SUPPORTING INFORMATION

Palygorskite-anchored Pd complex catalyzed the coupling reactions of pyrimidin-2-yl sulfonates

Huiying Zhan,*[a] Rongrong Zhou,[a] Xudong Chen,[a] Quanlu Yang,*[a] Hongyan Jiang,[b] Qiong Su,[b] Yanbin Wang,[b] Jia Li,[b] Lan Wu[b] and Shang Wu*[b]

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1. General Information

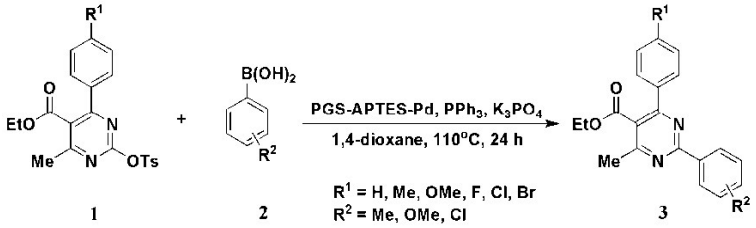
All reactions were carried out under an atmosphere of air atmosphere with dry solvents in flame-dried glassware unless otherwise noted. Binding energy was referred to C_{1s} (284.80 eV). FTIR spectroscopy patterns were obtained on an FT/IR-660 Plus system (Jasco, Tokyo, Japan). The samples were mixed with KBr powders and pressed into a disk suitable for FTIR measurement. The morphologies of the catalyst were examined with field emission scanning electron microscopy (FE-SEM, Ultra Plus, Carl Zeiss). Elemental analysis of the photocatalyst was conducted by an energy-dispersive X-ray spectrometer (EDX) attached to the scanning electron microscope. ^{1}H NMR and ^{13}C NMR data analyses were performed with a Varian Mercury plus-400 instrument unless otherwise specified. $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed.

Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shift for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. N-(pyrimidin-2-yl)-1H-indoles were prepared according to literature procedures[1]. Palladium (II) acetate, alkynes, carboxylic acids, Cu_2O, P ligands and solvents were all purchased from J&K Scientific Ltd.All other reagents were purchased from commercial sources and used as received.

[1] X. C. Wang, G. J. Yang, Z. J. Quan, P. Y. Ji, J. L. Liang and R. G. Ren, *Synlett,* 2010, 1657-1660.

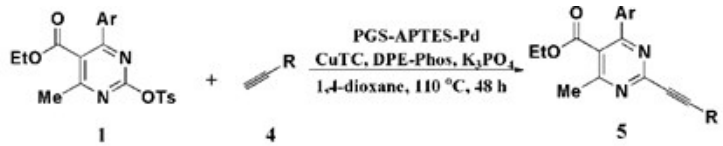
2. General procedure

2.1 General procedure for the Suzuki coupling reaction



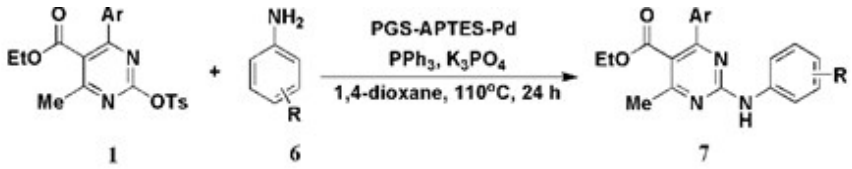
Schlenk tube (10 mL) was equipped with a magnetic stir bar, and **1a** (0.25 mmol), **2a** (1.5 equiv, 0.375 mmol), PPh_3 (20 mol%), PGS-APTES-Pd$(OAc)_2$ (20 mg, Pd 0.35 mol%), K_3PO_4 (2.0 equiv. 0.5 mmol), 1,4-dioxane (5 mL) were added under Ar. The mixture was stirred in at 110 ^oC for 24 h. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford the product.

2.2 General procedure for the Sonogashira coupling reaction



The Schlenk tube (10 mL) was equipped with a magnetic stir bar, and **1a** (0.25 mmol), **4a** (0.50 mmol), K_3P0_4 (3 equiv.), CuTC (10 mol%), DPE-Phos (2 mol%), PGS-APTES-Pd$(OAc)_2$ (Pd 0.463 wt%, 0.0435 mmol/g), 1,4-dioxane (5 mL) were added under Ar. The mixture was stirred in at 110 ^oC for 48 h. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford the product.

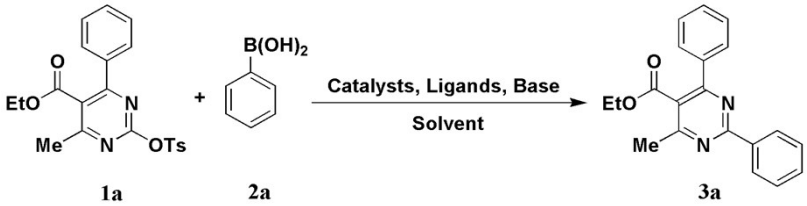
2.3 General procedure for the C-N coupling reaction



Schlenk tube (10 mL) was equipped with a magnetic stir bar, and **1a** (0.25 mmol), **6a** (0.38 mmol), PPh_3 (20 mol%), PGS-APTES-Pd$(OAc)_2$ (20 mg, Pd 0.35 mol%), K_3PO_4 (2.0 equiv. 0.5 mmol), 1,4-dioxane (5 mL) were added under Ar. The mixture was stirred in at 110 ^oC for 24 h. After the reaction was finished, the mixture was concentrated under vacuum to remove 1,4-dioxane, and the residue was purified by chromatography on silica gel to afford the product.

2.4 Optimization for the conditions of Suzuki reaction

Table S1. Optimization for the conditions of Suzuki reaction [a]

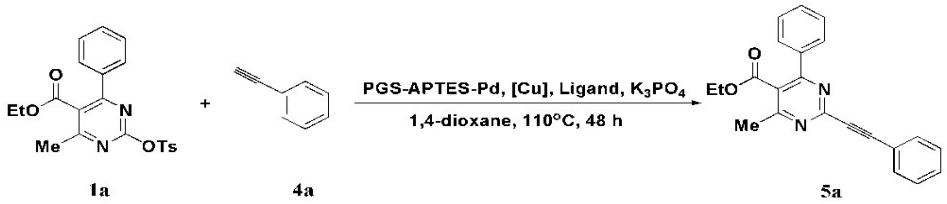


Entry	Catalyst	Base	Ligand	Solvent	Yield[b]
1	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_3PO_4	DPE-Phos	dioxane	72 %
2	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_3PO_4	X-Phos	dioxane	75 %
3	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_3PO_4	PPh_3	dioxane	88 %
4	PGS-APTES-Pd(OAc)$_2$ (20 mg)	NaOAc	PPh_3	dioxane	16 %
5	PGS-APTES-Pd(OAc)$_2$ (20 mg)	TBAB	PPh_3	dioxane	trace
6	PGS-APTES-Pd(OAc)$_2$ (20 mg)	Cs_2CO_3	PPh_3	dioxane	32 %
7	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_2CO_3	PPh_3	dioxane	37 %
8	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_3PO_4	PPh_3	toluene	trace
9	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_3PO_4	PPh_3	CCl_4	---
10	PGS-APTES-Pd(OAc)$_2$ (10 mg)	K_3PO_4	PPh_3	dioxane	57 %
11	PGS-APTES-Pd(OAc)$_2$ (15 mg)	K_3PO_4	PPh_3	dioxane	68 %
12	PGS-APTES-Pd(OAc)$_2$ (25 mg)	K_3PO_4	PPh_3	dioxane	88 %
13	PGS (20 mg)	K_3PO_4	PPh_3	dioxane	---
14	-	K_3PO_4	---	dioxane	---
15	PGS-APTES-Pd(OAc)$_2$ (20 mg)	K_3PO_4	---	dioxane	15 %
16	Pd(OAc)2 (0.35 mol%)	K_3PO_4	PPh_3	dioxane	14 %

[a] Reaction condition: 1a (0.25 mmol), 2a (1.5 equiv.), ligands (20 or 6 mol%), base (2.0 equiv.), catalyst (Pd 0.463 wt %), solvent (5 mL), 110 ^oC, 24 h. [b] Isolated yield of 3a by column chromatography.

2.5 Optimization for the conditions of Sonogashira reaction

Table S2. Optimization for the conditions of Sonogashira reaction [a]



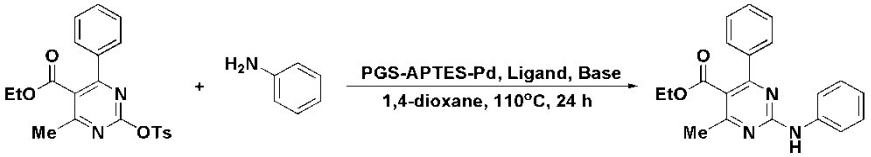
1a 4a 5a

Entry	Catalyst		Ligands	[Cu]	Solvent	Time	Yield[b]
1	PGS-APTES-Pd($OAc)_2$	(30 mg)	X-Phos	CuI	Dioxane	48 h	13 %
2	PGS-APTES-Pd($OAc)_2$	(30 mg)	X-Phos	Cu_2O	Dioxane	48 h	26 %
3	PGS-APTES-Pd($OAc)_2$	(30 mg)	X-Phos	CuTC	Dioxane	48 h	59 %
4	PGS-APTES-Pd($OAc)_2$	(30 mg)	X-Phos	Cu($OAc)_2$	Dioxane	48 h	n.d.[c]
5	PGS-APTES-Pd($OAc)_2$	(30 mg)	PPh_3	CuTC	Dioxane	48 h	22 %
6	PGS-APTES-Pd($OAc)_2$	(30 mg)	DPE-Phos	CuTC	Dioxane	48 h	81 %
7	PGS-APTES-Pd($OAc)_2$	(30 mg)	DPE-Phos	CuTC	Toluene	48 h	51 %
8	PGS-APTES-Pd($OAc)_2$	(30 mg)	DPE-Phos	CuTC	Xylene	48 h	67 %
9	PGS-APTES-Pd($OAc)_2$	(10 mg)	DPE-Phos	CuTC	Dioxane	48 h	33 %
10	PGS-APTES-Pd($OAc)_2$	(20 mg)	DPE-Phos	CuTC	Dioxane	48 h	80 %
11	PGS-APTES-Pd($OAc)_2$	(20 mg)	DPE-Phos	CuTC	Dioxane	12 h	32 %
12	PGS-APTES-Pd($OAc)_2$	(20 mg)	DPE-Phos	CuTC	Dioxane	24 h	68 %
13	PGS-APTES-Pd($OAc)_2$	(20 mg)	DPE-Phos	CuTC	Dioxane	72 h	79 %
14	-		-	CuTC	Dioxane	48 h	n.d.[c]
15	PGS-APTES-Pd($OAc)_2$	(20 mg)	-	CuTC	Dioxane	48 h	18 %

[a] Reaction condition: 1a (0.25 mmol), 4a (0.50 mmol), K_3P0_4 (equiv.), [Cu] (10 mol%), ligands (6 mol% PPh_3, 2 mol% DPE-Phos or X-phos), PGS-APTES-Pd($OAc)_2$ (Pd 0.463 wt%, 0.0435 mmol/g), solvent (5 mL); temperature: 110 ^oC for dioxane and toluene as solvent, 140 ^oC for xylene. [b] Isolated yield of 5a by column chromatography. [c] n.d. = No reaction was detected by TLC and ^1H NMR.

2.6 Optimization for the conditions of C-N coupling reactions

Table S3. Optimization for the conditions of C-N coupling reactions [a]

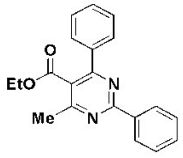


1a 6a 7a

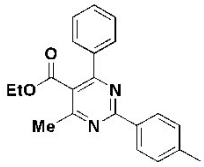
Entry	Base	Ligands	Yield [b]
1	DBU	PPh_3	13 %
2	Et_3N	PPh_3	45 %
3	K_2CO_3	PPh_3	21 %
4	Cs_2CO_3	PPh_3	17 %
5	K_3PO_4	DPE-Phos	67 %
6	K_3PO_4	X-Phos	54 %
7	K_3PO_4	-	41 %
8	K_3PO_4	PPh_3	76 %

[a] Reaction condition: 1a (0.25 mmol), 6a (0.38 mmol), PGS-APTES-Pd$(OAc)_2$ (Pd 0.463 wt%, 0.0435 mmol/g), ligands (20 mol% PPh_3, 6 mol% DPE-Phos or X-phos), base (2.0 equiv.), 1,4-dioxane (5 mL), 110 ^oC, 24 h. [b] Isolated yield of 7a by column chromatography.

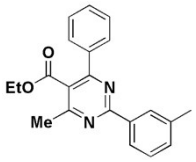
3. Characterization data for the products



Ethyl 4-methyl-2,6-diphenylpyrimidine-5-carboxylate (3a): White solid; m.p. 66-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62- 8.59 (dd, *J* = 2.8 Hz, 6.4 Hz, 2H), 7.81-7.79 (m, 2H), 7.54-7.52 (m, 6H), 4.28-4.22 (q, *J* = 7.2 Hz, 2H), 2.75 (s, 3H), 1.14-1.10 (t, J= 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ= 168.5, 165.4, 163.7, 163.7, 138.2, 137.1, 131.1, 130.0, 128.7, 128.6, 128.5, 128.5, 123.4, 61.8, 22.9, 13.7 ppm.

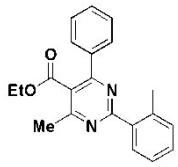


Ethyl 4-methyl-6-phenyl-2-p-tolylpyrimidine-5-carboxylate (3b): White solid; m.p. 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49-8.47 (d, *J* = 8.2 Hz, 2H), 7.79-7.77 (m, 2H), 7.54-7.46 (m, 3H), 7.33-7.31 (d, *J* = 8.1 Hz, 3H), 4.26-4.21 (q, *J* = 7.2 Hz, 2H), 2.72 (s, 3H), 2.46 (s, 3H), 1.12-1.10 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 165.3, 163.7, 163.6, 141.5, 138.3, 134.4, 130.0, 129.3, 128.7, 128.5, 128.5, 123.1, 61.8, 22.7, 21.6, 13.7 ppm.

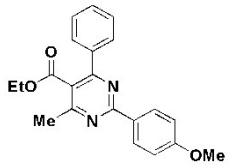


Ethyl 4-methyl-6-phenyl-2-m-tolylpyrimidine-5-carboxylate (3c): White solid, m.p. 69- 71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27- 8.29 (d, *J* = 7.4 Hz, 2H), 7.69-7.67 (dd, *J* = 6.5 Hz, 3.1 Hz, 2H), 7.42-7.39 (m, 3H), 7.33-7.29(t, *J* = 7.9 Hz, 1H), 7.25-7.23(t, *J* = 7.5 Hz, 1H), 4.16-4.11 (q, *J* = 7.2 Hz,

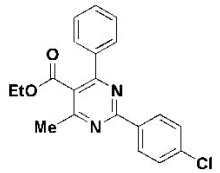
2H), 2.62 (s, 3H), 2.38 (s, 3H), 1.02-0.99 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 165.3, 163.8, 163.3, 138.2, 138.1, 137.0, 131.8, 129.9, 129.1, 128.5, 128.4, 125.8, 123.3, 61.7, 22.9, 21.5, 13.6 ppm.



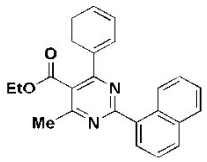
Ethyl 4-methyl-6-phenyl-2-o-tolylpyrimidine-5-carboxylate (3d): White solid; m.p. 77-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.79 (m, 1H), 7.73-7.57 (m, 2H), 7.46- 7.33 (m, 3H), 7.32-7.19 (m, 3H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 2.55 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.36, 166.75, 165.00, 163.12, 137.93, 137.62, 137.45, 131.31, 130.55, 129.97, 129.65, 128.48, 128.39, 125.93, 122.77, 61.86, 22.78, 21.32, 13.66 ppm.



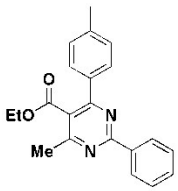
Ethyl 2-(4-methoxyphenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3e): White solid; m.p. 57-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49-8.39 (m, 2H), 7.72-7.60 (m, 2H), 7.46-7.32 (m, 3H), 6.95-6.85 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.59 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.54, 165.23, 163.53, 163.40, 162.13, 141.51, 138.41, 134.4, 130.34, 129.82, 128.39, 122.57, 113.79, 61.63, 55.33, 22.84, 13.63 ppm.



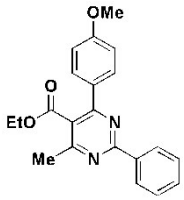
Ethyl 2-(4-chlorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3f): White solid; m.p. 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51-8.36 (m, 2H), 7.80-7.56 (m, 2H), 7.52-7.29 (m, 5H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.25, 165.48, 163.63, 162.64, 138.04, 137.29, 135.59, 130.00, 129.96, 128.70, 128.44, 128.41, 123.52, 61.80, 22.80, 13.64 ppm.



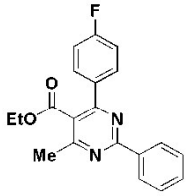
Ethyl 4-methyl-2-(naphthalen-1-yl)-6-phenylpyrimidine-5-carboxylate (3g): White solid; m.p. 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62-8.60 (m, 1H), 8.06 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.87-7.80 (m, 1H), 7.77-7.65 (m, 2H), 7.59-7.31 (m, 6H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.69 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.26, 166.35, 165.29, 163.53, 137.85, 135.41, 134.05, 130.96, 130.73, 130.06, 129.58, 128.55, 128.42, 126.85, 125.85, 125.70, 125.16, 123.18, 109.69, 61.93, 22.86, 13.67 ppm.



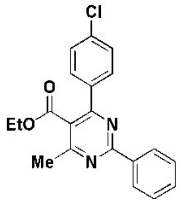
Ethyl 4-methyl-2-phenyl-6-p-tolylpyrimidine-5-carboxylate (3h): White solid; m.p. 66-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60-8.38 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.46-7.35 (m, 3H), 7.23-7.17 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.34 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.63, 165.14, 163.59, 163.34, 140.23, 137.23, 135.30, 130.91, 129.17, 128.58, 128.44, 128.41, 123.14, 61.72, 22.81, 21.38, 13.73 ppm.



Ethyl 4-(4-methoxyphenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3i): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54-8.43 (m, 2H), 7.77-7.62 (m, 2H), 7.45-7.36 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 2.56 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.72, 164.98, 163.36, 162.53, 161.17, 137.14, 130.82, 130.32, 130.01, 128.44, 128.36, 122.68, 113.80, 61.66, 55.24, 22.71, 13.73 ppm.

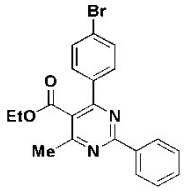


Ethyl 4-(4-fluorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3j): White solid; m.p. 85-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.77-7.62 (m, 2H), 7.48-7.33 (m, 3H), 7.11-7.06 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.33, 165.46, 165.20, 163.65, 162.71, 162.28, 136.97, 134.28, 131.10, 130.58, 130.50, 128.58, 128.50, 123.16, 115.66, 115.44, 61.84, 22.82, 13.74 ppm.

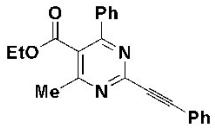


Ethyl 4-(4-chlorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3k): White solid; m.p. 83-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52-8.41 (m, 2H), 7.69-7.59 (m, 2H), 7.47-7.34 (m, 5H), 4.16

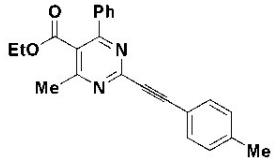
(q, *J* = 7.2 Hz, 2H), 2.62 (s, 3H), 1.07 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.15, 165.55, 163.66, 162.31, 136.81, 136.56, 136.36, 131.20, 129.85, 128.73, 128.63, 128.52, 123.19, 61.92, 22.79, 13.74 ppm.



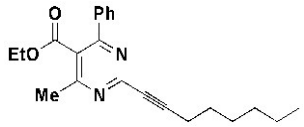
Ethyl 4-(4-bromophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3l): White solid; m.p. 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.47-7.37 (m, 5H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.52, 165.39, 163.06, 137.14, 137.00, 131.02, 128.94, 128.87, 128.60, 128.49, 127.78, 127.18, 127.16, 123.22, 61.82, 22.88, 13.72 ppm.



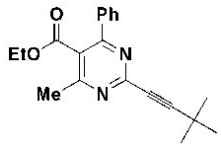
Ethyl 4-methyl-6-phenyl-2-(phenylethynyl)pyrimidine-5-carboxylate (5a): White solid; m.p. 161-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.66 (m, 4H), 7.48-7.39 (m, 3H), 7.38-7.27 (m, 3H), 4.22- 4.17 (q, *J* = 8.0 Hz,, 2H), 2.67 (s, 3H), 1.06 (t, *J* = 8.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.53, 165.59, 164.08, 152.38, 137.19, 132.85, 132.54, 130.40, 130.01, 129.91, 129.52, 128.75, 126.53, 128.38, 128.17, 124.19, 121.25, 88.53, 88.09, 61.98, 22.47, 13.48 ppm.



Ethyl 4-Methyl-6-phenyl-2-(p-tolylethynyl)pyrimidine-5-carboxylate (5b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65-7.56 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.45-7.33 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.12 (q, *J* = 7.2 Hz,, 2H), 2.58 (s, 3H), 2.30 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.57, 165.54, 164.05, 152.47, 140.17, 137.20, 132.65, 130.16, 129.13, 128.54, 128.29, 124.00, 118.09, 89.07, 87.66, 61.96, 22.61, 21.63, 13.58 ppm.

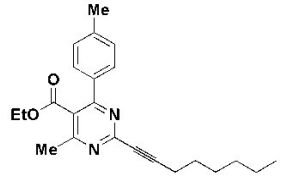


Ethyl 4-Methyl-2-(oct-1-ynyl)-6-phenylpyrimidine-5-carboxylate (5c): Yellow oil. ^{1}H NMR (400 MHz, CDCl3): δ = 7.63–7.49 (m, 2H), 7.47–7.28 (m, 3 H), 4.10 (q, *J* = 7.2 Hz, 2 H), 2.54 (s, 3 H), 2.40 (t, *J* = 7.3 Hz, 2 H), 1.65–1.53 (m, 2 H), 1.43–1.33 (m, 2 H),1.28–1.19 (m, 4 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 0.81 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl3): δ = 167.58, 165.39, 163.91, 152.27, 137.18, 130.06, 128.44, 128.25, 123.95, 91.65, 79.93, 61.87,31.25, 28.70, 27.89, 22.52, 22.43, 19.41, 13.99, 13.53 ppm.

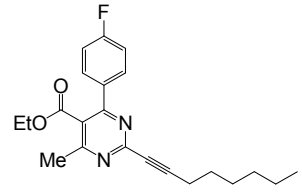


Ethyl 2-(3,3-Dimethylbut-1-ynyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (5d): White solid; m.p. 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57-7.36 (m, 2H), 7.46-7.25 (m, 3H), 4.10 (q, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.30 (s, 9H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.61, 165.29, 163.90, 152.51, 137.33, 129.99, 128.43, 128.29, 123.94, 98.45, 78.87, 61.82, 30.38,

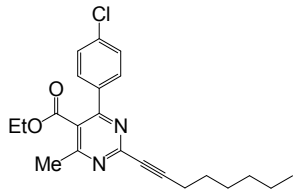
27.90, 22.52, 13.54 ppm.



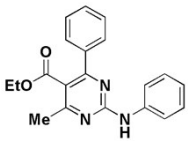
Ethyl 4-Methyl-2-(oct-1-ynyl)-6-p-tolylpyrimidine-5-carboxylate (5e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, *J* =8.2, 2.0 Hz, 2 H), 7.18–7.14 (m, 2H), 4.13 (dd, *J* = 7.2, 2.9 Hz, 2H), 2.52 (d, *J* = 2.5 Hz, 3 H), 2.42–2.37 (m, 2H), 2.31 (d, *J* =2.6 Hz, 3H), 1.64–1.54 (m, 2 H), 1.38 (dd, *J* = 13.1, 6.4 Hz, 2H),1.28–1.16 (m, 4H), 1.05–1.01 (m, 3H), 0.82–0.79 (m, 3 H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.83, 165.15, 163.72, 152.25,140.42, 134.27, 129.17, 128.28, 123.80, 91.41, 80.03, 61.86, 31.27,28.71, 27.92, 22.50, 22.45, 21.35, 19.43, 14.00, 13.64 ppm.



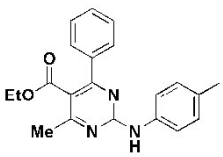
Ethyl 4-(4-Fluorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5f): Yellow oil (331 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.51 (m, 2H), 7.04 (dd, *J* = 11.9, 5.3 Hz, 2H), 3.71–3.55 (m, 3H),2.39 (t, *J* = 7.3 Hz, 2H), 1.67–1.50 (m, 2H), 1.41–1.32 (m, 2H),1.23 (t, *J* = 6.9 Hz, 9H), 0.80 (d, *J* = 1.2 Hz, 3H) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ = 173.16, 168.23, 165.03, 162.54, 162.20,152.74, 133.33, 130.29, 130.21, 122.79, 115.67, 115.66, 115.44,90.99, 80.23, 52.56, 33.35, 31.14, 28.60, 27.83, 22.33, 21.45, 19.37,13.86 ppm.



Ethyl 4-(4-Chlorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5g): Yellow oil (350 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.45 (m, 2H), 7.42–7.31 (m, 2H), 4.11–4.17 (m, 2H), 2.54 (d, *J* = 1.2 Hz, 3H), 2.40 (t, J = 7.3 Hz, 2H), 1.65–1.54 (m, 2H), 1.43–1.34 (m, 2H), 1.28–1.19 (m, 4H), 1.07–1.03 (m, 3H), 0.85–0.76(m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.43, 165.64,162.59, 152.33, 136.52, 135.59, 129.73, 128.75, 123.84, 92.04, 79.86,62.07, 31.27, 29.65, 28.72, 27.90, 22.56, 22.45, 19.44, 14.01,13.67 ppm.

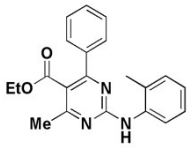


Ethyl 4-methyl-6-phenyl-2-(phenylamino)pyrimidine-5-carboxylate (7a): Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (s, 1H), 7.61-7.45 (m, 4H), 7.38-7.27 (m, 3H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.92 (dd, *J* = 11.4, 4.2 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.41, 167.17, 165.73, 158.71, 139.01, 138.52, 129.60, 128.71, 128.23, 127.96, 122.57, 119.16, 116.93, 61.19, 22.88, 13.46 ppm.

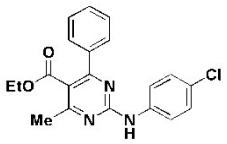


Ethyl 4-methyl-6-phenyl-2-(*p*-tolylamino)pyrimidines-5-carboxylate (7b): Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.64-7.56 (m, 2H), 7.50 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.42 (dd, *J* = 4.3,

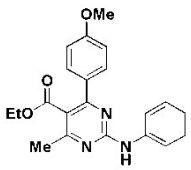
2.6 Hz, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 4.12-4.06 (m, 2H), 2.55 (d, *J* = 1.8 Hz, 3H), 2.30 (s, 3H), 0.99-0.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ =168.48, 167.17, 165.76, 158.79, 138.62, 136.38, 132.19, 129.55, 129.22, 128.21, 127.96, 119.42, 116.64, 61.15, 22.91, 20.70, 13.47 ppm.



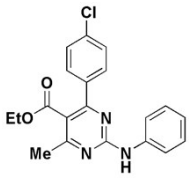
Ethyl 4-methyl-6-phenyl-2-(*o*-tolylamino)pyrimidine-5-carboxylate (7c): Brown oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.1 Hz, 1H), 7.61-7.46 (m, 2H), 7.35 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.20-7.10 (m, 2H), 6.97 (dd, *J* = 8.5, 11.1 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 2.26 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.51, 167.26, 165.88, 159.09, 138.59, 136.98, 130.40, 129.63, 128.30, 127.99, 126.50, 121.51, 117.02, 61.23, 22.92, 18.16, 13.53 ppm.



Ethyl 2-(4-chlorophenylamino)-4-methyl-6-phenylpyrimidine-5-carboxylate (7d): Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.97 (s, 1H), 7.71-7.57 (m, 2H), 7.56-7.47 (m, 2H), 7.41 (d, *J* = 5.8 Hz, 3H), 7.24-7.17 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 0.98 (dd, *J* = 7.7, 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.28, 167.24, 165.70, 158.53, 138.30, 137.63, 129.75, 128.60, 128.29, 127.95, 127.32, 120.40, 117.25, 61.30, 22.88, 13.52 ppm.



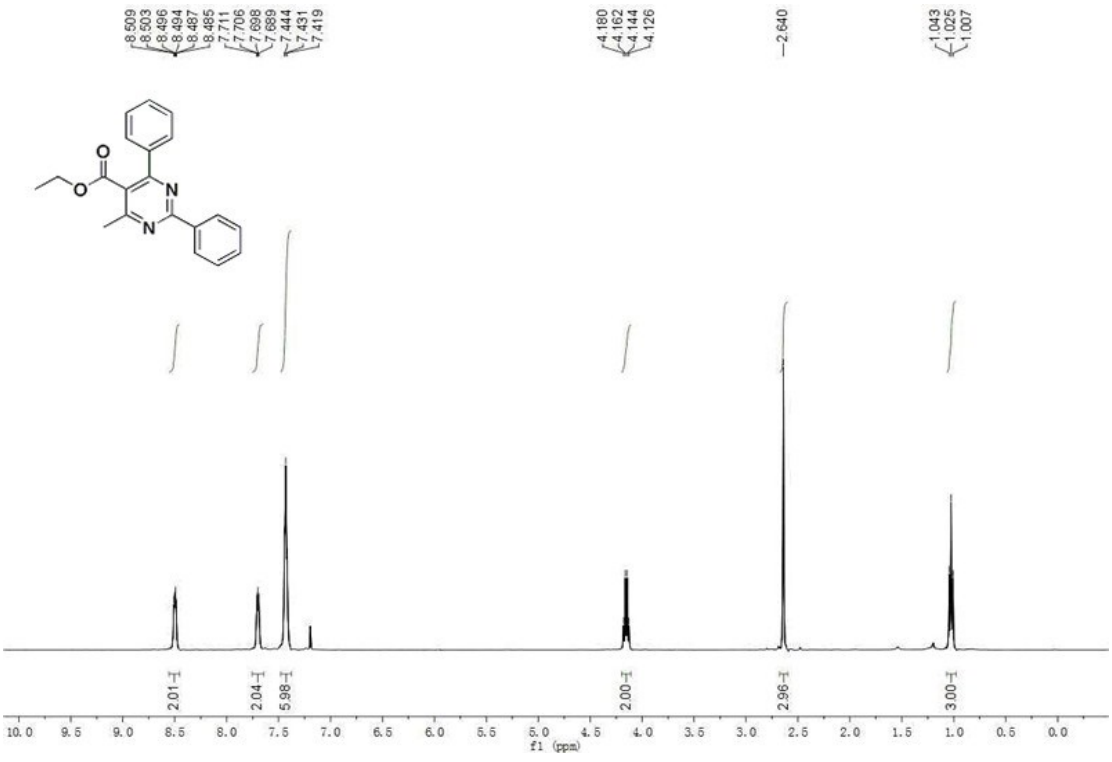
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-(phenylamino)pyrimidine-5-carboxylate (7e): Claybank oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 10.1 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 4H), 7.06-6.95 (m, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.68-6.61 (m, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 3.52 (s, 3H), 2.24 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.90, 166.83, 164.88, 161.05, 158.78, 139.26, 130.80, 129.77, 128.75, 122.55, 119.27, 116.67 , 113.75, 61.30, 55.28, 22.83, 13.75 ppm.

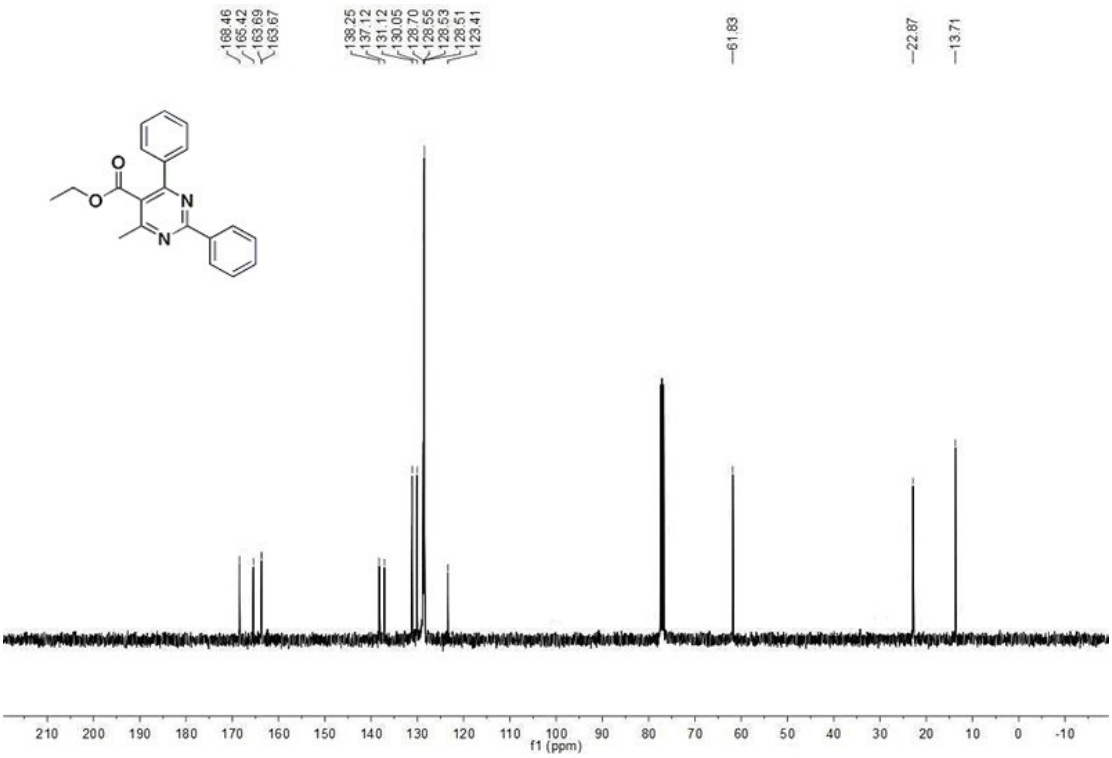


Ethyl 4-(4-chlorophenyl)-6-methyl-2-(phenylamino)pyrimidine-5-carboxylate (7f): White solid, m.p. 129-130 ^{o}C, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.54 (s, 1H), 7.46-7.27 (m, 4H), 7.19-7.14 (m, 2H), 7.09-7.04 (m, 2H), 6.87-6.75 (m, 1H), 3.98-3.86 (m, 2H), 2.42-2.26 (m, 3H), 0.92- 0.74 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.38, 167.60, 164.61, 158.92, 139.08, 137.15, 136.02, 129.62, 128.93, 128.65, 122.98, 119.50, 116.97, 61.52, 23.12, 13.78 ppm.

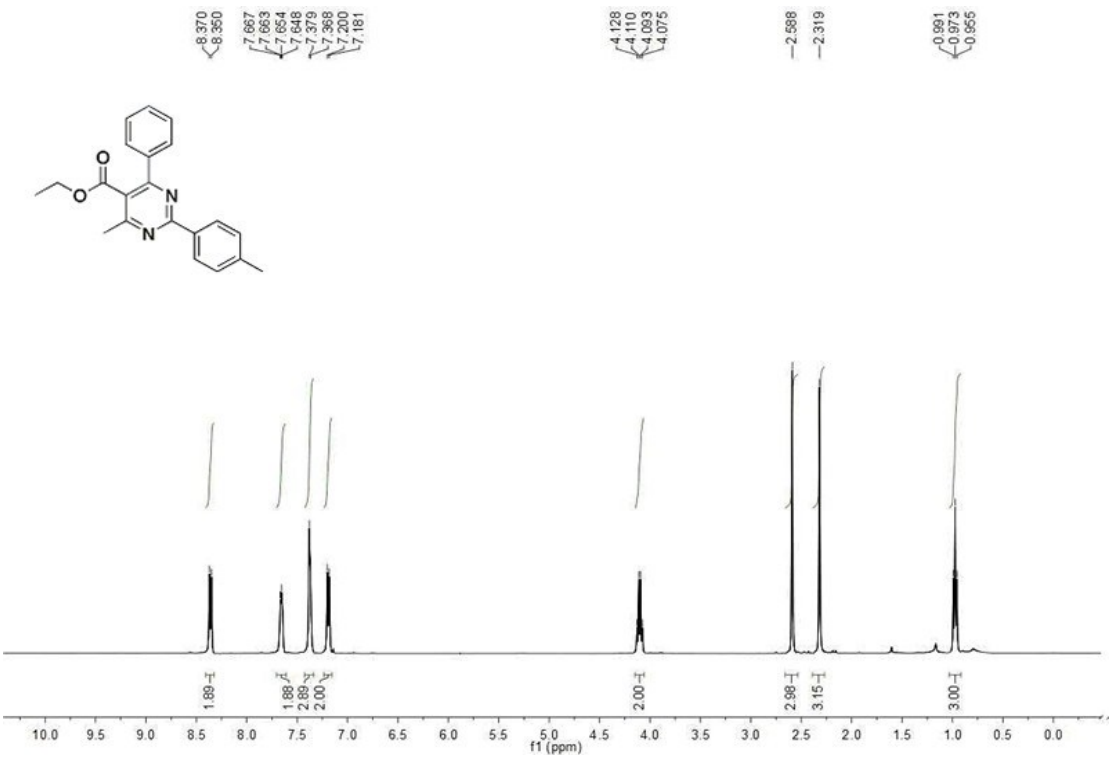
4. NMR Spectra for products

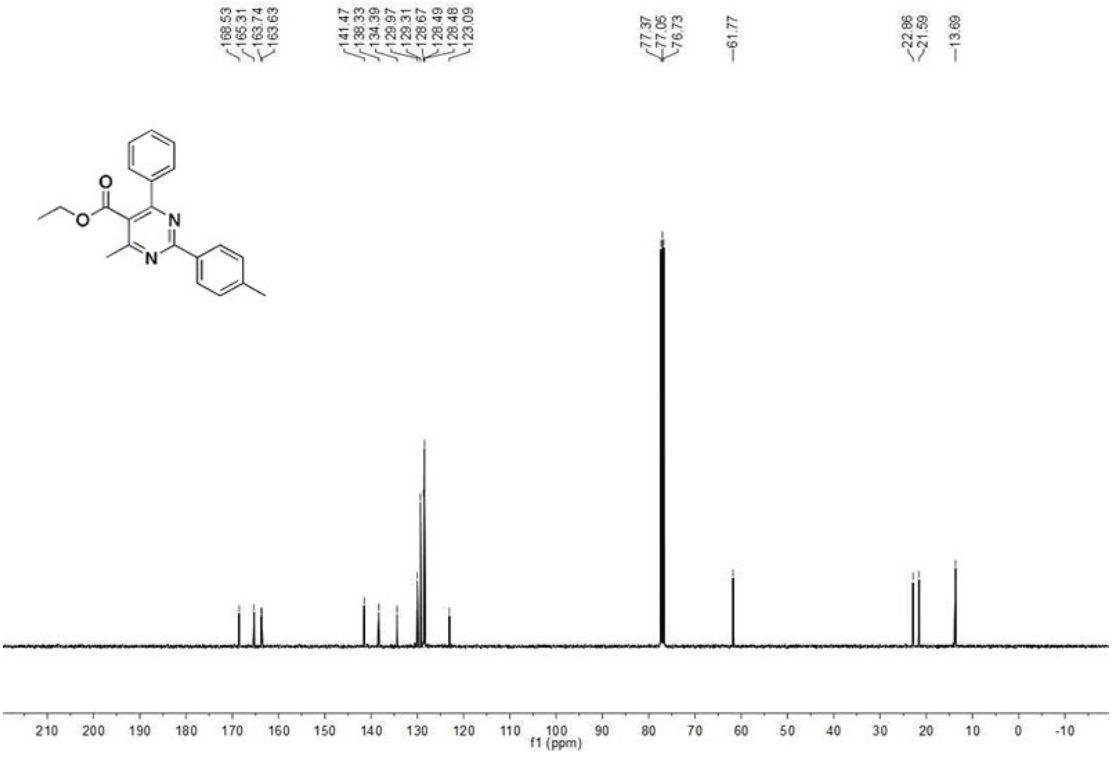
^{1}H and ^{13}C Spectra of compound 3a ($CDCl_3$, 400 MHz)



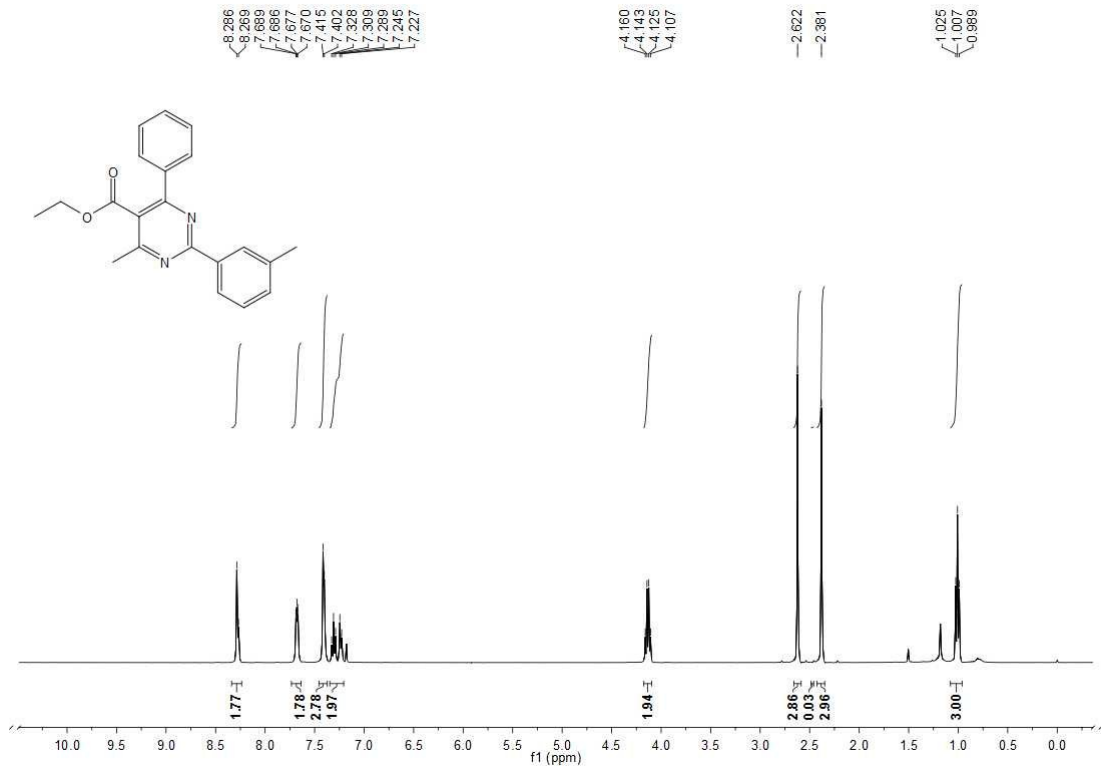


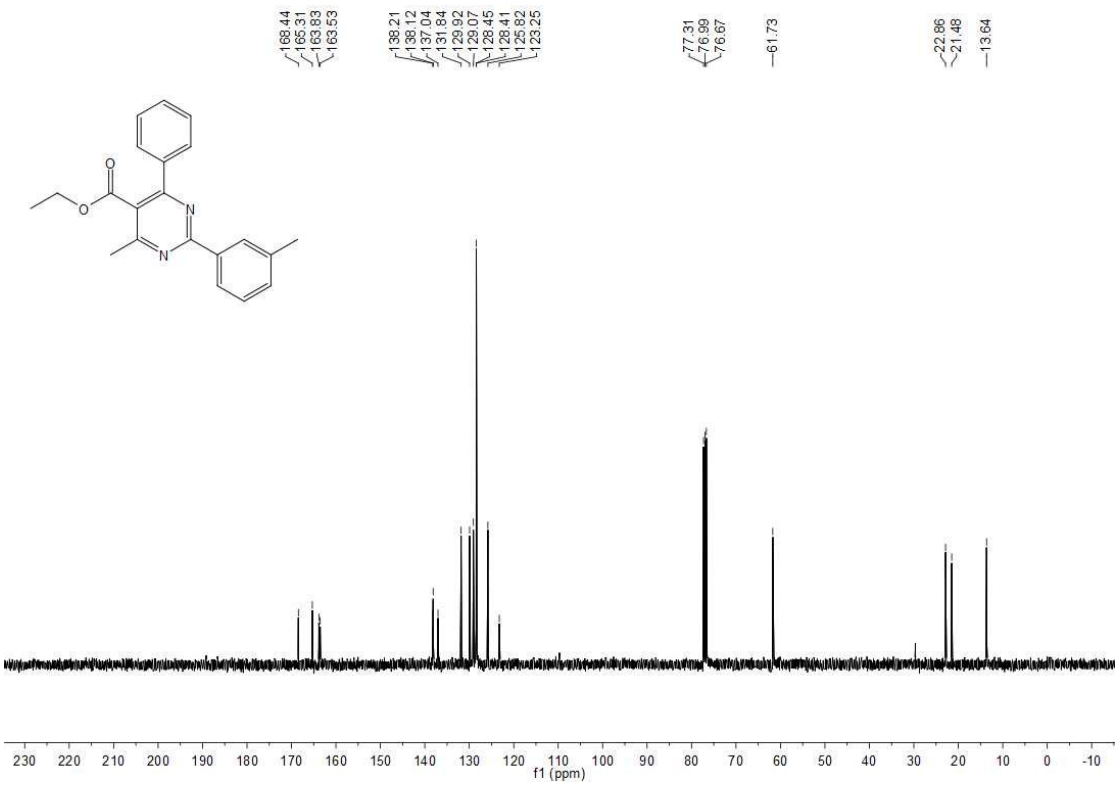
^{1}H and ^{13}C Spectra of compound 3b ($CDCl_3$, 400 MHz)



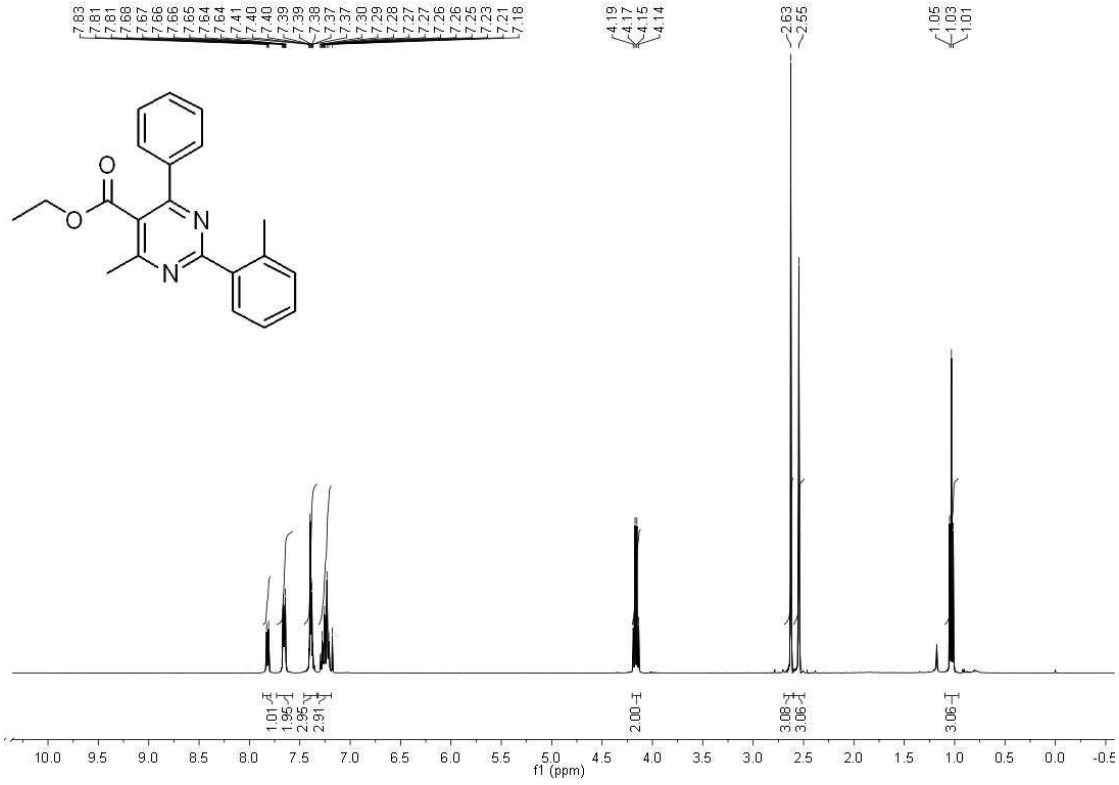


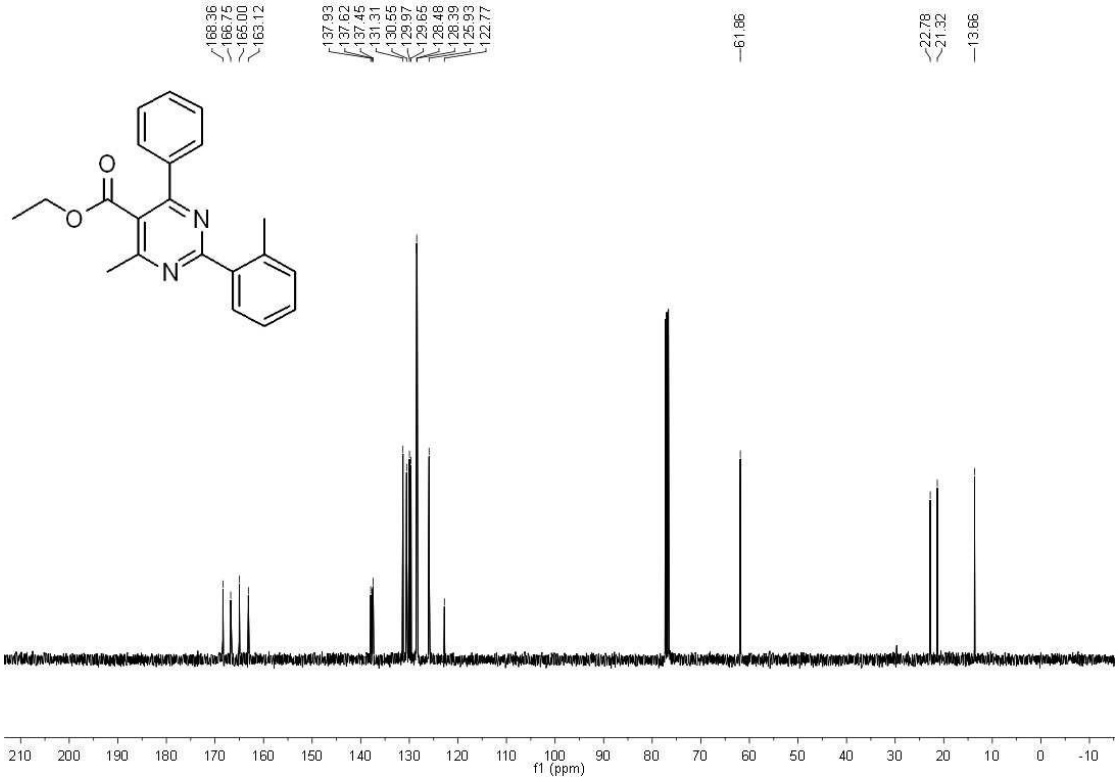
^{1}H and ^{13}C Spectra of compound 3c ($CDCl_3$, 400 MHz)



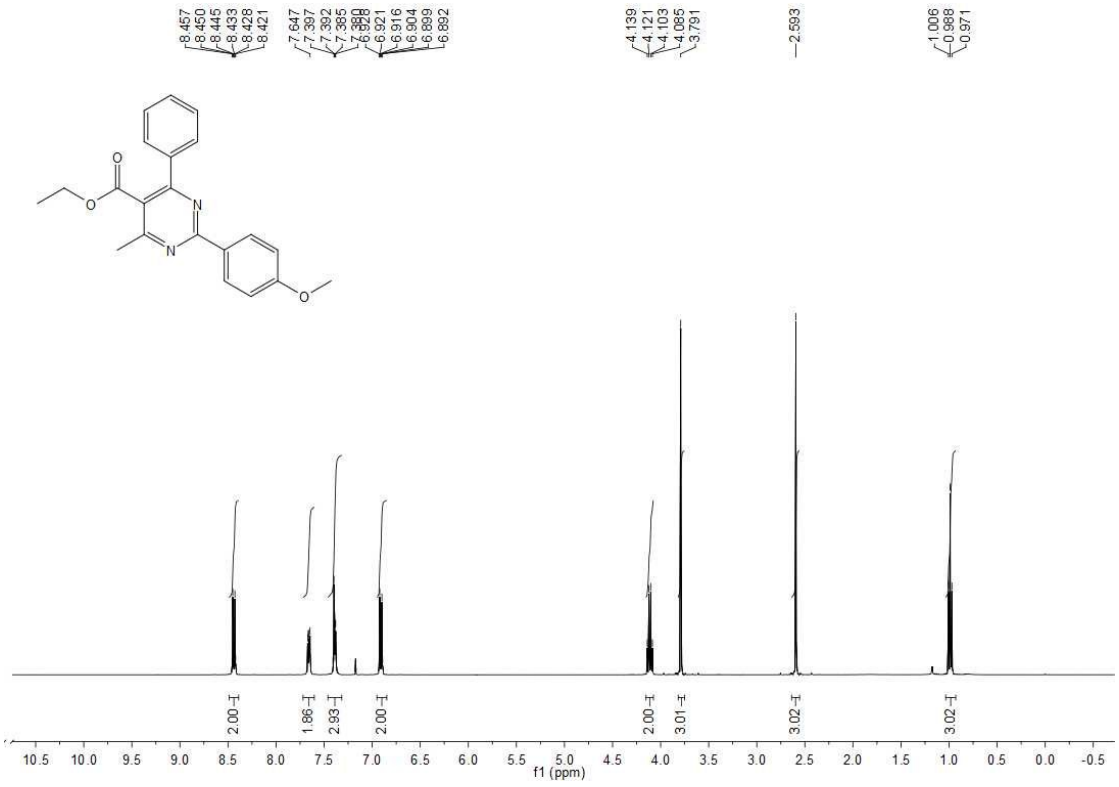


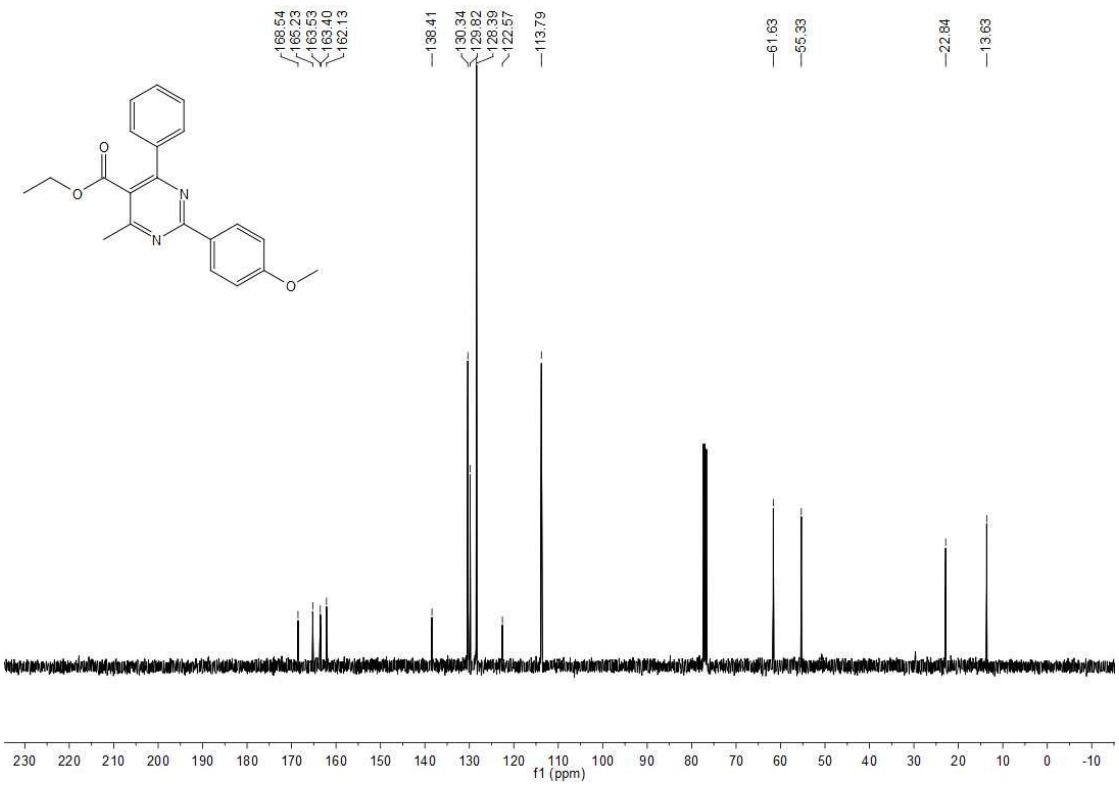
^{1}H and ^{13}C Spectra of compound 3d ($CDCl_3$, 400 MHz)



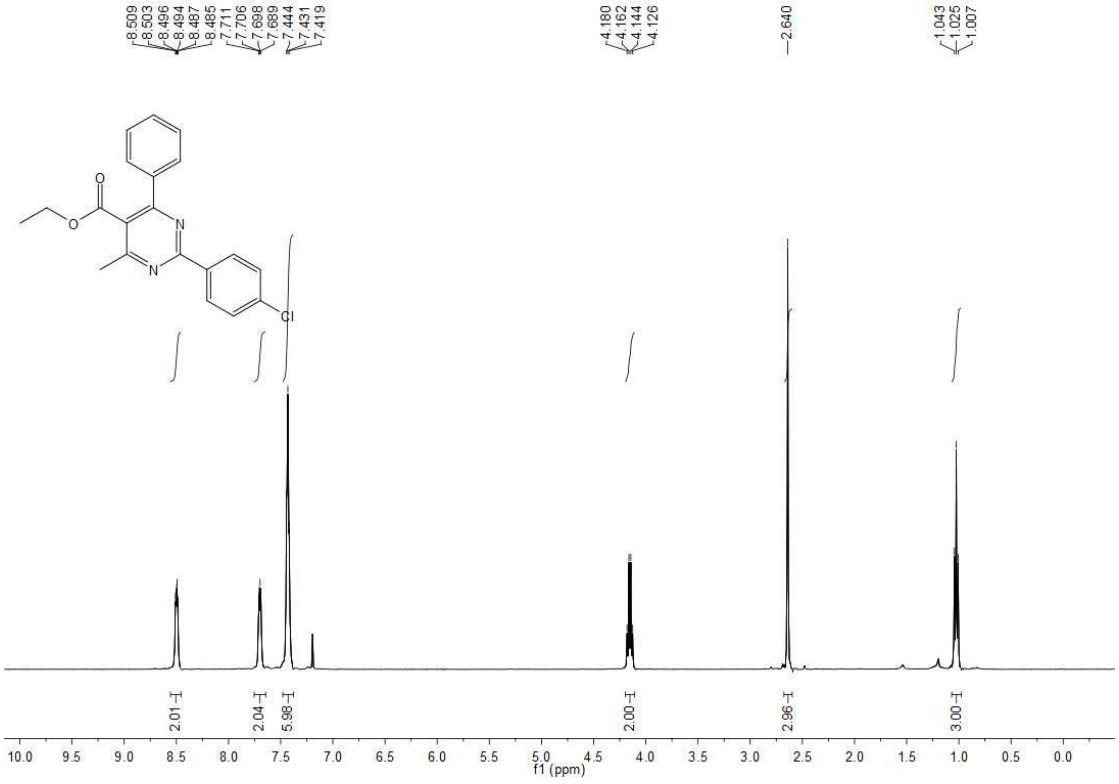


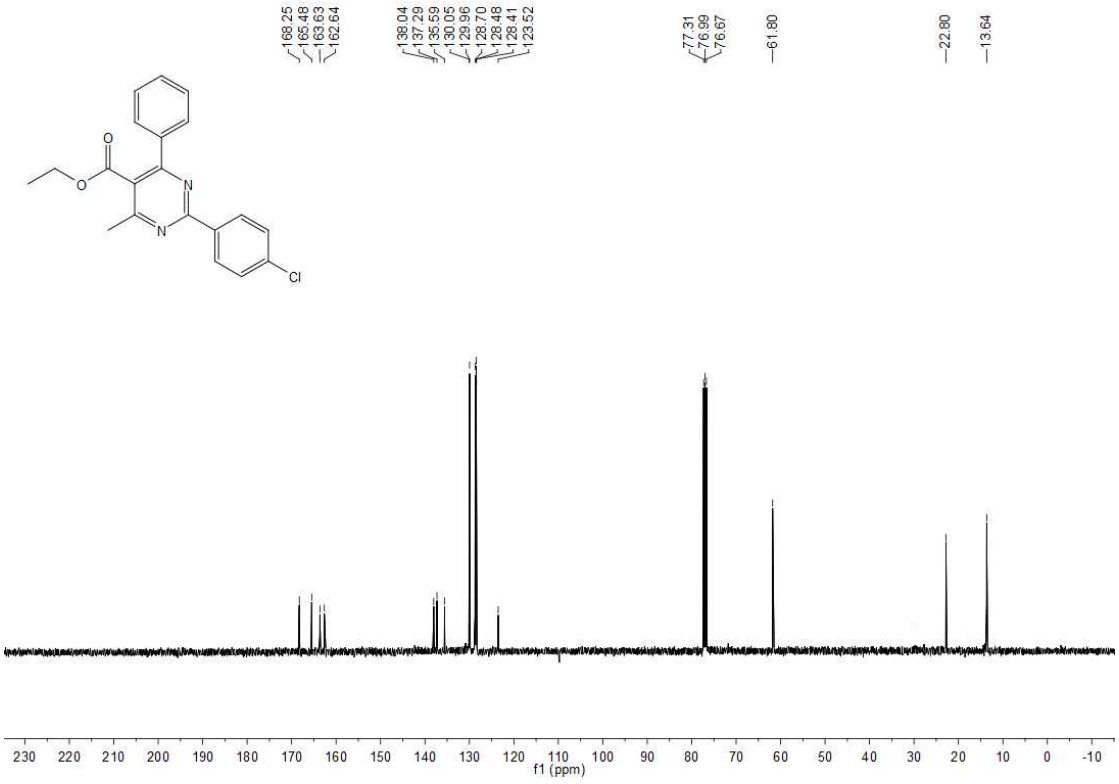
^{1}H and ^{13}C Spectra of compound 3e ($CDCl_3$, 400 MHz)



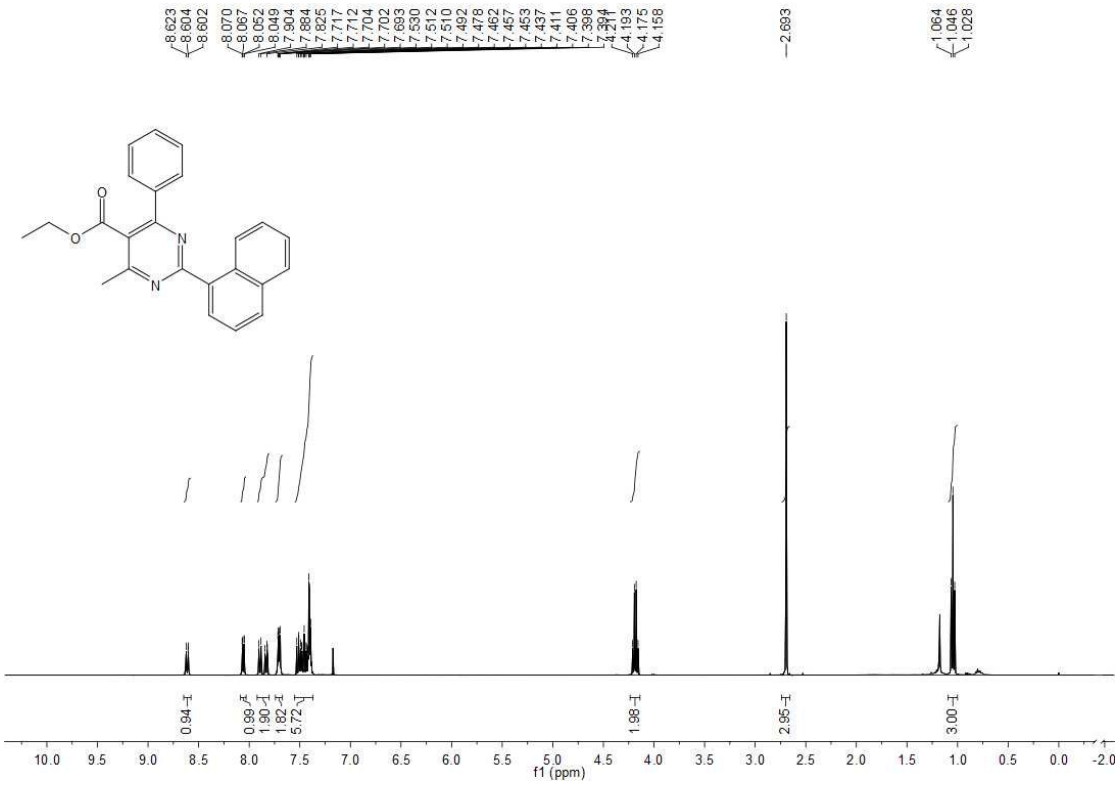


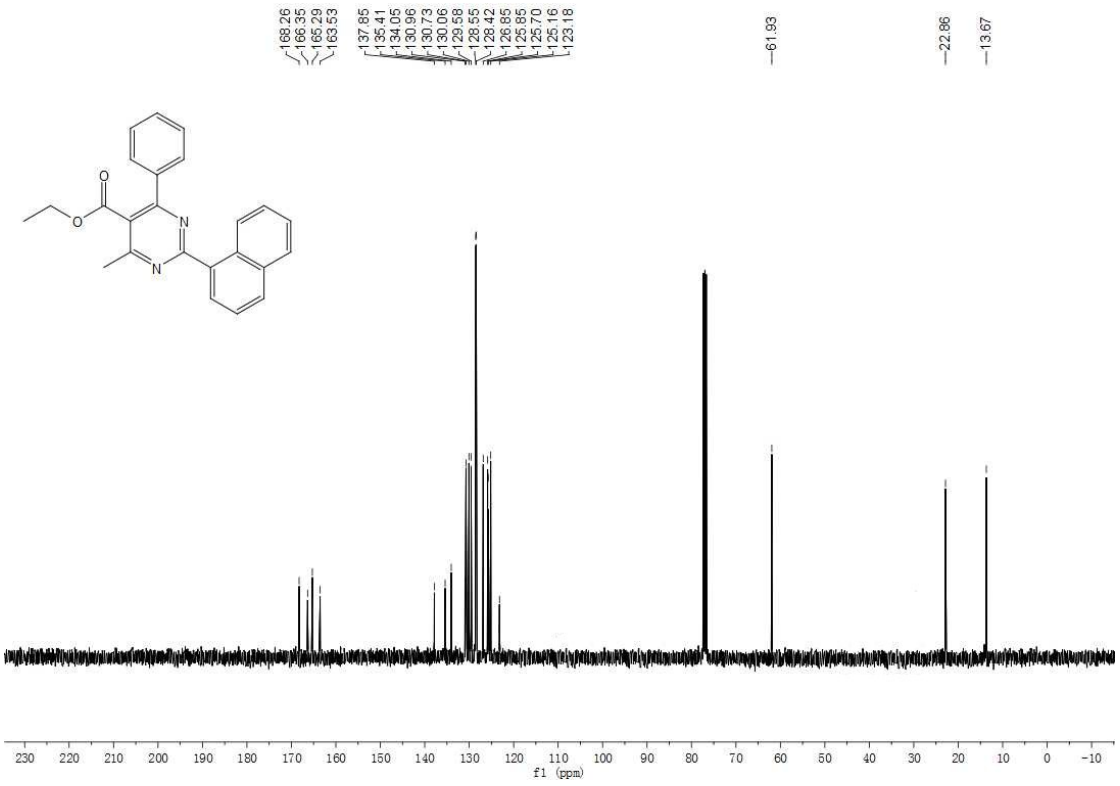
^{1}H and ^{13}C Spectra of compound 3f ($CDCl_3$, 400 MHz)



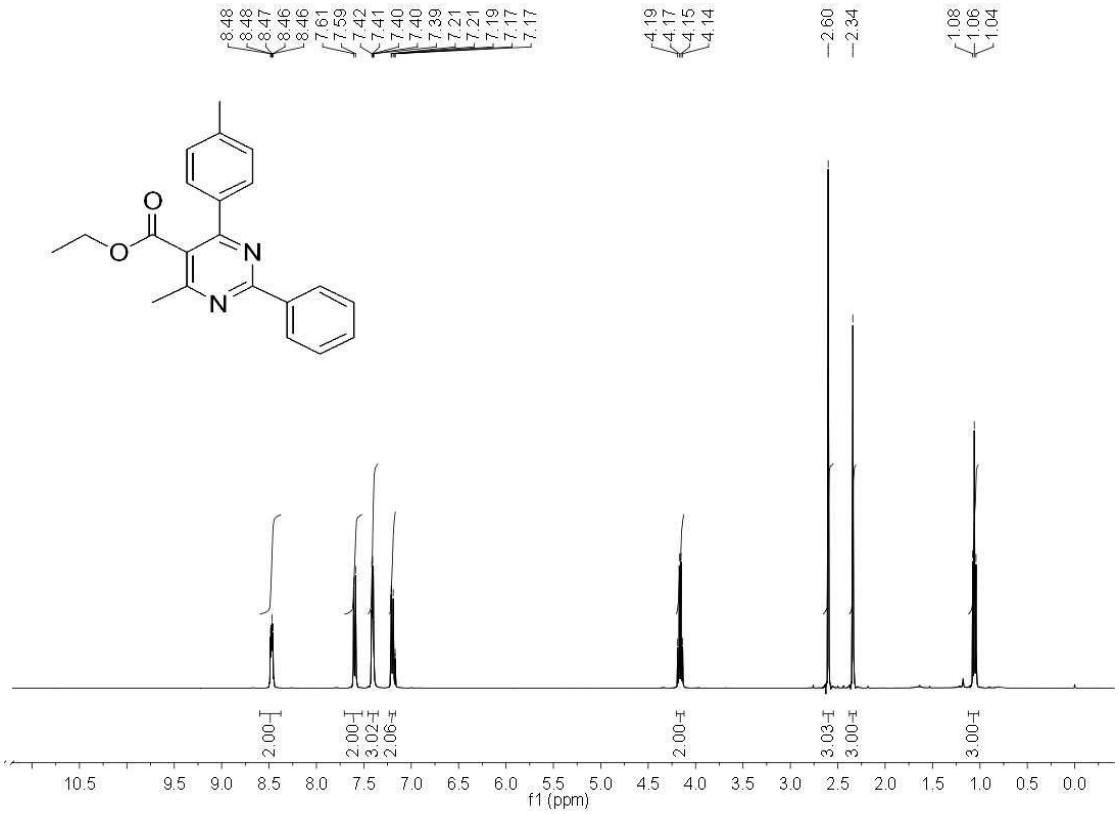


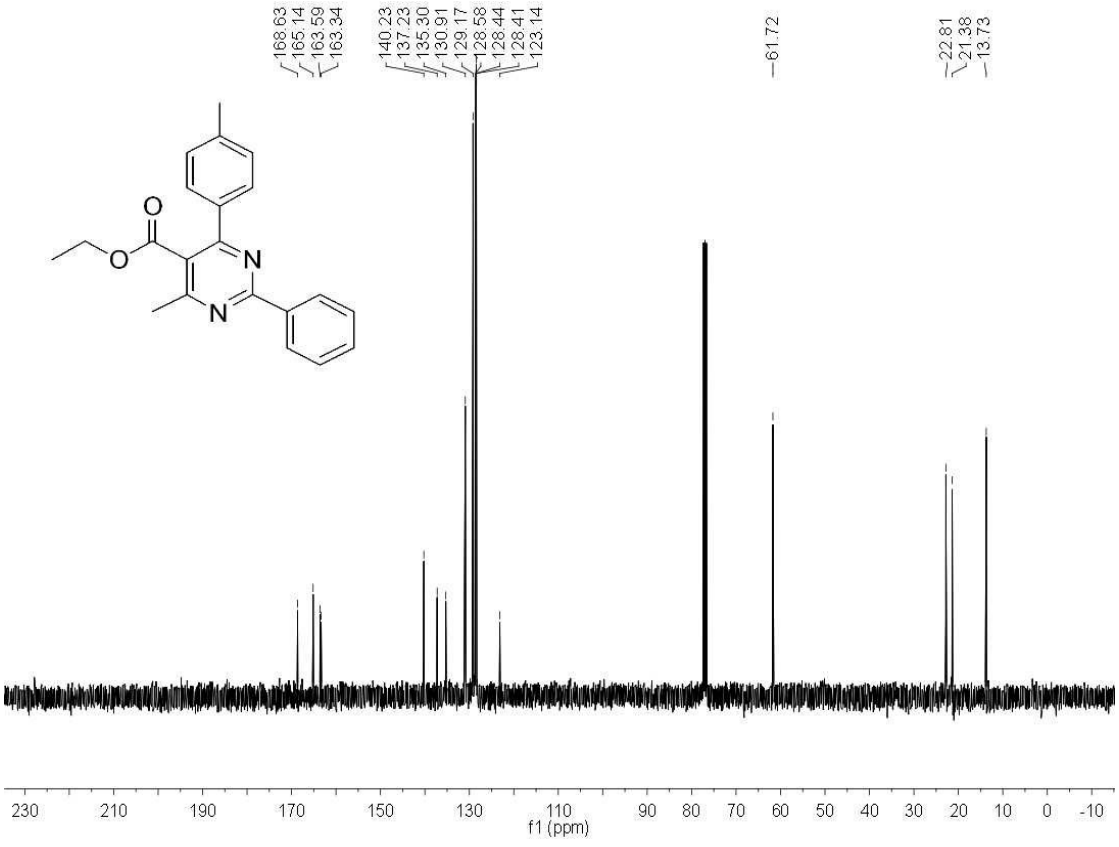
^{1}H and ^{13}C Spectra of compound 3g ($CDCl_3$, 400 MHz)



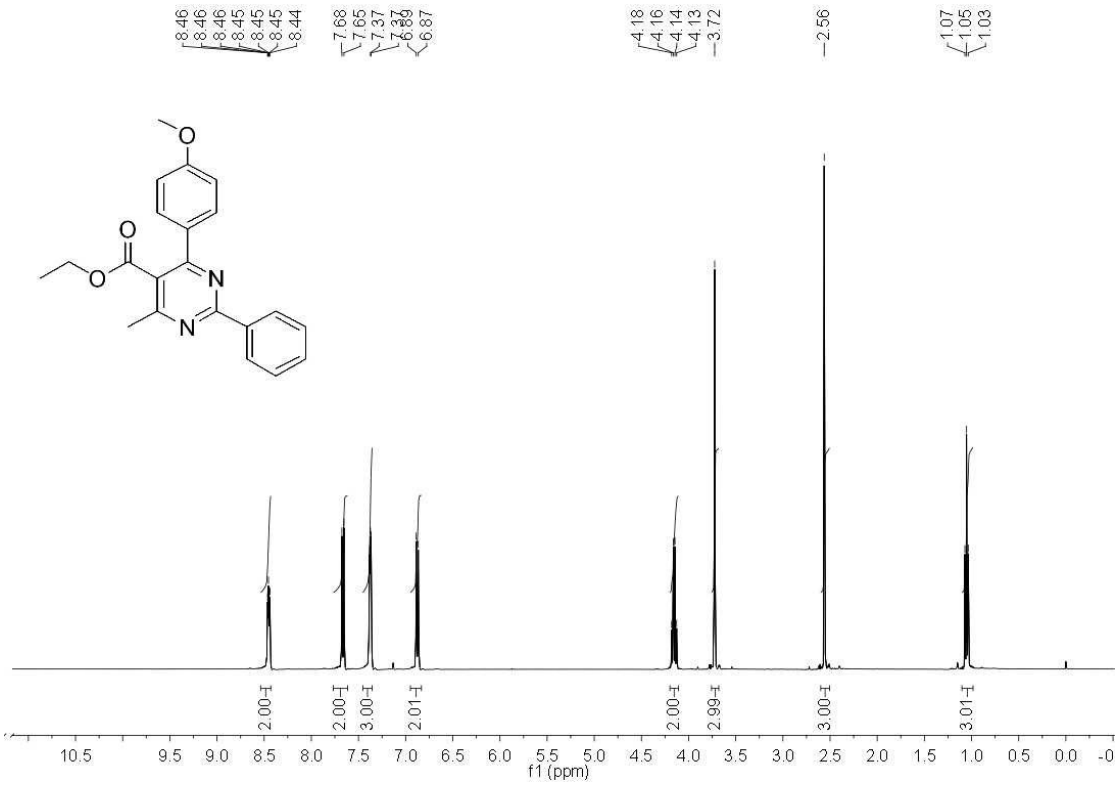


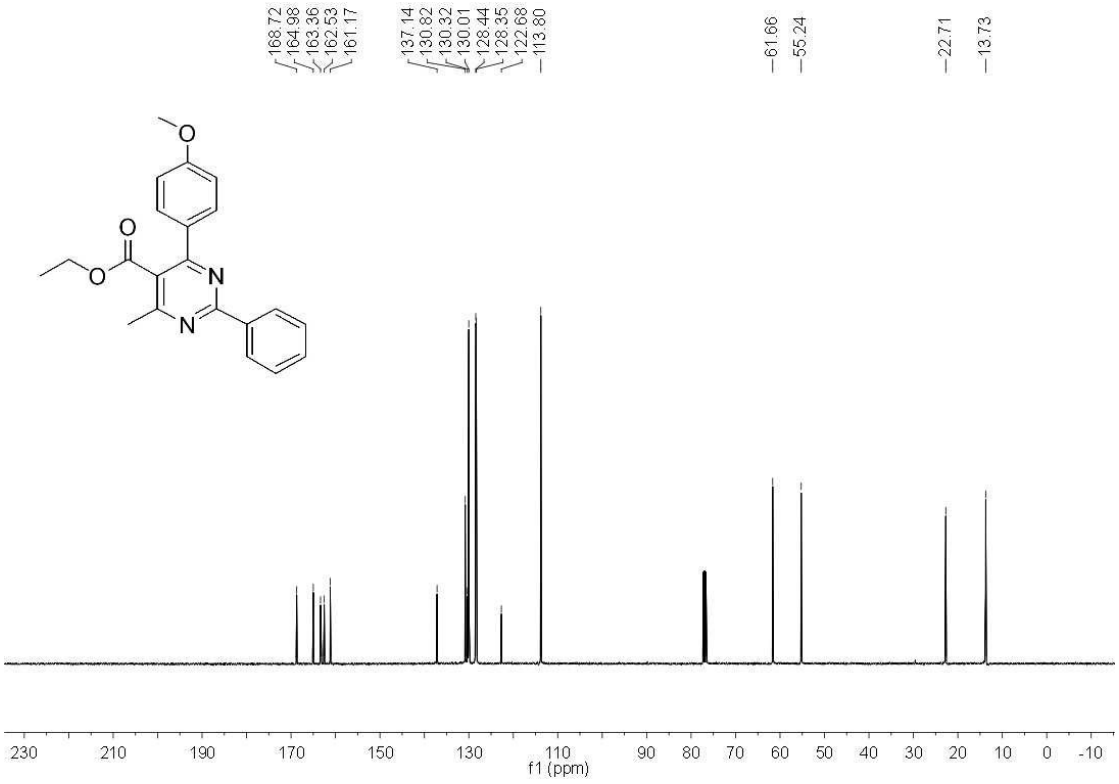
^{1}H and ^{13}C Spectra of compound 3h ($CDCl_3$, 400 MHz)



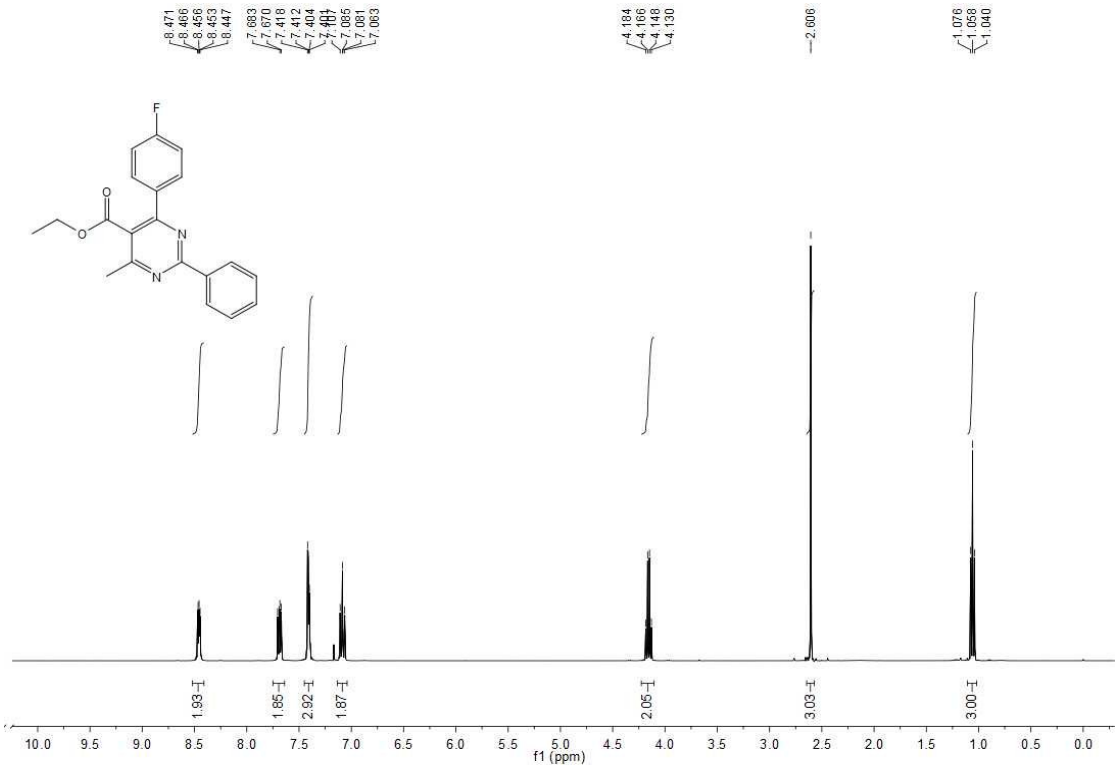


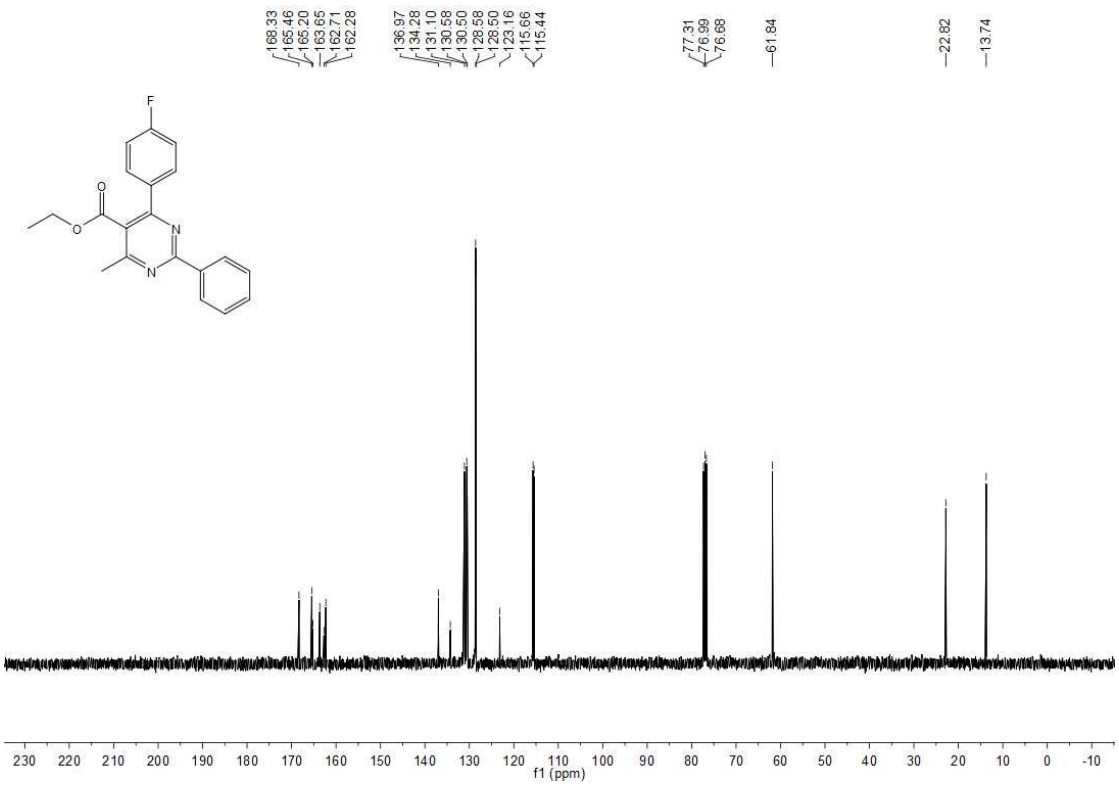
^{1}H and ^{13}C Spectra of compound 3i ($CDCl_3$, 400 MHz)



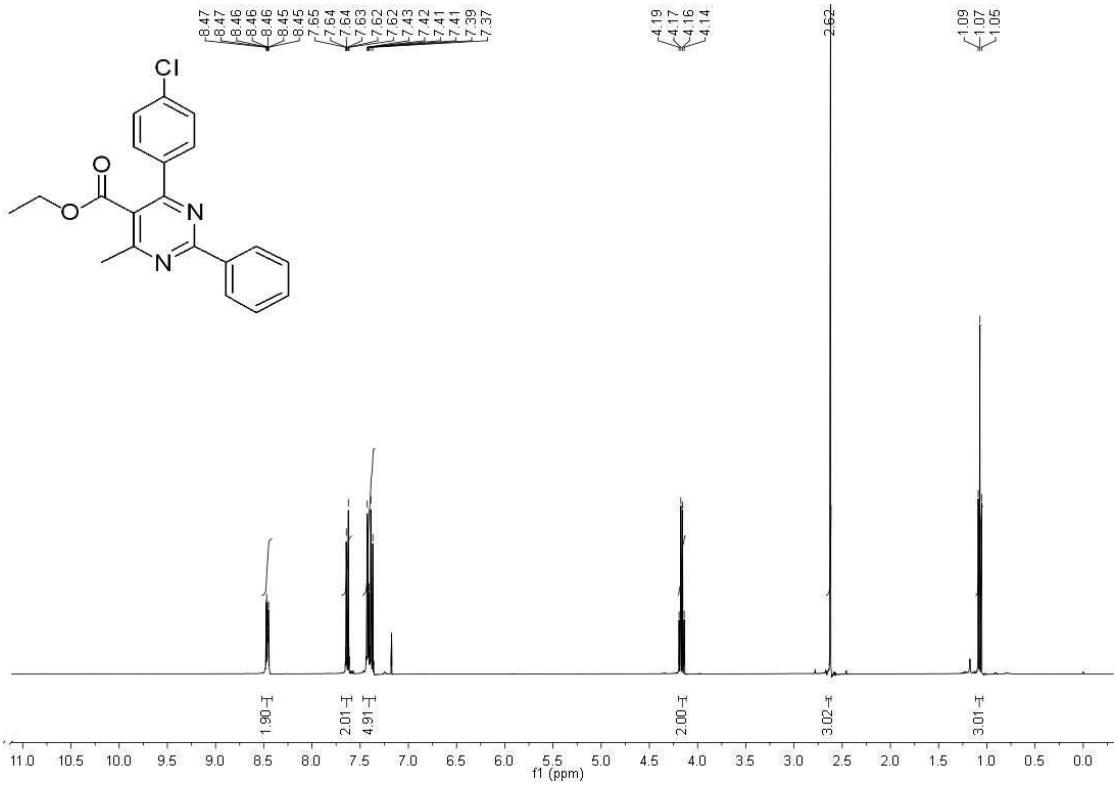


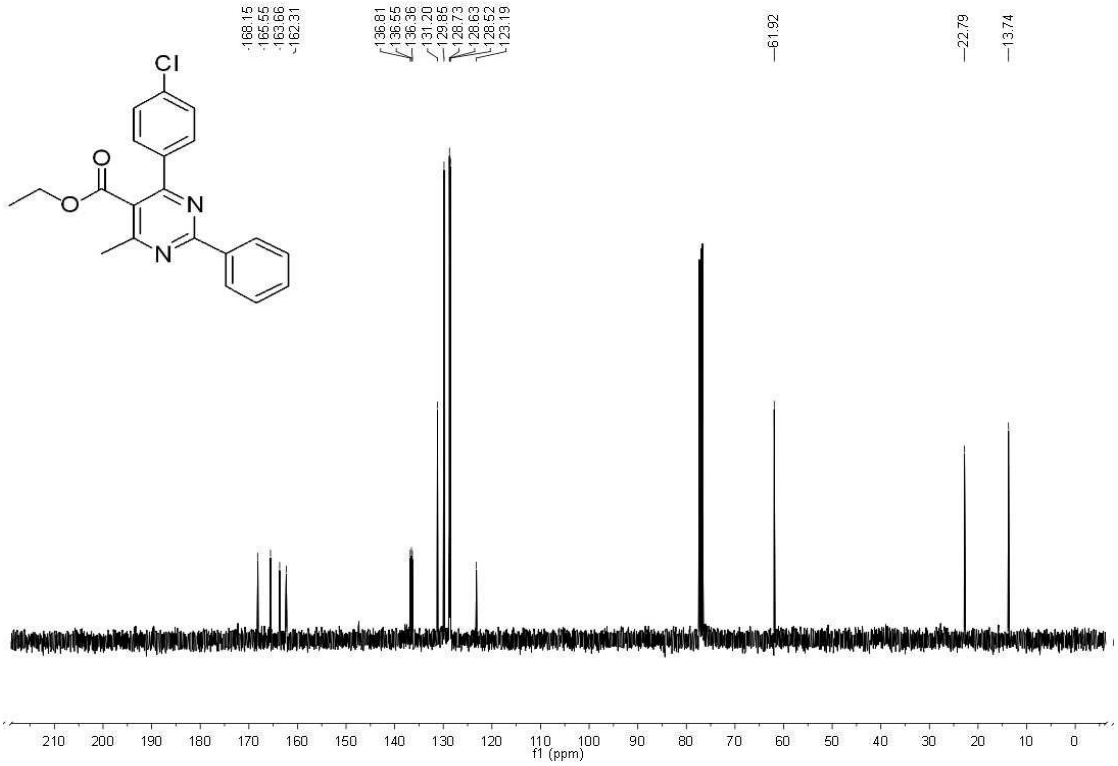
^{1}H and ^{13}C Spectra of compound 3j ($CDCl_3$, 400 MHz)



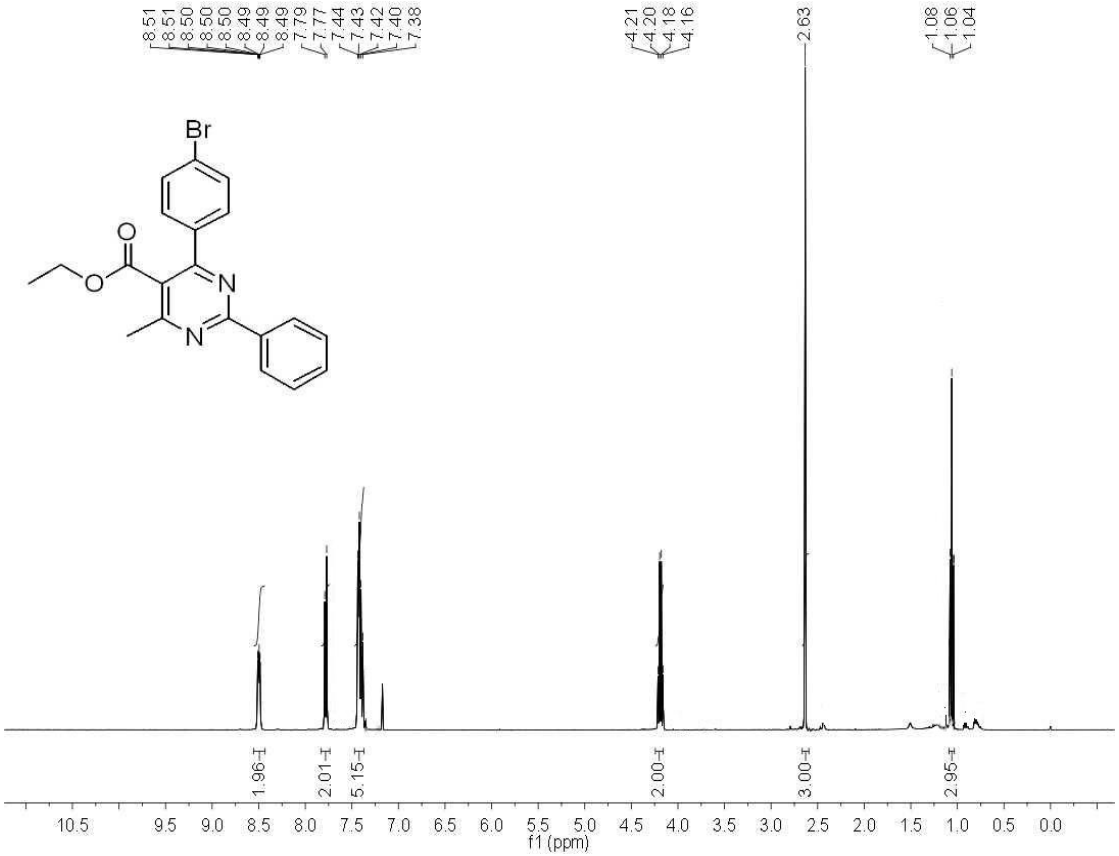


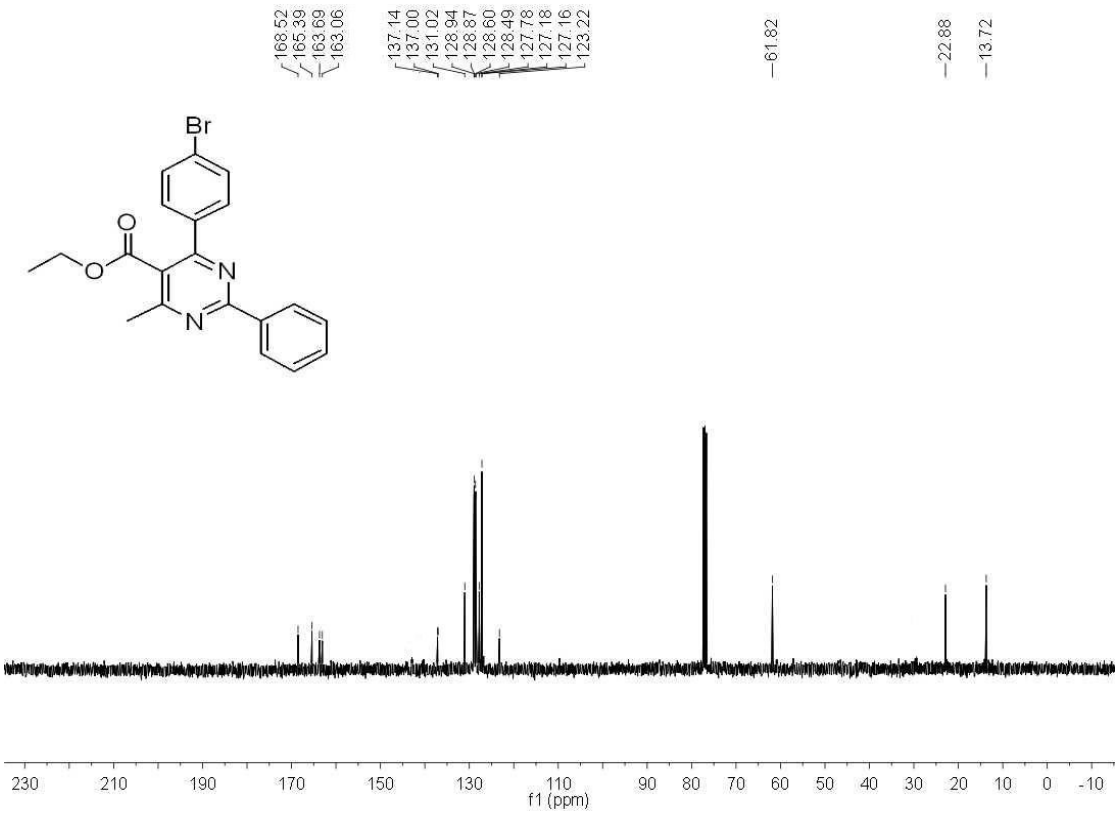
^{1}H and ^{13}C Spectra of compound 3k ($CDCl_3$, 400 MHz)



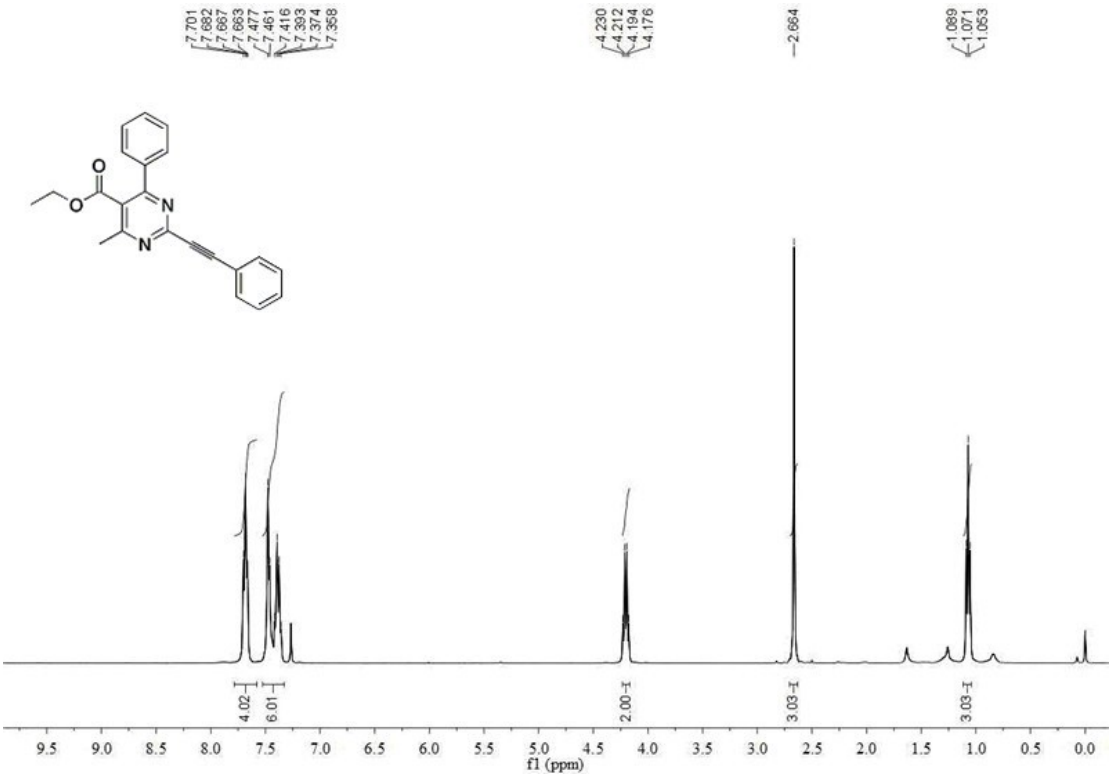


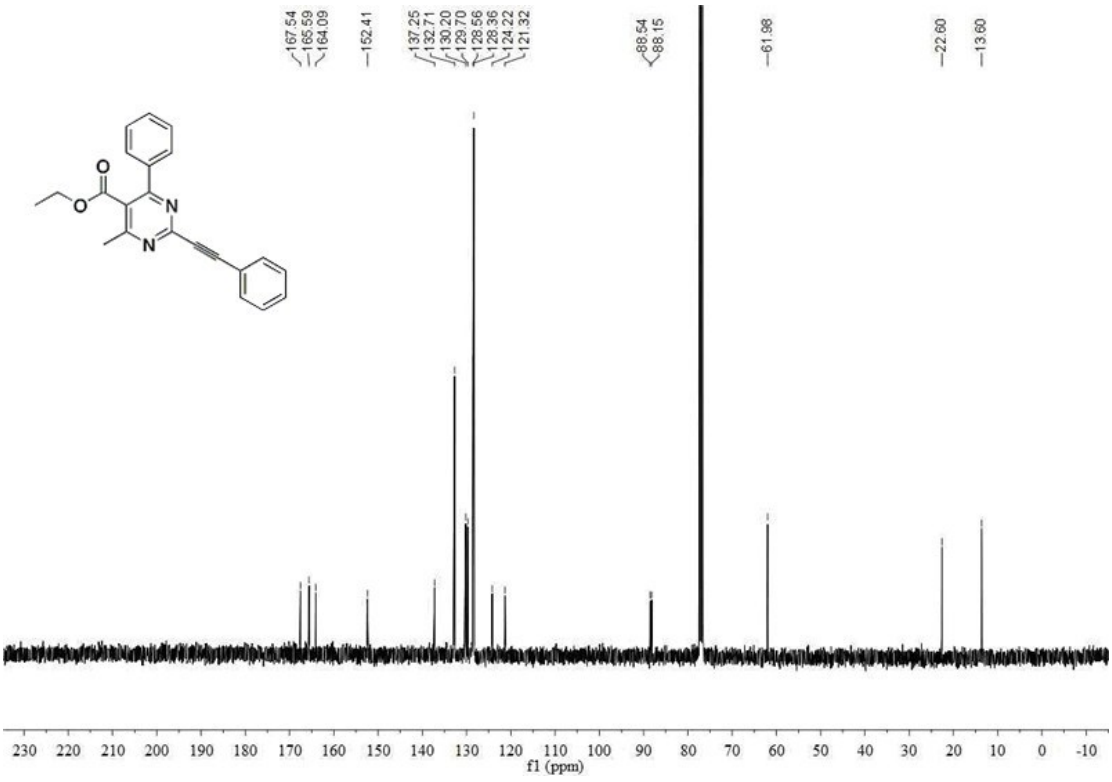
^{1}H and ^{13}C Spectra of compound 3l ($CDCl_3$, 400 MHz)



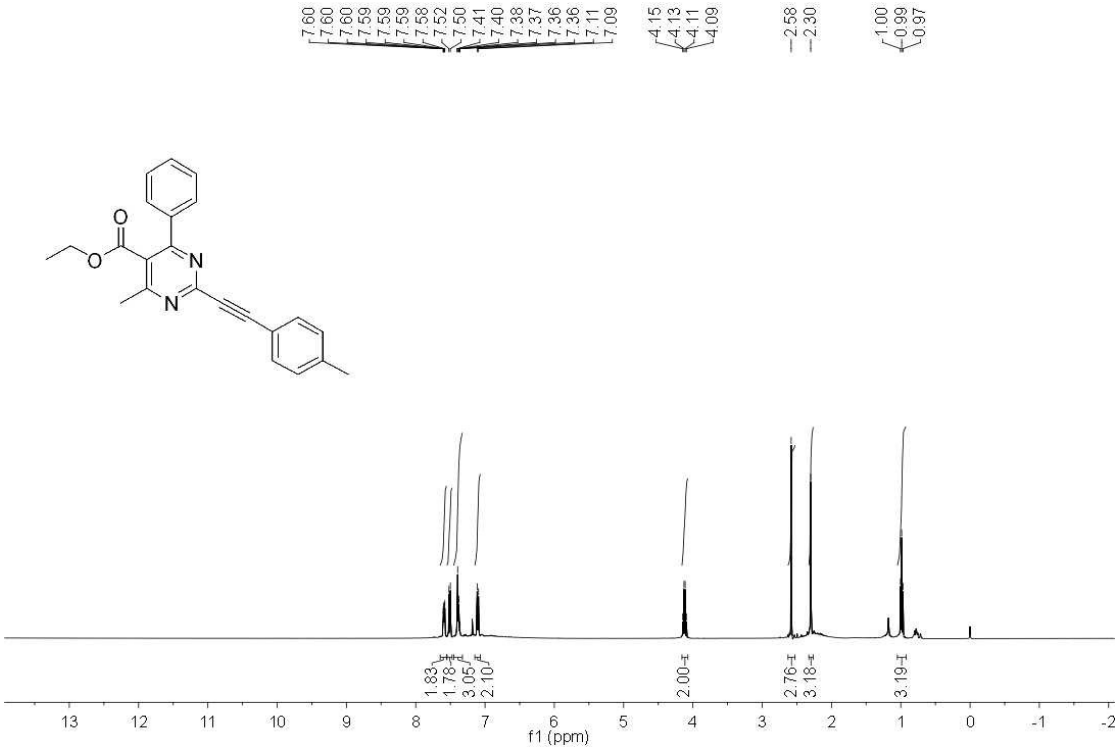


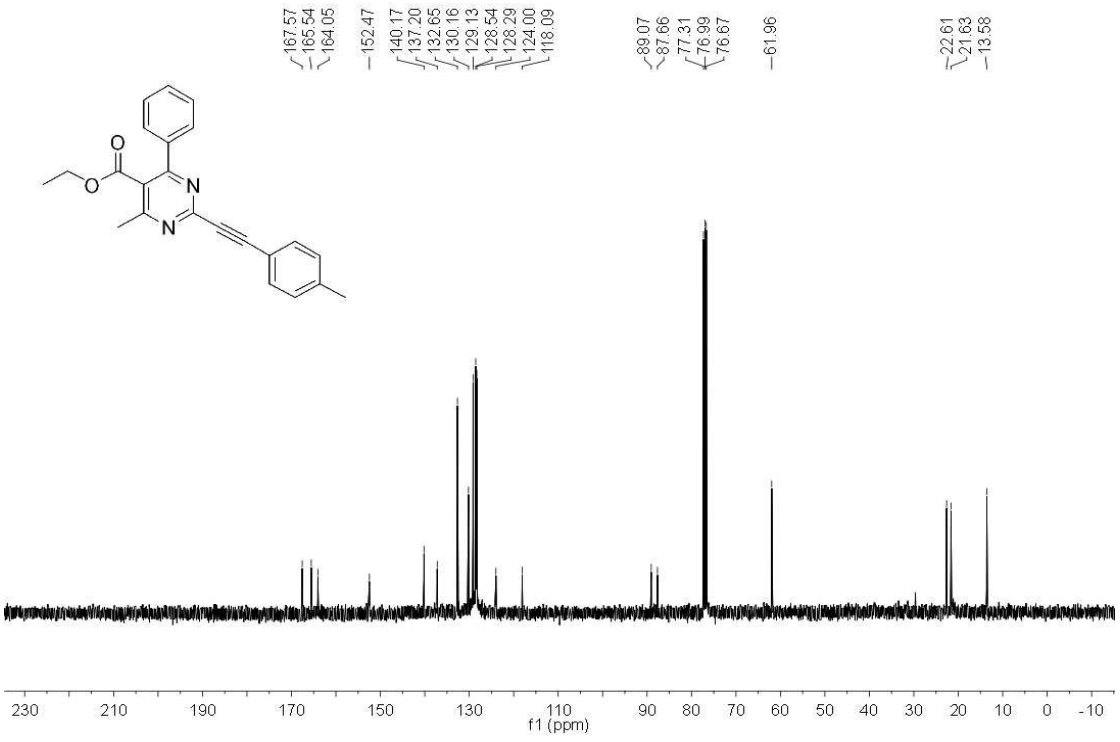
^{1}H and ^{13}C Spectra of compound 5a ($CDCl_3$, 400 MHz)



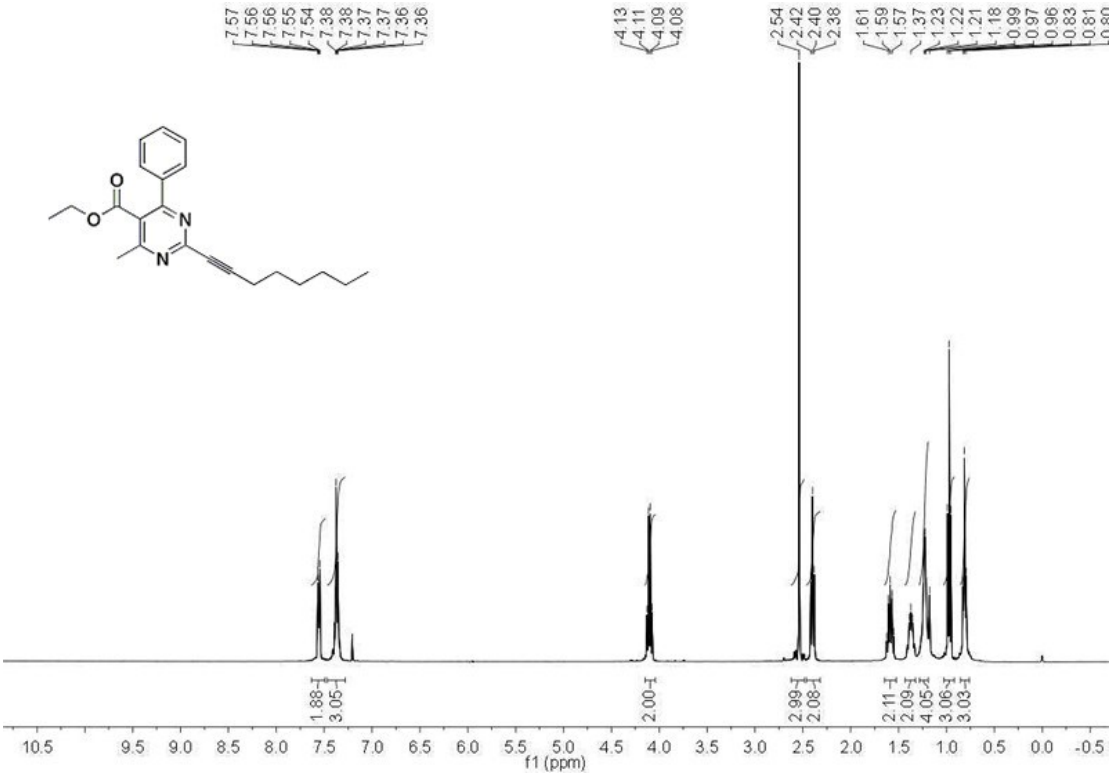


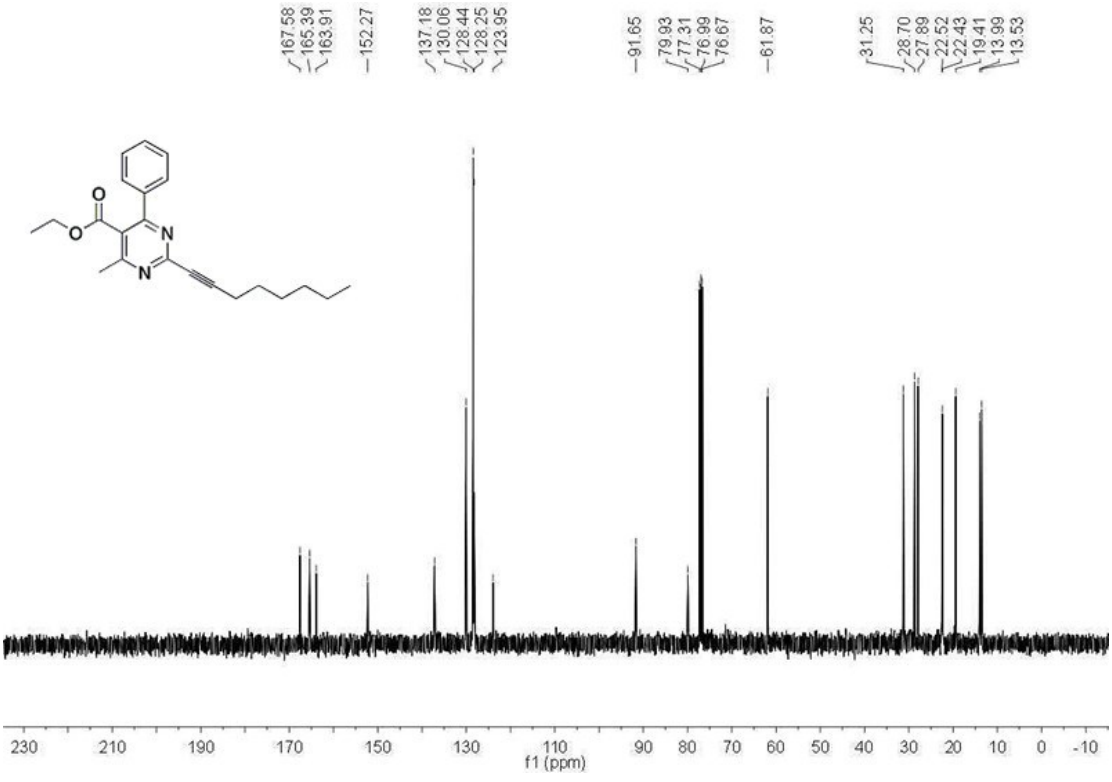
^{1}H and ^{13}C Spectra of compound 5b ($CDCl_3$, 400 MHz)



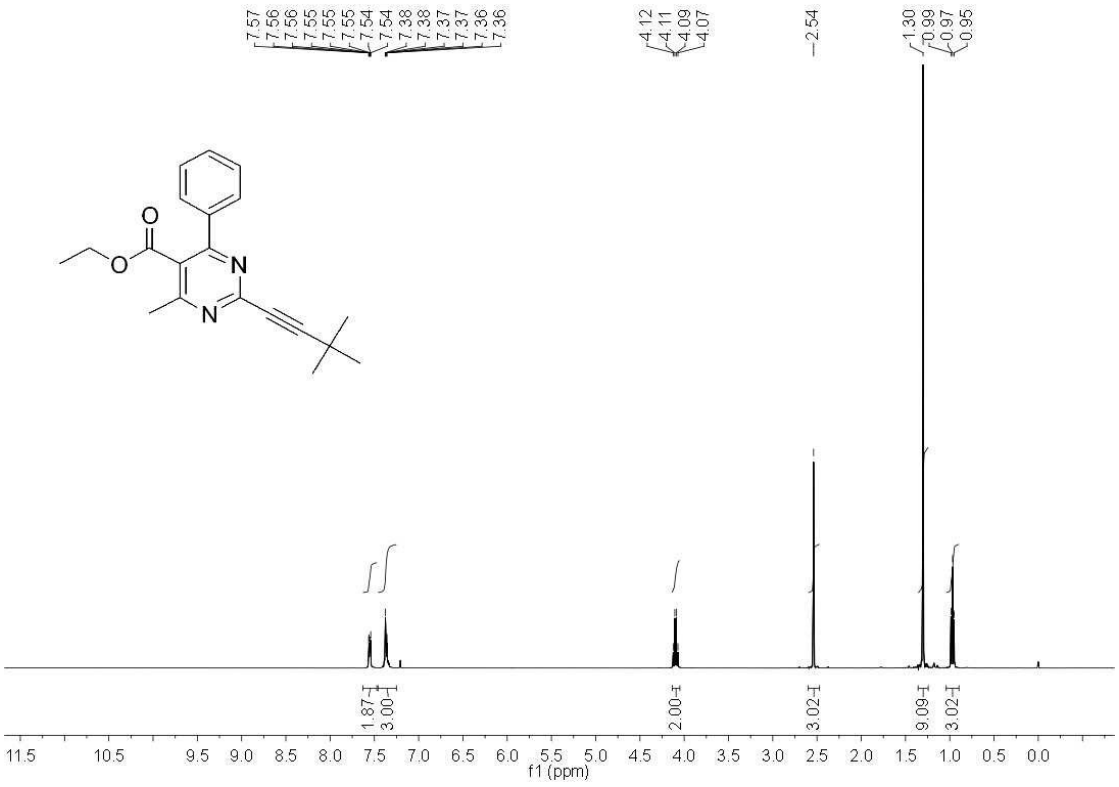


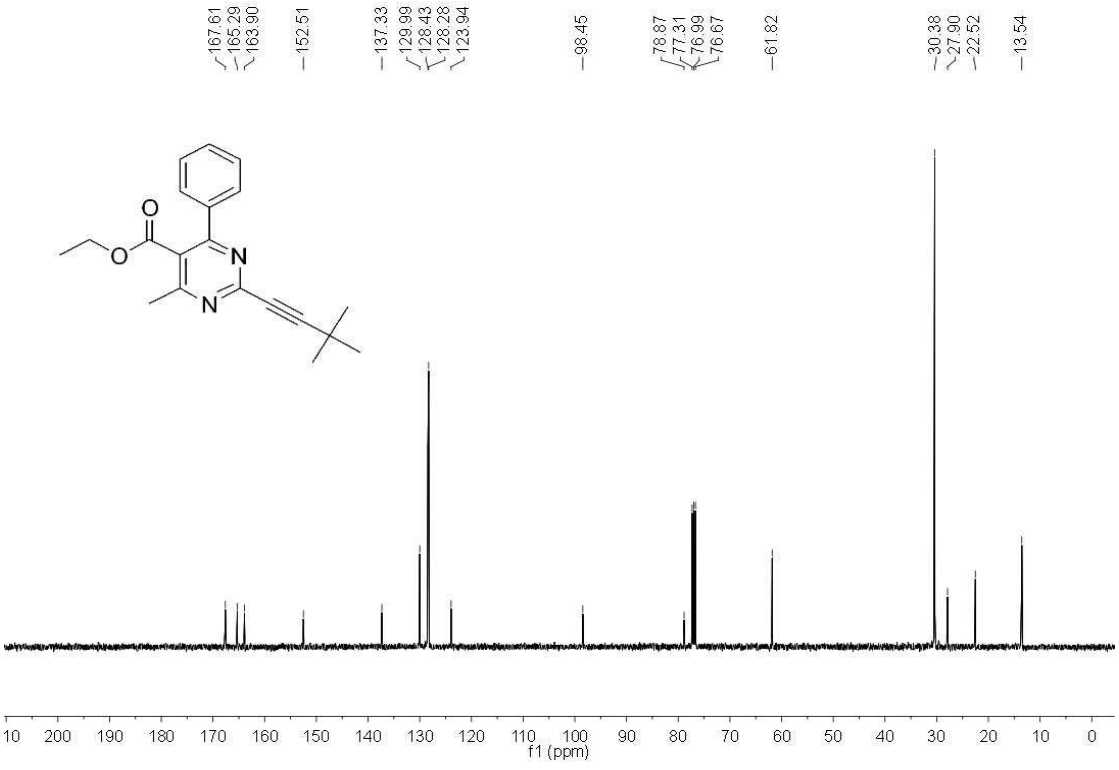
^{1}H and ^{13}C Spectra of compound 5c ($CDCl_3$, 400 MHz)



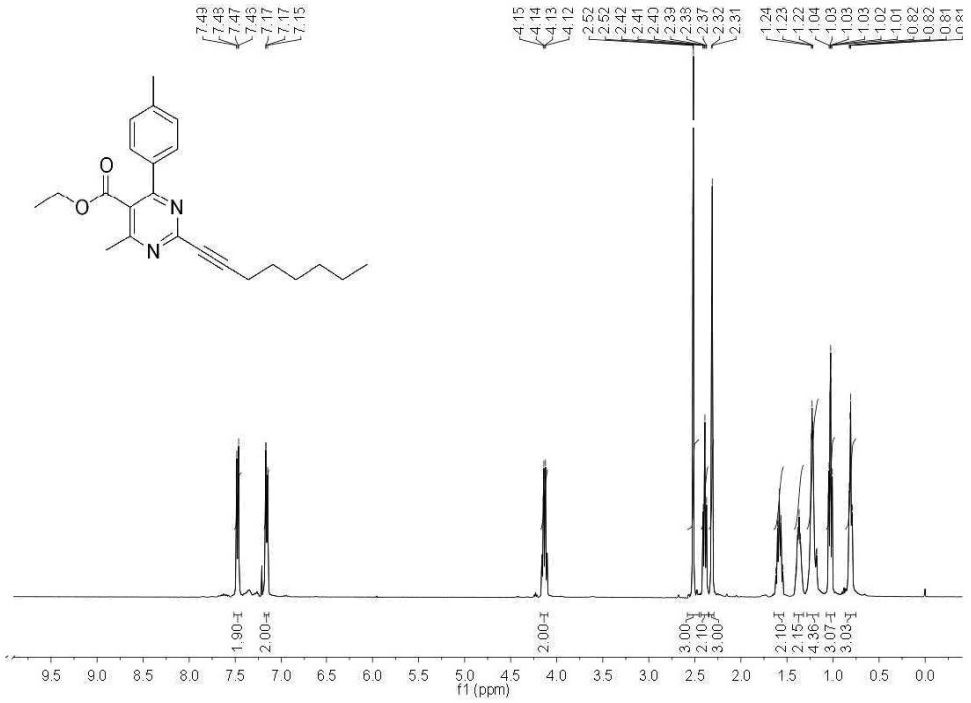


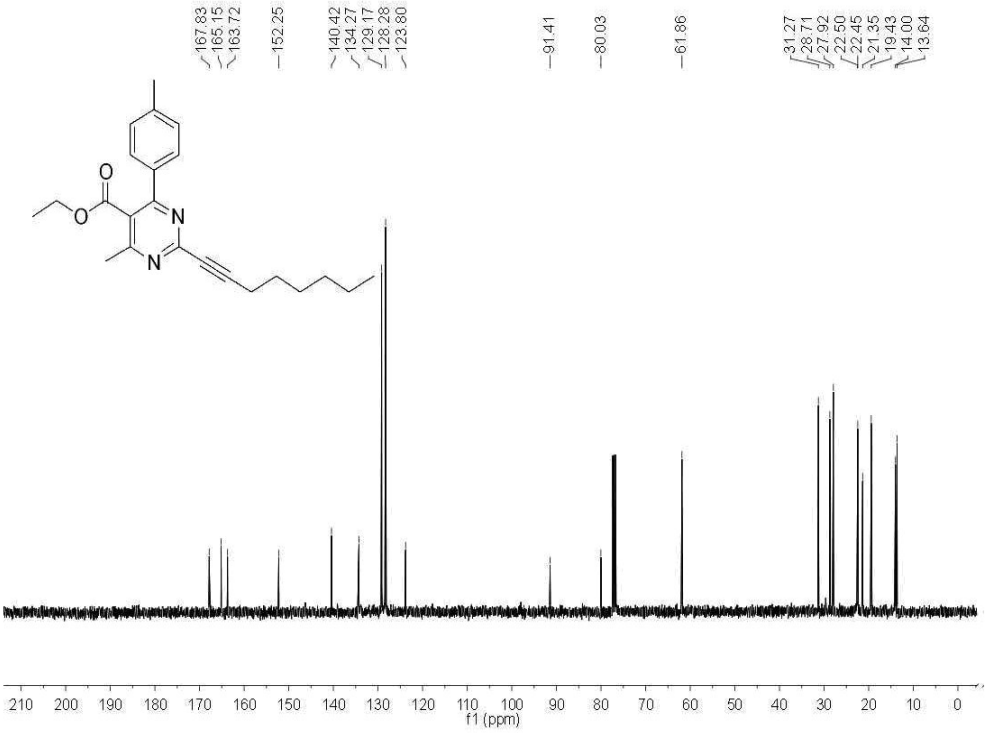
^{1}H and ^{13}C Spectra of compound 5d ($CDCl_3$, 400 MHz)



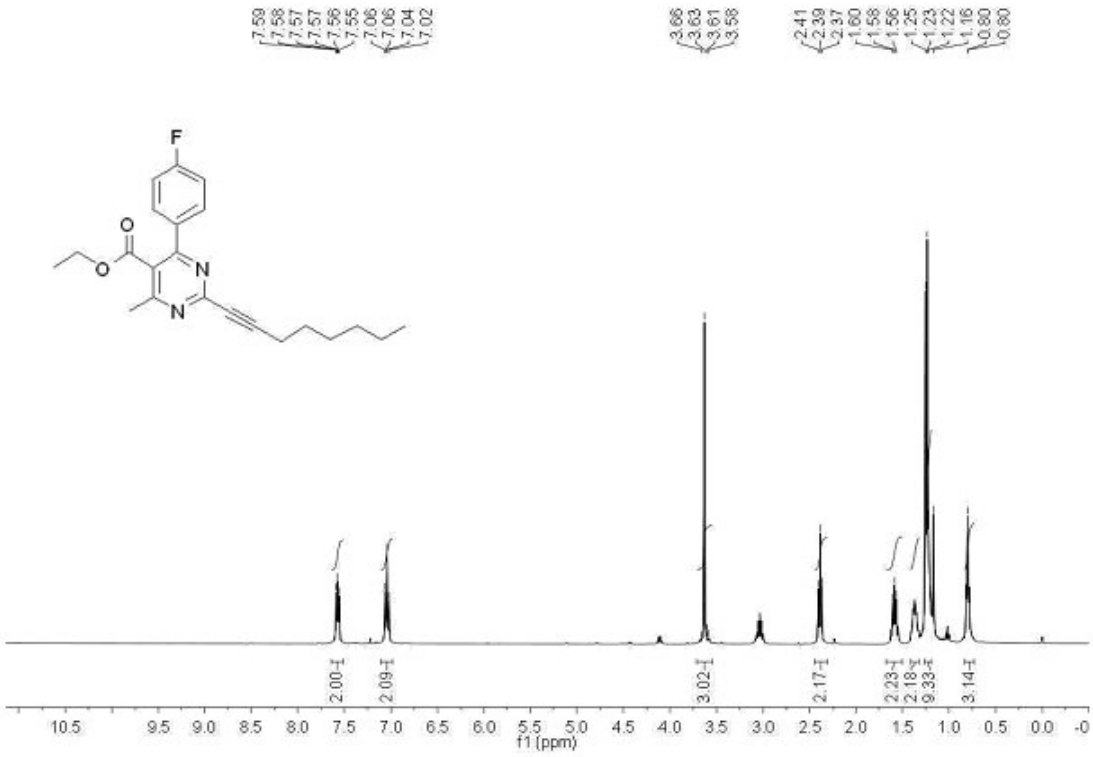


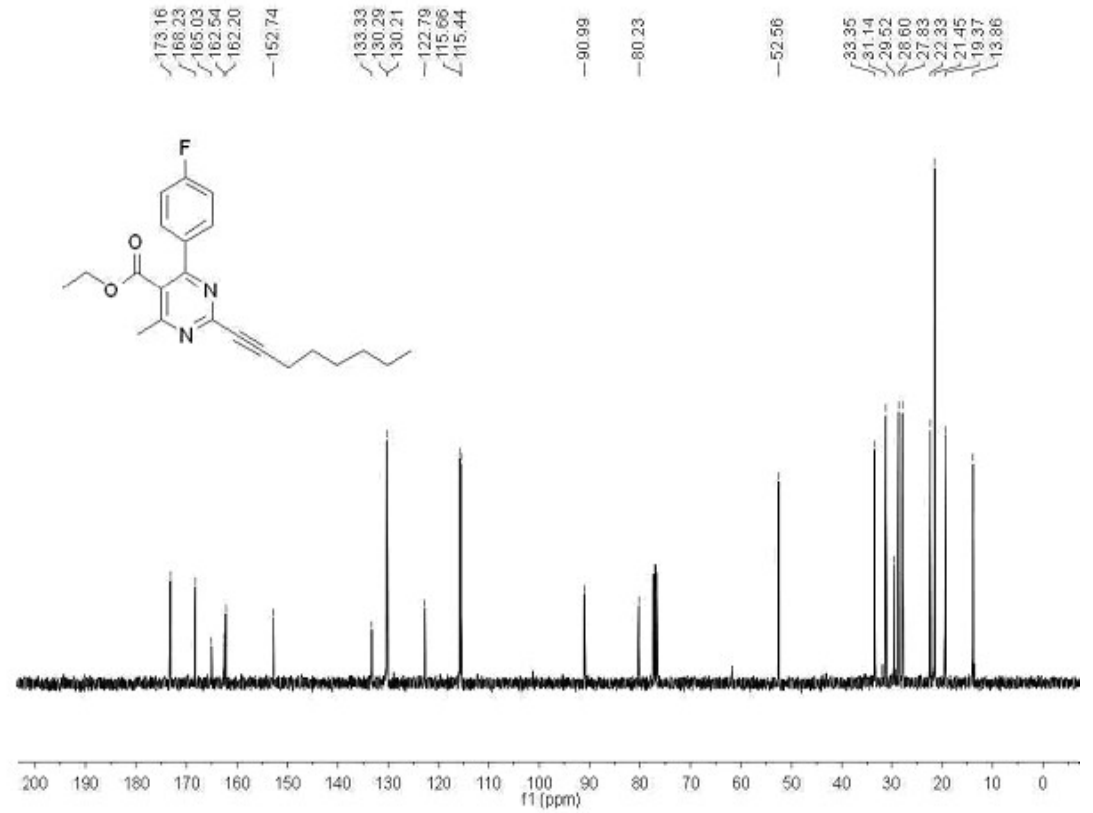
^{1}H and ^{13}C Spectra of compound 5e ($CDCl_3$, 400 MHz)



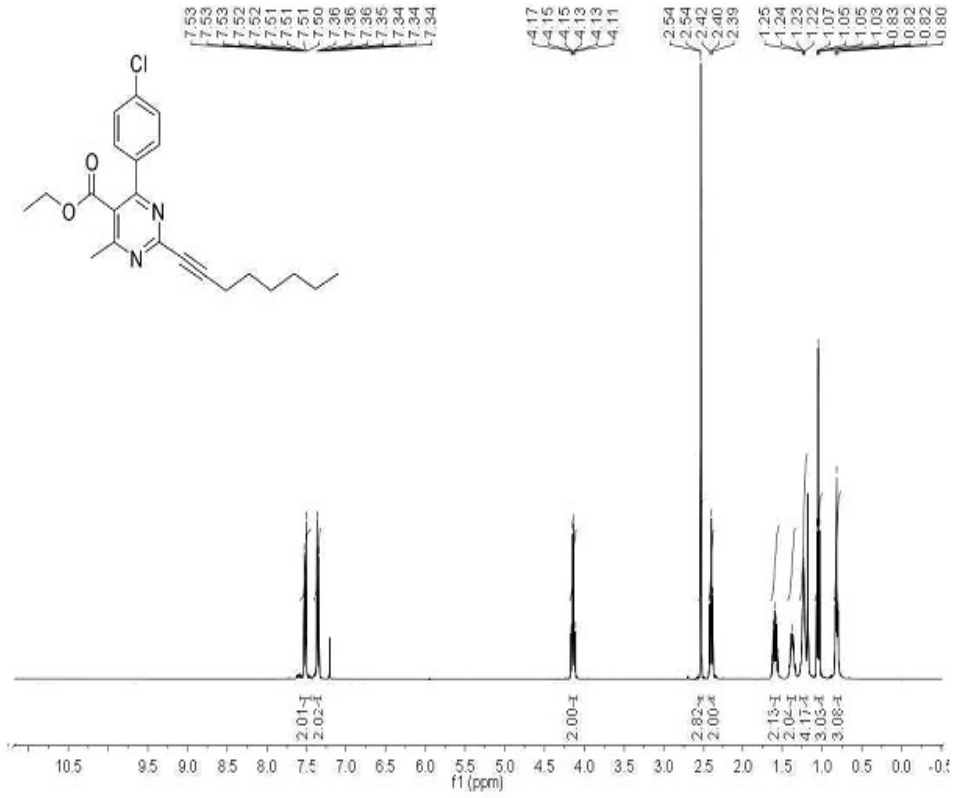


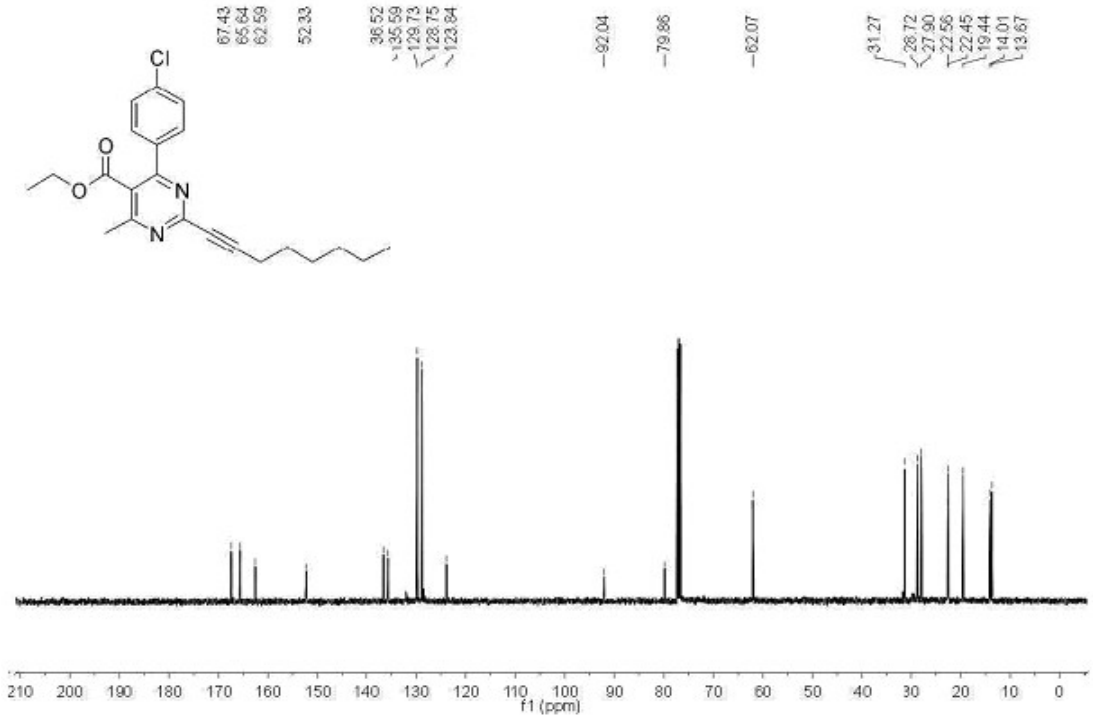
^{1}H and ^{13}C Spectra of compound 5f ($CDCl_3$, 400 MHz)



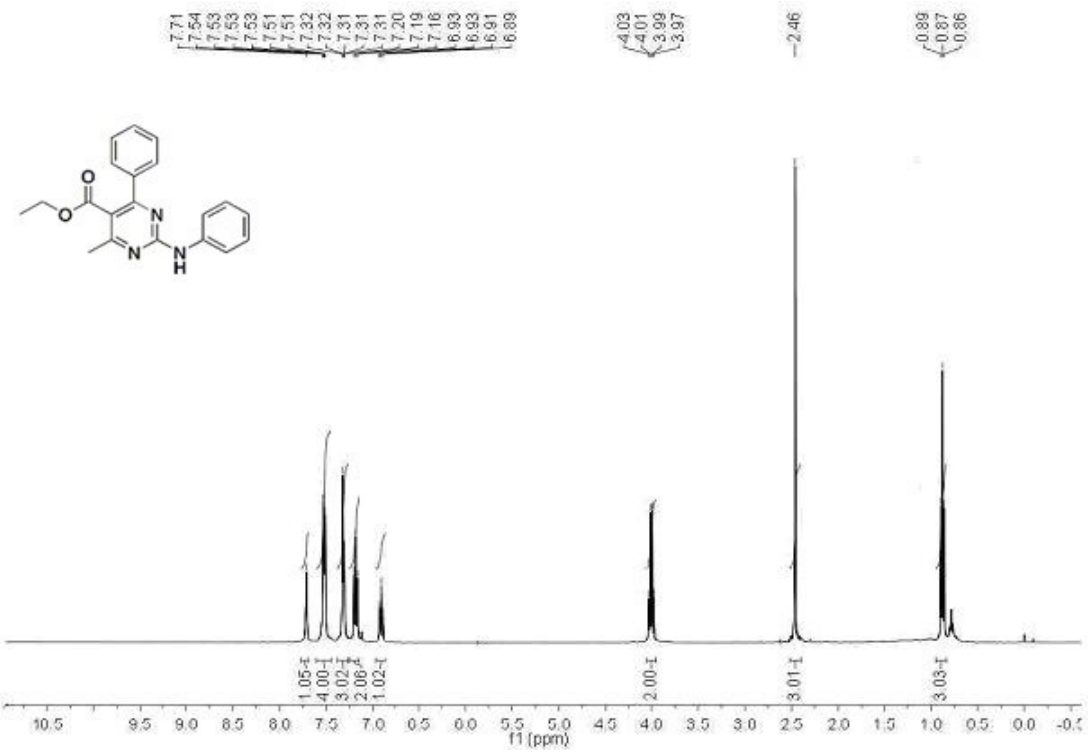


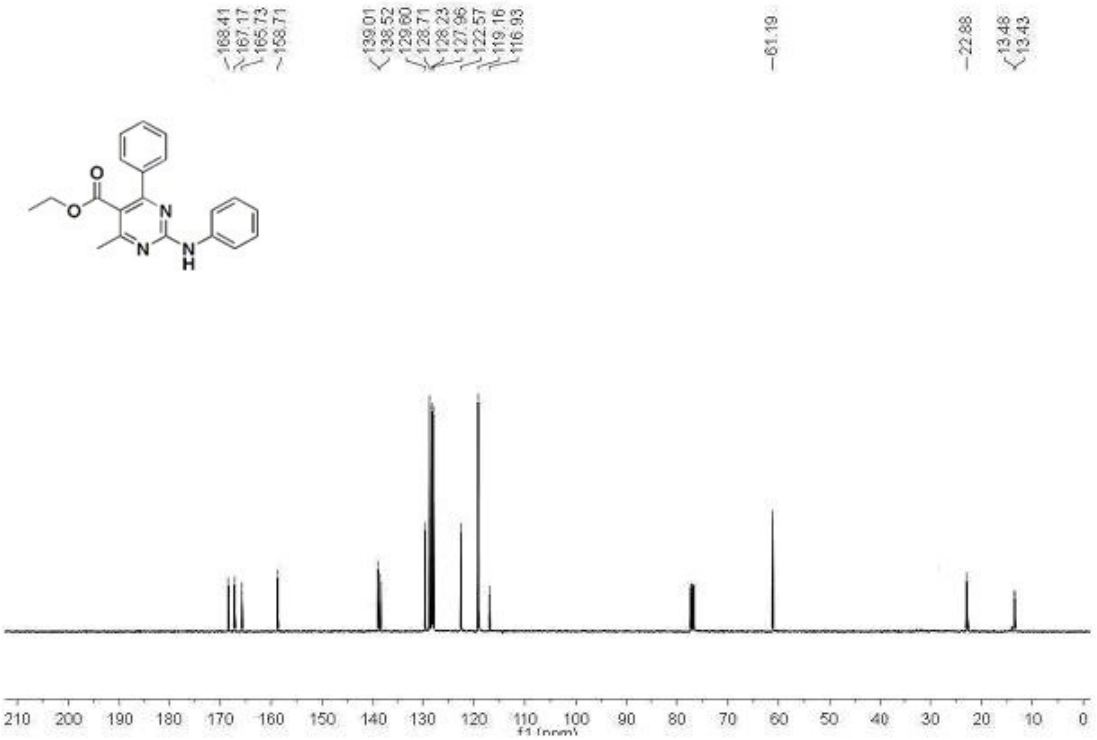
^{1}H and ^{13}C Spectra of compound 5g ($CDCl_3$, 400 MHz)



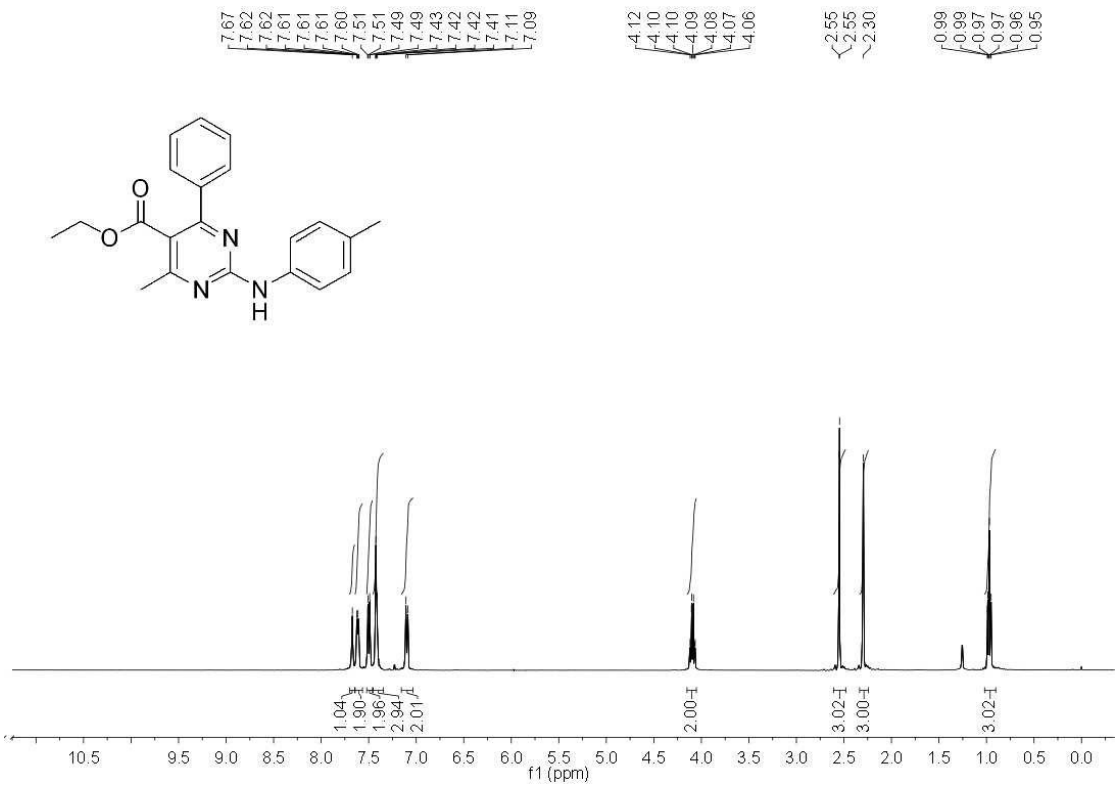


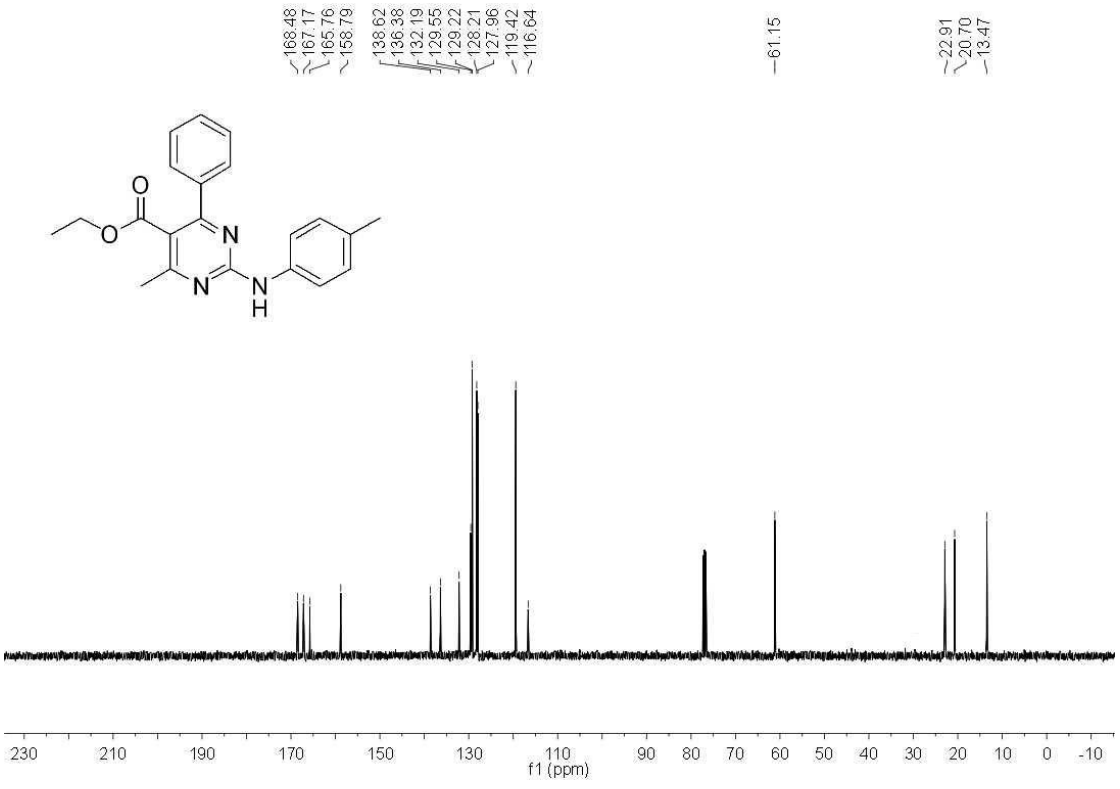
^{1}H and ^{13}C Spectra of compound 7a ($CDCl_3$, 400 MHz)



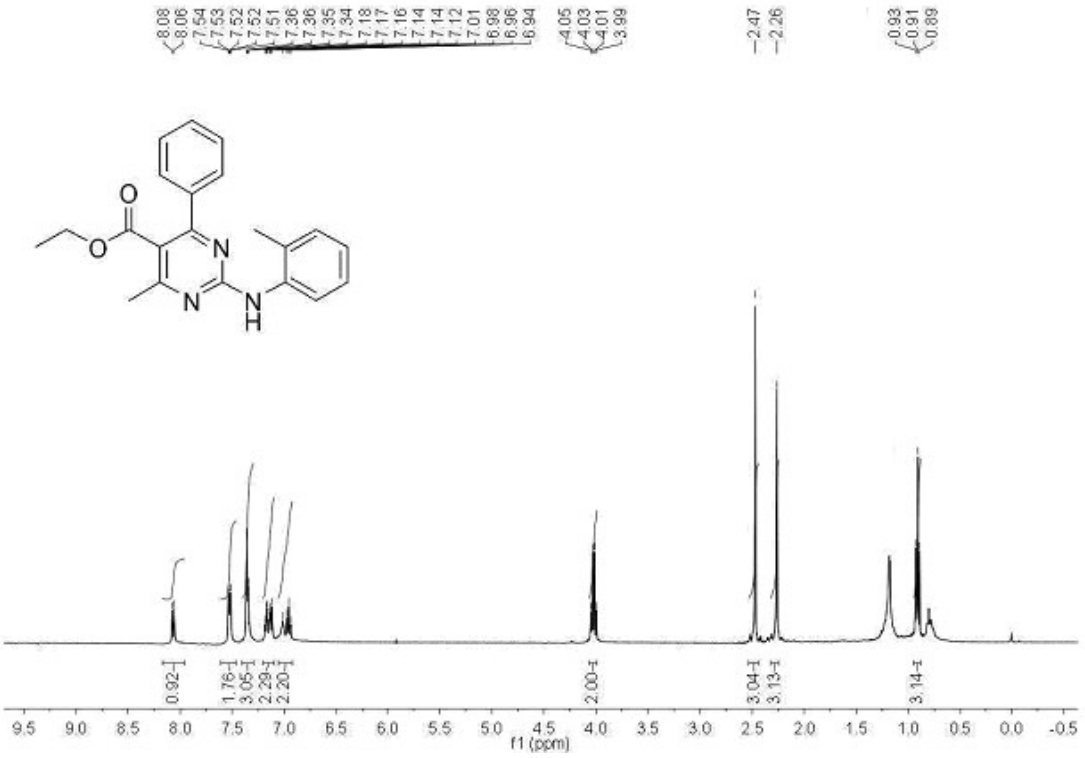


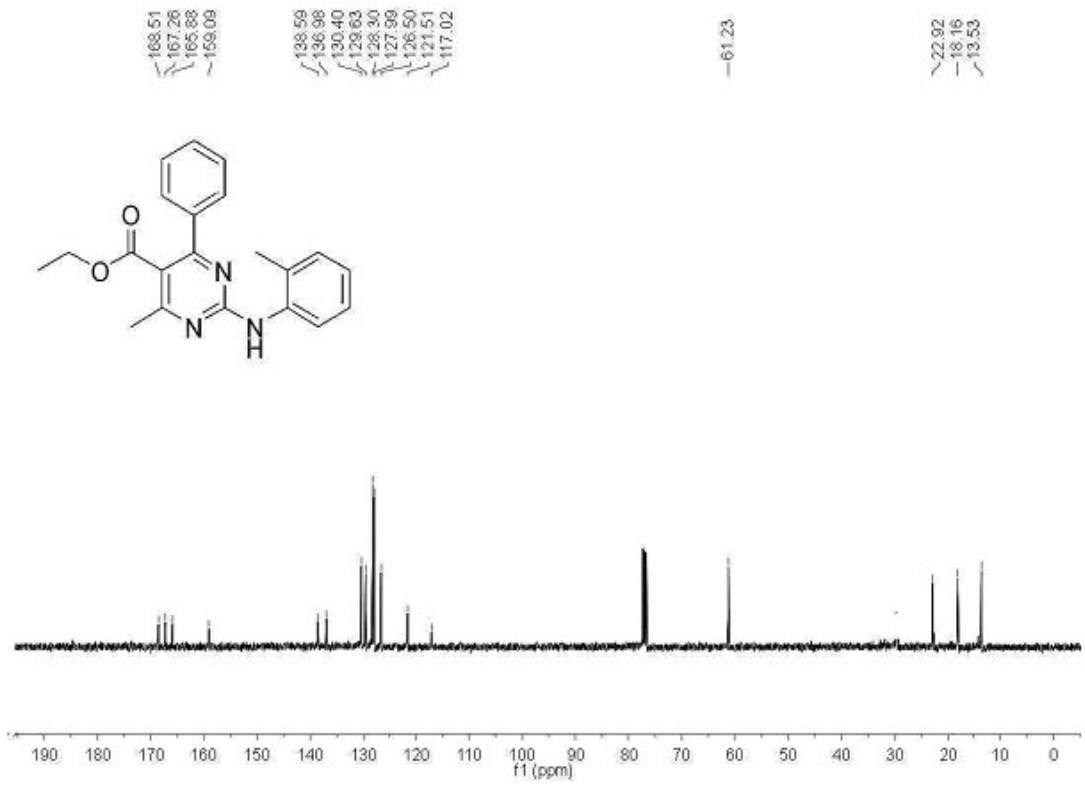
^{1}H and ^{13}C Spectra of compound 7b ($CDCl_3$, 400 MHz)



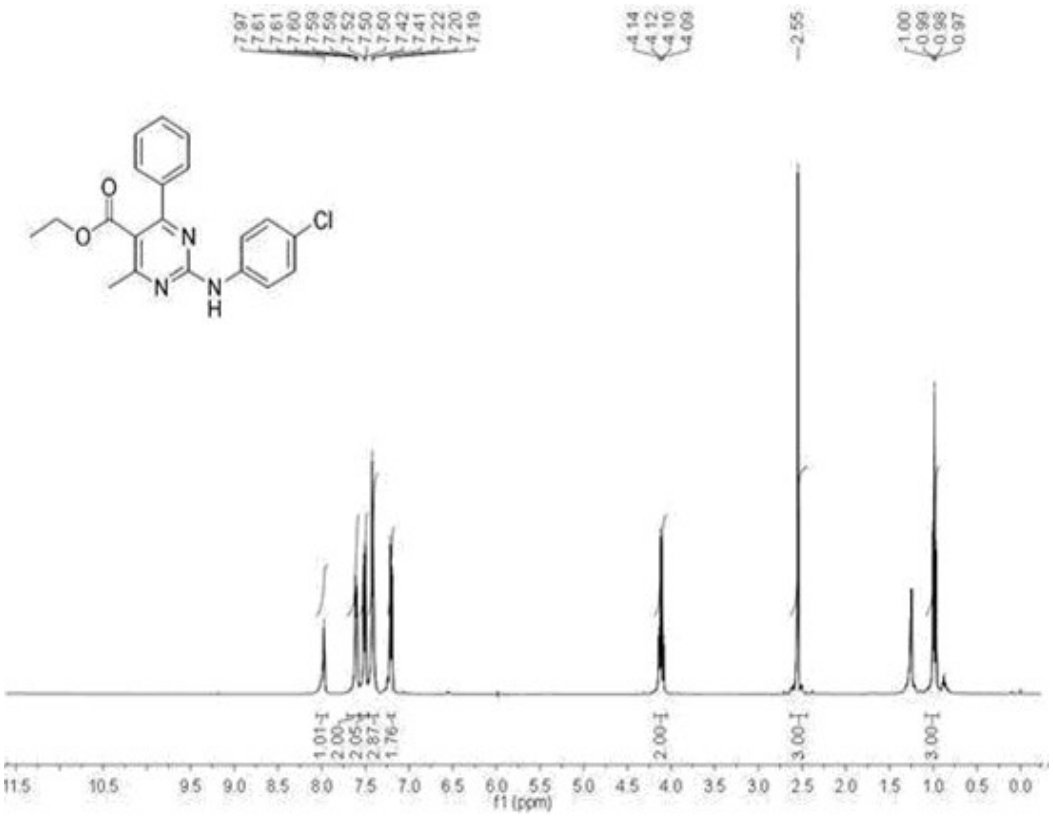


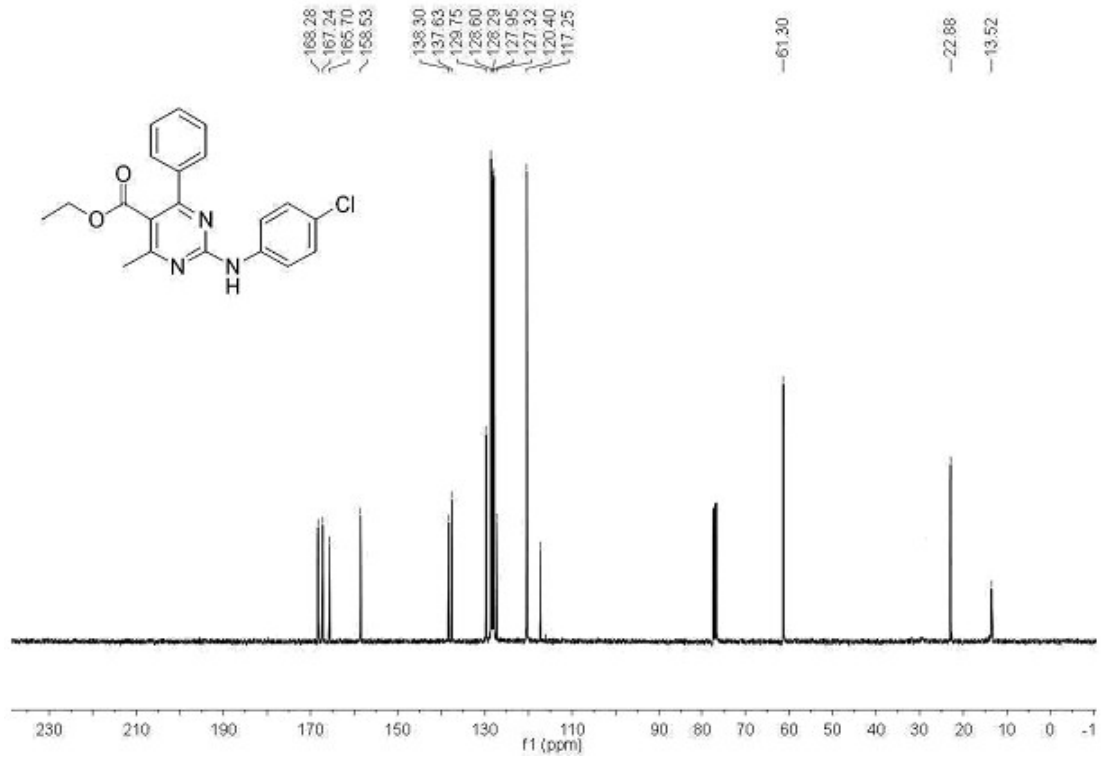
^{1}H and ^{13}C Spectra of compound 7c ($CDCl_3$, 400 MHz)



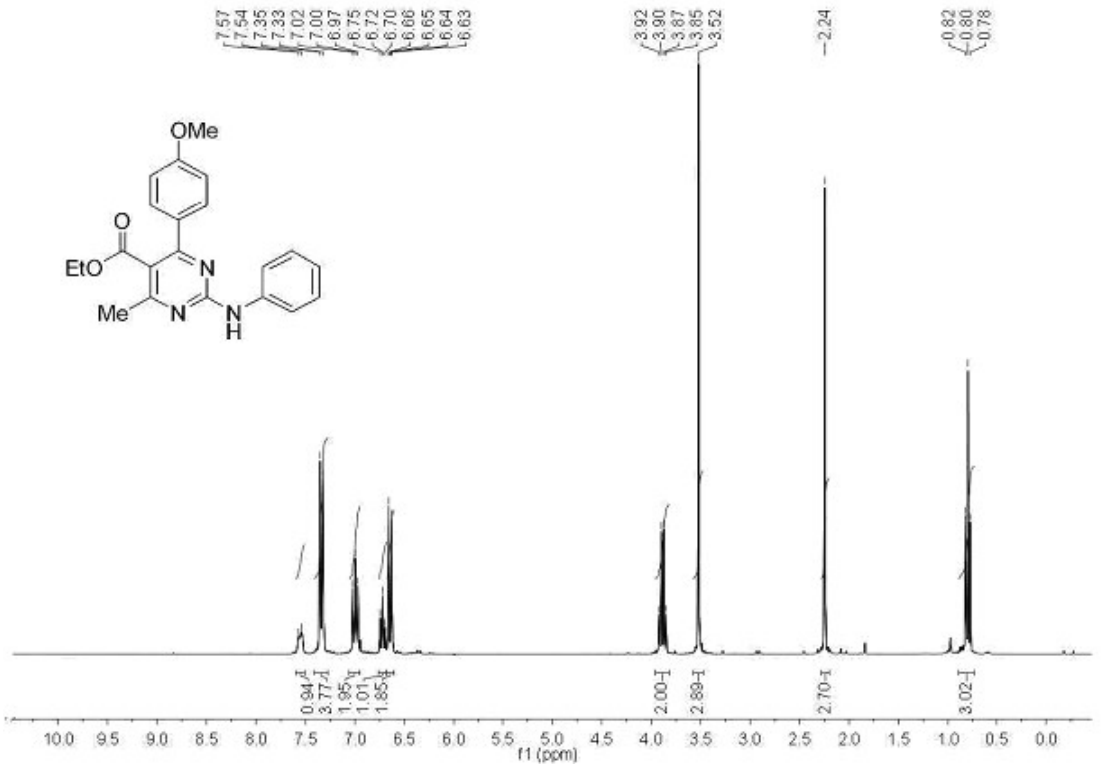


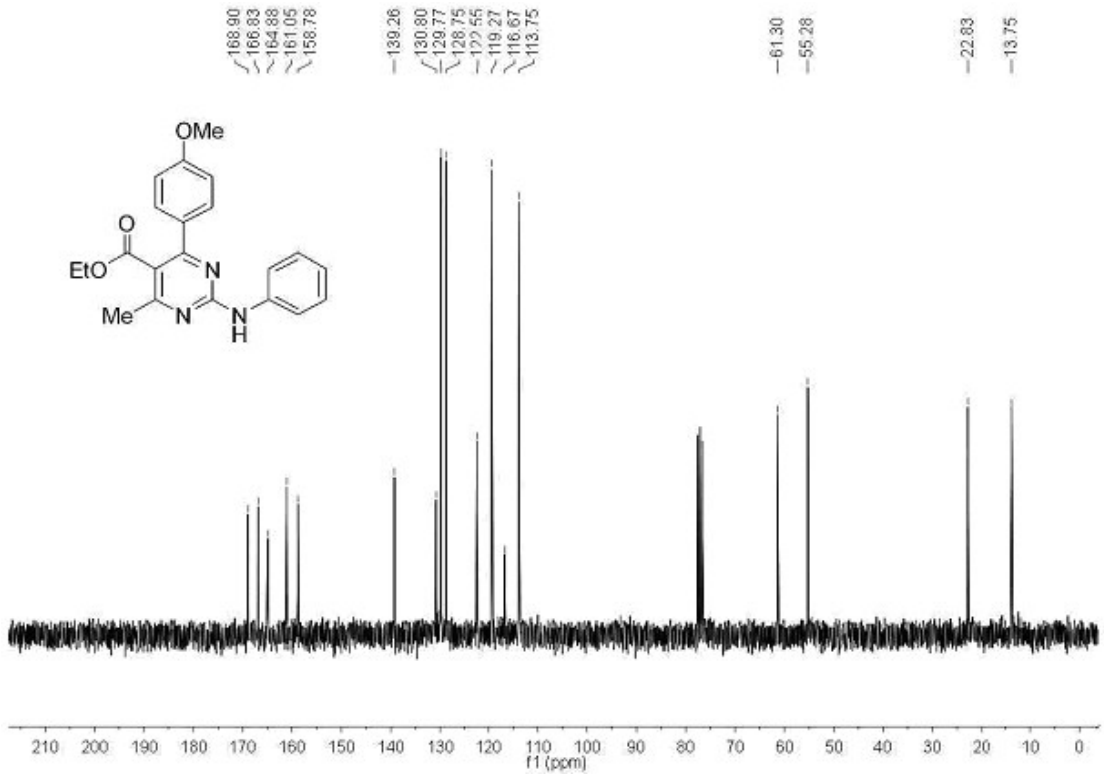
^{1}H and ^{13}C Spectra of compound 7d ($CDCl_3$, 400 MHz)





^{1}H and ^{13}C Spectra of compound 7e ($CDCl_3$, 400 MHz)





^{1}H and ^{13}C Spectra of compound 7f ($CDCl_3$, 400 MHz)