Supporting Information

Electrochemically Enabled Synthesis of Multi-substituted Pyrazoles *via* a Radical Cyclization Cascade

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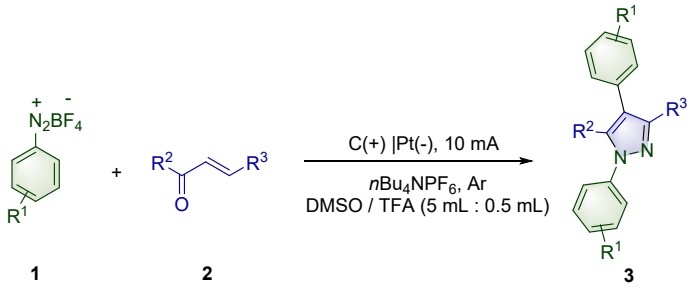
1. General information

Without special instructions, all reagents and solvents were commercially available and were not further purified. Column chromatography was carried out using silica gel (300-400 mesh). NMR spectroscopy was performed on Bruker AV-400 or Bruker AV-600 instruments. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-d (δ 7.26, singlet). The abbreviations used to explain the multiplicities were as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-d (δ 77.00, triplet). The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat. EPR spectra was recorded on Bruker A300.

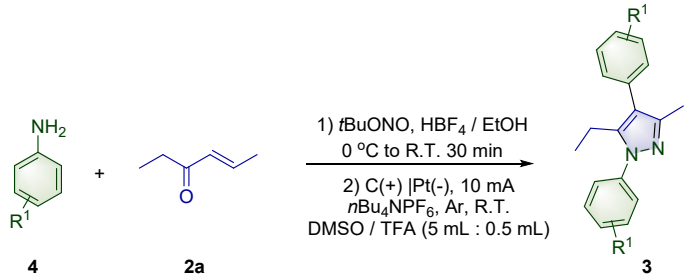
2. Procedures for the electrolysis

2.1 Synthesis of multi-substituted pyrazoles



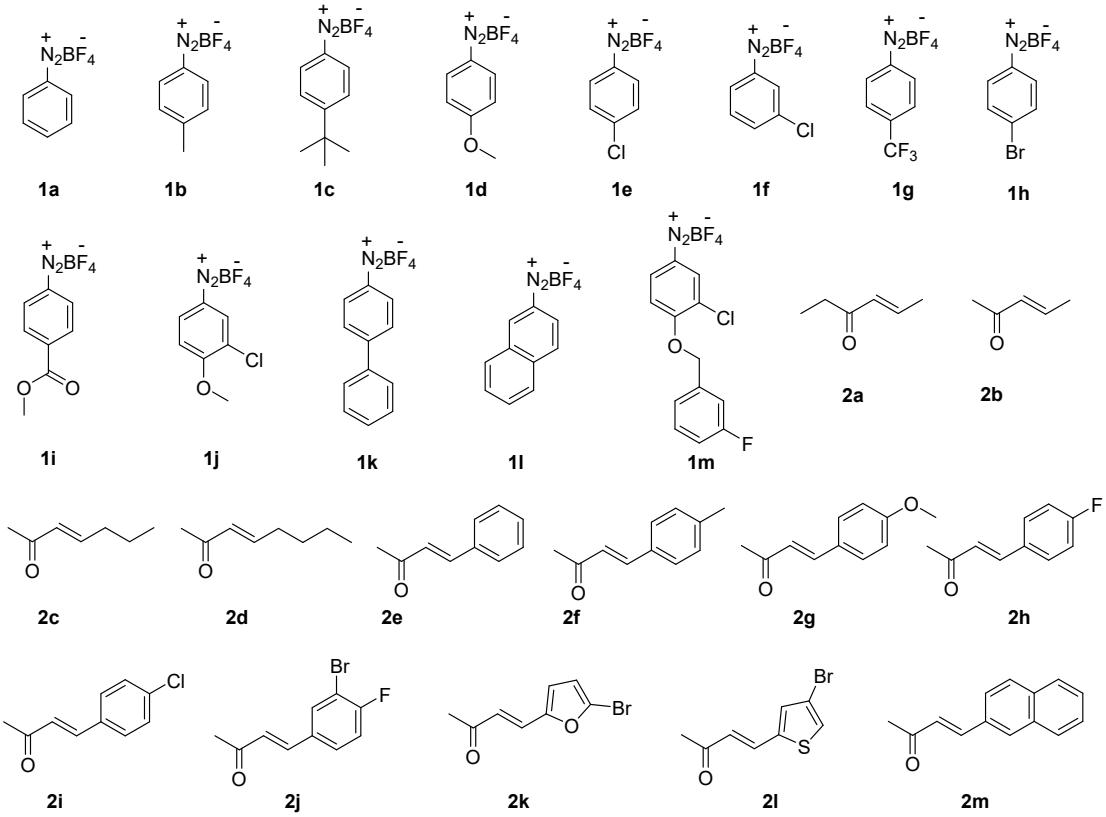
The aryl diazonium salts **1** (0.6 mmol, 1.0 equiv.) and enones **2** (0.9 mmol, 1.5 equiv.), nBu$_4$NPF$_6$ (0.5 equiv.), TFA (0.5 mL), were placed in a 10 mL three-necked round-bottomed flask. The flask was equipped a graphite rod (Φ 6 mm) anode and a platinum plate (1 cm x 1 cm) cathode and DMSO (5 mL) was added. Electrolysis was carried out at room temperature, which using a constant current of 10 mA in an argon atmosphere for 1.5 hours. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford **3**.

2.2 Two-step one-pot program using arylamines as starting materials



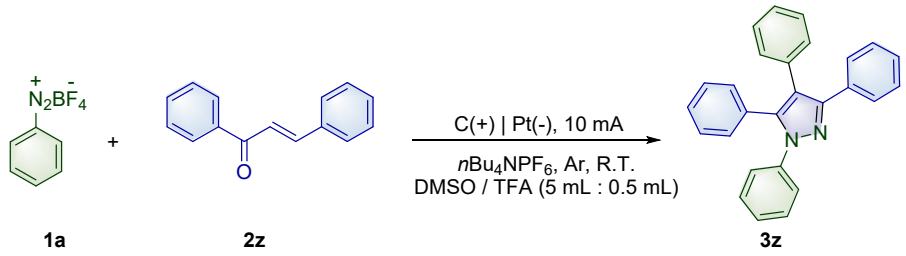
Firstly, the arylamines **4** (0.6 mmol, 1.0 equiv.), HBF_4 (48 wt% in H_2O, 0.1 mL), EtOH (0.5 mL), were placed in a 10 mL three-necked round-bottomed flask. The reaction mixture was cooled to 0 °C, tert-Butyl nitrite (0.9 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 0.5 hours. Secondly, enones **2** (1.8 mmol, 3 equiv.), nBu$_4$NPF$_6$ (0.3 mmol, 0.5 equiv.), TFA (0.5 mL), were placed in the three-necked round-bottomed flask. The flask was equipped a graphite rod (Φ 6 mm) anode and a platinum plate (1 cm x 1 cm) cathode and DMSO (5 mL) was added. Electrolysis was carried out at room temperature, which using a constant current of 10 mA in an argon atmosphere for 1.5 hours. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3×5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford **3**.

2.3 Substrates employed for the reaction



3. Other reaction attempts

3.1 Reaction attempts of chalcone

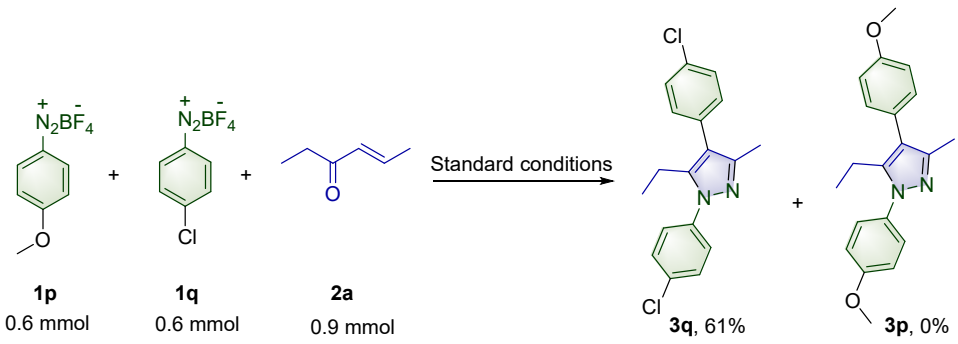


1a **2z** **3z**

Entry	Variation from standard conditions	Yield[b] (%)
1[a]	**None**	**0**
2	2 h instead of 1.5 h	0
3	60 °C instead of R.T.	0
4	Zn (-) instead of Pt (-)	0

[a]Standard conditions: undivided cell, graphite rod anode (∅ 6 mm), Pt plate cathode (1 cm × 1 cm), constant current = 10 mA, **1a** (0.6 mmol), **2z** (1.5 equiv.), nBu$_4$NPF$_6$ (0.5 equiv.), DMSO (5 mL), TFA (0.5 mL, 8.0 equiv. based on the amount of **2a**), Ar, R.T., 1.5 h.

3.2 Competitive reaction



1p 0.6 mmol **1q** 0.6 mmol **2a** 0.9 mmol

We used 0.3 mmol electron donating group functionalized aryl diazonium salts 1p and 0.3 mmol electron withdrawing group functionalized aryl diazonium salts **1q** and 4-Hexen-3-one (**2a**) under standard conditions, and finally only obtained the product **3q** corresponding to **1q**. As shown in the figure, we speculate that this may be due to the significantly lower reduction potential of 1q (-0.34 V) compared to 1p (-0.62 V), Therefore, the radicals generated by cathodic reduction of **1q** preferentially react with 4-Hexen-3-one (2a). Due to the low reduction potential and high activity of aryl radicals in the system (*Org. Chem. Front.*, 2024, **11**, 4318.), as well as the short half-life of aryl diazo radicals (*Chem. Rev.*, 1988, **88**, 765.; *J. Org. Chem.*, 2001, **66**, 1138.). The radicals generated by reducing **1p** were not captured in time and were directly quenched, resulting in only a single product of **3q** being obtained.

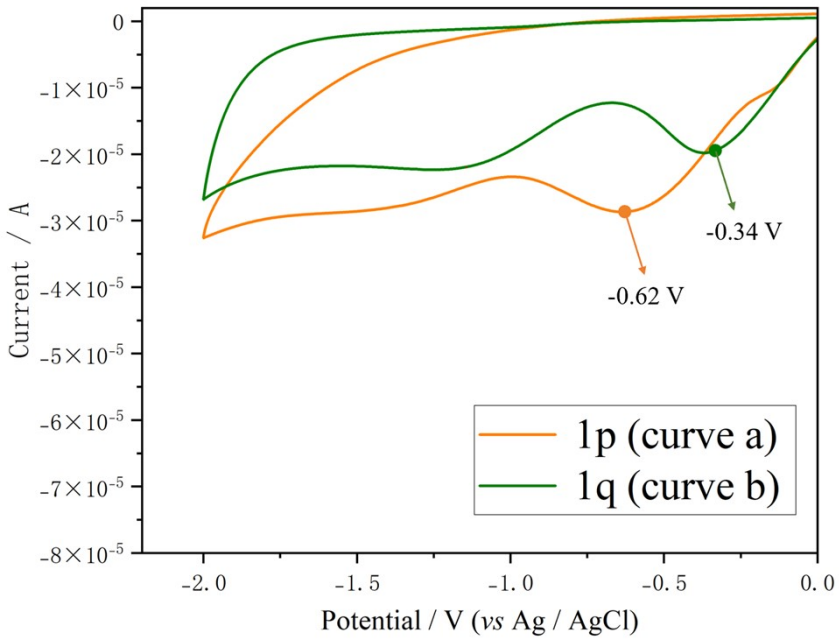


Figure S1. Cyclic voltammograms of 0.1 M nBu$_4$NPF$_6$ at room temperature, Pt disk and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate: (a) **1p** (10 mM) + DMSO (9 mL); (b) **1q** (10 mM) + DMSO (9 mL).

4. Procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three electrodes cell connected to a schlenk line at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was a Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. The cyclic voltammetry was given in Figure S1. 9.0 mL of DMSO containing 0.1 M nBu$_4$NPF$_6$ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to - 2.0 V. The results of cyclic voltammetry showed that the **1a** exhibited reduction potential at - 0.43V, as shown in Figure S1. In addition, after adding trifluoroacetic acid, the reduction potential slightly shifted positively to - 0.37 V, but the effect was not significant. It was proved that aryl diazonium salt **1a** was directly reduced on the anode.

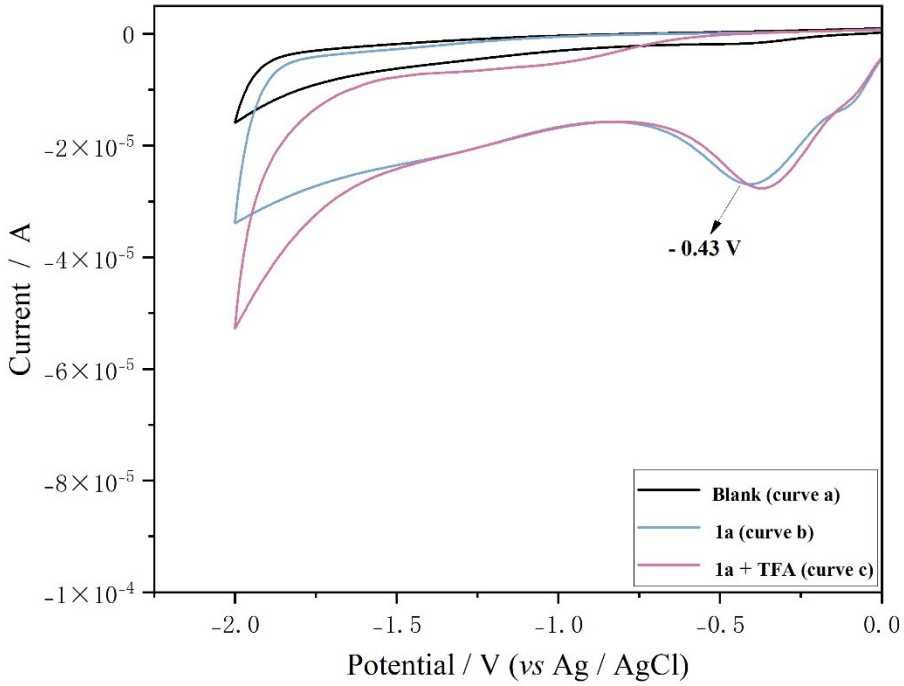


Figure S2. Cyclic voltammograms of 0.1 M nBu$_4$NPF$_6$ at room temperature, Pt disk and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate: (a) DMSO (9 mL); (b) **1a** (0.2 mmol) + DMSO (9 mL); (c) **1a** (10 mM) + DMSO (9 mL) + TFA (0.4 mmol).

Subsequently, we also investigated the reduction of **2a**, as shown in Figure S2. The reduction potential of **2a** was - 2.1 V, indicating that **2a** is difficult to reduce compared to **1a**. In order to further study the influence of the amount of trifluoroacetic acid on the reaction, we carried out more cyclic voltammetry experiments. When the amount of trifluoroacetic acid gradually increased from 2.0 equiv. to 8.0 equiv. (based on the amount of **2a**), and it was observed that the catalytic current of substrate **2a** also showed an increasing trend with the increase of TFA content, indicating that TFA has an activating effect on substrate **2a**. Therefore, we speculate that trifluoroacetic acid can form intermolecular hydrogen bonds with the carbonyl oxygen of **2a**, effectively activating **2a** (Scheme 5.) and better capturing transient aryl

diazo radicals for subsequent conversion.

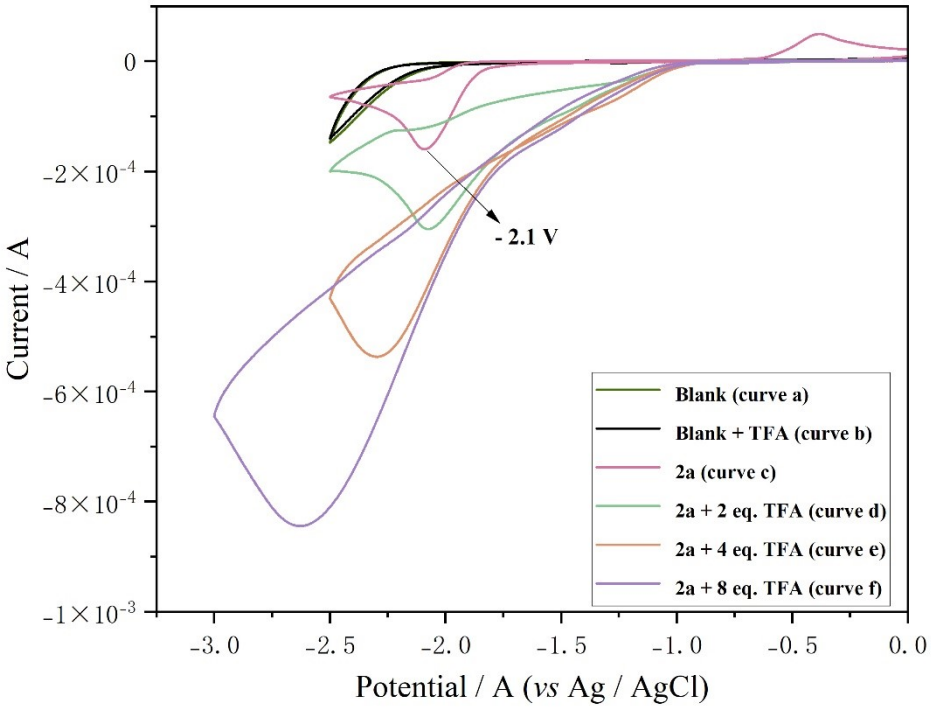
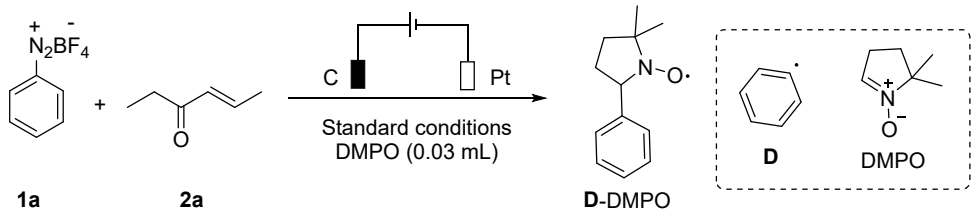


Figure S3. Cyclic voltammograms of 0.1 M nBu$_4$NPF$_6$ at room temperature, Pt disk and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate: (a) DMSO (9 mL); (b) TFA (0.2 mmol) + DMSO (9 mL); (c) **2a** (0.2 mmol, 1.0 equiv.) + DMSO (9 mL); (d) **2a** (0.2 mmol, 1.0 equiv.) + DMSO (9 mL) + TFA (0.4 mmol, 2.0 equiv.); (e) **2a** (0.2 mmol) + DMSO (9 mL) + TFA (0.8 mmol, 4.0 equiv.); (f) **2a** (0.2 mmol) + DMSO (9 mL) + TFA (1.6 mmol, 8.0 equiv.).

5. General procedure for the Electron Paramagnetic Resonance (EPR) experiment

The aryl diazonium salt **1a** (0.6 mmol, 1.0 equiv.) and 4-Hexen-3-one **2a** (0.9 mmol, 1.5 equiv.), nBu$_4$NPF$_6$ (0.5 equiv.), TFA (0.5 mL), were placed in a 10 mL three-necked round-bottomed flask. The flask was equipped a graphite rod (Φ 6 mm) anode and a platinum plate (1 cm x 1 cm) cathode and DMSO (5 mL) was added. Electrolysis was carried out at room temperature, which using a constant current of 10 mA in an argon atmosphere for 0.5 hours. Then the DMPO (30 μL) was added into the cell and reacted for 2 min. The mixture was put into a simple melting point tube for EPR test. EPR spectra was recorded at room temperature on Bruker A300 spectrometer. Typical spectrometer parameters were shown as follows, sweep width: 200.00 G; center field set: 3513.500 G; conversion time: 15.00 msec; time constant: 1.28 msec; sweep time: 15.36 sec; modulation amplitude: 1.00 G; microwave bridge frequeency: 9.85 GHz; receiver gain: 10×10^3; Number of X-Scans: 1. Phenyl radical trapped by DMPO was detected (g = 2.0065, A_N = 14.35 G, A_H = 20.99 G).



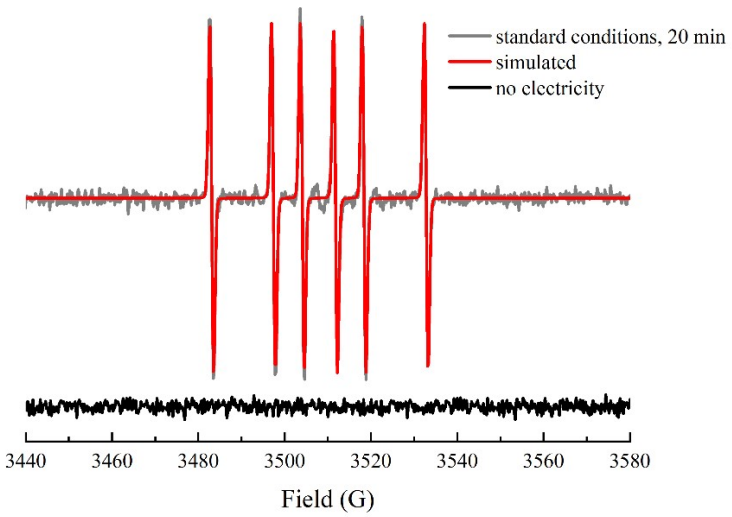
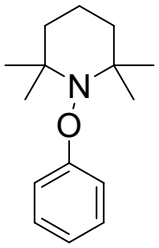


Figure S4. EPR experiment.

6. The HRMS spectra of compounds 5, 6, 8, 9, 11, 12 and intermediate C



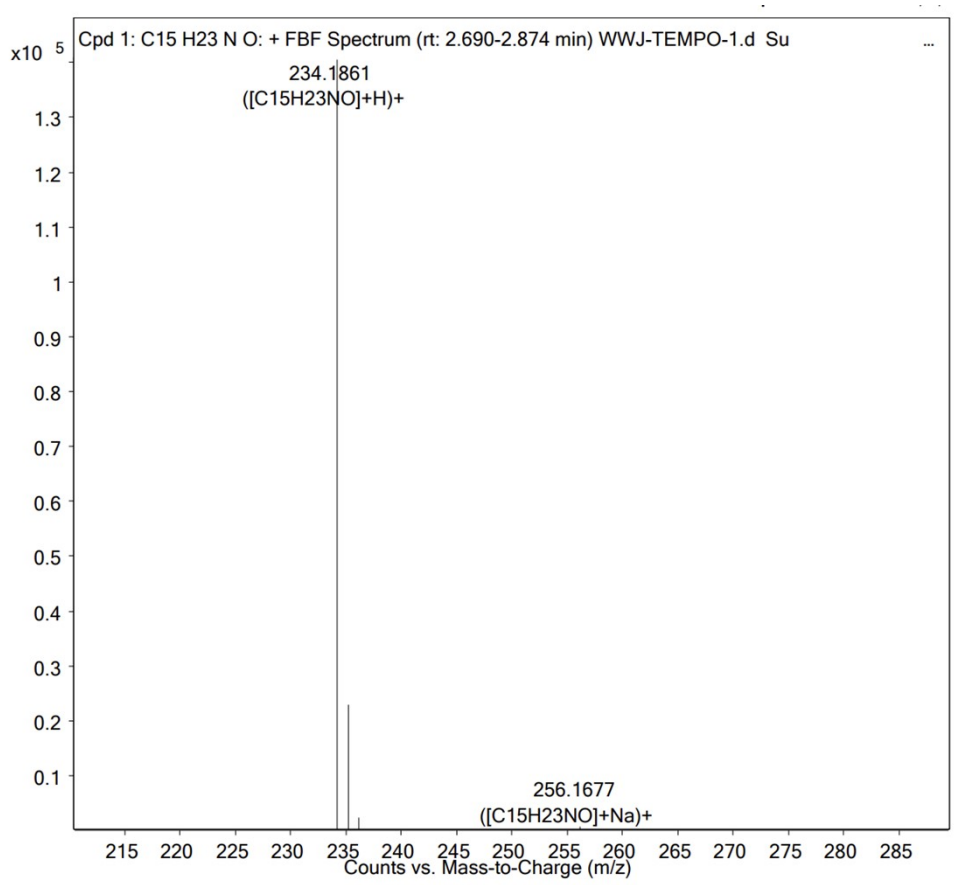


Figure S5 HRMS of compound **5**: calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1852, found 234.1861 (m/z) (ESI).

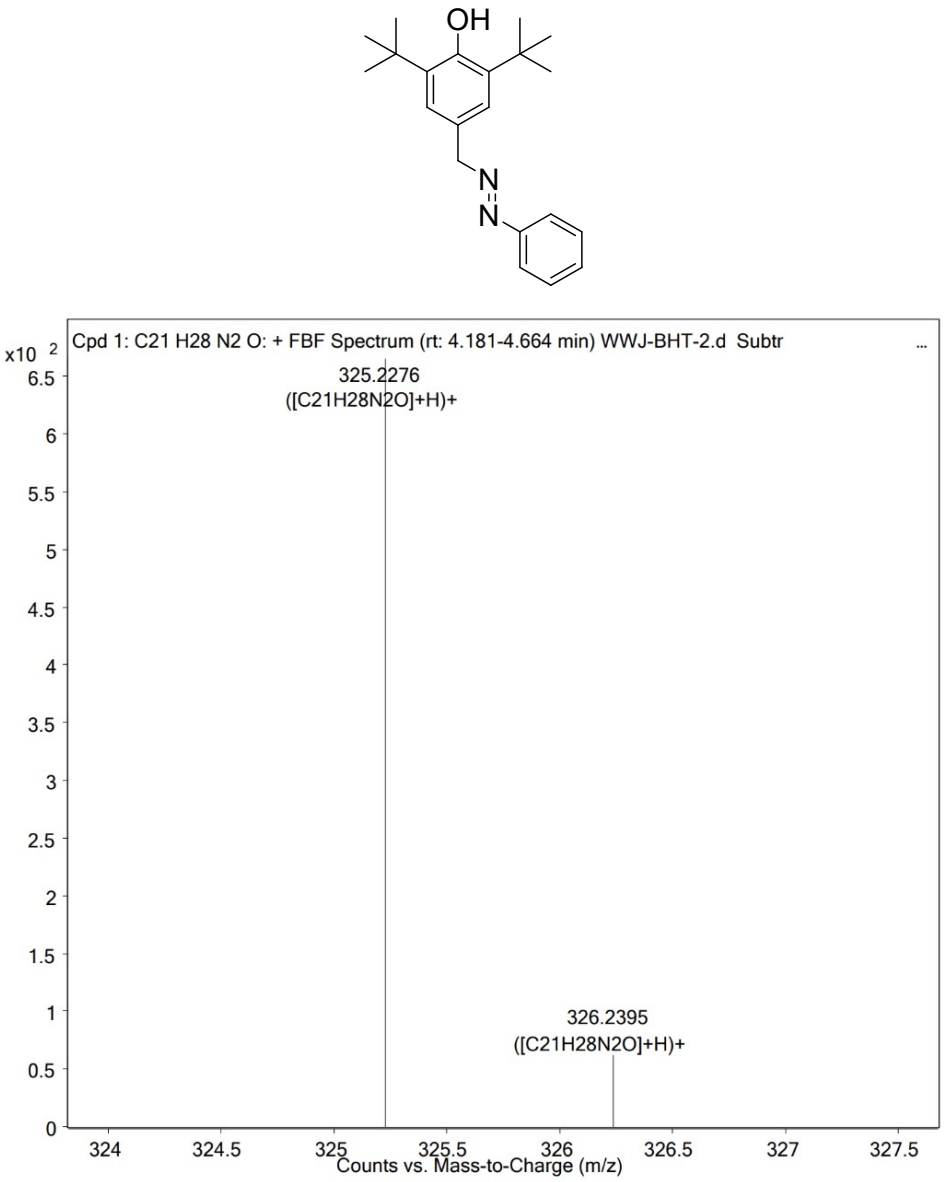


Figure S6 HRMS of compound **6**: calcd for $C_{21}H_{29}N_2O$ $[M+H]^+$ 325.2274, found 325.2276 (m/z) (ESI).

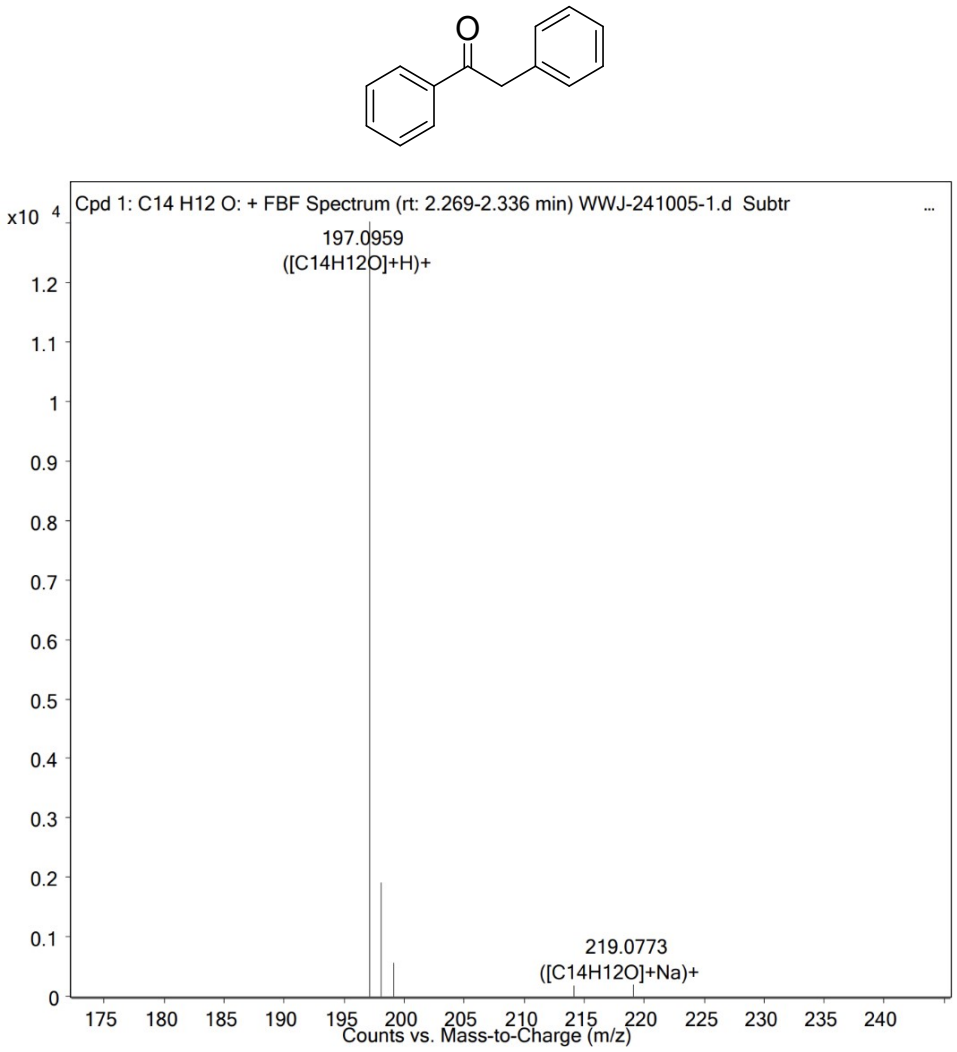


Figure S7 HRMS of compound **8**: calcd for $C_{14}H_{13}O$ $[M+H]^+$ 197.0961, found 197.0959 (m/z) (ESI).

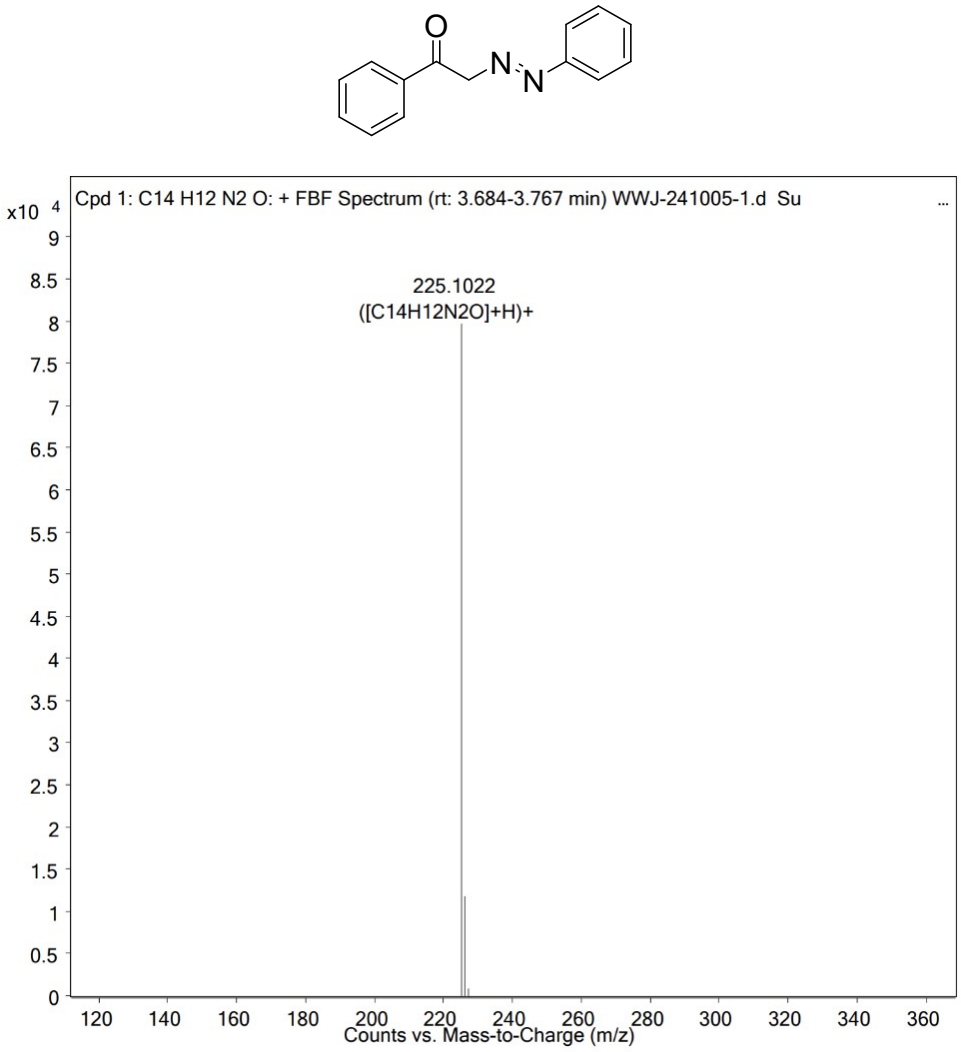


Figure S8 HRMS of compound **9**: calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1022, found 225.1022 (m/z) (ESI).

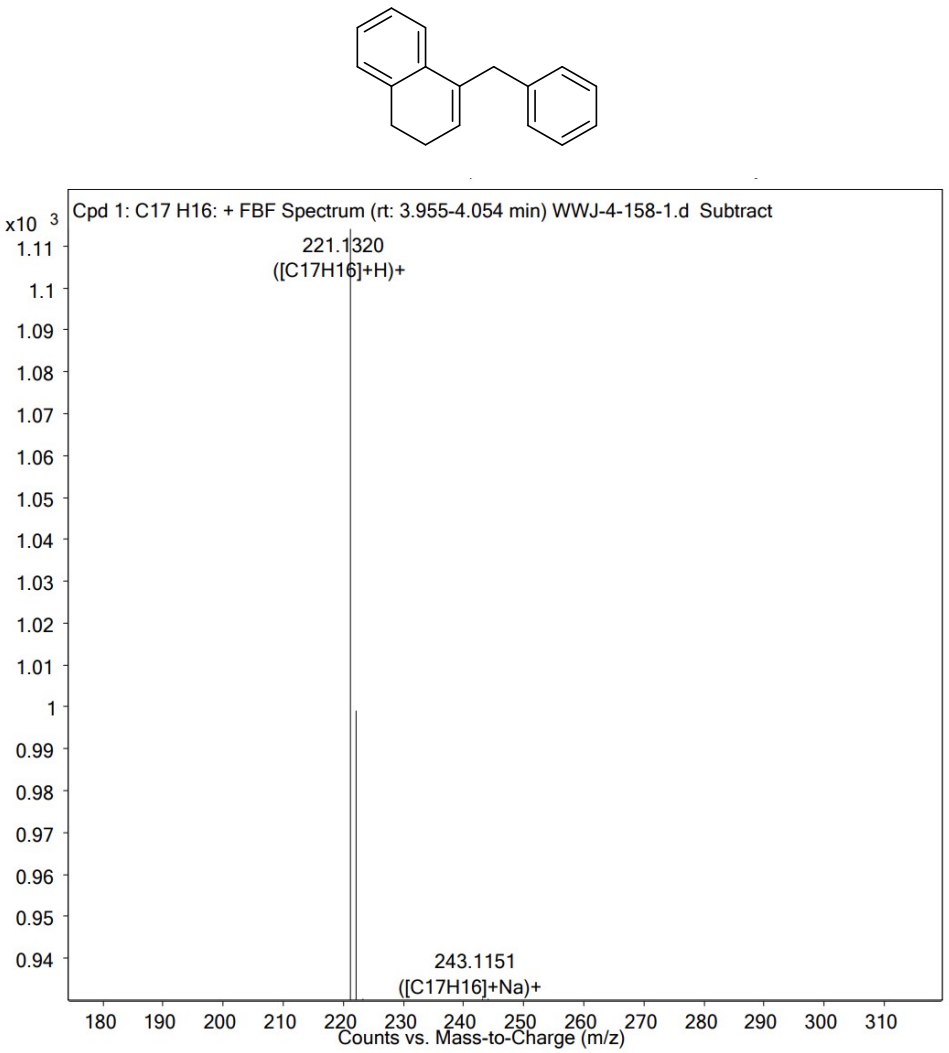
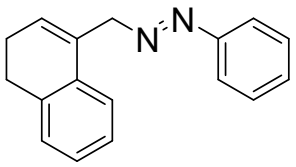


Figure S9 HRMS of compound **11**: calcd for $C_{17}H_{17}$ $[M+H]^+$ 221.1325, found 221.1320 (m/z) (ESI).



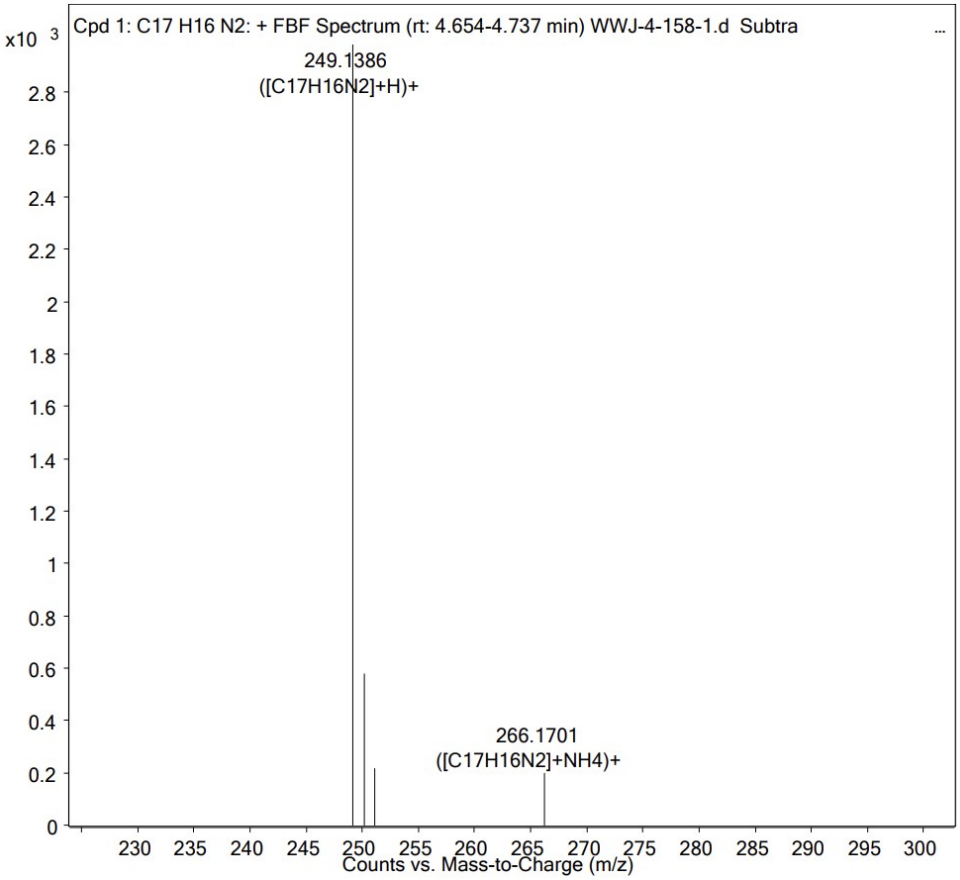
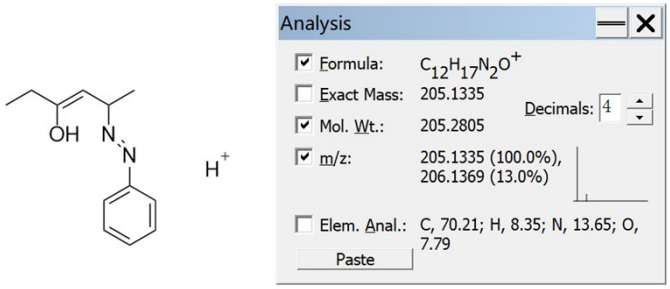


Figure S10 HRMS of compound **12**: calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386, found 249.1386(m/z) (ESI).



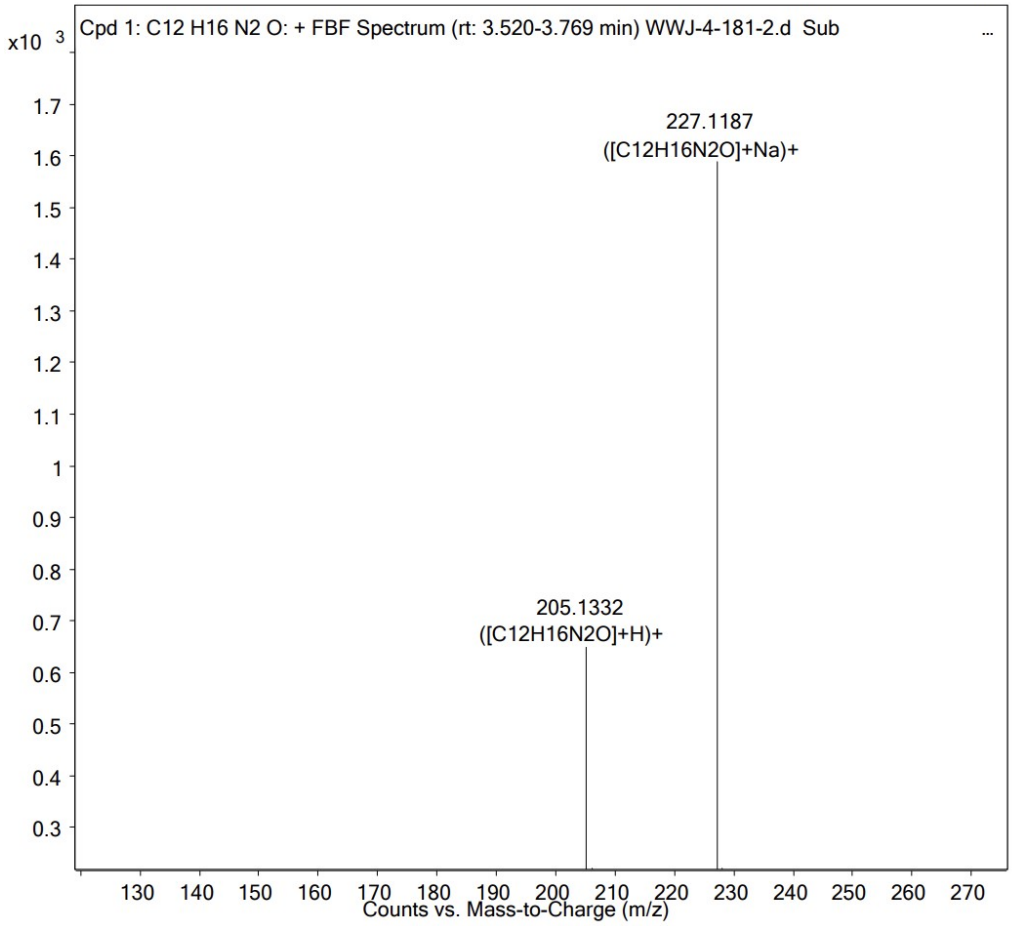
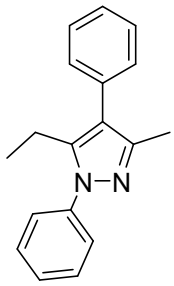
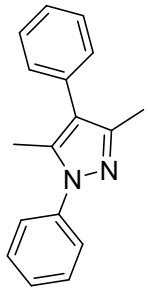


Figure S11 HRMS of intermediate **C** calcd for $C_{12}H_{17}N_2O$ $[M+H]^+$ 205.1335, found 205.1332 (m/z) (ESI)

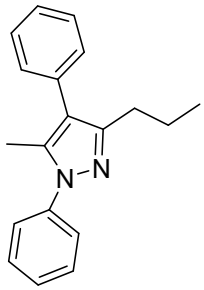
7. Characterization data of all products



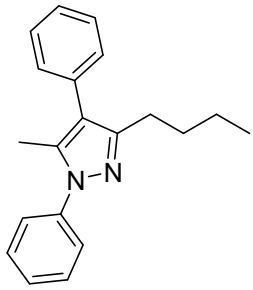
3-ethyl-5-methyl-1,4-diphenyl-1*H*-pyrazole (3a) yellow oil (78 %, 61.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 750-7.48 (m, 4H), 7.46-7.41 (m, 3H), 7.35-7.31 (m, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.20, 142.77, 139.94, 133.86, 129.85, 129.34, 128.62, 128.18, 126.82, 125.87, 120.43, 18.17, 13.83, 12.52. HRMS (m/z) (ESI): calcd for $C_{18}H_{19}N_2$ $[M+H]^+$ 263.1543, found 263.1550.



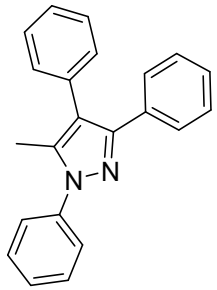
3,5-dimethyl-1,4-diphenyl-1*H*-pyrazole (3b) yellow oil (77 %, 57.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49-7.45 (m, 5H), 7.44-7.38 (m, 2H), 7.34-7.31 (m, 3H), 2.35 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.29, 140.00, 136.54, 133.92, 129.70, 129.22, 128.61, 127.60, 126.60, 125.12, 121.05, 12.79, 11.96. HRMS (m/z) (ESI): calcd for $C_{17}H_{17}N_2$ $[M+H]^+$ 249.1386, found 249.1392.



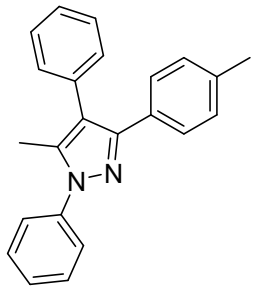
3-methyl-1,4-diphenyl-5-propyl-1*H*-pyrazole (3c) yellow oil (72 %, 59.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52-7.47 (m, 4H), 7.45-7.41 (m, 2H), 7.38-7.30 (m, 4H), 2.70-2.66 (m, 2H), 2.28 (s, 2H), 1.65-1.60 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.44, 139.99, 136.58, 134.02, 129.87, 129.21, 128.59, 127.56, 126.68, 125.14, 120.87, 29.04, 22.91, 14.27, 11.83. HRMS (m/z) (ESI): calcd for $C_{19}H_{21}N_2$ $[M+H]^+$ 277.1699, found 277.1690.



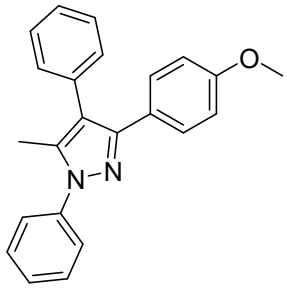
5-butyl-4-(cyclohexa-1,5-dien-1-yl)-3-methyl-1-phenyl-1*H*-pyrazole (3d) yellow oil (61 %, 53.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52-7.49 (m, 4H), 7.47-7.41 (m, 2H), 7.37-7.29 (m, 4H), 2.72-2.67 (m, 2H), 2.28 (s, 3H), 1.60-1.55 (m, 2H), 1.33 (d, *J* = 7.5 Hz, 2H), 0.85 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.53, 140.00, 136.32, 133.96, 129.74, 129.06, 128.44, 127.35, 126.50, 125.00, 120.68, 31.66, 26.63, 22.69, 13.87, 11.70. HRMS (m/z) (ESI): calcd for $C_{20}H_{22}N_2$ $[M+H]^+$ 290.1783, found 290.1778.



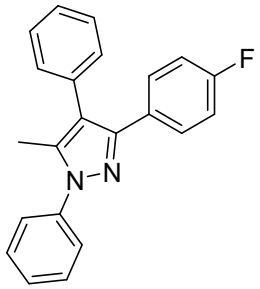
3-methyl-1,4,5-triphenyl-1*H*-pyrazole (3e) yellow oil (65 %, 60.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61-7.58 (m, 2H), 7.54-7.49 (m, 4H), 7.43-7.36 (m, 3H), 7.34-7.31 (m, 1H), 7.30-7.28 (m, 1H), 7.27-7.26 (m, 2H), 7.26-7.24 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.81, 140.05, 137.81, 133.99,133.39, 130.47, 129.28, 128.61, 128.27, 127.87, 127.61, 126.89, 125.29, 120.25, 11.85. HRMS (m/z) (ESI): calcd for $C_{22}H_{19}N_2$ $[M+H]^+$ 311.1543, found 311.1549.



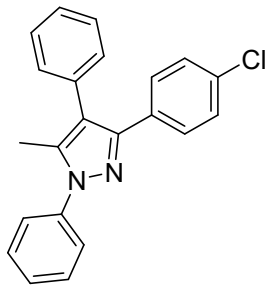
3-methyl-1,4-diphenyl-5-(p-tolyl)-1*H*-pyrazole (3f) yellow oil (66 %, 64.2 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60-7.58 (m, 2H), 7.52-7.48 (m, 2H), 7.40-7.36 (m, 5H), 7.34-7.30 (m, 1H), 7.29-2.27 (m, 2H), 7.08-7.06 (m, 2H), 2.32 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.82, 140.09, 137.71, 137.29, 134.14, 130.48, 129.25, 128.99, 128.58, 128.13, 127.78, 126.83, 125.28, 120.11, 21.39, 11.84. HRMS (m/z) (ESI): calcd for $C_{23}H_{21}N_2$ $[M+H]^+$ 325.1699, found 325.1670.



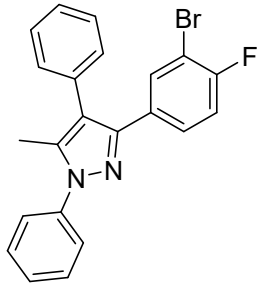
5-(4-methoxyphenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole (3g) yellow oil (65 %, 66.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60-7.57 (m, 2H), 7.52-7.48 (m, 2H), 7.45-7.42 (m, 2H), 7.41-7.37 (m, 3H), 7.33-7.31 (m, 1H), 7.29-7.27 (m, 2H), 6.81-6.78 (m, 2H), 3.78 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.23, 149.58, 140.10, 137.69, 134.15, 130.49, 129.48, 129.25, 128.60, 127.76, 126.83, 125.99, 125.25, 119.91, 113.71, 55.31, 11.86. HRMS (m/z) (ESI): calcd for $C_{23}H_{21}N_2O$ $[M+H]^+$ 341.1648, found 341.1658.



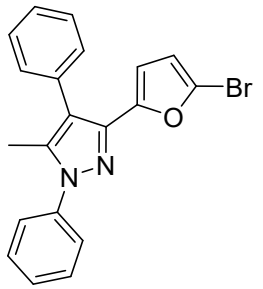
5-(4-fluorophenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole (3h) yellow oil (67 %, 66.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58-7.56 (m, 2H), 7.52-7.45 (m, 4H), 7.42-7.35 (m, 3H), 7.33-7.30 (m, 1H), 7.26-7.24 (m, 2H), 6.96-6.91 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.52 (d, J = 244.8 Hz, $^{1}J_{CF}$), 148.91, 139.96, 137.88, 133.79, 130.41, 129.92 (d, J = 8.0 Hz, $^{3}J_{CF}$), 129.53 (d, J = 3.1 Hz, $^{4}J_{CF}$), 129.30, 128.69, 127.93, 127.01, 125.24, 120.09, 115.21 (d, J = 21.4 Hz, $^{2}J_{CF}$), 11.81. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.64. HRMS (m/z) (ESI): calcd for $C_{22}H_{18}FN_2$ $[M+H]^+$ 329.1449, found 329.1456.



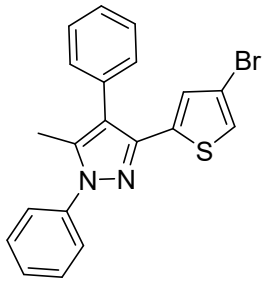
5-(4-chlorophenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole (3i) yellow oil (69 %, 71.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60-7.56 (m, 2H), 7.54-7.49 (m, 2H), 7.46-7.37 (m, 5H), 7.37-7.33 (m, 1H), 7.28-7.24 (m, 2H), 7.24-7.21 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.64, 139.93, 138.02, 133.69, 133.45, 131.94, 130.40, 129.47, 129.33, 128.74, 128.49, 128.01, 127.10, 125.26, 120.25, 11.79. HRMS (m/z) (ESI): calcd for $C_{22}H_{18}ClN_2$ $[M+H]^+$ 345.1153, found 345.1155.



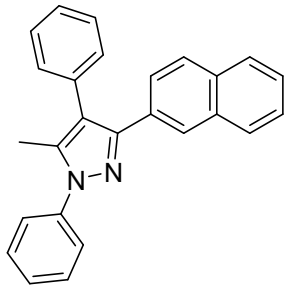
5-(3-bromo-4-fluorophenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole (3j) yellow oil (61 %, 74.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84-7.81 (m, 1H), 7.58-7.49 (m, 4H), 7.44-7.34 (m, 4H), 7.30-7.27 (m, 1H), 7.27-7.23 (m, 2H), 6.95 (t, *J* = 8.4 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.64 (d, *J* = 246.2 Hz, $^{1}J_{CF}$), 147.50, 139.82, 138.13, 133.37, 133.03, 131.10 (d, *J* = 3.8 Hz, $^{4}J_{CF}$), 130.36, 129.36, 128.82, 128.73 (d, *J* = 7.1 Hz, $^{3}J_{CF}$), 128.13, 127.28, 125.26, 120.23, 116.11 (d, *J* = 22.3 Hz, $^{2}J_{CF}$), 108.97 (d, *J* = 20.8 Hz, $^{2}J_{CF}$), 11.74. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.16. HRMS (m/z) (ESI): calcd for $C_{22}H_{17}BrFN_2$ $[M+H]^+$ 407.0554, found 407.0550.



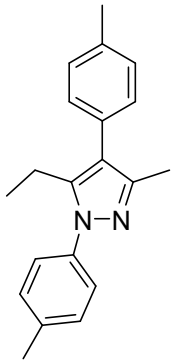
5-(5-bromofuran-2-yl)-3-methyl-1,4-diphenyl-1*H*-pyrazole (3k) yellow oil (63 %, 71.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56-7.48 (m, 4H), 7.44-7.41 (m, 3H), 7.39-7.34 (m, 3H), 6.22 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.14, 140.92, 139.72, 137.98, 132.98, 130.48, 129.29, 128.65, 128.21, 127.56, 125.50, 121.68, 119.70, 112.80, 110.54, 11.47. HRMS (m/z) (ESI): calcd for $C_{20}H_{16}BrN_2O$ $[M+H]^+$ 378.0368, found 378.0378.



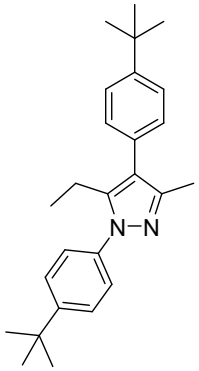
5-(4-bromothiophen-2-yl)-3-methyl-1,4-diphenyl-1*H*-pyrazole (3l) yellow oil (55 %, 65.2 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56-7.54 (m, 2H), 7.52-7.50 (m, 2H), 7.47-7.44 (m, 2H), 7.43-7.39 (m, 2H), 7.36-7.34 (m, 2H), 7.06 (d, *J* = 1.2 Hz, 1H), 6.83 (d, *J* = 0.8 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.51, 139.67, 138.38, 137.38, 132.89, 130.65, 129.34, 128.84, 128.15, 127.79, 127.41, 125.26, 122.06, 120.05, 109.70, 11.59. HRMS (m/z) (ESI): calcd for $C_{20}H_{15}BrN_2NaS$ $[M+Na]^+$ 417.0032, found 417.0040.



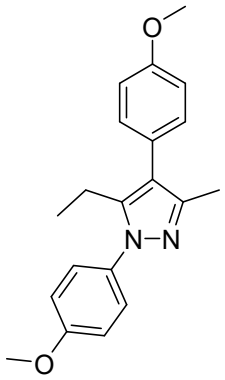
3-methyl-5-(naphthalen-2-yl)-1,4-diphenyl-1*H*-pyrazole (3m) yellow oil (62 %, 67.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02-8.01 (m, 1H), 7.79-7.77 (m, 1H), 7.74-7.69 (m, 2H), 7.65-7.62 (m, 3H), 7.56-7.51 (m, 2H), 7.45-7.40 (m, 3H), 7.40-7.36 (m, 2H), 7.37-7.31 (m, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.69, 140.06, 137.95, 133.98, 133.47, 132.91, 130.92, 130.51, 129.32, 128.65, 128.42, 127.94, 127.69, 127.10, 126.98, 126.46, 125.94, 125.92, 125.34, 120.49, 11.84. HRMS (m/z) (ESI): calcd for $C_{26}H_{21}N_2$ $[M+H]^+$ 361.1699, found 361.1697.



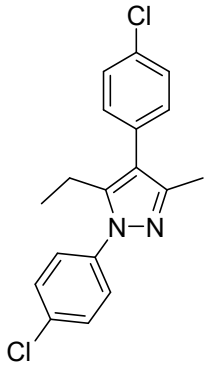
3-ethyl-5-methyl-1,4-di-*p*-tolyl-1*H*-pyrazole (3n) yellow oil (75 %, 65.3 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36-7.33 (m, 2H), 7.28-7.25 (m 3H), 7.23-7.19 (m, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.41 (d, *J* = 4.8 Hz, 6H), 2.28 (s, 3H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.05, 142.51, 137.90, 137.76, 136.27, 131.12, 129.81, 129.70, 129.30, 125.67, 119.98, 21.35, 21.30, 18.16, 13.90, 12.58. HRMS (m/z) (ESI): calcd for $C_{20}H_{23}N_2$ $[M+H]^+$ 291.1856, found 291.1857.



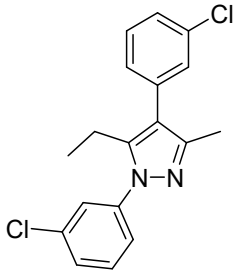
1,4-bis(4-(*tert*-butyl)phenyl)-3-ethyl-5-methyl-1*H*-pyrazole (3o) yellow oil (71 %, 79.8 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50-7.47 (m, 2H), 7.47-7.43 (m, 2H), 7.41-7.38 (m, 2H), 7.28-7.25 (m, 2H), 2.73 (q, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.38 (s, 9H), 1.37 (s, 9H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.05, 149.31, 147.08, 142.51, 137.69, 131.08, 129.34, 126.12, 125.42, 125.37, 119.87, 34.82, 34.66, 31.55, 31.49, 18.18, 14.06, 12.69. HRMS (m/z) (ESI): calcd for $C_{26}H_{34}N_2Na$ $[M+Na]^+$ 397.2614, found 397.2621.



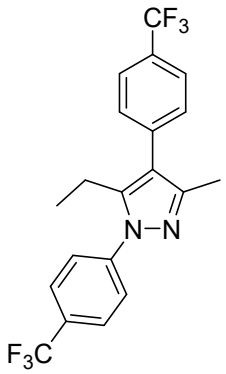
3-ethyl-1,4-bis(4-methoxyphenyl)-5-methyl-1*H*-pyrazole (3p) yellow oil (75 %, 72.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38-7.35 (m, 2H), 7.24-7.22 (m, 2H), 6.98-6.95 (m, 4H), 3.86 (s, 6H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.35, 158.49, 146.87, 142.76, 133.15, 130.89, 127.31, 126.31, 119.50, 114.37, 114.05, 55.69, 55.41, 18.13, 13.89, 12.48. HRMS (m/z) (ESI): calcd for $C_{20}H_{23}N_2O_2$ $[M+H]^+$ 323.1754 found 323.1764.



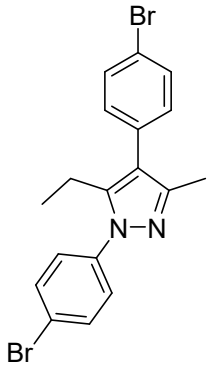
1,4-bis(4-chlorophenyl)-3-ethyl-5-methyl-1*H*-pyrazole (3q) yellow oil (67 %, 66.6 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50-7.47 (m, 2H), 7.45-7.42 (m, 4H), 7.30-7.25 (m, 2H), 2.71 (q, *J* = 7.5 Hz, 2H), 2.28 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.60, 142.62, 138.66, 133.85, 132.85, 132.32, 131.06, 129.50, 128.88, 126.85, 119.61, 18.14, 13.81, 12.49. HRMS (m/z) (ESI): calcd for $C_{18}H_{17}Cl_2N_2$ $[M+H]^+$ 331.0763 found 331.0770.



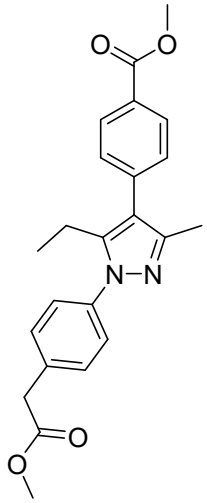
1,4-bis(3-chlorophenyl)-3-ethyl-5-methyl-1*H*-pyrazole (3r) yellow oil (61 %, 60.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.45-7.38 (m, 2H), 7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.19 (m, 1H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.78, 142.74, 141.14, 135.71, 134.99, 134.44, 130.27, 129.90, 129.76, 128.23, 128.01, 127.06, 125.99, 123.60, 119.67, 18.16, 13.84, 12.51. HRMS (m/z) (ESI): calcd for $C_{18}H_{17}Cl_2N_2$ $[M+H]^+$ 331.0763 found 331.0771.



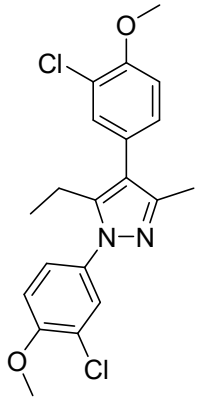
3-ethyl-5-methyl-1,4-bis(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (3s) yellow oil (65 %, 77.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77-7.75 (m, 2H), 7.71-7.69 (m, 2H), 7.64-7.62 (m, 2H), 7.44-7.42 (m, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.20, 142.91, 137.55, 130.03, 130.01 (d, *J* = 32.7 Hz, $^{2}J_{CF}$), 129.18 (d, *J* = 32.2 Hz, $^{2}J_{CF}$), 126.62 (d, *J* = 3.8 Hz, $^{3}J_{CF}$), 125.68 (d, *J* = 3.9 Hz, $^{3}J_{CF}$), 125.49, 123.95 (d, *J* = 271.0 Hz, $^{1}J_{CF}$),123.32, 120.19, 18.25, 13.83, 12.55. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.43, -62.46. HRMS (m/z) (ESI): calcd for $C_{20}H_{17}F_6N_2$ $[M+H]^+$ 399.1290 found 399.1297.



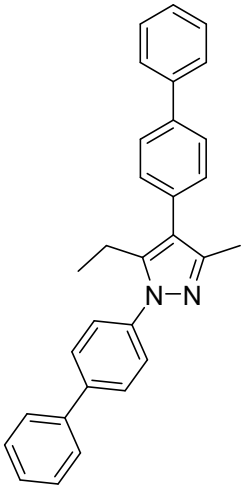
1,4-bis(4-bromophenyl)-5-ethyl-3-methyl-1*H*-pyrazole (3t) yellow oil (67 %, 84.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62-7.59 (m, 2H), 7.57-7.54 (m, 2H), 7.36-7.33 (m, 2H), 7.18-7.16 (m, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.25 (s, 3H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.59, 142.59, 139.07, 132.73, 132.50, 131.84, 131.40, 127.12, 121.82, 120.99, 119.68, 18.14, 13.81, 12.48. HRMS (m/z) (ESI): calcd for $C_{18}H_{16}Br_2NaN_2$ $[M+Na]^+$ 442.9552 found 442.9557.



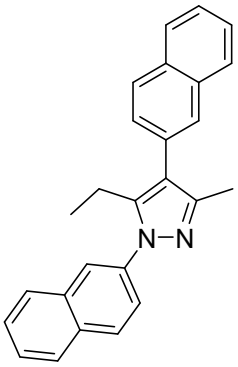
methyl 4-(5-ethyl-1-(4-(2-methoxy-2-oxoethyl)phenyl)-3-methyl-1*H*-pyrazol-4-yl)benzoate (3u) yellow oil (62 %, 73.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18-7.15 (m, 2H), 8.12-8.09 (m, 2H), 7.58-7.56 (m, 2H), 7.40-7.37 (m, 2H), 3.95 (d, *J* = 2.8 Hz, 6H), 2.78 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.11, 166.45, 148.13, 143.760, 142.82, 138.71, 130.86, 129.97, 129.65, 129.37, 128.61, 124.90, 120.49, 52.48, 52.30, 18.32, 13.70, 12.64. HRMS (m/z) (ESI): calcd for $C_{23}H_{24}N_2NaO_4$ $[M+Na]^+$ 415.1628 found 415.1619.



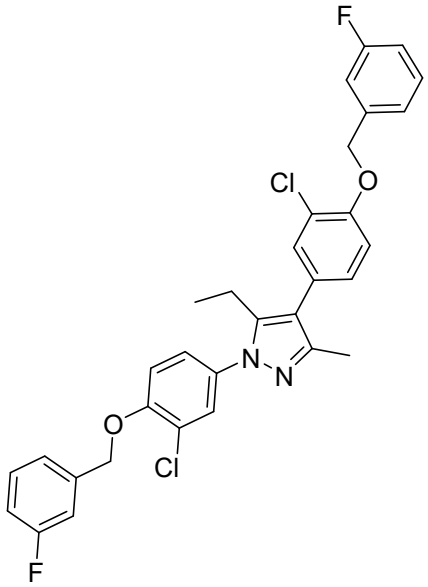
1,4-bis(3-chloro-4-methoxyphenyl)-5-ethyl-3-methyl-1*H*-pyrazole (3v) yellow oil (67 %, 78.6 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 2.5 Hz, 1H), 7.34-7.30 (m, 2H), 7.16-7.14 (m, 1H), 7.10-6.98 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 2.64 (q, *J* = 7.5 Hz, 2H), 2.24 (s, 3H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.98, 154.00, 147.32, 142.90, 133.21, 131.43, 129.15, 128.05, 127.10, 125.26, 122.91, 122.49, 118.80, 112.22, 111.96, 56.56, 56.33, 18.08, 13.88, 12.38. HRMS (m/z) (ESI): calcd for $C_{20}H_{21}Cl_2N_2O_2$ $[M+H]^+$ 391.0975 found 391.0979.



1,4-di([1,1'-biphenyl]-4-yl)-5-ethyl-3-methyl-1*H*-pyrazole (3w) yellow oil (70 %, 87.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75-7.63 (m, 8H), 7.59-7.55 (m, 2H), 7.50-7.45 (m, 4H), 7.43-7.37 (m, 4H), 2.82 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.50, 142.67, 140.94, 140.87, 140.28, 139.48, 139.38, 133.07, 130.16, 129.03, 128.95, 127.94, 127.79, 127.41, 127.30, 127.27, 127.16, 125.95, 120.08, 18.31, 13.99, 12.70. HRMS (m/z) (ESI): calcd for $C_{30}H_{27}N_2$ $[M+H]^+$ 415.2169 found 415.2160.



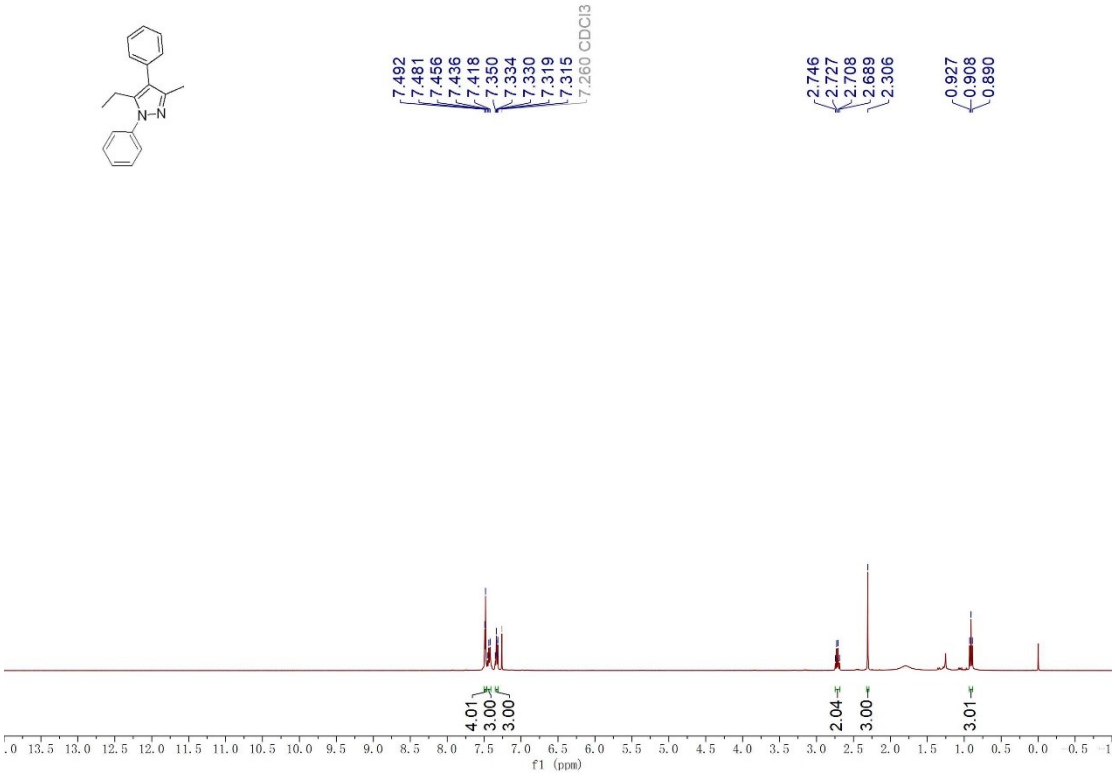
5-ethyl-3-methyl-1,4-di(naphthalen-2-yl)-1*H*-pyrazole (3x) yellow oil (60 %, 65.2 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80-7.97 (m, 2H), 7.94-7.87 (m, 5H), 7.82-7.80 (m, 1H), 7.67-7.64 (m, 1H), 7.57-7.49 (m, 5H), 2.85 (q, *J* = 7.6 Hz, 2H), 2.38 (s, 3H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.68, 143.27, 133.69, 133.44, 132.73, 132.37, 129.38, 128.48, 128.24, 128.34, 128.21, 127.99, 127.87, 127.01, 126.76, 126.37, 126.00, 124.06, 124.00, 120.56, 18.40, 13.94, 12.65. HRMS (m/z) (ESI): calcd for $C_{26}H_{23}N_2$ $[M+H]^+$ 363.1856 found 363.1851.

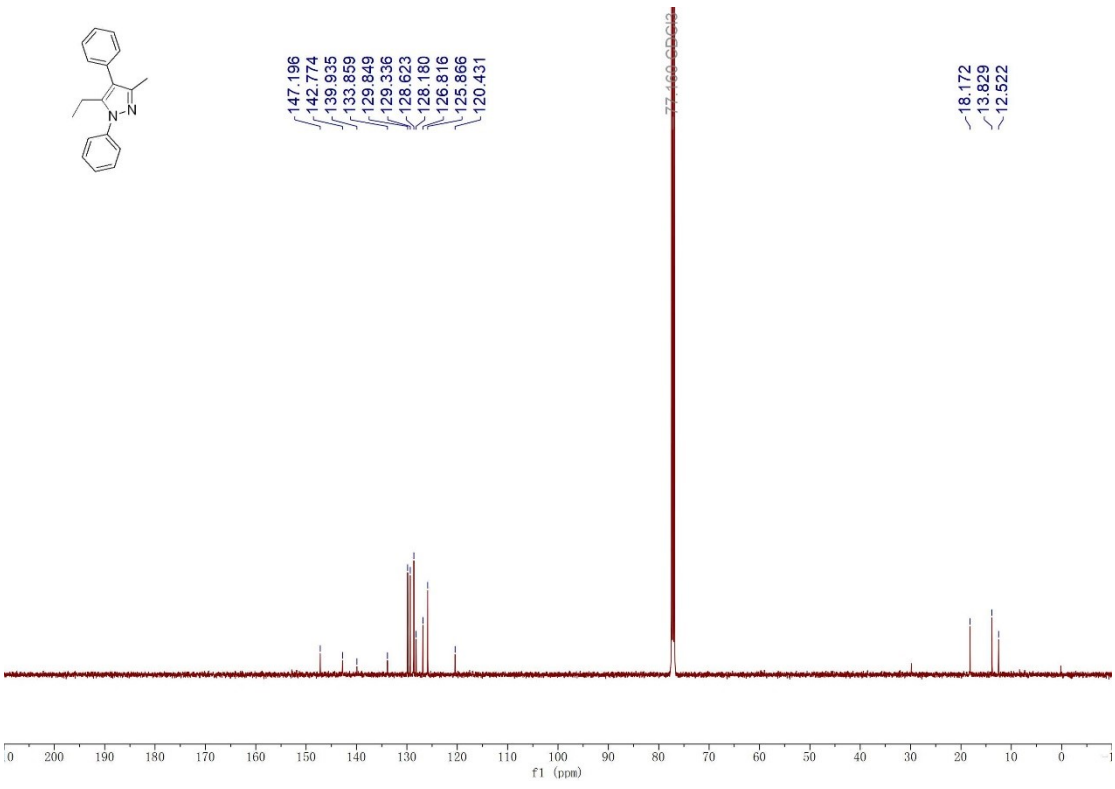


1,4-bis(3-chloro-4-((3-fluorobenzyl)oxy)phenyl)-5-ethyl-3-methyl-1*H*-pyrazole (3y) yellow oil (52 %, 90.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 2.4 Hz, 1H), 7.41 -7.32 (m, 4H), 7.32-7.26 (m, 2H), 7.25-7.20 (m, 4H), 7.13-7.10 (m, 1H), 7.06-6.99 (m, 5H), 5.20 (s, 2H), 5.19 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.25 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.17 (d, *J* = 245.5 Hz, $^{1}J_{CF}$), 154.14, 153.13, 147.25, 143.42, 139.22, 139.14, 138.68, 138.60, 132.86, 131.59, 130.43 (d, *J* = 8.2 Hz, $^{2}J_{CF}$), 130.37 (d, *J* = 8.0 Hz, $^{2}J_{CF}$), 129.10, 128.25, 127.16, 125.40, 123.85, 123.43, 122.58, 122.55, 122.51, 118.90, 115.25 (d, *J* = 20.9 Hz, $^{3}J_{CF}$), 115.10 (d, *J* = 20.9 Hz, $^{3}J_{CF}$), 114.23, 114.08, 114.01, 113.86, 70.41, 70.23, 18.02, 13.82, 12.08. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.42, -112.55. HRMS (m/z) (ESI): calcd for $C_{32}H_{27}Cl_2F_2N_2O_2$ $[M+H]^+$ 579.1412 found 579.1417.

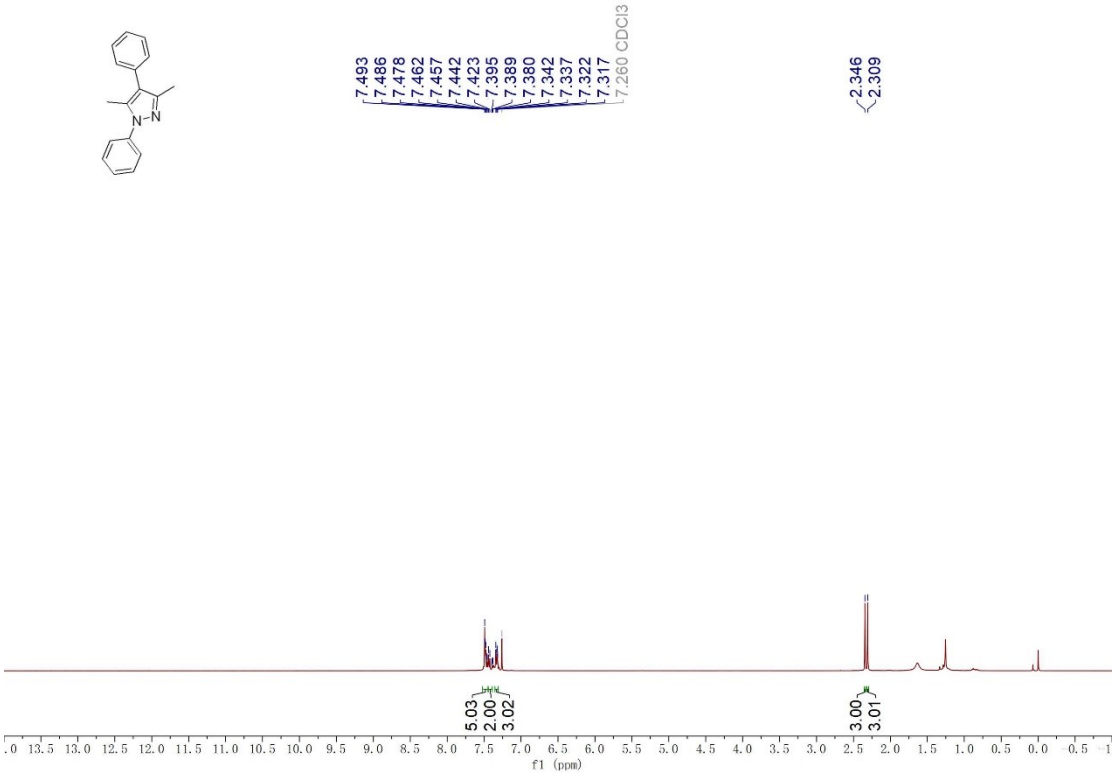
8. Copies of ^{13}C and ^{1}H NMR spectra of all products

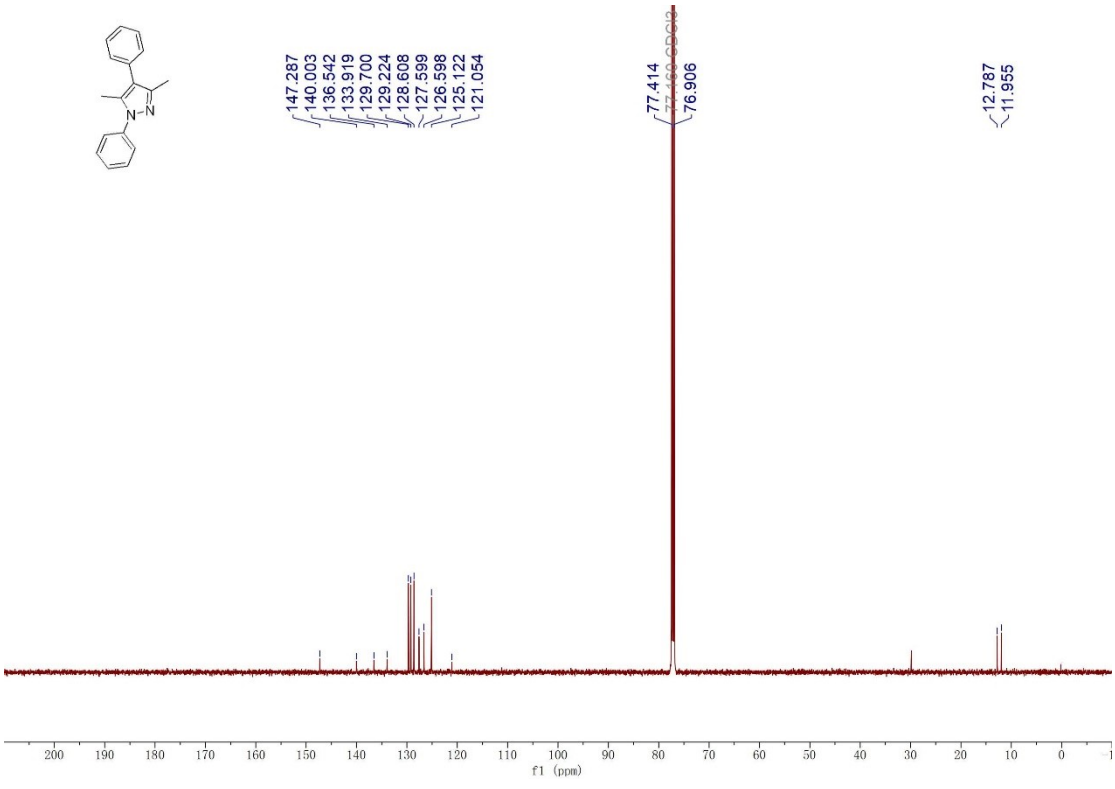
3-ethyl-5-methyl-1,4-diphenyl-1*H*-pyrazole **(3a)**



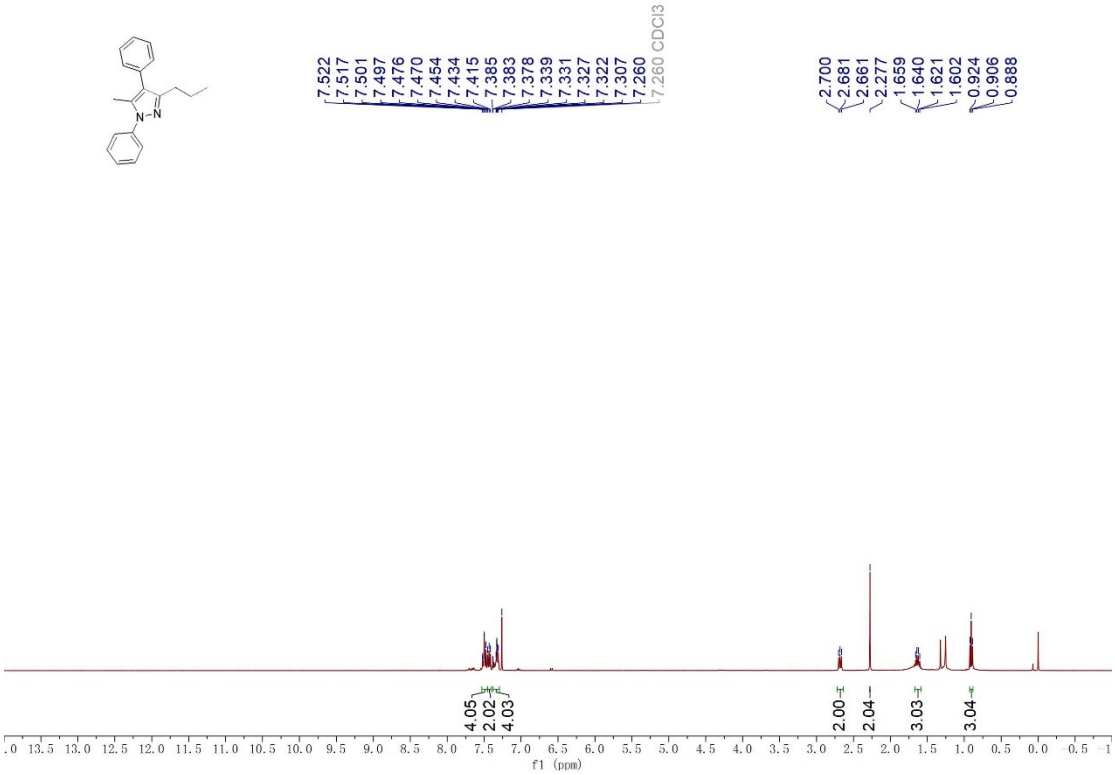


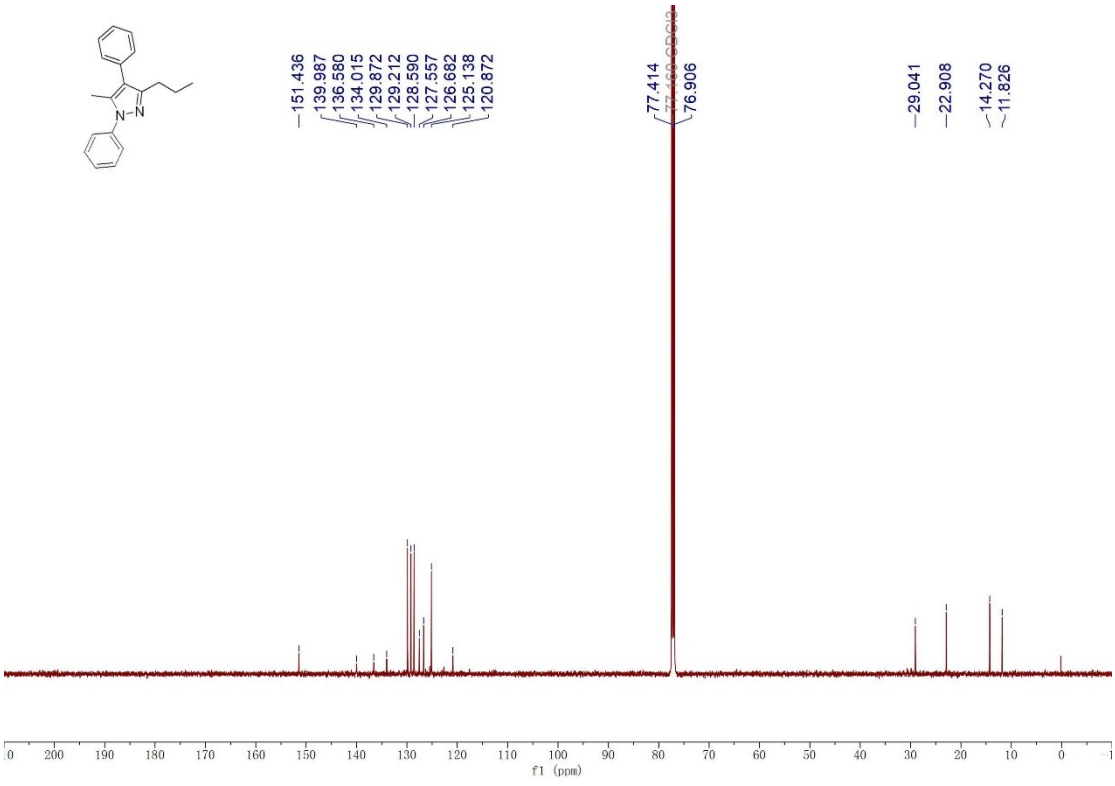
3,5-dimethyl-1,4-diphenyl-1*H*-pyrazole **(3b)**



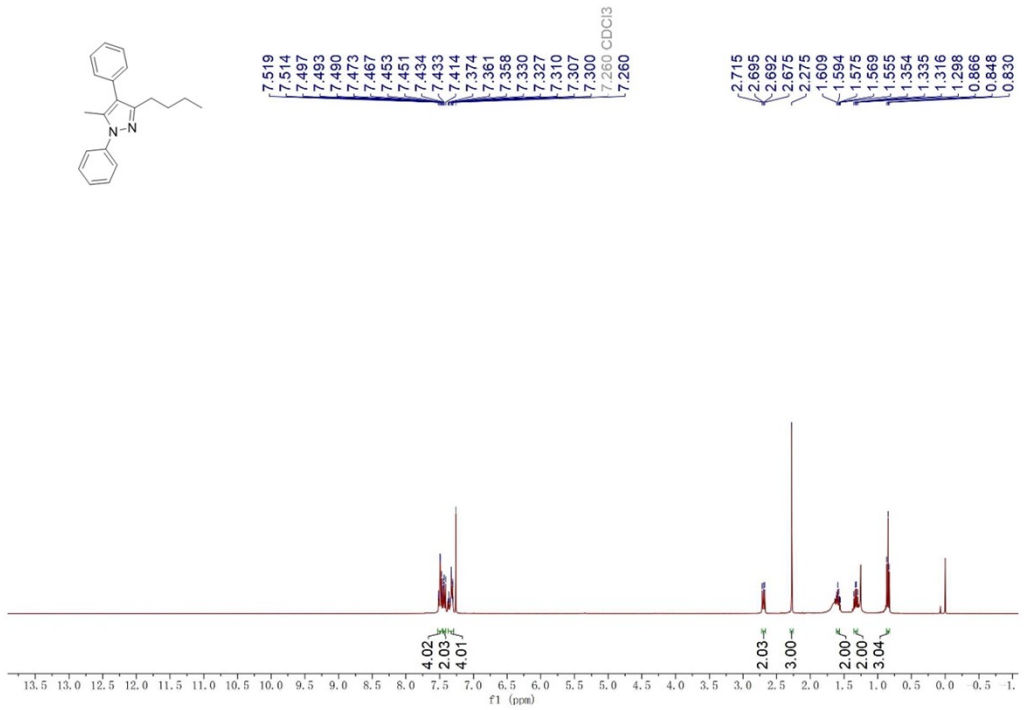


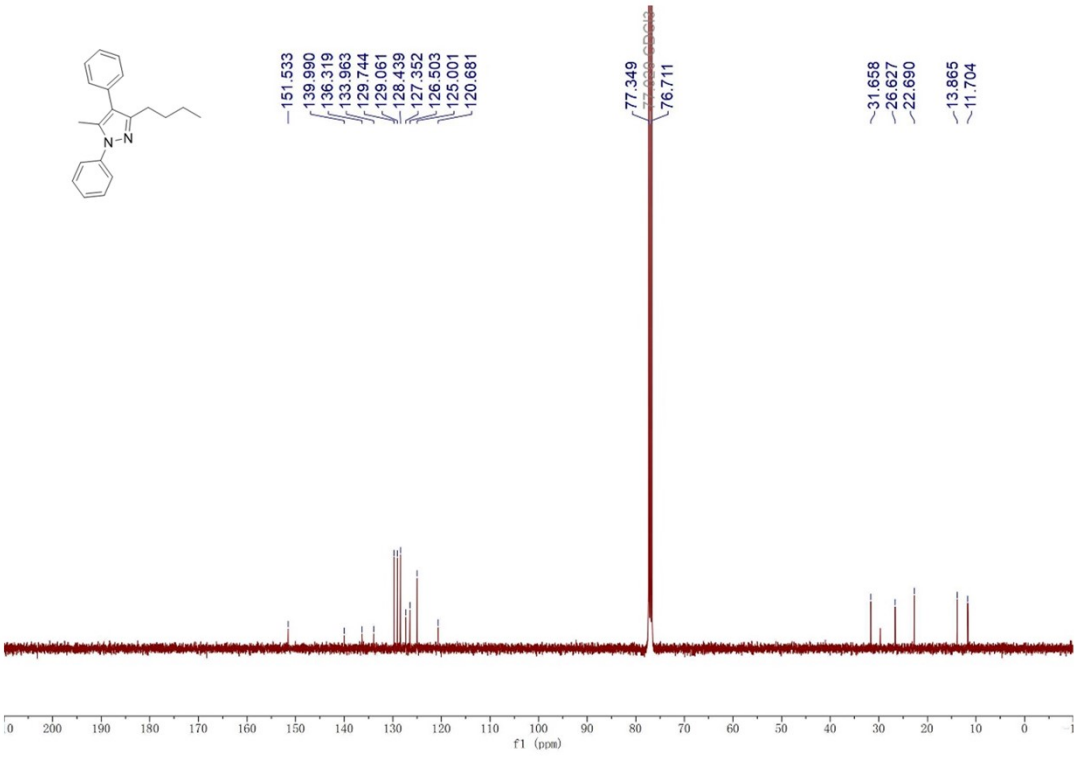
3-methyl-1,4-diphenyl-5-propyl-1*H*-pyrazole **(3c)**



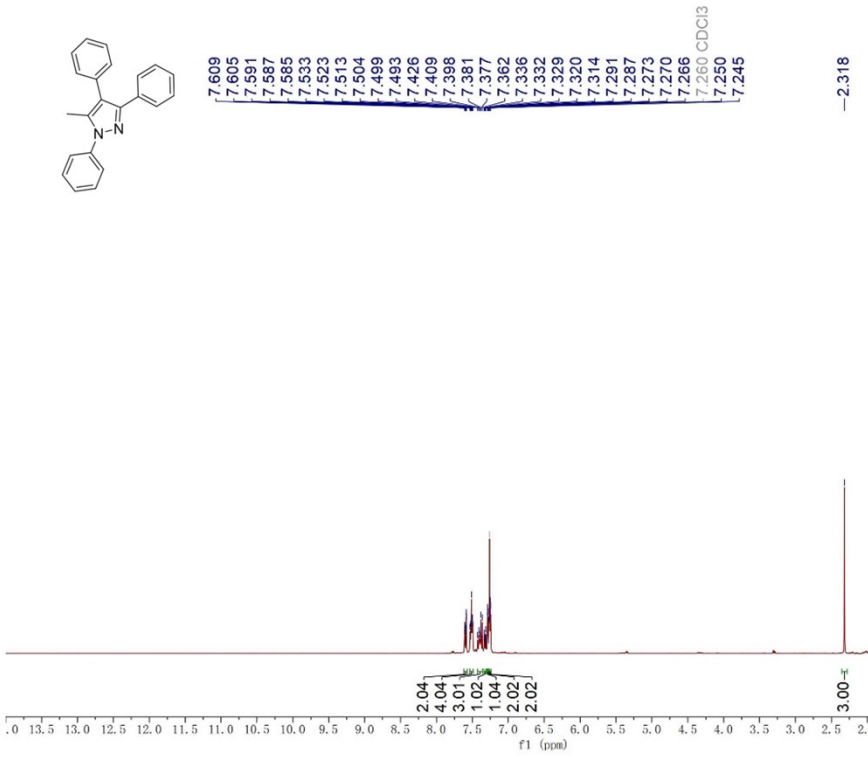


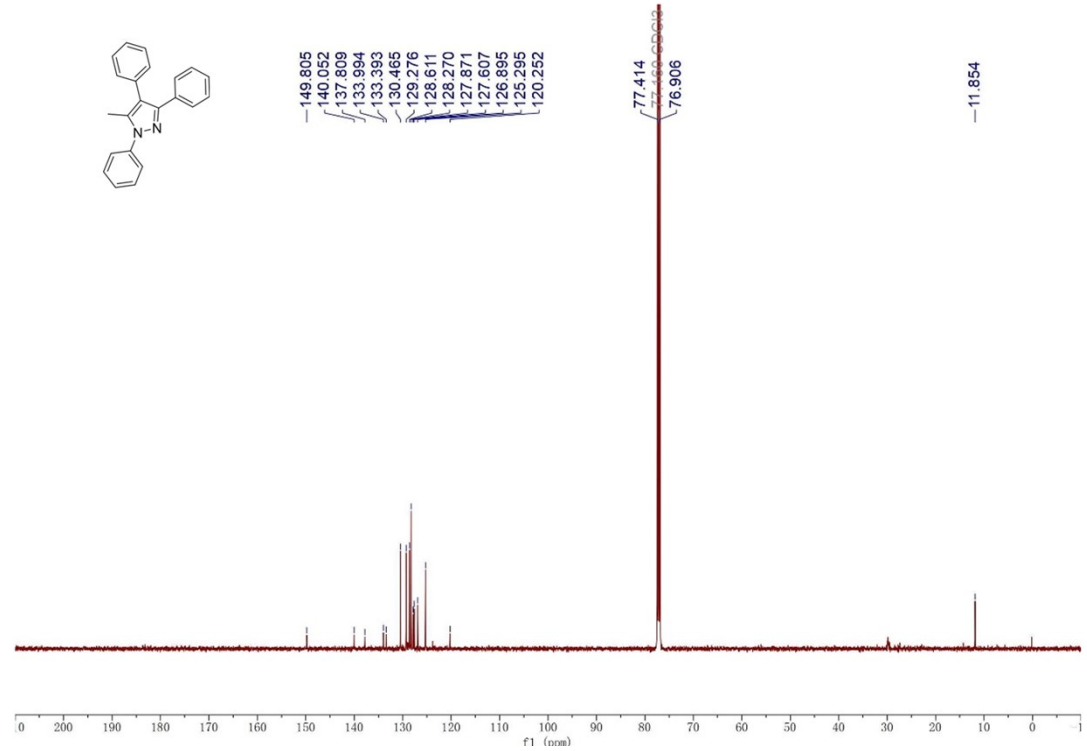
5-butyl-4-(cyclohexa-1,5-dien-1-yl)-3-methyl-1-phenyl-1*H*-pyrazole **(3d)**



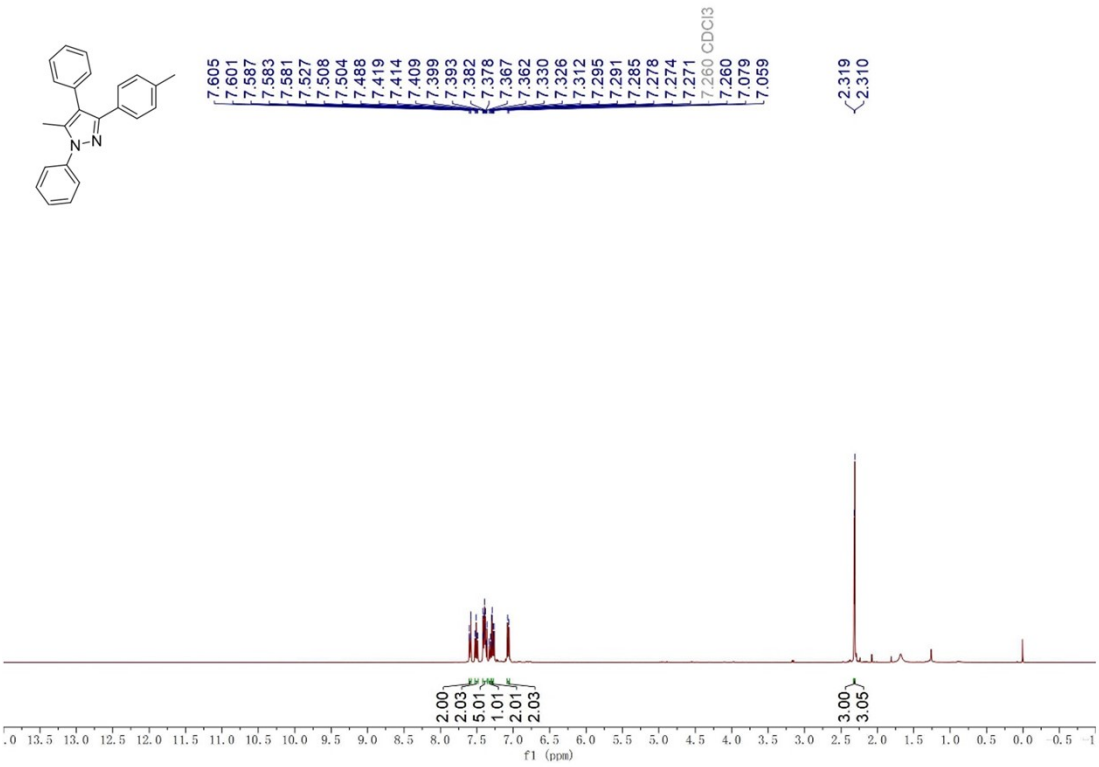


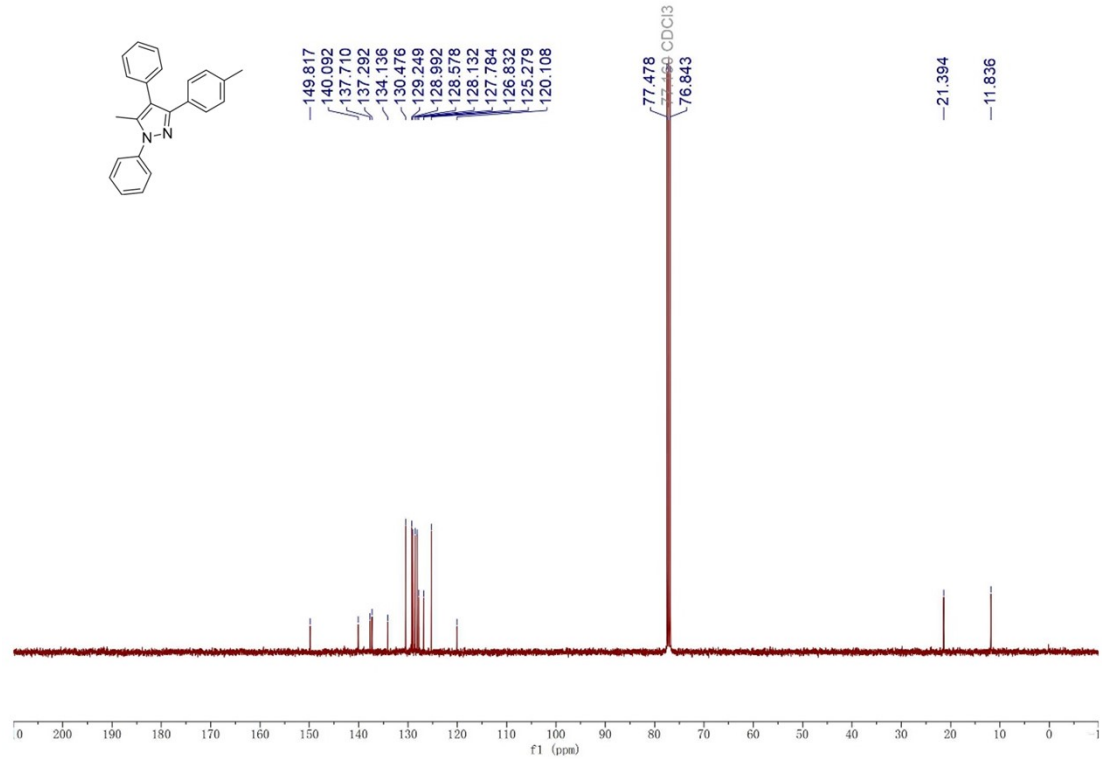
3-methyl-1,4,5-triphenyl-1*H*-pyrazole **(3e)**



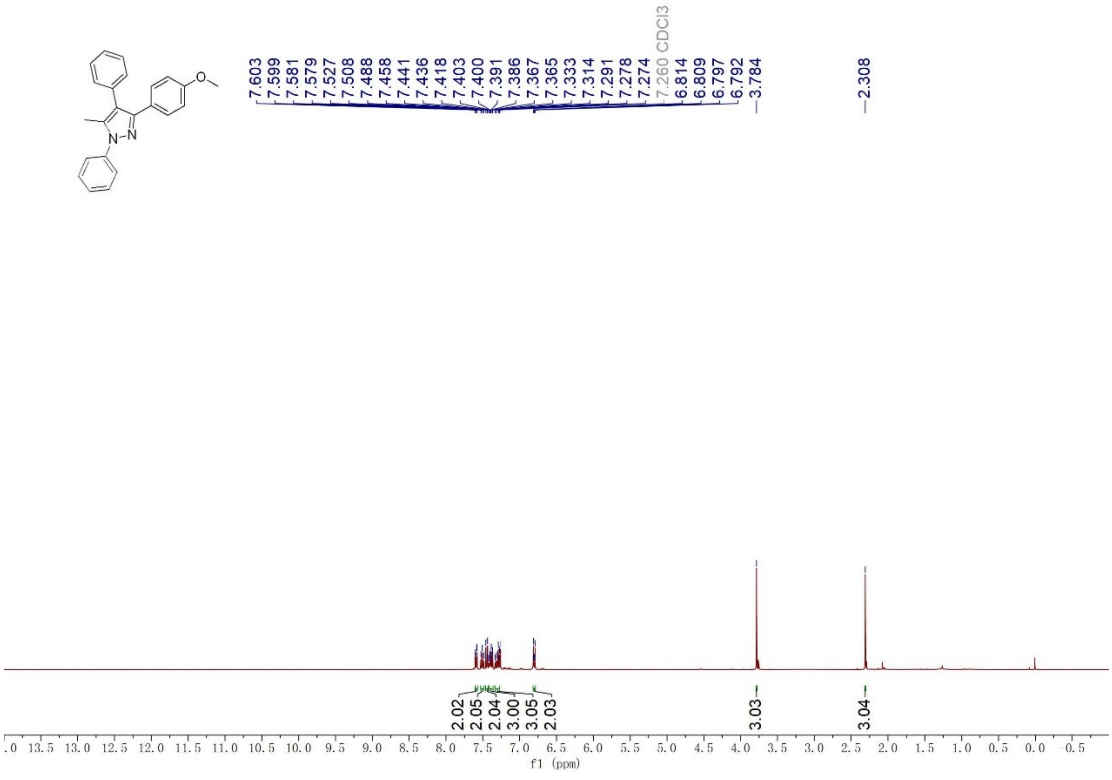


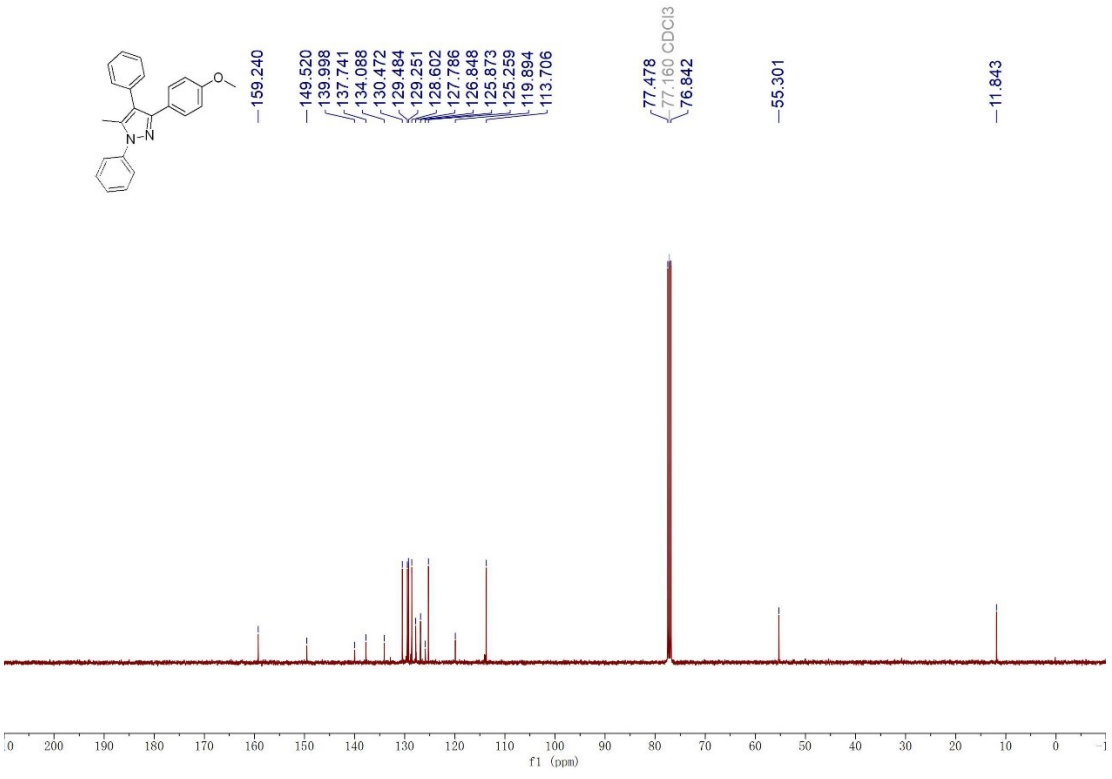
3-methyl-1,4-diphenyl-5-(p-tolyl)-1*H*-pyrazole **(3f)**



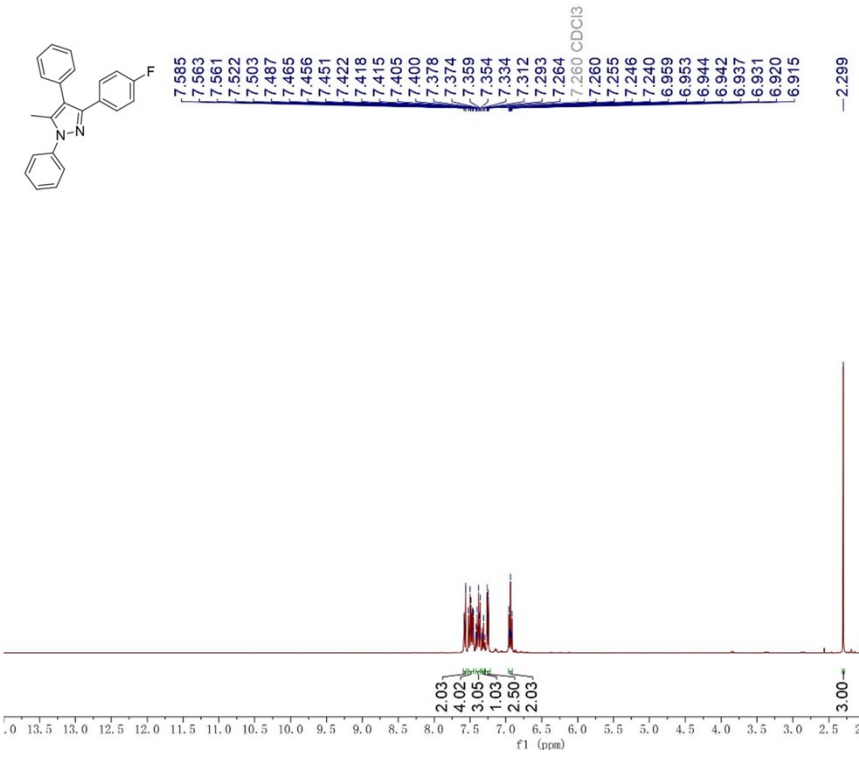


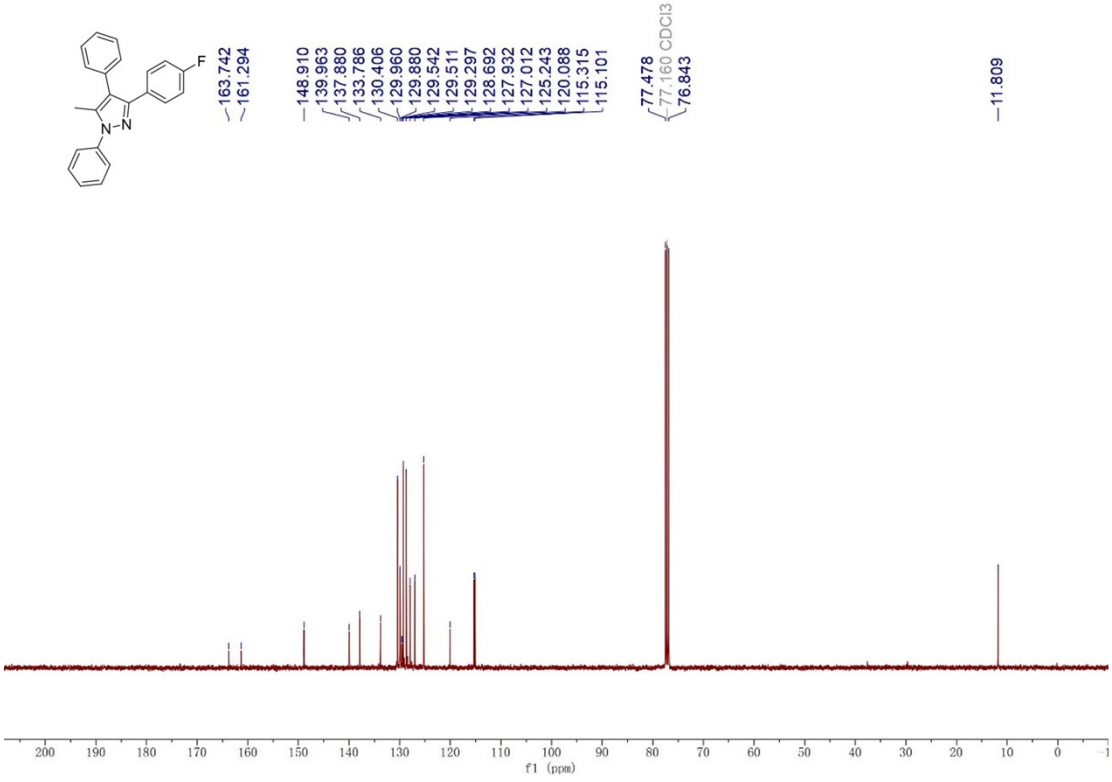
5-(4-methoxyphenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole **(3g)**

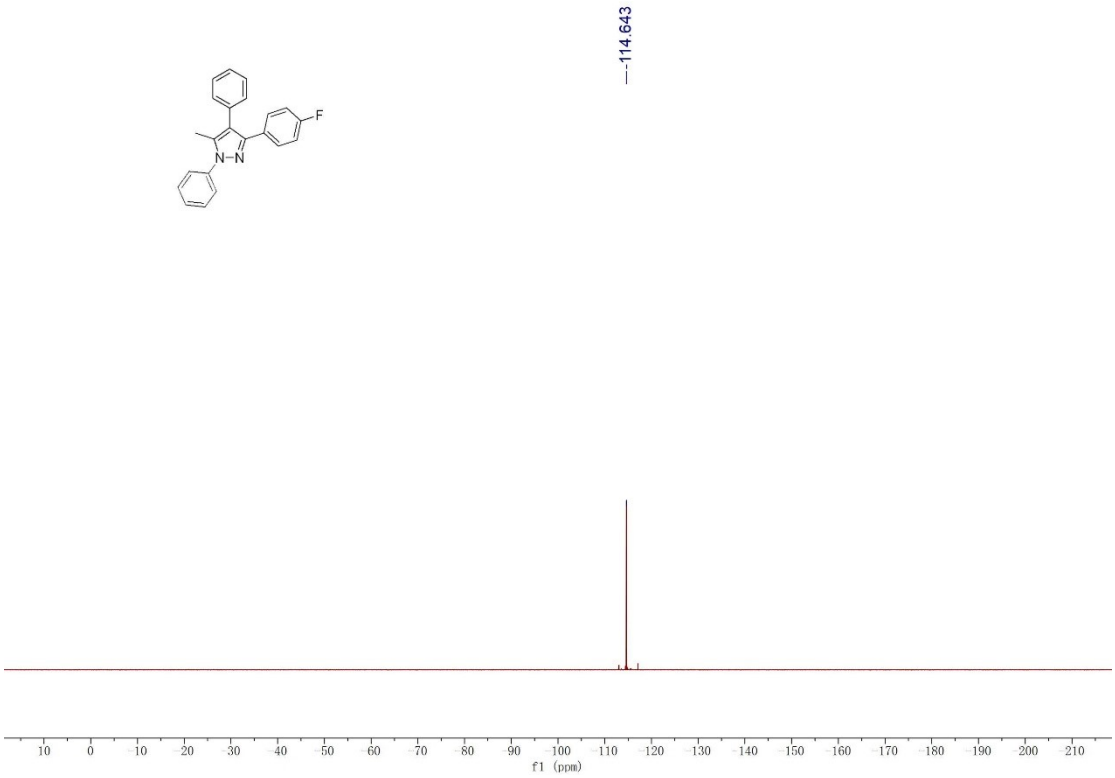




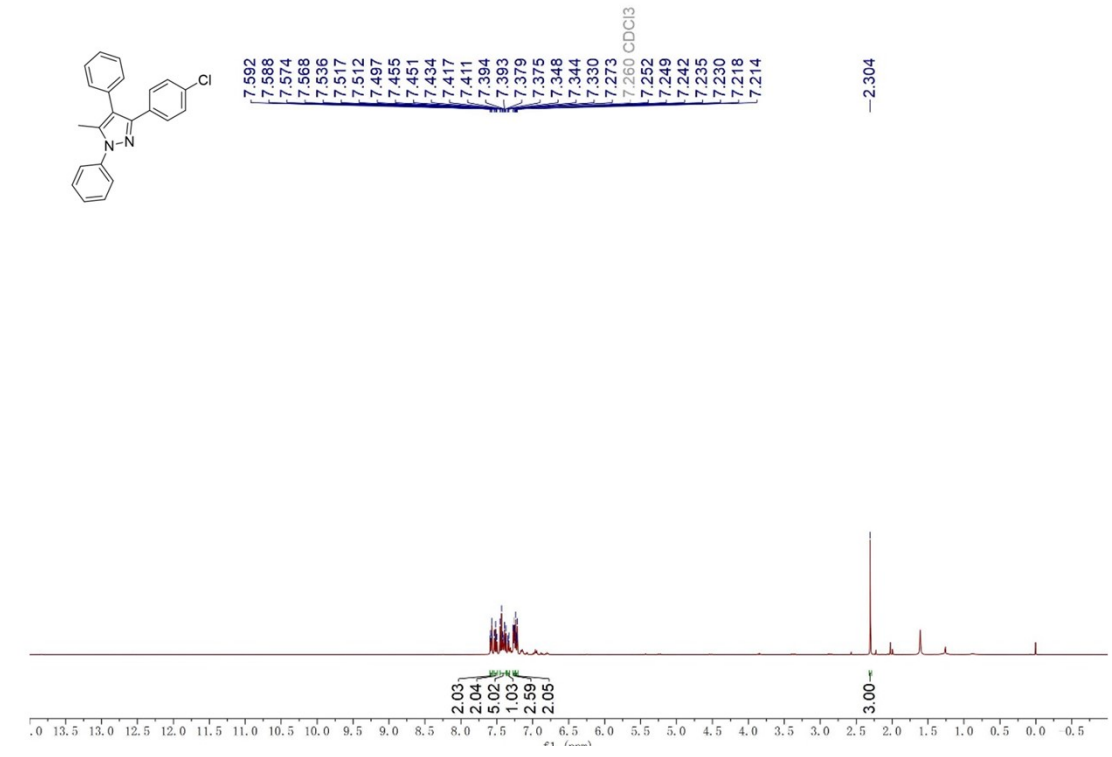
5-(4-fluorophenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole **(3h)**

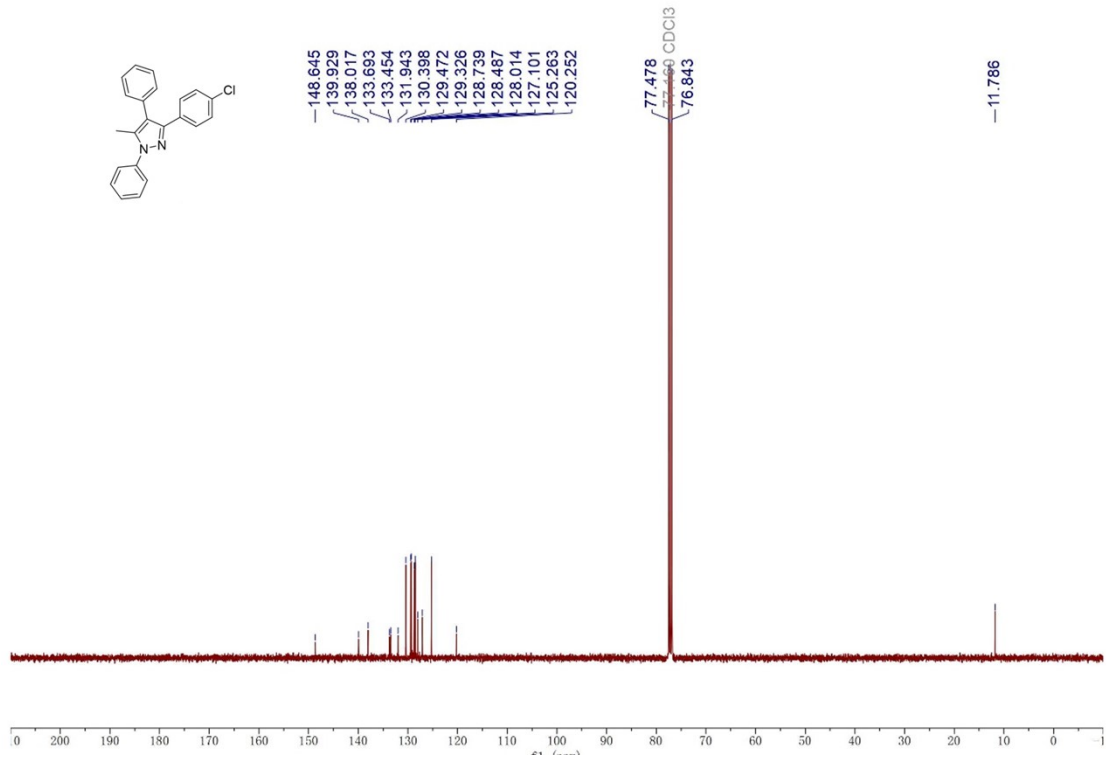




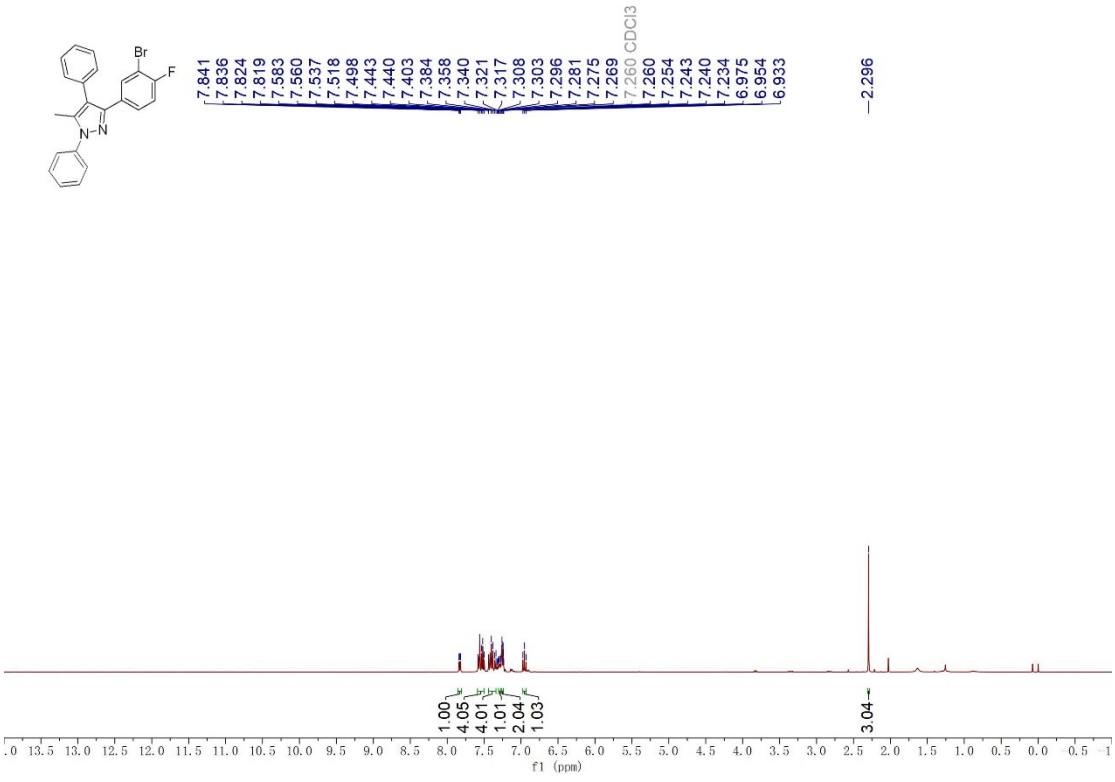


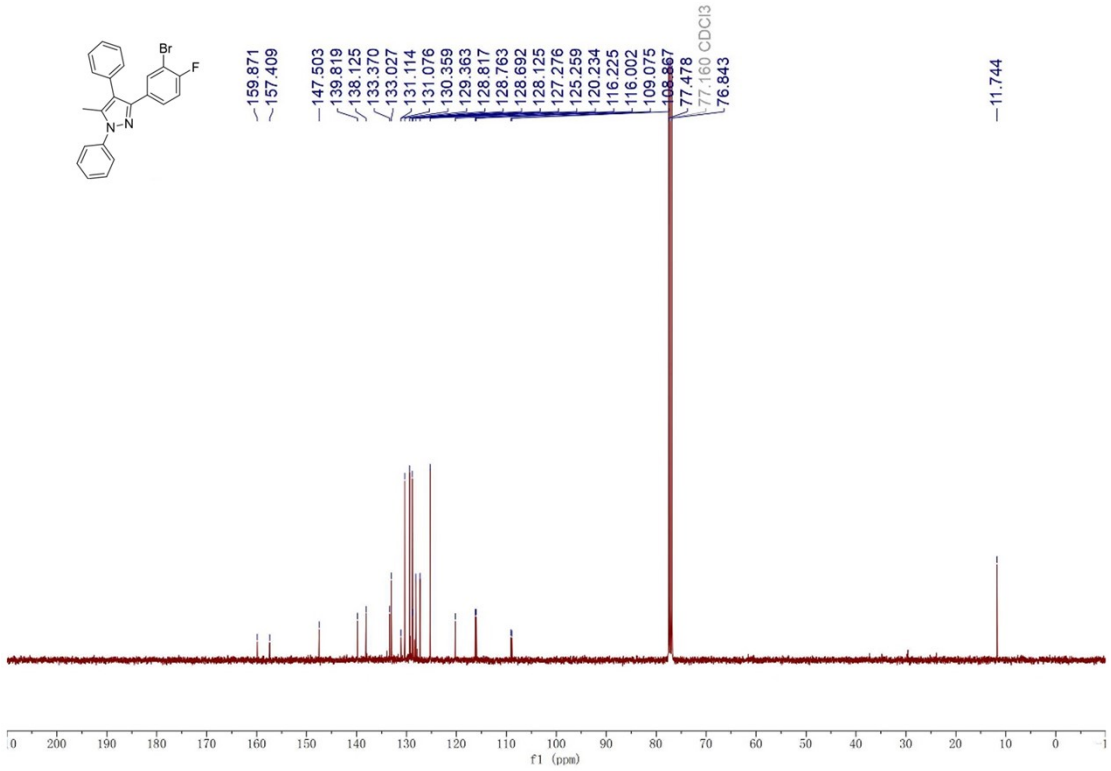
5-(4-chlorophenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole **(3i)**





5-(3-bromo-4-fluorophenyl)-3-methyl-1,4-diphenyl-1*H*-pyrazole **(3j)**




Br
F
N
N
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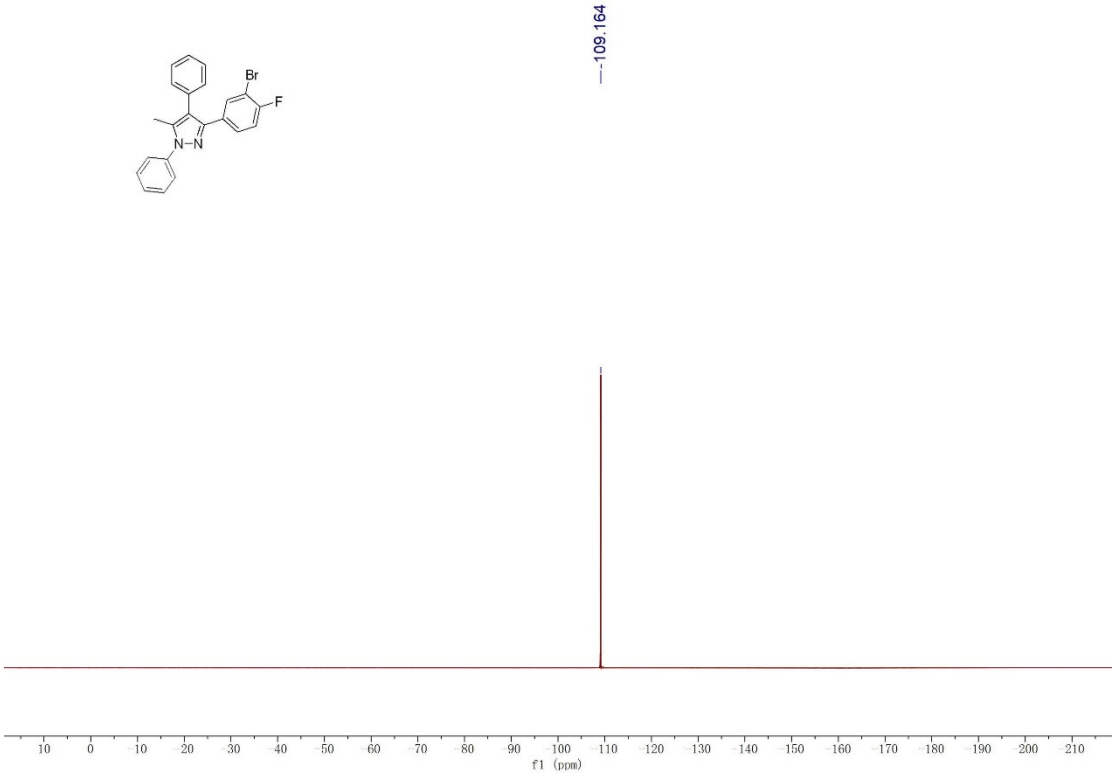
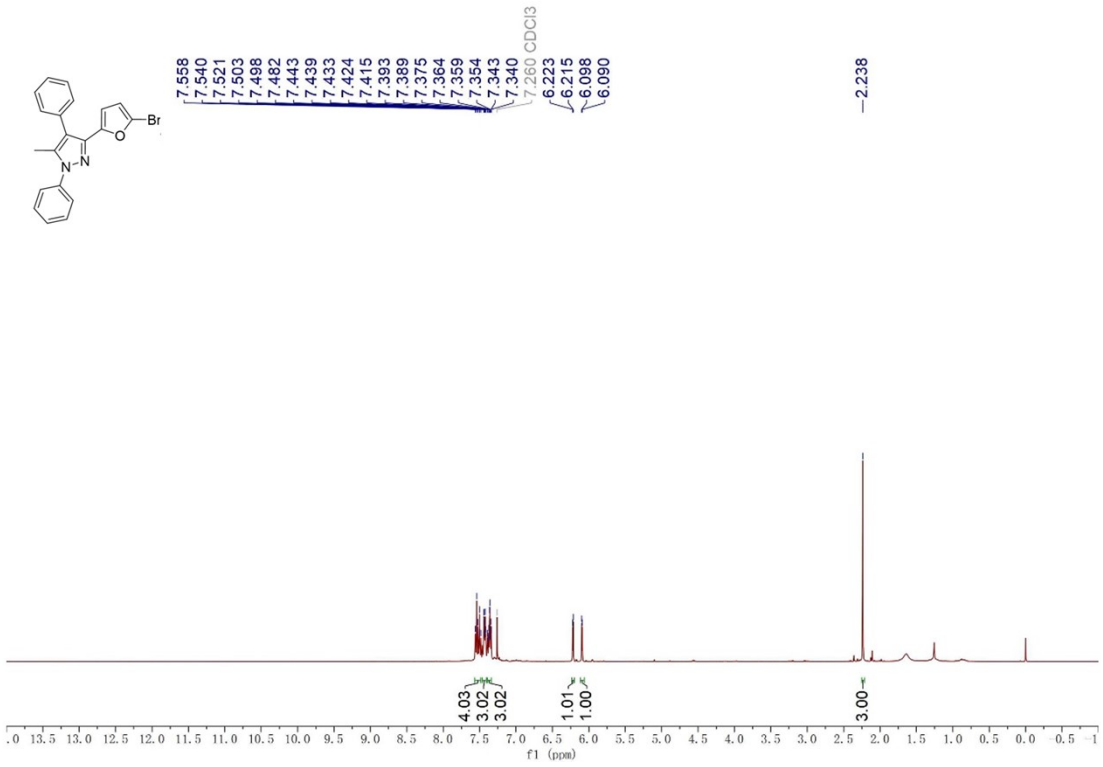
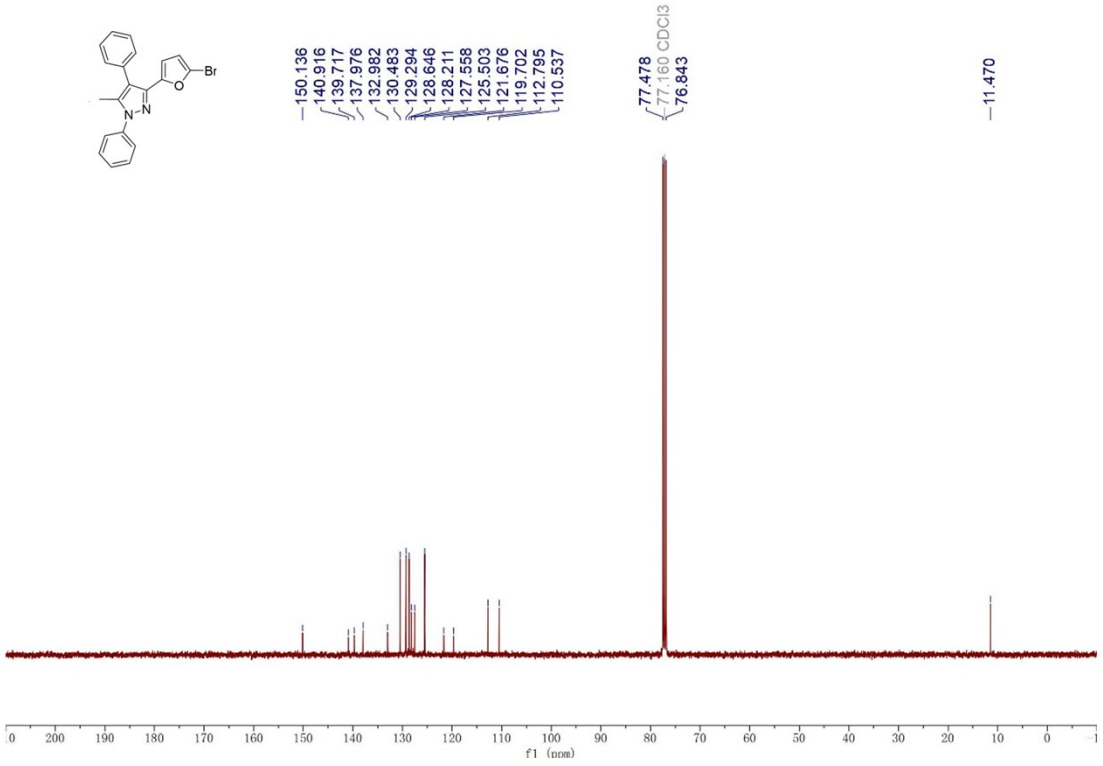
157.409
147.503
139.819
138.125
133.370
133.027
131.114
131.076
130.359
129.363
128.817
128.763
128.692
128.125
127.276
125.259
120.234
116.225
116.002
109.075
108.867
77.478
77.160 CDCl3
76.843
11.744
f1 (ppm)

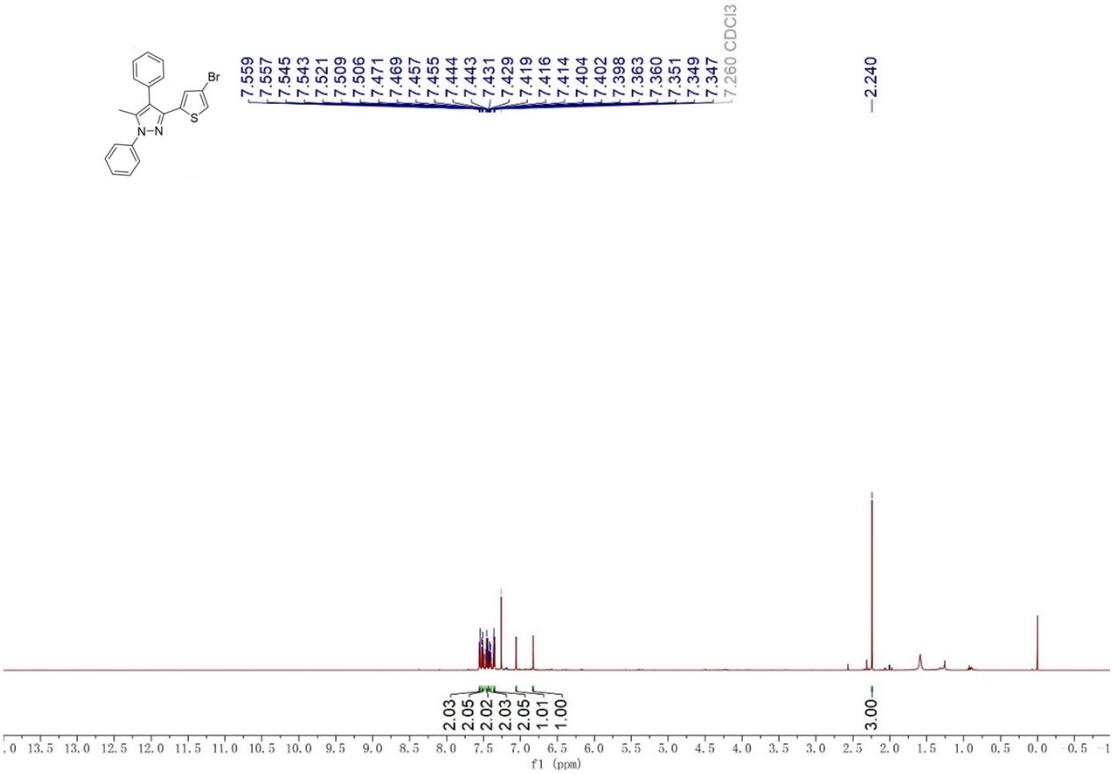

Br
F
N
N
109.164
f1 (ppm)

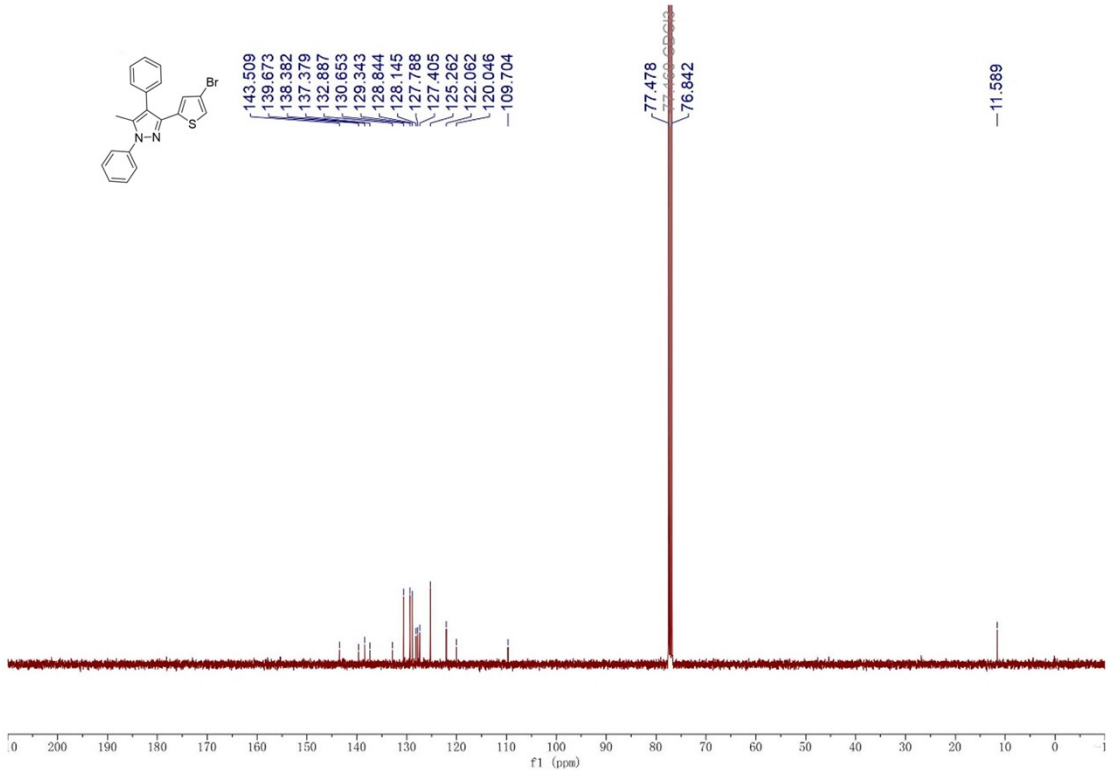
5-(5-bromofuran-2-yl)-3-methyl-1,4-diphenyl-1*H*-pyrazole **(3k)**



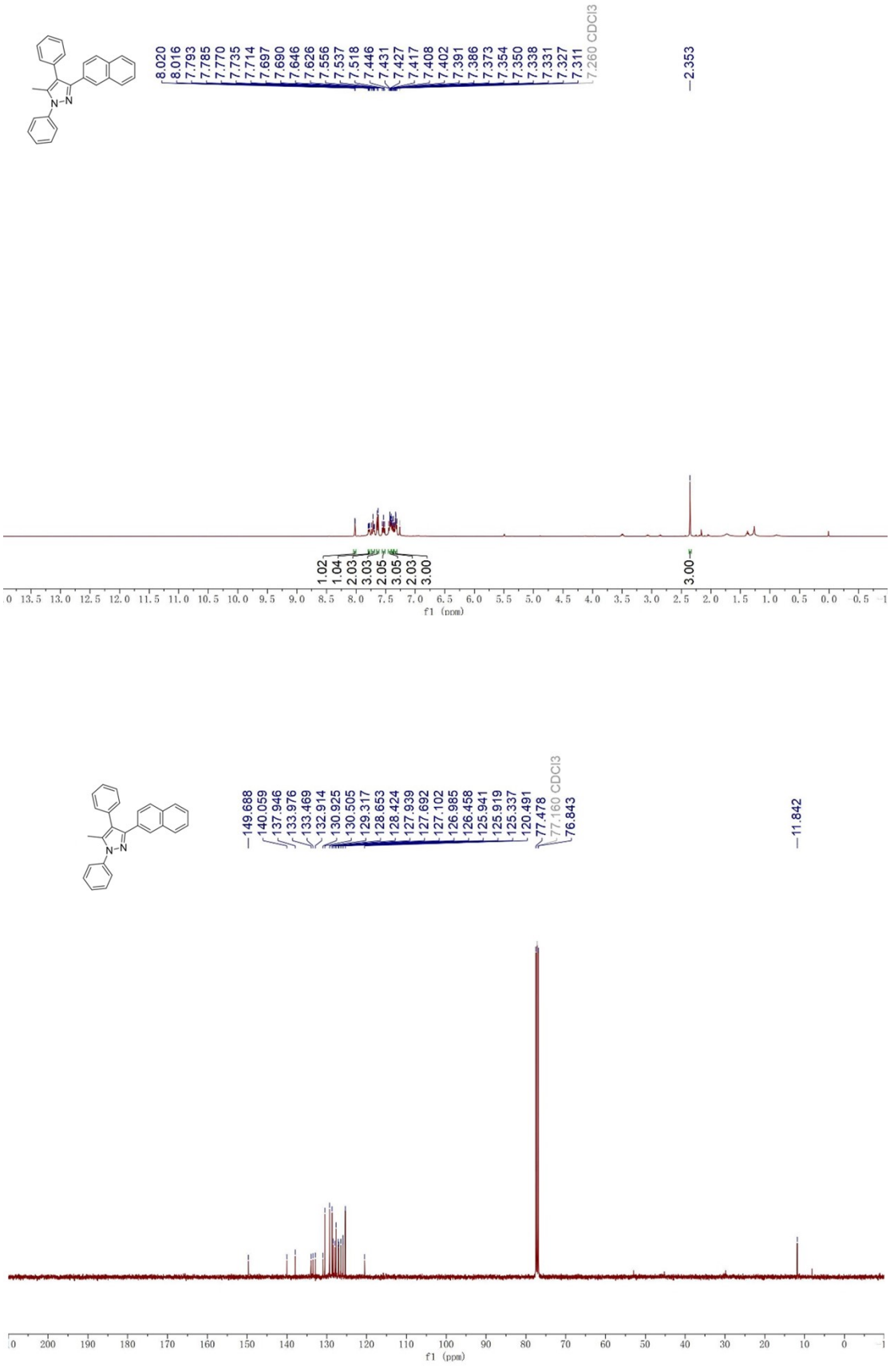


5-(4-bromothiophen-2-yl)-3-methyl-1,4-diphenyl-1*H*-pyrazole **(3l)**

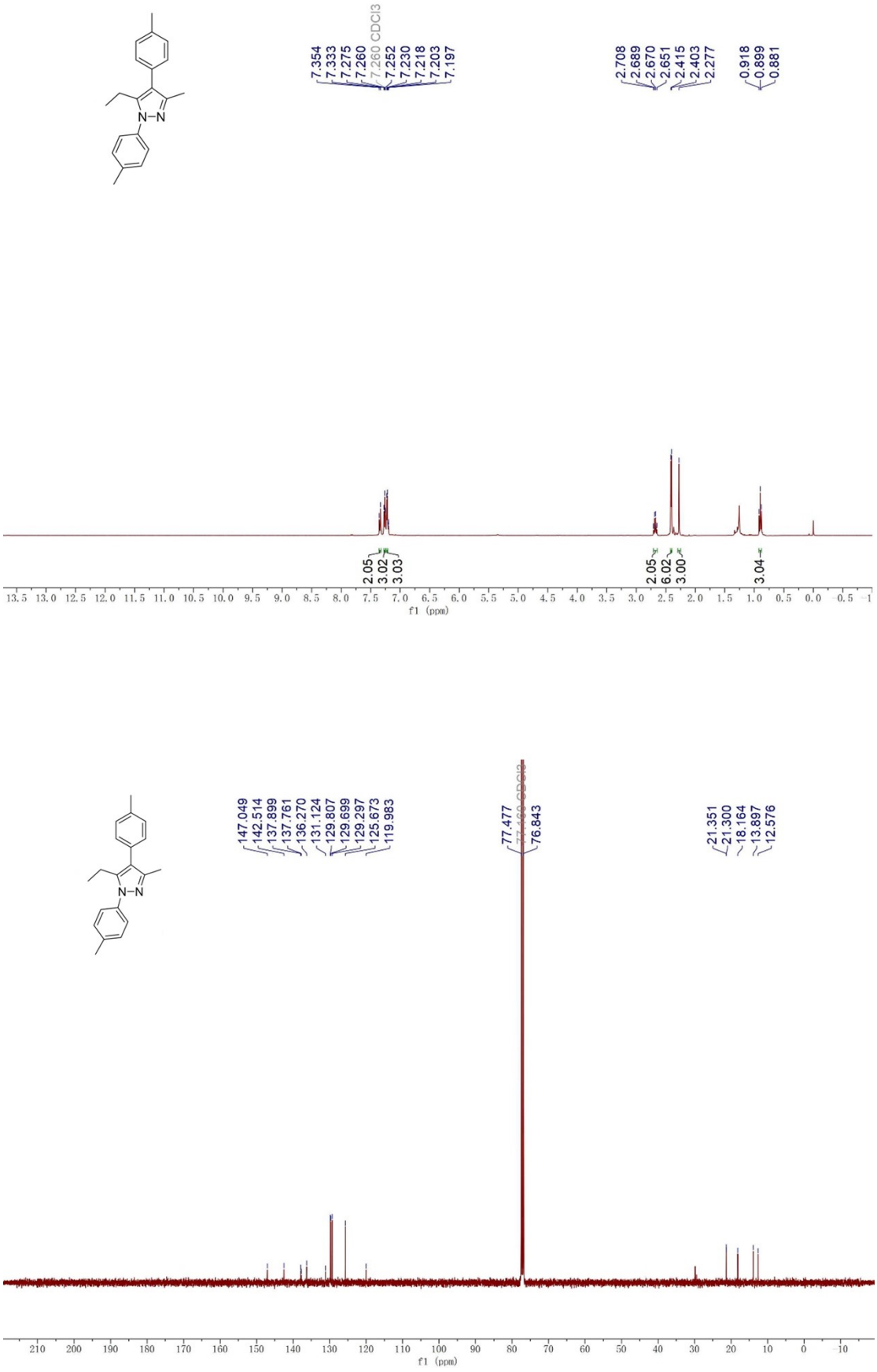




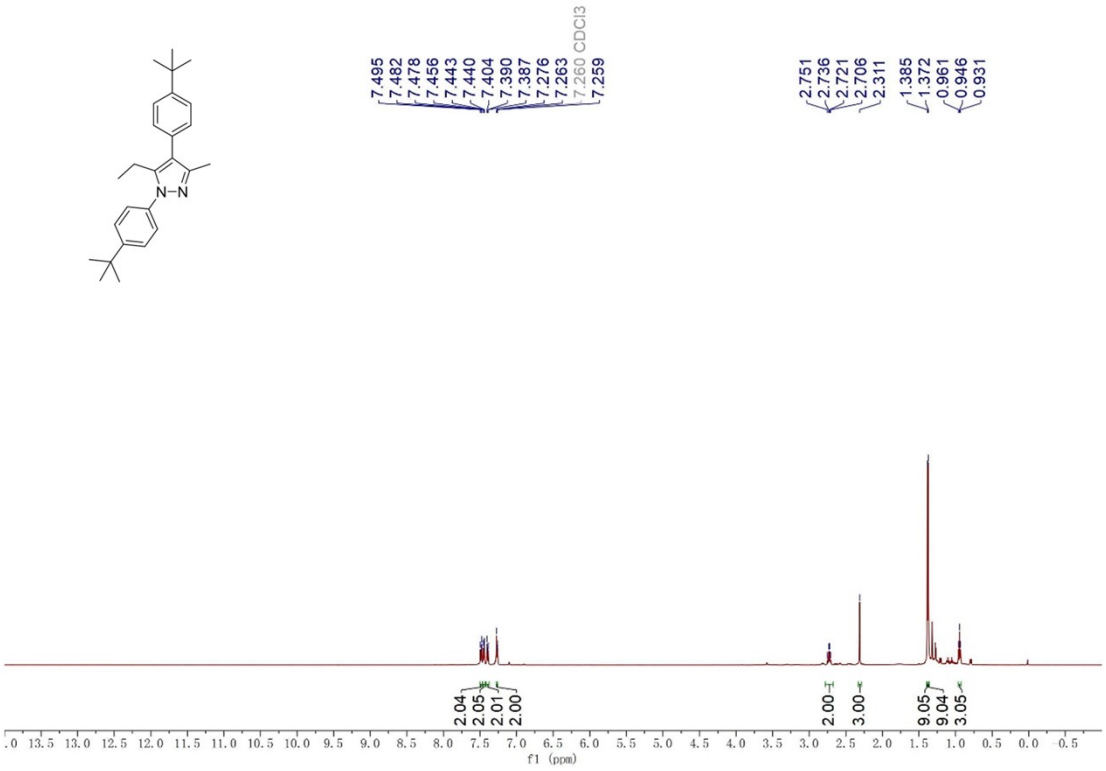
3-methyl-5-(naphthalen-2-yl)-1,4-diphenyl-1*H*-pyrazole **(3m)**

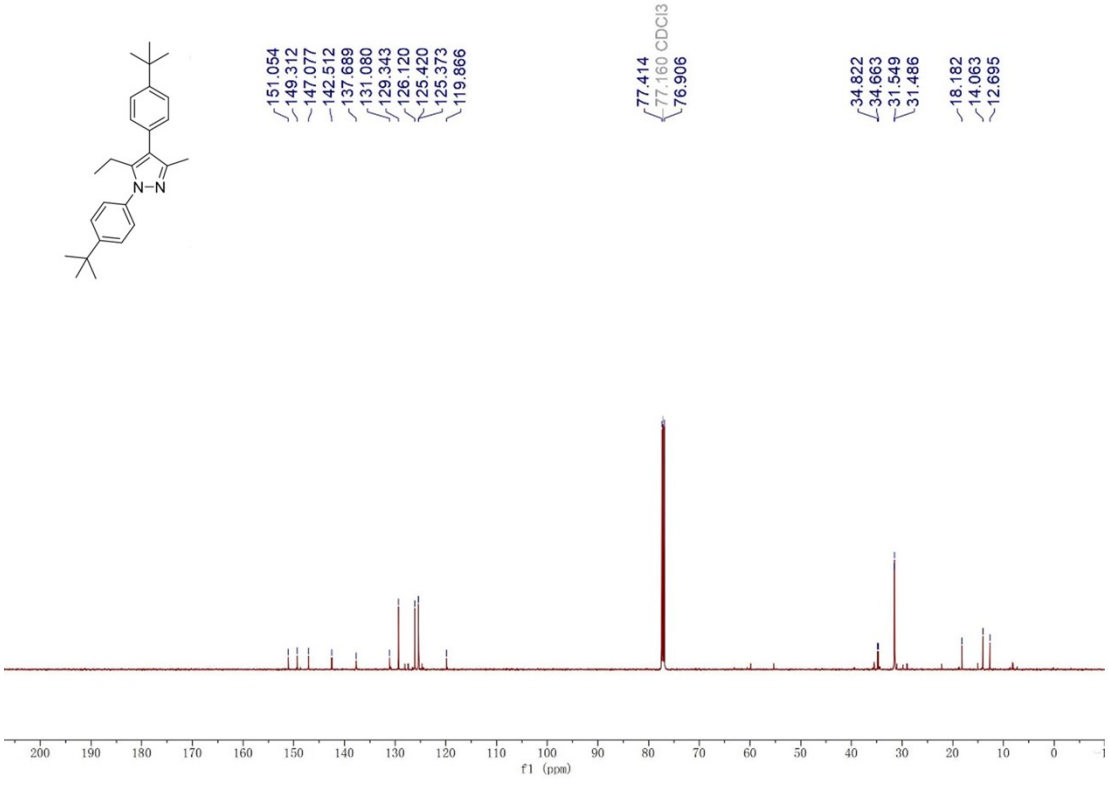


3-ethyl-5-methyl-1,4-di-*p*-tolyl-1*H*-pyrazole **(3n)**

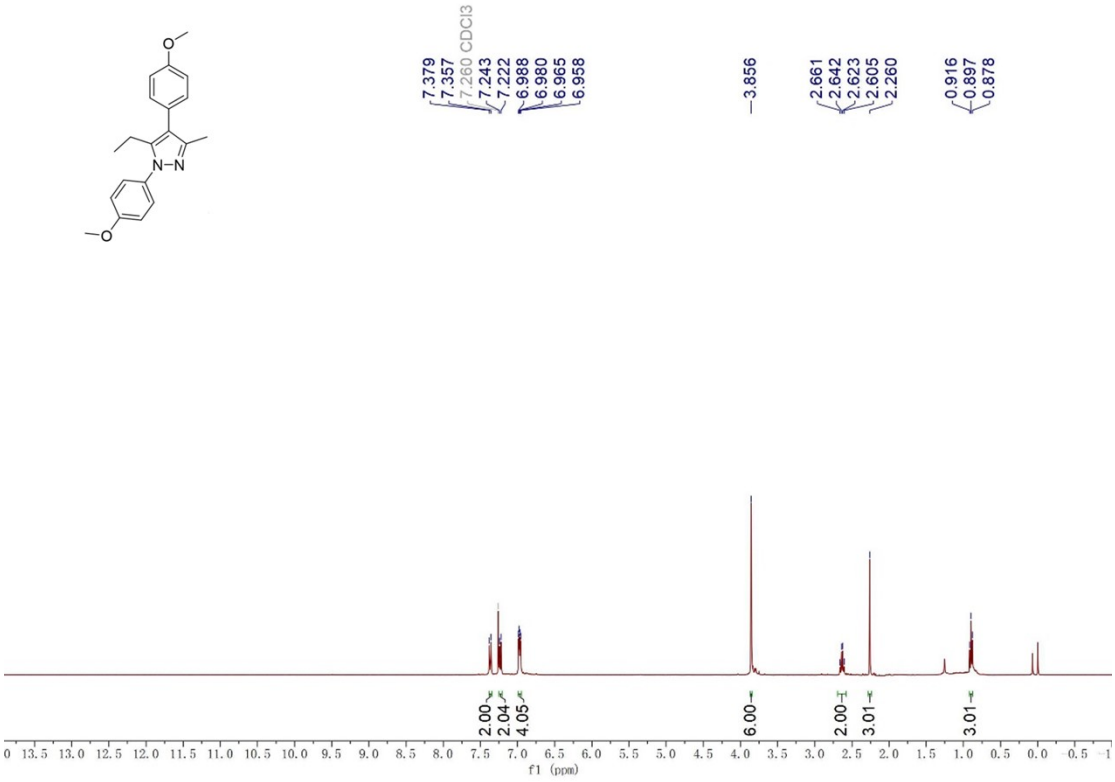


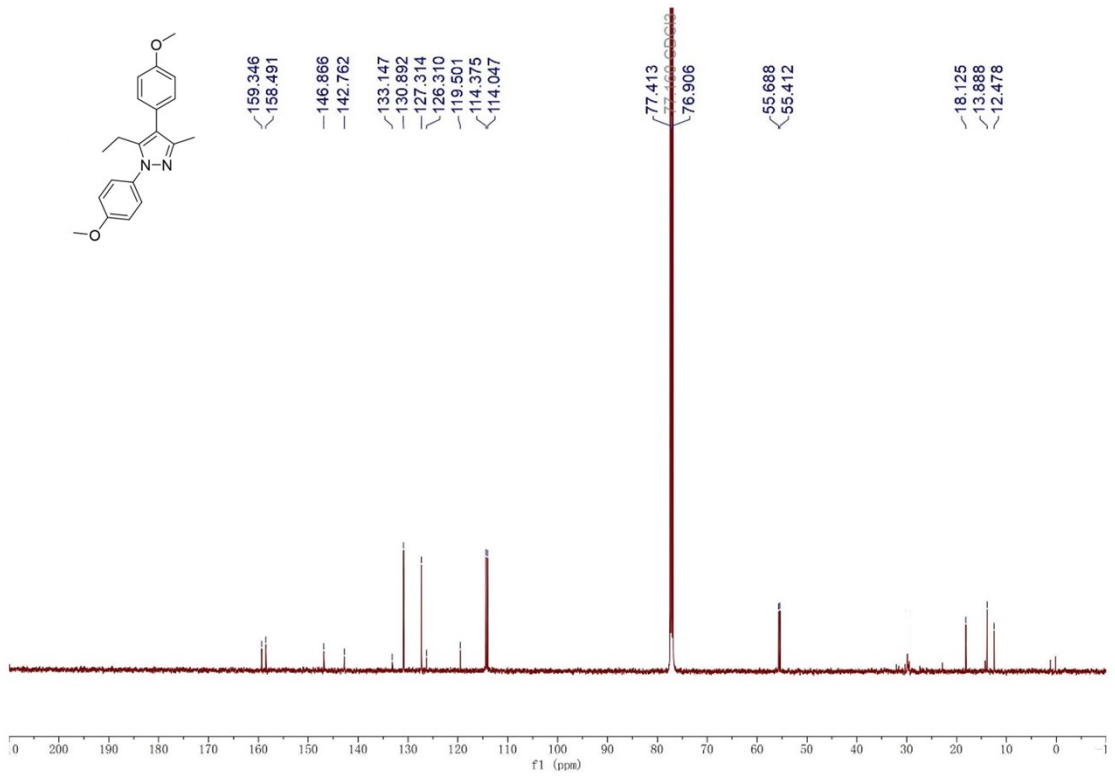
1,4-bis(4-(*tert*-butyl)phenyl)-3-ethyl-5-methyl-1*H*-pyrazole **(3o)**



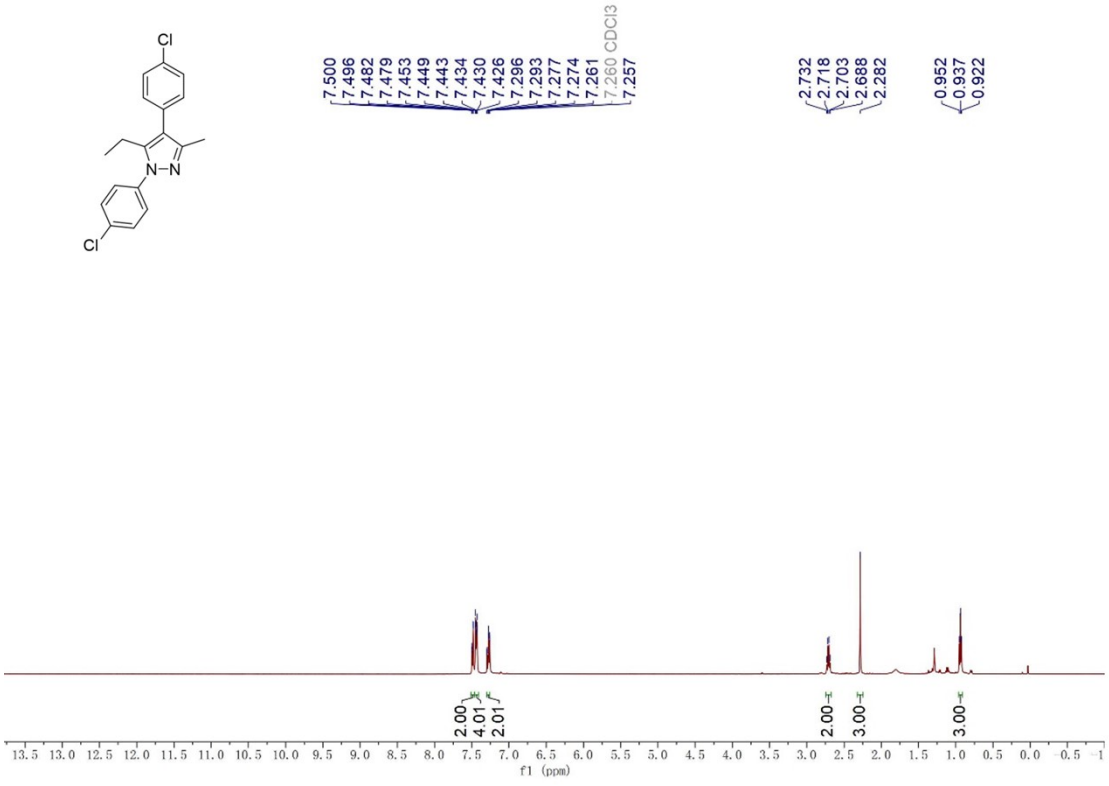


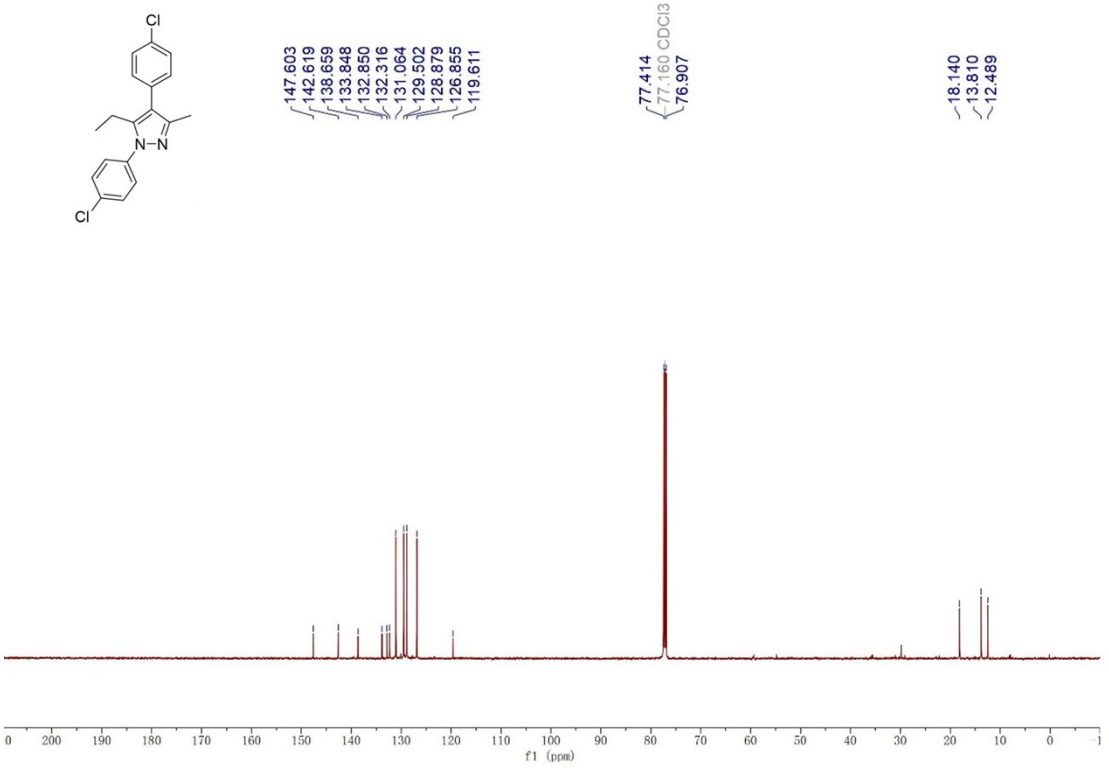
3-ethyl-1,4-bis(4-methoxyphenyl)-5-methyl-1*H*-pyrazole **(3p)**



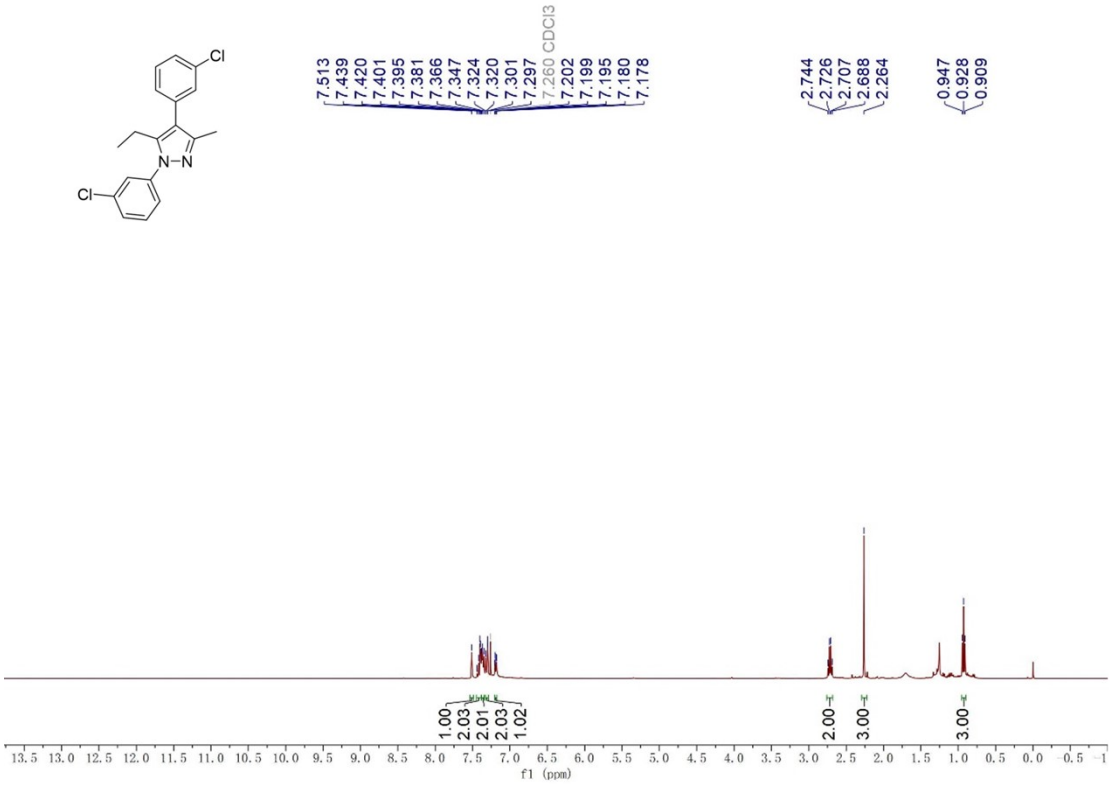


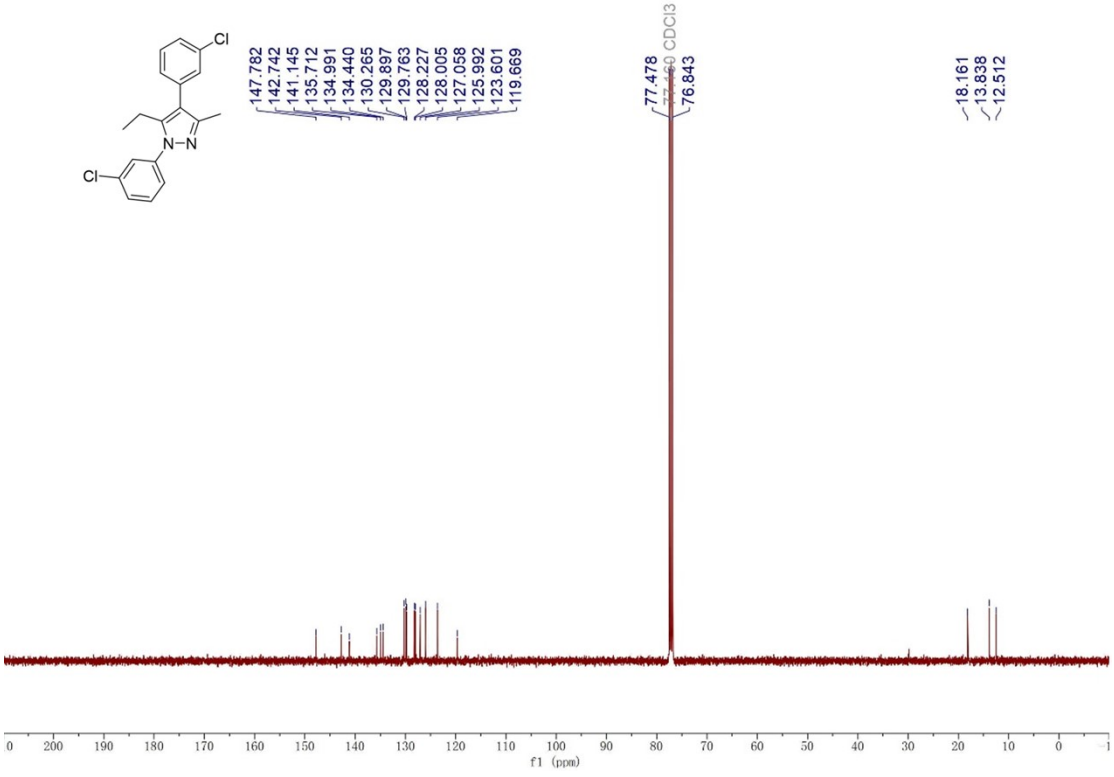
1,4-bis(4-chlorophenyl)-3-ethyl-5-methyl-1*H*-pyrazole **(3q)**



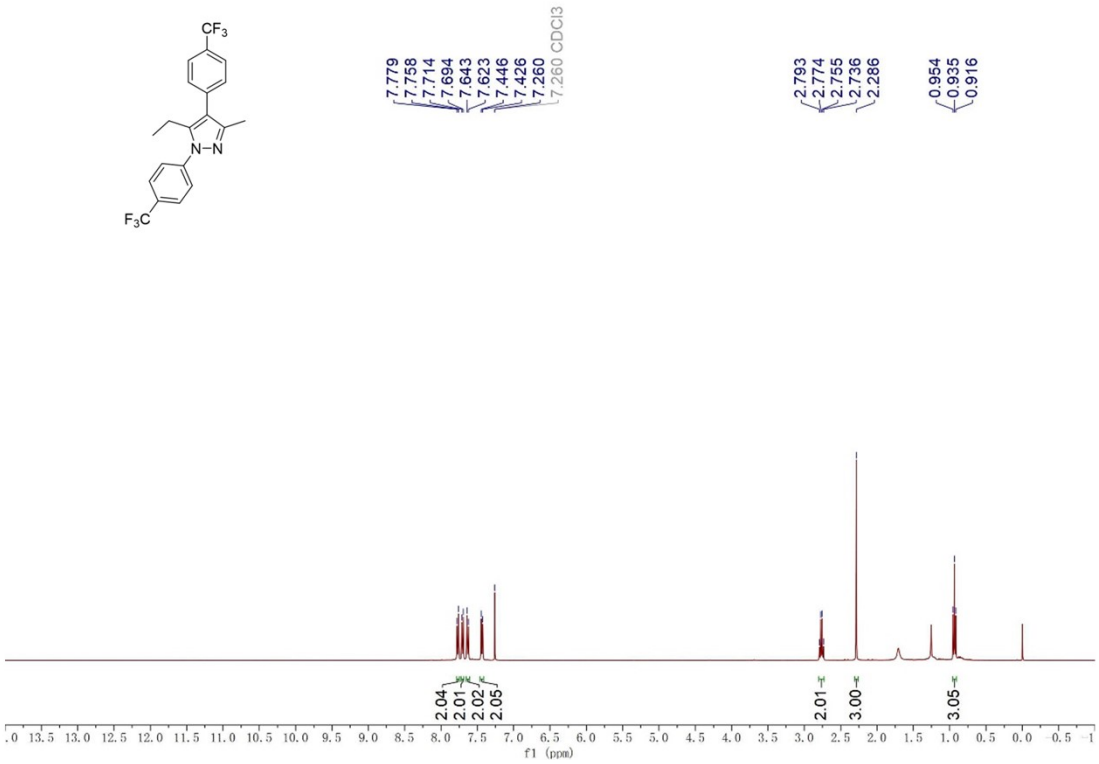


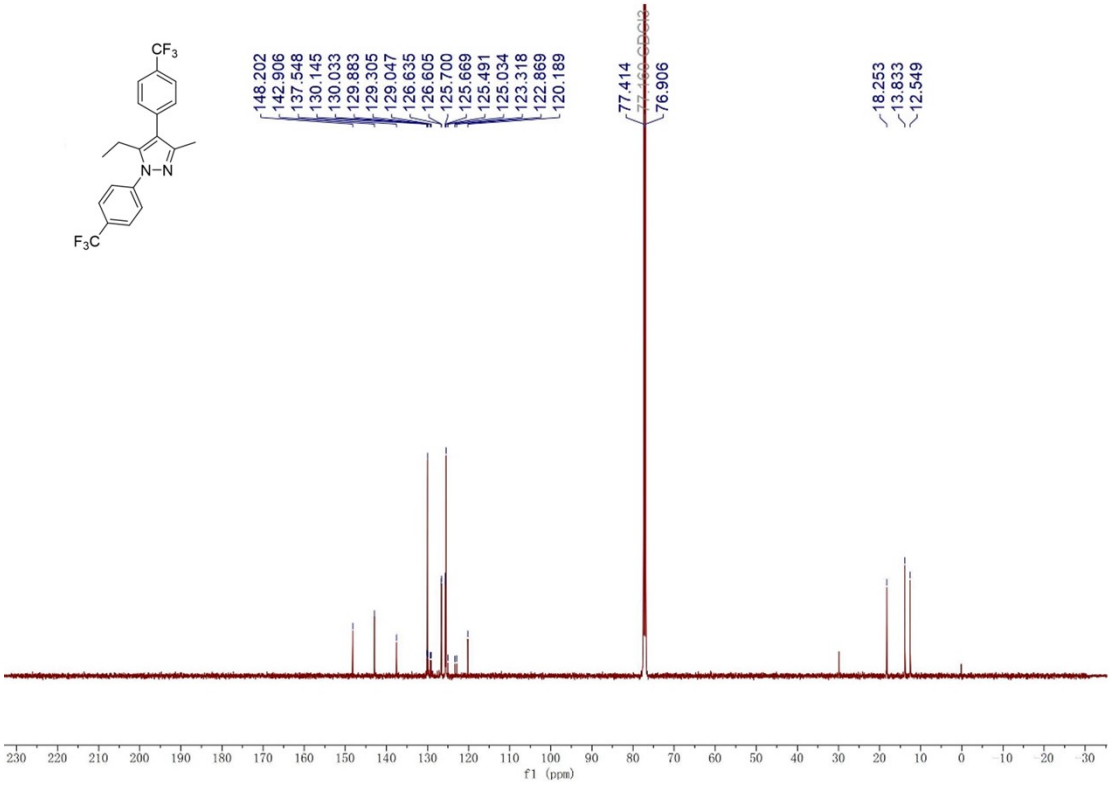
1,4-bis(3-chlorophenyl)-3-ethyl-5-methyl-1*H*-pyrazole **(3r)**

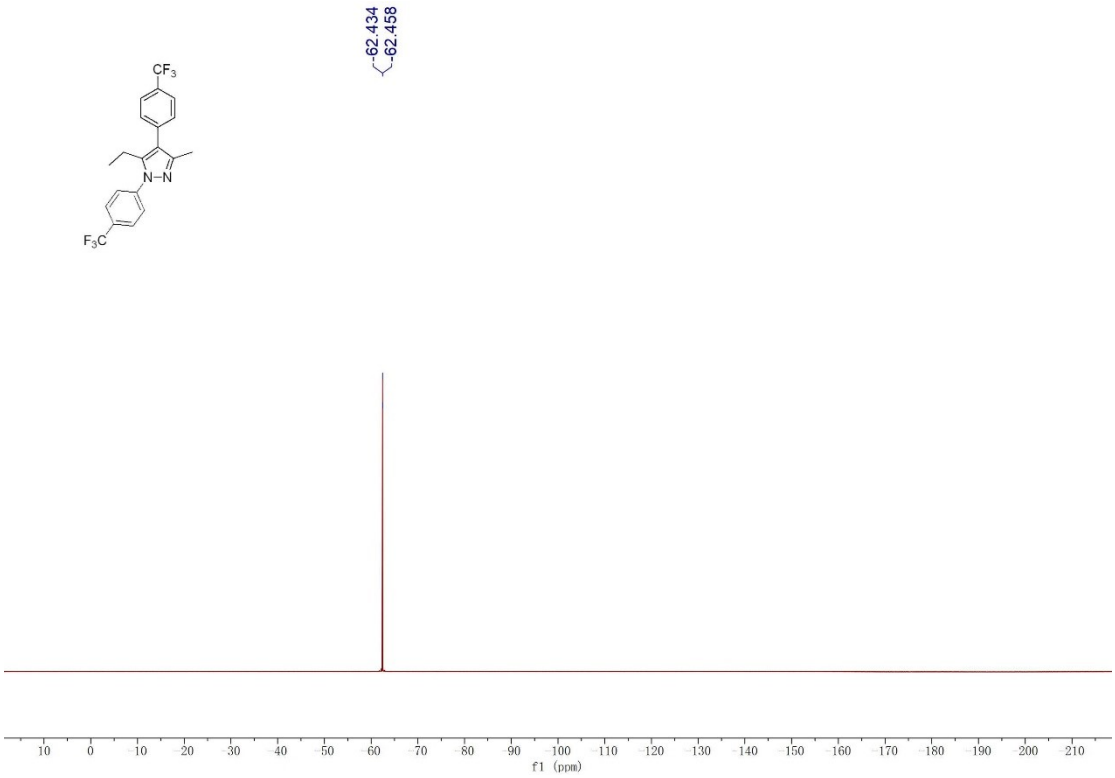




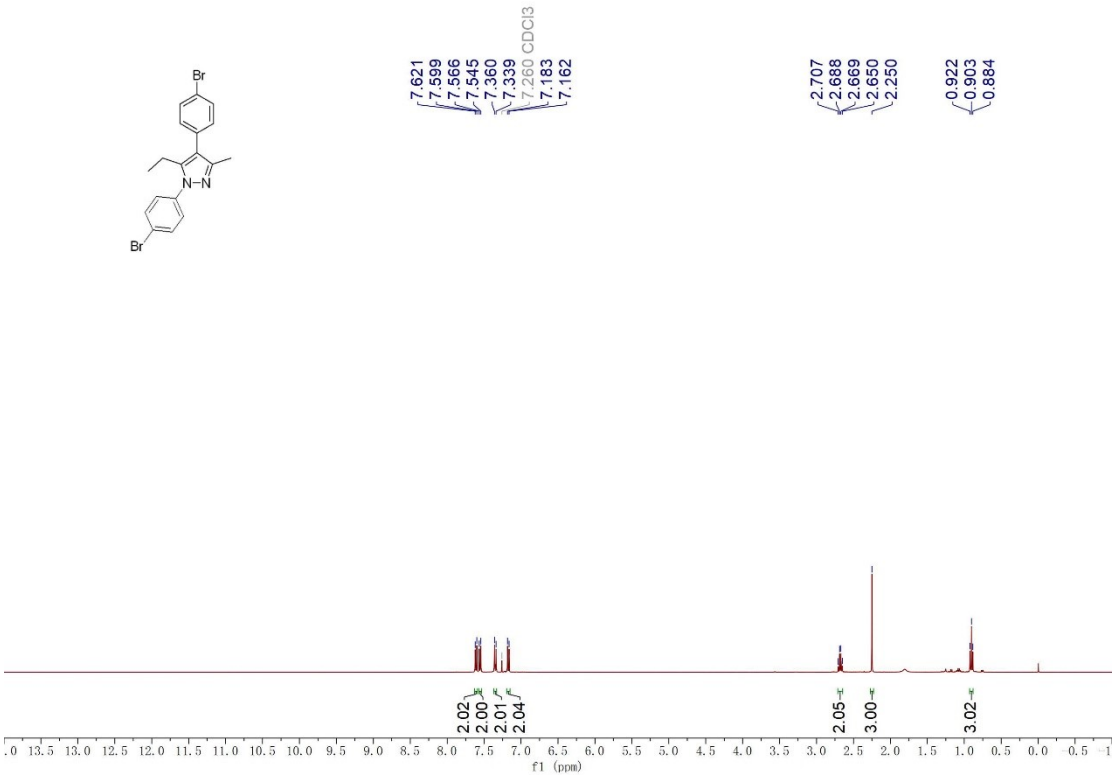
3-ethyl-5-methyl-1,4-bis(4-(trifluoromethyl)phenyl)-1*H*-pyrazole **(3s)**

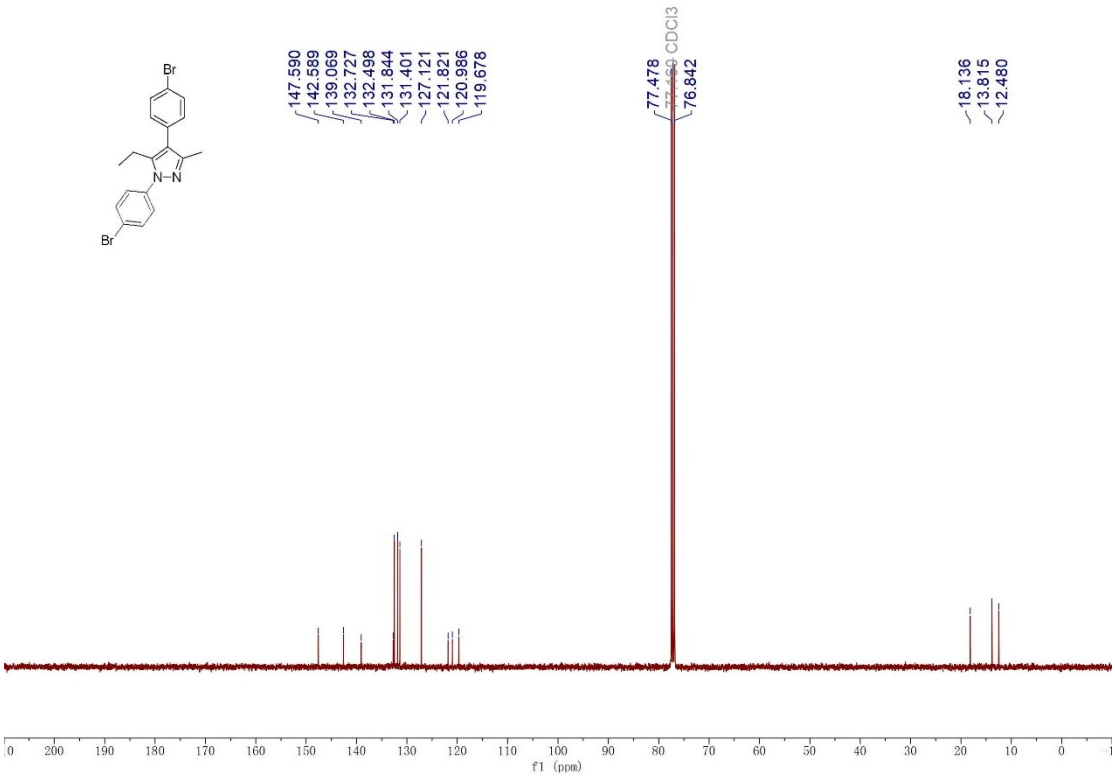




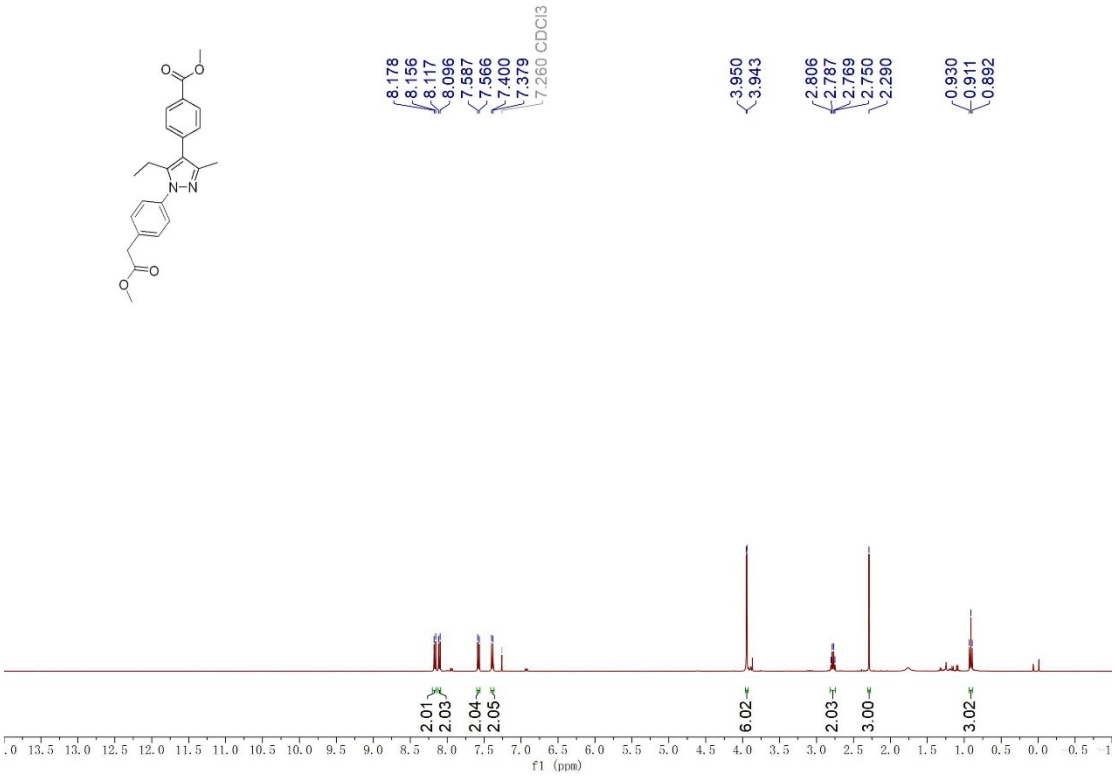


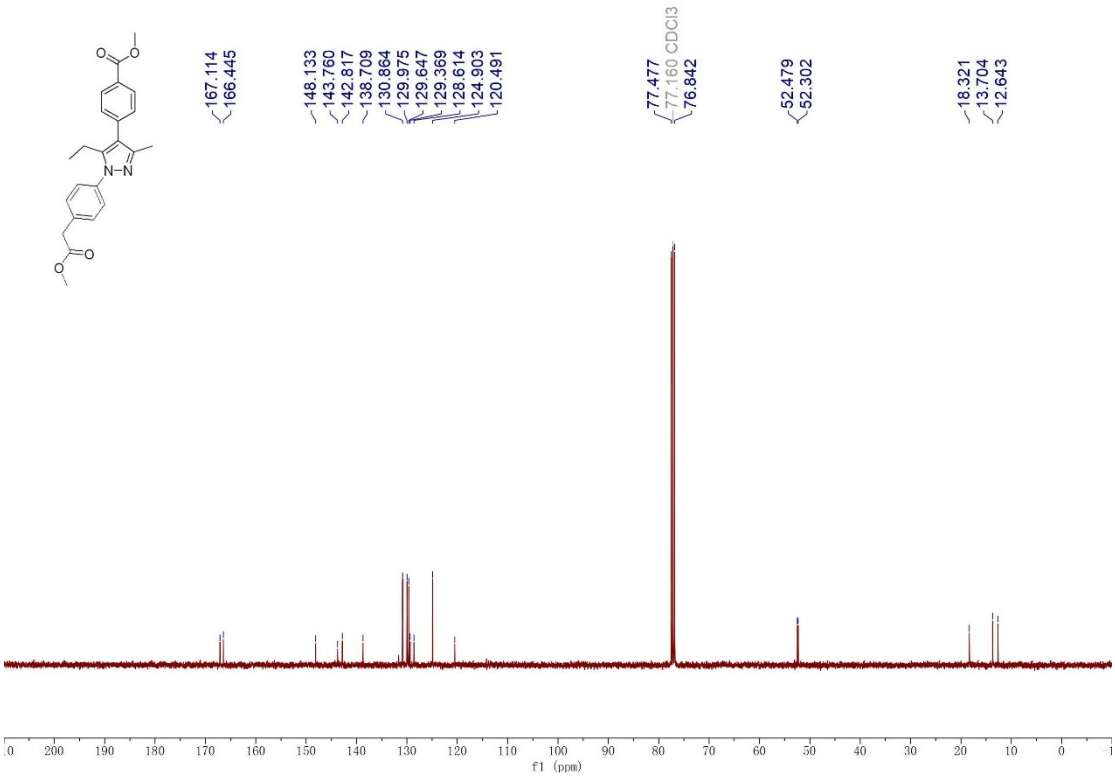
1,4-bis(4-bromophenyl)-5-ethyl-3-methyl-1*H*-pyrazole **(3t)**



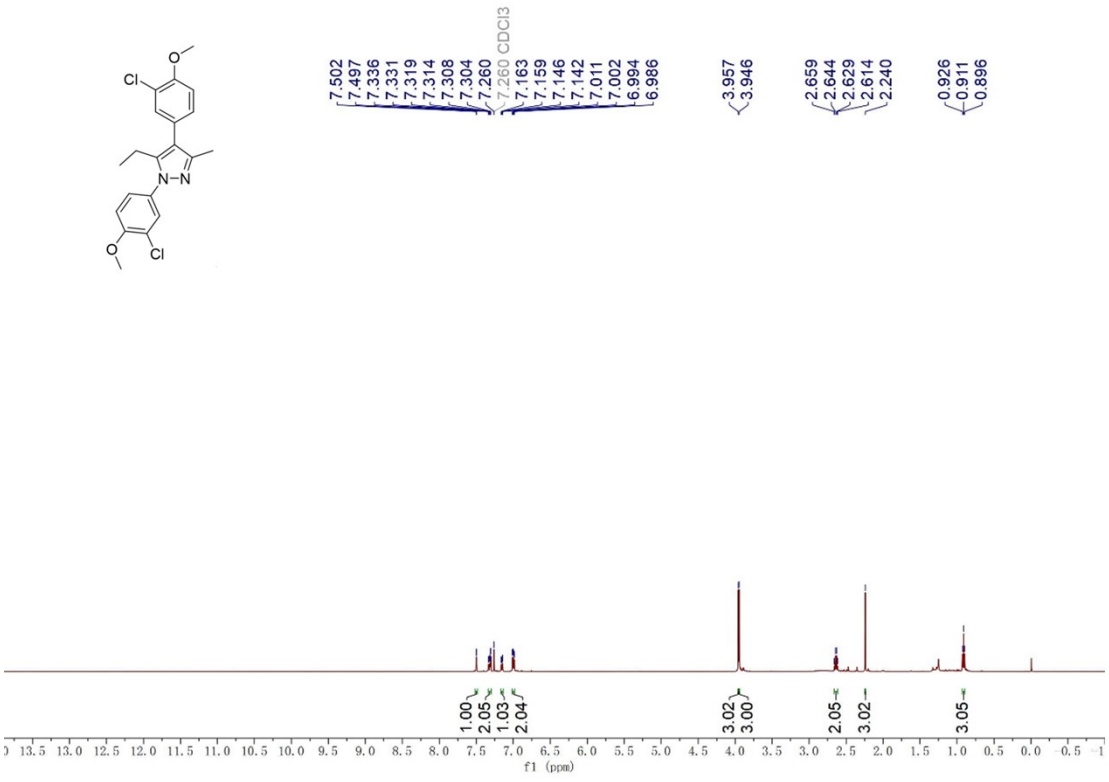


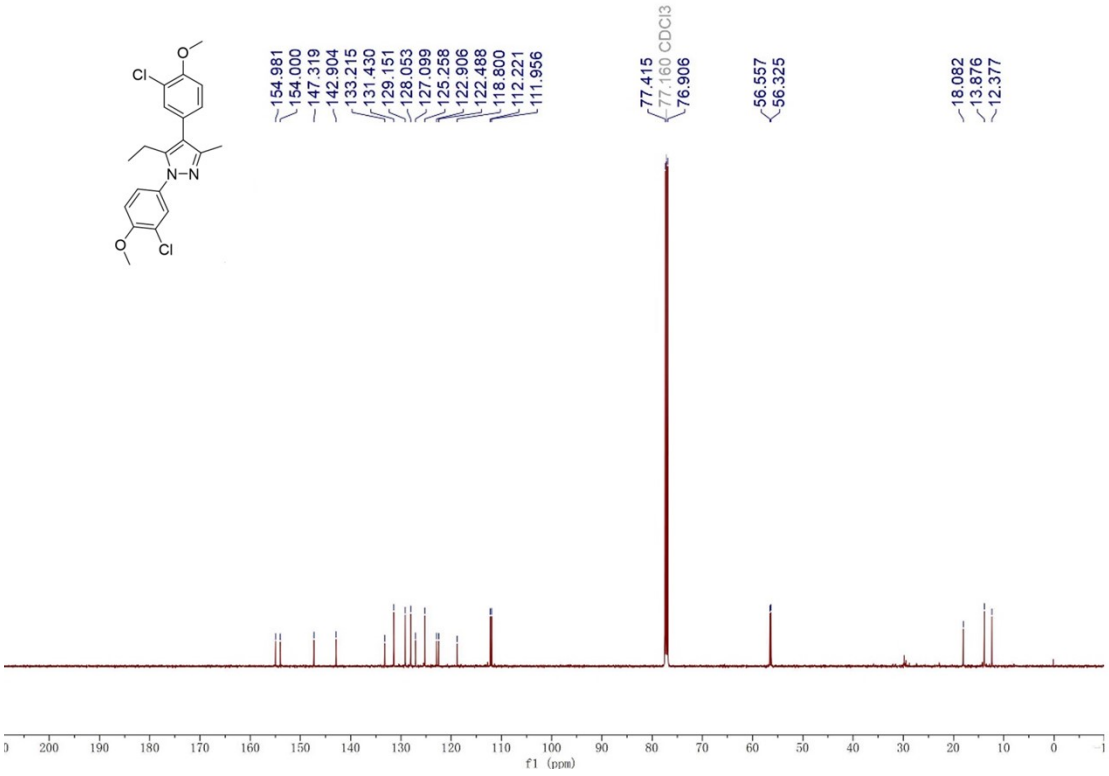
methyl 4-(5-ethyl-1-(4-(2-methoxy-2-oxoethyl)phenyl)-3-methyl-1*H*-pyrazol-4-yl)benzoate **(3u)**



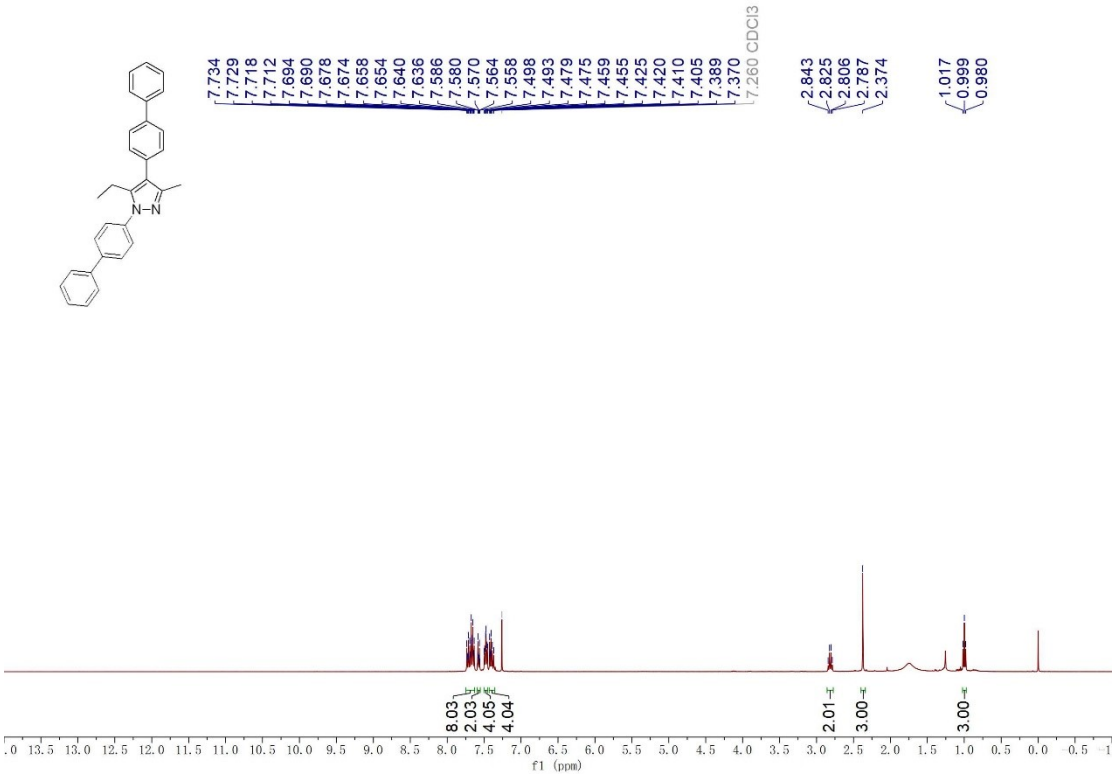


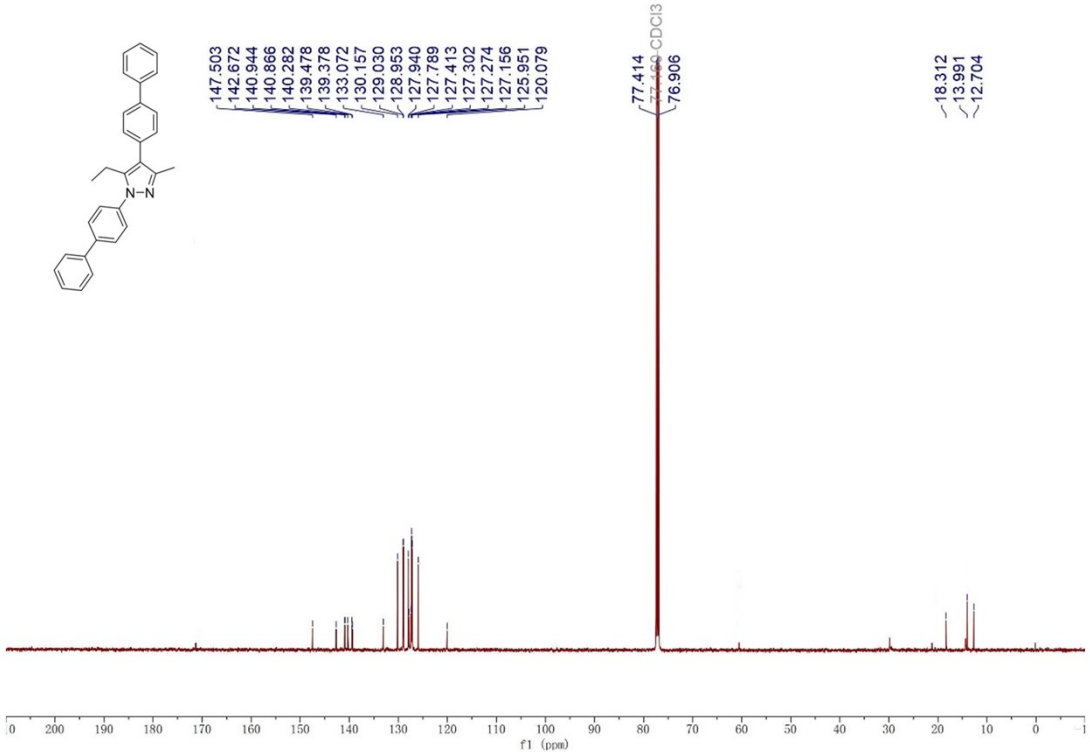
1,4-bis(3-chloro-4-methoxyphenyl)-5-ethyl-3-methyl-1*H*-pyrazole **(3v)**



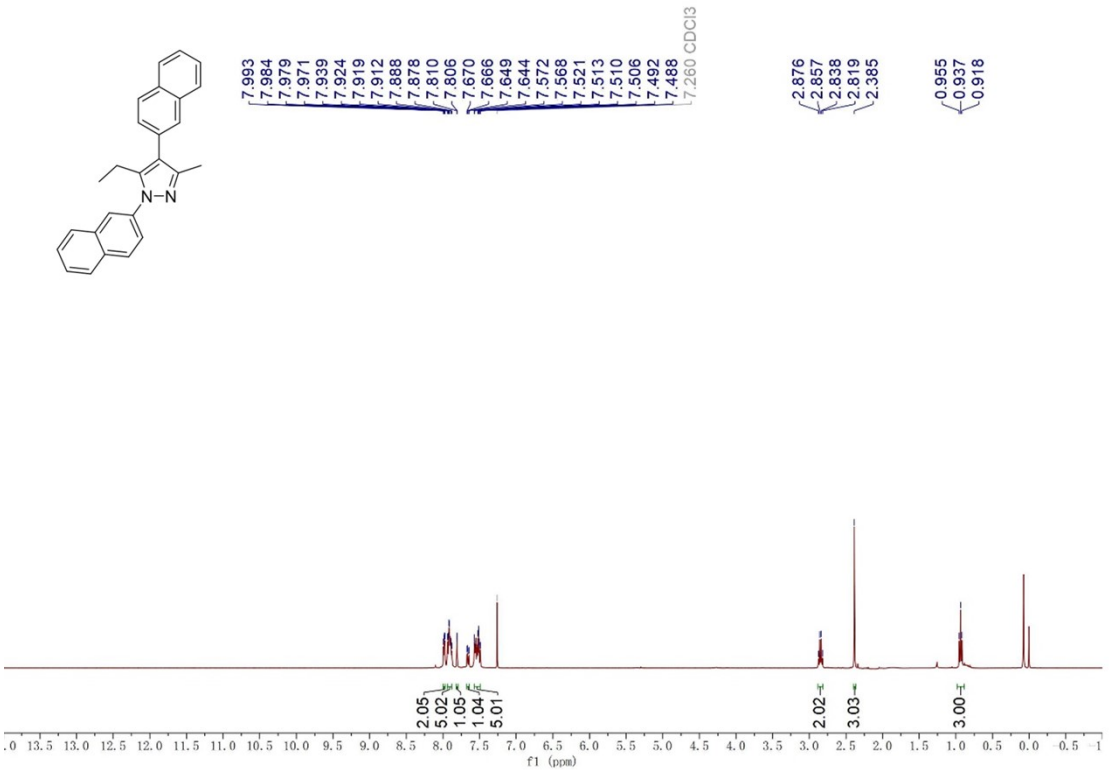


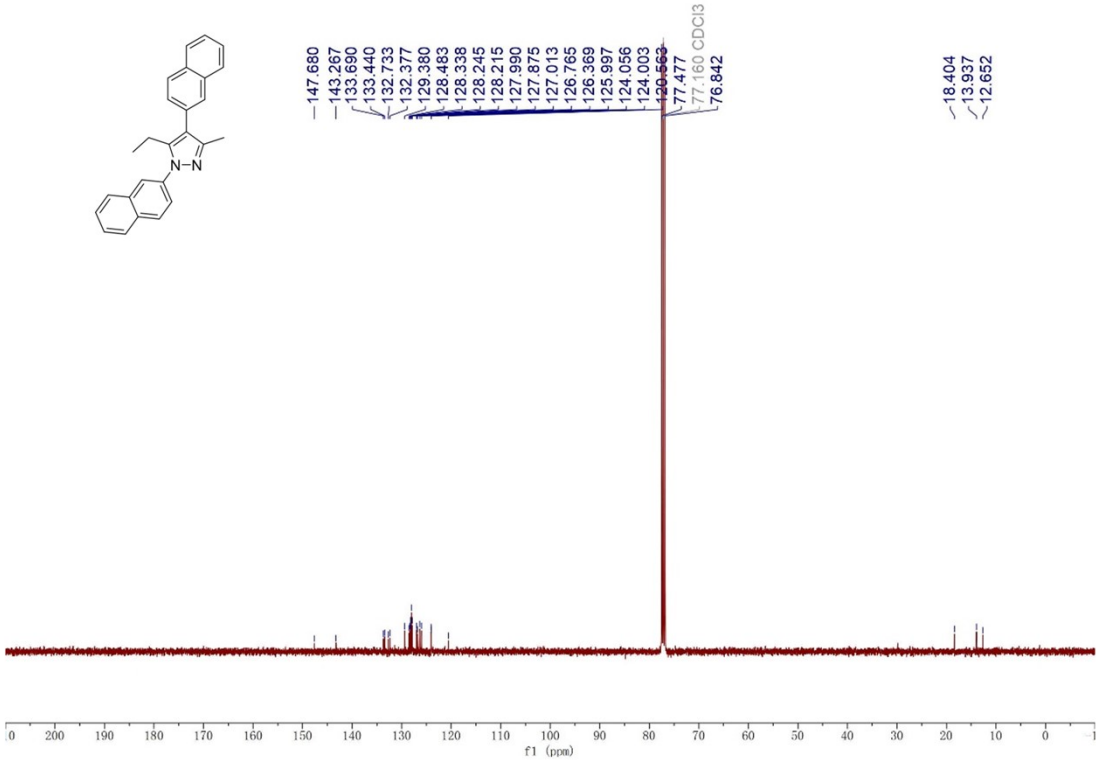
1,4-di([1,1'-biphenyl]-4-yl)-5-ethyl-3-methyl-1*H*-pyrazole **(3w)**



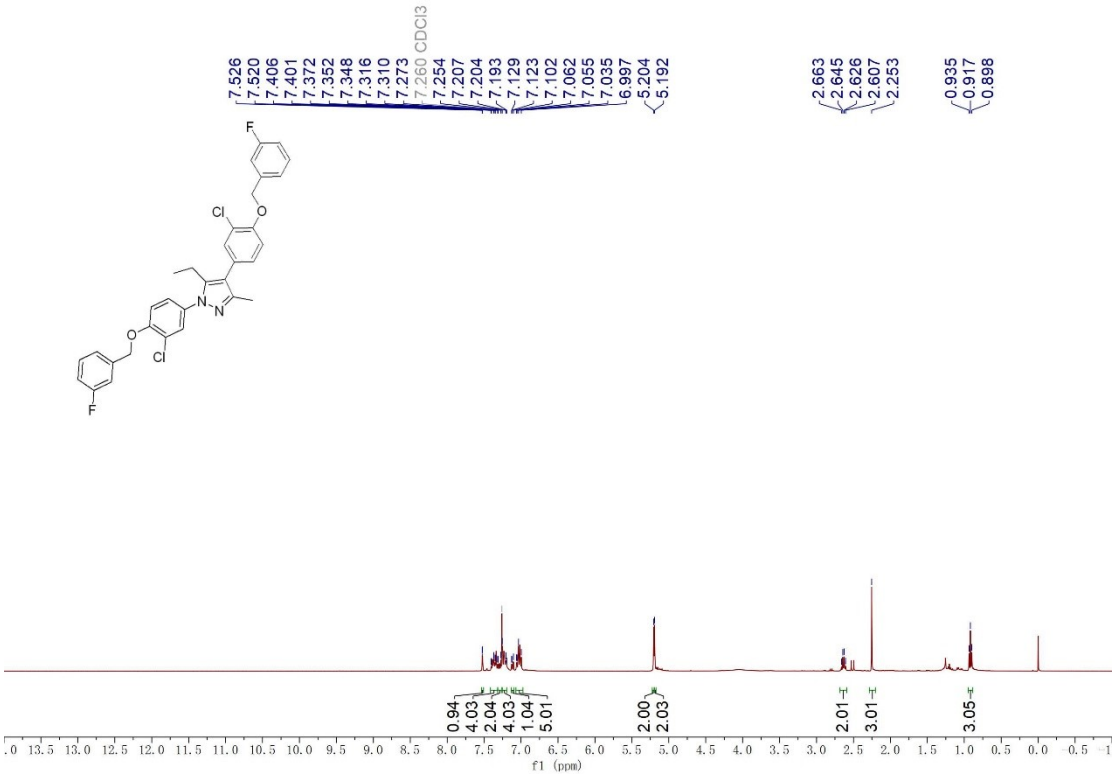


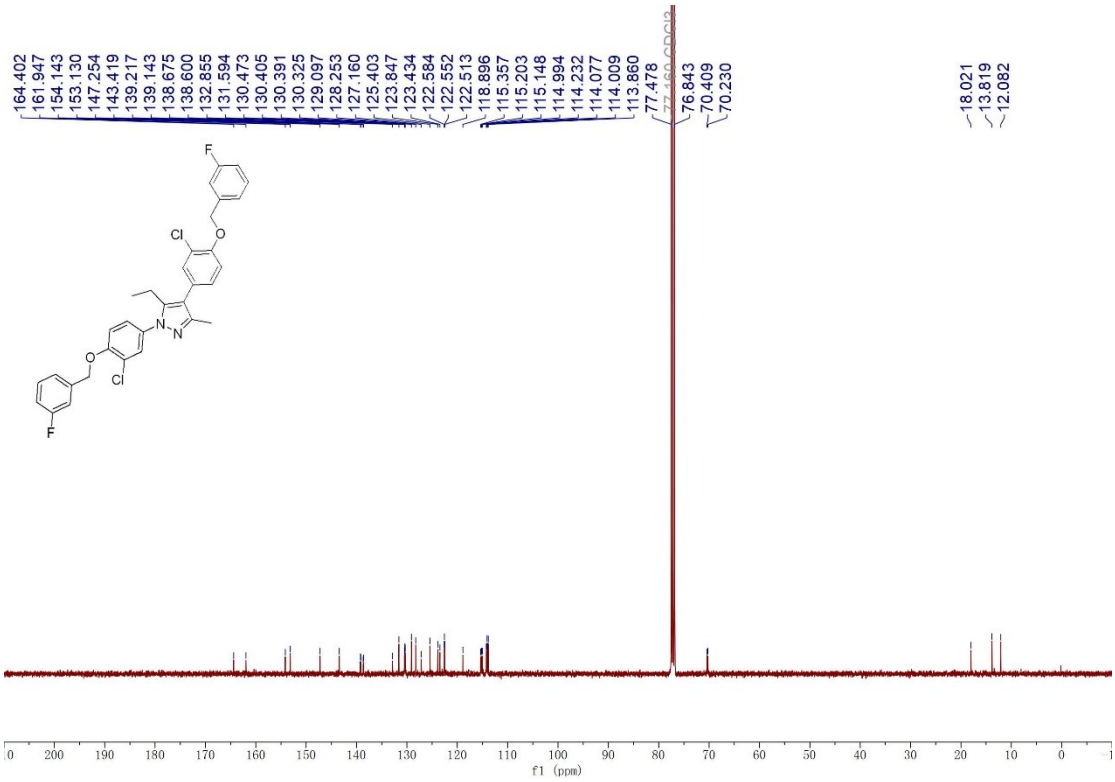
5-ethyl-3-methyl-1,4-di(naphthalen-2-yl)-1*H*-pyrazole **(3x)**





1,4-bis(3-chloro-4-((3-fluorobenzyl)oxy)phenyl)-5-ethyl-3-methyl-1*H*-pyrazole **(3y)**

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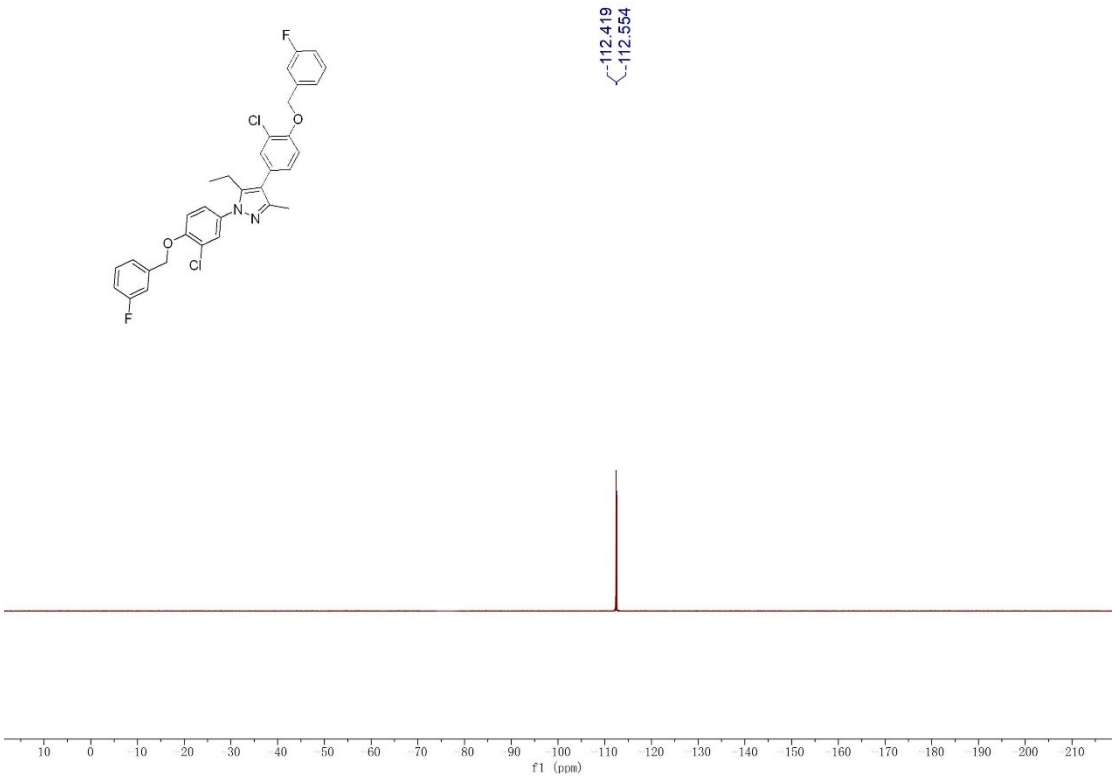
F
Cl
O
N
N
O
Cl
F
f1 (ppm)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F
Cl
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N
O
Cl
F
f1 (ppm)