Wool-anchored $Pd(OAc)_2$ complex: a highly active and reusable catalyst for the desulfurative coupling reactions

SUPPORTING INFORMATION

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Contents

1. General

All reactions were conducted under a nitrogen atmosphere with a dual-manifold Schlenk tube, unless otherwise mentioned, and in oven-dried glassware. 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 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. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Mass-spectra (EI) were recorded on a TRACE DSQ instrument. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC analyses were conducted on silica gel GF254 plates. Palladium (II) acetate, alkynes, carboxylic acids, Cu_2O, P ligands and solvents were all purchased from J&K Scientific Ltd. All reagents were directly used from purchased without any further purification unless otherwise specified. Wool was provided by Gansu Jingyuan Woolen Mill (Jingyuan town, Gansu province, PR China).

2. Experimental details and characterization for catalyst and all compounds

2.1 The wool-anchored palladium(II) was prepared following these procedures: 1.0 g the treated-wool pieces prepared in our laboratory[1-5] (a, Figure 1) and 0.2 g $Pd(OAc)_2$ were dipped in 30 mL of de-ionized water, the mixture was stirred at r.t. for 3 h until the white wool pieces become to brownish yellow. Then the biomacromolecule-$Pd(OAc)_2$ complex catalyst was filtered and washed with de-ionized water(3 × 20 mL) and acetone (3 × 20 mL), dryed in a vacuum oven at 50 °C for 4 h. (b, Figure 1) The palladium content in Wool-Pd(II) complex was determined by means of inductively coupled plasma equipped with atomic emission spectrometry (ICP-AES) and amounted to be 1.56 wt %. The possible structure of wool-$Pd(OAc)_2$ complex was shown in Figure 2.

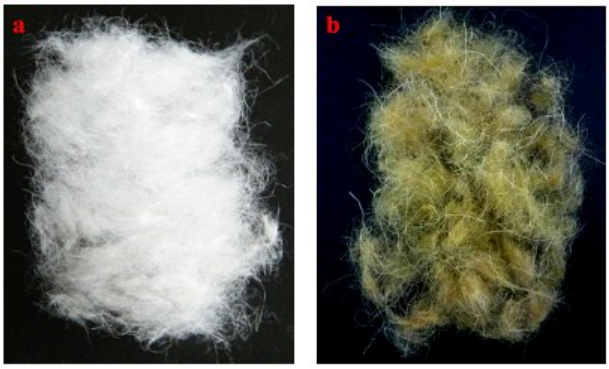


Figure 1. (a) Wool fibre, and (b) wool-$Pd(OAc)_2$ complex.

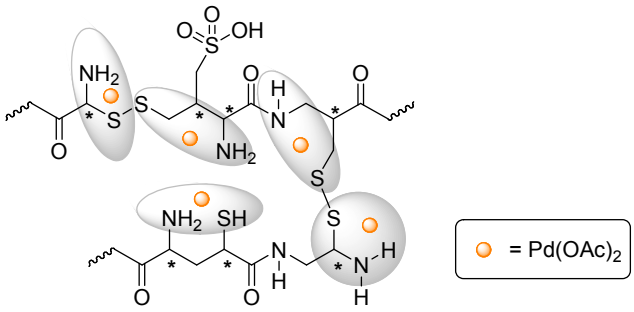
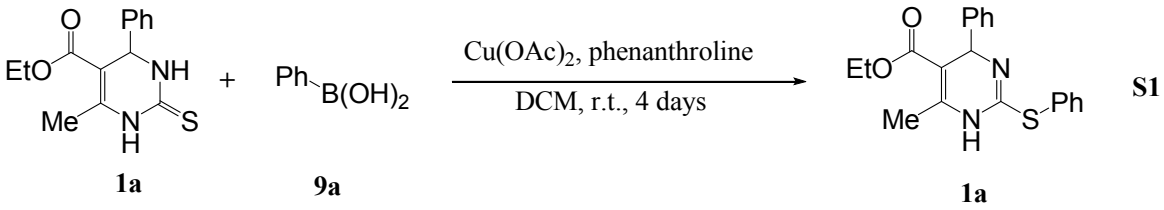


Figure 2. The possible structure of wool-$Pd(OAc)_2$ complex.

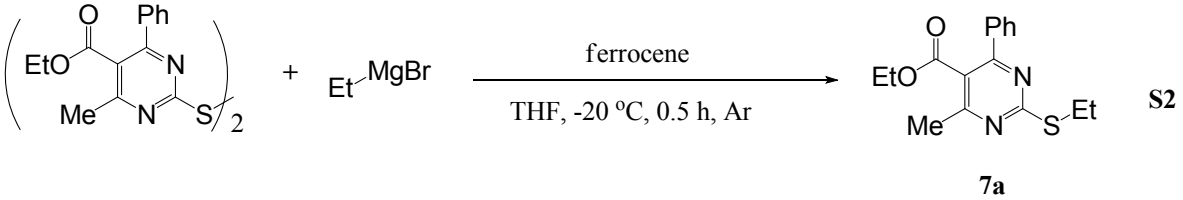
2.2 General procedures for preparation of substrates 1a (eq. S1).[6] The substrates **1a** was synthesized through the reactions between DHPM and phenylboronic acid. DHPM (90.6 mg; 0.33 mmol), $PhB(OH)_2$ (121.9 mg; 1 mmol), phenanthroline (118.9 mg; 0.66 mmol), $Cu(OAc)_2$ (59.9 mg; 0.33 mmol), 4Å molecularsieves powder (250 mg) and 1,2-dichlorethane (5 ml) were added into a reaction vessel. The mixture was stired for 4 days and then transferred to a round bottom flask, and was adsorbed on silica gel.

The residue was purified by flash chromatography on silica gel.



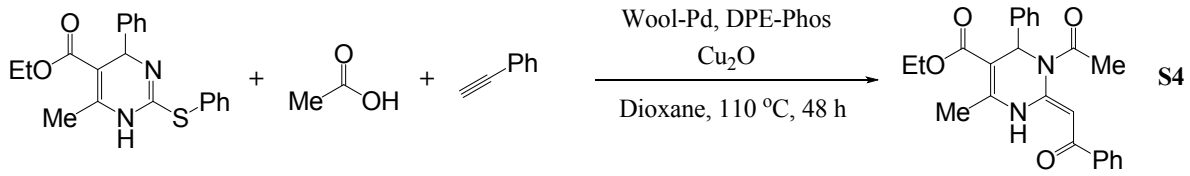
1a **9a** **1a** **S1**

2.3 General procedures for preparation of substrates 7 (eq. S2).[7] The substrates **7** were synthesized through the reactions between disulfides and Grignard reagent. Under argon atmosphere, disulfide (1 mmol), ferrocene (5 mol%) were added into a Schlenk tube dried by Hot-gun. The tube was stopped and degassed with argon for three times. Then EtMgBr (5 mmol), THF (6 mL) were added by syringe. The mixture was stirred under argon atmosphere at -20 °C for 0.5 h. Then 1 mL water was added to quench the reaction, and the organic components were extracted by acetic ether and evaporated in vacuum and further purified by column chromatography on silica gel.



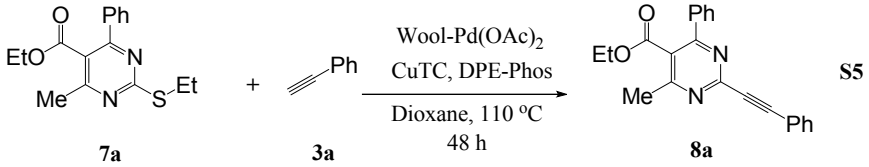
7a **S2**

2.4 General procedures for the domino process (eq. S4). Under argon atmosphere, **1a** (0.25 mmol, 69 mg), wool-Pd(OAc)$_2$ (10 mg, Pd 1.56 wt %), Cu_2O (0.25 mmol, 36 mg), DPE-Phos (5 μmol, 2.5 mg, 2 mol%) were added into a Schlenk tube dried by Hot-gun. The tube was stopped and degassed with argon for three times. Then **2a** (0.50 mmol, 30 mg), **3a** (0.375 mmol, 38 mg) and dioxane (2 mL) were added by syringe. The mixture was stirred under argon atmosphere at 110°C for 48 h. Then the mixture was cooled down to room temperature with 2 mL saturated solution of NH_4Cl added to quench the reaction and 1 mL dilute solution of NaOH to neutralize the excess **2a**. Then, the organic components were extracted by acetic ether and evaporated in vacuum and further purified by column chromatography on silica gel with petroleum ether/ethanol (60:1) to give the product **4a** (89 mg, 88%) as yellow solid.



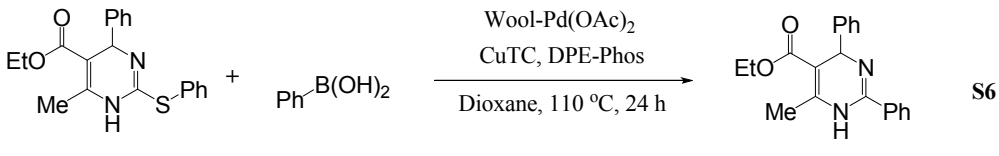
1a **2a** **3a** **4a** **S4**

2.5 General procedures for the Sonogashira reactions between 2-(ethylthio)pyrimidine derivatives and terminal alkynes (eq. S5). Under argon atmosphere, **7a** (0.25 mmol, 75 mg), wool-Pd(OAc)$_2$ (10 mg, Pd 1.56 wt %), CuTC (0.50 mmol, 95 mg), DPE-Phos (5 μmol, 2.5 mg, 2 mol%) were added into a Schlenk tube dried by Hot-gun. The tube was stopped and degassed with argon for three times. Then **3a** (0.50 mmol, 51 mg) and dioxane (2 mL) were added by syringe. The mixture was stirred under argon atmosphere at 110°C for 48 h. Then the mixture was cooled down to room temperature with 2 mL saturated solution of NH_4Cl added to quench the reaction and 1 mL dilute solution of NaOH to neutralize the excess acid. Then, the organic components were extracted by acetic ether and evaporated in vacuum and further purified by column chromatography on silica gel with petroleum ether/ethanol (60:1) to give the product **8a** (68 mg, 79%) as clear solid.



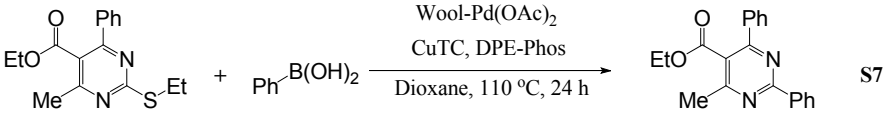
7a **3a** **8a** **S5**

2.6 General procedures for the reaction between 2-(phenylthio)-1,4-dihydropyrimidine derivatives and arylboronic acids (eq. S6). Under argon atmosphere, **1a** (0.25 mmol, 69 mg), **8a** (0.50 mmol, 61 mg), wool-Pd(OAc)$_2$ (10 mg, Pd 1.56 wt %), CuTC (0.50 mmol, 95 mg), DPE-Phos (5 μmol, 2.5 mg, 2 mol%) were added into a Schlenk tube dried by Hot-gun. The tube was stopped and degassed with argon for three times. Then dioxane (2 mL) was added by syringe. The mixture was stirred under argon atmosphere at 110°C for 24 h. Then the mixture was cooled down to room temperature with 2 mL saturated solution of NH_4Cl added to quench the reaction and 1 mL dilute solution of NaOH to neutralize the excess acid. Then, the organic components were extracted by acetic ether and evaporated in vacuum and further purified by column chromatography on silica gel with petroleum ether/ethanol (60:1) to give the product **10a** (53 mg, 65%) as yellow oil.



1a **8a** **10a** **S6**

2.7 General procedures for the reaction between 2-(ethylthio)pyrimidine derivatives and arylboronic acids (eq. S7). Under argon atmosphere, **7a** (0.25 mmol, 30 mg), **8a** (0.50 mmol, 61 mg), wool-Pd(OAc)$_2$ (10 mg, Pd 1.56 wt %), CuTC (0.50 mmol, 95 mg), DPE-Phos (5 μmol, 2.5 mg, 2 mol%) were added into a Schlenk tube dried by Hot-gun. The tube was stopped and degassed with argon for three times. Then dioxane (2 mL) was added by syringe. The mixture was stirred under argon atmosphere at 110°C for 24 h. Then the mixture was cooled down to room temperature with 2 mL saturated solution of NH_4Cl added to quench the reaction and 1 mL dilute solution of NaOH to neutralize the excess acid. Then, the organic components were extracted by acetic ether and evaporated in vacuum and further purified by column chromatography on silica gel with petroleum ether/ethanol (60:1) to give the product **11a** (65 mg, 82%) as clear solid.



7a **8a** **11a** **S7**

2.8 Procedures for the hot-filtration test.

The hot-filtration test was carried out with an investigation upon the reactions among **1a**, **2a** and **3a**. Two parallel reactions were undertaken under the identical standard conditions we use (see Part 2.5 above in this chapter). In one reaction, the mixture was quickly hot filtered with a Teflon syringe filter (0.2 mm pore size) after 12 h of reaction. The conversion of **1a** was immediately detected by HPLC (a conversion of 41%). The other reaction system was not intervened. Both reaction was continued thereafter for another 36 h and then quenched. The conversion of **1a** was detected by HPLC. As a result, the reaction that was handled by the hot-filtration remained the conversion of 41%; and the other reaction reached a conversion of 88%.

2.9 Procedures for the recycling test.

After the reactions among **1a**, **2a** and **3a**, the wool-Pd(OAc)$_2$ complex was filtrated, and washed with de-ionized water (3 × 10 mL) and acetone (3 × 10 mL), dried in a vacuum oven at 50 °C. Then it was used in a new round of the cycle, with new substrates and additives added. The catalyst was reused repeatedly for nine times and then was examined by ICP-AES analysis within very narrow scope (1.56% to 1.43%) to observe its palladium content. The total TON value is 1320. Only 68 parts per billion palladium was detected in the reaction phase, (ICP-MS) indicating quite a slender metal leaching of the catalyst during the reactions. Also, throughout the recycled tests of nine rounds, the yields of product **4a** were not declined all the while

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The NMR Data for the Products

(E)-ethyl 3-acetyl-6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-1,2,3,4-tetrahydro- pyrimidine-5-carboxylate (4a) Yellow solid (89 mg, 88%); m.p. = 197°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.2Hz, 3H), 2.55 (s, 3H), 2.58 (s, 3H), 4.18-4.23 (q, 2H), 6.00 (s, 1H), 6.70 (s, 1H), 7.25-7.32 (m, 5H), 7.42-7.51 (m, 3H), 7.84 (d, *J* = 7.2Hz, 2H), 12.78 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.26, 18.64, 24.61 52.15, 60.44, 90.88, 106.68, 126.92, 127.24, 128.04, 128.56, 128.67, 132.06, 138.95, 139.01, 144.28, 150.48, 165.17, 169.58, 189.25 ppm.

(E)-ethyl 3-acetyl-4-(2-methoxyphenyl)-6-methyl-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b) Yellow solid (61 mg, 56%); m.p. = 165~166°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.2Hz, 3H), 2.53 (s, 3H), 2.54 (s, 3H), 3.79 (s, 3H), 4.16-4.19 (m, 2H), 6.24 (s, 1H), 6.66 (s, 1H), 6.84-6.87 (m, 2H), 7.17-7.28 (m, 2H), 7.38-7.42 (m, 3H), 7.84 (d, *J* = 7.2Hz, 2H), 12.86 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17, 18.55, 24.15, 50.39, 55.11, 60.17, 91.27, 105.29, 111.00, 120.39, 125.89, 127.19, 128.35, 128.92, 129.58, 131.71, 139.17, 144.34, 150.28, 157.41, 165.15, 169.64, 189.58 ppm.

(E)-ethyl 3-acetyl-6-methyl-4-(4-nitrophenyl)-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c) Yellow solid (86 mg, 77%); m.p. = 178~179°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.2Hz, 3H), 2.53 (s, 3H), 2.56 (s, 3H), 4.15-4.20 (q, 2H), 5.90 (s, 1H), 6.65 (s, 1H), 6.96 (t, *J* = 8.8Hz, 2H), 7.26-7.50 (m, 5H), 7.81-7.83 (m, 2H), 12.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.15, 18.53, 24.48, 51.38, 60.38, 90.83, 106.46, 115.36, 115.57, 127.14, 128.71, 128.80, 132.06, 138.75, 144.22, 150.17, 164.93, 169.41, 189.18 ppm.

(E)-ethyl 3-acetyl-4-(2-chlorophenyl)-6-methyl-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d) Yellow solid (67 mg, 61%); m.p. = 222~223°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, 3H), 2.48 (d, *J* = 1.2Hz, 3H), 2.58 (s, 3H), 4.13-4.16 (q, 2H), 5.98 (d, *J* = 1.2Hz, 1H), 7.04 (s, 1H), 7.18 (s, 3H), 7.37-7.50 (m, 4H), 7.83 (d, *J* = 6.0Hz, 2H), 12.59 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.12, 18.45, 24.07, 49.73, 60.35, 92.95, 107.00, 127.04, 127.24, 128.49, 128.85, 129.51, 130.40, 132.15, 135.66, 138.61, 144.52, 150.02, 164.73, 168.53, 189.49 ppm.

(E)-ethyl 3-hexanoyl-6-methyl-2-(2-oxohexylidene)-4-phenyl-1,2,3,4-tetrahydro- pyrimidine-5-carboxylate (4e) Yellow oil (75 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (s, 6H), 1.22 (t, *J* = 6.8Hz, 3H), 1.32 (s, 6H), 1.55-1.58 (m, 2H), 1.72-1.74 (m, 2H), 2.30-2.40 (m, 2H), 2.48 (s, 3H), 2.71 (s, 2H), 2.13-2.18 (q, 2H), 5.31 (s, 1H), 6.59 (s, 1H), 7.25 (s, 5H), 12.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.67, 14.01, 18.34, 22.17, 25.45, 27.37, 31.14, 35.83, 42.63, 51.76, 60.05, 93.54, 105.76, 126.65, 127.63, 128.32, 139.04, 144.30, 148.47, 165.01, 172.69, 200.05 ppm.

(E)-ethyl 6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-3-(thiophene-2-carbonyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4f) Yellow solid (80 mg, 68%), m.p. = 157~158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.27 (t, *J* = 8.0 Hz, 3H), 2.62 (s, 3H), 4.20 (q, *J* = 8.0 Hz, 2H), 5.71 (s, 1H), 6.45 (s, 1H), 7.01-7.08 (m, 1H), 7.27–7.60 (m, 12H), 12.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.24, 18.86, 54.81, 60.49, 92.66, 106.89, 127.08, 127.43, 128.27, 128.37, 128.88, 131.84, 132.11, 132.46, 136.91, 138.91, 139.26, 144.35, 151.50, 163.16, 165.05, 188.75 ppm.

(E)-ethyl 3-(furan-2-carbonyl)-6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4g) Yellow solid (74 mg, 65%), m.p. = 159~160 °C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.27 (t, *J* = 8.0 Hz, 3H), 2.68 (s, 3H), 4.21 (q, *J* = 8.0 Hz, 2H), 5.50 (s, 1H), 6.45 (s, 1H), 6.55-6.60 (m, 1H), 7.27–7.55 (m, 12H), 12.70 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.26, 18.81, 54.31, 60.45, 90.50, 106.62, 112.25, 118.78, 127.02, 127.22, 128.12, 128.35, 128.61, 131.81, 138.91,

144.35, 145.35, 147.02, 150.55, 158.84, 165.11, 189.04 ppm.

(*E*)-Ethyl 6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-3-(2,4,6-triisopropylbenzoyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4h) Yellow solid (119 mg, 81%); m.p. = 138~139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.10 (d, *J* = 7.2 Hz, 3H), 1.13-1.20 (m, 9H), 1.27 (d, *J* = 6.8 Hz, 3H), 2.52 (s, 3H), 2.78-2.86 (m ,2H), 2.95-2.98 (m, 1H), 4.14 (q, *J* = 6.8 Hz, 2H), 5.15 (s, 1H), 6.85 (s, 1H), 6.95 (s, 1H), 7.03-7.28 (m, 11H), 12.78 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.08, 18.23, 22.73, 22.87, 23.72, 23.83, 24.08, 25.36, 25.42, 30.89, 31.34, 31.61, 34.29, 50.19, 60.29, 92.17, 105.89, 120.69, 121.38, 121.66, 126.15, 126.72, 126.93, 127.47, 127.86, 127.93, 128.53, 131.53, 131.73, 138.80, 139.14, 143.87, 144.53, 145.49, 149.92, 150.57, 165.14, 168.97, 189.38 ppm.

Ethyl 9-benzoyl-2-methyl-6-oxo-4-phenyl-4,6,7,8-tetrahydro-1H-pyrido[1,2-a]pyrimidine-3-carboxylate (6a) Yellow solid (82 mg, 79%), m.p. 222~223°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 6.8Hz, 3H), 2.57 (s, 3H), 2.62 (d, 8.0Hz, 4H), 4.14-4.19 (m, 2H), 6.71 (s, 1H), 7.29-7.36 (m, 3H), 7.41-7.45 (m, 7H), 13.27 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): = 14.24, 18.86, 21.55, 33.42, 49.82, 60.36, 91.57, 104.36, 126.90, 127.25, 128.09, 128.20, 128.70, 130.08, 140.55, 140.62, 143.79, 149.62, 165.05, 168.80, 193.93 ppm.

Ethyl 9-benzoyl-4-(2-methoxyphenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6b) Yellow solid (80 mg, 72%), m.p. = 189~190°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.23 (t, *J* = 7.2Hz, 3H), 2.47 (d, *J* = 0.4Hz, 3H), 2.51-2.56 (m, 4H), 3.75 (s, 3H), 4.07-4.13 (m, 2H), 6.59 (s, 1H), 6.86-6.92 (m, 2H), 7.21-7.53 (m, 7H), 13.41 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11, 18.72, 21.49, 33.23, 49.81, 54.82, 59.99, 90.37, 111.05, 119.96, 126.76, 128.08, 129.20, 131.63, 132.38, 140.85, 142.42, 150.57, 157.85, 165.25, 168.83, 193.30 ppm.

Ethyl 9-benzoyl-4-(3-methoxyphenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6c) Yellow solid (83 mg, 75%), m.p. = 159~160°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.24 (t, *J* = 7.2Hz, 3H), 2.54 (s, 3H), 2.57-2.62 (m, 4H), 3.78 (s, 3H), 4.13-4.19 (q, 2H), 6.68 (s, 1H), 6.82 (d, *J* = 8.0Hz, 1H), 6.96-6.99 (m, 2H), 7.22-7.27 (m, 1H), 7.40 (d, *J* = 3.6Hz, 5), 13.23 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.14, 18.73, 21.43, 33.31, 49.50, 55.07, 60.23, 91.45, 104.11, 113.01, 113.24, 119.24, 126.77, 128.06, 129.59, 129.94, 140.49, 141.87, 143.75, 149.48, 159.60, 164.92, 168.64, 193.76 ppm.

Ethyl 9-benzoyl-4-(4-methoxyphenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6d) Yellow solid (82 mg, 74%), m.p. = 153~154°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.23 (t, *J* = 7.2Hz, 3H), 2.55 (s, 3H), 2.59 (d, *J* = 6.8Hz, 4H), 3.78 (s, 3H), 4.12-4.17 (q, 2H), 6.63 (s, 1H), 6.84 (d, *J* = 8.4Hz, 1H), 7.33 (d, *J* = 8.4Hz, 2H), 7.36-7.42 (m, 5H), 13.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): = 14.13, 18.68, 21.45, 33.28, 49.25, 55.10, 60.19, 91.38, 104.51, 113.88, 126.77, 128.06, 128.48, 129.91, 132.68, 140.56, 143.36, 149.54, 159.24, 164.95, 168.67, 193.68 ppm.

Ethyl 9-benzoyl-2-methyl-4-(4-nitrophenyl)-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6e) Red solid (62 mg, 54%), m.p. = 201~202°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.21 (t, *J* = 6.8Hz, 3H), 2.54 (s, 3H), 2.59 (m, 4H), 4.13 (q, 2H), 6.68 (s, 1H), 7.39 (q, 5H), 7.56 (d, *J* = 8.4Hz, 2H), 8.15 (d, J = 8.8Hz, 2H), 13.22 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.14, 18.90, 21.44, 33.07, 49.37, 60.50, 91.82, 102.91, 123.92, 126.78, 128.15, 128.27, 130.24, 140.20, 144.51, 147.45, 147.52, 148.58, 164.59, 168.59, 194.40 ppm.

Ethyl 9-benzoyl-4-(4-chlorophenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6f) Yellow solid (76 mg, 68%), m.p. = 229°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.22 (t, *J* = 7.2Hz, 3H), 2.55 (s, 3H), 2.56-2.60 (m, 4H), 4.12-4.17 (q, 2H), 6.64 (s, 1H), 7.28 (d, *J* = 8.4Hz, 2H), 7.34-

7.41 (m, 7H), 13.25 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.06, 18.68, 21.35, 33.09, 49.11, 60.23, 91.49, 103.63, 126.71, 128.01, 128.62, 128.69, 129.98, 133.72, 138.90, 140.29, 143.82, 149.01, 164.67, 168.54, 193.89 ppm.

Ethyl 9-benzoyl-4-(2-chlorophenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6g) Yellow solid (102 mg, 91%), m.p. = 209~210°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.22 (t, *J* = 6.8Hz, 3H), 2.53 (s, 3H), 2.54-2.57 (m, 4H), 4.10-4.15 (m, 2H), 6.86 (s, 1H), 7.19-7.24 (m, 2H), 7.34-7.50 (m, 7H), 13.39 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.22, 18.84, 21.47, 33.34, 49.29, 60.33, 91.78, 103.72, 126.92, 127.10, 128.18, 129.31, 130.10, 130.31, 130.53, 133.21, 138.78, 140.59, 143.03, 149.52, 164.91, 168.86, 194.07 ppm.

Ethyl 9-benzoyl-4-(4-(diethylamino)phenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido [1,2-a]pyrimidine-3-carboxylate (6h) Yellow solid (85 mg, 70%), m.p. = 166~167°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.14 (t, *J* = 7.2Hz, 6H), 1.25 (t, *J* = 7.2Hz, 3H), 2.53 (s, 4H), 2.59-2.65 (m, 3H), 3.30-3.35 (q, 4H), 4.12-4.17 (q, 2H), 6.57-6.59 (m, 3H), 7.22 (d, *J* = 8.4Hz, 2H), 7.40 (d, *J* = 4.0Hz, 7H), 13.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.55, 14.18, 18.69, 21.50, 33.41, 44.16, 49.37, 60.15, 91.20, 105.06, 111.25, 126.81, 126.96, 128.05, 128.36, 129.80, 140.76, 142.88, 147.44, 150.00, 165.16, 168.74, 193.38 ppm.

Ethyl 9-benzoyl-2,7-dimethyl-6-oxo-4-phenyl-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6i) Yellow solid (80 mg, 75%), m.p. = 180~181°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.16-1.25 (m, 6H), 2.32-2.43 (m, 1H), 2.55 (s, 3H), 2.73-2.82 (m, 2H), 4.12-4.17 (q, 2H), 6.63 (d, *J* = 16.4Hz, 1H), 7.26-7.31 (m, 3H), 7.40 (s, 7H), 13.30 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.12, 15.32, 18.82, 28.12, 37.00, 50.11, 60.24, 88.55, 104.33, 126.72, 126.87, 127.16, 127.94, 128.09, 128.54, 129.78, 140.61, 140.68, 143.62, 148.72, 164.93, 171.97, 194.70 ppm.

Ethyl 9-benzoyl-4-(4-chlorophenyl)-2,7-dimethyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido [1,2-a]pyrimidine-3-carboxylate (6j) Yellow solid (84 mg, 72%), m.p. = 170~171°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.15-1.25 (m, 6H), 2.35 (d, *J* = 15.2Hz, 1H), 2.56 (s, 1H), 2.72-2.81 (m, 2H), 4.12-4.17 (q, 2H), 6.58 (d, *J* = 14.4Hz, 2H), 7.27-7.43 (m, 7H), 13.26 (d, *J* = 15.2Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.12, 15.29, 18.85, 28.10, 36.88, 49.59, 60.31, 88.67, 91.78, 103.78, 126.70, 128.11, 128.72, 129.87, 133.77, 139.10, 140.51, 143.83, 148.28, 148.88, 164.76, 171.91, 194.87 ppm.

Ethyl 9-benzoyl-4-(2-chlorophenyl)-2,7-dimethyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido [1,2-a]pyrimidine-3-carboxylate (6k) Yellow solid (99 mg, 83%), m.p. = 192~193°C. ^{1}H NMR (400 MHz, $CDCl_3$): = 1.12-1.25 (m, 6H), 2.33 (dd, *J* = 15.6, 2.8Hz, 1H), 2.53 (s, 3H), 2.67 (d, *J* = 4.8Hz, 1H), 2.76 (dd, *J* = 15.6, 5.4Hz, 1H), 4.11-4.14 (q, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 19.2Hz, 1H), 7.21 (s, 2H), 7.33-7.50 (m, 7H), 13.47 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11, 15.30, 18.82, 28.10, 36.81, 49.65, 60.19, 88.70, 103.56, 126.70, 126.88, 126.98, 128.07, 129.13, 129.78, 130.01, 130.13, 130.33, 133.12, 138.87, 138.91, 140.64, 142.86, 148.62, 164.78, 172.03, 194.78 ppm.

Ethyl 4-methyl-6-phenyl-2-(phenylethynyl)pyrimidine-5-carboxylate (8a): White solid (68 mg, 79%); 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 (8b): Yellow oil (73 mg, 81%). ^{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 (8c): Yellow oil (74 mg, 83%). ^{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 (8d): White solid (65 mg, 80%); 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-(4-Fluorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (8e): Yellow oil (70 mg, 76%). ^{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 (8f): Yellow oil (80 mg, 84%). ^{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-2-(oct-1-ynyl)-6-p-tolylpyrimidine-5-carboxylate (8g): Yellow oil (70 mg, 77%). ^{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 6-methyl-2,4-diphenyl-1,4-dihydropyrimidine-5-carboxylate (10a) Yellow oil (52 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 5.6 Hz, 3H), 2.41 (s, 3H), 4.05-4.06 (m, 2H), 5.68 (s, 1H), 7.18-7.26 (m, 3H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.52-7.57 (m, 3H), 7.63 (d, *J* = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.10, 29.49, 56.96, 59.44, 101.16, 126.93, 126.97, 128.12, 128.28, 128.40, 130.54, 131.71, 131.81, 132.49, 133.56, 145.27, 166.76 ppm.

Ethyl 4-(2-methoxyphenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10b) Yellow oil (41 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 5.6 Hz, 3H), 2.38 (s, 3H), 3.71 (s, 3H), 4.04 ((q, *J* = 5.6 Hz, 2H), 5.61 (s, 1H), 7.20-7.64 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.10, 29.49, 56.96, 58.10, 60.04, 105.15, 111.12, 126.73, 126.97, 127.92, 128.28, 128.42, 130.51, 131.53, 132.01, 132.49, 133.36, 146.27, 165.76 ppm.

Ethyl 4-(3-methoxyphenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10c) Yellow oil (44 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 5.6 Hz, 3H), 2.38 (s, 3H), 3.71 (s, 3H), 4.04 (q, *J* = 5.6 Hz, 2H), 5.60 (s, 1H), 7.04-7.60 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11, 29.46, 56.86, 58.12, 60.09, 105.25, 111.82, 126.03, 126.91, 127.22, 128.68, 128.92, 130.41, 131.73, 132.51,

132.79, 133.46, 146.07, 165.86 ppm.

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10d) Yellow oil (50 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (t, *J* = 5.6 Hz, 3H), 2.38 (s, 3H), 3.71 (s, 3H), 4.05 (q, *J* = 5.6 Hz, 2H), 5.61 (s, 1H), 7.16-7.57 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.04, 29.59, 56.90, 58.30, 59.95, 104.95, 112.02, 126.43, 126.87, 127.90, 128.29, 128.48, 130.53, 131.57, 132.09, 132.43, 133.39, 146.24, 165.79 ppm.

Ethyl 4-(2-chlorophenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10e) Yellow oil (61 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 5.6 Hz, 3H), 2.31 (s, 3H), 4.07 (q, *J* = 5.6 Hz, 2H), 5.91 (s, 1H), 7.17-7.73 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.10, 29.69, 56.96, 60.44, 107.15, 127.13, 128.12, 128.58, 129.40, 130.53, 131.67, 132.81, 135.49, 143.57, 150.27, 155.77, 167.38 ppm.

Ethyl 4-(4-chlorophenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10f) Yellow oil (54 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 5.6 Hz, 3H), 2.12 (s, 3H), 4.06 (q, *J* = 5.6 Hz, 2H), 5.82 (s, 1H), 7.27-7.76 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.12, 29.79, 54.93, 60.14, 107.35, 128.13, 128.42, 128.57, 129.10, 130.83, 132.11, 135.59, 143.07, 150.10, 156.38, 167.68 ppm.

Ethyl 6-methyl-4-phenyl-2-o-tolyl-1,4-dihydropyrimidine-5-carboxylate (10g) Yellow oil (43 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, *J* = 5.6 Hz, 3H), 2.22 (s, 3H), 2.26 (s, 3H), 4.04 (q, *J* = 5.6 Hz, 2H), 5.68 (s, 1H), 7.18-7.53 (m, 10H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.10, 20.26, 29.49, 54.96, 60.44, 104.16, 125.93, 126.93, 127.92, 128.26, 128.50, 129.68, 130.94, 134.71, 136.81, 143.46, 149.56, 155.26, 166.67 ppm.

Ethyl 4-methyl-2,6-diphenylpyrimidine-5-carboxylate (11a): White solid (66 mg, 82%); 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-(4-fluorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (11b): White solid (65 mg, 78%); 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 (11c): White solid (78 mg, 87%); 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 (11d): White solid (78 mg, 89%); 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-2-phenyl-6-p-tolylpyrimidine-5-carboxylate (11e): White solid (70 mg, 84%); 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-methyl-6-phenyl-2-o-tolylpyrimidine-5-carboxylate (11f): White solid (53 mg, 64%); 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 4-methyl-6-phenyl-2-m-tolylpyrimidine-5-carboxylate (11g): White solid (71 mg, 83%); 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-p-tolylpyrimidine-5-carboxylate (11h): White solid (70 mg, 85%); 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 2-(4-methoxyphenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (11i): White solid (32 mg, 91%); 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.

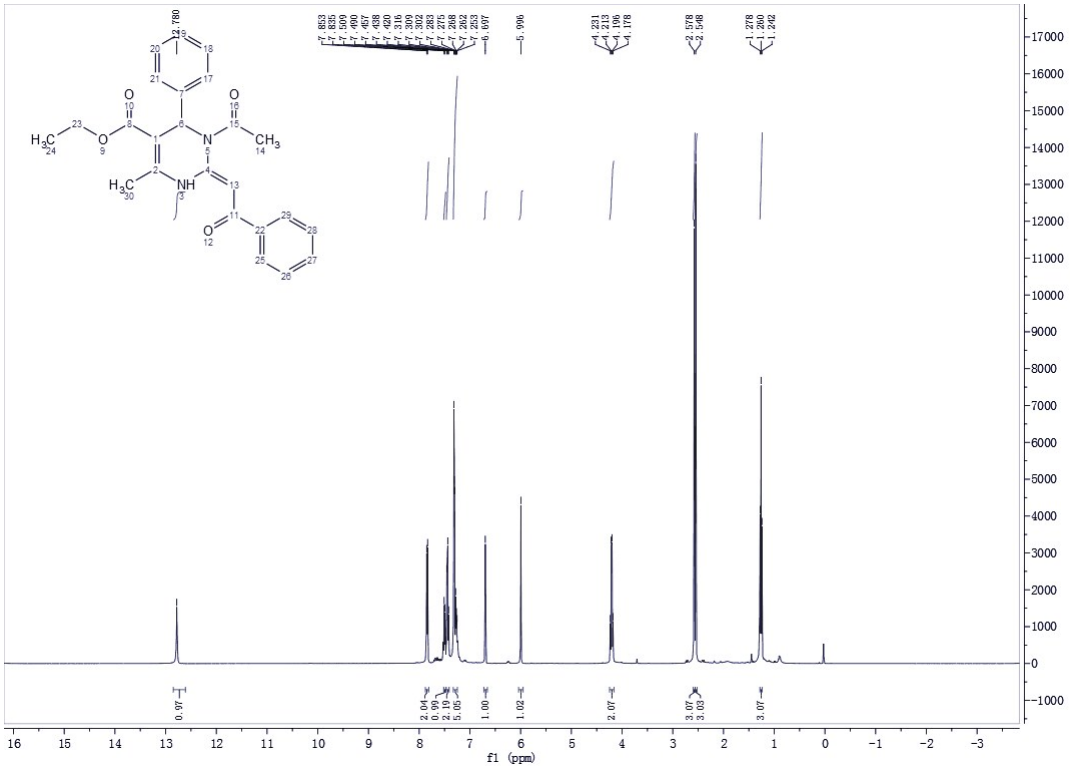
Ethyl 2-(4-chlorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (11j): White solid (75 mg, 85%); m.p. = 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51-8.36 (m, 2H), 7.80-7.56 (m, 2H), 7.52-7.29 (m, 5H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 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.

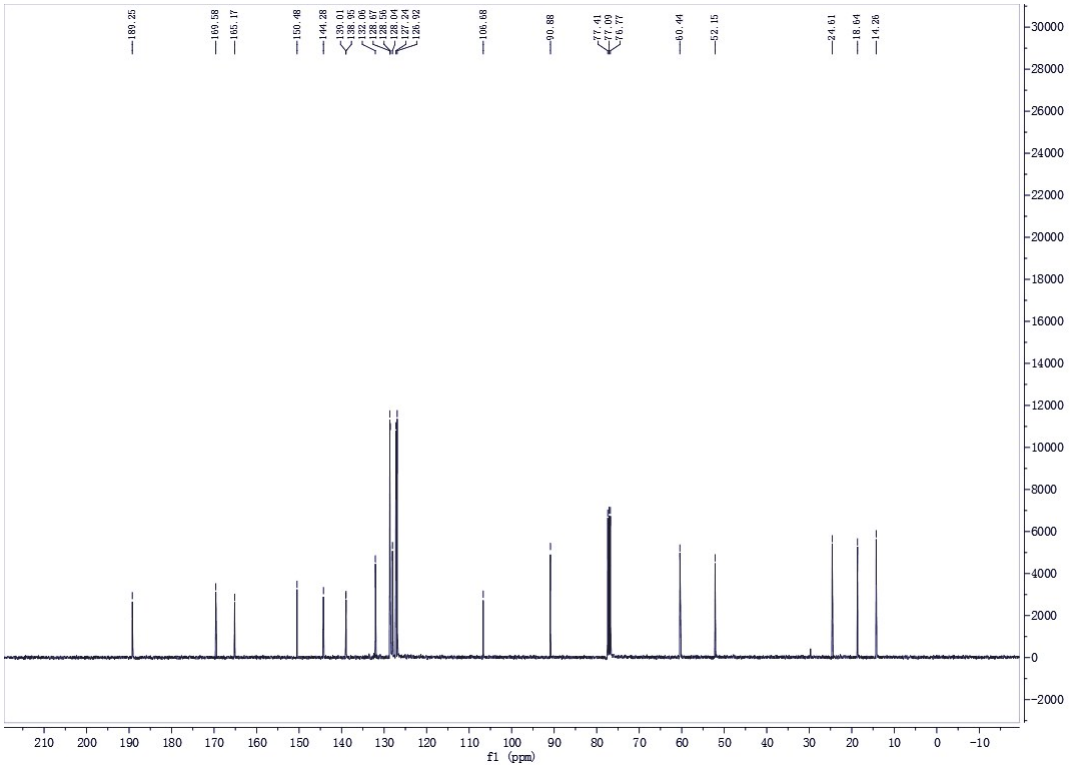
Ethyl 4-methyl-2-(naphthalen-1-yl)-6-phenylpyrimidine-5-carboxylate (11k): White solid (68 mg, 73%); m.p. = 83-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62-8.60 (m, 1H), 8.06 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.87-7.80 (m, 1H), 7.77-7.65 (m, 2H), 7.59-7.31 (m, 6H), 4.18 (q, *J* = 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-6-phenyl-2-(thiophen-2-yl)pyrimidine-5-carboxylate (11l): White solid (55 mg, 69%); m.p. = 89-91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.71-7.56 (m, 2H), 7.51-7.28 (m, 4H), 7.07 (dd, *J* = 4.9, 3.8Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.20, 165.54,163.67, 160.49, 142.96, 137.88, 130.54, 130.00, 129.82, 128.42, 128.29, 128.21, 122.77, 61.71, 22.70, 13.61 ppm.

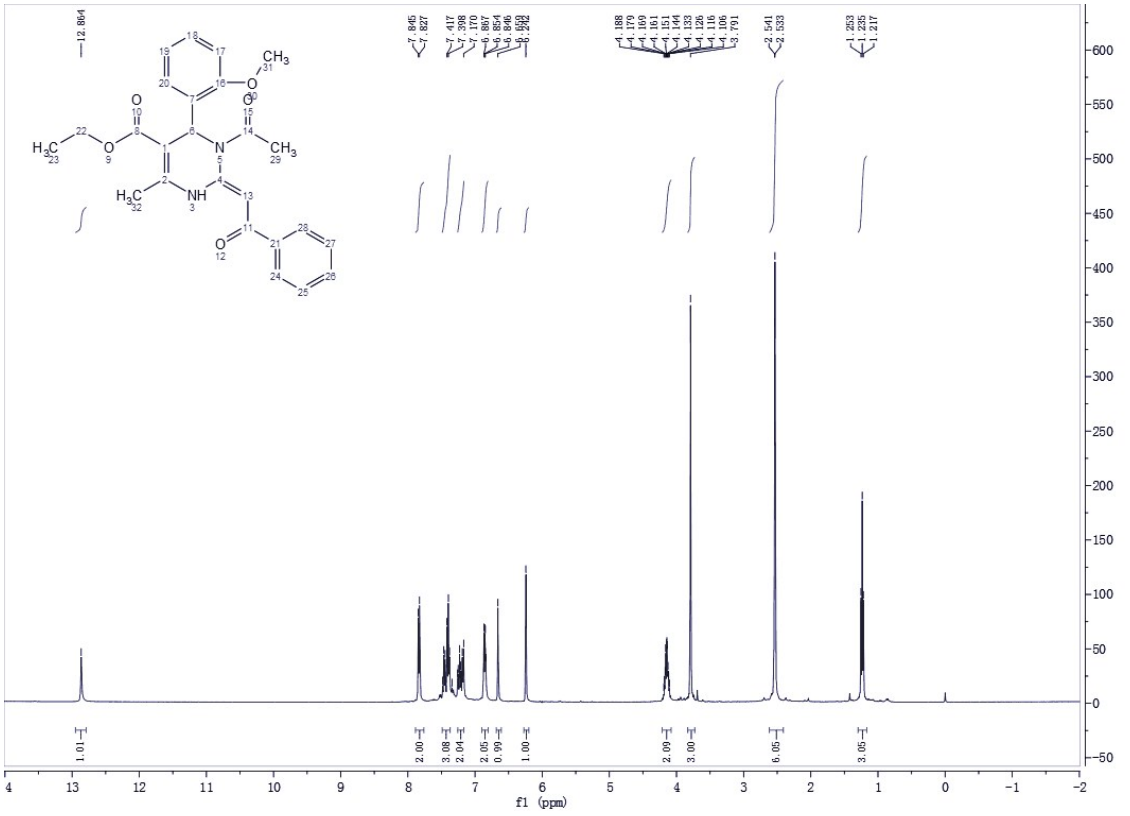
Copies of the NMR Spectra for New Products.

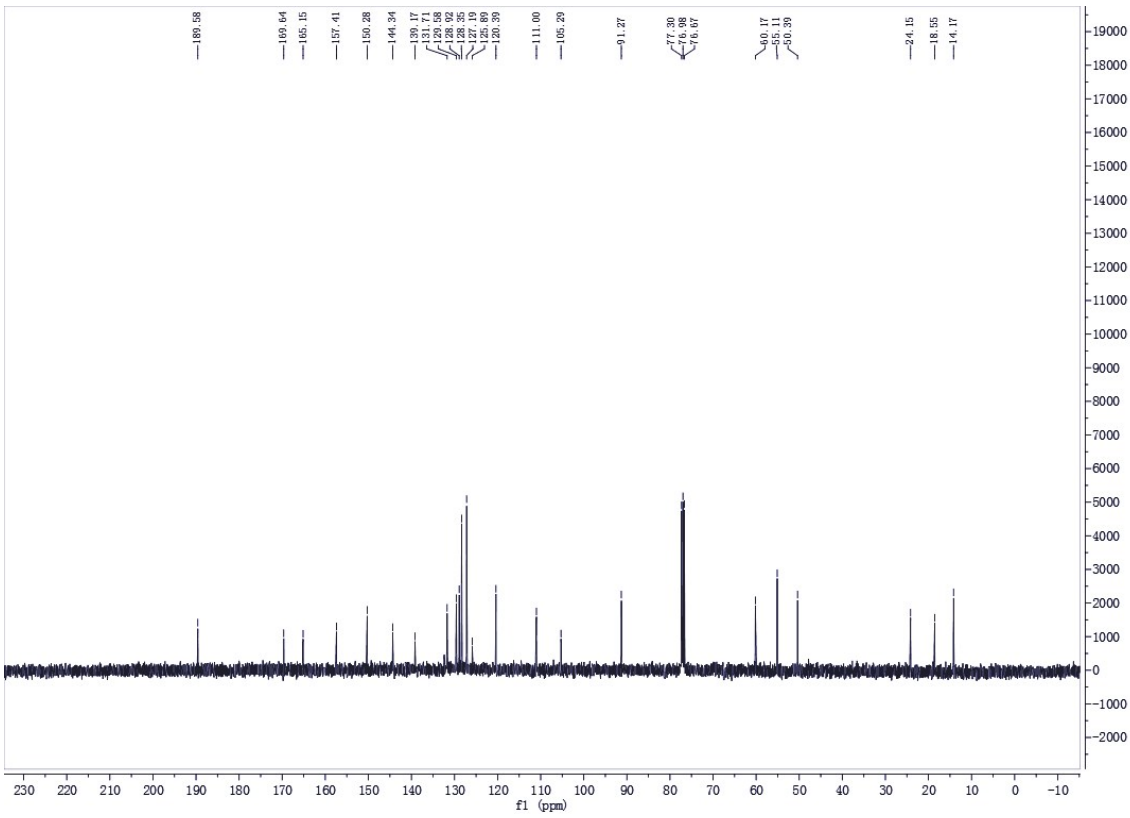
(*E*)-ethyl 3-acetyl-6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-1,2,3,4-tetrahydro-pyrimidine-5-carboxylate (4a)



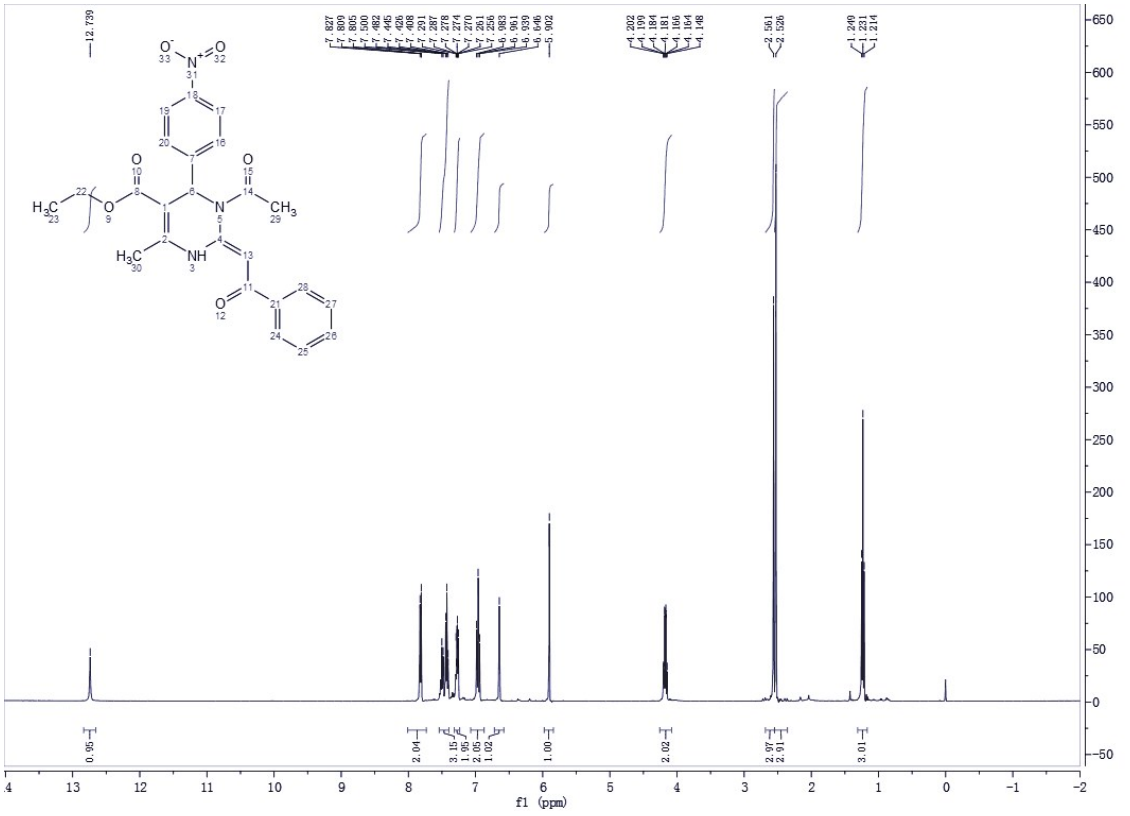


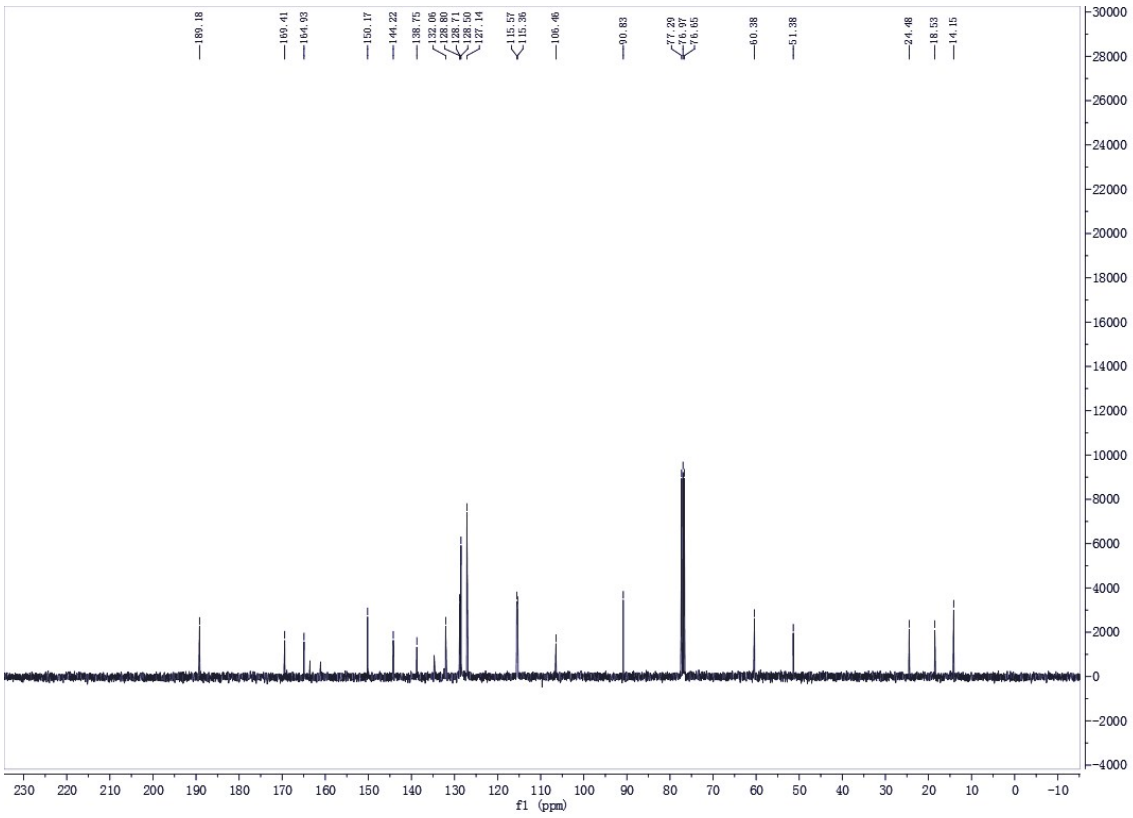
(*E*)-ethyl 3-acetyl-4-(2-methoxyphenyl)-6-methyl-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b)



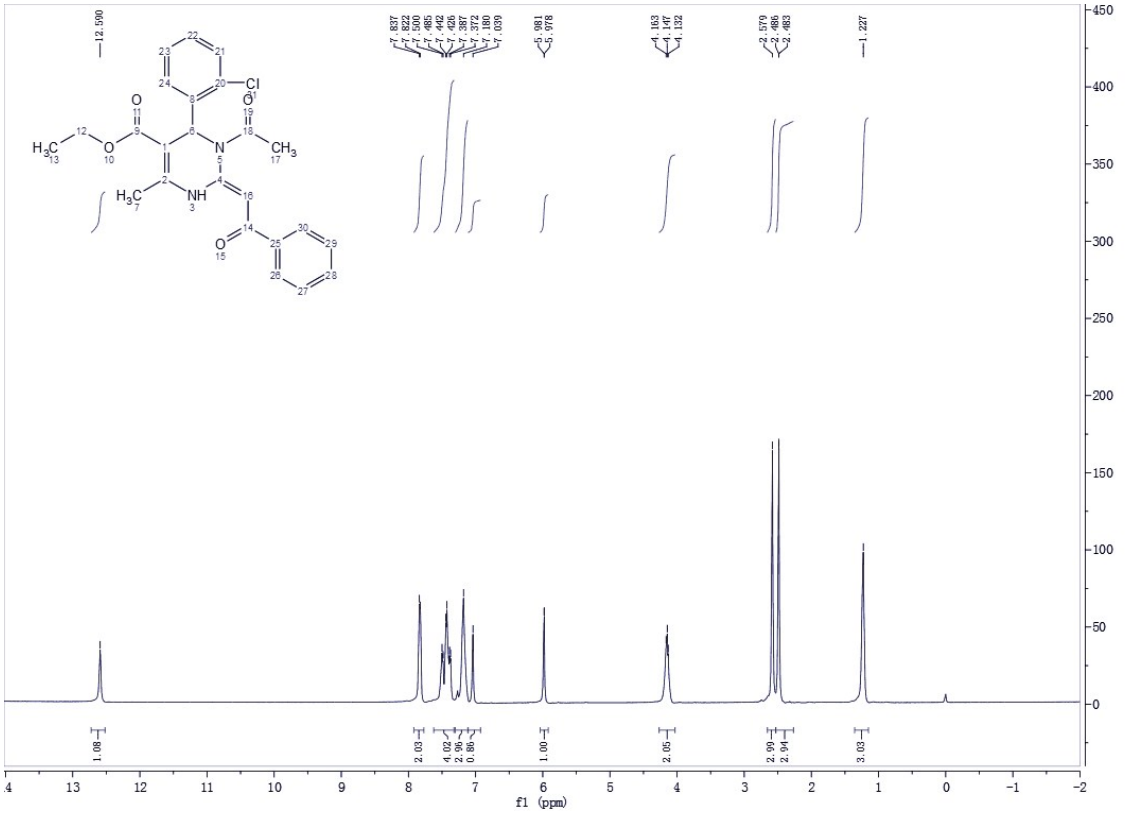


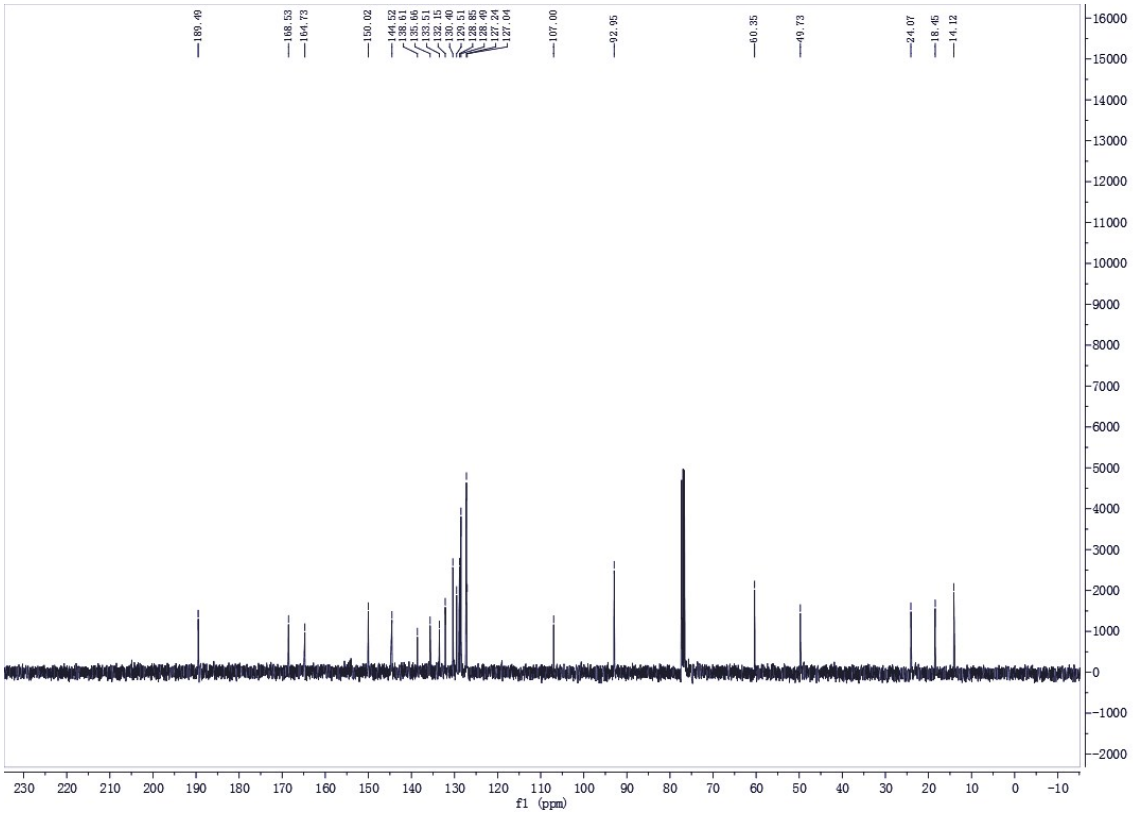
(*E*)-ethyl 3-acetyl-6-methyl-4-(4-nitrophenyl)-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c)



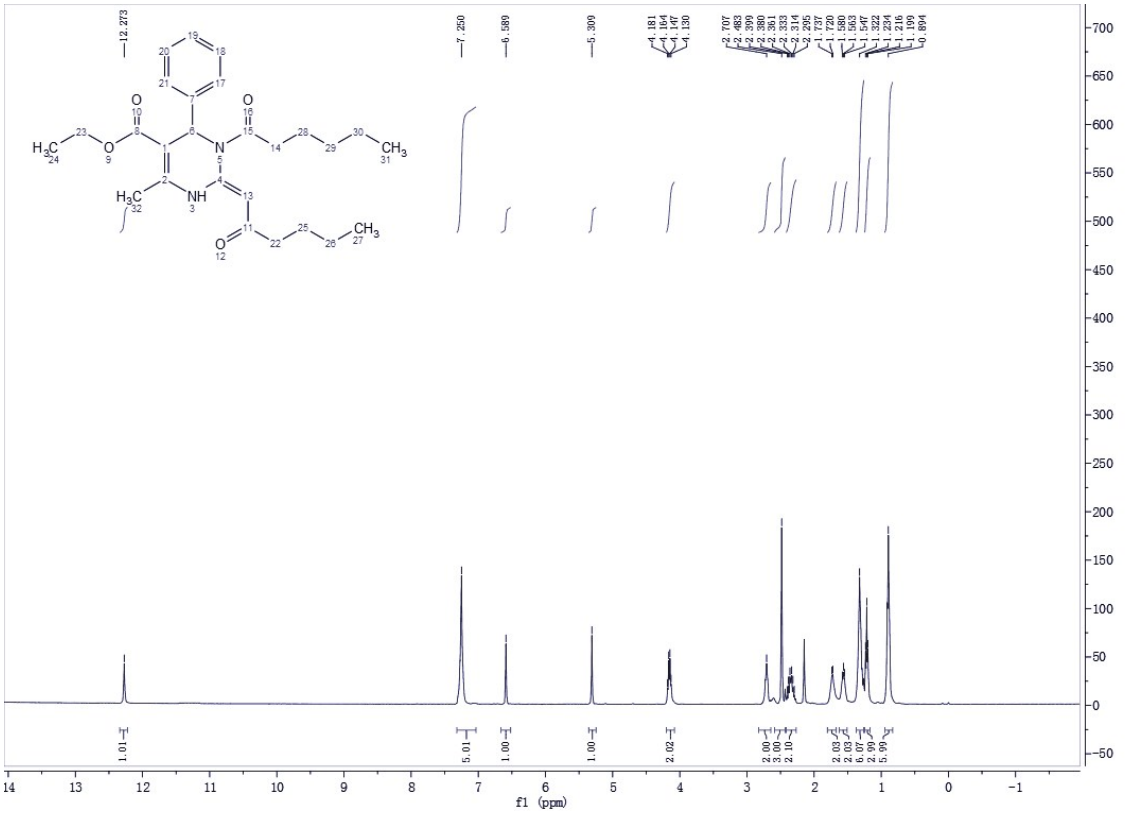


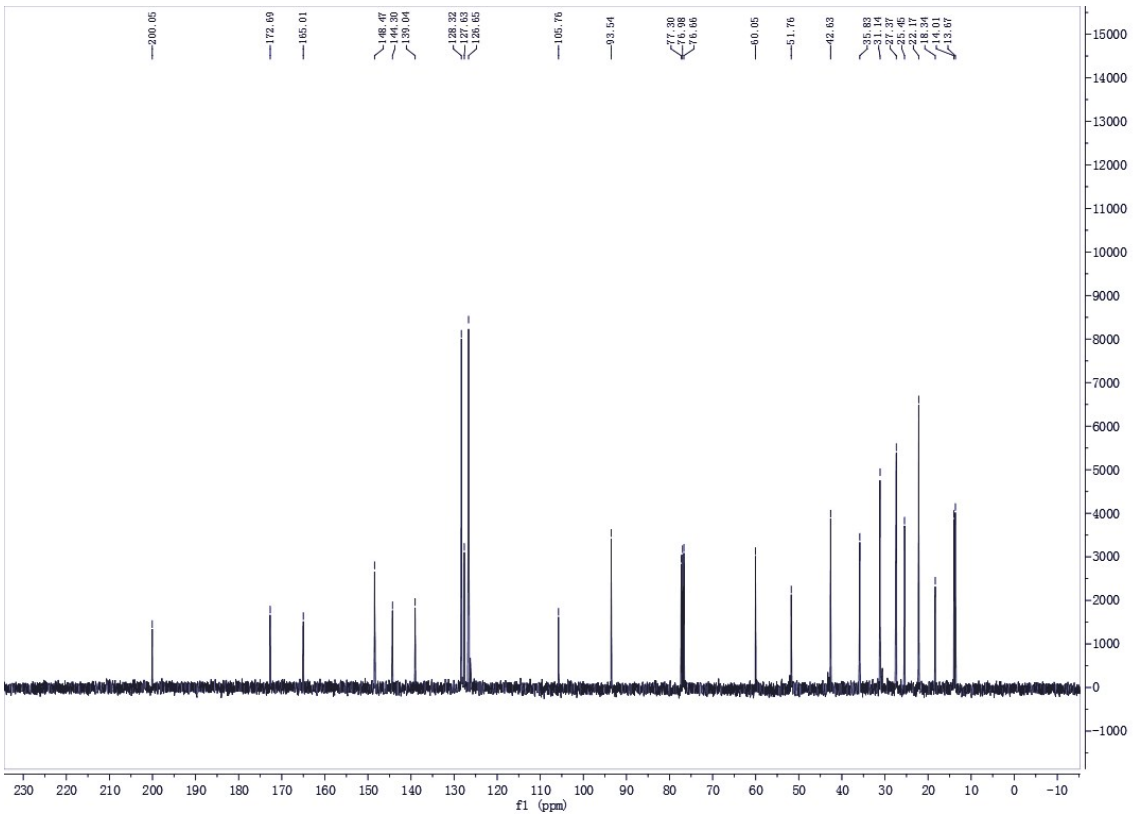
(E)-ethyl 3-acetyl-4-(2-chlorophenyl)-6-methyl-2-(2-oxo-2-phenylethylidene)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d)



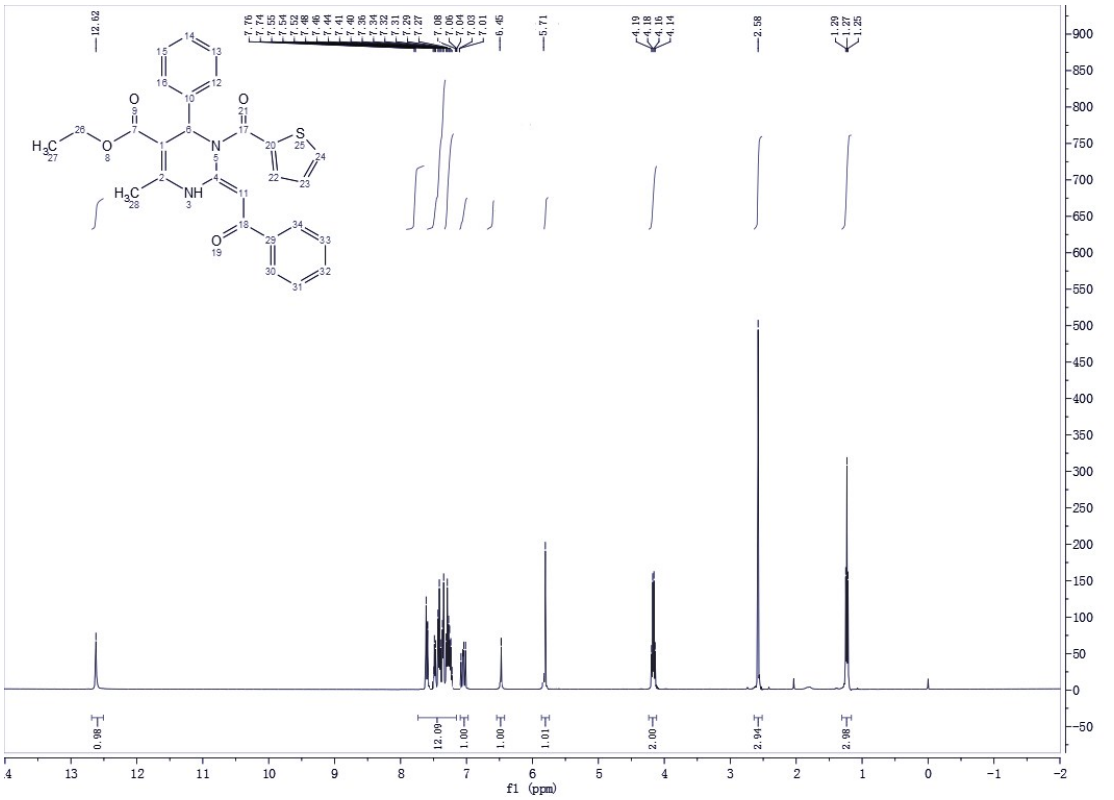


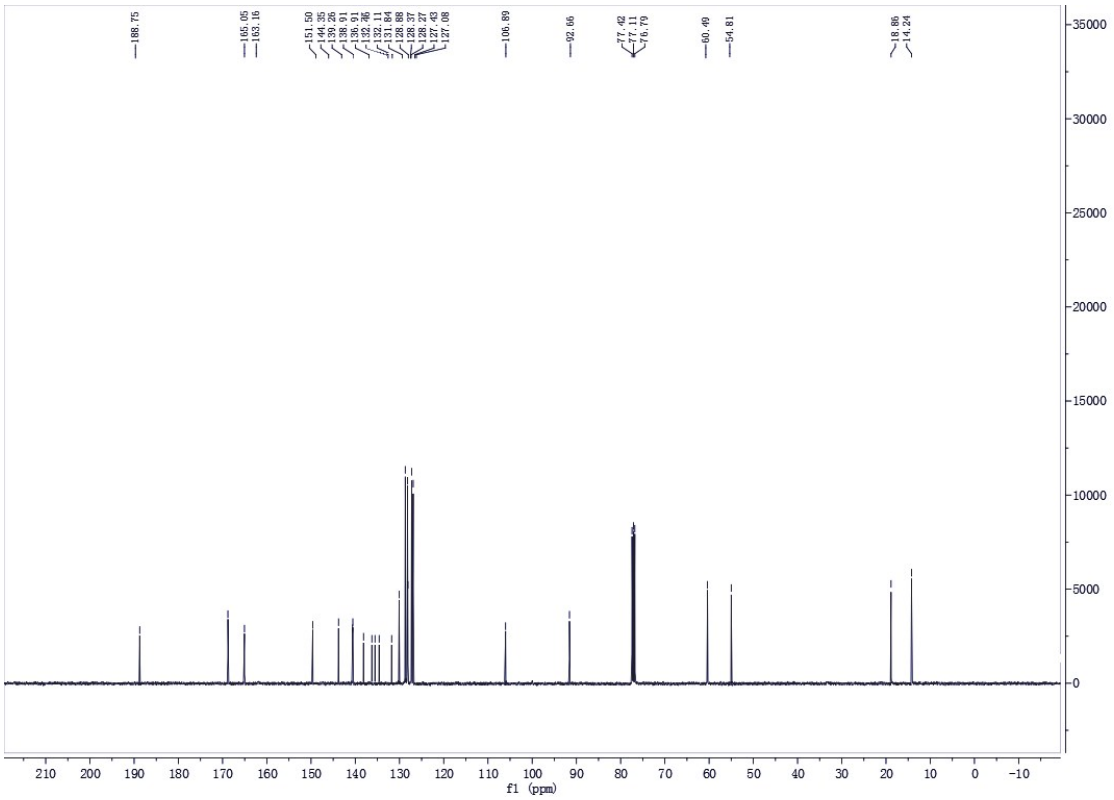
(*E*)-ethyl 3-hexanoyl-6-methyl-2-(2-oxohexylidene)-4-phenyl-1,2,3,4-tetrahydro-pyrimidine-5-carboxylate (4e)



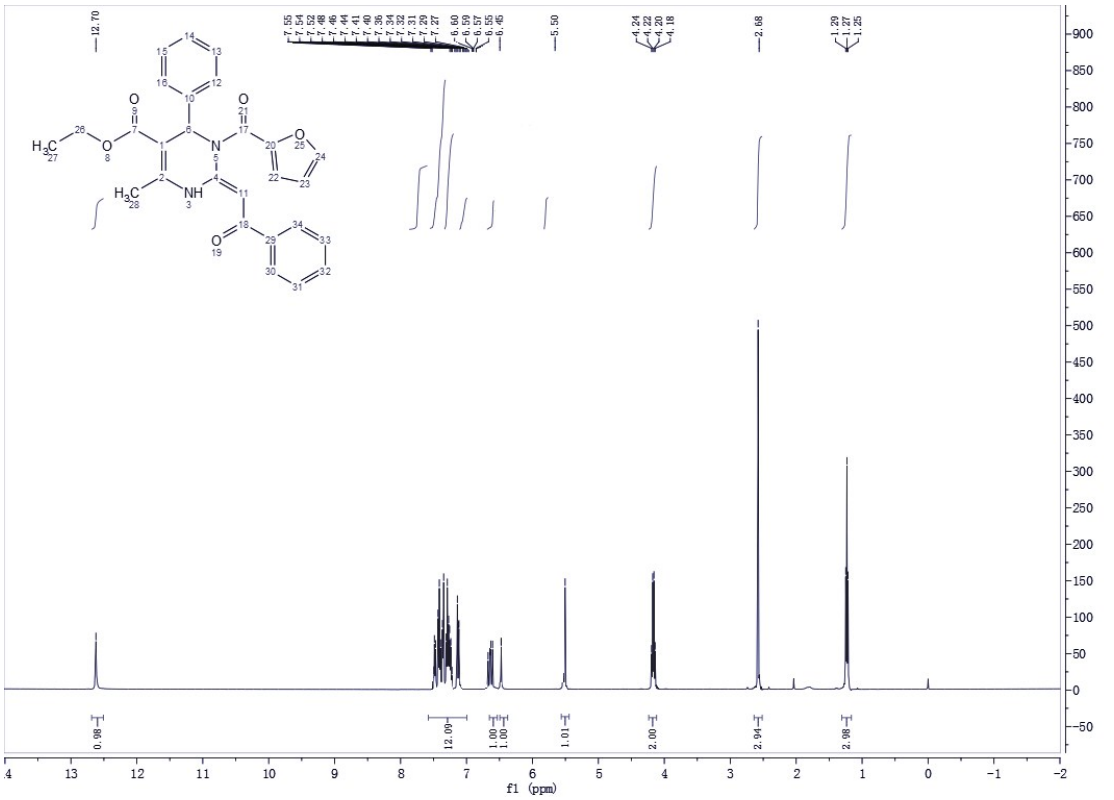


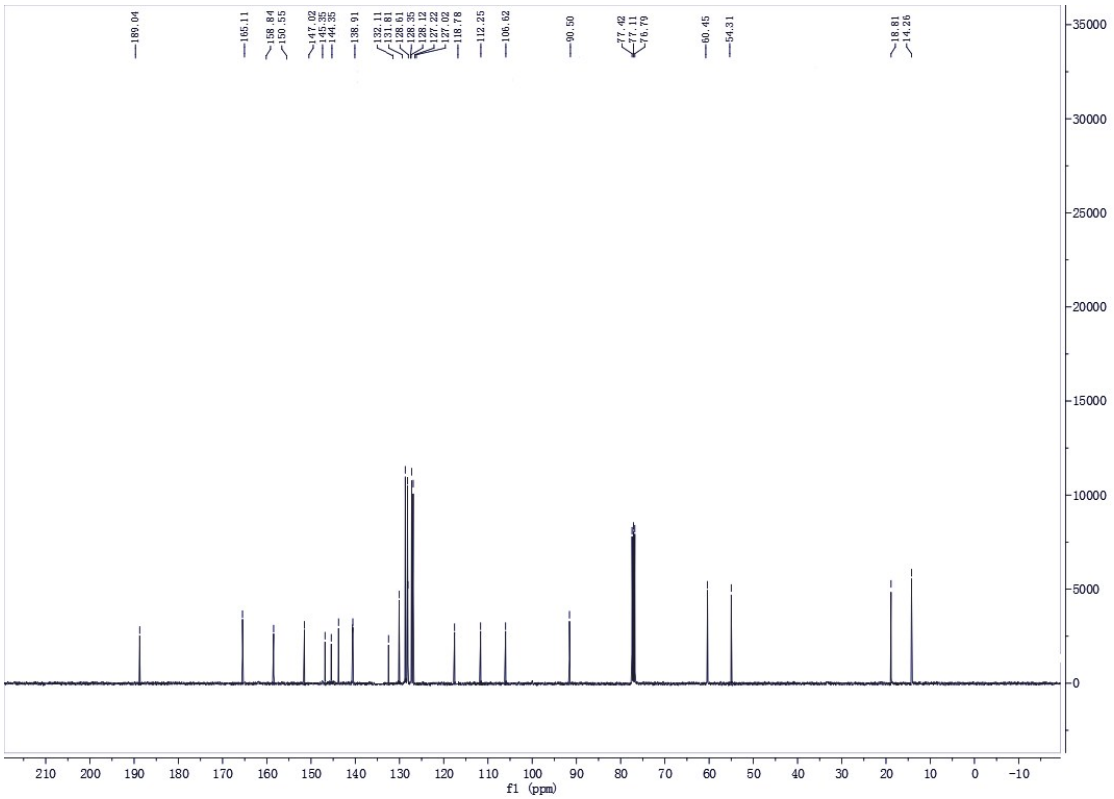
(E)-ethyl 6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-3-(thiophene-2-carbonyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4f)



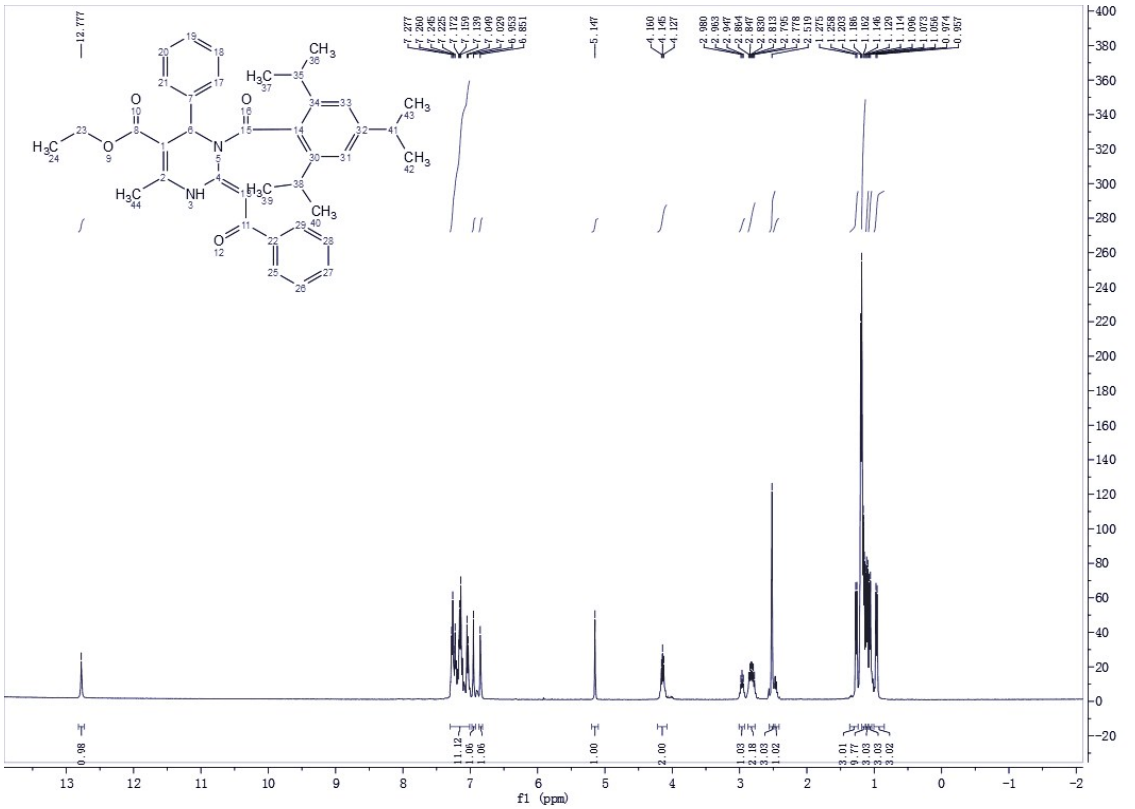


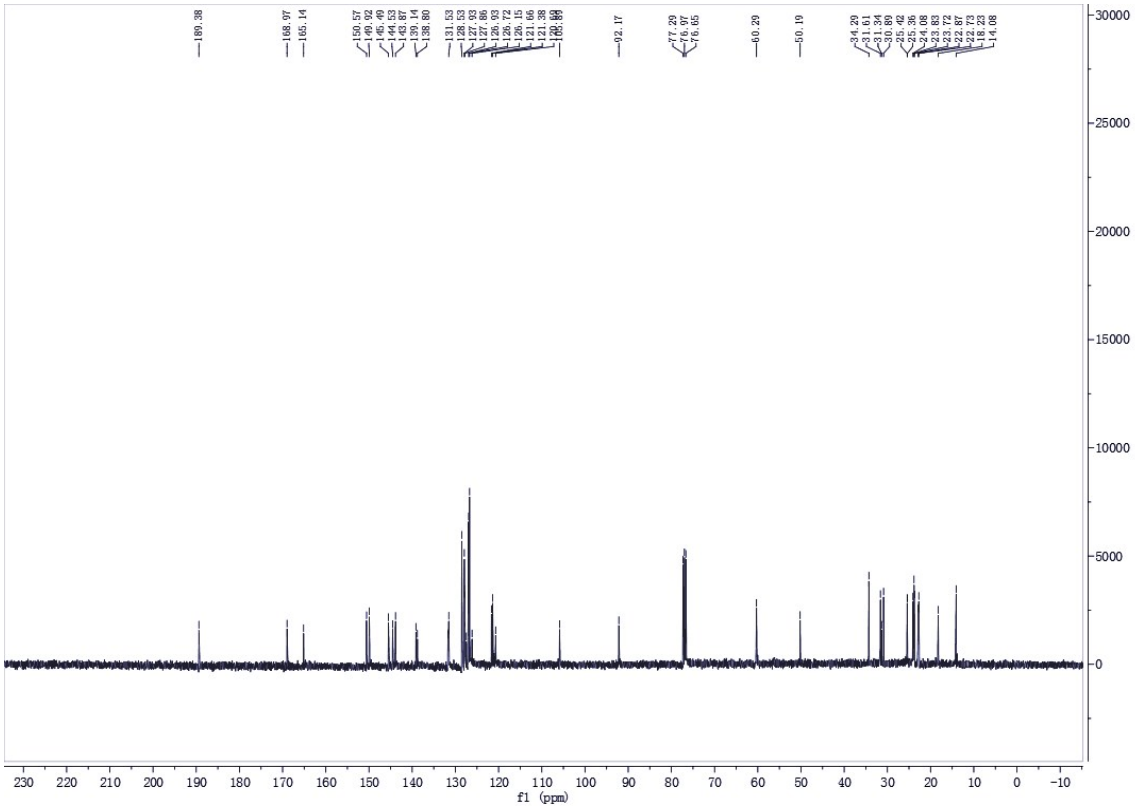
(E)-ethyl 3-(furan-2-carbonyl)-6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4g)



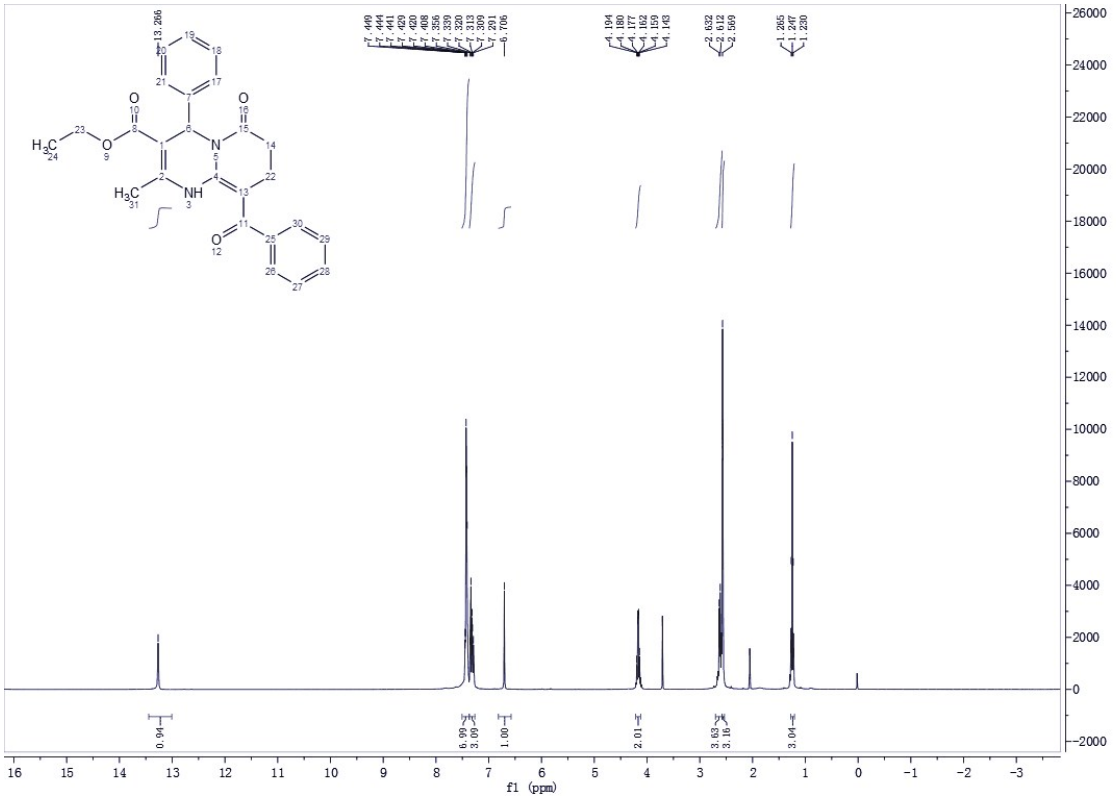


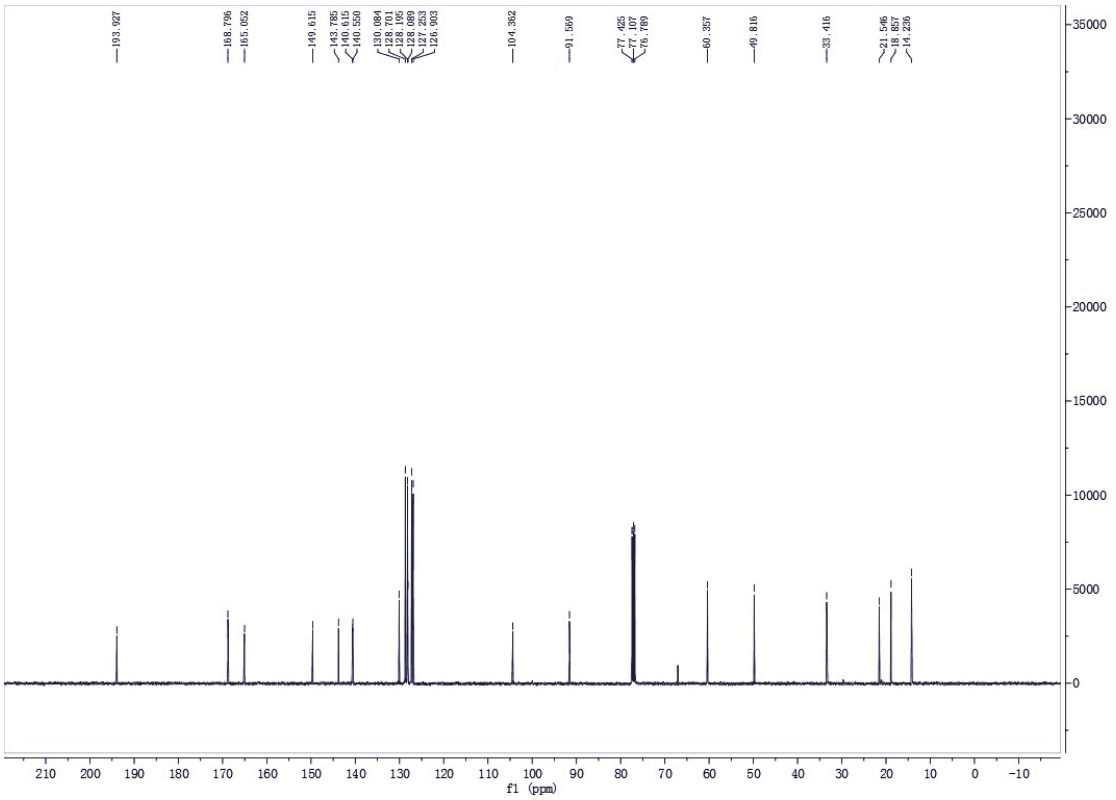
(*E*)-ethyl 6-methyl-2-(2-oxo-2-phenylethylidene)-4-phenyl-3-(2,4,6-triisopropylbenzoyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4h)



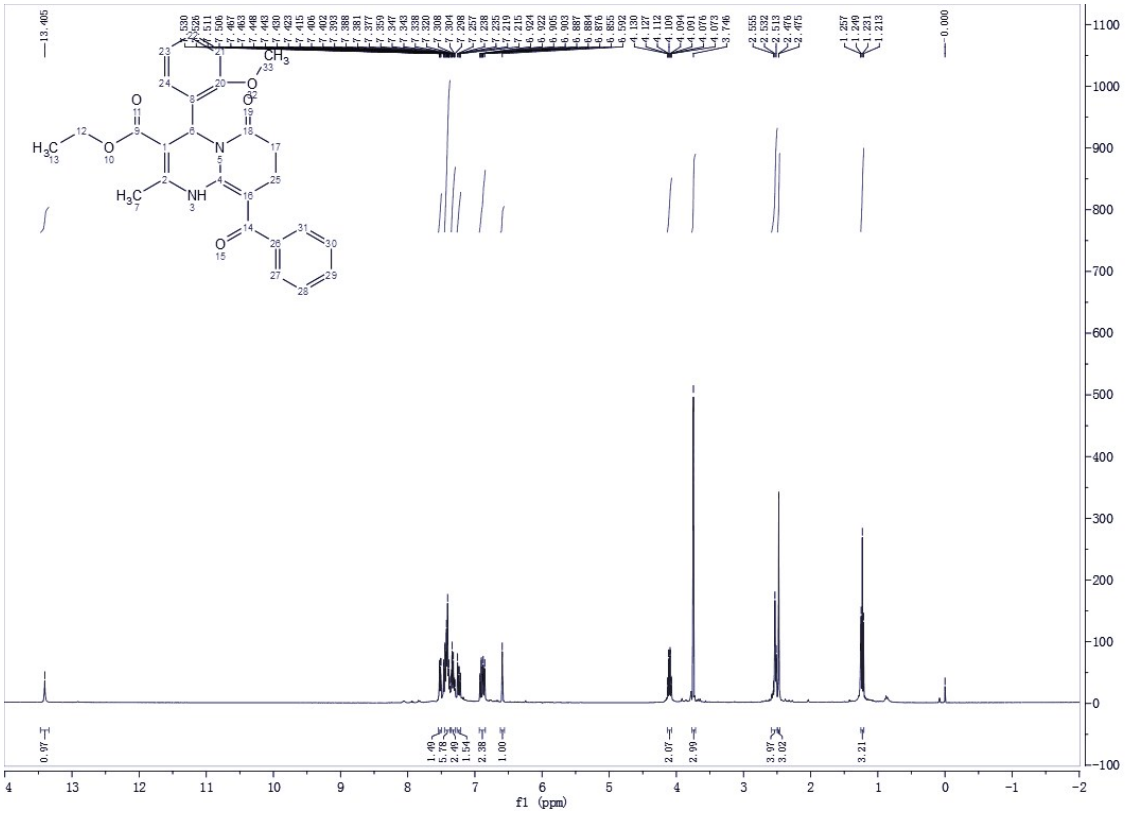


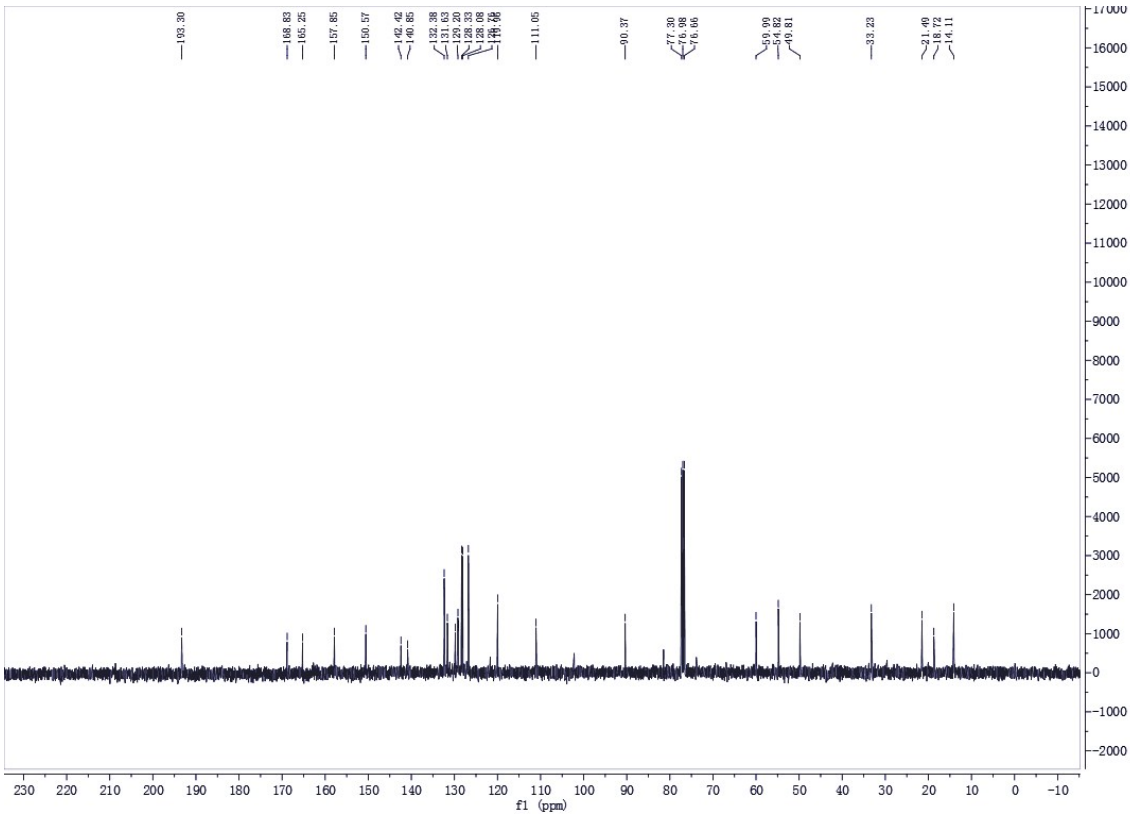
Ethyl 9-benzoyl-2-methyl-6-oxo-4-phenyl-4,6,7,8-tetrahydro-1H-pyrido[1,2-a]pyrimidine- 3-carboxylate (6a)



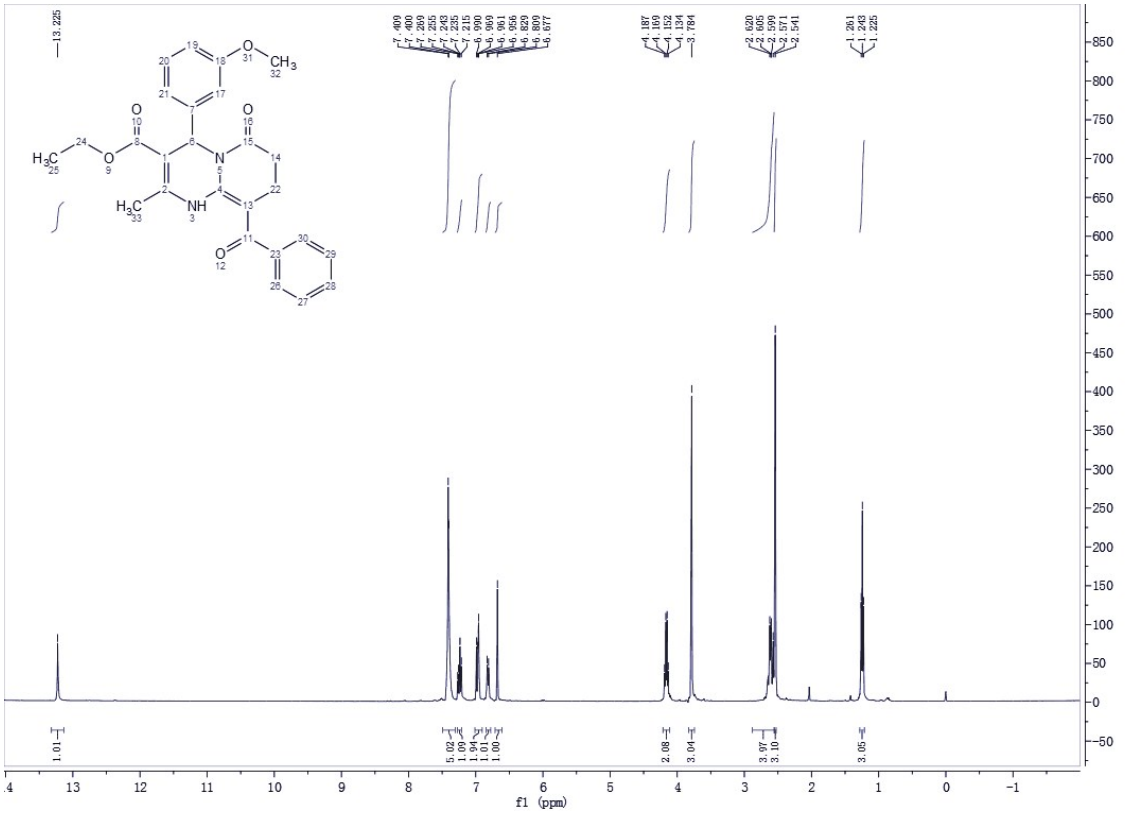


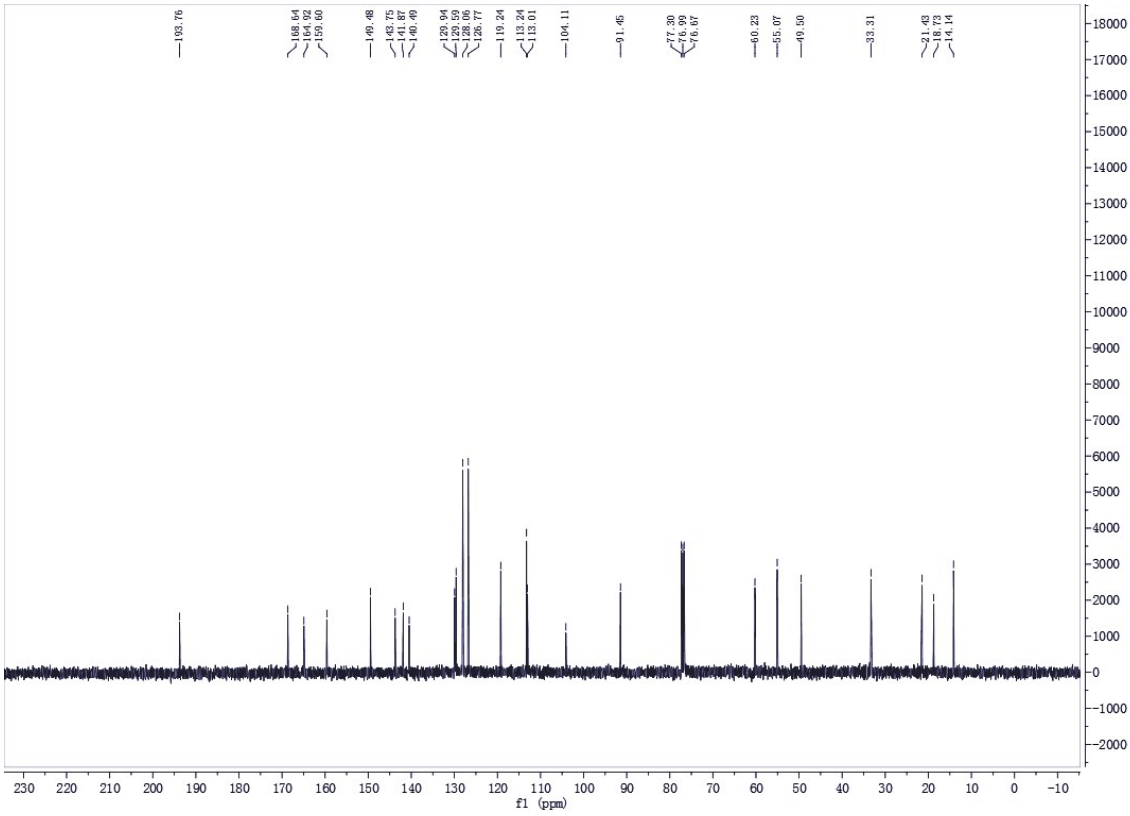
Ethyl 9-benzoyl-4-(2-methoxyphenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6b)



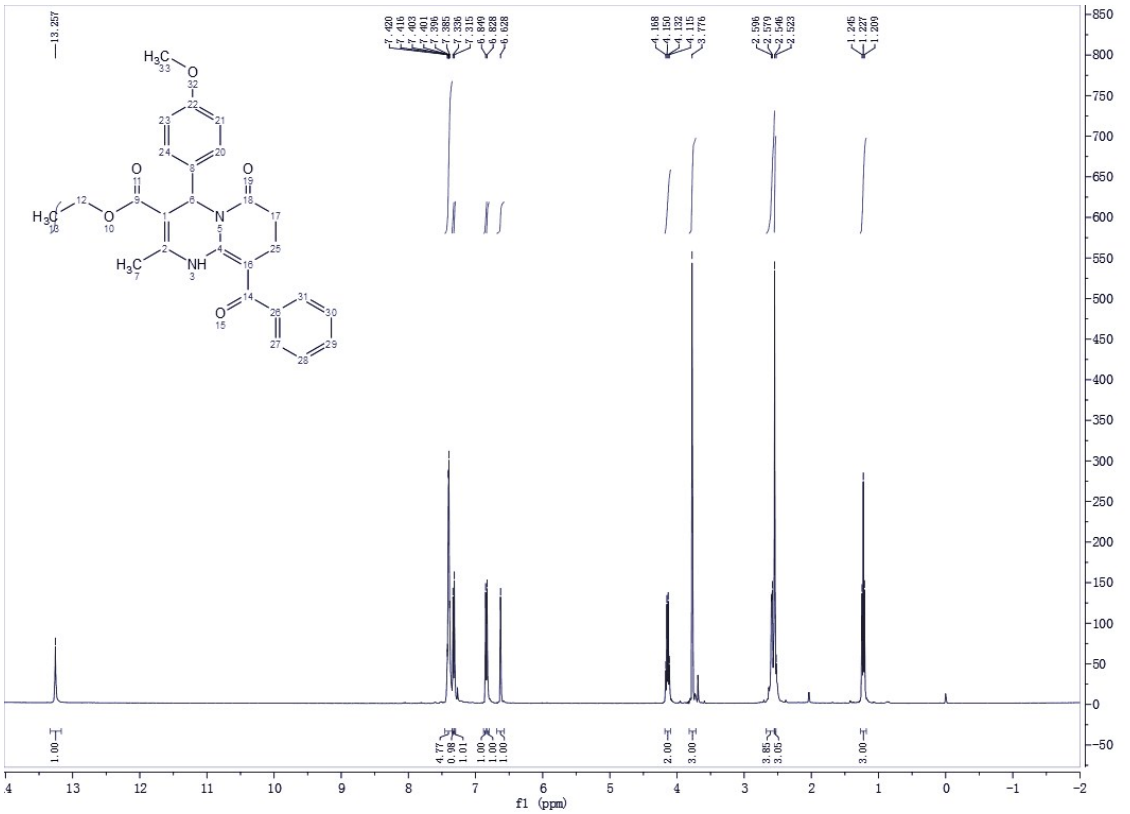


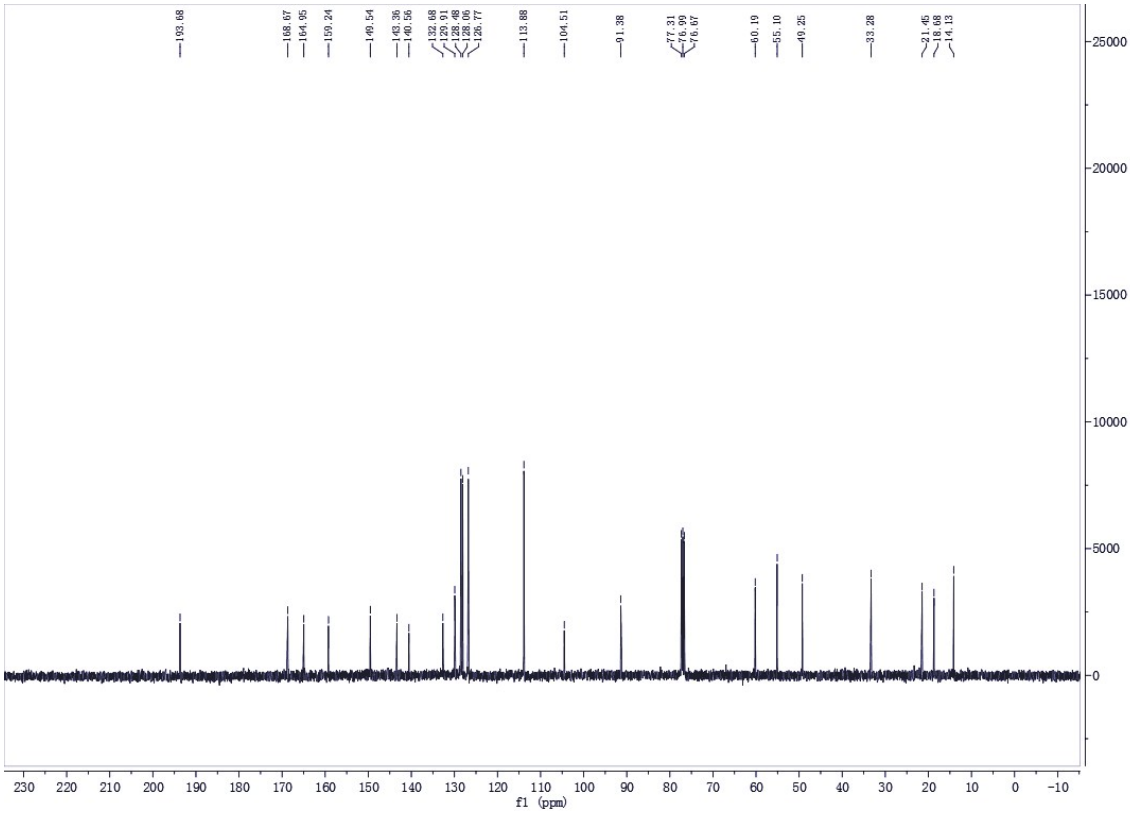
Ethyl 9-benzoyl-4-(3-methoxyphenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6c)



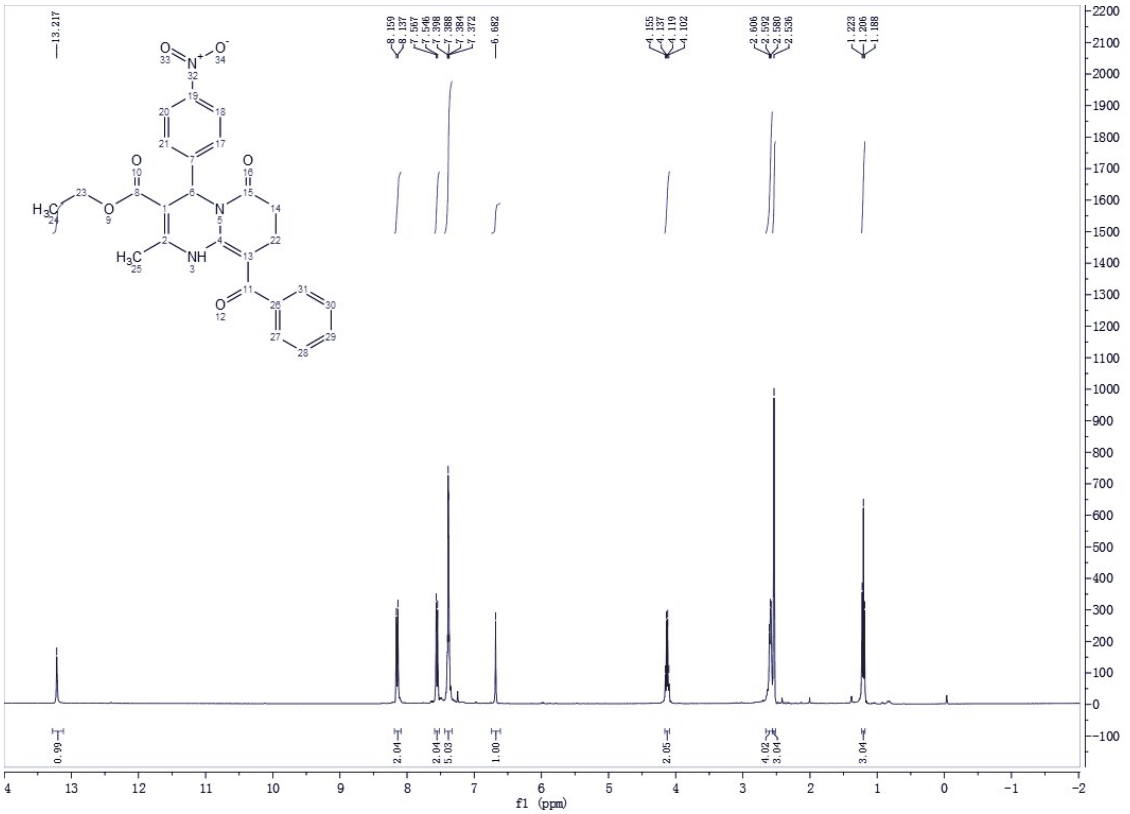


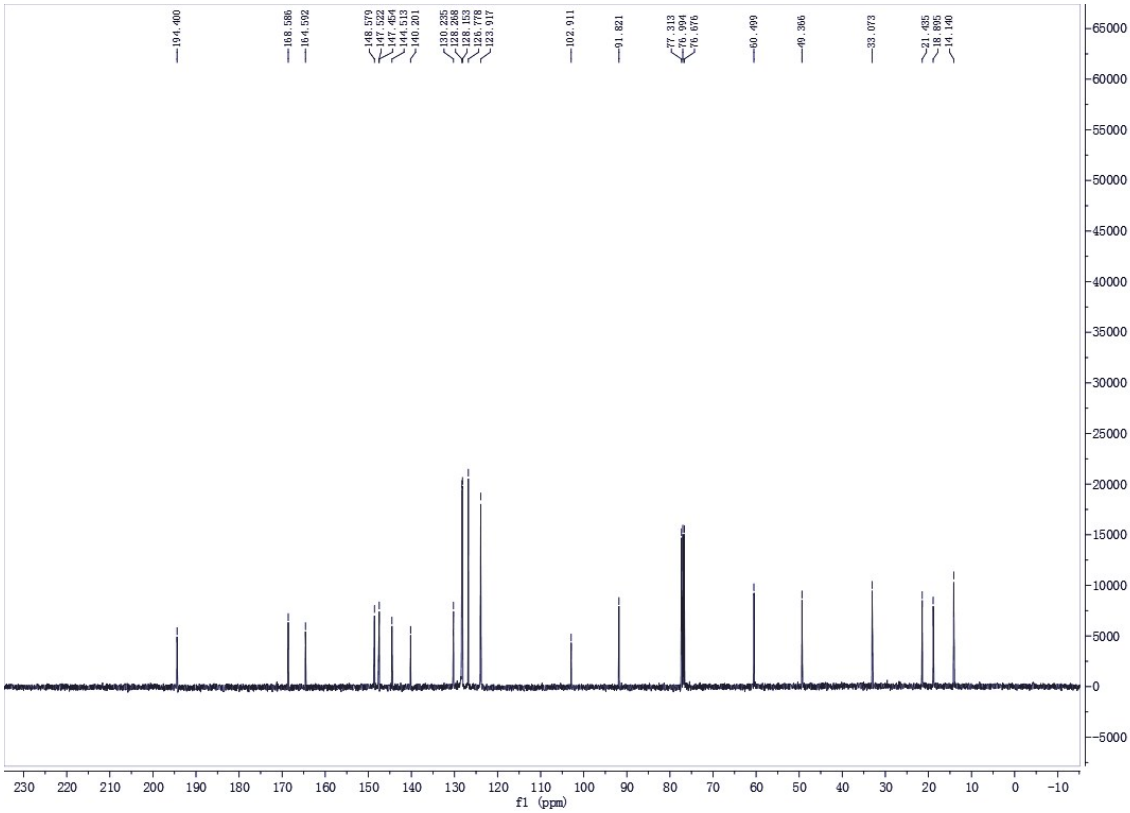
Ethyl 9-benzoyl-4-(4-methoxyphenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6d)



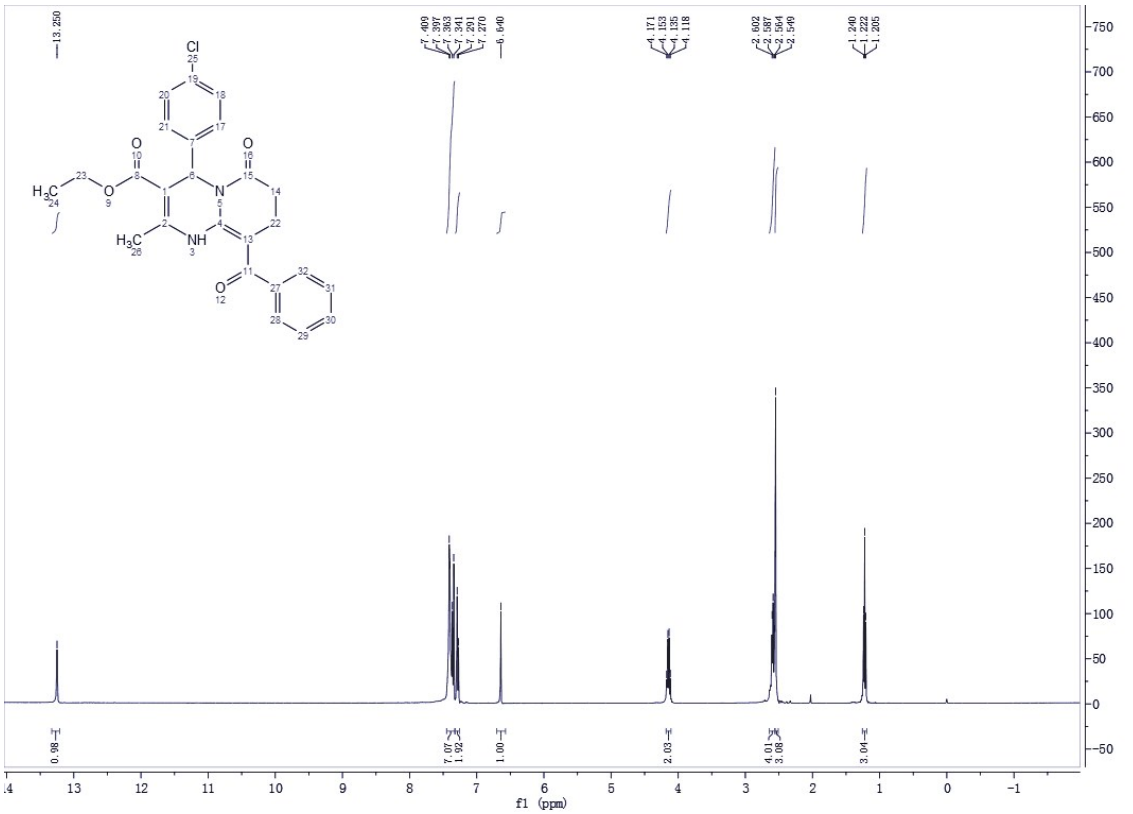


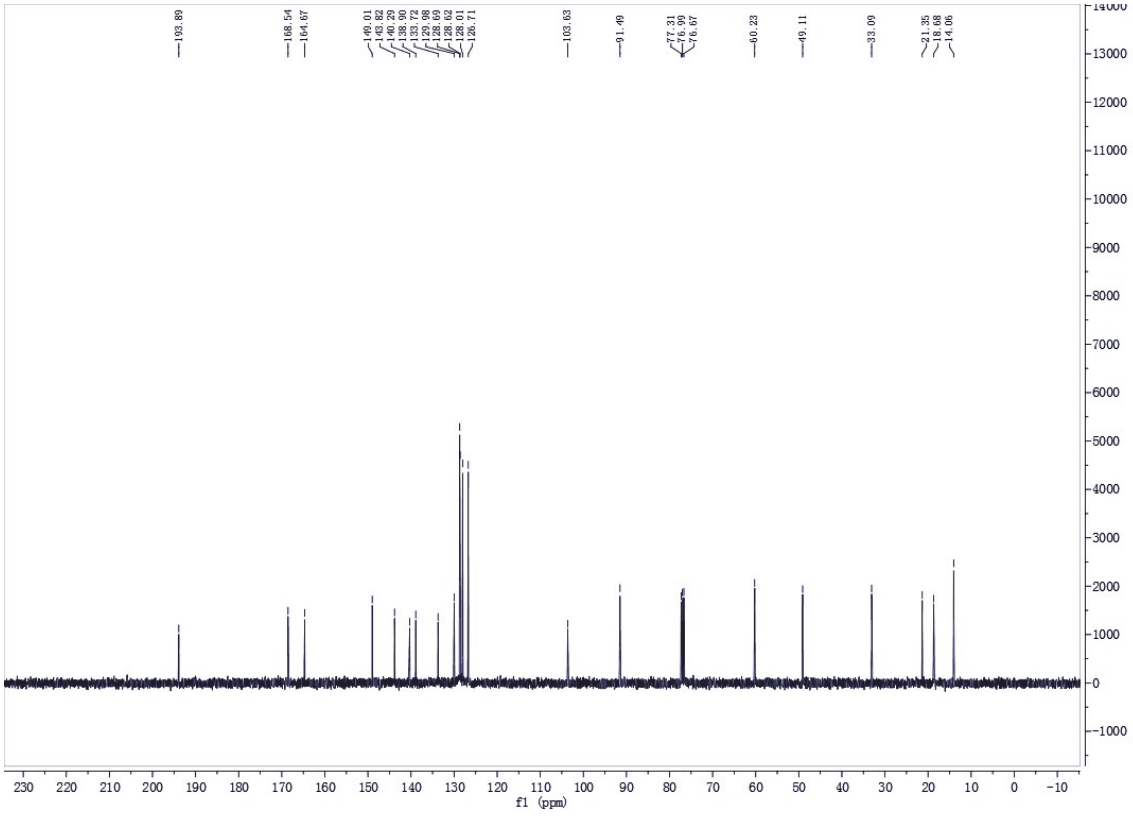
Ethyl 9-benzoyl-2-methyl-4-(4-nitrophenyl)-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6e)



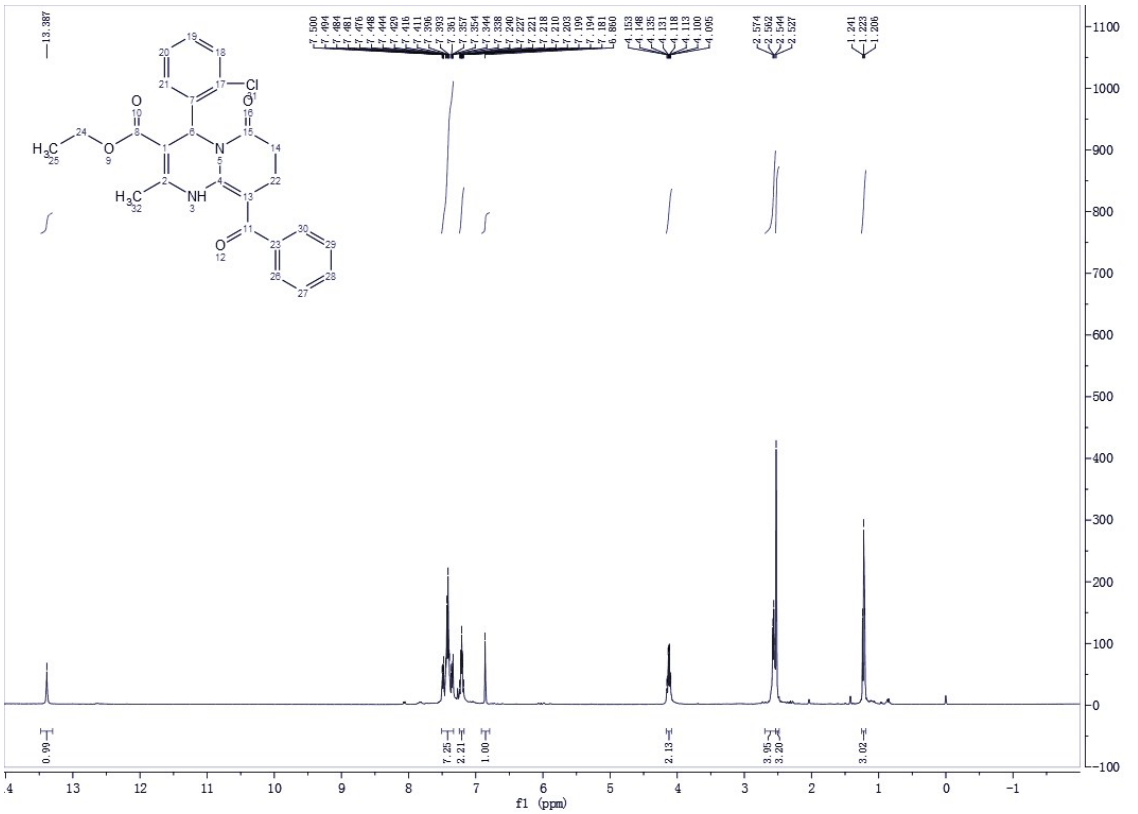


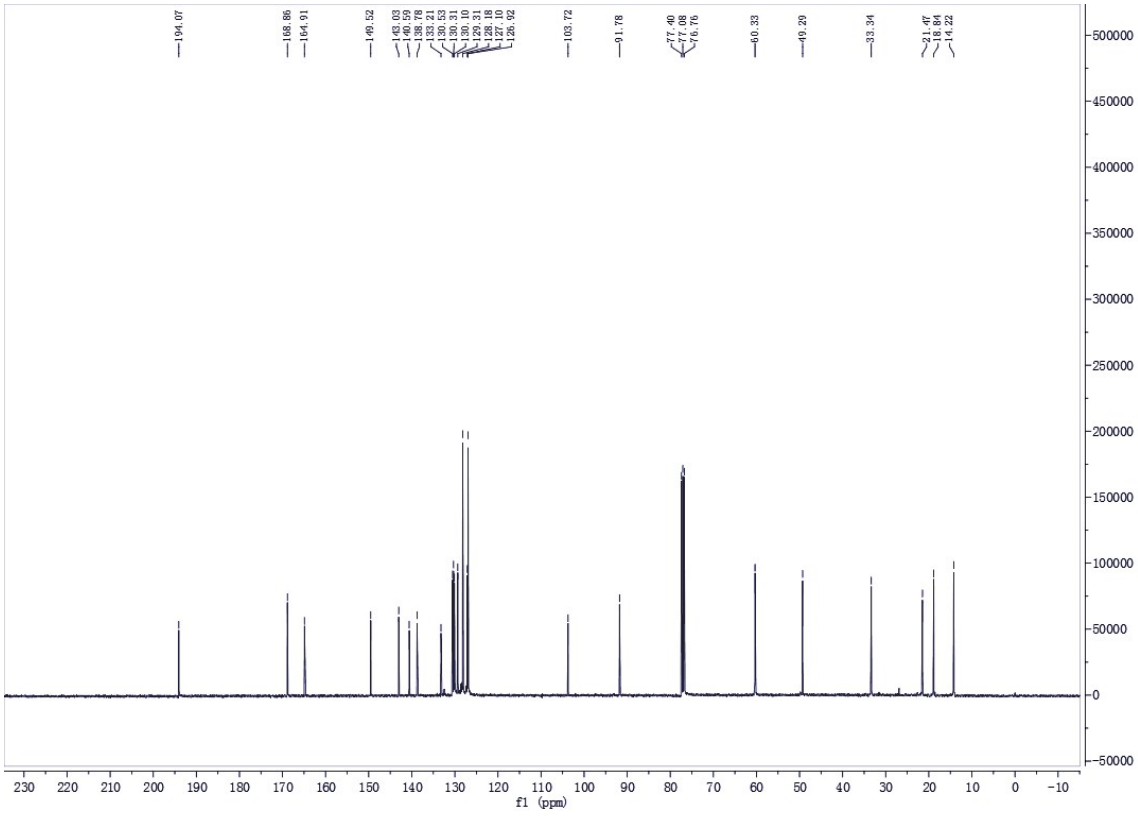
Ethyl 9-benzoyl-4-(4-chlorophenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6f)



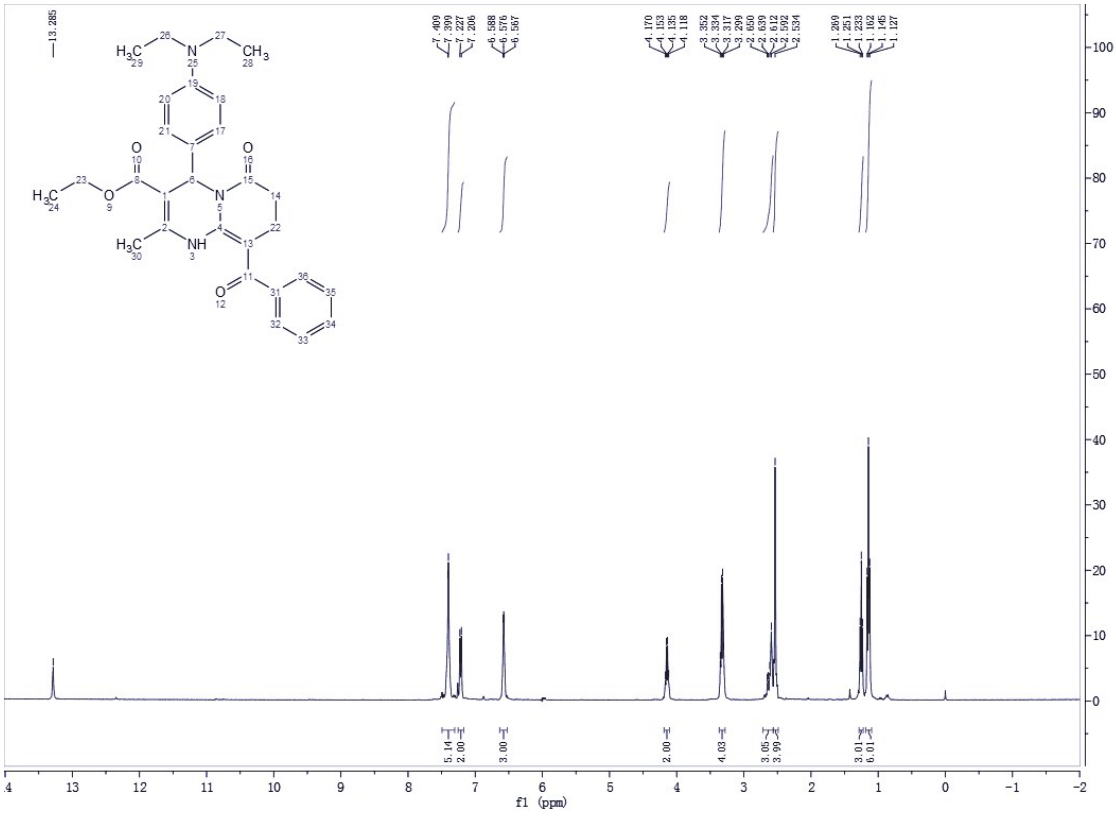


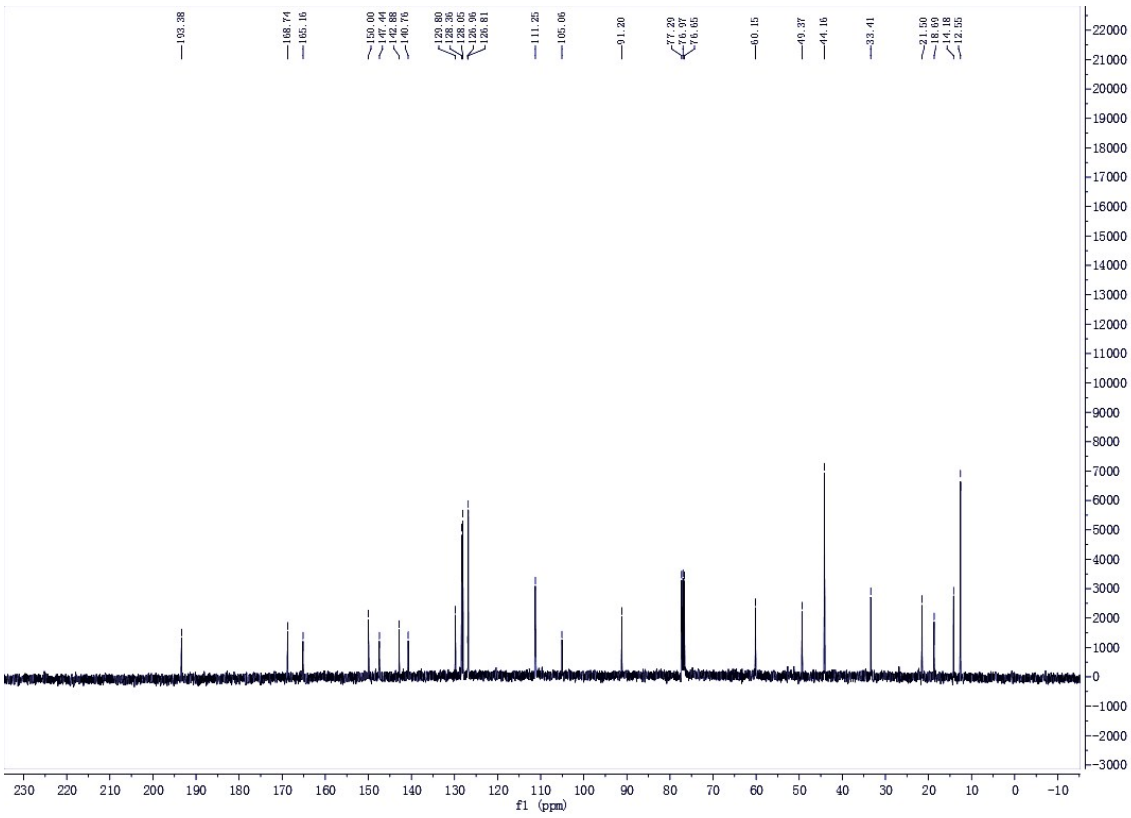
Ethyl 9-benzoyl-4-(2-chlorophenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6g)



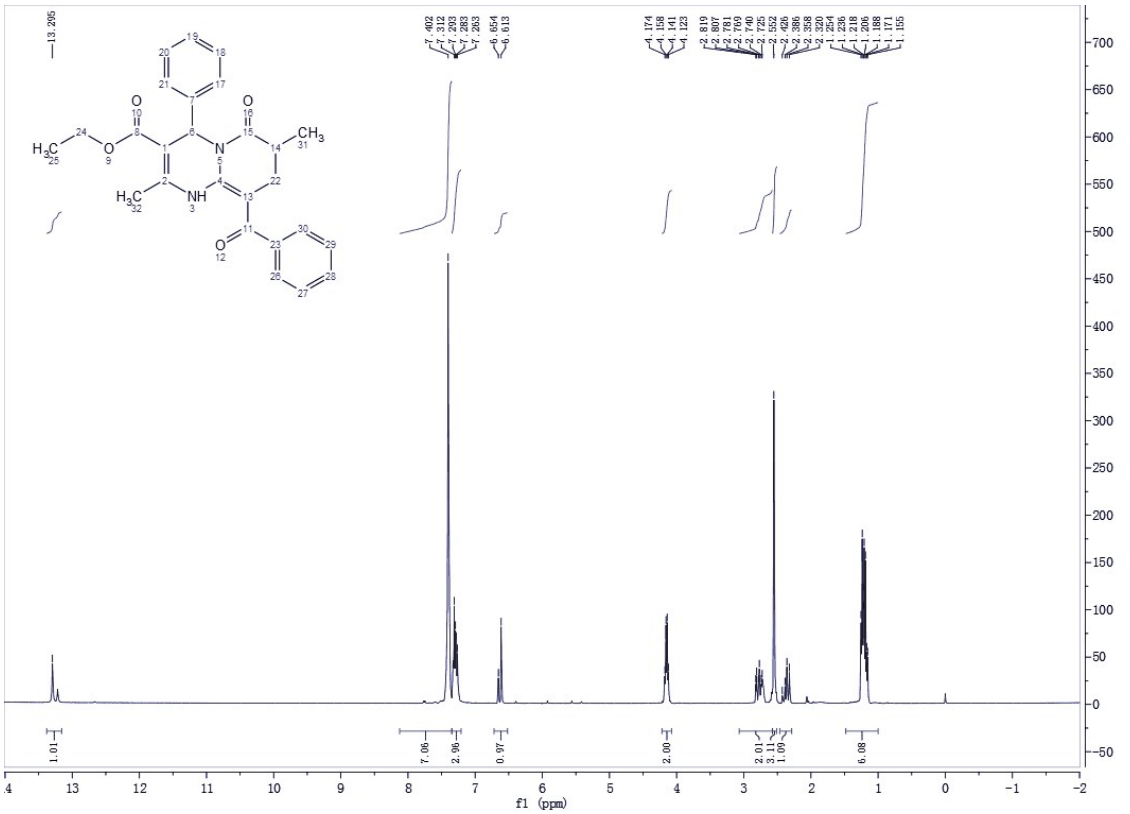


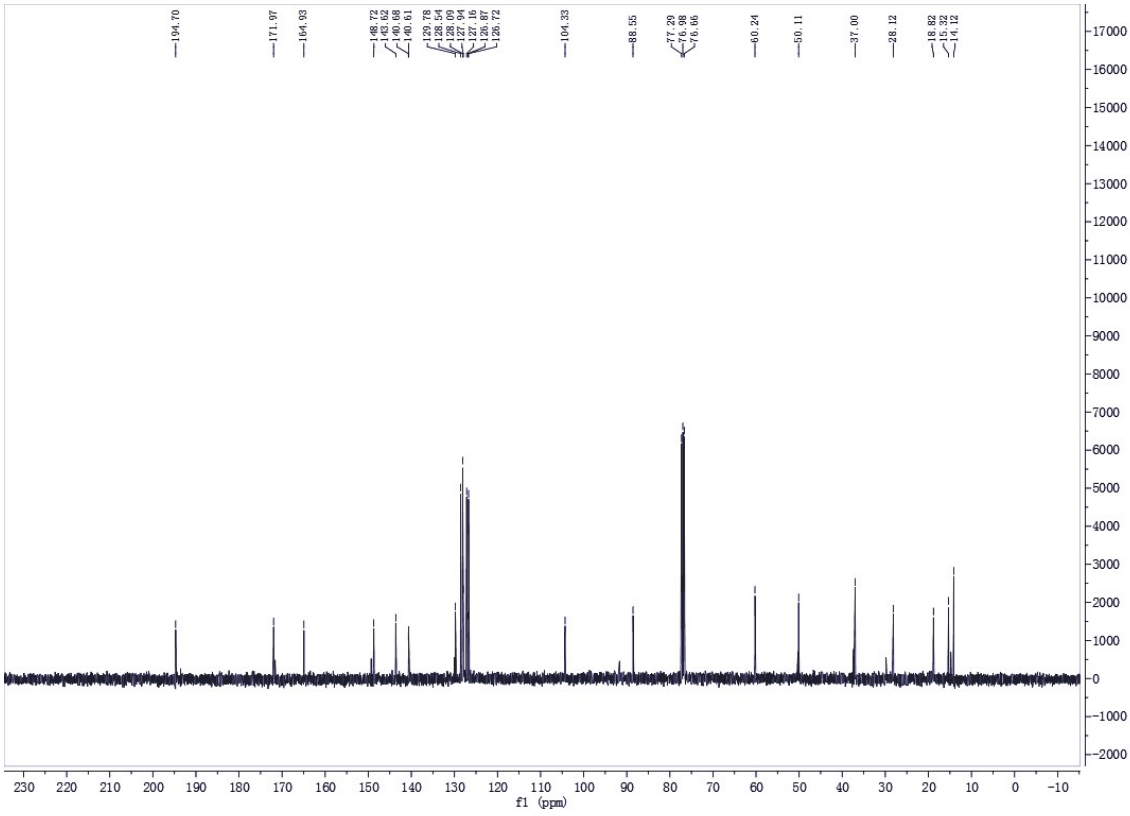
Ethyl 9-benzoyl-4-(4-(diethylamino)phenyl)-2-methyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido [1,2-a]pyrimidine-3-carboxylate (6h)



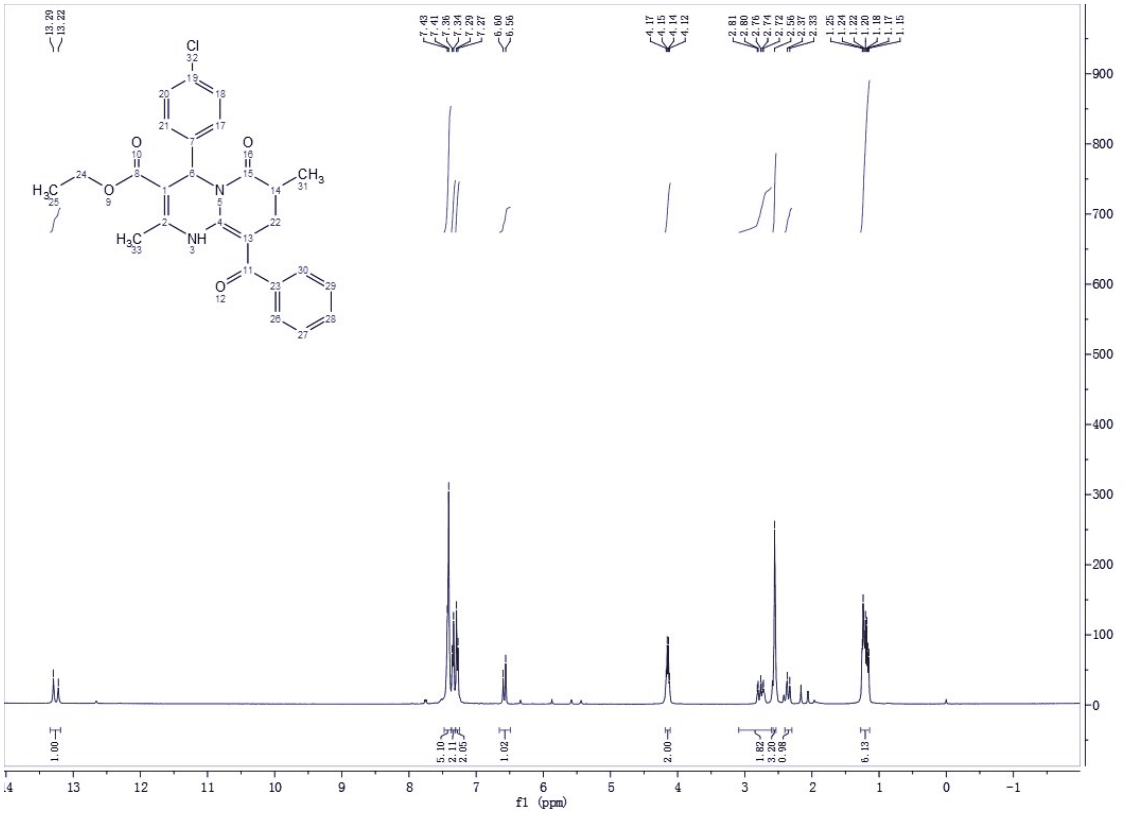


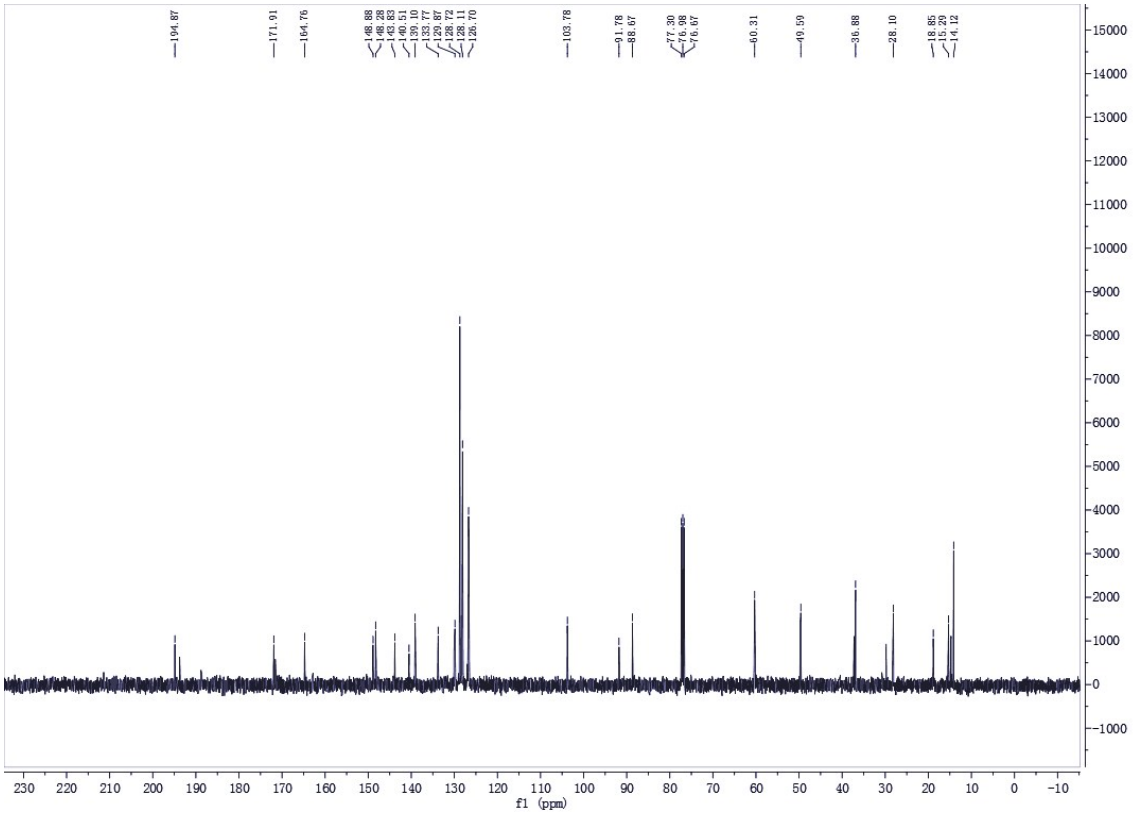
Ethyl 9-benzoyl-2,7-dimethyl-6-oxo-4-phenyl-4,6,7,8-tetrahydro-1H-pyrido[1,2-a] pyrimidine-3-carboxylate (6i)



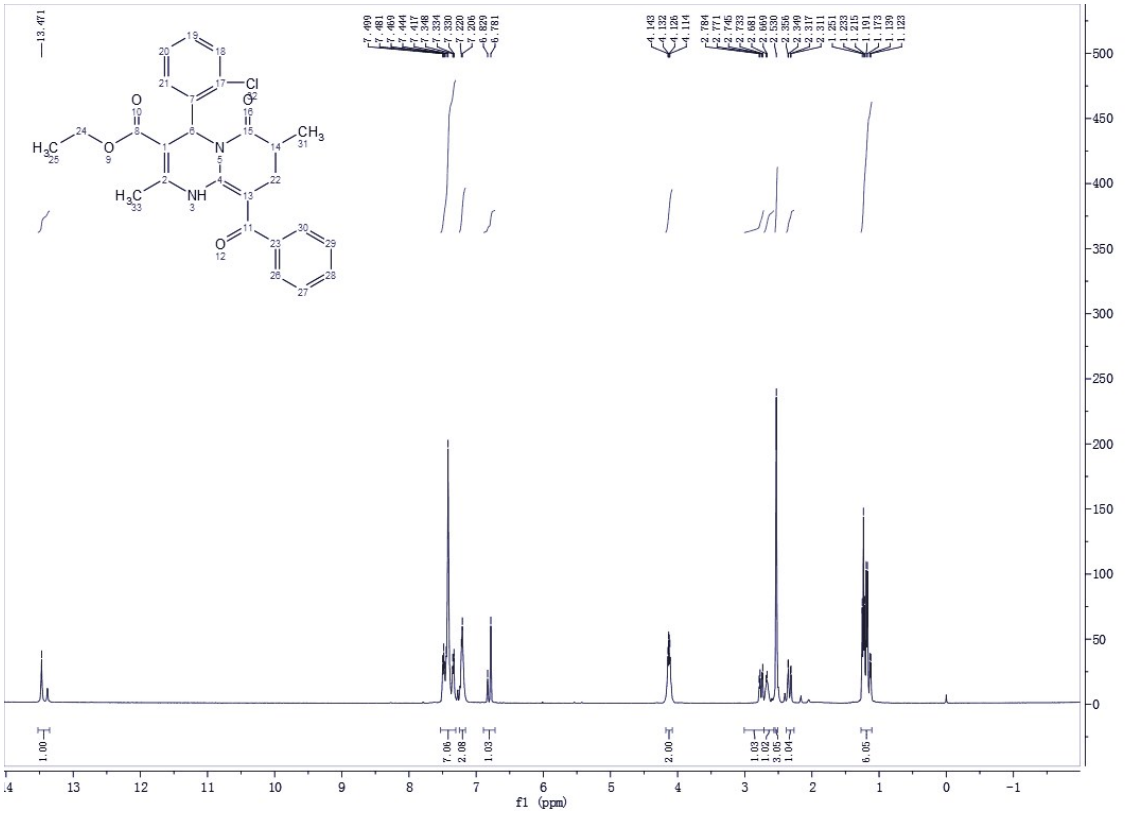


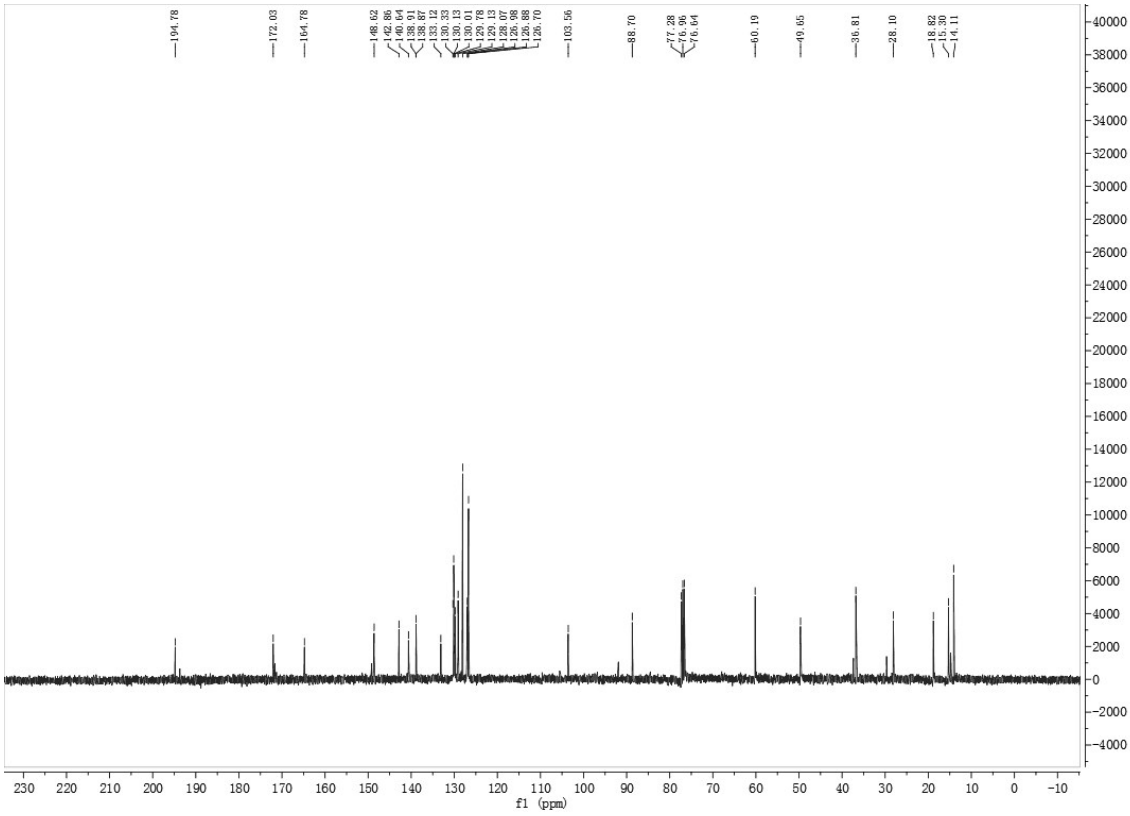
Ethyl 9-benzoyl-4-(4-chlorophenyl)-2,7-dimethyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido [1,2-a]pyrimidine-3-carboxylate (6j)



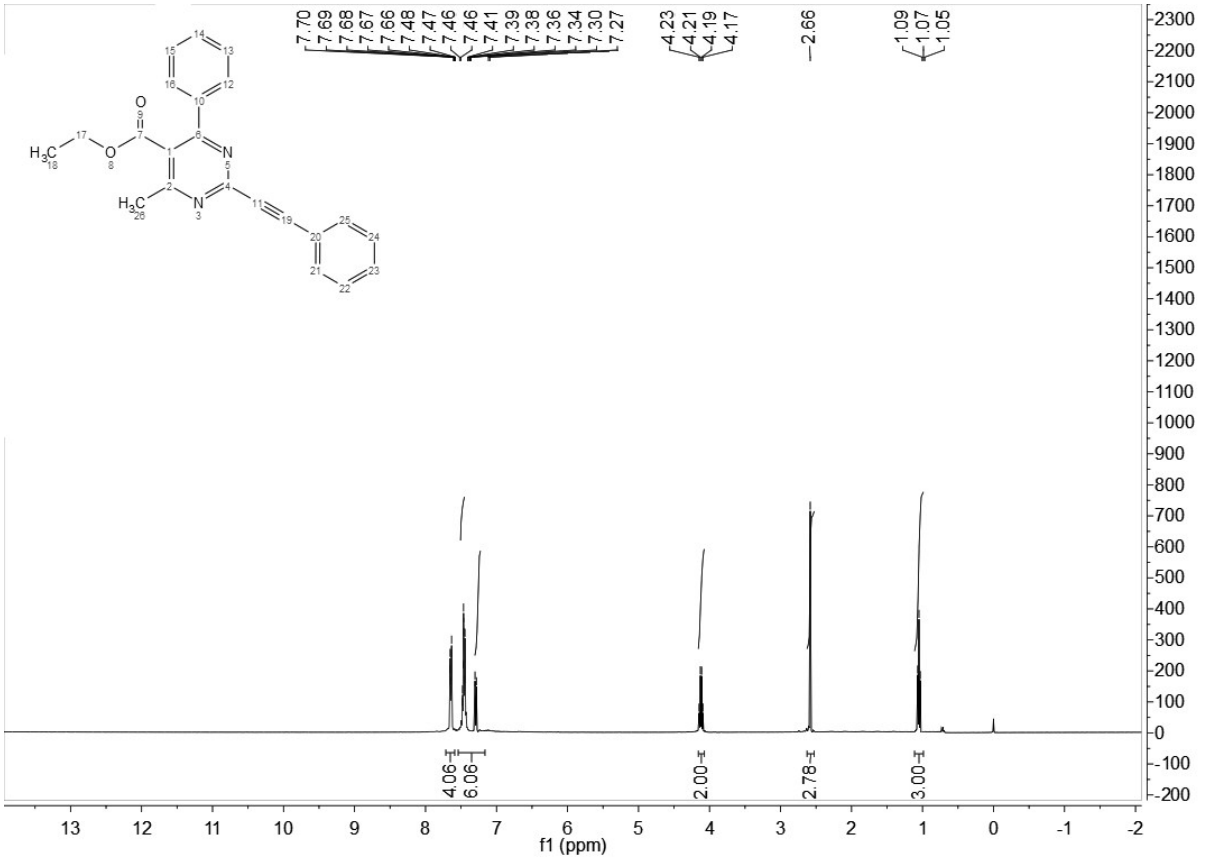


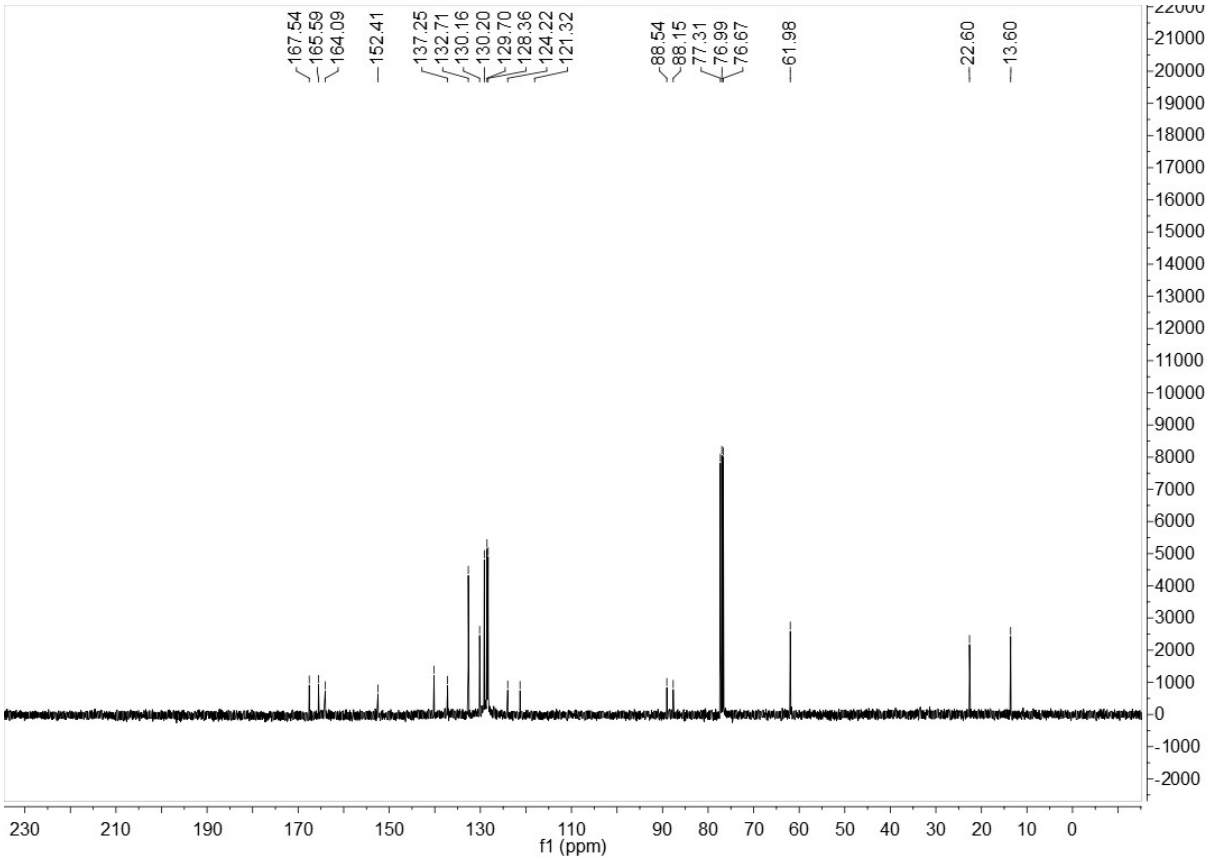
Ethyl 9-benzoyl-4-(2-chlorophenyl)-2,7-dimethyl-6-oxo-4,6,7,8-tetrahydro-1H-pyrido [1,2-a]pyrimidine-3-carboxylate (6k)



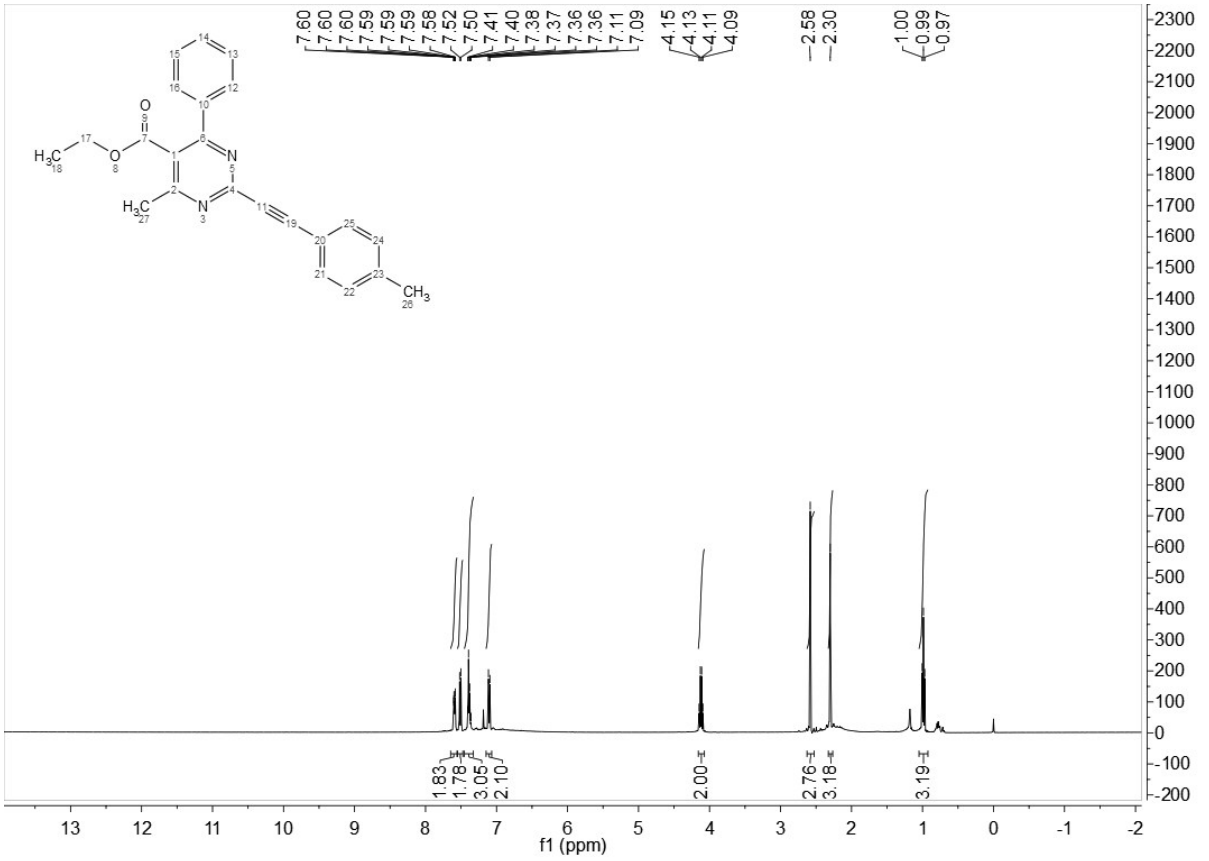


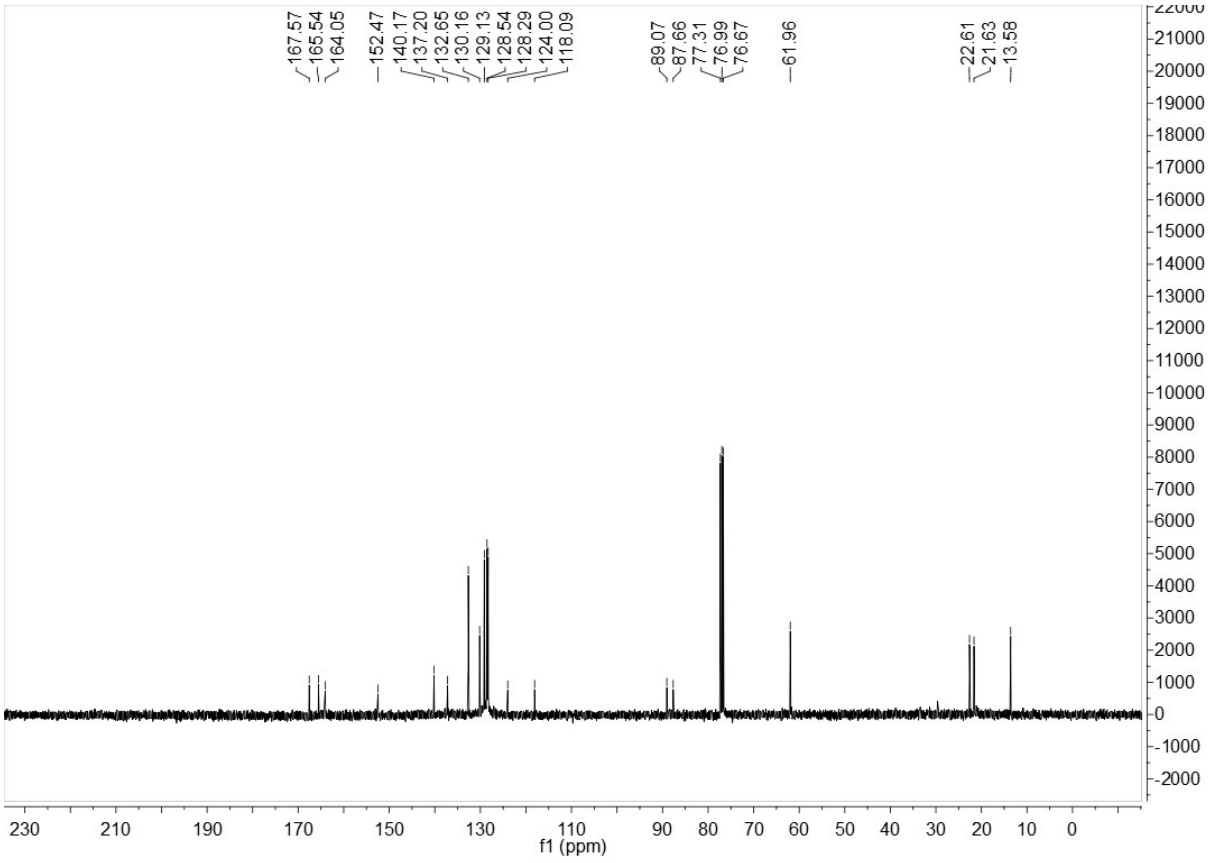
Ethyl 4-methyl-6-phenyl-2-(phenylethynyl)pyrimidine-5-carboxylate (8a)



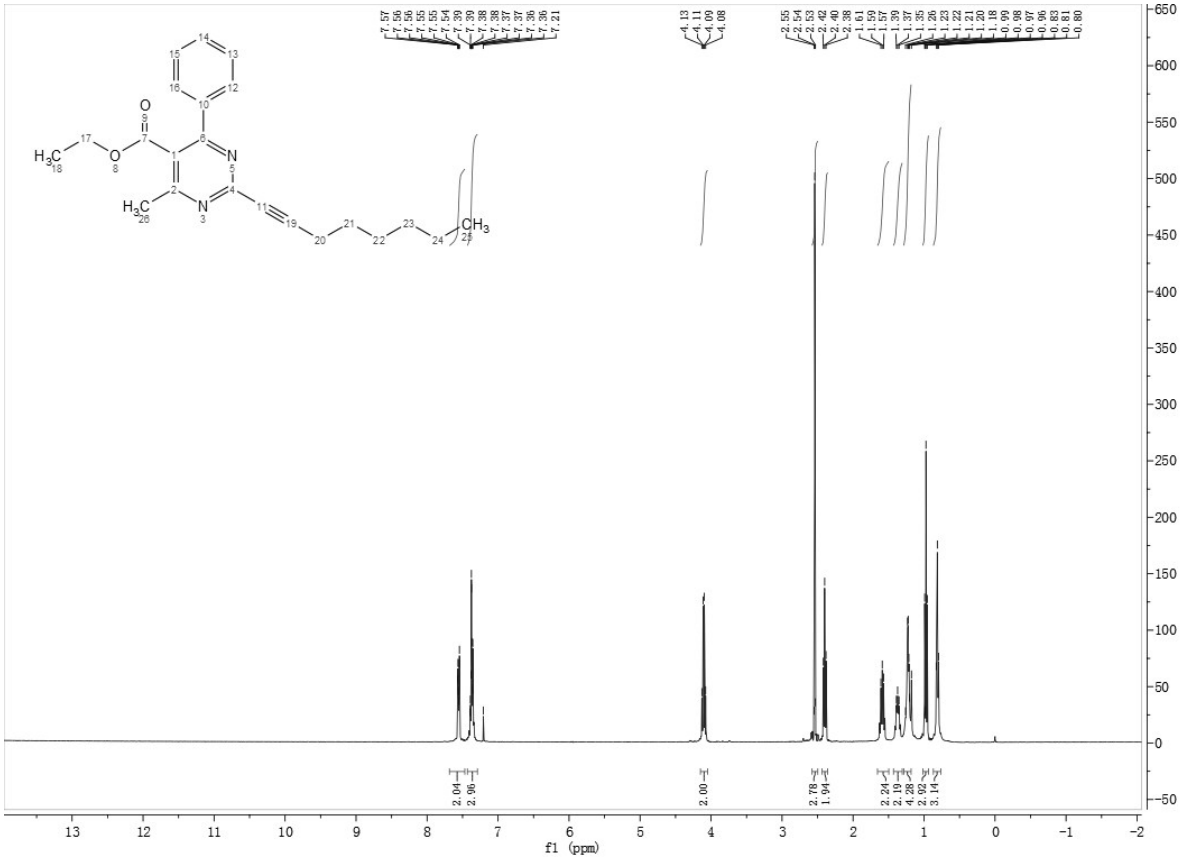


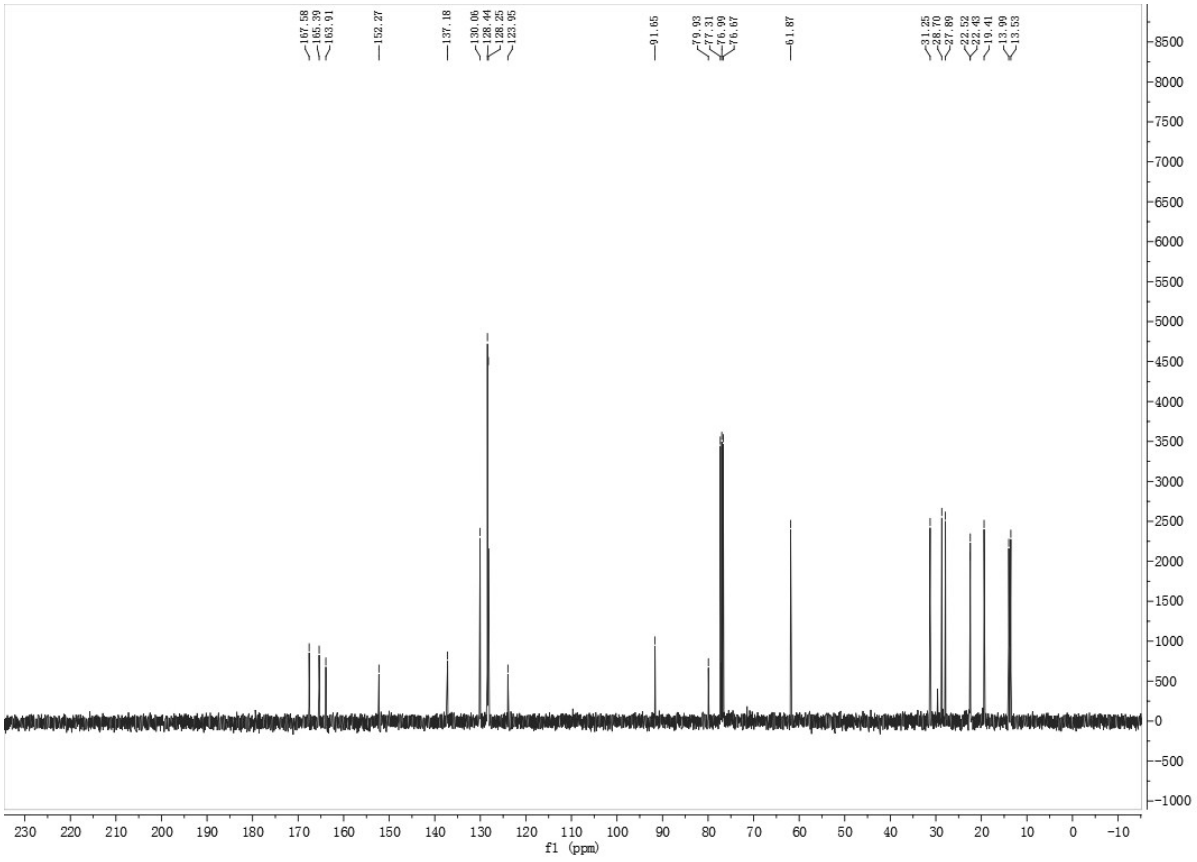
Ethyl 4-Methyl-6-phenyl-2-(p-tolylethynyl)pyrimidine-5-carboxylate (8b)



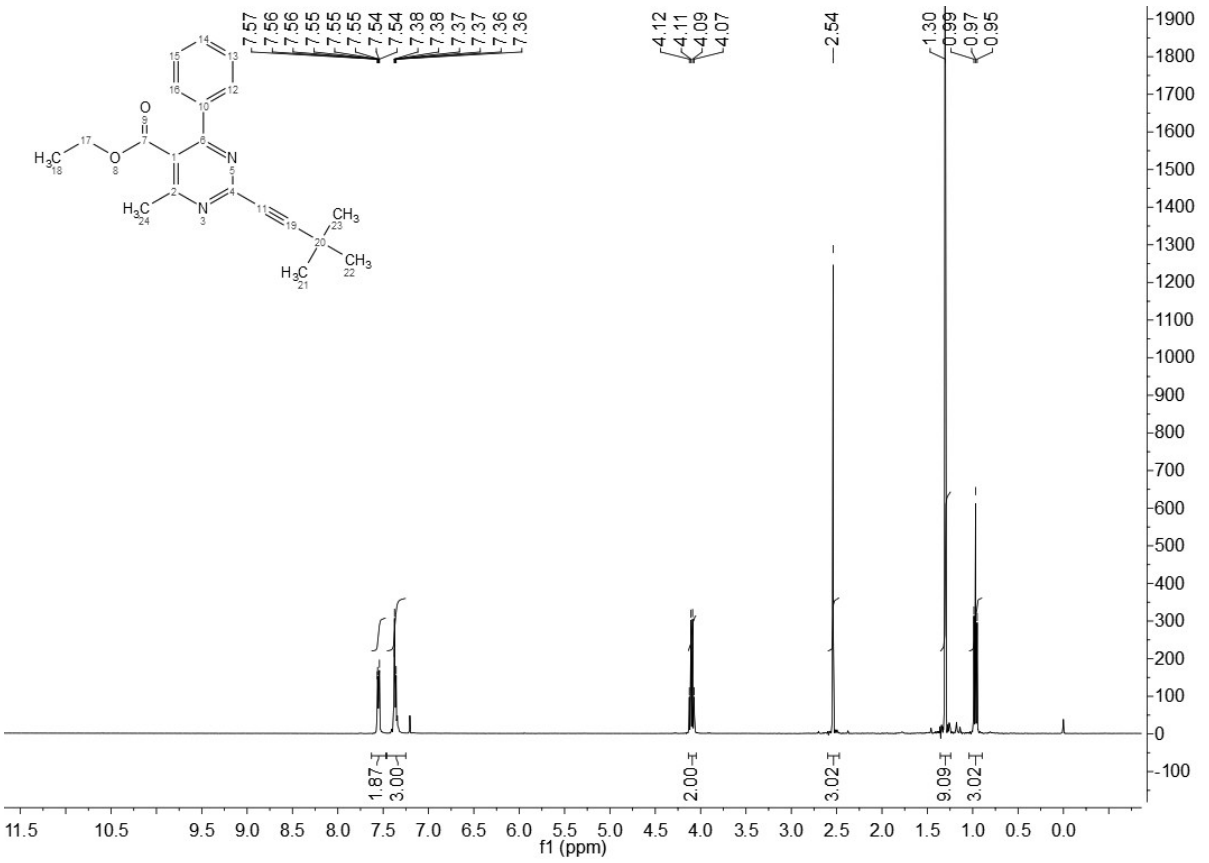


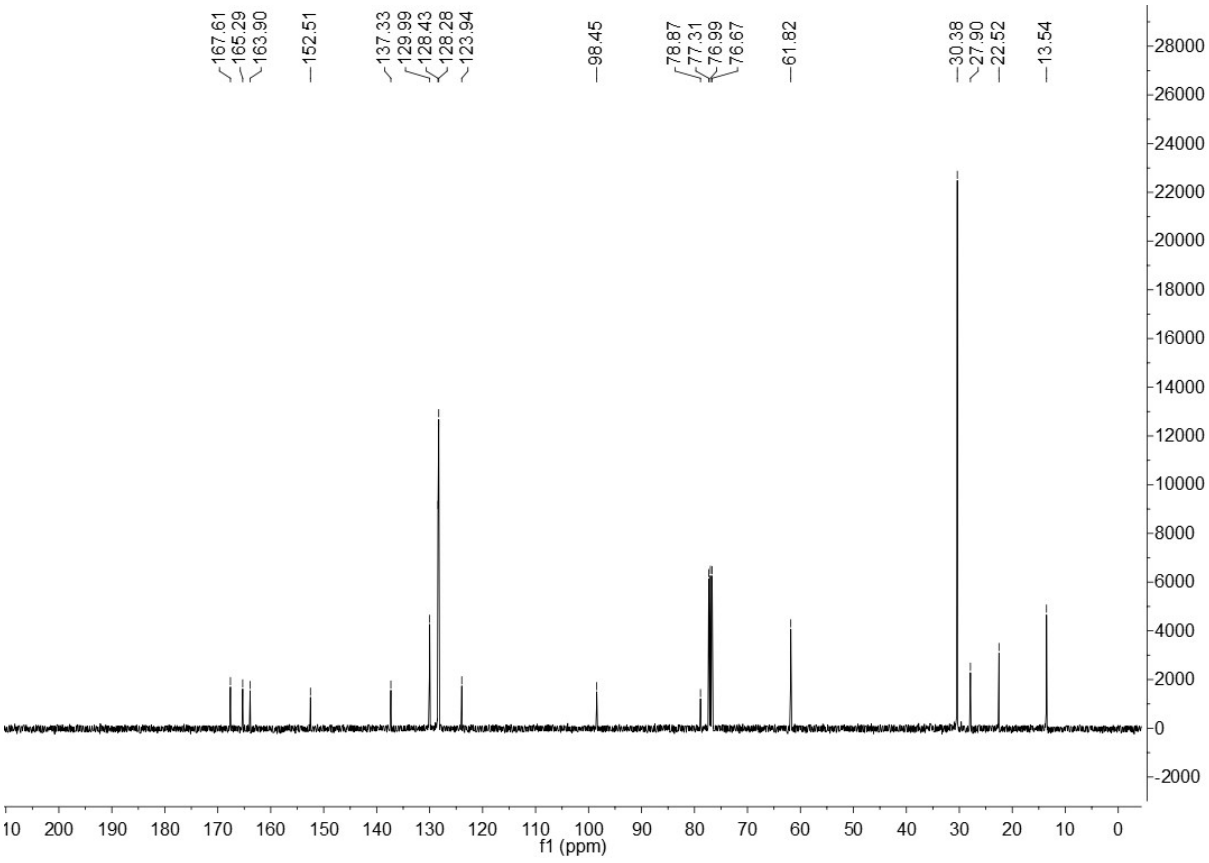
Ethyl 4-Methyl-2-(oct-1-ynyl)-6-phenylpyrimidine-5-carboxylate (8c)



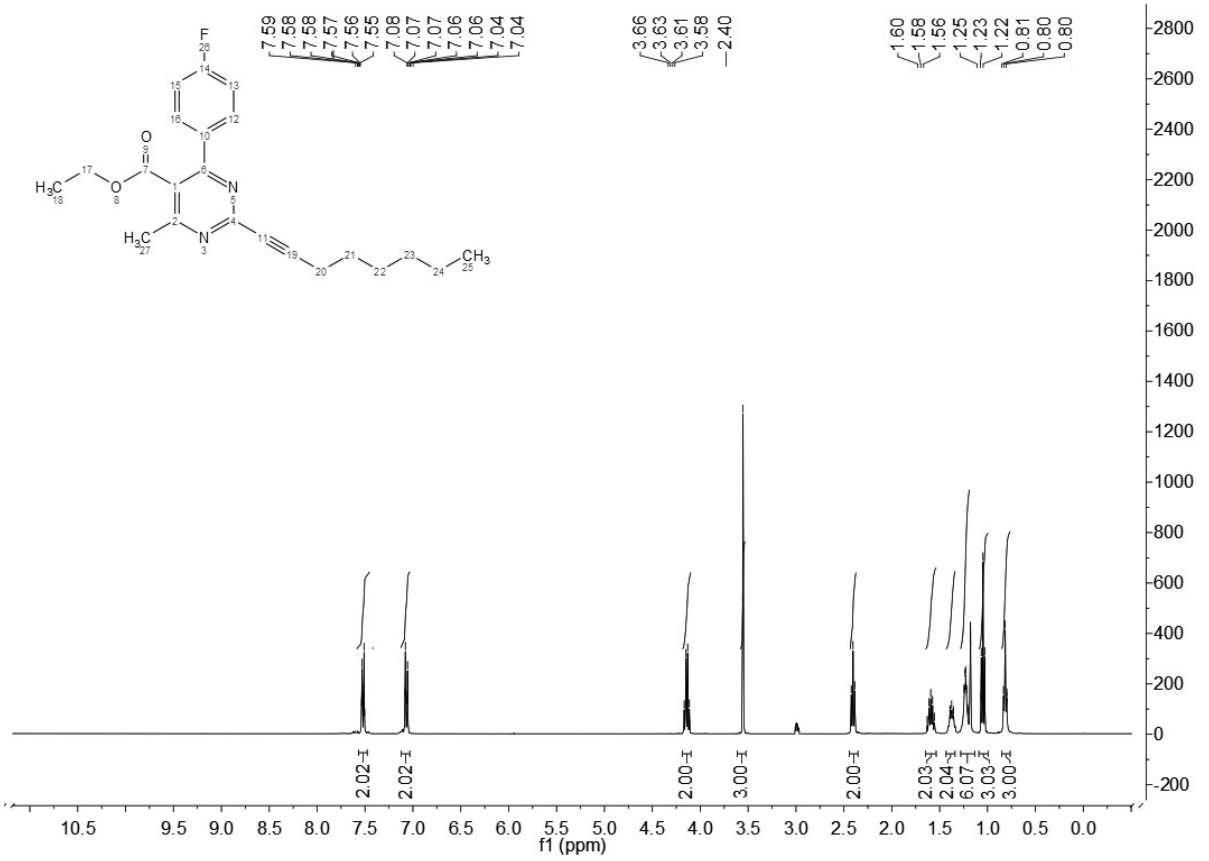


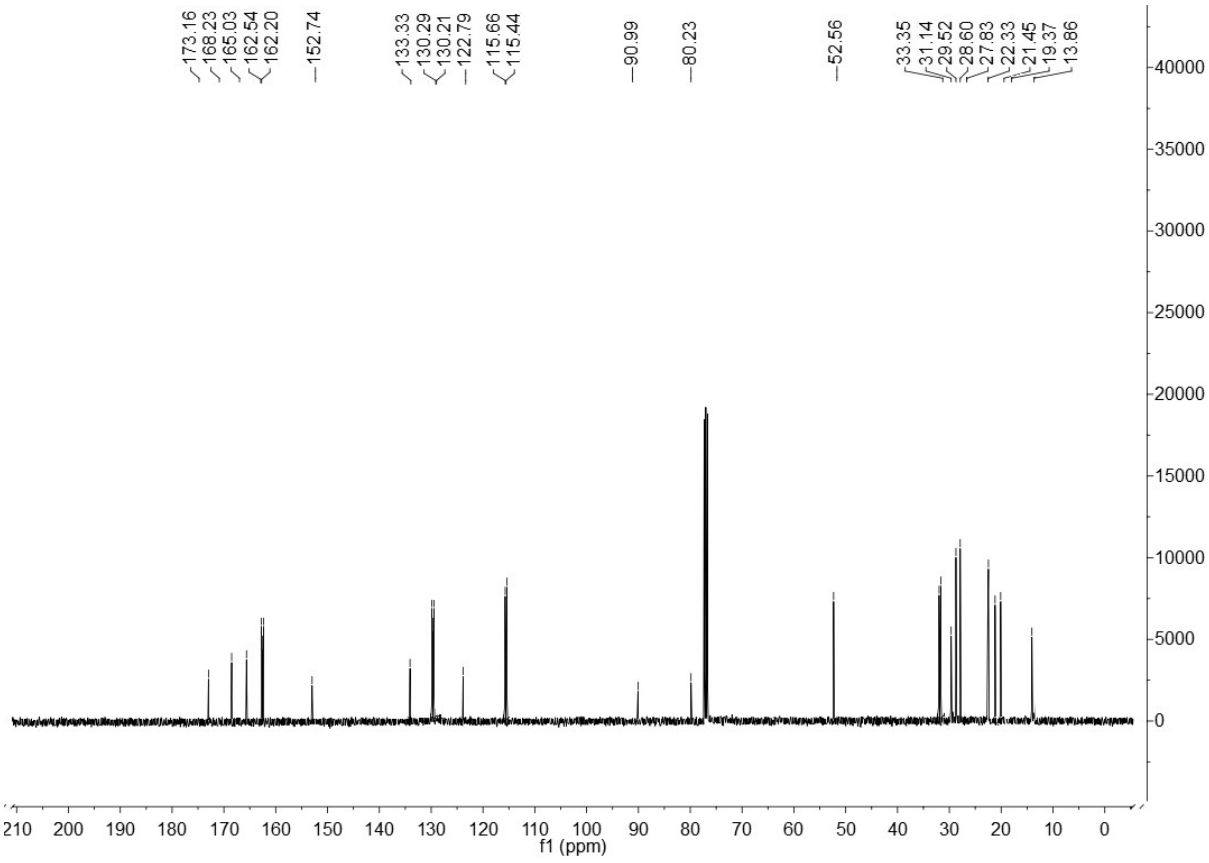
Ethyl 2-(3,3-Dimethylbut-1-ynyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (8d)



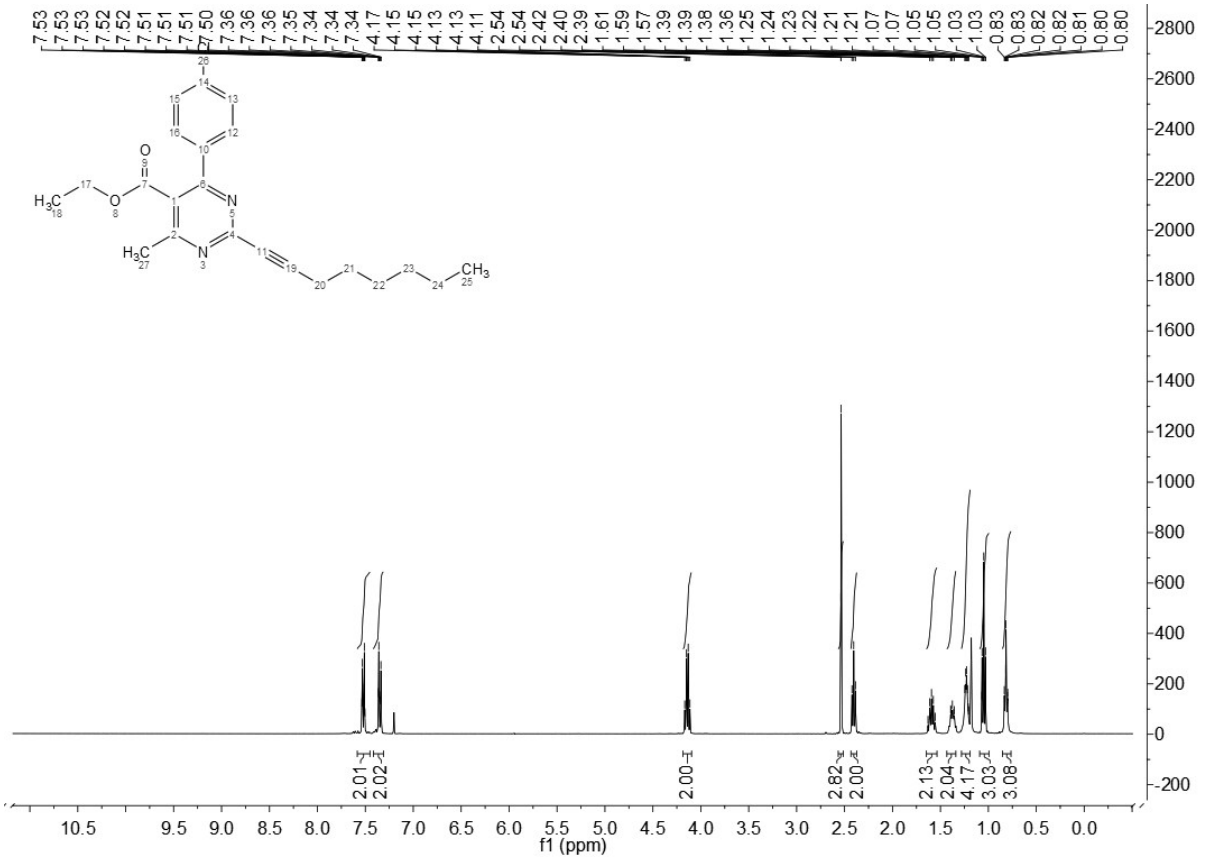


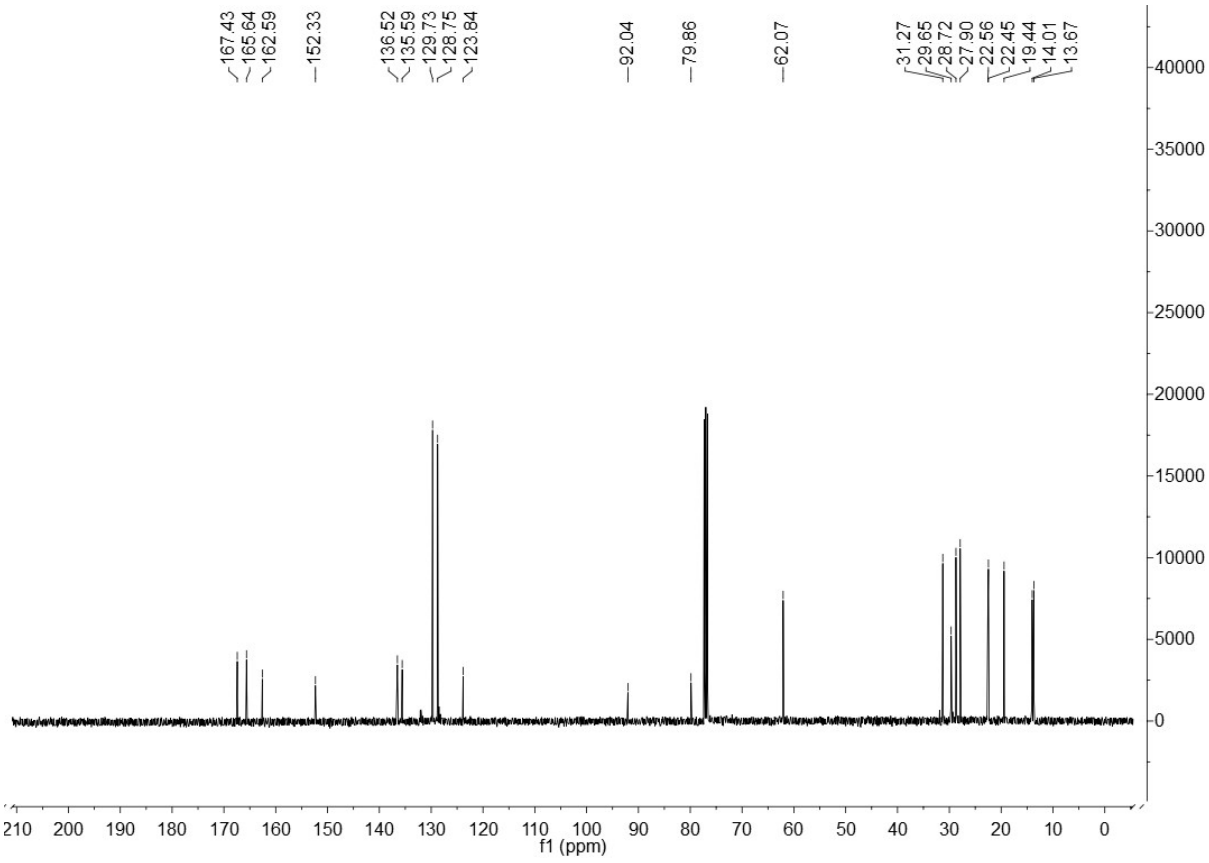
Ethyl 4-(4-Fluorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (8e)



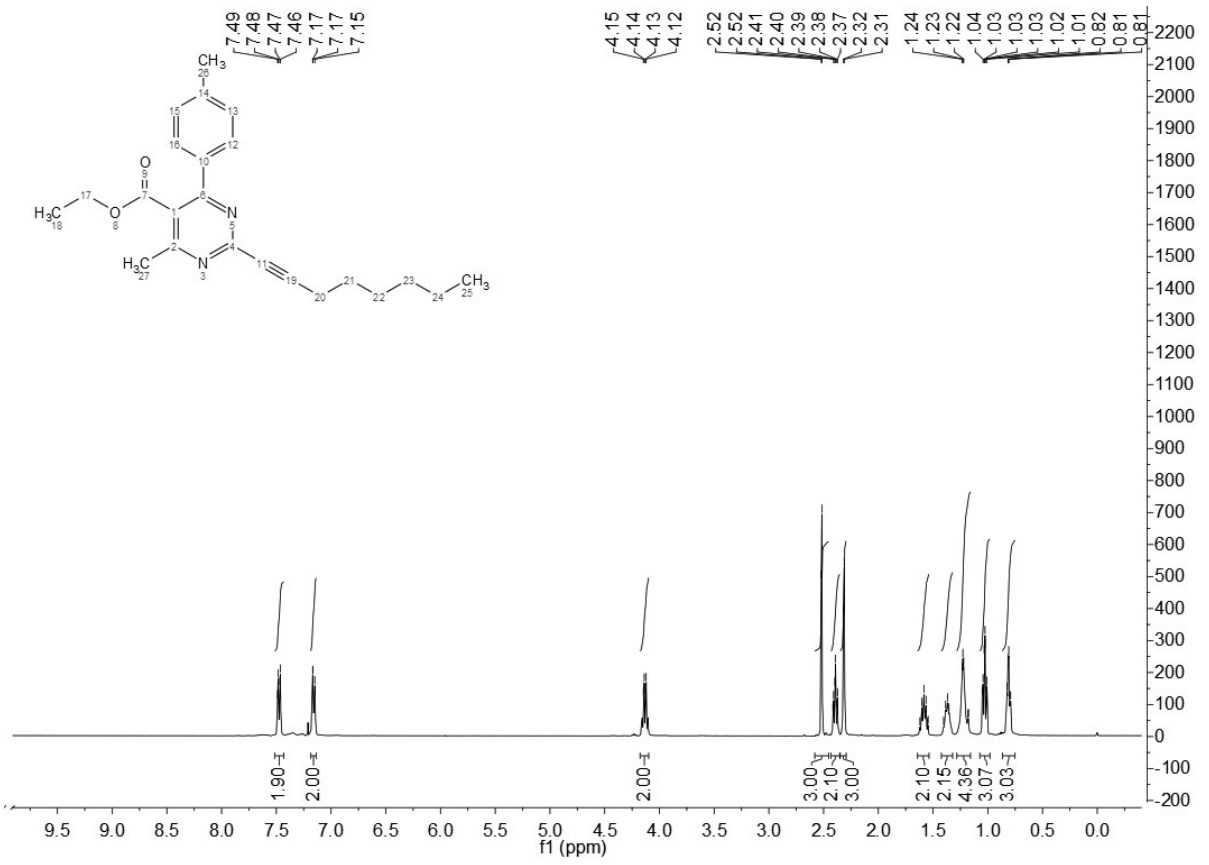


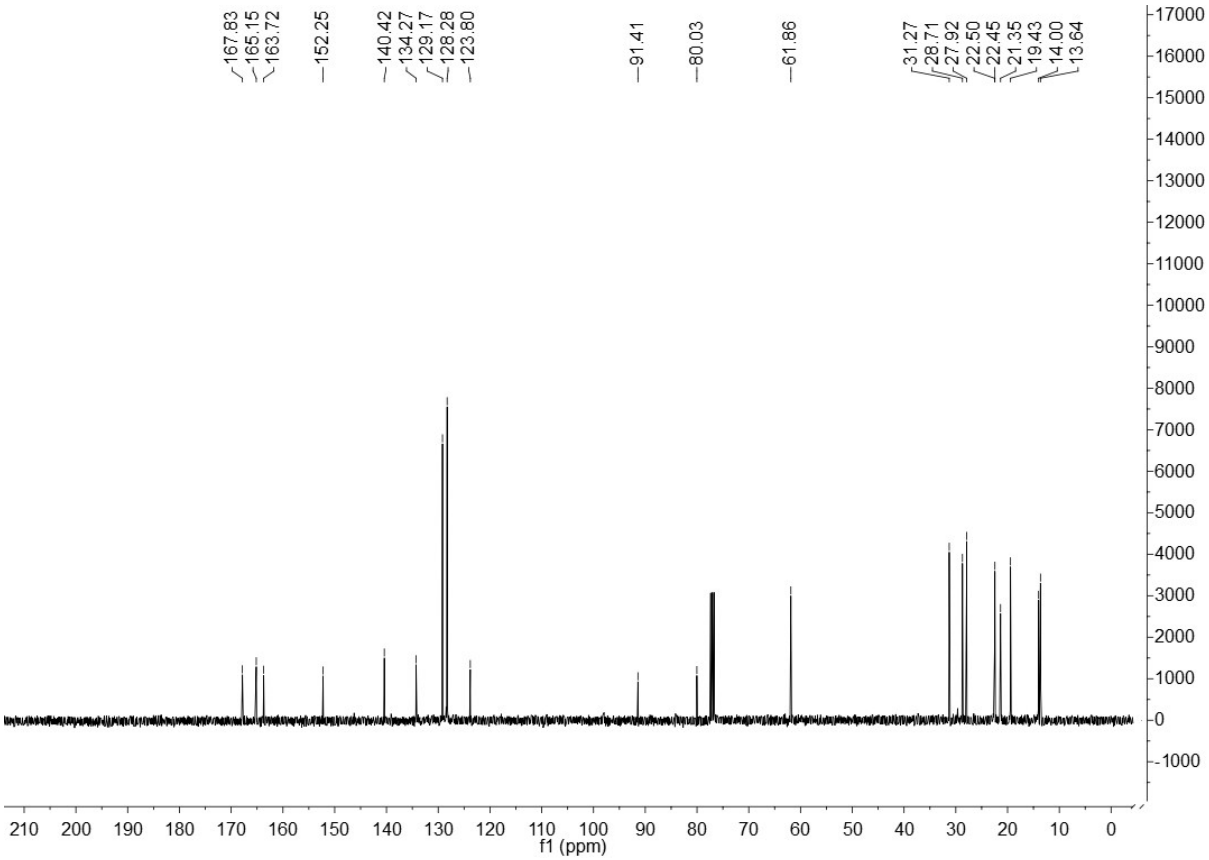
Ethyl 4-(4-Chlorophenyl)-6-methyl-2-(oct-1-ynyl)pyrimidine-5-carboxylate (8f)



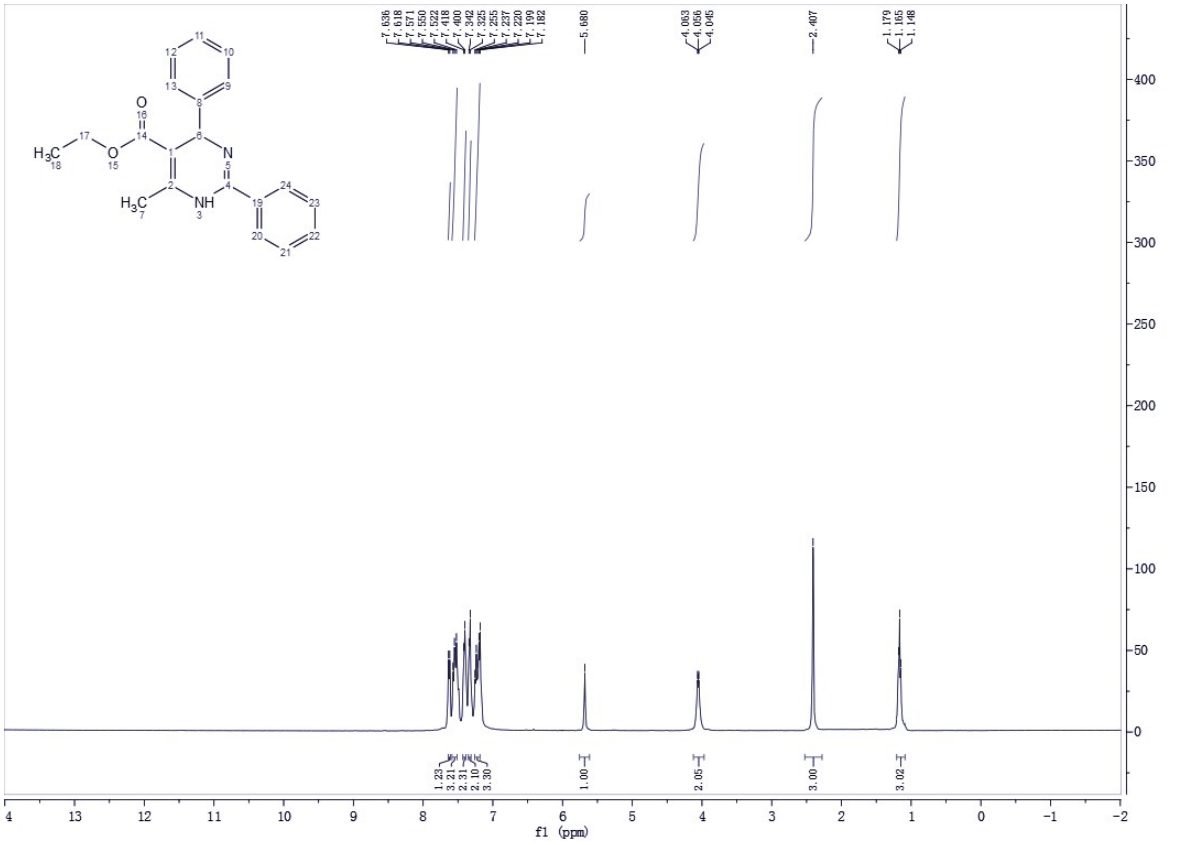


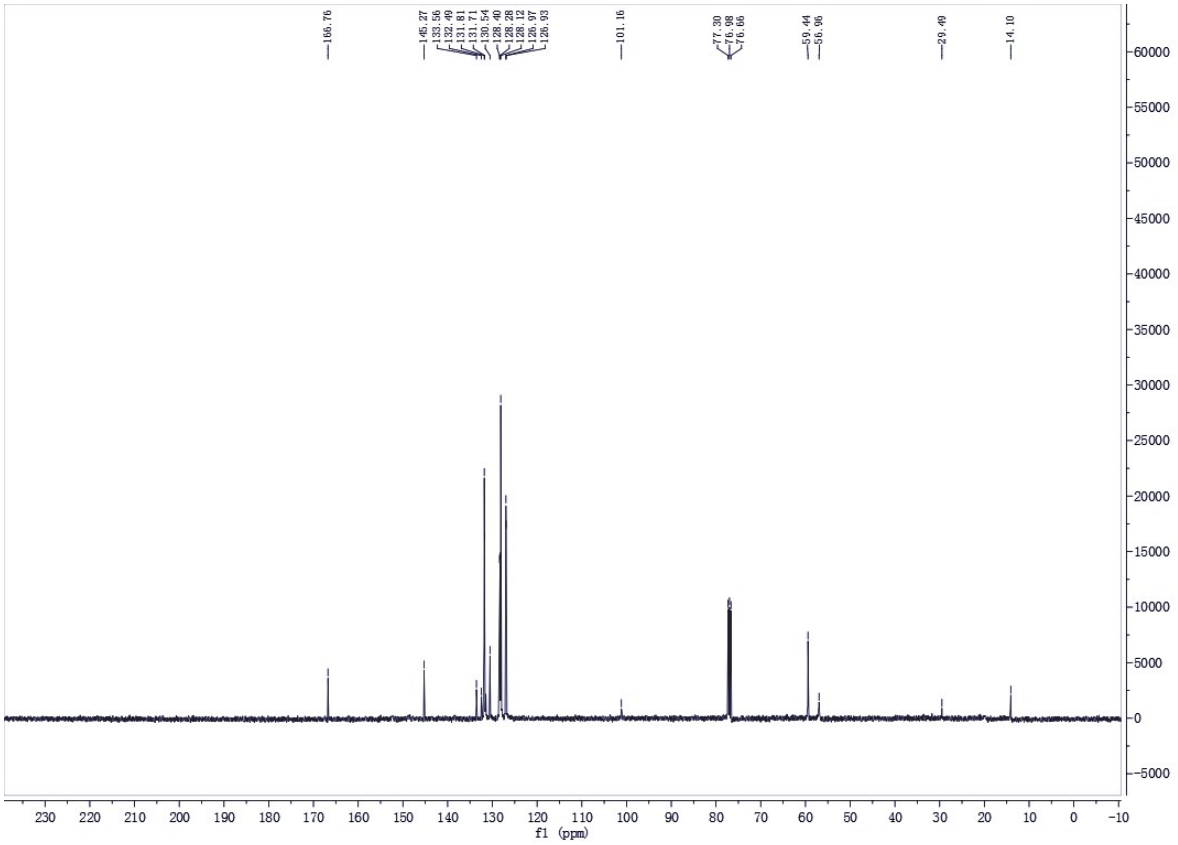
Ethyl 4-Methyl-2-(oct-1-ynyl)-6-p-tolylpyrimidine-5-carboxylate (8g)



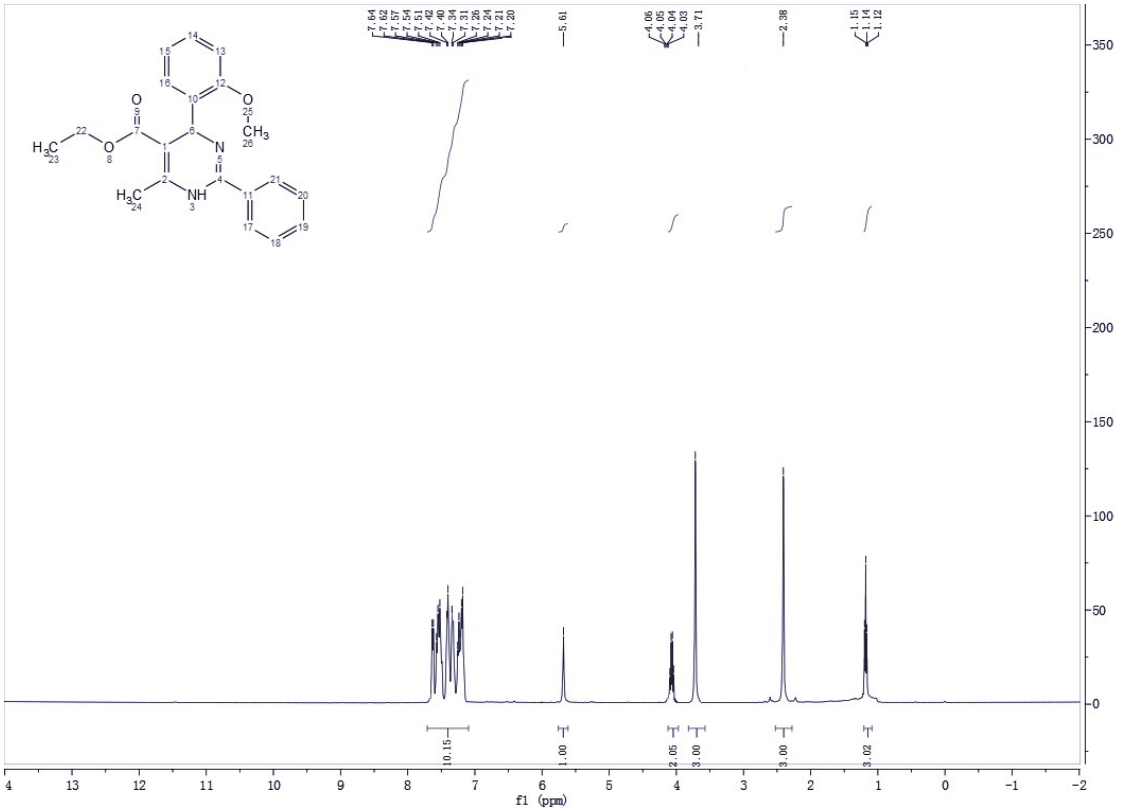


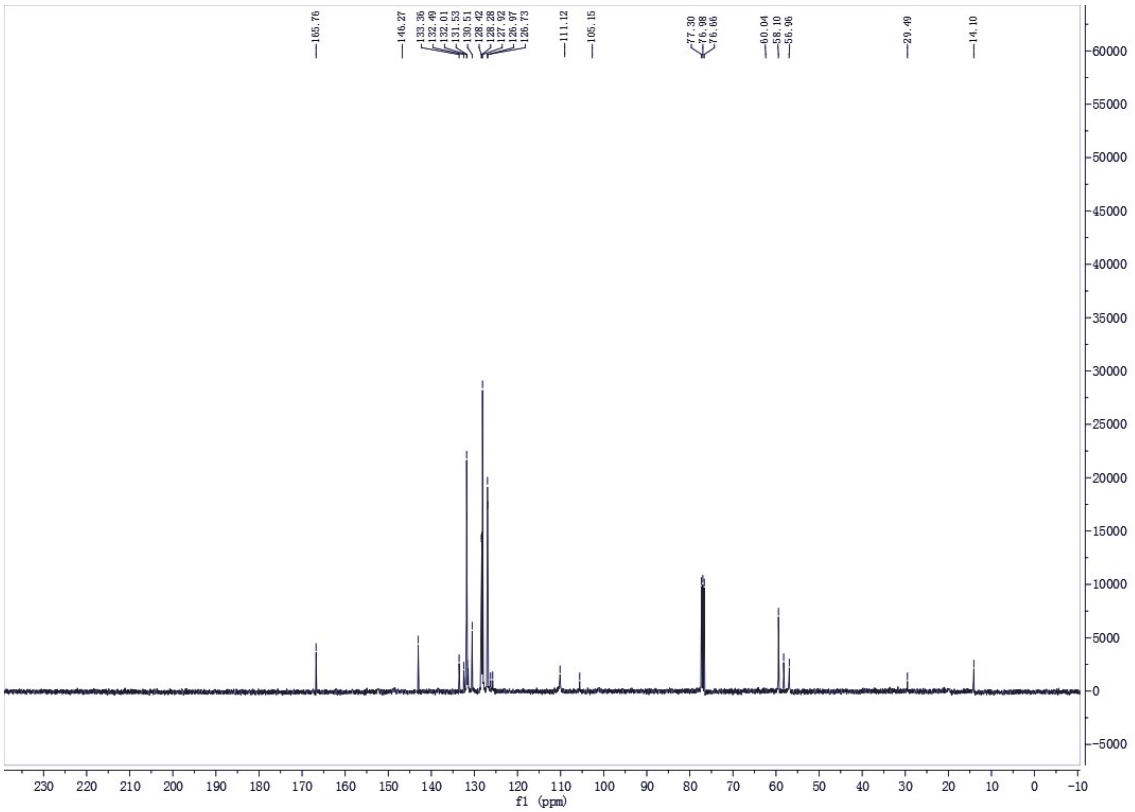
Ethyl 6-methyl-2,4-diphenyl-1,4-dihydropyrimidine-5-carboxylate (10a)



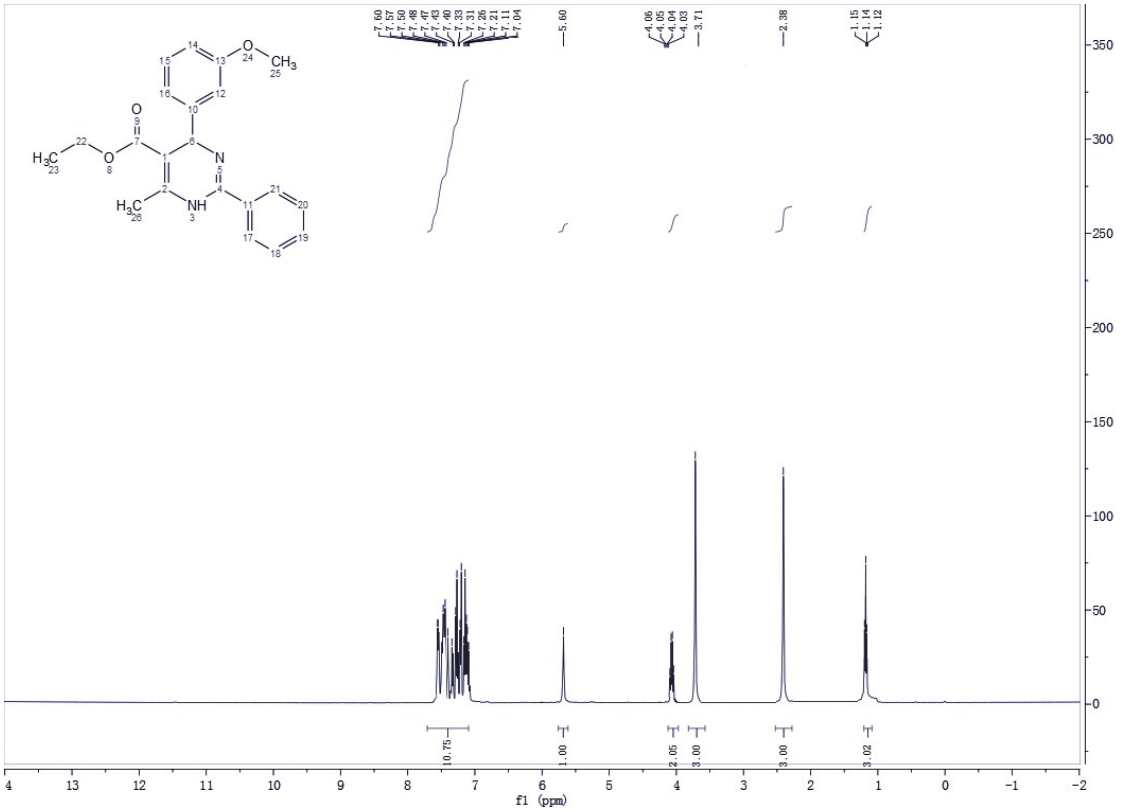


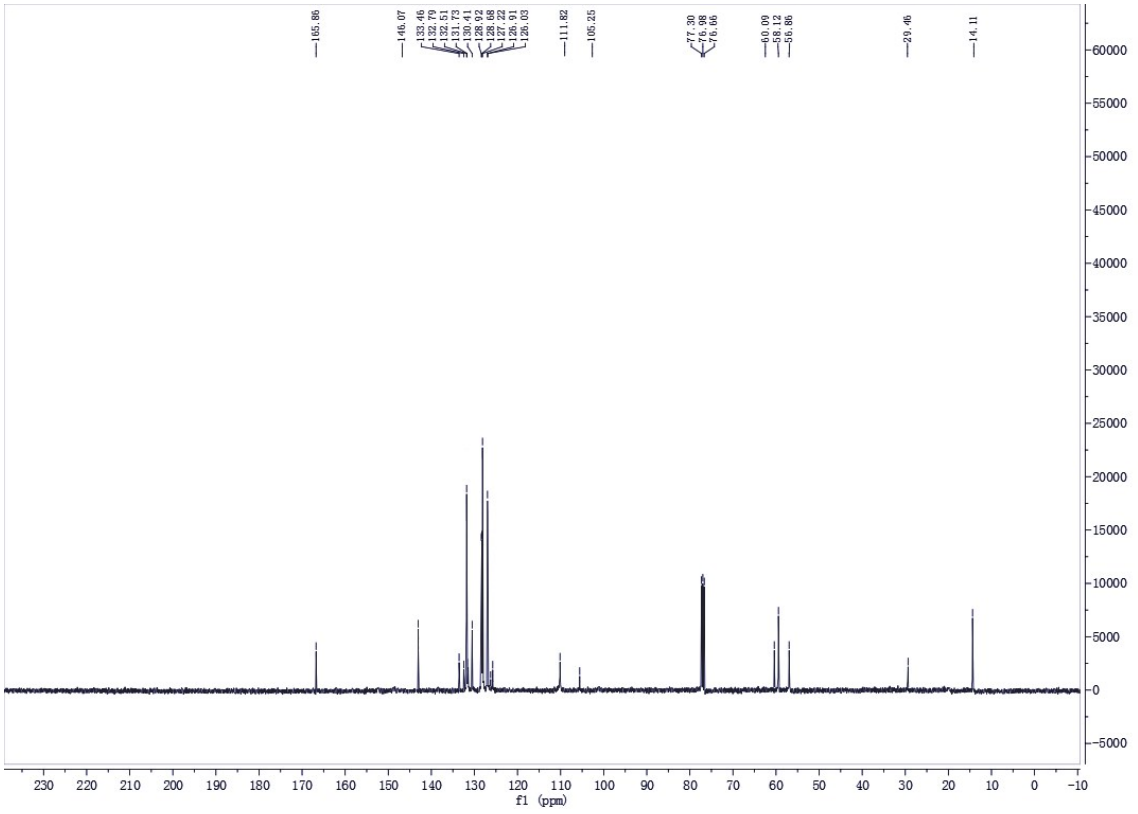
Ethyl 4-(2-methoxyphenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10b)



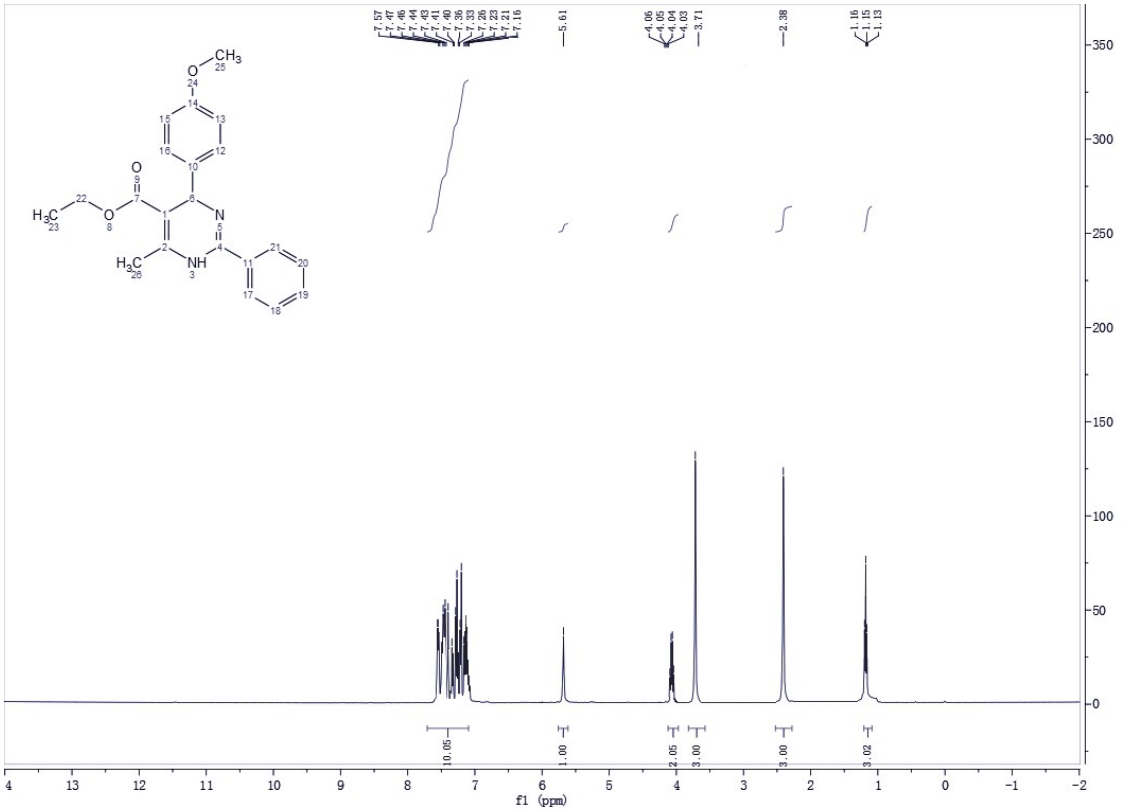


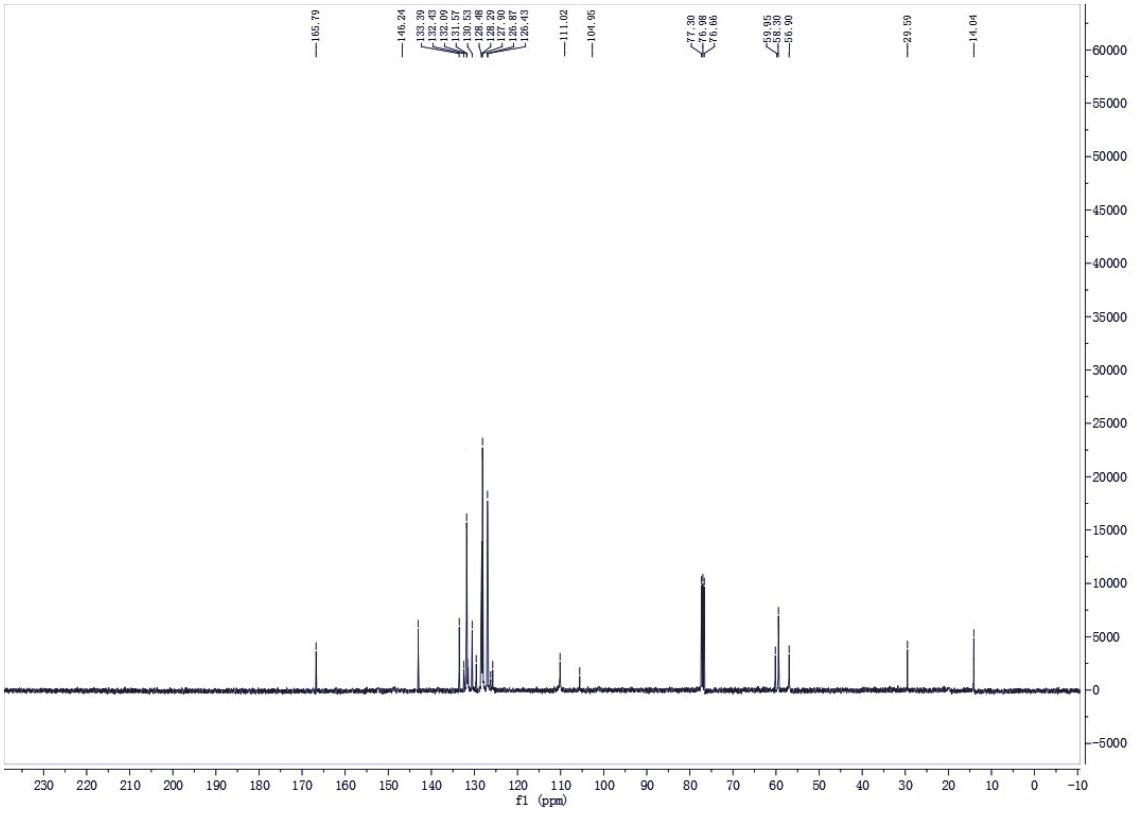
Ethyl 4-(3-methoxyphenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10c)



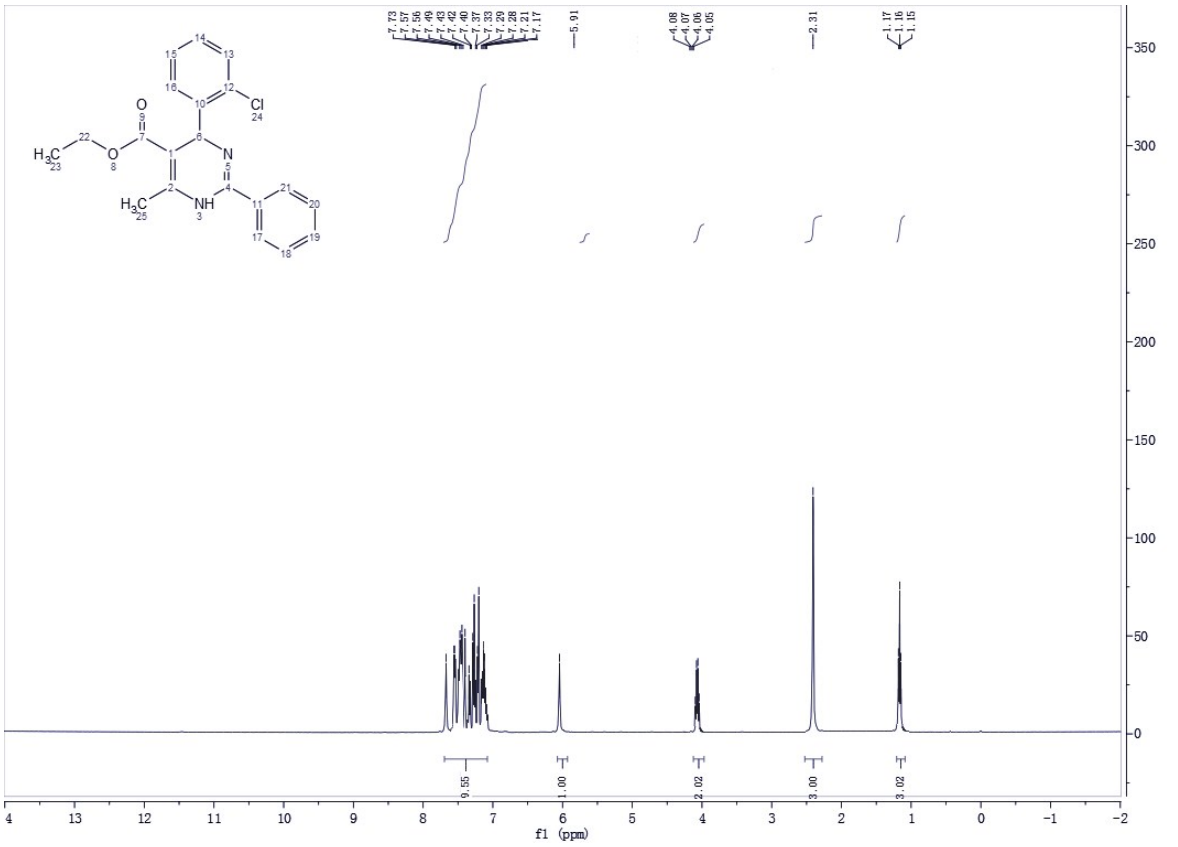


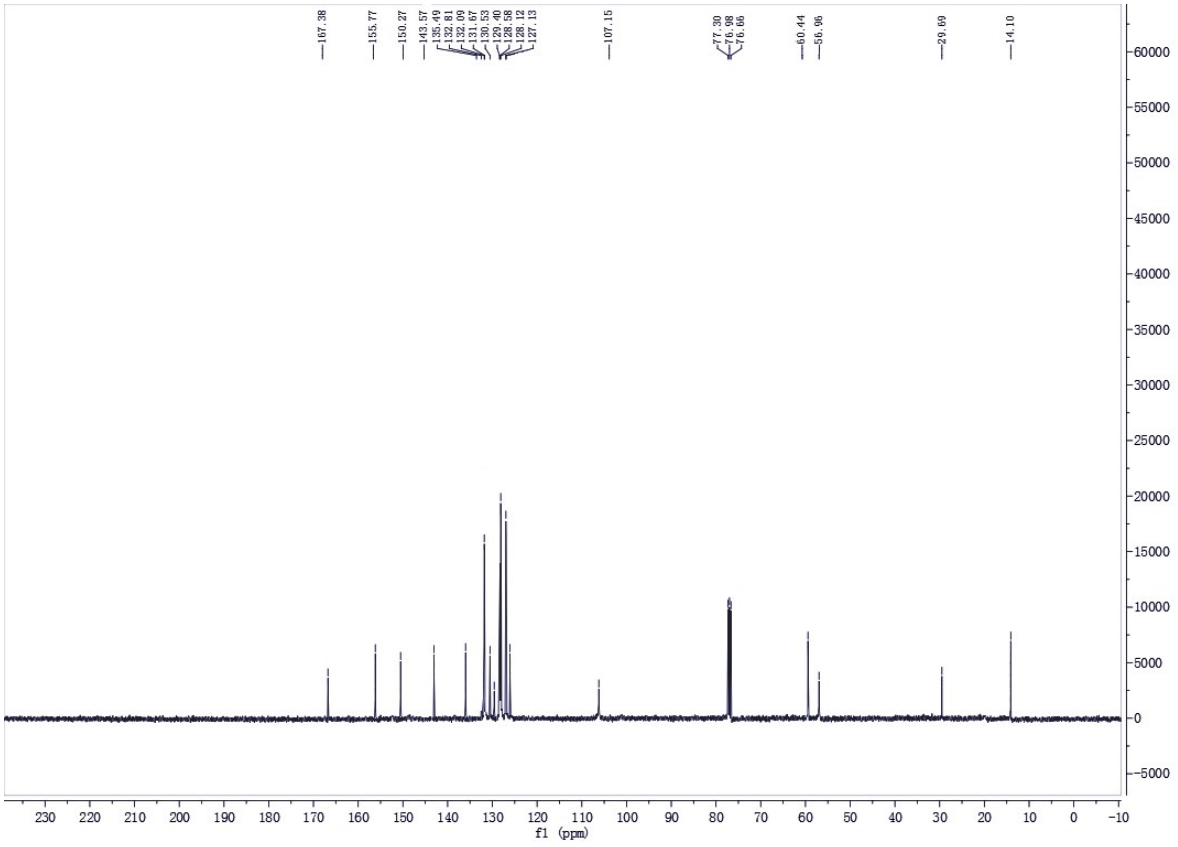
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10d)



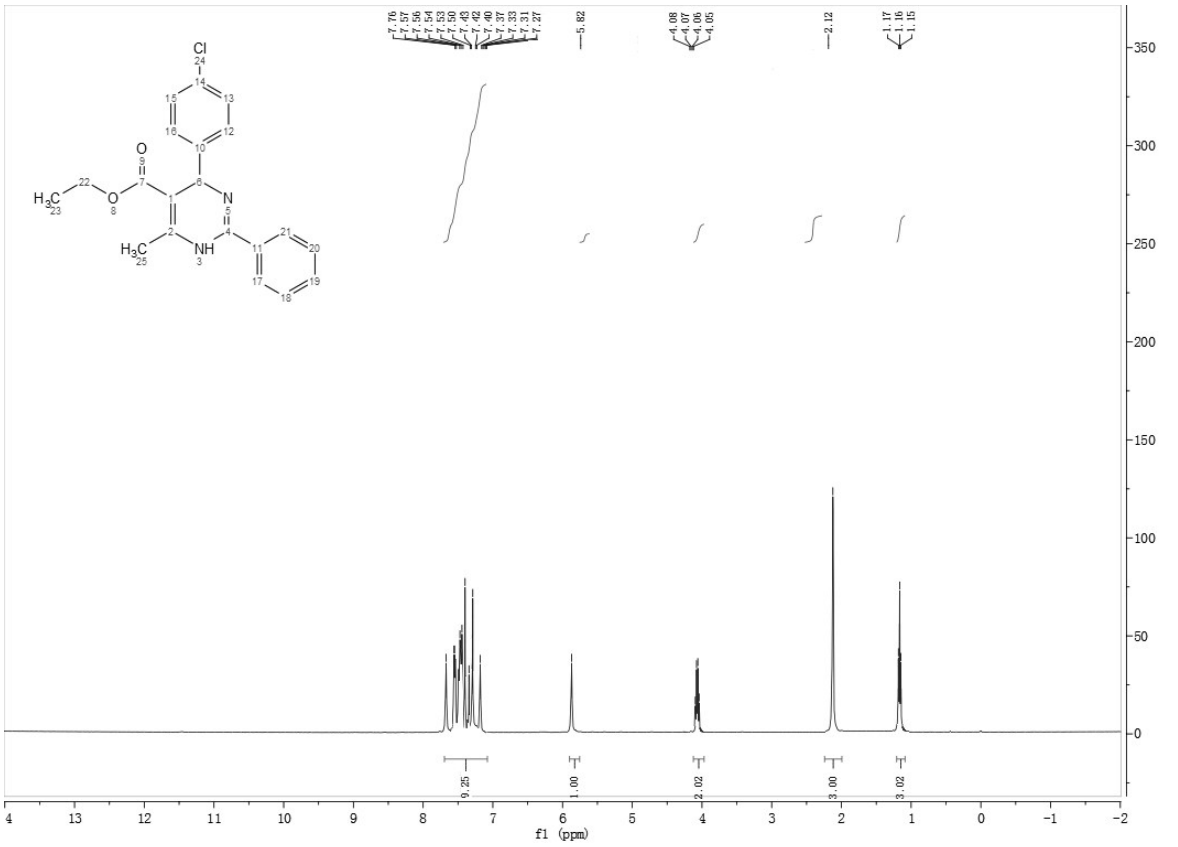


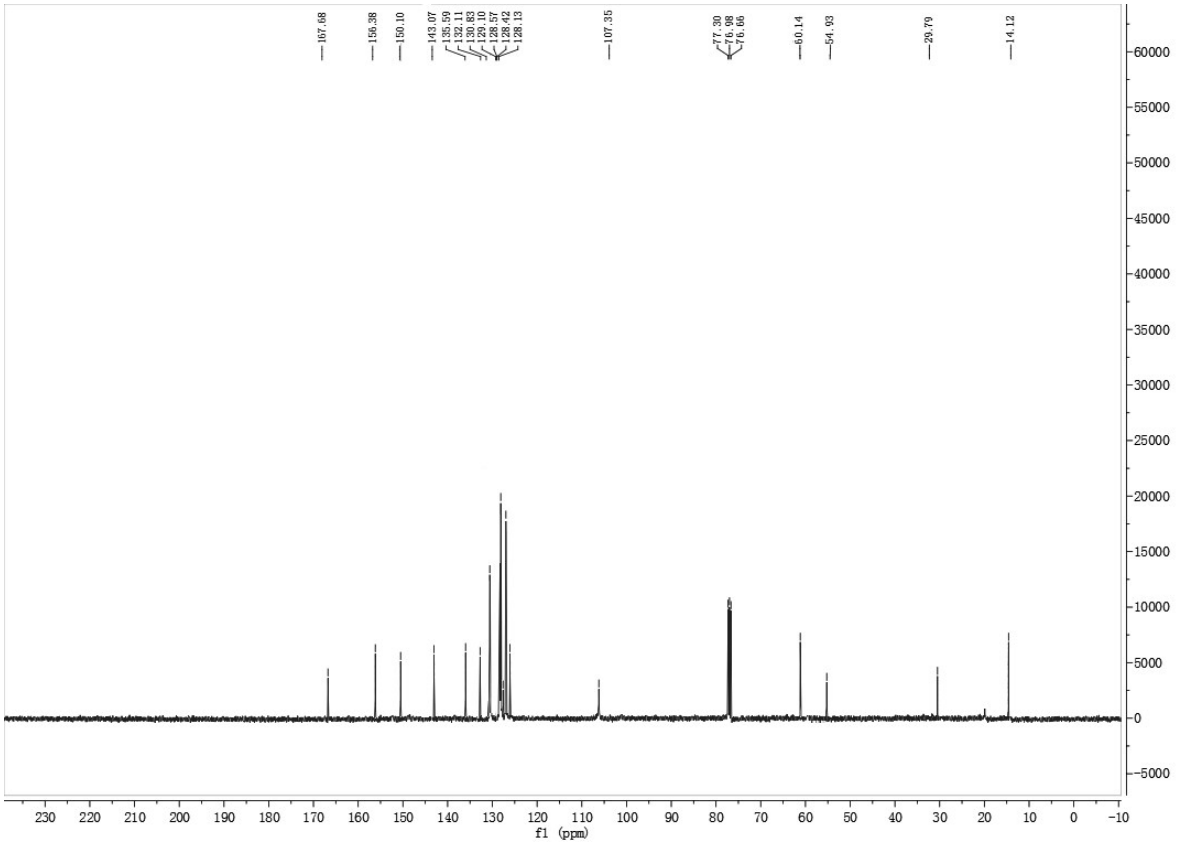
Ethyl 4-(2-chlorophenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10e)



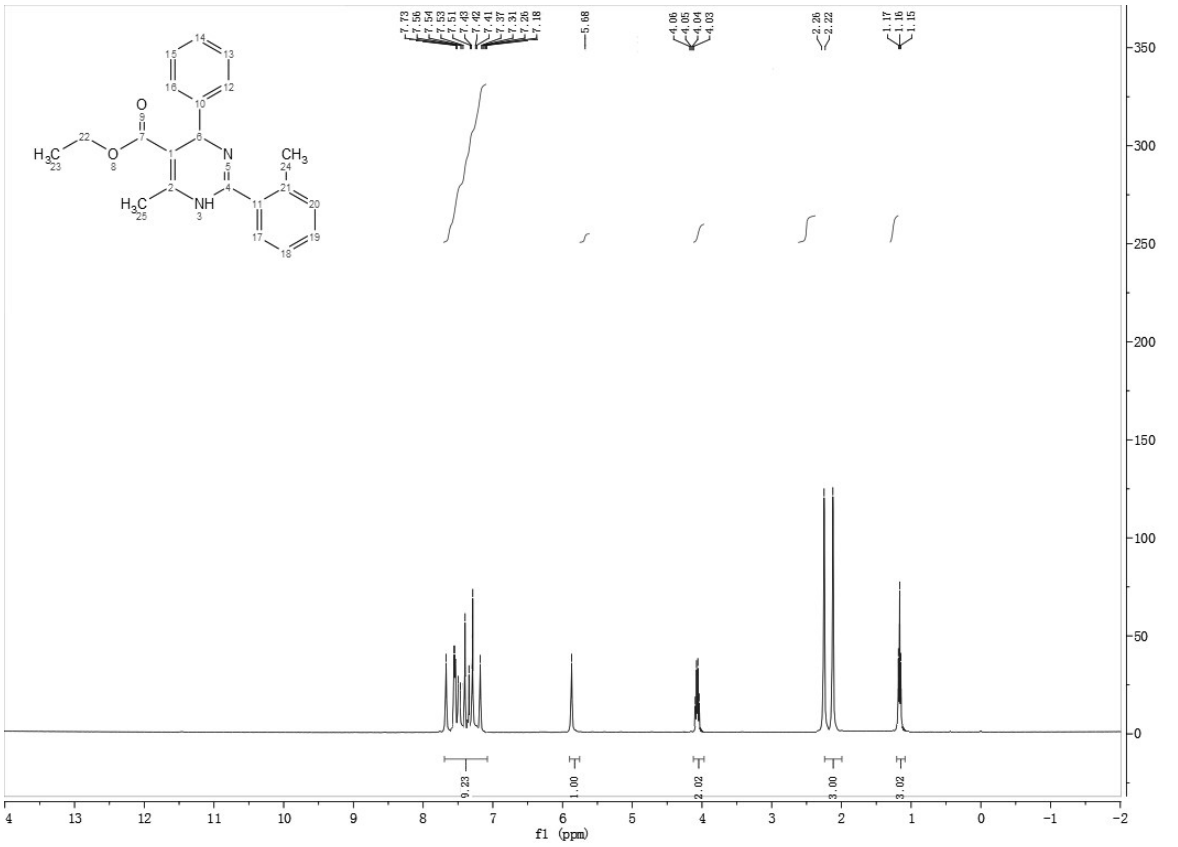


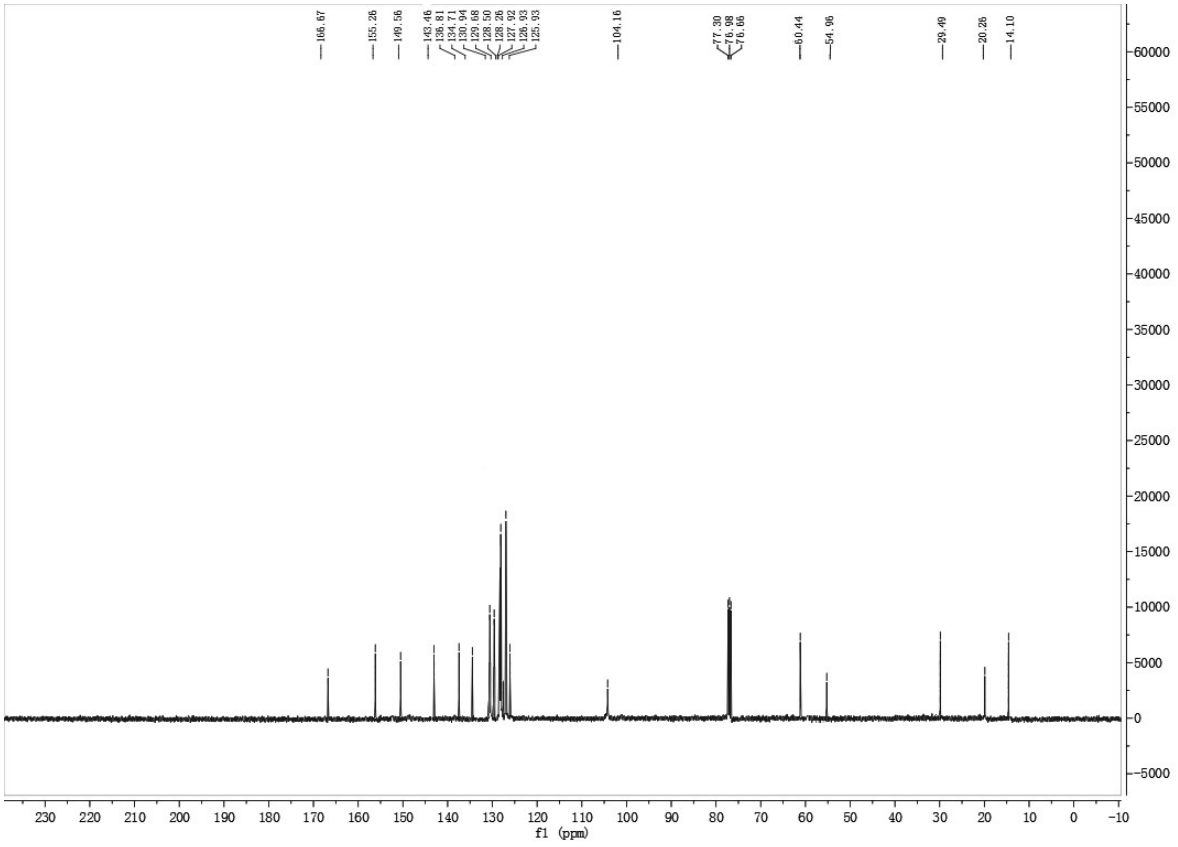
Ethyl 4-(4-chlorophenyl)-6-methyl-2-phenyl-1,4-dihydropyrimidine-5-carboxylate (10f)



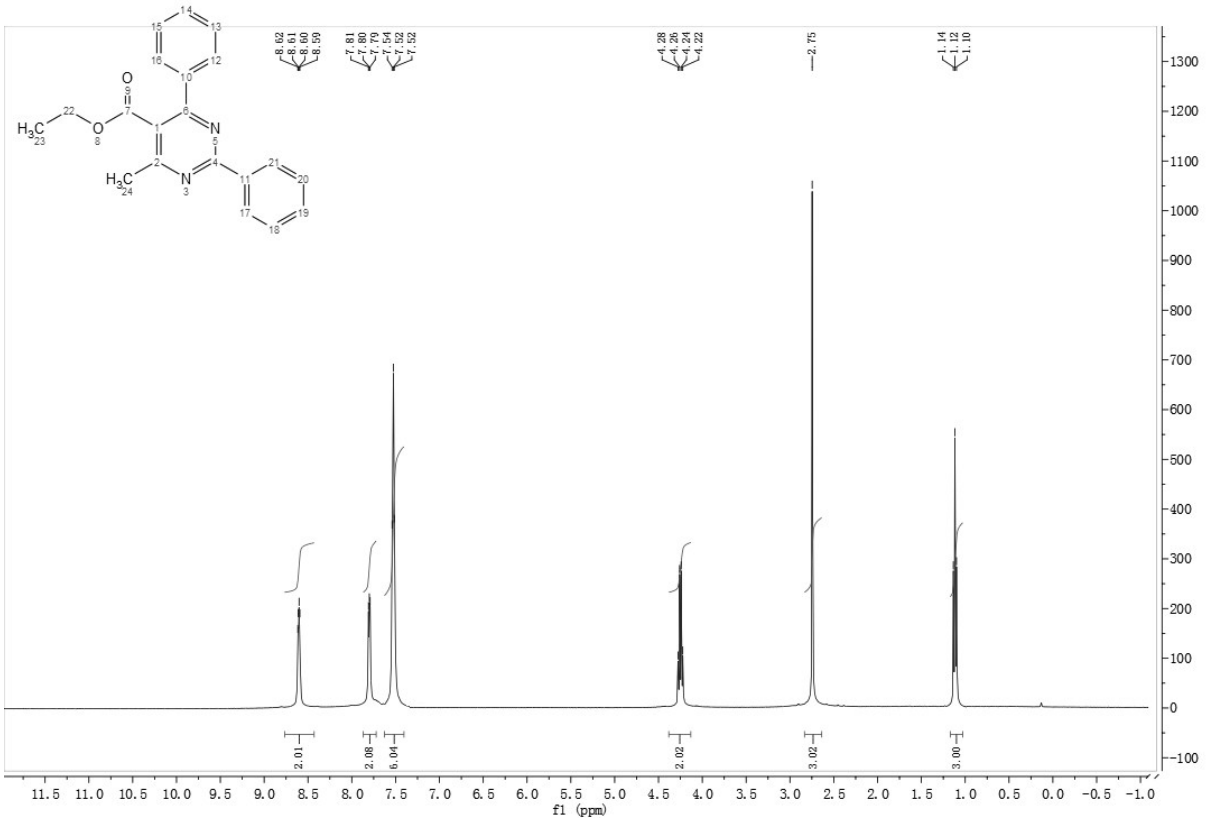


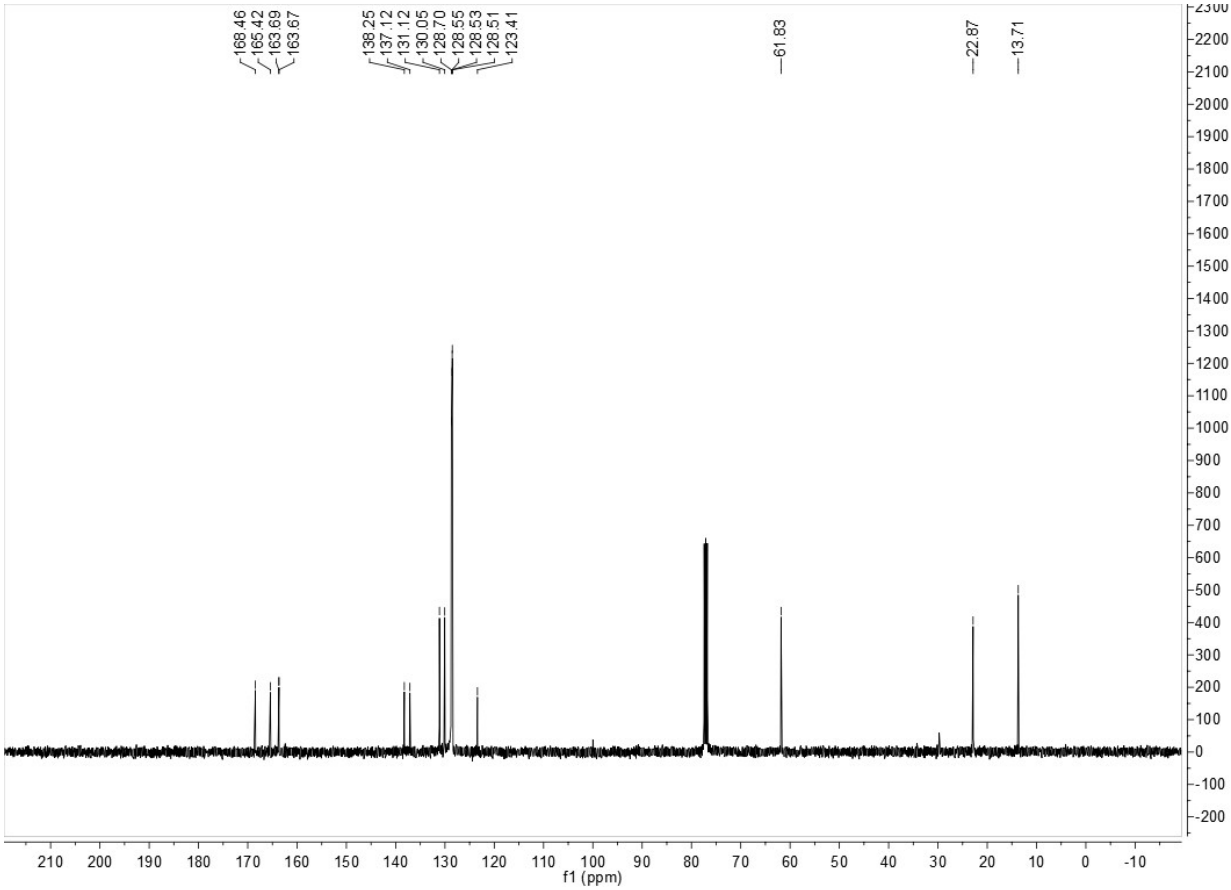
Ethyl 6-methyl-4-phenyl-2-o-tolyl-1,4-dihydropyrimidine-5-carboxylate (10g)



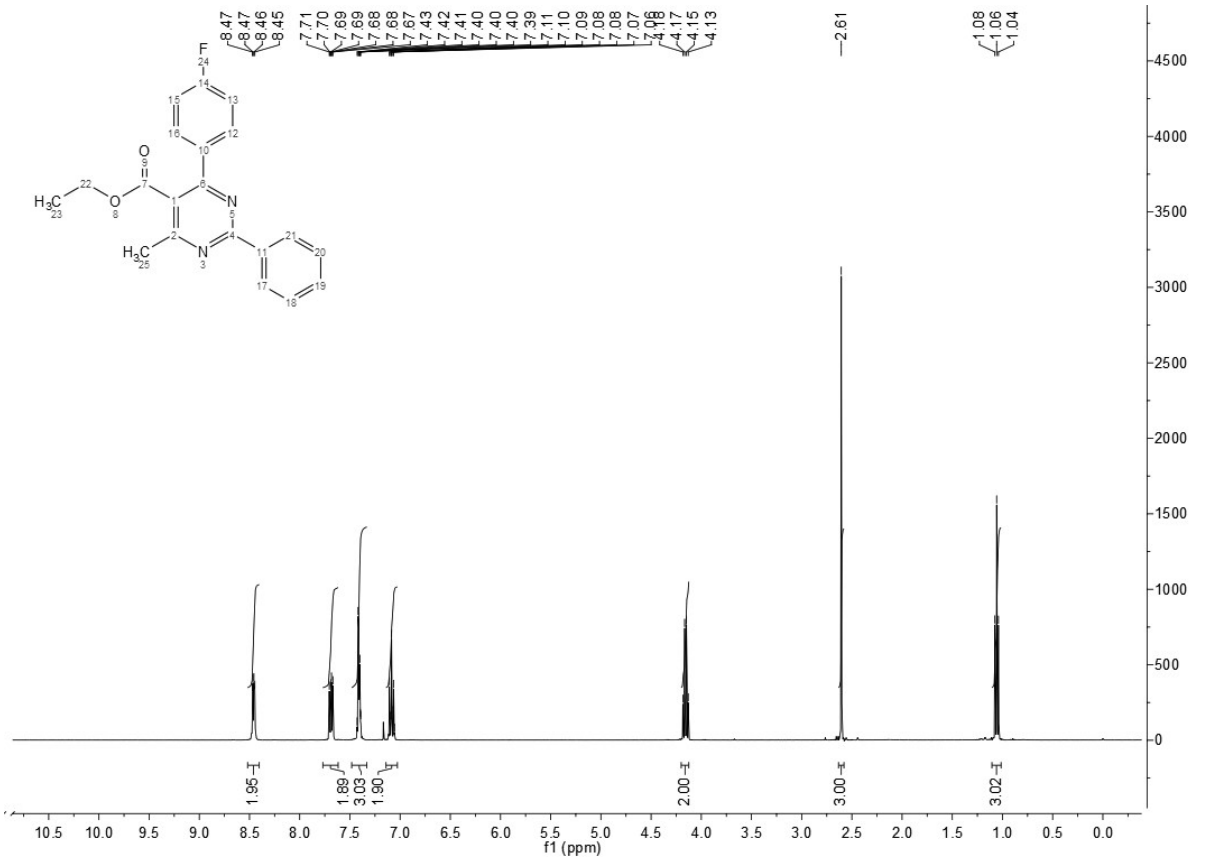


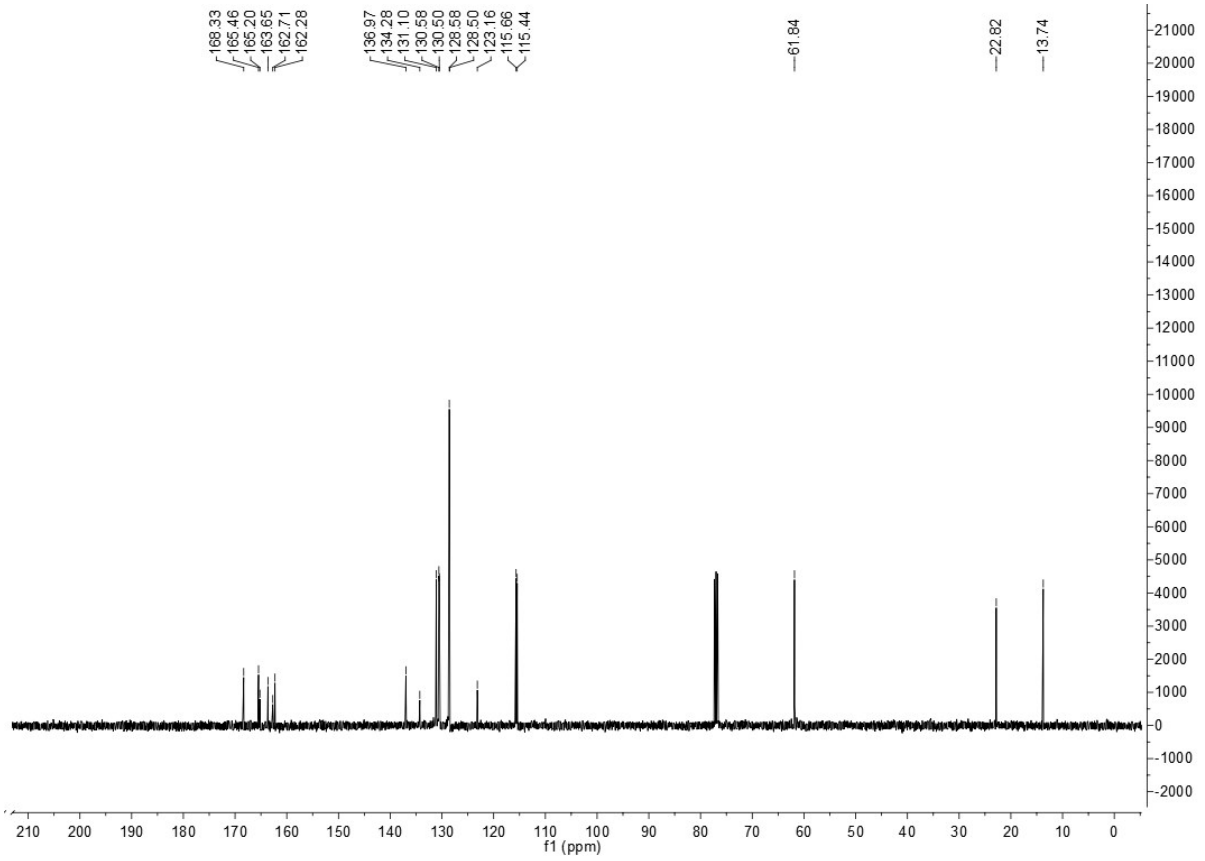
Ethyl 4-methyl-2,6-diphenylpyrimidine-5-carboxylate (11a)



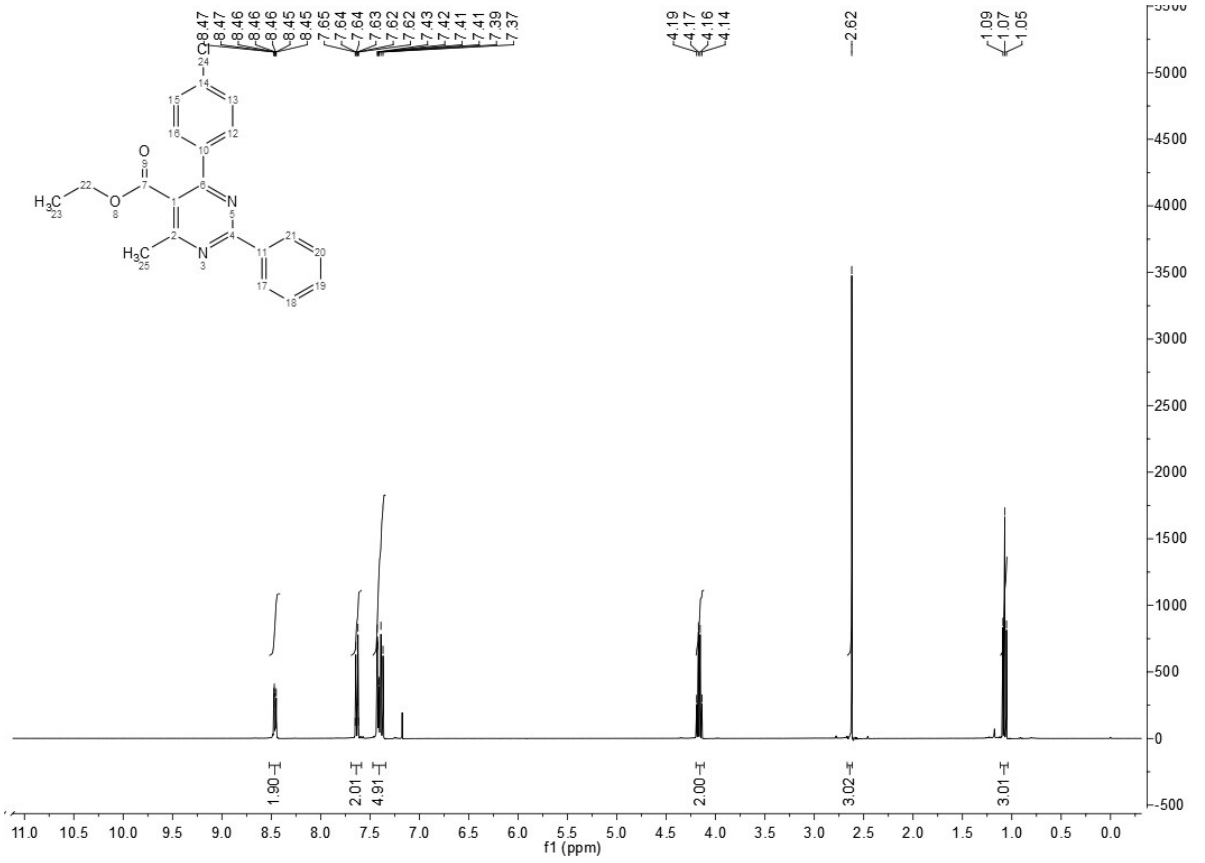


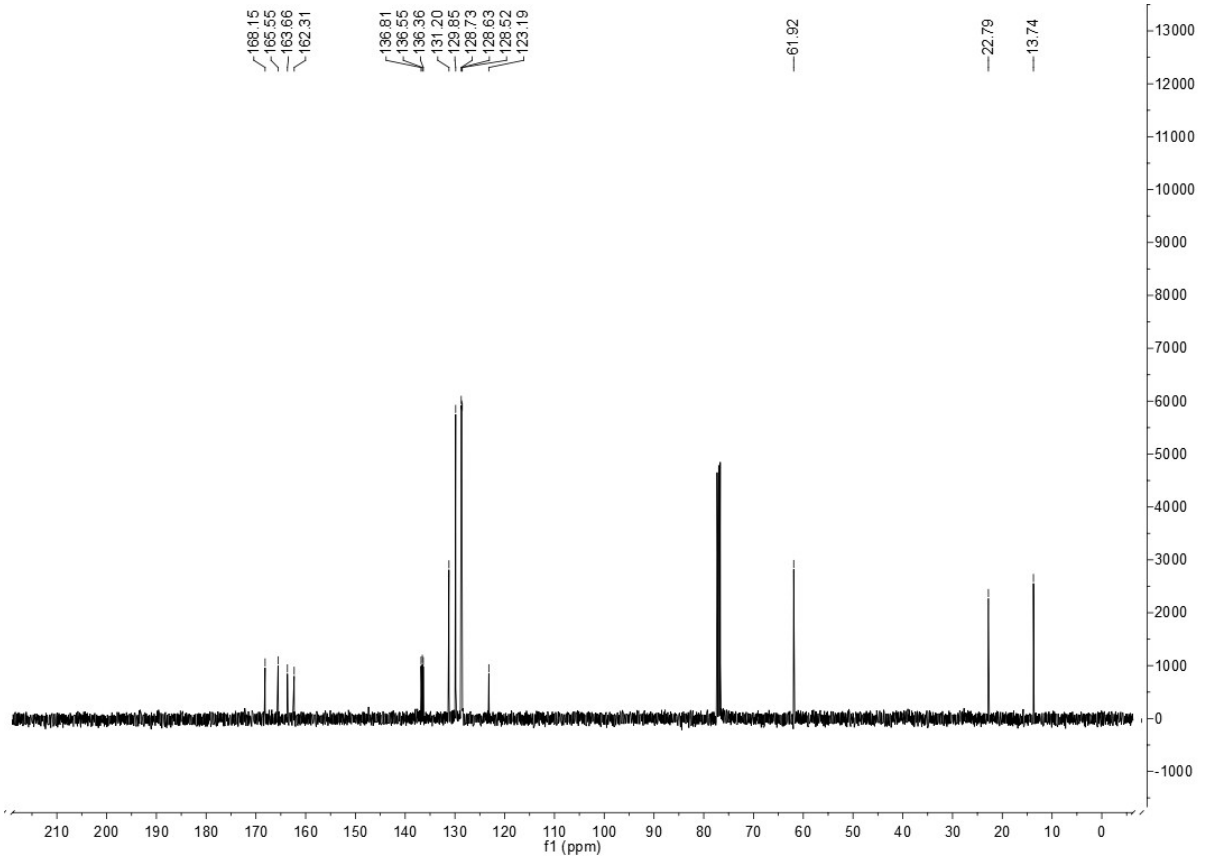
Ethyl 4-(4-fluorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (11b)



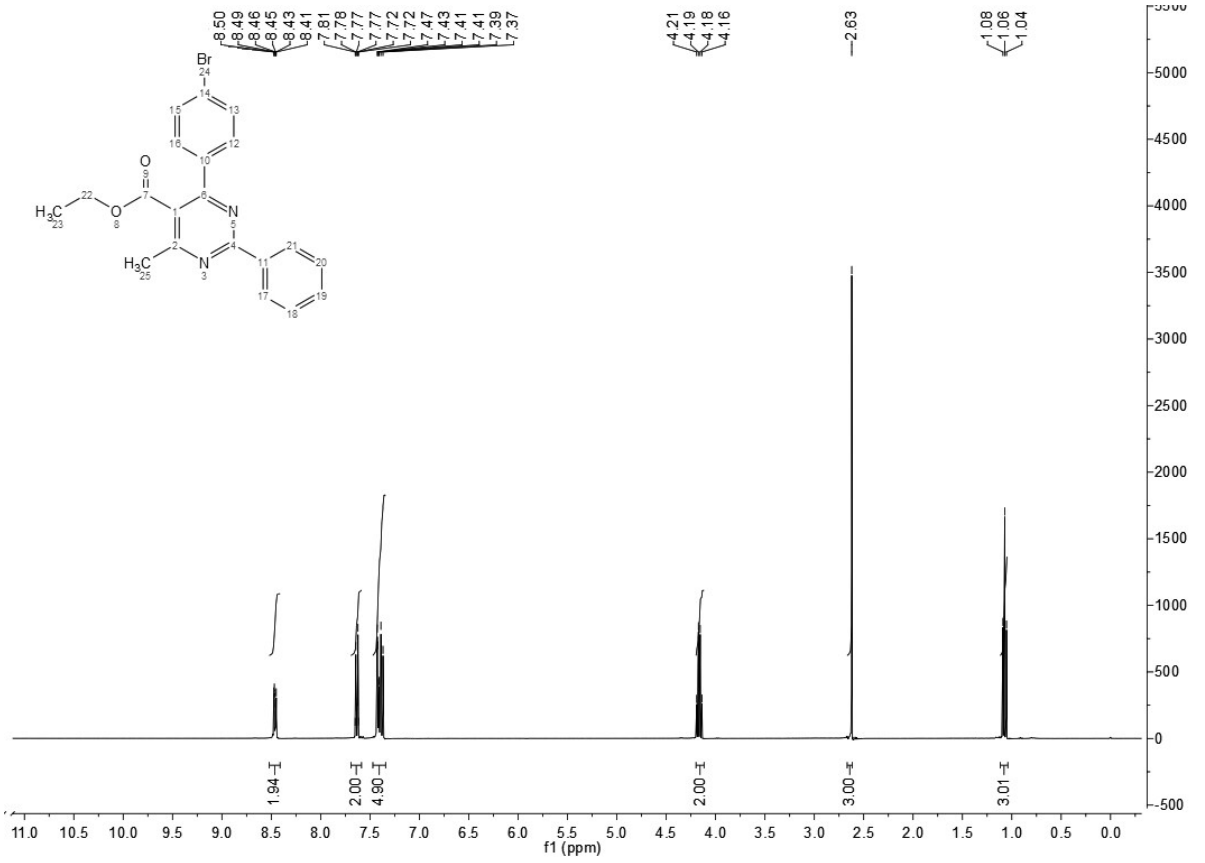


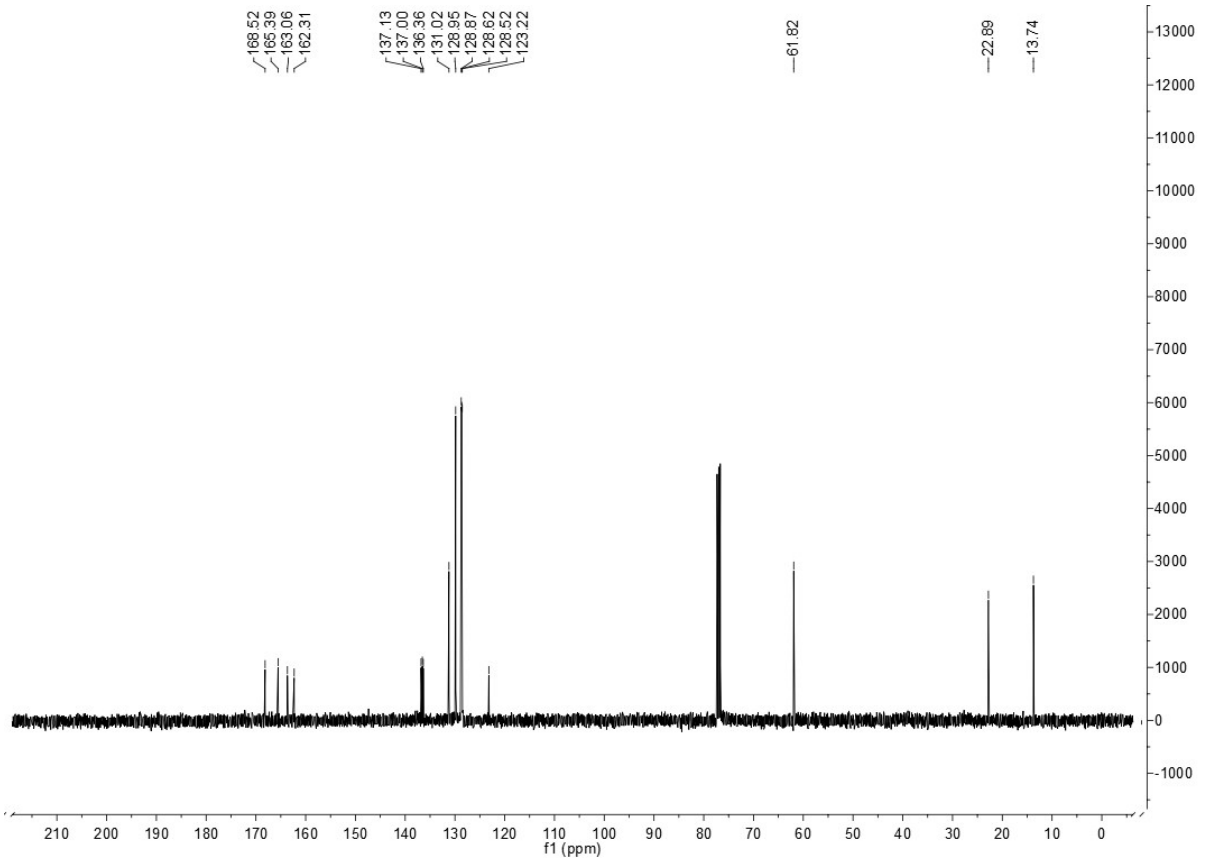
Ethyl 4-(4-chlorophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (11c)



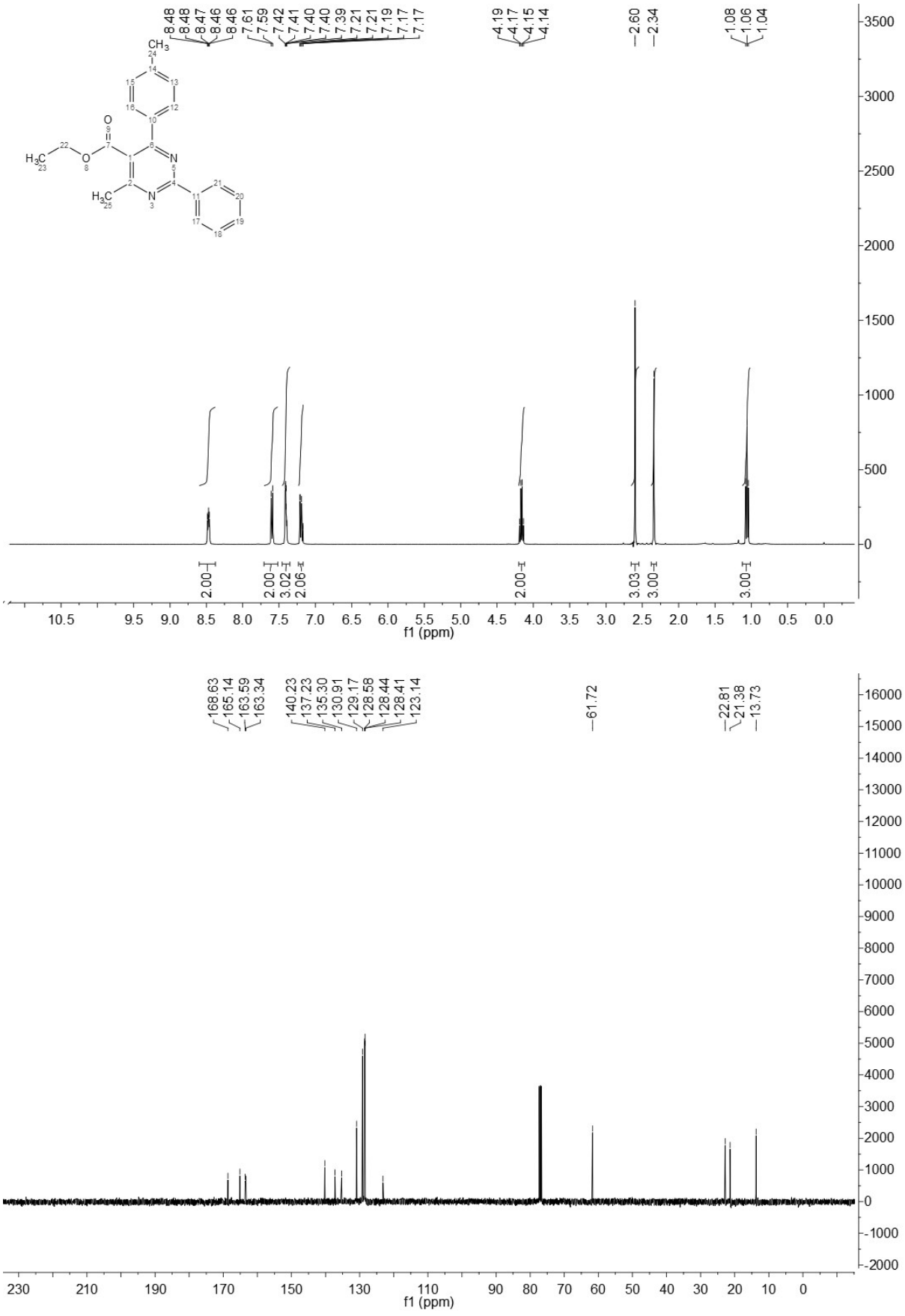


Ethyl 4-(4-bromophenyl)-6-methyl-2-phenylpyrimidine-5-carboxylate (11d)

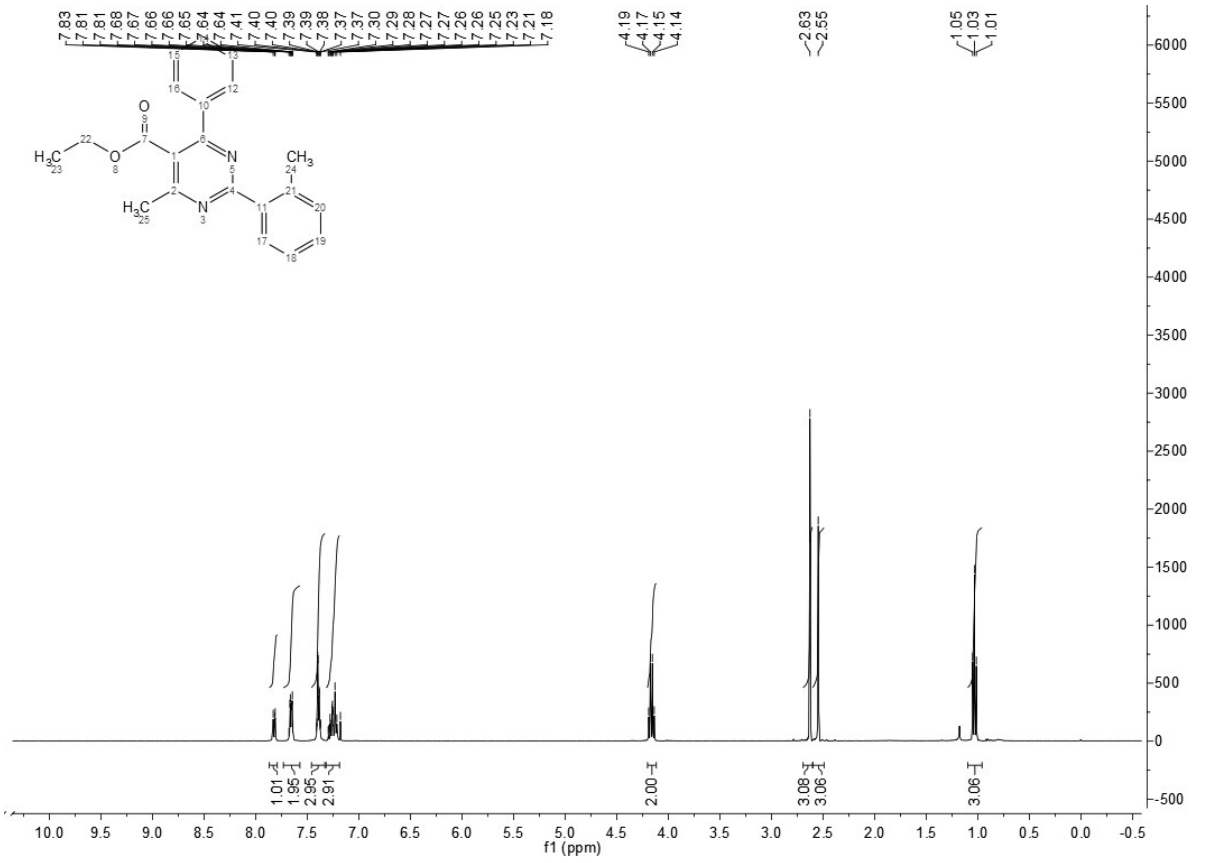


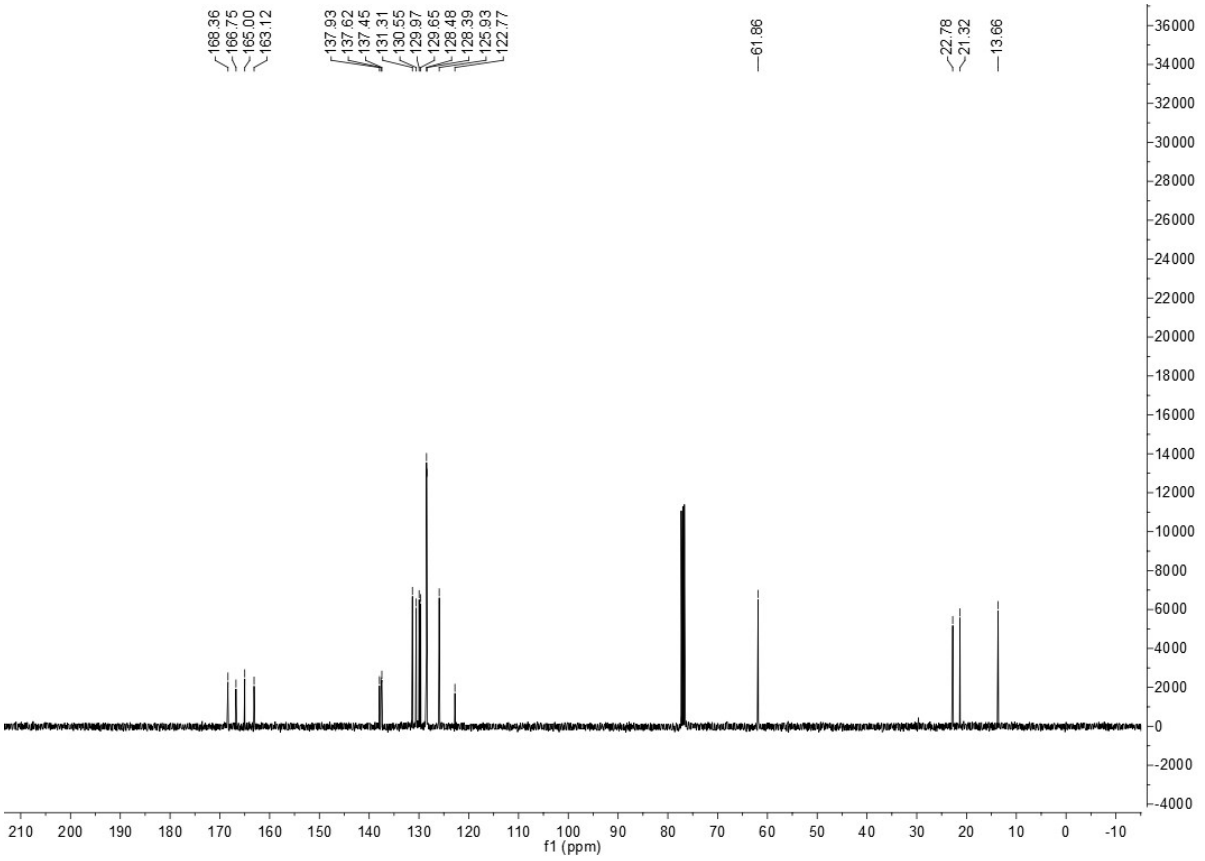


Ethyl 4-methyl-2-phenyl-6-p-tolylpyrimidine-5-carboxylate (11e)

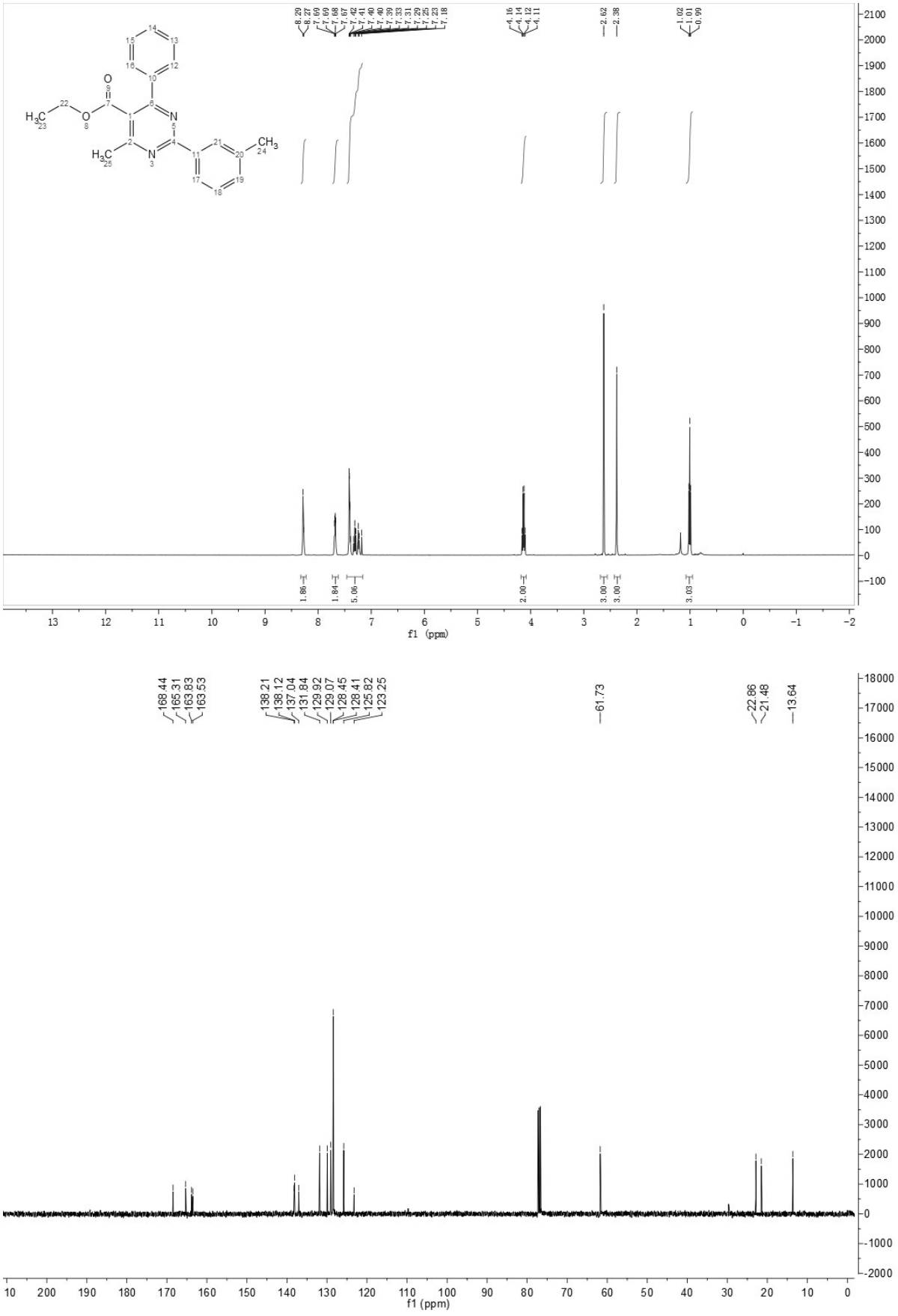


Ethyl 4-methyl-6-phenyl-2-o-tolylpyrimidine-5-carboxylate (11f)

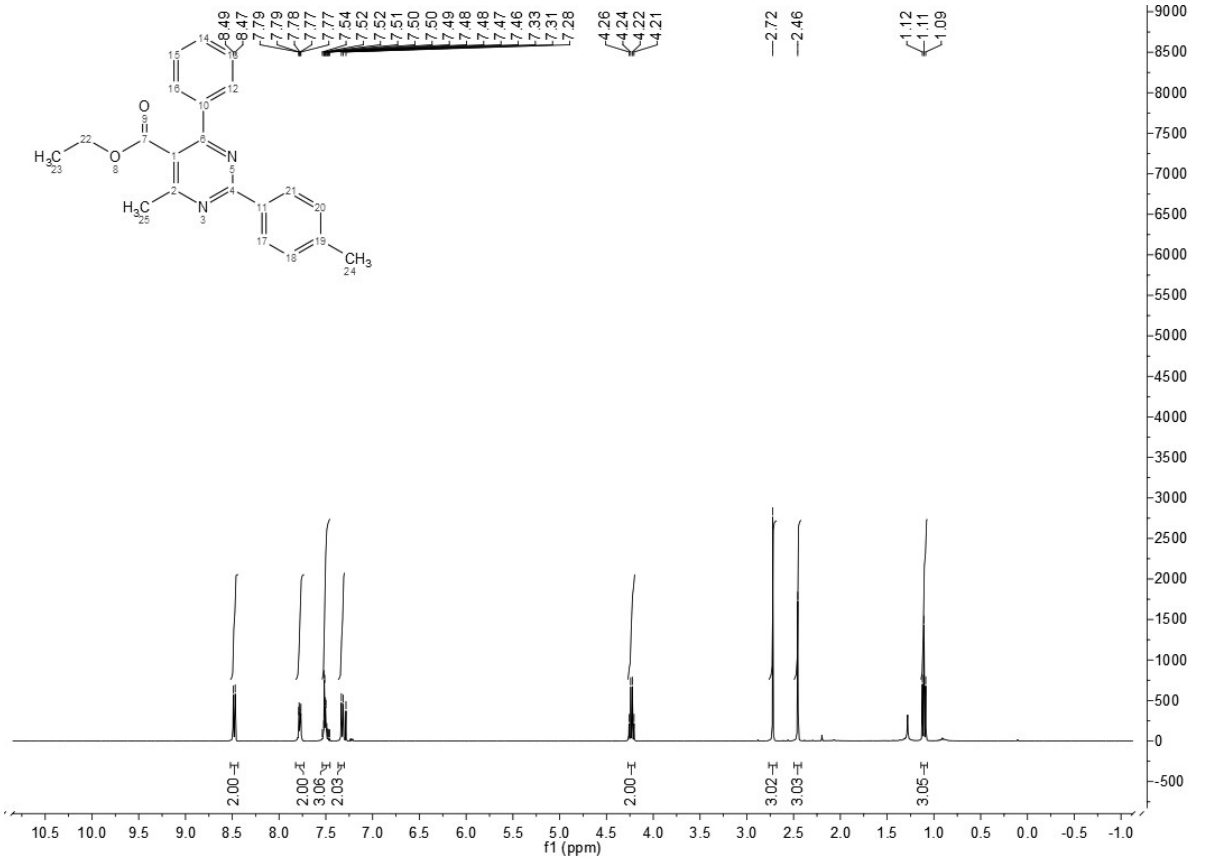


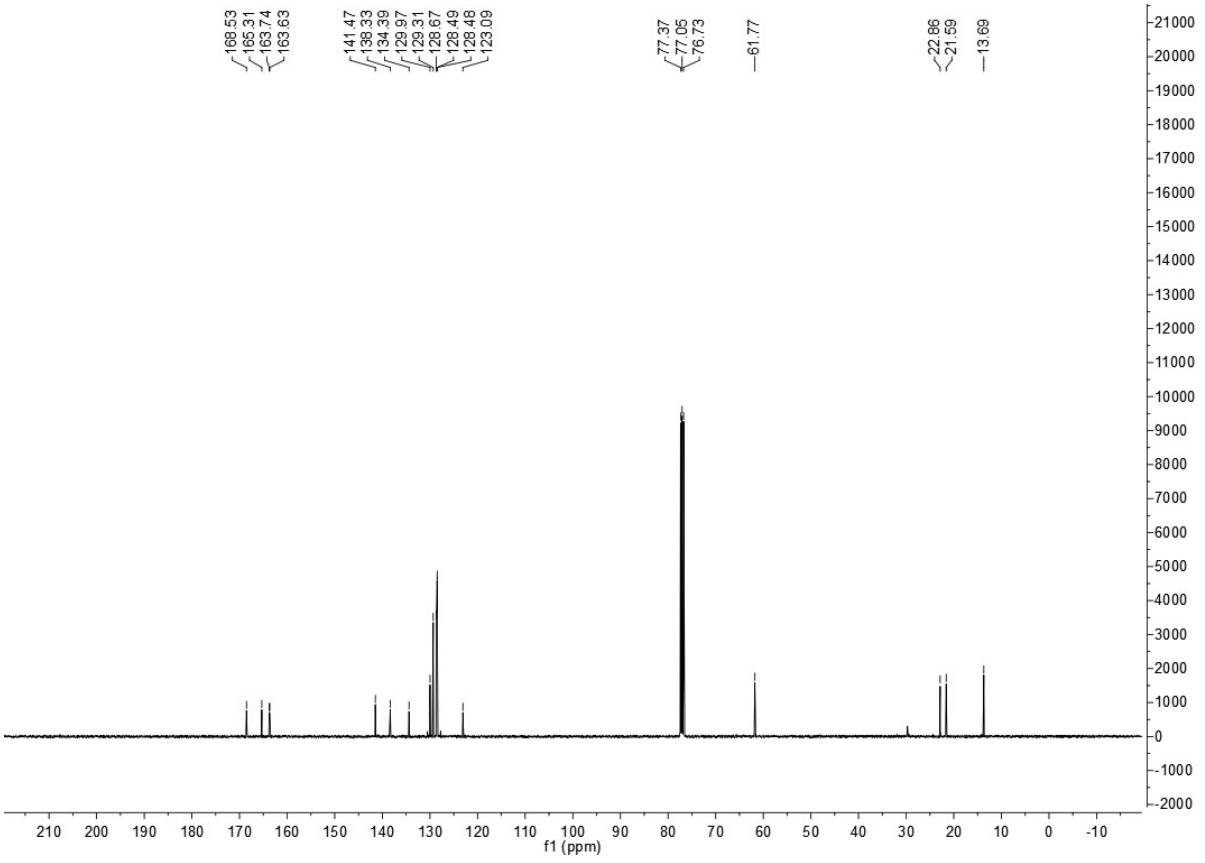


Ethyl 4-methyl-6-phenyl-2-m-tolylpyrimidine-5-carboxylate (11g)

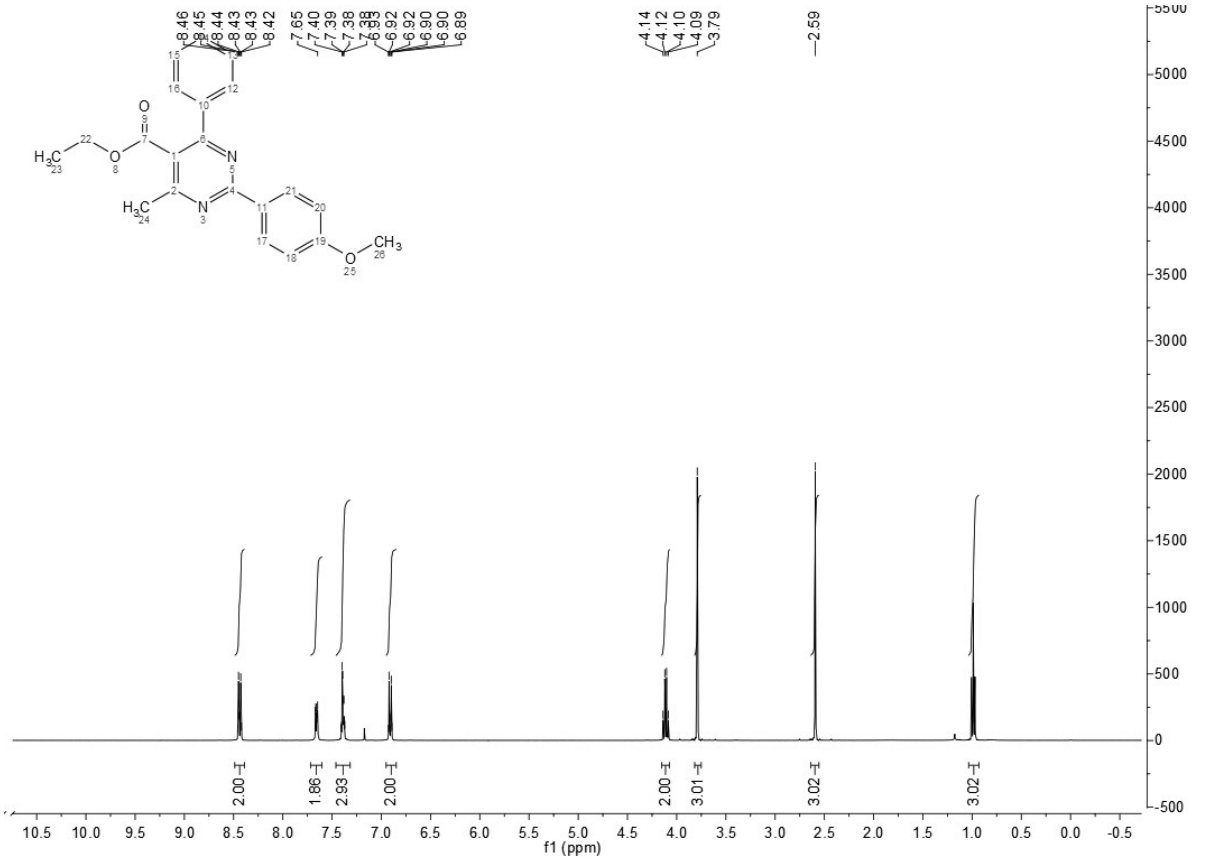


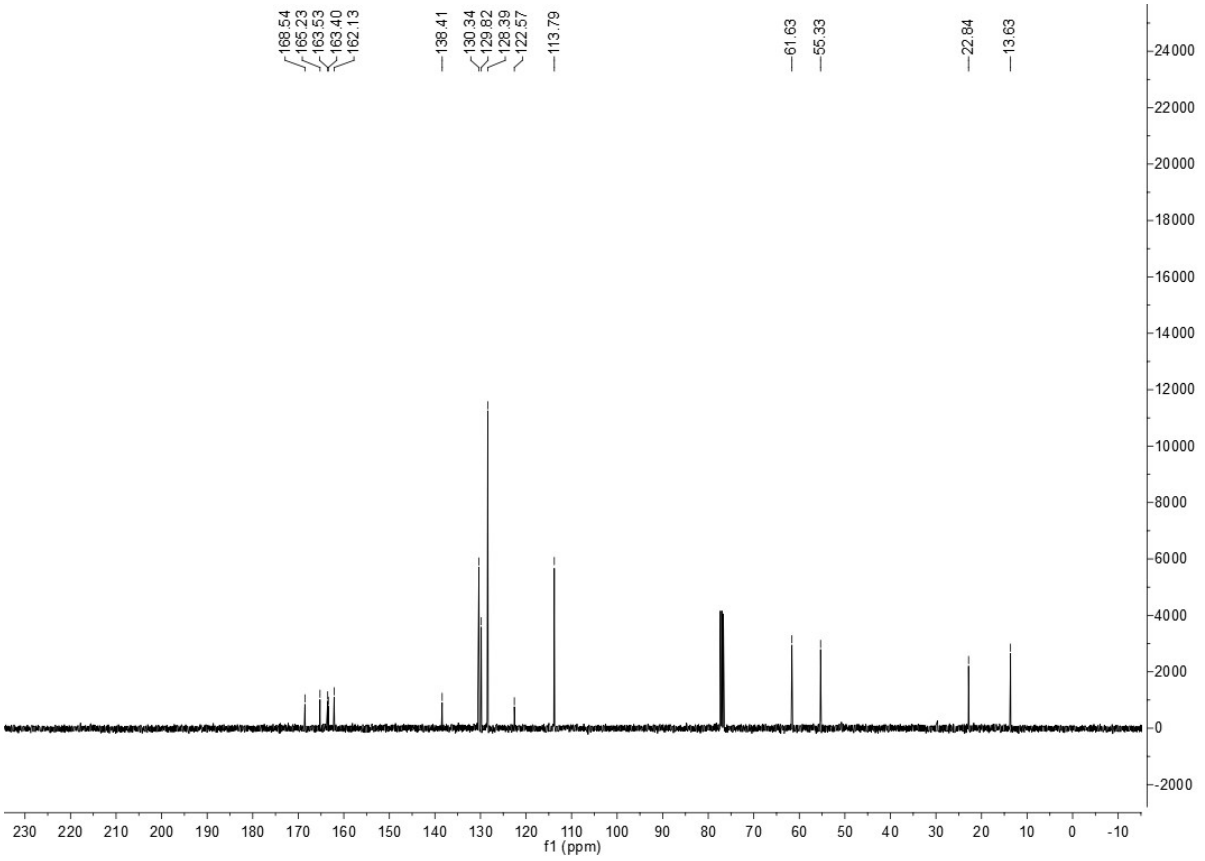
Ethyl 4-methyl-6-phenyl-2-p-tolylpyrimidine-5-carboxylate (11h)



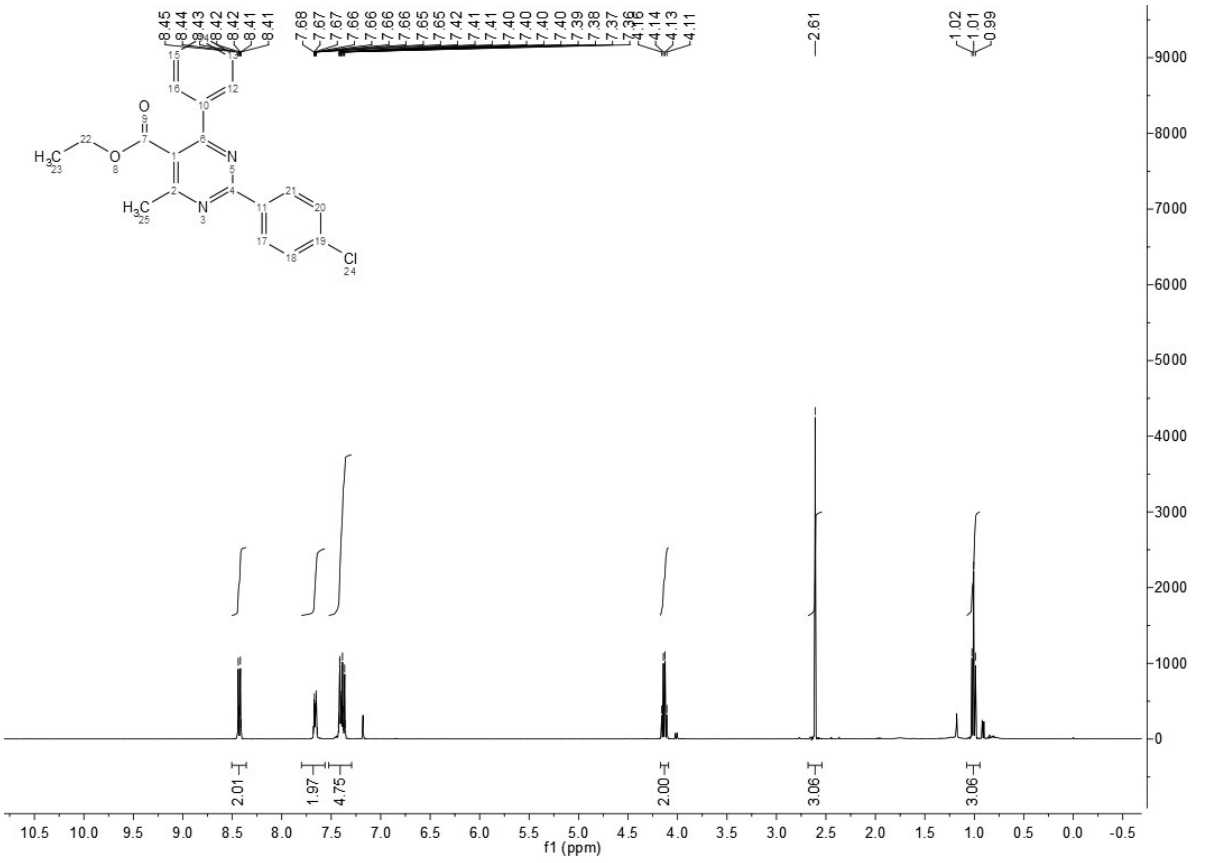


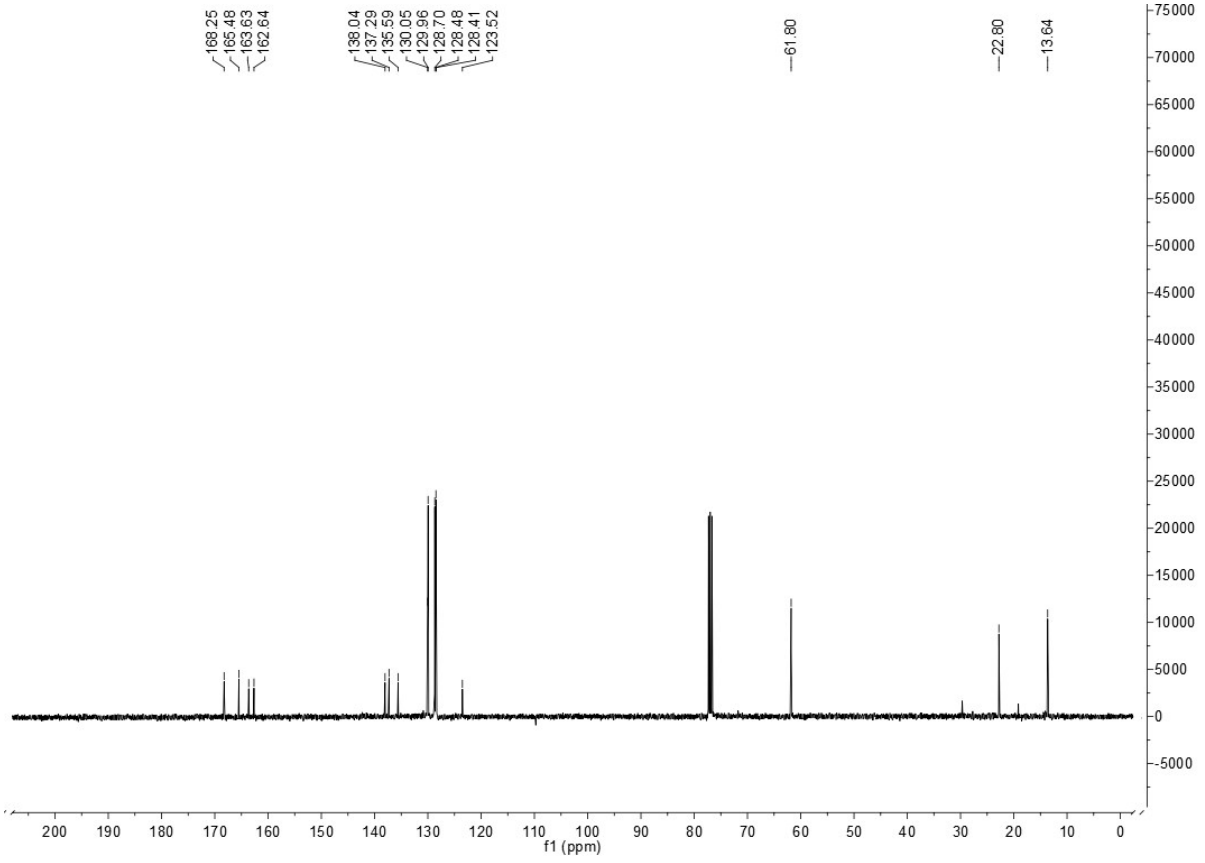
Ethyl 2-(4-methoxyphenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (11i)



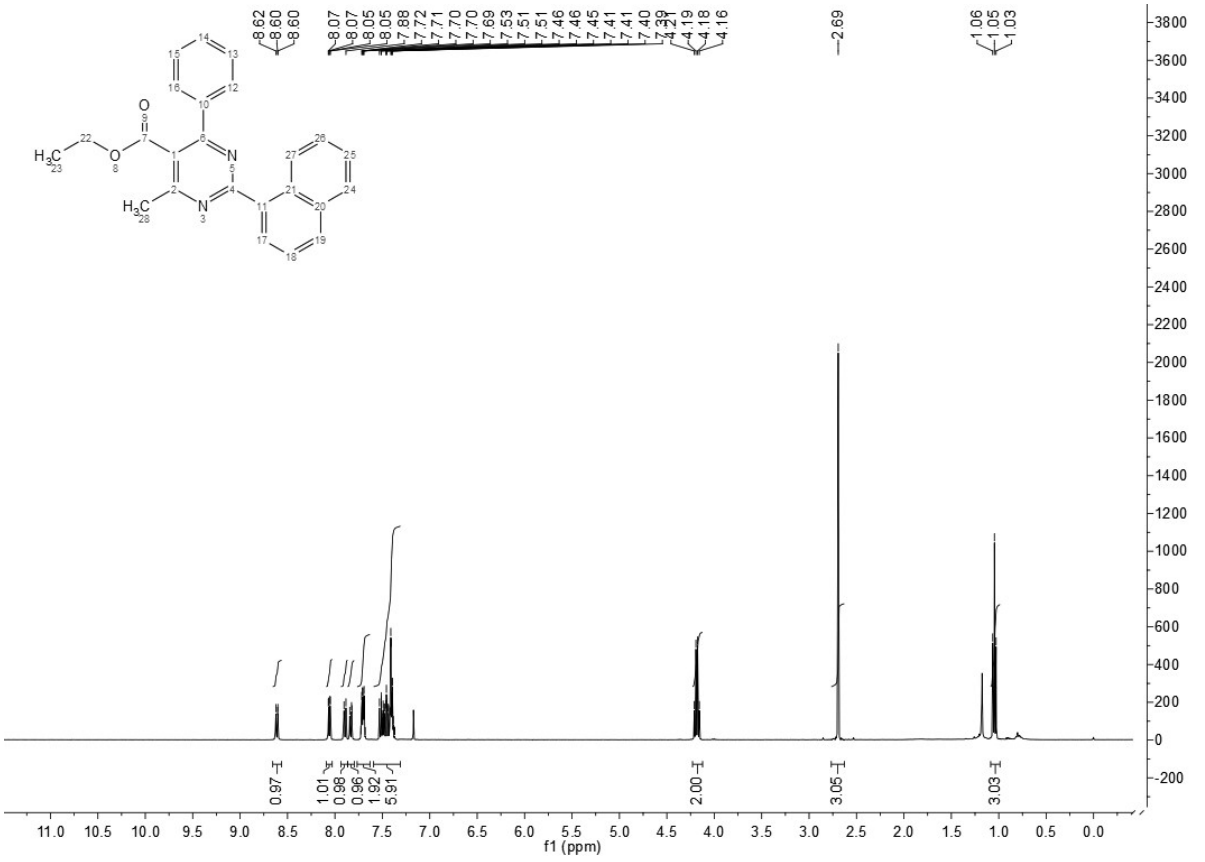


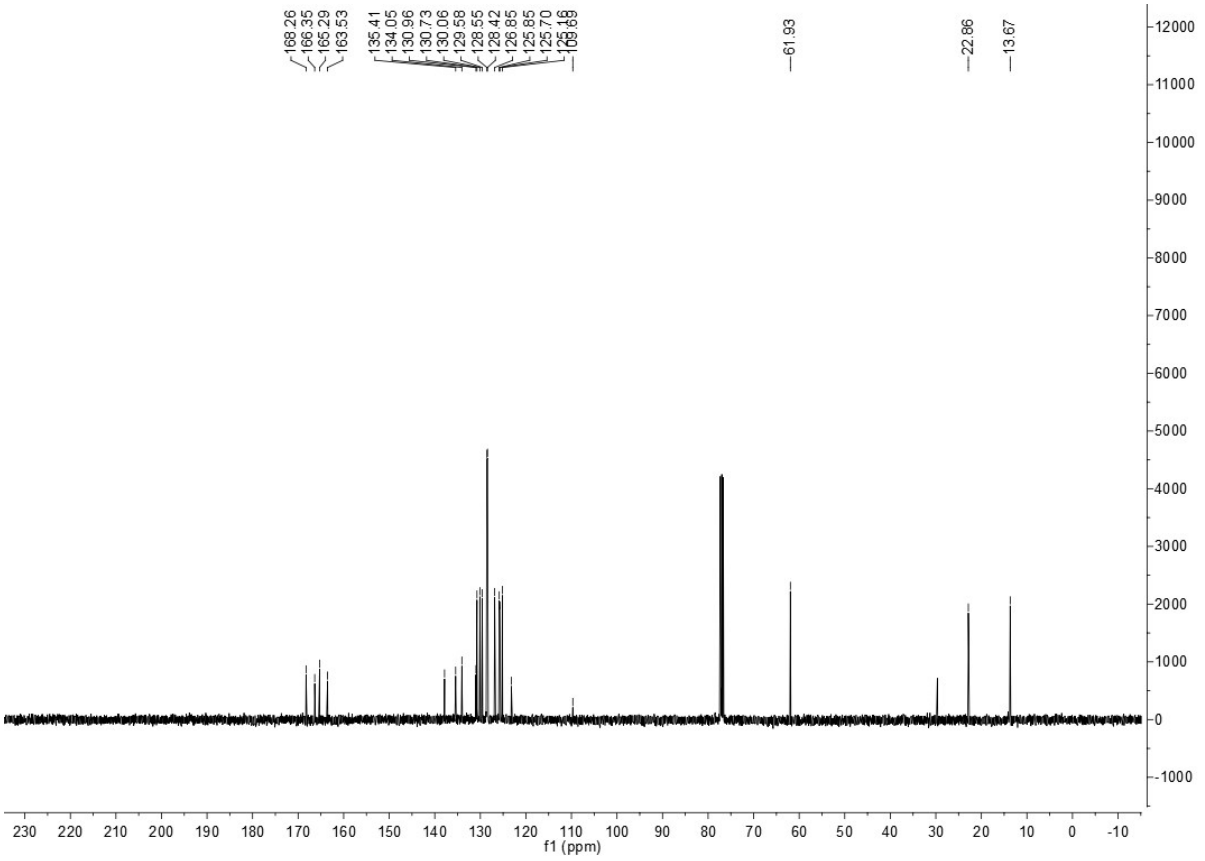
Ethyl 2-(4-chlorophenyl)-4-methyl-6-phenylpyrimidine-5-carboxylate (11j)



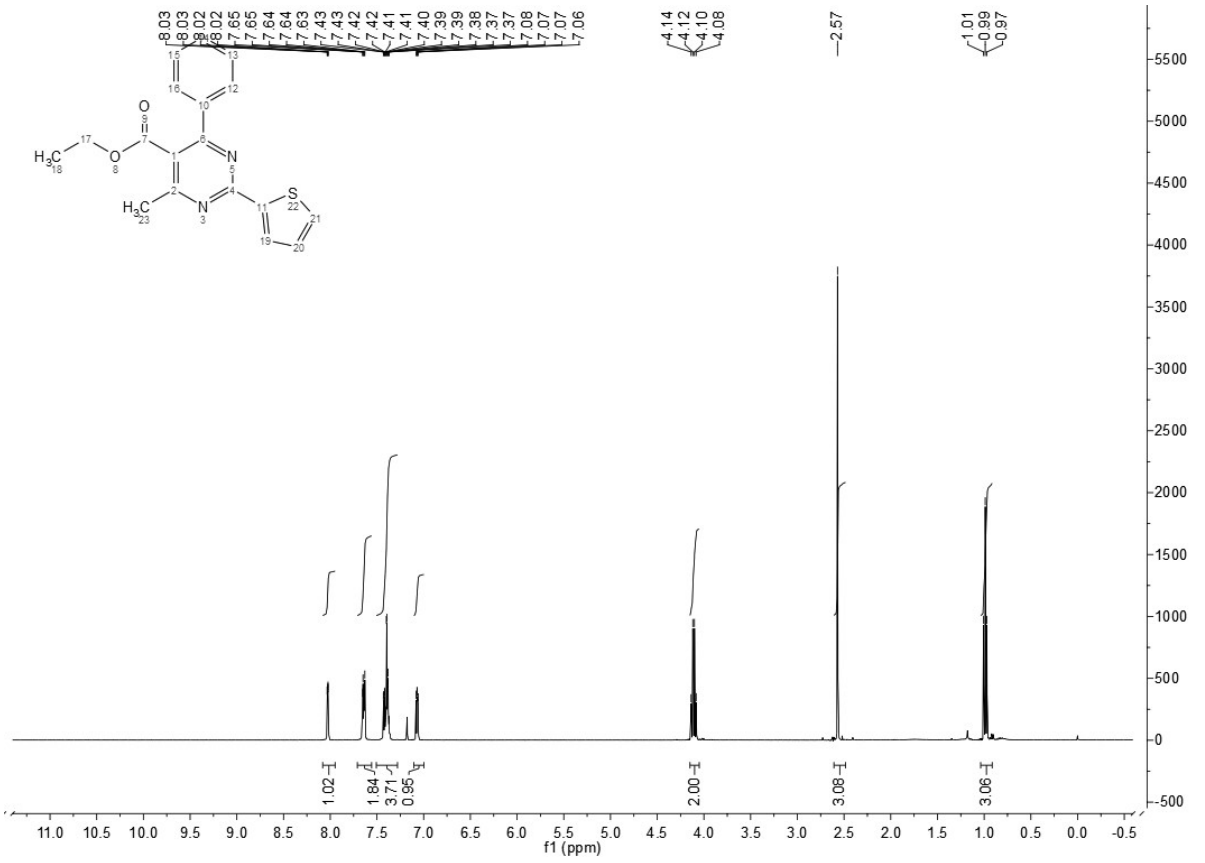


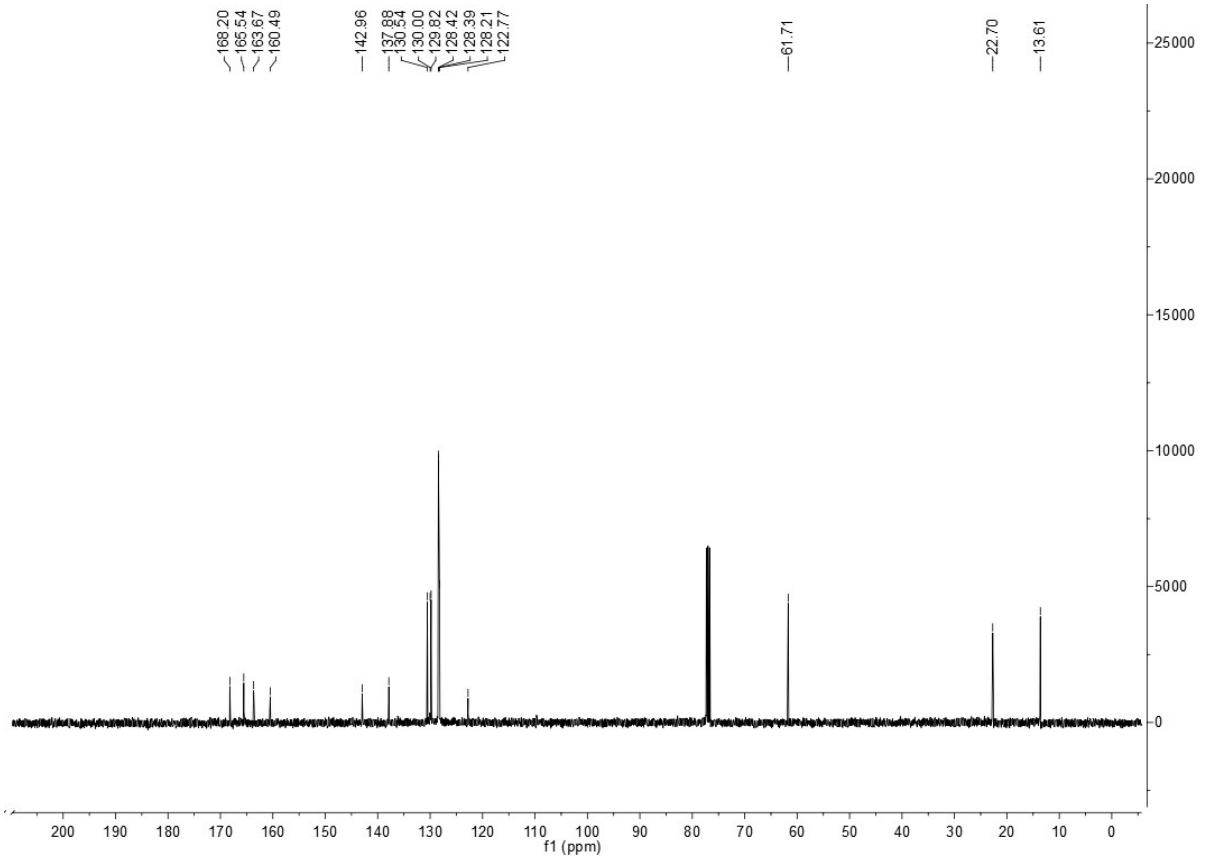
Ethyl 4-methyl-2-(naphthalen-1-yl)-6-phenylpyrimidine-5-carboxylate (11k)





Ethyl 4-methyl-6-phenyl-2-(thiophen-2-yl)pyrimidine-5-carboxylate (11l)


8.03
8.03
8.02
8.02
7.65
7.65
7.64
7.64
7.63
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.08
7.07
7.07
7.06
4.14
4.12
4.10
4.08
2.57
1.01
0.99
0.97
1.02
1.84
3.71
0.95
2.00
3.08
3.06
f1 (ppm)


168.20
165.54
163.67
160.49
142.96
137.88
130.54
130.00
129.82
128.42
128.39
128.21
122.77
61.71
22.70
13.61
f1 (ppm)