

## Supporting Information

Assembly of 1,3-Diaryl-1*H*-pyrazoles *via* Base-Mediated [3+2] cycloaddition

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## Table of Contents

1. General Information.....	S1
1.1. Chemicals .....	S1
1.2. Chromatography .....	S1
1.3. Nuclear Magnetic Resonance (NMR) Spectroscopy .....	S1
2. General Synthesis Procedure of Substrates <b>1</b> .....	S1
3. Reaction Optimization Tables .....	S2
4. General Synthesis Procedure of Substrates <b>3-6</b> .....	S2
4.1. General procedures for preparation of pyrazoline <b>3</b> and <b>5ai</b> .....	S2
4.2. General procedures for preparation of pyrazole <b>4</b> .....	S3
4.3. General procedures for preparation of pyrazole <b>5</b> .....	S5
4.4. General procedures for preparation of pyrazoline <b>6</b> .....	S5
5. Gram-scale reaction preparation.....	S5
6. References.....	S5
7. Characteristic data of Compounds .....	S6
8. The NMR Spectra of Compounds .....	S20

## 1. General Information

### 1.1. Chemicals

All the chemicals were purchased from commercial sources (Sigma-Aldrich, Merck, TCI, Energy Chemical, Bidepharm) and directly used as received without additional purification. Solvents (DMF) Extra Dry over Molecular Sieve, were purchased from Energy Chemical.

### 1.2. Chromatography

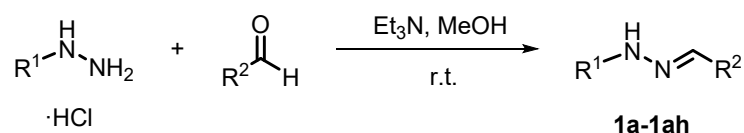
Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum 60 F254 plates. TLC was visualized using a UV lamp (254 nm, 365 nm). Column chromatography was carried out with silica gel (200-300 mesh, and 300-400 mesh) to purify products using proper solvents as the eluent system. All the yields of the products are referred to chromatography pure compounds.

### 1.3. Nuclear Magnetic Resonance (NMR) Spectroscopy

$^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectra were recorded on the nuclear magnetic resonance (NMR) spectrometer used Bruker 500 and Bruker 400. The sample to be analyzed was dissolved in chloroform-*d*, solvent. For  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR, chemical shifts are reported in parts per million referenced to the center of a triplet at 77.16 ppm and 7.26 ppm of chloroform-*d*, respectively. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. Coupling constants are reported in hertz. The data of HRMS was carried out on Agilent LC 1200 / MS QTOF6520. The data of IR was carried out on Fourier transform infrared spectrometer (Nicolet5700). The data of melting point was carried out on SGWX-4 Microscopic Melting Point Analyzer.

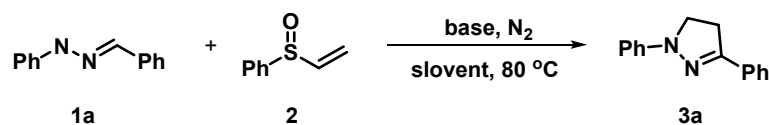
## 2. General Synthesis Procedure of Substrates 1

General procedures for preparation of hydrazone **1**<sup>[1]</sup>



In a 100 mL round-bottomed flask, substituted phenylhydrazine hydrochloride derivatives (1.0 equiv., 5 mmol), methanol (10 mL), and triethylamine (1.5 equiv., 7.5 mmol) were added sequentially and stirred until the substituted phenylhydrazine hydrochloride derivatives solid disappeared, then benzaldehyde (1.5 equiv., 7.5 mmol) was added, and the reaction was carried out under room temperature conditions and monitored by TLC. When the reaction was complete, methanol was evaporated under reduced pressure. The reaction mixture was extracted three times with ethyl acetate and saturated salt solution. The combined organic phases were dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. Then the crude product was directly used in the preparation of the next raw material.

### 3. Reaction Optimization Tables

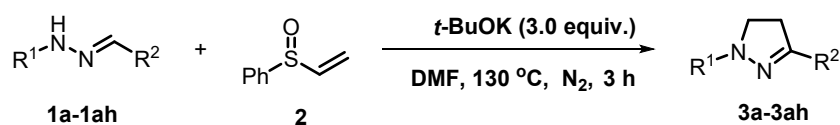


Entry	Base	Solvent	Temp.(°C)	Time (h)	Yield <b>3a</b> (%)
1	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMSO	80	12	43
2	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	THF	80	12	trace
3	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	Toluene	80	12	trace
4	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	MTBE	80	12	NR
5	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	80	12	45
6	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	80	8	47
7	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	100	8	62
8	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	120	8	70
9	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	130	8	77
10	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	130	6	79
11	<i>n</i> -C <sub>3</sub> H <sub>7</sub> ONa	DMF	130	4	64
12	<i>n</i> -C <sub>5</sub> H <sub>11</sub> OK	DMF	130	6	59
13	MeONa	DMF	130	6	69
14	EtONa	DMF	130	6	57
15	<i>t</i> -BuOK	DMF	130	6	67
16	<i>t</i> -BuOK	DMF	130	4	76
17	<b><i>t</i>-BuOK</b>	<b>DMF</b>	<b>130</b>	<b>3</b>	<b>87</b>
18	<i>t</i> -BuOK	DMF	130	2	84

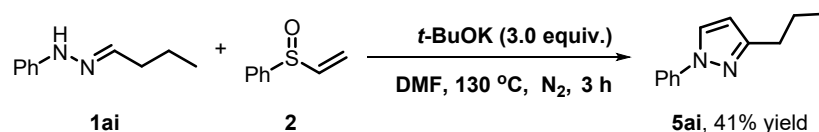
Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), base (3.0 equiv.), in slovent (5.0 mL), N<sub>2</sub>.

### 4. General Synthesis Procedure of Substrates 3-6

#### 4.1. General procedures for preparation of pyrazoline **3** and **5ai**

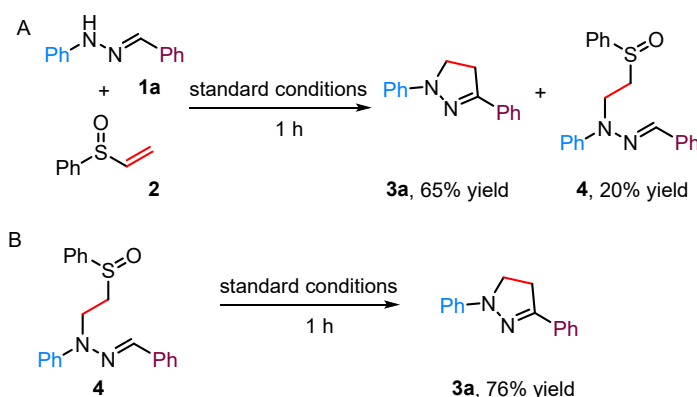


An oven-dried 20 mL pressure-resistant tube equipped with a stir bar, DMF (5 mL), hydrazone (1.0 equiv., 0.5 mmol), (Vinylsulfonyl)benzene **2** (1.2 equiv., 0.6 mmol) and *t*-BuOK (3.0 equiv., 1.5 mmol) were added under nitrogen. The reaction was stirred at 130 °C for 3 h, then quenched with 3 mL of H<sub>2</sub>O. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were concentrated in vacuo. The crude product was separated by column chromatography on silica gel with petroleum ether/ethyl acetate.



An oven-dried 20 mL pressure-resistant tube equipped with a stir bar, DMF (5 mL), hydrazone **1ai** (1.0 equiv., 0.5 mmol), (Vinylsulfinyl)benzene **2** (1.2 equiv., 0.6 mmol) and *t*-BuOK (3.0 equiv., 1.5 mmol) were added under nitrogen. The reaction was stirred at 130 °C for 3 h, then quenched with 3 mL of H<sub>2</sub>O. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were concentrated in vacuo. The crude product was separated by column chromatography on silica gel with petroleum ether/ethyl acetate to give *l*-phenyl-3-propyl-1*H*-pyrazole (**5ai**) in 41% yield as yellow liquid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.4 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.28 – 7.18 (m, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 2.69 – 2.66 (m, 2H), 1.79 – 1.67 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 155.4, 140.4, 129.5, 127.4, 126.1, 119.1, 106.6, 30.5, 23.1, 14.1. HRMS ESI (*m/z*): calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 187.1230, found: 187.1238.

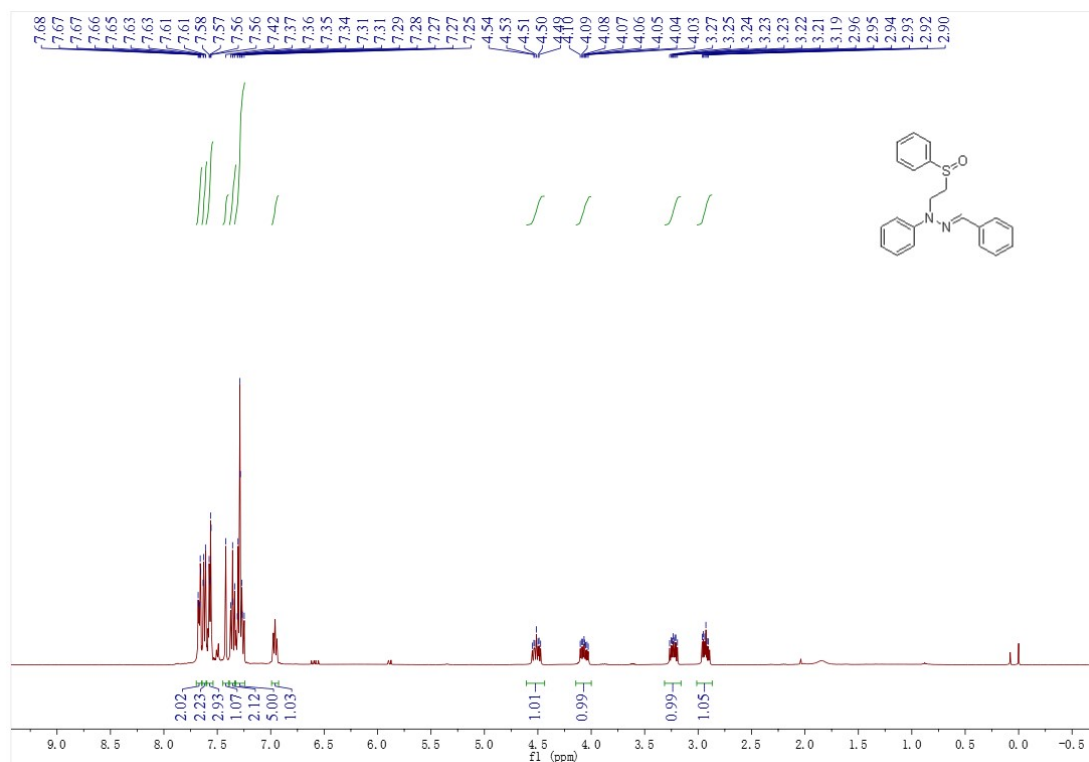
#### 4.2. General procedures for preparation of pyrazole 4



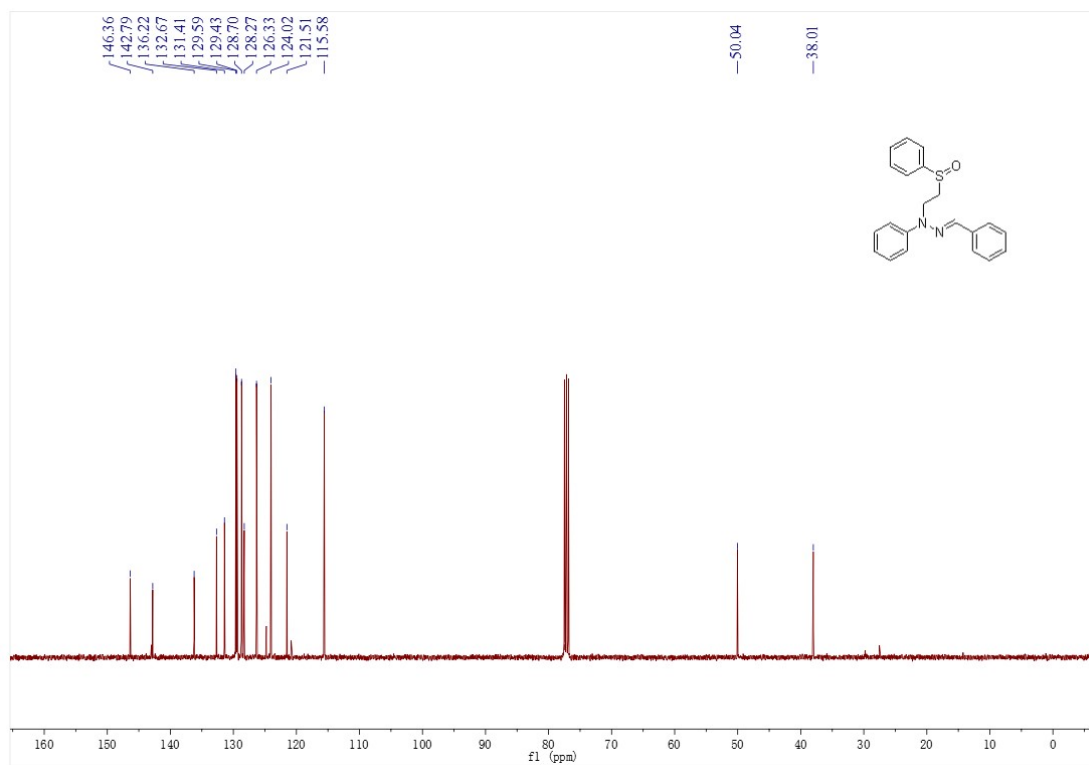
An oven-dried 20 mL pressure-resistant tube equipped with a stir bar, DMF (5 mL), hydrazone **1a** (1.0 equiv., 0.5 mmol), (Vinylsulfinyl)benzene **2** (1.2 equiv., 0.6 mmol) and *t*-BuOK (3.0 equiv., 1.5 mmol) were added under nitrogen. The reaction was stirred at 130 °C for 1 h, then quenched with 3 mL of H<sub>2</sub>O. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were concentrated in vacuo. The crude product was separated by column chromatography on silica gel with petroleum ether:ethyl acetate = 5:1 to give (*E*)-2-benzylidene-1-phenyl-1-(2-(phenylsulfinyl)ethyl)hydrazine (**4**) (34.8 mg, 20% yield) as a white solid; mp: 94–95 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.66 (m, 2H), 7.64 – 7.60 (m, 2H), 7.59 – 7.55 (m, 3H), 7.42 (s, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.24 (m, 5H), 6.98 – 6.95 (m, 1H), 4.53 – 4.50 (m, 1H), 4.09 – 4.05 (m, 1H), 3.25 – 3.21 (m, 1H), 2.95 – 2.91 (m, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 146.4, 142.8, 136.2, 132.8, 131.4, 129.6, 129.4, 128.7, 128.3, 126.3, 124.0, 121.5, 115.6, 50.0, 38.0. HRMS ESI (*m/z*): calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>: 349.1369, found: 349.1372.

An oven-dried 20 mL pressure-resistant tube equipped with a stir bar, compound **4** (1.0 equiv., 0.1 mmol, 34.8 mg), *t*-BuOK (3.0 equiv., 1.5 mmol) and DMF (1 mL) were added under nitrogen. The reaction was stirred at 130 °C for 1 h, then quenched with 3 mL of H<sub>2</sub>O. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were concentrated in vacuo. The yield of product **3a** obtained after purification by column chromatography on silica gel was 76%.

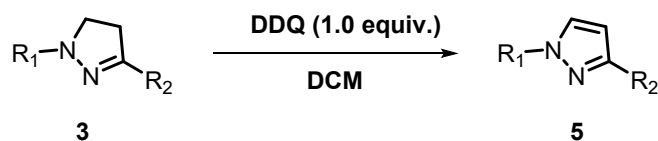
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-2-benzylidene-1-phenyl-1-(2-(phenylsulfinyl)ethyl)hydrazine (**4**)



$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of (*E*)-2-benzylidene-1-phenyl-1-(2-(phenylsulfinyl)ethyl)hydrazine (**4**)



#### 4.3. General procedures for preparation of pyrazole **5**



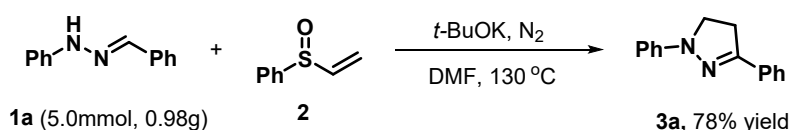
A mixture of pyrazoline **3a** (0.2 mmol) and DDQ (0.2 mmol) in DCM (5 mL) was stirred at room temperature for 3 h. The reaction mixture was diluted with water (10 mL) and extracted with AcOEt (3 x 15 mL). The organic extract was washed with H<sub>2</sub>O (3 x 5 mL). The solvent was removed and the crude product was separated by column chromatography eluted with petroleum ether/ethyl acetate.

#### 4.4. General procedures for preparation of pyrazoline **6**<sup>[2]</sup>



To a stirred solution of POCl<sub>3</sub> (3.0 equiv., 0.6 mmol) in DMF (3 mL) was added a solution of pyrazoline **3a** (0.2 mmol) in DMF (2 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was then quenched by dropwise adding KOH solution 3.8 M in H<sub>2</sub>O, extracted with AcOEt (3 x 15 mL). The combined organic layers were washed with H<sub>2</sub>O several times and once with brine (100 mL), then were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a crude product. Following purification by column chromatography (eluted with petroleum ether:ethyl acetate = 20:1) to give a pure sample of 4-(3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)benzaldehyde (**6**) (34.5 mg, 69% yield) as a yellow solid; mp: 101–102 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 7.77 – 7.71 (m, 2H), 7.71 – 7.64 (m, 2H), 7.41 – 7.31 (m, 3H), 7.06 (s, 2H), 3.84 (t, *J* = 10.5 Hz, 2H), 3.25 – 3.21 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 190.7, 152.2, 149.4, 132.1, 129.6, 128.8, 127.6, 126.2, 112.2, 47.2, 32.2. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 251.1179, found: 251.1178.

### 5. Gram-scale reaction preparation



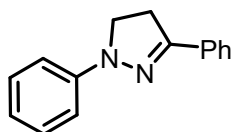
Under nitrogen atmosphere, DMF (50 mL), hydrazone **1a** (1.0 equiv., 5.0 mmol), sulfoxide **2** (1.0 equiv., 5.0 mmol), and *t*-BuOK (3.0 equiv., 15.0 mmol) were added to a 100mL round bottom flask equipped with a magnetic stir bar. The mixture was stirred at 130 °C in an oil bath, and the reaction was monitored by TLC. After the reaction was complete, it was quenched with H<sub>2</sub>O. The aqueous layer was extracted with ethyl acetate, and the organic layer was concentrated using a rotary evaporator. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent. Finally, 0.85g of the target product **3a** was obtained, and the isolated yield was 78%.

### 6. References

- [1] X. Wang, D. P. Chen, W. P. Wang, C. H. Yang, M. Li, W. B. Xu, X. C. Wang and Z. J. Quan, *Org. Lett.*, 2024, **17**, 3575–3580.
- [2] T. Phumjan, T. Yazawa, S. Harada and T. Nemoto, *Org. Lett.*, 2025, **6**, 1549–1554.

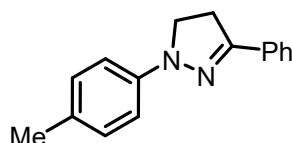
## 7. Characteristic data of Compounds

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



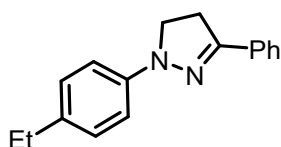
The product **3a** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3a** (96.7 mg, 87% yield) as a white solid; mp: 151–153 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.77 – 7.72 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.19 – 7.12 (m, 2H), 6.87 (t, *J* = 7.5 Hz, 1H), 3.89 (t, *J* = 10.5 Hz, 2H), 3.28 – 3.21 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.2, 146.0, 133.0, 129.6, 129.3, 128.7, 125.8, 119.2, 113.1, 48.4, 32.1. IR (KBr): 3037, 2925, 2858, 1588, 1489, 1298, 1114, 735, 677, 486 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 223.1230, found: 223.1238.

### 3-phenyl-1-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3b**)



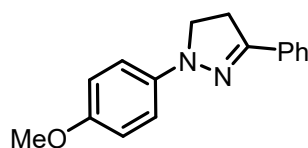
The product **3b** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3b** (49.6 mg, 42% yield) as a white solid; mp: 131–133 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.69 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.13 – 7.08 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.84 (t, *J* = 10.4 Hz, 2H), 3.25 – 3.21 (m, 2H), 2.29 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.8, 144.0, 136.3, 133.1, 129.7, 128.6, 125.8, 119.2, 113.2, 48.8, 32.1, 20.7. IR (KBr): 3673, 2916, 2861, 1518, 1448, 1357, 1260, 1040, 935, 809, 744, 694, 495 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 237.1386, found: 237.1379.

### 1-(4-ethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3c**)



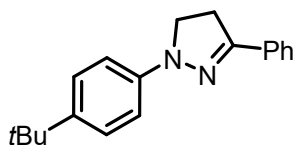
The product **3c** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:400) to give **3c** (86.5 mg, 69% yield) as a white solid; mp: 135–136 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 3.87 (t, *J* = 10.5 Hz, 2H), 3.23 (t, *J* = 10.5 Hz, 2H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.3, 146.1, 145.1, 130.5, 129.2, 128.2, 125.9, 119.0, 113.0, 48.3, 32.2, 28.9, 15.7. IR (KBr): 2973, 2918, 2875, 1561, 1487, 1443, 1375, 1284, 1116, 835, 741, 683, 498 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 251.1543, found: 251.1537.

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



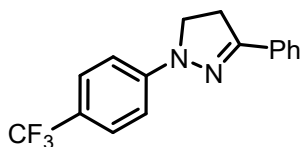
The product **3d** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3d** (112.3 mg, 89% yield) as a white solid; mp: 163–165 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 2H), 7.41 – 7.36 (m, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.92 – 6.88 (m, 2H), 3.87 – 3.97 (m, 5H), 3.22 (t, *J* = 10.0 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 153.5, 148.8, 140.9, 133.2, 128.6, 128.5, 125.7, 114.8, 114.5, 55.9, 55.8, 49.5, 32.2. IR (KBr): 3837, 3762, 3654, 2900, 2813, 1506, 1451, 1258, 1179, 1037, 835, 789, 721, 611, 502 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 253.1335, found: 253.1342.

1-(4-(tert-butyl)phenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3e**)



The product **3e** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:400) to give **3e** (97.4 mg, 70% yield) as a white solid; mp: 152–155 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.77 – 7.73 (m, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.36 (m, 3H), 7.12 (d, *J* = 8.5 Hz, 2H), 3.88 (t, *J* = 10.5 Hz, 2H), 3.25 – 3.21 (m, 2H), 1.35 (s, 9H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.7, 143.8, 142.0, 133.2, 128.6, 126.0, 125.8, 119.0, 112.8, 48.7, 32.1, 31.7, 31.5. IR (KBr): 3299, 2953, 2898, 2867, 1608, 1501, 1211, 1118, 1035, 741, 683, 541 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 279.1856, found: 279.1860.

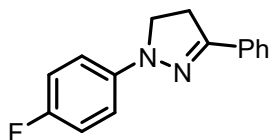
3-phenyl-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-pyrazole (**3f**)



The product **3f** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3f** (49.4 mg, 34% yield) as a white solid; mp: 101–102 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.74 – 7.72 (m, 2H), 7.44 – 7.37 (m, 3H), 7.26 – 7.22 (m, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 3.86 (t, *J* = 10.5 Hz, 2H), 3.29 – 3.24 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) 164.2, 161.7, 148.0, 145.8, 129.4 (q, *J* = 3.3 Hz), 129.1, 127.4, 127.3, 119.1, 119.0, 118.7, 115.7, 115.4, 112.9, 48.3, 32.1. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -61.23. IR (KBr): 3021, 2957, 1658, 1571, 1501, 13890, 1263, 1274, 1138, 798, 685, 578, 493 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 291.1104, found: 291.1106.

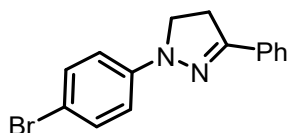
1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3g**)





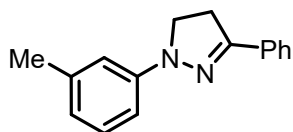
The product **3g** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3g** (62.5 mg, 52% yield) as a yellow solid; mp: 95–96 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.75 – 7.72 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.10 – 7.06 (m, 2H), 7.03 – 6.99 (m, 2H), 3.84 (t, *J* = 10.5 Hz, 2H), 3.27 – 3.24 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 156.9 (d, <sup>1</sup>*J*<sub>CF</sub> = 235 Hz), 149.2, 142.6(1), 142.6(9), 132.7, 128.6, 128.5, 125.7, 115.5 (d, <sup>2</sup>*J*<sub>CF</sub> = 22.3 Hz), 113.8 (d, <sup>3</sup>*J*<sub>CF</sub> = 7.4 Hz), 48.8, 32.1. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -124.79. IR (KBr): 2926, 2853, 1608, 1501, 1449, 1370, 1256, 1204, 1038, 745, 683, 541, 462 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub>FN<sub>2</sub> [*M*+*H*]<sup>+</sup>: 241.1136, found: 241.1137.

1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3h**)



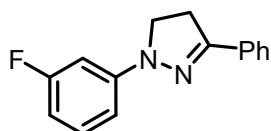
The product **3h** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3h** (36.0 mg, 24% yield) as a yellow solid; mp: 102–103 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.68 (m, 2H), 7.40 – 7.32 (m, 5H), 6.98 (d, *J* = 9.2 Hz, 2H), 3.81 (t, *J* = 10.4 Hz, 2H), 3.25 – 3.21 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.8, 144.9, 132.6, 132.0, 128.9, 128.7, 125.9, 120.5, 114.6, 48.2, 32.3. IR (KBr): 2925, 2852, 1588, 1489, 1351, 1257, 1070, 812, 744, 685, 501 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub><sup>79</sup>BrN<sub>2</sub> [*M*+*H*]<sup>+</sup>: 301.0335, found: 301.0342.

3-phenyl-1-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3i**)



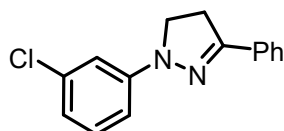
The product **3i** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3i** (66.3 mg, 56% yield) as a white solid; mp: 152–153 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.03 (s, 1H), 6.96 – 6.92 (m, 1H), 6.73 – 6.69 (m, 1H), 3.88 (t, *J* = 10.5 Hz, 2H), 3.26 – 3.22 (m, 2H), 2.39 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 148.9, 146.0, 139.0, 133.1, 129.1, 128.6(1), 128.5(5), 125.8, 120.2, 113.8, 110.2, 48.4, 32.0, 21.9. IR (KBr): 3121, 2935, 2857, 1612, 1543, 1422, 1216, 1186, 743, 654, 549, 463 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> [*M*+*H*]<sup>+</sup>: 237.1386, found: 237.1395.

1-(3-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3j**)



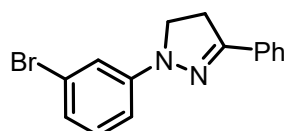
The product **3j** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3j** (64.8 mg, 54% yield) as a yellow solid; mp: 112–113 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 2H), 7.40 – 7.36 (m, 3H), 7.25 – 7.19 (m, 1H), 6.93 – 6.87 (m, 1H), 6.83 – 6.80 (m, 1H), 6.56 – 6.52 (m, 1H), 3.87 (t, *J* = 10.5 Hz, 2H), 3.29 – 3.25 (m, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) 163.8 (d, <sup>1</sup>*J*<sub>CF</sub> = 241.2 Hz), 149.7, 147.2 (d, <sup>3</sup>*J*<sub>CF</sub> = 10.9 Hz), 132.5, 130.2 (d, <sup>3</sup>*J*<sub>CF</sub> = 9.9 Hz), 128.8, 128.5, 125.8, 108.2 (d, <sup>4</sup>*J*<sub>CF</sub> = 2.3 Hz), 105.4 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.5 Hz), 100.1 (d, <sup>2</sup>*J*<sub>CF</sub> = 26.4 Hz), 48.0, 32.0. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -112.20. IR (KBr): 2929, 2852, 1609, 1486, 1454, 1380, 1184, 1180, 1072, 861, 738, 680, 504, 442 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub>FN<sub>2</sub> [M+H]<sup>+</sup>: 241.1136, found: 241.1140.

1-(3-chlorophenyl)-3-phenyl-4,5-dihydro-1H-pyrazole (**3k**)



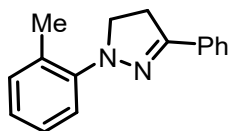
The product **3k** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3k** (55.2 mg, 43% yield) as a yellow solid; mp: 103–104 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 2H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.22 – 7.17 (m, 1H), 7.16 (t, *J* = 2.0 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.83 – 6.79 (m, 1H), 3.86 (t, *J* = 10.5 Hz, 2H), 3.29 – 3.26 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 150.0, 146.8, 135.1, 132.6, 130.2, 129.0, 128.7, 126.0, 118.9, 113.0, 111.0, 48.1, 32.2. IR (KBr): 2926, 2865, 1595, 1487, 1446, 1189, 1063, 978, 855, 779, 694, 485 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub><sup>35</sup>ClN<sub>2</sub> [M+H]<sup>+</sup>: 257.0840, found: 257.0845.

1-(3-bromophenyl)-3-phenyl-4,5-dihydro-1H-pyrazole (**3l**)



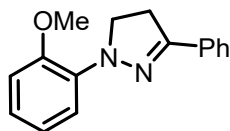
The product **3l** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3l** (103.9 mg, 69% yield) as a yellow solid; mp: 111–112 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.72 (m, 2H), 7.44 – 7.34 (m, 3H), 7.31 (t, *J* = 3.2 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.02 – 6.92 (m, 2H), 3.85 (t, *J* = 6.4 Hz, 2H), 3.26 (t, *J* = 6.4 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 150.1, 147.0, 132.7, 130.5, 129.0, 128.7, 126.0, 123.3, 121.8, 115.9, 111.5, 48.1, 32.2. IR (KBr): 3054, 2934, 1597, 1495, 1439, 1257, 1078, 955, 829, 738, 691, 507 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub><sup>79</sup>BrN<sub>2</sub> [M+H]<sup>+</sup>: 301.0335, found: 301.0328.

3-phenyl-1-(*o*-tolyl)-4,5-dihydro-1H-pyrazole (**3m**)



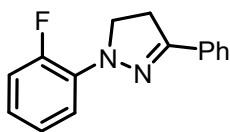
The product **3m** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3m** (50.7 mg, 43% yield) as a white solid; mp: 147–148 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.74 (m, 2H), 7.43 – 7.38 (m, 2H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.04 – 7.00 (m, 1H), 3.76 (t, *J* = 10.0 Hz, 2H), 3.22 (t, *J* = 10.0 Hz, 2H), 2.49 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.8, 146.0, 139.4, 138.9, 133.1, 128.8, 128.6, 125.8, 121.3, 117.1, 111.0, 48.5, 32.0, 21.8. IR (KBr): 3035, 2925, 2853, 1589, 1497, 1395, 1192, 1139, 812, 731, 675, 532, 449 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 237.1386, found: 237.1392.

1-(2-methoxyphenyl)-3-phenyl-4,5-dihydro-1H-pyrazole (**3n**)



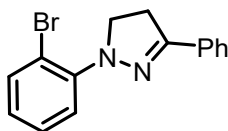
The product **3n** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3n** (74.3 mg, 59% yield) as a white solid; mp: 153–154 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.77 (m, 2H), 7.57 – 7.53 (m, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.33 (m, 1H), 7.06 – 7.02 (m, 1H), 6.99 – 6.92 (m, 2H), 3.98 (t, *J* = 10.0 Hz, 2H), 3.91 (s, 3H), 3.23 (t, *J* = 10.0 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 151.0, 150.1, 138.3, 133.2, 128.8, 128.6, 126.1, 123.3, 121.4, 119.9, 111.9, 55.9, 53.6, 33.2. IR (KBr): 3854, 2919, 2829, 1597, 1504, 1465, 1238, 1024, 955, 745, 693, 486 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 253.1335, found: 253.1337.

1-(2-fluorophenyl)-3-phenyl-4,5-dihydro-1H-pyrazole (**3o**)



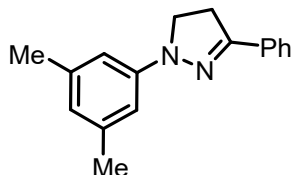
The product **3o** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3o** (50.1 mg, 42% yield) as a yellow solid; mp: 98–99 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.67 – 7.63 (m, 1H), 7.45 – 7.36 (m, 3H), 7.13 – 7.04 (m, 2H), 6.93 – 6.87 (m, 1H), 4.08 – 4.03 (m, 2H), 3.25 (t, *J* = 10.0 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) 151.4 (d, <sup>1</sup>*J*<sub>CF</sub> = 241.2 Hz), 150.5, 135.6 (d, <sup>3</sup>*J*<sub>CF</sub> = 9.0 Hz), 132.6, 128.8, 128.5, 126.0, 124.5 (d, <sup>4</sup>*J*<sub>CF</sub> = 3.2 Hz), 121.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 7.2 Hz), 118.9 (d, <sup>4</sup>*J*<sub>CF</sub> = 3.3 Hz), 116.1 (d, <sup>2</sup>*J*<sub>CF</sub> = 20.1 Hz), 52.2, 32.9. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -137.11. IR (KBr): 2927, 2849, 1612, 1573, 1453, 1376, 1269, 1214, 1029, 739, 685, 542, 473 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub>FN<sub>2</sub> [M+H]<sup>+</sup>: 241.1136, found: 241.1137.

1-(2-bromophenyl)-3-phenyl-4,5-dihydro-1H-pyrazole (**3p**)



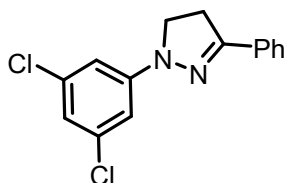
The product **3p** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3p** (67.7 mg, 45% yield) as a yellow solid; mp: 105–106 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 6.4 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.43 – 7.36 (m, 3H), 7.32 – 7.27 (m, 1H), 7.17 – 7.12 (m, 1H), 6.99 – 6.94 (m, 1H), 3.98 (t, *J* = 9.6 Hz, 2H), 3.27 (t, *J* = 9.6 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 152.5, 146.4, 132.8, 130.5, 129.2, 128.8, 128.7, 127.6, 126.3, 124.4, 122.2, 53.5, 33.5. IR (KBr): 3062, 2958, 1617, 1515, 1489, 1307, 1115, 878, 767, 691, 535 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub><sup>79</sup>BrN<sub>2</sub> [M+H]<sup>+</sup>: 301.0335, found: 301.0342.

1-(3,5-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3q**)



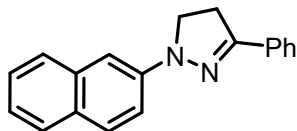
The product **3q** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3q** (62.5 mg, 50% yield) as a white solid; mp: 146–147 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 2H), 7.42 – 7.38 (m, 2H), 7.34 (d, *J* = 7.0 Hz, 1H), 6.81 (d, *J* = 4.5 Hz, 2H), 6.55 (s, 1H), 3.88 (t, *J* = 10.5 Hz, 2H), 3.25 – 3.21 (m, 2H), 2.34 (s, 6H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.7, 146.0, 138.8, 133.1, 128.6, 128.5, 125.8, 121.2, 110.9, 48.4, 31.9, 21.8. IR (KBr): 3734, 3031, 2919, 2846, 1583, 1477, 1383, 1196, 1119, 809, 741, 685, 542, 454 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 251.1543, found: 251.1548.

1-(3,5-dichlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3r**)



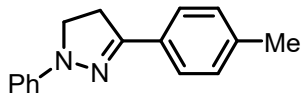
The product **3r** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3r** (75.7 mg, 52% yield) as a yellow solid; mp: 155–156 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.76 – 7.72 (m, 2H), 7.43 – 7.35 (m, 3H), 6.98 (d, *J* = 4.0 Hz, 2H), 6.79 (t, *J* = 5.0 Hz, 1H), 3.88 – 3.84 (m, 2H), 3.33 – 3.29 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.8, 144.1, 133.2, 129.8, 128.6, 128.5, 125.8, 119.2, 113.2, 48.8, 32.1. IR (KBr): 2916, 2855, 1591, 1480, 1457, 1199, 1078, 958, 853, 773, 694, 642, 483 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>13</sub><sup>35</sup>Cl<sub>2</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 291.0450, found: 291.0462.

1-(naphthalen-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3s**)



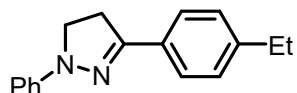
The product **3s** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3s** (51.6 mg, 38% yield) as a yellow solid; mp: 142–143 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.90 (m, 1H), 7.78 – 7.72 (m, 5H), 7.41 – 7.35 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.06 (d, *J* = 4.8 Hz, 1H), 3.91 (t, *J* = 10.4 Hz, 2H), 3.25 – 3.21 (m, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.3, 143.6, 134.9, 132.9, 129.1, 128.7, 127.9, 126.6, 126.5, 125.8, 122.7, 116.4, 106.1, 48.2, 32.1. IR (KBr): 2916, 2850, 1628, 1594, 1501, 1452, 1356, 1256, 959, 817, 738, 683, 465 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 273.1386, found: 273.1392.

1-phenyl-3-(*p*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3t**)



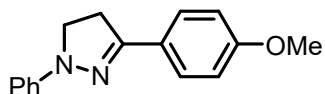
The product **3t** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3t** (75.5 mg, 64% yield) as a white solid; mp: 165–167 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 2H), 7.34 – 7.30 (m, 2H), 7.21 (d, *J* = 6.0 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.90 – 6.83 (m, 1H), 3.87 (t, *J* = 6.4 Hz, 2H), 3.23 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 149.3, 146.2, 138.7, 130.3, 129.3, 129.2, 125.8, 119.0, 113.0, 48.3, 32.2, 21.5. IR (KBr): 3683, 2911, 2865, 1508, 1458, 1362, 1257, 1040, 815, 752, 699, 489 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 237.1386, found: 237.1385.

3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3u**)



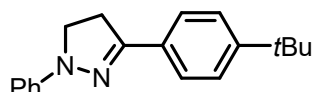
The product **3u** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3u** (62.5 mg, 50% yield) as a white solid; mp: 153–154 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.12 (m, 2H), 6.87 – 6.82 (m, 1H), 3.88 (t, *J* = 10.5 Hz, 2H), 3.27 – 3.22 (m, 2H), 2.68 (q, *J* = 7.5 Hz, 2H), 1.27 (d, *J* = 7.5 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.3, 146.1, 145.0, 130.5, 129.2, 128.1, 125.9, 119.0, 113.0, 48.3, 32.2, 28.9, 15.6. IR (KBr): 3048, 2963, 2922, 2870, 1591, 1498, 1445, 1386, 1295, 1116, 826, 741, 683, 548, 498 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 251.1543, found: 251.1540.

3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3v**)



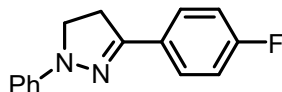
The product **3v** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3v** (84.4 mg, 67% yield) as a white solid; mp: 141–142 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.16 – 7.10 (m, 2H), 6.95 – 6.90 (m, 2H), 6.87 – 6.83 (m, 1H), 3.89 – 3.82 (m, 5H), 3.22 (t, *J* = 10.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 160.1, 149.2, 146.3, 129.2, 127.3, 125.8, 118.9, 114.1, 113.0, 55.4, 48.3, 32.3. IR (KBr): 3825, 3758, 3685, 2922, 2843, 1506, 1451, 1248, 1172, 1031, 820, 747, 694, 600, 498 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 253.1335, found: 253.1341.

3-(4-(tert-butyl)phenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3w**)



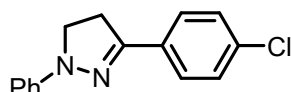
The product **3w** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3w** (83.4 mg, 60% yield) as a white solid; mp: 156–157 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.18 – 7.13 (m, 2H), 6.89 – 6.84 (m, 1H), 3.88 (t, *J* = 10.5 Hz, 2H), 3.27 – 3.23 (m, 2H), 1.36 (s, 9H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 151.9, 149.2, 146.2, 130.3, 129.2, 125.7, 125.6, 119.1, 113.1, 48.4, 34.9, 32.2, 31.4. IR: 3049, 2938, 2929, 2874, 2827, 1606, 1541, 1347, 1262, 1138, 920, 787, 687, 518 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 279.1856, found: 279.1863.

3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3x**)



The product **3x** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3x** (96.0 mg, 80% yield) as a yellow solid; mp: 75–76 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.68 (m, 2H), 7.34 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 7.09 (t, *J* = 8.8 Hz, 2H), 6.93 – 6.81 (m, 1H), 3.88 (t, *J* = 10.4 Hz, 2H), 3.21 (t, *J* = 10.4 Hz, 2H). <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 162.9 (d, <sup>1</sup>*J*<sub>CF</sub> = 247.1 Hz), 152.0, 148.0, 129.4, 129.1, 128.1, 127.5 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.0 Hz), 127.4 (d, <sup>3</sup>*J*<sub>CF</sub> = 8.0 Hz), 126.4, 119.0, 115.5 (d, <sup>2</sup>*J*<sub>CF</sub> = 21.4 Hz), 112.9, 48.3, 32.0. <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -112.69. IR (KBr): 2928, 2837, 1608, 1513, 1453, 1377, 1264, 1213, 1021, 749, 684, 553, 475 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>14</sub>FN<sub>2</sub> [M+H]<sup>+</sup>: 241.1136, found: 241.1148.

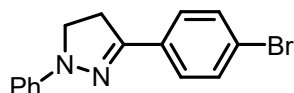
3-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3y**)



The product **3y** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3y** (55.0 mg, 43% yield) as a yellow solid; mp: 78–79 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.08 – 7.03 (m, 2H), 6.83 – 6.77 (m, 1H),

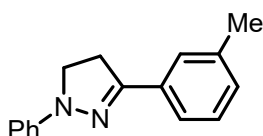
3.81 (t,  $J = 10.4$  Hz, 2H), 3.14 – 3.11 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform- $d$ )  $\delta$  149.7, 143.1, 131.4, 129.6, 128.7, 125.9, 124.8, 120.8, 114.1, 48.3, 32.2. IR (KBr): 2936, 2875, 1610, 1490, 1497, 1213, 1128, 978, 863, 793, 642, 445  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{14}^{35}\text{ClN}_2$   $[\text{M}+\text{H}]^+$ : 257.0840, found: 257.0845.

3-(4-bromophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3z**)



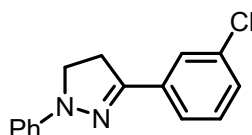
The product (**3z**) was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3z** (91.8 mg, 61% yield) as a yellow solid; mp: 82–83 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.58 (d,  $J = 8.4$  Hz, 2H), 7.50 (d,  $J = 8.8$  Hz, 2H), 7.32 – 7.27 (m, 2H), 7.15 – 7.09 (m, 2H), 6.90 – 6.85 (m, 1H), 3.89 (t,  $J = 10.4$  Hz, 2H), 3.22 – 3.18 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  147.8, 145.6, 132.0, 131.7, 129.2, 127.2, 122.4, 119.4, 113.0, 48.3, 31.8. IR (KBr): 2985, 2872, 1573, 1492, 1276, 1070, 925, 822, 744, 655, 499  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{14}^{79}\text{BrN}_2$   $[\text{M}+\text{H}]^+$ : 301.0335, found: 301.0342.

1-phenyl-3-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3aa**)



The product **3aa** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3aa** (83.8 mg, 71% yield) as a white solid; mp: 124–126 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.60 (s, 1H), 7.53 (d,  $J = 7.6$  Hz, 1H), 7.35 – 7.27 (m, 3H), 7.19 – 7.13 (m, 3H), 6.90 – 6.84 (m, 1H), 3.88 (t,  $J = 10.4$  Hz, 2H), 3.25 (t,  $J = 10.4$  Hz, 2H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  149.4, 146.0, 138.2, 132.9, 129.5, 129.2, 128.5, 126.4, 123.1, 119.2, 113.1, 48.3, 32.1, 21.6. IR (KBr): 3618, 2937, 2879, 1575, 1473, 1369, 1247, 1140, 859, 763, 512  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 237.1386, found: 237.1390.

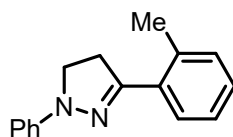
3-(3-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ab**)



The product (**3ab**) was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3ab** (76.8 mg, 60% yield) as a yellow solid; mp: 104–105 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.72 (s, 1H), 7.57 (d,  $J = 7.2$  Hz, 1H), 7.35 – 7.27 (m, 4H), 7.16 – 7.12 (m, 2H), 6.91 – 6.86 (m, 1H), 3.90 (t,  $J = 10.4$  Hz, 2H), 3.22 – 3.18 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  147.5, 145.5, 134.9, 134.7, 129.9, 129.3, 128.4, 125.7, 123.8, 119.6, 113.1, 48.4, 31.9. IR (KBr): 3018, 2957, 1583, 1499, 1442,

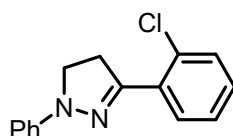
1237, 1078, 957, 831, 738, 695, 513  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{14}^{35}\text{ClN}_2$   $[\text{M}+\text{H}]^+$ : 257.0840, found: 257.0835.

1-phenyl-3-(*o*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3ac**)



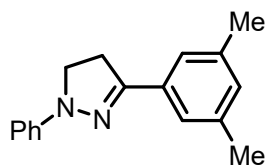
The product **3ac** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3ac** (57.8 mg, 49% yield) as a white solid; mp: 114–115 °C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.38 – 7.34 (m, 1H), 7.34 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.14 – 7.08 (m, 2H), 6.89 – 6.81 (m, 1H), 3.82 (t,  $J$  = 10.4 Hz, 2H), 3.35 – 3.31 (m, 2H), 2.71 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  149.9, 146.2, 137.6, 131.8, 131.5, 129.3, 128.1, 127.9, 125.8, 119.1, 113.0, 47.5, 34.2, 24.0. IR (KBr): 3525, 2937, 2879, 1575, 1473, 1369, 1247, 1140, 859, 763, 512  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 237.1386, found: 237.1393.

3-(2-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ad**)



The product **3ad** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3ad** (71.9 mg, 56% yield) as a yellow solid; mp: 134–136 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.81 – 7.76 (m, 1H), 7.43 – 7.38 (m, 1H), 7.33 – 7.24 (m, 4H), 7.17 – 7.11 (m, 2H), 6.91 – 6.84 (m, 1H), 3.90 (t,  $J$  = 10.4 Hz, 2H), 3.46 – 3.43 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  148.5, 145.9, 132.3, 132.0, 130.9, 130.2, 129.5, 129.3, 126.9, 119.6, 113.3, 48.9, 35.0. IR (KBr): 3175, 2979, 2901, 1535, 1486, 1375, 1198, 1132, 859, 763, 684, 512  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{14}^{35}\text{ClN}_2$   $[\text{M}+\text{H}]^+$ : 257.0840, found: 257.0837.

3-(3,5-dimethylphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ae**)

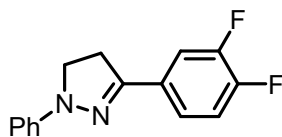


The product **3ae** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3ae** (86.3 mg, 69% yield) as a white solid; mp: 143–144 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.38 (d,  $J$  = 3.2 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.19 – 7.14 (m, 2H), 6.99 (s, 1H), 6.89 – 6.86 (m, 1H), 3.87 (t,  $J$  = 10.4 Hz, 2H), 3.23 (t,  $J$  = 10.4 Hz, 2H), 2.38 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  149.4, 146.1, 138.1, 132.9, 130.4, 129.2, 123.7, 119.0, 113.0, 48.2, 32.2, 21.4(4), 21.4(2). IR (KBr): 3721,



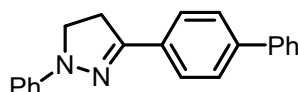
3168, 2935, 2876, 1586, 1467, 1374, 1235, 1137, 821, 759, 643, 542  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 251.1543, found: 251.1545.

3-(3,4-difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3af**)



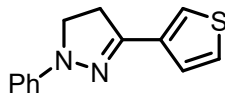
The product **3af** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give **3af** (59.3 mg, 46% yield) as a yellow solid; mp: 87–88 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.48 (m, 1H), 7.34 – 7.28 (m, 4H), 7.15 – 7.10 (m, 2H), 6.92 – 6.86 (m, 1H), 3.98 – 3.82 (m, 2H), 3.19 (t,  $J$  = 10.4 Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*) 160.9 (d,  $^1J_{\text{CF}}$  = 247 Hz), 146.1 (d,  $^1J_{\text{CF}}$  = 220.8 Hz), 134.4 (d,  $^3J_{\text{CF}}$  = 7.9 Hz), 132.9 (d,  $^4J_{\text{CF}}$  = 1.8 Hz), 131.1, 129.2 (d,  $^2J_{\text{CF}}$  = 23.6 Hz), 127.5, 121.7(4), 121.7(1), 119.5, 113.0, 112.5 (d,  $^2J_{\text{CF}}$  = 23.8 Hz), 48.3, 31.6.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -122.20, -124.79. IR (KBr): 2927, 2873, 1594, 1497, 1252, 1121, 907, 835, 752, 683, 445  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{15}\text{H}_{13}\text{F}_2\text{N}_2$   $[\text{M}+\text{H}]^+$ : 259.1041, found: 259.1045.

3-([1,1'-biphenyl]-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ag**)



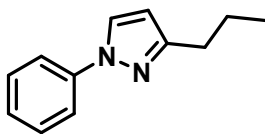
The product **3ag** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:300) to give **3ag** (93.9 mg, 63% yield) as a yellow solid; mp: 134–135 °C.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.73 (d,  $J$  = 8.4 Hz, 2H), 7.58 – 7.52 (m, 4H), 7.41 – 7.36 (m, 3H), 7.31 – 7.25 (m, 3H), 7.11 – 7.06 (m, 2H), 6.82 – 6.76 (m, 1H), 3.84 (t,  $J$  = 10.4 Hz, 2H), 3.23 – 3.20 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  148.8, 145.9, 141.2, 140.7, 132.1, 129.3, 129.0, 127.6, 127.3, 127.1, 126.3, 119.3, 113.1, 48.4, 32.1. IR (KBr): 3014, 2967, 1594, 1480, 1252, 1121, 907, 835, 752, 683, 445  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 299.1543, found: 299.1537.

1-phenyl-3-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrazole (**3ah**)



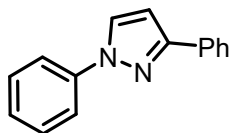
The product **3ah** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:400) to give **3ah** (61.6 mg, 54% yield) as a white solid; mp: 103–104 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.63 – 7.60 (m, 1H), 7.36 – 7.28 (m, 4H), 7.15 – 7.10 (m, 2H), 6.89 – 6.83 (m, 1H), 3.85 (t,  $J$  = 10.5 Hz, 2H), 3.26 – 3.18 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  146.1(4), 146.1(0), 135.7, 129.2, 126.3, 125.8, 122.4, 119.2, 113.1, 48.3, 33.0. IR(KBr): 3840, 3754, 3088, 3029, 1583, 1480, 1249, 1114, 848, 783, 735, 683, 624, 500  $\text{cm}^{-1}$ . HRMS ESI ( $m/z$ ): calcd for  $\text{C}_{13}\text{H}_{13}\text{SN}_2$   $[\text{M}+\text{H}]^+$ : 229.0794, found: 229.0795.

1-phenyl-3-propyl-1*H*-pyrazole (**5ai**)



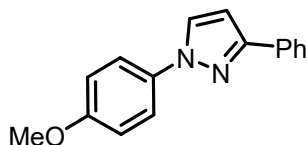
The product **5ai** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:400) to give **5ai** (38.2 mg, 41% yield) as yellow liquid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 2.4 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.28 – 7.18 (m, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 2.69 – 2.66 (m, 2H), 1.79 – 1.67 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 155.4, 140.4, 129.5, 127.4, 126.1, 119.1, 106.6, 30.5, 23.1, 14.1. HRMS ESI (*m/z*): calcd for C<sub>12</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 187.1230, found: 187.1238.

1,3-diphenyl-1*H*-pyrazole (**5a**)



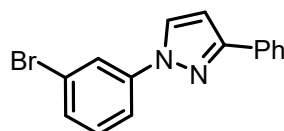
The product **5a** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 1,3-diphenyl-1*H*-pyrazole (**5a**) (39.2 mg, 89% yield) as a yellow solid; mp: 81–83 °C. <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.81 – 7.76 (m, 2H), 7.50 – 7.41 (m, 4H), 7.36 – 7.32 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 2.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 153.0, 140.3, 133.2, 129.5, 128.8, 128.1(4), 128.1(1), 126.4, 125.9, 119.1, 105.1. IR (KBr): 1600, 1530, 1505, 1455, 1362, 1044, 954 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 221.1073, found: 221.1078.

1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole (**5d**)



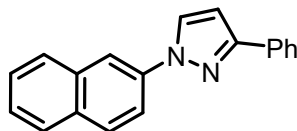
The product **5d** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole (**5d**) (43.6 mg, 87% yield) as a white solid; mp: 105–106 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.86 (d, *J* = 4.8 Hz, 1H), 7.67 (d, *J* = 9.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.30 (m, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 4.8 Hz, 1H), 3.85 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 158.3, 152.7, 134.2, 133.4, 128.8, 128.2, 128.0, 125.9, 120.9, 114.6, 104.7, 55.7. IR (KBr): 3146, 2963, 2838, 1598, 1530, 1518, 1456, 1257, 1046, 956, 830, 748 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 251.1179, found: 251.1182.

1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole (**5l**)



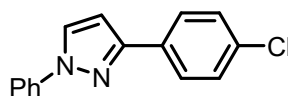
The product **5l** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole (**5l**) (47.3 mg, 79% yield) as a yellow solid; mp: 121–123 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.00 (t, *J* = 2.0 Hz, 1H), 7.95 – 7.90 (m, 3H), 7.71 – 7.66 (m, 1H), 7.48 – 7.39 (m, 3H), 7.39 – 7.29 (m, 2H), 6.79 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 153.5, 141.3, 132.9, 130.8, 129.3, 128.8, 128.4, 128.1, 126.0, 123.3, 122.2, 117.3, 105.7. IR (KBr): 3050, 1597, 1503, 1448, 1386, 1348 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub><sup>79</sup>Br [M+H]<sup>+</sup>: 299.0178, found: 299.0180.

#### 1-(naphthalen-2-yl)-3-phenyl-1*H*-pyrazole (**5s**)



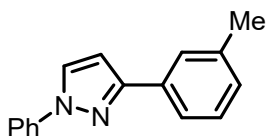
The product **5s** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 1-(naphthalen-2-yl)-3-phenyl-1*H*-pyrazole (**5s**) (44.3 mg, 82% yield) as a white solid; mp: 113–114 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 2.0 Hz, 1H), 8.10 (d, *J* = 2.4 Hz, 1H), 8.00 – 7.93 (m, 4H), 7.91 – 7.87 (m, 2H), 7.56 – 7.52 (m, 1H), 7.51 – 7.42 (m, 3H), 7.40 – 7.33 (m, 1H), 6.84 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 153.3, 137.8, 133.8, 133.2, 132.0, 129.6, 128.8, 128.4, 128.2, 128.1, 128.0, 127.1, 126.0(3), 126.0(5), 118.6, 116.2, 105.4. IR (KBr): 1598, 1547, 1528, 1509, 1464, 1391, 1368, 1336 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 271.1230, found: 271.1228.

#### 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (**5y**)



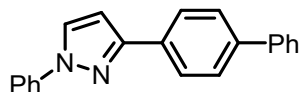
The product **5y** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (**5y**) (38.2 mg, 75% yield) as a yellow solid; mp: 131–133 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.4 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.78 – 7.74 (m, 2H), 7.50 – 7.45 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 141.6, 139.6, 135.0, 132.4, 129.0, 128.8, 128.7, 126.5, 120.7, 114.6, 106.9. IR (KBr): 3052, 2924, 1596, 1507, 1442, 1410, 1262 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub><sup>35</sup>Cl [M+H]<sup>+</sup>: 255.0684, found: 255.0680.

#### 1-phenyl-3-(*m*-tolyl)-1*H*-pyrazole (**5aa**)



The product **5aa** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 1-phenyl-3-(m-tolyl)-1*H*-pyrazole (**5aa**) (40.2 mg, 86% yield) as a white solid; mp: 110–111 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.89 (m, 3H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.29 – 7.24 (m, 2H), 6.76 (d, *J* = 2.4 Hz, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 152.8, 138.1, 136.3, 133.3, 130.1, 128.8, 128.1, 128.1, 126.0, 119.2, 104.9, 21.1. IR (KBr): 3145, 3029, 1605, 1521, 1453, 1389, 1364 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 235.1230, found: 235.1238.

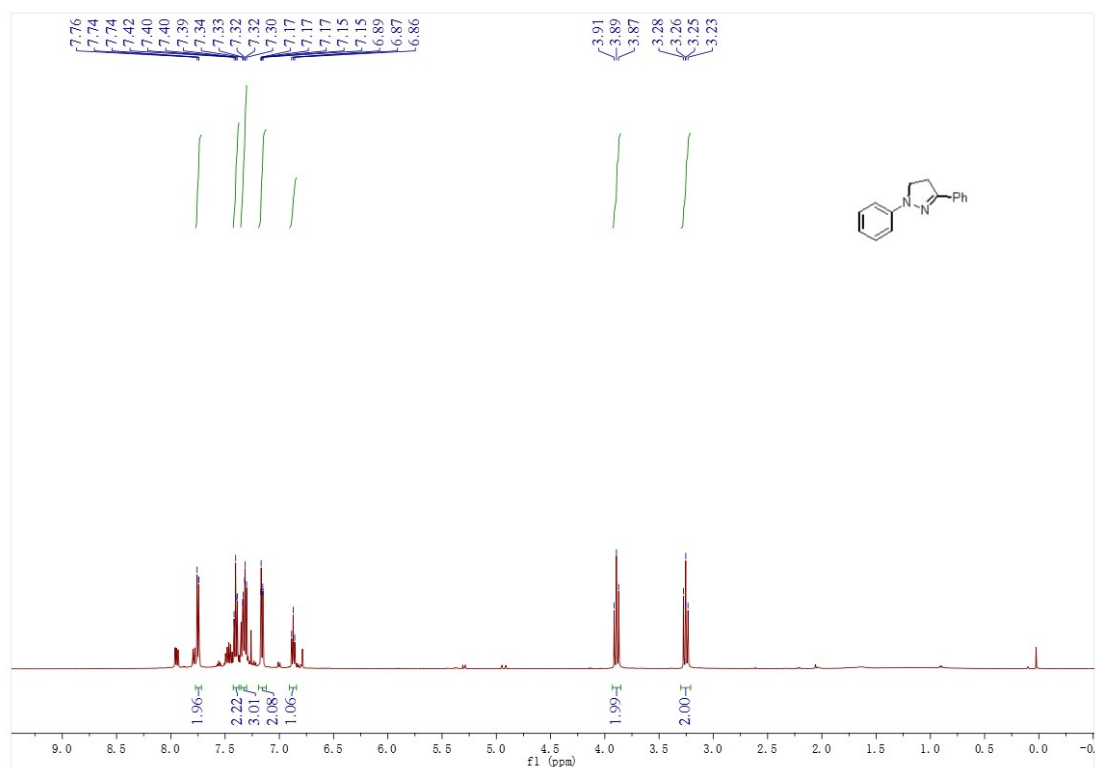
3-([1,1'-biphenyl]-4-yl)-1-phenyl-1*H*-pyrazole (**5ag**)



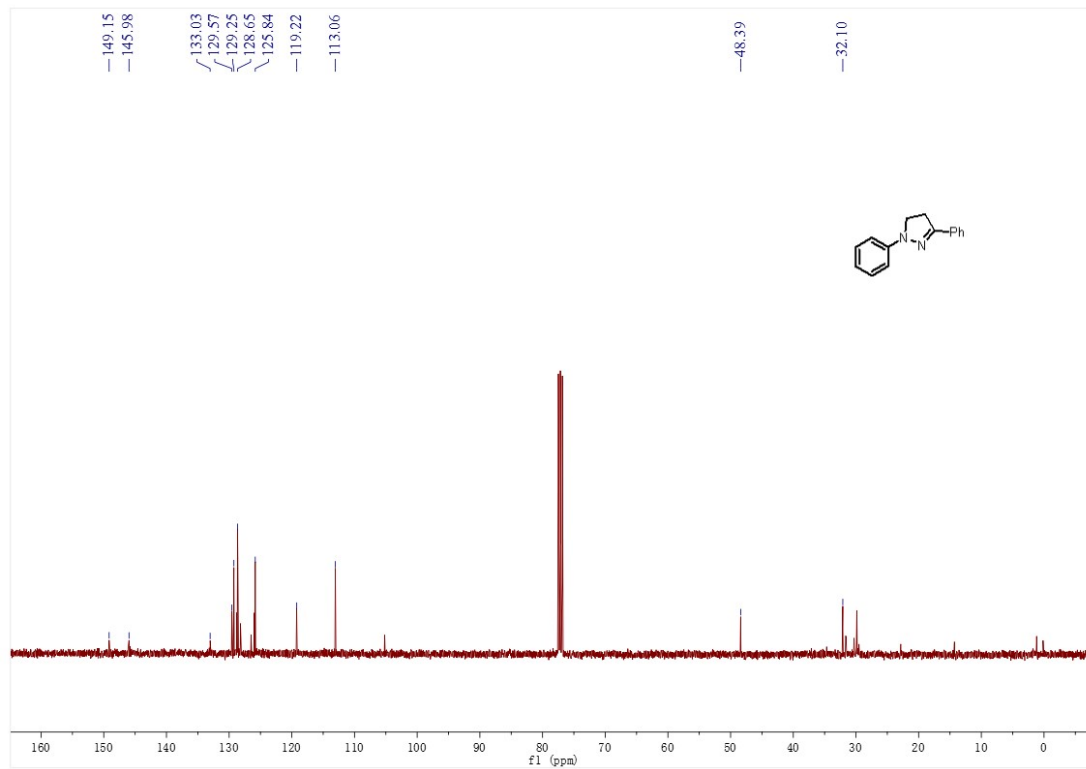
The product **5ag** was performed following the General Procedure. The product was separated by flash chromatography on silica gel (ethyl acetate: petroleum ether = 1:500) to give a pure sample of 3-([1,1'-biphenyl]-4-yl)-1-phenyl-1*H*-pyrazole (**5ag**) (51.6 mg, 87% yield) as a white solid; mp: 131–132 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.97 (m, 3H), 7.82 – 7.77 (m, 2H), 7.70 – 7.64 (m, 4H), 7.49 – 7.47 (m, 4H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 152.7, 140.9, 140.4, 132.2, 129.6, 128.9, 128.2, 127.5, 127.2, 126.5, 126.4, 124.6, 124.1, 119.2, 105.2. IR (KBr): 3014, 2967, 1594, 1480, 1252, 1439, 1397, 1357, 1121, 907 cm<sup>-1</sup>. HRMS ESI (*m/z*): calcd for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 297.1386, found: 297.1391.

## 8. The NMR Spectra of Compounds

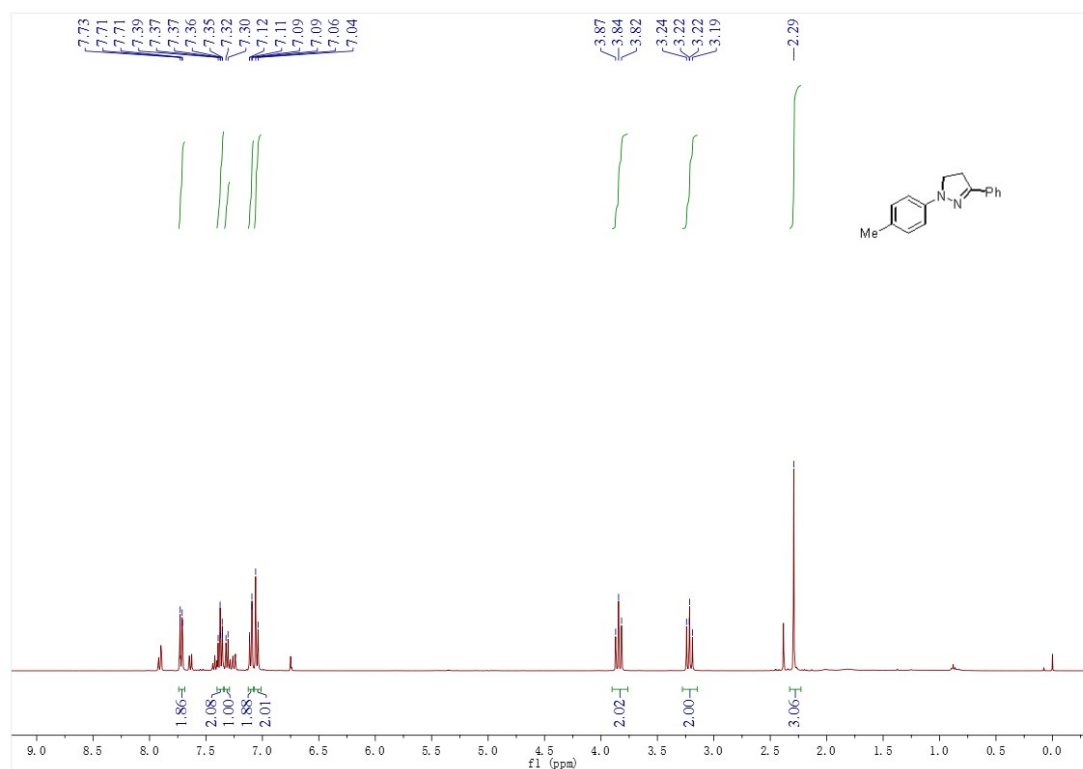
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1,3-diphenyl-4,5-dihydro-1*H*-pyrazole (**3a**)



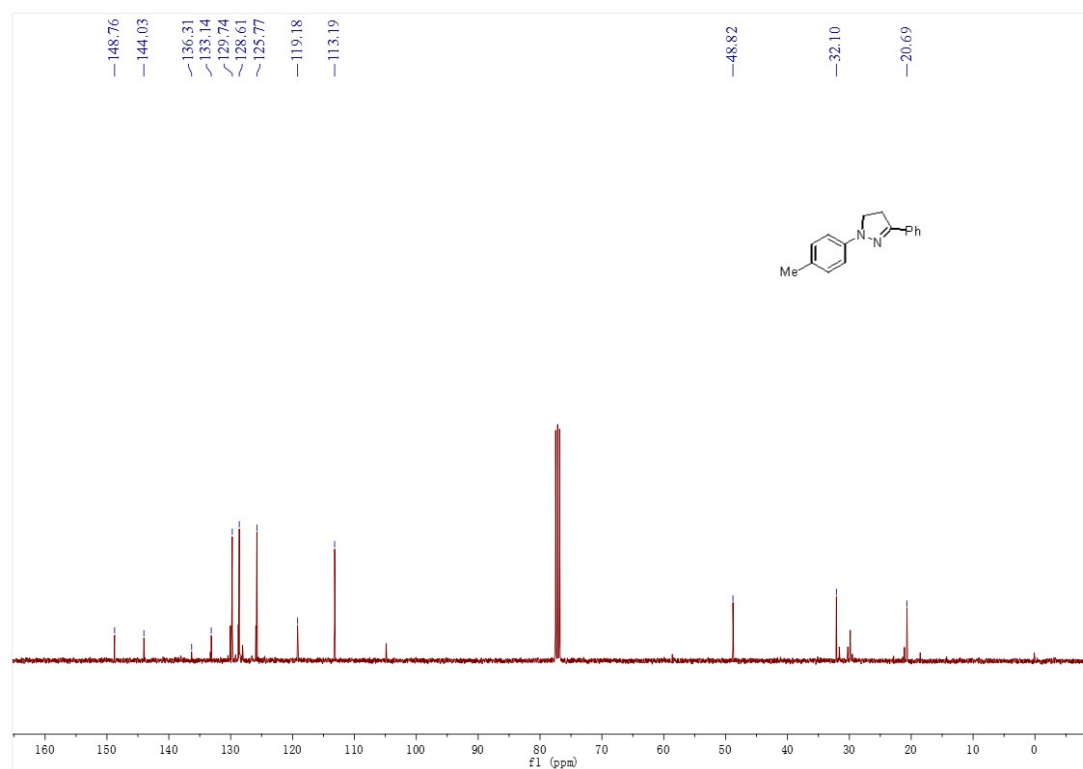
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1,3-diphenyl-4,5-dihydro-1*H*-pyrazole (**3a**)



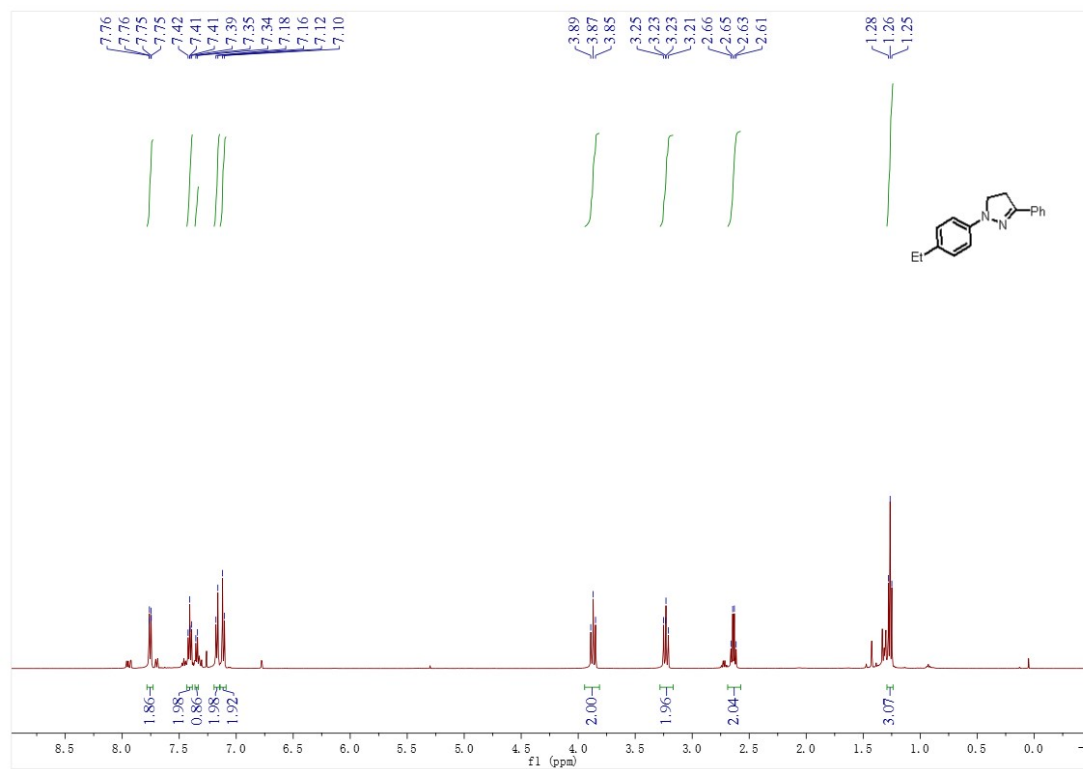
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-phenyl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrazole (**3b**)



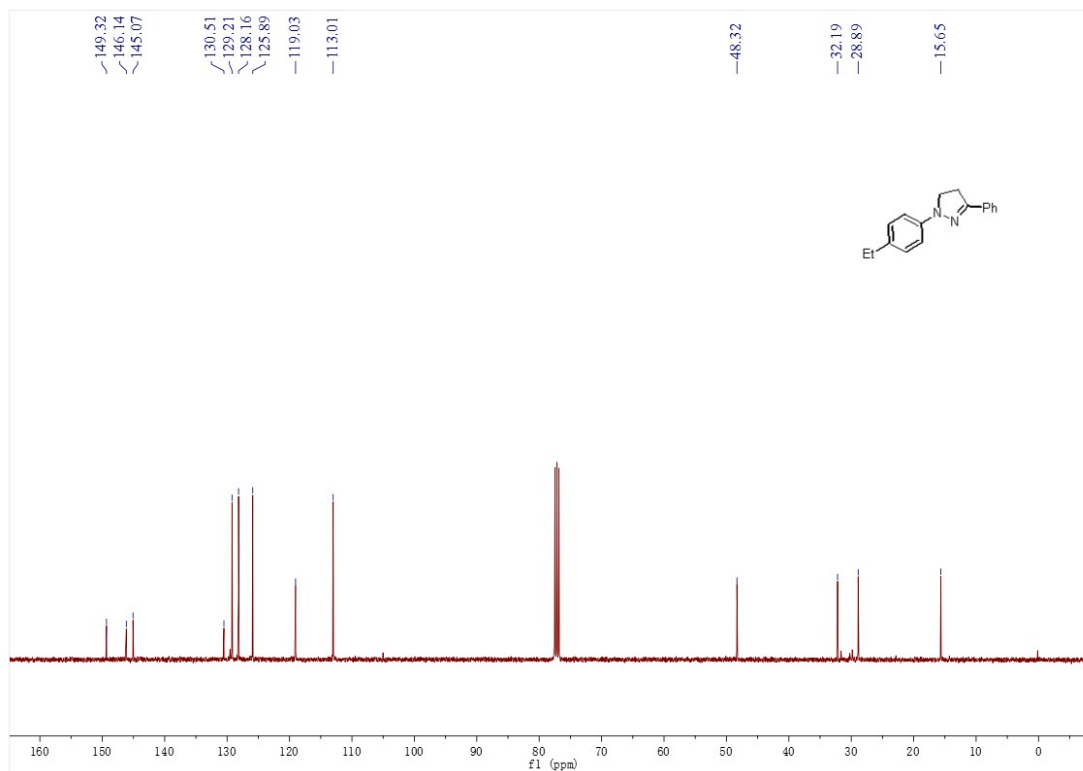
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-phenyl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrazole (**3b**)



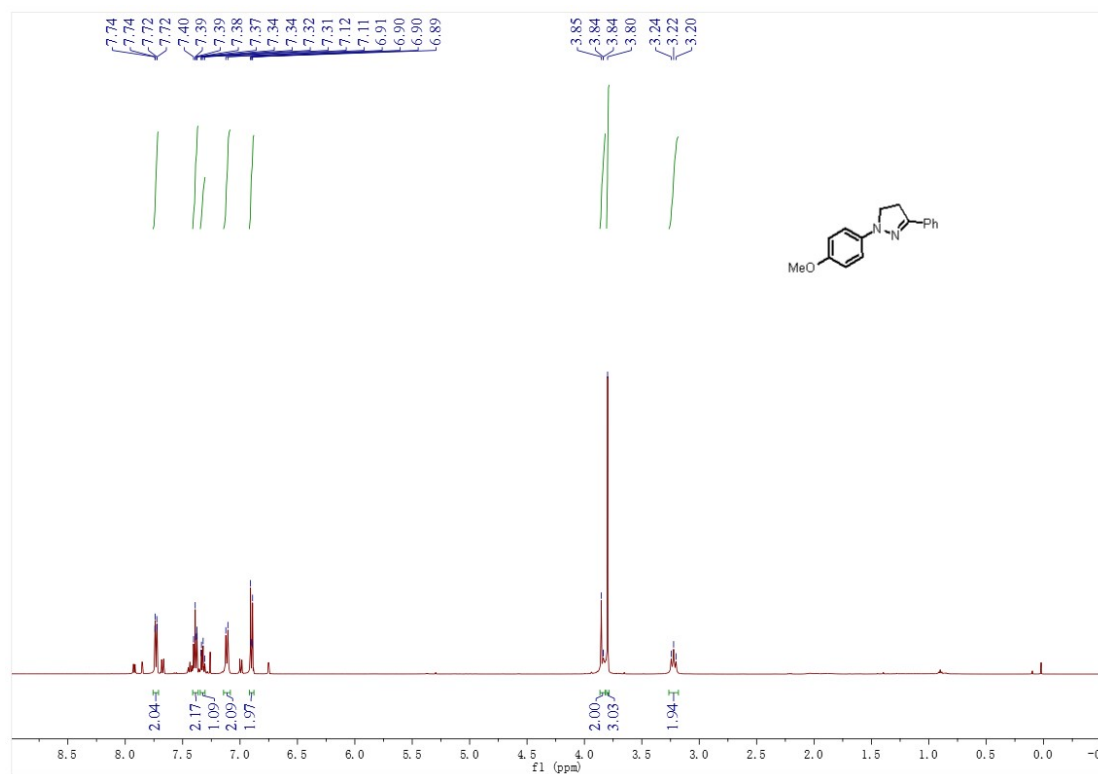
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(4-ethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3c**)



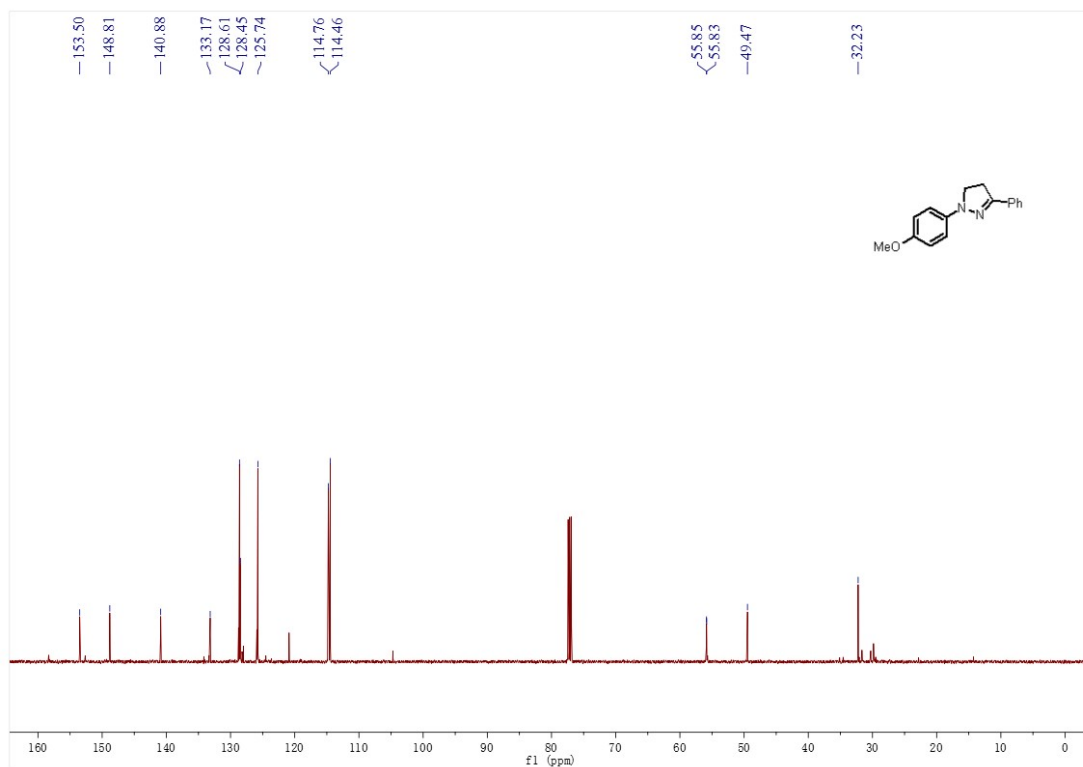
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(4-ethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3c**)



$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3d**)

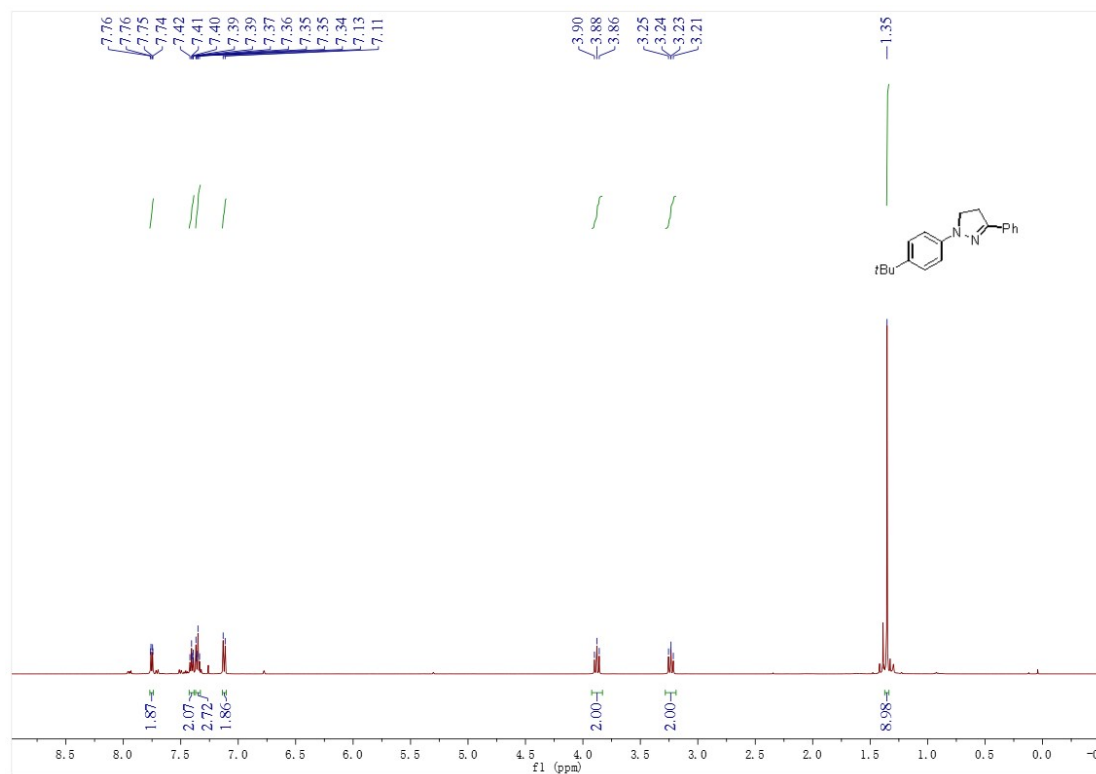


$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 1-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3d**)

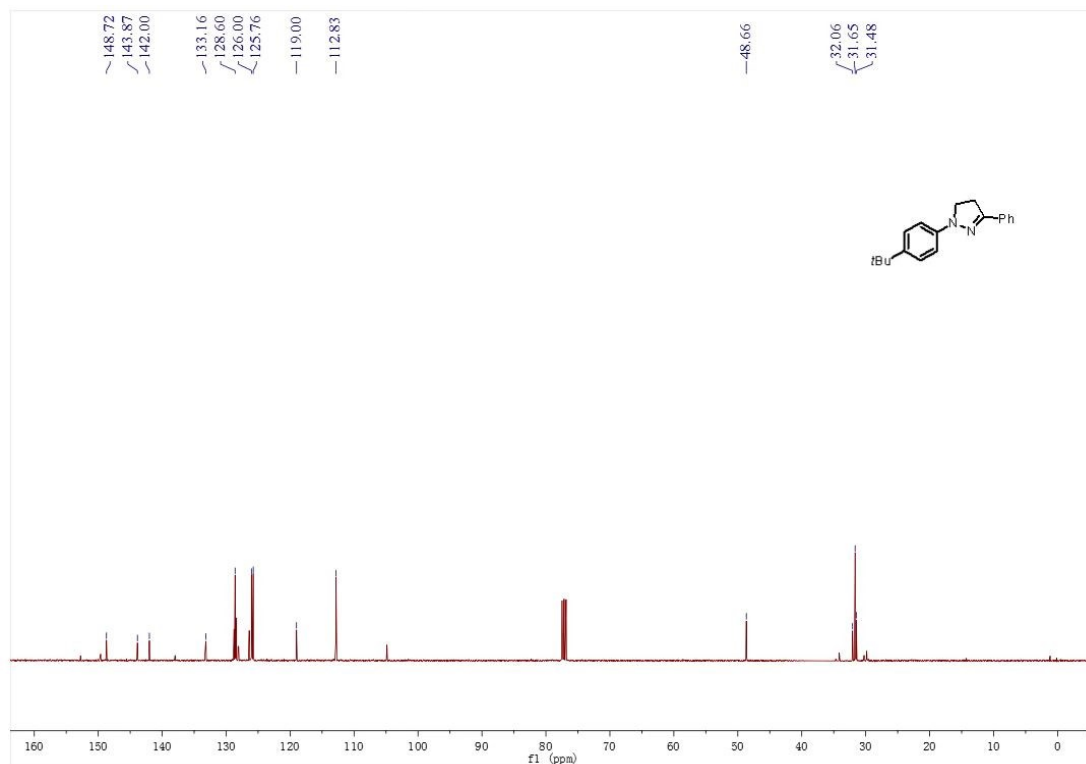




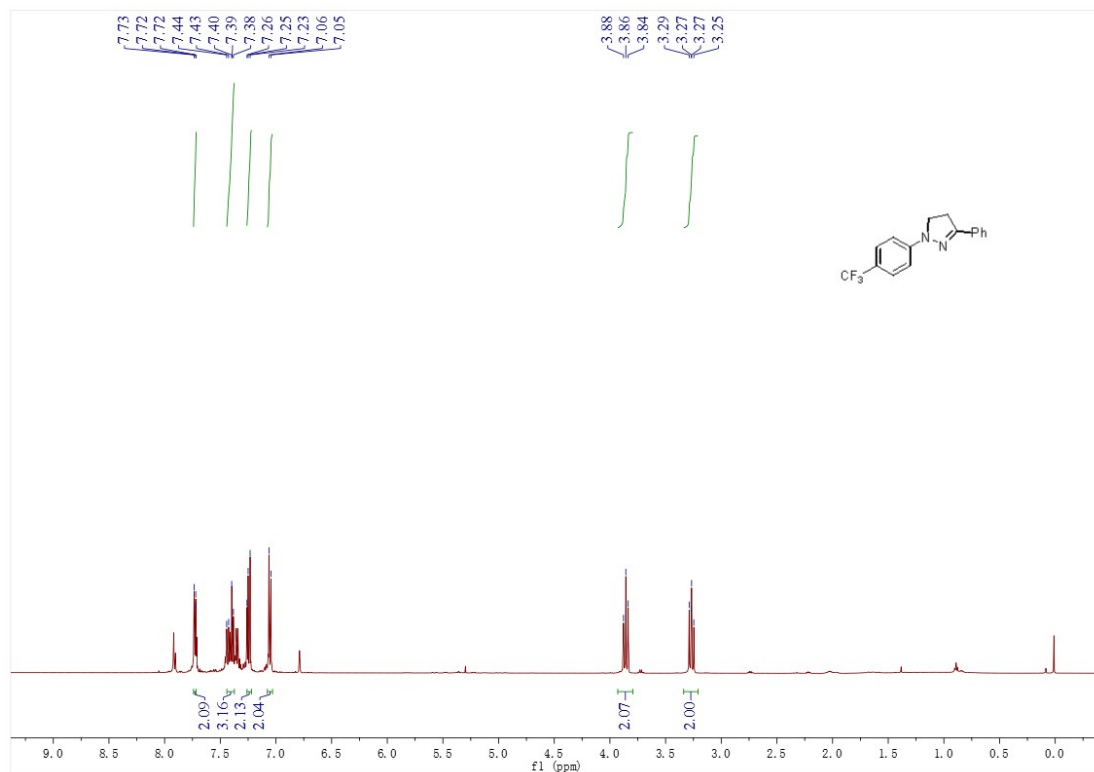
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(4-(tert-butyl)phenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3e**)



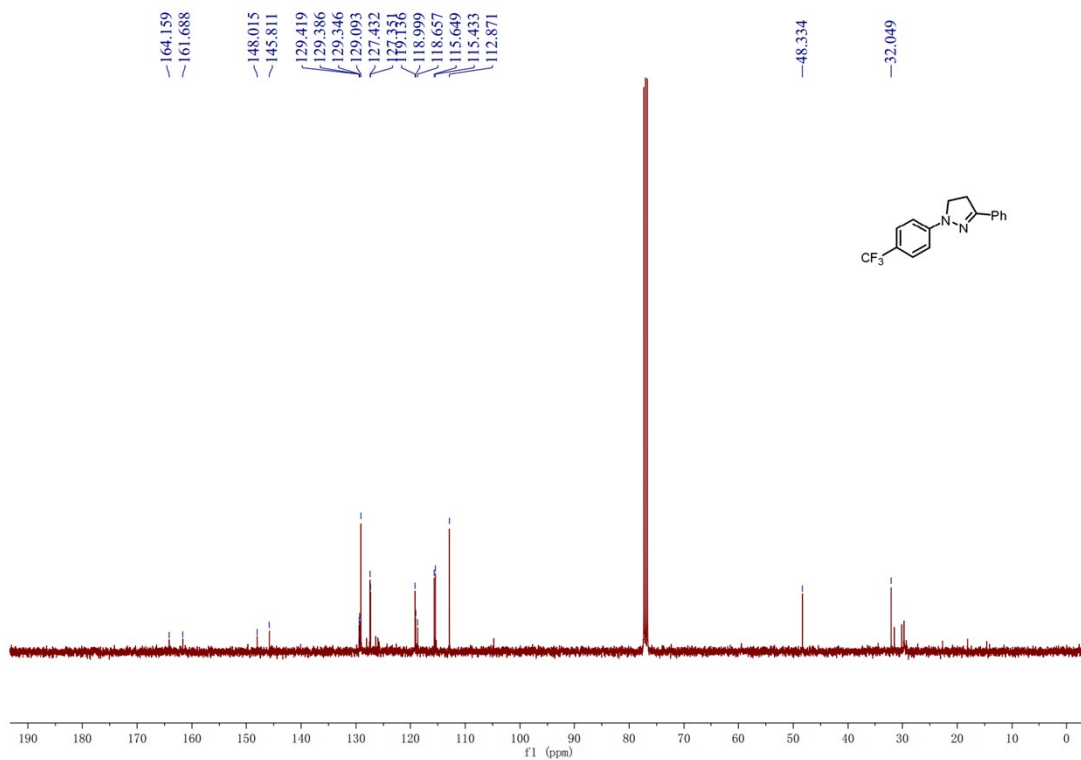
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(4-(tert-butyl)phenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3e**)



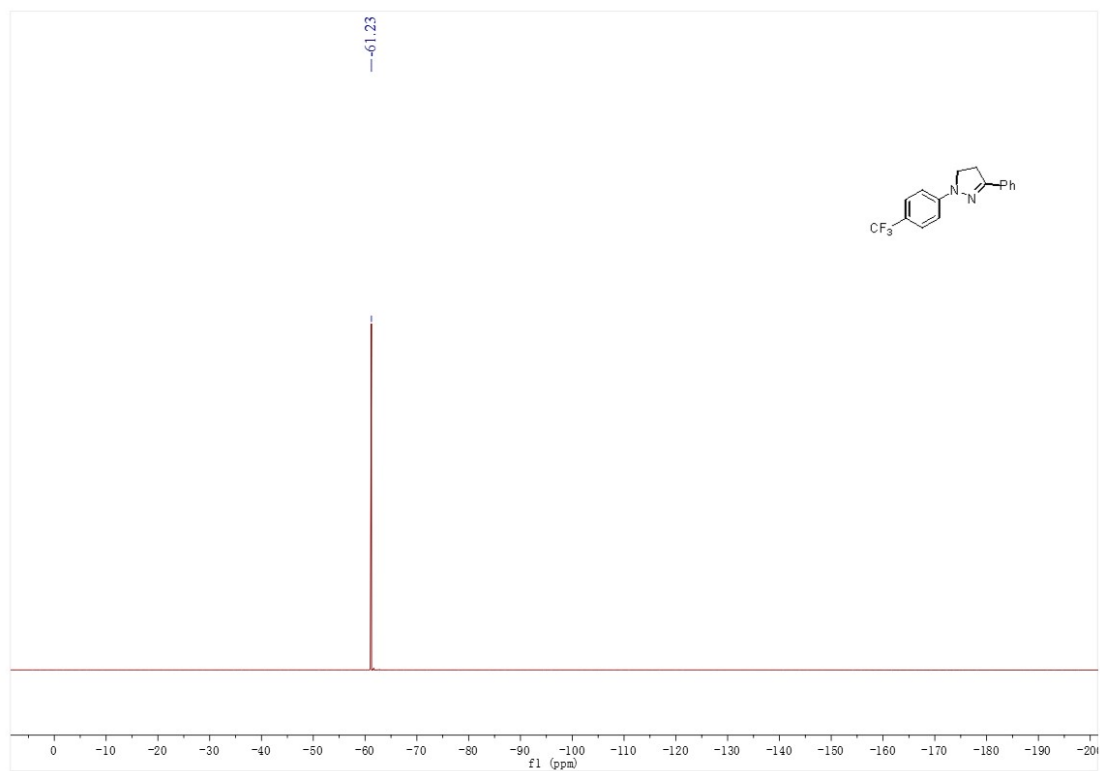
$^1\text{H}$  NMR spectra (500 MHz, Chloroform- $d$ ) of 3-phenyl-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (**3f**)



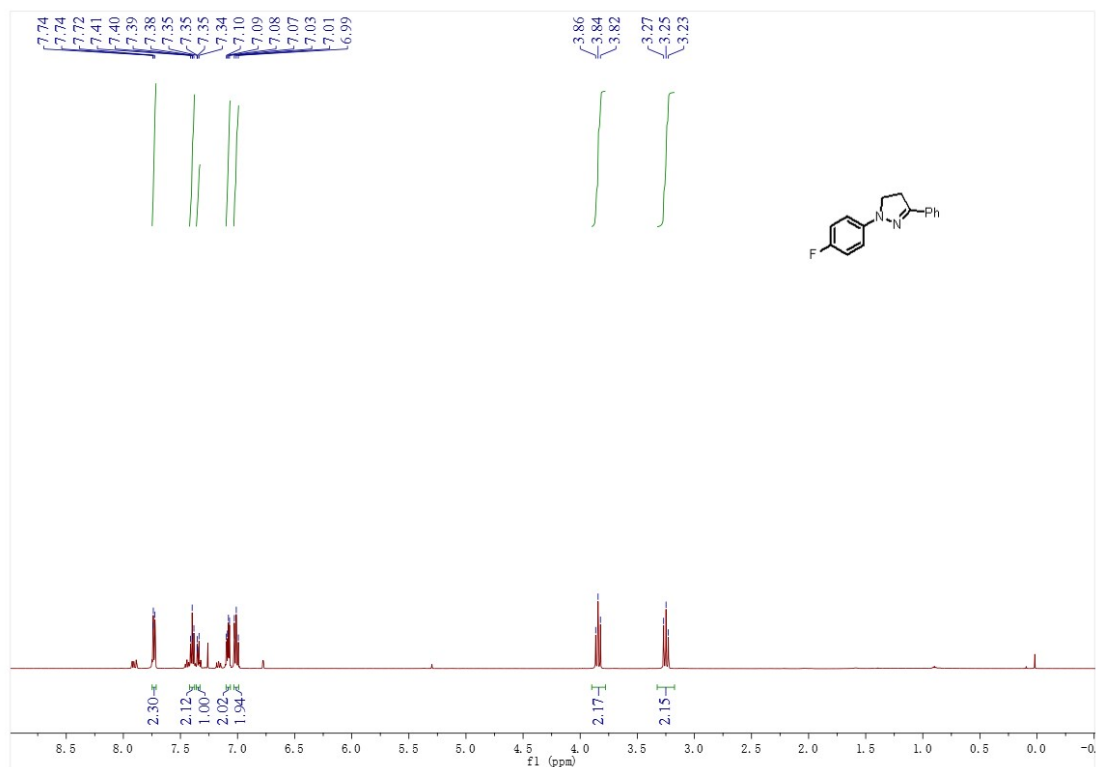
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform- $d$ ) of 3-phenyl-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (**3f**)



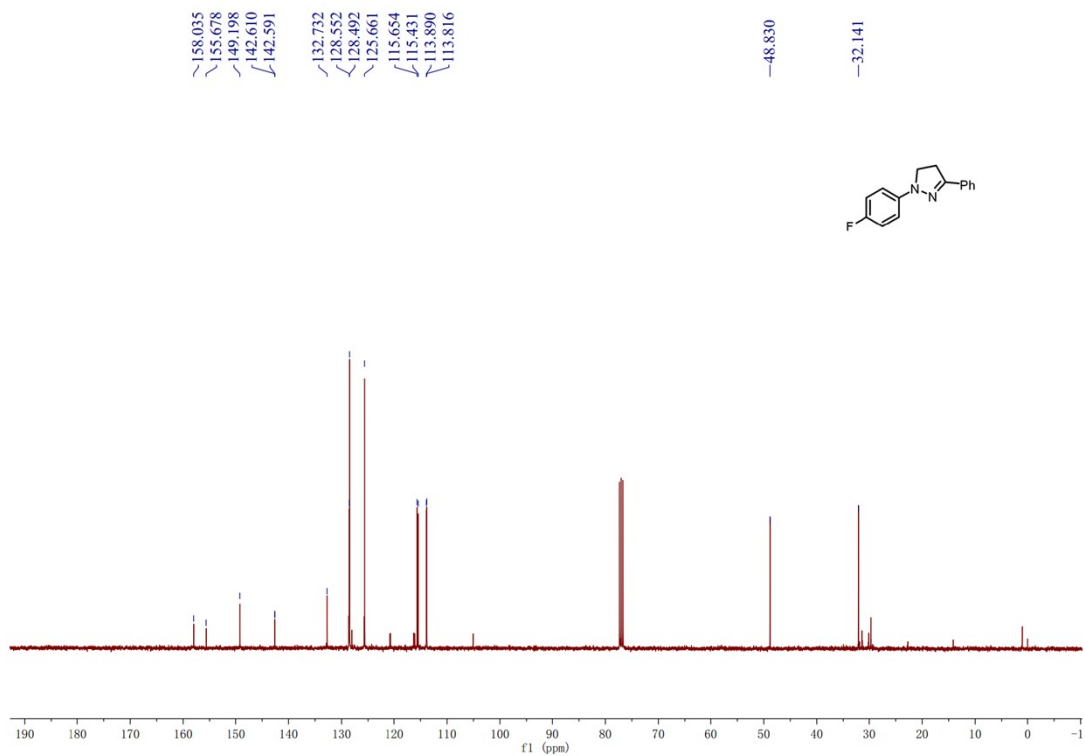
$^{19}\text{F}$  NMR spectra (376 MHz, Chloroform-*d*) of 3-phenyl-1-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-pyrazole (**3f**)



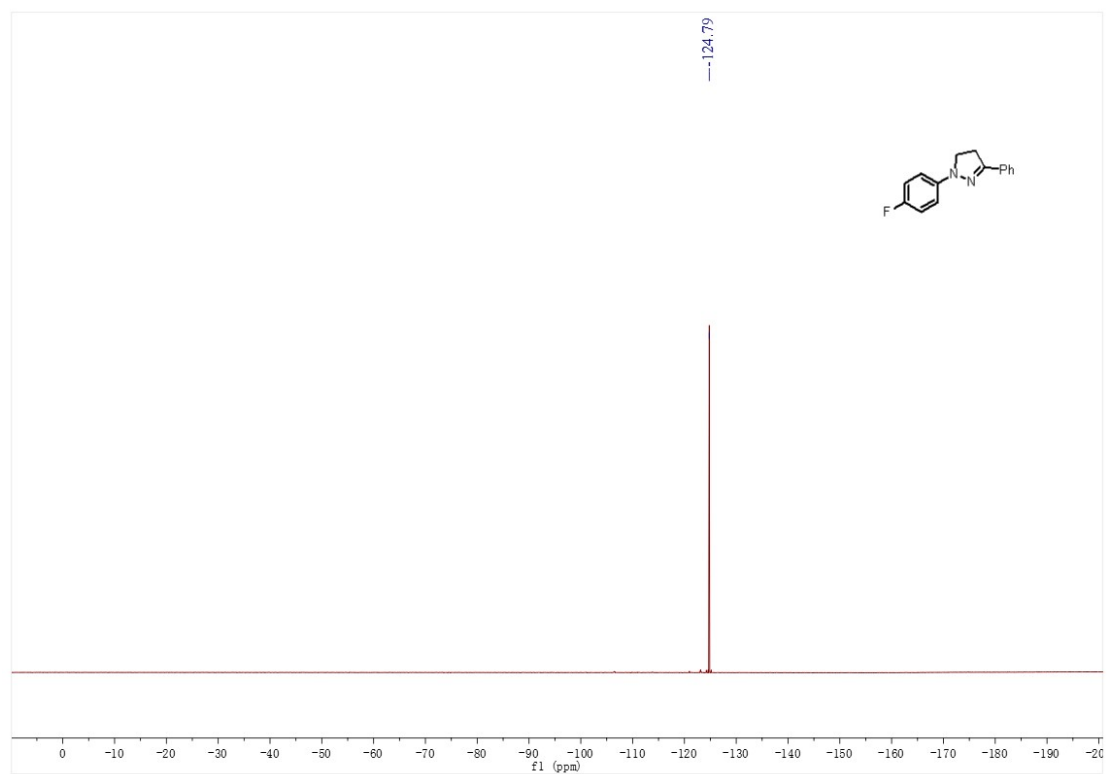
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3g**)



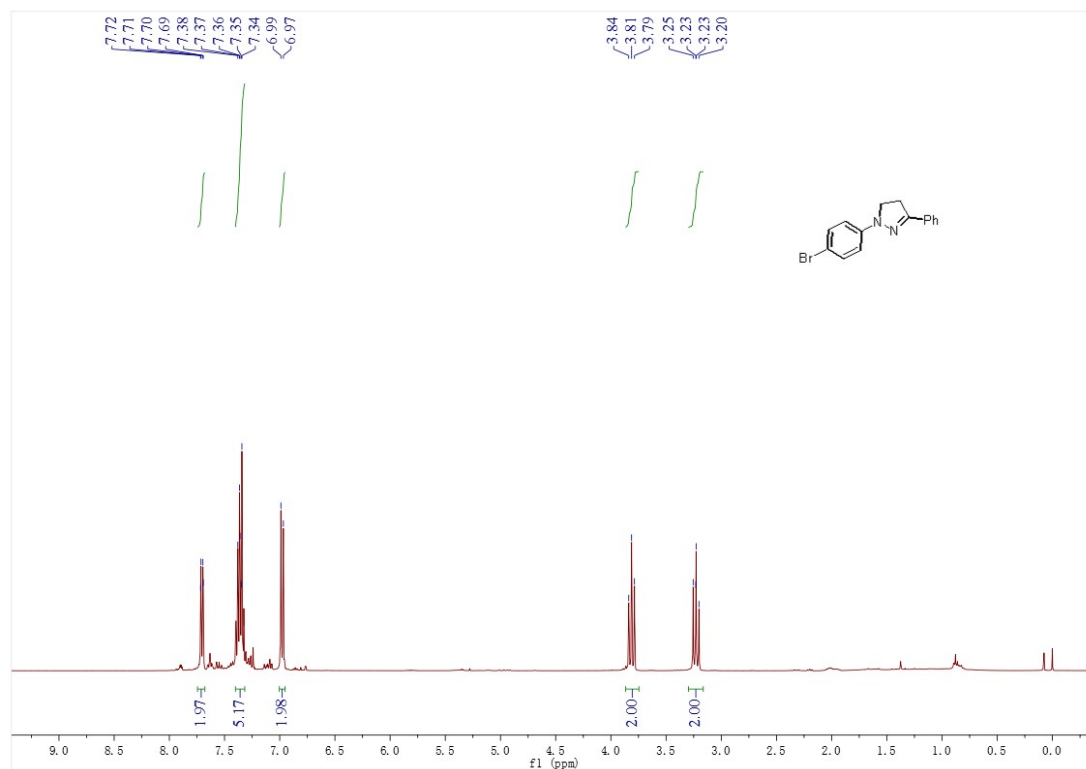
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3g**)



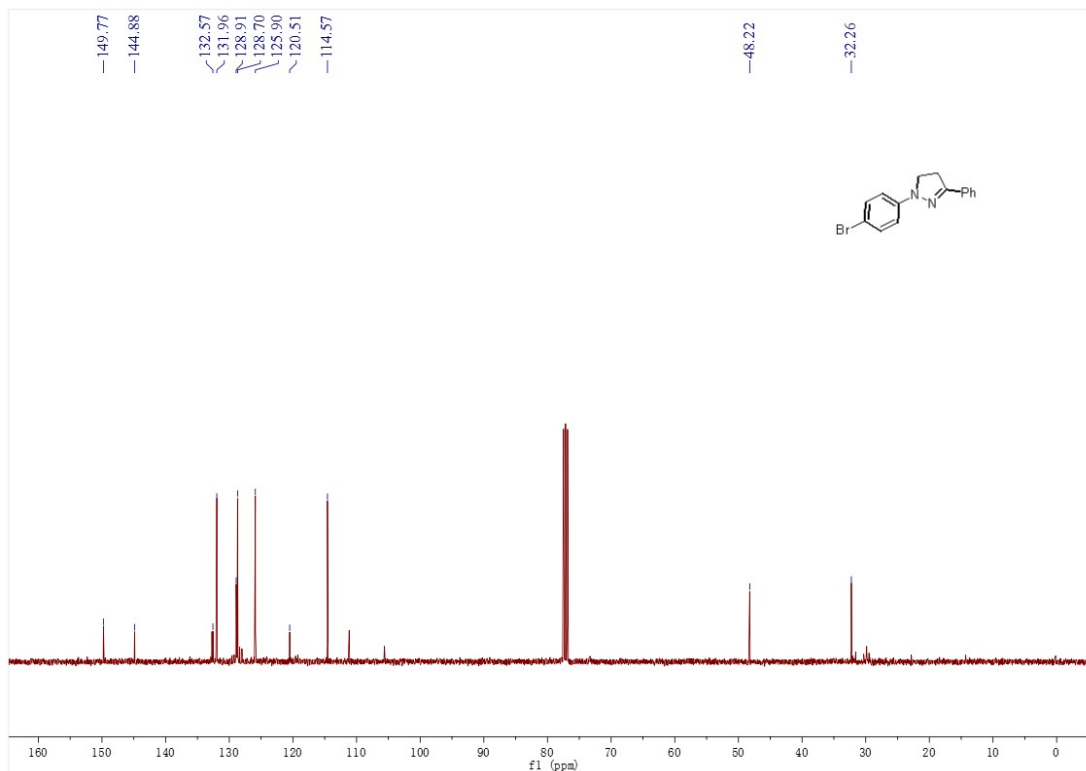
$^{19}\text{F}$  NMR spectra (376 MHz, Chloroform-*d*) of 1-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3g**)



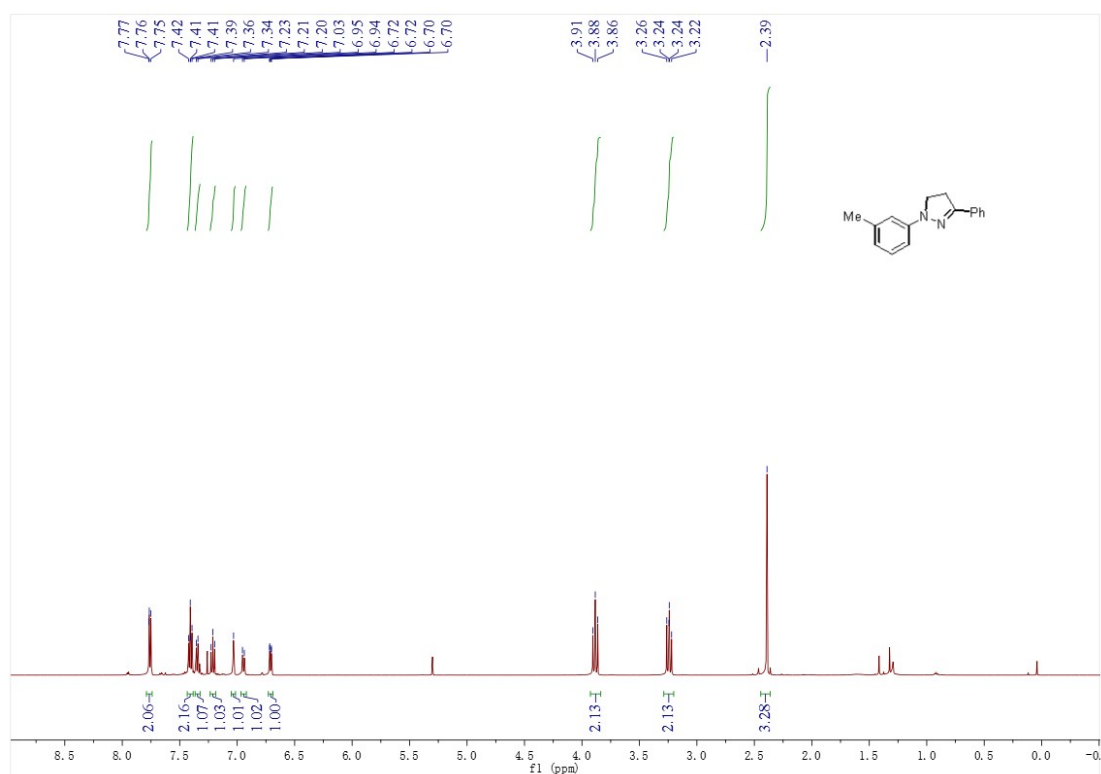
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3h**)



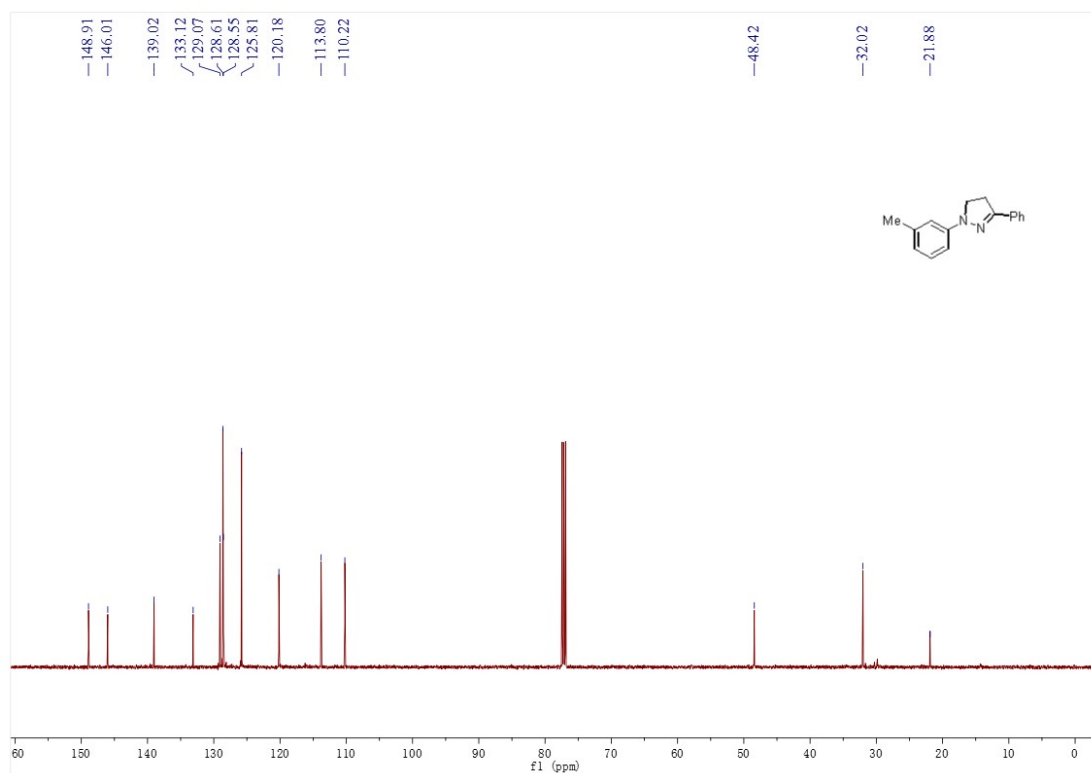
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3h**)



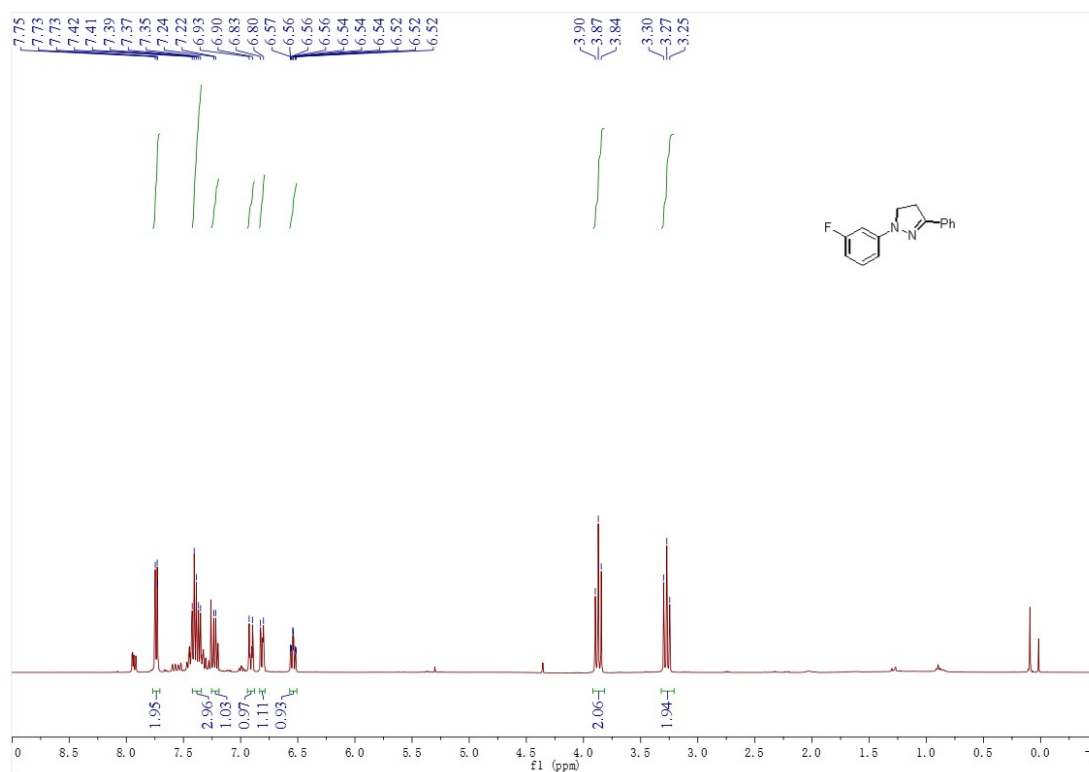
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 3-phenyl-1-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3i**)



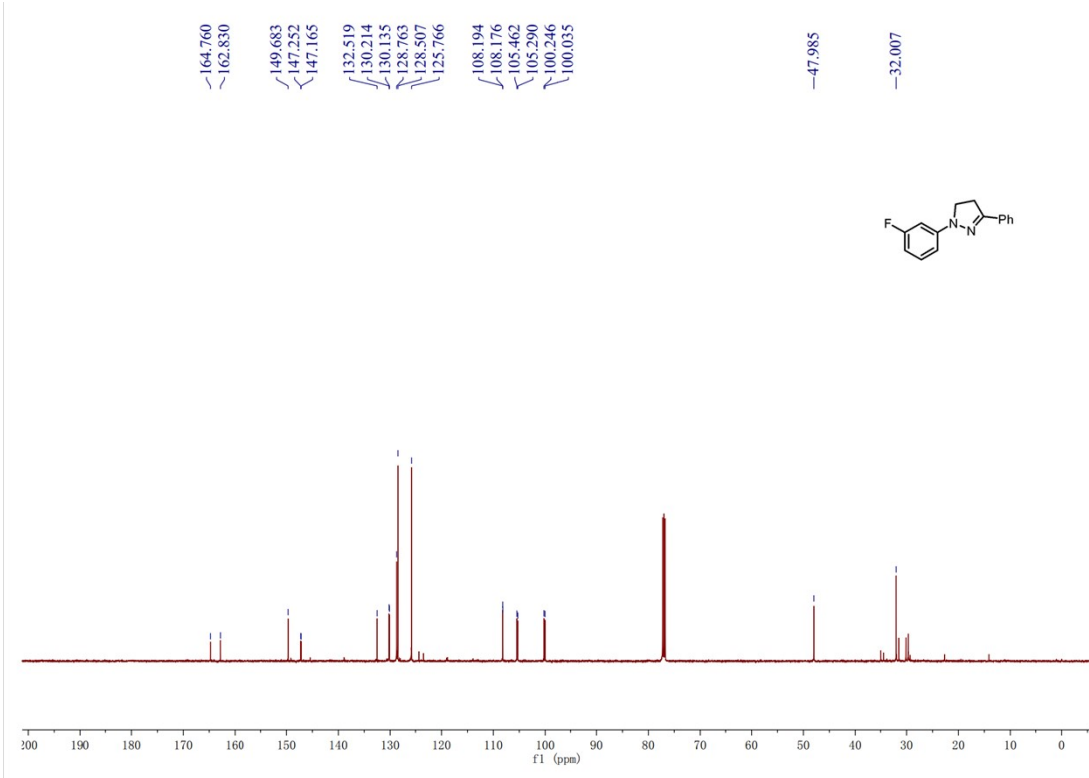
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 3-phenyl-1-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3i**)



$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(3-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3j**)

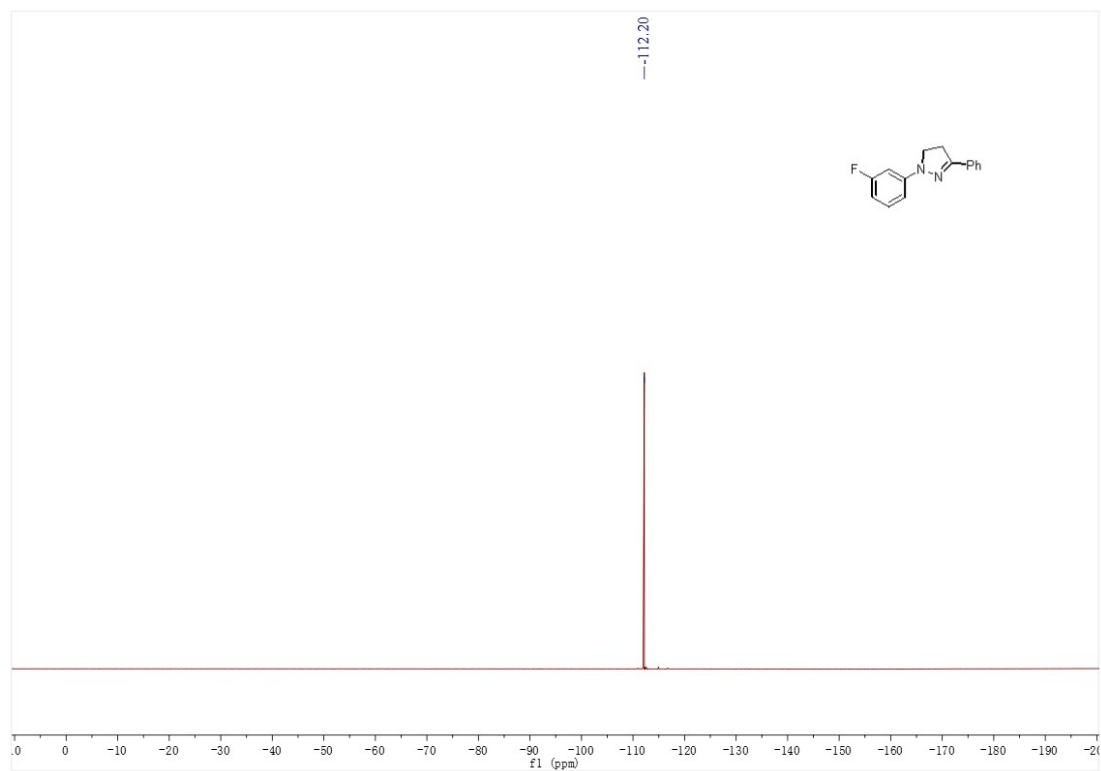


$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 1-(3-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3j**)

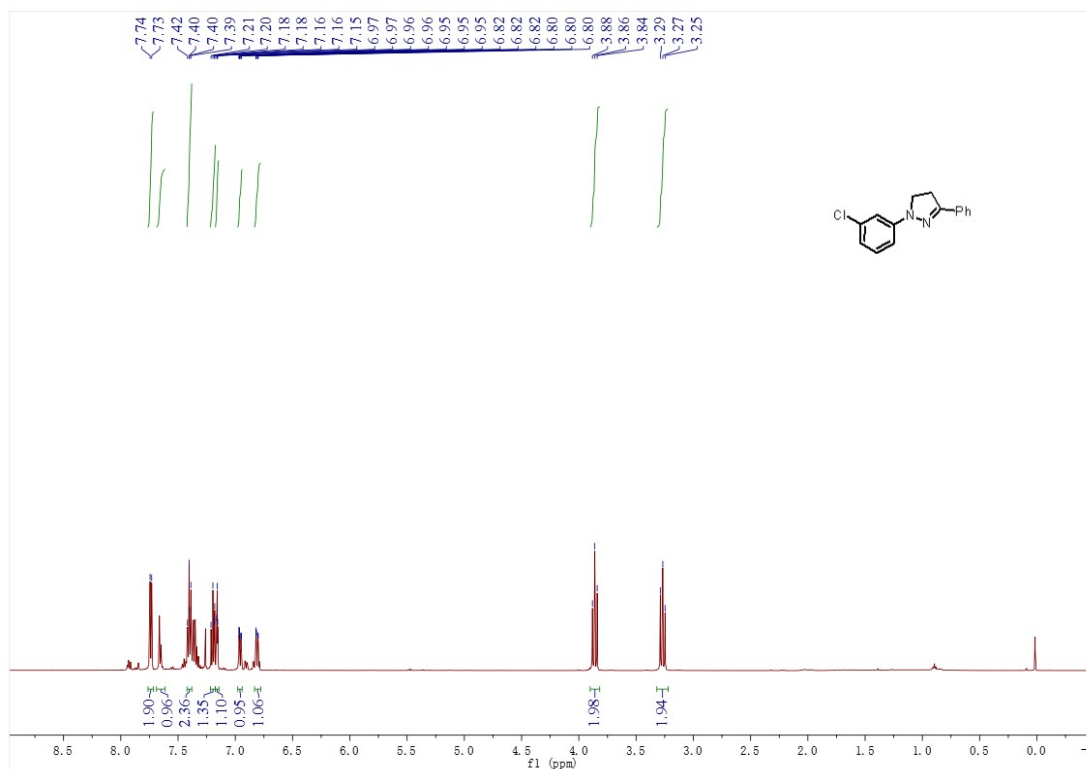




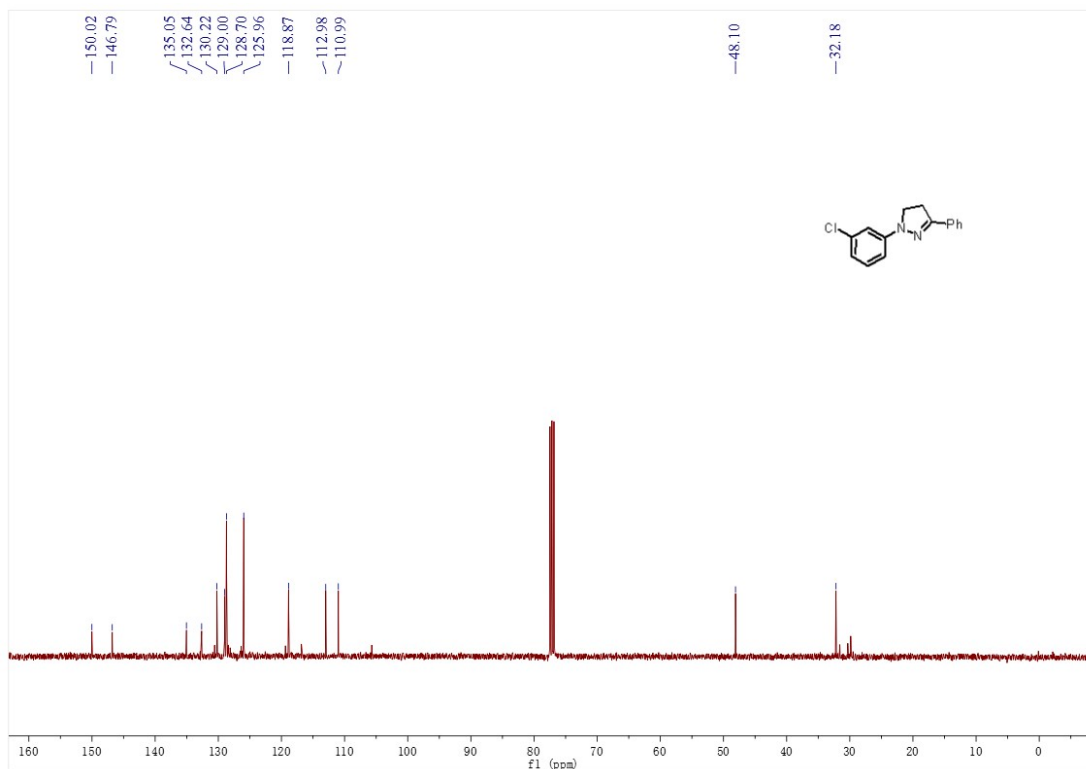
$^{19}\text{F}$  NMR spectra (376 MHz, Chloroform-*d*) of 1-(3-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3j**)



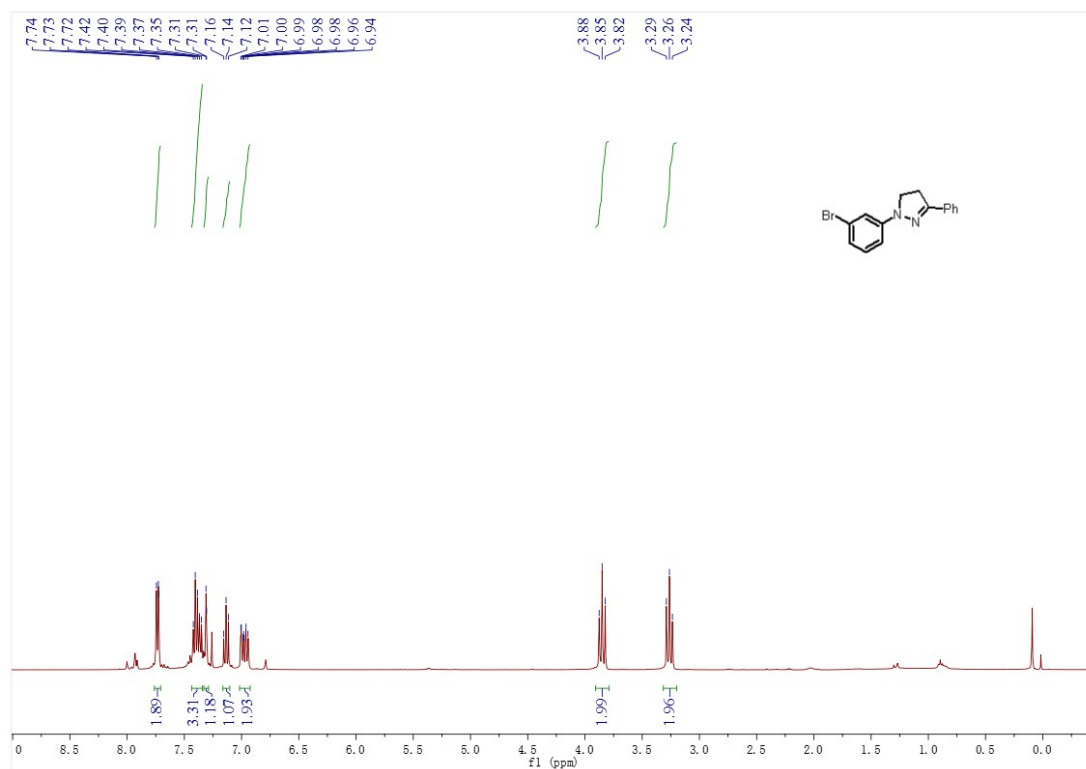
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(3-chlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3k**)



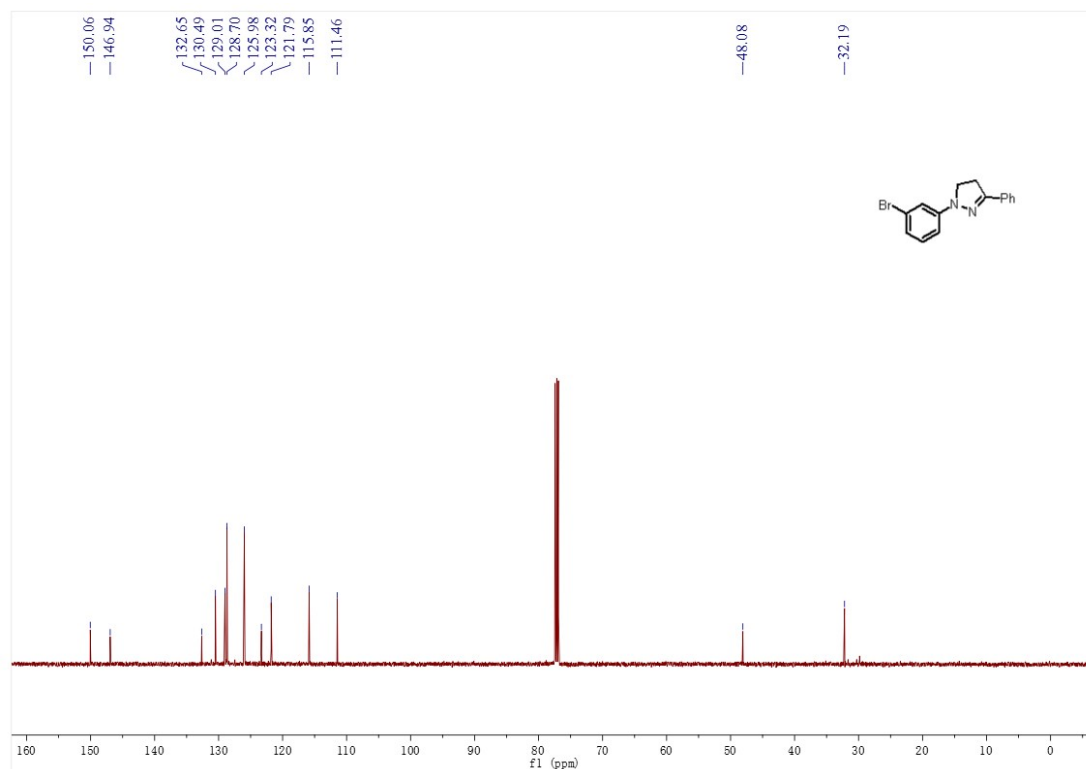
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(3-chlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3k**)



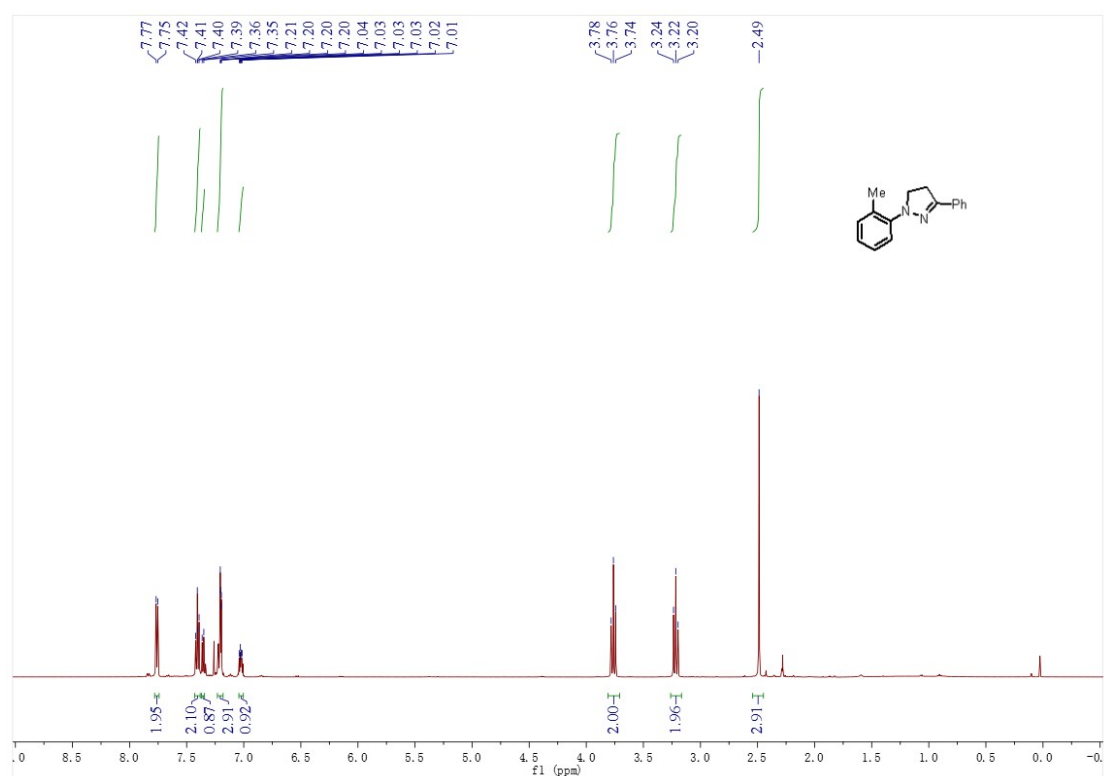
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(3-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3l**)



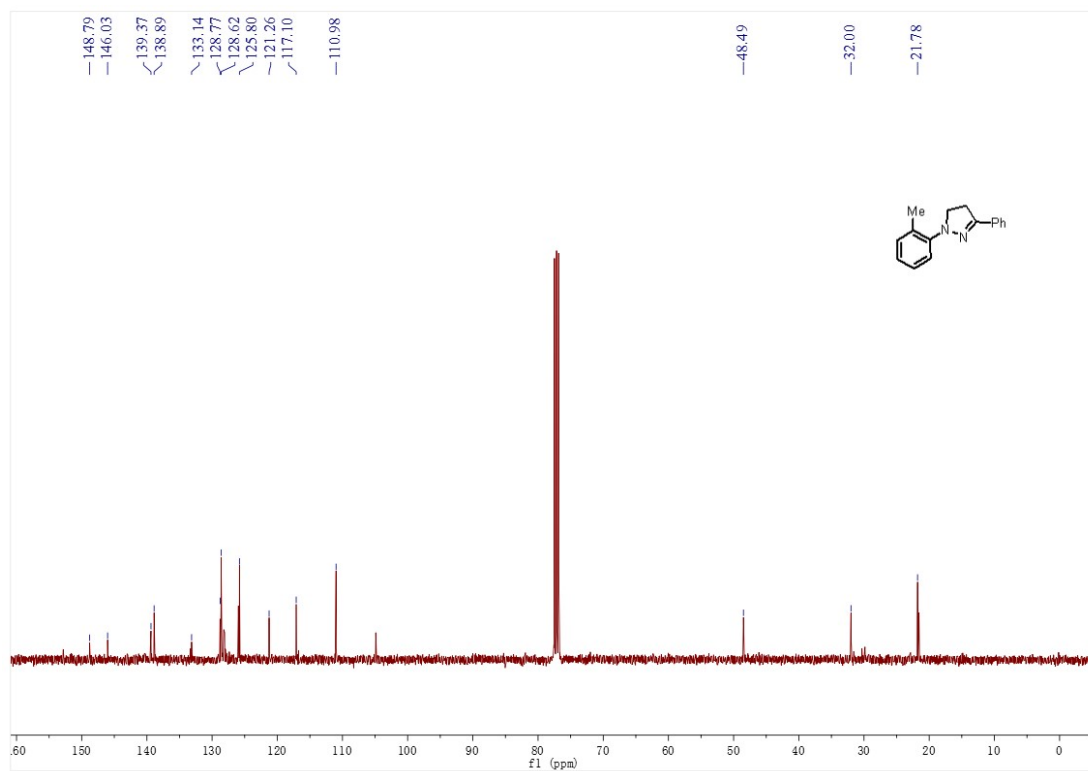
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 1-(3-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3l**)



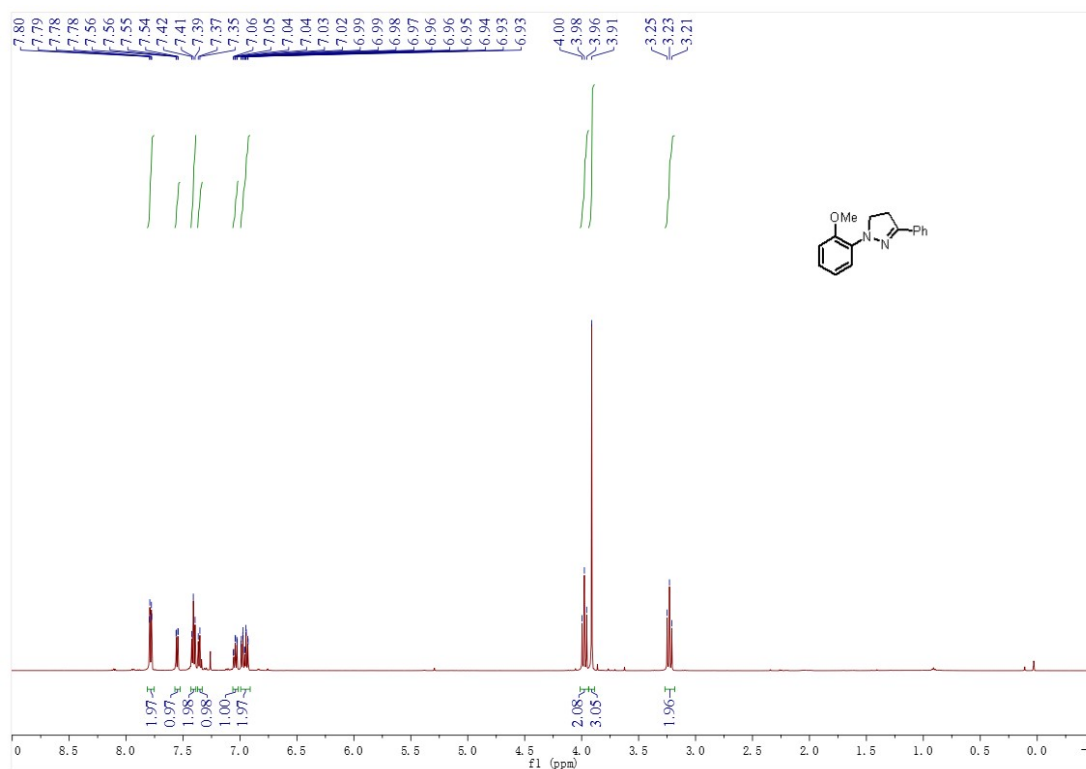
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 3-phenyl-1-(*o*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3m**)



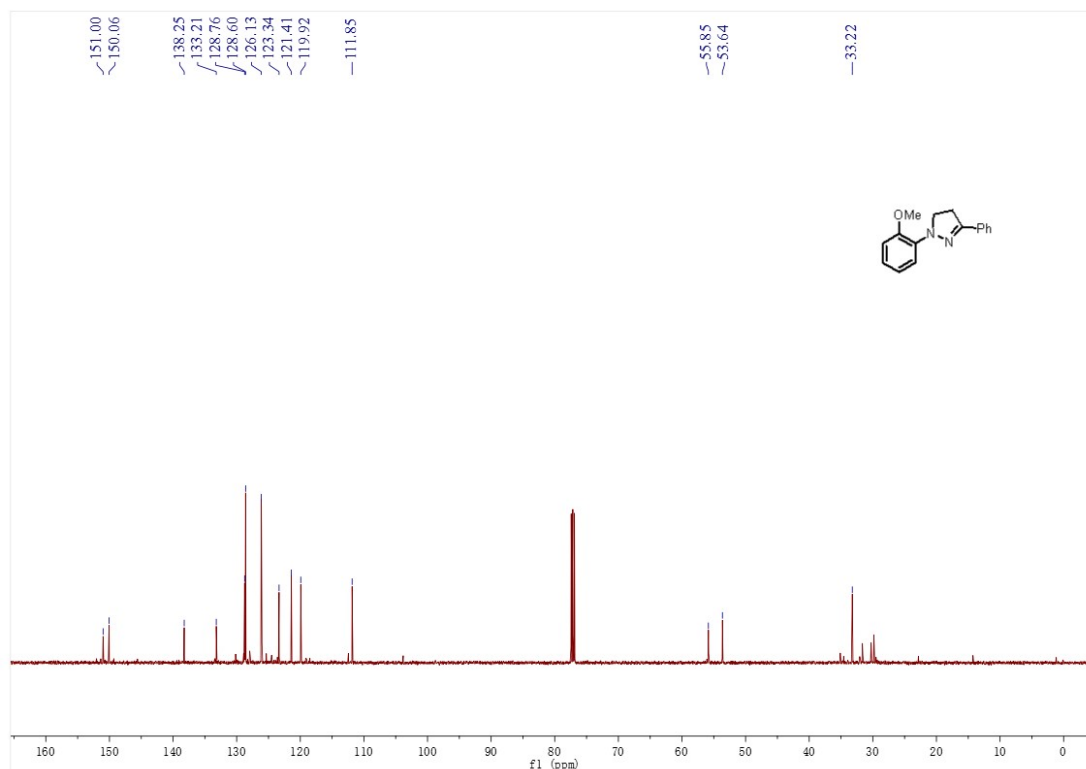
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-phenyl-1-(*o*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3m**)



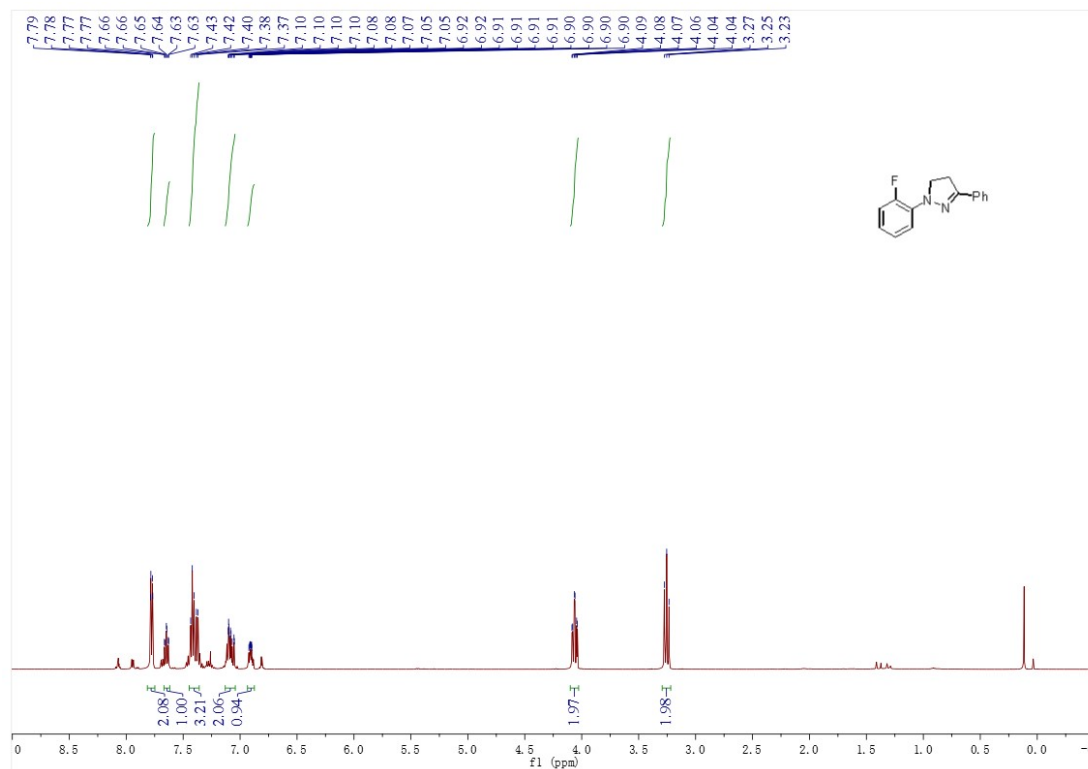
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(2-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3n**)



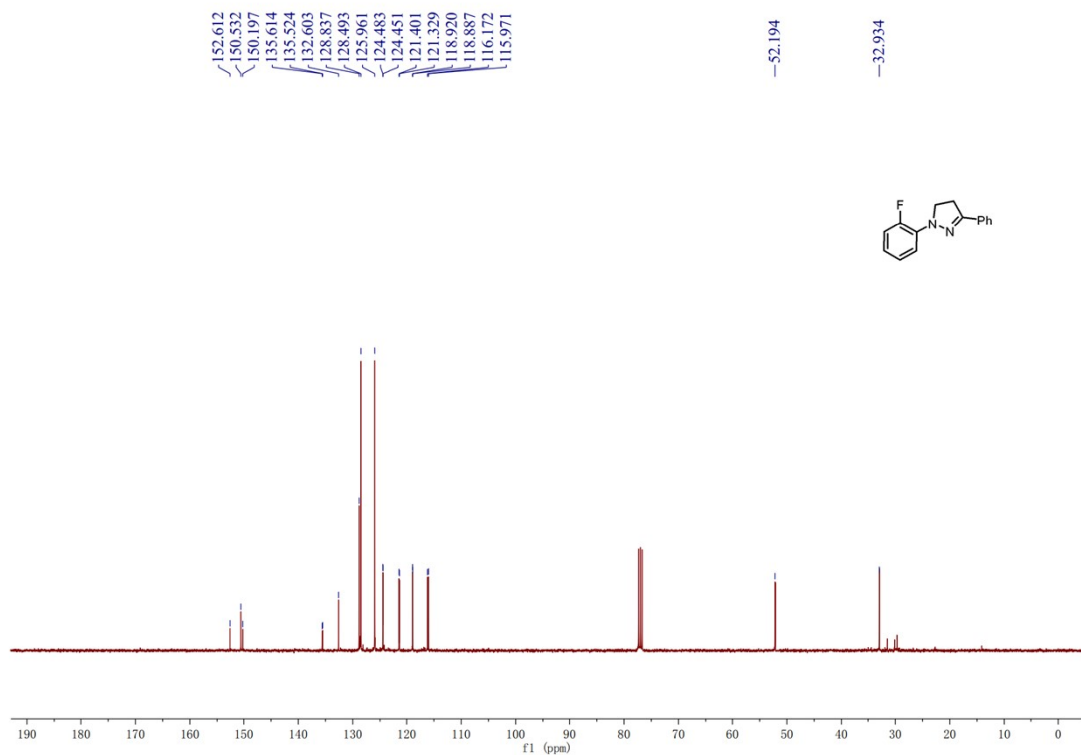
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 1-(2-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3n**)



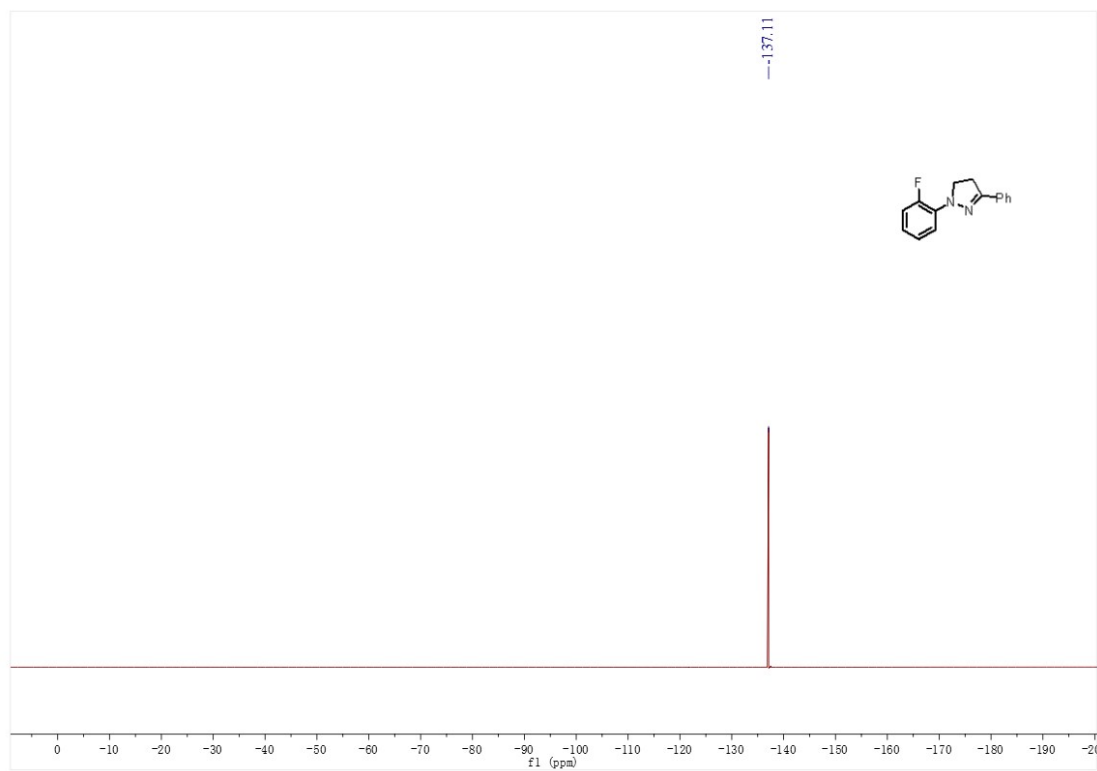
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(2-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3o**)



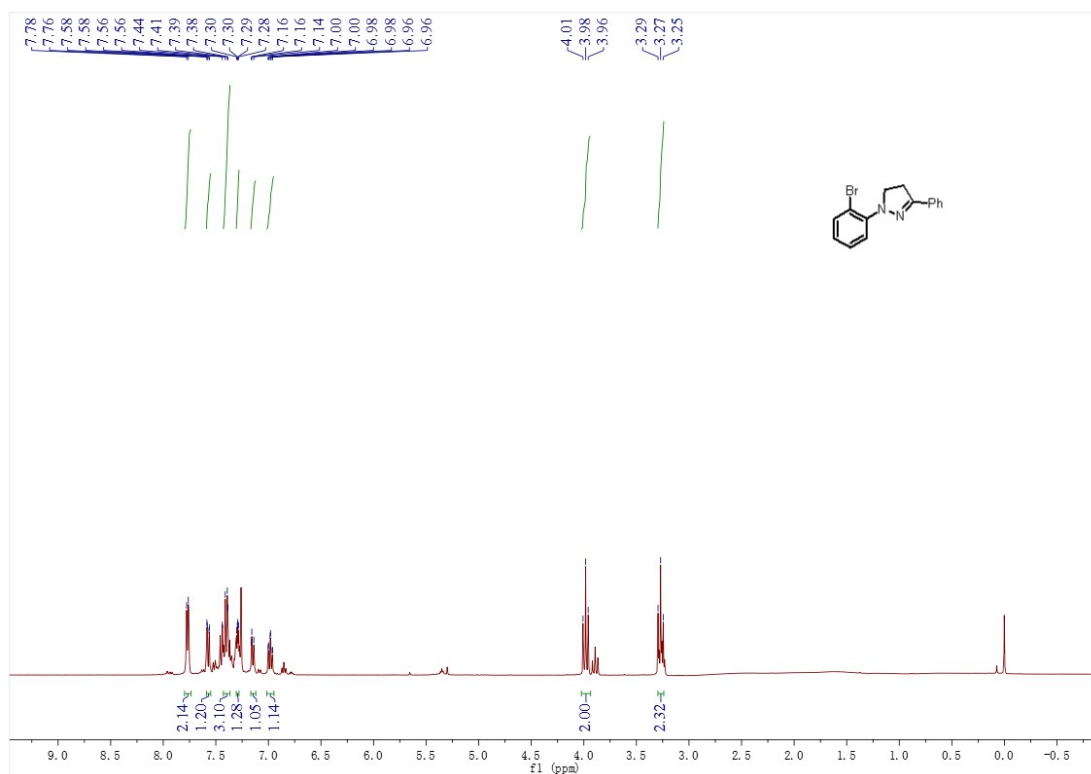
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(2-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3o**)



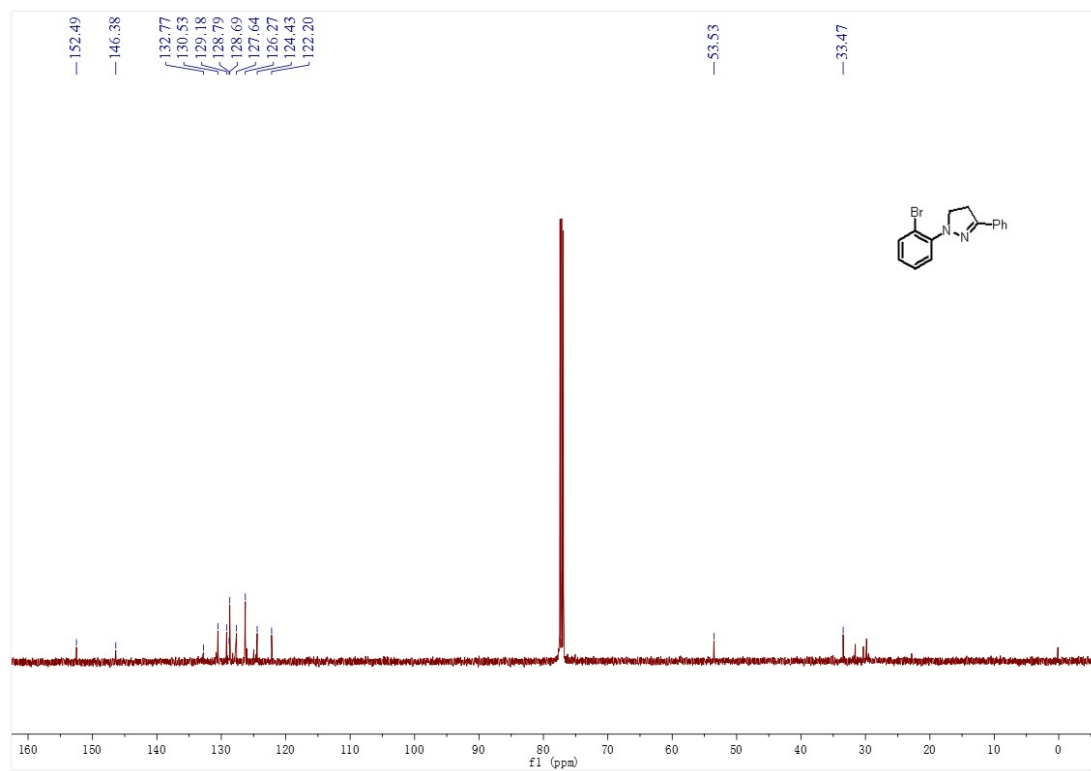
$^{19}\text{F}$  NMR spectra (376 MHz, Chloroform-*d*) of 1-(2-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3o**)



$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(2-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3p**)

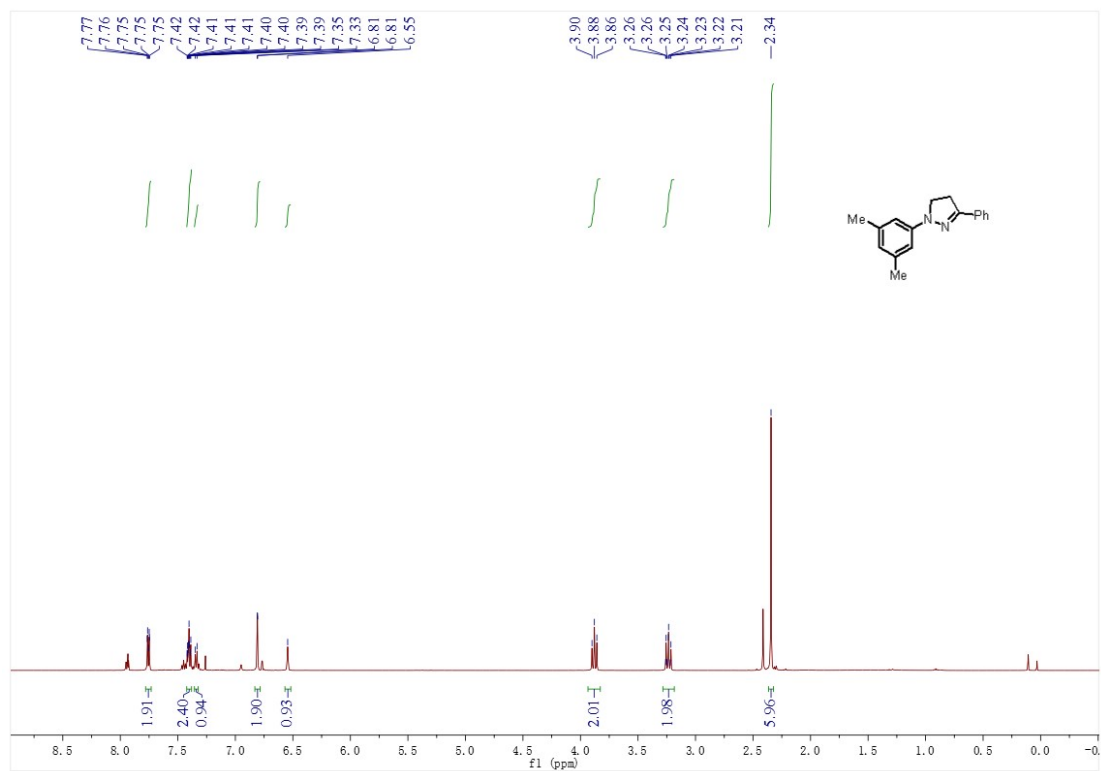


$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 1-(2-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3p**)

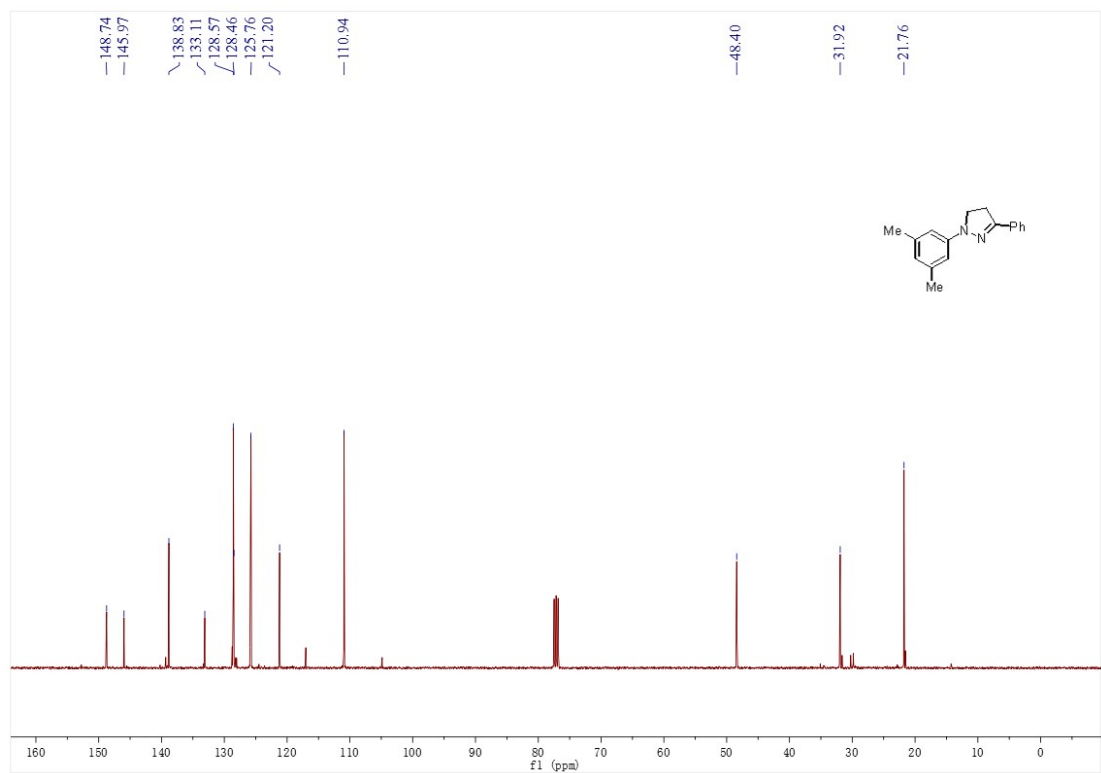




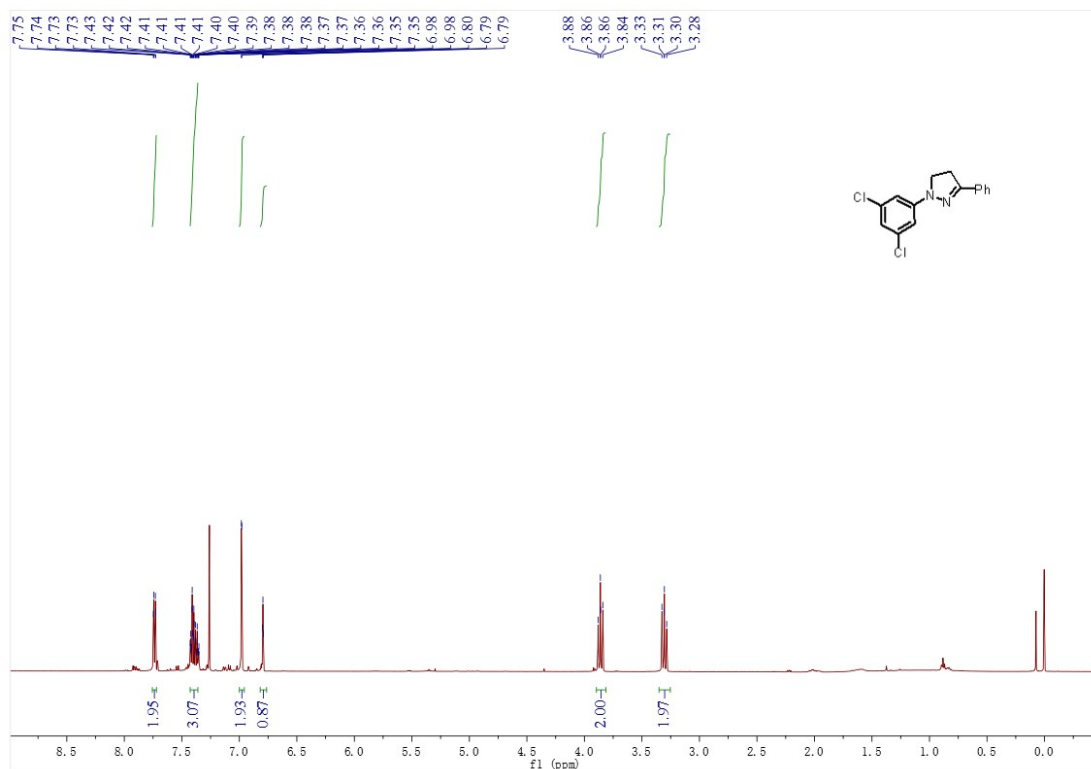
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(3,5-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3q**)



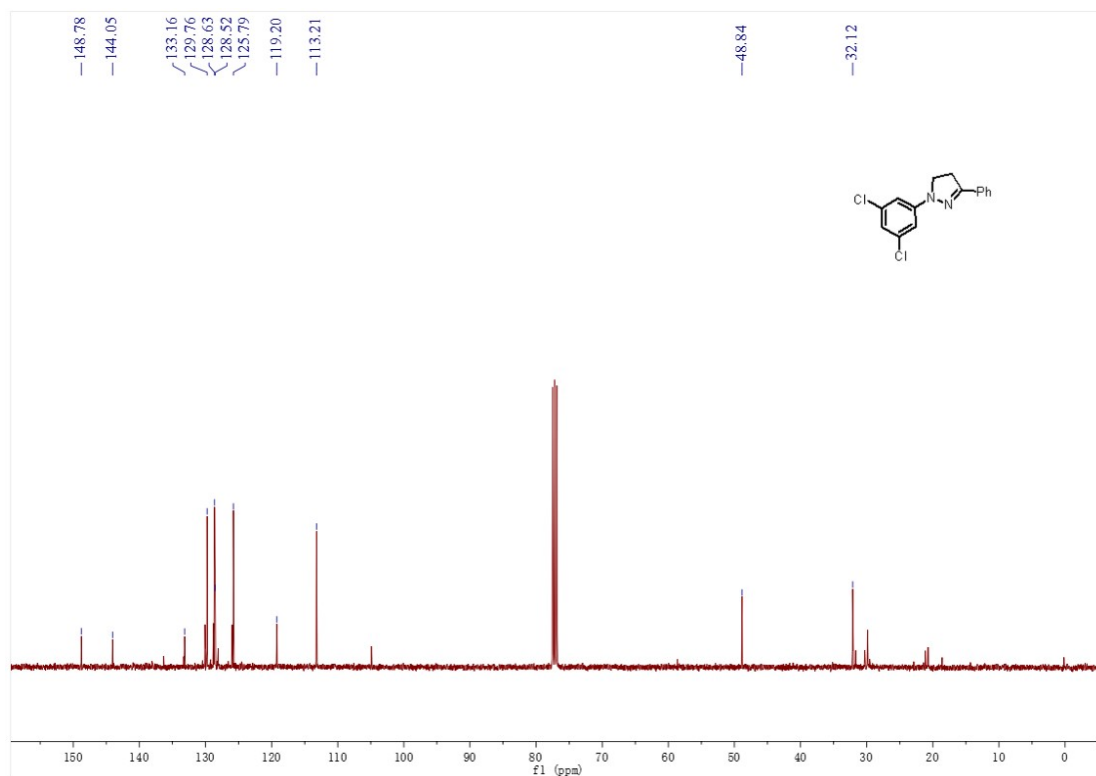
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(3,5-dimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3q**)



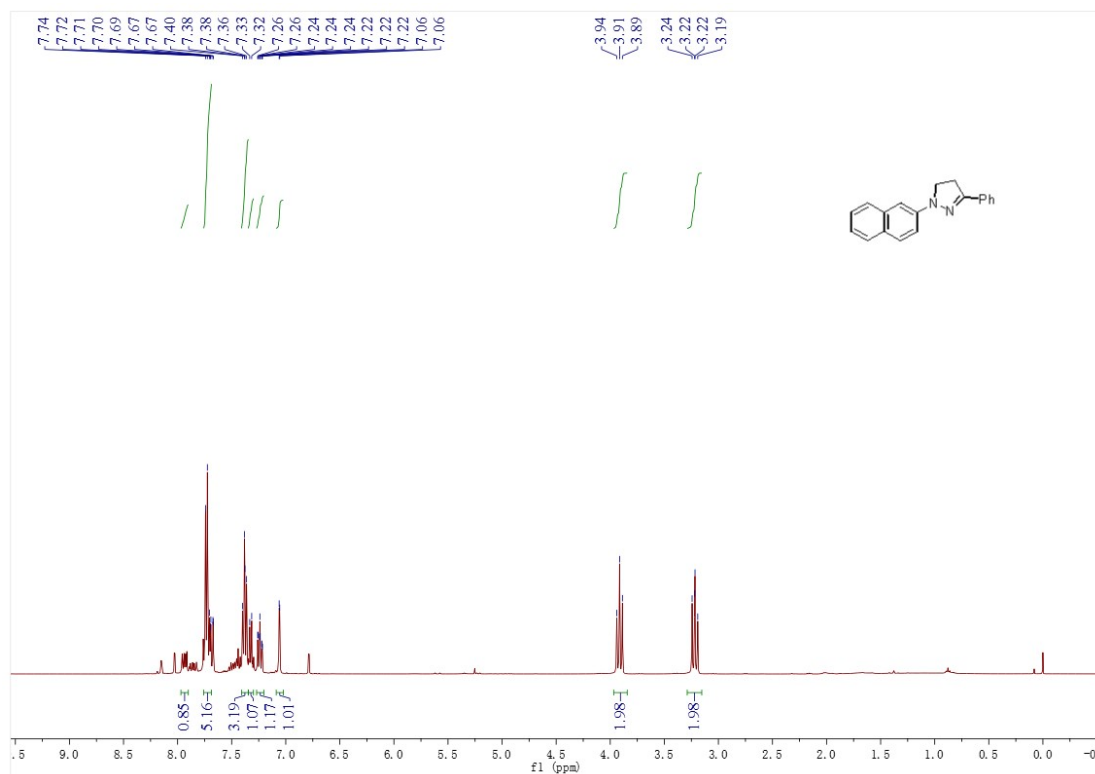
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1-(3,5-dichlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3r**)



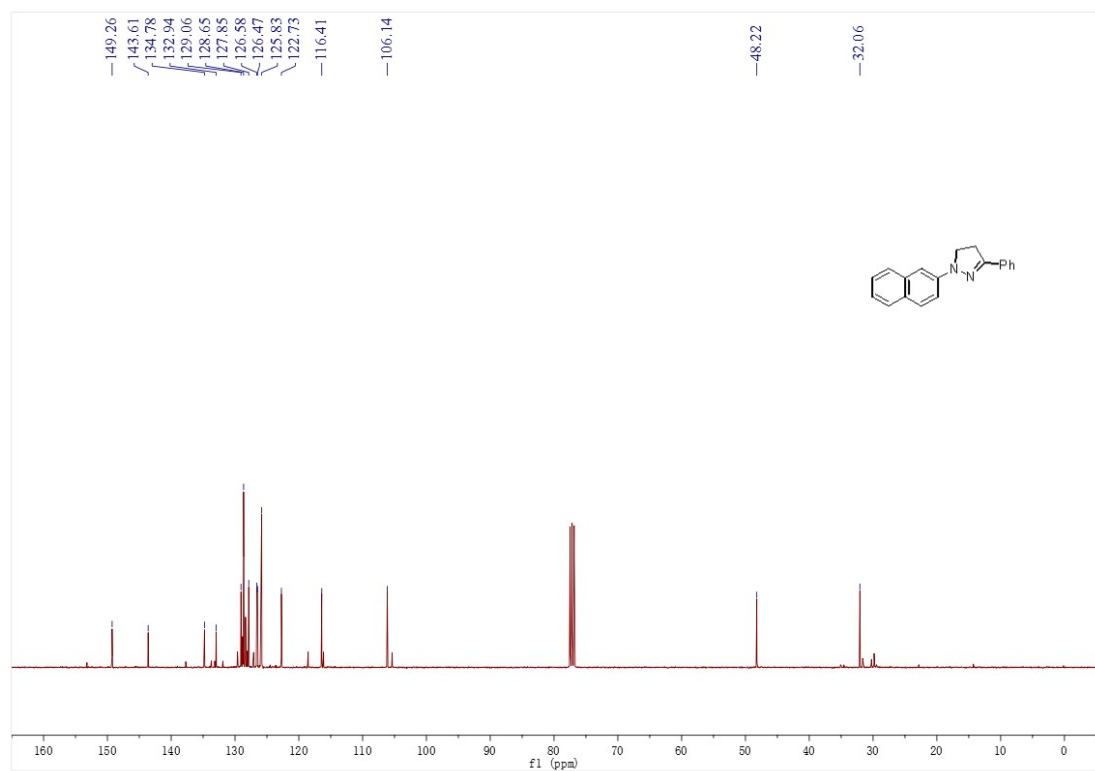
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(3,5-dichlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3r**)



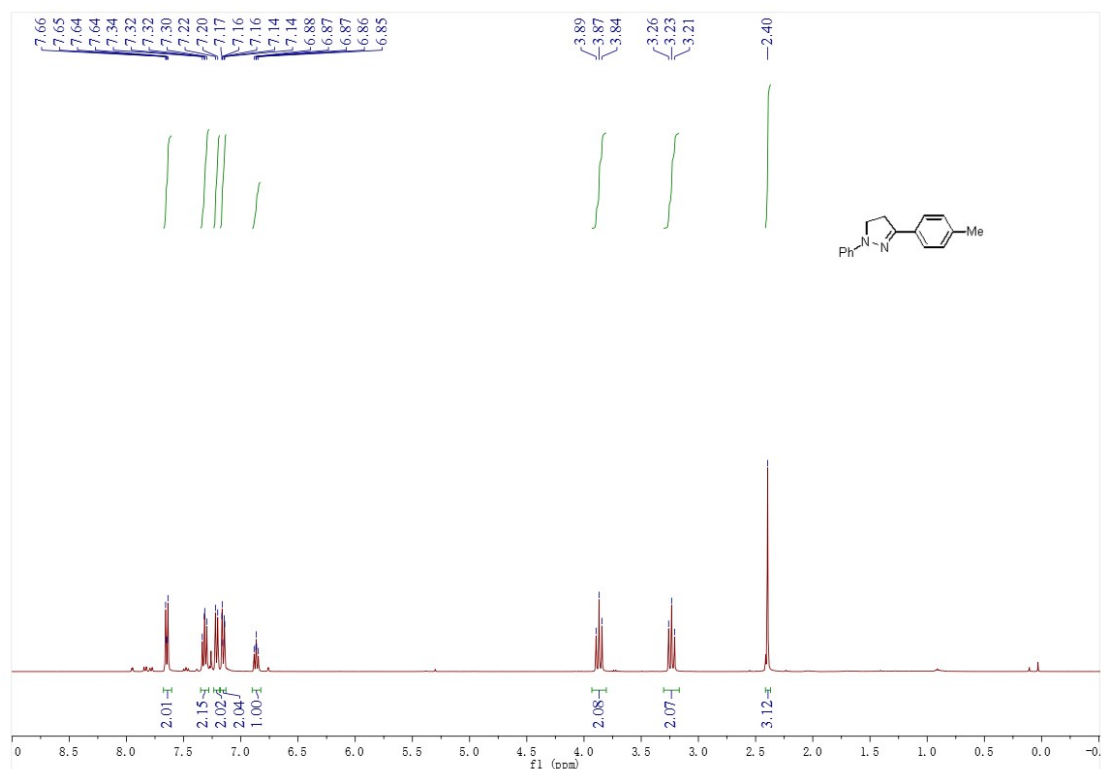
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(naphthalen-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3s**)



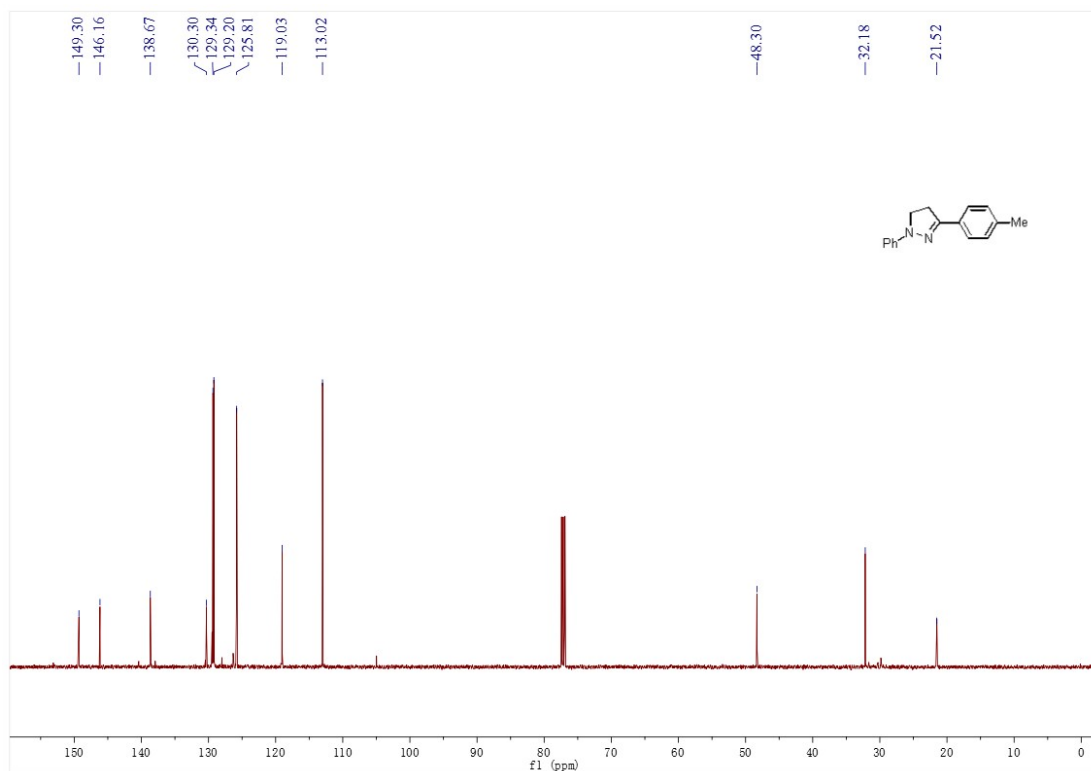
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(naphthalen-2-yl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**3s**)



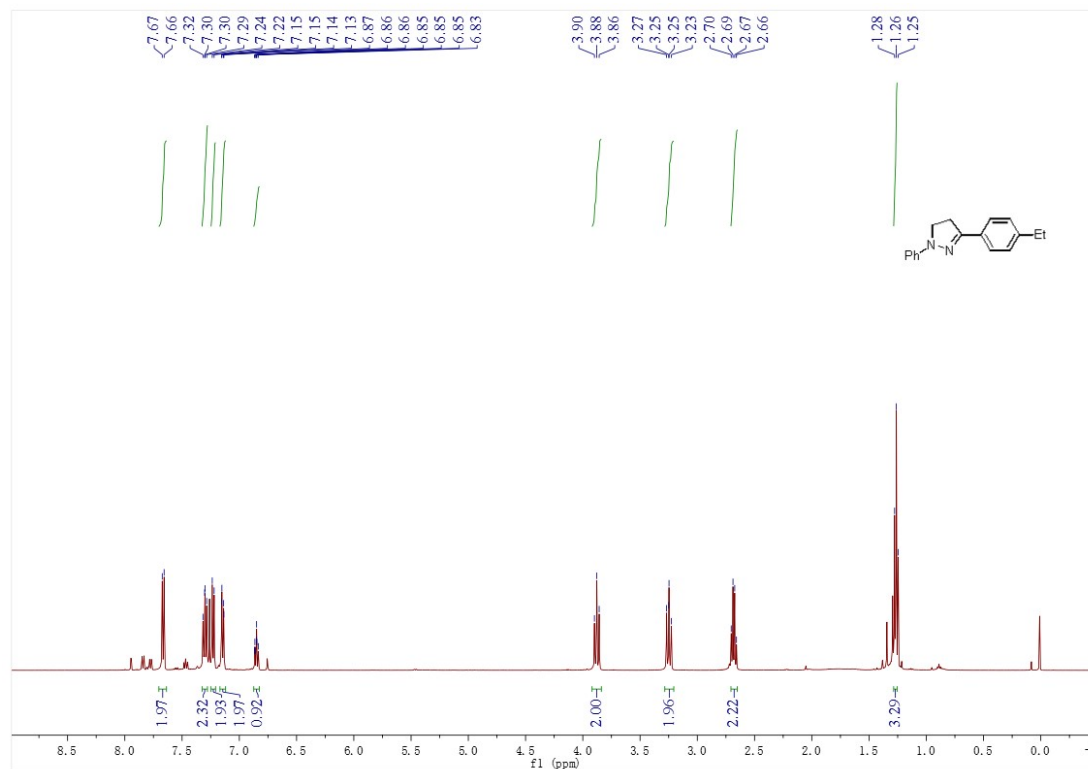
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-phenyl-3-(p-tolyl)-4,5-dihydro-1*H*-pyrazole (**3t**)



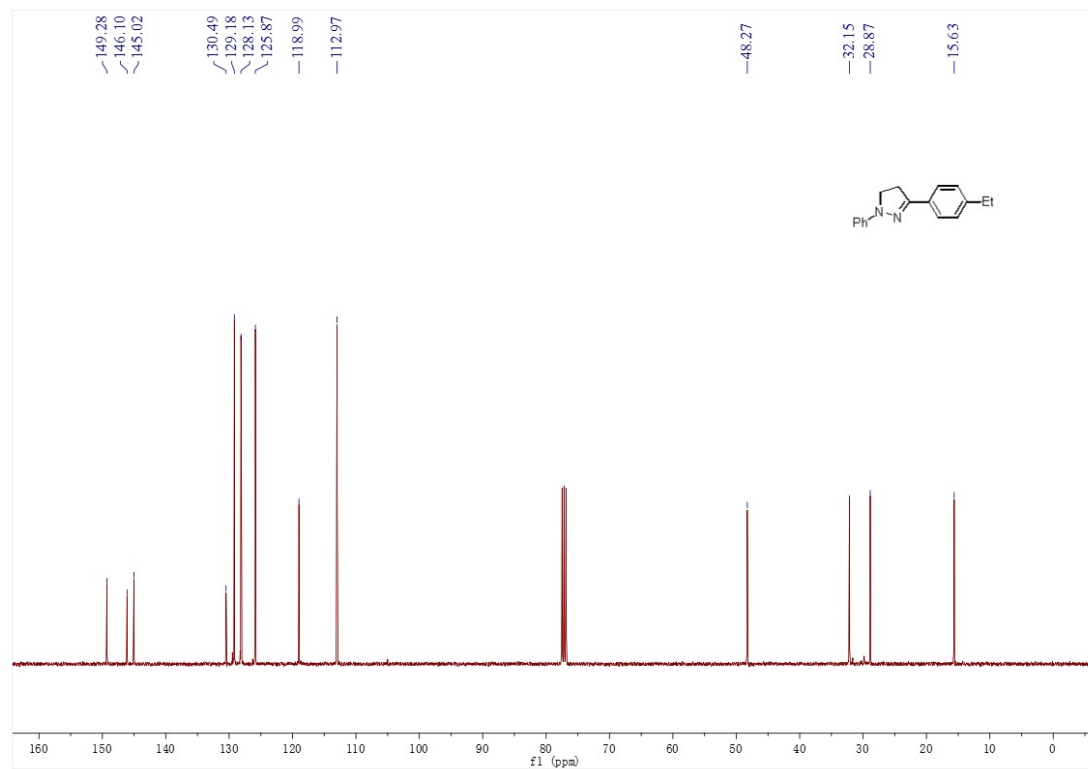
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 1-phenyl-3-(p-tolyl)-4,5-dihydro-1*H*-pyrazole (**3t**)



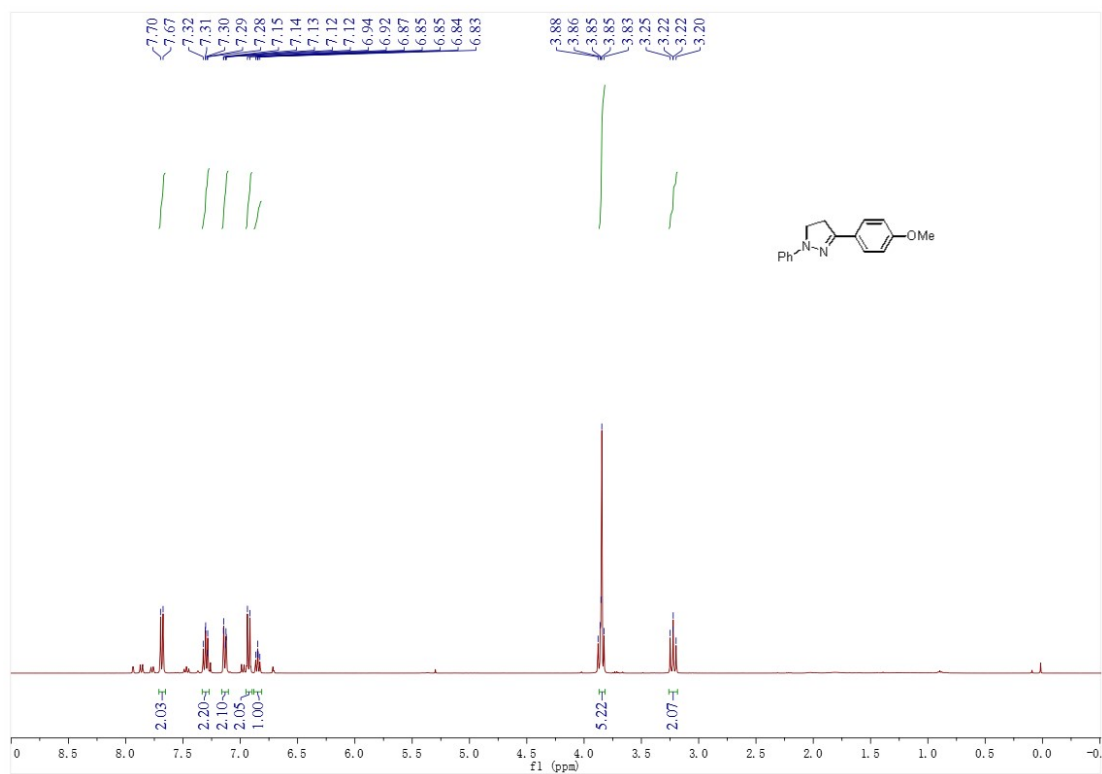
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3u**)



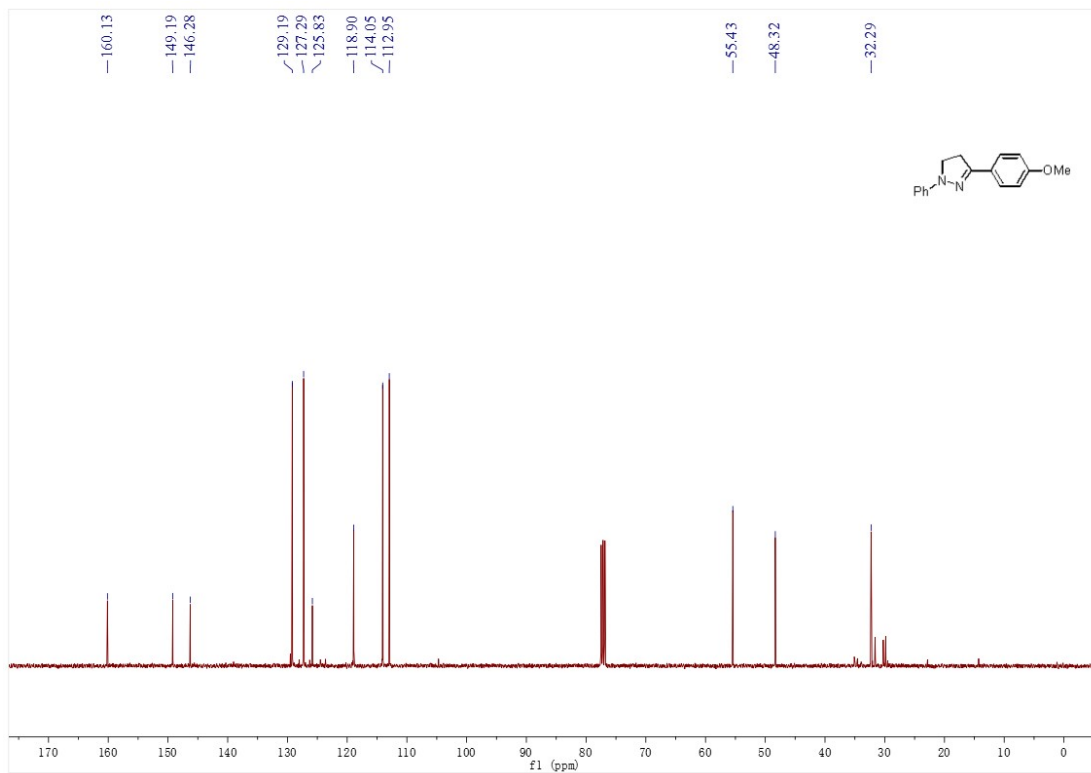
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-(4-ethylphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3u**)



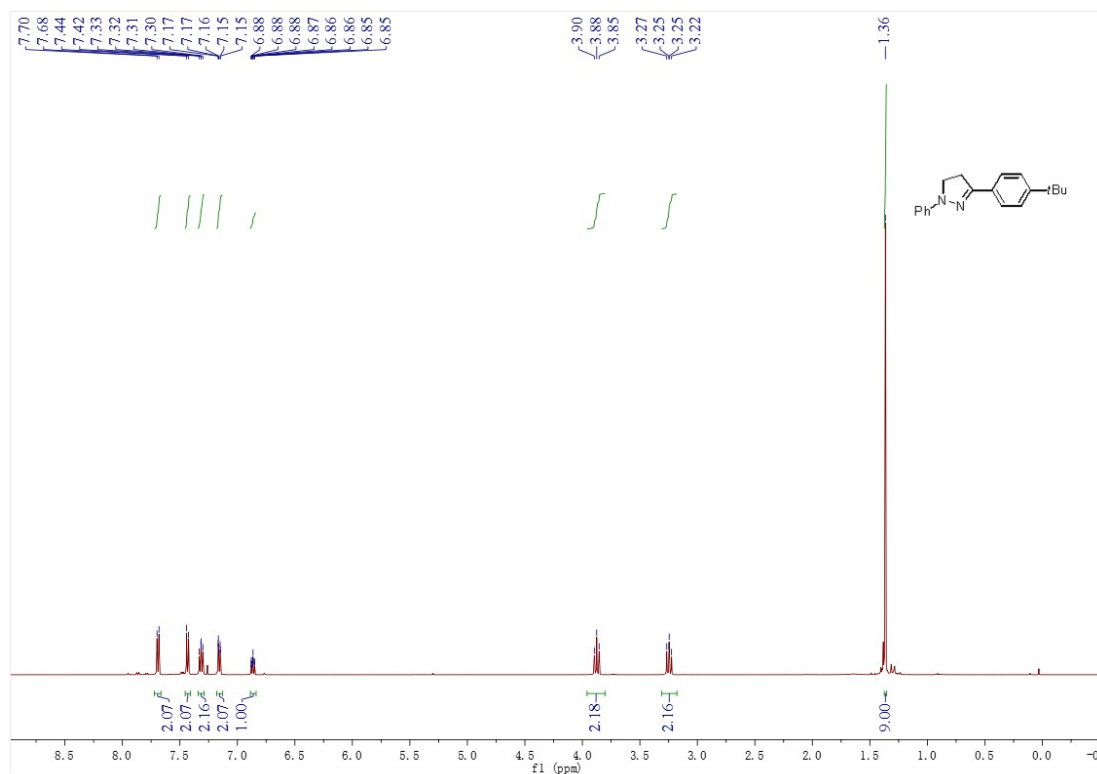
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3v**)



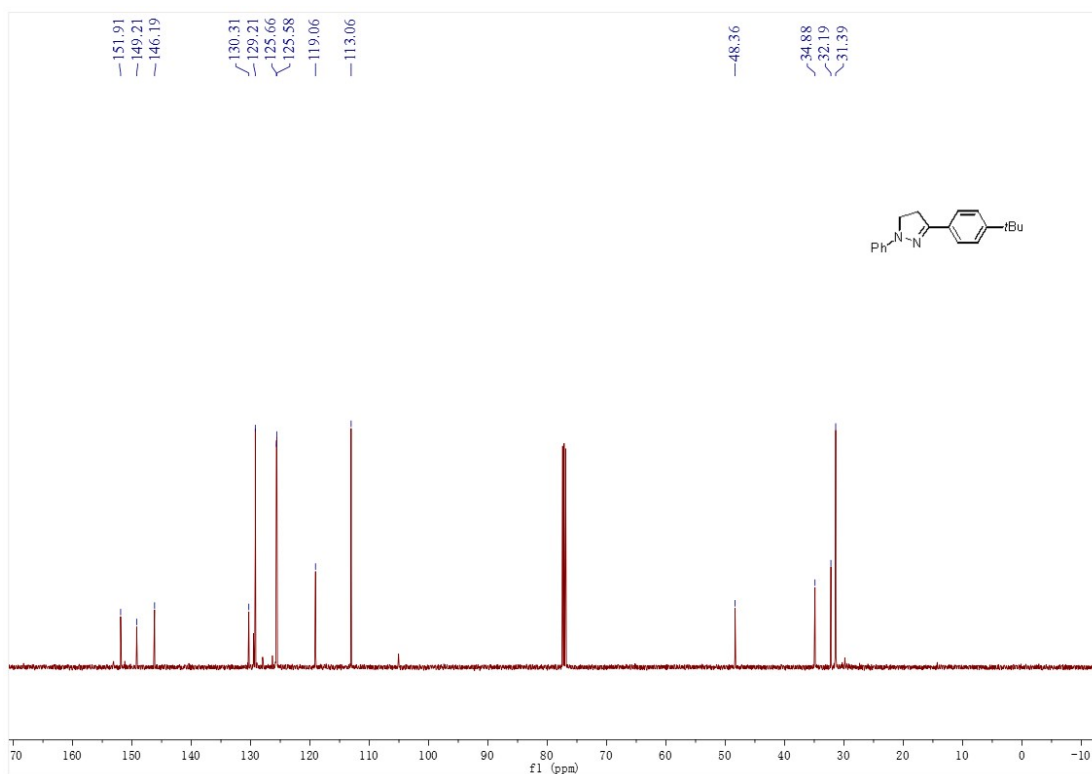
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3v**)



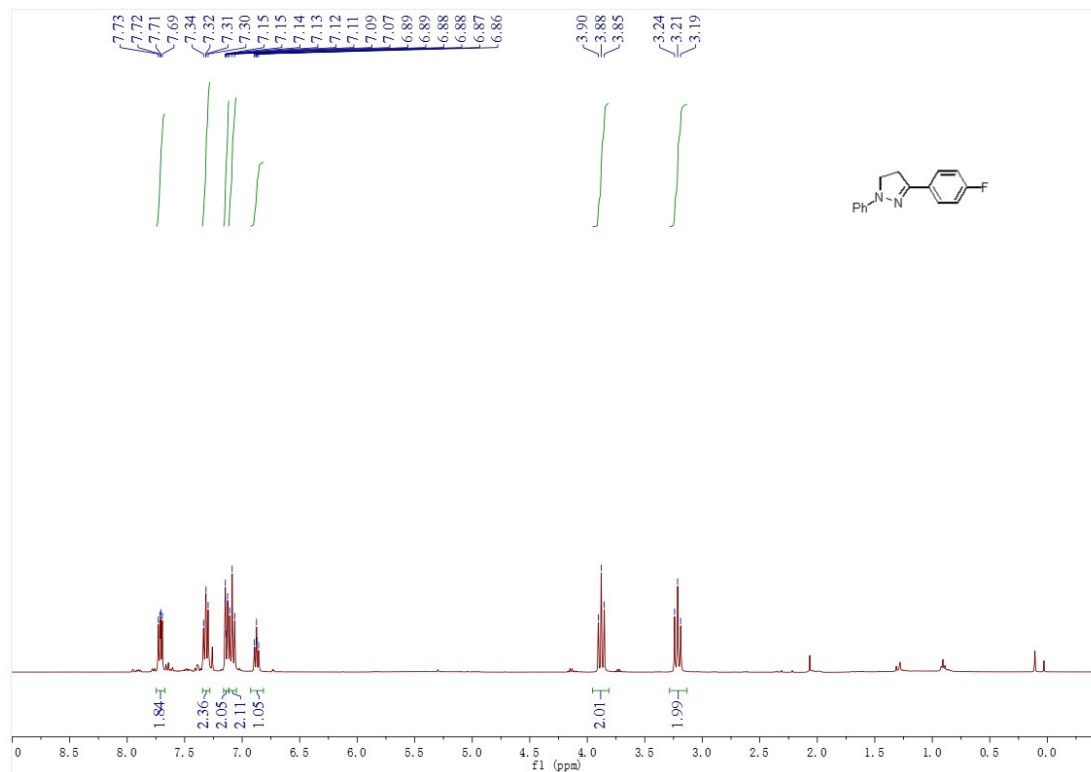
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 3-(4-(tert-butyl)phenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3w**)



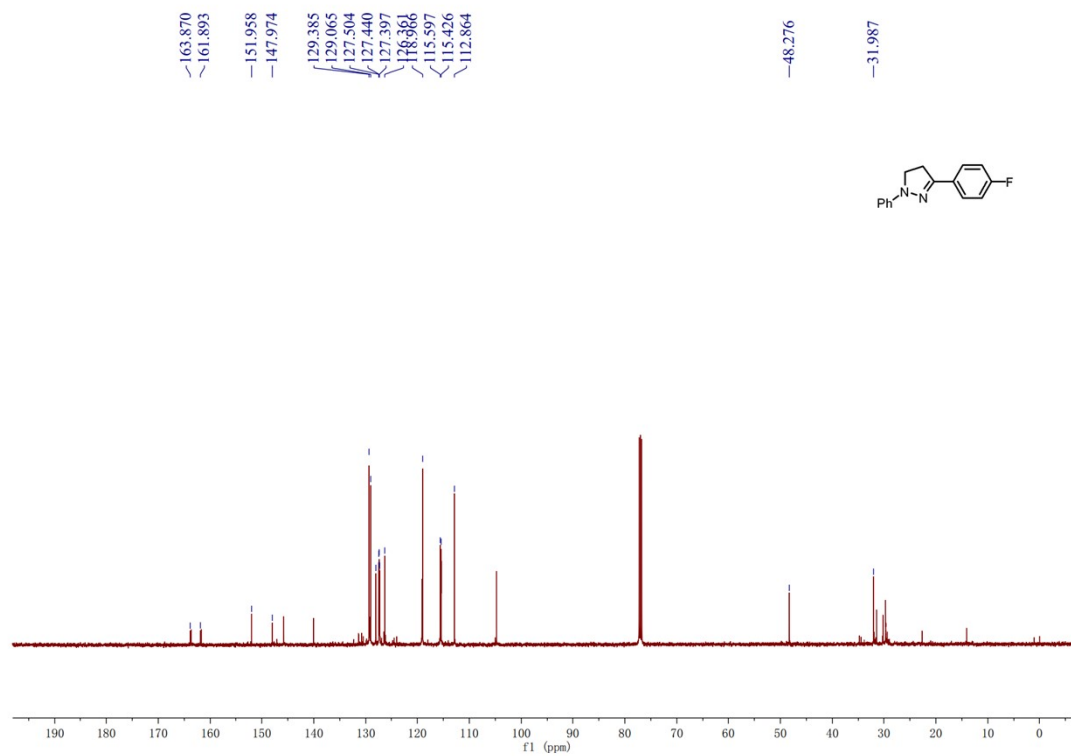
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 3-(4-(tert-butyl)phenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3w**)



$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3x**)

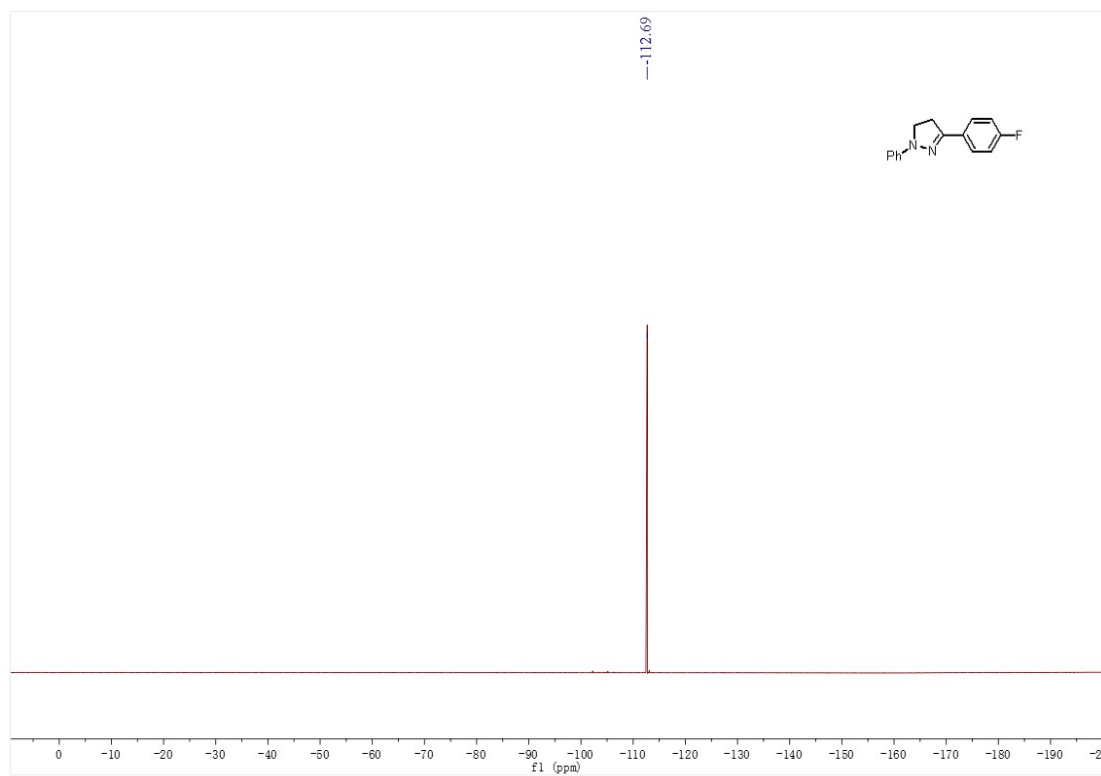


$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3x**)

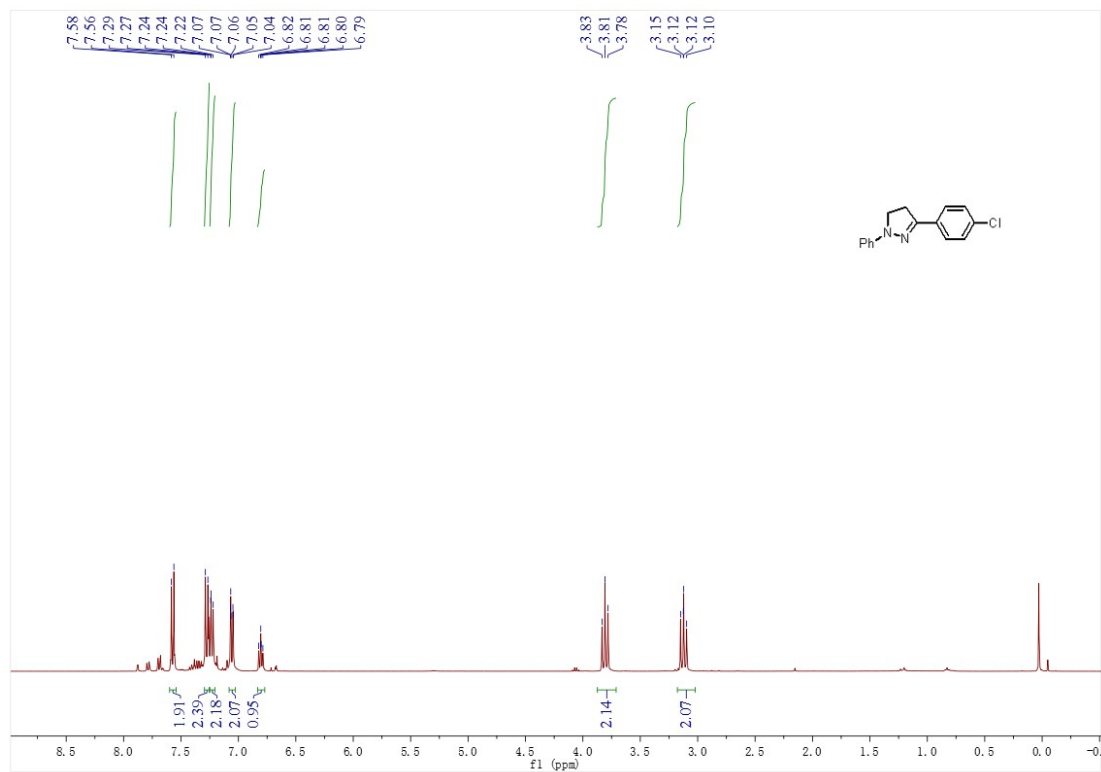




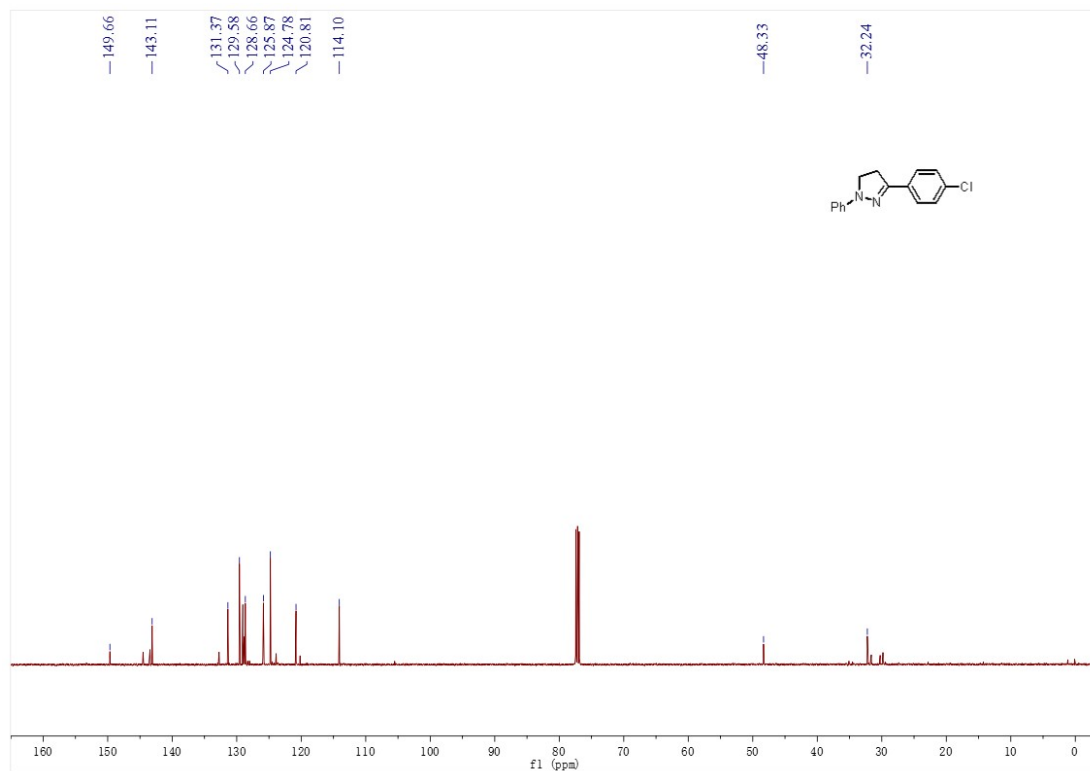
$^{19}\text{F}$  NMR spectra (376 MHz, Chloroform-*d*) of 3-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3x**)



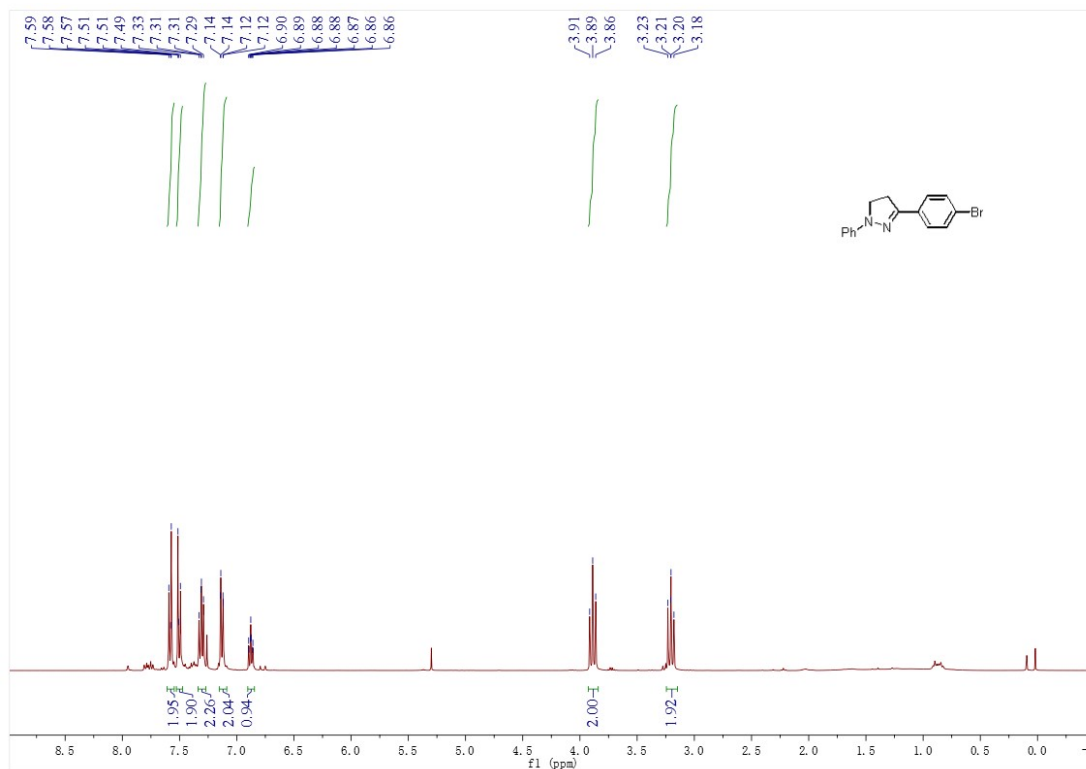
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3y**)



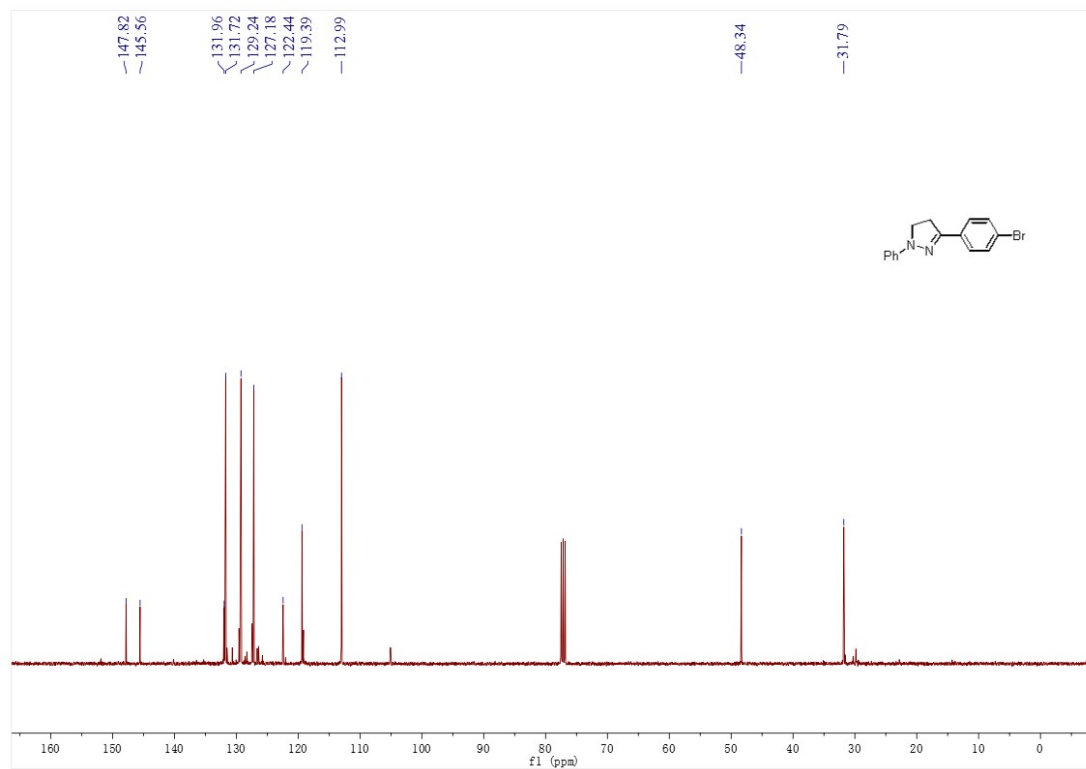
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 3-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3y**)



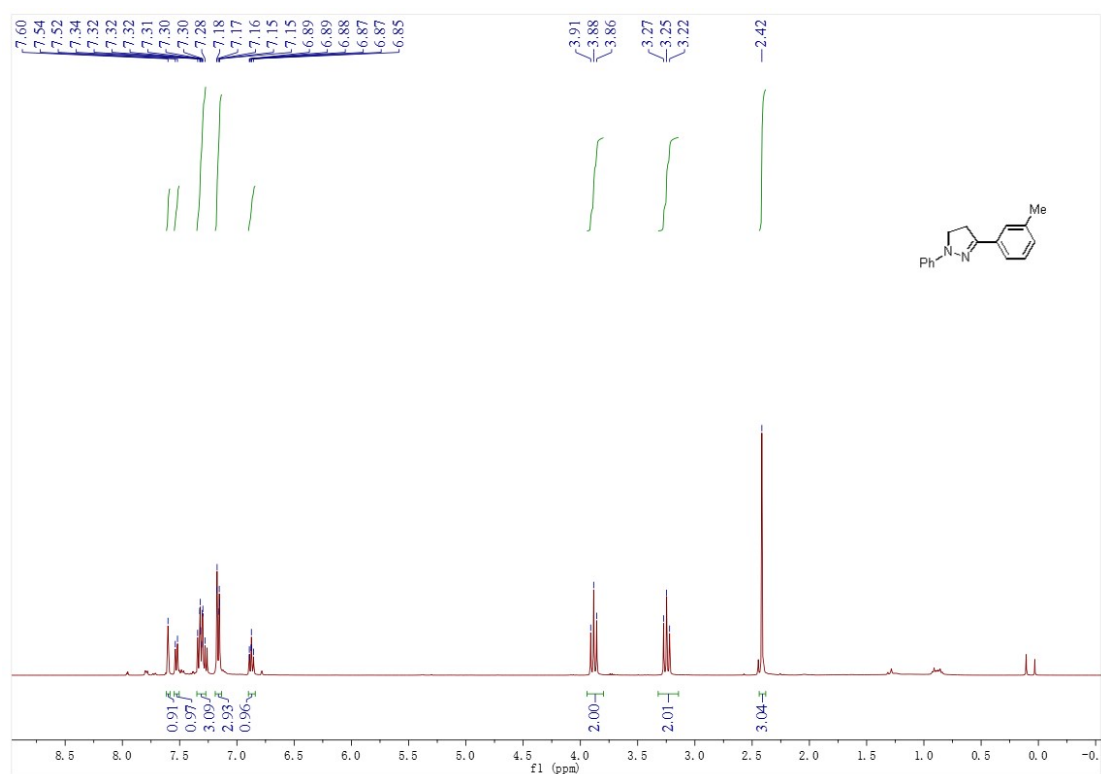
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(4-bromophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3z**)



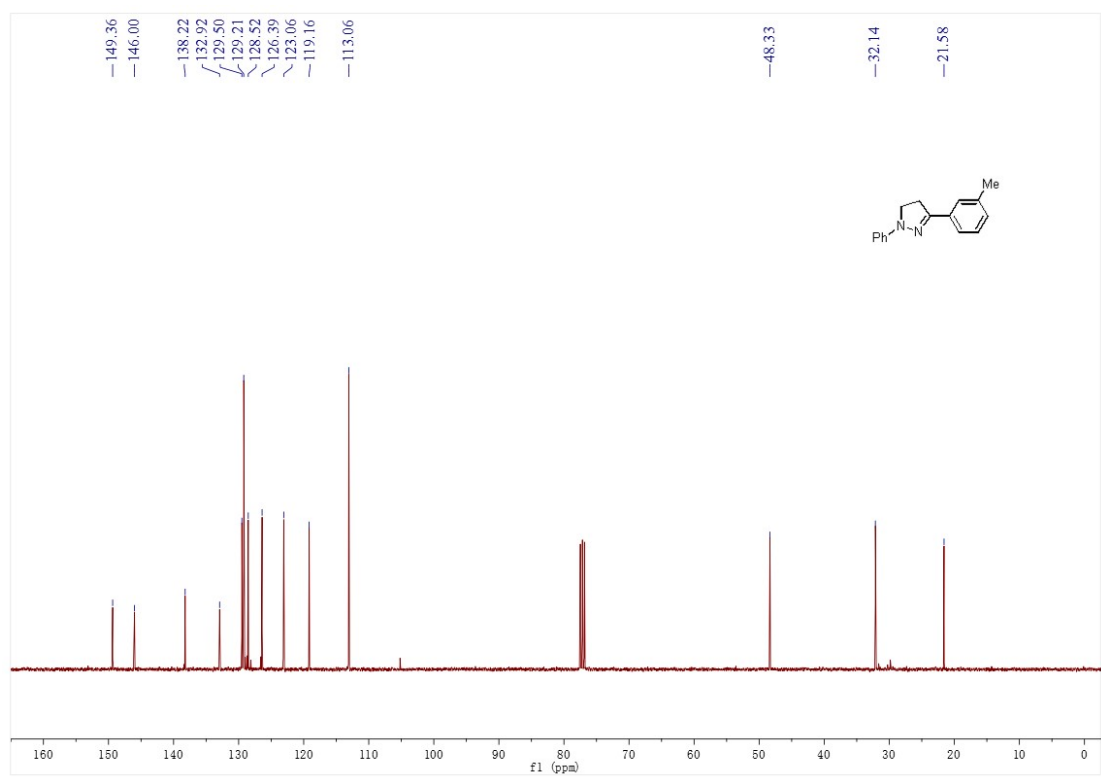
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-(4-bromophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3z**)



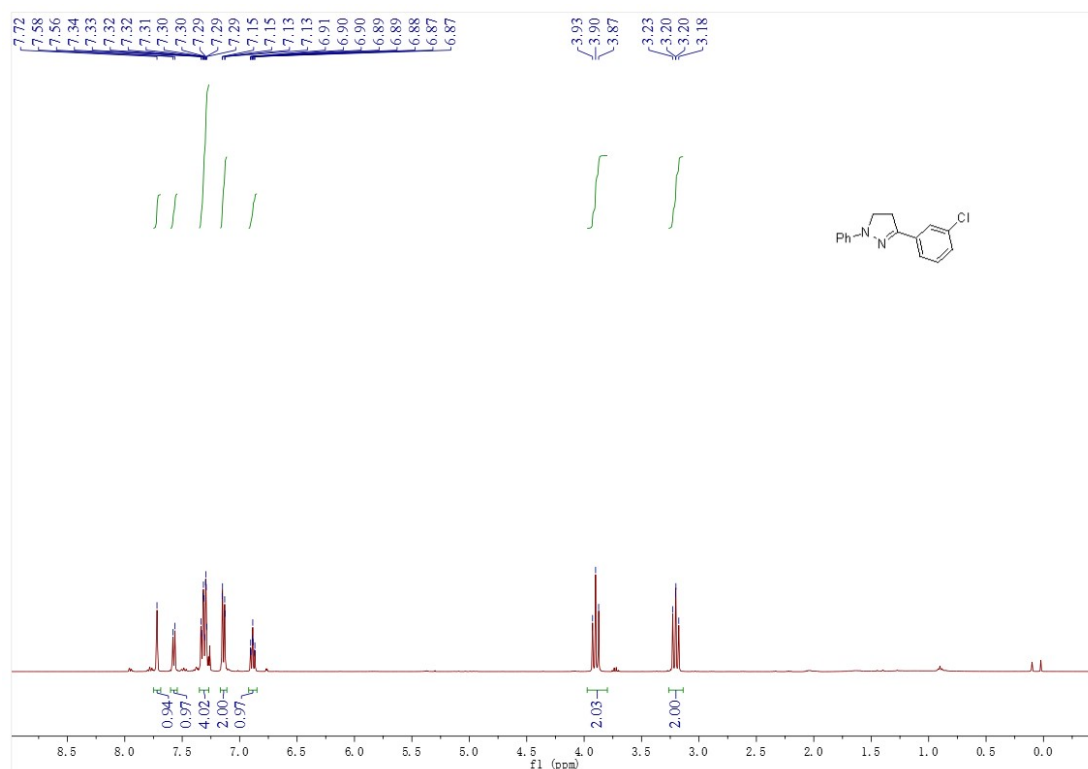
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-phenyl-3-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3aa**)



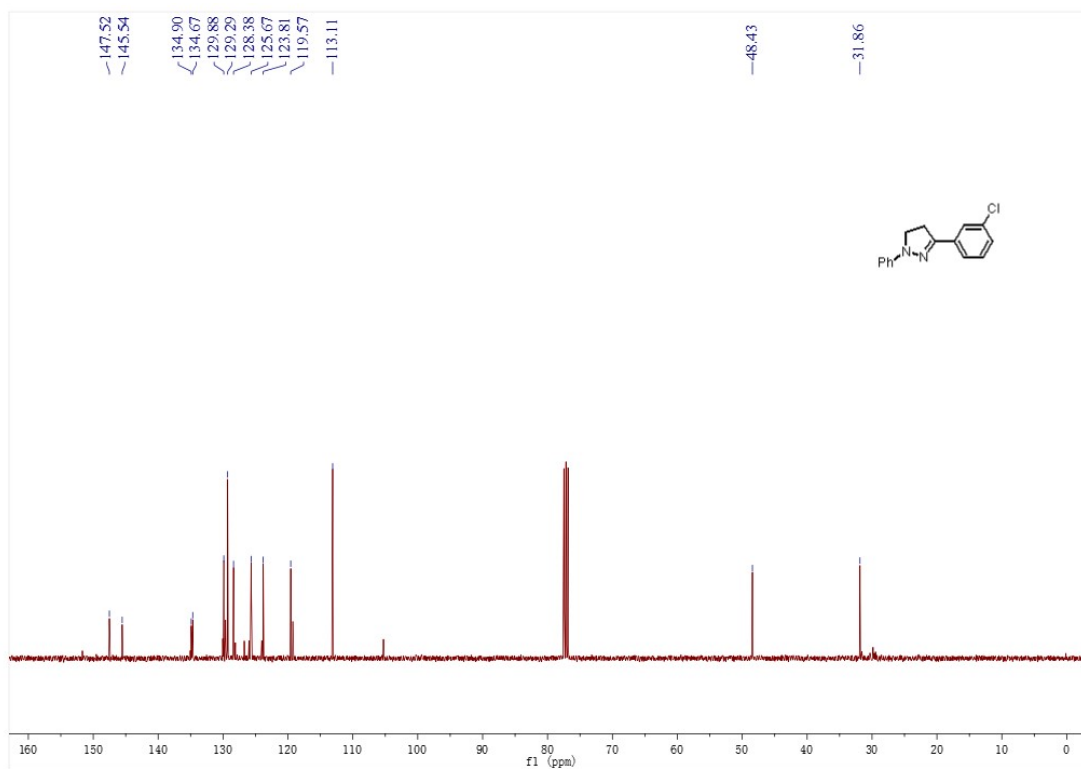
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-phenyl-3-(*m*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3aa**)



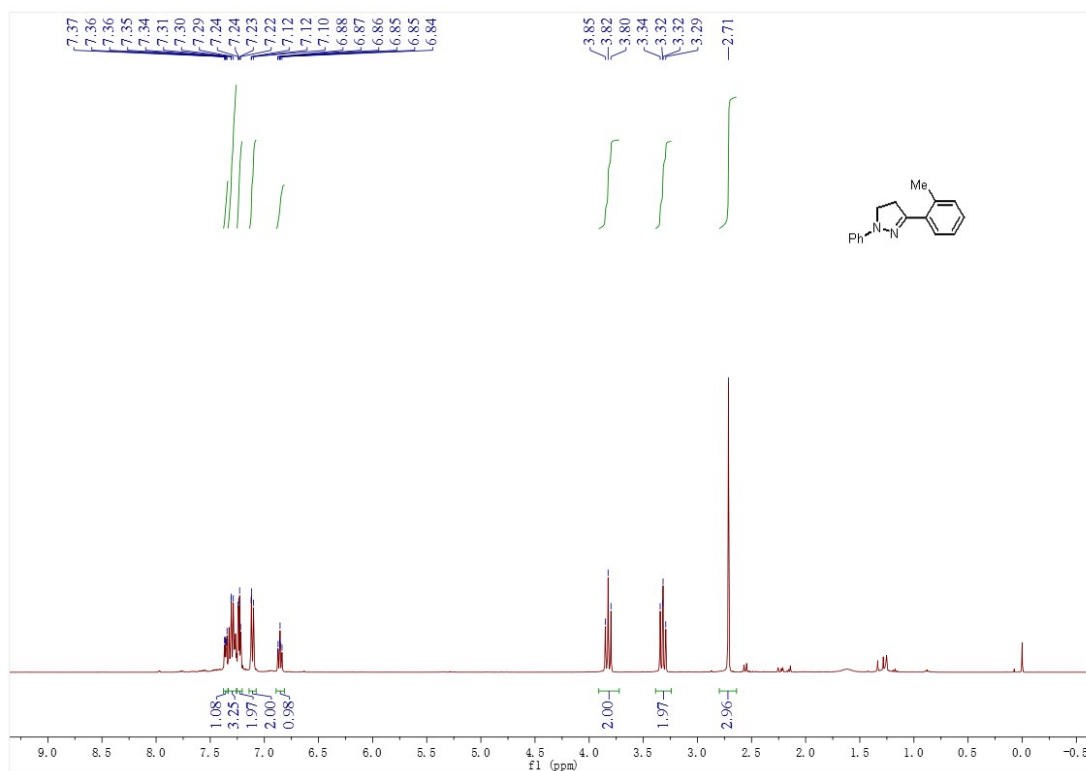
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(3-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ab**)



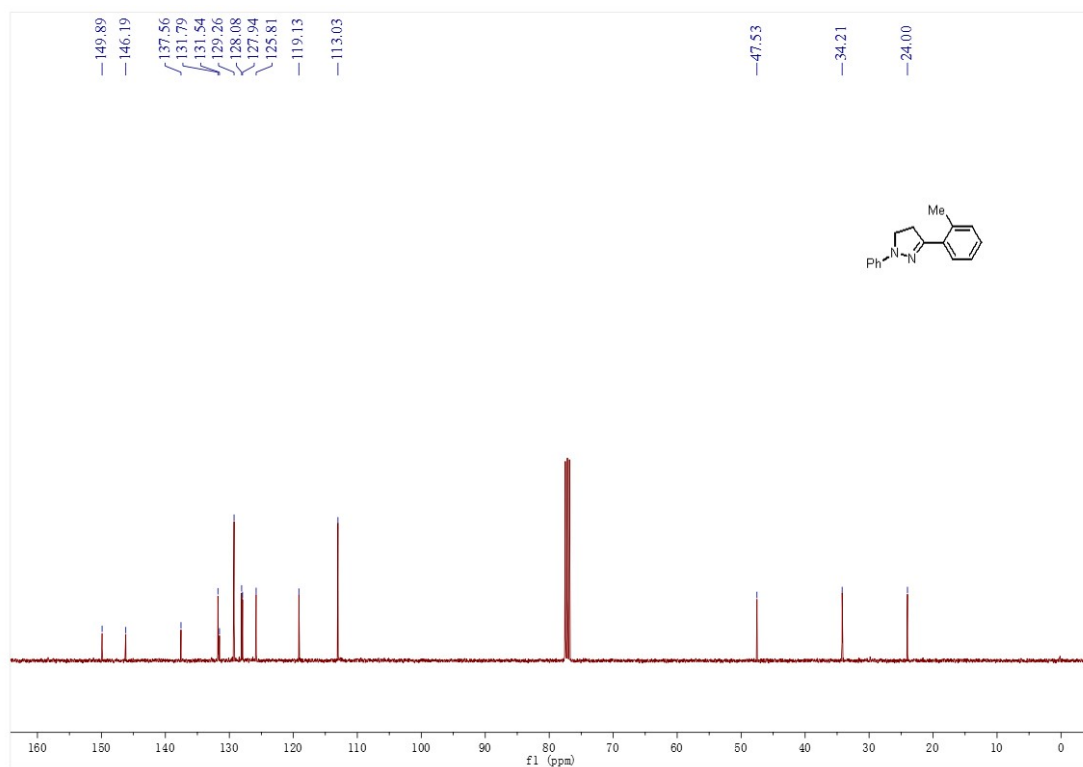
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-(3-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ab**)



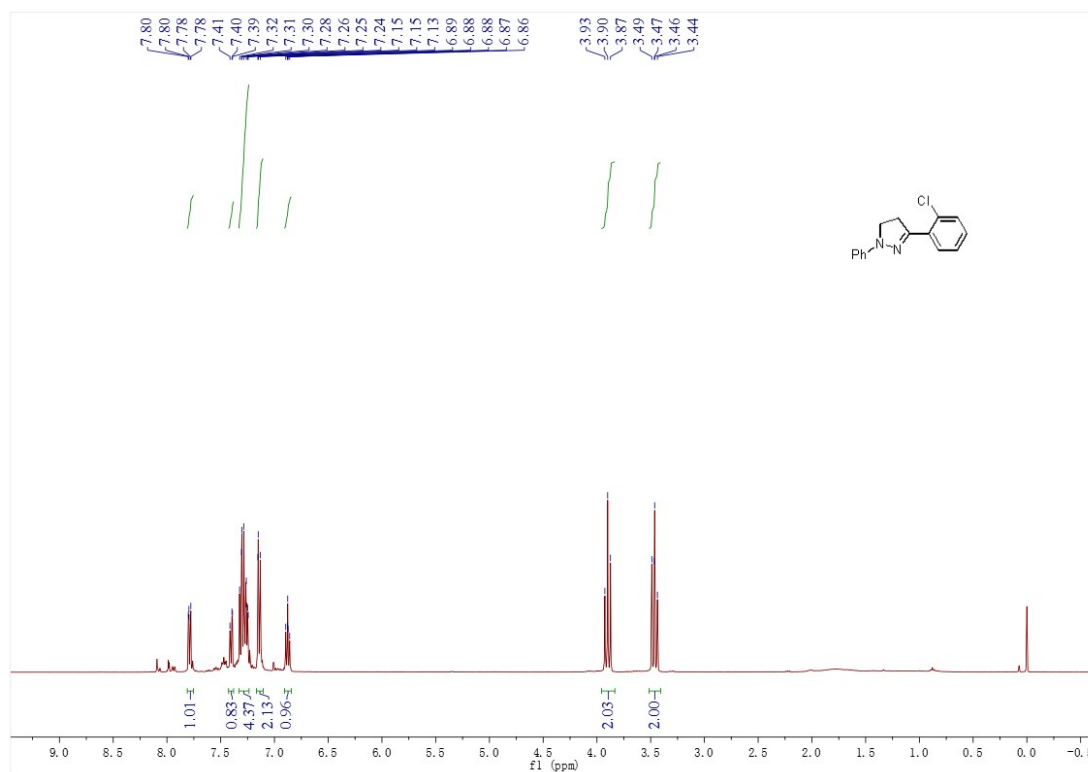
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-phenyl-3-(*o*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3ac**)



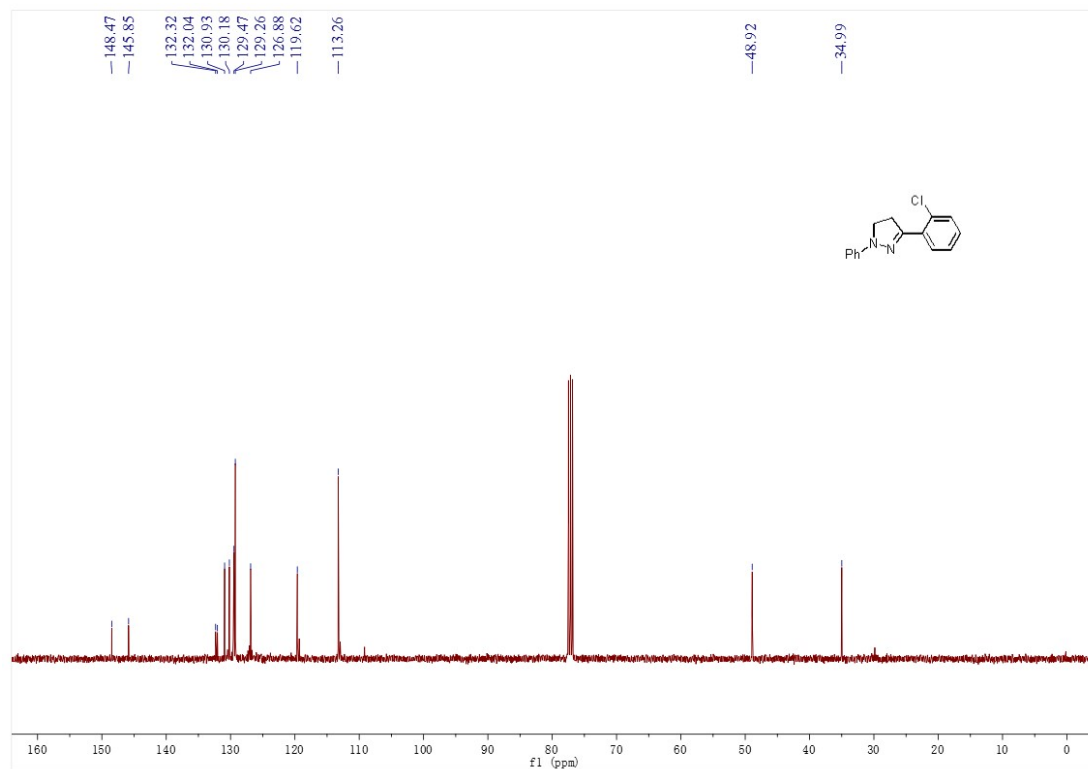
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) 1-phenyl-3-(*o*-tolyl)-4,5-dihydro-1*H*-pyrazole (**3ac**)



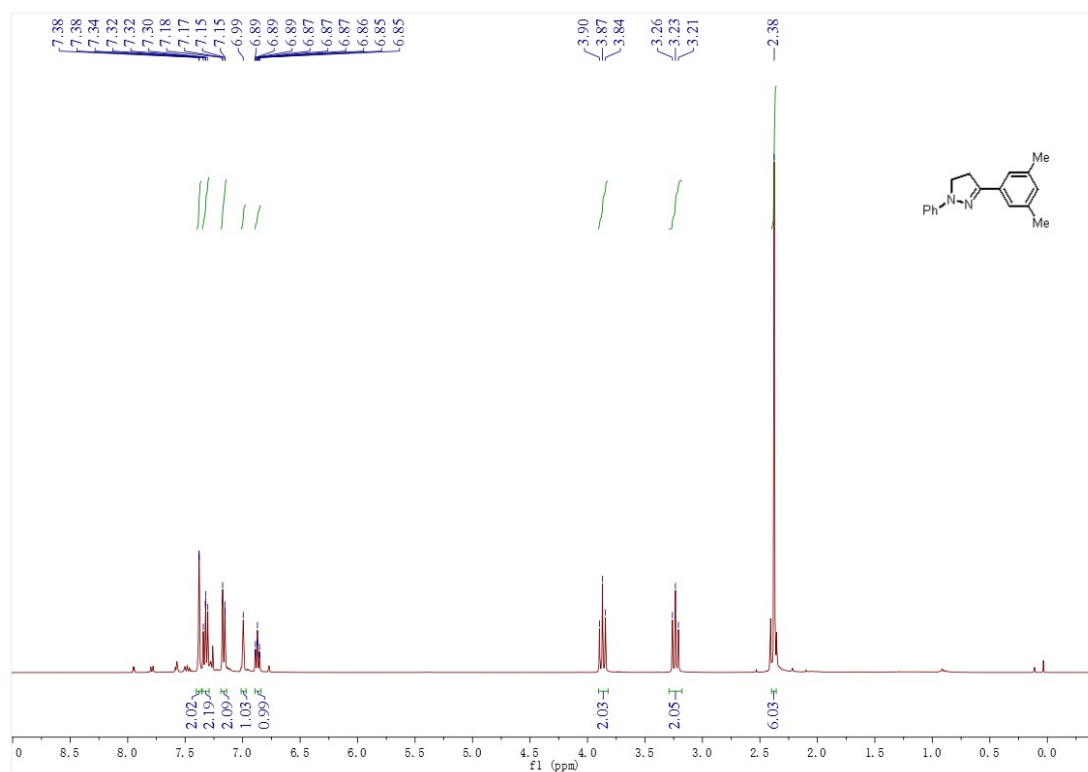
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(2-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ad**)



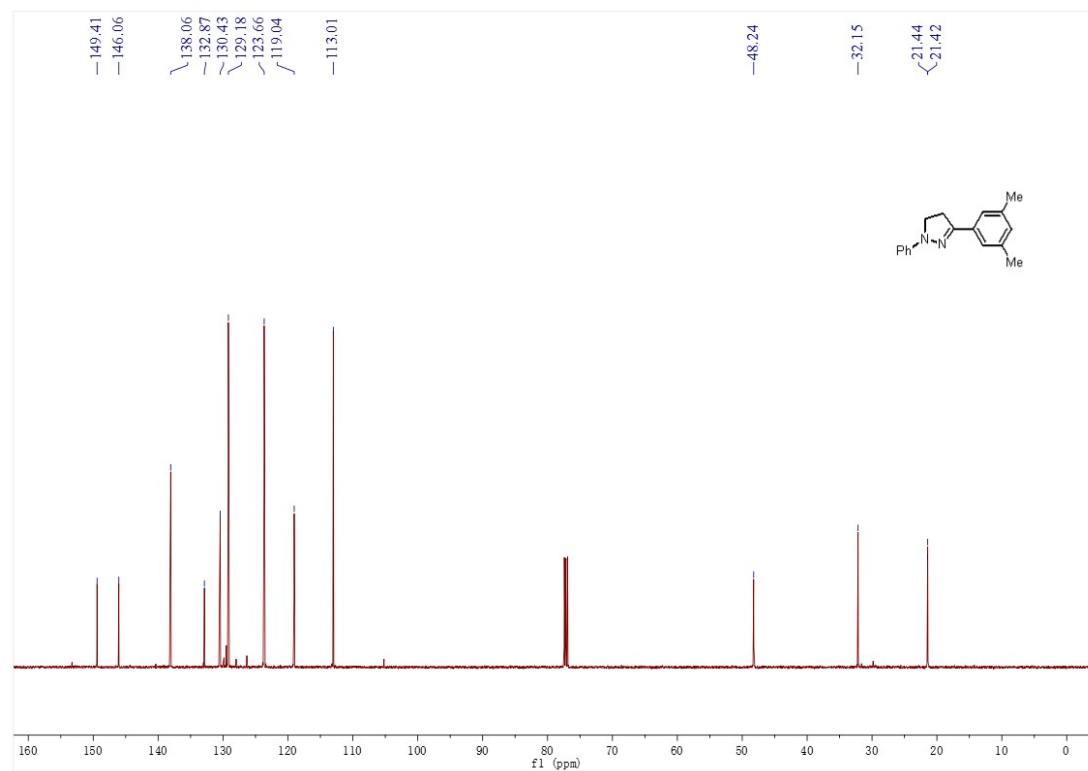
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-(2-chlorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ad**)



$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(3,5-dimethylphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ae**)

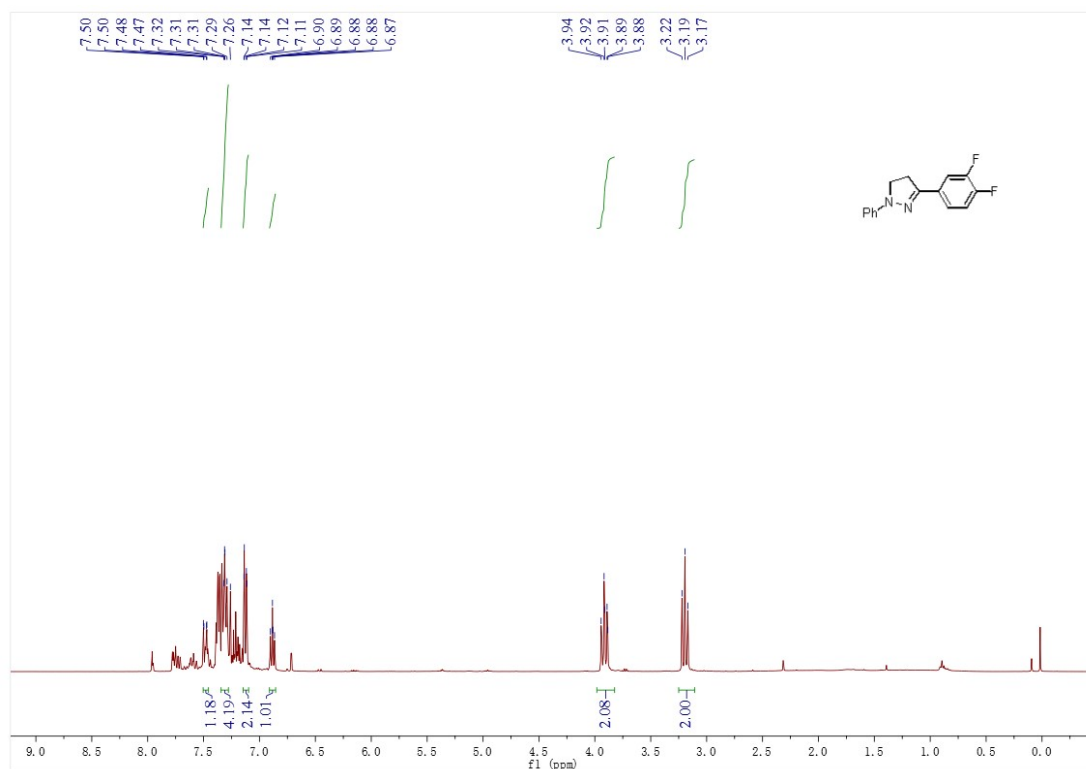


$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 3-(3,5-dimethylphenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ae**)

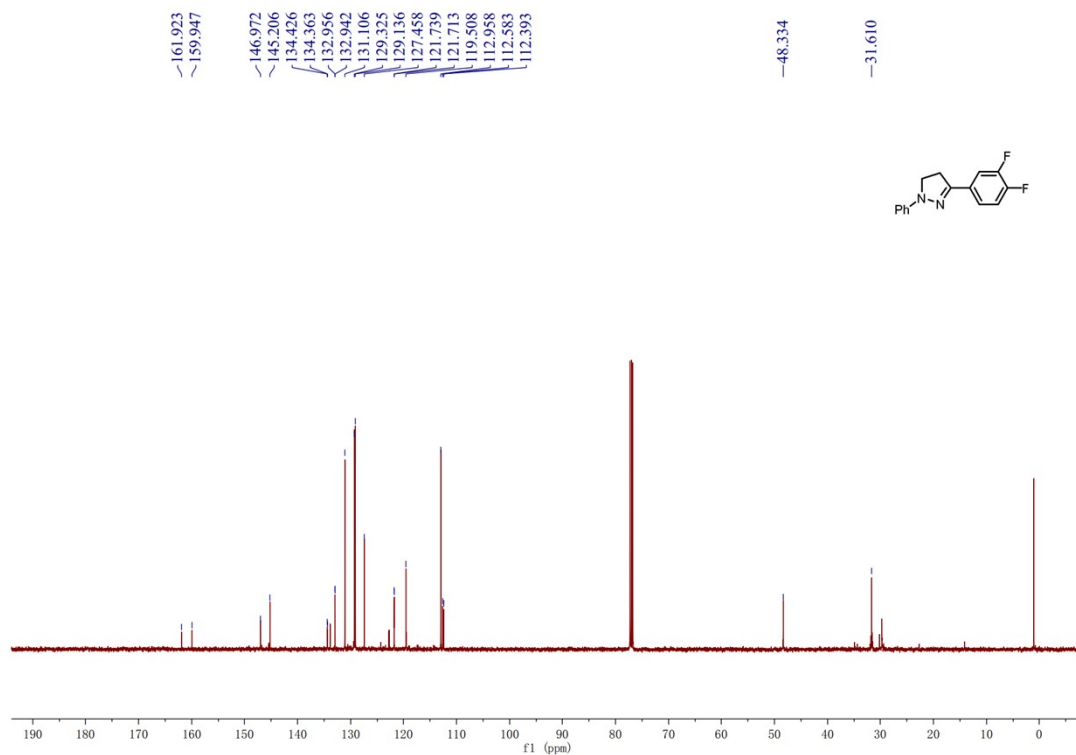




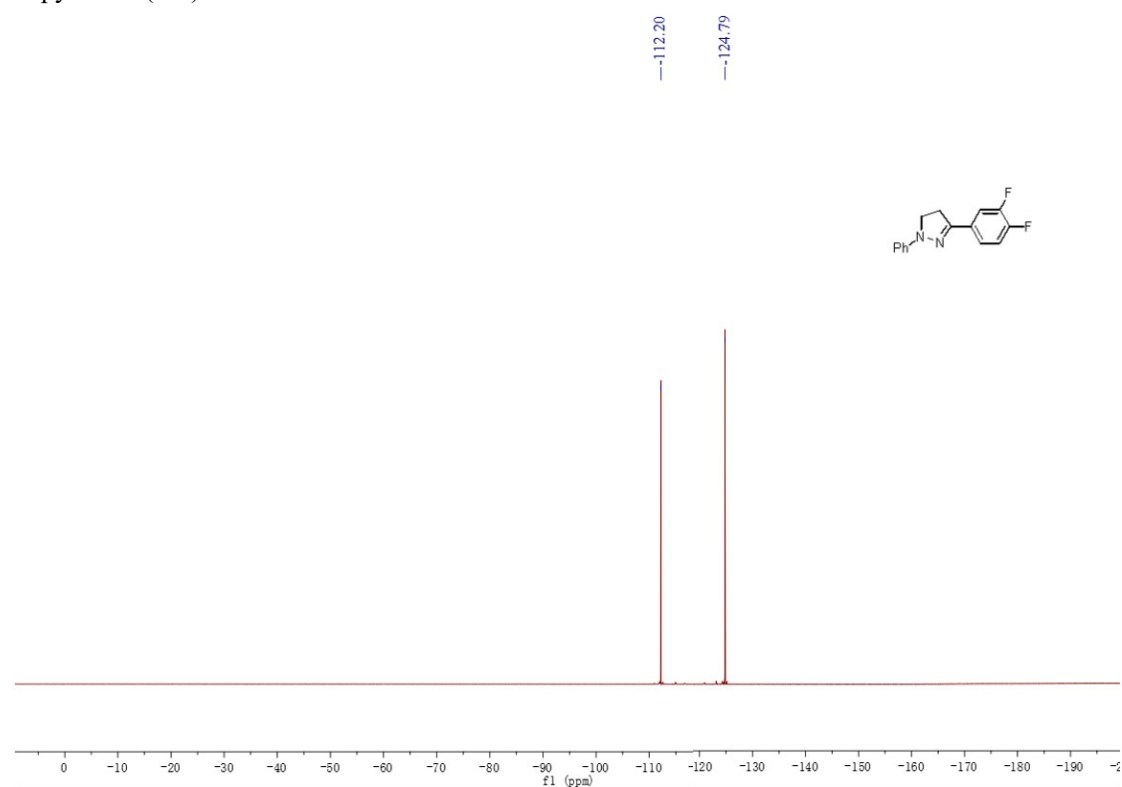
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-(3,4-difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3af**)



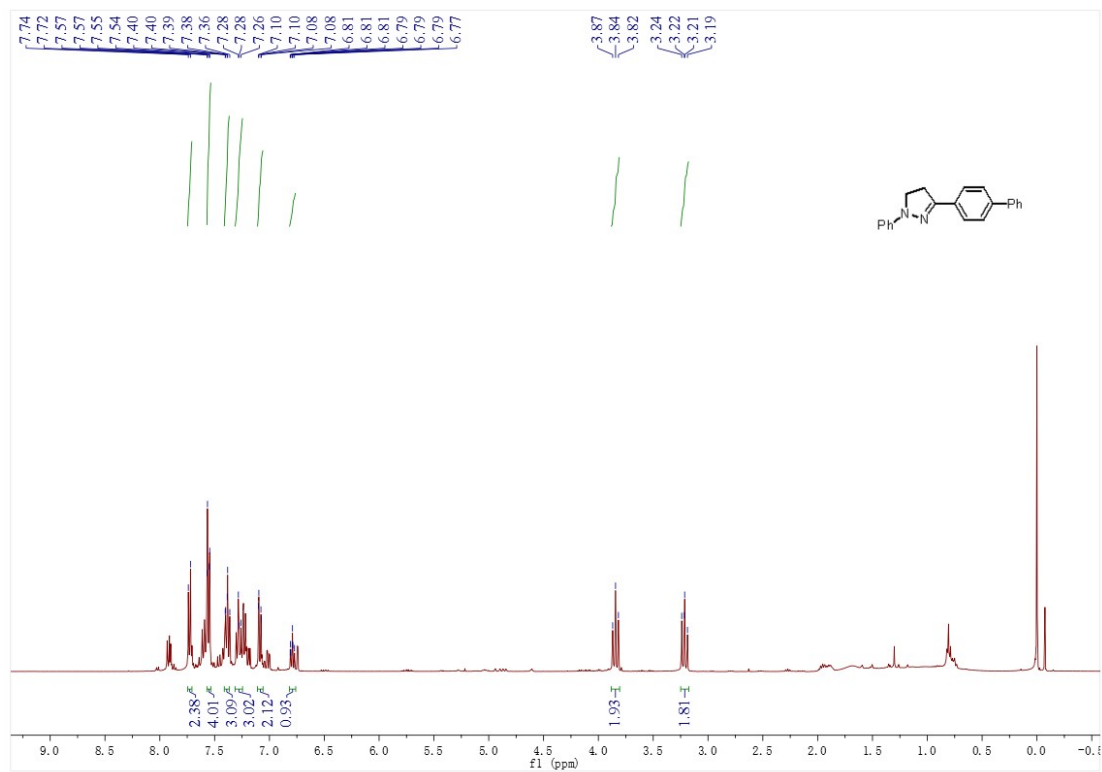
$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 3-(3,4-difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3af**)



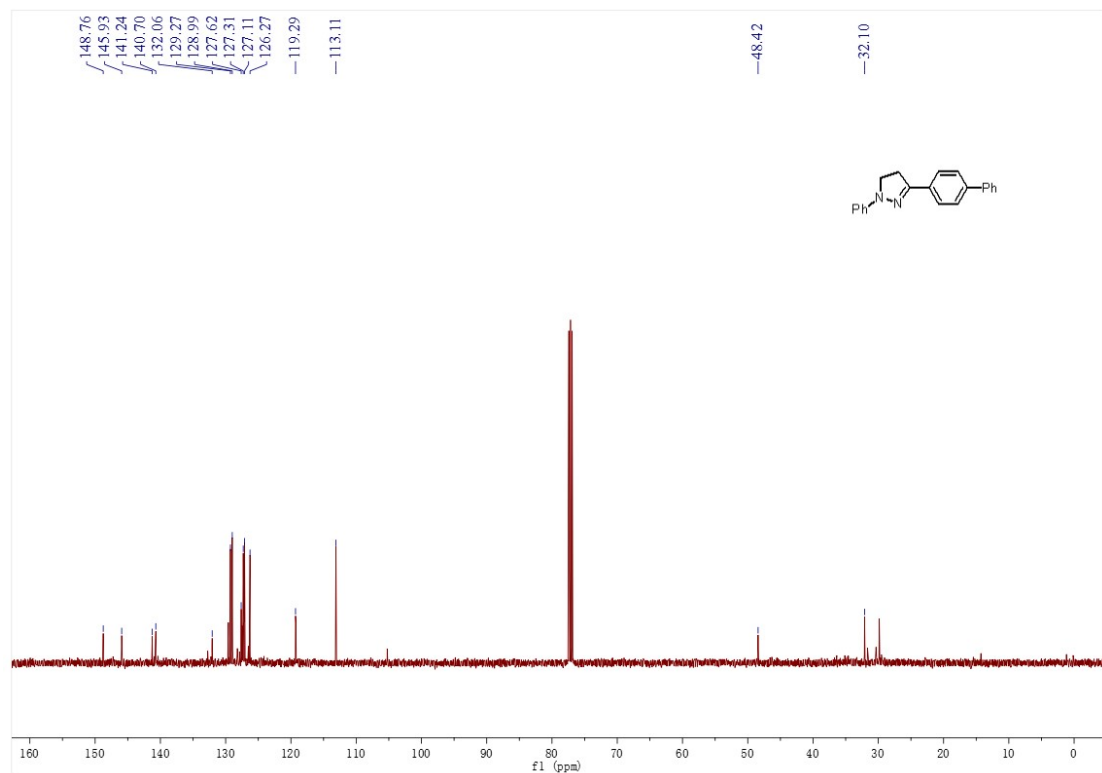
$^{19}\text{F}$  NMR spectra (376 MHz, Chloroform-*d*) of 3-(3,4-difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3af**)



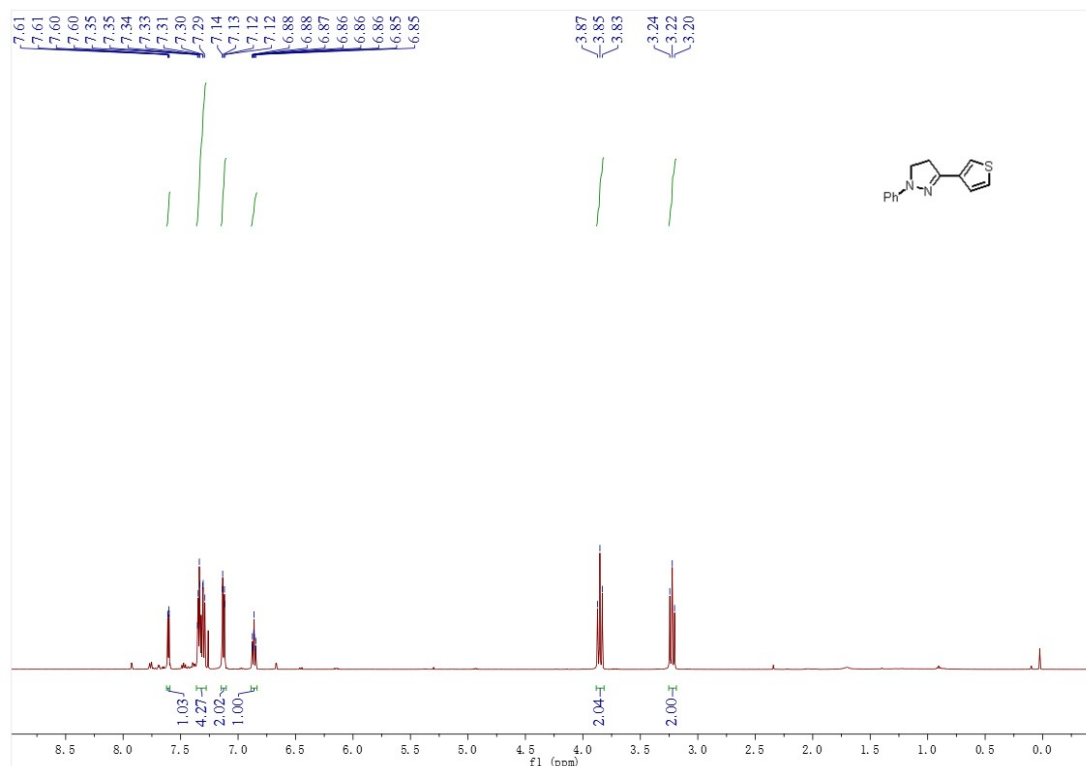
<sup>1</sup>H NMR spectra (400 MHz, Chloroform-*d*) of 3-([1,1'-biphenyl]-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ag**)



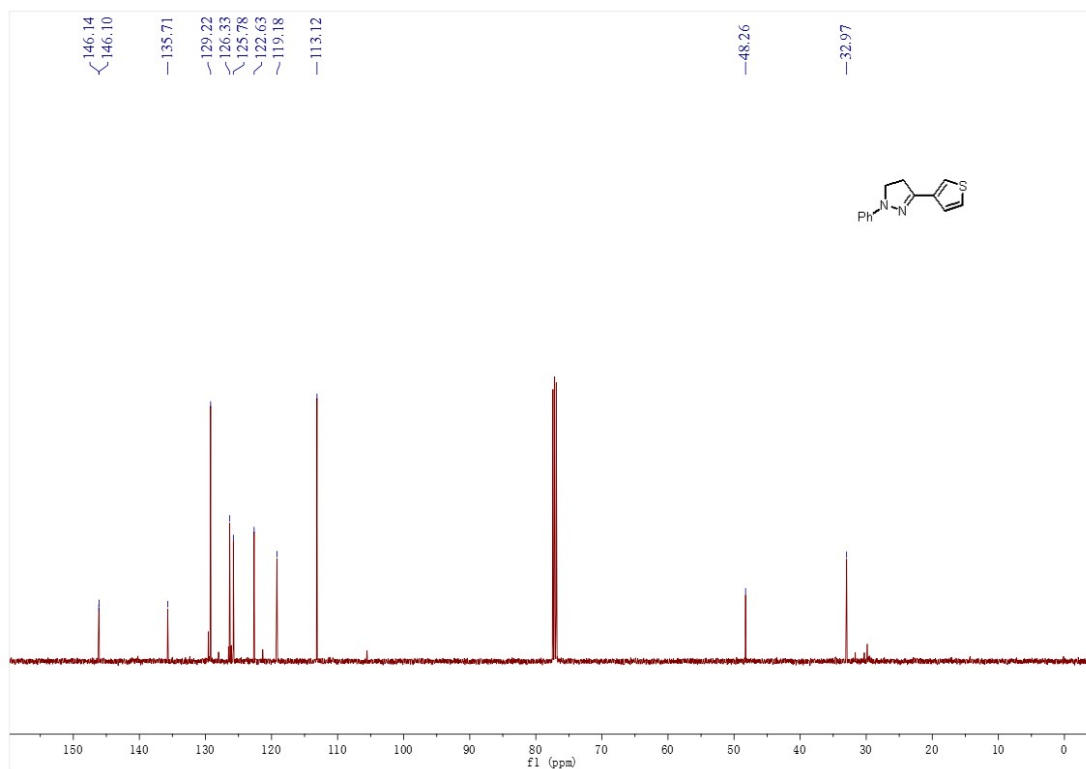
<sup>13</sup>C NMR spectra (126 MHz, Chloroform-*d*) of 3-([1,1'-biphenyl]-4-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole (**3ag**)



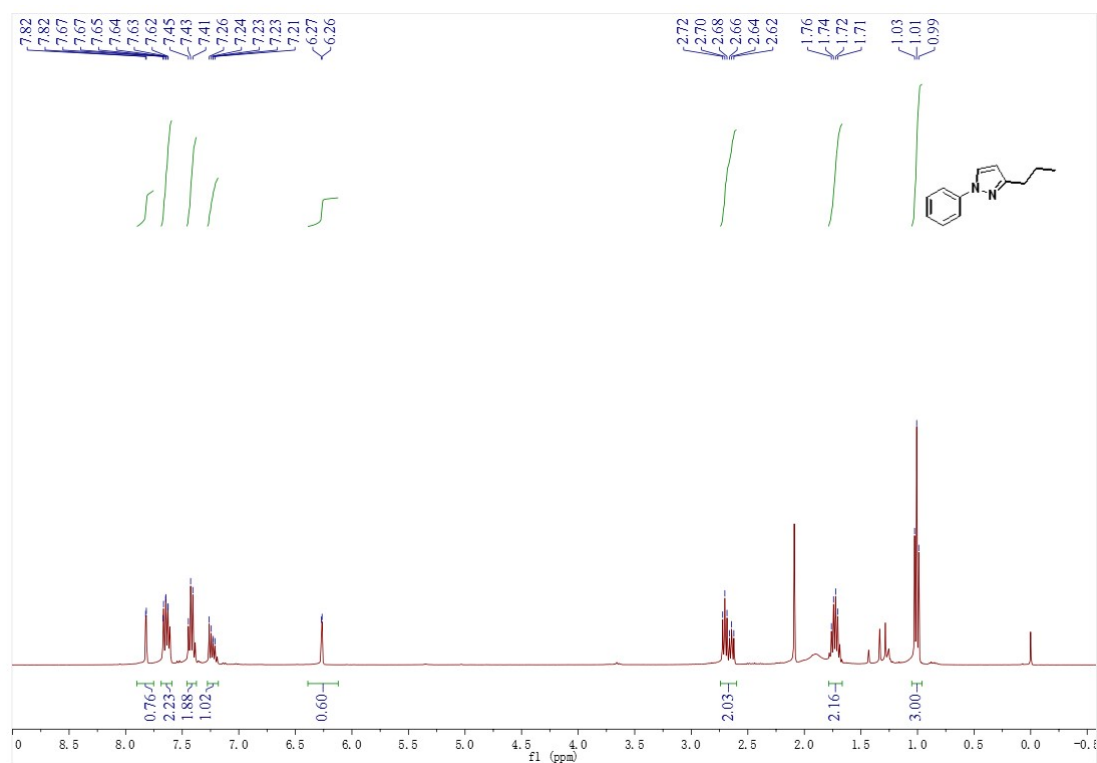
<sup>1</sup>H NMR spectra (500 MHz, Chloroform-*d*) of 1-phenyl-3-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrazole (**3ah**)



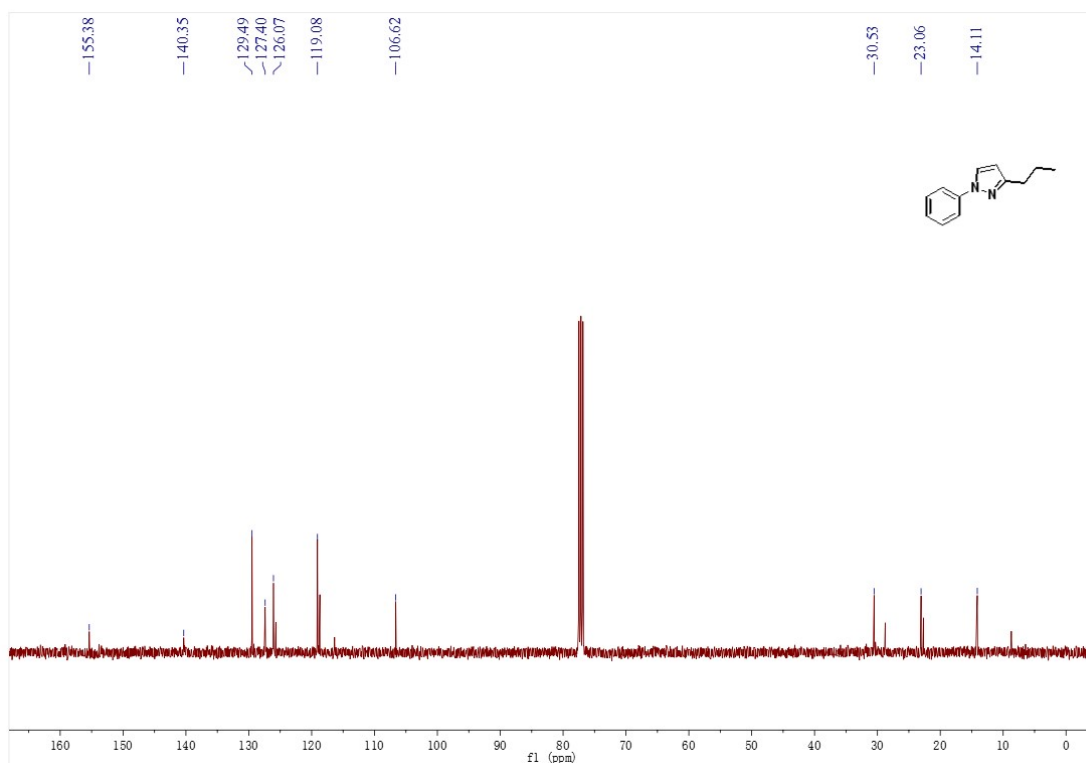
<sup>13</sup>C NMR spectra (126 MHz, Chloroform-*d*) of 1-phenyl-3-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrazole (**3ah**)



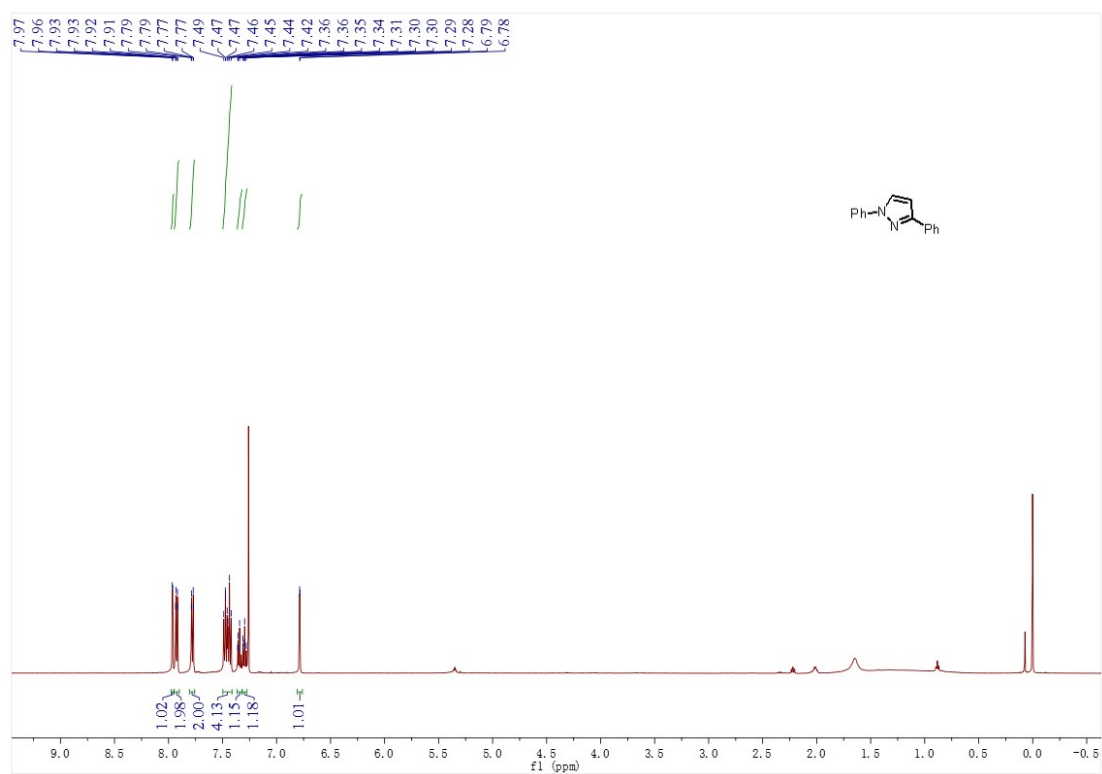
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-phenyl-3-propyl-1*H*-pyrazole (**5ai**)



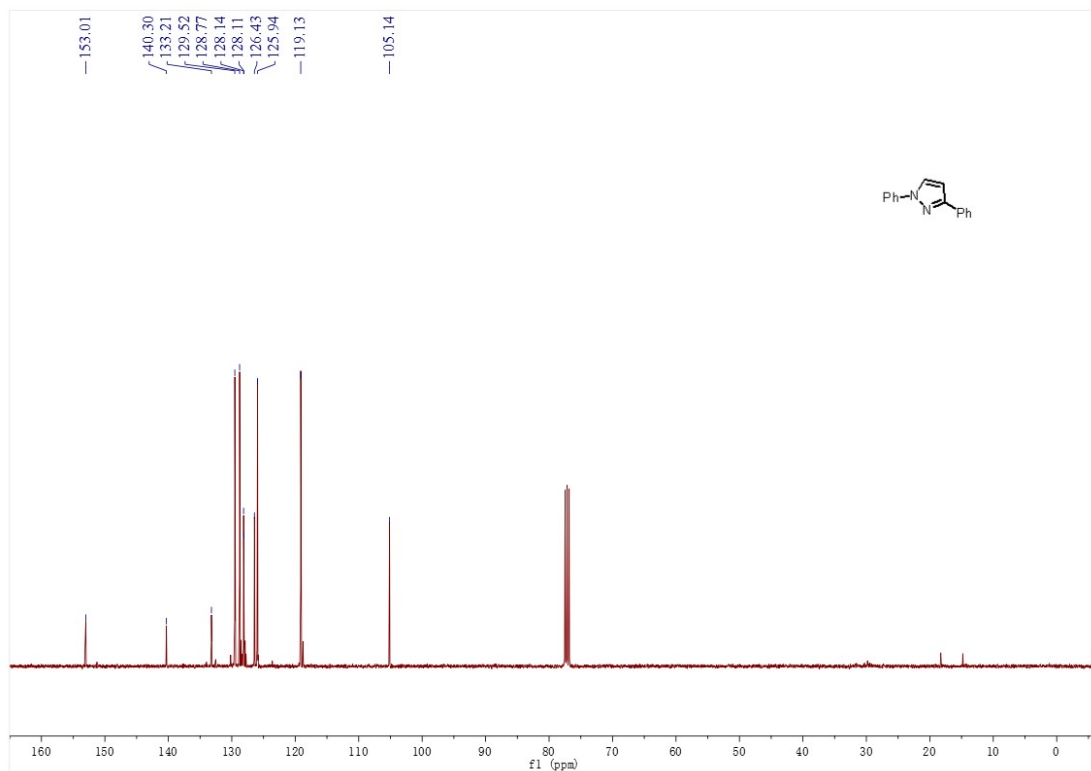
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-phenyl-3-propyl-1*H*-pyrazole (**5ai**)



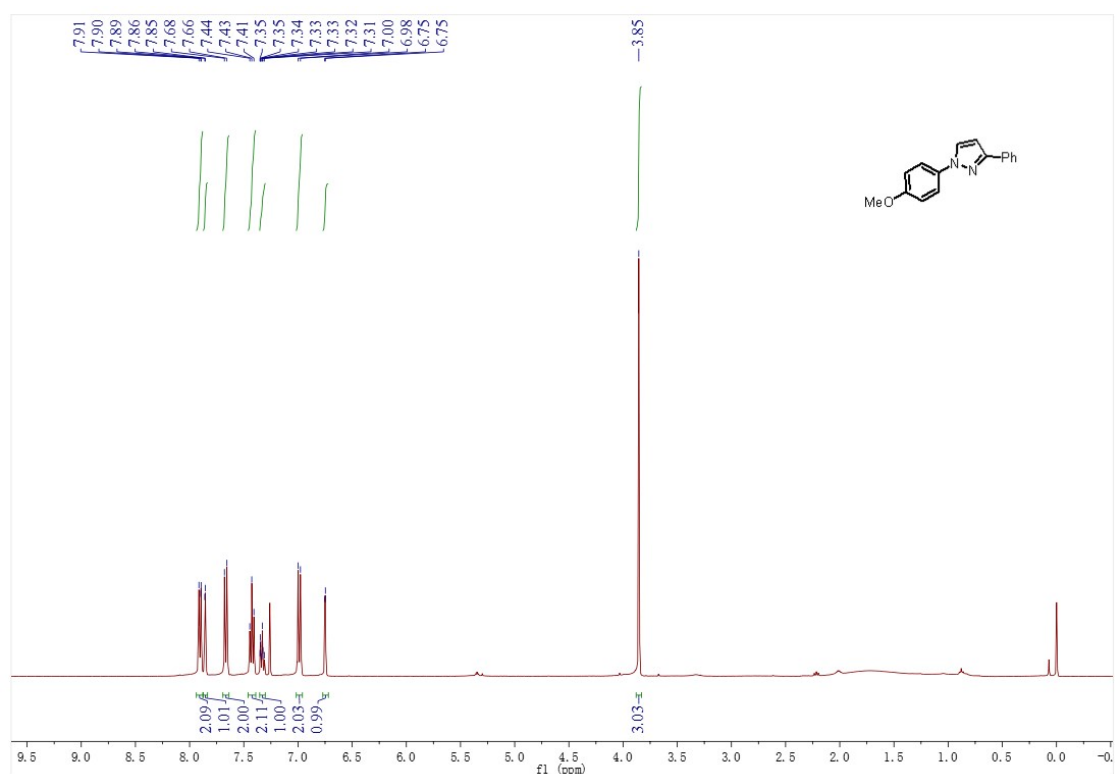
$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 1,3-diphenyl-1*H*-pyrazole (**5a**)



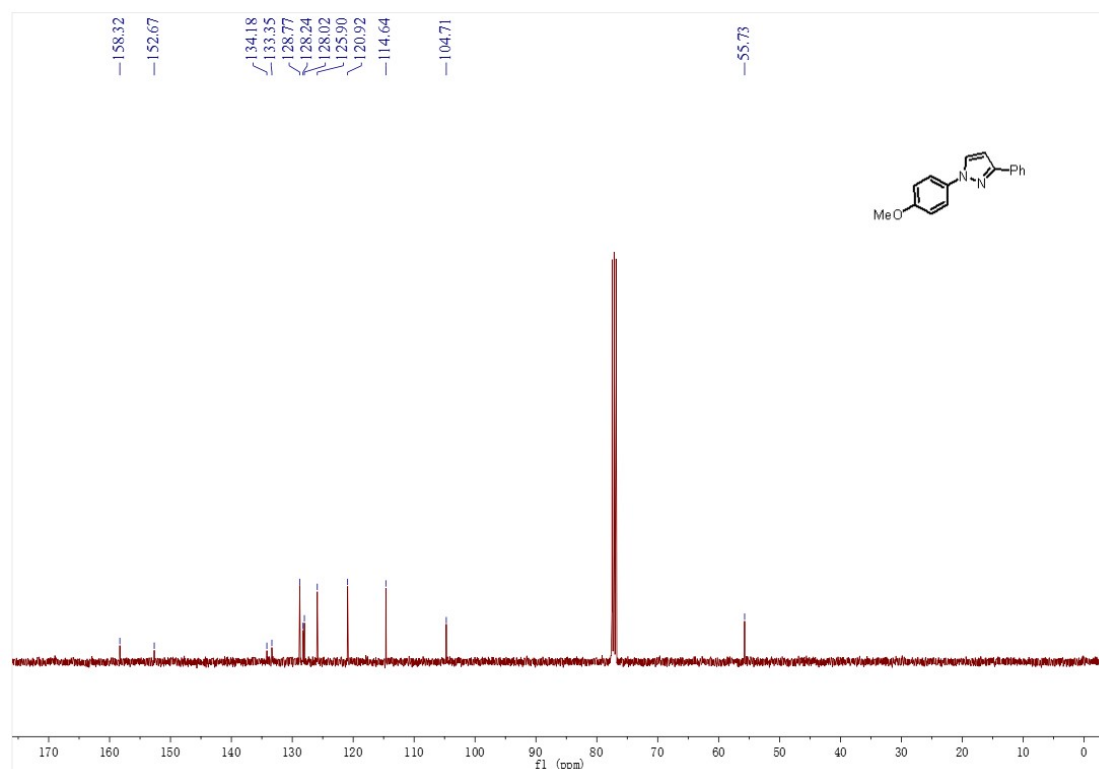
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1,3-diphenyl-1*H*-pyrazole (**5a**)



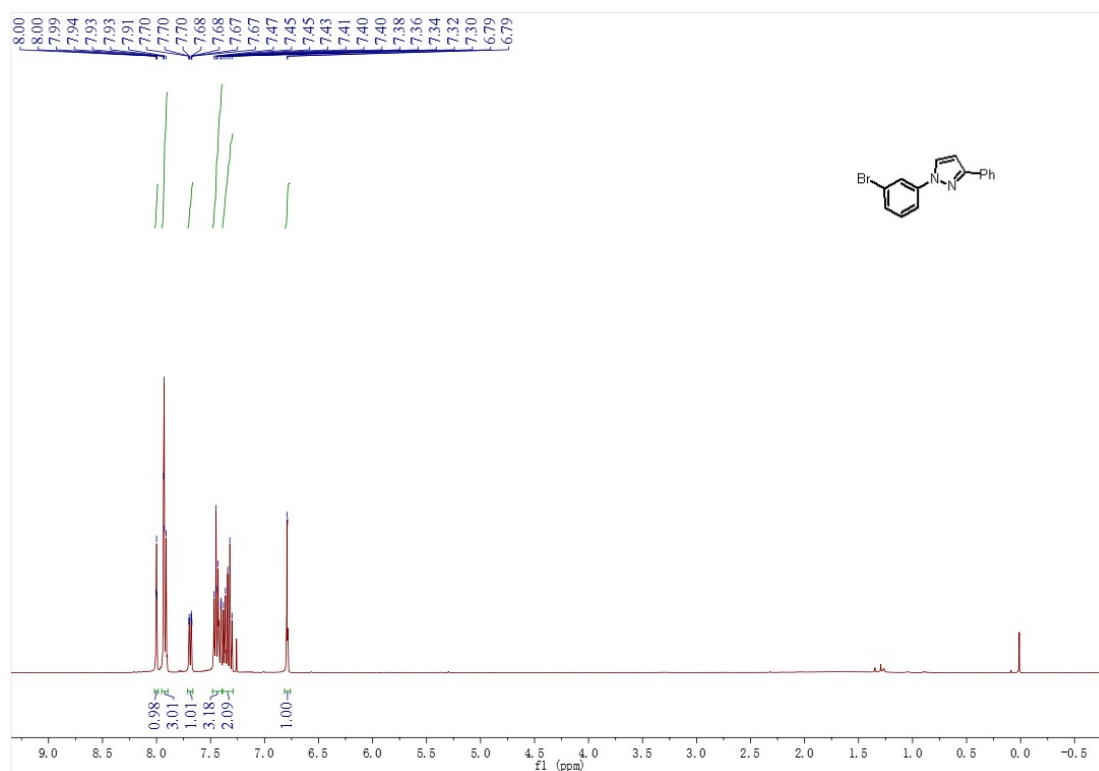
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole (**5d**)



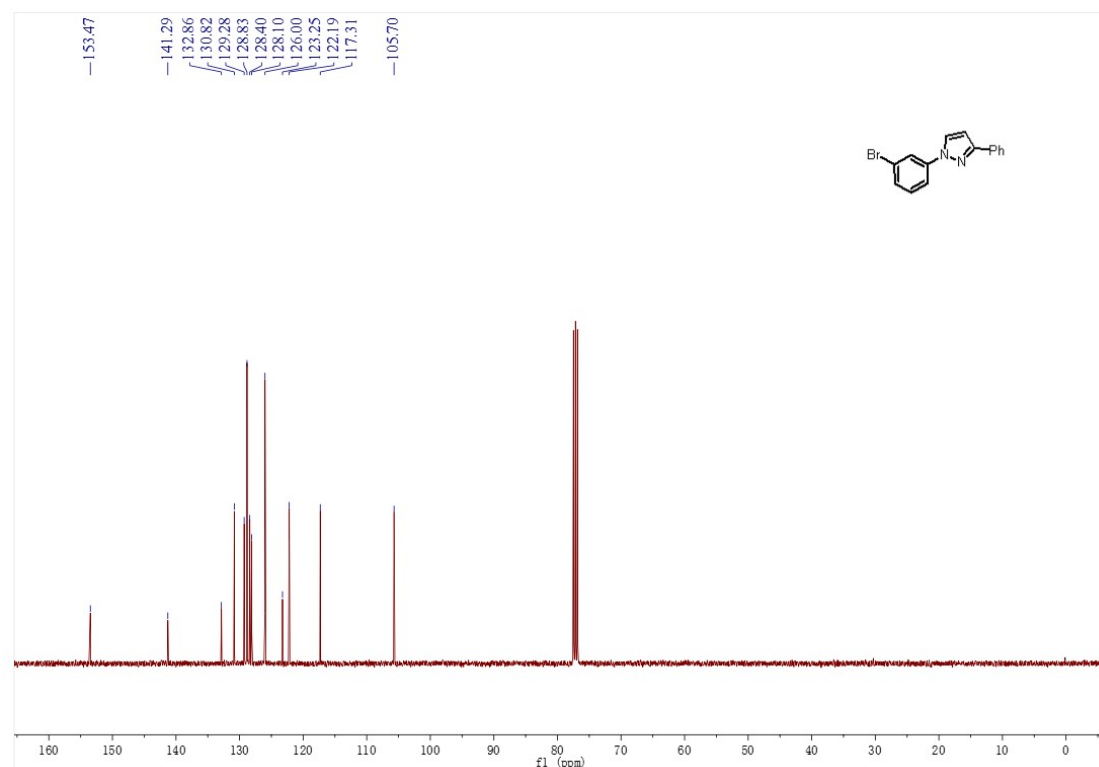
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(4-methoxyphenyl)-3-phenyl-1*H*-pyrazole (**5d**)



$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole (**51**)

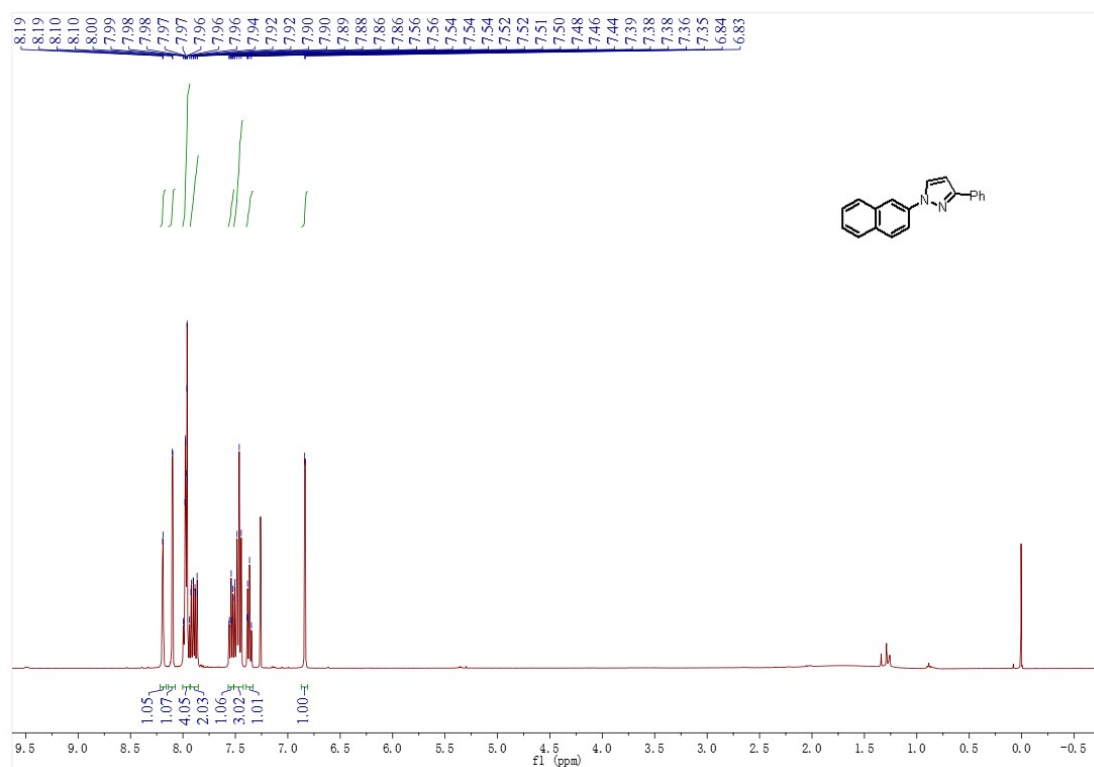


$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(3-bromophenyl)-3-phenyl-1*H*-pyrazole (**51**)

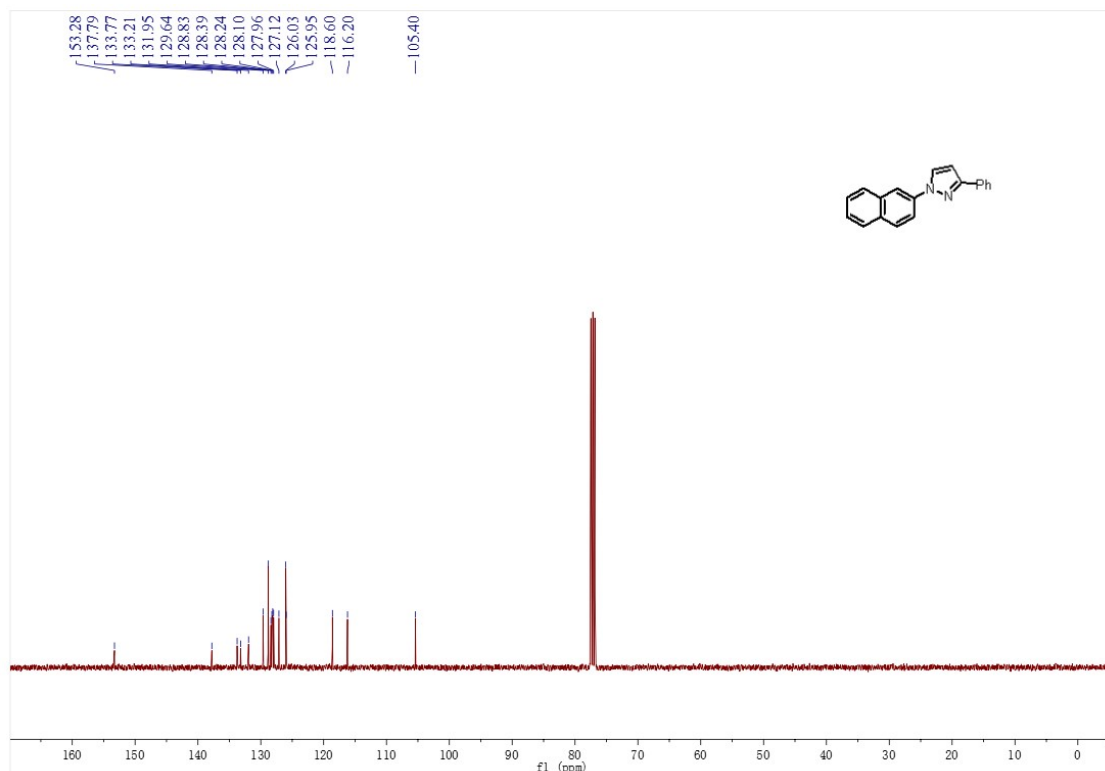




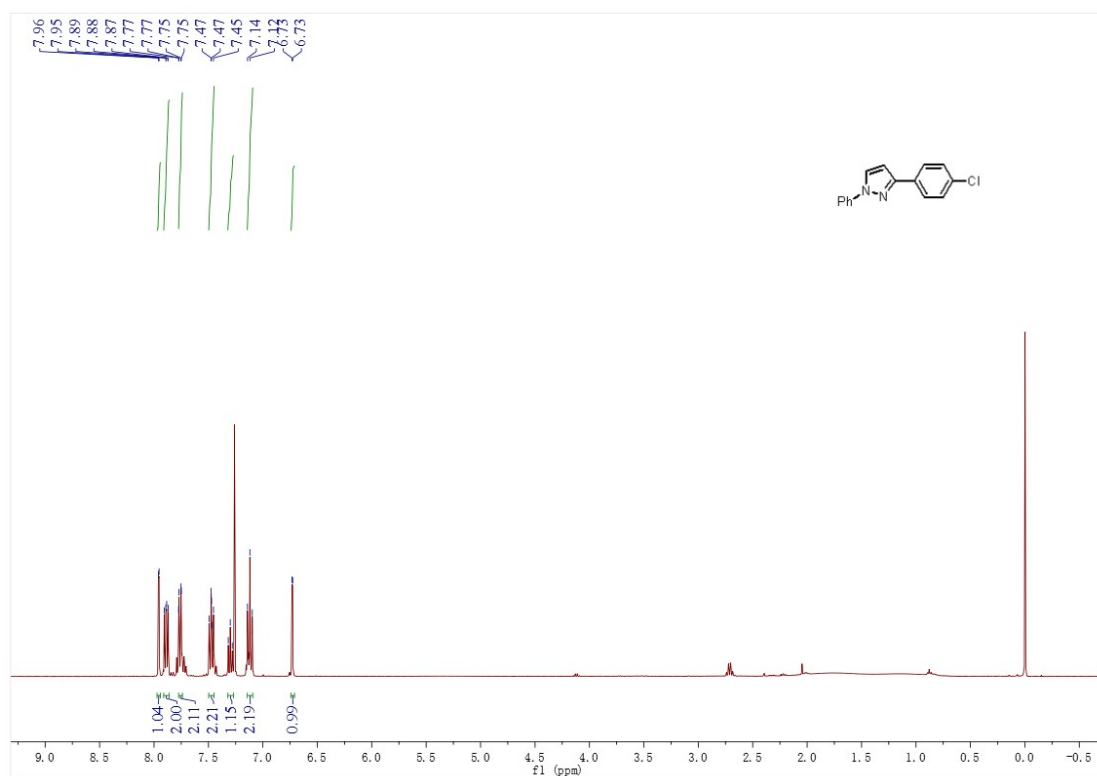
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-(naphthalen-2-yl)-3-phenyl-1*H*-pyrazole (**5s**)



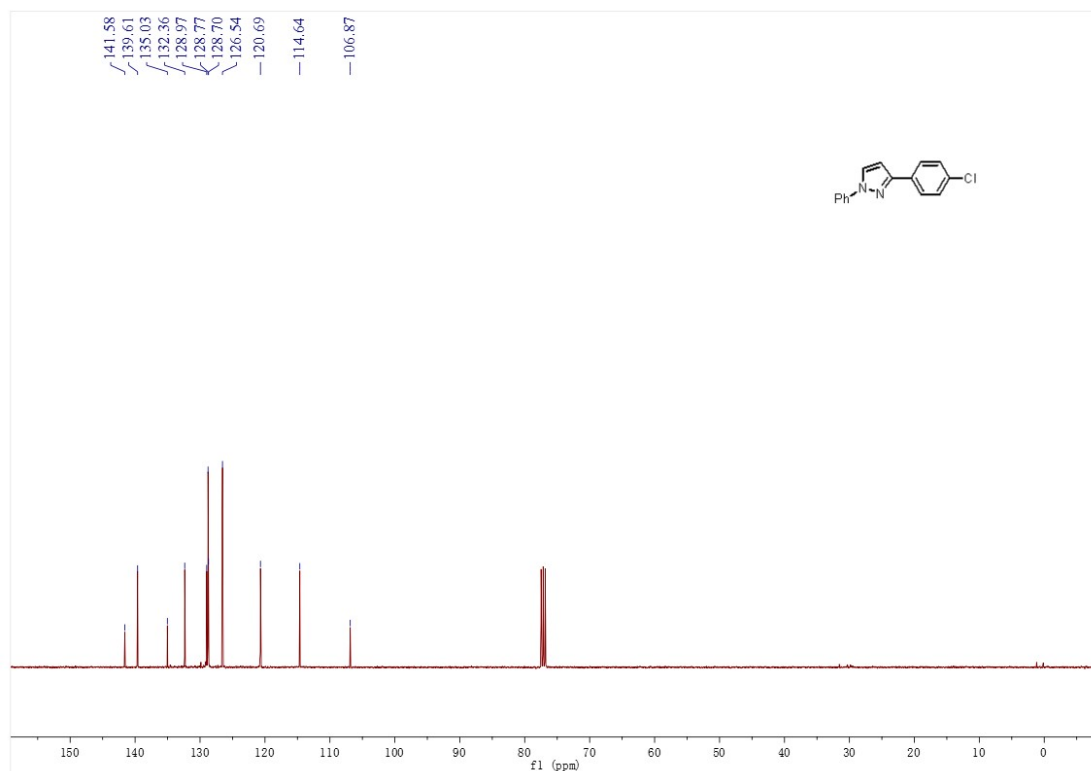
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-(naphthalen-2-yl)-3-phenyl-1*H*-pyrazole (**5s**)



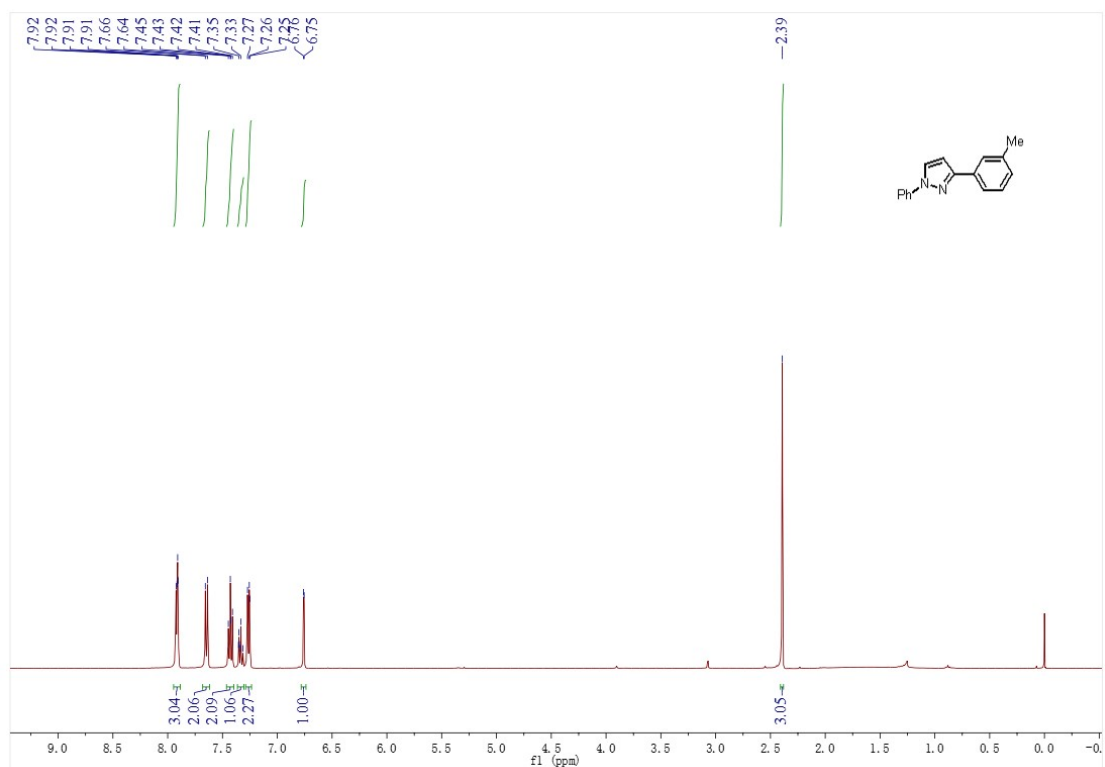
$^1\text{H}$  NMR spectra (400 MHz, Chloroform- $d$ ) of 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (**5y**)



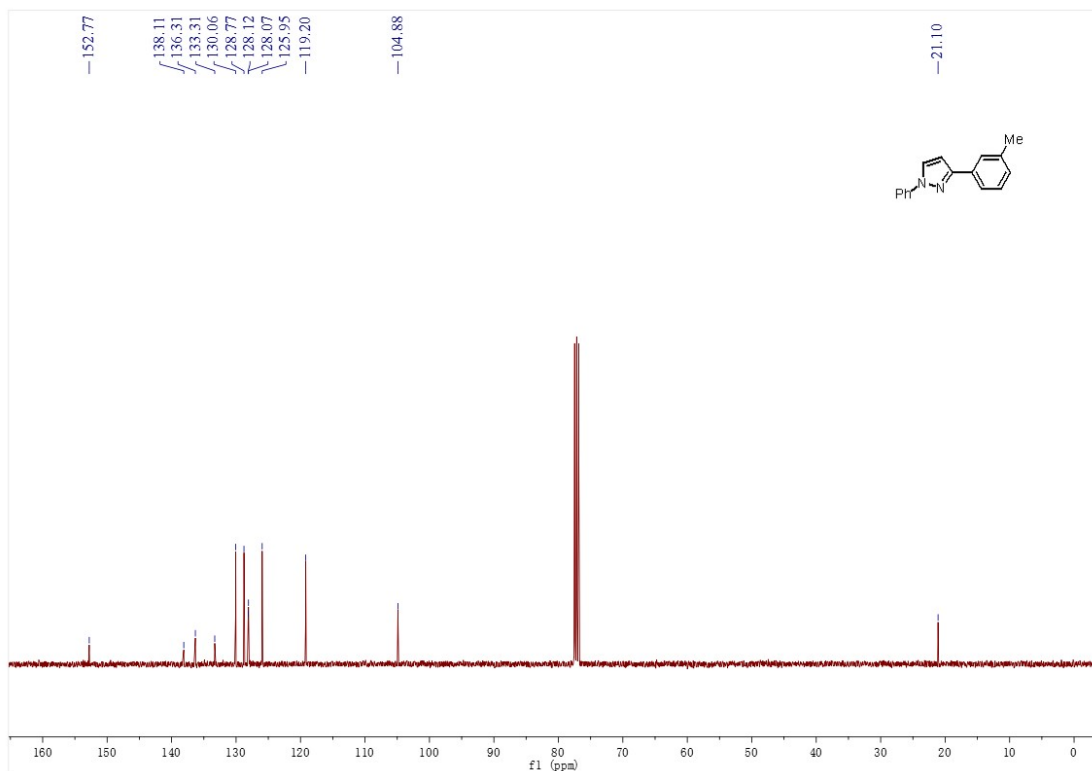
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform- $d$ ) of 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole (**5y**)



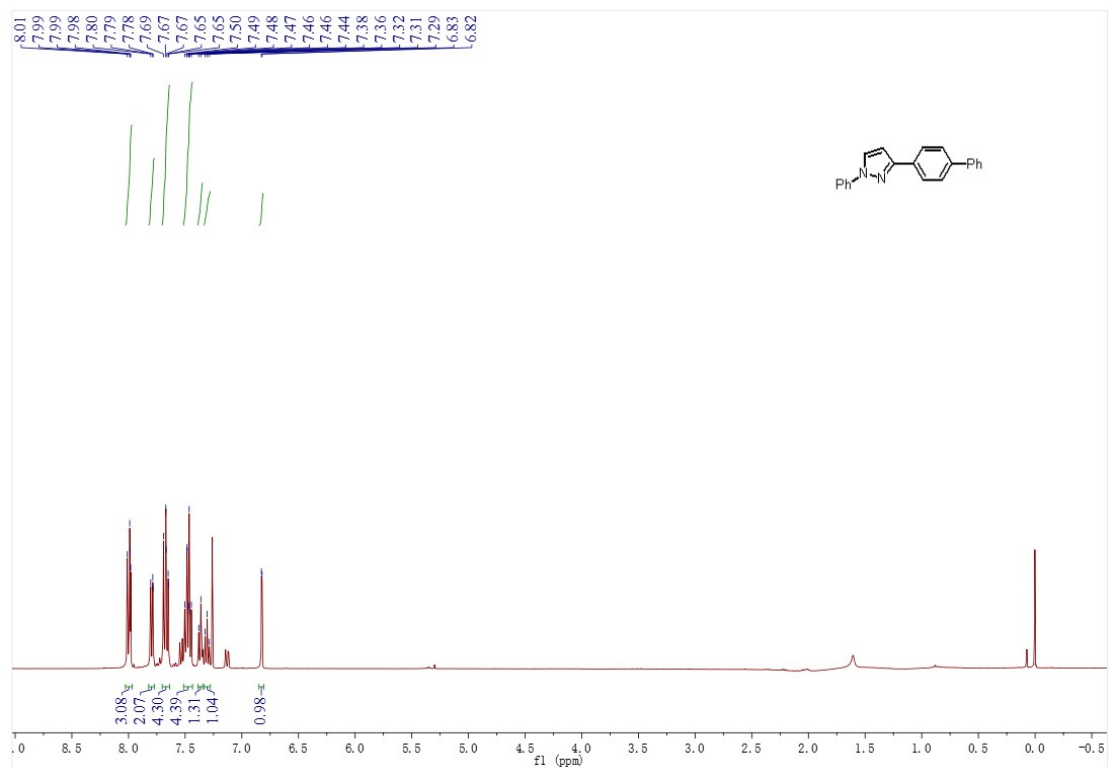
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 1-phenyl-3-(*m*-tolyl)-1*H*-pyrazole (**5aa**)



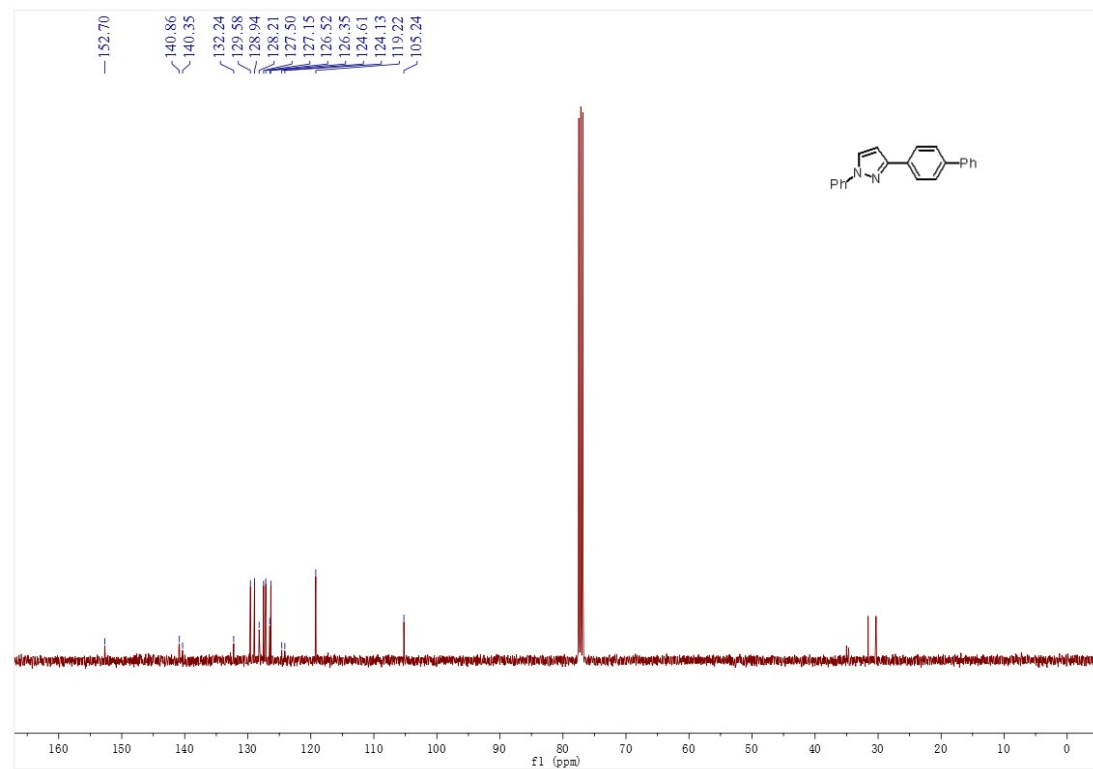
$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 1-phenyl-3-(*m*-tolyl)-1*H*-pyrazole (**5aa**)



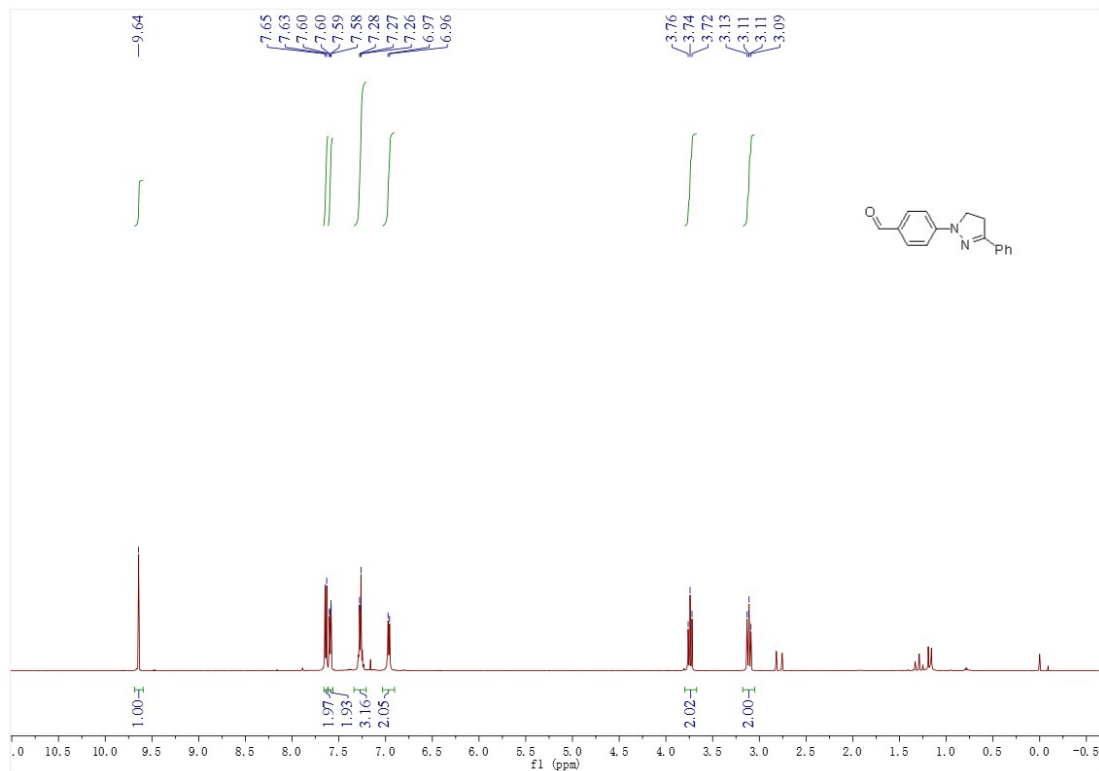
$^1\text{H}$  NMR spectra (400 MHz, Chloroform-*d*) of 3-([1,1'-biphenyl]-4-yl)-1-phenyl-1*H*-pyrazole (**5ag**)



$^{13}\text{C}$  NMR spectra (101 MHz, Chloroform-*d*) of 3-([1,1'-biphenyl]-4-yl)-1-phenyl-1*H*-pyrazole (**5ag**)



$^1\text{H}$  NMR spectra (500 MHz, Chloroform-*d*) of 4-(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)benzaldehyde (**6**)



$^{13}\text{C}$  NMR spectra (126 MHz, Chloroform-*d*) of 4-(3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl)benzaldehyde (**6**)

