Supporting Information

A Regioselective Approach to Tri-substituted Pyrazoles via Palladium-Catalyzed Oxidative Sonogashira-Carbonylation of Arylhydrazines

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General Information：

All reactions were carried out in oven-dried glassware. All Aryl hydrazine hydrochloride and Aryl acetylene were obtained from commercial sources and used as received. All the reactions were monitored by thin-layer chromatography (TLC). Products purification was done using silica gel column chromatography.

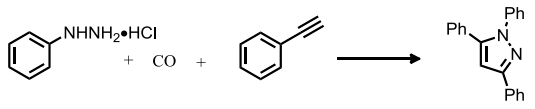
$^{1}H/^{13}C$ NMR spectra were recorded on Bruker Avance 400 MHz and Bruker AMX 400 MHz spectrometer at 400/100 MHz, respectively, in $CDCl_3$ unless otherwise stated, using either TMS or the undeuterated solvent residual signal as the reference. Chemical shifts are given in ppm and are measured relative to $CDCl_3$ or DMSO-d_6 as an internal standard. Mass spectra were obtained by the electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. GC yields were obtained with naphthalene as the internal standard. Flash column chromatography purification of compounds was carried out by gradient elution using ethyl acetate (EA) in light petroleum ether (PE).

General experimental procedure:

Aryl hydrazine hydrochloride (0.8 mmol, 4.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol, 5 mol %), PPh_3 (10.5 mg, 0.04 mmol, 20 mol %) and were combined in an oven-dried Schlenk tube equipped with a stir-bar. After the addition of all soild reagents, a balloon filled with CO and O_2 (the ratio is 3:1) was connected to the Schlenk tube via the side tube and purged 3 times. Then phenylacetylene (22.0 μL, 0.2 mmol, 1.0 equiv), Et_3N (111.1 μL, 0.8 mmol, 4.0 equiv) and DMF (2.0 mL) were added to the tube via a syringe. The Schlenk tube was heated at 100 °C for 8 h. After the reaction was completion, the contents were cooled to room temperature and then the balloon gas was released carefully. The reaction was quenched by water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleum ether/ ethyl acetate.

Optimization of Reaction Conditions

Table S1. Optimization of reaction temperature

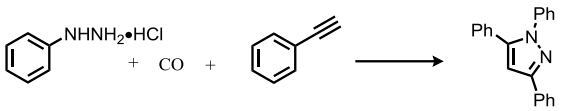


1a **2a** **3a**

Entry	T [°C]	yield[%][b]
1	40	25
2	60	60
3	80	68
4	100	76

[a] Reaction condition: **1a** (4.0 equiv), **2a** (0.2 mmol), Et_3N (4.0 equiv) in the presence of $Pd(OAc)_2$ (5 mol %), 4 Å molecular sieve (50 mg), and PPh_3 (20 mol %) in DMF (2.0 mL) for 8 h, with an balloon (CO/O_2 = 3:1); [b] GC yield with naphthalene as the internal standard.

Table S2. Optimization of reaction time

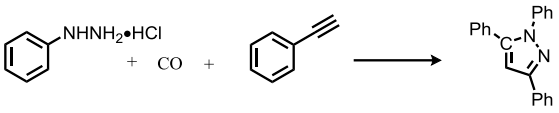


1a **2a** **3a**

Entry	Time [h]	yield[%][b]
1	4	64
2	6	63
3	8	79
4	10	65
5	12	70
6	16	68
7	20	65
8	24	63

[a] Reaction condition: **1a** (4.0 equiv), **2a** (0.2 mmol), Et_3N (4.0 equiv) in the presence of $Pd(OAc)_2$ (5 mol %), 4 Å molecular sieve (50 mg), and PPh_3 (20 mol %) in DMF (2.0 mL) at 100 °C, with an balloon (CO/O_2 = 3:1); [b] GC yield with naphthalene as the internal standard.

Table S3. Screening of transition-metal-catalyst

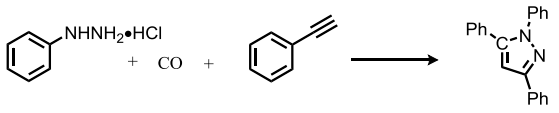


1a **2a** **3a**

Entry	Cat [mol %]	yield[%][b]
1	NiCl	ND
2	CuCl	ND
3	$CuCl_2$	ND
4	$FeCl_2$	ND
5	$FeCl_3$	ND
6	$Co(acac)_2$	ND
4[c]	$Pd(OAc)_2$	56
5	$Pd(OAc)_2$	81
6[d]	$Pd(OAc)_2$	78

[a] Reaction condition: **1a** (4.0 equiv), **2a** (0.2 mmol), Et_3N (4.0 equiv) in the presence of cat (5 mol %), 4 A molecular sieve (50 mg), and PPh_3 (20 mol %) in DMF (2.0 mL) at 100 °C for 8 h, with an balloon (CO/O_2 = 3:1); [b] GC yield with naphthalene as the internal standard; [c] $Pd(OAc)_2$ (3 mol %); [d] $Pd(OAc)_2$ (10 mol %).

Table S4. Screening of solvent

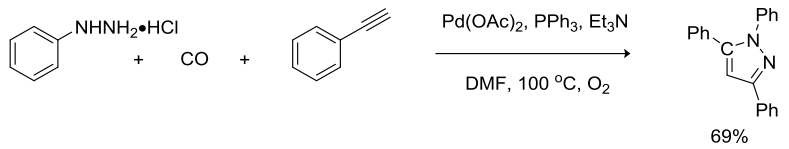


1a **2a** **3a**

Entry	Solvent	yield[%][b]
1	PhMe	2
2	DCM	0
3	dioxane	15
4	NMP	24
5	$PhCF_3$	4
6	MeCN	ND
7	DMSO	43
8	EtOH	6
9	THF	trace
10	DMF	83

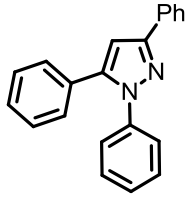
[a] Reaction condition: **1a** (4.0 equiv), **2a** (0.2 mmol), Et_3N (4.0 equiv) in the presence of $Pd(OAc)_2$ (5 mol %), 4 Å molecular sieve (50 mg), and PPh_3 (20 mol %) in solvent (2.0 mL) at 100 °C for 8 h, with an balloon (CO/O_2 = 3:1); [b[GC yield with naphthalene as the internal standard.

Large Scale Experiment



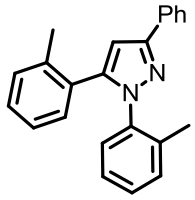
Aryl hydrazine hydrochloride (20 mmol, 2.89 g), $Pd(OAc)_2$ (0.25 mmol, 56.0 mg), 4 Å molecular sieve (600 mg) and PPh_3 (1 mmol, 262.5 mg) were combined in an oven-dried Schlenk tube equipped with a stir-bar. After the addition of all soild reagents, a balloon filled with CO and O_2 (the ratio is 3:1) was connected to the Schlenk tube via the side tube and purged 3 times. Then Et_3N (20 mmol, 2.78 mL) in 6 mL of DMF were added to the tube via a syringe. The Schlenk tube was heated at 100 °C. A solution of phenylacetylene (0.55 mL, 5.0 mmol) in 5 ml of DMF was added slowly to the flask over 4 h by using a syringe pump. After addition of phenylacetylene/DMF solution, the reaction mixture was allowed to stir at 100 °C for another 12 h and then cooled to room temperature. The reaction was quenched by water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with petroleum ether/ ethyl acetate.

Characterization of products:



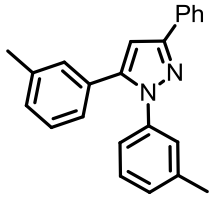
1,3,5-Triphenyl-1H-pyrazole (3aa)[1]

Yellow solid, 46.2 mg (78%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37-7.26 (m, 11H), 6.82 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.0, 144.4, 140.2, 133.1, 130.6, 128.9, 128.8, 128.7, 128.5, 128.3, 128.0, 127.4, 125.8, 125.3, 105.2.



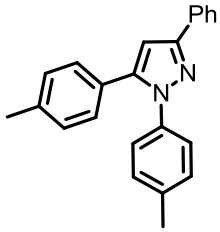
3-Phenyl-1,5-di-o-tolyl-1H-pyrazole (3ba)

Yellow liquid, 54.4 mg (84%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.21-7.15 (m, 4H), 7.12-7.08 (m, 2H), 7.08-7.04 (m, 2H), 6.74 (s, 1H), 2.24 (s, 3H), 2.17 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.3, 144.6, 136.9, 135.2, 133.4, 131.1, 130.6, 130.4, 130.2, 128.7, 128.4, 127.9, 127.8, 126.2, 125.8, 125.5, 104.9, 20.3, 18.1; **IR (KBr)** $\tilde{\nu}$ 1646, 1609, 1556, 1509, 1493, 1458 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{23}H_{21}N_2$ ($M + H^+$) 325.1699, found 325.1695.



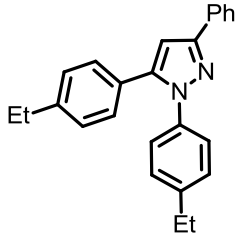
3-Phenyl-1,5-di-m-tolyl-1H-pyrazole (3ca)

Yellow liquid, 46.7 mg (72%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87-7.82 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29-7.22 (m, 2H), 7.12-7.00 (m, 5H), 6.94 (t, *J* = 7.9 Hz, 2H), 6.72 (s, 1H), 2.26 (s, 3H), 2.23 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.8, 144.5, 140.1, 139.0, 138.1, 133.2, 130.6, 129.47, 129.1, 128.6, 128.5, 128.3, 128.2, 127.9, 125.9, 125.9, 125.9, 122.5, 105.0, 21.4, 21.4; **IR (KBr)** $\tilde{\nu}$ 1653, 1595, 1549, 1498, 1479, 1456, cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{23}H_{21}N_2$ ($M + H^+$) 325.1699, found 325.1696.



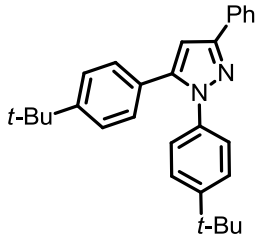
3-Phenyl-1,5-di-p-tolyl-1H-pyrazole (3da)[2]

Yellow solid, 49.9 mg (77%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.18-7.08 (m, 6H), 6.77 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.7, 144.4, 138.2, 137.9, 137.3, 133.2, 129.5, 129.2, 128.6, 128.6, 127.9, 127.8, 125.81, 125.2, 104.7, 21.3, 21.1.



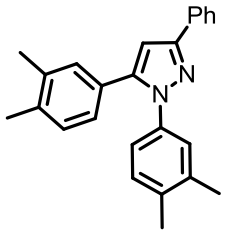
1,5-Bis(4-ethylphenyl)-3-phenyl-1H-pyrazole (3ea)

Yellow solid, 52,8 mg (75%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34-7.25 (m, 3H), 7.21-7.11 (m, 6H), 6.78 (s, 1H), 2.65 (m, 4H), 1.23 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.7, 144.4, 144.4, 143.6, 138.1, 133.3, 128.7, 128.6, 128.3, 128.0, 128.0, 127.9, 125.8, 125.3, 104.7, 28.6, 28.5, 15.5, 15.3; **IR (KBr)** $\tilde{\nu}$ 1647, 1604, 1512, 1492, 1458, 1436 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{25}H_{25}N_2$ ($M + H^+$) 353.2012, found 353.1999.



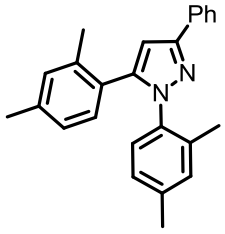
1,5-Bis(4-(tert-butyl)phenyl)-3-phenyl-1H-pyrazole (3fa)

Yellow solid, 62.0 mg (76%), purification by chromatography (petroleum ether/EtOAc = 200:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.46-7.29 (m, 9H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.80 (s, 1H), 1.34 (s, 18H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.7, 151.3, 150.5, 144.3, 137.9, 133.3, 128.6, 128.3, 127.8, 127.7, 125.8, 125.8, 125.4, 124.8, 104.8, 34.7, 34.7, 31.4, 31.3; **IR (KBr)** $\tilde{\nu}$ 1656, 1595, 1549, 1498, 1479, 1456 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{29}H_{33}N_2$ (M + H$^+$) 409.2638, found 409.2637.



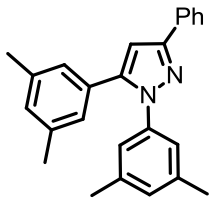
1,5-Bis(3,4-dimethylphenyl)-3-phenyl-1H-pyrazole (3ga)

Yellow solid, 52.1 mg (74%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.37-7.30 (m, 2H), 7.17 (s, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.78 (s, 1H), 2.25 (s, 9H), 2.22 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.5, 144.5, 138.2, 137.4, 136.7, 136.7, 135.9, 133.4, 129.8, 129.7, 129.6, 128.6, 128.2, 127.8, 126.4, 126.1, 125.8, 122.7, 104.5, 19.8, 19.8, 19.6, 19.5; **IR (KBr)** $\tilde{\nu}$ 1686, 1611, 1587, 1548, 1505, 1458 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{25}H_{25}N_2$ (M + H$^+$) 353.2012, found 353.1997.



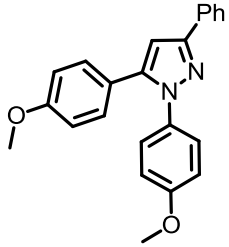
1,5-Bis(2,4-dimethylphenyl)-3-phenyl-1H-pyrazole (3ha)

Yellow liquid, 52.1 mg (74%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.05-6.94 (m, 4H), 6.92-6.84 (m, 2H), 6.69 (s, 1H), 2.27 (s, 6H), 2.20 (s, 3H), 2.10 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.1, 144.7, 138.3, 138.2, 136.8, 136.7, 134.8, 133.5, 131.7, 131.1, 130.5, 128.6, 127.7, 127.6, 127.4, 126.8, 126.2, 125.7, 104.7, 21.2, 21.1, 20.2, 18.0; **IR (KBr)** $\tilde{\nu}$ 1654, 1595, 1549, 1498, 1479, 1456 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{25}H_{25}N_2$ (M + H$^+$) 353.2012, found 353.2010.



1,5-Bis(3,5-dimethylphenyl)-3-phenyl-1H-pyrazole (3ia)

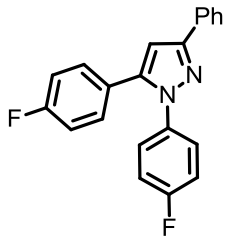
Yellow solid, 51.4 mg (73%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.99 (s, 2H), 6.93 (d, *J* = 6.0 Hz, 2H), 6.90 (s, 2H), 6.77 (s, 1H), 2.26 (s, 6H), 2.24 (s, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.6, 144.6, 140.1, 138.4, 137.8, 133.3, 130.5, 129.8, 129.1, 128.6, 127.8, 126.5, 125.9, 123.1, 104.8, 21.3, 21.2; **IR (KBr)** $\tilde{\nu}$ 1646, 1609, 1556, 1509, 1494, 1458 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{25}H_{25}N_2$ (M + H$^+$) 353.2012, found 353.2009.



1,5-Bis(4-methoxyphenyl)-3-phenyl-1H-pyrazole (3ja)

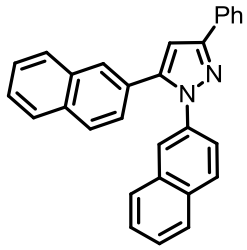
Yellow solid, 48.4 mg (68%), purification by chromatography (petroleum ether/EtOAc = 20:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.93-7.88 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.34-7.24 (m, 3H), 7.21-7.16 (m, 2H), 6.88-6.81 (m, 4H), 6.74 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 159.5, 158.8, 151.5, 144.2, 133.6, 133.3, 123.0, 128.6, 127.8, 126.8, 125.8, 123.1, 114.1,

113.9, 104.1, 55.5, 55.3; **IR (KBr)** $\tilde{\nu}$ 1657, 1612, 1552, 1511, 1492, 1458 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{23}H_{21}N_2O_2$ ($M + H^+$) 357.1598, found 357.1595.



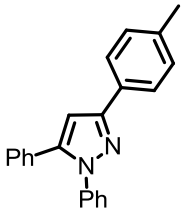
1,5-Bis(4-fluorophenyl)-3-phenyl-1H-pyrazole (3ka)

Yellow solid, 41.8 mg (63%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93-7.87 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37-7.29 (m, 3H), 7.26-7.21 (m, 2H), 7.07-6.99 (m, 4H), 6.78 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.8 (d, J_{C-F} = 247.6 Hz), 161.8 (d, J_{C-F} = 246.4 Hz), 152.1, 143.5, 136.14 (d, J_{C-F} = 3.0 Hz), 132.8, 130.6 (d, J_{C-F} = 8.2 Hz), 128.7, 128.2, 127.0 (d, J_{C-F} = 8.6 Hz), 126.5 (d, J_{C-F} = 3.5 Hz), 125.8, 115.9 (d, J_{C-F} =22.8 Hz), 115.8 (d, J_{C-F} =21.6 Hz), 105.2; **IR (KBr)** $\tilde{\nu}$ 1646, 1609, 1556, 1509, 1494, 1458 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{21}H_{15}F_2N_2$ ($M + H^+$) 333.1198, found 333.1196.



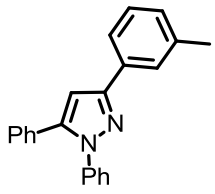
1,5-Di(naphthalen-2-yl)-3-phenyl-1H-pyrazole (3la)

Yellow solid, 56.2 mg (71%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.95 (s, 1H), 7.89 (s, 1H), 7.80-7.70 (m, 5H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.47-7.41 (m, 7H), 7.37-7.32 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.95 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.3, 144.6, 137.8, 133.4, 133.2, 133.1, 132.9, 132.3, 128.8, 128.8, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 126.7, 126.7, 126.6, 126.4, 126.3, 126.0, 123.6, 123.4, 105.9; **IR (KBr)** $\tilde{\nu}$ 1646, 1609, 1556, 1509, 1494, 1458 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{29}H_{21}N_2$ ($M + H^+$) 397.1699, found 397.1693.



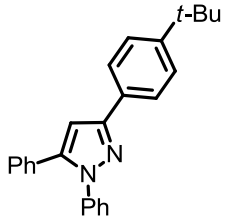
1,5-Diphenyl-3-(p-tolyl)-1H-pyrazole (3ab)[3]

Yellow solid, 38.4 mg (62%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.38-7.23 (m, 12H), 6.79 (s, 1H), 2.38 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.1, 144.3, 140.2, 137.8, 130.7, 130.3, 129.4, 128.9, 128.8, 128.5, 128.3, 127.4, 125.8, 125.3, 105.1, 21.4.



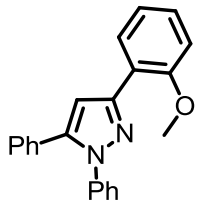
1,5-Diphenyl-3-(m-tolyl)-1H-pyrazole (3ac)[1]

Yellow liquid, 44.6 mg (72%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.39-7.33 (m, 4H), 7.32-7.29 (m, 5H), 7.29-7.26 (m, 2H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 2.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.1, 144.4, 140.2, 138.3, 133.0, 130.6, 129.0, 128.8, 128.8, 128.6, 128.5, 128.3, 127.5, 126.5, 125.4, 123.0, 105.3, 21.5.



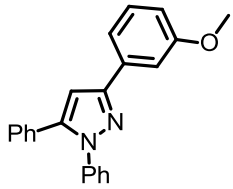
3-(4-(*tert*-Butyl)phenyl)-1,5-diphenyl-1H-pyrazole (3ad)[3]

Yellow solid, 50.7 mg (72%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.39-7.33 (m, 4H), 7.32-7.27 (m, 6H), 6.79 (s, 1H), 1.35 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.0, 151.0, 144.3, 140.3, 130.8, 130.3, 128.9, 128.8, 128.5, 128.2, 127.3, 125.6, 125.6, 125.3, 105.2, 34.7, 31.4.



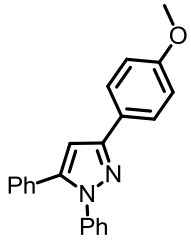
3-(2-Methoxyphenyl)-1,5-diphenyl-1H-pyrazole (3ae)[4]

Yellow solid, 32.6 mg (50%), purification by chromatography (petroleum ether/EtOAc = 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (dd, *J* = 1.6 Hz, 7.6 Hz, 1H), 7.37-7.29 (m, 11H), 7.08 (s, 1H), 7.06-7.00 (m, 2H), 3.94 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 157.0, 149.0, 143.4, 140.3, 130.9, 129.1, 128.9, 128.9, 128.9, 128.4, 128.1, 127.3, 125.3, 121.9, 120.9, 111.2, 109.4, 55.5.



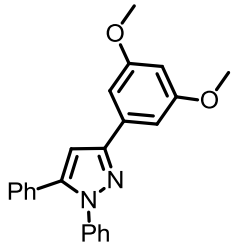
3-(3-Methoxyphenyl)-1,5-diphenyl-1H-pyrazole (3af)[5]

Yellow solid, 46.3 mg (71%), purification by chromatography (petroleum ether/EtOAc = 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51-7.47 (m, 2H), 7.38-7.25 (m, 11H), 6.91-6.87 (m, 1H), 6.81 (s, 1H), 3.87 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.0, 151.9, 144.4, 140.2, 134.5, 130.6, 129.7, 128.9, 128.8, 128.5, 128.3, 127.5, 125.4, 118.5, 114.2, 110.9, 105.4, 55.4.



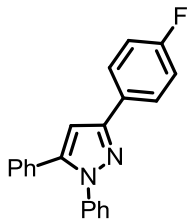
3-(4-Methoxyphenyl)-1,5-diphenyl-1H-pyrazole (3ag)[5]

Yellow solid, 39.1 mg (60%), purification by chromatography (petroleum ether/EtOAc = 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.9 Hz, 2H), 7.37-7.26 (m, 10H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.75 (s, 1H), 3.84 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.6, 151.8, 144.3, 140.2, 130.7, 128.9, 128.8, 128.5, 128.3, 127.3, 127.1, 125.9, 125.3, 114.1, 104.8, 55.3.



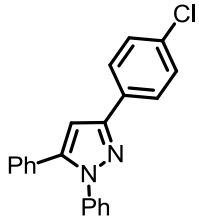
3-(2,5-Dimethoxyphenyl)-1,5-diphenyl-1H-pyrazole (3ah)

Yellow solid, 41.3 mg (58%), purification by chromatography (petroleum ether/EtOAc = 20:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.25 (m, 10H), 7.10 (d, *J* = 2.3 Hz, 2H), 6.80 (s, 1H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.86 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 161.1, 151.9, 144.4, 140.1, 135.0, 130.5, 129.0, 128.8, 128.5, 128.4, 127.5, 125.4, 105.5, 103.8, 100.6, 55.5; **IR (KBr)** $\tilde{\nu}$ 1655, 1596, 1552, 1499, 1485, 1468 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{23}H_{21}N_2O_2$ ($M + H^+$) 357.1598, found 357.1590.



3-(4-Fluorophenyl)-1,5-diphenyl-1H-pyrazole (3ai)[1]

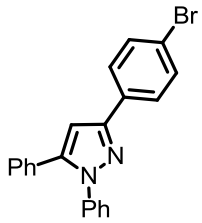
Yellow solid, 39.6 mg (63%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92-7.87 (m, 2H), 7.37-7.34 (m, 4H), 7.33-7.30 (m, 4H), 7.28-7.25 (m, 2H), 7.11 (t, *J* = 8.7 Hz, 2H), 6.77 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.8 (d, $J_{C\text{-}F}$ = 246.6 Hz), 151.1, 144.6, 140.1, 130.5, 129.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.0, 128.7, 128.5, 128.4, 127.5 (d, $J_{C\text{-}F}$= 8.0 Hz), 127.5, 125.3, 115.6 (d, $J_{C\text{-}F}$ = 21.6 Hz), 105.0.



3-(4-Chlorophenyl)-1,5-diphenyl-1H-pyrazole (3aj)[1]

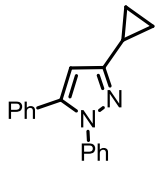
Yellow solid, 40.3 mg (61%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.36-7.34 (m, 4H), 7.32-7.30 (m, 4H), 7.28-7.25 (m, 2H), 6.78 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.9, 144.6, 140.1, 133.7, 131.7,

130.5, 128.9, 128.8, 128.8, 128.5, 128.4, 127.6, 127.1, 125.3, 105.1.



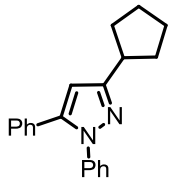
3-(4-Bromophenyl)-1,5-diphenyl-1H-pyrazole (3ak)[1]

Yellow solid, 21.7 mg (29%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.36-7.34 (m, 4H), 7.33-7.30 (m, 4H), 7.29-7.25 (m, 2H), 6.80 (s, 1H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 150.9, 144.6, 140.0, 132.1, 131.8, 130.4, 129.0, 128.8, 128.6, 128.5, 127.6, 127.4, 125.3, 121.9, 105.1.



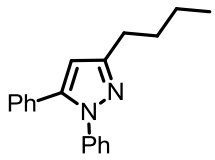
3-Cyclopropyl-1,5-diphenyl-1H-pyrazole (3am)[6]

Yellow liquid, 33.8 mg (65%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.30-7.25 (m, 8H), 7.21-7.18 (m, 2H), 6.15 (s, 1H), 2.09-2.02 (m, 1H), 1.02-0.96 (m, 2H), 0.86-0.80 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 156.0, 143.6, 140.2, 130.8, 128.8, 128.7, 128.4, 128.1, 127.1, 125.2, 104.1, 9.2, 8.1.



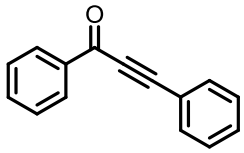
3-Cyclopentyl-1,5-diphenyl-1H-pyrazole (3an)

Yellow liquid, 25.9 mg (45%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.36-7.12 (m, 10H), 6.34 (s, 1H), 3.24-3.15 (m, 1H), 2.17-2.09 (m, 2H), 1.82-1.67 (m, 6H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 158.3, 143.4, 140.3, 131.0, 128.8, 128.7, 128.4, 128.0, 127.0, 125.2, 105.4, 39.2, 33.6, 25.5; **IR (KBr)** $\tilde{\nu}$ 1655, 1585, 1549, 1498, 1479, 1456 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{20}H_{21}N_2$ (M + H$^+$) 289.1699, found 289.1691.



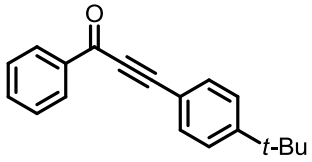
3-Butyl-1,5-diphenyl-1H-pyrazole (3ao)

Yellow liquid, 21.0 mg (38%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.31 – 7.22 (m, 10H), 6.33 (s, 1H), 2.76 – 2.70 (m, 2H), 1.75 – 1.69 (m, 2H), 1.50 – 1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** 154.3, 143.5, 140.2, 130.9, 128.8, 128.7, 128.4, 128.0, 127.0, 125.2, 106.7, 31.9, 28.1, 22.7, 14.0; **IR (KBr)** $\tilde{\nu}$ 1646, 1609, 1556, 1509, 1494, 1459 cm^{-1}; **HRMS (ESI-TOF)** calcd for $C_{19}H_{21}N_2$ (M + H$^+$) 277.1699, found 277.1694.



1,3-Diphenylprop-2-yn-1-one[3]

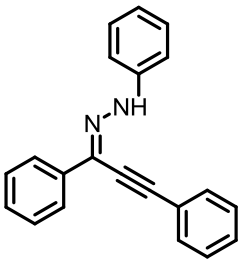
Yellow liquid, (4a), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.24 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.55-7.46 (m, 3H), 7.42 (t, *J* = 7.2 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 178.1, 136.9, 134.2, 133.1, 130.9, 129.6, 128.7, 128.7, 120.1, 93.2, 86.9.



3-(4-(*tert*-Butyl)phenyl)-1-phenylprop-2-yn-1-one[7]

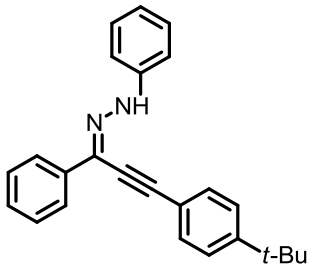
Yellow liquid, (4b), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.24 (d, *J* = 7.2 Hz,, 2H), 7.62 (t, *J* = 7.6 Hz, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* =

8.4 Hz, 2H), 1.34 (s, 9H); **^{13}C (100 MHz, $CDCl_3$)** δ 178.0, 154.6, 137.1, 134.0, 133.0, 129.6, 128.6, 125.8, 117.1, 93.8, 86.8, 35.1, 31.1.



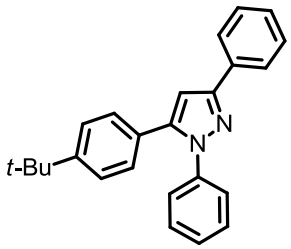
1-(1,3-Diphenylprop-2-yn-1-ylidene)-2-phenylhydrazine (5a)[8]

Yellow solid, purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (s, 1H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.64 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.48-7.38 (m, 5H), 7.32 (t, *J* = 7.8 Hz, 3H), 7.25 (s, 1H), 7.23 (s, 1H), 6.94 (t, *J* = 7.2 Hz, 1H); **^{13}C (100 MHz, $CDCl_3$)** δ 143.6, 135.9, 131.9, 129.6, 129.4, 128.7, 128.4, 128.2, 125.7, 125.5, 121.6, 121.1, 113.6, 103.7, 78.9.



1-(3-(4-(*tert*-Butyl)phenyl)-1-phenylprop-2-yn-1-ylidene)-2-phenylhydrazine (5b)

Yellow solid, purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.73 (s, 1H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 3H), 7.26-7.20 (m, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 1.35 (s, 9H); **^{13}C (100 MHz, $CDCl_3$)** δ 153.2, 143.7, 136.0, 131.7, 129.4, 128.4, 128.2, 125.9, 125.8, 125.6, 121.0, 118.5, 113.5, 104.1, 78.4, 35.0, 31.2. **HRMS (ESI-TOF)** calcd for $C_{25}H_{25}N_2$ (M + H^+) 353.2012, found 353.1997.



5-(4-(*tert*-Butyl)phenyl)-1,3-diphenyl-1H-pyrazole (6a)

Yellow solid, 16.3 mg (48%), purification by chromatography (petroleum ether/EtOAc = 100:1); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.44-7.31 (m, 10H), 7.21 (d, *J* = 8.3 Hz, 2H), 6.80 (s, 1H), 1.32 (s, 9H); **^{13}C (100 MHz, $CDCl_3$)** δ 151.9, 151.4, 144.5, 140.4, 133.2, 132.7, 128.9, 128.6, 128.3, 127.9, 127.6, 127.4, 125.8, 125.4, 105.0, 34.9, 31.3; **HRMS (ESI-TOF)** calcd for $C_{25}H_{25}N_2$ (M + H^+) 353.2012, found 353.1999.

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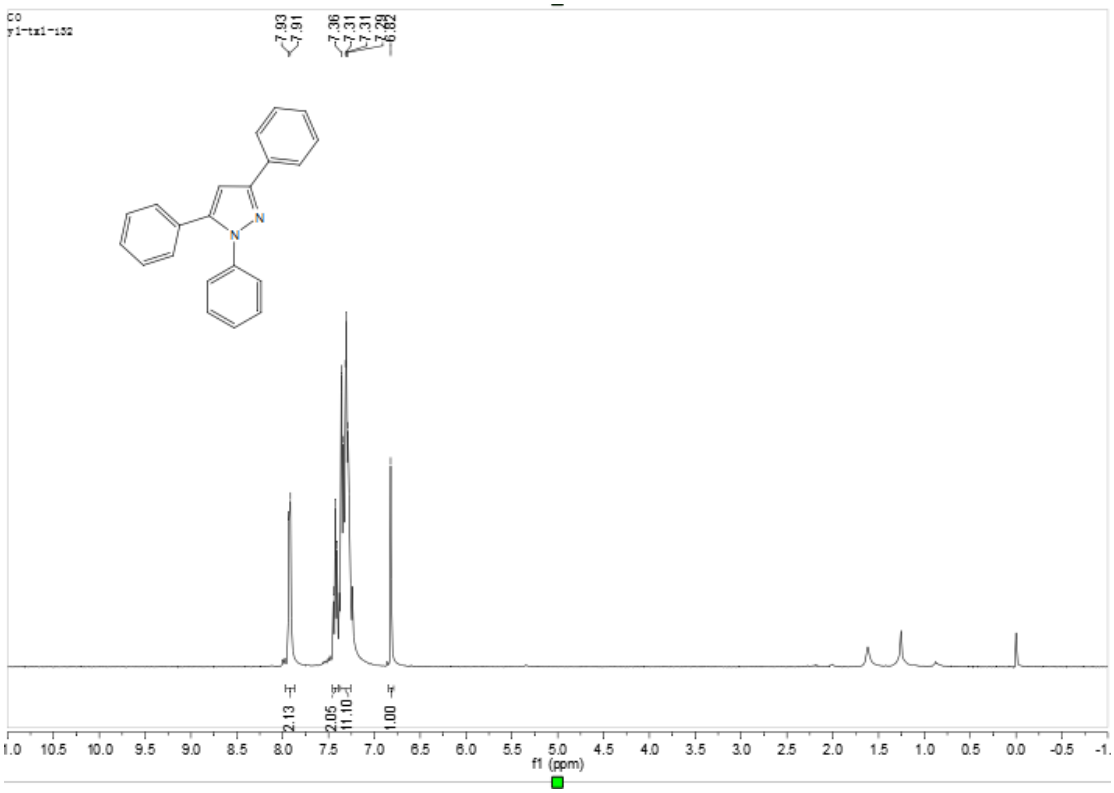
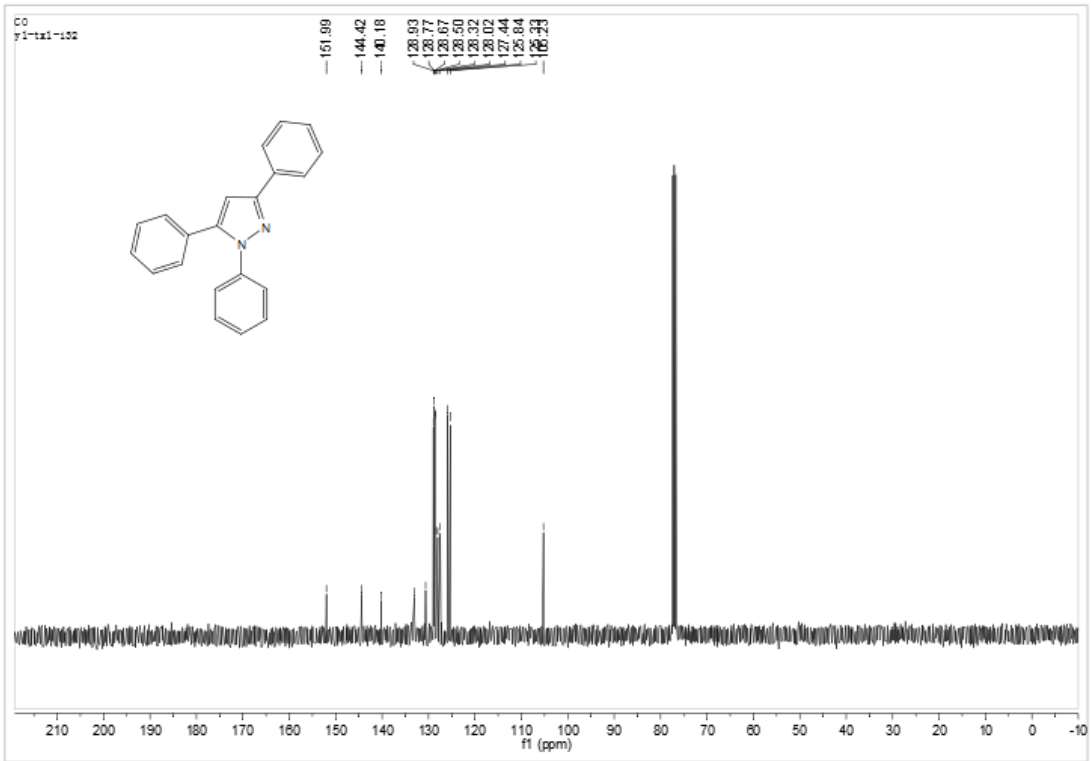
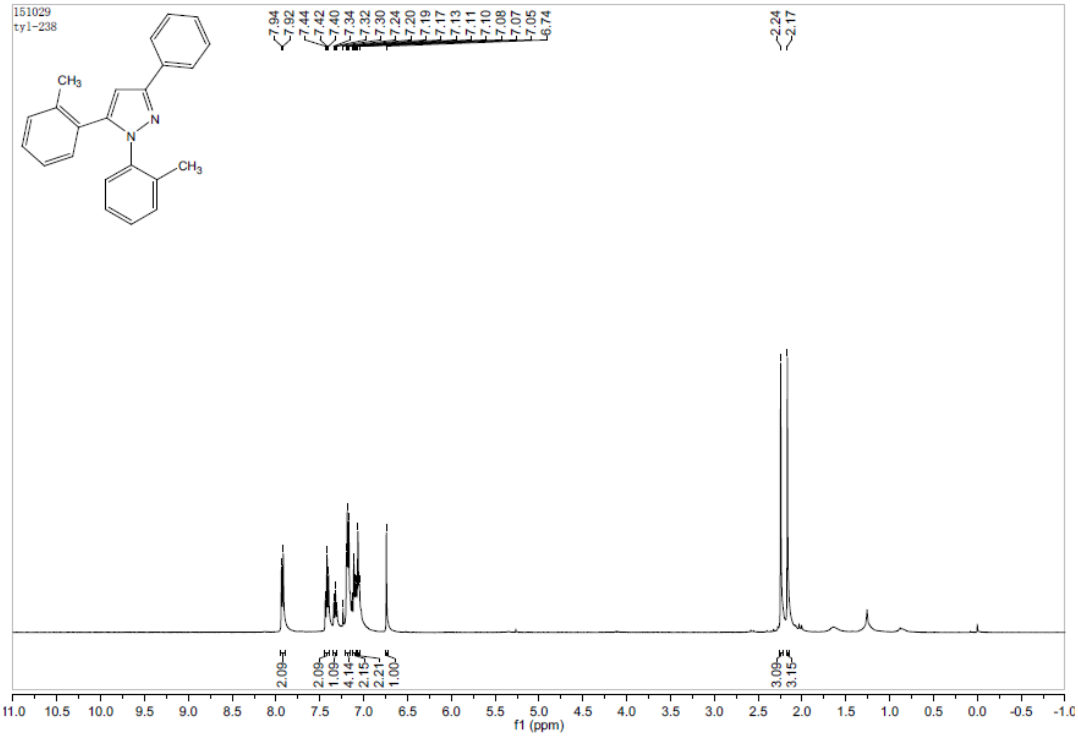
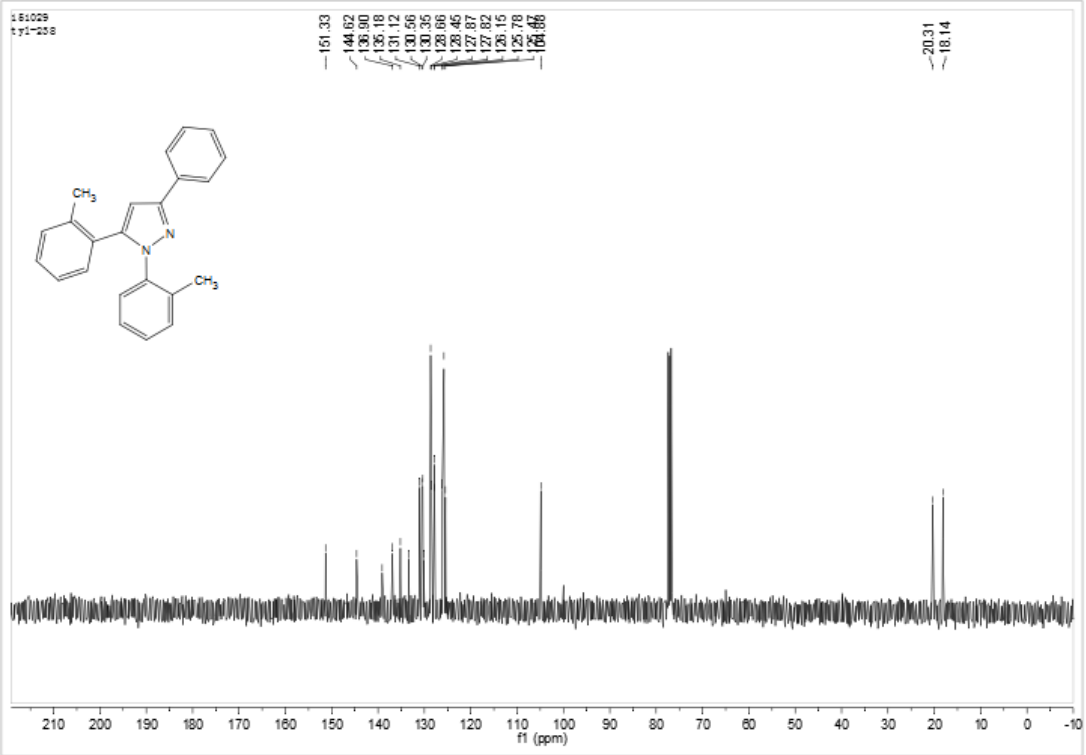
Copies of ^{1}H-NMR & ^{13}C-NMR spectrum



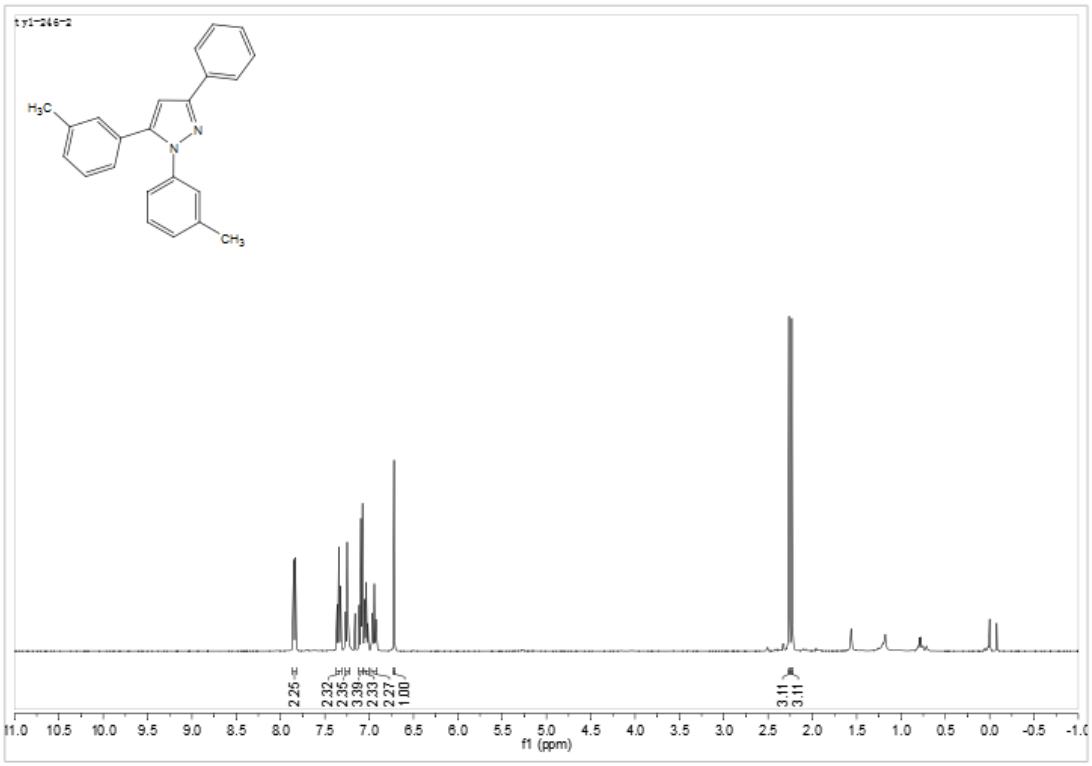


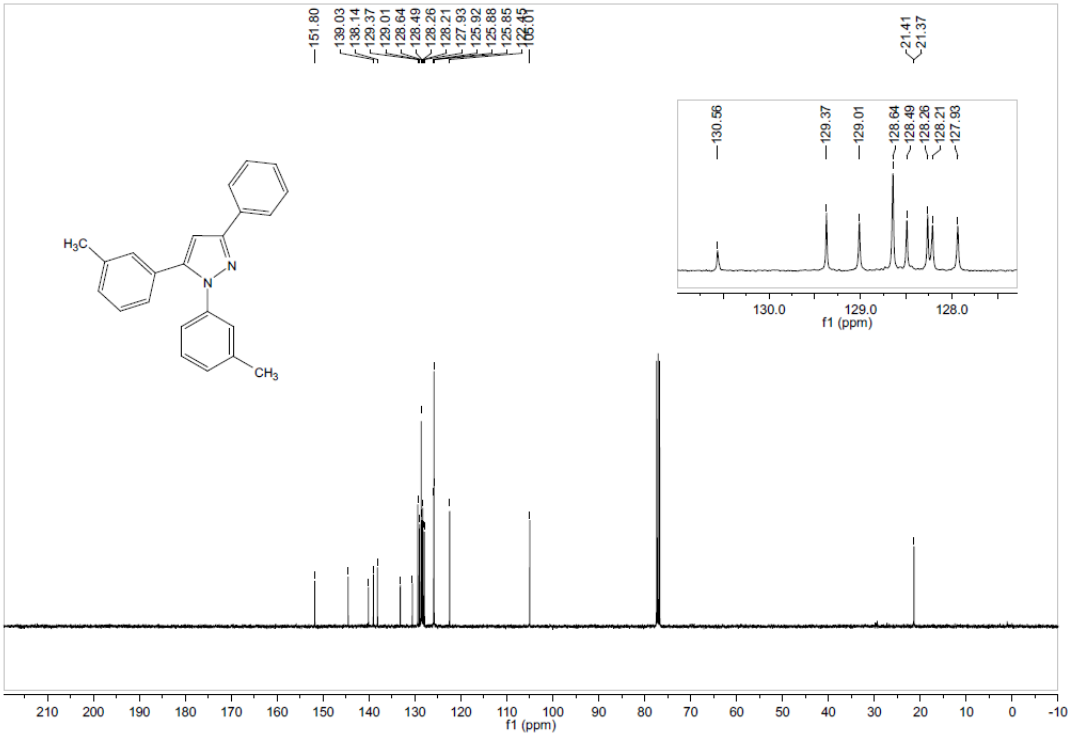
^{1}H NMR and ^{13}C NMR for compound **3aa**



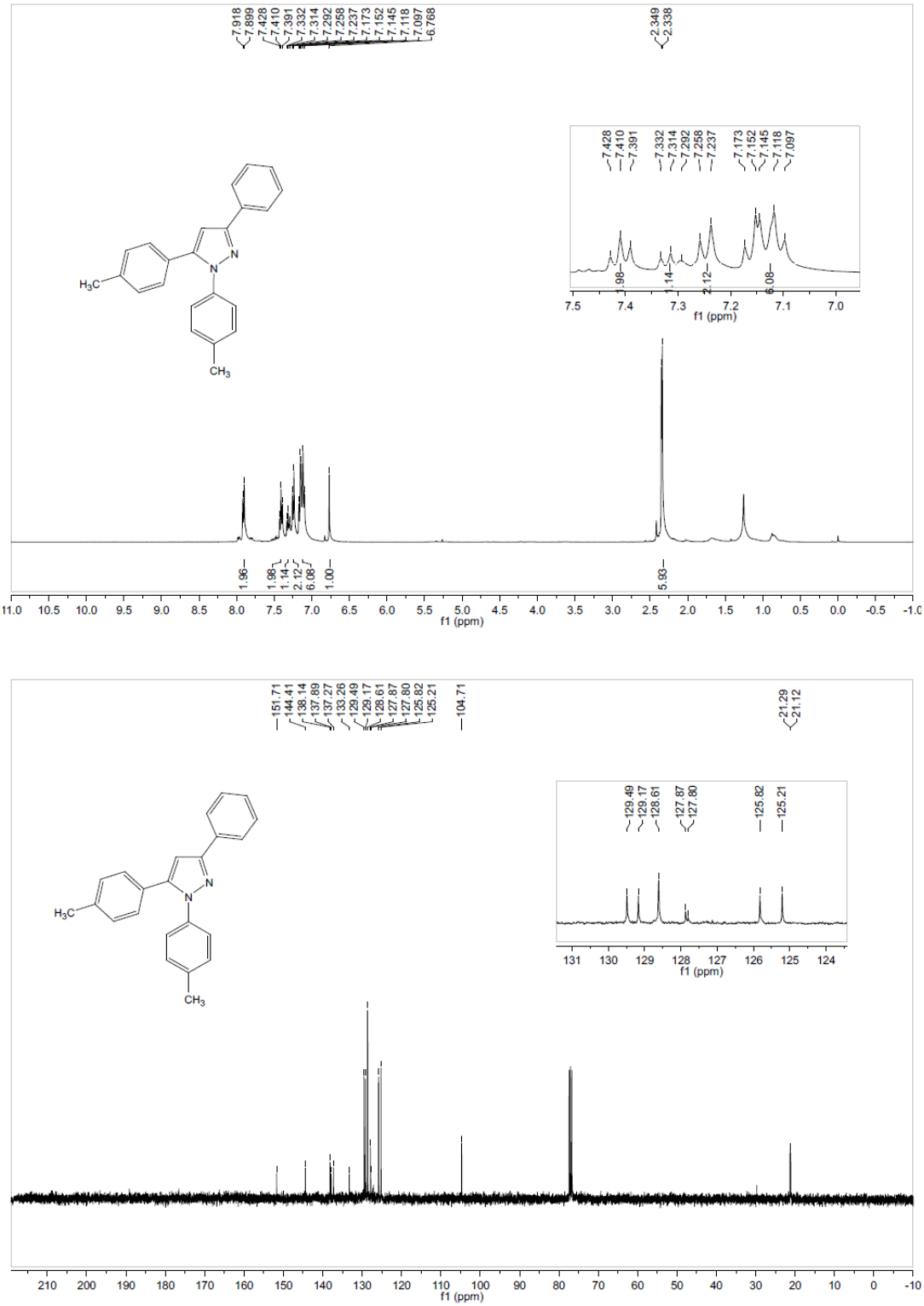


^{1}H NMR and ^{13}C NMR for compound **3ba**

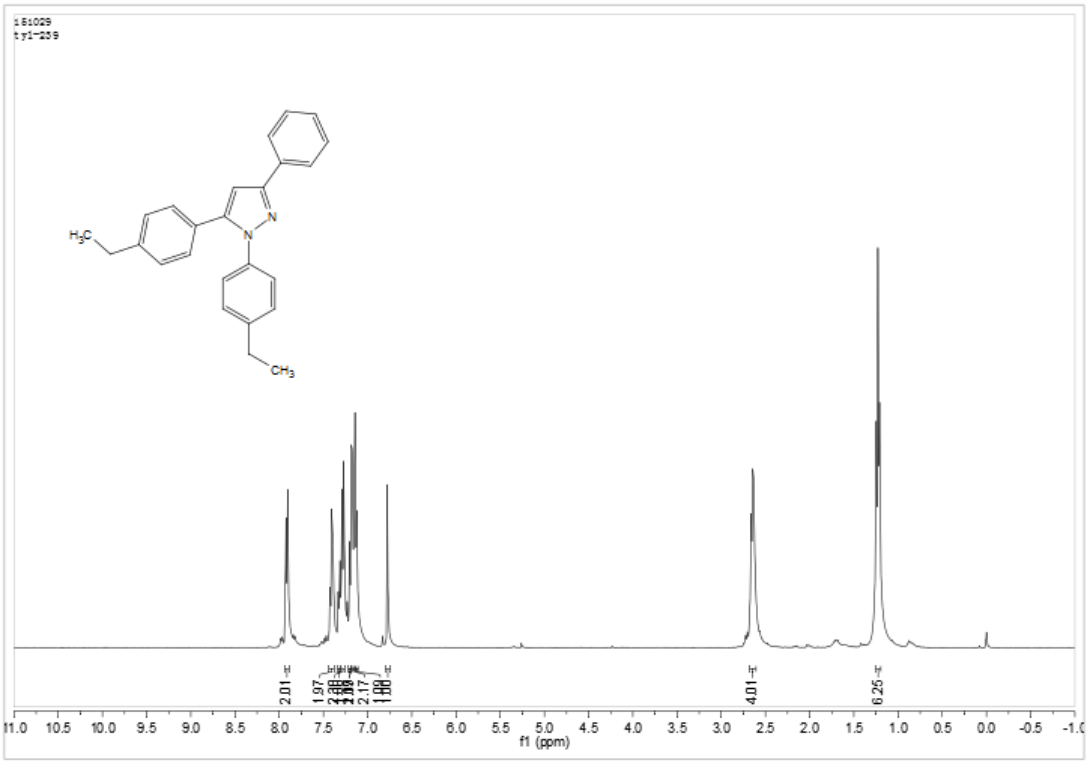


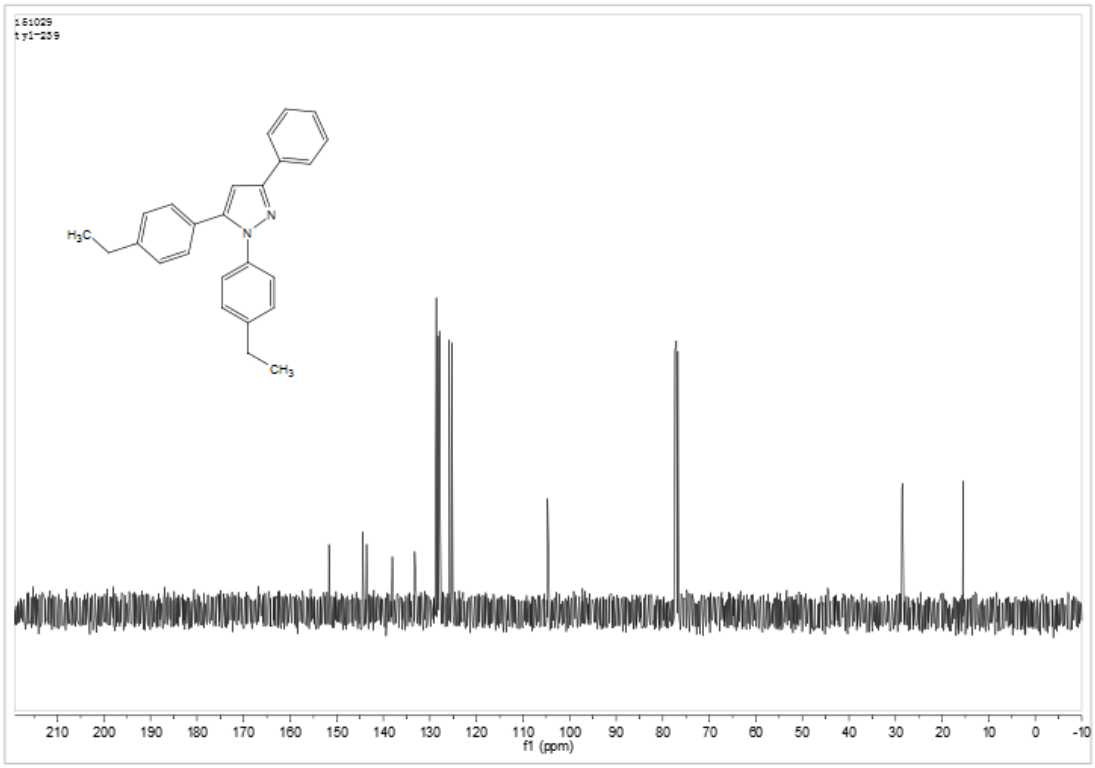


^{1}H NMR and ^{13}C NMR for compound **3ca**

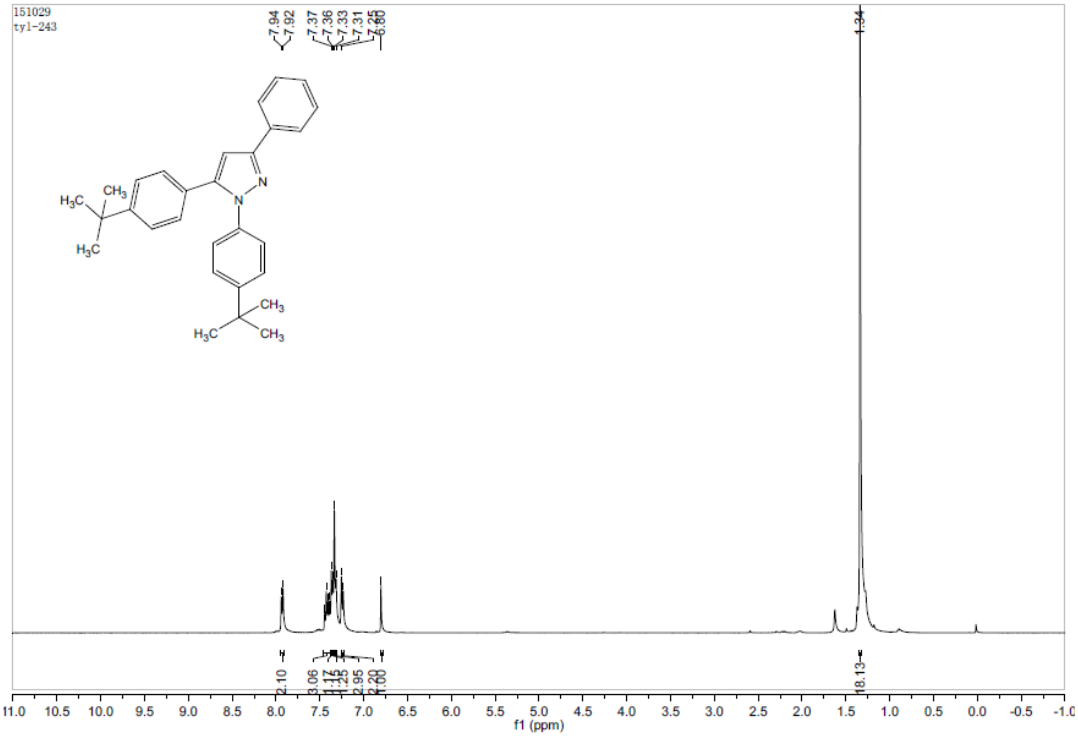


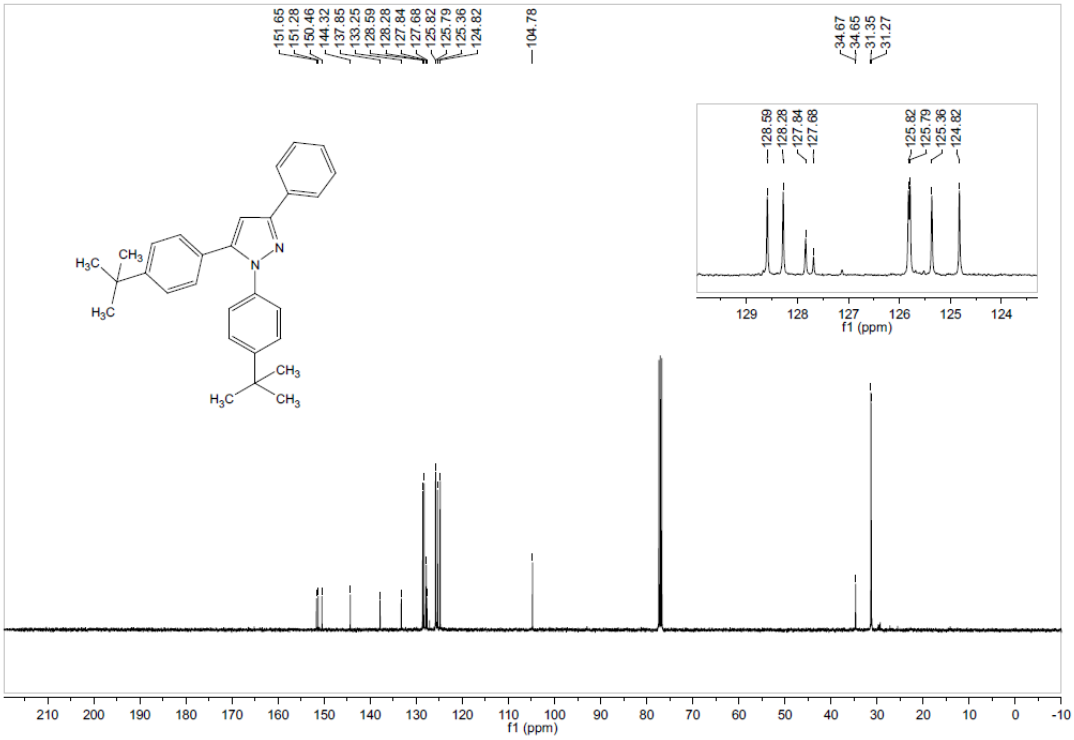
^{1}H NMR and ^{13}C NMR for compound **3da**



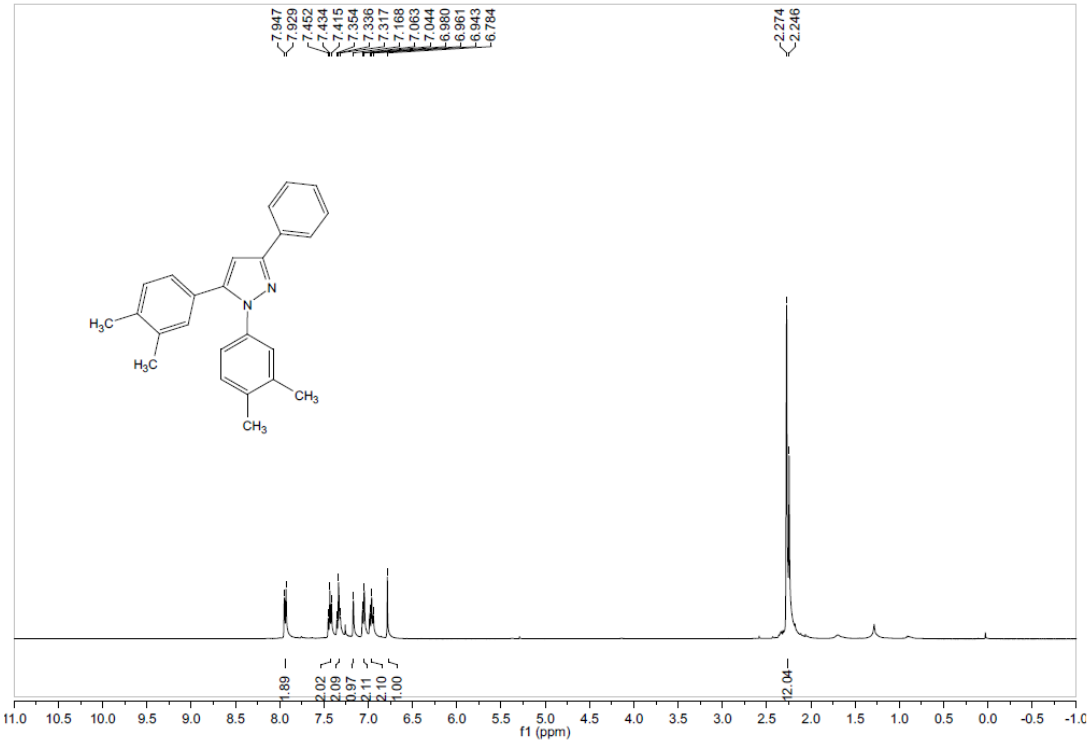


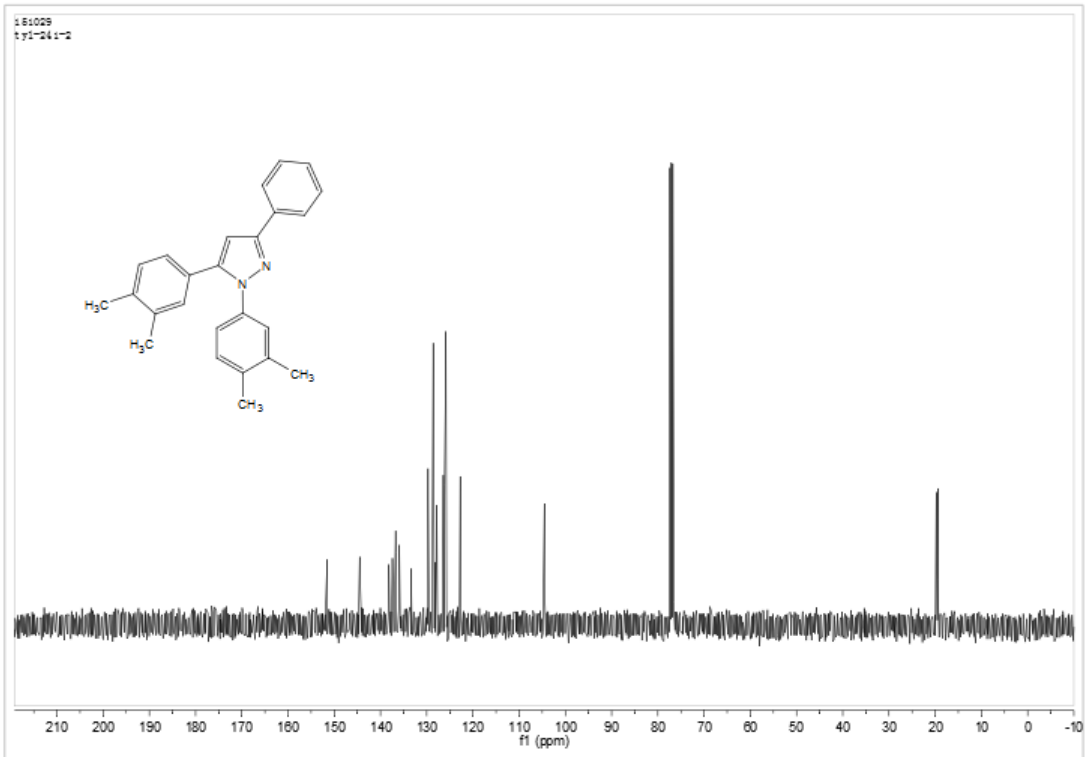
^{1}H NMR and ^{13}C NMR for compound **3ea**



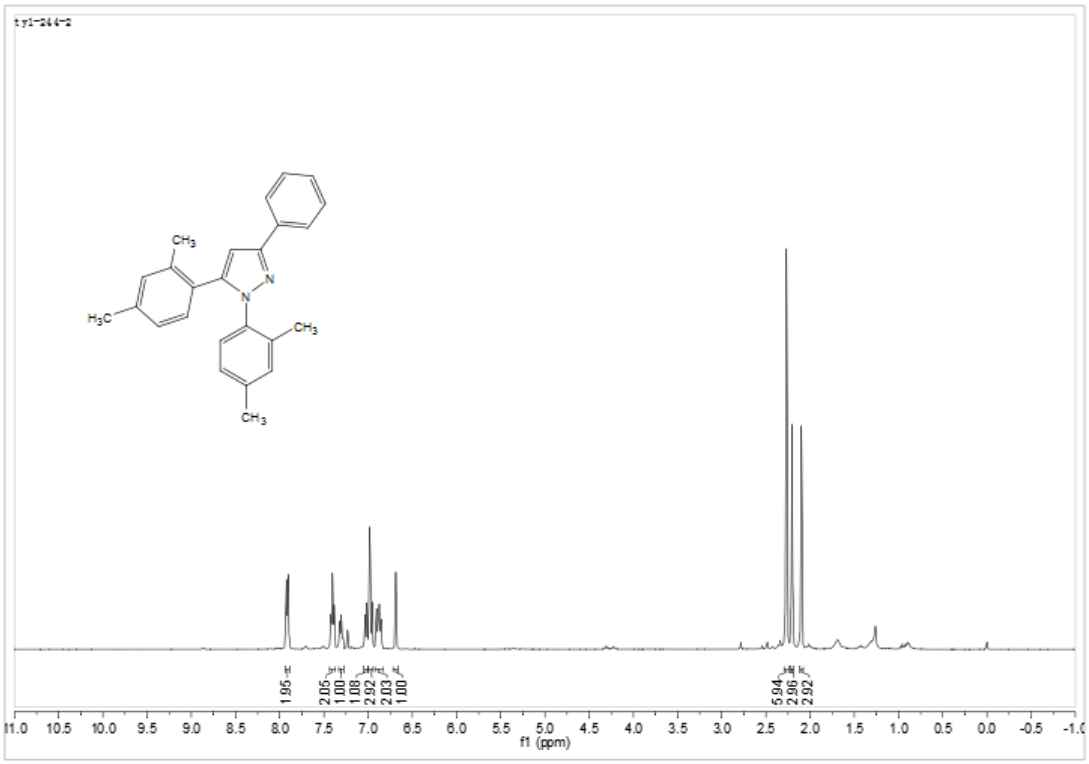


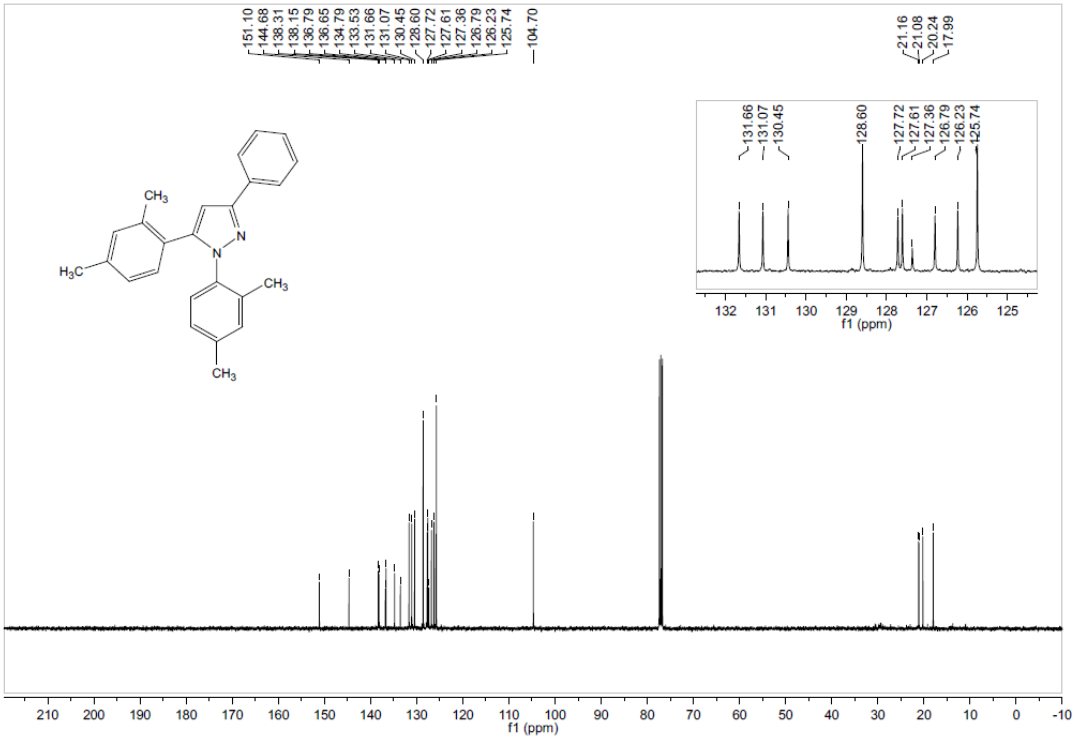
^{1}H NMR and ^{13}C NMR for compound **3fa**



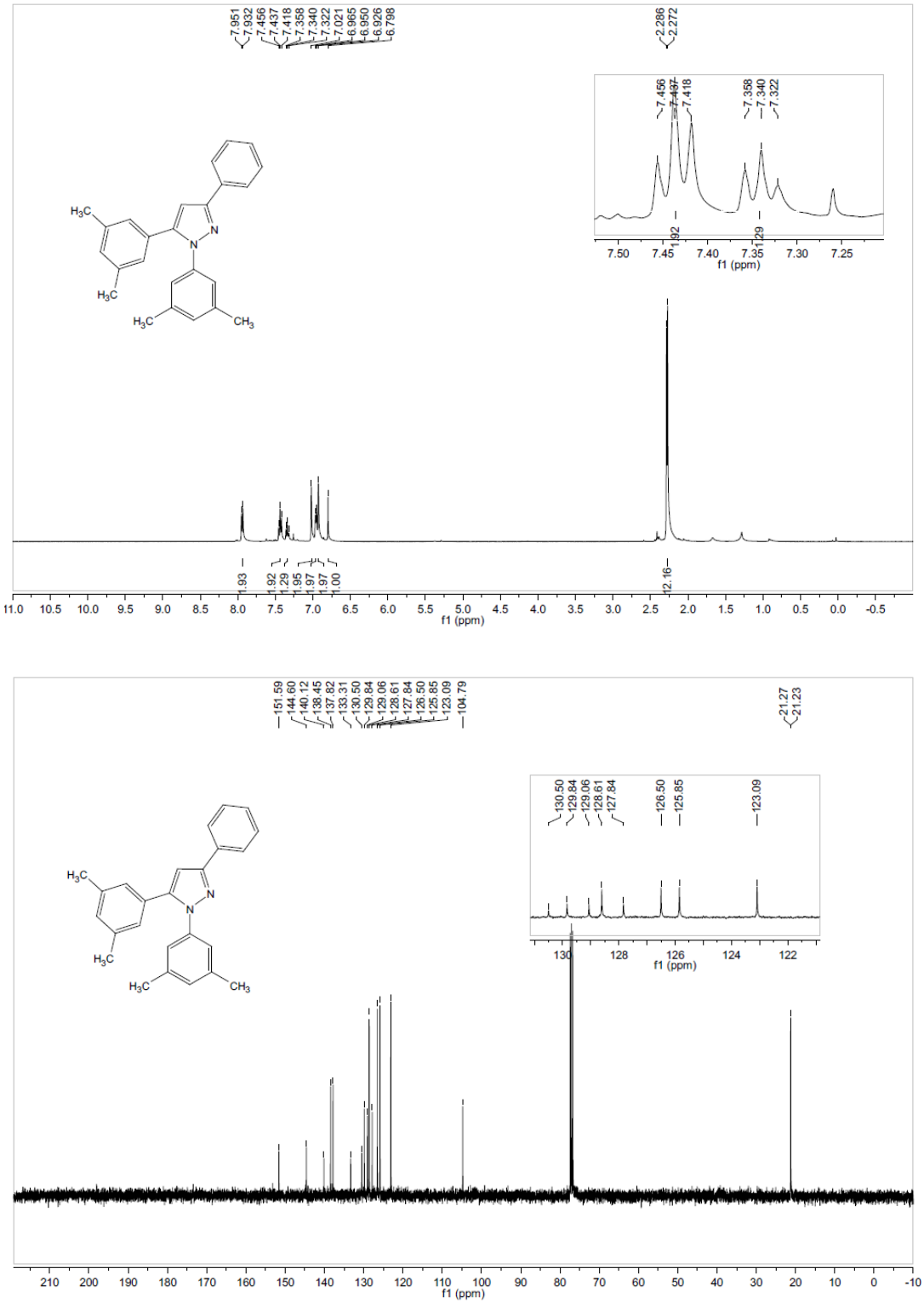


^{1}H NMR and ^{13}C NMR for compound **3ga**

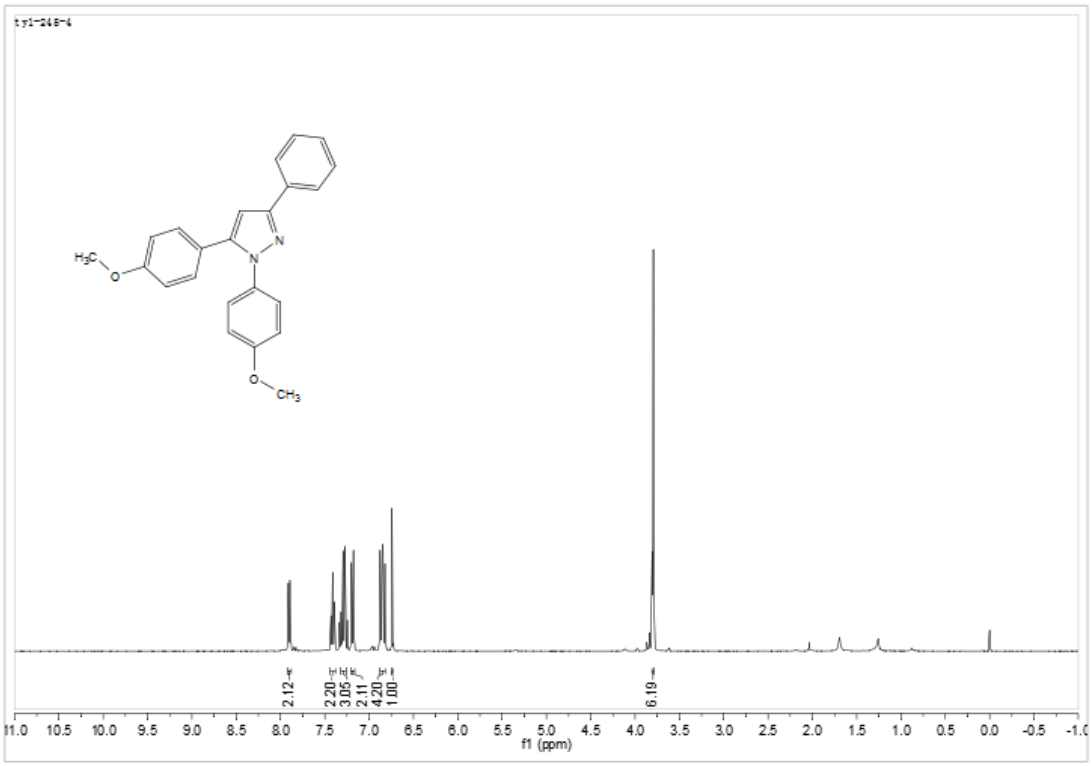


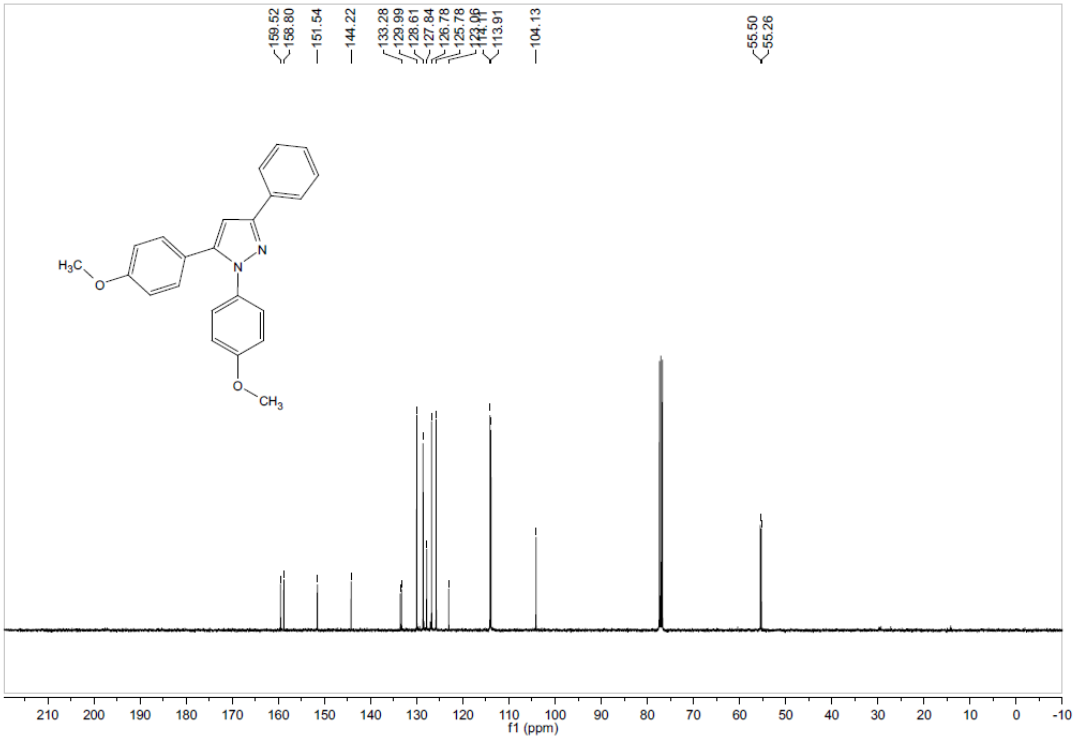


^{1}H NMR and ^{13}C NMR for compound **3ha**

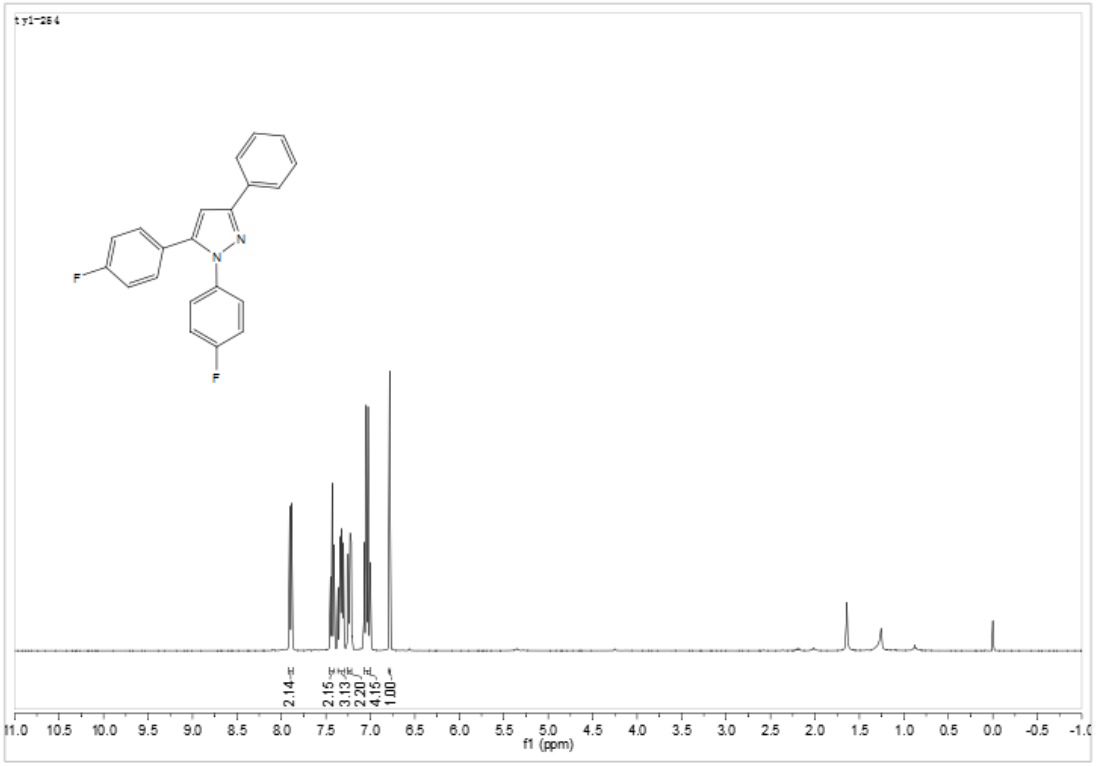


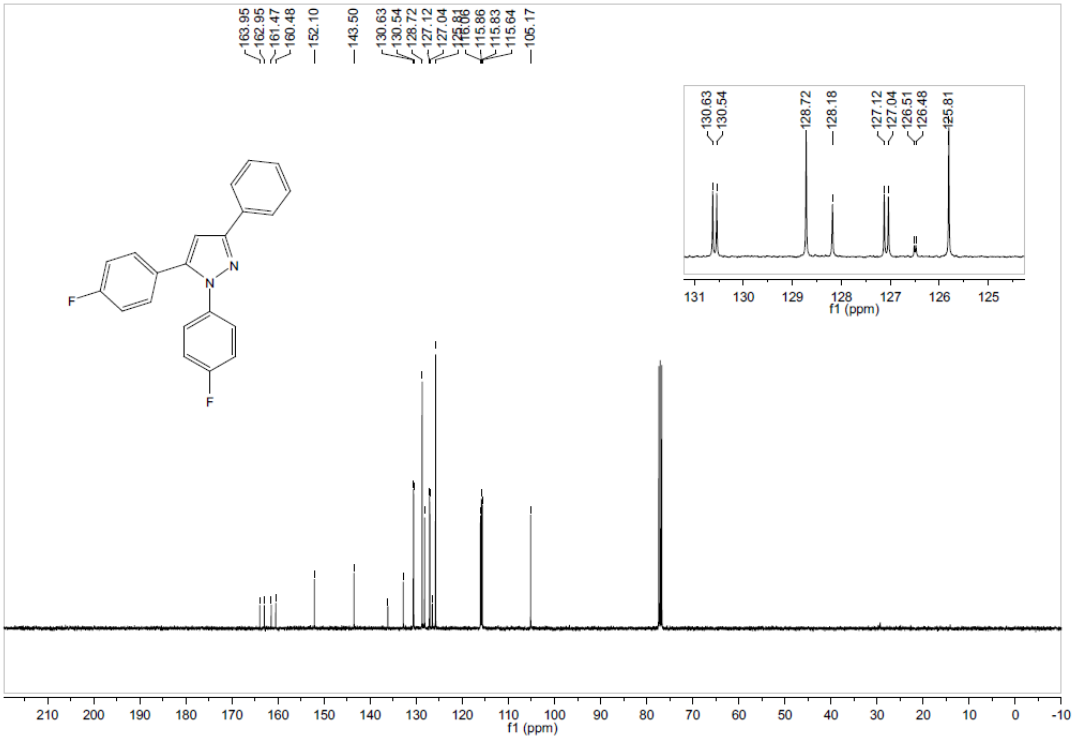
^{1}H NMR and ^{13}C NMR for compound **3ia**



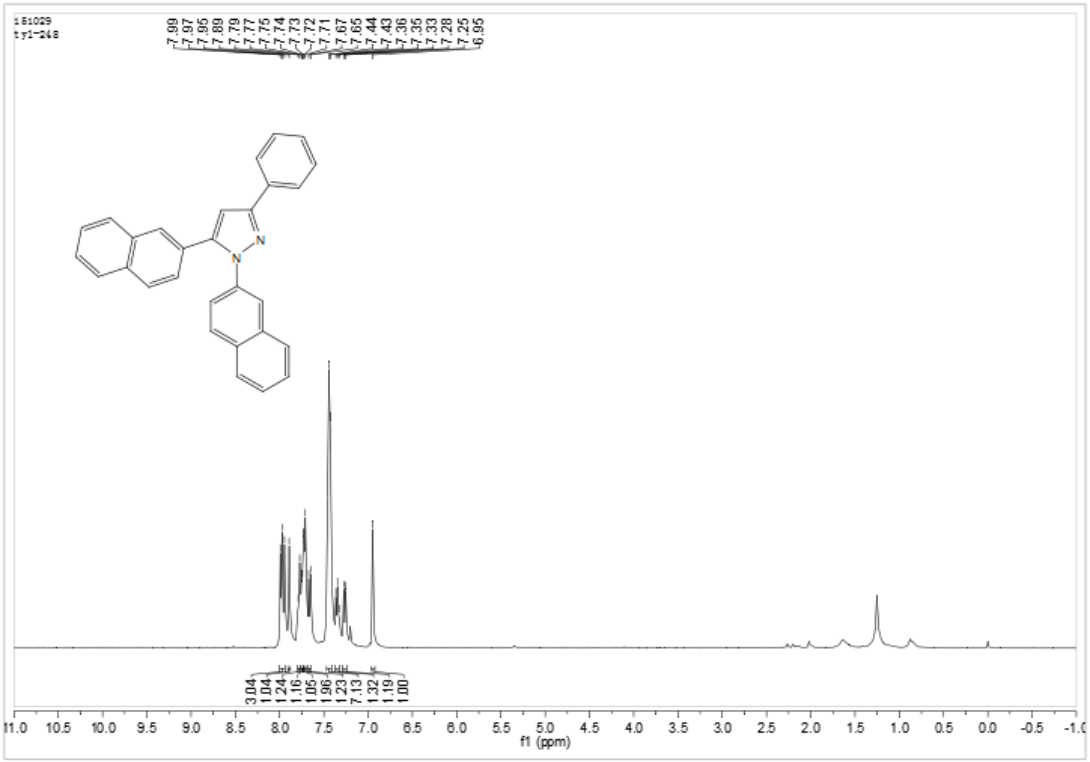


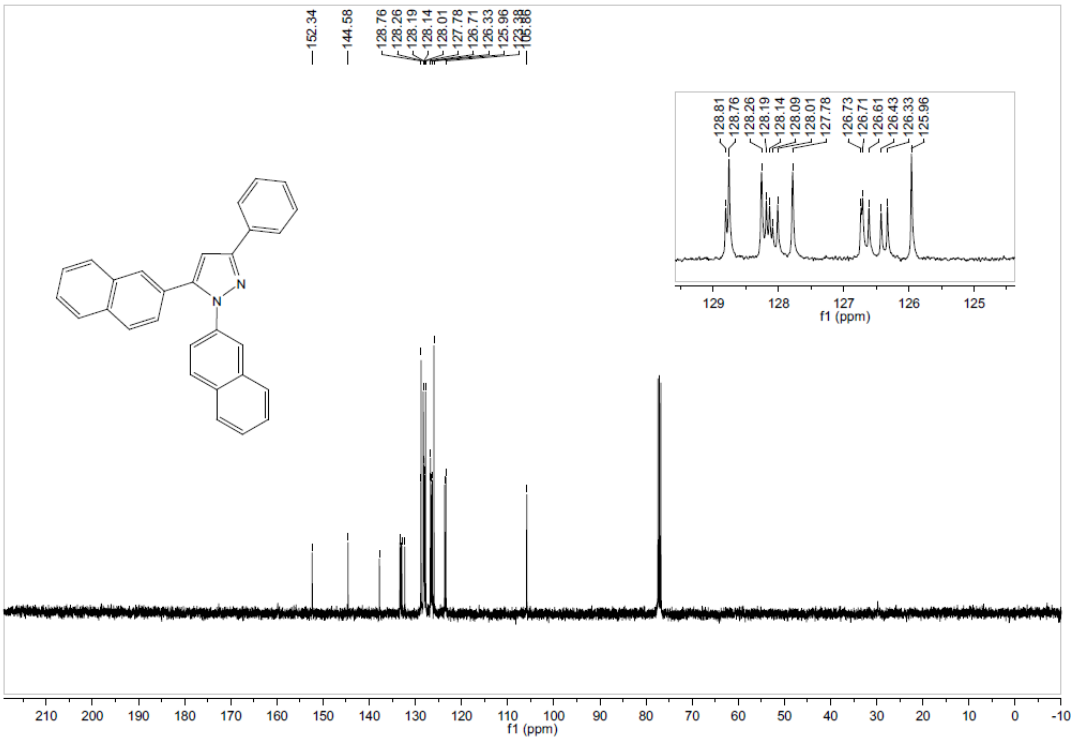
^{1}H NMR and ^{13}C NMR for compound **3ja**



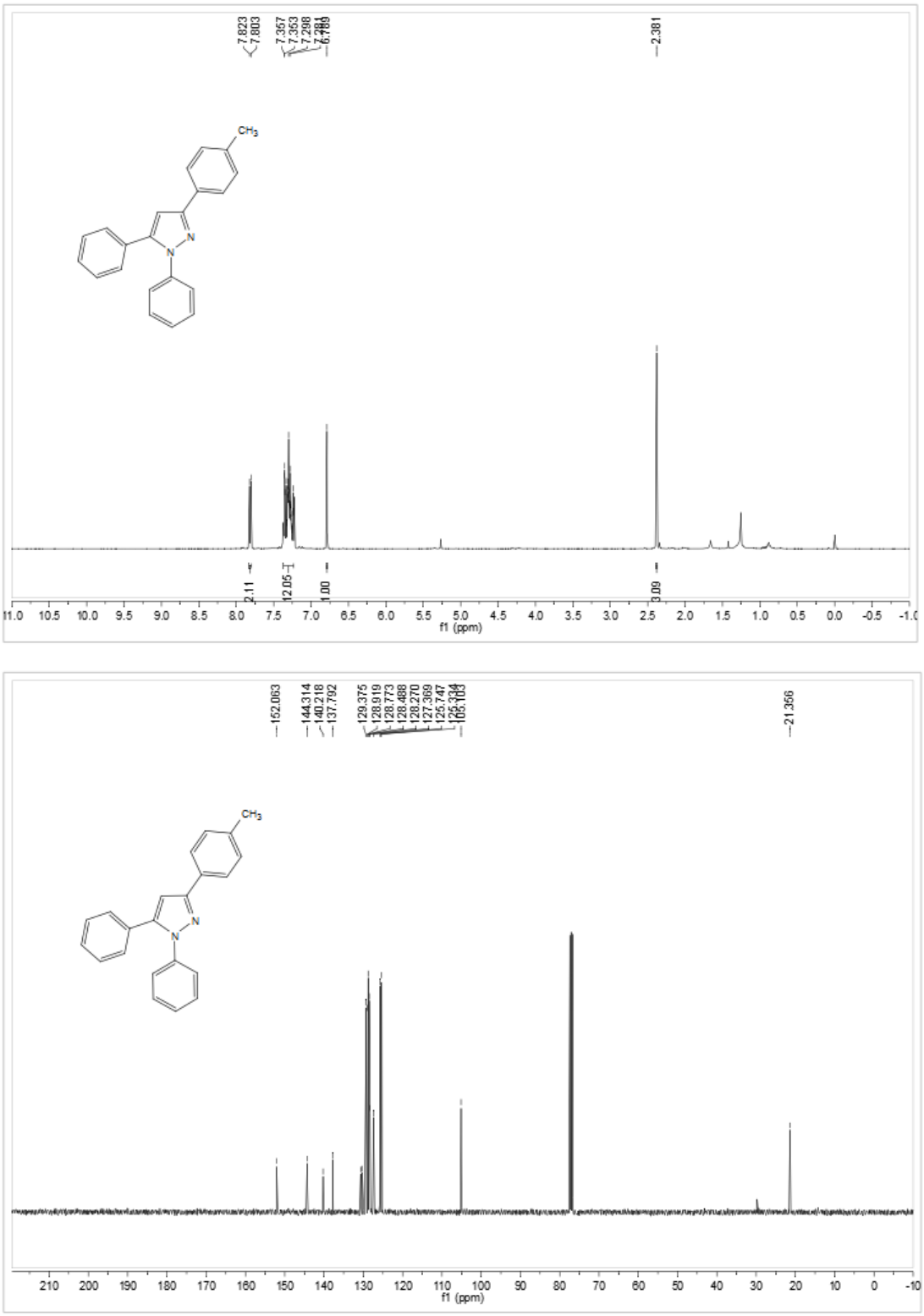


^{1}H NMR and ^{13}C NMR for compound **3ka**

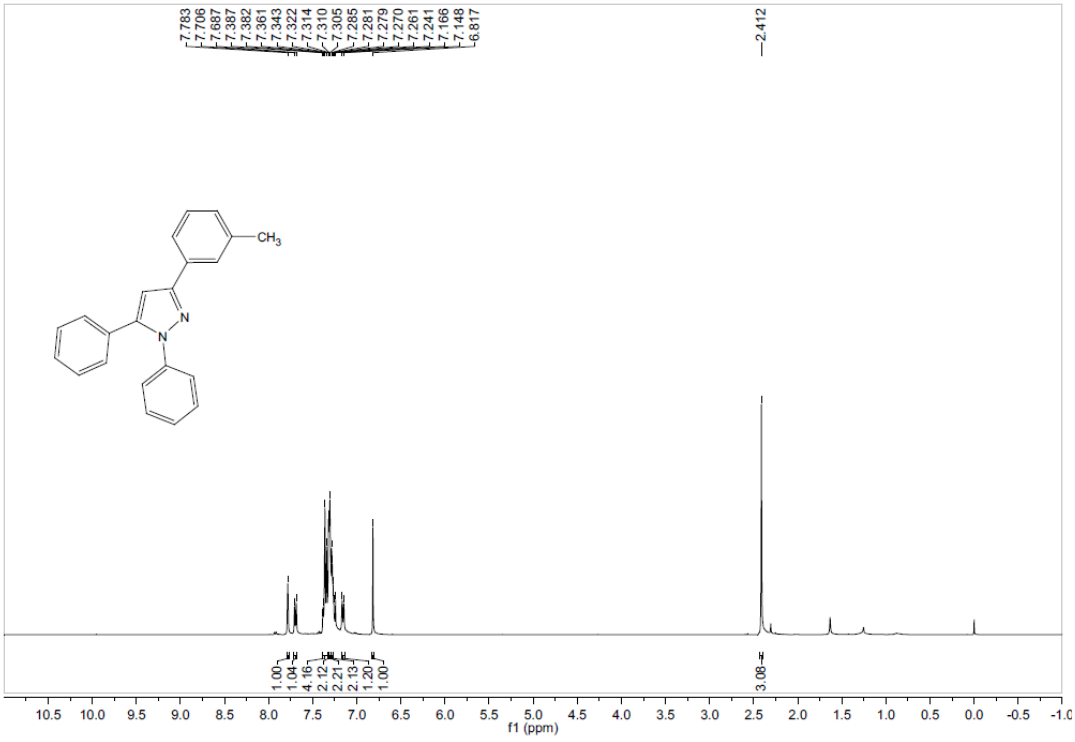


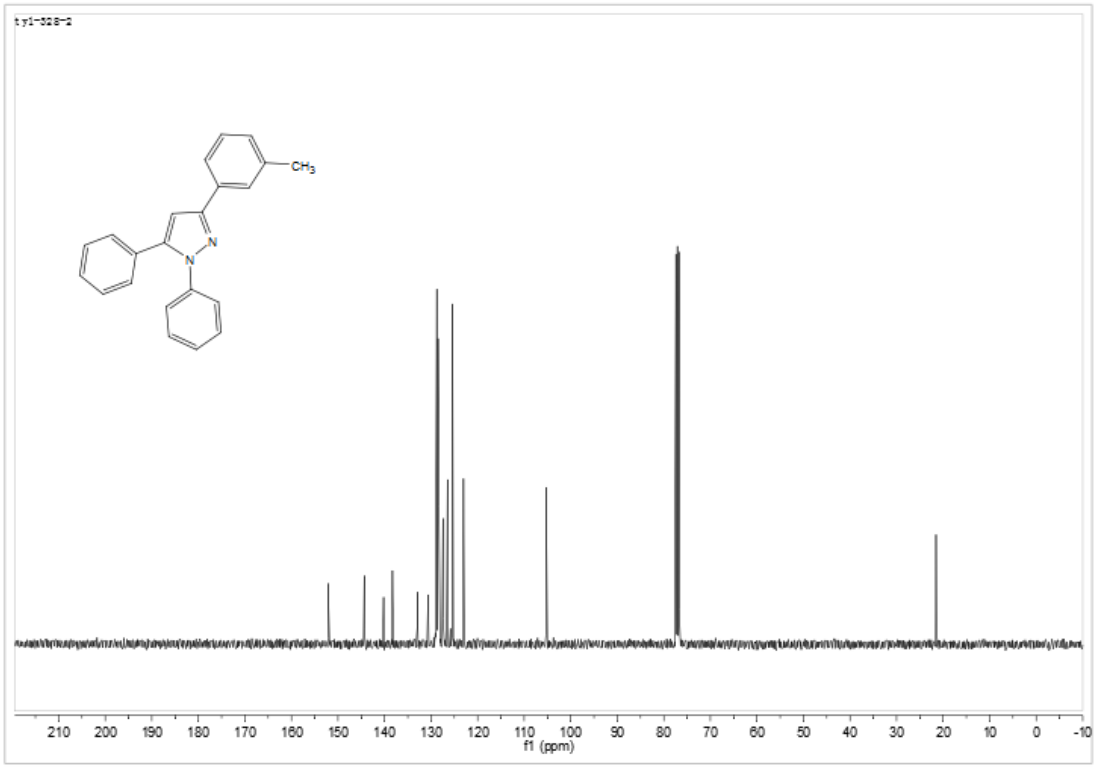


^{1}H NMR and ^{13}C NMR for compound **3la**

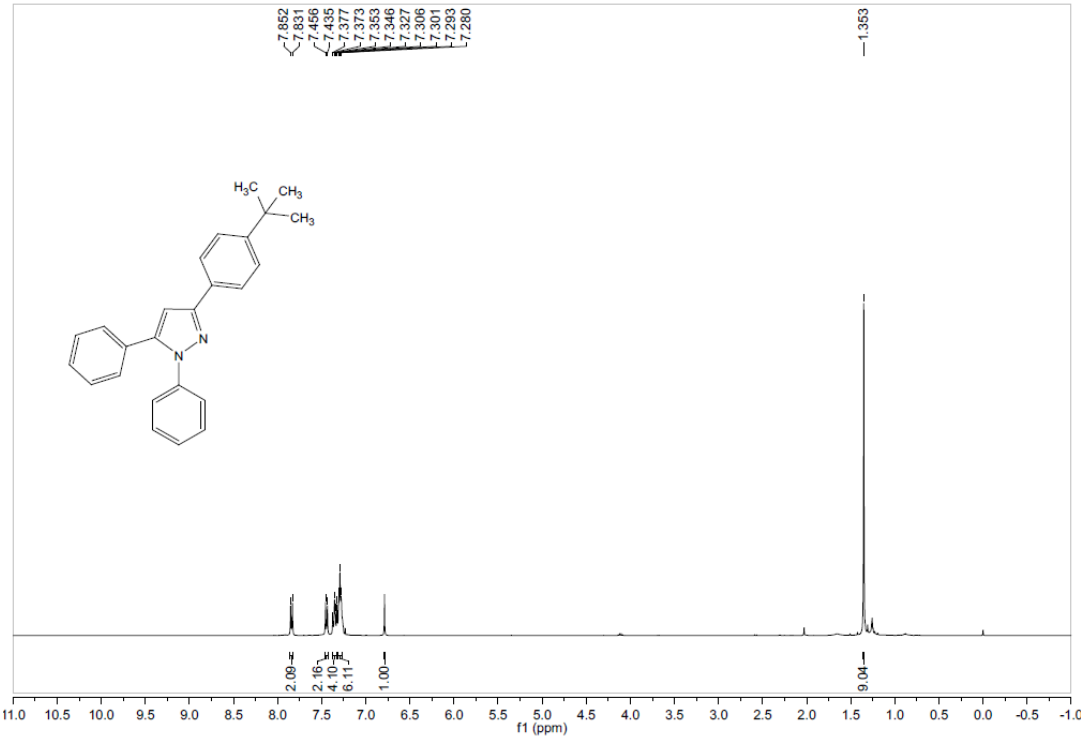


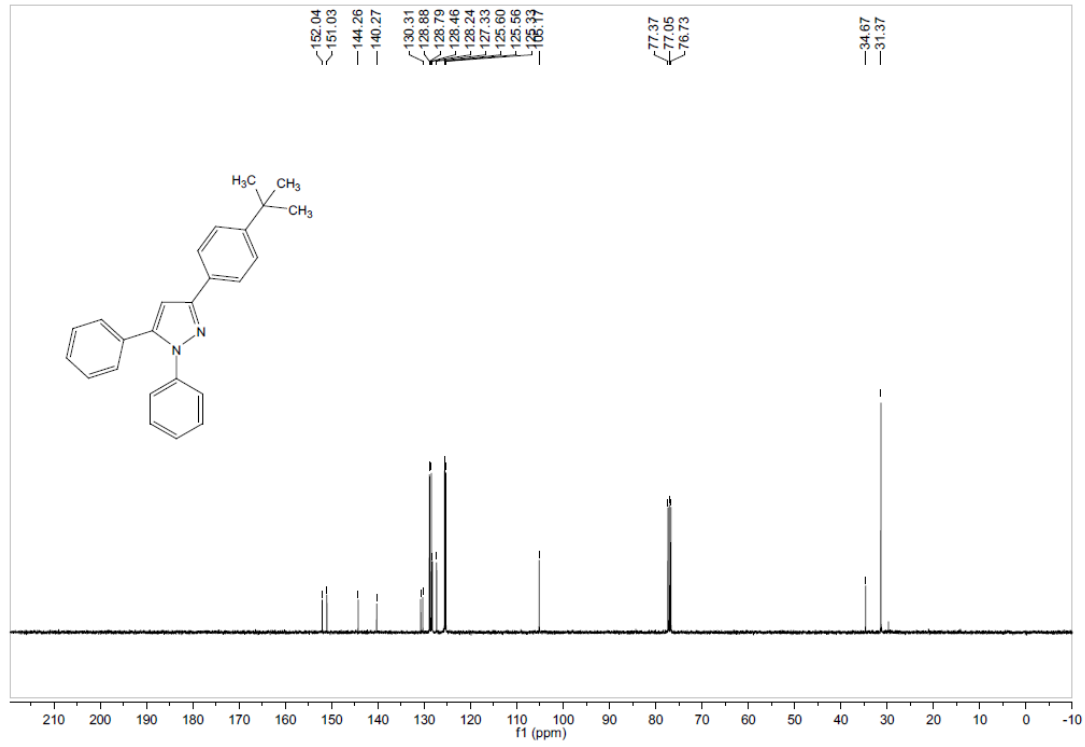
^{1}H NMR and ^{13}C NMR for compound **3ab**



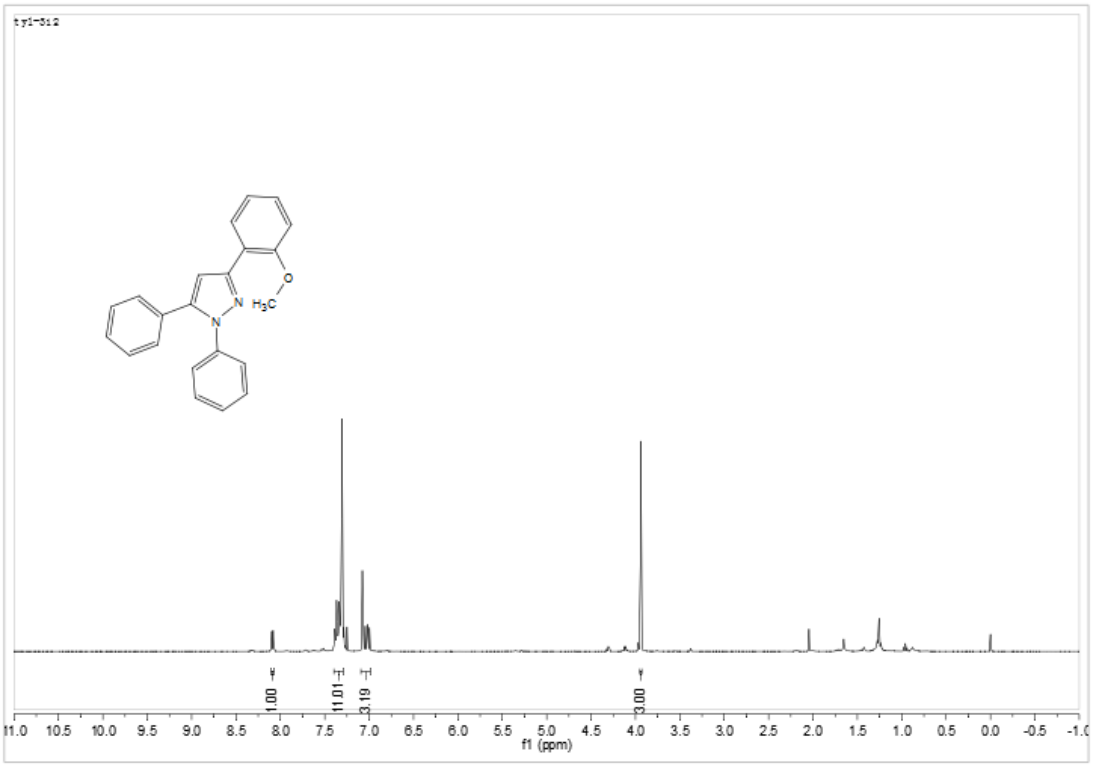


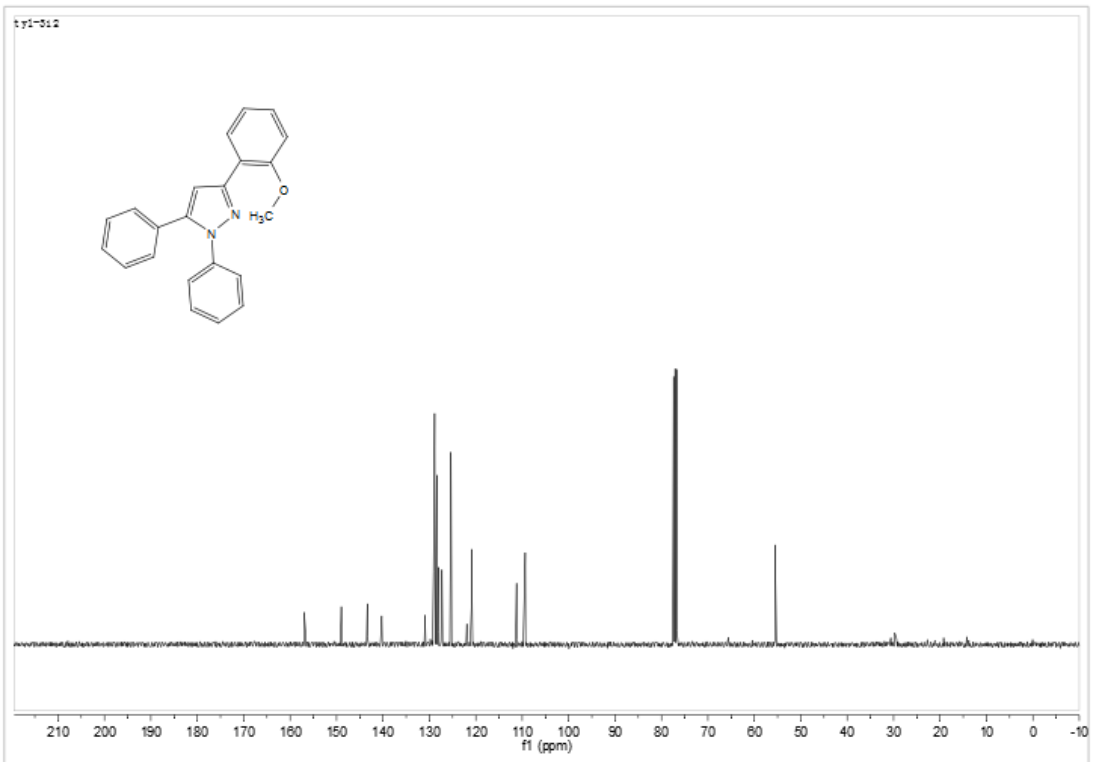
^{1}H NMR and ^{13}C NMR for compound **3ac**



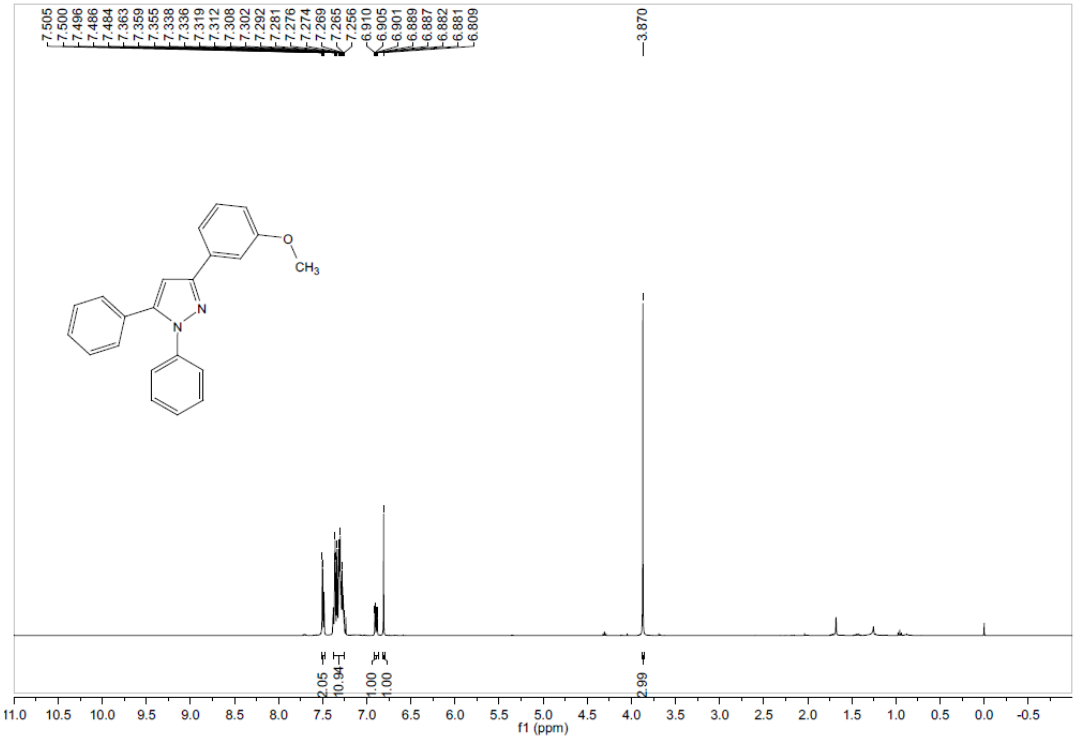


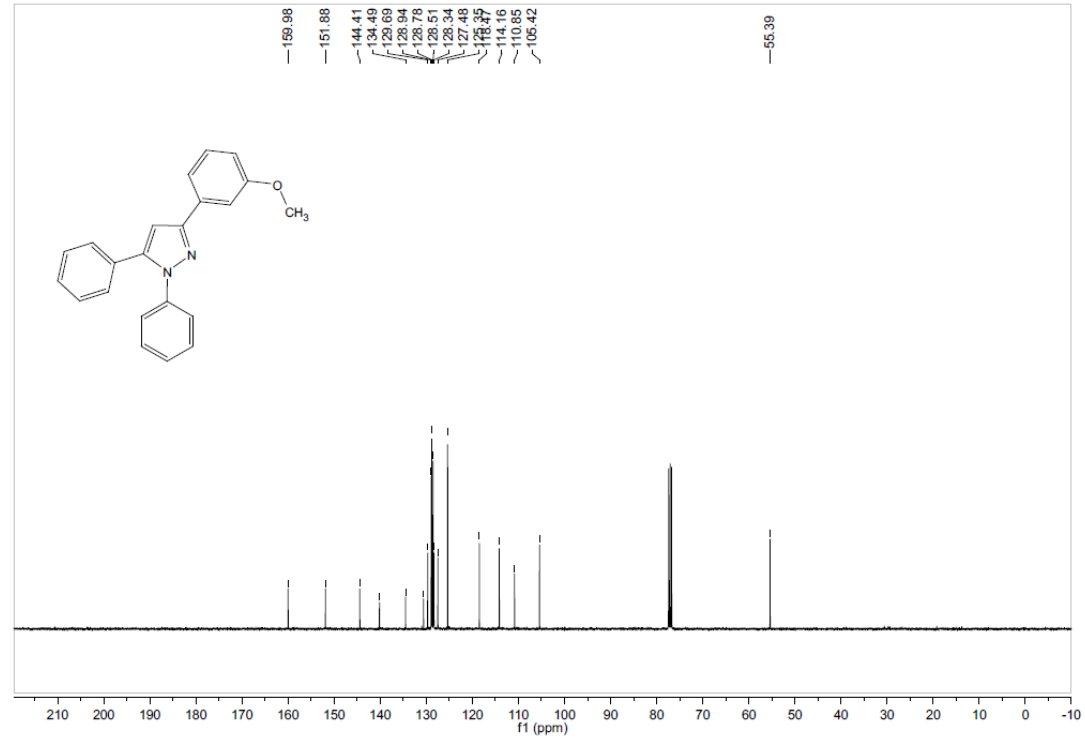
^{1}H NMR and ^{13}C NMR for compound **3ad**



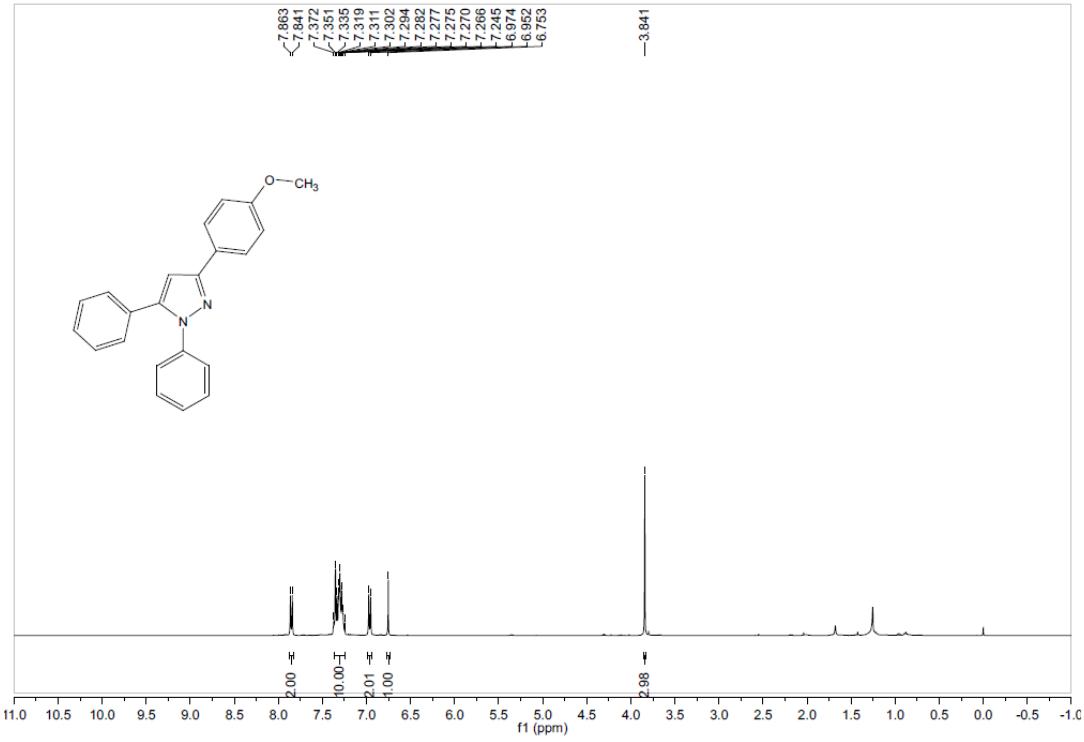


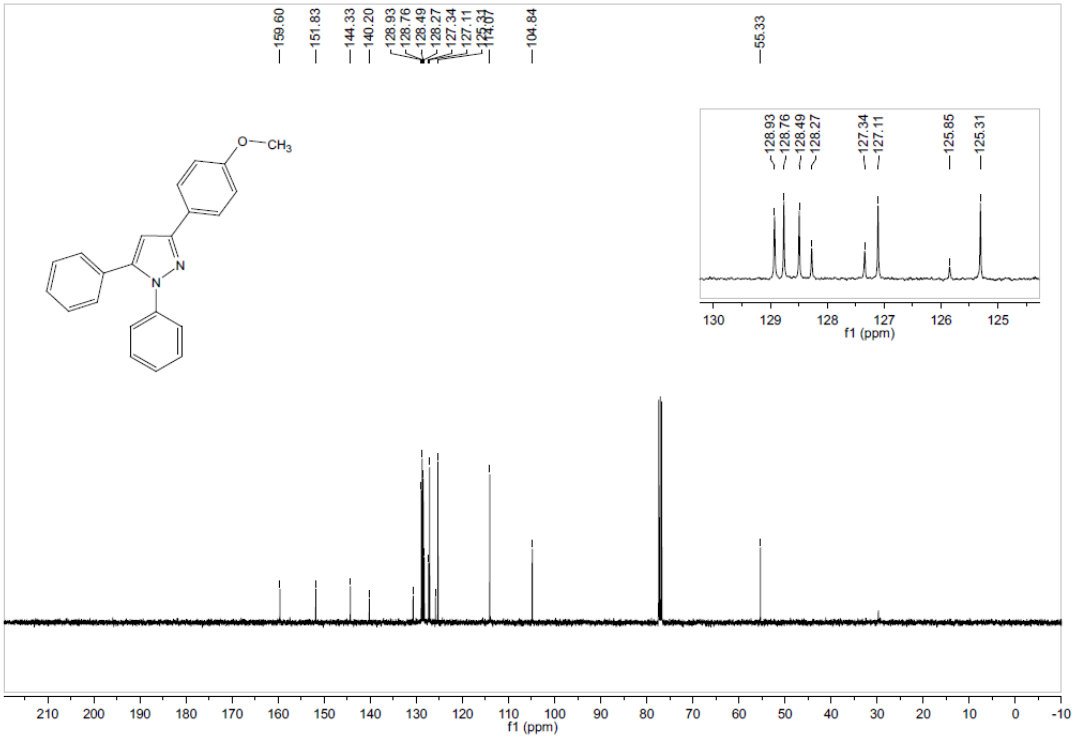
^{1}H NMR and ^{13}C NMR for compound **3ae**



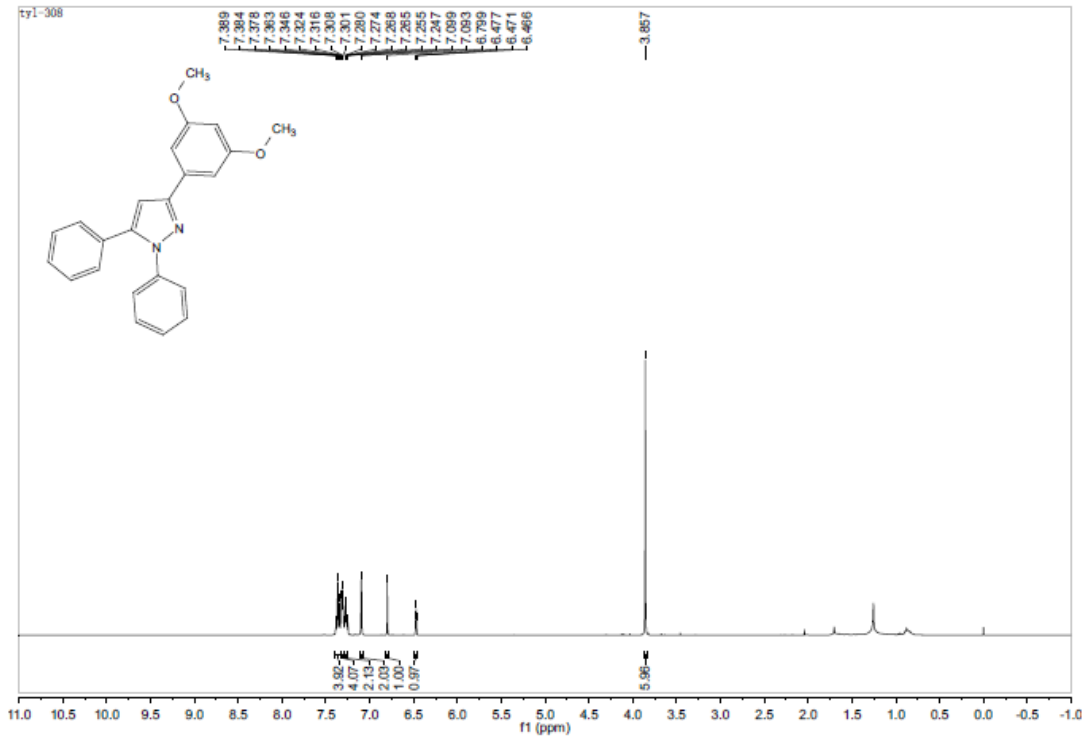


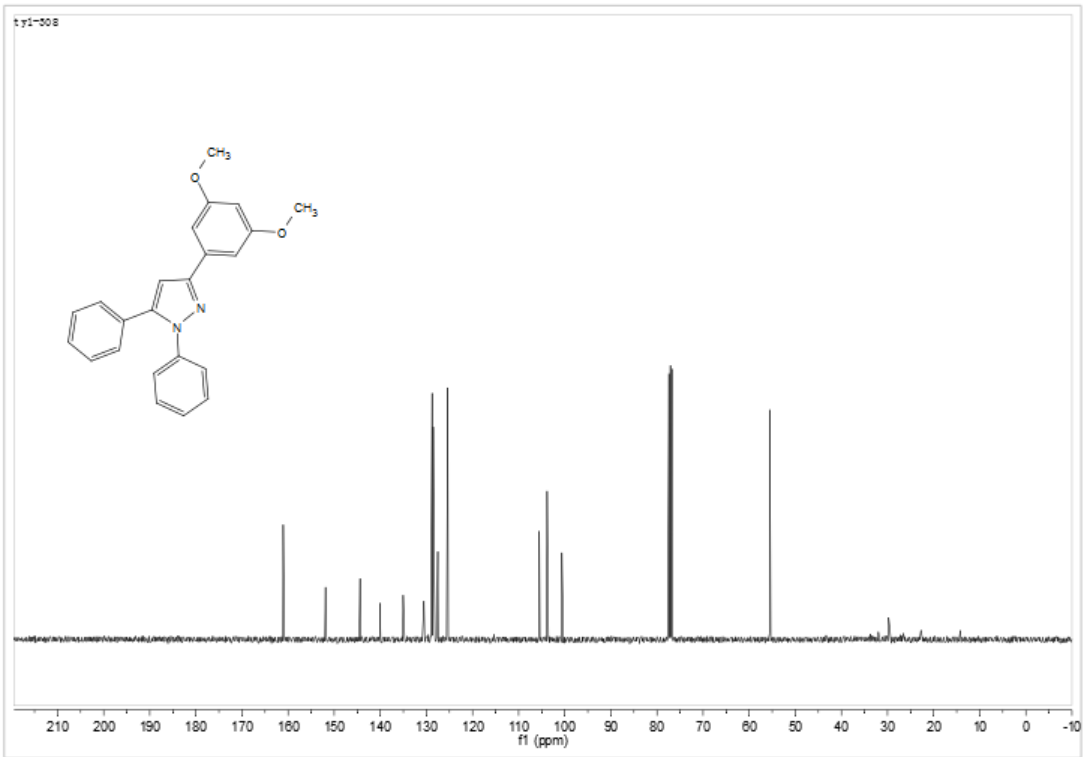
^{1}H NMR and ^{13}C NMR for compound **3af**



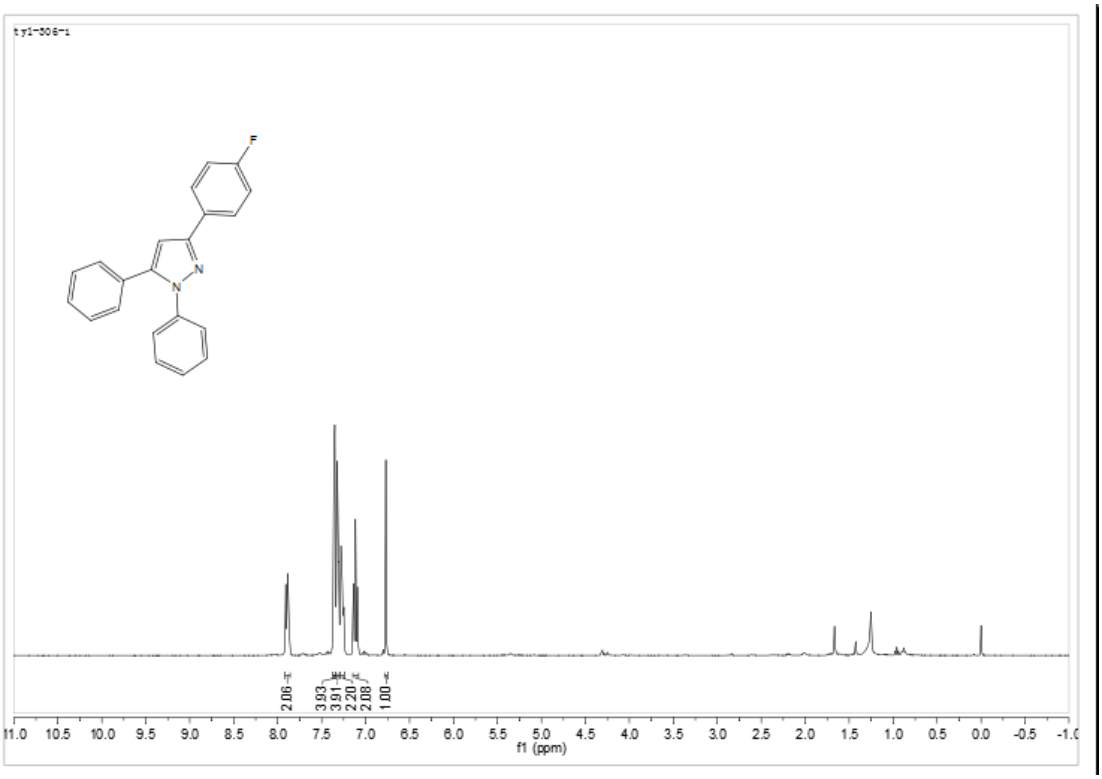


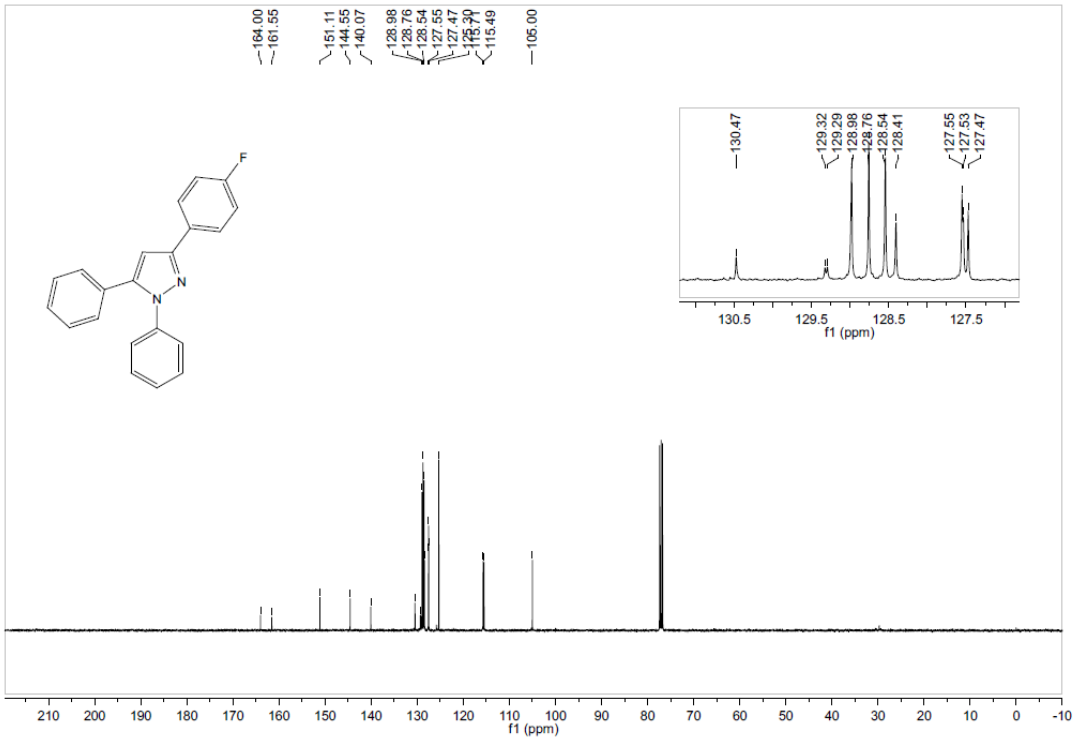
^{1}H NMR and ^{13}C NMR for compound **3ag**





^{1}H NMR and ^{13}C NMR for compound **3ah**





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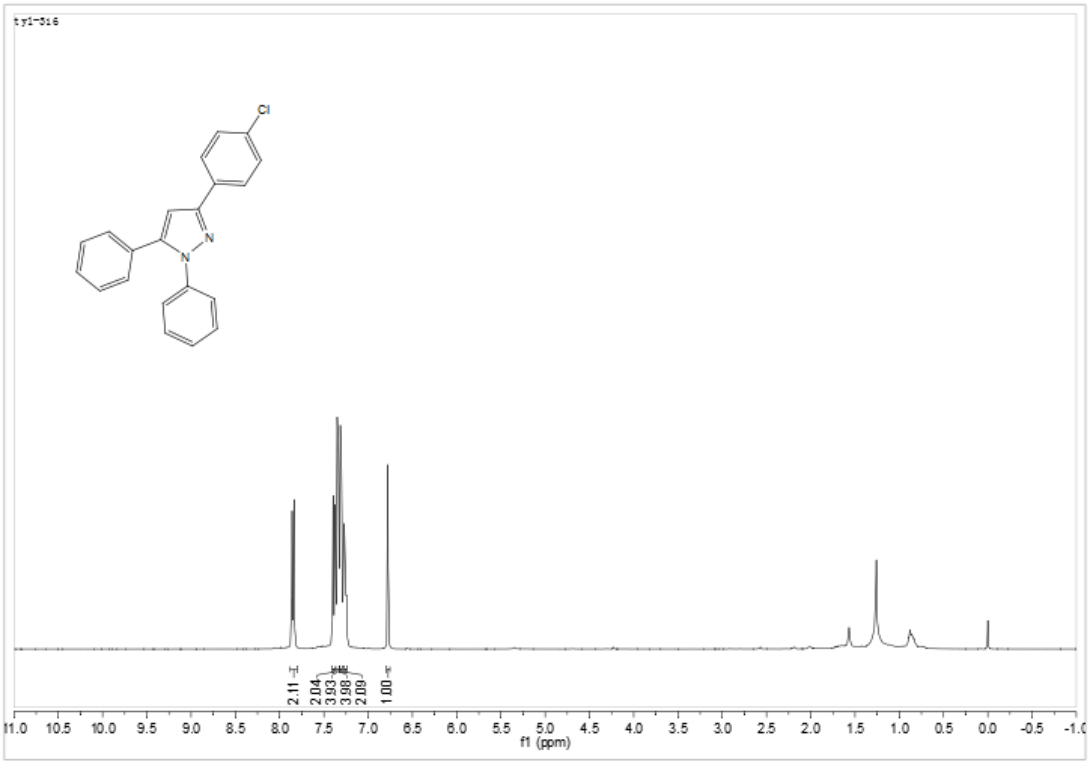

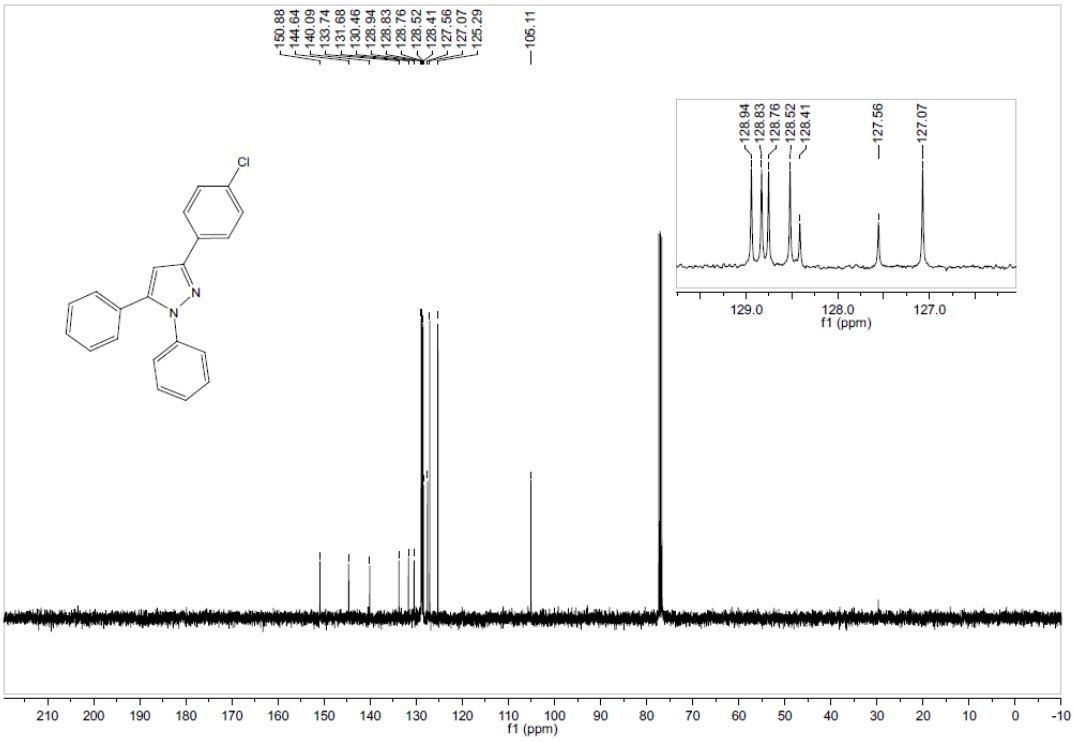

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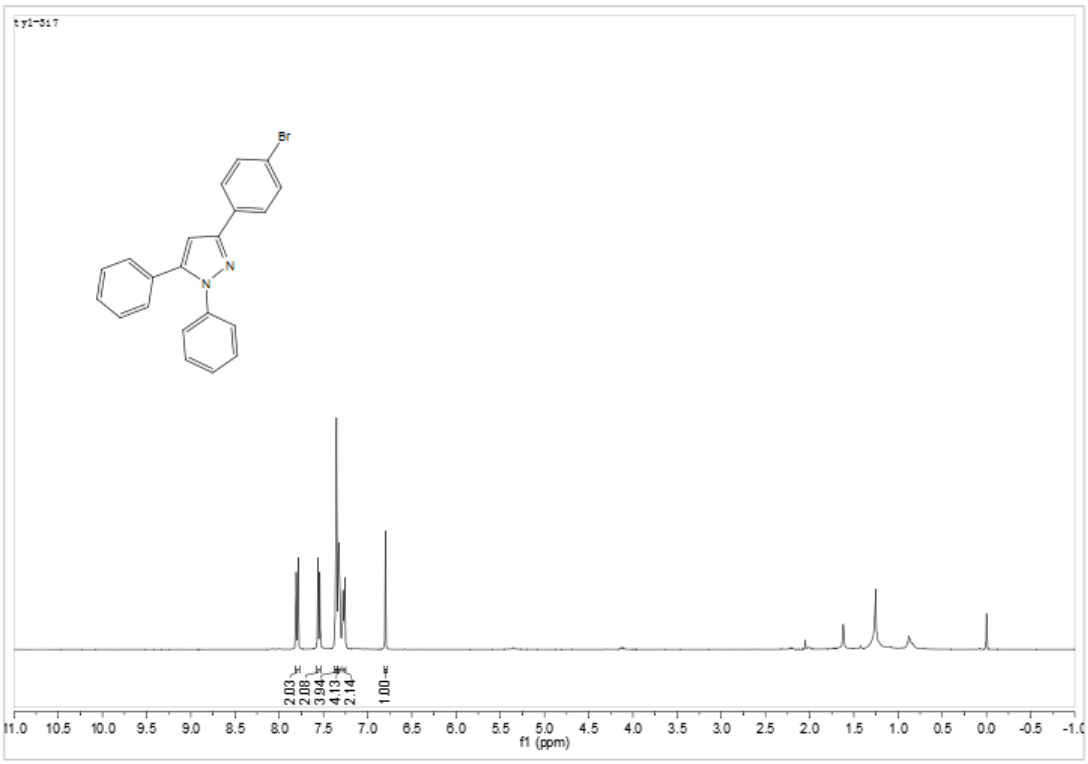
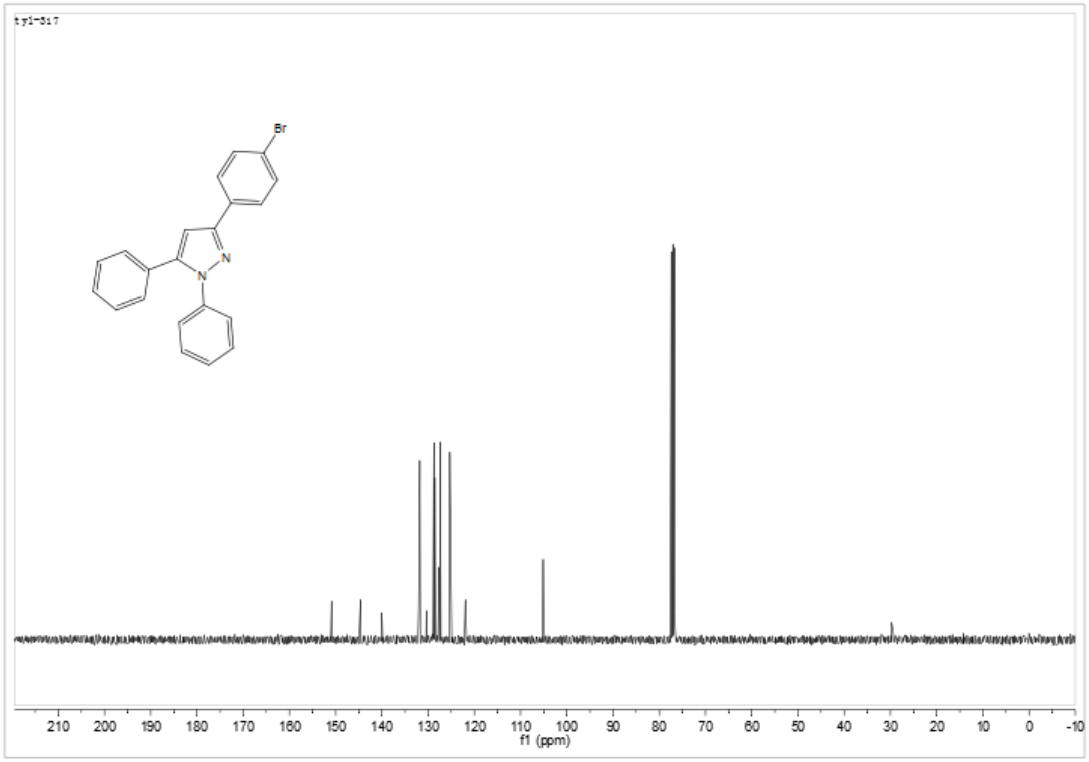
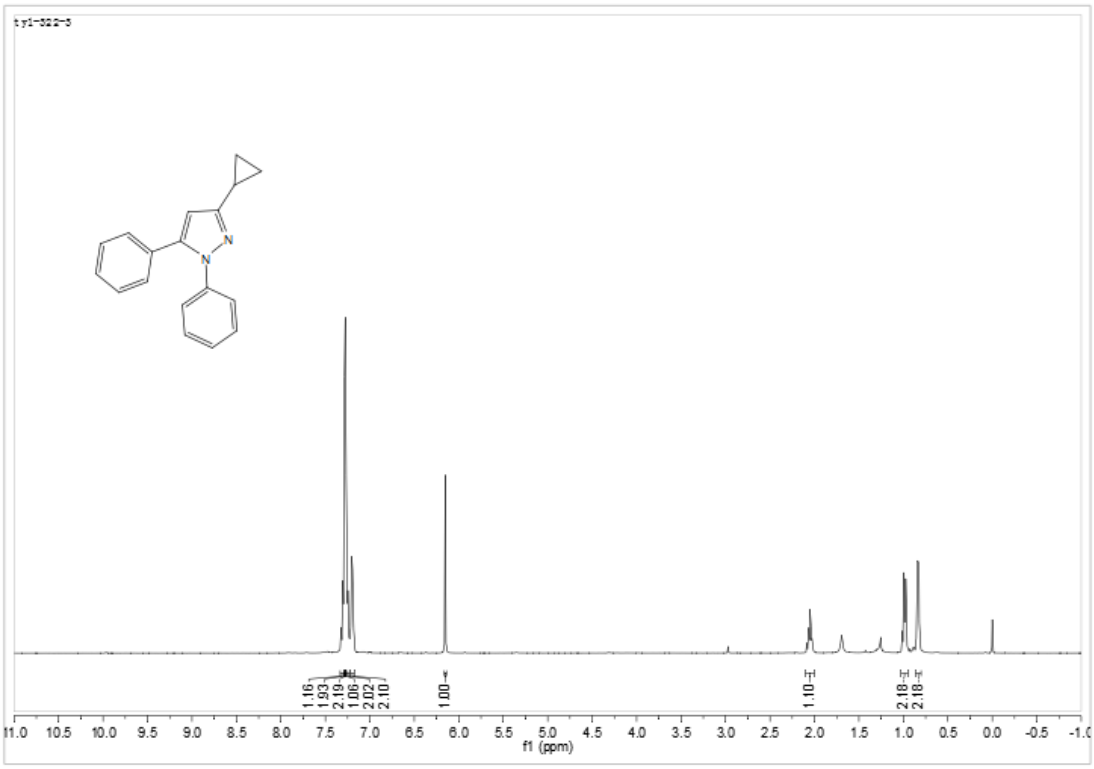
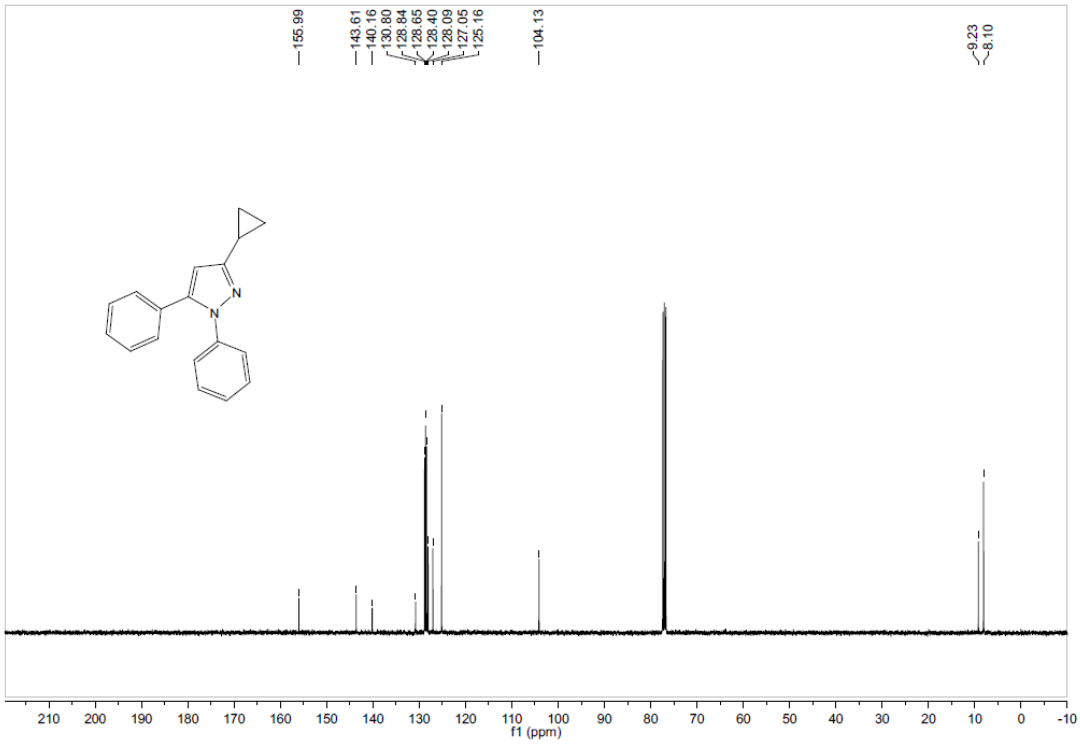


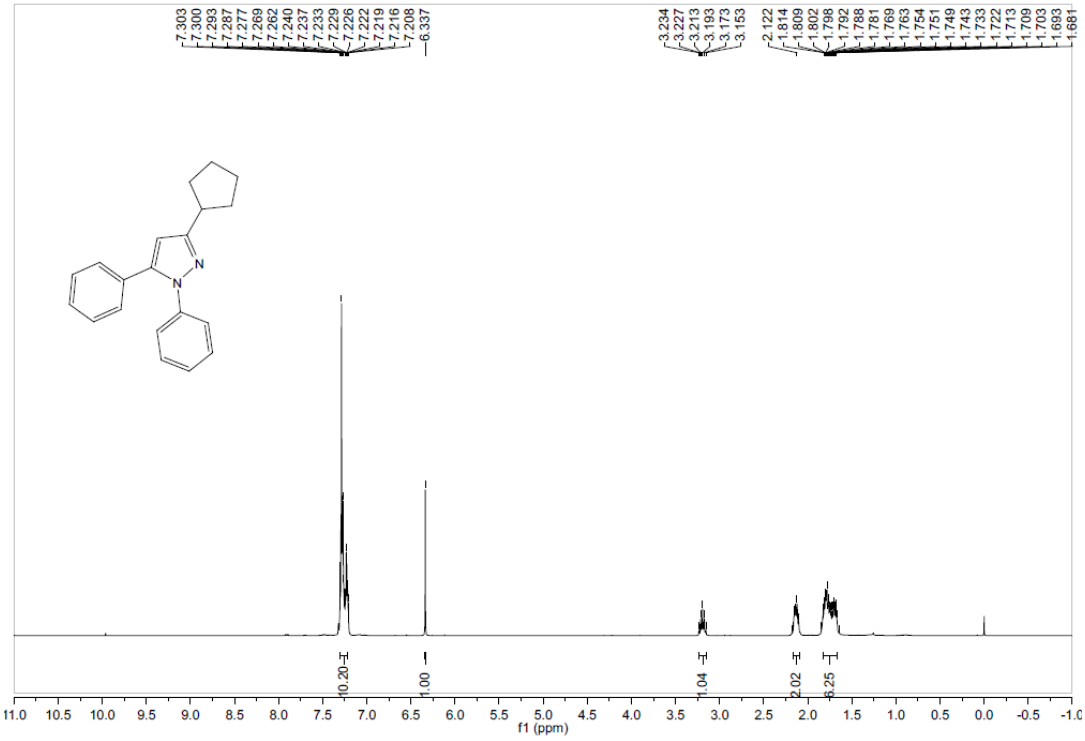


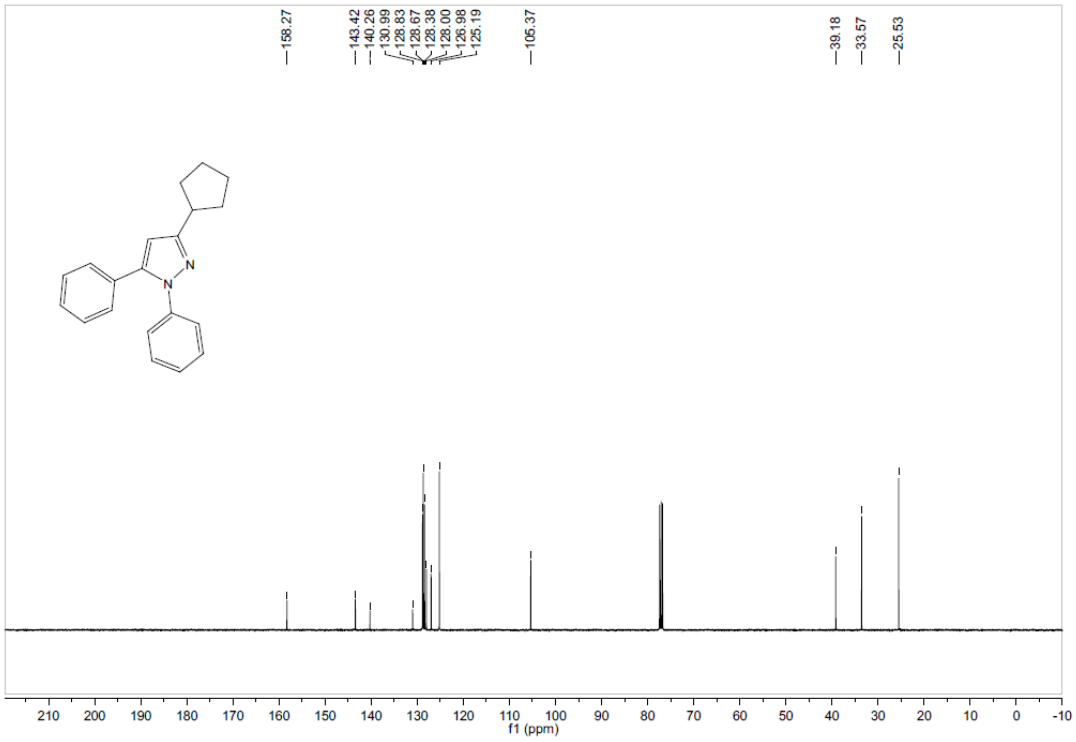
^{1}H NMR and ^{13}C NMR for compound **3ak**



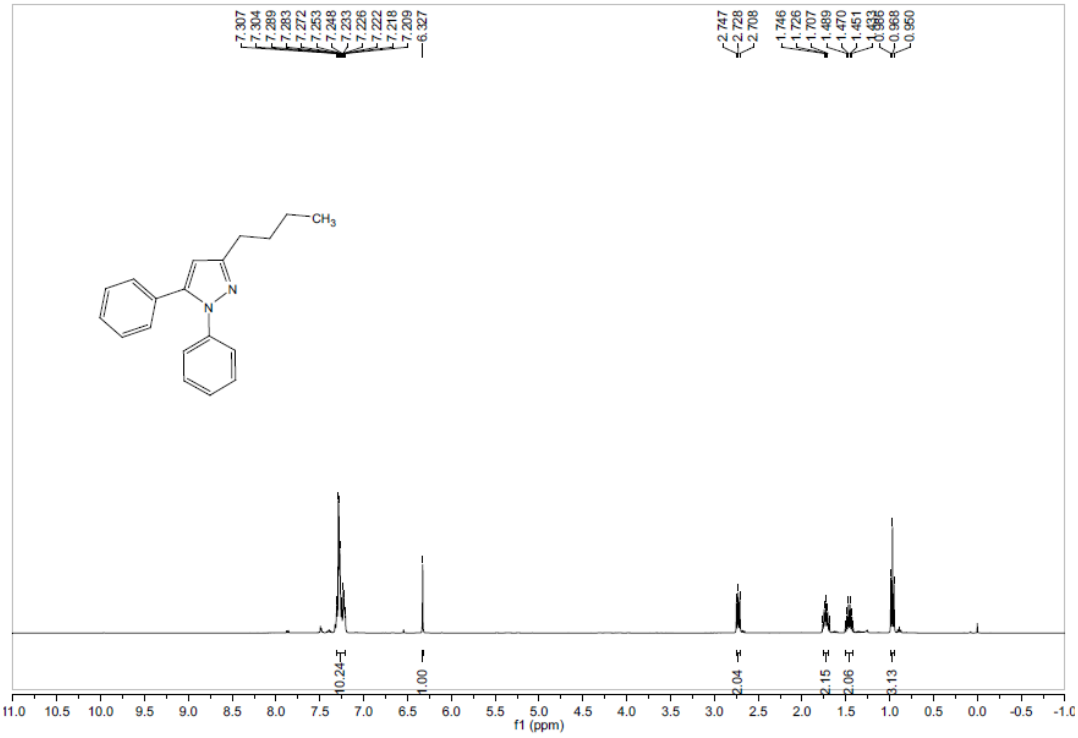


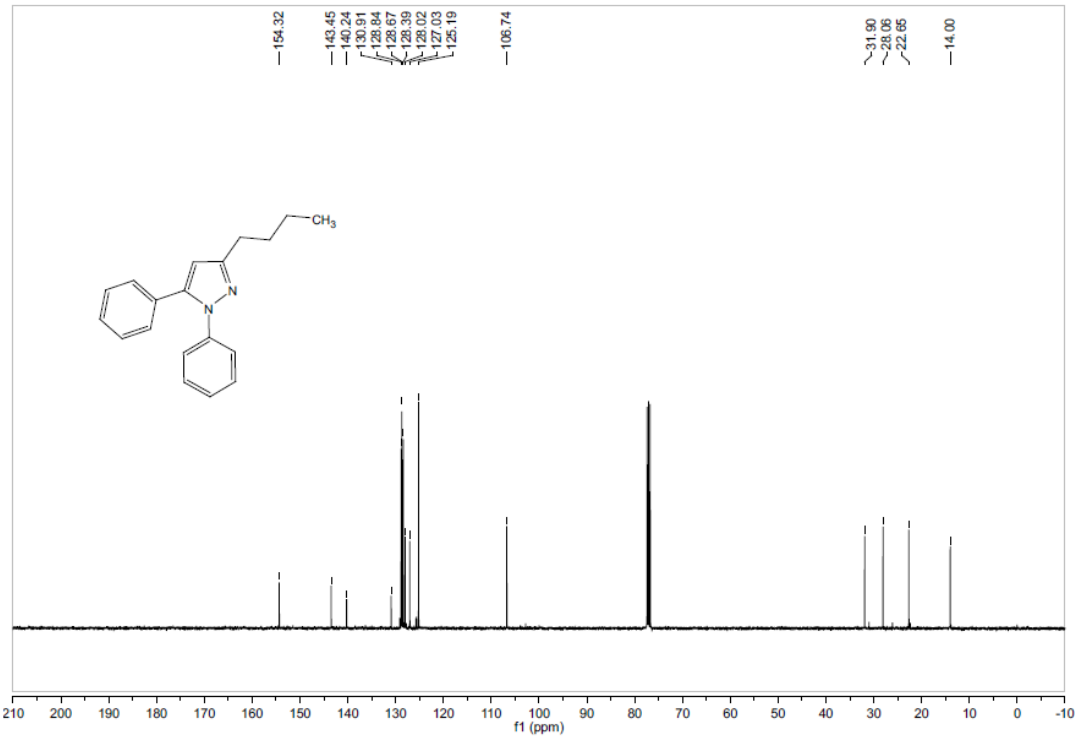
^{1}H NMR and ^{13}C NMR for compound **3am**



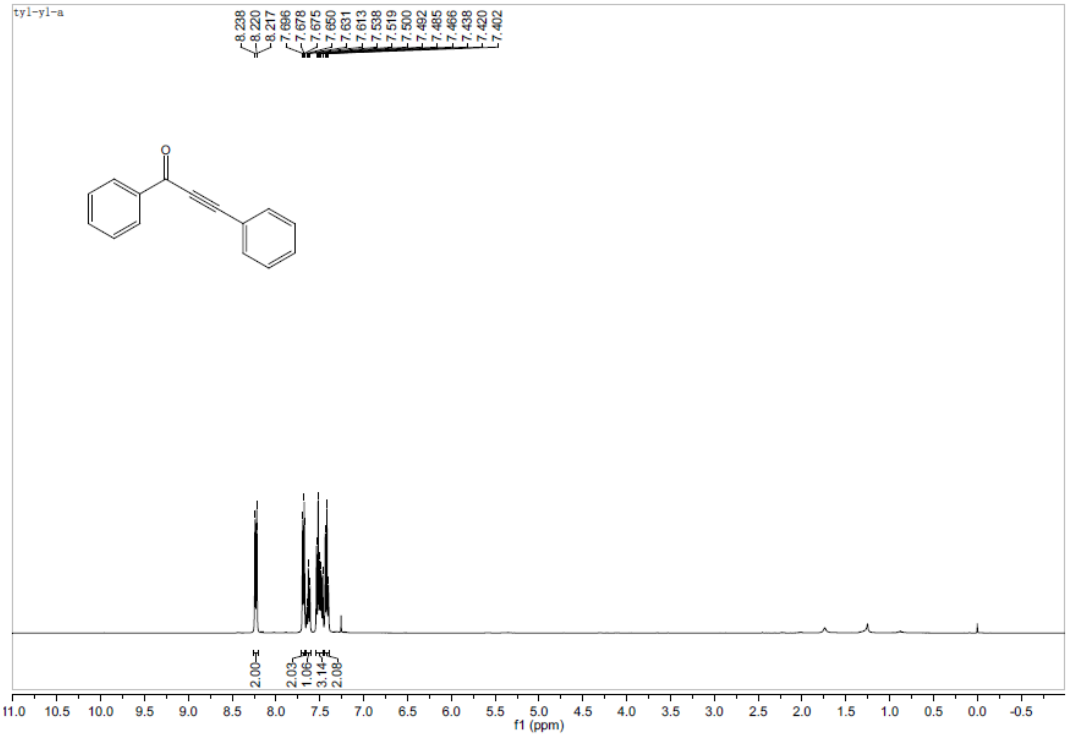


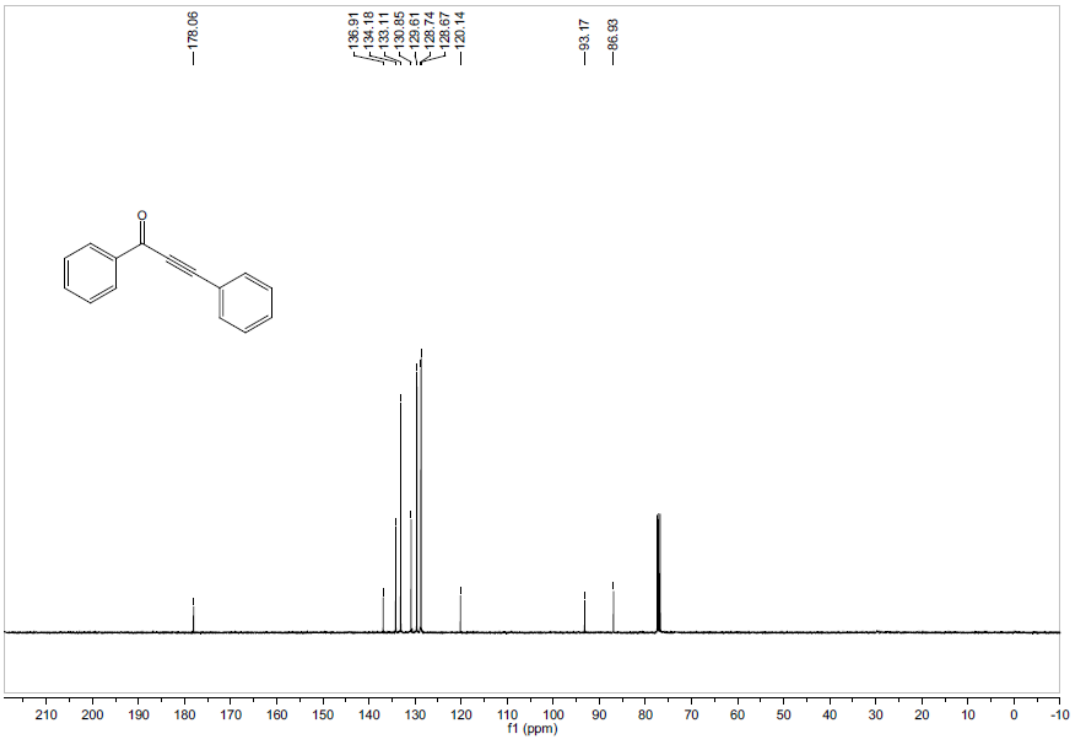
^{1}H NMR and ^{13}C NMR for compound **3an**



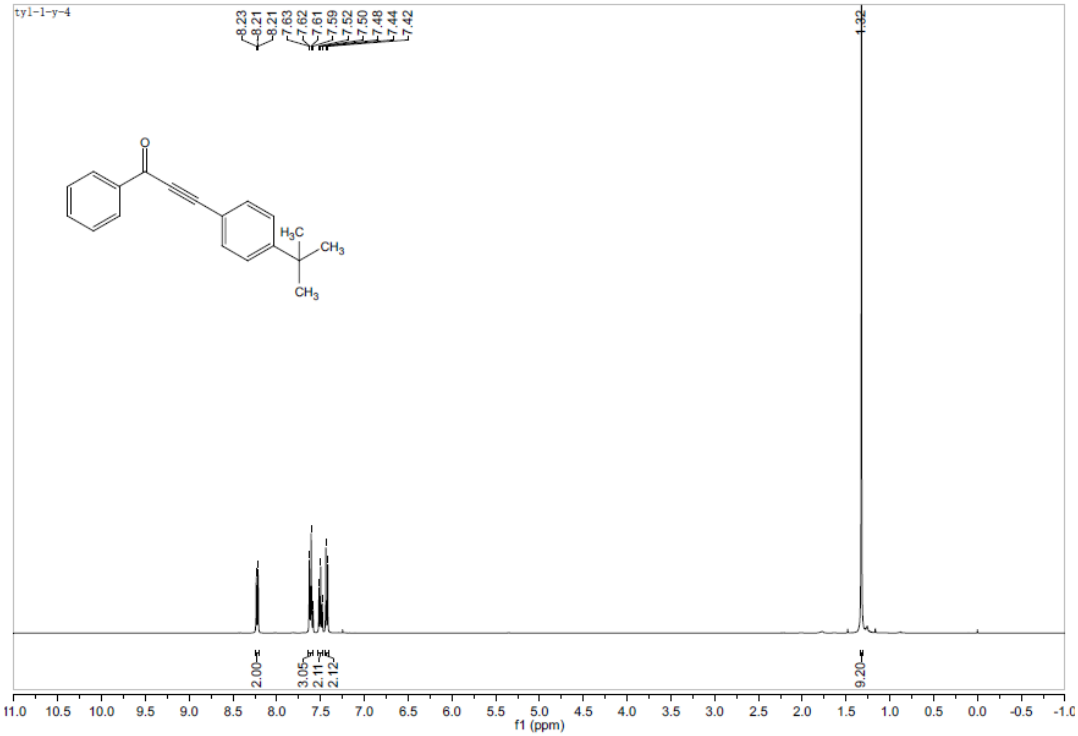


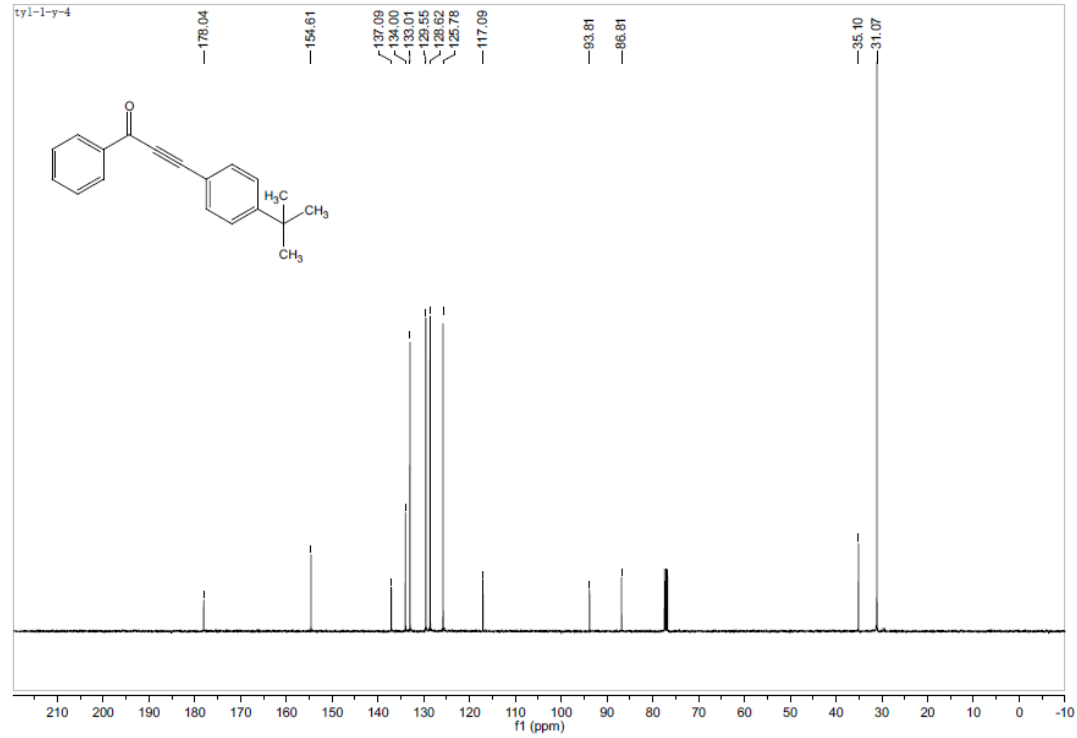
^{1}H NMR and ^{13}C NMR for compound **3ao**



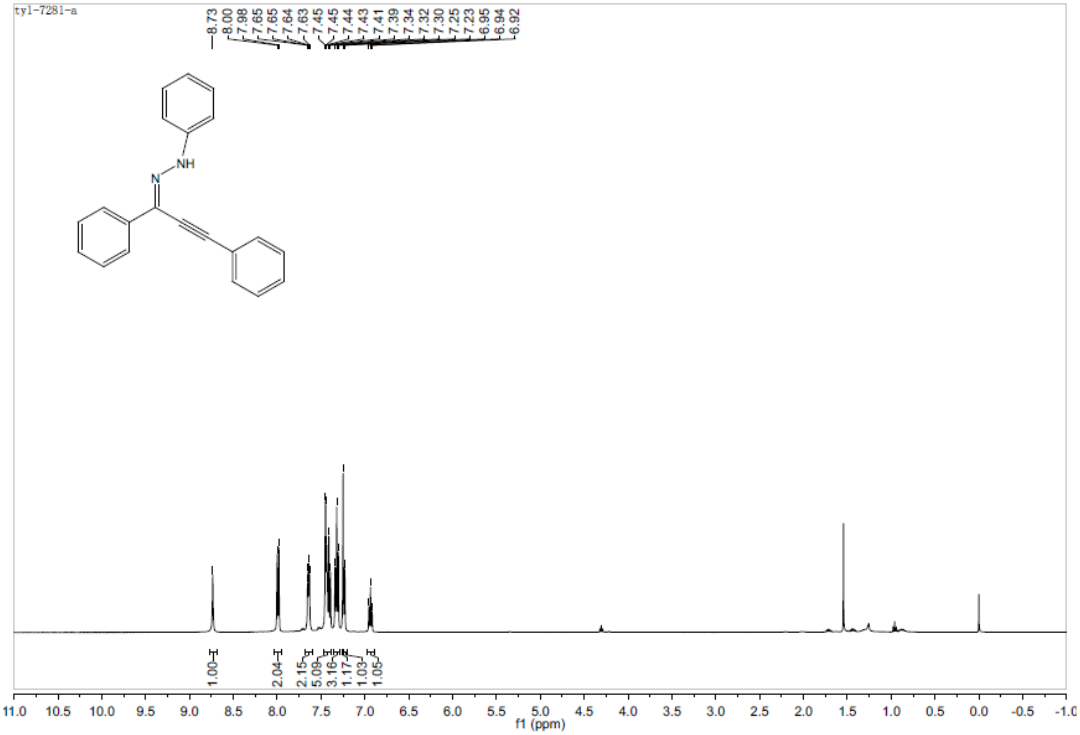


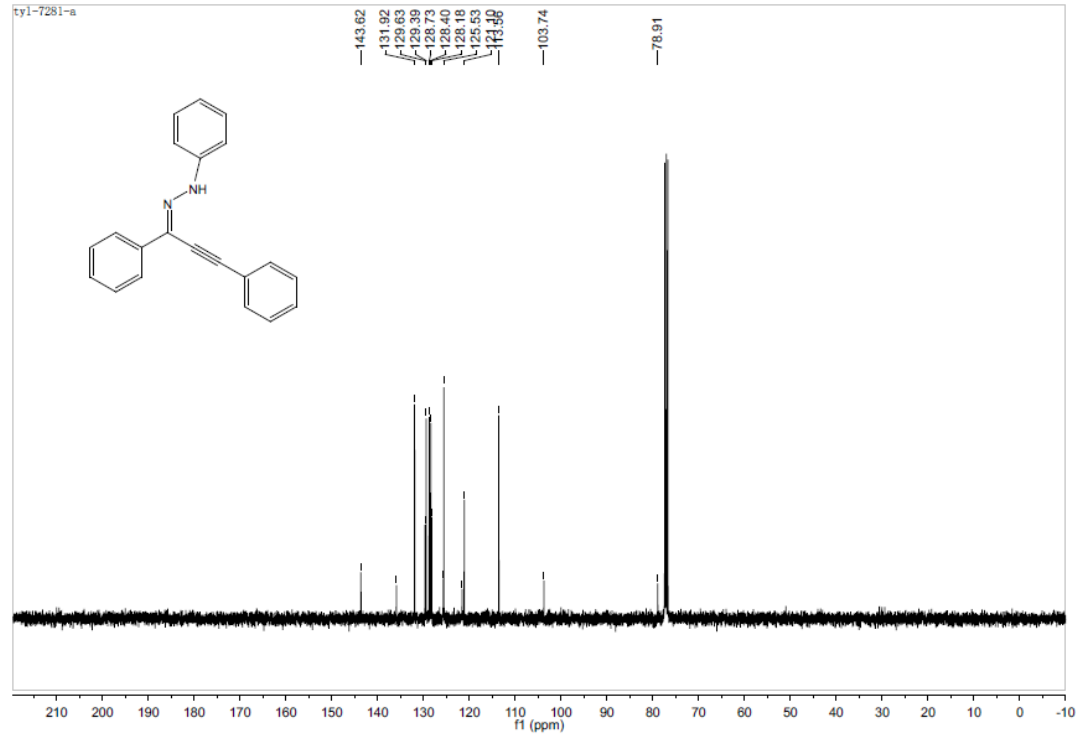
^{1}H NMR and ^{13}C NMR for compound **4a**



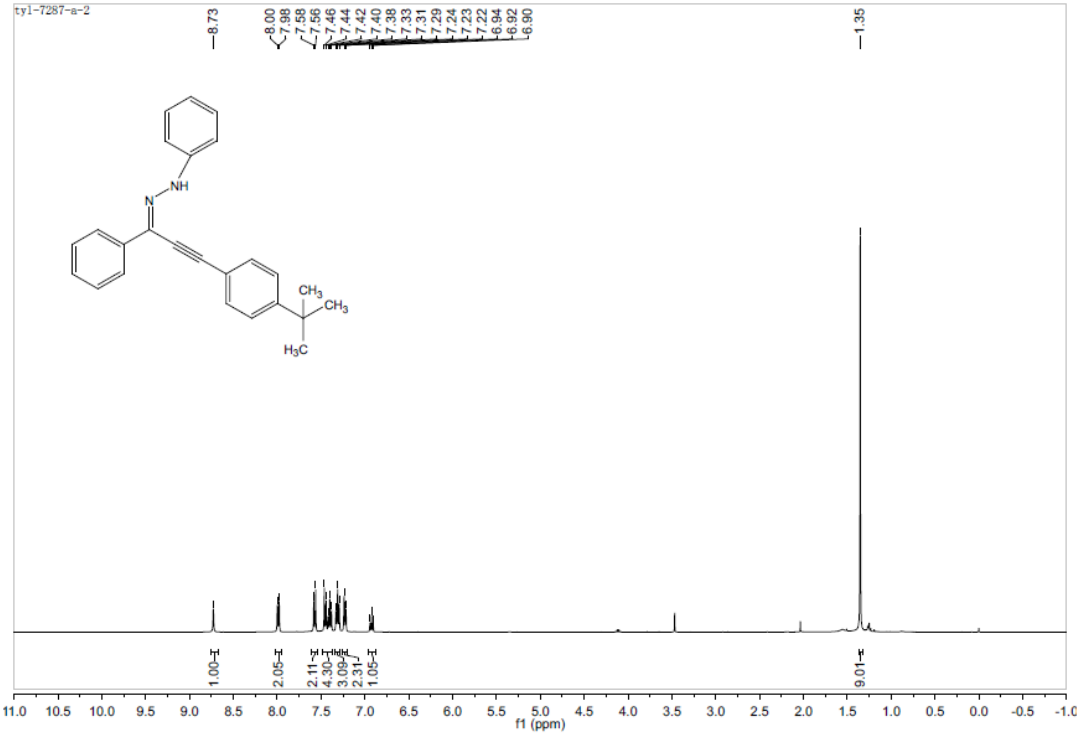


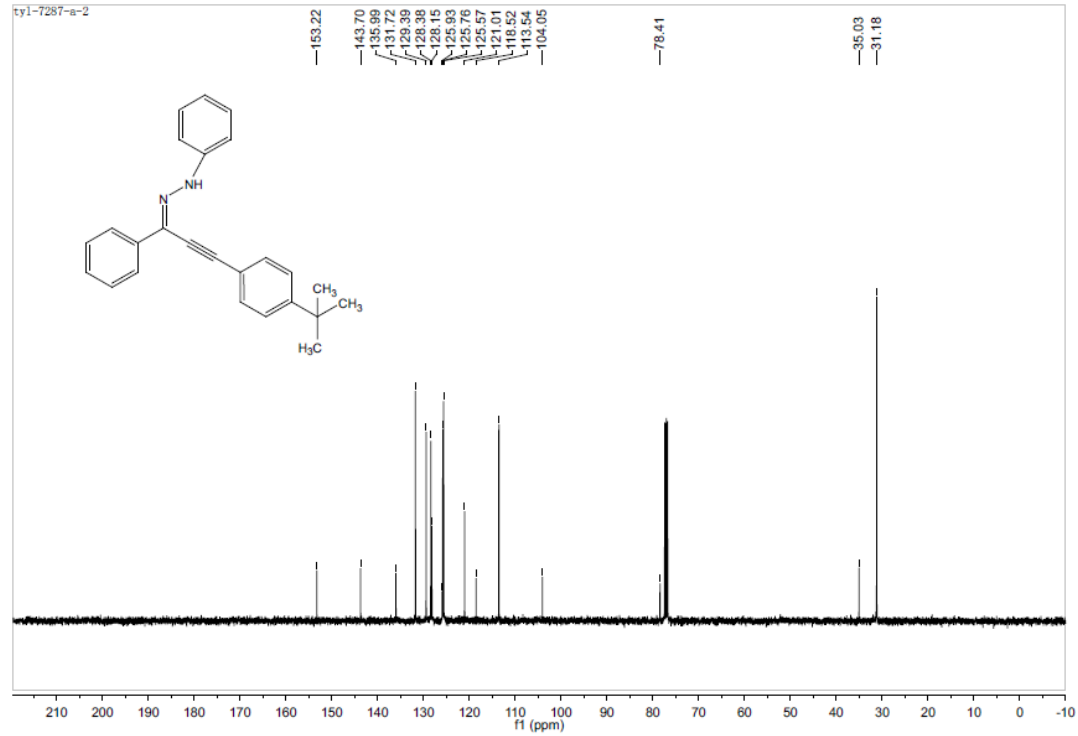
^{1}H NMR and ^{13}C NMR for compound **4b**



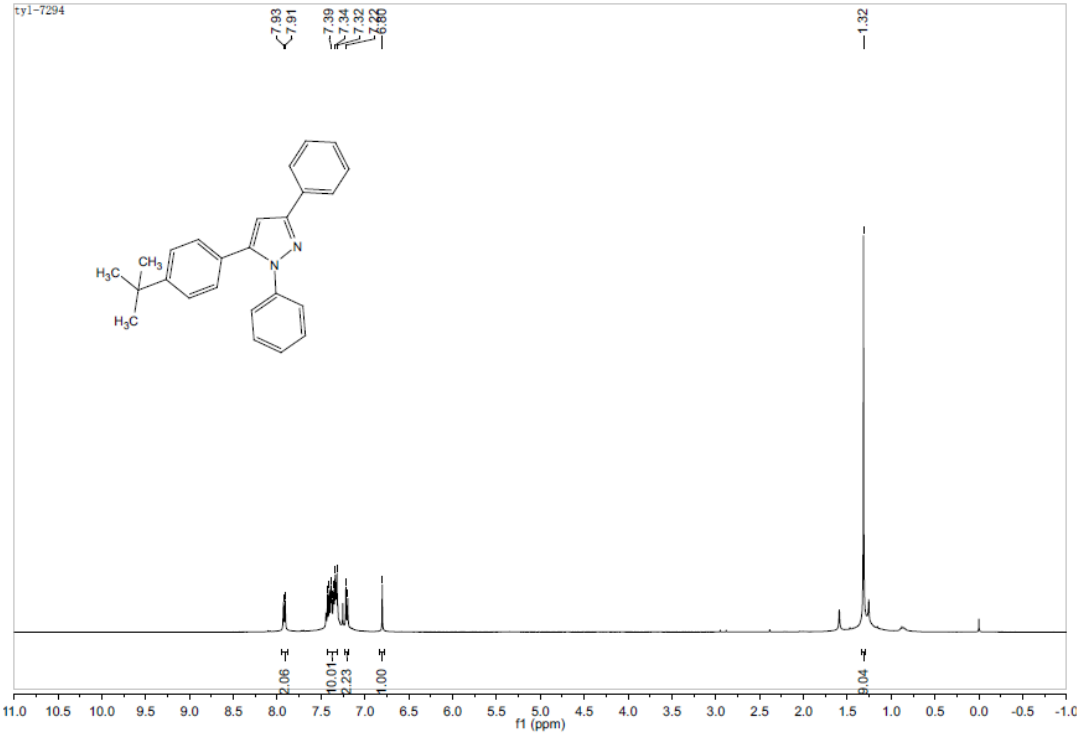


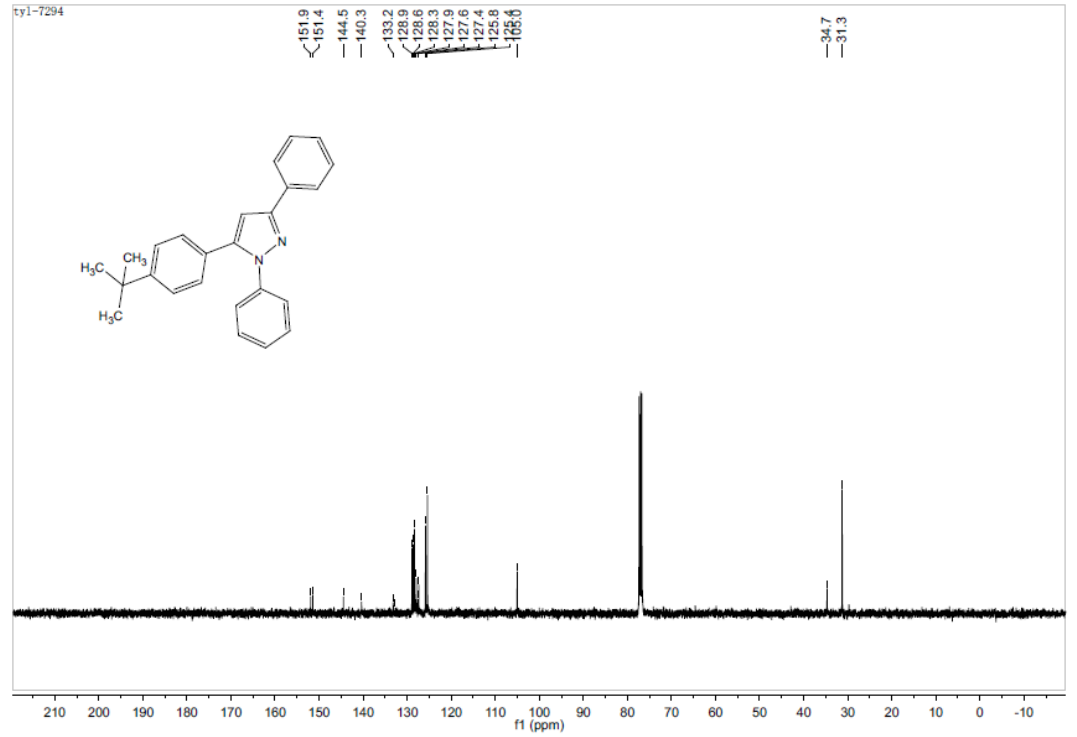
^{1}H NMR and ^{13}C NMR for compound **5a**





^{1}H NMR and ^{13}C NMR for compound **5b**





^{1}H NMR and ^{13}C NMR for compound **6a**

5. X-ray Structure for compound 3ak

The CCDC no. of compound **3ak** is 1548912

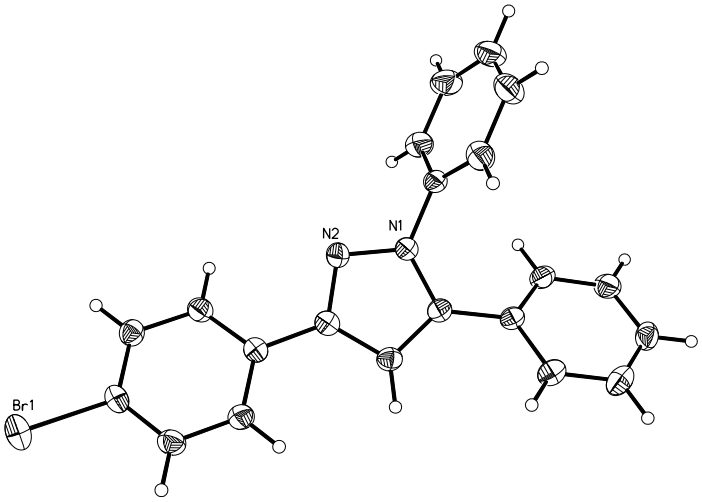


Figure 1 ORTEP representation of compound 3ak. Thermal ellipsoids are drawn at the 50% probability level.