

Supporting Information

Cobalt(III)-Catalyzed Synthesis of Pyrroles from Enamides and Alkynes.

Wenlong Yu,^a Wei Zhang,^a Yue Liu,^a Yougui Zhou,^a Zhanxiang Liu,^a Yuhong

Zhang^{*,a,b}

^aDepartment of Chemistry, Zhejiang University, Hangzhou 310027, China

^bState Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

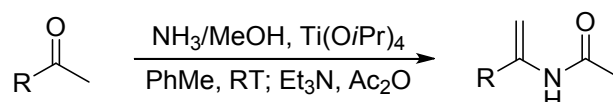
E-mail: yhzhang@zju.edu.cn

Content

General Information.....	S2
Preparation of Enamides.....	S2
The optimization of reaction conditions.....	S3
Gram-Scale Reaction.....	S3
Characterization of products.....	S4
References.....	S13
¹ H NMR and ¹³ C NMR Spectra.....	S14

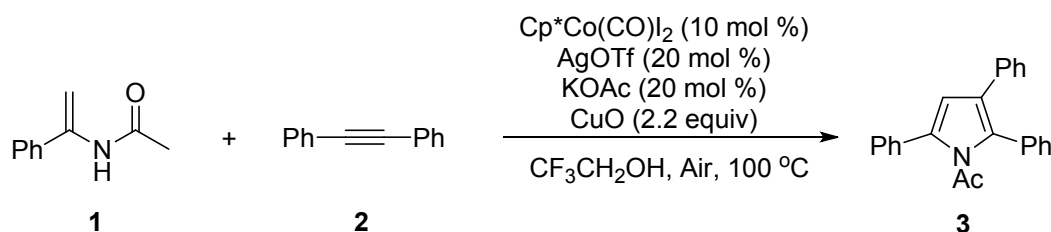
General All reactions were performed under air in a flame-dried reaction flask. N-acyl enamides¹ were synthesized according to published procedures. Methyl 2-acetamidoacrylate (**1l**) and N-vinylacetamide (**1n**) were purchased from Tokyo Chemical Industry Co., Ltd. The other materials and solvents were purchased from common commercial sources and used without additional purification, if there is no special version. ¹H NMR spectra were recorded at 400 MHz using TMS as internal standard. ¹³C NMR spectra were recorded at 100 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonances (br). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

Preparation of Enamides¹



10 mmol (1 equiv) of the acetophenone was dissolved in 6 mL of toluene taken in a dry 3-necked 50 mL RB flask under nitrogen. The resultant solution was stirred and cooled in an ice/water bath. To the resultant cold stirring solution was added 7N NH₃ in MeOH (2.14 mL, 15.0 mmol, 1.5 equiv) followed by dropwise addition of Ti(Oi-Pr)₄ (5.92 mL, 20.0 mmol, 2.0 equiv). After 10 min, the ice/water cooling bath was removed, and the solution was stirred at rt for 20 h. Then the reaction mixture was then cooled in an ice/water bath (~5 °C) and treated with Et₃N (5.58 mL, 40.0 mmol, 4.0 equiv) followed by Ac₂O (1.89 mL, 20.0 mmol, 2.0 equiv). The cooling bath was then removed and the solution was stirred at rt for 3 h. The reaction mixture was then treated with EDTE (*N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine) (4.51 mL, 21.0 mmol, 2.1 equiv) at rt, and the solution was then heated at about 55 °C for 15 min. The reaction mixture was allowed to cool to rt, and was then poured into a separatory funnel containing a solution made from water (30 mL) and NH₄OH (10 mL) and also EtOAc (50 mL). Additional water and EtOAc were used to rinse all the flask contents into the separatory funnel. The mixture was shaken, and from the resultant two clear phases the lower aqueous phase was removed. The aqueous phase was extracted again with EtOAc (50 mL), and the combined organic extracts were dried (Na₂SO₄), filtered, and concentrated to give the crude product. The pure product was isolated by flash column chromatography (Petroleum ether /ethyl acetate = 5/1).

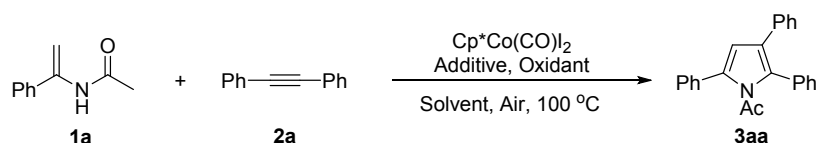
Typical Procedure for the Product



Enamides **1** (0.1 mmol) and Alkynes **2** (0.15 mmol) was added to a mixture of

Cp*Co(CO)I₂ (10 mol %), CuO (0.22 mmol), AgOTf (20 mol %), KOAc (20 mol %) in CF₃CH₂OH (1 mL). The mixture was stirred at 100 °C in air for 8 h. After completion the reaction mixture was cooled to ambient temperature and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel to afford pure products **3**.

The optimization of reaction conditions



entry	Additive 1	Additive 2	Oxidant	Solvent	Yield ^b (%)
1 ^c	Na ₂ CO ₃	TBAI	Ag ₂ CO ₃	CF ₃ CH ₂ OH	NR
2	AgOTf	KOAc	Cu(OAc) ₂	CF ₃ CH ₂ OH	30
3	AgOTf	KOAc	AgOAc	CF ₃ CH ₂ OH	22
4	AgOTf	KOAc	Ag ₂ CO ₃	CF ₃ CH ₂ OH	16
5	AgOTf	KOAc	O ₂	CF ₃ CH ₂ OH	30
6	AgOTf	KOAc	BQ	CF ₃ CH ₂ OH	trace
7	AgOTf	KOAc	CuO	CF ₃ CH ₂ OH	91
8	AgOTs	KOAc	CuO	CF ₃ CH ₂ OH	45
9	AgBF ₄	KOAc	CuO	CF ₃ CH ₂ OH	NR
10	AgOTFA	KOAc	CuO	CF ₃ CH ₂ OH	30
11	AgSbF ₆	KOAc	CuO	CF ₃ CH ₂ OH	40
12	AgOTf	NaOAc	CuO	CF ₃ CH ₂ OH	79
13	AgOTf	LiOAc	CuO	CF ₃ CH ₂ OH	64
14	AgOTf	KOAc	CuO	PhMe	32
15	AgOTf	KOAc	CuO	DCE	45
16	AgOTf	KOAc	CuO	DMF	trace
17	AgOTf	KOAc	CuO	Dioxane	12
18	-	AgOAc	CuO	CF ₃ CH ₂ OH	80
19	-	KOAc	CuO	CF ₃ CH ₂ OH	Trace
20	AgOTf	-	CuO	CF ₃ CH ₂ OH	Trace

^a Reactions were carried out by using **1a** (0.1 mmol), **2a** (0.15 mmol), Cp*Co(CO)I₂ (10 mol %), oxidant (2.2 equiv), additive **1** (20 mol %), additive **2** (20 mol %), Solvent (1.0 mL), 100 °C, air, 8 h. ^b Isolated yield. ^cCo(OAc)₂·4H₂O (10 mol %), Ag₂CO₃ (4 equiv), TBAI (3 equiv), Na₂CO₃ (3 equiv), pyridine (2 equiv), PhCF₃ (1.0 mL), 100 °C. TBAI = Tetrabutylammonium Iodide.

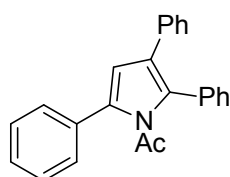
Gram-Scale Reaction

Enamides **1a** (5 mmol) and Alkynes **2a** (7.5 mmol) was added to a mixture of

Cp*Co(CO)I₂ (5 mol %), CuO (0.22 mmol), AgOTf (20 mol %), KOAc (20 mol %) in CF₃CH₂OH (5 mL). The mixture was stirred at 100 °C in air for 8 h. After completion the reaction mixture was cooled to ambient temperature and the solvent was removed in vacuo to provide a crude product, which was purified by column chromatography on silica gel to afford pure products **3a** (1.1g, 66%).

Characterization of products

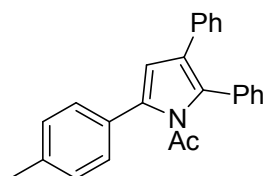
1-(2,3,5-triphenyl-1H-pyrrol-1-yl)ethanone



3aa

Yield: 91%; white solid; m.p = 129-130 °C ; ¹H NMR (CDCl₃, 400 MHz) δ 7.35-7.43 (m, 10H), 7.16-7.18 (m, 5H), 6.53 (s, 1H), 2.02 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 172.9, 134.9, 134.8, 133.5, 132.9, 131.0, 130.9, 128.5, 128.5, 128.5, 128.2, 128.1, 127.7, 126.3, 125.6, 113.6, 28.7. HRMS (EI-TOF) calcd for C₂₄H₁₉NO (M⁺): 337.1467, found: 337.1465

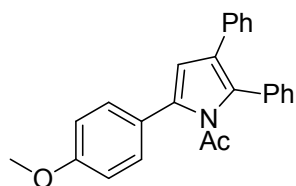
1-(2,3-diphenyl-5-(p-tolyl)-1H-pyrrol-1-yl)ethanone



3ba

Yield: 93%; Yellow solid; m.p = 123-124 °C ; ¹H NMR (CDCl₃, 400 MHz) δ 7.31-7.35 (m, 7H), 7.17-7.25 (m, 7H), 6.49 (s, 1H), 2.39 (s, 3H), 2.02 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 173.0, 134.9, 134.9, 137.5, 132.9, 131.0, 130.7, 130.6, 129.2, 128.4, 128.2, 128.2, 128.1, 126.2, 125.5, 113.3, 28.7, 21.3. HRMS (EI-TOF) calcd for C₂₅H₂₁NO (M⁺): 351.1623, found: 351.1619.

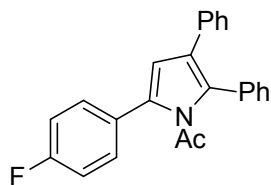
1-(5-(4-methoxyphenyl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone



3ca

Yield: 90%; Yellow solid; m.p = 118-119 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.34-7.37 (m, 7H), 7.15-7.19 (m, 5H), 6.95 (d, 2H, $J = 8\text{Hz}$), 6.46 (s, 1H), 3.84 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.0, 159.3, 135.0, 134.7, 133.0, 131.0, 130.5, 129.9, 128.4, 128.2, 128.2, 128.0, 126.2, 125.9, 125.5, 114.0, 113.1, 55.4, 28.7. HRMS (EI-TOF) calcd for $\text{C}_{25}\text{H}_{21}\text{NO}_2$ (M^+): 367.1572, found: 367.1568.

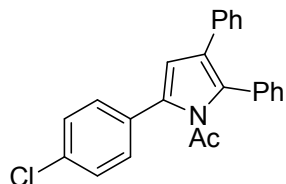
1-(5-(4-fluorophenyl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone



3da

Yield: 60%; Yellow solid; m.p = 141-142 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.36-7.41 (m, 7H), 7.07-7.19 (m, 7H), 6.48 (s, 1H), 1.99 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.8, 163.7, 161.2 (d, $J_{\text{C-F}} = 251.0\text{ Hz}$), 134.8, 134.0, 132.9, 130.9, 130.8, 130.5, 130.4 (d, $J_{\text{C-F}} = 8.1\text{ Hz}$), 129.6 (d, $J_{\text{C-F}} = 3.7\text{ Hz}$), 128.6, 128.3, 128.2, 126.4, 125.6, 115.6, 115.3 (d, $J_{\text{C-F}} = 21.7\text{ Hz}$), 113.8, 28.6. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{18}\text{FNO}$ (M^+): 355.1372, found: 355.1369.

1-(5-(4-chlorophenyl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone

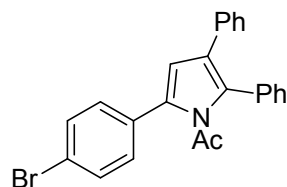


3ea

Yield: 84%; Yellow solid; m.p = 124-125 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.34-7.38 (m, 10H), 7.15-7.19 (m, 10H), 6.51 (s, 1H), 2.01 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.7, 134.6, 133.8, 133.6, 132.7, 131.9, 131.1, 130.9, 129.8, 128.6, 128.6,

128.3, 128.2, 128.2, 126.4, 125.8, 114.0, 28.4. HRMS (EI-TOF) calcd for $C_{24}H_{18}ClNO$ (M^+): 371.1077, found: 371.1075.

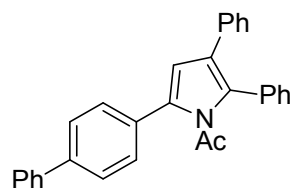
1-(5-(4-bromophenyl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone



3fa

Yield: 71%; Yellow solid; m.p = 127-128 °C ; 1H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, 2H, J = 8Hz), 7.28-7.38 (m, 7H), 7.14-7.20 (m, 5H), 2.01 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.7, 134.6, 133.8, 132.7, 132.4, 131.6, 131.1, 130.9, 130.1, 128.6, 128.4, 128.2, 128.2, 126.4, 125.8, 121.7, 114.1, 28.6. HRMS (EI-TOF) calcd for $C_{24}H_{18}BrNO$ (M^+): 415.0572, found: 415.0568.

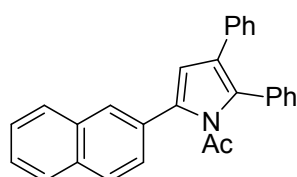
1-(5-([1,1'-biphenyl]-4-yl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone



3ga

Yield: 75%; Yellow solid; m.p = 165-166 °C ; 1H NMR ($CDCl_3$, 400 MHz) δ 6.74-6.77 (m, 4H), 6.64 (d, 2H, J = 7Hz), 6.60 (t, 2H, J = 8Hz), 6.53 (s, 6H), 6.38-6.39 (m, 5H), 5.88 (s, 1H), 2.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.1, 140.5, 140.4, 134.9, 134.6, 132.9, 132.4, 131.1, 131.1, 128.9, 128.8, 128.5, 128.3, 127.5, 127.2, 127.1, 126.3, 125.7, 113.8, 28.8. HRMS (EI-TOF) calcd for $C_{30}H_{23}NO$ (M^+): 413.1780, found: 413.1782.

1-(5-(naphthalen-2-yl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone

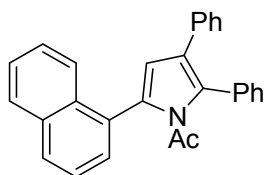


3ha

Yield: 90%; Yellow solid; m.p = 141-142 °C ; 1H NMR ($CDCl_3$, 400 MHz) δ 7.84-

7.91 (m, 4H), 7.47-7.55 (m, 3H), 7.37 (s, 5H), 7.13-7.21 (m, 5H), 6.64 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.1, 134.9, 134.9, 133.4, 132.9, 132.7, 131.3, 131.1, 131.0, 128.5, 128.3, 128.2, 128.1, 128.1, 127.8, 127.0, 126.7, 126.6, 126.3, 125.8, 114.2, 28.7. HRMS (EI-TOF) calcd for $\text{C}_{28}\text{H}_{21}\text{NO}$ (M^+): 387.1623, found: 387.1629.

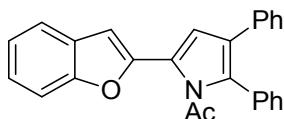
1-(5-(naphthalen-1-yl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone



3ia

Yield: 85%; White Solid; m.p = 167-168 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.88-7.94 (m, 3H), 7.48-7.56 (m, 4H), 7.36-7.40 (m, 5H), 7.15-7.21 (m, 5H), 6.60 (s, 1H), 1.80 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.9, 134.9, 133.6, 133.4, 133.0, 132.5, 131.7, 130.9, 130.7, 128.8, 128.5, 128.5, 128.3, 128.3, 128.2, 128.0, 126.8, 126.3, 126.2, 125.7, 125.6, 125.3, 115.2, 27.7. HRMS (EI-TOF) calcd for $\text{C}_{28}\text{H}_{21}\text{NO}$ (M^+): 387.1623, found: 387.1622.

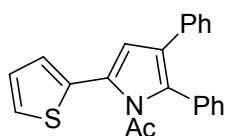
1-(5-(benzofuran-2-yl)-2,3-diphenyl-1H-pyrrol-1-yl)ethanone



3ja

Yield: 75%; Green Solid; m.p = 104-105 °C ; ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 7.68 (d, 1H, $J = 8\text{Hz}$), 7.59 (d, 1H, $J = 8\text{Hz}$), 7.44-7.45 (m, 3H), 7.17-7.38 (m, 9H), 7.12 (s, 1H), 7.07 (s, 1H), 2.12 (s, 3H). ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz) δ 172.3, 154.1, 148.0, 133.9, 131.8, 131.6, 130.7, 128.7, 128.4, 128.3, 127.8, 126.5, 124.9, 124.6, 123.3, 123.3, 121.2, 114.8, 111.0, 104.2, 27.2. HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{19}\text{NO}_2$ (M^+): 377.1416, found: 377.1417.

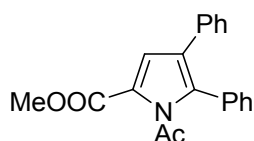
1-(2,3-diphenyl-5-(thiophen-2-yl)-1H-pyrrol-1-yl)ethanone



3ka

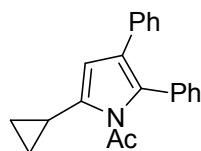
Yield: 40%; Yellow Solid; m.p = 169-170 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.33-7.36 (m, 6H), 7.15-7.20 (m, 6H), 7.07 (dd, $J = 8\text{Hz}$, 1H), 6.60 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.9, 134.8, 134.1, 132.9, 131.0, 130.6, 128.6, 128.3, 128.2, 128.2, 127.6, 127.3, 127.1, 126.4, 126.1, 125.6, 114.9, 28.4. HRMS (EI-TOF) calcd for $\text{C}_{22}\text{H}_{17}\text{NOS}$ (M^+): 343.1031, found: 343.1035.

Methyl 1-acetyl-4,5-diphenyl-1H-pyrrole-2-carboxylate

**3la**

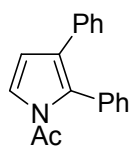
Yield: 80%; Yellow liquid; ^1H NMR (CDCl_3 , 400 MHz) δ 7.28-7.38 (m, 5H), 7.12-7.21 (m, 6H), 3.88 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 174.0, 161.2, 134.6, 134.0, 130.7, 129.0, 128.6, 128.3, 128.1, 126.5, 124.9, 123.0, 118.5, 51.9, 28.9. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{17}\text{NO}_3$ (M^+): 319.1208, found: 319.1217.

1-(5-cyclopropyl-2,3-diphenyl-1H-pyrrol-1-yl)ethanone

**3ma**

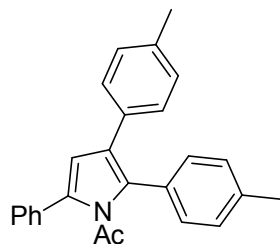
Yield: 30%; Yellow Solid; m.p = 97-98 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.33-7.35 (m, 3H), 7.26-7.28 (m, 2H), 7.08-7.18 (m, 5H), 6.10 (s, 1H), 2.18-2.25 (m, 1H), 2.04 (s, 3H), 0.90-0.93 (m, 2H), 0.69-0.70 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.5, 138.2, 134.7, 133.1, 130.0, 129.9, 128.5, 128.2, 127.7, 127.6, 127.4, 125.6, 124.7, 109.2, 27.7, 8.9, 6.6. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}$ (M^+): 301.1467, found: 301.1469.

1-(2,3-diphenyl-1H-pyrrol-1-yl)ethanone

**3na**

Yield: 20%; Yellow Solid; m.p = 111-112 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.44 (d, 1H, J = 4Hz), 7.36-7.37 (m, 3H), 7.30-7.32 (m, 2H), 7.10-7.20 (m, 5H), 6.53 (d, 1H, J = 4Hz), 2.22 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 169.2, 134.7, 133.5, 131.0, 128.4, 128.2, 128.1, 128.1, 128.0, 126.3, 120.9, 112.6, 24.9. HRMS (EI-TOF) calcd for $\text{C}_{18}\text{H}_{15}\text{NO}$ (M^+): 261.1154, found: 261.1150.

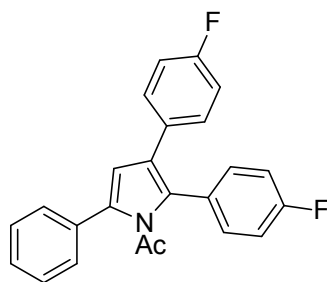
1-(5-phenyl-2,3-di-p-tolyl-1H-pyrrol-1-yl)ethanone



3ab

Yield: 81%; Brown liquid; m.p = 128-129 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.41 (m, 4H), 7.33-7.35 (m, 1H), 7.22-7.24 (m, 2H), 7.16 (d, 2H, J = 8Hz), 7.07 (d, 2H, J = 8Hz), 7.01 (d, 2H, J = 8Hz), 6.50 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.0, 137.9, 135.8, 134.6, 133.6, 132.0, 130.9, 129.9, 129.2, 128.9, 128.5, 128.4, 128.0, 127.5, 125.3, 113.7, 28.7, 21.4, 21.1. HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$ (M^+): 365.1780, found: 365.1783.

1-(2,3-bis(4-fluorophenyl)-5-phenyl-1H-pyrrol-1-yl)ethanone

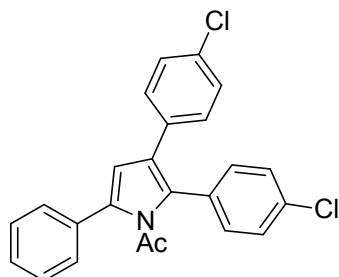


3ac

Yield: 89%; Yellow Solid; m.p = 125-126 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.42 (d, 4H, J = 4 Hz), 7.35-7.38 (m, 1H), 7.28-7.32 (m, 2H), 7.03-7.11 (m, 2H), 6.48 (s, 1H), 2.03 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.7, 162.6 (d, $J_{\text{C-F}}$ = 247.3 Hz), 161.6 (d, $J_{\text{C-F}}$ = 243.8 Hz), 134.8, 133.3, 132.9 (d, $J_{\text{C-F}}$ = 8.1 Hz), 130.7 (d, $J_{\text{C-F}}$ = 3.6 Hz), 130.0, 129.7 (d, $J_{\text{C-F}}$ = 7.2 Hz), 128.7, 128.6 (d, $J_{\text{C-F}}$ = 3.6 Hz), 128.4, 127.9, 125.0, 115.5 (d, $J_{\text{C-F}}$ = 21.6 Hz), 115.2 (d, $J_{\text{C-F}}$ = 20.7 Hz), 113.5, 28.7. HRMS (EI-TOF)

calcd for $C_{24}H_{17}F_2NO$ (M^+): 373.1278, found: 373.1279.

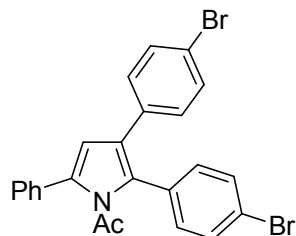
1-(2,3-bis(4-chlorophenyl)-5-phenyl-1H-pyrrol-1-yl)ethanone



3ad

Yield: 90%; Yellow Solid; m.p = 151-152 °C ; 1H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.43 (m, 5H), 7.33 (d, 2H, J = 8Hz), 7.25 (d, 2H, J = 8Hz), 7.18 (d, 2H, J = 8Hz), 7.06 (d, 2H, J = 8Hz), 6.48 (s, 1H), 2.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.6, 135.1, 134.3, 133.2, 133.1, 132.4, 132.3, 130.9, 130.0, 129.5, 128.7, 128.5, 128.4, 128.0, 124.9, 113.4, 28.8. HRMS (EI-TOF) calcd for $C_{24}H_{17}Cl_2NO$ (M^+): 405.0687, found: 405.0686.

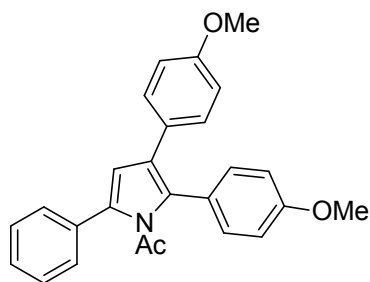
1-(2,3-bis(4-bromophenyl)-5-phenyl-1H-pyrrol-1-yl)ethanone



3ae

Yield: 71%; Yellow solid; m.p = 161-162 °C ; 1H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, 2H, J = 8Hz), 7.37-7.43 (m, 5H), 7.33 (d, 2H, J = 8Hz), 7.18 (d, 2H, J = 8Hz), 7.00 (d, 2H, J = 8Hz), 6.48 (s, 1H), 2.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.6, 135.2, 133.5, 133.1, 132.7, 131.7, 131.5, 131.4, 130.0, 129.8, 138.8, 128.4, 128.0, 124.9, 122.6, 120.4, 113.4, 28.8. HRMS (EI-TOF) calcd for $C_{24}H_{17}Br_2NO$ (M^+): 492.9677, found: 492.9675.

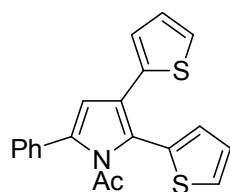
1-(2,3-bis(4-methoxyphenyl)-5-phenyl-1H-pyrrol-1-yl)ethanone



3af

Yield: 60%; Yellow liquid; m.p = 108-109 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.32-7.41 (m, 5H), 7.26 (d, 2H, J = 8Hz), 7.10 (d, 2H, J = 8Hz), 6.89 (d, 2H, J = 8Hz), 6.74 (d, 2H, J = 8Hz), 6.48 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.1, 159.4, 158.0, 134.5, 133.7, 132.4, 130.3, 129.2, 128.5, 128.3, 127.5, 127.4, 125.2, 125.1, 113.9, 113.7, 113.6, 55.2, 55.2, 28.7. HRMS (EI-TOF) calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_3$ (M^+): 397.1678, found: 397.1682.

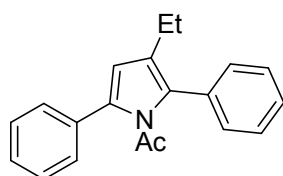
1-(5-phenyl-2,3-di(thiophen-2-yl)-1H-pyrrol-1-yl)ethanone



3ag

Yield: 80%; Yellow Solid; m.p = 131-132 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (d, 1H, J = 0.8Hz), 7.34-7.53 (m, 5H), 7.09-7.20 (m, 3H), 6.91-6.93 (m, 2H), 6.58 (s, 1H), 2.07 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.8, 136.6, 136.1, 133.2, 132.6, 131.6, 128.9, 128.6, 128.3, 128.0, 127.4, 127.0, 124.4, 124.3, 122.7, 121.6, 112.6, 27.9. HRMS (EI-TOF) calcd for $\text{C}_{20}\text{H}_{15}\text{NOS}_2$ (M^+): 349.0595, found: 349.0591.

1-(3-ethyl-2,5-diphenyl-1H-pyrrol-1-yl)ethanone

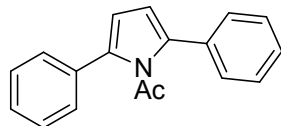


3ah

Yield: 80%; Yellow Solid; m.p = 81-82 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.30-7.41 (m, 10H), 6.25 (s, 1H), 2.36 (q, 2H, J = 8Hz), 1.99 (s, 3H), 1.13 (t, 3H, J = 8Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.5, 134.8, 134.0, 133.3, 130.9, 130.2, 128.6, 128.3,

127.6, 127.6, 127.3, 113.8, 28.4, 19.0, 15.2. HRMS (EI-TOF) calcd for C₂₀H₁₉NO (M⁺): 289.1467, found: 289.1473.

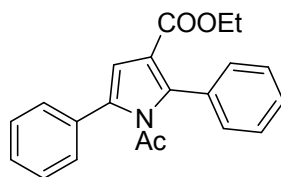
1-(2,5-diphenyl-1H-pyrrol-1-yl)ethanone



3ai

Yield: 60%; Yellow Solid; m.p = 105-106 °C ; ¹H NMR (CDCl₃, 400 MHz) δ 7.31-7.39 (m, 10H), 6.30 (s, 2H), 2.10 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 173.1, 135.9, 133.6, 128.7, 128.4, 127.6, 112.9, 28.7. HRMS (EI-TOF) calcd for C₁₈H₁₅NO (M⁺): 261.1154, found: 261.1160.

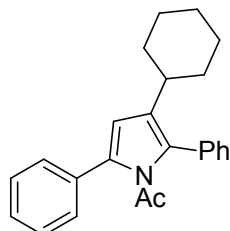
Ethyl 1-acetyl-2,5-diphenyl-1H-pyrrole-3-carboxylate



3aj

Yield: 25%; Yellow Solid; m.p = 92-94 °C ; ¹H NMR (CDCl₃, 400 MHz) δ 7.42 (s, 5H), 7.35-7.40 (m, 5H), 6.77 (s, 1H), 4.13 (q, 2H, *J* = 8Hz), 1.99 (s, 3H), 1.14 (t, 3H, *J* = 8Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 172.9, 164.1, 138.4, 134.3, 132.5, 131.7, 130.6, 128.8, 128.6, 128.0, 127.9, 116.3, 112.9, 60.0, 28.6, 14.1. HRMS (EI-TOF) calcd for C₂₁H₁₉NO₃ (M⁺): 333.1365, found: 333.1366.

1-(3-cyclohexyl-2,5-diphenyl-1H-pyrrol-1-yl)ethanone

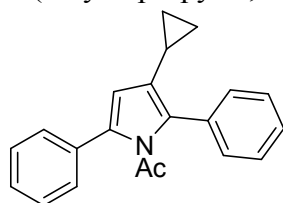


3ak

Yield: 35%; Yellow solid; m.p = 127-128 °C ; ¹H NMR (CDCl₃, 400 MHz) δ 7.30-7.42 (m, 10H), 6.26 (s, 1H), 2.31 (t, 1H, *J* = 8Hz), 1.98 (s, 3H), 1.72-1.74 (m, 4H),

1.56 (s, 1H), 1.38 (q, 2H, $J = 12\text{Hz}$), 1.18-1.20 (m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.4, 134.7, 134.1, 133.4, 131.9, 130.3, 130.3, 128.5, 128.3, 127.6, 127.2, 112.3, 34.9, 34.5, 28.4, 26.6, 26.1. HRMS (EI-TOF) calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$ (M^+): 343.1936, found: 343.1934.

1-(3-cyclopropyl-2,5-diphenyl-1H-pyrrol-1-yl)ethanone

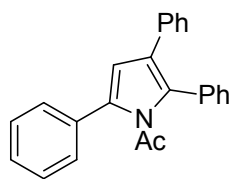


3al

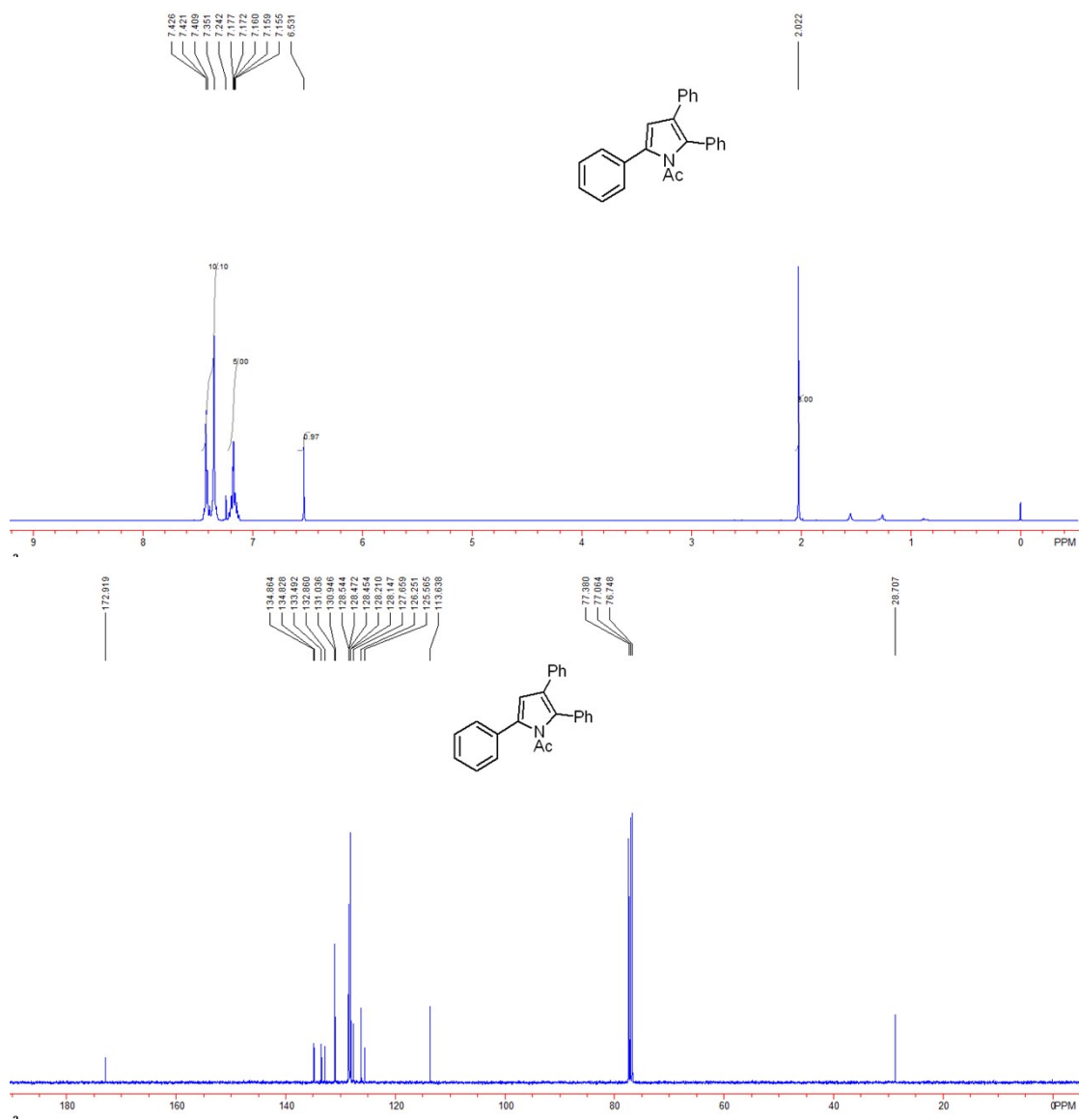
Yield: 20%; Yellow Solid; m.p = 117-118 °C ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.43 (m, 4H), 7.30-7.37 (m, 6H), 5.88 (s, 1H), 2.00 (s, 3H), 1.61-1.68 (m, 1H), 0.77-0.82 (m, 2H), 0.57-0.61 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.6, 134.5, 133.4, 132.7, 131.1, 129.8, 128.1, 127.8, 127.8, 127.5, 127.0, 126.9, 109.5, 27.9, 7.5, 6.7. HRMS (EI-TOF) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}$ (M^+): 301.1467, found: 301.1470.

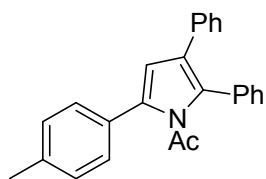
References

- 1 Reeves, J. T.; Tan, Z.; Han, Z.; Li, G.; Zhang, Y.; Xu, Y.; Reeves, D. C.; Gonnella, D. C.; Ma, S. L.; Lee, H. W.; Lu, B. Z.; Senanayake, C. H. *Angew. Chem. Int. Ed.* 2012, *51*, 1400–1404.

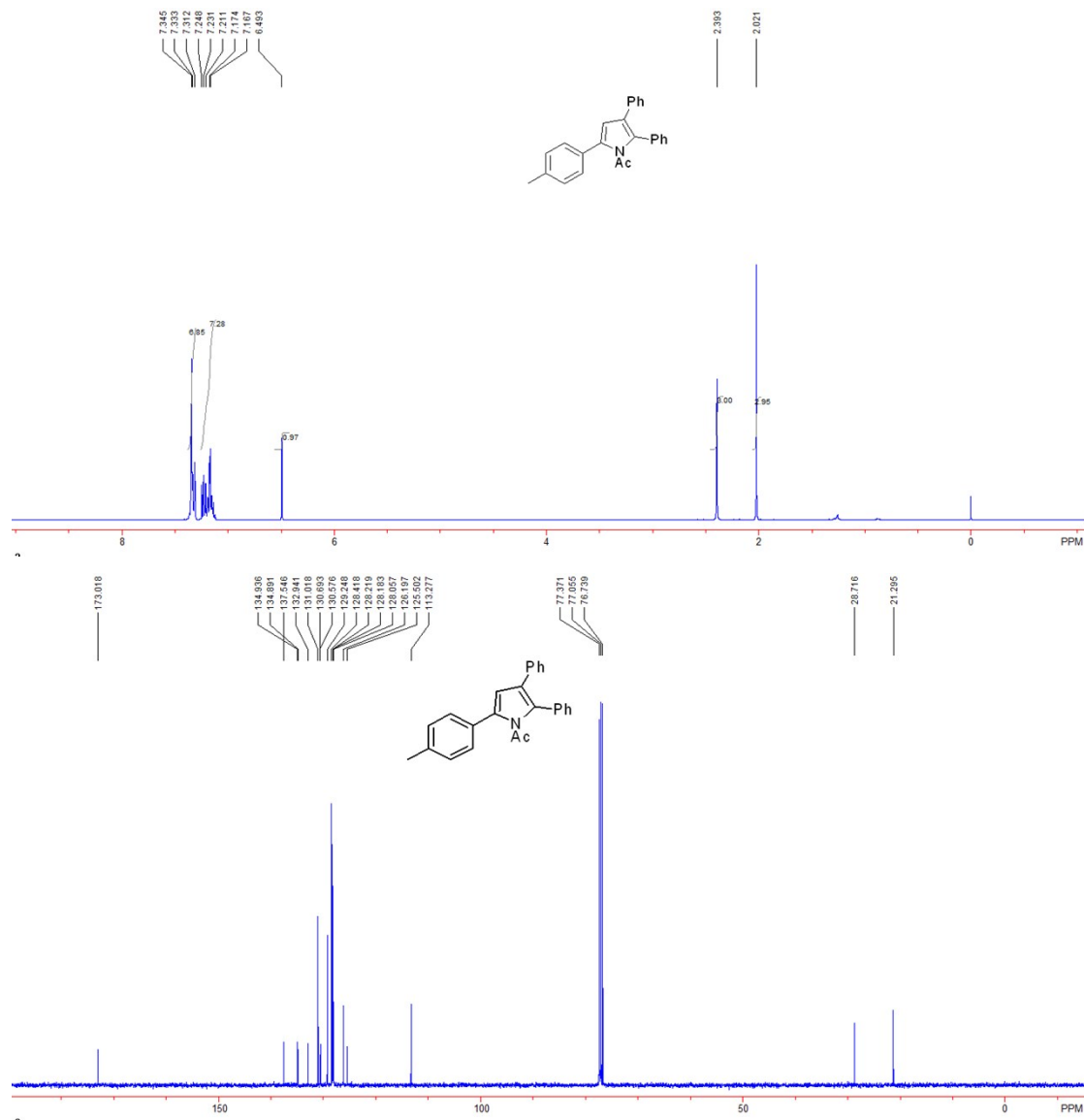


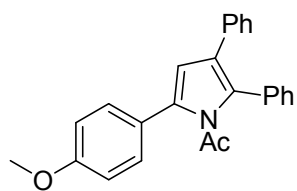
3aa



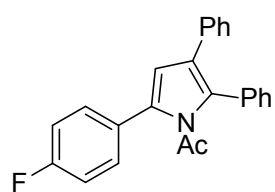
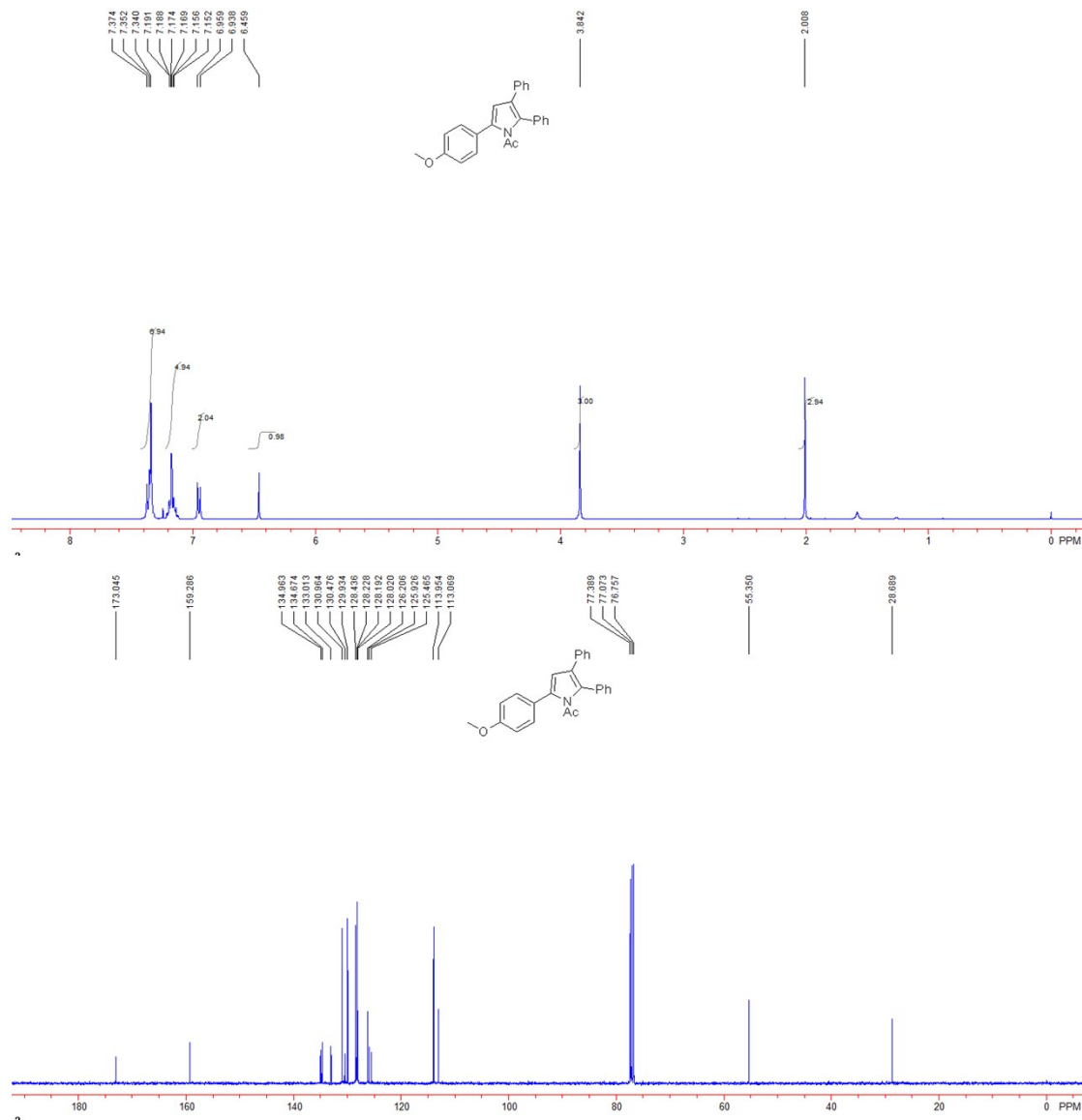


3ba

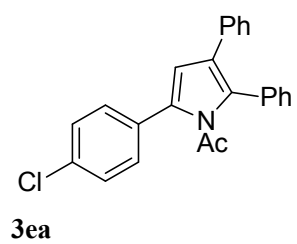
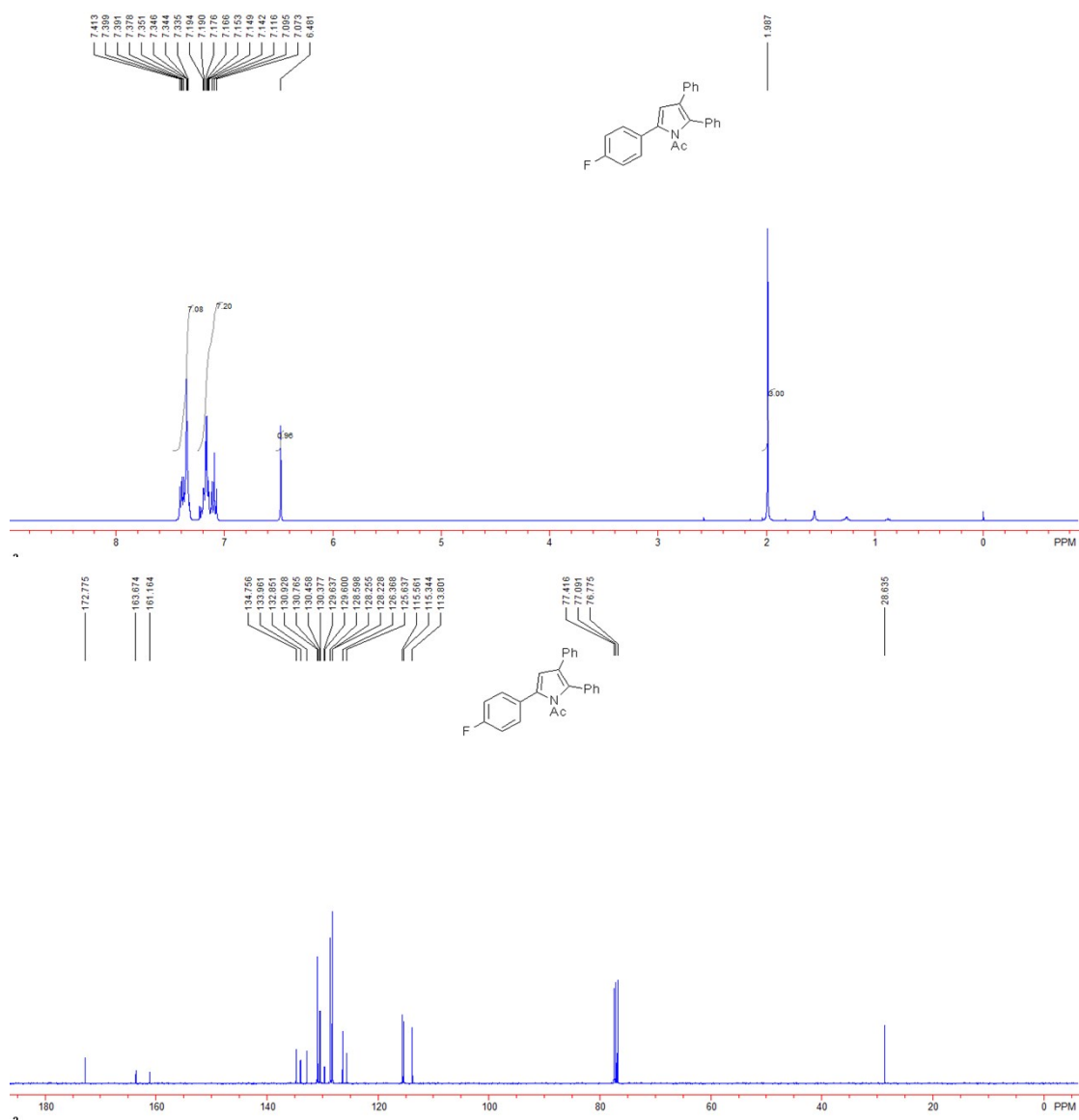


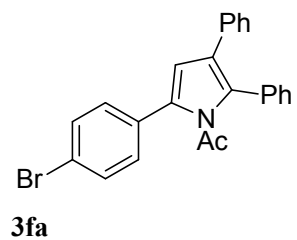
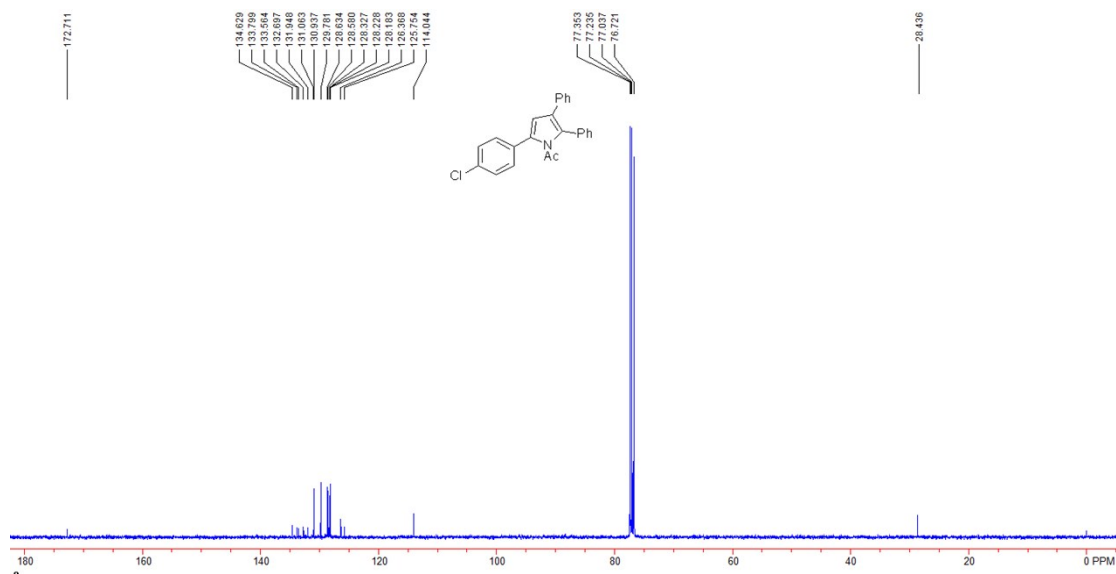
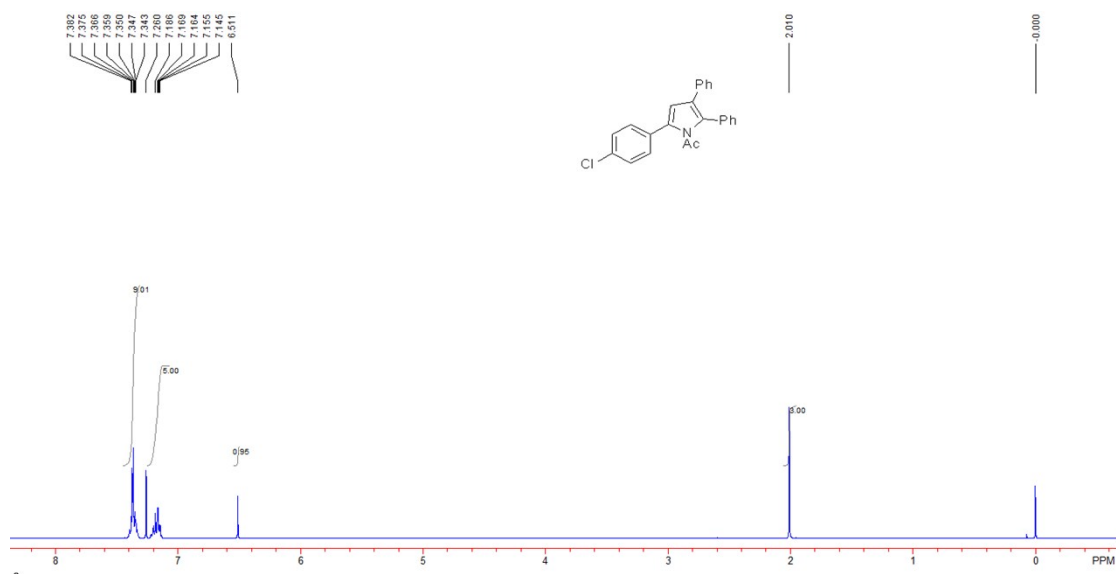


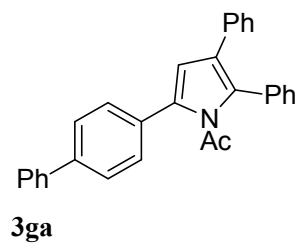
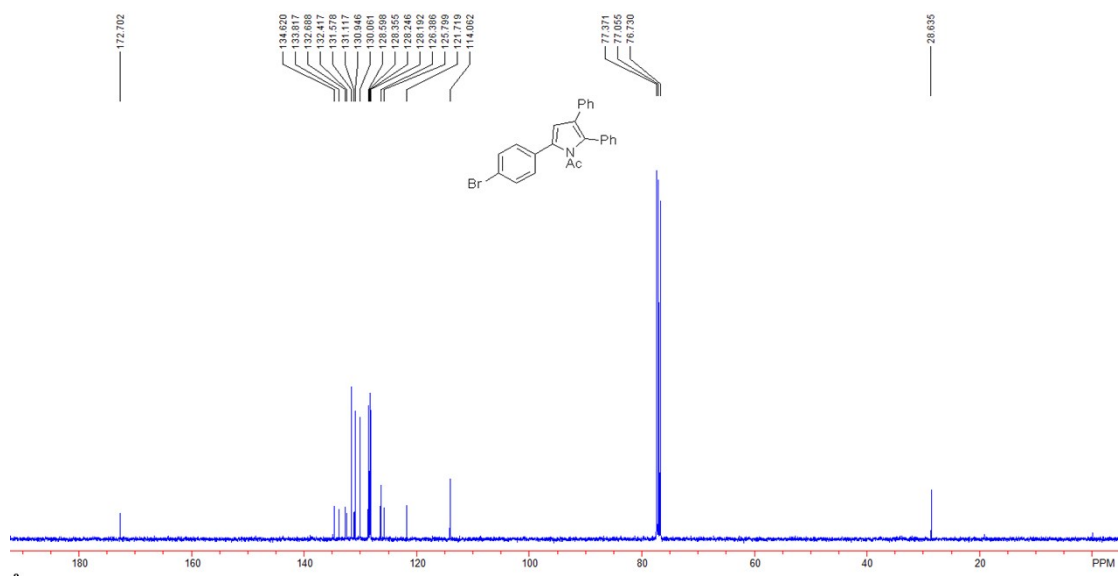
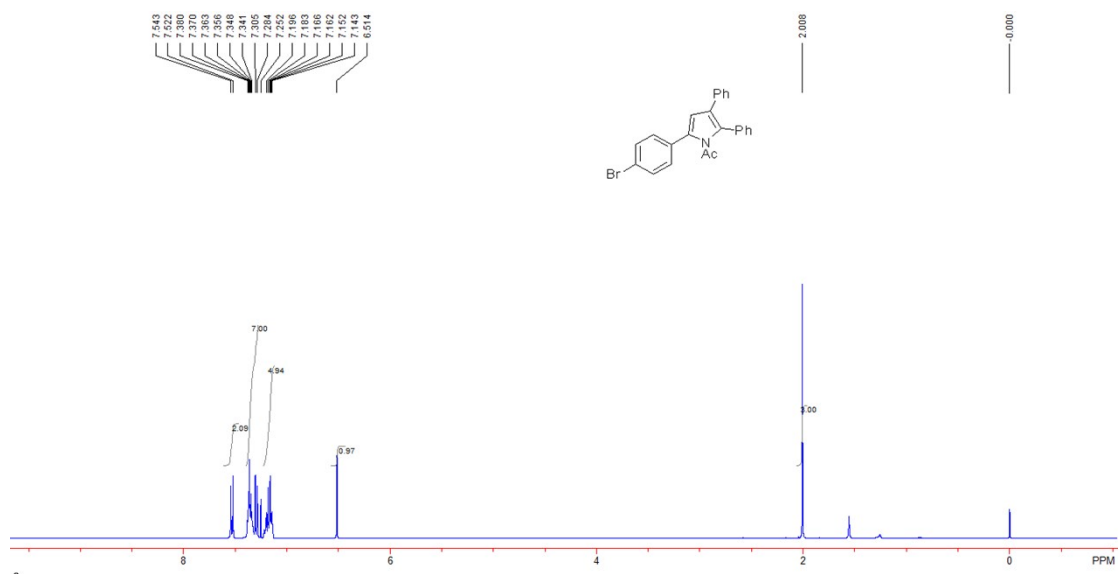
3ca

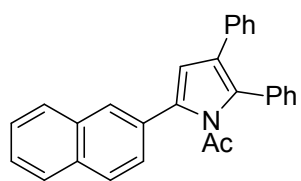
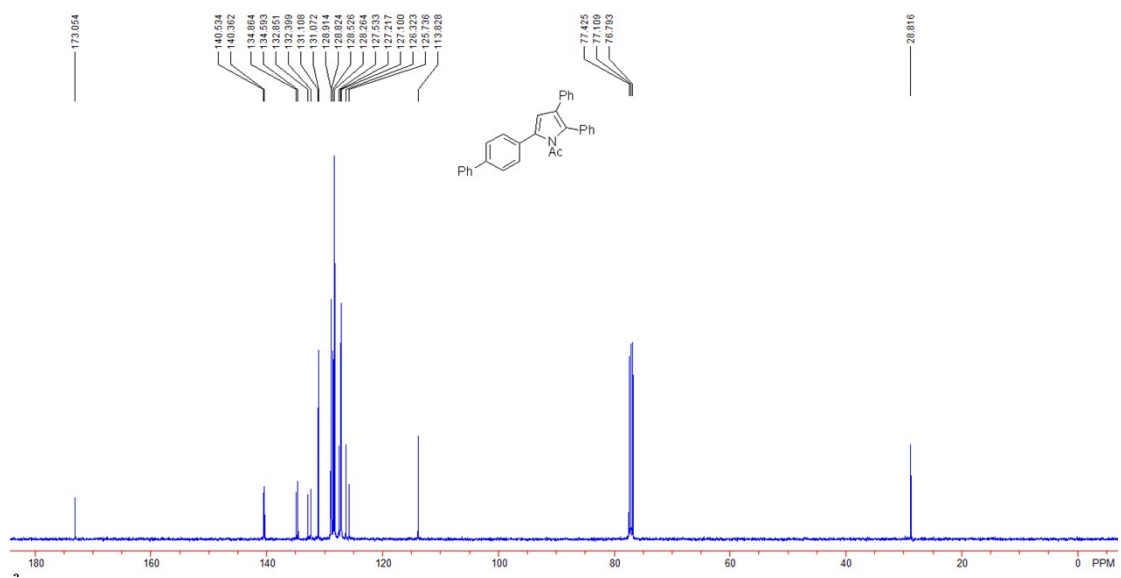
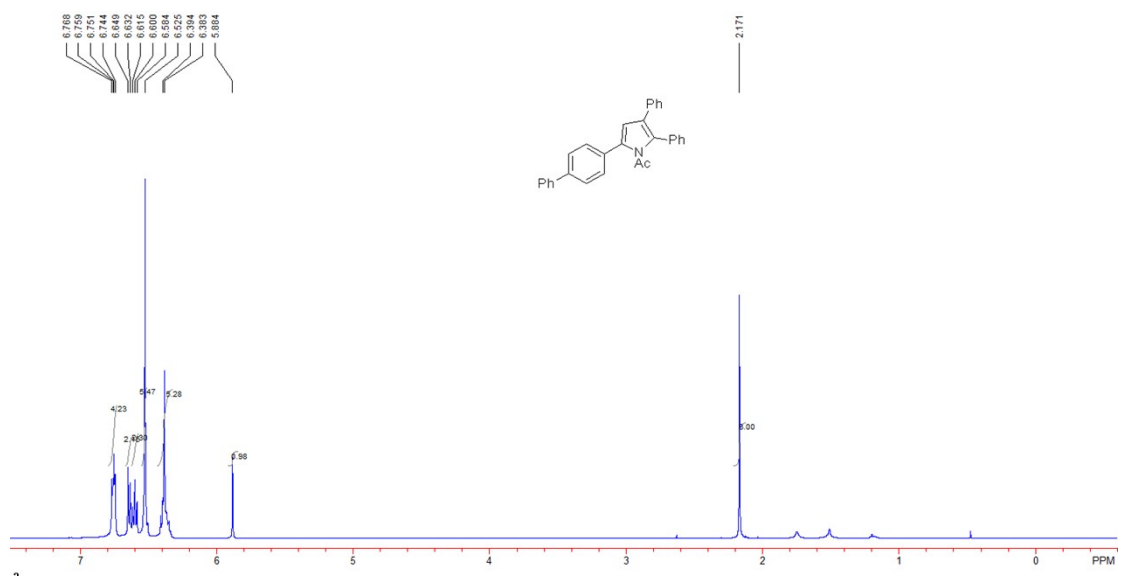


3da

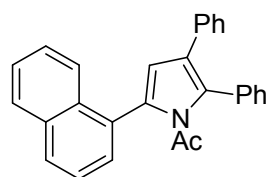
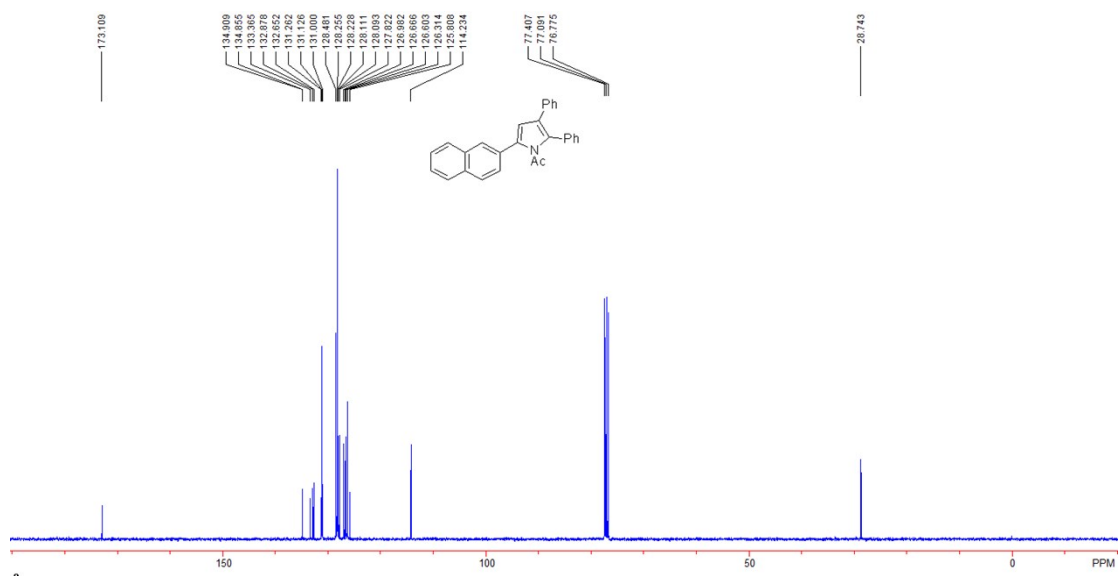
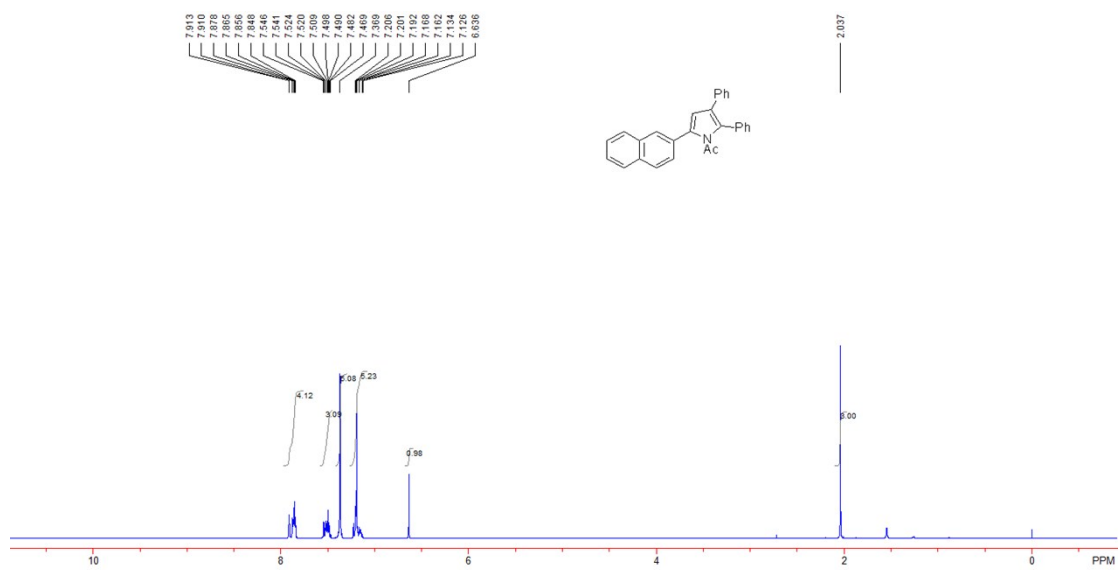




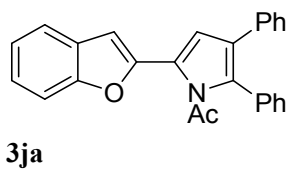
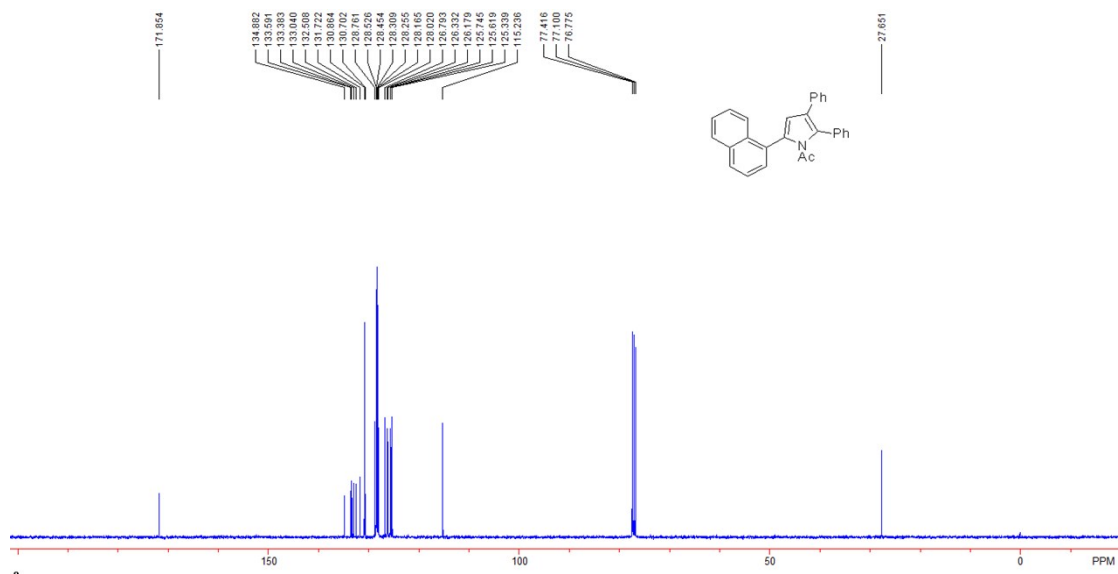
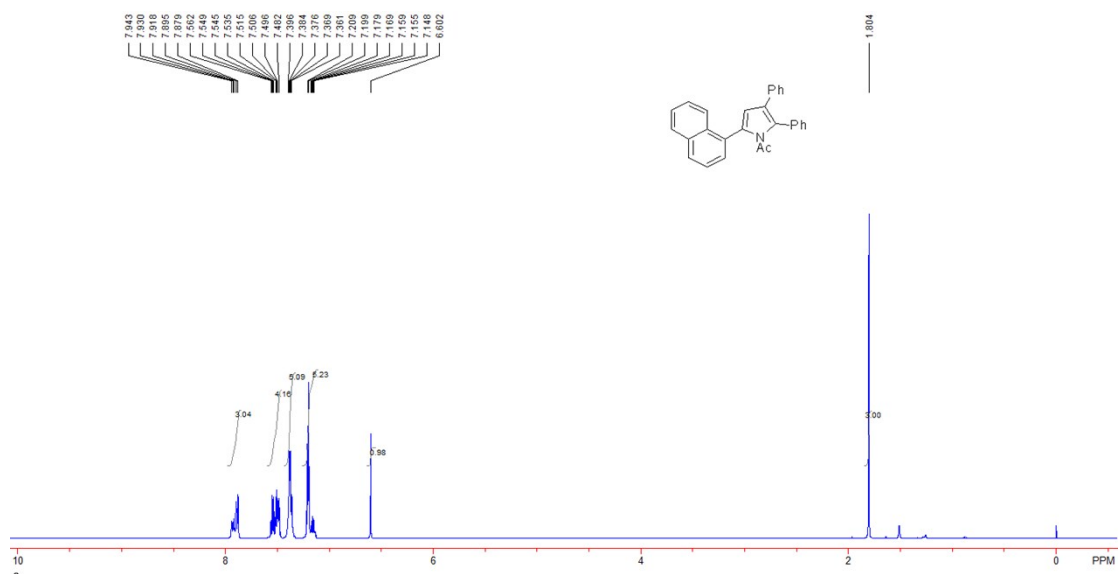


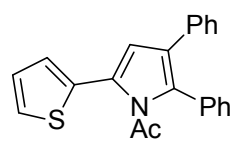
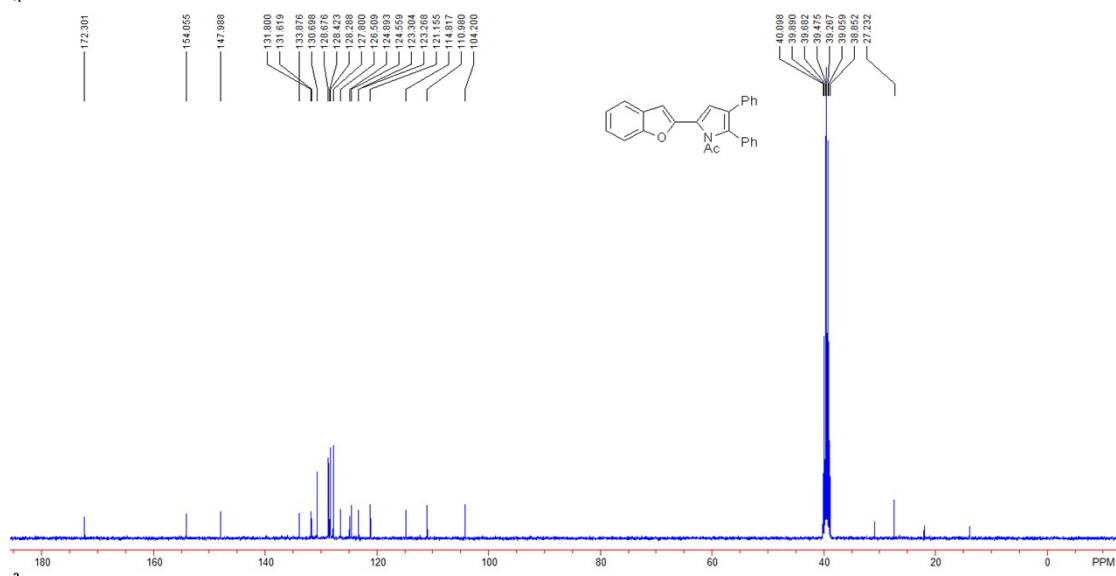
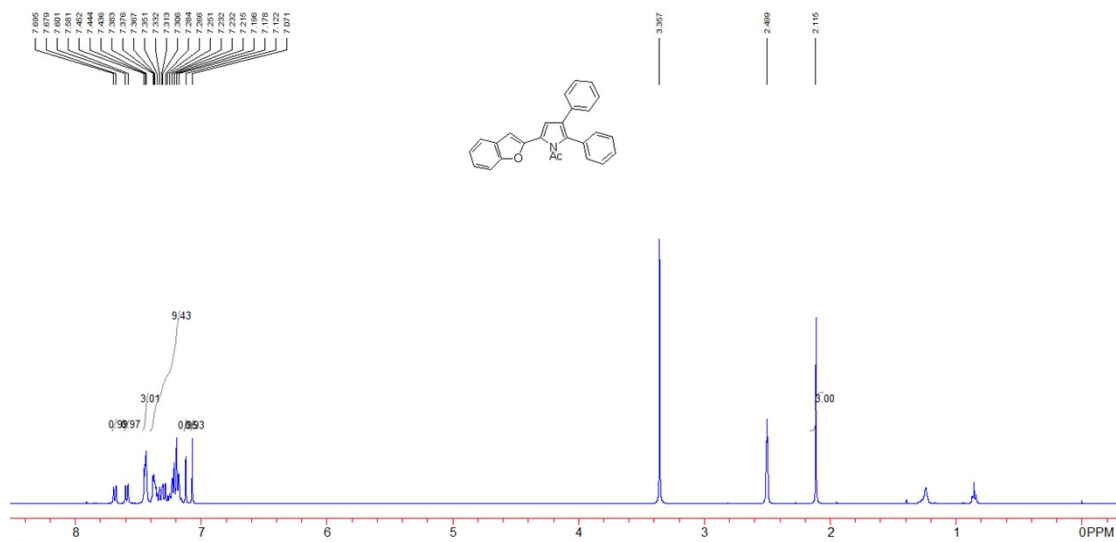


3ha

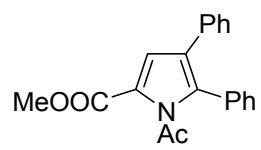
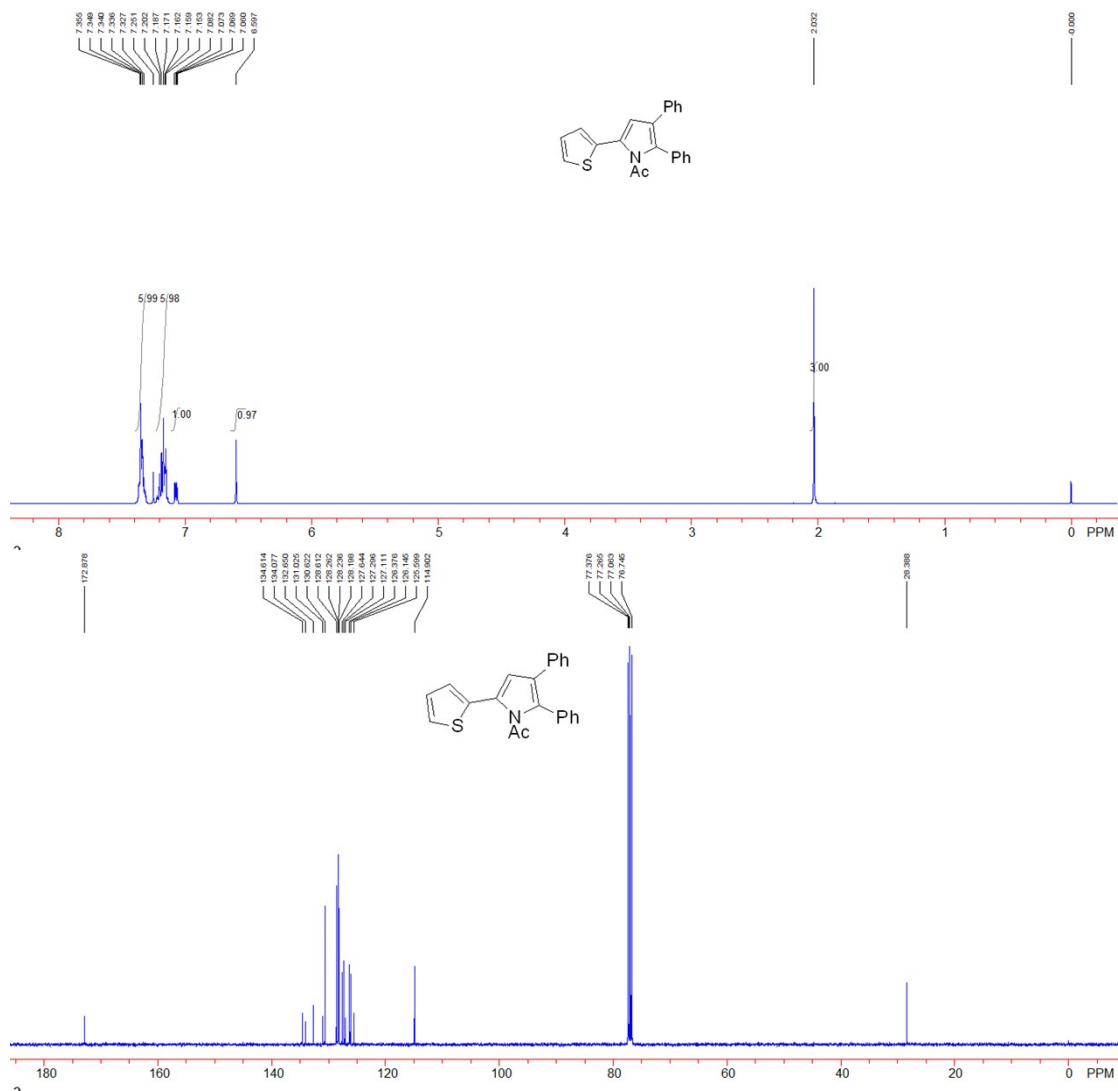


3ia

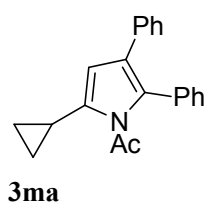
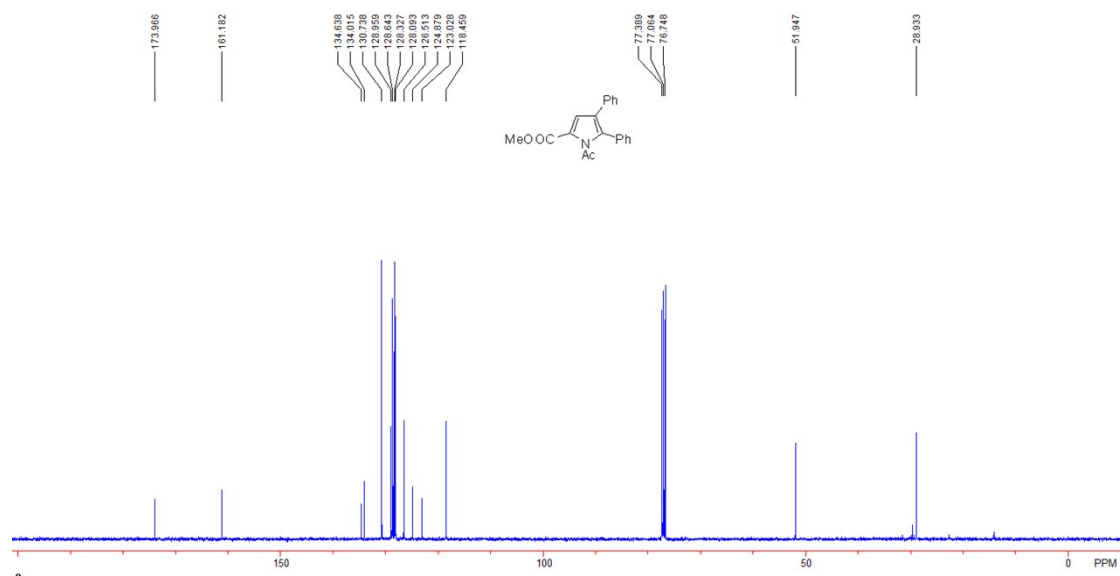
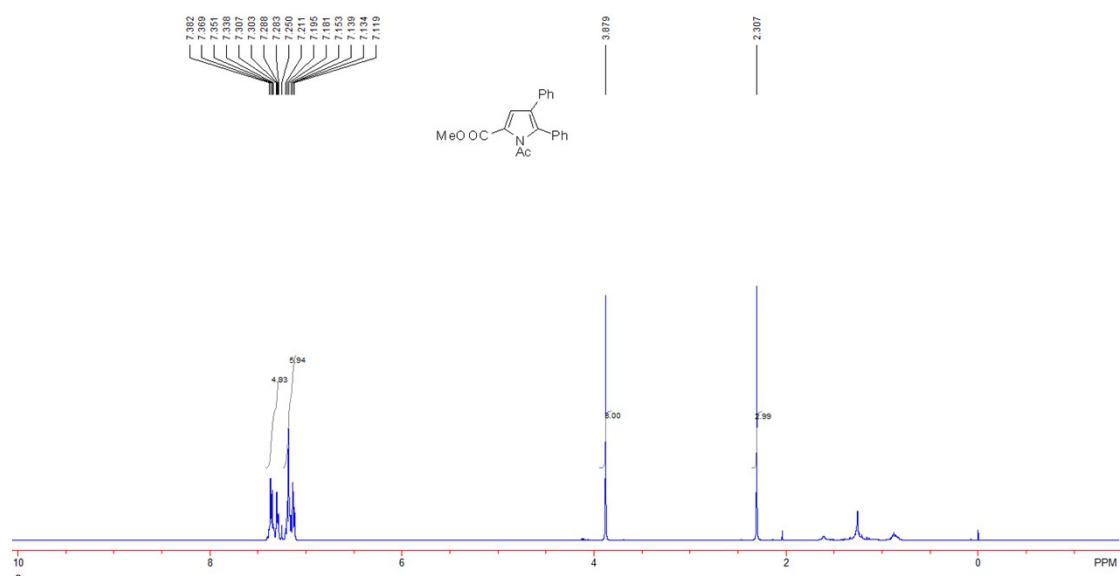


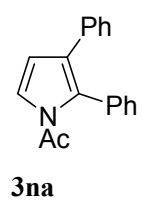
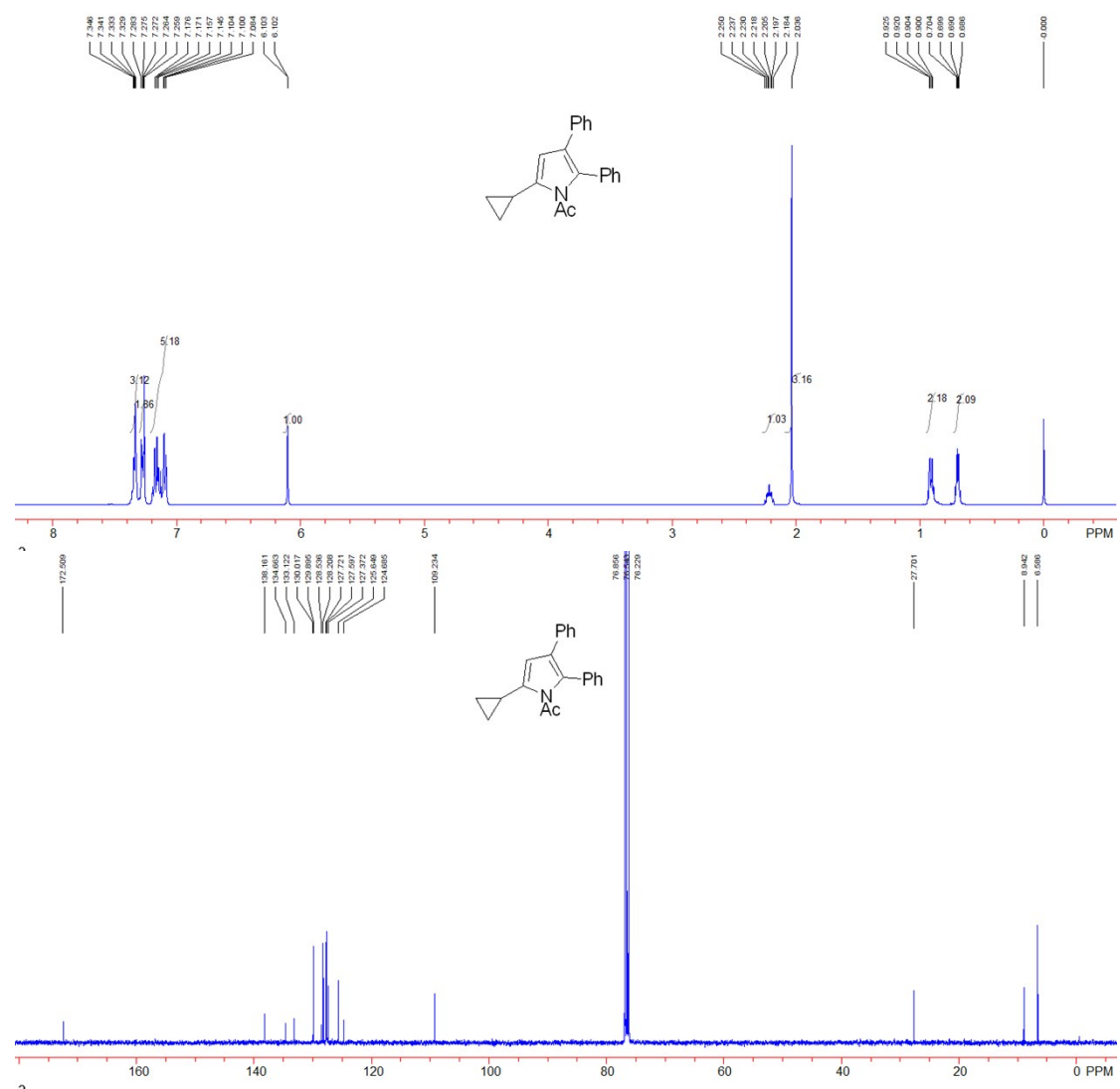


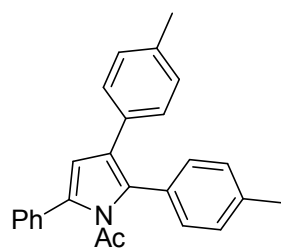
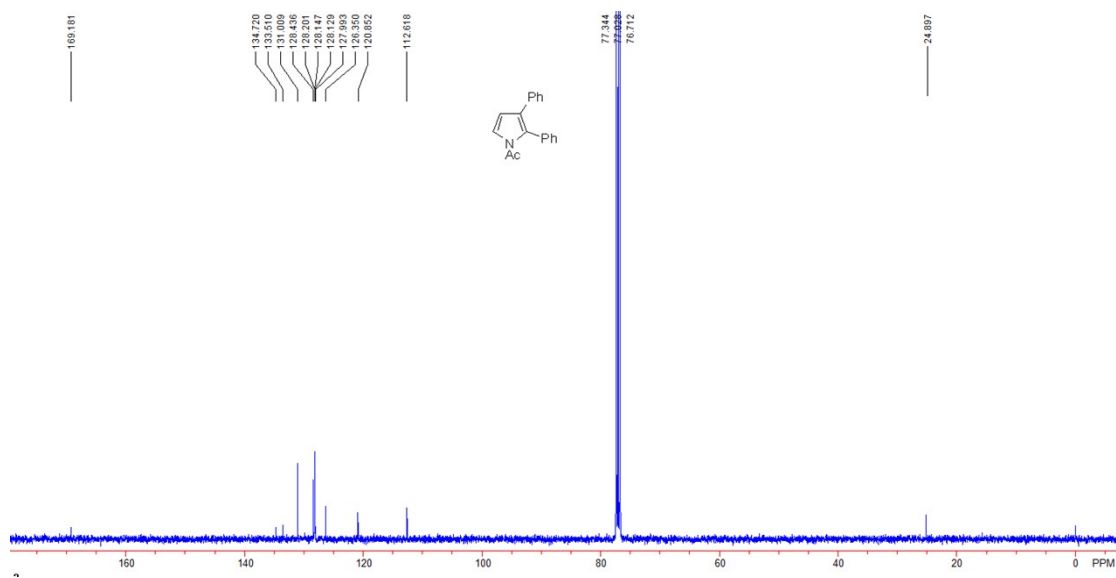
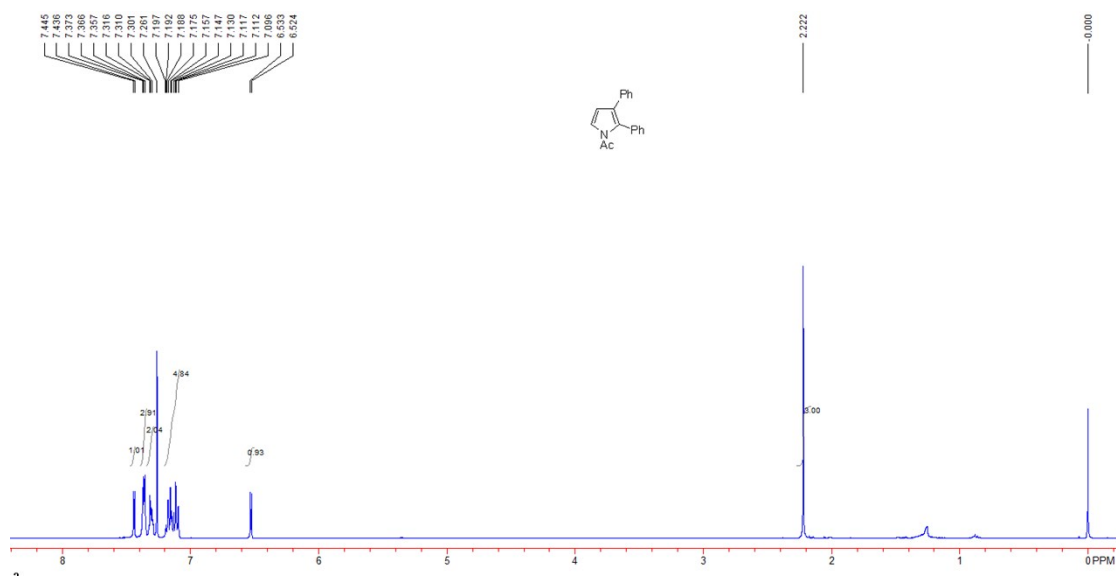
3ka



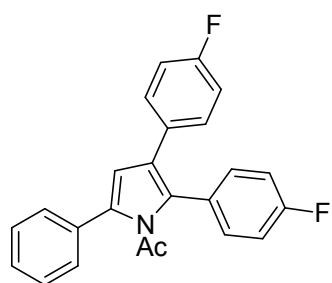
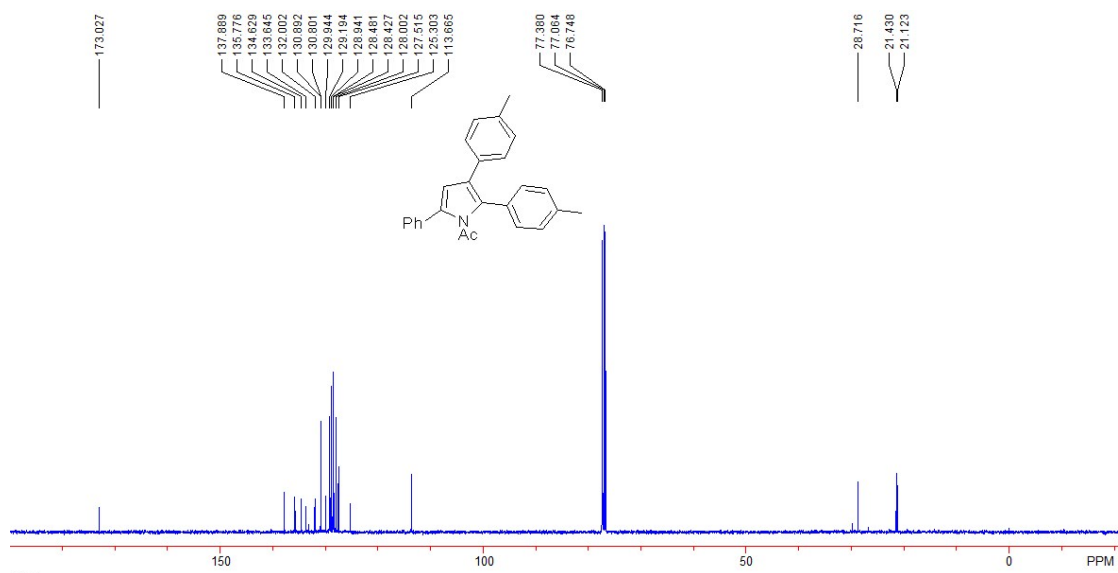
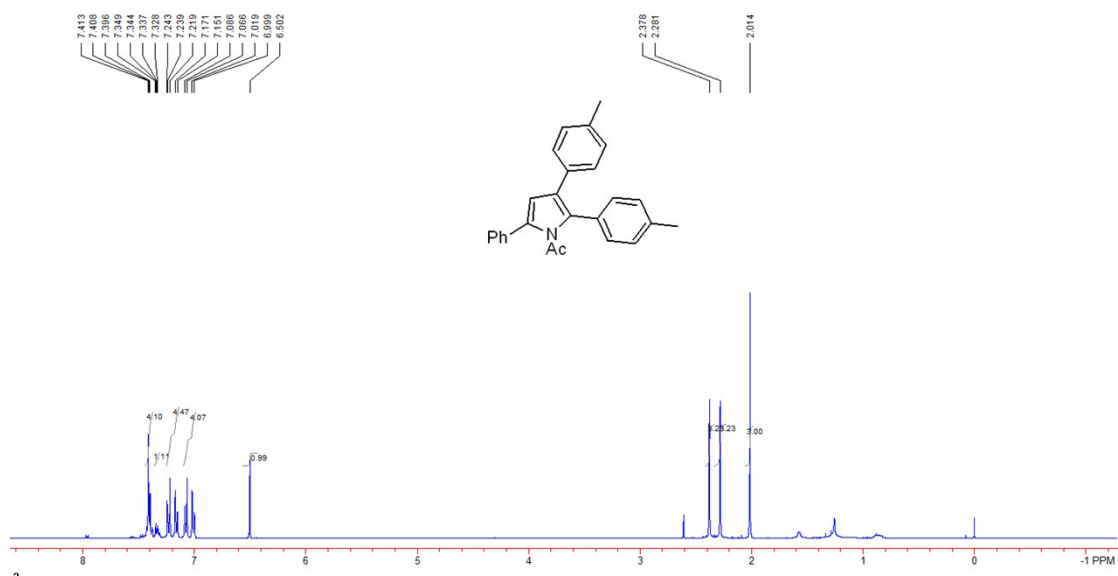
3la



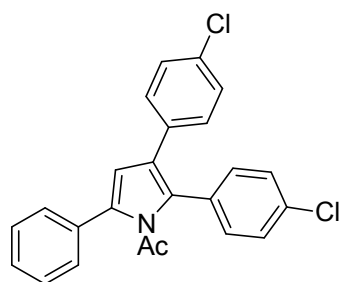
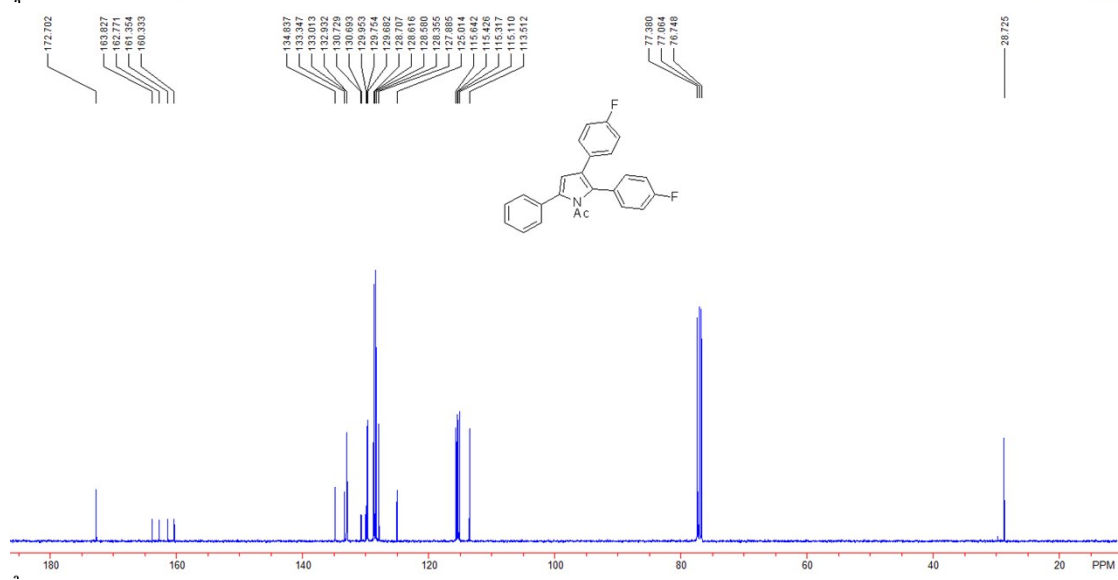
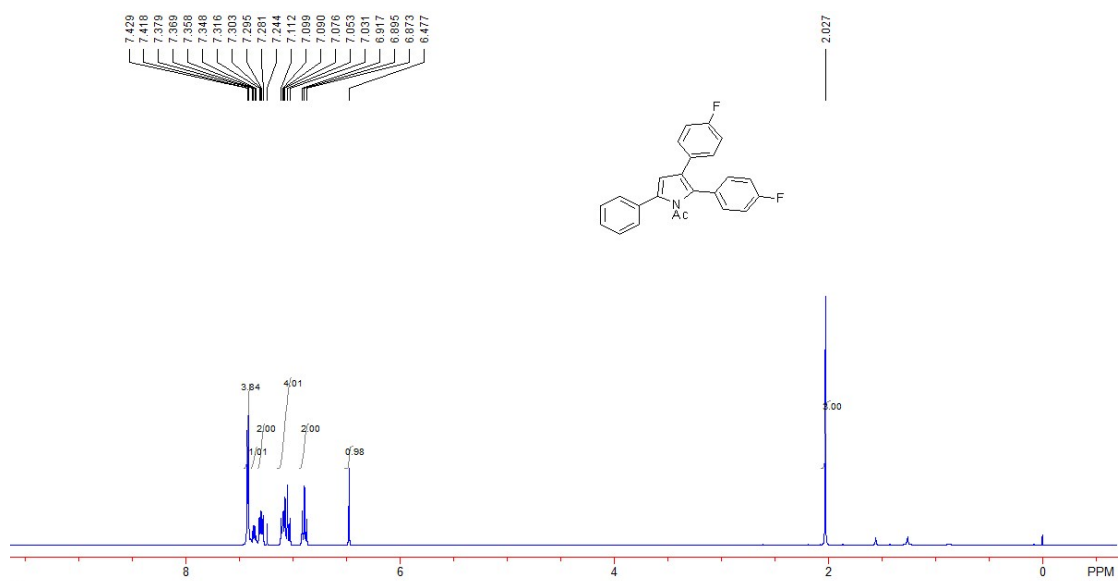


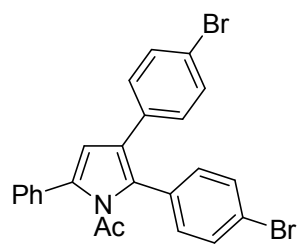
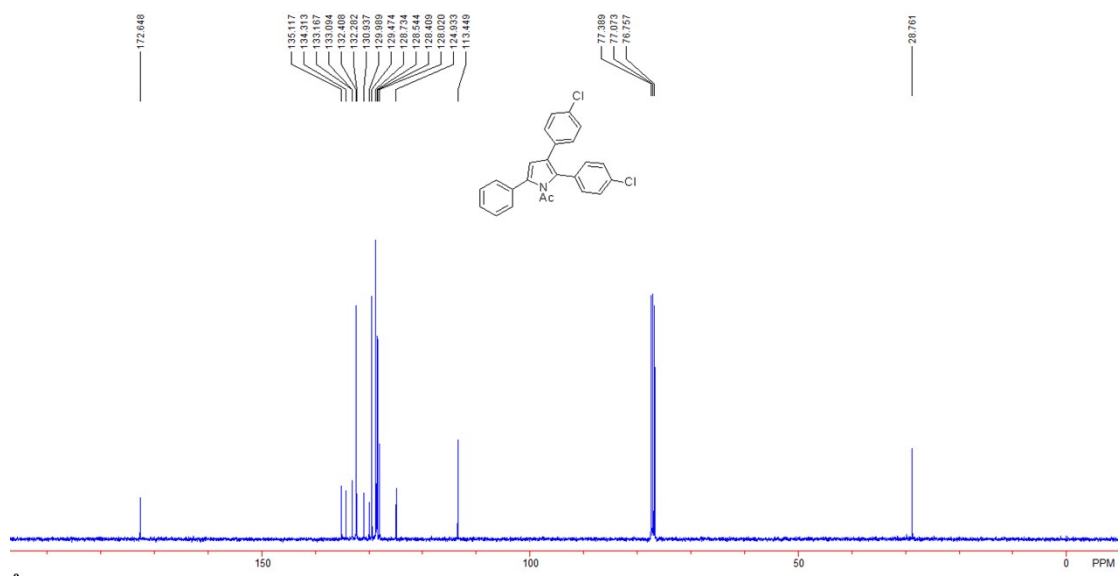
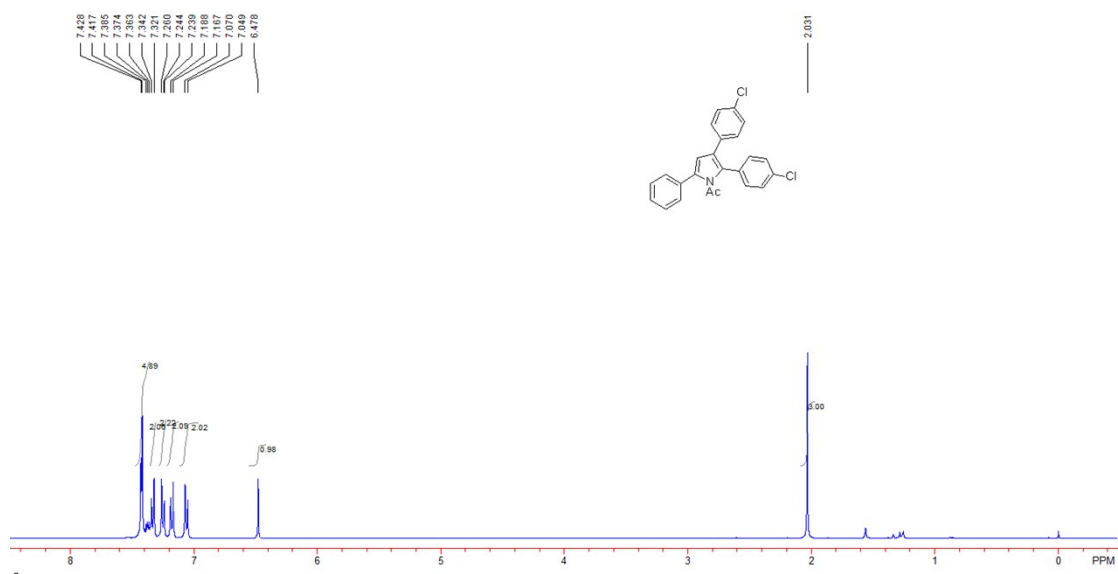


3ab

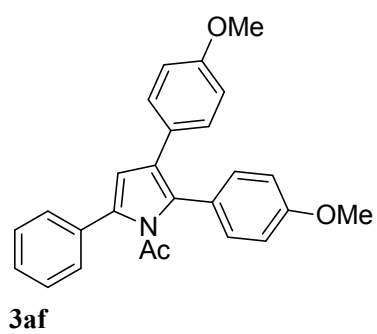
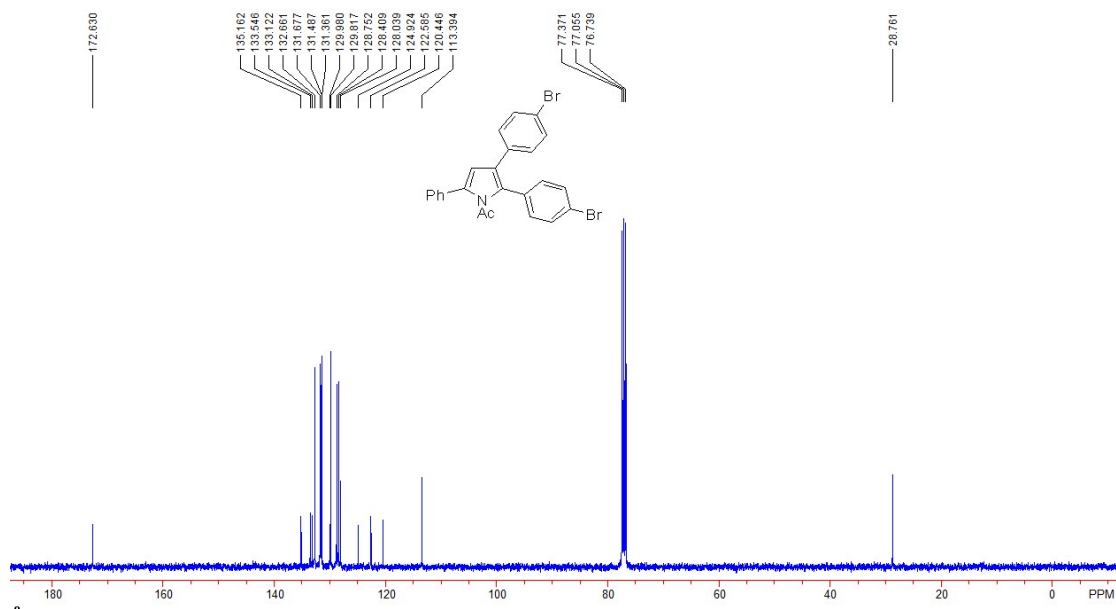
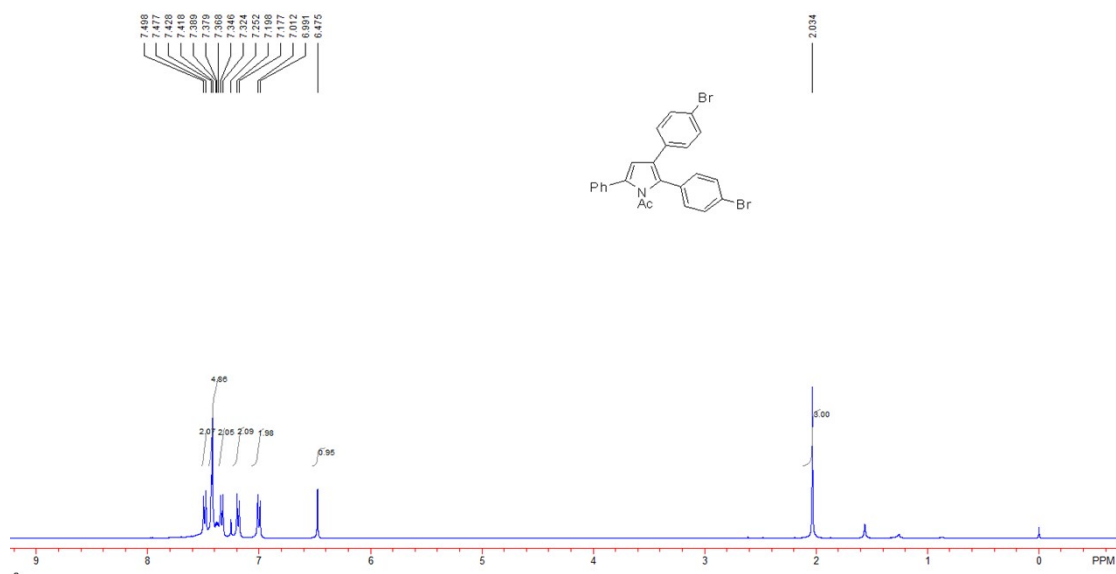


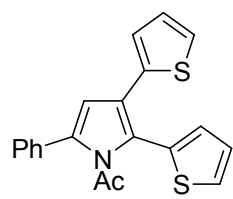
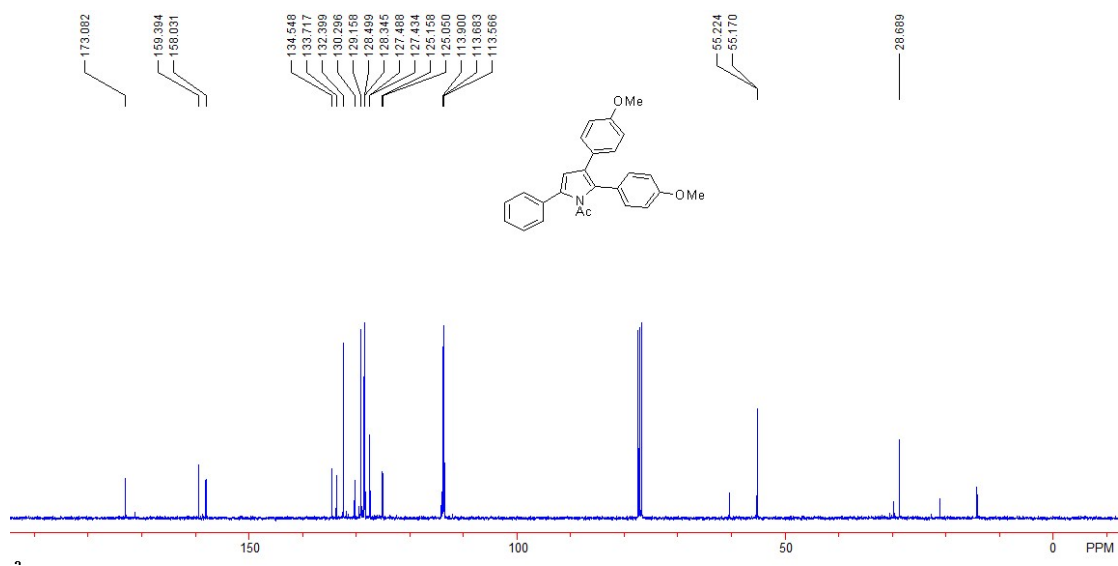
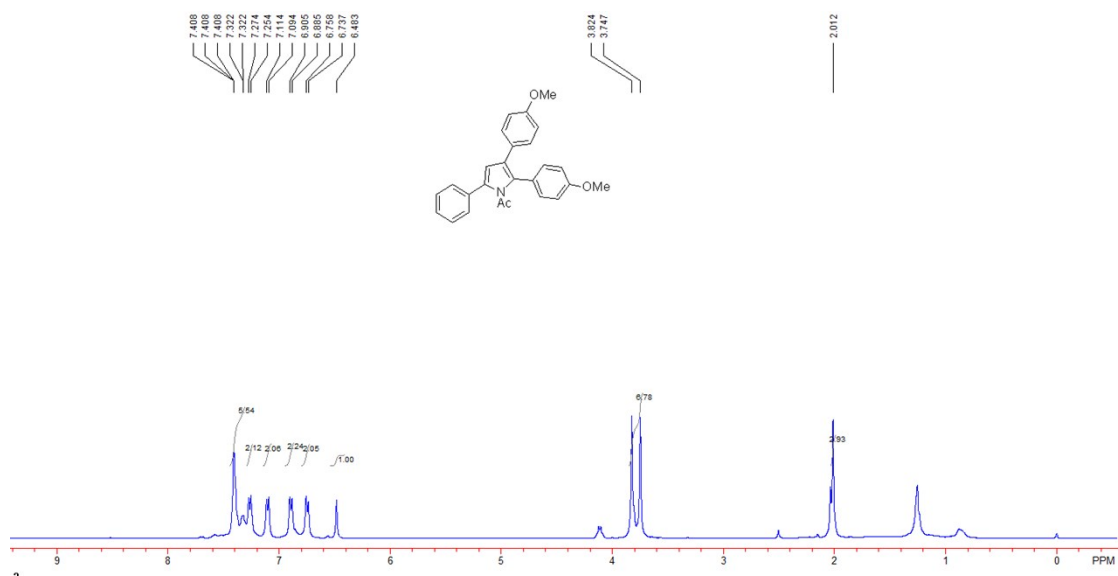
3ac



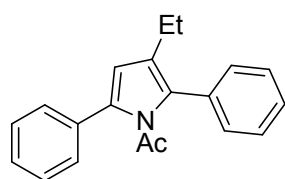
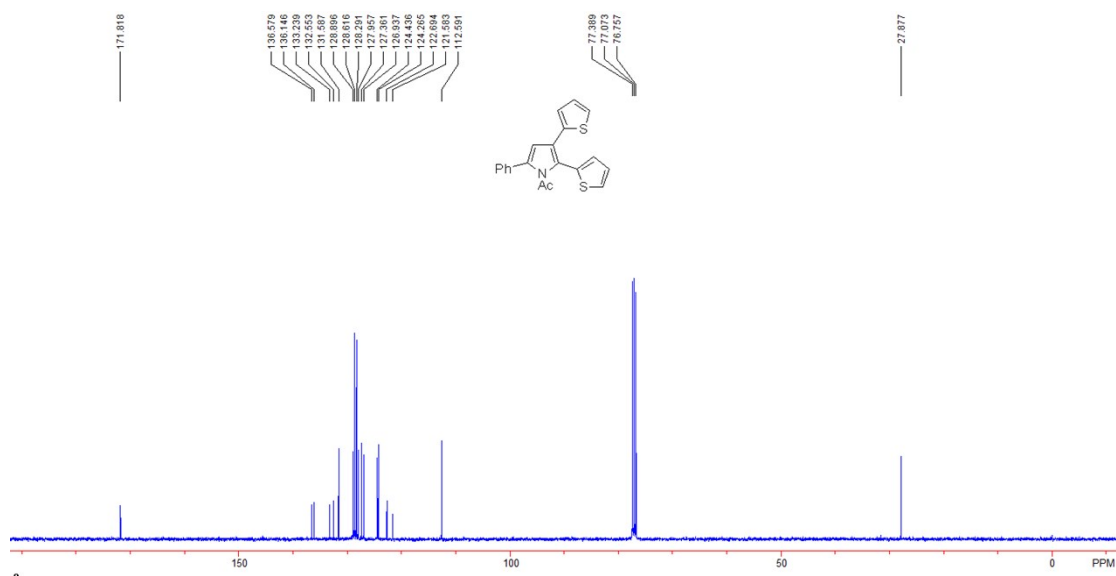
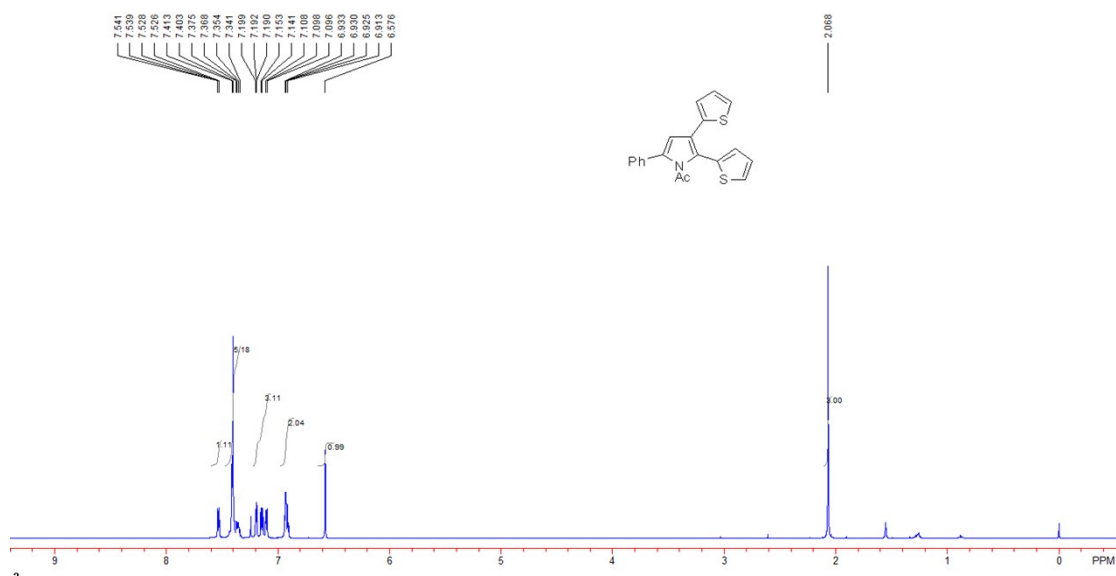


3ae

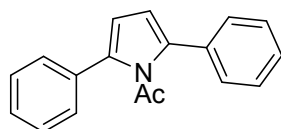
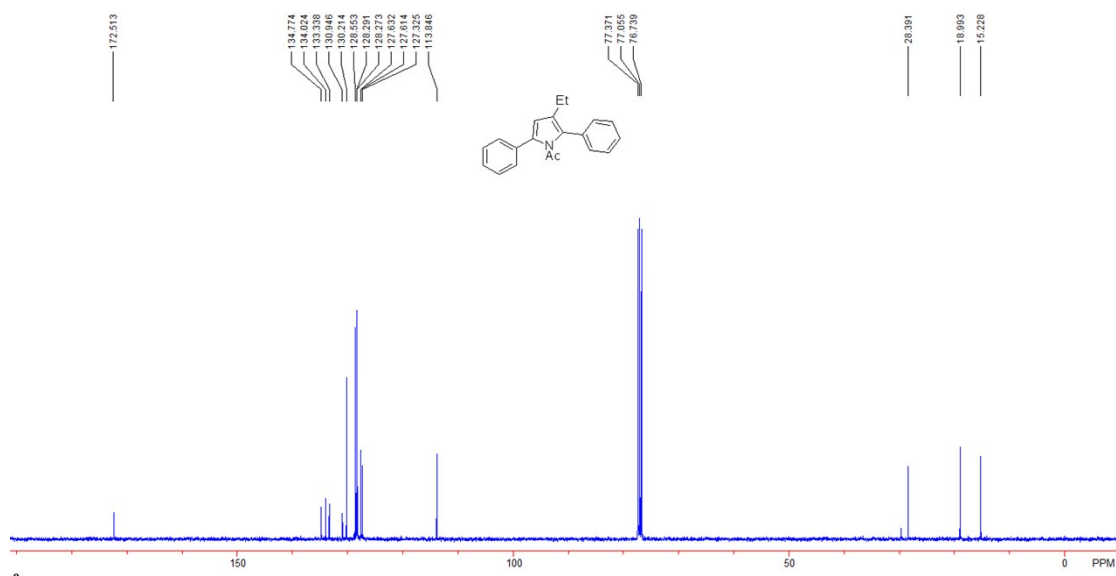
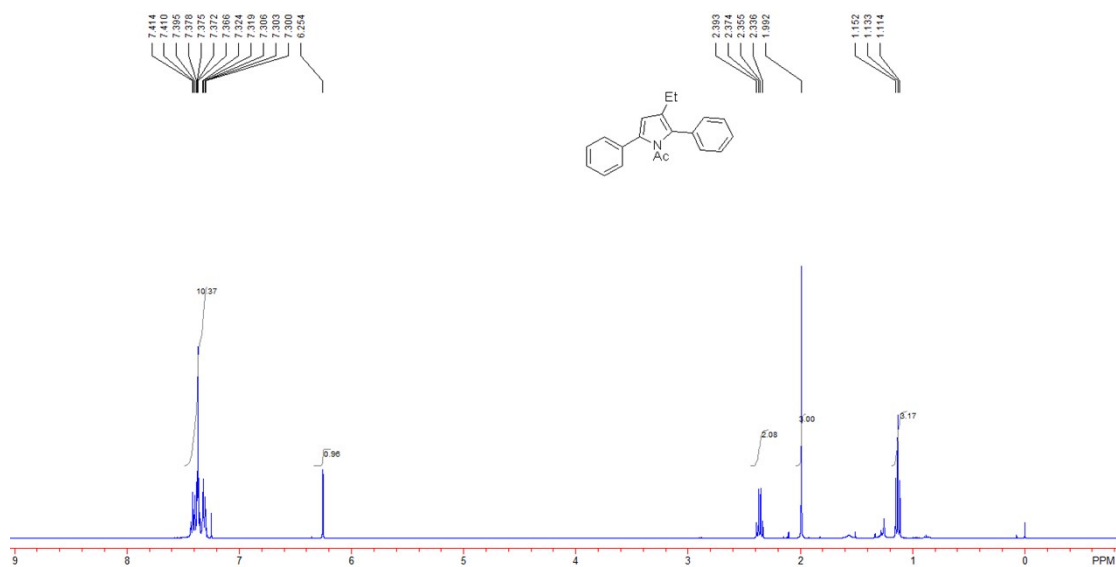




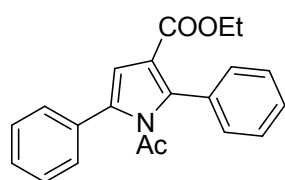
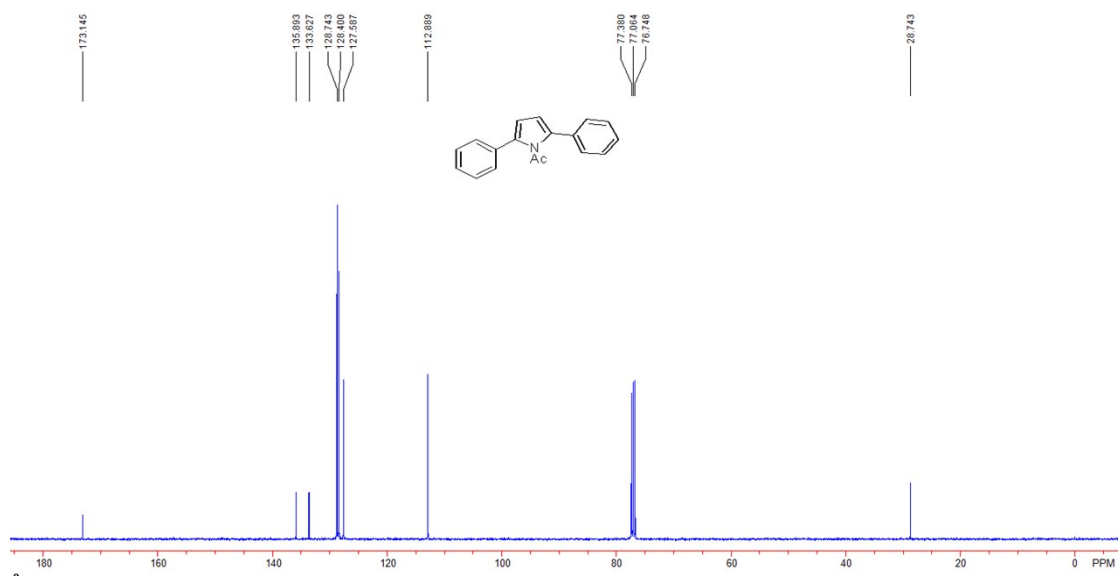
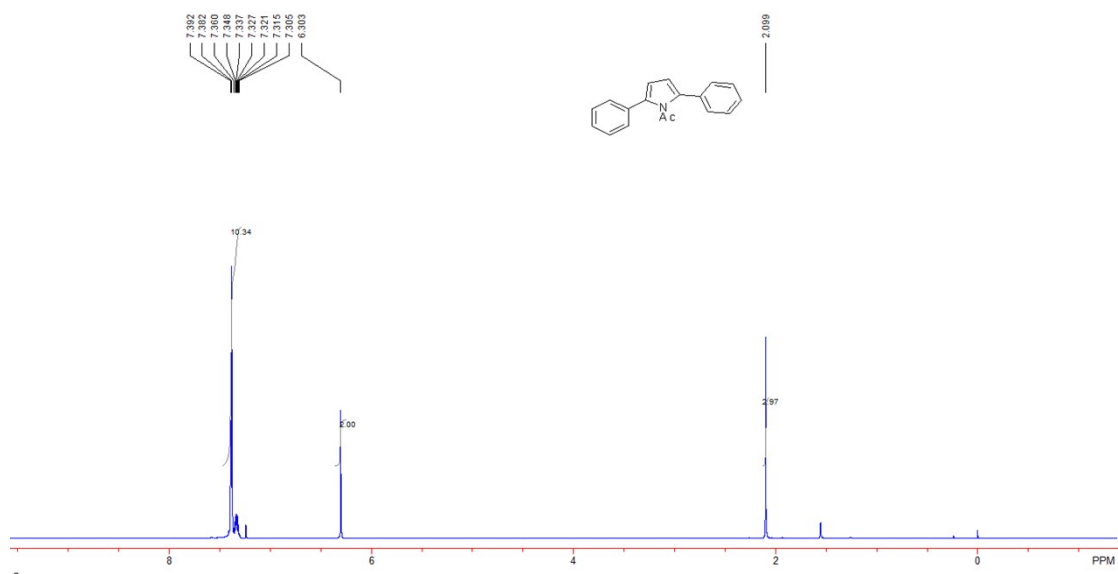
3ag



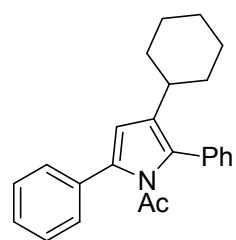
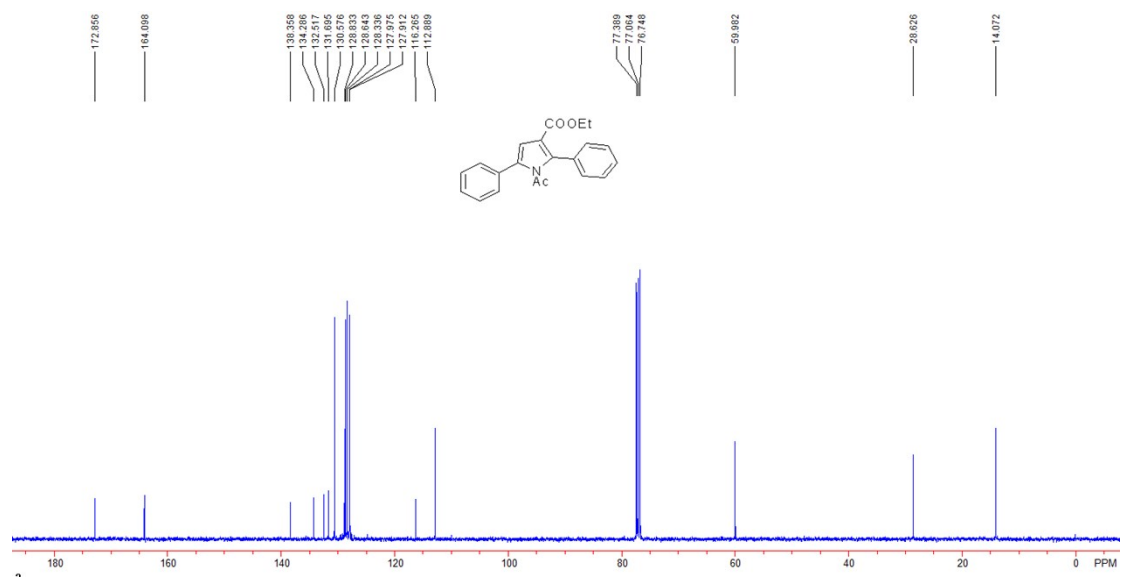
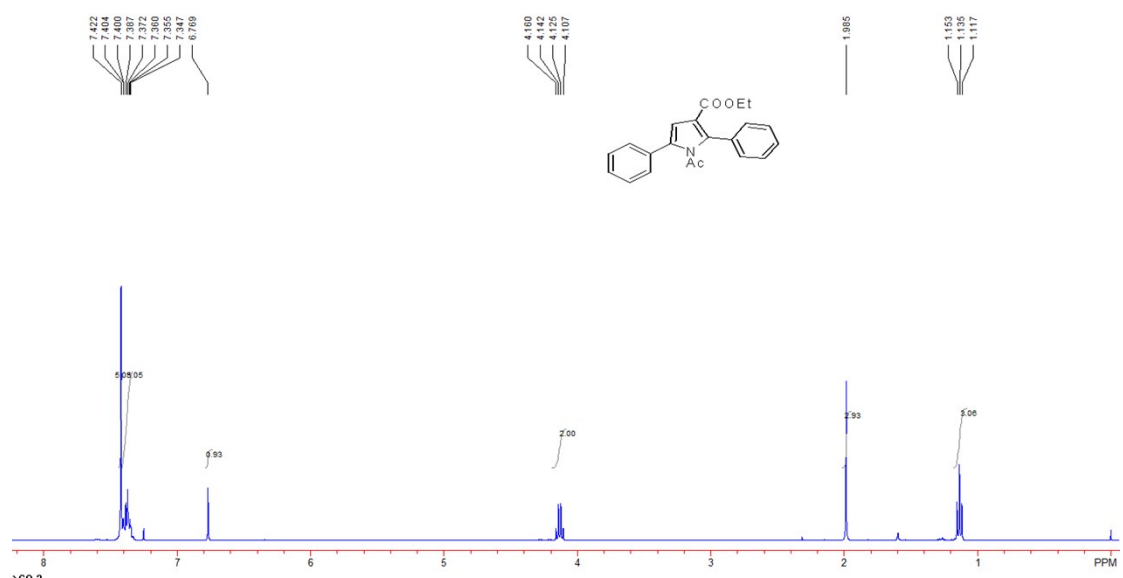
3ah



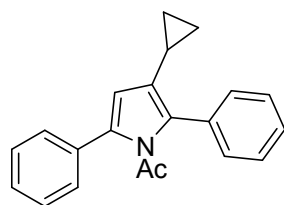
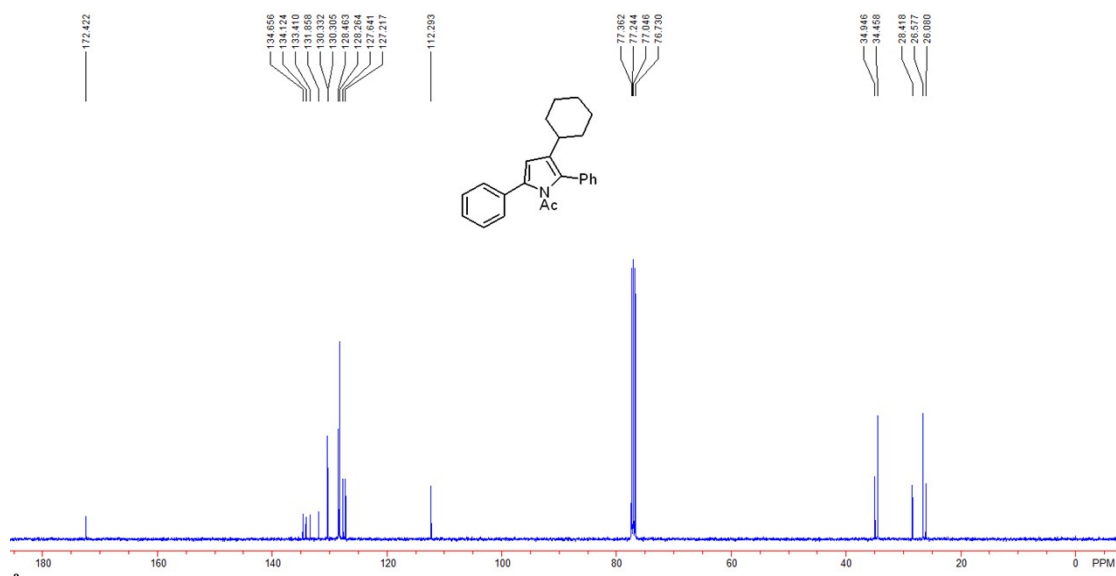
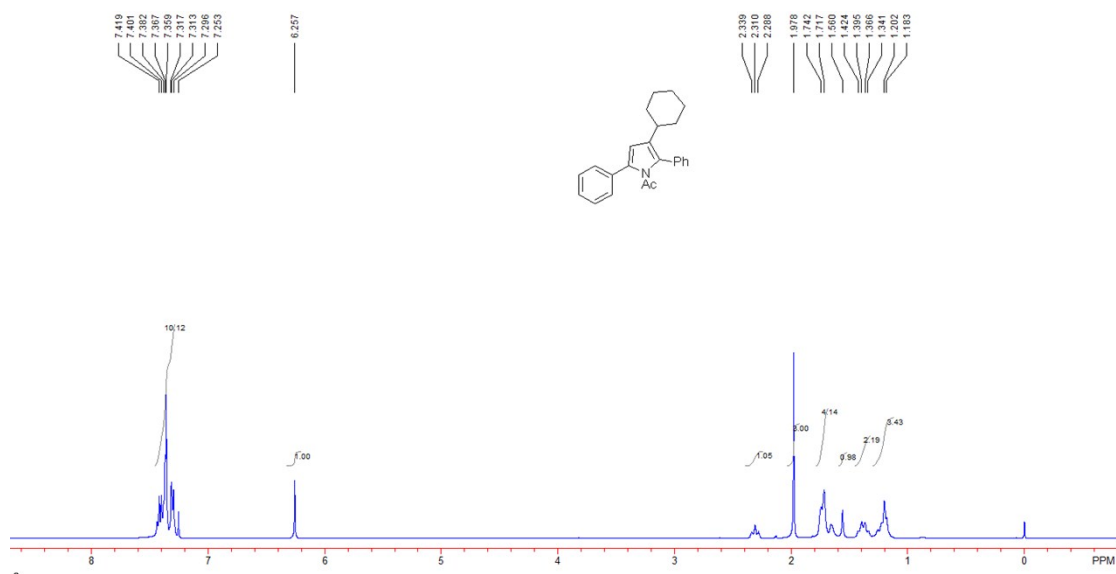
3ai



3aj



3ak



3al

