Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Metal-free Cyclization of Unsaturated Hydrazones for the Divergent Assembly of Pyrazolones and Pyrazolines

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Table of Contents

1. General information

All chemicals were purchased from Adamas Reagent, Ltd, Energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. CH_3CN was dried by CaH prior to use. Unless otherwise stated, all experiments were conducted in a 25 mL Schlenk reaction tube under O_2 or N_2 atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

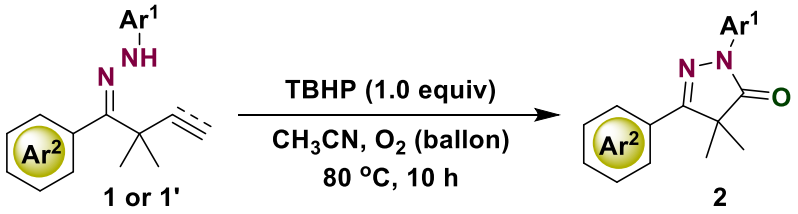
^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) or DMSO-d_6 (δ = 2.50 for ^{1}H-NMR, δ = 39.60 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz).

The starting materials **1a**-**1u**, **2a'**, **2c'**, **2g'**, **2i'** were synthetized according to methods reported previous literatures.[1,2]

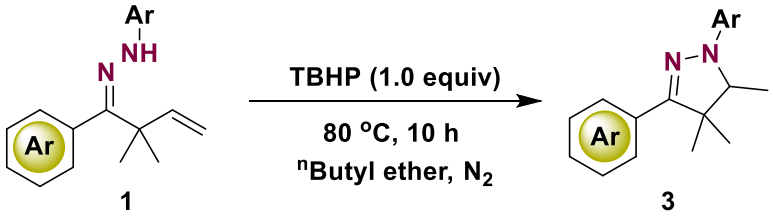
[1] M. Chen, L. Wang, P. Ren, X. Hou, Z. Fang, M. Han and W. Li, *Org. Lett.*, **2018**, *20*, 510.

[2] X. Peng, D. Wei, W. Han, F. Chen, W. Yu and B. Han, *ACS Catal.*, **2017**, *7*, 7830.

2. General procedure for the synthesis of 2 and 3



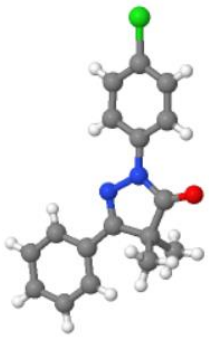
A mixture of β,γ-unsaturated hydrazone **1** or **1'** (0.2 mmol) and TBHP (40 μL, 1.0 equiv, 5.0-6.0 mol/L in decane) in CH_3CN (2 mL) was charged in a 25 mL Schlenk reaction tube . Then the Schlenk reaction tube was stirred at 80 ^oC under O_2 (1 atm, balloon) for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph to give the desired product **2**.



A mixture of β,γ-unsaturated hydrazone **1** (0.2 mmol) and TBHP (40 μL, 1.0 equiv, 5.0-6.0 mol/L in decane) in ^{n}Butyl ether (2 mL) was charged in a 25 mL Schlenk reaction tube under N_2. Then the Schlenk reaction tube was stirred at 80 ^oC for 10 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph to give the desired product **3**.

3. Crystal data of 2c, 4, 3f

Crystallographic data for compound **2c** (CCDC-1916783) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



ORTEP view with ellipsoids (at the 30% probability level)

```
Bond precision:  C-C = 0.0038 A          Wavelength=0.71073

Cell:            a=5.9361(7)    b=26.091(3)         c=10.7999(11)
                 alpha=90       beta=98.444(11)     gamma=90
Temperature:     298 K

                 Calculated                 Reported
Volume           1654.5(3)                  1654.6(3)
Space group      P 21/n                     P 1 21/n 1
Hall group       -P 2yn                     -P 2ybc (x-
Moiety formula   C18 H17 N3 O4              C18 H17 N3 O4
Sum formula      C18 H17 N3 O4              C18 H17 N3 O4
Mr               339.35                     339.35
Dx,g cm-3        1.362                      1.362
Z                4                          4
Mu (mm-1)        0.098                      0.098
F000             712.0                      712.4
F000'            712.35
h,k,lmax         7,31,12                    7,30,12
Nref             2905                       2898
Tmin,Tmax                                   0.501,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.501 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.000

R(reflections)= 0.0591( 2078)     wR2(reflections)= 0.1542( 2898)

S = 1.083                 Npar= 229
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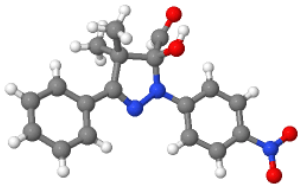
Crystallographic data for compound **4** (CCDC-1876777) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



ORTEP view with ellipsoids (at the 30% probability level)

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=5.9361(7) b=26.091(3) c=10.7999(11)
alpha=90 beta=98.444(11) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	1654.5(3)	1654.6(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2ybc (x-
Moiety formula	C18 H17 N3 O4	C18 H17 N3 O4
Sum formula	C18 H17 N3 O4	C18 H17 N3 O4
Mr	339.35	339.35
Dx,g cm-3	1.362	1.362
Z	4	4
Mu (mm-1)	0.098	0.098
F000	712.0	712.4
F000'	712.35	
h,k,lmax	7,31,12	7,30,12
Nref	2905	2898
Tmin,Tmax		0.501,1.000
Tmin'		

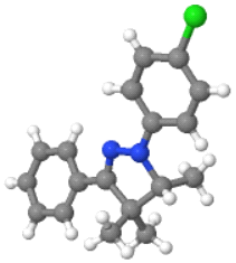
Correction method= # Reported T Limits: Tmin=0.501 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.000

R(reflections)= 0.0591(2078) wR2(reflections)= 0.1542(2898)

S = 1.083 Npar= 229

Crystallographic data for compound **3f** (CCDC-1916788) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



ORTEP view with ellipsoids (at the 30% probability level)

Bond precision: C-C = 0.0052 A Wavelength=0.71073

Cell: a=8.2526(9) b=9.1103(10) c=21.0646(18)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1583.7(3)	1583.7(3)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C18 H19 Cl N2	C18 H19 Cl N2
Sum formula	C18 H19 Cl N2	C18 H19 Cl N2
Mr	298.80	298.80
Dx,g cm-3	1.253	1.253
Z	4	4
Mu (mm-1)	0.236	0.236
F000	632.0	632.0
F000'	632.78	
h,k,lmax	11,12,28	11,12,28
Nref	4320[2475]	3381
Tmin,Tmax	0.972,0.977	0.951,1.000
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.951 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.37/0.78 Theta(max)= 29.259

R(reflections)= 0.0608(2179) wR2(reflections)= 0.1062(3381)

S = 1.010 Npar= 193

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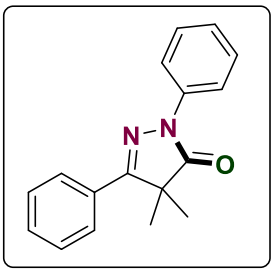
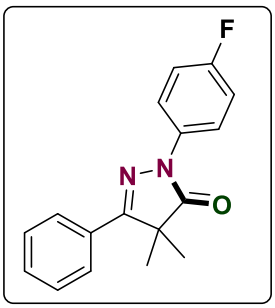
4. Characterization data for products

4,4-dimethyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (2a)



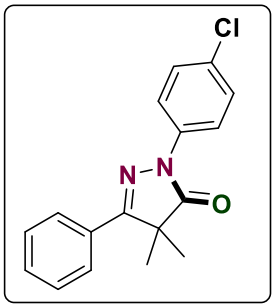
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (44.8 mg, 85%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 2H), 7.95 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.53 – 7.43 (m, 5H), 7.25 (t, *J* = 7.4 Hz, 1H), 1.64 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 162.4, 138.3, 130.7, 130.4, 128.9, 128.9, 126.6, 125.2, 118.9, 49.9, 23.0. HRMS (ESI, m/z) calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335; found: 265.1338.

2-(4-fluorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2b)



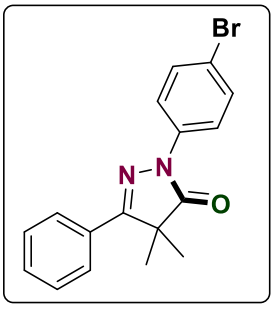
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (36.7 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.96 – 7.90 (m, 2H), 7.53 – 7.47 (m, 3H), 7.18 – 7.11 (m, 2H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 162.6, 160.0 (*J* = 243.8 Hz), 134.4 (*J* = 2.5 Hz), 130.6, 130.5, 128.9, 126.6, 120.6 (*J* = 7.5 Hz), 115.6 (*J* = 22.5 Hz), 49.9, 23.0. HRMS (ESI, m/z) calcd for $C_{17}H_{16}FN_2O$ $[M+H]^+$: 283.1241; found: 283.1240.

2-(4-chlorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2c)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (49.8 mg, 83%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.91 – 7.87 (m, 2H), 7.50 – 7.43 (m, 4H), 7.25 (tt, *J* = 7.2, 1.2 Hz, 1H), 1.62 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 161.3, 138.1, 136.4, 129.2, 129.1, 128.9, 127.8, 125.3, 118.9, 49.7, 22.3. HRMS (ESI, m/z) calcd for $C_{17}H_{16}ClN_2O$ $[M+H]^+$: 299.0946; found: 299.0947.

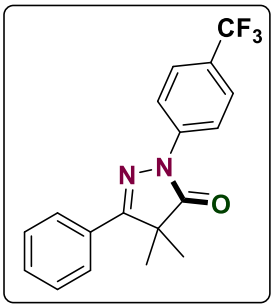
2-(4-bromophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2d)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (47.6 mg, 70%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.93 (ddd, *J* = 6.9, 2.8, 1.5 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.53 – 7.47 (m, 3H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 162.7, 137.4, 131.9, 130.6, 130.5, 128.9, 126.6, 120.3, 118.0, 50.0, 23.0. HRMS (ESI, m/z) calcd for $C_{17}H_{16}BrN_2O$ $[M+H]^+$: 343.0441; found:

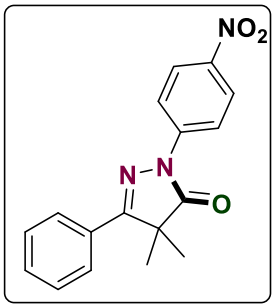
343.0442.

4,4-dimethyl-5-phenyl-2-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (2e)



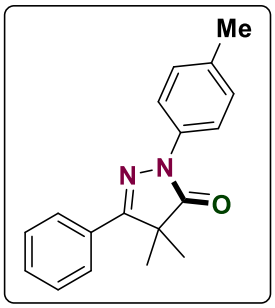
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 15:1, v/v) to give the product as a white solid (46.2 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 2H), 7.99 – 7.92 (m, 2H), 7.74 – 7.69 (m, 2H), 7.52 (tt, *J* = 3.8, 2.8 Hz, 3H), 1.65 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.6, 163.0, 141.0, 130.7, 130.4, 129.0, 126.7, 126.6 (q, *J* = 32.5 Hz), 126.1 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.0 Hz), 118.4, 50.1, 23.0.^{19}F NMR (470 MHz, $CDCl_3$) δ -62.1. HRMS (ESI, m/z) calcd for $C_{18}H_{16}F_3N_2O$ $[M+H]^+$: 333.1209; found: 333.1211.

4,4-dimethyl-2-(4-nitrophenyl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2f)



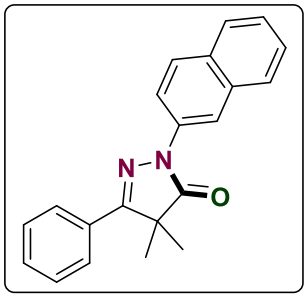
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 5:1, v/v) to give the product as a yellow solid 31.6 mg, 69%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.33 (s, 4H), 8.00 – 7.92 (m, 2H), 7.53 (qd, *J* = 4.4, 1.5 Hz, 3H), 1.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 163.6, 144.0, 143.3, 131.0, 130.1, 129.1, 126.8, 124.9, 118.2, 50.2, 23.1. HRMS (ESI, m/z) calcd for $C_{17}H_{16}N_3O$ $[M+H]^+$: 310.1186; found: 310.1188.

4,4-dimethyl-5-phenyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (2g)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (25.6 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 4H), 7.52 – 7.46 (m, 3H), 7.26 (dd, *J* = 7.7, 1.3 Hz, 2H), 2.40 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 162.2, 135.9, 134.8, 130.8, 130.3, 129.4, 128.9, 126.6, 119.0, 49.8, 23.0, 21.0. HRMS (ESI, m/z) calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$: 279.1492; found: 279.1498.

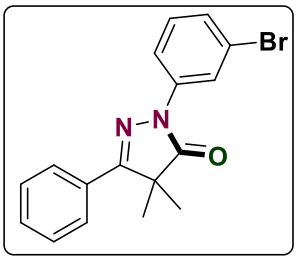
4,4-dimethyl-2-(naphthalen-2-yl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2h)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (44.0 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.2 Hz, 1H), 8.28 (dd, *J* = 8.9, 2.2 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.94 (t, *J* = 9.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.46 (m, 5H), 1.68 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 162.6, 135.9, 133.6, 131.1, 130.7, 130.5, 128.9, 128.8,

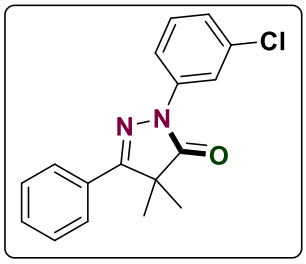
128.1, 127.7, 126.7, 126.5, 125.4, 118.5, 116.1, 50.0, 23.1. HRMS (ESI, m/z) calcd for $C_{21}H_{19}N_2O$ $[M+H]^+$: 315.1492; found: 315.1490.

2-(3-bromophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2i)



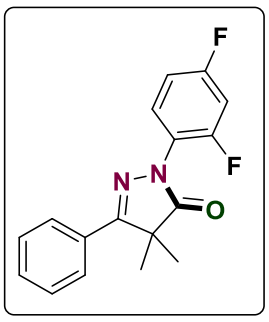
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (34.2 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (t, *J* = 2.0 Hz, 1H), 8.09 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.51 (q, *J* = 3.2, 2.6 Hz, 3H), 7.40 – 7.30 (m, 2H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 162.7, 139.4, 130.6, 130.4, 130.3, 129.0, 128.0, 126.7, 122.6, 121.6, 117.1, 50.0, 23.0. HRMS (ESI, m/z) calcd for $C_{17}H_{16}BrN_2O$ $[M+H]^+$: 343.0441; found: 343.0443.

2-(3-chlorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2j)



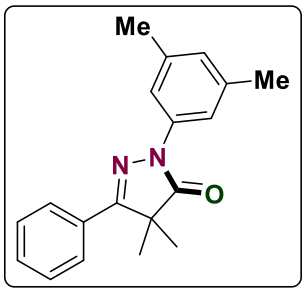
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (44.8 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (t, *J* = 2.1 Hz, 1H), 8.05 (ddd, *J* = 8.3, 2.1, 1.0 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.50 (dp, *J* = 4.9, 1.8 Hz, 3H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.21 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 162.7, 139.3, 134.7, 130.6, 130.4, 130.0, 129.0, 126.7, 125.0, 118.8, 116.6, 50.0, 23.0. HRMS (ESI, m/z) calcd for $C_{17}H_{16}ClN_2O$ $[M+H]^+$: 299.0946; found: 299.0944.

2-(2,4-difluorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2k)



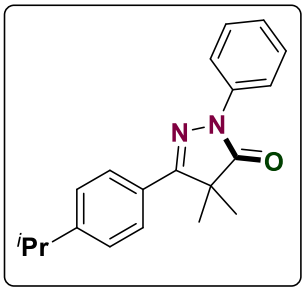
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 15:1, v/v) to give the product as a pale yellow oil (26.4 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.52 (tdd, J = 8.4, 5.9, 0.9 Hz, 1H), 7.47 – 7.43 (m, 3H), 7.01 – 6.95 (m, 2H), 1.63 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 163.2, 160.1 (dd, *J* = 250.0, 10.0 Hz), 157.1 (dd, *J* = 255.0, 12.5 Hz), 130.5, 130.4, 128.9, 128.4 (dd, *J* = 10.0, 2.5 Hz), 126.5, 121.3 (dd, *J* = 12.5, 3.8 Hz), 111.6 (dd, *J* = 22.5, 3.8 Hz), 105.2 (dd, *J* = 26.3, 23.8 Hz), 48.4, 22.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -109.1 (d, *J* = 7.9 Hz), -114.1 (d, *J* = 7.5 Hz). HRMS (ESI, m/z) calcd for $C_{17}H_{15}F_2N_2O$ $[M+H]^+$: 301.1147; found: 301.1149.

2-(3,5-dimethylphenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2l)



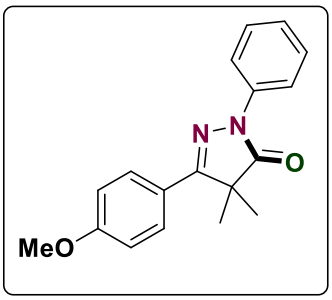
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (31.2 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.70 (d, *J* = 1.5 Hz, 2H), 7.49 (dd, *J* = 5.2, 2.0 Hz, 3H), 6.92 – 6.85 (m, 1H), 2.40 (s, 6H), 1.62 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 162.3, 138.6, 138.1, 130.8, 130.3, 128.9, 127.0, 126.6, 116.8, 49.9, 23.0, 21.6. HRMS (ESI, m/z) calcd for $C_{19}H_{21}N_2O$ $[M+H]^+$: 293.1648; found: 293.1650.

5-(4-isopropylphenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2m)



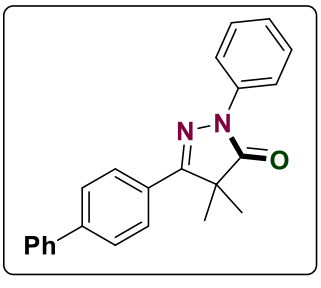
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as pale yellow oil (33.6 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.92 – 7.86 (m, 2H), 7.51 – 7.43 (m, 2H), 7.39 – 7.33 (m, 2H), 7.27 – 7.20 (m, 1H), 2.99 (hept, *J* = 6.8 Hz, 1H), 1.63 (s, 6H), 1.33 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 162.4, 151.6, 138.4, 128.9, 128.3, 127.0, 126.7, 125.1, 118.9, 49.9, 34.1, 23.8, 23.1. HRMS (ESI, m/z) calcd for $C_{20}H_{23}N_2O$ $[M+H]^+$: 307.1805; found: 307.1807.

5-(4-methoxyphenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2n)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 15:1, v/v) to give the product as pale yellow oil (37.6 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H), 7.94 – 7.87 (m, 2H), 7.50 – 7.41 (m, 2H), 7.26 – 7.19 (m, 1H), 7.04 – 6.95 (m, 2H), 3.90 (s, 3H), 1.62 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 162.2, 161.3, 138.4, 128.9, 128.2, 125.0, 123.4, 118.9, 114.3, 55.4, 49.9, 23.1. HRMS (ESI, m/z) calcd for $C_{18}H_{18}N_2NaO_2$ $[M+Na]^+$: 317.1260; found: 317.1265.

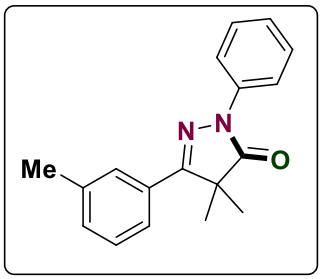
5-([1,1'-biphenyl]-4-yl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2o)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (32.2 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (ddd, *J* = 8.9, 2.6, 1.3 Hz, 2H), 8.07 – 7.96 (m, 2H), 7.77 – 7.70 (m, 2H), 7.70 – 7.61 (m, 2H), 7.50 (ddd, *J* = 15.2, 8.6, 7.3 Hz, 4H), 7.45 – 7.38 (m, 1H), 7.26 (ddd, *J* = 8.7, 6.8, 1.3 Hz, 1H), 1.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 162.0, 143.1, 140.1, 138.3, 129.5, 129.0,

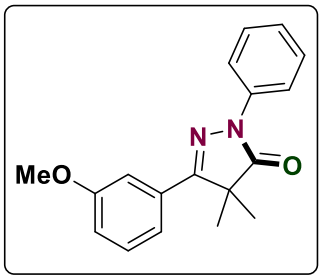
128.9, 128.0, 127.5, 127.1, 127.0, 125.2, 119.0, 49.9, 23.1. HRMS (ESI, m/z) calcd for $C_{23}H_{21}N_2O$ $[M+H]^+$: 341.1648; found: 333.1249.

4,4-dimethyl-2-phenyl-5-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (2p)



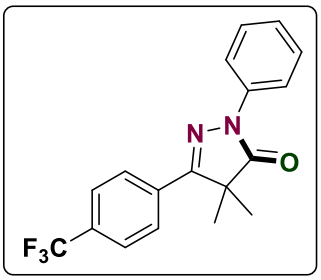
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (37.2 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dt, *J* = 8.0, 1.1 Hz, 2H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.25 (td, *J* = 7.4, 1.1 Hz, 1H), 2.46 (s, 3H), 1.63 (d, *J* = 0.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 162.6, 138.7, 138.3, 131.2, 130.7, 128.9, 128.7, 127.2, 125.2, 123.8, 119.0, 50.0, 23.1, 21.6. HRMS (ESI, m/z) calcd for $C_{18}H_{19}N_2O$ $[M+H]^+$: 279.1492; found: 279.1495.

5-(3-methoxyphenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2q)



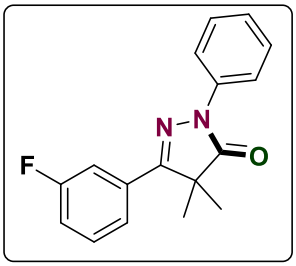
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 15:1, v/v) to give the product as a pale yellow oil (35.9 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 2H), 7.52 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.25 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.04 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 3.91 (s, 3H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 162.2, 159.9, 138.2, 132.0, 129.9, 128.9, 125.2, 119.1, 119.0, 116.0, 112.0, 55.4, 49.9, 23.1. HRMS (ESI, m/z) calcd for $C_{18}H_{19}N_2O_2$ $[M+H]^+$: 295.1441; found: 295.1440.

4,4-dimethyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (2r)



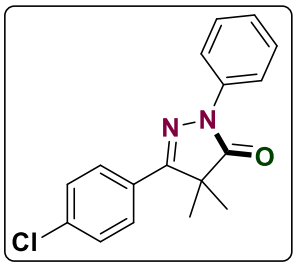
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (45.2 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 4H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.44 (m, 2H), 7.29 – 7.24 (m, 1H), 1.64 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 160.9, 138.0, 134.0, 131.9 (q, *J* = 32.5 Hz), 129.0, 126.8, 125.9 (q, *J* = 3.8 Hz), 125.5, 123.8 (q, *J* = 270.0 Hz), 119.0, 49.68, 22.89.^{19}F NMR (470 MHz, $CDCl_3$) δ -62.9. HRMS (ESI, m/z) calcd for $C_{18}H_{16}F_3N_2O$ $[M+H]^+$: 333.1209; found: 333.1212.

5-(3-fluorophenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2s)



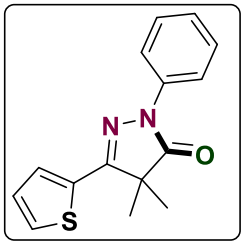
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (32.2 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.72 – 7.65 (m, 2H), 7.50 – 7.42 (m, 3H), 7.28 – 7.22 (m, 1H), 7.19 (tdd, *J* = 8.3, 2.5, 1.0 Hz, 1H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 163.0 (d, *J* = 245.0 Hz), 161.2 (d, *J* = 3.1 Hz), 138.1, 132.8 (d, *J* = 7.9 Hz), 130.5 (d, *J* = 7.5 Hz), 129.0, 125.3, 122.2 (d, *J* = 2.5 Hz), 118.9, 117.4 (d, *J* = 21.3 Hz), 113.4 (d, *J* = 23.2 Hz), 49.7, 23.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -111.5.

5-(4-chlorophenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2t)



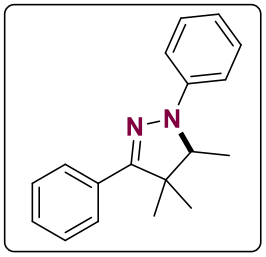
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (43.8 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.96 – 7.91 (m, 2H), 7.52 – 7.48 (m, 3H), 7.44 – 7.40 (m, 2H), 1.63 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 162.7, 136.9, 130.6, 130.5, 130.2, 128.9, 126.6, 120.0, 50.0, 23.0. HRMS (ESI, m/z) calcd for $C_{17}H_{16}ClN_2O$ $[M+H]^+$: 299.0946; found: 299.0949.

4,4-dimethyl-2-phenyl-5-(thiophen-2-yl)-2,4-dihydro-3H-pyrazol-3-one (2u)



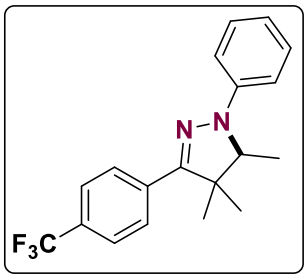
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (31.3 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.51 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.23 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.15 (dd, *J* = 5.1, 3.7 Hz, 1H), 1.62 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7, 158.7, 138.1, 134.2, 128.9, 128.3, 127.7, 127.3, 125.2, 118.9, 50.0, 23.1. HRMS (ESI, m/z) calcd for $C_{15}H_{15}N_2OS$ $[M+H]^+$: 271.0900; found: 271.0903.

4,4,5-trimethyl-1,3-diphenyl-4,5-dihydro-1H-pyrazole (3a)



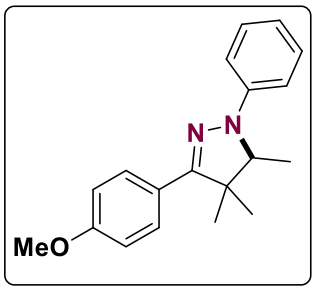
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (41.7 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.47 – 7.39 (m, 2H), 7.40 – 7.32 (m, 3H), 7.27 – 7.22 (m, 2H), 6.92 (tt, *J* = 7.2, 1.2 Hz, 1H), 3.96 (q, *J* = 6.5 Hz, 1H), 1.47 (s, 3H), 1.42 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 144.9, 133.0, 129.1, 128.4, 128.2, 126.7, 119.6, 115.0, 68.0, 50.0, 26.4, 19.4, 11.9. HRMS (ESI, m/z) calcd for $C_{18}H_{21}N_2$ $[M+H]^+$: 265.1699; found: 265.1701

4,4,5-trimethyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (3b)



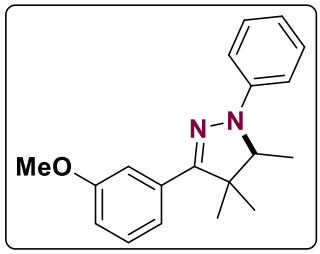
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (41.8 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.27 – 7.21 (m, 2H), 6.98 – 6.90 (m, 1H), 4.01 (q, *J* = 6.5 Hz, 1H), 1.46 (s, 3H), 1.43 (s, 3H), 1.21 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 144.3, 136.5, 129.6 (q, *J* = 32.5 Hz), 129.1, 127.5, 126.6, 125.3 (q, *J* = 3.8 Hz), 123.2, 120.2, 115.1, 68.2, 49.5, 26.4, 19.3, 11.9.^{19}F NMR (470 MHz, $CDCl_3$) δ -62.9. HRMS (ESI, m/z) calcd for $C_{19}H_{20}F_3N_2$ $[M+H]^+$: 333.1573; found: 333.1573.

3-(4-methoxyphenyl)-4,4,5-trimethyl-1-phenyl-4,5-dihydro-1H-pyrazole (3c)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a pale yellow oil (38.8 mg, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.36 – 7.29 (m, 2H), 7.23 – 7.18 (m, 2H), 6.98 – 6.91 (m, 2H), 6.89 (tt, *J* = 7.3, 1.2 Hz, 1H), 3.90 (q, *J* = 6.5 Hz, 1H), 3.87 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.19 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 155.1, 145.1, 129.0, 128.1, 125.5, 119.4, 114.9, 113.8, 67.8, 55.3, 49.8, 26.4, 19.5, 11.9. HRMS (ESI, m/z) calcd for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1805; found: 295.1808.

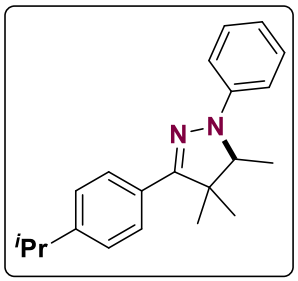
3-(3-methoxyphenyl)-4,4,5-trimethyl-1-phenyl-4,5-dihydro-1H-pyrazole (3d)



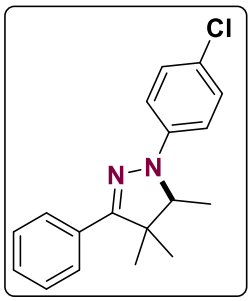
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (44.7 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dt, *J* = 7.5, 1.6 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.26 – 7.19 (m, 2H), 6.97 – 6.86 (m, 2H), 3.95 (q, *J* = 6.5 Hz, 1H), 3.89 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.20 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 154.9, 144.8, 134.3, 129.3, 129.1, 119.6, 119.2, 115.0, 114.0, 112.2, 68.0, 55.3, 49.8, 26.5, 19.4, 11.9. HRMS (ESI, m/z) calcd for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1805; found: 295.1808.

3-(4-isopropylphenyl)-4,4,5-trimethyl-1-phenyl-4,5-dihydro-1H-pyrazole (3e)

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (50.6 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.24 – 7.20 (m, 2H), 6.94 – 6.86 (m, 1H), 3.94 (q, *J* = 6.5 Hz, 1H), 2.97 (hept, *J* = 7.0 Hz, 1H), 1.45 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.20 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 149.1, 145.0, 130.4, 129.0, 126.7, 126.5, 119.4, 114.9, 67.8, 49.8, 34.0, 26.5, 23.0, 23.9, 19.4, 11.9. HRMS (ESI, m/z) calcd for $C_{21}H_{27}N_2$ $[M+H]^+$: 307.2169; found: 307.2167.

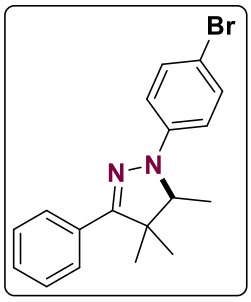


1-(4-chlorophenyl)-4,4,5-trimethyl-3-phenyl-4,5-dihydro-1H-pyrazole (3f)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (40.8 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.47 – 7.33 (m, 3H), 7.30 – 7.25 (m, 2H), 7.17 – 7.11 (m, 2H), 3.91 (q, *J* = 6.5 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.17 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 143.5, 132.6, 128.9, 128.4, 126.8, 124.3, 116.0, 68.0, 50.0, 26.4, 19.4, 11.8. HRMS (ESI, m/z) calcd for $C_{18}H_{20}ClN_2$ $[M+H]^+$: 299.1310; found: 299.1311.

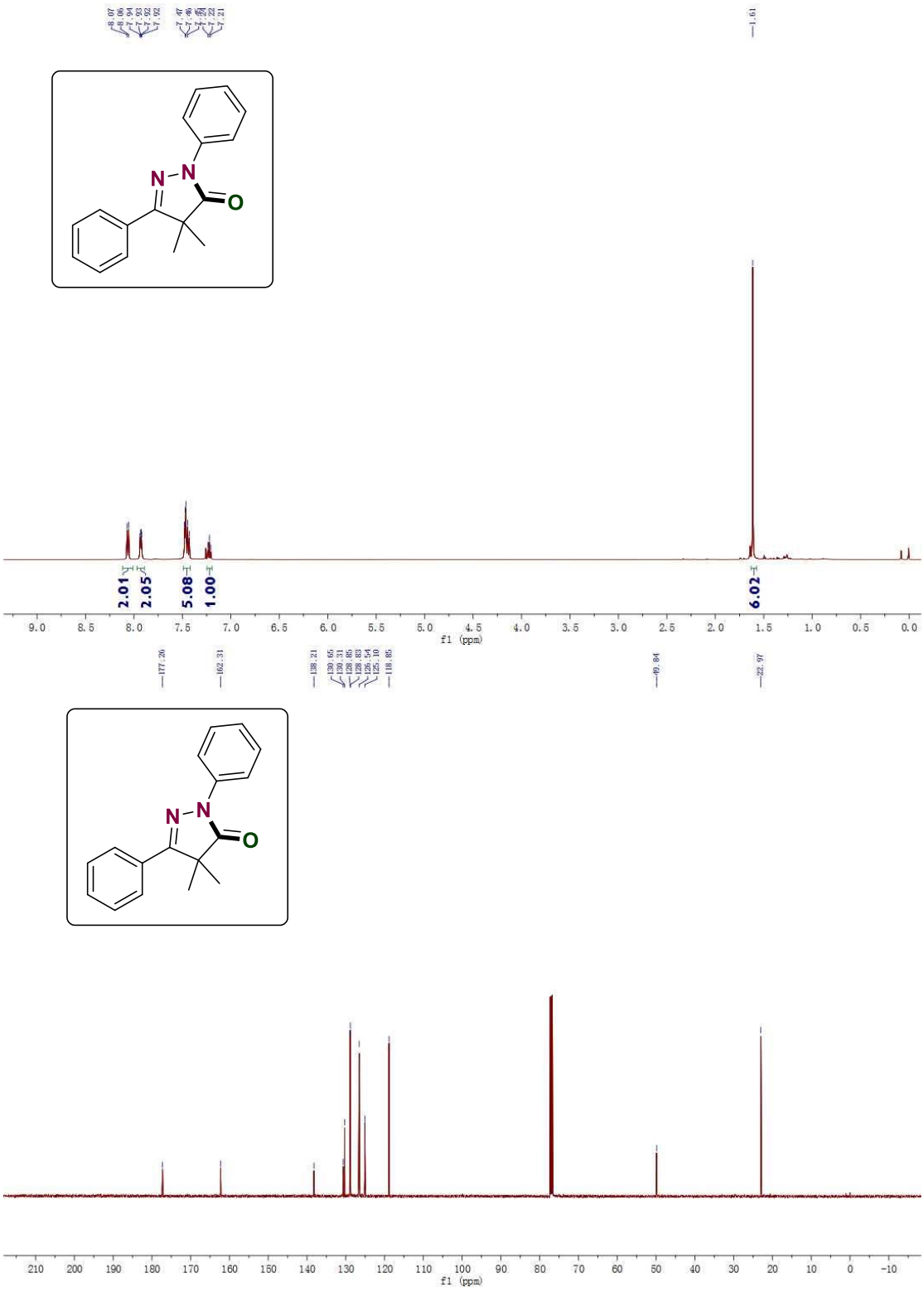
1-(4-bromophenyl)-4,4,5-trimethyl-3-phenyl-4,5-dihydro-1H-pyrazole (3g)



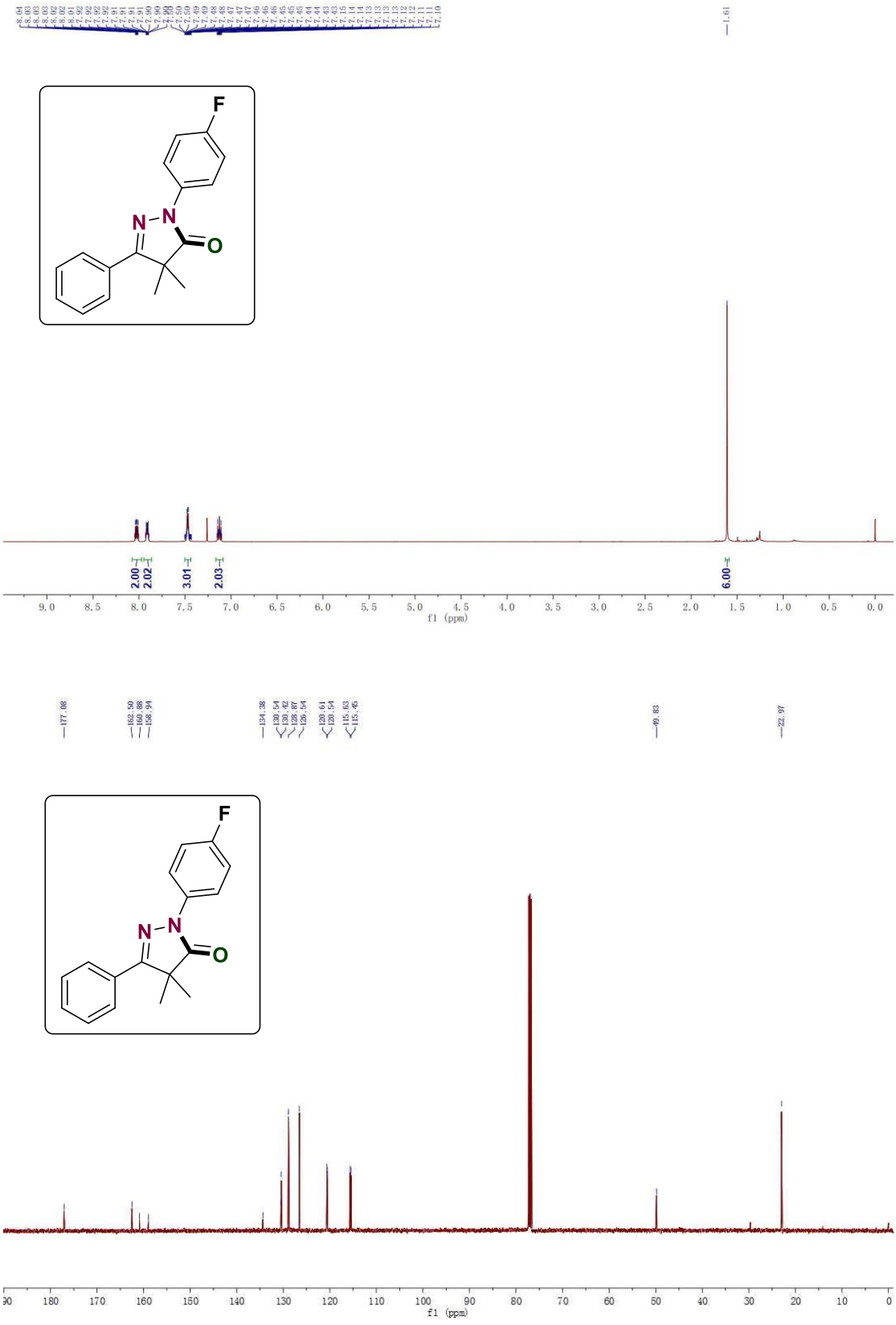
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (40.8 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.40 (dq, *J* = 8.4, 6.9 Hz, 5H), 7.11 – 7.06 (m, 2H), 3.92 (q, *J* = 6.5 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 143.8, 132.6, 131.8, 128.5, 128.4, 126.8, 116.3, 111.5, 67.8, 50.0, 26.5, 19.4, 11.8. HRMS (ESI, m/z) calcd for $C_{18}H_{20}BrN_2$ $[M+H]^+$: 343.0804; found: 343.0804.

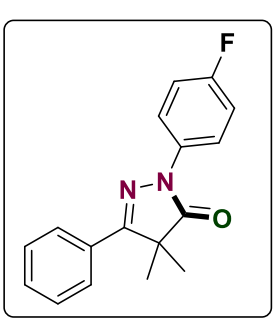
5. NMR spectroscopic data

4,4-dimethyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (2a)



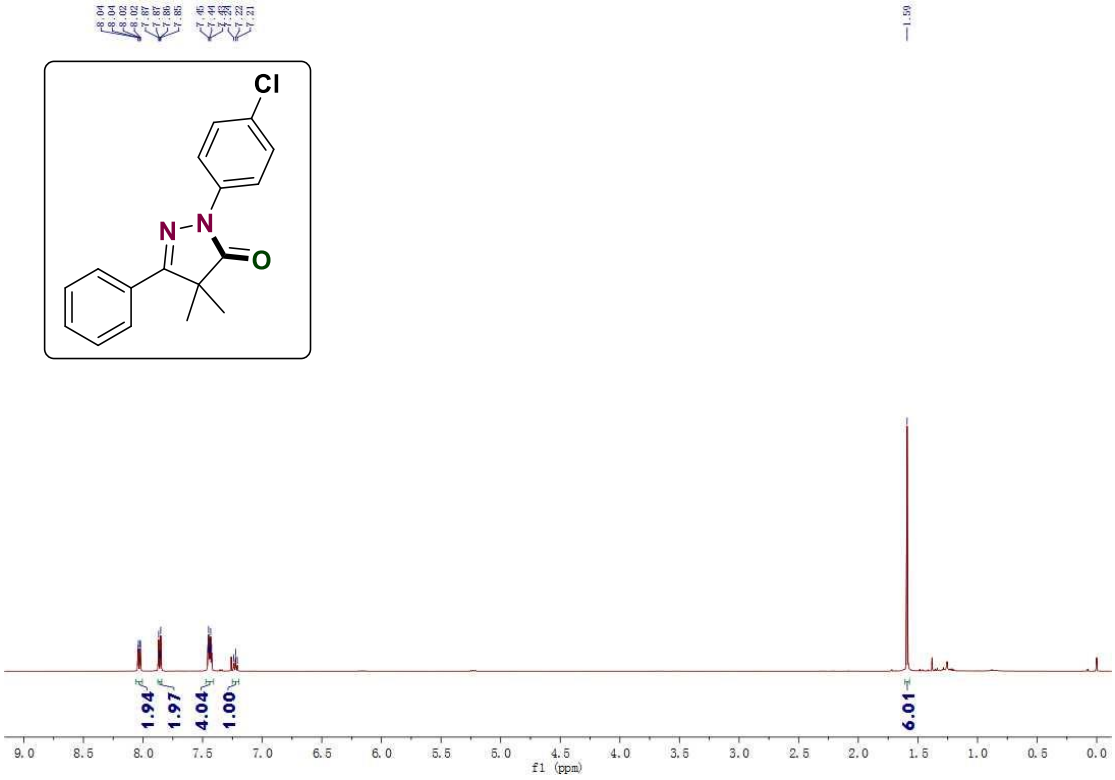
2-(4-fluorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2b)

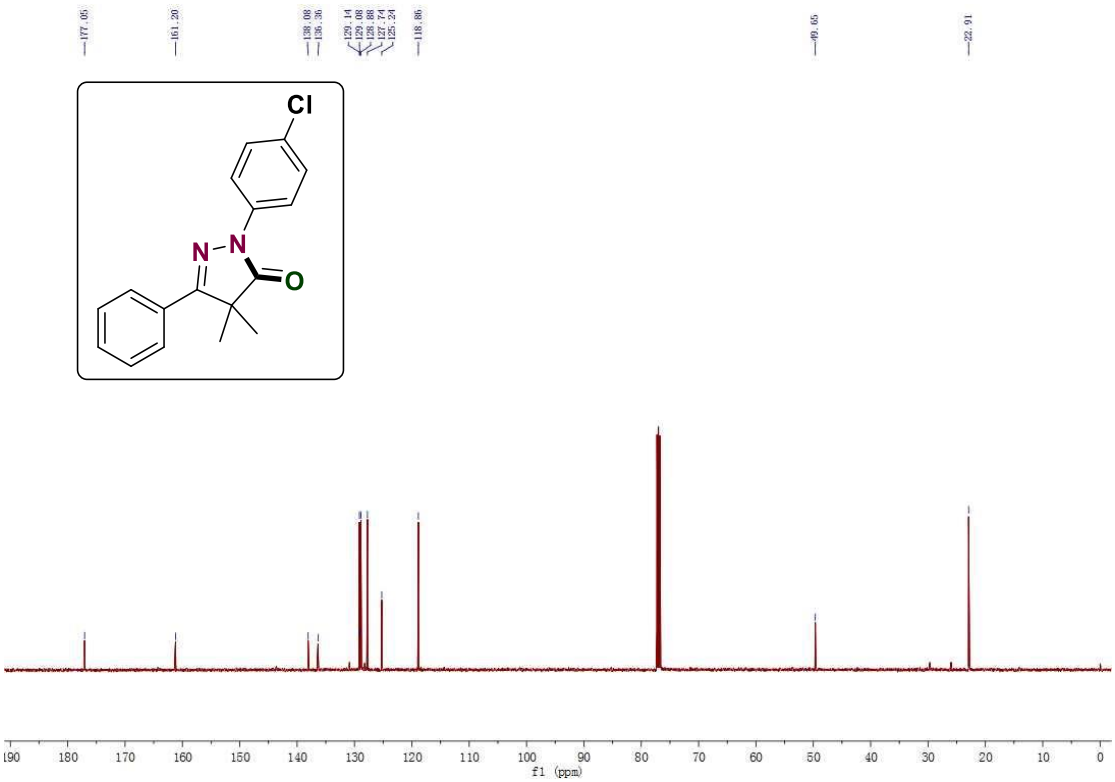



F
N
N
O

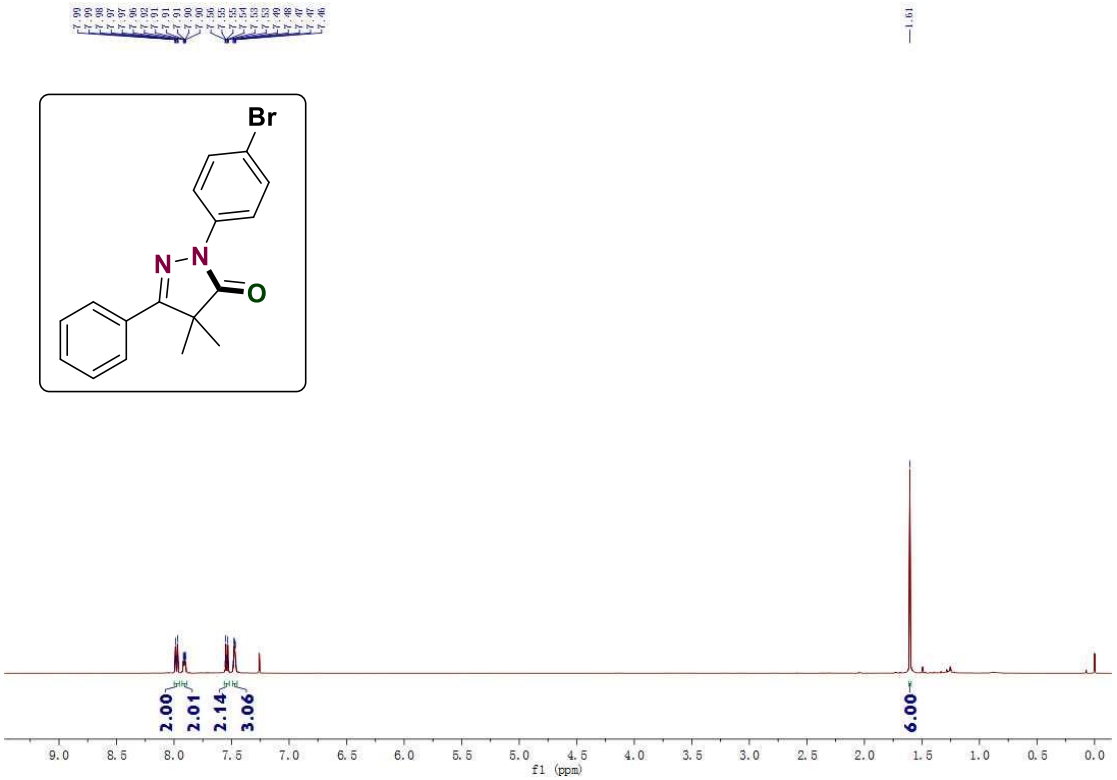
-117.14
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

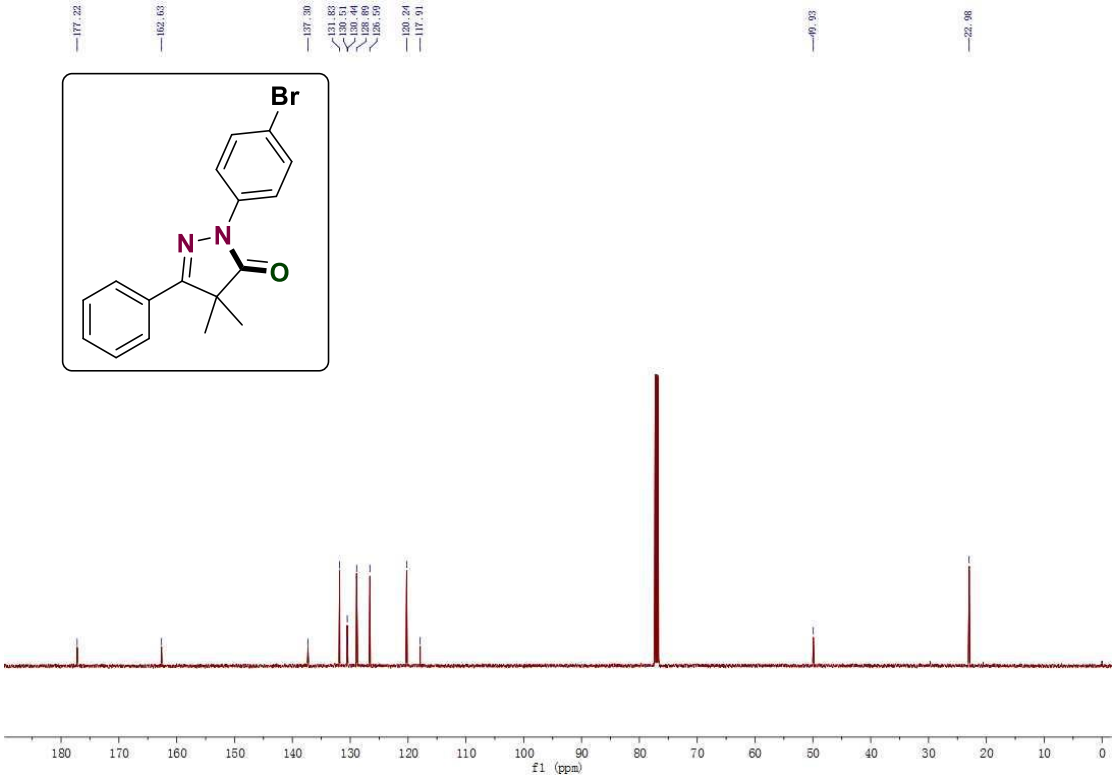
2-(4-chlorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2c)



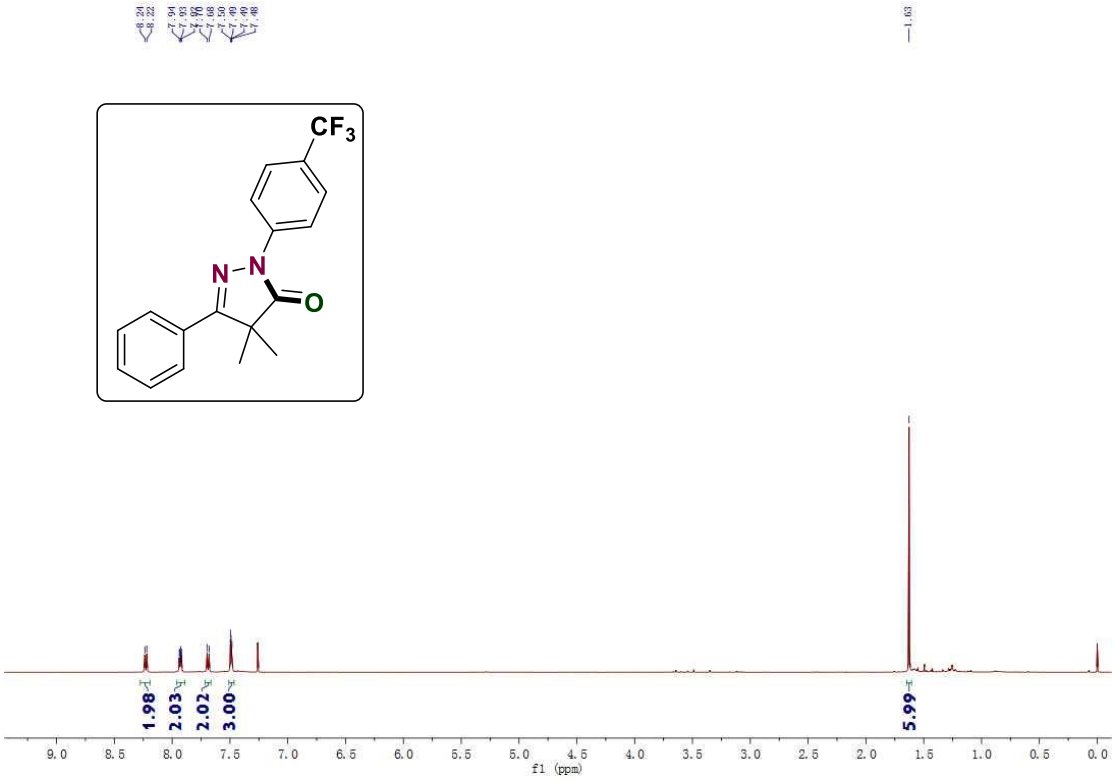


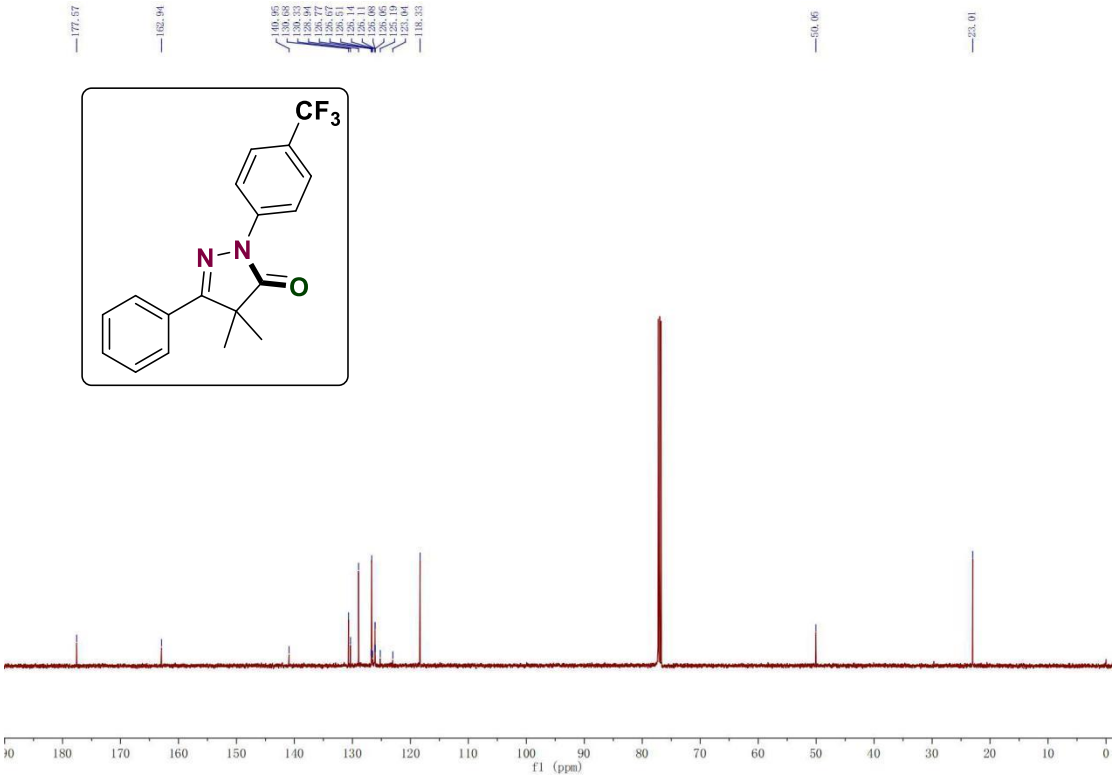
2-(4-bromophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2d)

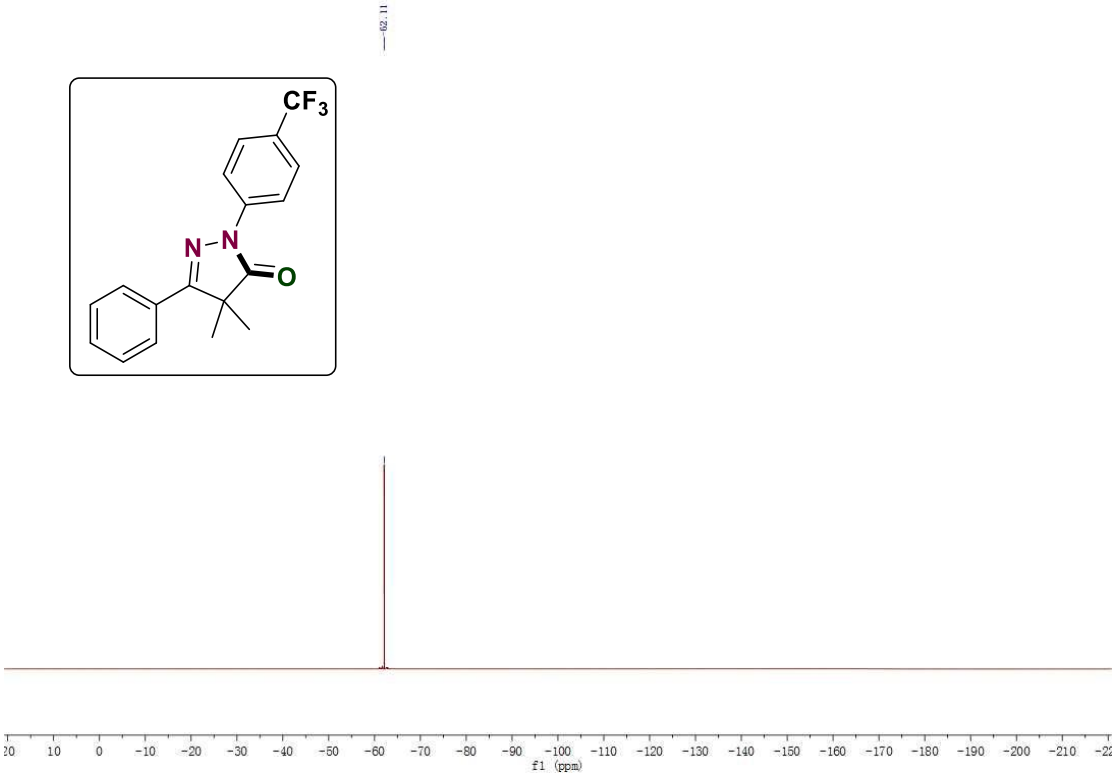




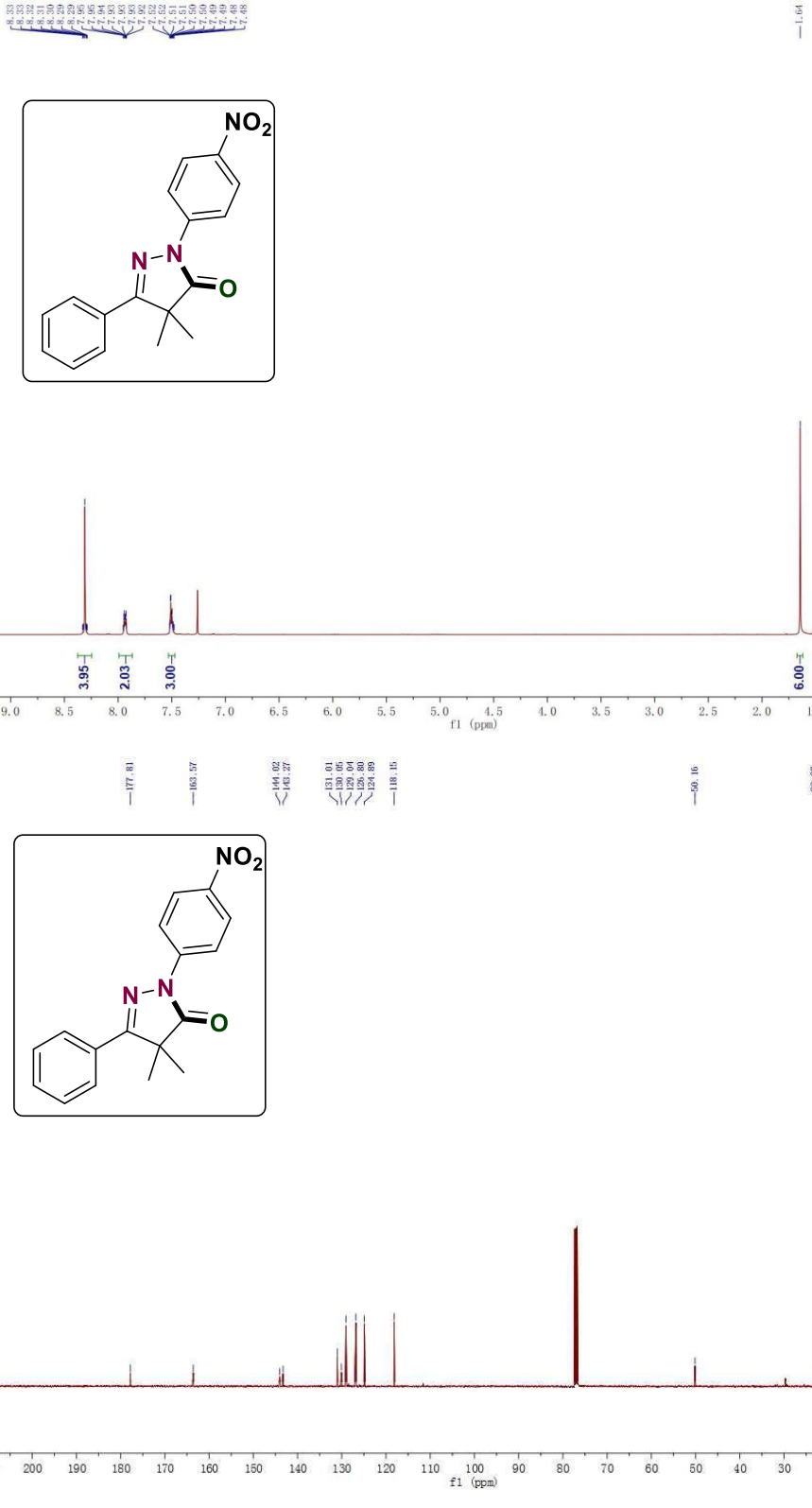
4,4-dimethyl-5-phenyl-2-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (2e)



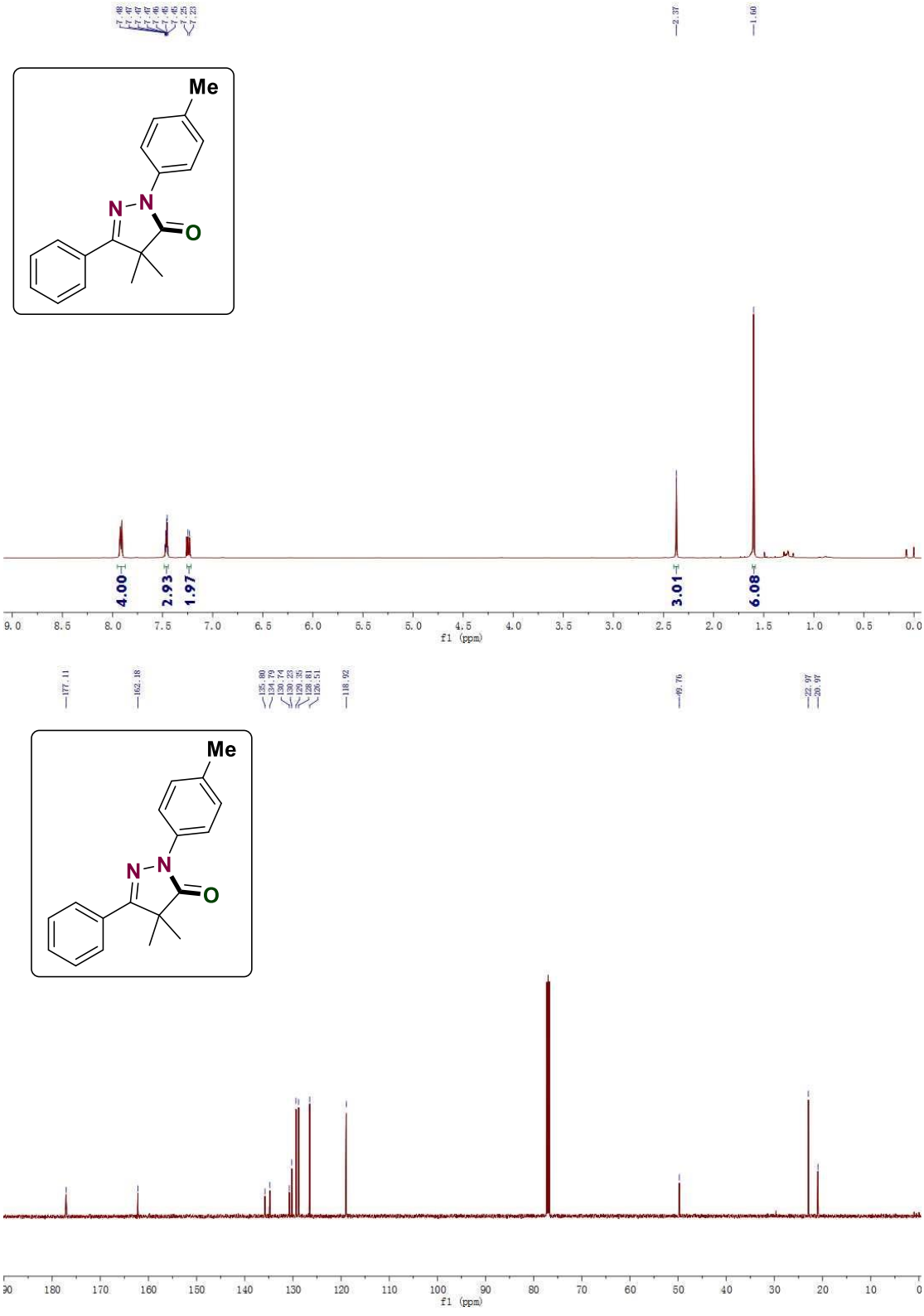



CF3
N
N
O
-62.11
f1 (ppm)

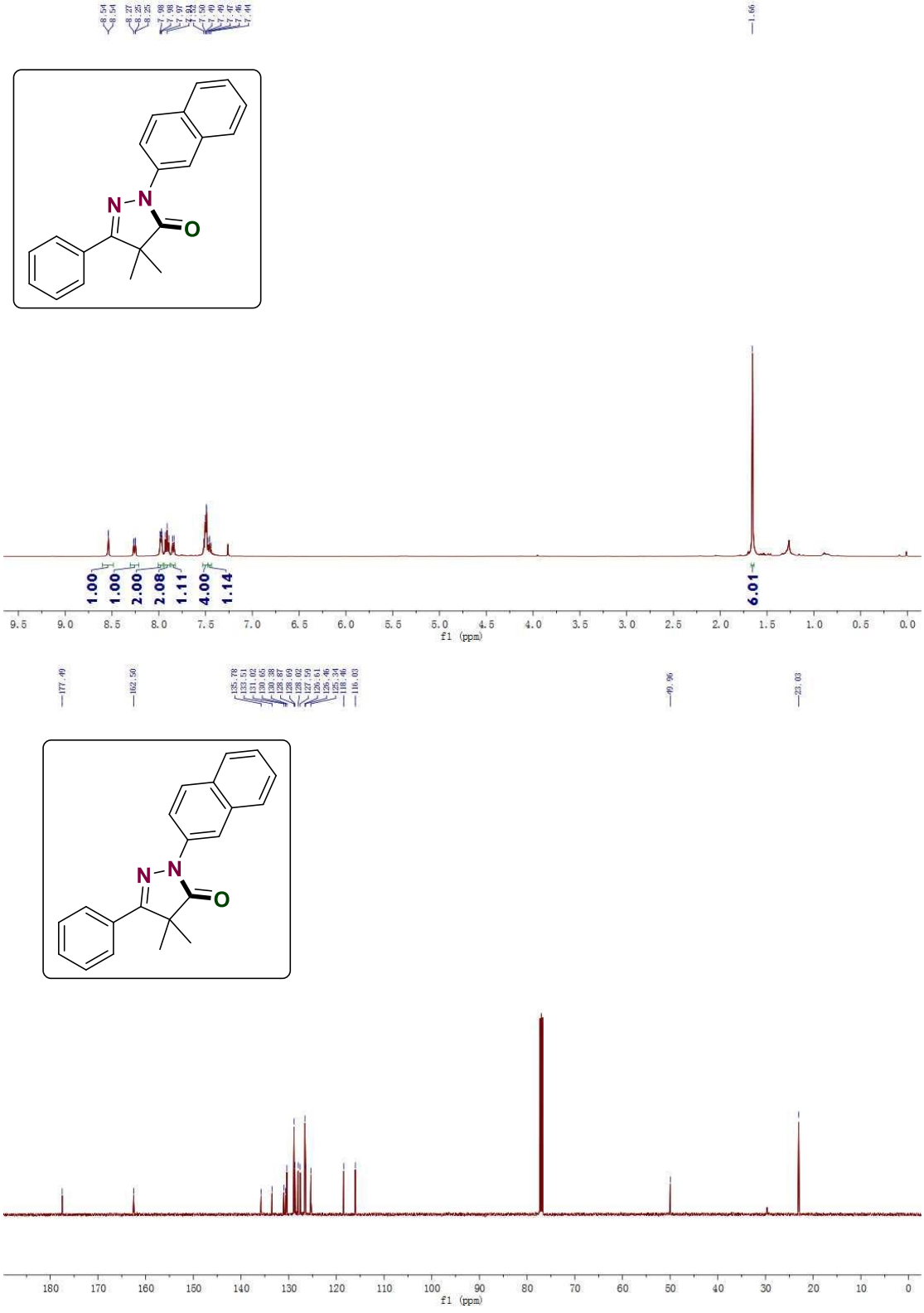
4,4-dimethyl-2-(4-nitrophenyl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2f)



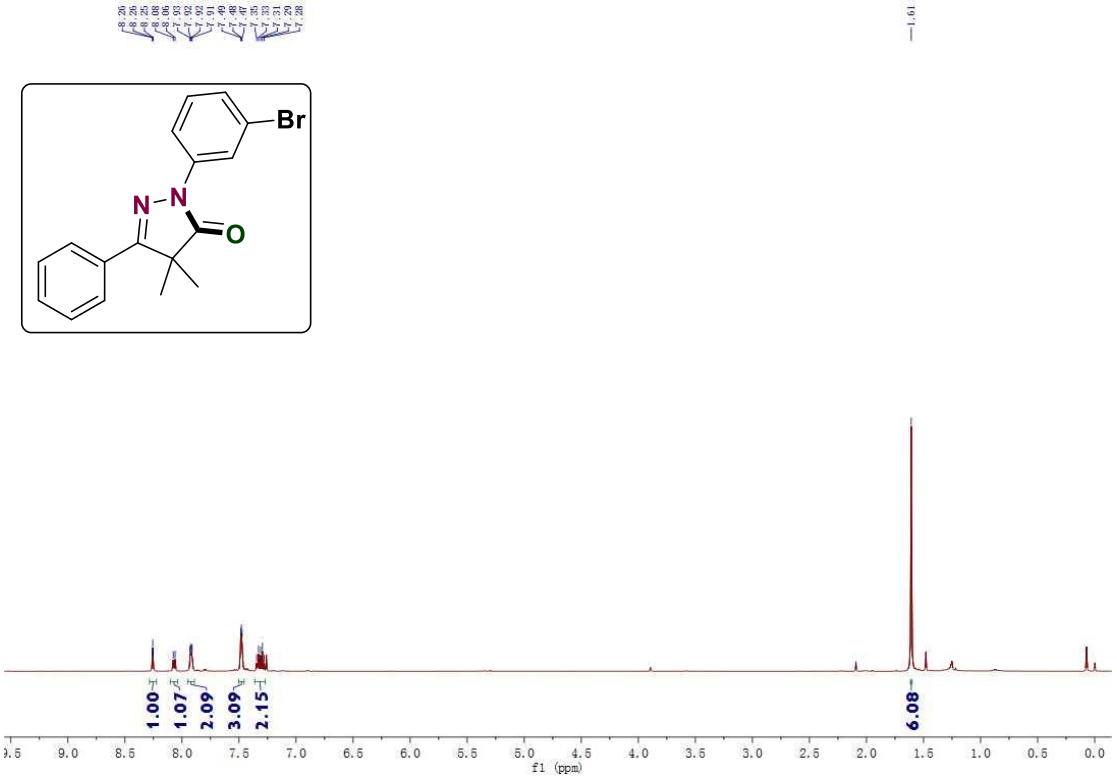
4,4-dimethyl-5-phenyl-2-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (2g)

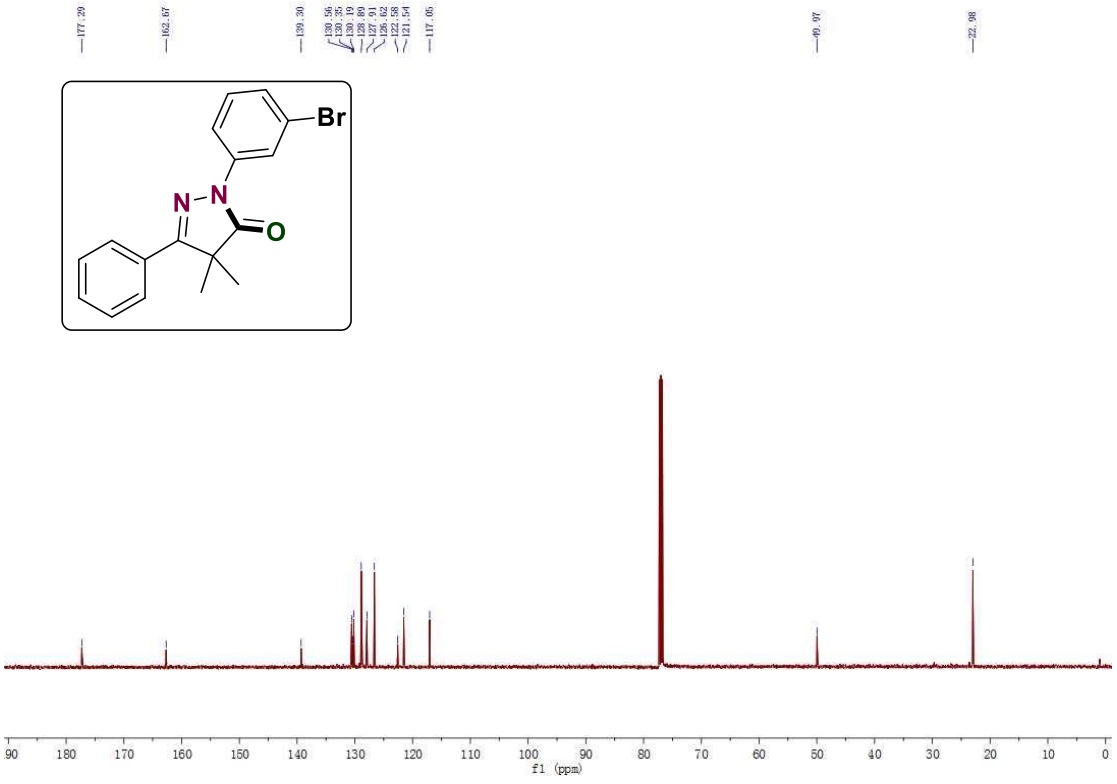


4,4-dimethyl-2-(naphthalen-2-yl)-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2h)

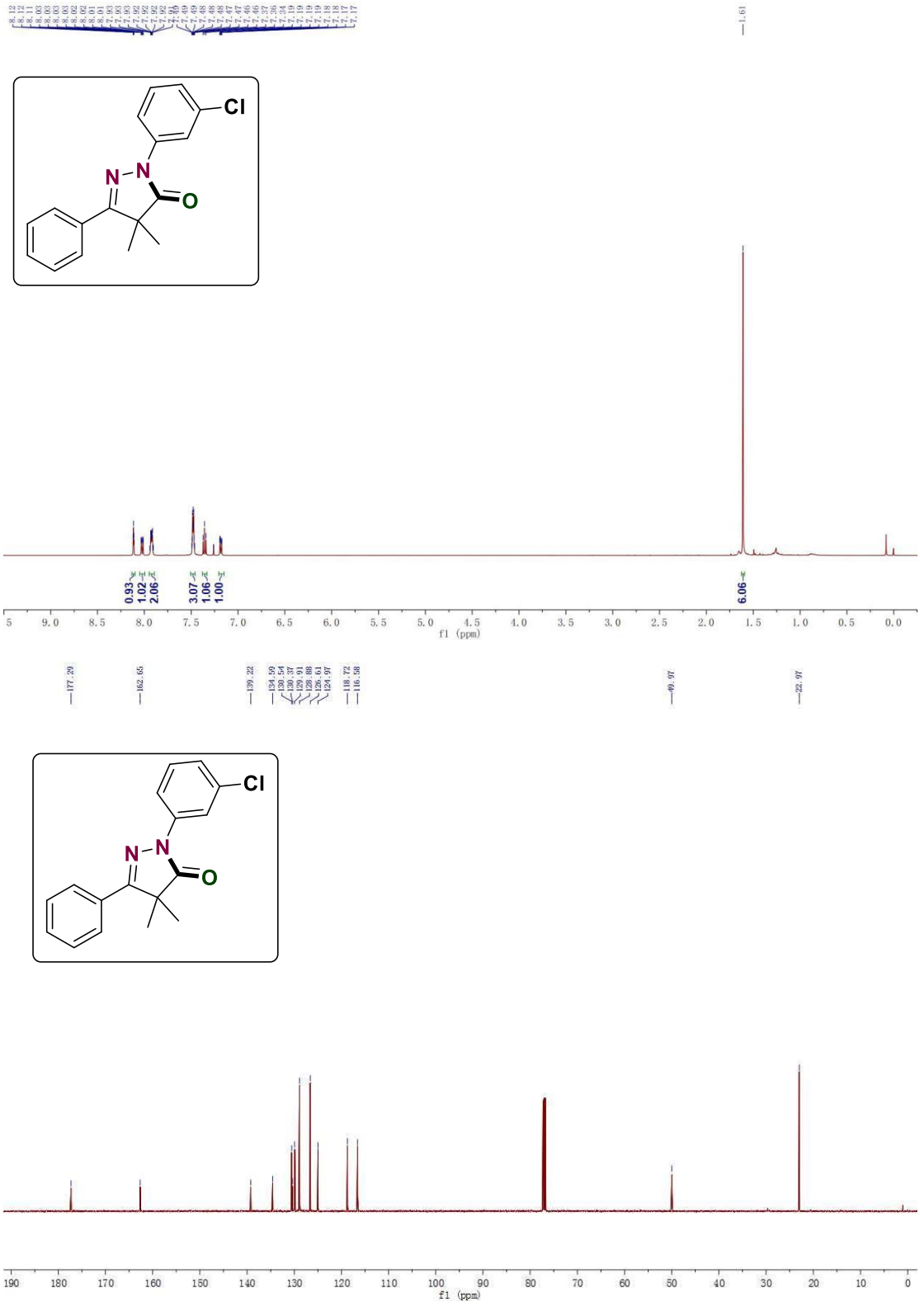


2-(3-bromophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2i)

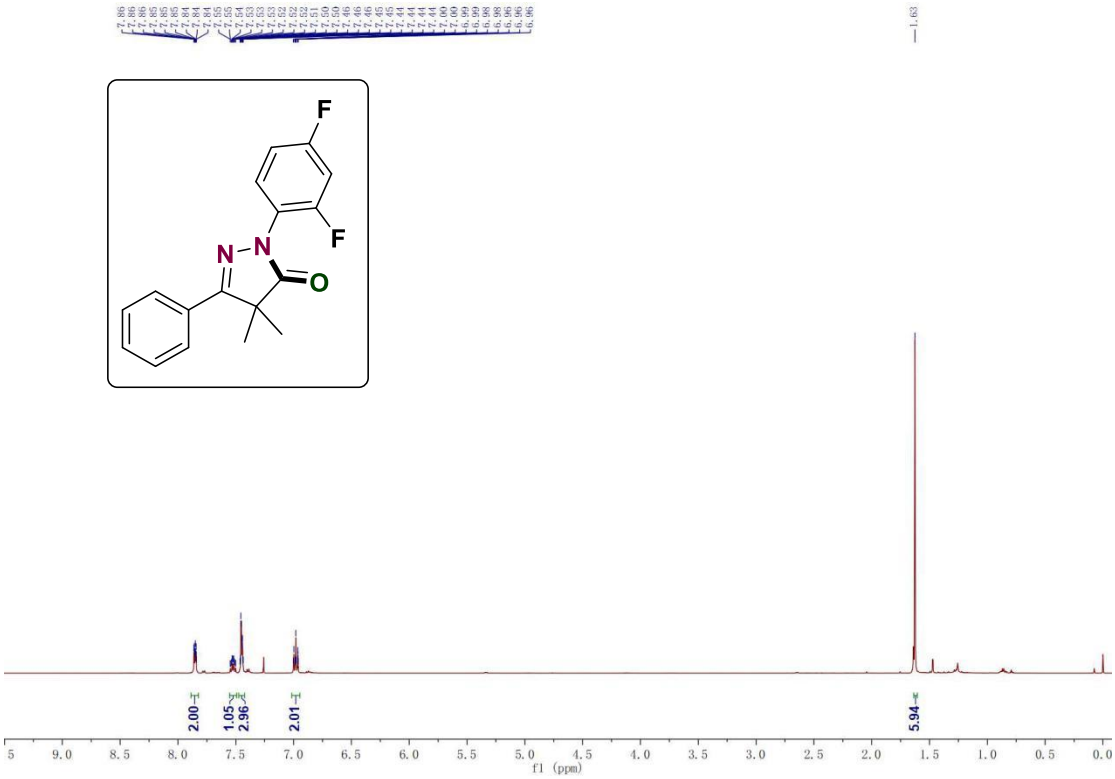


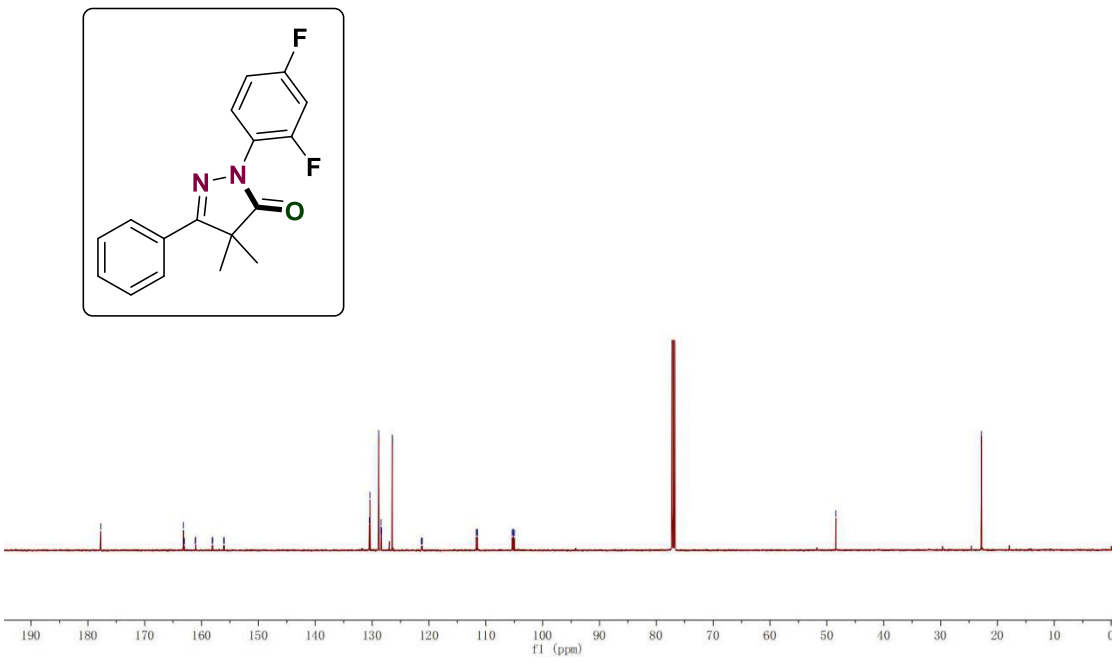


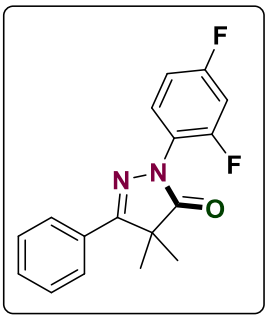
2-(3-chlorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2j)



2-(2,4-difluorophenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2k)

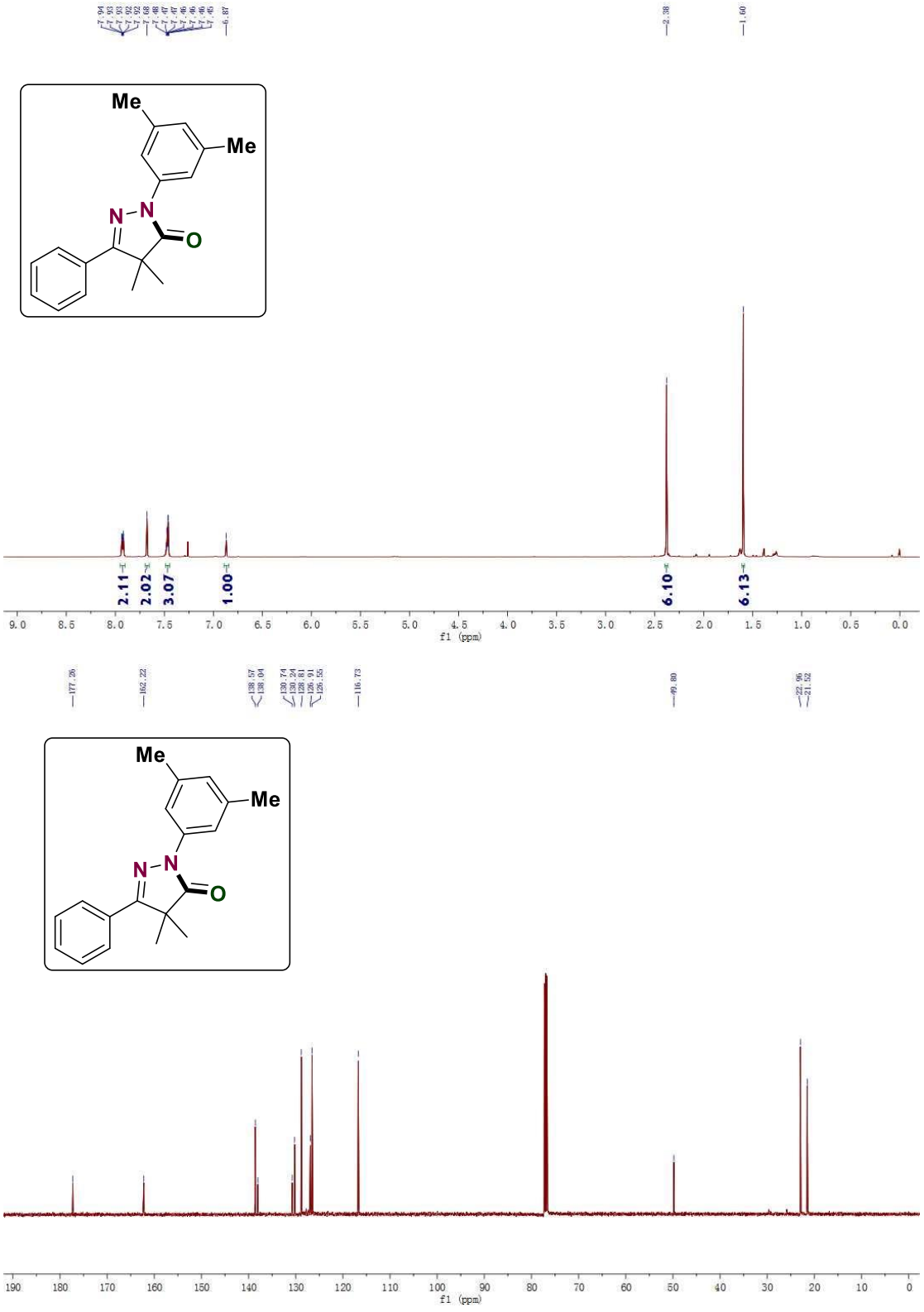




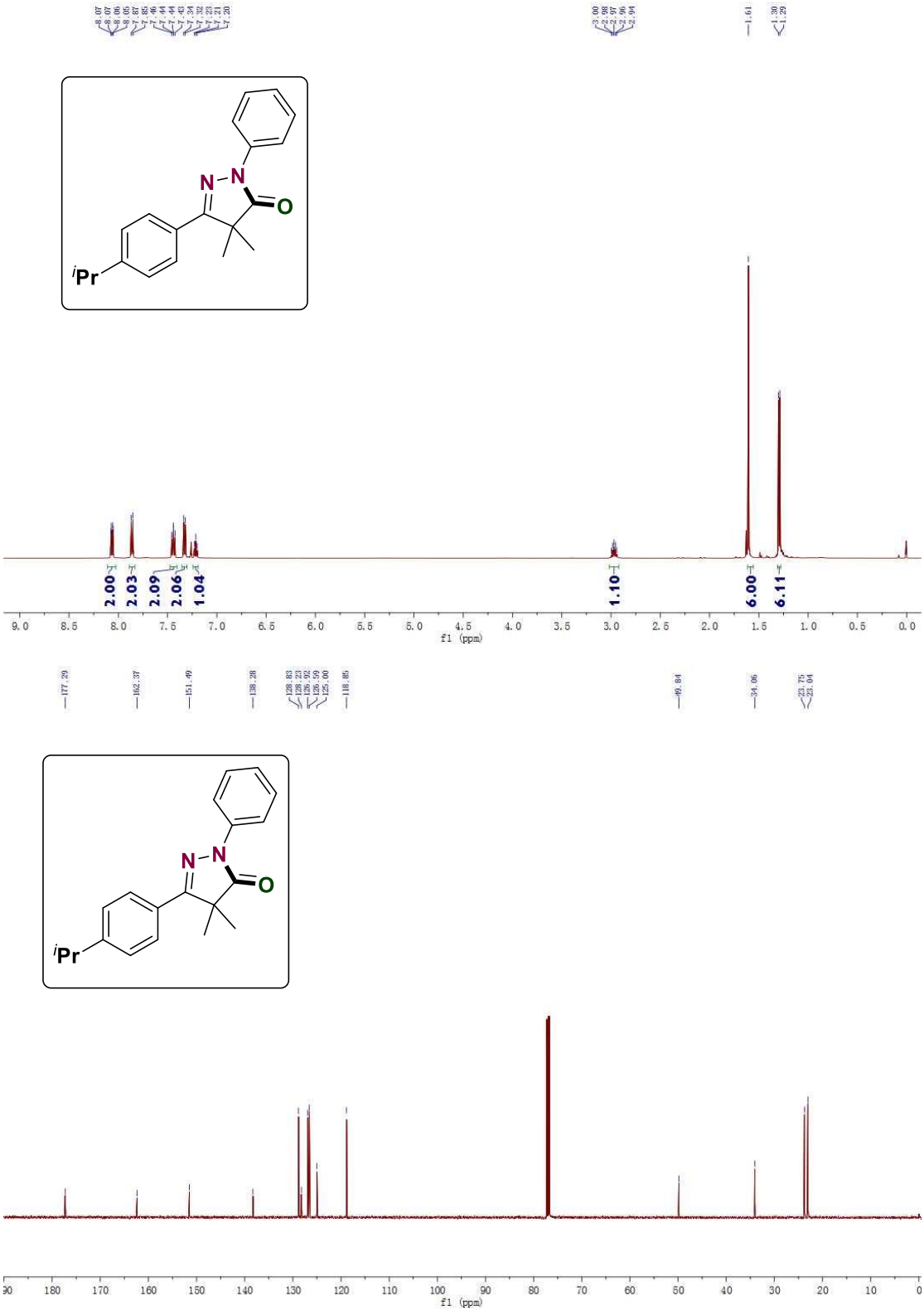

F
F
N
N
O

-109.67
-109.69
-114.69
-114.71
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

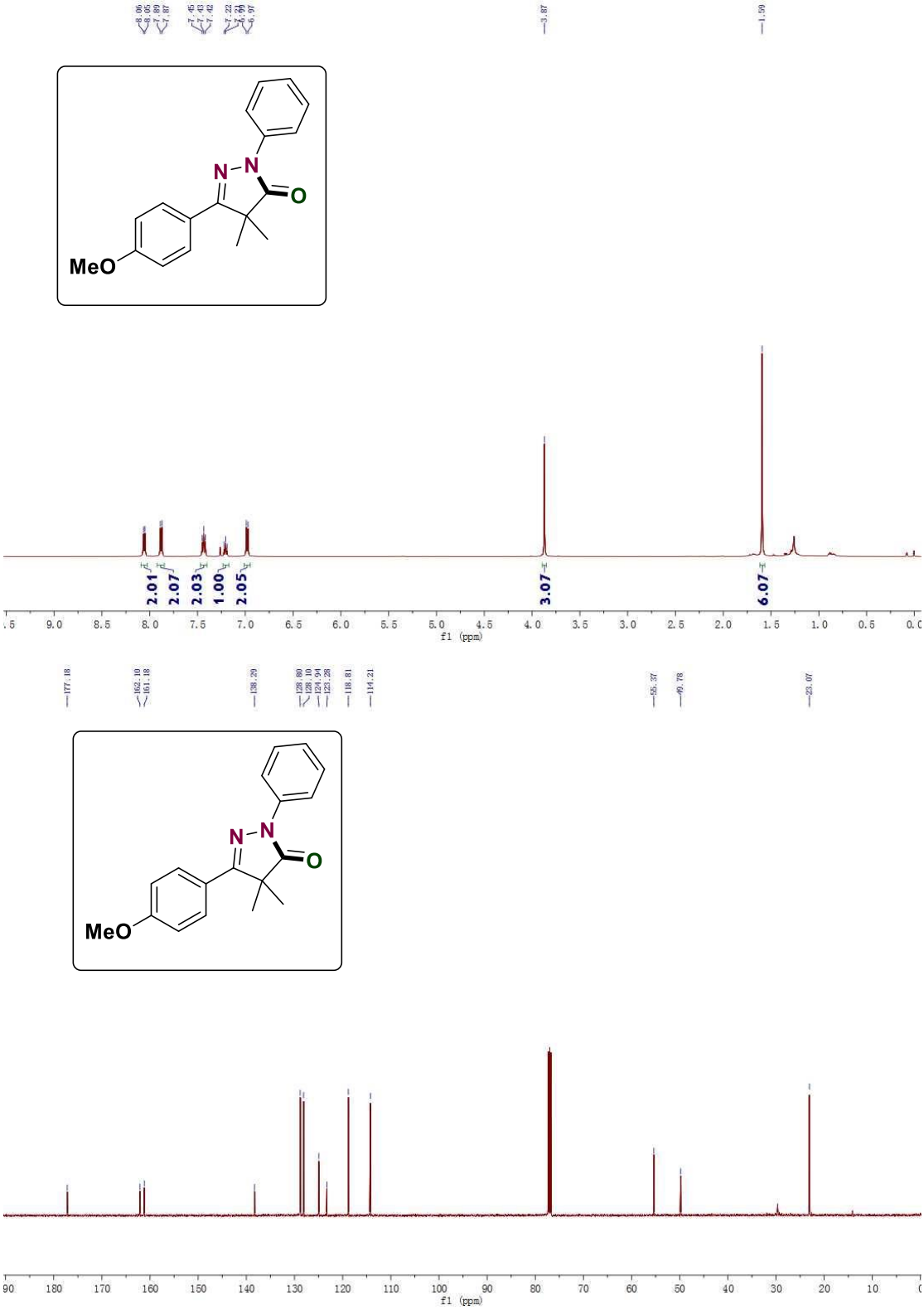
2-(3,5-dimethylphenyl)-4,4-dimethyl-5-phenyl-2,4-dihydro-3H-pyrazol-3-one (2l)



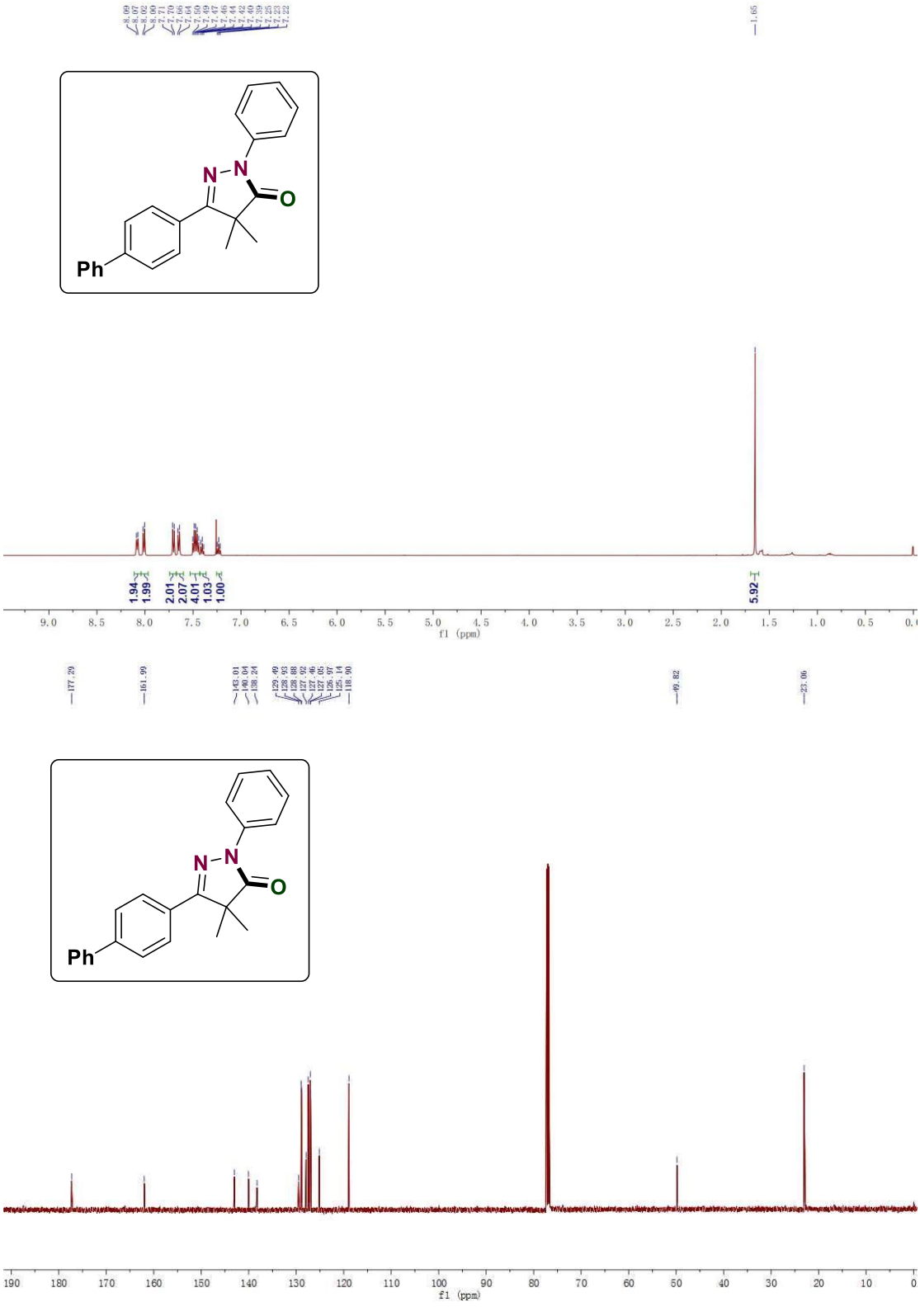
5-(4-isopropylphenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2m)



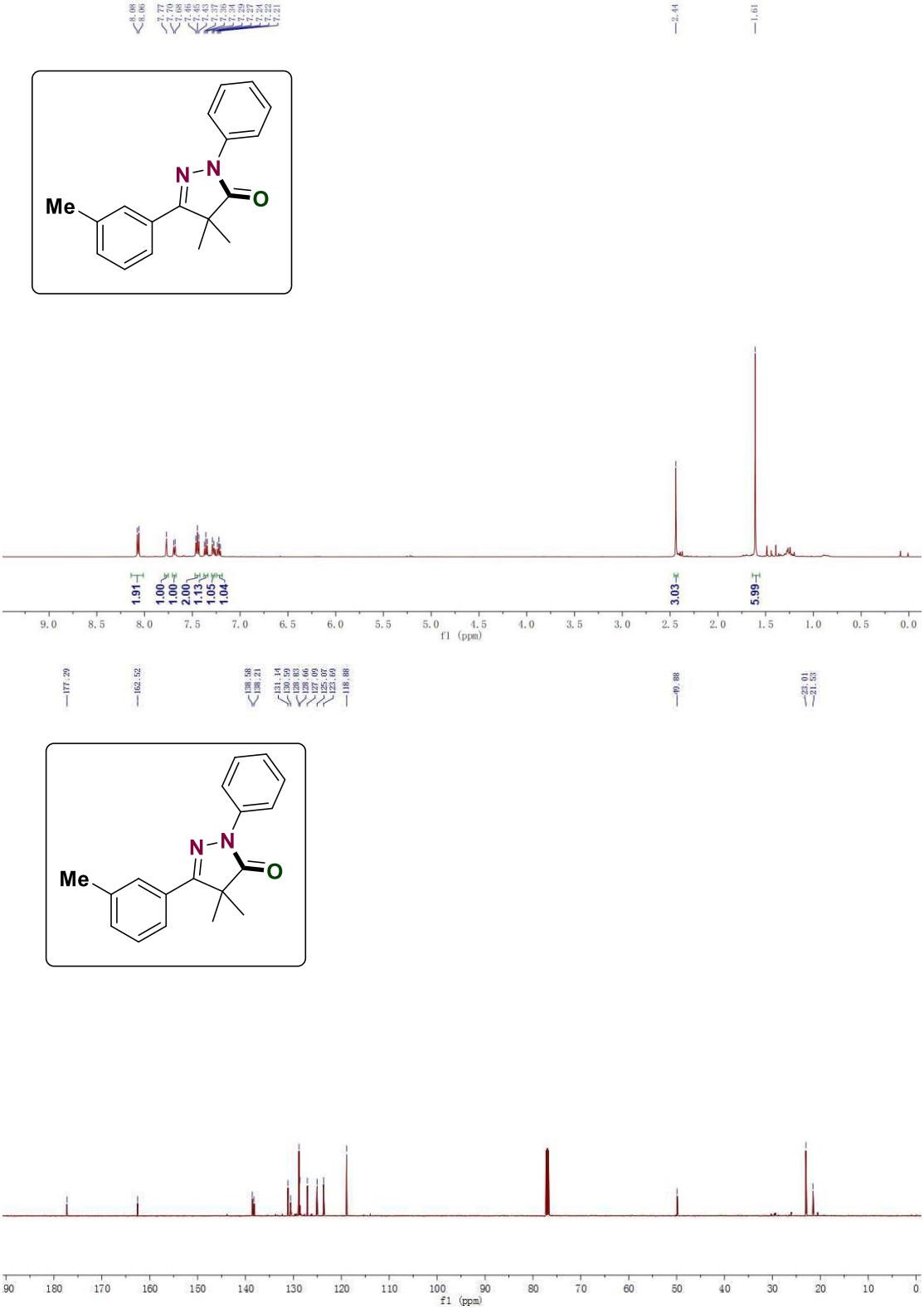
5-(4-methoxyphenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2n)



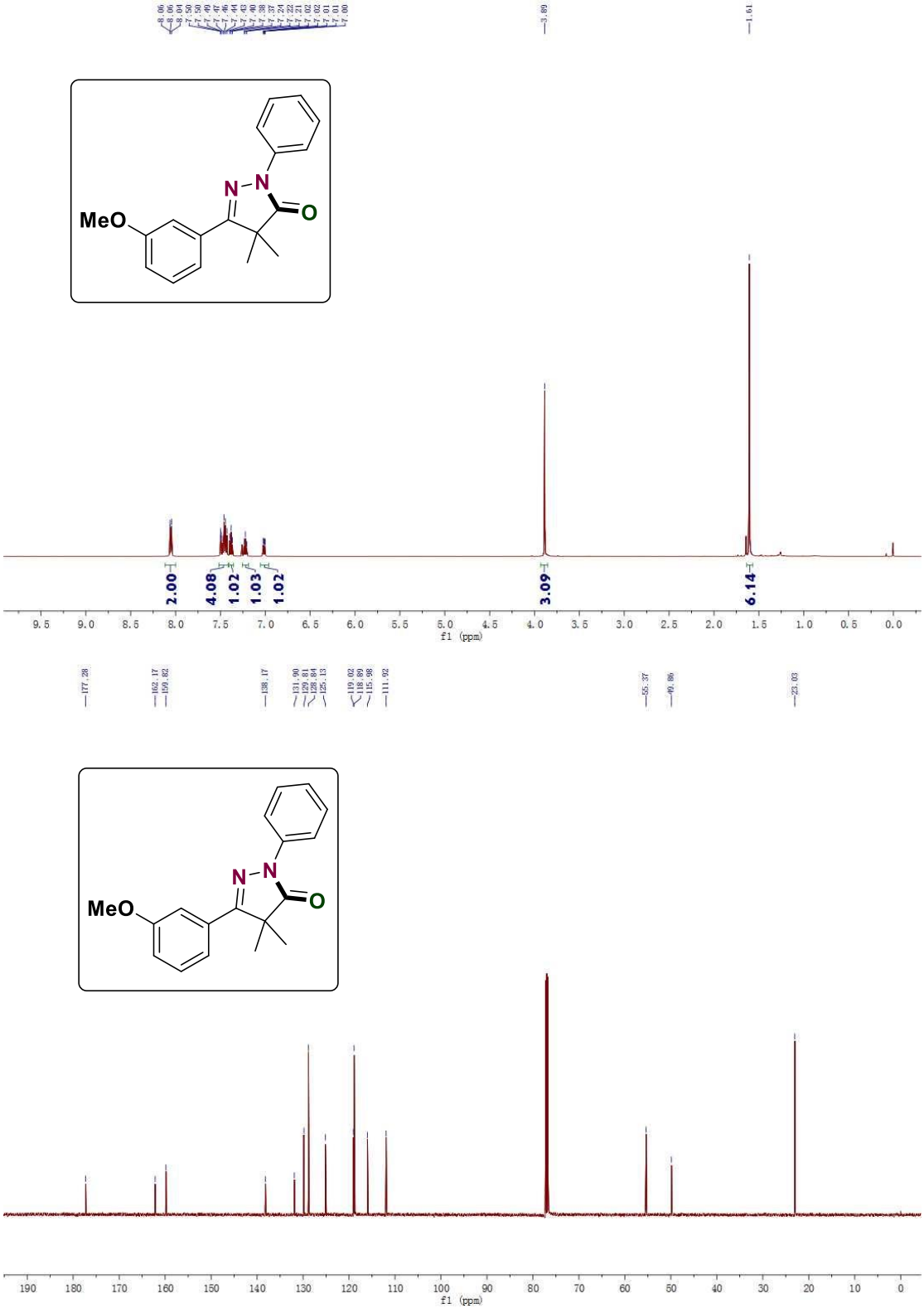
5-([1,1'-biphenyl]-4-yl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2o)



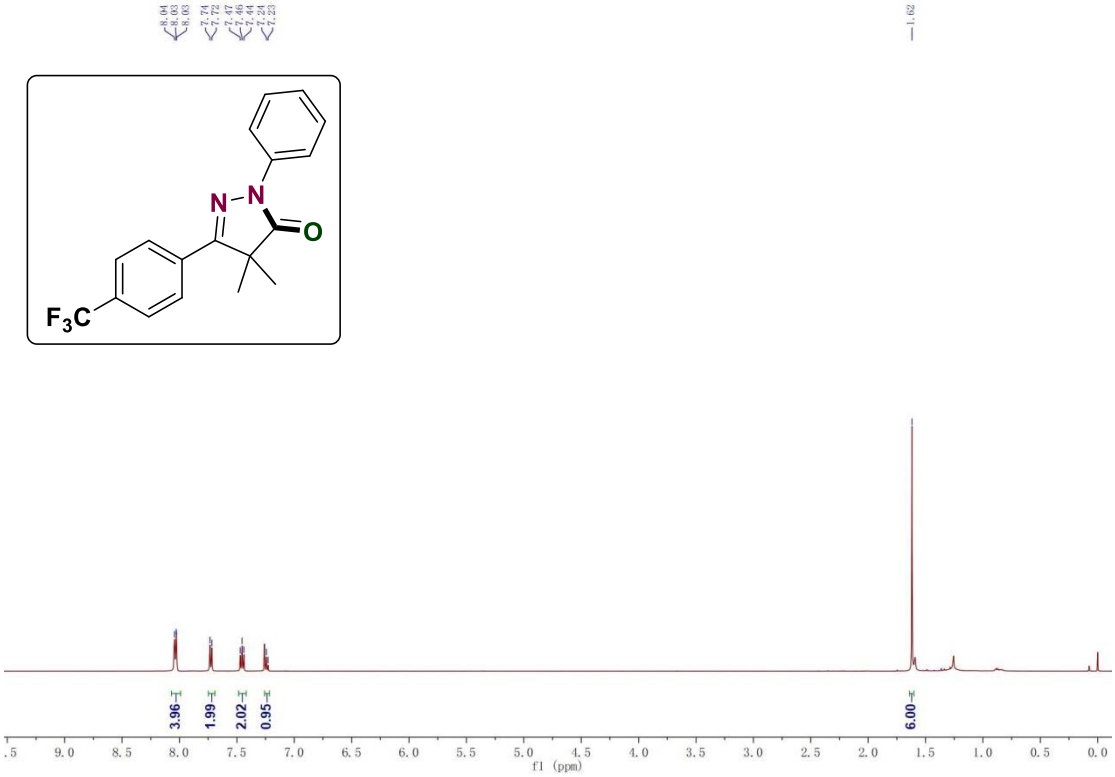
4,4-dimethyl-2-phenyl-5-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (2p)

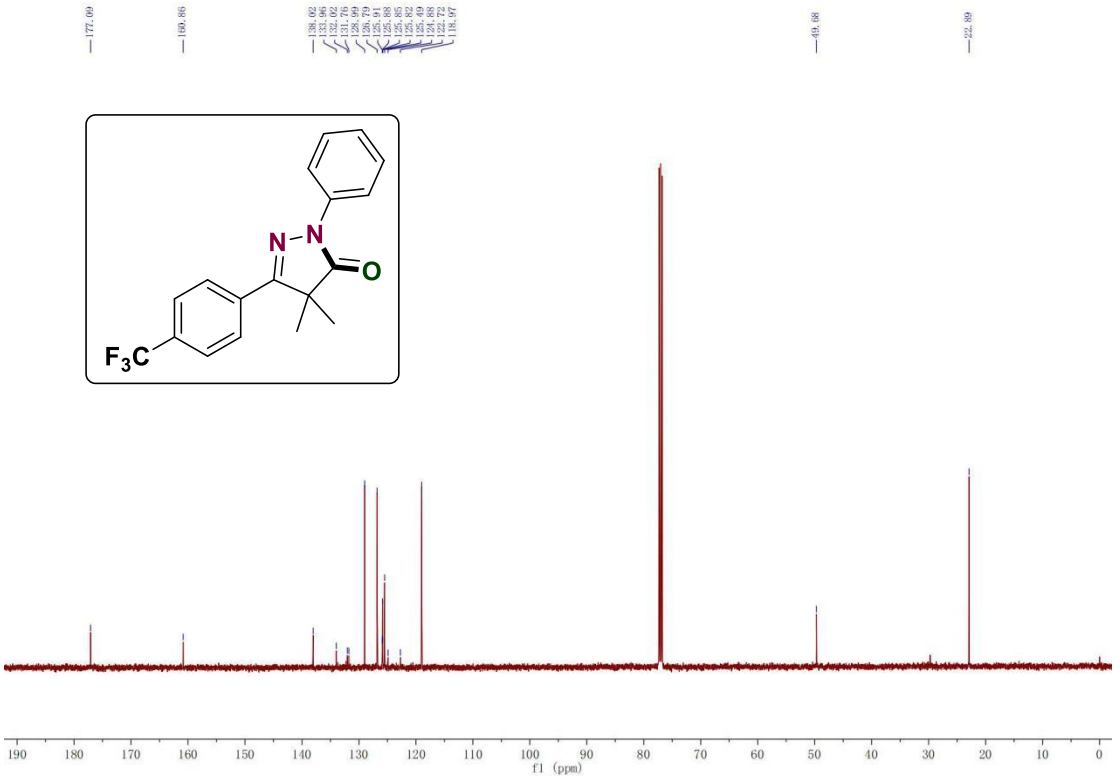


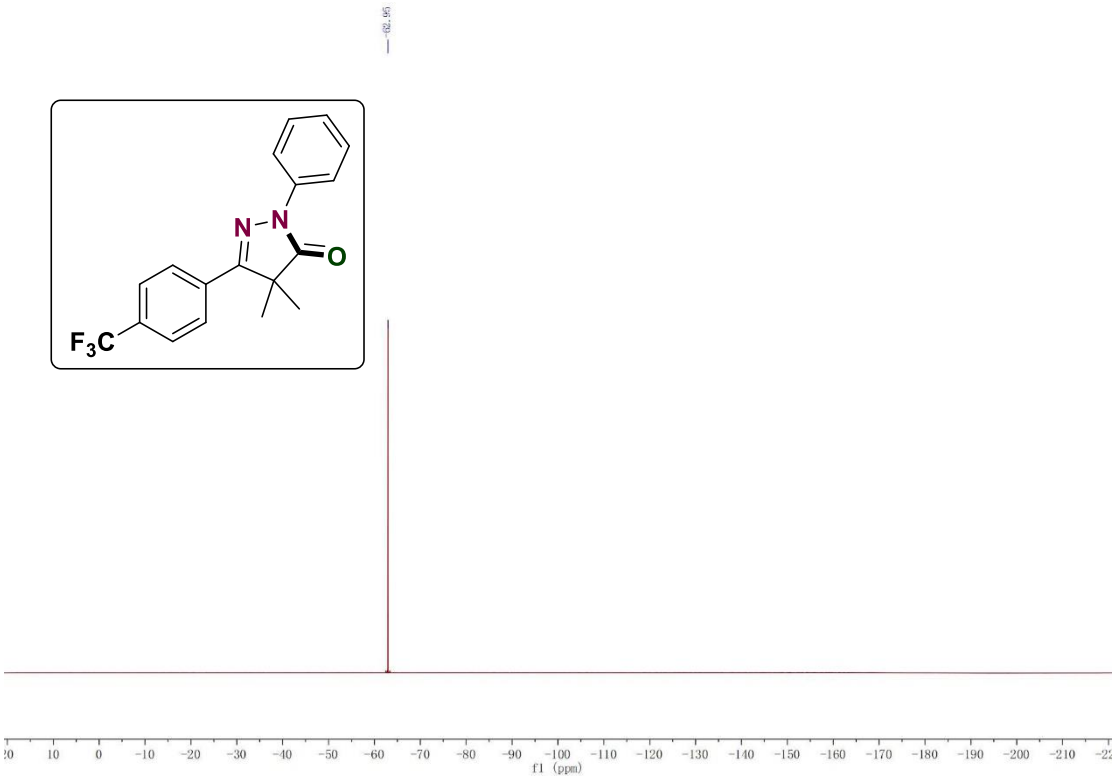
5-(3-methoxyphenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2q)



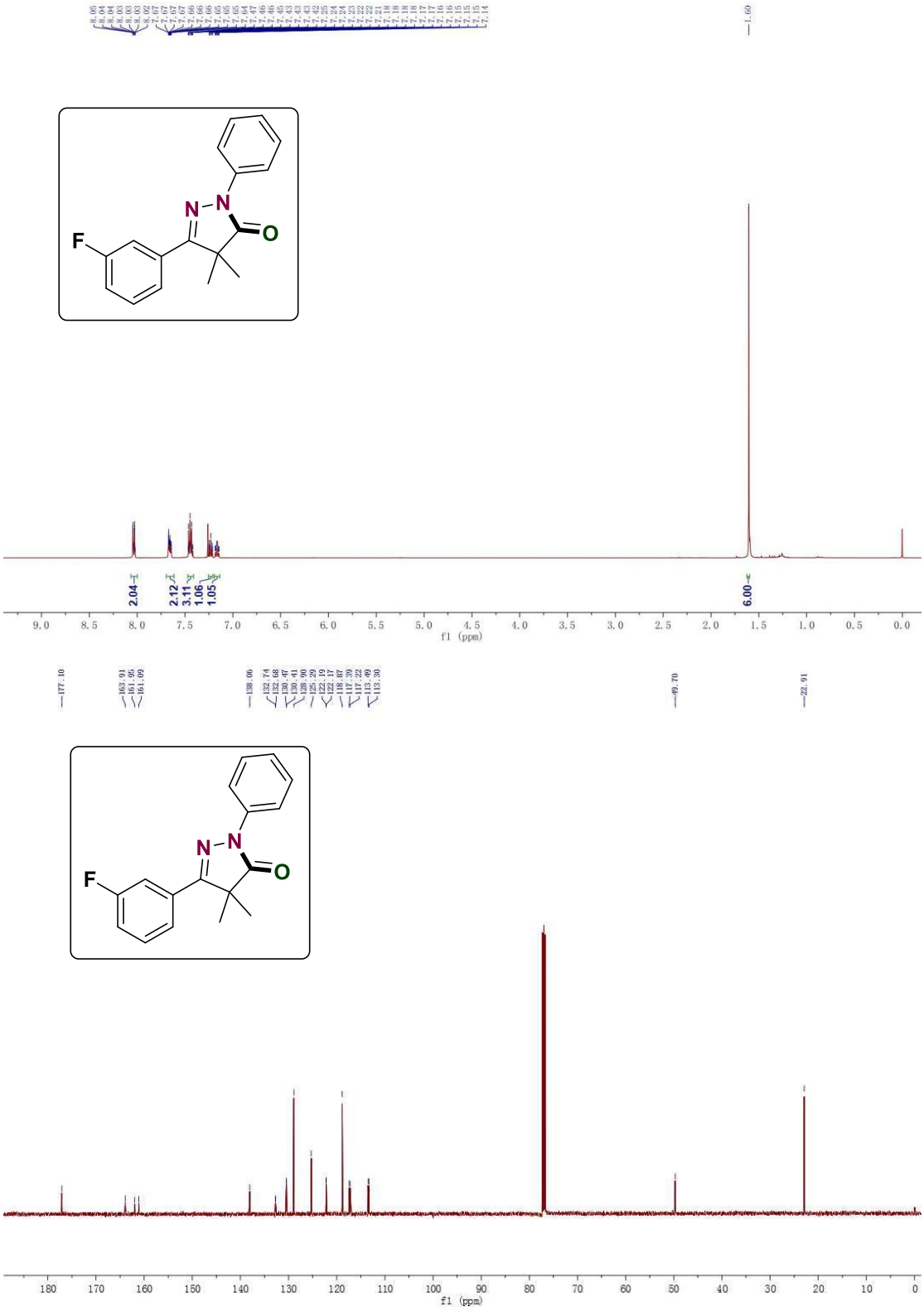
4,4-dimethyl-2-phenyl-5-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (2r)

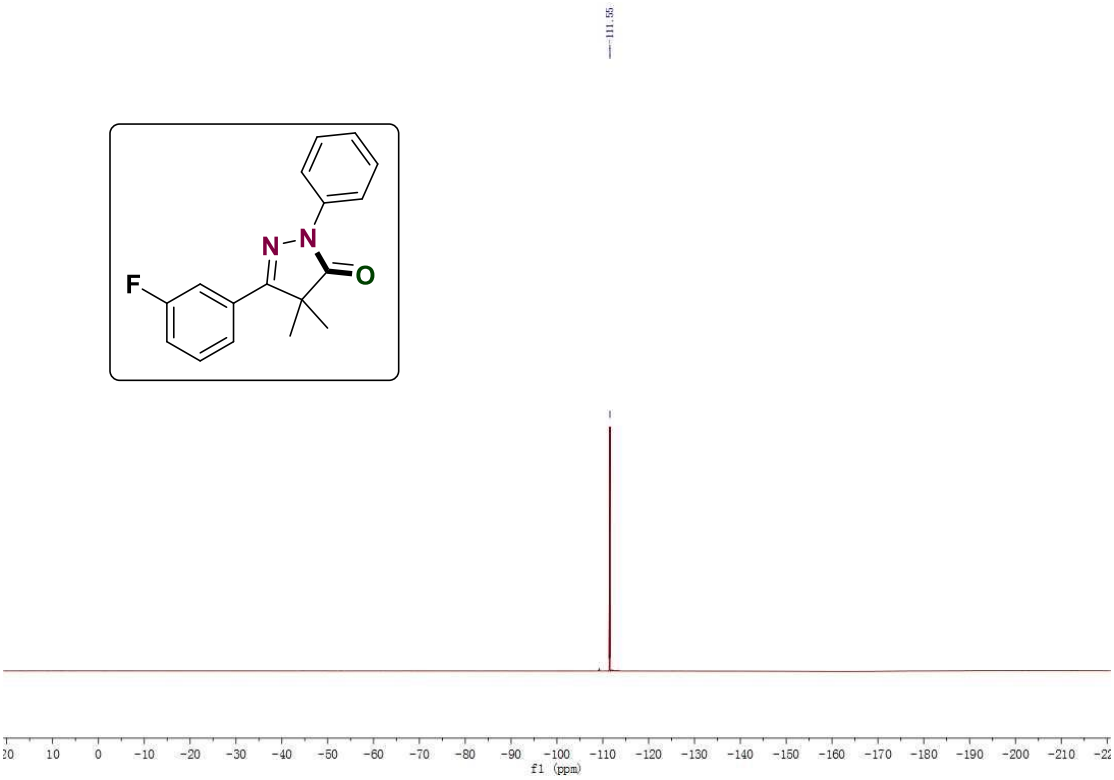




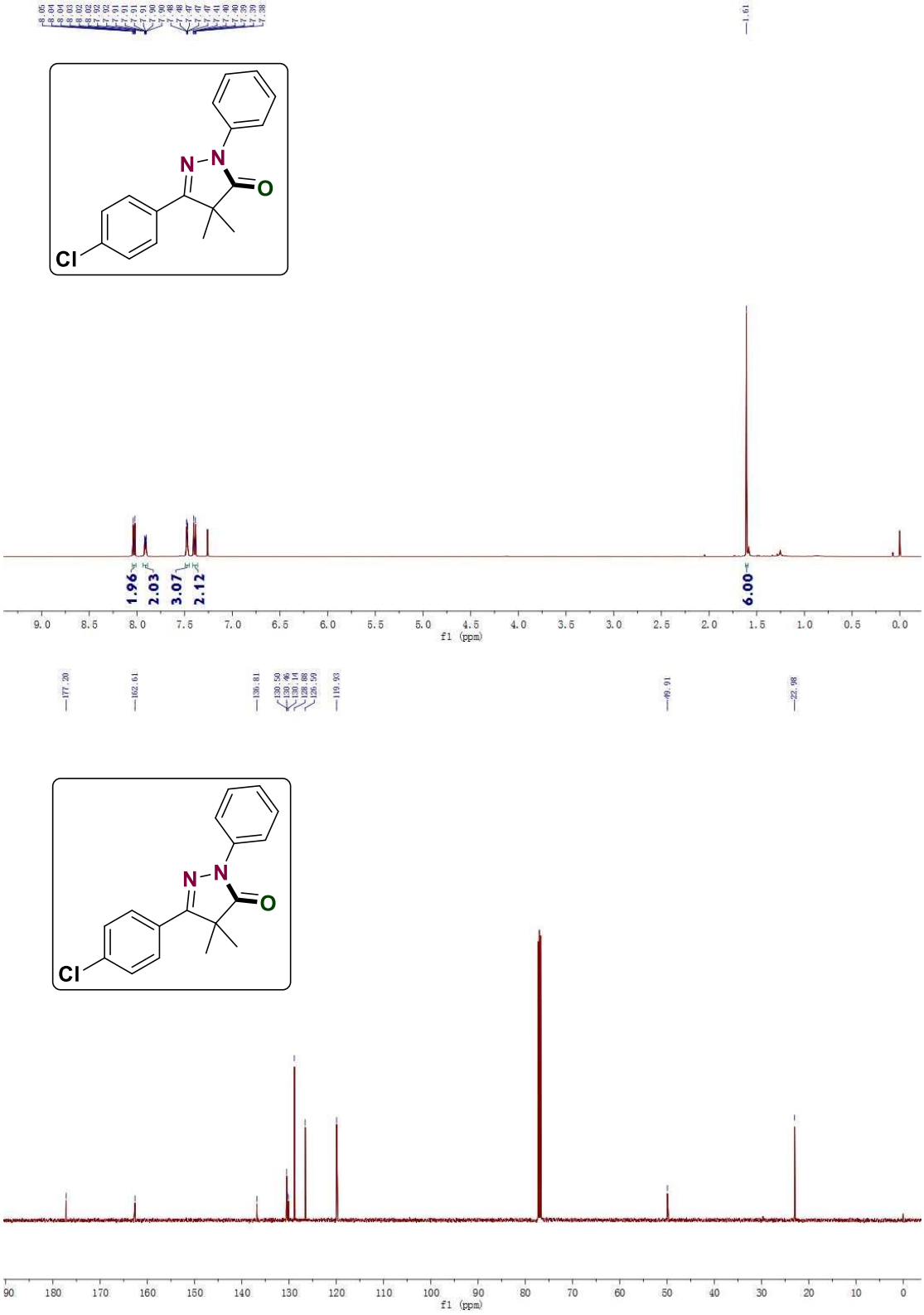

N
N
O
F3C
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

5-(3-fluorophenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2s)

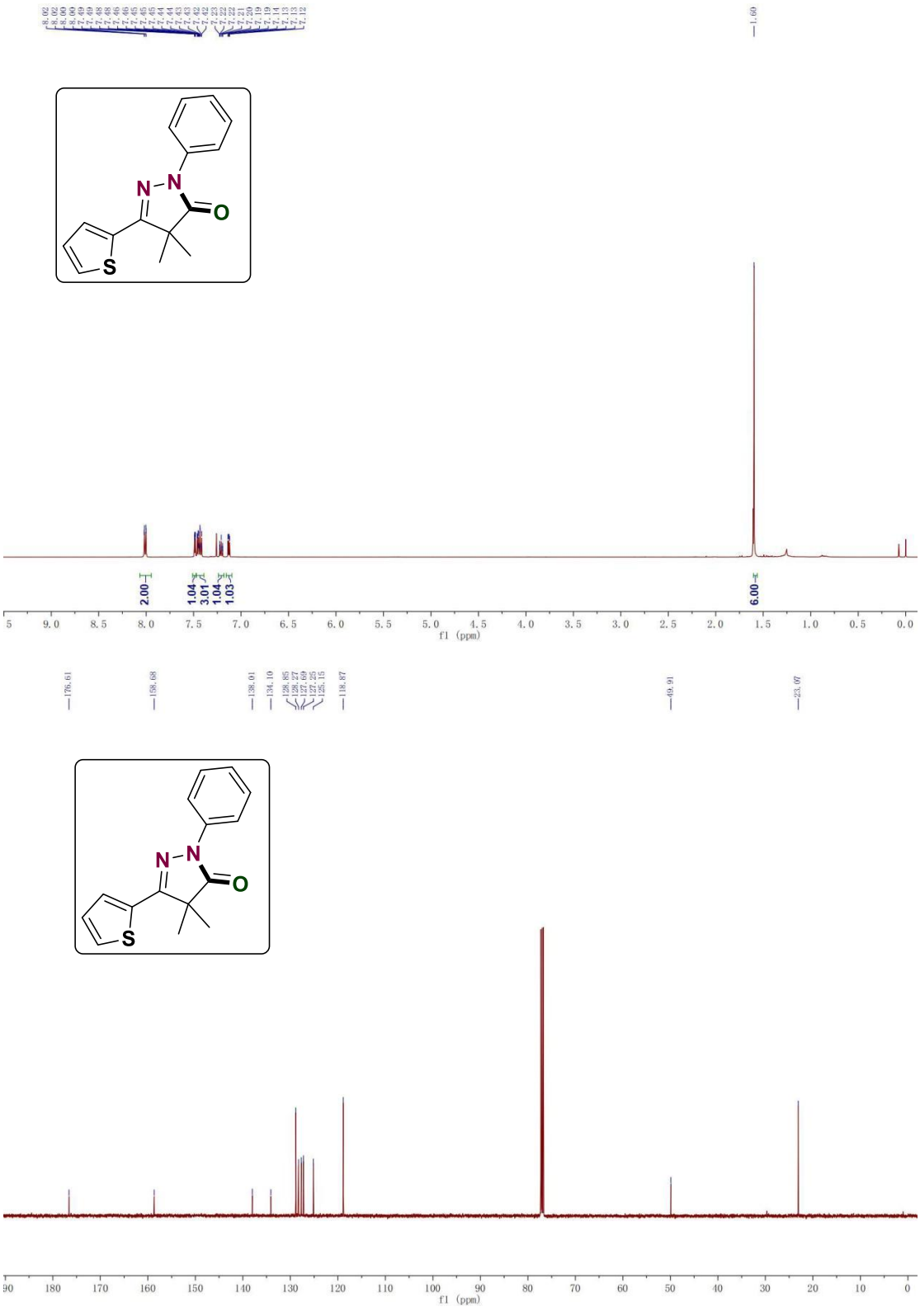



111.55
F
N
N
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

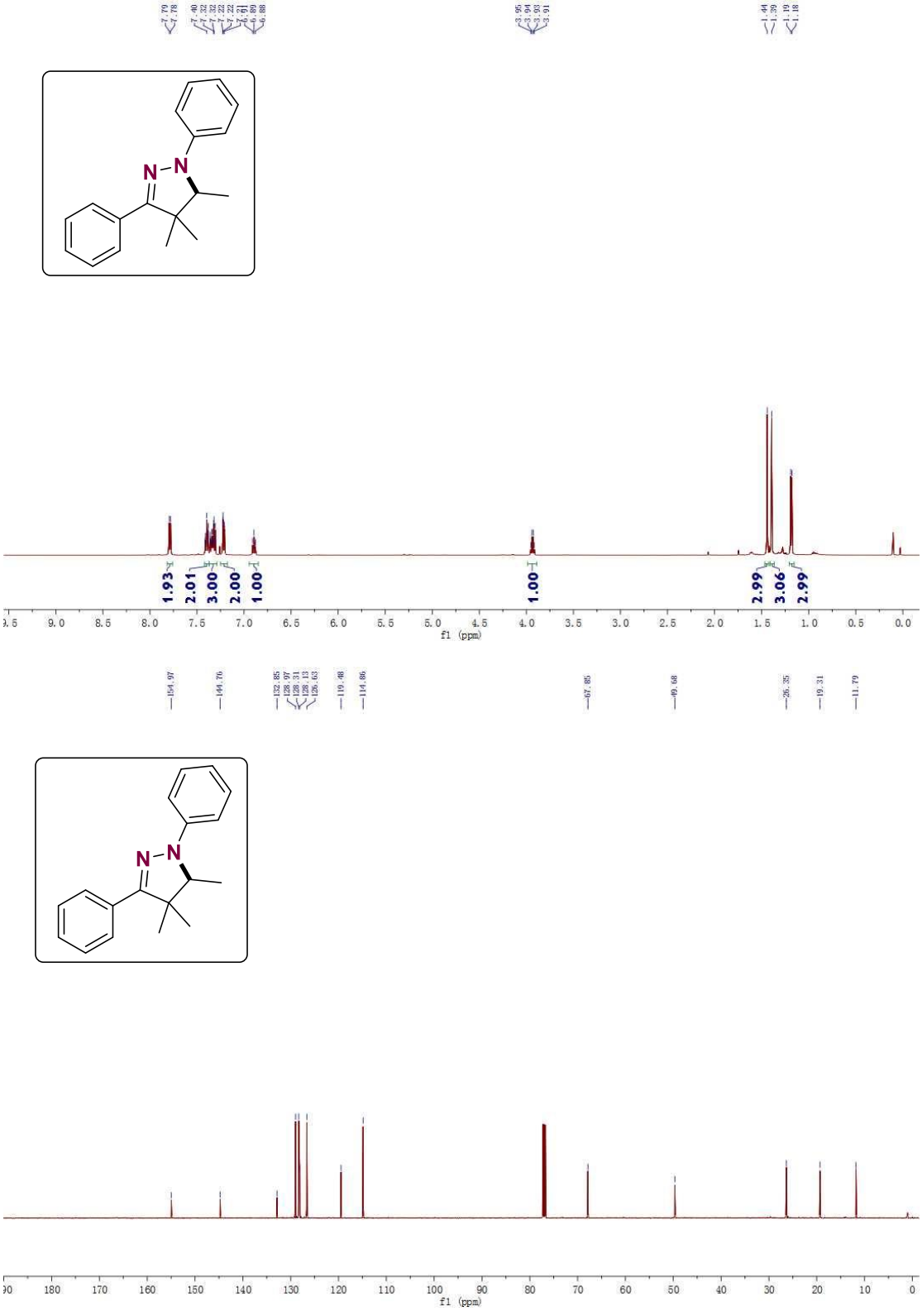
5-(4-chlorophenyl)-4,4-dimethyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (2t)



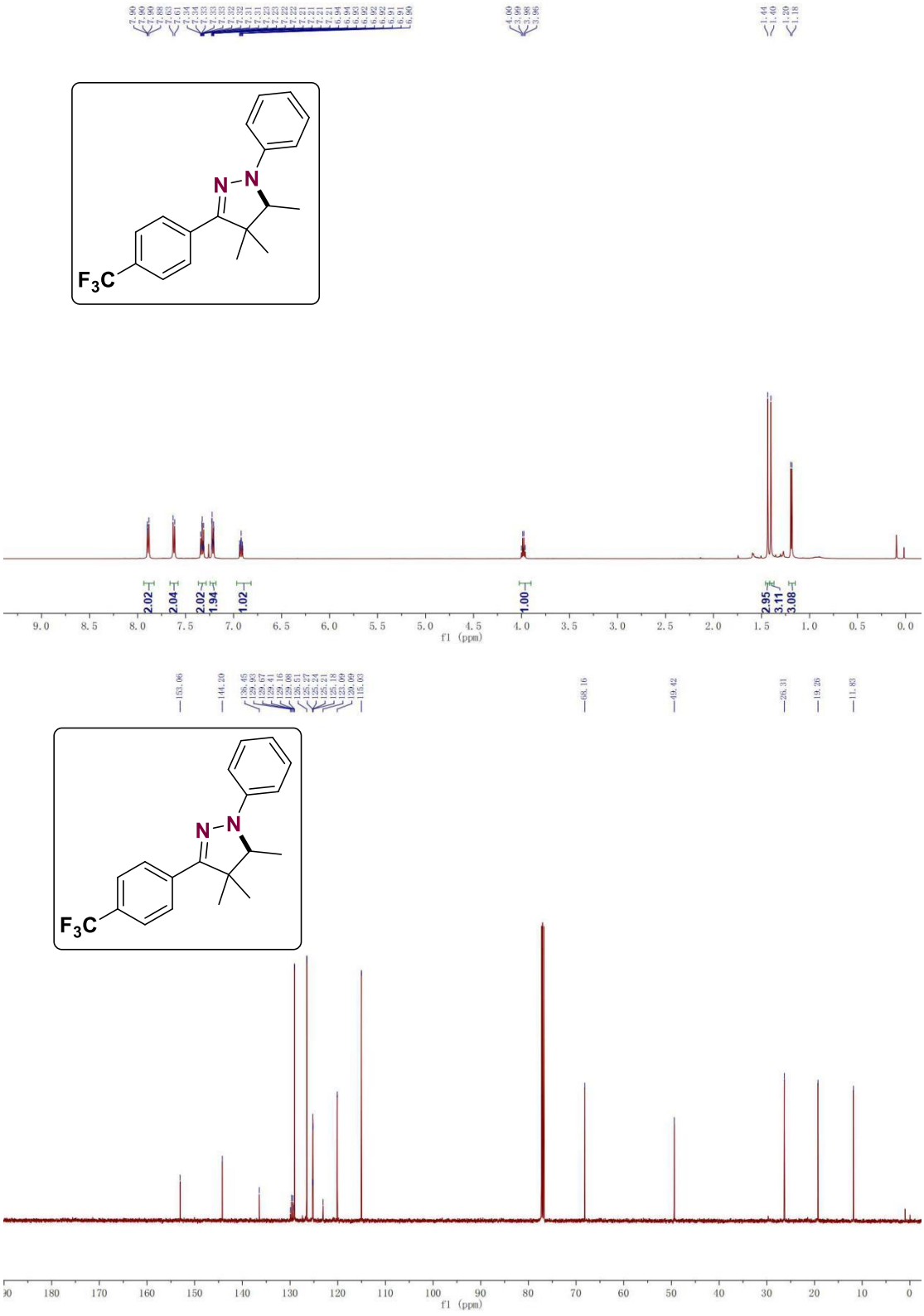
4,4-dimethyl-2-phenyl-5-(thiophen-2-yl)-2,4-dihydro-3H-pyrazol-3-one (2u)



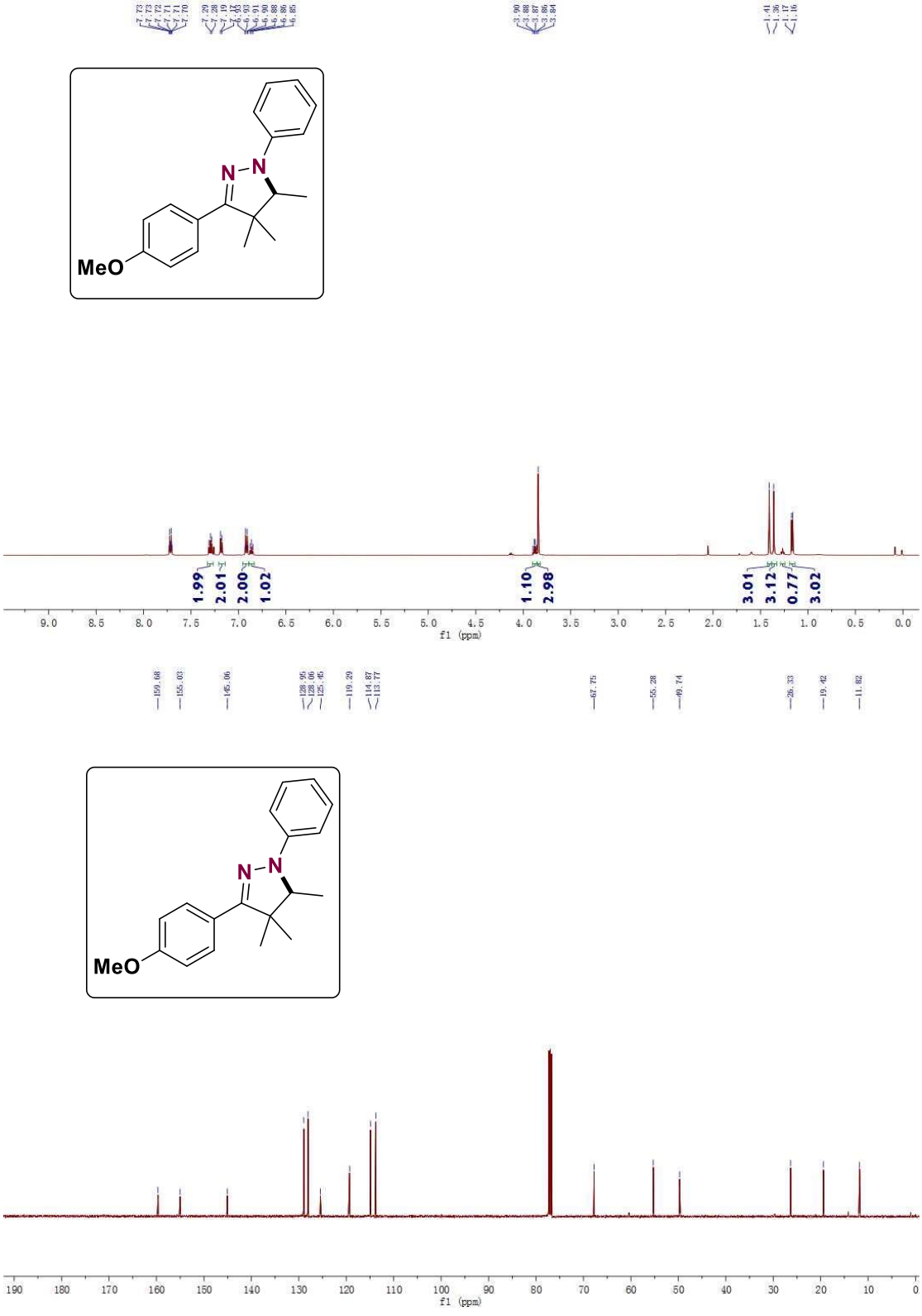
4,4,5-trimethyl-1,3-diphenyl-4,5-dihydro-1H-pyrazole (3a)



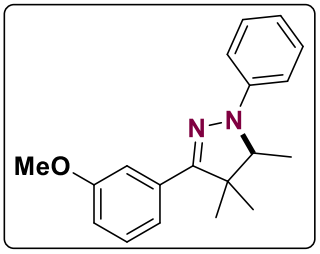
4,4,5-trimethyl-1-phenyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (3b)

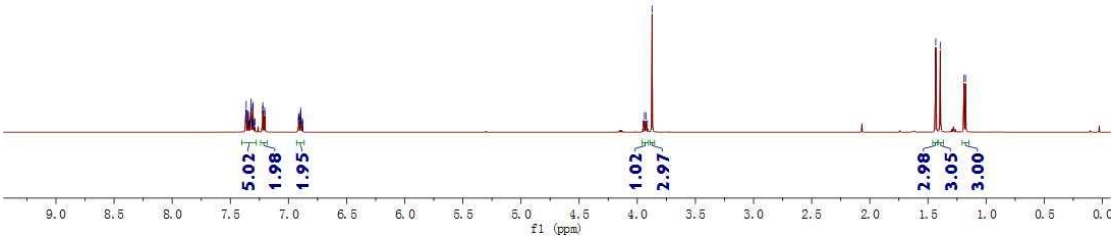


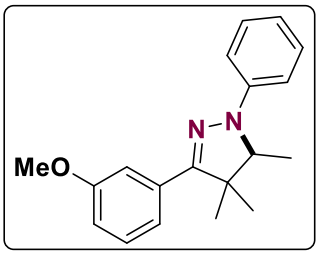
3-(4-methoxyphenyl)-4,4,5-trimethyl-1-phenyl-4,5-dihydro-1H-pyrazole (3c)

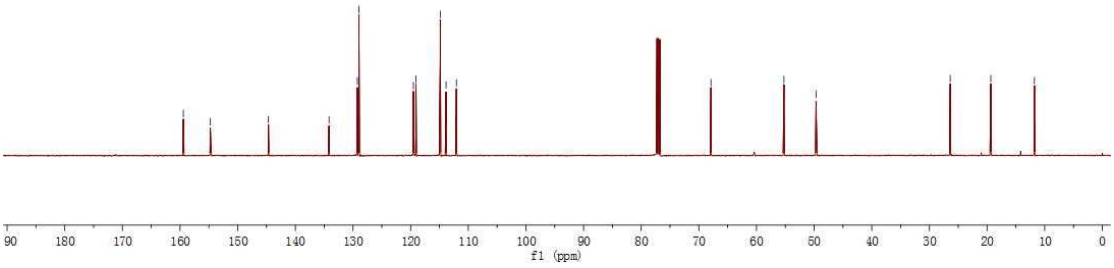


3-(3-methoxyphenyl)-4,4,5-trimethyl-1-phenyl-4,5-dihydro-1H-pyrazole (3d)

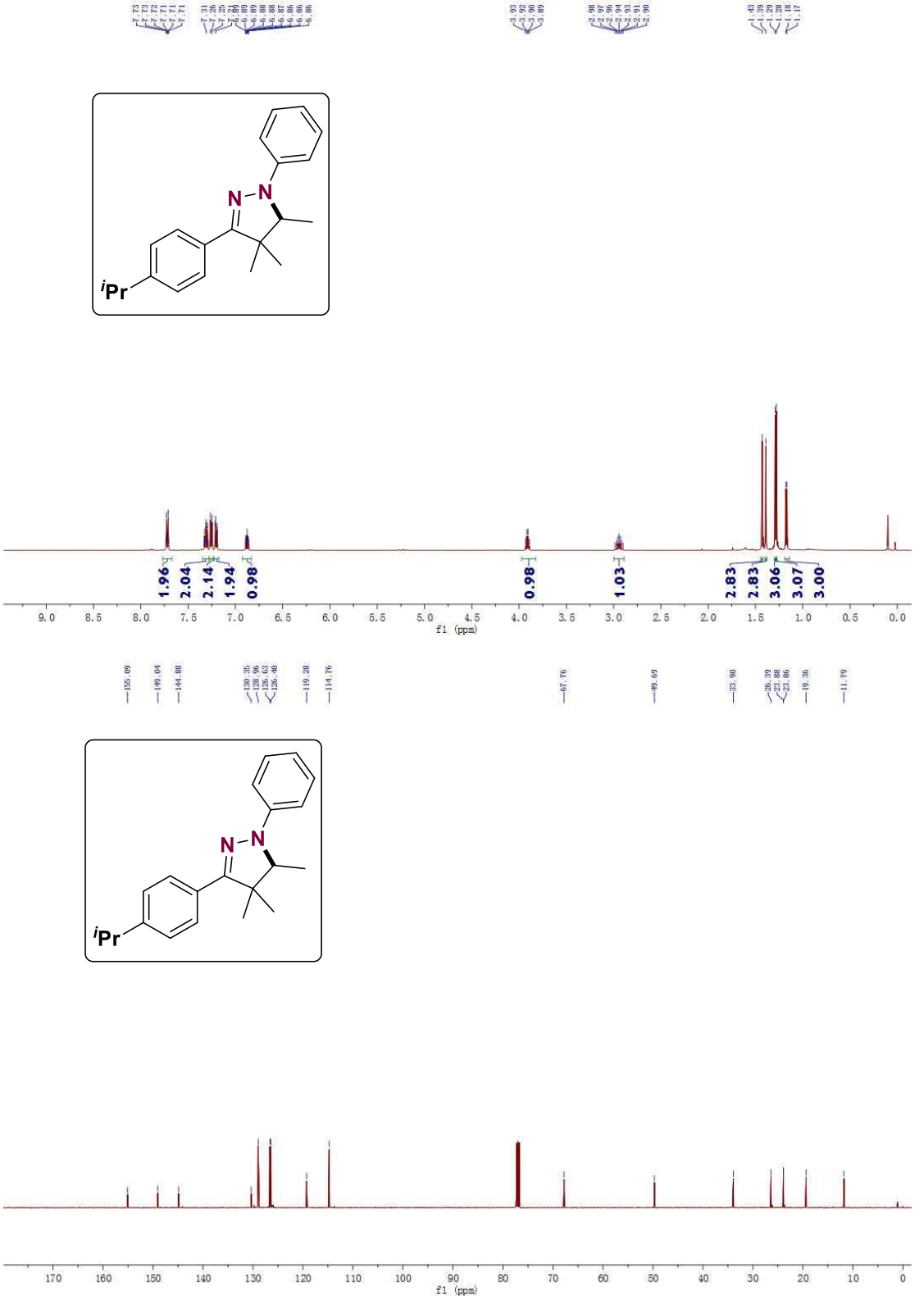




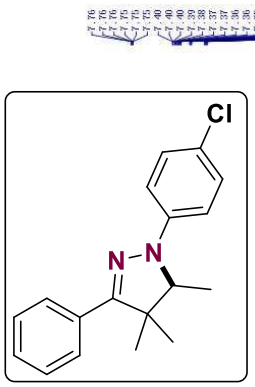


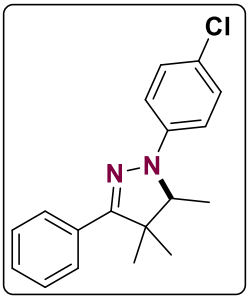


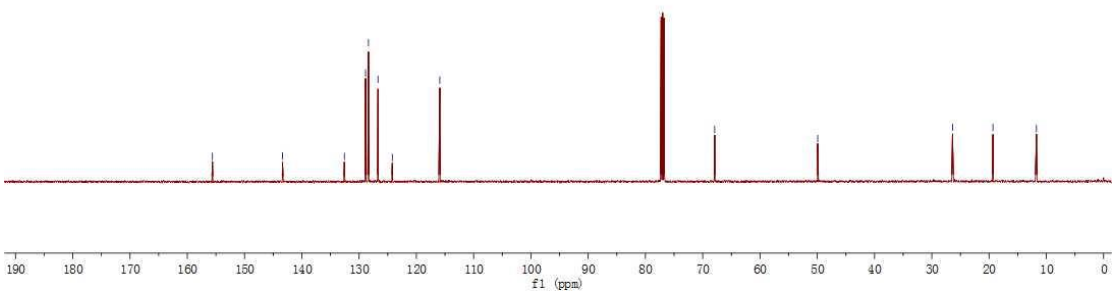
3-(4-isopropylphenyl)-4,4,5-trimethyl-1-phenyl-4,5-dihydro-1H-pyrazole (3e)



1-(4-chlorophenyl)-4,4,5-trimethyl-3-phenyl-4,5-dihydro-1H-pyrazole (3f)







1-(4-bromophenyl)-4,4,5-trimethyl-3-phenyl-4,5-dihydro-1H-pyrazole (3g)