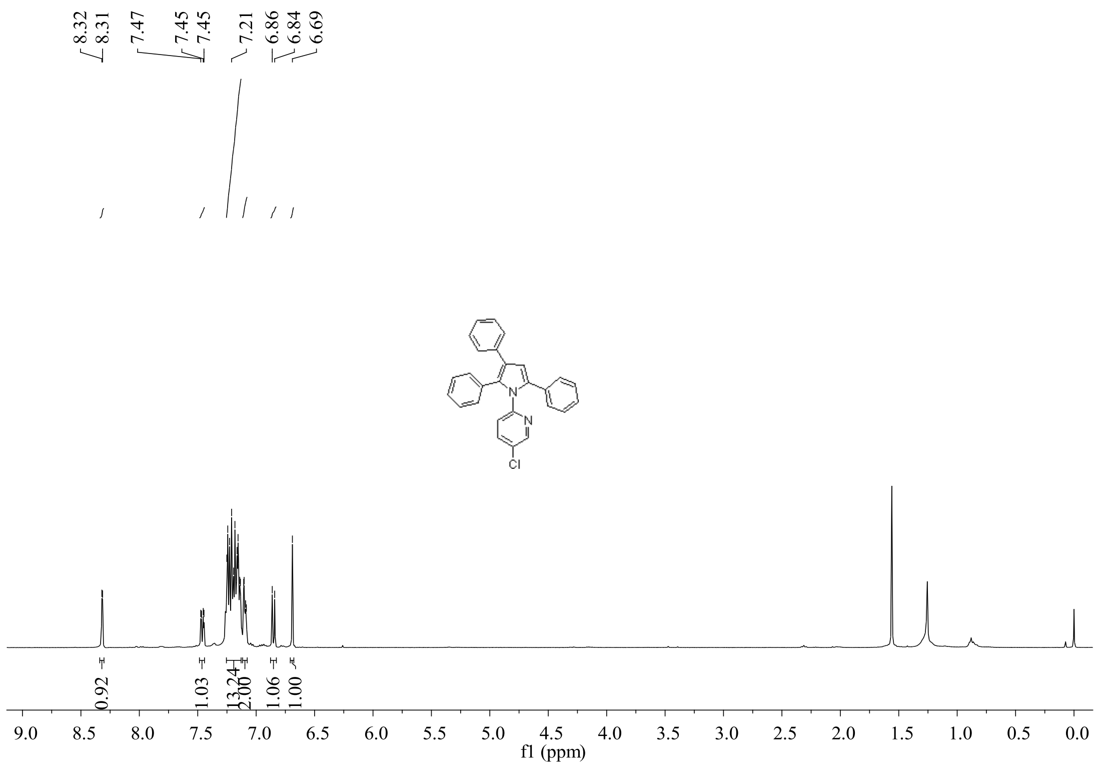


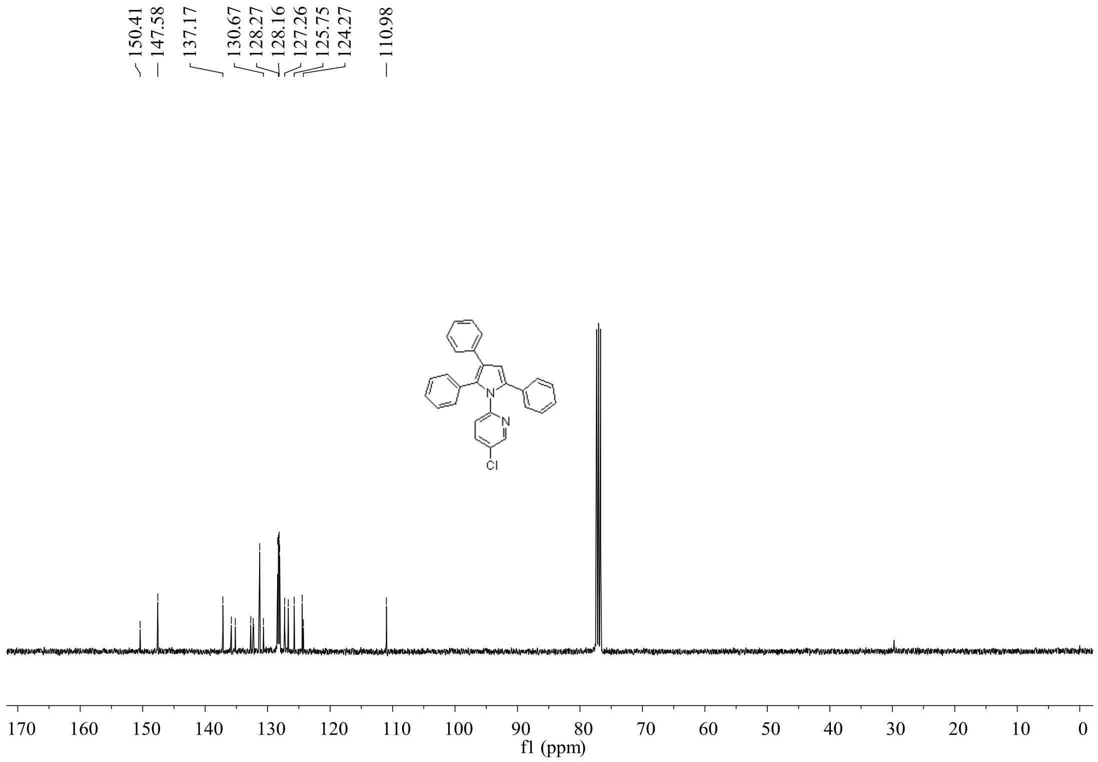
22) 5-Methyl-2-(2, 3, 5-triphenyl-pyrrol-1-yl)-pyridine **(3o)** (Using $CDCl_3$ as solvent)



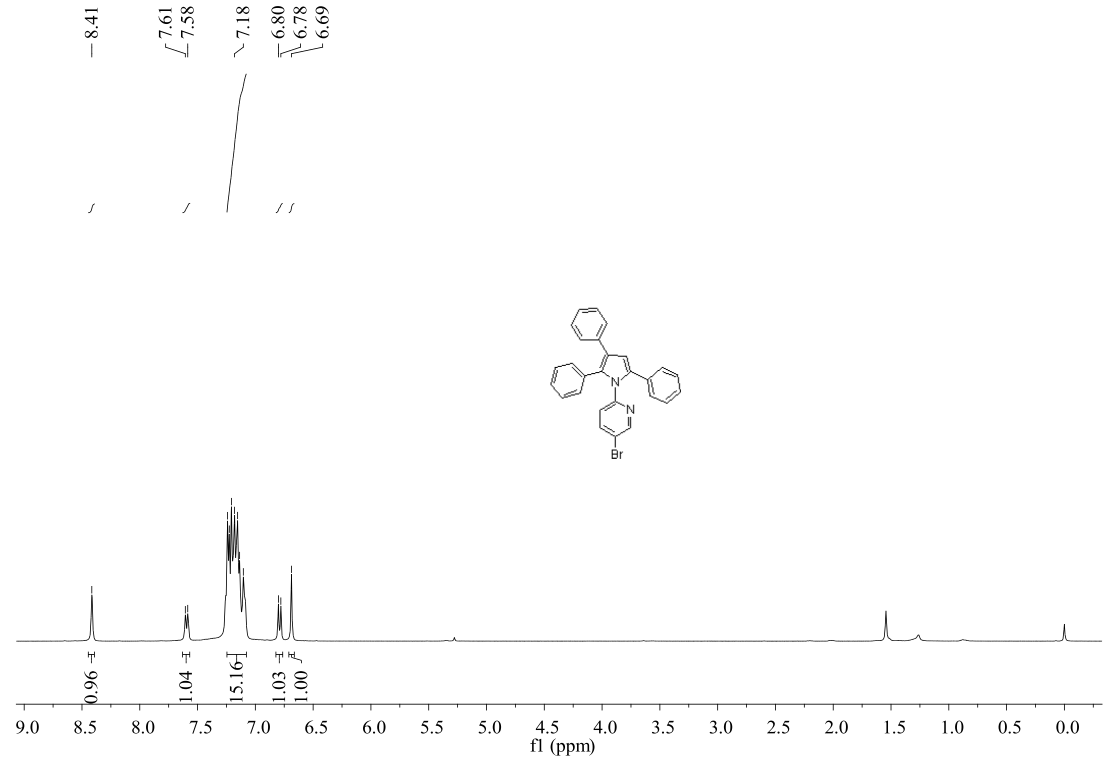


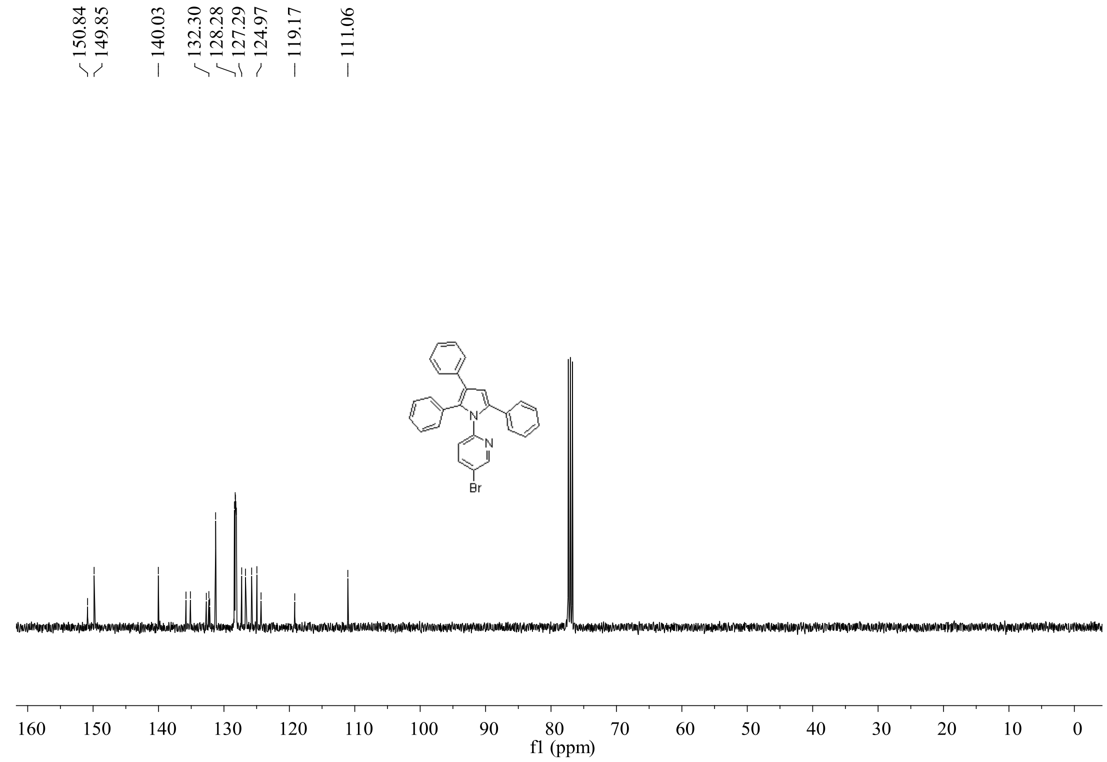
23) 5-Chloro-2-(2, 3, 5-triphenyl-pyrrol-1-yl)-pyridine **(3p)** (Using $CDCl_3$ as solvent)



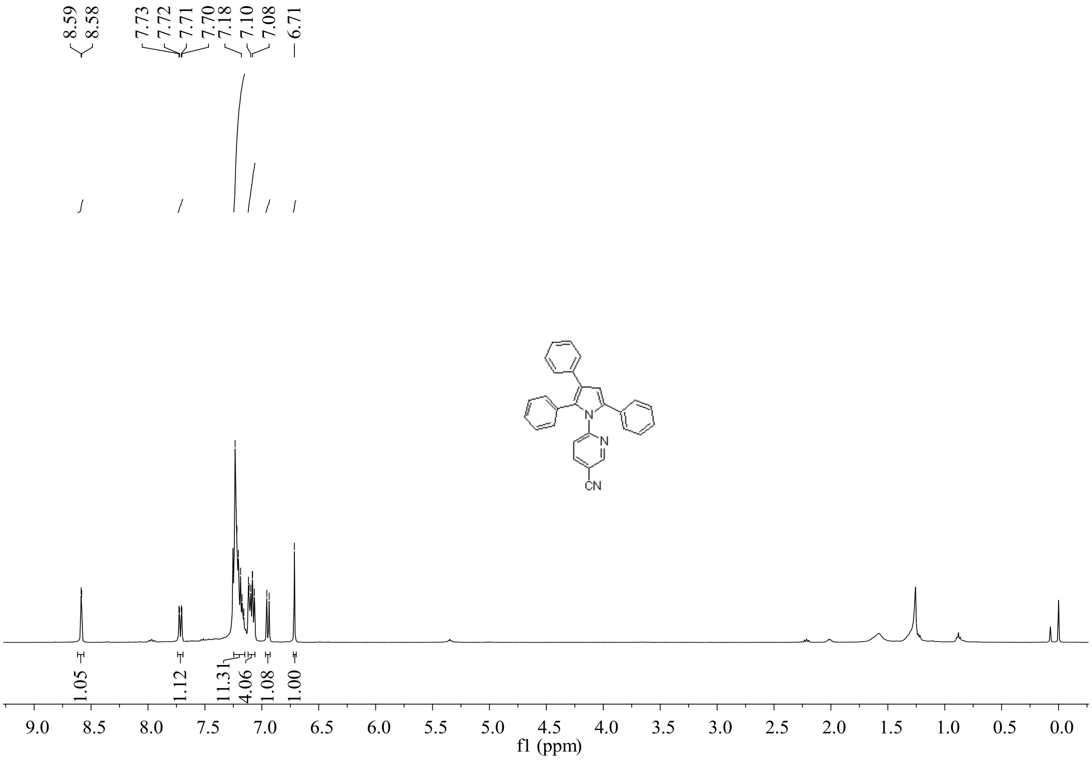


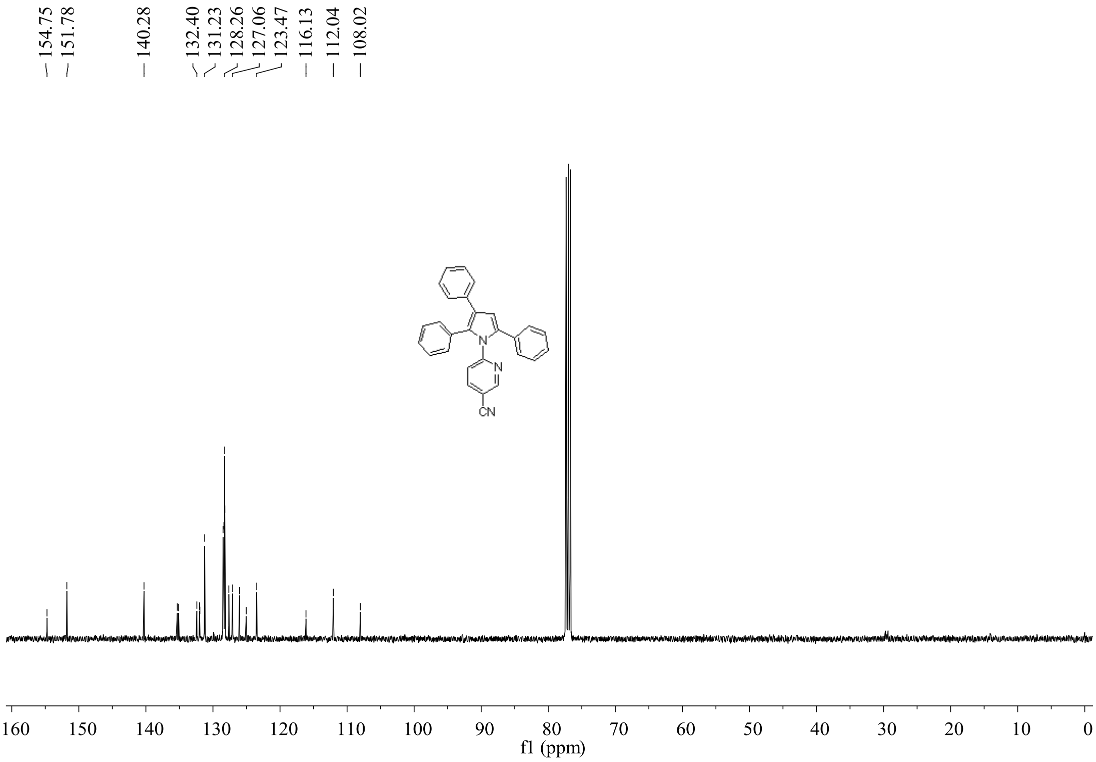
24) 5-Bromo-2-(2, 3, 5-triphenyl-pyrrol-1-yl)-pyridine **(3q)** (Using $CDCl_3$ as solvent)



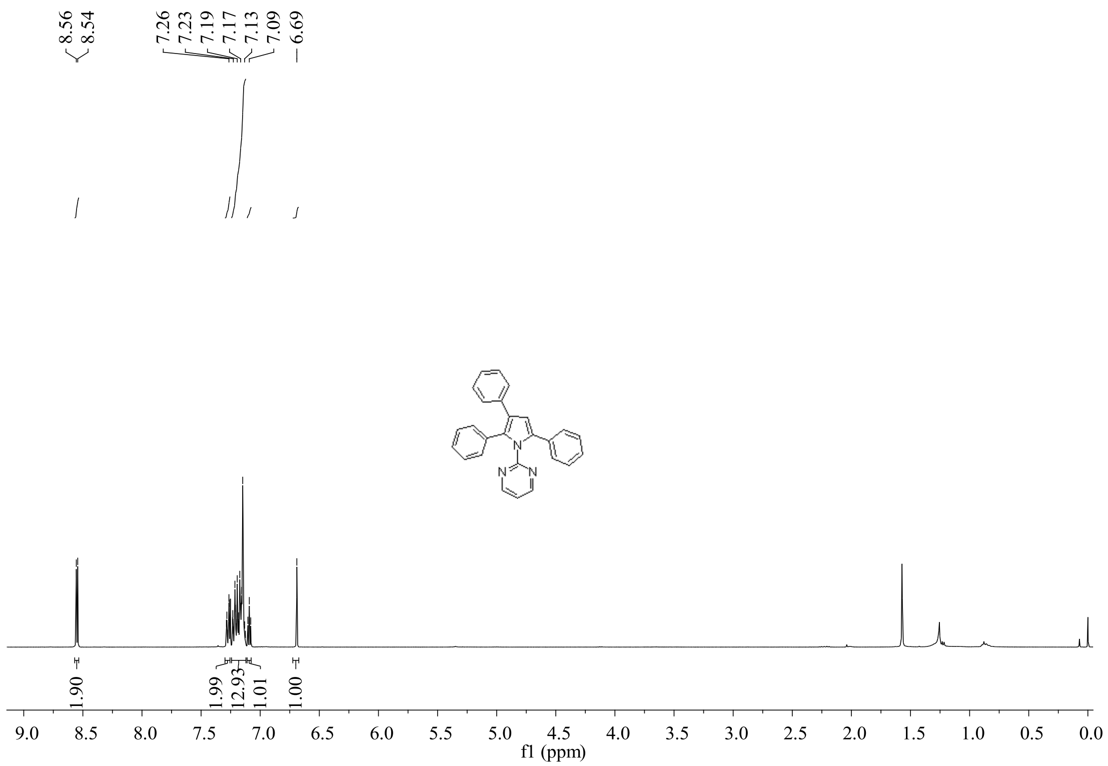


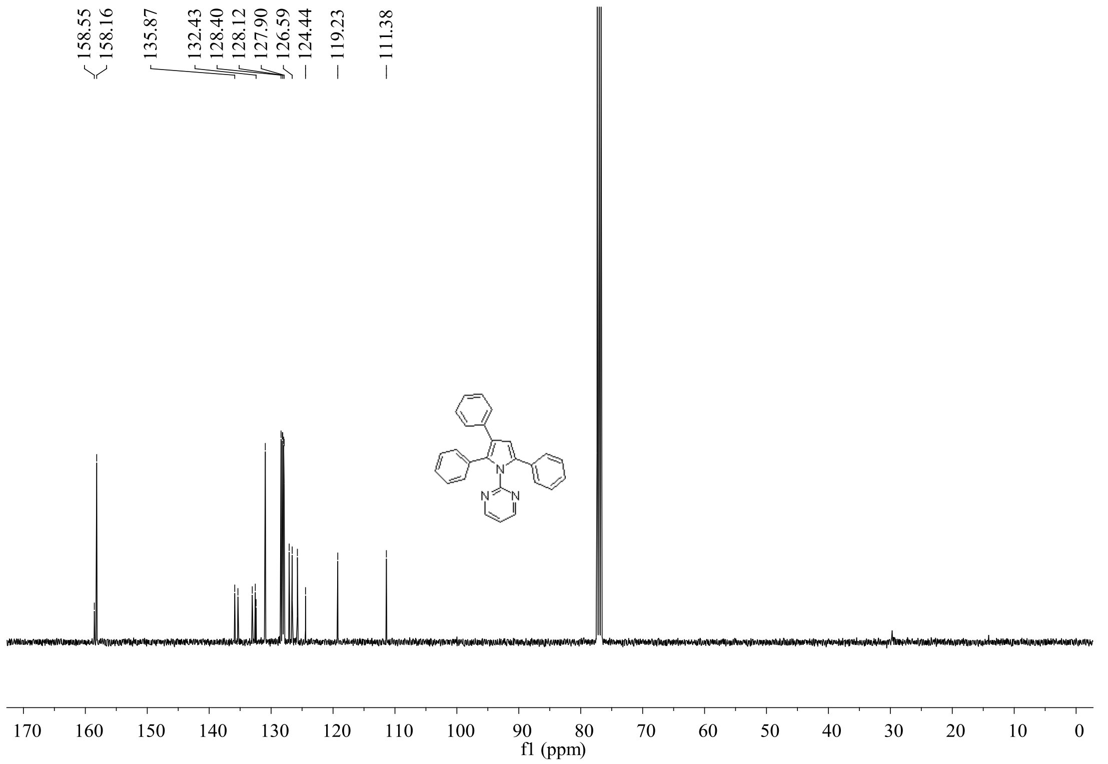
25) 6-(2, 3, 5-Triphenyl-pyrrol-1-yl)-nicotinonitrile **(3r)** (Using $CDCl_3$ as solvent)



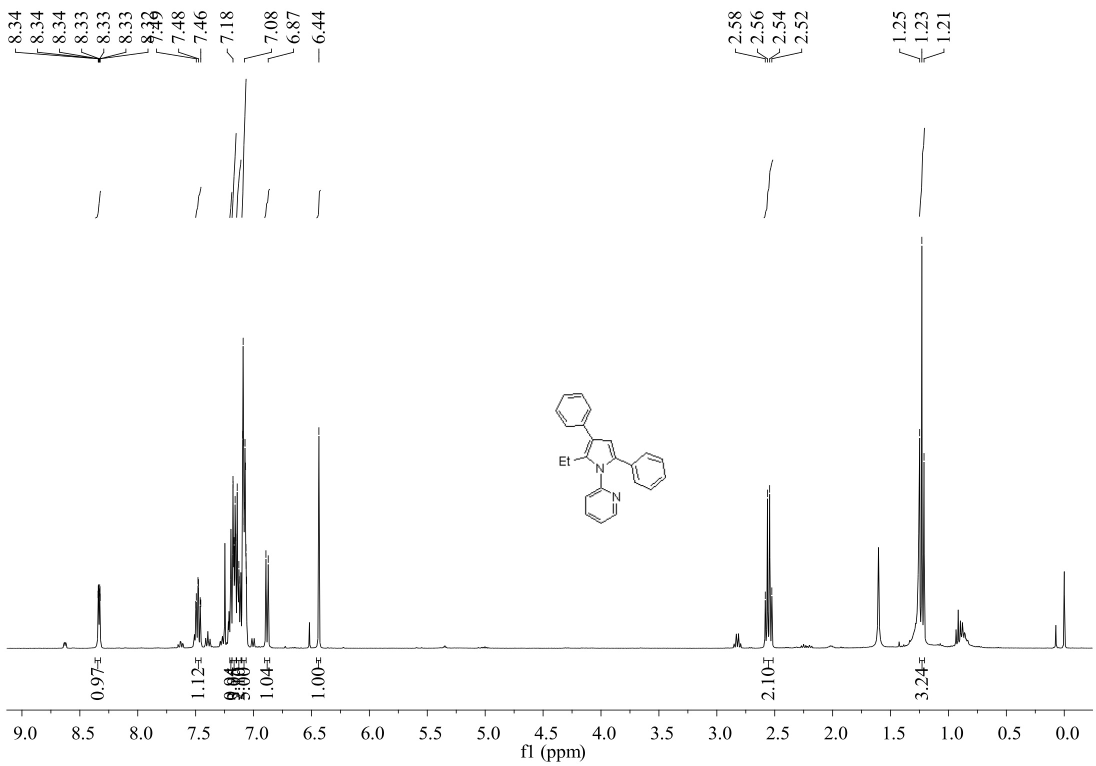


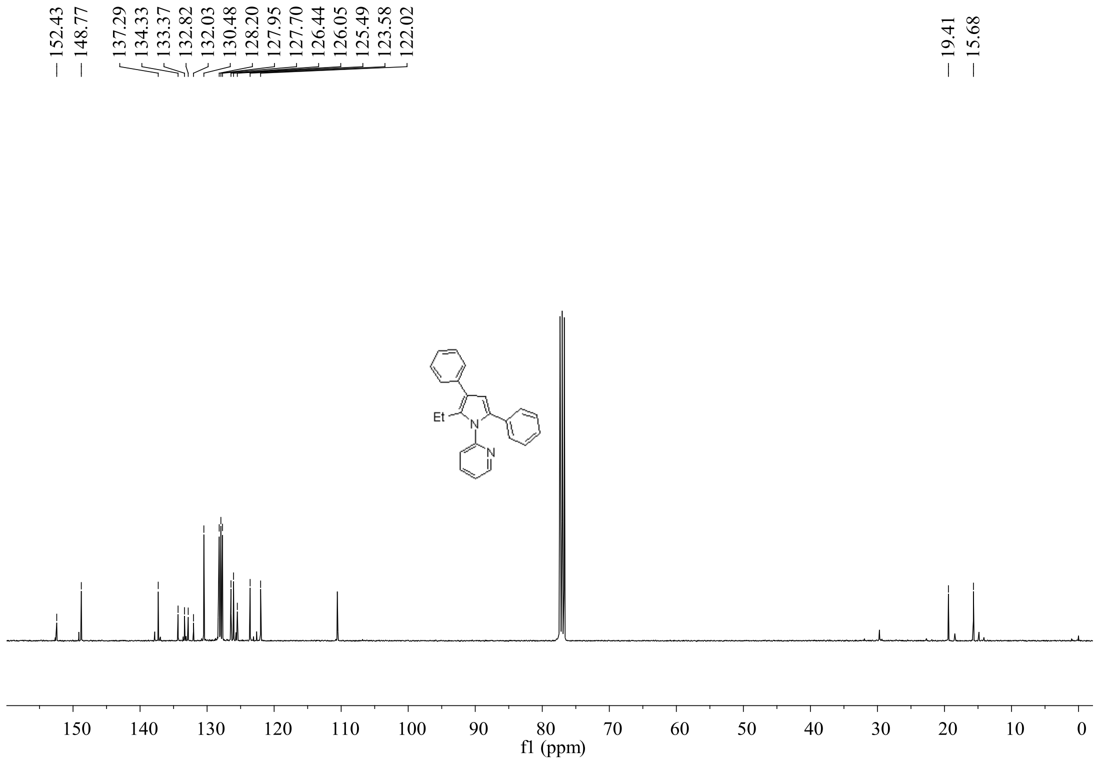
26) 2-(2, 3, 5-Triphenyl-pyrrol-1-yl)-pyrimidine **(3s)** (Using $CDCl_3$ as solvent)



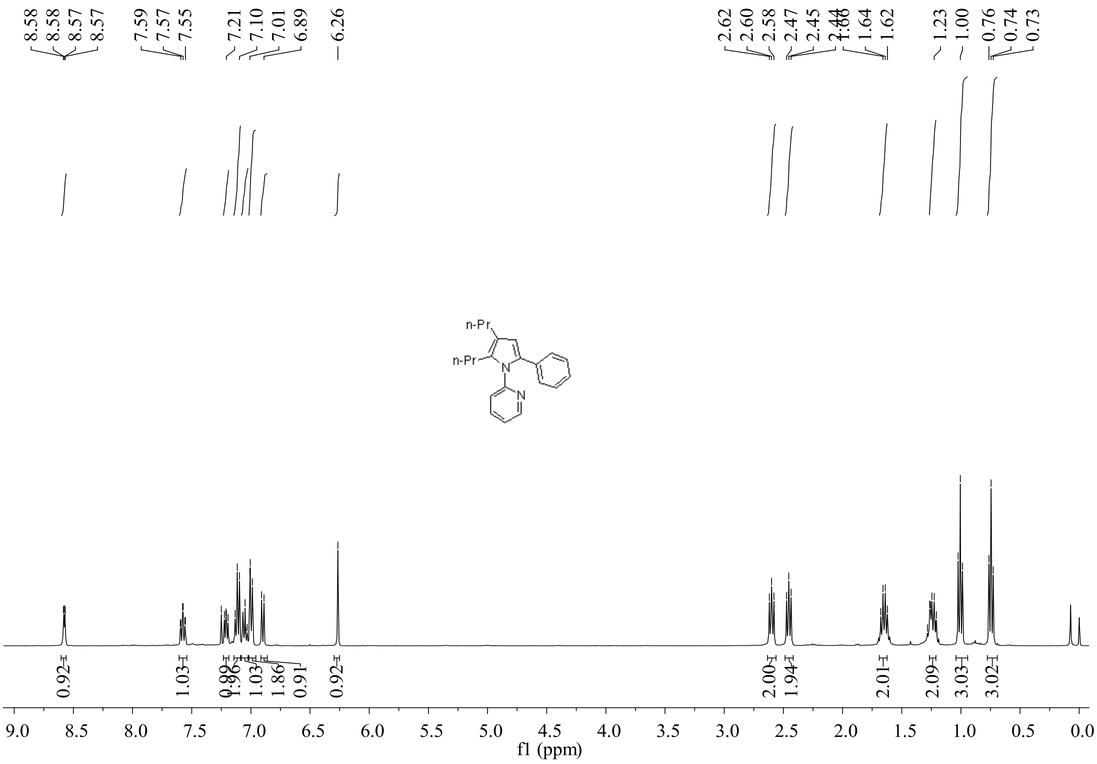


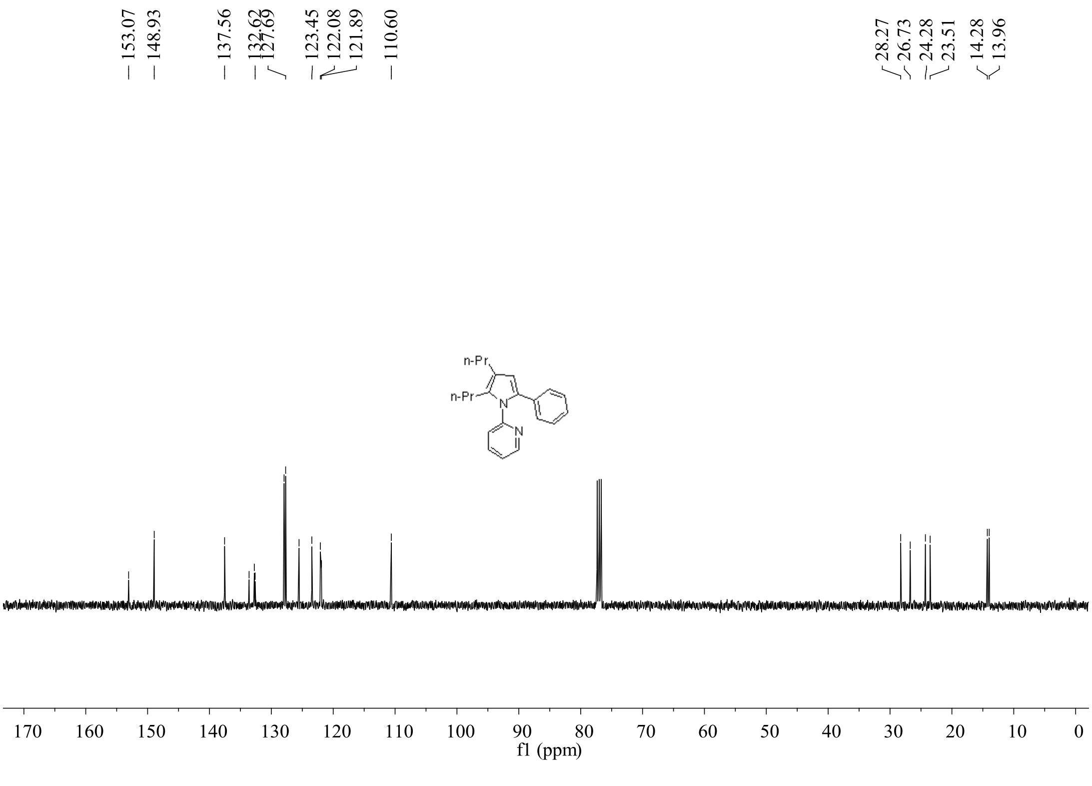
27) 2-(2-Ethyl-3, 5-diphenyl-pyrrol-1-yl)-pyridine **(3t)** (rr=9:1) (Using $CDCl_3$ as solvent)



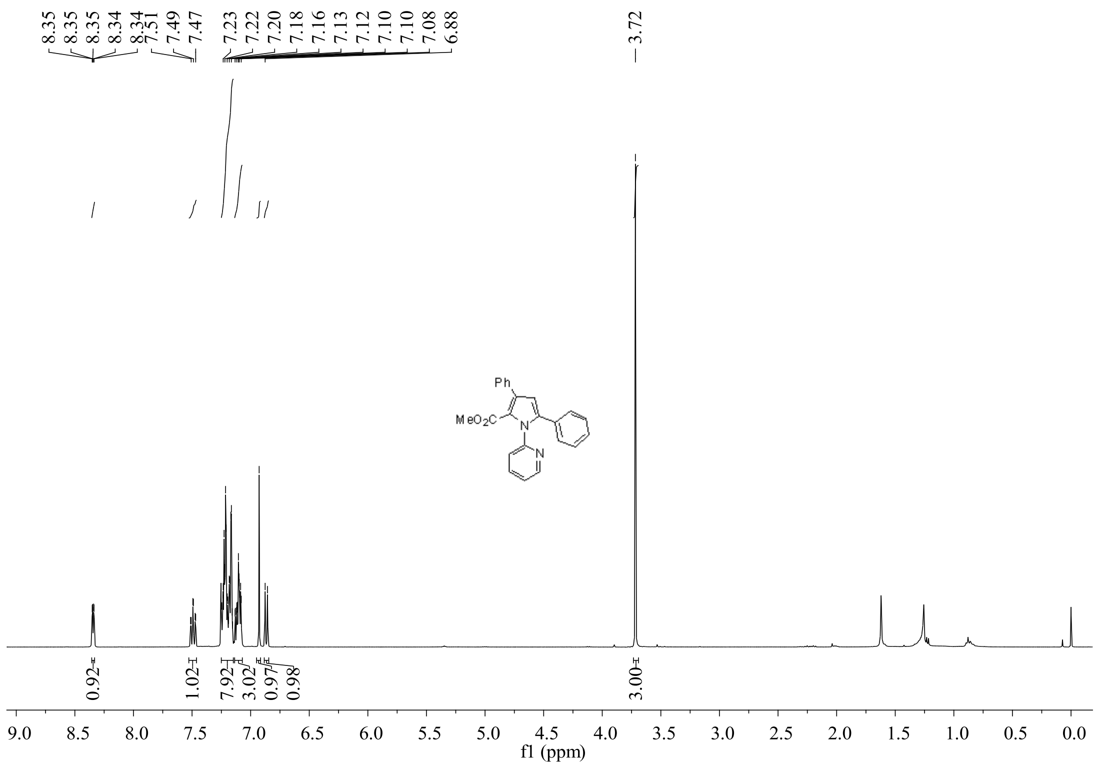


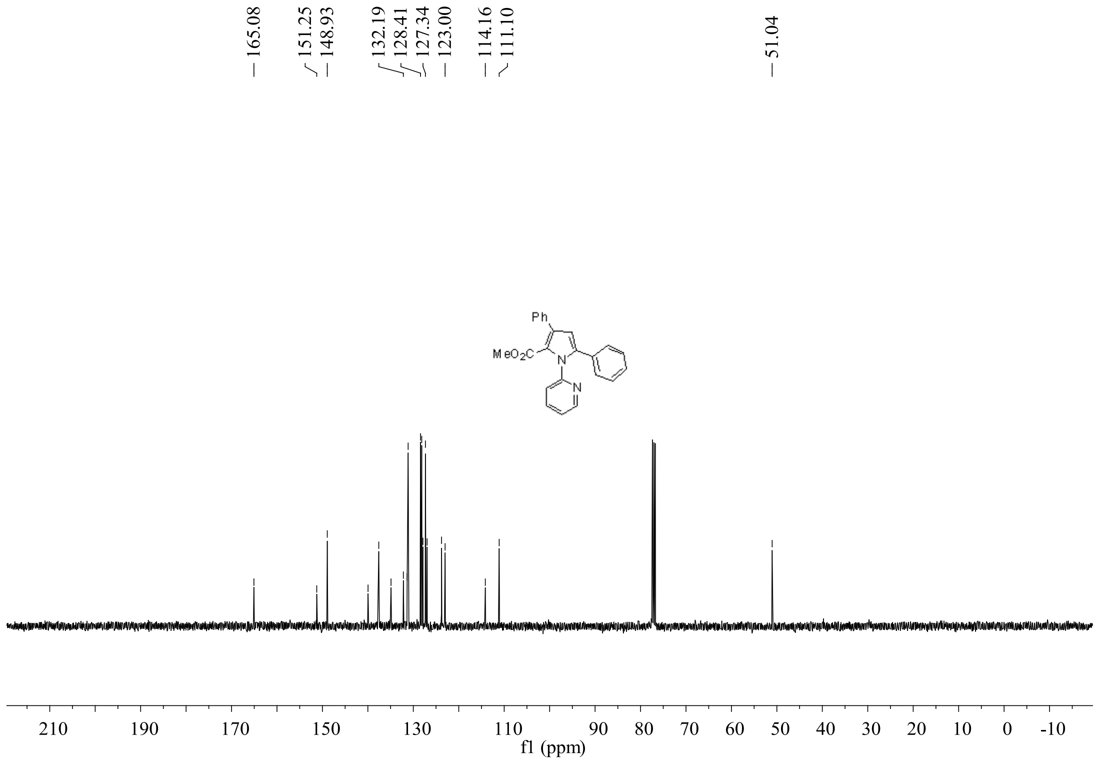
28) 2-(5-Phenyl-2,3-dipropyl-pyrrol-1-yl)-pyridine **(3u)** (Using $CDCl_3$ as solvent)



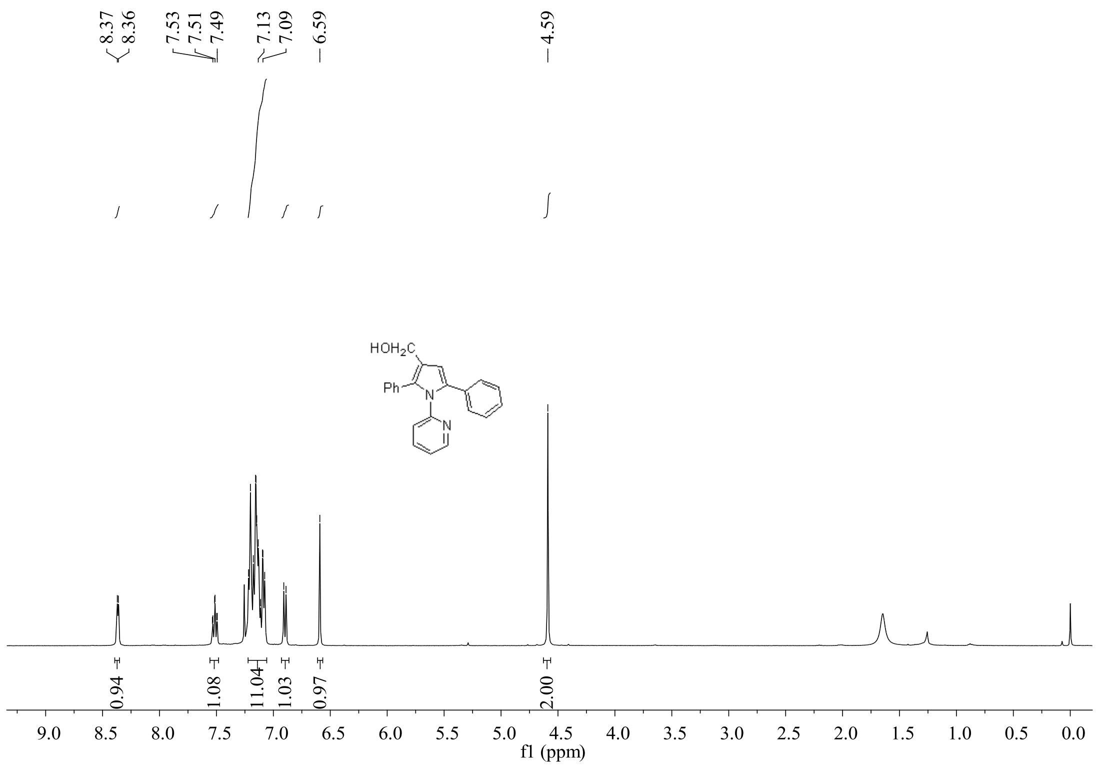


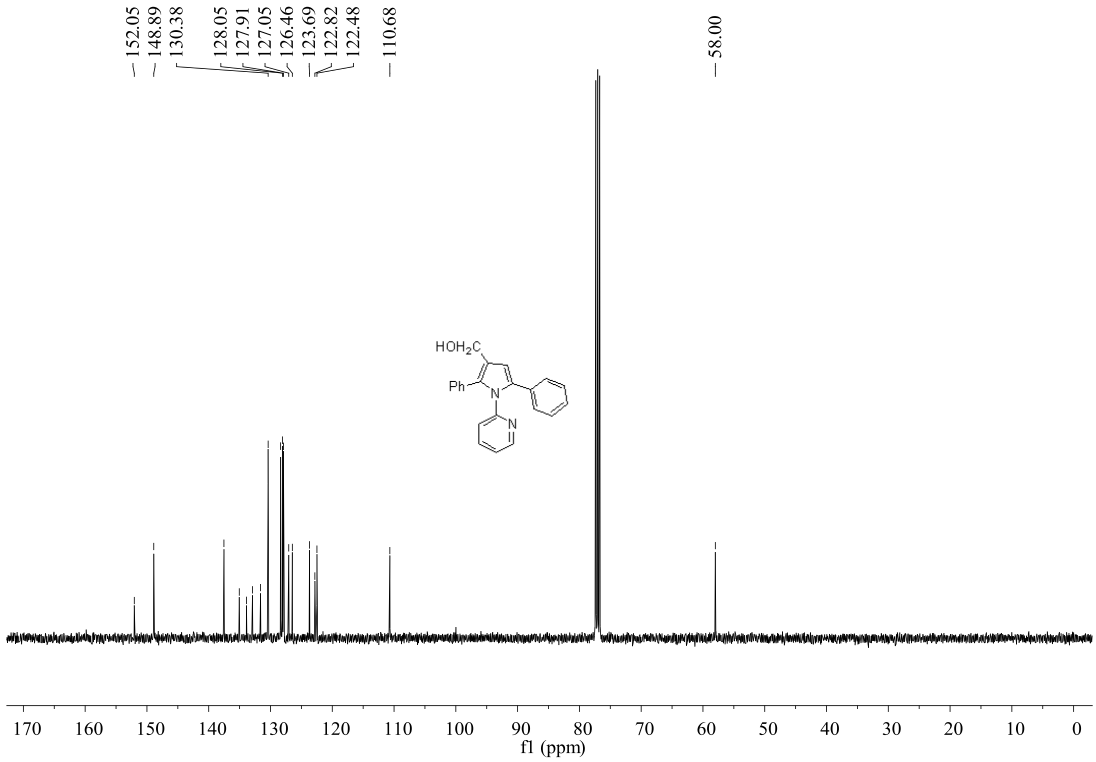
29) 3, 5-Diphenyl-1-pyridin-2-yl-1H-pyrrole-2-carboxylic acid methyl ester **(3v)** (Using $CDCl_3$ as solvent)



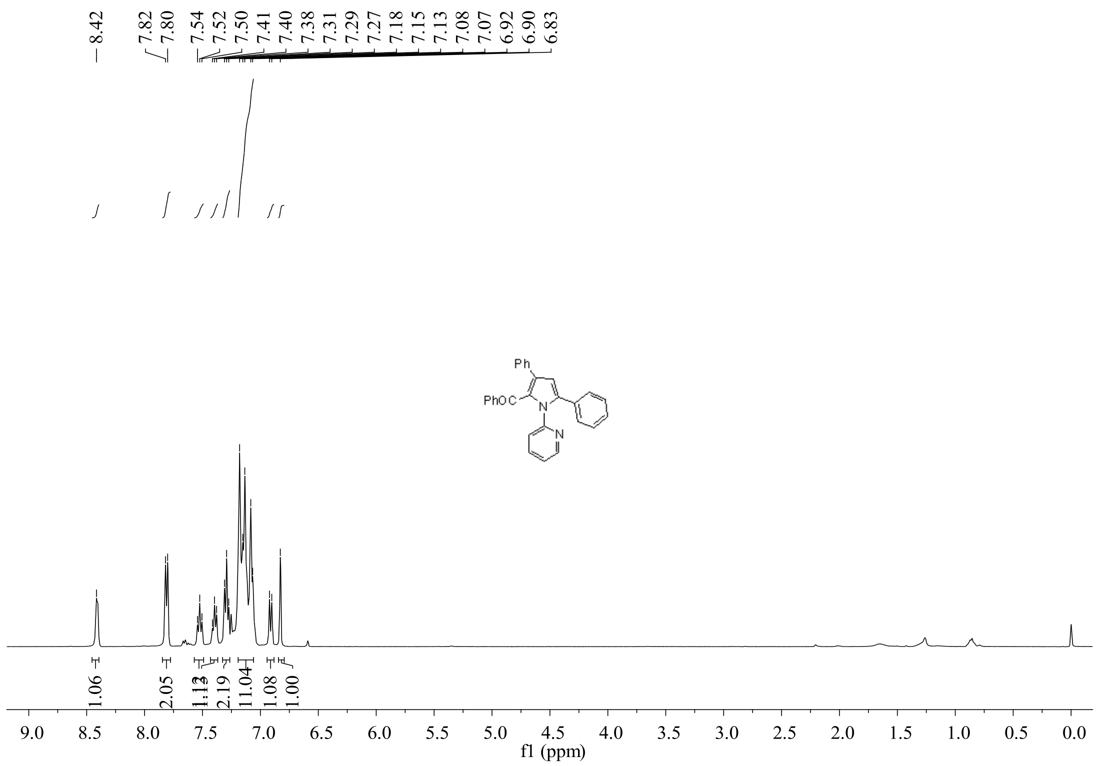


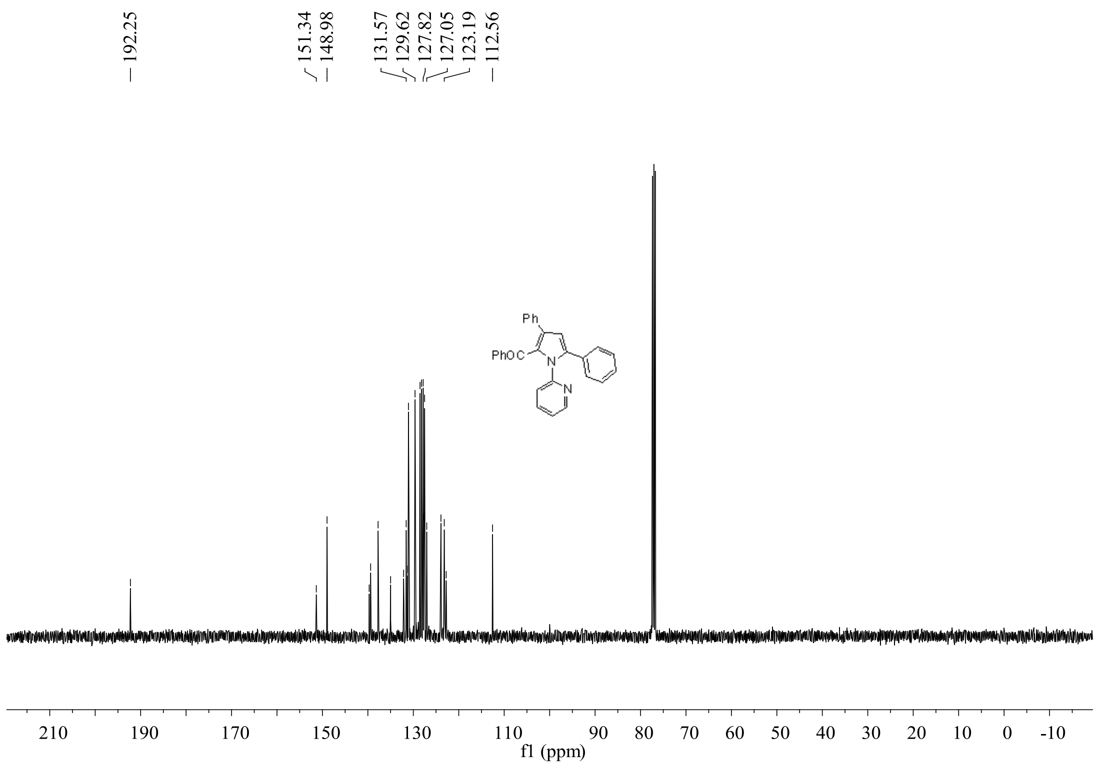
30) (3, 5-Diphenyl-1-pyridin-2-yl-1H-pyrrol-2-yl)-methanol **(3w)** (Using $CDCl_3$ as solvent)



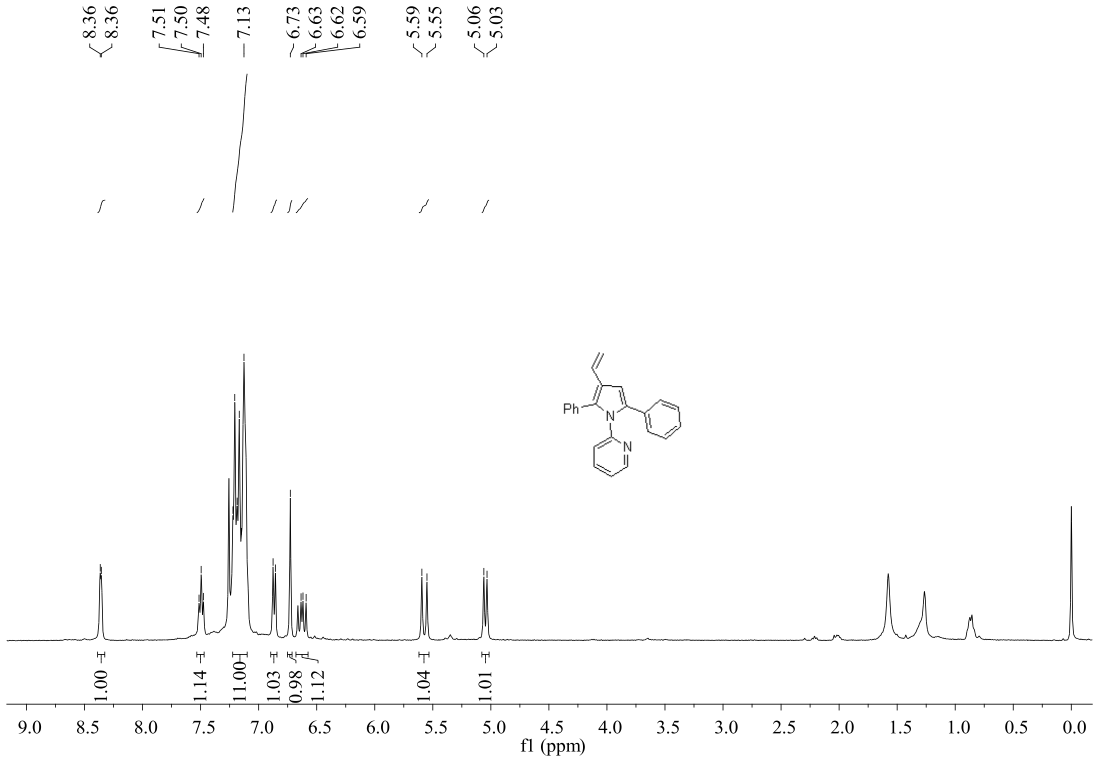


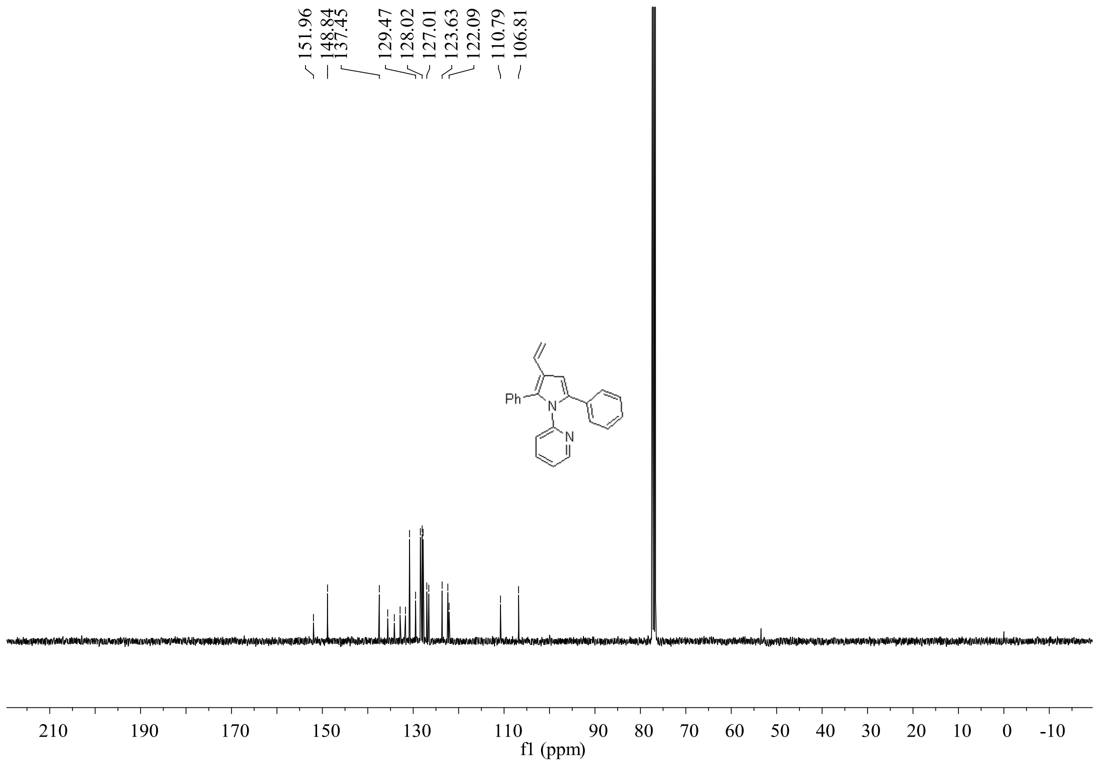
31) (3, 5-Diphenyl-1-pyridin-2-yl-1H-pyrrol-2-yl)-phenyl-methanone **(3x)** (Using $CDCl_3$ as solvent)



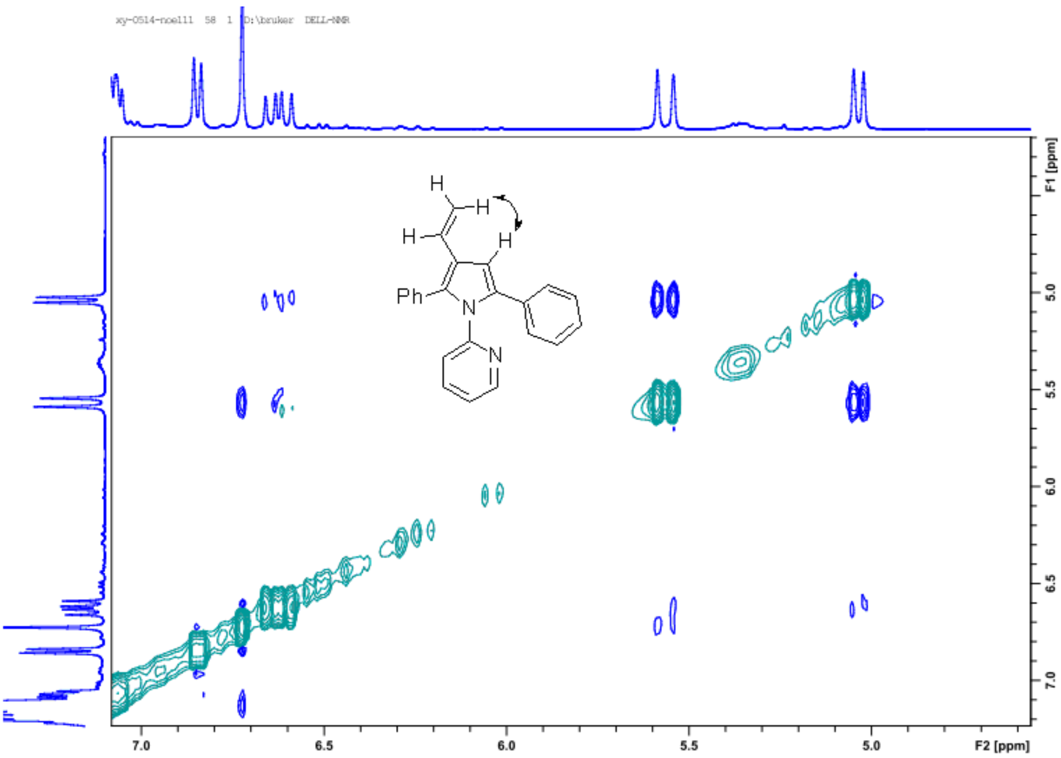


32) 2-(3, 5-Diphenyl-2-vinyl-pyrrol-1-yl)-pyridine **(3y)** (Using $CDCl_3$ as solvent)

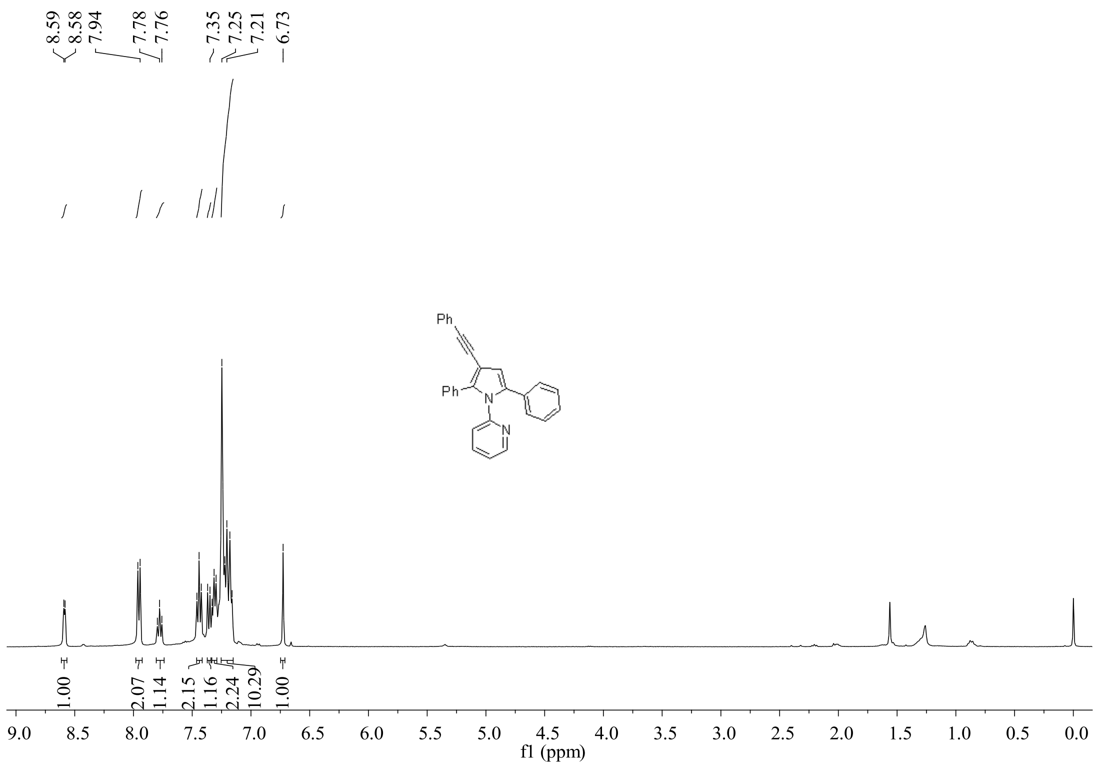


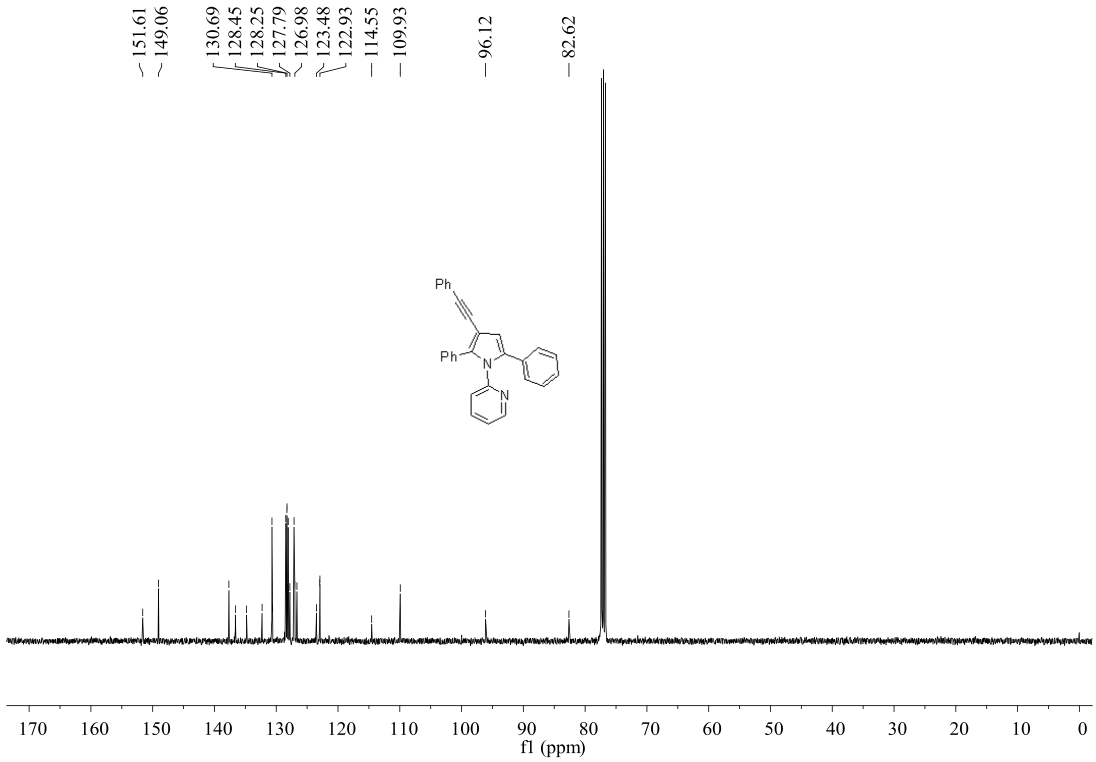


[1]H-[1]H NOE NMR spectrum of **3y**

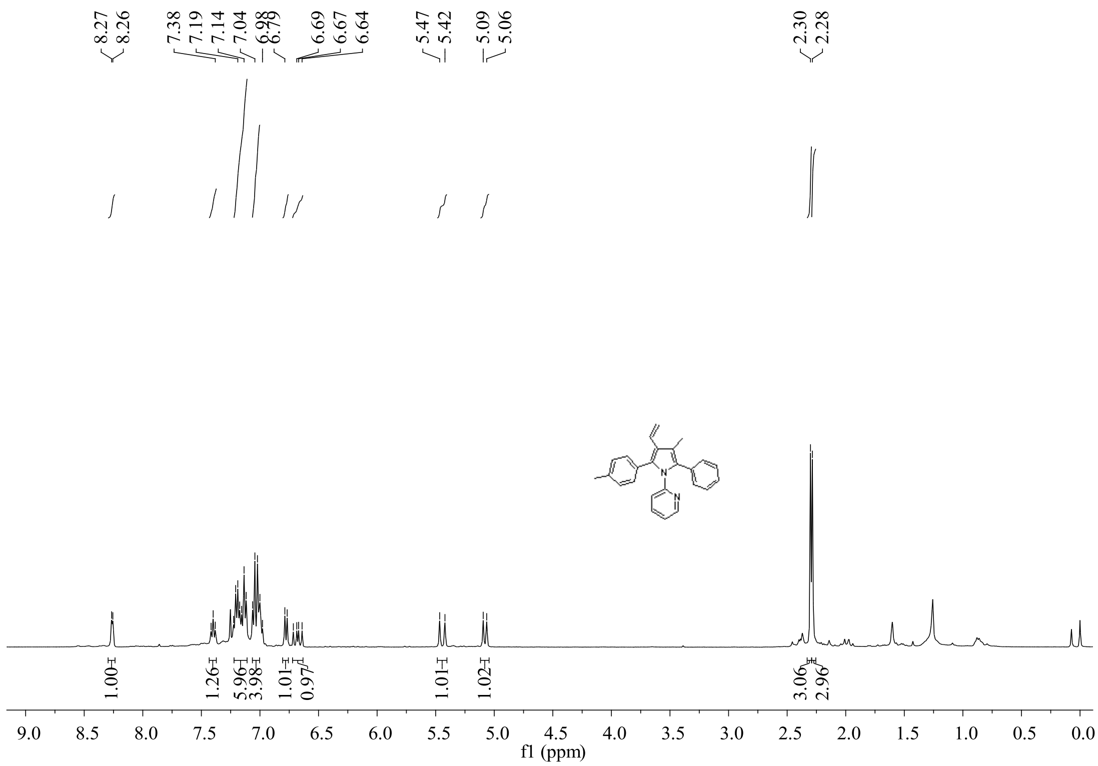


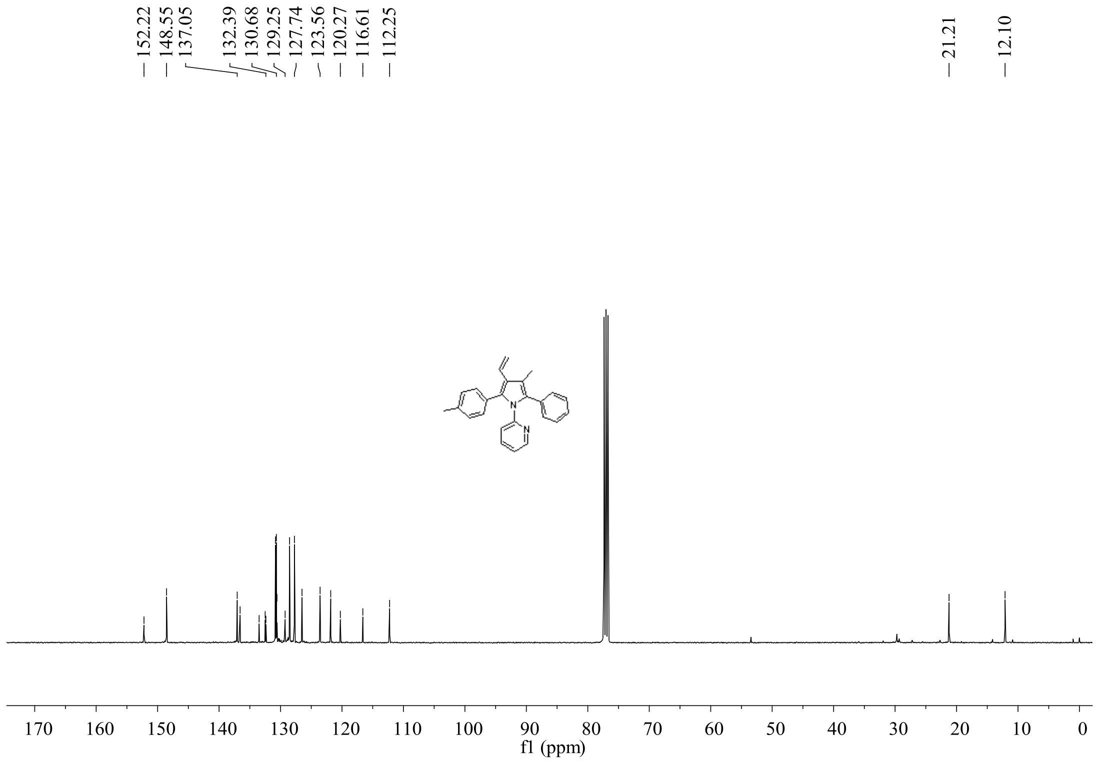
33) 2-(3, 5-Diphenyl-2-phenylethynyl-pyrrol-1-yl)-pyridine **(3z)** (Using $CDCl_3$ as solvent)



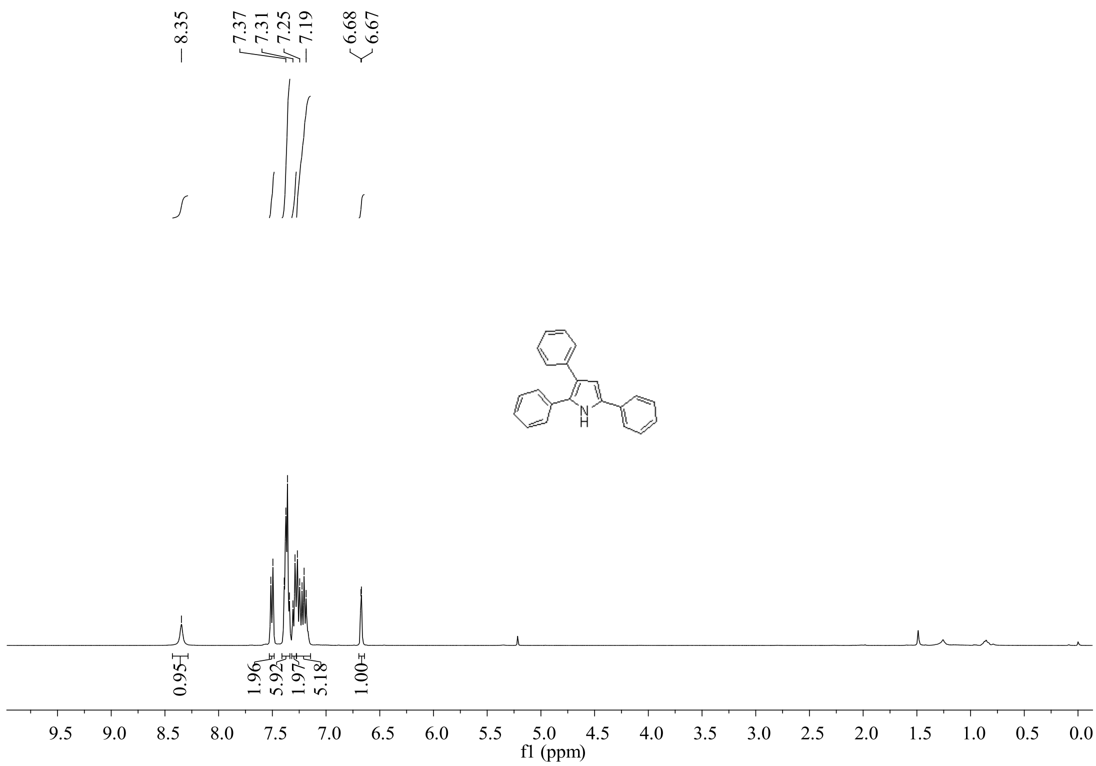


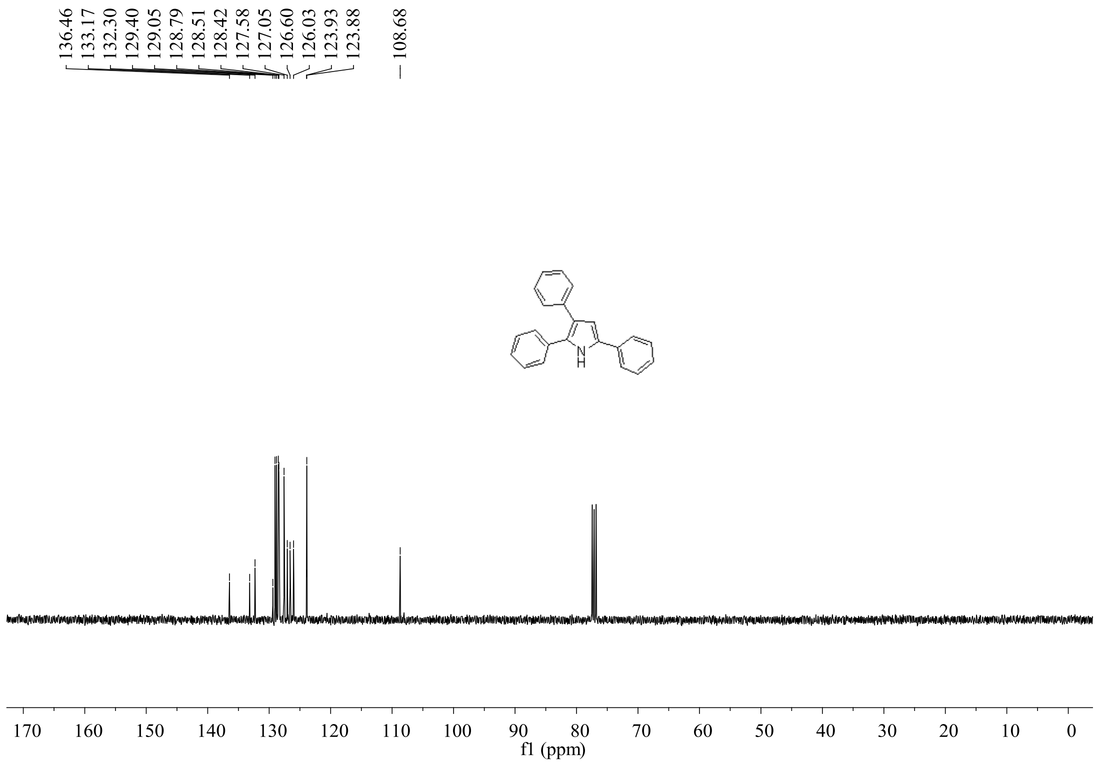
34) 2-(3-Methyl-2-phenyl-4-p-tolyl-5-vinyl-pyrrol-1-yl)-pyridine **(3za)** (Using $CDCl_3$ as solvent)



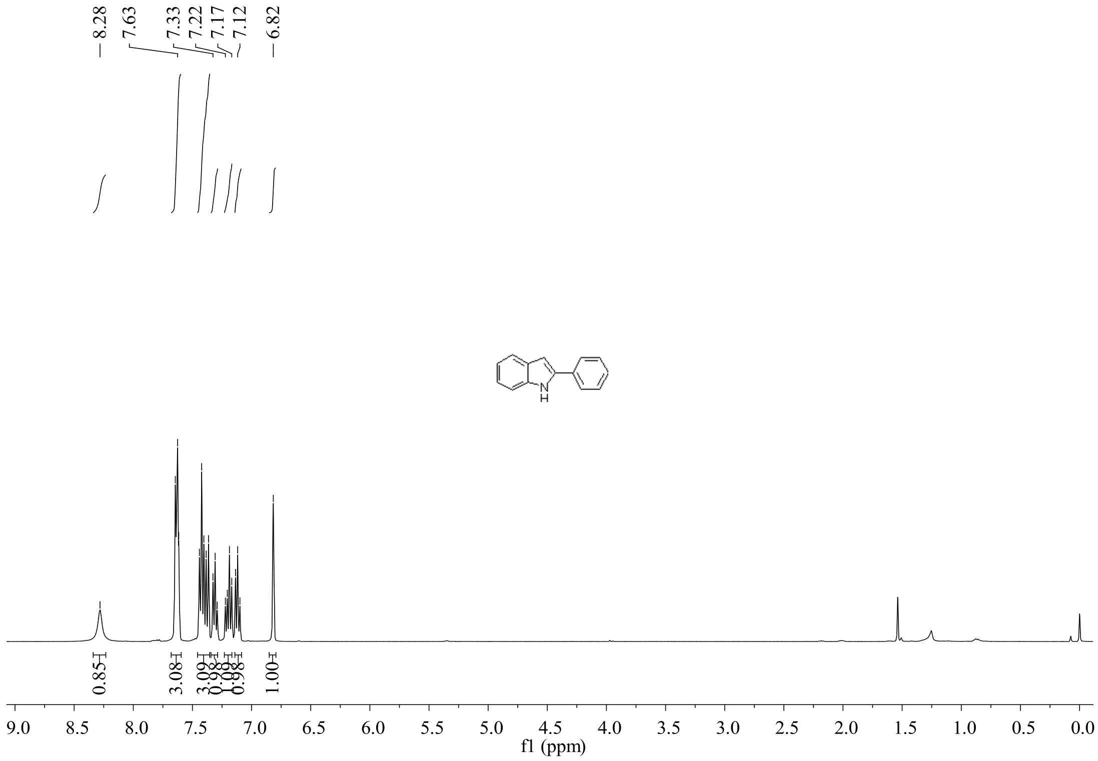


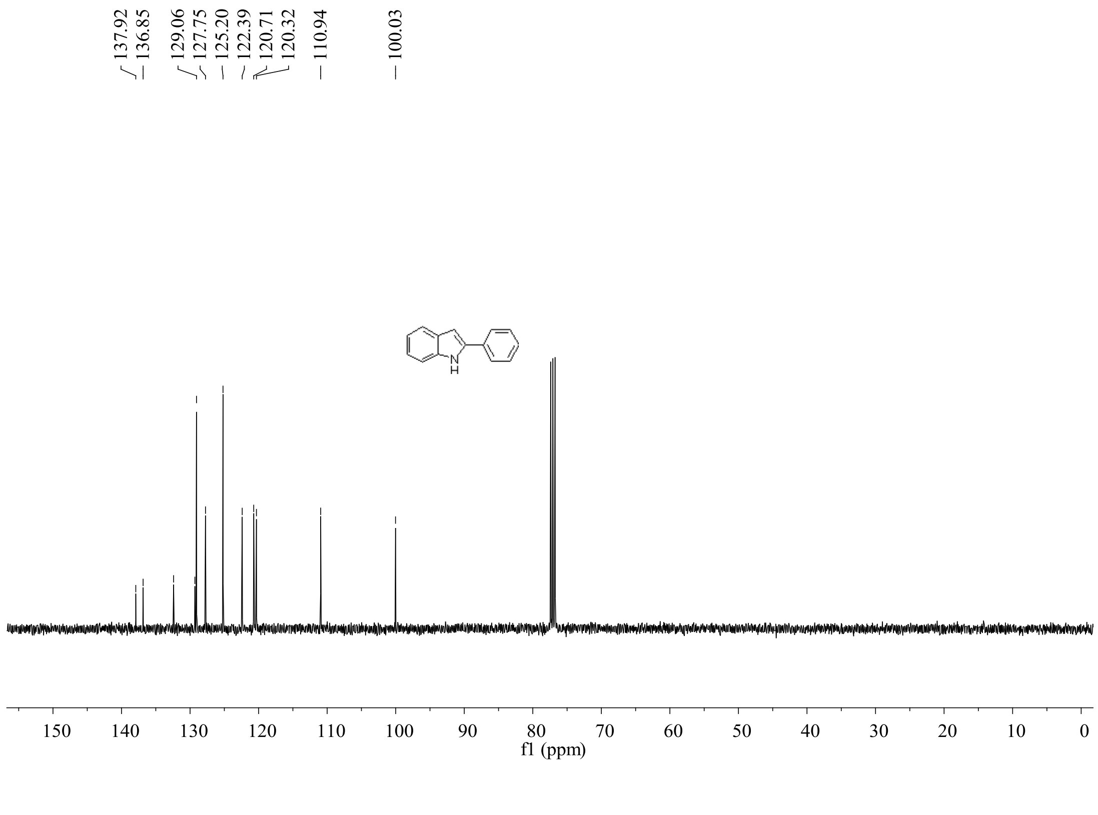
35) 2, 3, 5-Triphenyl-1H-pyrrole **(4a)** (Using $CDCl_3$ as solvent)



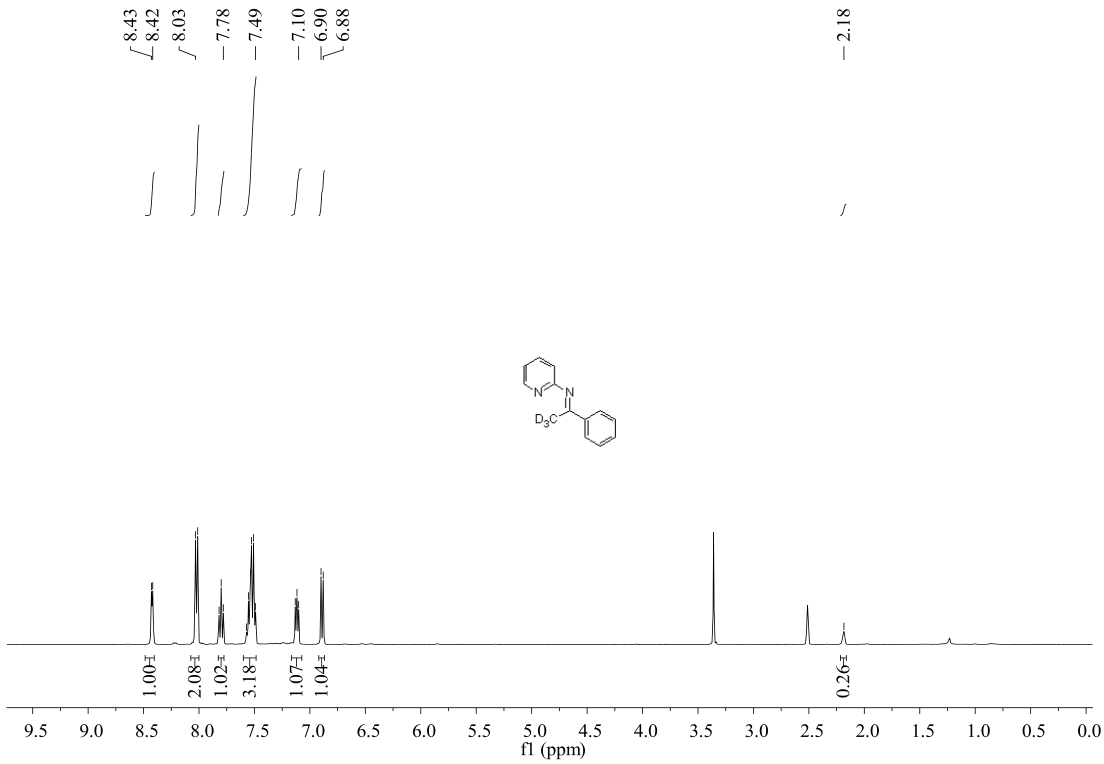


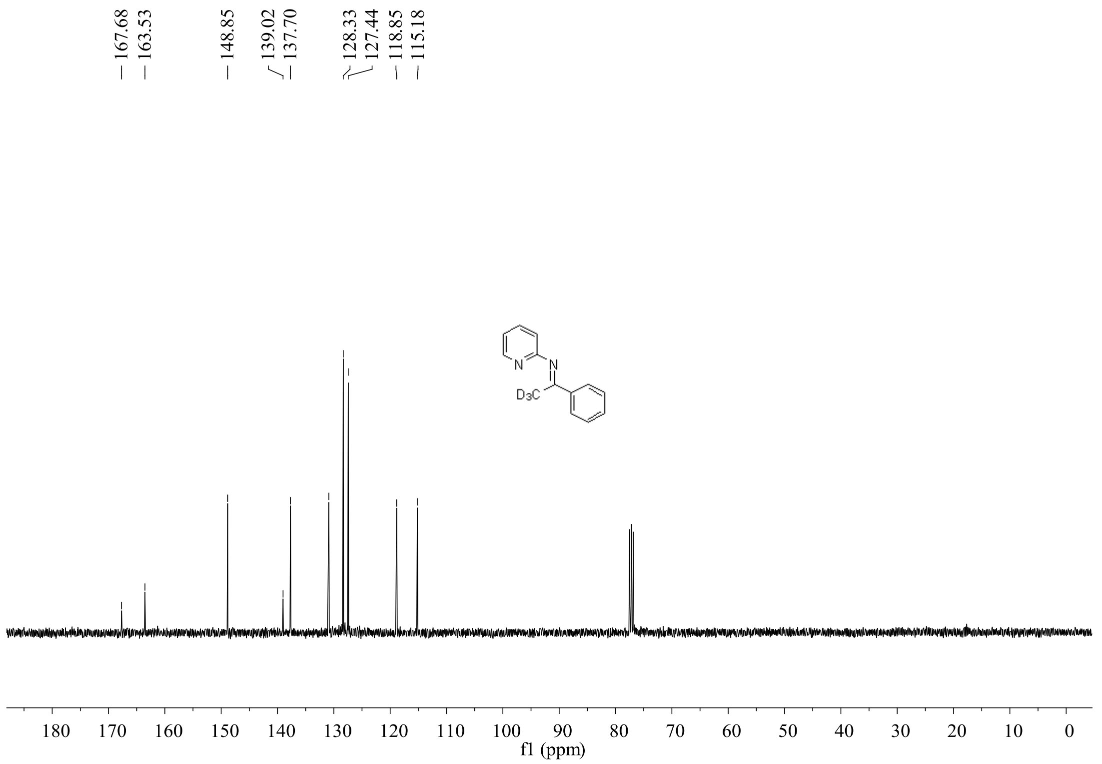
36) 2-phenyl-1H-indole **(4c)** (Using $CDCl_3$ as solvent)



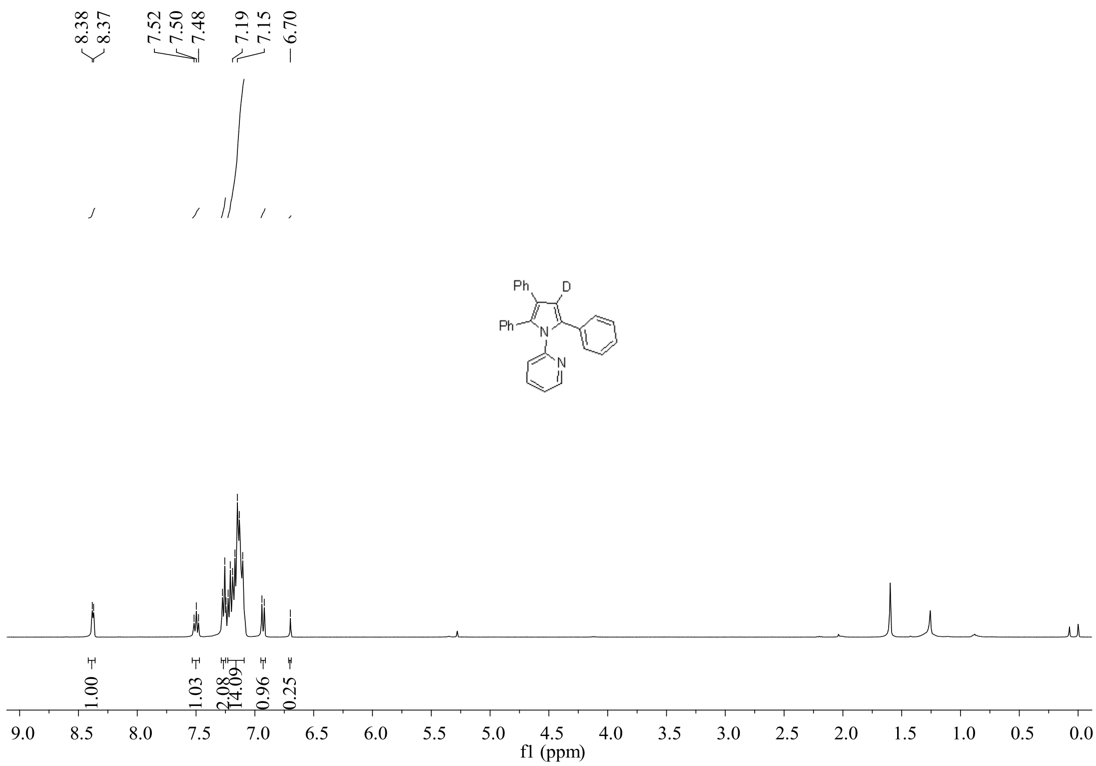


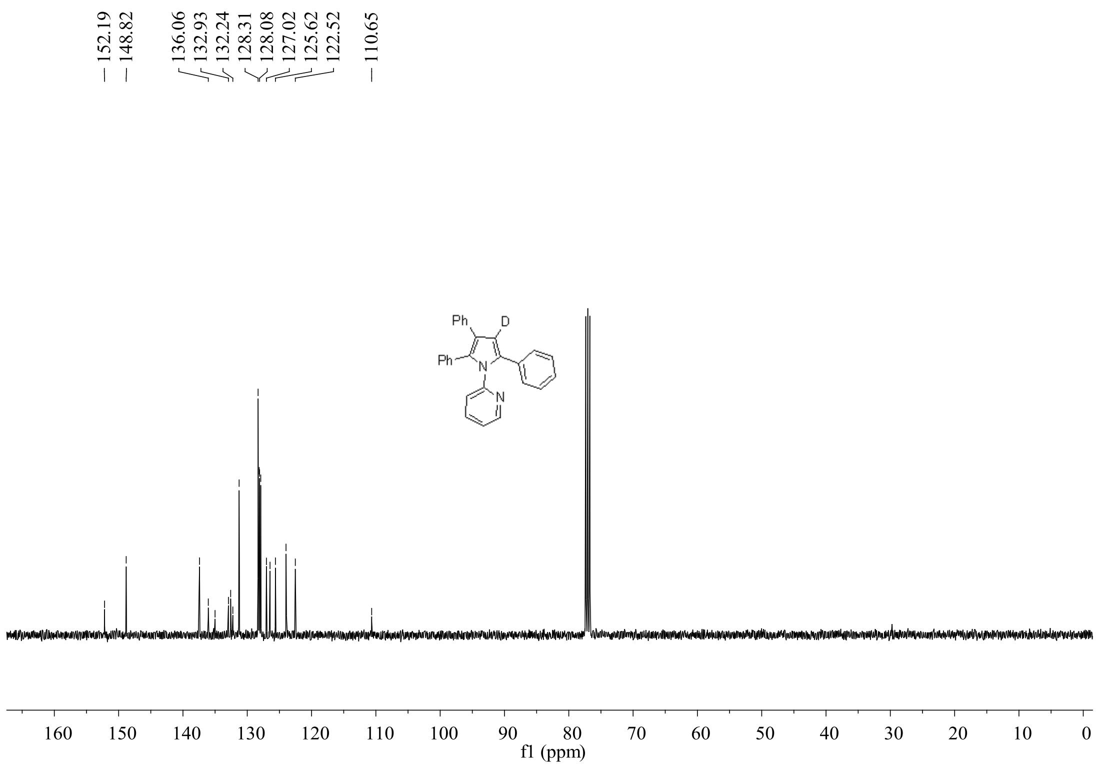
37) H/D Exchange of *N*-pyridyl ketoimine **(*d*-1a)** (Using *d*6-DMSO as solvent for ^{1}H NMR and using $CDCl_3$ as solvent for ^{13}C NMR)





38) ^{1}H and ^{13}C NMR spectrum for ***d*-3a** (Using $CDCl_3$ as solvent)

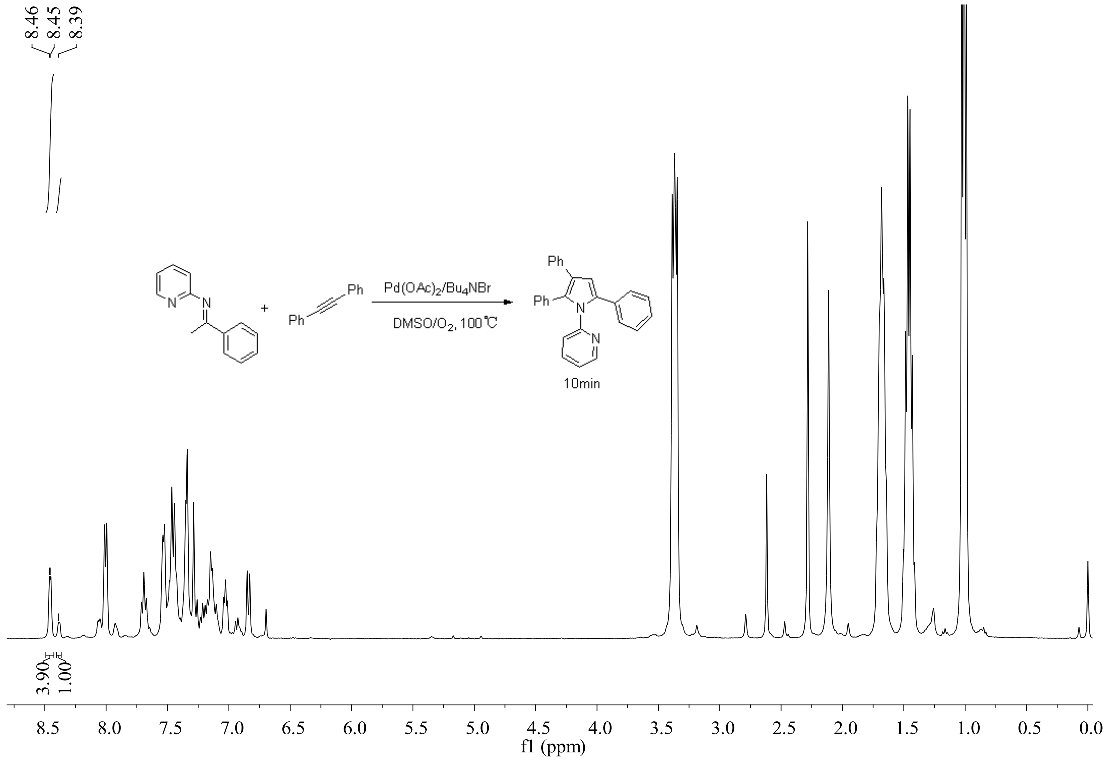


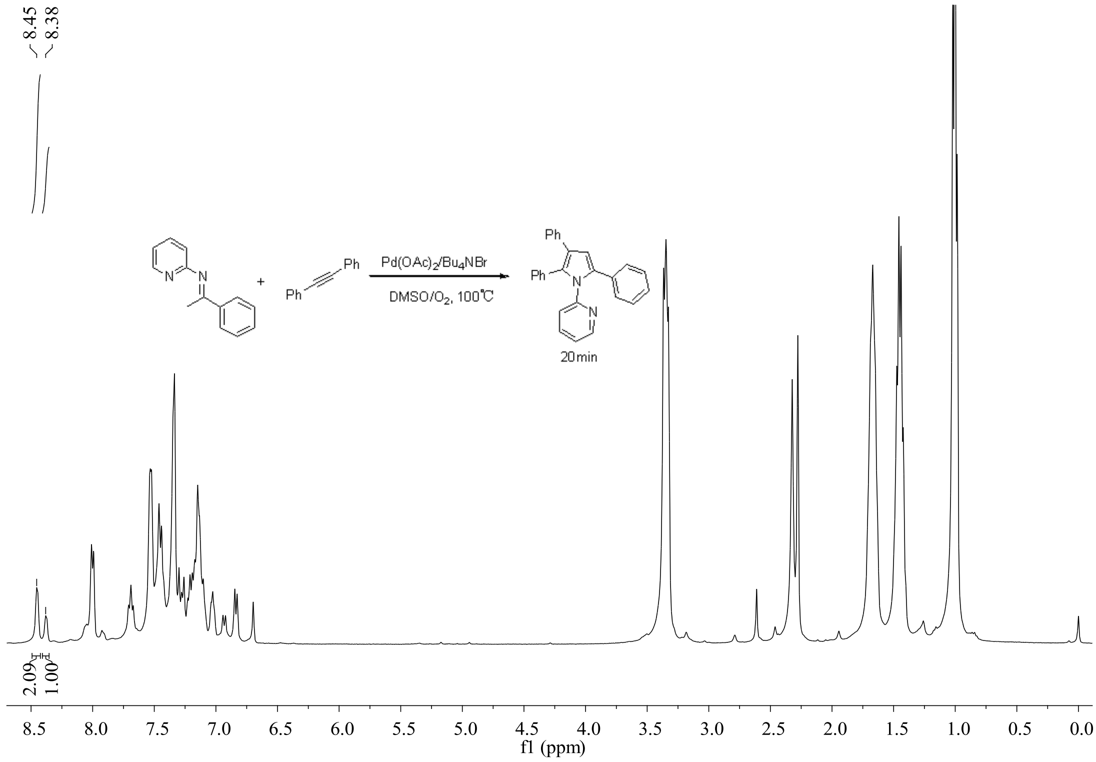


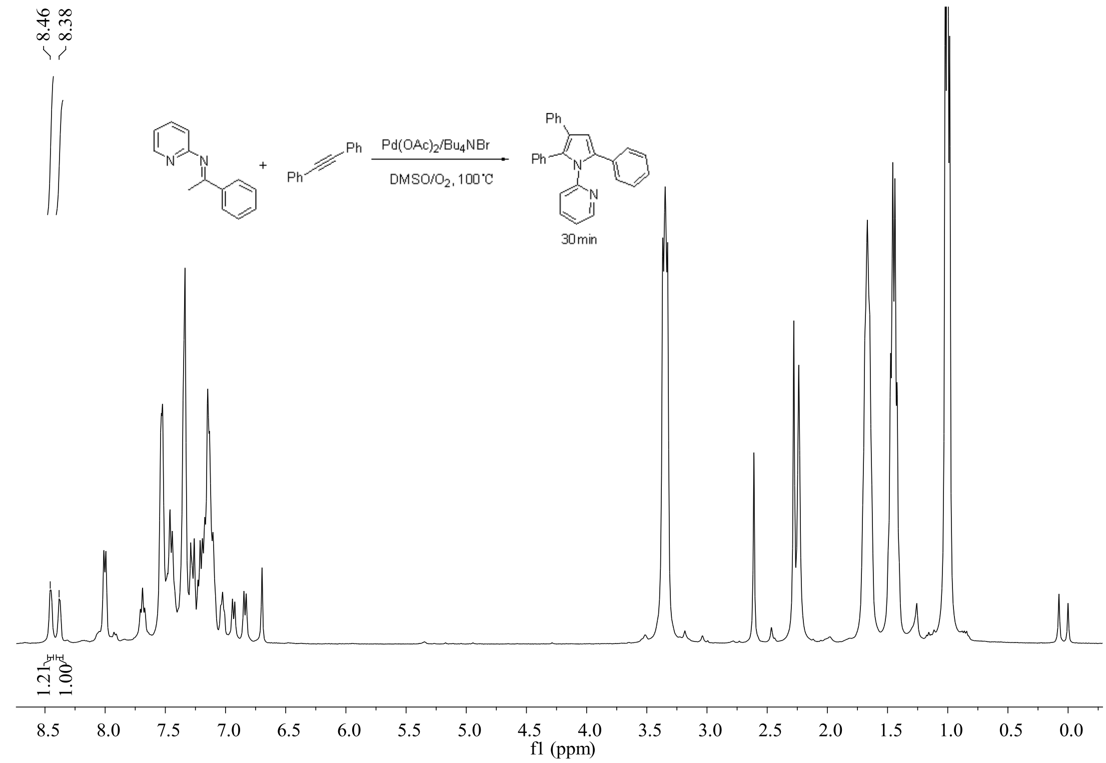
39) The crude ^{1}H NMR spectrum for calculating **KIE** value via parallel reactions (Using $CDCl_3$ as

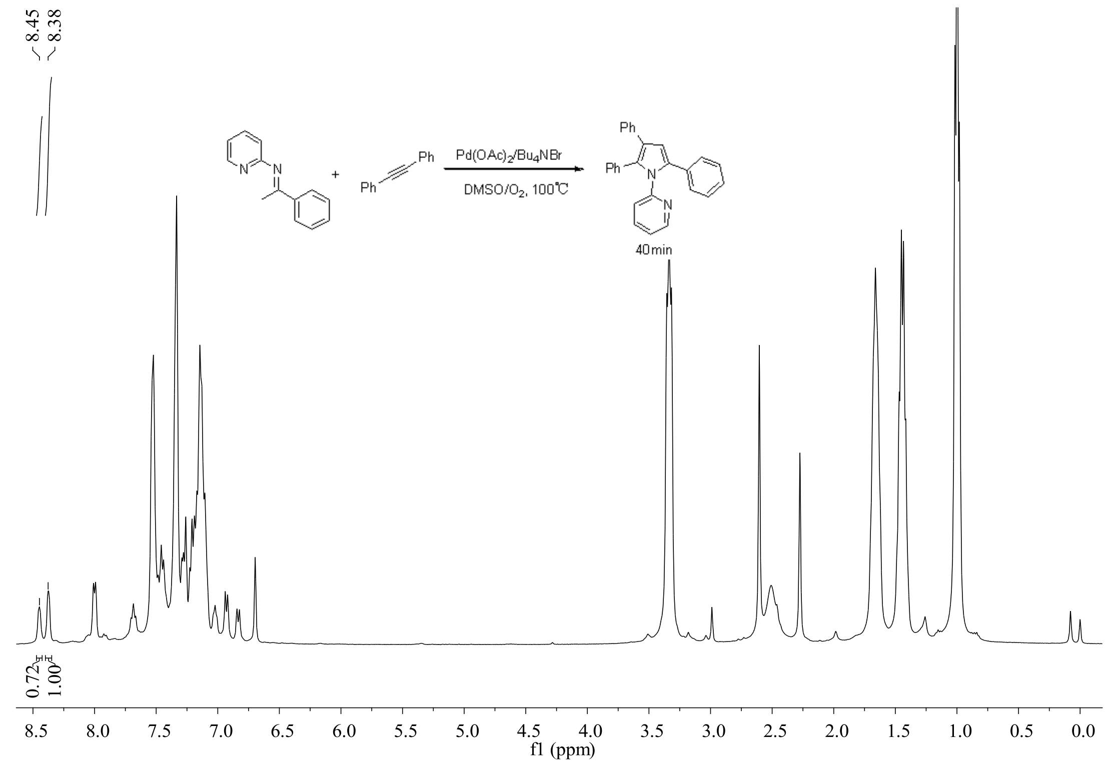
solvent)

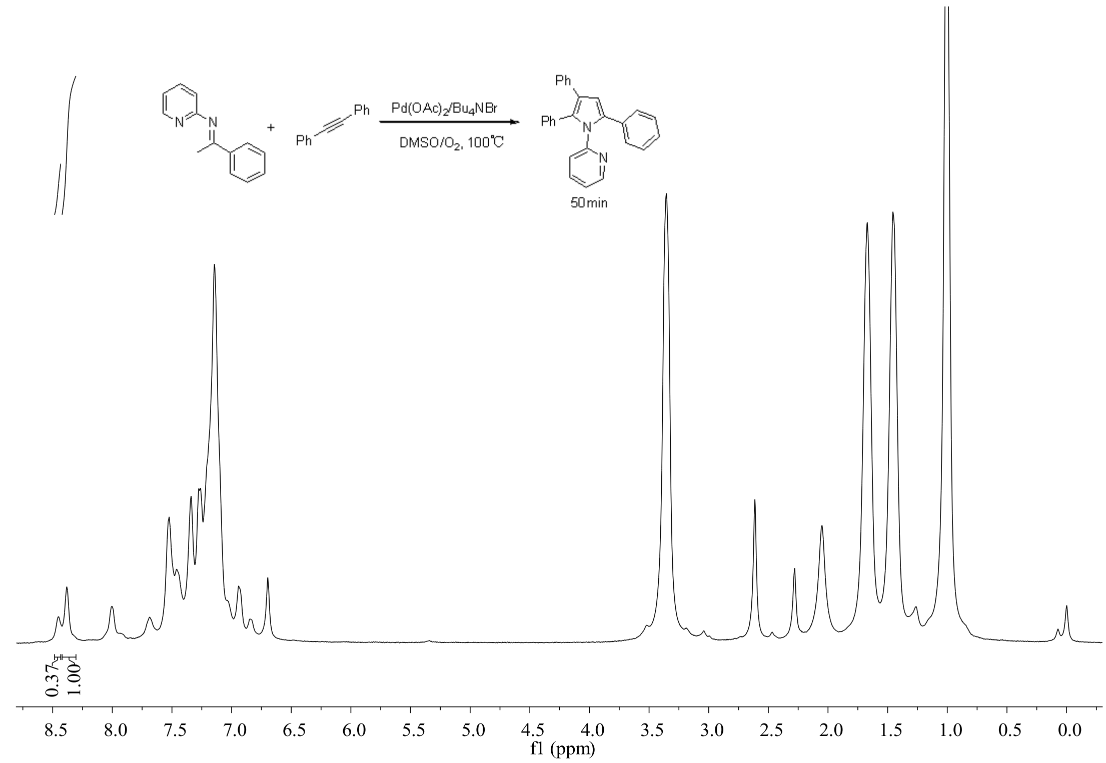
a. The crude ^{1}H NMR spectrum for the reaction of **1a** with **2a**.



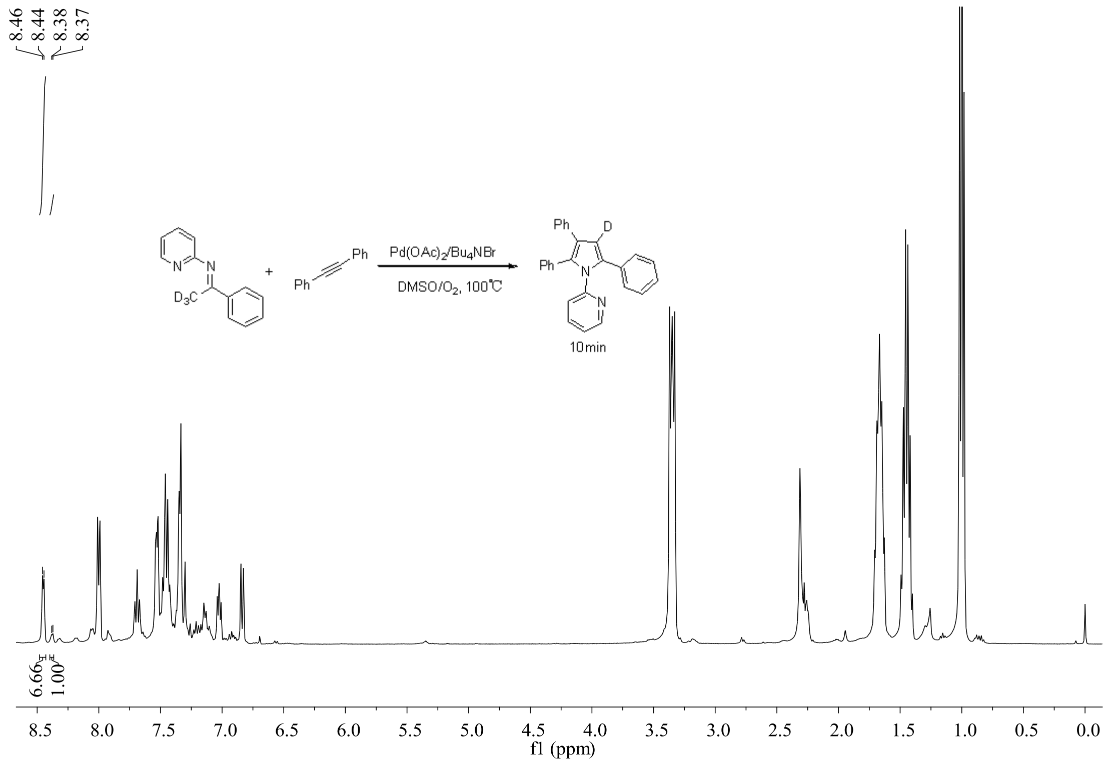


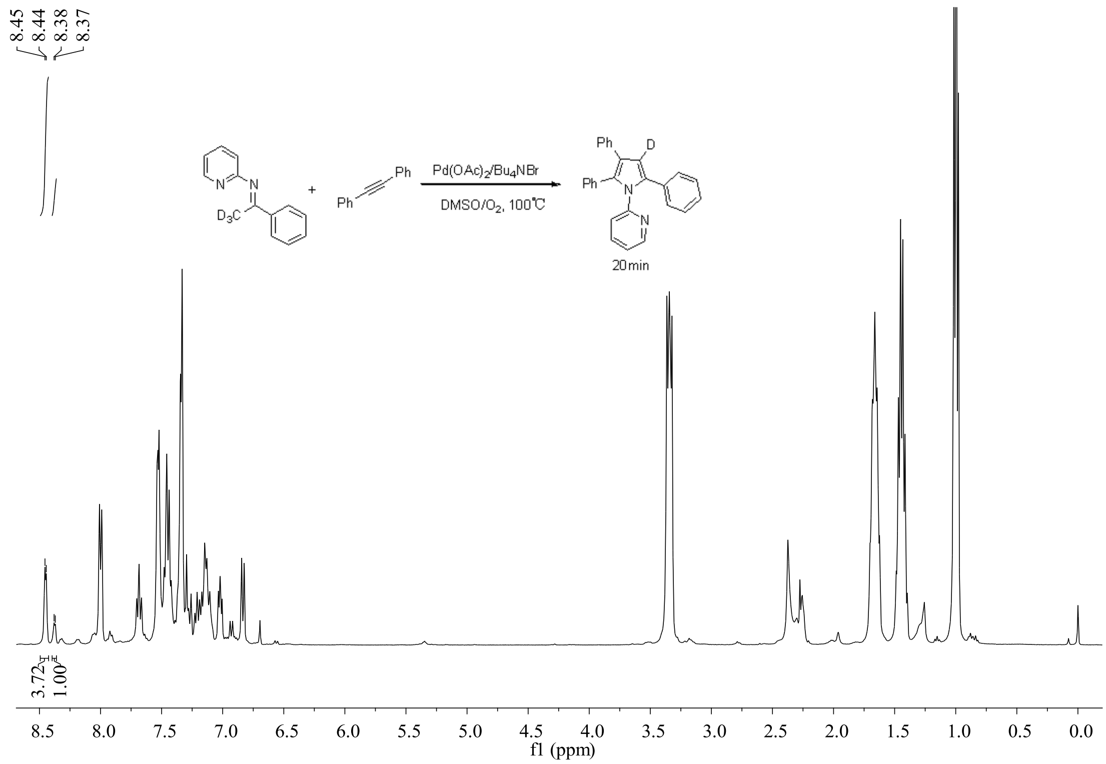

8.46
8.38
Ph
Pd(OAc)2/Bu4NBr
DMSO/O2, 100℃
Ph
Ph
Ph
N
N
N
30min
1.21
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

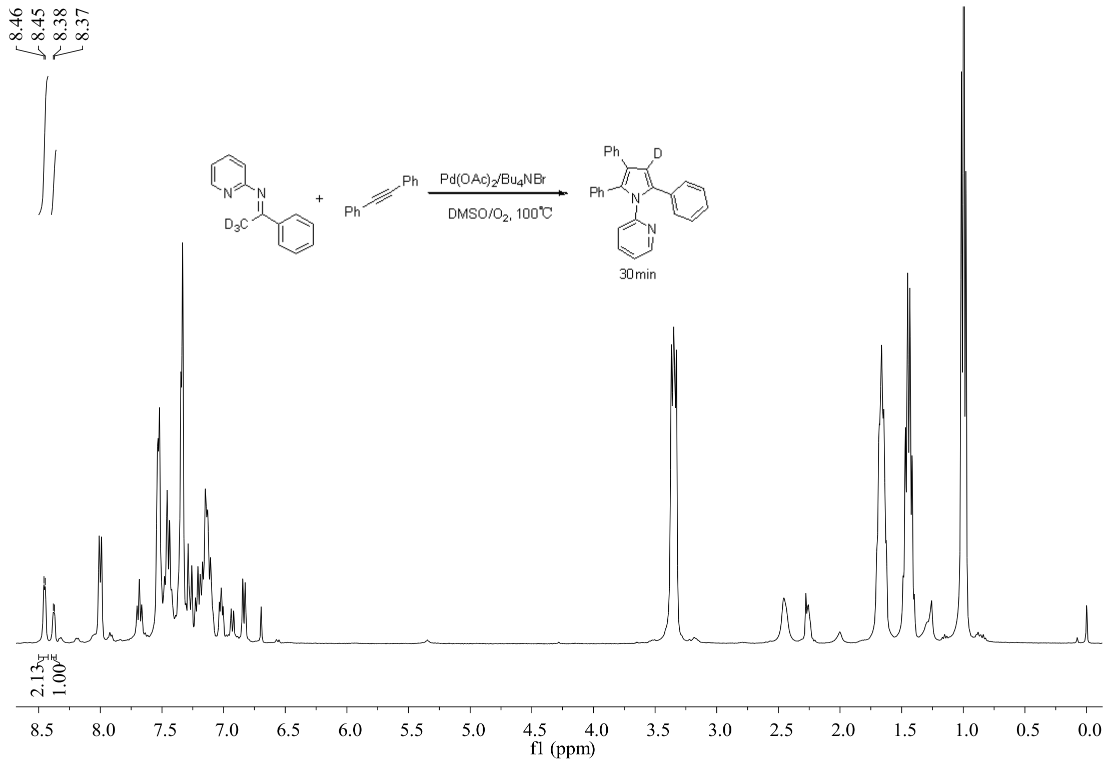

8.45
8.38
Ph
Pd(OAc)2/Bu4NBr
DMSO/O2, 100℃
Ph
Ph
Ph
N
N
N
40min
0.72
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

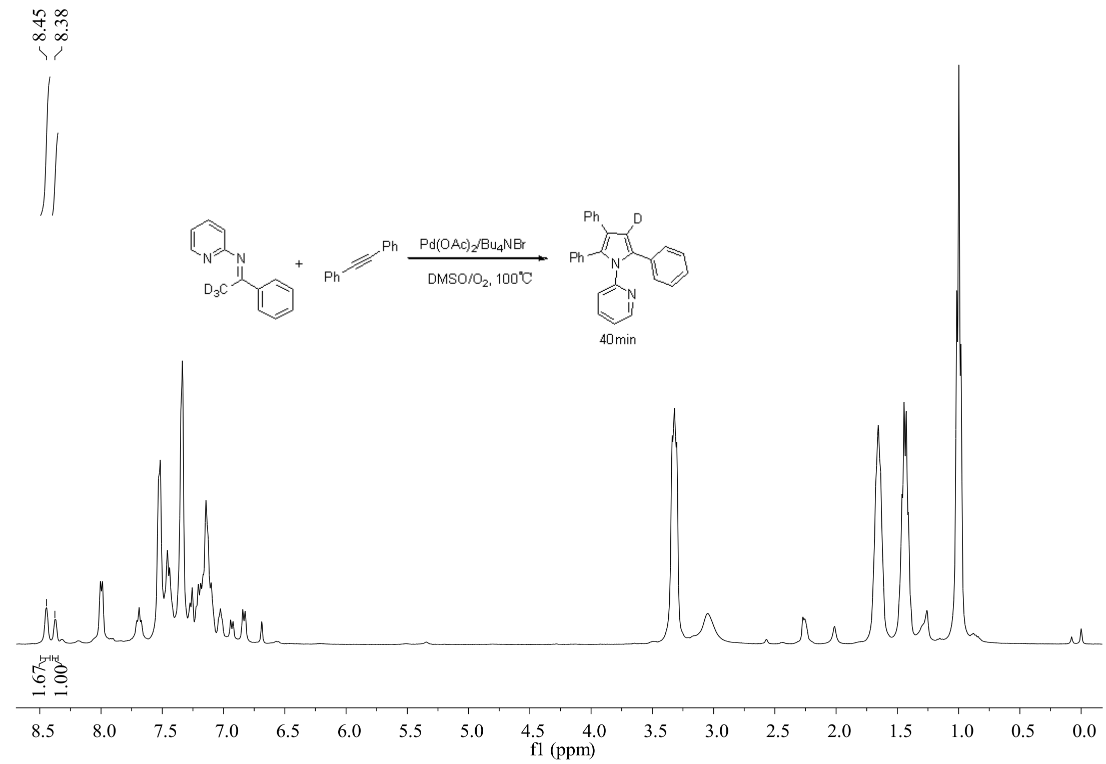

Pd(OAc)2/Bu4NBr
DMSO/O2, 100°C
Ph
Ph
Ph
Ph
N
N
N
50min
0.37
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

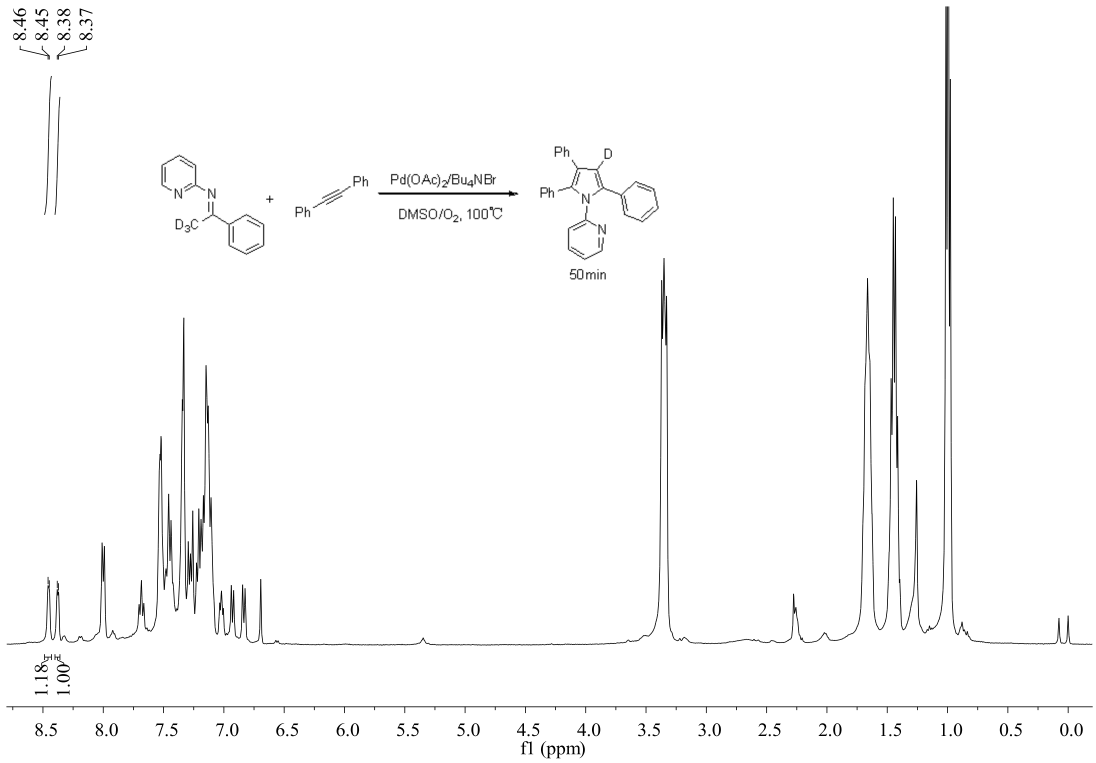
b. The crude ^{1}H NMR spectrum for the reaction of *d*-**1a** with **2a**.



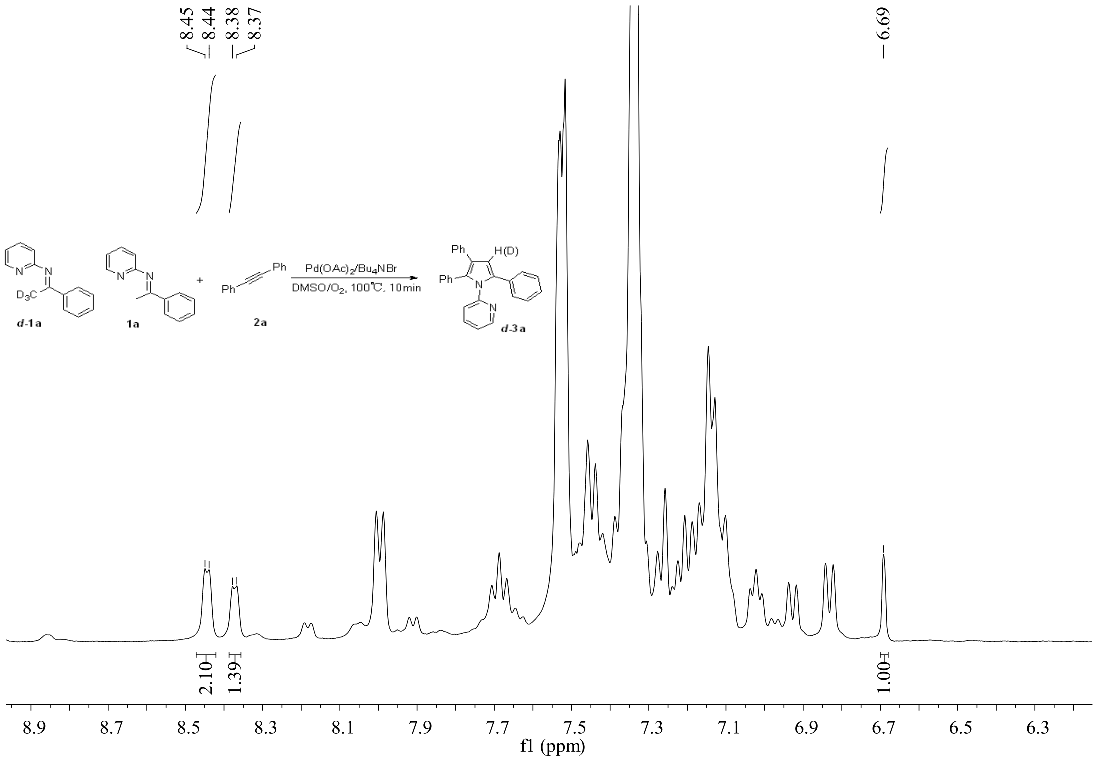


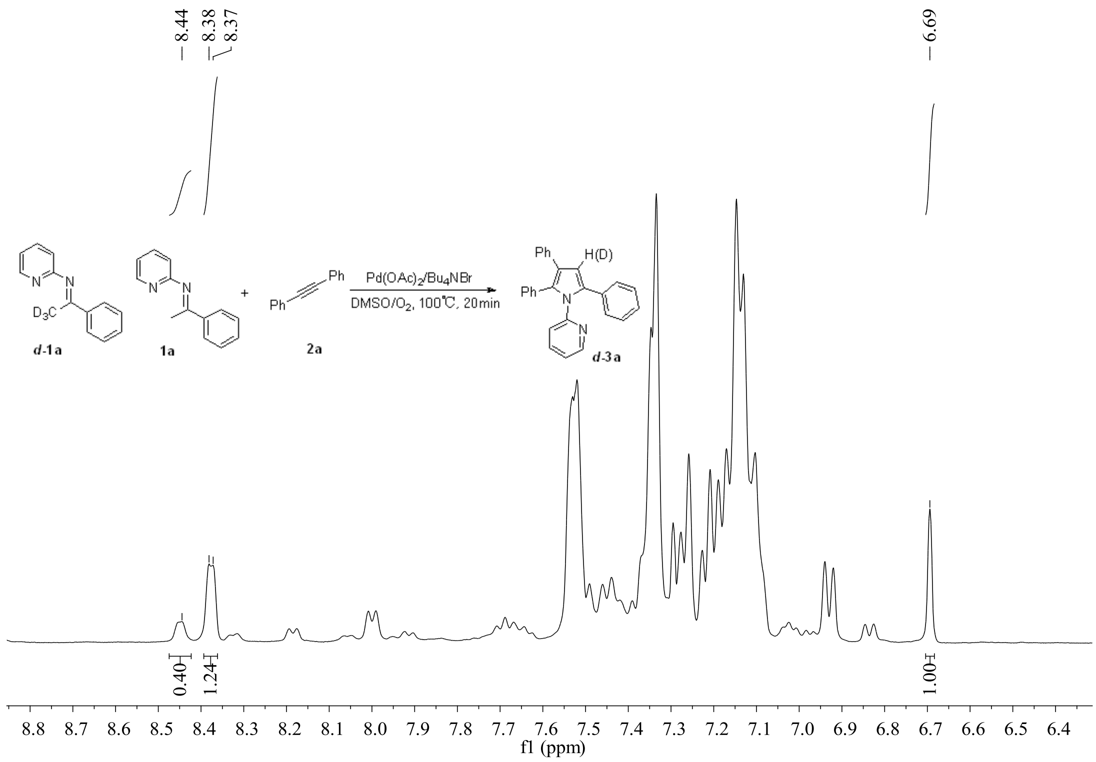

8.46
8.45
8.38
8.37
Pd(OAc)2/Bu4NBr
DMSO/O2, 100℃
30min
2.13
1.00
f1 (ppm)


8.45
8.38
Pd(OAc)2/Bu4NBr
DMSO/O2, 100℃
40min
1.67
1.00
f1 (ppm)

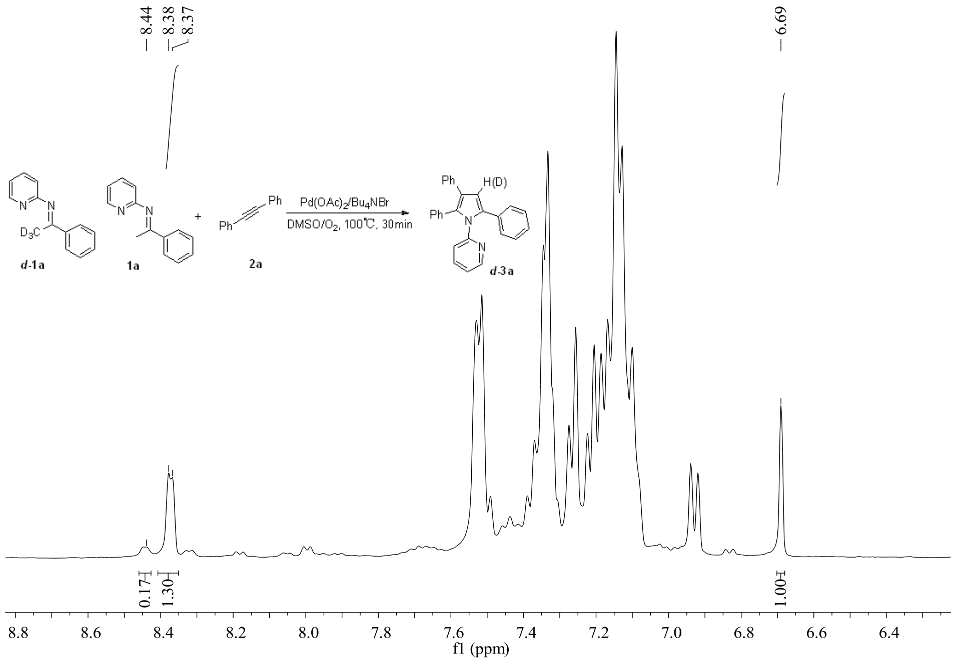


40) The crude [1]H NMR spectrum for calculating **KIE** value via competition reactions (Using $CDCl_3$ as solvent)





8.44
8.38
8.37
6.69
Ph
H(D)
Ph
N
N
D3C
d-1a
1a
+
Ph
Ph
2a
Pd(OAc)2/Bu4NBr
DMSO/O2, 100℃, 20min
d-3a
0.40
1.24
1.00
8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)



8.44
8.38
8.37
6.69
Ph
H(D)
Ph
N
N
D3C
d-1a
1a
+
Ph
Ph
2a
Pd(OAc)2/Bu4NBr
DMSO/O2, 100℃, 30min
d-3a
0.17
1.30
1.00
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)