# Supporting Information

## Synthesis of substituted pyrroles using a silver-catalysed reaction between isocyanoacetates/benzyl isocyanides and chromones.

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## 1、 General Methods

Unless otherwise noted, all solvents and other reagents are commercially available and used without further purification. All reagents were weighed and handled in air at room temperature. Column chromatography was performed on silica gel (200~300 mesh). NMR spectra were recorded on Bruker AVANCE 300 NMR spectrometer or Bruker AVANCE III 400 NMR spectrometer or Bruker AVANCE III 500 NMR spectrometer or Bruker AVANCE III 600 NMR spectrometer. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), heptet (hept), multipet (m) and broad (br). Low and high-resolution mass spectra (LRMS and HRMS) were recorded on a Finnigan/MAT-95 (EI), Finnigan LCQ/DECA and Micromass Ultra Q-TOF (ESI) spectrometer. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and uncorrected.

## 2、 Experimental Procedures

**General procedure for the synthesis of chromenones.**

The chromenones were prepared by the addition of the corresponding substituted o-hydroxyacetophenone with N,N-dimethylformamide dimethyl acetal (DMFDMA), followed by cyclization by methylene chloride according to a reported protocol.[1]

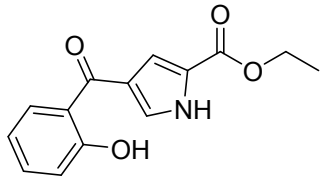
**General procedure for the synthesis of pyrroles.**

To a 10 mL of round bottomed flask was added the chromenones (0.5 mmol), isocyanoacetate (0.75 mmol), Silver carbonate (0.1 mmol), potassium carbonate (1 mmol), DMF (3 mL) in sequence. This mixture was heated to 100 °C with stirring for 1 h under air atmosphere, after that the reaction mixture was cooled down to room temperature, washed with ammonium chloride, and extracted with ethyl acetate (10 mL×3), washed with brine (10 mL), dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo to give the crude product, which was further purified by silica gel chromatography using an ethyl acetate/petroleum ether gradient mixture to afford the desired product.

1. M. Khoobi, M. Alipour, S. Zarei, F. Jafarpour and A. Shafiee, *Chem Commun*, 2012, **48**, 2985.

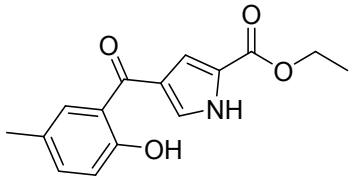
## 3、 Analytical Characterization Data of Products

### Ethyl 4-(2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3a)



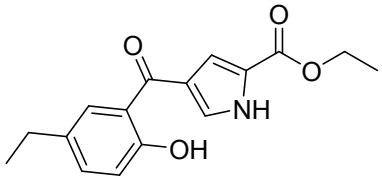
As a light yellow solid (127 mg, 98%), m. p. 110-112 ºC. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.70 (s, 1H), 10.95 (s, 1H), 7.60 (dd, $J$ = 7.7, 1.5 Hz, 1H), 7.56 (dd, $J$ = 3.4, 1.6 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.13 – 7.10 (m, 1H), 6.99 – 6.91 (m, 2H), 4.27 (d, $J$ = 7.1 Hz, 2H), 1.29 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.85 , 160.52 , 158.62 , 134.00 , 130.81 , 129.79 , 125.25 , 124.27 , 124.19 , 119.48 , 117.52 , 116.23 , 60.67 , 14.74 . LRMS (EI$^+$) found m/z 259. HRMS (EI$^+$) calculated for $C_{14}H_{13}NO_4$, 259.0845; found, 259.0840.

### Ethyl 4-(2-hydroxy-5-methylbenzoyl)-1*H*-pyrrole-2-carboxylate (3b)



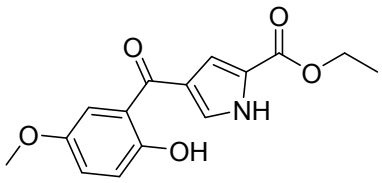
As a light yellow solid (128 mg, 94%), m. p. 120-122 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.66 (s, 1H), 10.70 (s, 1H), 7.57 (dd, $J$ = 3.2, 1.5 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.25 (dd, $J$ = 8.3, 1.8 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.88 (d, $J$ = 8.3 Hz, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 2.27 (s, 3H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.88 , 160.53 , 156.35 , 134.61 , 130.62 , 129.79 , 128.11 , 125.33 , 124.13 , 117.37 , 116.22 , 60.66 , 20.48 , 14.75 . LRMS (EI$^+$) found m/z 273. HRMS (EI$^+$) calculated for $C_{15}H_{15}NO_4$, 273.1001; found, 273.0993.

### Ethyl 4-(5-ethyl-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3c)



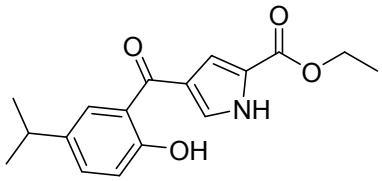
As a light yellow solid (141 mg, 98%), m. p. 135-137 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.65 (s, 1H), 10.70 (s, 1H), 7.56 (dd, $J$ = 3.4, 1.6 Hz, 1H), 7.39 (d, $J$ = 2.1 Hz, 1H), 7.29 (dd, $J$ = 8.4, 2.1 Hz, 1H), 7.13 – 7.11 (m, 1H), 6.90 (d, $J$ = 8.4 Hz, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 2.58 (q, $J$ = 7.6 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H), 1.16 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.91 , 160.52 , 156.49 , 134.58 , 133.46 , 129.75 , 129.48 , 125.35 , 124.19 , 124.13 , 117.43 , 116.23 , 60.66 , 27.60 , 16.22 , 14.75 . LRMS (EI$^+$) found m/z 287. HRMS (EI$^+$) calculated for $C_{16}H_{17}NO_4$, 287.1158; found, 287.1159.

### Ethyl 4-(2-hydroxy-5-methoxybenzoyl)-1*H*-pyrrole-2-carboxylate (3d)



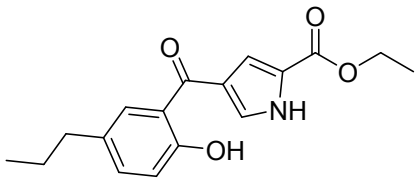
As a yellow solid (133 mg, 92%), m. p. 135-138 ºC. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 12.61 (s, 1H), 10.16 (s, 1H), 7.53 (dd, $J$ = 2.9, 1.4 Hz, 1H), 7.07 (t, $J$ = 1.6 Hz, 1H), 7.02 (dd, $J$ = 8.7, 3.2 Hz, 1H), 6.98 (d, $J$ = 2.8 Hz, 1H), 6.88 (d, $J$ = 8.7 Hz, 1H), 4.25 (q, $J$ = 7.1 Hz, 2H), 3.70 (s, 3H), 1.28 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.21 , 160.51 , 152.06 , 151.72 , 129.82 , 125.44 , 125.16 , 124.18 , 120.07 , 118.34 , 116.14 , 114.24 , 60.65 , 55.96 , 14.74 . LRMS (EI$^+$) found m/z 289. HRMS (EI$^+$) calculated for $C_{15}H_{15}NO_5$, 289.0950; found, 289.0947.

**Ethyl 4-(2-hydroxy-5-isopropylbenzoyl)-1*H*-pyrrole-2-carboxylate (3e)**



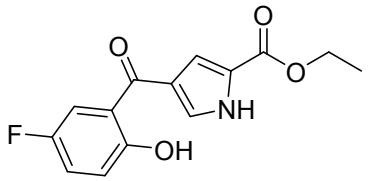
As a light yellow solid (149 mg, 99%), m. p. 121-125 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.64 (s, 1H), 10.67 (s, 1H), 7.55 – 7.53 (m, 1H), 7.40 (d, $J$ = 2.3 Hz, 1H), 7.33 (dd, $J$ = 8.5, 2.3 Hz, 1H), 7.11 (s, 1H), 6.91 (d, $J$ = 8.4 Hz, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 2.88 (p, $J$ = 6.9 Hz, 1H), 1.29 (t, $J$ = 7.1 Hz, 3H), 1.18 (d, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.93 , 160.51 , 156.50 , 139.19 , 131.98 , 129.70 , 128.05 , 125.38 , 124.16 , 124.13 , 117.41 , 116.23 , 60.65 , 32.87 , 24.39 , 14.74 . LRMS (EI$^+$) found m/z 301. HRMS (EI$^+$) calculated for $C_{17}H_{19}NO_4$, 301.1314; found, 301.1305.

**Ethyl 4-(2-hydroxy-5-propylbenzoyl)-1*H*-pyrrole-2-carboxylate (3f)**



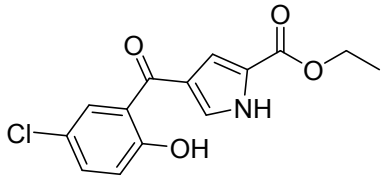
As a light yellow solid (149 mg, 99%), m. p. 133-135 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.65 (s, 1H), 10.71 (s, 1H), 7.55 (dd, $J$ = 3.3, 1.6 Hz, 1H), 7.38 (d, $J$ = 2.1 Hz, 1H), 7.27 (dd, $J$ = 8.4, 2.1 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.90 (d, $J$ = 8.4 Hz, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 2.52 (d, $J$ = 7.4 Hz, 2H), 1.56 (q, $J$ = 7.4 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H), 0.89 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.92 , 160.51 , 156.60 , 134.04 , 132.91 , 130.13 , 129.71 , 125.33 , 124.13 , 124.01 , 117.39 , 116.25 , 60.66 , 36.61 , 24.65 , 14.73 , 13.97 . LRMS (EI$^+$) found m/z 301. HRMS (EI$^+$) calculated for $C_{17}H_{19}NO_4$, 301.1314; found, 301.1312.

**Ethyl 4-(5-fluoro-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3g)**



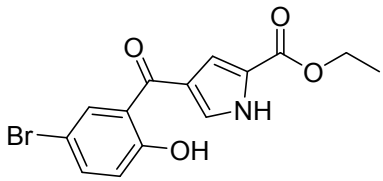
As a light yellow solid (125 mg, 90%), m. p. 148-150 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.71 (s, 1H), 11.52 (s, 1H), 7.71 (dd, $J$ = 8.2, 7.0 Hz, 1H), 7.59 (dd, $J$ = 3.2, 1.5 Hz, 1H), 7.14 – 7.12 (m, 1H), 6.82 – 6.76 (m, 2H), 4.28 (q, $J$ = 7.1 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 190.81 , 165.38 (d, $J$ = 249.9 Hz), 161.07 (d, $J$ = 13.0 Hz), 160.50 , 133.36 (d, $J$ = 11.3 Hz), 129.87 , 125.04 , 124.26 , 121.12 , 116.18 , 106.93 (d, $J$ = 22.1 Hz), 104.30 (d, $J$ = 23.8 Hz), 60.70 , 14.74 . LRMS (EI$^+$) found m/z 277. HRMS (EI$^+$) calculated for $C_{14}H_{12}FNO_4$, 277.0750; found, 277.0751.

### Ethyl 4-(5-chloro-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3h)



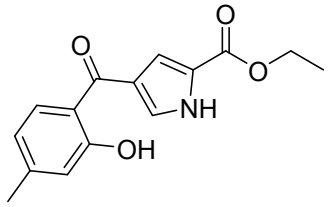
As a light yellow solid (122 mg, 83%), m. p. 164-167 ºC. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.65 (s, 1H), 10.45 (s, 1H), 7.48 (dd, $J$ = 3.4, 1.6 Hz, 1H), 7.39 (dd, $J$ = 8.7, 2.7 Hz, 1H), 7.34 (d, $J$ = 2.7 Hz, 1H), 7.02 (dd, $J$ = 2.4, 1.7 Hz, 1H), 6.95 (d, $J$ = 8.7 Hz, 1H), 4.25 (q, $J$ = 7.1 Hz, 2H), 1.27 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 189.38 , 160.49 , 155.37 , 132.24 , 130.02 , 128.99 , 128.17 , 125.56 , 124.29 , 122.89 , 119.00 , 115.89 , 60.68 , 14.73 . LRMS (EI$^+$) found m/z 293. HRMS (EI$^+$) calculated for $C_{14}H_{12}NClO_4$, 293.0455; found, 293.0452.

### Ethyl 4-(5-bromo-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3i)



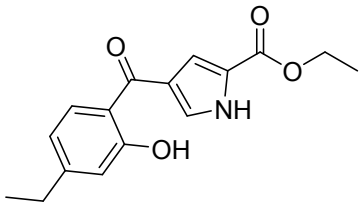
As a yellow solid (143 mg, 85%), m. p. 175-178 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.64 (s, 1H), 10.48 (s, 1H), 7.52 (dd, $J$ = 8.7, 2.5 Hz, 1H), 7.49 (dd, $J$ = 3.3, 1.5 Hz, 1H), 7.47 (d, $J$ = 2.5 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.93 (d, $J$ = 8.7 Hz, 1H), 4.27 (q, $J$ = 7.1 Hz, 2H), 1.29 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 189.26 , 160.50 , 155.73 , 135.06 , 131.79 , 130.01 , 128.84 , 125.59 , 124.29 , 119.47 , 115.88 , 110.33 , 60.68 , 14.74 . LRMS (EI$^+$) found m/z 337. HRMS (EI$^+$) calculated for $C_{14}H_{12}NBrO_4$, 336.9950; found, 336.9943.

### Ethyl 4-(2-hydroxy-4-methylbenzoyl)-1*H*-pyrrole-2-carboxylate (3j)



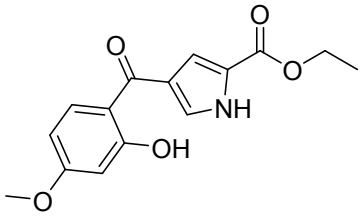
As a light yellow solid (123 mg, 90%), m. p. 138-140 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.71 (s, 1H), 11.49 (s, 1H), 7.65 (d, $J$ = 7.9 Hz, 1H), 7.62 (dd, $J$ = 3.4, 1.7 Hz, 1H), 7.18 – 7.13 (m, 1H), 6.81 (s, 1H), 6.80 (d, $J$ = 8.0 Hz, 1H), 4.29 (q, $J$ = 7.1 Hz, 2H), 2.33 (s, 3H), 1.31 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 192.14 , 160.51 , 160.23 , 145.67 , 131.42 , 129.63 , 124.80 , 124.15 , 120.63 , 120.18 , 117.96 , 116.33 , 60.69 , 21.75 , 14.75 . LRMS (EI$^+$) found m/z 273. HRMS (EI$^+$) calculated for $C_{15}H_{15}NO_4$, 273.1001; found, 273.1006.

### Ethyl 4-(4-ethyl-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3k)



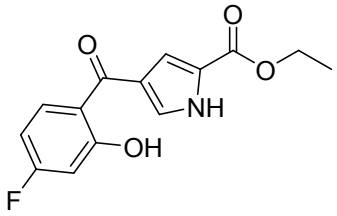
As a light yellow solid (133 mg, 93%), m. p. 139-142 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.71 (s, 1H), 11.49 (s, 1H), 7.68 (d, $J$ = 8.4 Hz, 1H), 7.63 (dd, $J$ = 3.3, 1.6 Hz, 1H), 7.18 – 7.15 (m, 1H), 6.86 – 6.81 (m, 2H), 4.29 (q, $J$ = 7.1 Hz, 2H), 2.62 (q, $J$ = 7.6 Hz, 2H), 1.31 (t, $J$ = 7.1 Hz, 3H), 1.20 (t, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 192.14 , 160.51 , 160.35 , 151.73 , 131.54 , 129.66 , 124.79 , 124.14 , 120.37 , 119.43 , 116.76 , 116.34 , 60.69 , 28.70 , 15.35 , 14.76 . LRMS (EI$^+$) found m/z 287. HRMS (EI$^+$) calculated for $C_{16}H_{17}NO_4$, 287.1158; found, 287.1157.

### Ethyl 4-(2-hydroxy-4-methoxybenzoyl)-1*H*-pyrrole-2-carboxylate (3l)



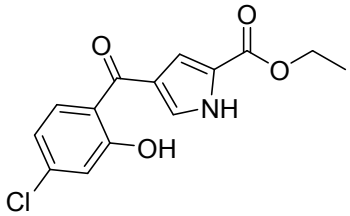
As a yellow solid (130 mg, 90%), m. p. 138-141 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.73 (s, 1H), 12.55 (s, 1H), 7.85 (d, $J$ = 8.9 Hz, 1H), 7.67 (s, 1H), 7.19 (s, 1H), 6.57 (dd, $J$ = 8.9, 2.3 Hz, 1H), 6.53 (d, $J$ = 2.3 Hz, 1H), 4.29 (q, $J$ = 7.1 Hz, 2H), 3.84 (s, 3H), 1.31 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.79 , 165.37 , 164.38 , 160.51 , 133.81 , 129.30 , 124.28 , 124.10 , 116.33 , 114.59 , 107.47 , 101.66 , 60.69 , 56.10 , 14.77 . LRMS (EI$^+$) found m/z 289. HRMS (EI$^+$) calculated for $C_{15}H_{15}NO_5$, 289.0950; found, 289.0953.

### Ethyl 4-(4-fluoro-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3m)



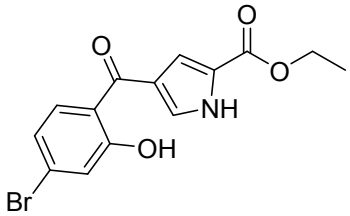

As a light yellow solid (129 mg, 93%), m. p. 143-145 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.71 (s, 1H), 11.51 (s, 1H), 7.73 – 7.68 (m, 1H), 7.59 (d, $J$ = 1.2 Hz, 1H), 7.12 (d, $J$ = 1.4 Hz, 1H), 6.83 – 6.76 (m, 2H), 4.28 (d, $J$ = 7.1 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 190.80 , 165.37 (d, $J$ = 249.8 Hz), 161.04 (d, $J$ = 12.9 Hz), 160.50 , 133.35 (d, $J$ = 11.5 Hz), 129.87 , 125.05 , 124.26 , 121.15 , 116.17 , 106.93 (d, $J$ = 22.1 Hz), 104.30 (d, $J$ = 23.9 Hz), 60.70 , 14.75 . LRMS (EI$^+$) found m/z 277. HRMS (EI$^+$) calculated for $C_{14}H_{12}NFO_4$, 277.0750; found, 277.0745.

### Ethyl 4-(4-chloro-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3n)



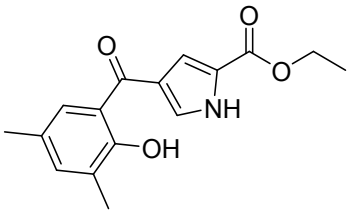

As a light yellow solid (126 mg, 86%), m. p. 151-155 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.68 (s, 1H), 11.05 (s, 1H), 7.53 (d, $J$ = 8.4 Hz, 2H), 7.09 (d, $J$ = 1.4 Hz, 1H), 7.03 (d, $J$ = 2.0 Hz, 1H), 6.98 (dd, $J$ = 8.3, 2.0 Hz, 1H), 4.27 (q, $J$ = 7.1 Hz, 2H), 1.29 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 190.33 , 160.50 , 158.65 , 137.25 , 131.98 , 129.97 , 125.37 , 124.44 , 124.29 , 119.58 , 117.06 , 116.02 , 60.69 , 14.74 . LRMS (EI$^+$) found m/z 293. HRMS (EI$^+$) calculated for $C_{14}H_{12}NClO_4$, 293.0455; found, 293.0456.

### Ethyl 4-(4-bromo-2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3o)



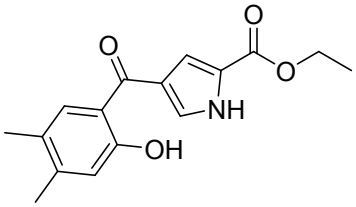

As a light yellow solid (145 mg, 86%), m. p. 175-178 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.68 (s, 1H), 10.98 (s, 1H), 7.54 (s, 1H), 7.45 (d, $J$ = 8.2 Hz, 1H), 7.18 (d, $J$ = 1.8 Hz, 1H), 7.12 (dd, $J$ = 8.2, 1.8 Hz, 1H), 7.08 (s, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 190.34 , 160.49 , 158.41 , 132.00 , 129.98 , 125.86 , 125.42 , 124.97 , 124.29 , 122.45 , 119.95 , 115.99 , 60.69 , 14.74 . LRMS (EI$^+$) found m/z 337. HRMS (EI$^+$) calculated for $C_{14}H_{12}BrNO_4$, 336.9950; found, 336.9953.

### Ethyl 4-(2-hydroxy-3,5-dimethylbenzoyl)-1*H*-pyrrole-2-carboxylate (3p)



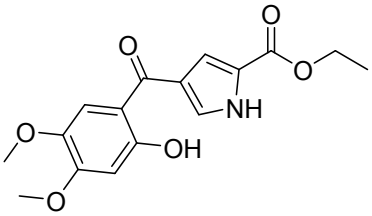
As a light yellow solid (136 mg, 95%), m. p. 150-153 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.64 (s, 1H), 11.74 (s, 1H), 7.59 – 7.56 (m, 1H), 7.37 (s, 1H), 7.13 (s, 1H), 7.09 – 7.05 (m, 1H), 4.18 (q, $J$ = 7.1 Hz, 2H), 2.14 (s, 3H), 2.06 (s, 3H), 1.19 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 193.44 , 160.49 , 157.53 , 137.46 , 129.90 , 129.19 , 127.61 , 126.41 , 124.35 , 124.27 , 120.15 , 116.49 , 60.72 , 20.57 , 15.85 , 14.75 . LRMS (EI$^+$) found m/z 287. HRMS (EI$^+$) calculated for $C_{16}H_{17}NO_4$, 287.1158; found, 287.1162.

**Ethyl 4-(2-hydroxy-4,5-dimethylbenzoyl)-1*H*-pyrrole-2-carboxylate (3q)**



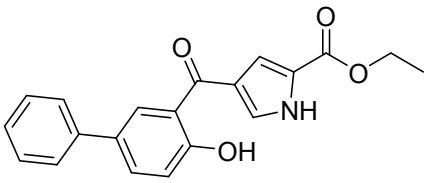
As a light yellow solid (128 mg, 89%), m. p. 155-160 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.68 (s, 1H), 11.26 (s, 1H), 7.63 (s, 1H), 7.48 (s, 1H), 7.16 (d, $J$ = 1.3 Hz, 1H), 6.80 (s, 1H), 4.29 (q, $J$ = 7.1 Hz, 2H), 2.23 (s, 3H), 2.19 (s, 3H), 1.31 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 192.13 , 160.52 , 158.30 , 144.52 , 131.54 , 129.61 , 127.31 , 124.89 , 124.09 , 120.30 , 118.52 , 116.32 , 60.65 , 20.28 , 18.88 , 14.74 . LRMS (EI$^+$) found m/z 287. HRMS (EI$^+$) calculated for $C_{16}H_{17}NO_4$, 287.1158; found, 287.1160.

**Ethyl 4-(2-hydroxy-4,5-dimethoxybenzoyl)-1*H*-pyrrole-2-carboxylate (3r)**



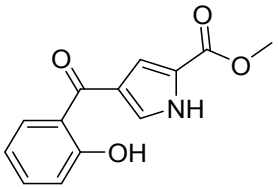
As a yellow solid (113 mg, 71%), m. p. 155-159 ºC. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.67 (s, 1H), 12.41 (s, 1H), 7.73 (s, 1H), 7.29 (s, 1H), 7.21 (s, 1H), 6.61 (s, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 3.85 (s, 3H), 3.74 (s, 3H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 191.59 , 160.48 , 159.02 , 156.12 , 141.99 , 129.10 , 124.42 , 124.16 , 116.30 , 113.73 , 112.20 , 101.23 , 60.65 , 56.43 , 56.40 , 14.74 . LRMS (EI$^+$) found m/z 319. HRMS (EI$^+$) calculated for $C_{16}H_{17}NO_6$, 319.1056; found, 319.1052.

**Ethyl 4-(4-hydroxy-[1,1'-biphenyl]-3-carbonyl)-1*H*-pyrrole-2-carboxylate (3s)**



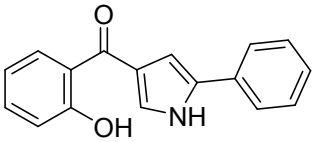

As a light yellow solid (156 mg, 93%), m. p. 216-220 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.65 (s, 1H), 10.71 (s, 1H), 7.76 – 7.70 (m, 2H), 7.62 (d, $J$ = 8.0 Hz, 2H), 7.59 (dd, $J$ = 3.3, 1.6 Hz, 1H), 7.44 (t, $J$ = 7.7 Hz, 2H), 7.32 (t, $J$ = 7.4 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.08 (d, $J$ = 8.9 Hz, 1H), 4.28 (q, $J$ = 7.1 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.29 , 160.52 , 157.18 , 139.82 , 131.62 , 131.45 , 129.90 , 129.39 , 128.30 , 127.36 , 126.64 , 125.94 , 125.66 , 124.23 , 117.96 , 116.13 , 60.66 , 14.75 . LRMS (EI$^+$) found m/z 335. HRMS (EI$^+$) calculated for $C_{20}H_{17}NO_4$, 335.1158; found, 335.1151.

### Methyl 4-(2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (3t)




As a light yellow solid (121 mg, 99%), m. p. 145-150 ºC. $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 12.71 (s, 1H), 10.94 (s, 1H), 7.59 (dd, $J$ = 7.7, 1.6 Hz, 1H), 7.55 (dd, $J$ = 3.4, 1.6 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.13 – 7.09 (m, 1H), 6.96 (d, $J$ = 8.4 Hz, 1H), 6.95 – 6.90 (m, 1H), 3.80 (s, 3H). $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ 191.82 , 160.95 , 158.59 , 134.01 , 130.82 , 129.89 , 125.29 , 124.28 , 123.89 , 119.49 , 117.52 , 116.36 , 52.05 . LRMS (EI$^+$) found m/z 245. HRMS (EI$^+$) calculated for $C_{13}H_{11}NO_4$, 245.0688; found, 245.0686.

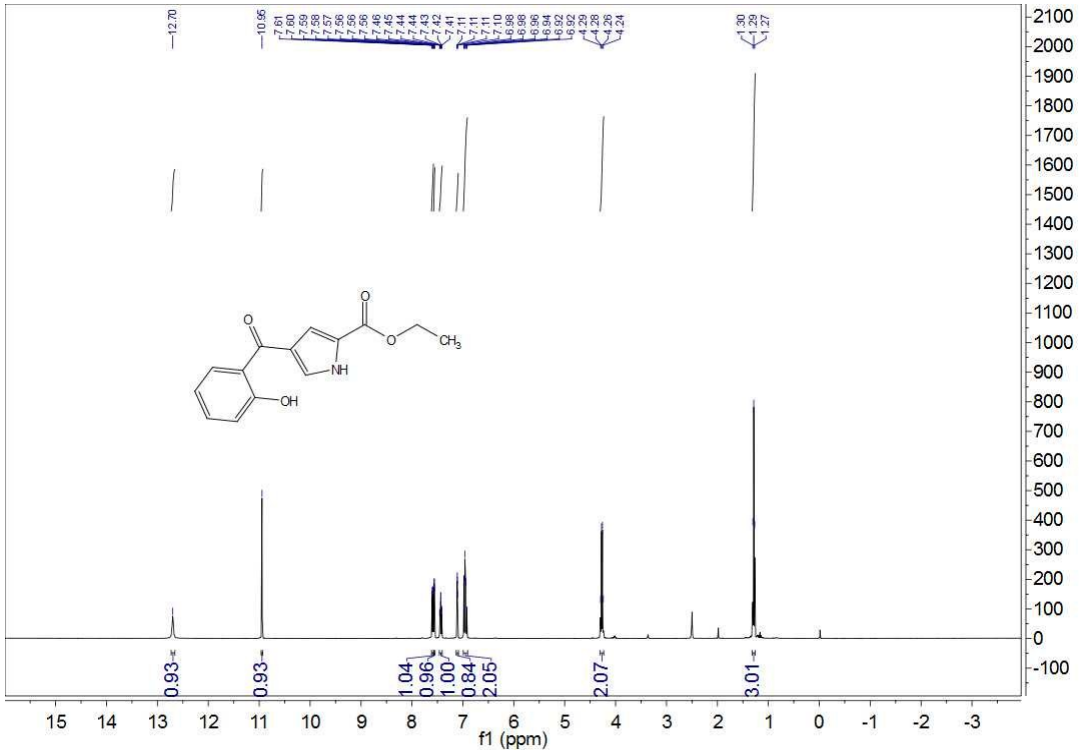
### (2-Hydroxyphenyl)(5-phenyl-1*H*-pyrrol-3-yl)methanone (3u)



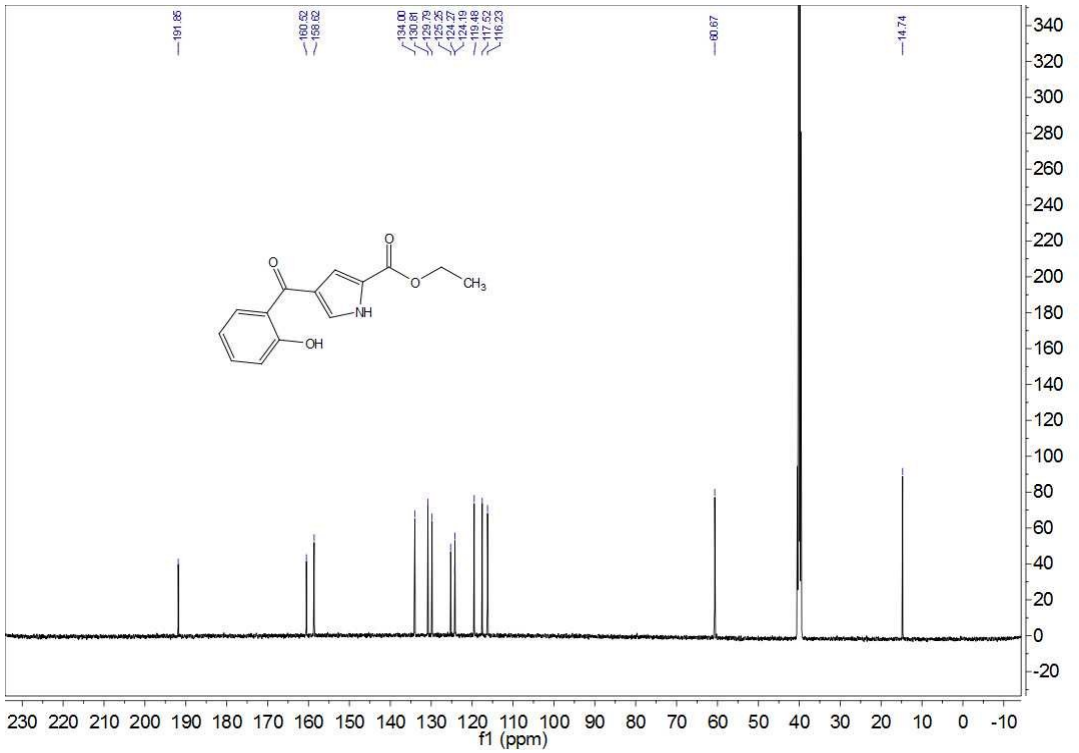

As a light yellow solid (67mg, 51%), m. p. 165-167 ºC. $^{1}$H NMR (600 MHz, DMSO-$d_6$) δ 12.20 (s, 1H), 11.39 (s, 1H), 7.79 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.74 (d, $J$ = 7.7 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.50 – 7.44 (m, 1H), 7.44 – 7.38 (m, 2H), 7.29 – 7.24 (m, 1H), 7.04 – 7.01 (m, 1H), 7.00 – 6.94 (m, 2H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 193.51 , 160.67 , 135.23 , 134.85 , 133.14 , 132.33 , 130.48 , 129.11 , 128.39 , 126.26 , 125.73 , 124.79 , 120.54 , 118.74 , 108.09 . LRMS (EI$^+$) found m/z 263. HRMS (EI$^+$) calculated for $C_{17}H_{13}NO_2$, 263.0946; found, 263.0949.

## 4、 Copies of $^{1}$H NMR and $^{13}$C NMR Spectra for the Products

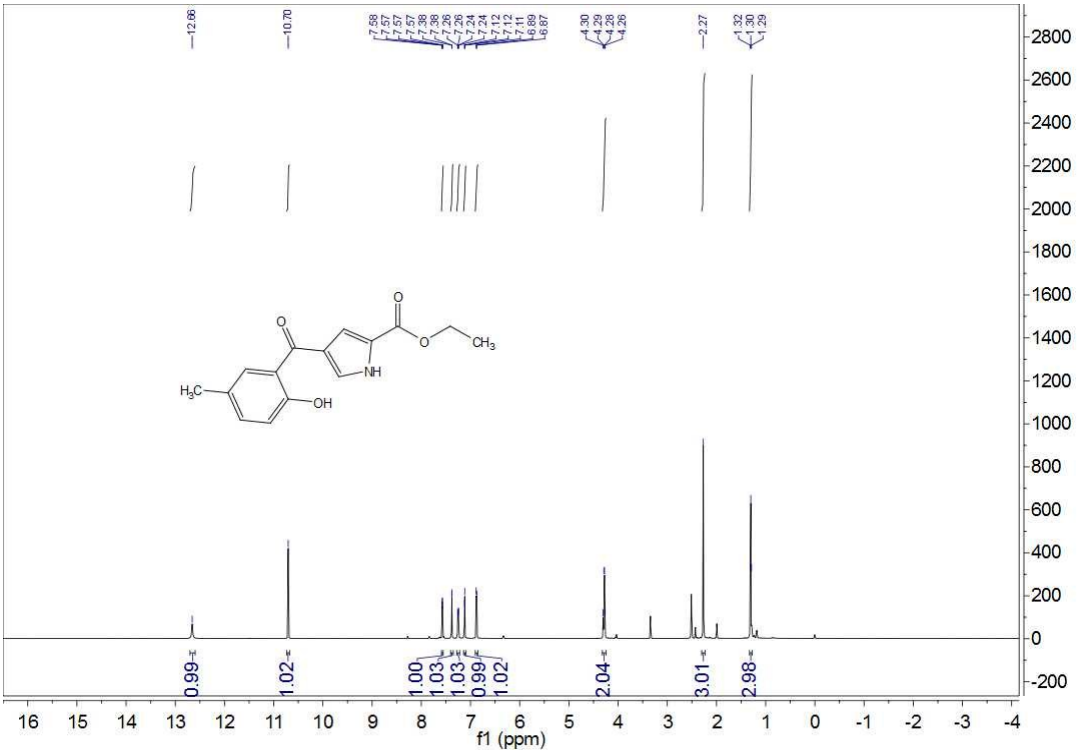
$^{1}$H NMR spectrum of **3a**



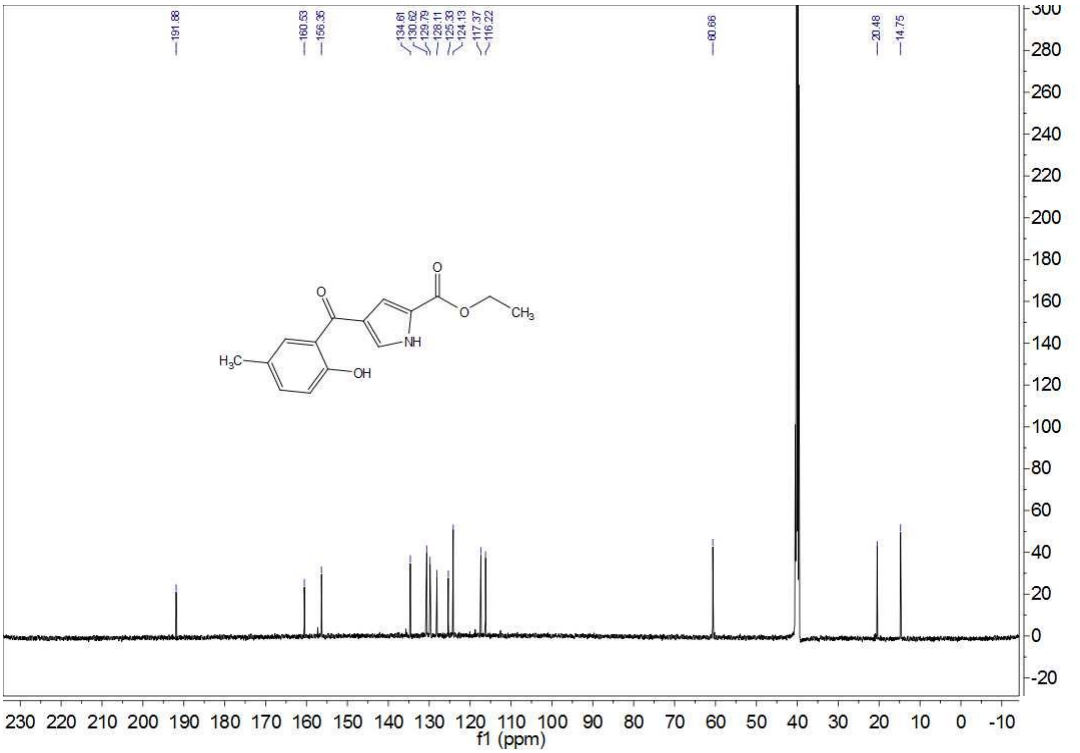

$^{13}$C NMR spectrum of **3a**



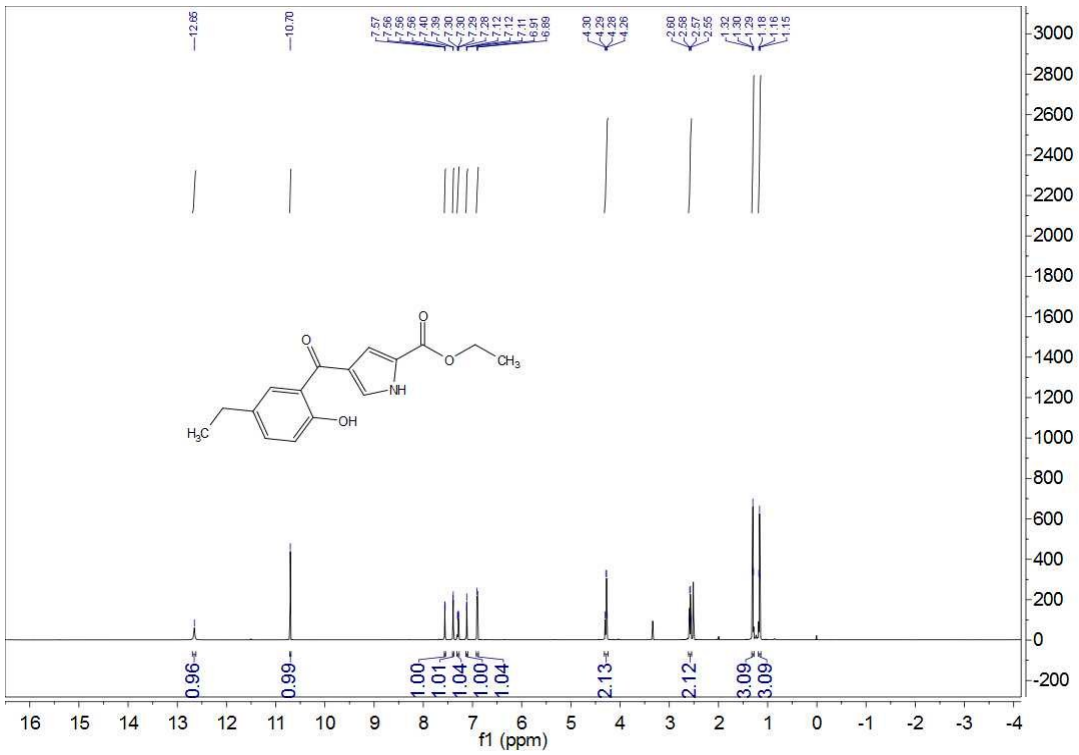
$^{1}$H NMR spectrum of **3b**



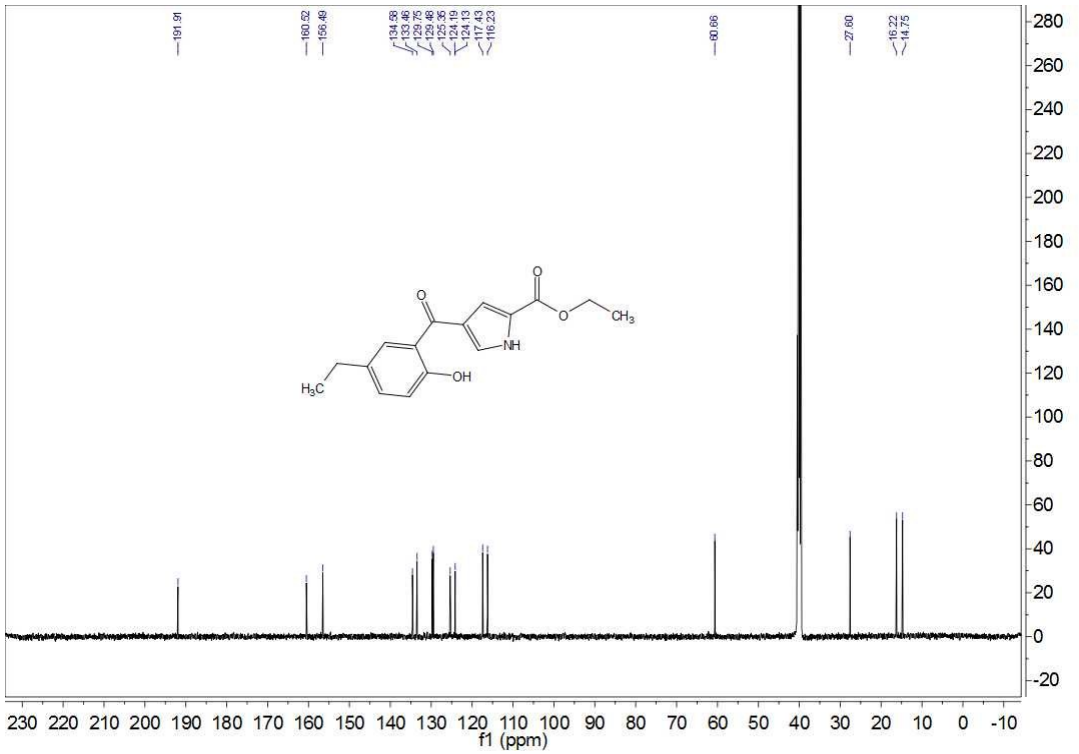

$^{13}$C NMR spectrum of **3b**



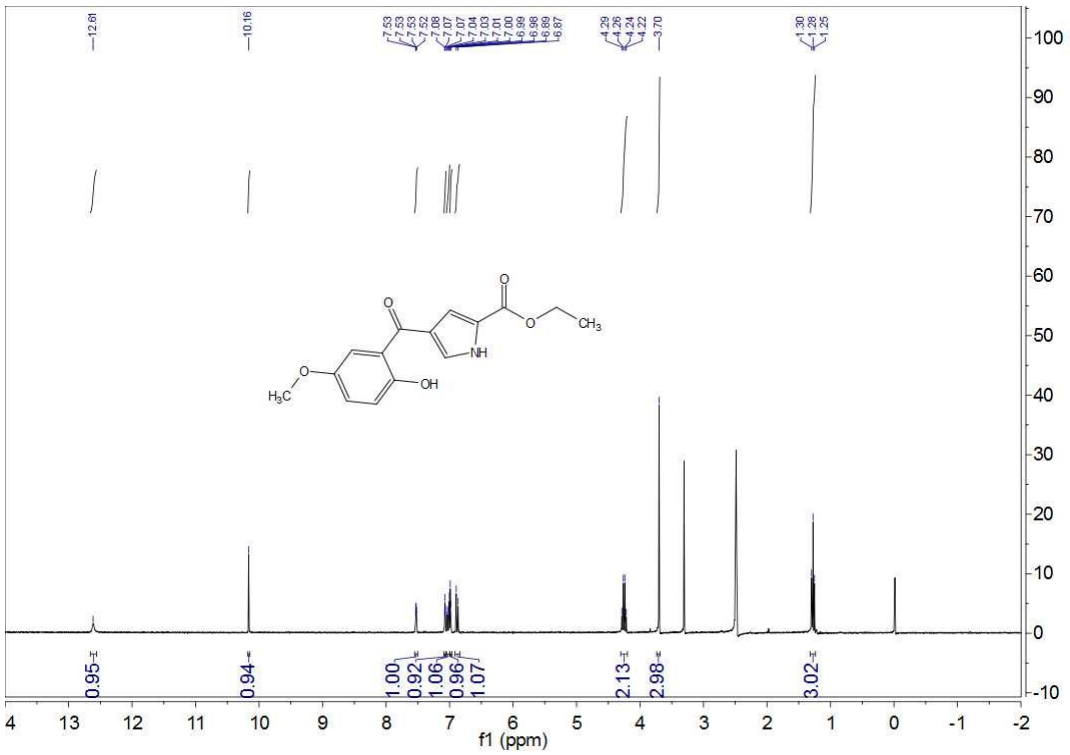

$^{1}$H NMR spectrum of **3c**



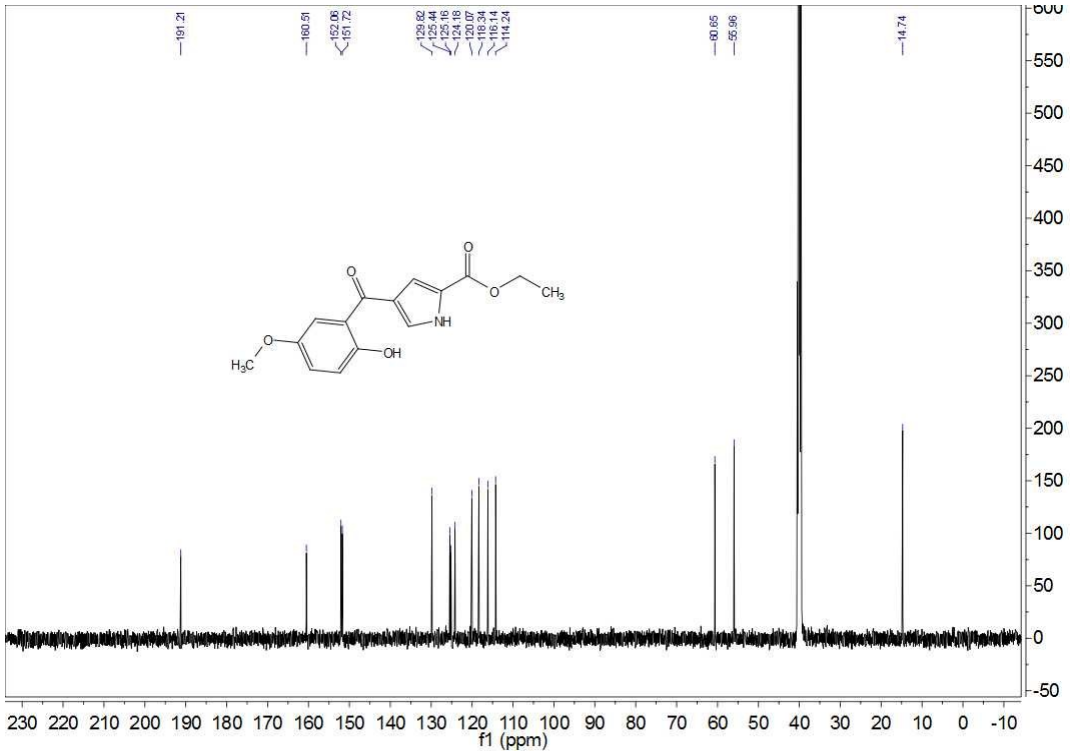

$^{13}$C NMR spectrum of **3c**



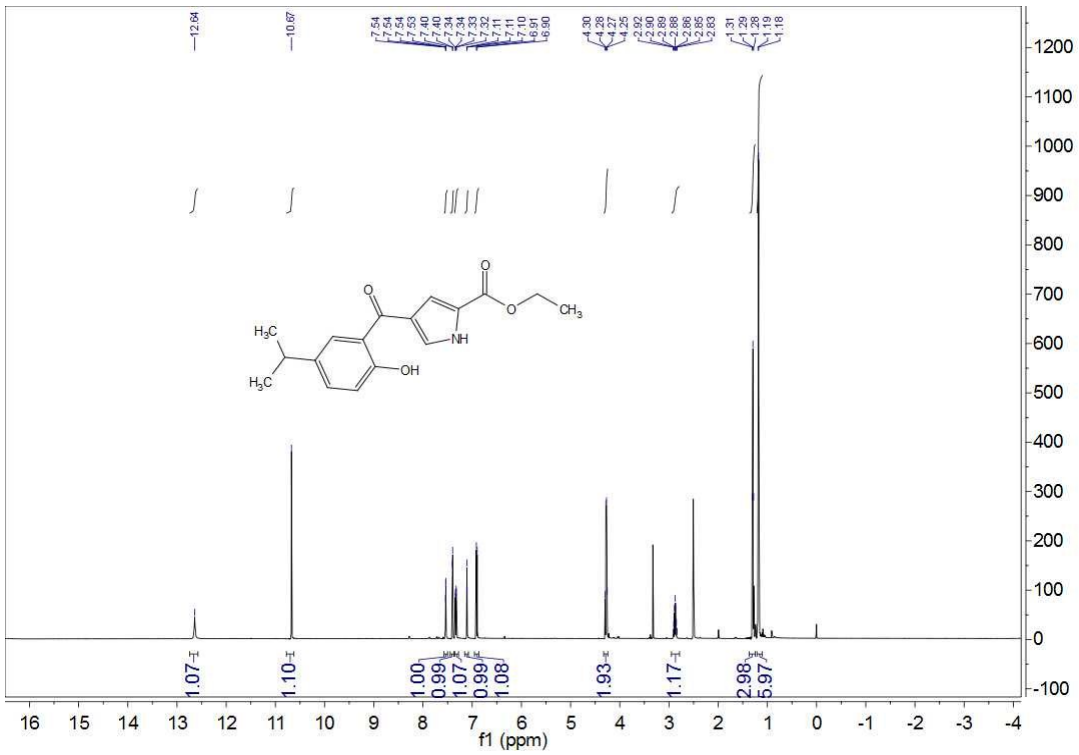

$^{1}$H NMR spectrum of **3d**



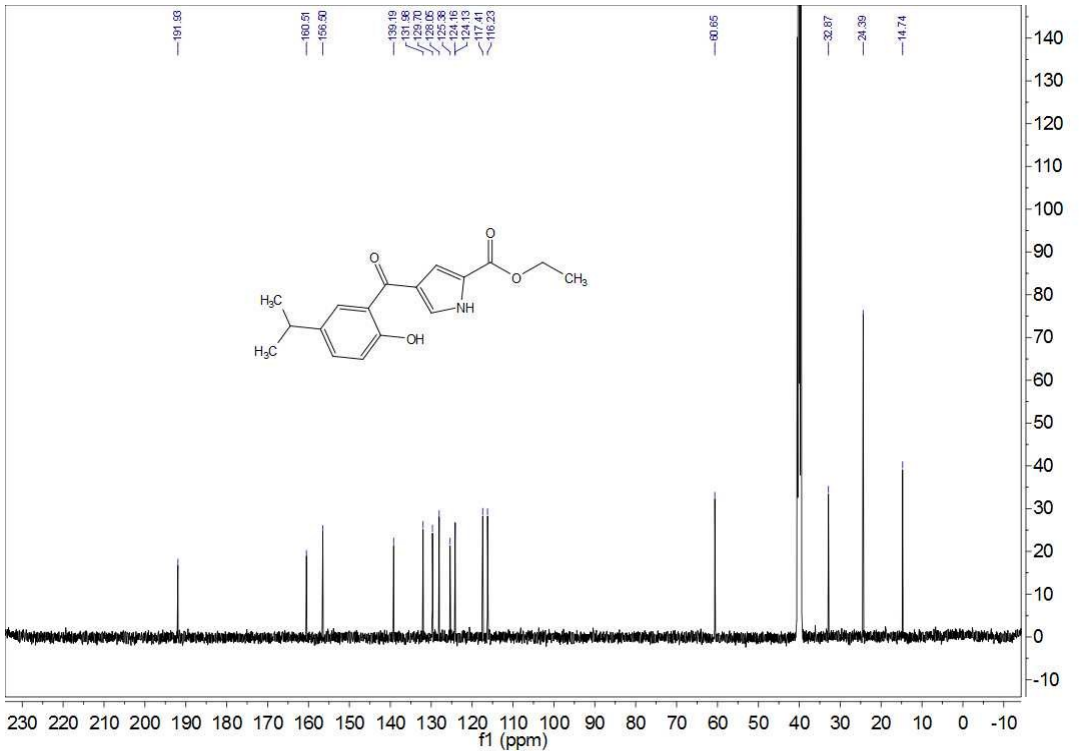

$^{13}$C NMR spectrum of **3d**



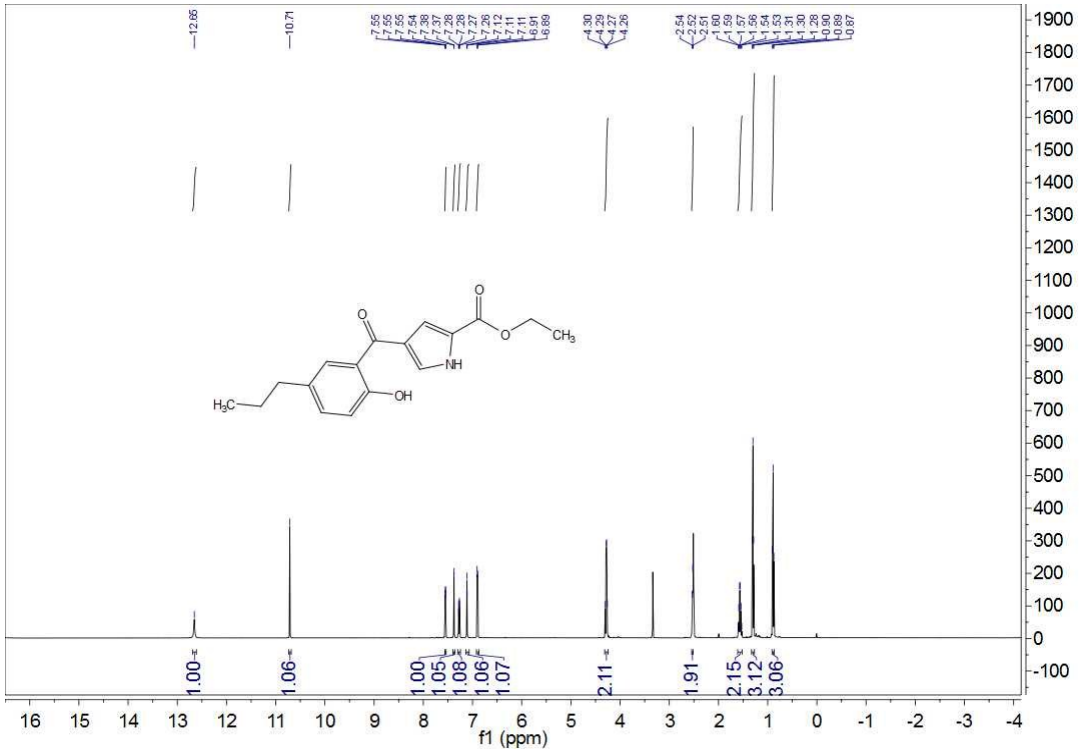

$^{1}$H NMR spectrum of **3e**



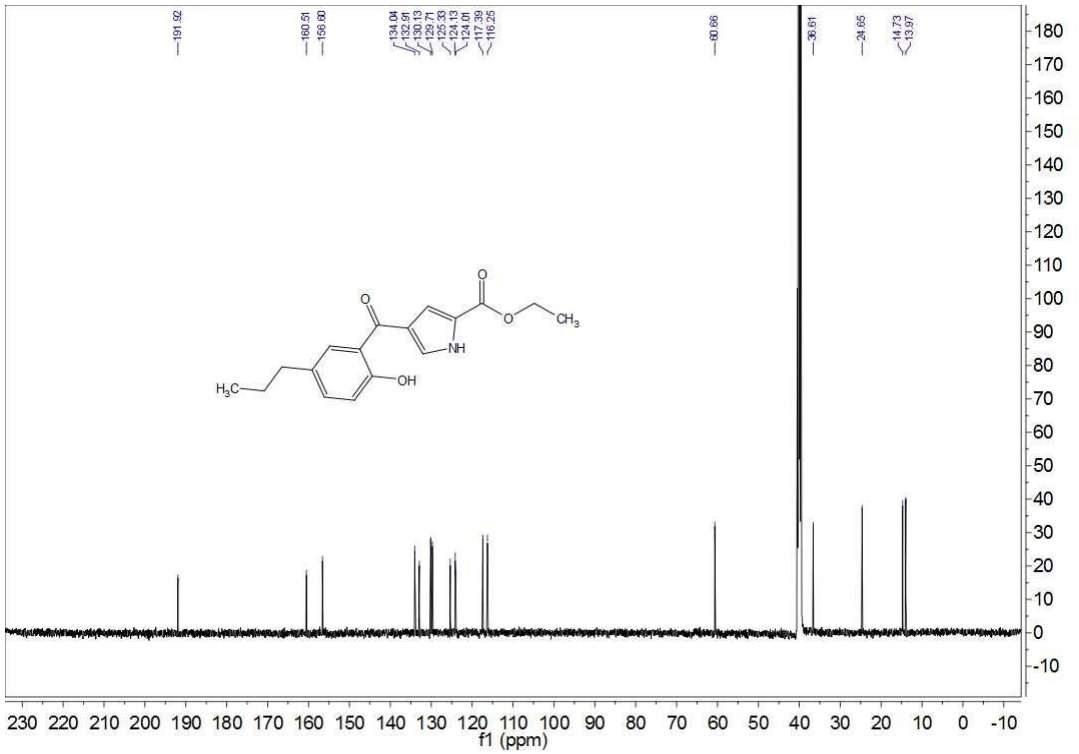

$^{13}$C NMR spectrum of **3e**



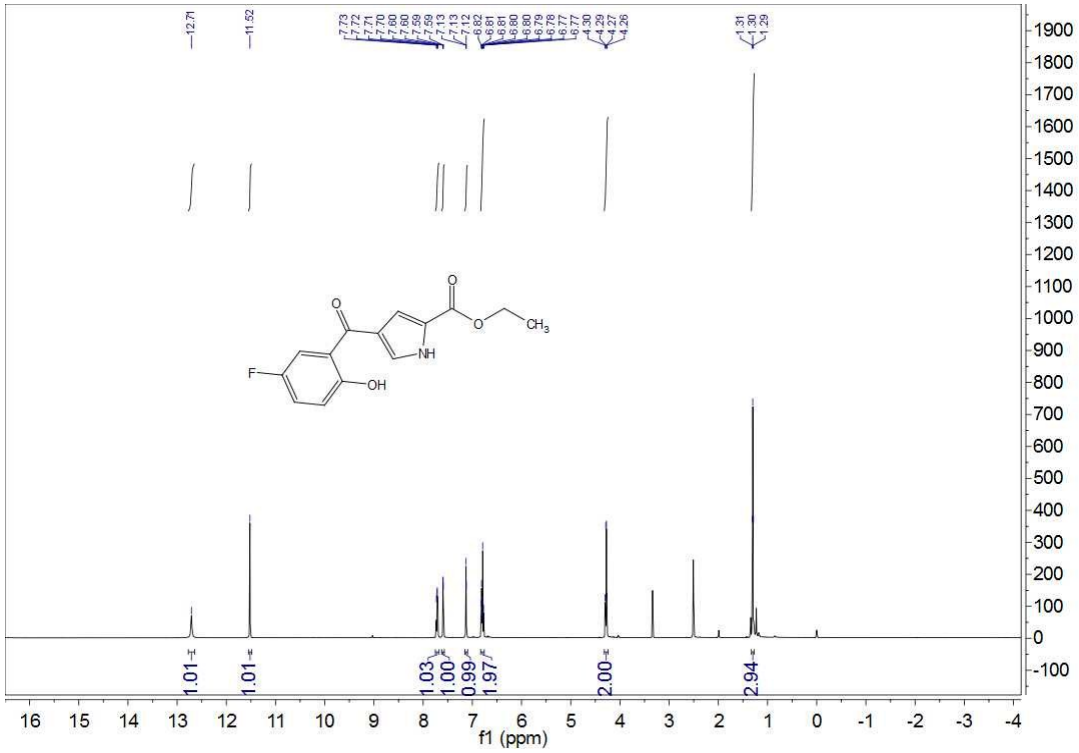

$^{1}$H NMR spectrum of **3f**



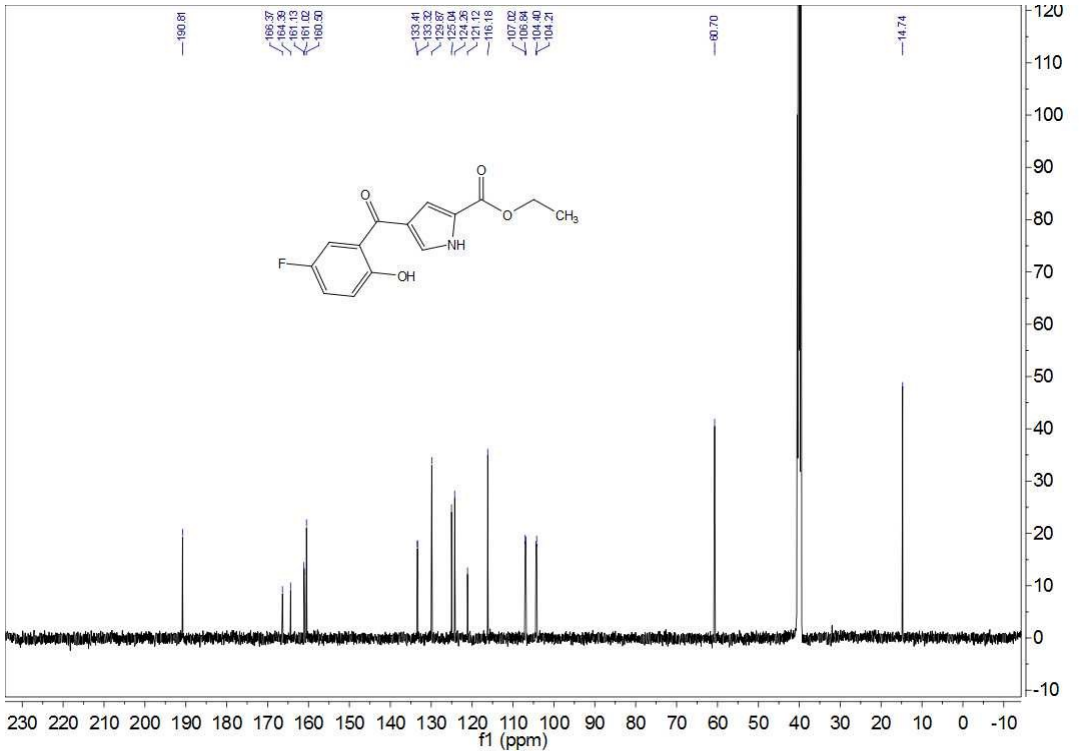

$^{13}$C NMR spectrum of **3f**



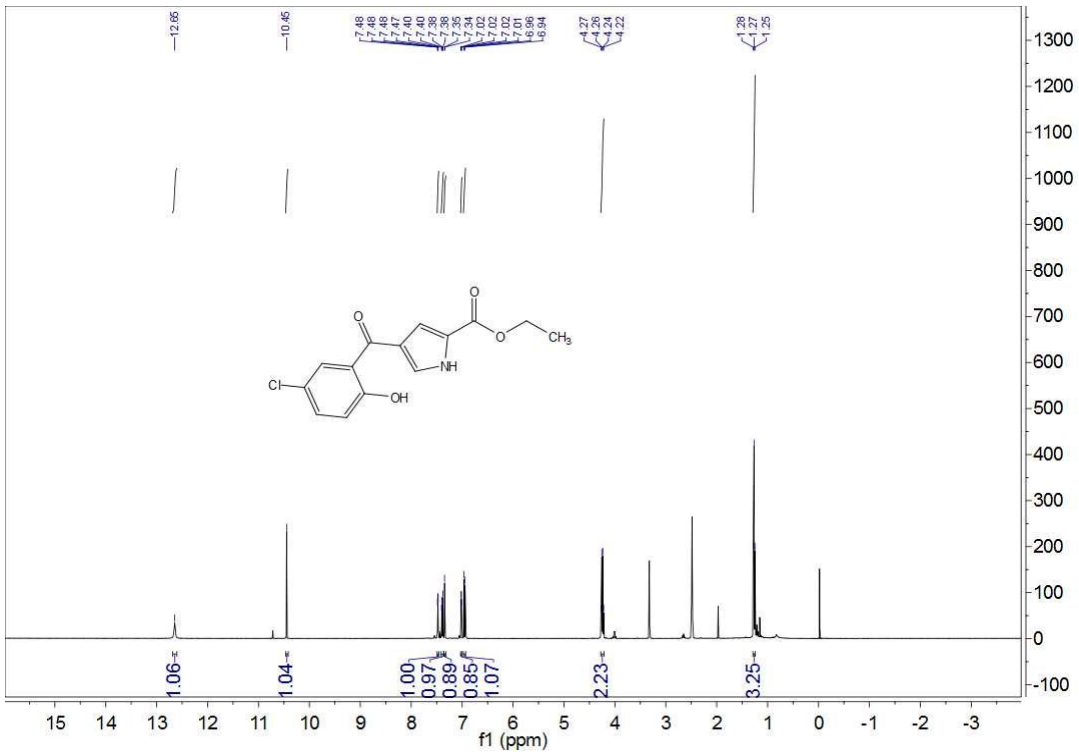

$^{1}$H NMR spectrum of **3g**



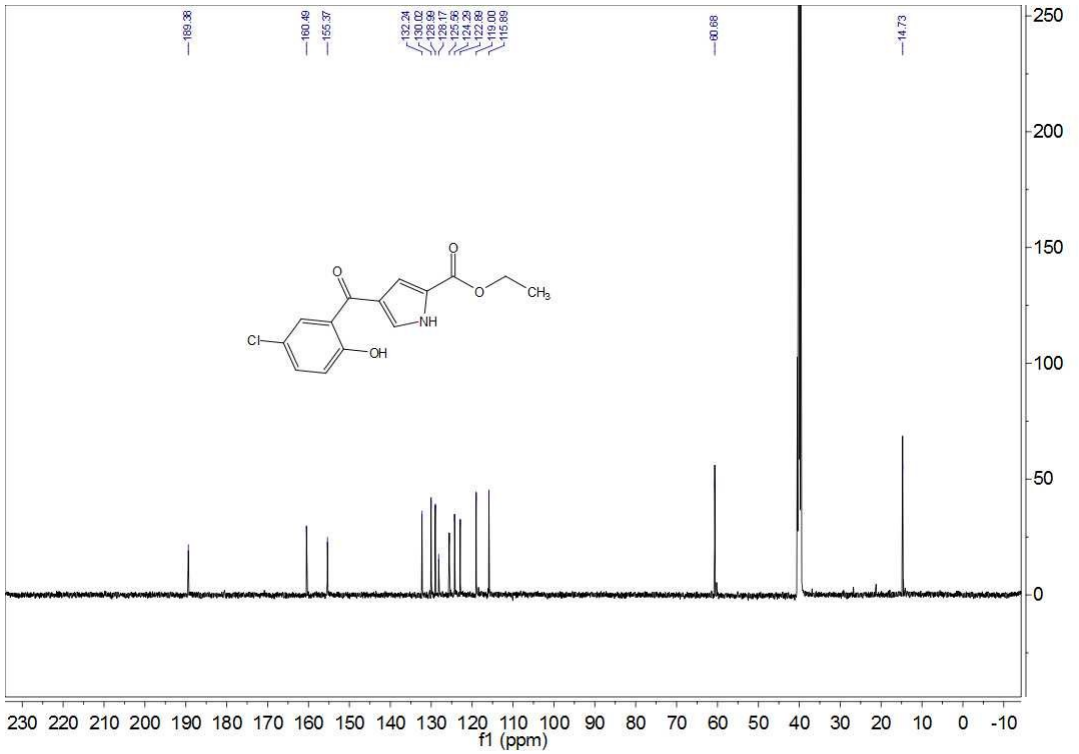

$^{13}$C NMR spectrum of **3g**



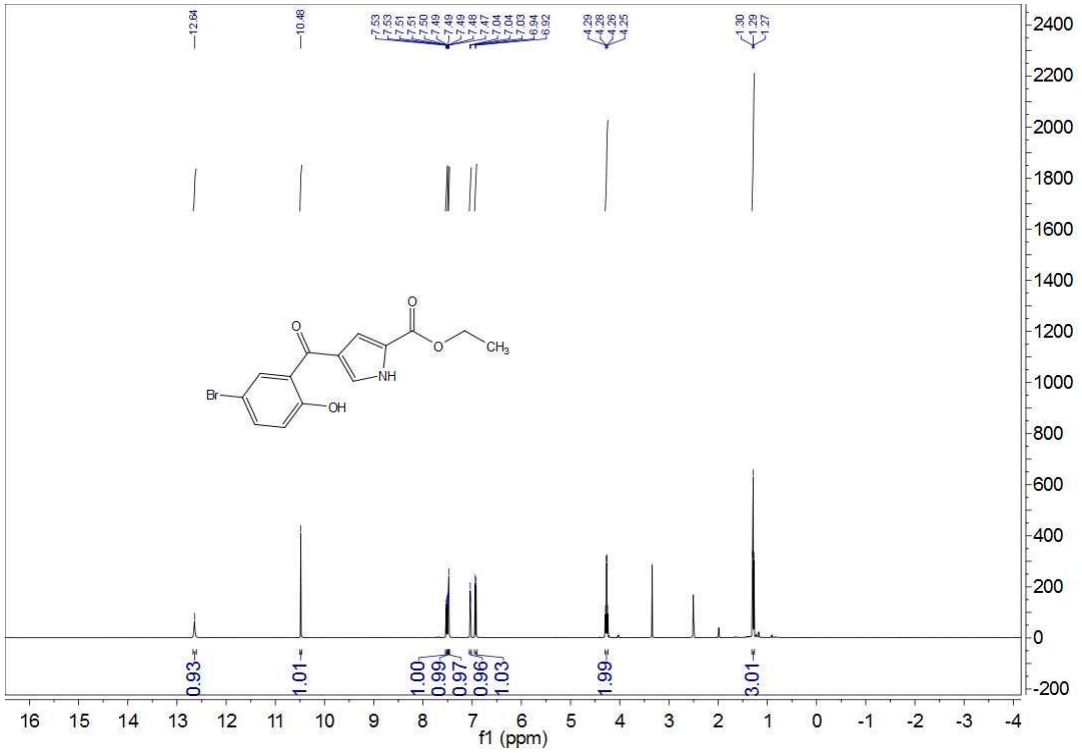

$^{1}$H NMR spectrum of **3h**



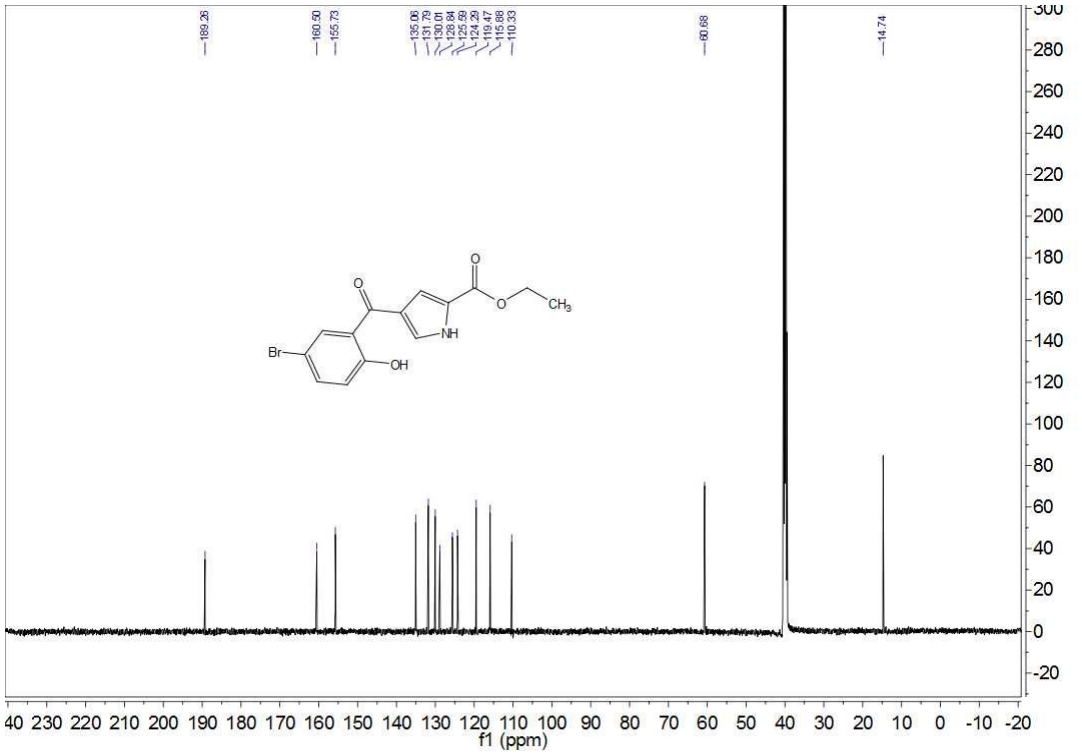

$^{13}$C NMR spectrum of **3h**



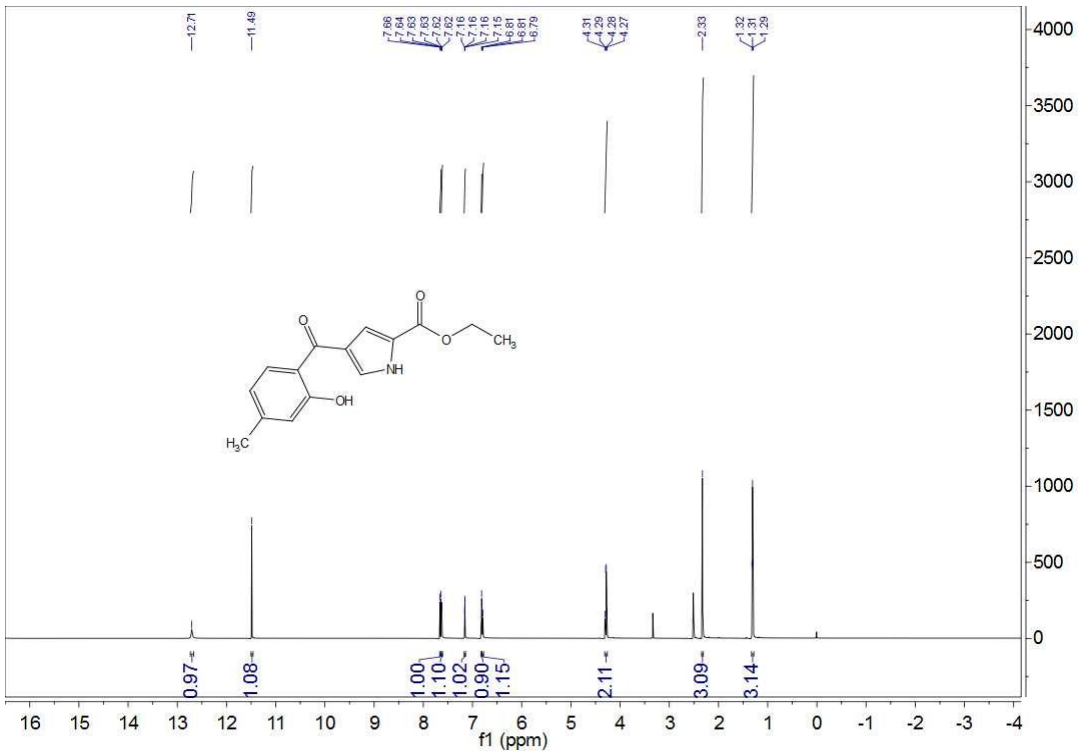

$^{1}$H NMR spectrum of **3i**



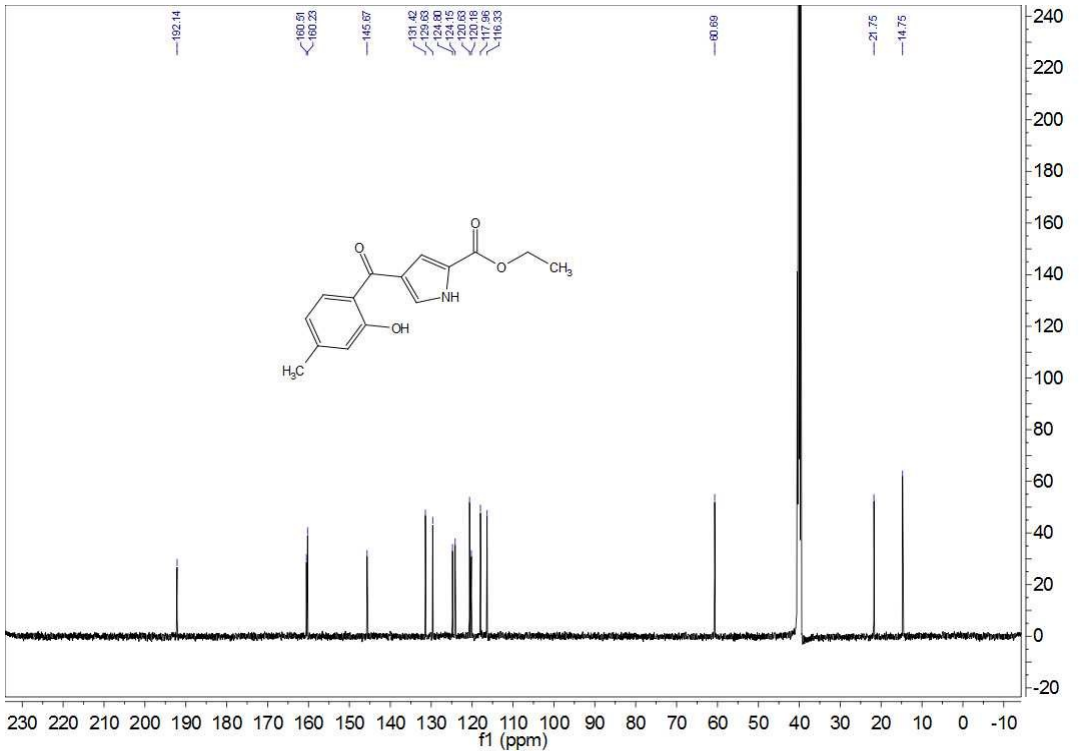

$^{13}$C NMR spectrum of **3i**



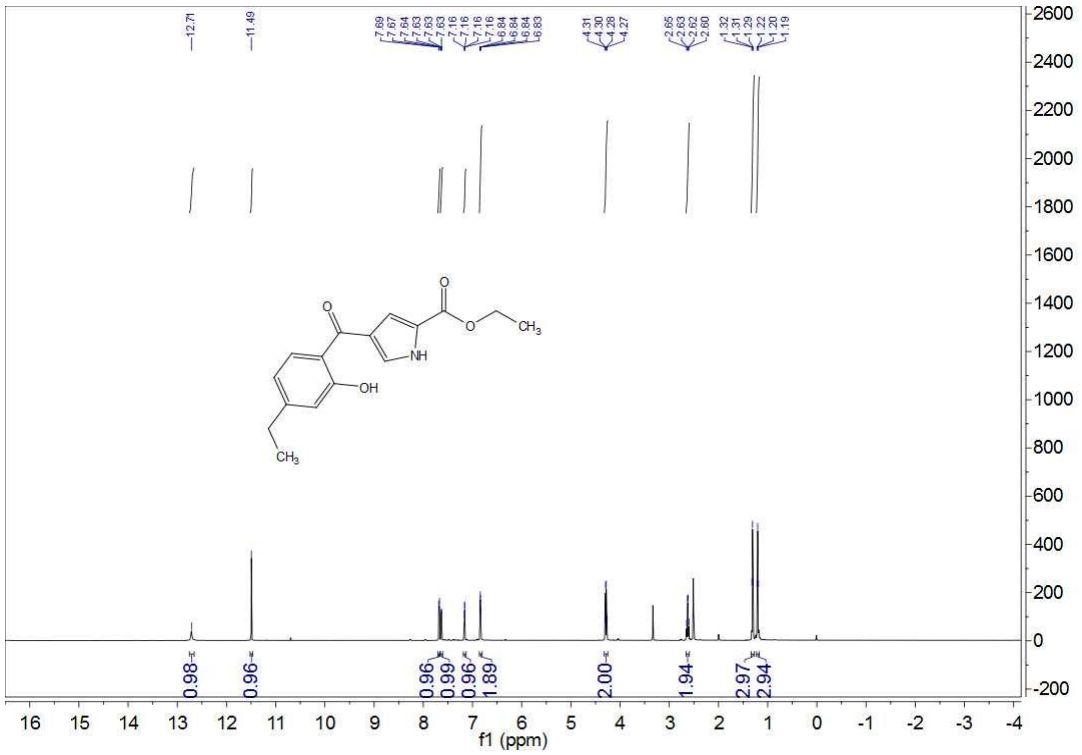

$^{1}$H NMR spectrum of **3j**



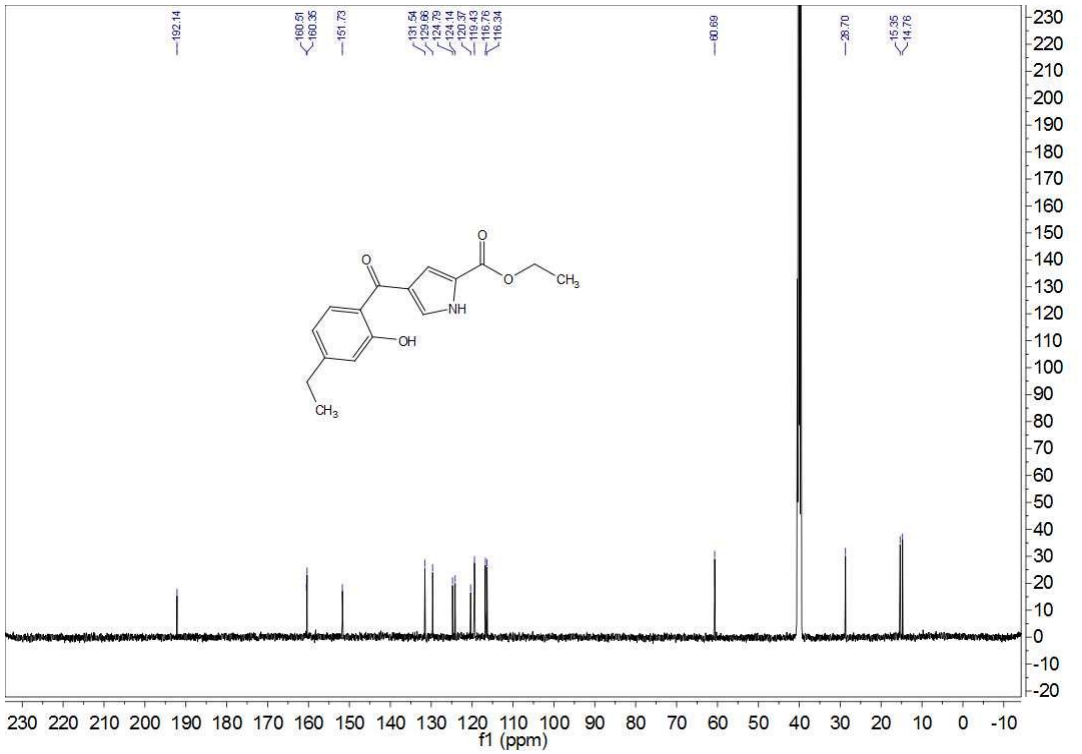

$^{13}$C NMR spectrum of **3j**



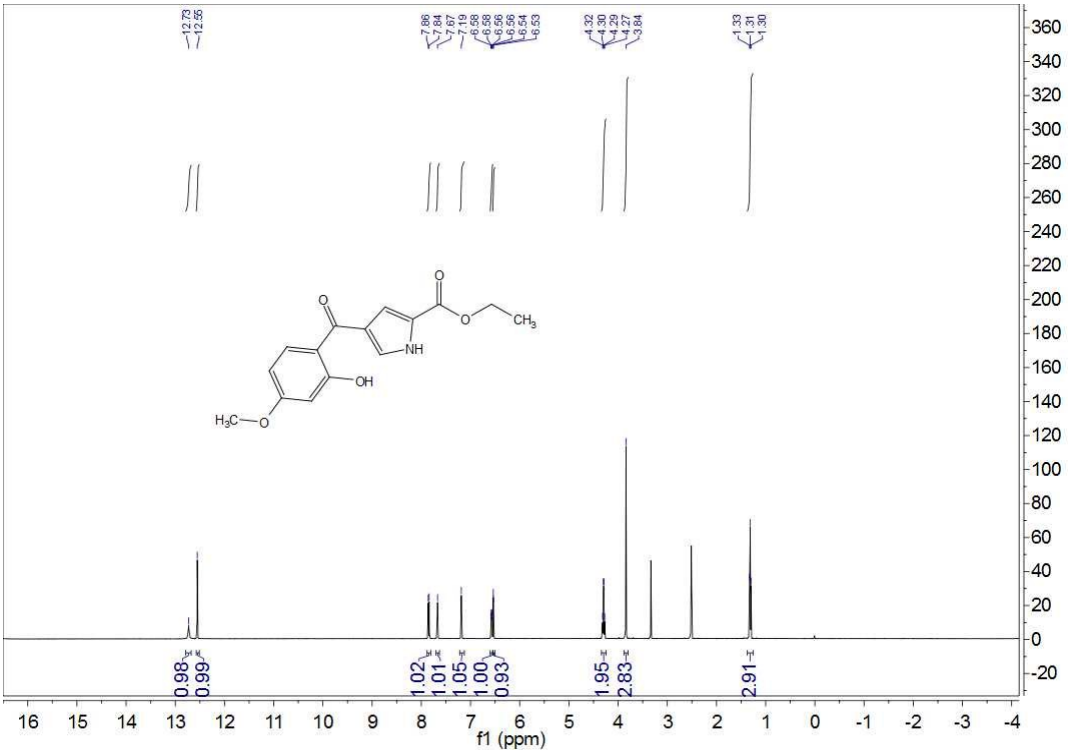

$^{1}$H NMR spectrum of **3k**



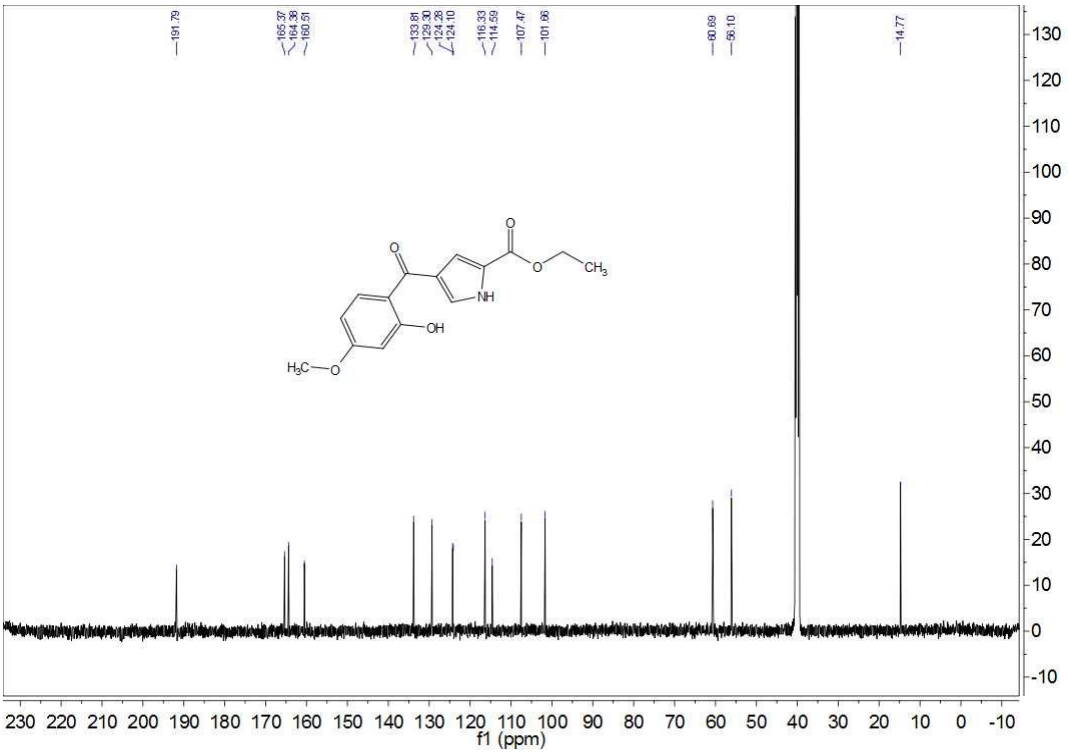

$^{13}$C NMR spectrum of **3k**



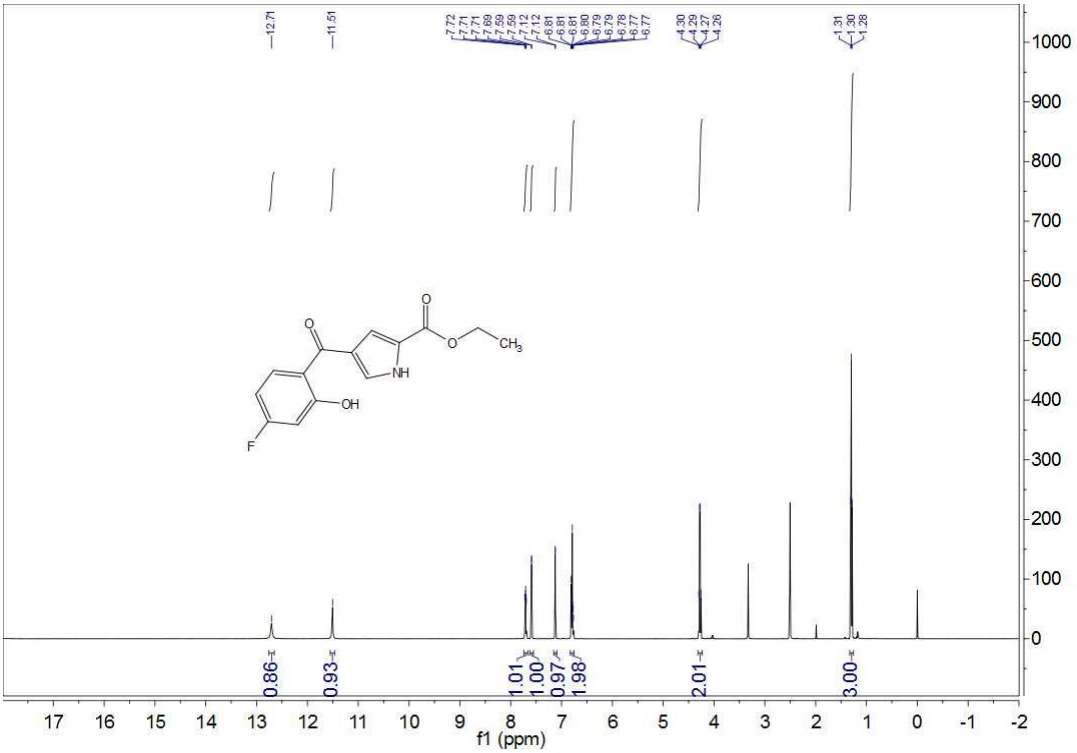
$^{1}$H NMR spectrum of **3l**



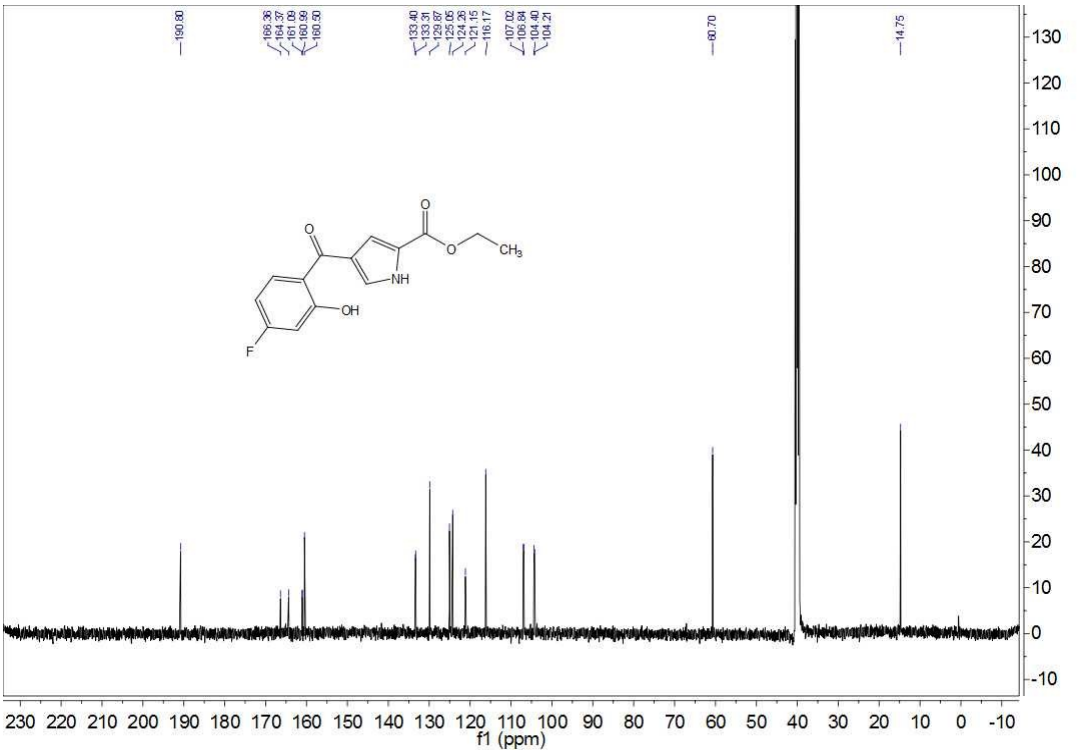

$^{13}$C NMR spectrum of **3l**



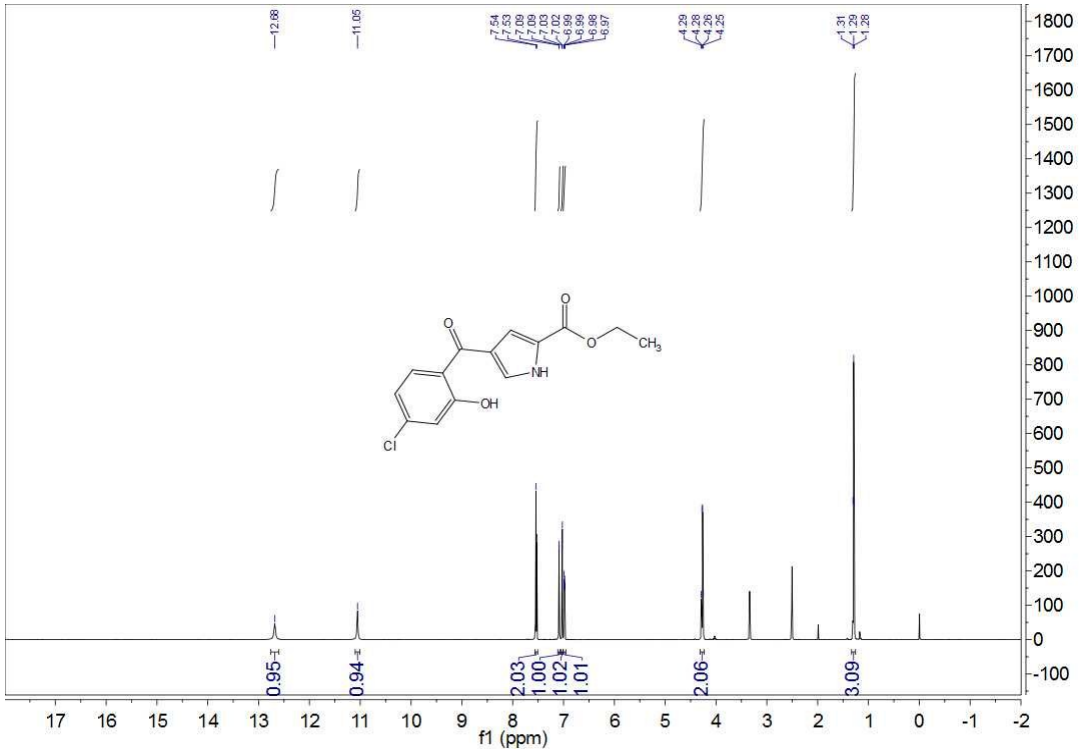
$^{1}$H NMR spectrum of **3m**



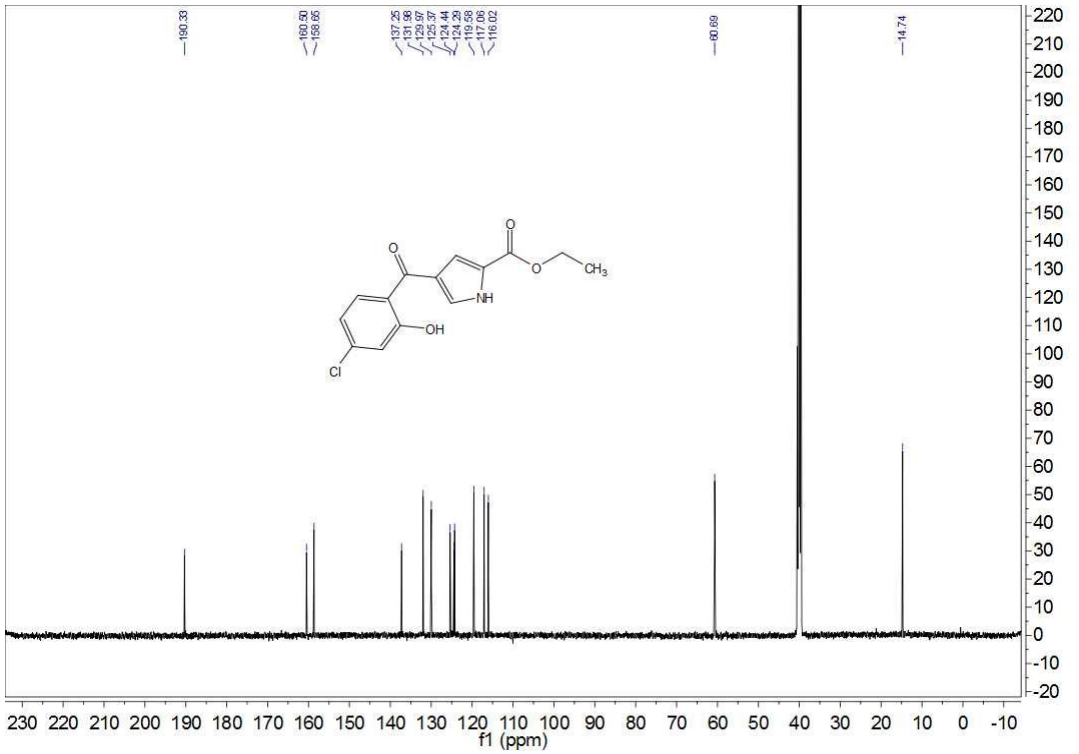

$^{13}$C NMR spectrum of **3m**



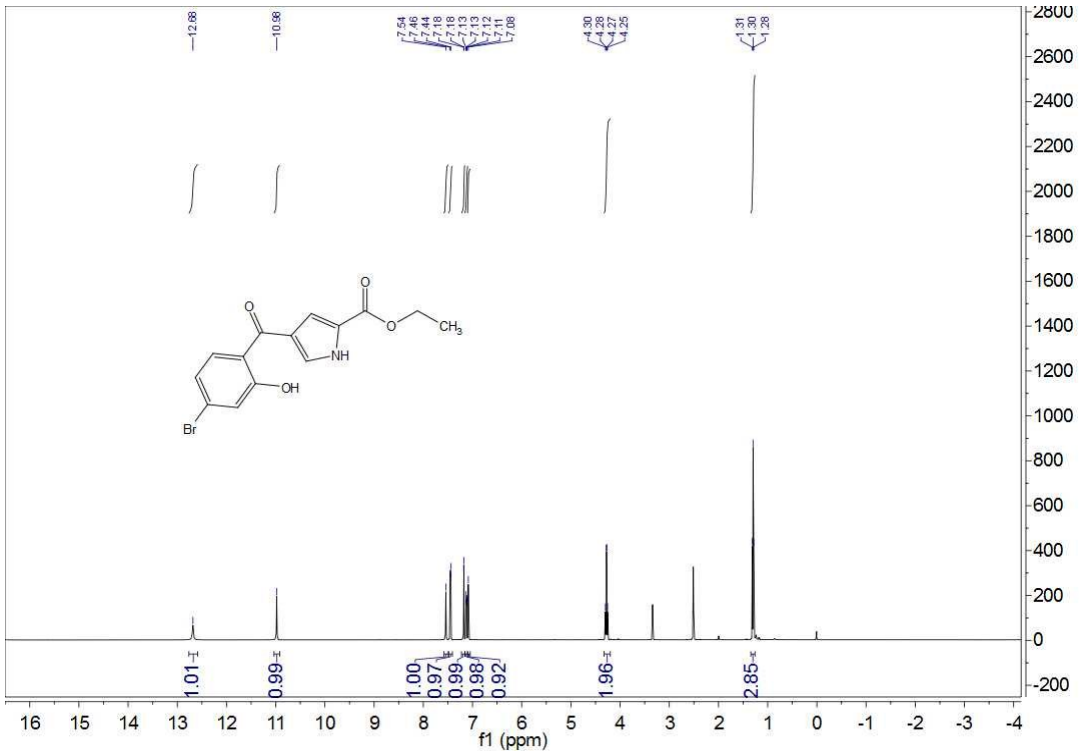

$^{1}$H NMR spectrum of **3n**



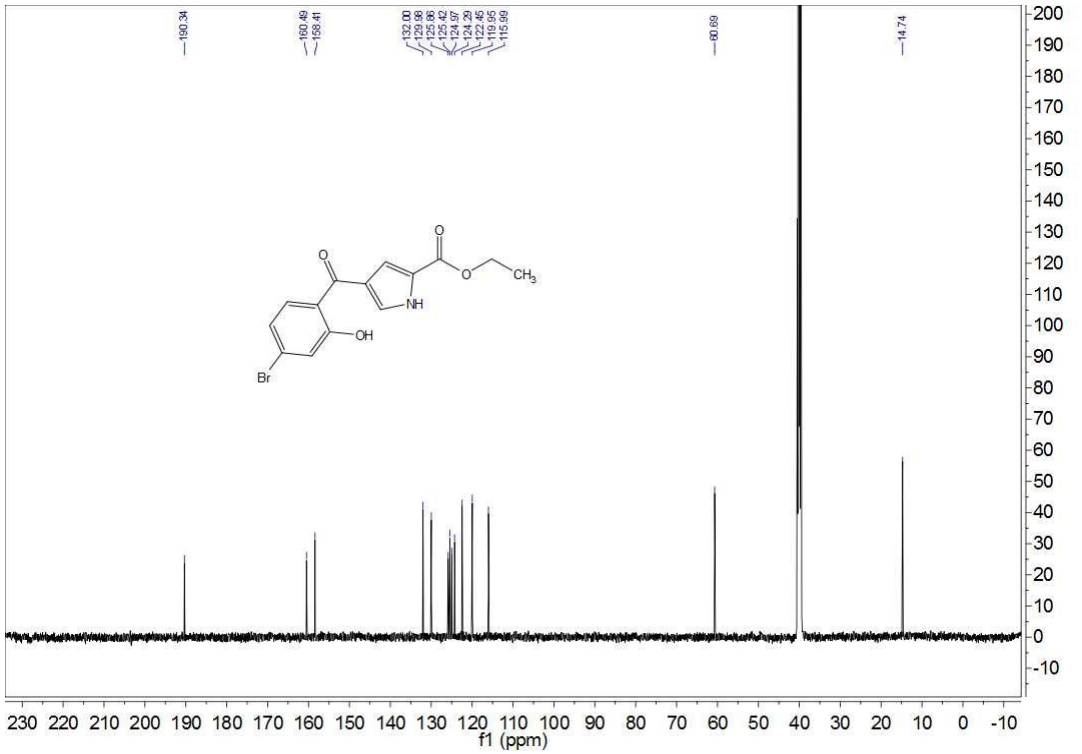

$^{13}$C NMR spectrum of **3n**



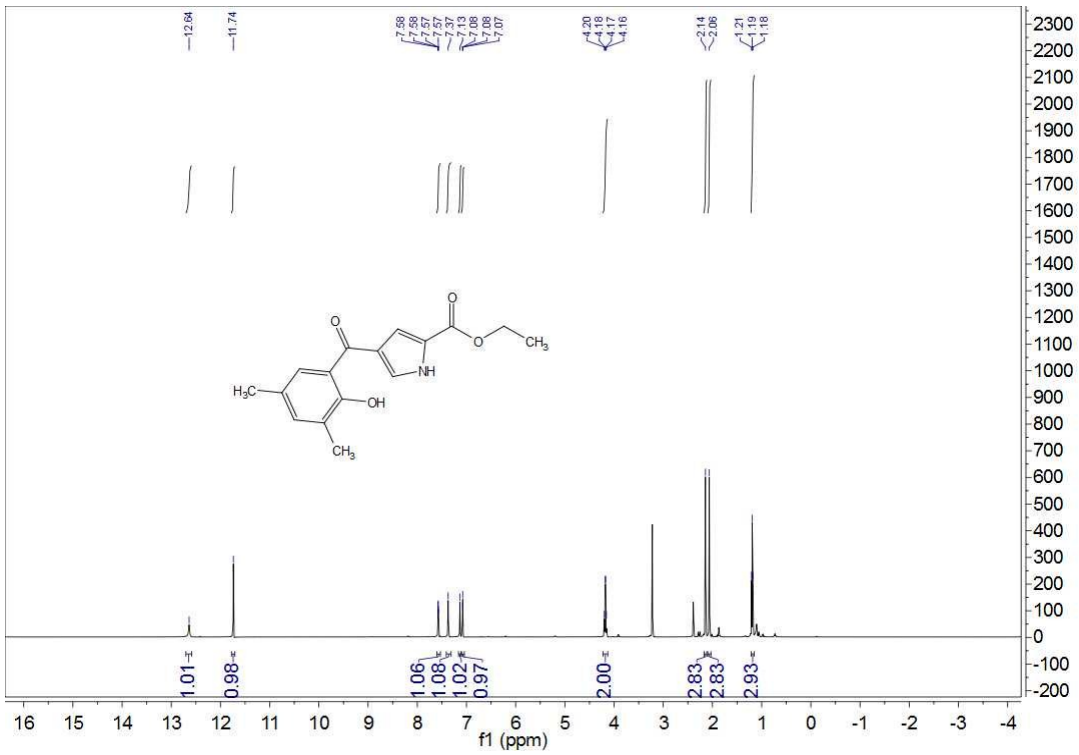

$^{1}$H NMR spectrum of **3o**



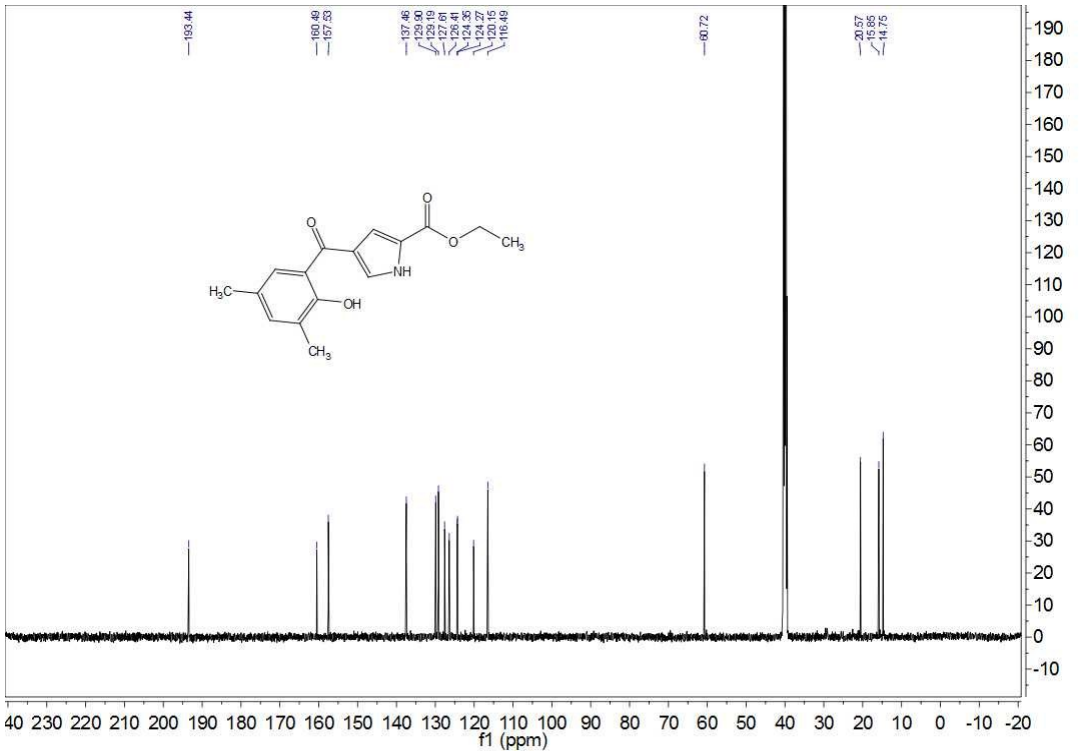

$^{13}$C NMR spectrum of **3o**



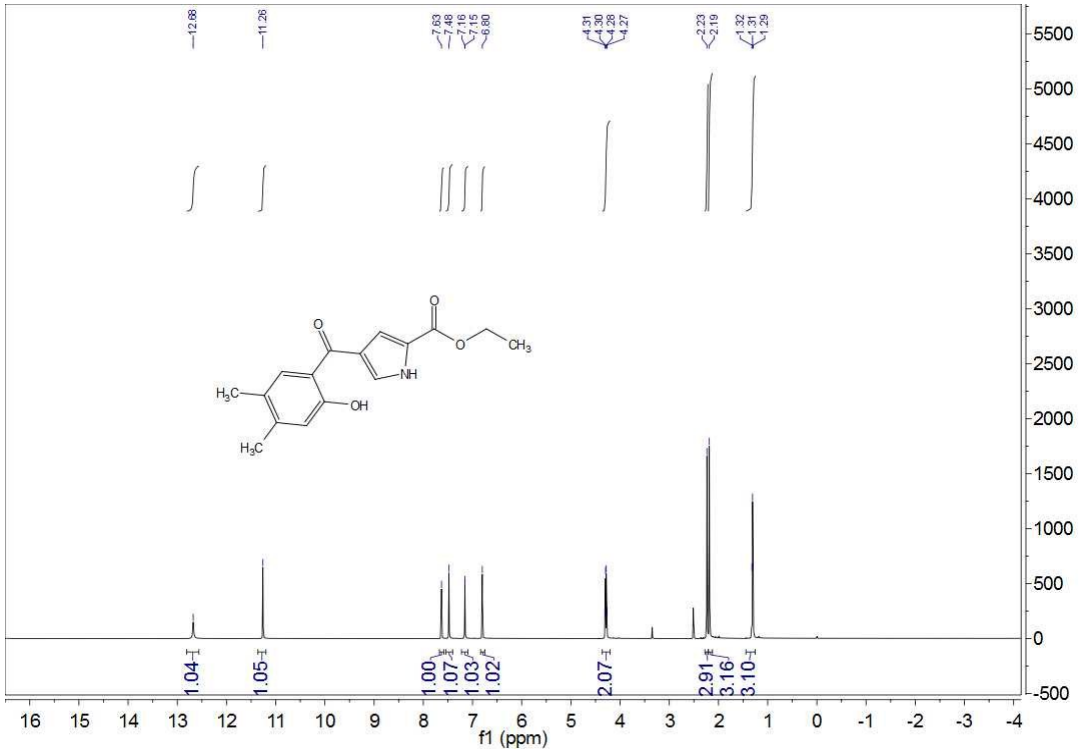

$^{1}$H NMR spectrum of **3p**



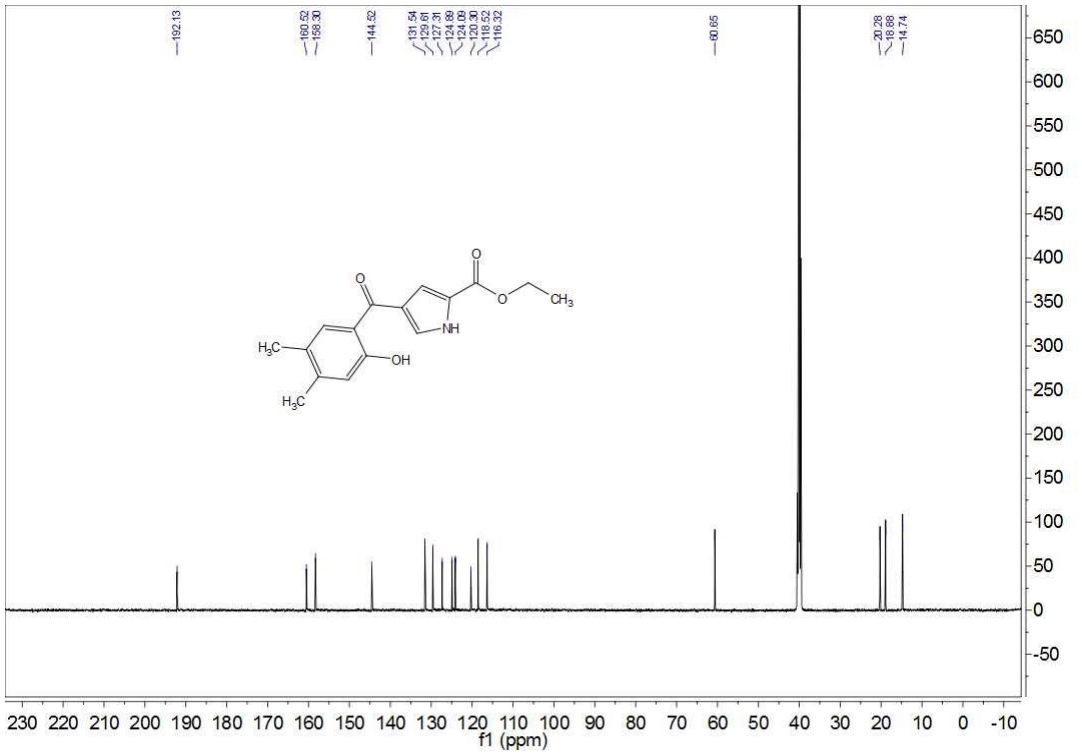

$^{13}$C NMR spectrum of **3p**



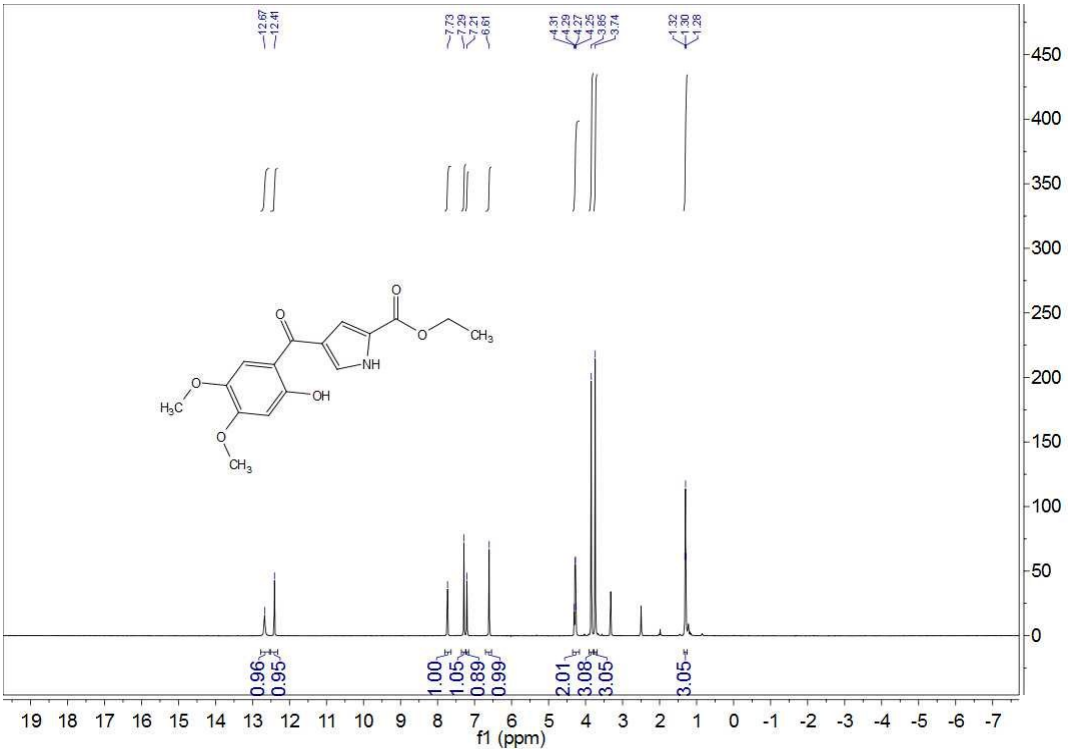

$^{1}$H NMR spectrum of **3q**



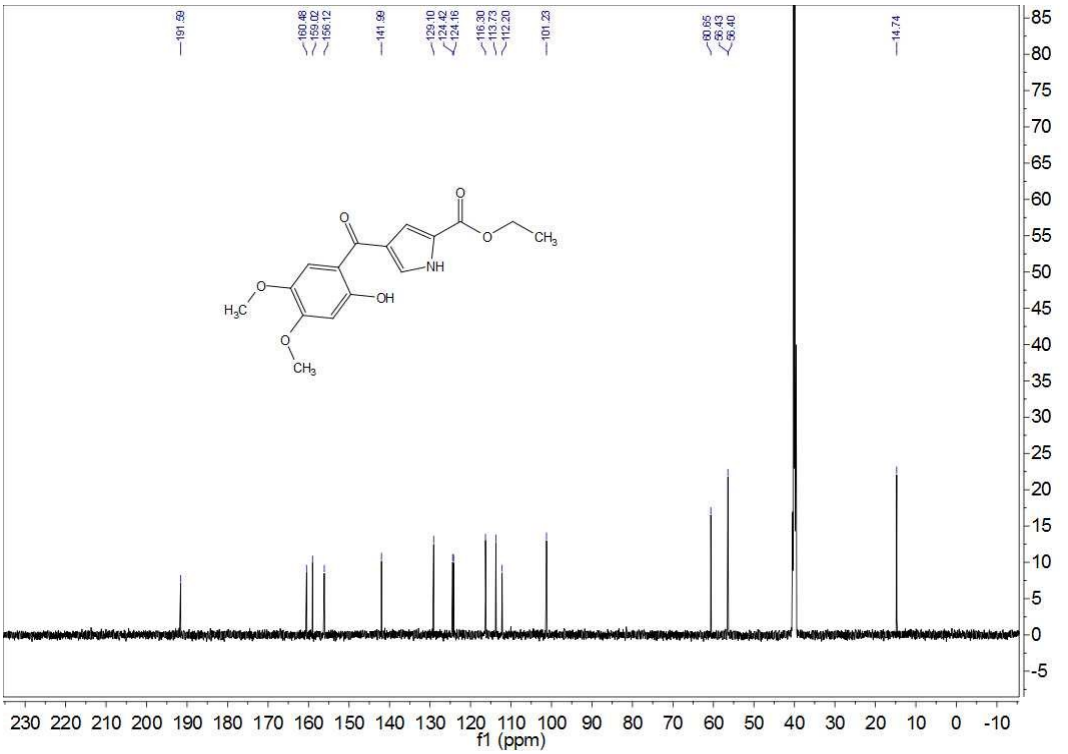

$^{13}$C NMR spectrum of **3q**



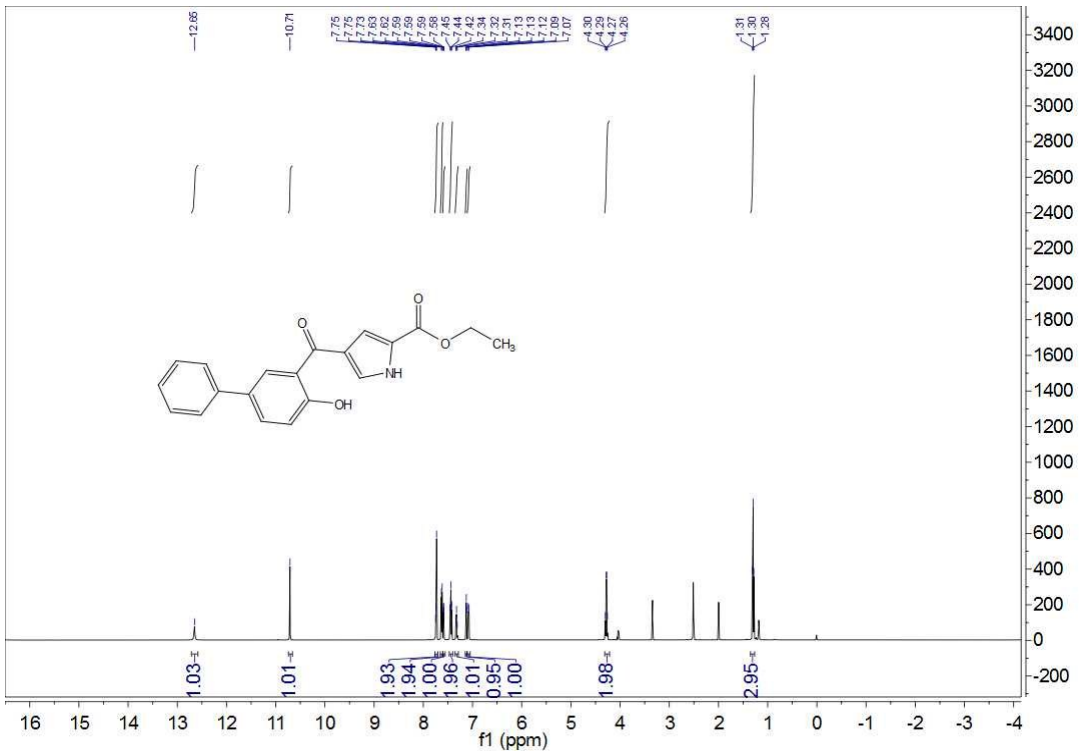

$^{1}$H NMR spectrum of **3r**



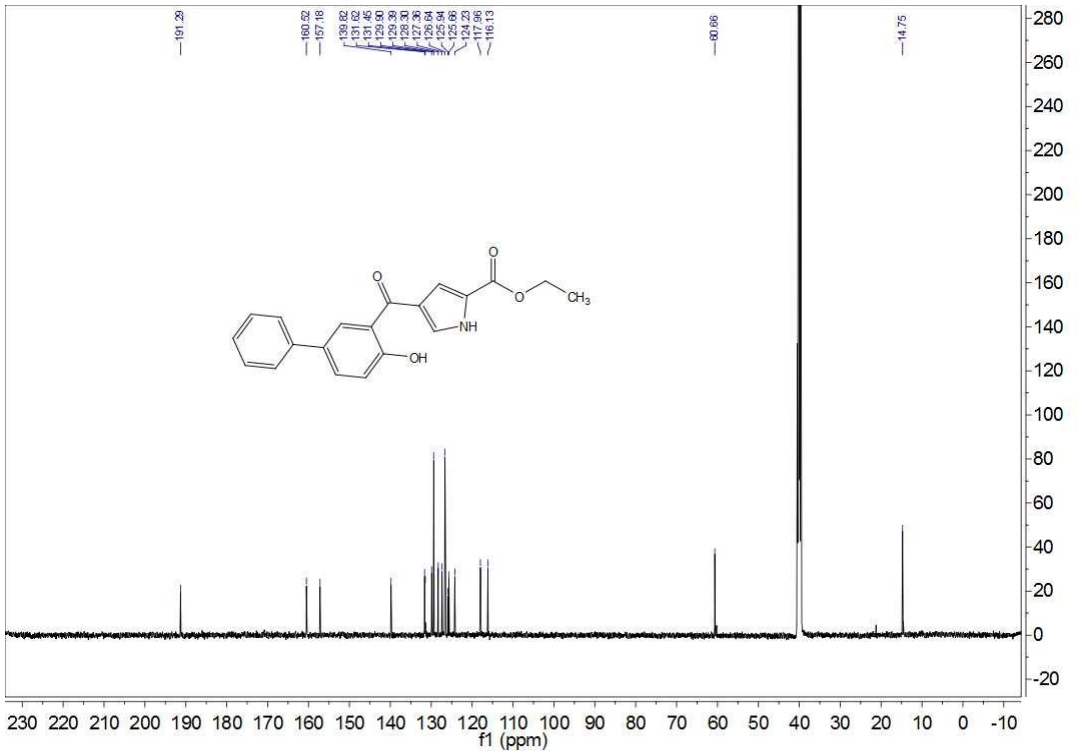

$^{13}$C NMR spectrum of **3r**



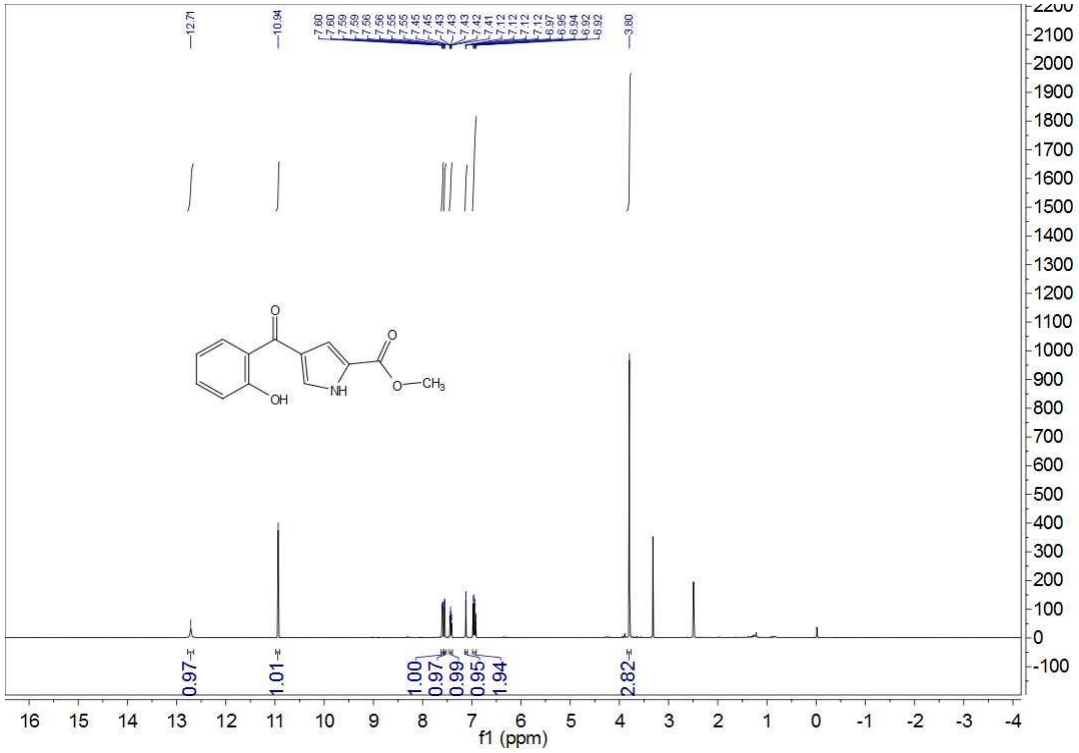

$^{1}$H NMR spectrum of **3s**



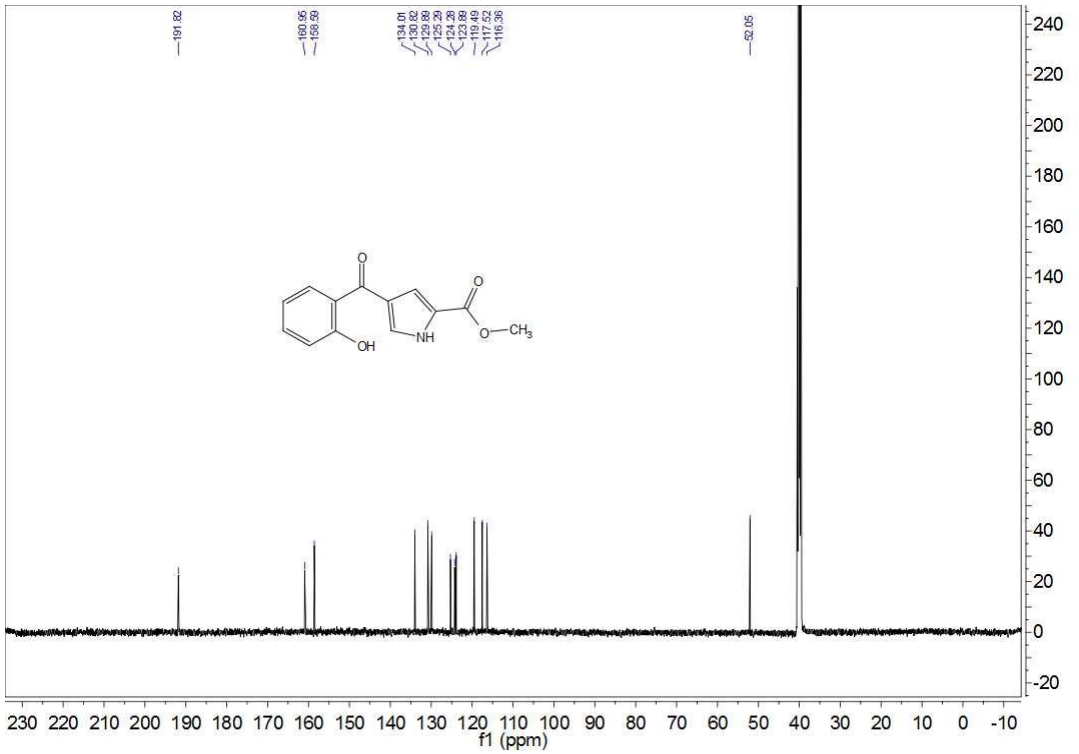

$^{13}$C NMR spectrum of **3s**



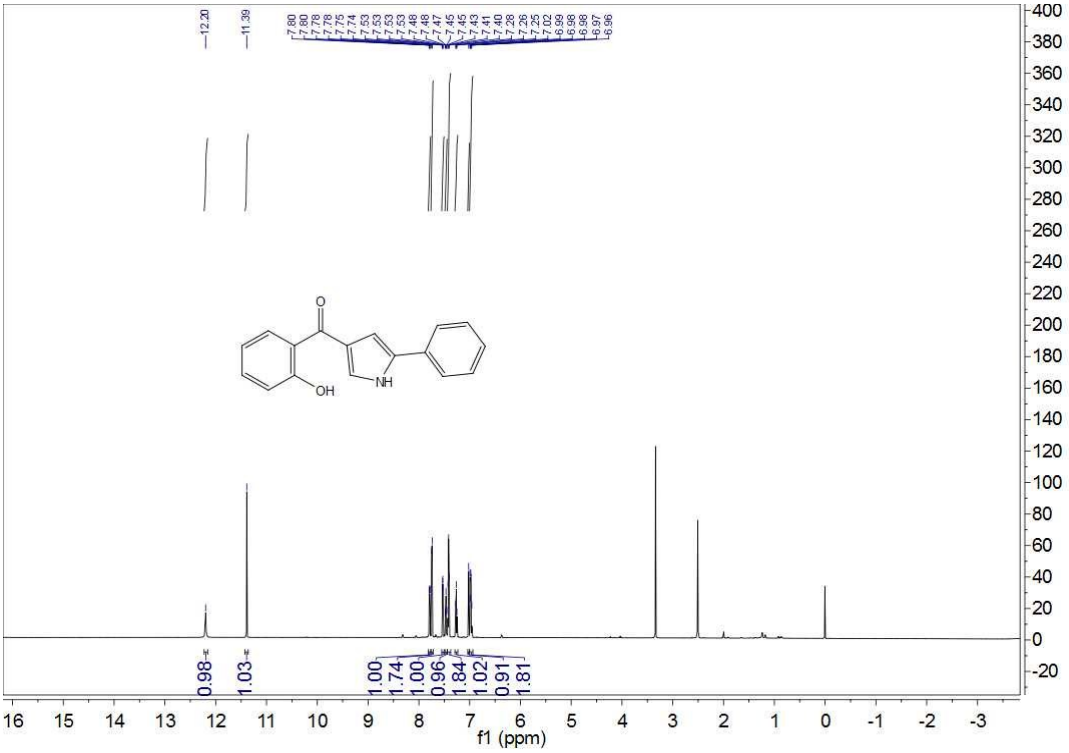

$^{1}$H NMR spectrum of **3t**



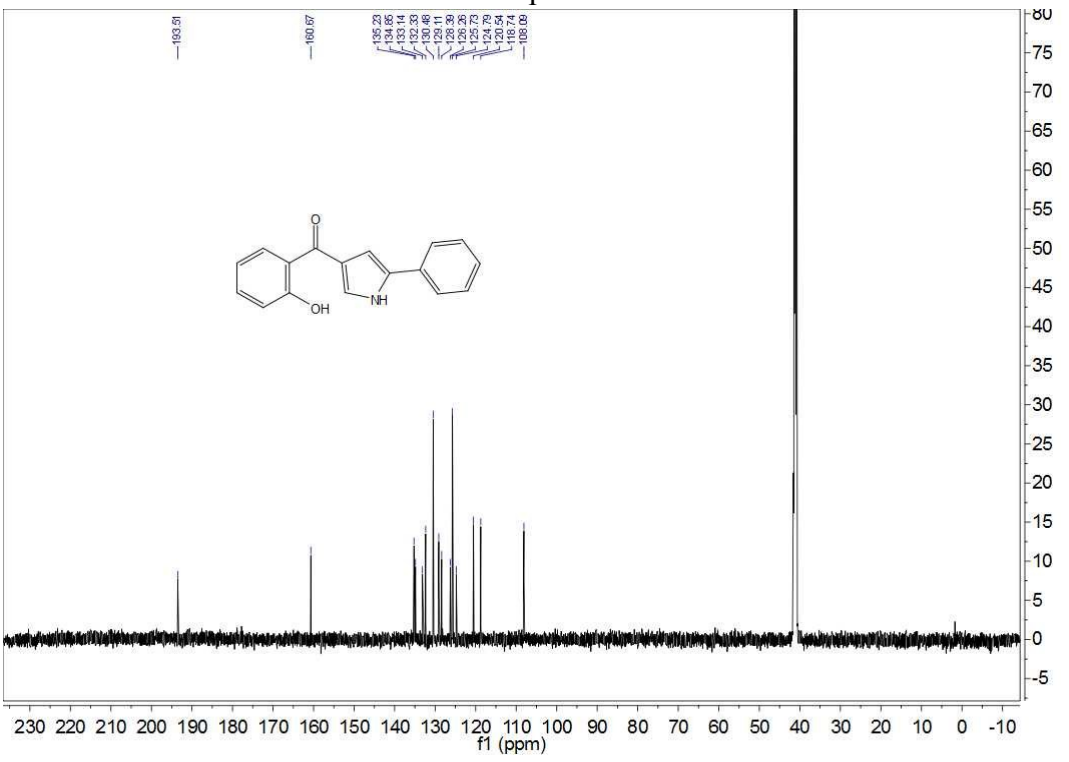

$^{13}$C NMR spectrum of **3t**




$^{1}$H NMR spectrum of **3u**




$^{13}$C NMR spectrum of **3u**



## 5、 X-ray Crystallography of ethyl 4-(2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate 3a

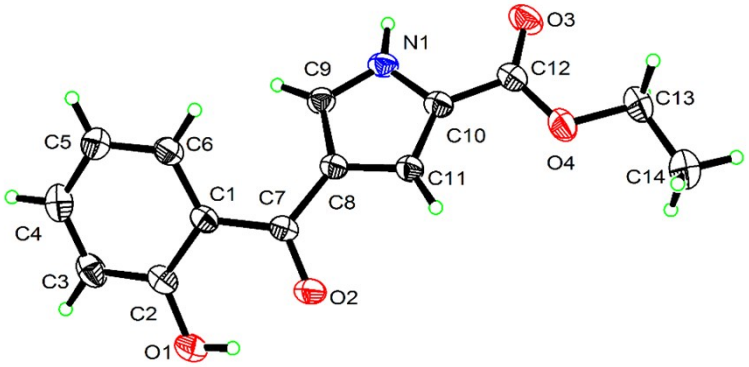



**Table 1.** Crystal data and structure refinement for **3a** (probability 30%).

| | |
|---|---|
| CCDC number: | 1412634 |
| Empirical formula: | $C_{14}H_{13}NO_4$ |
| Formula weight: | 259.25 |
| Temperature: | 296 K |
| Wavelength: | 0.71073Å |
| Crystal system: | Orthorhombic |
| Unit cell dimensions: | |
| a = 6.0219 (6) Å □ | α = 90 |
| b = 10.9014 (10) Å □ | β = 90 |
| c = 19.3876 (19) Å □ | γ = 90 |
| Volume: | 1272.7(2) $Å^3$ |
| Z | 4 |
| Density (calculated): | 1.353 $g/cm^3$ |
| Absorption coefficient: | 0.100 $mm^{-1}$ |
| F(000) | 544 |