Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ruthenium-catalyzed acceptorless dehydrogenative coupling of amino alcohols and ynones to access 3-acylpyrroles

Mingshi Pan, Xiabin Wang, Yixin Tong, Xiaodong Qiu, Xiaobao Zeng and Biao Xiong*

School of Pharmacy, Nantong University, 19 Qixiu Road, Nantong, Jiangsu Province 226001, China.

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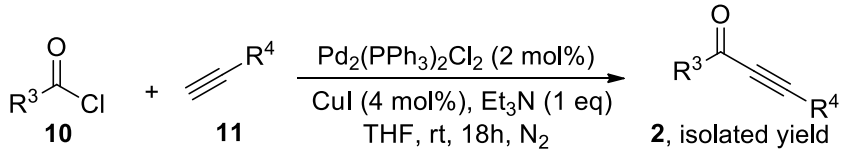
General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR and infrared spectra (IR). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 and referenced to 7.19 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated,, all the reagents were purchased from commercial sources (J&KChemic, TCI, Bidepharm, Aladdin, SCRC), used without further purification.

Preparation of Ynones (2a-2t)

The preparation of alkynone **2** was similar to the literature procedures.[1, 2] **4** (5 mmol), **5** (5.5 mmol), triethylamine (5 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol %), CuI (4 mol %), and Anhydrous tetrahydrofuran (16 mL) were introduced in a flask (50 mL). Then, it was stirred at 30 ^{o}C under N_2 for 18 hours. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography.

Table S1. Synthesis of Ynones (**2a**-**2t**)



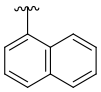
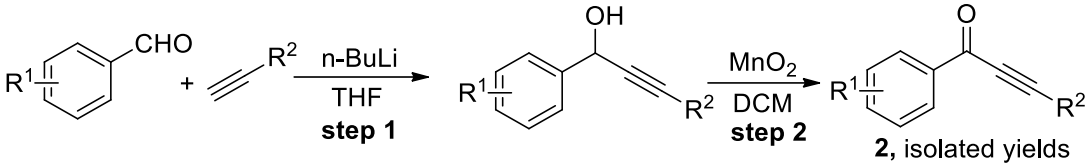
Entry	R^3	R^4	**2**[ref.], Yield
1	4-MeC_6H_4	Ph	**2a**[2], 90%
2	3-Me C_6H_4	Ph	**2b**[3], 92%
3	2-MeC_6H_4	Ph	**2c**[2], 91%
4	C_6H_5	Ph	**2d**[1], 86%
5	4-FC_6H_4	Ph	**2e**[4], 90%
6	4-ClC_6H_4	Ph	**2f**[2], 88%
7	4-BrC_6H_4	Ph	**2g**[5], 84%
8	4-$CF_3C_6H_4$	Ph	**2h**[3],87%
9	4-CNC_6H_4	Ph	**2i**[2], 91%
10	4-$OMeC_6H_4$	Ph	**2j**[2], 84%
11	3,4-$OMeC_6H_3$	Ph	**2k**[2], 85%
12	4-$OMeC_6H_4$	4-MeC_6H_4	**2l**[3], 87%
13	4-$OMeC_6H_4$	4-CNC_6H_4	**2m**[3], 86%
14	4-$CF_3C_6H_4$	4-MeC_6H_4	**2n**[3], 90%
15	4-CNC_6H_4	4-CNC_6H_4	**2o**[3], 83%
16		Ph	**2p**[2], 79%
17		Ph	**2q**[3], 75%
18		Ph	**2r**[3], 81%
19	*t*-Bu	Ph	**2s**[2], 89%
20	*n*-propyl	Ph	**2t**[3], 76%

Table S2. Preparation of Ynones (2u and 2v)



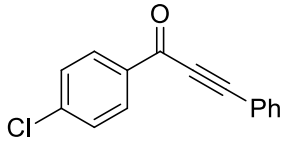
Entry	R^1	R^2	**2**[ref.], Yield
1	H	n-butyl	**2u**[7], 86%
2	H	cyclopropyl	**2v**[8], 85%

Step 1[6]: To a solution of alkyne (5.5 mmol) in THF (20 mL) at -40 °C was added n-BuLi (1.6 M in hexane, 5.5 mmol) dropwise. After stirring for 30 min, aldehyde (5.0 mmol) was added and the solution was warmed to RT. After the consumption of aldehyde, the reaction was quenched with saturated solution of NH_4Cl and the mixture was extracted with ethyl acetate (30 mL×3). Then, the organic phase was dried by Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude propargylic alcohol, which could be used directly in the next step without further purification.

Step 2[7]: The obtained crude propargylic alcohol was added to a suspension of MnO_2 (3.6 g, 40.0 mmol) in dichloromethane (35 mL) at 0 °C, and the mixture was stirred for 1 hour at 0 °C. After filtered through celite, the solvent was removed under vacuum. The residue was purified by silica column chromatography (EA: PE = 1: 50) to afford the alkyone.

Analytical data of synthesized ynones

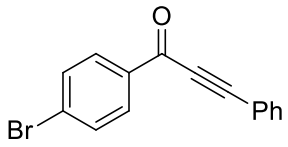
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (2f)



Yellow solid (1.06 g, 88% yield), m.p: 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.13 (m, 2H), 7.73-7.66 (m, 2H), 7.52-7.41 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.70, 140.75, 135.32, 133.14, 131.02, 130.90, 129.04, 128.77, 119.91,

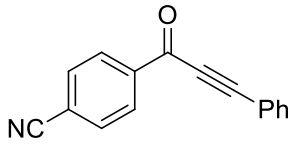
93.66, 86.60. MS (EI, m/z): 240 [M]+.

1-(4-bromophenyl)-3-phenylprop-2-yn-1-one (2g)



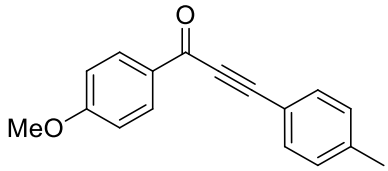
Yellow solid (1.19 g, 84% yield), m.p: 108-110 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.06 (m, 2H), 7.71-7.50 (m, 4H), 7.53-7.48 (m, 1H), 7.47-7.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.90, 135.72, 133.15, 132.03, 131.03, 130.97, 129.60, 128.77, 119.90, 93.71, 86.58. MS (EI, m/z): 284 [M]+.

4-(3-phenylpropioloyl)benzonitrile (2i)



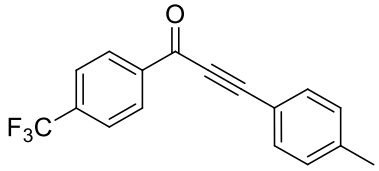
Yellow solid (1.05 g, 91% yield), m.p: 139-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35-8.29 (m, 2H), 7.86-7.81 (m, 2H), 7.73-7.69 (m, 2H), 7.56-7.51 (m, 1H), 7.48-7.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.24, 139.67, 133.28, 132.53, 131.41, 129.84, 128.87, 119.48, 117.91, 117.19, 95.17, 86.44. MS (EI, m/z): 231 [M]+.

1-(4-methoxyphenyl)-3-(p-tolyl)prop-2-yn-1-one (2l)



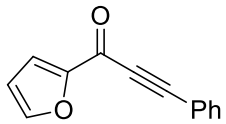
Brown solid (1.09 g, 87% yield), m.p: 78-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.78, 164.42, 141.32, 133.02, 131.97, 130.43, 129.47, 117.26, 113.87, 93.00, 86.79, 55.62, 21.78. MS (EI, m/z): 250 [M]+.

3-(p-tolyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (2n)



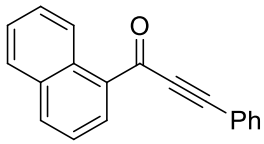
Yellow solid (1.30 g, 90% yield), m.p: 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.78, 142.11, 139.50, 135.10 (q, J_{C-F} = 32.3 Hz), 133.30, 129.80, 129.63, 125.70 (q, J_{C-F} = 4.1 Hz), 123.58 (d, J_{C-F} = 274.7 Hz), 116.56, 95.28, 86.57, 21.85. MS (EI, m/z): 288 [M]+.

1-(furan-2-yl)-3-phenylprop-2-yn-1-one (2p)



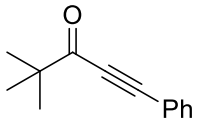
Brown solid (0.77 g, 79% yield), m.p: 50-51 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.69 (m, 1H), 7.68-7.64 (m, 2H), 7.52-7.46 (m, 1H), 7.45-7.39 (m, 3H), 6.61 (dd, *J* = 3.6 Hz, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.80, 153.24, 148.08, 133.08, 130.91, 128.71, 120.97, 119.90, 112.69, 91.92, 86.24. MS (EI, m/z): 196 [M]+.

1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one (2r)



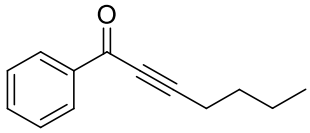
Yellow solid (1.04 g, 81% yield), m.p: 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (d, *J* = 8.4 Hz, 1H), 8.65 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.72-7.67 (m, 3H), 7.64-7.56 (m, 2H), 7.50-7.40 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 179.78, 135.14, 134.57, 133.91, 132.99, 130.78, 130.65, 129.00, 128.70, 128.61, 126.81, 126.04, 124.51, 120.39, 91.73, 88.52. MS (EI, m/z): 256 [M]+.

4,4-dimethyl-1-phenylpent-1-yn-3-one (2s)



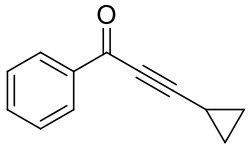
Yellow oil (0.83 g, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.56 (m, 2H), 7.48-7.43 (m, 1H), 7.41-7.36 (m, 2H), 1.28 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 194.31, 132.98, 130.58, 128.63, 120.27, 92.24, 86.01, 44.91, 26.16. MS (EI, m/z): 186 [M]+.

1-phenylhept-2-yn-1-one (2u)



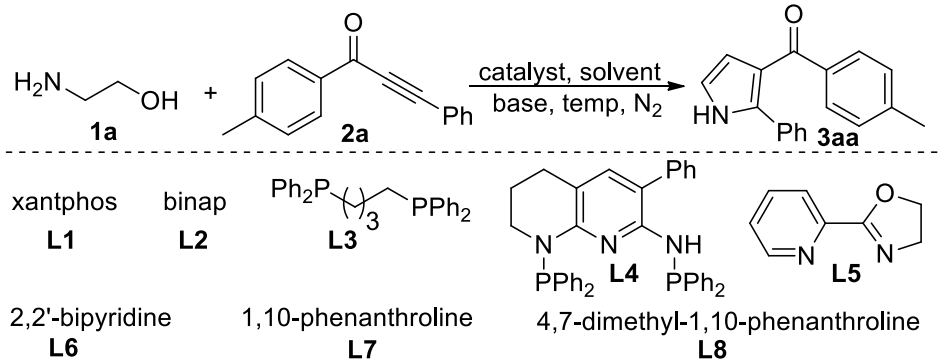
Colorless oil (0.80 g, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-7.17 (m, 2H), 7.55-7.48 (m, 1H), 7.46-7.33 (m, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.59 (p, *J* = 7.2 Hz, 2H), 1.43 (h, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.31, 136.91, 133.91, 129.57, 128.52, 96.92, 79.67, 29.85, 22.11, 18.94, 13.57. MS (EI, m/z): 186 [M]+.

3-cyclopropyl-1-phenylprop-2-yn-1-one (2v)



Colorless oil (0.72 g, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.53-7.46 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 1.50-1.39 (m, 1H), 1.01-1.89 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.92, 136.87,133.79, 129.41, 128.44, 101.14, 75.51, 9.92, . MS (EI, m/z): 170 [M]+.

Table S3. **Screening of reaction conditions**[a]

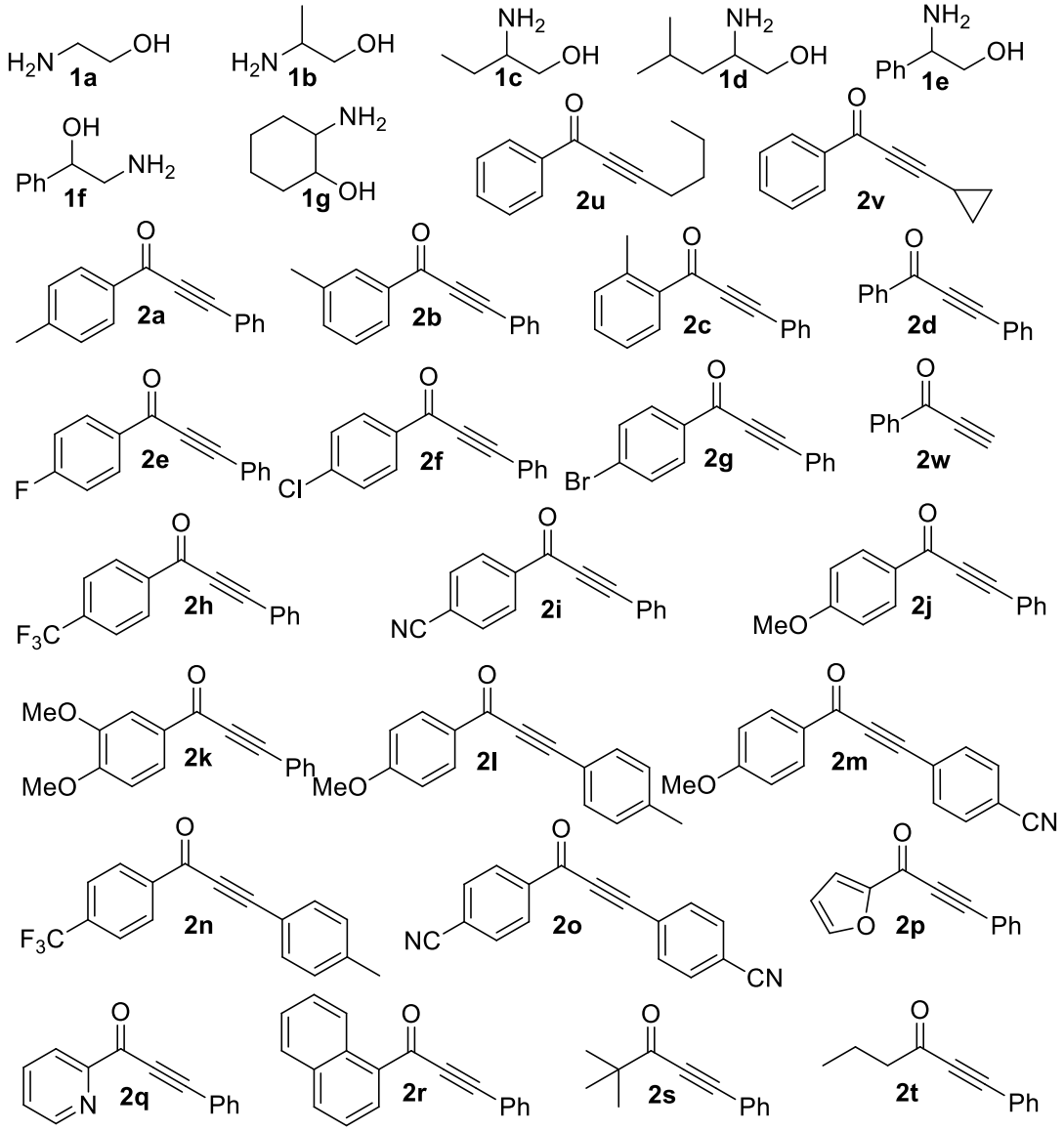


Entry	Catalyst	Ligand	Solvent	Base	Yield(%)[b]
1	$Mn_2(CO)_{10}$	**L1**	*t*-amyl alcohol	Cs_2CO_3	trace
2	$Co_2(CO)_8$	**L1**	*t*-amyl alcohol	Cs_2CO_3	trace
3	$Ru_3(CO)_{12}$	**L1**	*t*-amyl alcohol	Cs_2CO_3	59
4	$RuCl_2(PPh_3)_3$	**L1**	*t*-amyl alcohol	Cs_2CO_3	42
5	$RuCl_2(CO)_2(PPh_3)_2$	**L1**	*t*-amyl alcohol	Cs_2CO_3	48
6	$[Ru(p\text{-cymene})Cl_2]_2$	**L1**	*t*-amyl alcohol	Cs_2CO_3	31
7		**L1**	*t*-amyl alcohol	Cs_2CO_3	0
8	$Ru_3(CO)_{12}$	**L2**	*t*-amyl alcohol	Cs_2CO_3	52
9	$Ru_3(CO)_{12}$	**L3**	*t*-amyl alcohol	Cs_2CO_3	21
10	$Ru_3(CO)_{12}$	**L4**	*t*-amyl alcohol	Cs_2CO_3	37
11	$Ru_3(CO)_{12}$	**L5**	*t*-amyl alcohol	Cs_2CO_3	54
12	$Ru_3(CO)_{12}$	**L6**	*t*-amyl alcohol	Cs_2CO_3	58
13	$Ru_3(CO)_{12}$	**L7**	*t*-amyl alcohol	Cs_2CO_3	72
14	$Ru_3(CO)_{12}$	**L8**	*t*-amyl alcohol	Cs_2CO_3	78
15	$Ru_3(CO)_{12}$	**L8**	*t*-amyl alcohol	Base	(56, 39, 0)[c]
16	$Ru_3(CO)_{12}$	**L8**	*t*-amyl alcohol	Base	(43, 18, 0)[d]
17	$Ru_3(CO)_{12}$	**L8**	1,4-Dioxane	Cs_2CO_3	72
18	$Ru_3(CO)_{12}$	**L8**	Toluene	Cs_2CO_3	70
19	$Ru_3(CO)_{12}$	**L8**	Chlorobenzene	Cs_2CO_3	70
20	$Ru_3(CO)_{12}$	**L8**	DMF	Cs_2CO_3	47
21	$Ru_3(CO)_{12}$	**L8**	DMSO	Cs_2CO_3	12
22	$Ru_3(CO)_{12}$	**L8**	*t*-amyl alcohol	Cs_2CO_3	(23, 89, 89)[e]

[a] Unless otherwise stated, the reaction was performed with **1a** (0.3 mmol), **2a** (0.3 mmol), catalyst (1 mol%), ligand (3 mol%), base (100 mmol%) in *t*-amyl alcohol (1.5 mL) at 130 °C for 16 h under N_2. [b] GC yield. [c] Yields are with respect to use of K_2CO_3, CsOH and *t*-BuOK as the bases, respectively. [d] Yields are with respect to use of Na_2CO_3, NaOH and *t*-BuONa as the bases, respectively. [e] Yields are with respect to the temperature at 120 °C, 140 °C and 150 °C, respectively.

Typical procedure for the synthesis of 3aa

Under N_2 atmosphere, 2-aminoethanol hydrochloride **1a** (29 mg, 0.3 mmol), alkynone **2a** (66 mg, 0.3 mmol), 4,7-dimethyl-1,10-phenanthroline (1.9 mg, 3 mol %), Ru_3CO_{12} (2.0 mg, 1 mol %), Cs_2CO_3 (97 mg, 100 mol %), and *t*-Amyl alcohol (1.5 mL) were introduced in a Schlenk tube (25 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 140 ^oC for 16 h. Then, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether: ethyl acetate (10:1) to give (2-phenyl-1H-pyrrol-3-yl)(p-tolyl) methanone **3aa** as a canary yellow solid.



Scheme S1. Substrates employed for synthesizing pyrroles

Reference

[1] Y. Tohda, K. Sonogashira, N. Hagihara; *Synthesis* **1977**, 777-778.

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[4] X. F. Wu, H. Neumann, M. Beller; *Chem.-Eur. J*. **2010**, 16, 12104-12107.

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[7] R. Shintani; T. Hayashi. *Org. Lett*. **2005**, *7*, 2071-2073.

[8] D. Zhai, S. M. Ma; *Org. Chem. Front.* **2019**, *6*, 3101-3106.

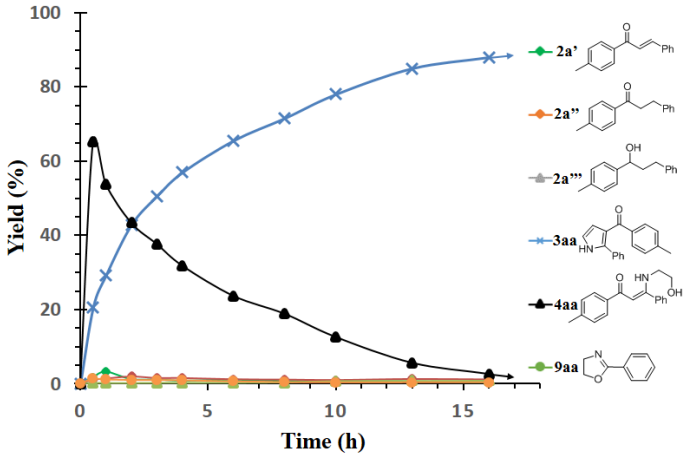


Fig S1. Representative time course of the reaction

A time-concentration profile of different components of the model reaction under the standard conditions is depicted in Figure S1. Initially, intermediate **4aa** was almost formed quantitatively in a short time and converted into target product **3aa** efficiently in the first 2 hours. Meanwhile, due to the auto transfer hydrogenation, a small amount of reduction product of **2a** were detected which had no increase over the whole reaction time, indicating the protocol has good selectivity on the catalytic acceptorless dehydrogenation coupling rather than auto transfer hydrogenation. Moreover, **4aa** could be completely transformed into the product **3aa** within 16 h. The above-results indicate that the compound **4aa** is a key intermediate.

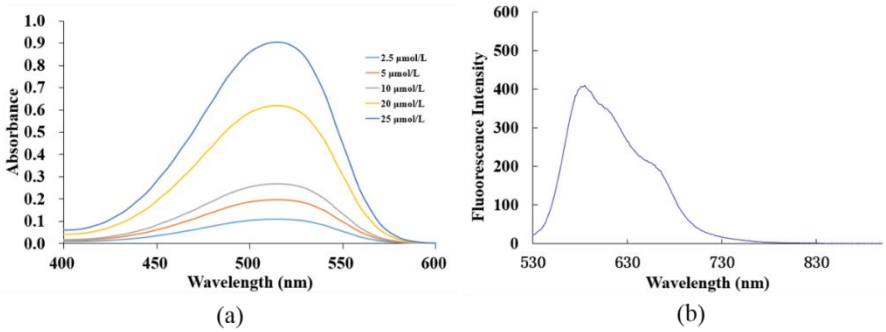


Figure S2. UV (a) and fluorescence emission spectrums (b) of **3aaa**

An obvious absorbance peak at 515 nm of this synthesized BODIPY (**3aaa**) was observed from UV-vis absorption spectra and the maximum emission wavelength was located at 585 nm under the excitation wavelength at 520 nm (5 μM **3aaa** in DMSO).

Mechanism investigation

1. GC-MS spectrums of control experiments

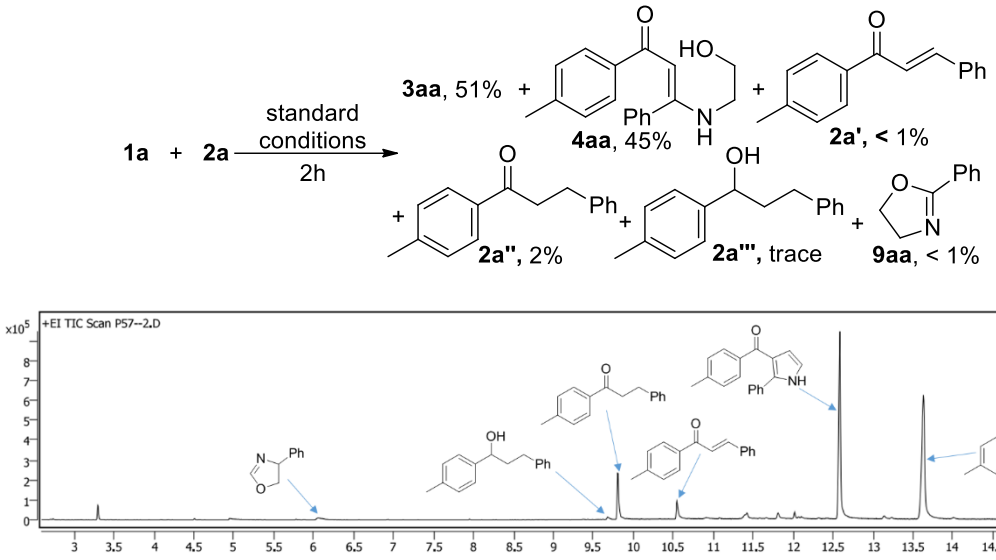


Figure S3 GC-MS of the model reaction under standard conditions after 2 hours.

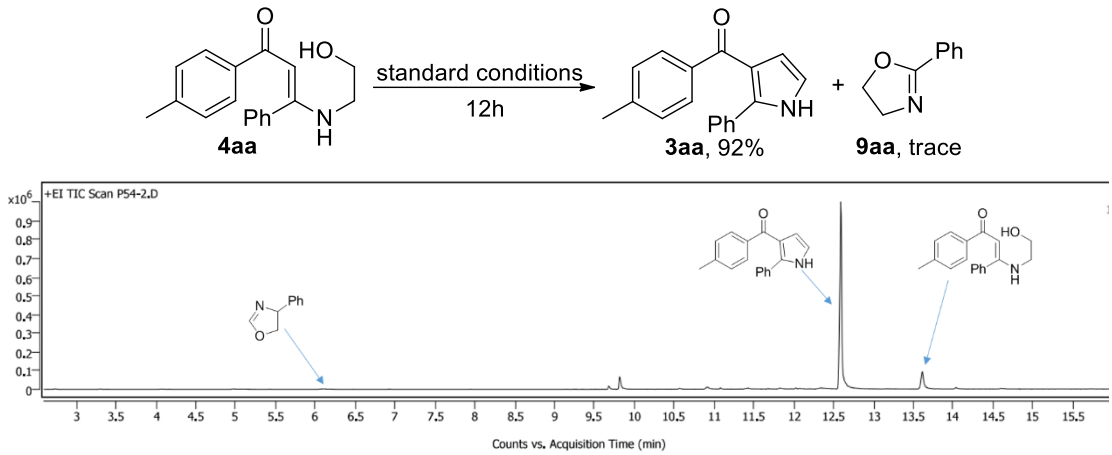


Figure S4 GC-MS of the reaction from **4aa** after 12 hours.

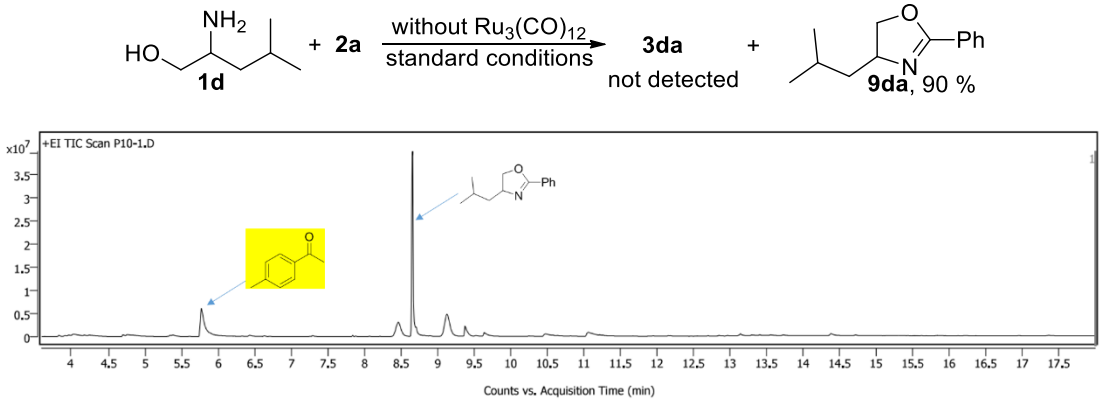


Figure S5 GC-MS of the reaction from **1d** and **2a** without catalyst after12 hours.

2. Detection of hydrogen gas

The model reaction of **1a** (0.3 mmol) and **2a** (0.3 mmol) was stirred at 140 °C under N_2 atmosphere for 12 h. After cooling to room temperature, the head gas was collected by a gas-tight syringe and analyzed by GC. (Instrument model: GC9790plus. The peak time has very slight deviation because of the manual injection mode.)

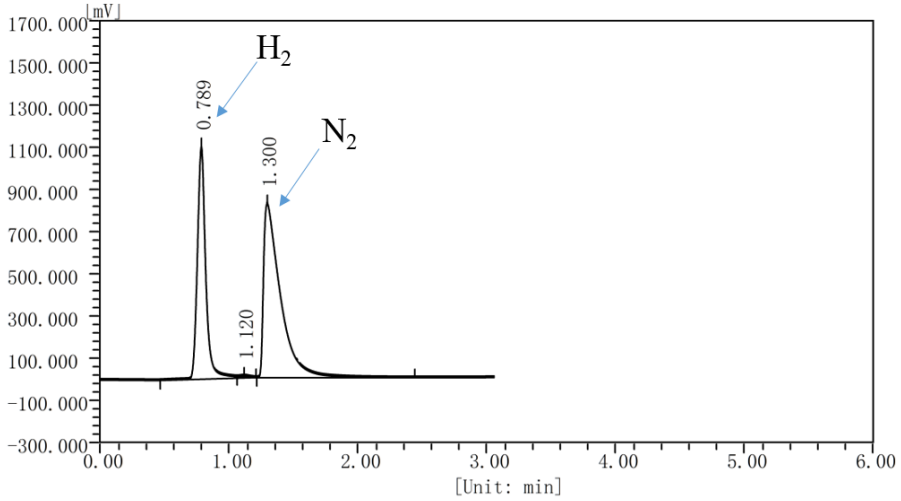


Fig S6 GC of the standard mixture of N_2 and H_2 (V_{N2} / V_{H2} = 95 / 5)

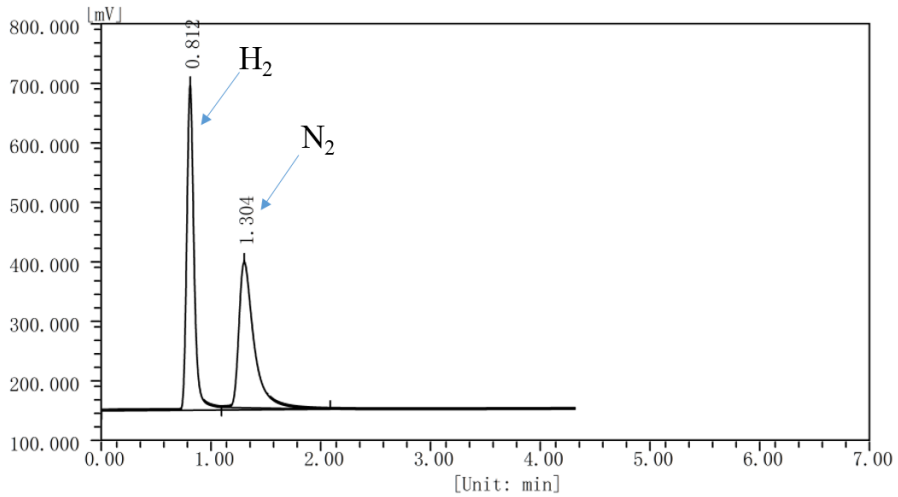
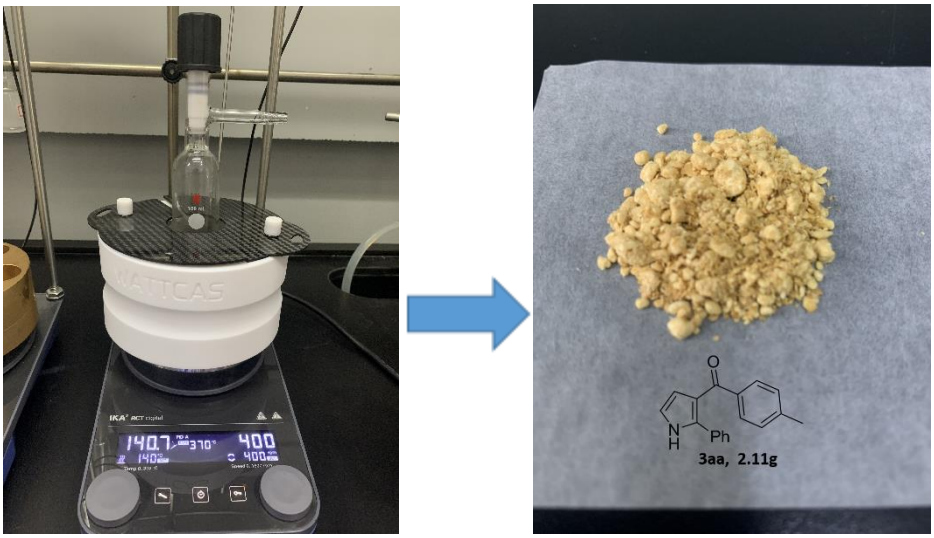


Fig S7 GC of the head gas of model reaction

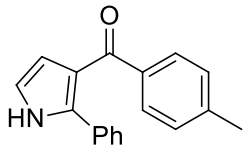
Details of the gram reaction

Under N_2 atmosphere, 2-aminoethanol hydrochloride **1a** (0.61 g, 10.0 mmol), alkynone **2a** (2.20 g, 10.0 mmol), 4,7-dimethyl-1,10-phenanthroline (62.5 mg, 3 mol %), Ru_3CO_{12} (64.0 mg, 1 mol %), Cs_2CO_3 (3.2 g, 100 mol %), and *t*-Amyl alcohol (20 mL) were introduced in a Schlenk tube (100 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 140 ^oC for 24 h. Then, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by silica-gel column chromatography, eluting with petroleum ether: ethyl acetate (20:1) to give (2-phenyl-1H-pyrrol-3-yl)(p-tolyl) methanone **3aa** (2.11g, 81%).



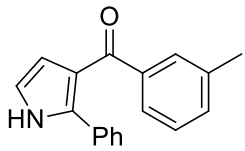
Analytic data of the obtained compounds

(1) (2-phenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3aa)



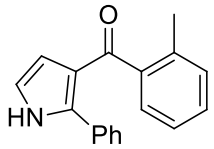
Yellow solid, 88% yield, m.p: 155-157 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.38-7.32 (m, 2H), 7.24-7.12 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.69 (m, 1H), 6.52-6.46 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.37, 142.25, 136.85, 136.77, 132.10, 129.91, 128.57, 128.37, 128.34, 127.86, 120.52, 117.61, 113.68, 21.57. IR (KBr): 3243, 1615, 1597, 1566, 1557, 1495, 1472, 1432, 1399, 1312, 1292, 1164, 1112, 1034, 883, 779, 760, 735, 696 cm^{-1}. MS (EI, m/z): 261 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1226; found: 262.1224.

(2) (2-phenyl-1H-pyrrol-3-yl)(m-tolyl)methanone (3ab)



Yellow solid, 81% yield, m.p: 92-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.57-7.46 (m, 2H), 7.38-7.31 (m, 2H), 7.23-7.19 (m, 3H), 7.17-7.10 (m, 2H), 6.74 (t, *J* = 2.8 Hz, 1H), 6.54 (t, *J* = 2.8 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.61, 138.40, 136.49, 135.97, 131.29, 131.08, 129.25, 127.36, 127.30, 126.91, 126.69, 125.87, 119.57, 116.60, 112.66, 20.19. MS (EI, m/z): 261 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1226; found: 262.1223.

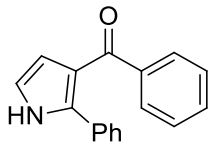
(3) (2-phenyl-1H-pyrrol-3-yl)(o-tolyl)methanone (3ac)



Yellow solid, 77% yield, m.p: 134-136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.38-7.34 (m, 2H), 7.26-7.19 (m, 4H), 7.16-7.10 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.67 (t, *J* = 2.8 Hz, 1H), 6.40 (t, *J* = 2.8 Hz, 1H), 2.29 (s, 3H). ^{13}C

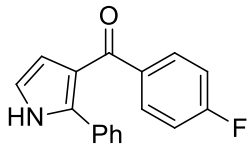
NMR (101 MHz, $CDCl_3$) δ 194.23, 140.62, 137.60, 136.25, 131.90, 130.56, 129.52, 128.61, 128.54, 128.20, 128.14, 124.83, 121.67, 117.75, 113.78, 19.91. MS (EI, m/z): 261 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{15}NO$ $[M+H]^+$: 262.1226; found: 262.1225.

(4) phenyl(2-phenyl-1H-pyrrol-3-yl)methanone (3ad)



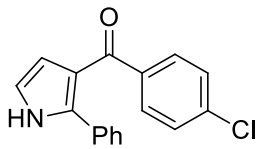
Red solid, 83% yield, m.p: 131-134 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.72-7.67 (m, 2H), 7.39-7.31 (m, 3H), 7.27-7.21 (m, 2H), 7.20-7.15 (m, 3H), 6.70 (t, *J* = 2.8 Hz, 1H), 6.51 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.60, 139.56, 137.17, 132.02, 131.61, 129.67, 128.44, 128.35, 127.97, 127.85, 120.40, 117.75, 113.71. MS (EI, m/z): 247 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{13}NO$ $[M+H]^+$: 268.1070; found: 248.1068.

(5) (4-fluorophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (3ae)



Yellow solid, 78% yield, m.p: 123-125 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.75-7.68 (m, 2H), 7.36-7.28 (m, 2H), 7.24-7.19 (m, 3H), 6.94-6.86 (m, 2H), 6.76 (t, *J* = 2.8 Hz, 1H), 6.53 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.97, 163.82 (d, J_{C-F} = 253.5 Hz), 135.99, 134.68 (d, J_{C-F} = 3.0 Hz), 131.08 (d, J_{C-F} = 9.0 Hz), 130.85, 127.39, 127.07, 119.28, 116.83, 113.82 (d, J_{C-F} = 21.2 Hz), 112.45. MS (EI, m/z): 265 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{12}FNO$ $[M+H]^+$: 266.0976; found: 266.0974.

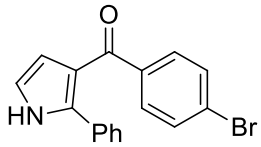
(6) (4-chlorophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (3af)



Yellow solid, 73% yield, m.p: 108-110 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H),

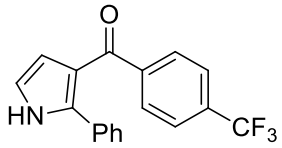
7.62 (d, *J* = 8.0 Hz, 2H), 7.47-7.28 (m, 2H), 7.26-7.09 (m, 5H), 6.73 (t, *J* = 2.8 Hz, 1H), 6.50 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.16, 137.87, 137.82, 137.28, 131.84, 131.05, 128.47, 128.45, 128.18, 128.12, 120.14, 117.94, 113.50. MS (EI, m/z): 281 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{12}ClNO$ $[M+H]^+$: 282.0680; found: 282.0678.

(7) (4-bromophenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (3ag)



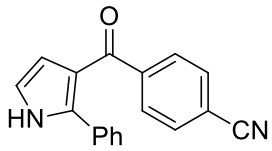
Yellow solid, 71% yield, m.p: 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.71-7.49 (m, 2H), 7.43-7.27 (m, 4H), 7.23-7.13 (m, 3H), 6.70 (s, 1H), 6.54-6.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.33, 138.33, 137.36, 131.20, 131.10, 129.67, 128.48, 128.43, 128.17, 126.43, 120.05, 117.98, 113.49. IR (KBr): 3151, 3040, 2919, 1591, 1570, 1489, 1453, 1429, 1343, 1256, 1190, 1153, 1065, 1013, 901, 801, 760, 730, 691 cm^{-1}. MS (EI, m/z): 325 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{12}BrNO$ $[M+H]^+$: 326.0175; found: 326.0172.

(8) (2-phenyl-1H-pyrrol-3-yl)(4-(trifluoromethyl)phenyl)methanone (3ah)



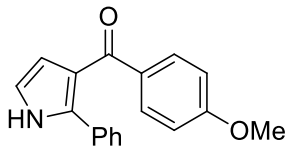
Red solid, 70% yield, m.p: 131-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.36-7.28 (m, 2H), 7.24-7.17 (m, 3H), 6.76 (t, *J* = 2.8 Hz, 1H), 6.53 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.09, 142.73, 137.89, 132.79 (q, J_{C-F} = 32.3 Hz), 131.69, 129.67, 128.60, 128.42, 128.37, 124.83 (q, J_{C-F} = 3.6 Hz), 123.75 (d, J_{C-F} = 271.7 Hz), 120.03, 118.10, 113.53. MS (EI, m/z): 315 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{12}F_3NO$ $[M+H]^+$: 316.0944; found: 316.0943.

(9) 4-(2-phenyl-1H-pyrrole-3-carbonyl)benzonitrile (3ai)



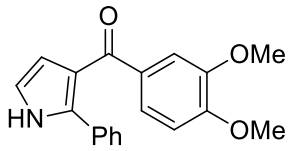
Yellow solid, 80% yield, m.p: 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.30-7.24 (m, 2H), 7.21-7.14 (m, 3H), 6.74 (t, *J* = 2.8 Hz, 1H), 6.51 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.63, 142.30, 137.10, 130.63, 130.52, 128.76, 127.65, 127.42, 127.36, 118.70, 117.42, 117.27, 113.45, 112.26. MS (EI, m/z): 272 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{12}N_2O$ $[M+H]^+$: 273.1022; found: 273.1020.

(10) (4-methoxyphenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (3aj)



Yellow solid, 86% yield, m.p: 179-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.39-7.34 (m, 2H), 7.26-7.15 (m, 3H), 6.79-6.72 (m, 3H), 6.52 (t, *J* = 2.8 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.31, 161.52, 135.22, 131.09, 130.99, 127.41, 127.21, 126.81, 119.68, 116.50, 112.48, 112.07, 53.34. MS (EI, m/z): 277 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{15}NO_2$ $[M+H]^+$: 278.1176; found: 278.1174.

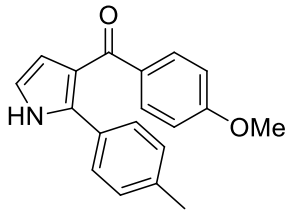
(11) (3,4-dimethoxyphenyl)(2-phenyl-1H-pyrrol-3-yl)methanone (3ak)



Black solid, 70% yield, m.p: 58-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.40 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.38-7.31 (m, 3H), 7.24-7.14 (m, 3H), 6.75 (t, *J* = 2.8 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.54 (d, *J* = 2.8 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.31, 151.24, 147.41, 135.21, 131.13, 131.06, 127.43, 127.18, 126.84, 123.61, 119.59, 116.66, 112.49, 111.13, 108.64, 54.95, 54.84. MS (EI,

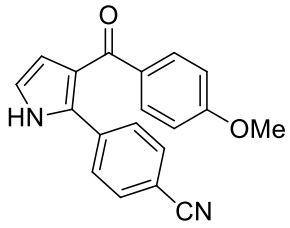
m/z): 307 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{17}NO_3$ $[M+H]^+$: 308.1281; found: 308.1280.

(12) (4-methoxyphenyl)(2-(m-tolyl)-1H-pyrrol-3-yl)methanone (3al)



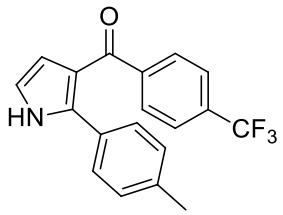
Red solid, 77% yield, m.p: 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.76 (t, *J* = 2.8 Hz, 1H), 6.55 (t, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.41, 162.52, 137.70, 136.58, 132.27, 132.04, 129.27, 129.12, 128.13, 120.31, 117.28, 113.45, 113.11, 55.39, 21.24. MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{17}NO_2$ $[M+H]^+$: 292.1332; found: 292.1330.

(13) 3-(3-(4-methoxybenzoyl)-1H-pyrrol-2-yl)benzonitrile (3am)



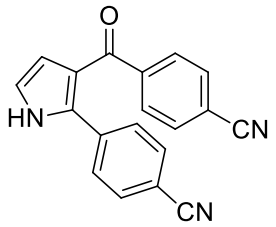
Crimson solid, 67% yield, m.p: 86-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.49 (s, 4H), 6.81 (d, *J* = 8.4 Hz, 3H), 6.51 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.22, 163.07, 136.40, 133.51, 132.20, 131.64, 128.44, 122.25, 118.96, 118.76, 114.25, 113.40, 110.94, 55.48. MS (EI, m/z): 302 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{14}N_2O_2$ $[M+H]^+$: 303.1128; found: 303.1126.

(14) (2-(m-tolyl)-1H-pyrrol-3-yl)(4-(trifluoromethyl)phenyl)methanone (3an)



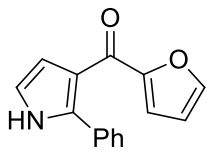
Red solid, 80% yield, m.p: 165-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 2.8 Hz, 1H), 6.52 (t, *J* = 2.8 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.02, 141.83, 137.37, 137.16, 131.58 (q, J_{C-F} = 32.3 Hz), 128.57, 128.03, 127.74, 127.46, 123.73 (q, J_{C-F} = 3.6 Hz), 122.58 (d, J_{C-F} = 271.7 Hz), 118.80, 116.79, 112.35, 20.12. MS (EI, m/z): 329 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{14}F_3NO$ $[M+H]^+$: 330.1100; found: 330.1099.

(15) 3-(3-(4-cyanobenzoyl)-1H-pyrrol-2-yl)benzonitrile (3ao)



Yellow solid, 62% yield, m.p: 222-223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.86-7.76 (m, 2H), 7.70-7.62 (m, 2H), 7.59 (s, 4H), 6.87 (t, *J* = 2.8 Hz, 1H), 6.47 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.07, 141.84, 134.85, 134.16, 131.27, 131.02, 128.84, 127.91, 119.67, 118.27, 117.45, 117.09, 114.26, 113.40, 110.89. MS (EI, m/z): 297 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{11}N_3O$ $[M+H]^+$: 298.0975; found: 298.0973.

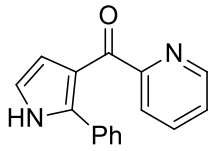
(16) furan-2-yl(2-phenyl-1H-pyrrol-3-yl)methanone (3ap)



Yellow solid, 69% yield, m.p: 141-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H),

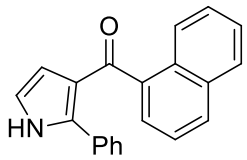
7.50-7.37 (m, 3H), 7.33-7.20 (m, 3H), 7.07-6.99 (m, 1H), 6.80 (t, *J* = 2.8 Hz, 1H), 6.75 (t, *J* = 2.8 Hz, 1H), 6.38 (dd, *J* = 3.5, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.47, 153.64, 145.73, 137.17, 132.17, 128.43, 128.39, 128.10, 119.45, 118.48, 117.94, 112.69, 111.84. MS (EI, m/z): 237 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{11}NO_2$ $[M+H]^+$: 238.0863; found: 238.0861.

(17) (2-phenyl-1H-pyrrol-3-yl)(pyridin-2-yl)methanone (3aq)



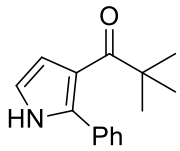
Black solid, 58% yield, m.p: 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.71-7.64 (m, 1H), 7.44-7.34 (m, 2H), 7.28-7.16 (m, 4H), 6.85 (t, *J* = 2.8 Hz, 1H), 6.75 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.73, 155.56, 147.18, 137.78, 135.57, 131.41, 127.62, 127.24, 127.04, 124.41, 122.80, 118.42, 116.93, 113.19. MS (EI, m/z): 248 $[M]^+$. HRMS (ESI): Calcd. for $C_{16}H_{12}N_2O$ $[M+H]^+$: 249.1022; found: 249.1020.

(18) naphthalen-1-yl(2-phenyl-1H-pyrrol-3-yl)methanone (3ar)



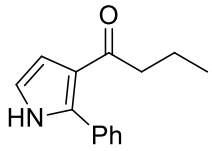
Crimson solid, 85% yield, m.p: 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (brs, 1H), 8.15 (d, *J* = 3.6 Hz, 1H), 7.77-7.67 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.44-7.35 (m, 2H), 7.32-7.25 (m, 2H), 7.25-7.17 (m, 1H), 7.14-7.00 (m, 3H), 6.71-6.60 (m, 1H), 6.50-6.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.47, 138.32, 138.09, 133.54, 131.87, 130.88, 130.44, 128.48, 128.09, 128.04, 127.41, 126.78, 125.97, 125.80, 124.21, 122.24, 117.85, 113.80. MS (EI, m/z): 297 $[M]^+$. HRMS (ESI): Calcd. for $C_{21}H_{15}NO$ $[M+H]^+$: 298.1226; found: 298.1224.

(19) 2,2-dimethyl-1-(2-phenyl-1H-pyrrol-3-yl)propan-1-one (3as)



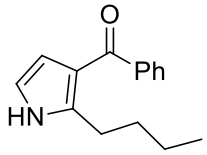
Crimson solid, 73% yield, m.p: 55-56 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.37-7.33 (m, 2H), 7.31-7.22 (m, 3H), 6.64 (t, *J* = 2.8 Hz, 1H), 6.58 (t, *J* = 2.8 Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.69, 136.54, 133.12, 128.50, 127.86, 119.21, 116.98, 111.00, 44.32, 27.95. MS (EI, m/z): 227 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383; found: 228.1381.

(20) 1-(2-phenyl-1H-pyrrol-3-yl)butan-1-one (3at)



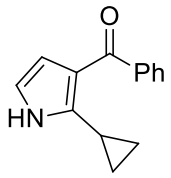
Red solid, 65% yield, m.p: 82-84 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.52-7.44 (m, 2H), 7.36-7.27 (m, 3H), 6.68 (t, *J* = 2.8 Hz, 1H), 6.62 (t, *J* = 2.8 Hz, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 1.58 (h, *J* = 7.2 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.29, 136.14, 132.55, 129.04, 128.43, 128.29, 121.32, 117.68, 111.54, 42.79, 18.09, 13.95. MS (EI, m/z): 213 $[M]^+$. HRMS (ESI): Calcd. for $C_{14}H_{15}NO$ $[M+H]^+$: 214.1226; found: 214.1224.

(21) 1-(2-phenyl-1H-pyrrol-3-yl)butan-1-one (3au)



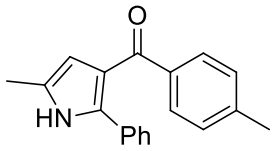
Yellow oil, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.53-7.47 (m, 1H), 7.46-7.39 (m, 2H), 6.51 (t, *J* = 2.8 Hz, 1H), 6.37 (t, *J* = 2.8 Hz, 1H), 2.96 (t, *J* = 7.6 Hz, 2H), 1.62 (p, *J* = 7.6 Hz, 2H), 1.32 (h, *J* = 7.6 Hz, 2H), 0.87 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.07, 141.77, 140.85, 131.19, 129.08, 128.06, 119.01, 115.81, 122.69, 31.50, 27.46, 22.62, 13.92. MS (EI, m/z): 227 $[M]^+$. HRMS (ESI): Calcd. for $C_{15}H_{17}NO$ $[M+H]^+$: 228.1383; found: 228.1381.

(22) (2-cyclopropyl-1H-pyrrol-3-yl)(phenyl)methanone (3av)



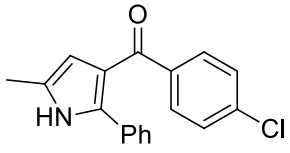
White solid, 77% yield; m.p: 106-107 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.86-7.78 (m, 2H), 7.53-7.48 (m, 1H), 7.47-7.41 (m, 2H), 6.45 (dd, *J* = 5.6 Hz, 2.4 Hz, 1H), 6.34 (t, *J* = 2.8 Hz, 1H), 2.72-2.54 (m, 1H), 1.01-0.93 (m, 2H), 0.79-0.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.92,142.05, 140.82, 131.21, 129.16, 128.04, 120.61, 115.52, 112.79, 29.74, 9.09, 8.22. MS (EI, m/z): 211 $[M]^+$. HRMS (ESI): Calcd. for $C_{14}H_{13}NO$ $[M+H]^+$: 212.1070; found: 212.1068.

(23) (5-methyl-2-phenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3ba)



Yellow solid, 85% yield, m.p: 142-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0, 2H), 7.16-7.09 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.13 (d, *J* = 2.8 Hz, 1H), 2.27 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.35, 140.94, 135.96, 134.76, 131.21, 128.79, 127.41, 127.16, 127.13, 126.66, 126.39, 119.59, 110.12, 20.47, 11.64. MS (EI, m/z): 275 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{17}NO$ $[M+H]^+$: 276.1383; found: 276.1382.

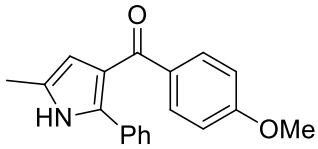
(24) (4-chlorophenyl)(5-methyl-2-phenyl-1H-pyrrol-3-yl)methanone (3bf)



Black solid, 79% yield, m.p: 52-53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 6.4, 2.8 Hz, 2H), 7.19-7.12 (m, 5H), 6.15 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.20, 136.98, 136.55, 135.38, 130.95, 127.29,

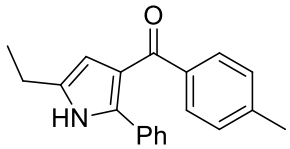
127.27, 126.97, 126.77, 119.19, 109.89, 11.66. MS (EI, m/z): 295 $[M]^+$. HRMS (ESI): Calcd. for $C_{18}H_{14}ClNO$ $[M+H]^+$: 296.0837; found: 296.0837.

(25) (4-methoxyphenyl)(5-methyl-2-phenyl-1H-pyrrol-3-yl)methanone (3bj)



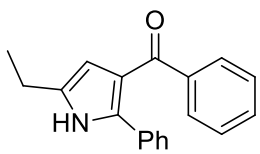
Yellow solid, 81% yield, m.p: 112-113 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 2H), 7.20-7.07 (m, 3H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.15 (s, 1H), 3.73 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.50, 161.38, 134.31, 131.25, 131.23, 130.95, 127.24, 127.05, 126.71, 126.37, 119.73, 111.98, 109.96, 54.32, 11.70. MS (EI, m/z): 291 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{17}NO_2$ $[M+H]^+$: 292.1332; found: 292.1331.

(26) (5-ethyl-2-phenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3ca)



Green solid, 80% yield, m.p: 162-163 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.31 (d, *J* = 4.8 Hz, 2H), 7.23-7.07 (m, 6H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.10 (s, 1H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.28 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.15, 139.75, 135.59, 135.07, 133.19, 131.05, 129.39, 128.27, 127.47, 127.47, 127.02, 126.77, 123.71, 120.58, 108.28, 19.43, 18.82, 12.14. MS (EI, m/z): 289 $[M]^+$. HRMS (ESI): Calcd. for $C_{20}H_{19}NO$ $[M+H]^+$: 290.1539; found: 290.1538.

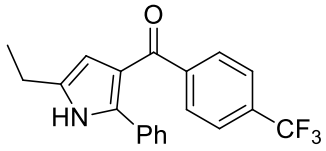
(27) (5-ethyl-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (3cd)



Yellow solid, 82% yield, m.p: 79-80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H),

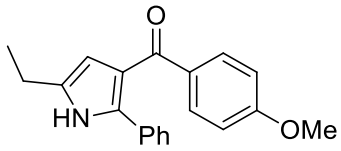
7.68 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 3H), 7.24-7.14 (m, 5H), 6.23 (s, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.56, 139.72, 136.06, 134.22, 132.27, 131.39, 129.62, 128.35, 128.28, 127.76, 127.68, 120.48, 109.54, 20.57, 13.29. MS (EI, m/z): 275 $[M]^+$. HRMS (ESI): Calcd. for $C_{19}H_{17}NO$ $[M+H]^+$: 276.1383; found: 276.1380.

(28) (5-ethyl-2-phenyl-1H-pyrrol-3-yl)(4-(trifluoromethyl)phenyl)methanone (3ch)



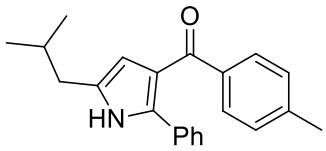
Yellow solid, 79% yield, m.p: 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.27-7.11 (m, 5H), 6.20 (d, *J* = 2.8 Hz, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.27, 142.95, 137.04, 134.77, 132.56 (q, J_{C-F} = 32.3 Hz), 131.92, 129.61, 128.55, 128.27, 128.02, 124.74 (q, J_{C-F} = 3.6 Hz), 123.81 (q, J_{C-F} = 271.7 Hz), 120.03, 109.20, 20.50, 13.24. MS (EI, m/z): 343 $[M]^+$. HRMS (ESI): Calcd. for $C_{20}H_{16}F_3NO$ $[M+H]^+$: 344.1257; found: 344.1255.

(29) (5-ethyl-2-phenyl-1H-pyrrol-3-yl)(4-methoxyphenyl)methanone (3cj)



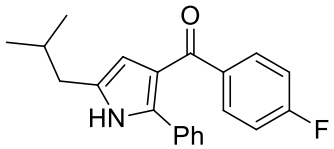
Yellow solid, 77% yield, m.p: 60-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18-7.11 (m, 3H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 3.74 (s, 3H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.47, 161.37, 134.12, 133.09, 131.34, 131.25, 130.94, 127.28, 127.10, 126.44, 119.68, 111.99, 108.34, 54.31, 19.54, 12.27. MS (EI, m/z): 305 $[M]^+$. HRMS (ESI): Calcd. for $C_{20}H_{19}NO_2$ $[M+H]^+$: 306.1489; found: 306.1487.

(30) (5-isobutyl-2-phenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3da)



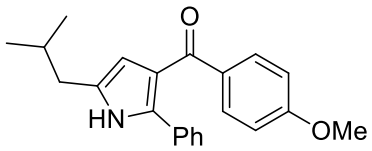
Yellow solid, 74% yield, m.p: 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.35-7.30 (m, 2H), 7.25-7.20 (m, 1H), 7.17-7.10 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.07 (d, *J* = 2.8 Hz, 1H), 2.35 (d, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.84-1.73 (m, 1H), 0.87 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.23, 135.41, 135.12, 131.08, 130.80, 129.42, 128.31, 127.56, 127.39, 127.05, 126.76, 123.74, 120.66, 110.08, 35.67, 27.88, 21.36, 18.86. MS (EI, m/z): 317 $[M]^+$. HRMS (ESI): Calcd. for $C_{22}H_{23}NO$ $[M+H]^+$: 318.1852; found: 318.1848.

(31) (4-fluorophenyl)(5-isobutyl-2-phenyl-1H-pyrrol-3-yl)methanone (3de)



Yellow solid, 81% yield, m.p: 96-97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.77-7.64 (m, 2H), 7.34-7.27 (m, 3H), 7.17-7.15 (m, 2H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 2.8 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.89-1.78 (m, 1H), 0.90 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.09, 164.76 (d, $J_{C\text{-}F}$ = 252.5 Hz), 135.91, 132.13, 132.04, 131.97, 129.26, 128.36, 128.32, 127.79, 120.39, 114.79 (d, $J_{C\text{-}F}$ = 21.21 Hz), 111.06, 36.79, 29.00, 22.43. MS (EI, m/z): 321 $[M]^+$. HRMS (ESI): Calcd. for $C_{21}H_{20}FNO$ $[M+H]^+$: 322.1602; found: 322.1598.

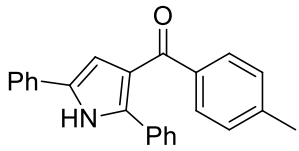
(32) (5-isobutyl-2-phenyl-1H-pyrrol-3-yl)(4-methoxyphenyl)methanone (3dj)



Yellow solid, 76% yield, m.p: 40-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.43-7.35 (m, 2H), 7.24-7.16 (m, 3H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.24 (s, 1H), 3.81 (s, 3H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.95-1.83 (m, 1H), 0.95 (d, *J* = 7.2

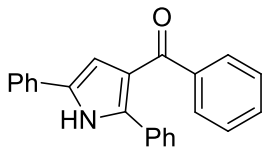
Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.67, 162.43, 135.25, 132.38, 132.04, 131.78, 128.30, 128.17, 127.43, 120.65, 113.05, 111.15, 55.38, 36.78, 29.00, 22.46. MS (EI, m/z): 333 $[M]^+$. HRMS (ESI): Calcd. for $C_{22}H_{23}NO_2$ $[M+H]^+$: 334.1802; found: 334.1797.

(33) (2,5-diphenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3ea)



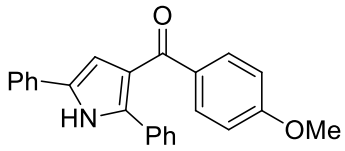
Yellow solid, 78% yield, m.p: 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.46-7.38 (m, 4H), 7.34-7.26 (m, 3H), 7.23-7.13 (m, 5H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.02-6.95 (m, 1H), 6.67 (d, *J* = 2.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.03, 139.34, 137.27, 135.34, 130.79, 130.62, 130.23, 129.58, 128.61, 128.00, 127.66, 127.53, 127.27, 127.21, 126.15, 123.85, 123.01, 109.34, 18.91. MS (EI, m/z): 337 $[M]^+$. HRMS (ESI): Calcd. for $C_{24}H_{19}NO$ $[M+H]^+$: 338.1539; found: 338.1536.

(34) (2,5-diphenyl-1H-pyrrol-3-yl)(phenyl)methanone (3ed)



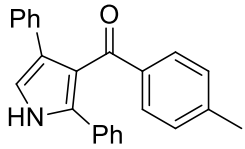
Yellow solid, 79% yield, m.p: 148-149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 7.76-7.68 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.39-7.28 (m, 5H), 7.25-7.14 (m, 6H), 6.76 (d, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.48, 138.31, 136.87, 130.85, 130.69, 130.37, 128.66, 127.99, 127.43, 127.32, 127.06, 126.85, 126.08, 123.09, 120.85, 109.43. MS (EI, m/z): 323 $[M]^+$. HRMS (ESI): Calcd. for $C_{23}H_{17}NO$ $[M+H]^+$: 324.1383; found: 324.1380.

(35) (2,5-diphenyl-1H-pyrrol-3-yl)(4-methoxyphenyl)methanone (3ej)



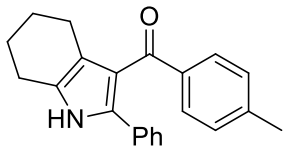
Yellow solid, 72% yield, m.p: 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.49-7.45 (m, 2H), 7.38-7.28 (m, 4H), 7.21-7.13 (m, 4H), 6.74 (dd, *J* = 6.4 Hz, 3.0 Hz, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.40, 161.63, 136.07, 131.06, 130.88, 130.78, 130.49, 127.98, 127.38, 127.24, 126.88, 125.98, 123.07, 121.11, 112.13, 109.31, 54.36. IR (KBr): 3137, 3001, 2969, 2842, 1589, 1562, 1508, 1452, 1432, 1339, 1243, 1170, 1152, 1032, 903, 846, 762, 695 cm^{-1}. MS (EI, m/z): 353 $[M]^+$. HRMS (ESI): Calcd. for $C_{24}H_{19}NO_2$ $[M+H]^+$: 354.1489; found: 354.1487.

(36) (2,4-diphenyl-1H-pyrrol-3-yl)(p-tolyl)methanone (3fa)



Yellow solid, 76% yield, m.p: 193-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.78-7.69 (m, 2H), 7.54-7.47 (m, 2H), 7.45-7.38 (m, 2H), 7.37-7.30 (m, 1H), 7.29-7.22 (m, 1H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.01-6.93 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 2.8 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.98, 137.08, 136.47, 135.26, 134.46, 131.37, 130.05, 129.82, 128.49, 128.38, 128.01, 127.35, 127.19, 126.95, 126.45, 124.16, 109.32, 20.03. MS (EI, m/z): 337 $[M]^+$. HRMS (ESI): Calcd. for $C_{24}H_{19}NO$ $[M+H]^+$: 338.1539; found: 338.1536.

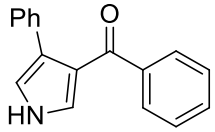
(37) (2-phenyl-4,5,6,7-tetrahydro-1H-indol-3-yl)(p-tolyl)methanone (3ga)



Yellow solid, 65% yield, m.p: 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.15-7.00 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.46 (t, *J* = 6.4 Hz, 2H), 2.20 (s, 3H), 1.82-1.73 (m, 2H), 1.70-1.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.94, 142.13, 136.89, 134.32, 132.60, 129.97, 128.40, 128.26, 127.94, 126.96, 120.39, 119.57, 23.43, 22.94, 22.79, 22.64, 21.51. MS (EI,

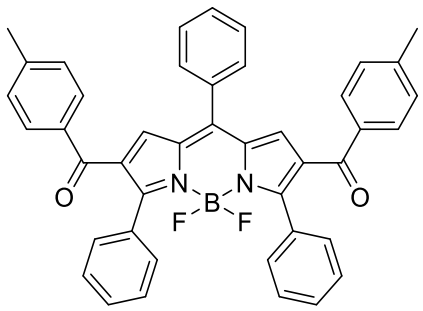
m/z): 315 $[M]^+$. HRMS (ESI): Calcd. for $C_{22}H_{21}NO$ $[M+H]^+$: 316.1696; found: 316.1690.

(38) phenyl(4-phenyl-1H-pyrrol-3-yl)methanone (3fw)



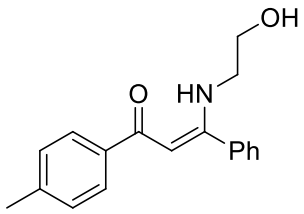
White solid, 80% yield, m.p: 229-231 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76-7.72 (m, 2H), 7.59-7.53 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.39-7.35 (m, 2H), 7.30-7.19 (m, 3H), 7.19-7.14 (m, 1H), 7.08 (t, J = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.80, 140.44, 135.71, 132.01, 129.42, 128.82, 128.63, 128.58, 128.20, 126.11, 125.95, 120.98, 120.10. MS (EI, m/z): 247 $[M]^+$. HRMS (ESI): Calcd. for $C_{17}H_{13}NO$ $[M+H]^+$: 248.1070; found: 248.1067.

(39) (5,5-difluoro-3,7,10-triphenyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine-2,8-diyl)bis(p-tolylmethanone) (3aaa)



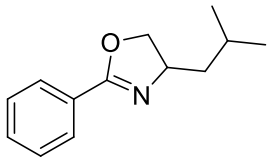
Red solid, 90% yield, m.p: 253-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.74 (m, 8H), 7.59-7.55 (m, 2H), 7.48-7.44 (m, 2H), 7.41-7.36 (m, 6H), 7.18 (d, J = 8.0 Hz, 4H), 6.99 (s, 2H), 5.30 (s, 1H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.15, 155.70, 143.66, 140.11, 135.82, 133.71, 132.57, 130.78, 130.16, 129.99, 129.73, 129.58, 129.04, 128.64, 128.56, 128.18, 21.68. HRMS (ESI): Calcd. for $C_{43}H_{31}BF_2N_2O_2$ $[M+e]^-$: 656.2452; found: 656.2446.

(40) phenyl(4-phenyl-1H-pyrrol-3-yl)methanone (intermidate 4aa)



White solid, 62% yield, m.p: 114-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.41 (br, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.44-7.36 (m, 3H), 7.36-7.31 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 4.06 (br, 1H), 3.71 (t, *J* = 5.2 Hz, 2H), 3.35 (q, *J* = 5.2 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ188.38, 167.18, 141.16, 137.56, 135.58, 129.49, 128.99, 128.53, 127.87, 127.18, 93.78, 61.84, 47.09, 21.49. MS (EI, m/z): 281 $[M]^+$.

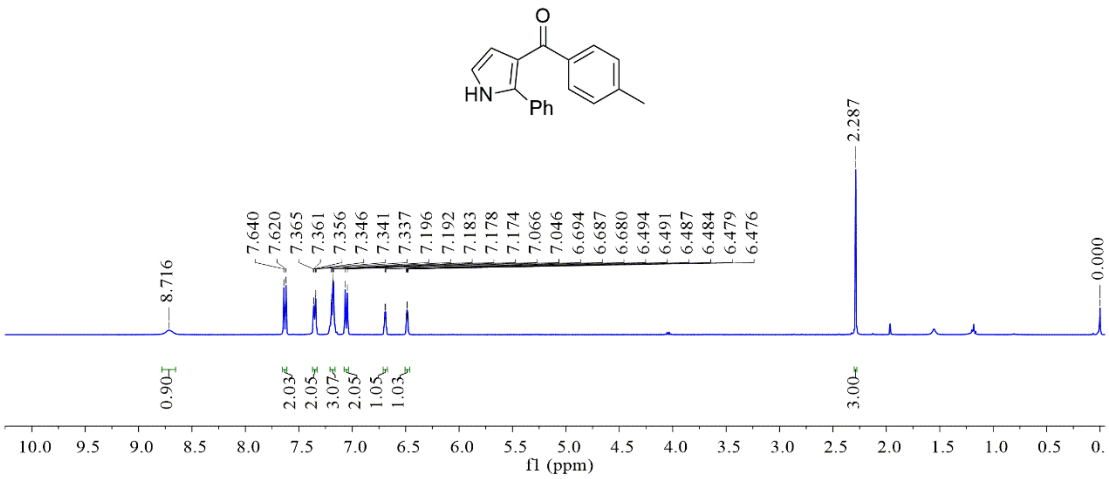
(41) 4-isobutyl-2-phenyl-4,5-dihydrooxazole (9da)



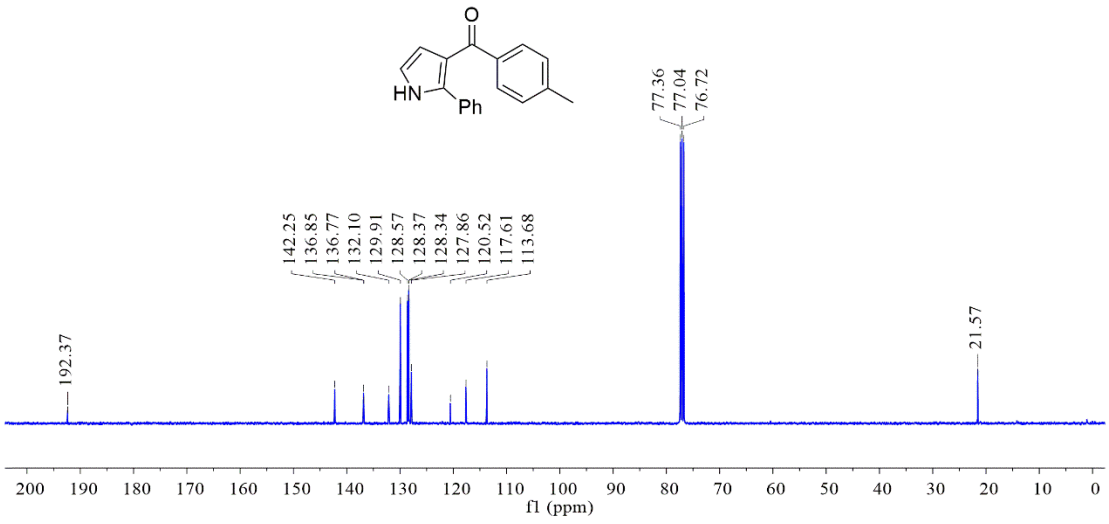
Yellow oil, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.83 (m, 2H), 7.42-7.37 (m, 1H), 7.36-7.29 (m, 2H), 4.46-4.41 (m, 1H), 4.31-4.22 (m, 1H), 3.92 (t, *J* = 8.0 Hz, 1H), 1.77-1.73 (m, 1H), 1.69-1.62 (m, 1H), 1.35-1.29 (m, 1H), 0.91 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.31, 131.19, 128.30, 128.22, 127.95, 73.13, 65.14, 45.61, 25.51, 22.95, 22.70. MS (EI, m/z): 203 $[M]^+$.

NMR spectra of the obtained compounds

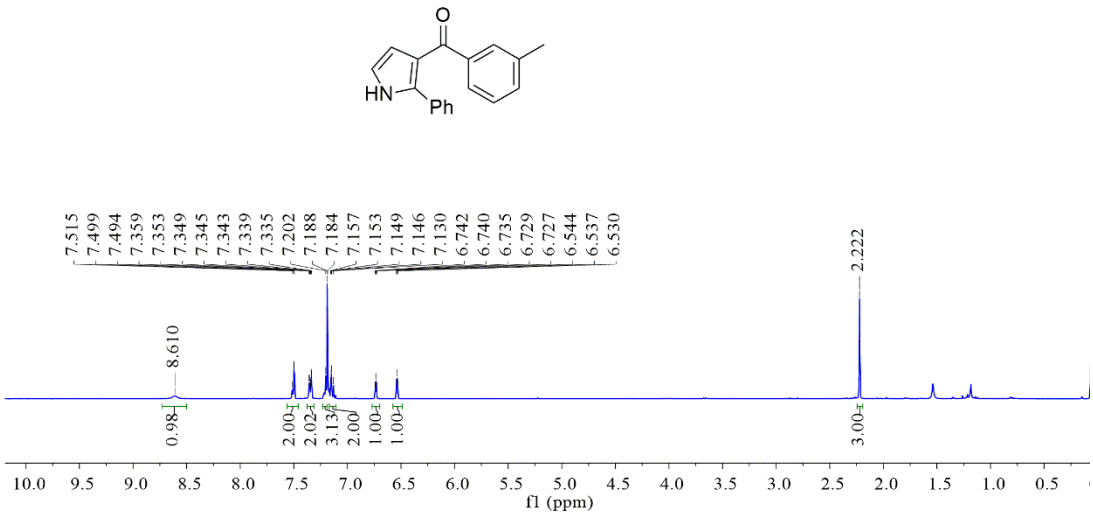
^{1}H- NMR spectrum of 3aa



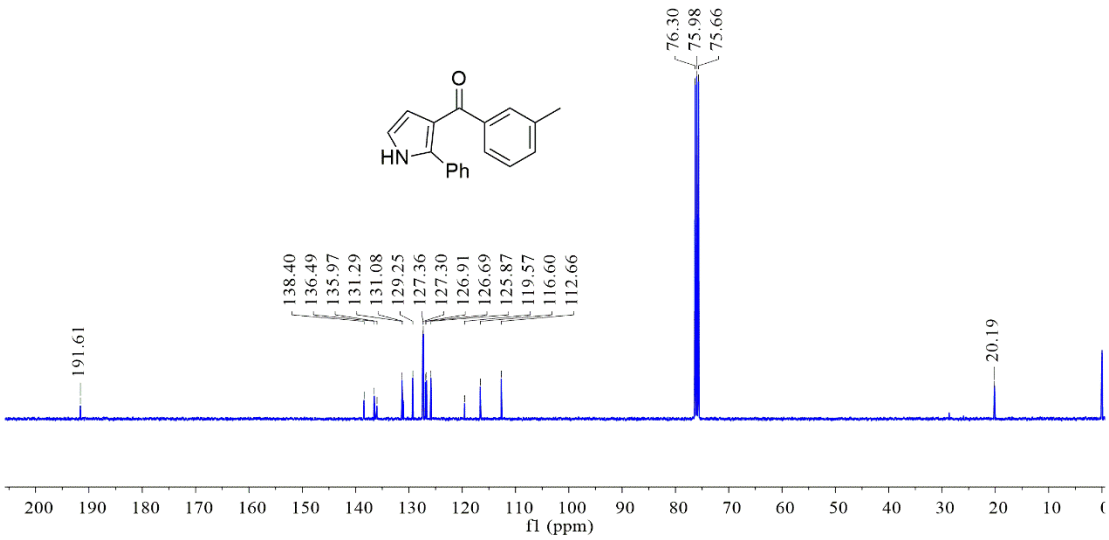
^{13}C-NMR spectrum of 3aa



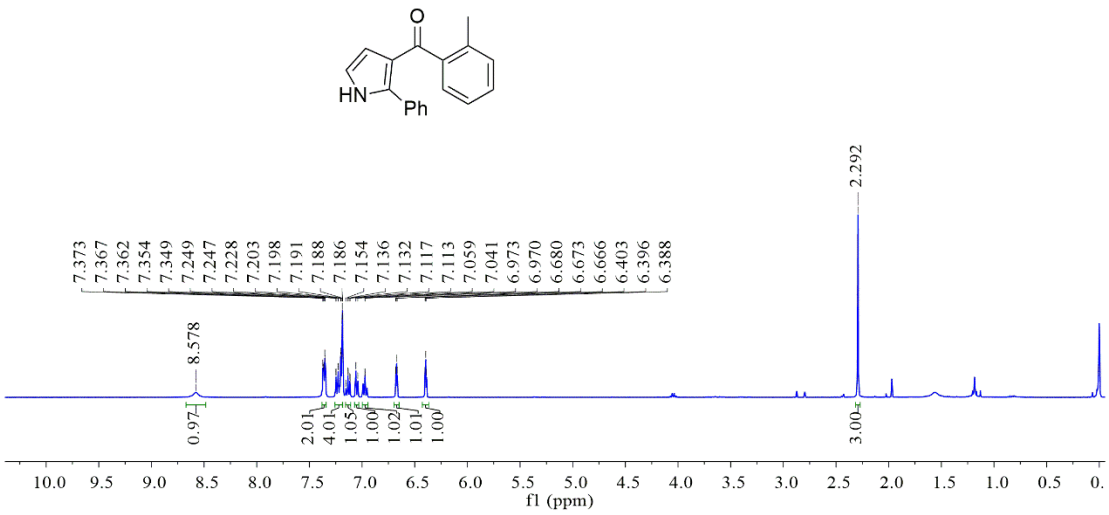
^{1}H- NMR spectrum of 3ab



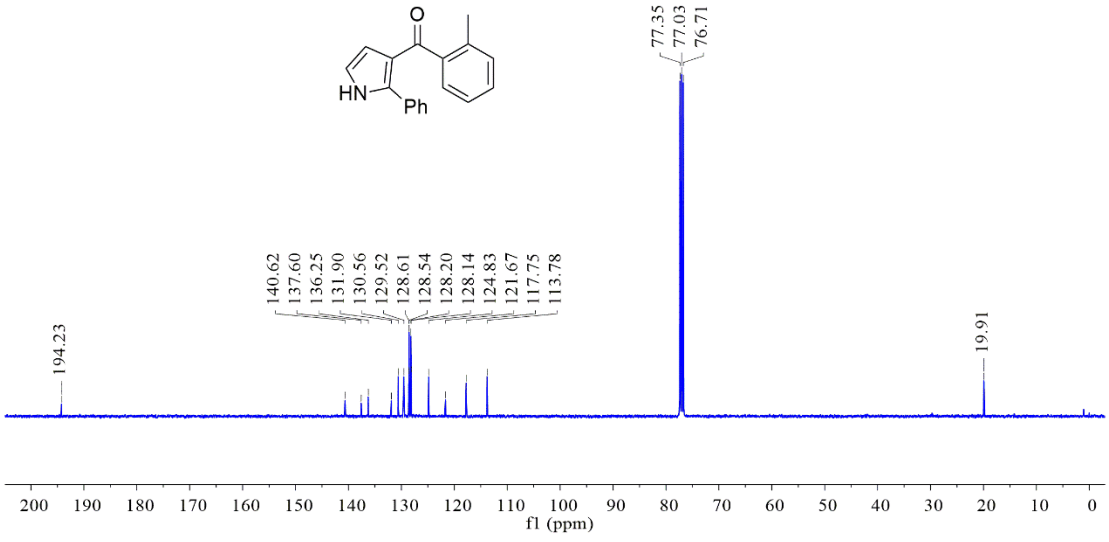
^{13}C-NMR spectrum of 3ab



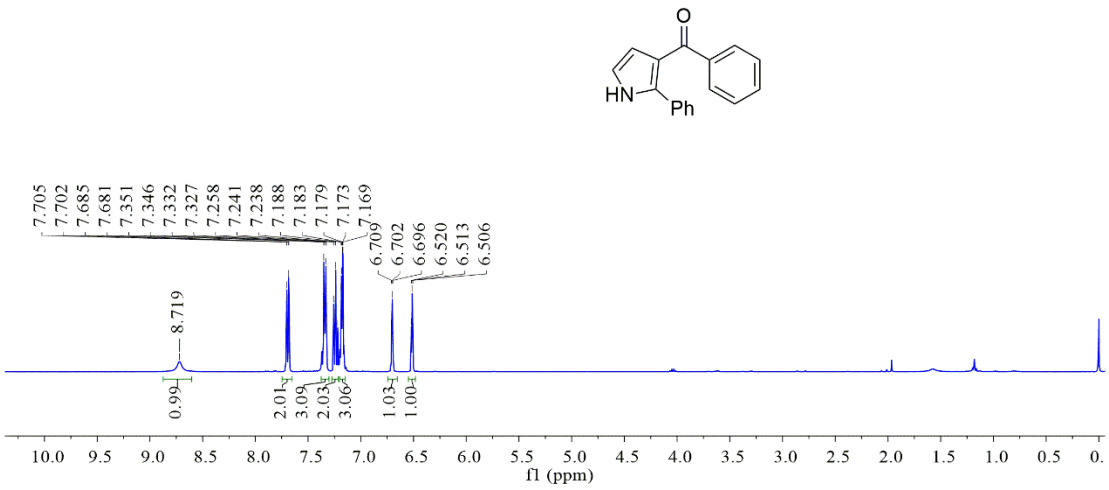
^{1}H- NMR spectrum of 3ac



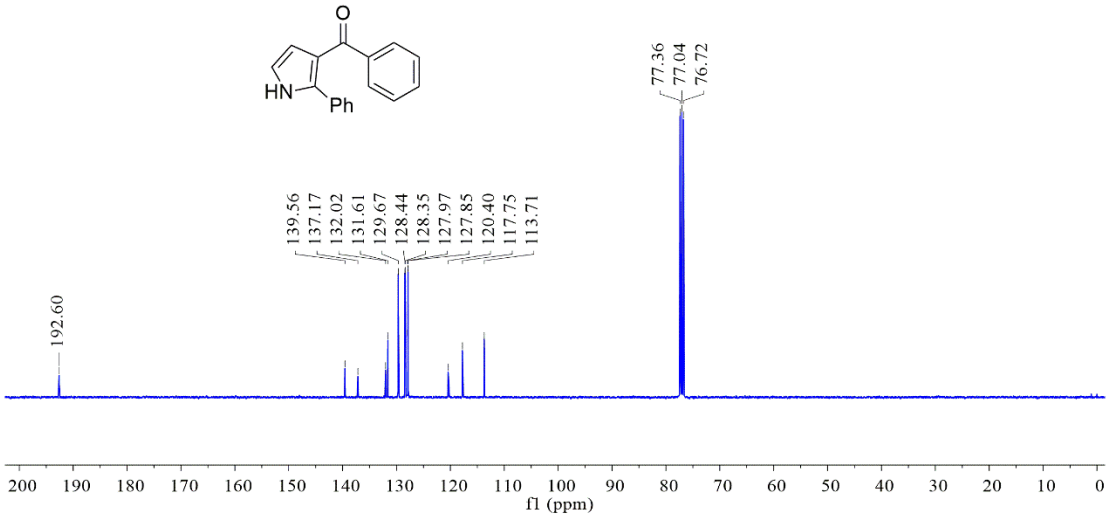
^{13}C-NMR spectrum of 3ac



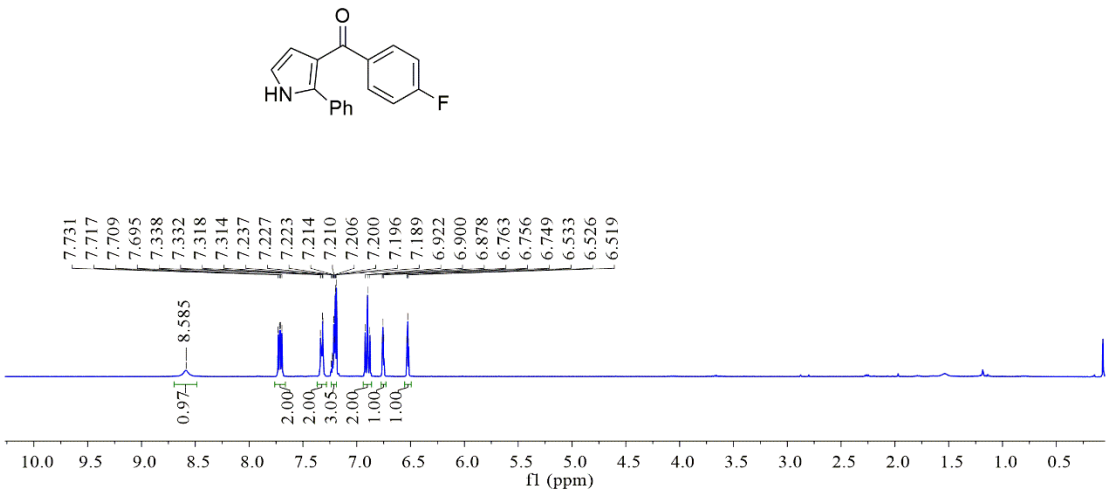
^{1}H- NMR spectrum of 3ad



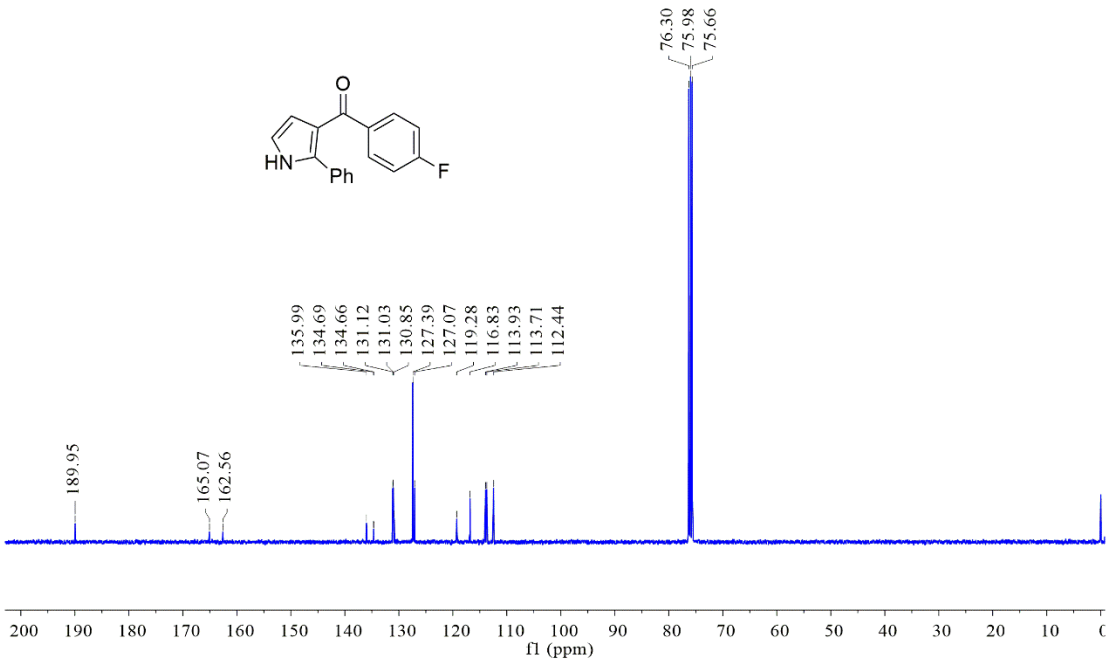
^{13}C-NMR spectrum of 3ad



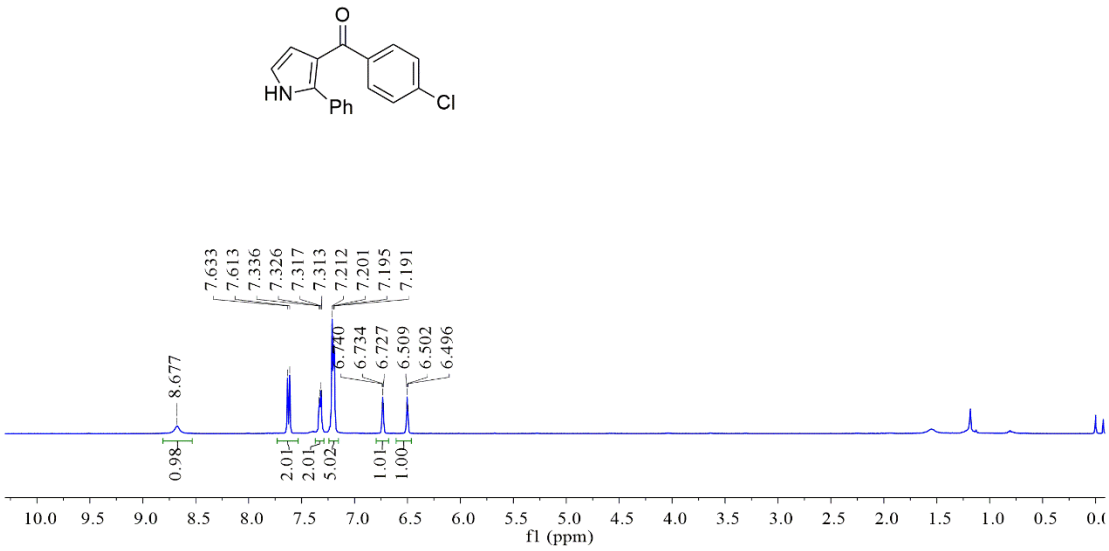
^{1}H- NMR spectrum of 3ae



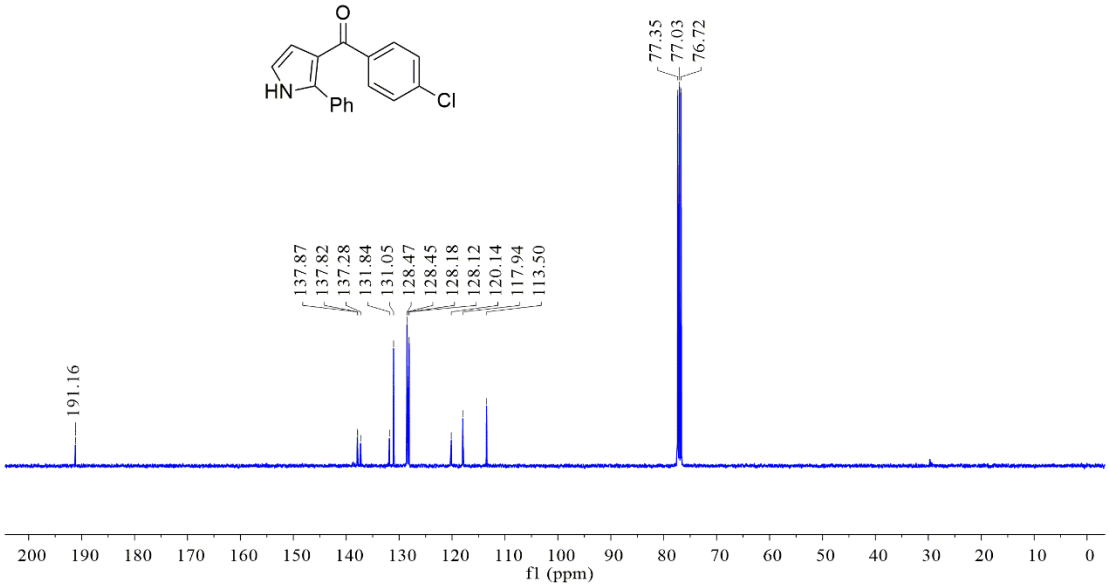
^{13}C-NMR spectrum of 3ae



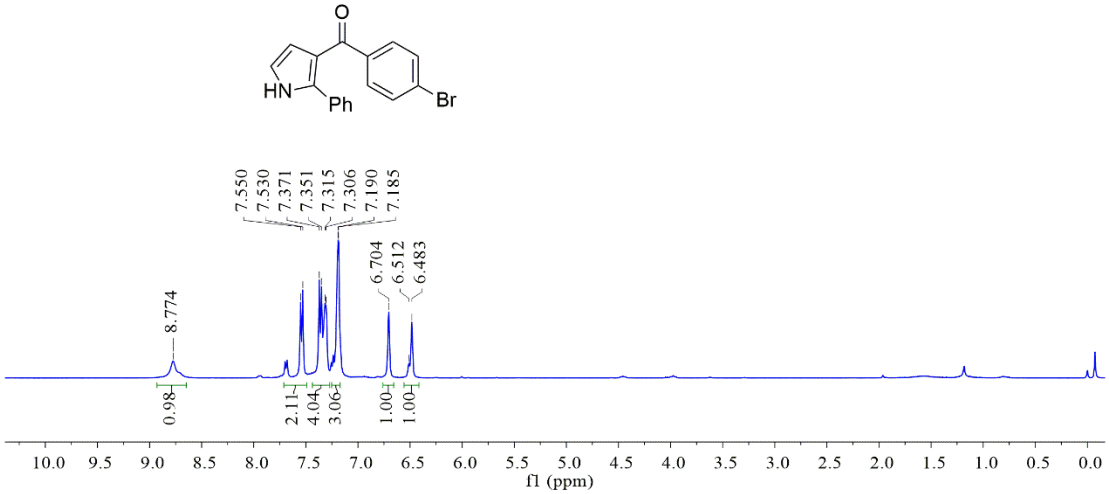
^{1}H- NMR spectrum of 3af



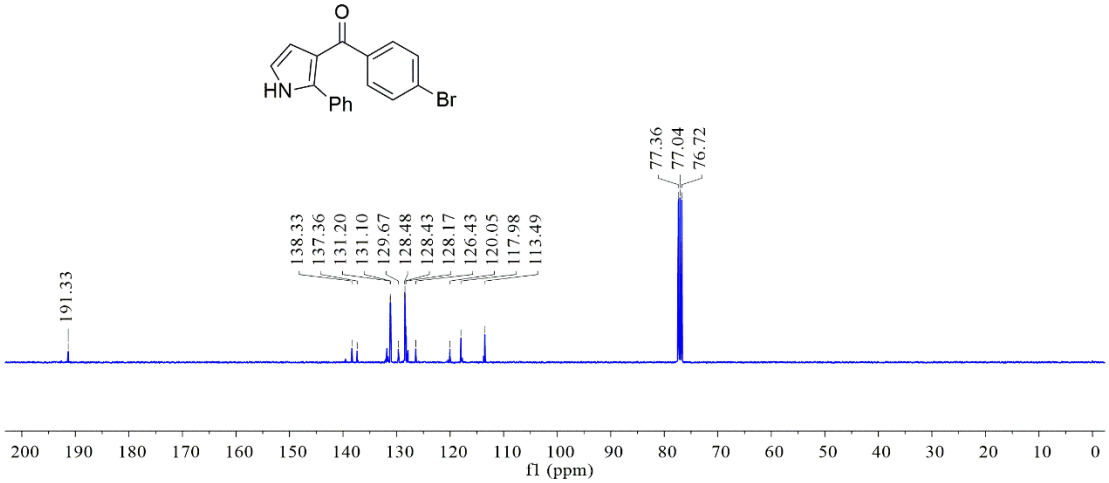
^{13}C-NMR spectrum of 3af



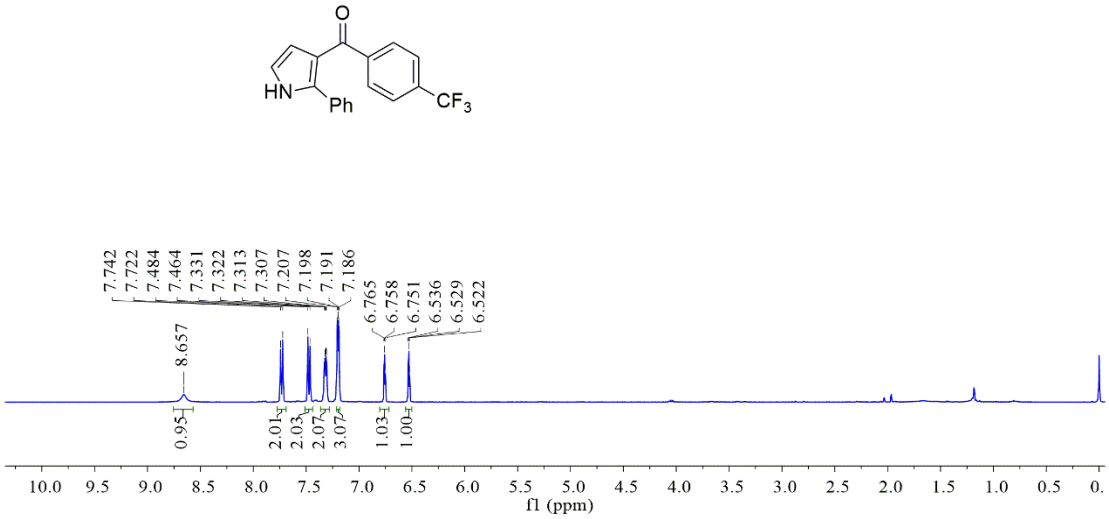
^{1}H- NMR spectrum of 3ag



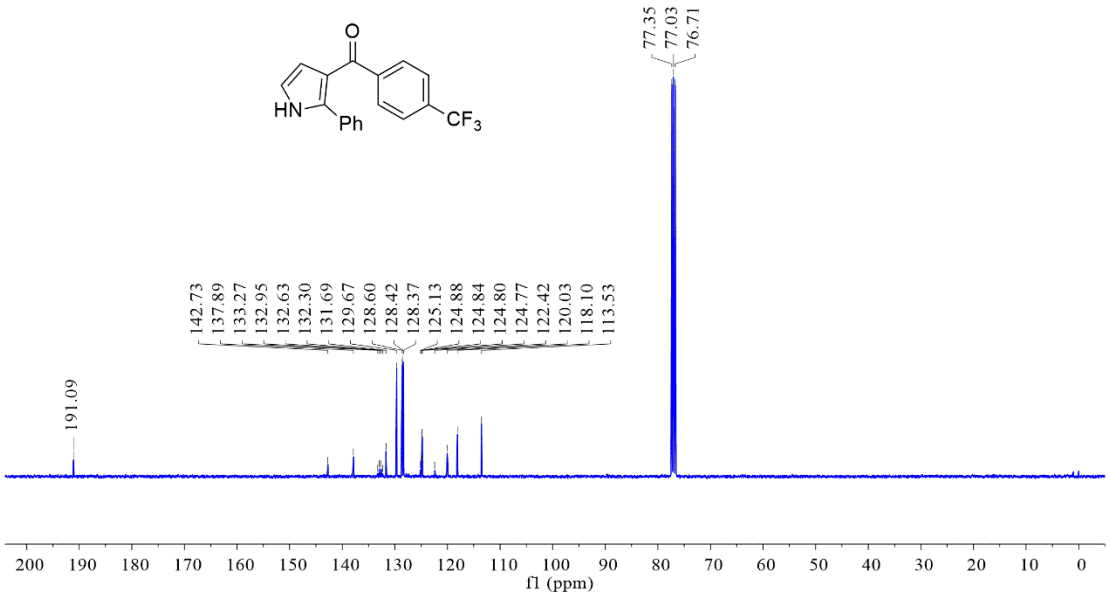
^{13}C-NMR spectrum of 3ag



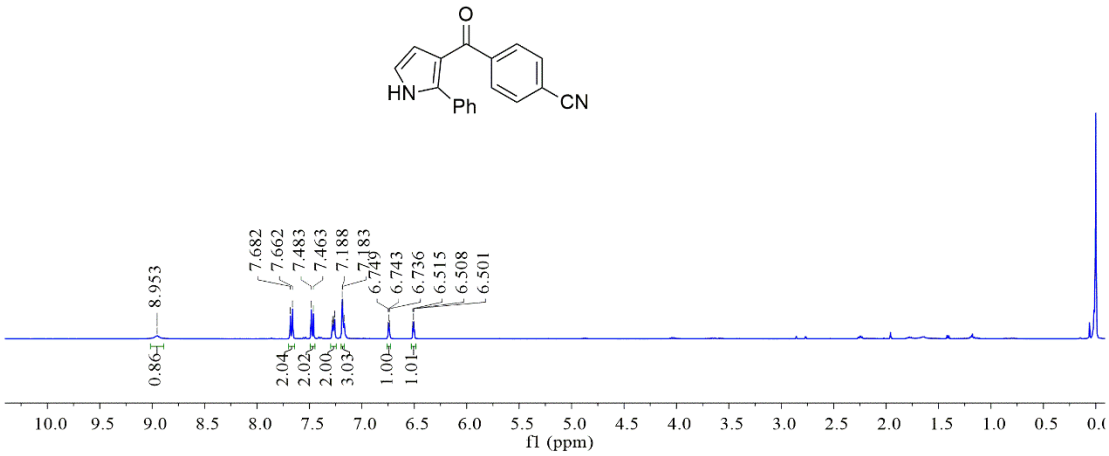
^{1}H- NMR spectrum of 3ah



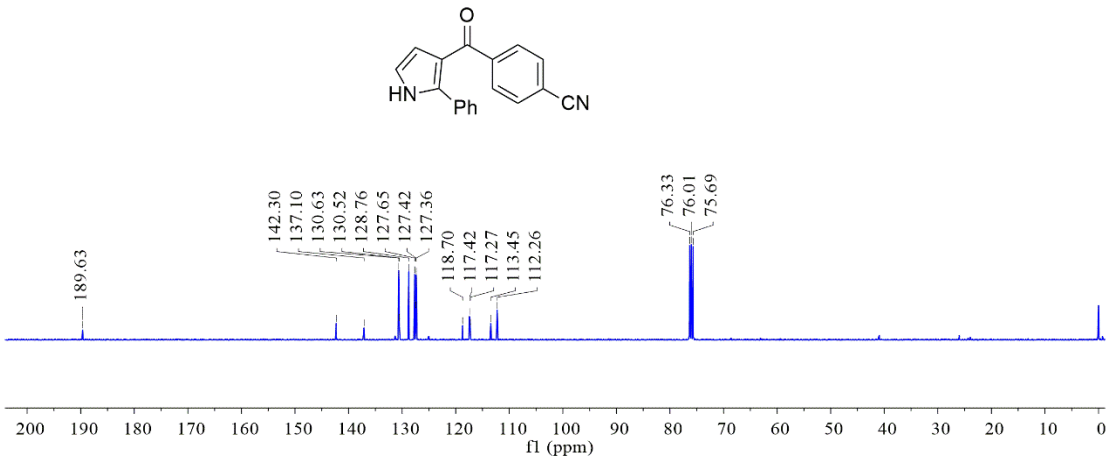
^{13}C-NMR spectrum of 3ah



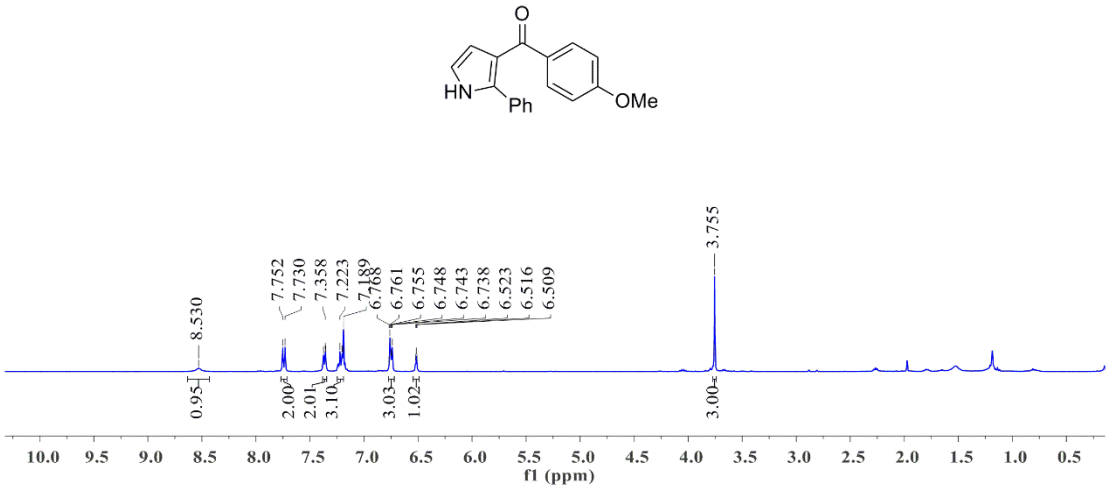
^{1}H- NMR spectrum of 3ai



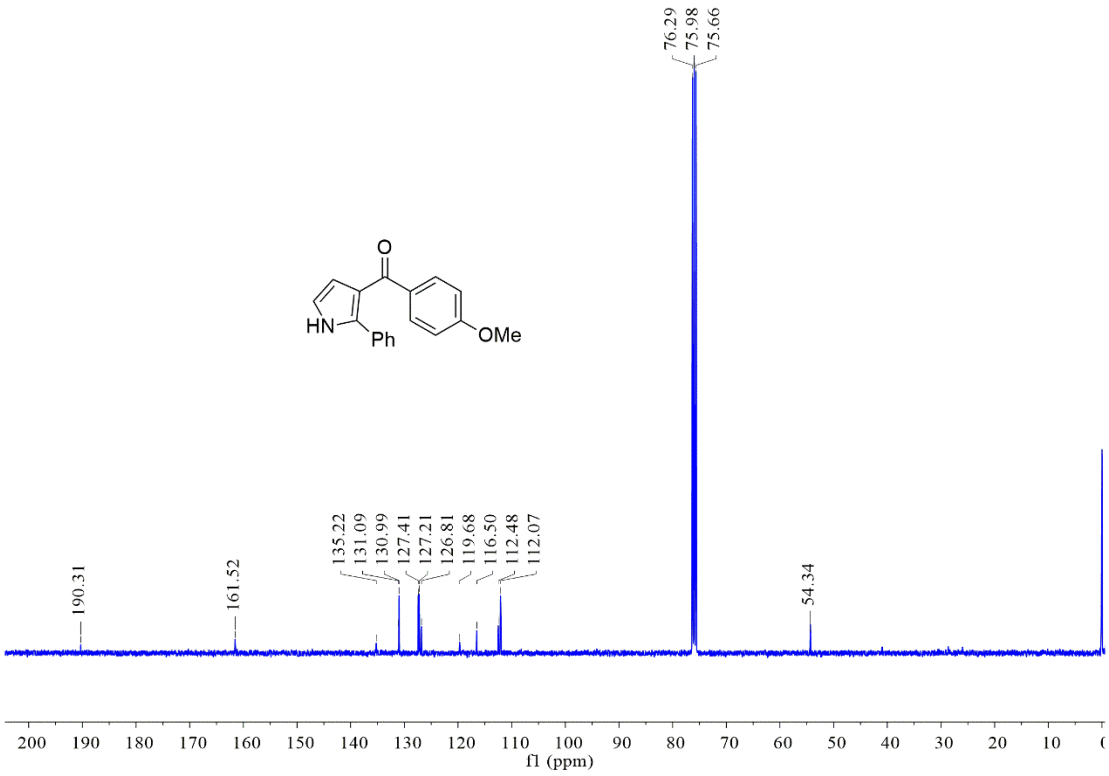
^{13}C-NMR spectrum of 3ai



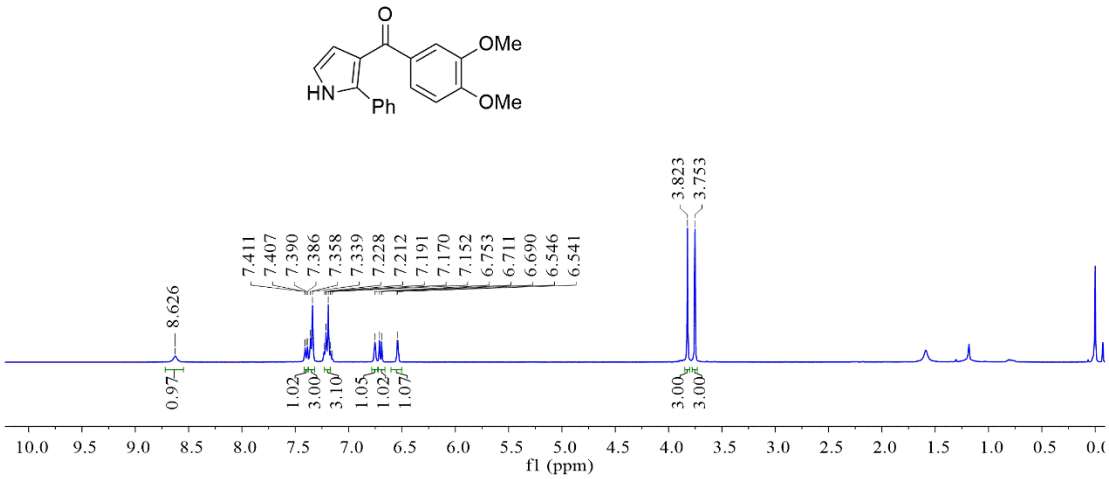
^{1}H- NMR spectrum of 3aj



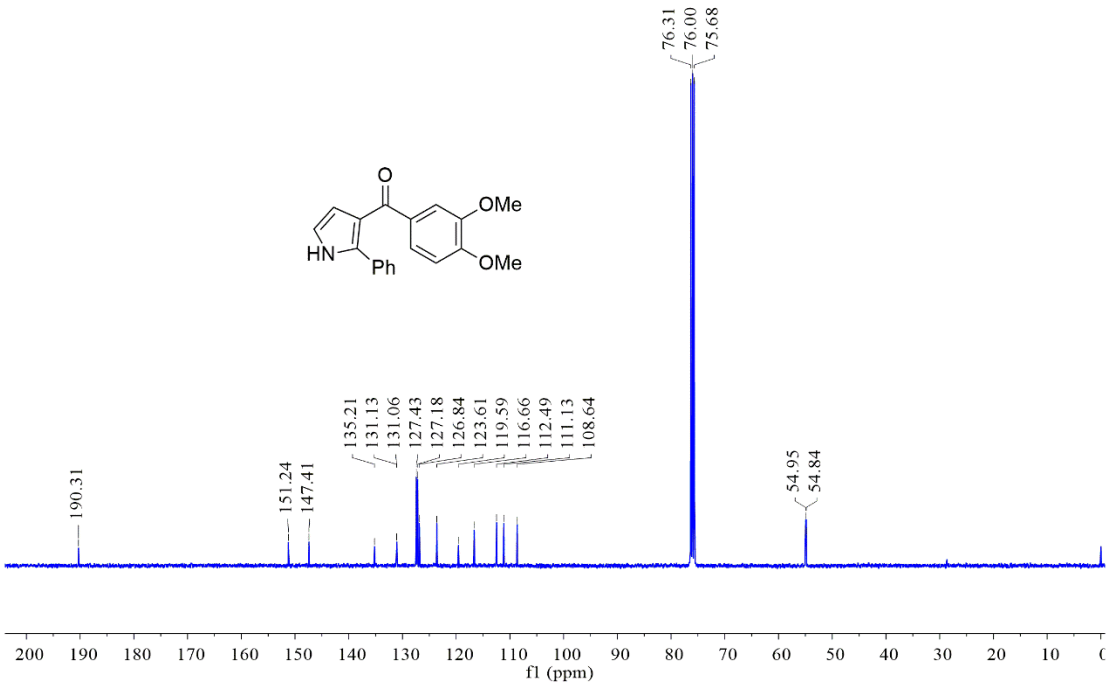
^{13}C-NMR spectrum of 3aj



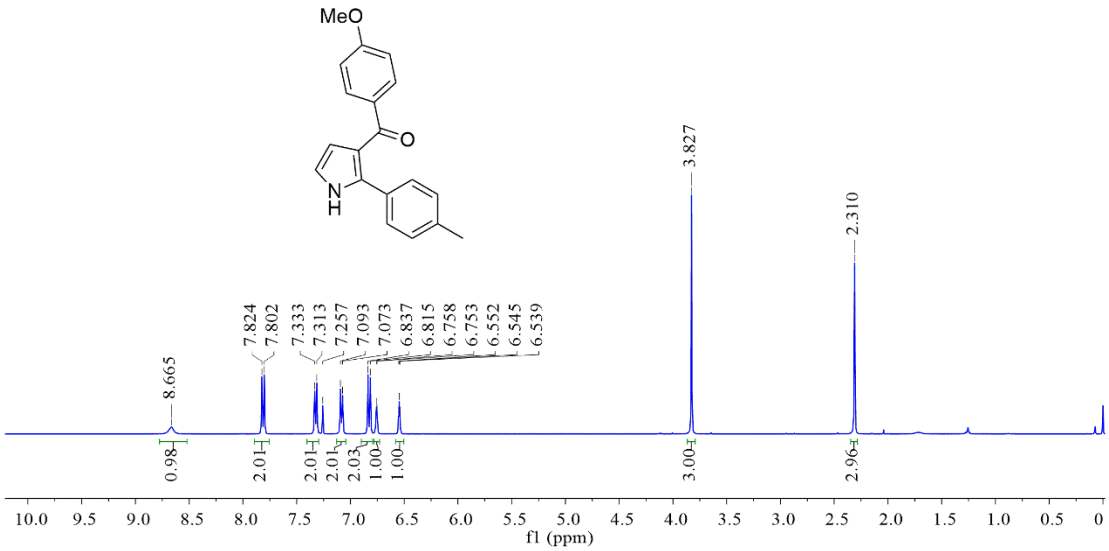
^{1}H- NMR spectrum of 3ak



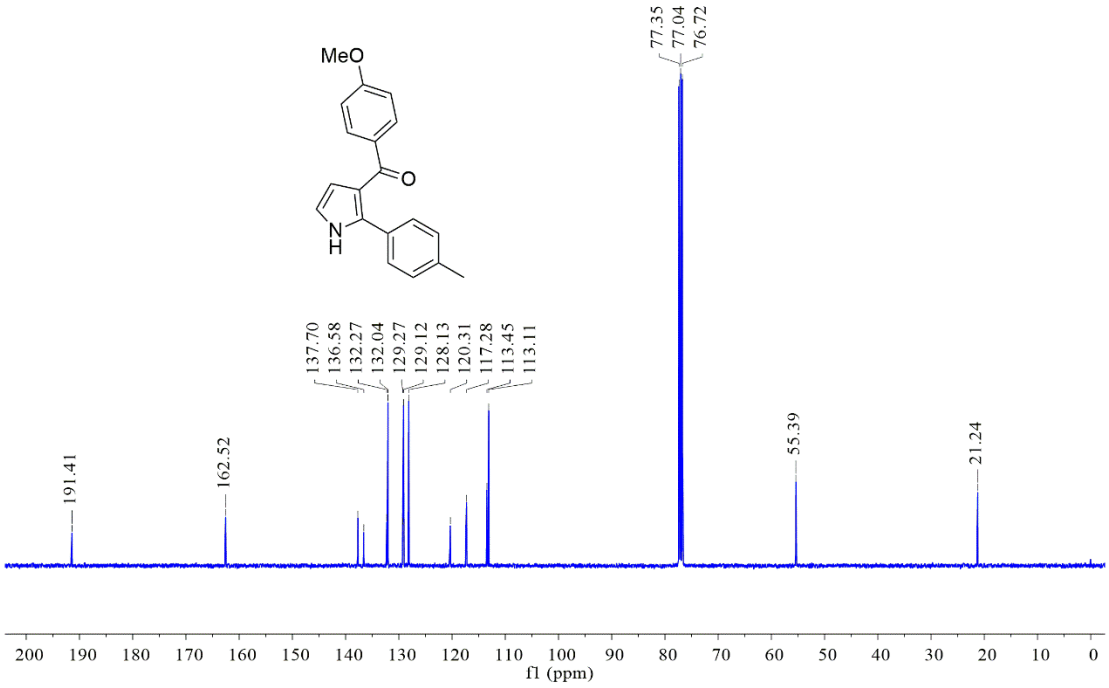
^{13}C-NMR spectrum of 3ak



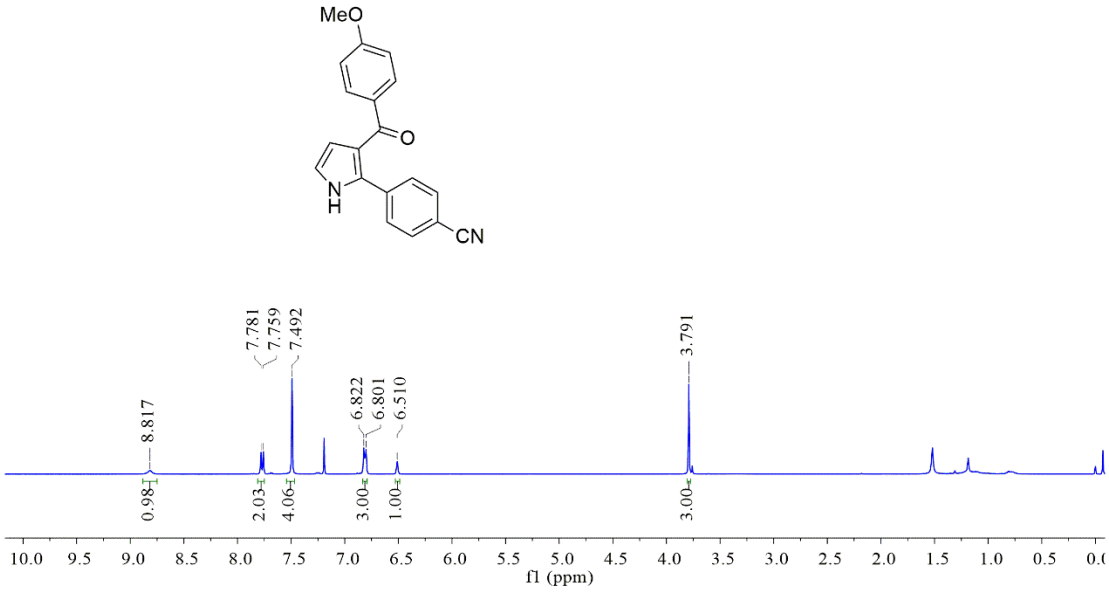
^{1}H- NMR spectrum of 3al



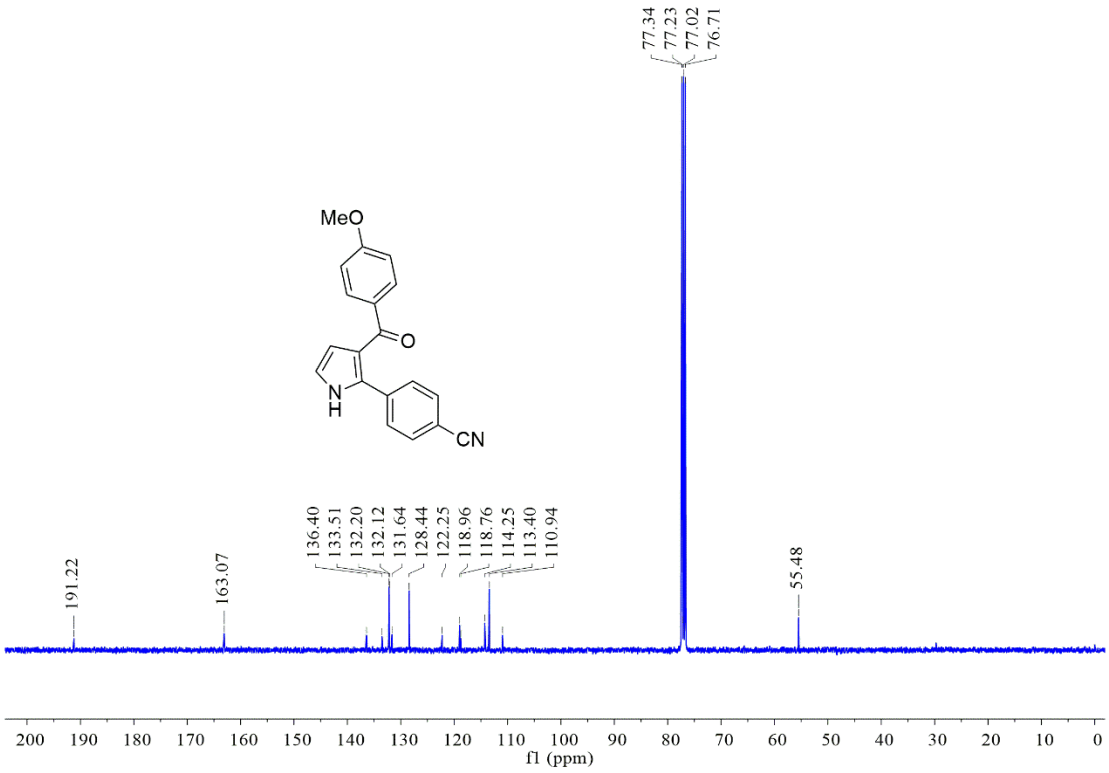
^{13}C-NMR spectrum of 3al



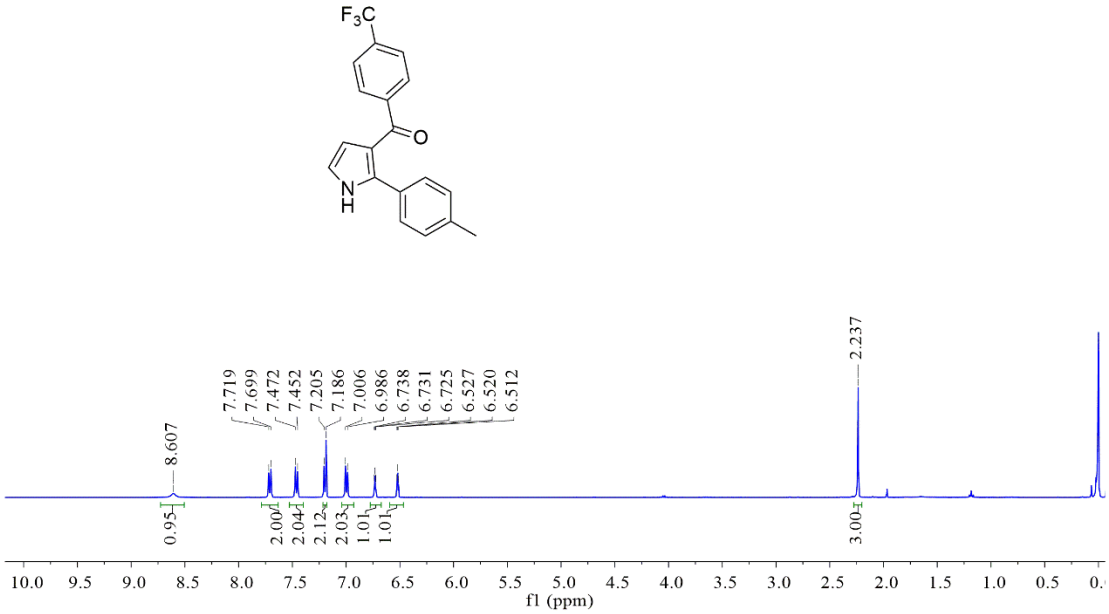
^{1}H- NMR spectrum of 3am



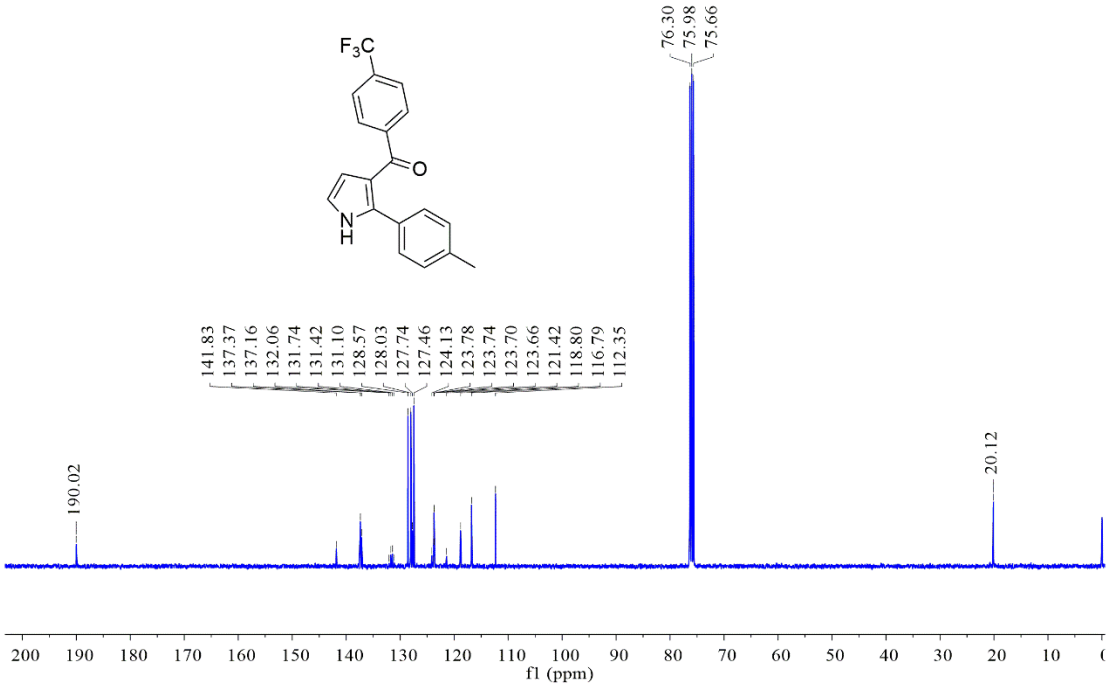
^{13}C-NMR spectrum of 3am



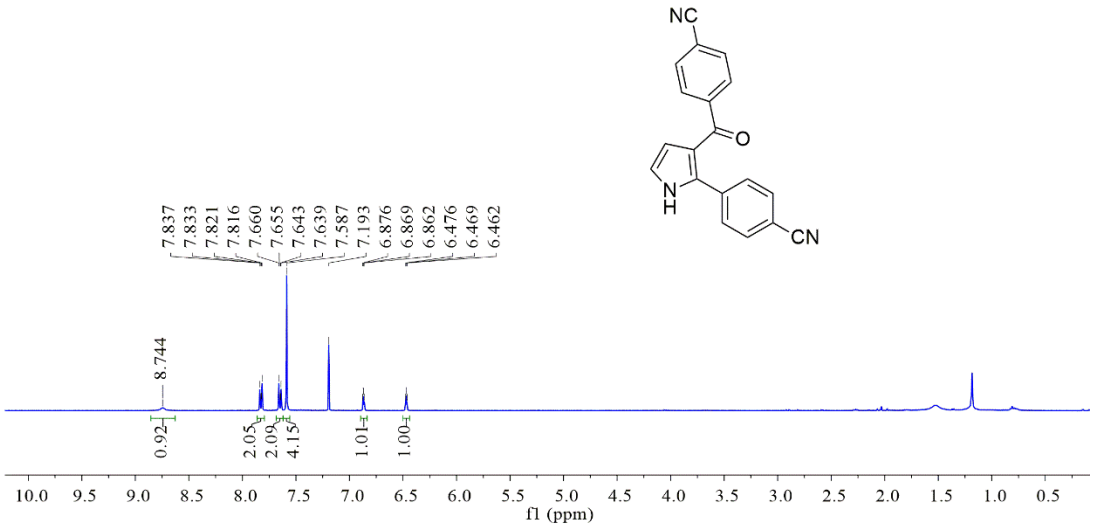
^{1}H- NMR spectrum of 3an



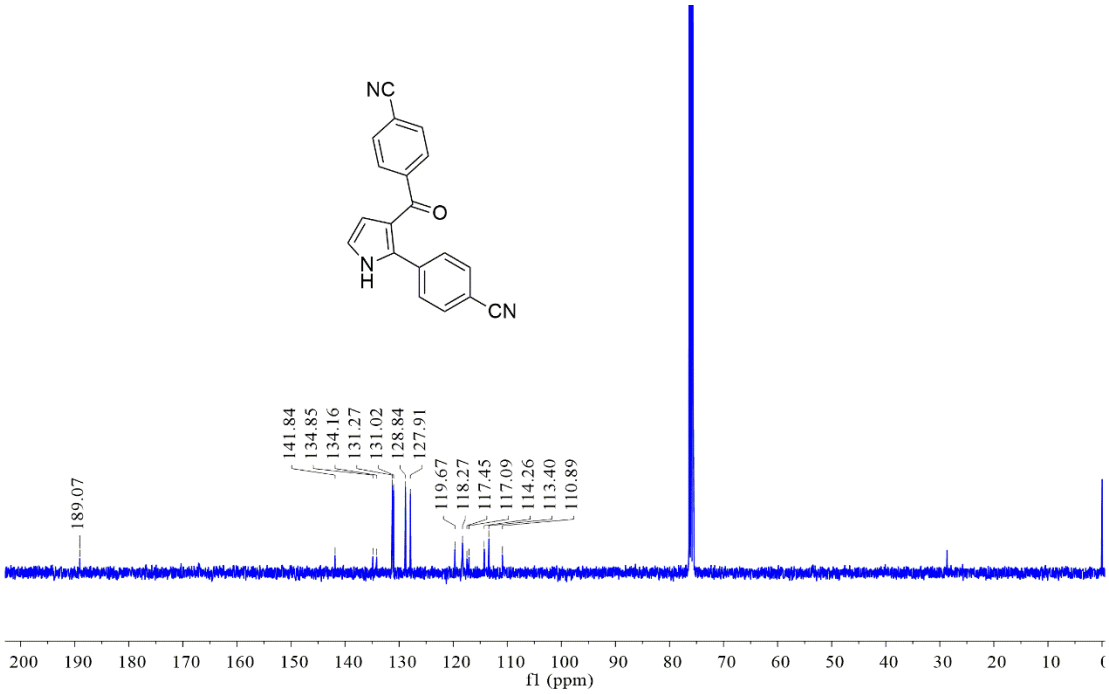
^{13}C-NMR spectrum of 3an



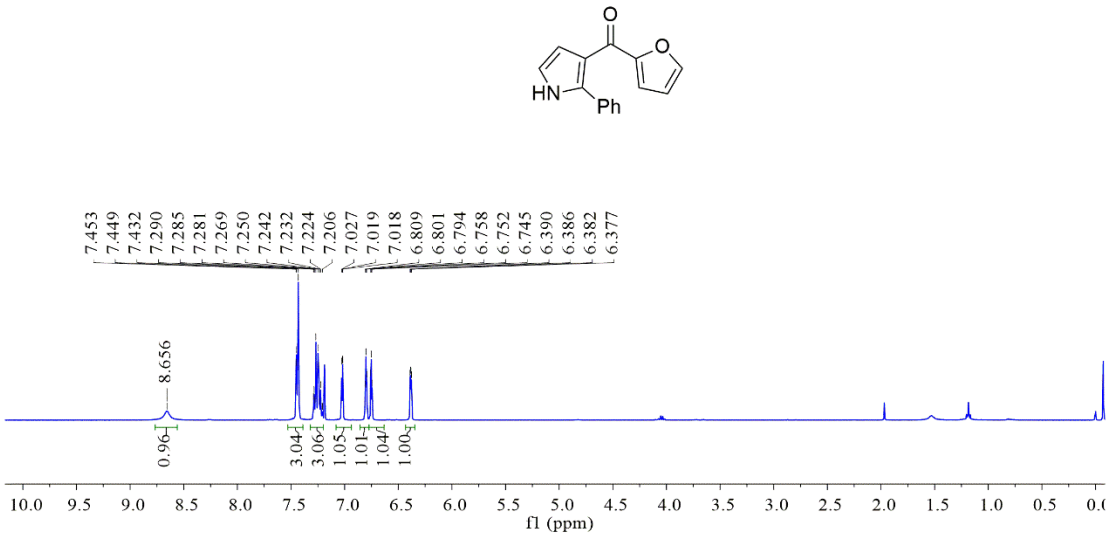
^{1}H- NMR spectrum of 3ao



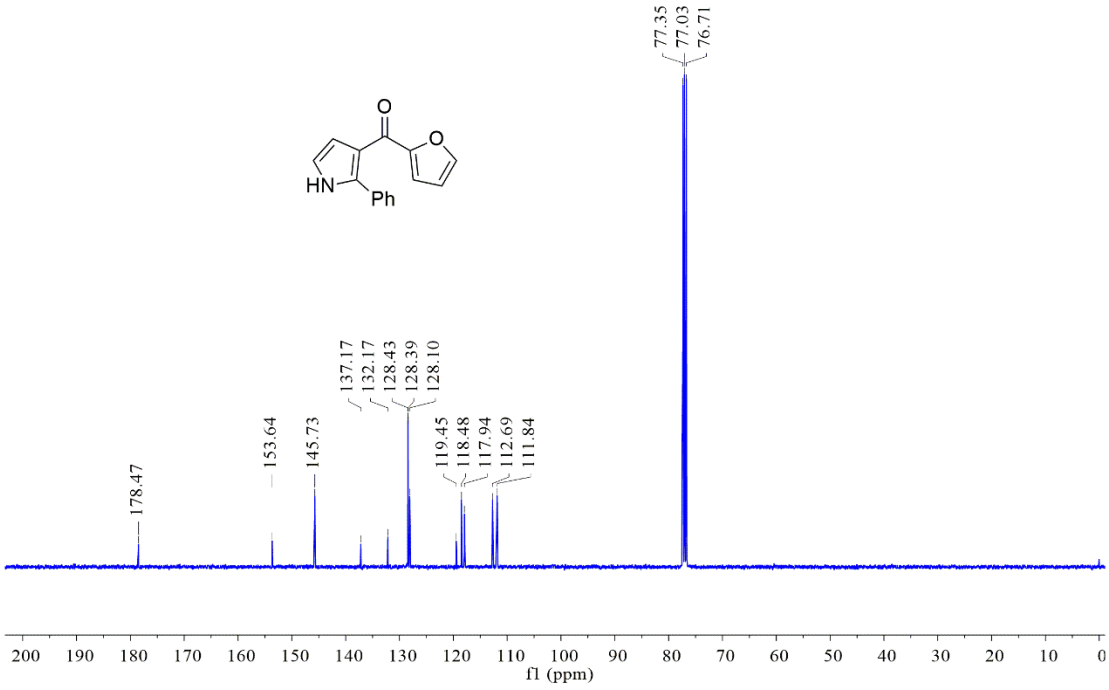
^{13}C-NMR spectrum of 3ao



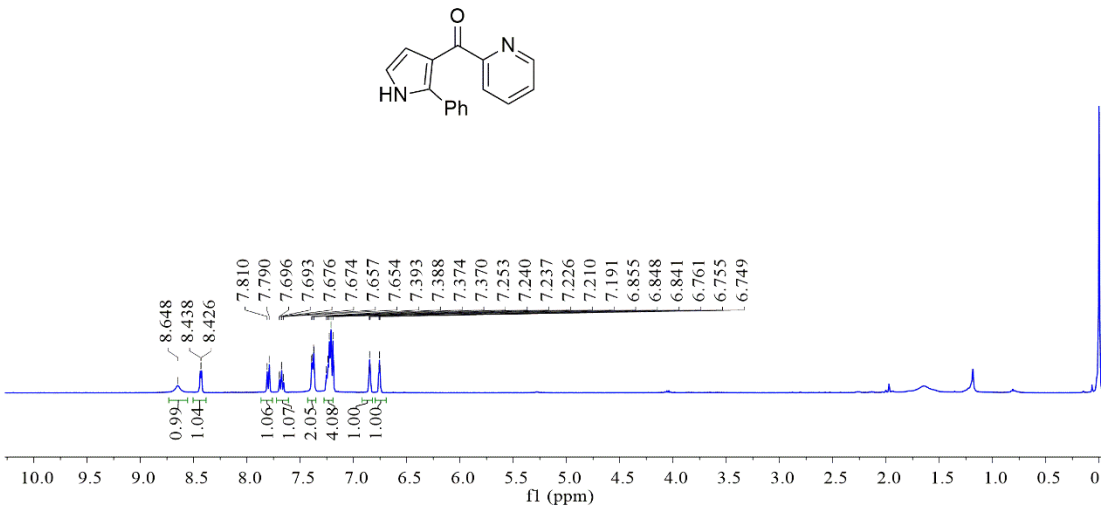
^{1}H- NMR spectrum of 3ap



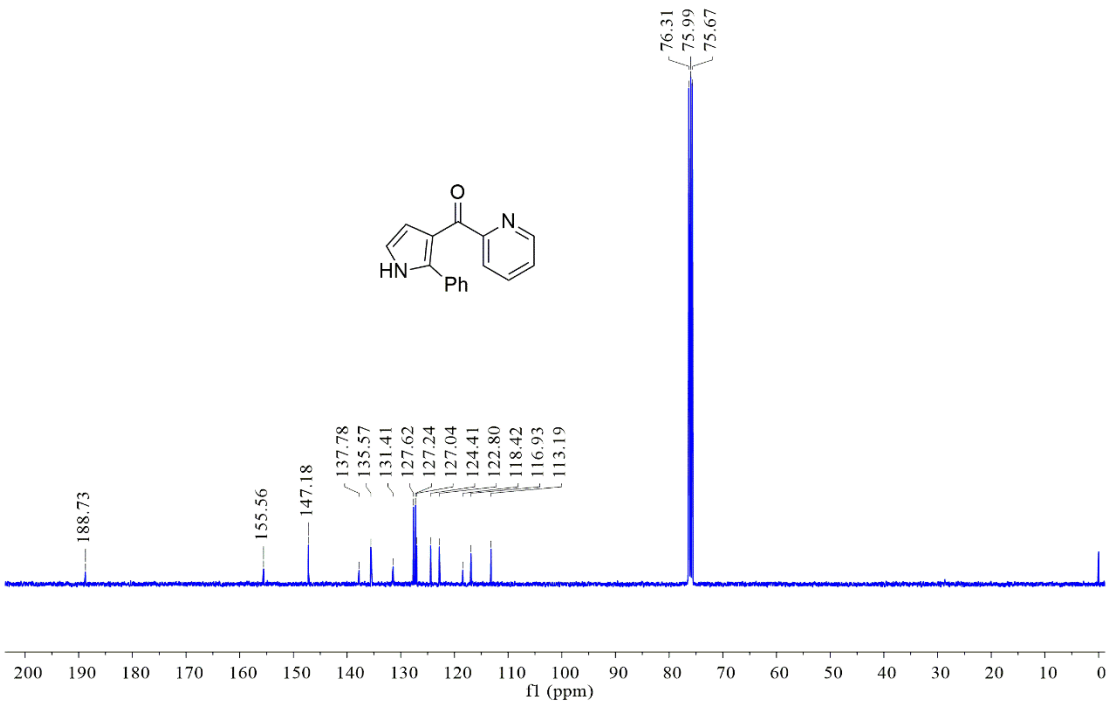
^{13}C-NMR spectrum of 3ap



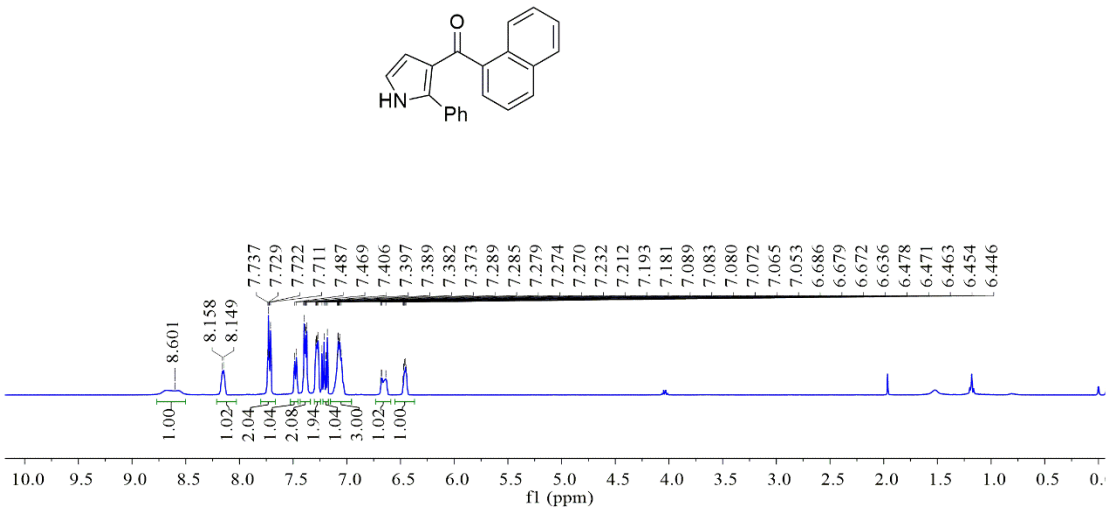
^{1}H- NMR spectrum of 3aq



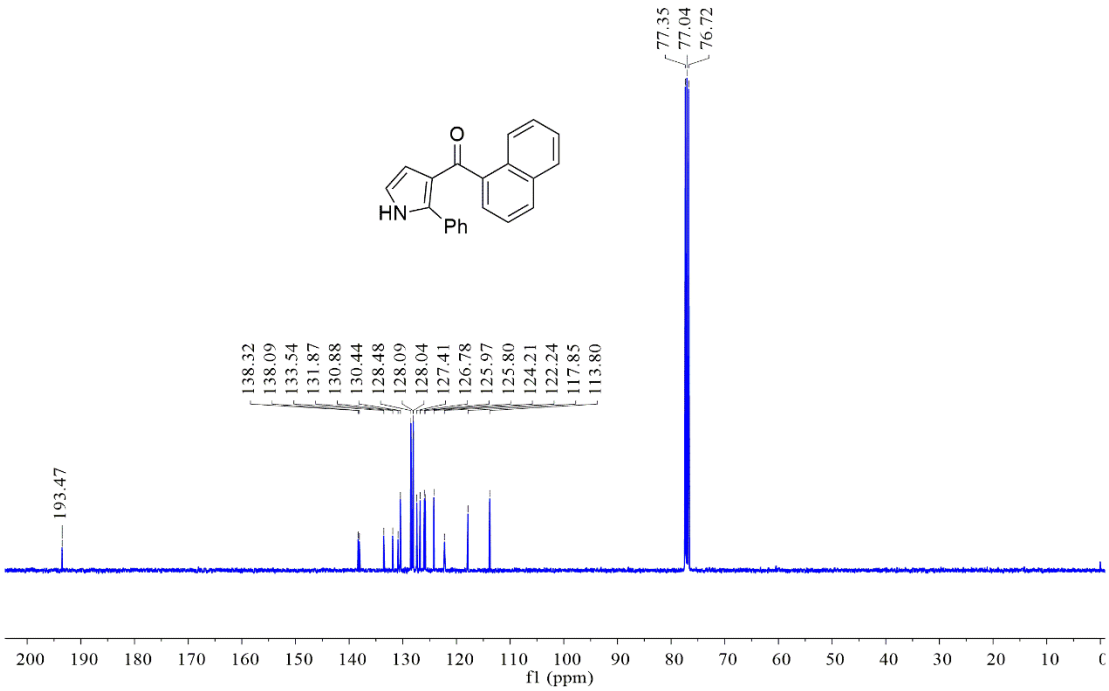
^{13}C-NMR spectrum of 3aq



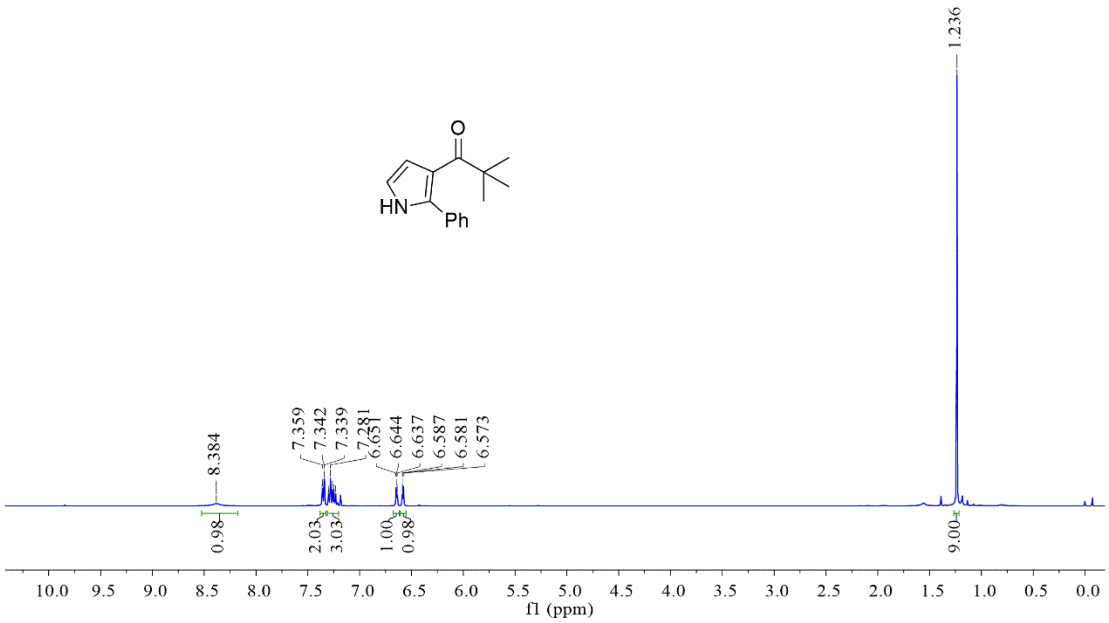
^{1}H- NMR spectrum of 3ar



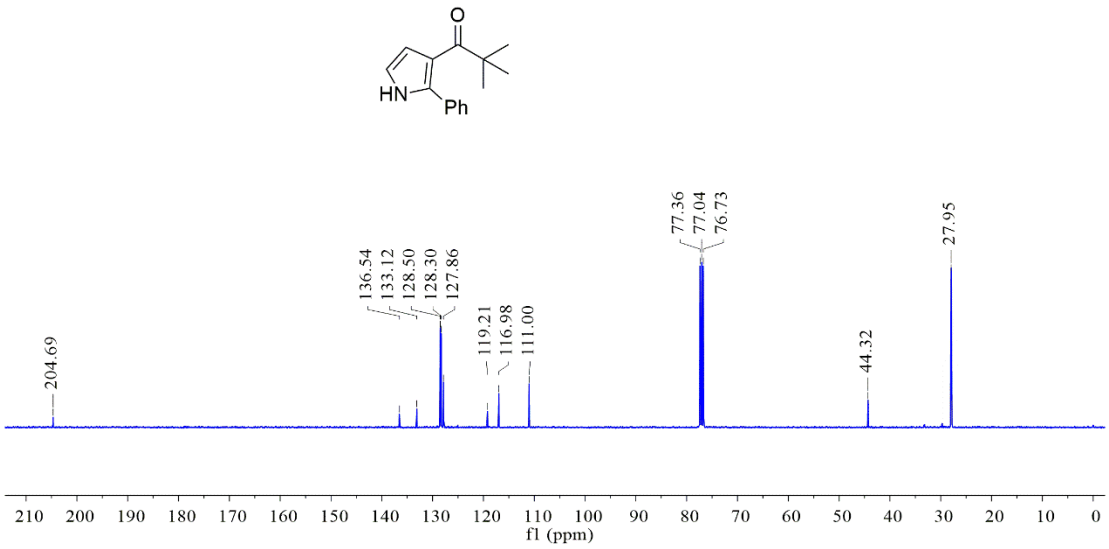
^{13}C-NMR spectrum of 3ar



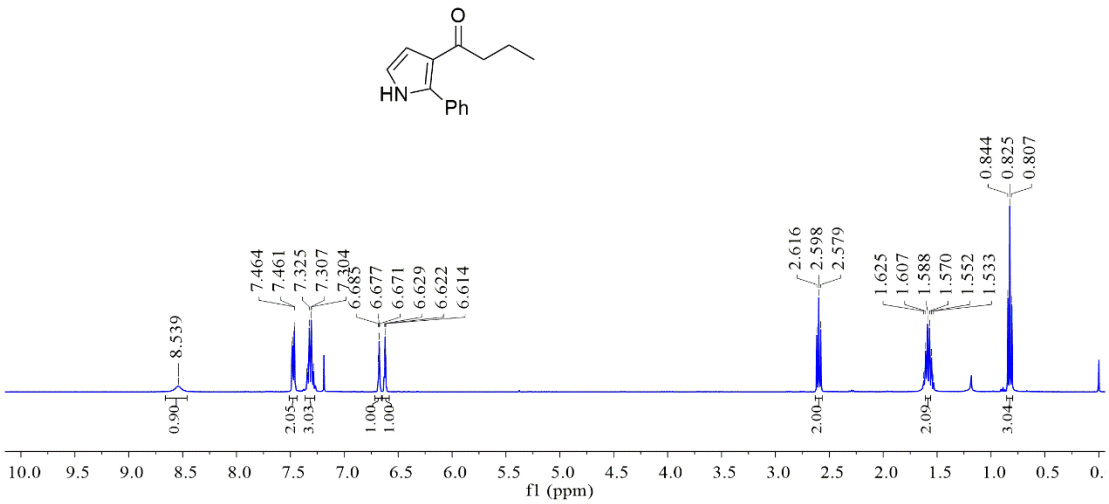
^{1}H- NMR spectrum of 3as



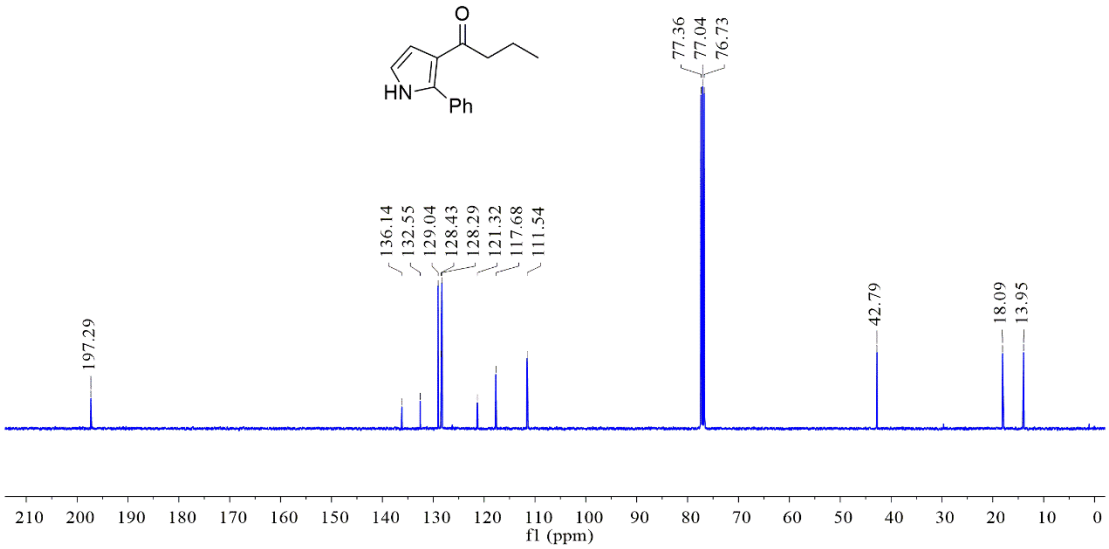
^{13}C-NMR spectrum of 3as



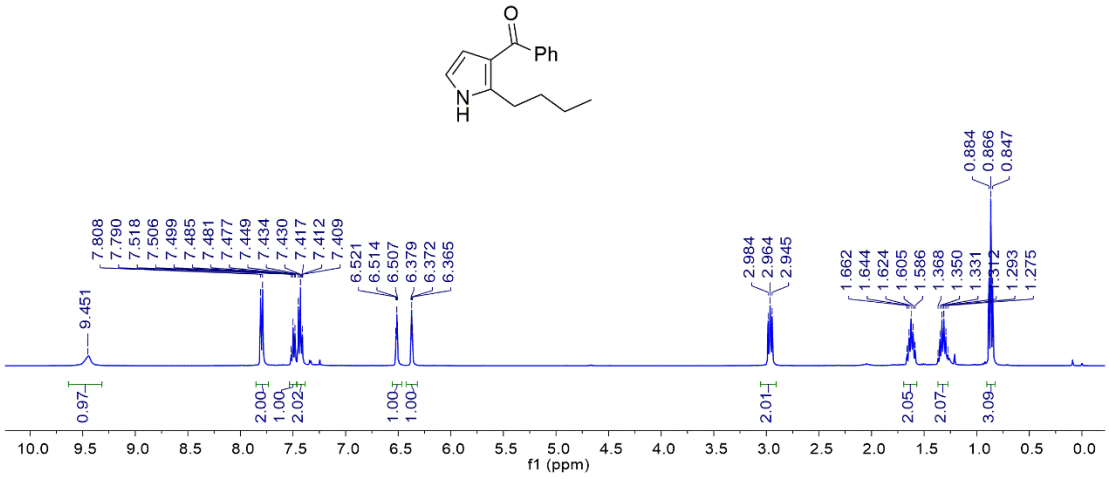
^{1}H- NMR spectrum of 3at



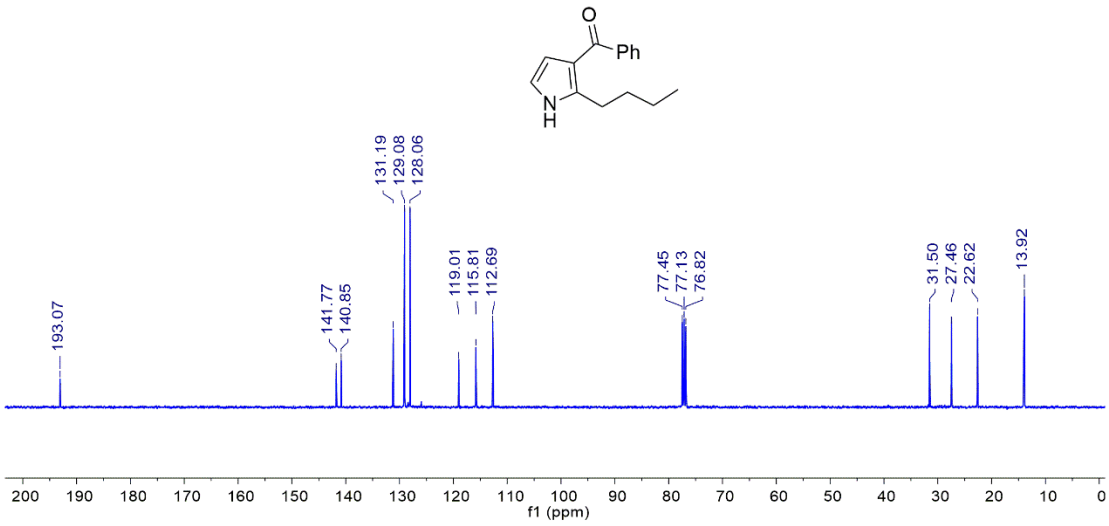
^{13}C-NMR spectrum of 3at



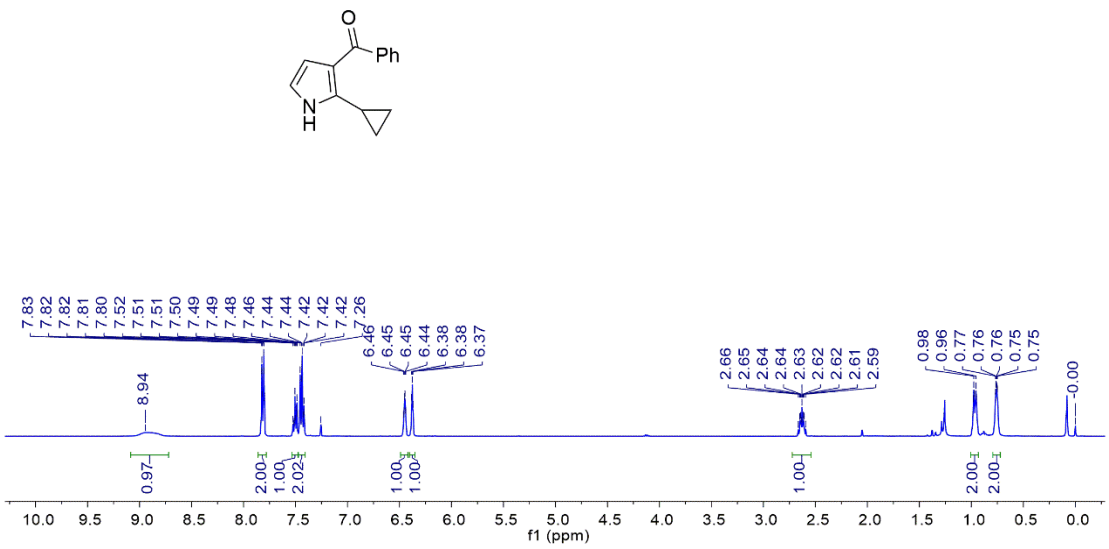
^{1}H- NMR spectrum of 3au



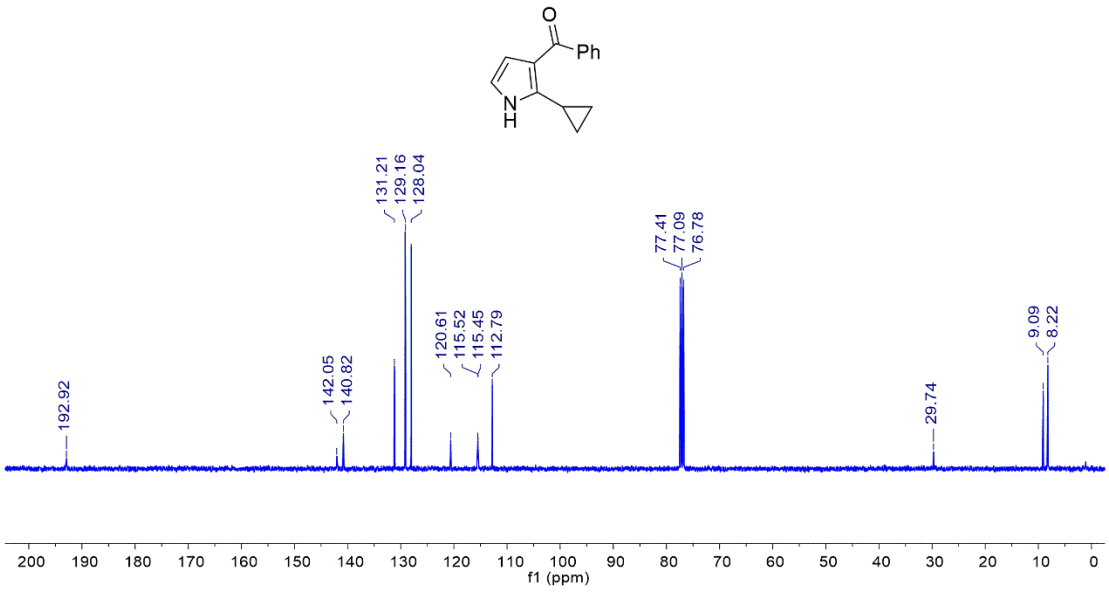
^{13}C-NMR spectrum of 3au



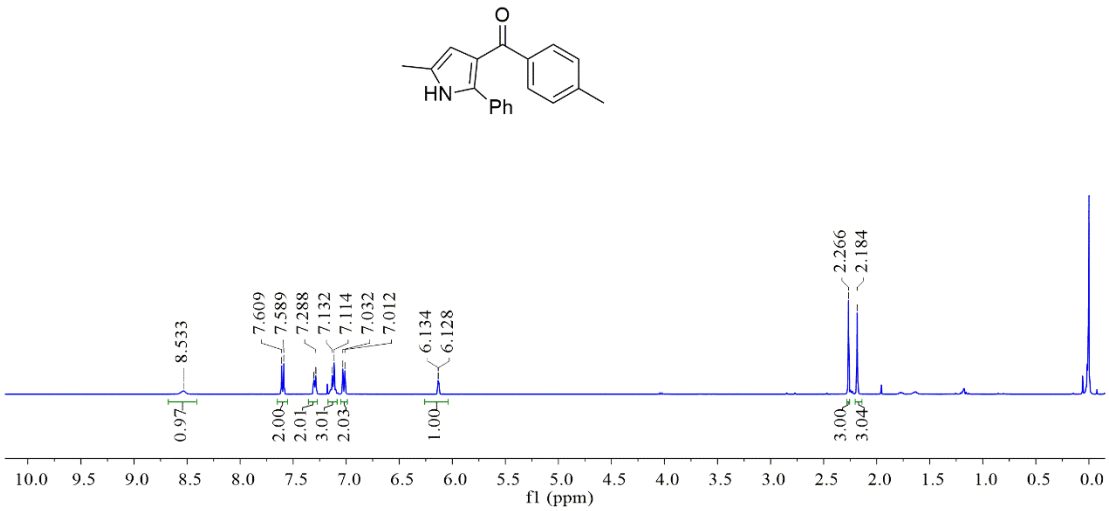
^{1}H- NMR spectrum of 3av



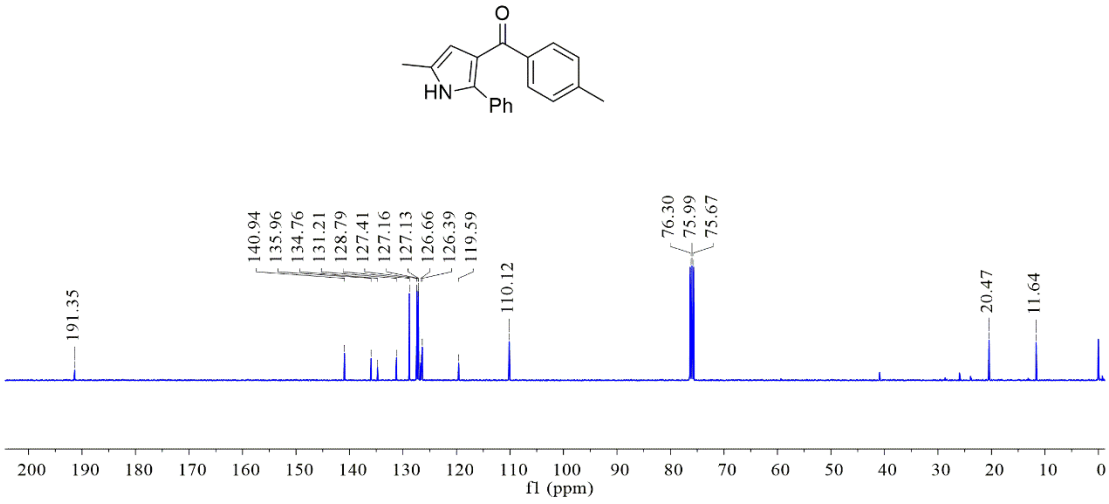
^{13}C-NMR spectrum of 3av



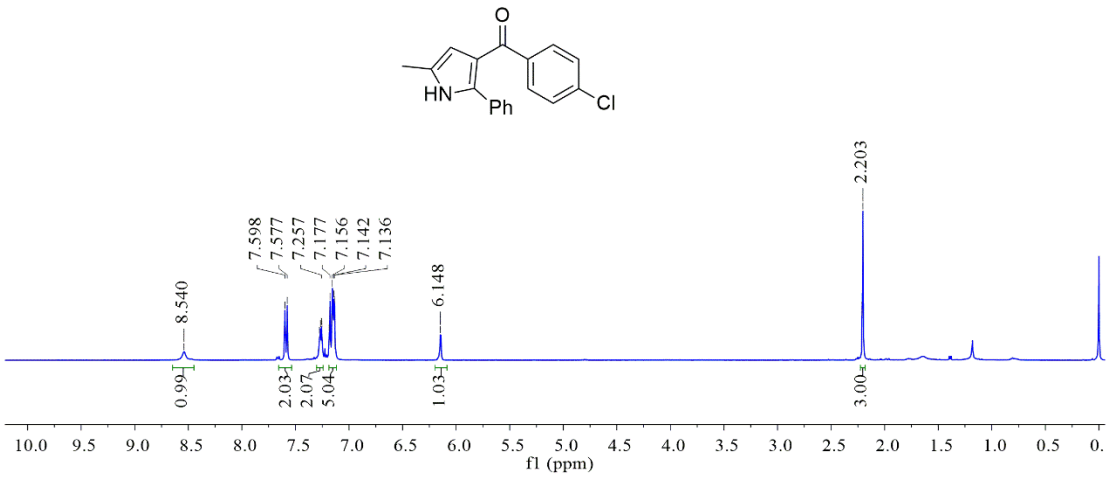
^{1}H- NMR spectrum of 3ba



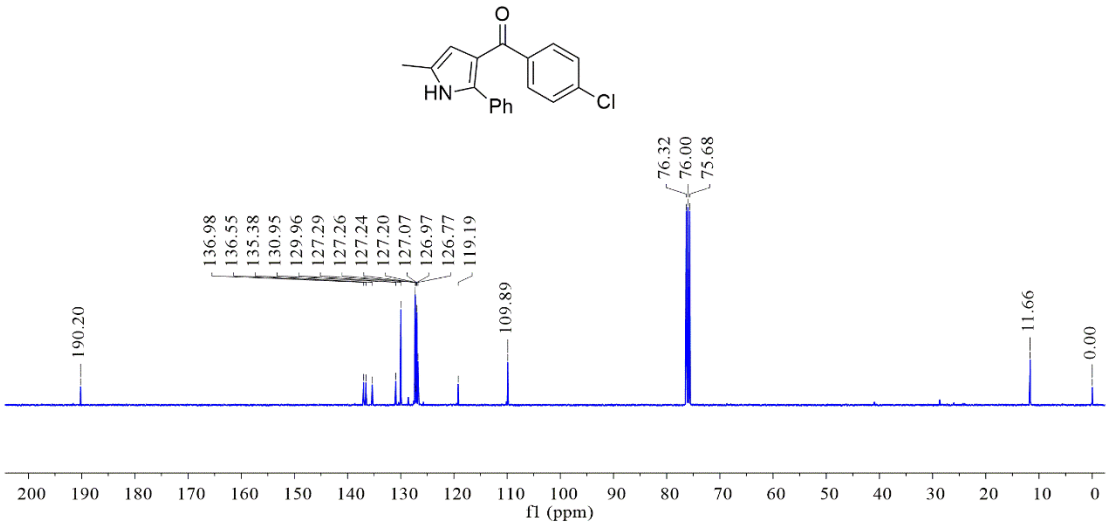
^{13}C-NMR spectrum of 3ba



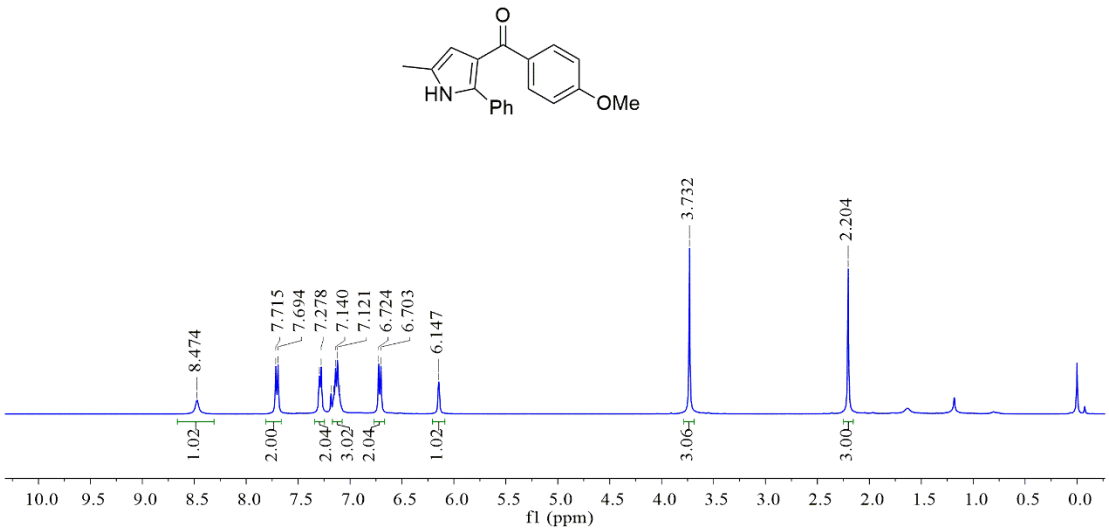
^{1}H- NMR spectrum of 3bf



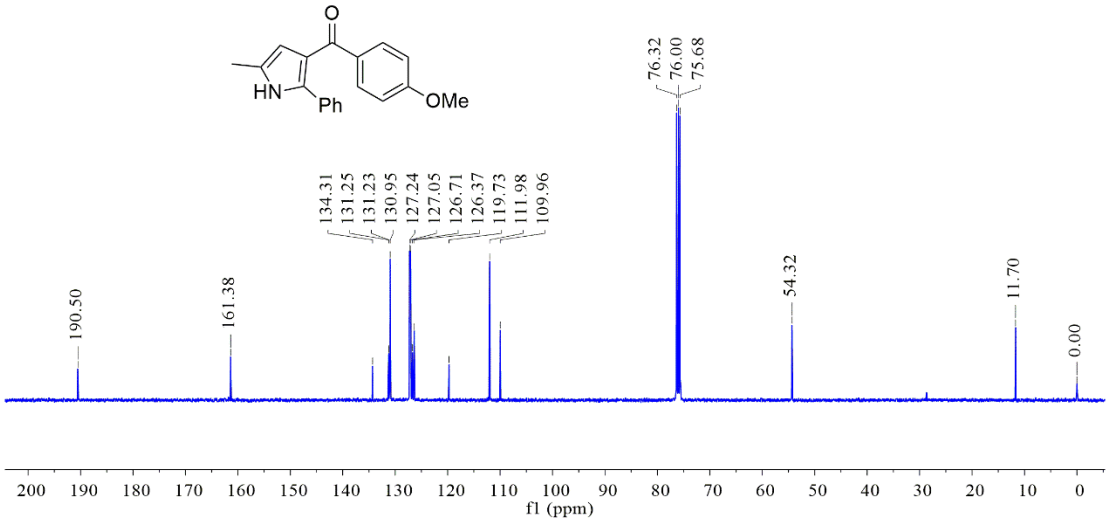
^{13}C-NMR spectrum of 3bf



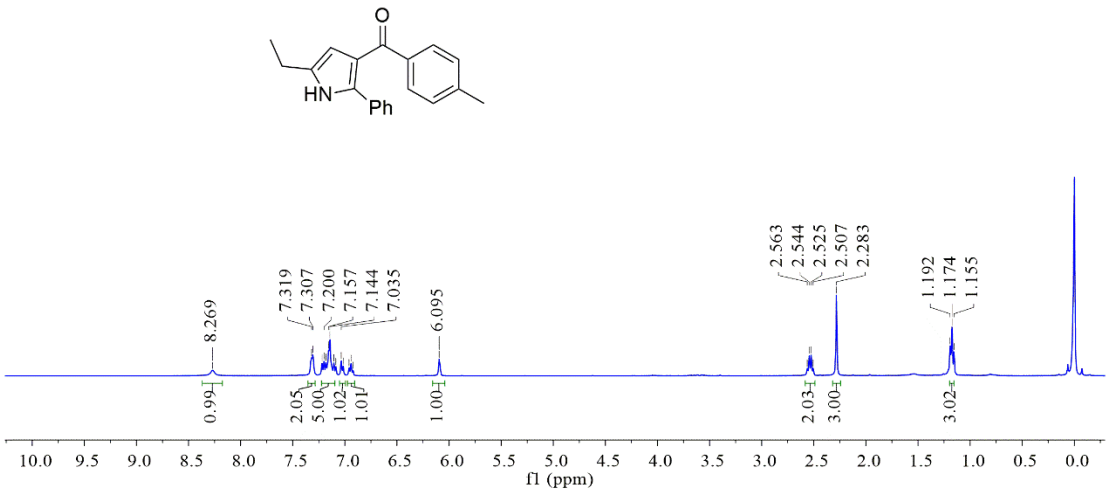
^{1}H- NMR spectrum of 3bj



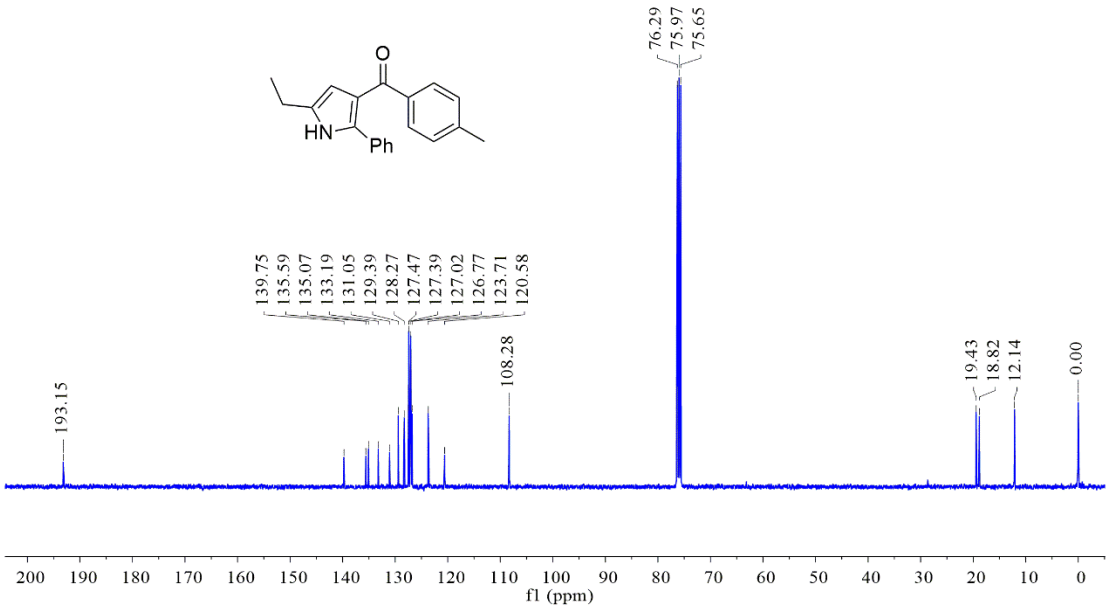
^{13}C-NMR spectrum of 3bj



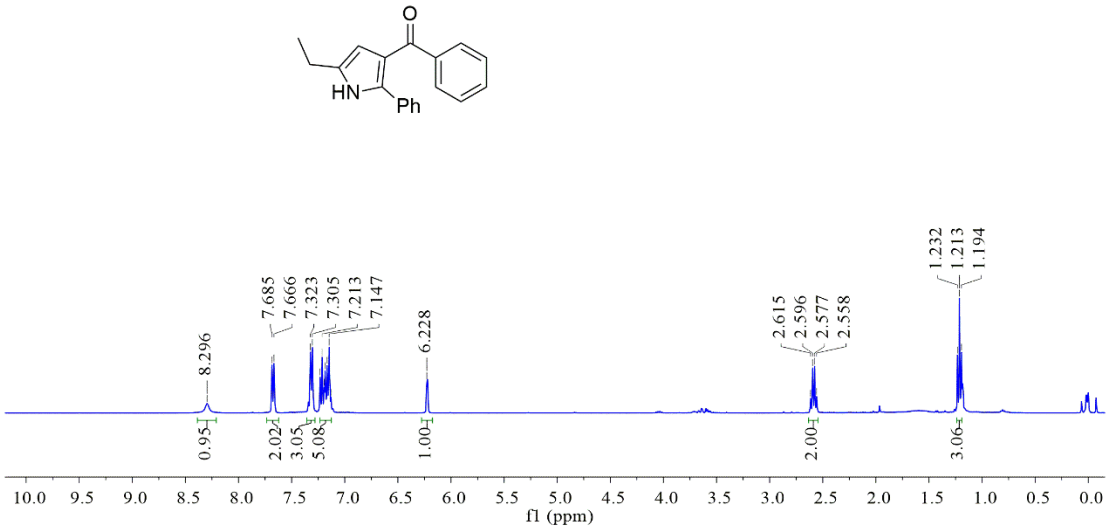
^{1}H- NMR spectrum of 3ca



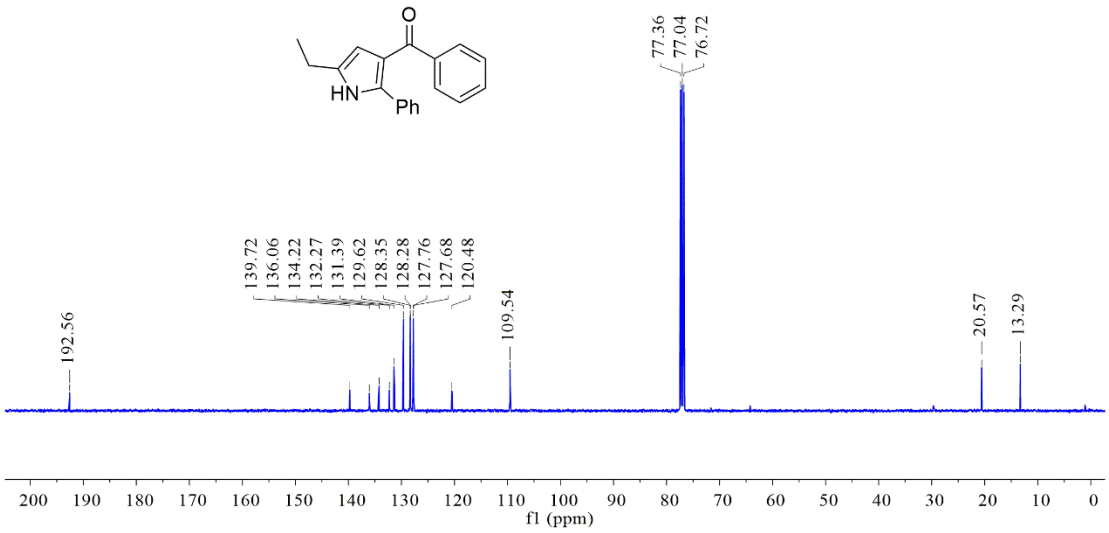
^{13}C-NMR spectrum of 3ca



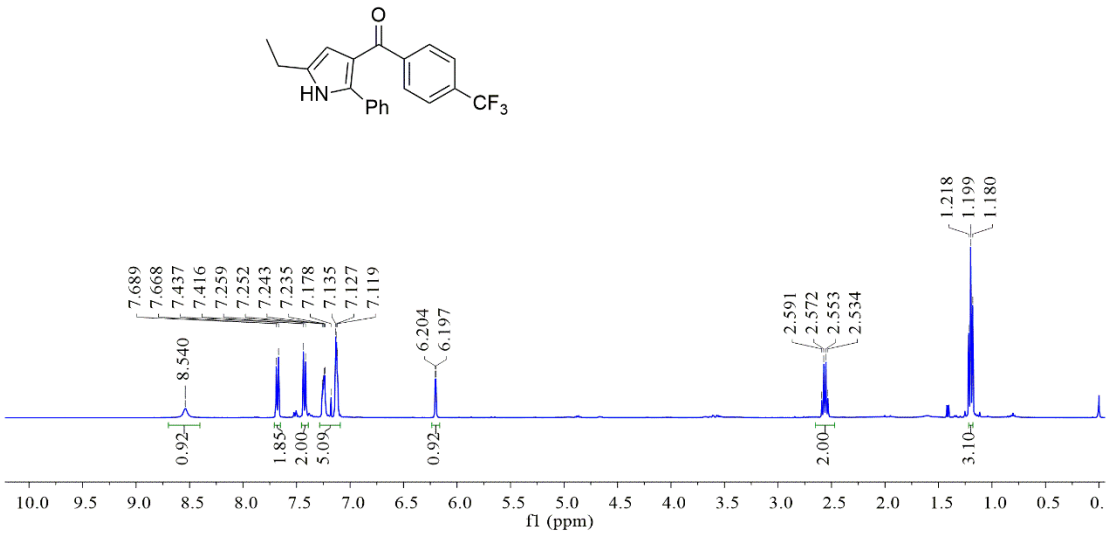
^{1}H- NMR spectrum of 3cd



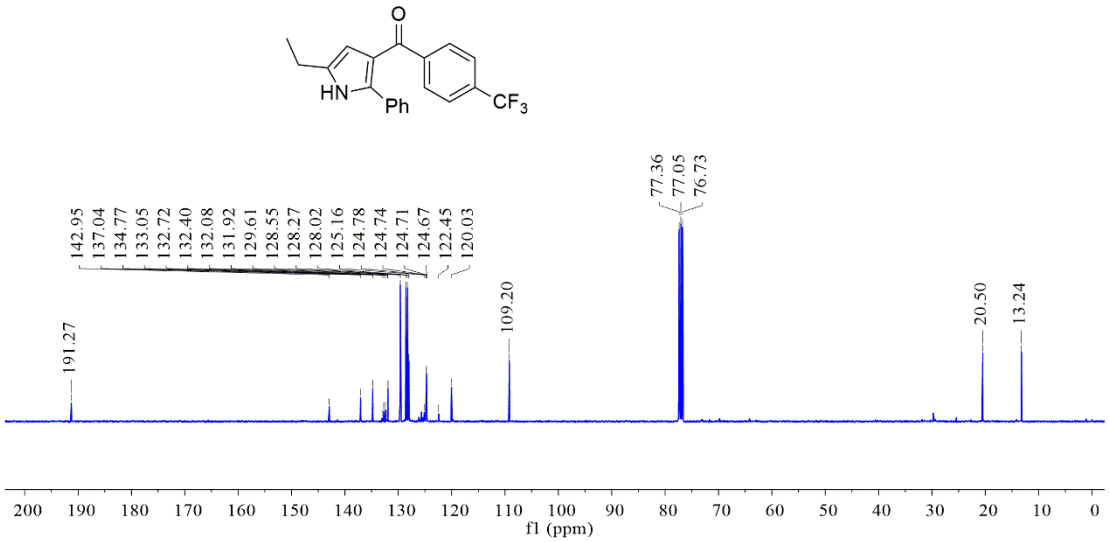
^{13}C-NMR spectrum of 3cd



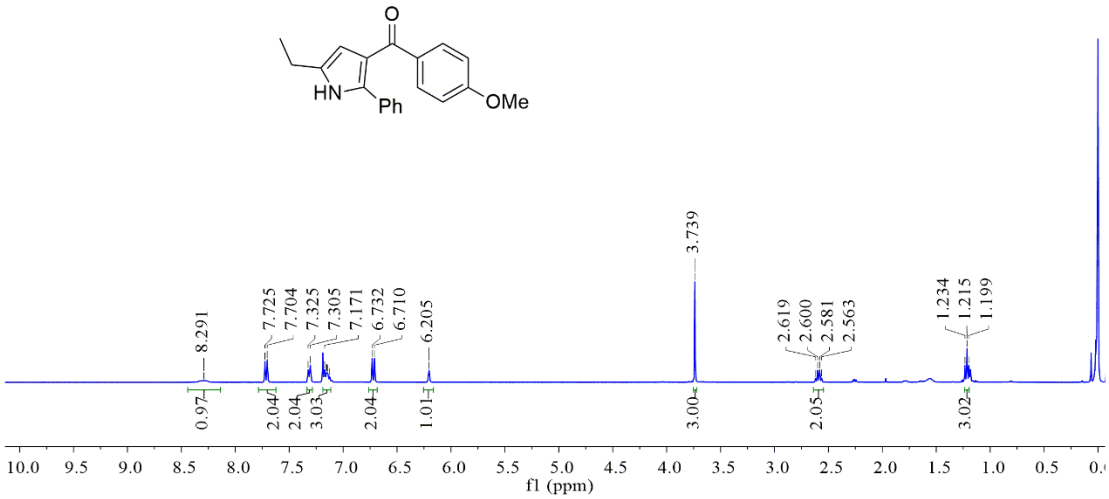
^{1}H- NMR spectrum of 3ch



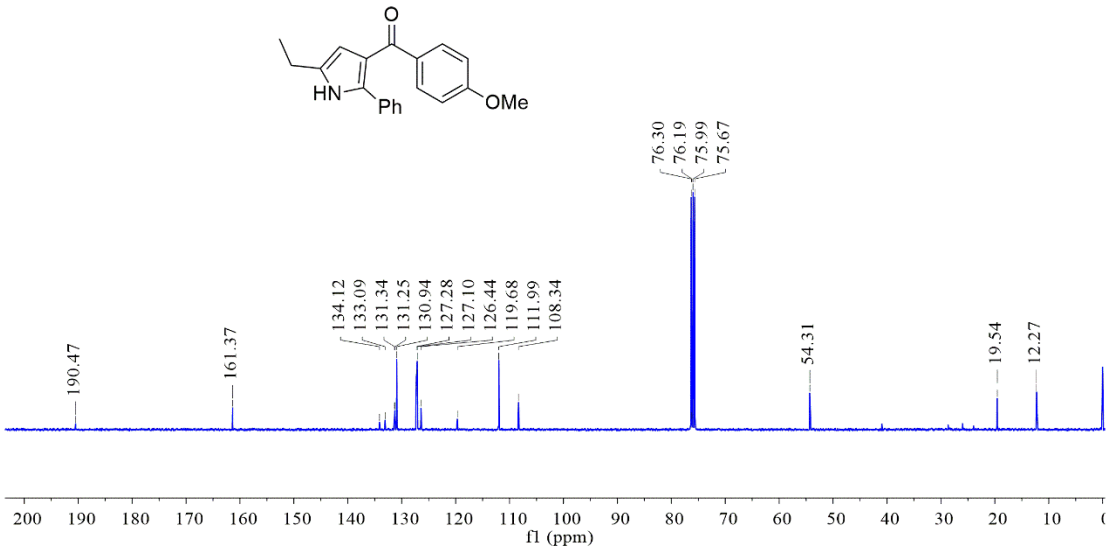
^{13}C-NMR spectrum of 3ch



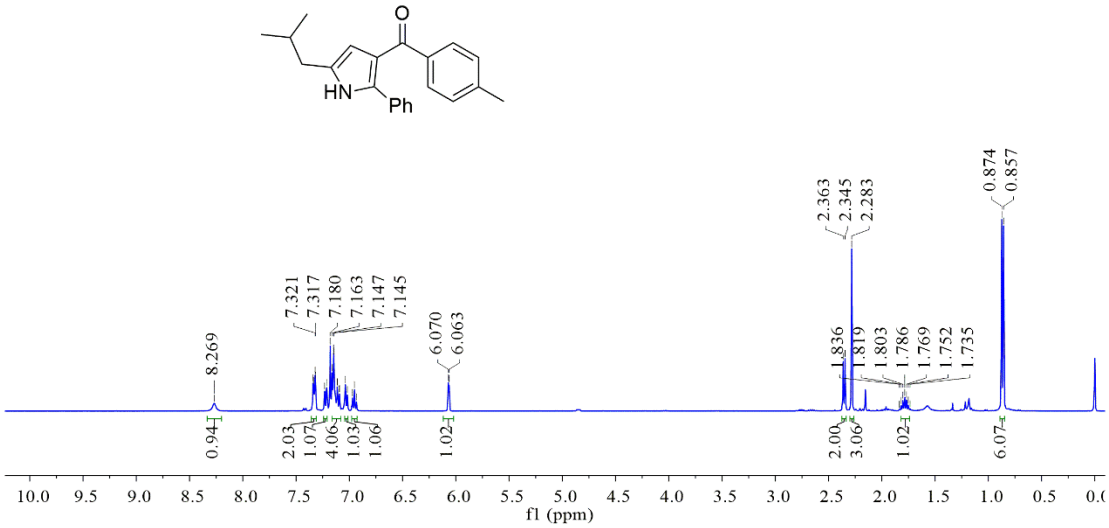
^{1}H- NMR spectrum of 3cj



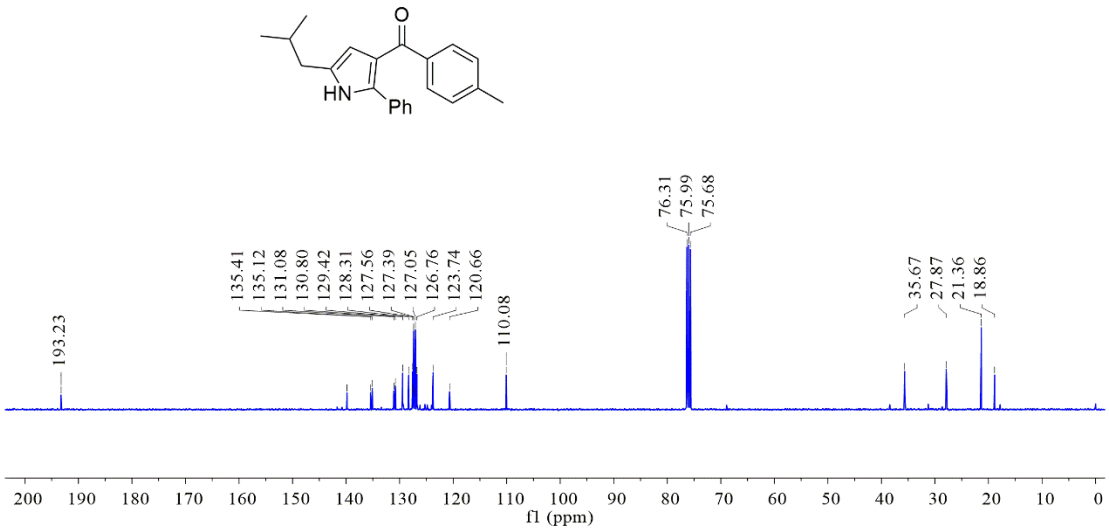
^{13}C-NMR spectrum of 3cj



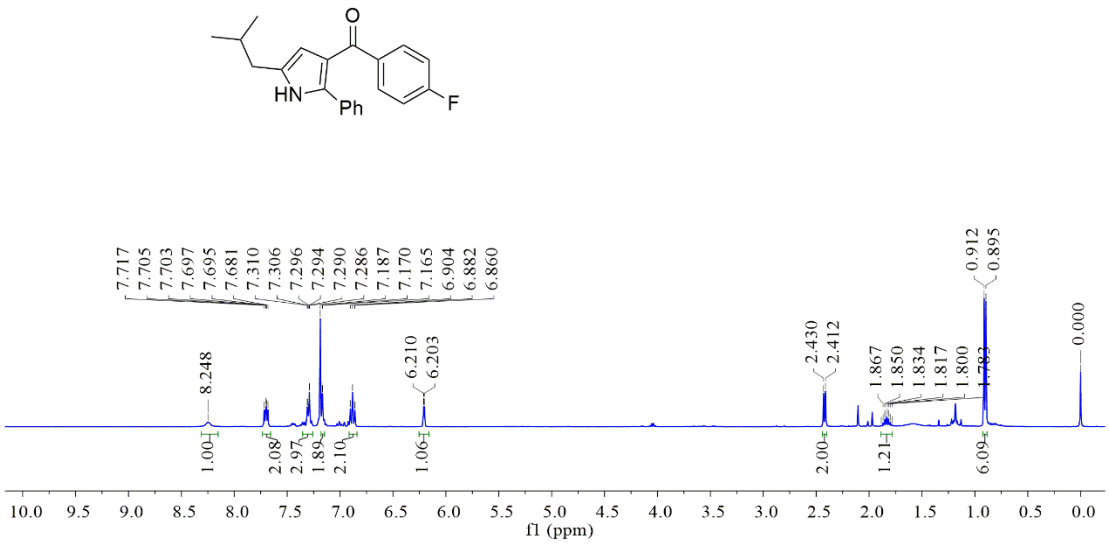
^{1}H- NMR spectrum of 3da



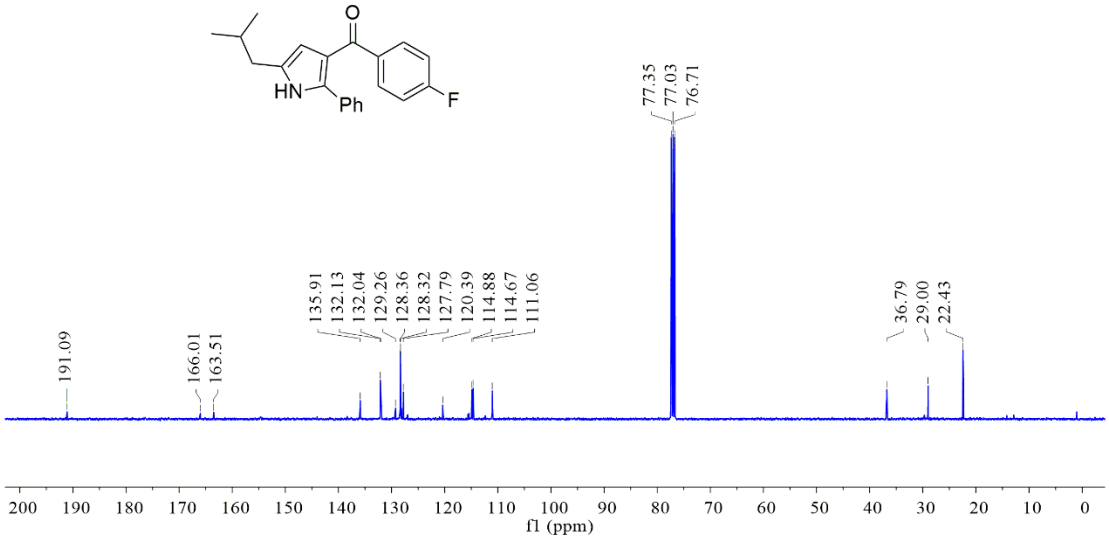
^{13}C-NMR spectrum of 3da



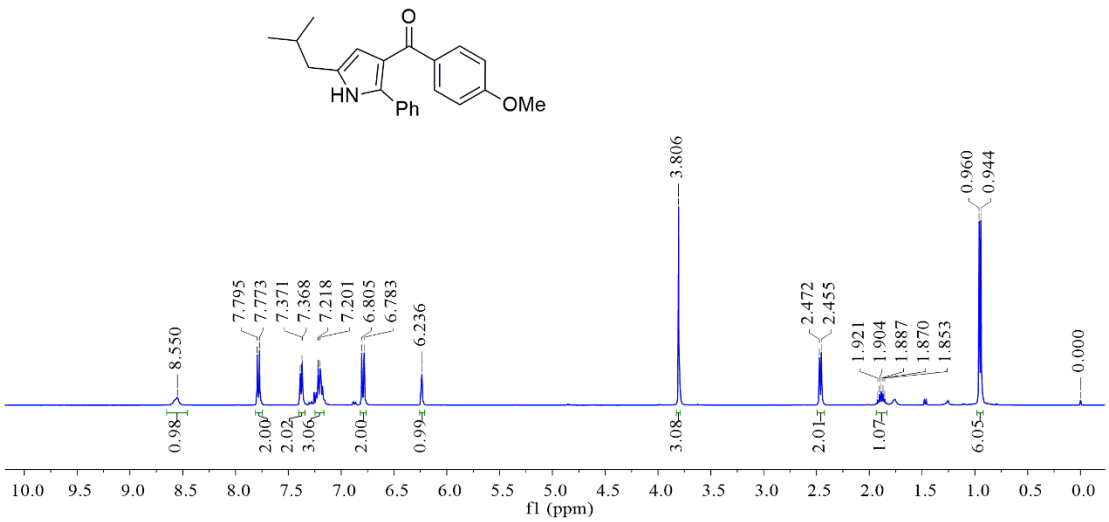
^{1}H- NMR spectrum of 3de



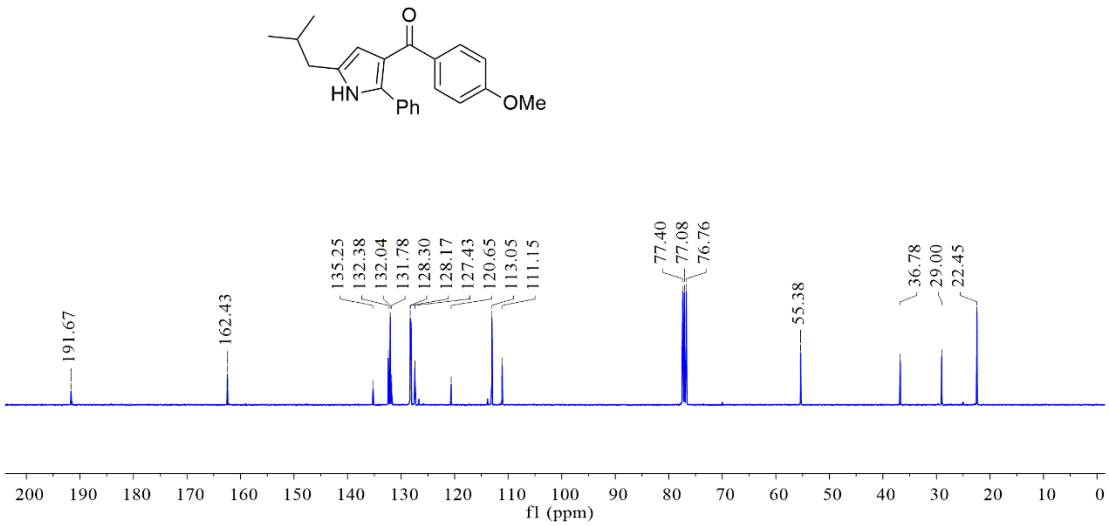
^{13}C-NMR spectrum of 3de



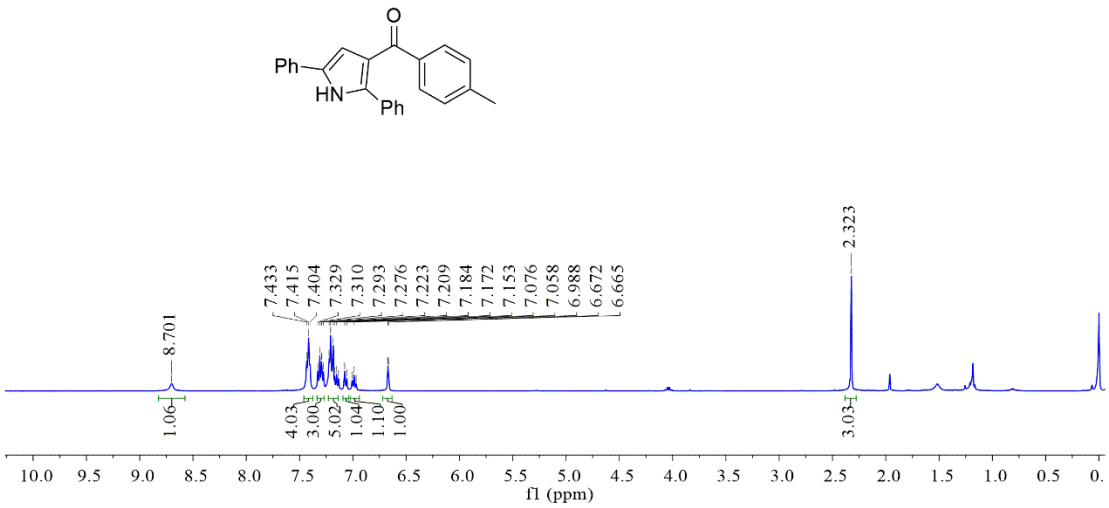
^{1}H- NMR spectrum of 3dj



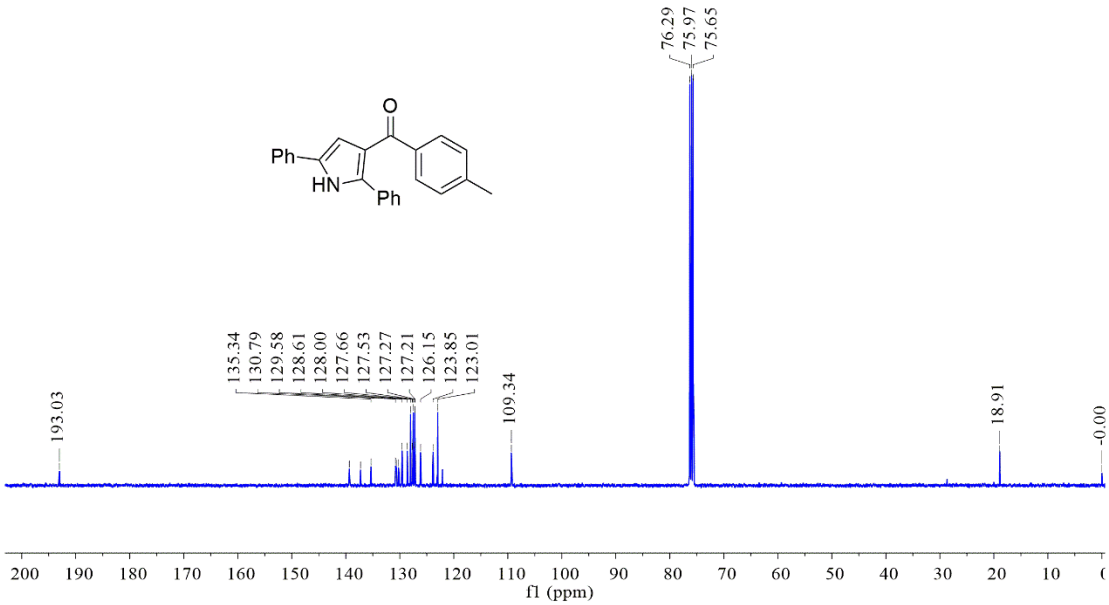
^{13}C-NMR spectrum of 3dj



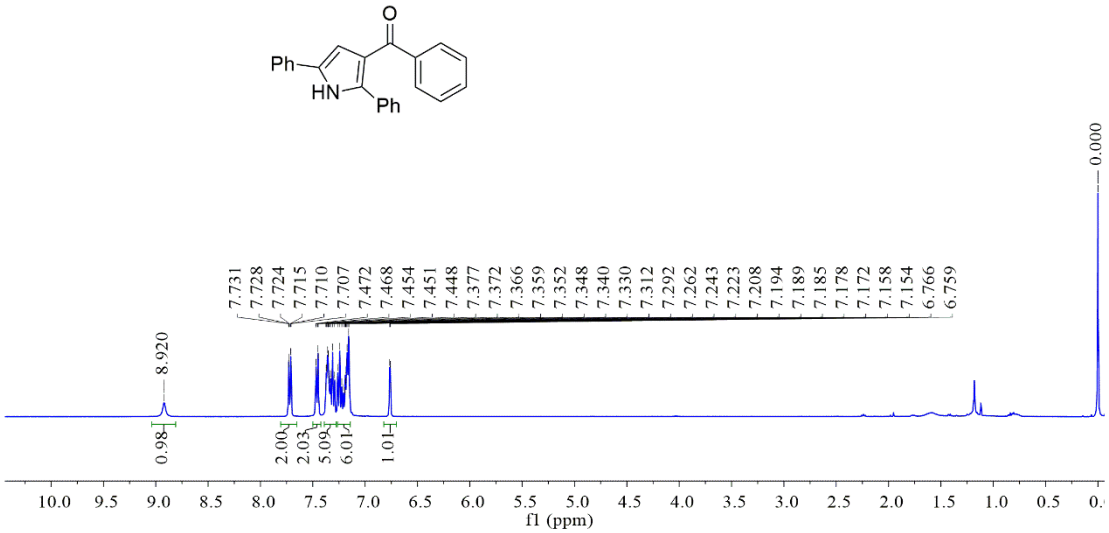
^{1}H- NMR spectrum of 3ea



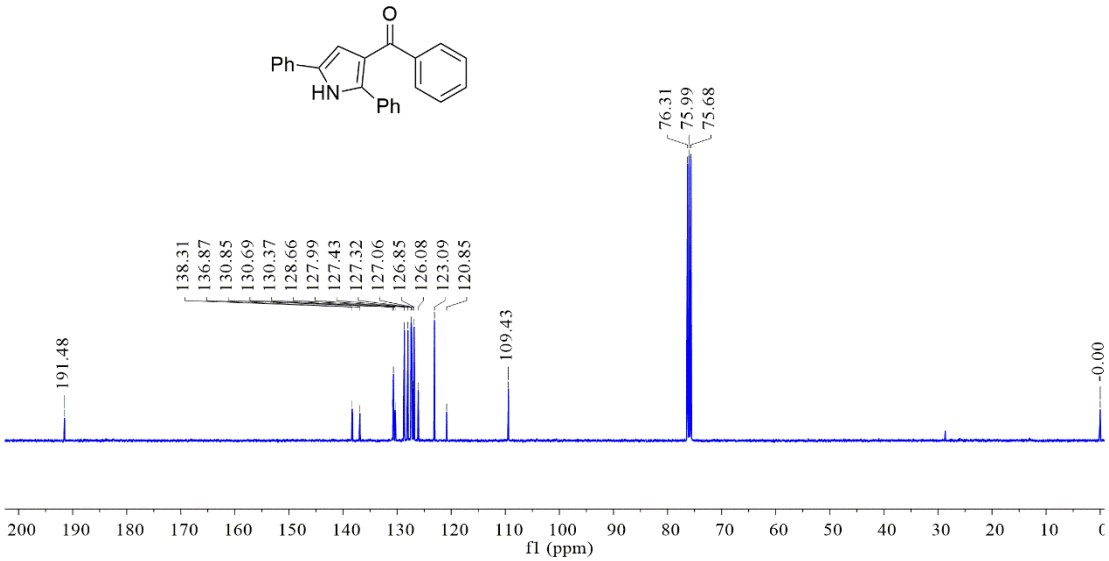
^{13}C-NMR spectrum of 3ea



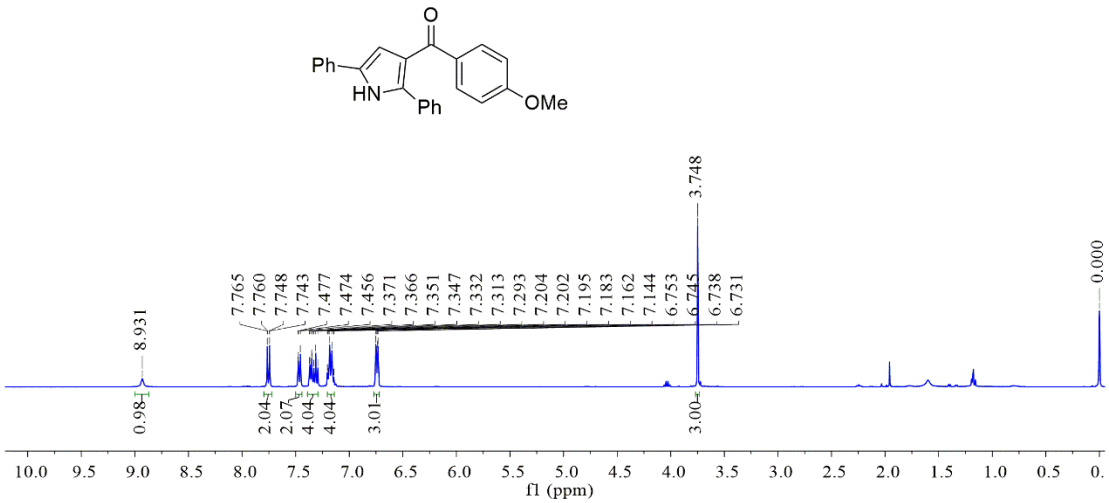
^{1}H- NMR spectrum of 3ed



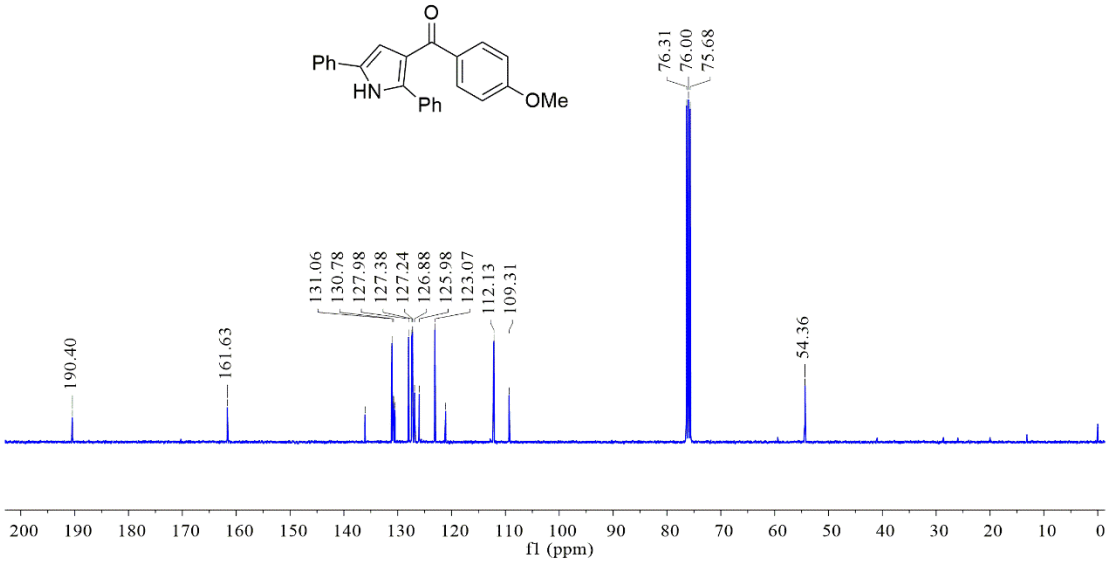
^{13}C-NMR spectrum of 3ed



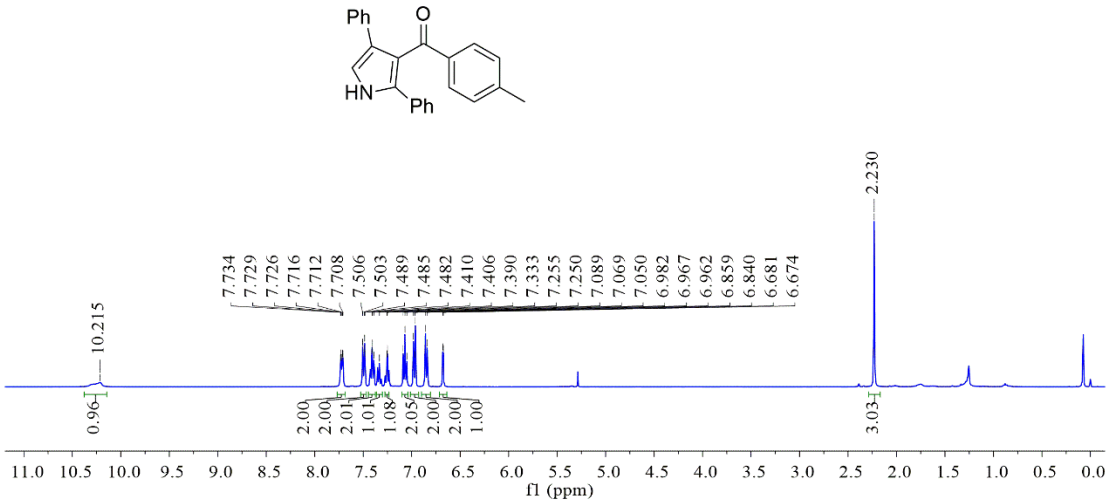
^{1}H- NMR spectrum of 3ej



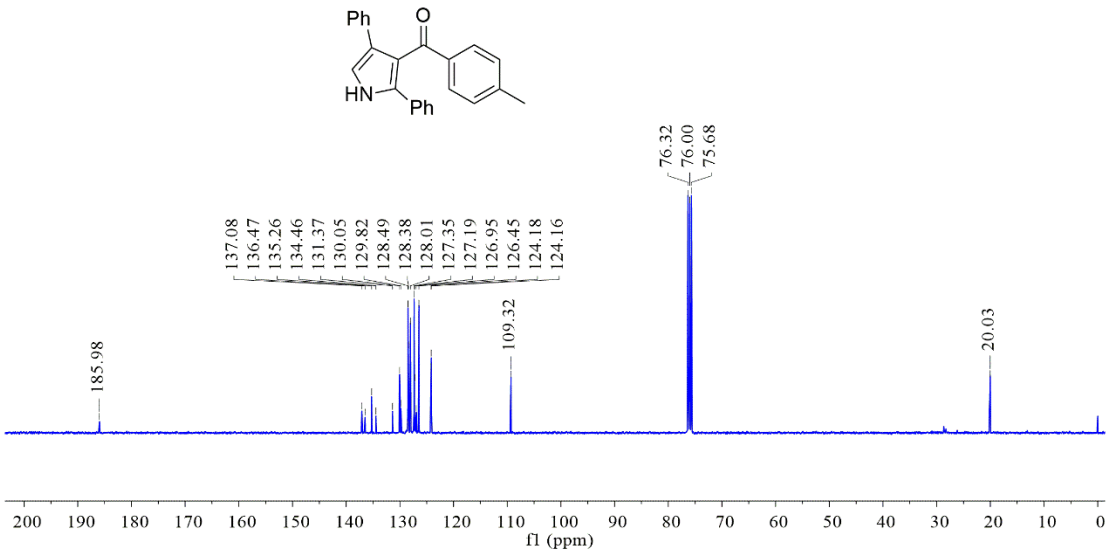
^{13}C-NMR spectrum of 3ej



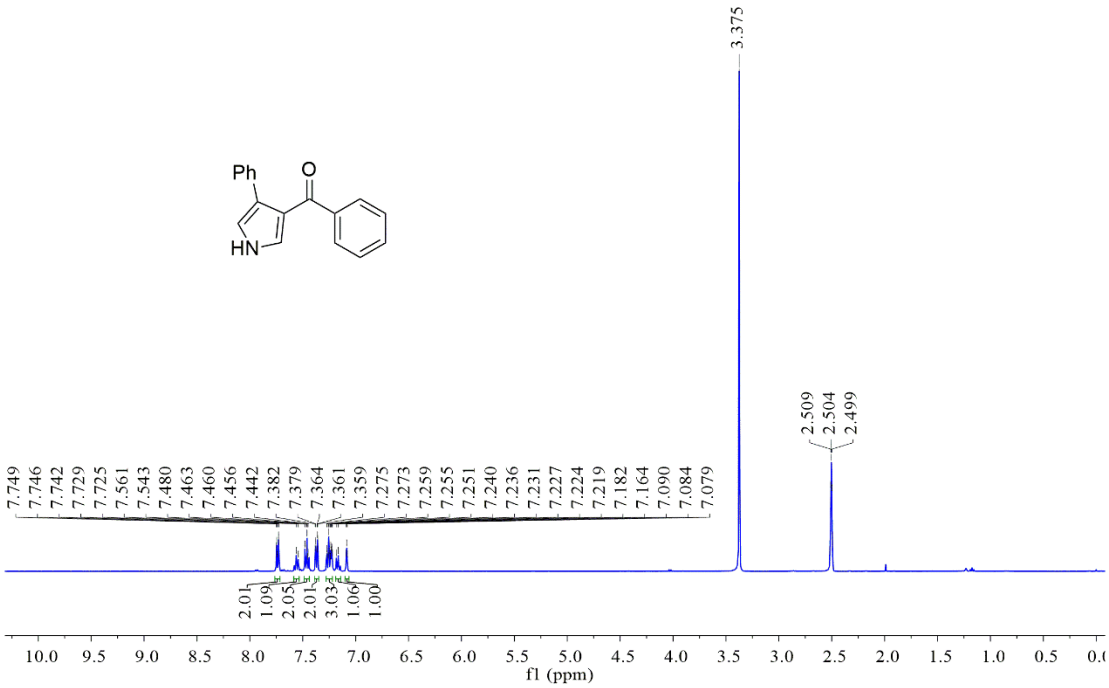
^{1}H- NMR spectrum of 3fa



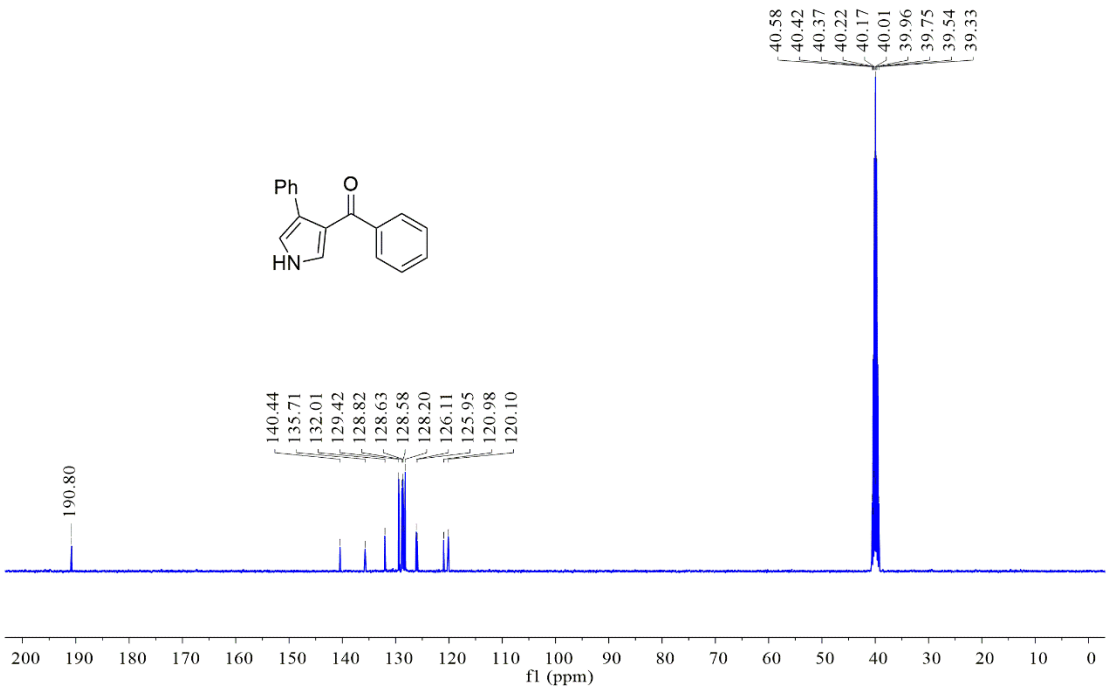
^{13}C-NMR spectrum of 3fa



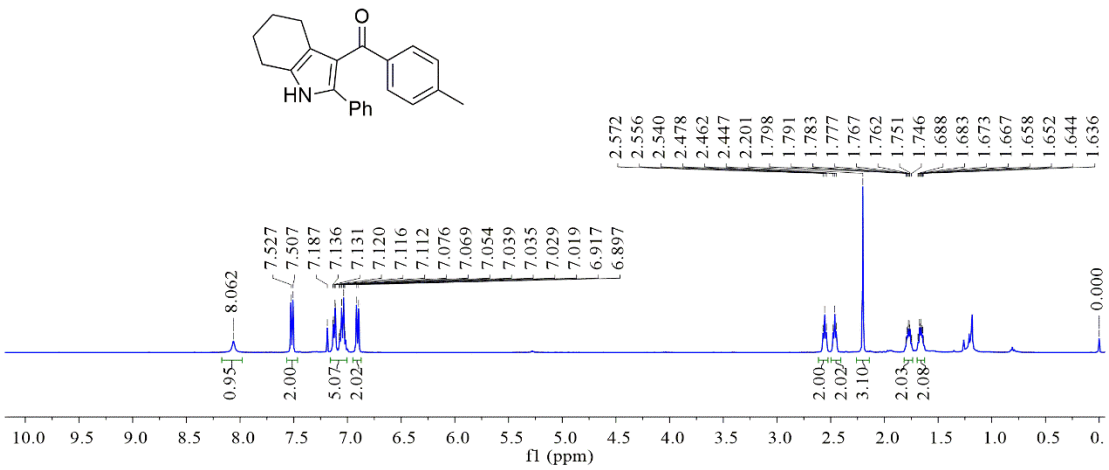
^{1}H- NMR spectrum of 3fw



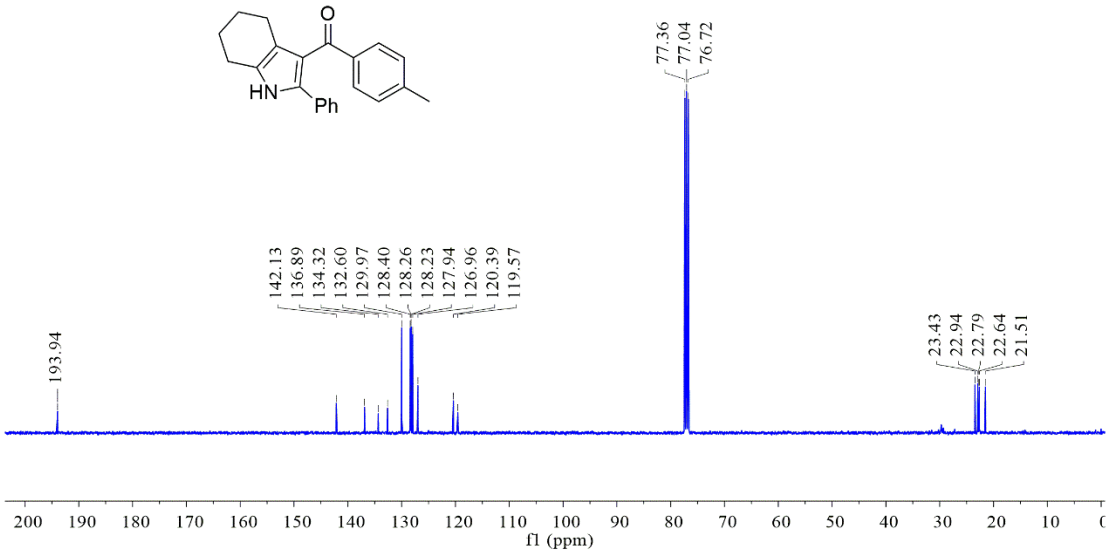
^{13}C-NMR spectrum of 3fw



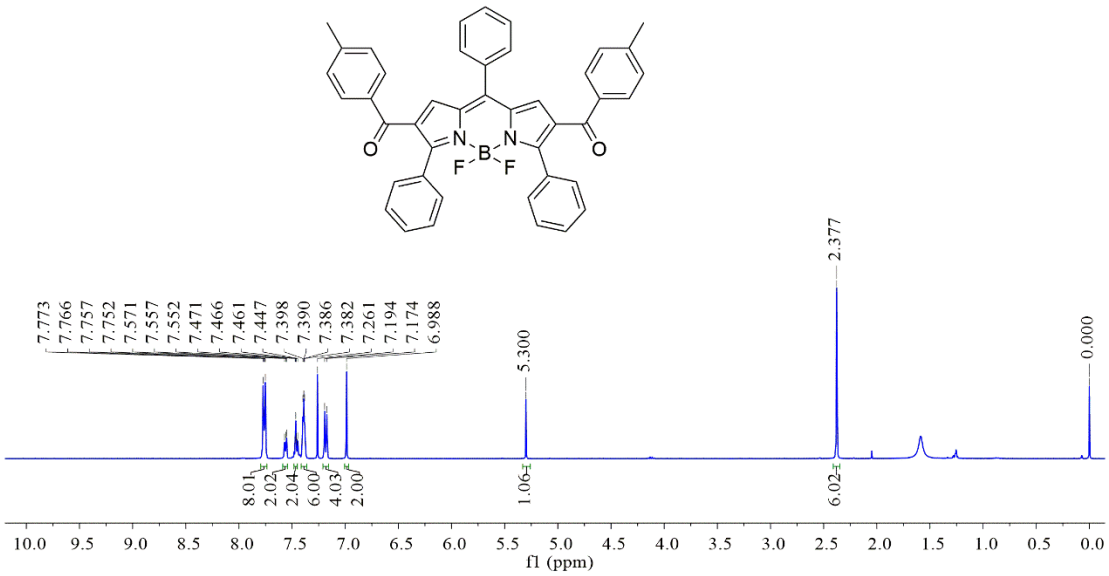
^{1}H- NMR spectrum of 3ga



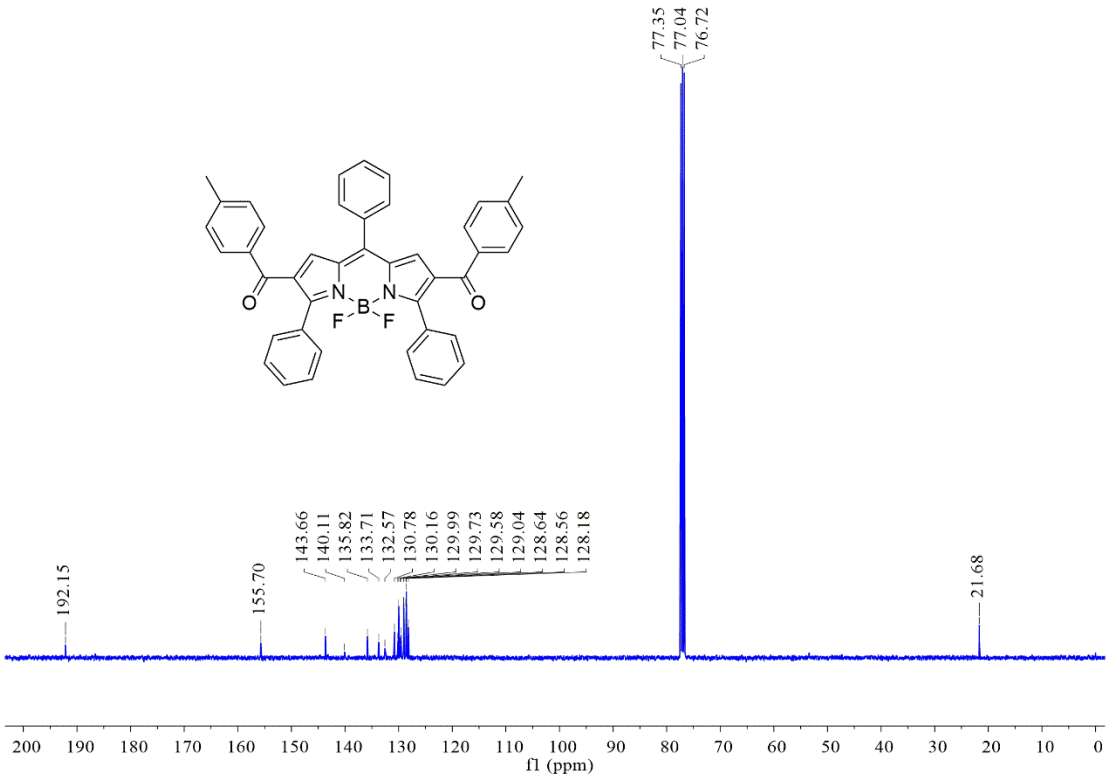
^{13}C-NMR spectrum of 3ga



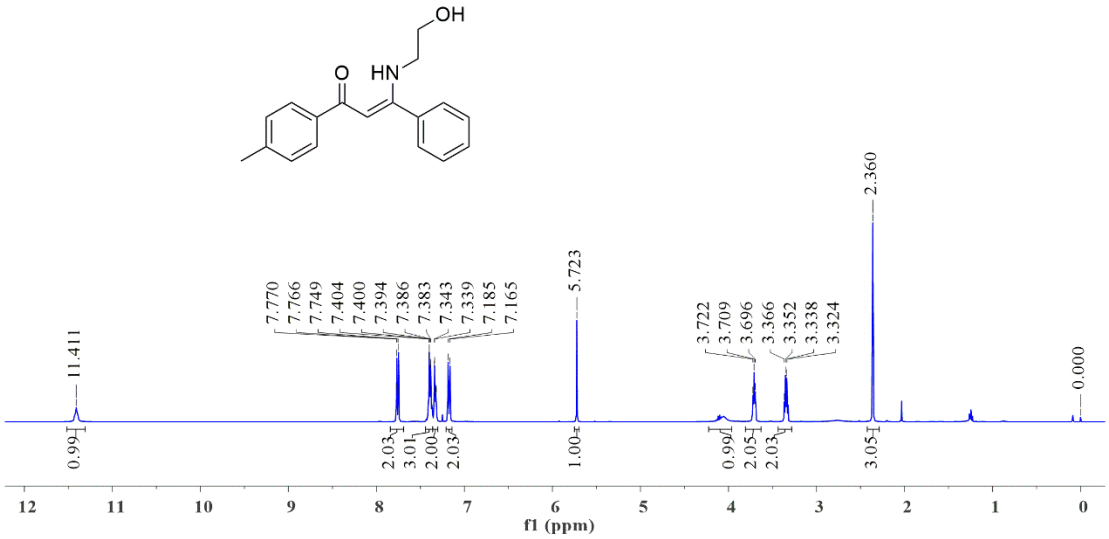
^{1}H- NMR spectrum of 3aaa



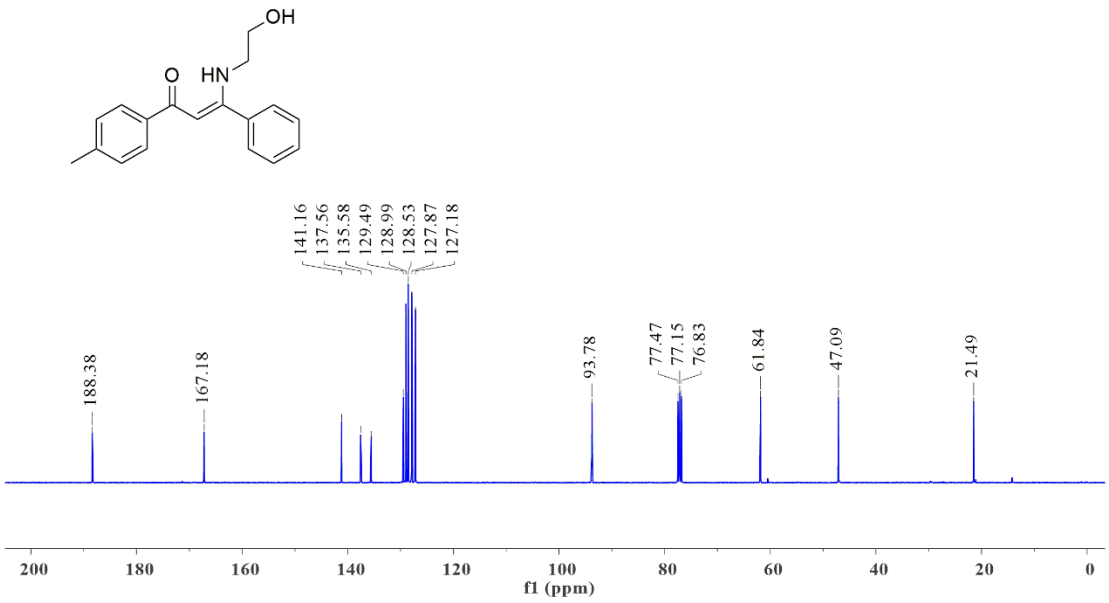
^{13}C-NMR spectrum of 3aaa



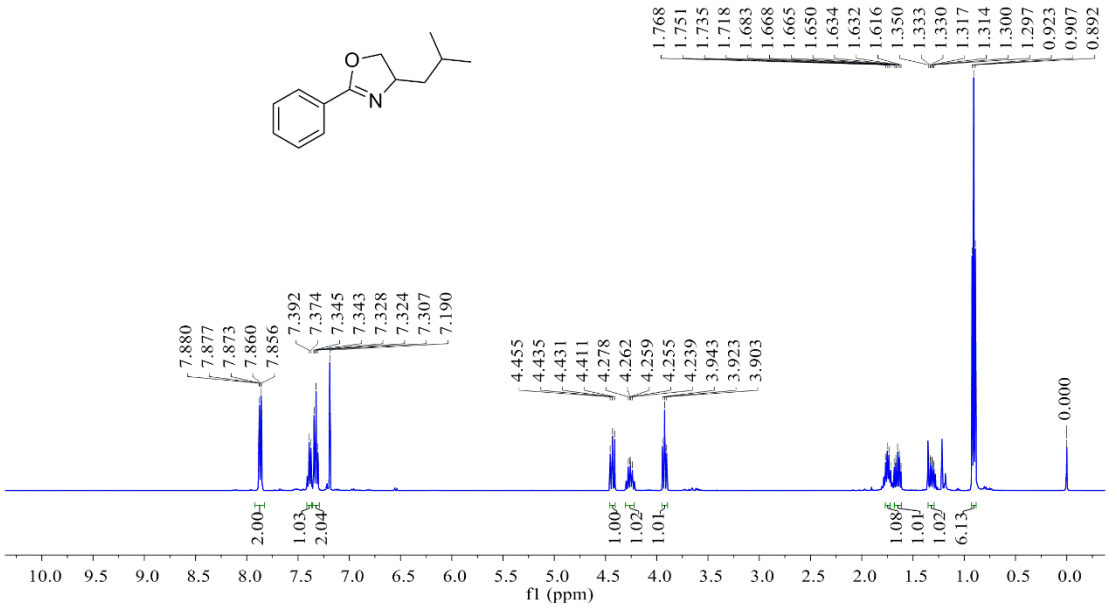
^{1}H- NMR spectrum of 4aa



^{13}C-NMR spectrum of 4aa



^{1}H- NMR spectrum of 9da



^{13}C-NMR spectrum of 9da