DMSO as C1 Source for the [2+2+1] Pyrazole Ring Construction via Metal-Free Annulation with Enaminones and Hydrazines

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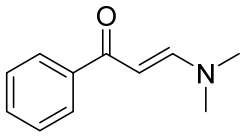
Contents

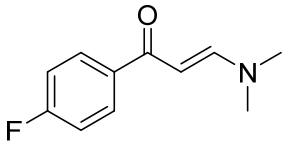
General experimental information

Enaminones **1a-x**, **1z,**[1a-e] enaminoester **1y**,[1f] and enaminone **10**[1g] were synthesized following literature process (characterization data and $^{1}H/^{13}C$ NMR spectra for new compounds are provided below). All other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further purification. The organic solvents were treated following standard procedures before use. The NMR spectra were recorded in 400 MHz apparatus, and the frequencies for ^{1}H NMR and ^{13}C NMR test are 400 MHz and 100 MHz, respectively. The chemical shifts were reported in ppm with TMS as internal standard. HMRS data for new compounds were acquired in the mass spectrometer equipped with TOF analyzer. Melting points were rested in an X-4A apparatus without correcting temperature.

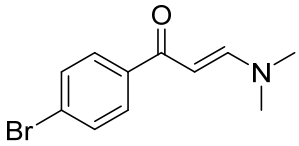
Characterization data of enaminone substrates 1 and 10 (new compounds and compounds reported in references using other synthetic methods)



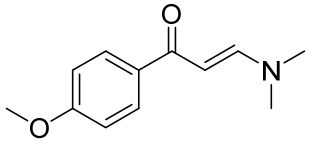
(*E*)-3-(Dimethylamino)-1-phenylprop-2-en-1-one (**1a**).[1a] Yellow solid; mp 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 6.8 Hz, 2H), 7.80 (d, *J* = 12.4 Hz, 1H), 7.47-7.37 (m, 3H), 5.71 (d, *J* = 12.4 Hz, 1H), 3.12 (s, 3H), 2.91 (s, 3H).



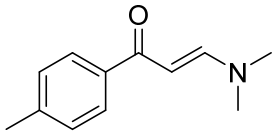
(*E*)-3-(Dimethylamino)-1-(4-fluorophenyl)prop-2-en-1-one (**1b**).[1h] Yellow solid; mp 83-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.6, 5.8 Hz, 2H), 7.80 (d, *J* = 12.4 Hz, 1H), 7.07 (t, *J* = 8.8 Hz, 2H), 5.67 (d, *J* = 12.4 Hz, 1H), 3.13 (s, 3H), 2.91 (s, 3H).



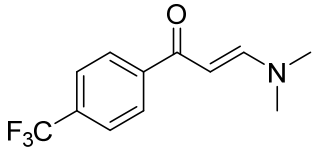
(*E*)-1-(4-Bromophenyl)-3-(dimethylamino)prop-2-en-1-one (**1c**).[1a] Yellow solid; mp 74-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.74 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 2H), 5.65 (d, *J* = 12.4 Hz, 1H), 3.14 (s, 3H), 2.91 (s, 3H).



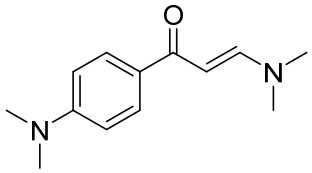
(*E*)-3-(Dimethylamino)-1-(4-methoxyphenyl)prop-2-en-1-one (**1d**).[1c] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 12.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.71 (d, *J* = 12.4 Hz, 1H), 3.84 (s, 3H), 3.09 (s, 3H), 2.93 (s, 3H).



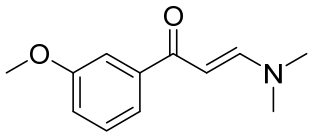
(*E*)-3-(Dimethylamino)-1-(*p*-tolyl)prop-2-en-1-one (**1e**).[1a] Yellow solid; mp 89-91°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.75 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 12.4 Hz, 1H), 3.09 (s, 3H), 2.89 (s, 3H), 2.38 (s, 3H).



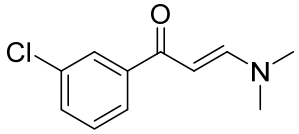
(*E*)-3-(Dimethylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**1f**).[1h] Yellow solid; mp 107-109 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 12.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 5.69 (d, *J* = 12.2 Hz, 1H), 3.18 (s, 3H), 2.95 (s, 3H).



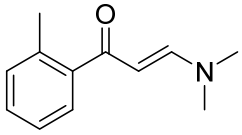
(*E*)-3-(Dimethylamino)-1-(4-(dimethylamino)phenyl)prop-2-en-1-one (**1g**). Yellow solid; mp 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 12.4 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.74 (d, *J* = 12.4 Hz, 1H), 3.01 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 153.0, 152.4, 129.4, 128.0, 110.8, 91.7, 40.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{19}N_2O$ 219.1492; Found 219.1490.



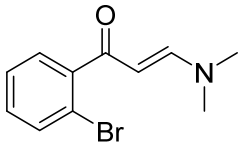
(*E*)-3-(Dimethylamino)-1-(3-methoxyphenyl)prop-2-en-1-one (**1h**).[1i] Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 12.4 Hz, 1H), 7.50-7.43 (m, 2H), 7.31 (t, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 12.4 Hz, 1H), 3.85 (s, 3H), 3.13 (s, 3H), 2.90 (s, 3H).



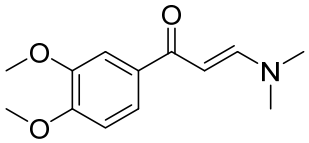
(*E*)-1-(3-Chlorophenyl)-3-(dimethylamino)prop-2-en-1-one (**1i**).[1j] Yellow solid; mp 67-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.81 (d, *J* = 12.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 5.64 (d, *J* = 12.4 Hz, 1H), 3.15 (s, 3H), 2.92 (s, 3H).



(*E*)-3-(Dimethylamino)-1-(o-tolyl)prop-2-en-1-one (**1j**).[1k] Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.11 (m, 5H), 5.33 (d, *J* = 12.8 Hz, 1H), 3.03 (s, 3H), 2.83 (s, 3H), 2.39 (s, 3H).

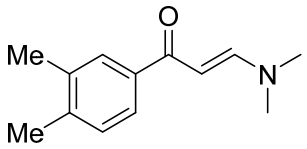


(*E*)-1-(2-Bromophenyl)-3-(dimethylamino)prop-2-en-1-one (**1k**).[1h] Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.36-7.29 (m, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 5.31 (d, *J* = 12.8 Hz, 1H), 3.08 (s, 3H), 2.87 (s, 3H).

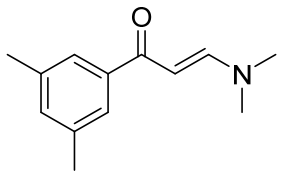


(*E*)-1-(3,4-Dimethoxyphenyl)-3-(dimethylamino)prop-2-en-1-one (**1l**).[1d] Yellow solid; mp 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 12.4 Hz, 1H), 7.56

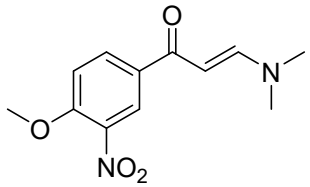
(s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.72 (d, *J* = 12.4 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.11 (s, 3H), 2.95 (s, 3H).



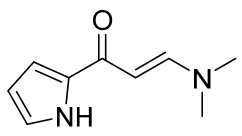
(*E*)-3-(Dimethylamino)-1-(3,4-dimethylphenyl)prop-2-en-1-one (**1m**). Yellow solid; mp 101-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 12.4 Hz, 1H), 7.69 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 5.72 (d, *J* = 12.4 Hz, 1H), 3.12 (s, 3H), 2.93 (s, 3H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 154.1, 140.0, 138.2, 136.4, 129.4, 128.8, 125.1, 92.2, 19.8, 19.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO$ 204.1383; Found 204.1386.



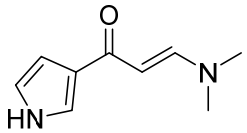
(*E*)-3-(Dimethylamino)-1-(3,5-dimethylphenyl)prop-2-en-1-one (**1n**). Yellow solid; mp 77-79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 12.4 Hz, 1H), 7.50 (s, 2H), 7.09 (s, 1H), 5.69 (d, *J* = 12.4 Hz, 1H), 3.12 (s, 3H), 2.93 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 154.1, 140.7, 137.6, 132.5, 125.3, 92.5, 21.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{18}NO$ 204.1383; Found 204.1383.



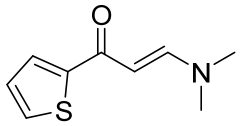
(*E*)-3-(Dimethylamino)-1-(4-methoxy-3-nitrophenyl)prop-2-en-1-one (**1o**).[1e] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.0 Hz, 1H), 8.17 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.85 (d, *J* = 12.2 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.66 (d, *J* = 12.2 Hz, 1H), 4.01 (s, 3H), 3.19 (s, 3H), 2.97 (s, 3H).



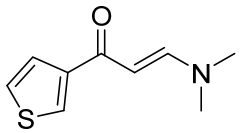
(*E*)-3-(Dimethylamino)-1-(1H-pyrrol-2-yl)prop-2-en-1-one (**1p**).[11] Brown solid; mp 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.75 (d, *J* = 12.6 Hz, 1H), 6.95 (s, 1H), 6.77 (s, 1H), 6.24 (s, 1H), 5.58 (d, *J* = 12.6 Hz, 1H), 2.99 (s, 6H).



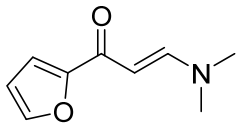
(*E*)-3-(Dimethylamino)-1-(1*H*-pyrrol-3-yl)prop-2-en-1-one (**1q**). Yellow solid; mp 194-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.75 (d, *J* = 12.6 Hz, 1H), 6.95 (s, 1H), 6.77 (s, 1H), 6.24 (d, *J* = 3.4 Hz, 1H), 5.58 (d, *J* = 12.6 Hz, 1H), 2.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 152.4, 133.6, 122.1, 111.8, 109.8, 91.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{13}N_2O$ 165.1022; Found 165.1025.



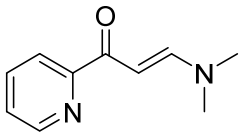
(*E*)-3-(Dimethylamino)-1-(thiophen-2-yl)prop-2-en-1-one (**1r**).[1h] Yellow solid; mp 117-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 12.3 Hz, 1H), 7.63 (d, *J* = 3.3 Hz, 1H), 7.47 (d, *J* = 4.9 Hz, 1H), 7.11-7.04 (m, 1H), 5.63 (d, *J* = 12.3 Hz, 1H), 3.14 (s, 3H), 2.92 (s, 3H).



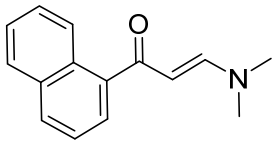
(*E*)-3-(Dimethylamino)-1-(thiophen-3-yl)prop-2-en-1-one (**1s**).[1m] Brown solid; mp 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.89 (m, 1H), 7.76 (d, *J* = 12.4 Hz, 1H), 7.53 (d, *J* = 5.0 Hz, 1H), 7.29-7.24 (m, 1H), 5.58 (d, *J* = 12.4 Hz, 1H), 3.10 (s, 3H), 2.89 (s, 3H).



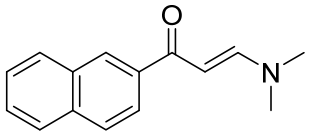
(*E*)-3-(Dimethylamino)-1-(furan-2-yl)prop-2-en-1-one (**1t**).[1h] Yellow solid; mp 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 12.6 Hz, 1H), 7.49 (s, 1H), 7.06 (s, 1H), 6.48 (s, 1H), 5.68 (d, *J* = 12.6 Hz, 1H), 3.13 (s, 3H), 2.91 (s, 3H).



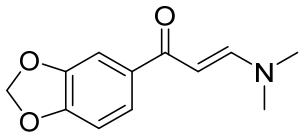
(*E*)-3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (**1u**).[1h] Yellow solid; mp 124-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.2 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 12.8 Hz, 1H), 7.80 (t, *J* = 8.4 Hz, 1H), 7.39-7.34 (m, 1H), 6.45 (d, *J* = 12.8 Hz, 1H), 3.17 (s, 3H), 2.99 (s, 3H).



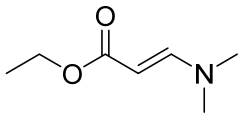
(*E*)-3-(Dimethylamino)-1-(naphthalen-1-yl)prop-2-en-1-one (**1v**).[1c] Brown liquid ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.91-7.78 (m, 2H), 7.69-7.31 (m, 5H), 5.50 (d, *J* = 12.8 Hz, 1H), 3.00 (s, 3H), 2.83 (s, 3H).



(*E*)-3-(Dimethylamino)-1-(naphthalen-2-yl)prop-2-en-1-one (**1w**).[1h] Yellow solid; mp 113-115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.87-7.80 (m, 3H), 7.54-7.45 (m, 2H), 5.84 (d, *J* = 12.4 Hz, 1H), 3.07 (s, 3H), 2.89 (s, 3H).

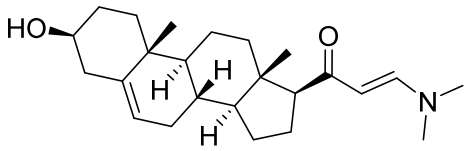


(*E*)-1-(Benzo[d][1,3]dioxol-5-yl)-3-(dimethylamino)prop-2-en-1-one (**1x**).[1n] Yellow solid; mp 127-129 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 12.4 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.43 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.00 (s, 2H), 5.65 (d, *J* = 12.4 Hz, 1H), 3.13 (s, 3H), 2.92 (s, 3H).

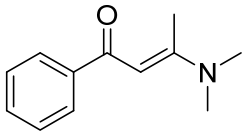


Ethyl (*E*)-3-(dimethylamino)acrylate (**1y**).[1o] Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 13.0 Hz, 1H), 4.51 (d, *J* = 13.0 Hz, 1H), 4.12 (q, *J* = 7.2 Hz,

2H), 2.89 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 3H).



(*E*)-3-(Dimethylamino)-1-((3S,8S,9S,10R,13S,14S,17S)-3-hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)prop-2-en-1-one (**1z**). White solid; mp 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 12.6 Hz, 1H), 5.35 (d, *J* = 4.8 Hz, 1H), 4.99 (d, *J* = 12.6 Hz, 1H), 3.53 (tt, *J* = 10.8, 4.4 Hz, 1H), 3.02 (s, 3H), 2.84 (s, 3H), 2.45 (t, *J* = 9.0 Hz, 1H), 2.37-2.21 (m, 3H), 2.05-1.92 (m, 4H), 1.85 (d, *J* = 10.2 Hz, 2H), 1.72-1.60 (m, 2H), 1.53-1.40 (m, 3H), 1.38-1.05 (m, 5H), 1.00 (s, 3H), 0.99-0.93 (m, 1H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 151.7, 140.8, 121.6, 97.1, 71.7, 62.1, 57.1, 50.3, 44.1, 42.3, 39.0, 37.3, 36.6, 32.0, 31.9, 31.6, 24.7, 22.9, 21.1, 19.4, 13.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ $C_{24}H_{38}NO_2$ 372.2897; Found 372.2908.



(*E*)-3-(Dimethylamino)-1-phenylbut-2-en-1-one (**10**).[1g] White solid; mp 65-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.2 Hz, 2H), 7.39 (q, *J* = 5.6 Hz, 3H), 5.67 (s, 1H), 3.06 (s, 6H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 164.0, 143.1, 130.3, 128.0, 127.3, 92.6, 40.1, 16.5.

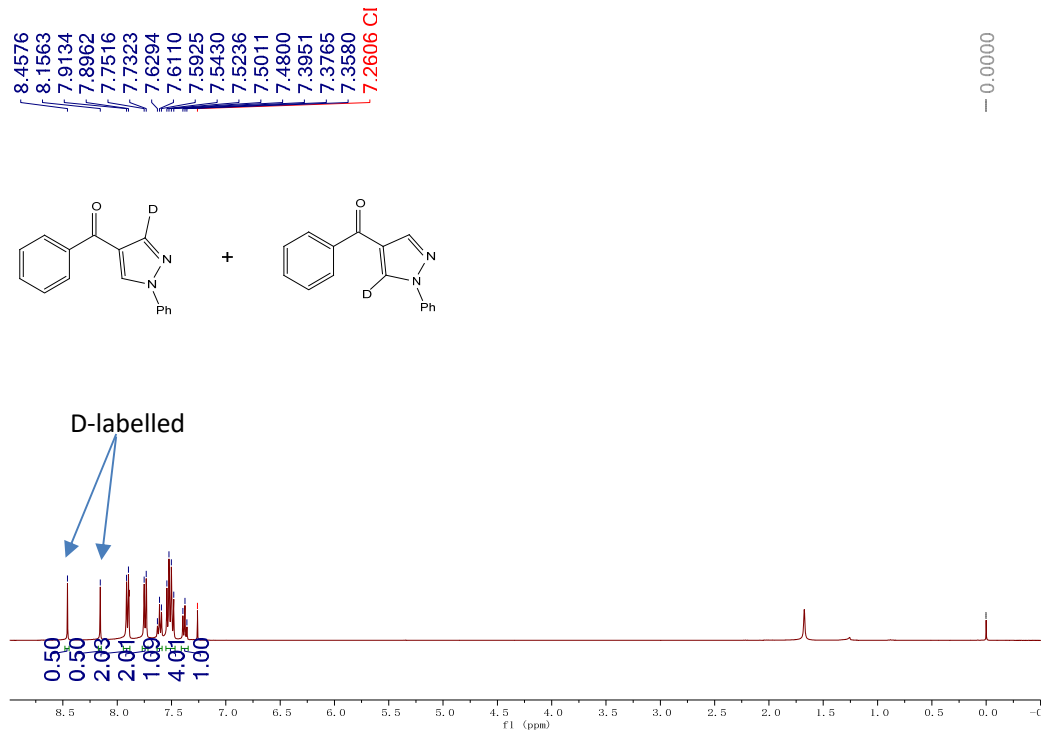


Figure S1 ^{1}H NMR spectra of the D-labelled products

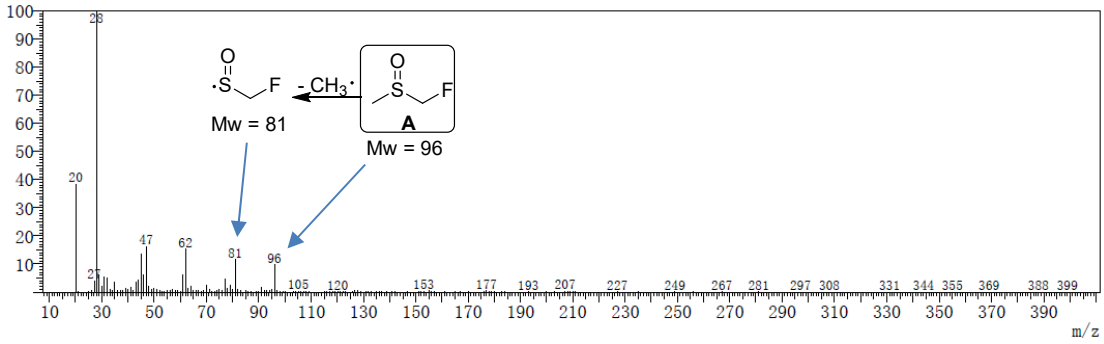


Figure S2 GC-MS analysis on intermediate **A** (reaction mixture at the stage of 5 min)

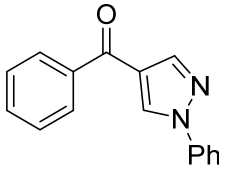
General procedure for the synthesis and characterization data of 3 and 11/11'

To a 25 mL round-bottom flask were added enaminone **1** (0.2 mmol, 1.0 equiv), hydrazine hydrochloride **2** (0.4 mmol, 2.0 equiv), I_2 (0.02 mmol, 10 mol%), selectfluor (1 mmol, 5.0 equiv) and DMSO (2 mL). Then, the mixture was stirred at 90 °C with oil bath heating for 10 min. After being cooled down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The organic phases were collected and washed with a small amount of water for three times. After being dried with anhydrous Na_2SO_4, the solid was removed by filtration. The solvent in the resulting solution was removed at reduced pressure. The residue obtained

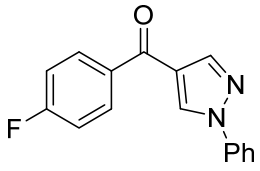
therein was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed petroleum ether and ethyl acetate (v/v = 3:1~15:1).

Procedure for the 1 mmol scale reaction for of 3a synthesis

To a 25 mL round-bottom flask were added enaminone **1** (1 mmol, 1.0 equiv), hyrazine **2a** (2 mmol, 2.0 equiv), I_2 (0.1 mmol, 10 mol%), selectfluor (5 mmol, 5.0 equiv) and DMSO (6 mL). The mixture was then stirred at 90 °C with oil bath heating for 15 min. After being cooled down to room temperature, 20 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 50 mL). The organic phases were collected and washed with a small amount of water for three times. After being dried with anhydrous Na_2SO_4, the solid was removed by filtration. The solvent in the resulting solution was removed at reduced pressure. The residue obtained therein was subjected to flash silica gel column chromatography to provide pure product **3a** (55% yield, 136.0 mg) with the elution of mixed petroleum ether and ethyl acetate (v/v = 15:1).

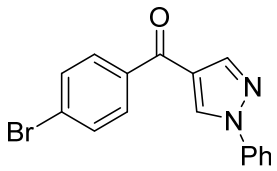


Phenyl(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3a**).[2] Eluent: V_{PET}/V_{EA} = 15:1; white soild (37.2 mg, 75% yield); mp 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.16 (s, 1H), 7.91 (d, *J* = 6.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.56-7.48 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 142.8, 139.4, 139.0, 132.4, 130.7, 129.7, 128.9, 128.6, 127.8, 124.2, 119.8.

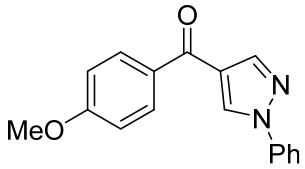


(4-Fluorophenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3b**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (36.7 mg, 69% yield); mp 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.13 (s, 1H), 7.96-7.93(m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz,

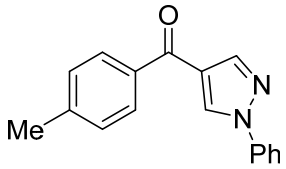
$CDCl_3$) δ 187.2, 165.4 (d, *J* = 252.6 Hz), 142.6, 139.3, 135.1, 131.4 (d, *J* = 9.2 Hz), 130.7, 129.7, 127.9, 124.0, 119.8, 115.8 (d, *J* = 22.6 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}FN_2O$ 267.0928; Found 267.0928.



(4-Bromophenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3c**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (39.7 mg, 61% yield); mp 192-194 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 1H), 8.26 (s, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.55 (t, 2H), 7.41 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.3, 142.9, 139.4, 137.8, 132.5, 132.3, 131.3, 130.1, 128.0, 126.9, 123.6, 119.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrN_2O$ 327.0128; Found 327.0130.

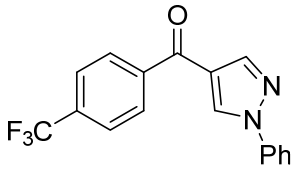


(4-Methoxyphenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3d**). Eluent: V_{PET}/V_{EA} = 10:1; white solid (36.4 mg, 65% yield); mp 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.14 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 163.2, 142.6, 139.4, 131.5, 131.3, 130.5, 129.7, 127.7, 124.3, 119.7, 113.9, 55.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O_2$ 279.1128; Found 279.1126.

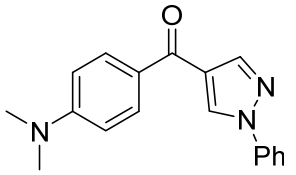


(1-Phenyl-1*H*-pyrazol-4-yl)(*p*-tolyl)methanone (**3e**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (28.8 mg, 55% yield); mp 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45

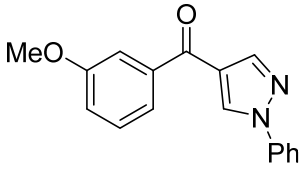
(s, 1H), 8.15 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 143.3, 142.8, 139.4, 136.2, 130.6, 129.7, 129.3, 129.1, 127.7, 124.3, 119.7, 21.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1179; Found 263.1177.



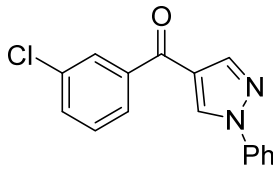
(1-Phenyl-1*H*-pyrazol-4-yl)(4-(trifluoromethyl)phenyl)methanone (**3f**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (36.7 mg, 58% yield); mp 169-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.14 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 142.7, 141.9, 139.1, 133.9,(d, *J* = 32.2 Hz), 130.9, 129.7, 129.1, 128.0, 125.7 (q, *J* = 3.6 Hz), 123.7, 123.6 (d, *J* = 271.0 Hz), 119.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}F_3N_2O$ 317.0896; Found 317.0897.



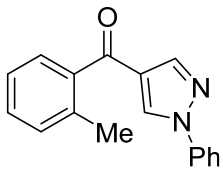
(4-(Dimethylamino)phenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3g**). Eluent: V_{PET}/V_{EA} = 7:1; yellow solid (42.1 mg, 72% yield); mp 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.14 (s, 1H), 7.92 (d, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 3.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.8, 153.2, 142.5, 139.5, 131.4, 130.1, 129.6, 127.4, 126.3, 124.8, 119.6, 111.1, 40.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}N_3O$ 292.1444; Found 292.1442.



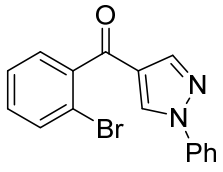
(3-Methoxyphenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3h**). Eluent: V_{PET}/V_{EA} = 15:1; brown liquid (31.1 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.16 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 8.0 Hz, 3H), 7.44-7.40 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.17-7.12 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 159.8, 142.8, 140.2, 139.3, 130.8, 129.7, 129.6, 127.8, 124.2, 121.4, 119.8, 118.8, 113.4, 55.5; HRMS (ESI-TOF) m/z: $[M + H]^+$Calcd for $C_{17}H_{15}N_2O_2$ 279.1128; Found 279.1127.



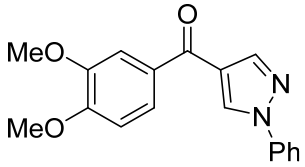
(3-Chlorophenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3i**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (29.3 mg, 52% yield); mp 148-150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.14 (s, 1H), 7.87 (s, 1H), 7.79-7.72 (m, 3H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54-7.45 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 142.7, 140.5, 139.2, 134.9, 132.4, 130.8, 130.0, 129.7, 128.9, 127.9, 126.9, 123.7, 119.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}ClN_2O$ 283.0633; Found 283.0633.



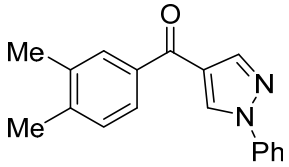
(1-Phenyl-1*H*-pyrazol-4-yl)(o-tolyl)methanone (**3j**). Eluent: V_{PET}/V_{EA} = 15:1; brown liquid (28.9 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.04 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 3H), 7.43-7.36 (m, 2H), 7.33-7.28 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 142.9, 139.3, 139.2, 136.7, 131.4, 130.8, 130.5, 129.7, 127.9, 127.8, 125.7, 125.4, 119.8, 19.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1179; Found 263.1177.



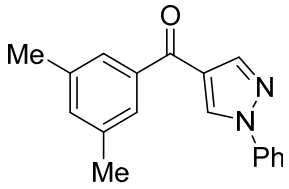
(2-Bromophenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3k**). Eluent: V_{PET}/V_{EA} = 15:1; brown liquid (25.6 mg, 39% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.02 (s, 1H), 7.69 (t, *J* = 7.8 Hz, 3H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 3.6 Hz, 2H), 7.39-7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 142.8, 141.2, 139.2, 133.6, 131.4, 131.0, 129.7, 128.6, 127.9, 127.4, 124.6, 119.8, 119.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}BrN_2O$ 327.0128; Found 327.0129.



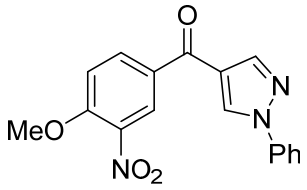
(3,4-Dimethoxyphenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3l**). Eluent: V_{PET}/V_{EA} = 5:1; yellow solid (49.3 mg, 80% yield); mp 151-153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.15 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 6.4 Hz, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 153.0, 149.2, 142.6, 139.4, 131.6, 130.5, 129.7, 127.7, 124.3, 123.6, 119.7, 111.4, 110.1, 56.1, 56.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O_3$ 309.1234; Found 309.1232.



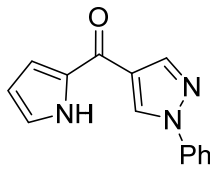
(3,4-Dimethylphenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3m**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (32.6 mg, 59% yield); mp 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.15 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.70 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 142.8, 142.0, 139.4, 137.1, 136.6, 130.6, 130.1, 129.8, 129.7, 127.7, 126.7, 124.4, 119.7, 20.0, 19.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O$ 277.1335; Found 277.1334.



(3,5-Dimethylphenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3n**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (34.2 mg, 62% yield); mp 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.14 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 142.9, 139.4, 139.1, 138.3, 134.1, 130.7, 129.7, 127.7, 126.6, 124.4, 119.7, 21.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2O$ 277.1335; Found 277.1335.

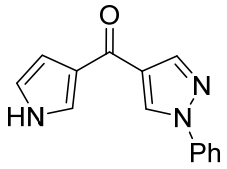


(4-Methoxy-3-nitrophenyl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3o**). Eluent: V_{PET}/V_{EA} = 3:1; yellow solid (45.0 mg, 70% yield); mp 164-166 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 1H), 8.39 (s, 1H), 8.30 (s, 1H), 8.25 (d, *J* = 9.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.58-7.52 (m, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 185.2, 155.4, 142.9, 139.6, 139.4, 135.4, 132.4, 130.7, 130.1, 128.0, 126.3, 123.3, 119.9, 114.9, 57.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}N_3O_4$ 324.0979; Found 324.0977.

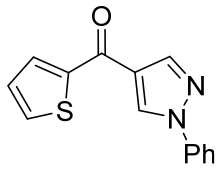


(1-Phenyl-1*H*-pyrazol-4-yl)(1*H*-pyrrol-2-yl)methanone (**3p**). Eluent: V_{PET}/V_{EA} = 3:1; yellow solid (41.7 mg, 88% yield); mp 189-191 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H), 9.15 (s, 1H), 8.32 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 (s, 1H), 7.19 (s, 1H), 6.30 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.0, 142.1, 139.6, 131.6, 130.5, 130.0, 127.7, 126.2,

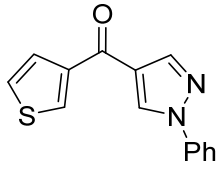
124.2, 119.7, 117.6, 110.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_3O$ 238.0975; Found 238.0974.



(1-Phenyl-1*H*-pyrazol-4-yl)(1*H*-pyrrol-3-yl)methanone (**3q**). Eluent: V_{PET}/V_{EA} = 3:1; yellow solid (44.5 mg, 94% yield); mp 201-203 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H), 9.15 (s, 1H), 8.32 (s, 1H), 8.01 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.31 (s, 1H), 7.19 (s, 1H), 6.30 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.0, 142.1, 139.6, 131.6, 130.5, 130.0, 127.7, 126.2, 124.2, 119.7, 117.6, 110.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}N_3O$ 238.0975; Found 238.0974.

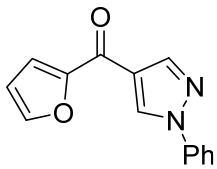


(1-Phenyl-1*H*-pyrazol-4-yl)(thiophen-2-yl)methanone (**3r**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (35.0 mg, 69% yield); mp 122-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.27 (s, 1H), 7.88 (d, J = 3.8 Hz, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.71 (d, J = 5.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.24-7.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 144.1, 141.9, 139.3, 133.4, 132.5, 130.2, 129.7, 128.1, 127.8, 124.1, 119.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_2OS$ 255.0587; Found 255.0586.

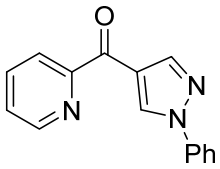


(1-Phenyl-1*H*-pyrazol-4-yl)(thiophen-3-yl)methanone (**3s**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (31.5 mg, 62% yield); mp 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.20 (s, 1H), 8.09 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 5.2 Hz,

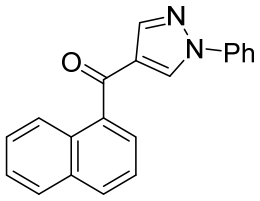
1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.44-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.9, 142.4, 142.2, 139.3, 131.8, 130.2, 129.7, 127.8, 127.8, 126.6, 124.9, 119.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_2OS$ 255.0587; Found 255.0585.



Furan-2-yl(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3t**). Eluent: V_{PET}/V_{EA} = 10:1; yellow solid (23.8 mg, 50% yield); mp 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.43 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.42-7.34 (m, 2H), 6.63 (dd, *J* = 3.8, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 153.4, 146.0, 142.6, 139.4, 130.7, 129.6, 127.7, 123.1, 119.8, 117.9, 112.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_2O_2$ 239.0815; Found 239.0814.

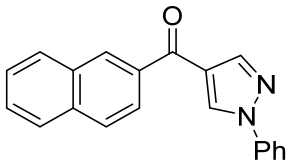


(1-Phenyl-1*H*-pyrazol-4-yl)(pyridin-2-yl)methanone (**3u**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (21.0 mg, 42% yield); mp 93-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.76 (d, *J* = 4.8 Hz, 1H), 8.58 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.90 (td, *J* = 7.8, 1.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 154.7, 148.7, 144.2, 139.5, 137.1, 132.8, 129.6, 127.5, 126.8, 123.6, 122.7, 119.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{12}N_3O$ 250.0975; Found 250.0974.

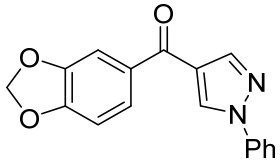


Naphthalen-1-yl(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3v**). Eluent: V_{PET}/V_{EA} = 15:1; brown liquid (31.2 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.27 (dd, *J* = 6.4, 3.6 Hz, 1H), 8.10 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 6.4,

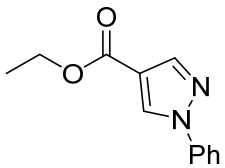
3.4 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.58-7.52 (m, 3H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 143.0, 139.3, 137.2, 133.9, 131.5, 131.0, 130.4, 129.7, 128.4, 127.8, 127.4, 126.9, 126.6, 126.2, 125.5, 124.5, 119.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}N_2O$ 299.1179; Found 299.1178.



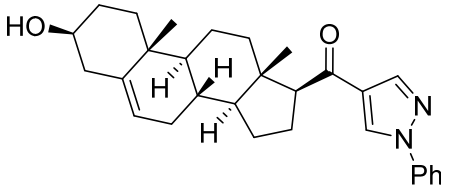
Naphthalen-2-yl(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3w**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (35.3 mg, 59% yield); mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.42 (s, 1H), 8.22 (s, 1H), 7.97 (s, 3H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.64-7.55 (m, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 142.9, 139.3, 136.2, 135.3, 132.5, 130.8, 130.2, 129.7, 129.4, 128.7, 128.3, 127.9, 127.8, 127.0, 125.0, 124.4, 119.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}N_2O$ 299.1179; Found 299.1179.



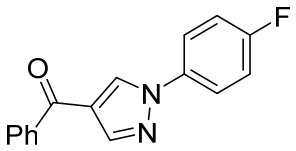
Benzo[*d*][1,3]dioxol-5-yl(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3x**). Eluent: V_{PET}/V_{EA} = 10:1; yellow solid (36.3 mg, 62% yield); mp 156-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.13 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.54-7.47 (m, 3H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.07 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 151.5, 148.2, 142.6, 139.3, 133.2, 130.5, 129.7, 127.7, 125.1, 124.1, 119.7, 109.0, 108.0, 101.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2O_3$ 293.0921; Found 293.0919.



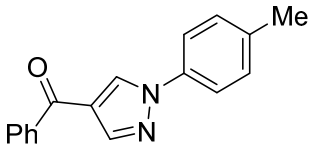
Ethyl 1-phenyl-1*H*-pyrazole-4-carboxylate (**3y**).[3] Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (17.2 mg, 40% yield); mp 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.10 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 142.2, 139.5, 130.0, 129.6, 127.5, 119.6, 117.0, 60.4, 14.4.



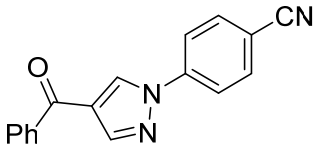
((3S,8S,9S,10R,13S,14S,17S)-3-Hydroxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)(1-phenyl-1*H*-pyrazol-4-yl)methanone (**3z**). Eluent: V_{PET}/V_{EA} = 4:1; yellow solid (37.6 mg, 42% yield); mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.09 (s, 1H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz,1H), 5.37 (d, *J* = 5.3 Hz, 1H), 3.58-3.48 (m, 1H), 3.11 (t, *J* = 8.8 Hz, 1H), 2.43 (q, *J* = 11.0 Hz, 1H), 2.33-2.21 (m, 2H), 2.09-2.00 (m, 1H), 1.88-1.73 (m, 7H), 1.56-1.27 (m, 7H), 1.14-1.01 (m, 2H), 0.99 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)δ 195.4, 141.8, 140.8, 139.4, 129.6, 129.2, 127.6, 127.1, 121.4, 119.7, 71.7, 60.3, 57.5, 50.1, 45.1, 42.2, 39.5, 37.3, 36.6, 32.1, 31.9, 31.60, 24.9, 23.6, 21.1, 19.4, 13.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{37}N_2O_2$ 445.2850; Found 445.2849.



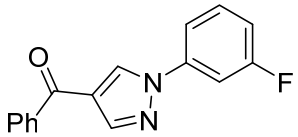
(1-(4-Fluorophenyl)-1*H*-pyrazol-4-yl)(phenyl)methanone (**3aa**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (37.6 mg, 71% yield); mp 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.14 (s, 1H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.74-7.68 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 161.8 (d, *J* = 246.4 Hz) 142.8, 138.8, 135.6, 132.5, 130.8, 128.9, 128.7, 124.3, 121.7 (d, *J* = 8.4 Hz), 116.6 (d, *J* = 23.0 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}FN_2O$ 267.0928; Found 267.0926.



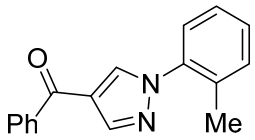
Phenyl(1-(*p*-tolyl)-1*H*-pyrazol-4-yl)methanone (**3ab**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (30.6 mg, 58% yield); mp 94-96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.13 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 8.2 Hz, 3H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 142.6, 139.0, 137.8, 137.1, 132.4, 130.7, 130.2, 128.9, 128.6, 124.0, 119.7, 21.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1179; Found 263.1177.



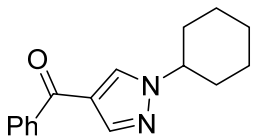
4-(4-Benzoyl-1*H*-pyrazol-1-yl)benzonitrile (**3ac**). Eluent: V_{PET}/V_{EA} = 8:1; yellow solid (32.8 mg, 60% yield); mp 178-180 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.19 (s, 1H), 7.94-7.88 (m, 4H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 143.6, 142.1, 138.5, 133.8, 132.8, 130.7, 128.9, 128.8, 125.1, 119.7, 118.0, 111.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}N_3O$ 274.0975; Found 274.0975.



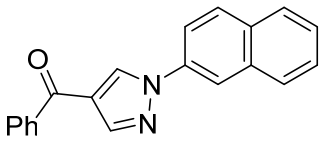
(1-(3-Fluorophenyl)-1*H*-pyrazol-4-yl)(phenyl)methanone (**3ad**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (33.0 mg, 62% yield); mp 106-108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.15 (s, 1H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 4H), 7.51-7.41 (m, 2H), 7.12-7.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 163.2 (d, *J* = 246.4 Hz), 143.0, 140.6 (d, *J* = 10.2 Hz), 138.7, 132.6, 131.0 (d, *J* = 9.0 Hz), 130.8, 128.9, 128.7, 124.5, 114.9 (d, *J* = 3.2 Hz), 114.6 (d, *J* = 21.2 Hz), 107.6 (d, *J* = 26.2 Hz); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{12}FN_2O$ 267.0928; Found 267.0926.



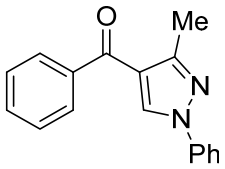
Phenyl(1-(*o*-tolyl)-1*H*-pyrazol-4-yl)methanone (**3ae**). Eluent: V_{PET}/V_{EA} = 15:1; brown liquid (25.3 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.15 (s, 1H), 7.91 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.39-7.30 (m, 4H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 142.2, 139.0, 134.7, 133.7, 132.4, 131.5, 129.3, 128.9, 128.6, 126.8, 126.0, 123.3, 18.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1179; Found 263.1178.



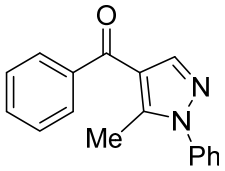
(1-Cyclohexyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**3af**). Eluent: V_{PET}/V_{EA} = 10:1; yellow liquid (18.3 mg, 36% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.93 (s, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 4.21-4.11 (m, 1H), 2.21 (d, *J* = 13.0 Hz, 2H), 1.93 (d, *J* = 13.6 Hz, 2H), 1.80-1.71 (m, 3H), 1.45 (q, *J* = 13.0 Hz, 2H), 1.33-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 141.2, 139.2, 132.1, 131.0, 128.8, 128.5, 122.2, 61.8, 38.5, 33.3, 25.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}N_2O$ 255.1492; Found 255.1491.



(1-(Naphthalen-2-yl)-1*H*-pyrazol-4-yl)(phenyl)methanone (**3ag**). Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (35.4 mg, 59% yield); mp 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.21 (s, 1H), 8.18 (s, 1H), 7.99-7.87 (m, 6H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.58-7.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 143.0, 138.9, 136.7, 133.4, 132.5, 132.4, 131.0, 129.9, 128.9, 128.7, 128.2, 127.9, 127.4, 126.6, 124.3, 118.4, 117.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}N_2O$ 299.1179; Found 299.1178.



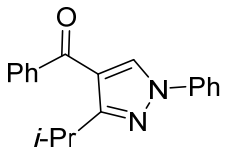
(3-Methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**11a**).[5] Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (18.7 mg, 36% yield); mp 80-82 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.82 (s, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.58-7.48 (m, 4H), 7.36 (t, J = 7.4 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.5, 152.4, 139.6, 139.3, 133.4, 132.7, 129.9, 129.3, 129.1, 127.5, 120.6, 119.6, 14.3.



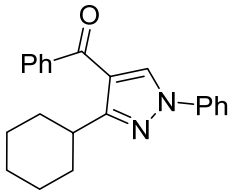
(5-Methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**11a′**).[5] Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (6.5 mg, 12% yield); mp 84-86 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.83 (d, J = 7.0 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.62-7.53 (m, 7H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.0, 144.5, 142.9, 139.6, 138.8, 132.6, 129.8, 129.2, 129.1, 129.0, 125.9, 120.0, 12.6.

General procedure for the synthesis and characterization data of 5

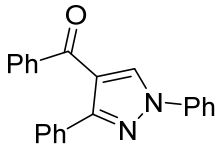
To a 25 mL round-bottom flask were added enaminone **1** (0.2 mmol, 1.0 equiv), hydrazine hydrochloride **2** (0.3 mmol, 1.5 equiv), aldehydes **4** (0.4 mmol, 2.0 equiv) and MeOH (2 mL). Then, the mixture was stirred at room temperature for 6 h. Subsequently, the mixture was directly employed to reduced pressure to remove the solvent, and the resulting residue was purified by flash column chromatography to give pure product by using mixed ethyl acetate and petroleum ether as eluent (v/v = 10:1~20:1).



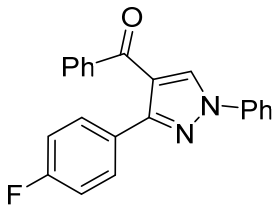
(3-Isopropyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5a**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (41.9 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.82 (d, *J* = 6.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.60-7.54 (m, 1H), 7.51-7.42 (m, 4H), 7.30 (t, *J* = 7.4 Hz, 1H), 3.73-3.61 (m, 1H), 1.42 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 162.3, 140.3, 139.5, 132.3, 132.0, 129.5, 128.8, 128.5, 127.1, 120.1, 119.5, 27.4, 21.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}N_2O$ 291.1492; Found 291.1490.



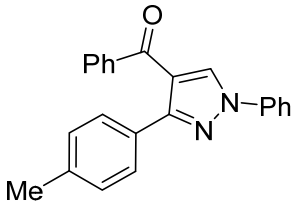
(3-Cyclohexyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5b**). Eluent: V_{PET}/V_{EA} = 20:1; yellow liquid (36.3 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.52-7.41 (m, 4H), 7.30 (t, *J* = 7.4 Hz, 1H), 3.34 (tt, *J* = 11.8, 3.4 Hz, 1H), 2.07 (d, *J* = 13.0 Hz, 2H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.74-1.62 (m, 3H), 1.51-1.39 (m, 2H), 1.33 (tt, *J* = 12.6, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.6, 140.3, 139.5, 132.1, 132.0, 129.5, 128.8, 128.5, 127.1, 120.1, 119.5, 37.0, 32.2, 26.6, 26.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O$ 331.1805; Found 331.1804.



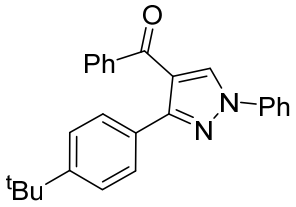
(1,3-Diphenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5c**).[4] Eluent: V_{PET}/V_{EA} = 15:1; white solid (44.0 mg, 68% yield); mp 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.83 (d, *J* = 7.0 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.76-7.70 (m, 2H), 7.54-7.46 (m, 3H), 7.42-7.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 154.0, 139.3, 138.9, 132.6, 132.3, 132.1, 129.6, 129.5, 128.9, 128.6, 128.4, 128.1, 127.5, 121.3, 119.6.



(3-(4-Fluorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5d**).[4] Eluent: V_{PET}/V_{EA} = 15:1; white solid (31.0 mg, 45% yield); mp 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.83 (d, *J* = 6.8 Hz, 2H), 7.81-7.73 (m, 4H), 7.57-7.47 (m, 3H), 7.45-7.33 (m, 3H), 7.08-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 163.1 (d, *J* = 246.6 Hz), 153.1, 139.1 (d, *J* = 21.6 Hz), 132.7, 132.5, 130.9, 130.8, 129.6, 129.4, 128.4, 127.6, 121.1, 119.6, 115.1 (d, *J* = 21.4 Hz).

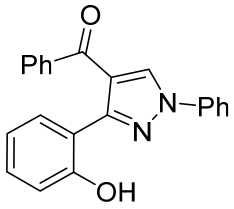


Phenyl(1-phenyl-3-(*p*-tolyl)-1*H*-pyrazol-4-yl)methanone (**5e**).[4] Eluent: V_{PET}/V_{EA} = 15:1; yellow solid (39.9 mg, 59% yield); mp 109-111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.55-7.45 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 154.1, 139.3, 139.0, 138.5, 132.5, 132.2, 129.6, 129.5, 129.2, 128.9, 128.8, 128.4, 127.4, 121.1, 119.6, 21.3.

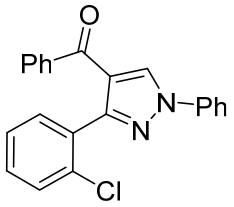


(3-(4-(*tert*-Butyl)phenyl)-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5f**). Eluent: V_{PET}/V_{EA} = 15:1; yellow liquid (44.0 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.83 (d, *J* = 6.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.54-7.45 (m, 3H), 7.43-7.32 (m, 5H), 1.31 (s, 9H); ^{13}C NMR (100 MHz,

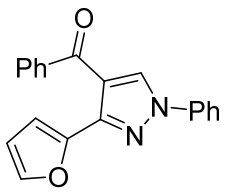
$CDCl_3$) δ 190.0, 154.1, 151.6, 139.3, 139.1, 132.4, 132.2, 129.6, 129.4, 129.2, 128.6, 128.3, 127.4, 125.1, 121.1, 119.5, 34.6, 31.3; HRMS (ESI-TOF) m/z: Calcd for $C_{26}H_{25}N_2O$ $[M + H]^+$ 381.1961; Found 381.1961.



(3-(2-Hydroxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5g**). Eluent: V_{PET}/V_{EA} = 10:1; yellow solid (28.1 mg, 41% yield); mp 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 8.24 (s, 1H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 2H), 7.60-7.55 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.47-7.36 (m, 3H), 7.25-7.20 (m, 1H), 7.05 (d, *J* = 9.4 Hz, 1H), 6.76 (t, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 155.9, 151.8, 138.5, 133.2, 132.2, 130.5, 130.1, 129.8, 129.8, 128.6, 128.0, 121.6, 119.4, 119.3, 117.3, 115.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}N_2O_2$ 341.1285; Found 341.1284.



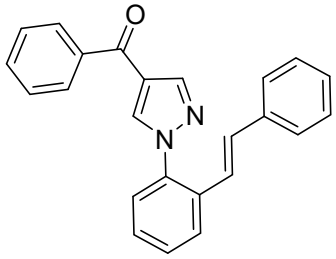
(3-(2-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5h**). Eluent: V_{PET}/V_{EA} = 15:1; yellow liquid (31.5 mg, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.80 (t, *J* = 7.8 Hz, 4H), 7.58 (d, *J* = 9.2 Hz, 1H), 7.52-7.46 (m, 3H), 7.40-7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 139.3, 152.0, 138.5, 133.6, 132.4, 132.0, 131.6, 131.1, 129.8, 129.6, 129.5, 129.3, 128.2, 127.6, 126.7, 122.9, 119.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}ClN_2O$ 359.0946; Found 359.0948.



(3-(Furan-2-yl)-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone (**5i**).[4] Eluent: V_{PET}/V_{EA} = 15:1; brown liquid (28.3 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$ δ 8.20 (s, 1H), 7.86 (d, *J* = 7.0 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52-7.45 (m, 5H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 3.4 Hz, 1H), 6.50-6.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 145.4, 143.9, 142.1, 138.5, 138.1, 131.6, 131.5, 128.6, 128.2, 127.5, 126.7, 119.3, 118.9, 111.3, 110.4.

Procedure for the synthesis of pyrazole 7

To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added sequentially **3a** (0.2 mmol, 1.0 equiv), styrene **6** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), $Cu(OAc)_2$ (0.4 mmol, 2.0 equiv), and DMF (2 mL). After vacuuming and backfilling with argon for three times, the Schlenk tube with an argon balloon was stirred at 100 °C (oil bath) for 12 h. After being cooled down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The organic phases were collected and washed with a small amount of water for three times. The solution was dried with anhydrous Na_2SO_4, and the solid was filtered. The solvent was removed from the solution at reduced pressure. The residue obtained therein was subjected to flash silica gel column chromatography to provide pure products with the elution of mixed petroleum ether and ethyl acetate (v/v = 15:1).

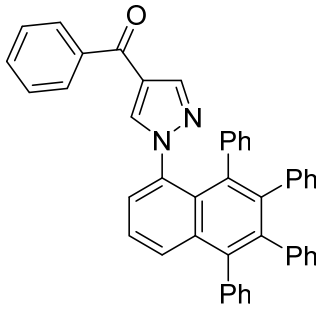


(*E*)-Phenyl(1-(2-styrylphenyl)-1*H*-pyrazol-4-yl)methanone (**7**). Eluent: V_{PET}/V_{EA} = 15:1; white solid (40.5 mg, 58% yield); mp 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.17 (s, 1H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.50-7.45 (m, 2H), 7.45-7.32 (m, 7H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.09 (d, *J* = 16.4 Hz, 1H), 7.00 (d, *J* = 16.4 Hz, 1H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7,

142.6, 139.0, 137.7, 136.7, 135.6, 133.2, 132.4, 132.4, 129.3, 128.9, 128.8, 128.5, 128.3, 128.3, 127.0, 126.8, 126.2, 123.4, 123.2.; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{19}N_2O$ 351.1492; Found 351.1502.

Procedure for the synthesis of pyrazole 9

To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added sequentially **3a** (0.2 mmol, 1.0 equiv), 1,2-diphenylacetylene **8** (0.4 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), $Cu(OAc)_2$ (0.4 mmol, 2.0 equiv), and DMF (2 mL). After vacuuming and backfilling with argon for three times, the Schlenk tube with an argon balloon was stirred at 80 °C (oil bath) for 12 h. After being cooled down to room temperature, 5 mL of water was added, and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The organic phases were collected and washed with a small amount of water for three times. The solution was dried with anhydrous Na_2SO_4, and the solid was removed from the solution by filtration. The solvent was removed at reduced pressure, and the residue was subjected to flash silica gel column chromatography to provide pure product with the elution of mixed petroleum ether and ethyl acetate (v/v = 5:1).



Phenyl(1-(5,6,7,8-tetraphenylnaphthalen-1-yl)-1*H*-pyrazol-4-yl)methanone (**9**). Eluent: V_{PET}/V_{EA} = 5:1; white solid (102.3 mg, 85% yield); mp 96-98 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (s, 1H), 7.69 (d, J = 8.4 Hz, 3H), 7.64-7.49 (m, 6H), 7.34-7.20 (m, 5H), 6.91-6.61 (m, 15H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.5, 142.8, 141.7, 140.3, 140.1, 140.1, 139.4, 139.2, 139.0, 138.1, 137.2, 136.1, 133.8, 132.5, 131.3, 131.1, 129.5, 129.0, 128.9, 128.2, 127.3, 127.1, 126.9, 126.6, 126.0, 125.9, 125.7, 125.6, 122.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{31}N_2O$ 603.2431; Found 603.2438.

References

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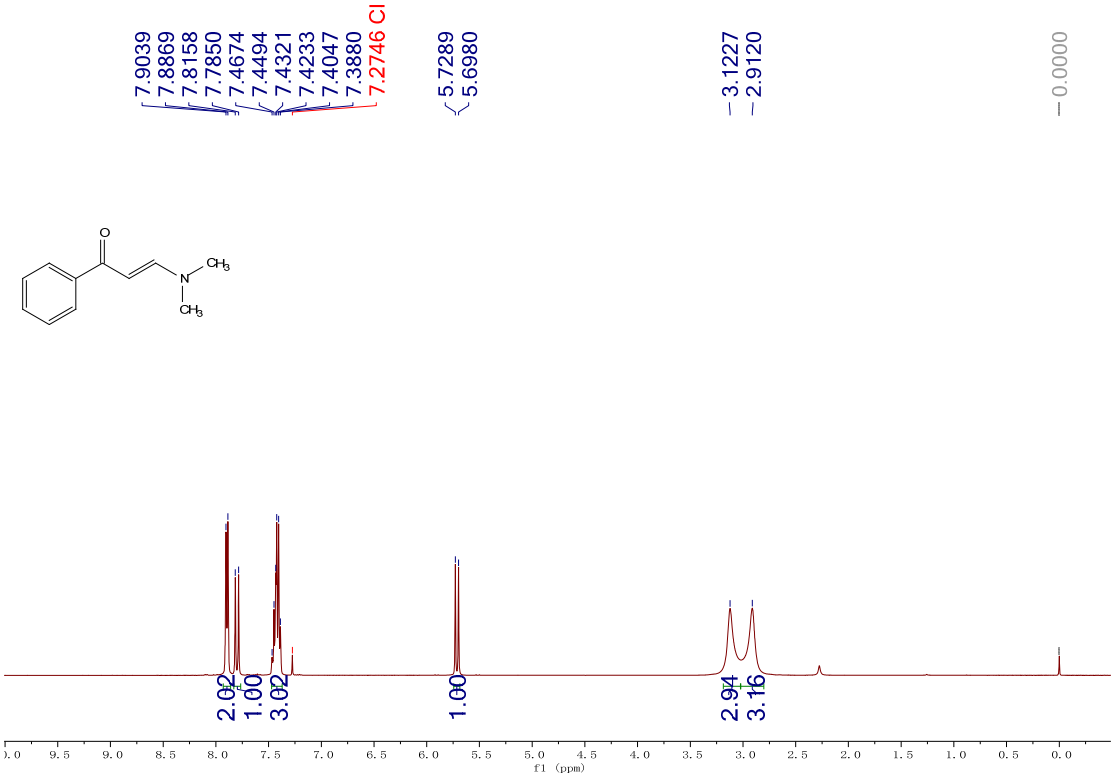
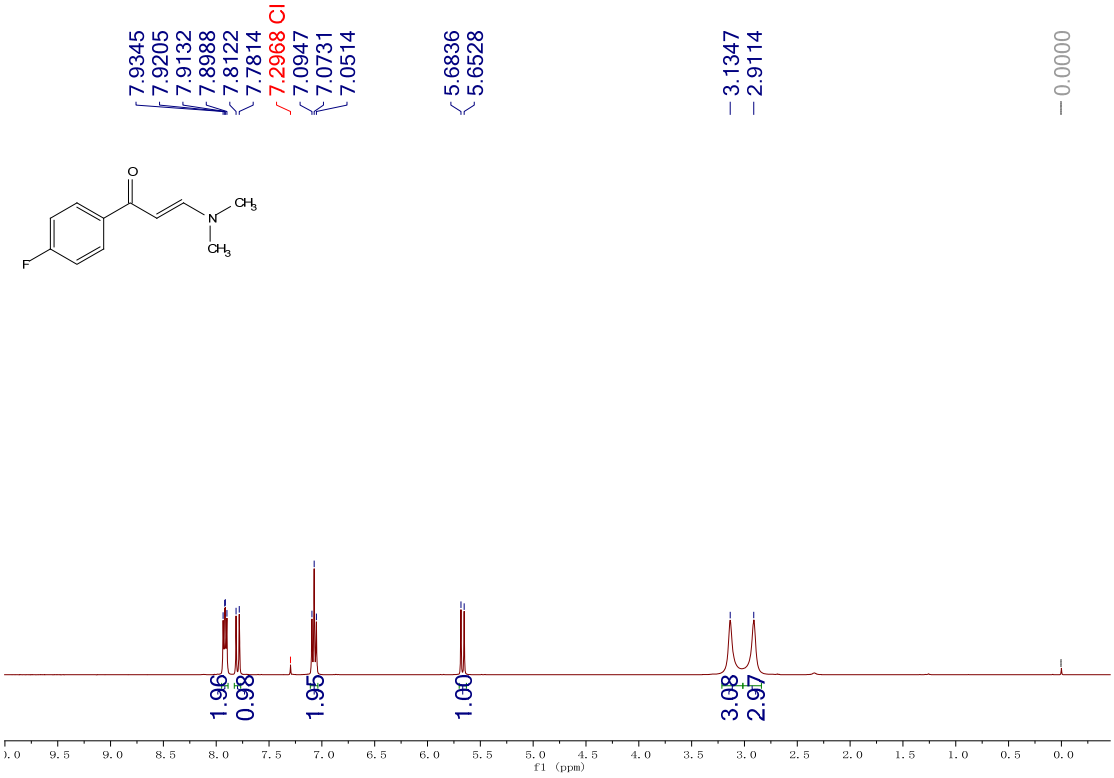
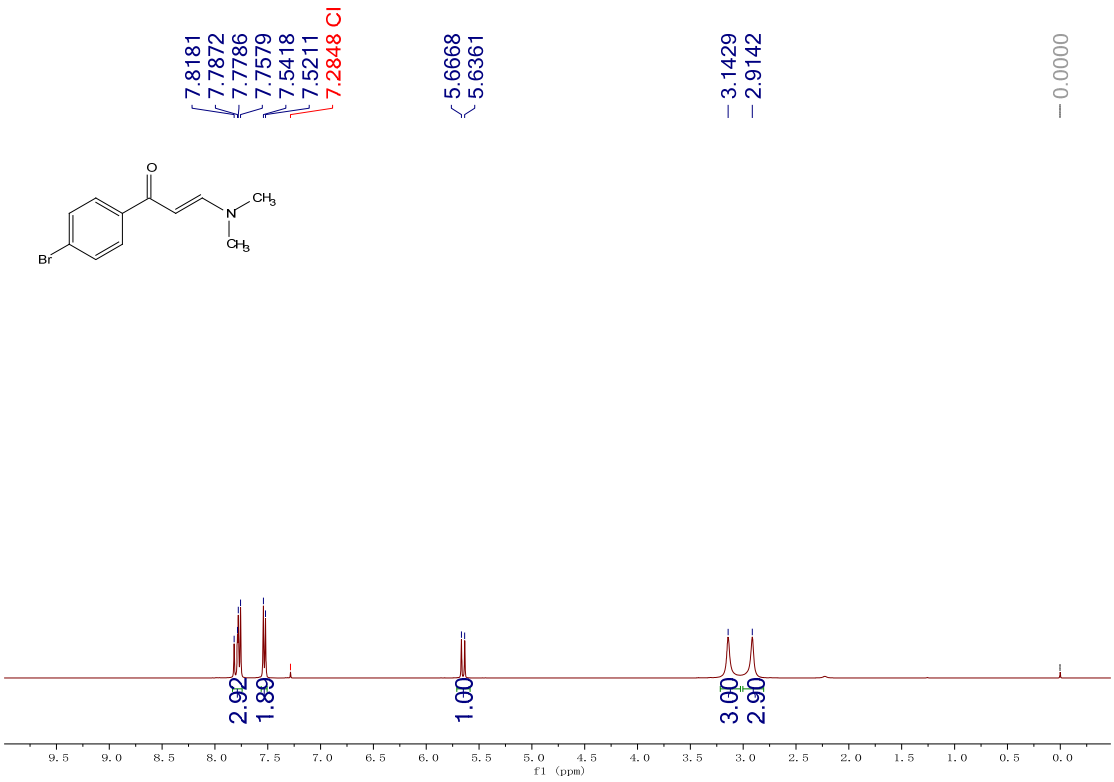
The ^{1}H and ^{13}C NMR spectra



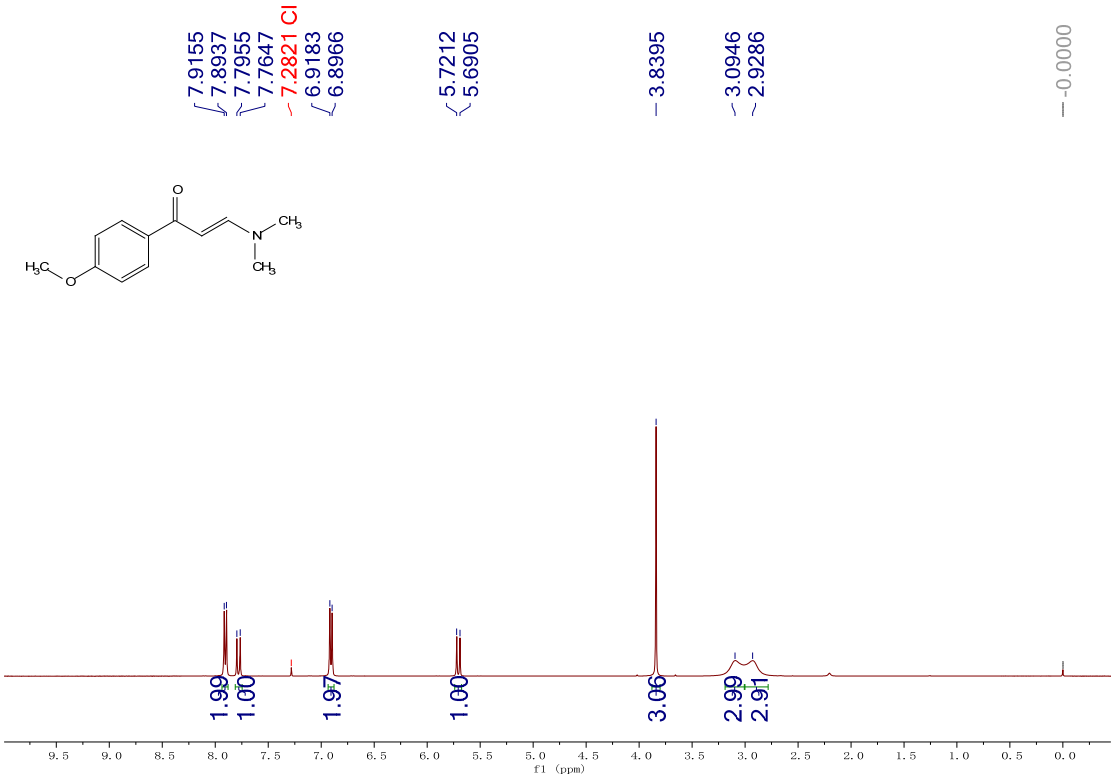
^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$)



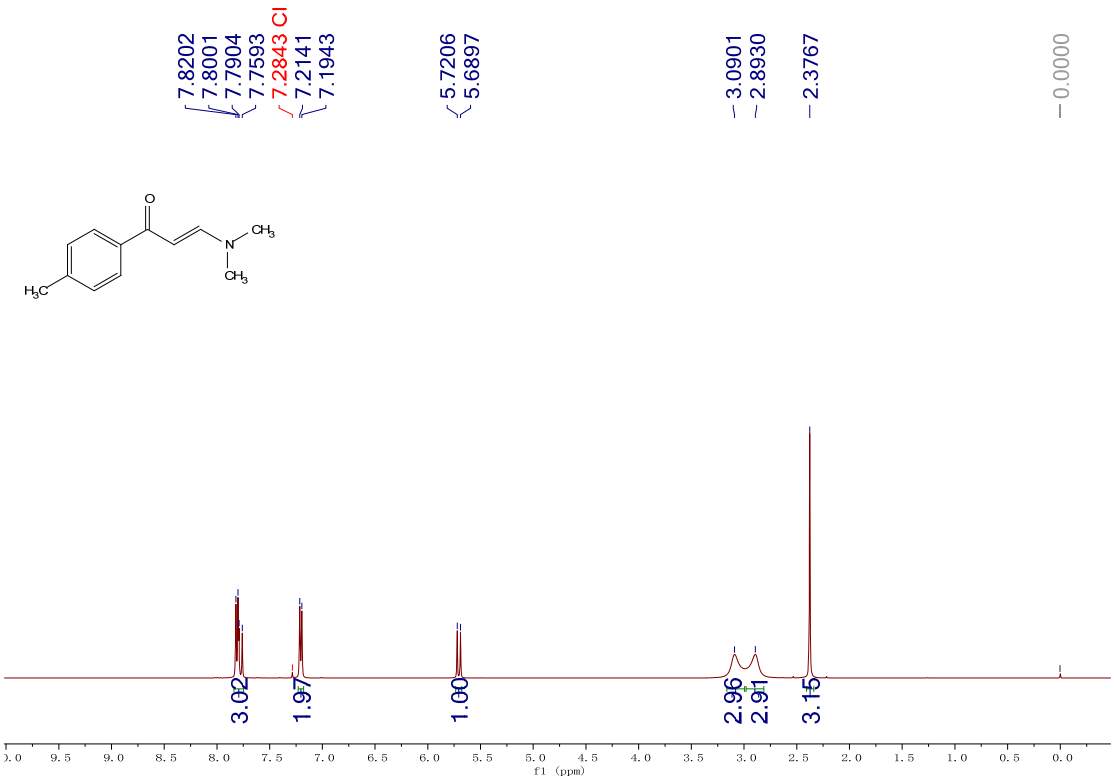
^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1d** (400 MHz, $CDCl_3$)



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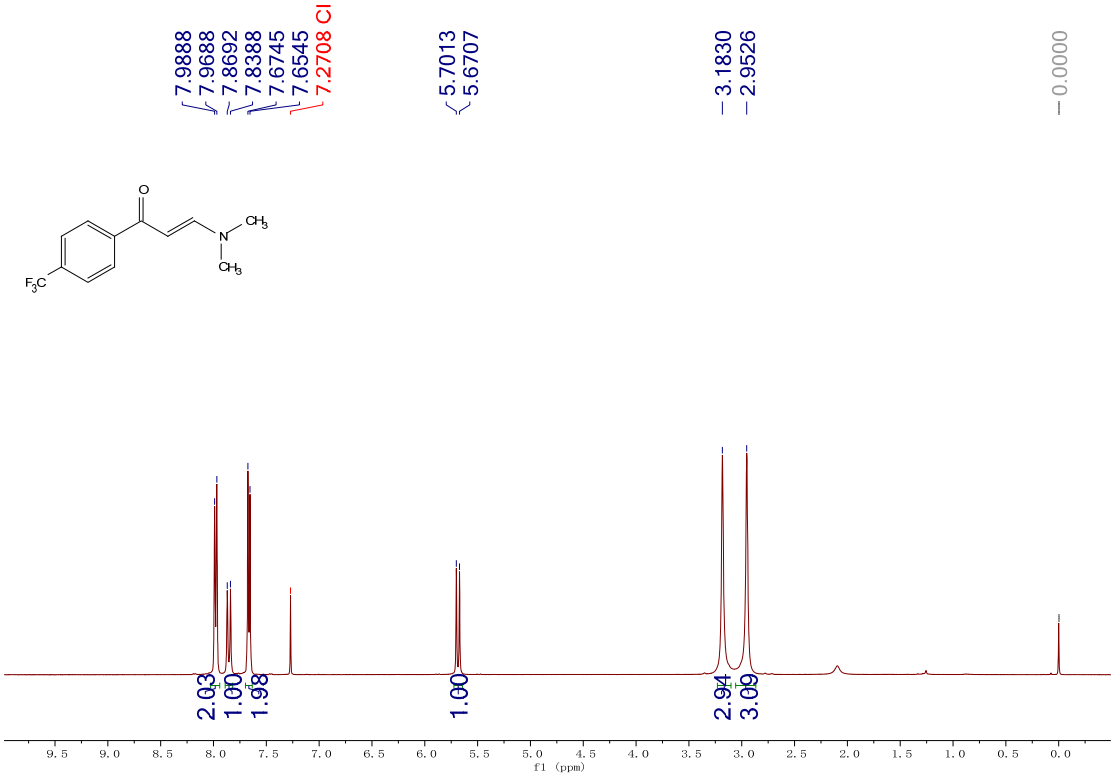
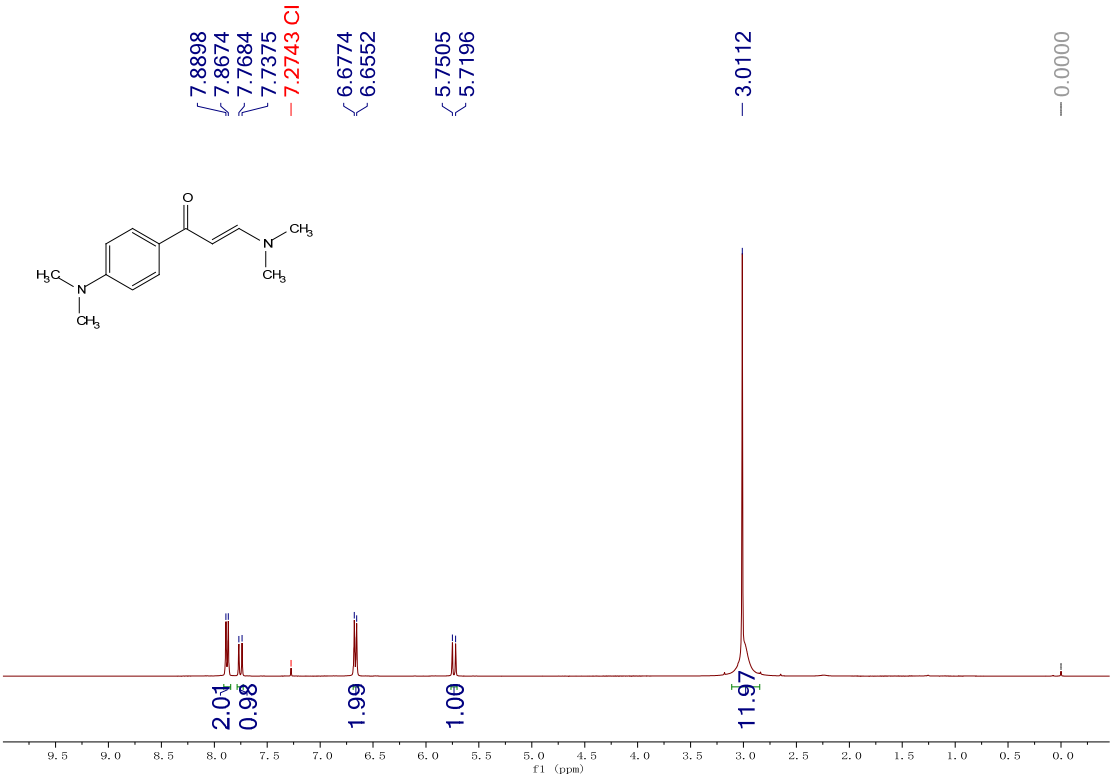
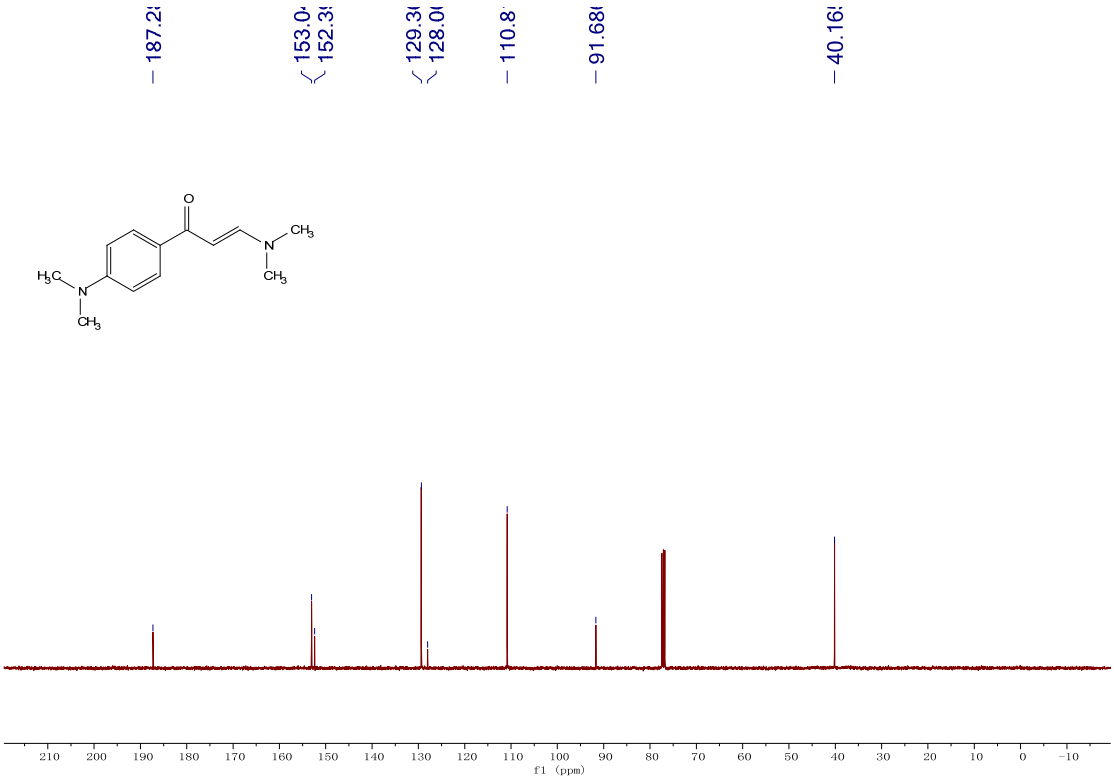


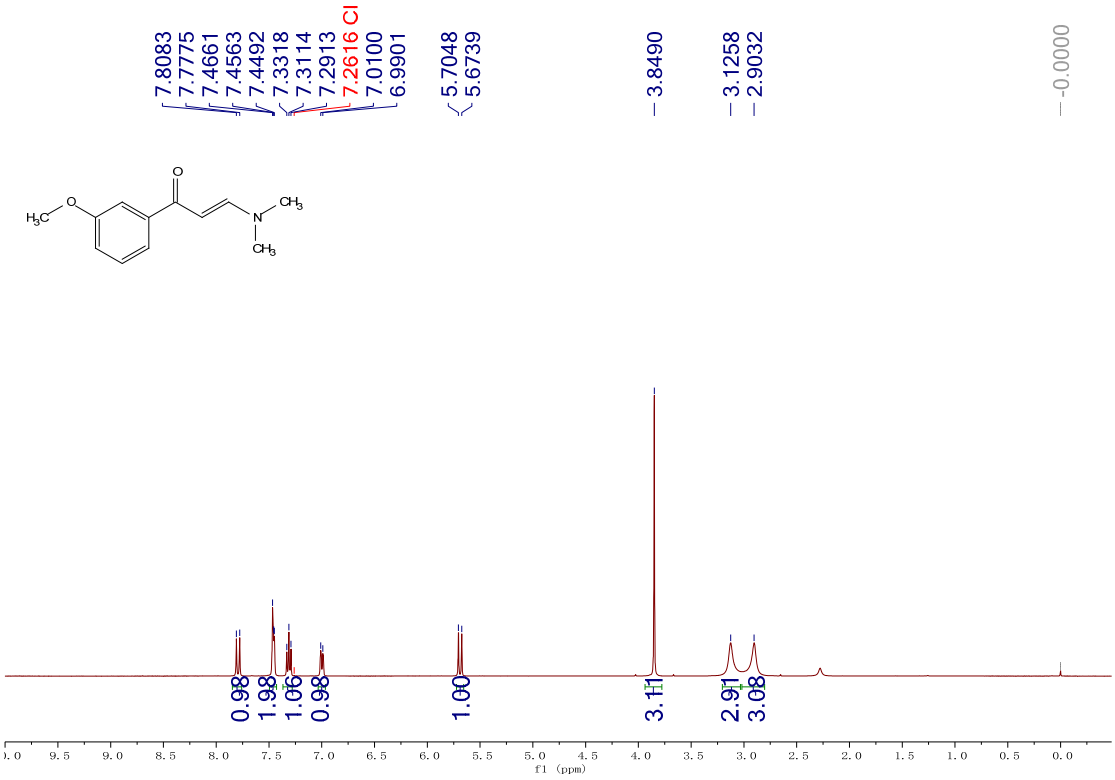
^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1g** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1g** (100 MHz, $CDCl_3$)



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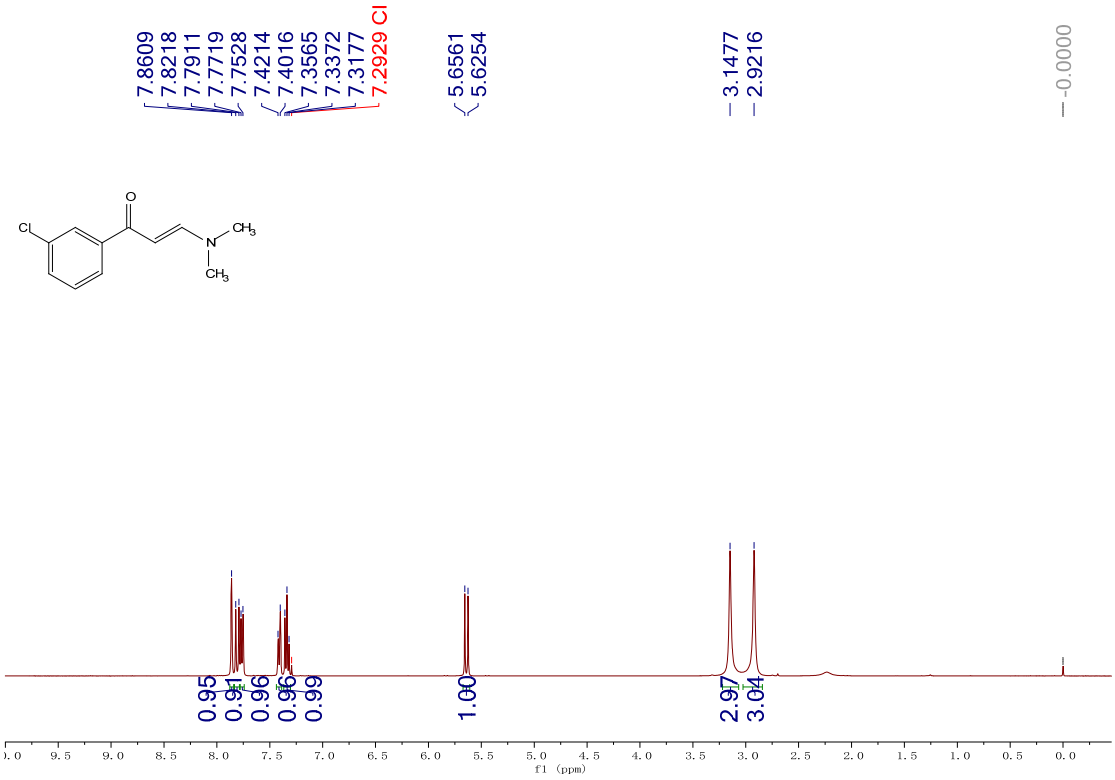

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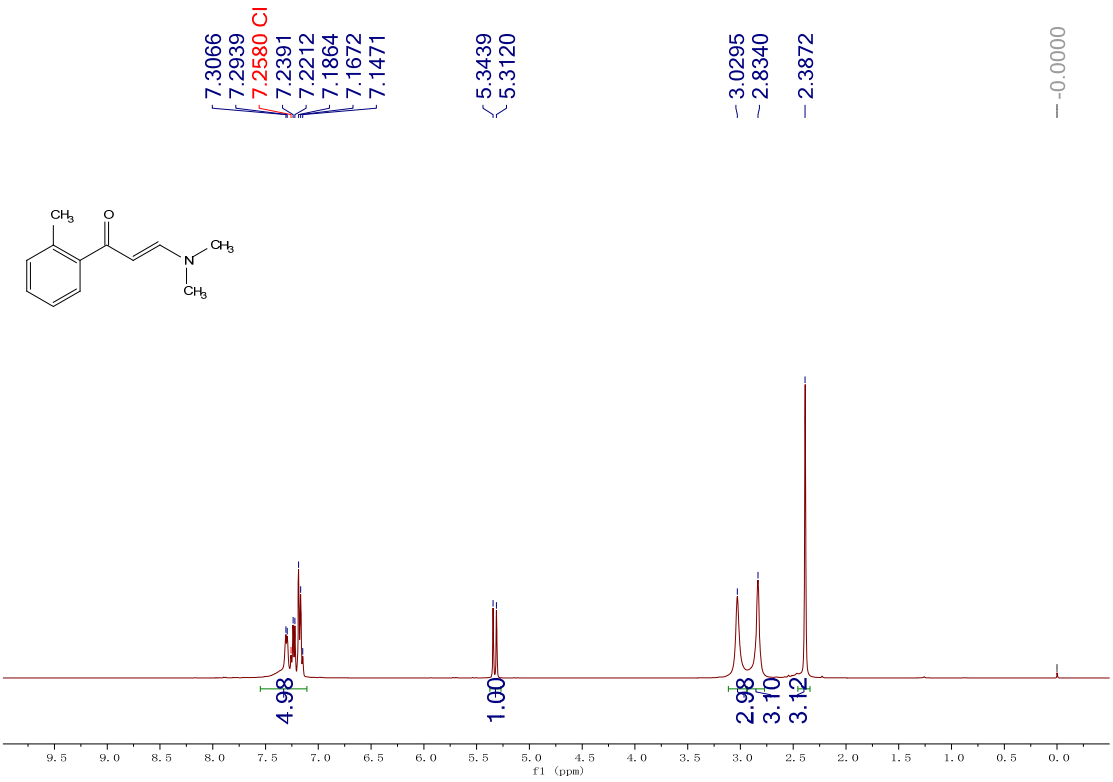

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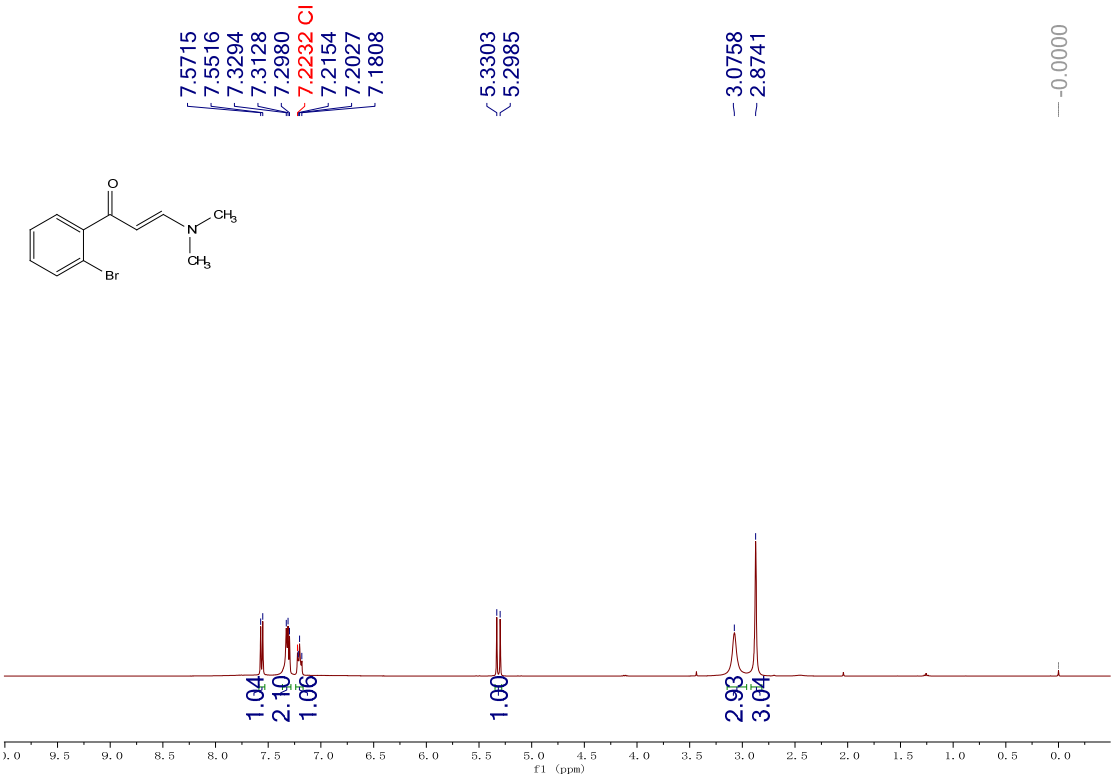
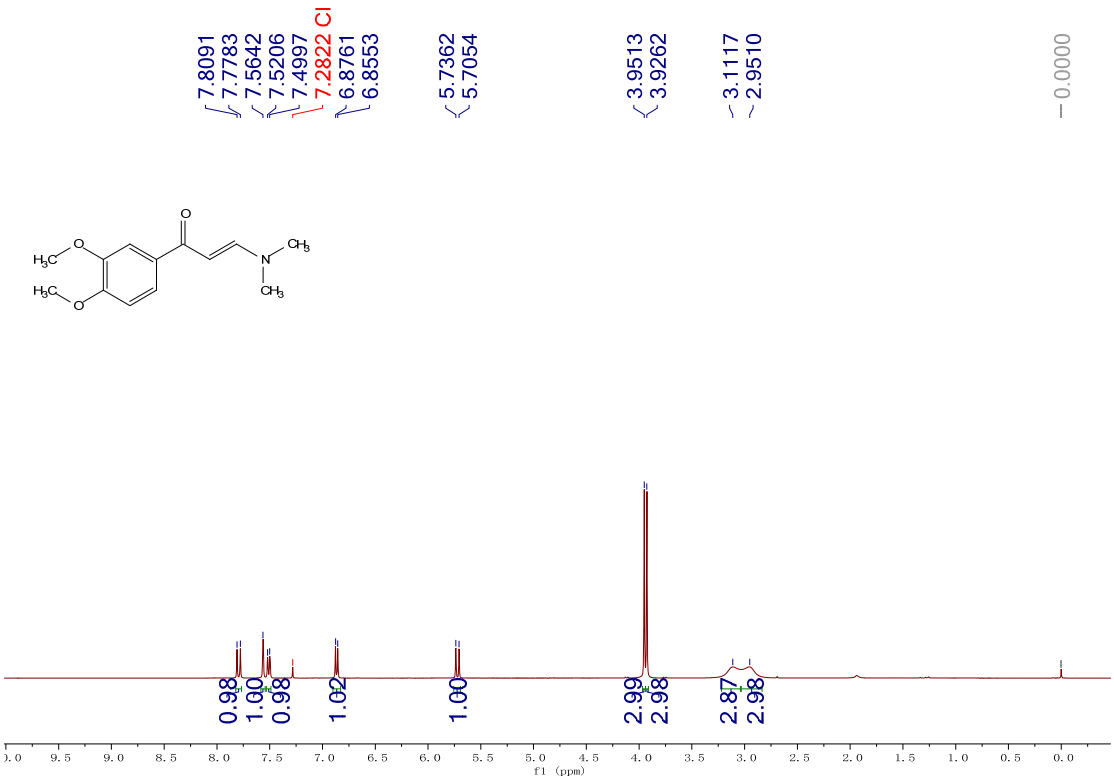
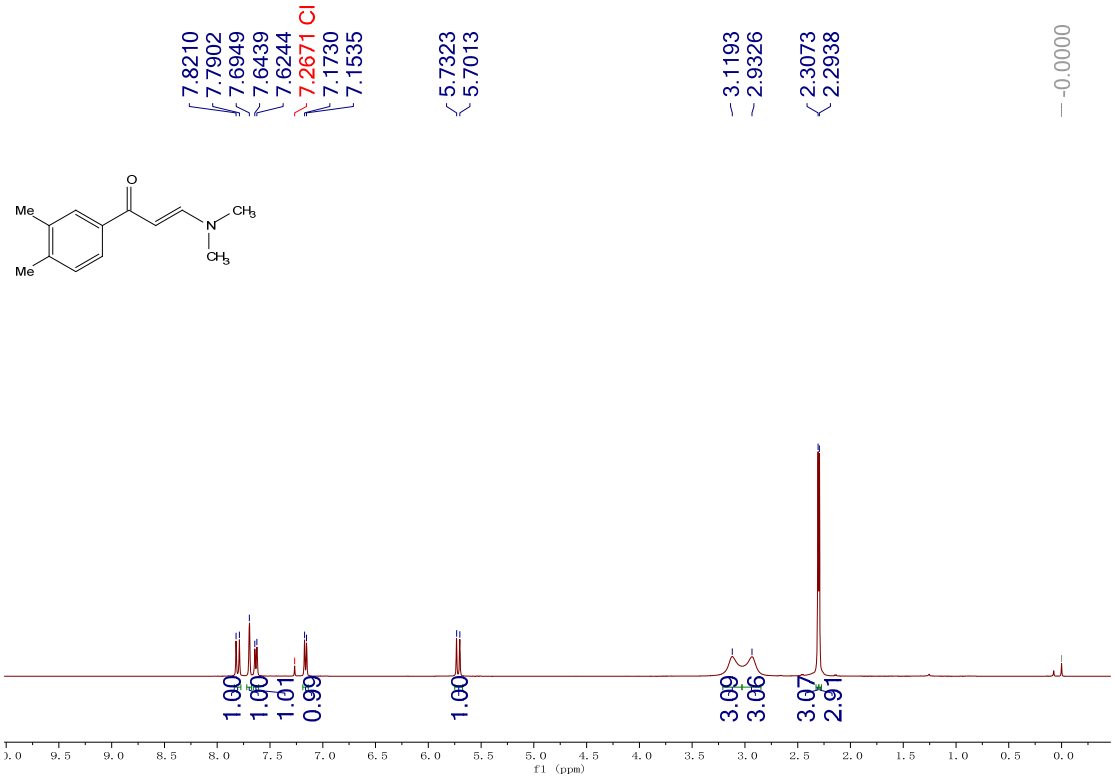


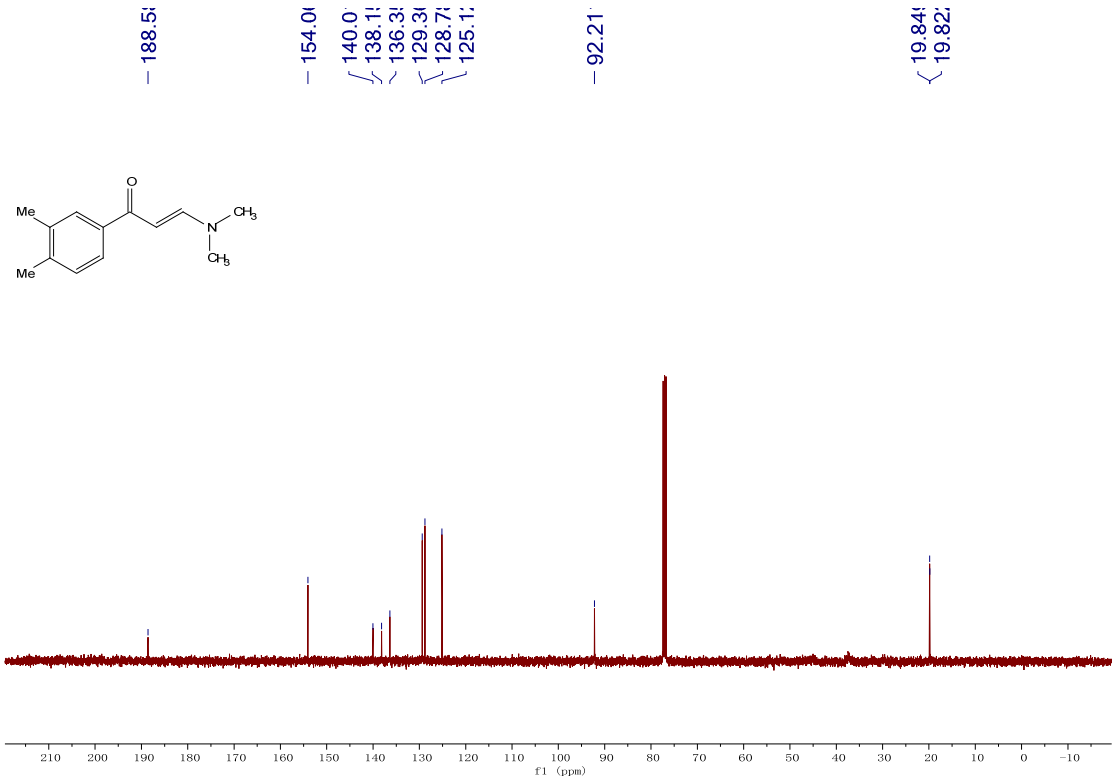
^{1}H NMR spectrum of **1k** (400 MHz, $CDCl_3$)



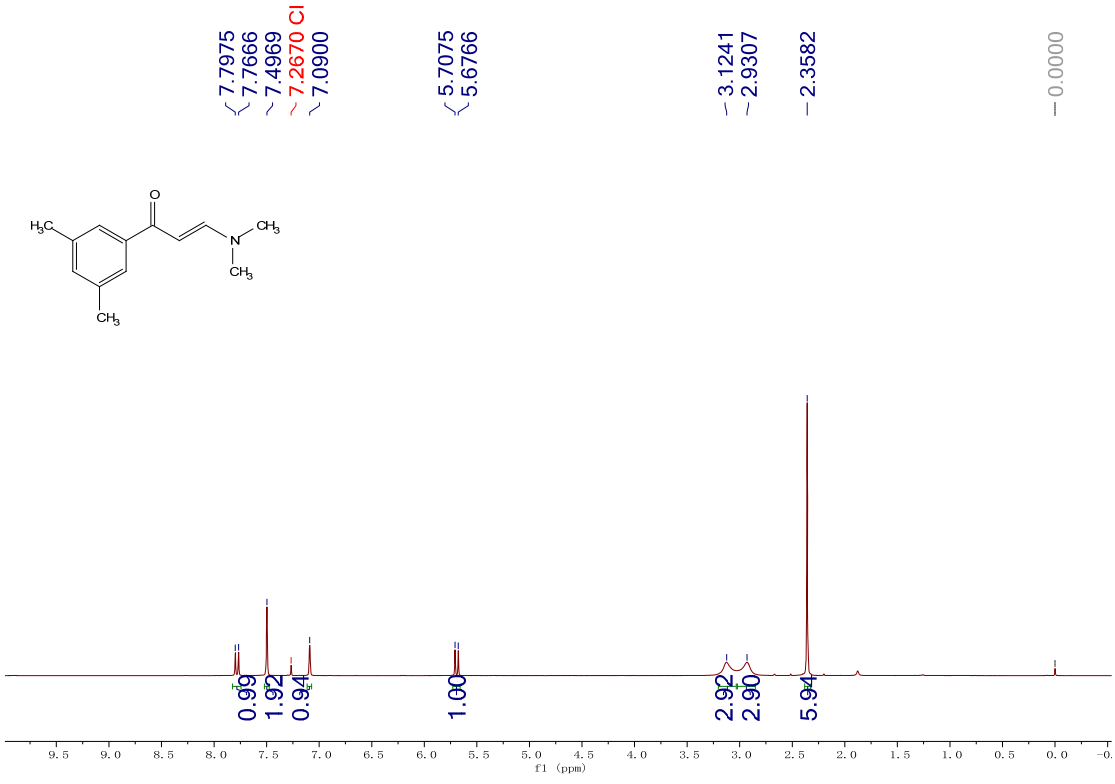
^{1}H NMR spectrum of **1l** (400 MHz, $CDCl_3$)



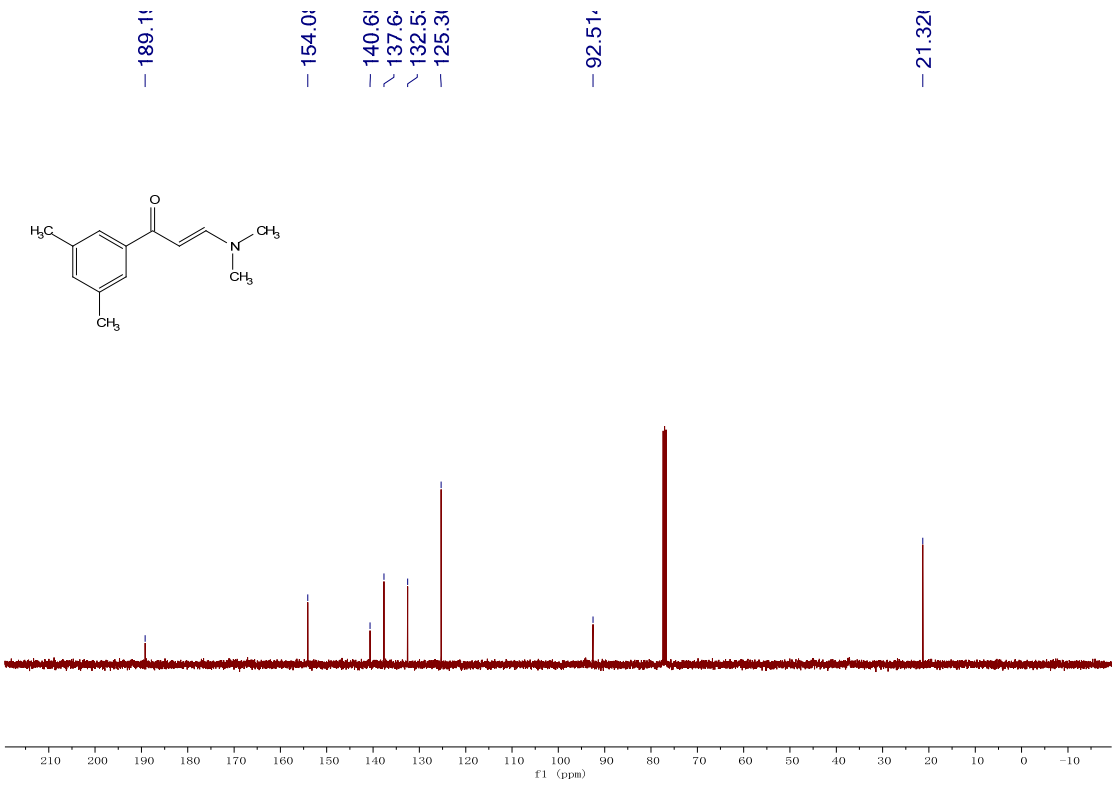
^{1}H NMR spectrum of **1m** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1m** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1n** (400 MHz, $CDCl_3$)



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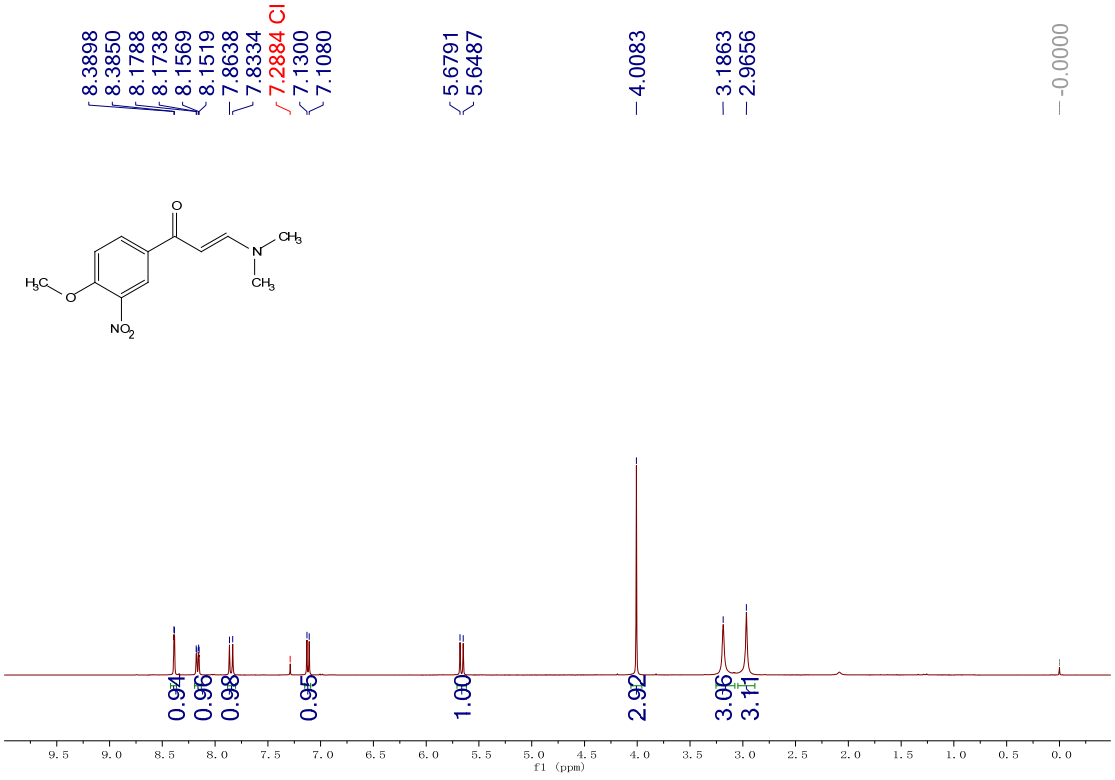
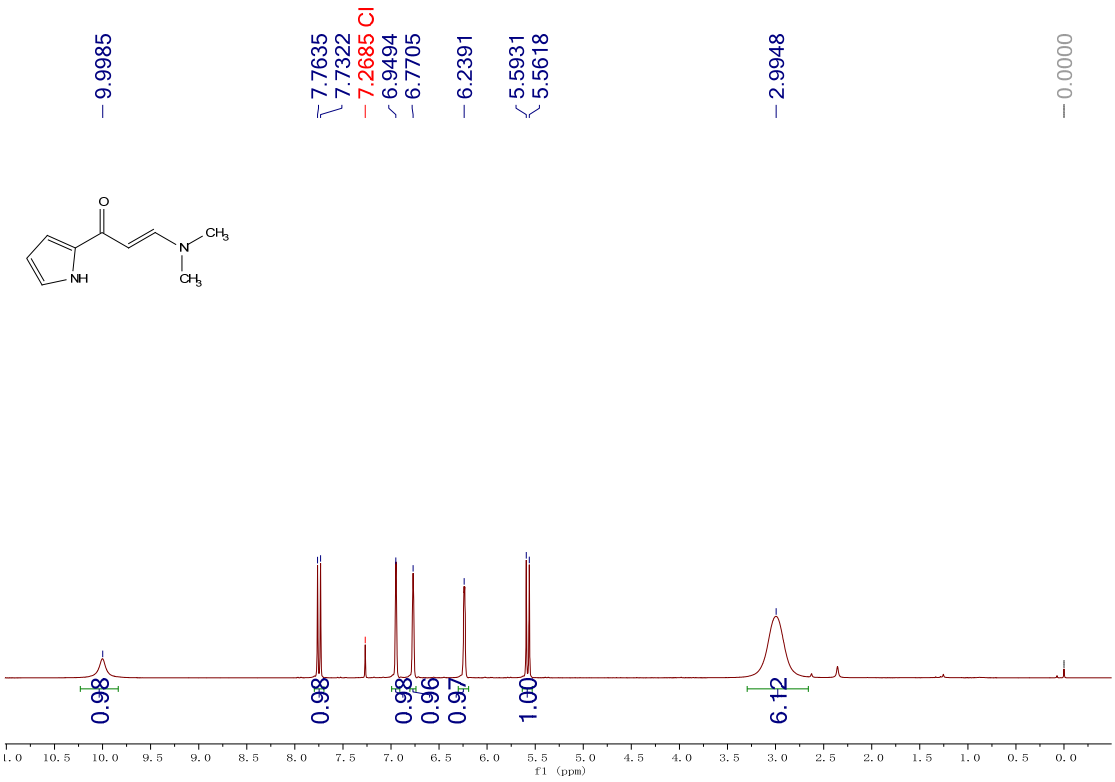
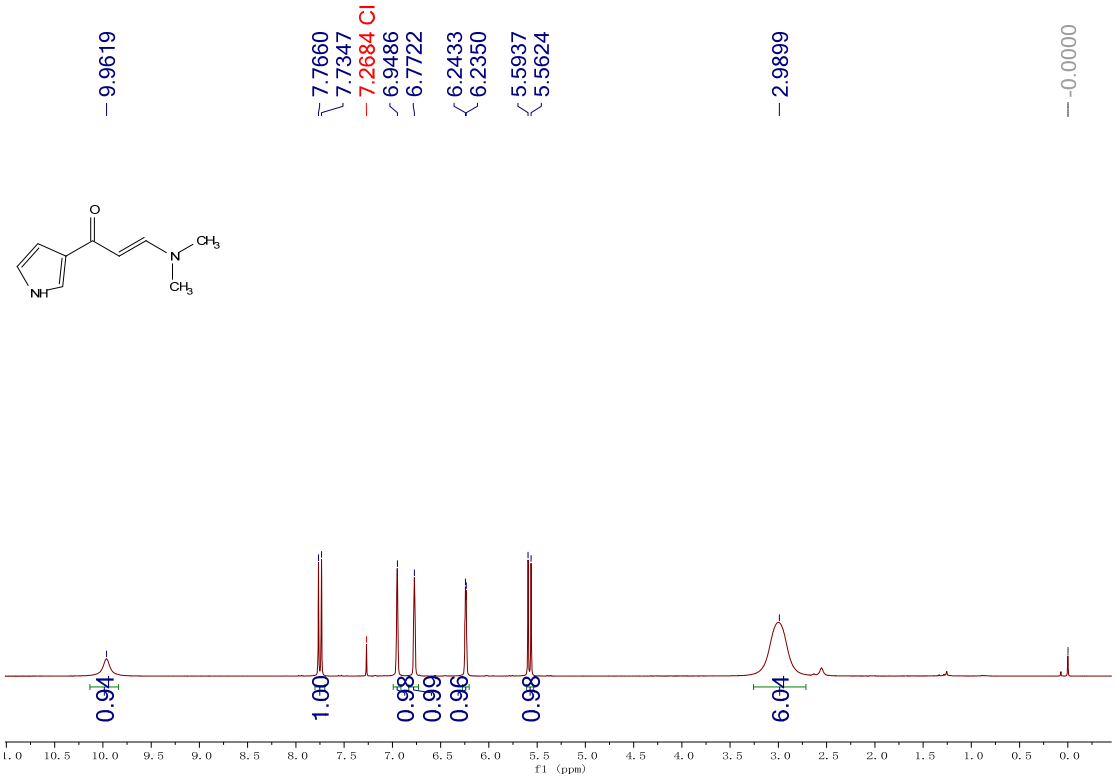


^{1}H NMR spectrum of **1o** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1p** (400 MHz, $CDCl_3$)



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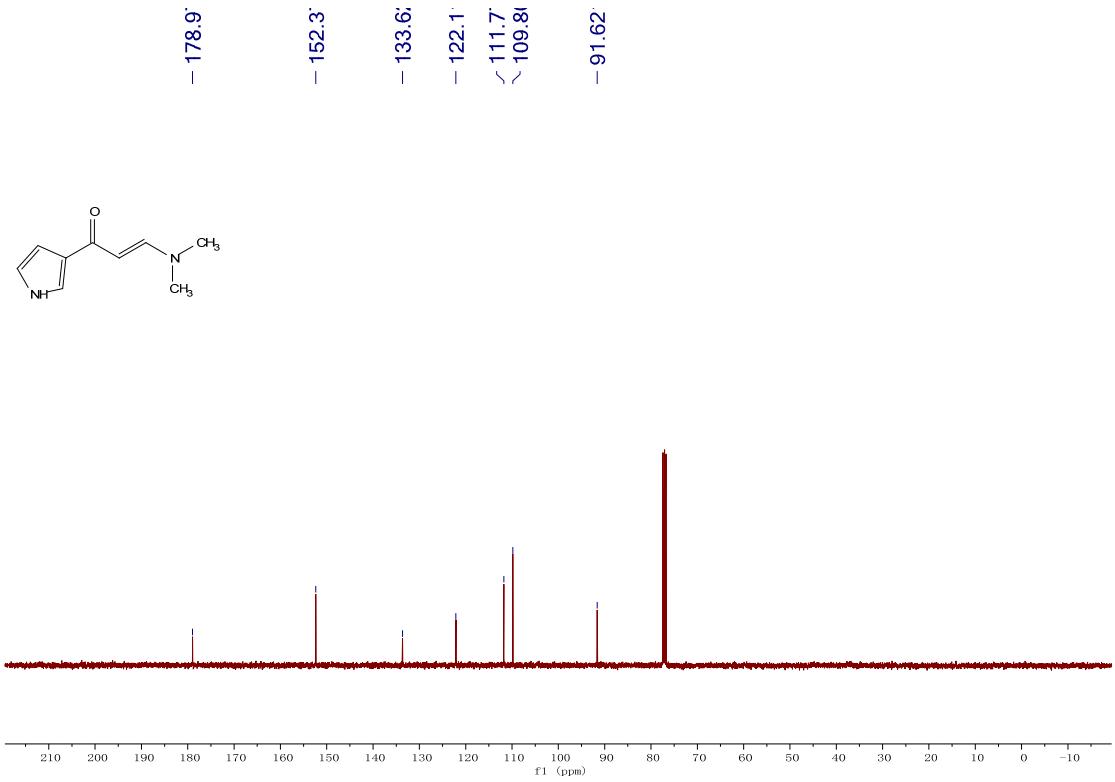

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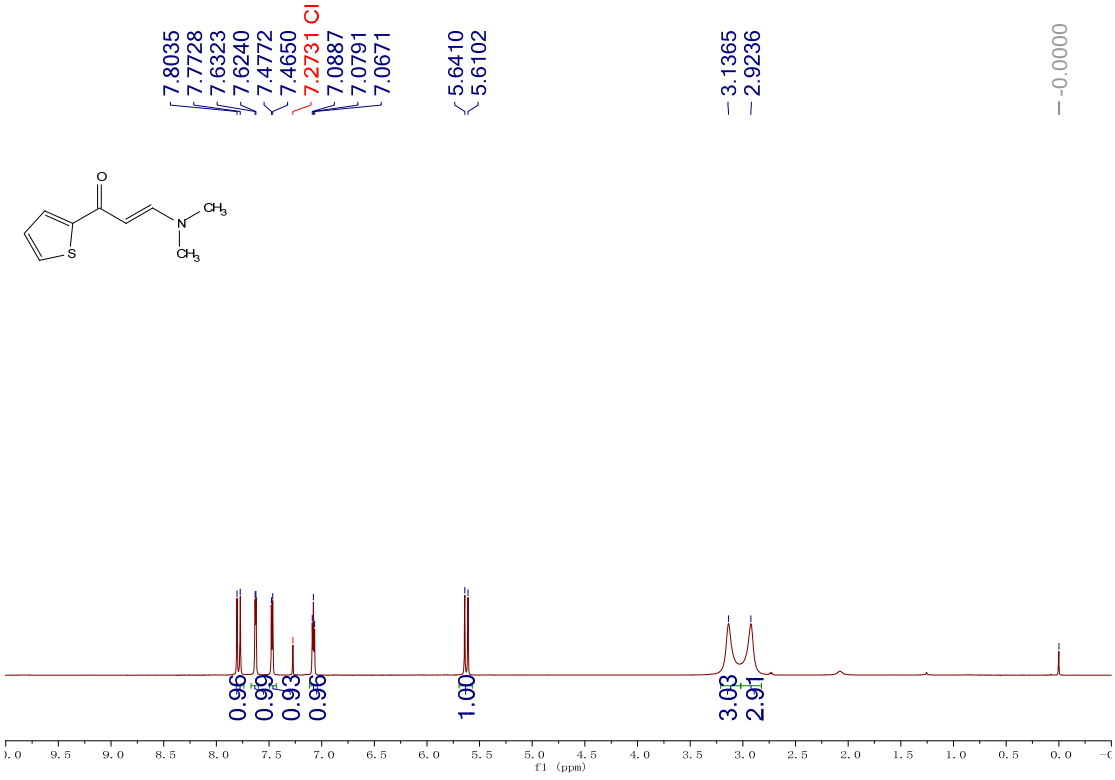
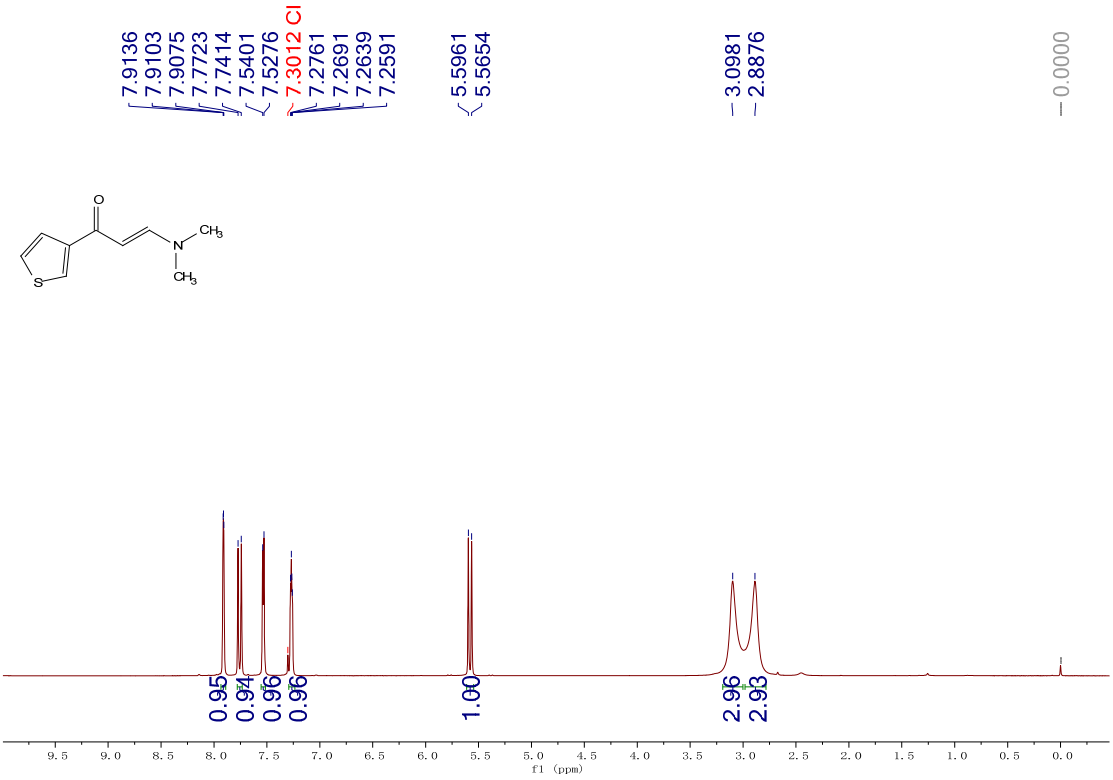
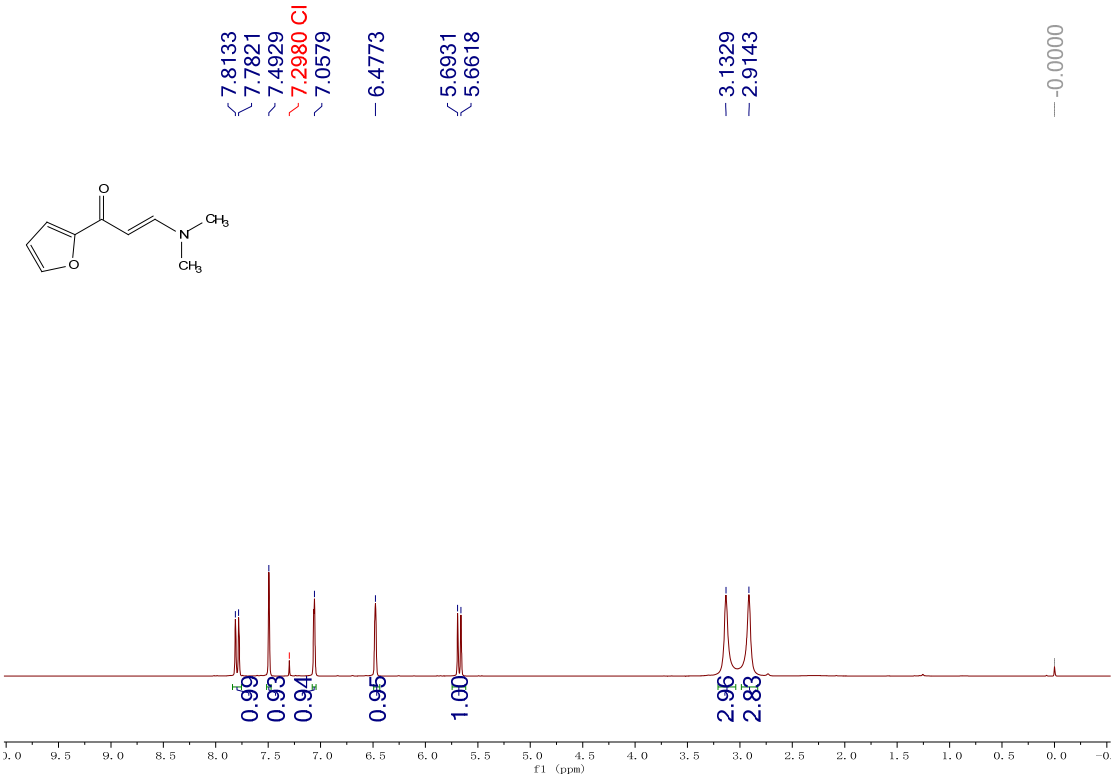


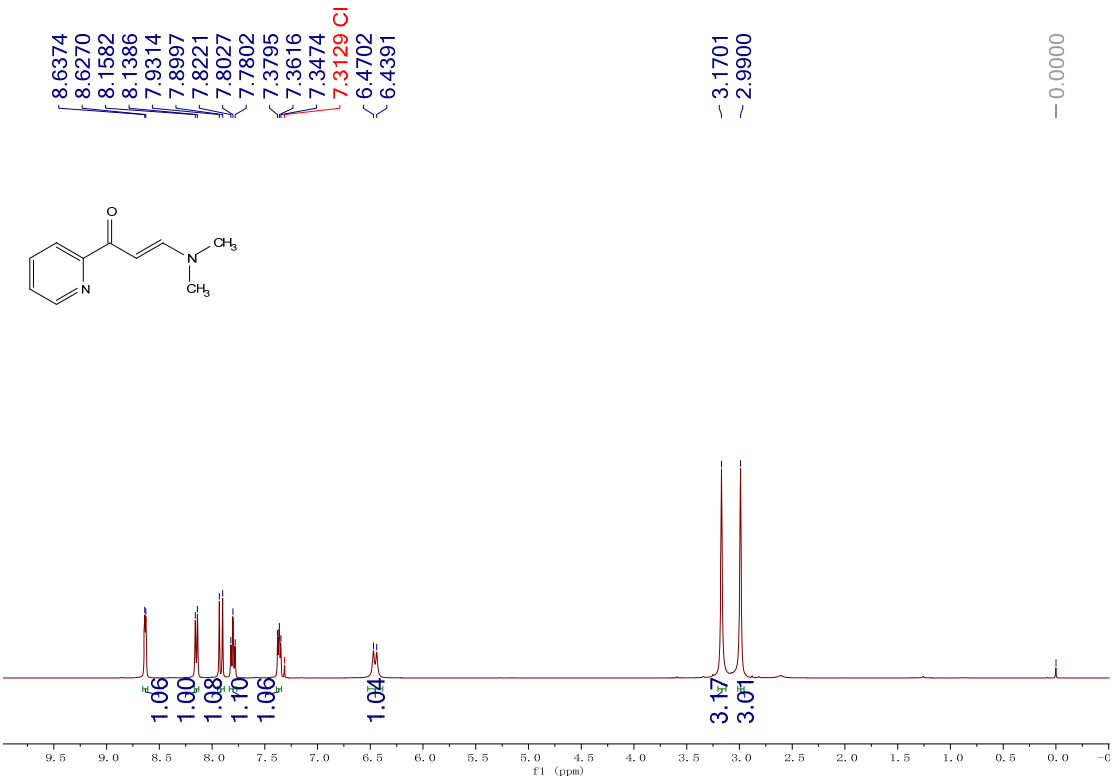
^{1}H NMR spectrum of **1r** (400 MHz, $CDCl_3$)



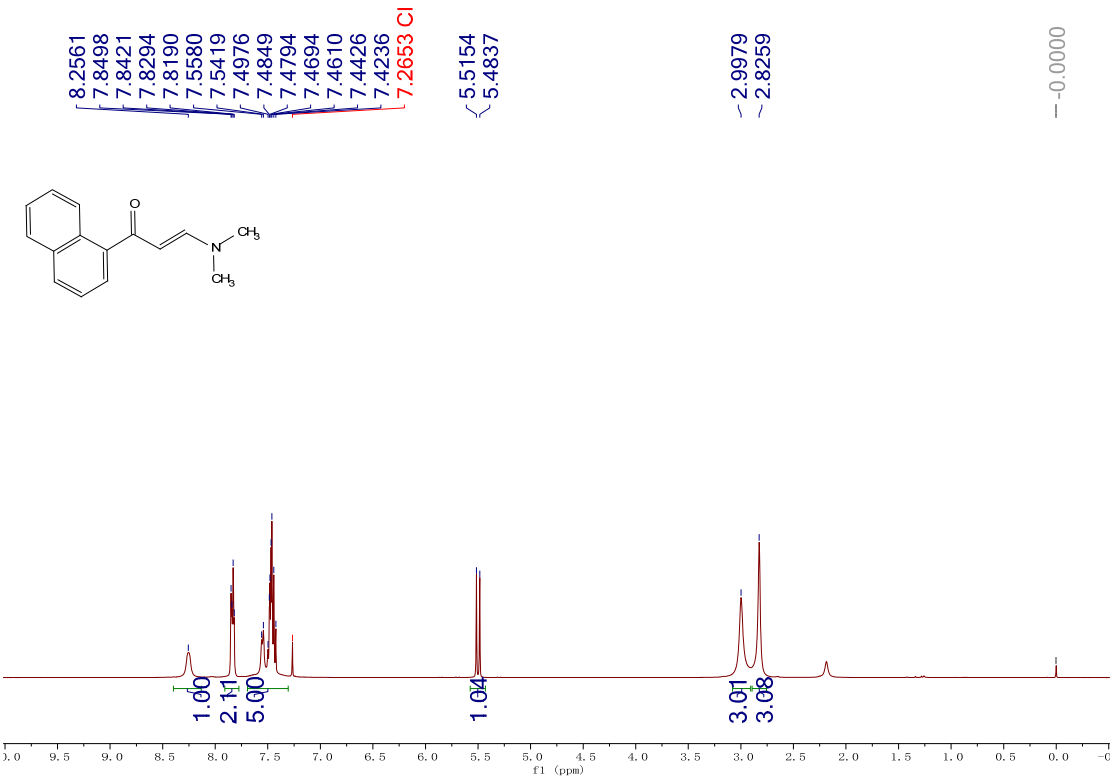
^{1}H NMR spectrum of **1s** (400 MHz, $CDCl_3$)



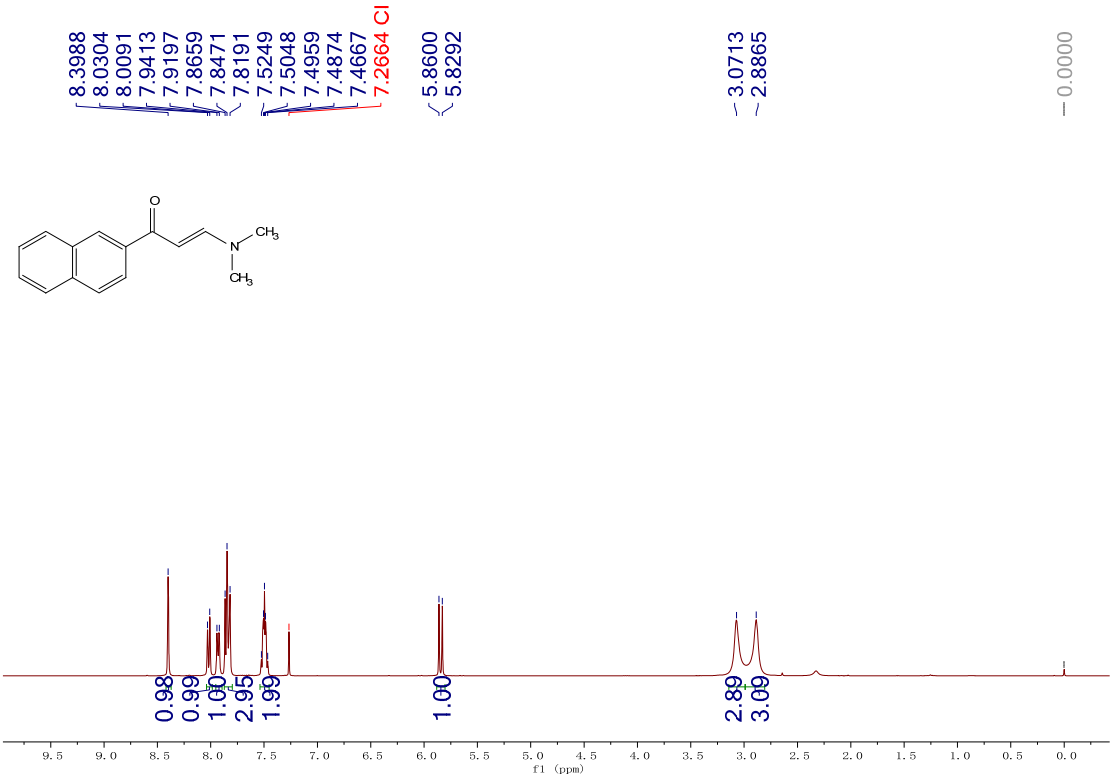
^{1}H NMR spectrum of **1t** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1u** (400 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1v** (400 MHz, $CDCl_3$)



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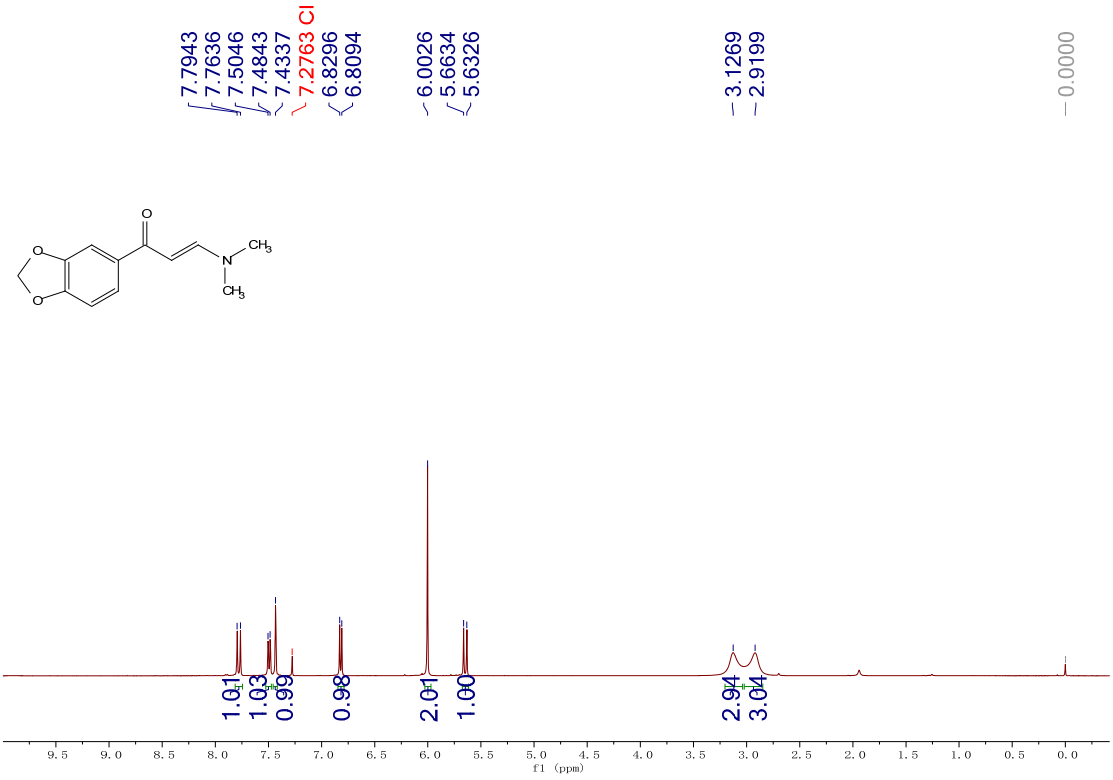

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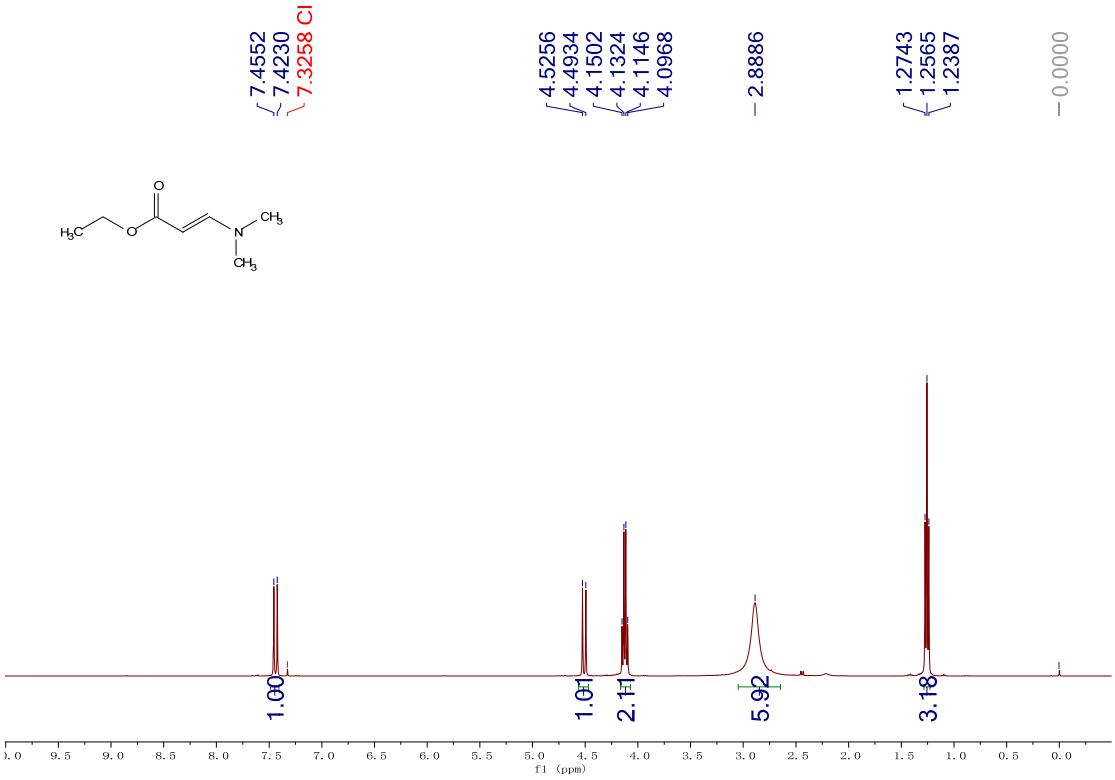

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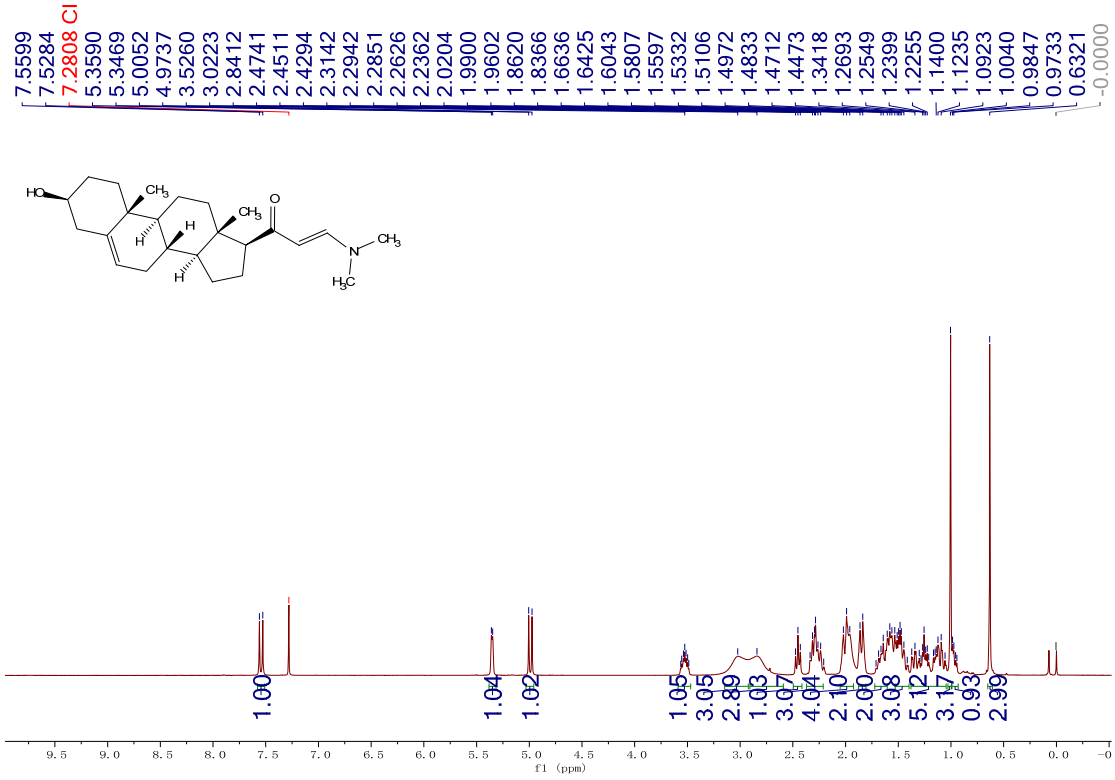

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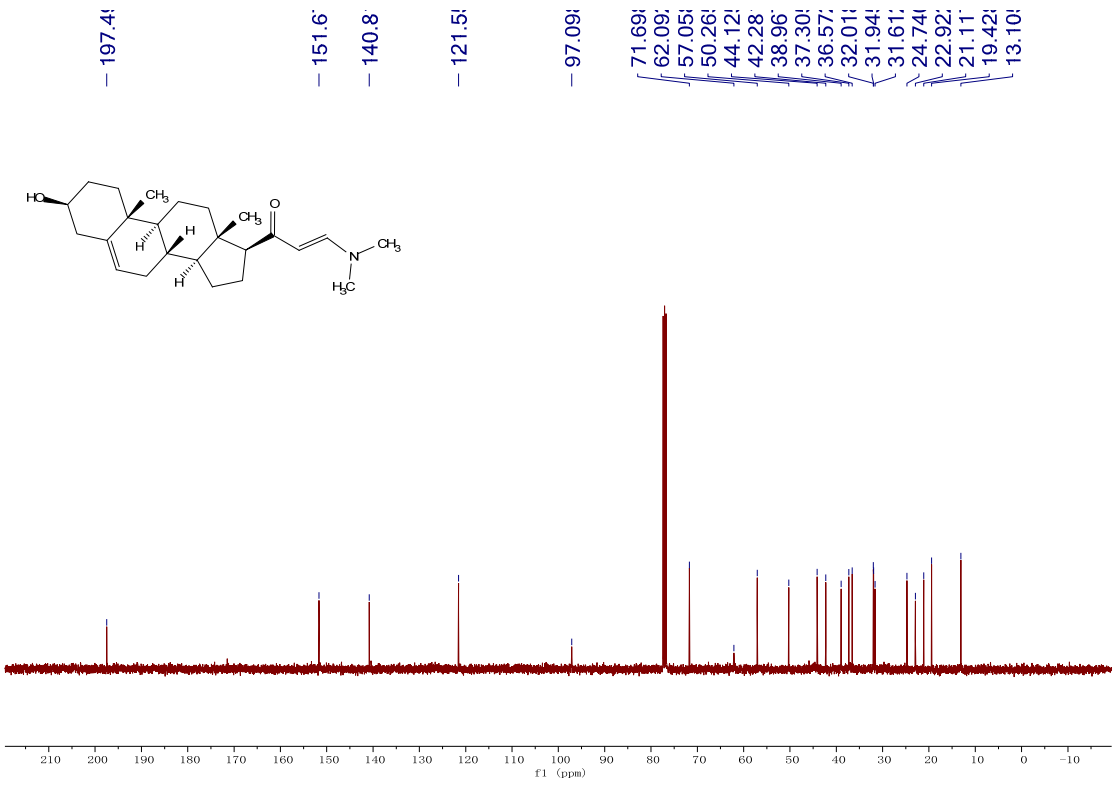

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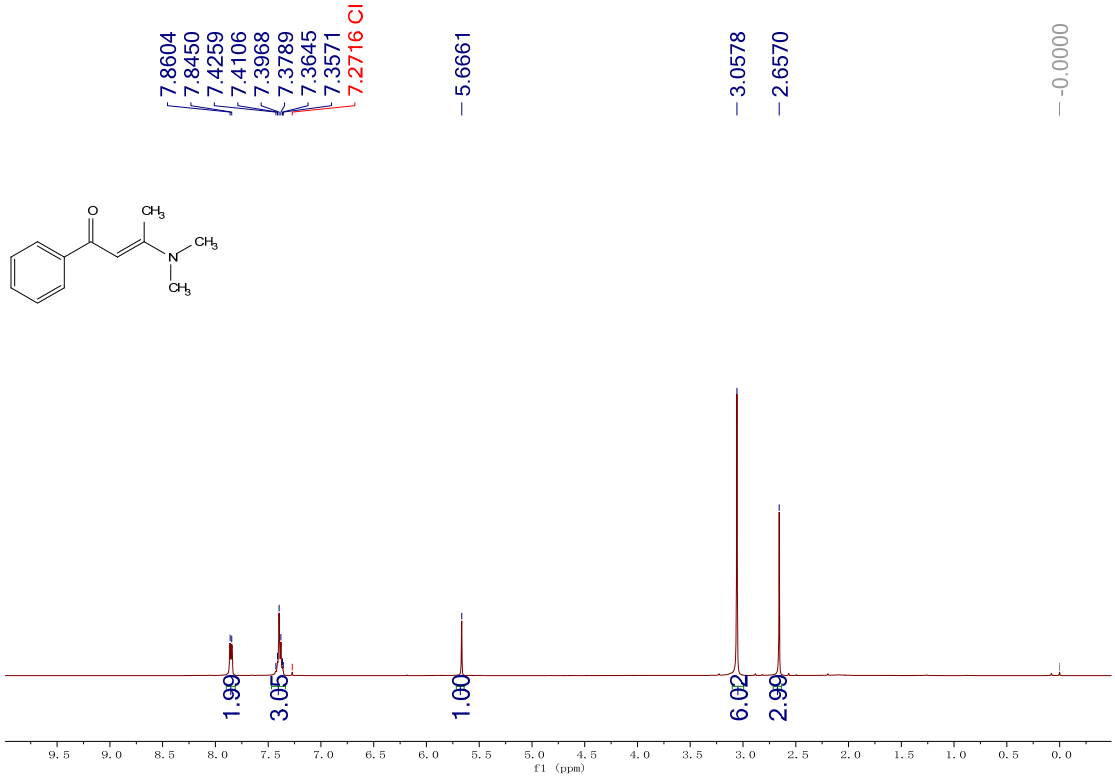

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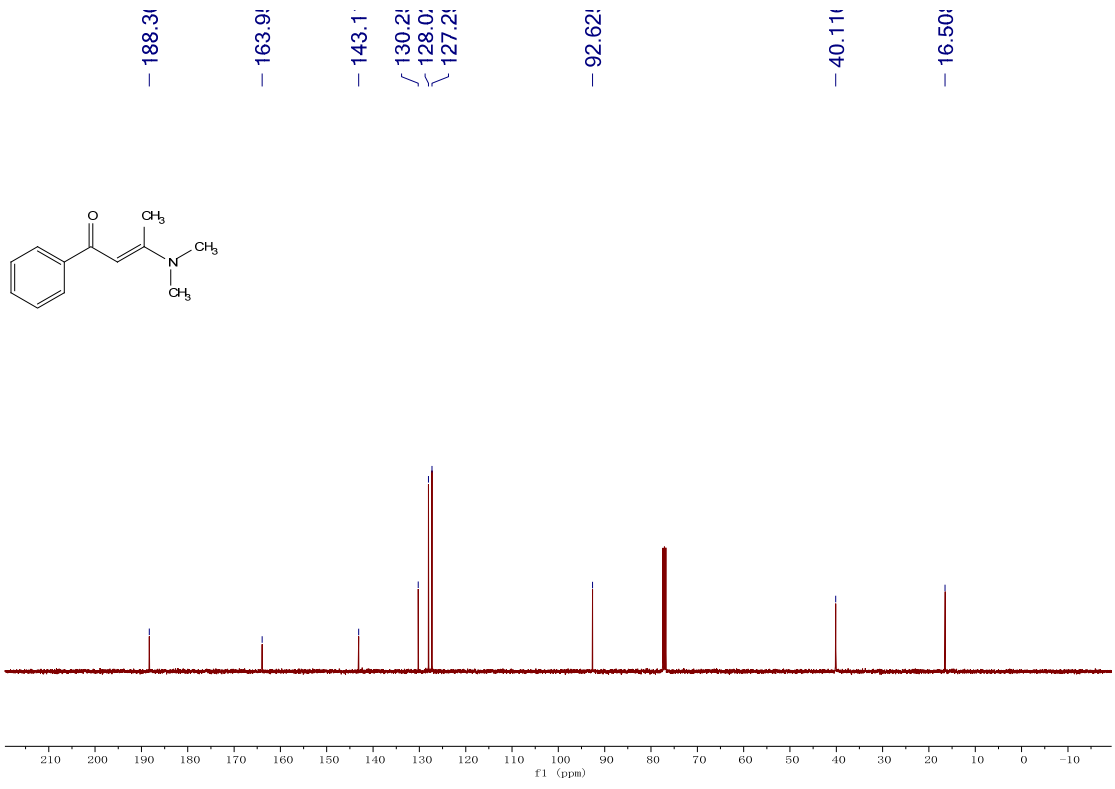
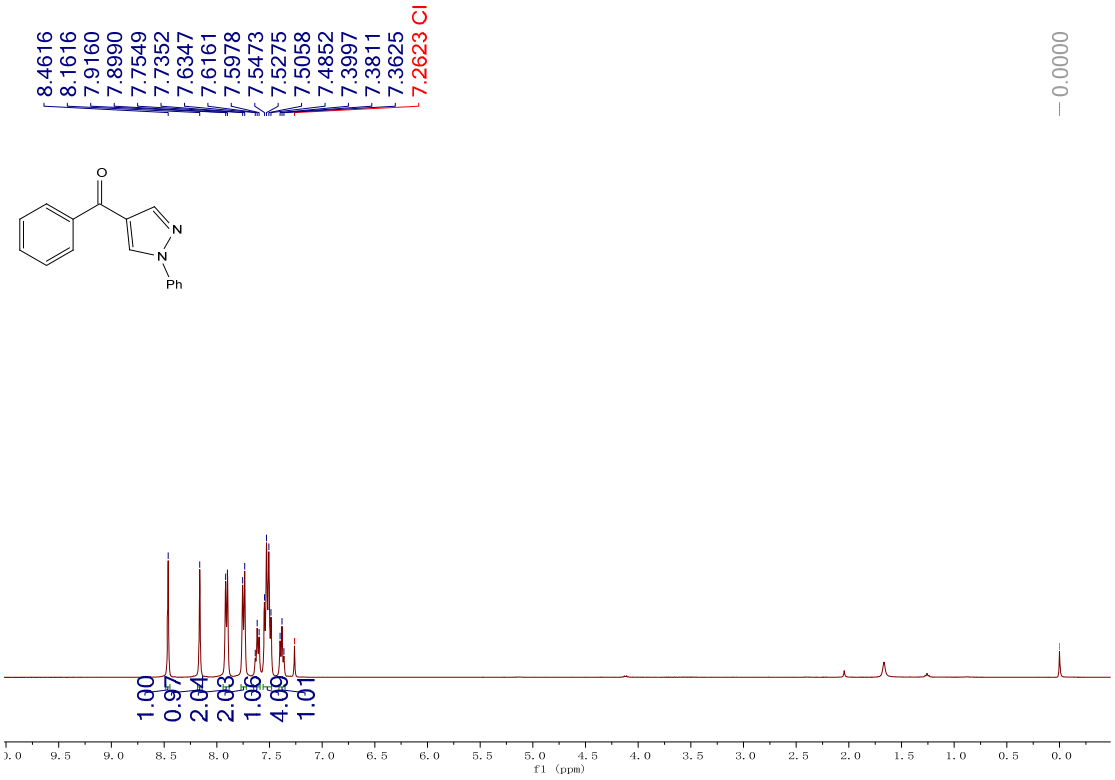
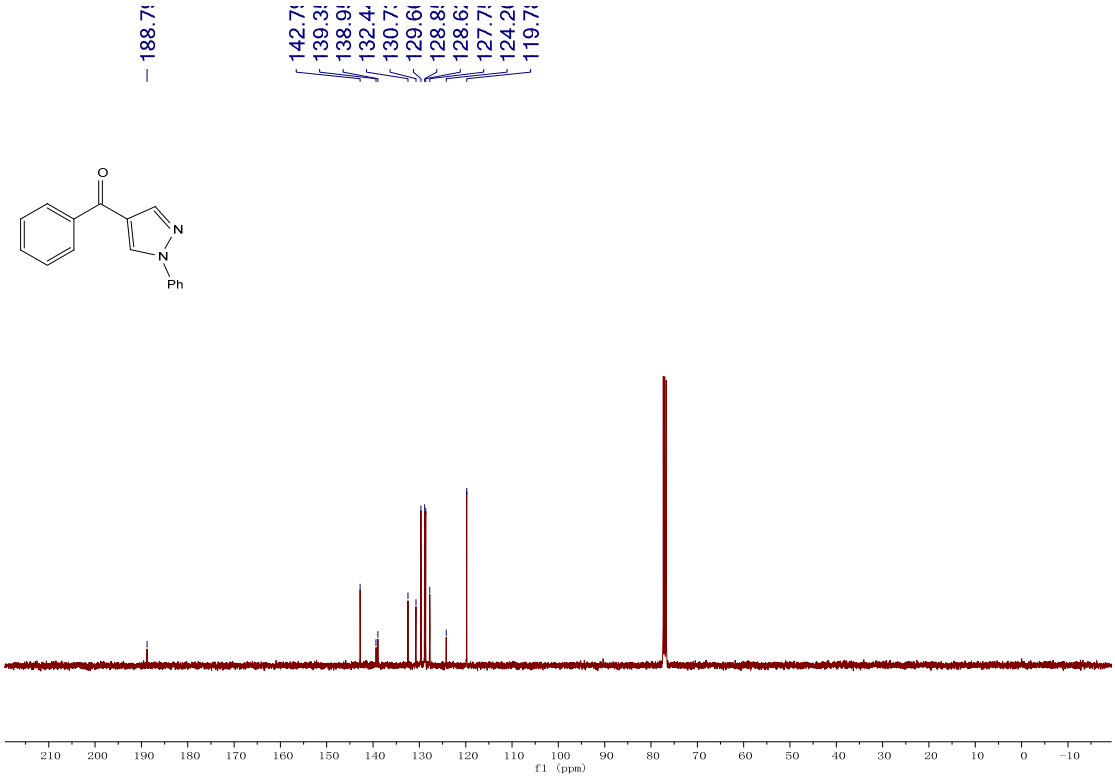


^{13}C NMR spectrum of 10 (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



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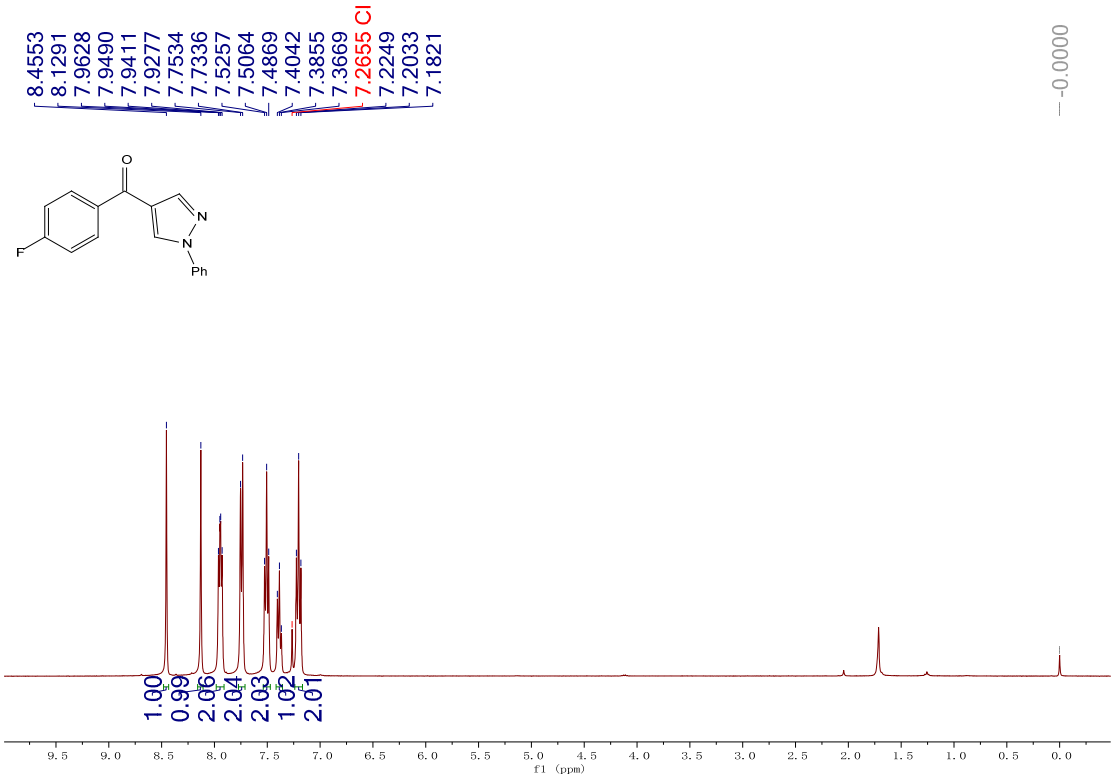
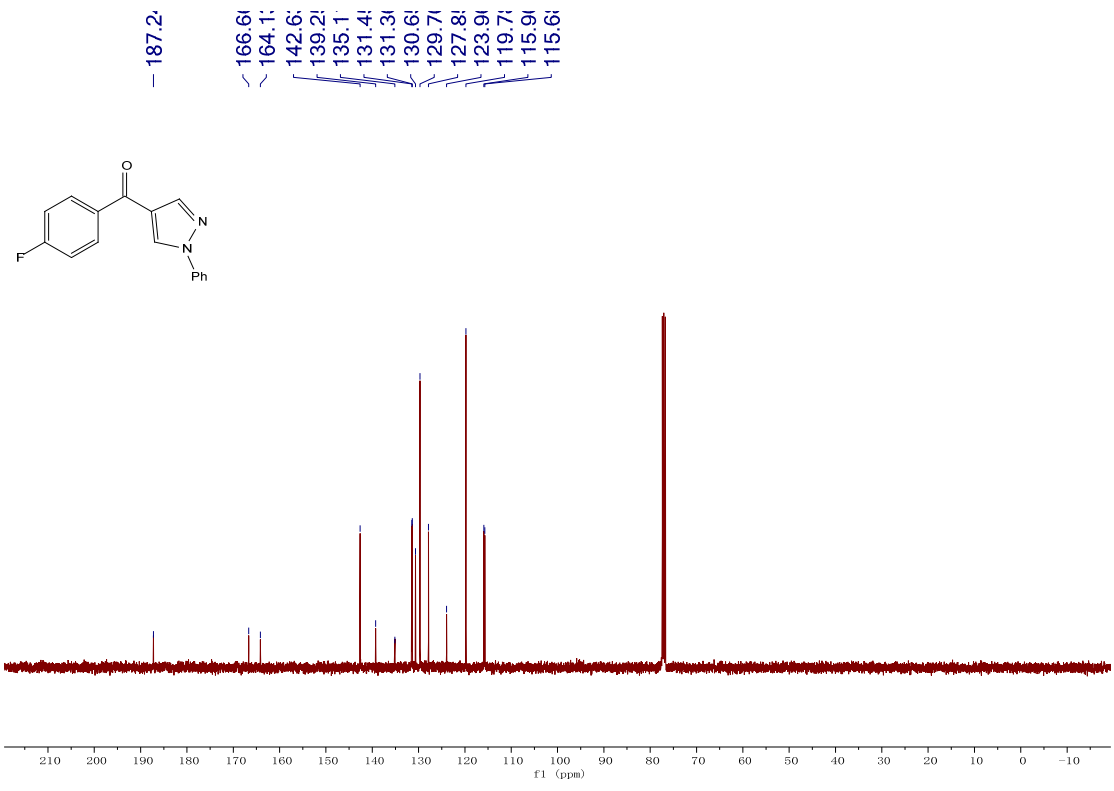
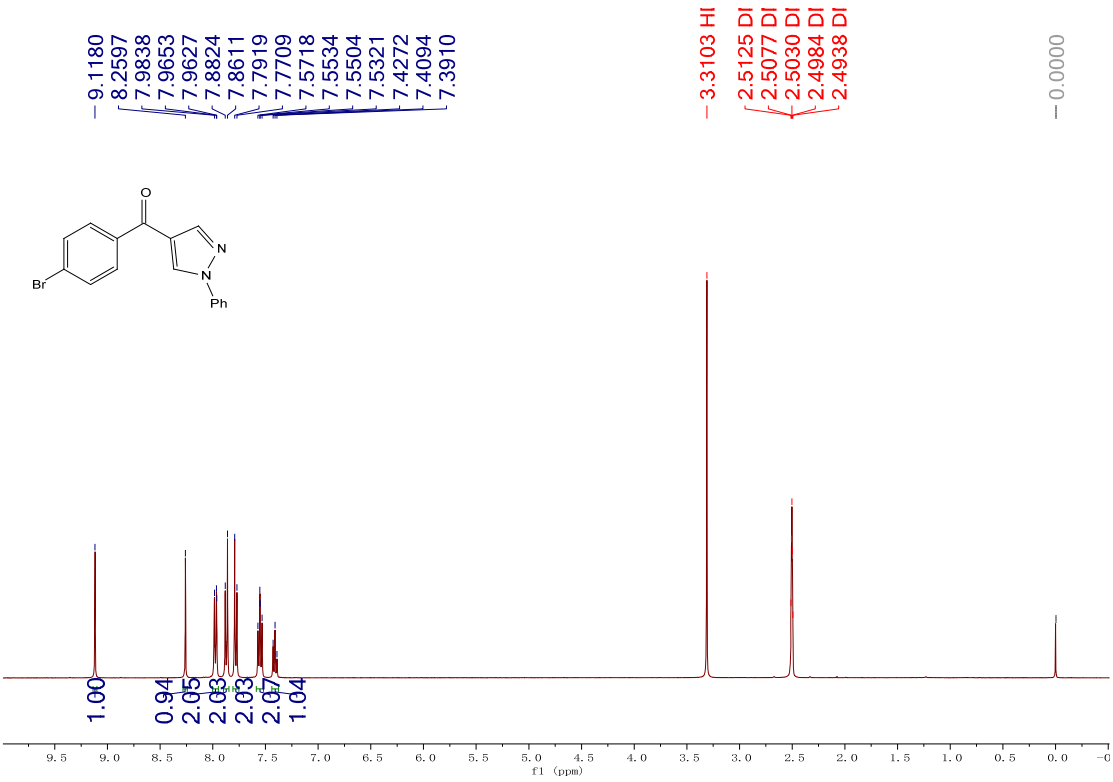


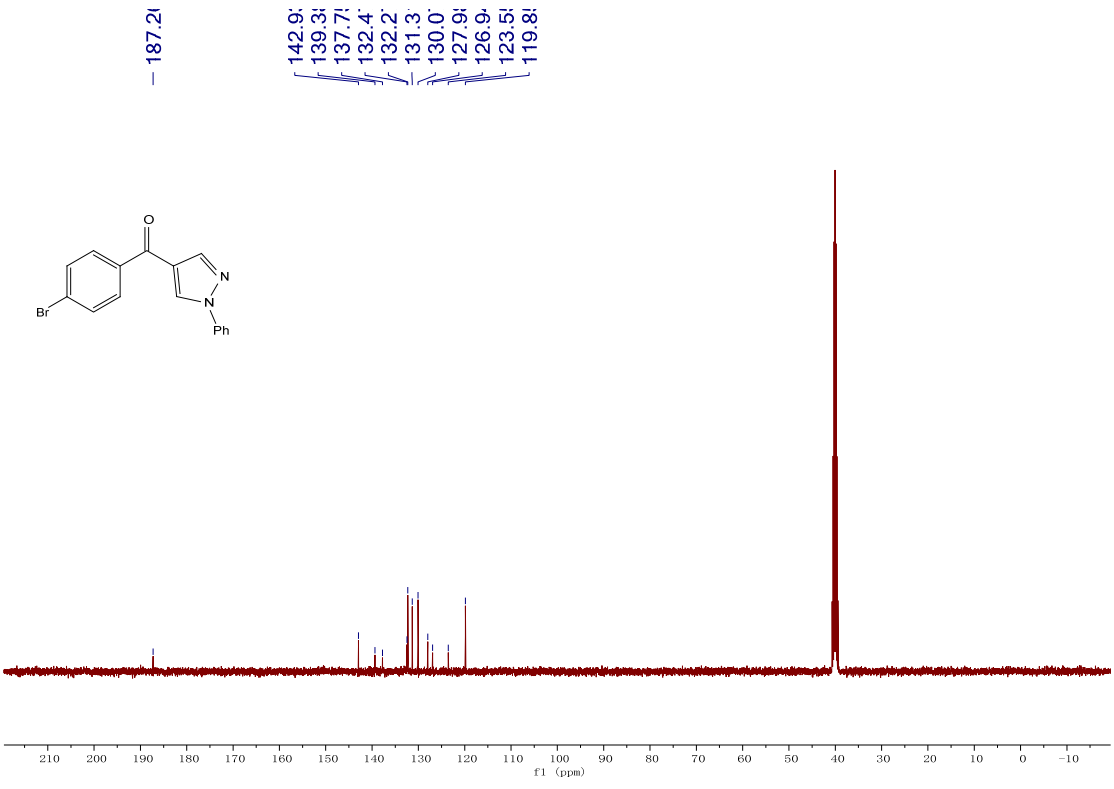
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



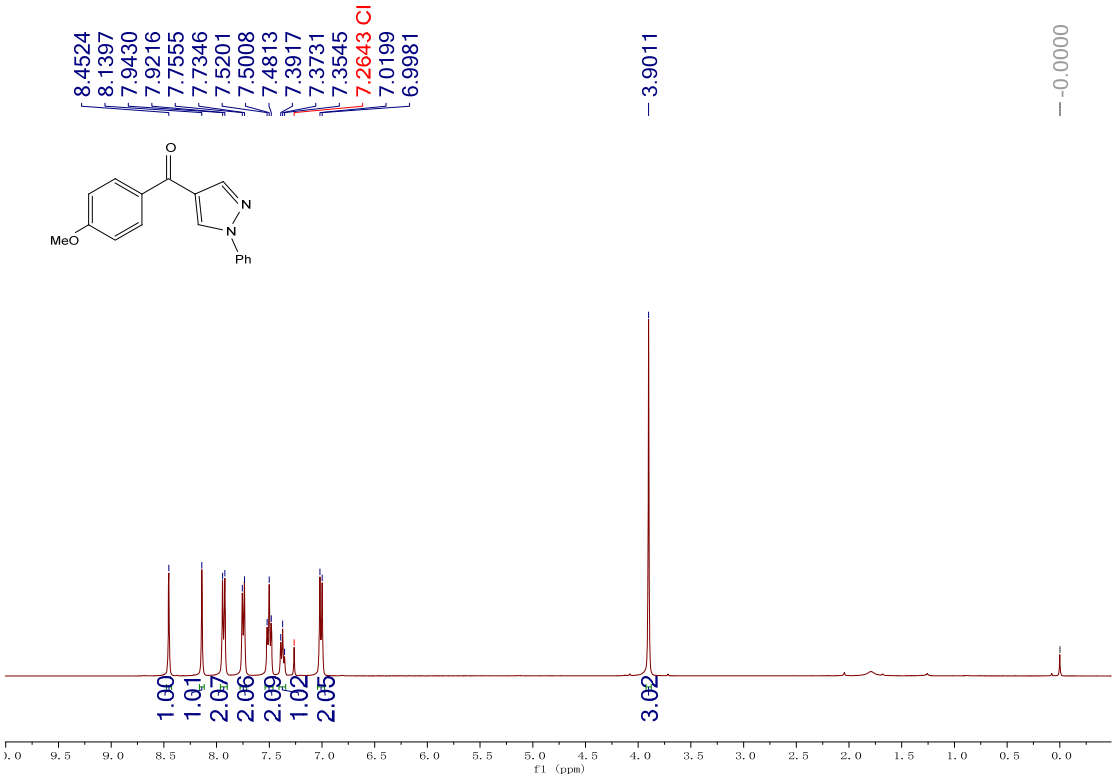
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



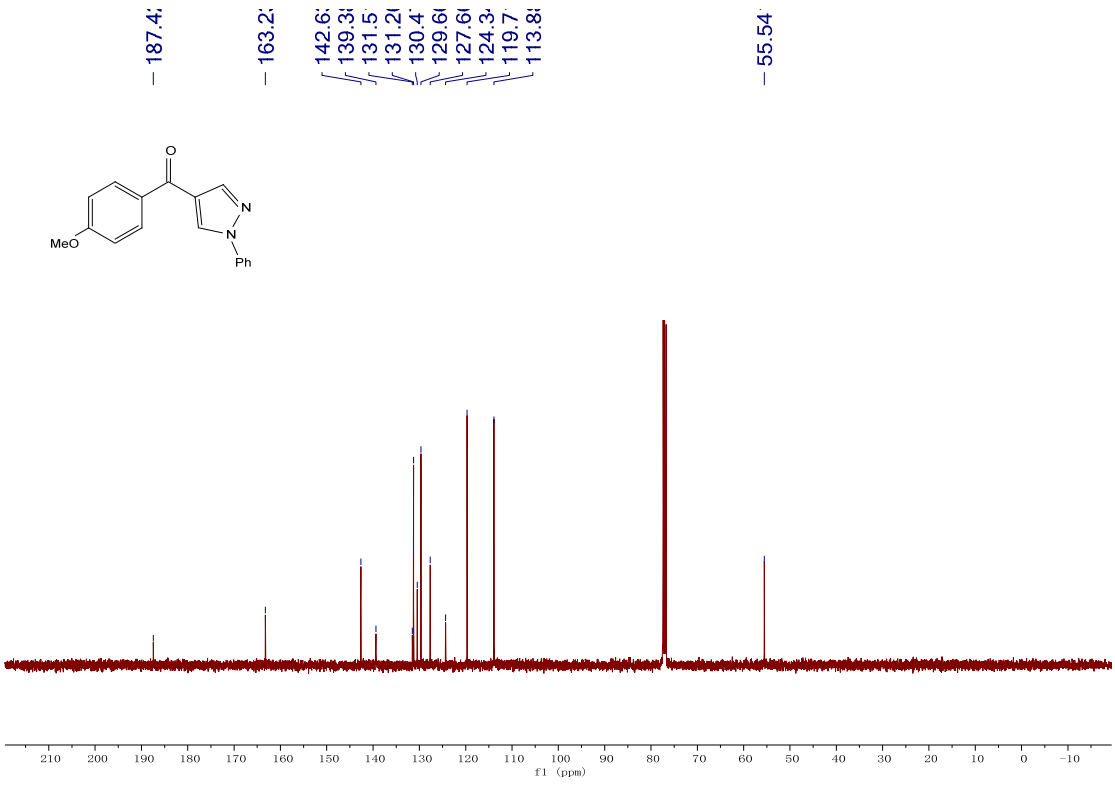
^{1}H NMR spectrum of **3c** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of **3c** (100 MHz, DMSO-d_6)



^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



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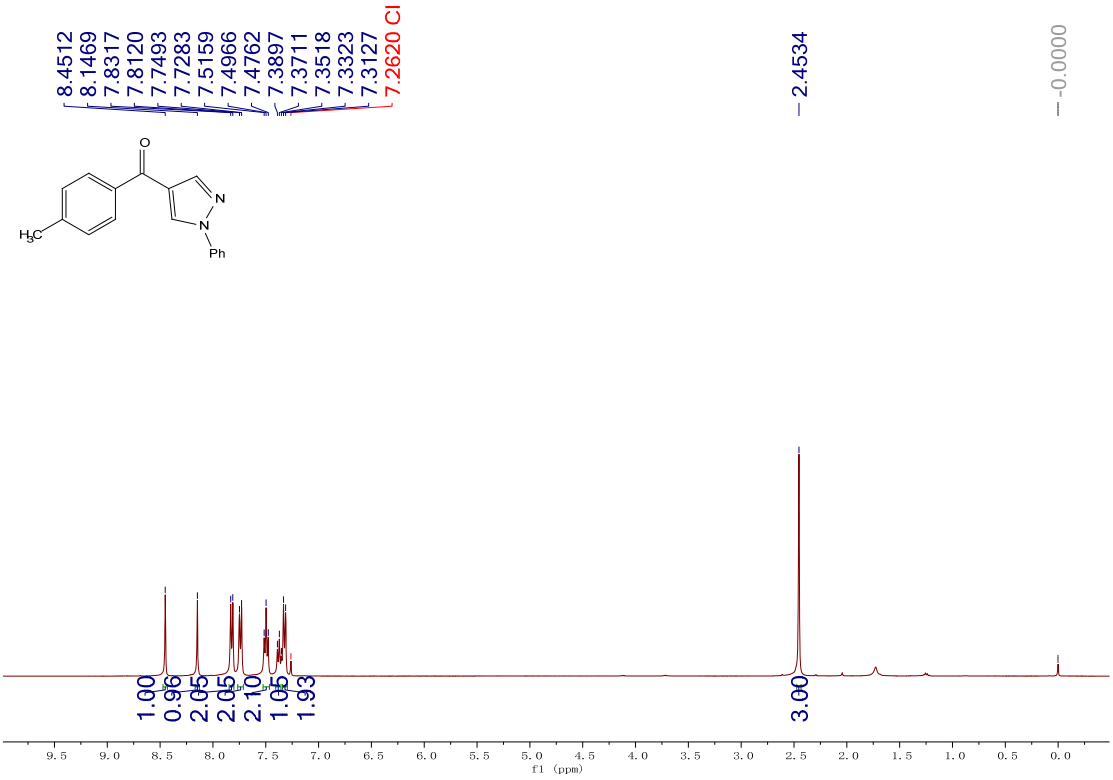

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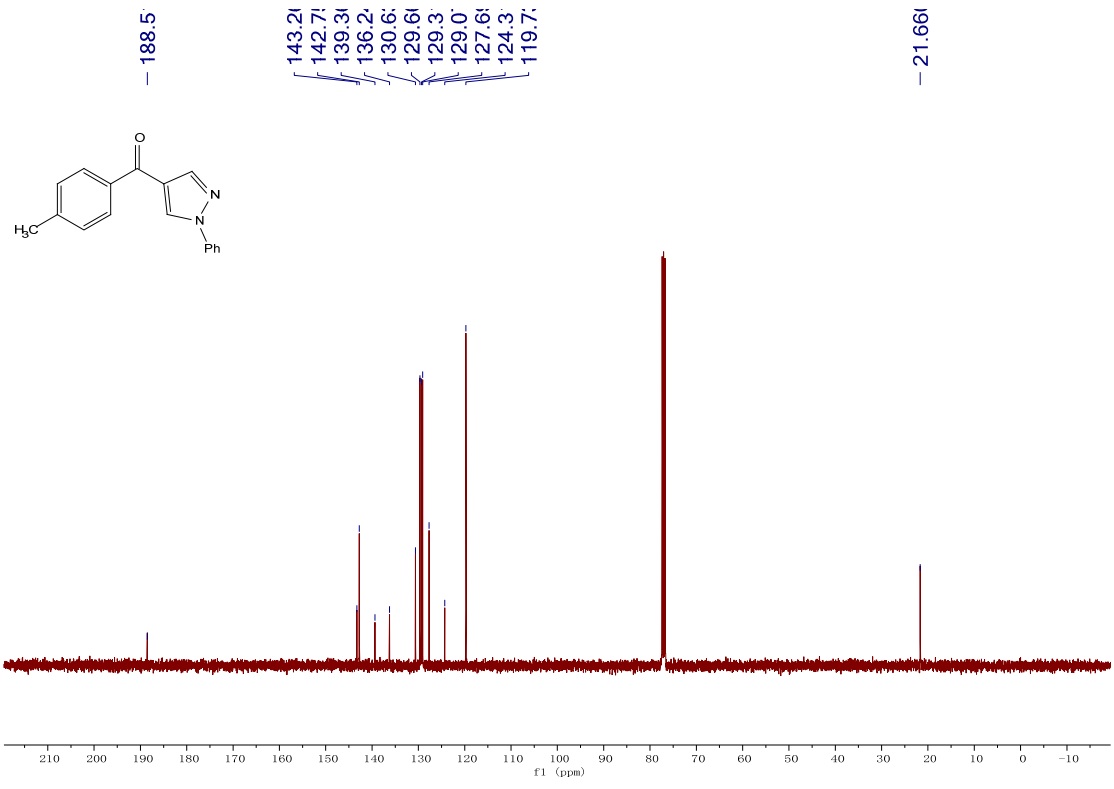

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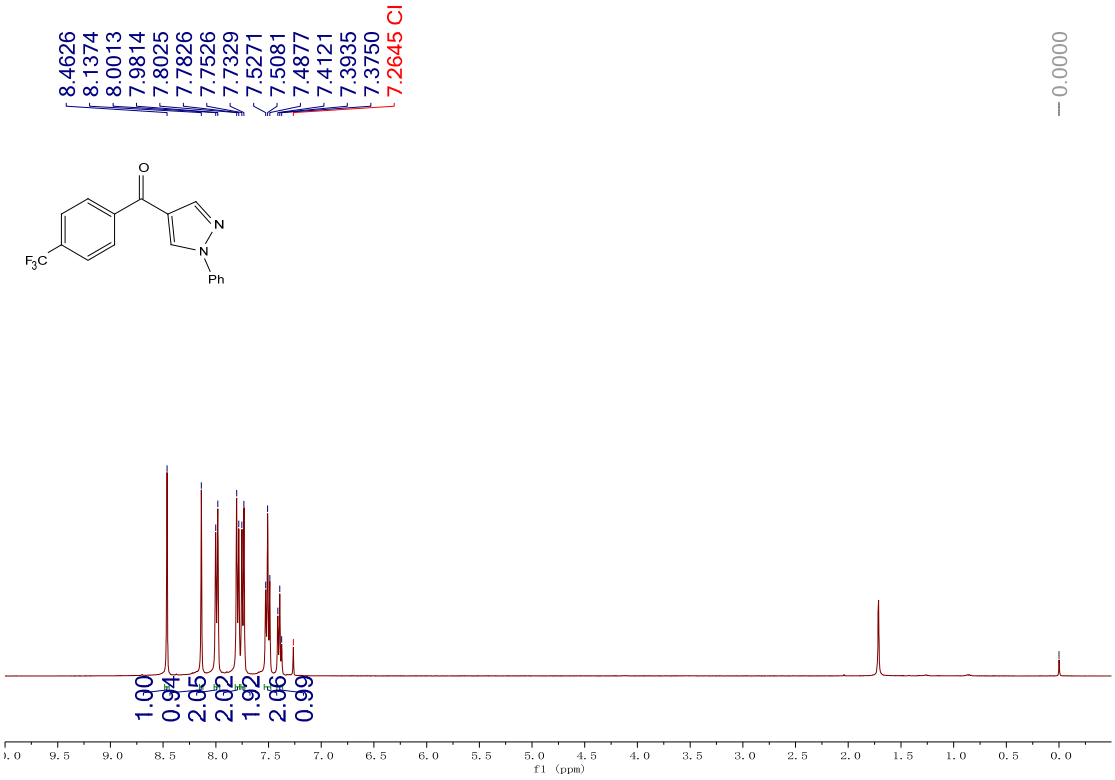

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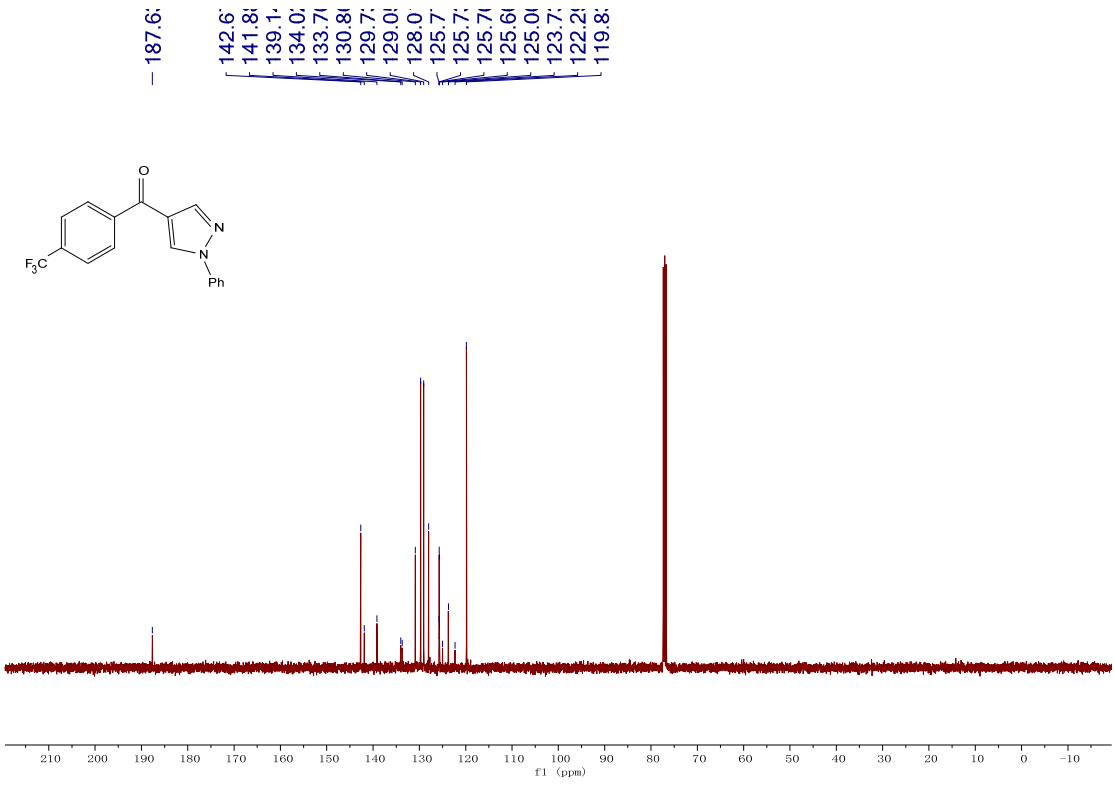
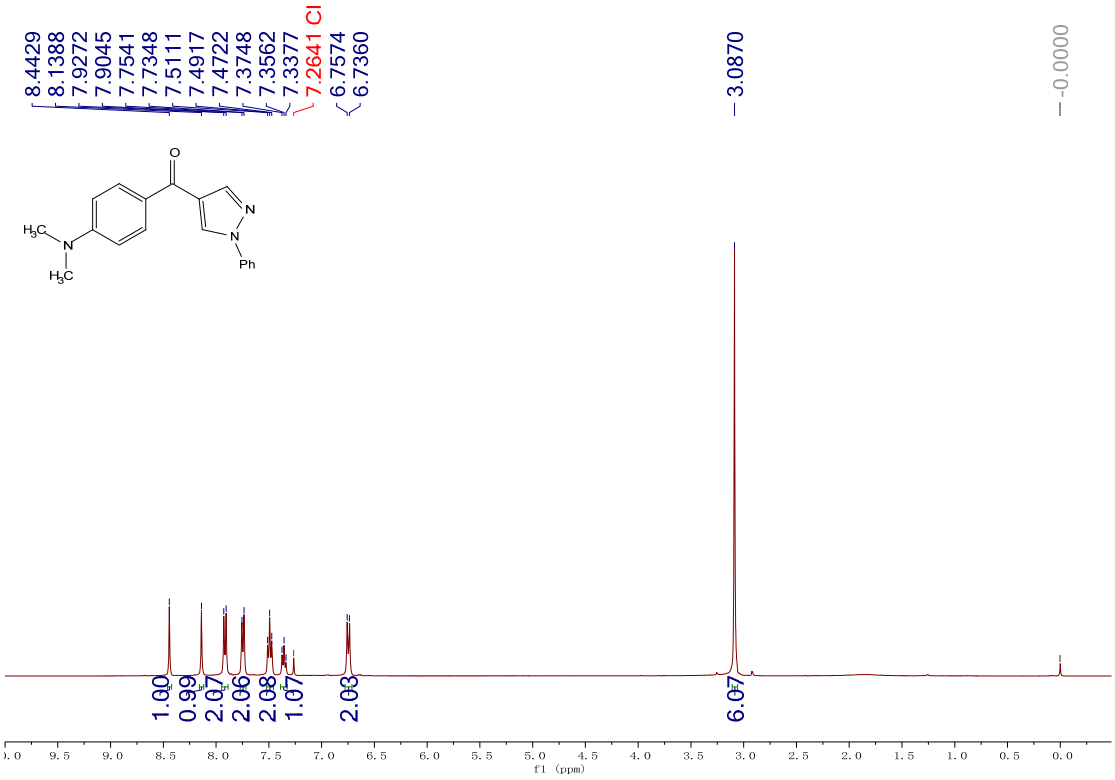
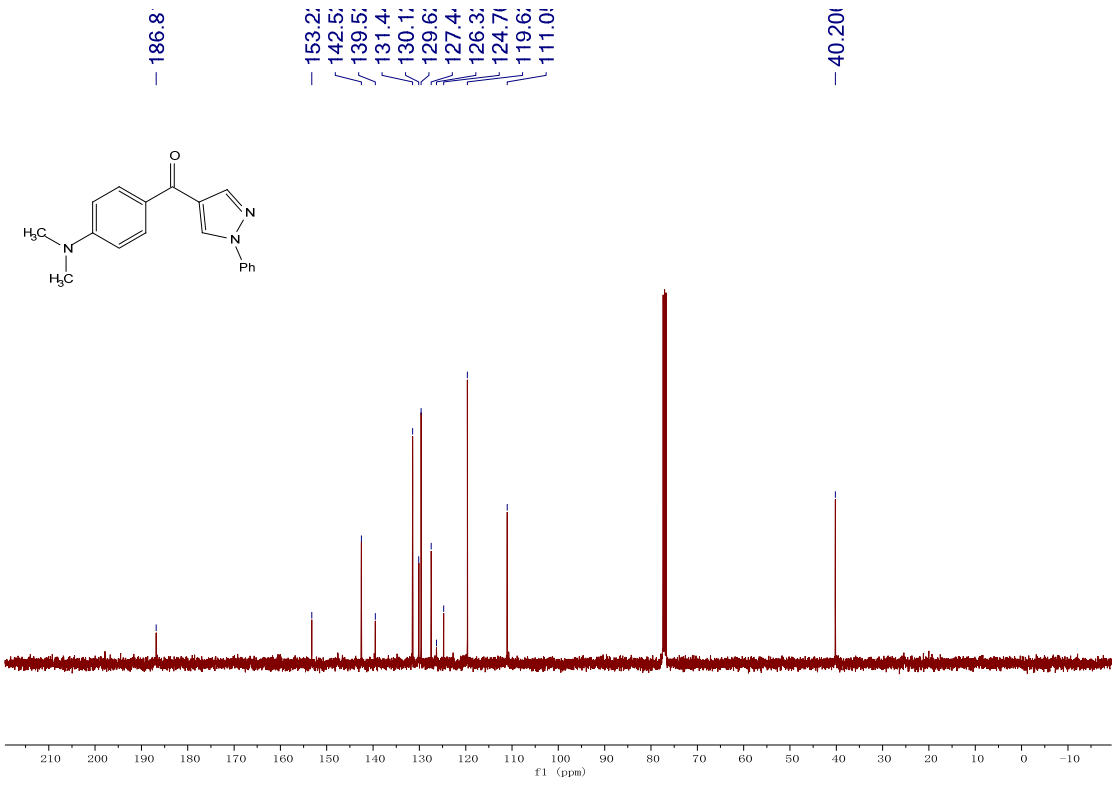


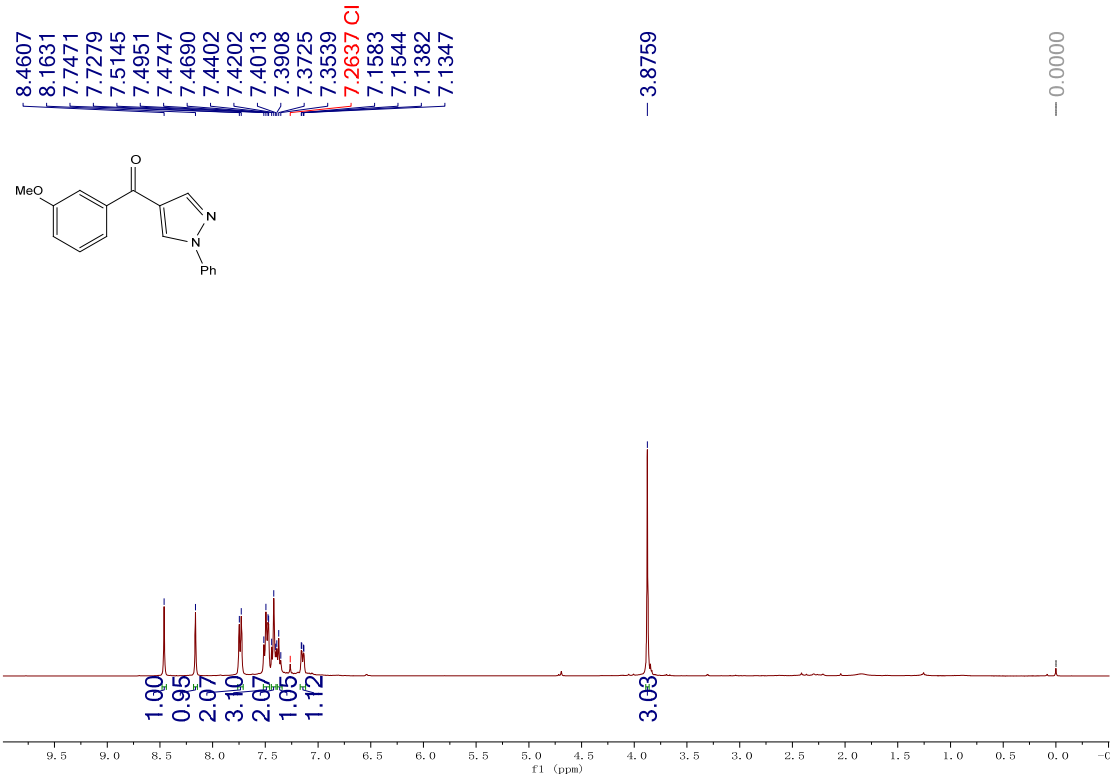
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



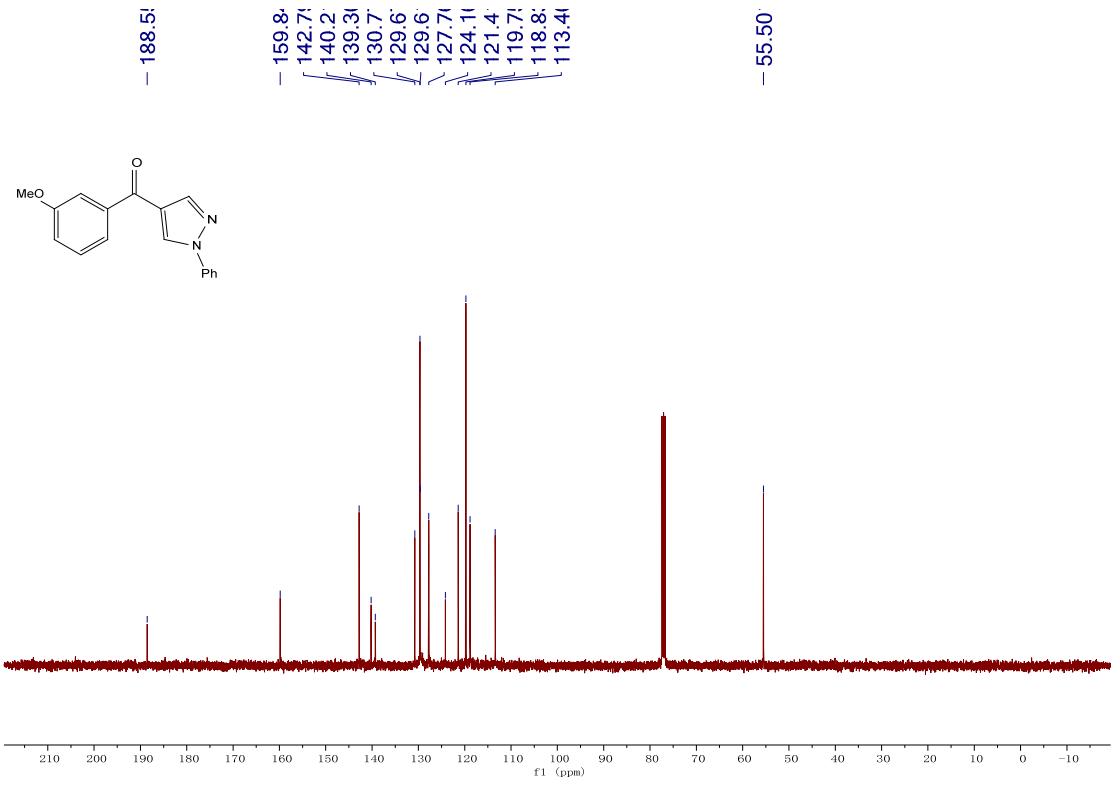
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



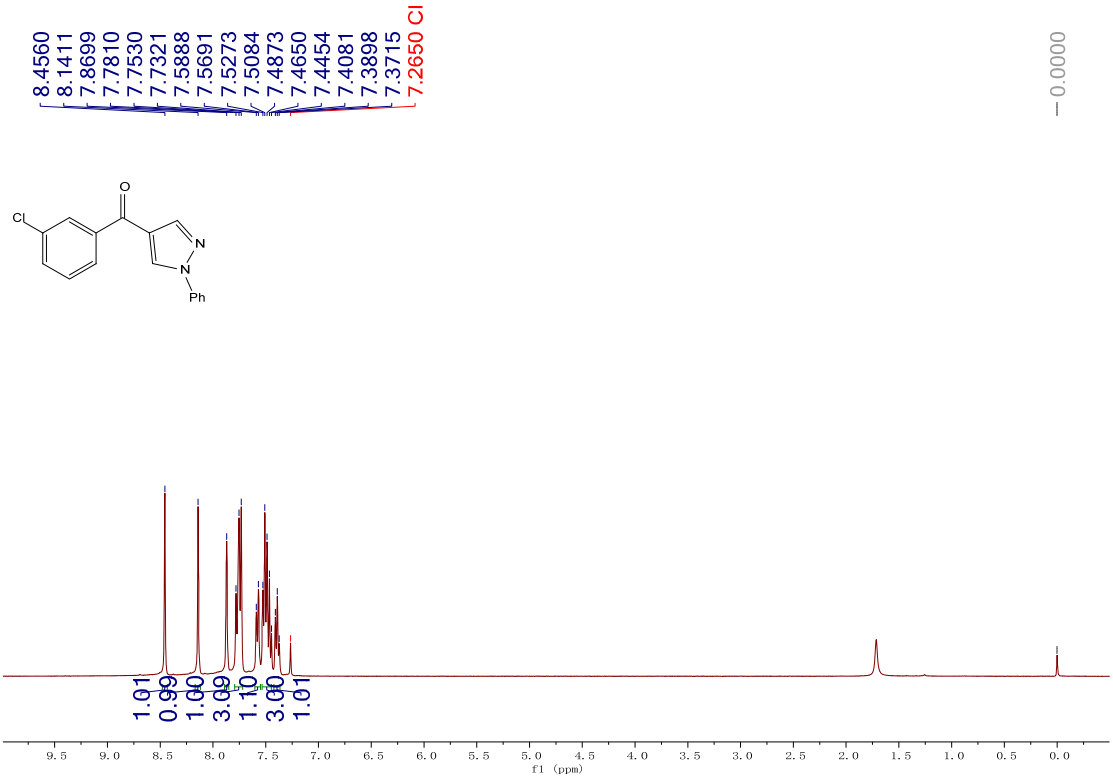
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



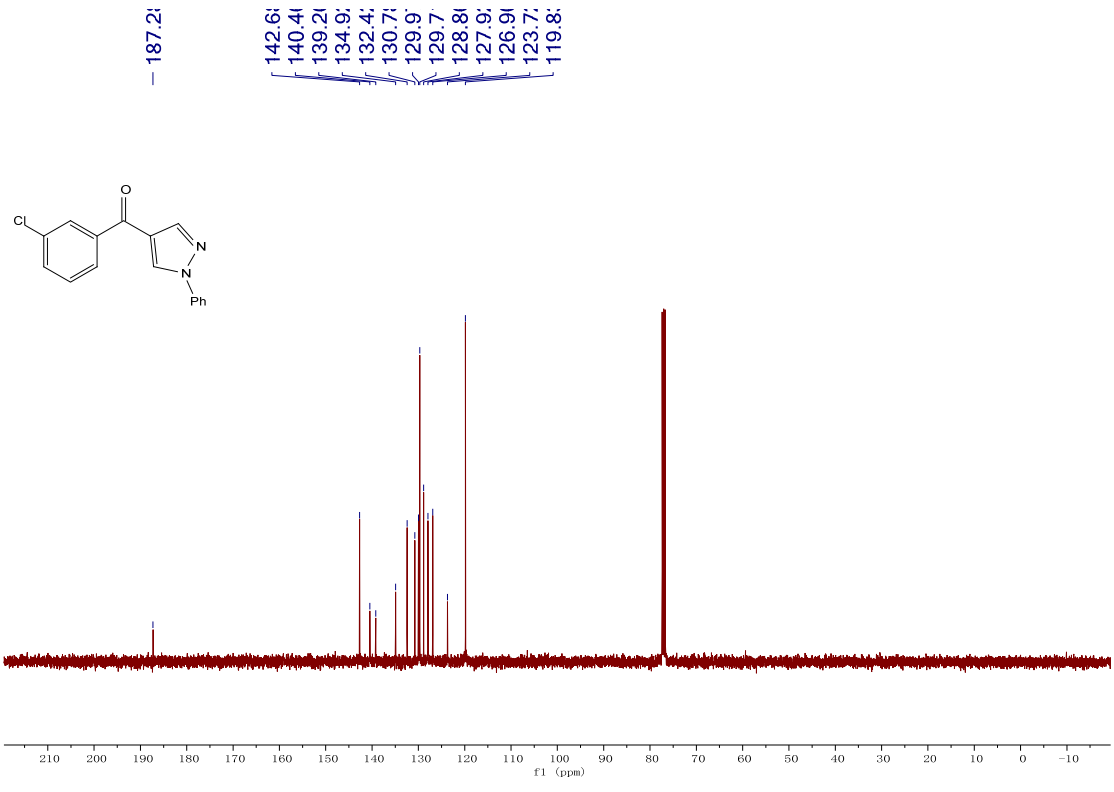
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



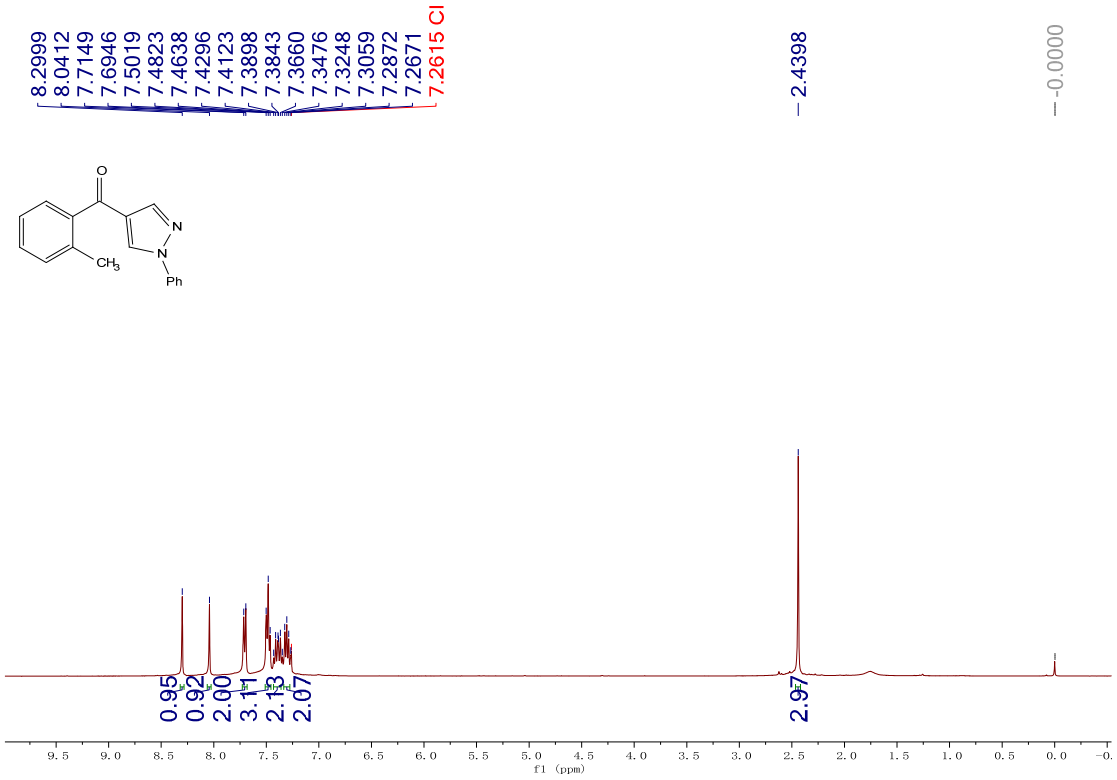
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



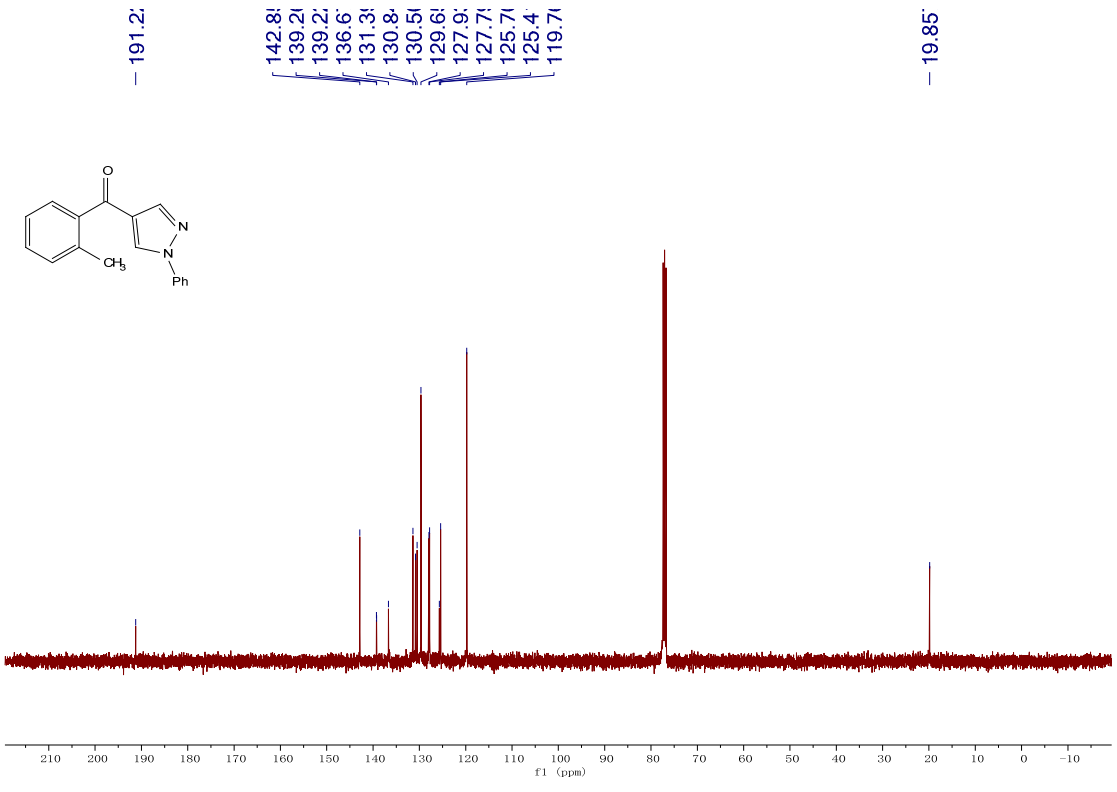
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



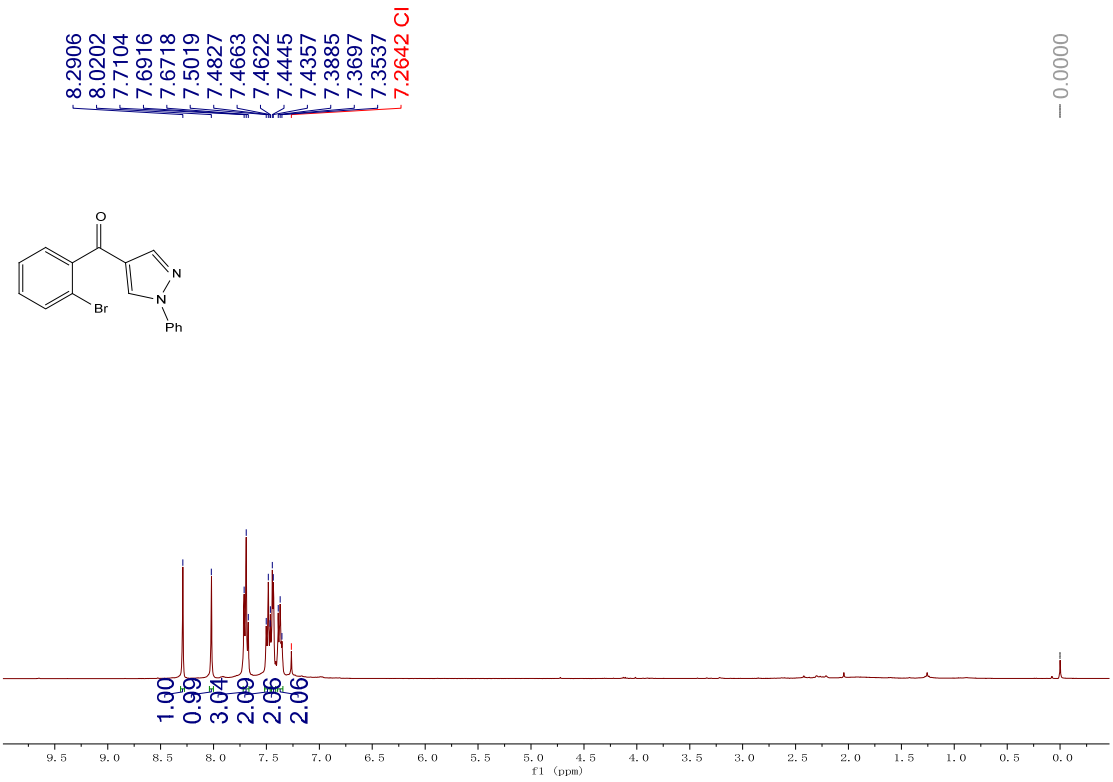
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



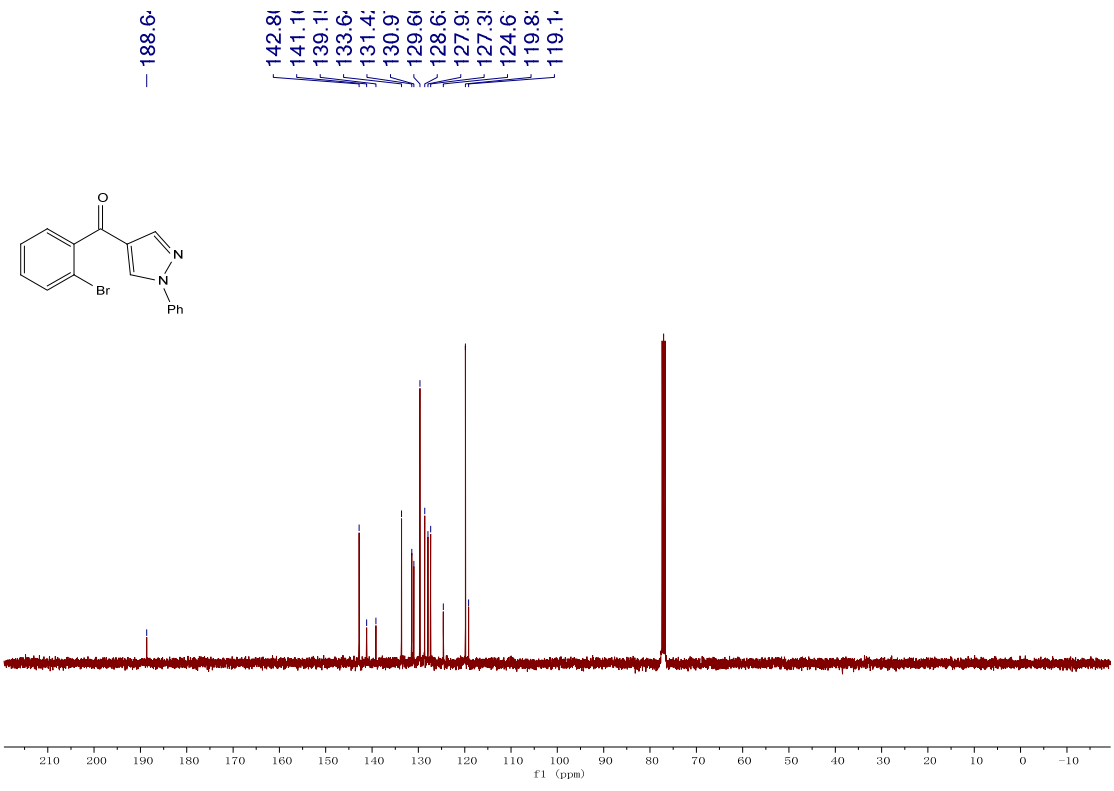
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



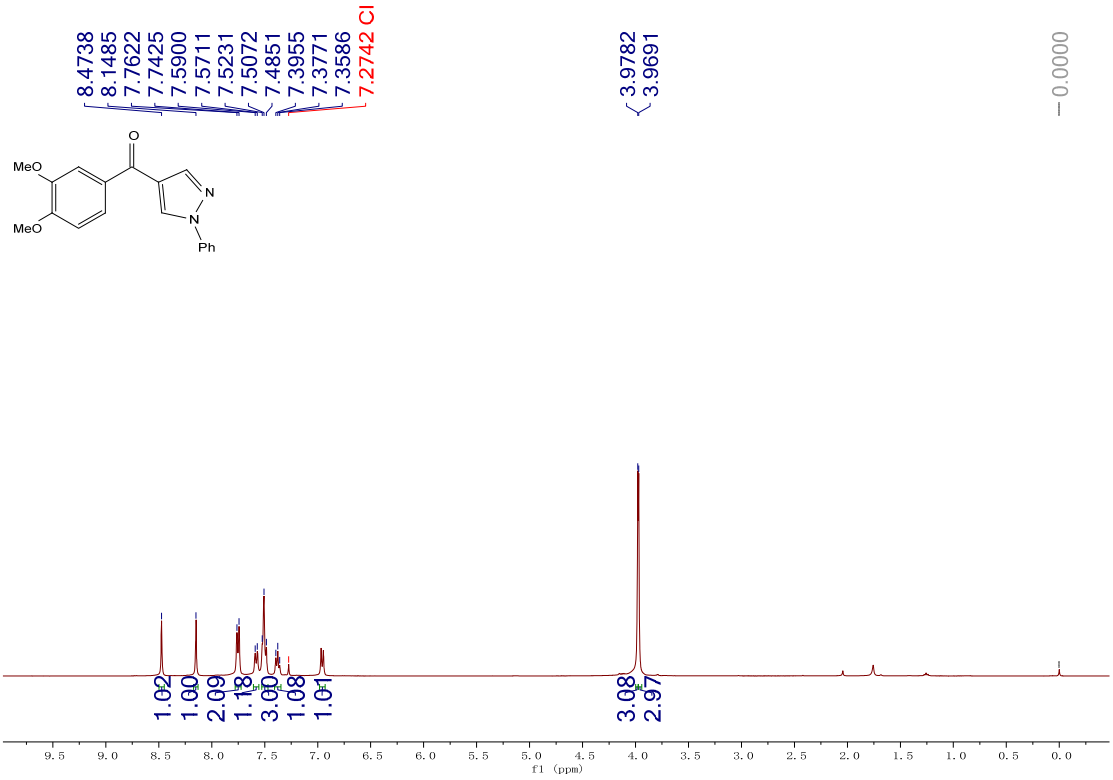
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



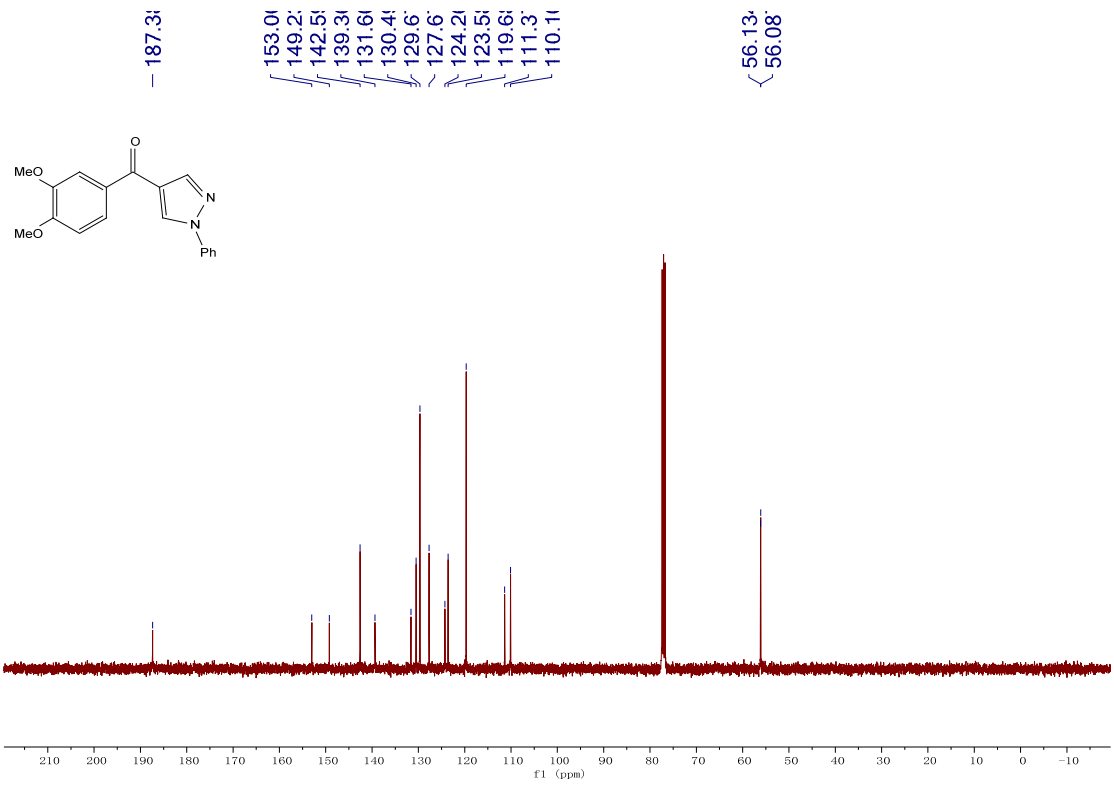
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



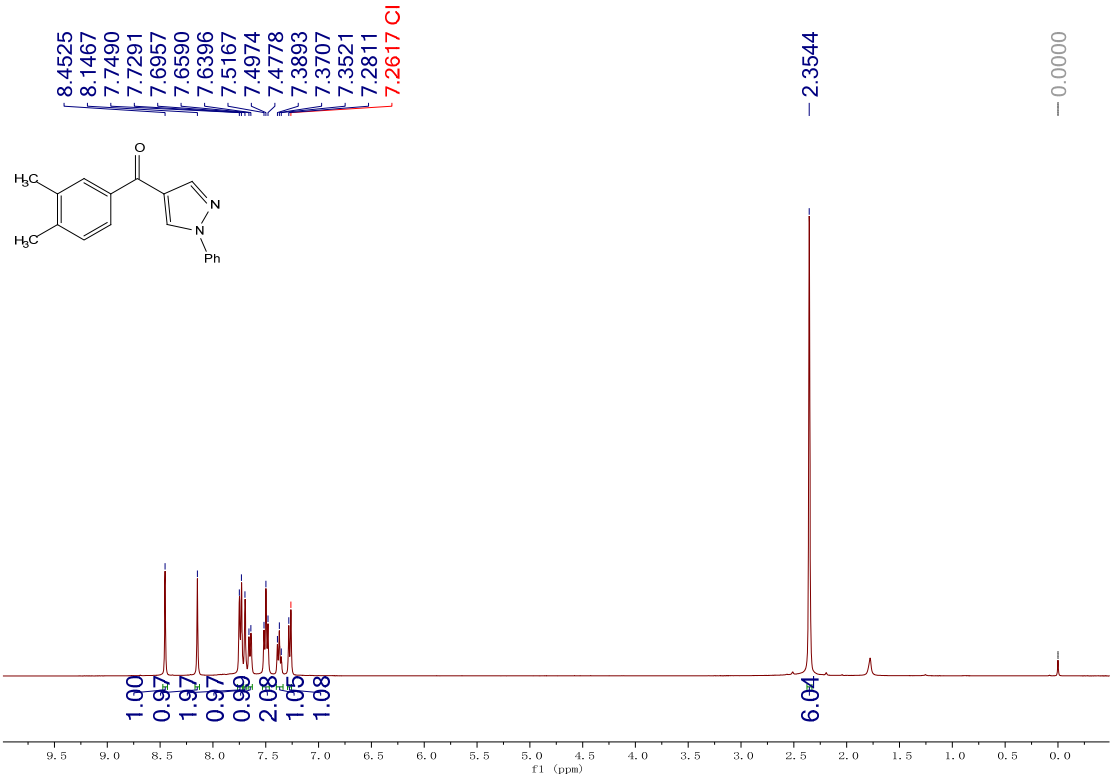
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



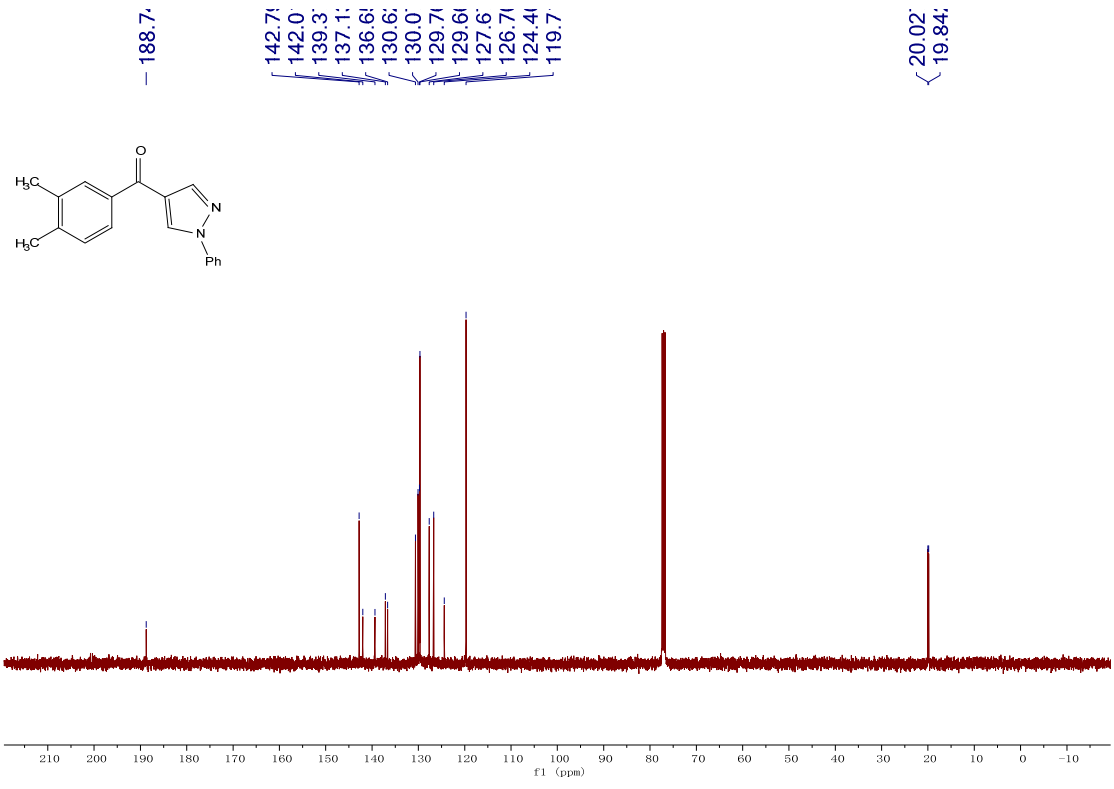
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



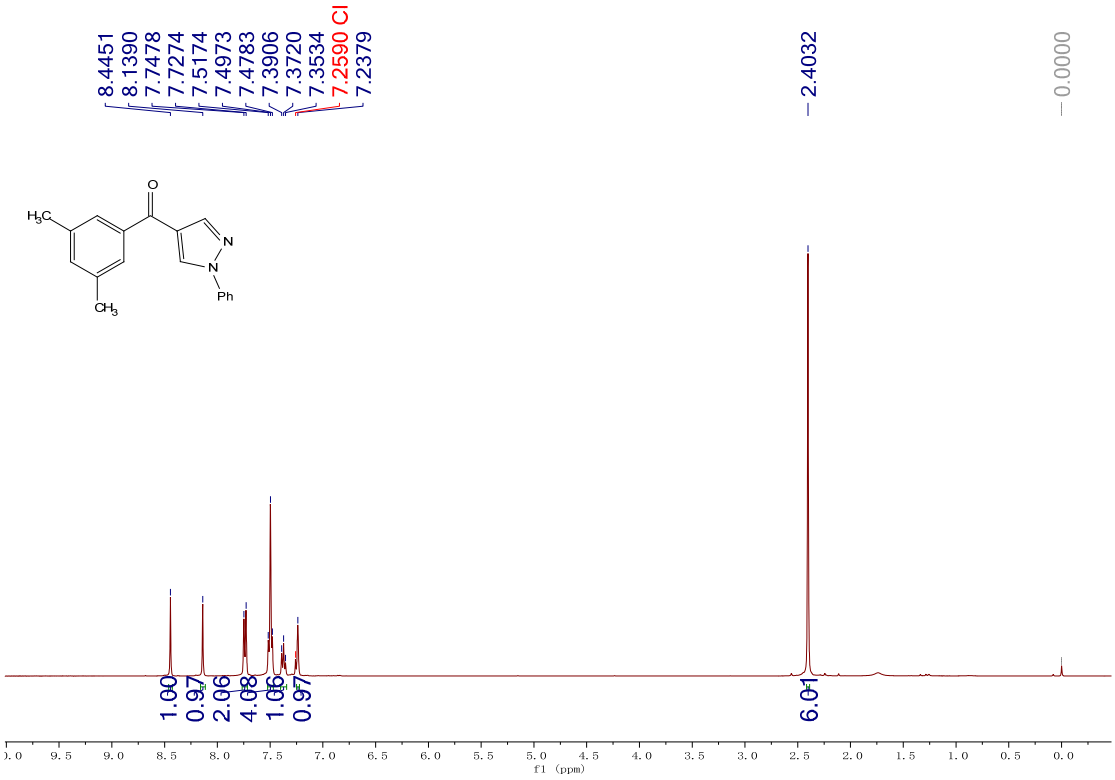
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



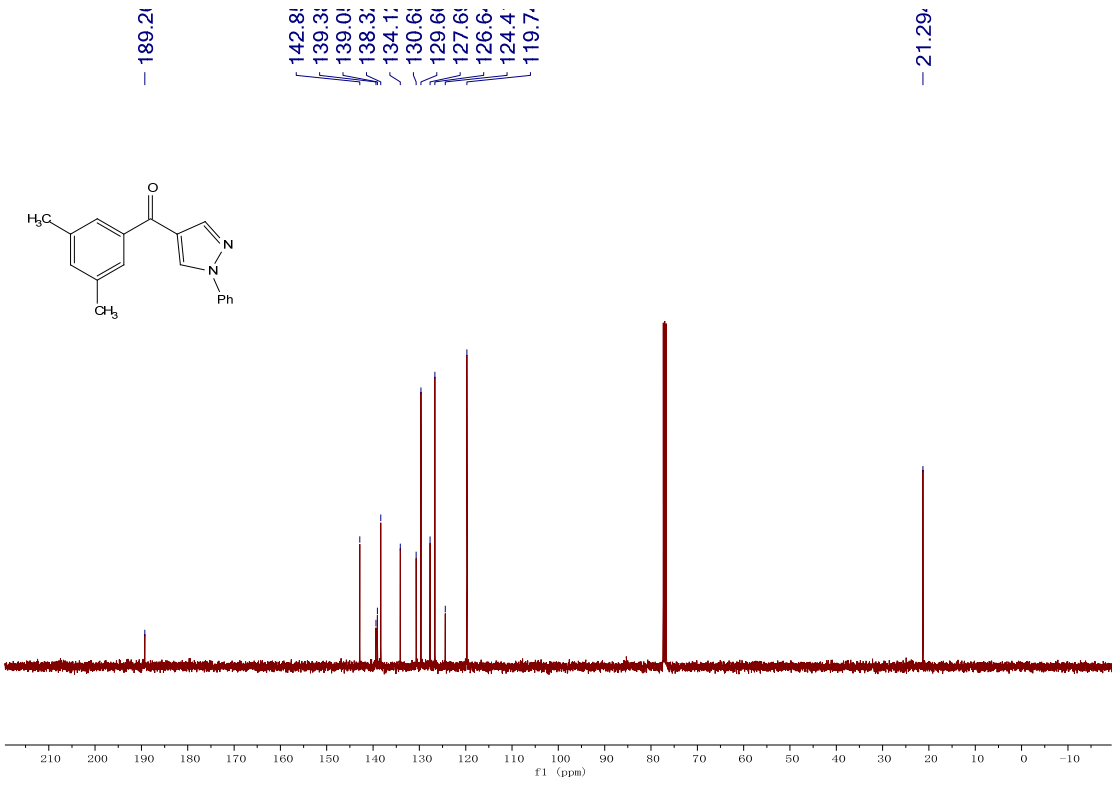
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



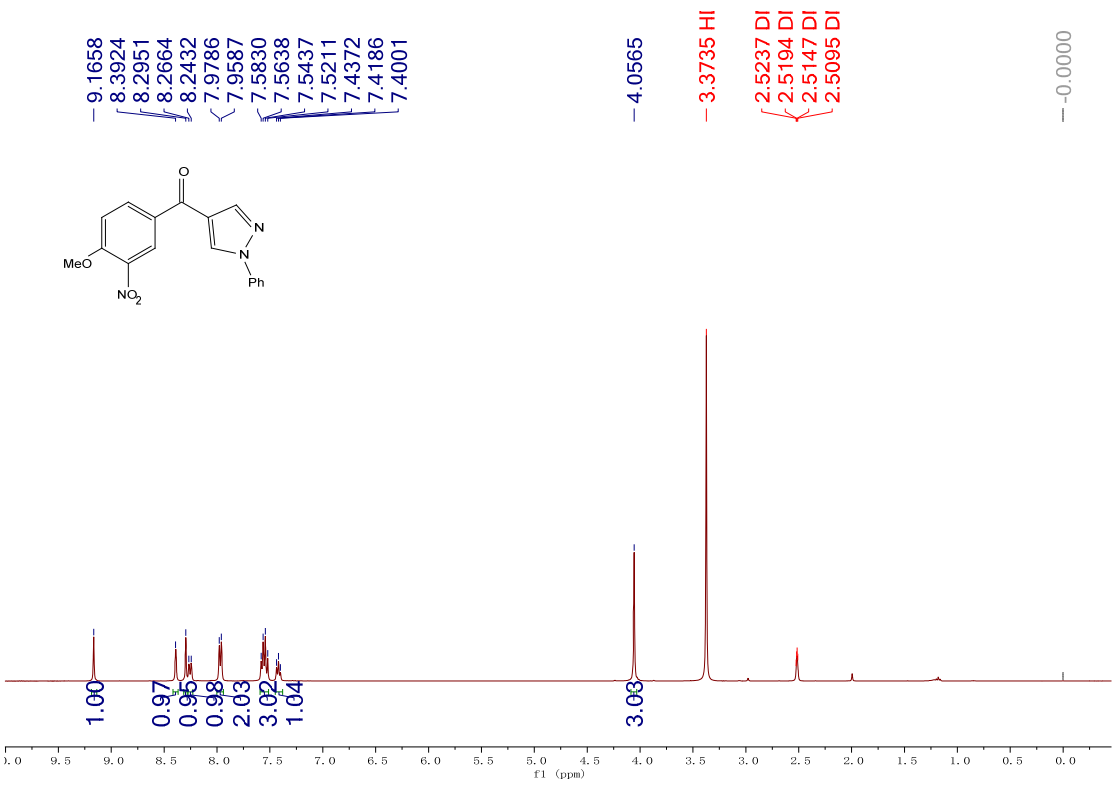
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



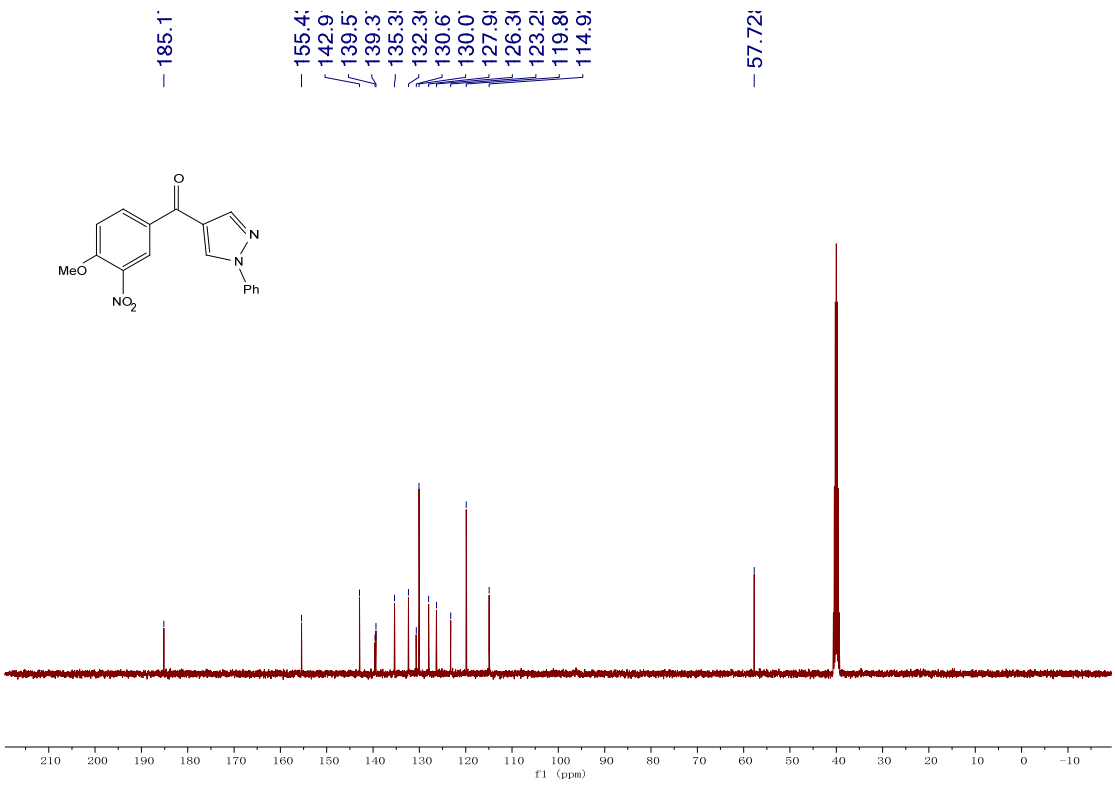
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



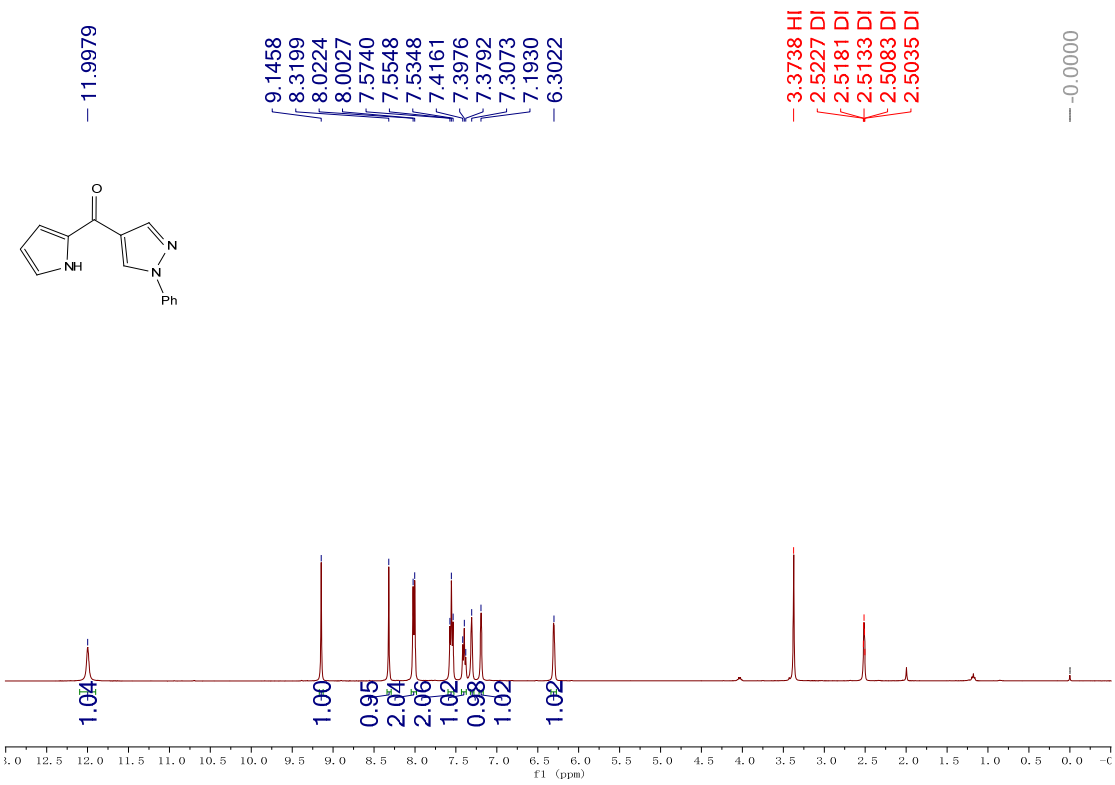
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



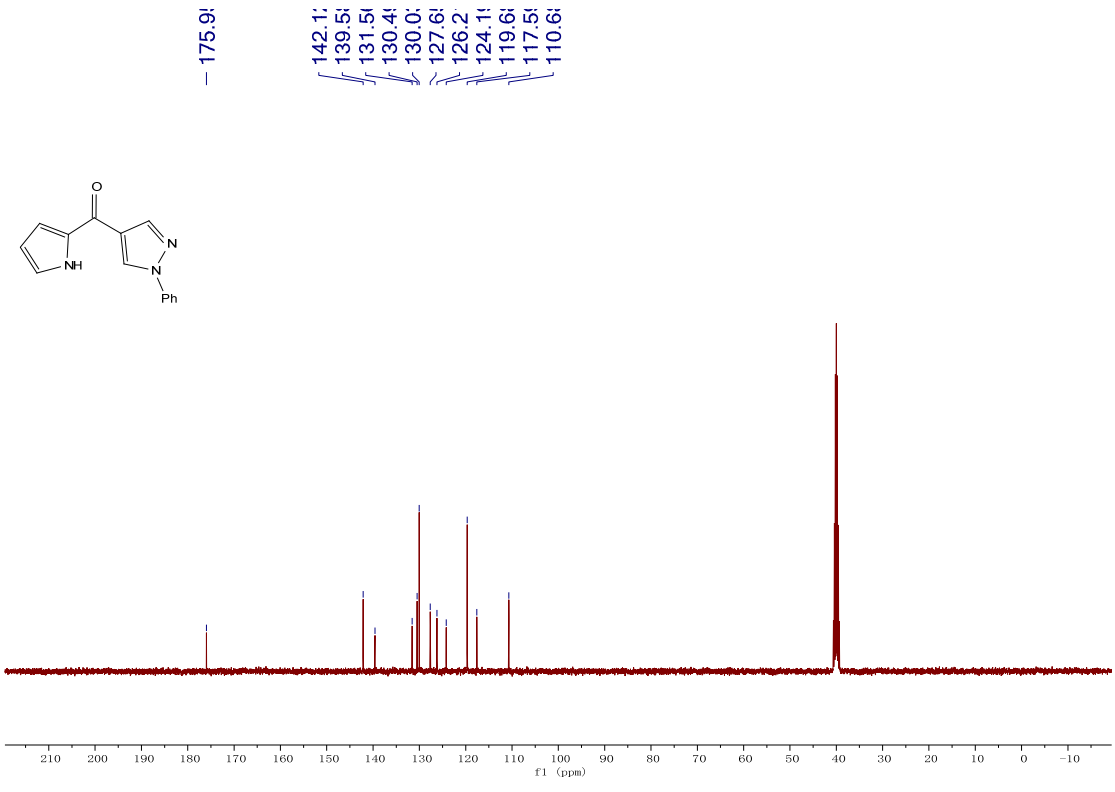
^{1}H NMR spectrum of **3o** (400 MHz, DMSO-d_6)



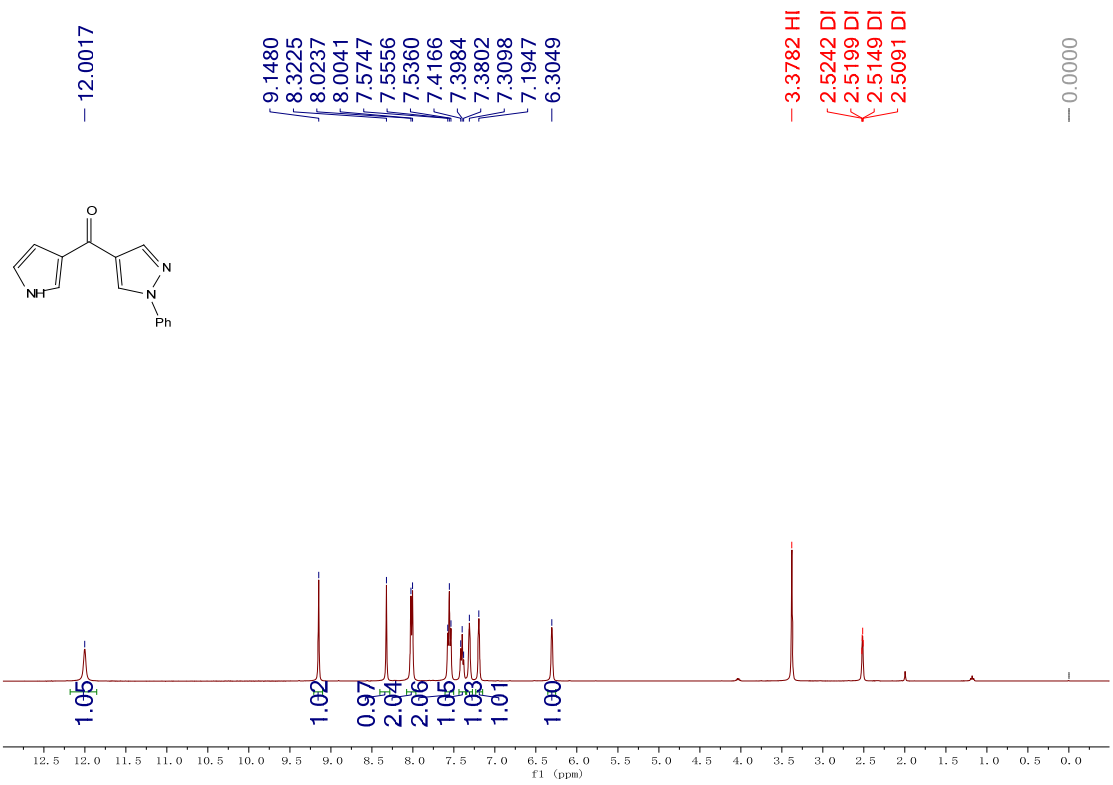
^{13}C NMR spectrum of **3o** (100 MHz, DMSO-d_6)



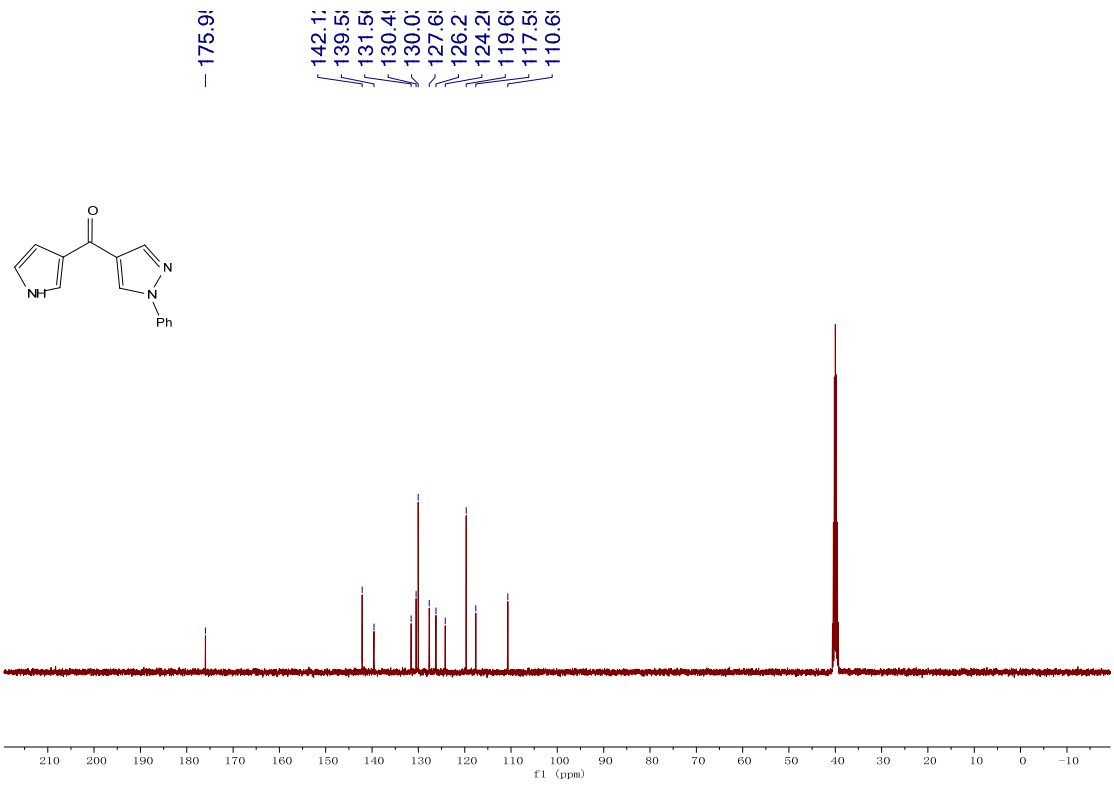
^{1}H NMR spectrum of **3p** (400 MHz, DMSO-d_6)



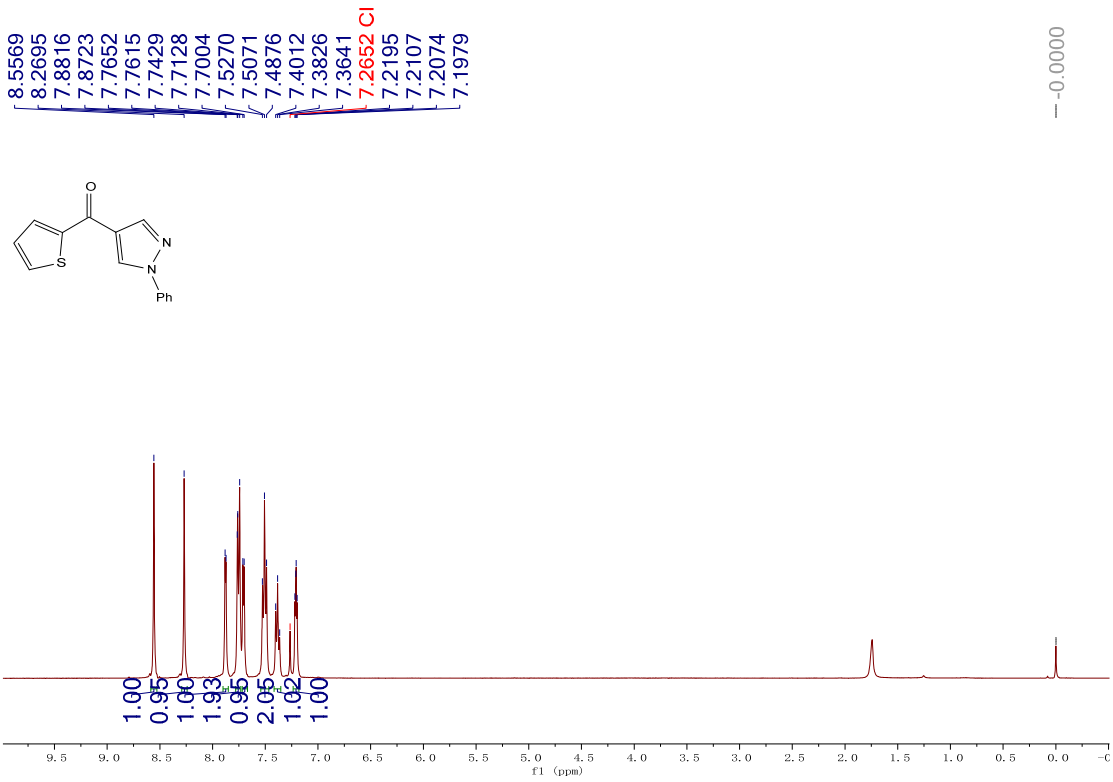
^{13}C NMR spectrum of **3p** (100 MHz, DMSO-d_6)



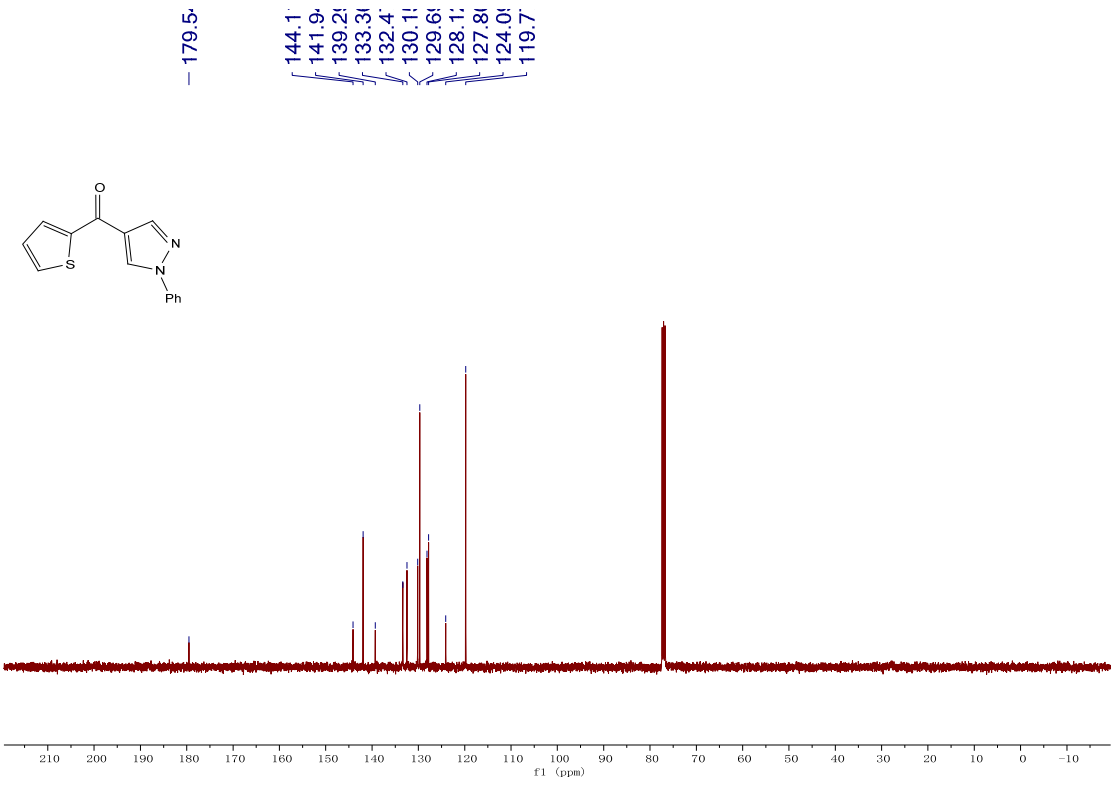
^{1}H NMR spectrum of **3q** (400 MHz, DMSO-d_6)



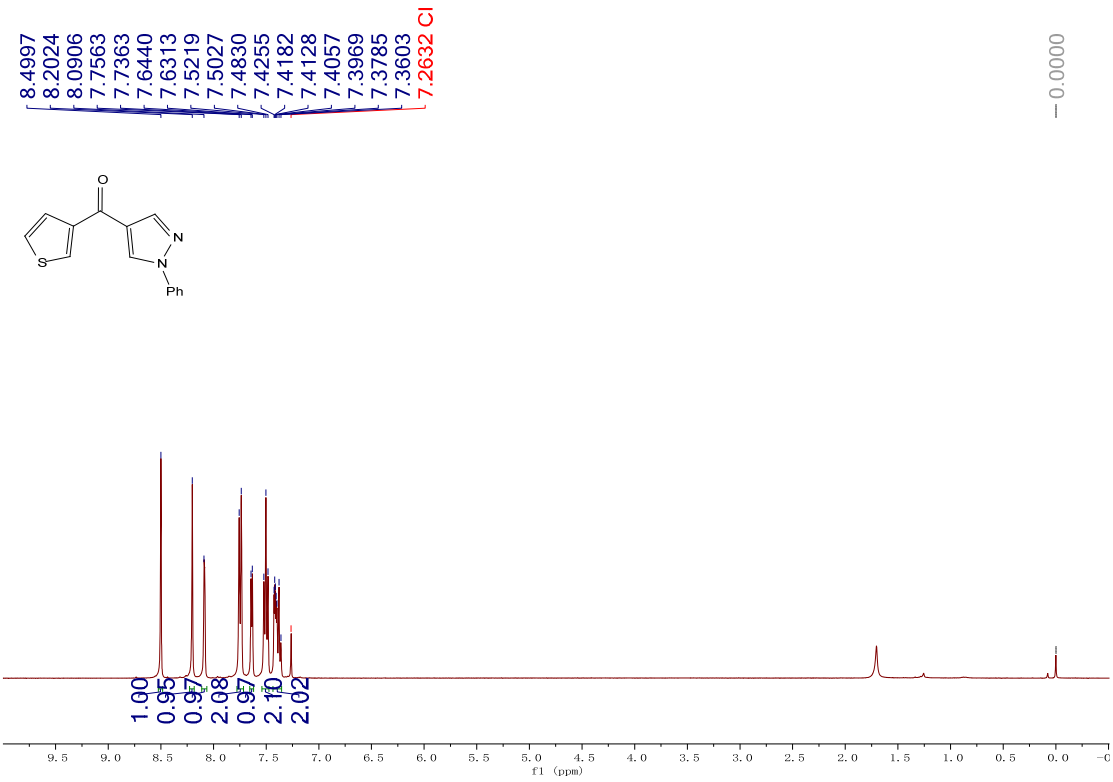
^{13}C NMR spectrum of **3q** (100 MHz, DMSO-d_6)



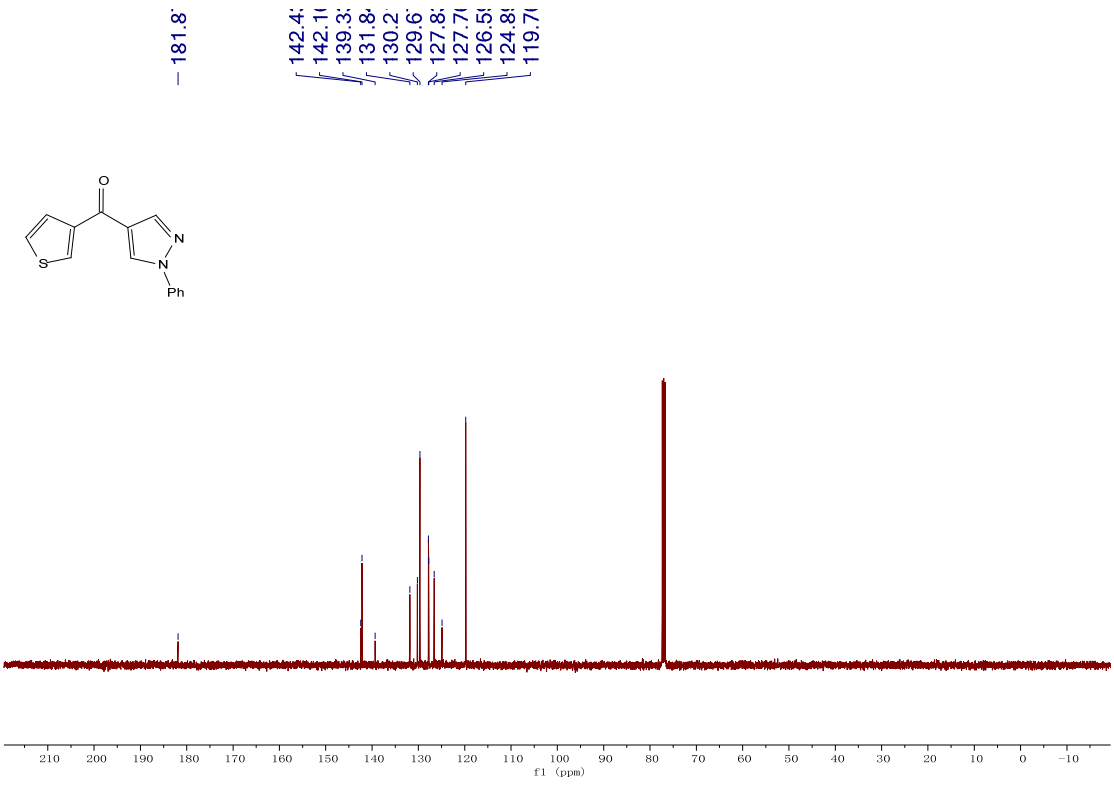
^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)



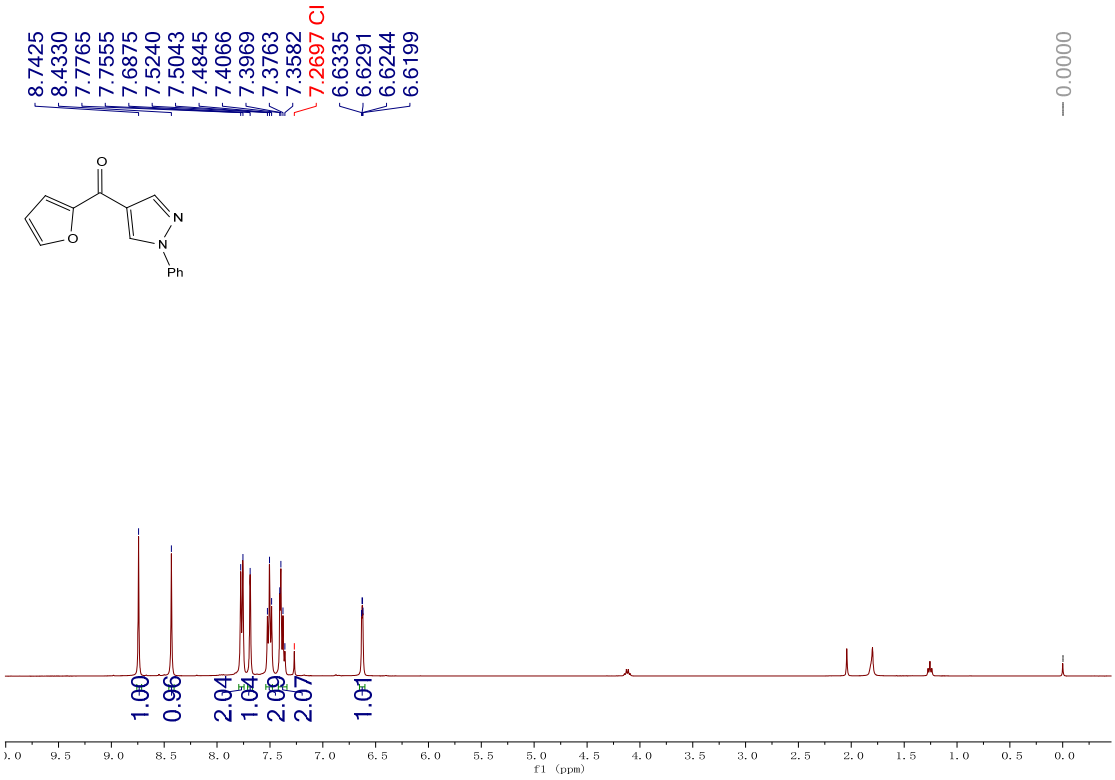
^{13}C NMR spectrum of **3r** (100 MHz, $CDCl_3$)



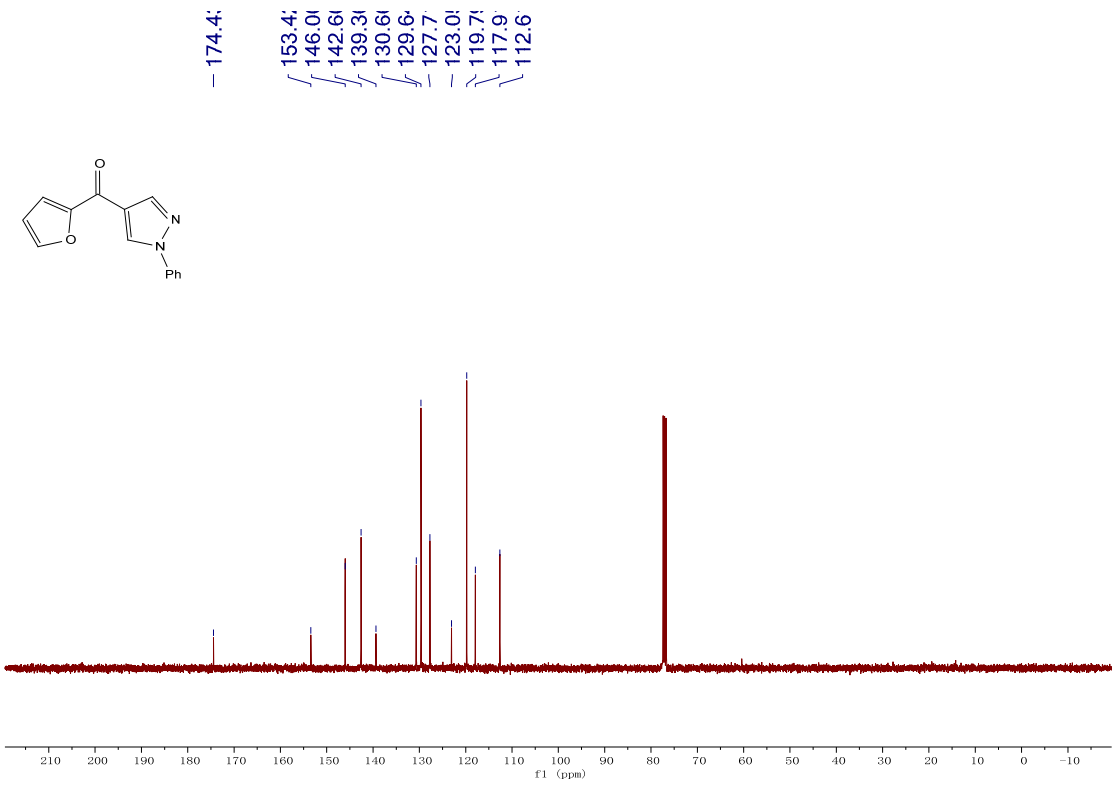
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)



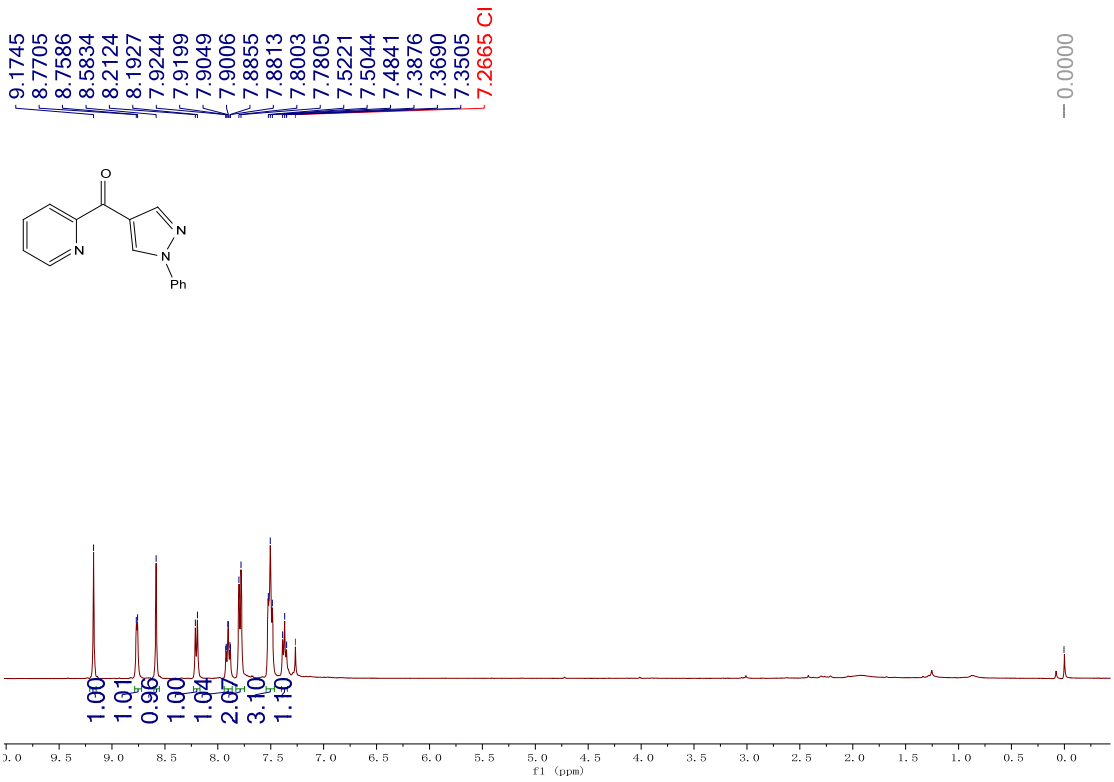
^{13}C NMR spectrum of **3s** (100 MHz, $CDCl_3$)



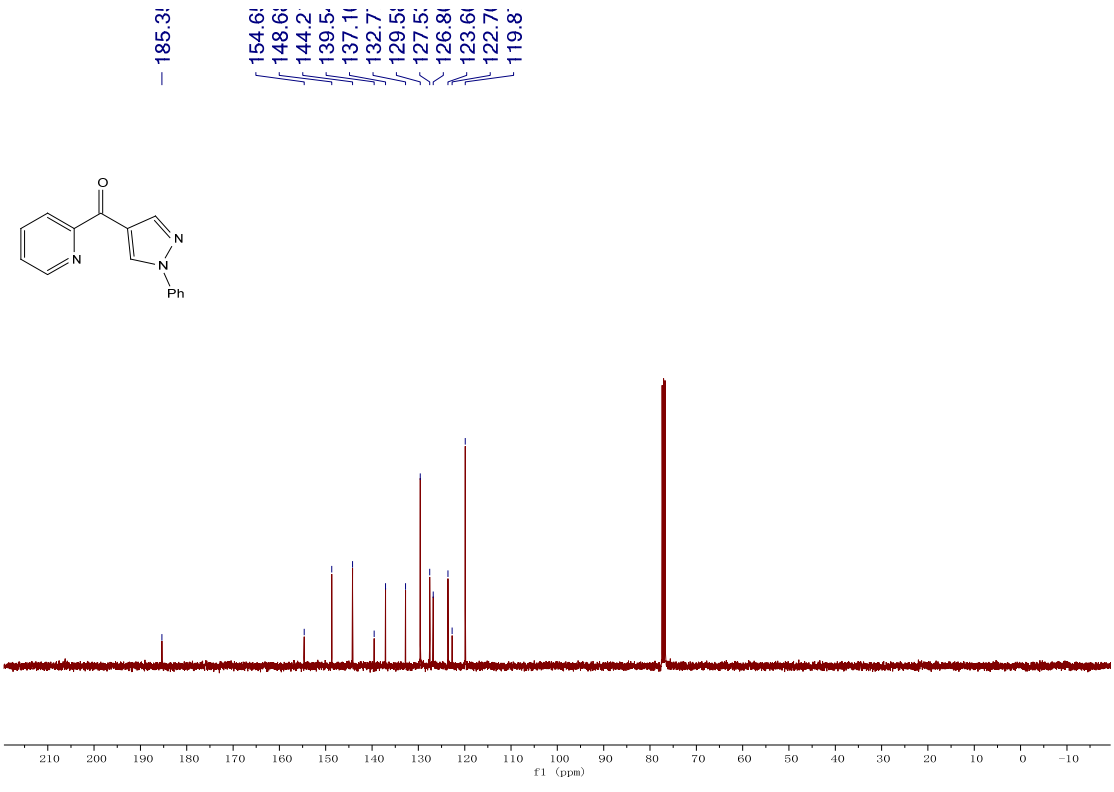
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



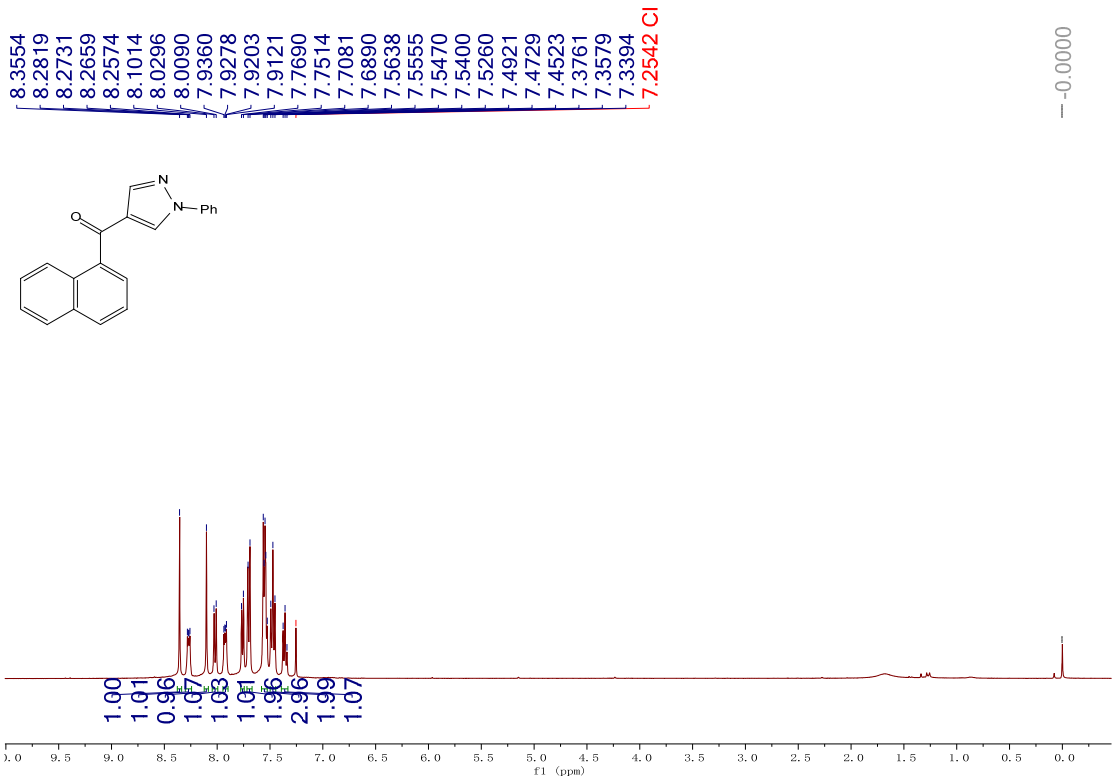
^{13}C NMR spectrum of **3t** (100 MHz, $CDCl_3$)



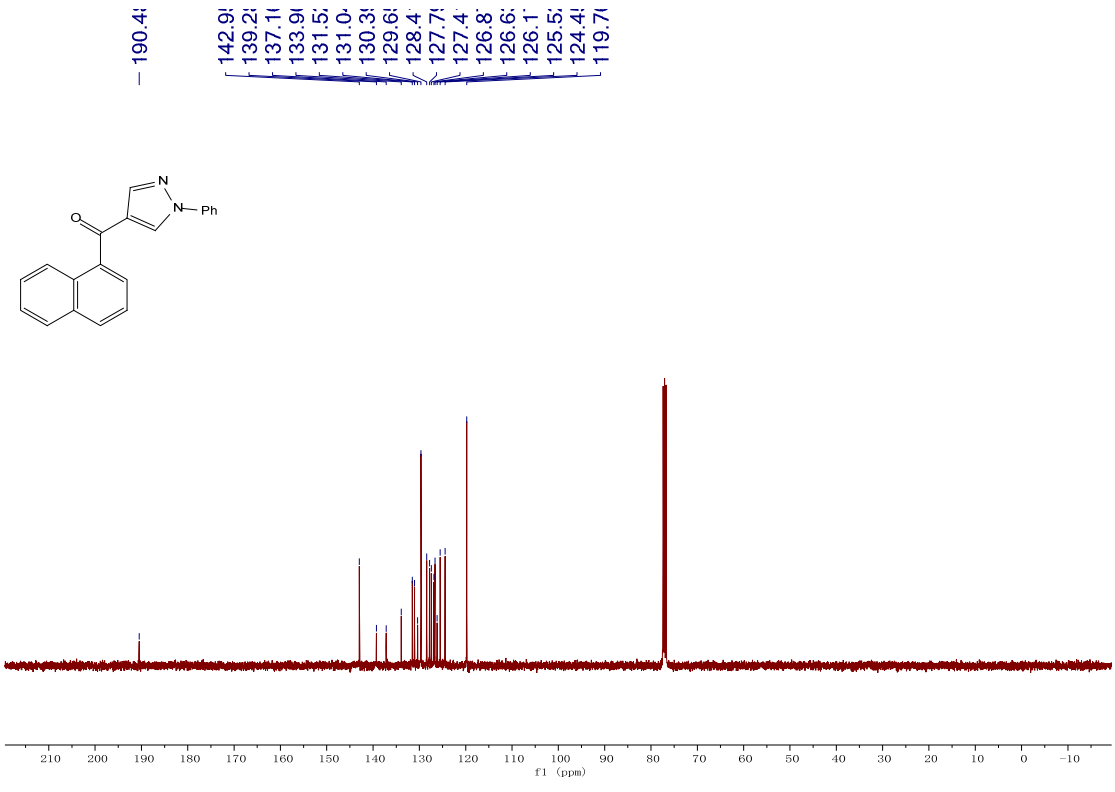
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)



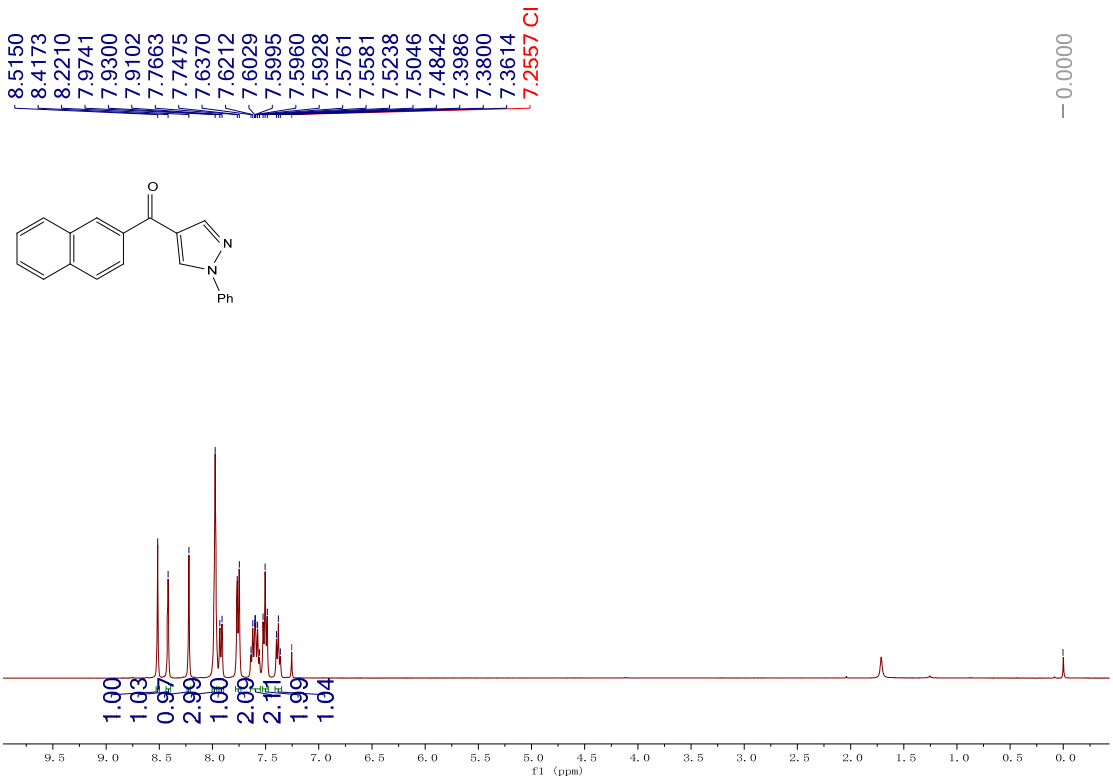
^{13}C NMR spectrum of **3u** (100 MHz, $CDCl_3$)



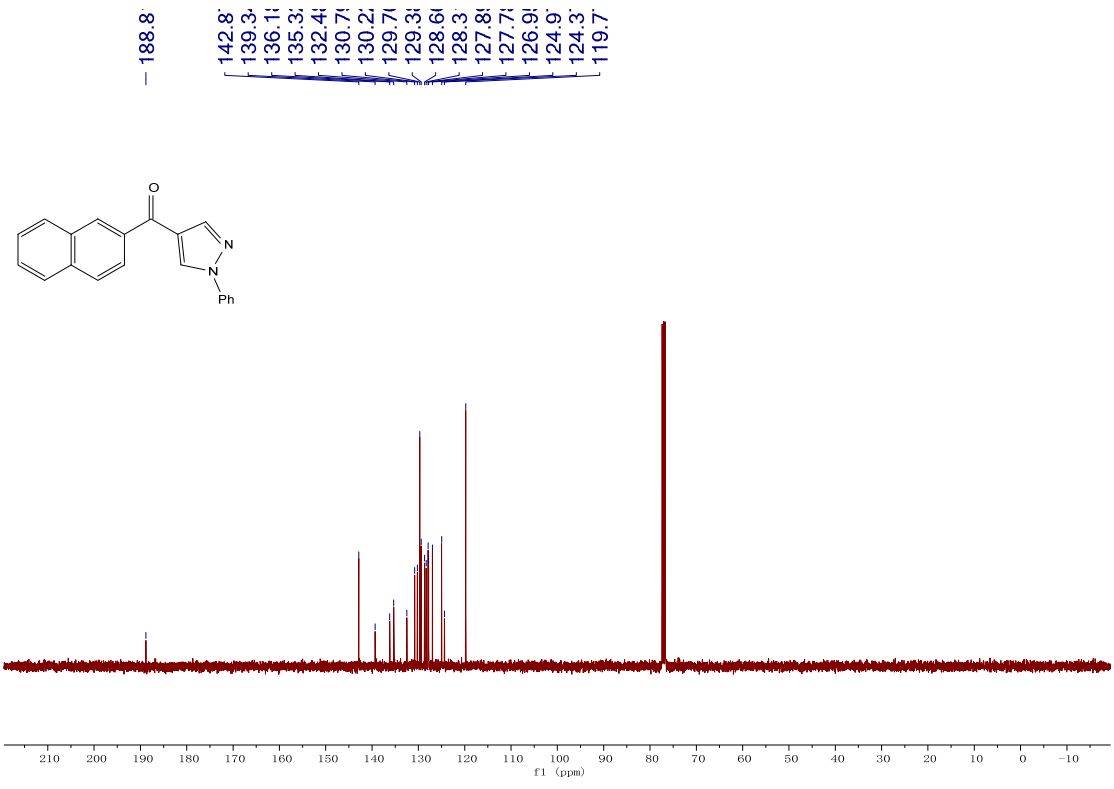
^{1}H NMR spectrum of **3v** (400 MHz, $CDCl_3$)



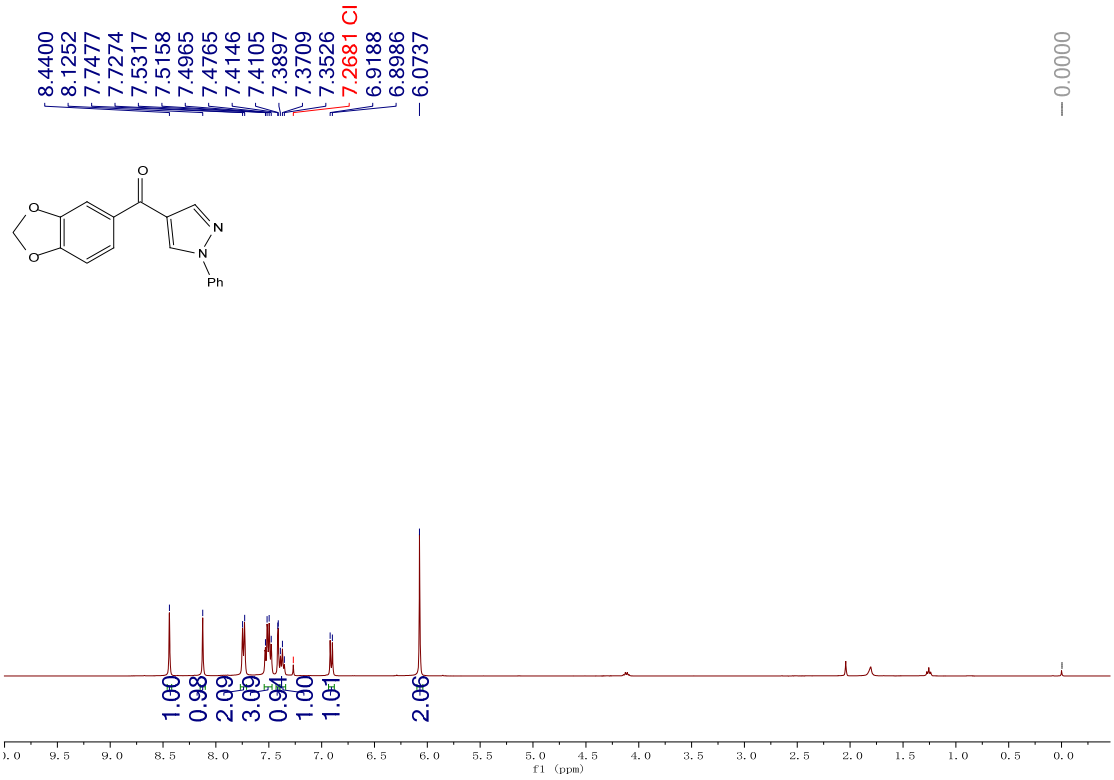
^{13}C NMR spectrum of **3v** (100 MHz, $CDCl_3$)



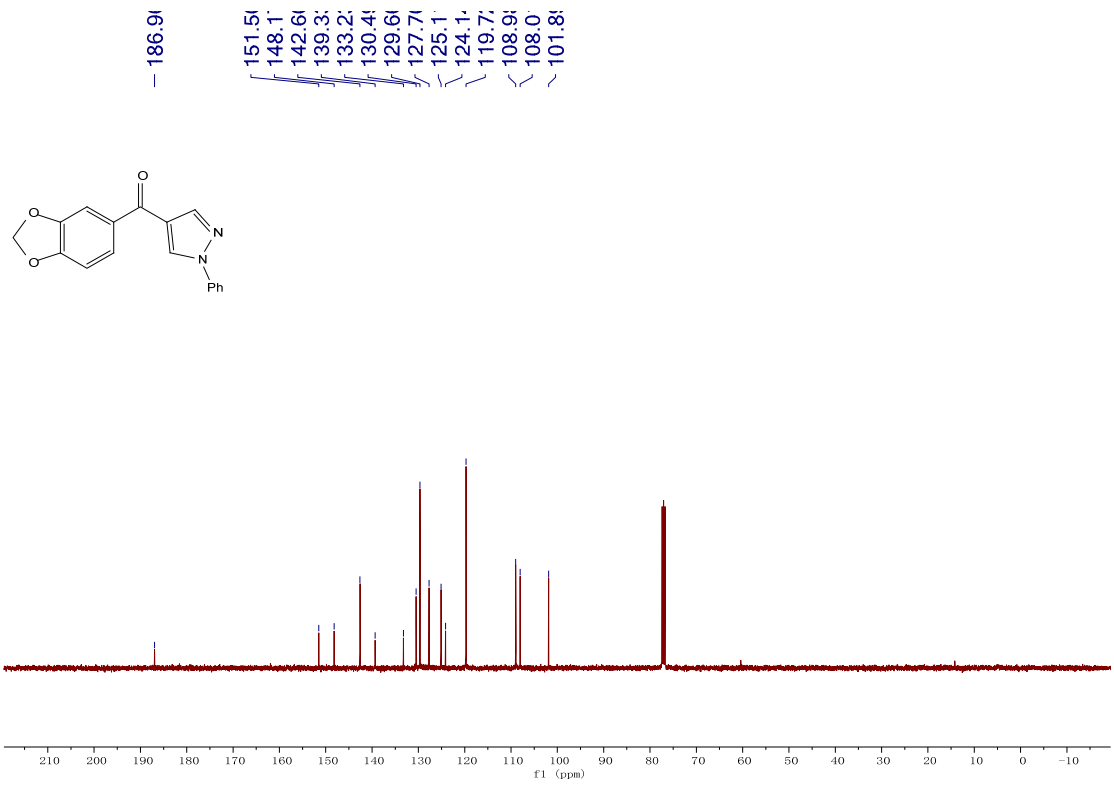
^{1}H NMR spectrum of **3w** (400 MHz, $CDCl_3$)



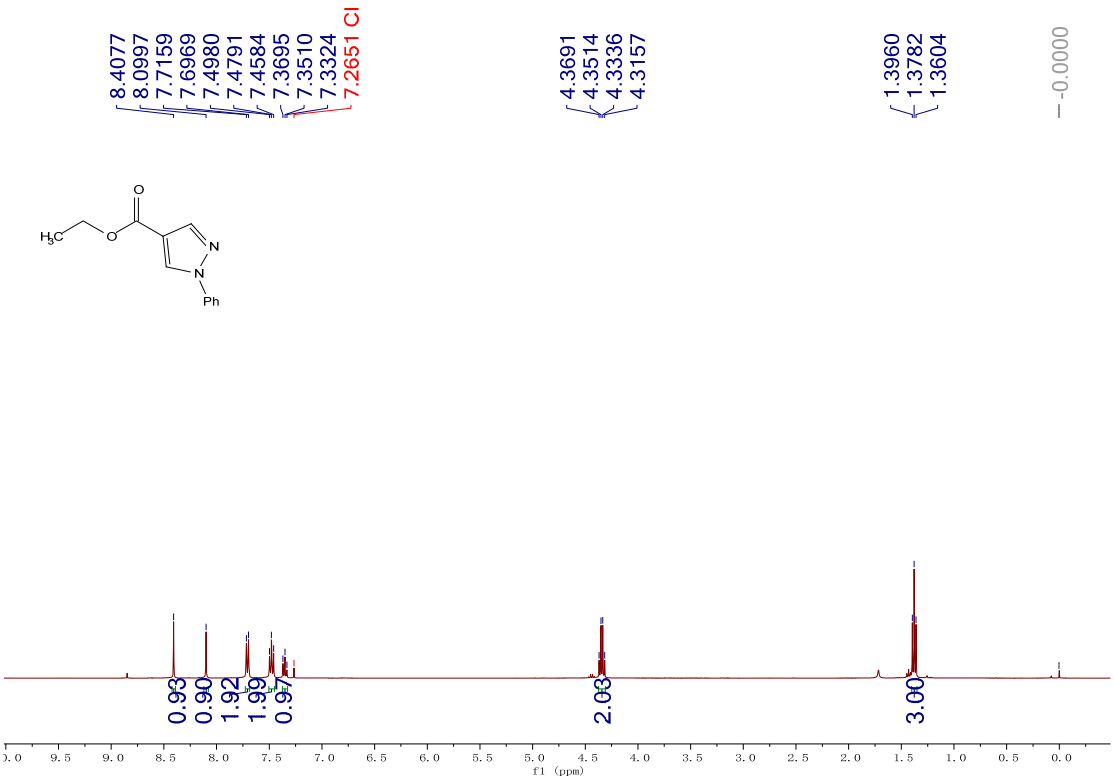
^{13}C NMR spectrum of **3w** (100 MHz, $CDCl_3$)



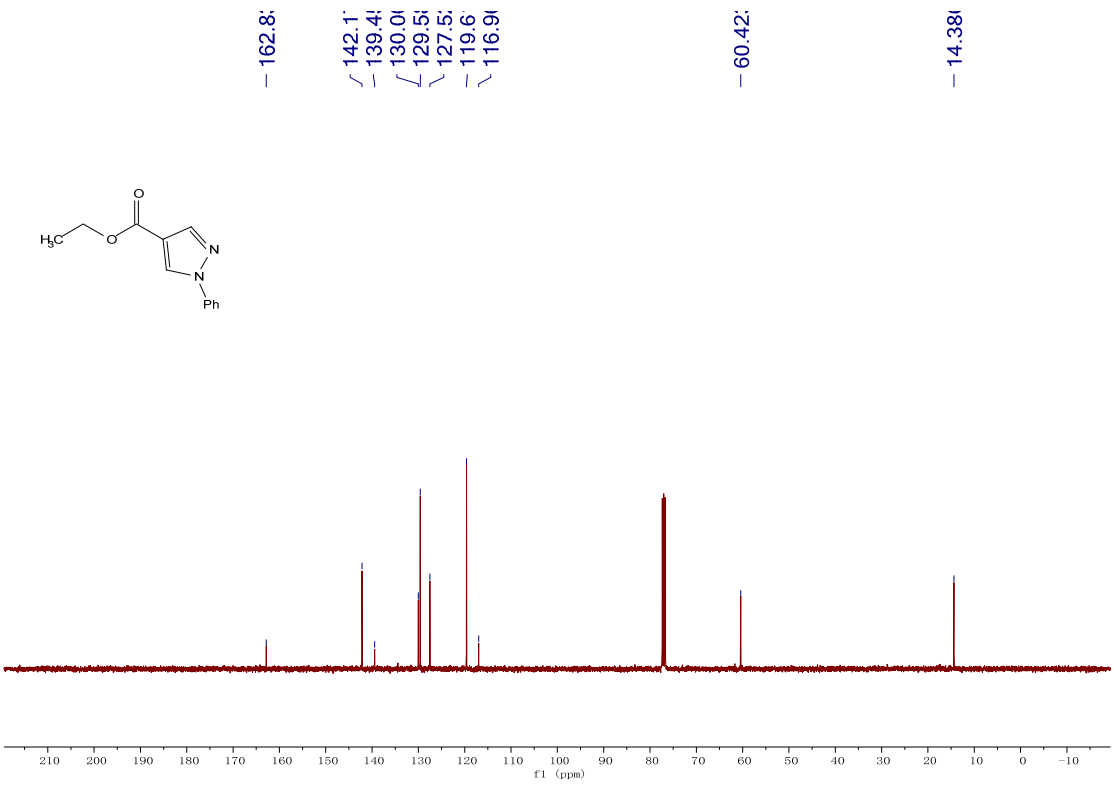
^{1}H NMR spectrum of **3x** (400 MHz, $CDCl_3$)



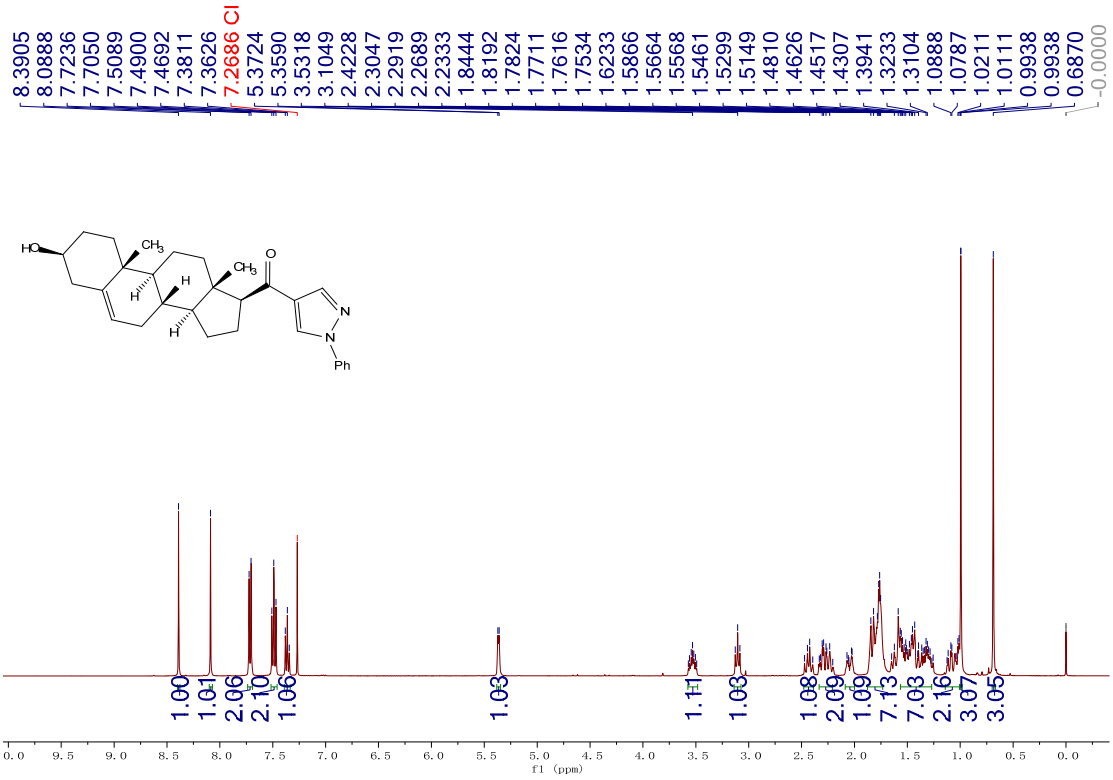
^{13}C NMR spectrum of **3x** (100 MHz, $CDCl_3$)



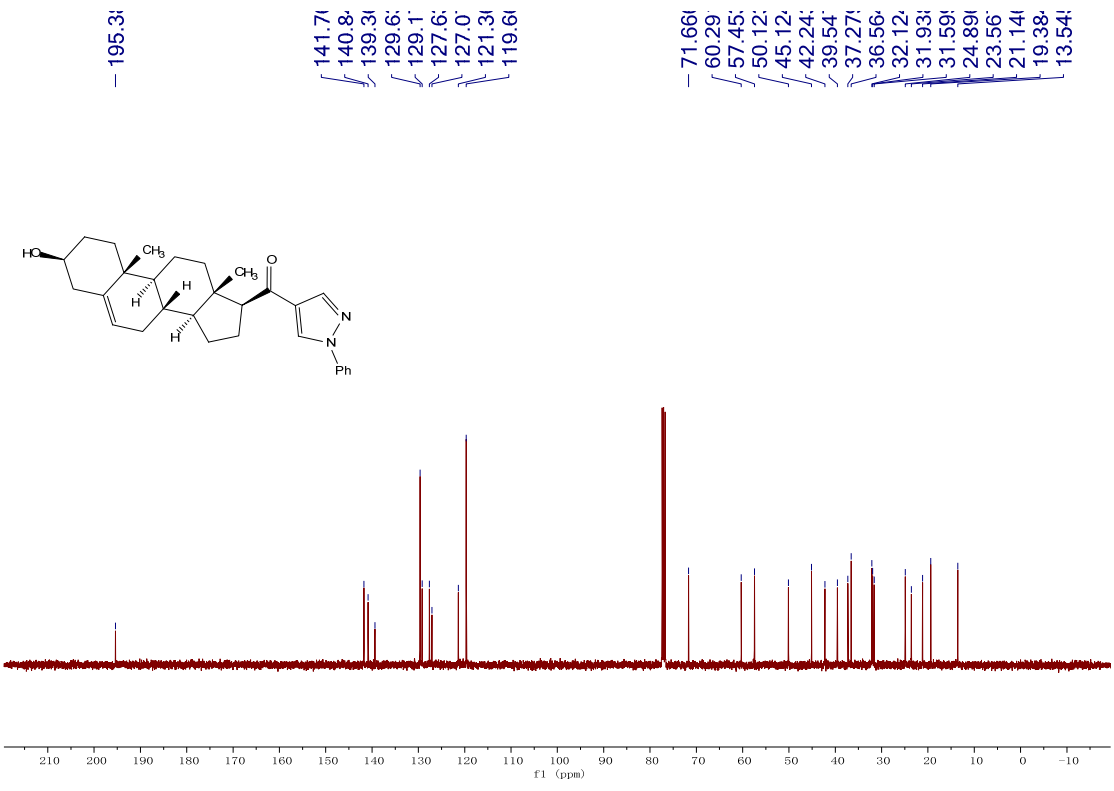
^{1}H NMR spectrum of **3y** (400 MHz, $CDCl_3$)



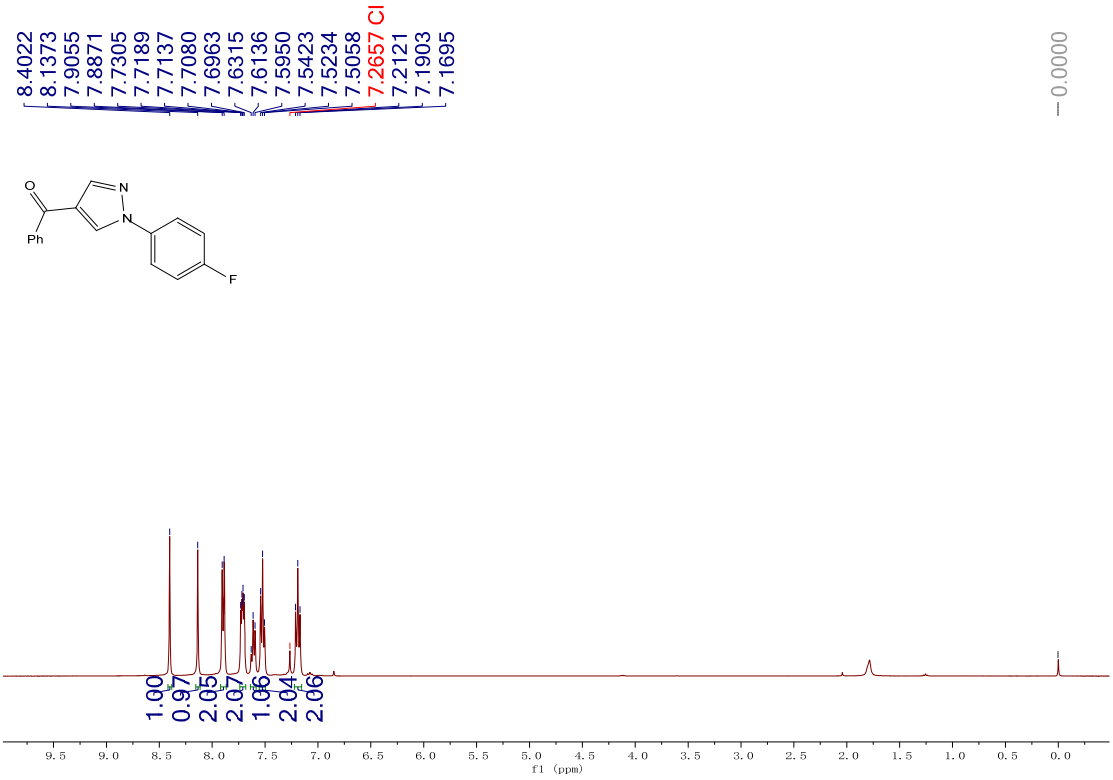
^{13}C NMR spectrum of **3y** (100 MHz, $CDCl_3$)



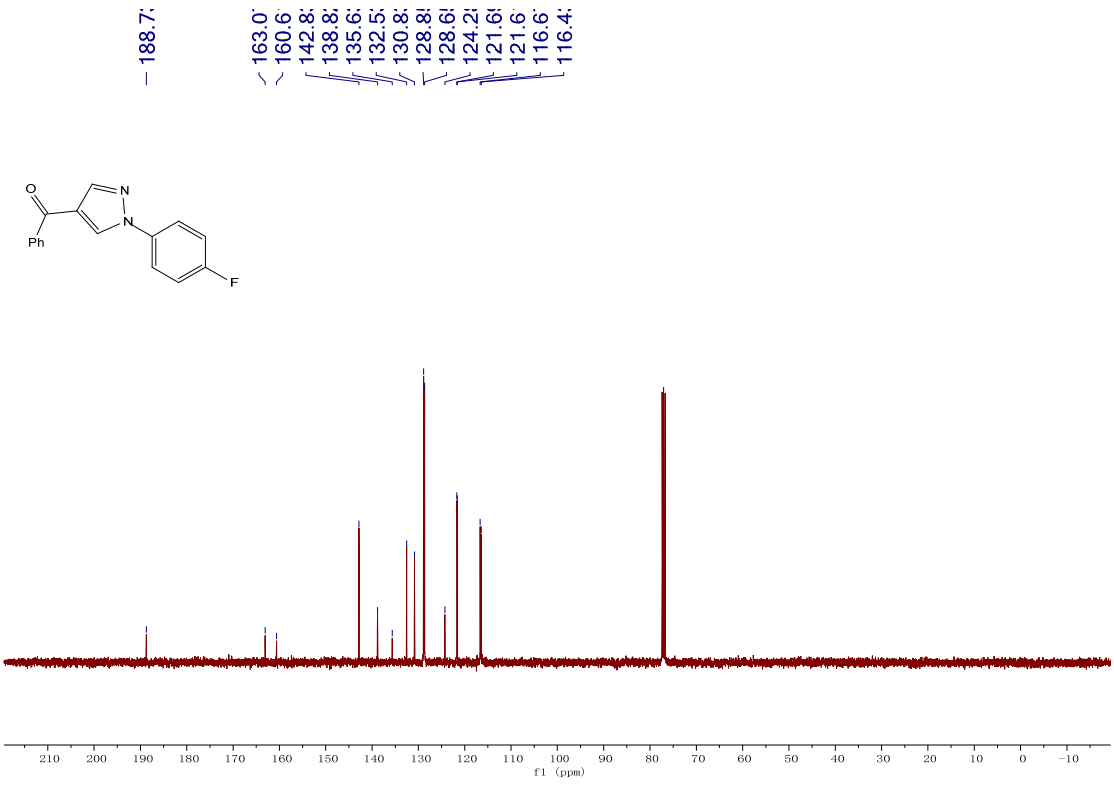
^{1}H NMR spectrum of **3z** (400 MHz, $CDCl_3$)



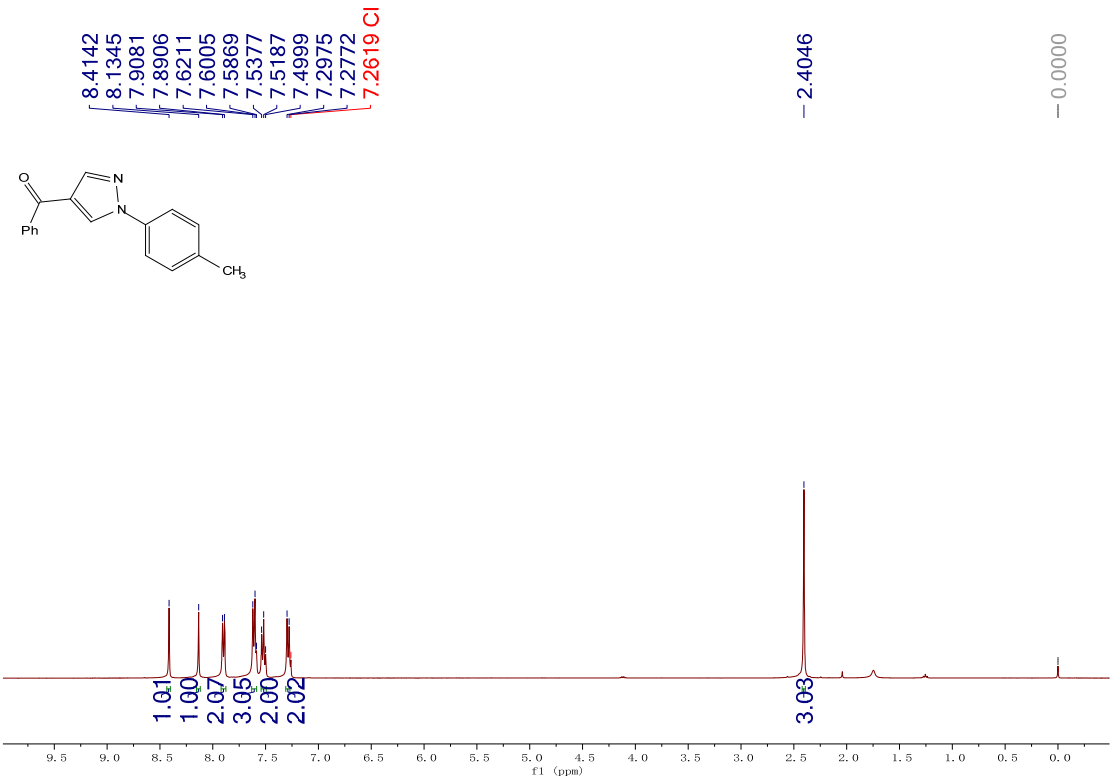
^{13}C NMR spectrum of **3z** (100 MHz, $CDCl_3$)



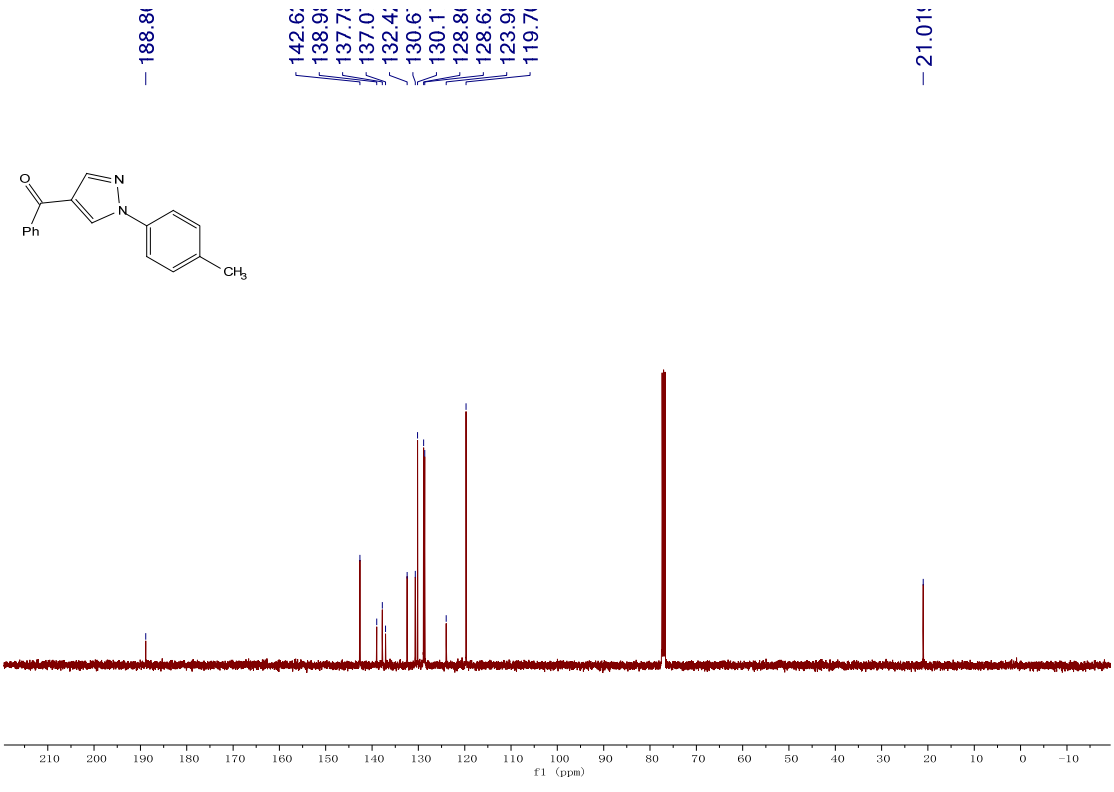
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



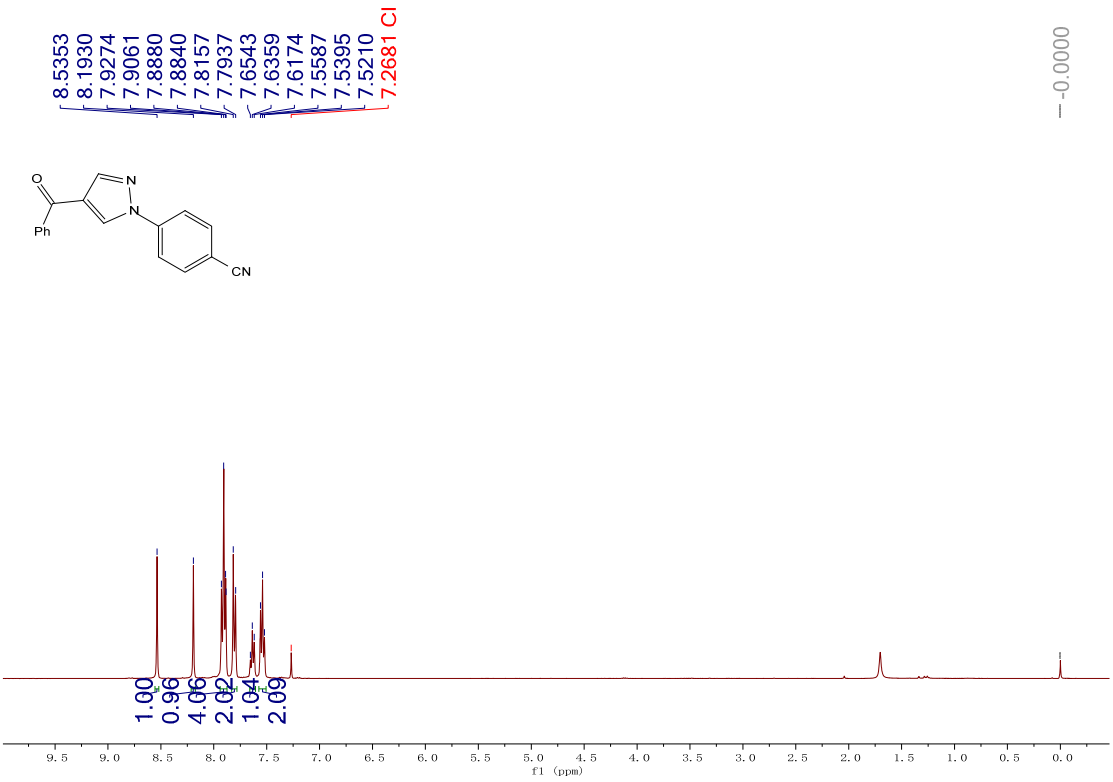
^{13}C NMR spectrum of **3aa** (100 MHz, $CDCl_3$)



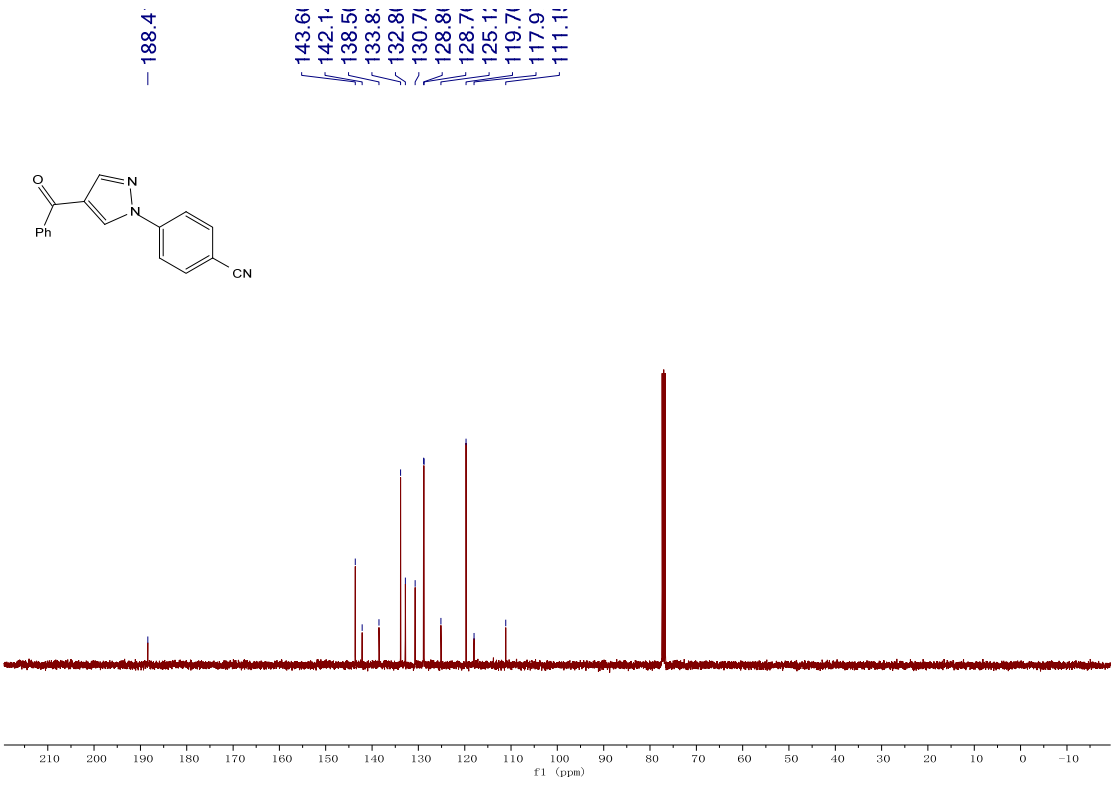
^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$)



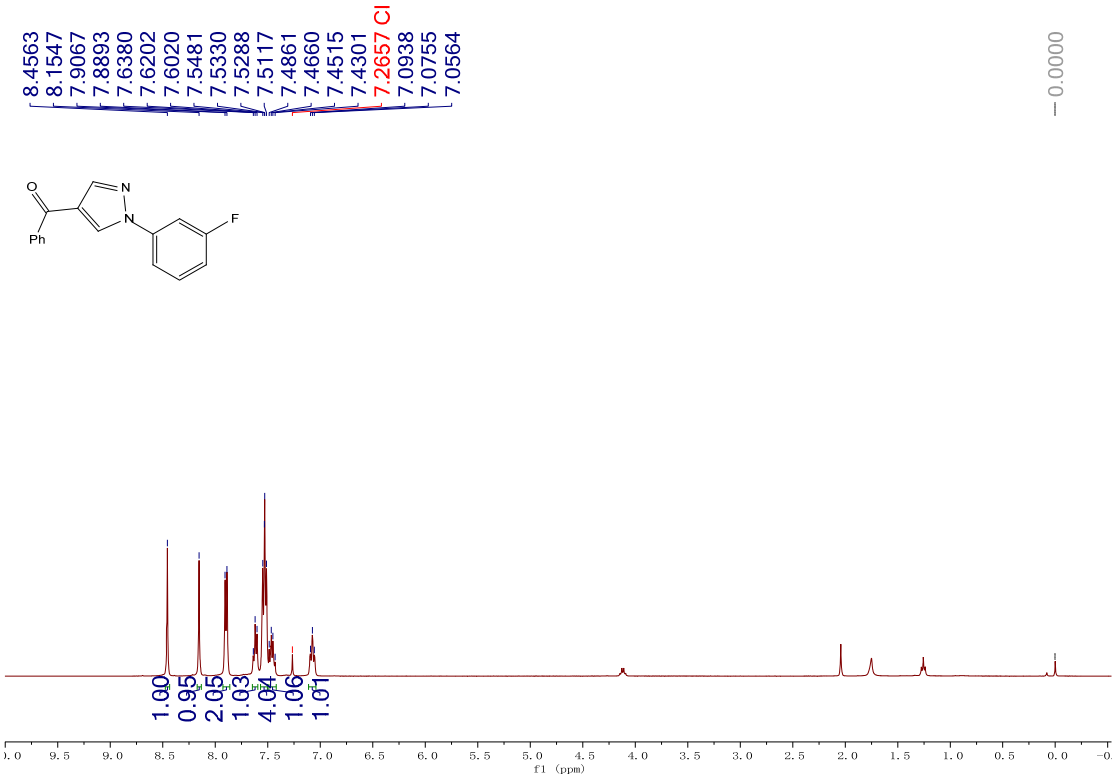
^{13}C NMR spectrum of **3ab** (100 MHz, $CDCl_3$)



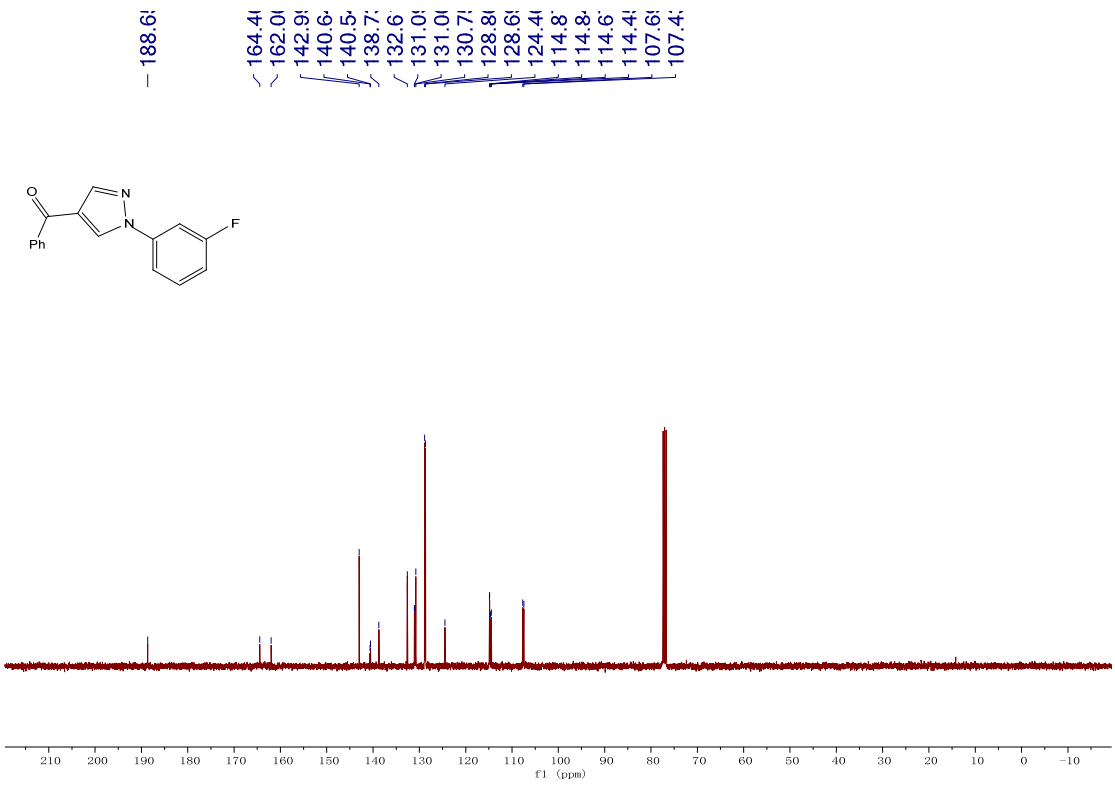
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



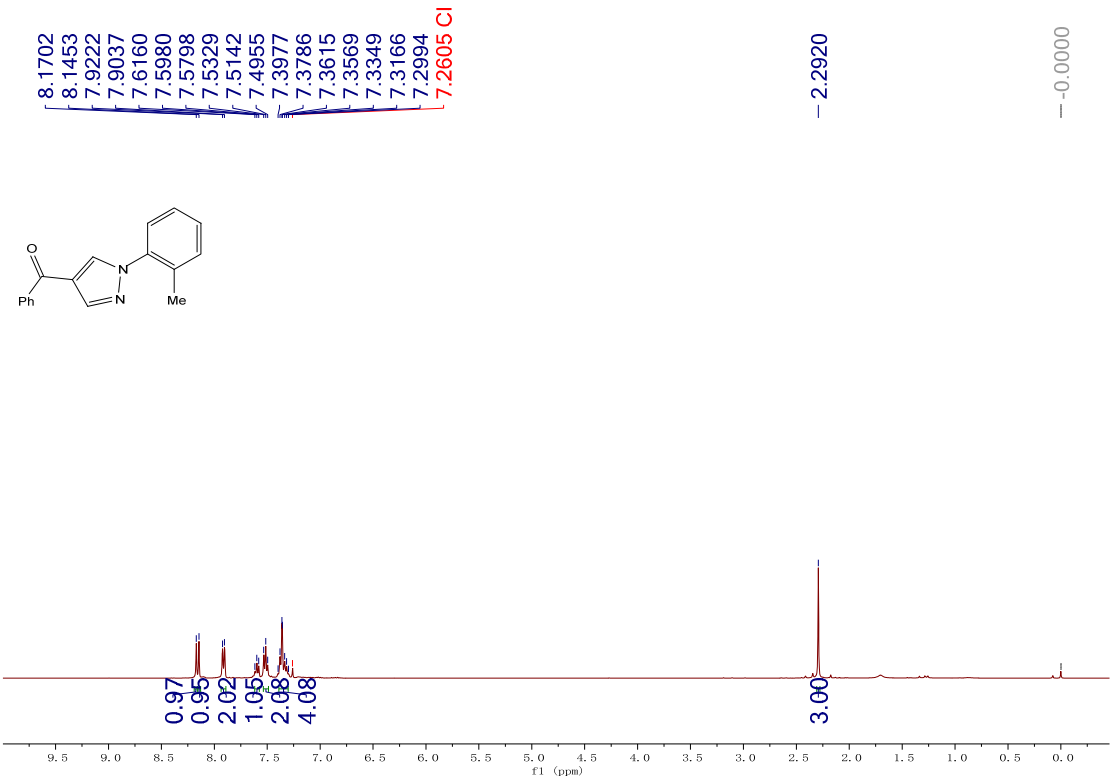
^{13}C NMR spectrum of **3ac** (100 MHz, $CDCl_3$)



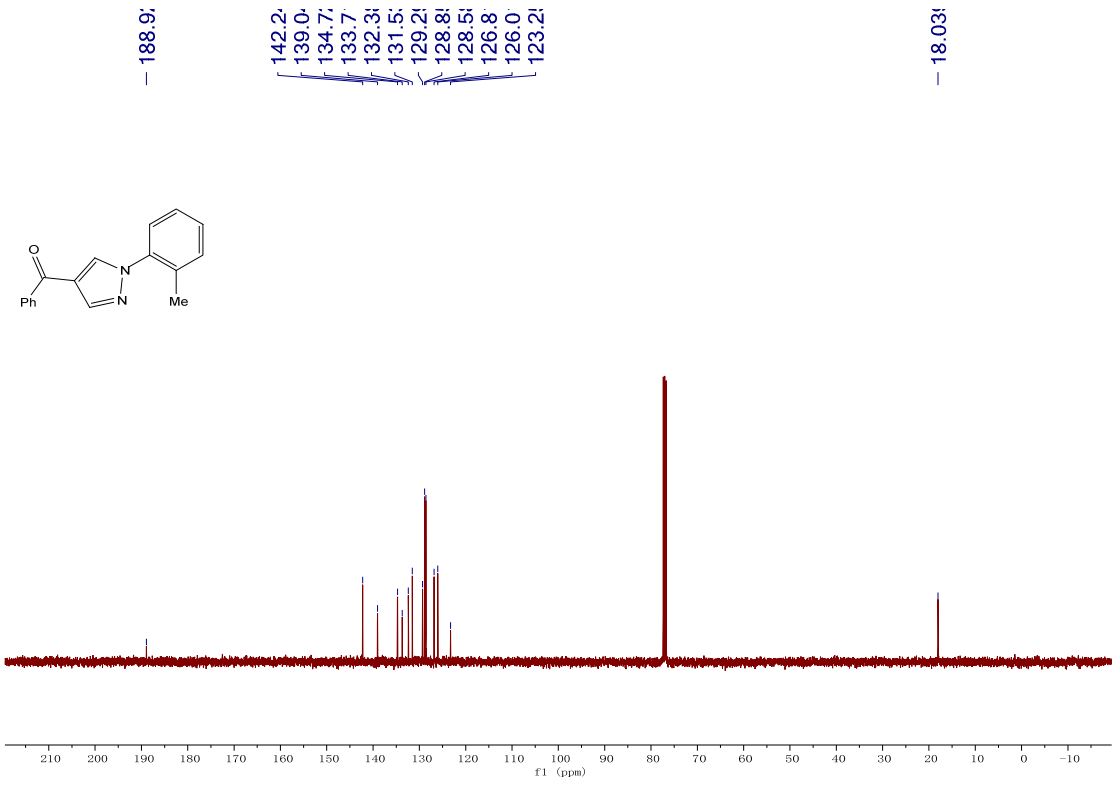
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)



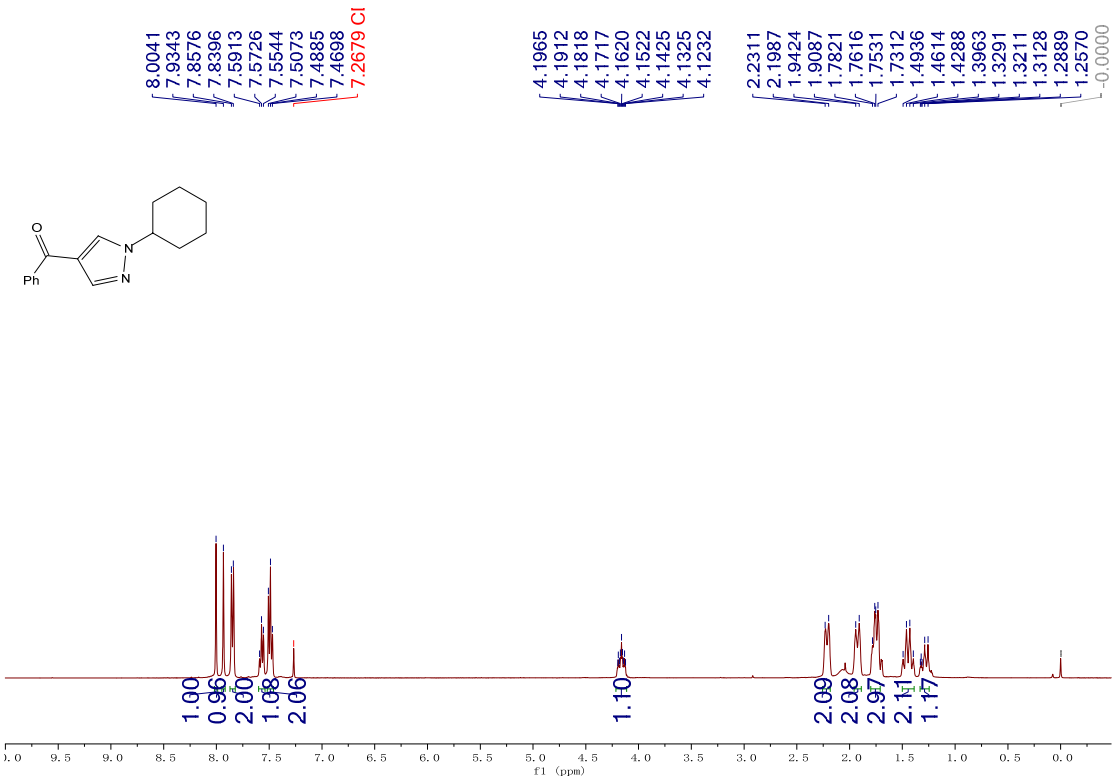
^{13}C NMR spectrum of **3ad** (100 MHz, $CDCl_3$)



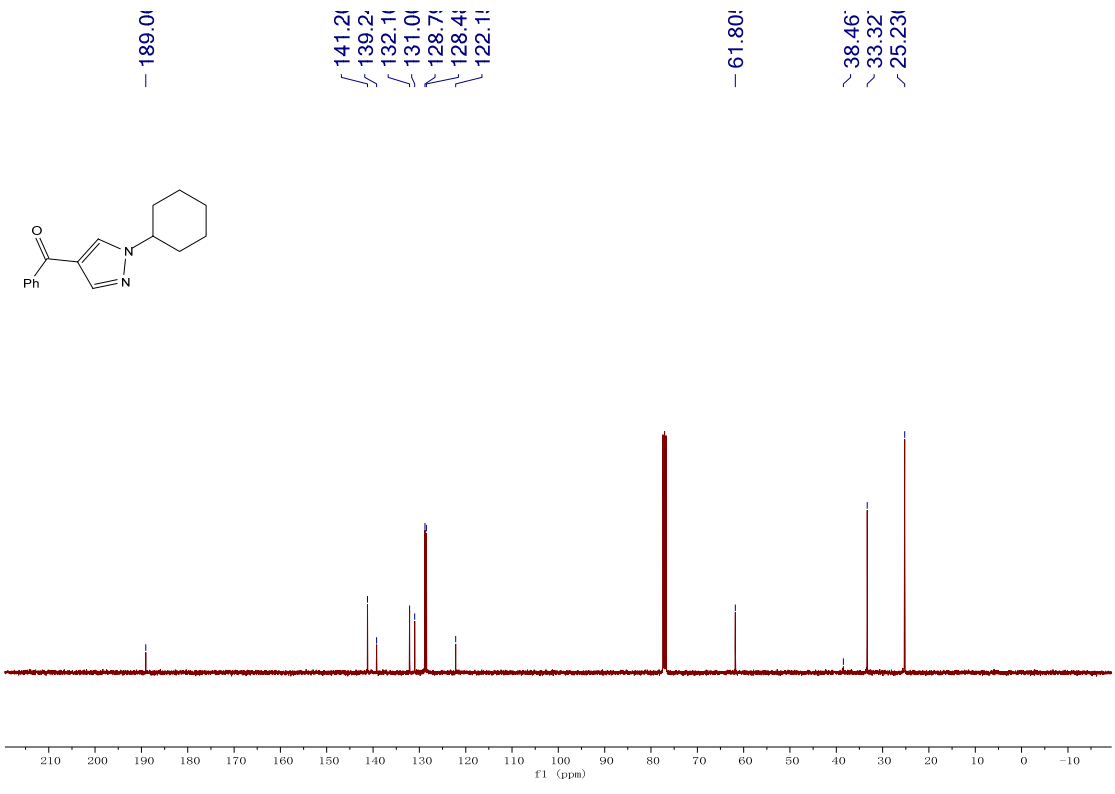
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



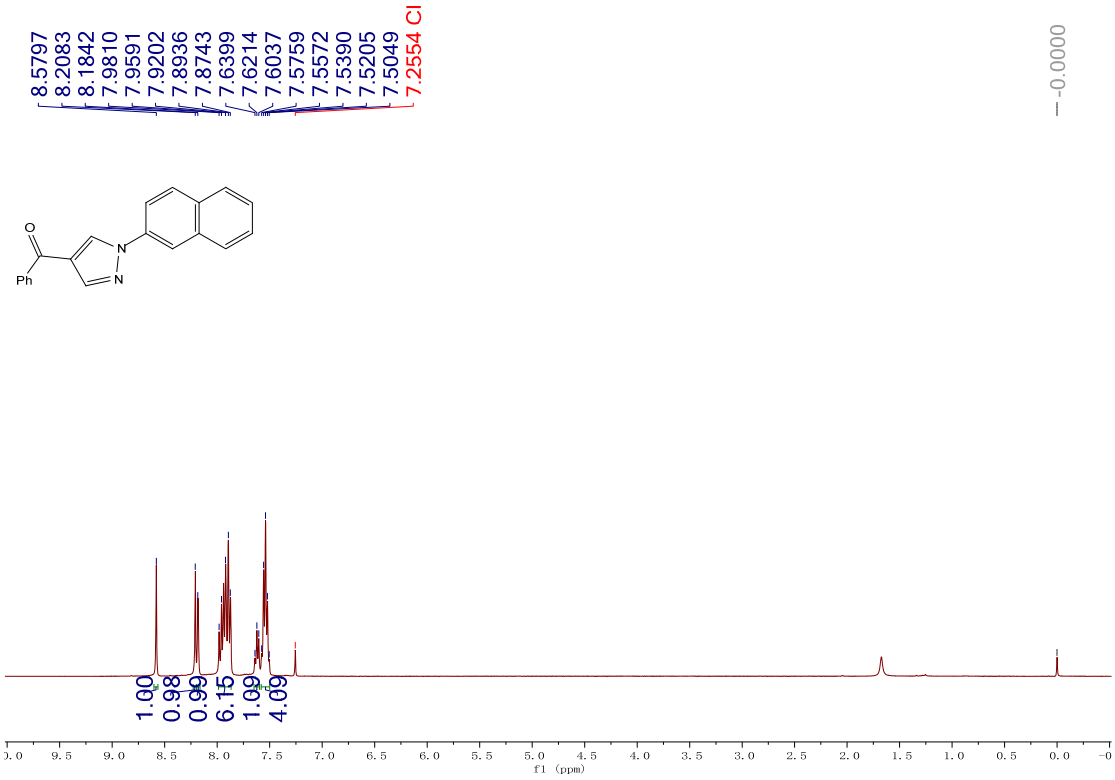
^{13}C NMR spectrum of **3ae** (100 MHz, $CDCl_3$)



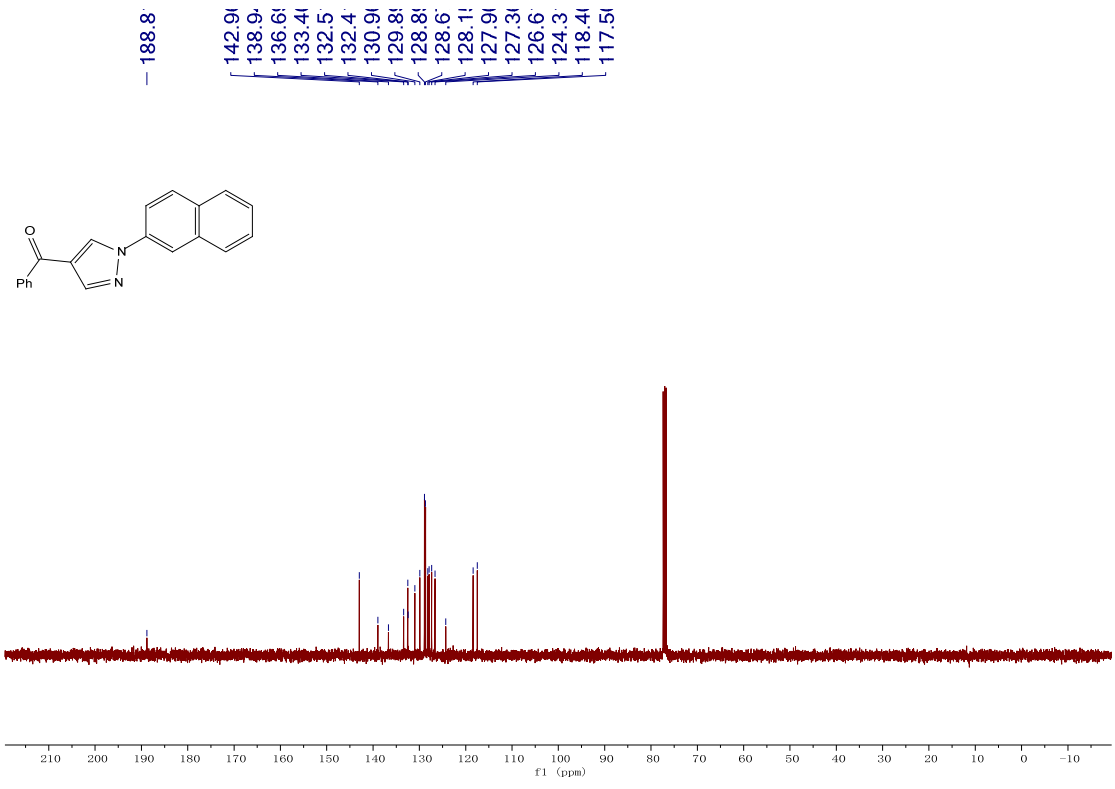
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



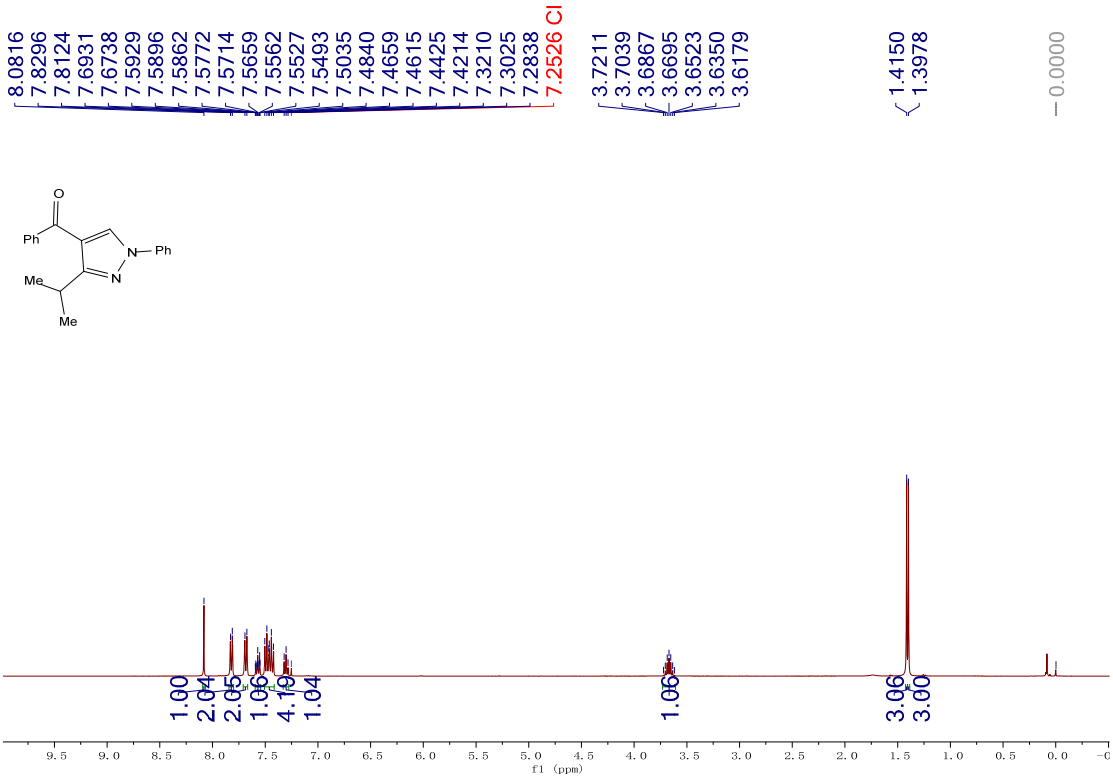
^{13}C NMR spectrum of **3af** (100 MHz, $CDCl_3$)



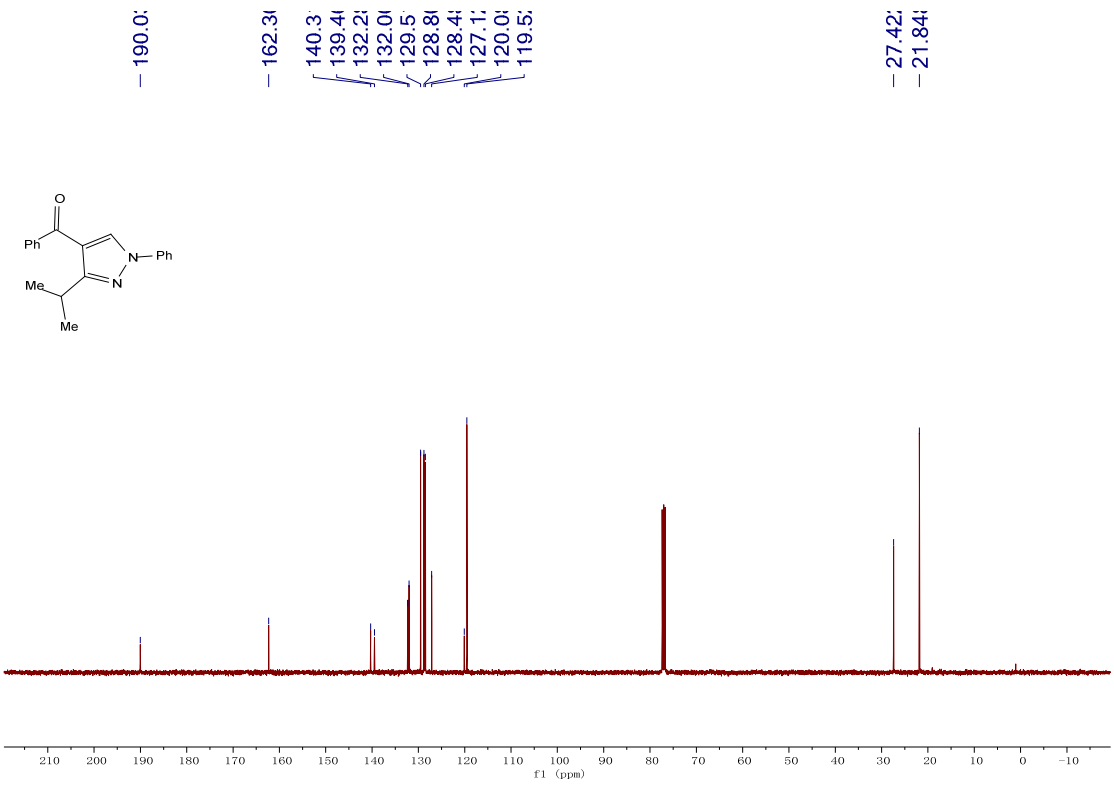
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)



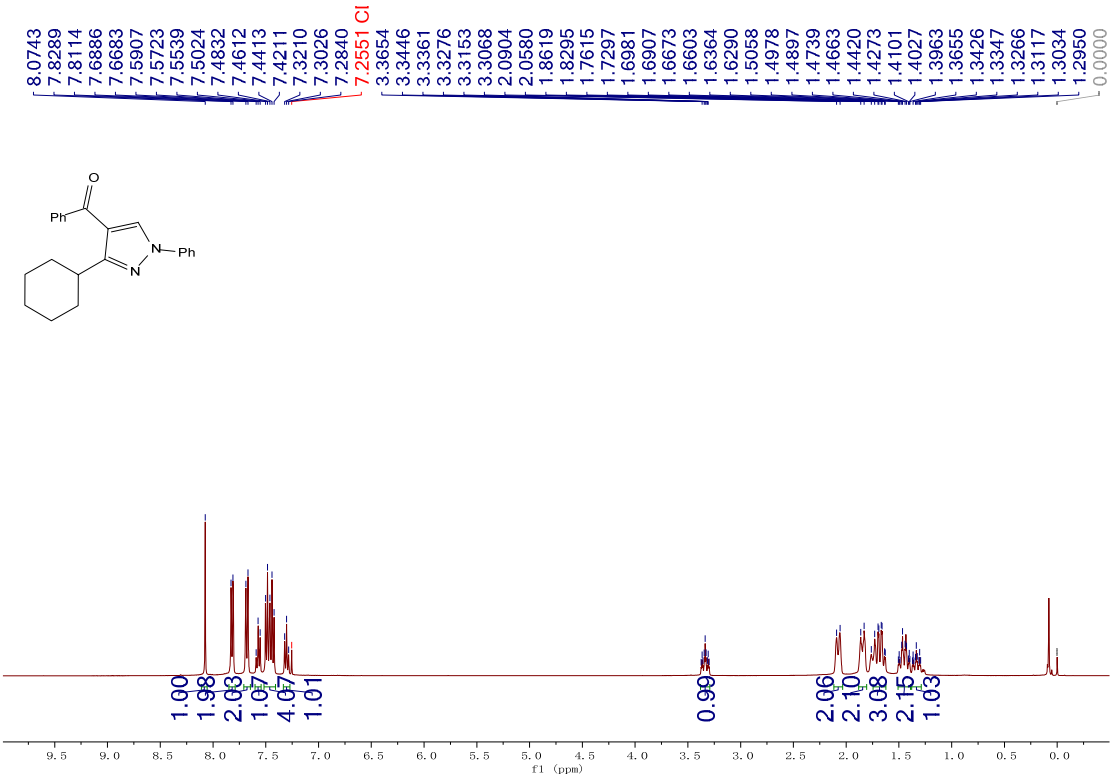
^{13}C NMR spectrum of **3ag** (100 MHz, $CDCl_3$)



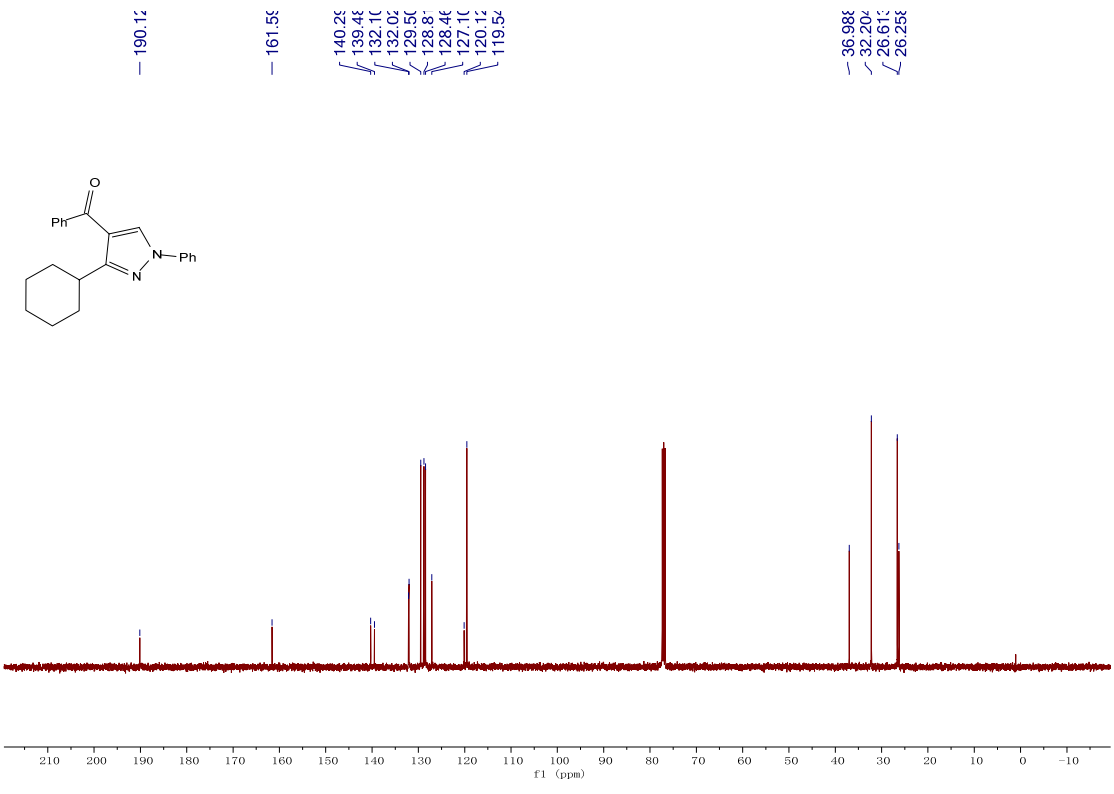
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



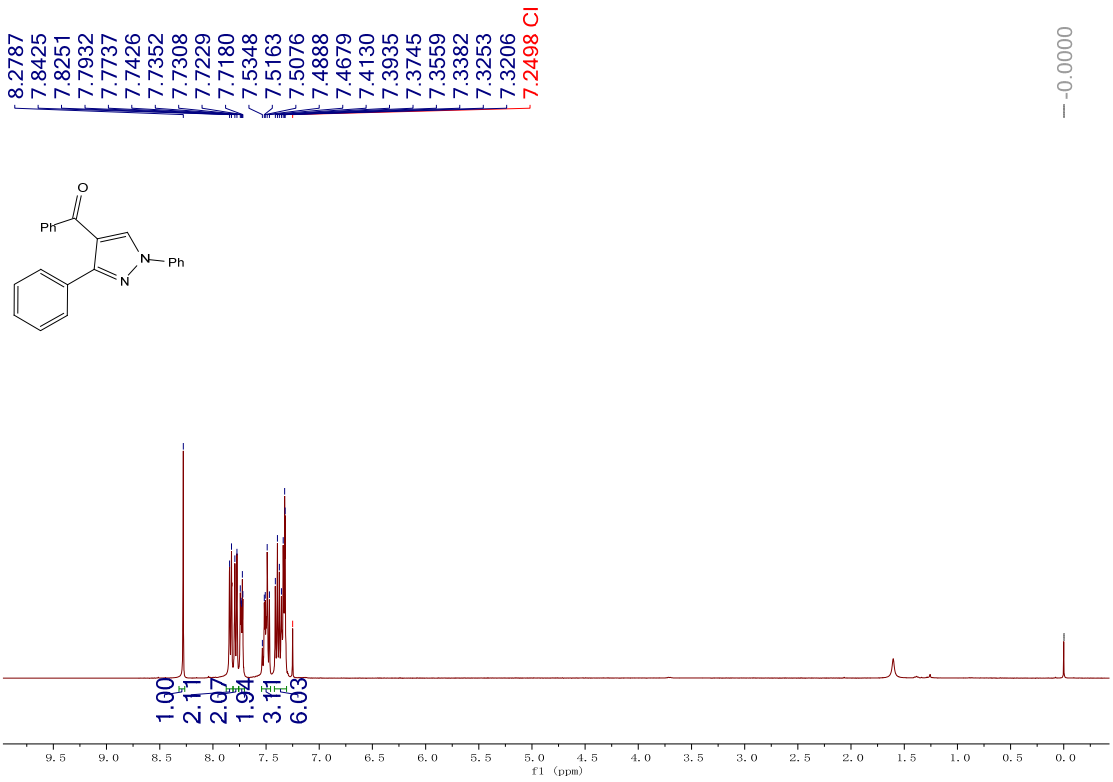
^{13}C NMR spectrum of **5a** (100 MHz, $CDCl_3$)



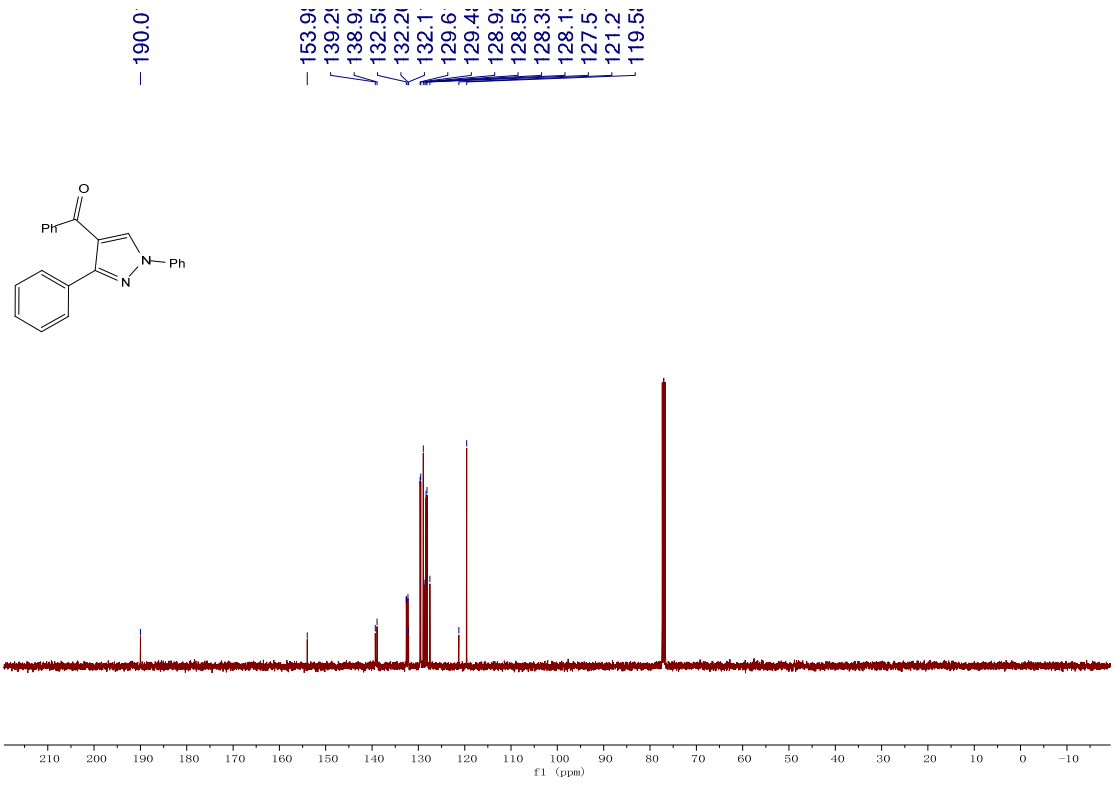
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



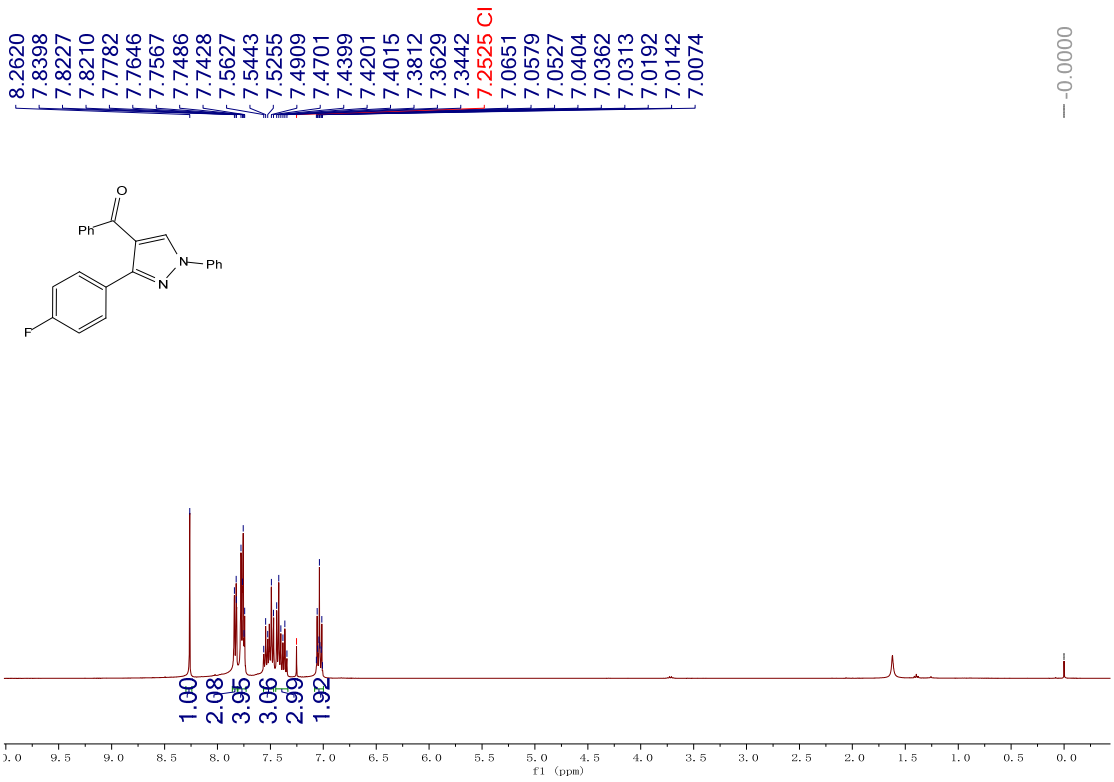
^{13}C NMR spectrum of **5b** (100 MHz, $CDCl_3$)



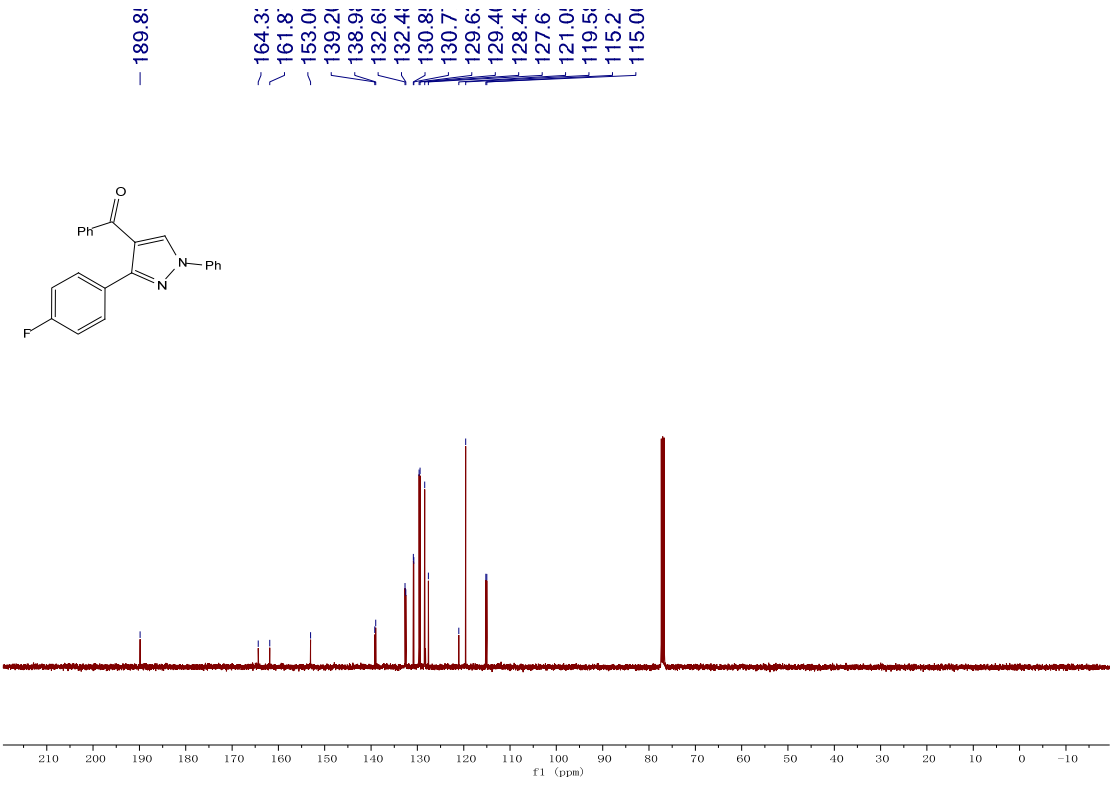
^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)



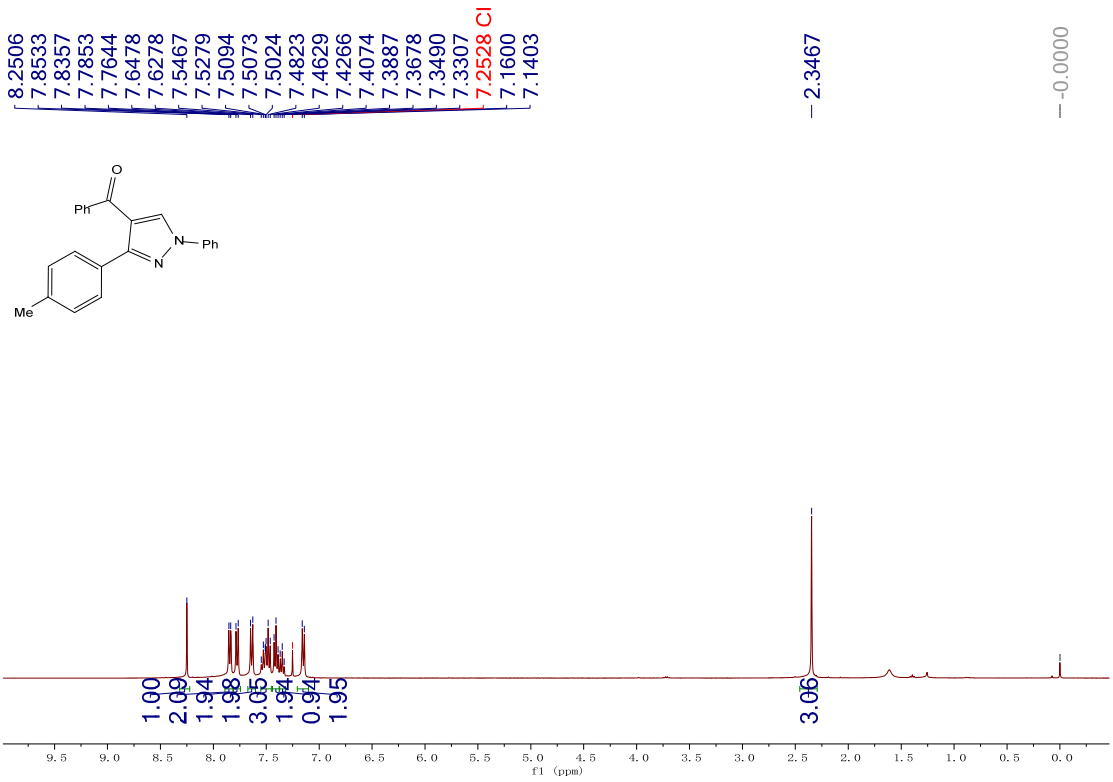
^{13}C NMR spectrum of **5c** (100 MHz, $CDCl_3$)



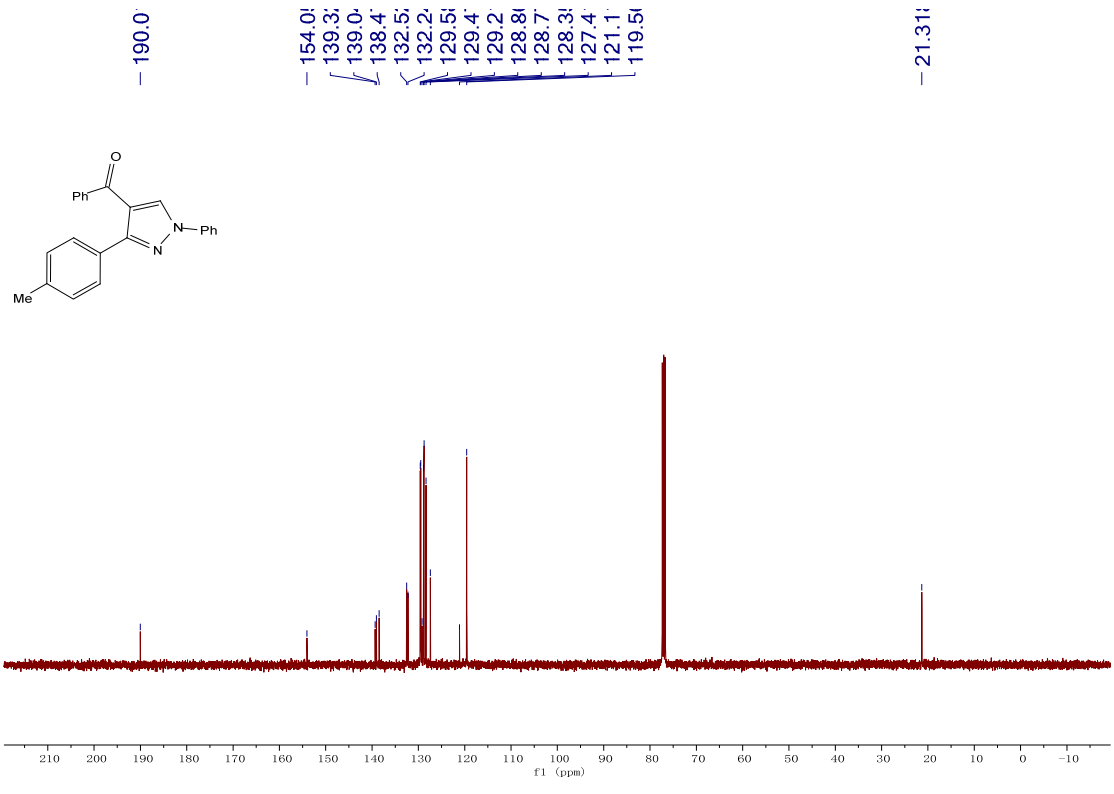
^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)



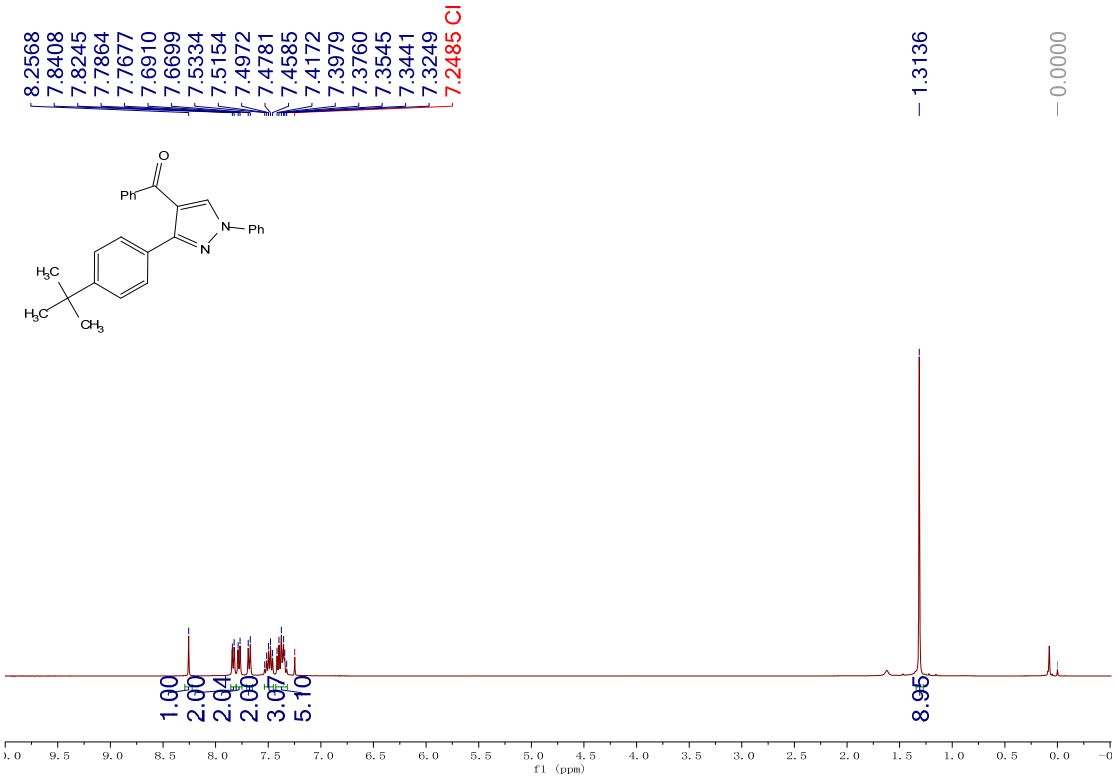
^{13}C NMR spectrum of **5d** (100 MHz, $CDCl_3$)



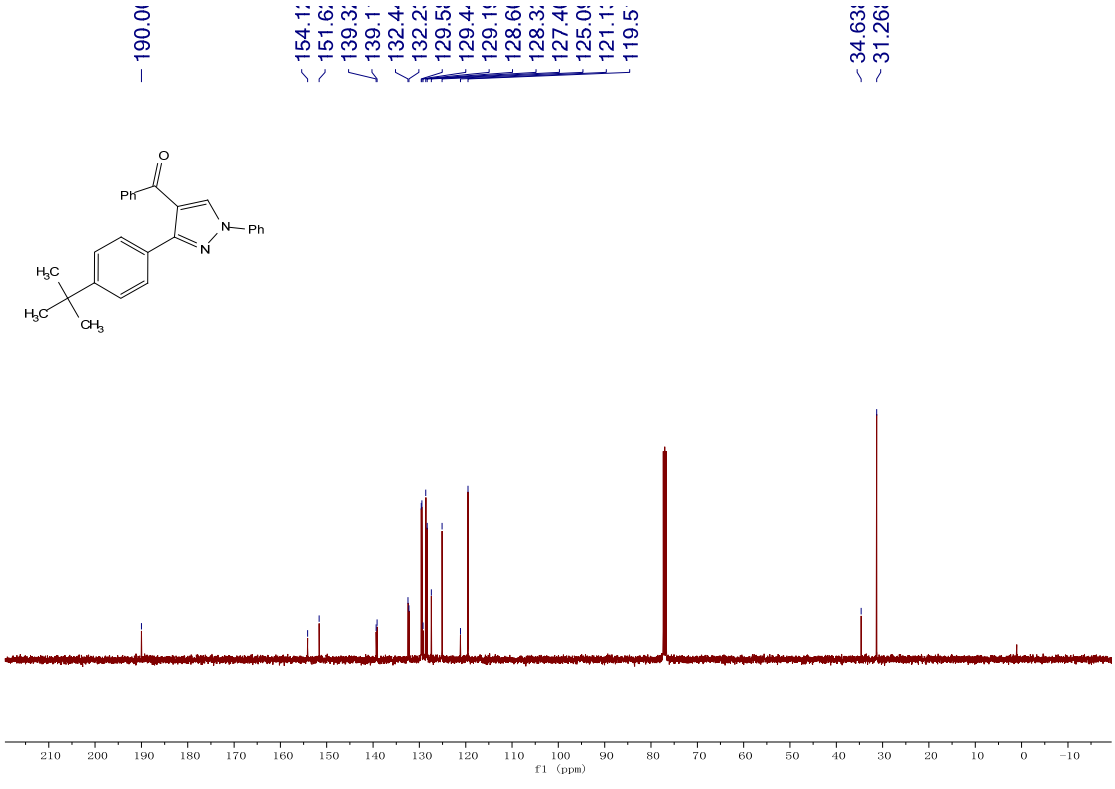
^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)



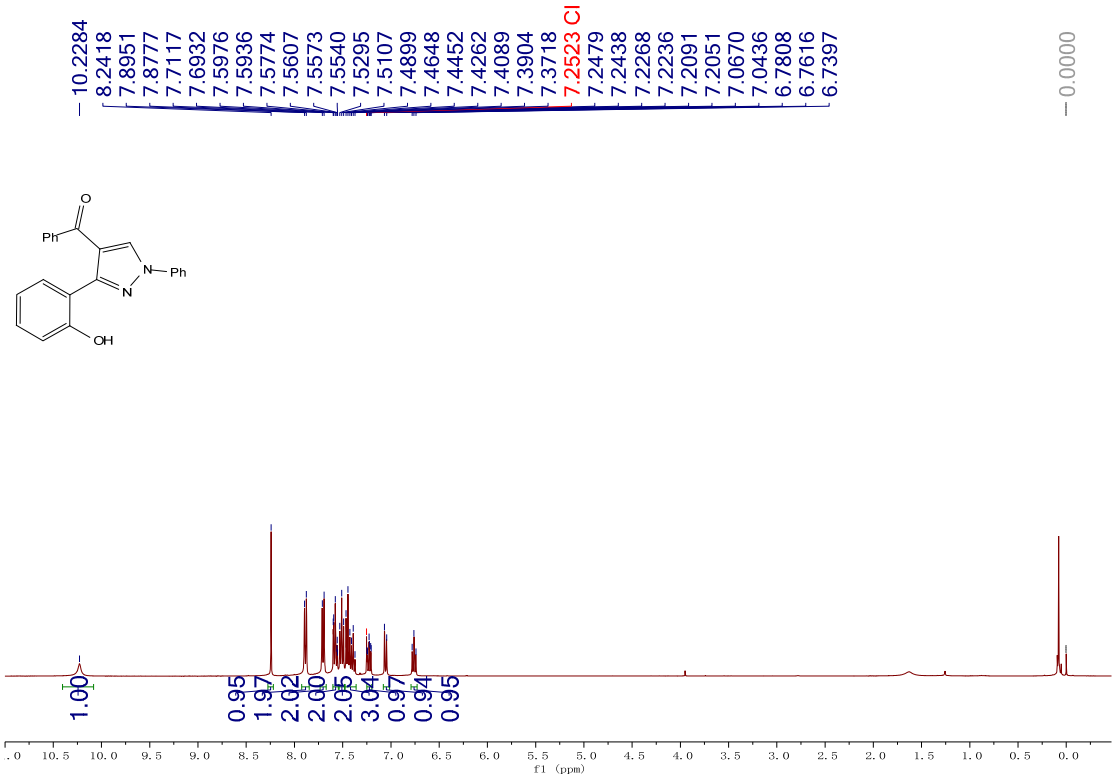
^{13}C NMR spectrum of **5e** (100 MHz, $CDCl_3$)



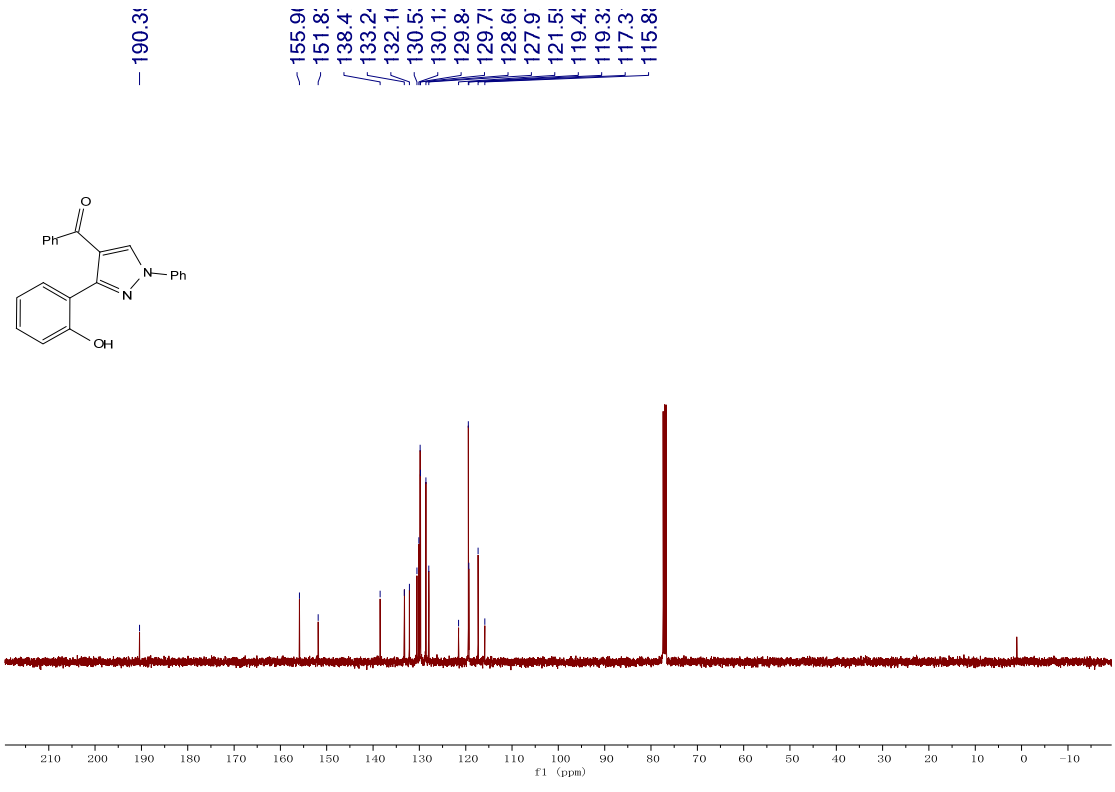
^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)



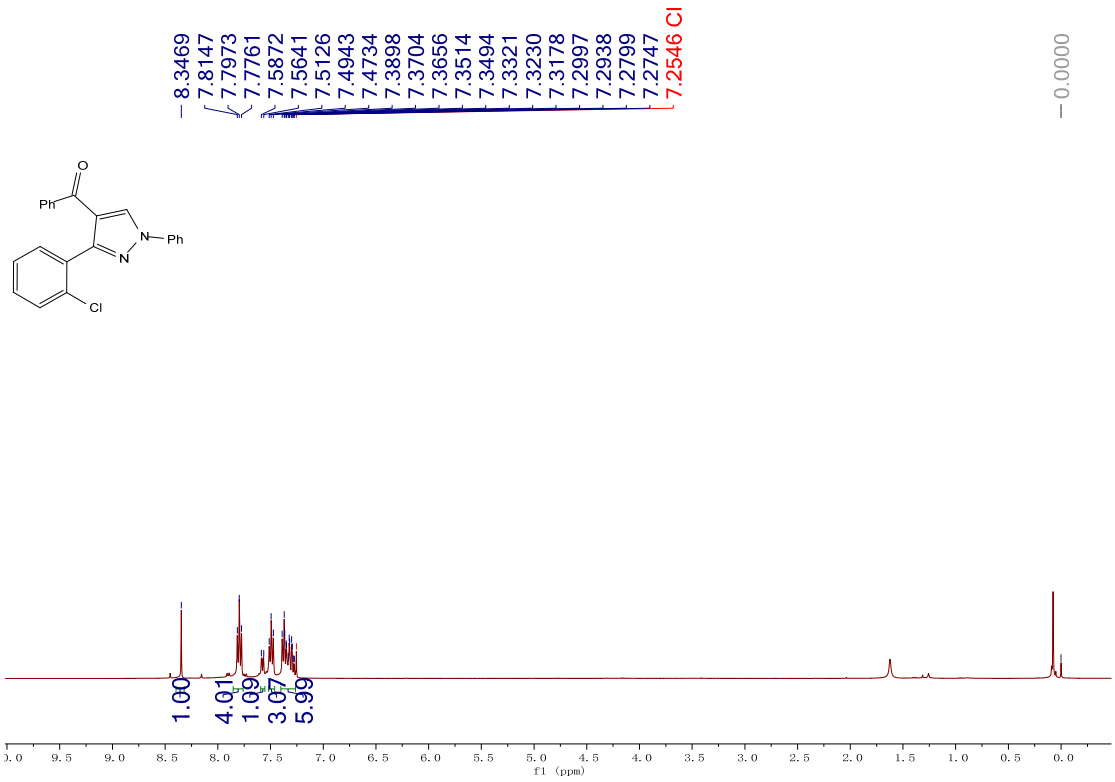
^{13}C NMR spectrum of **5f** (100 MHz, $CDCl_3$)



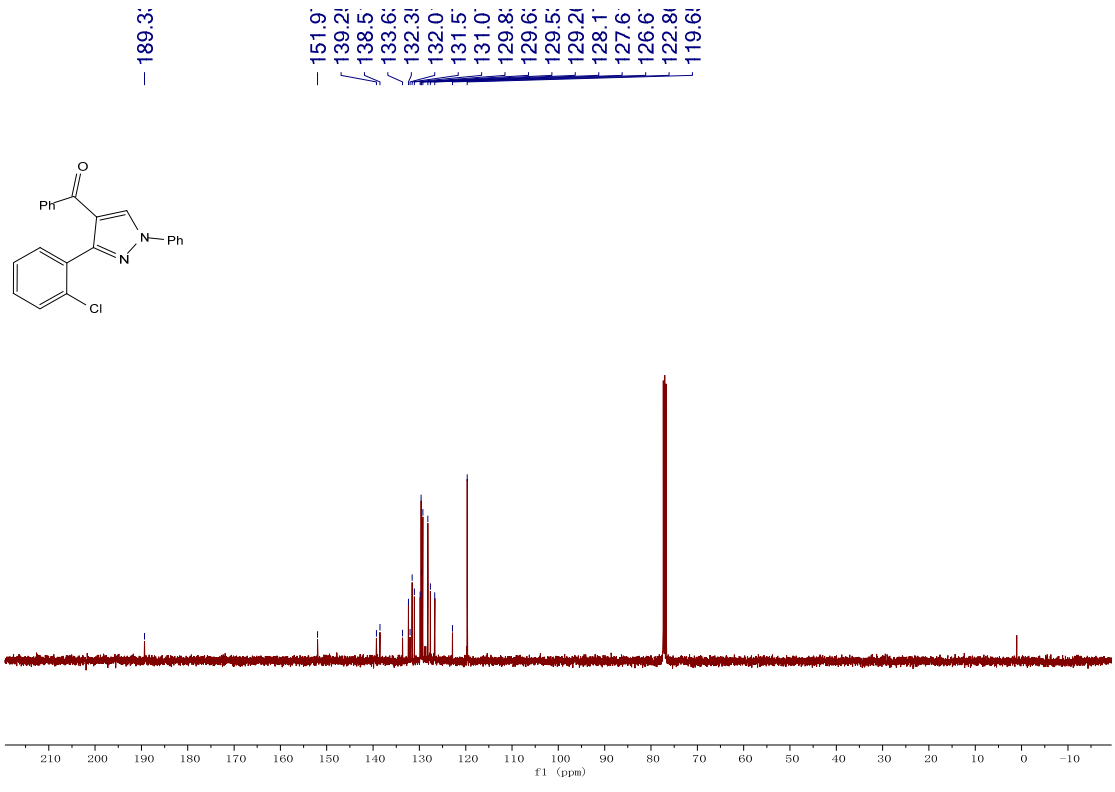
^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)



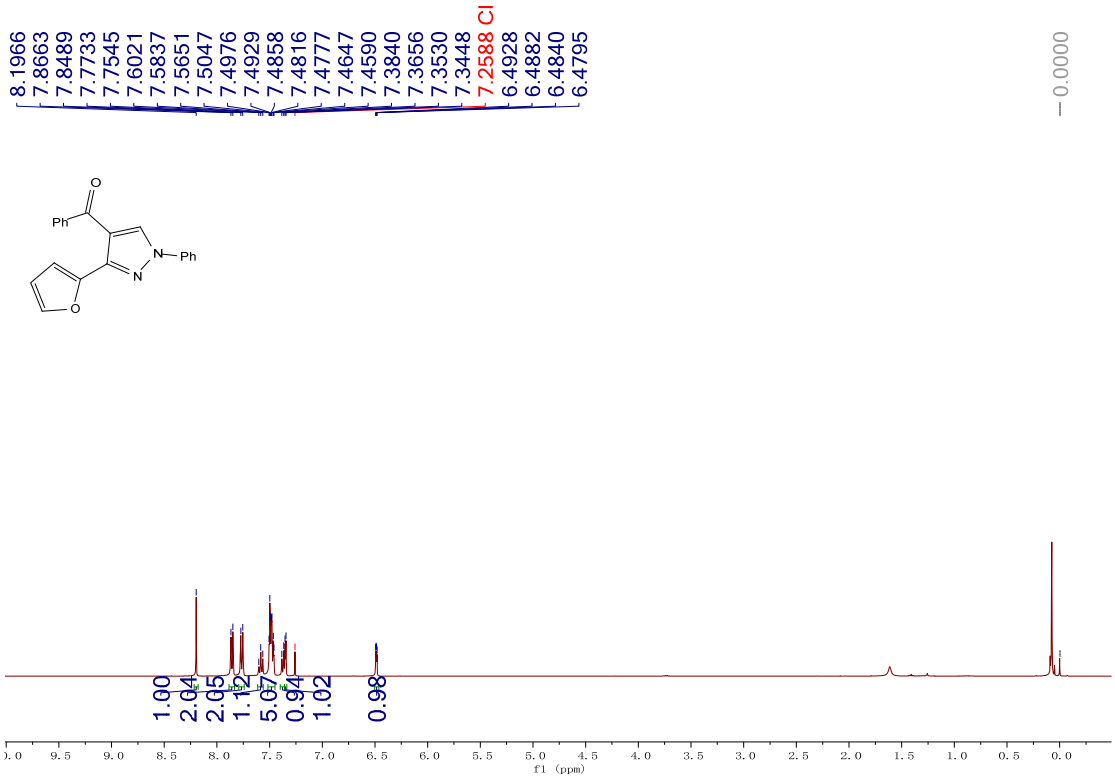
^{13}C NMR spectrum of **5g** (100 MHz, $CDCl_3$)



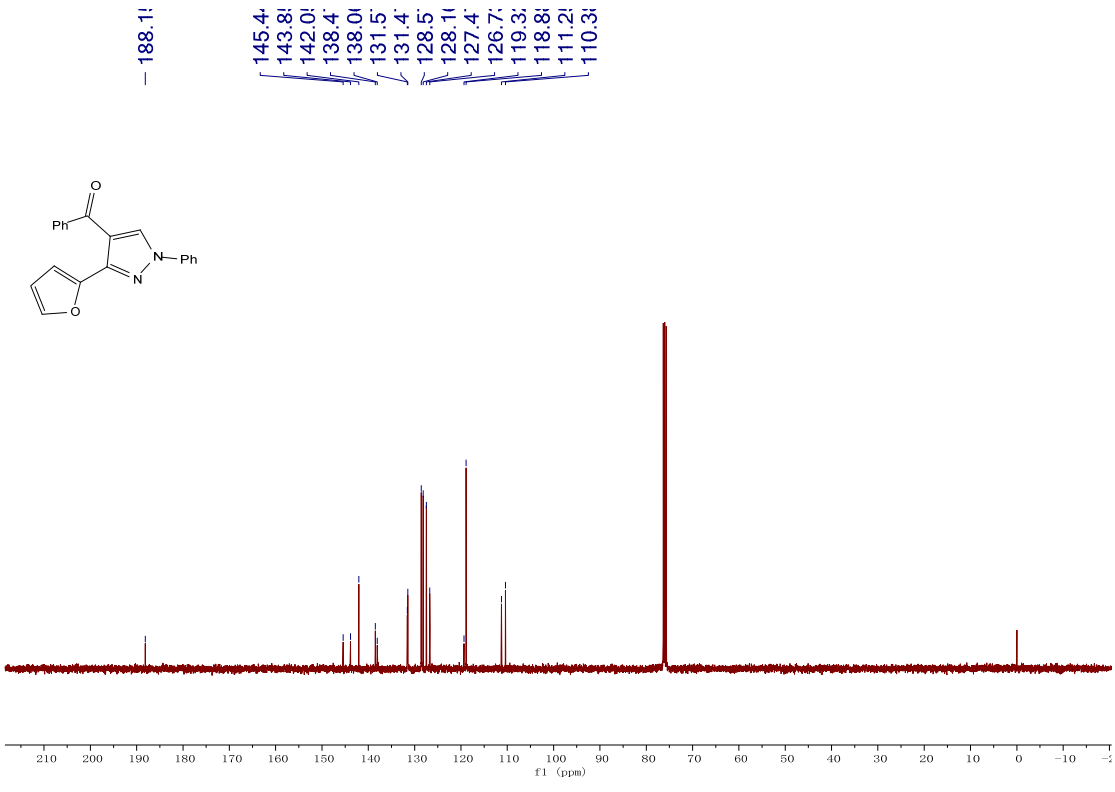
^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)



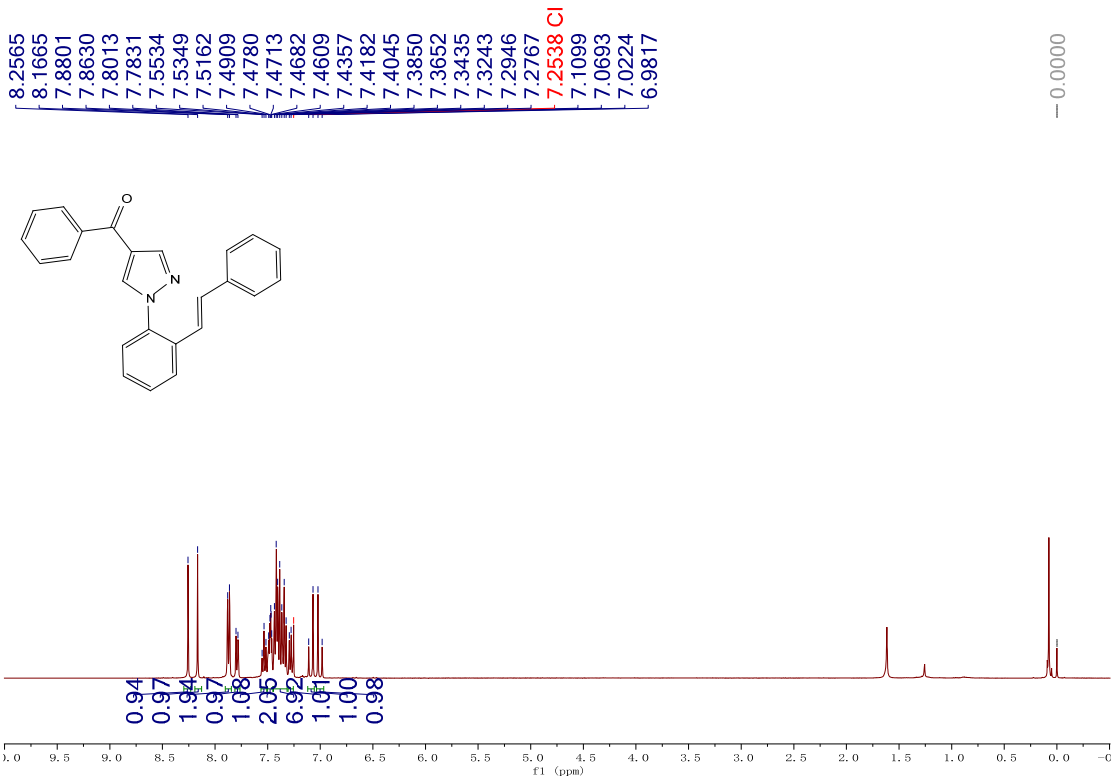
^{13}C NMR spectrum of **5h** (100 MHz, $CDCl_3$)



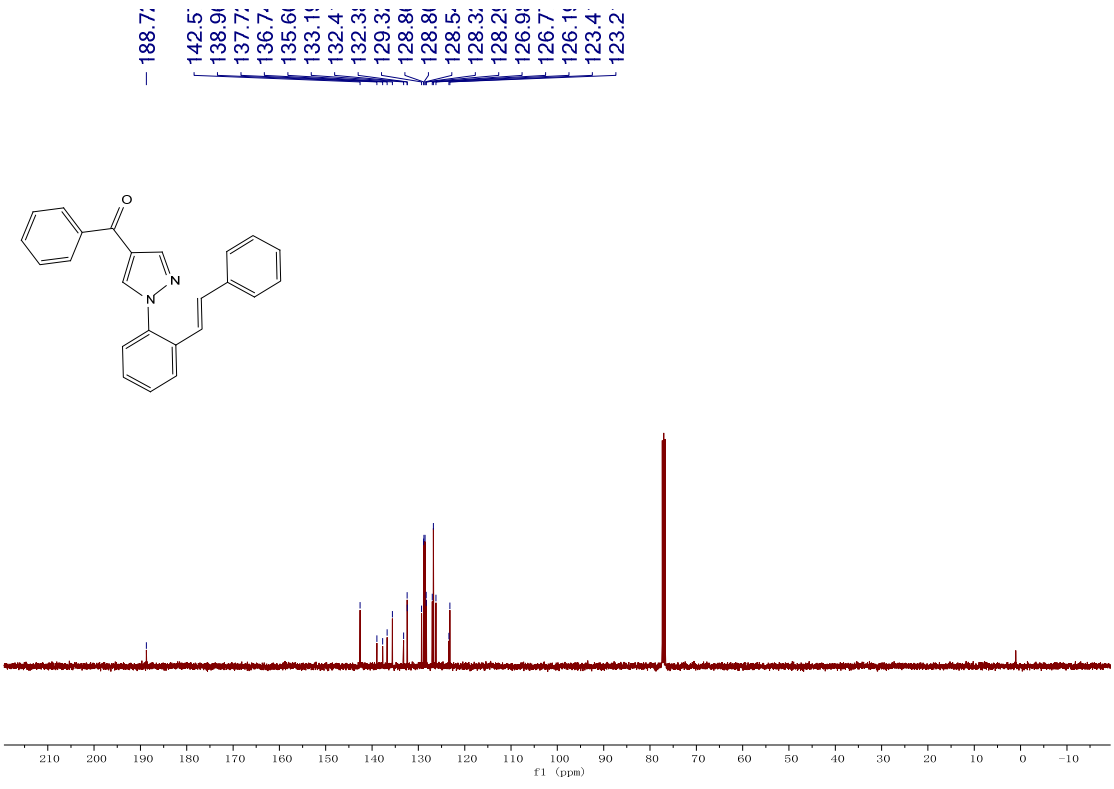
^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)



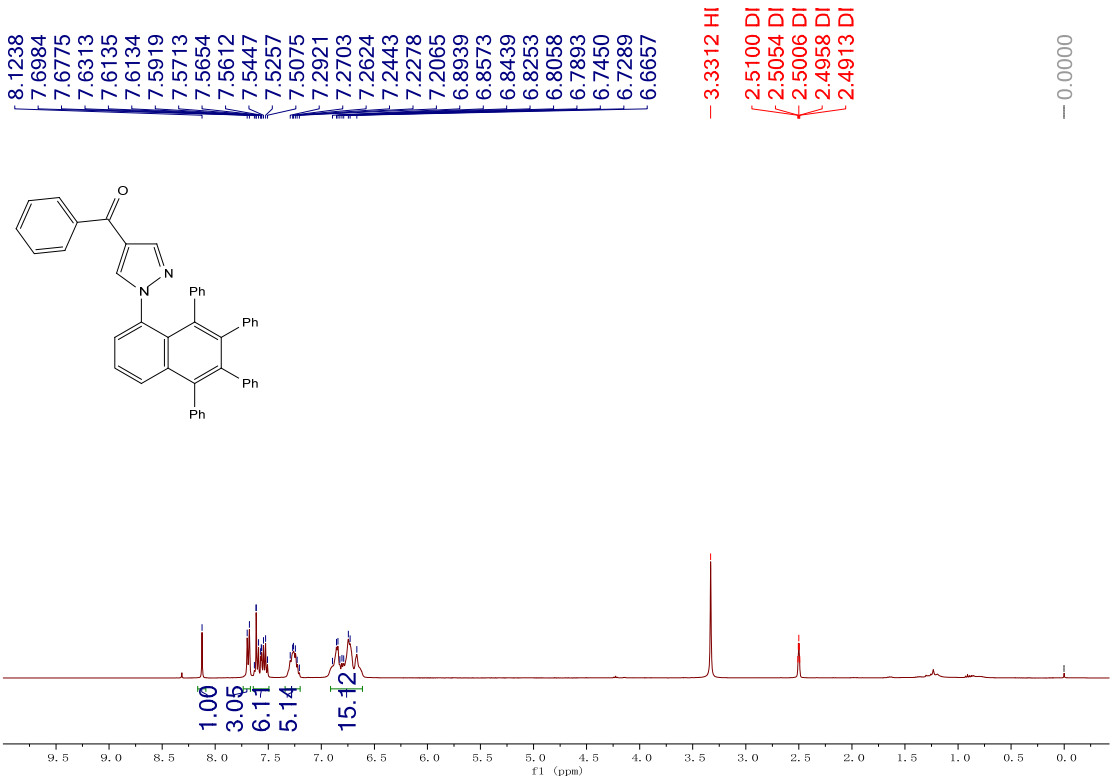
^{13}C NMR spectrum of **5i** (100 MHz, $CDCl_3$)



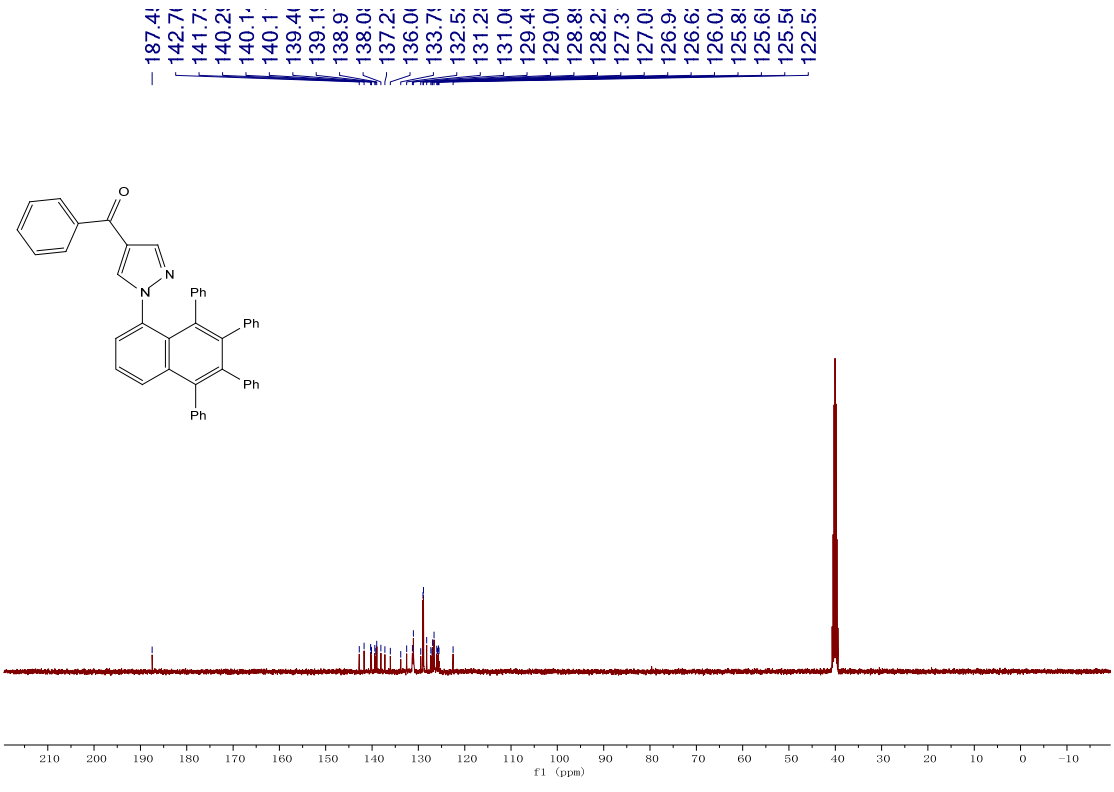
^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$)



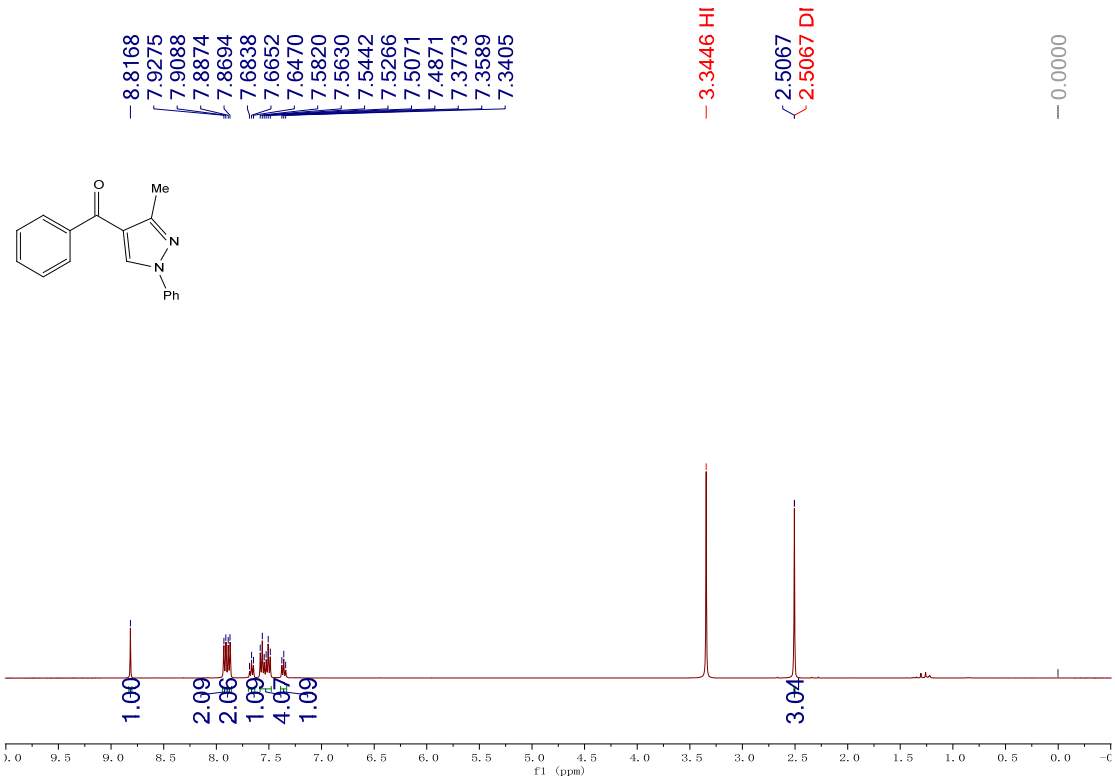
^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$)



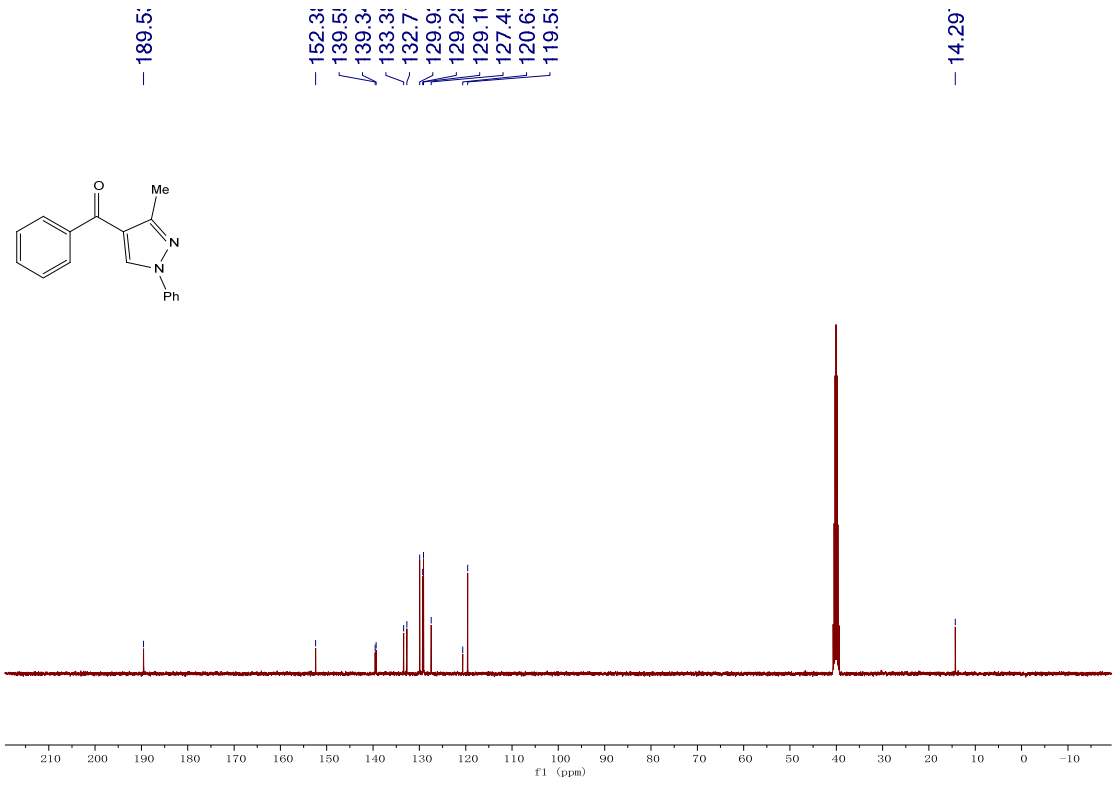
^{1}H NMR spectrum of **9** (400 MHz, DMSO-d_6)



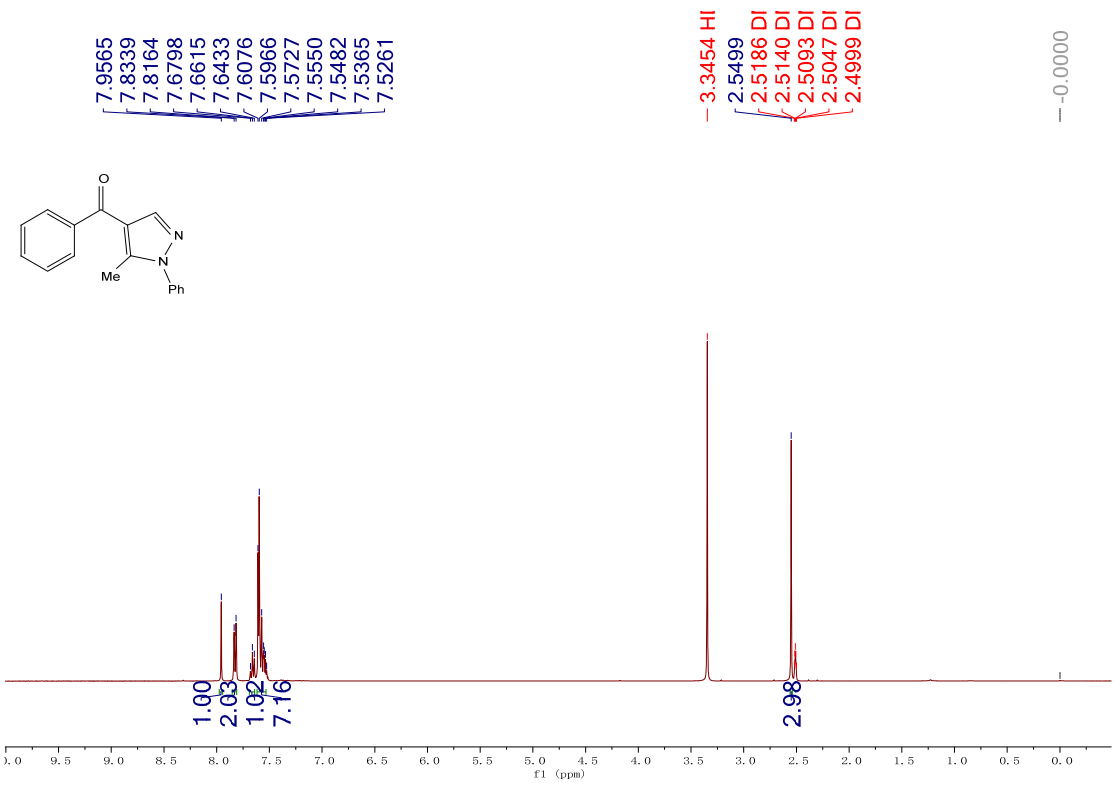
^{13}C NMR spectrum of **9** (100 MHz, DMSO-d_6)



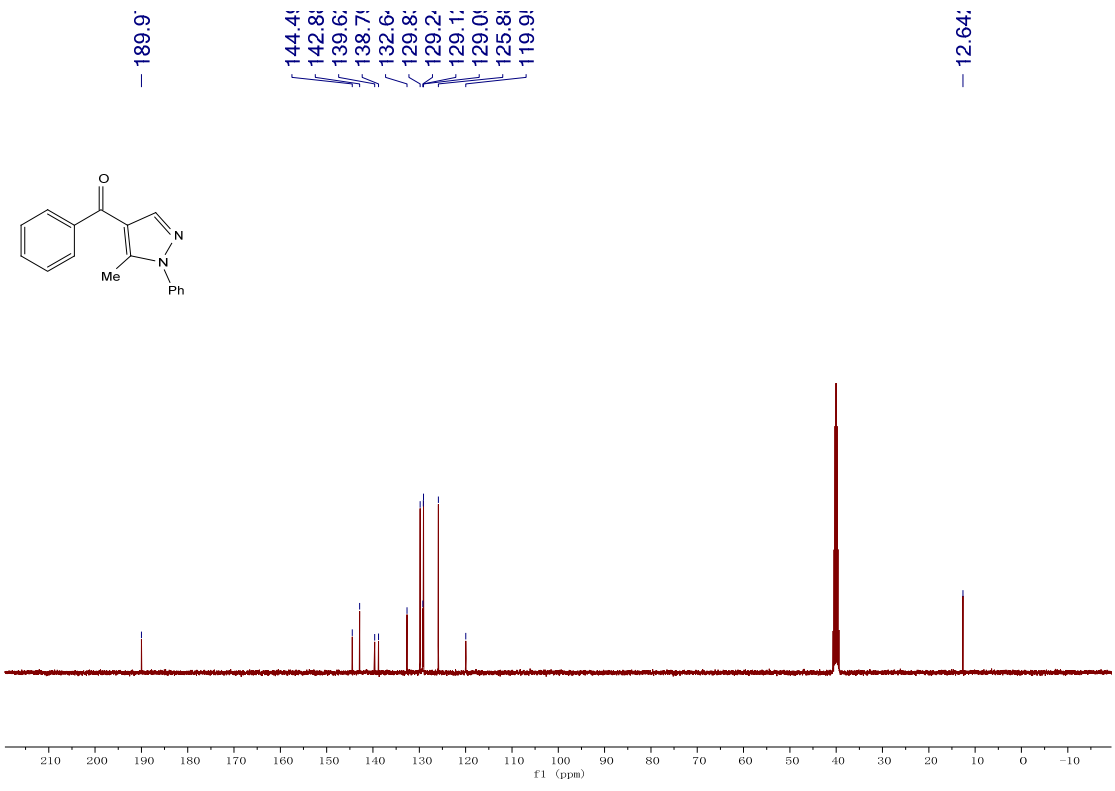
^{1}H NMR spectrum of **11a** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of **11a** (100 MHz, DMSO-d_6)



^{1}H NMR spectrum of **11a′** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of **11a′** (100 MHz, DMSO-d_6)