Palladium-catalyzed dehydrogenation of dihydro-heterocycles using isoprene as the hydrogen acceptors without oxidants

Xiao-Jun Liu, Wen-Peng Wang, Cong-De Huo, Xi-Cun Wang,* Zheng-Jun Quan*

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education; Gansu Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Anning East Road 967#, Lanzhou, Gansu 730070, PR China

Supporting Informations

Contents

1. General Information

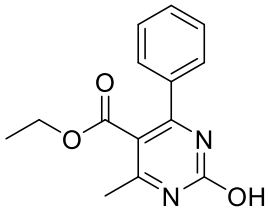
^{1}H NMR and ^{13}C NMR data analyses were performed with a Varian Mercury plus-400 instrument unless otherwise specified. $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR 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 $CDCl_3$ (77.0 ppm) 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. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC analyses were conducted on silica gel GF254 plates. All reagents were directly used from purchased without any further purification unless otherwise specified.

2. Experimental Details and Analytic Data of Products

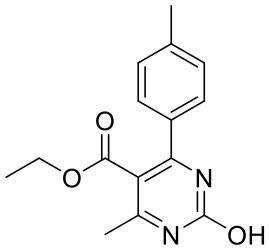
General Procedure

A 10 mL schlenk tube was charged with $Pd(OAc)_2$ (2.8 mg, 2.5 mol %), DPEphos (13.46 mg, 5 mol %), DHPM **1** (0.5 mmol), isoprene (68 mg, 2 eq.), Cs_2CO_3 (81.25 mg, 0.5 eq.) and toluene (5 mL) under argon atmosphere. The reaction is allowed to be heated under 120 °C for 36 h. Afterward, the reaction mixture is cooled to room temperature. EtOAc (15 mL) with NH_4Cl solution were then added to the reaction mixture. The organic phase was collected and washed with brine (10 mL) and evaporated to remove solvents. Pure product was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate ratio of 2:1). (**2a-2h** [1],**4a-4k** [2, 3],**6a-6f** [4,5]).

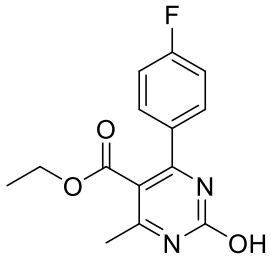
Analytic Data of Products



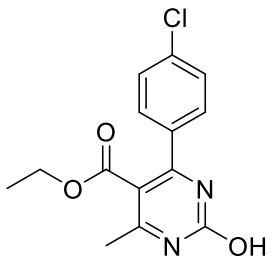
Ethyl 2-hydroxy-4-methyl-6-phenylpyrimidine-5-carboxylate (2a): White solid, m.p. = 195 - 196 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.89 (s, 1H), 8.47 (d, *J* = 2.1 Hz, 1H), 8.38 – 8.30 (m, 1H), 7.94 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.62 (t, *J* = 7.9 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.67 (s, 3H), 1.02 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.10, 158.10, 147.98, 133.94, 129.40, 125.20, 123.23, 111.21, 61.99, 18.80, 13.62 ppm.



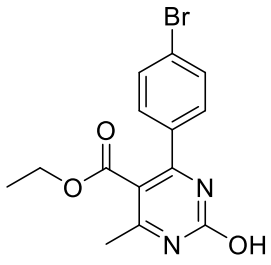
Ethyl 2-hydroxy-4-methyl-6-(*p*-tolyl)pyrimidine-5-carboxylate (2b): Pale yellow solid, m.p. = 168-169 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.67 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.36 (s, 3H), 0.96 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.32, 158.35, 141.36, 129.06, 128.10, 111.38, 61.58, 21.43, 13.52 ppm.



Ethyl 4-(4-fluorophenyl)-2-hydroxy-6-methylpyrimidine-5-carboxylate (2c): Pale brown solid, m.p. = 185-186 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.75 (s, 1H), 7.60 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 0.99 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.93, 158.26, 130.36, 130.30, 115.56, 115.42, 111.32, 61.70,18.41, 13.56 ppm.

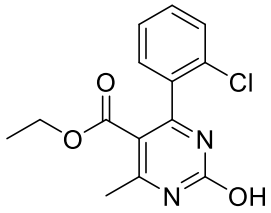


Ethyl 4-(4-chlorophenyl)-2-hydroxy-6-methylpyrimidine-5-carboxylate (2d): Yellow solid, m.p. = 187-188 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.76 (s, 1H), 7.53 – 7.48 (m, 2H), 7.38 – 7.34 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 3H), 0.96 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.74, 158.21, 137.12, 129.46, 128.56, 111.26, 61.72, 19.38, 13.54 ppm.



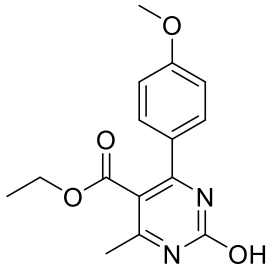
Ethyl 4-(4-bromophenyl)-2-hydroxy-6-methylpyrimidine-5-carboxylate (2e):

White solid, m.p. = 190-191 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.75 (s, 1H), 7.64 – 7.56 (m, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 0.99 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.93, 158.26, 130.36, 130.30, 115.56, 115.42, 111.32, 61.70, 20.05, 13.56 ppm.



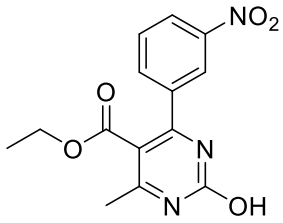
Ethyl 4-(2-chlorophenyl)-2-hydroxy-6-methylpyrimidine-5-carboxylate (2f):

Yellow solid, m.p. = 192-193 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.58 (s, 1H), 7.33 (dt, *J* = 24.0, 7.6 Hz, 4H), 4.01 – 3.96 (m, 2H), 2.67 (s, 3H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.33, 157.84, 148.52, 129.76, 129.43, 128.06, 127.55, 126.71, 111.47, 61.24, 18.29, 13.26 ppm.



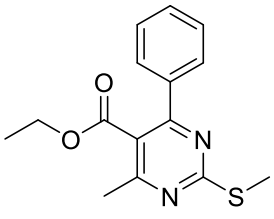
Ethyl 2-hydroxy-4-(4-methoxyphenyl)-6-methylpyrimidine-5-carboxylate (2g):

White solid, m.p. = 183-184 ºC. **^{1}H NMR (600 MHz, $CDCl_3$):** δ = 13.67 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 2.55 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.54, 162.04, 158.38, 130.09, 113.80, 111.13, 61.61, 55.37, 18.27, 13.66 ppm.

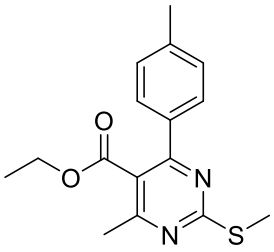


Ethyl 2-hydroxy-4-methyl-6-(3-nitrophenyl)pyrimidine-5-carboxylate (2h):

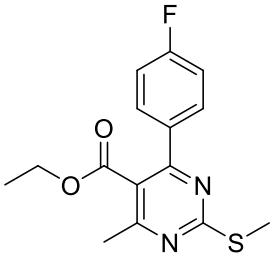
Pale yellow solid, m.p. = 209-210 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 13.89 (s, 1H), 8.47 (d, *J* = 2.1 Hz, 1H), 8.35 – 8.32 (m, 1H), 7.96 – 7.92 (m, 1H), 7.62 (t, *J* = 8.1 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.67 (s, 3H), 1.02 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.10, 158.10, 147.98, 133.94, 129.40, 125.20, 123.23, 111.21, 61.99, 18.80, 13.62 ppm.



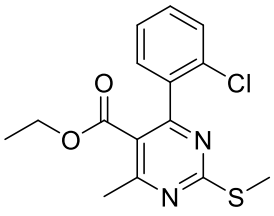
Ethyl 4-methyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (4a): Reddish brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 – 7.62 (m, 2H), 7.44 (dd, *J* = 10.8, 7.0 Hz, 3H), 4.15 (q, *J* = 7.0 Hz, 2H), 2.61 (s, 3H), 2.56 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.47, 168.10, 165.44, 163.56, 130.04, 128.46, 128.41, 128.30, 126.97, 120.93, 61.66, 22.60, 14.15, 13.59 ppm.



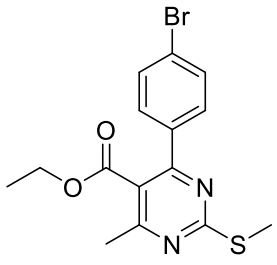
Ethyl 4-methyl-2-(methylthio)-6-(*p*-tolyl)pyrimidine-5-carboxylate (4b): Reddish brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.18 (dd, *J* = 7.2, 1.6 Hz, 2H), 2.60 (s, 3H), 2.54 (s, 3H), 2.40 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.31, 168.33, 165.22, 163.35, 140.41, 134.83, 129.14, 128.31, 120.76, 61.66, 22.56, 21.38, 14.14, 13.67 ppm.



Ethyl 4-(4-fluorophenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (4c): Reddish brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 – 7.63 (m, 2H), 7.14 (t, *J* = 8.7 Hz, 2H), 4.20 (q, *J* = 7.6 Hz, 2H), 2.62 (s, 3H), 2.57 (s, 3H), 1.11 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.56, 168.04, 165.54, 162.30, 130.50, 130.44, 120.79, 115.61, 115.47, 61.76, 22.61, 14.14, 13.70 ppm.

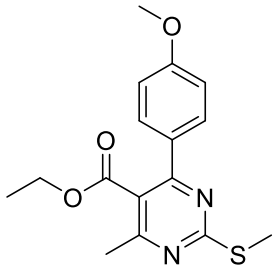


Ethyl 4-(2-chlorophenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate (4d): brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 11.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 4.04 (q, *J* = 6.9 Hz, 2H), 2.65 (s, 3H), 2.58 (s, 3H), 0.92 – 0.89 (t, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.70, 166.33, 163.70, 137.64, 130.09, 129.95, 129.43, 126.57, 121.31, 61.35, 23.49, 14.20, 13.39 ppm.



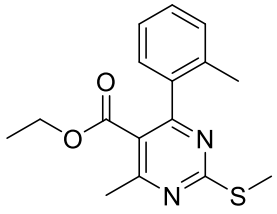
Ethyl 4-(4-bromophenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate

(4e): Reddish brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.53 – 7.49 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 2.55 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.68, 167.87, 165.67, 162.32, 136.61, 131.65, 129.93, 124.76, 61.83, 22.65, 14.16, 13.70 ppm.



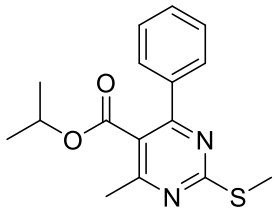
Ethyl4-(4-methoxyphenyl)-6-methyl-2-(methylthio)pyrimidine-5-carboxylate

(4f): Yellow oil . ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 – 7.62 (m, 2H), 6.96 – 6.91 (m, 2H), 4.20 (q, *J* = 7.1, 6.7 Hz, 2H), 3.84 (s, 3H), 2.60 (s, 3H), 2.52 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.16, 168.51, 165.13, 162.63, 161.37, 130.03, 129.95, 120.40, 113.88, 61.68, 55.36, 22.53, 14.13, 13.77 ppm.



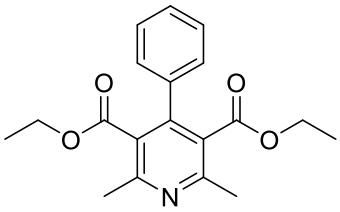
Ethyl 4-methyl-2-(methylthio)-6-(*o*-tolyl)pyrimidine-5-carboxylate (4g):

Reddish brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 6.6 Hz, 1H), 7.20 (d, *J* = 6.6 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 4.06 – 3.91 (m, 2H), 2.61 (s, 3H), 2.58 (s, 3H), 2.27 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.13, 165.89, 165.75, 137.74, 135.85, 130.33, 129.02, 128.04, 125.41, 122.13, 61.32, 22.88, 19.66, 14.13, 13.39 ppm.

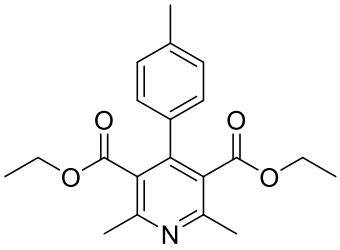


Isopropyl 4-methyl-2-(methylthio)-6-phenylpyrimidine-5-carboxylate (4h):

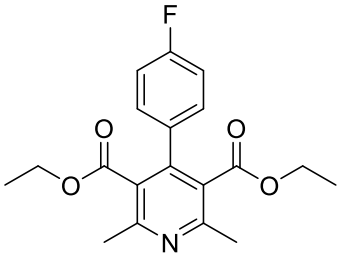
Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.1 Hz, 2H), 7.46 (d, *J* = 9.0 Hz, 3H), 5.15 – 4.99 (m, 1H), 2.63 (s, 3H), 2.58 (s, 3H), 1.09 (d, *J* = 3.1 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.32, 167.57, 165.17, 163.45, 137.80, 129.98, 128.41, 121.47, 69.56, 22.52, 21.29, 14.15 ppm.



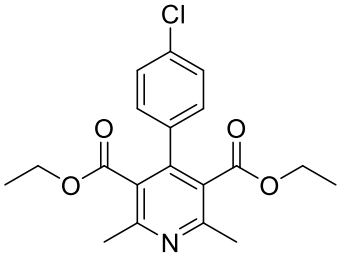
Diethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6a): Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 – 7.31 (m, 3H), 7.23 (dq, *J* = 5.8, 2.3, 1.8 Hz, 2H), 3.97 (qd, *J* = 7.1, 1.2 Hz, 4H), 2.58 (d, *J* = 1.2 Hz, 6H), 0.87 (td, *J* = 7.1, 1.3 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.80, 155.35, 146.05, 136.54, 128.34, 128.05, 128.01, 126.87, 61.26, 22.86, 13.49 ppm.



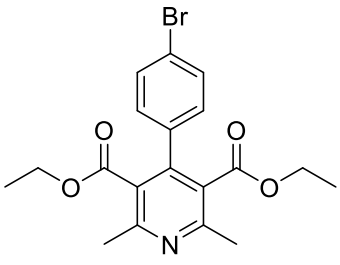
Diethyl 2,6-dimethyl-4-(*p*-tolyl)pyridine-3,5-dicarboxylate (6b): Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 – 7.45 (m, 2H), 7.22 – 7.19 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.52, 168.37, 156.35, 155.15, 142.61, 138.74, 136.78, 129.00, 128.17, 61.61, 61.46, 23.10, 21.24, 16.84, 14.17, 13.65 ppm.



Diethyl 4-(4-fluorophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6c): Pale brown oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.58 – 7.53 (m, 2H), 7.09 (t, *J* = 8.8 Hz, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.59 (s, 3H), 2.34 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 168.26, 155.28, 142.85, 130.25, 130.20, 128.50, 128.16, 127.19, 115.38, 115.24, 61.71, 61.58, 23.06, 16.85, 14.16, 13.67 ppm.

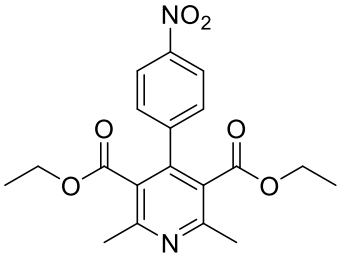


Diethyl 4-(4-chlorophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6d): Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.17 (dd, *J* = 8.2, 1.5 Hz, 2H), 4.04 – 3.99 (m, 4H), 2.57 (d, *J* = 1.6 Hz, 6H), 0.95 (td, *J* = 7.1, 1.7 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.54, 155.54, 134.92, 129.54, 128.25, 126.73, 61.41, 22.89, 13.60 ppm.



Diethyl 4-(4-bromophenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6e):

Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 4H), 2.59 (s, 6H), 0.97 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.55, 155.59, 135.41, 131.23, 129.82, 126.67, 122.80, 61.46, 22.91, 13.62 ppm.



Diethyl 2,6-dimethyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate (6f):

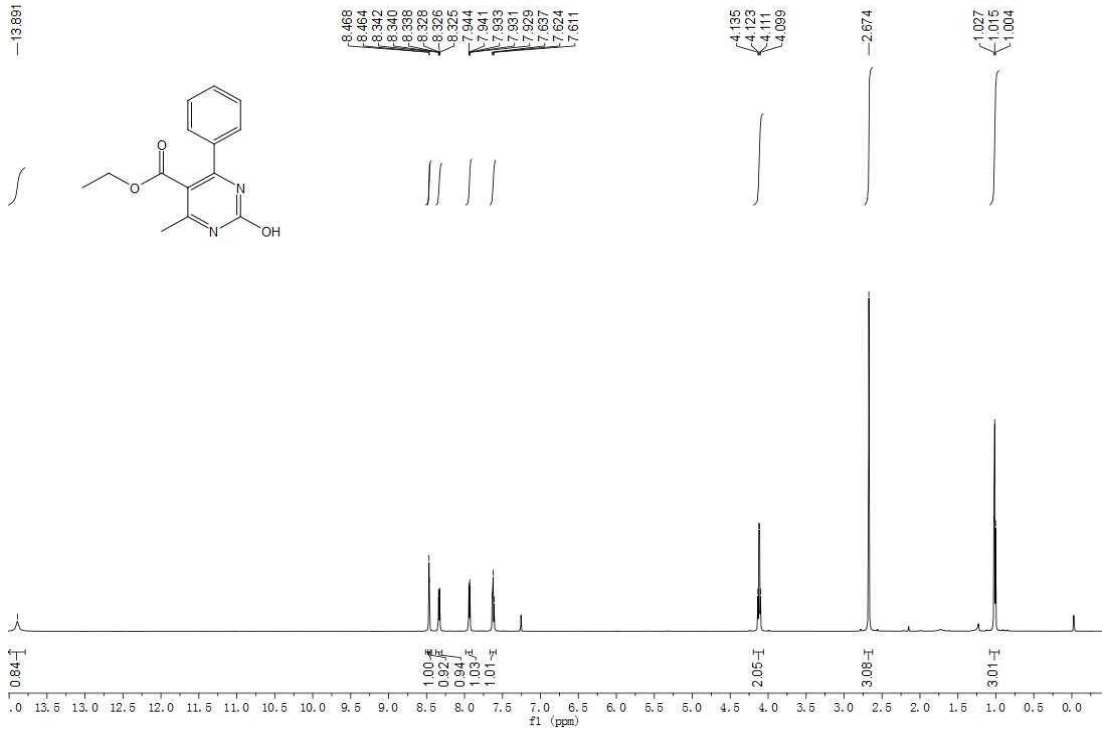
Pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.27 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.60 (s, 3H), 2.37 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.82, 167.68, 153.85, 147.99, 145.77, 143.31, 129.55, 129.41, 127.48, 123.48, 61.90, 61.85, 23.02, 16.91, 14.16, 13.69 ppm.

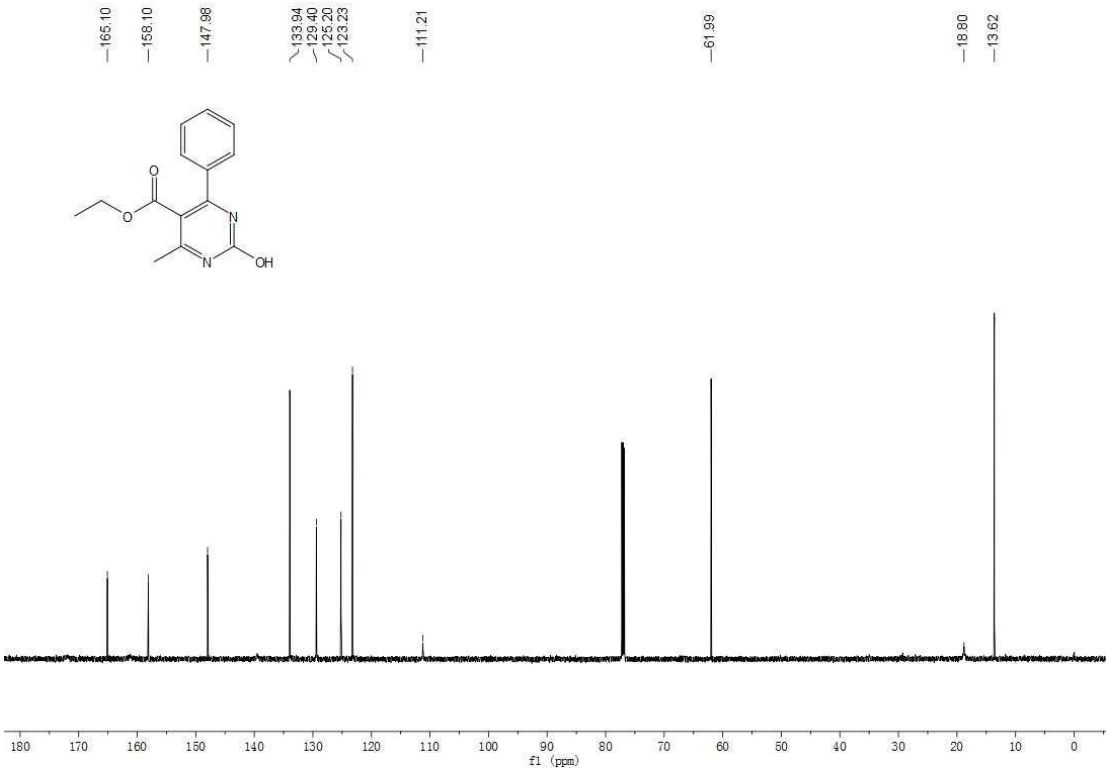
3. References

1. Yamamoto, K.; Chen, Y. G.; Buono, F. G. *Organic Lett*. **2005**, 7, 4673-4676.
2. Phan, N. H. T.; Sohn, J.-H. *Tetrahedron* **2014**, *70*, 7929-7935.
3. Wang, L, Ma, Z.-G., Wei, X.-J., Meng, Q.-Y., Yang, D.-T., Du, S.-F., Chen, Z.-F., Wu, L.-Z. and Liu, Q.. *Green Chem*. **2014**, *16*, 3752-3757.
4. Wei, X.-j., Wang, L., Jia, W.-L., Du, S.-F., Wu, L.-Z. Liu, Q.. *Chin. J. Chem.* **2014**, *32*, 1245-1250.
5. Han, B., Liu, Z.-G., Liu, Q., Yang, L., Liu, Z.-L. and Yu, W.. *Tetrahedron* **2006,** *62*, 2492-2496.

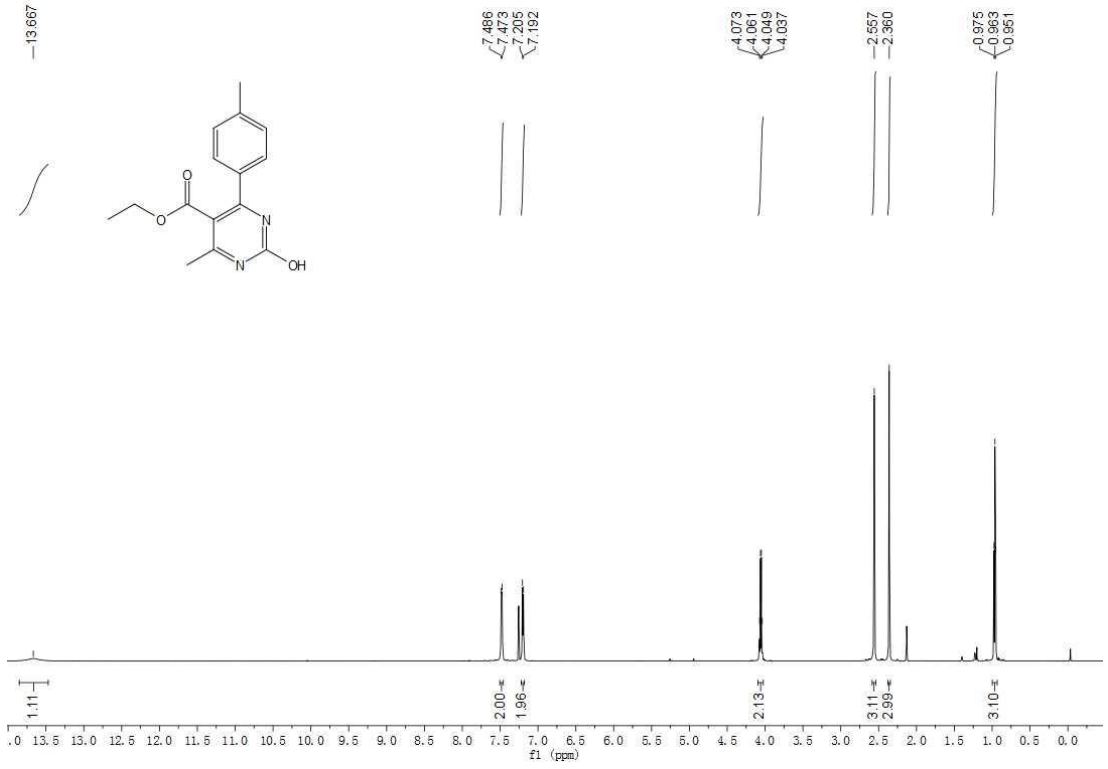
4. Copies of the NMR Spectra for all products

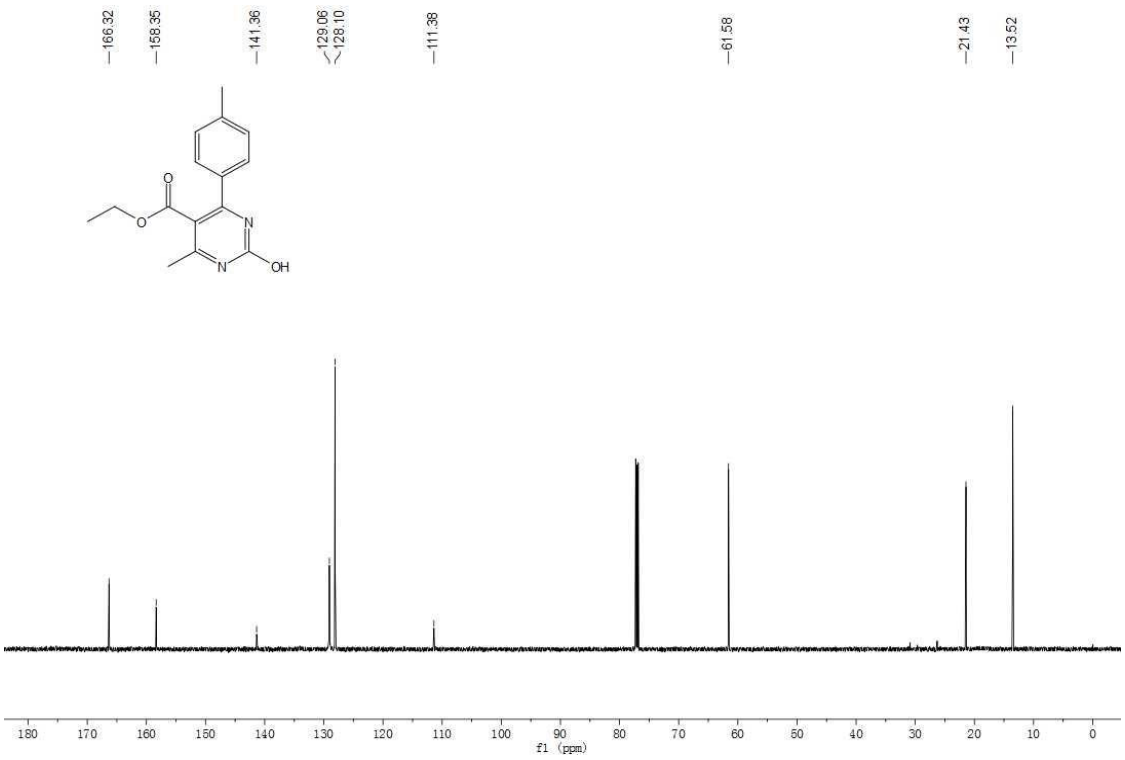
^{1}H and ^{13}C Spectra of compound 2a ($CDCl_3$, 600 MHz)



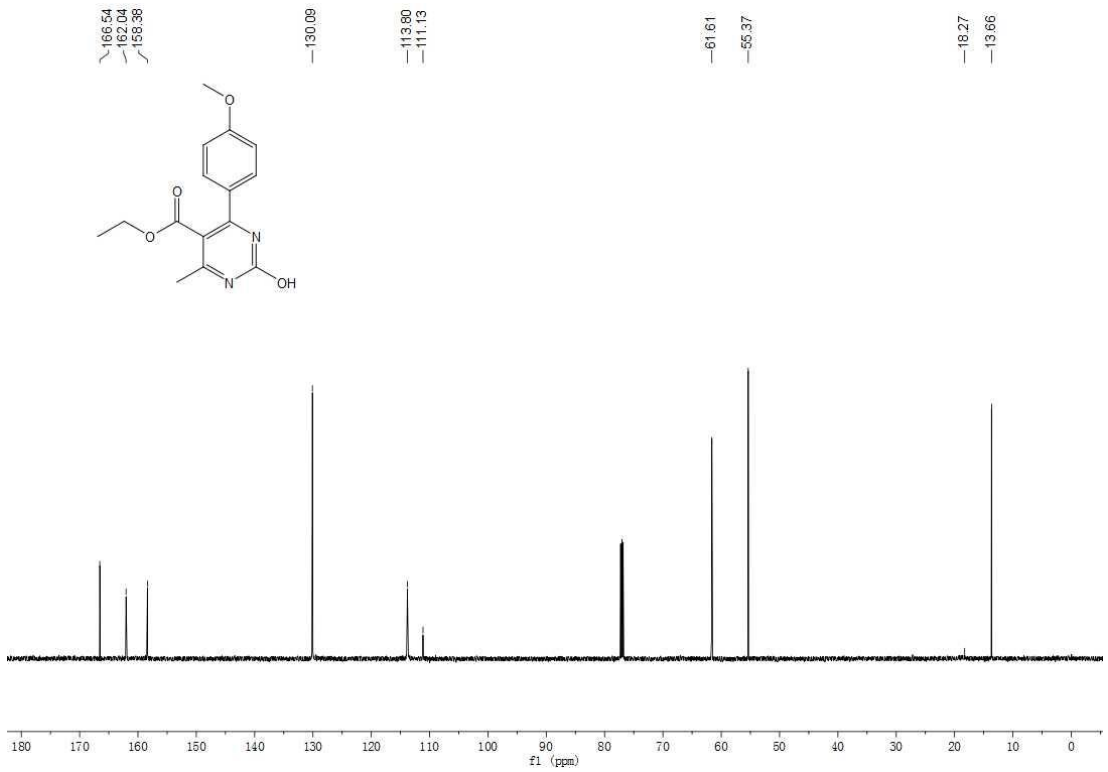


^{1}H and ^{13}C Spectra of compound 2b ($CDCl_3$, 600 MHz)

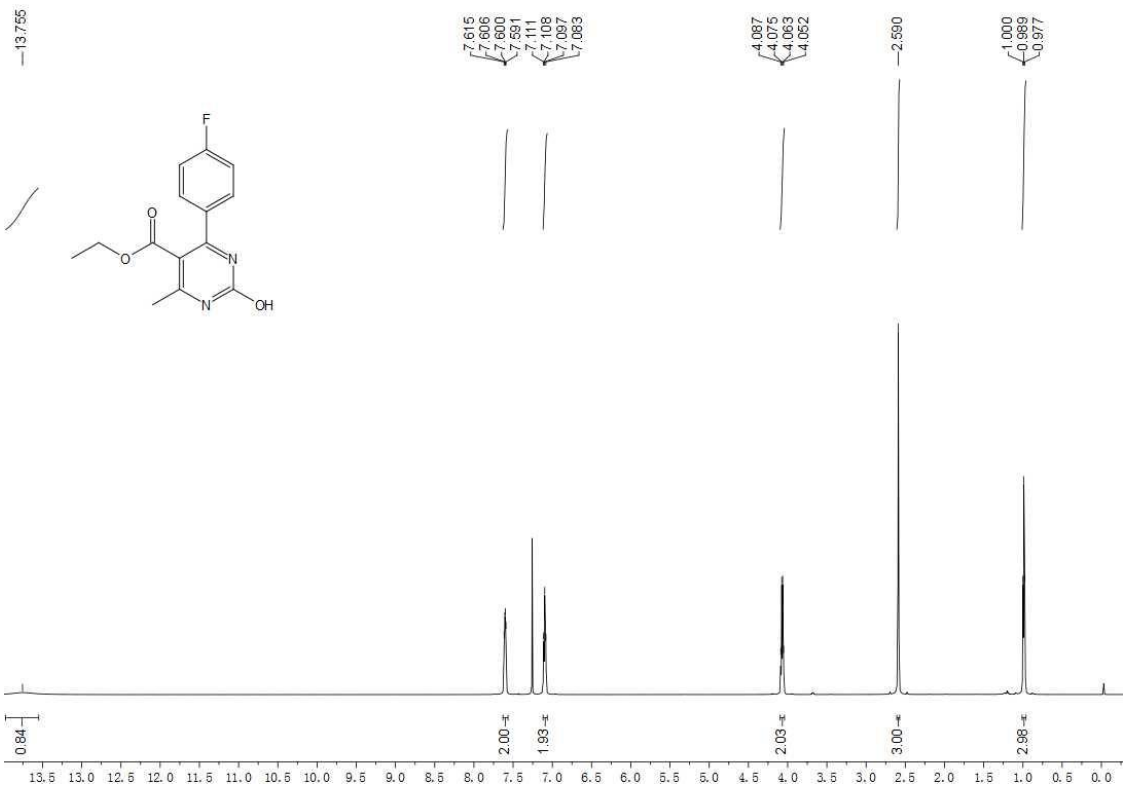


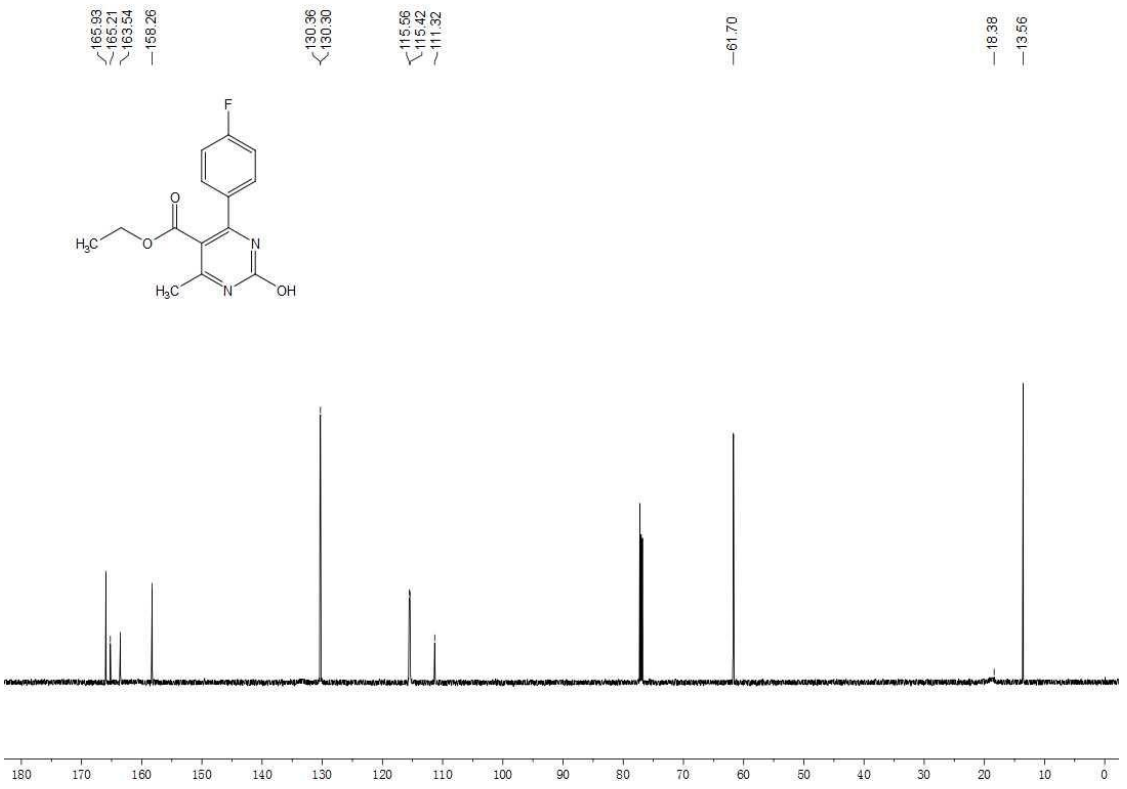


^{1}H and ^{13}C Spectra of compound 2c ($CDCl_3$, 600 MHz)

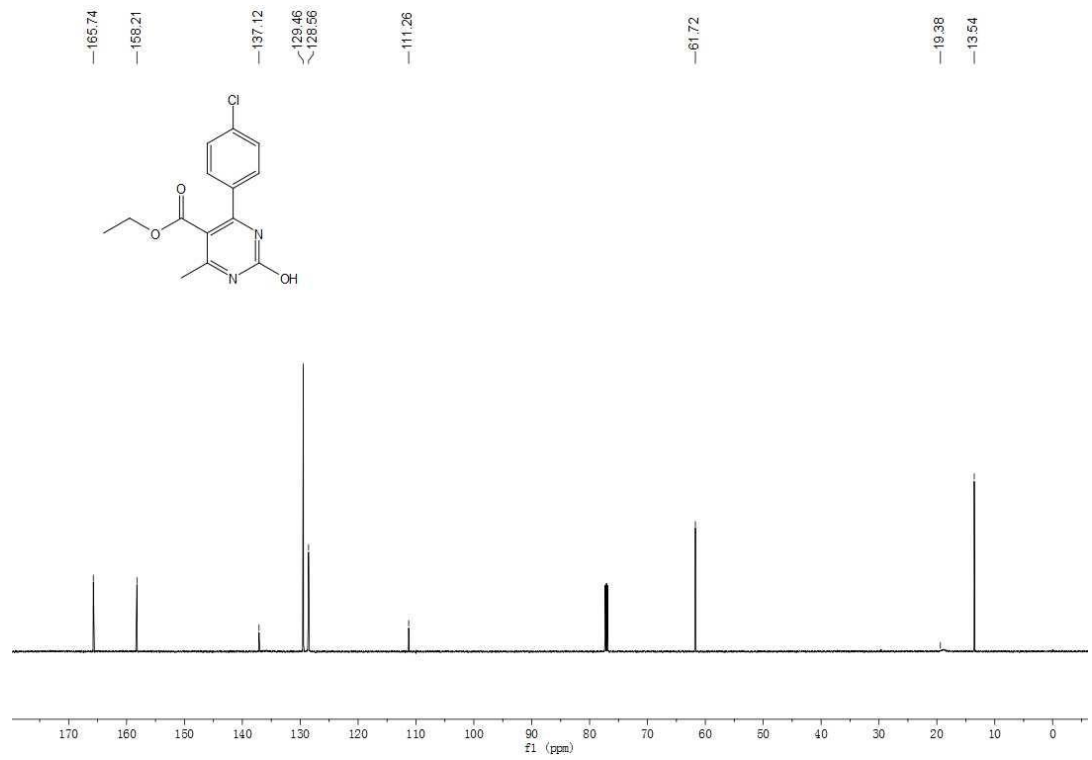


^{1}H and ^{13}C Spectra of compound 2d ($CDCl_3$, 600 MHz)

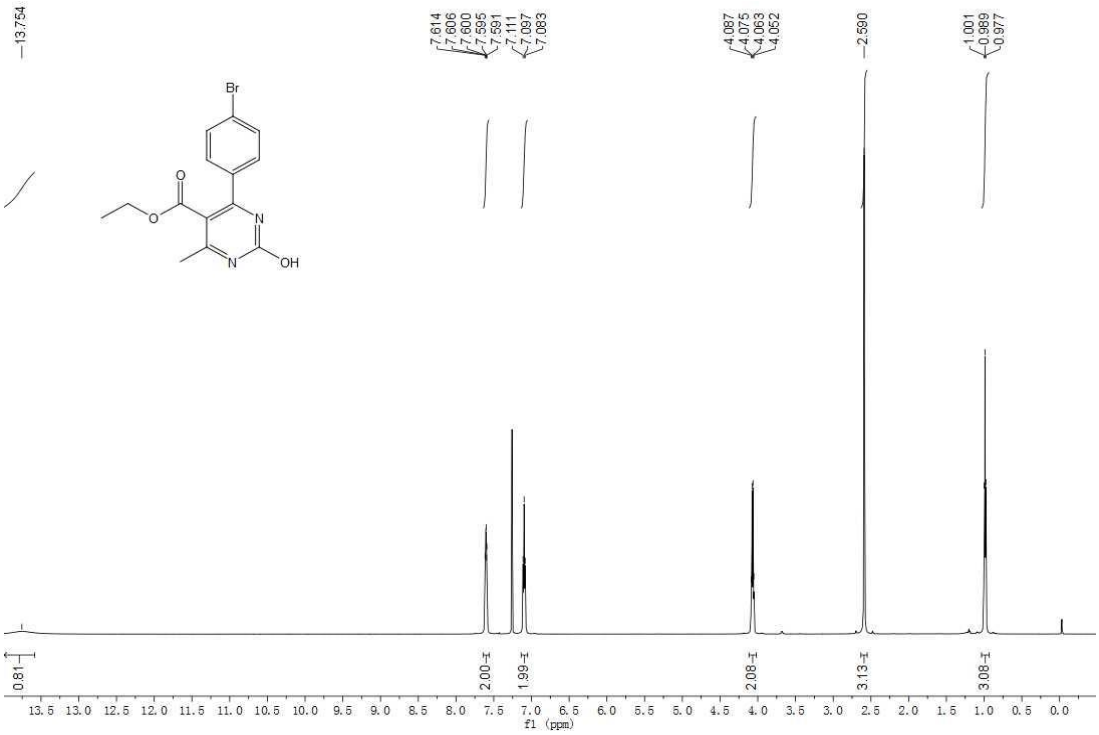


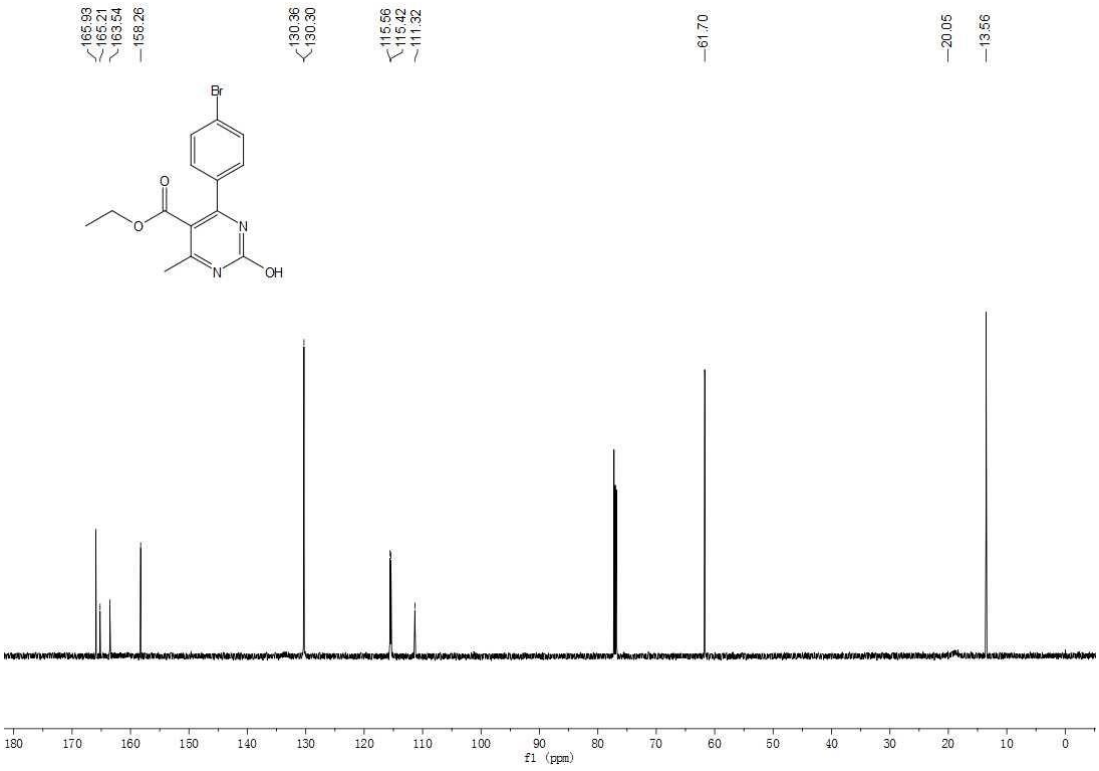


^{1}H and ^{13}C Spectra of compound 2e ($CDCl_3$, 600 MHz)

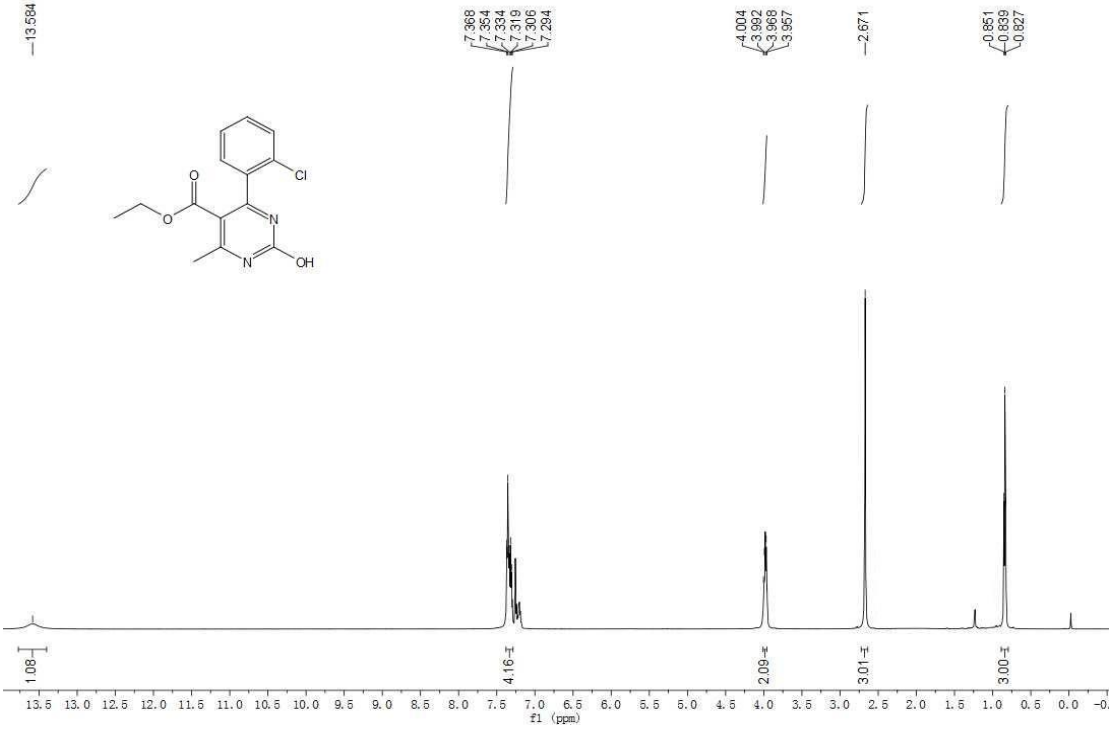


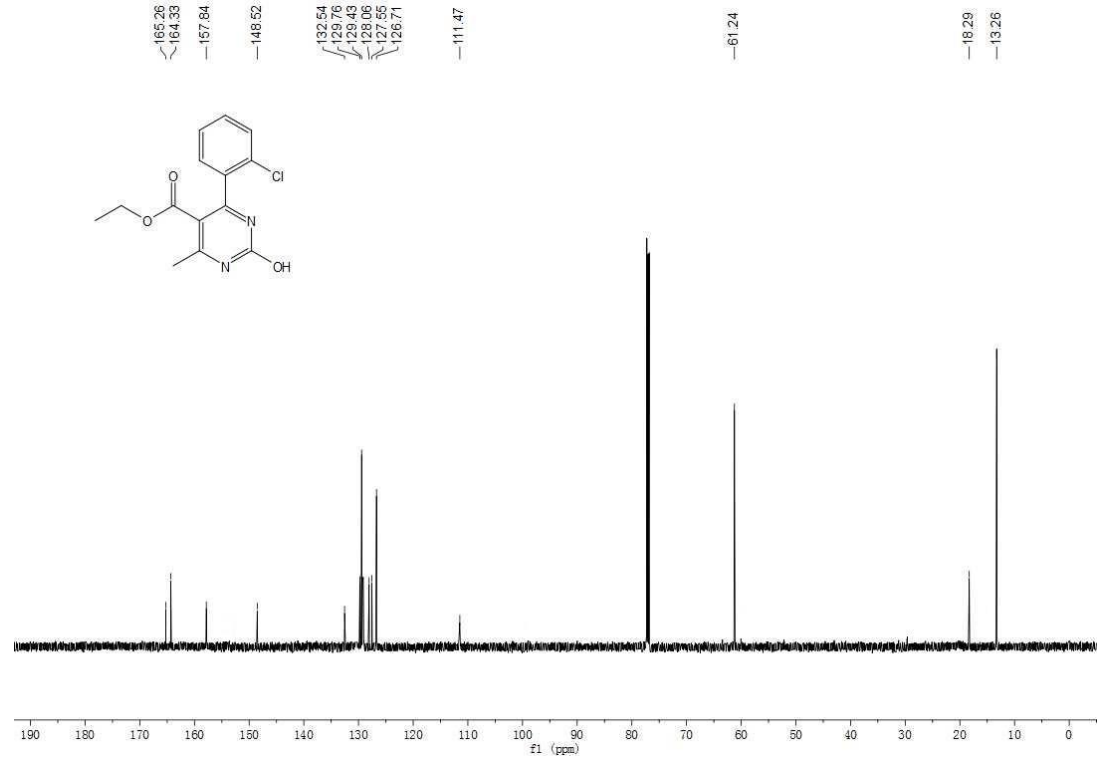
^{1}H and ^{13}C Spectra of compound 2f ($CDCl_3$, 600 MHz)



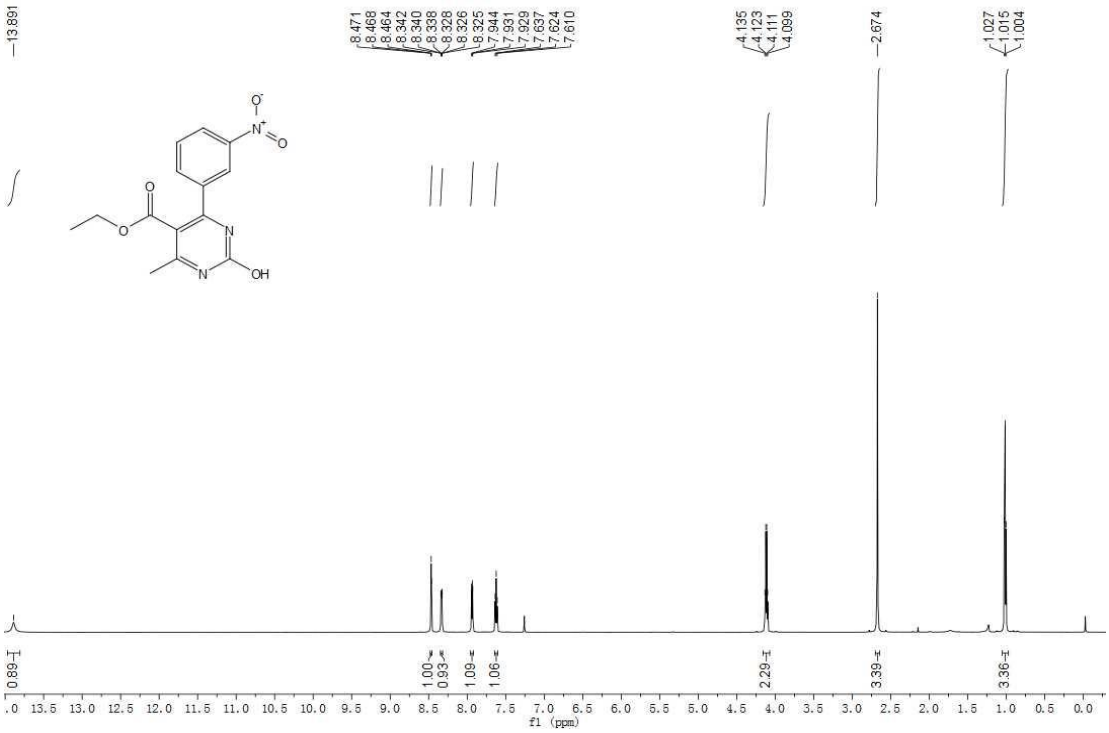


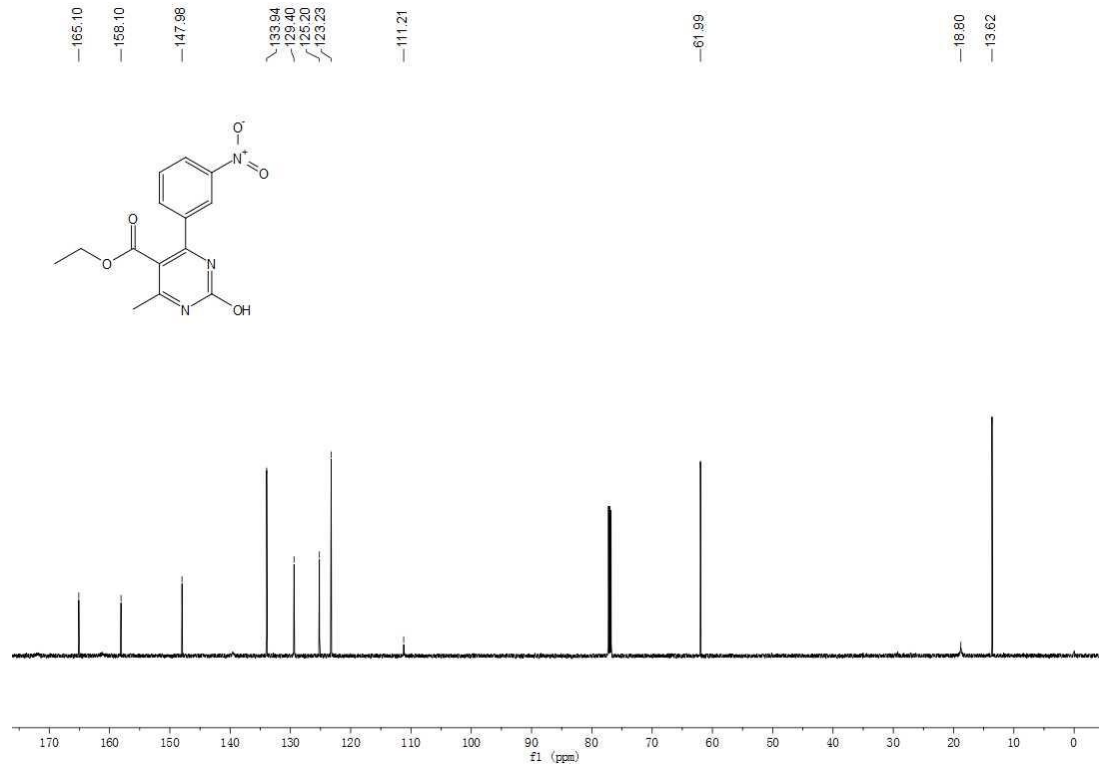
^{1}H and ^{13}C Spectra of compound 2g ($CDCl_3$, 600 MHz)



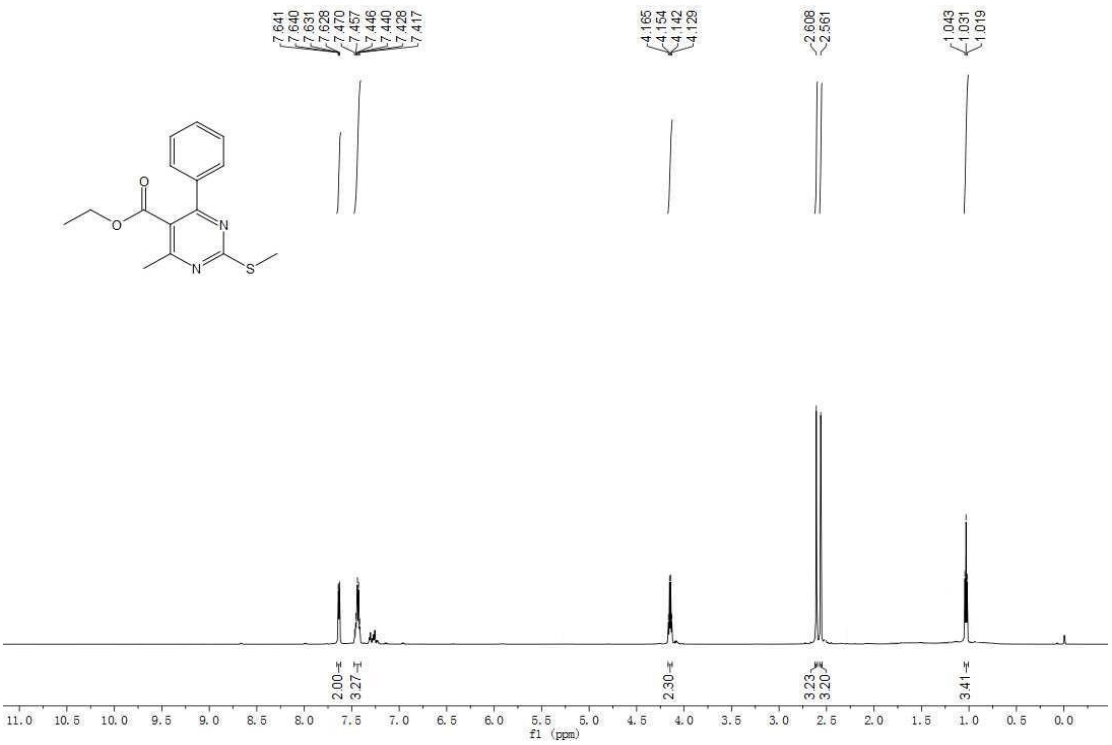


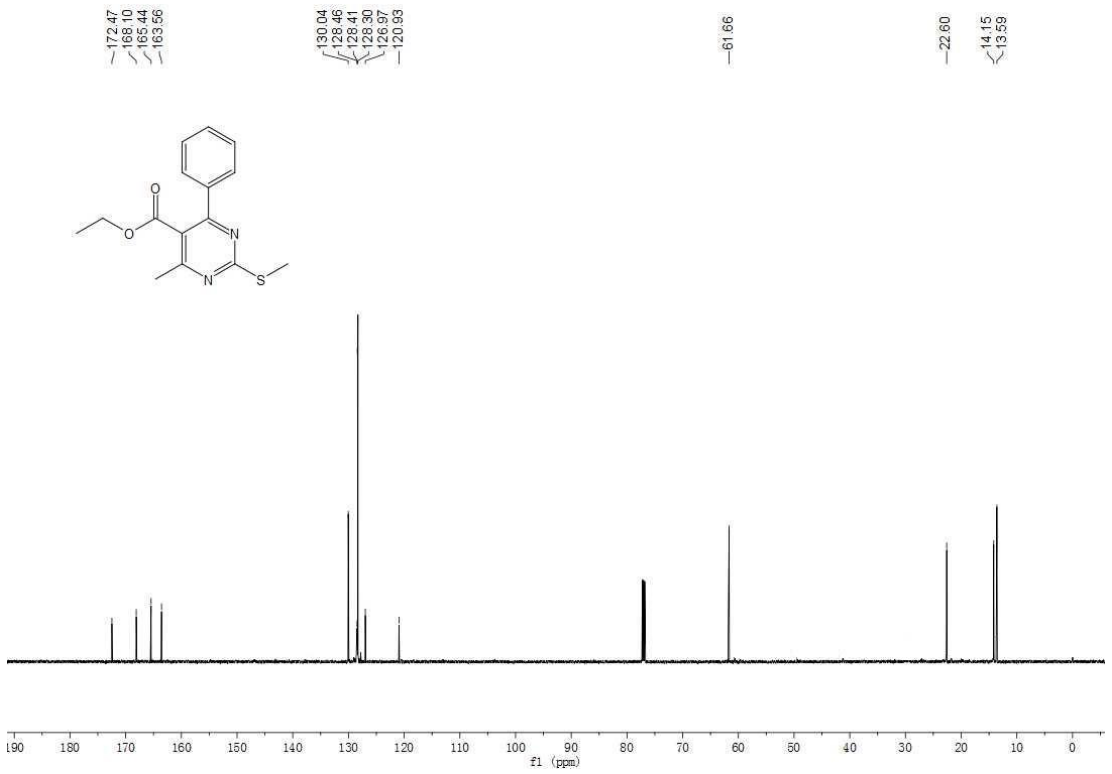
^{1}H and ^{13}C Spectra of compound 2h ($CDCl_3$, 600 MHz)



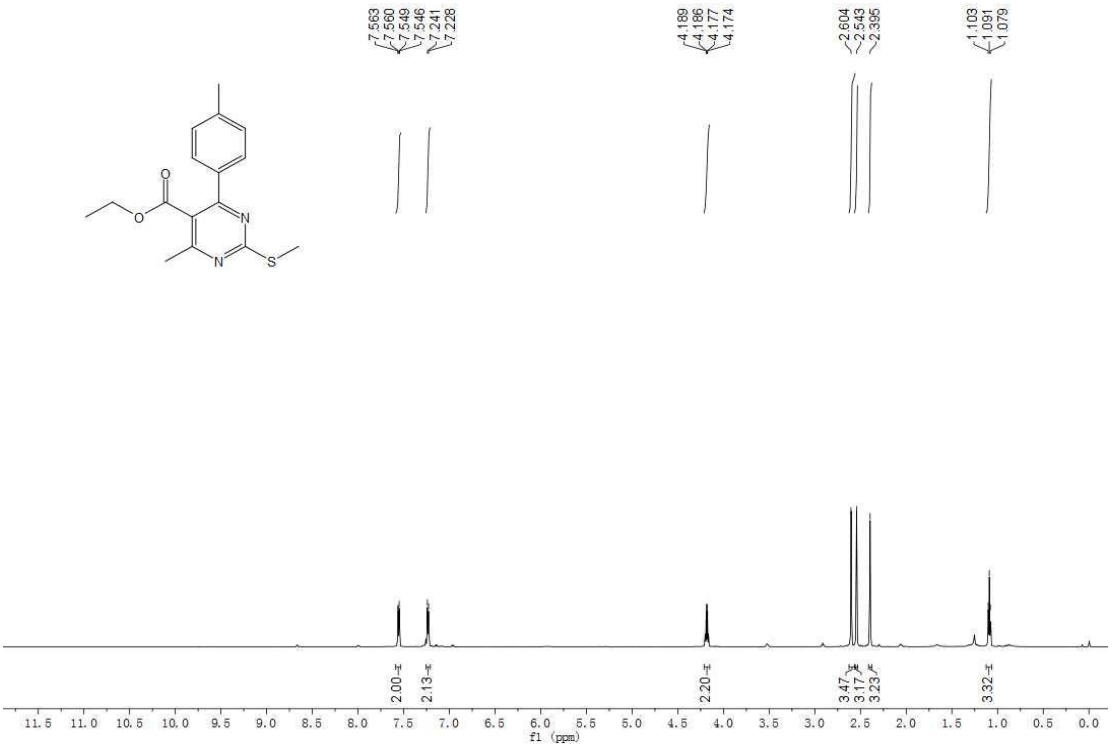


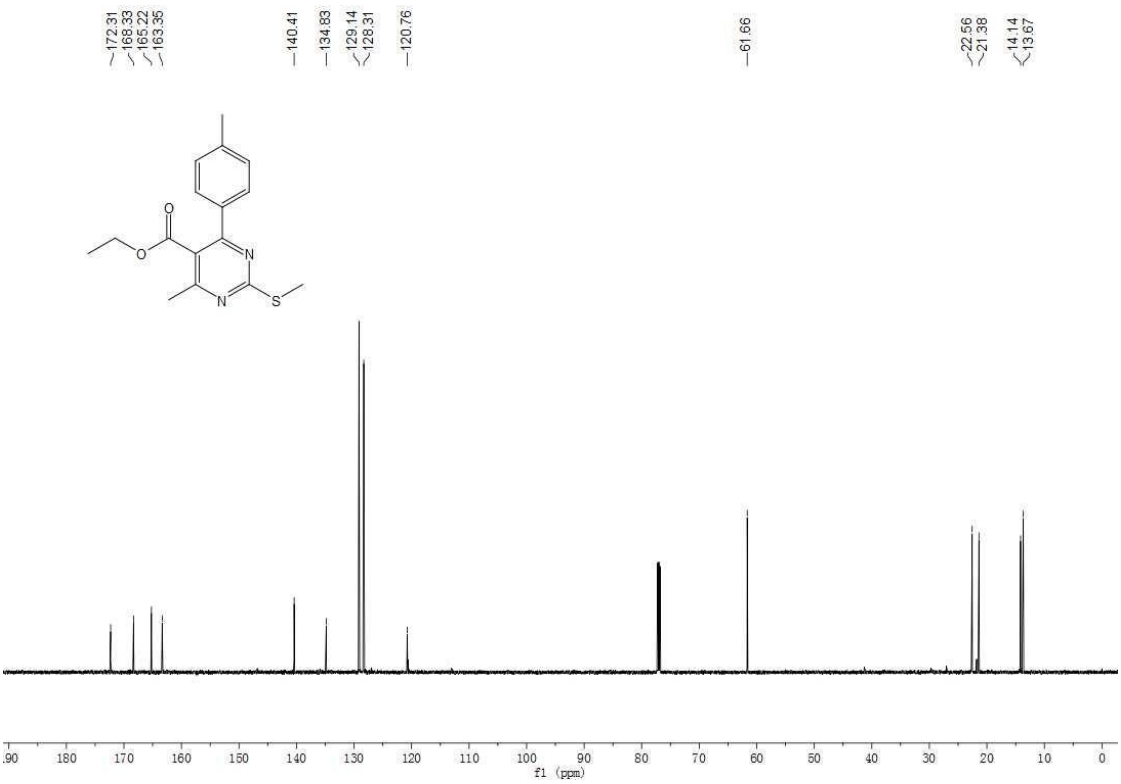
^{1}H and ^{13}C Spectra of compound 4a ($CDCl_3$, 600 MHz)



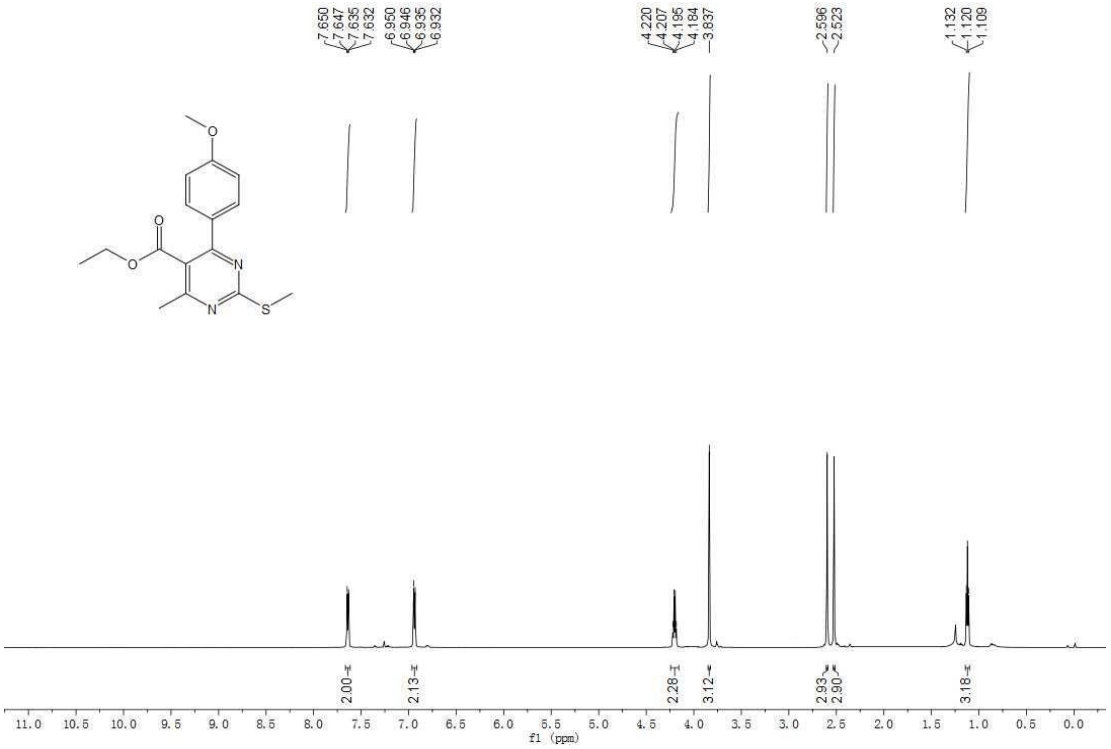


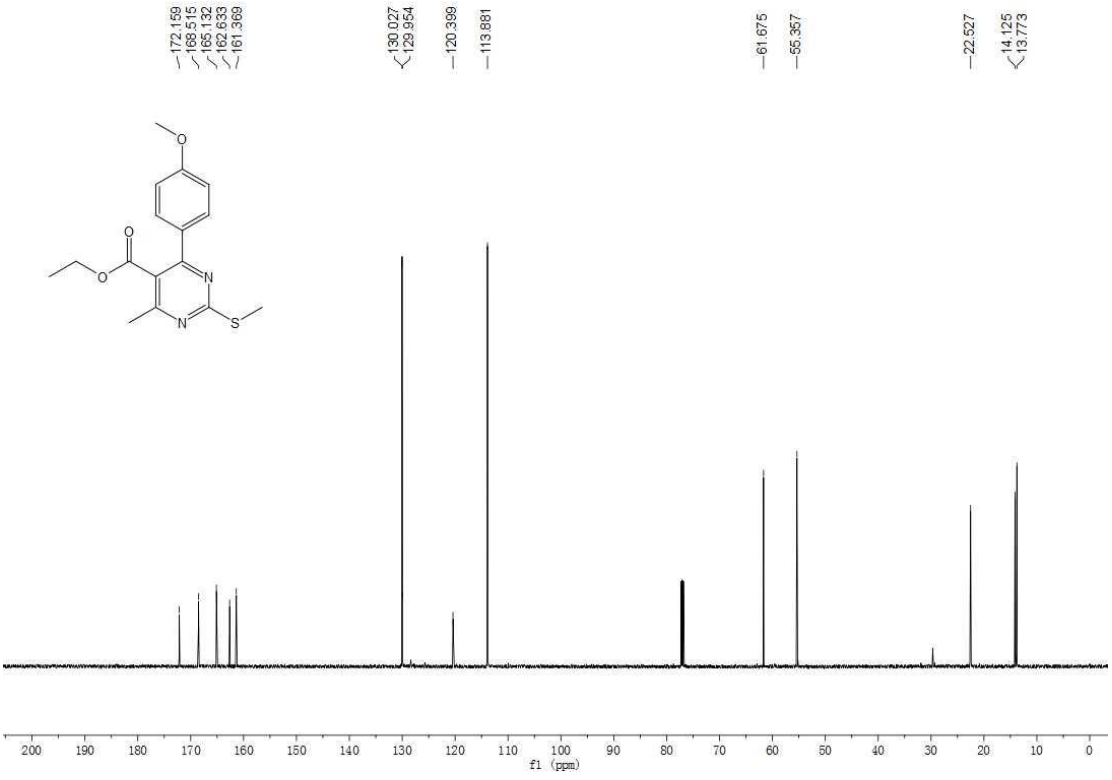
^{1}H and ^{13}C Spectra of compound 4b ($CDCl_3$, 600 MHz)



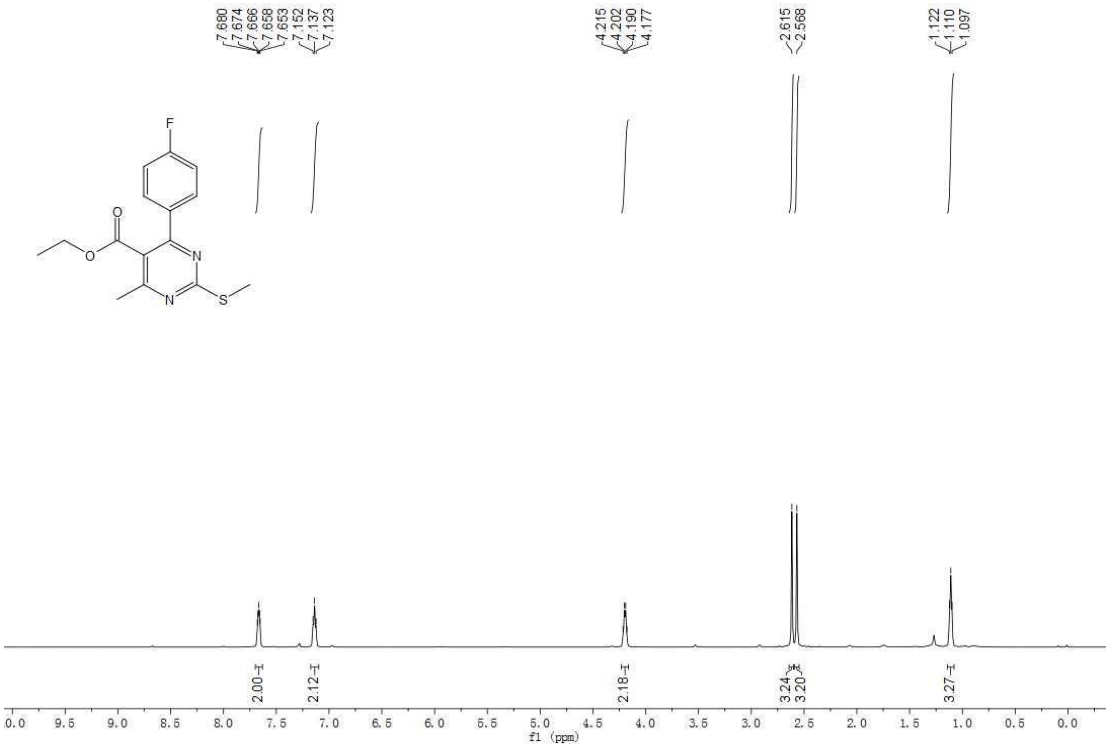


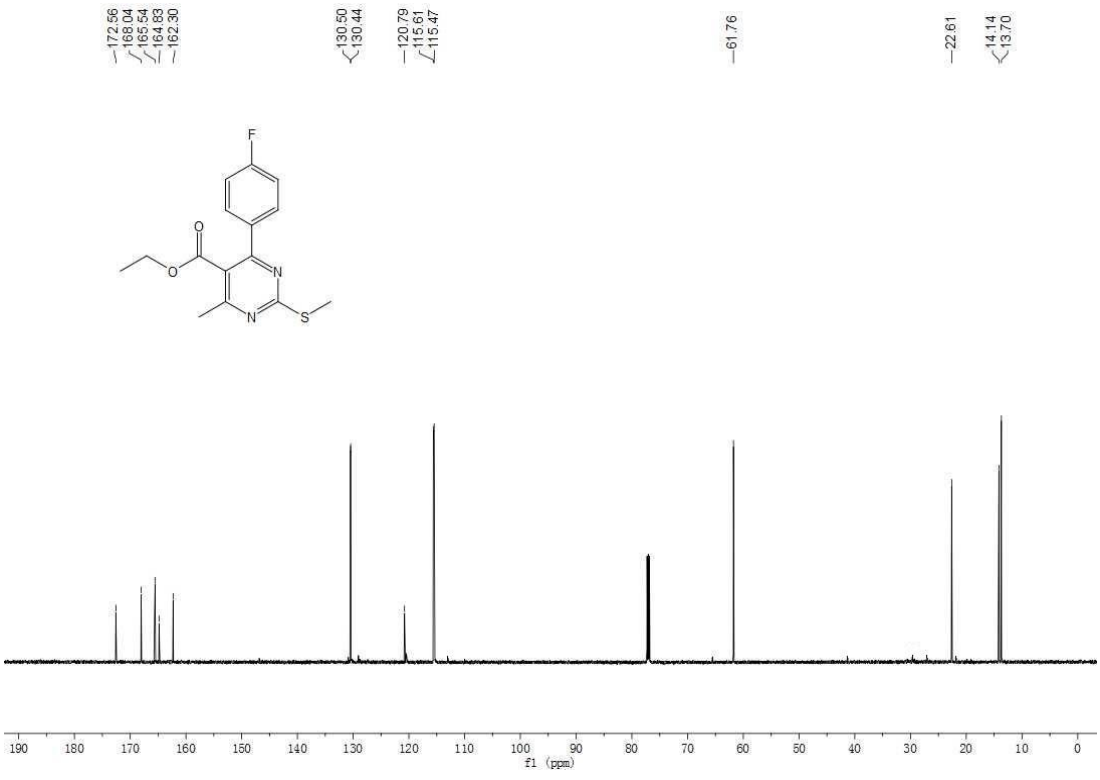
^{1}H and ^{13}C Spectra of compound 4c ($CDCl_3$, 600 MHz)



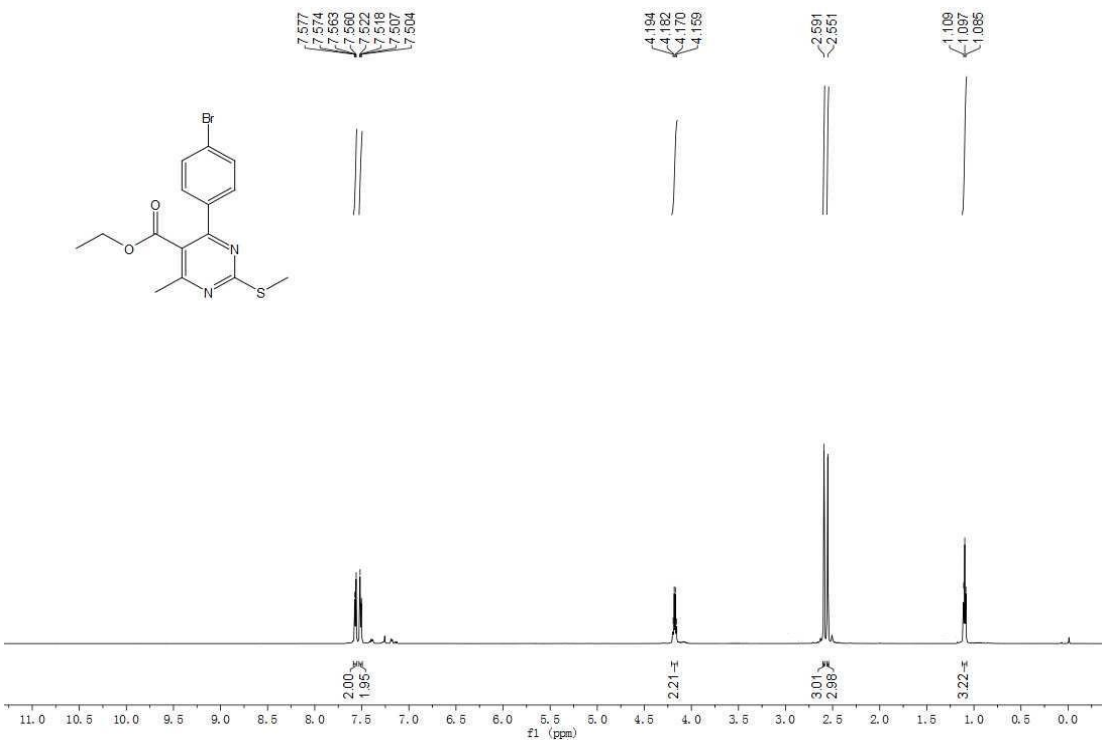


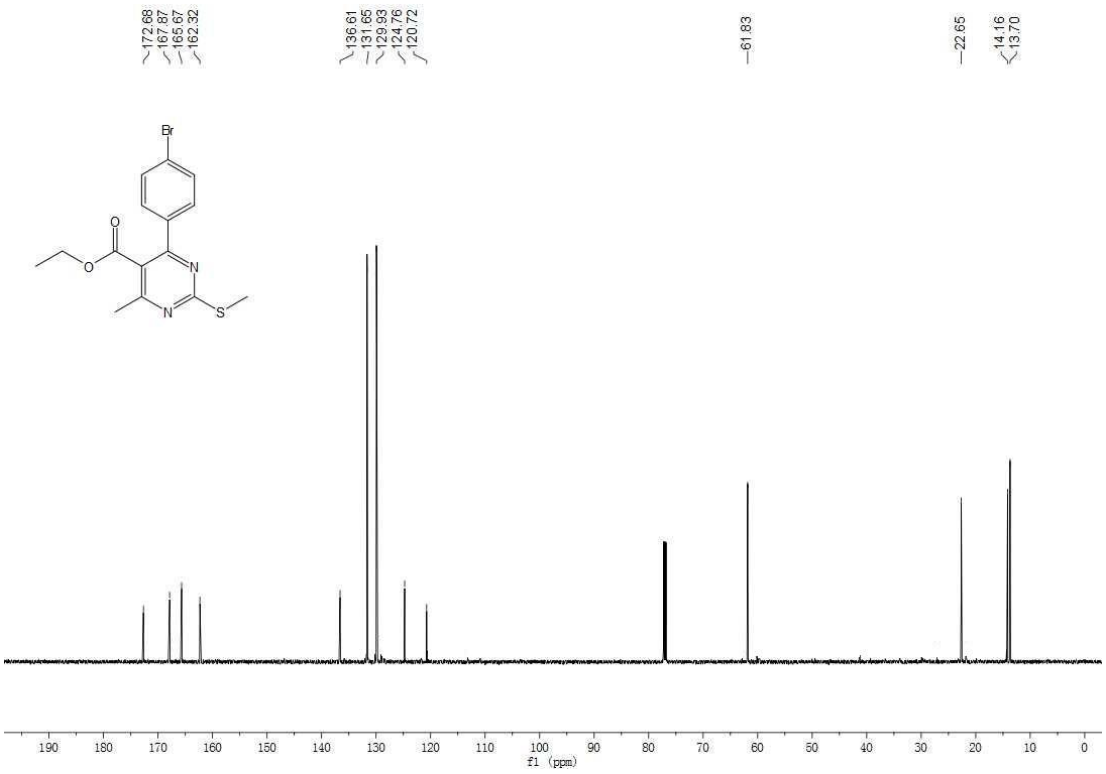
^{1}H and ^{13}C Spectra of compound 4d ($CDCl_3$, 600 MHz)



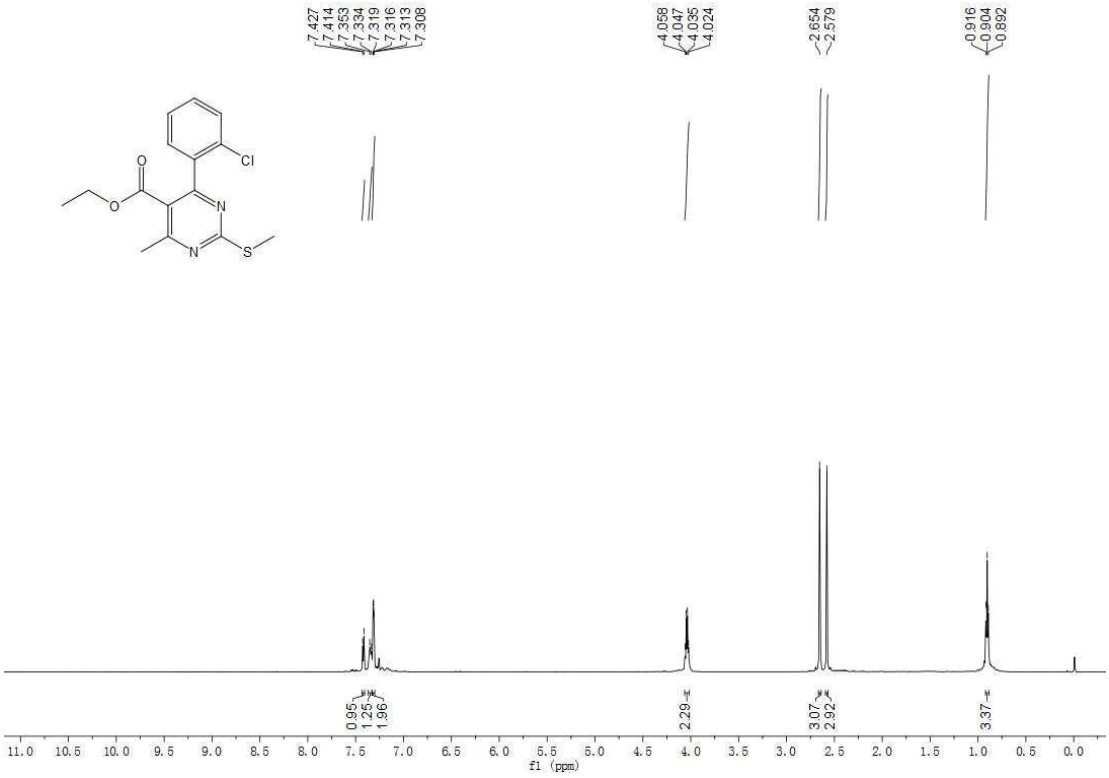


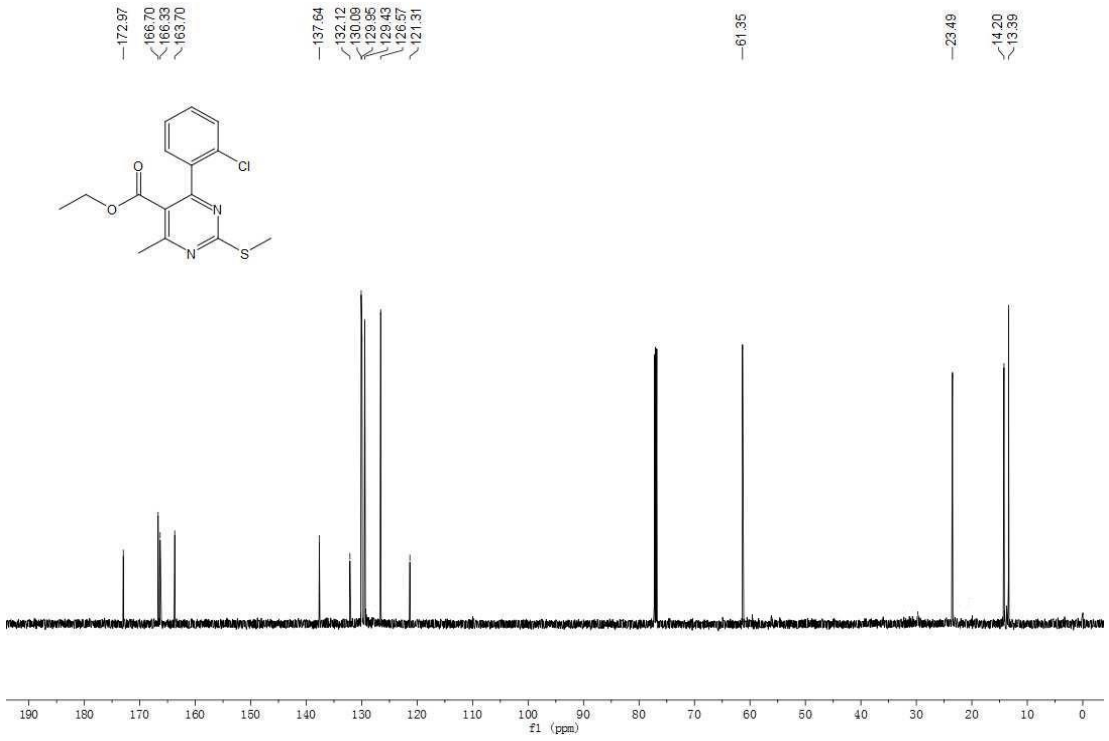
^{1}H and ^{13}C Spectra of compound 4e ($CDCl_3$, 600 MHz)



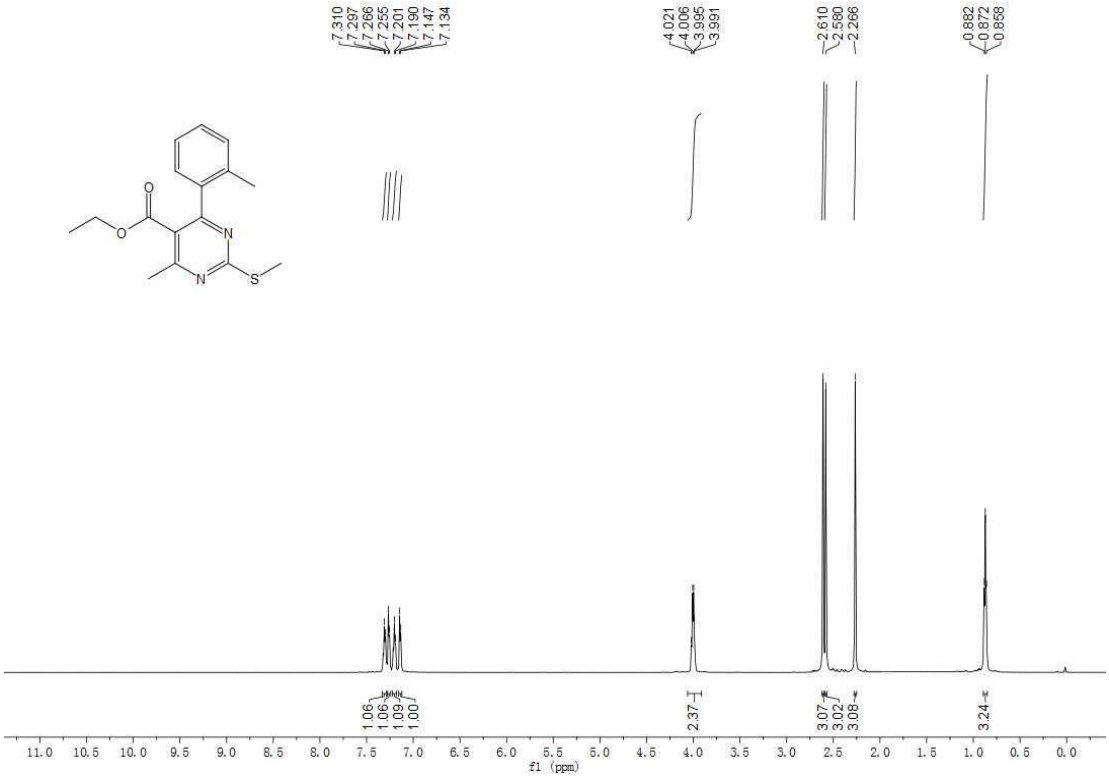


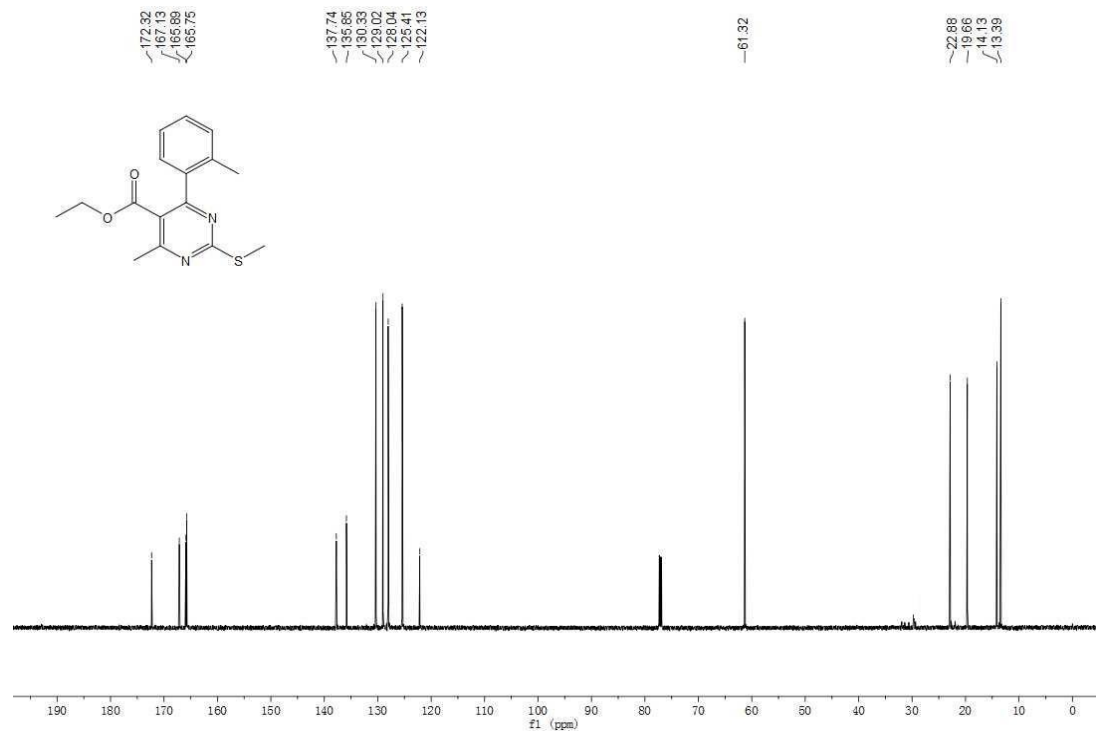
^{1}H and ^{13}C Spectra of compound 4f ($CDCl_3$, 600 MHz)



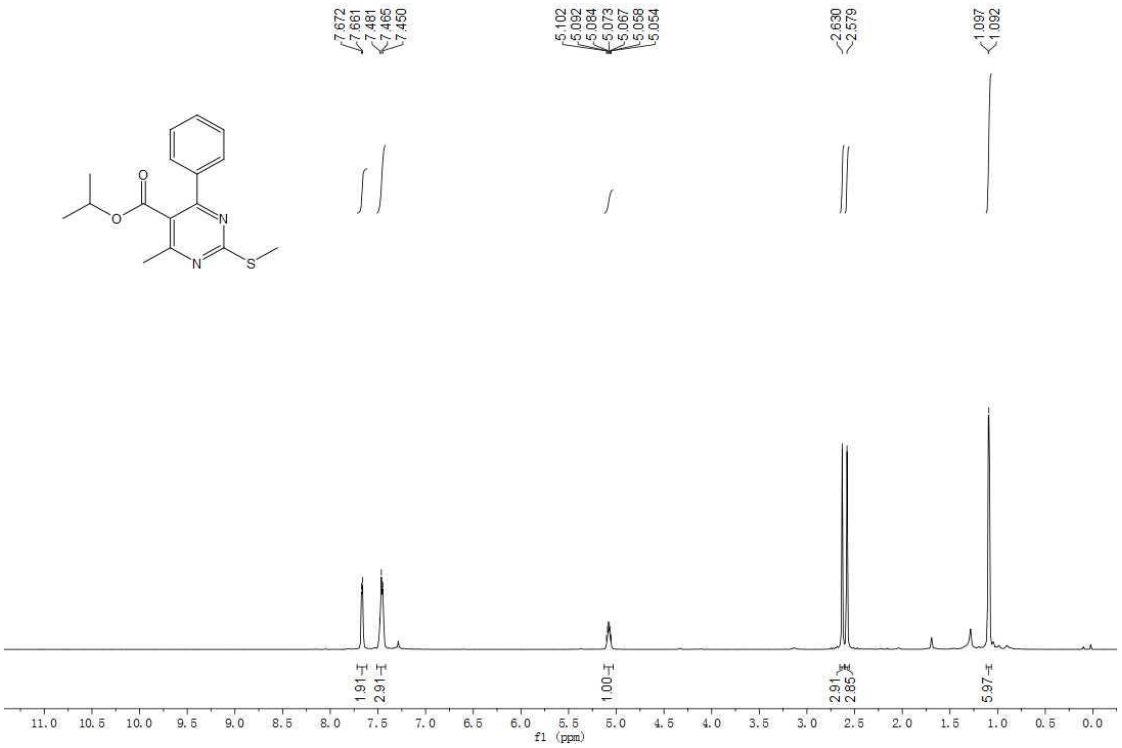


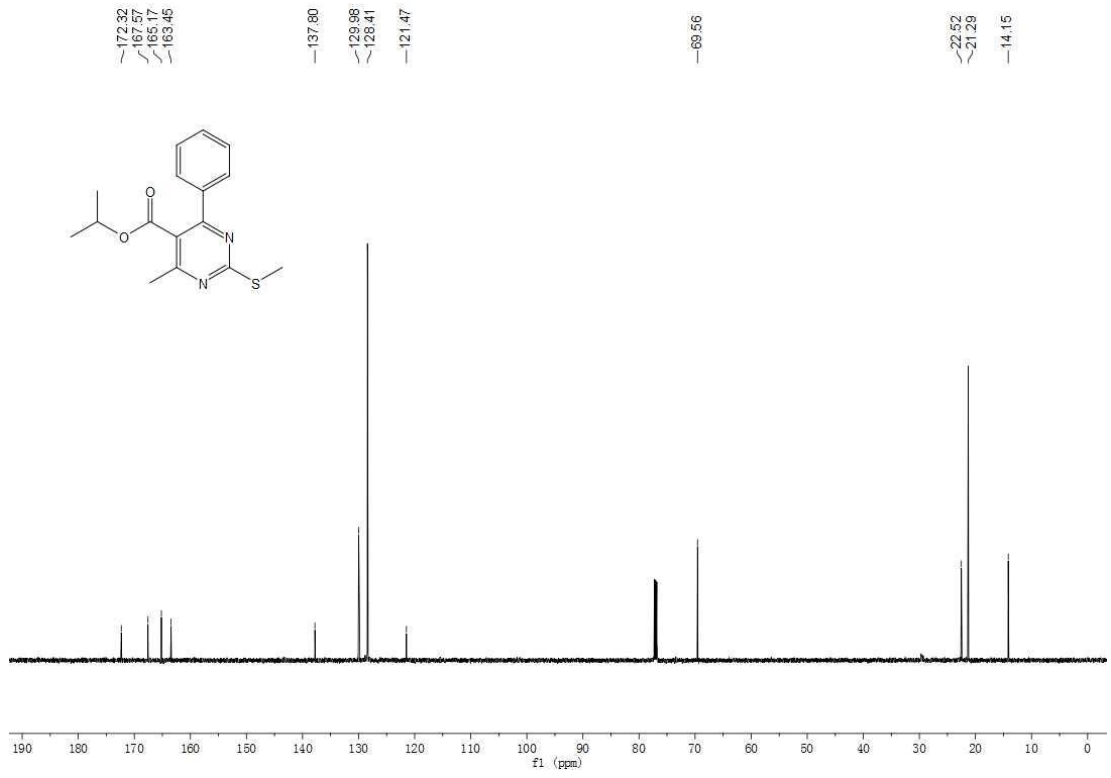
^{1}H and ^{13}C Spectra of compound 4g ($CDCl_3$, 600 MHz)



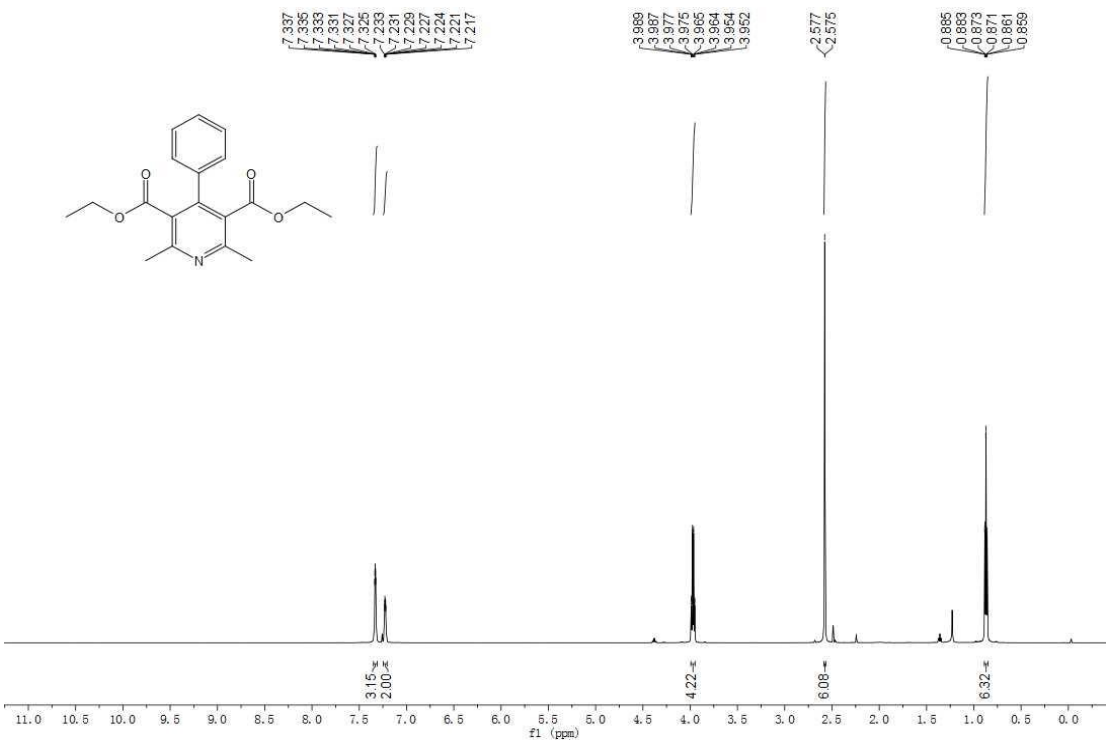


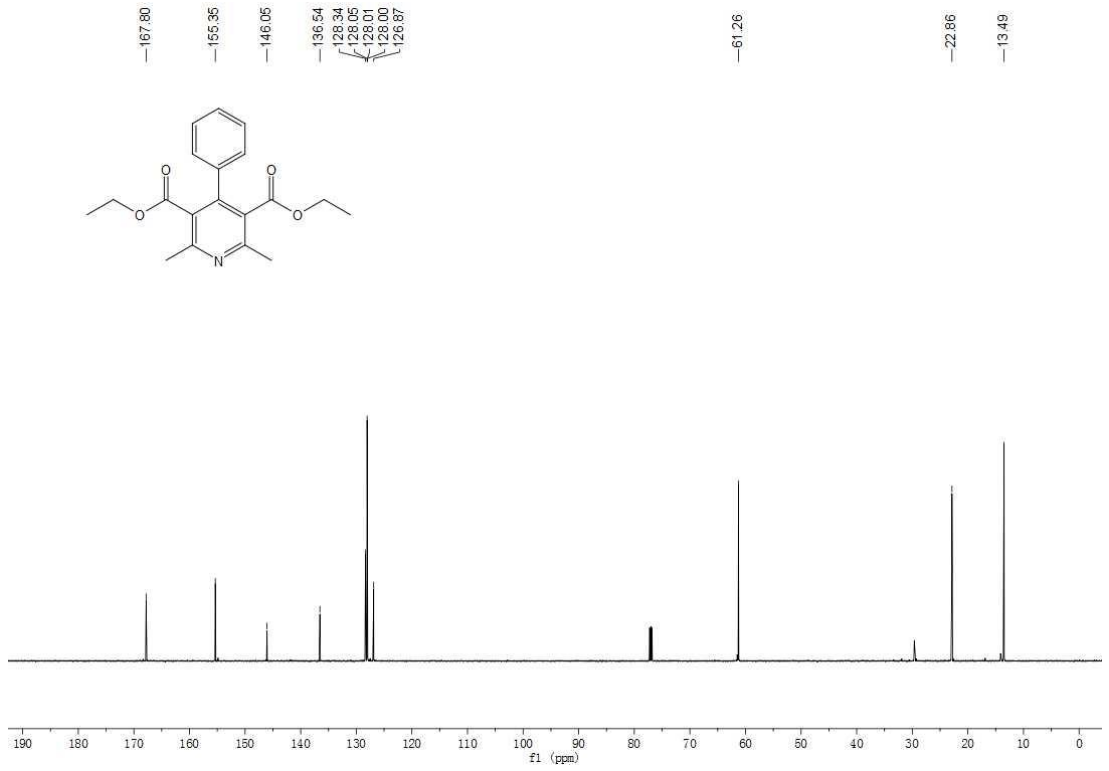
^{1}H and ^{13}C Spectra of compound 4h ($CDCl_3$, 600 MHz)



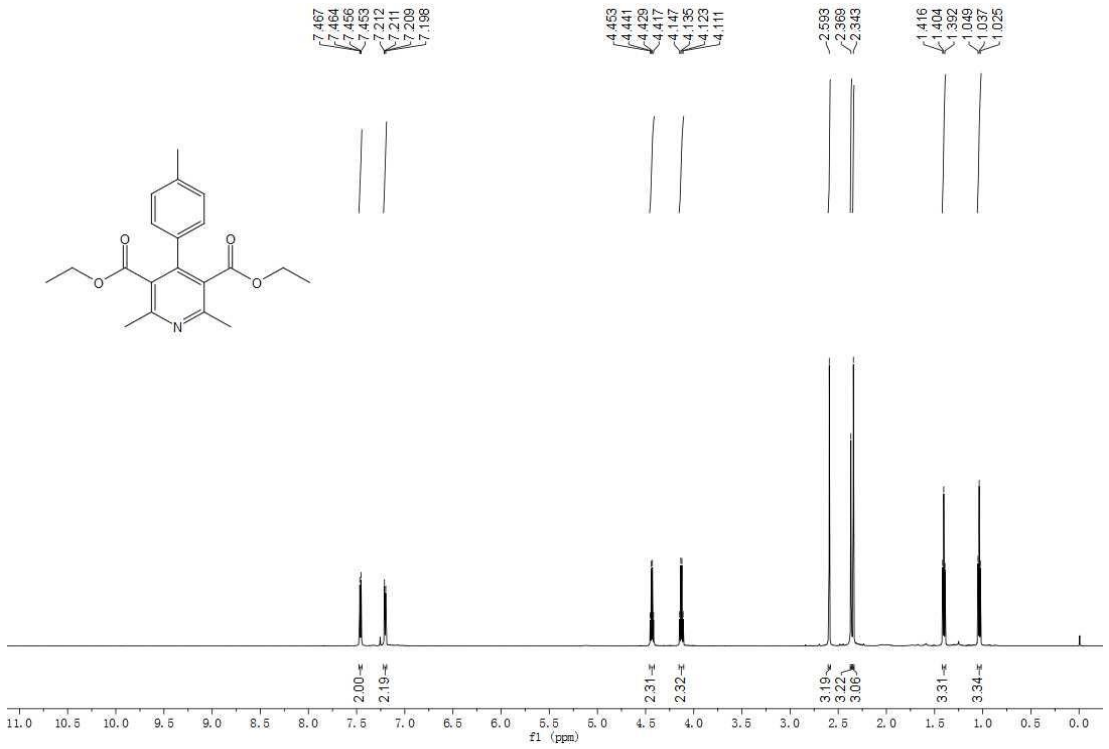


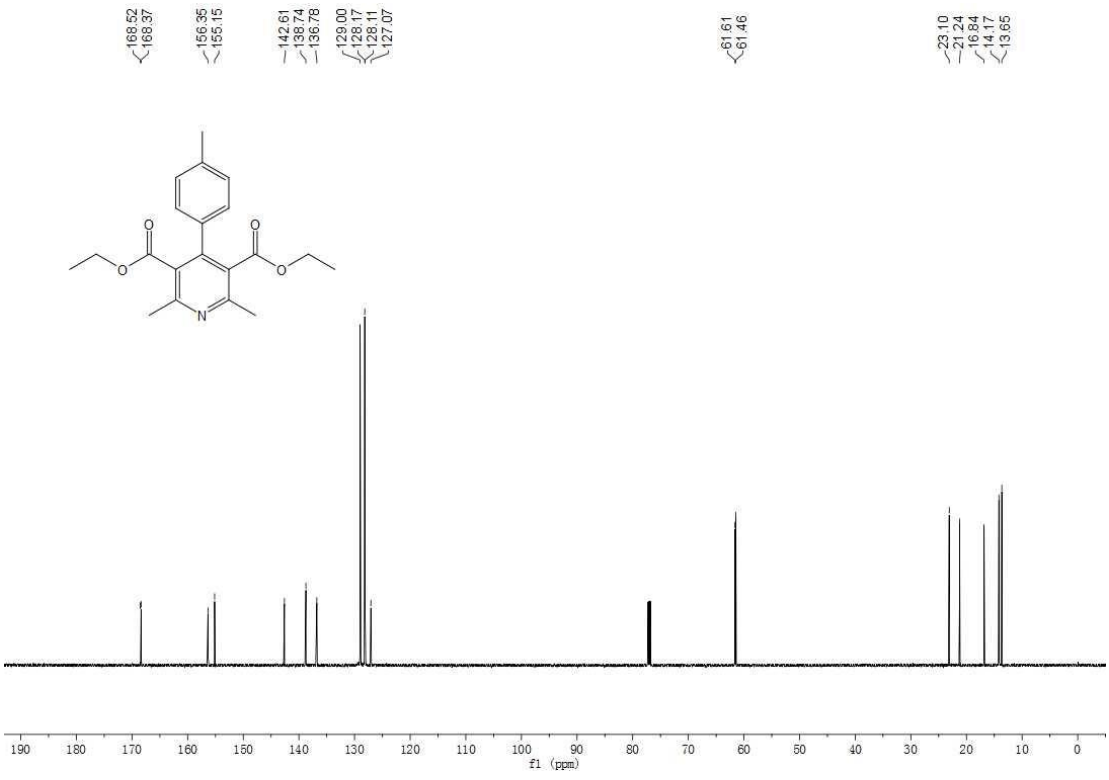
^{1}H and ^{13}C Spectra of compound 6a ($CDCl_3$, 600 MHz)



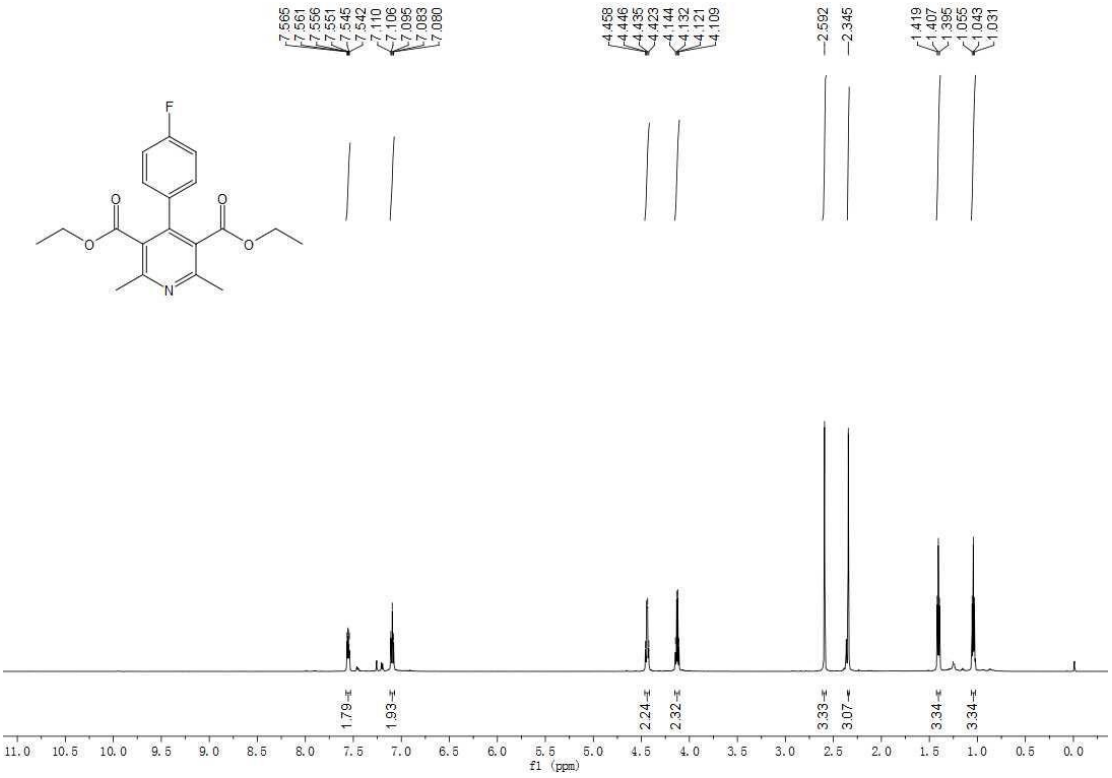


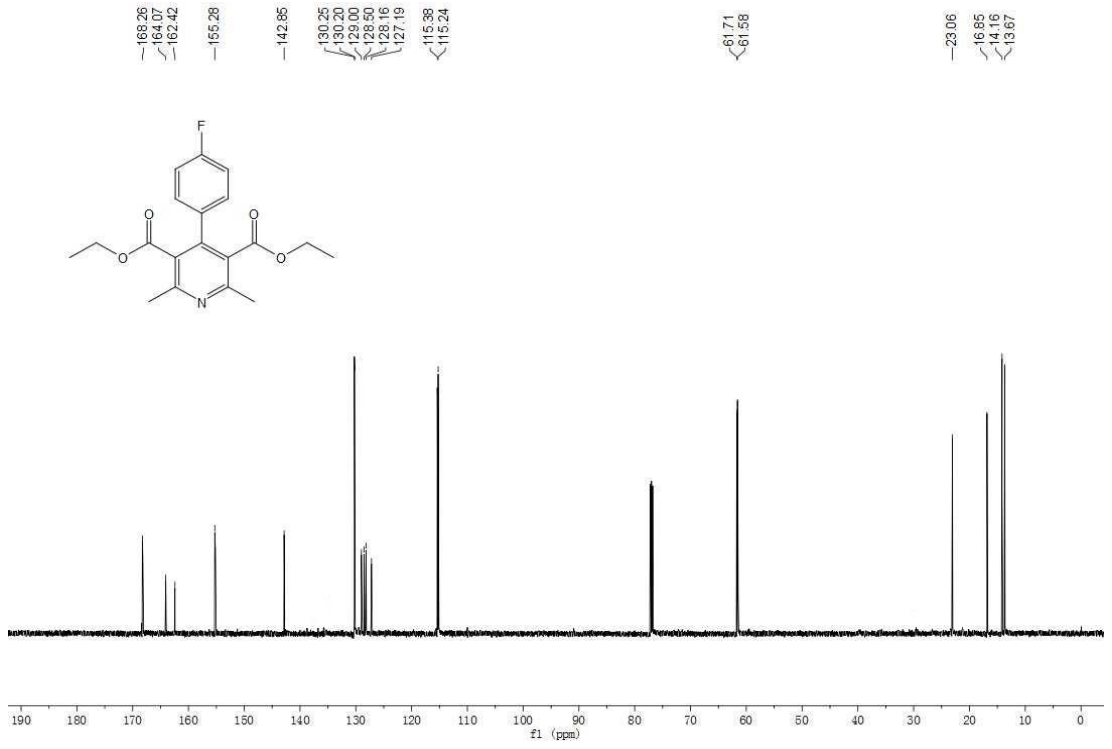
^{1}H and ^{13}C Spectra of compound 6b ($CDCl_3$, 600 MHz)



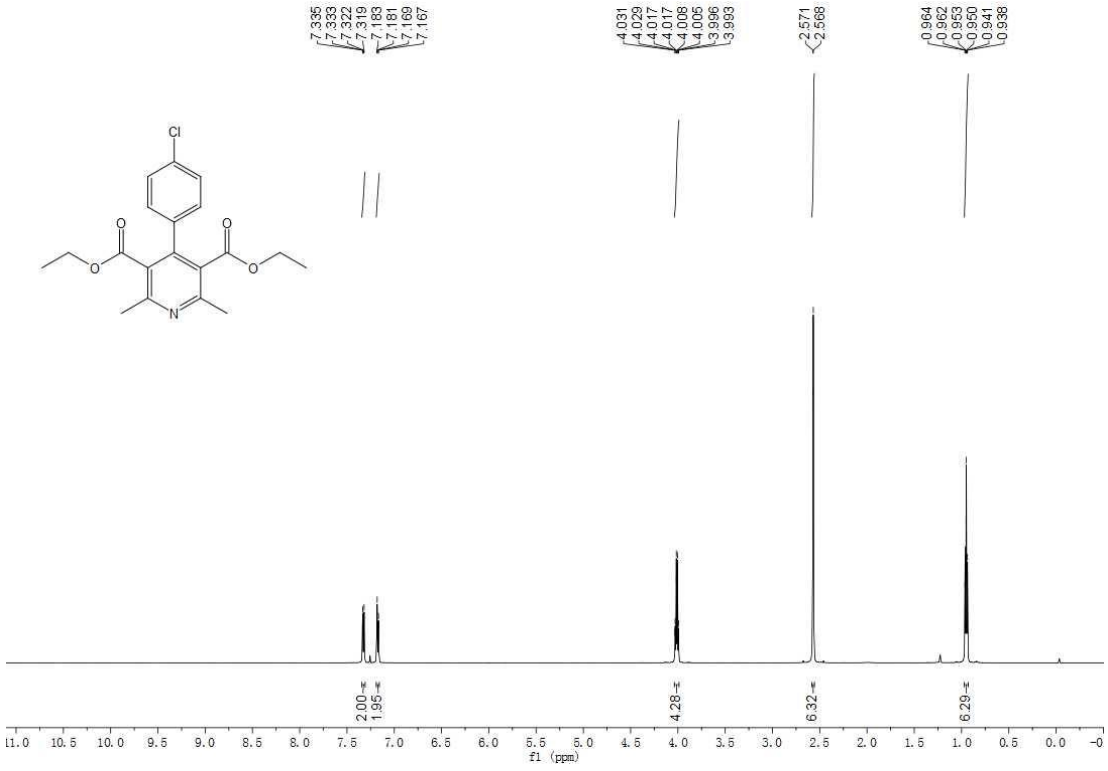


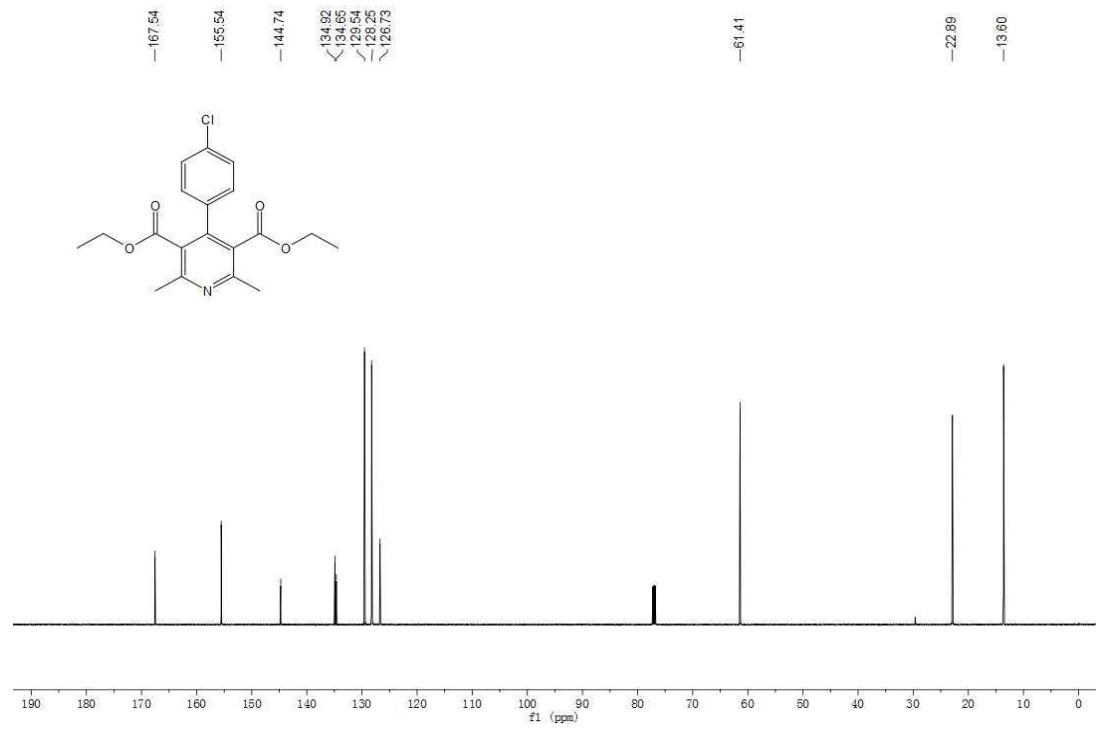
^{1}H and ^{13}C Spectra of compound 6c ($CDCl_3$, 600 MHz)





^{1}H and ^{13}C Spectra of compound 6d ($CDCl_3$, 600 MHz)





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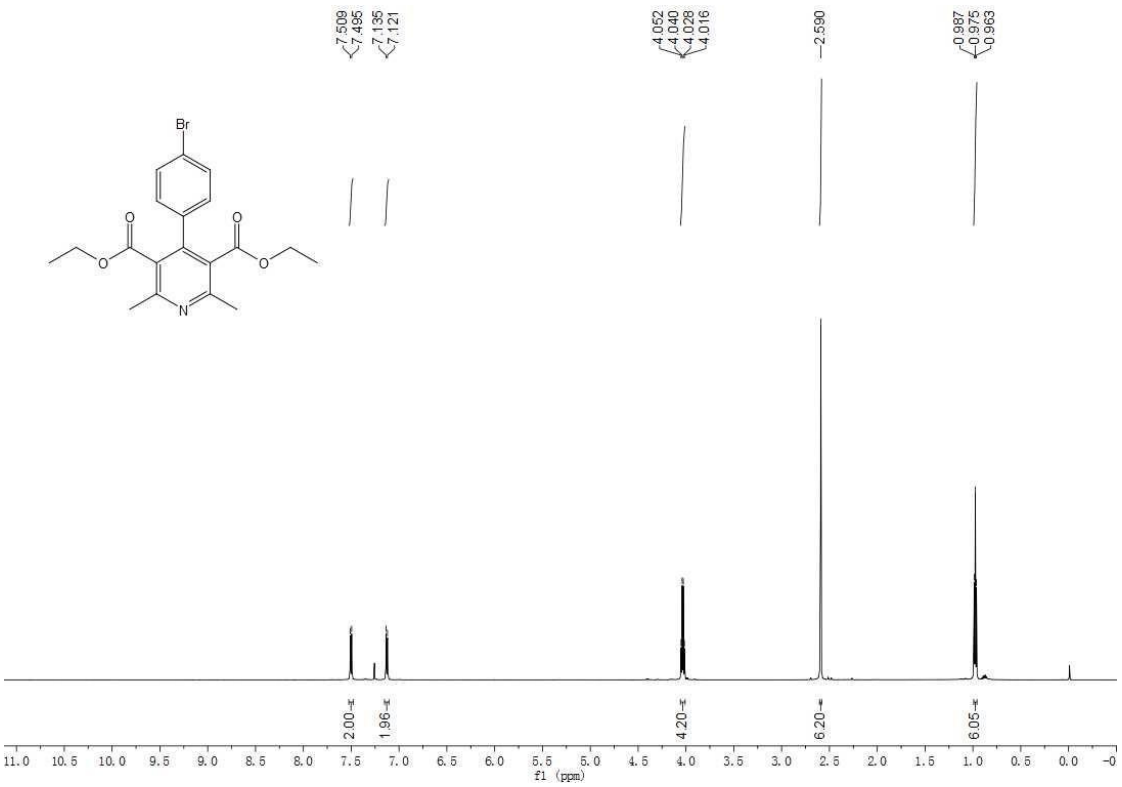

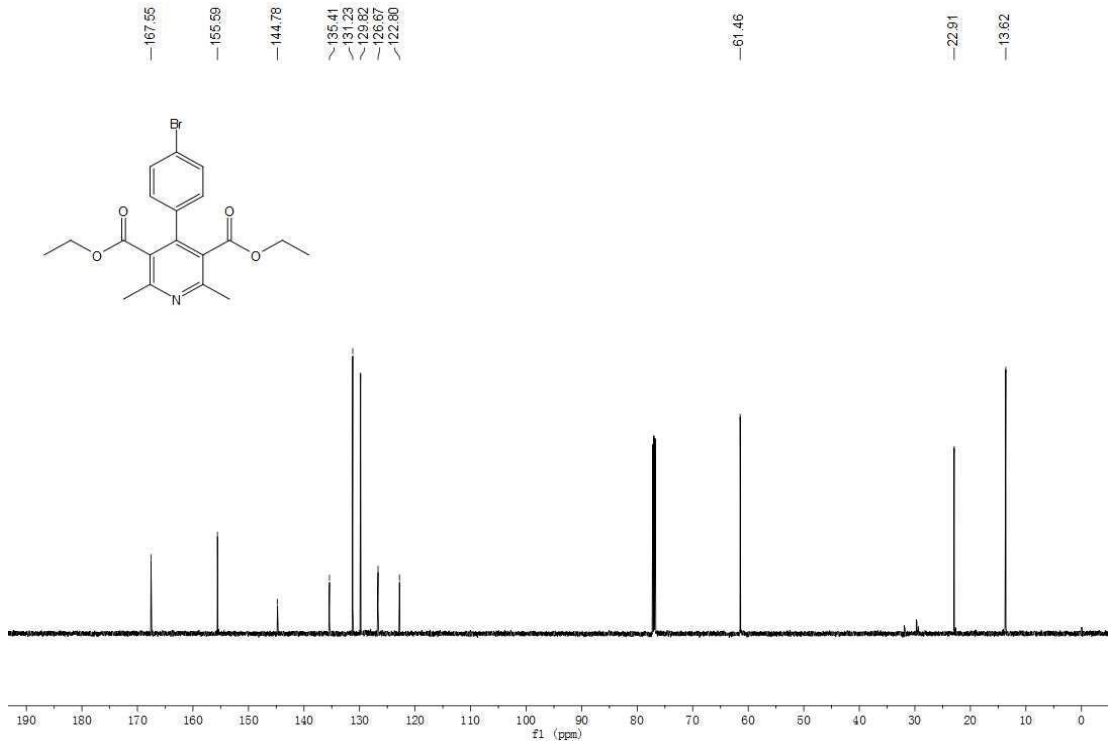

^{1}H and ^{13}C Spectra of compound 6f ($CDCl_3$, 600 MHz)