Electronic Supplementary Information for Photocatalytic Radical Cyclization of α-halo Hydrazones with β-ketocarbonyls: Facile Access to Substituted Dihydropyrazoles

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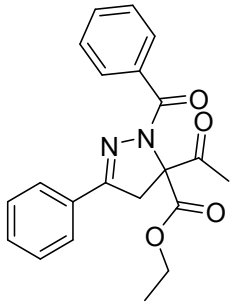
1. General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, MS. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light.^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. Mass spectra are taken on a Waters UPLC H-class LC-MS instrument in the electrospray ionization (ESI) mode. Only molecular ions (M + 1) are given for the ESI-MS analysis. Melting points were determined in open capillaries using a hot stage microscope by XI melting point apparatus, and are uncorrected.

2. General Procedure

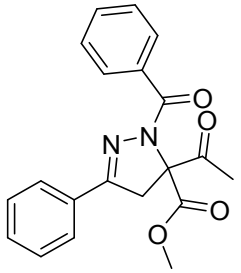
General procedure for Photocatalytic radical cyclization of a-halo hydrazones with β ketocarbonyls: facile access to substituted dihydropyrazoles: A 10 mL reaction vessel with a magnetic stirring bar was equipped with $Ru(bpy)_3Cl_2$ (2 mol %), a-bromo-hydrazones (**1**) (0.2 mmol), 1,3-dicarbonyl compounds (**2**) (0.25 mmol), tBuOK (0.3 mmol) and MeCN (2 mL). The mixture was irradiated with a blue LED (5 W) and stirred under air atmosphere at r.t. for 24 h. The reaction solution was diluted with ethyl acetate, washed with water, dried over anhydrous Na_2SO_4. After the solvent had been removed under reduced pressure, the residue was purified by flash chromatography using PE-AcOEt (10:1-5:1, v/v) as the eluent to functionalized 4, 5-dihydropyrazoles (**3**).

3. Characterization Data



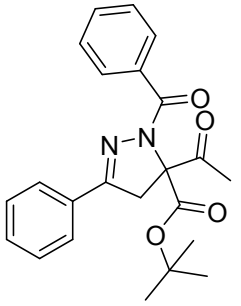
3aa

Ethyl 5-acetyl-1-benzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3aa**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 7.71 – 7.62 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 (p, *J* = 6.4 Hz, 3H), 4.33 (p, *J* = 7.3 Hz, 2H), 3.92 (d, *J* = 17.6 Hz, 1H), 3.64 (d, *J* = 17.6 Hz, 1H), 2.56 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.67, 167.64, 165.97, 152.53, 132.37, 130.53, 129.89, 129.10, 127.86, 126.84, 125.90, 61.83, 41.52, 26.88, 13.07. ESI-MS *m/z*: 365 $[M+1]^+$.



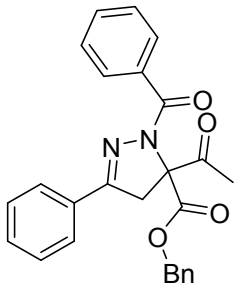
3ab

Methyl 5-acetyl-1-benzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3ab**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.61 – 7.56 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.33 (qd, *J* = 8.7, 7.8, 3.7 Hz, 3H), 3.82 (d, *J* = 17.7 Hz, 1H), 3.78 (s, 3H), 3.58 (d, *J* = 17.7 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.53, 168.21, 165.92, 152.59, 132.18, 130.61, 129.92, 129.21, 127.86, 126.83, 125.89, 52.54, 41.50, 26.70. ESI-MS *m/z*: 351 $[M+1]^+$.



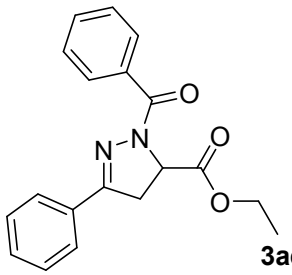
3ac

Tert-butyl 5-acetyl-1-benzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3ac**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.62 – 7.55 (m, 2H), 7.47 – 7.41 (m, 1H), 7.40 – 7.31 (m, 5H), 3.84 (dd, *J* = 17.5, 0.9 Hz, 1H), 3.50 (dd, *J* = 17.6, 0.9 Hz, 1H), 2.48 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.09, 166.44, 165.92, 152.33, 132.72, 130.31, 129.75, 129.44, 128.94, 127.80, 126.78, 125.87, 83.12, 76.73, 41.59, 27.11, 26.88. ESI-MS *m/z*: 393 $[M+1]^+$.



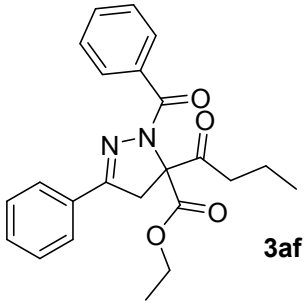
3ad

Benzyl 5-acetyl-1-benzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3ad**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.56 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.40 – 7.36 (m, 2H), 7.35 – 7.29 (m, 3H), 7.28 – 7.22 (m, 5H), 5.21 (d, *J* = 2.8 Hz, 2H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.55 (d, *J* = 17.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.37, 167.46, 166.00, 152.53, 133.79, 132.25, 130.54, 129.90, 129.14, 127.84, 127.66, 127.32, 126.82, 125.90, 67.34, 41.47, 26.86. ESI-MS *m/z*: 427 $[M+1]^+$.



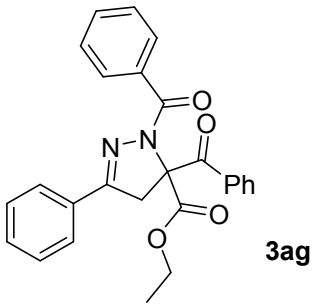
3ae'

Ethyl 1-benzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3ae'**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.99 (m, 2H), 7.69 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.46 (ddt, *J* = 8.4, 6.6, 1.6 Hz, 2H), 7.44 – 7.37 (m, 3H), 5.22 (dd, *J* = 12.4, 6.3 Hz, 1H), 4.28 (qd, *J* = 7.1, 2.8 Hz, 2H), 3.63 (dd, *J* = 17.6, 12.4 Hz, 1H), 3.33 (dd, *J* = 17.6, 6.2 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.02, 165.71, 153.24, 132.49, 130.28, 129.83, 129.61, 129.16, 127.79, 126.75, 125.76, 60.95, 58.17, 35.52, 13.17. ESI-MS *m/z*: 323 $[M+1]^+$.



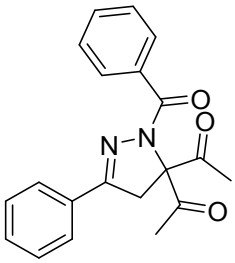
3af

Ethyl 1-benzoyl-5-butyryl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3af**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.58 – 7.53 (m, 2H), 7.44 – 7.39 (m, 1H), 7.35 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.33 – 7.26 (m, 3H), 4.31 – 4.13 (m, 2H), 3.80 (d, *J* = 17.6 Hz, 1H), 3.54 (d, *J* = 17.6 Hz, 1H), 2.79 (qdd, *J* = 18.3, 8.1, 6.4 Hz, 2H), 1.59 (dddd, *J* = 17.1, 15.3, 8.4, 4.4 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.99, 167.71, 166.01, 152.56, 132.54, 130.41, 129.81, 129.36, 129.06, 127.82, 126.78, 125.88, 61.74, 41.66, 40.58, 16.26, 13.04, 12.65. ESI-MS *m/z*: 393 $[M+1]^+$.



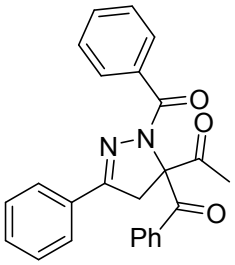
3ag

Ethyl 1,5-dibenzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3ag**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.94 – 7.87 (m, 2H), 7.71 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.45 (dq, *J* = 16.3, 7.1, 6.7 Hz, 7H), 4.42 – 4.28 (m, 2H), 4.17 (d, *J* = 17.8 Hz, 1H), 3.90 (d, *J* = 17.9 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.26, 167.97, 165.96, 151.65, 133.11, 132.66, 132.09, 130.31, 129.84, 129.38, 129.07, 127.93, 127.86, 127.53, 126.74, 125.87, 61.94, 42.60, 12.94. ESI-MS *m/z*: 427 $[M+1]^+$.



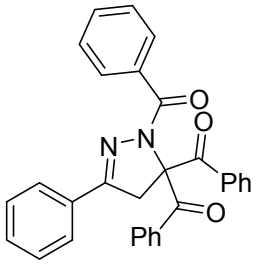
3ah

1,1'-(1-Benzoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5,5-diyl)bis(ethan-1-one) **3ah**, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 2H), 7.74 – 7.67 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 (qd, *J* = 8.6, 7.8, 3.6 Hz, 3H), 3.70 (s, 2H), 2.43 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.16, 166.34, 153.50, 131.98, 130.85, 130.11, 129.18, 129.05, 127.90, 126.95, 125.95, 81.10, 40.17, 26.11. ESI-MS *m/z*: 335 $[M+1]^+$.



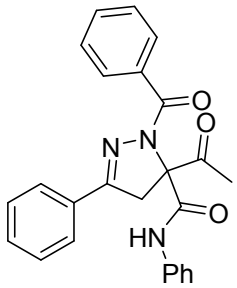
3ai

(5-Acetyl-3-phenyl-4,5-dihydro-1H-pyrazole-1,5-diyl)bis(phenylmethanone) **3ai**, light yellow solid, mp 138-139℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.81 – 7.78 (m, 2H), 7.76 – 7.73 (m, 2H), 7.53 – 7.50 (m, 2H), 7.44 (q, *J* = 7.3, 6.0 Hz, 5H), 7.39 (t, *J* = 7.7 Hz, 2H), 4.36 (d, *J* = 18.2 Hz, 1H), 3.67 (d, *J* = 18.2 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.01, 192.03, 166.35, 153.80, 133.01, 132.37, 130.59, 130.18, 129.22, 128.95, 127.92, 126.99, 126.86, 126.11, 80.04, 39.80, 27.12. ESI-MS *m/z*: 397 $[M+1]^+$.



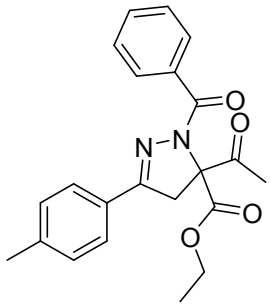
3aj

(3-Phenyl-4,5-dihydro-1H-pyrazole-1,5,5-triyl)tris(phenylmethanone) **3aj**, pale solid, mp 143-144℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.83 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.65 – 7.60 (m, 2H), 7.45 – 7.42 (m, 3H), 7.39 – 7.36 (m, 3H), 7.36 – 7.31 (m, 6H), 4.08 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.33, 166.32, 151.61, 133.19, 132.63, 132.14, 130.33, 129.94, 129.31, 129.10, 128.49, 127.91, 127.56, 126.73, 125.89, 80.03, 42.95. ESI-MS *m/z*: 459 $[M+1]^+$.



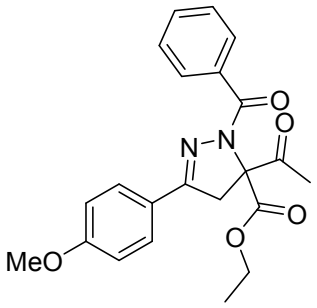
3ak

5-Acetyl-1-benzoyl-N,3-diphenyl-4,5-dihydro-1H-pyrazole-5-carboxamide **3ak**, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.36 (p, *J* = 7.5 Hz, 3H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.53 (d, *J* = 18.2 Hz, 1H), 3.29 (d, *J* = 18.2 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.46, 168.42, 163.92, 154.34, 136.84, 132.03, 131.01, 130.27, 129.35, 128.93, 128.03, 127.92, 126.94, 126.14, 123.74, 119.37, 79.24, 40.33, 24.40. ESI-MS *m/z*: 412 $[M+1]^+$.



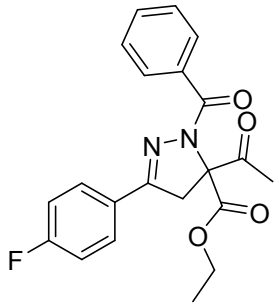
3ba

Ethyl 5-acetyl-1-benzoyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ba**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.48 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.34 (p, *J* = 7.1 Hz, 2H), 3.91 (d, *J* = 17.7 Hz, 1H), 3.64 (d, *J* = 17.5 Hz, 1H), 2.57 (s, 3H), 2.40 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.71, 167.63, 165.85, 152.63, 140.31, 132.46, 130.43, 129.10, 128.54, 126.79, 126.51, 125.85, 124.44, 61.75, 41.51, 26.82, 20.59, 13.05. ESI-MS *m/z*: 379 $[M+1]^+$.



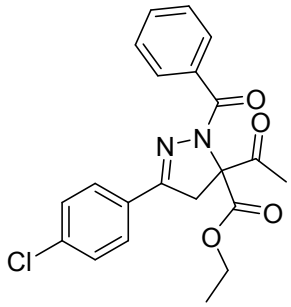
3ca

Ethyl 5-acetyl-1-benzoyl-3-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ca**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.68 – 7.59 (m, 2H), 7.57 – 7.52 (m, 1H), 7.50 – 7.44 (m, 2H), 6.98 – 6.88 (m, 2H), 4.34 (p, *J* = 7.2 Hz, 2H), 3.93 – 3.82 (m, 4H), 3.62 (d, *J* = 17.5 Hz, 1H), 2.57 (d, *J* = 1.4 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.85, 167.65, 165.76, 160.72, 152.38, 132.50, 130.40, 129.08, 127.56, 126.78, 121.86, 113.24, 61.75, 54.46, 41.49, 26.81, 13.04. ESI-MS *m/z*: 395 $[M+1]^+$.



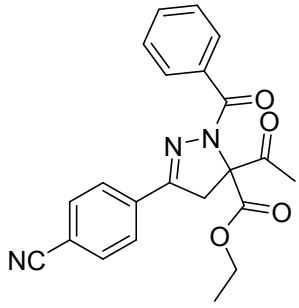
3da

Ethyl 5-acetyl-1-benzoyl-3-(4-fluorophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3da**, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.57 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 4.25 (p, *J* = 7.2 Hz, 2H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.52 (d, *J* = 17.6 Hz, 1H), 2.48 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -108.35. ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.60, 167.52, 165.97, 151.49, 132.34, 130.52, 129.01, 127.97, 127.90, 126.83, 125.60, 115.15, 114.97, 61.84, 41.47, 26.89, 13.04. ESI-MS *m/z*: 383 $[M+1]^+$.



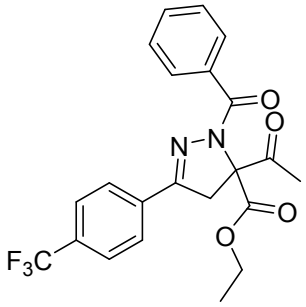
3ea

Ethyl 5-acetyl-1-benzoyl-3-(4-chlorophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ea**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.33 (p, *J* = 7.3 Hz, 2H), 3.89 (d, *J* = 17.6 Hz, 1H), 3.60 (d, *J* = 17.6 Hz, 1H), 2.56 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.51, 167.47, 165.99, 151.41, 135.88, 132.26, 130.58, 129.02, 128.13, 127.80, 127.10, 126.86, 61.87, 41.35, 26.92, 13.05. ESI-MS *m/z*: 399 $[M+1]^+$.



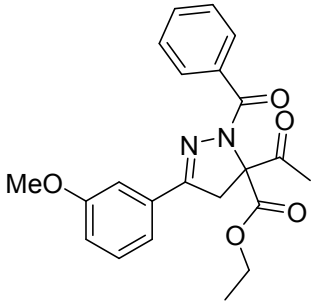
3fa

Ethyl 5-acetyl-1-benzoyl-3-(4-cyanophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3fa**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 4.40 – 4.29 (m, 2H), 3.92 (d, *J* = 17.7 Hz, 1H), 3.61 (d, *J* = 17.7 Hz, 1H), 2.57 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.24, 167.30, 166.21, 150.43, 133.50, 131.97, 131.57, 130.80, 128.98, 126.95, 126.27, 117.23, 112.95, 62.03, 41.16, 27.01, 13.04. ESI-MS *m/z*: 390 $[M+1]^+$.



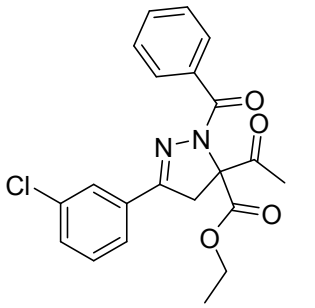
3ga

Ethyl 5-acetyl-1-benzoyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ga**, colorless luquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.83 (m, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.42 – 7.36 (m, 2H), 4.32 – 4.20 (m, 2H), 3.85 (d, *J* = 17.7 Hz, 1H), 3.55 (d, *J* = 17.7 Hz, 1H), 2.49 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).^{19}F NMR (470 MHz, $CDCl_3$) δ -62.91. ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.38, 167.40, 166.15, 150.95, 132.68, 132.11, 131.45, 130.92, 130.70, 129.02, 126.90, 126.11, 124.81, 61.95, 41.34, 26.97, 13.03. ESI-MS *m/z*: 433 $[M+1]^+$.



3ha

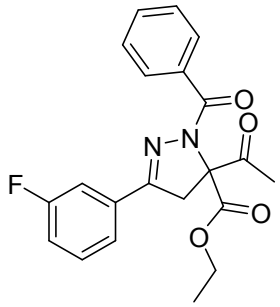
Ethyl 5-acetyl-1-benzoyl-3-(3-methoxyphenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ha**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.95 (m, 2H), 7.55 – 7.50 (m, 1H), 7.46 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.01 – 6.94 (m, 1H), 4.39 – 4.27 (m, 2H), 3.90 (d, *J* = 17.7 Hz, 1H), 3.81 (s, 3H), 3.63 (d, *J* = 17.7 Hz, 1H), 2.56 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.57, 167.55, 165.95, 158.79, 152.40, 132.35, 130.52, 129.10, 128.91, 126.80, 118.49, 115.55, 111.09, 61.79, 54.40, 41.56, 26.84, 13.05. ESI-MS *m/z*: 395 $[M+1]^+$.



3ia

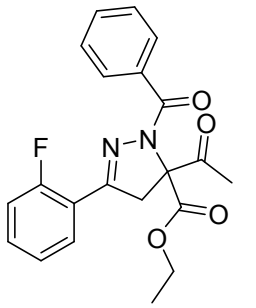
Ethyl 5-acetyl-1-benzoyl-3-(3-chlorophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ia**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.56 (dd, *J* = 11.0, 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 4.35 (p, *J* = 7.4 Hz, 2H), 3.91 (d, *J* = 17.7 Hz, 1H), 3.62 (d, *J* = 17.6 Hz, 1H), 2.58 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.40, 167.43, 166.07, 151.14, 133.96, 132.17, 131.10, 130.64, 129.77, 129.02, 126.91,

125.82, 123.98, 61.89, 41.37, 26.92, 13.05. ESI-MS *m/z*: 399 $[M+1]^+$.



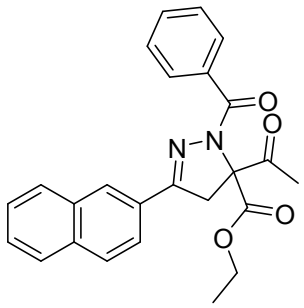
3ja

Ethyl 5-acetyl-1-benzoyl-3-(3-fluorophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ja**, colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.48 – 7.43 (m, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (tt, *J* = 7.9, 3.3 Hz, 3H), 7.08 – 7.00 (m, 1H), 4.30 – 4.20 (m, 2H), 3.81 (d, *J* = 17.7 Hz, 1H), 3.53 (d, *J* = 17.7 Hz, 1H), 2.48 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.79. ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.43, 167.44, 166.06, 162.81, 160.84, 151.32, 132.19, 131.45, 130.62, 129.54, 129.47, 129.02, 126.88, 121.71, 116.90, 116.73, 112.65, 112.47, 61.87, 41.41, 26.91, 13.04. ESI-MS *m/z*: 383 $[M+1]^+$.



3ka

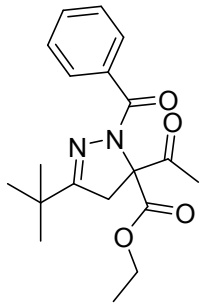
Ethyl 5-acetyl-1-benzoyl-3-(2-fluorophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ka**, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.75 (td, *J* = 7.8, 1.8 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32 (dddd, *J* = 8.7, 7.1, 5.1, 1.8 Hz, 1H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (ddd, *J* = 11.6, 8.4, 1.1 Hz, 1H), 4.32 – 4.21 (m, 2H), 3.88 (dd, *J* = 18.5, 2.6 Hz, 1H), 3.67 (dd, *J* = 18.4, 2.8 Hz, 1H), 2.48 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.94. ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.36, 167.51, 165.97, 161.23, 159.22, 149.01, 132.26, 131.46, 130.53, 129.09, 128.06, 126.81, 123.59, 117.48, 117.39, 115.69, 115.52, 61.77, 43.80, 26.89, 13.05. ESI-MS *m/z*: 383 $[M+1]^+$.



3la

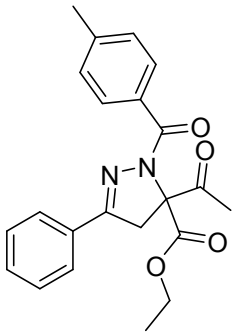
Ethyl 5-acetyl-1-benzoyl-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3la**, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.95 – 7.90 (m, 2H), 7.88 – 7.81 (m, 3H), 7.55 (td, *J* = 6.5, 2.9 Hz, 3H), 7.50 (t, *J* = 7.6 Hz, 2H), 4.40 – 4.31 (m, 2H), 4.05 (d, *J* = 17.5 Hz, 1H), 3.78 (d, *J* = 17.5 Hz, 1H), 2.59 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.65, 167.62, 165.99, 152.59, 133.36, 132.40, 131.92, 130.57, 129.15, 127.71, 127.54, 126.95, 126.88, 126.65, 125.96, 122.34, 61.84, 41.46, 26.90, 13.08. ESI-MS *m/z*: 415 $[M+1]^+$.



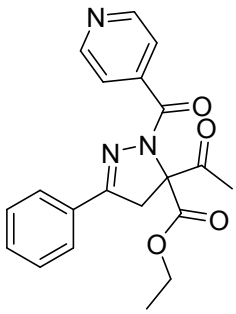
3ma

Ethyl 5-acetyl-1-benzoyl-3-(tert-butyl)-4,5-dihydro-1H-pyrazole-5-carboxylate **3ma**, colorless luquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.50 – 7.46 (m, 1H), 7.41 (dd, *J* = 8.2, 6.8 Hz, 2H), 4.31 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.53 (d, *J* = 17.7 Hz, 1H), 3.20 (d, *J* = 17.7 Hz, 1H), 2.50 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.19 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.99, 167.72, 165.49, 164.39, 132.36, 130.32, 129.21, 126.62, 61.55, 40.61, 33.21, 26.90, 25.11, 13.05. ESI-MS *m/z*: 345 $[M+1]^+$.



3na

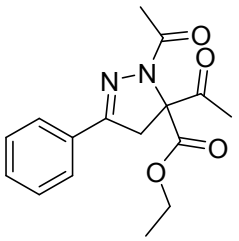
Ethyl 5-acetyl-1-(4-methylbenzoyl)-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3na**, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.68 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.27 (d, *J* = 7.9 Hz, 2H), 4.37 – 4.27 (m, 2H), 3.91 (d, *J* = 17.7 Hz, 1H), 3.63 (d, *J* = 17.6 Hz, 1H), 2.55 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.74, 167.65, 165.88, 152.29, 141.01, 129.78, 129.42, 129.25, 127.81, 127.51, 125.86, 61.72, 41.38, 26.81, 20.62, 13.03. ESI-MS *m/z*: 379 $[M+1]^+$.



3oa

Ethyl 5-acetyl-1-isonicotinoyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3oa**, colorless liquid.

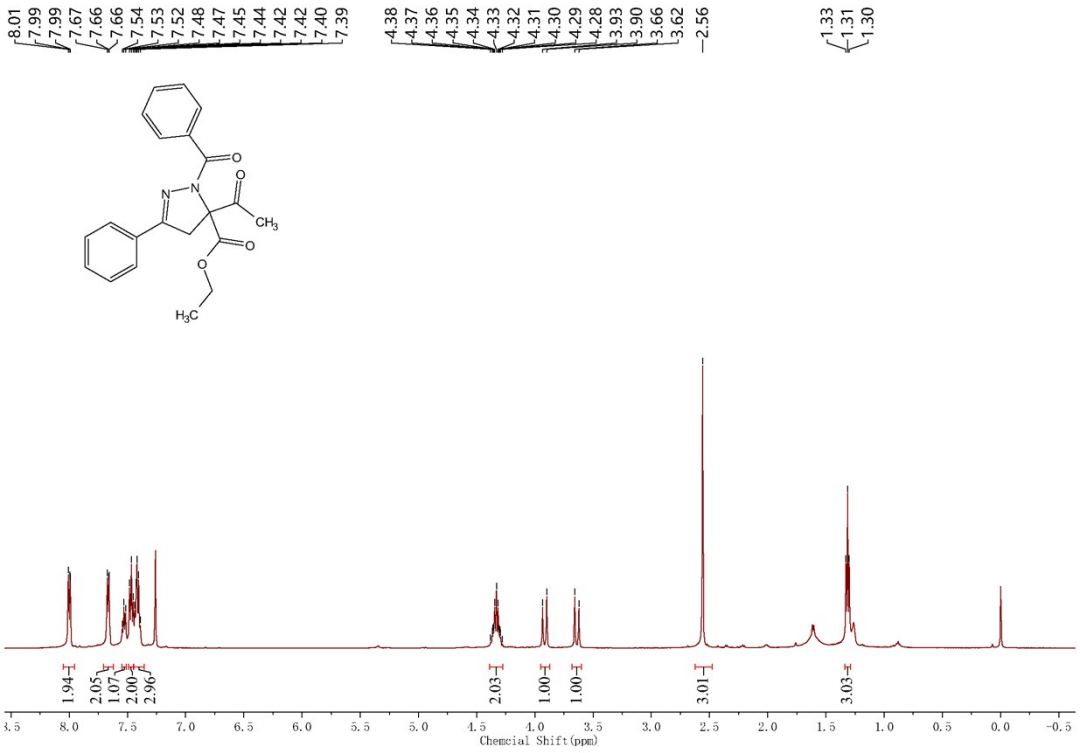
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.2 Hz, 2H), 7.72 (d, *J* = 6.0 Hz, 2H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.35 (dt, *J* = 14.5, 6.8 Hz, 3H), 4.26 (p, *J* = 7.2 Hz, 2H), 3.83 (d, *J* = 17.7 Hz, 1H), 3.59 (d, *J* = 17.7 Hz, 1H), 2.48 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.76, 167.11, 163.94, 153.54, 148.85, 139.90, 130.26, 128.80, 127.94, 125.95, 122.49, 62.03, 41.74, 26.90, 13.04. ESI-MS *m/z*: 366 $[M+1]^+$.



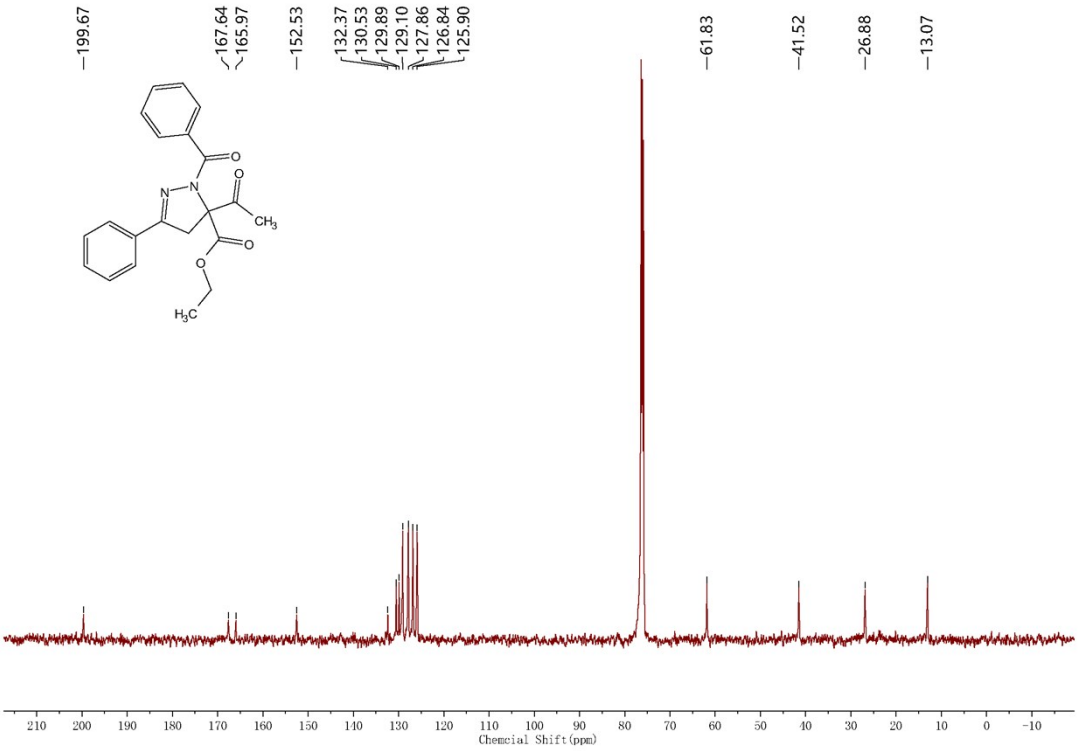
3pa

Ethyl 1,5-diacetyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate **3pa**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.36 – 7.31 (m, 3H), 4.21 (dtt, *J* = 10.2, 7.0, 3.4 Hz, 2H), 3.83 (d, *J* = 17.7 Hz, 1H), 3.50 (d, *J* = 17.6 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.79, 168.41, 167.51, 151.93, 129.80, 129.31, 127.84, 125.72, 75.18, 61.75, 42.07, 26.67, 20.93, 12.98. ESI-MS *m/z*: 303 $[M+1]^+$.

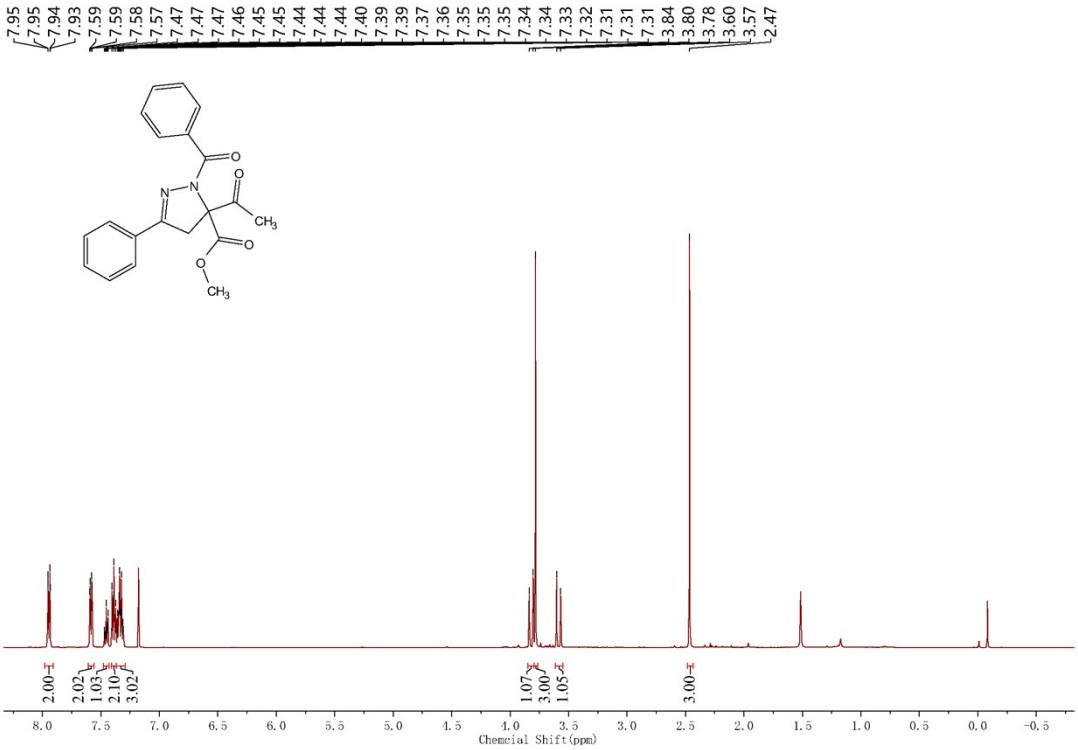
4. NMR Spectra of All Products



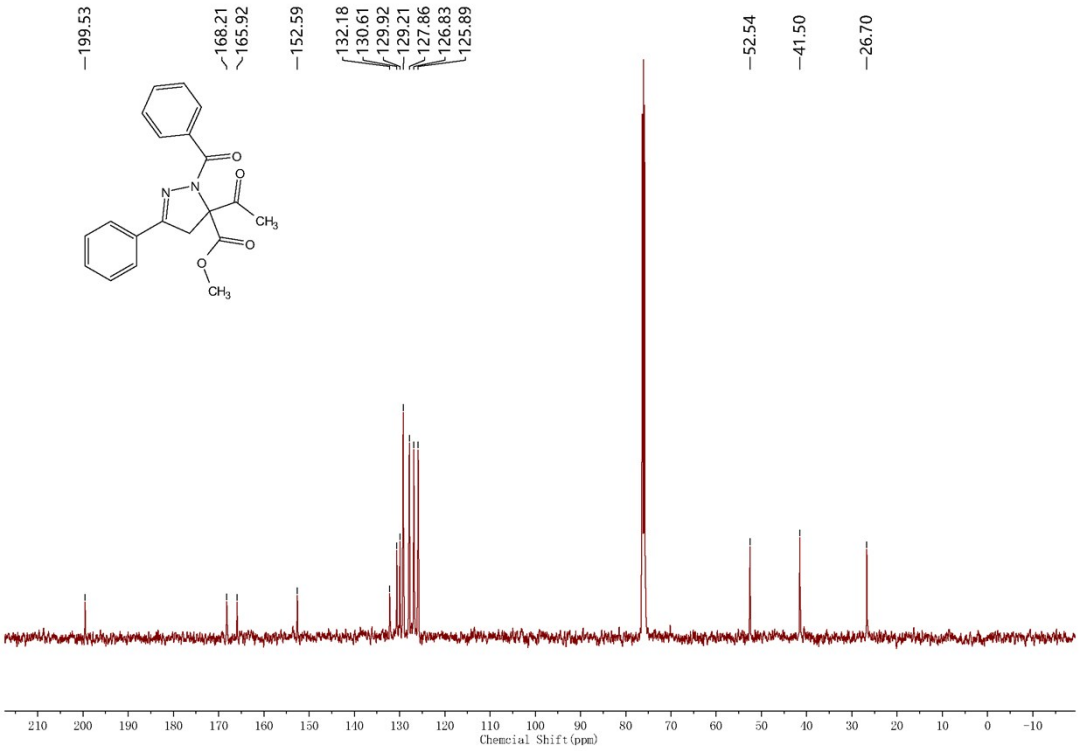
^{1}H NMR Spectrum of Compound **3aa** (500MHz, $CDCl_3$)



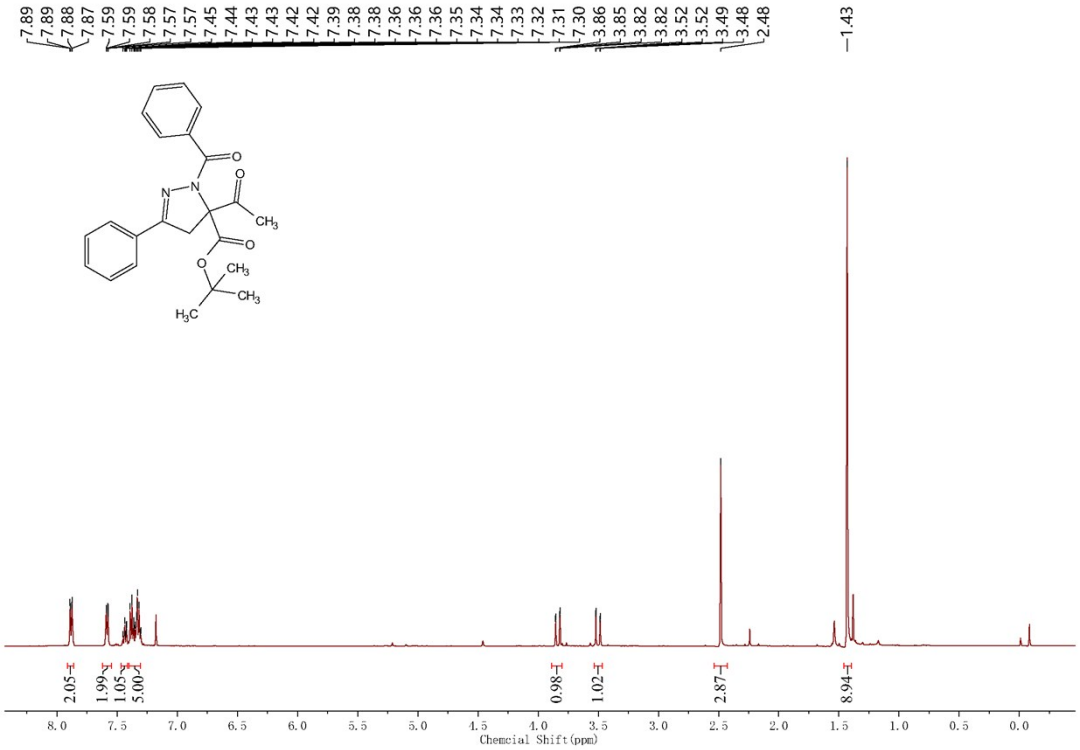
^{13}C NMR Spectrum of Compound **3aa** (125MHz, $CDCl_3$)



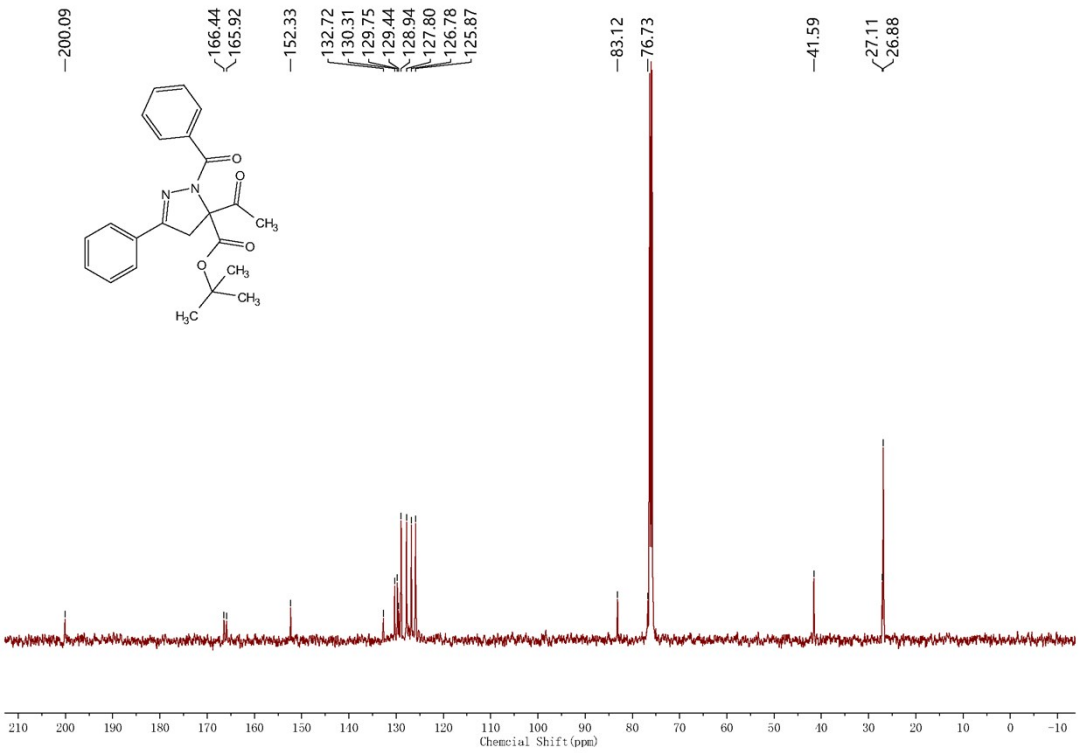
^{1}H NMR Spectrum of Compound **3ab** (500MHz, $CDCl_3$)



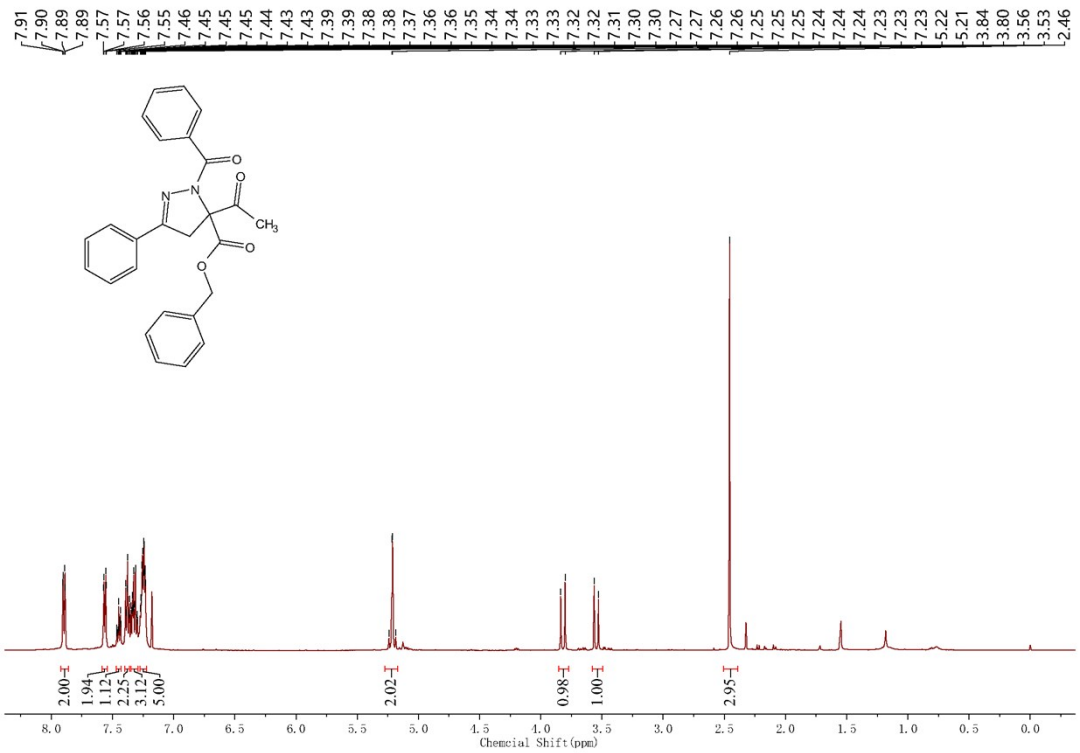
^{13}C NMR Spectrum of Compound **3ab** (125MHz, $CDCl_3$)



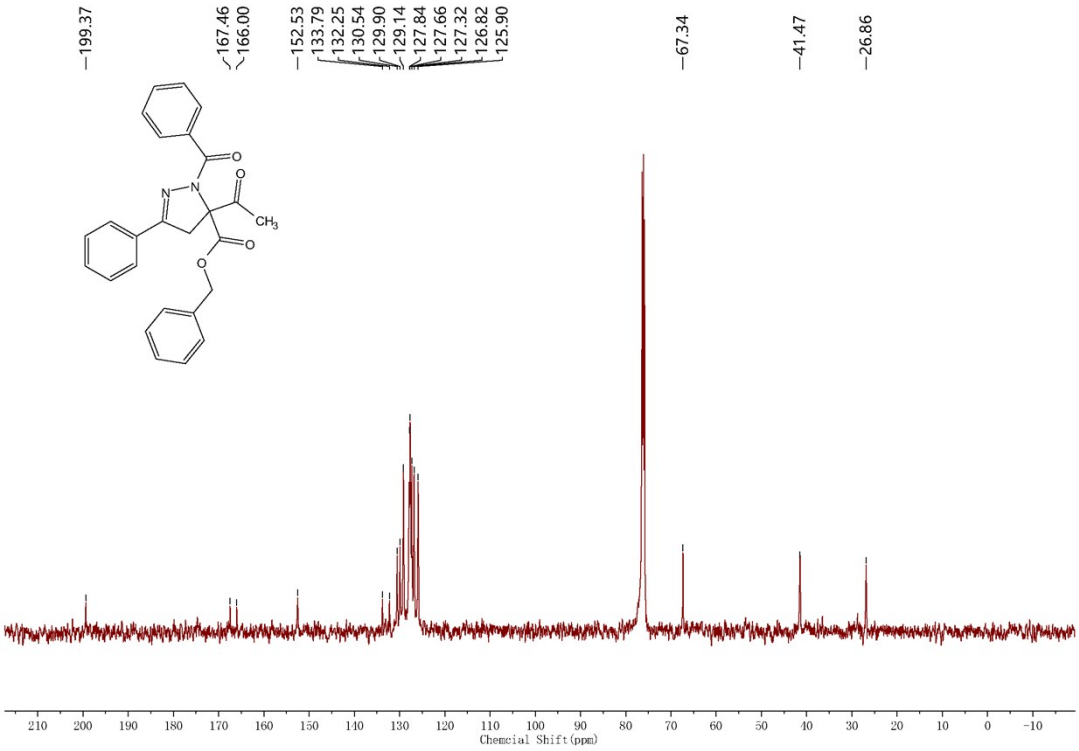
^{1}H NMR Spectrum of Compound **3ac** (500MHz, $CDCl_3$)



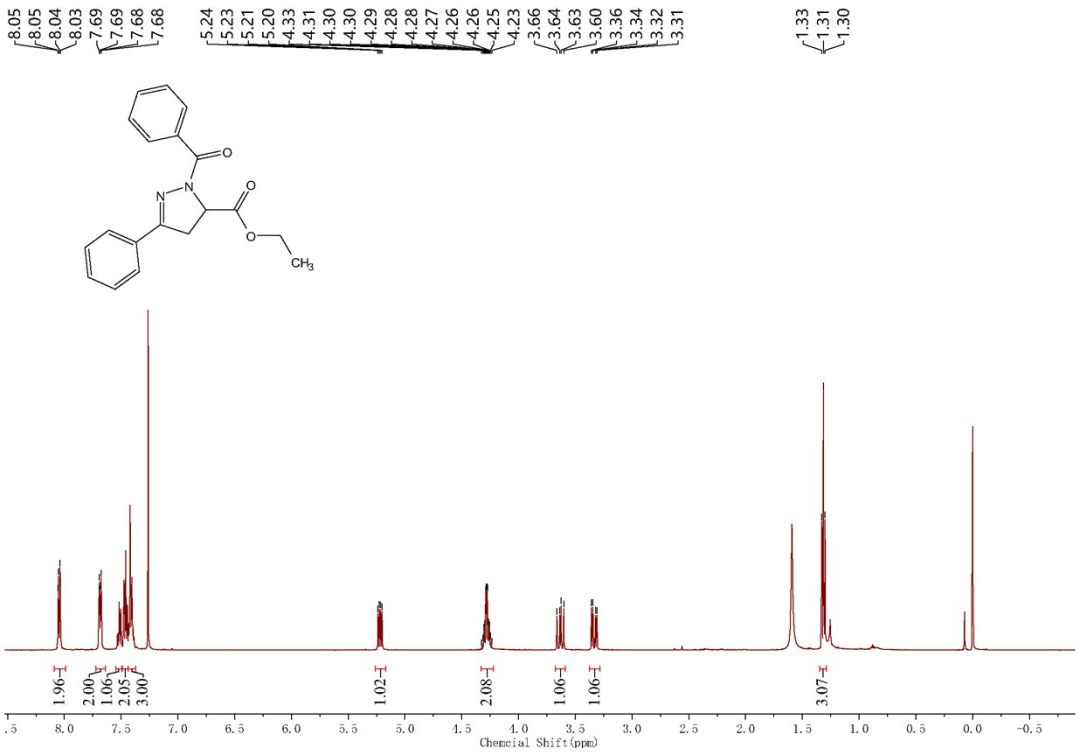
^{13}C NMR Spectrum of Compound **3ac** (125MHz, $CDCl_3$)



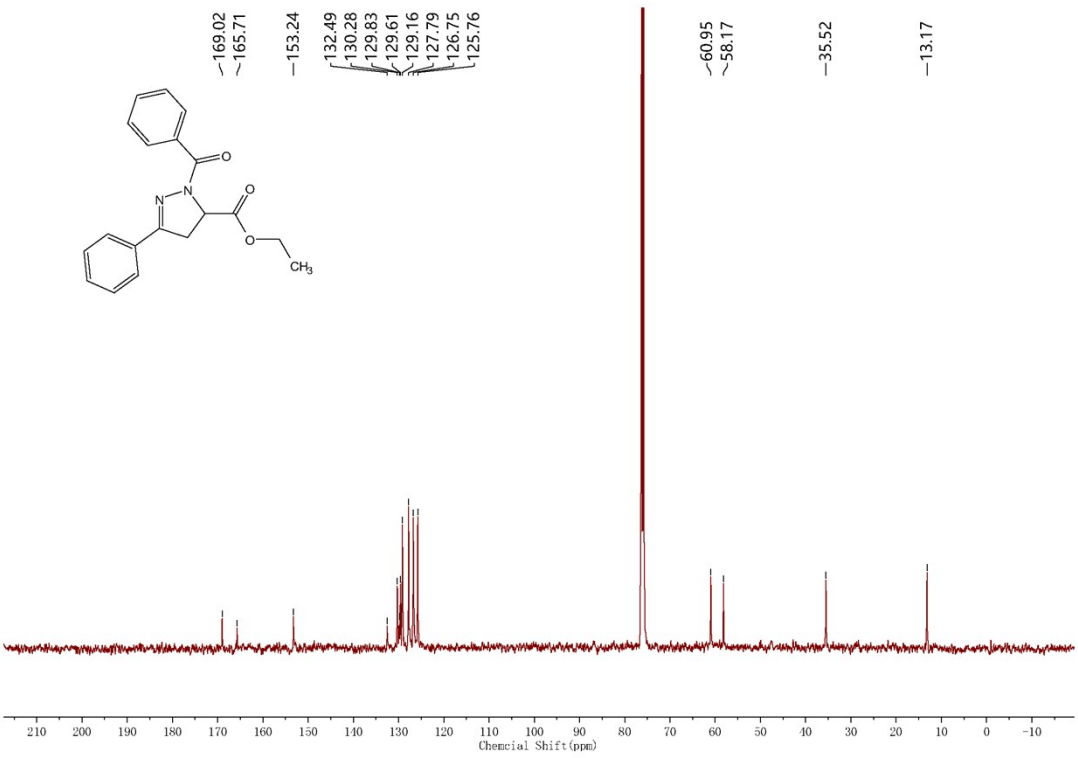
^{1}H NMR Spectrum of Compound **3ad** (500MHz, $CDCl_3$)



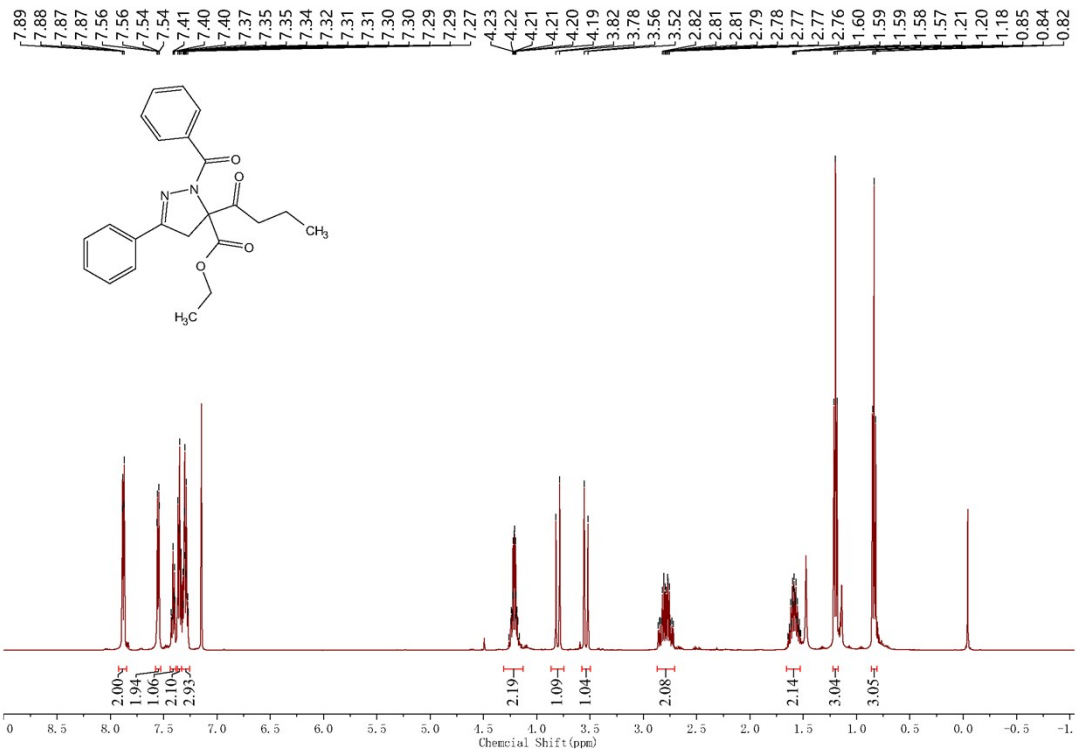
^{13}C NMR Spectrum of Compound **3ad** (125MHz, $CDCl_3$)



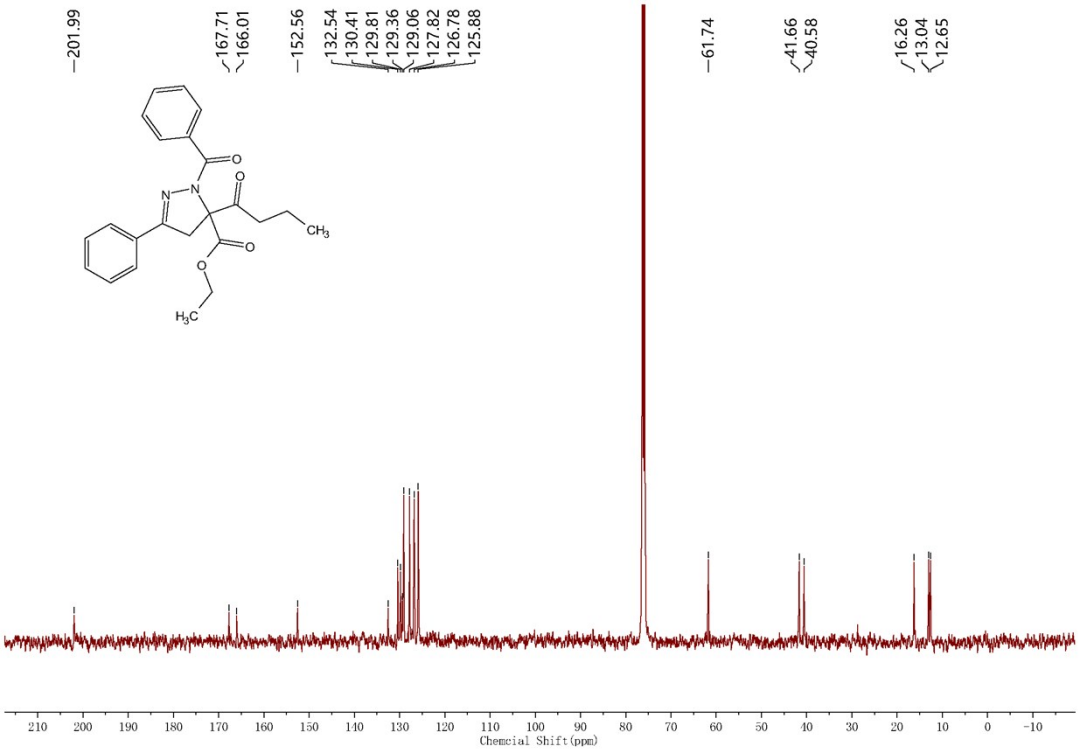
^{1}H NMR Spectrum of Compound **3ae'** (500MHz, $CDCl_3$)



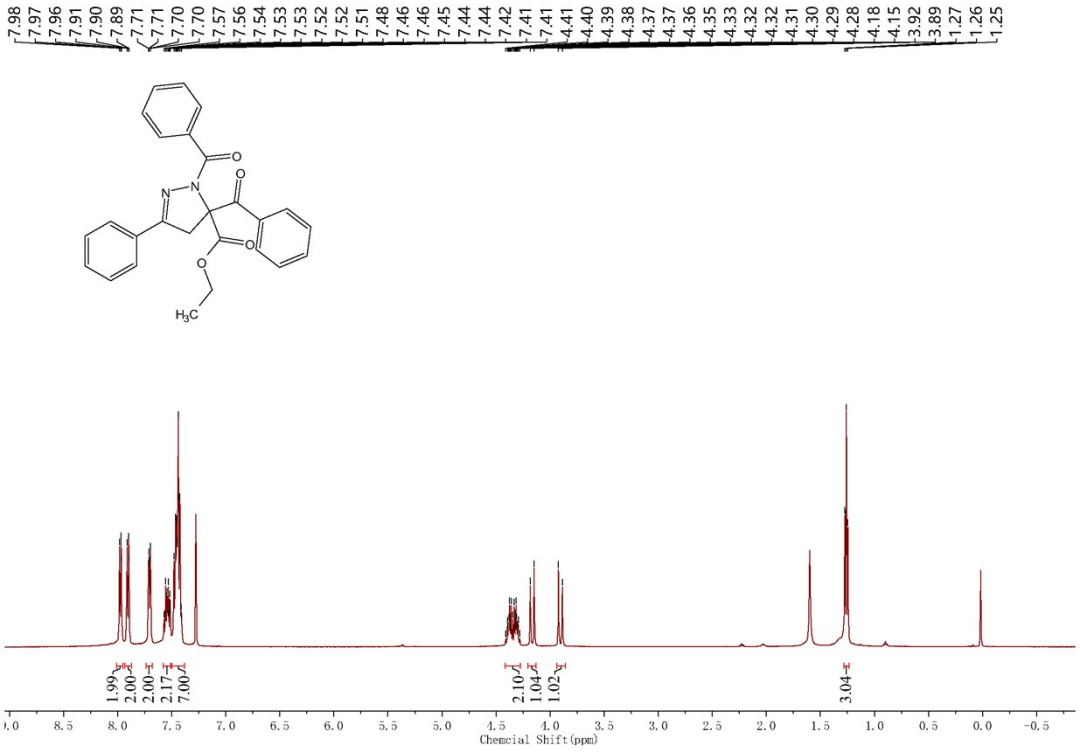
^{13}C NMR Spectrum of Compound **3ae'** (125MHz, $CDCl_3$)



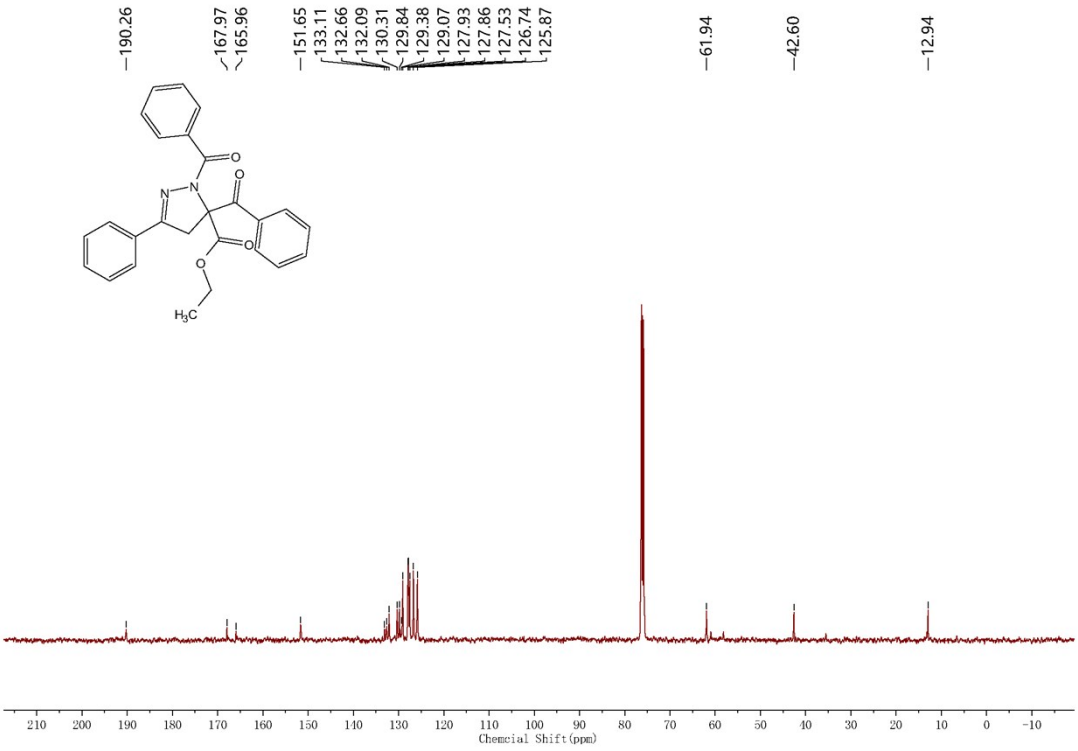
^{1}H NMR Spectrum of Compound **3af** (500MHz, $CDCl_3$)



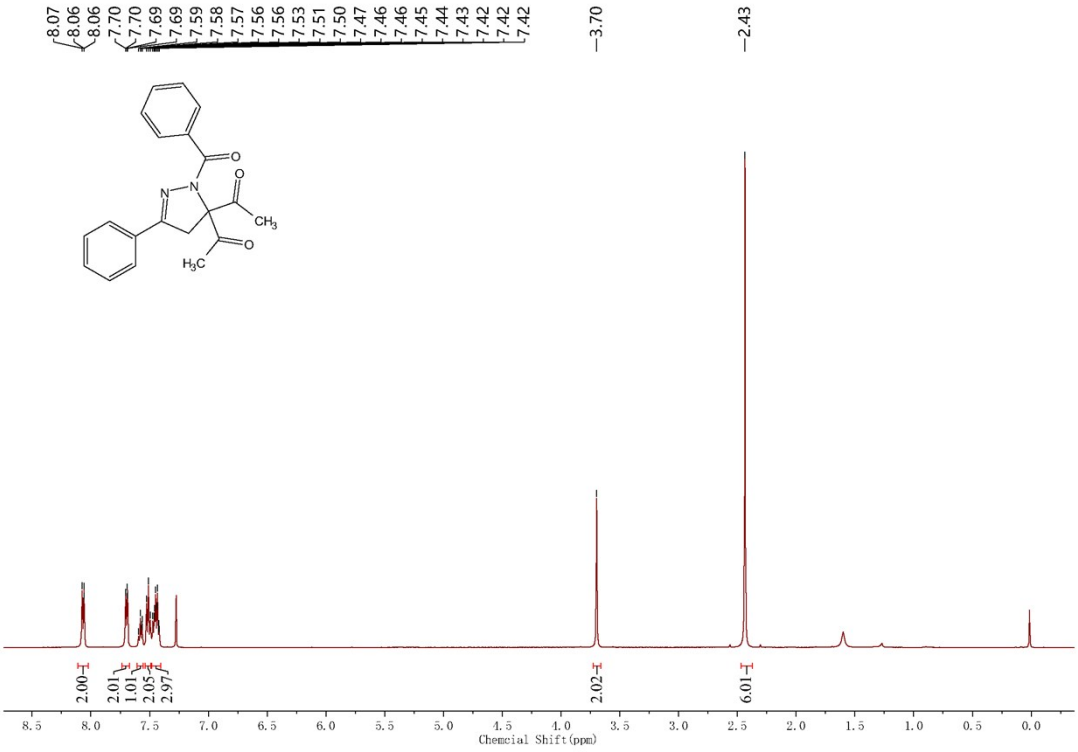
^{13}C NMR Spectrum of Compound **3af** (125MHz, $CDCl_3$)



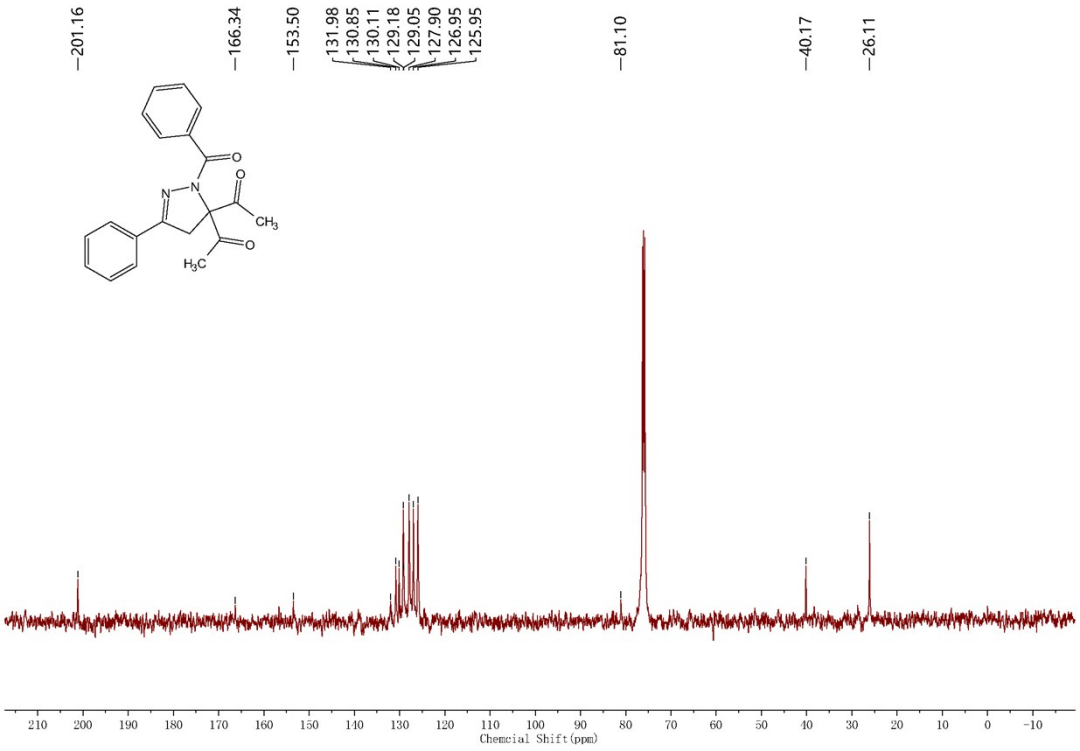
^{1}H NMR Spectrum of Compound **3ag** (500MHz, $CDCl_3$)



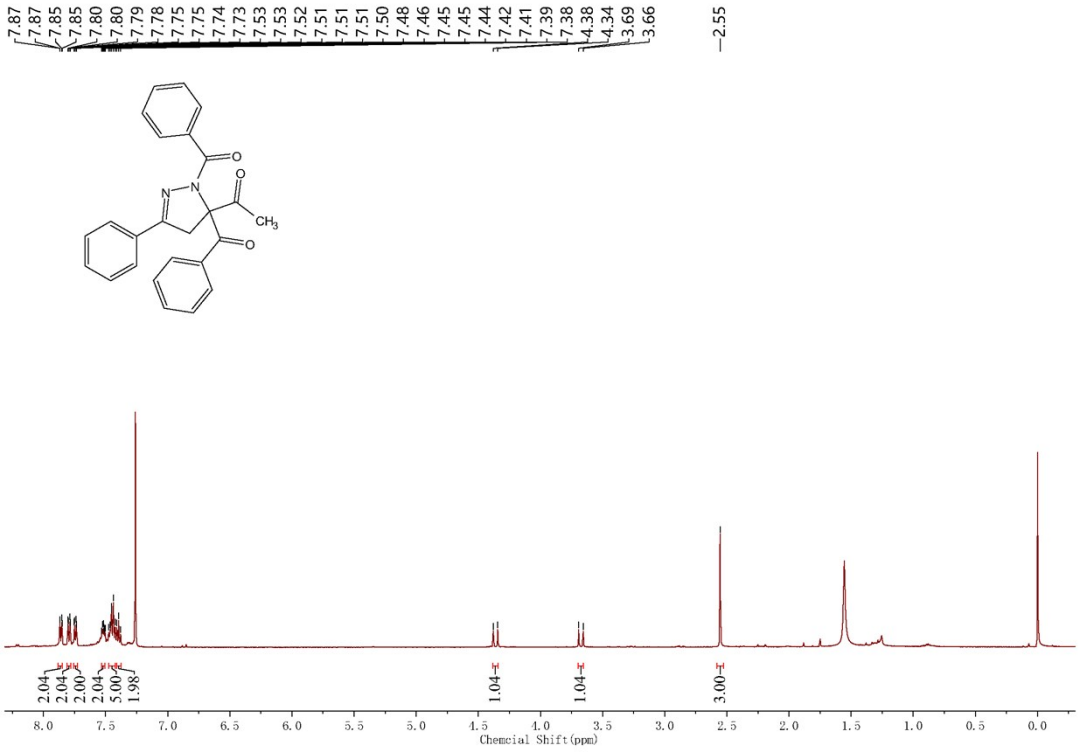
^{13}C NMR Spectrum of Compound **3ag** (125MHz, $CDCl_3$)



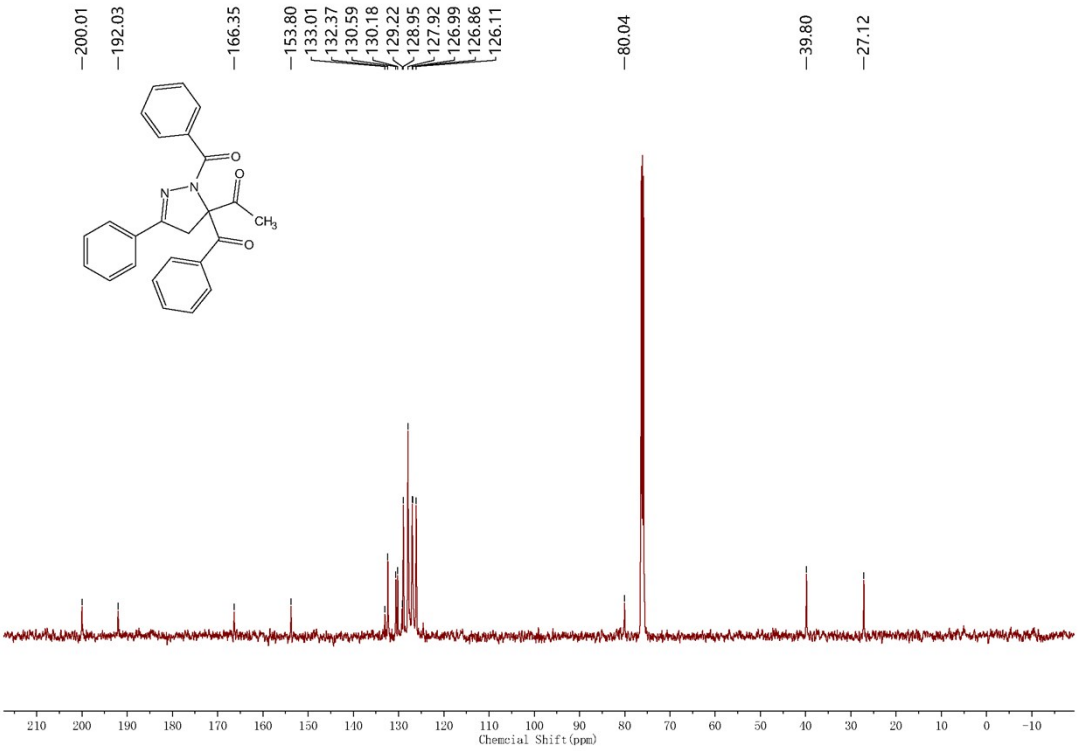
^{1}H NMR Spectrum of Compound **3ah** (500MHz, $CDCl_3$)



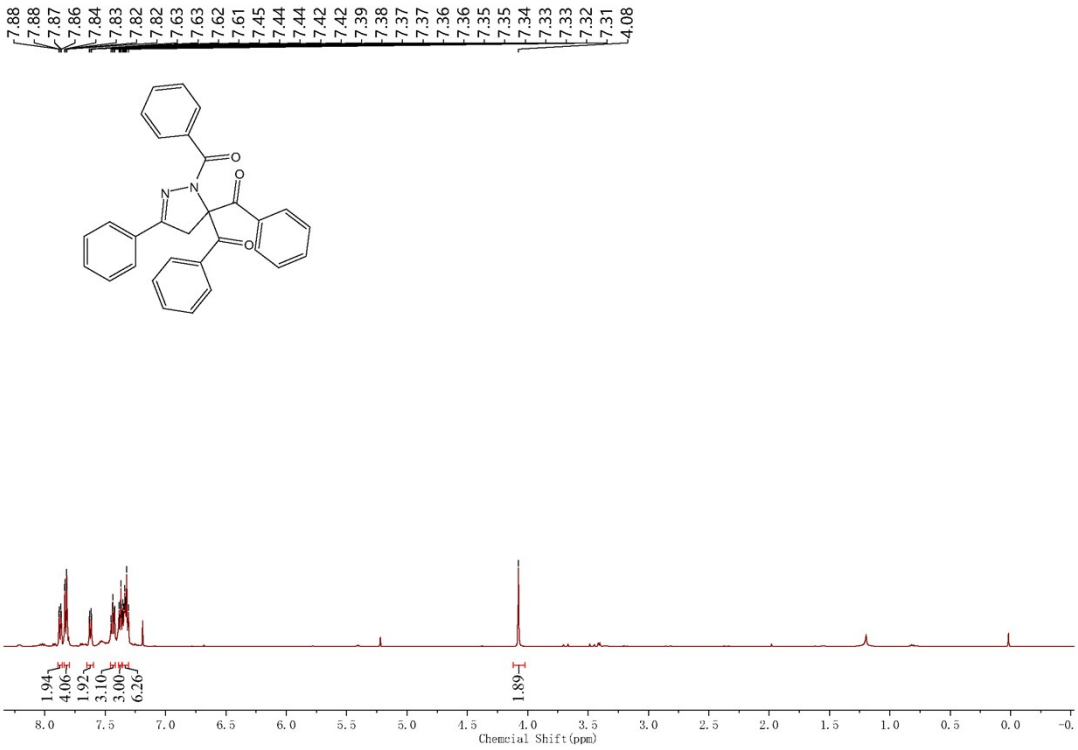
^{13}C NMR Spectrum of Compound **3ah** (125MHz, $CDCl_3$)



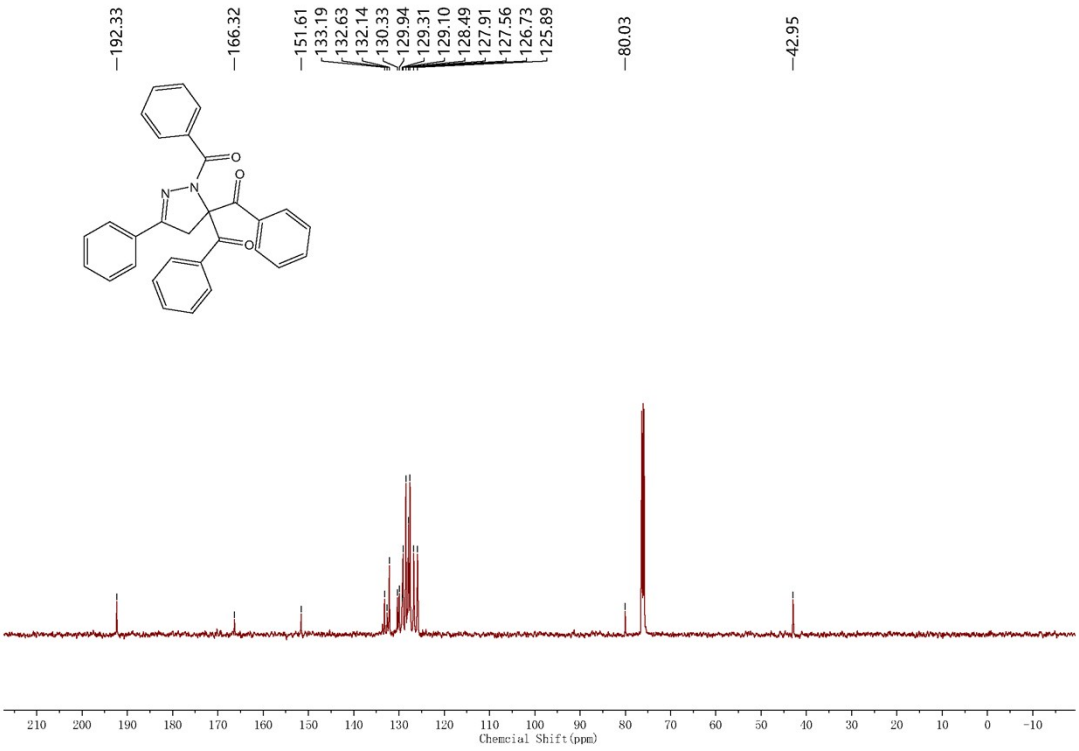
^{1}H NMR Spectrum of Compound **3ai** (500MHz, $CDCl_3$)



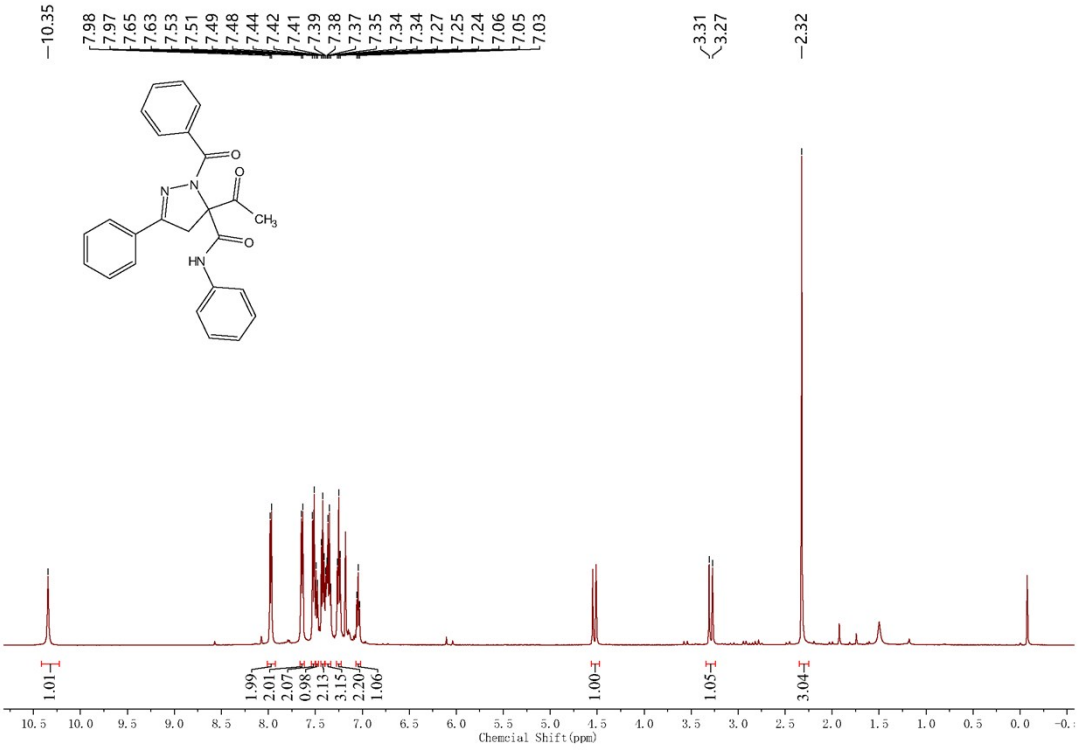
^{13}C NMR Spectrum of Compound **3ai** (125MHz, $CDCl_3$)



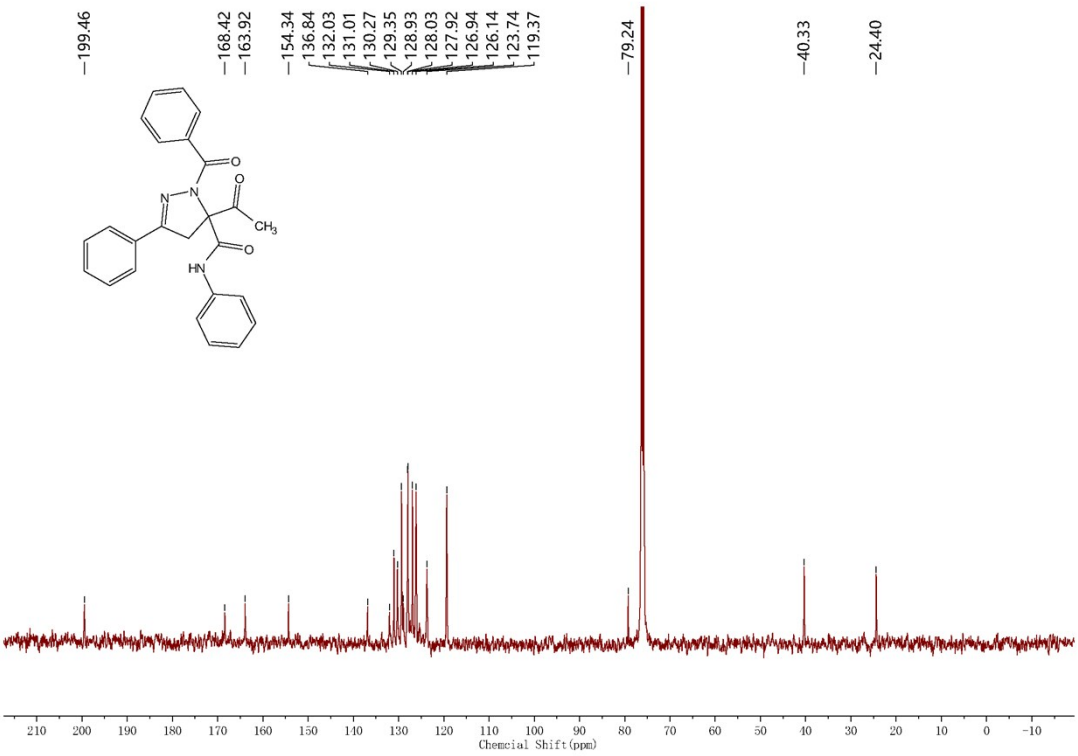
^{1}H NMR Spectrum of Compound **3aj** (500MHz, $CDCl_3$)



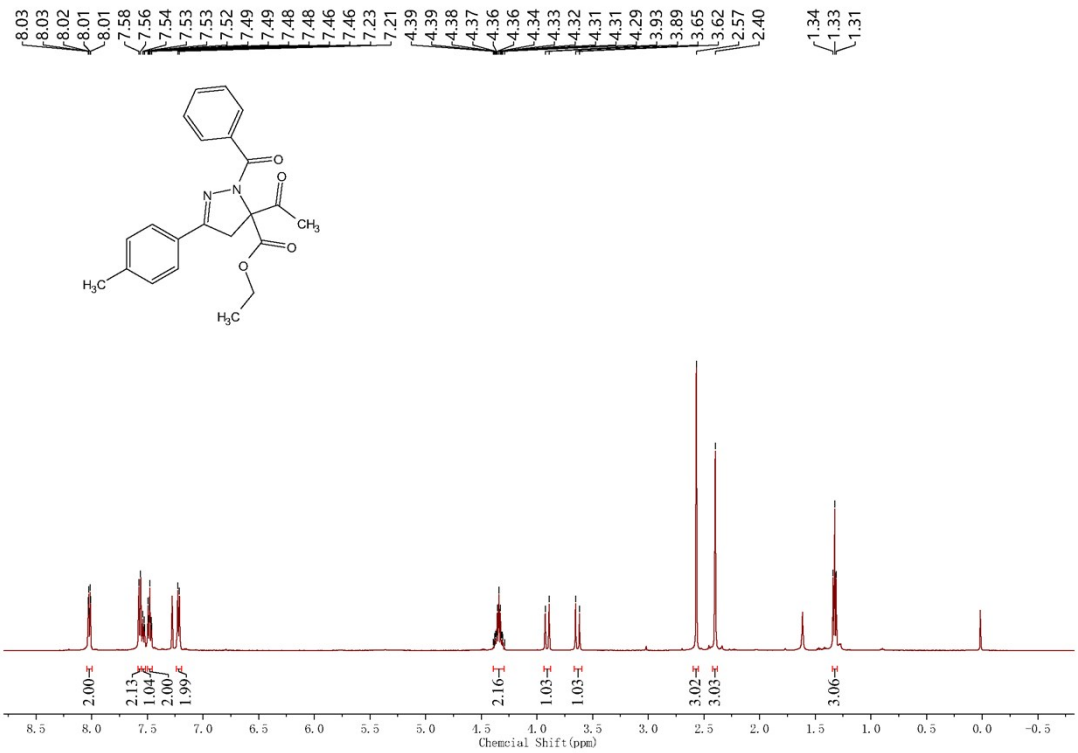
^{13}C NMR Spectrum of Compound **3aj** (125MHz, $CDCl_3$)



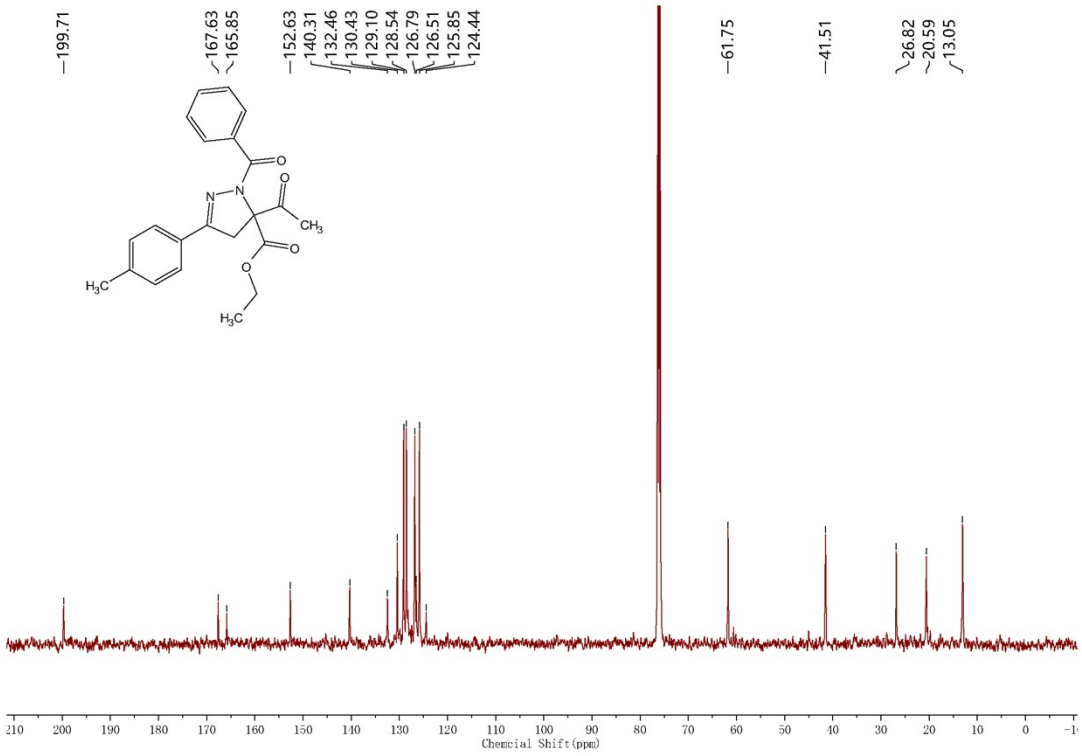
^{1}H NMR Spectrum of Compound **3ak** (500MHz, $CDCl_3$)



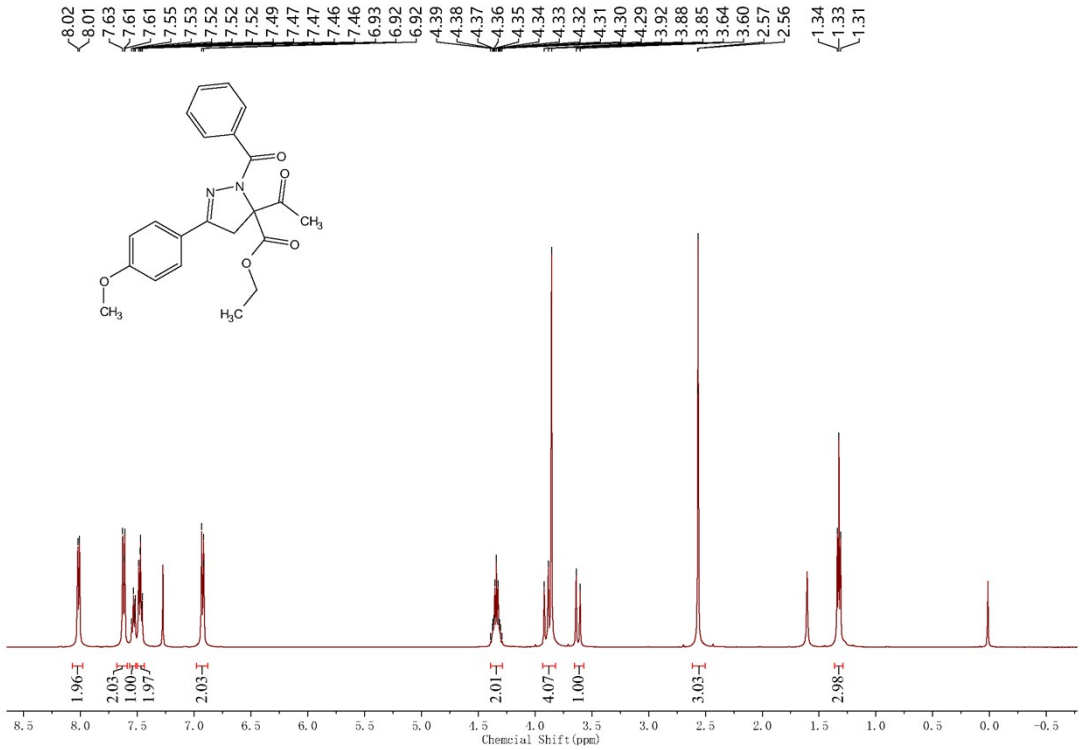
^{13}C NMR Spectrum of Compound **3ak** (125MHz, $CDCl_3$)



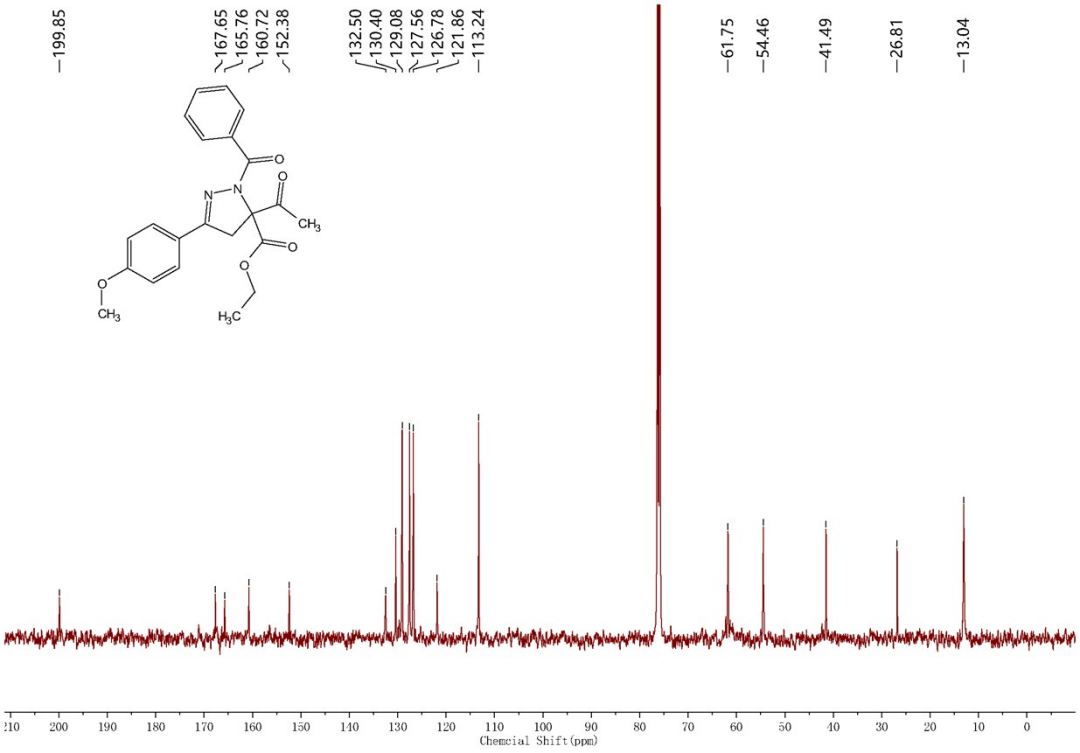
^{1}H NMR Spectrum of Compound **3ba** (500MHz, $CDCl_3$)



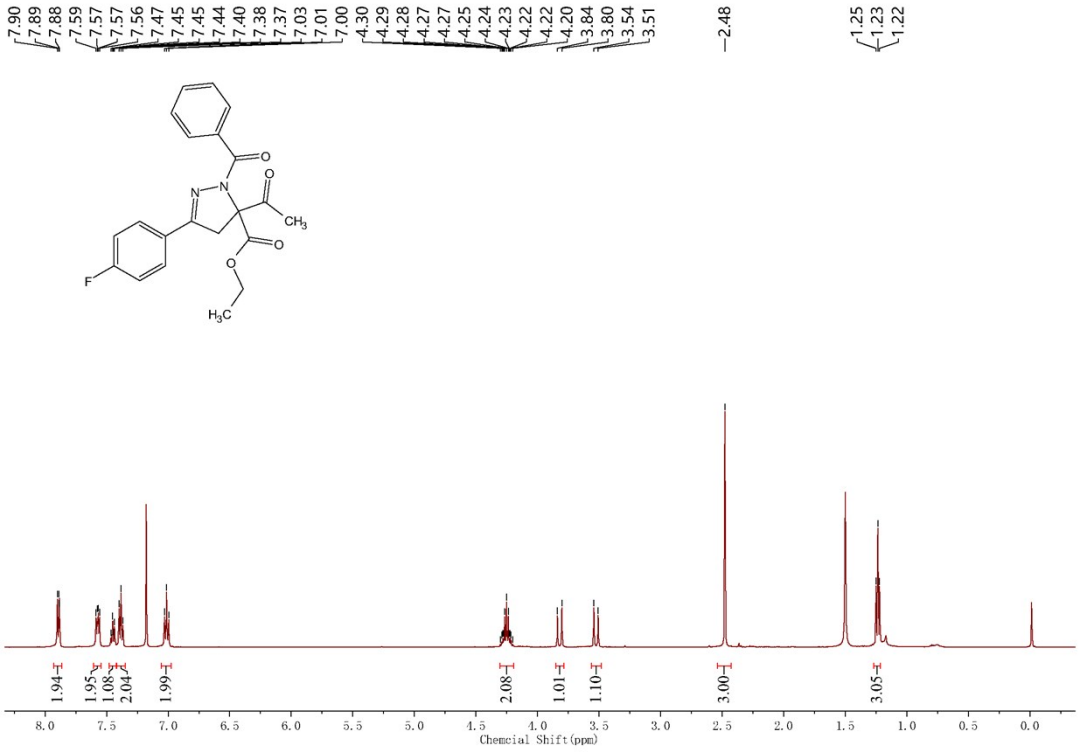
^{13}C NMR Spectrum of Compound **3ba** (125MHz, $CDCl_3$)



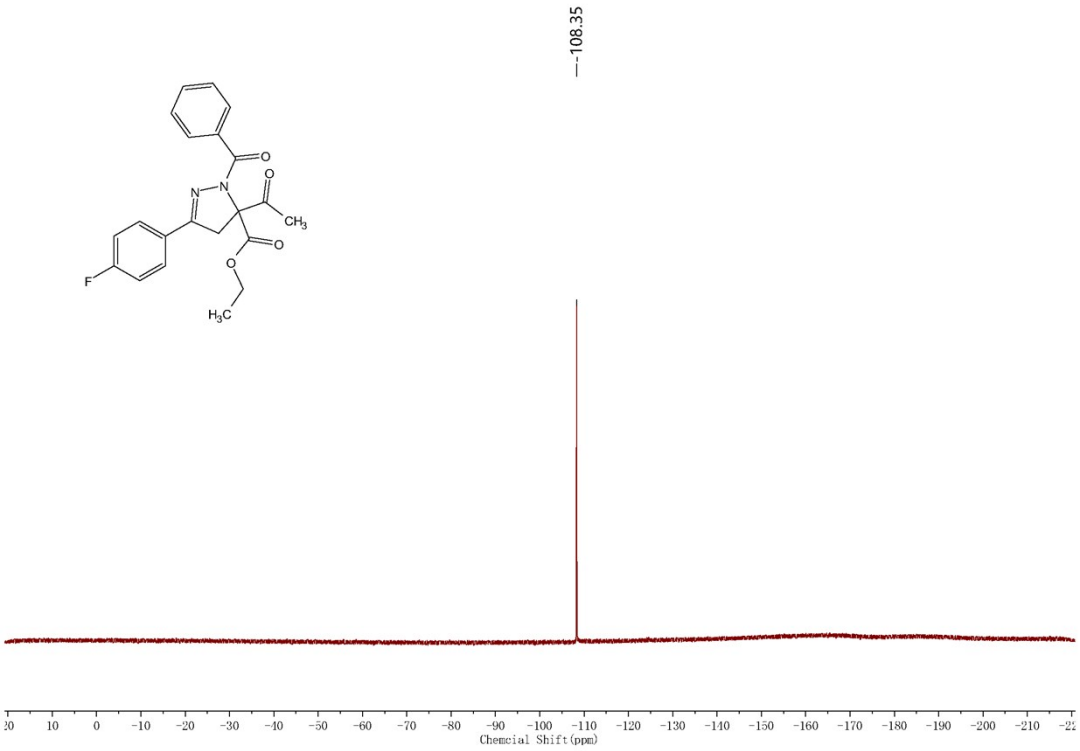
^{1}H NMR Spectrum of Compound **3ca** (500MHz, $CDCl_3$)



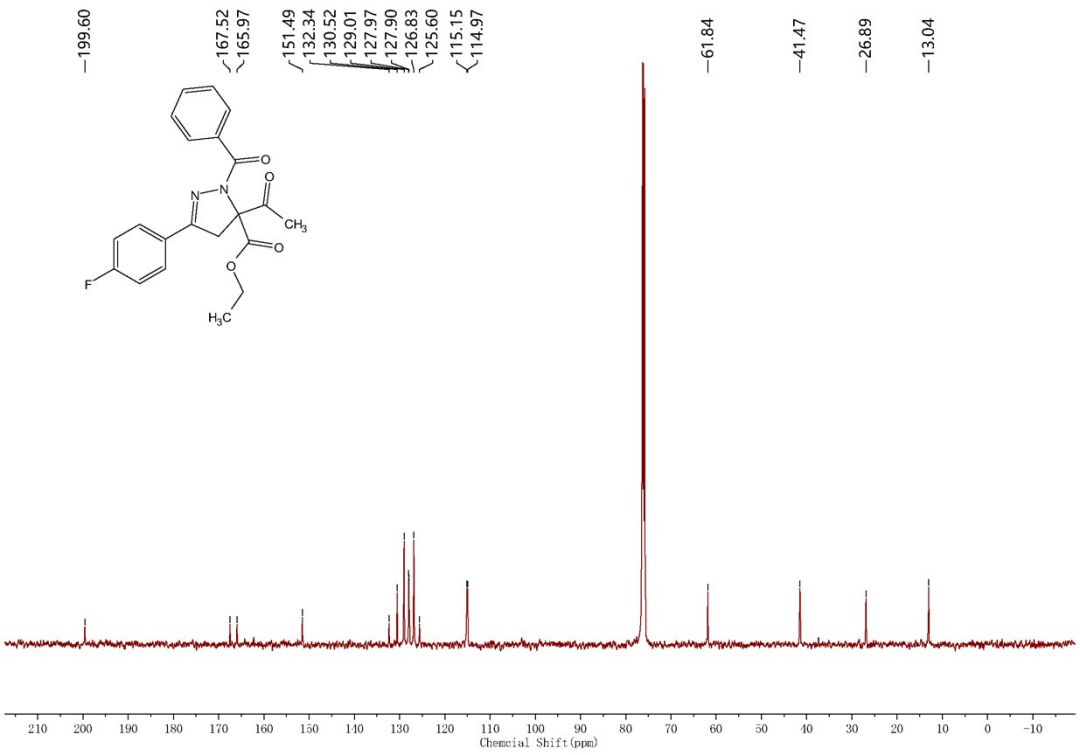
^{13}C NMR Spectrum of Compound **3ca** (125MHz, $CDCl_3$)



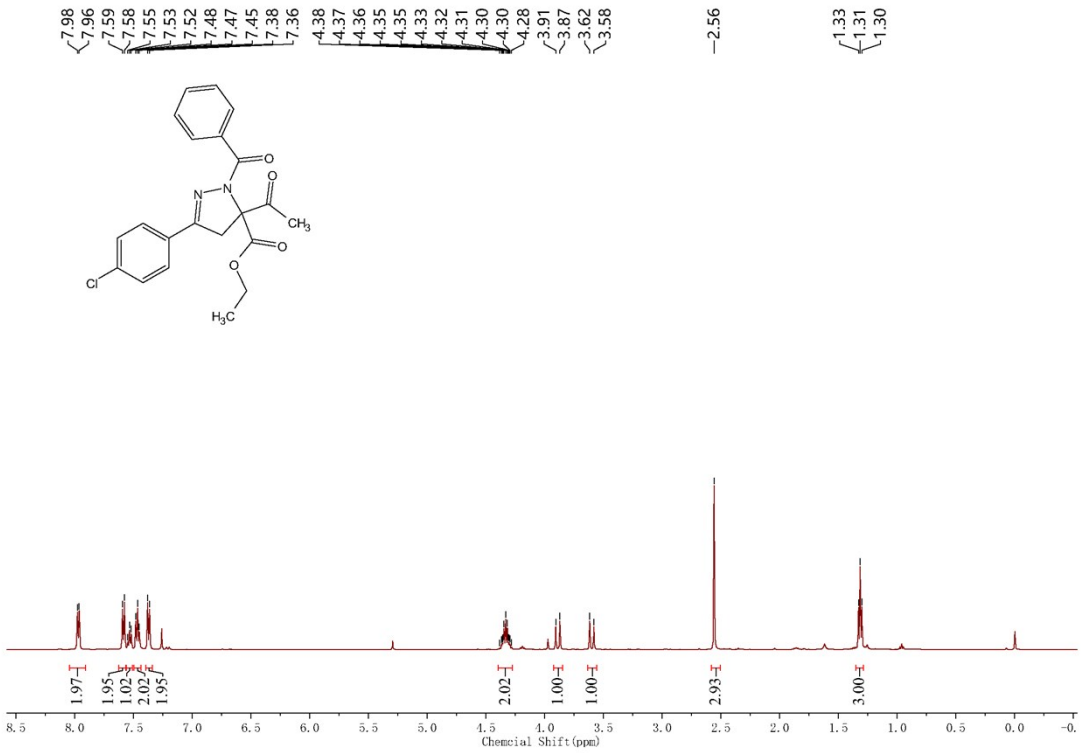
^{1}H NMR Spectrum of Compound **3da** (500MHz, $CDCl_3$)



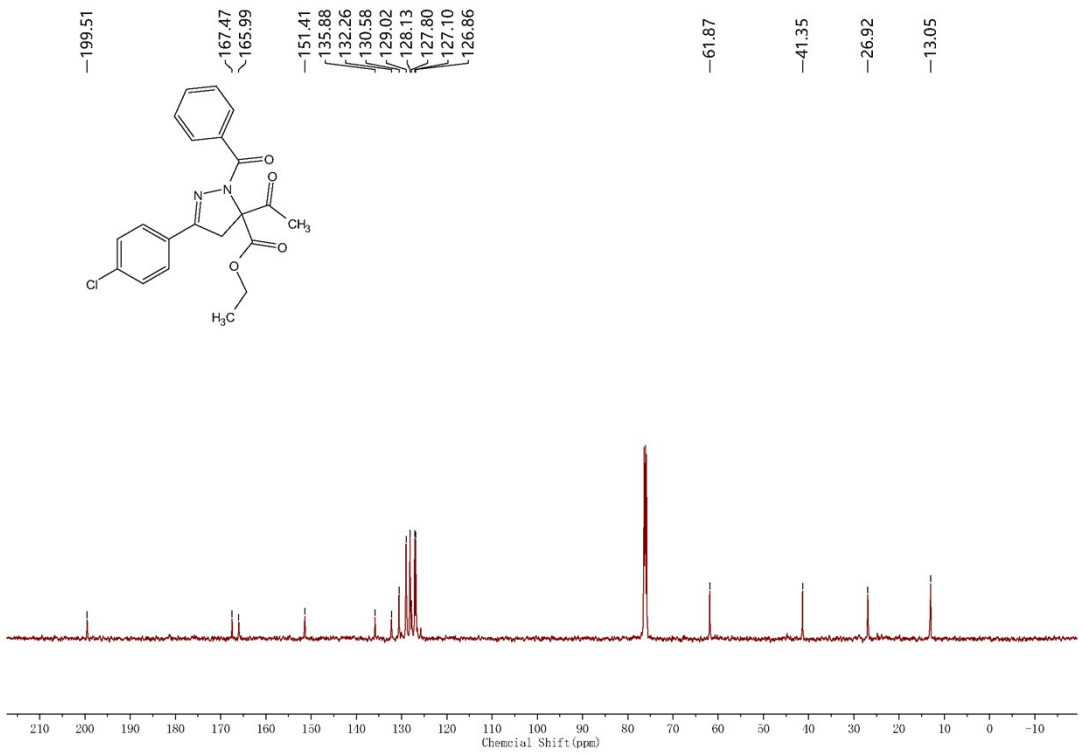
^{19}F NMR Spectrum of Compound **3da** (470MHz, $CDCl_3$)



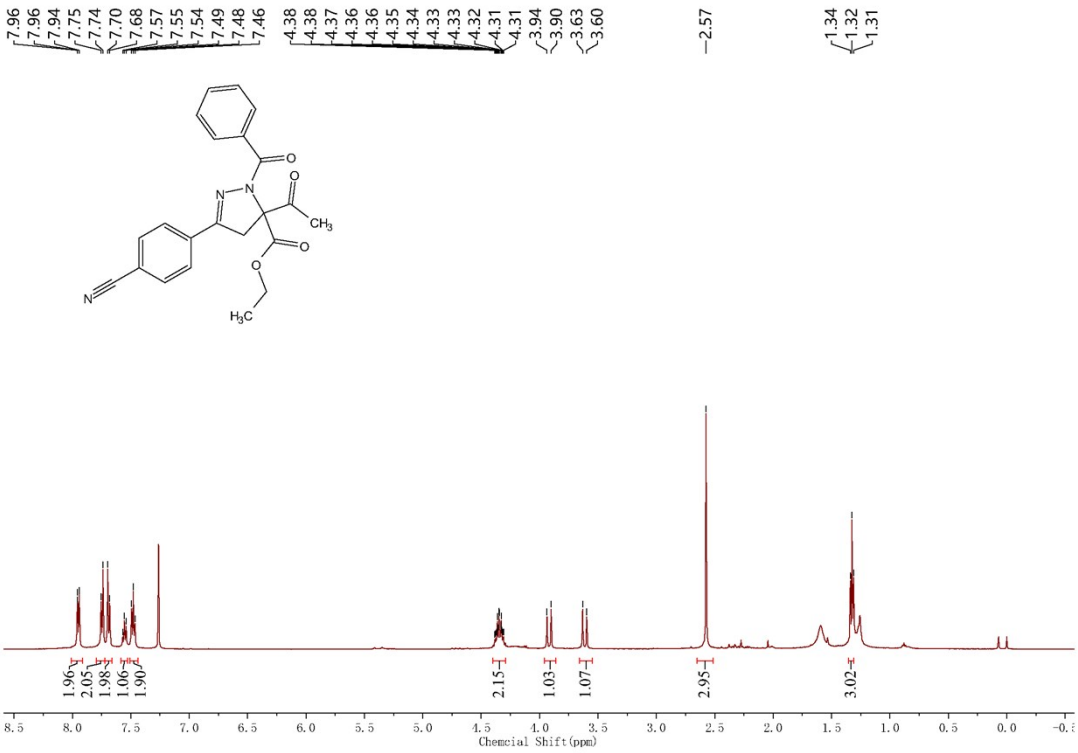
^{13}C NMR Spectrum of Compound **3da** (125MHz, $CDCl_3$)



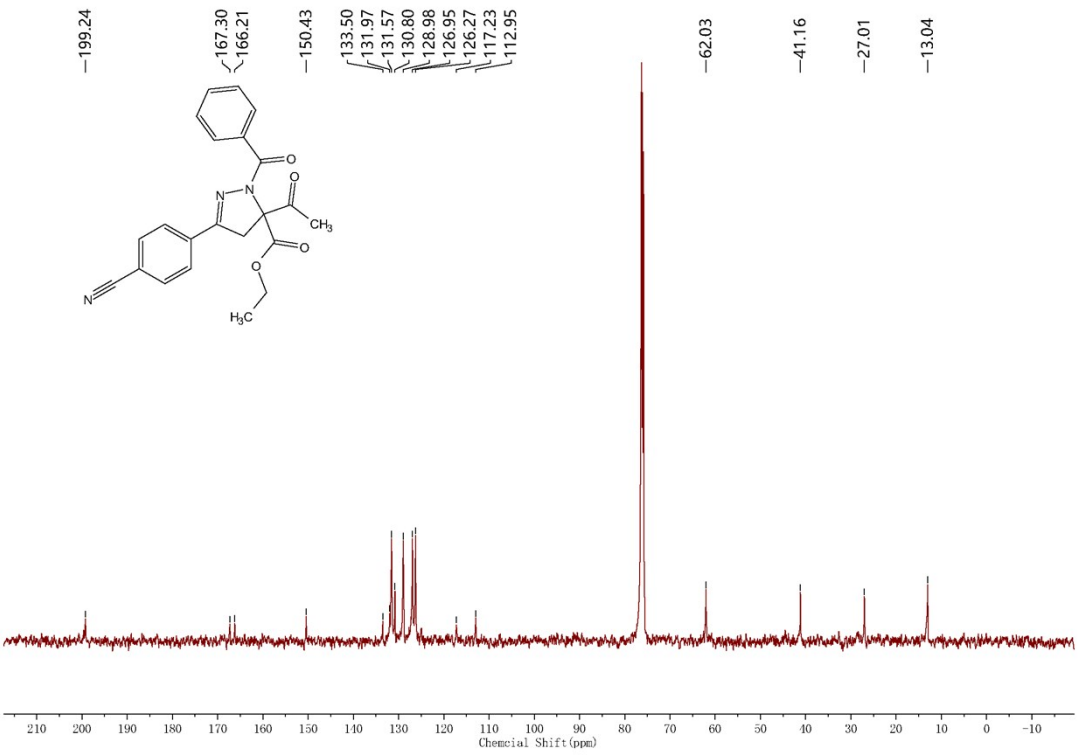
^{1}H NMR Spectrum of Compound **3ea** (500MHz, $CDCl_3$)



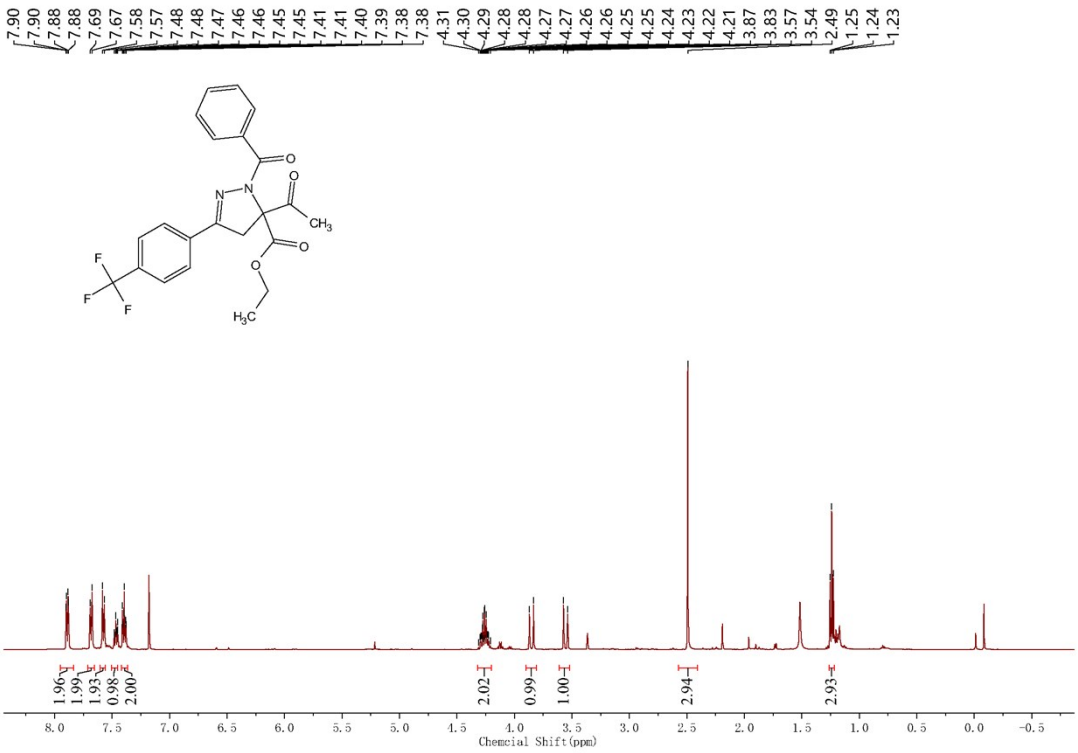
^{13}C NMR Spectrum of Compound **3ea** (125MHz, $CDCl_3$)



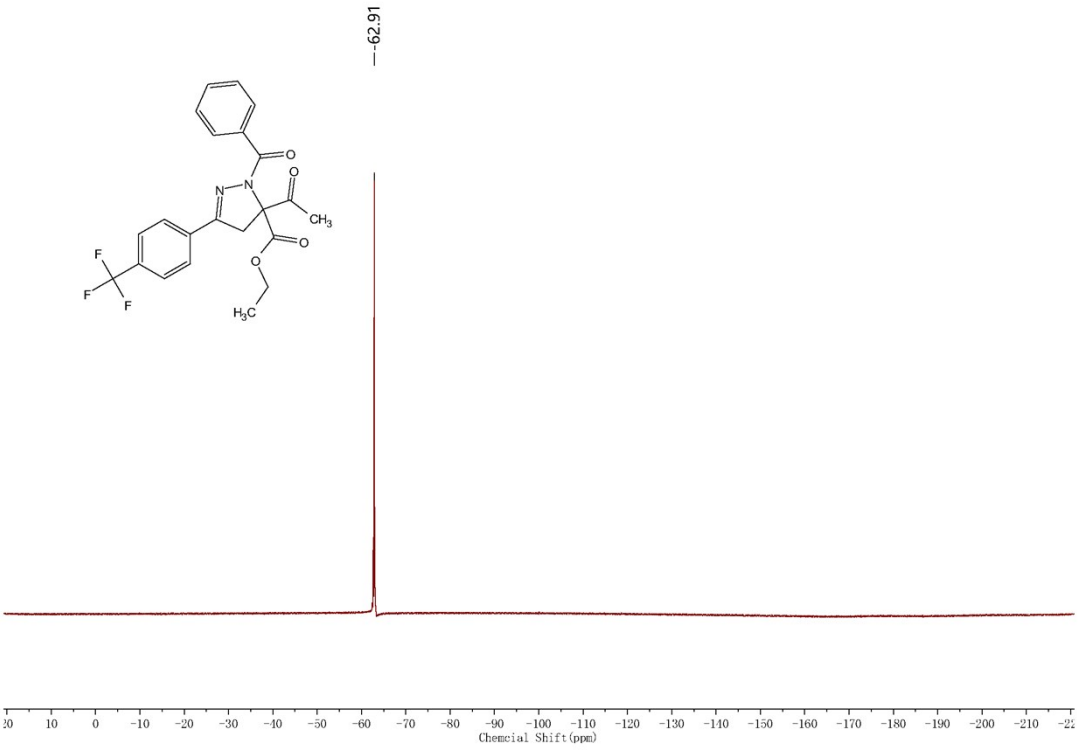
^{1}H NMR Spectrum of Compound **3fa** (500MHz, $CDCl_3$)



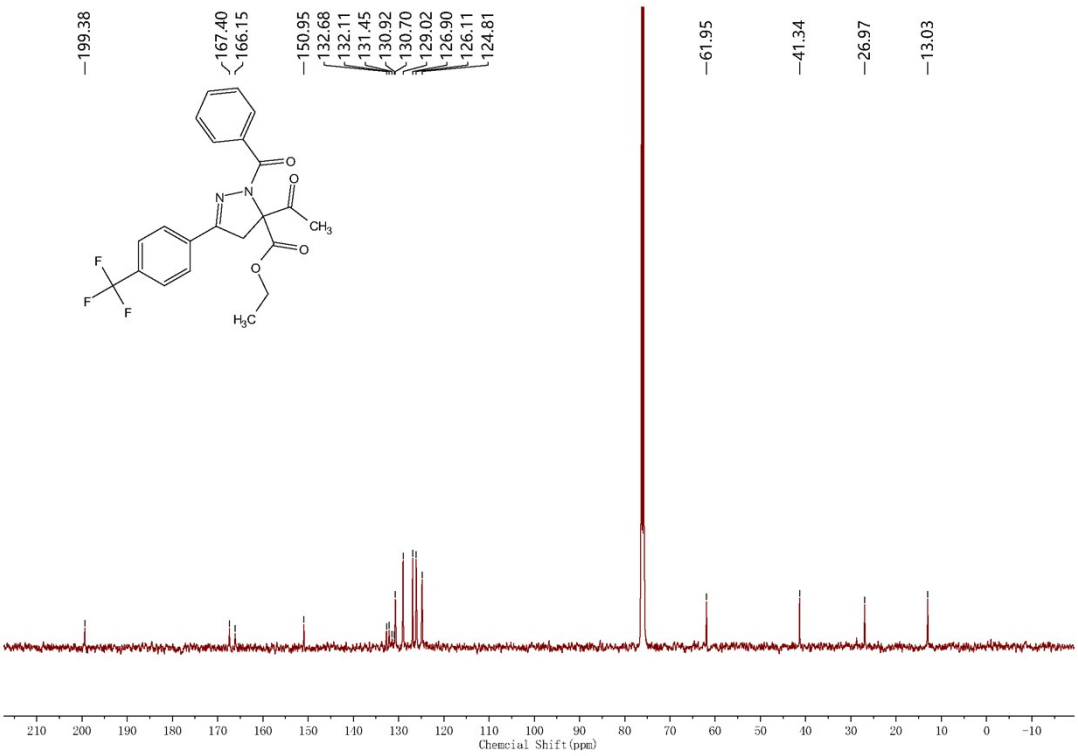
^{13}C NMR Spectrum of Compound **3fa** (125MHz, $CDCl_3$)



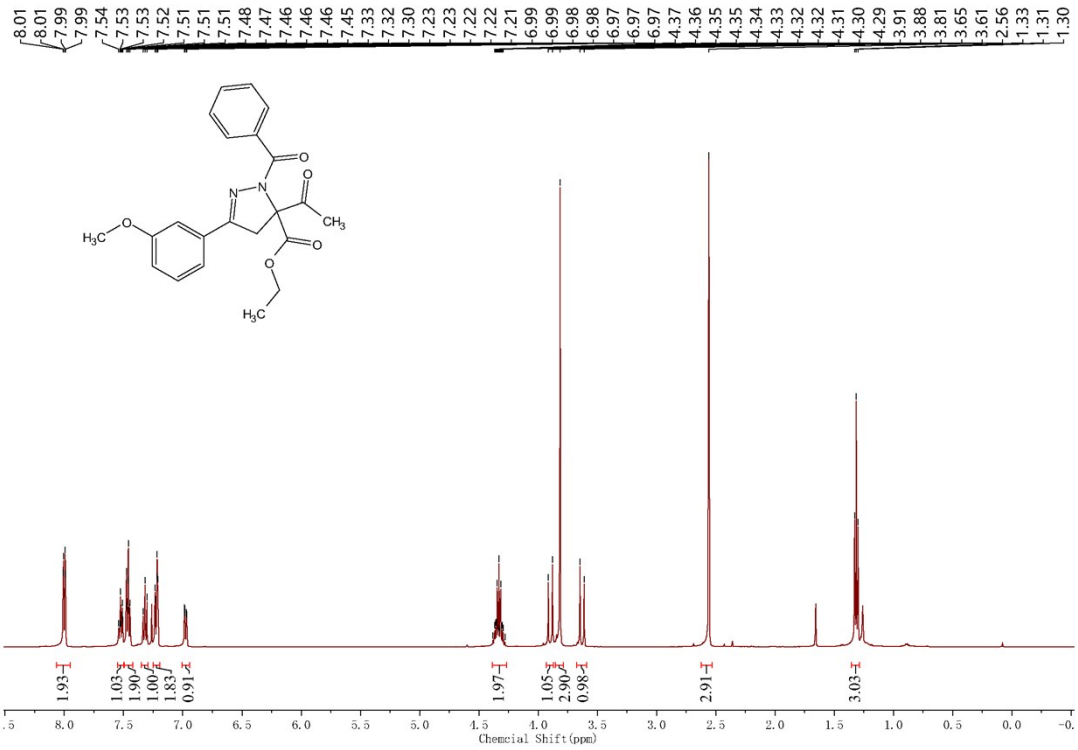
^{1}H NMR Spectrum of Compound **3ga** (500MHz, $CDCl_3$)



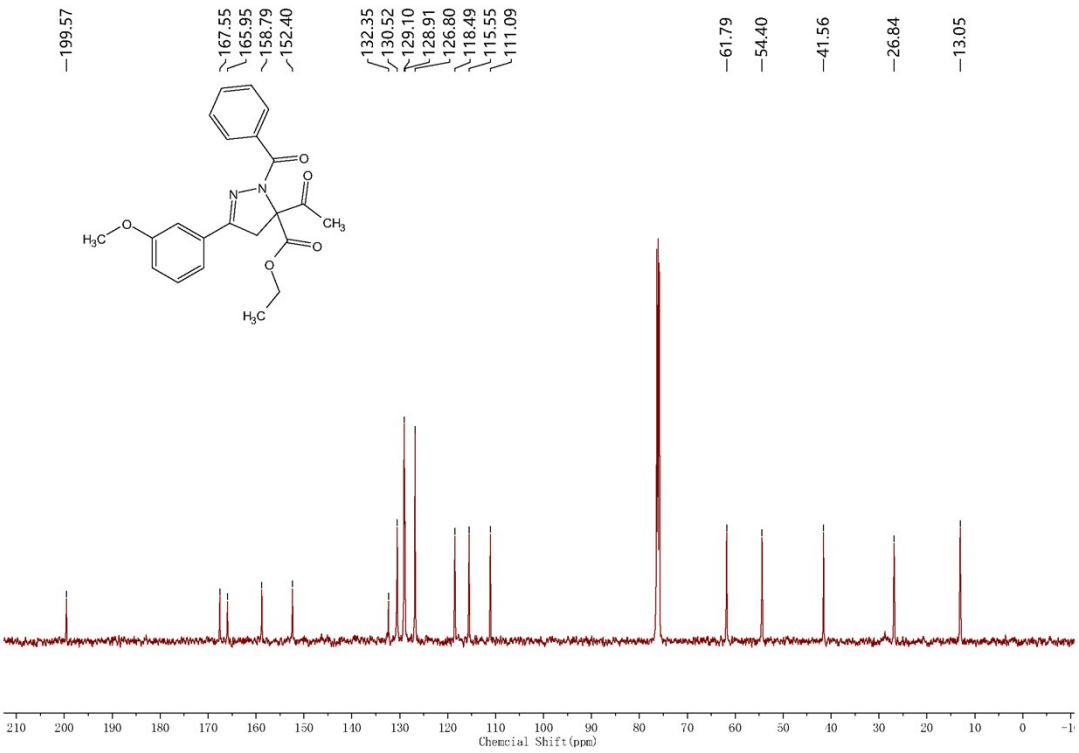
^{19}F NMR Spectrum of Compound **3ga** (470MHz, $CDCl_3$)



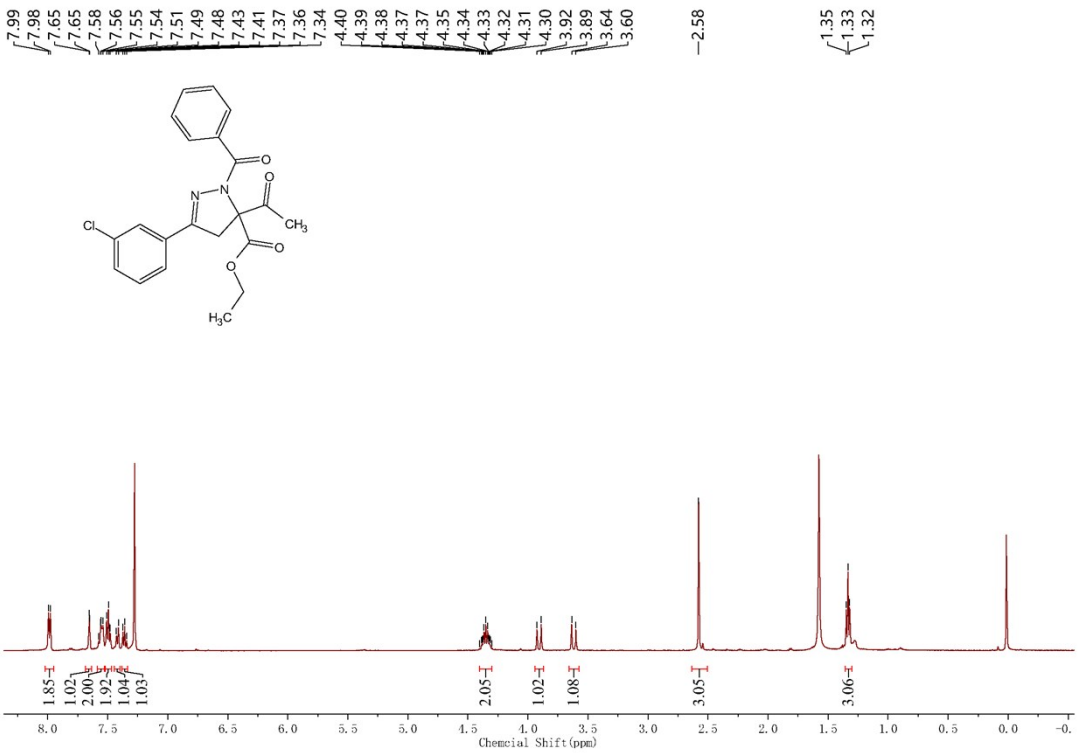
^{13}C NMR Spectrum of Compound **3ga** (125MHz, $CDCl_3$)



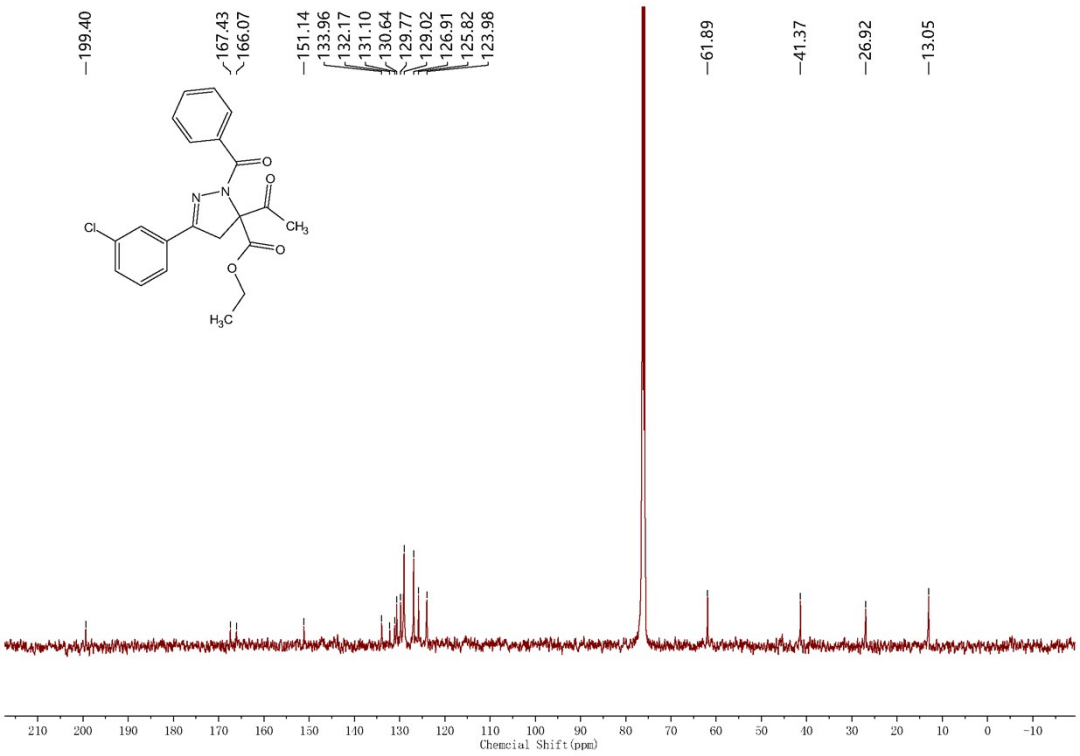
^{1}H NMR Spectrum of Compound **3ha** (500MHz, $CDCl_3$)



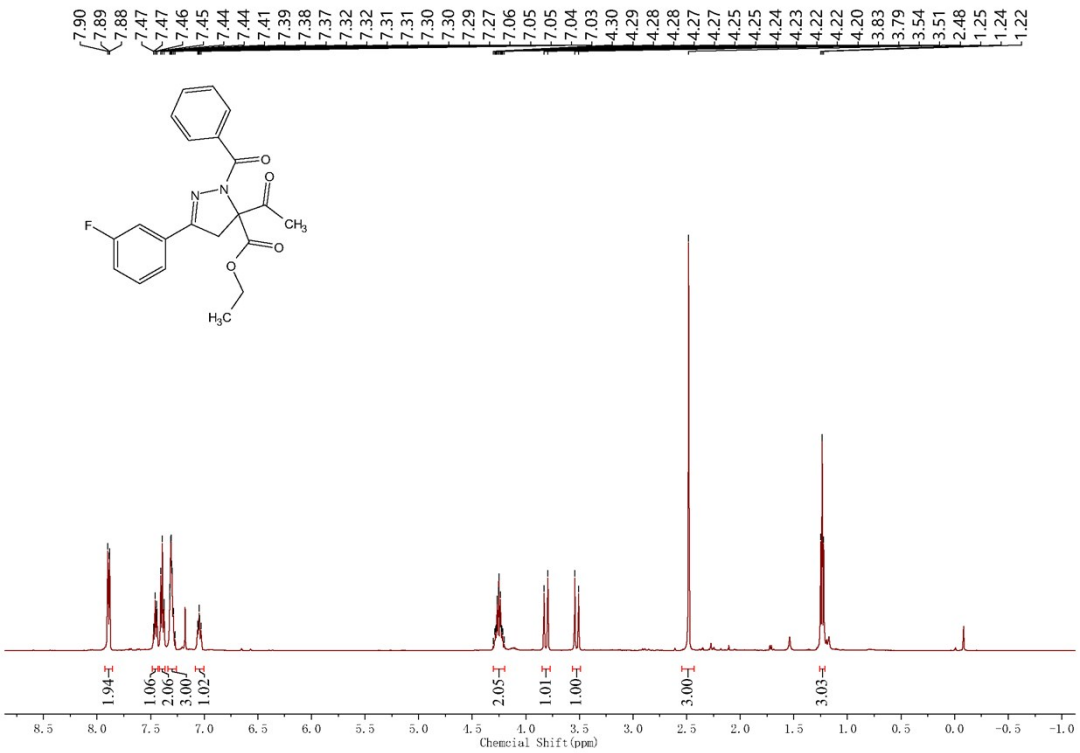
^{13}C NMR Spectrum of Compound **3ha** (125MHz, $CDCl_3$)



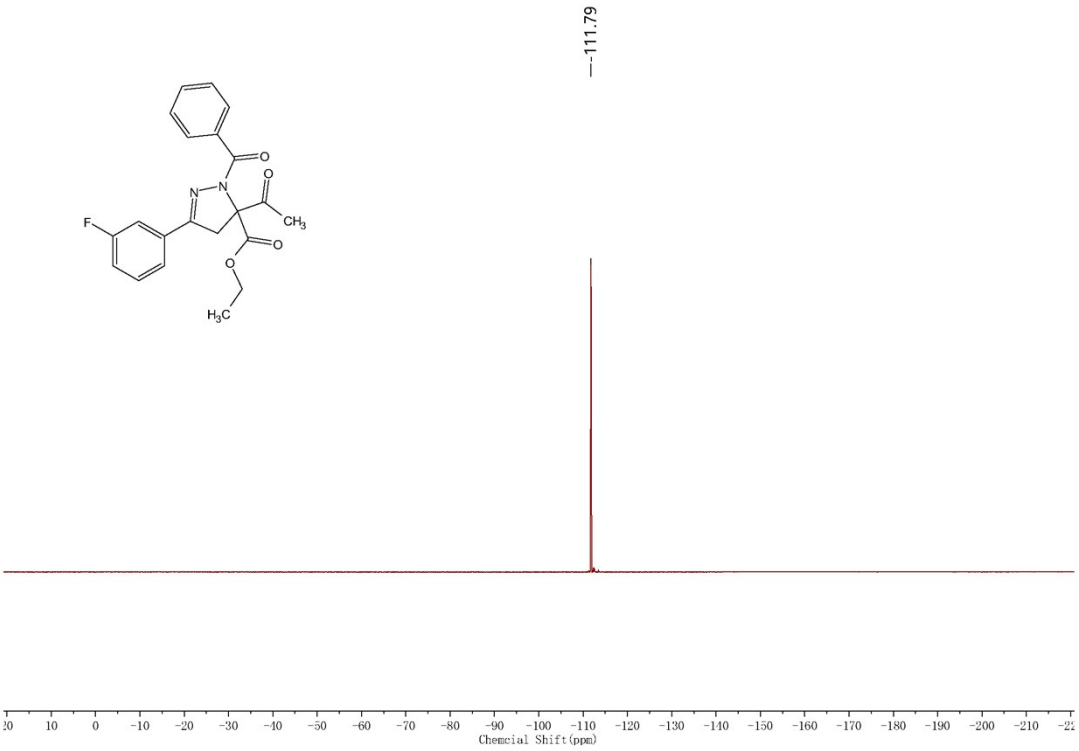
^{1}H NMR Spectrum of Compound **3ia** (500MHz, $CDCl_3$)



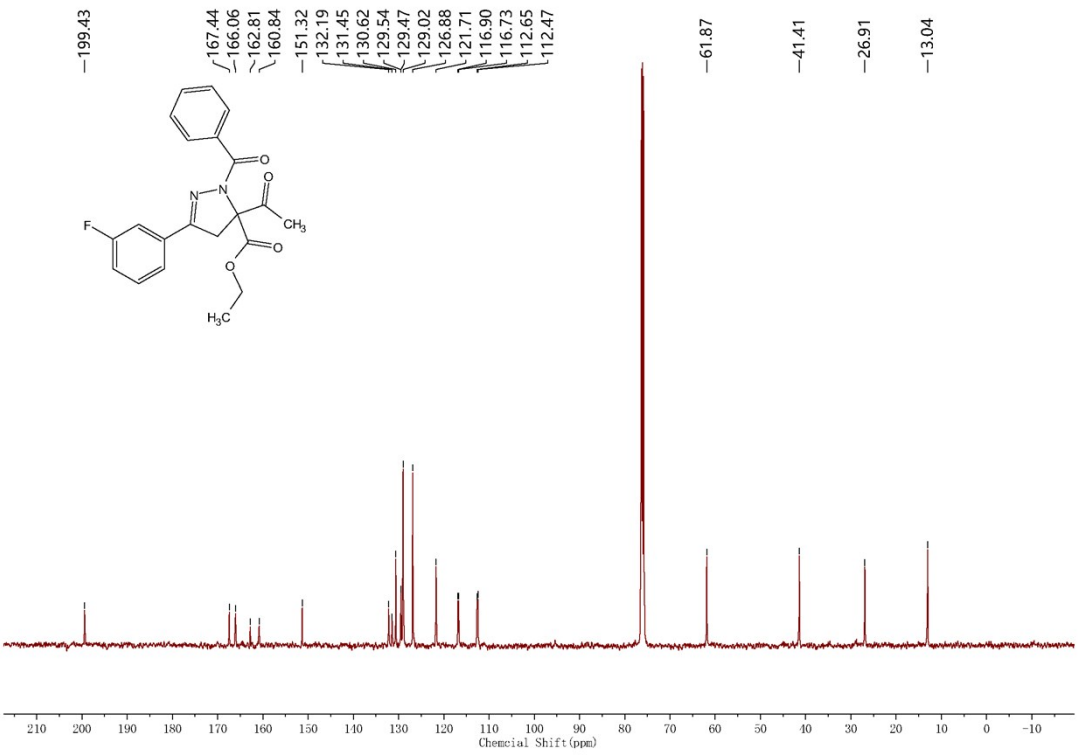
^{13}C NMR Spectrum of Compound **3ia** (125MHz, $CDCl_3$)



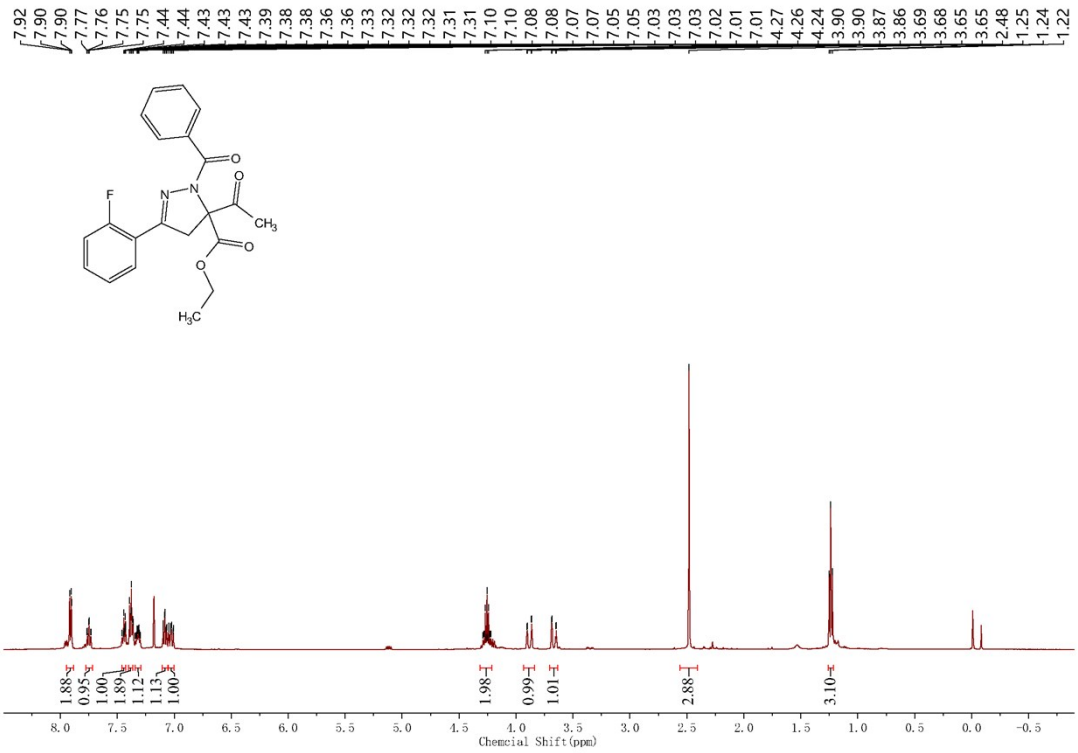
^{1}H NMR Spectrum of Compound **3ja** (500MHz, $CDCl_3$)



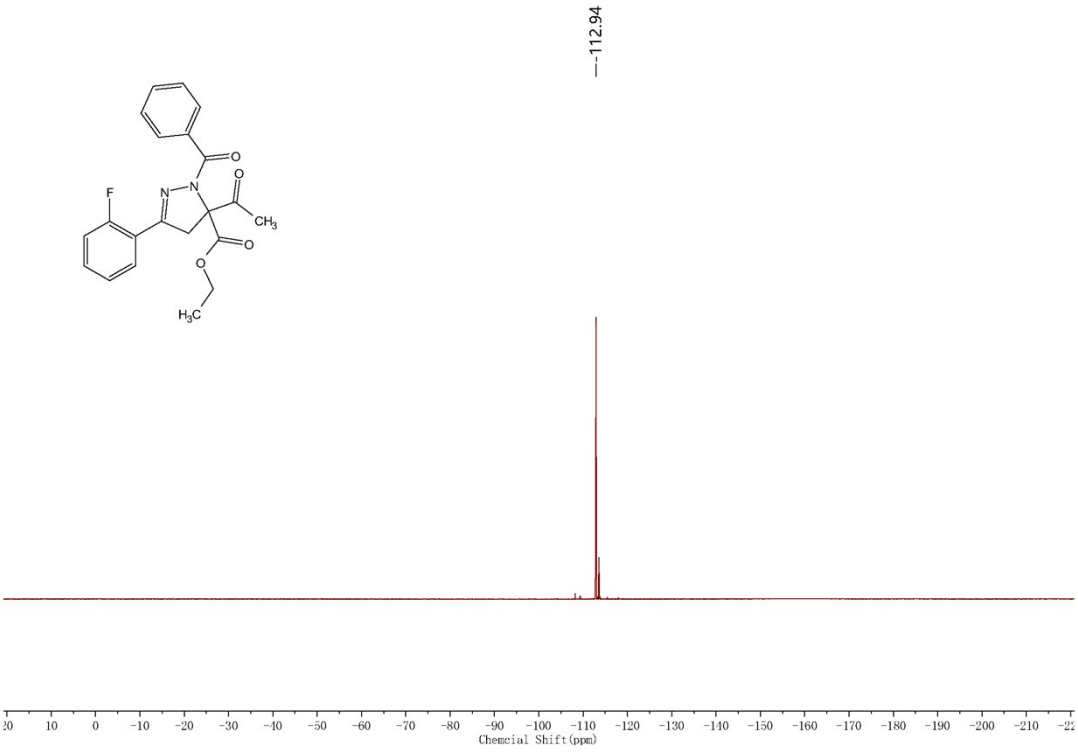
^{19}F NMR Spectrum of Compound **3ja** (470MHz, $CDCl_3$)



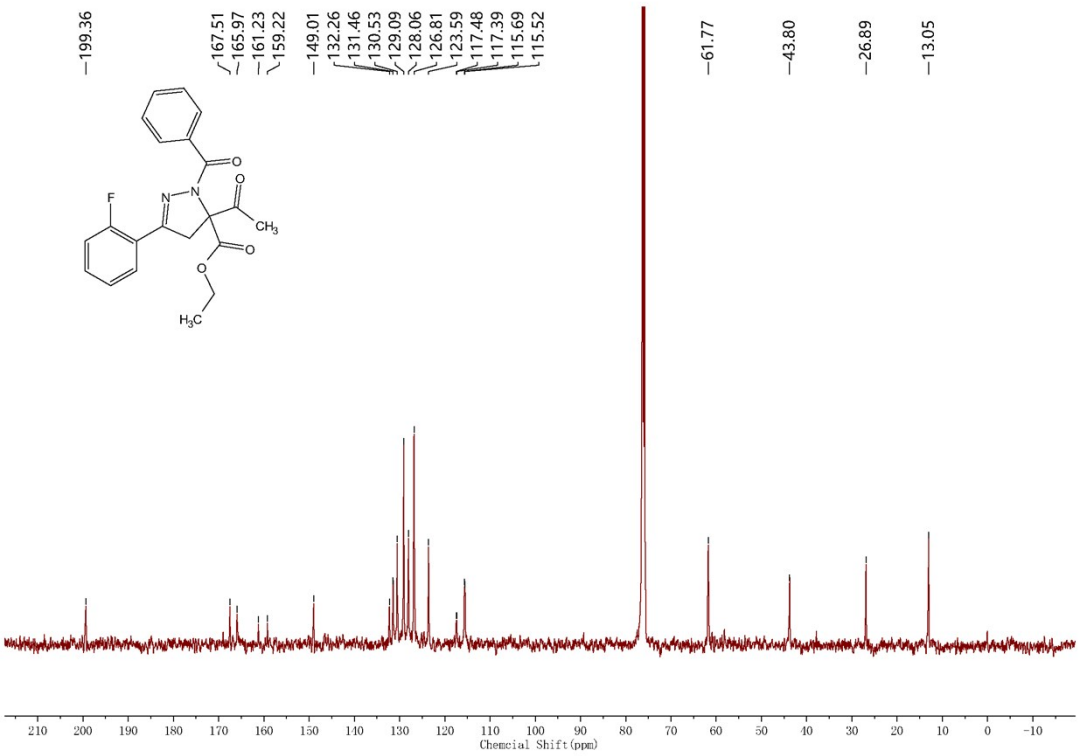
^{13}C NMR Spectrum of Compound **3ja** (125MHz, $CDCl_3$)



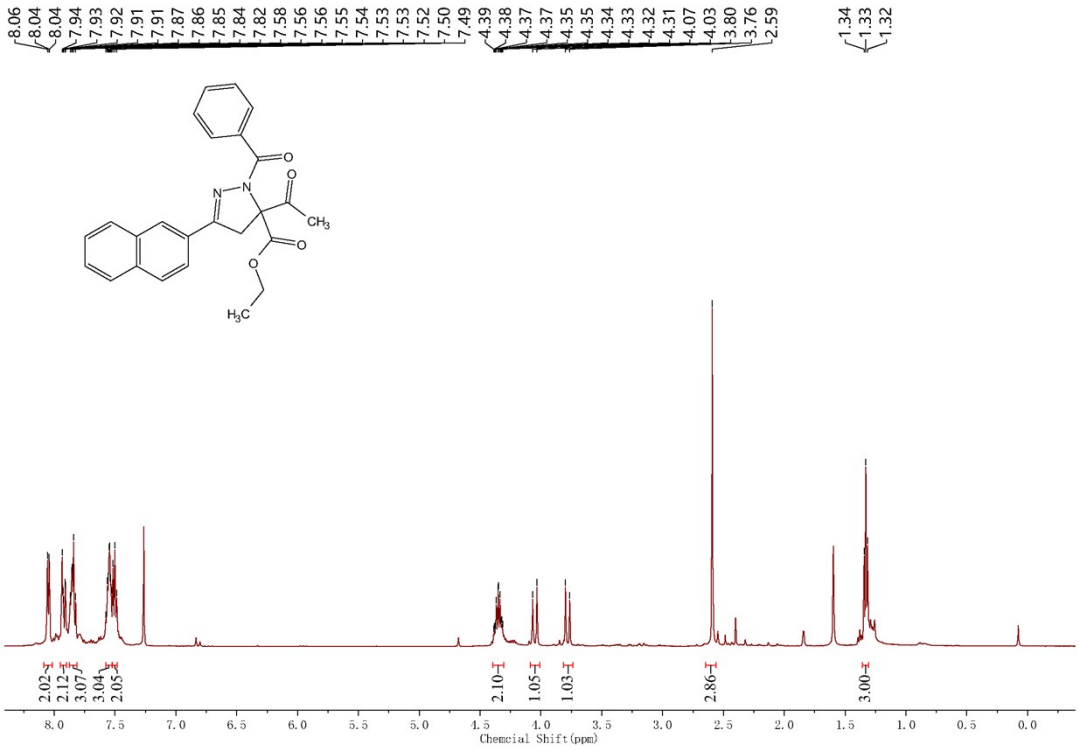
^{1}H NMR Spectrum of Compound **3ka** (500MHz, $CDCl_3$)



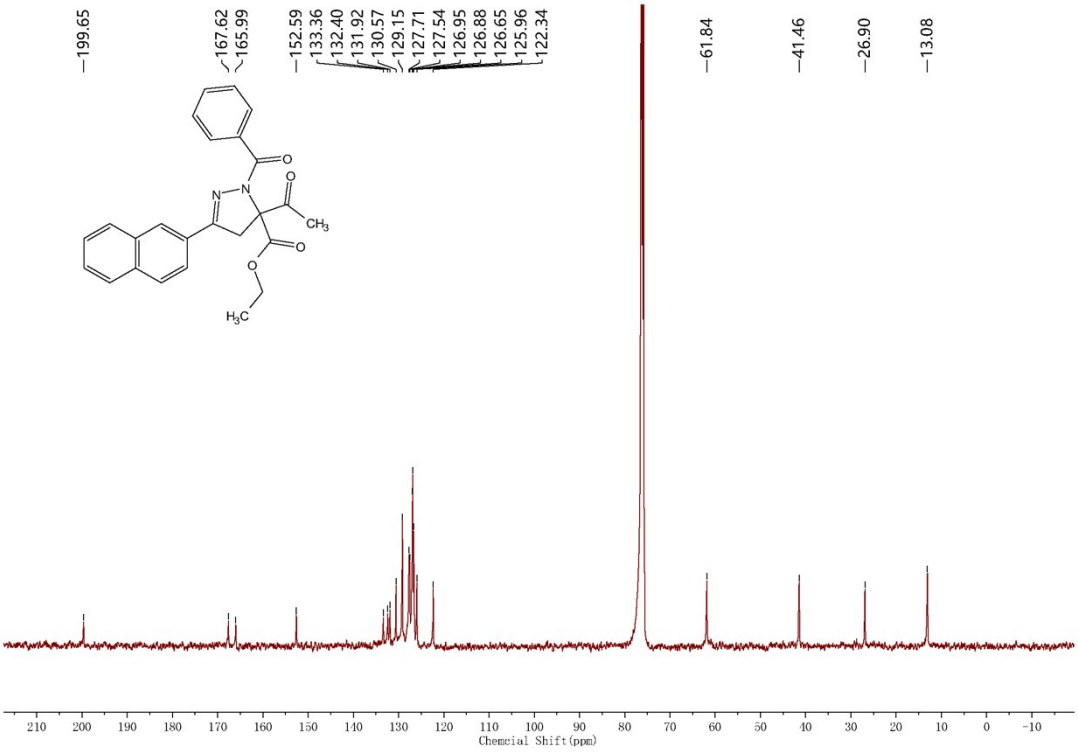
^{19}F NMR Spectrum of Compound **3ka** (470MHz, $CDCl_3$)



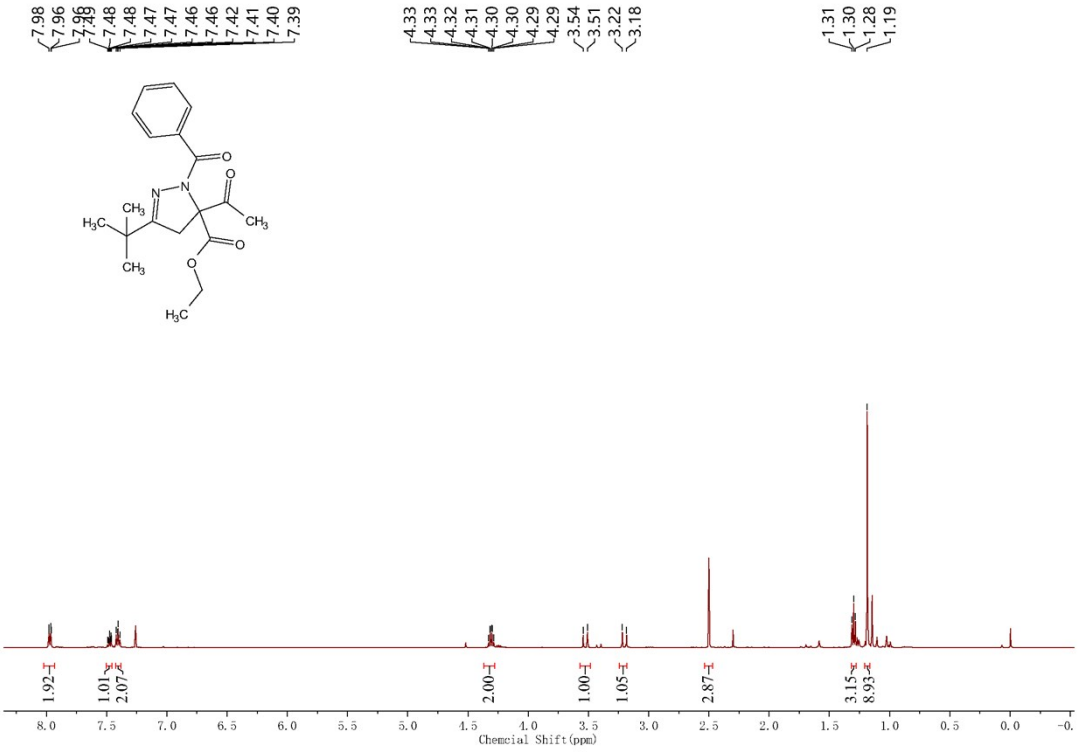
^{13}C NMR Spectrum of Compound **3ka** (125MHz, $CDCl_3$)



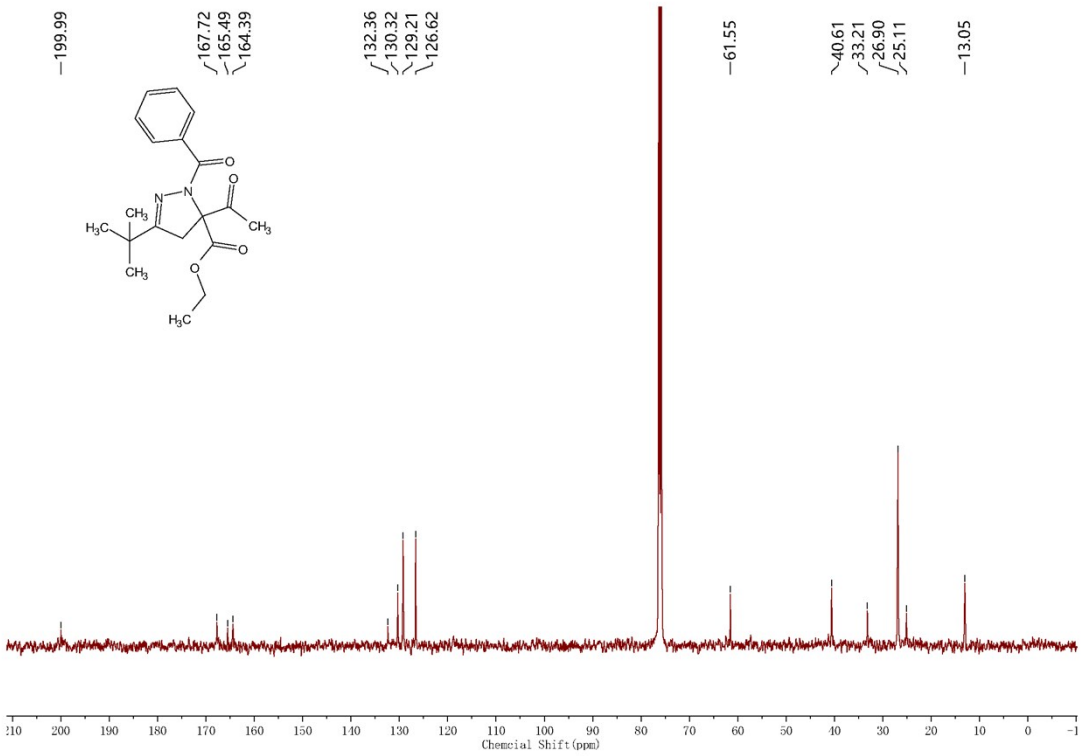
^{1}H NMR Spectrum of Compound **3la** (500MHz, $CDCl_3$)



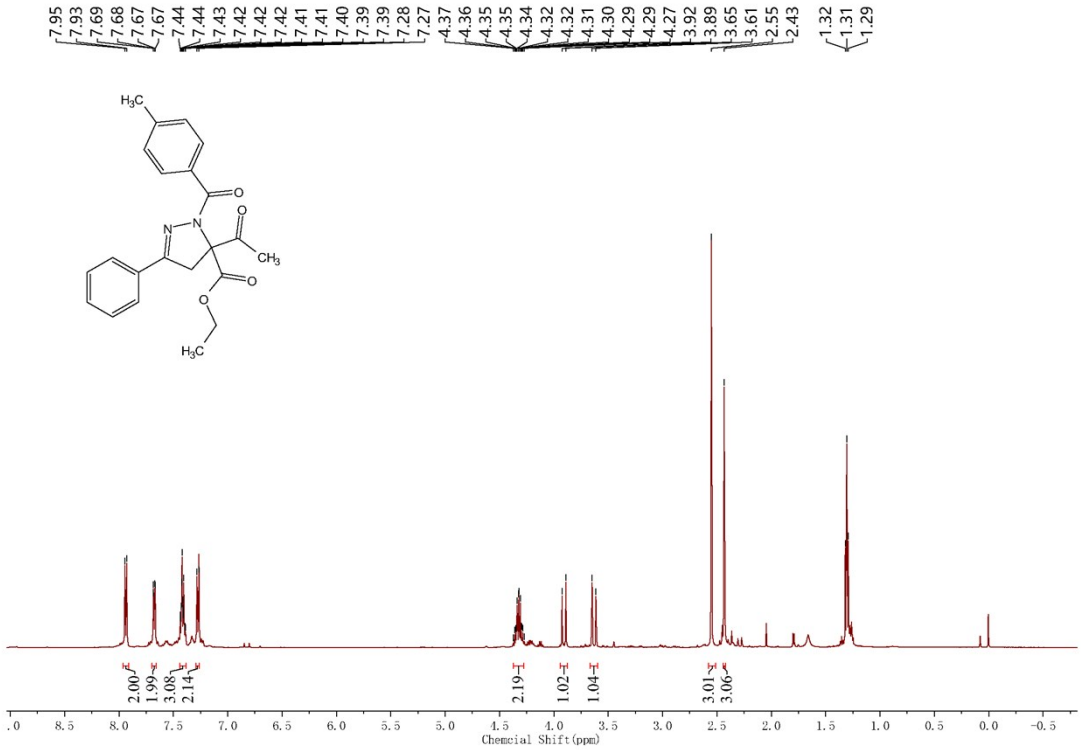
^{13}C NMR Spectrum of Compound **3la** (125MHz, $CDCl_3$)



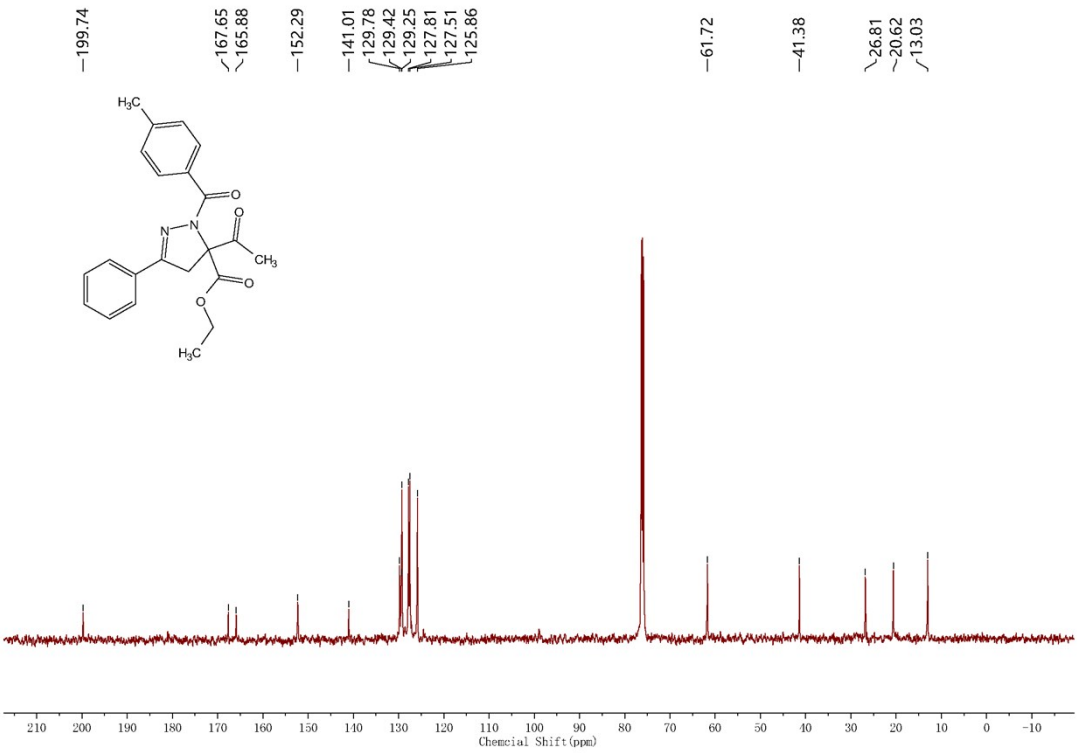
^{1}H NMR Spectrum of Compound **3ma** (500MHz, $CDCl_3$)



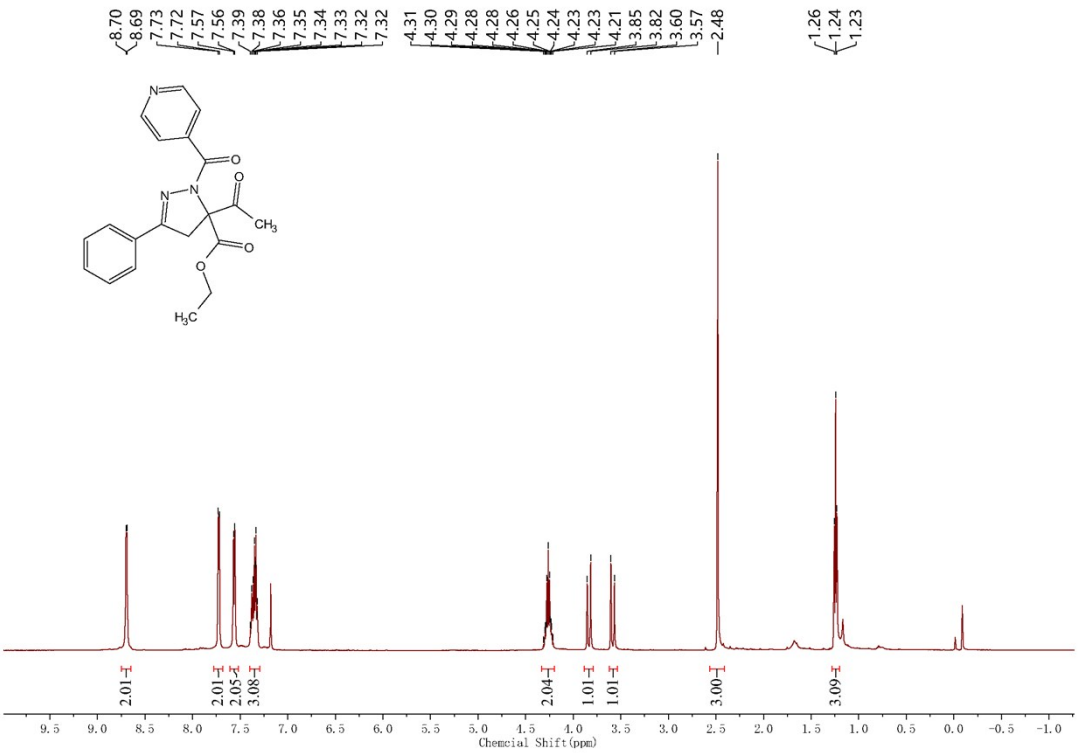
^{13}C NMR Spectrum of Compound **3ma** (125MHz, $CDCl_3$)



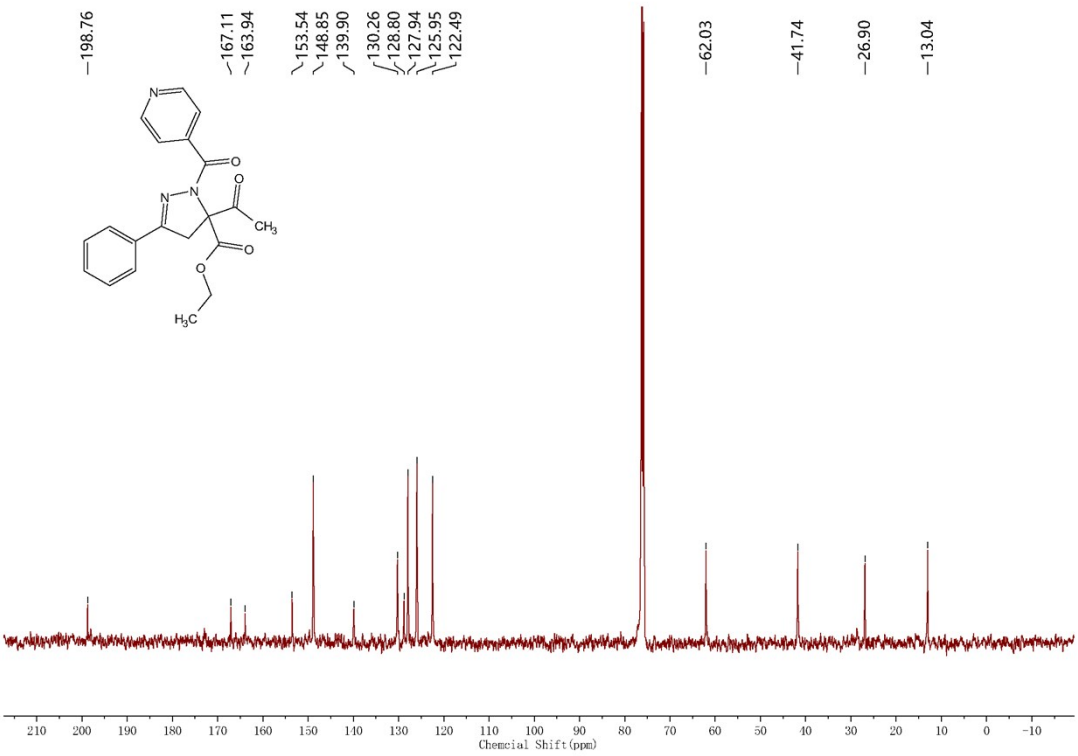
^{1}H NMR Spectrum of Compound **3na** (500MHz, $CDCl_3$)



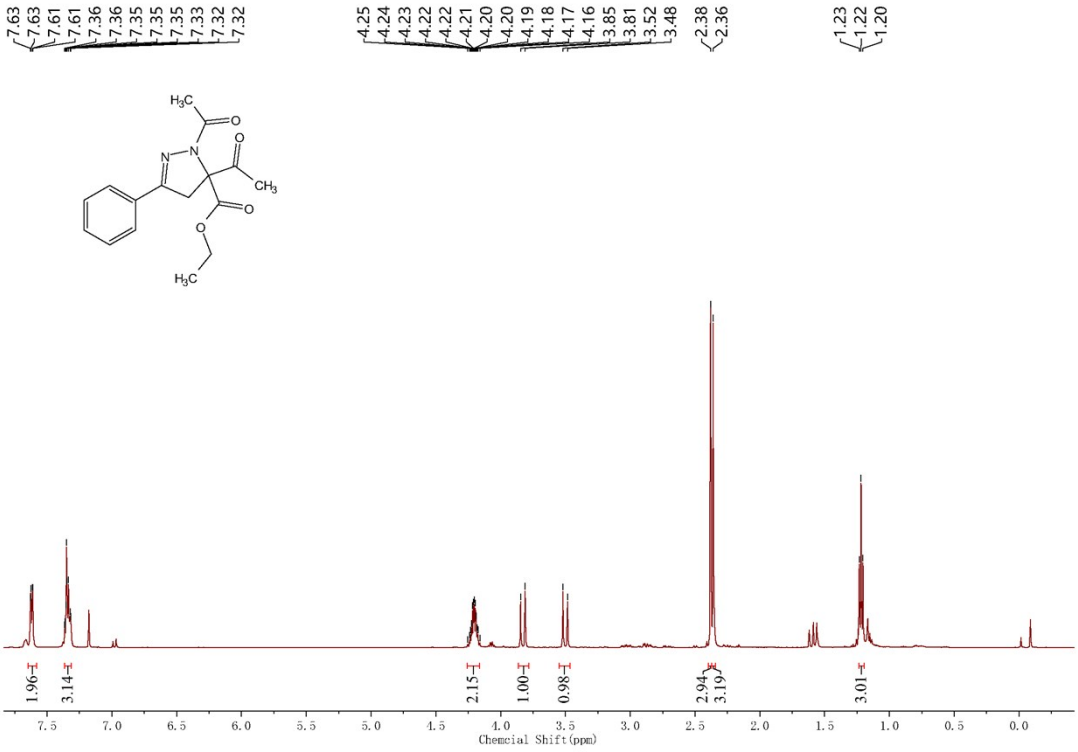
^{13}C NMR Spectrum of Compound **3na** (125MHz, $CDCl_3$)



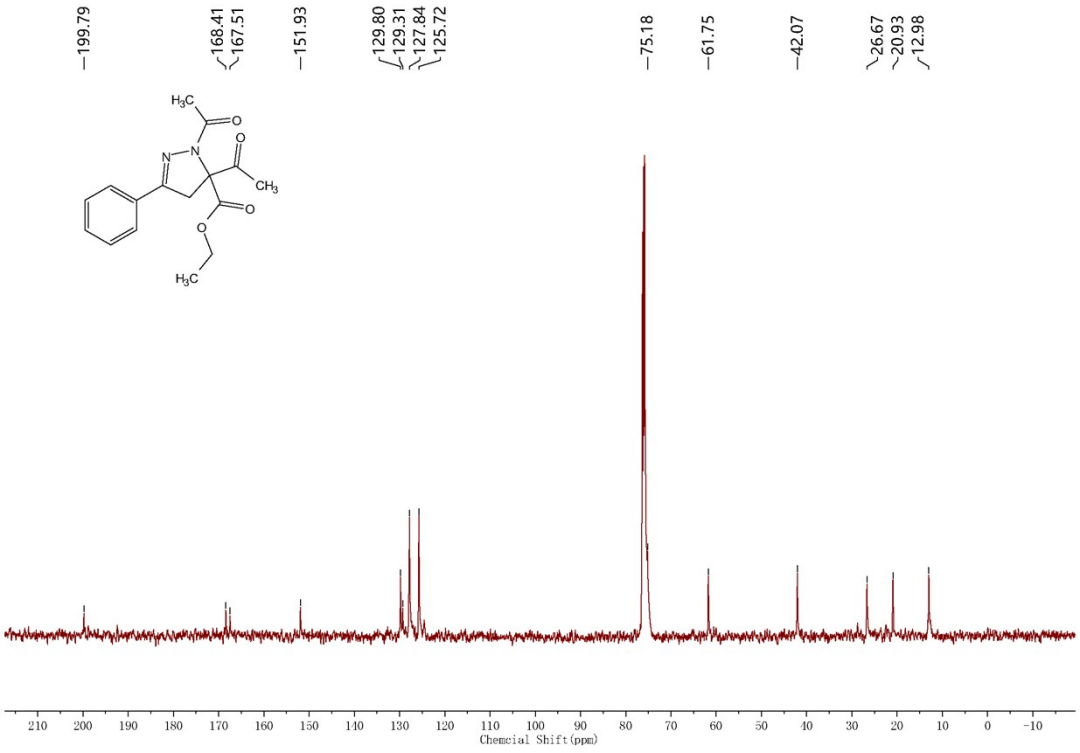
^{1}H NMR Spectrum of Compound **3oa** (500MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound **3oa** (125MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound **3pa** (500MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound **3pa** (125MHz, $CDCl_3$)