Electronic Supplementary Material (ESI) for RSC Advances.

(2-Chlorobenzoyloxy)copper(I) catalyzed C-S cross-coupling of di(hetero)aryl disulfides with aryl boronic acids under base-free conditions

Yan Guo, Zheng-Jun Quan,* Yu-Xia Da, Zhang Zhang, and Xi-Cun Wang*

SUPPORTING INFORMATIONs

Contents

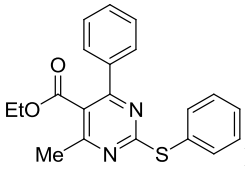
1. General

^{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. Column chromatography was generally performed on silica gel (200–300 mesh) and TLC analyses were conducted on silica gel GF254 plates. Palladium catalysts, Cu catalysts, phenylboronic acid, 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. Disulfides were prepared according to our previous reported prcedures.[1]

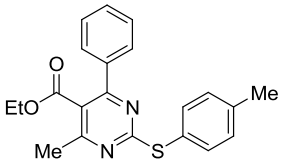
2. Experimental details and characterization data for all compounds

A sealed tube was charged with the mixture of disulfide **1** (0.5 mmol), aryl boronic acid **2** (1.5 mmol), CuCBC (20 mol%) and then stirred in toluene (3.0 mL) at 90 °C under air atmosphere for indicated time. After completion, H_2O (5 mL) was added, and the mixture was extracted with EtOAc (10 mL × 3) and dried by anhydrous $MgSO_4$. Evaporation of the solvent followed by purification on silica gel (petroleum ether) provided the corresponding product **3**.

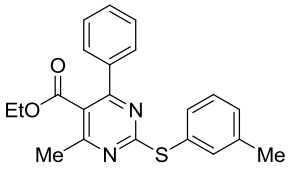
Characterization Data for the Isolated Products



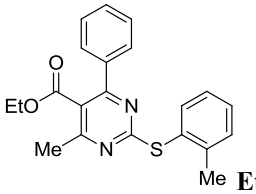
Ethyl 4-methyl-6-phenyl-2-(phenylthio)pyrimidine-5-carboxylate (3a)[3], white solid, (128 mg, 0.366 mmol, 92%), m.p. = 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 3.6 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.24-7.31 (m, 6H), 4.07 (q, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 0.95 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.08, 168.05, 165.91, 163.53, 137.37, 135.19, 130.16, 129.53, 129.04, 128.91, 128.41, 128.35, 121.51, 61.74, 22.59, 13.63 ppm.



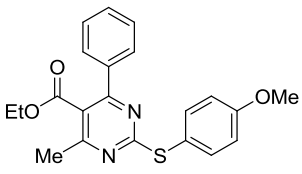
Ethyl 4-methyl-6-phenyl-2-(*p*-tolylthio)pyrimidine-5-carboxylate (3b)[2]**,** white solid, (123 mg, 0.338 mmol, 85%), m.p. = 64-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 6.8 Hz, 4H), 7.42-7.37 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 2.39 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.33, 168.04, 165.76, 163.46, 139.10, 137.37, 135.03, 130.02, 129.6, 128.30, 125.88, 121.34, 61.64, 22.54, 21.28, 13.55 ppm.



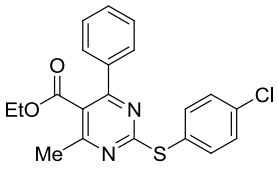
Ethyl 4-methyl-6-phenyl-2-(*m*-tolylthio)pyrimidine-5-carboxylate (3c)[2], colourless oil, (123 mg, 0.338 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.44 (m, 7H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 2.52 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.10, 167.54, 166.43, 162.83, 160.27), 136.11, 133.69, 131.69, 130.02(2C), 127.20(2C), 125.04, 122.25, 114.51, 61.97, 55.30, 22.59, 13.65 ppm.



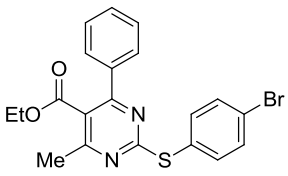
Ethyl 4-methyl-6-phenyl-2-(*o*-tolylthio)pyrimidine-5-carboxylate (3d), colourless oil, (121 mg, 0.332 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 1H), 7.49 (d, *J* = 6.8 Hz, 2H), 7.38 – 7.33 (m, 5H), 7.22 (s, 1H), 4.16 (d, *J* = 6.8 Hz, 2H), 2.49 (s, 3H), 2.44 (s, 3H), 1.05 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.79, 168.08, 165.80, 163.39, 142.95, 137.29, 136.47, 130.38, 130.03, 129.76, 128.64, 128.28, 126.31, 121.17, 77.30, 76.98, 76.66, 61.65, 22.53, 20.90, 13.48 ppm. HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{21}H_{20}N_2O_2S$: 365.1318; Found 365.1321.



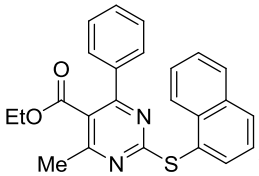
Ethyl 2-(4-methoxyphenylthio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3e)[2], white solid, (135 mg, 0.355 mmol, 89%), m.p. = 91-93 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 8.6 Hz, 4H), 7.40-7.36 (m, 3H), 6.94 (d, *J* = 6.8 Hz, 2H), 4.15 (q, *J* = 5.8 Hz, 2H), 3.82 (s, 3H), 2.50 (s, 3H), 1.03 (t, *J* = 5.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.60, 167.97, 165.69, 163.38, 160.38, 137.34, 136.83, 129.97, 128.28, 128.21, 121.23, 120.03, 114.43, 61.57, 55.21, 22.47, 13.49 ppm.



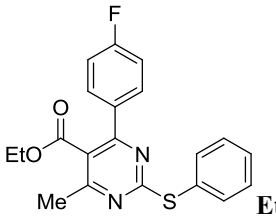
Ethyl 2-(4-chlorophenylthio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3f)[3], white solid, (143 mg, 0.372 mmol, 93%), m.p. = 41-43 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.35-7.30 (m, 5H), 4.08 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 0.97 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.66, 168.14, 166.26, 163.90, 137.47, 136.66, 135.58, 130.47, 129.34, 128.64 , 128.57, 128.27, 121.98, 77.58, 77.27, 76.95, 62.02, 22.80, 13.84 ppm.



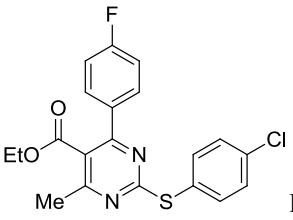
Ethyl 2-((4-bromophenyl)thio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3g), white solid, (161 mg, 0.376 mmol, 94%), m.p. = 59-61 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 5.6 Hz, 6H), 7.28 (d, *J* = 7.2 Hz, 3H), 4.05 (d, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.24, 167.86, 166.00, 163.63, 137.20, 136.58, 136.39, 132.02, 130.20, 129.07, 128.67, 128.38, 128.31, 123.53, 121.75, 77.32, 77.00, 76.68, 61.74, 22.53, 13.57 ppm. HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{20}H_{18}BrN_2O_2S$: 429.0267; Found 429.0271.



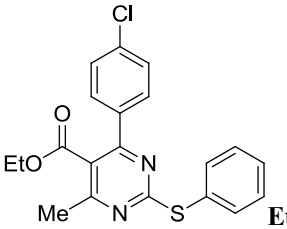
Ethyl 4-methyl-2-(naphthalen-1-ylthio)-6-phenylpyrimidine-5-carboxylate (3h)[2], white solid, (128 mg, 0.320 mmol, 80%), m.p.=87-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.91 (d, *J* = 6.8 Hz, 3H), 7.52-7.47 (m, 3H), 7.26 (d, *J* = 32.6 Hz, 5H), 4.13-4.16 (m, 2H), 2.43 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.99, 168.07, 165.80, 163.26, 137.12, 135.28, 134.90, 134.14, 130.69 (2C), 129.96, 128.43, 128.25, 128.13, 126.87, 126.12, 125.55, 121.31, 61.68, 22.48, 13.55 ppm.



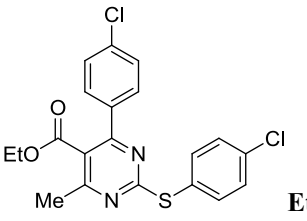
Ethyl 4-(4-fluorophenyl)-6-methyl-2-(phenylthio)pyrimidine-5-carboxylate (3i)[2], white solid, (132 mg, 0.359 mmol, 90%), m.p. =108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 2H), 7.52 (d, *J* = 4.8 Hz, 2H), 7.42 (s, 3H), 7.05 (t, *J* = 7.4 Hz, 2H), 4.19 (d, *J* = 6.4 Hz, 2H), 2.50 (s, 3H), 1.10 (t, *J* = 6.4 Hz, 3H) ppm. ^{13}C NMR (100MHz, $CDCl_3$): δ = 172.13, 167.95, 165.96, 165.26, 162.76, 162.15, 135.20, 133.38, 130.51 (d, *J* = 8.6 Hz), 129.22 (d, *J* = 30.5 Hz), 128.88, 121.22, 115.53, 115.32, 61.79, 22.54, 13.66 ppm.



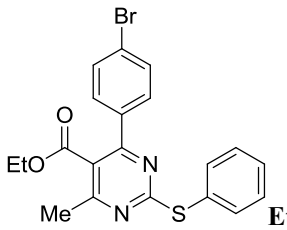
Ethyl 2-((4-chlorophenyl)thio)-4-(4-fluorophenyl)-6-methylpyrimidine-5-carboxylate (3j), white solid, (148 mg, 0.368 mmol, 92%), m.p.=88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.57 – 7.53 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.10-7.06 (m, 2H), 4.20 (q, *J* = 6.8 Hz, 2H), 2.51 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (150MHz, $CDCl_3$): δ =171.48, 167.81, 166.11, 164.88, 163.21, 162.31, 136.45, 135.40 , 133.27 (d, *J* = 3.1 Hz), 130.48 (d, *J* = 8.7 Hz), 129.12, 127.86, 121.49, 115.62, 115.47, 77.28, 77.07, 76.86, 61.87, 22.57, 13.69 ppm. HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{20}H_{16}ClFN_2O_2S$: 403.0678; Found 403.0674.



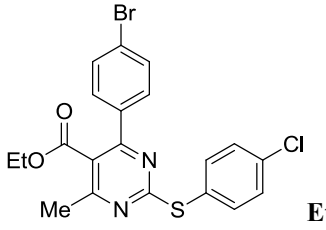
Ethyl 4-(4-chlorophenyl)-6-methyl-2-(phenylthio)pyrimidine-5-carboxylate (3k)[3], white solid, (140 mg, 0.365 mmol, 91%), m.p. = 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 2H), 7.48 – 7.42 (m, 5H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.21 – 4.18 (m, 2H), 2.52 (s, 3H), 1.11(t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ= 172.26 , 167.83, 166.09 , 162.10, 136.52, 135.71, 135.23, 129.76, 129.27, 129.14, 128.93, 128.61, 121.23, 77.28, 77.07, 76.86, 61.88, 22.62, 13.71 ppm.



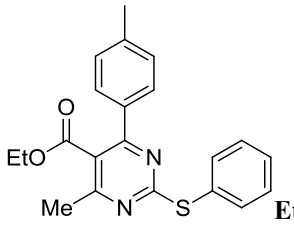
Ethyl 4-(4-chlorophenyl)-2-((4-chlorophenyl)thio)-6-methylpyrimidine-5-carboxylate (3l), white solid, (156 mg, 0.373 mmol, 93%), m.p. = 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 6.8 Hz, 2H), 7.47 – 7.45 (m, 2H), 7.39-7.35 (m, 4H), 4.20 (q, *J* = 6.8 Hz, 2H), 2.51 (s, 3H), 1.11 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 171.61, 167.69, 166.22, 162.26, 136.63, 136.46, 135.59, 135.44, 129.70, 129.13, 128.69, 127.79, 121.51, 77.28, 77.06, 76.85, 61.93, 22.60 , 13.70 ppm. HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{20}H_{17}Cl_2N_2O_2S$: 419.0382; Found 419.0379.



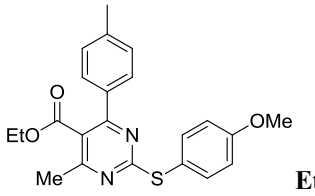
Ethyl 4-(4-bromophenyl)-6-methyl-2-(phenylthio)pyrimidine-5-carboxylate (3m)[3], white solid, (157 mg, 0.367 mmol, 92%), m.p. = 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (s, 2H), 7.49 (d, *J* = 3.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 5H), 4.19 (q, *J* = 1.8Hz, 2H), 2.51 (s, 3H), 1.10 (d, *J* = 3.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.23, 167.79, 166.08, 162.12, 136.07, 135.19, 131.60, 131.52, 129.90, 129.13, 128.89, 124.89, 121.11, 77.31, 76.99, 76.67, 61.88, 22.60, 13.66 ppm.



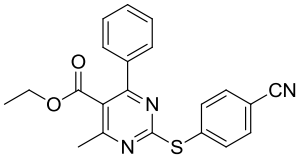
Ethyl 4-(4-bromophenyl)-2-((4-chlorophenyl)thio)-6-methylpyrimidine-5-carboxylate (3n), white solid, (168 mg, 0.364 mmol, 91%), m.p. = 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 – 7.52 (m, 4H), 7.38 (d, *J* = 6.4 Hz, 4H), 4.19 (q, *J* = 4.4 Hz, 2H), 2.51 (d, *J* = 2.0Hz, 3H), 1.12 (t, J=4.8Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.62, 167.64, 166.21, 162.32, 136.43, 136.03, 135.44, 131.62, 129.88, 129.11, 127.77, 125.00, 121.46, 77.31, 76.99, 76.67, 61.90, 22.56, 13.66 ppm.



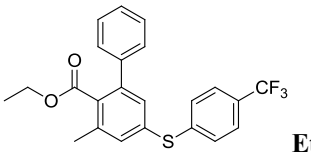
Ethyl 4-methyl-2-(phenylthio)-6-(p-tolyl)pyrimidine-5-carboxylate (3o)[3], white solid, (137 mg, 0.376 mmol, 94%), m.p. = 67-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (s, 2H), 7.41 (s, 5H), 7.16 (d, *J* = 7.2Hz, 2H), 4.20– 4.19 (m, 2H), 2.50 (s, 3H), 2.35 (s, 3H), 1.10 (t, *J* = 6.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.83, 168.27, 165.65, 163.19, 140.54, 135.15, 134.27, 129.40, 129.12, 129.05, 128.97, 128.83, 128.31, 121.13, 77.32, 77.00, 76.68, 61.72, 22.54, 21.33, 13.65 ppm.



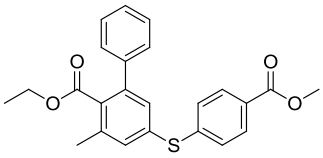
Ethyl 2-((4-methoxyphenyl)thio)-4-methyl-6-(p-tolyl)pyrimidine-5-carboxylate (3p), white solid, (118 mg, 0.300 mmol, 75%), m.p. = 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.2 Hz, 2H), 4.19 – 4.16(m, 2H), 3.81 (s, 3H), 2.49 (s, 3H), 2.34 (s, 3H), 1.09 (t, *J* = 6.8Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.42, 168.25, 165.49, 163.12, 160.28, 140.40, 136.86, 134.32, 128.98, 128.26, 120.95, 119.98, 114.35, 77.31, 76.99, 76.67, 61.62, 55.22, 22.49, 21.27, 13.60 ppm. HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{22}H_{22}N_2O_3S$: 395.1424; Found 395.1421.



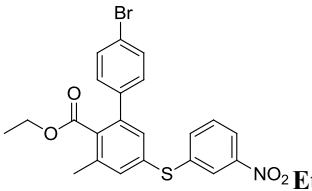
Ethyl 2-((4-cyanophenyl)thio)-4-methyl-6-phenylpyrimidine-5-carboxylate (3q), white solid, (116 mg, 0.309 mmol, 78%), m.p. = 110-112 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 – 7.76 (m, 2H), 7.68 – 7.66 (m, 2H), 7.51 – 7.49 (m, 2H), 7.45 – 7.43(m, 1H), 7.40-7.38 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.06 (s), 167.65 (s), 166.29 (s), 163.87 (s), 136.97 (s), 136.30 (s), 134.84 (s), 132.21 (s), 130.43 (s), 128.50 (s), 128.25 (s), 122.28 (s), 118.40 (s), 112.36 (s), 77.22 (s), 77.01 (s), 76.80 (s), 61.91 (s), 22.56 (s), 13.59 (s). HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{21}H_{17}N_3O_2S$: 376.1114; Found 376.1111



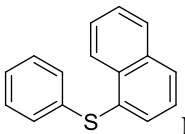
Ethyl 3-methyl-5-((4-(trifluoromethyl)phenyl)thio)-[1,1'-biphenyl]-2-carboxylate (3r), white solid, (117 mg, 0.281 mmol, 71%), m.p. = 109-111 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 4.16 (q, *J* = 6.6 Hz, 2H), 2.51 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.70 (s), 167.78 (s), 166.15 (s), 163.69 (s), 137.05 (s), 134.91 (s), 130.31 (s), 128.41 (s), 128.28 (s), 125.90 – 125.47 (m), 121.97 (s), 77.18 (s), 76.97 (s), 76.76 (s), 61.83 (s), 22.54 (s), 13.56 (s). HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{21}H_{17}F_3N_2O_2S$: 419.1036; Found 419.1039.



Ethyl 5-((4-(methoxycarbonyl)phenyl)thio)-3-methyl-[1,1'-biphenyl]-2-carboxylate (3s), white solid, (96 mg, 0.236 mmol, 60%), m.p. = 83-85 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 2.51 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.85 (s), 167.81 (s), 166.56 (s), 166.08 (s), 163.75 (s), 137.12 (s), 135.56 (s), 134.27 (s), 130.24 (d, *J* = 3.1 Hz), 129.80 (s), 128.35 (d, *J* = 18.9 Hz), 121.94 (s), 77.17 (s), 76.96 (s), 76.75 (s), 61.79 (s), 52.21 (s), 22.53 (s), 13.56 (s). HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{22}H_{20}N_2O_4S$: 409.1215; Found 409.1213.

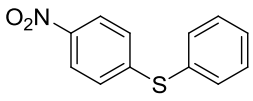


Ethyl 4'-bromo-3-methyl-5-((3-nitrophenyl)thio)-[1,1'-biphenyl]-2-carboxylate (3t),white solid, (169 mg, 0.359 mmol, 90%), m.p. = 106-108 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.61– 8.60(m, 1H), 8.26-8.24 (m, 1H), 7.92 – 7.91(m, 1H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.41 – 7.39 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 170.20 (s), 167.41 (s), 166.56 (s), 162.62 (s), 148.26 (s), 140.31 (s), 135.81 (s), 131.97 (s), 131.72 (s), 129.84 (t, *J* = 17.2 Hz), 129.51 (s), 125.19 (s), 123.79 (s), 122.06 (s), 77.18 (s), 76.97 (s), 76.76 (s), 62.05 (s), 29.64 (s), 22.58 (s), 13.66 (s). HRMS (ESI$^+$) m/z: ([M+H]$^+$) Calcd for $C_{20}H_{16}BrN_3O_4S$: 474.0118; Found 474.0115.

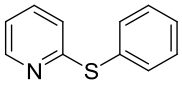


Naphthalen-1-yl(phenyl)sulfane (3u)[4]**,** colourless oil, (77 mg, 0.326 mmol, 82%). ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 8.55 (d, *J* = 4.8 Hz, 1H), 8.07-7.93 (m, 2H), 7.80 (d, *J* = 6.4 Hz, 1H), 7.62-7.55 (m, 3H), 7.33 (s, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.87, 134.17, 133.54, 132.43, 131.25, 129.09, 128.99, 128.48, 126.85, 126.34, 126.06, 125.73, 125.56 ppm.



4-Nitrophenyl phenyl sulfide (**3v**)[4], yellow solid, (79 mg, 0.342 mmol, 86%), m.p. = 53-56°C. CAS 952-97-6. ^1H NMR (400 MHz, $CDCl_3$) : δ = 7.91 (d, *J* = 8.8Hz, 2H), 7.41 (s, 2H), 7.33 (s, 3H), 7.03 (d, *J* = 8.8 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) : δ = 148.26, 145.05, 134.49, 130.15, 129.81, 129.45, 126.39, 123.76 ppm.



2-(Phenylthio)pyridine (**3w**)[4], colourless oil (72 mg, 0.385 mmol, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, *J* = 3.2 Hz, 1H), 7.57 (d, *J* = 3.2 Hz, 2H), 7.43-7.39 (m, 4H), 6.95 (t, *J* = 5.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.32, 149.41, 136.61, 134.78, 130.90, 129.52, 128.92, 121.28, 191.80 ppm.

3. References:

1. Z.-J. Quan, Y. Lv, F.-Q. Jing, X.-D. Jia and X.-C. Wang, *Adv. Synth. Catal*., 2014, **356**, 325-332.

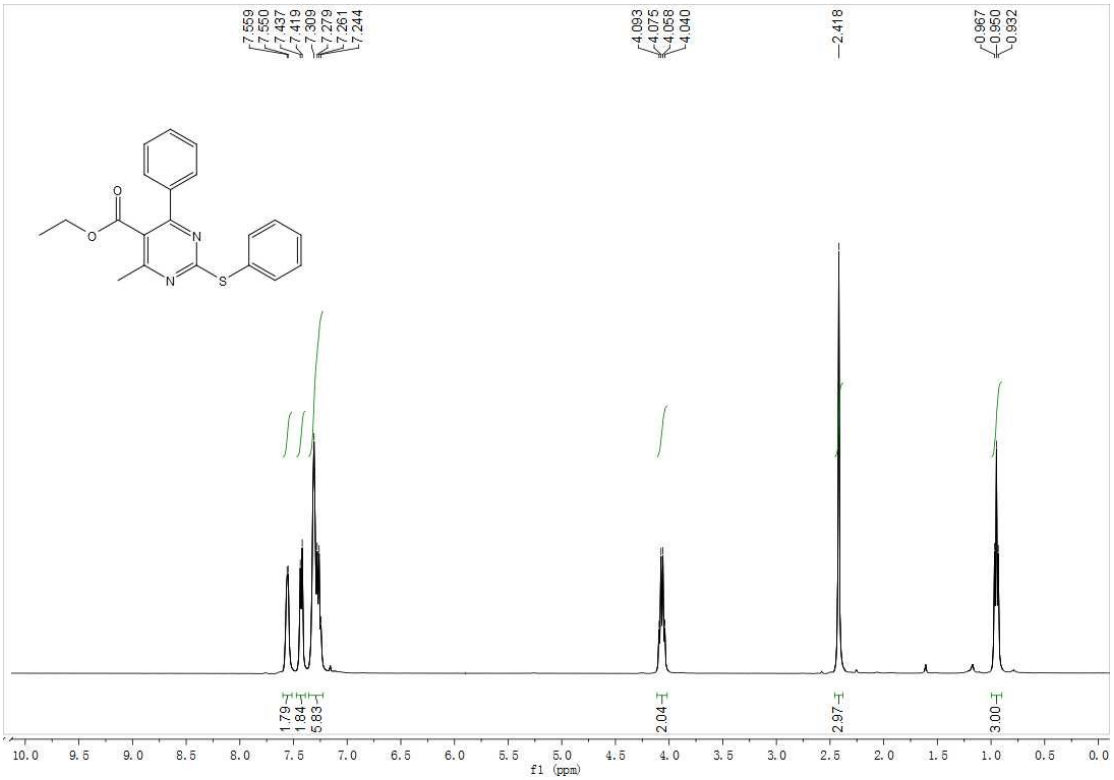
2. B.-X. Du, Z.-J. Quan, Y.-X. Da, Z. Zhang and X.-C. Wang, *Adv. Synth. Catal*., 2015, **357**, 1270-1276.

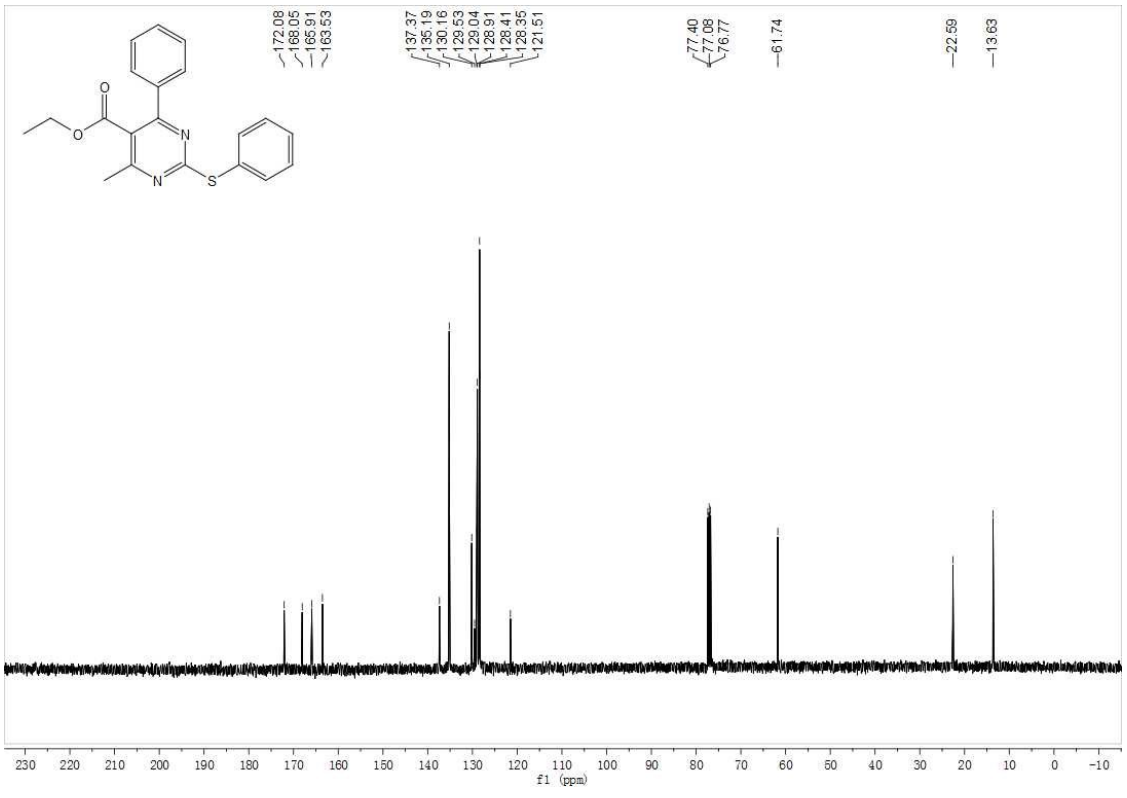
3. B. Y. Bhong, A. V. Shelke and N. N. Karade, *Tetrahedron Lett.*, 2013,**54**, 739–743.

4. N. Taniguchi and T. Onami, *J. Org. Chem.,* 2004, **69**, 915-920.

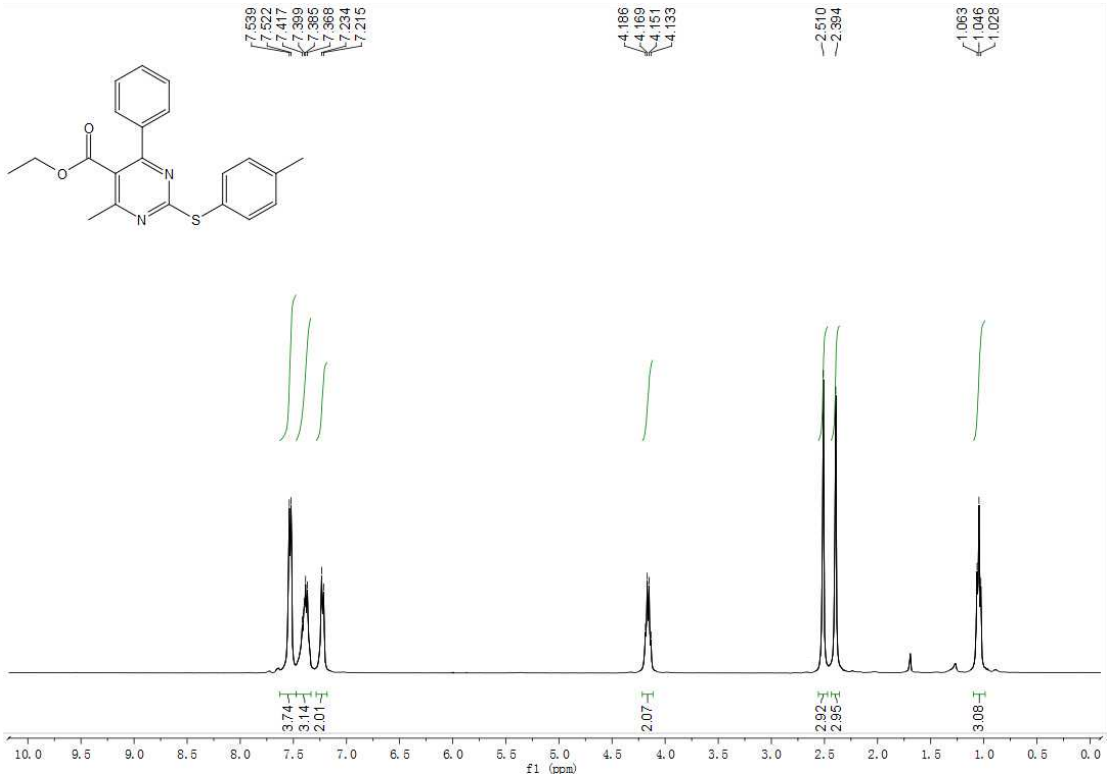
4. **Copies of the NMR Spectra for the Synthesized Products.**

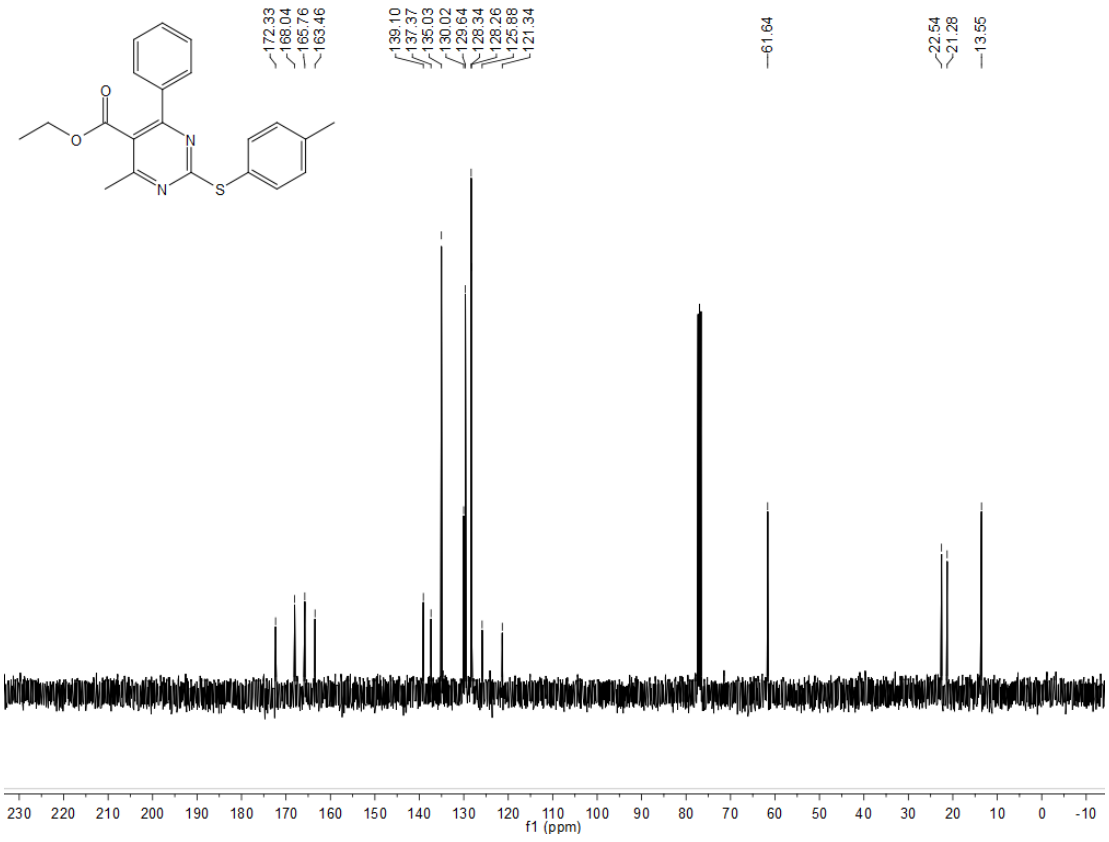
^{1}H and ^{13}C Spectra of compound 3a ($CDCl_3$, 400 MHz)



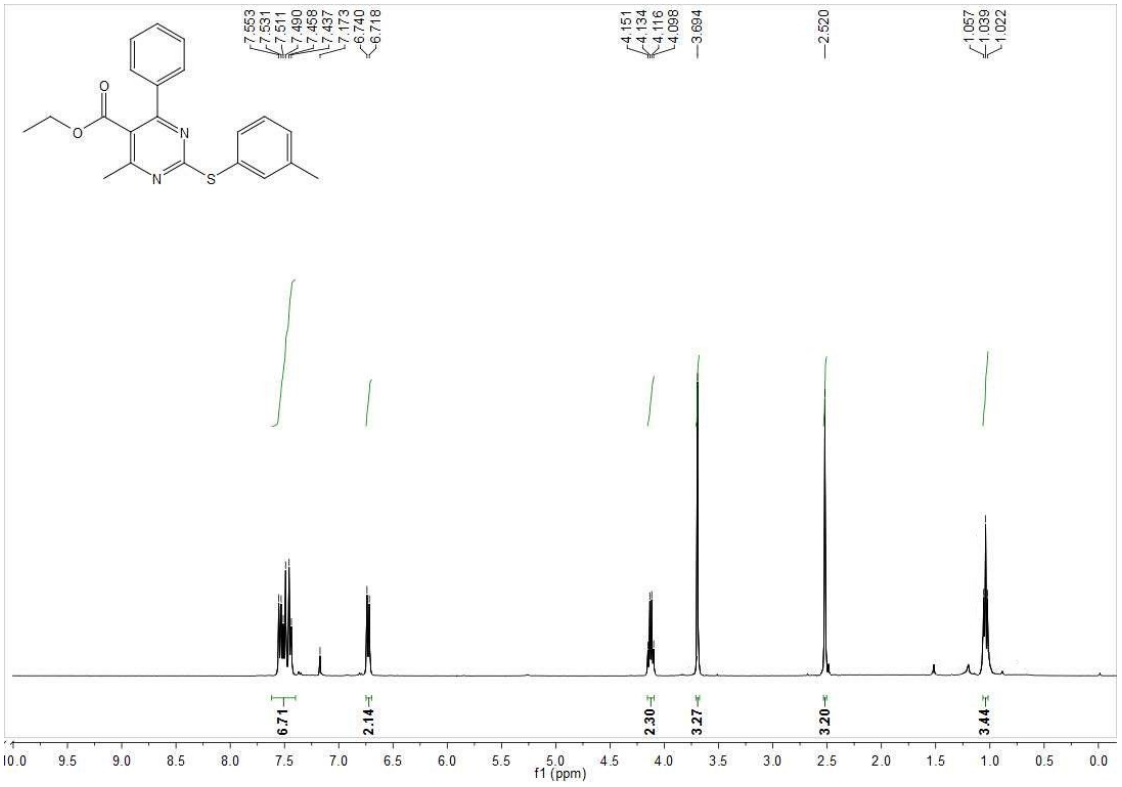


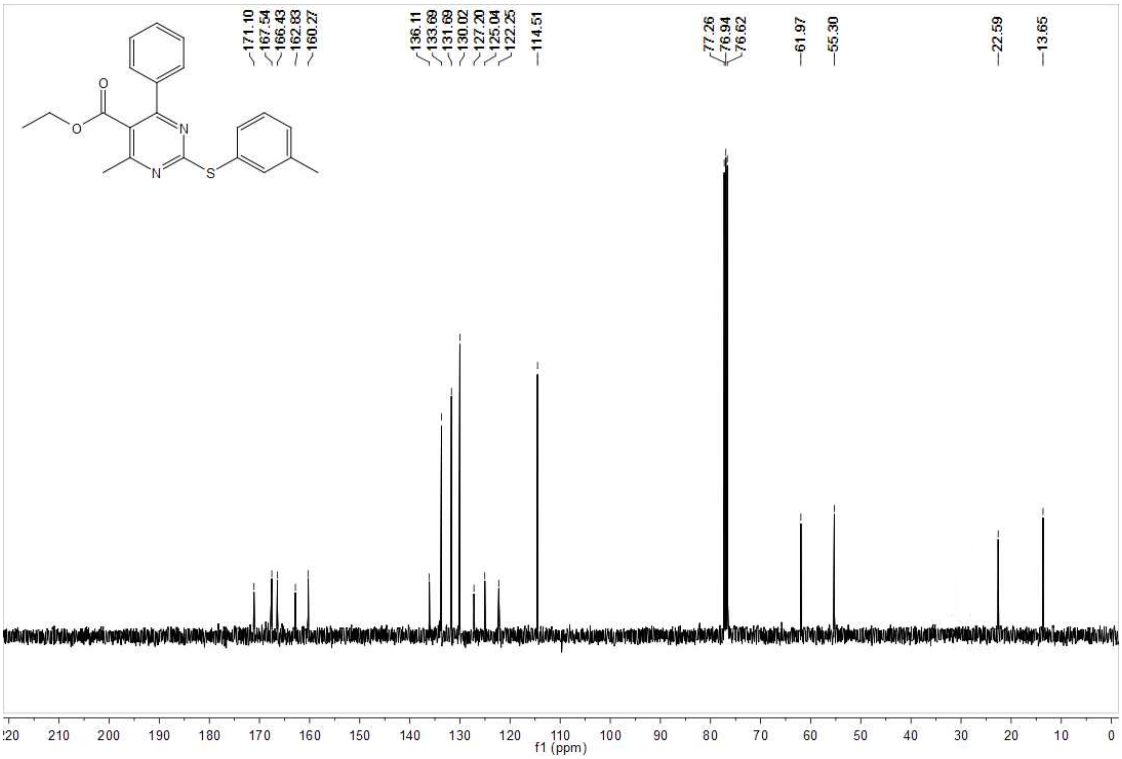
^{1}H and ^{13}C Spectra of compound 3b ($CDCl_3$, 400 MHz)



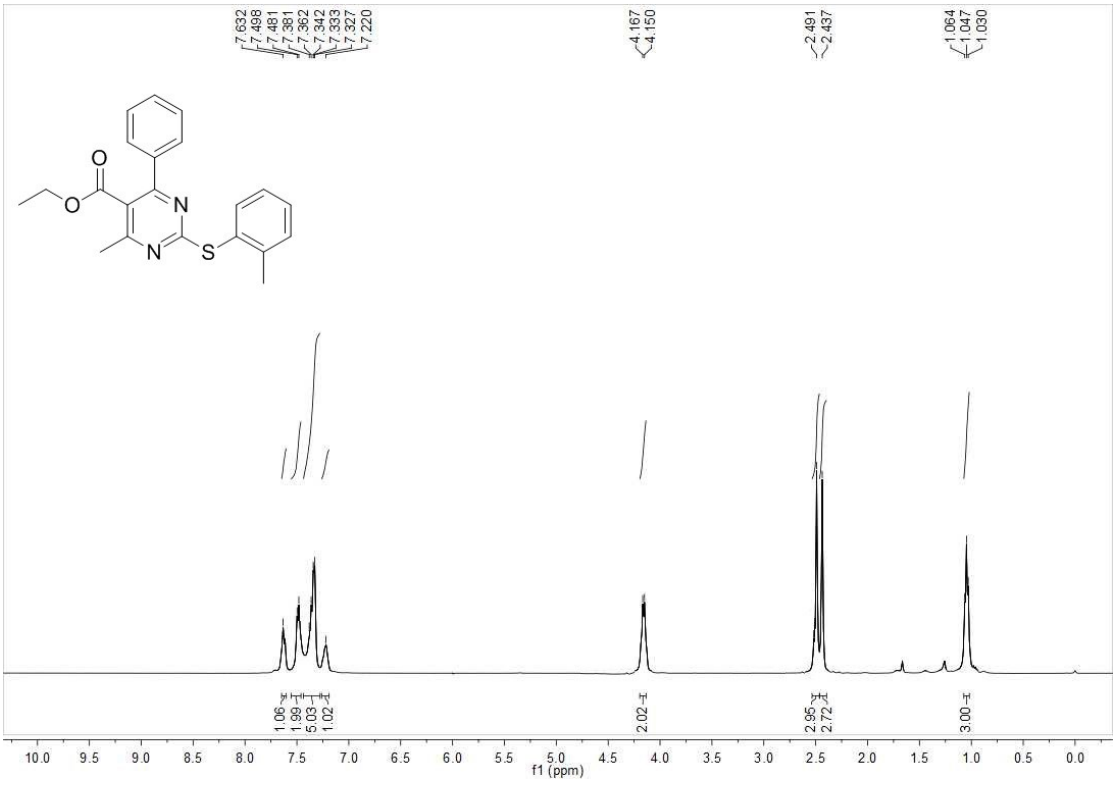


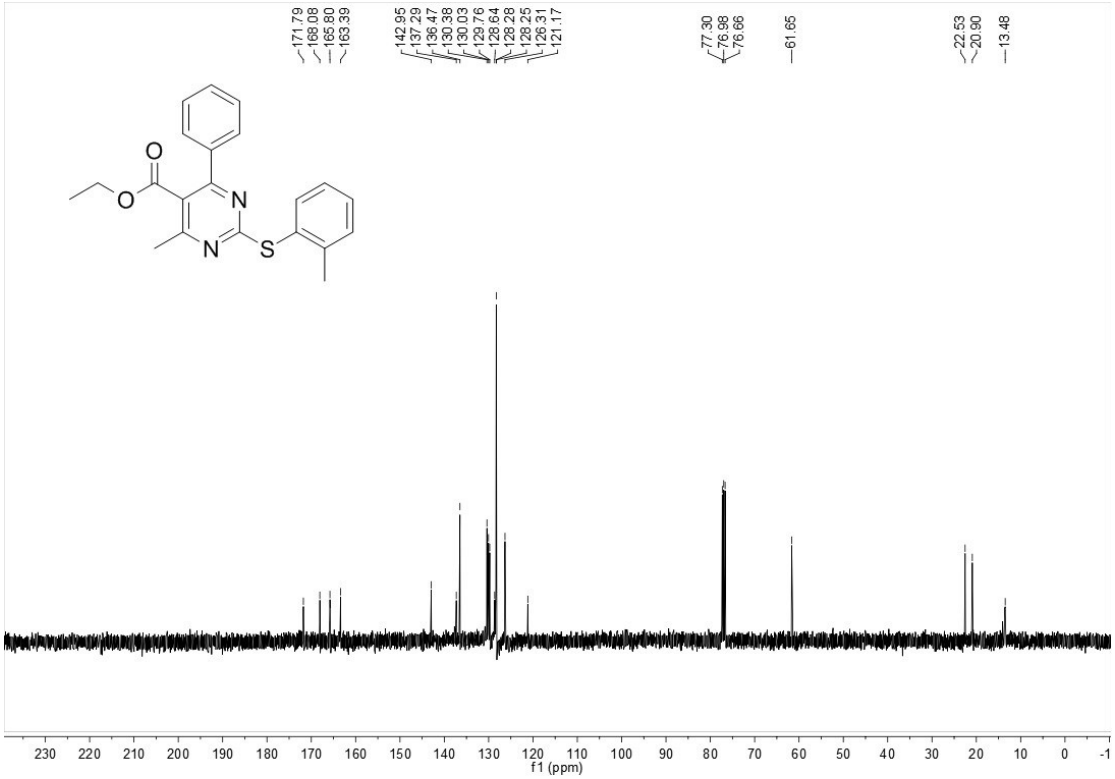
^{1}H and ^{13}C Spectra of compound 3c ($CDCl_3$, 400 MHz)



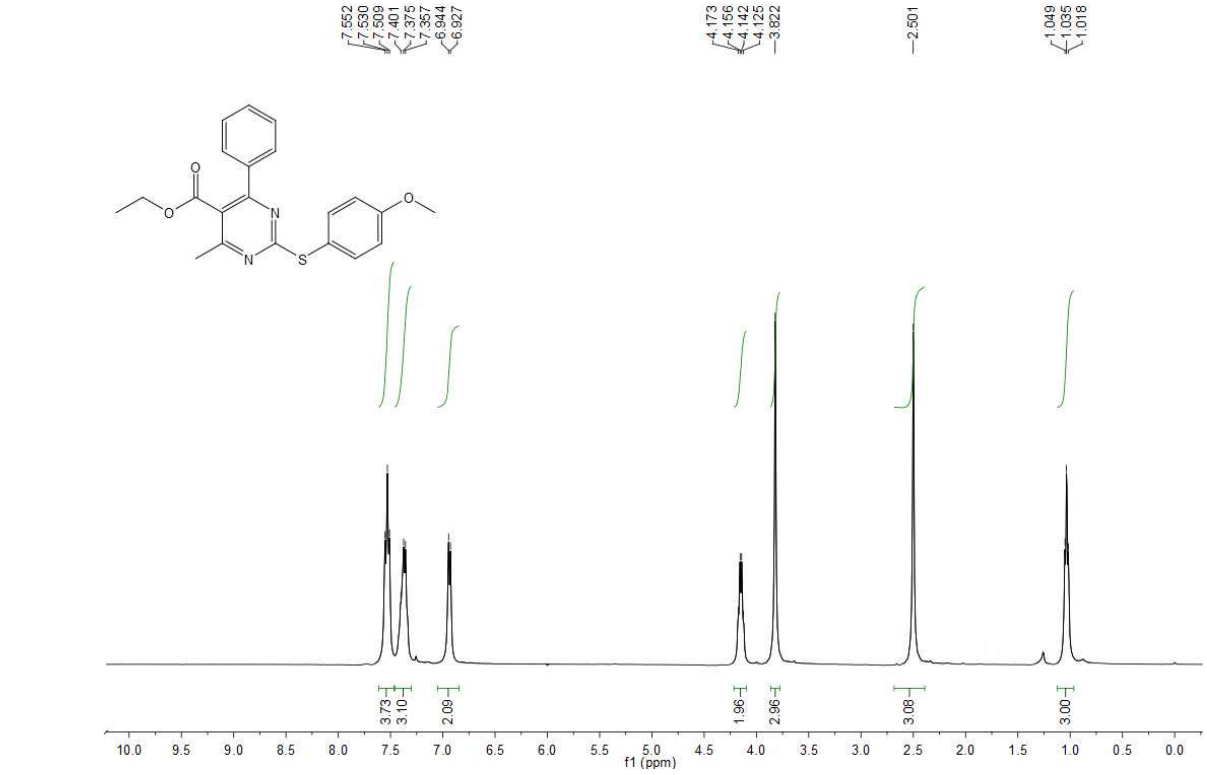


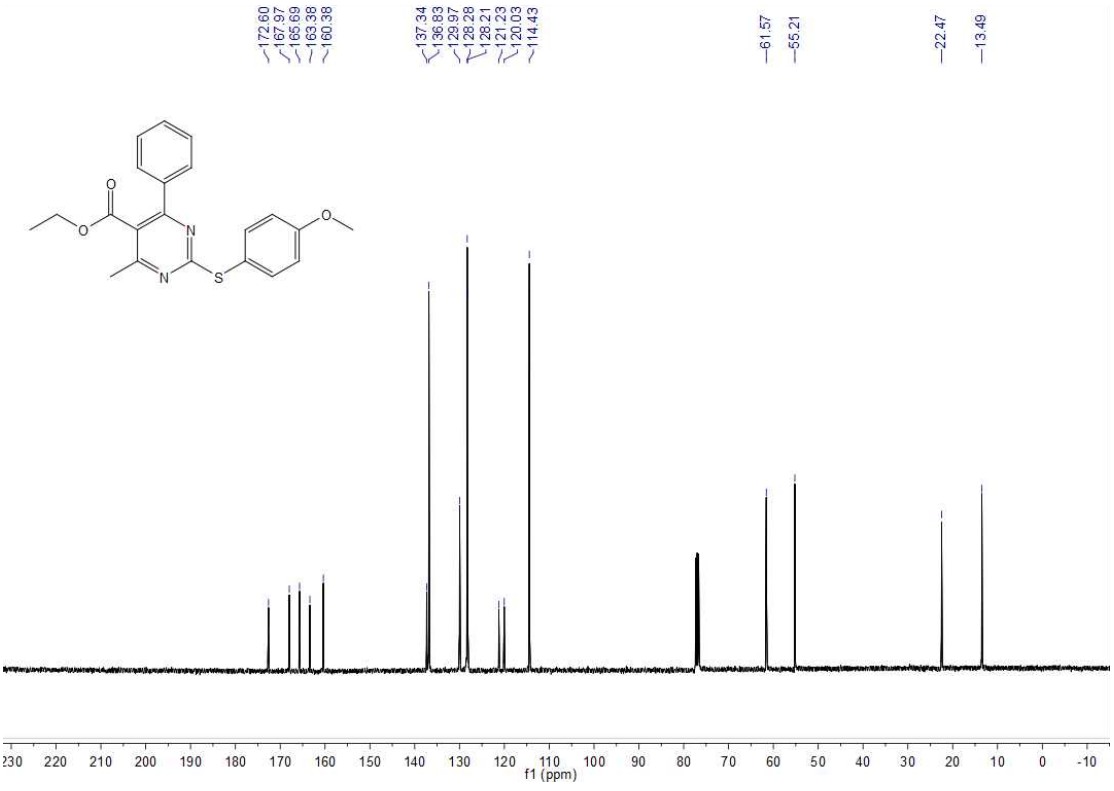
^{1}H and ^{13}C Spectra of compound 3d ($CDCl_3$, 400 MHz)



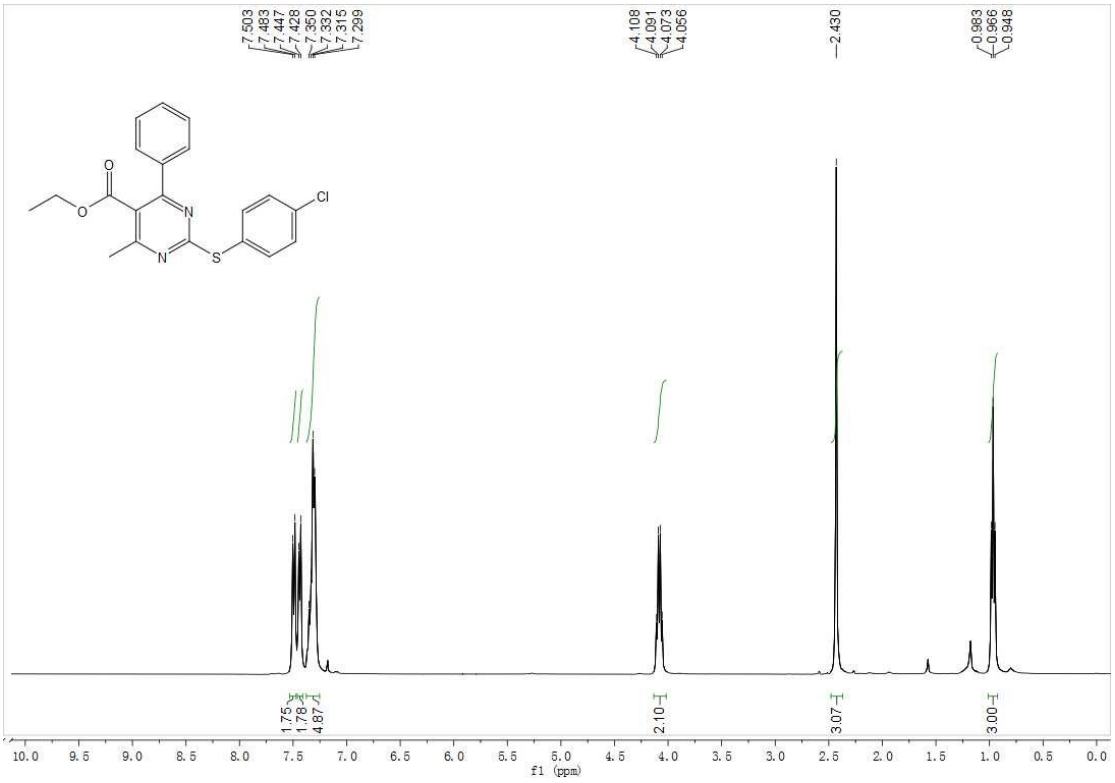


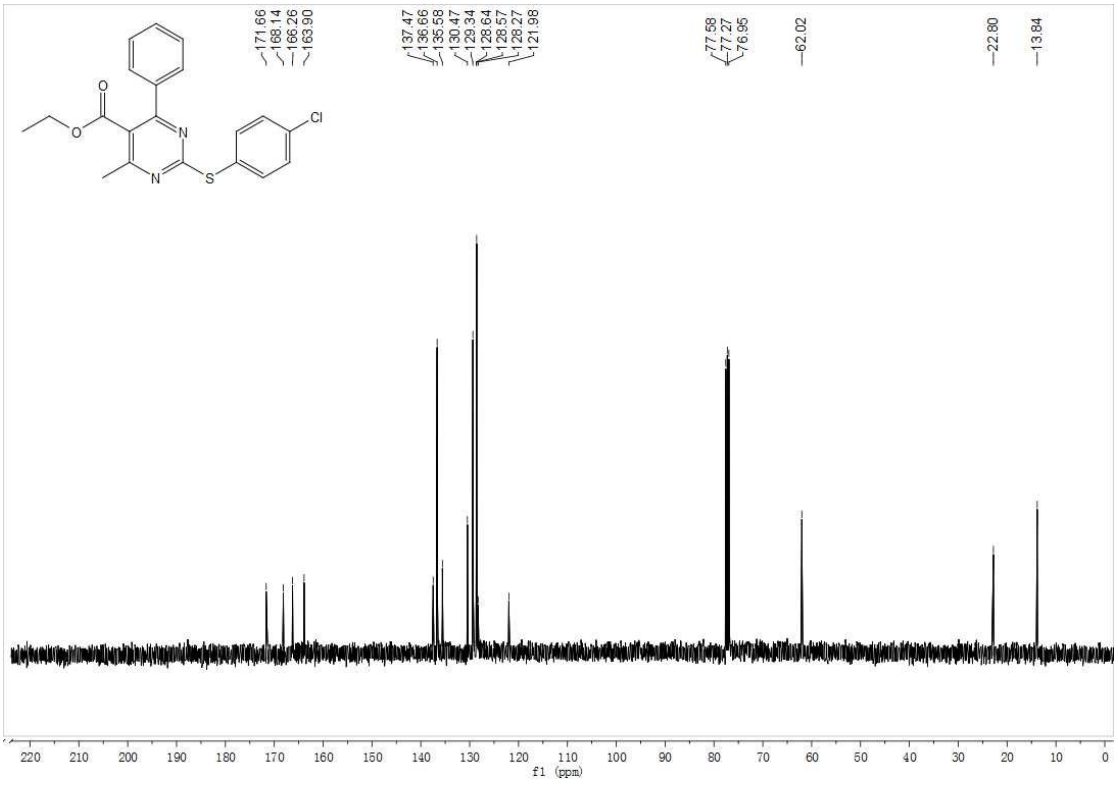
^{1}H and ^{13}C Spectra of compound 3e ($CDCl_3$, 400 MHz)



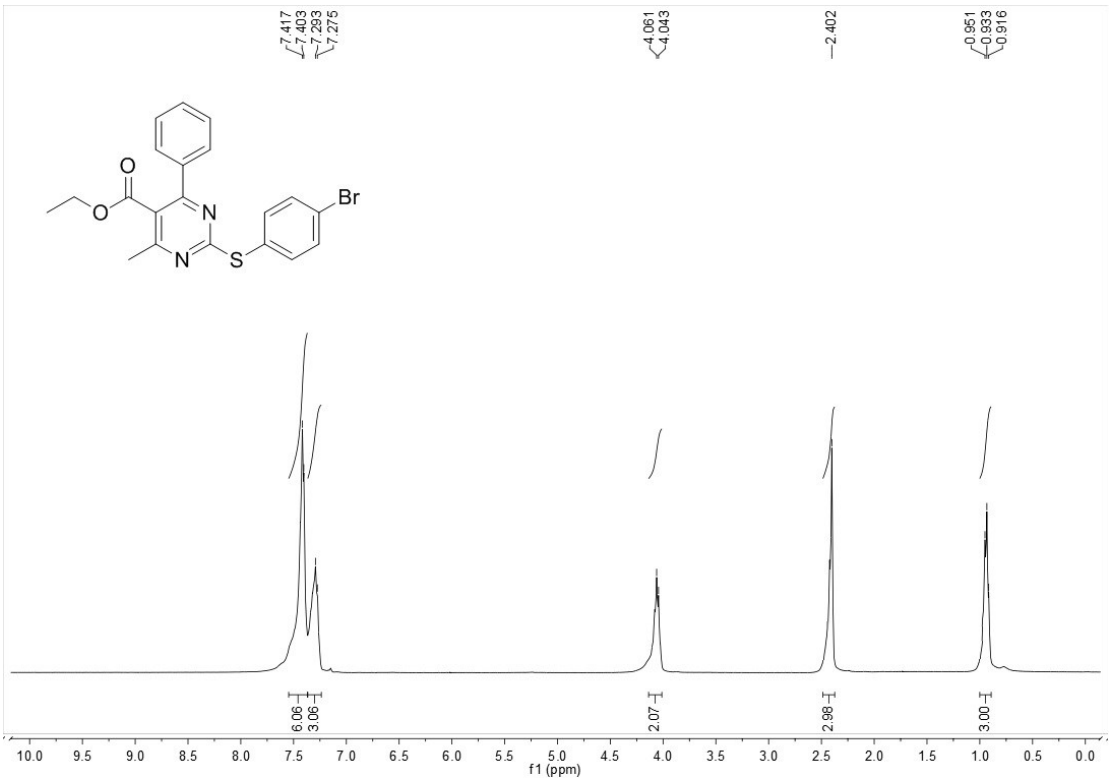


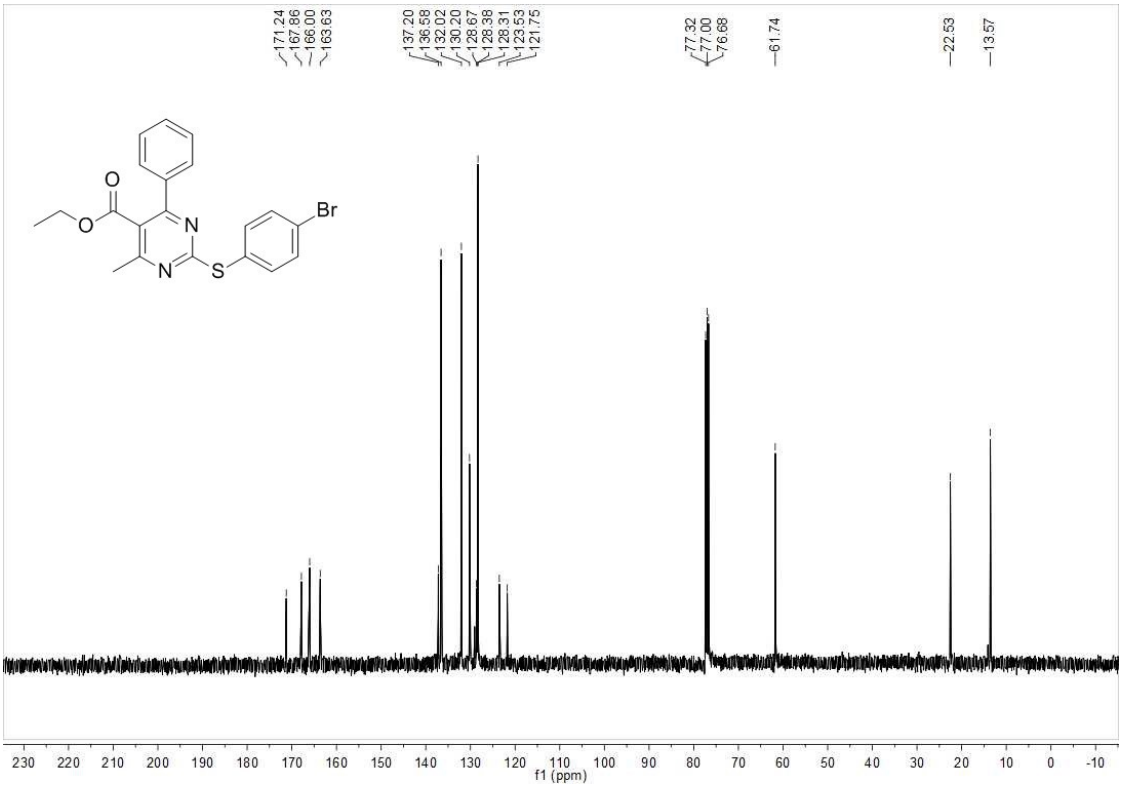
^{1}H and ^{13}C Spectra of compound 3f ($CDCl_3$, 400 MHz)



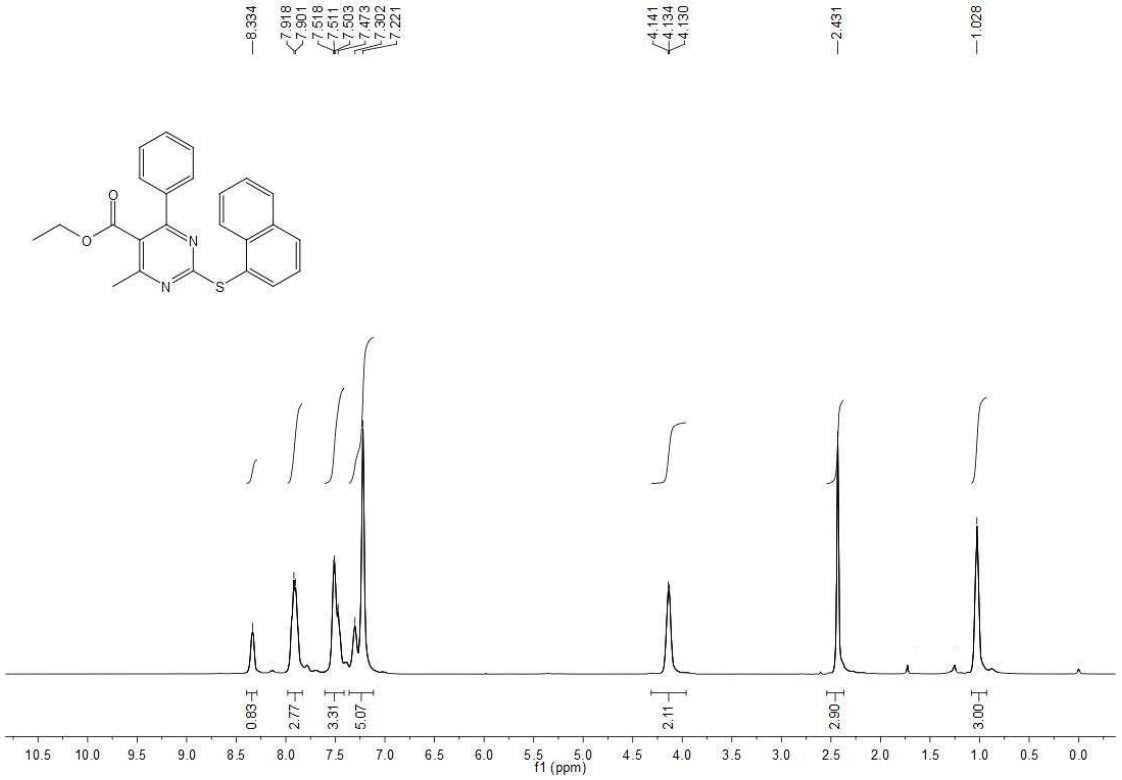


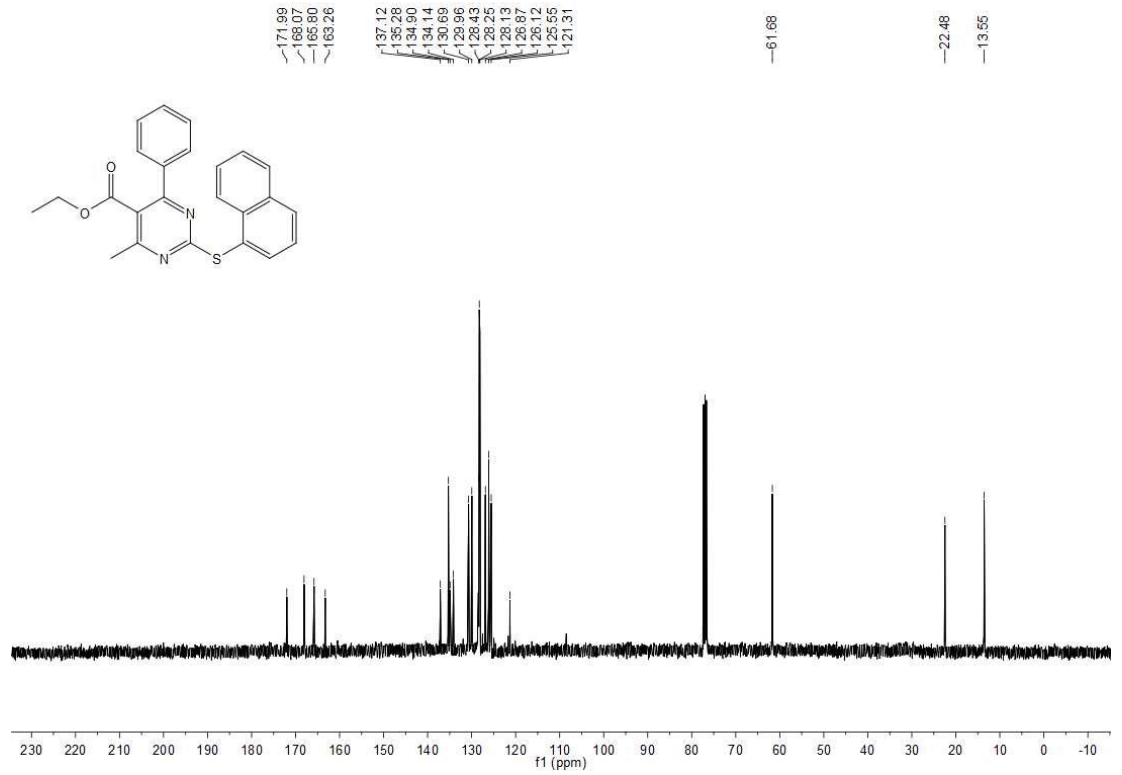
^{1}H and ^{13}C Spectra of compound 3g ($CDCl_3$, 400 MHz)



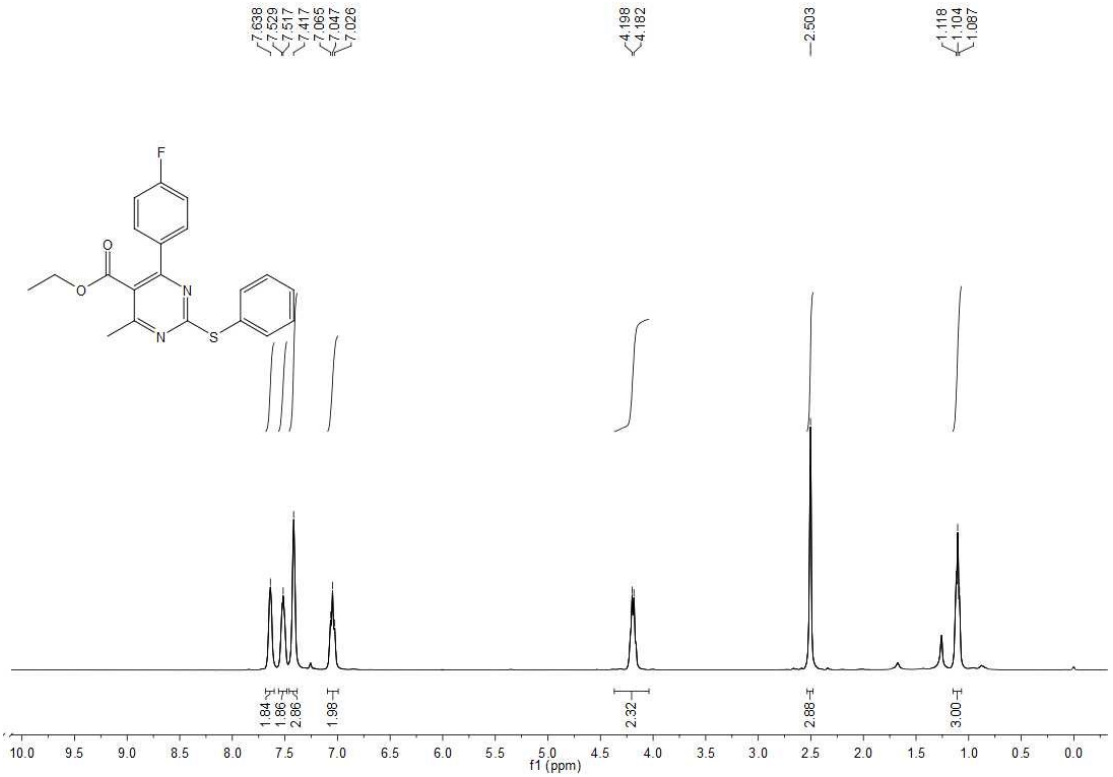


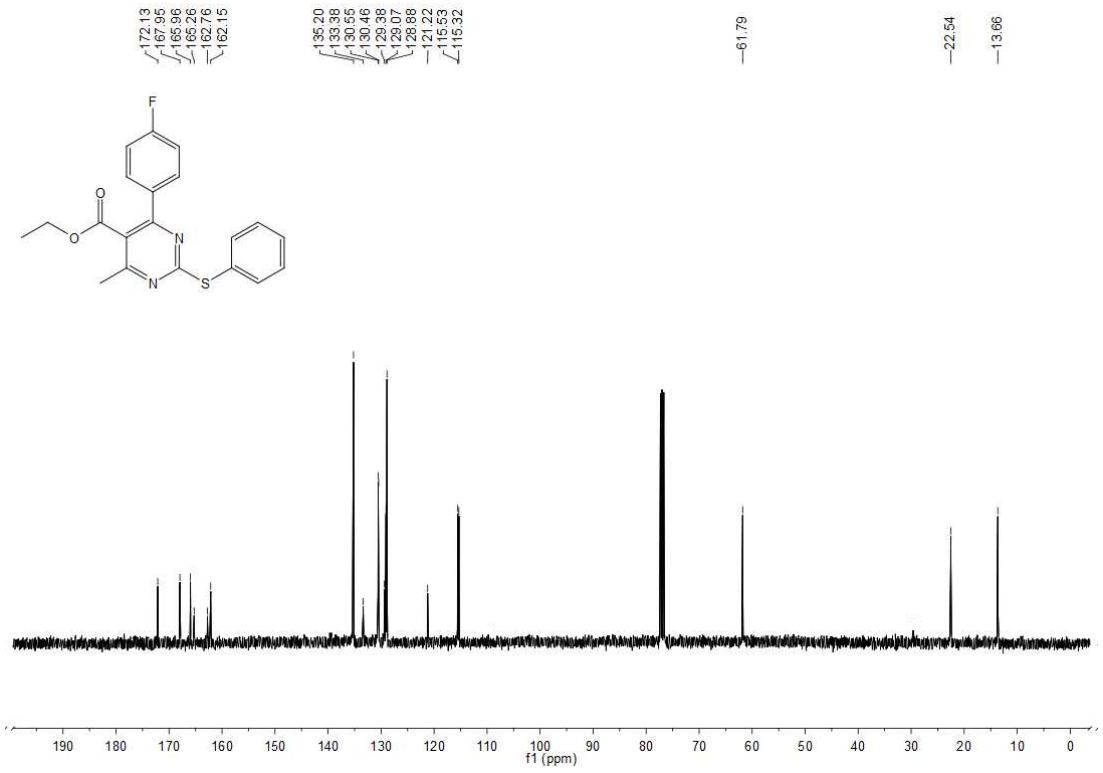
^{1}H and ^{13}C Spectra of compound 3h ($CDCl_3$, 400 MHz)



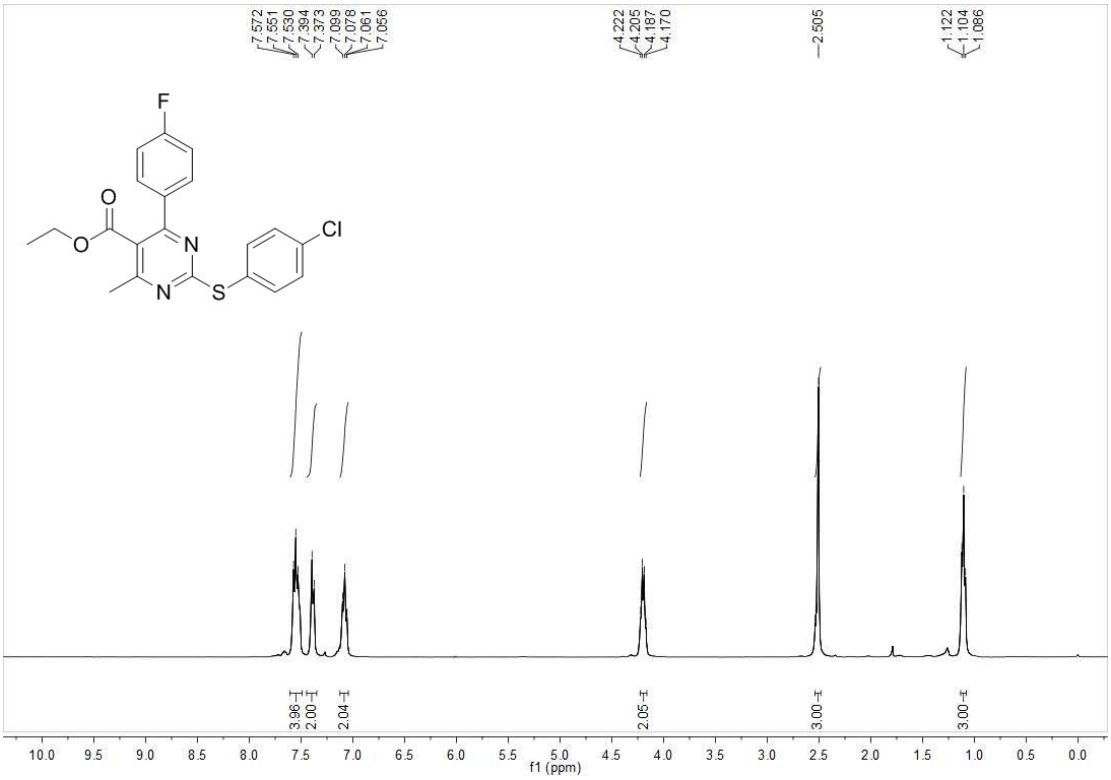


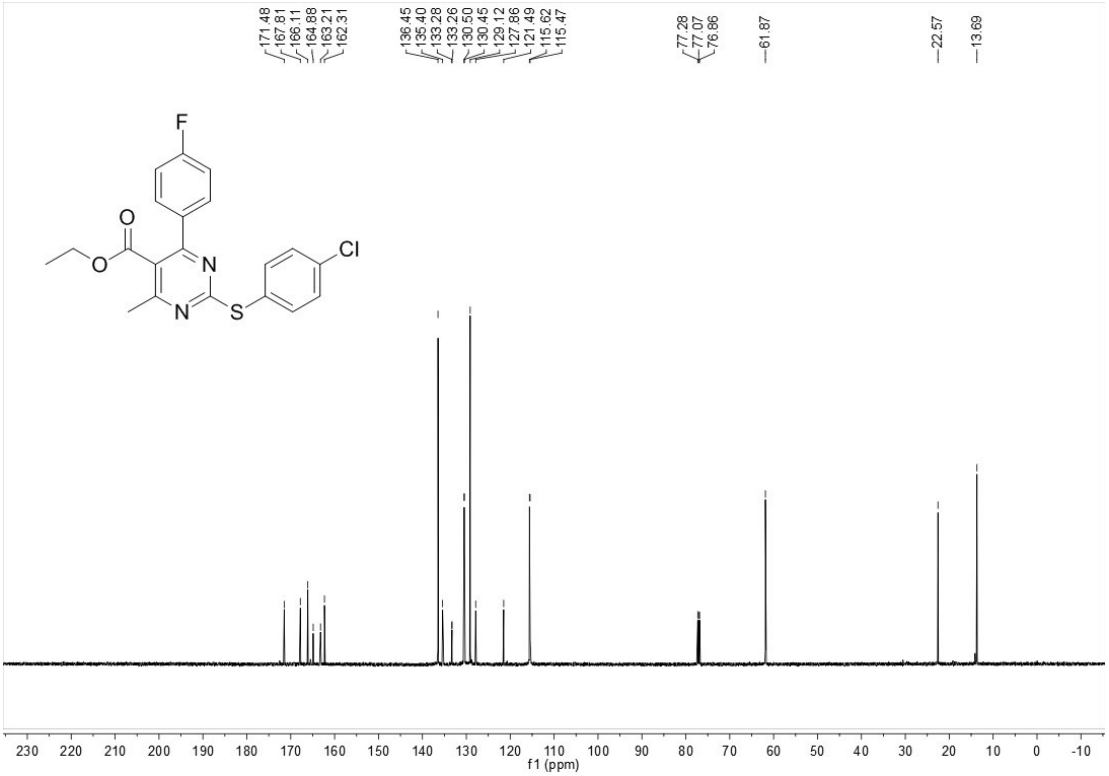
^{1}H and ^{13}C Spectra of compound 3i ($CDCl_3$, 400 MHz)



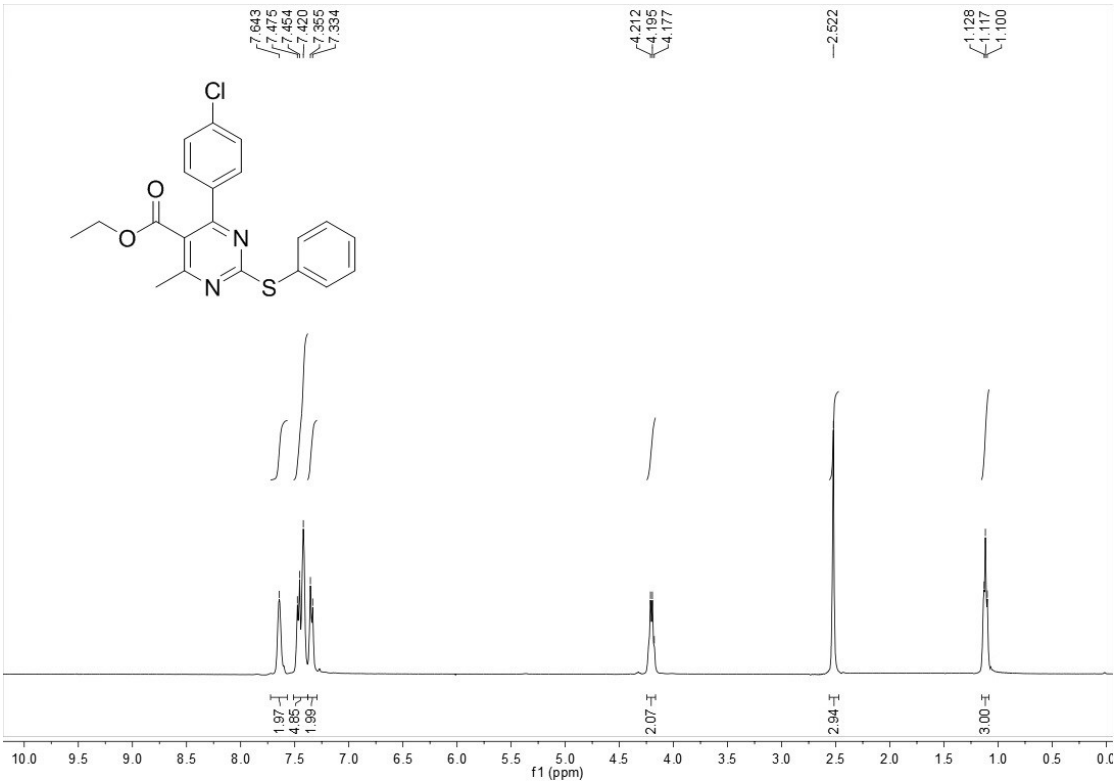


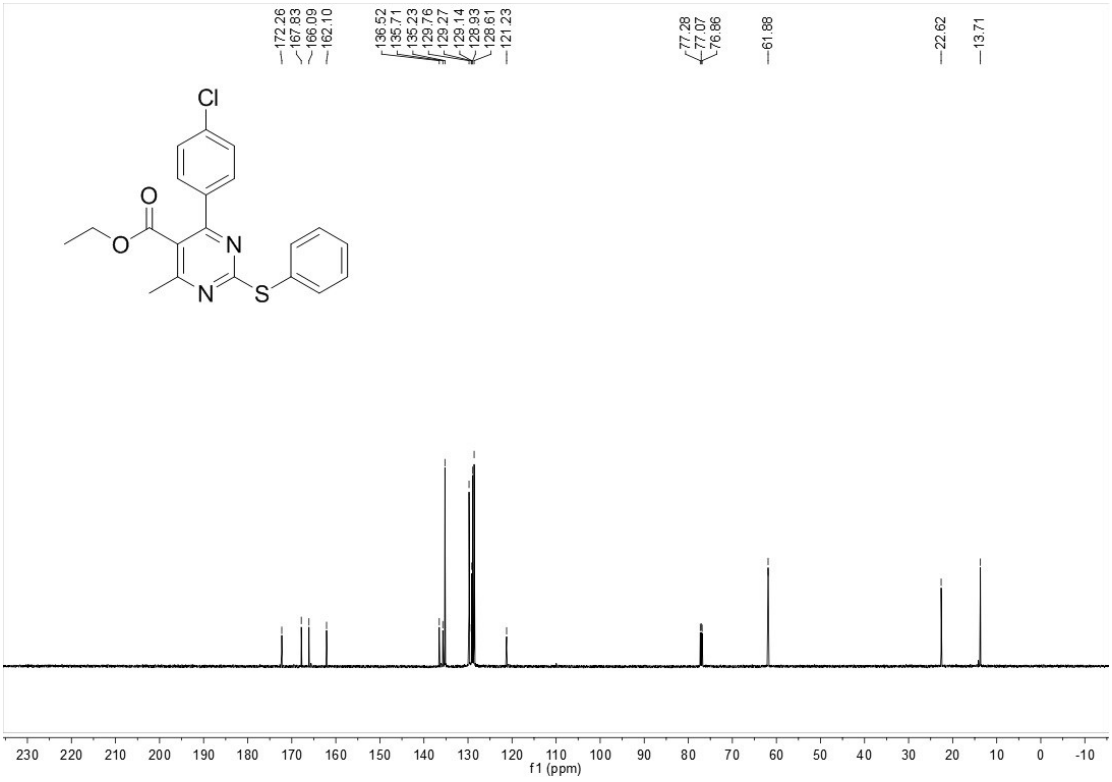
^{1}H and ^{13}C Spectra of compound 3j ($CDCl_3$, 400 MHz and 600MHz)



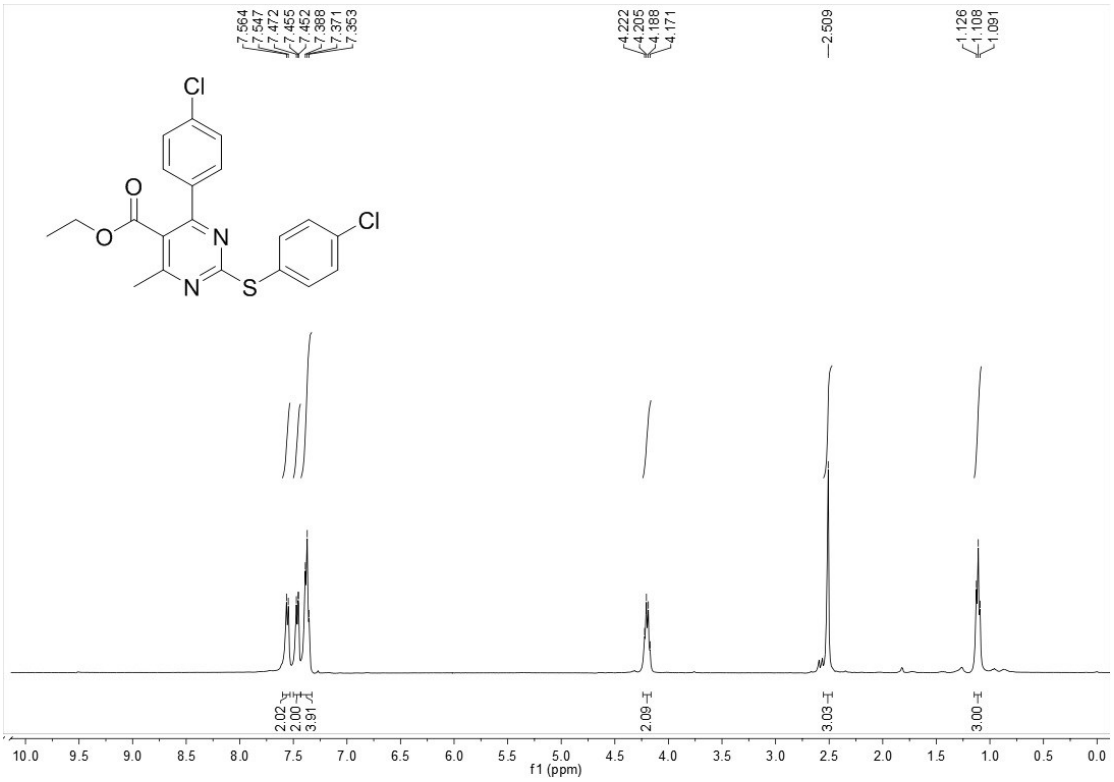


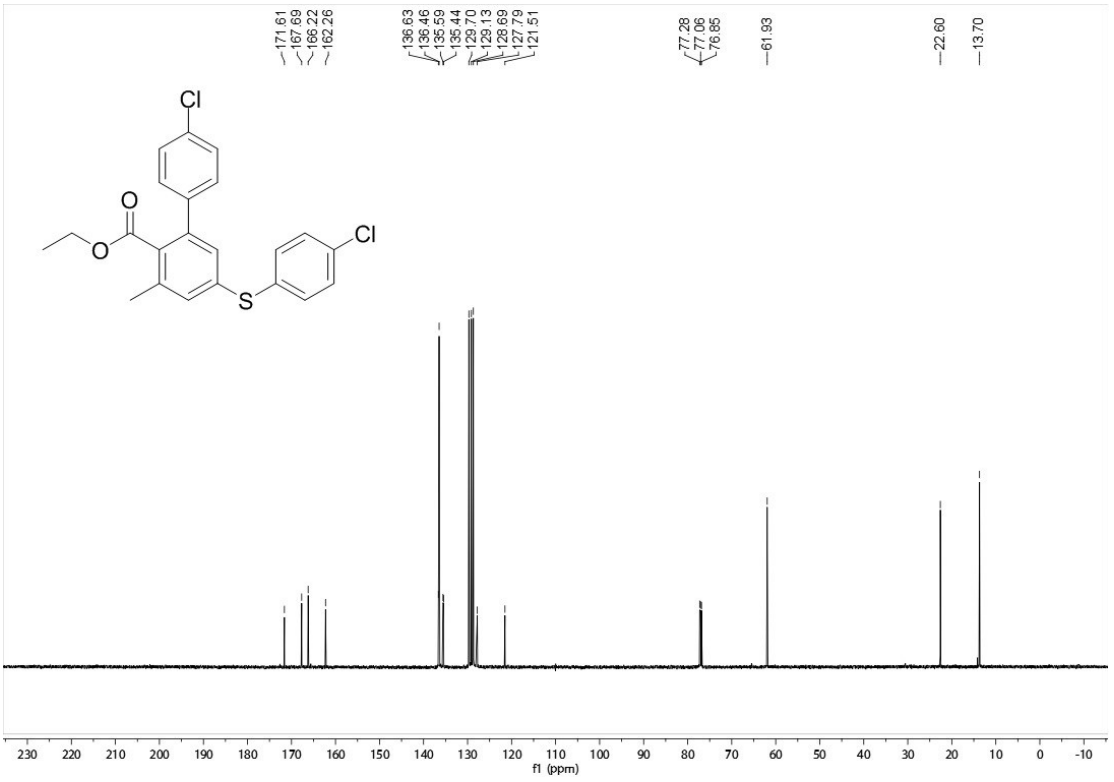
^{1}H and ^{13}C Spectra of compound 3k ($CDCl_3$, 400 MHz and 600MHz)



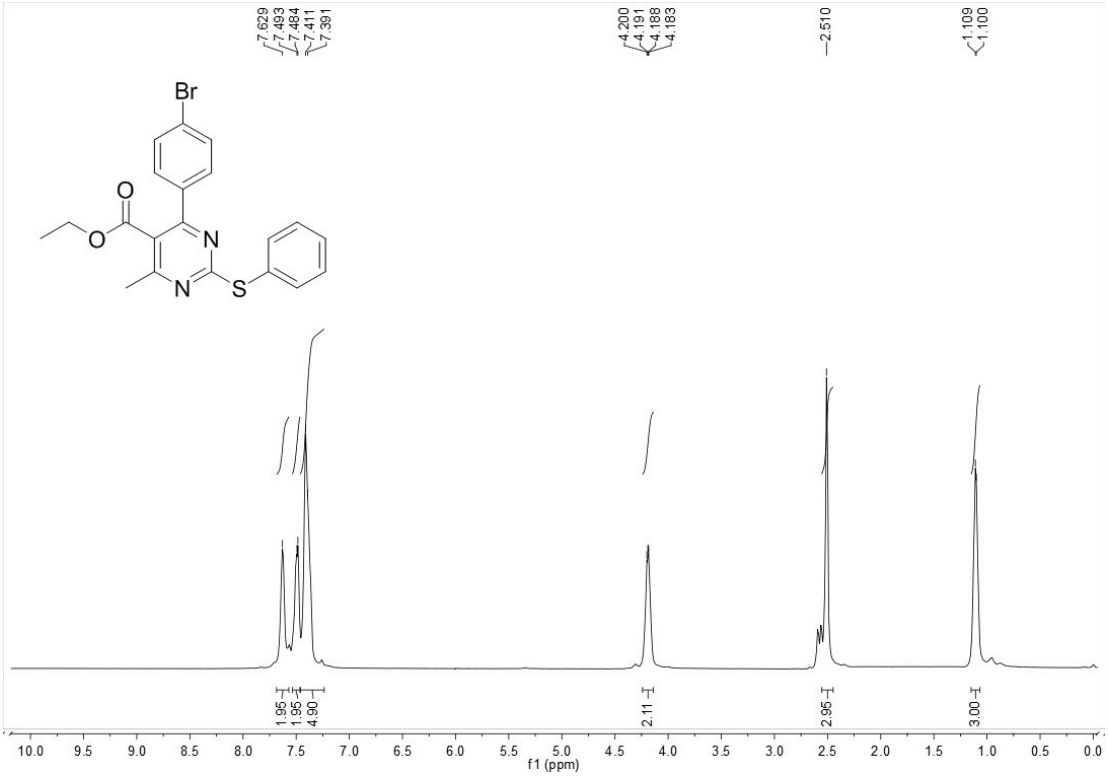


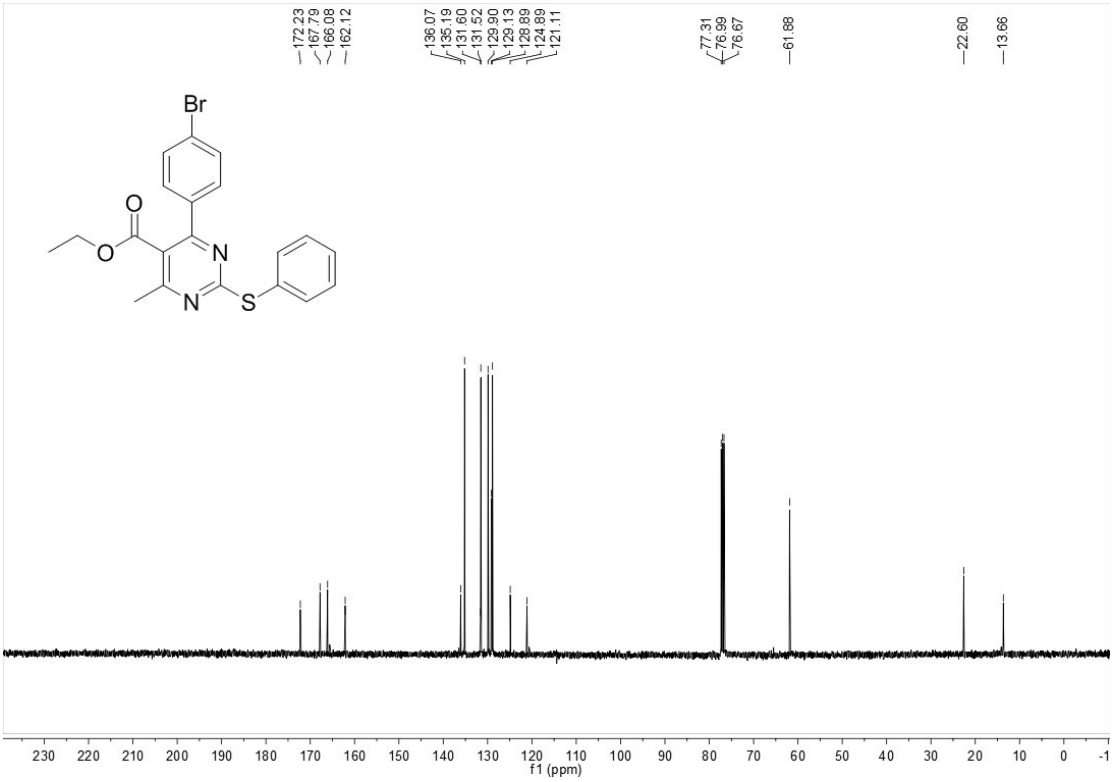
^{1}H and ^{13}C Spectra of compound 3l ($CDCl_3$, 400 MHz and 600MHz)



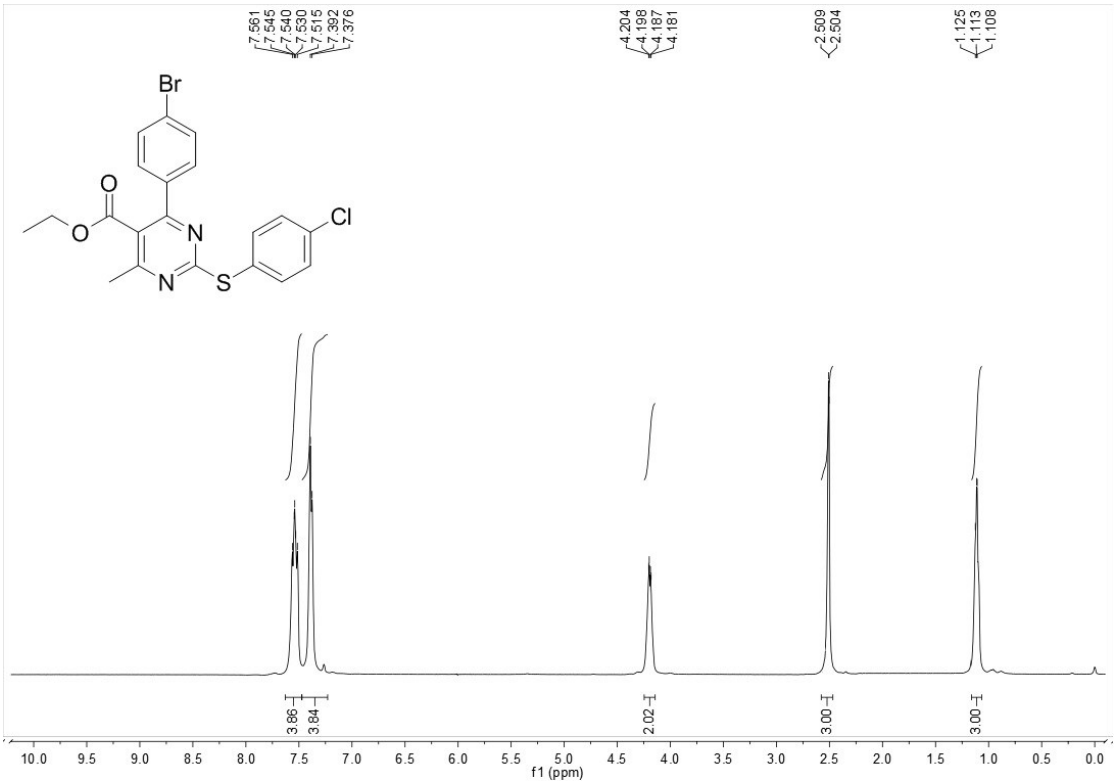


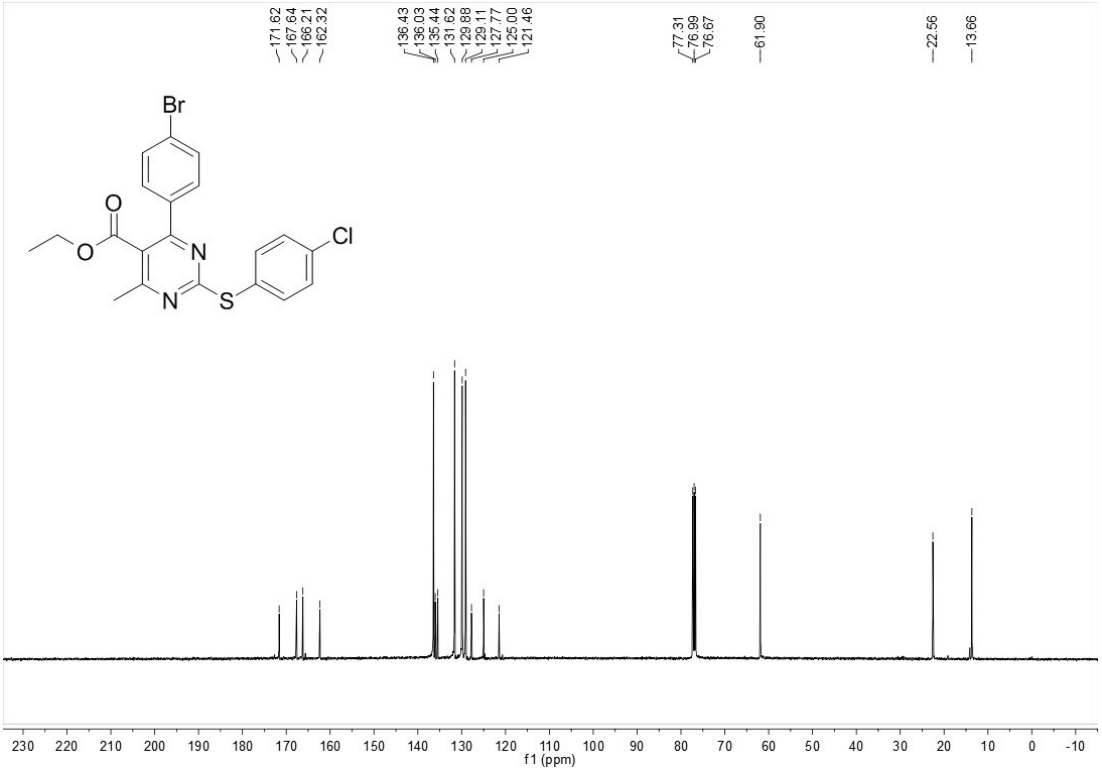
^{1}H and ^{13}C Spectra of compound 3m ($CDCl_3$, 400 MHz)



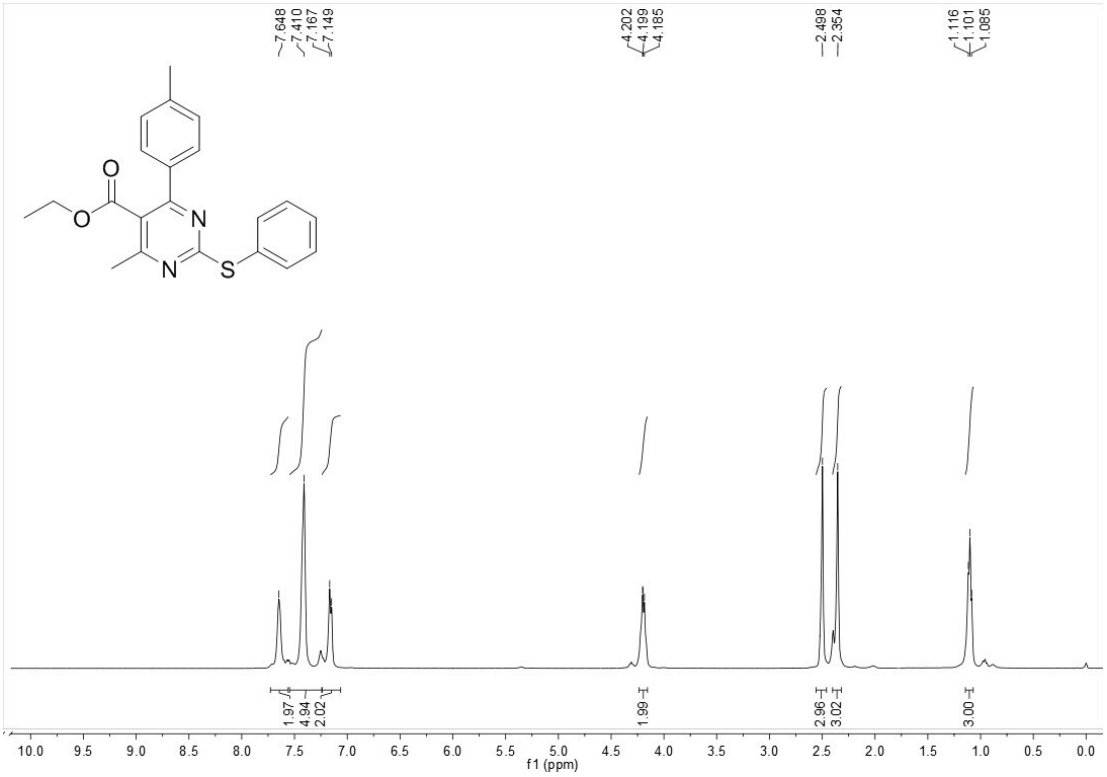


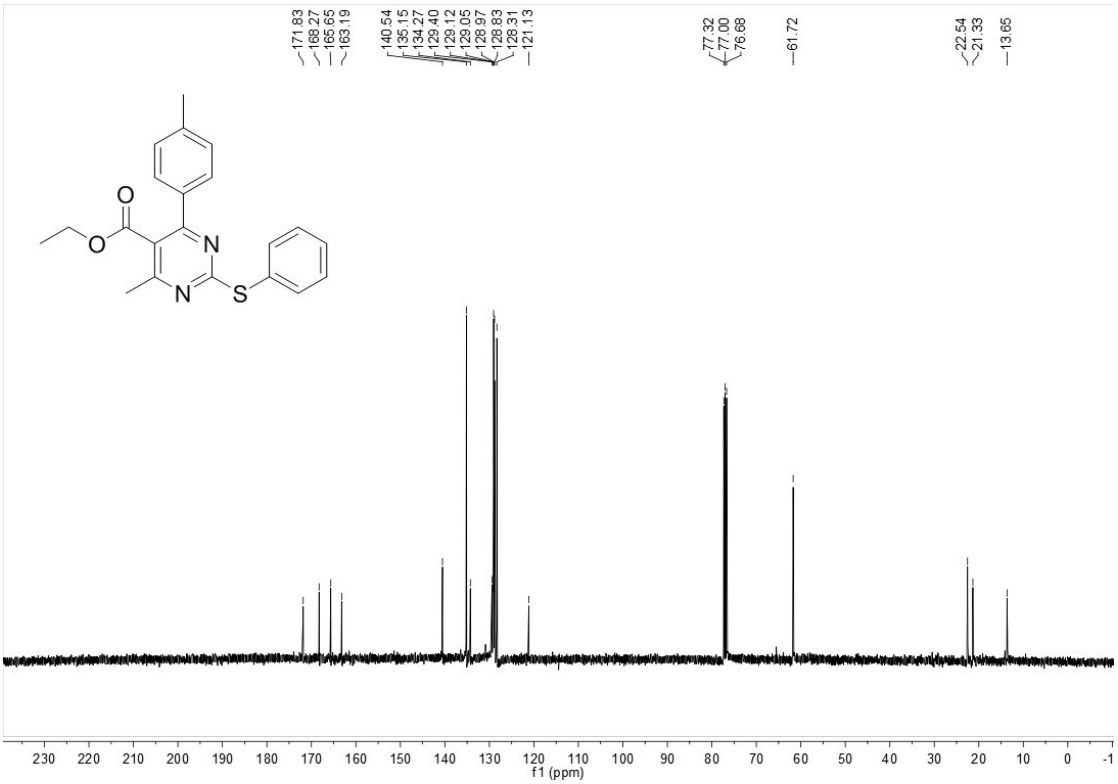
^{1}H and ^{13}C Spectra of compound 3n ($CDCl_3$, 400 MHz)



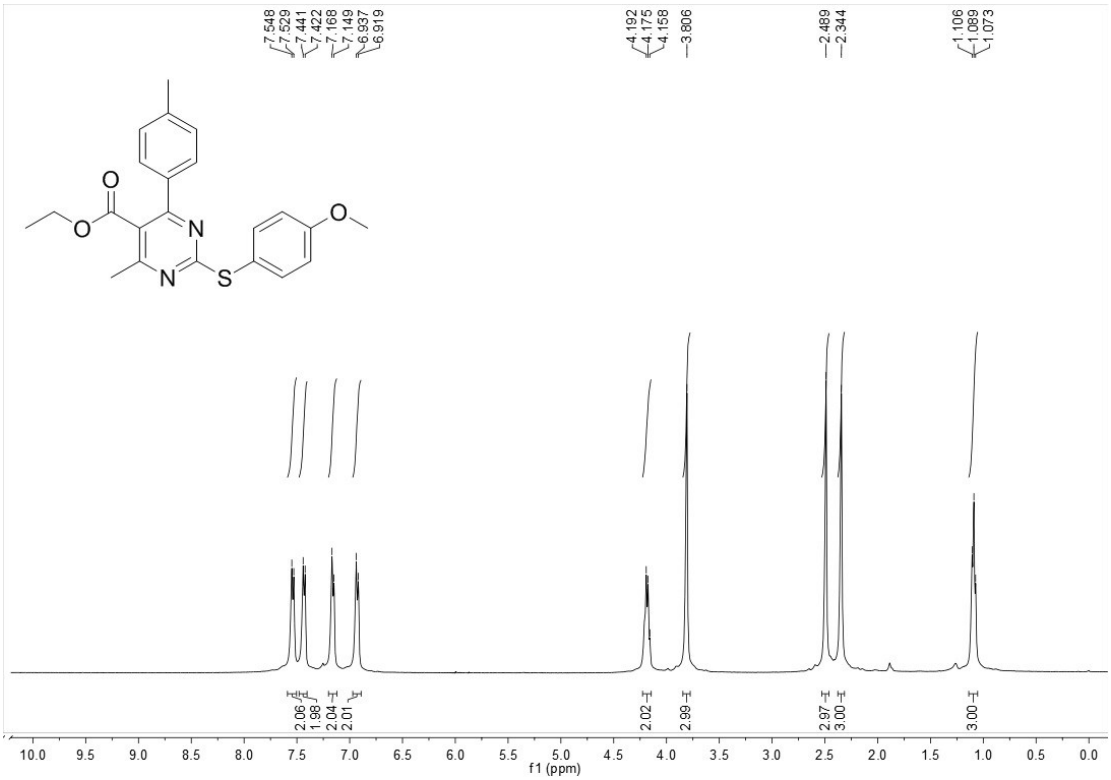


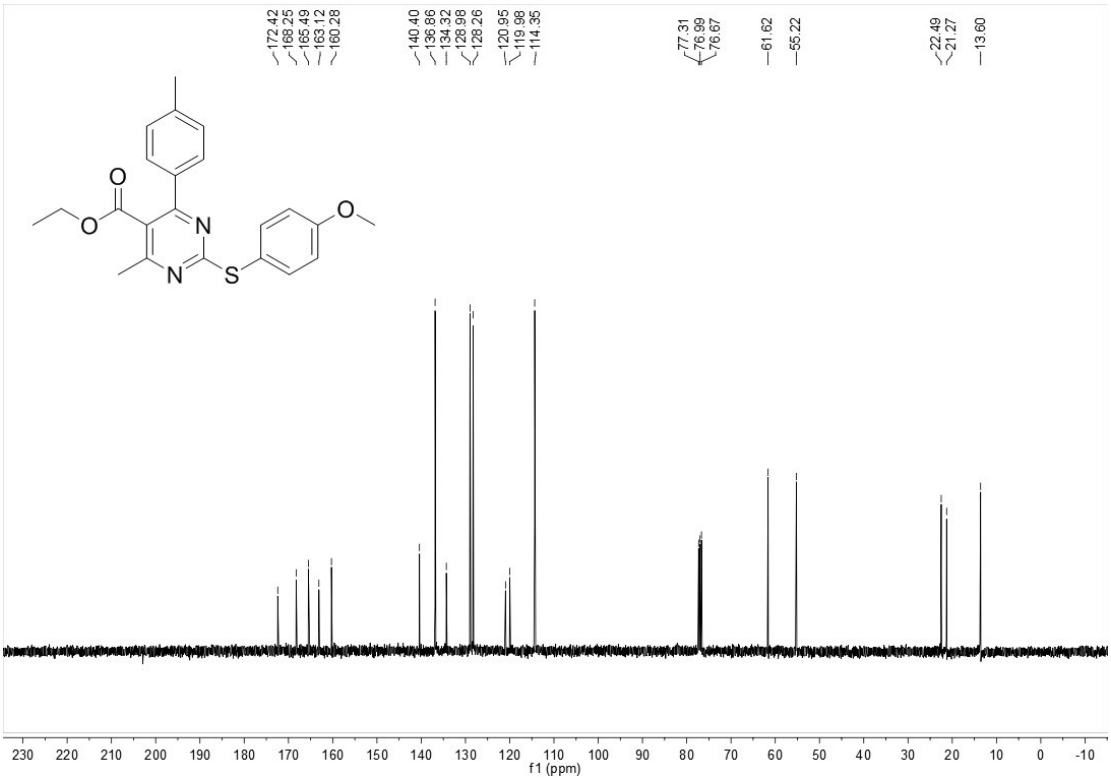
^{1}H and ^{13}C Spectra of compound 3o ($CDCl_3$, 400 MHz)



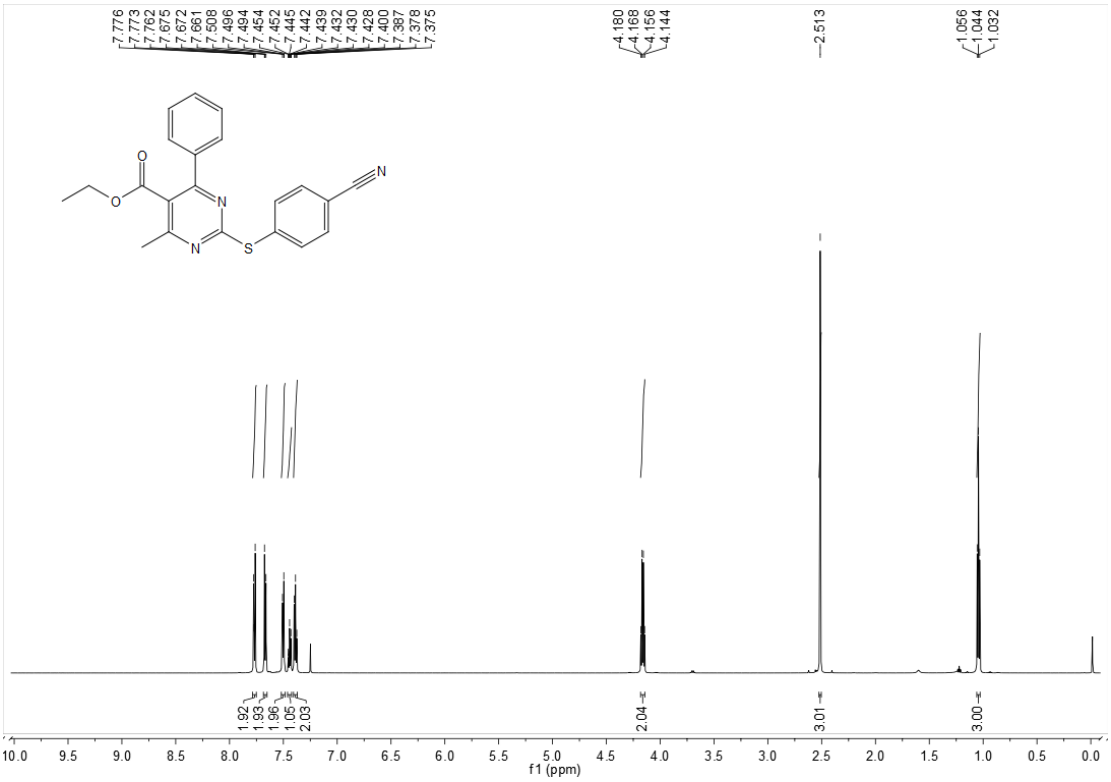


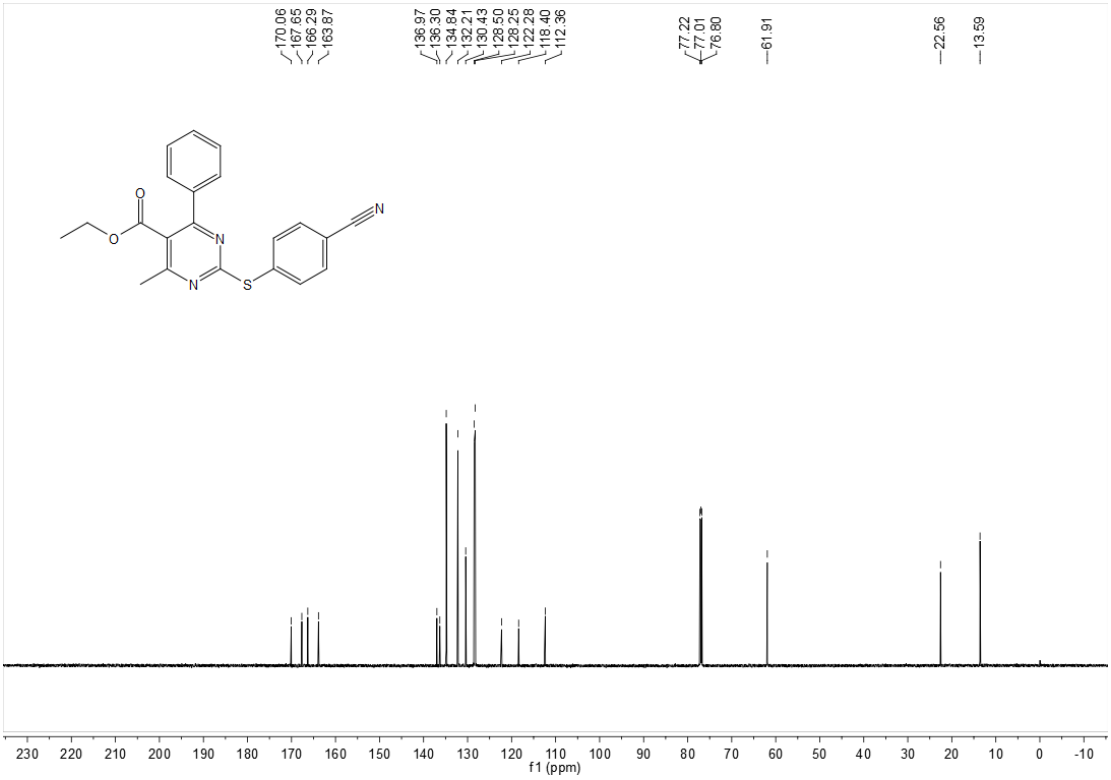
^{1}H and ^{13}C Spectra of compound 3p ($CDCl_3$, 400 MHz)



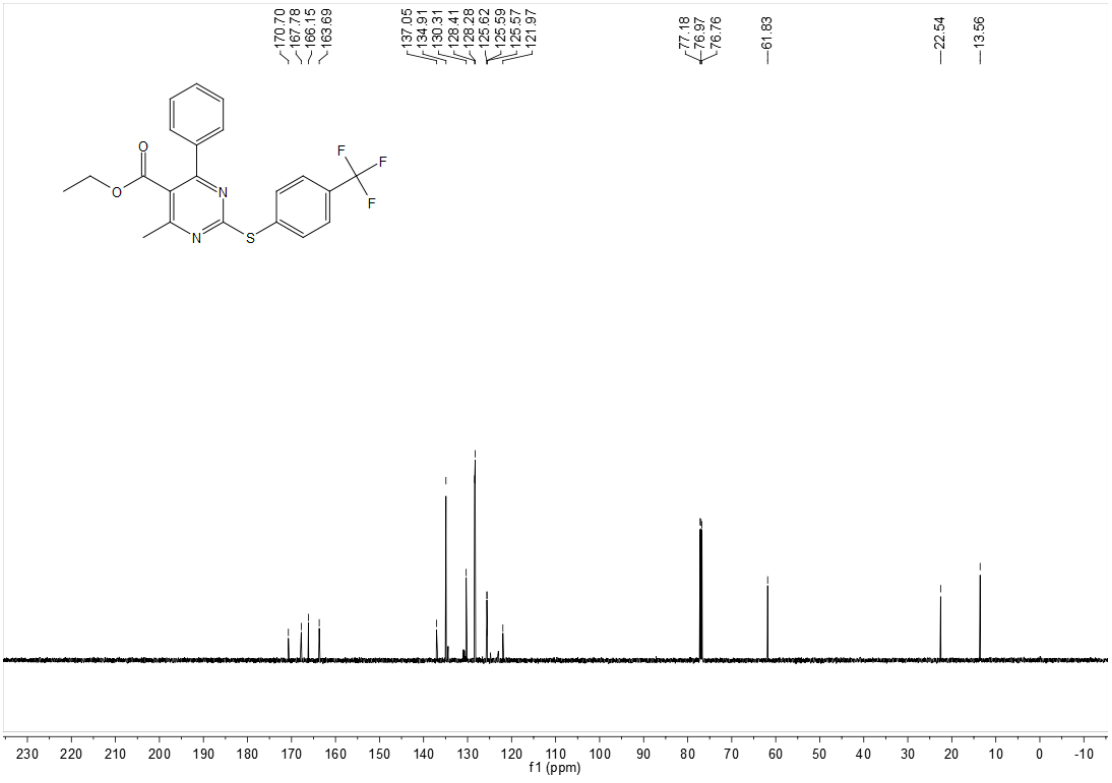


^{1}H and ^{13}C Spectra of compound 3q ($CDCl_3$, 600 MHz)

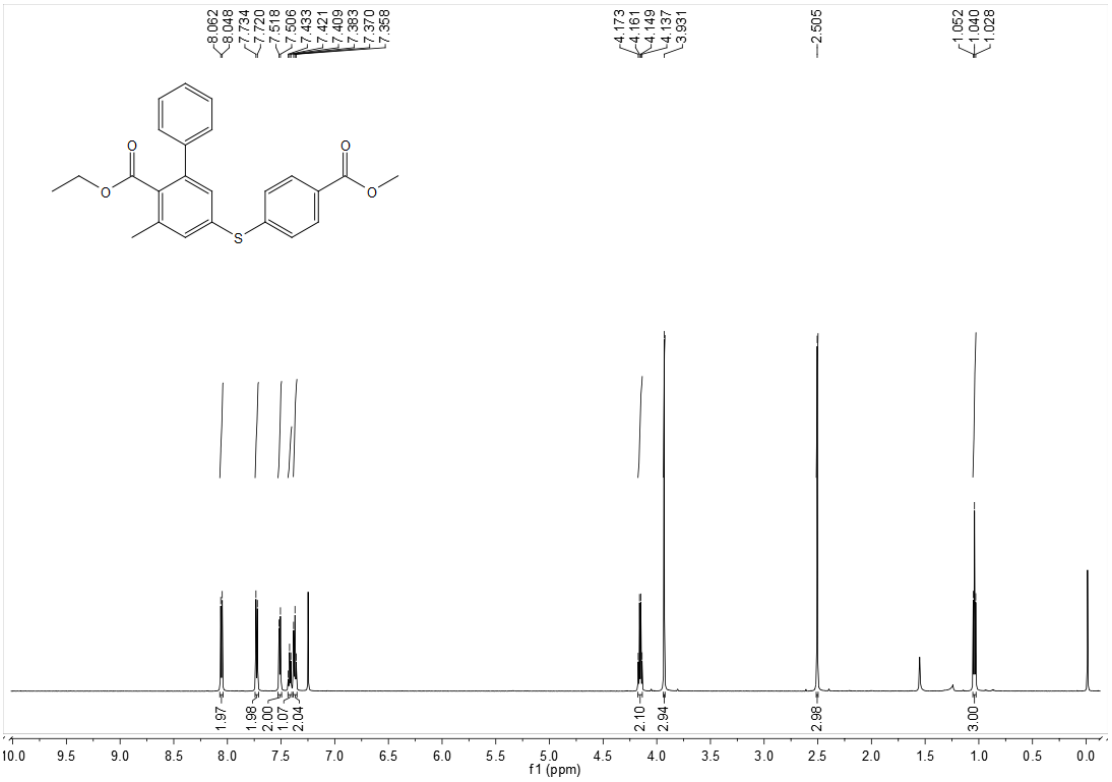


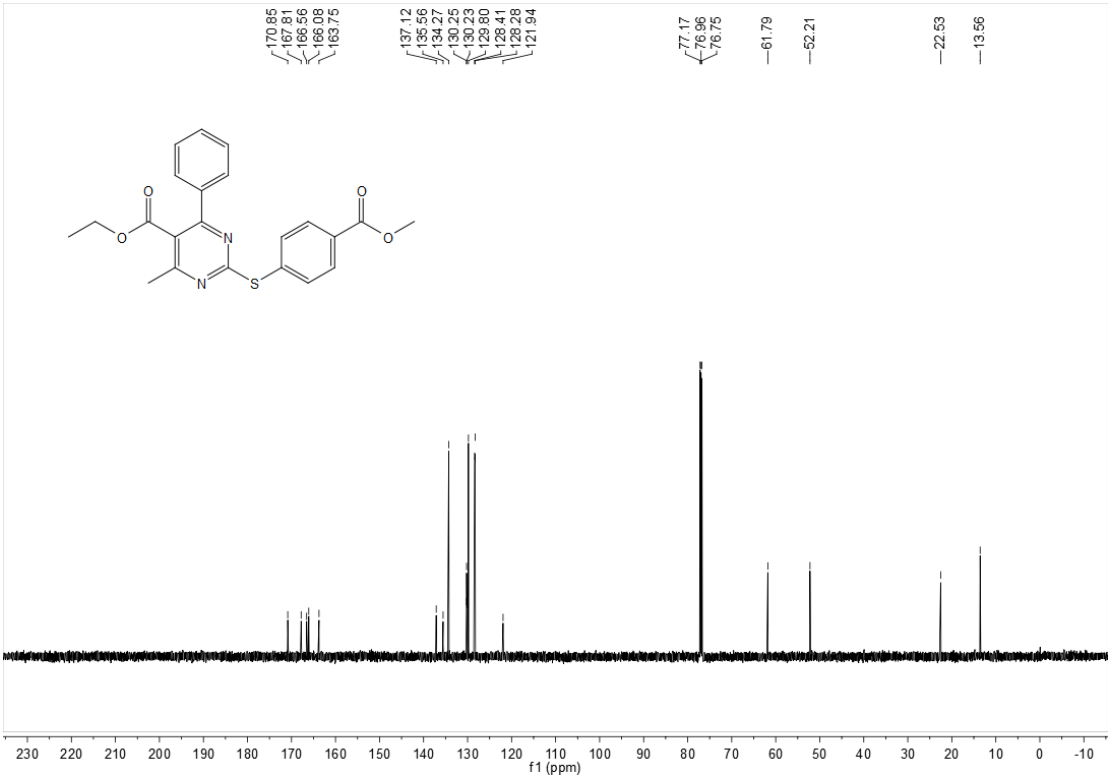


^{1}H and ^{13}C Spectra of compound 3r ($CDCl_3$, 600 MHz)

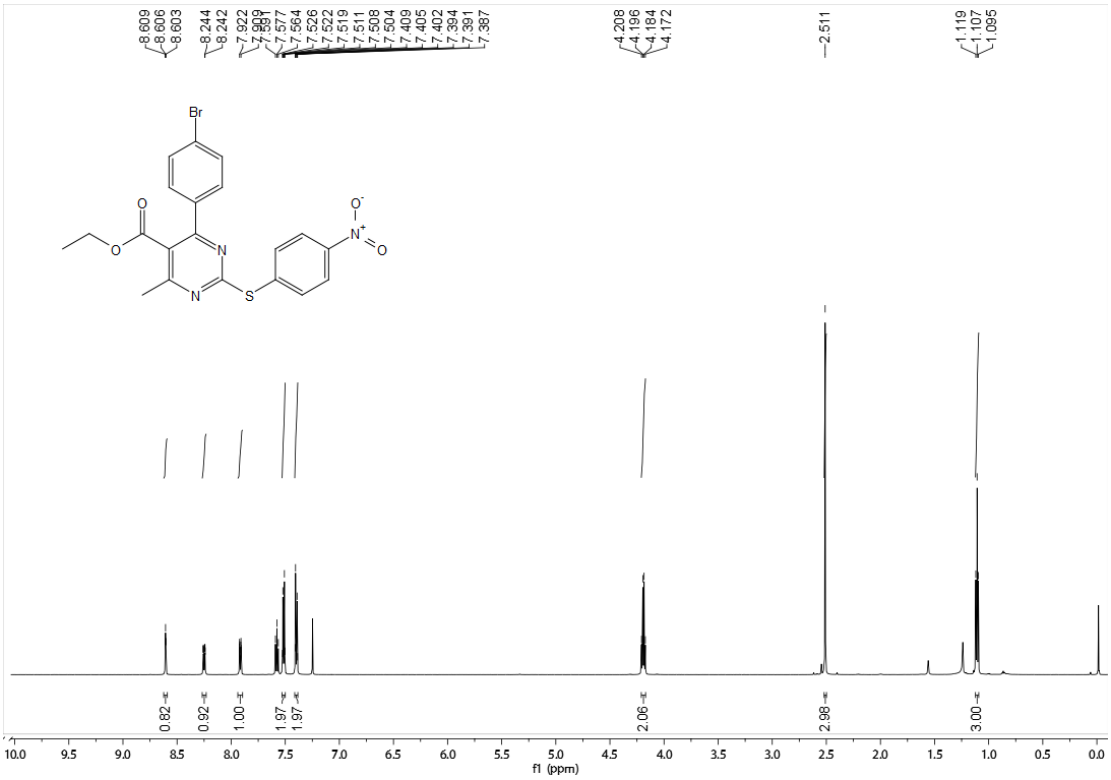


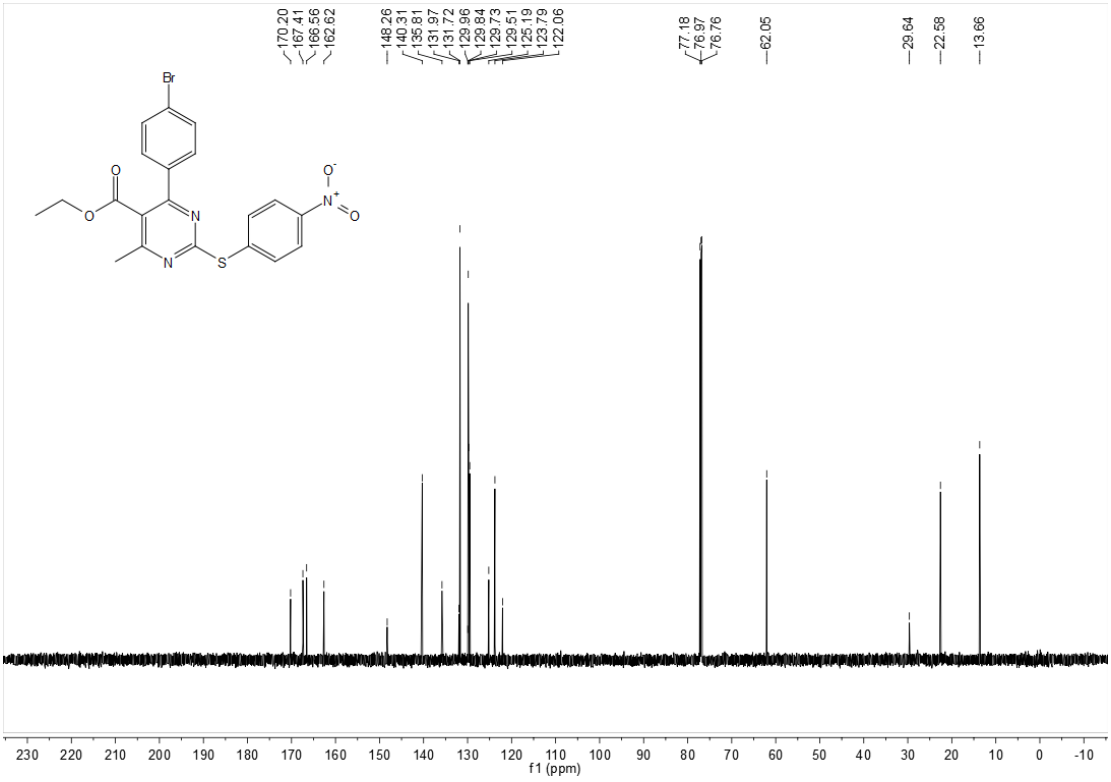
[1] H and [13]C Spectra of compound 3s ($CDCl_3$, 600 MHz)



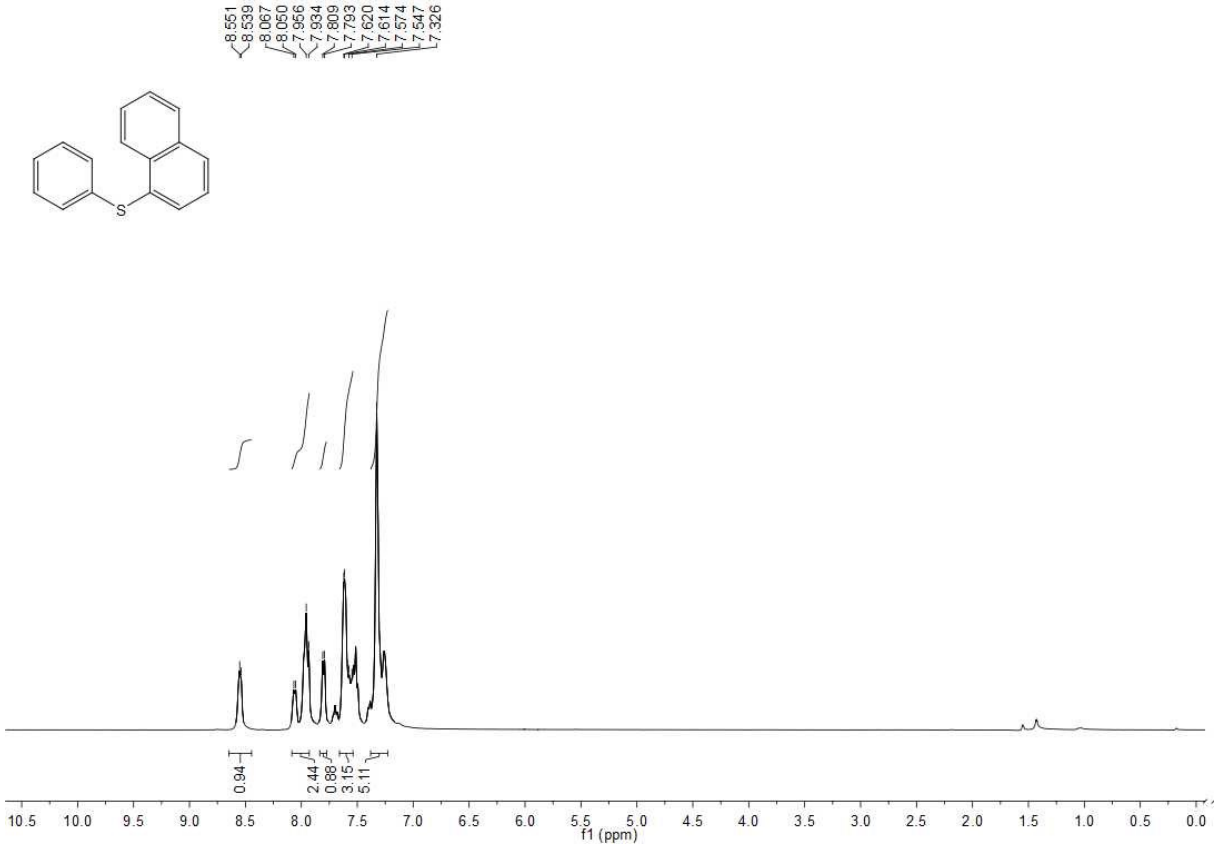


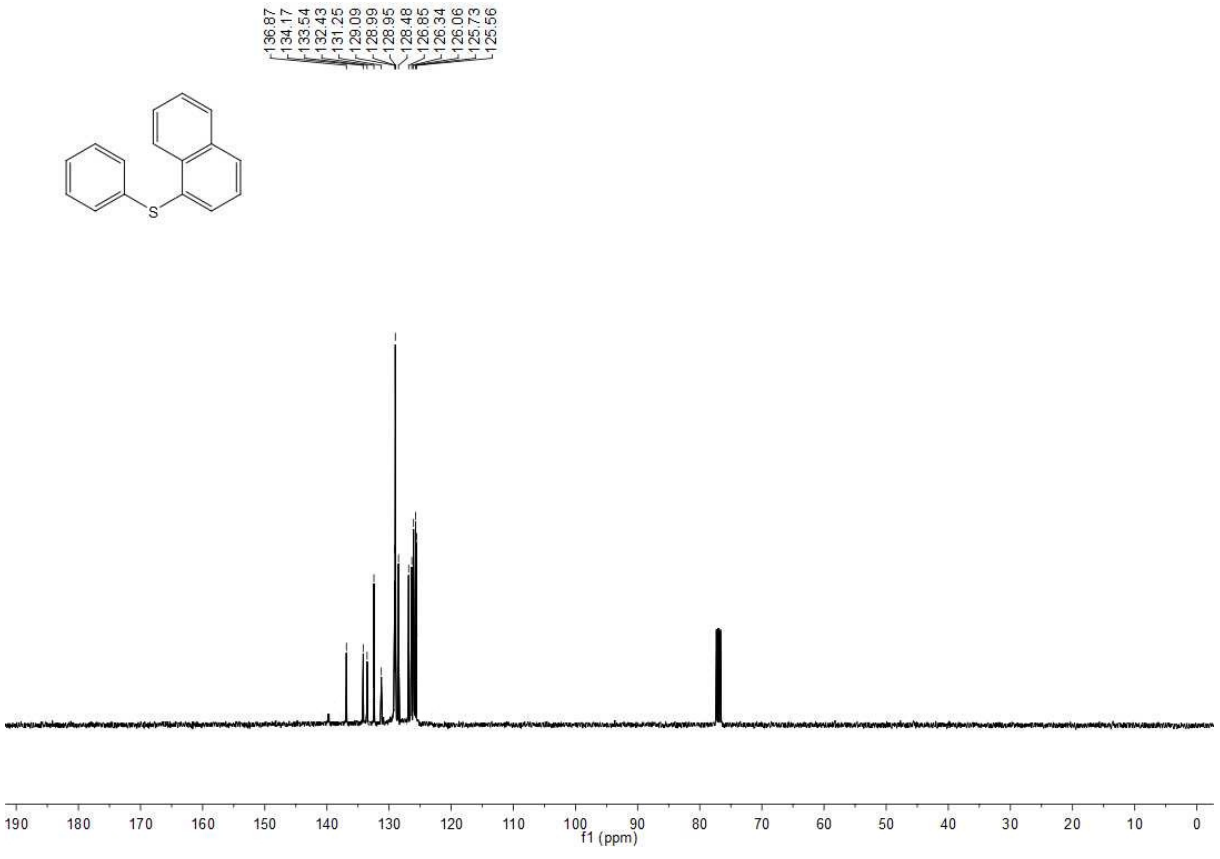
^{1}H and ^{13}C Spectra of compound 3t ($CDCl_3$, 600 MHz)



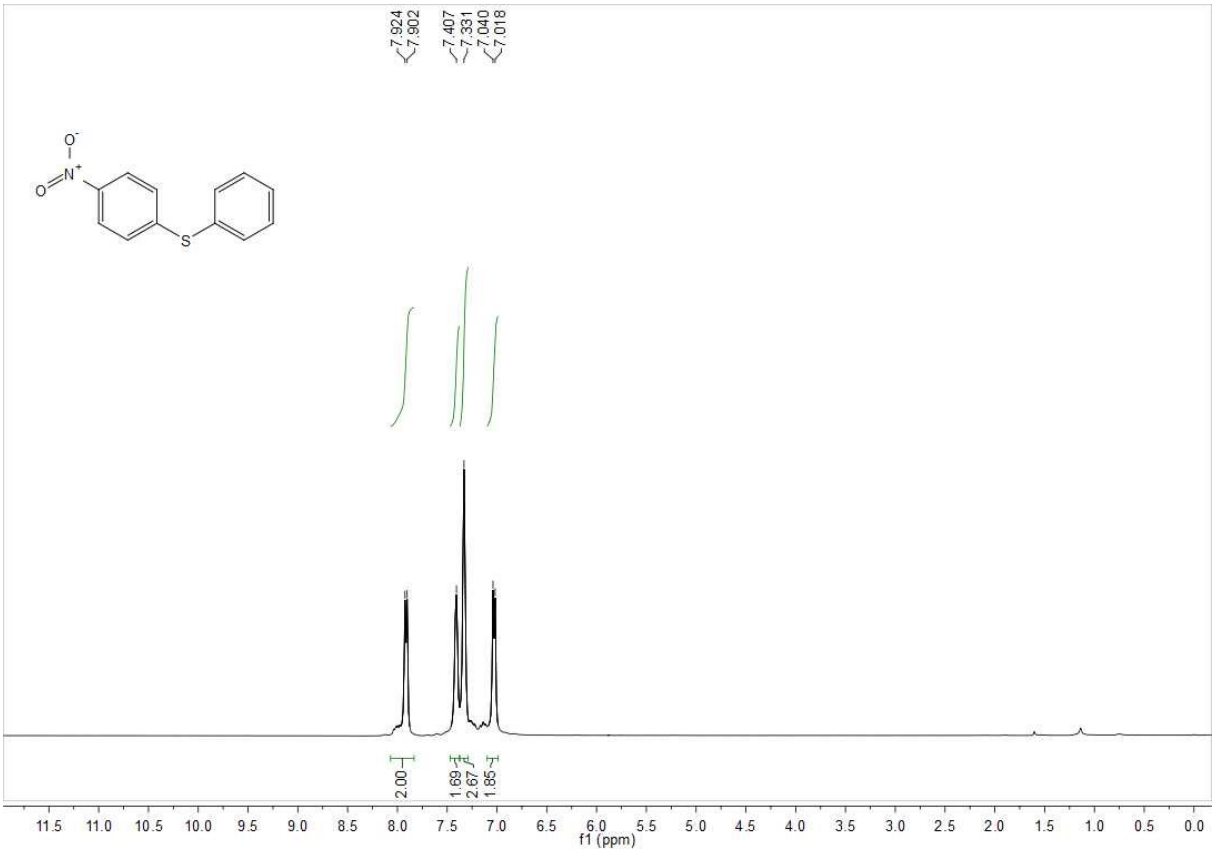


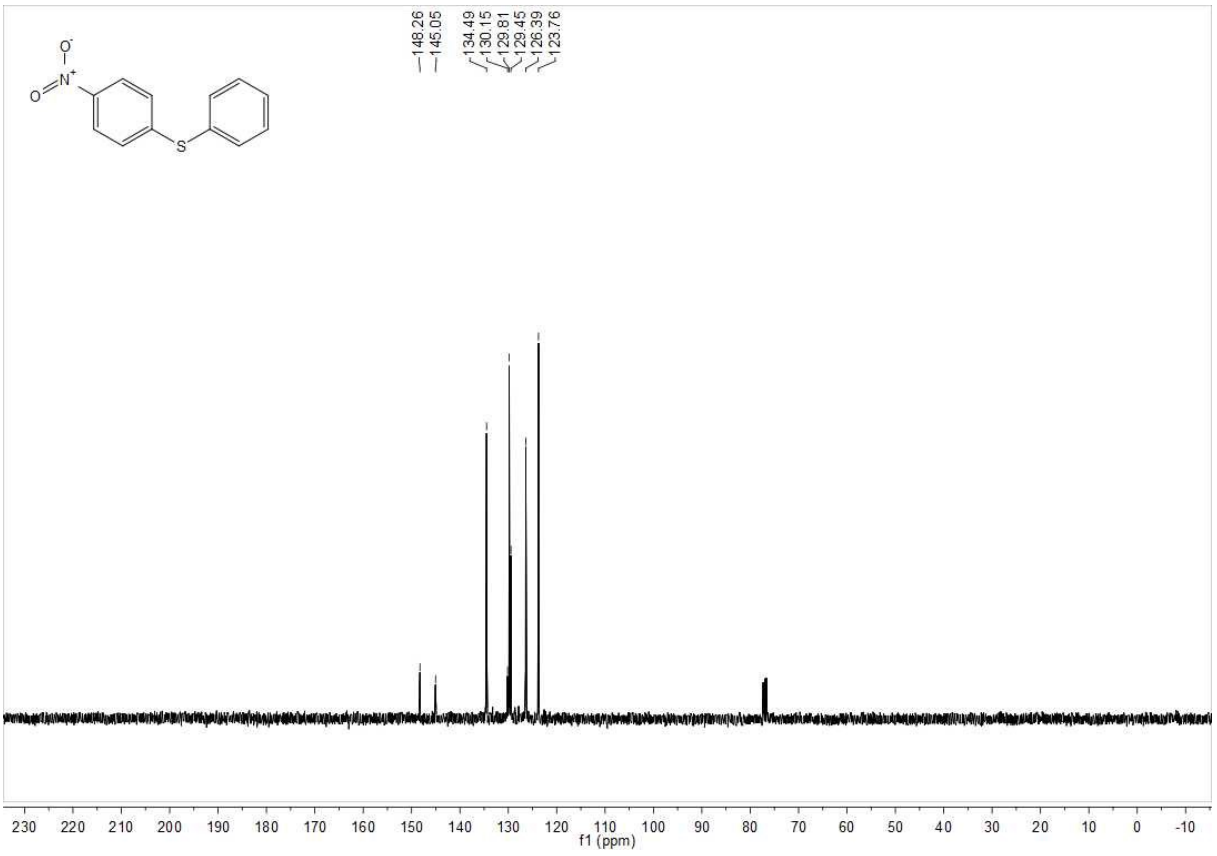
^{1}H and ^{13}C Spectra of compound 3u ($CDCl_3$, 400 MHz)





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





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