Supplementary Data

Base Promoted Direct C4-Arylation of 4-Substituted-pyrazolin-5-ones with Diaryliodonium Salts

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Part 1. General Information

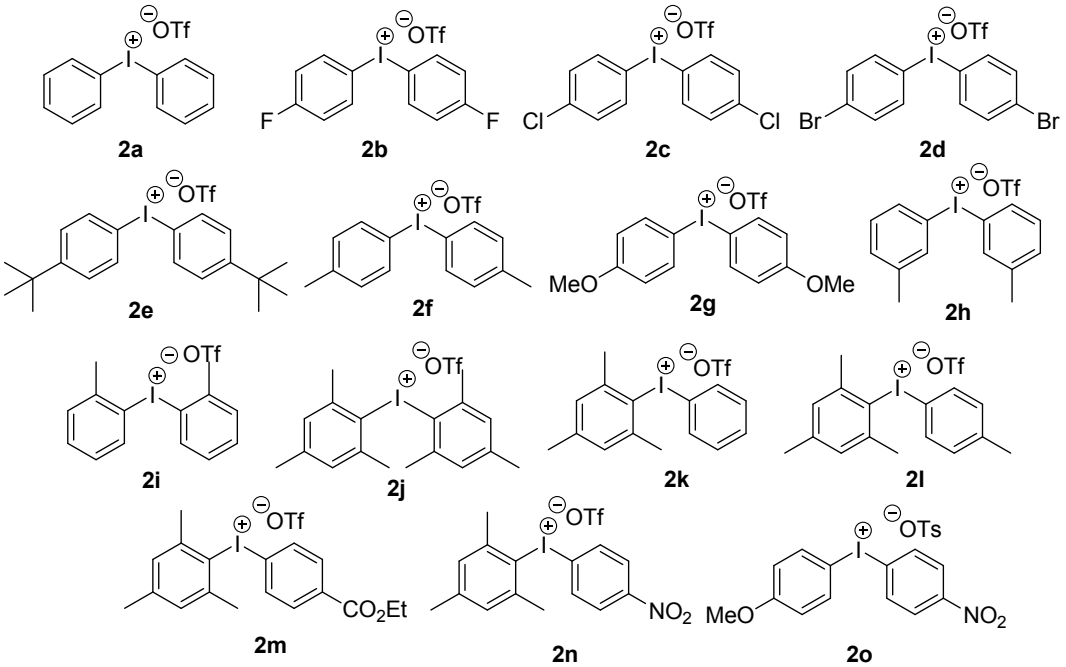
a. Methods:

NMR spectrum: ^{1}H and ^{13}C were recorded on a Bruker AVANCE 400 spectrometer, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

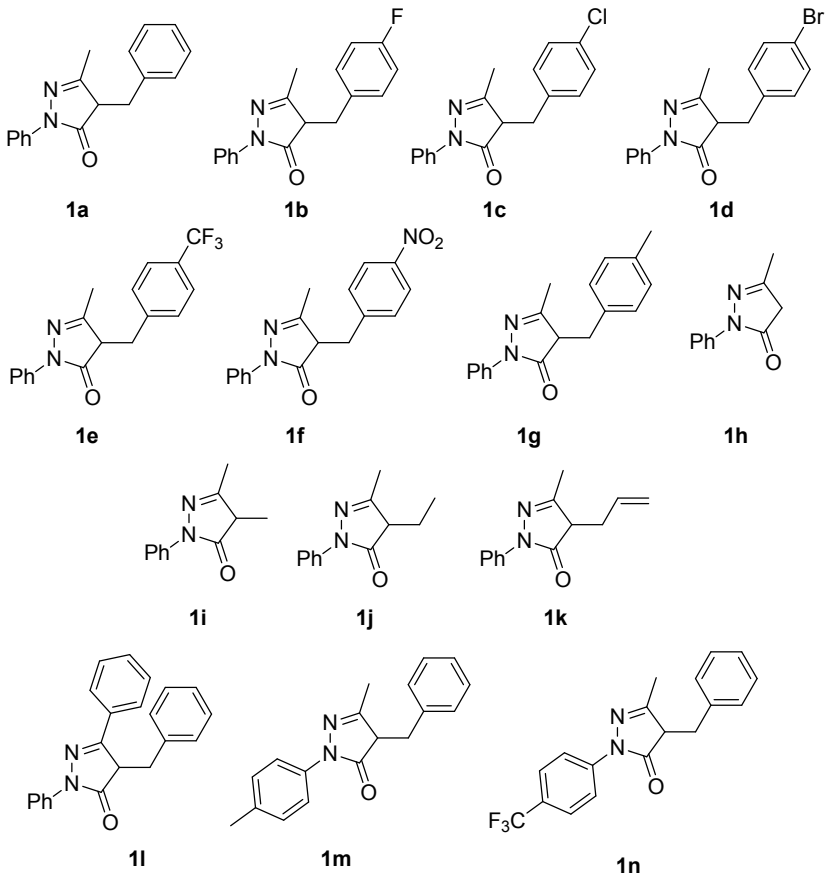
Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

Chromatography: Column chromatography was performed with silica gel (300-400 mesh ASTM).

b. Materials: All solvents were dried and/or distilled by standard methods. All reagents were purchased from commercial sources and used without further purification. All the diaryliodonium salts were synthesized according to the literature procedures. Salts **2a-2e**, **2j** were prepared from corresponding arenes and iodine in the presence of *m*CPBA and TfOH described by Olofsson and co-workers.[1] **2f** was prepared from toluene and 4-iodotoluene in the presence of *m*CPBA and TfOH described by Olofsson and co-workers.[1] **2k-2n** was prepared from corresponding aryl iodides and mesitylene in the presence of *m*CPBA and TfOH described by Olofsson and co-workers.[1] **2h** and **2i** were prepared from corresponding arylboronic acids and aryl iodides in the presence of *m*CPBA, $BF_3{\cdot}OEt_2$, and TfOH described by Onomura and co-workers.[2] **2g** was prepared from di(4-methoxyphenyl)iodonium tosylate in the presence of TfOH by in situ anion exchange described by Olofsson and co-workers..[3] **2o** was prepared from [Hydroxy-(4-tosyloxy)iodo]-4-nitrobenzene and anisole in 1:1 CH_2Cl_2:CF_3CH_2OH co-solvent described by Olofsson and co-workers.[4]



All 4-substituted pyrazolones **1** were prepared according to the literature and references therein.[4]

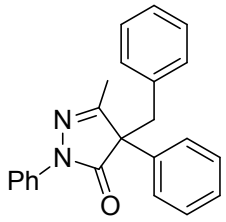


Part2. General procedure for the C4-arylation of 4-substitued-pyrazolin-5-ones with diaryliodonium salts (Table 2, 3)

A mixture of 4-substitued-pyrazolin-5-ones **1** (0.2 mmol, 1 equiv.), diaryliodonium salt **2** (0.4 mmol, 2 equiv.), DMAP (0.4 mmol, 2 equiv.), and toluene (3 mL) was taken in a 10 mL reaction tube at room temperature for 15-120 min under vigorous stirring. After completion of the reaction, as indicated by TLC, the reaction mixture was concentrated under reduced pressure, and the crude compound was purified by chromatography on a silica gel column (ethyl acetate/petroleum ether (1/10)) to afford the desired product **3**.

Part3. Characterization of the Products

4-benzyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3aa)



The product (64 mg, 94% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

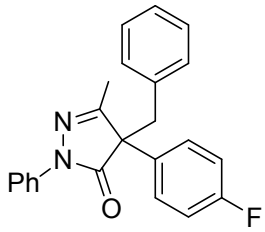
m.p. 109-112 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.48-7.34 (m, 7H), 7.24-7.16 (m, 6H), 3.84 (d, *J* = 13.2 Hz, 1H), 3.43 (d, *J* = 13.2 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 162.1, 137.6, 135.7, 134.4, 129.4, 129.2, 128.7, 128.5, 128.4 127.5, 126.5, 125.3, 119.5, 64.8, 38.9, 15.0.

HRMS (ESI+): Calcd. for $C_{23}H_{21}N_2O$ ($[M+H]^+$): 341.1654, Found: 341.1655.

4-benzyl-4-(4-fluorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (3ab)



The product (66 mg, 93% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

m.p. 89-92 °C.

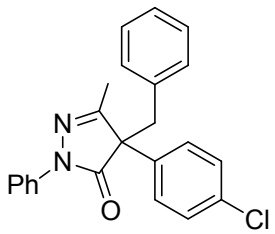
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.39-7.31 (m, 4H), 7.24-7.20 (m, 5H), 7.19-7.12 (m, 3H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 162.5 (d, *J* = 246.6 Hz), 161.8, 137.5, 134.1, 131.5 (d, *J* = 3.3 Hz), 129.2, 128.8, 128.5, 128.4 (d, *J* = 8.1 Hz), 127.6, 125.4, 119.5, 116.4 (d, *J* = 21.5 Hz), 64.1, 39.2, 15.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4.

HRMS (ESI+): Calcd. for $C_{23}H_{20}FN_2O$ ($[M+H]^+$): 359.1560, Found: 359.1553.

4-benzyl-4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (3ac)



The product (64 mg, 85% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

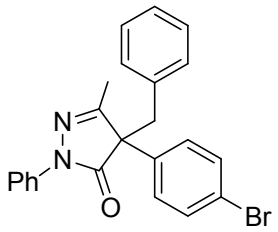
m.p. 96-98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.60 (m, 2H), 7.41-7.37 (m, 2H), 7.35-7.32 (m, 2H), 7.27-7.23 (m, 2H), 7.21-7.12 (m, 6H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.33 (d, *J* = 13.2 Hz, 1H) 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 161.6, 137.4, 134.4, 134.2, 134.0, 129.6, 129.2, 128.8, 128.6, 128.0, 127.6, 125.4, 119.5, 64.2, 39.0, 15.0.

HRMS (ESI+): Calcd. for $C_{23}H_{20}ClN_2O$ ($[M+H]^+$): 375.1264, Found: 375.1258.

4-benzyl-4-(4-bromophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (3ad)



The product (79 mg, 95% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

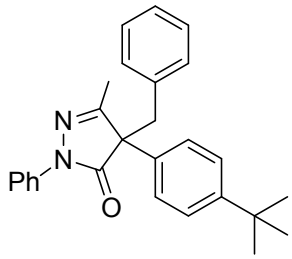
m.p. 112-115 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.57-7.54 (m, 2H), 7.38-7.31 (m, 2H), 7.24-7.14 (m, 8H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.34 (d, *J* = 13.2 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 161.5, 137.4, 134.8, 134.0, 132.5, 129.2, 128.8, 128.5, 128.3, 127.6, 125.4, 122.6, 119.5, 64.3, 39.0, 15.0.

HRMS (ESI+): Calcd. for $C_{23}H_{20}BrN_2O$ ($[M+H]^+$): 419.0759, Found: 419.0751.

4-benzyl-4-(4-(tert-butyl)phenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (3ae)



The product (74 mg, 93% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

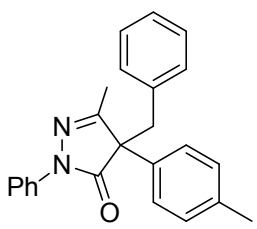
m.p. 145-147 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.34-7.29 (m, 2H), 7.25-7.22 (m, 2H), 7.19-7.11 (m, 6H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.36 (d, *J* = 13.2 Hz, 1H), 2.09 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 162.3, 151.3, 137.7, 134.6, 132.7, 129.2, 128.7, 128.5, 127.5, 126.4, 126.2, 125.2, 119.5, 64.5, 39.0, 34.6, 31.3, 15.1.

HRMS (ESI+): Calcd. for $C_{27}H_{29}N_2O$ ($[M+H]^+$): 397.2280, Found: 397.2272.

4-benzyl-3-methyl-1-phenyl-4-(p-tolyl)-1H-pyrazol-5(4H)-one (3af)



The product (67 mg, 95% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

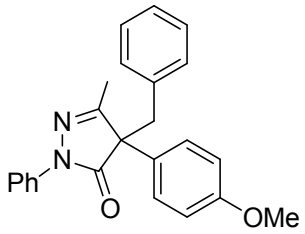
m.p. 86-88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.34-7.29 (m, 2H), 7.24-7.11 (m, 10H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 2.35 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 162.2, 138.2, 137.7, 134.6, 132.7, 130.1, 129.2, 128.7, 128.5, 127.5, 126.4, 125.2, 119.5, 64.5, 38.9, 21.1, 15.0.

HRMS (ESI+): Calcd. for $C_{24}H_{23}N_2O$ ($[M+H]^+$): 355.1810, Found: 355.1805.

4-benzyl-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (3ag)



The product (61 mg, 82% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

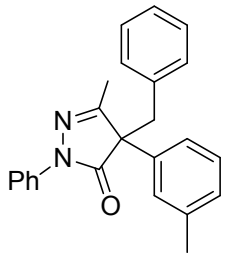
m.p. 90-93 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.34-7.29 (m, 2H), 7.25-7.11 (m, 8H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 3.76 (d, *J* = 13.2 Hz, 1H), 3.34 (d, *J* = 13.2 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 162.3, 159.5, 137.6, 134.5, 129.2, 128.7, 128.5, 127.7, 127.47, 125.2, 119.5, 114.8, 64.1, 55.4, 39.1, 15.0.

HRMS (ESI+): Calcd. for $C_{24}H_{23}N_2O_2$ ($[M+H]^+$): 371.1760, Found: 371.1752.

4-benzyl-3-methyl-1-phenyl-4-(m-tolyl)-1H-pyrazol-5(4H)-one (3ah)



The product (65 mg, 92% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

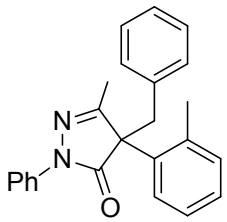
m.p. 89-91 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 2H), 7.35-7.28 (m, 3H), 7.20-7.09 (m, 9H), 3.79 (d, *J* = 12.8 Hz, 1H), 3.37 (d, *J* = 12.8 Hz, 1H), 2.37 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 162.2, 139.2, 137.6, 135.6, 134.5, 129.2, 129.1, 128.7, 128.5, 127.5, 127.1, 125.2, 123.5, 119.5, 64.7, 38.9, 21.7, 15.0.

HRMS (ESI+): Calcd. for $C_{24}H_{23}N_2O$ ([M+H]$^+$): 355.1810, Found: 355.1803.

4-benzyl-3-methyl-1-phenyl-4-(o-tolyl)-1H-pyrazol-5(4H)-one (3ai)



The product (14 mg, 20% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

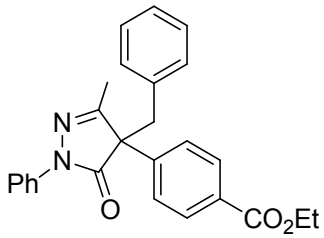
m.p. 140-142 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.41-7.32 (m, 3H), 7.31-7.25 (m, 3H), 7.19-7.09 (m, 7H), 3.64 (d, *J* = 12.0 Hz, 1H), 3.54 (d, *J* = 12.4 Hz, 1H), 2.05 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 160.1, 137.3, 137.2, 133.6, 133.2, 132.2, 129.73, 128.6, 128.5, 128.1, 127.6, 127.2, 126.7, 125.3, 119.7, 64.1, 40.6, 19.3, 14.6.

HRMS (ESI+): Calcd. for $C_{24}H_{23}N_2O$ ([M+H]$^+$): 355.1810, Found: 355.1807.

ethyl 4-(4-benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)benzoate (3ak)



The product (65 mg, 79% yield) as a yellow solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

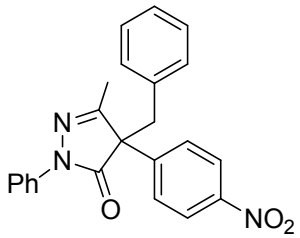
m.p. 142-145 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35-7.30 (m, 2H), 7.20-7.13 (m, 6H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.08 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 166.0, 161.4, 140.4, 137.4, 134.0, 130.5, 130.5, 129.2, 128.8, 128.5, 127.7, 126.7, 125.5, 119.5, 64.8, 61.2, 39.0, 15.0, 14.5.

HRMS (ESI+): Calcd. for $C_{26}H_{25}N_2O_3$ ([M+H]$^+$): 413.1865, Found: 413.1858.

4-benzyl-3-methyl-4-(4-nitrophenyl)-1-phenyl-1H-pyrazol-5(4H)-one (3al)



The product (34 mg, 44% yield) as a yellow solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

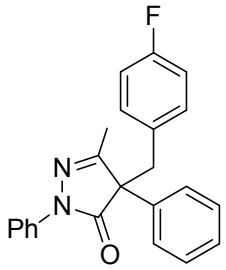
m.p. 136-138 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.39-7.34 (m, 2H), 7.25-7.18 (m, 6H), 3.85 (d, *J* = 13.2 Hz, 1H), 3.44 (d, *J* = 13.2 Hz, 1H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 160.7, 147.7, 142.7, 137.2, 133.4, 129.2, 128.8, 128.6, 127.9, 127.8, 125.7, 124.5, 119.5, 64.6, 39.2, 15.1.

HRMS (ESI+): Calcd. for $C_{23}H_{30}N_3O_3$ ($[M+H]^+$): 386.1505, Found: 386.1497.

4-(4-fluorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3ba)



The product (70 mg, 98% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

m.p. 87-90 °C.

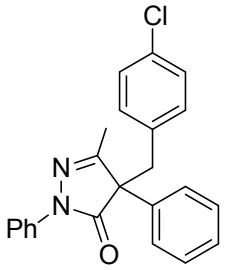
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.48-7.31 (m, 7H), 7.21-7.17 (m, 3H), 6.95-6.89 (m, 2H), 3.78 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 162.1 (d, *J* = 244.7 Hz), 161.9, 137.5, 135.5, 130.9 (d, *J* = 8.0 Hz), 130.2 (d, *J* = 3.3 Hz), 129.4, 128.8, 128.4, 126.5, 125.4, 119.4, 115.4 (d, *J* = 21.2 Hz), 64.8, 38.0, 15.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9.

HRMS (ESI+): Calcd. for $C_{23}H_{20}FN_2O$ ($[M+H]^+$): 359.1560, Found: 359.1554.

4-(4-chlorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3ca)



The product (68 mg, 91% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

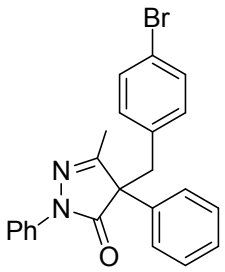
m.p. 93-96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.43-7.27 (m, 7H), 7.18-7.10 (m, 5H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.34 (d, *J* = 13.2 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 161.8, 137.5, 135.4, 133.4, 133.0, 130.6, 129.5, 128.8, 128.68, 128.5, 126.4, 125.4, 119.4, 64.6, 38.2, 15.0.

HRMS (ESI+): Calcd. for $C_{23}H_{20}ClN_2O$ ($[M+H]^+$): 375.1264, Found: 375.1257.

4-(4-bromobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3da)



The product (79 mg, 95% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

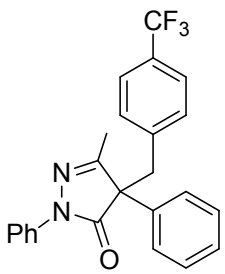
m.p. 124-127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.43-7.27 (m, 9H), 7.18-7.14 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 3.73 (d, *J* = 13.2 Hz, 1H), 3.33 (d, *J* = 13.2 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 161.8, 137.5, 135.4, 133.5, 131.6, 131.0, 129.5, 128.8, 128.5, 126.4, 125.4, 121.6, 119.4, 64.5, 38.2, 15.0.

HRMS (ESI+): Calcd. for $C_{23}H_{20}BrN_2O$ ($[M+H]^+$): 419.0759, Found: 419.0751.

3-methyl-1,4-diphenyl-4-(4-(trifluoromethyl)benzyl)-1H-pyrazol-5(4H)-one (3ea)



The product (77 mg, 94% yield) as a white solid was purified with silica gel chromatography

(EtOAc/*n*-hexane = 1/10). This compound is unknown.

m.p. 95-97 °C.

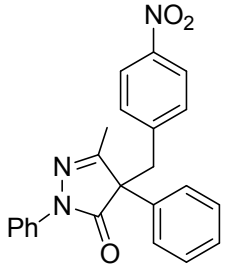
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.51-7.33 (m, 11H), 7.22-7.18 (m, 1H), 3.87 (d, *J* = 13.2 Hz, 1H), 3.48 (d, *J* = 13.2 Hz, 1H), 2.13 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 161.7, 138.7, 137.3, 135.2, 129.8 (q, $J_{C\text{-}F}$ = 32.3 Hz), 129.7, 129.5, 128.8, 128.6, 126.4, 125.6, 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.0 (q, $J_{C\text{-}F}$ = 270.4 Hz), 119.5, 64.5, 38.5, 15.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.65.

HRMS (ESI+): Calcd. for $C_{24}H_{20}F_3N_2O$ ($[M+H]^+$): 409.1528, Found: 409.1521.

3-methyl-4-(4-nitrobenzyl)-1,4-diphenyl-1H-pyrazol-5(4H)-one (3fa)



The product (71 mg, 92% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

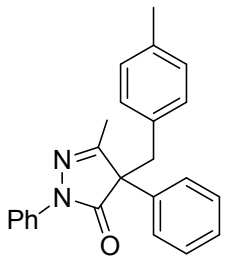
m.p. 147-149 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.46-7.29 (m, 9H), 7.19-7.14 (m, 1H), 3.87 (d, *J* = 13.2 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 161.4, 147.4, 142.2, 137.3, 134.9, 130.3, 129.6, 128.9, 128.7, 126.3, 125.6, 123.7, 119.1, 64.4, 38.4, 15.0.

HRMS (ESI+): Calcd. for $C_{23}H_{20}N_3O_3$ ($[M+H]^+$): 386.1505, Found: 386.1498.

3-methyl-4-(4-methylbenzyl)-1,4-diphenyl-1H-pyrazol-5(4H)-one (3ga)



The product (62 mg, 88% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

m.p. 116-118 °C.

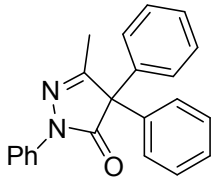
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 2H), 7.43-7.38 (m, 2H), 7.36-7.29 (m, 5H), 7.16-7.12 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 3.77 (d, *J* = 13.2 Hz, 1H), 3.34(d, *J* =

13.2 Hz, 1H), 2.23 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 162.2, 137.7, 137.1, 135.8, 131.3, 129.4, 129.2, 129.1, 128.7, 128.3, 126.5, 125.2, 119.5, 64.8, 38.6, 21.1, 15.0.

HRMS (ESI+): Calcd. for $C_{24}H_{23}N_2O$ ($[M+H]^+$): 355.1810, Found: 355.1803.

3-methyl-1,4,4-triphenyl-1H-pyrazol-5(4H)-one (3ha)



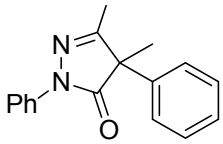
The product (47 mg, 72% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.41-7.30 (m, 8H), 7.24-7.15 (m, 5H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 161.8, 138.1, 137.2, 129.1, 128.9, 128.5, 128.2, 125.2, 118.9, 69.0, 15.5.

HRMS (ESI+): Calcd. for $C_{22}H_{18}N_2ONa$ ($[M+Na]^+$): 349.1318, Found: 265.1337.

3,4-dimethyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3ia)



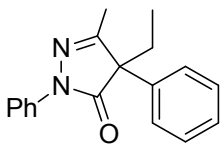
The product (48 mg, 91% yield) as a yellow oil was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.95 (m, 2H), 7.43-7.29 (m, 5H), 7.22-7.16 (m, 3H), 2.03 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 164.3, 138.2, 135.8, 129.3, 128.9, 128.2, 126.2, 125.0, 118.8 58.5, 18.5, 13.4.

HRMS (ESI+): Calcd. for $C_{17}H_{17}N_2O$ ($[M+H]^+$): 265.1341, Found: 265.1338.

4-ethyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3ja)



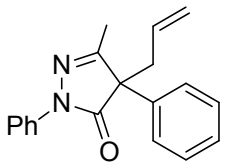
The product (50 mg, 90% yield) as a yellow oil was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.44-7.28 (m, 5H), 7.25-7.16 (m, 3H), 2.51-2.41 (m, 1H), 2.17-2.07 (m, 1H), 2.02 (s, 3H), 0.89 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 162.9, 138.1, 135.9, 129.3, 128.9, 128.2, 126.4, 125.1, 118.9, 63.9, 25.6, 14.2, 8.6.

HRMS (ESI+): Calcd. for $C_{18}H_{19}N_2O$ ($[M+H]^+$): 279.1497, Found: 279.1494.

4-allyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (3ka)



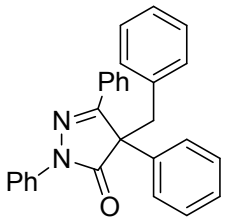
The product (48 mg, 82% yield) as a colorless oil was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.42-7.30 (m, 5H), 7.25-7.16 (m, 3H), 5.63-5.51 (m, 1H), 5.26 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 3.18, (dd, *J* = 6.8, 13.6 Hz, 1H), 2.85 (dd, *J* = 7.6, 13.2 Hz, 1H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 162.4, 138.0, 135.3, 130.7, 129.3, 128.9, 128.3, 126.4, 125.1, 120.3, 118.9, 63.1, 37.0, 14.6.

HRMS (ESI+): Calcd. for $C_{19}H_{19}N_2O$ ($[M+H]^+$): 291.1497, Found: 291.1491.

4-benzyl-1,3,4-triphenyl-1H-pyrazol-5(4H)-one (3ka)



m.p. 163-165 ^{o}C.

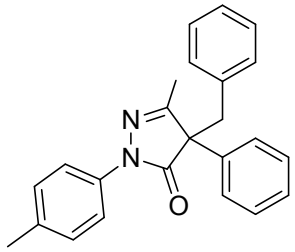
The product (48 mg, 82% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.60-7.57 (m, 2H), 7.43-7.30 (m, 10H), 7.19-7.14 (m, 1H), 7.11-6.99 (3H), 6.85-6.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 159.6, 137.7, 136.6, 134.2, 130.9, 130.3, 129.6, 129.5, 128.8, 128.7, 128.4, 128.1, 127.3, 127.0, 126.5, 125.5, 119.7, 63.6, 40.0.

HRMS (ESI+): Calcd. for $C_{28}H_{23}N_2O$ ($[M+H]^+$): 403.1810, Found: 403.1802.

4-benzyl-3-methyl-4-phenyl-1-(p-tolyl)-1H-pyrazol-5(4H)-one (3ma)



The product (59 mg, 83% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

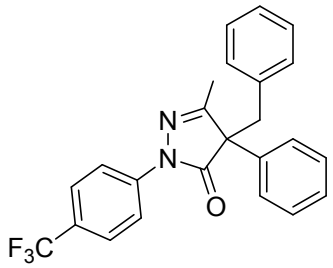
m.p. 101-102 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.45-7.39 (m, 2H), 7.38-7.29 (m, 3H), 7.22-7.17 (m, 5H), 7.14-7.11 (m, 2H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.38 (d, *J* = 13.2 Hz, 1H), 2.32 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 161.9, 135.8, 135.1, 135.0, 134.5, 129.4, 129.3, 128.5, 128.3, 127.5, 126.5, 119.7, 64.6, 38.9, 21.0, 15.0.

HRMS (ESI+): Calcd. for $C_{24}H_{23}N_2O$ ($[M+H]^+$): 355.1810, Found: 355.1807.

4-benzyl-3-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5(4H)-one (3na)



The product (78 mg, 95% yield) as a white solid was purified with silica gel chromatography (EtOAc/*n*-hexane = 1/10). This compound is unknown.

m.p. 123-125 °C.

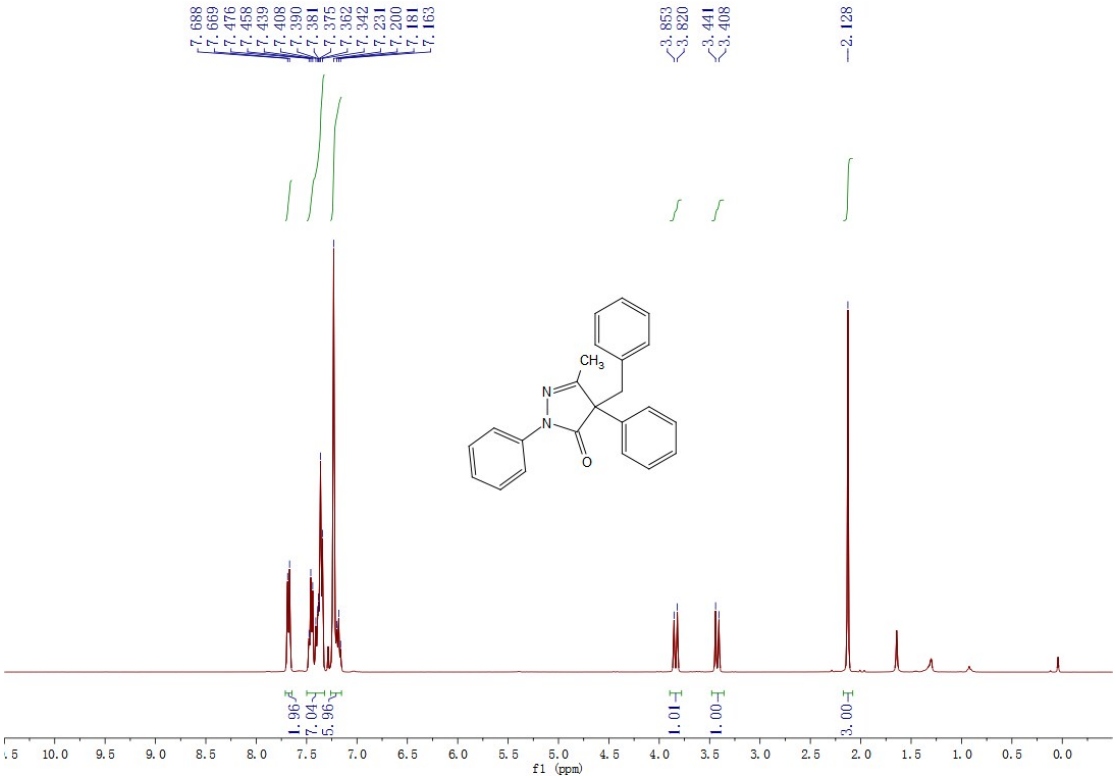
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.46-7.35 (m, 3H), 7.32-7.29 (m, 2H), 7.22-7.15 (m, 5H), 3.81 (d, *J* = 13.2 Hz, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 162.8, 140.3, 135.3, 134.1, 129.5, 129.1, 128.55, 128.53, 127.64, 127.6, 126.6 (q, $J_{C\text{-}F}$ = 32.4 Hz), 126.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 122.6 (q, $J_{C\text{-}F}$ = 270.0 Hz), 118.5, 65.0, 39.0, 15.0.

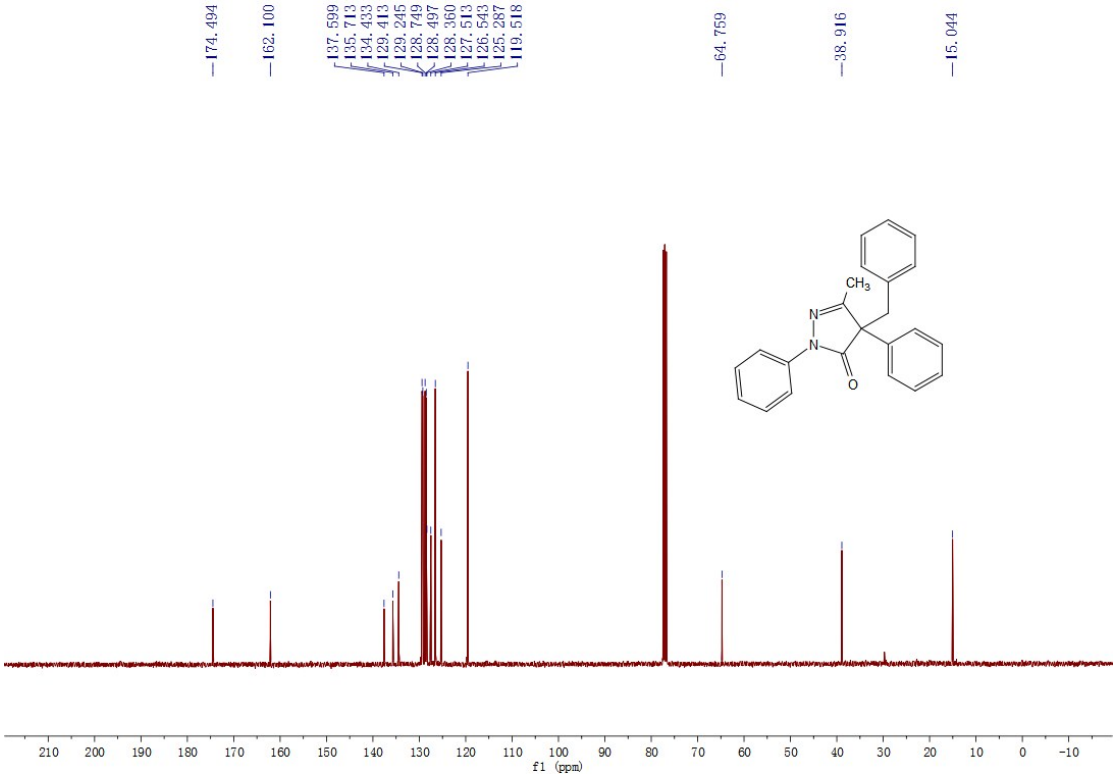
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.14.

HRMS (ESI+): Calcd. for $C_{24}H_{20}F_3N_2O$ ($[M+H]^+$): 409.1528, Found: 409.1521.

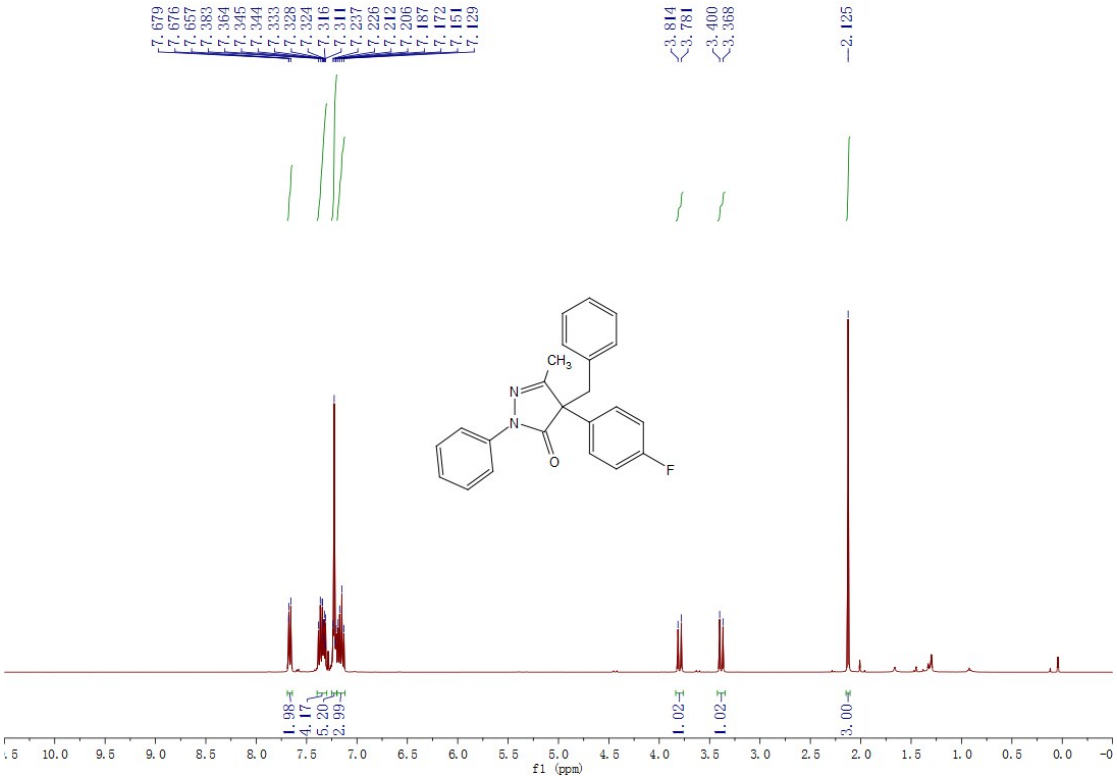
^{1}H NMR of 4-benzyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3aa)**



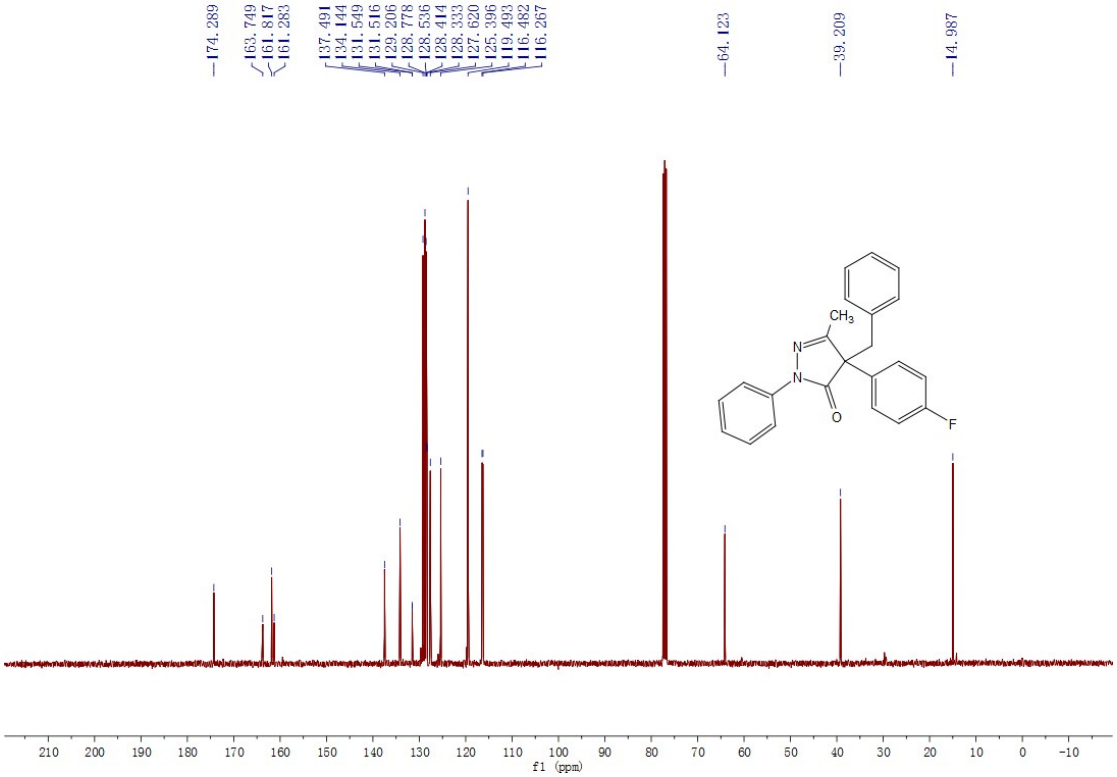
^{13}C NMR of 4-benzyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3aa)**



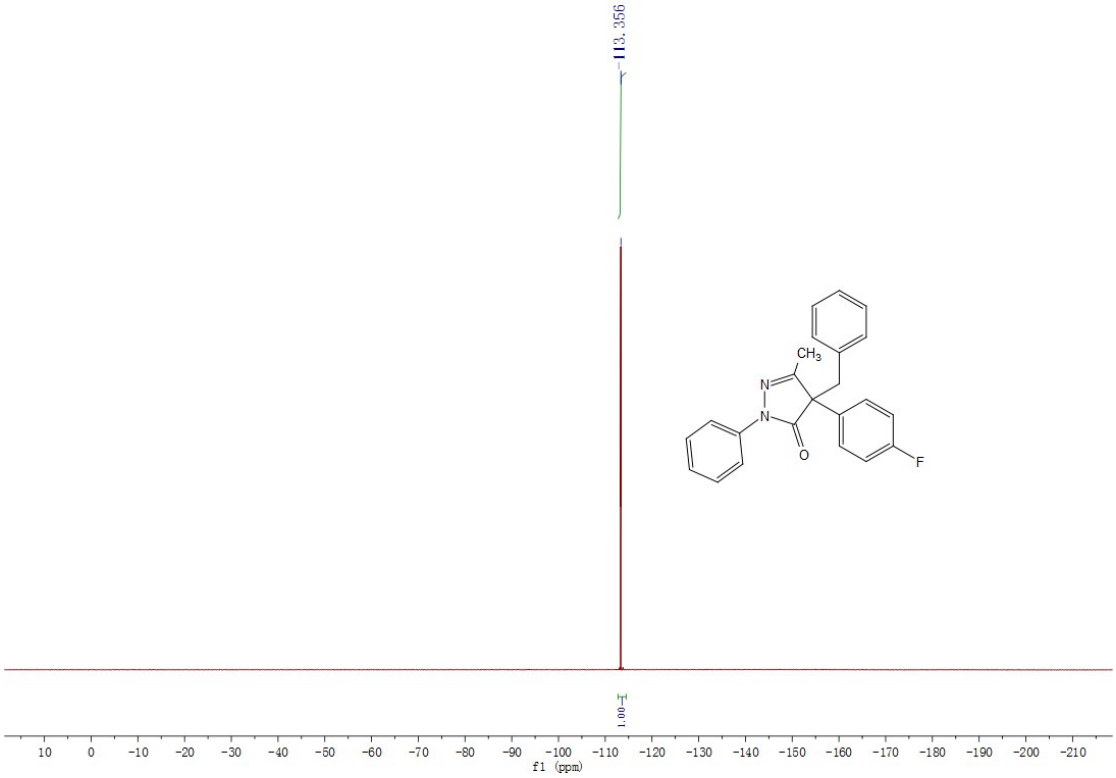
^{1}H NMR of 4-benzyl-4-(4-fluorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ab)**



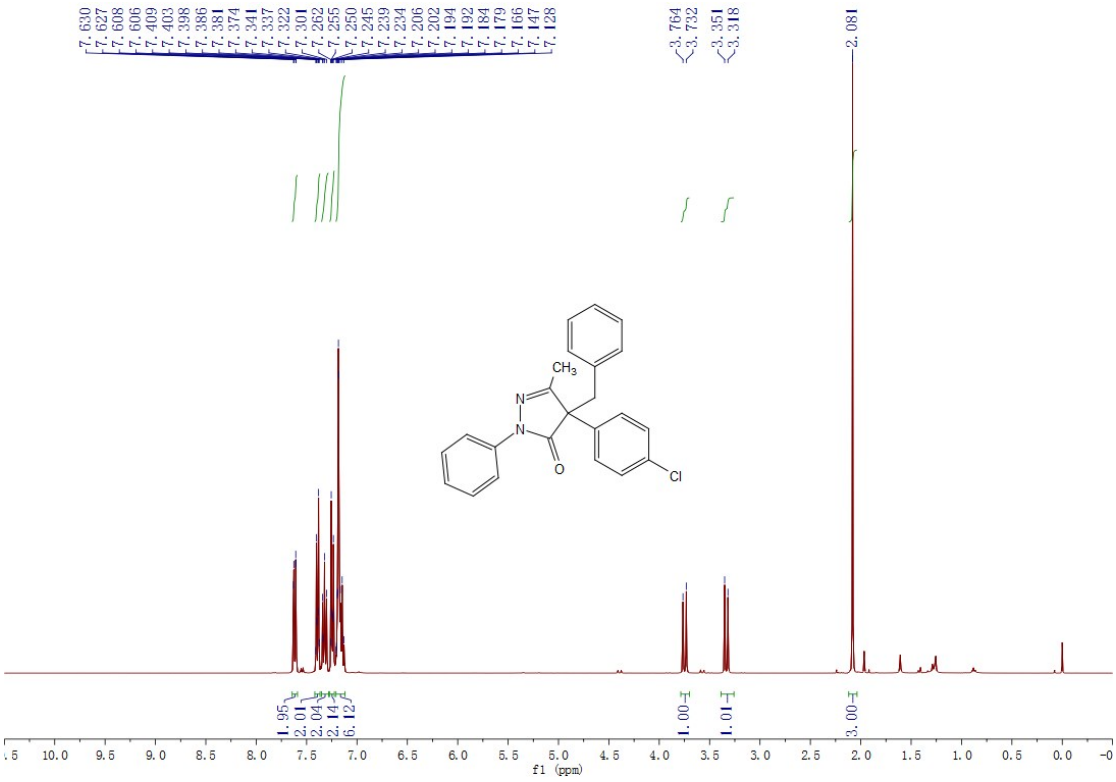
^{13}C NMR of 4-benzyl-4-(4-fluorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ab)**



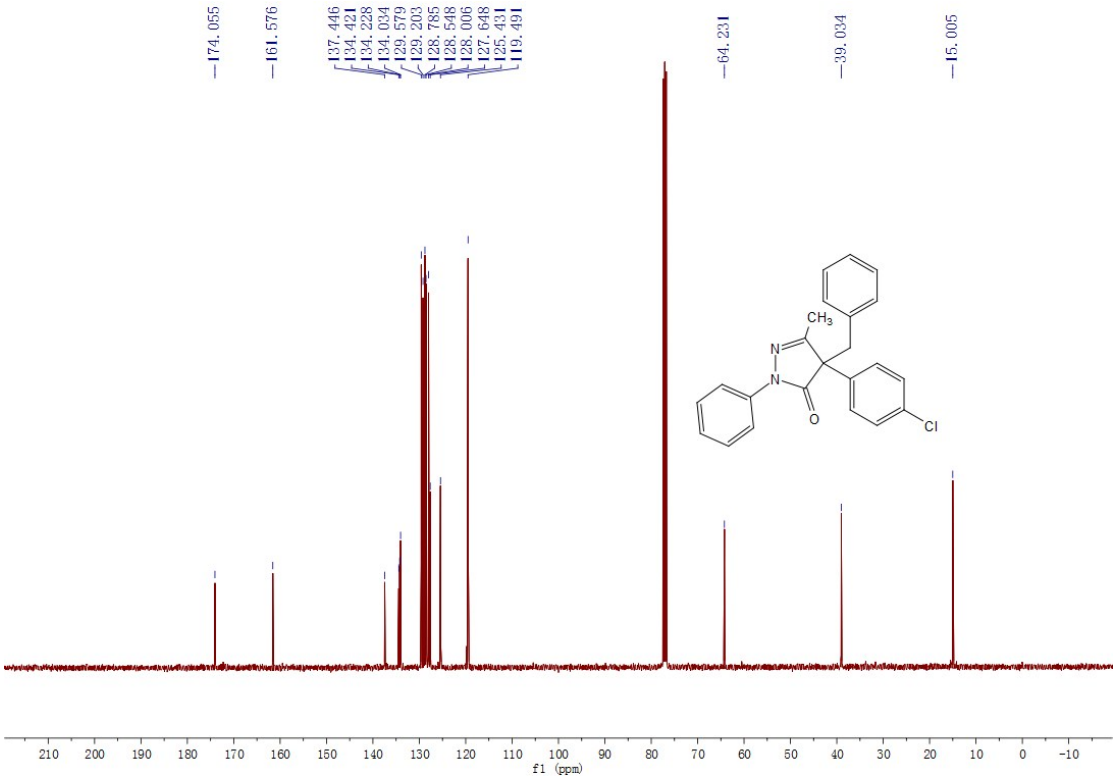
^{19}F NMR of 4-benzyl-4-(4-fluorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ab)**



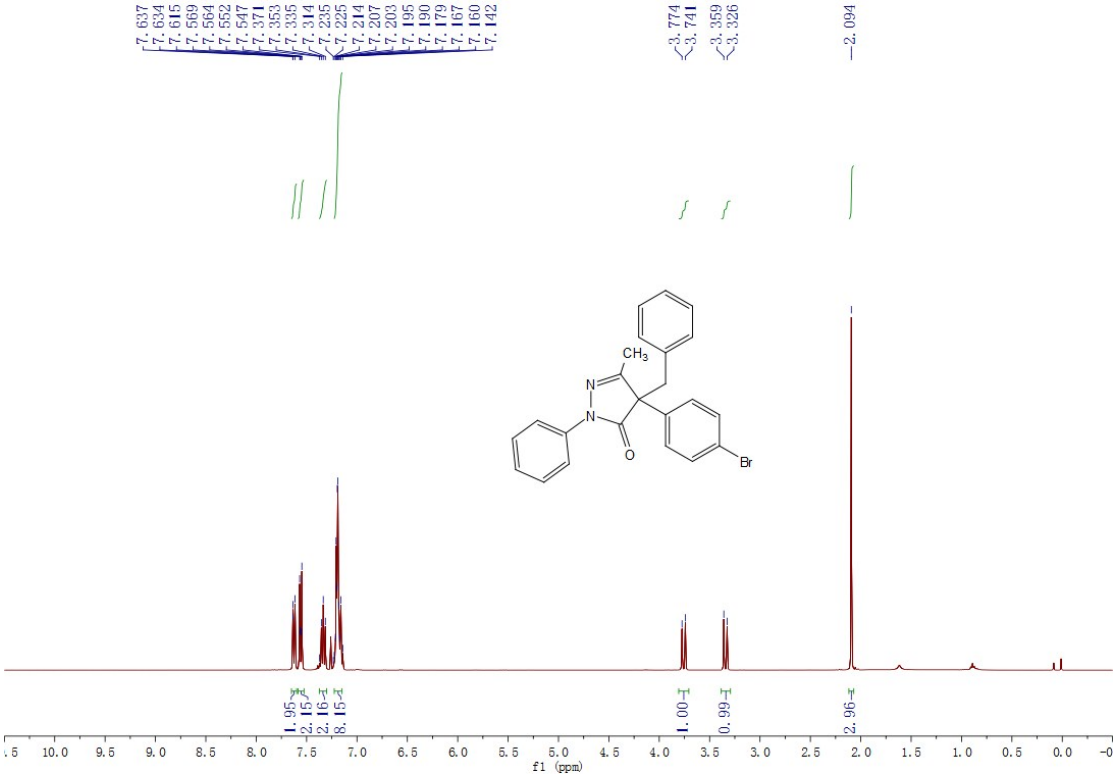
^{1}H NMR of 4-benzyl-4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ac)**



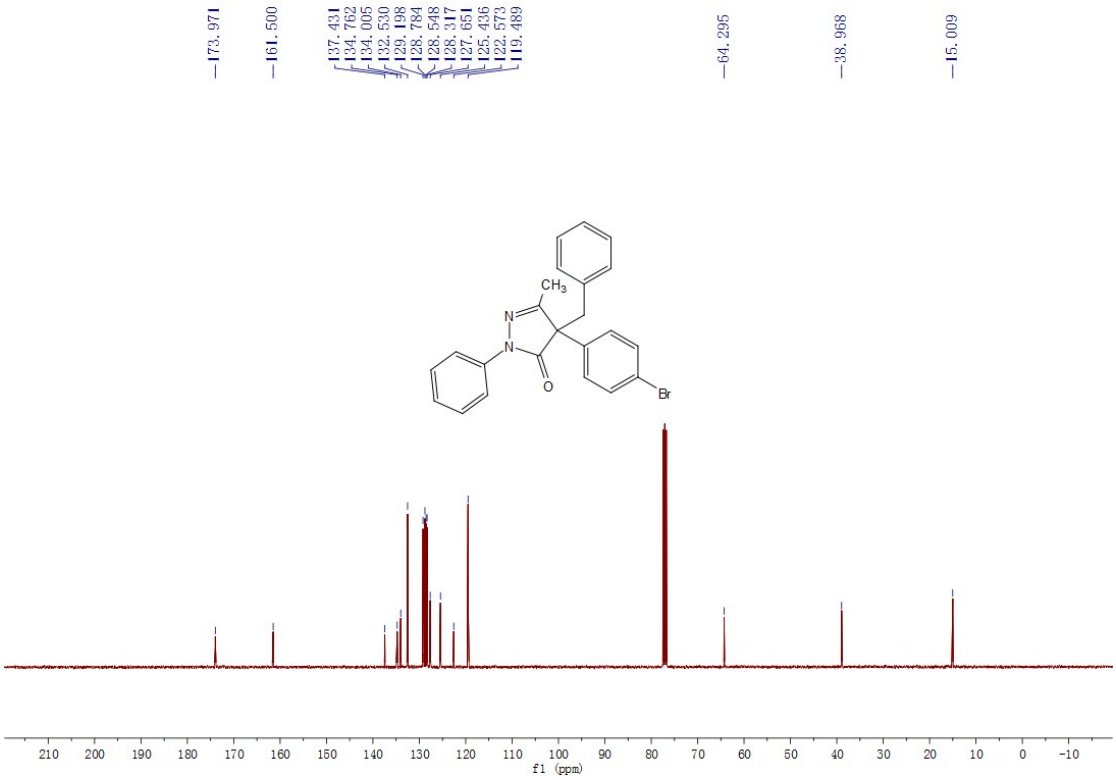
^{13}C NMR of 4-benzyl-4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ac)**



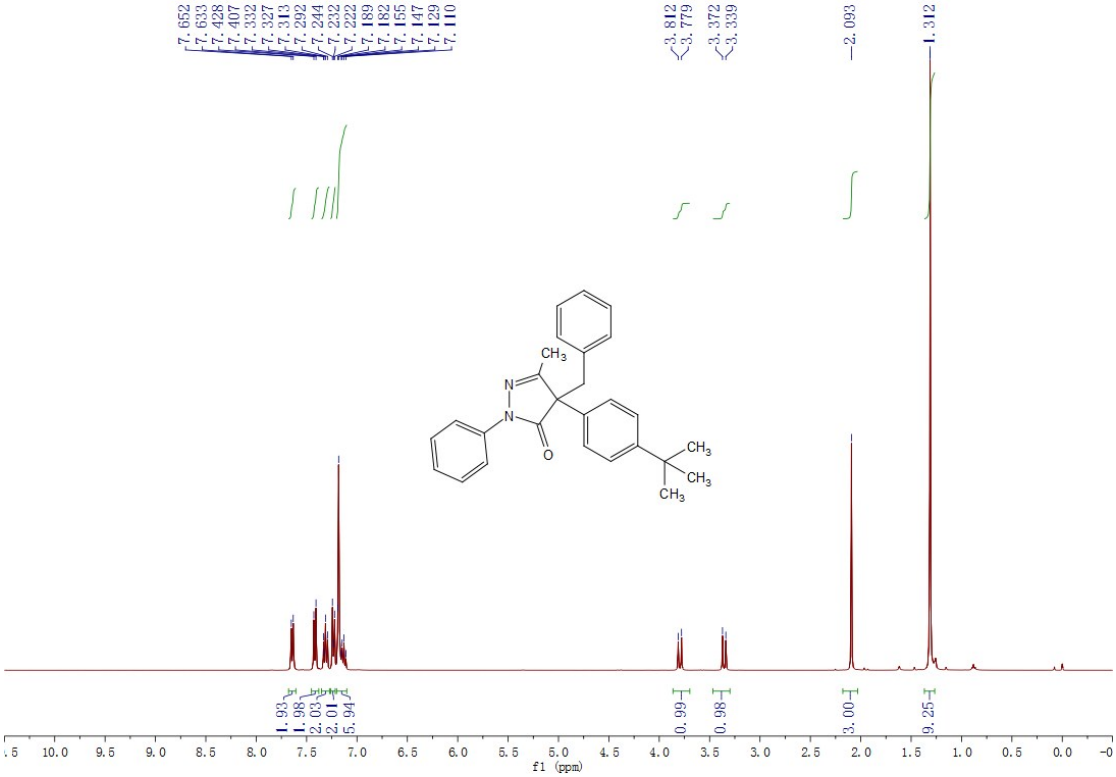
^{1}H NMR of 4-benzyl-4-(4-bromophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ad)**



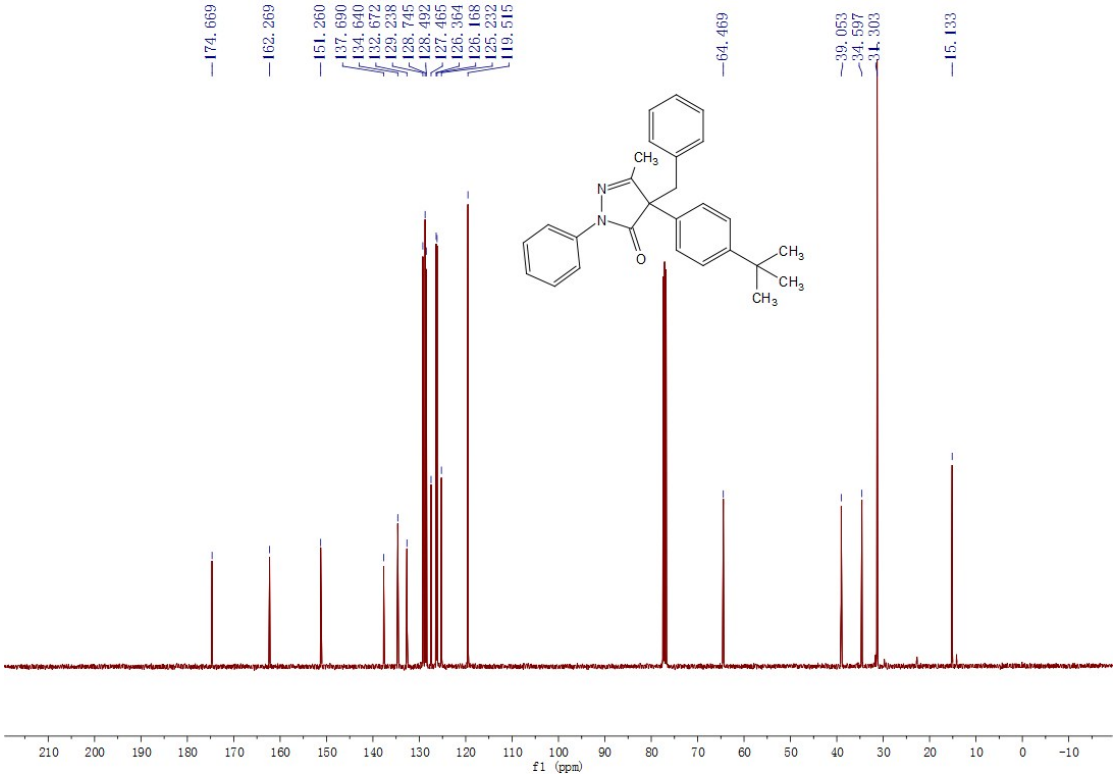
^{13}C NMR of 4-benzyl-4-(4-bromophenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ad)**



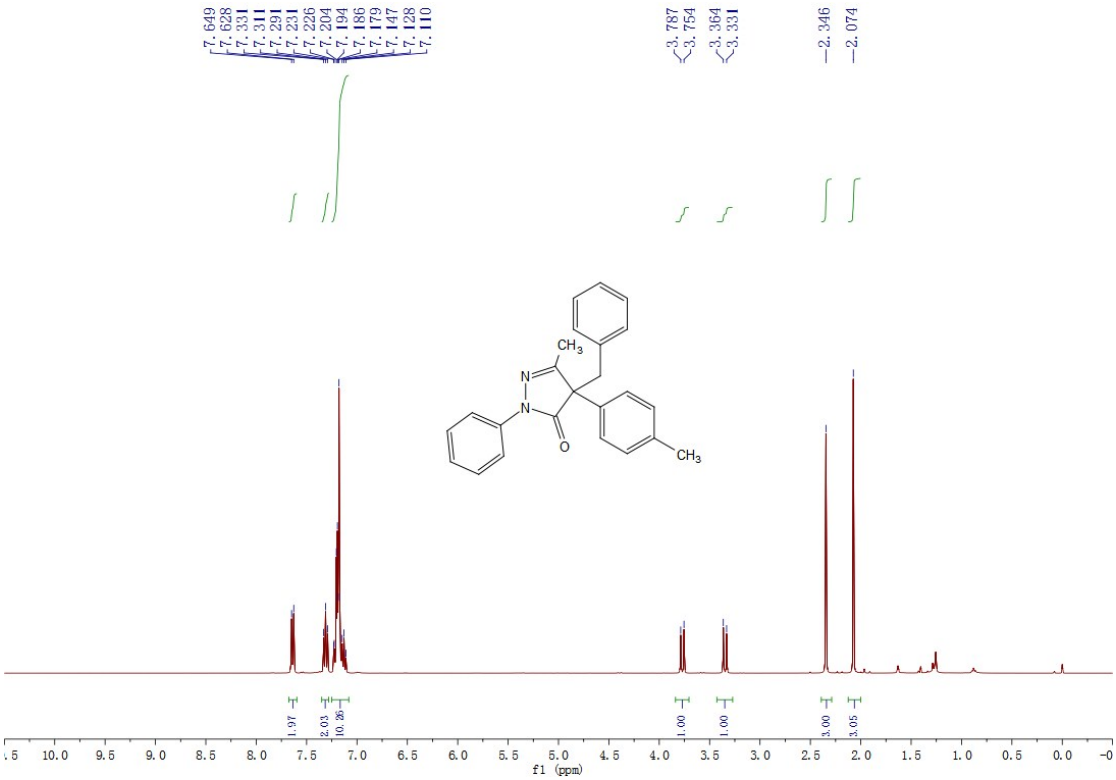
^{1}H NMR of 4-benzyl-4-(4-(tert-butyl)phenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ae)**



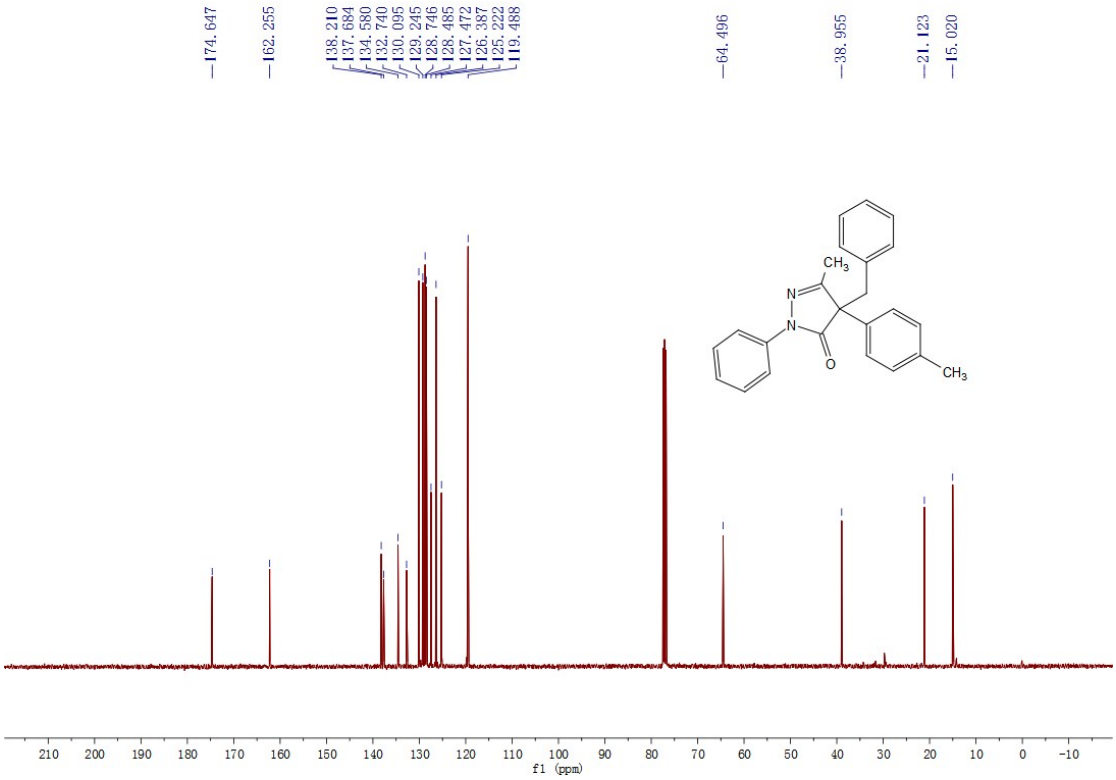
^{13}C NMR of 4-benzyl-4-(4-(tert-butyl)phenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ae)**



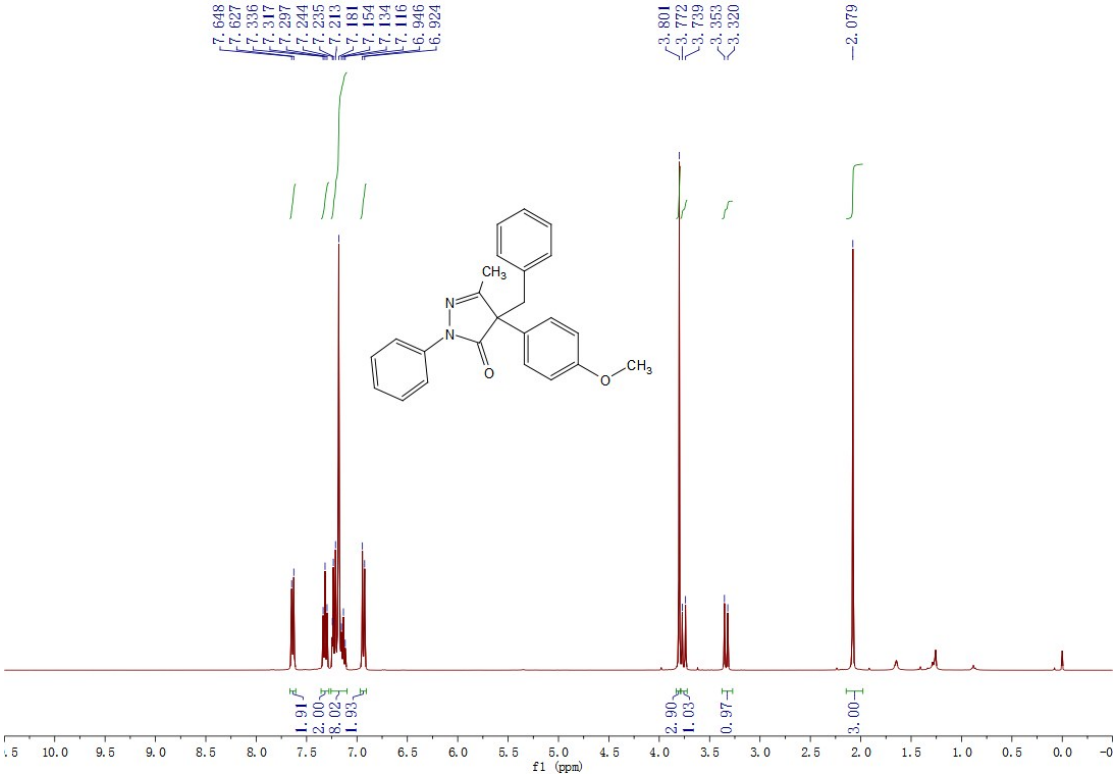
^{1}H NMR of 4-benzyl-3-methyl-1-phenyl-4-(p-tolyl)-1H-pyrazol-5(4H)-one **(3af)**



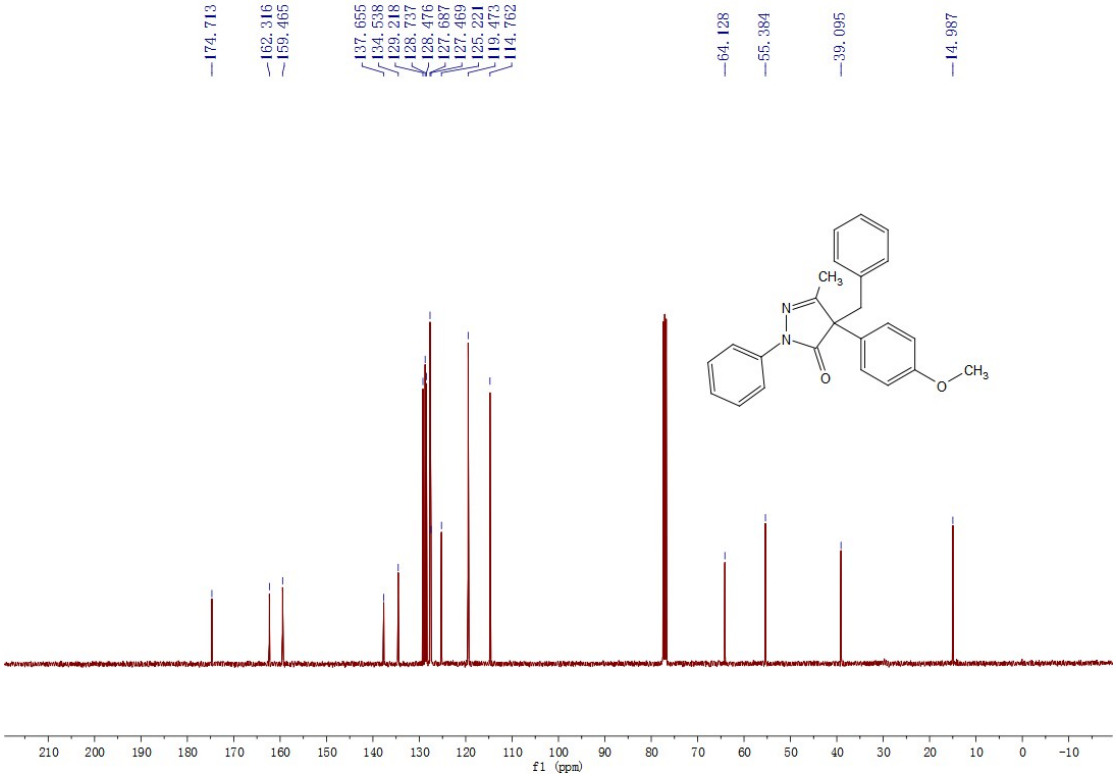
^{13}C NMR of 4-benzyl-3-methyl-1-phenyl-4-(p-tolyl)-1H-pyrazol-5(4H)-one **(3af)**



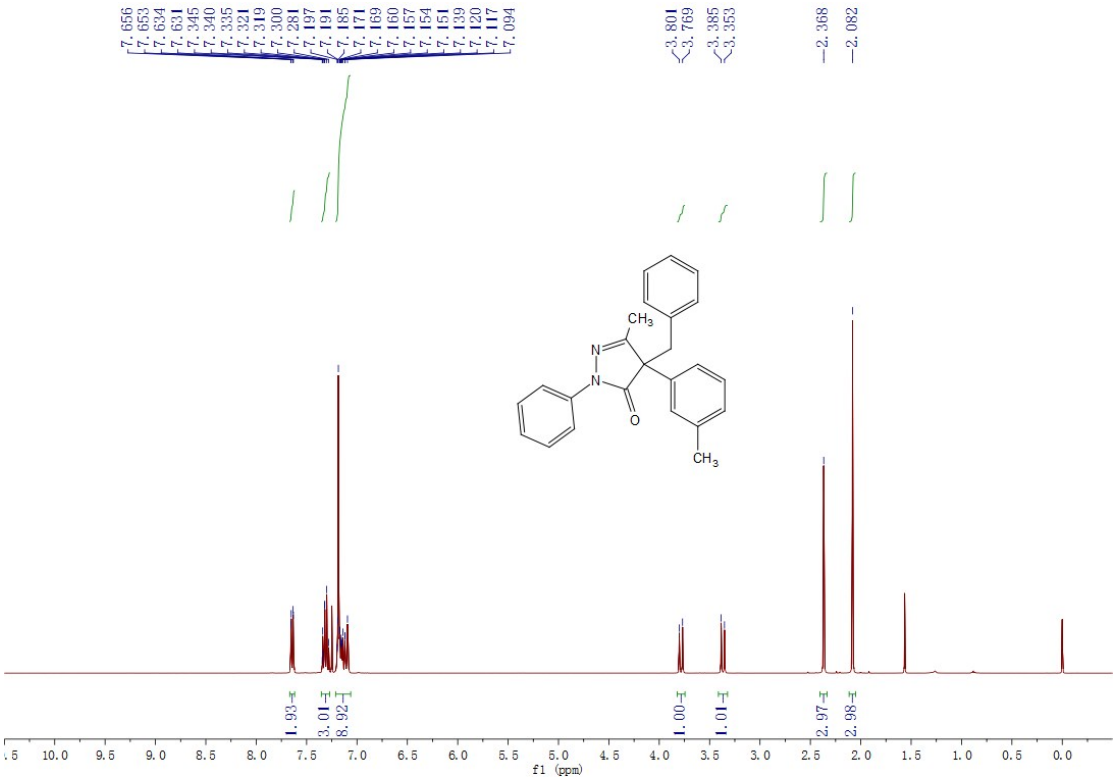
^{1}H NMR of 4-benzyl-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ag)**



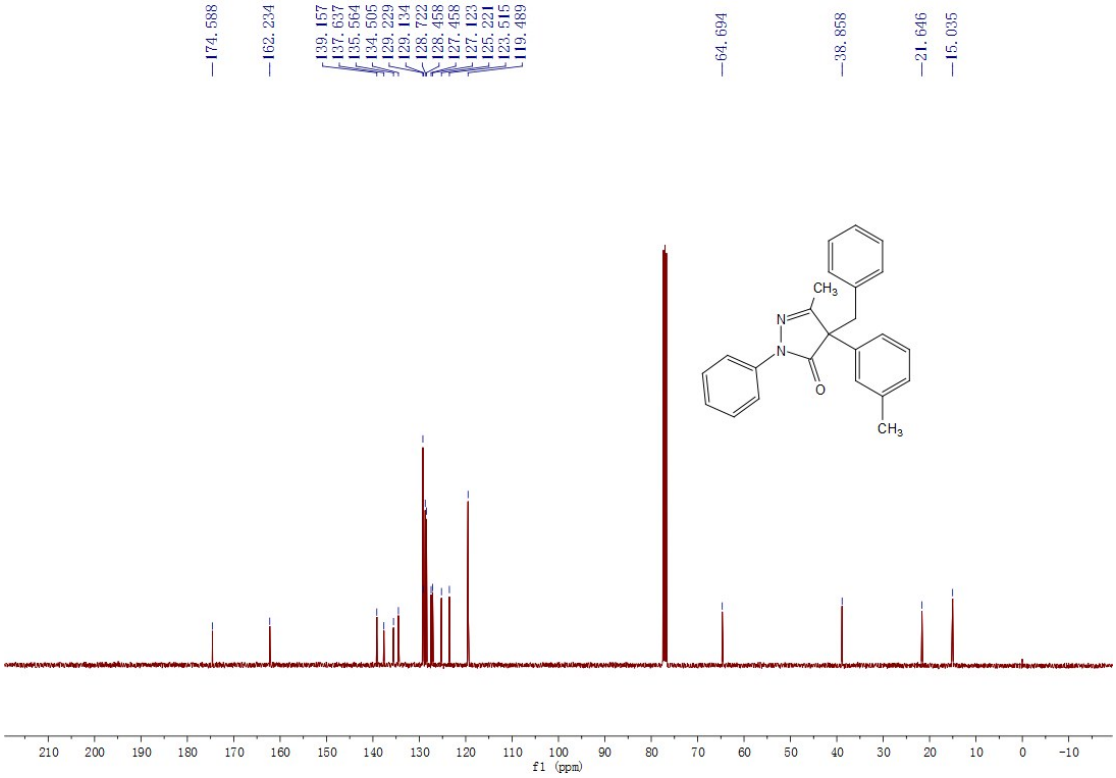
^{13}C NMR of 4-benzyl-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one **(3ag)**



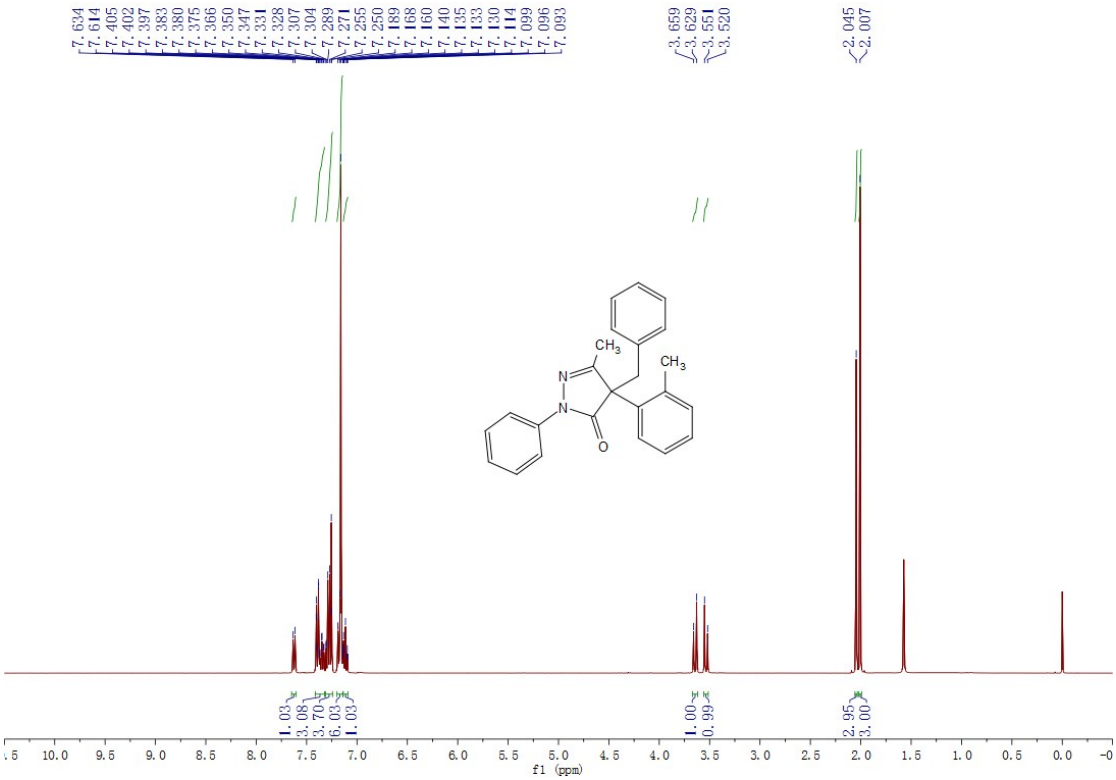
^{1}H NMR of 4-benzyl-3-methyl-1-phenyl-4-(m-tolyl)-1H-pyrazol-5(4H)-one **(3ah)**



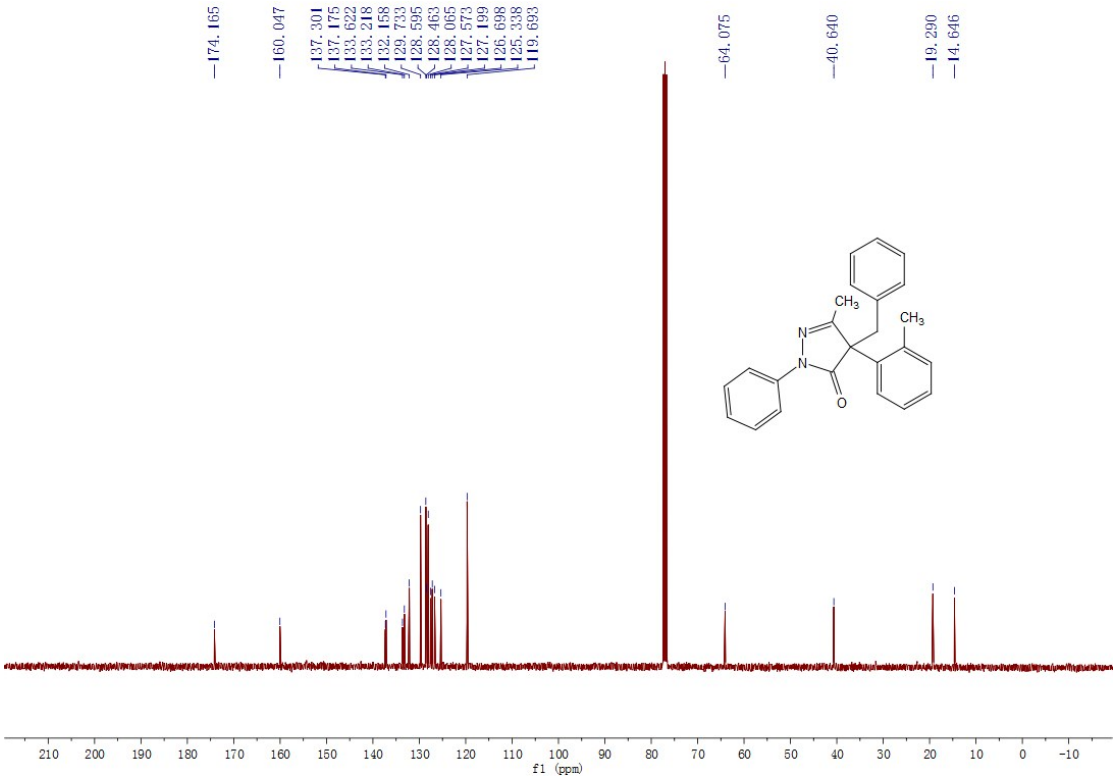
^{13}C NMR of of 4-benzyl-3-methyl-1-phenyl-4-(m-tolyl)-1H-pyrazol-5(4H)-one **(3ah)**



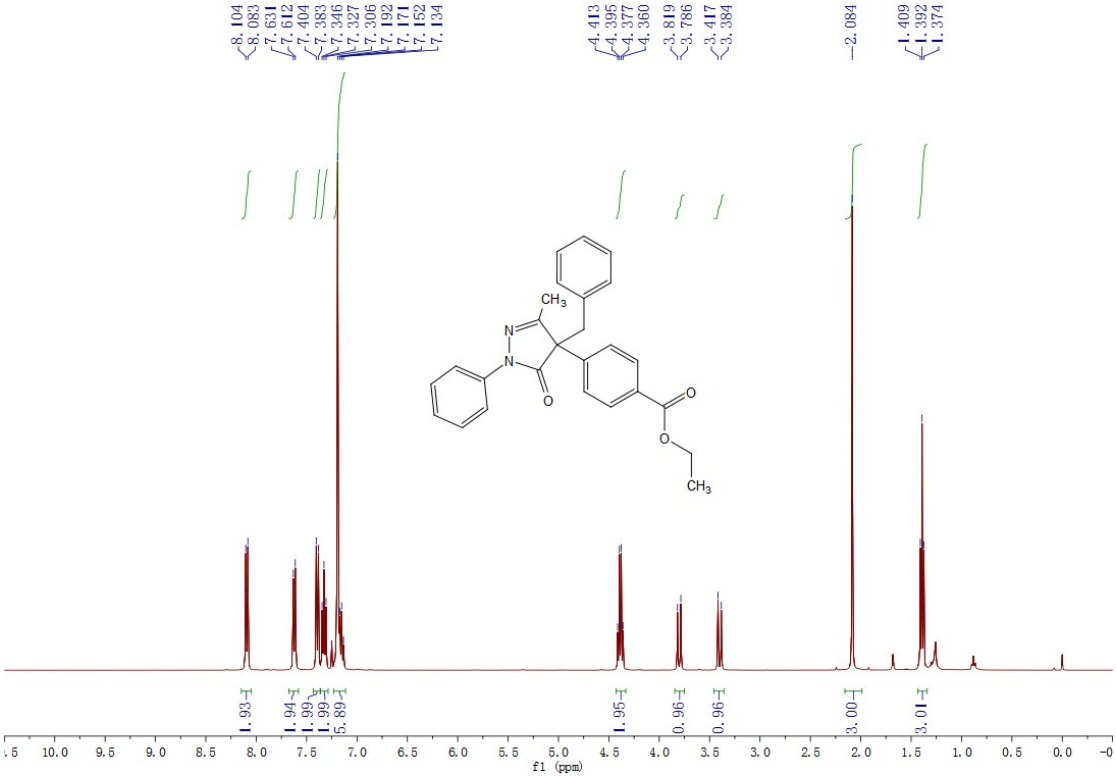
^{1}H NMR of 4-benzyl-3-methyl-1-phenyl-4-(o-tolyl)-1H-pyrazol-5(4H)-one **(3ai)**



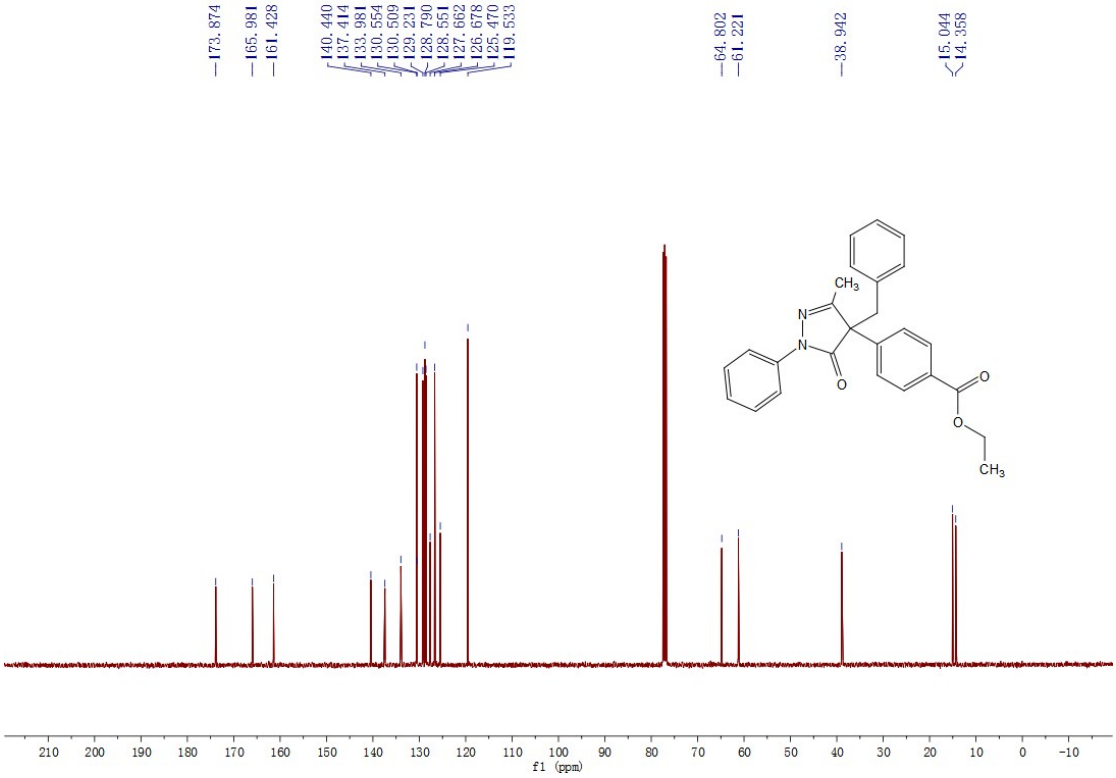
^{13}C NMR of 4-benzyl-3-methyl-1-phenyl-4-(o-tolyl)-1H-pyrazol-5(4H)-one **(3ai)**



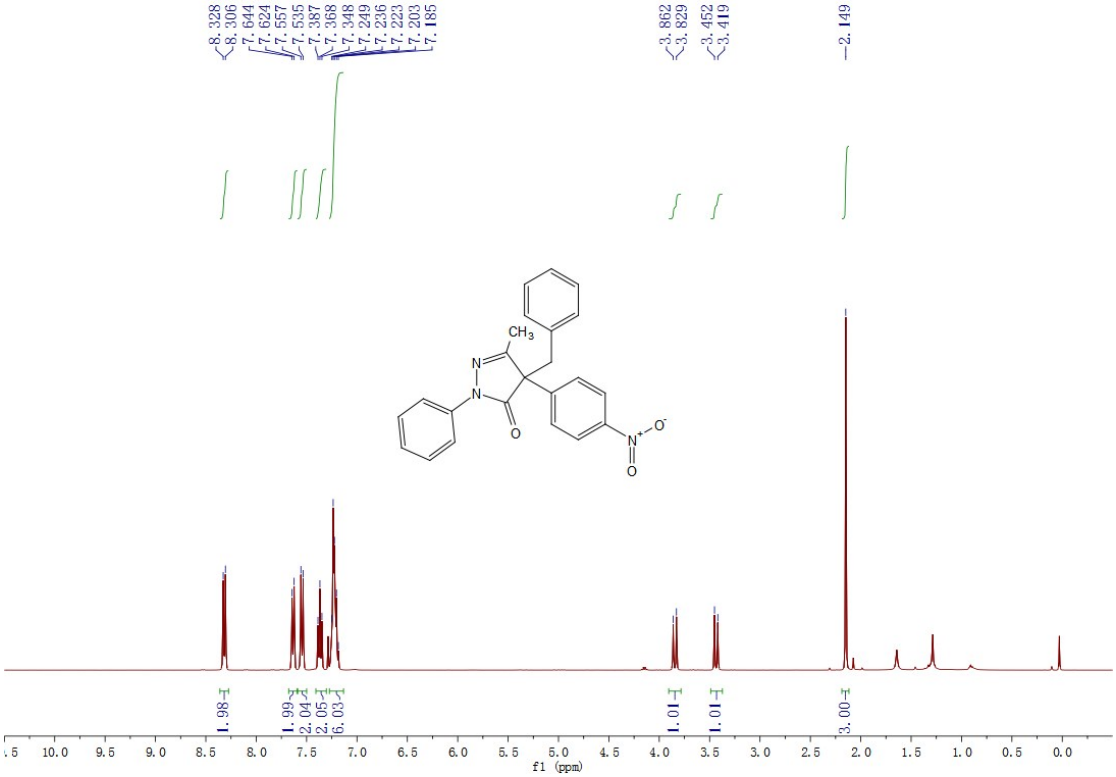
^{1}H NMR of ethyl 4-(4-benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)benzoate **(3ak)**



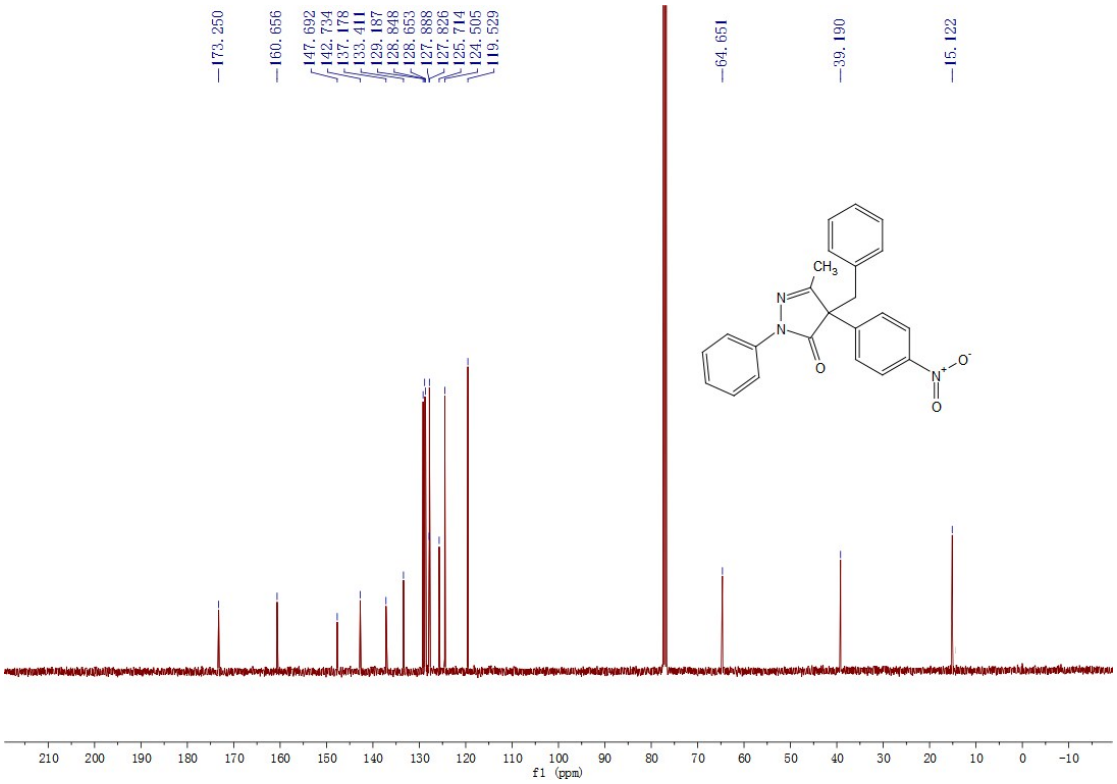
^{13}C NMR of ethyl 4-(4-benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)benzoate **(3ak)**



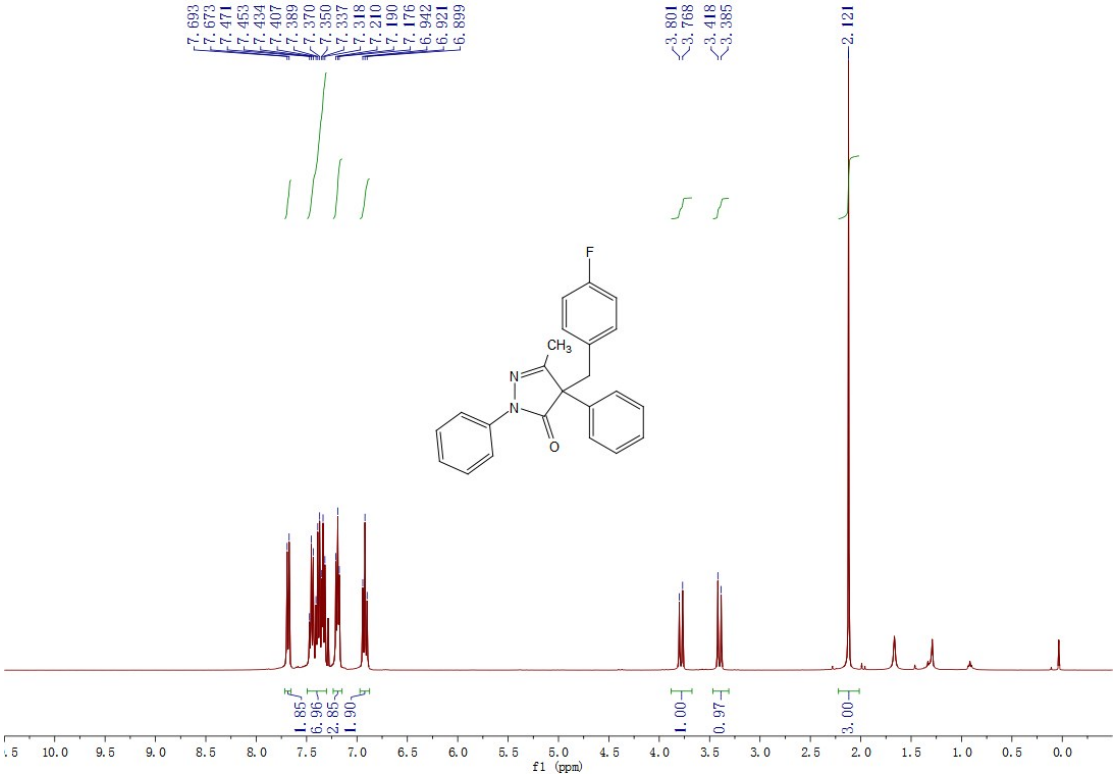
^{1}H NMR of 4-benzyl-3-methyl-4-(4-nitrophenyl)-1-phenyl-1H-pyrazol-5(4H)-one **(3al)**



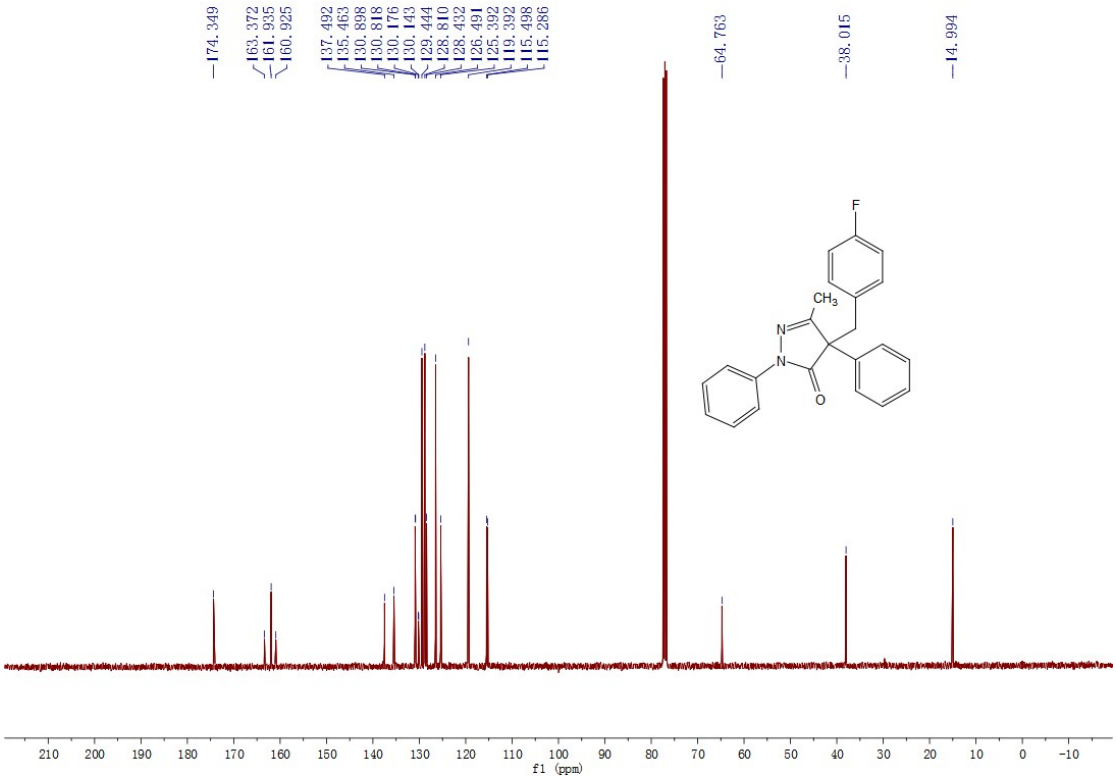
^{13}C NMR of 4-benzyl-3-methyl-4-(4-nitrophenyl)-1-phenyl-1H-pyrazol-5(4H)-one **(3al)**



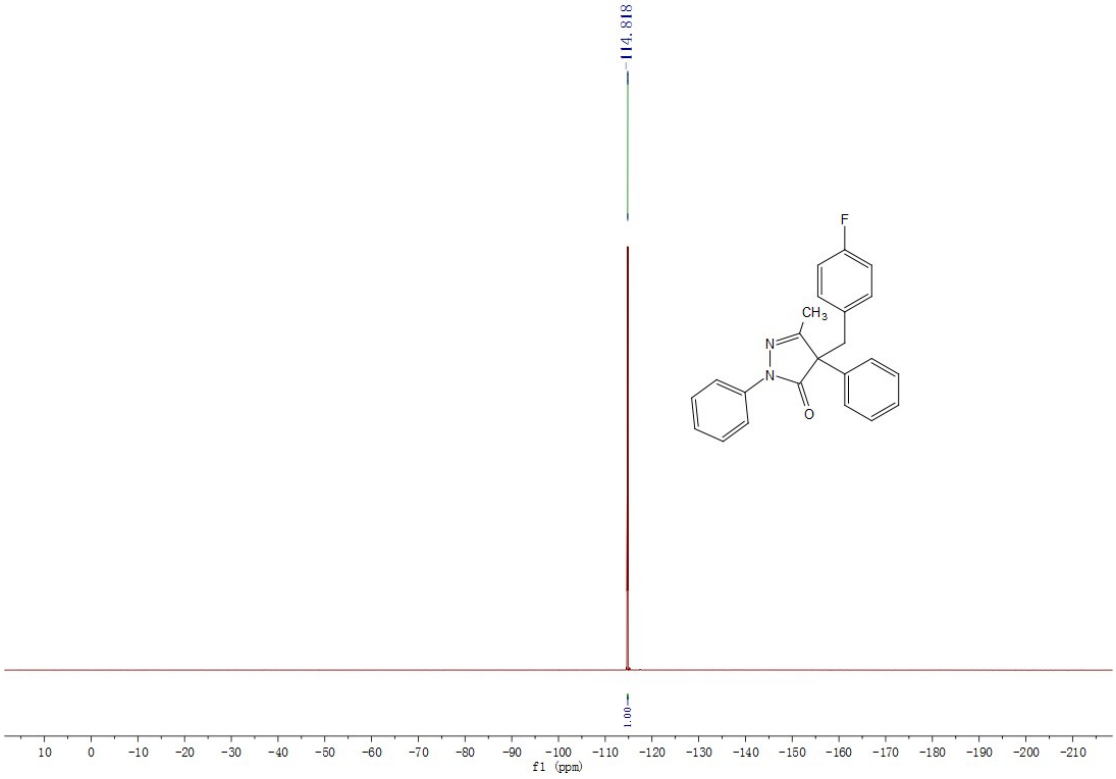
^{1}H NMR of 4-(4-fluorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ba)**



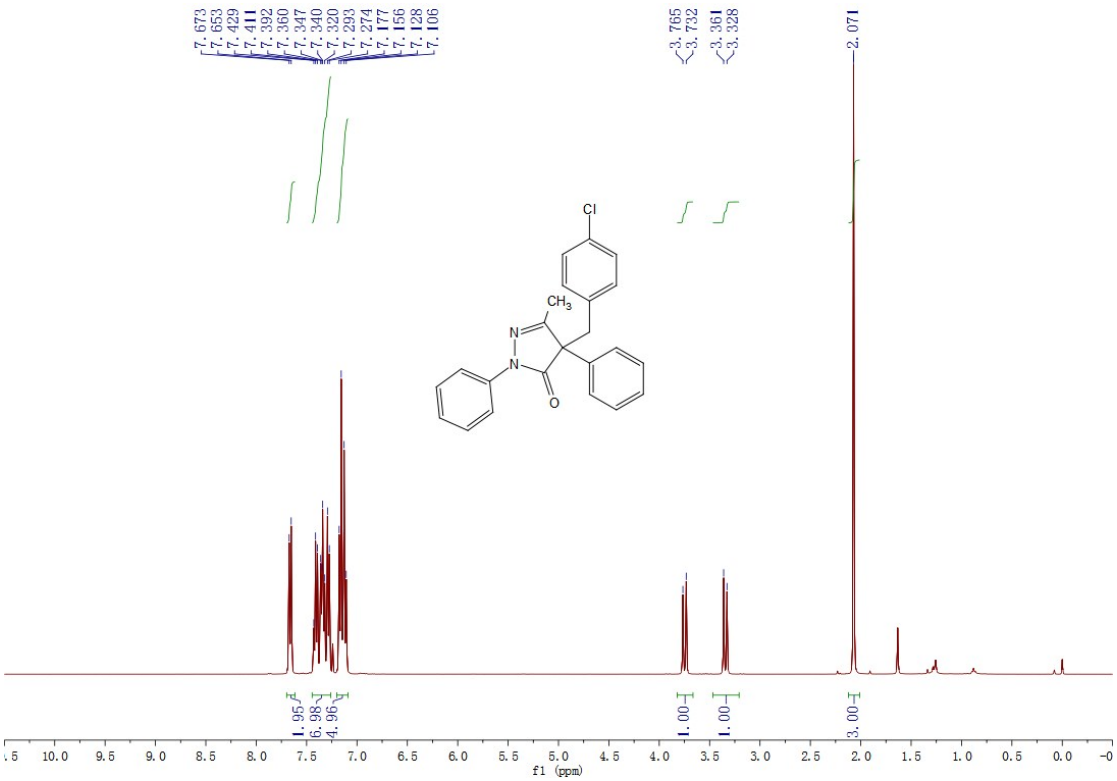
^{13}C NMR of 4-(4-fluorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ba)**



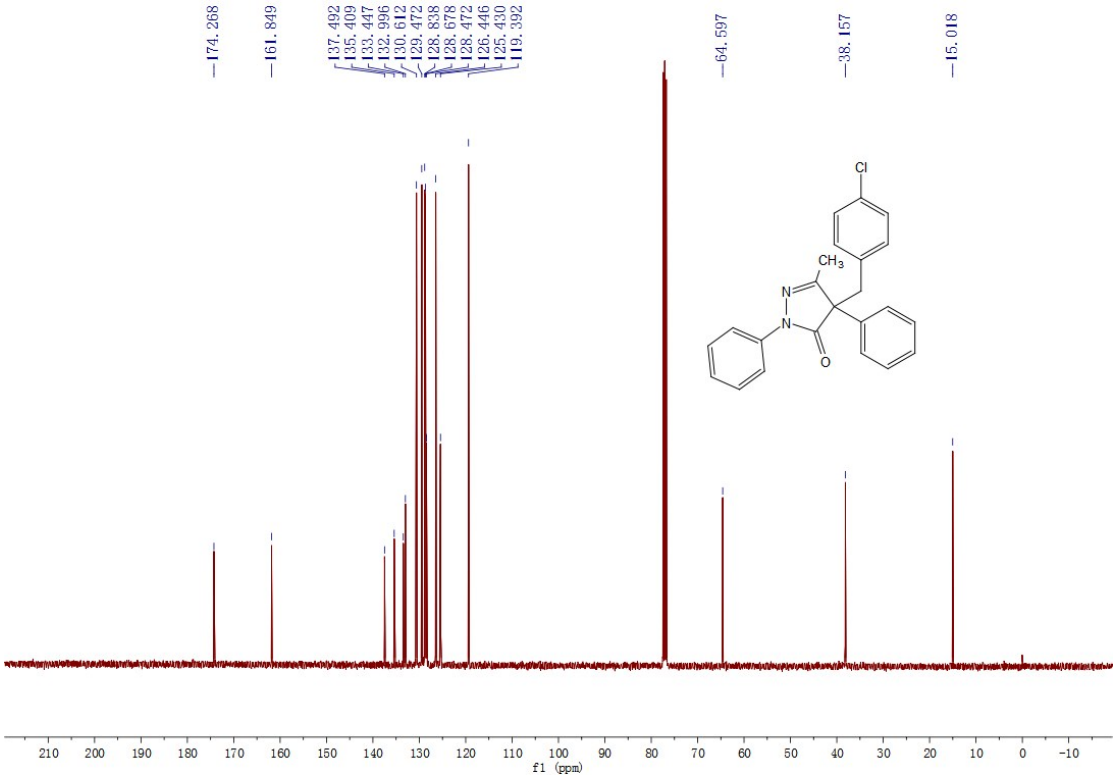
^{19}F NMR of 4-(4-fluorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ba)**



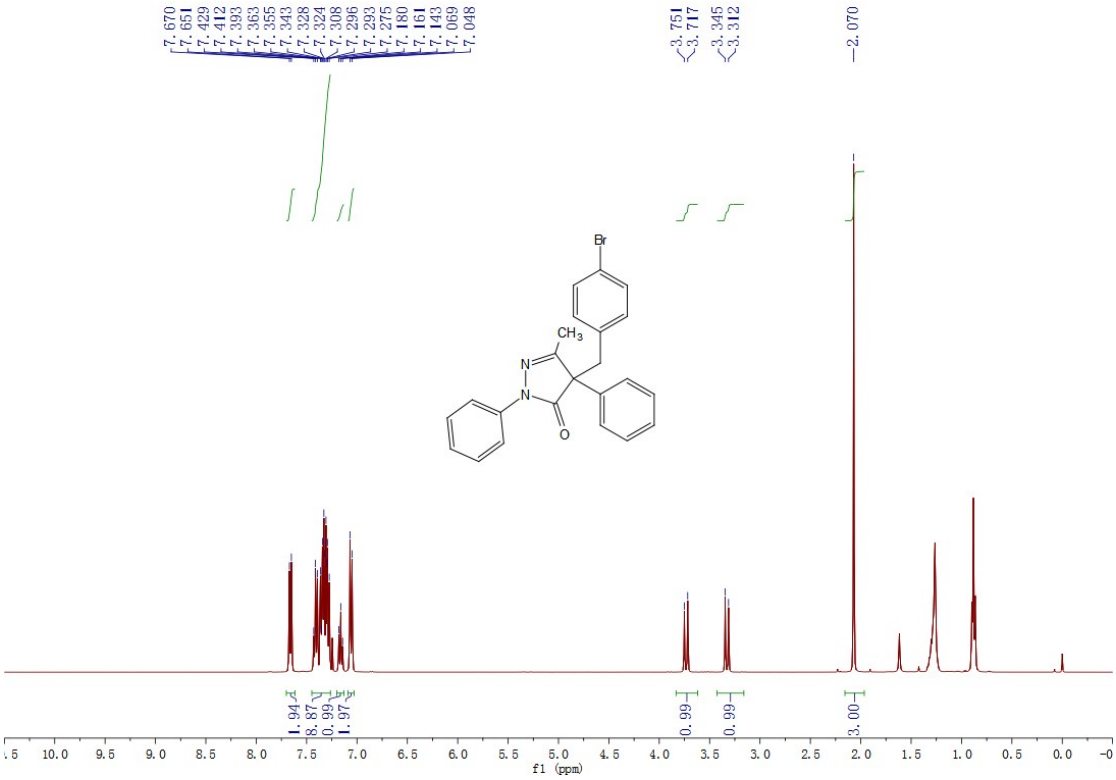
^{1}H NMR of 4-(4-chlorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ca)**



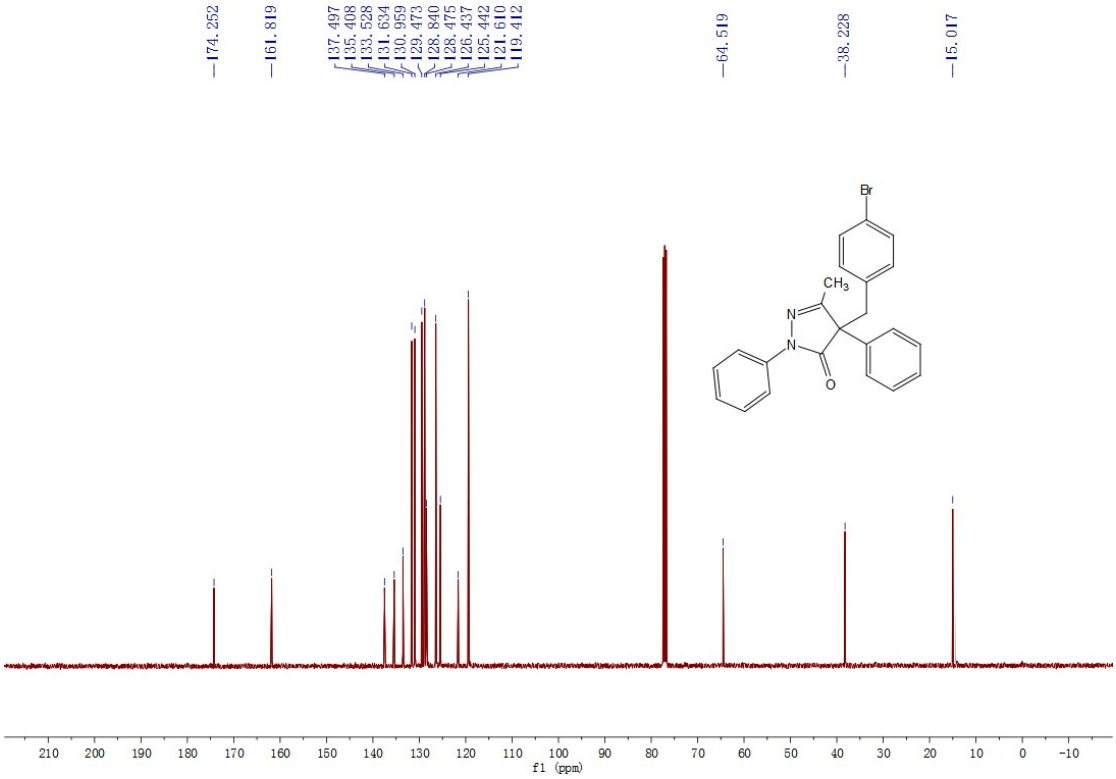
^{13}C NMR of 4-(4-chlorobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ca)**



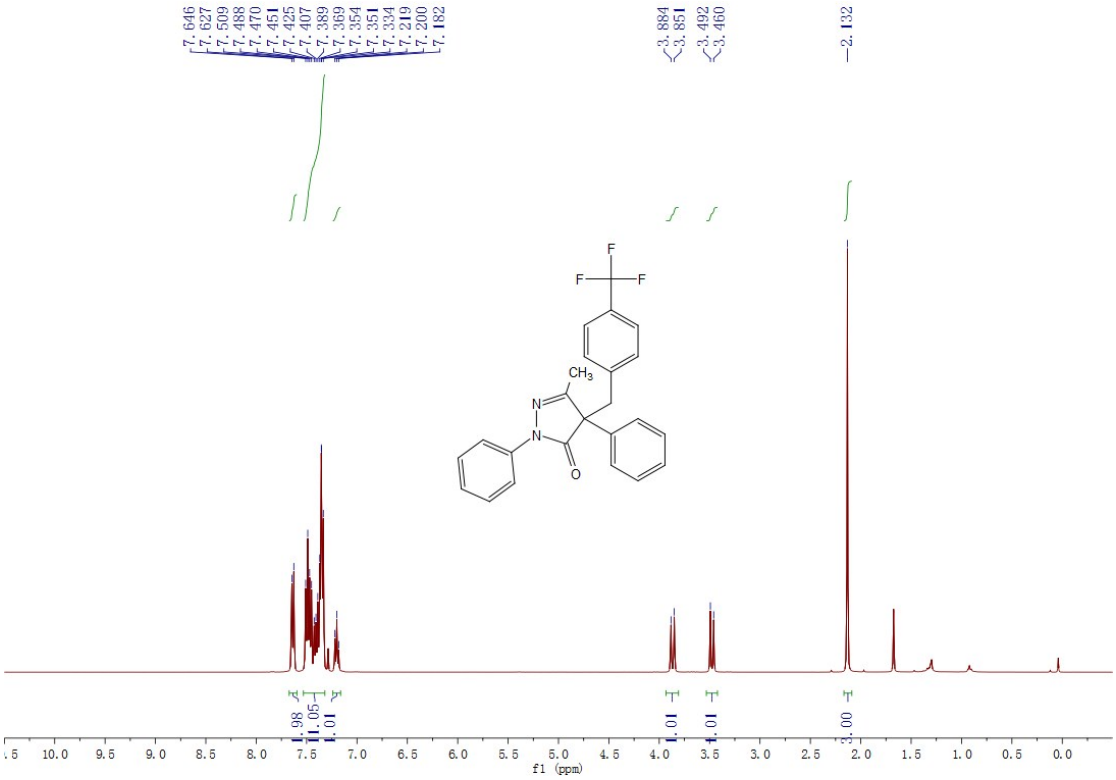
^{1}H NMR of 4-(4-bromobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3da)**



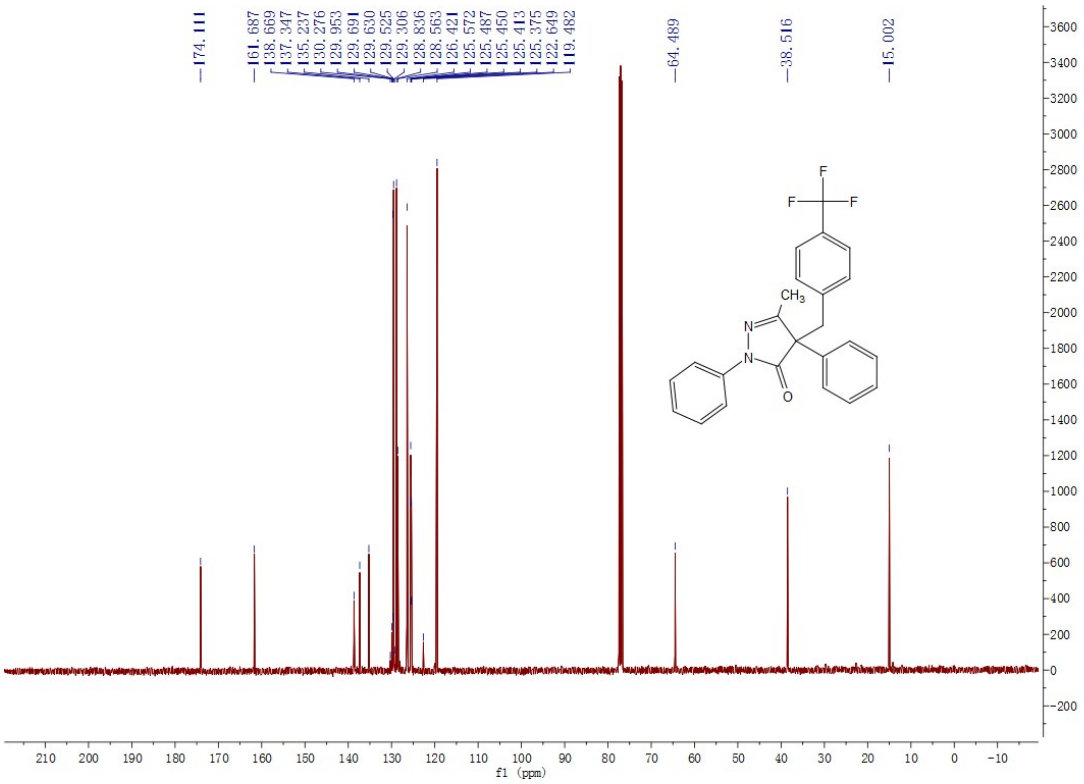
^{13}C NMR of 4-(4-bromobenzyl)-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3da)**



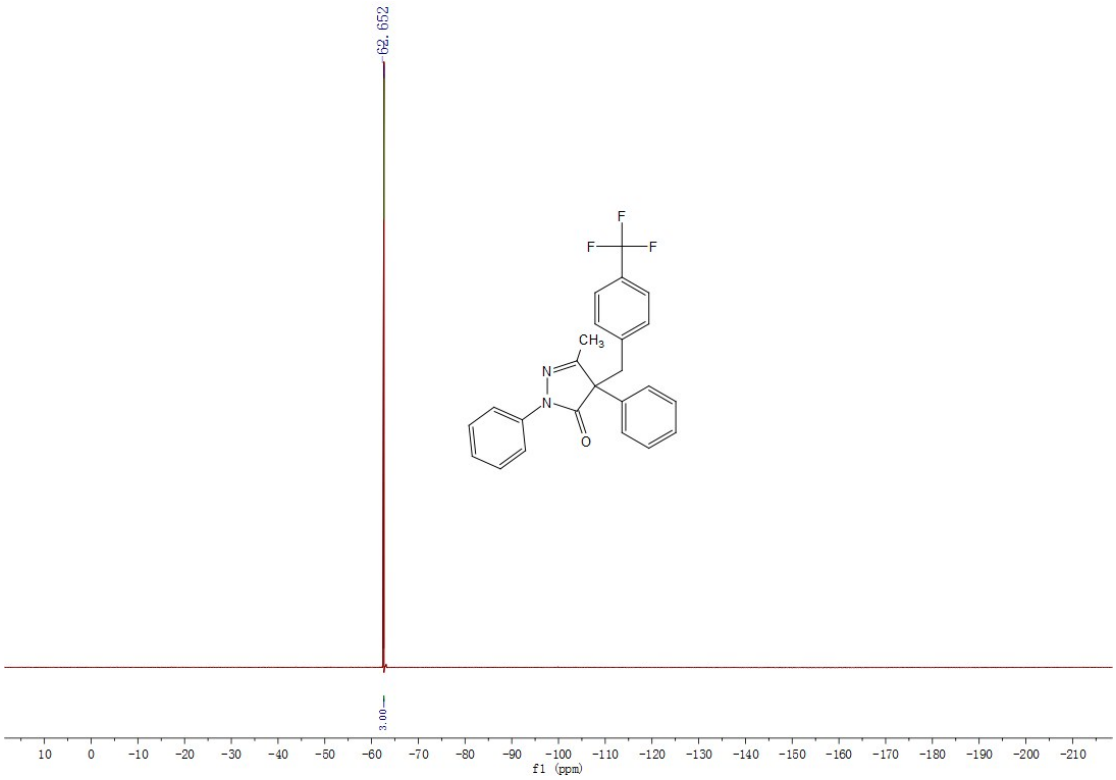
^{1}H NMR of 3-methyl-1,4-diphenyl-4-(4-(trifluoromethyl)benzyl)-1H-pyrazol-5(4H)-one **(3ea)**



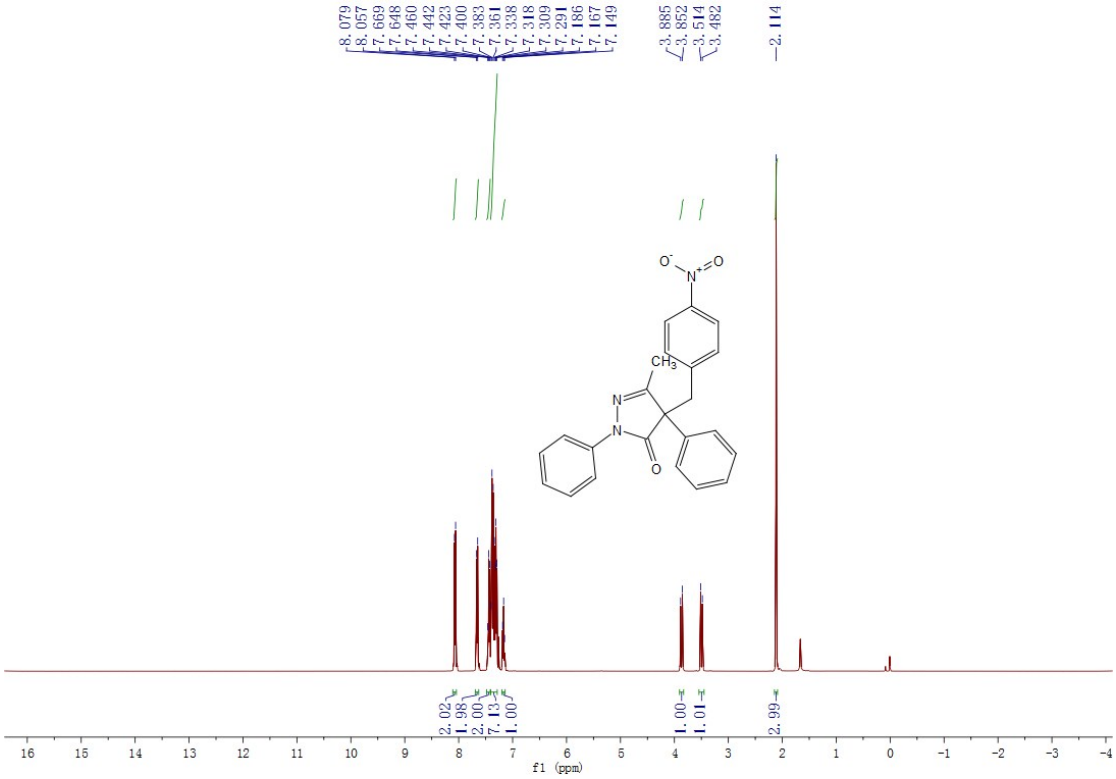
^{13}C NMR of 3-methyl-1,4-diphenyl-4-(4-(trifluoromethyl)benzyl)-1H-pyrazol-5(4H)-one **(3ea)**



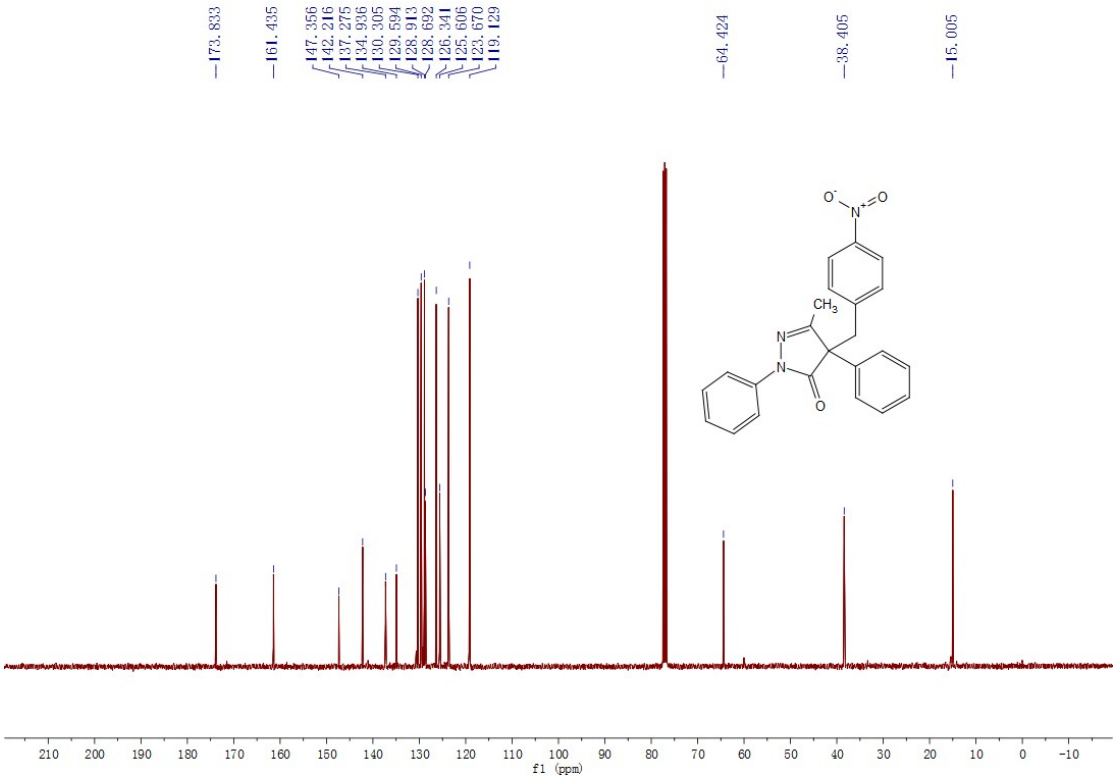
^{19}C NMR of 3-methyl-1,4-diphenyl-4-(4-(trifluoromethyl)benzyl)-1H-pyrazol-5(4H)-one **(3ea)**



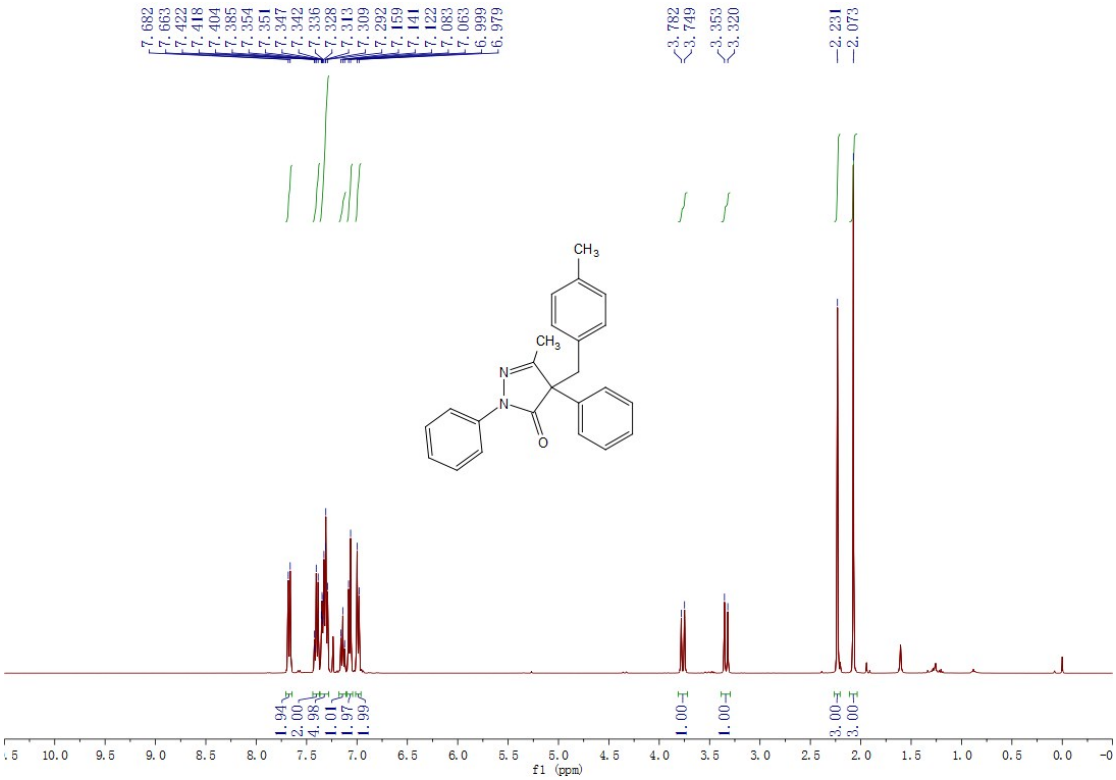
^{1}H NMR of 3-methyl-4-(4-nitrobenzyl)-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3fa)**



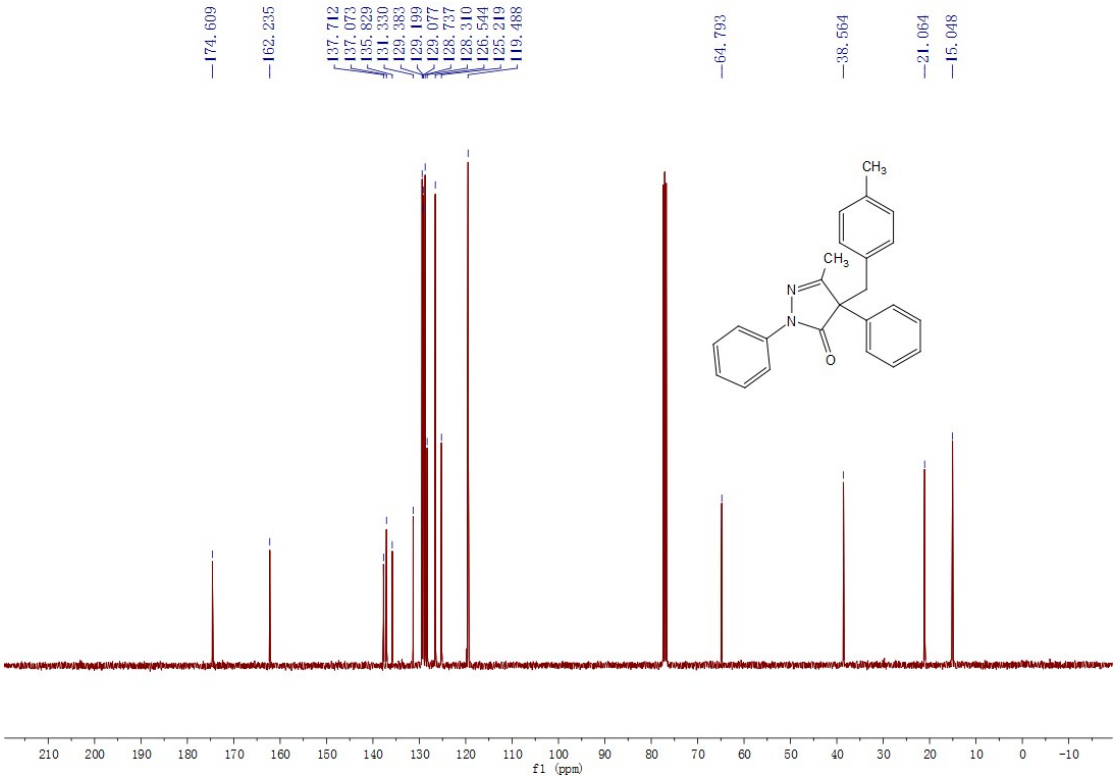
^{13}C NMR of 3-methyl-4-(4-nitrobenzyl)-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3fa)**



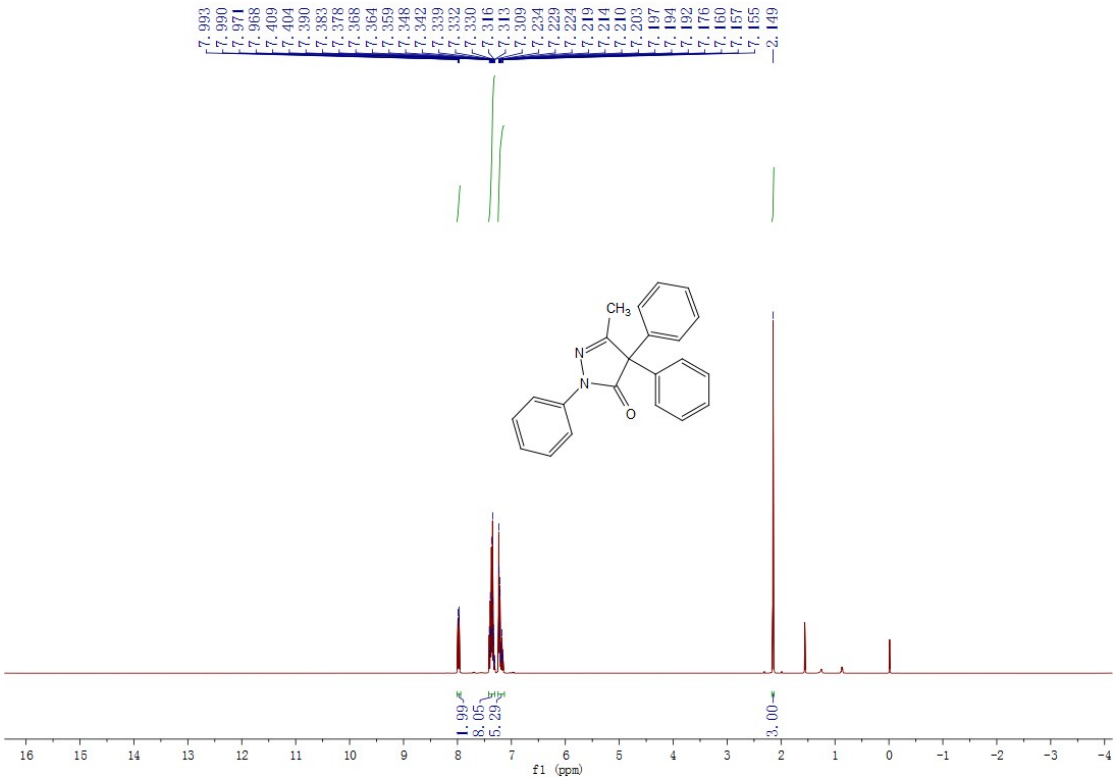
^{1}H NMR of 3-methyl-4-(4-methylbenzyl)-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ga)**



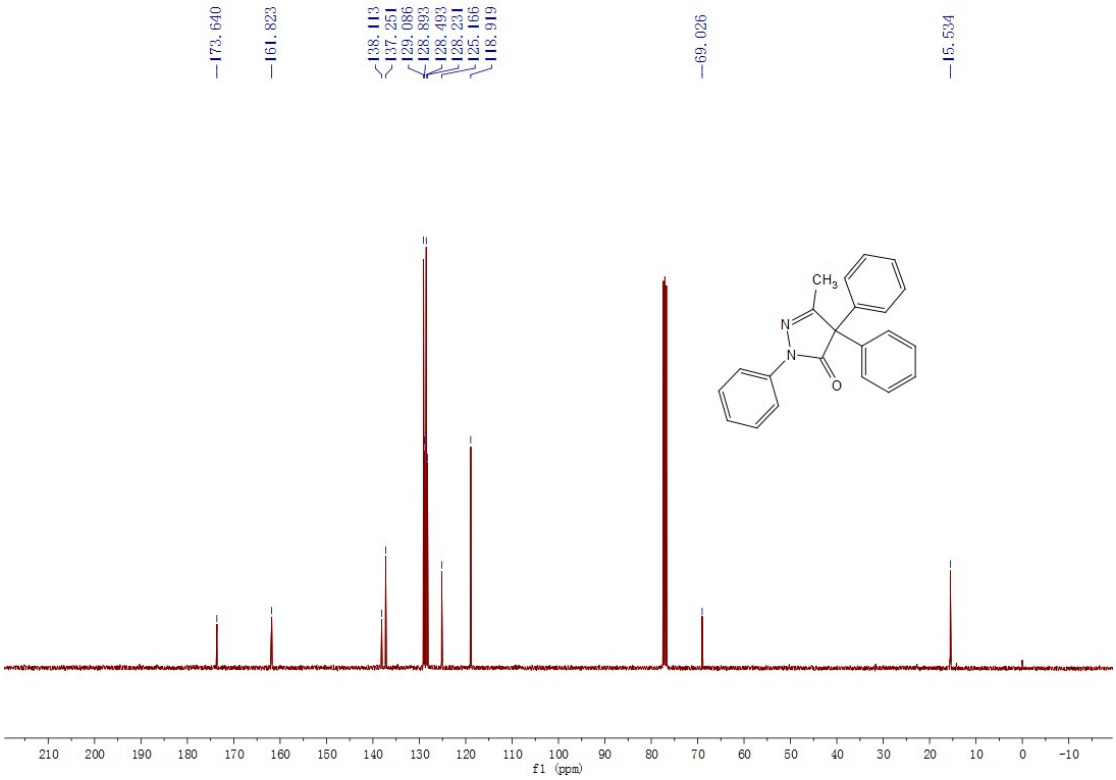
^{13}C NMR of 3-methyl-4-(4-methylbenzyl)-1,4-diphenyl-1H-pyrazol-5(4H)-one (**3ga)**



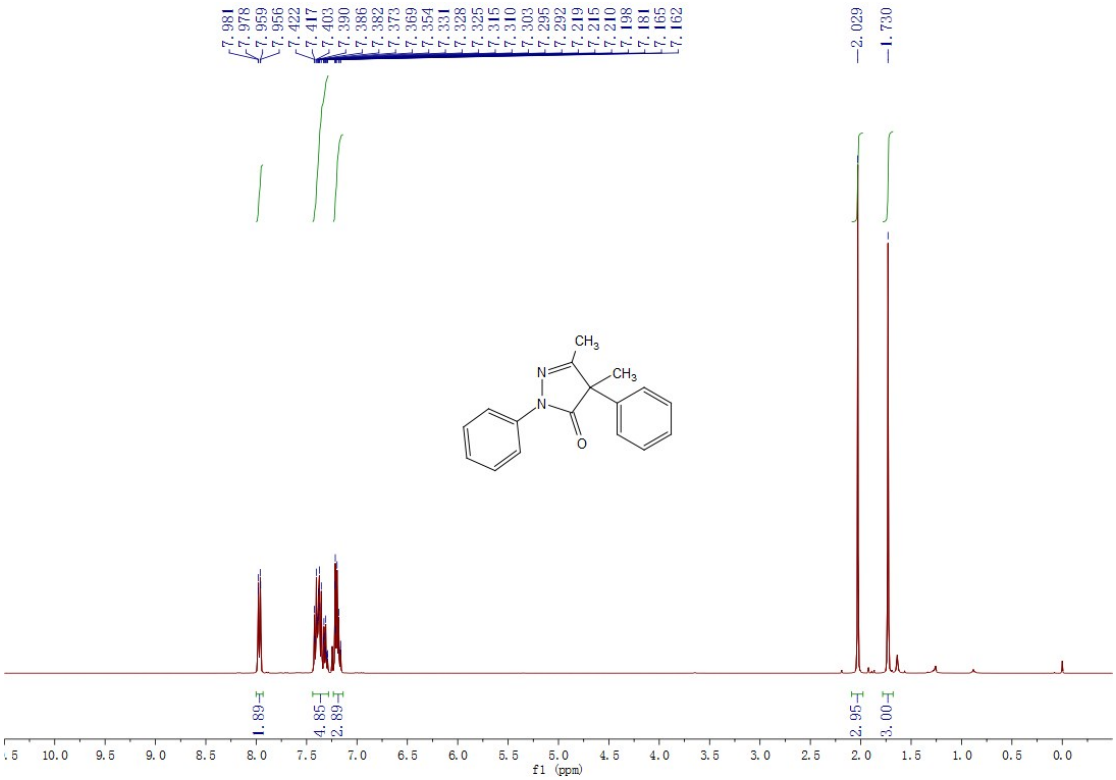
^{1}H NMR of 3-methyl-1,4,4-triphenyl-1H-pyrazol-5(4H)-one **(3ha)**



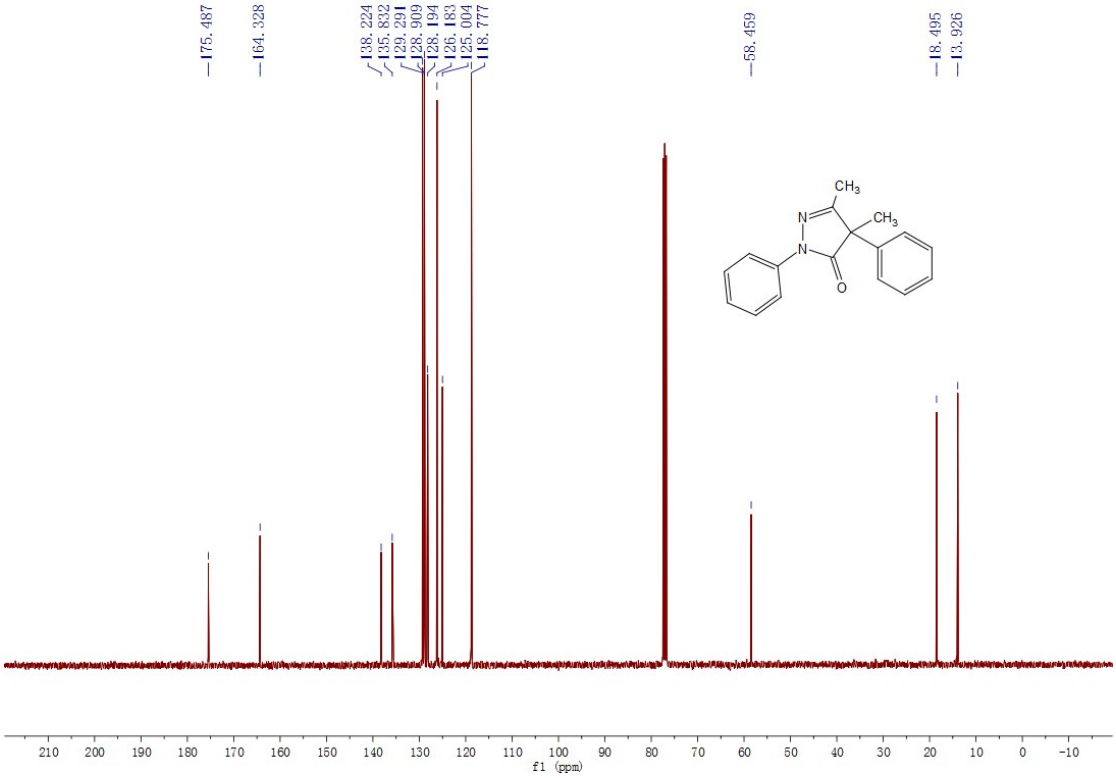
^{13}C NMR of 3-methyl-1,4,4-triphenyl-1H-pyrazol-5(4H)-one **(3ha)**



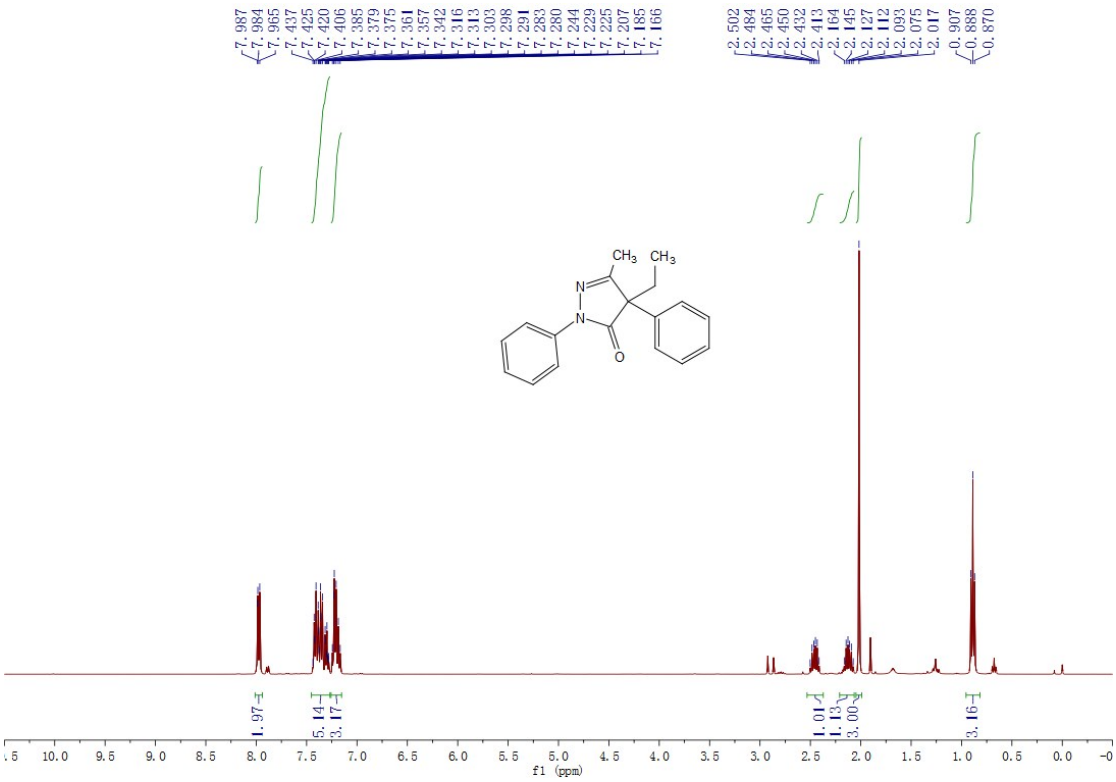
^{1}H NMR of 3,4-dimethyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ia)**



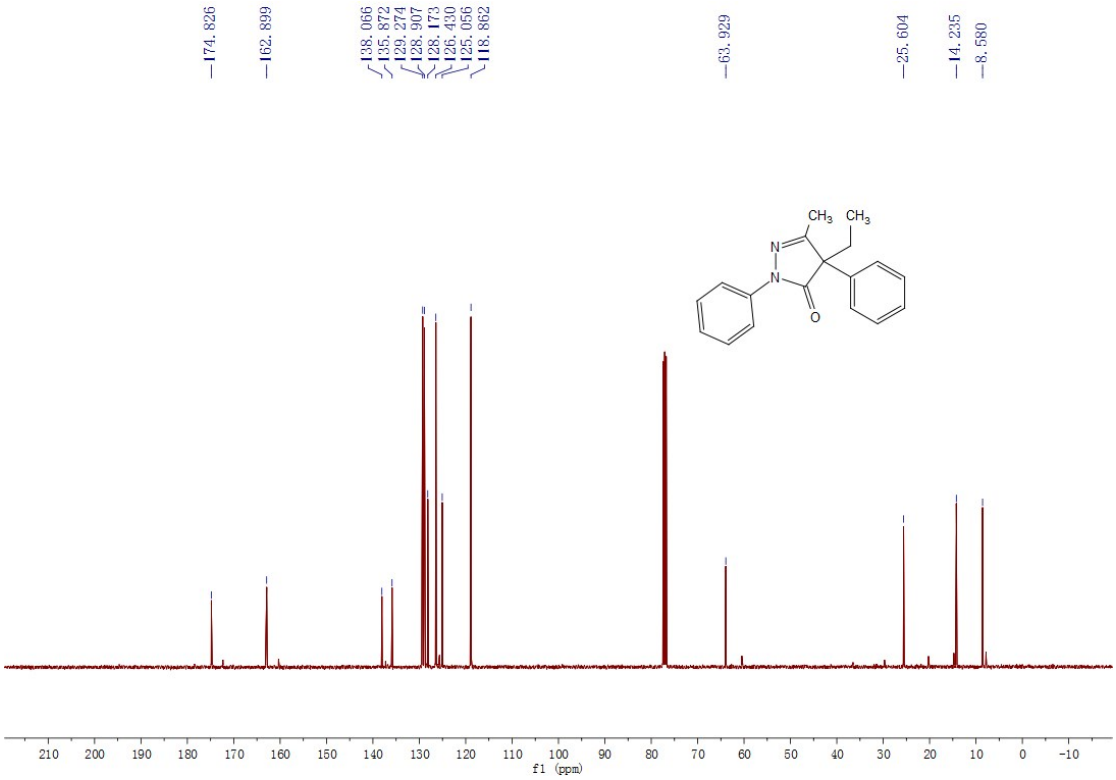
^{13}C NMR of 3,4-dimethyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (**3ia)**



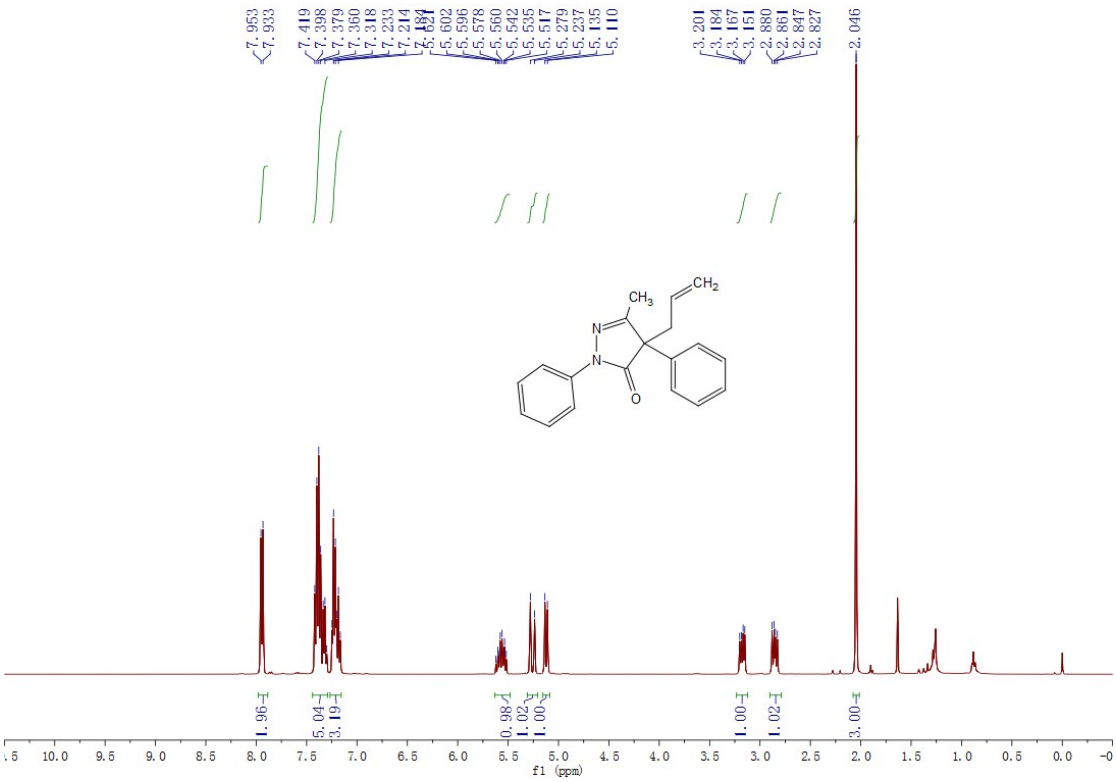
^{1}H NMR of 4-ethyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ja)**



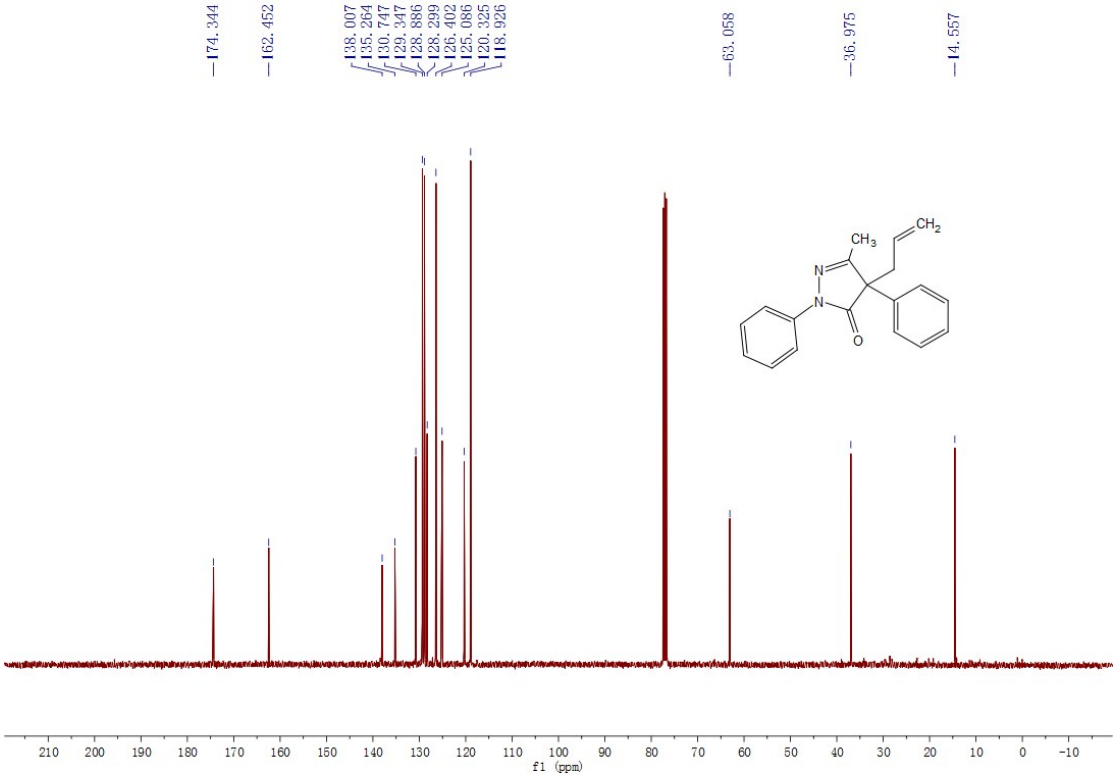
^{13}C NMR of 4-ethyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (**3ja)**



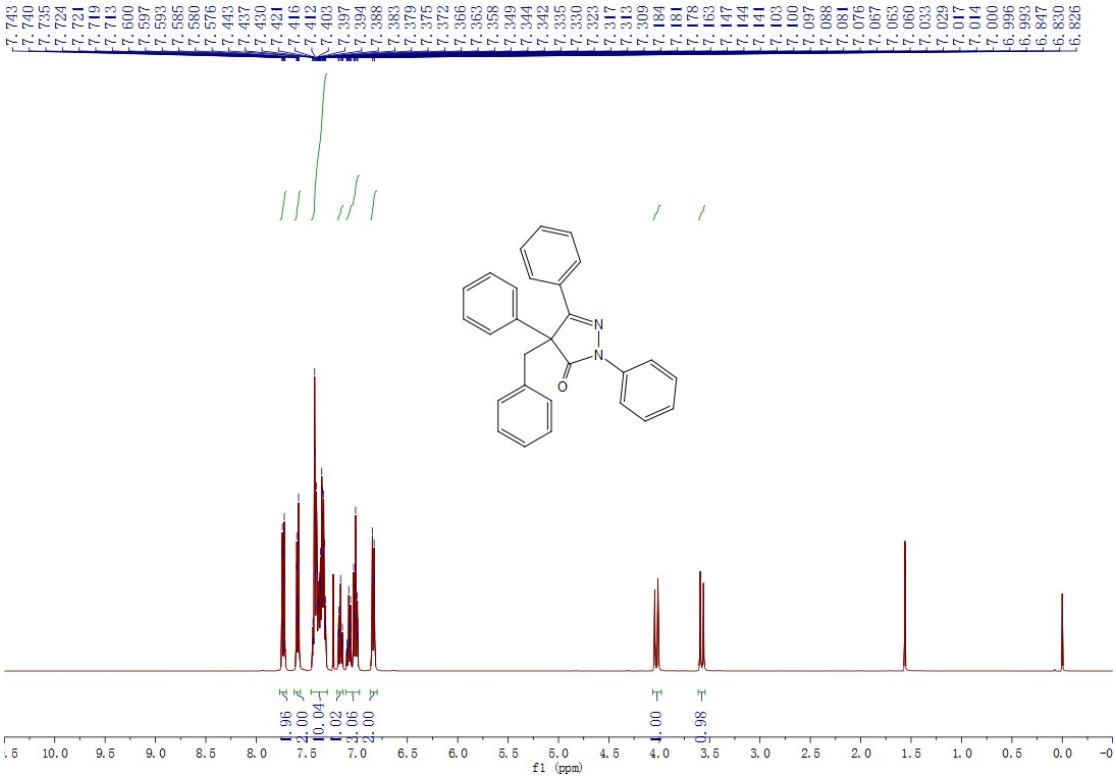
^{1}H NMR of 4-allyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one **(3ka)**



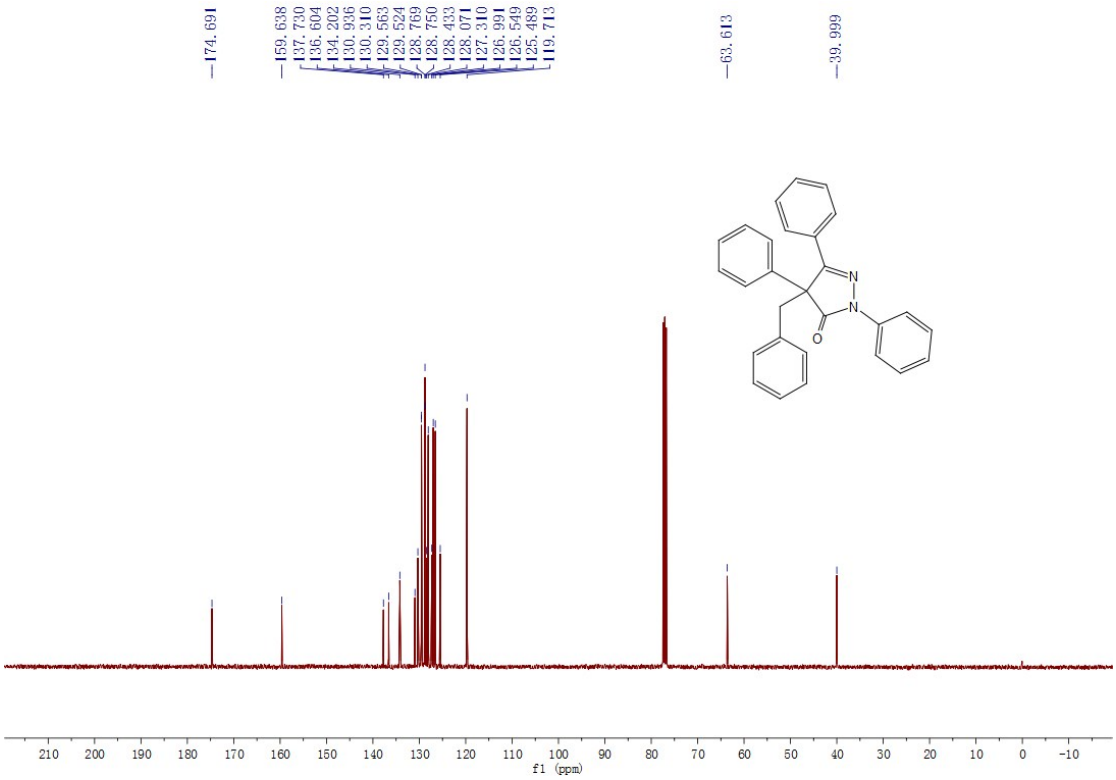
^{13}C NMR of 4-allyl-3-methyl-1,4-diphenyl-1H-pyrazol-5(4H)-one (**3ka)**



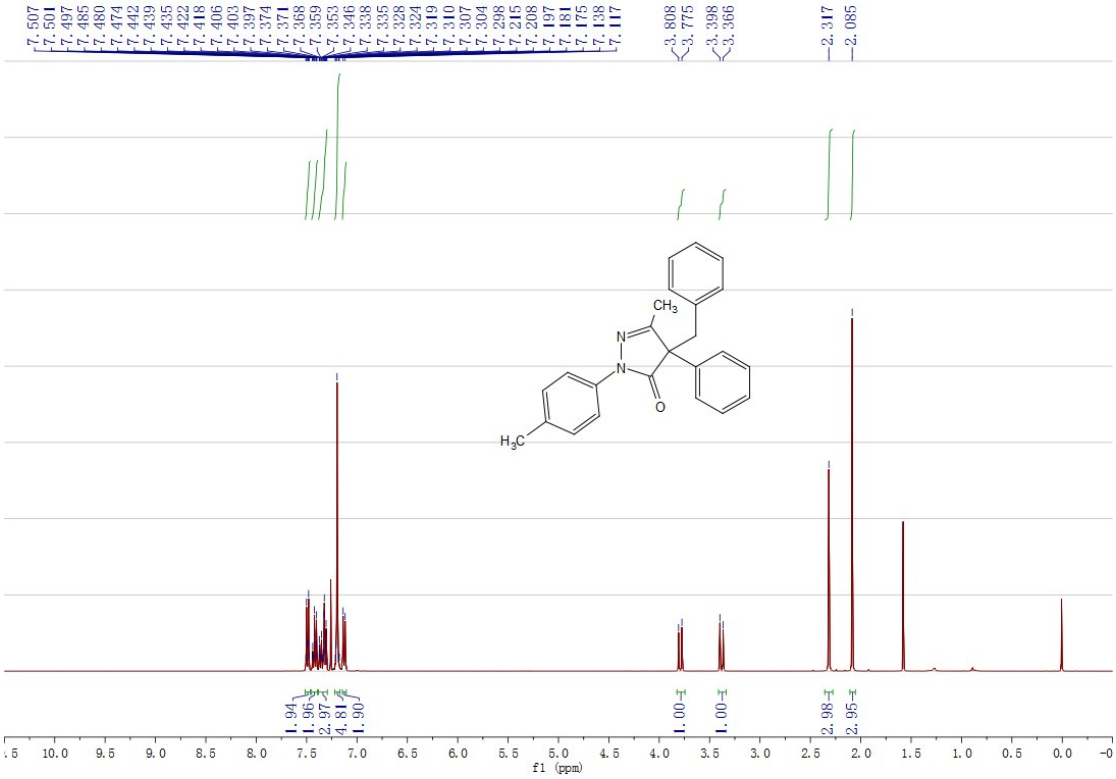
^{1}H NMR of 4-benzyl-1,3,4-triphenyl-1H-pyrazol-5(4H)-one **(3la)**



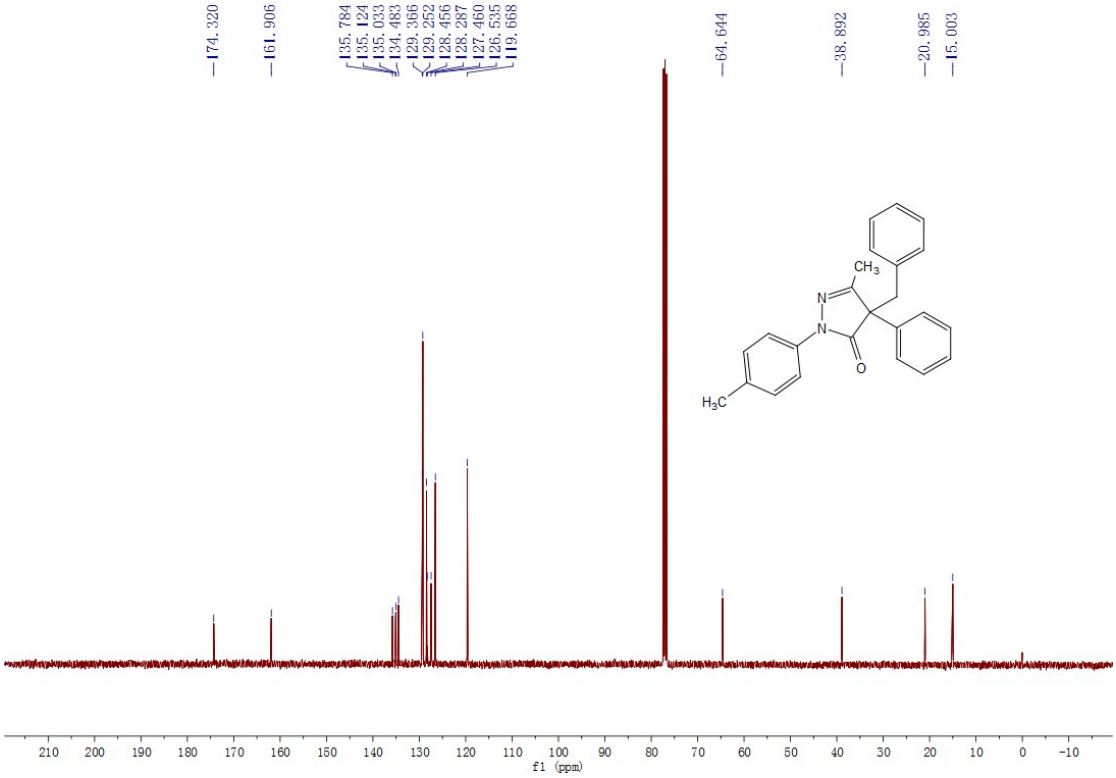
^{13}C NMR of 4-benzyl-1,3,4-triphenyl-1H-pyrazol-5(4H)-one **(3la)**



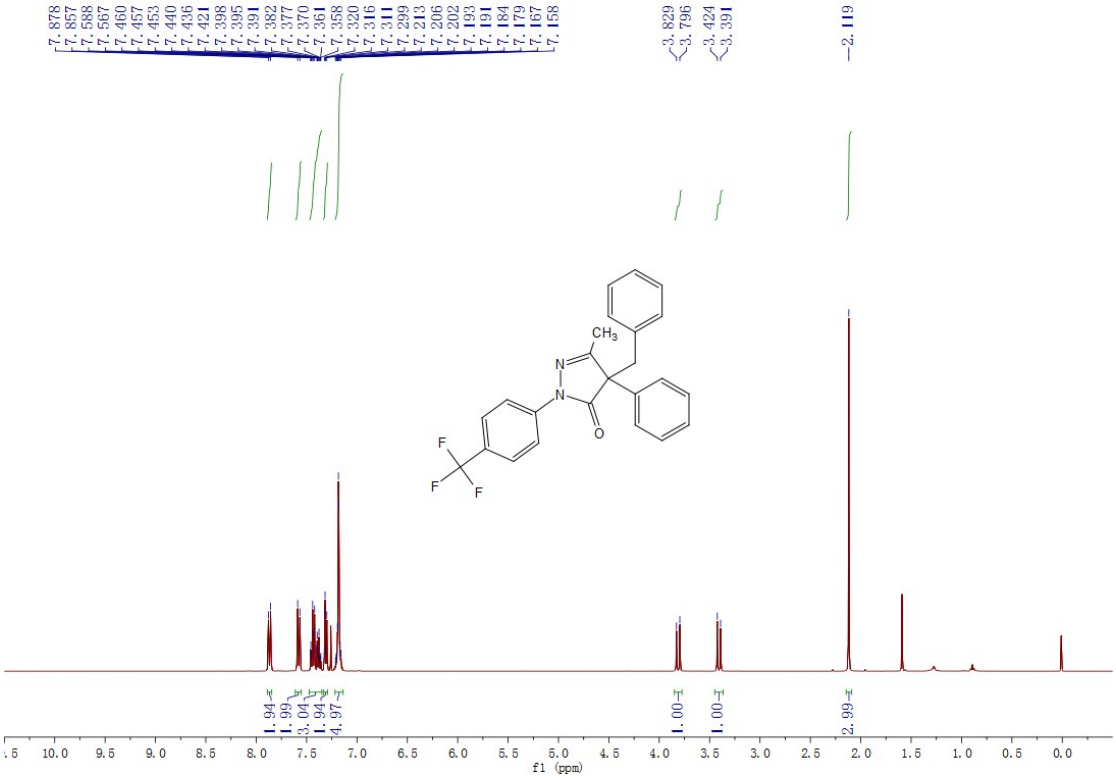
^{1}H NMR of 4-benzyl-3-methyl-4-phenyl-1-(p-tolyl)-1H-pyrazol-5(4H)-one **(3ma)**



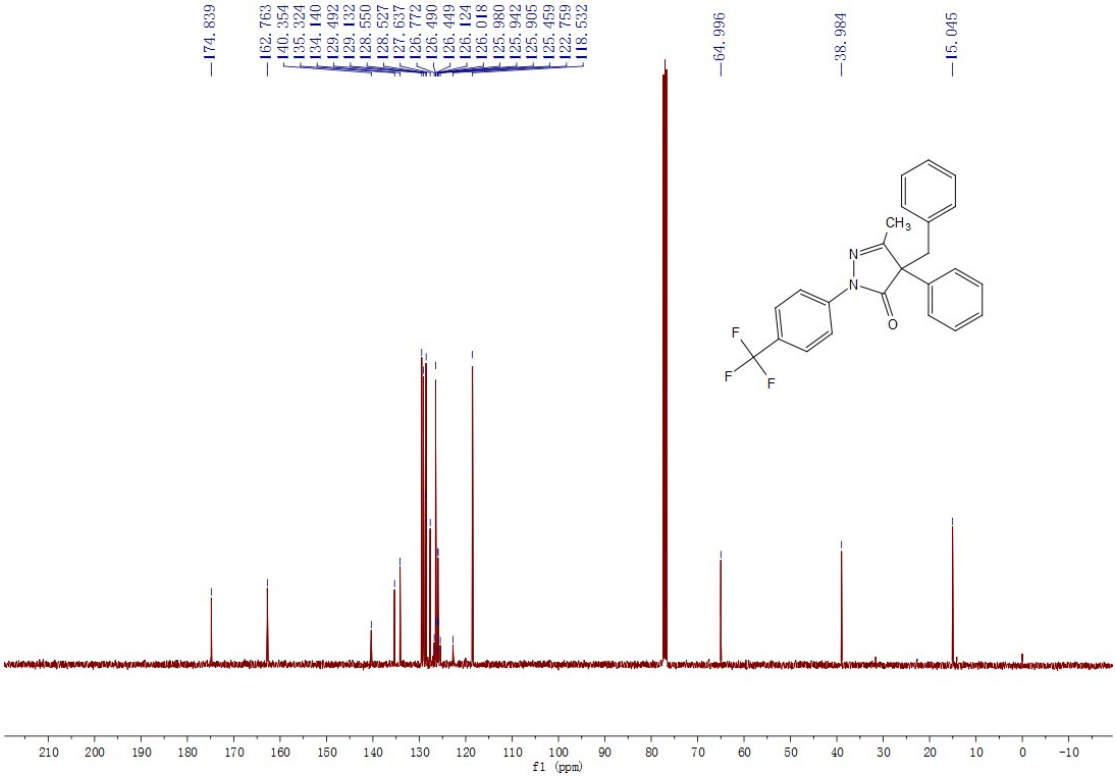
^{13}C NMR of 4-benzyl-3-methyl-4-phenyl-1-(p-tolyl)-1H-pyrazol-5(4H)-one **(3ma)**



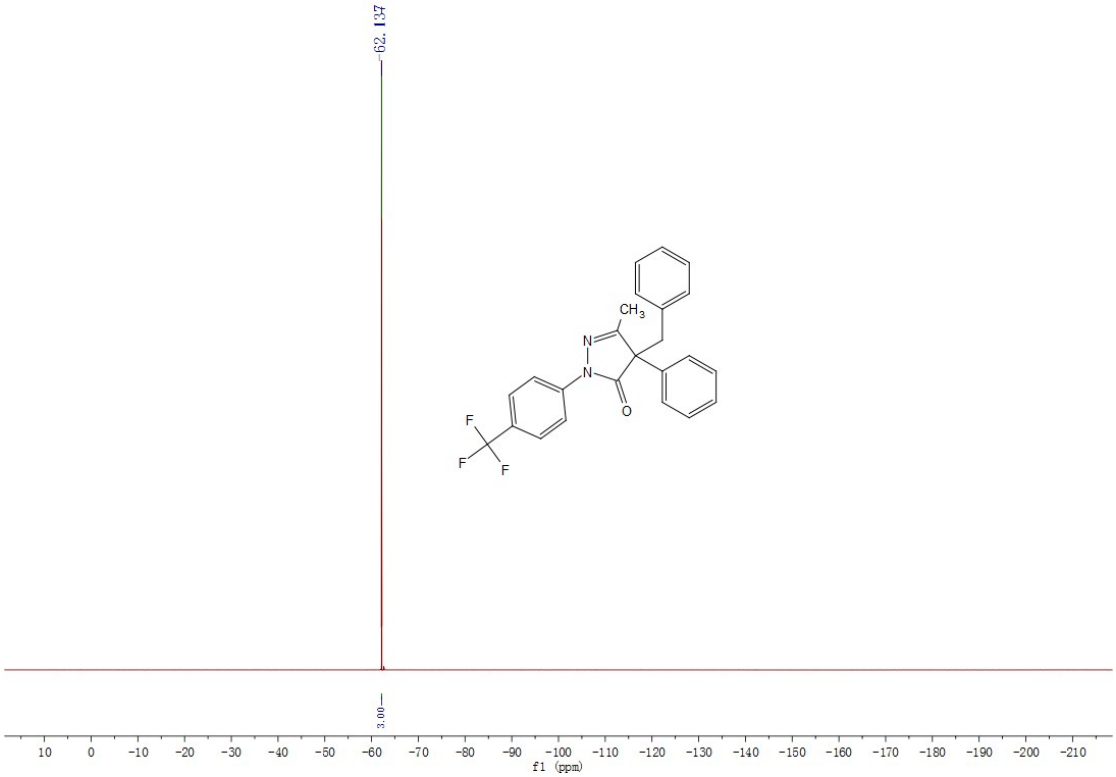
^{1}H NMR of 4-benzyl-3-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5(4H)-one **(3na)**



^{13}C NMR of 4-benzyl-3-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5(4H)-one **(3na)**



^{19}F NMR of 4-benzyl-3-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazol-5(4H)-one **(3na)**



Part4. References

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2. M. Kuriyama, N. Hamaguchi and O. Onomura, *Chem. Eur. J.* 2012, **18**, 1591.
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4. T. B. Petersen, R. Khan and B. Olofsson, *Org. Lett.* 2011, **13**, 3462.
5. (a) L. A. Carpino, *J. Am. Chem. Soc.* 1958, **80**, 599; (b) S. A. Shiba, N. M. S. Harb, M. A. El-kassaby and Mohsen Abou El-Regal, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 1995, **104**, 15; (c) J. Sun, C.-G. Yan and Y. Han, Synthetic Communications, 2001, **31**, 151; (d) R V. Hangarge, D. V. Jarikote and M. S. Shingare, Green Chemistry, 2002, **4**, 266.