

Supporting Information

Base-mediated unprecedented tandem cyclization reaction of nitrilimines and sulfur ylides: facile approaches to multifunctionalized pyrazolines

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1. General Informations:

The ^1H and ^{13}C NMR spectra were recorded on a 400 or 500 MHz spectrometer with chloroform-*d* as a solvent at 20–25 °C. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High-resolution mass spectra (HRMS) were recorded on FT-ICR MS spectrometer. Melting points are uncorrected. Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60 Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Hydrazonoyl chlorides **1**¹ and sulfonium salts **2**² were synthesized according to literature methods, respectively.

2. General procedure for the tandem reaction of hydrazoneyl chlorides **1 with sulfonium salts **2****

To a mixture of hydrazoneyl chlorides **1** (0.2 mmol) and sulfonium salts **2** (0.6 mmol) in 1,4-dioxane (3.0 mL) was added trimethylamine (1.0 mmol, 101 mg) at room temperature. The resulting mixture was stirred at room temperature until the starting material **1** was consumed (monitored by TLC, 6h). The mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10-1:5) to provide the desired products **3**.

3. Experimental procedure for the scaled-up synthesis of compound **3ba**

To a mixture of hydrazoneyl chloride **1b** (1.8 mmol, 547 mg) and sulfonium salts **2a** (5.4 mmol, 1.48 g) in 1,4-dioxane (20.0 mL) was added trimethylamine (9.0 mmol, 909 mg) at room temperature. The resulting mixture was stirred at room temperature until the starting material **1b** was consumed. The mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10-1:5) to provide the desired products **3ba** (690 mg) in 72% yield.

4. Experimental procedure for the scaled-up synthesis of compound **3dd**

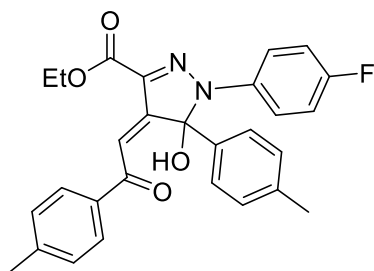
To the mixture of hydrazoneyl chlorides **1d** (4.4 mmol, 1.0 g), sulfonium bromide **2d** (13.0 mmol, 3.38 g), and triethylamine (22.0 mmol, 2.22 g) was added 1,4-dioxane (50.0 mL). The resulting mixture was stirred at room temperature until the starting material **1d** was consumed. The mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10-1:5) to provide the desired product **3dd** (1.37g) in 73% yield.

5. Control experiment

To the mixture of hydrazoneyl chlorides **1a** (0.2 mmol, 48.8 mg), sulfur ylide **2a'** (0.6 mmol, 116.4 mg), and triethylamine (0.3 mmol, 30.3 mg) was added 1,4-dioxane (3.0 mL). The resulting mixture was stirred at room temperature until the starting material **1a** was consumed. The mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10-1:5) to provide the desired product **3aa**

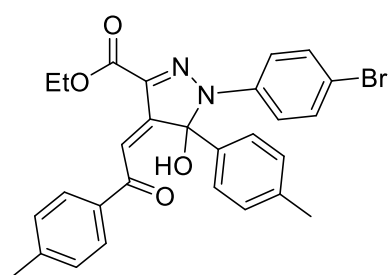
(80 mg) in 85% yield.

6. Characterization data for compounds 3



Ethyl (*Z*)-1-(4-fluorophenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3aa**)

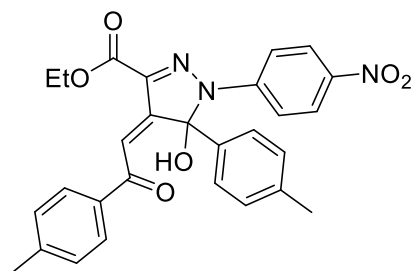
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (83 mg, 88% yield); **mp**: 159.2-159.7 °C; **¹H NMR** (500 MHz, CDCl₃) δ 8.16 (s, 1H), 8.14 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.48–7.46 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.88 (t, *J* = 8.5 Hz, 2H), 4.48–4.46 (m, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.67, 162.19, 159.86 (d, *J* = 242.9 Hz), 158.25, 144.97, 138.49, 135.52 (d, *J* = 2.1 Hz), 135.04, 134.78, 132.17, 129.34, 129.07, 128.67, 125.61, 120.02 (d, *J* = 7.9 Hz), 118.16, 115.39 (d, *J* = 22.7 Hz), 98.20, 61.23, 21.73, 21.05, 14.42. **HRMS** (ESI) calcd for C₂₈H₂₅FN₂NaO₄ [M + Na]⁺ 495.16906, found 495.16807.



Ethyl (*Z*)-1-(4-bromophenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ba**)

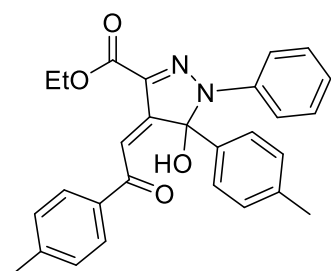
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford yellow solid (82 mg, 77% yield); **mp**: 180.6-181.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.18 (s, 1H), 8.14 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz,

2H), 4.50–4.44 (m, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 1.48 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.66, 162.08, 158.02, 145.09, 138.56, 138.20, 134.81, 134.64, 132.67, 131.59, 129.36, 129.13, 129.05, 128.72, 125.60, 119.30, 118.56, 118.51, 117.23, 97.91, 61.37, 21.79, 21.72, 21.02, 14.40. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{BrN}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 555.08899, found 555.08629.



Ethyl (*Z*)-5-hydroxy-1-(4-nitrophenyl)-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ca**)

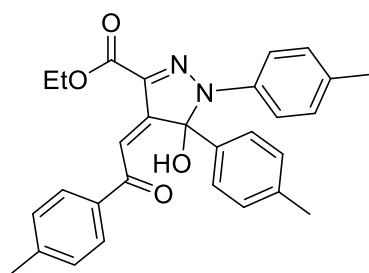
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford orange solid (50 mg, 50% yield); **mp**: 192.7-193.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 8.14 (s, 1H), 8.06 (d, $J = 9.2$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 9.2$ Hz, 2H), 7.23 (t, $J = 8.1$ Hz, 4H), 7.00 (d, $J = 7.9$ Hz, 2H), 4.54–4.46 (m, 2H), 2.39 (s, 3H), 2.19 (s, 3H), 1.51 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.70, 161.65, 156.83, 145.57, 144.03, 142.96, 138.95, 135.37, 134.42, 134.30, 130.05, 129.48, 129.19, 128.91, 125.58, 124.81, 120.49, 116.55, 97.30, 61.81, 21.80, 21.05, 14.35. HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{N}_3\text{NaO}_6$ $[\text{M} + \text{Na}]^+$ 522.16356, found 522.16205.



Ethyl (*Z*)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-1-phenyl-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3da**)

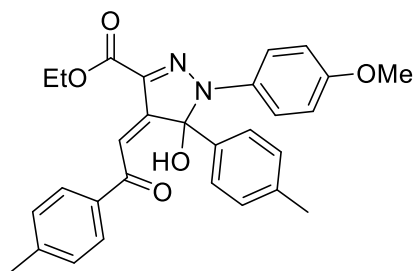
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (86 mg, 94% yield); **mp**: 169.7-170.1 °C; ^1H NMR (400 MHz, CDCl_3) δ

8.21 (s, 1H), 8.13 (s, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H), 7.28–7.26 (m, 2H), 7.19 (t, $J = 7.8$ Hz, 4H), 7.01–6.99 (m, 1H), 6.96 (d, $J = 8.1$ Hz, 2H), 4.50–4.44 (m, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 1.48 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.68, 162.26, 158.51, 144.90, 139.15, 138.32, 135.17, 134.78, 132.03, 129.31, 129.05, 128.61, 125.63, 124.39, 118.02, 117.84, 98.14, 61.20, 21.72, 21.02, 14.42. **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 477.17848, found 477.17675.



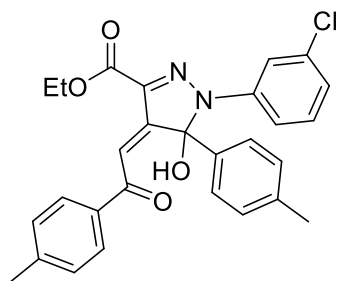
Ethyl (*Z*)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-1,5-di-*p*-tolyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ea**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (80 mg, 85% yield); **mp**:164.1-164.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.23 (s, 1H), 8.11 (s, 1H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.27–7.26 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.00–6.95 (m, 4H), 4.50–4.44 (m, 2H), 2.38 (s, 3H), 2.23 (s, 3H), 2.17 (s, 3H), 1.48 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.65, 162.36, 158.72, 144.80, 138.28, 136.84, 135.25, 134.90, 134.26, 131.48, 129.30, 129.21, 129.05, 128.61, 125.63, 118.20, 117.38, 98.32, 61.14, 21.75, 21.08, 20.86, 14.46. **HRMS** (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 491.19413, found 491.19306.



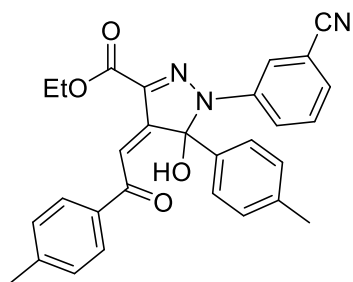
Ethyl (*Z*)-5-hydroxy-1-(4-methoxyphenyl)-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3fa**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford purplish red solid (80 mg, 83% yield); **mp**: 159.9-160.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.22 (s, 1H), 8.12 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 9.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 9.1 Hz, 2H), 4.50–4.42 (m, 2H), 3.72 (s, 3H), 2.37 (s, 3H), 2.17 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.60, 162.37, 158.70, 156.98, 144.75, 138.32, 135.27, 134.94, 132.87, 131.16, 129.29, 129.02, 128.60, 125.59, 120.34, 117.16, 113.82, 98.56, 61.07, 55.33, 21.72, 21.06, 14.46. **HRMS** (ESI) calcd for C₂₉H₂₈N₂NaO₅ [M + Na]⁺ 507.18904, found 507.18668.



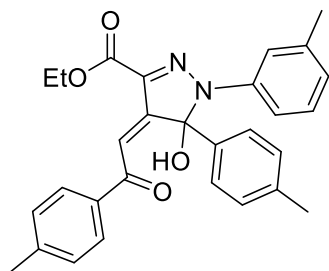
Ethyl (*Z*)-1-(3-chlorophenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ga**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (81 mg, 83% yield); **mp**: 154.5-155.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.16 (s, 1H), 8.14 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.58 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.26–7.24 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.48 (q, *J* = 6.9 Hz, 2H), 2.37 (s, 3H), 2.17 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.64, 162.03, 157.95, 145.11, 140.15, 138.54, 134.80, 134.61, 134.40, 132.98, 129.59, 129.36, 129.09, 128.71, 125.61, 124.05, 118.78, 117.82, 115.70, 97.83, 61.41, 21.75, 21.04, 14.40. **HRMS** (ESI) calcd for C₂₈H₂₅CIN₂NaO₄ [M + Na]⁺ 511.13951, found 511.14160.



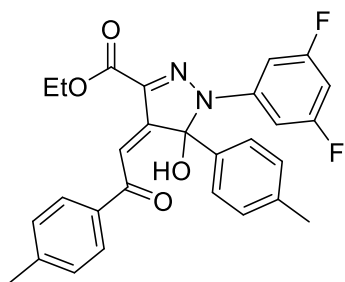
Ethyl (*Z*)-1-(3-cyanophenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ha**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (79 mg, 82% yield); **mp**: 175.9-176.3 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.17 (s, 1H), 8.14 (s, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.25–7.20 (m, 6H), 6.99 (d, *J* = 7.3 Hz, 2H), 4.52–4.46 (m, 2H), 2.38 (s, 3H), 2.18 (s, 3H), 1.50 (t, *J* = 6.6 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.65, 161.82, 157.39, 145.34, 139.73, 138.80, 134.46, 134.44, 133.89, 129.47, 129.42, 129.14, 128.86, 127.01, 125.59, 121.35, 120.56, 119.67, 118.61, 112.66, 97.54, 61.59, 21.77, 21.04, 14.37. **HRMS** (ESI) calcd for C₂₉H₂₅N₃NaO₄ [M + Na]⁺ 502.17373, found 502.17260.



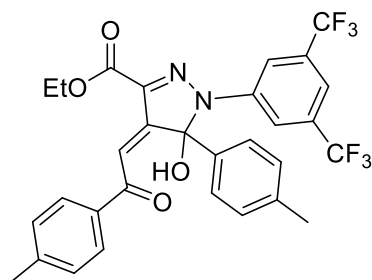
Ethyl (*Z*)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-1-(*m*-tolyl)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ia**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (89 mg, 95% yield); **mp**: 169.3-170 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (s, 1H), 8.12 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.38 (s, 1H), 7.31–7.26 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.4 Hz, 1H), 4.51–4.45 (m, 2H), 2.38 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.62, 162.27, 158.59, 144.82, 139.03, 138.45, 138.23, 135.19, 134.78, 131.79, 129.27, 129.01, 128.55, 128.32, 125.59, 125.36, 118.67, 117.64, 115.21, 98.18, 61.17, 21.67, 21.48, 21.01, 14.41. **HRMS** (ESI) calcd for C₂₉H₂₈N₂NaO₄ [M + Na]⁺ 491.19413, found 491.19294.



Ethyl (*Z*)-1-(3,5-difluorophenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ja**)

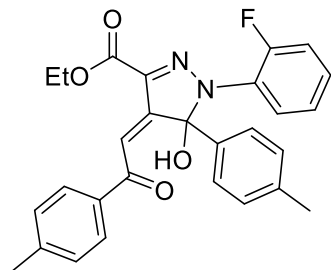
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (80 mg, 82% yield); **mp**: 185.5-185.7 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.15 (s, 1H), 8.12 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.25–7.19 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.40 (t, *J* = 8.4 Hz, 1H), 4.47 (q, *J* = 7.0 Hz, 2H), 2.37 (s, 3H), 2.18 (s, 3H), 1.49 (t, *J* = 6.9 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.64, 162.95 (dd, *J*₁ = 244.0 Hz, *J*₂ = 14.7 Hz), 161.84, 157.51, 145.30, 141.03 (t, *J* = 13.3 Hz), 138.72, 134.59, 134.47, 133.71, 129.40, 129.13, 128.81, 125.58, 119.51, 100.74 (dd, *J*₁ = 21.0 Hz, *J*₂ = 9.1 Hz), 98.97 (t, *J* = 25.9 Hz), 97.52, 61.55, 21.76, 21.04, 14.35. **HRMS** (ESI) calcd for C₂₈H₂₄F₂N₂NaO₄ [M + Na]⁺ 513.15963, found 513.15884.



Ethyl (*Z*)-1-(3,5-bis(trifluoromethyl)phenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ka**)

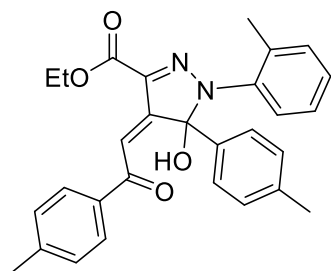
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (73 mg, 62% yield); **mp**: 157.9-158.4 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.21 (s, 1H), 8.08 (s, 1H), 7.96 (s, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.42 (s, 1H), 7.27–7.25 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 2H), 4.51 (q, *J* = 7.0 Hz, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.56, 161.70, 157.05, 145.46, 140.17, 138.98, 134.71, 134.36, 134.21, 131.85 (q,

$J = 33.5$ Hz), 129.45, 129.17, 128.84, 125.67, 123.09 (q, $J = 271.2$ Hz), 120.45, 116.89, 116.87, 116.58, 97.41, 61.77, 21.78, 21.02, 14.35. **HRMS** (ESI) calcd for $C_{30}H_{24}F_6N_2NaO_4$ $[M + Na]^+$ 613.15325, found 613.15121.



Ethyl (*Z*)-1-(2-fluorophenyl)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**31a**)

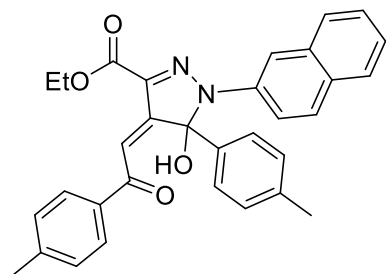
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford yellow solid (40 mg, 42% yield); **mp**: 135.5-136.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.29 (s, 1H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.46 (s, 1H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 7.9$ Hz, 2H), 7.18–7.12 (m, 1H), 7.02–6.95 (m, 2H), 6.91 (d, $J = 8.1$ Hz, 2H), 4.53–4.40 (m, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 1.45 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.61, 162.13, 157.68 (d, $J = 253.0$ Hz), 156.95, 144.83, 138.35, 135.39, 134.84, 132.99, 129.30, 129.02, 128.89 (d, $J = 7.7$ Hz), 128.42, 127.91, 127.07 (d, $J = 10.3$ Hz), 125.50, 123.59 (d, $J = 3.7$ Hz), 119.52, 116.44 (d, $J = 20.2$ Hz), 98.28, 61.21, 21.70, 21.04, 14.43. **HRMS** (ESI) calcd for $C_{28}H_{25}FN_2NaO_4$ $[M + Na]^+$ 495.16906, found 495.16809.



Ethyl (*Z*)-5-hydroxy-4-(2-oxo-2-(*p*-tolyl)ethylidene)-1-(*o*-tolyl)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3ma**)

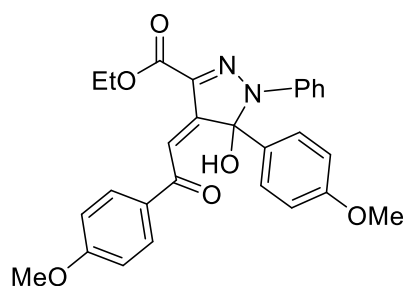
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford yellow solid (70 mg, 75% yield); **mp**: 129.4-130.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.81 (d, $J = 7.3$ Hz, 2H), 7.45 (s, 1H), 7.21–7.18 (m, 4H), 7.13 (d, $J =$

6.5 Hz, 2H), 7.07–7.03 (m, 2H), 6.92 (d, $J = 7.6$ Hz, 2H), 4.46–4.40 (m, 2H), 2.37 (s, 3H), 2.18 (s, 3H), 1.96 (s, 3H), 1.43 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.60, 162.42, 157.19, 144.61, 138.41, 137.48, 136.95, 135.55, 135.07, 130.95, 130.74, 129.25, 128.96, 128.51, 128.36, 128.31, 125.64, 125.57, 118.32, 98.73, 60.90, 21.69, 21.08, 18.14, 14.46. HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 491.19413, found 491.19289.



Ethyl (*Z*)-5-hydroxy-1-(naphthalen-2-yl)-4-(2-oxo-2-(*p*-tolyl)ethylidene)-5-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3na**)

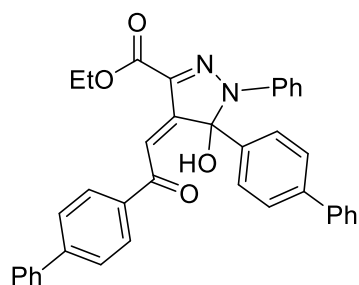
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (94 mg, 93% yield); mp: 182.7-183 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 1H), 8.16 (s, 1H), 7.90 (s, 1H), 7.81–7.79 (m, 3H), 7.72–7.66 (m, 3H), 7.40–7.36 (m, 1H), 7.34–7.32 (m, 3H), 7.21 (d, $J = 7.8$ Hz, 2H), 6.95 (d, $J = 7.9$ Hz, 2H), 4.53–4.48 (m, 2H), 2.38 (s, 3H), 2.13 (s, 3H), 1.51 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.66, 162.25, 158.45, 144.93, 138.38, 136.81, 135.13, 134.78, 133.34, 132.29, 130.64, 129.32, 129.07, 128.64, 128.52, 127.86, 127.47, 126.26, 125.64, 124.93, 118.04, 117.94, 114.79, 98.41, 61.29, 21.72, 20.99, 14.45. HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 527.19413, found 527.19199.



Ethyl (*Z*)-5-hydroxy-5-(4-methoxyphenyl)-4-(2-(4-methoxyphenyl)-2-oxoethylidene)-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3db**)

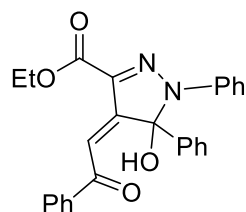
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford

red solid (81 mg, 83% yield); **mp**: 167.2-167.4 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.28 (s, 1H), 8.12 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 4.50–4.44 (m, 2H), 3.84 (s, 3H), 3.66 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 191.47, 164.18, 162.31, 159.39, 158.05, 139.20, 131.99, 131.43, 130.53, 130.32, 128.61, 127.11, 124.35, 118.07, 113.85, 113.18, 97.95, 61.18, 55.54, 55.02, 29.69, 14.44. **HRMS** (ESI) calcd for C₂₈H₂₆N₂NaO₆ [M + Na]⁺ 509.16831, found 509.16645.



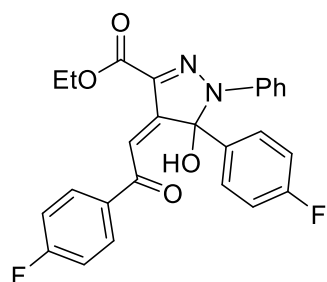
Ethyl (*Z*)-5-([1,1'-biphenyl]-4-yl)-4-(2-([1,1'-biphenyl]-4-yl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dc**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (107 mg, 93% yield); **mp**: 154.6-155.2 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.23 (s, 1H), 8.22 (s, 1H), 7.97 (d, *J* = 6.9 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 4H), 7.50–7.32 (m, 11H), 7.29–7.27 (m, 1H), 7.24–7.20 (m, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.53–4.48 (m, 2H), 1.51 (td, *J* = 7.1, 1.6 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.67, 162.23, 158.52, 146.54, 141.18, 139.95, 139.51, 139.10, 136.96, 135.88, 132.14, 129.53, 128.92, 128.70, 128.63, 128.39, 127.44, 127.24, 126.88, 126.60, 126.22, 124.57, 118.09, 117.99, 98.08, 61.30, 14.44. **HRMS** (ESI) calcd for C₃₈H₃₀N₂NaO₄ [M + Na]⁺ 601.20978, found 601.20737.



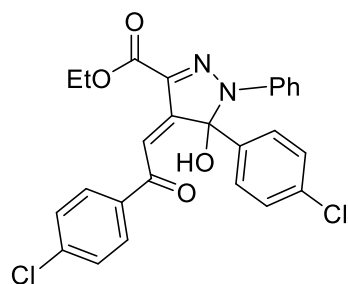
Ethyl (*Z*)-5-hydroxy-4-(2-oxo-2-phenylethylidene)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dd**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (68 mg, 80% yield); **mp**: 167.2-168.2 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.15 (s, 1H), 8.09 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.55–7.50 (m, 3H), 7.41–7.38 (m, 4H), 7.21–7.17 (m, 4H), 7.14–7.10 (m, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 4.50–4.44 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 193.27, 162.20, 158.71, 139.07, 137.94, 137.14, 133.78, 132.07, 128.82, 128.63, 127.91, 125.76, 124.56, 118.11, 117.96, 98.05, 61.27, 14.42. **HRMS** (ESI) calcd for C₂₆H₂₂N₂ NaO₄ [M + Na]⁺ 449.14718, found 449.14581.



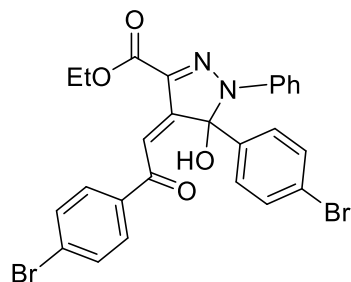
Ethyl (*Z*)-5-(4-fluorophenyl)-4-(2-(4-fluorophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3de**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (86 mg, 93% yield); **mp**: 142.3-143.5 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (s, 1H), 8.01 (s, 1H), 7.90 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 8.5 Hz, 2H), 4.50–4.45 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 191.59, 166.19 (d, *J* = 257.3 Hz), 162.50 (d, *J* = 248.2 Hz), 162.12, 158.59, 138.91, 133.88 (d, *J* = 2.8 Hz), 133.41 (d, *J* = 2.7 Hz), 131.94, 131.65 (d, *J* = 9.5 Hz), 128.72, 127.70 (d, *J* = 8.4 Hz), 124.82, 118.23, 117.74, 115.91 (d, *J* = 22.0 Hz), 114.96 (d, *J* = 21.9 Hz), 97.61, 61.34, 14.39. **HRMS** (ESI) calcd for C₂₆H₂₀F₂N₂NaO₄ [M + Na]⁺ 485.12833, found 485.12656.



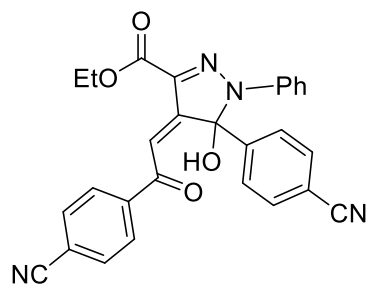
Ethyl (*Z*)-5-(4-chlorophenyl)-4-(2-(4-chlorophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3df**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (88 mg, 89% yield); **mp**: 174.5-175.2 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.99 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 4.51–4.43 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 191.87, 162.09, 158.71, 140.65, 138.86, 136.42, 135.31, 134.67, 132.04, 130.29, 129.07, 128.79, 128.25, 127.20, 124.95, 118.24, 117.51, 97.68, 61.41, 14.42. **HRMS** (ESI) calcd for C₂₆H₂₀Cl₂N₂NaO₄ [M + Na]⁺ 517.06923, found 517.06746.



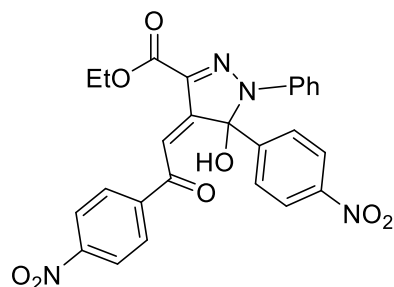
Ethyl (*Z*)-5-(4-bromophenyl)-4-(2-(4-bromophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dg**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (84 mg, 72% yield); **mp**: 190.8-191.3 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.99 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.32–7.30 (m, 2H), 7.27–7.26 (m, 2H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 4.49–4.45 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.03, 162.04, 158.68, 138.81, 136.88, 135.69, 132.05, 131.17, 130.33, 129.50, 128.78, 127.45, 124.95, 122.99, 118.20, 117.40, 97.71, 61.39, 14.40. **HRMS** (ESI) calcd for C₂₆H₂₀Br₂N₂NaO₄ [M + Na]⁺ 604.96820, found 604.96656.



Ethyl (*Z*)-5-(4-cyanophenyl)-4-(2-(4-cyanophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dh**)

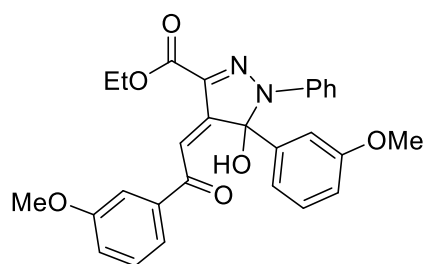
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (82 mg, 86% yield); **mp**: 177.1-177.8 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.19 (s, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.80 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.54–7.49 (m, 4H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 4.51–4.46 (m, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 191.56, 161.81, 159.24, 142.16, 139.71, 138.53, 132.56, 132.21, 131.93, 129.15, 128.93, 126.51, 125.51, 118.38, 117.93, 117.57, 117.16, 116.97, 112.91, 97.57, 61.60, 14.36. **HRMS** (ESI) calcd for C₂₈H₂₀N₄NaO₄ [M + Na]⁺ 499.13768, found 499.13580.



Ethyl (*Z*)-5-hydroxy-5-(4-nitrophenyl)-4-(2-(4-nitrophenyl)-2-oxoethylidene)-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3di**)

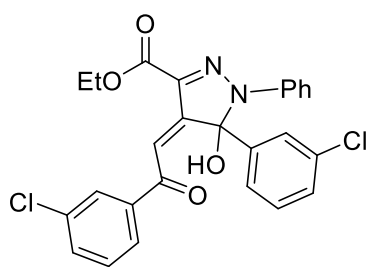
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (101 mg, 98% yield); **mp**: 177.0-177.9 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.7 Hz, 2H), 8.24 (s, 1H), 8.07 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.80 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 4.55–4.44 (m, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 191.40, 161.83, 159.43, 150.74, 148.02, 143.93, 141.19, 138.57, 132.33, 129.89, 129.01, 126.90, 125.70, 123.97, 123.37, 118.55, 117.08,

97.61, 61.68, 14.39. **HRMS** (ESI) calcd for C₂₆H₂₀N₄NaO₈ [M + Na]⁺ 539.11733, found 539.11533.



Ethyl (*Z*)-5-hydroxy-5-(3-methoxyphenyl)-4-(2-(3-methoxyphenyl)-2-oxoethylidene)-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dj**)

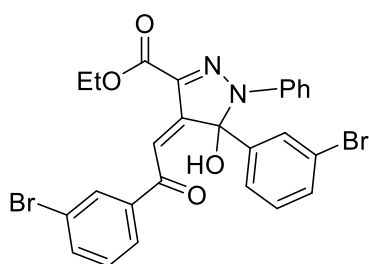
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (92 mg, 95% yield); **mp**: 171.2-172.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (s, 1H), 8.08 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.20 (t, *J* = 7.9 Hz, 2H), 7.12–7.08 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.97–6.95 (m, 2H), 6.67 (d, *J* = 7.4 Hz, 1H), 4.49–4.44 (m, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 193.02, 162.12, 159.76, 159.07, 158.28, 139.55, 139.10, 138.49, 132.10, 129.61, 128.98, 128.64, 124.60, 121.75, 120.45, 118.25, 118.18, 113.76, 112.70, 112.10, 97.88, 61.25, 55.41, 55.24, 14.42. **HRMS** (ESI) calcd for C₂₈H₂₆N₂NaO₆ [M + Na]⁺ 509.16831, found 509.16685.



Ethyl (*Z*)-5-(3-chlorophenyl)-4-(2-(3-chlorophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dk**)

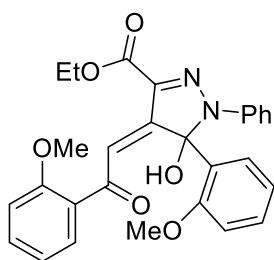
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (93 mg, 94% yield); **mp**: 169.8-170.4 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.12 (s, 1H), 7.92 (s, 1H), 7.84 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.53–7.49 (m, 3H), 7.39–7.32 (m, 3H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.17–7.13 (m, 2H), 7.05 (t, *J* = 7.3 Hz,

1H), 4.51–4.46 (m, 2H), 1.49 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.88, 162.00, 158.75, 139.68, 138.78, 138.45, 135.09, 134.18, 133.86, 132.07, 130.01, 129.24, 129.11, 128.79, 127.03, 125.90, 125.02, 124.06, 118.29, 117.52, 97.48, 61.45, 14.40. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 517.06923, found 517.06742.



Ethyl (*Z*)-5-(3-bromophenyl)-4-(2-(3-bromophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dl**)

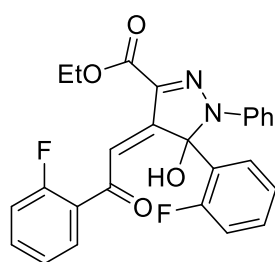
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (94 mg, 81% yield); **mp**: 149.4-149.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1H), 8.00 (s, 1H), 7.90 (s, 1H), 7.81 (d, $J = 7.7$ Hz, 1H), 7.68 (d, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 7.8$ Hz, 3H), 7.38 (d, $J = 7.8$ Hz, 1H), 7.33–7.29 (m, 2H), 7.23 (t, $J = 7.9$ Hz, 2H), 7.11–7.03 (m, 2H), 4.52–4.46 (m, 2H), 1.50 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.74, 161.95, 158.67, 139.85, 138.72, 138.59, 136.73, 132.00, 131.64, 130.20, 129.49, 128.77, 128.69, 127.45, 124.99, 124.49, 123.04, 122.29, 118.24, 117.48, 97.36, 61.43, 14.38. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{Br}_2\text{N}_2\text{NaO}_4$ $[\text{M} + \text{Na}]^+$ 604.96820, found 604.96569.



Ethyl (*Z*)-5-hydroxy-5-(2-methoxyphenyl)-4-(2-(2-methoxyphenyl)-2-oxoethylidene)-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dm**)

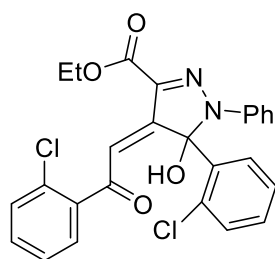
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (82 mg, 84% yield); **mp**: 165.3-165.9 °C; ^1H NMR (400 MHz, CDCl_3) δ

8.01 (d, $J = 7.7$ Hz, 1H), 7.86 (d, $J = 1.1$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.42–7.37 (m, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 1.4$ Hz, 1H), 7.16–7.10 (m, 3H), 6.96–6.91 (m, 2H), 6.90–6.85 (m, 2H), 6.63 (d, $J = 8.1$ Hz, 1H), 4.52–4.38 (m, 2H), 3.82 (s, 3H), 3.59 (s, 3H), 1.44 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.43, 162.39, 158.70, 156.33, 156.25, 139.74, 134.13, 133.59, 130.50, 129.97, 129.89, 128.28, 128.01, 126.04, 123.75, 122.24, 120.56, 119.22, 118.21, 111.77, 111.70, 94.96, 60.78, 55.77, 55.54, 14.45. **HRMS** (ESI) calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{NaO}_6$ [$\text{M} + \text{Na}$] $^+$ 509.16831, found 509.16826.



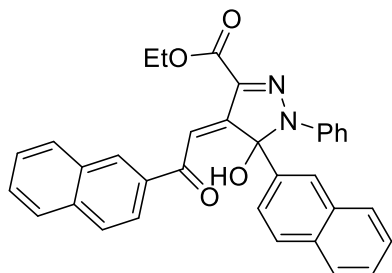
Ethyl (*Z*)-5-(2-fluorophenyl)-4-(2-(2-fluorophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dn**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (89 mg, 96% yield); **mp**: 141.3-142.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.02–7.99 (m, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.50–7.45 (m, 3H), 7.32 (s, 1H), 7.20–7.04 (m, 6H), 6.99 (t, $J = 7.3$ Hz, 1H), 6.81–6.77 (m, 1H), 4.50–4.41 (m, 2H), 1.45 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.11, 161.97, 161.60 (d, $J = 239.2$ Hz), 159.08 (d, $J = 233.1$ Hz), 157.04, 139.21, 135.31 (d, $J = 8.9$ Hz), 133.00, 130.84, 130.79, 130.03, 128.54, 125.80 (d, $J = 11.3$ Hz), 124.65, 124.50, 124.38 (d, $J = 3.2$ Hz), 122.61 (d, $J = 2.8$ Hz), 121.61 (d, $J = 6.9$ Hz), 118.31, 116.73 (d, $J = 23.1$ Hz), 115.90 (d, $J = 21.3$ Hz), 94.32, 61.23, 14.31. **HRMS** (ESI) calcd for $\text{C}_{26}\text{H}_{20}\text{F}_2\text{N}_2\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$ 485.12833, found 485.12837.



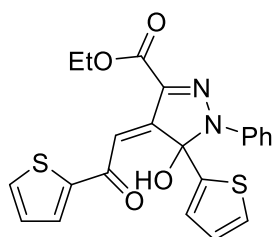
Ethyl (*Z*)-5-(2-chlorophenyl)-4-(2-(2-chlorophenyl)-2-oxoethylidene)-5-hydroxy-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3do**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (30 mg, 30% yield); **mp**: 153.4-154.1 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.22 (d, *J* = 7.9 Hz, 1H), 7.77 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.38–7.28 (m, 4H), 7.24–7.23 (m, 1H), 7.19–7.16 (m, 4H), 7.01 (t, *J* = 7.3 Hz, 1H), 6.74 (s, 1H), 4.52–4.36 (m, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 194.71, 162.12, 155.54, 139.31, 137.46, 133.99, 133.46, 132.90, 132.36, 132.16, 131.37, 130.65, 130.46, 130.22, 130.18, 128.48, 126.84, 125.29, 124.67, 122.32, 118.86, 94.97, 61.21, 14.36. **HRMS** (ESI) calcd for C₂₆H₂₀Cl₂N₂NaO₄ [M + Na]⁺ 517.06923, found 517.06889.



Ethyl (*Z*)-5-hydroxy-5-(naphthalen-2-yl)-4-(2-(naphthalen-2-yl)-2-oxoethylidene)-1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dp**)

It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford yellow solid (89 mg, 85% yield); **mp**: 174.6-175.3 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.43 (s, 1H), 8.36 (s, 1H), 8.35 (s, 1H), 8.07 (s, 1H), 7.89–7.84 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 2H), 7.65–7.62 (m, 2H), 7.58–7.53 (m, 3H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.42–7.34 (m, 3H), 7.18–7.14 (m, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 4.58–4.49 (m, 2H), 1.54 (t, *J* = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 192.93, 162.31, 158.51, 139.08, 135.69, 135.27, 134.41, 133.04, 132.26, 132.23, 132.14, 131.12, 129.69, 128.91, 128.66, 128.49, 128.12, 127.63, 127.37, 126.81, 126.47, 126.24, 125.58, 124.55, 123.91, 122.94, 118.17, 118.04, 98.28, 61.34, 14.44. **HRMS** (ESI) calcd for C₃₄H₂₆N₂NaO₄ [M + Na]⁺ 549.17848, found 549.17747.

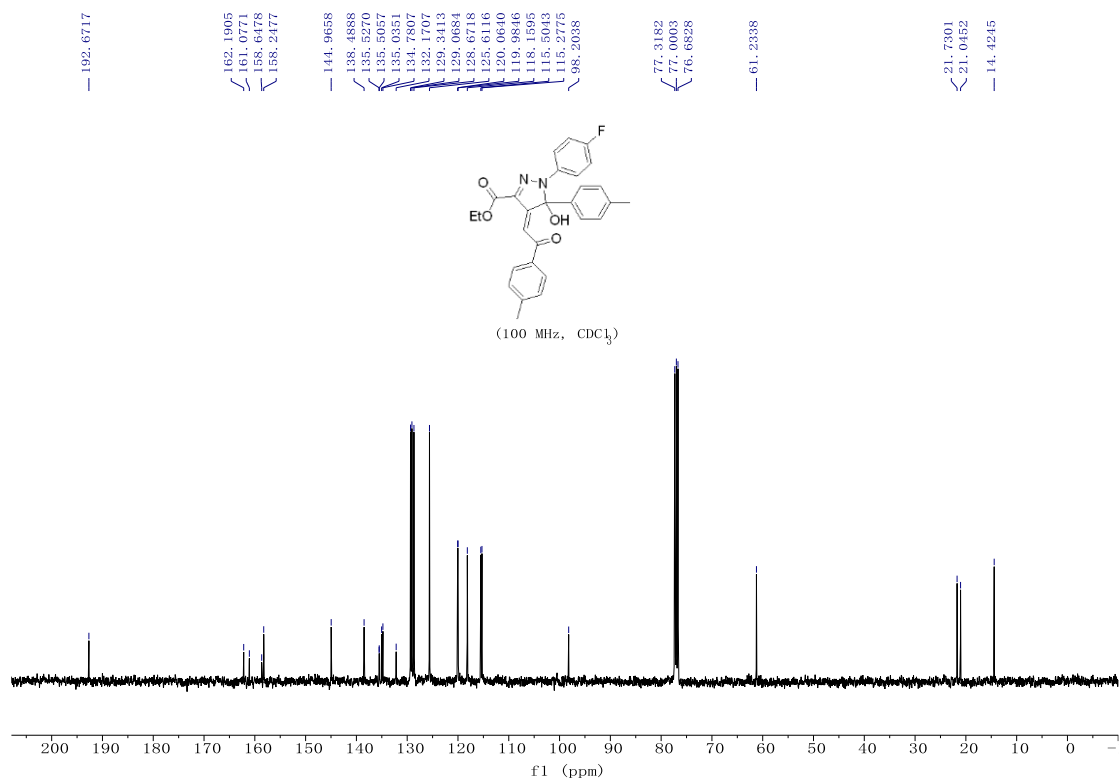
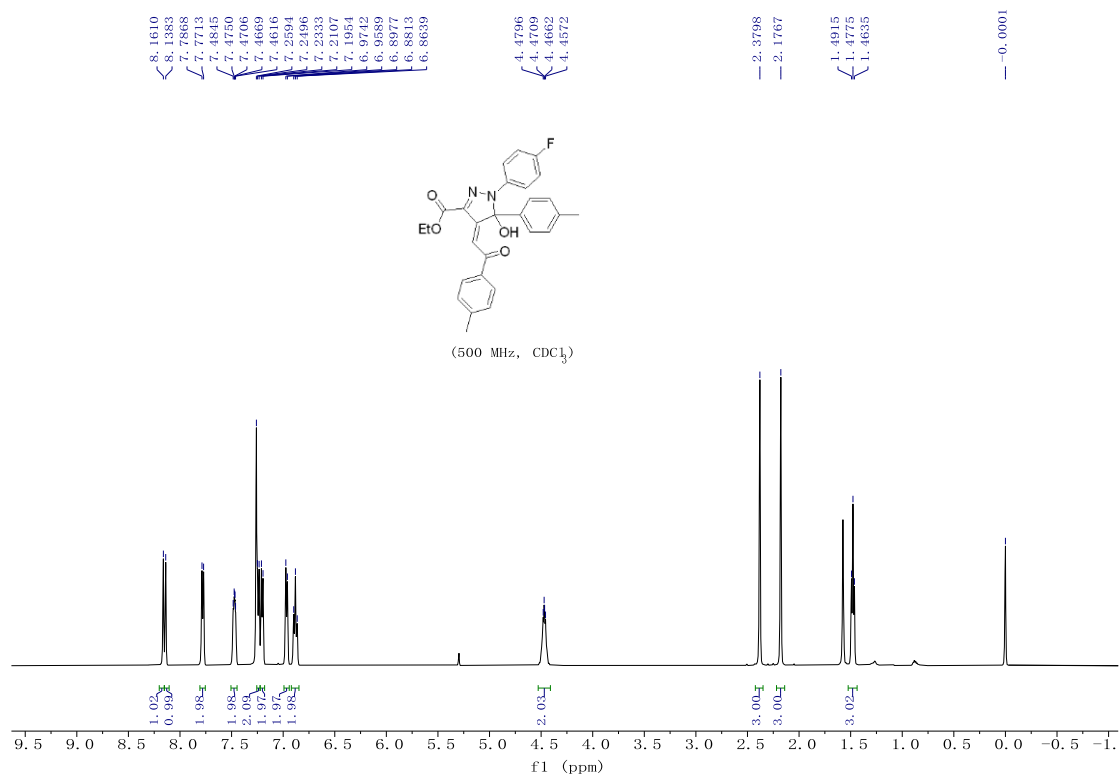


Ethyl (*Z*)-5-hydroxy-4-(2-oxo-2-(thiophen-2-yl)ethylidene)-1-phenyl-5-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (**3dq**)

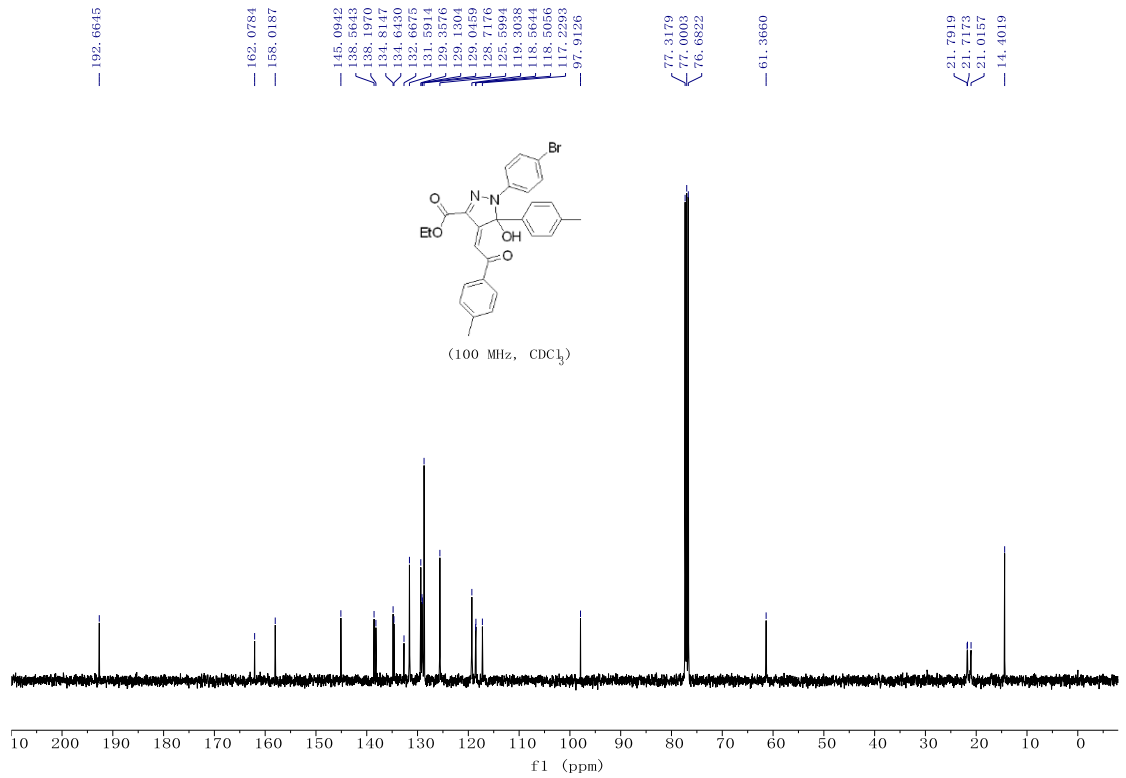
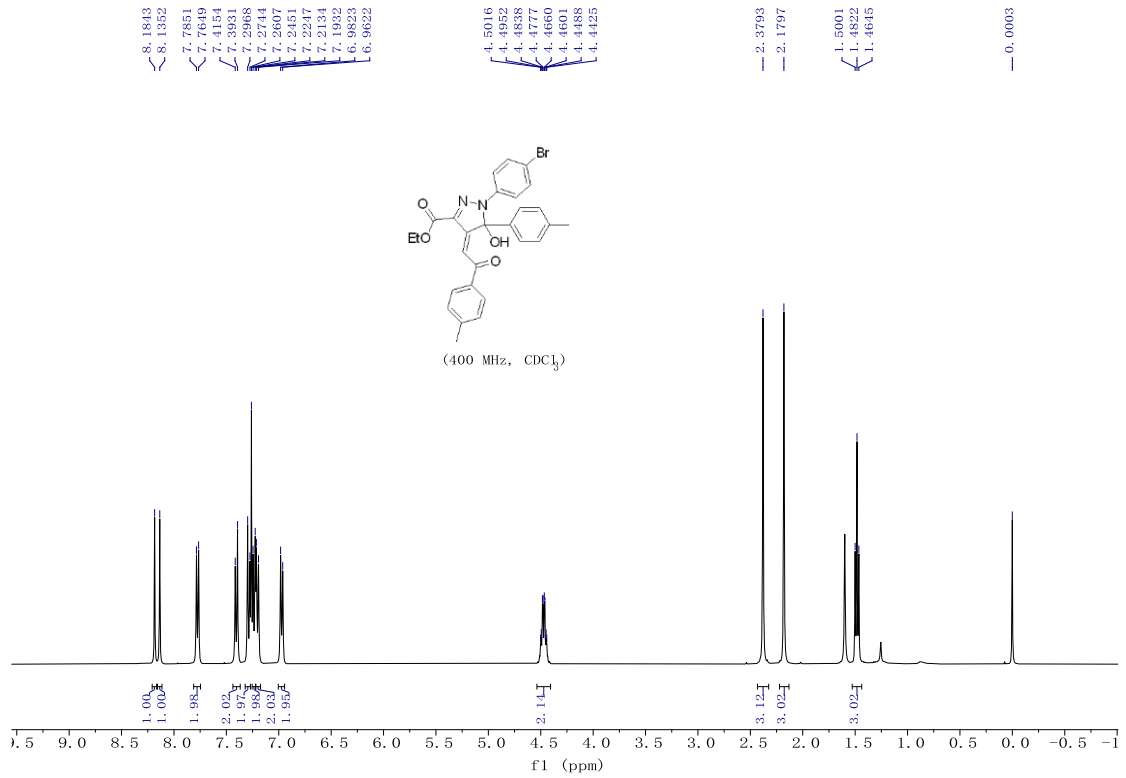
It was purified by flash chromatography (EtOAc/petroleum ether, 1:10-1:5) to afford red solid (49 mg, 56% yield); **mp**: 156.7-157.5 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.42 (s, 1H), 8.12 (s, 1H), 7.84 (d, *J* = 3.5 Hz, 1H), 7.70 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.28–7.24 (m, 2H), 7.15–7.13 (m, 1H), 7.11–7.07 (m, 2H), 7.04 (d, *J* = 2.8 Hz, 1H), 6.78–6.76 (m, 1H), 4.53–4.41 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 184.85, 162.03, 156.96, 144.89, 141.85, 139.09, 135.98, 134.01, 131.96, 128.67, 128.62, 126.42, 126.30, 126.18, 125.18, 119.28, 118.08, 96.74, 61.31, 14.41. **HRMS** (ESI) calcd for C₂₂H₁₈N₂NaO₄S₂ [M + Na]⁺ 461.06002, found 461.05873.

7. NMR spectra of compounds 3

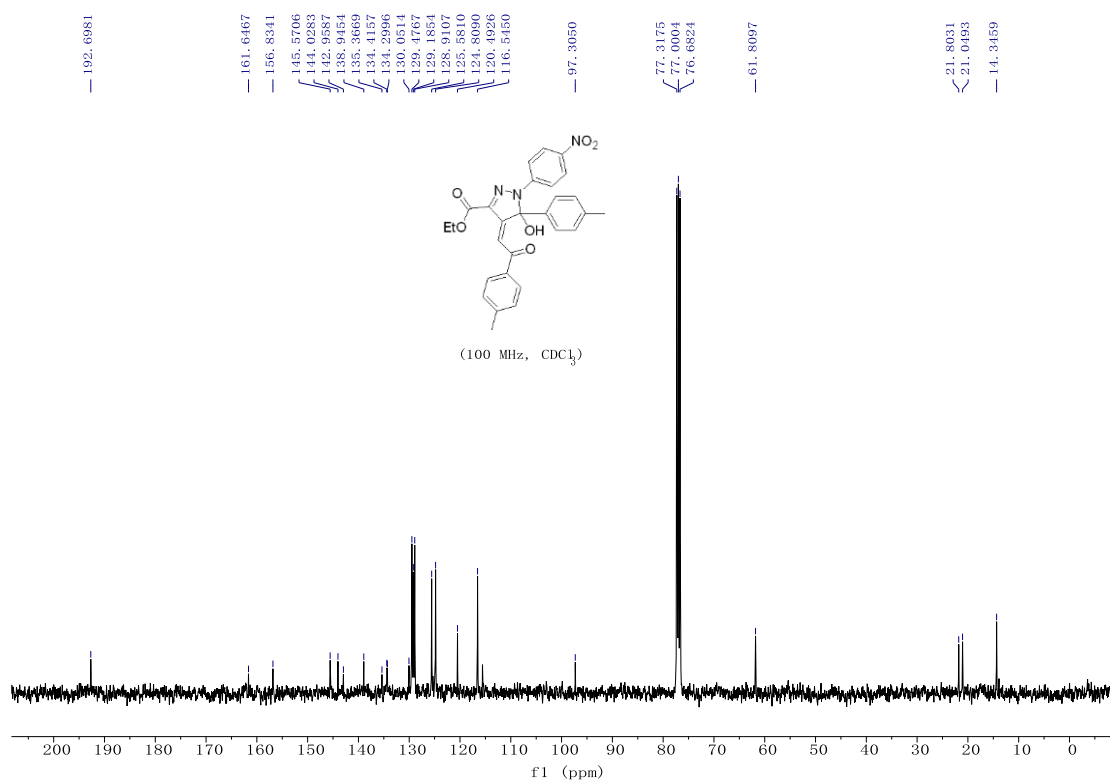
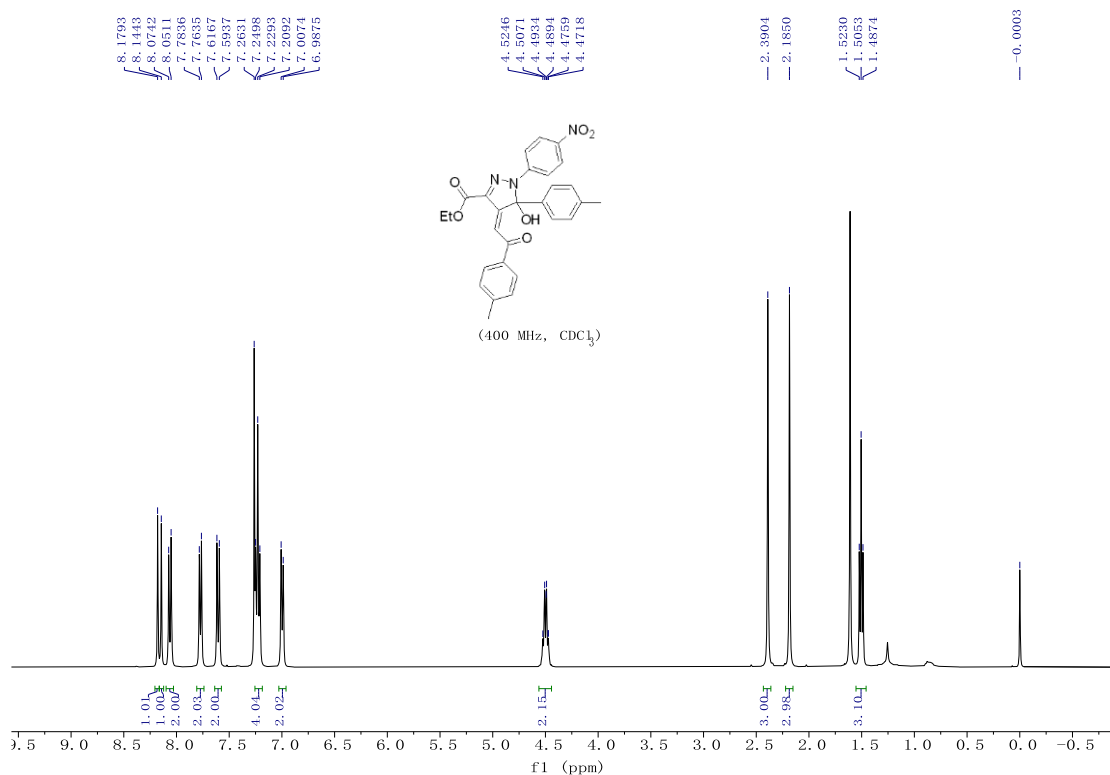
^1H NMR and ^{13}C NMR spectrums of **3aa**



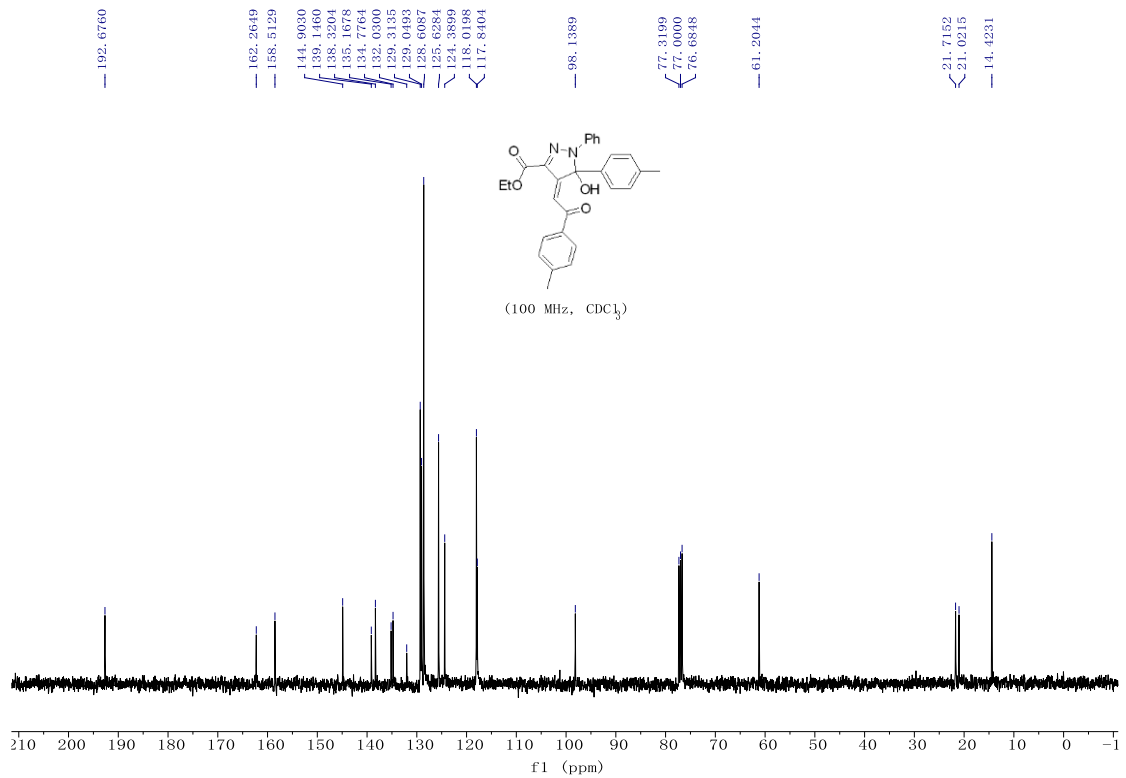
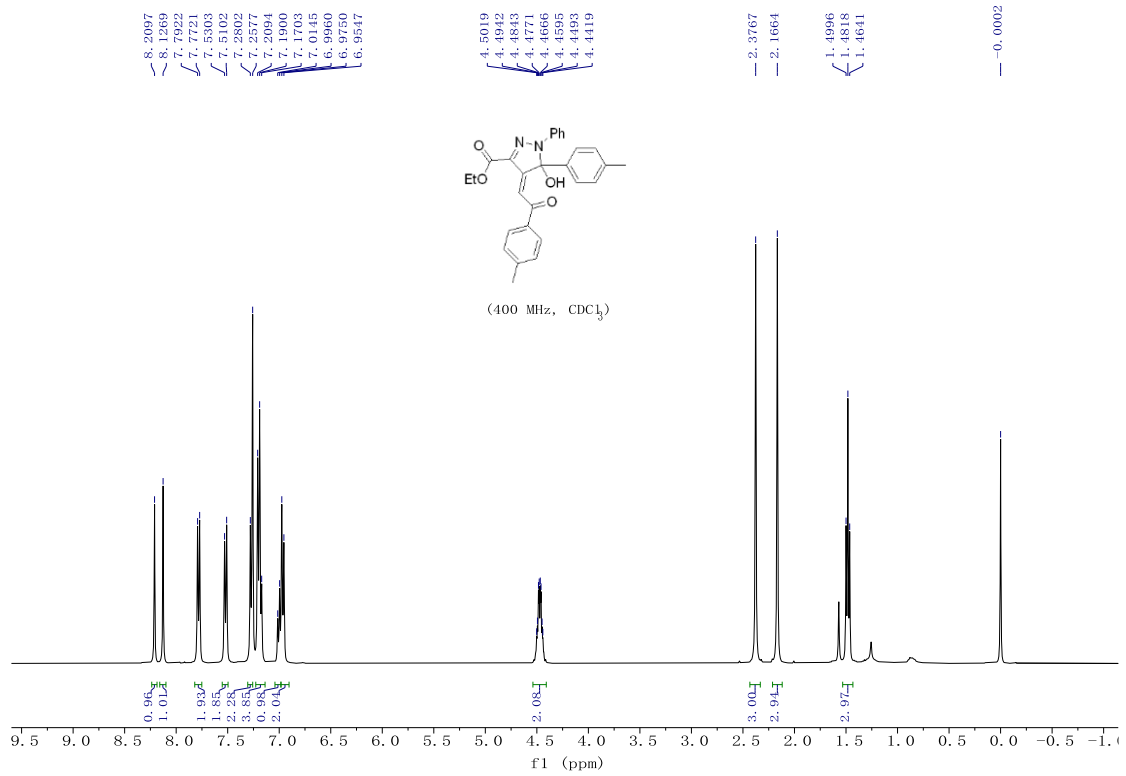
¹H NMR and ¹³C NMR spectrums of **3ba**



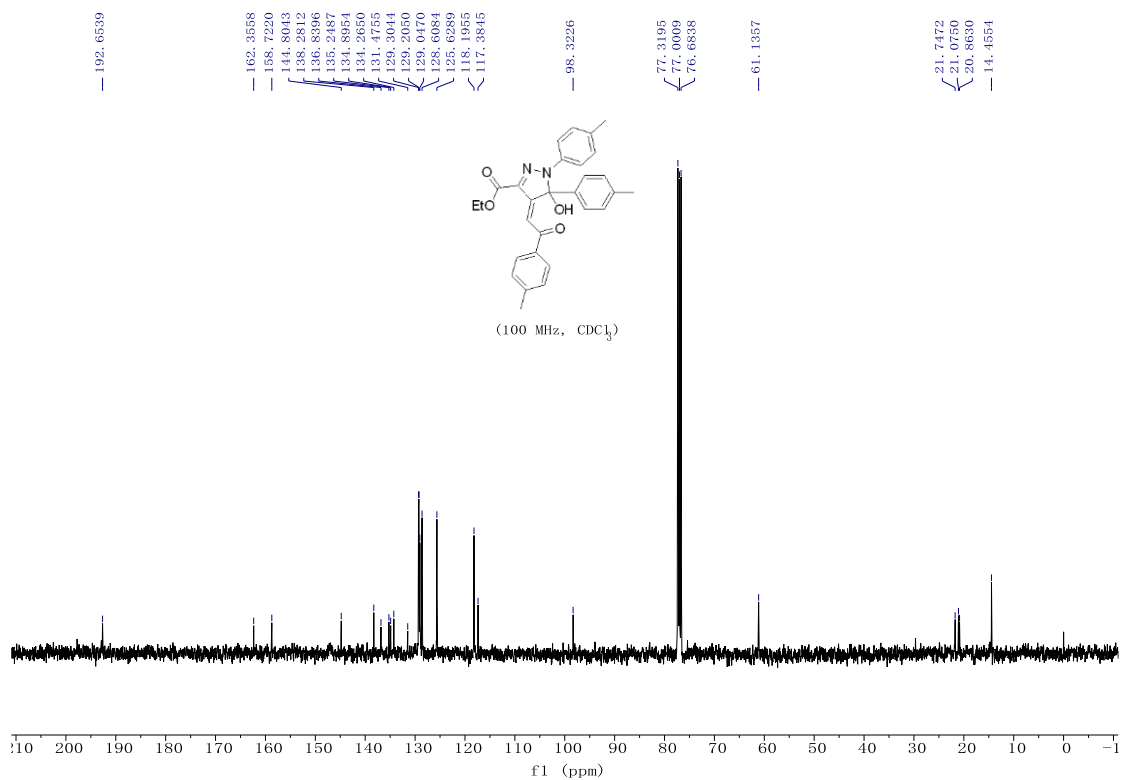
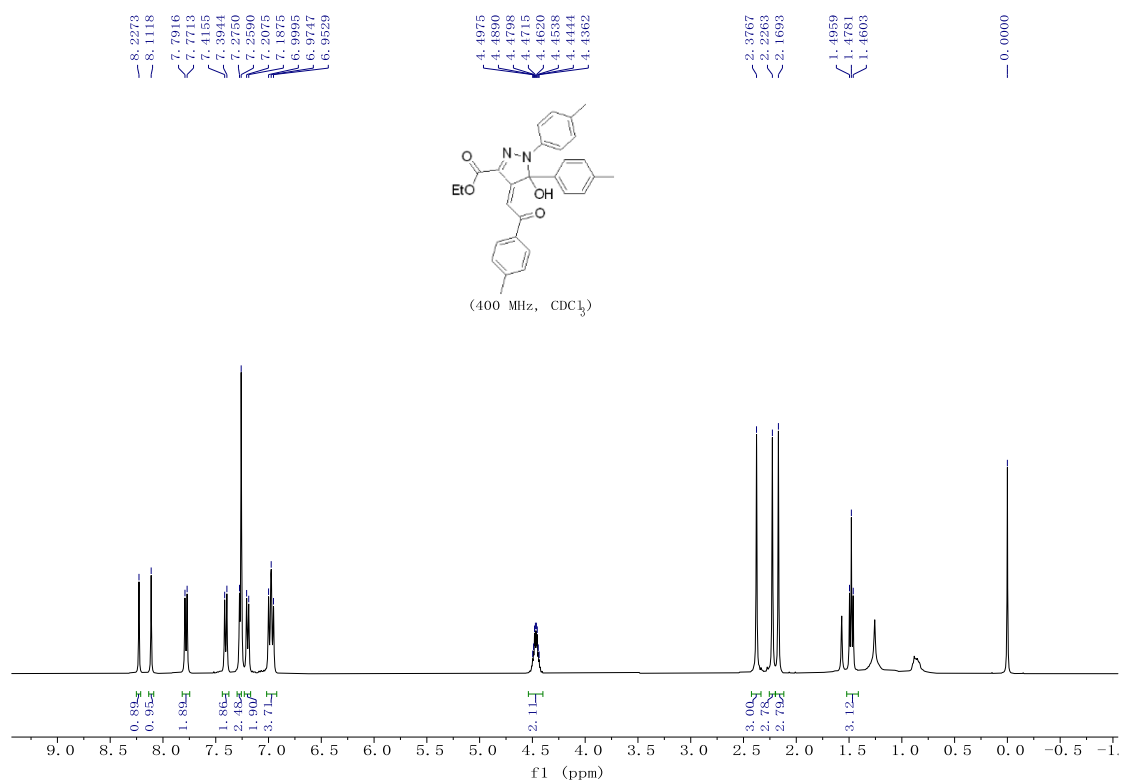
¹H NMR and ¹³C NMR spectrums of **3ca**



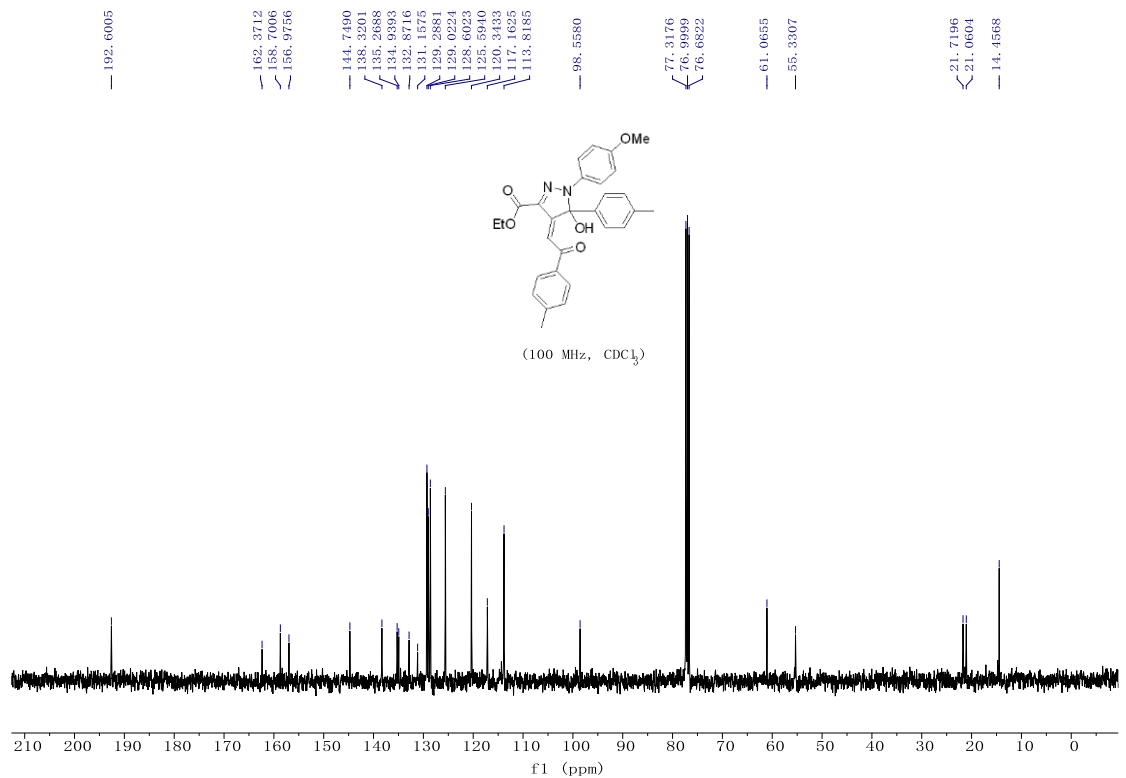
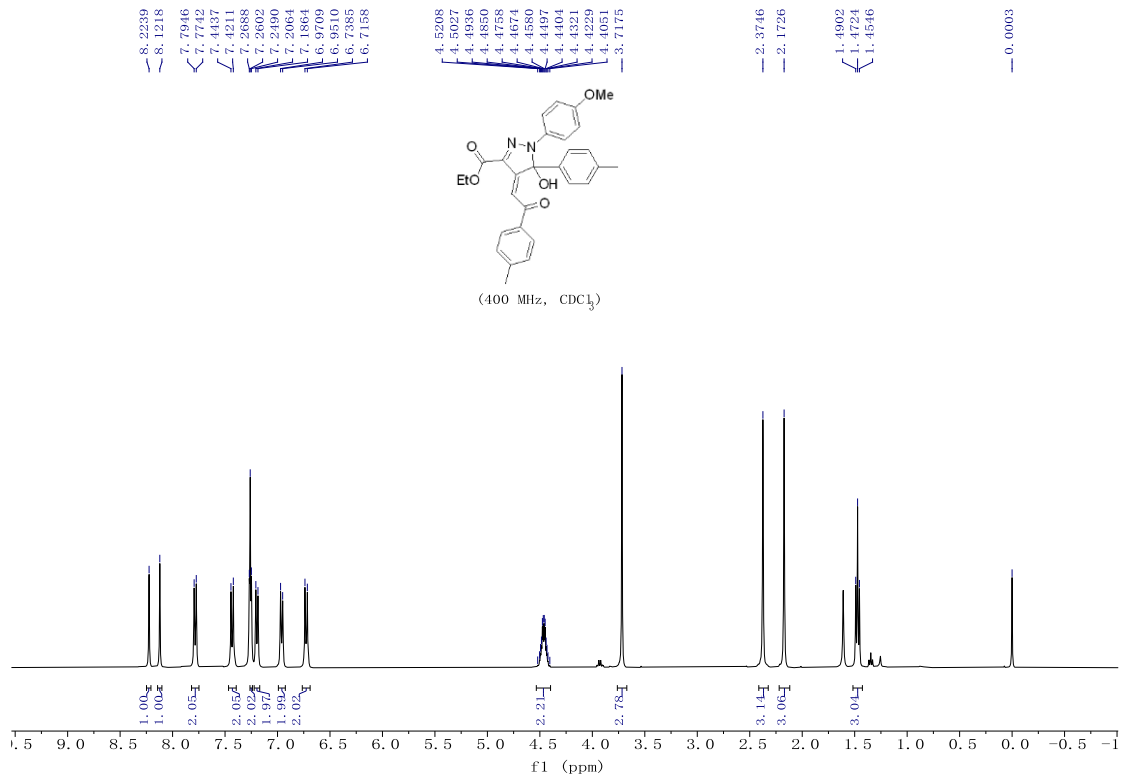
¹H NMR and ¹³C NMR spectrums of **3da**



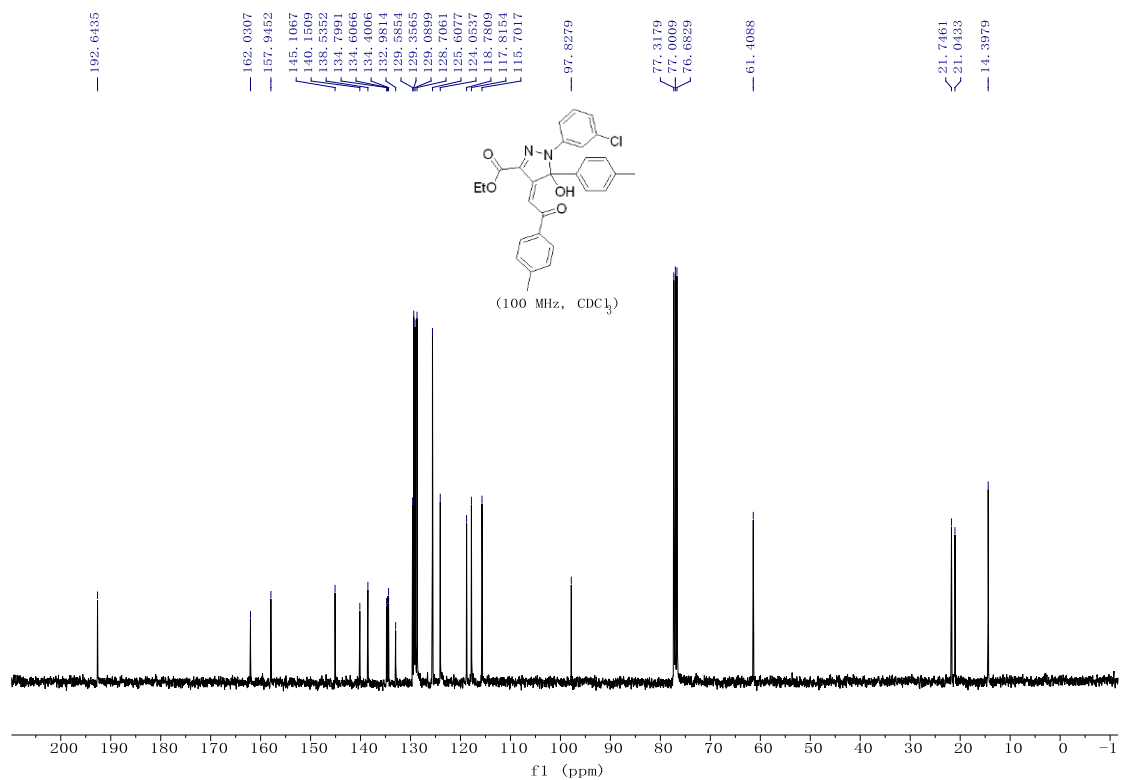
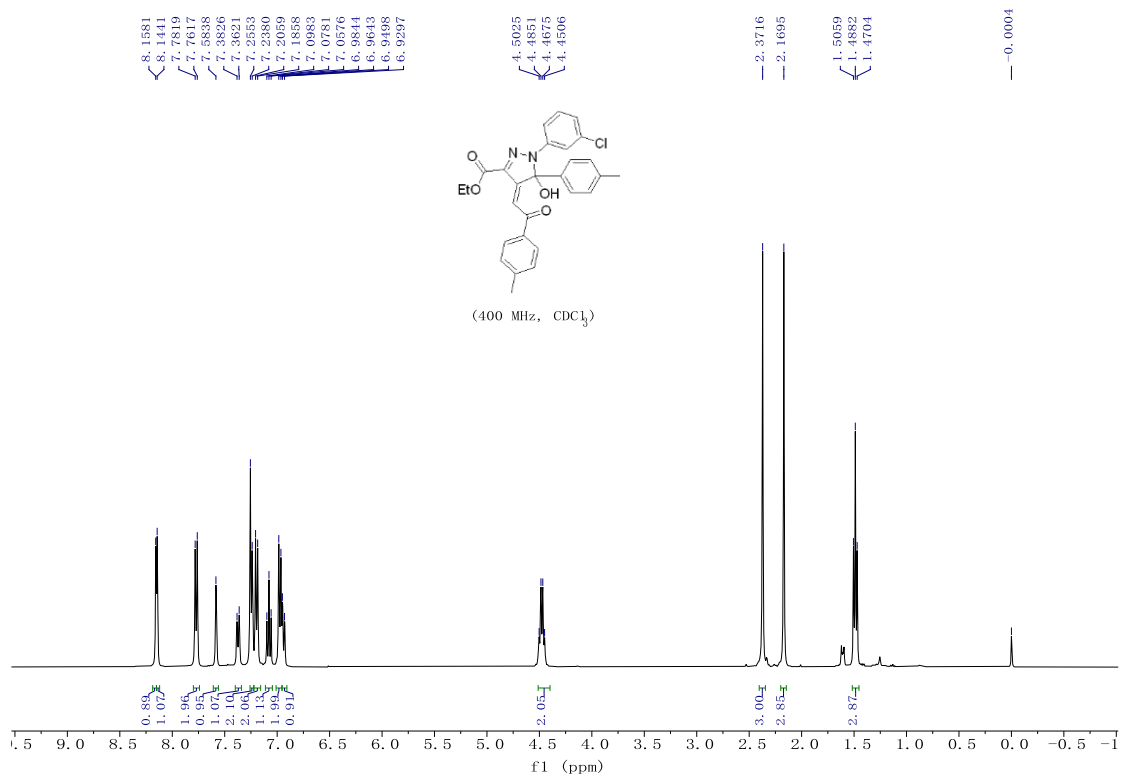
¹H NMR and ¹³C NMR spectrums of **3ea**



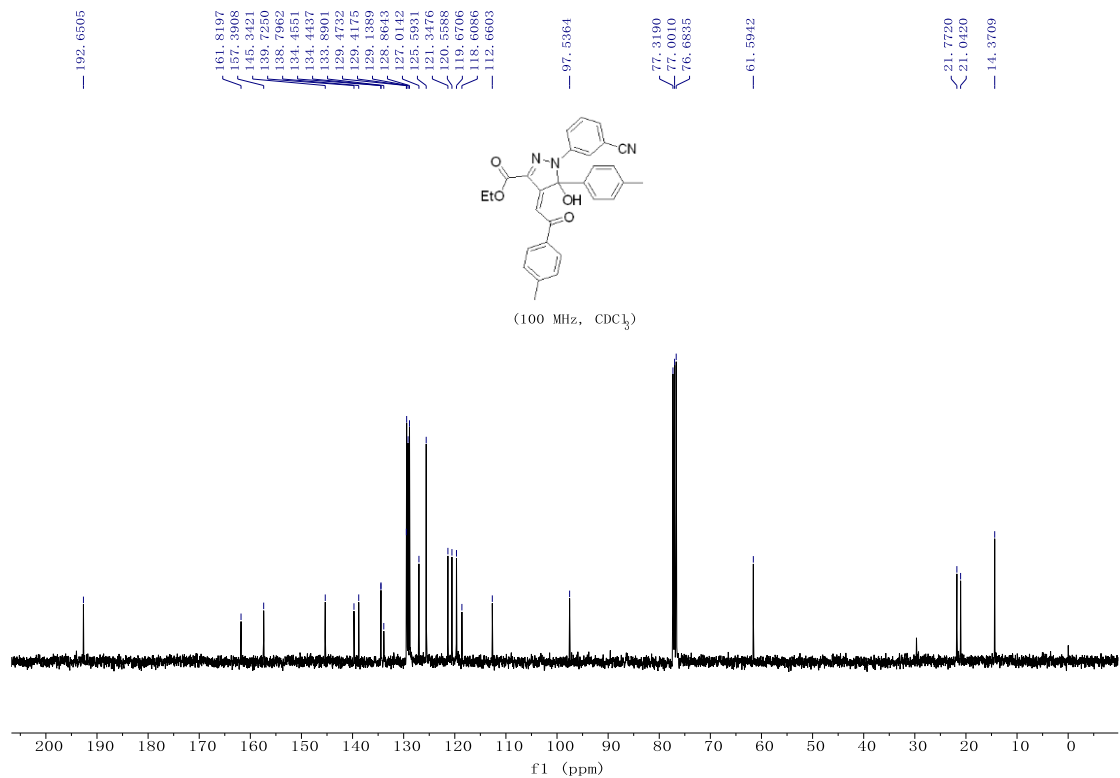
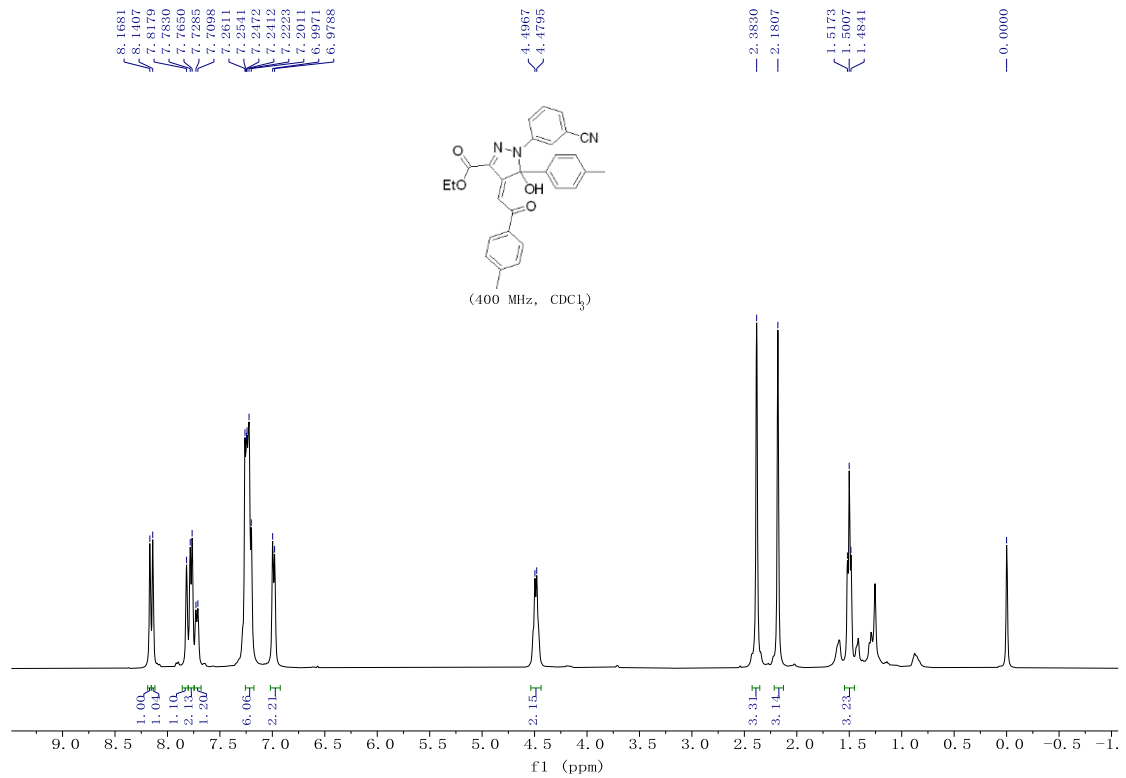
¹H NMR and ¹³C NMR spectra of **3fa**



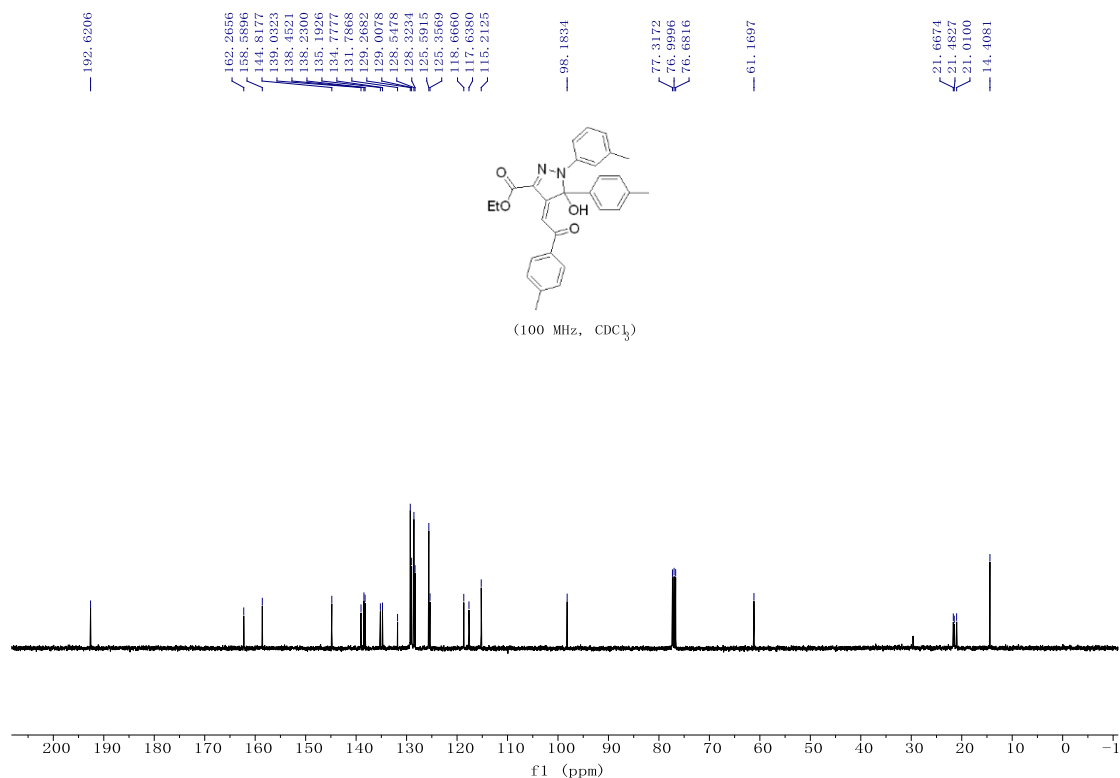
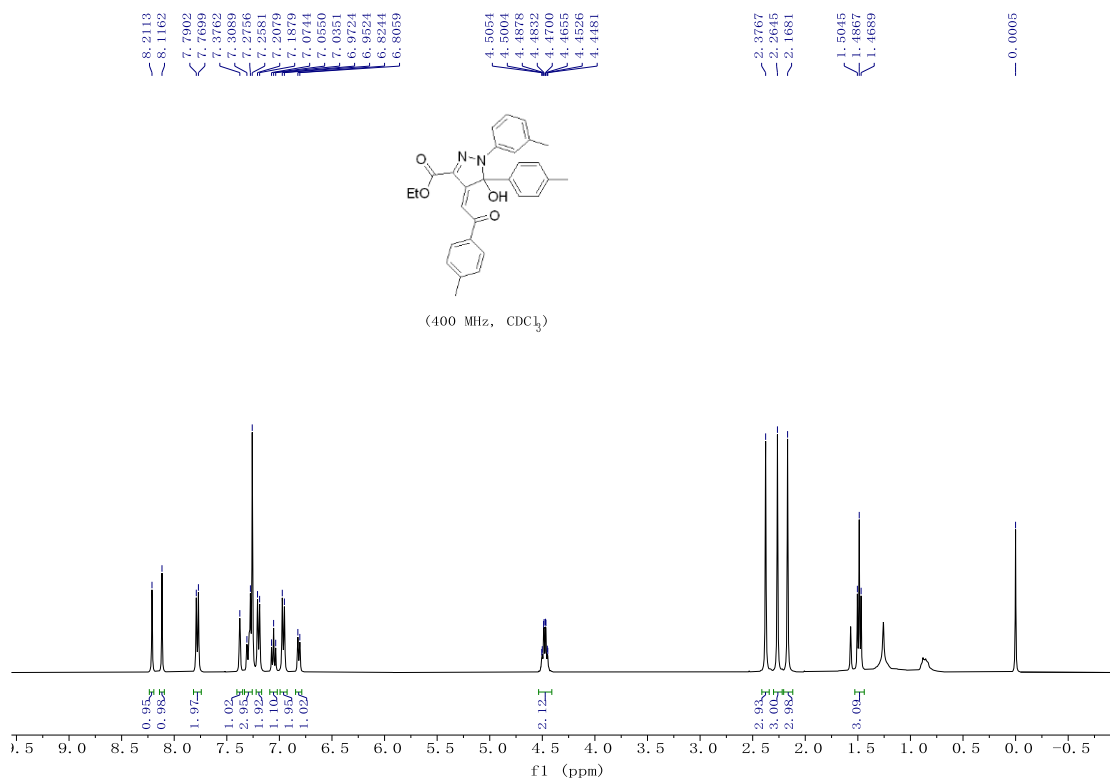
¹H NMR and ¹³C NMR spectrums of **3ga**



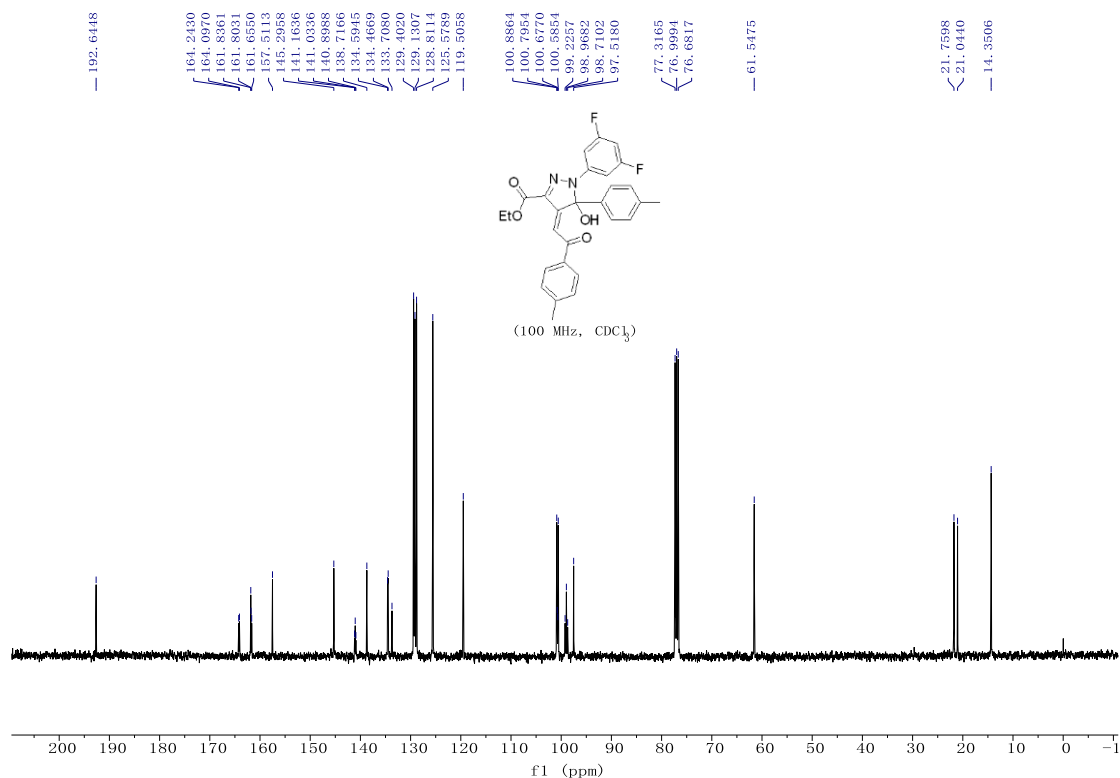
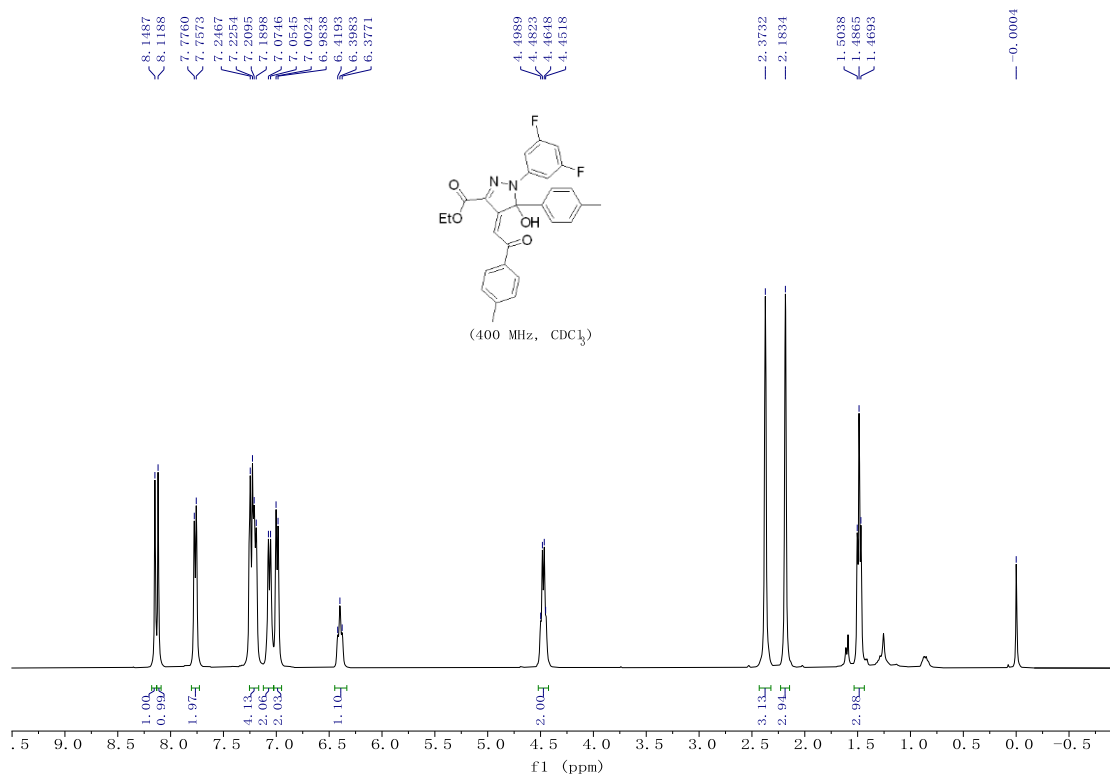
¹H NMR and ¹³C NMR spectrums of **3ha**



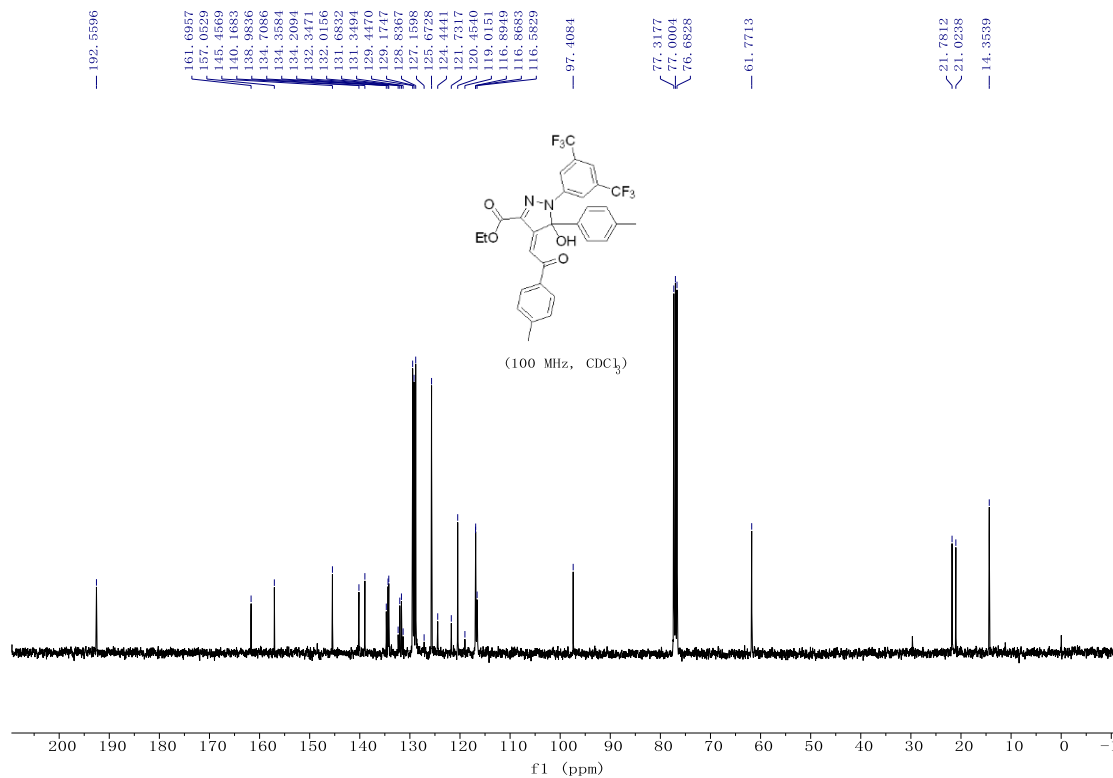
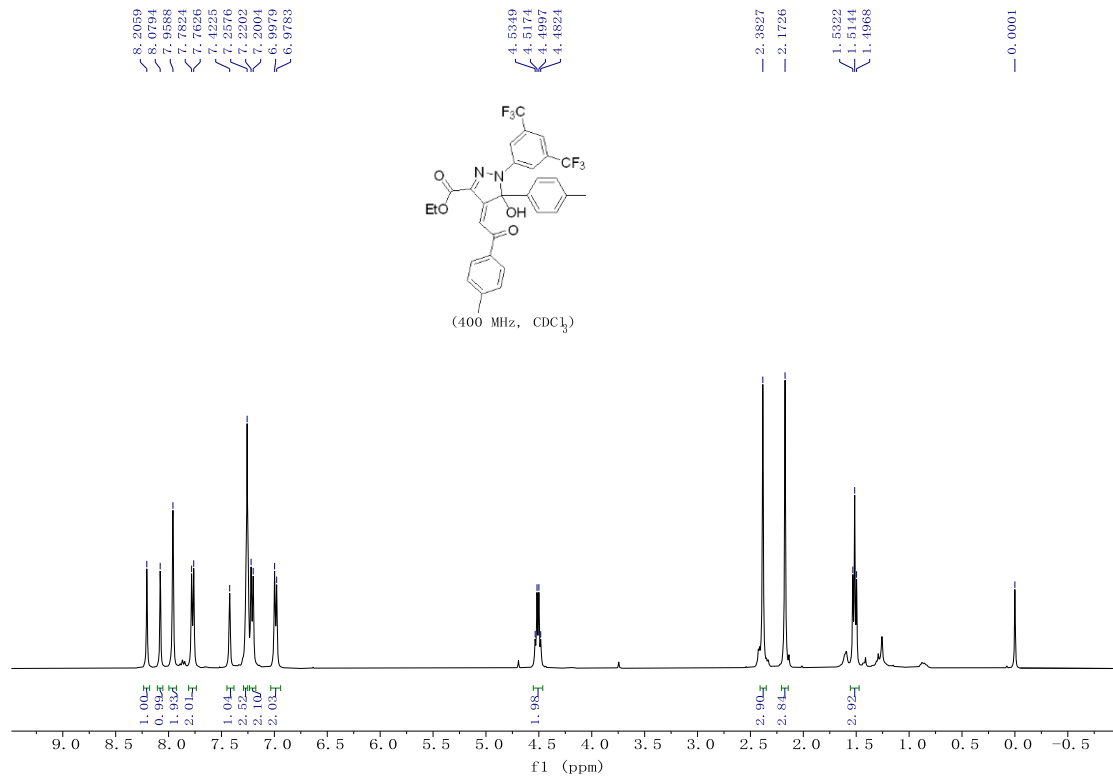
¹H NMR and ¹³C NMR spectra of **3ia**



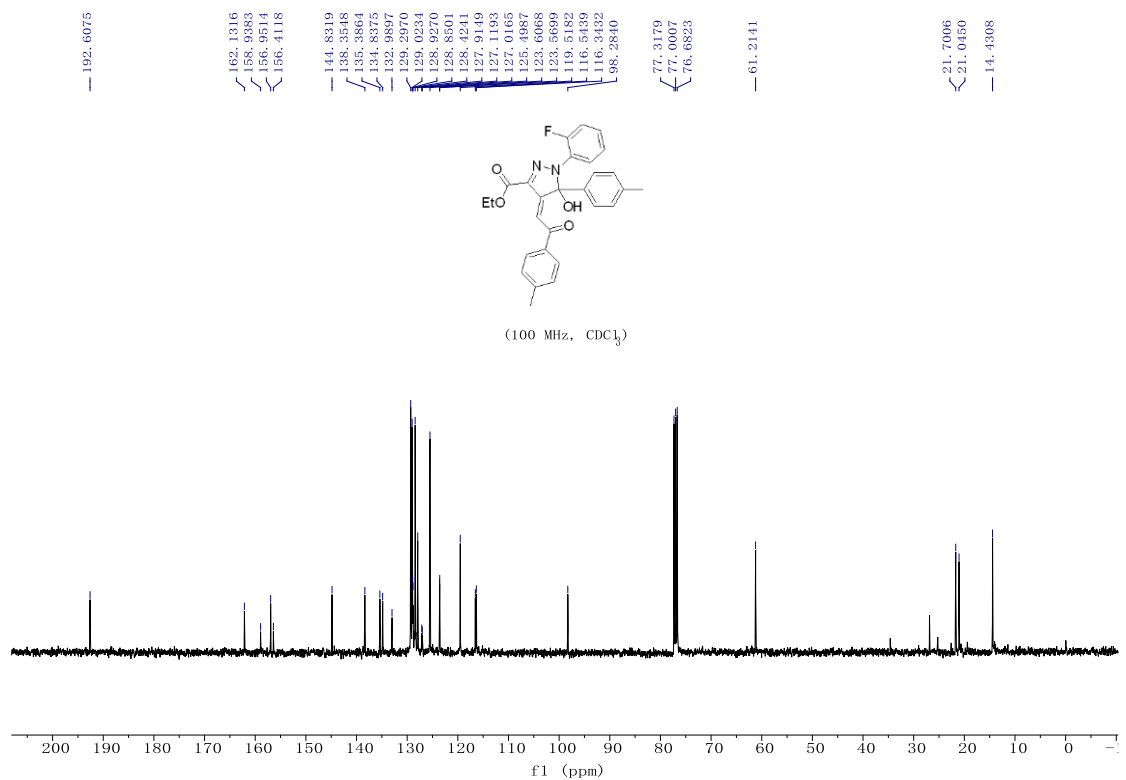
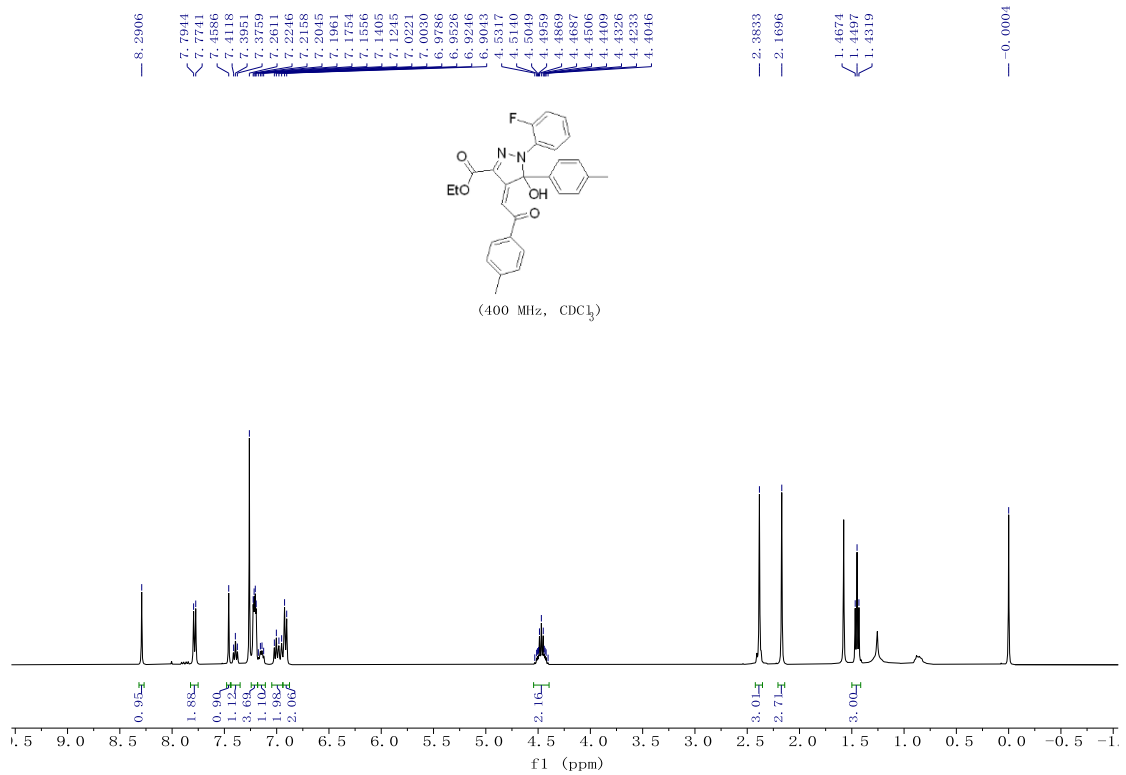
¹H NMR and ¹³C NMR spectra of **3ja**



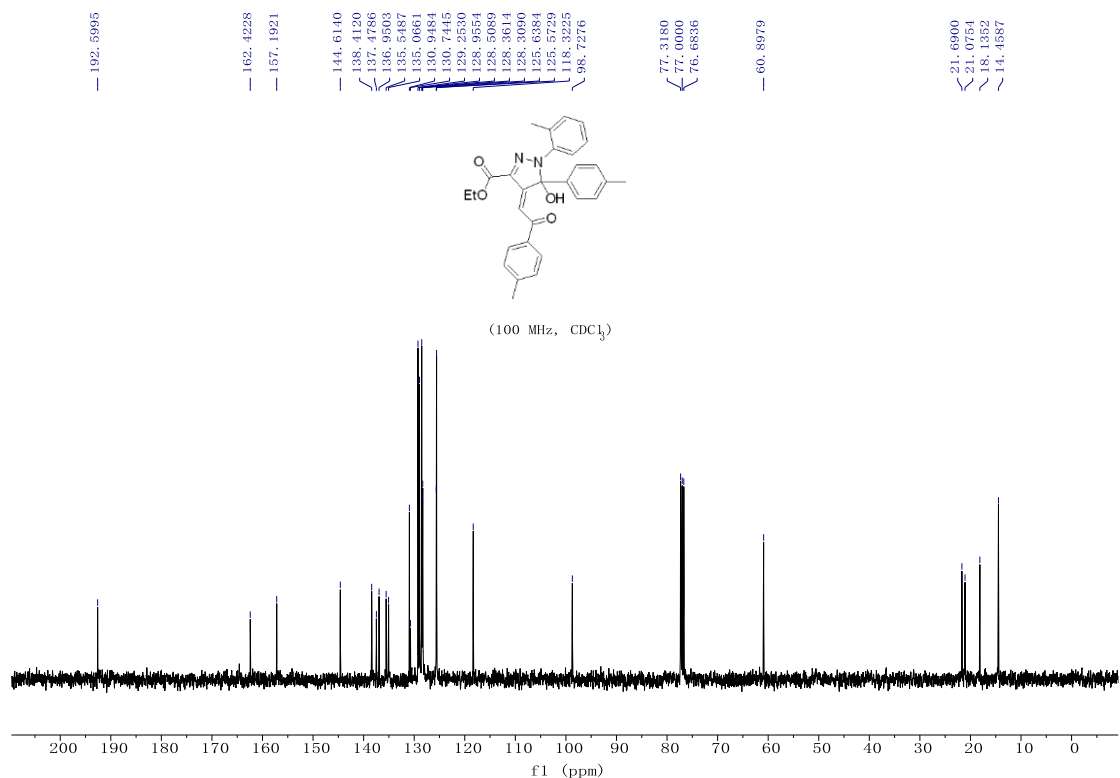
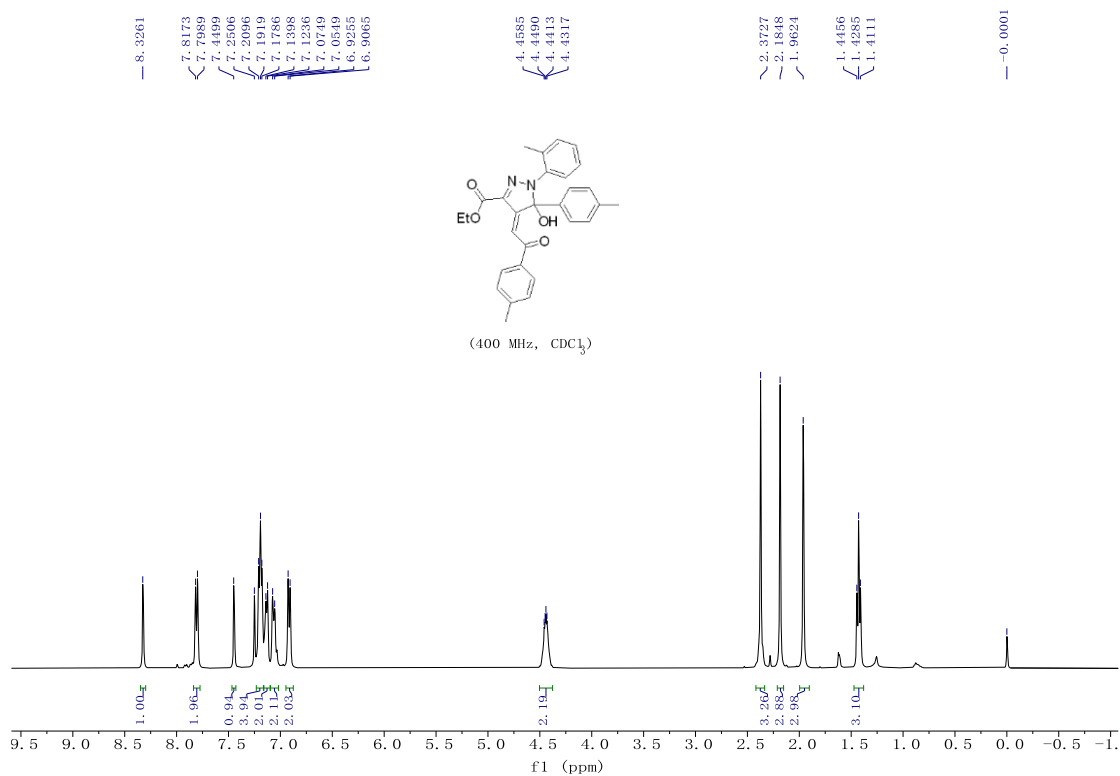
¹H NMR and ¹³C NMR spectrums of **3ka**



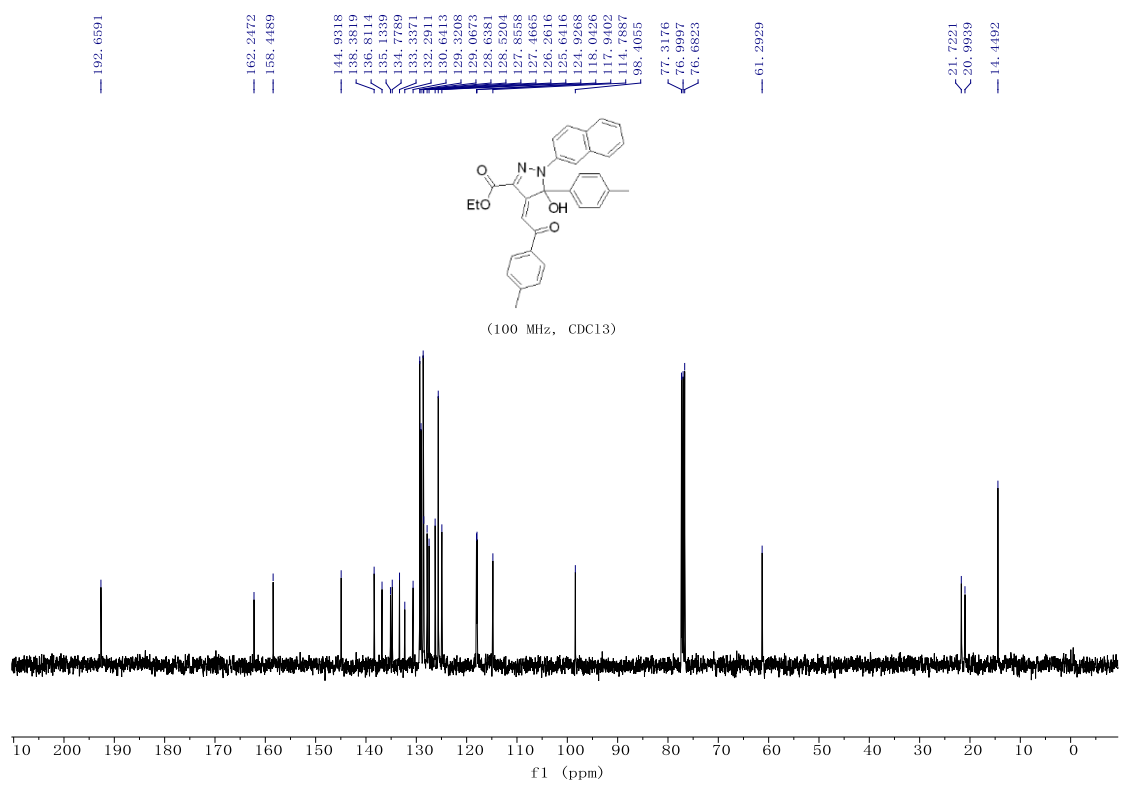
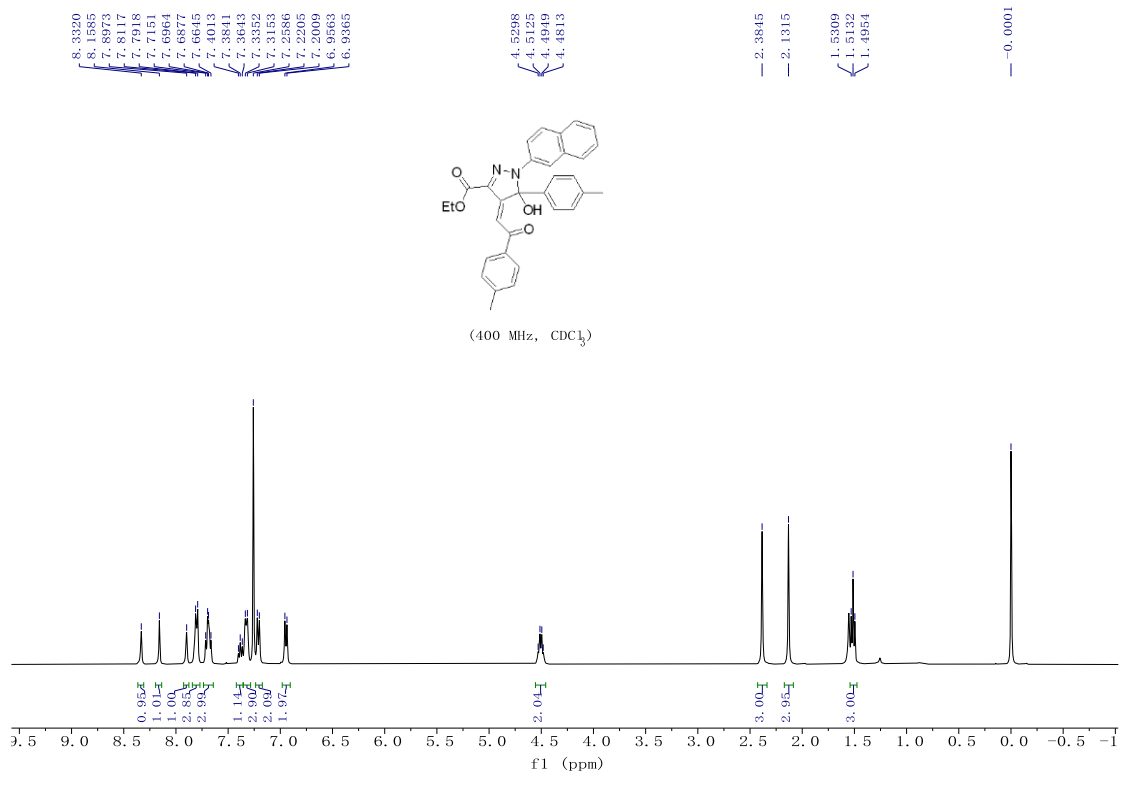
^1H NMR and ^{13}C NMR spectra of **31a**



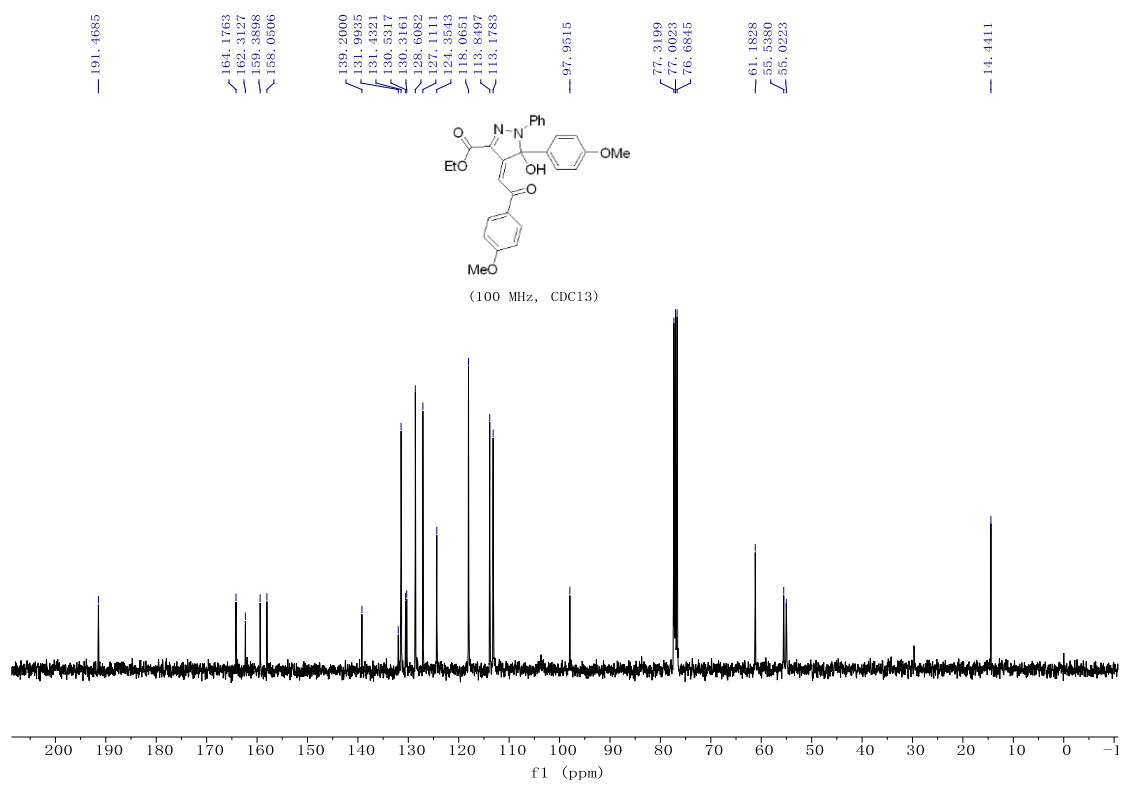
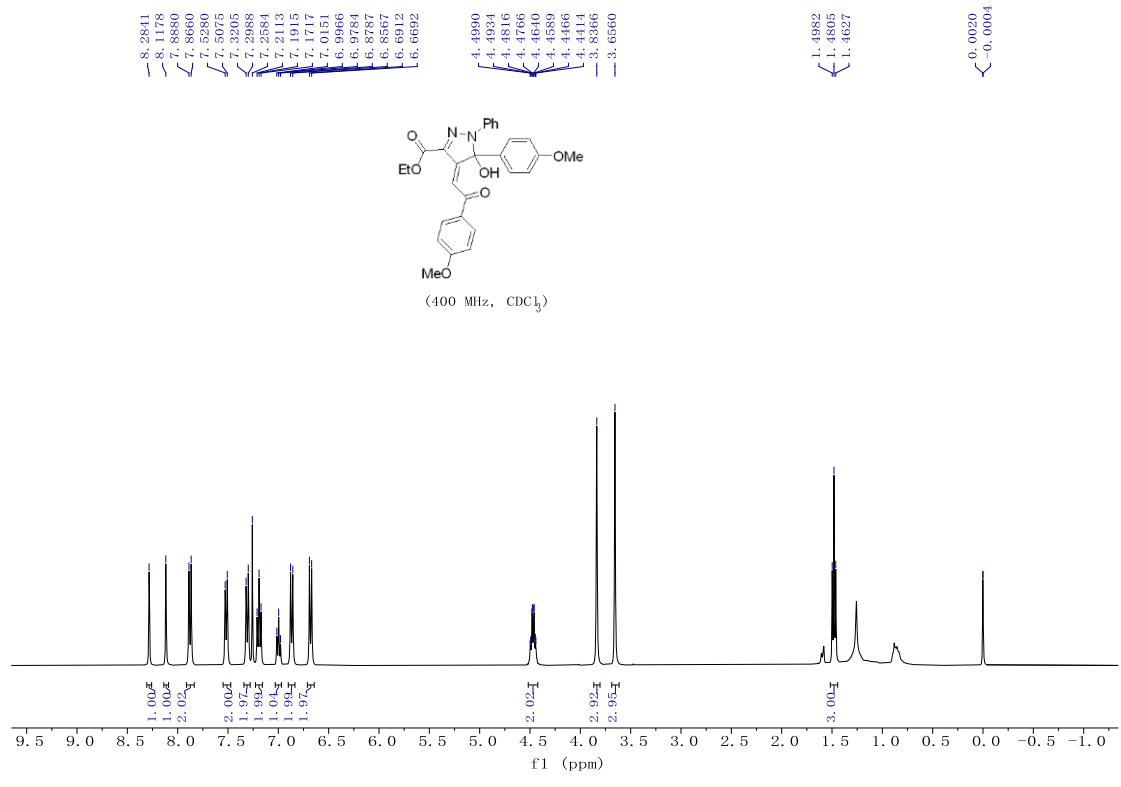
¹H NMR and ¹³C NMR spectrums of **3ma**



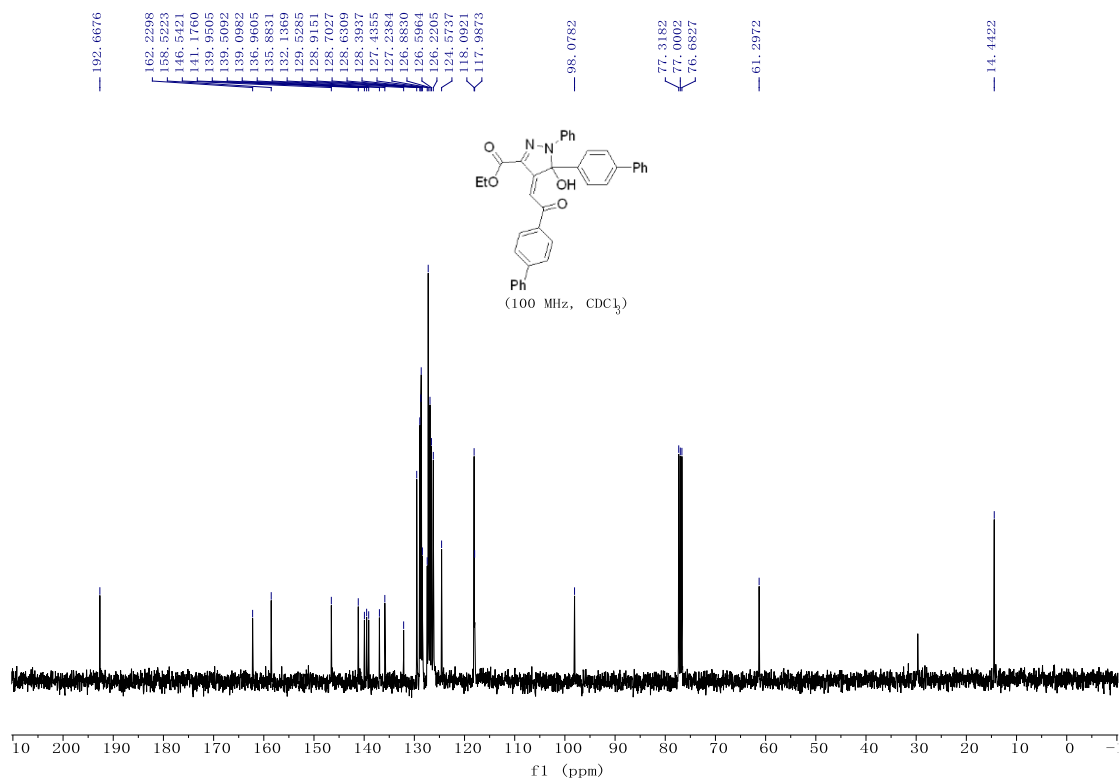
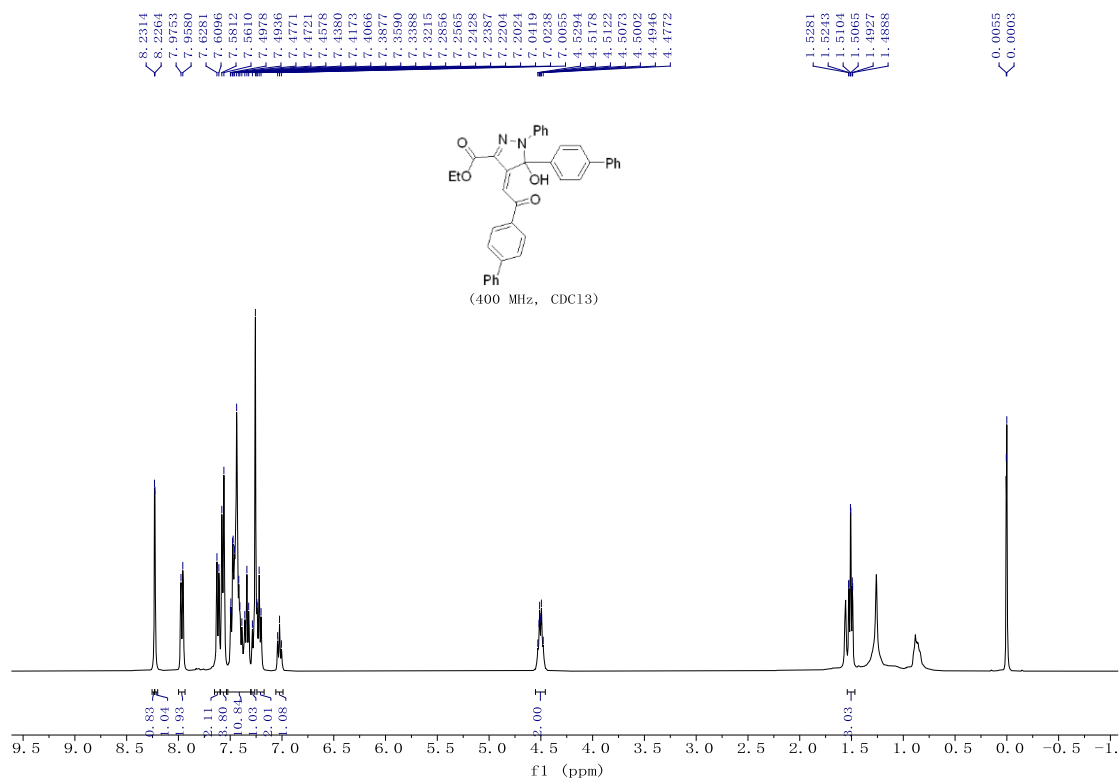
¹H NMR and ¹³C NMR spectrums of **3na**



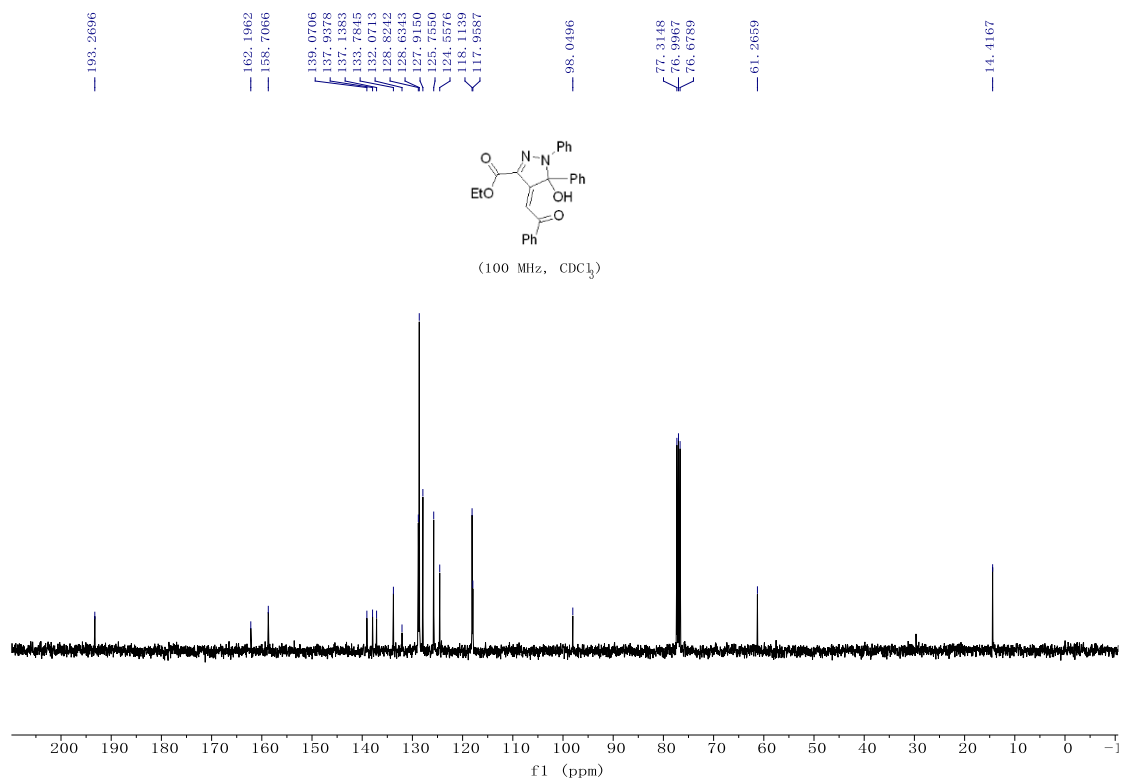
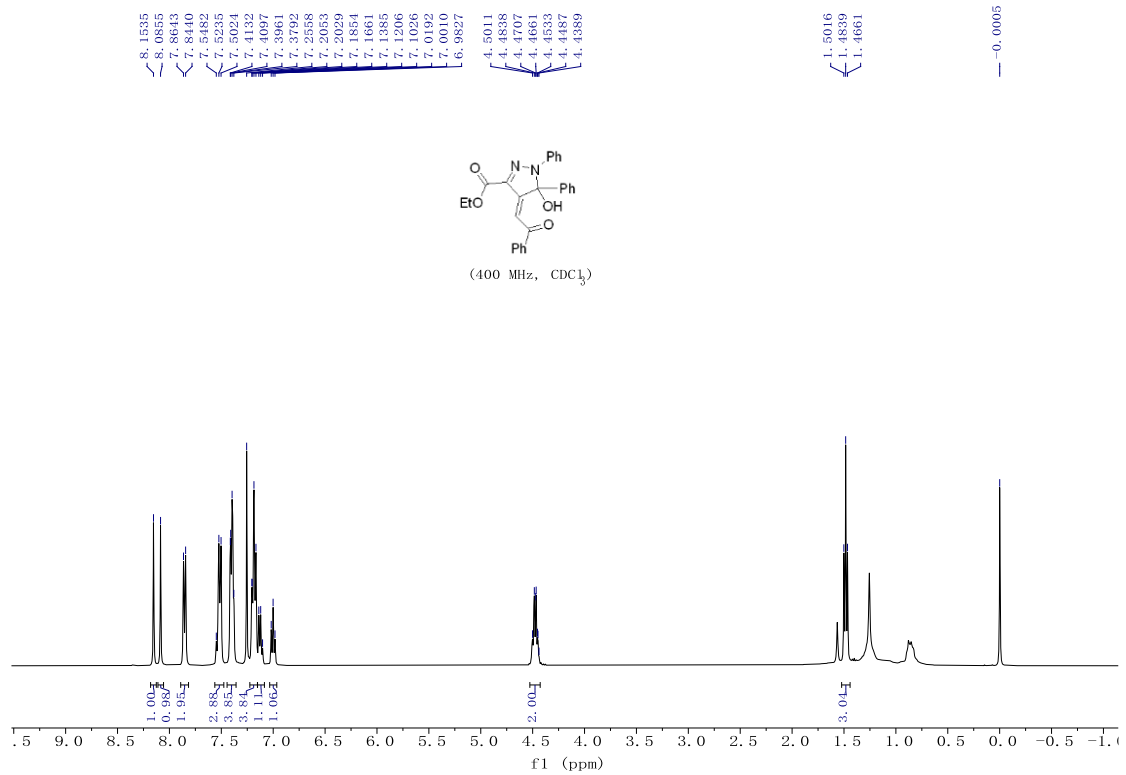
¹H NMR and ¹³C NMR spectrums of **3db**



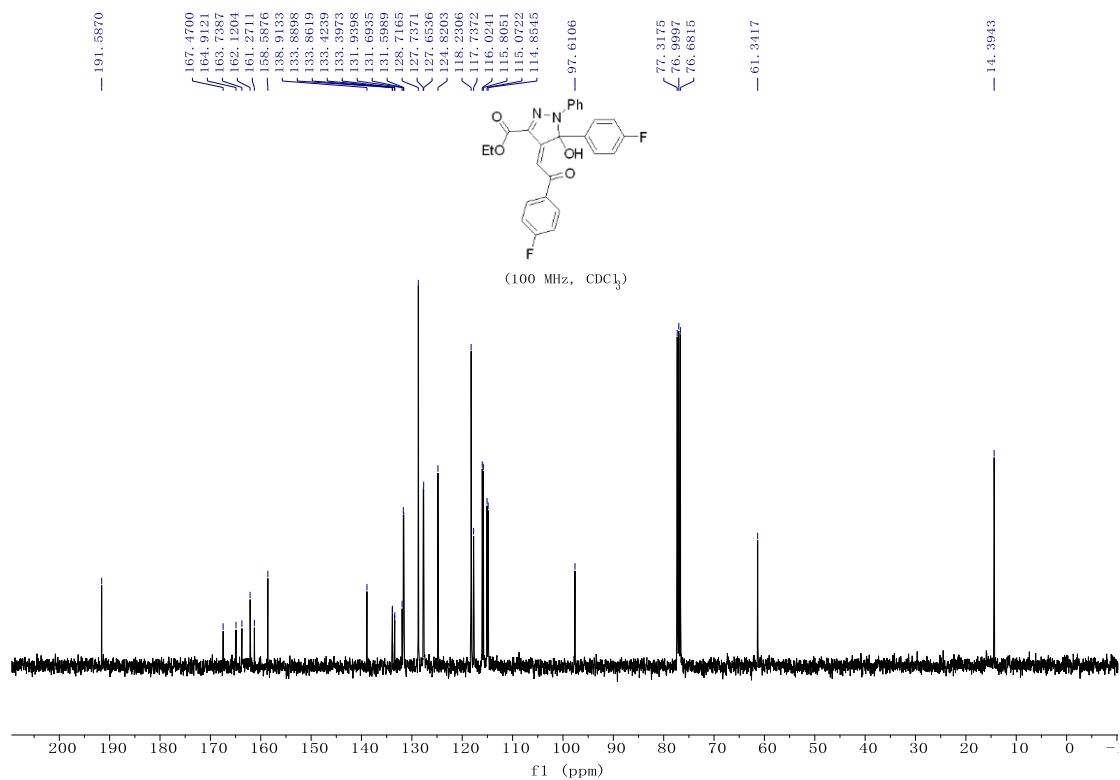
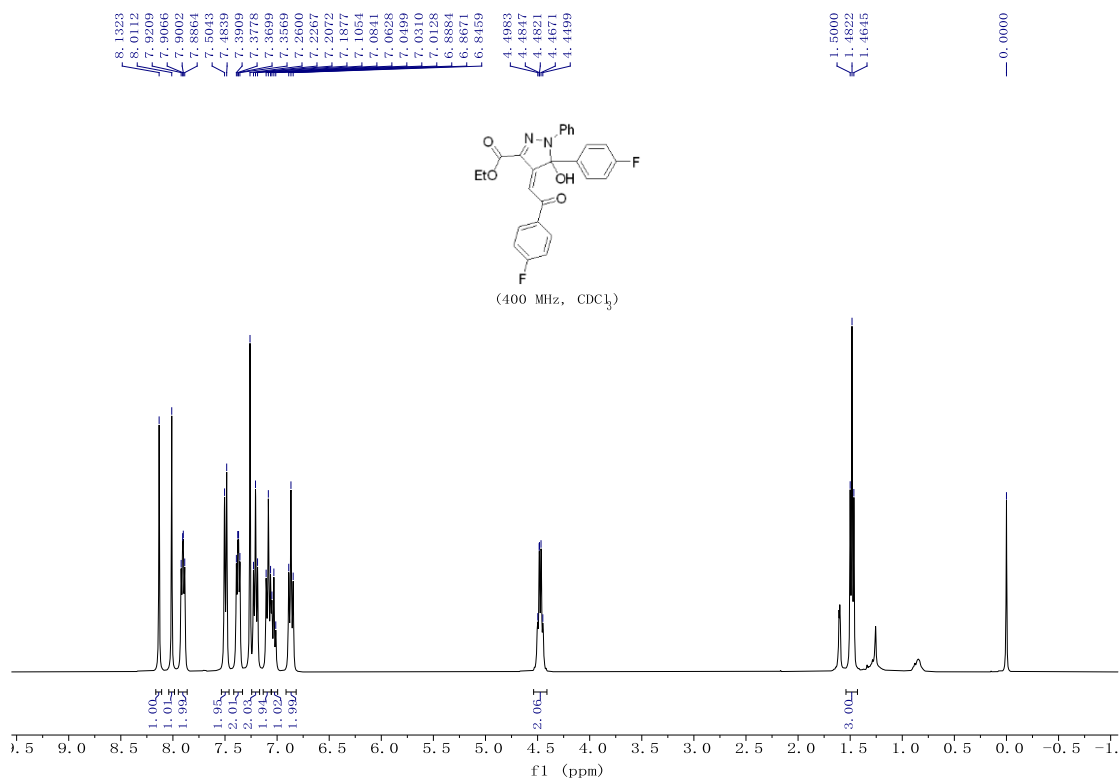
¹H NMR and ¹³C NMR spectra of 3dc



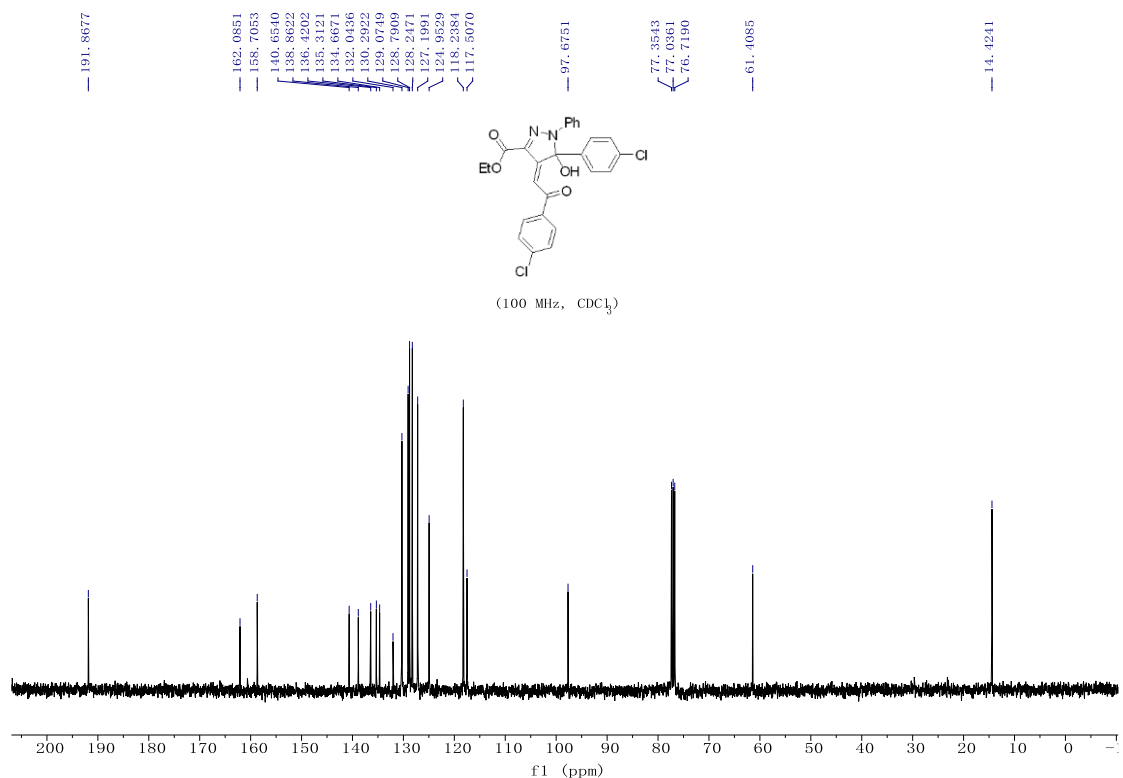
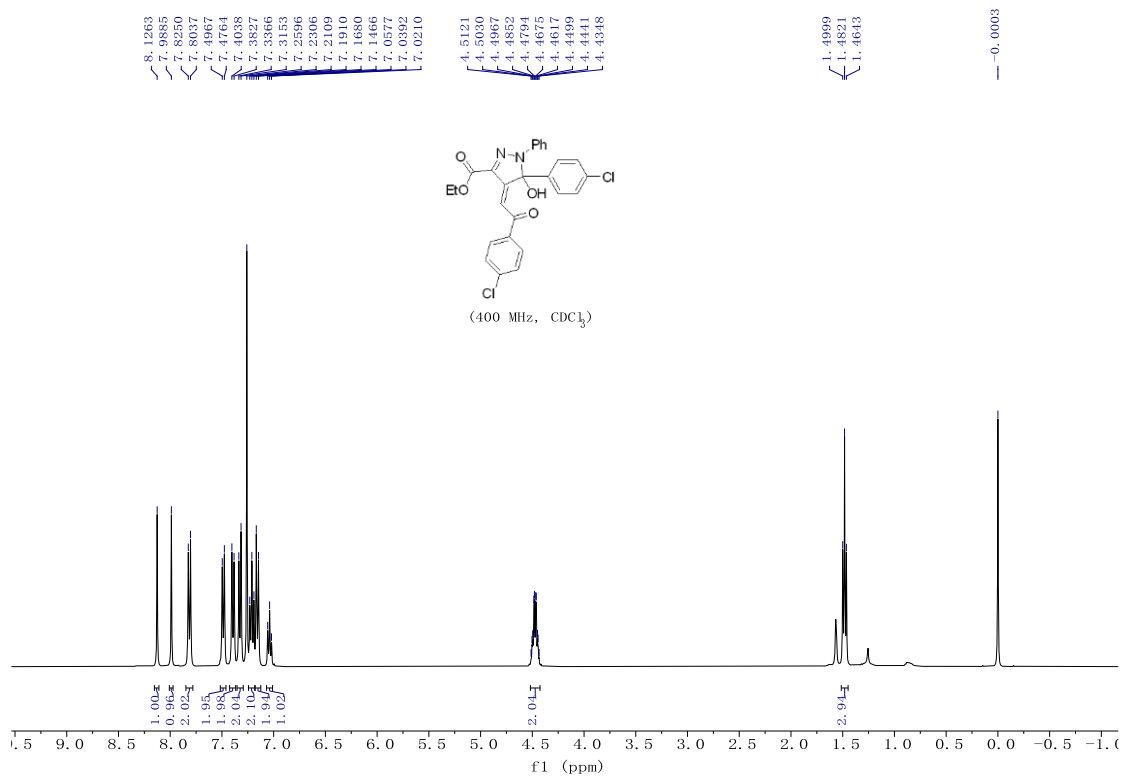
¹H NMR and ¹³C NMR spectra of **3dd**



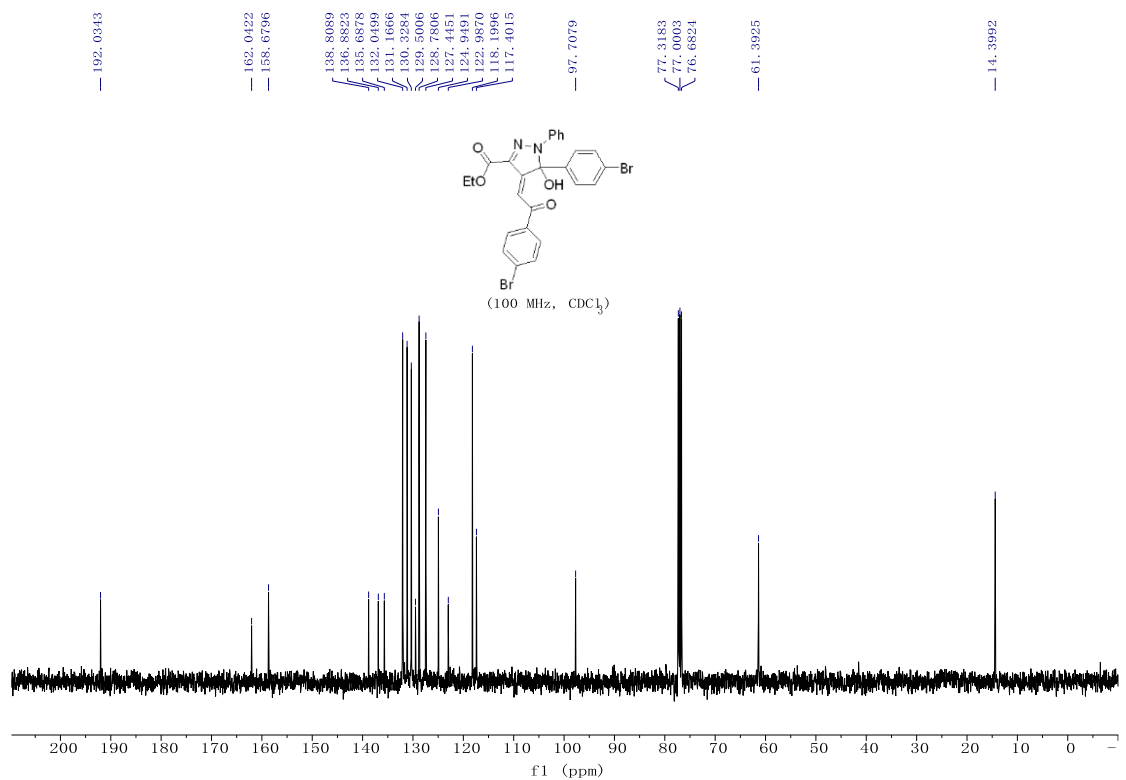
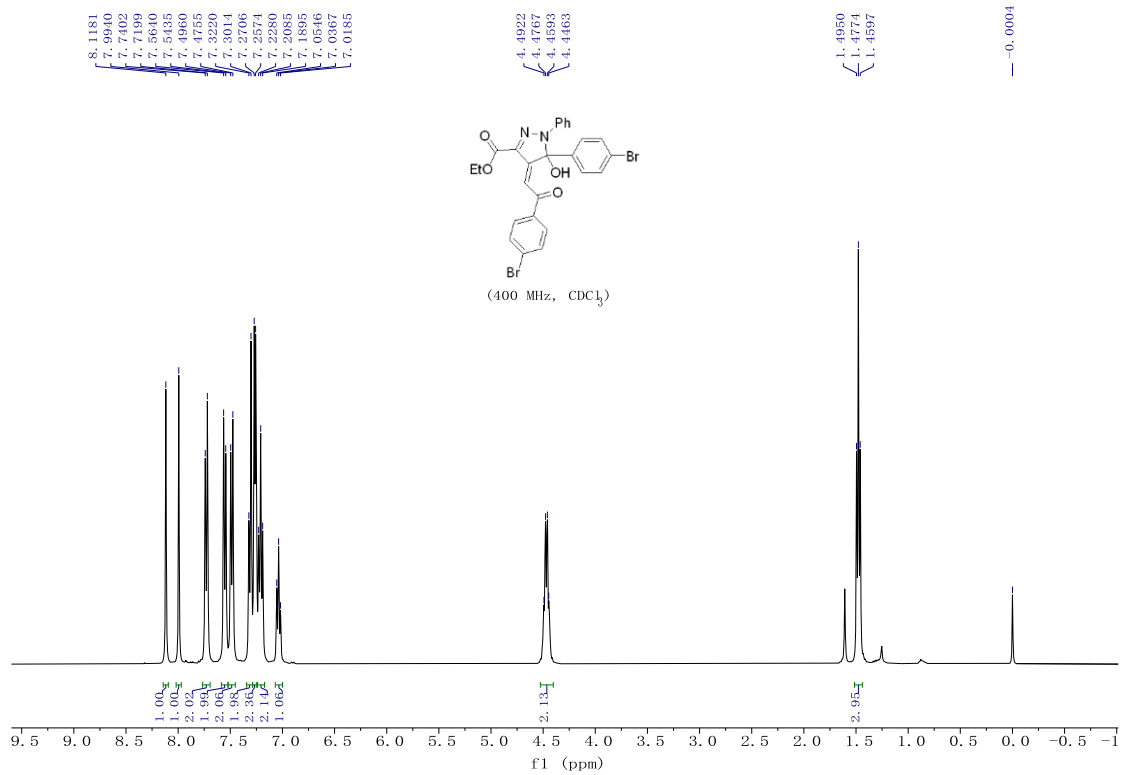
¹H NMR and ¹³C NMR spectrums of **3de**



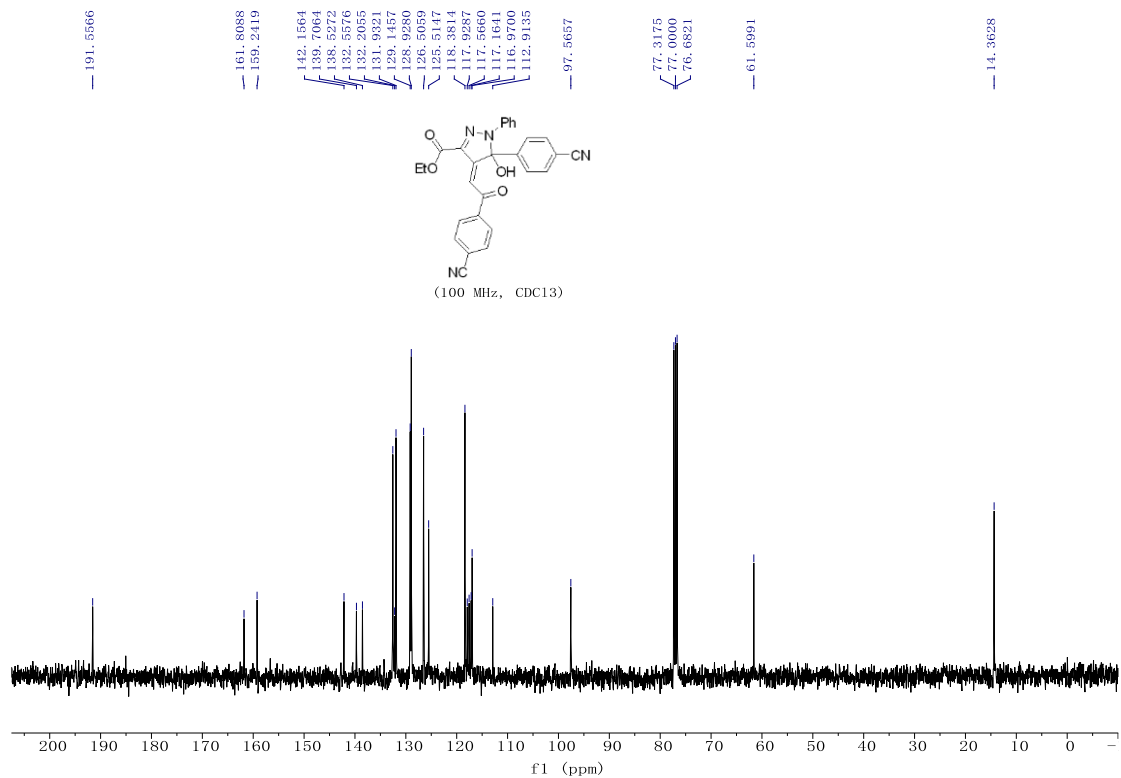
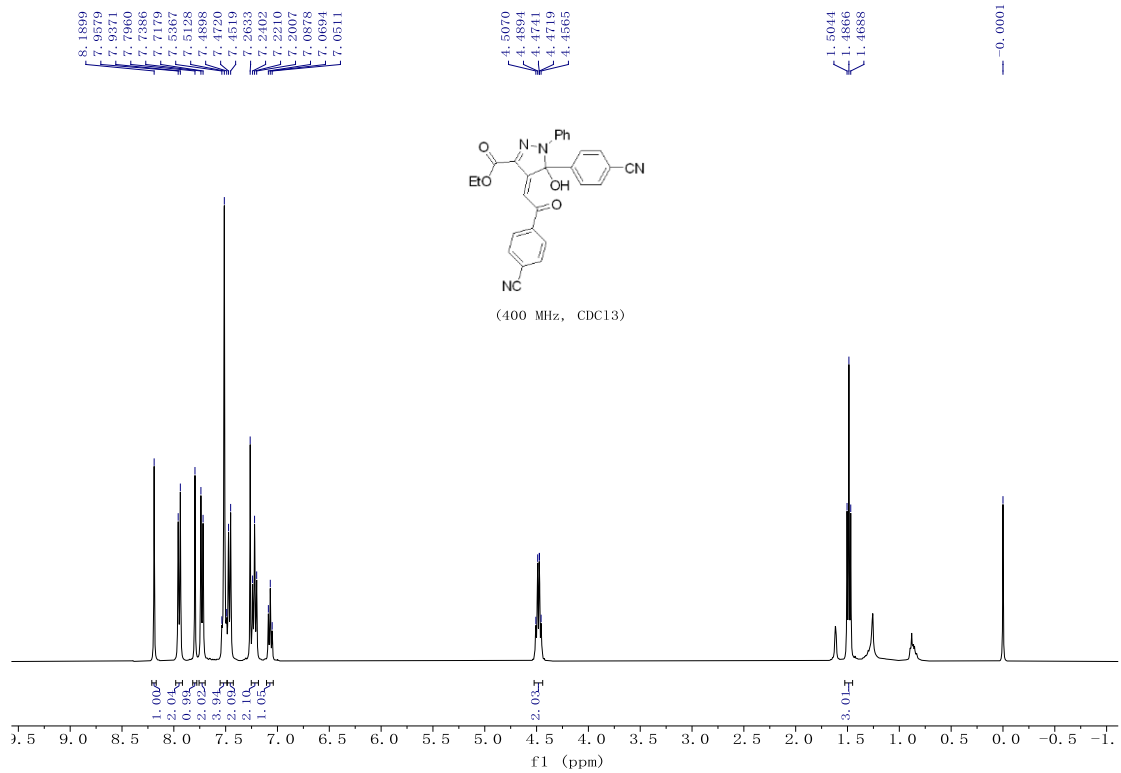
¹H NMR and ¹³C NMR spectra of **3df**



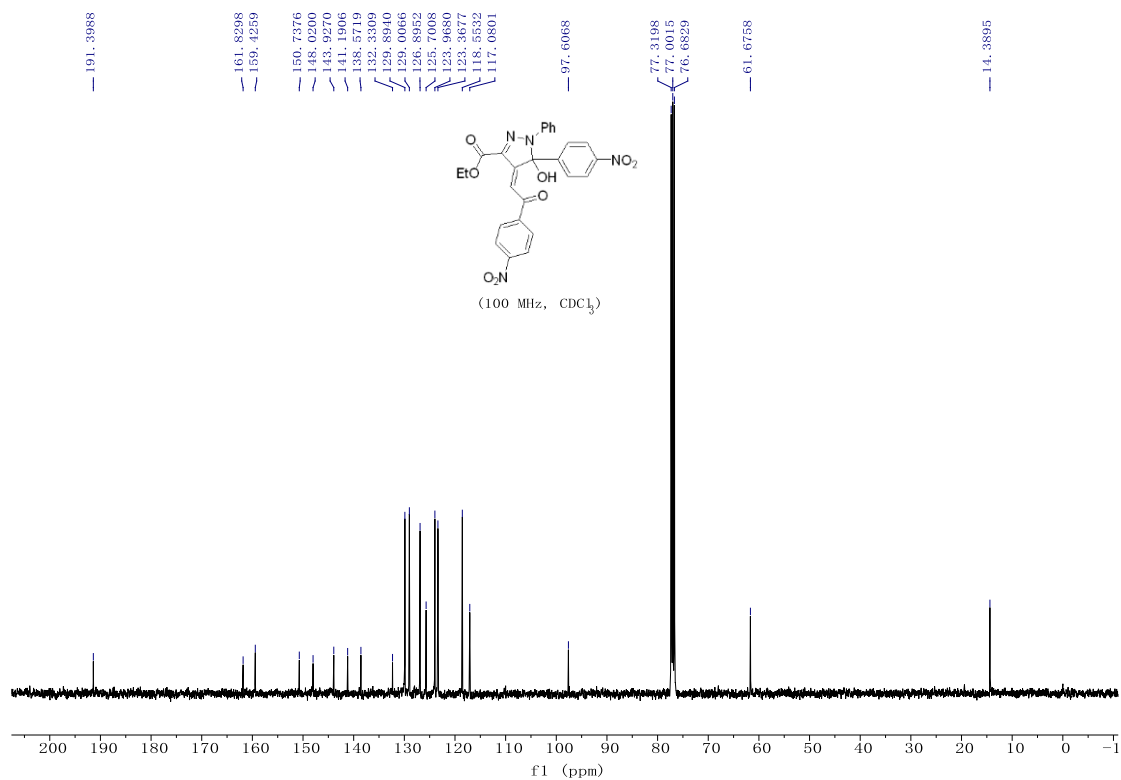
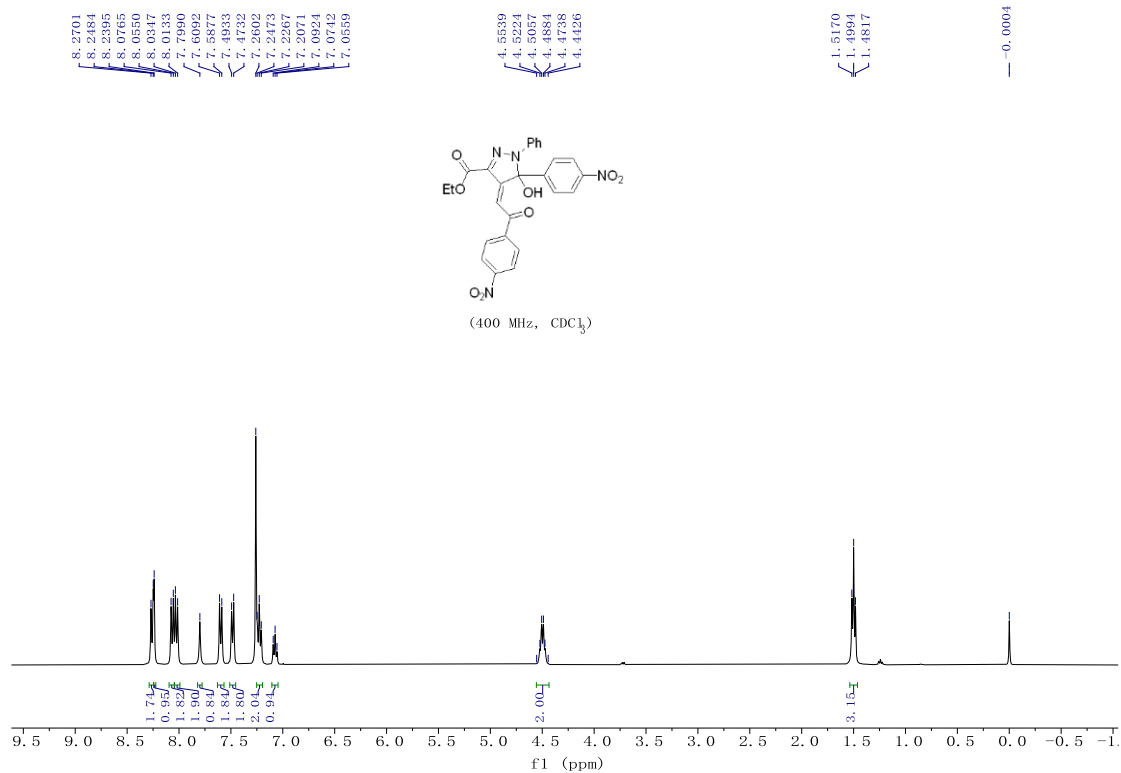
¹H NMR and ¹³C NMR spectrums of **3dg**



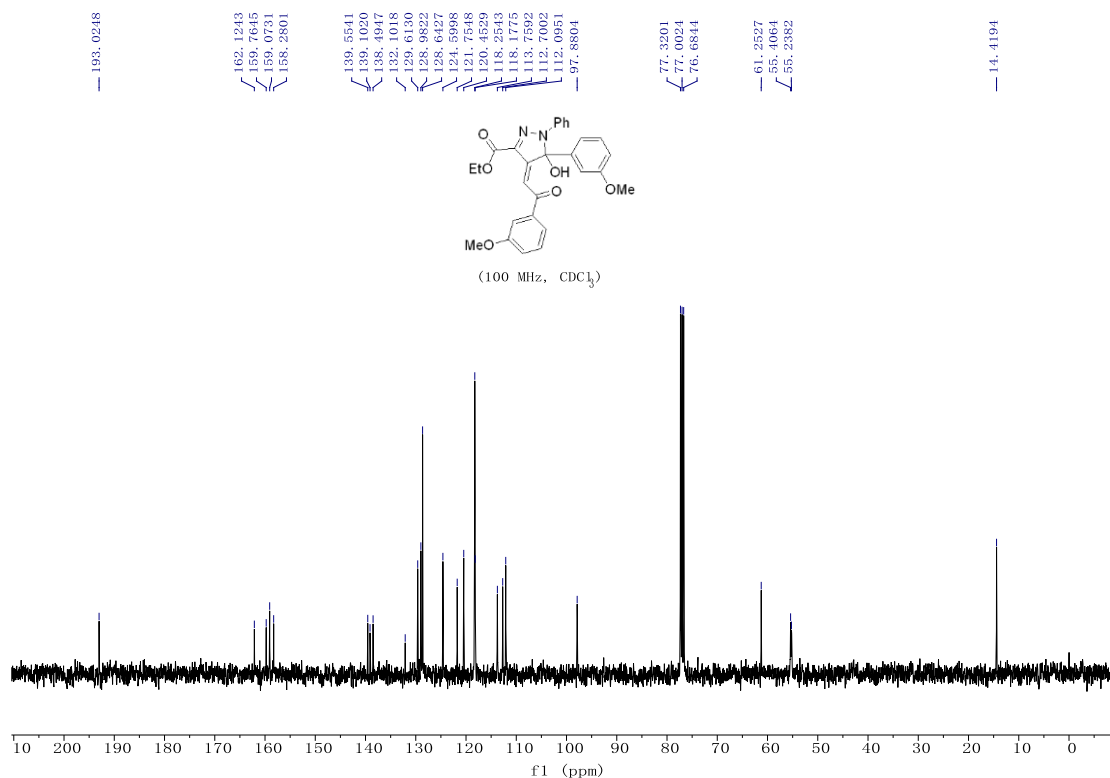
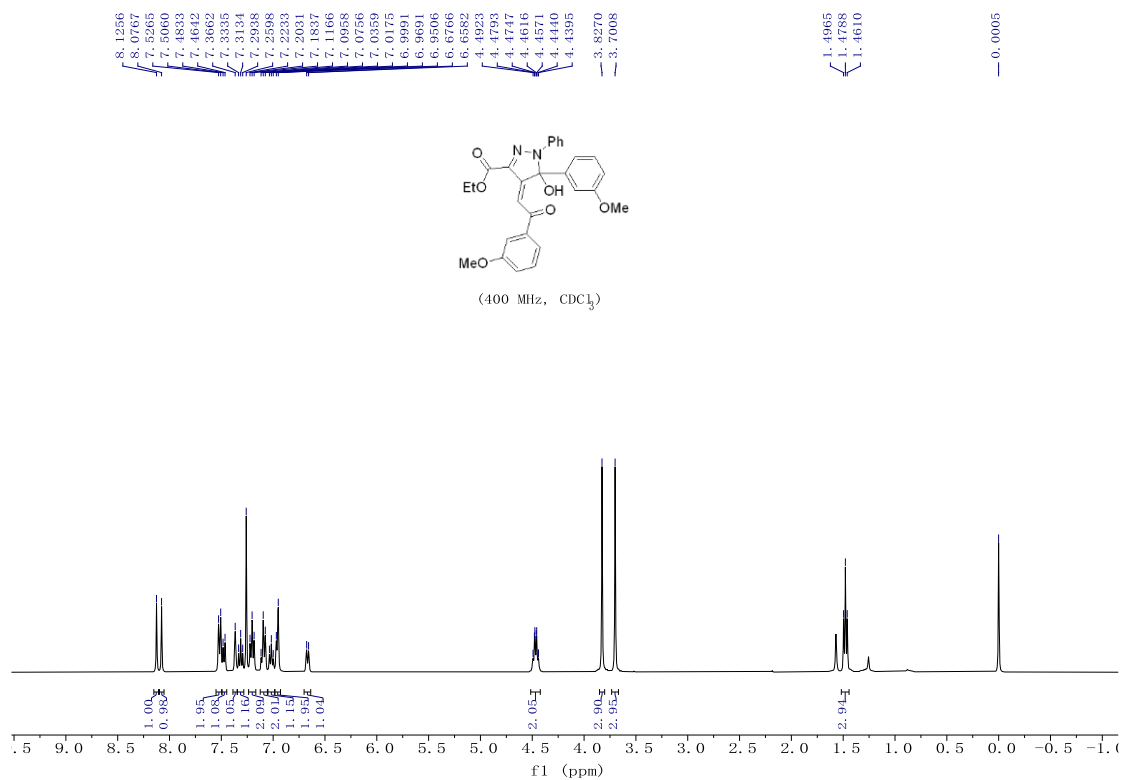
¹H NMR and ¹³C NMR spectrums of **3dh**



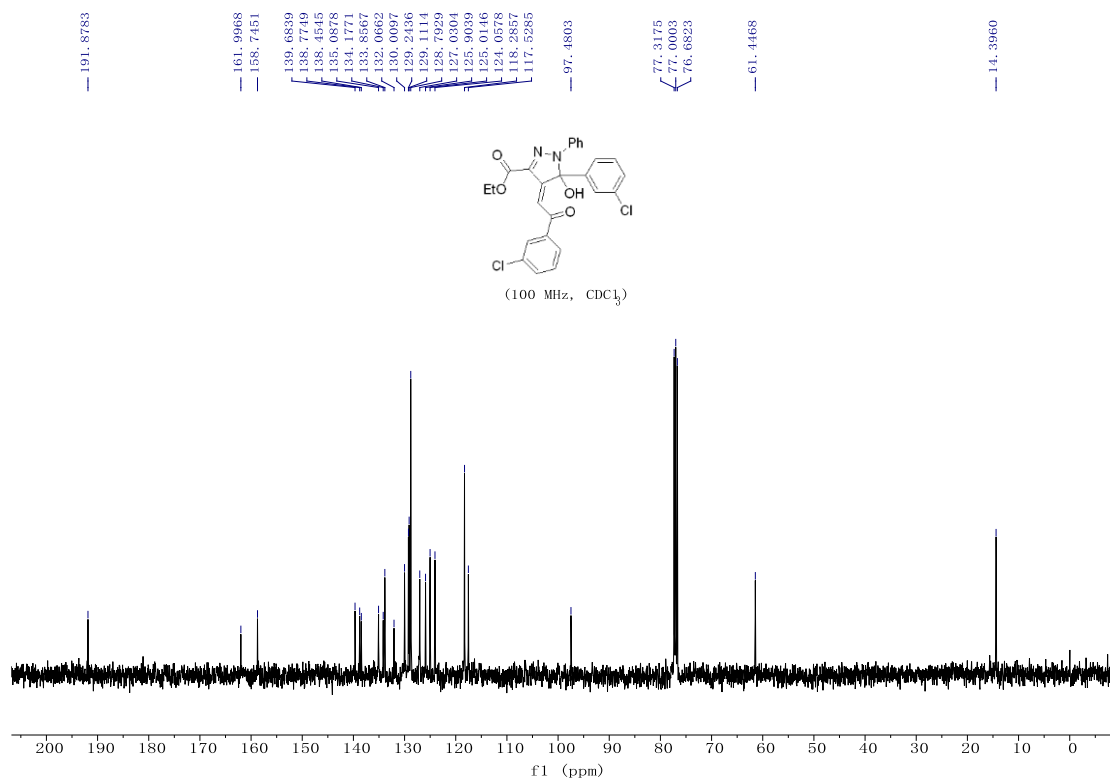
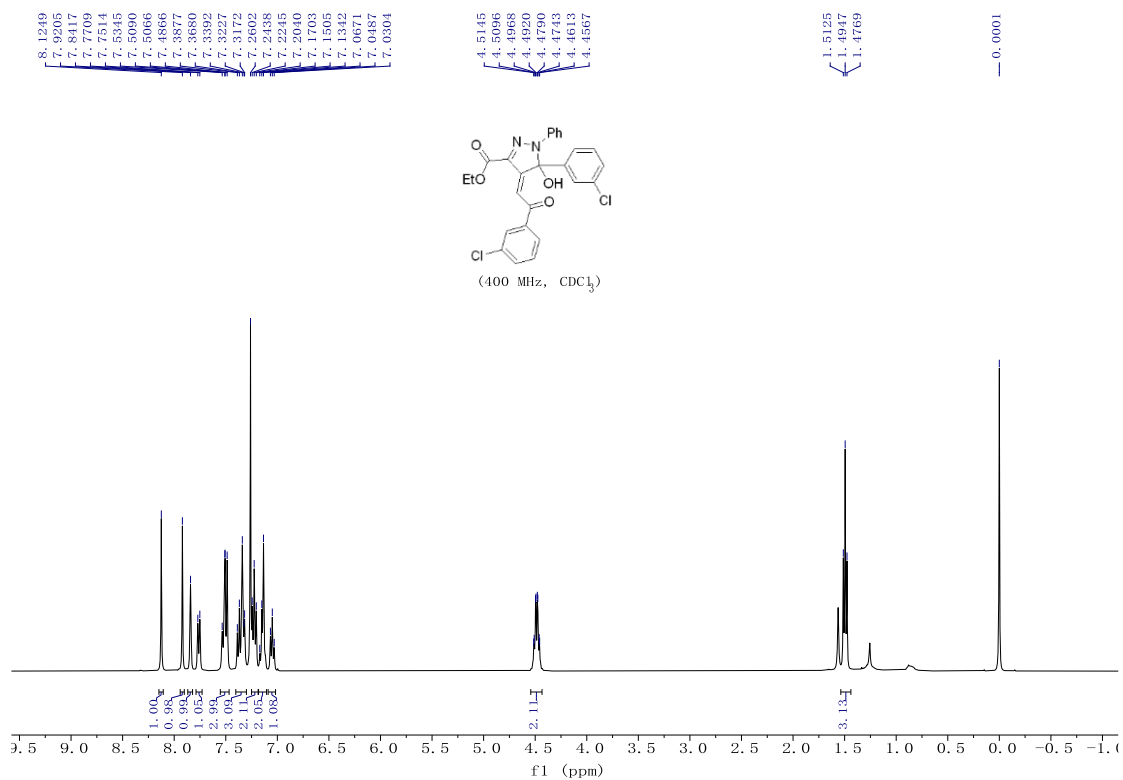
¹H NMR and ¹³C NMR spectra of **3di**



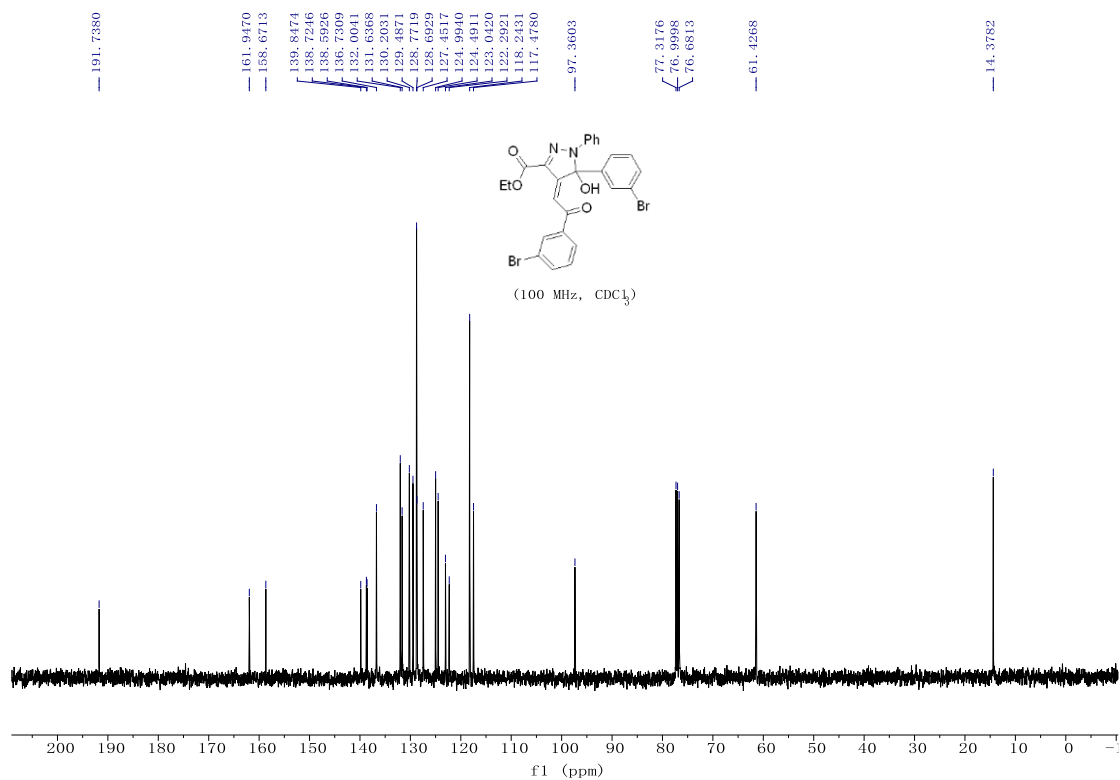
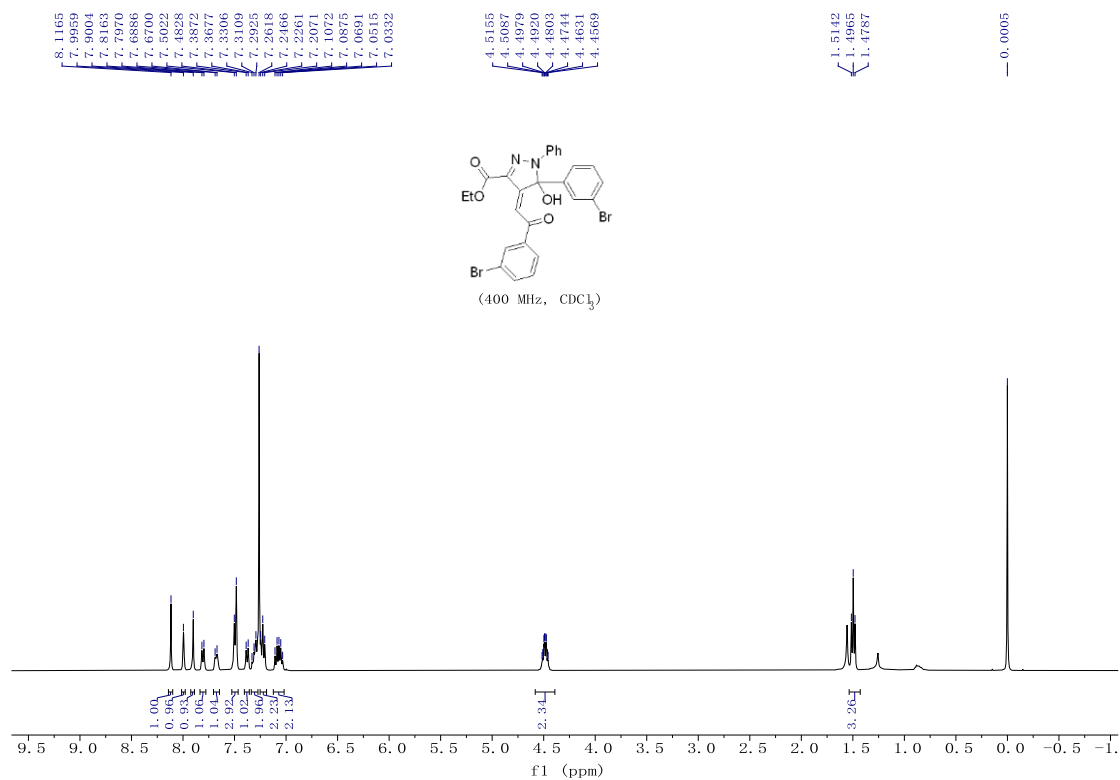
¹H NMR and ¹³C NMR spectrums of **3dj**



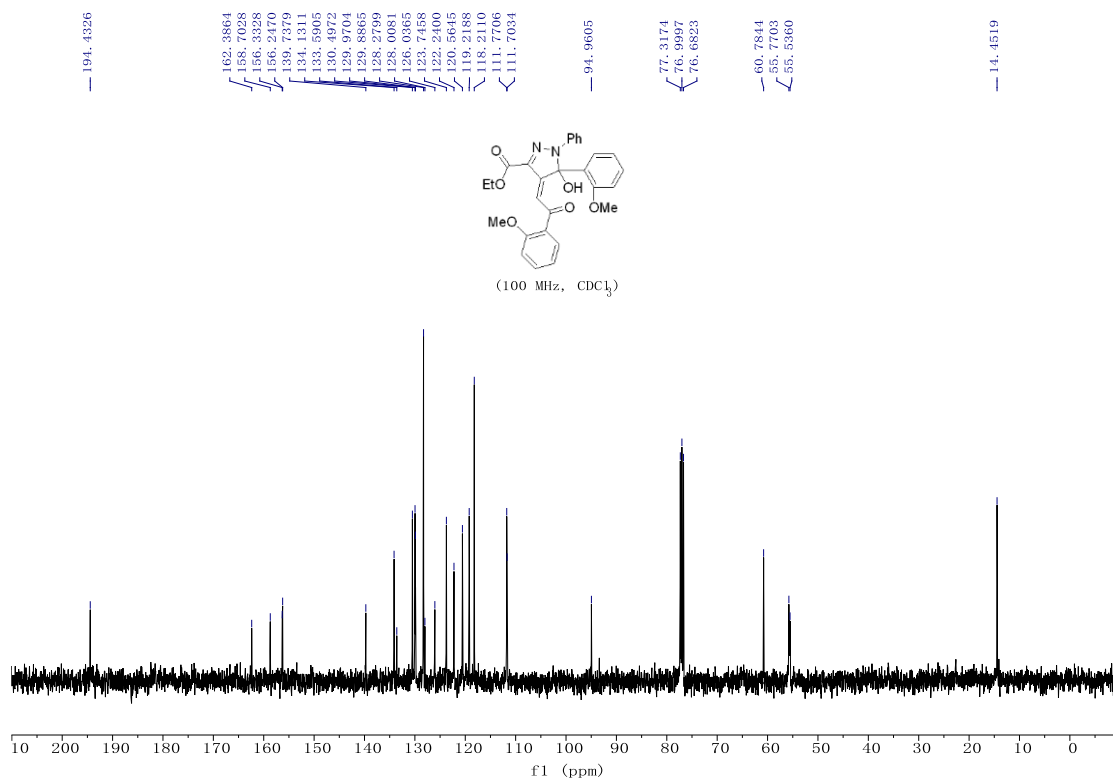
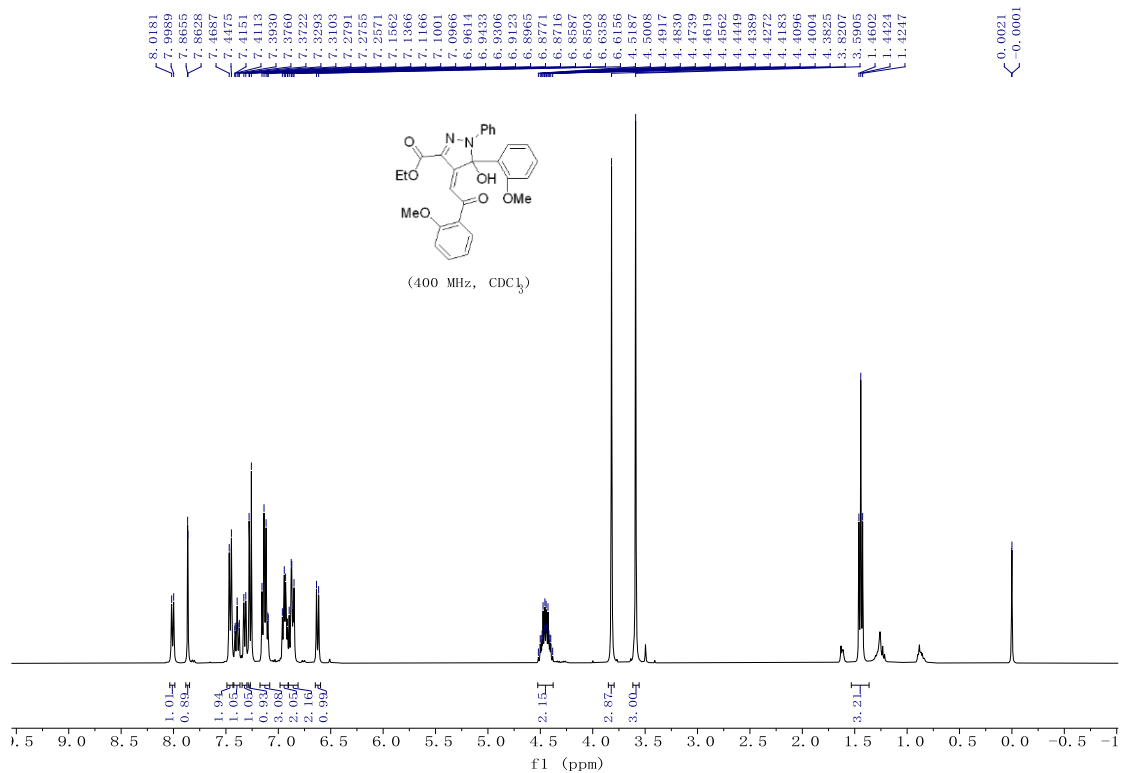
¹H NMR and ¹³C NMR spectrums of **3dk**



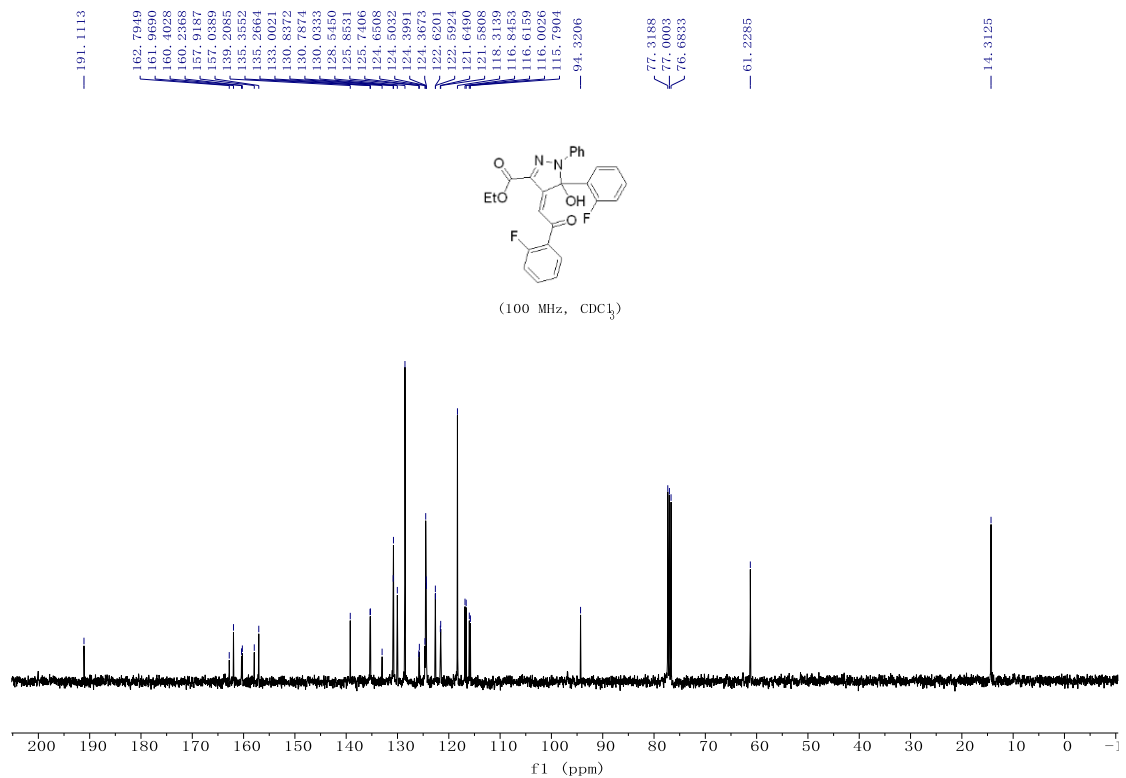
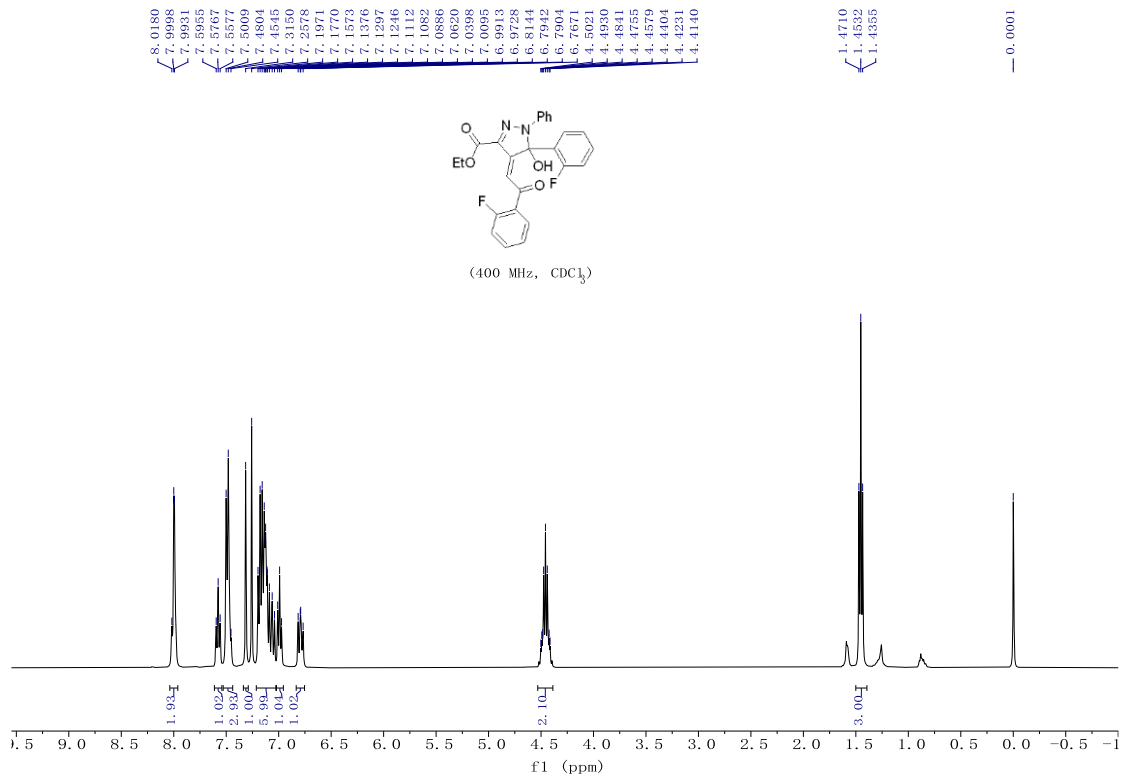
¹H NMR and ¹³C NMR spectra of **3dl**



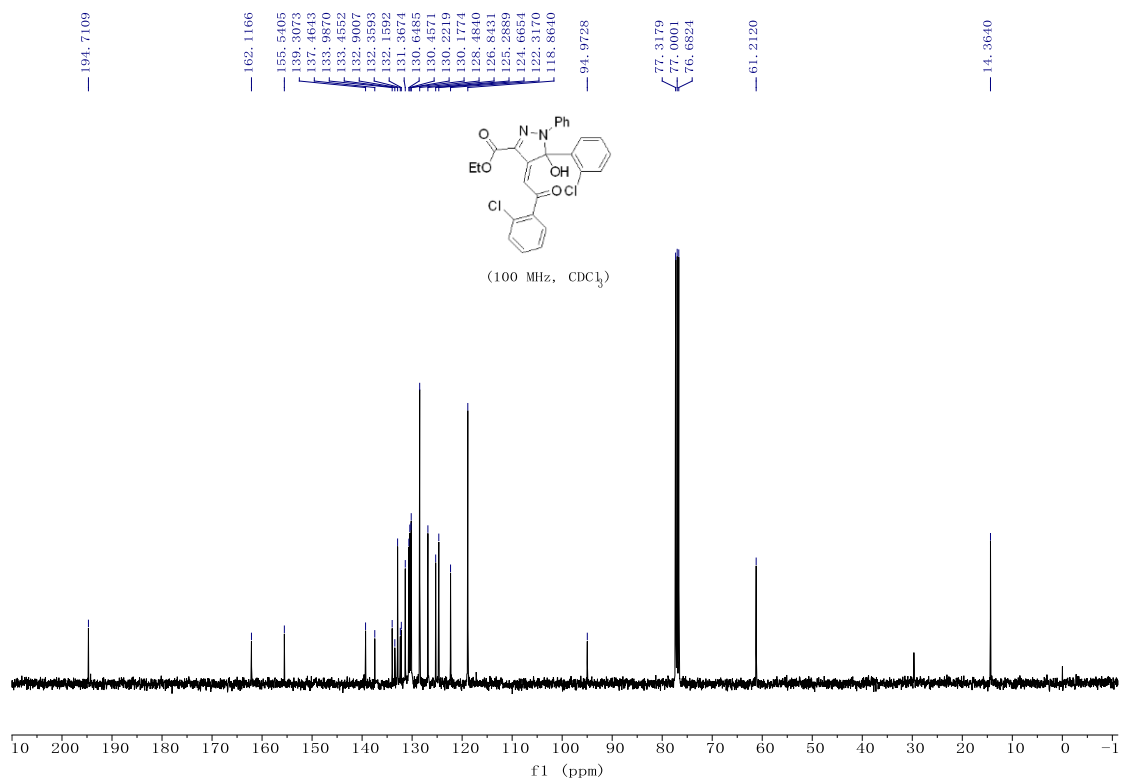
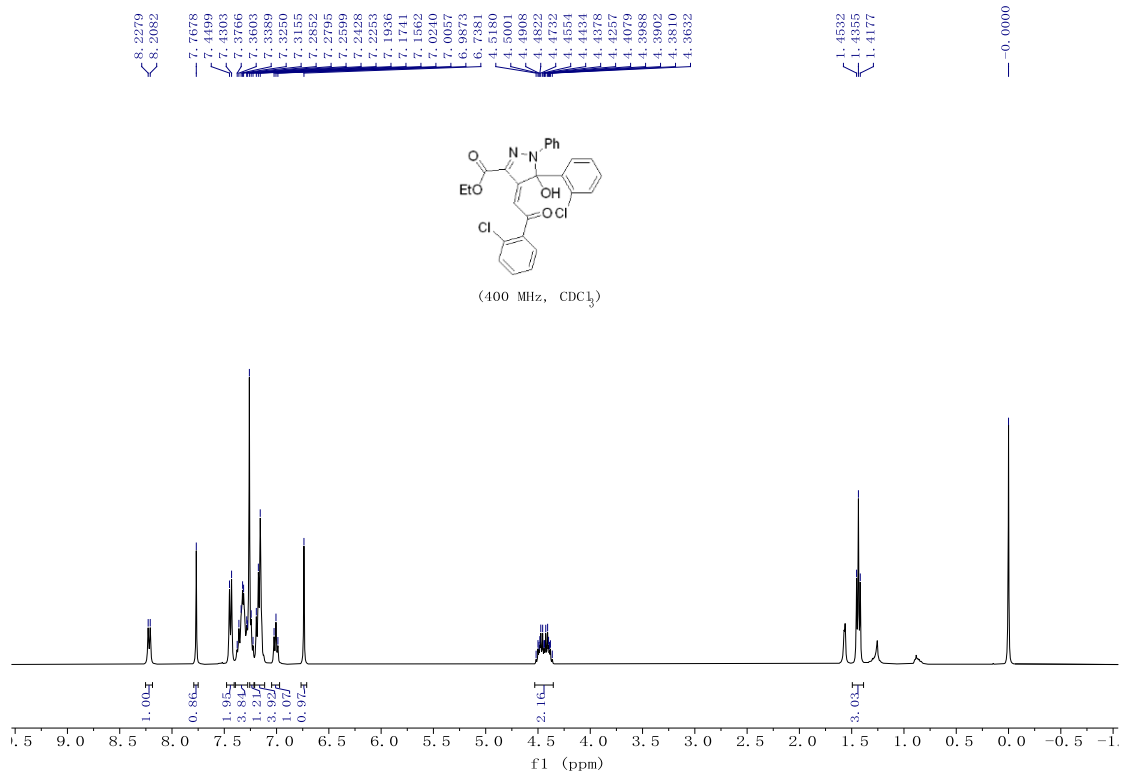
¹H NMR and ¹³C NMR spectrums of **3dm**



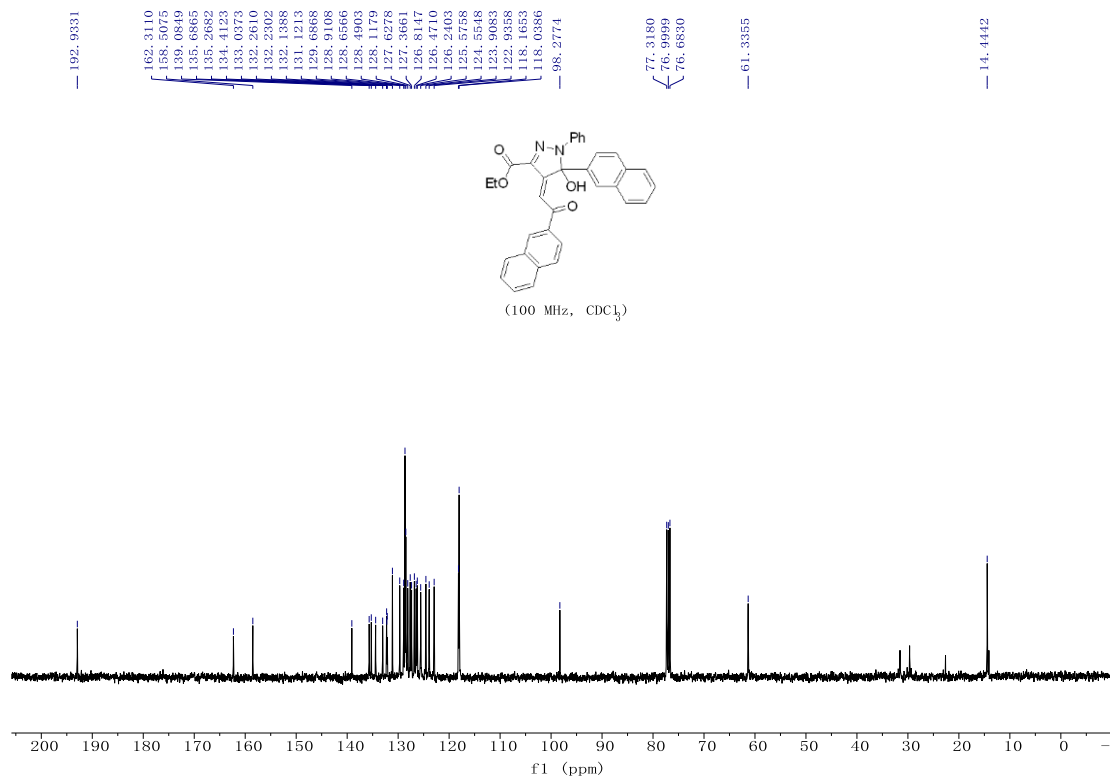
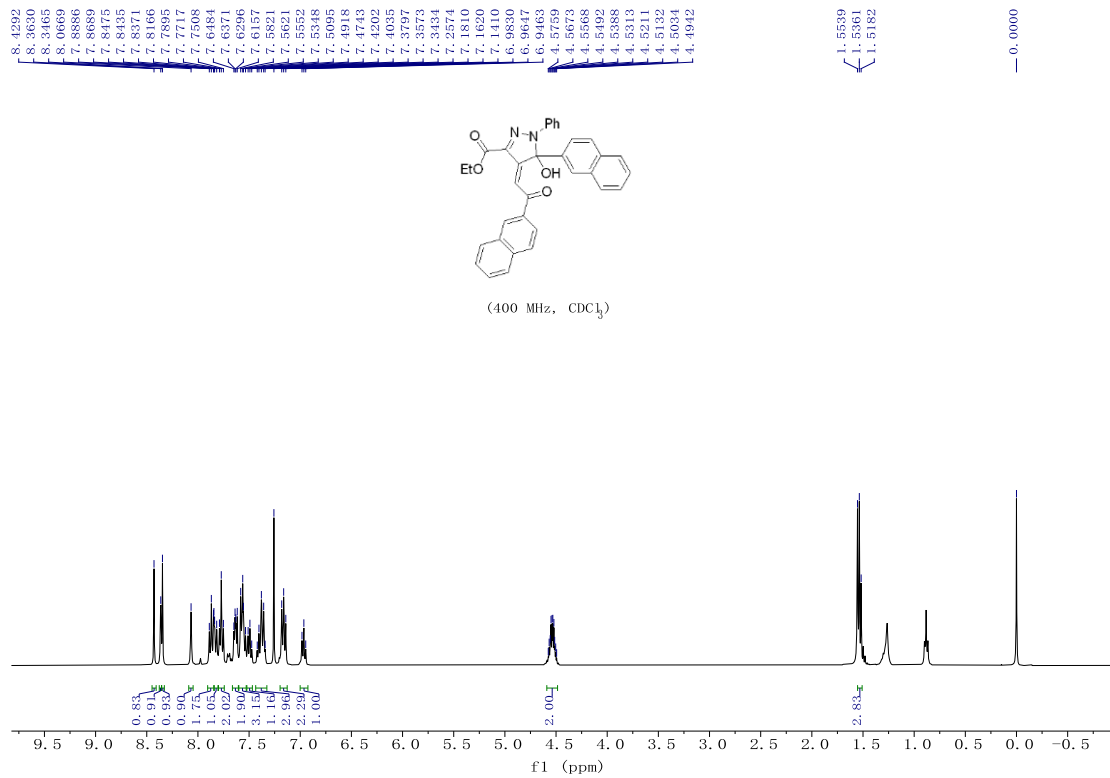
¹H NMR and ¹³C NMR spectrums of **3dn**



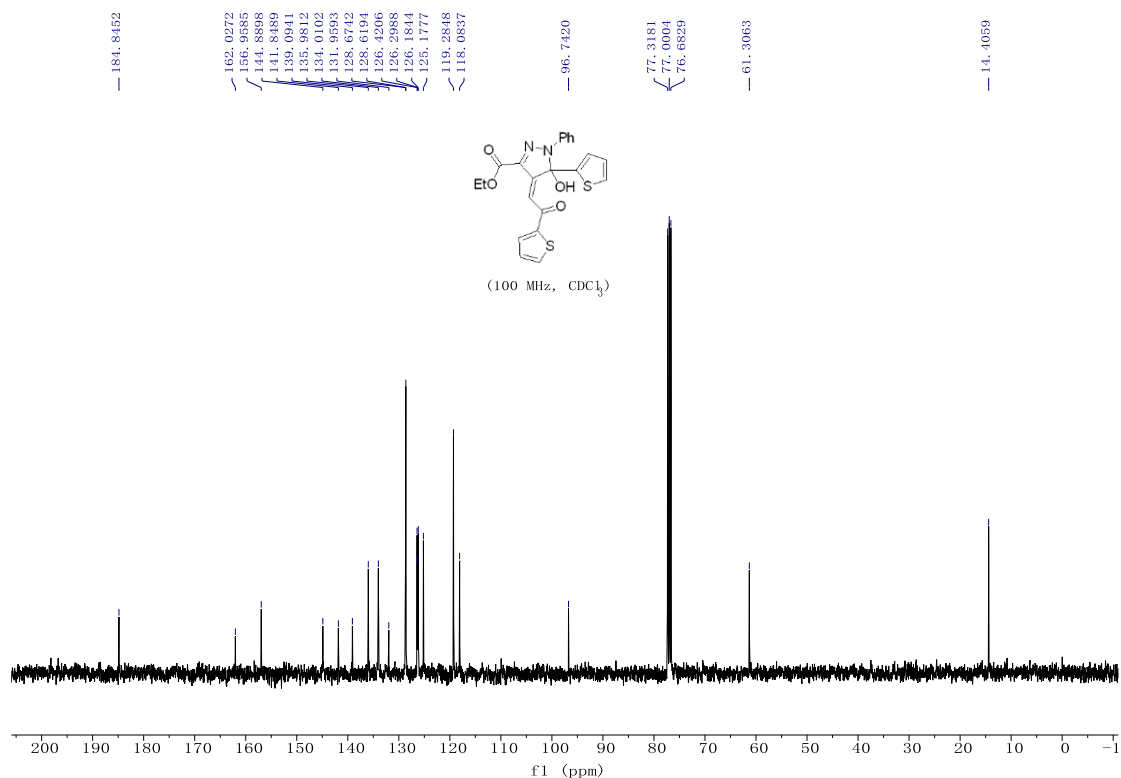
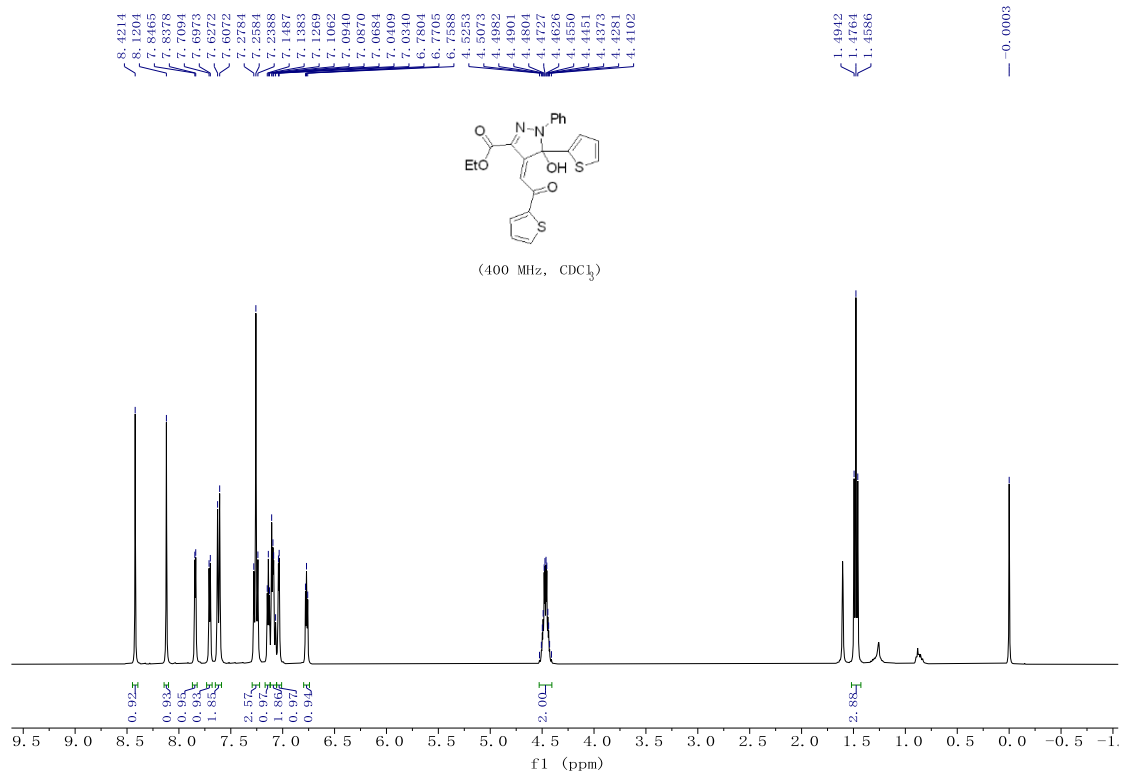
¹H NMR and ¹³C NMR spectra of **3do**



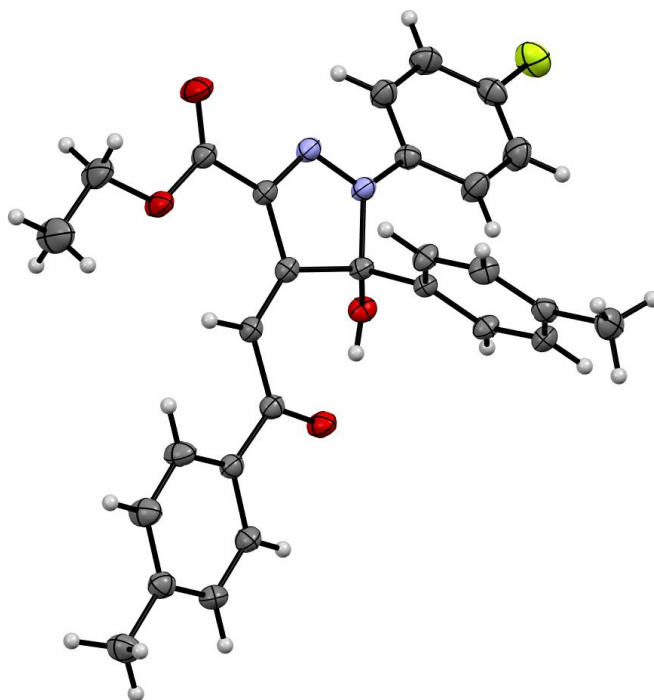
¹H NMR and ¹³C NMR spectrums of **3dp**



¹H NMR and ¹³C NMR spectra of **3dq**



8. Crystal Structure Information of Compound **3aa**



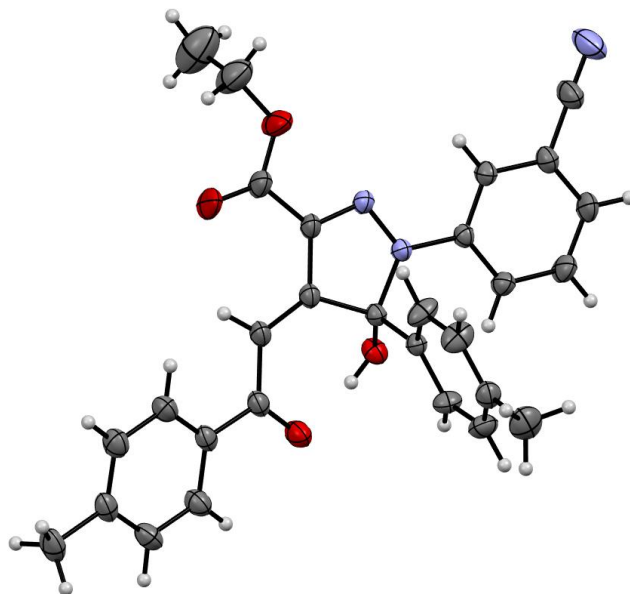
Thermal ellipsoids are drawn at the 30% probability levels

Red crystals of **3aa** were grown by layering a CH_2Cl_2 solution with hexanes, which has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition number CCDC 2126471. Single crystals were mounted on a sample holder and diffraction data were collected on an Agilent SuperNova diffractometer with Mo K_α radiation at 295(2) K.

Table 1 Crystal data and structure refinement for 3aa.

Identification code	3aa
Empirical formula	C ₂₈ H ₂₅ FN ₂ O ₄
Formula weight	472.50
Temperature/K	295(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.0400(10)
b/Å	11.4719(7)
c/Å	12.7098(13)
α/°	87.546(7)
β/°	86.892(9)
γ/°	87.682(8)
Volume/Å ³	1168.6(2)
Z	2
ρ _{calc} /cm ³	1.343
μ/mm ⁻¹	0.096
F(000)	496.0
Crystal size/mm ³	0.35 × 0.33 × 0.3
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.69 to 58.07
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -17 ≤ l ≤ 12
Reflections collected	8810
Independent reflections	5290 [R _{int} = 0.0236, R _{sigma} = 0.0485]
Data/restraints/parameters	5290/0/320
Goodness-of-fit on F ²	1.037
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0615, wR ₂ = 0.1564
Final R indexes [all data]	R ₁ = 0.0907, wR ₂ = 0.1792
Largest diff. peak/hole / e Å ⁻³	0.31/-0.21

9. Crystal Structure Information of Compound 3ha



Thermal ellipsoids are drawn at the 30% probability levels

Red crystals of **3ha** were grown by layering a CH_2Cl_2 solution with hexanes, which has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition number CCDC 2126472. Single crystals were mounted on a sample holder and diffraction data were collected on an Agilent SuperNova diffractometer with Mo K_α radiation at 293(2) K.

Table 1 Crystal data and structure refinement for **3ha**.

Identification code	3ha
Empirical formula	C ₂₉ H ₂₅ N ₃ O ₄
Formula weight	479.52
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.9777(10)
b/Å	11.6675(11)
c/Å	13.8578(15)
α/°	84.971(8)
β/°	80.812(10)
γ/°	75.327(10)
Volume/Å ³	1230.3(2)
Z	2
ρ _{calc} /cm ³	1.294
μ/mm ⁻¹	0.087
F(000)	504.0
Crystal size/mm ³	0.71 × 0.45 × 0.42
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.82 to 58.114
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -16 ≤ l ≤ 18
Reflections collected	9051
Independent reflections	5591 [R _{int} = 0.0220, R _{sigma} = 0.0469]
Data/restraints/parameters	5591/2/329
Goodness-of-fit on F ²	1.042
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0704, wR ₂ = 0.1754
Final R indexes [all data]	R ₁ = 0.1055, wR ₂ = 0.2087
Largest diff. peak/hole / e Å ⁻³	0.50/-0.44

10. References

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