C-C/C-N Cross-Coupling Reactions of Aryl Sulfonates Catalyzed by a Reusable Heterogeneous Catalyst: Wool-Pd Complex

SUPPORTING INFORMATION

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General

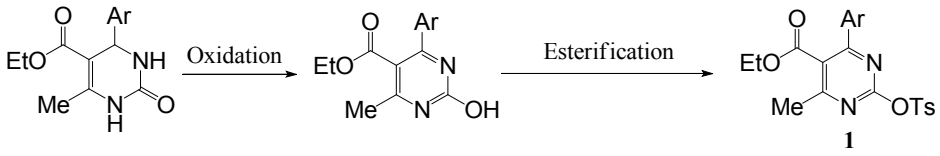
All starting materials and reagents were commercially available and used without further purification unless otherwise noted. Solvents were purified and dried by standard methods prior to use. All products have been previously reported and characterized. All known products gave satisfactory analytical data corresponding to the reported literature values. Wool was provided by Gansu Jingyuan Woolen Mill.

All reactions were conducted under a nitrogen atmosphere with a dual-manifold Schlenk tube, unless otherwise mentioned, and in oven-dried glassware. All NMR spectra are recorded on MERCURY (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometers; chemical shifts are expressed in ppm (δunits) relative to TMS signal as internal reference in $CDCl_3$. Gas chromatography (GC) analysis was performed on a Shimadezu GC-2010 equipped with a 15 m × 0.53 mm × 1.5 μm RTX-1 capillary column and a oxyhydrogen flame detector. ICP-AES were measured on IRIS Advantage. XPS measurement was recorded on PHI5702 photoelectron spectrometer. 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 catalyst was conducted by an energy-dispersive X-ray spectrometer (EDX) attached to the scanning electron microscope. The sample coating procedure consisted of plasma magnetron sputtering using a standard gold target, applying 20 mA plasma current for 60 s in argon atmosphere (0.1 mbar chamber pressure). This is the default procedure for depositing a 4 nm-thick gold coating in the main menu of the Quorum Technologies (Quorum Technologies Ltd., Ashford,Kent,UK) Q150R plasma coater used for this work. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC analyses were conducted on silica gel GF254 plates.

Preparation of the reaction substrates

The Preparation of Pyrimidin-2-yl Sulfonates

The pyrimidin-2-yl sulfonates **1** were readily prepared according to the procedures via sequential functionalization of easily available Biginelli 3,4-dihydropyrimidine-2(1H)-ones via oxidation, esterification [1]



1

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

The Characterization and the data of the catalyst

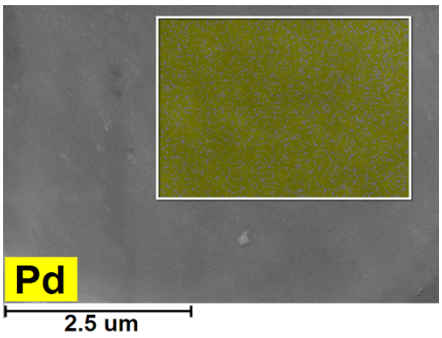


Figure 1. The SEM images and the corresponding EDS mapping of Pd of fresh catalyst at a high magnification.

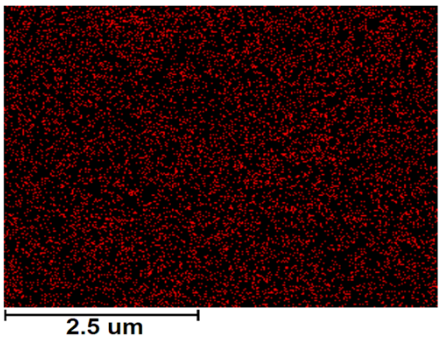


Figure 2. The corresponding EDS mapping of Pd of reused catalyst.

Table 1. The quantification of EDX data of the fresh catalyst.

Element	k Ration	wt%	wt% Sigma
C	1.00414	39.52	2.36
N	0.20615	12.81	1.28
O	0.27408	13.19	0.89
S	0.21153	5.41	0.91
Pd	0.78539	29.07	3.03
Total content:		100.00	

The NMR 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 2-(4-fluorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3f): White solid; m.p. 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54-8.42 (m, 2H), 7.75-7.57 (m, 2H), 7.49-7.28 (m, 3H), 7.07 (t, *J* = 8.7 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.32, 166.13, 165.42, 163.59, 162.68, 138.12, 133.32, 130.82, 130.73, 129.98, 128.45, 128.35, 123.24, 115.52, 115.31, 61.75, 22.80, 13.62 ppm. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 2-(4-chlorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3g): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of

ethyl acetate and petroleum ether (1:60).

Ethyl 4-methyl-2-(naphthalen-1-yl)-6-phenylpyrimidine-5-carboxylate (3h): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 4-methyl-2-phenyl-6-p-tolylpyrimidine-5-carboxylate (3i): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3j): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 4-(4-fluorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3k): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 4-(4-chlorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3l): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

Ethyl 4-(4-bromophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3m): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:60).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

Ethyl 4-Methyl-2-(oct-1-ynyl)-6-phenylpyrimidine-5-carboxylate (5b): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

Ethyl 2-(3,3-Dimethylbut-1-ynyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (5c): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

Ethyl 4-Methyl-6-phenyl-2-(p-tolylethynyl)pyrimidine-5-carboxylate (5d): 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

Ethyl 4-(4-Chlorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5f): Brown oil. ^{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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

Ethyl 4-(4-Fluorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5g): Yellow oil. ^{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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

Ethyl 4-(4-Methoxyphenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5h): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.56 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.15 (q, *J* =7.2 Hz, 2H), 3.75 (s, 3H), 2.50 (s, 3H), 2.39 (t, *J* = 7.2 Hz, 2H),1.65–1.52 (m, 2H), 1.36 (m, 2H), 1.28–1.16 (m, 4H), 1.06 (t, *J* =7.2 Hz, 3H), 0.80 (t, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.90, 164.95,

162.91, 161.24, 152.07, 129.92, 129.32, 123.32, 113.79, 91.09, 79.95, 61.75, 55.18, 31.15, 28.59, 27.81, 22.33, 19.29, 13.88, 13.62 ppm. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:40).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:30).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:30).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:30).

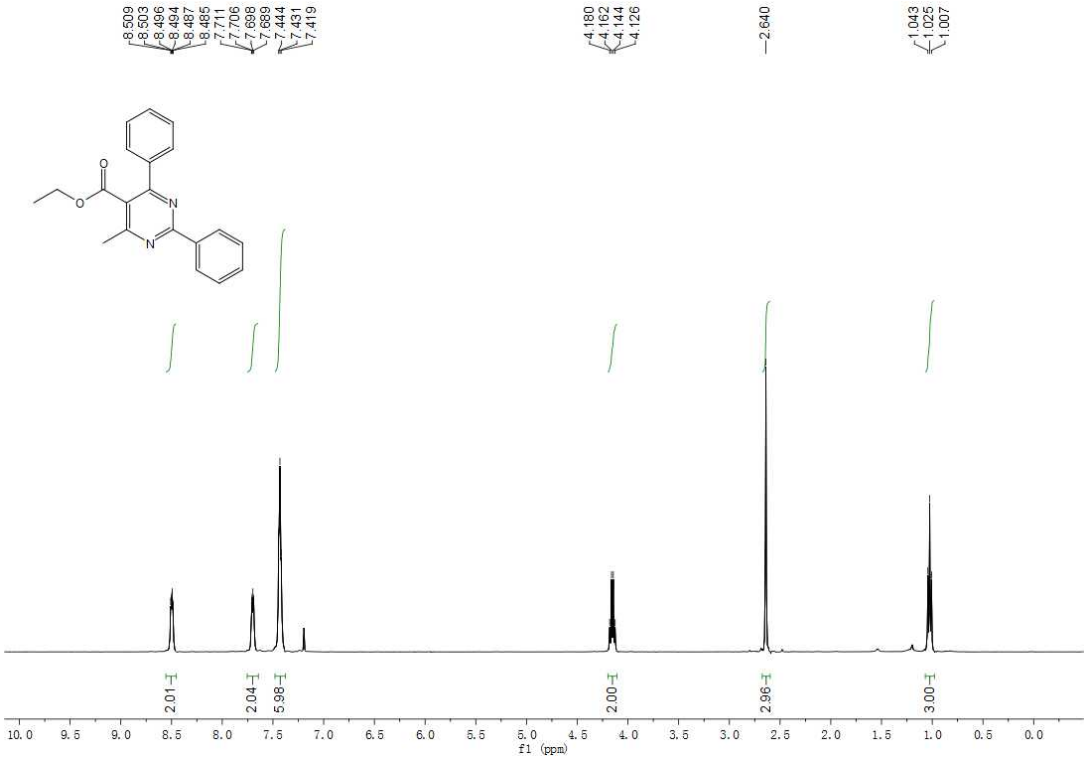
Ethyl 2-(4-chlorophenylamino)-4-methyl-6-phenylpyrimidine-5-carboxylate (7d): Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.97 (s, 1H), 7.71-7.57 (m, 2H), 7.56-7.47 (m, 2H), 7.41 (d, *J* = 5.8 Hz, 3H), 7.24-7.17 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 3H), 0.98 (dd, *J* = 7.7, 6.6 Hz, 3H). ^{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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:30).

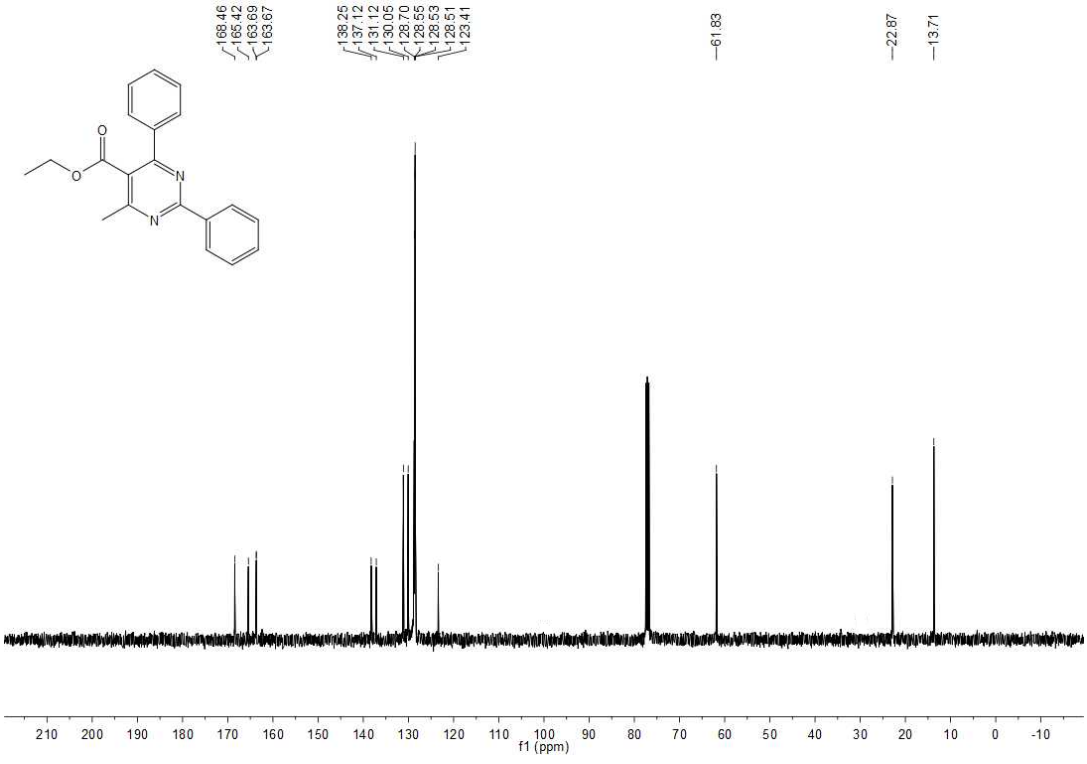
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-(phenylamino)pyrimidine-5-carboxylate (7e): Claybank oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 10.1 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 4H), 7.06-6.95 (m, 2H), 6.72 (t, *J* = 7.4 Hz, 1H), 6.68-6.61 (m, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 3.52 (s, 3H), 2.24 (s, 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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:30).

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. The crude product was purified by silica gel column chromatography, eluting with a mixture of ethyl acetate and petroleum ether (1:30).

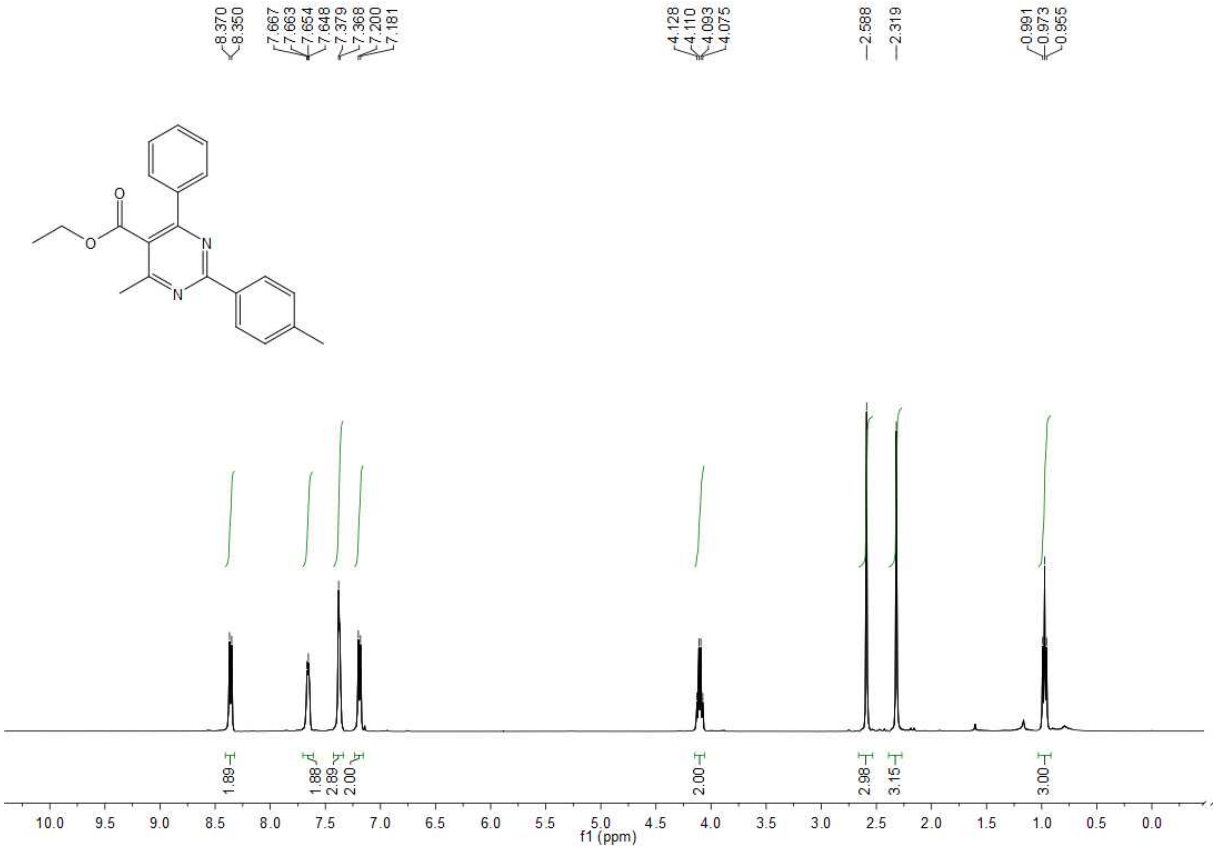
Copies of the NMR Spectra for Products

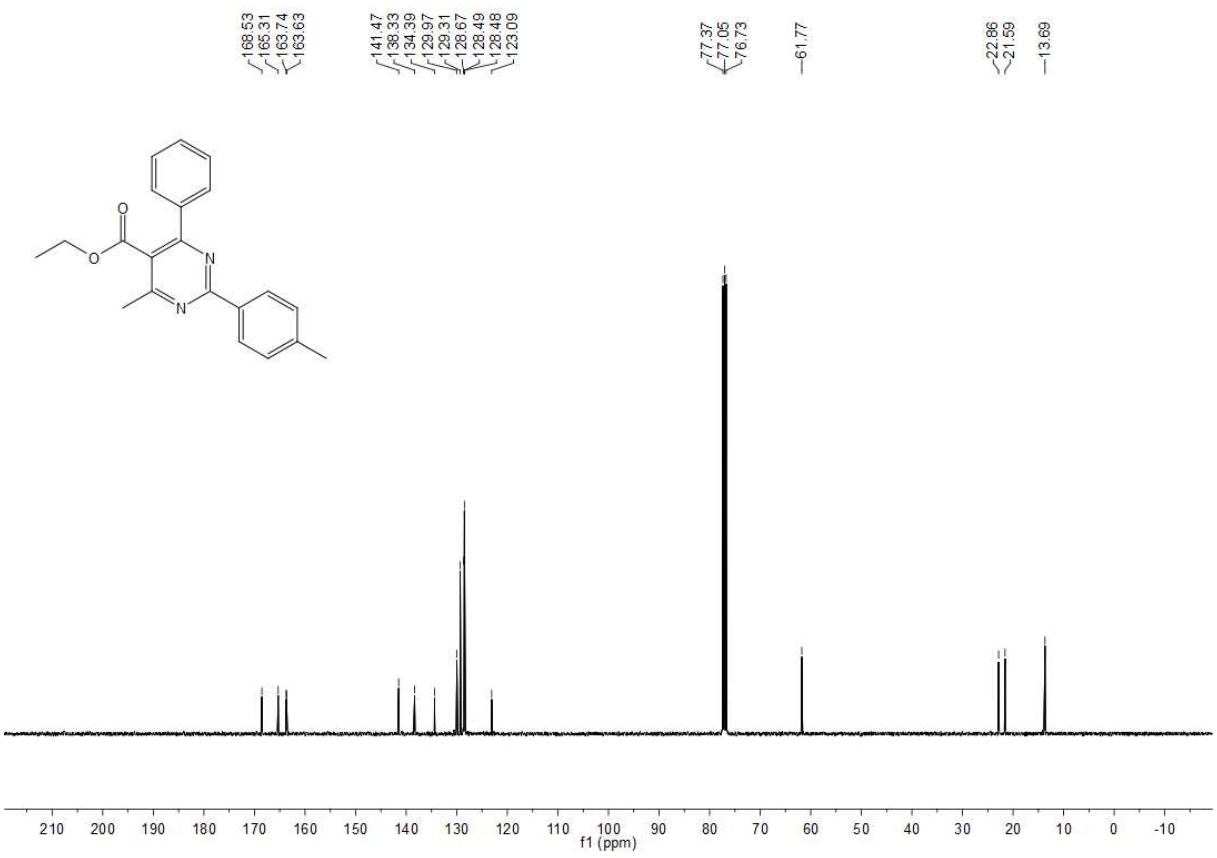
Ethyl 4-methyl-2,6-diphenylpyrimidine-5-carboxylate (3a)



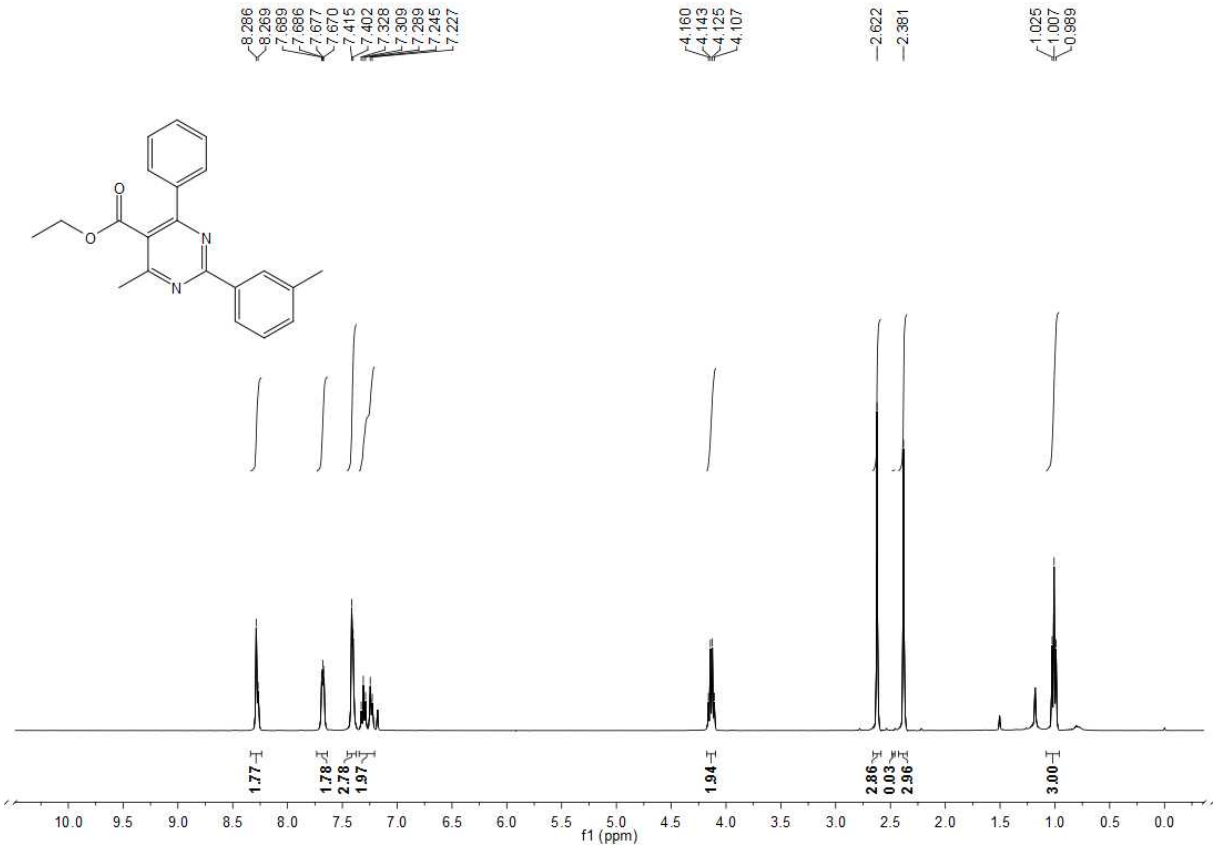


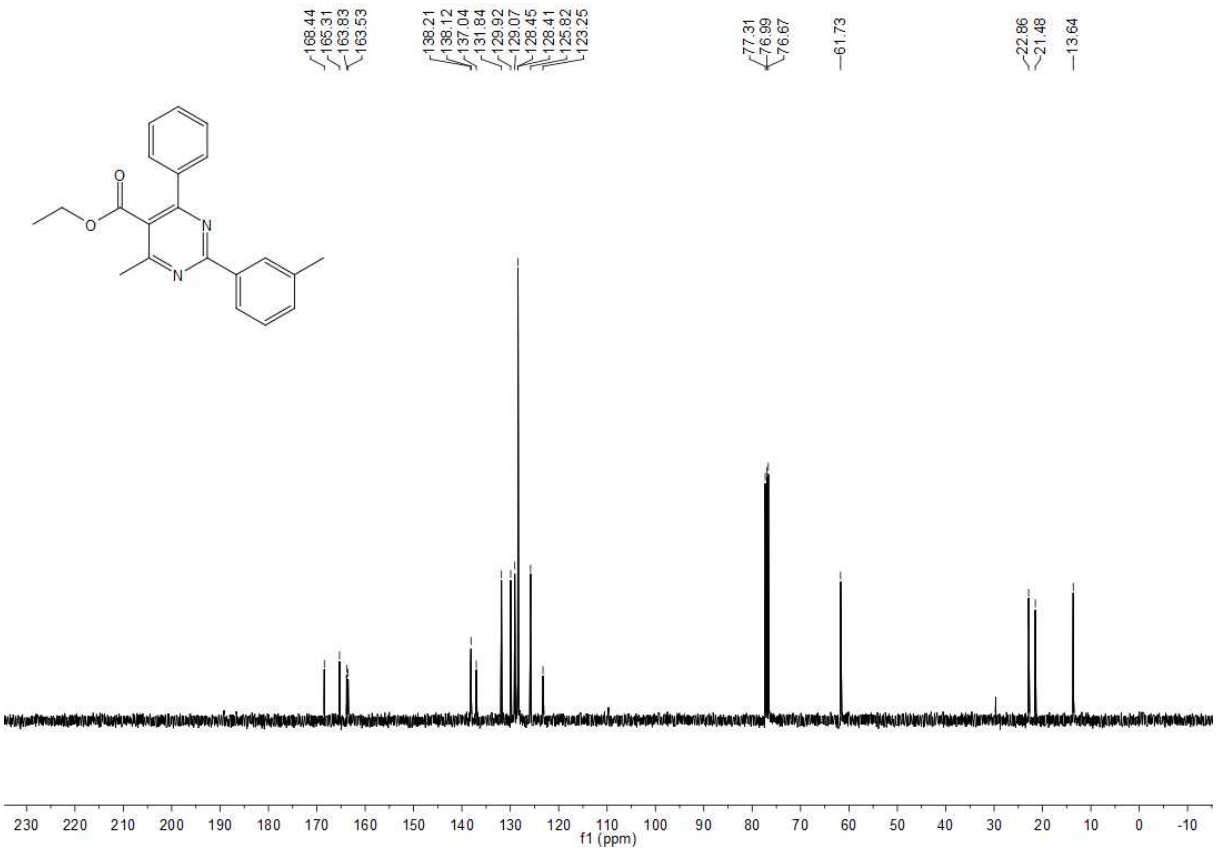
Ethyl 4-methyl-6-phenyl-2-p-tolylpyrimidine-5-carboxylate (3b)



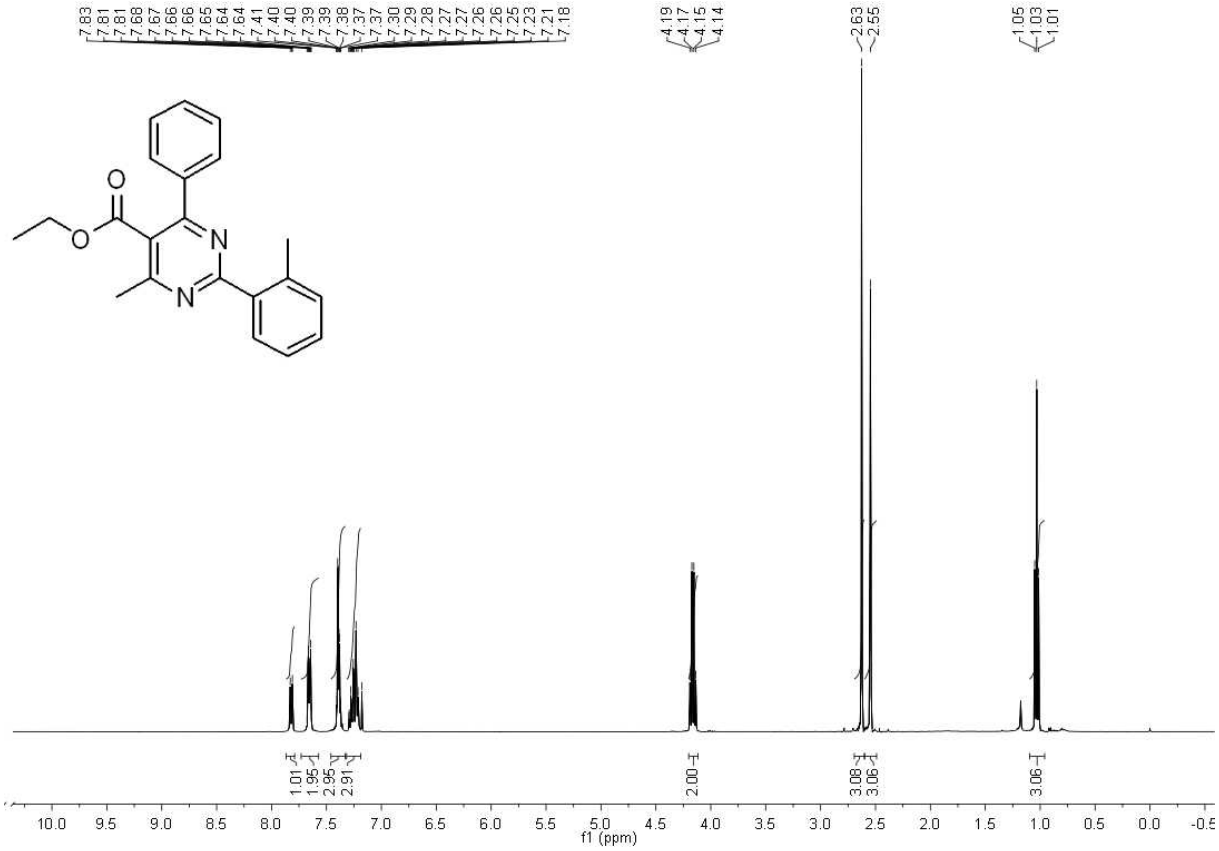


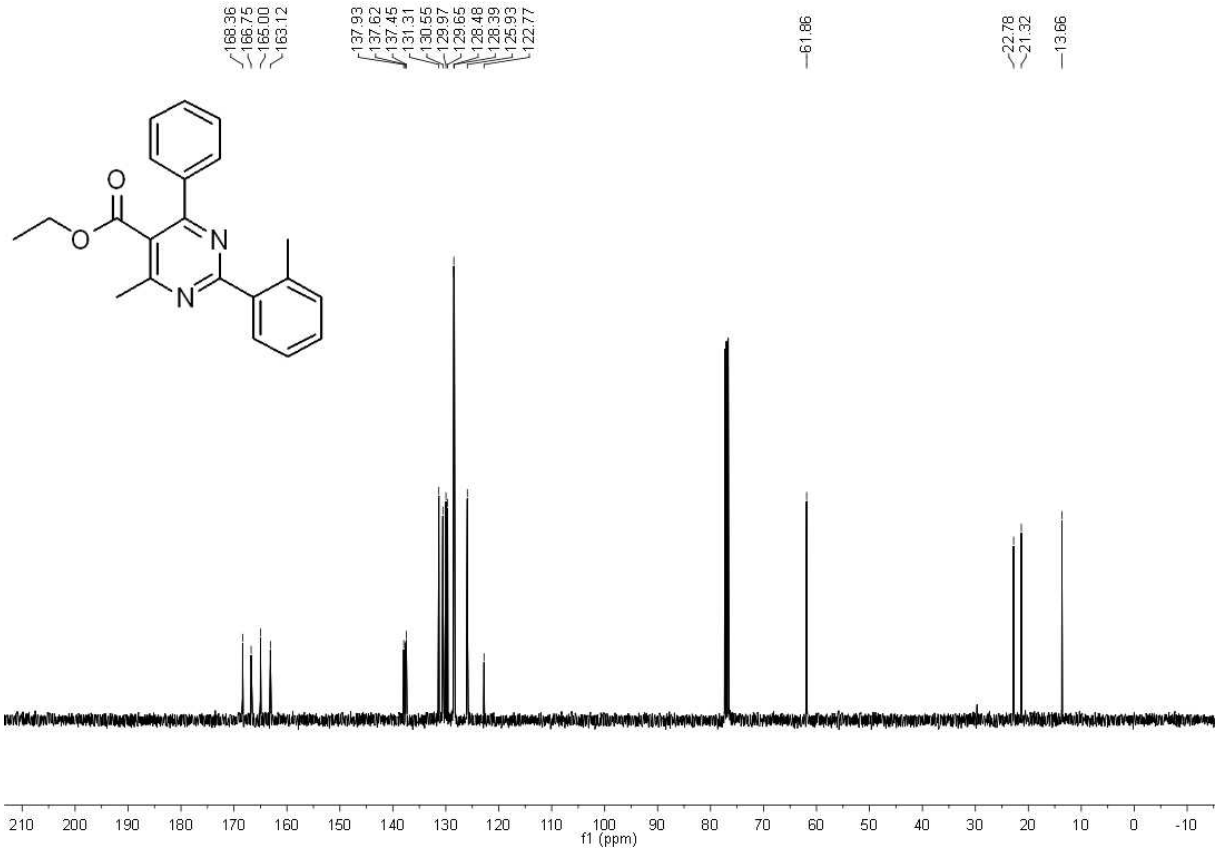
Ethyl 4-methyl-6-phenyl-2-m-tolylpyrimidine-5-carboxylate (3c)



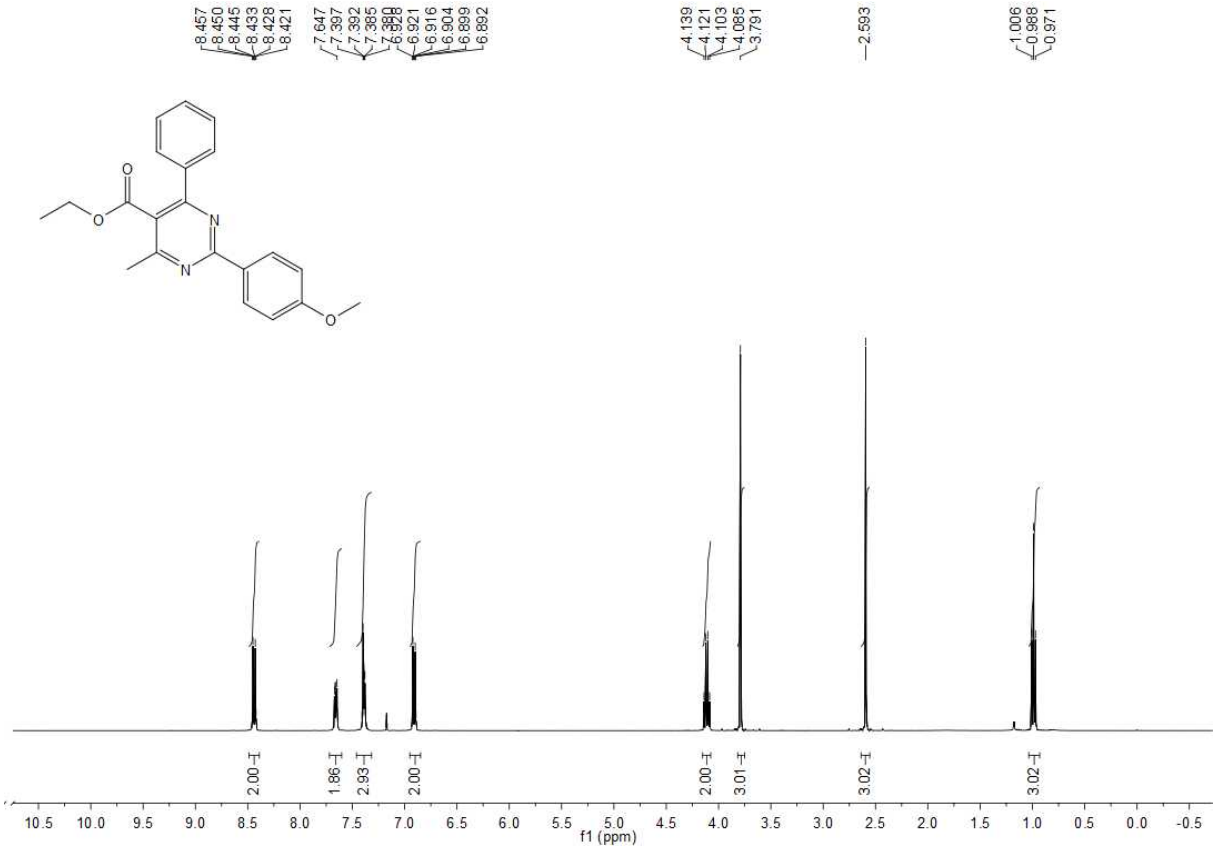


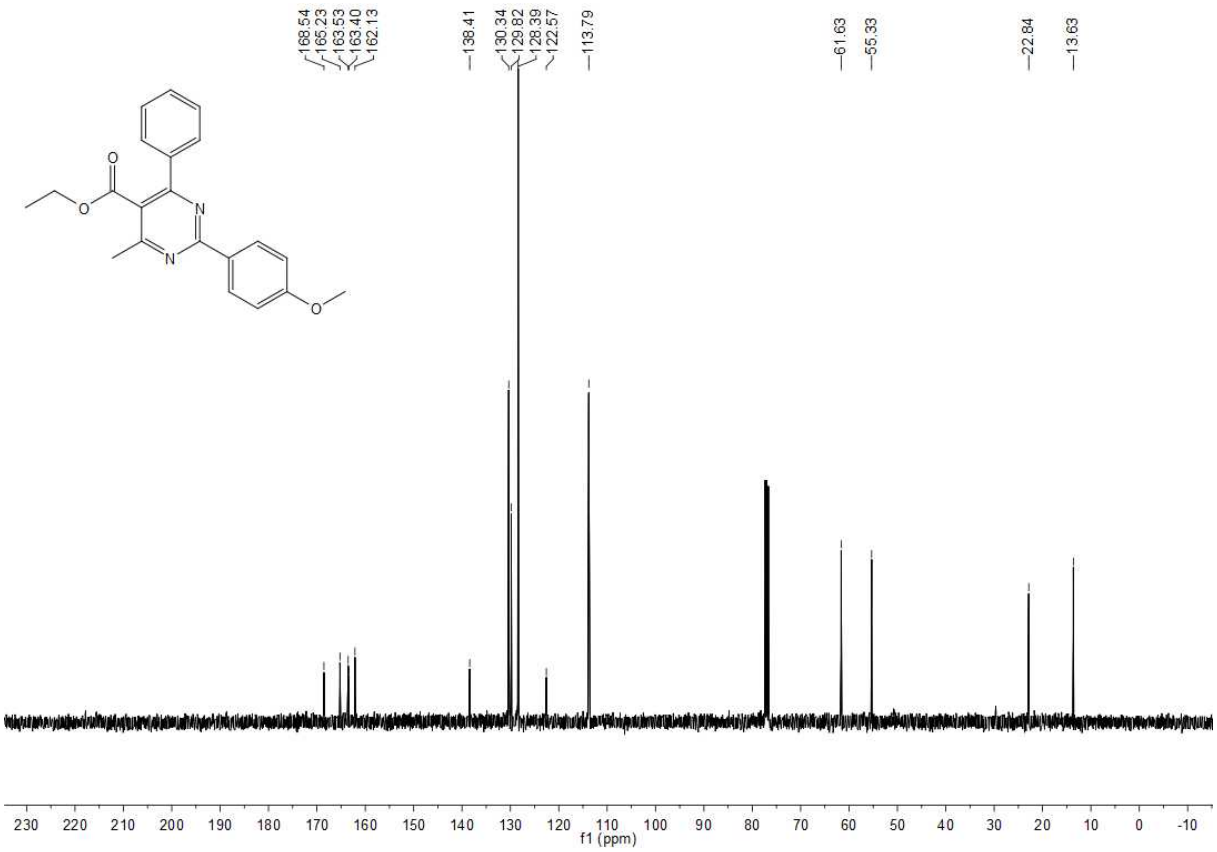
Ethyl 4-methyl-6-phenyl-2-o-tolylpyrimidine-5-carboxylate (3d)



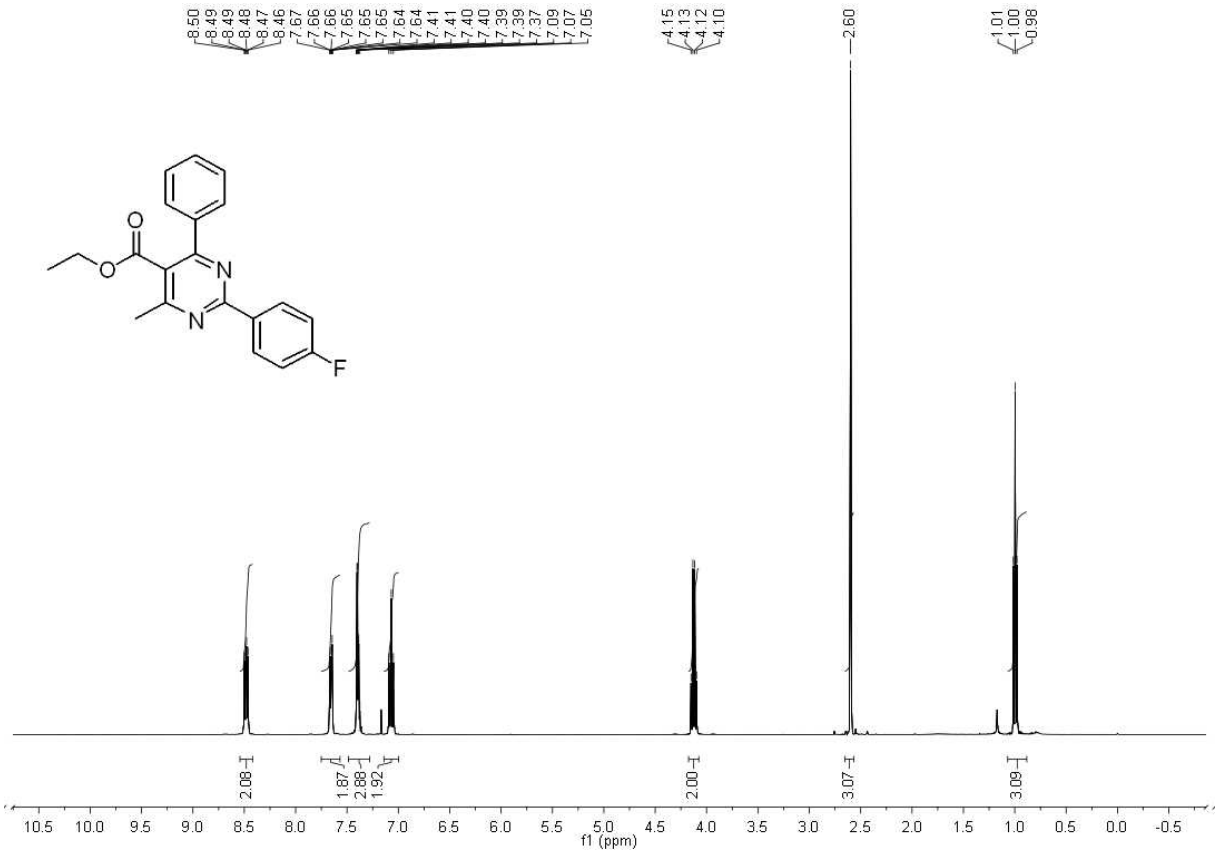


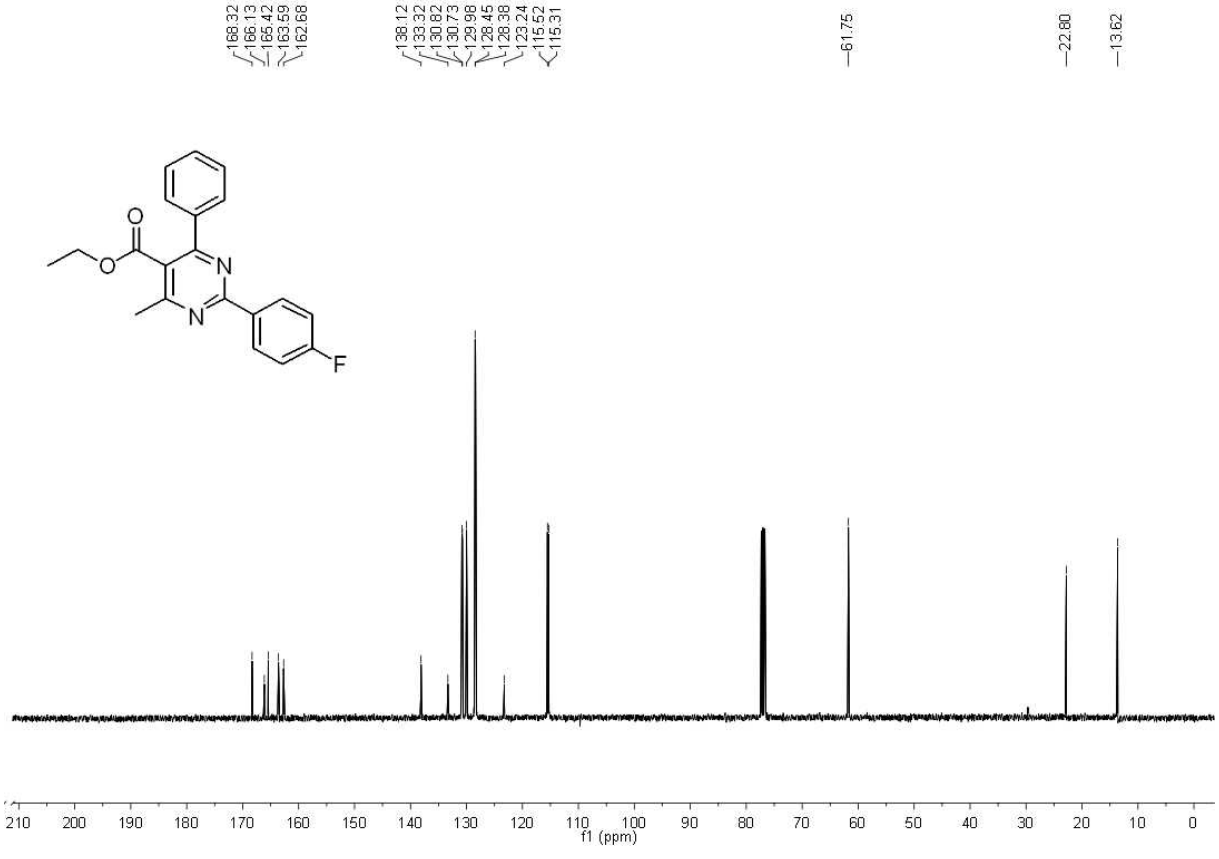
Ethyl 2-(4-methoxyphenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3e)



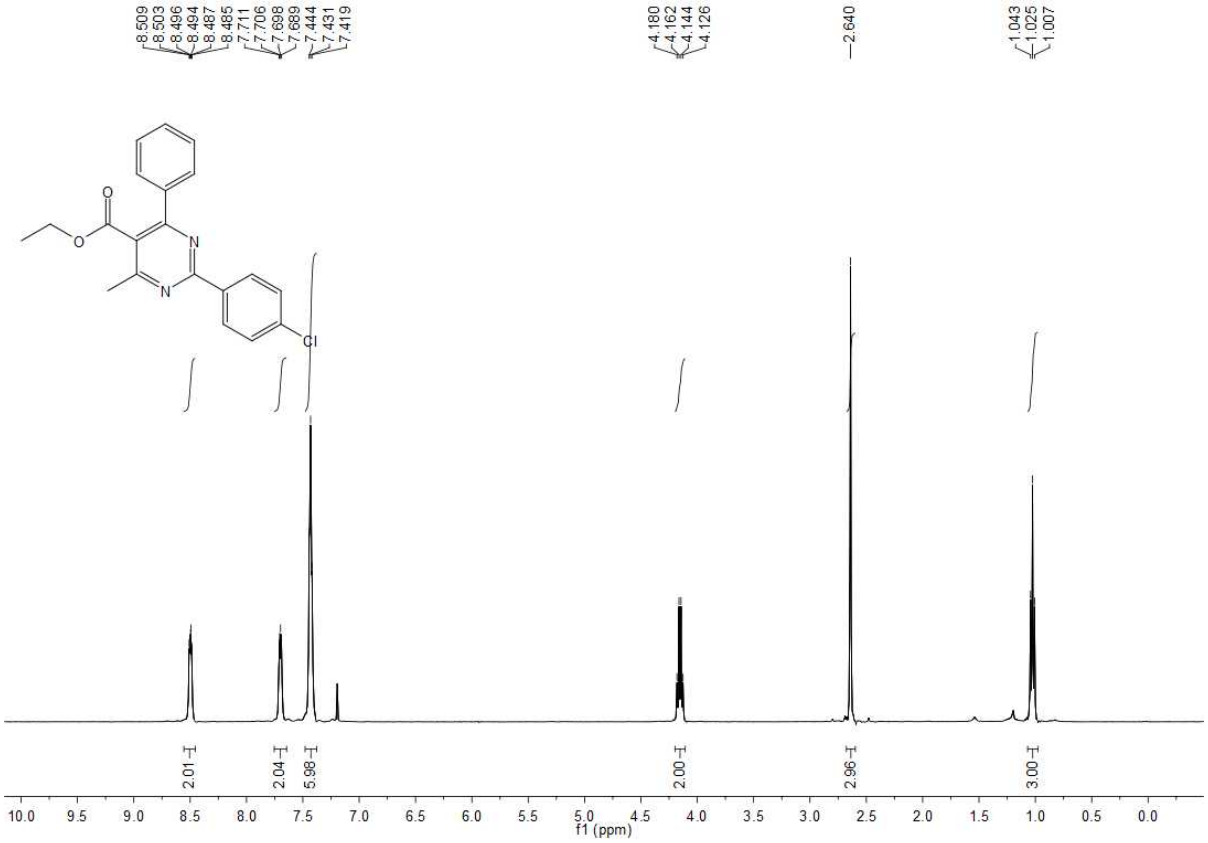


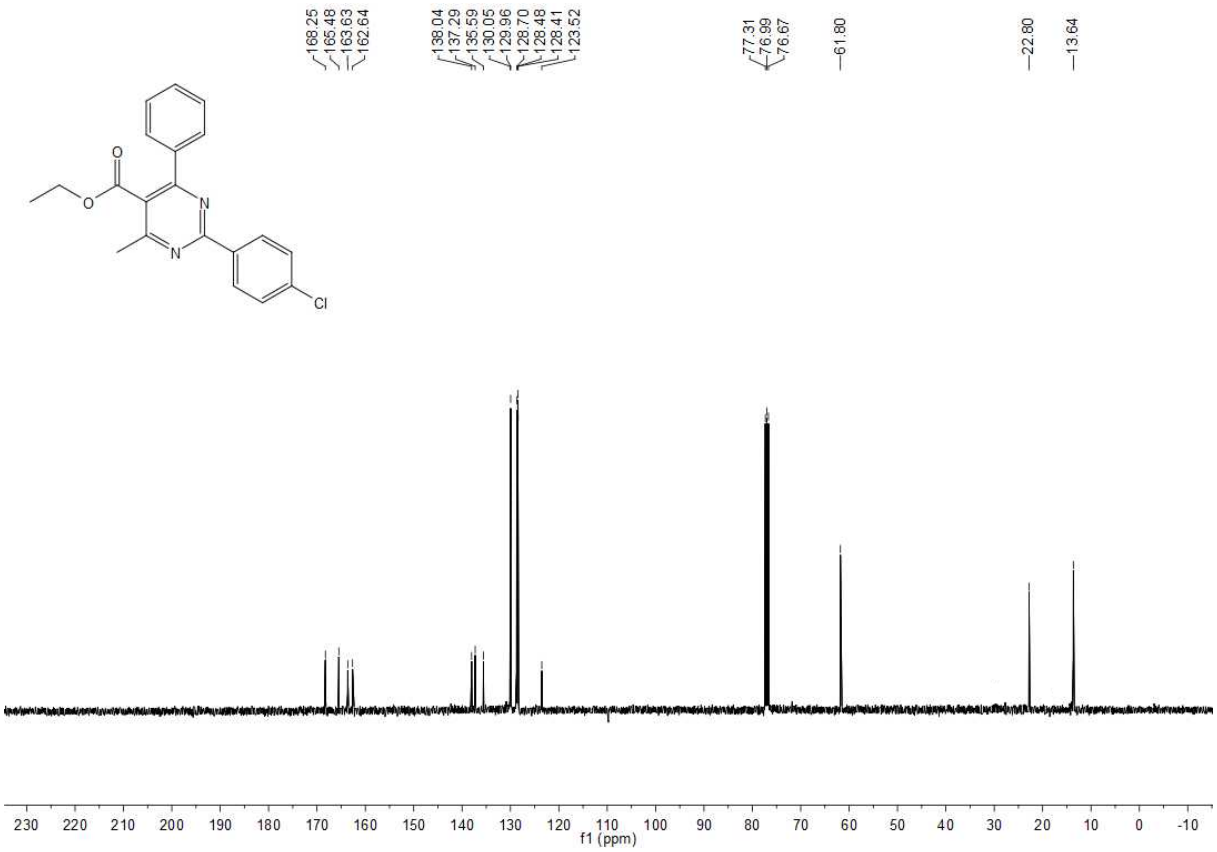
Ethyl 2-(4-fluorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3f)



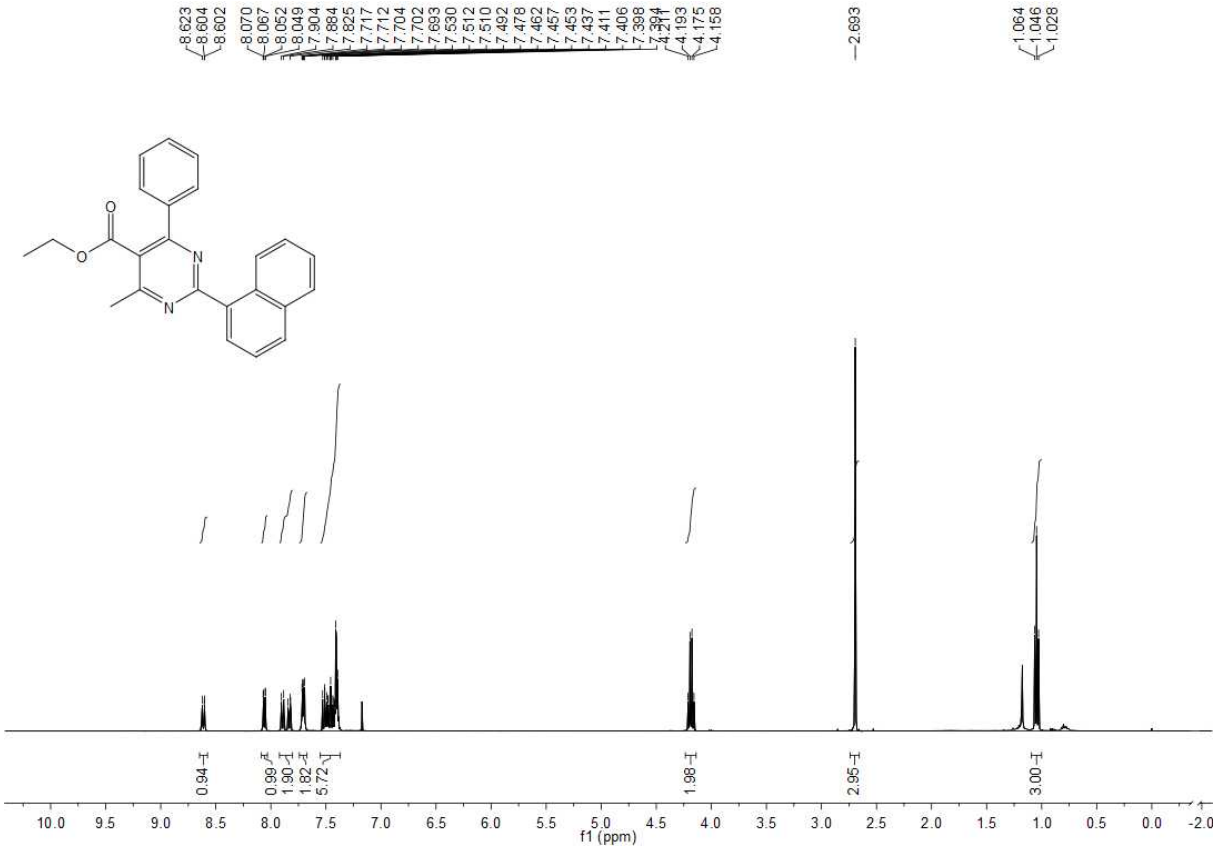


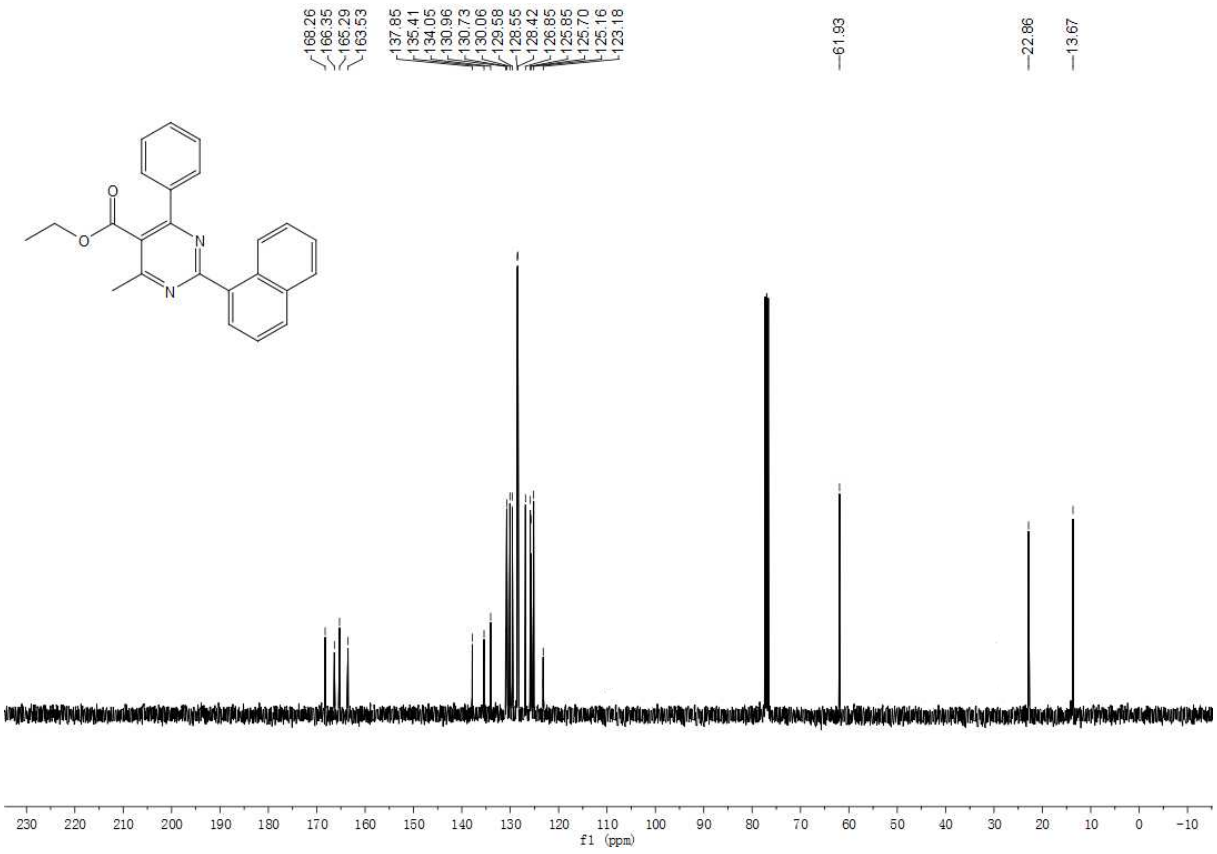
Ethyl 2-(4-chlorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (3g)



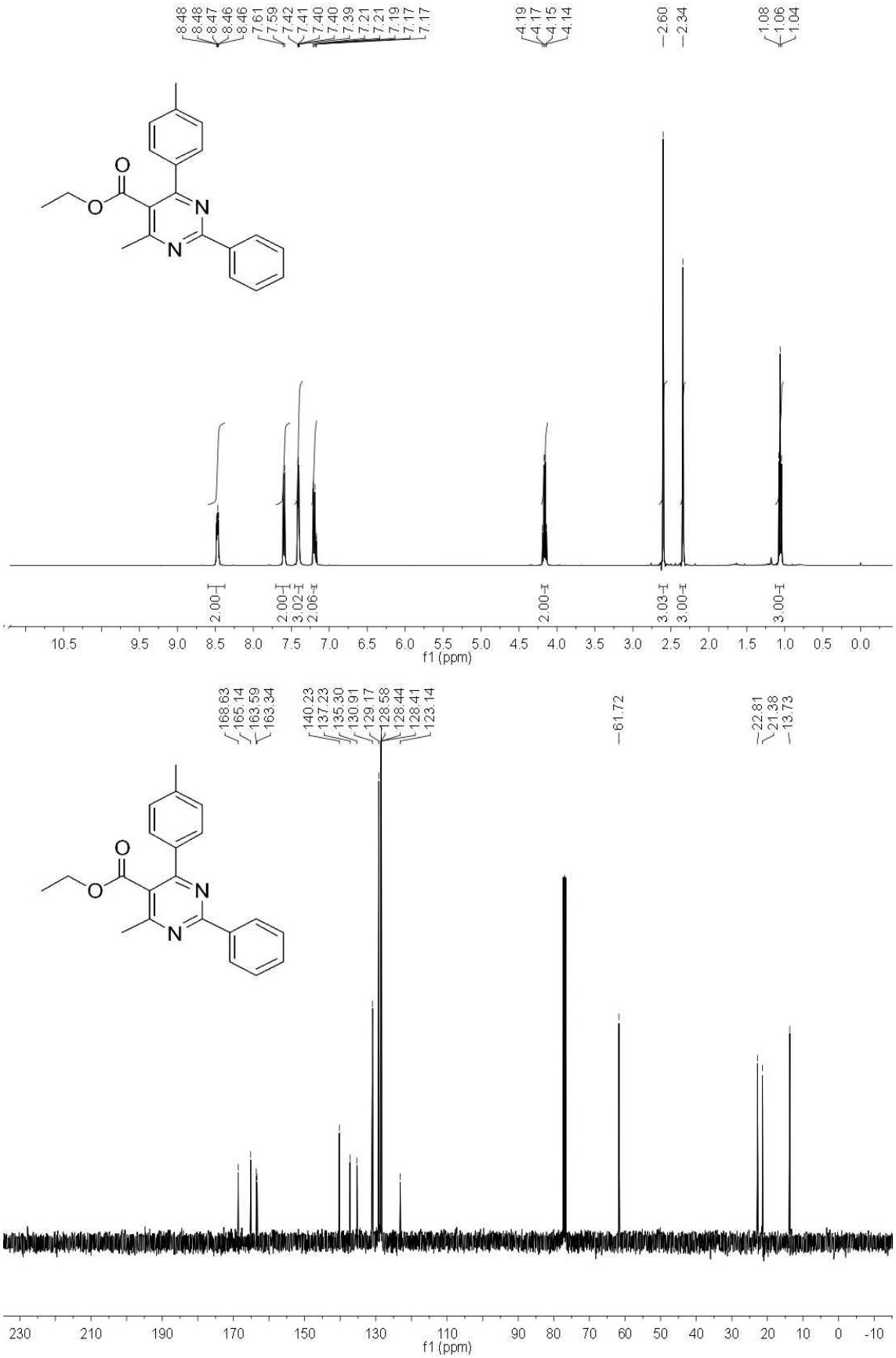


Ethyl 4-methyl-2-(naphthalen-1-yl)-6-phenylpyrimidine-5-carboxylate (3h)

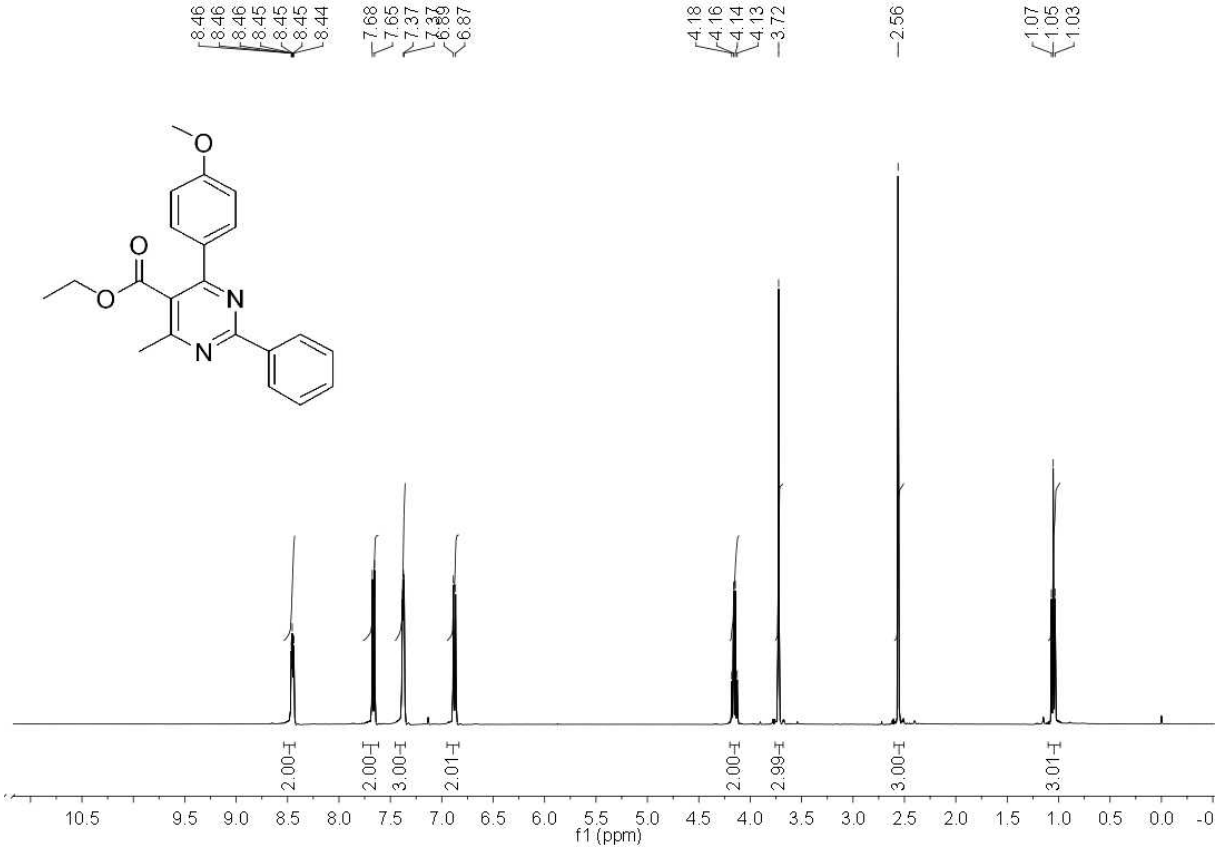


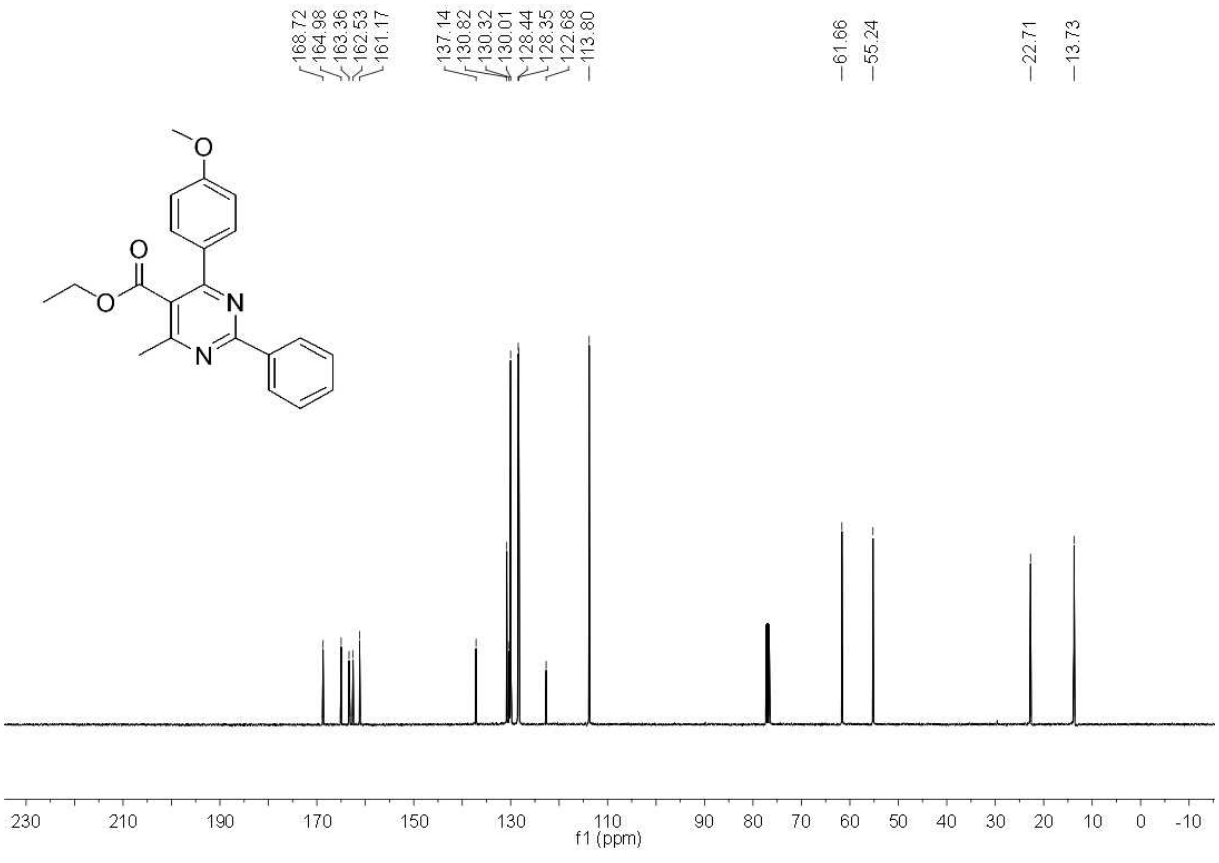


Ethyl 4-methyl-2-phenyl-6-p-tolylpyrimidine-5-carboxylate (3i)

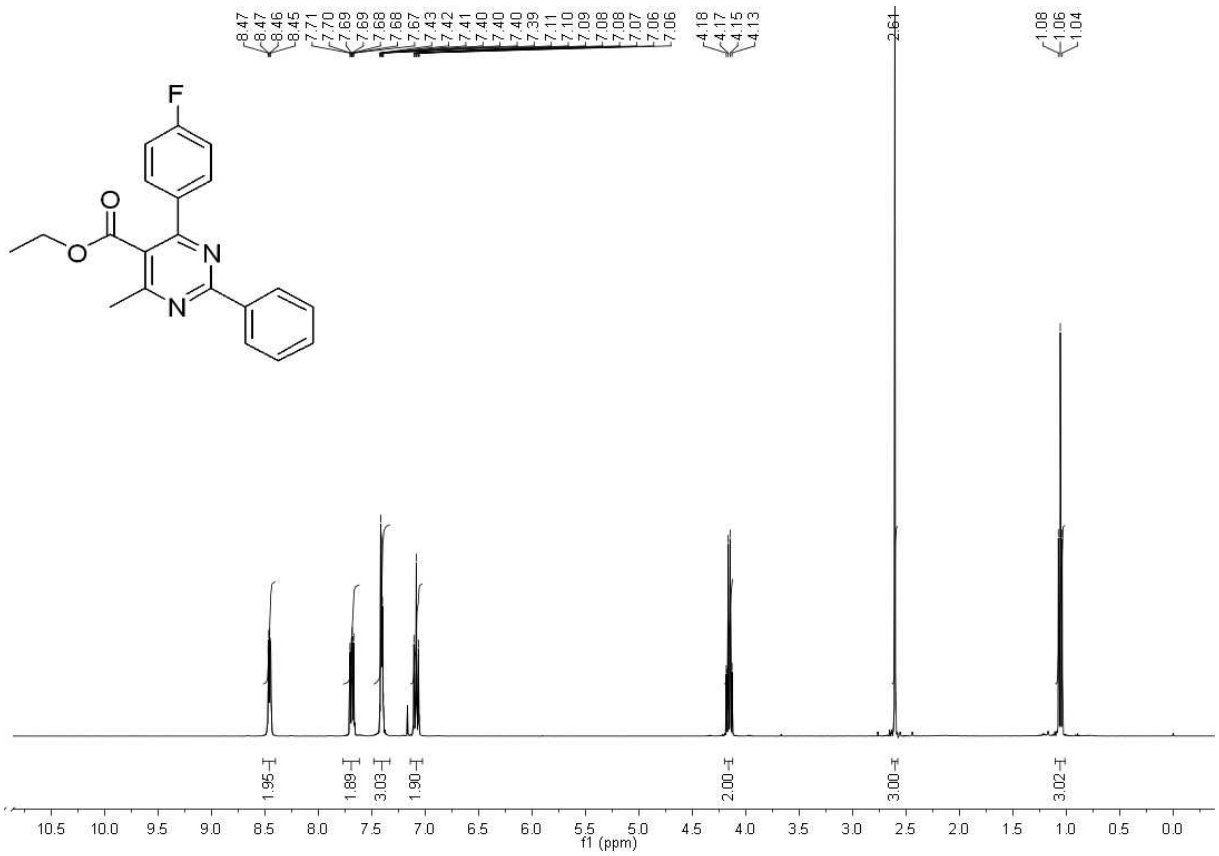


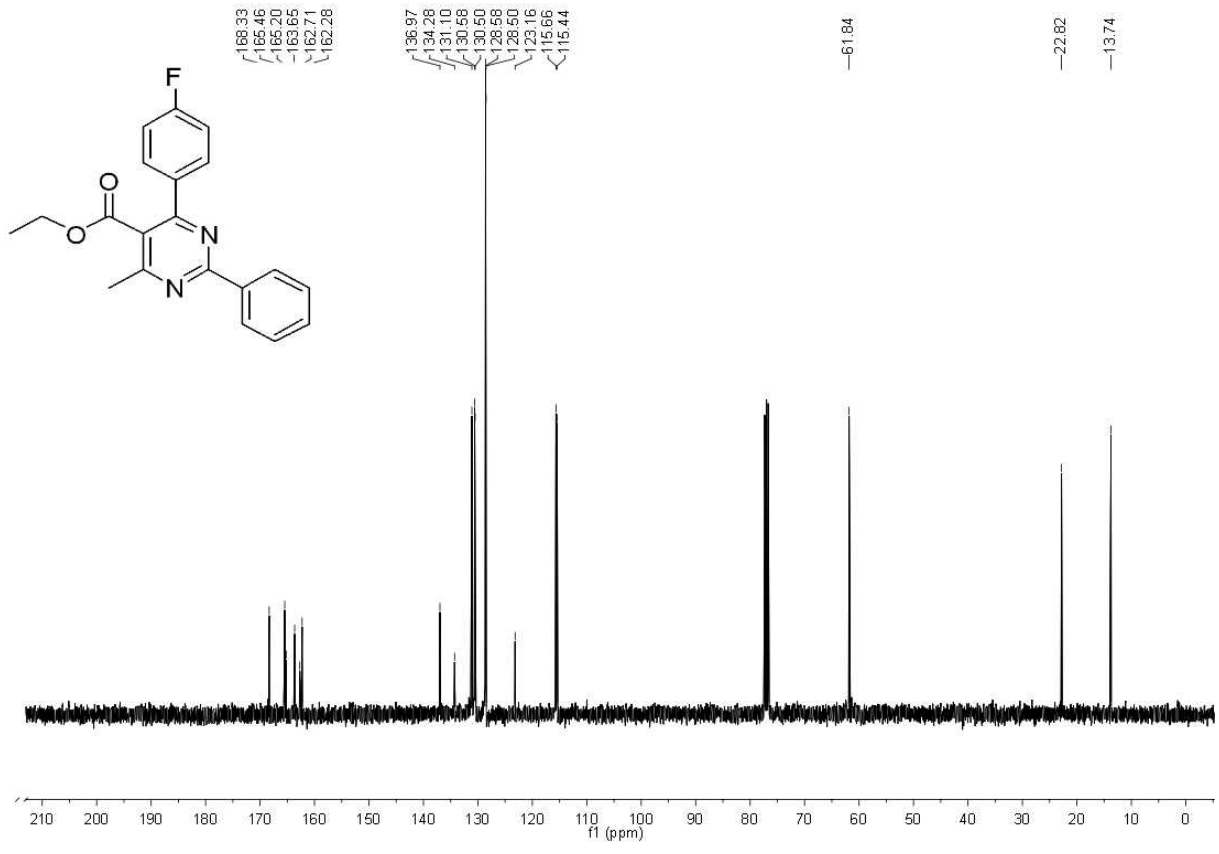
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3j)



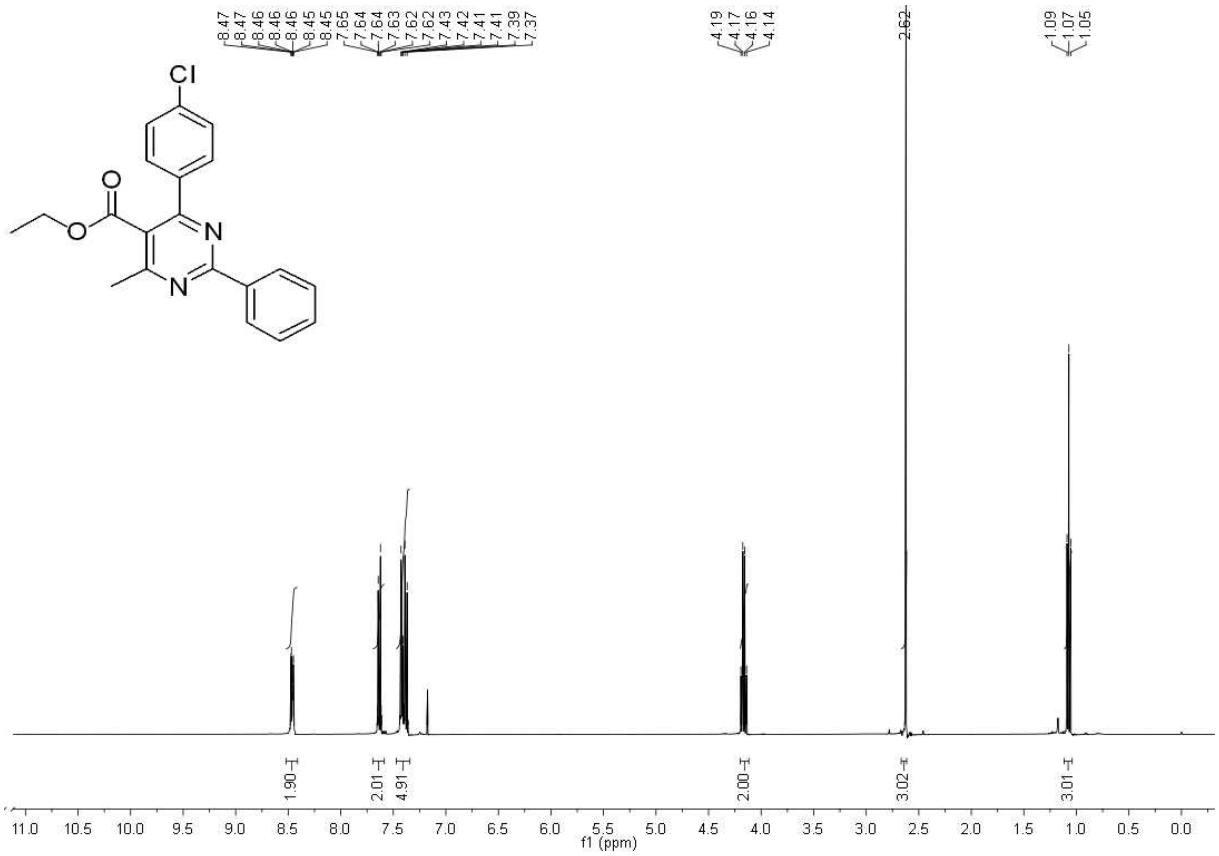


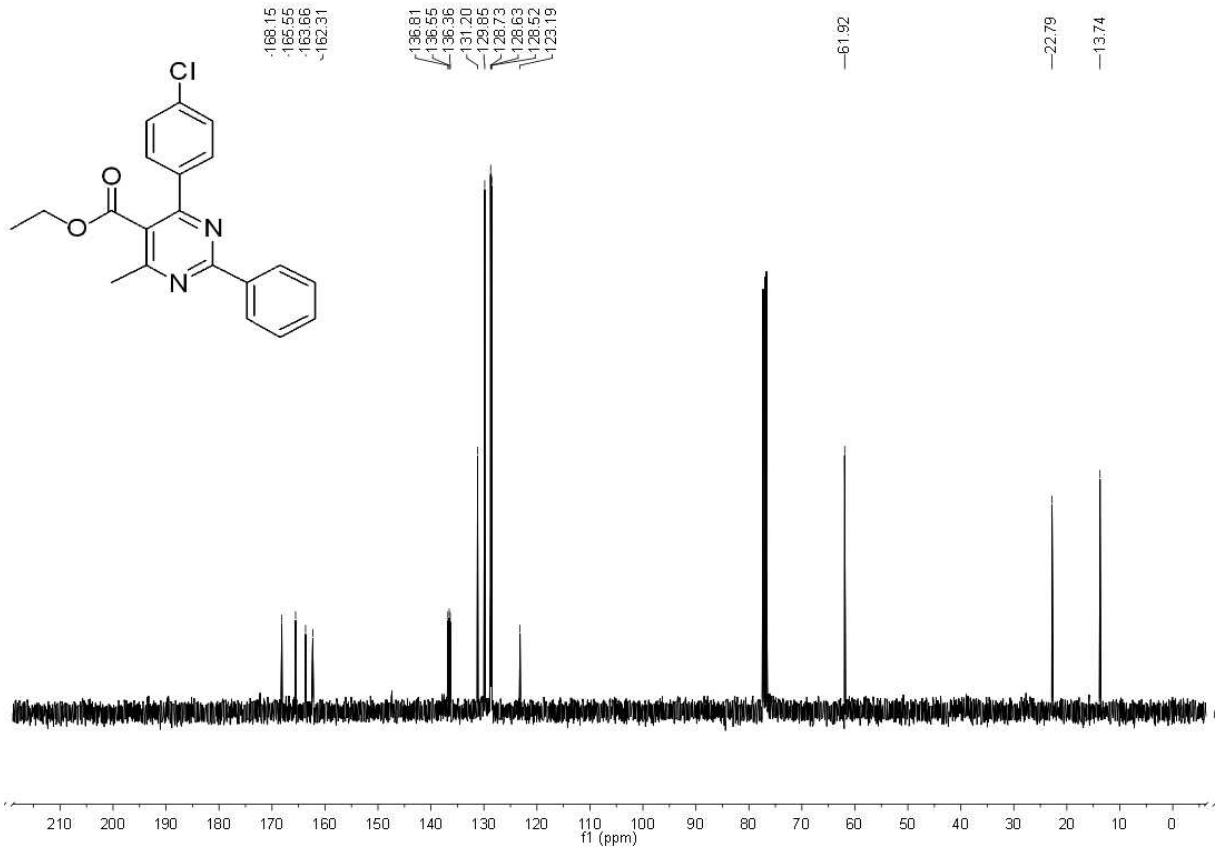
Ethyl 4-(4-fluorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3k)



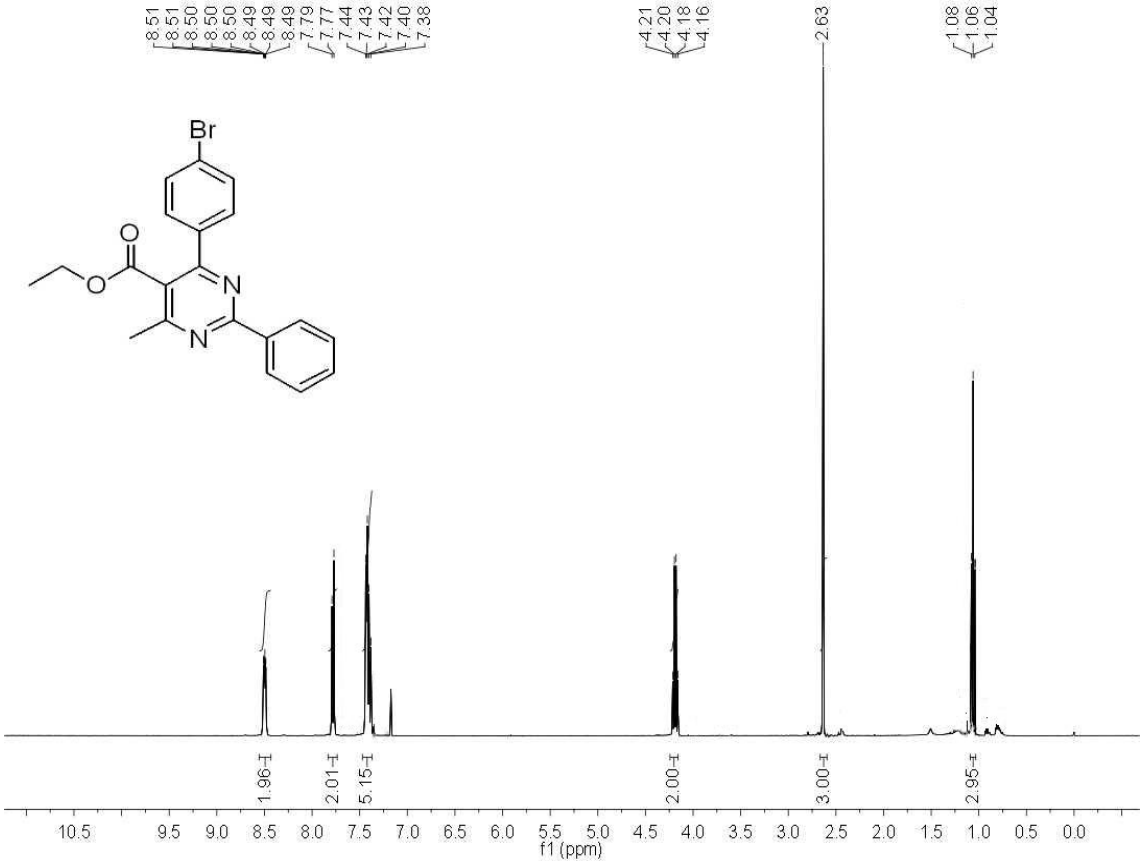


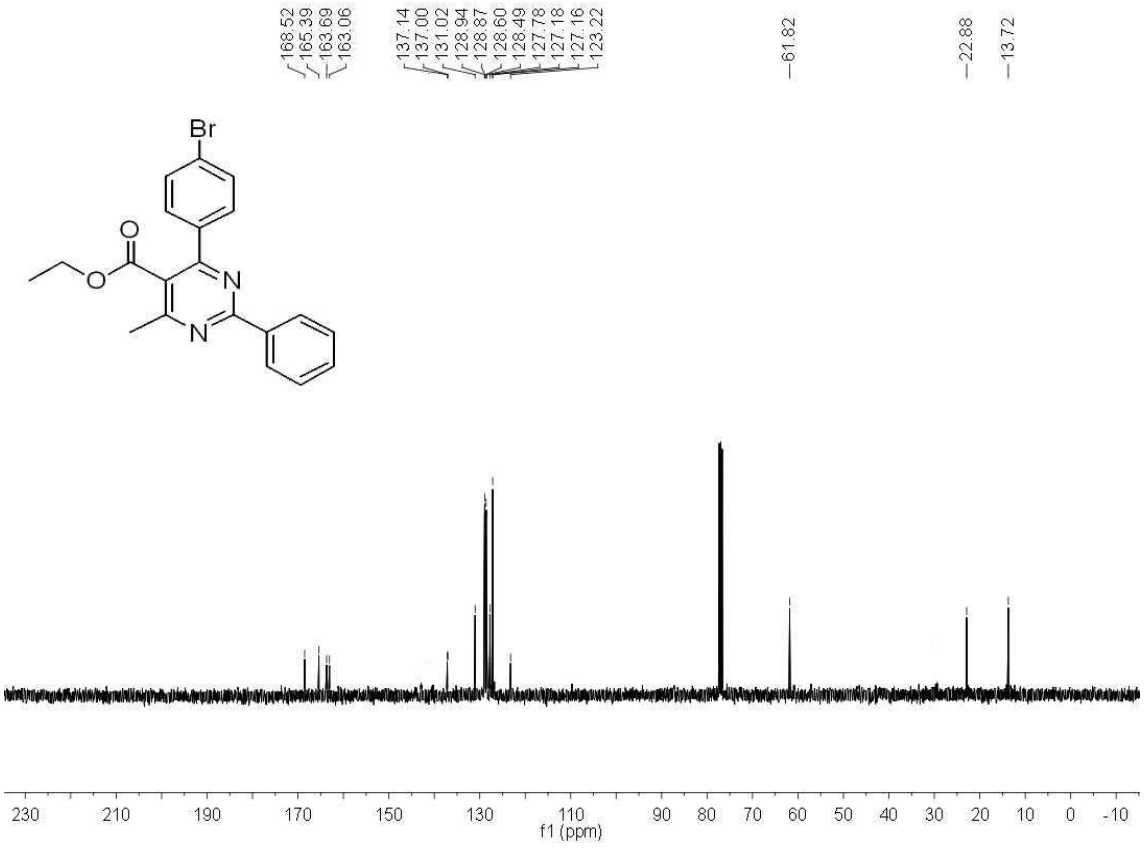
Ethyl 4-(4-chlorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3l)



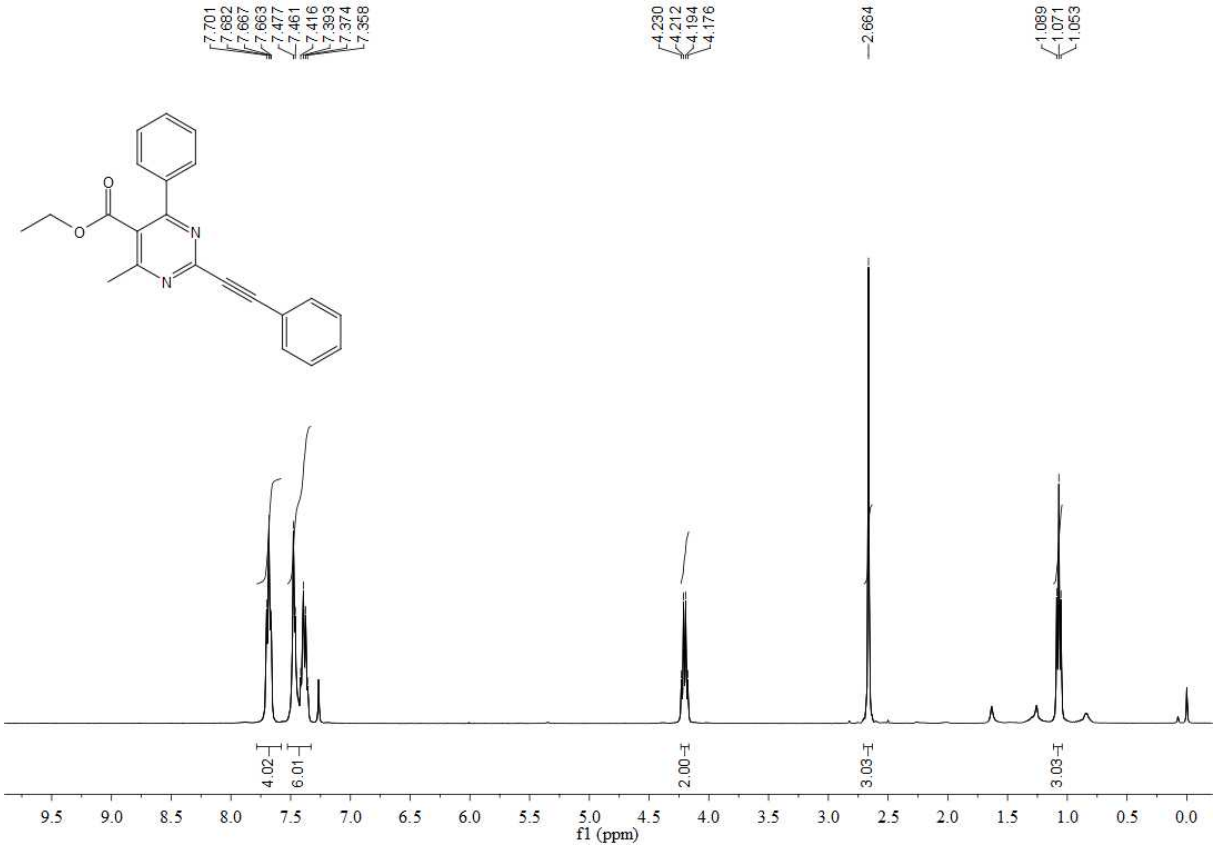


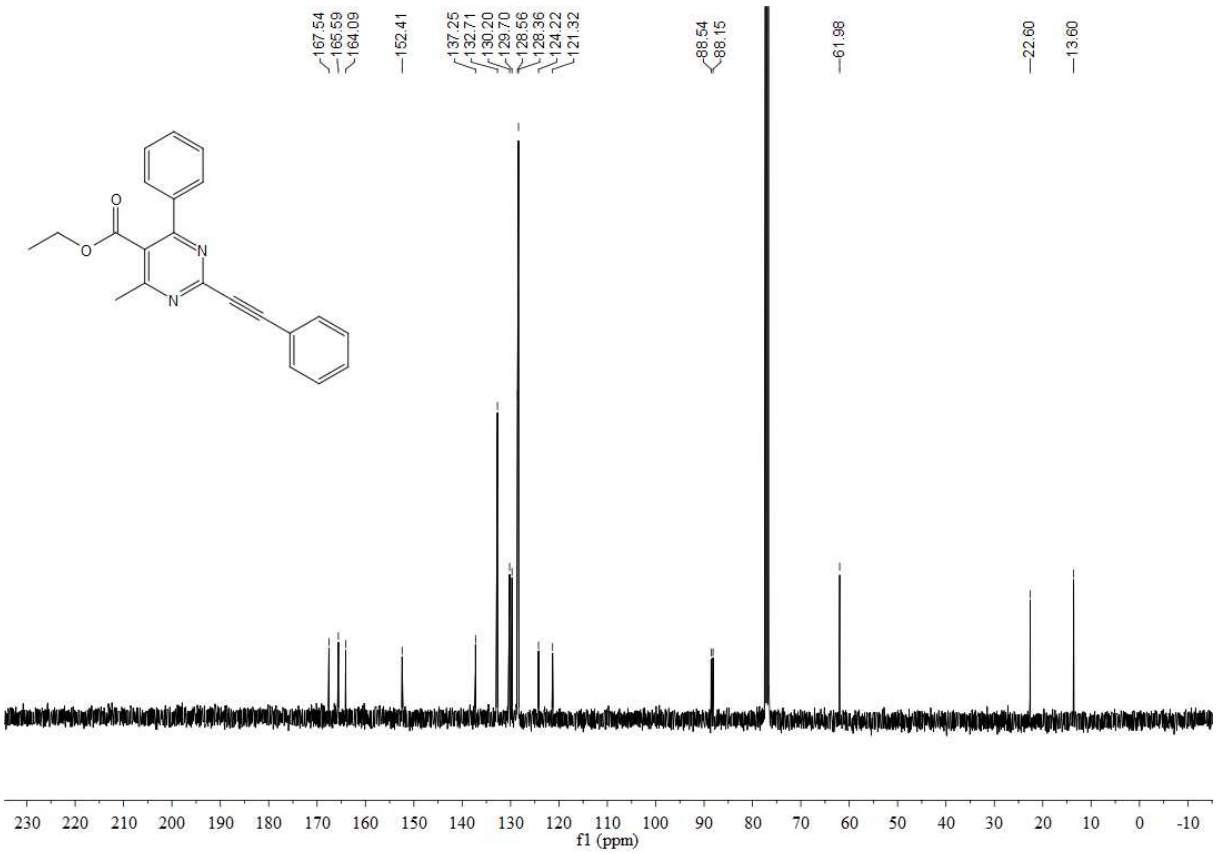
Ethyl 4-(4-bromophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (3m)



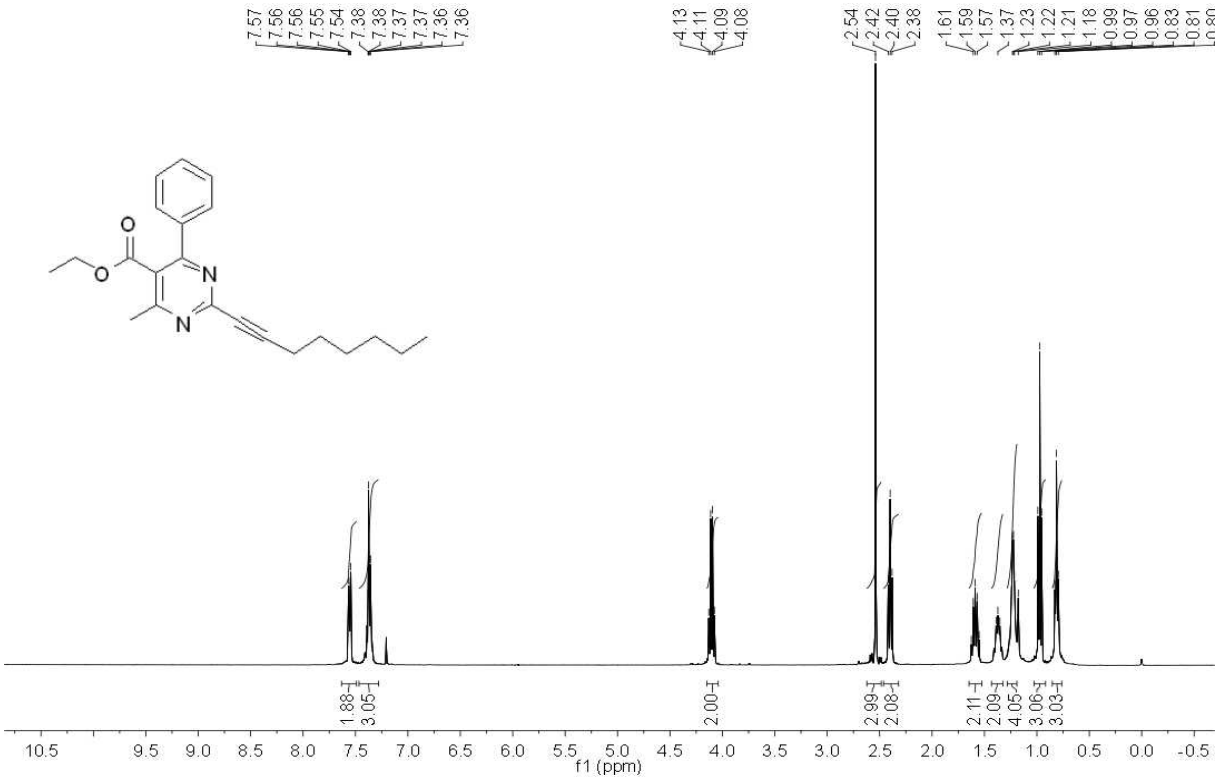


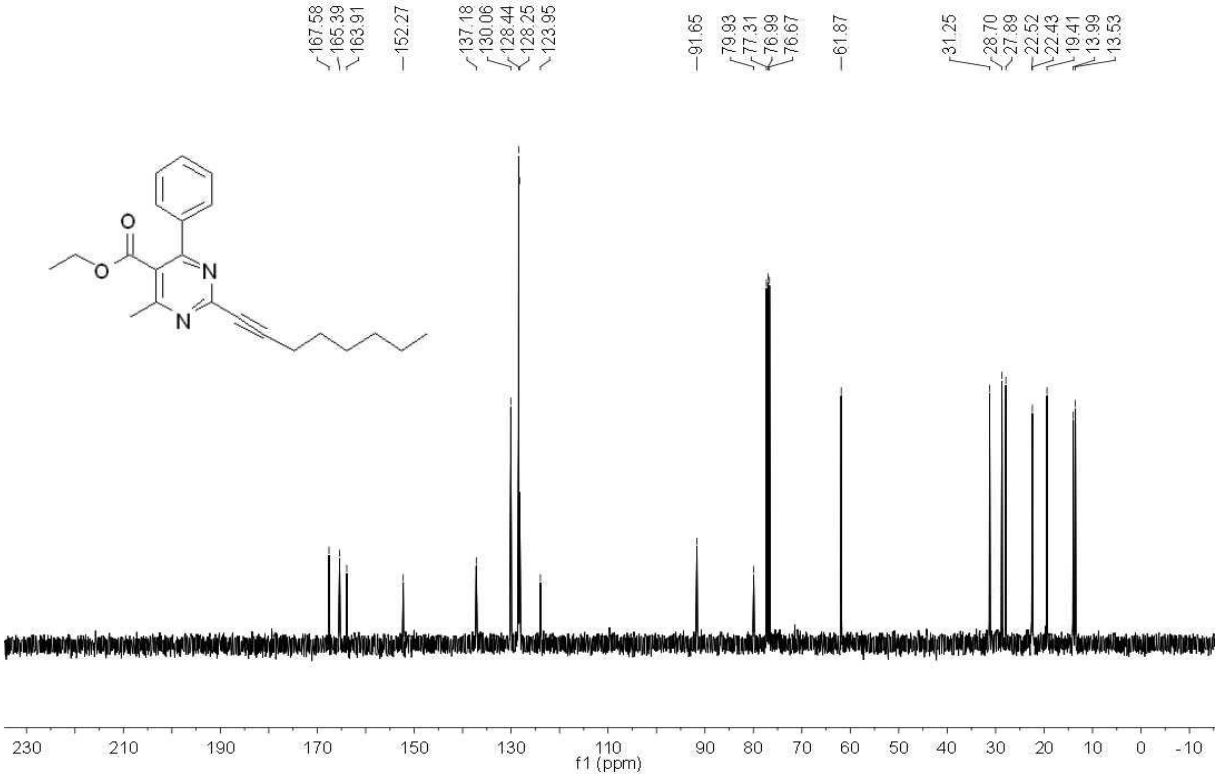
Ethyl 4-methyl-6-phenyl-2-(phenylethynyl)pyrimidine-5-carboxylate (5a)



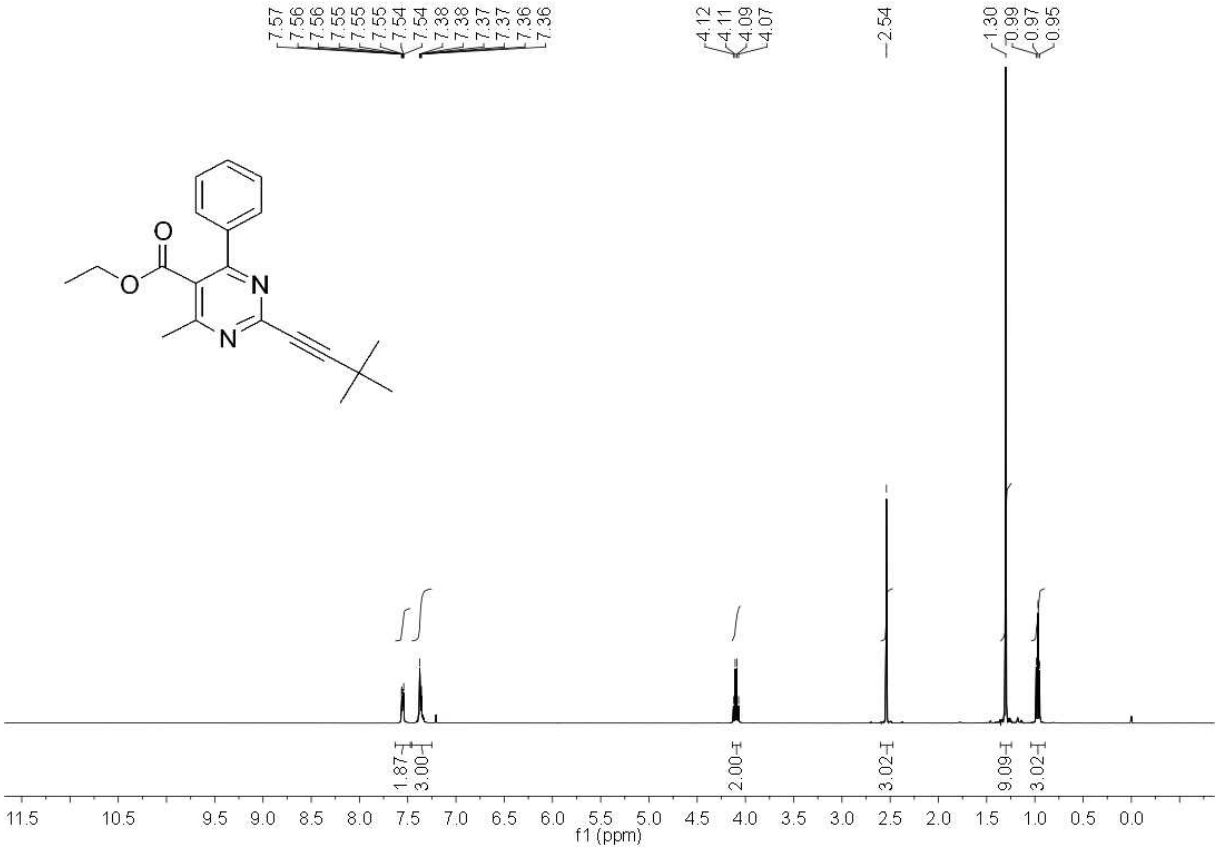


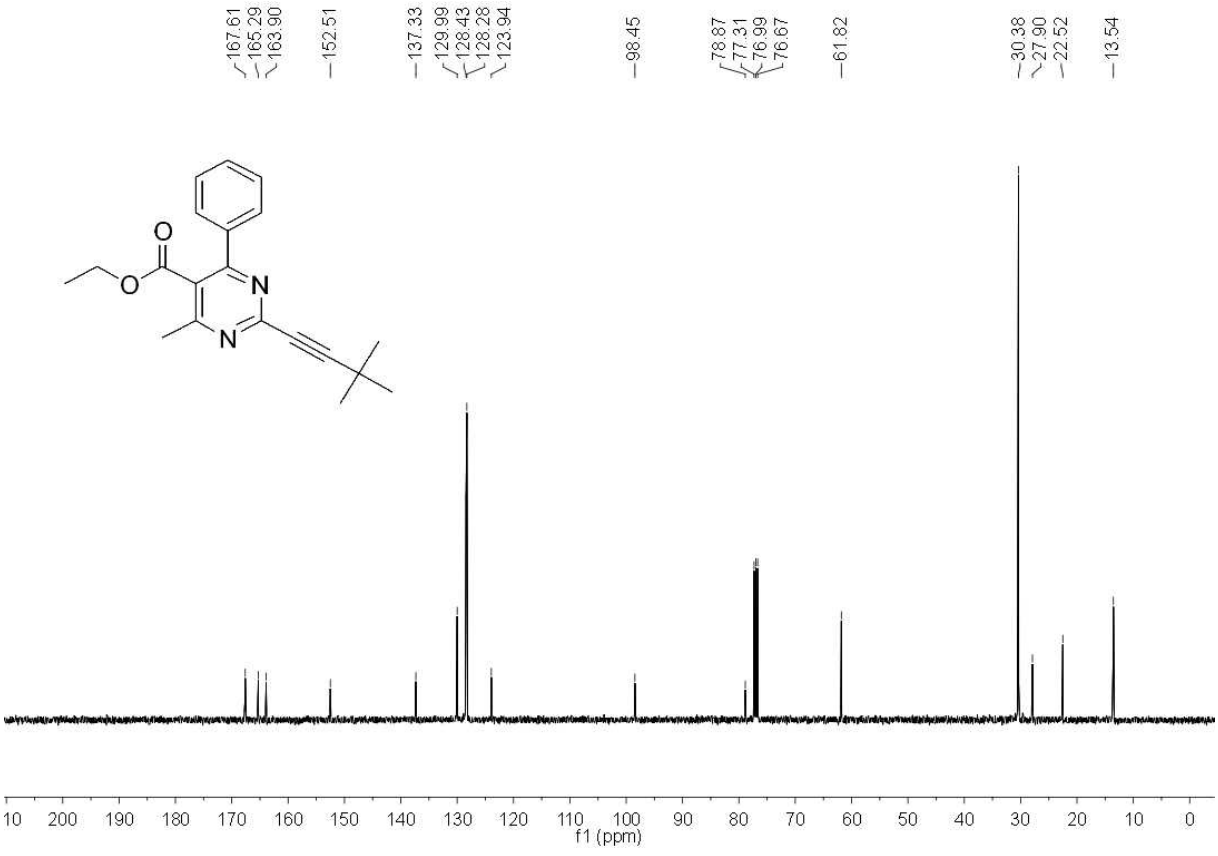
Ethyl 4-Methyl-2-(oct-1-ynyl)-6-phenylpyrimidine-5-carboxylate (5b)



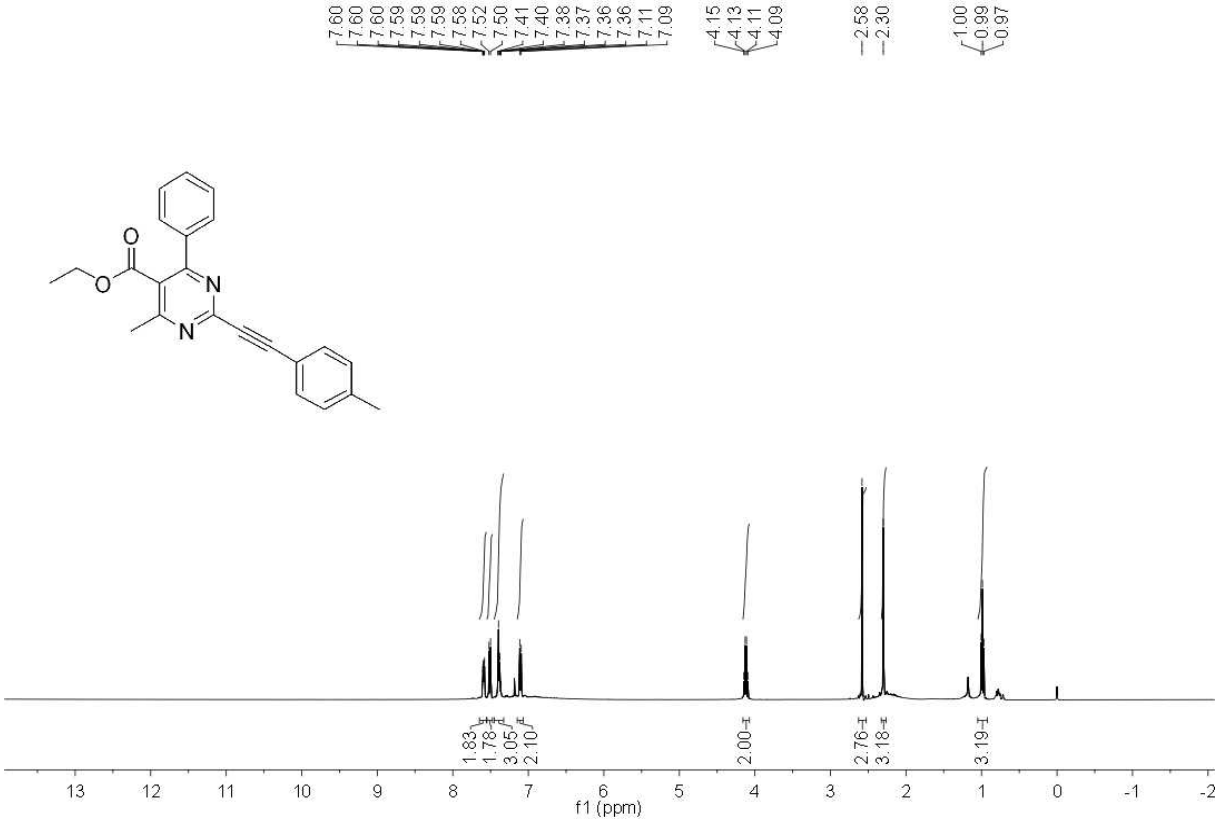


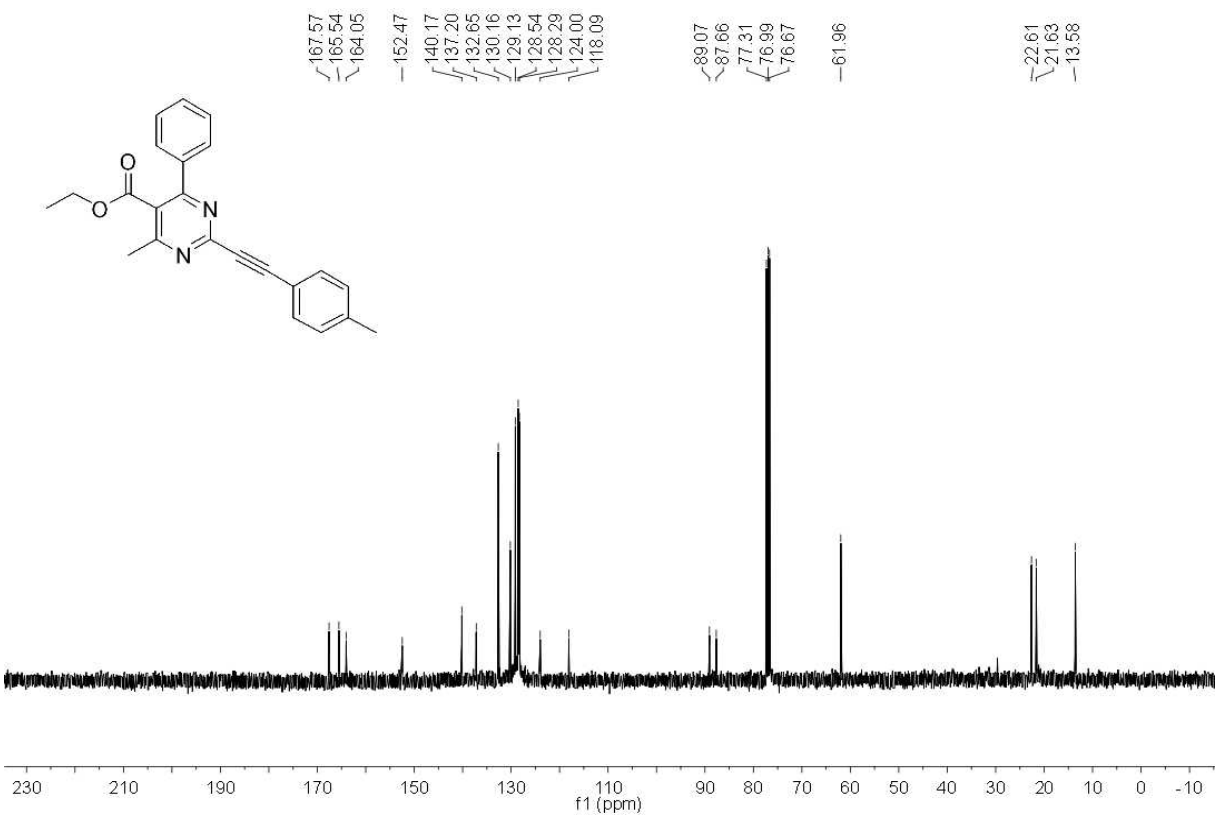
Ethyl 2-(3,3-Dimethylbut-1-ynyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (5c)



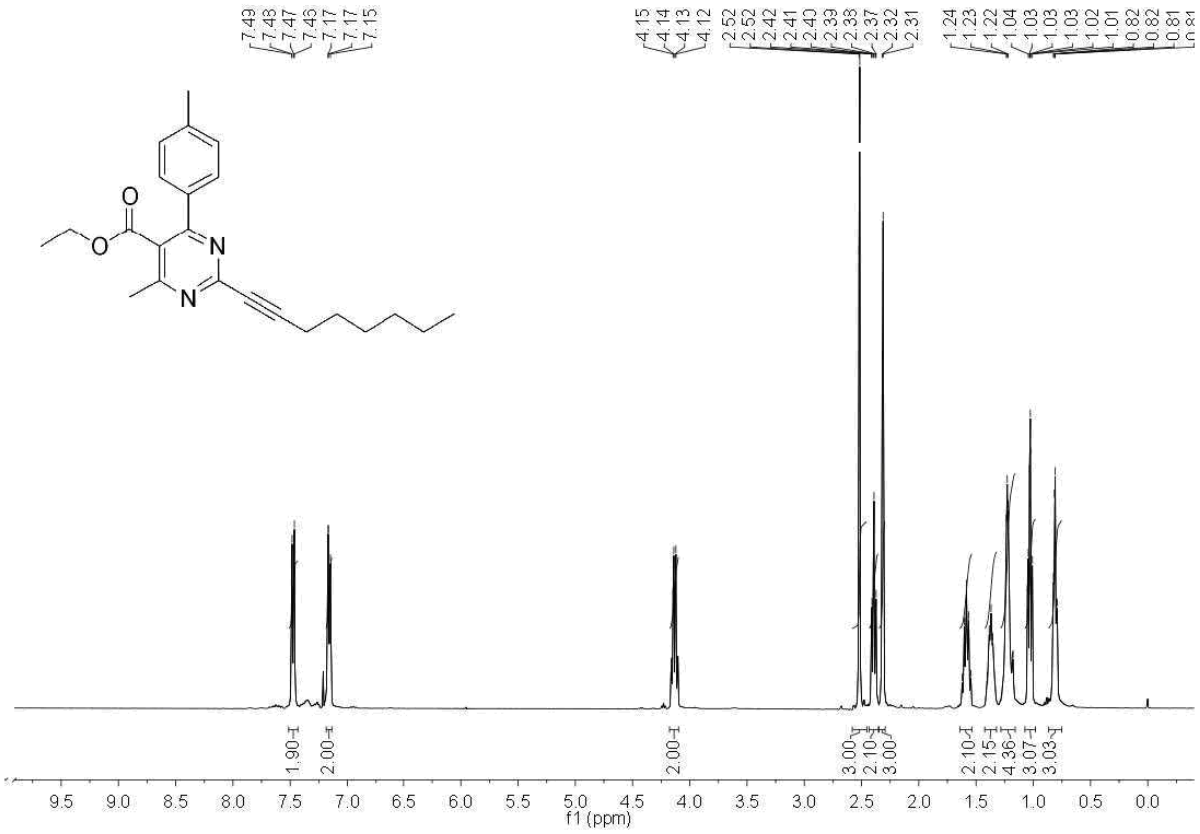


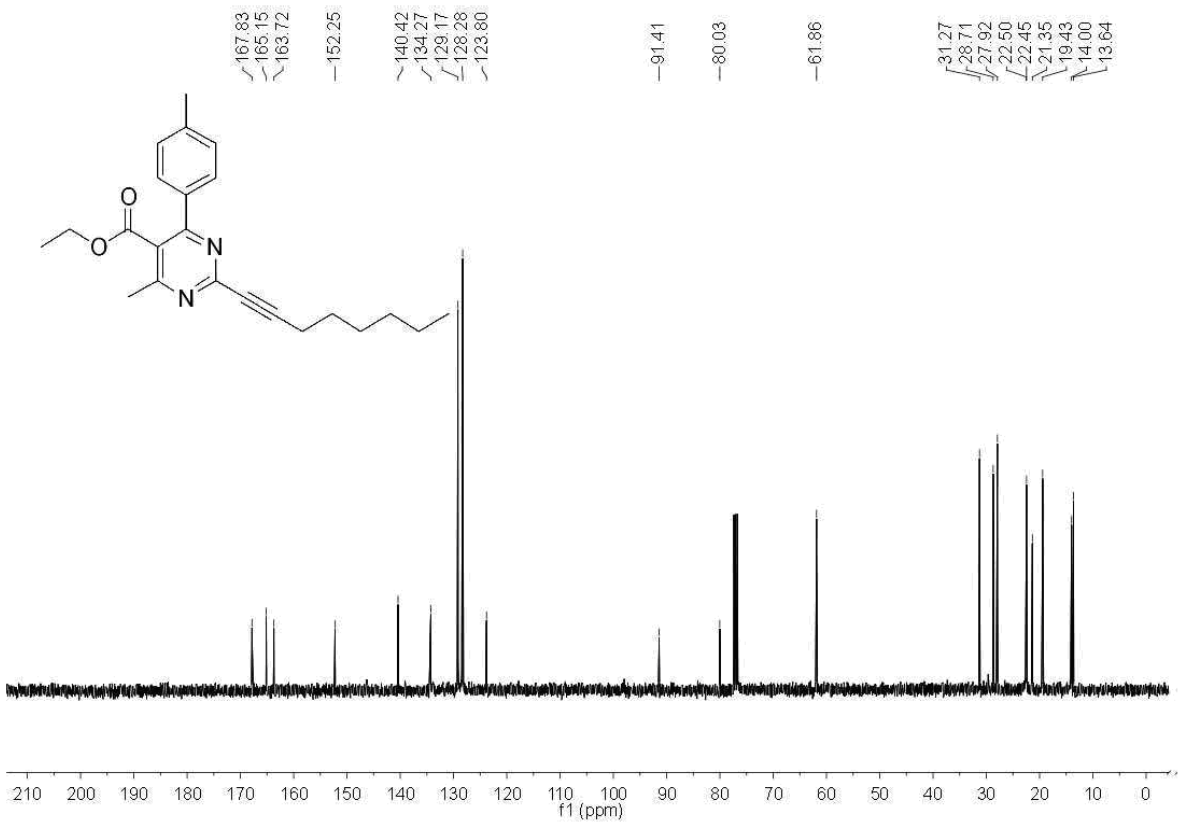
Ethyl 4-Methyl-6-phenyl-2-(p-tolylethynyl)pyrimidine-5-carboxylate (5d)



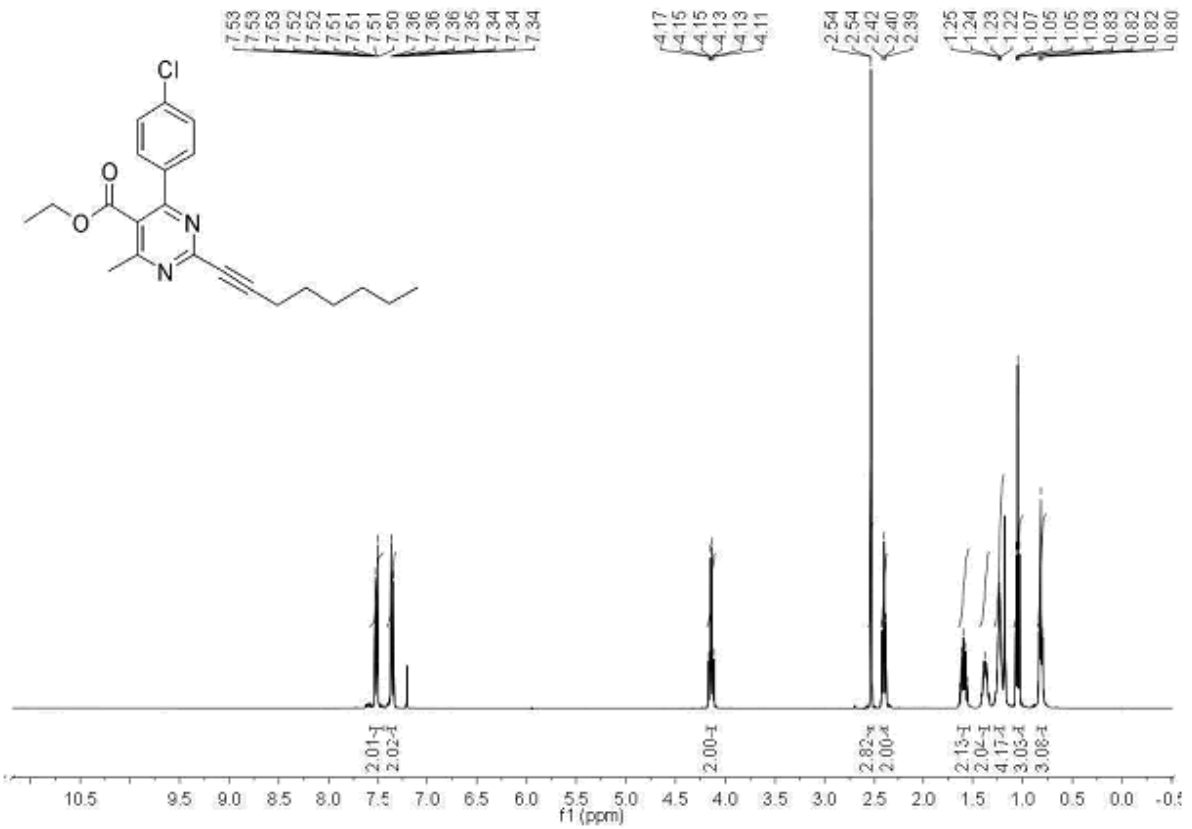


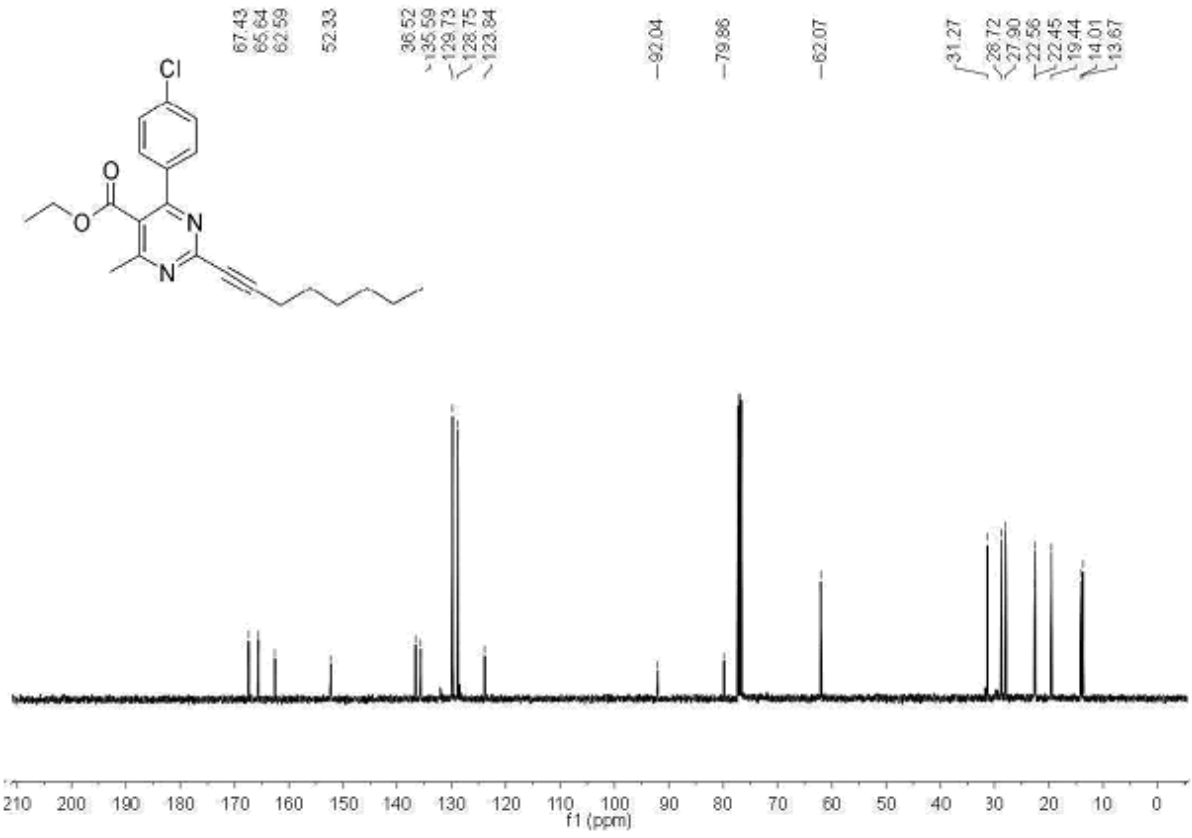
Ethyl 4-Methyl-2-(oct-1-ynyl)-6-p-tolylpyrimidine-5-carboxylate (5e)



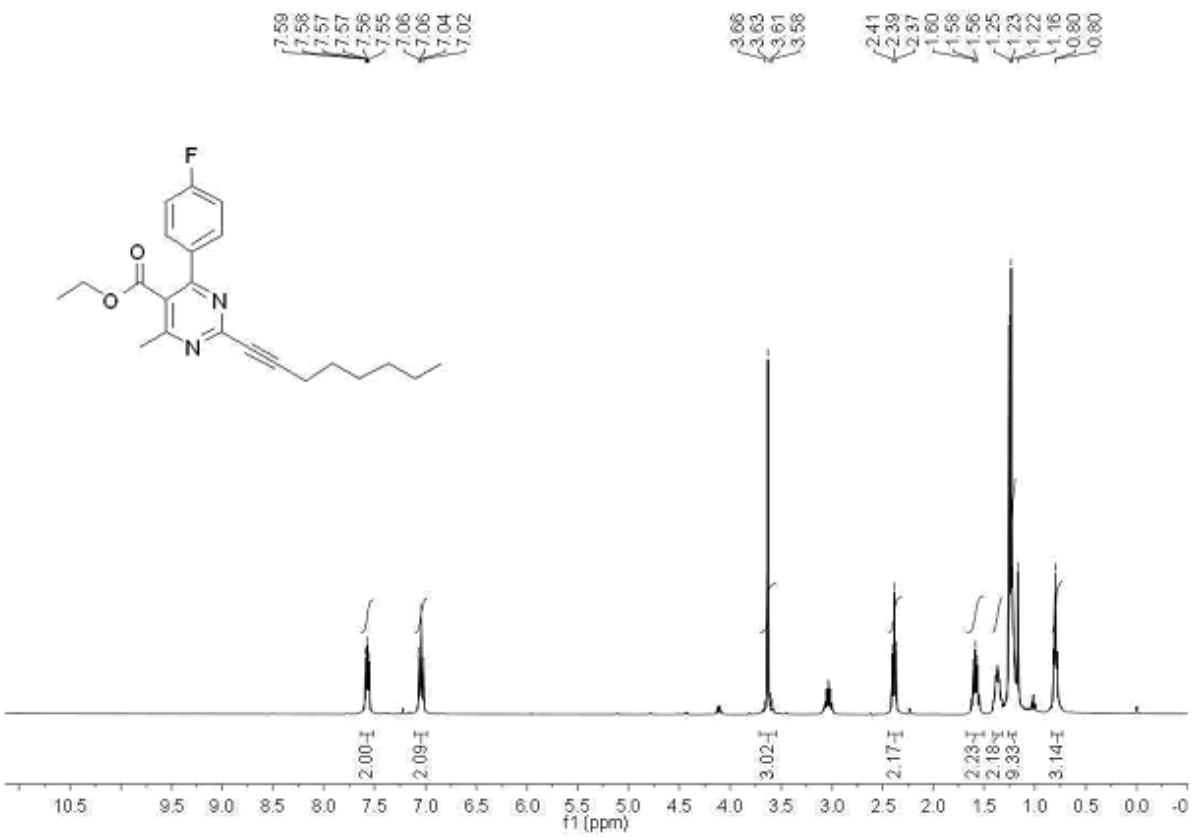


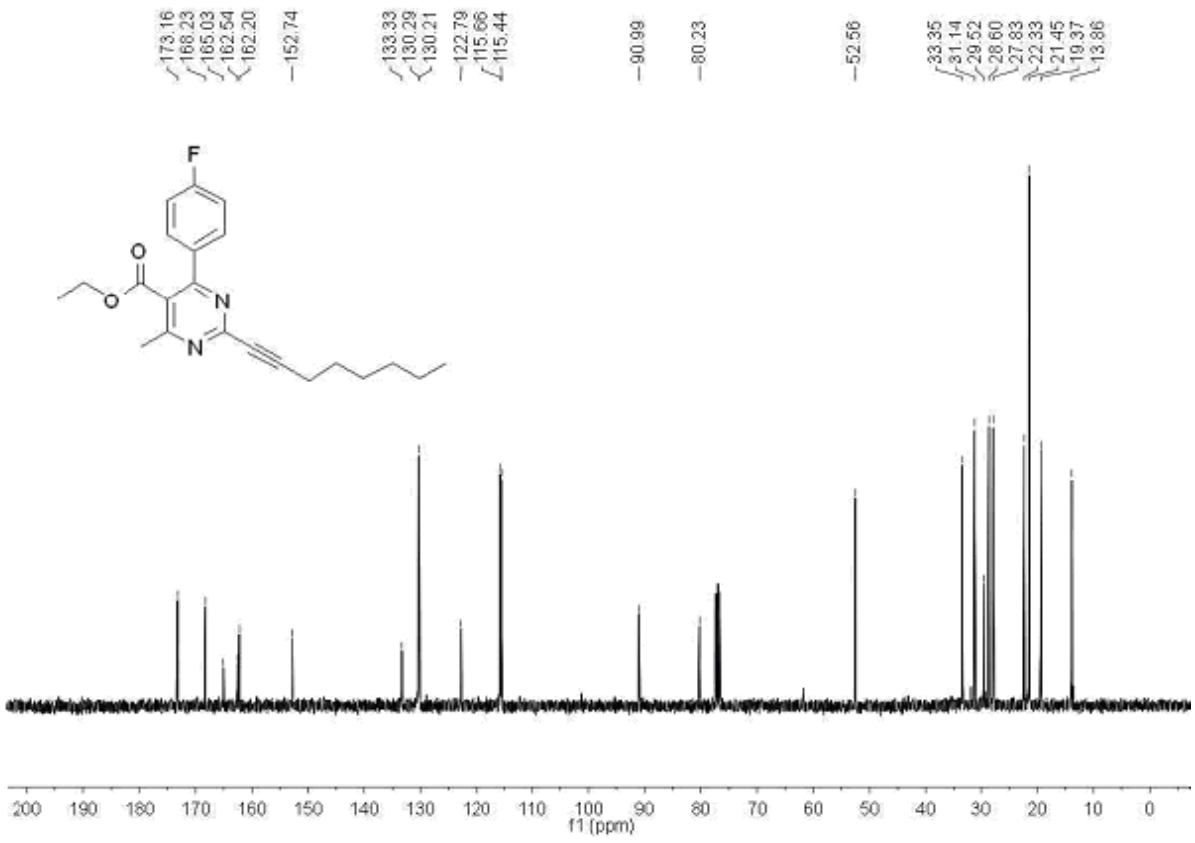
Ethyl 4-(4-Chlorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5f)



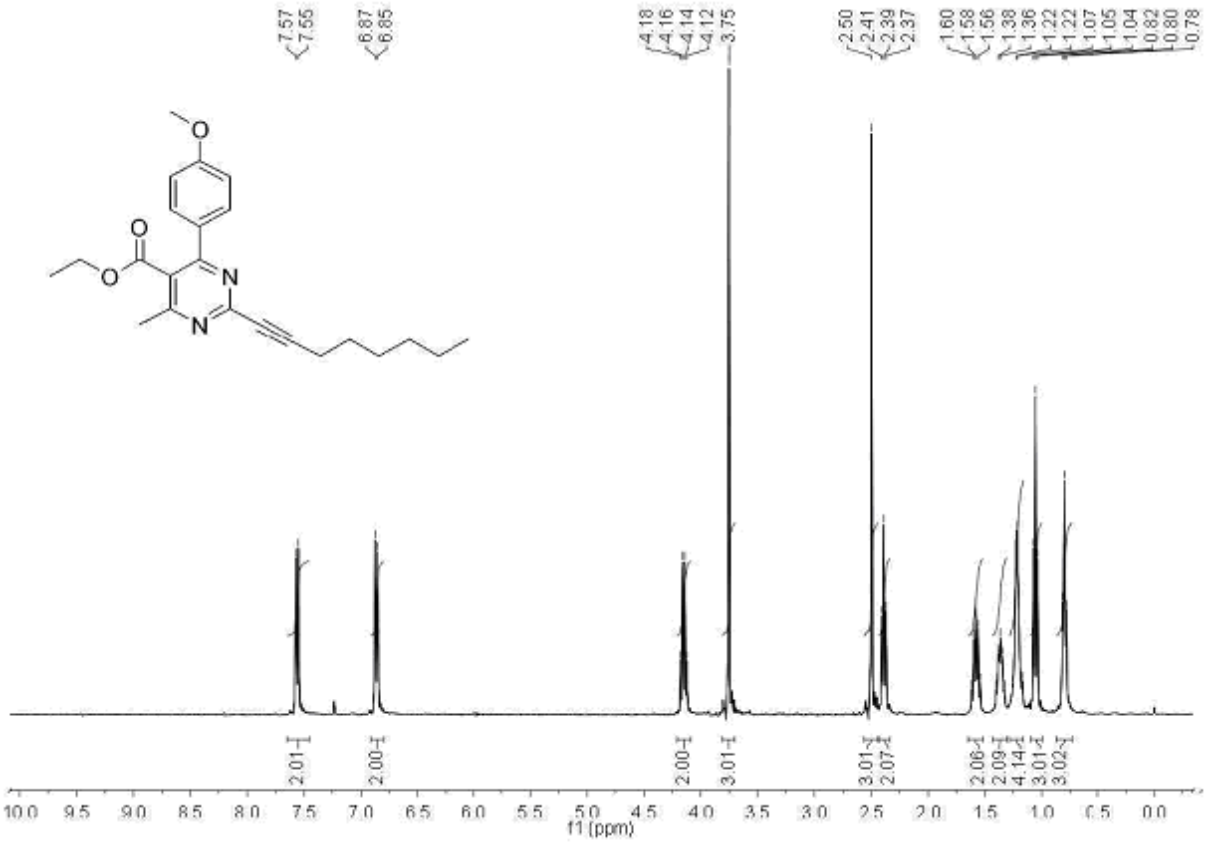


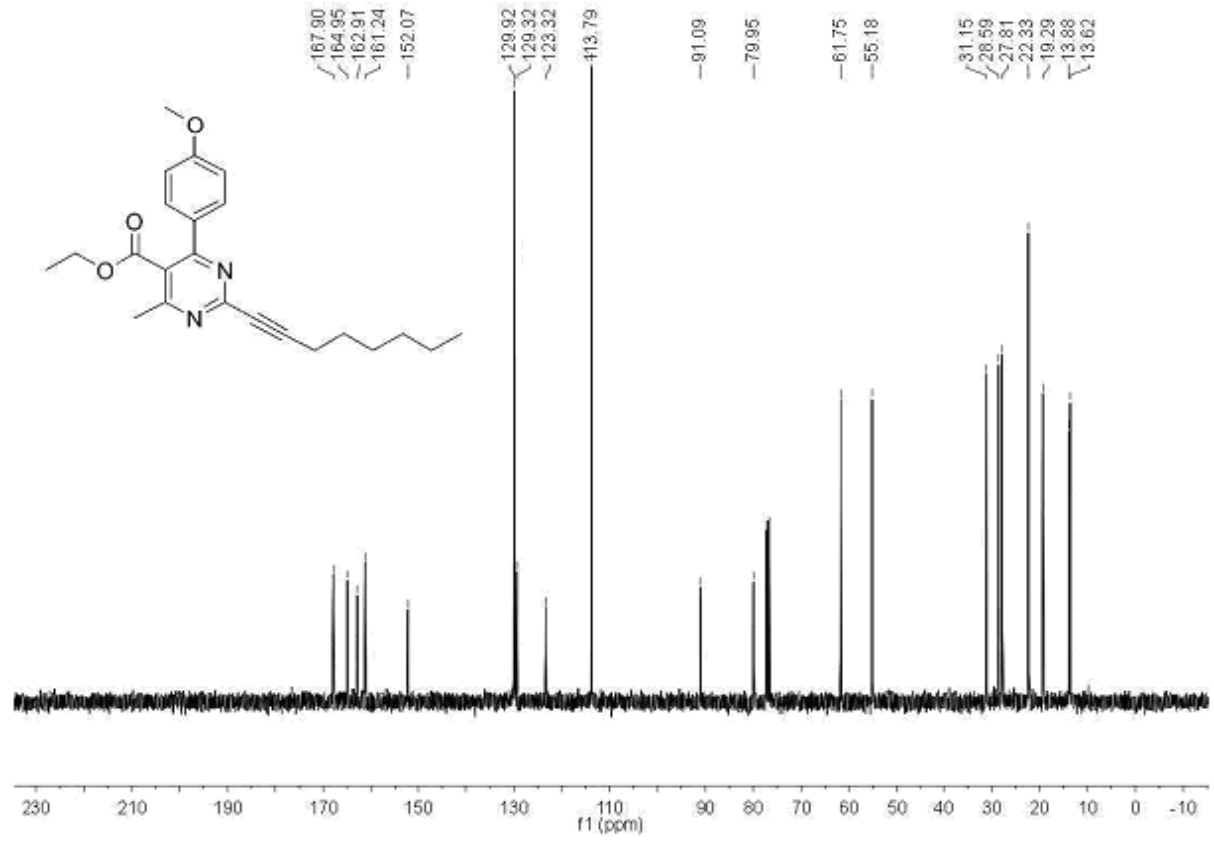
Ethyl 4-(4-Fluorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5g)



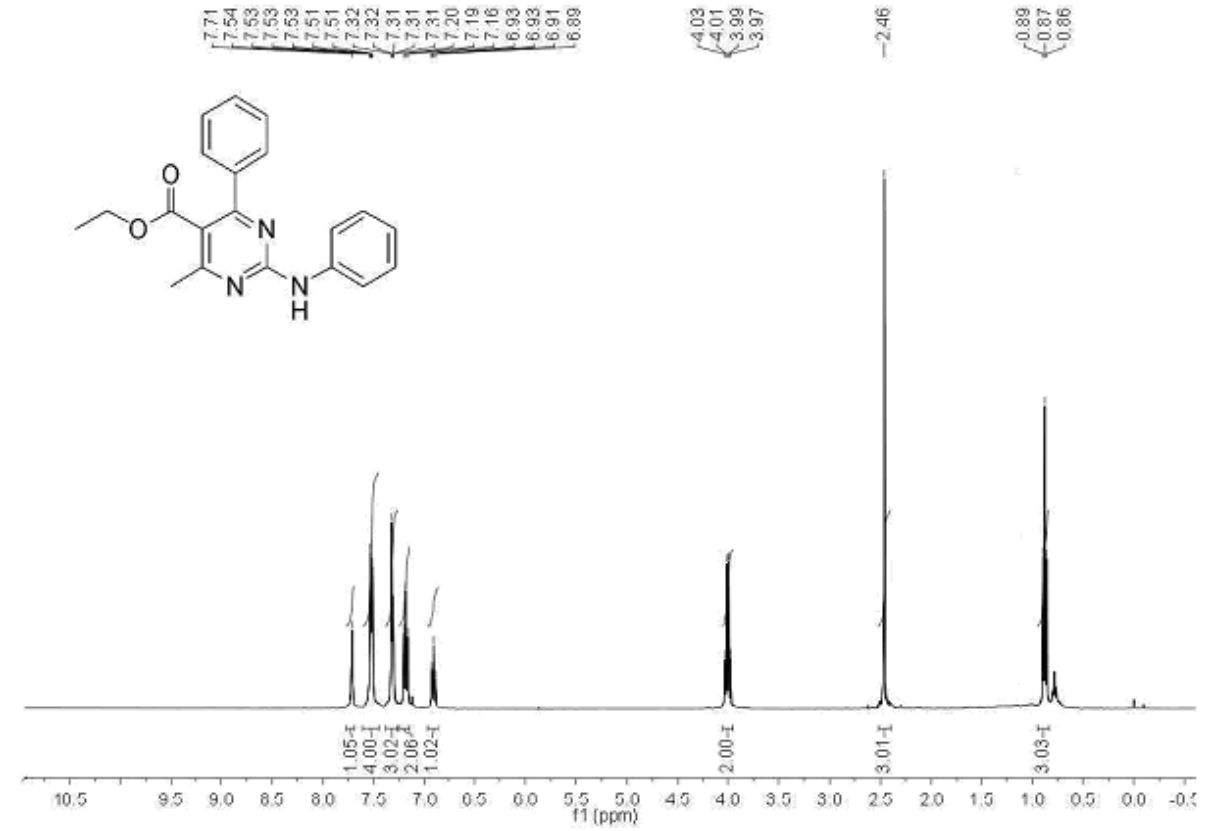


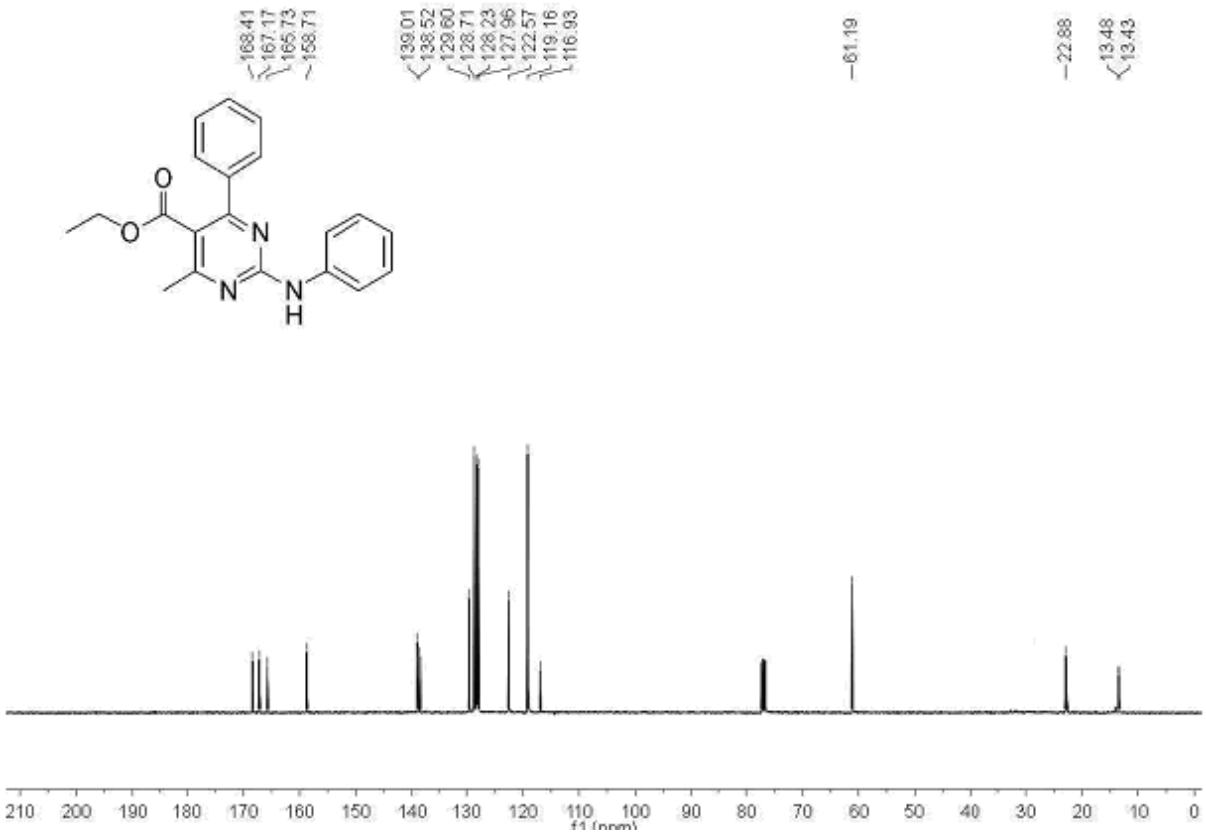
Ethyl 4-(4-Methoxyphenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (5h)



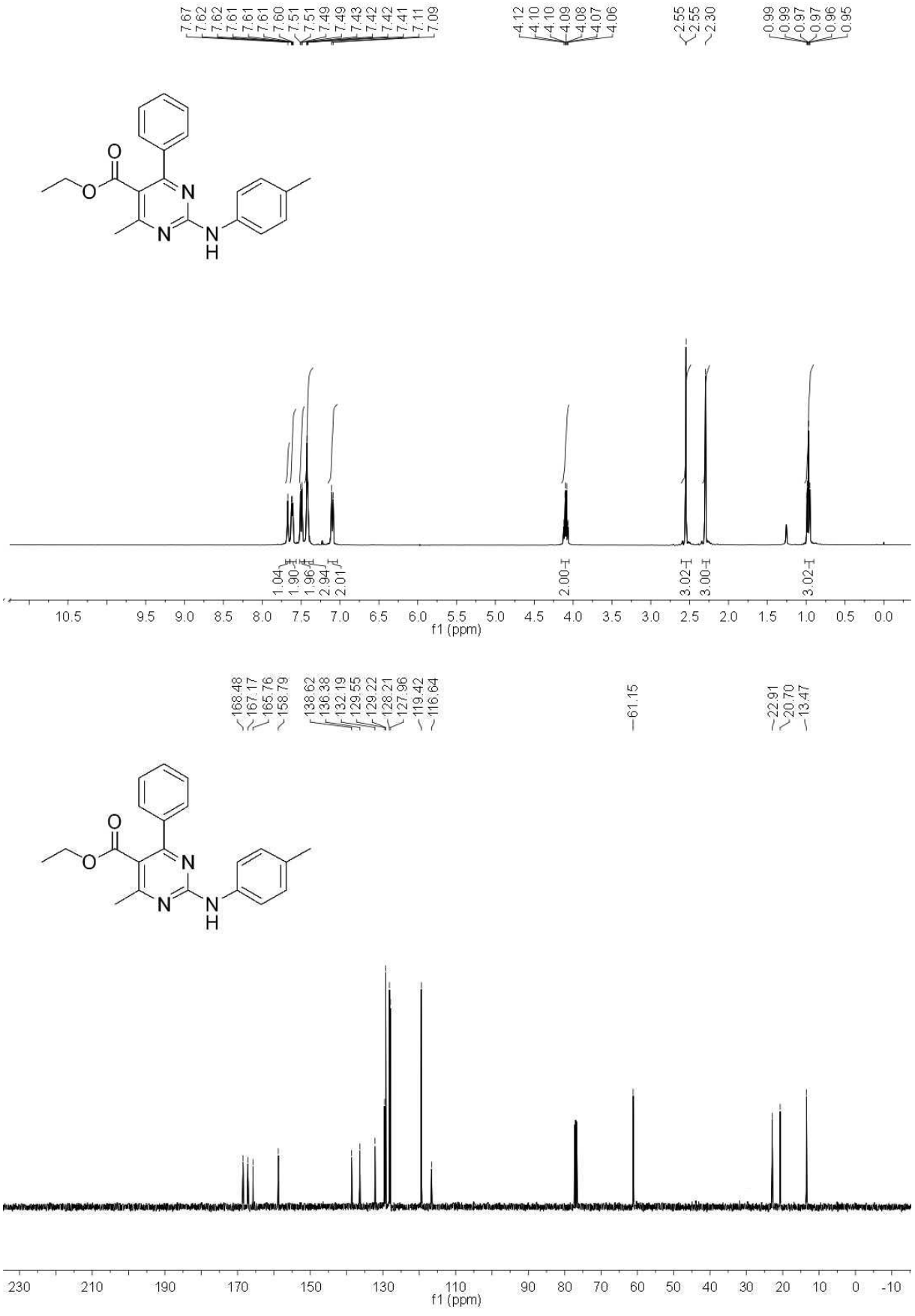


Ethyl 4-methyl-6-phenyl-2-(phenylamino)pyrimidine-5-carboxylate (7a)

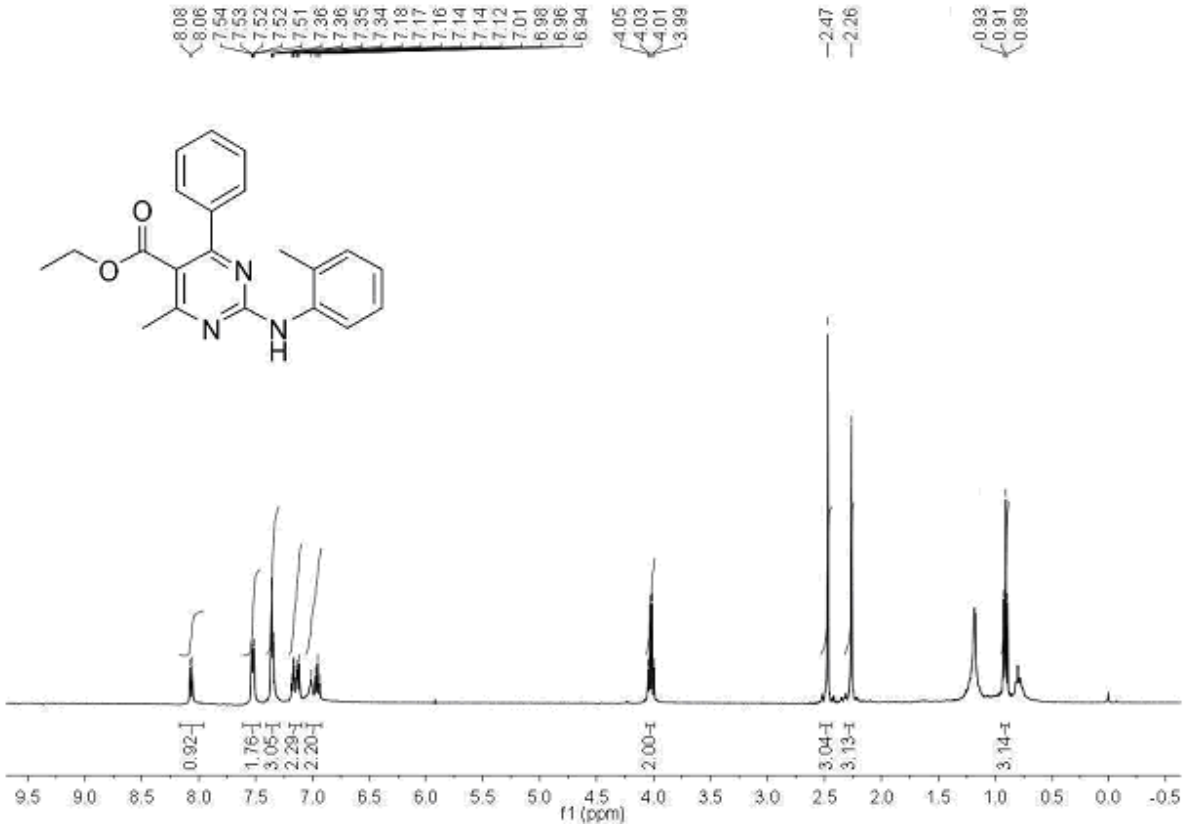


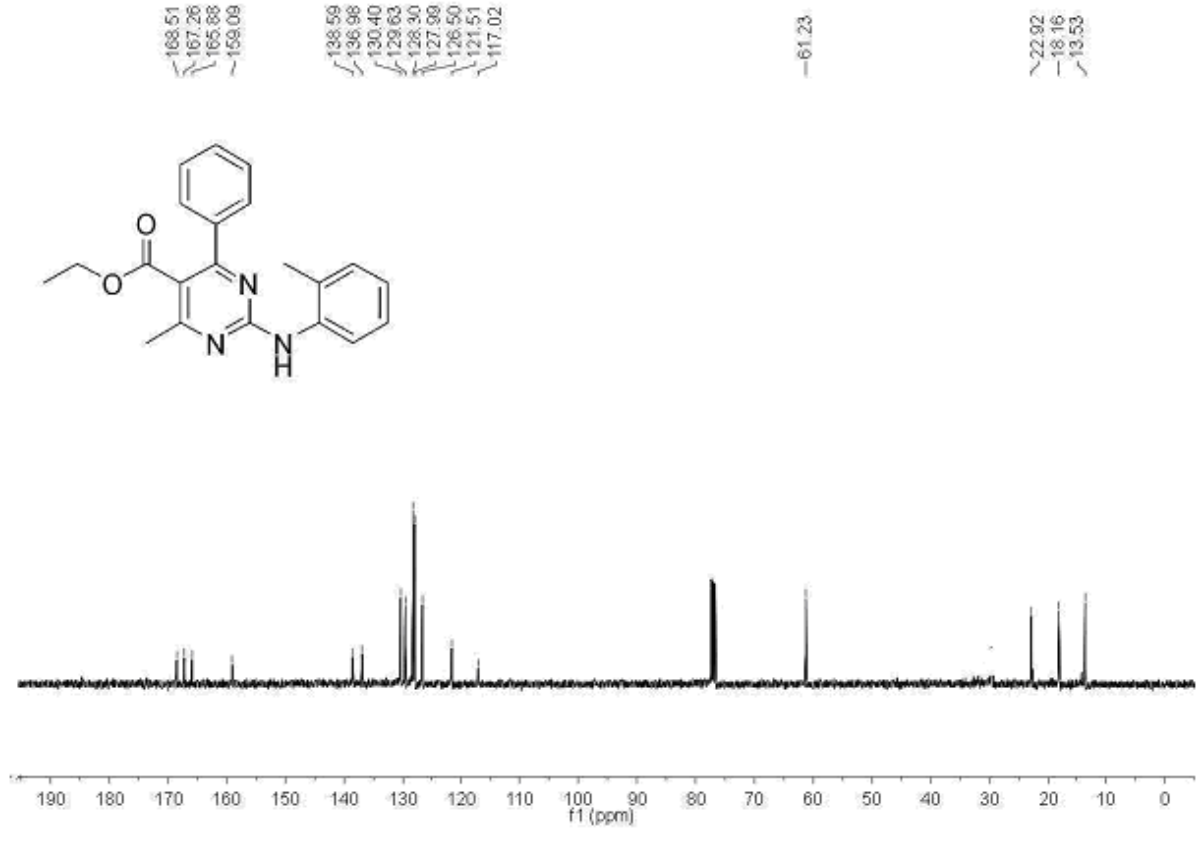


Ethyl 4-methyl-6-phenyl-2-(*p*-tolylamino)pyrimidines-5-carboxylate (7b)

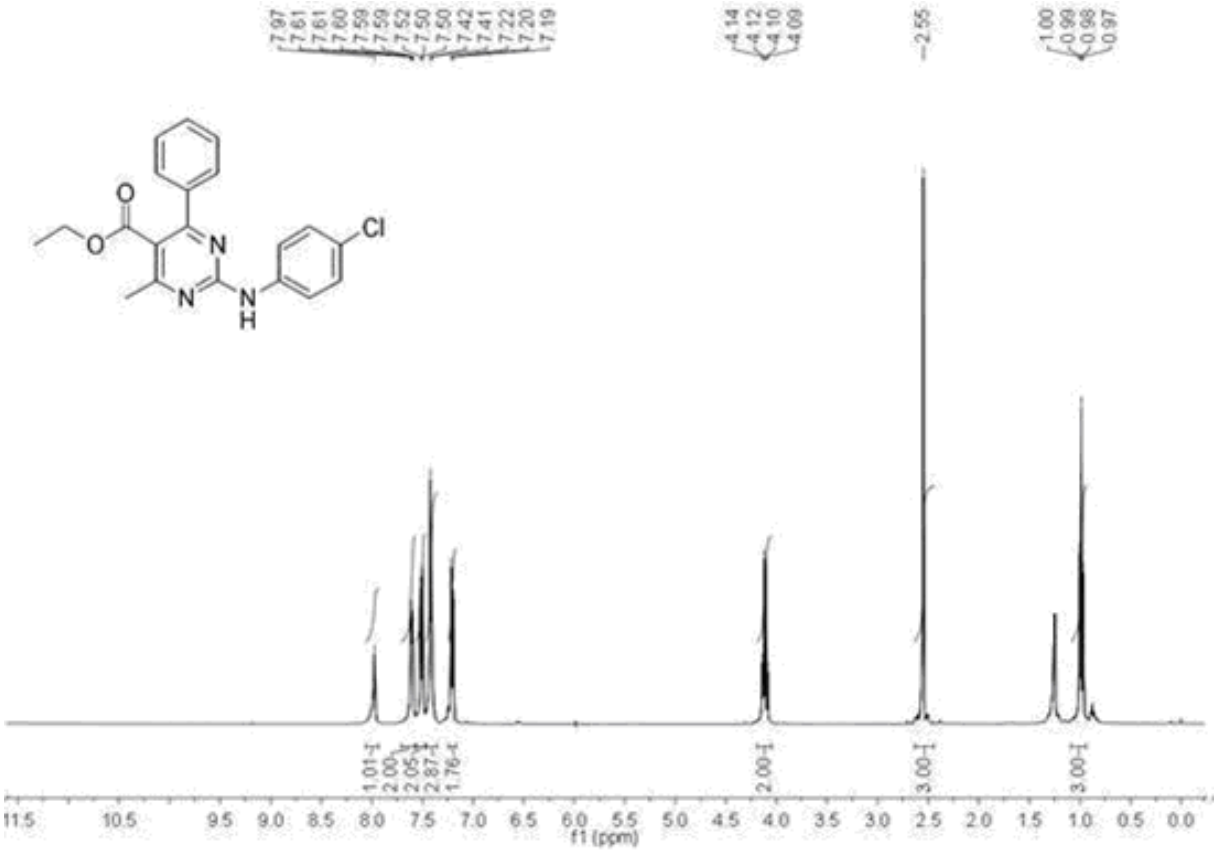


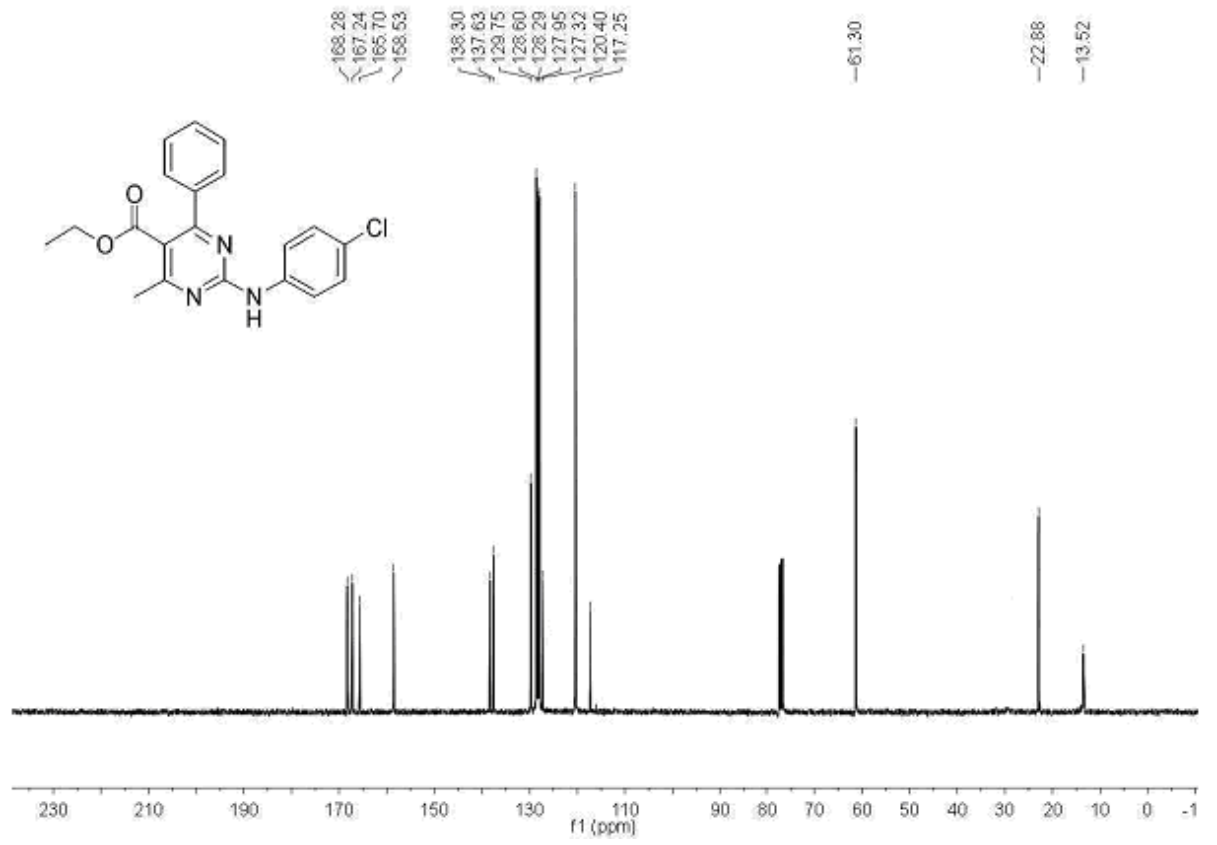
Ethyl 4-methyl-6-phenyl-2-(*o*-tolylamino)pyrimidine-5-carboxylate (7c)



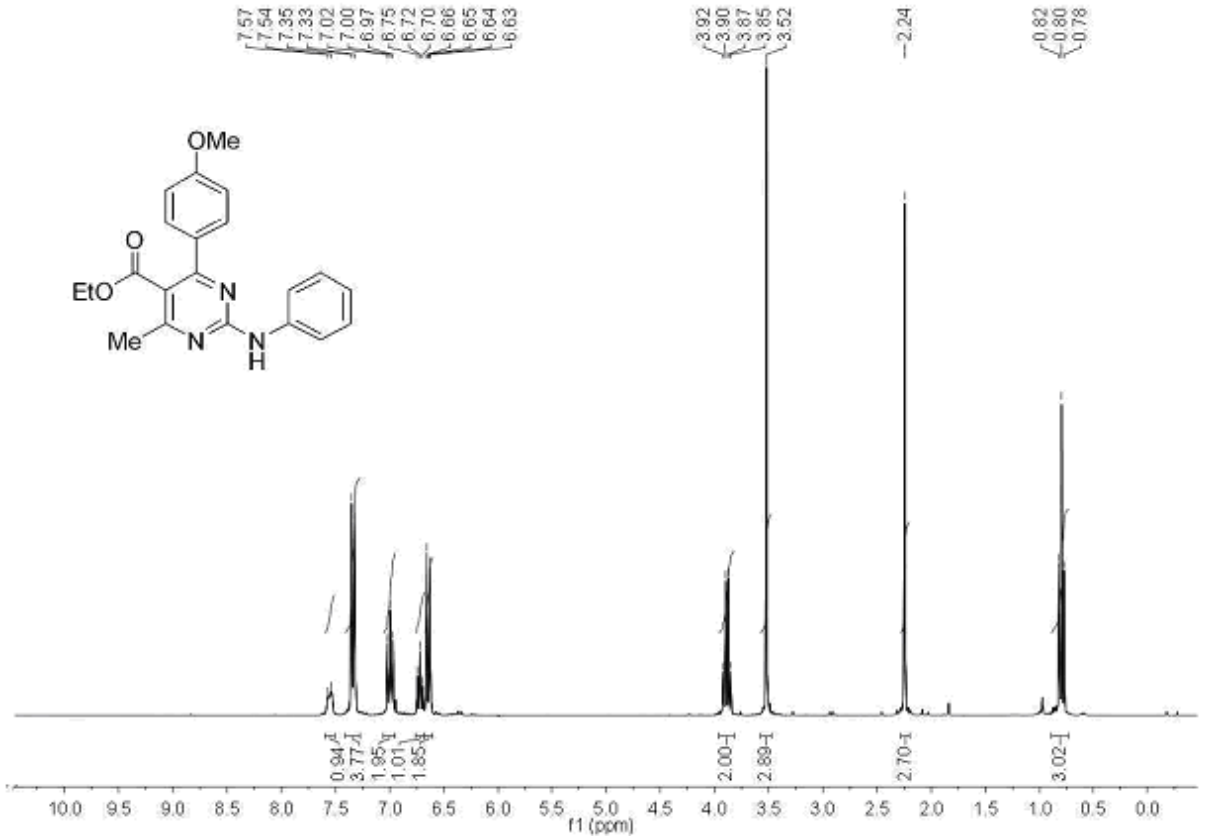


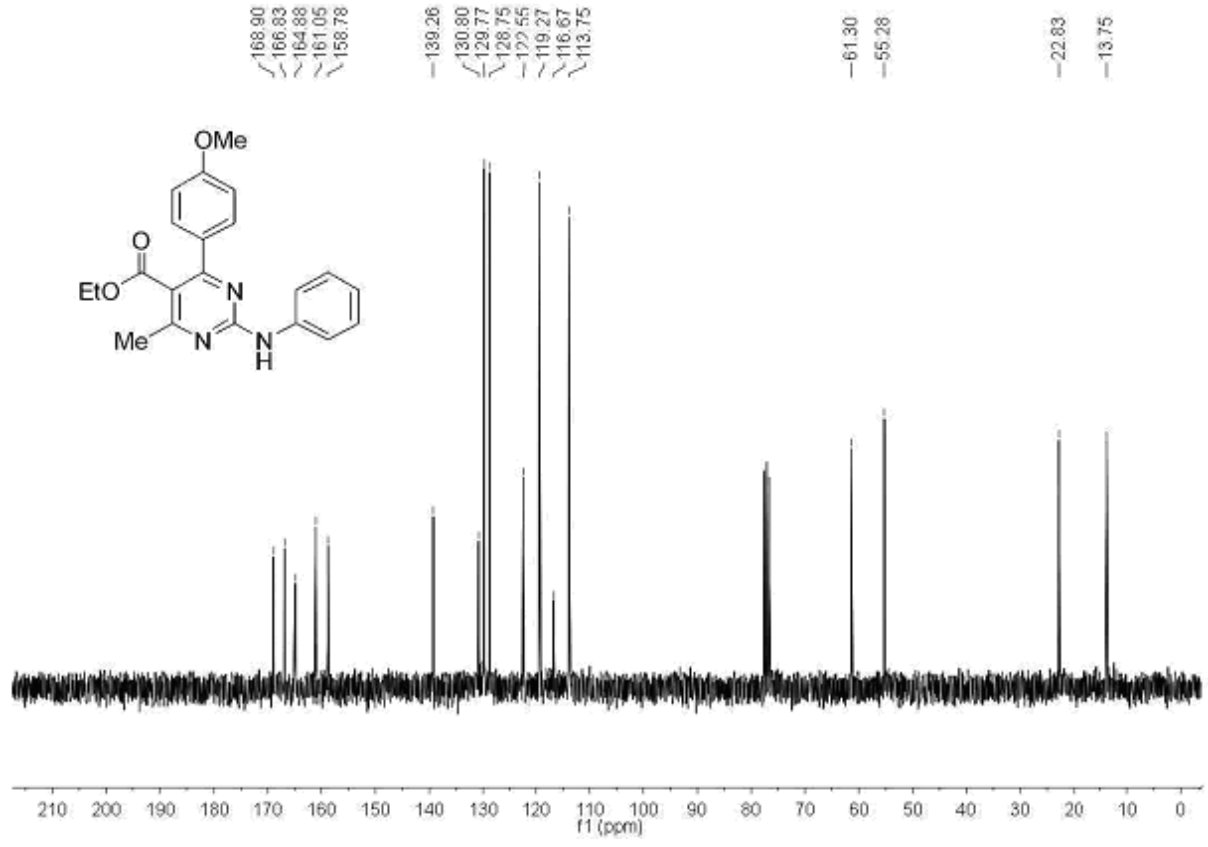
Ethyl 2-(4-chlorophenylamino)-4-methyl-6-phenylpyrimidine-5-carboxylate (7d)





Ethyl 4-(4-methoxyphenyl)-6-methyl-2-(phenylamino)pyrimidine-5-carboxylate (7e)





Ethyl 4-(4-chlorophenyl)-6-methyl-2-(phenylamino)pyrimidine-5-carboxylate (7f)