Photoinduced alkylation of pyrazolones *via* β-scission of unstrained aliphatic alcohol derivatives

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Content

1 General Experiment Details

All required fine chemicals were used directly without purification unless stated otherwise. All air and moisture sensitive reactions were carried out under nitrogen atmosphere using standard Schlenk manifold technique. All solvents were bought from *J&K Scientific* as 99.9% purity under 4 Å molecular sieves. Other commercial reagents were purchased from Adamas, TCI, Aldrich, Bidepharm and Alfa. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates. Flash chromatography columns were packed with 200-300 mesh silica gel. NMR-spectra were recorded on Bruker AVANCE III HD-400 or 600 spectrometers. All spectral data was acquired at 295 K. Deuterated solvents were purchased from Adamas. ^{1}H and ^{13}C chemicals shifts (δ) are quoted in parts per million (ppm) against tetramethylsilane (TMS, δ = 0.00 ppm) and were internally referenced to residual $CDCl_3$ (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C) or DMSO (2.50 ppm for ^{1}H, 39.5 ppm for ^{13}C). ^{19}F chemicals shifts (δ) are quoted in parts per million (ppm) and were calibrated using absolute referencing to the ^{1}H NMR spectrum. Coupling constants (J) are reported in Hertz (Hz) to the nearest 0.1 Hz. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High-resolution mass spectra (HRMS) were recorded on a UPLC of Thermo Q Exactive Focus. Experimental data of crystallography was recorded on a Bruker D8 Photon II. UV-Vis absorption spectra were recorded using 1 cm quartz cuvettes on a Thermo Scientific NanoDrop 2000C spectrophotometer. Fluorescence spectra were recorded using 1 cm quartz cuvettes on a HORIBA Fluoromax-4 Spectrofluorometer at 25 ºC. Emission spectrum of the light source was measured on a RF-5301PC Spectrofluorophotometer. Cyclic voltammograms were obtained on a CHI 600E potentiostat. Yields refer to isolated materials of >95% purity, as determined by ^{1}H NMR analysis. Regioselectivity and diastereoselectivity ratio (d.r.) also determined by ^{1}H NMR analysis.

2 Standard Reaction Setup

The setup (shown below **Figure S1**) is employed to photochemical organic synthesis reaction, which is made up of separable base and reaction hole (PhotoSyn 3.0 reactor). The integrated light panel with certain wavelength can be embedded into the sliding groove of the base. Due to the hollow design, the reaction can be kept at an ideal temperature through cold or hot medium. In a typical reaction, Schlenk tube was inserted into the hole and the reaction mixture is irradiated under 10 W LEDs with 1.0 cm distance.

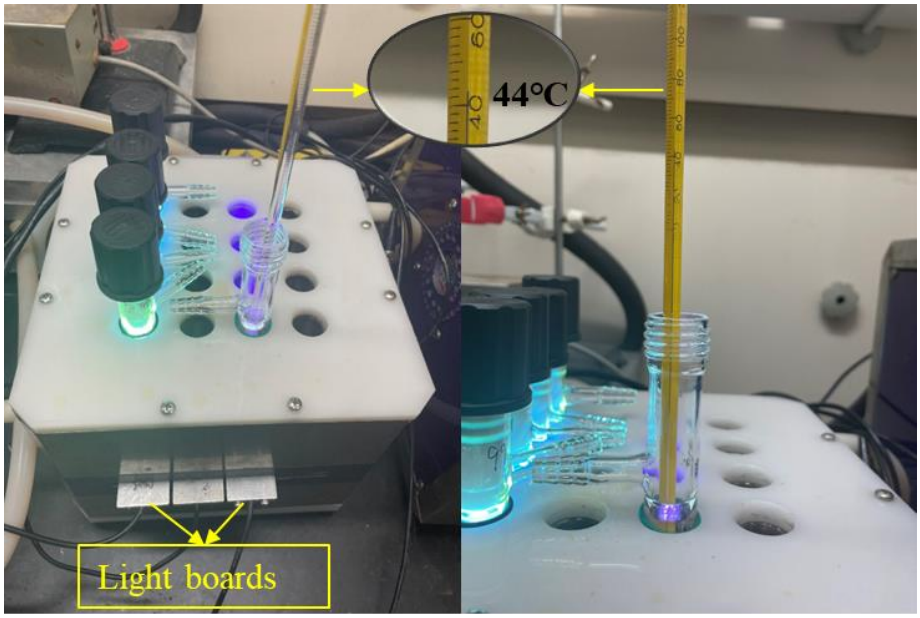


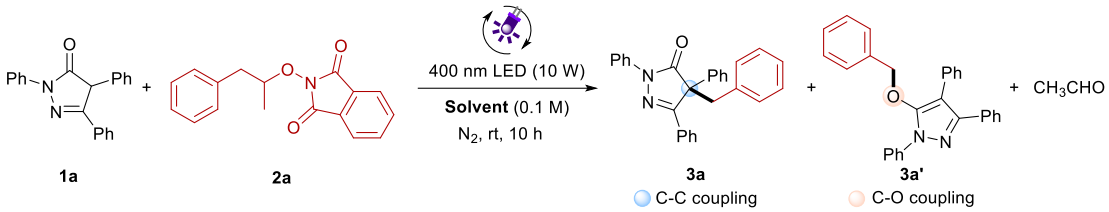
Figure S1. 16-hole parallel photoreactor (PhotoSyn 3.0)

3 Reaction Optimization and General Procedure

The oven-dried 10 mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone (0.05 mmol, 1.0 equiv.) and *N*-alkoxyphthalimides derivatives (0.1 mmol, 2.0 equiv.). Then, the solvent (0.05 M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction tube was inserted into the PhotoSyn 3.0 reactor and irradiated using a 10 W LED lamp (400 nm) at a specific temperature. Continuous circulating water at a specific temperature was introduced to ensure that the reaction is carried out at a specific temperature. Monitored by TLC until the completely consumption of pyrazolinone, the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times, the organic phase with water three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 50/1) to afford the product.

3.1 Reaction Optimization

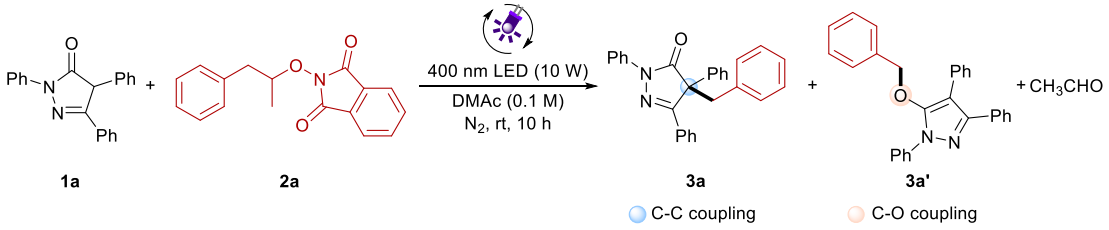
Table S1 Screening of solvents.



Entry	Solvent	Yield (%)
1	DMAc	54 (**3a**/**3a'** > 30:1)
2	1,4-dioxane	41 (**3a**/**3a'** = 2:1)
3	MeCN	Trace
4	$PhCF_3$	ND
5	DCM	Trace
6	DMF	30 (**3a**/**3a'** > 30:1)

Reaction condition: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), solvent (1.0 mL), 400 nm (10 W), rt, under N_2, 10 h, isolated yield. ND, not detected.

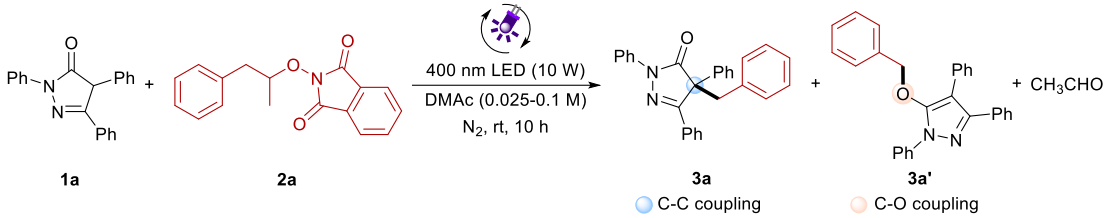
Table S2 Ratio of two substrates.



Entry	Ratio (**1a**: **2a**)	Yield (%)
1	1:1.2	48 (**3a**/**3a'** > 30:1)
2	1:1.5	51 (**3a**/**3a'** > 30:1)
3	1:2	56 (**3a**/**3a'** > 30:1)
4	1:3	56 (**3a**/**3a'** > 30:1)
5	1:4	49 (**3a**/**3a'** > 30:1)

Reaction condition: **1a** (0.1 mmol, 1.0 equiv.), **2a** (x equiv.), DMAc (1.0 mL), 400 nm (10 W), rt, under N_2, 10 h, isolated yield.

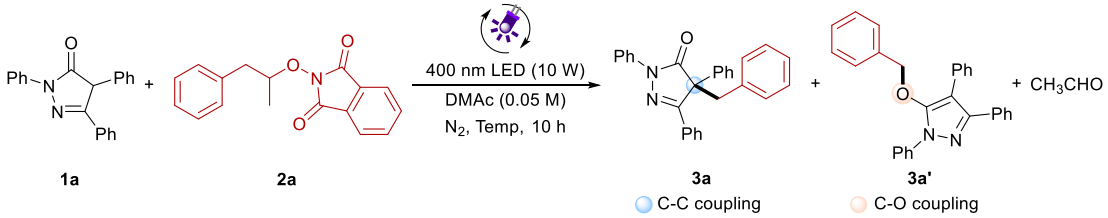
Table S3 Investigation of reaction concentration.



Entry	**1a** (x mmol)	Concentration	Yield (%)
1	0.1	0.1 M (1 mL)	54 (**3a**/**3a'** > 30:1)
2	0.1	0.05 M (2 mL)	59 (**3a**/**3a'** > 30:1)
3	0.05	0.05 M (1 mL)	68 (**3a**/**3a'** > 30:1)
4	0.05	0.025 M (2 mL)	68 (**3a**/**3a'** > 30:1)

Reaction condition: **1a** (x mmol, 1.0 equiv.), **2a** (y mmol, 2.0 equiv.), ratio (**1a**:**2a**=1:2), DMAc (z M), 400 nm (10 W), rt, under N_2, 10 h, isolated yield. ND, not detected.

Table S4 Investigation of temperature.

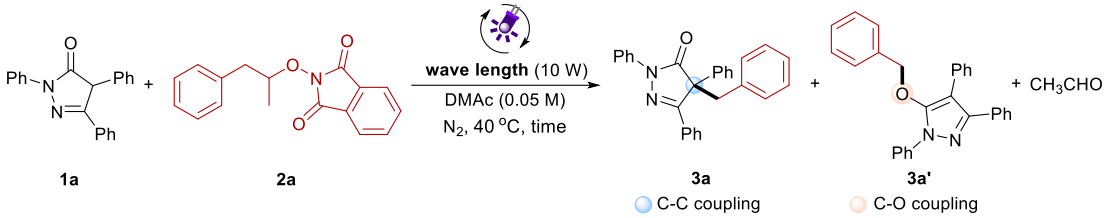


Entry	Temp (°C)	Yield (%)
1	rt	66 (**3a**/**3a'** > 30:1)
2	40	87 (**3a**/**3a'** > 30:1)
3	60	64 (**3a**/**3a'** > 30:1)

Reaction condition: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.1 mmol, 2.0 equiv.), DMAc (1.0 mL), 400 nm (10 W), rt, under N_2, 10 h, isolated yield.

***Note**: For entry 2, the yield is the average of three times.*

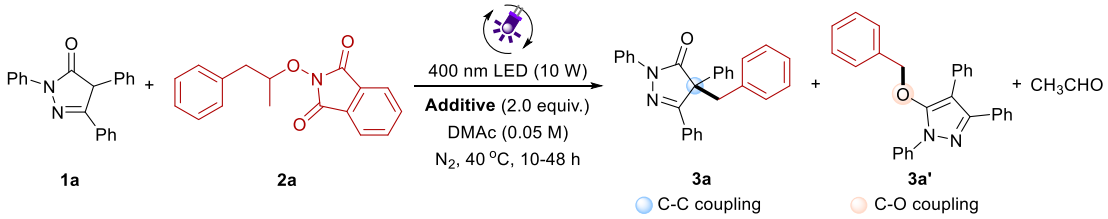
Table S5 Investigation of light sources.



Entry	wave length	Time (h)	Yield (%)
1	395 nm	10	81 (**3a**/**3a'** > 30:1)
2	400 nm	10	87 (**3a**/**3a'** > 30:1)
3	410 nm	36	72 (**3a**/**3a'** > 30:1)
4	420 nm	48	60 (**3a**/**3a'** > 30:1)
5	430 nm	60	24 (**3a**/**3a'** > 30:1)
6	white LEDs	20	78 (**3a**/**3a'** > 30:1)
7	460 nm	48	0

Reaction condition: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.1 mmol, 2.0 equiv.), DMAc (1.0 mL), 400 nm (10 W), 40 °C, under N_2, 10-60 h, isolated yield.

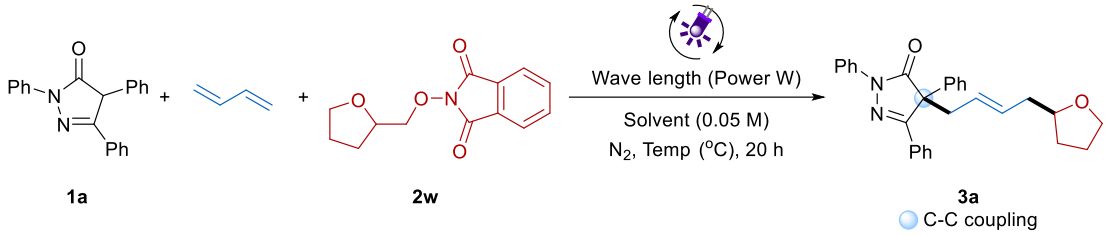
Table S6. Investigation of additives.



Entry	Additive (2.0 equiv.)	Yield (%)
1	none	87 (**3a**/**3a'** > 30:1)
2	DMAP	63 (**3a**/**3a'** > 30:1)
3	DIPEA	65 (**3a**/**3a'** > 30:1)
4	Cs_2CO_3	0
5	(R)-BNDHP	90 (**3a**/**3a'** = 3.33:1)

Reaction condition: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.1 mmol, 2.0 equiv.), additive (2.0 equiv.), DMAc (1.0 mL), 400nm (10 W), 40 °C, under N_2, 10-48 h, isolated yield.

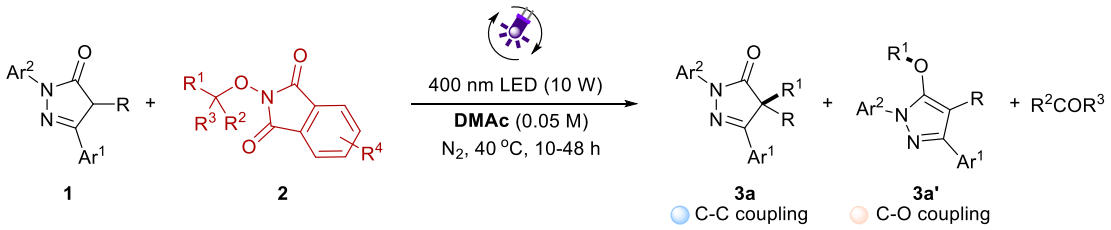
Table 7S. Optimization of three-component reaction.



Entry	Solvent (1 mL)	Wave length (nm)	Power (W)	Temp (°C)	Yield (%)
1	DMAc	400	10	40	29
2	DMSO	410	10	40	40
3	DMSO	410	20	40	41
4	DMSO	410	10	rt	48

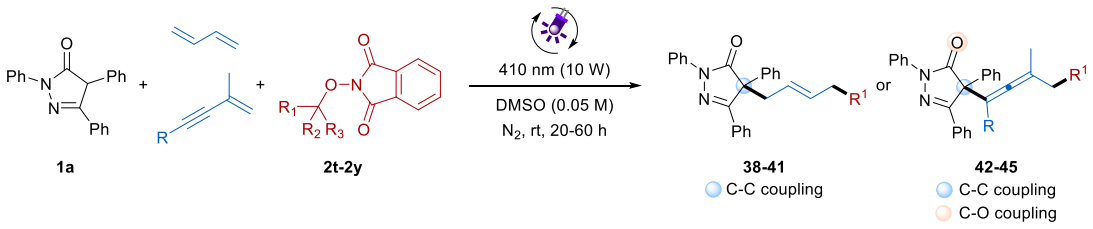
Reaction condition: **1a** (0.05 mmol, 1.0 equiv.), **2v** (0.1 mmol, 2.0 equiv.), 1,3-butadiene (2.0 equiv.), solvent (1.0 mL, 0.05 M), wave length (Power W), Temp (°C), under N_2, 15 h, isolated yield.

3.2 General procedure for two-component coupling reaction



Procedure A (**When R^1 is the primary, secondary or tertiary benzyl group**): The oven-dried 10 mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone (0.05 mmol, 1.0 equiv.) and *N*-alkoxyphthalimides derivatives **2**(0.1 mmol, 2.0 equiv). Then, DMAc (0.05M) was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction tube was inserted into the PhotoSyn 3.0 reactor and irradiated using a 400 nm LED lamp (10 W) at 40 °C for 10-20 h. Monitored by TLC until the completely consumption of pyrazolinone, the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times, the organic phase with water three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 50/1) to afford the product.

3.2 General procedure for three-component coupling reaction



Procedure B (**When R^1 is the alkyl group**): The oven-dried 10 mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.05 mmol, 1.0 equiv.) and *N*-alkoxyphthalimides derivatives **2t-y** (0.1 mmol, 2.0 equiv). Then, DMSO (0.05 M) and 1,3-butadiene (50 uL, 0.1 mmol, 2.0 equiv, 2 mol/L in THF), was added in glove box. The tube was sealed with a screw cap and took out from glove box. The reaction tube was inserted into the PhotoSyn 3.0 reactor and irradiated using a 410 nm LED lamp (10 W) at 25 ºC for 20-60 h. Monitored by TLC until the completely consumption of pyrazolinone, the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times, the organic phase with water three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 30/1) to afford the product.

4.The Application of the Reaction

4.1 Gram-scale experiment

A 50 mL round bottom flask was equipped with a magnetic stir bar, 2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one **1a** (1.250 g, 4.0 mmol), 2-((1-phenylpropan-2-yl)oxy)isoindoline-1,3-dione **2a** (2.248 g, 8.0 mmol) was added. In glove box, dry DMAc (0.1 M, 40 mL) was added. The colorless clear solution showed blue-green brightness under purple light. Then, the round bottom flask was irradiated by 395-400 nm LED lamp (45 W) for 15 h. The temperature range of mixture was 30-40 ºC. Monitored by TLC until the completely consumption of pyrazolinone, the mixture was diluted with water, then extracted with ethyl acetate (EA) for three times, the organic phase with water three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica (petroleum ether/EA = 50/1) to afford the product **3a** and **3a'** (1.014 g, 63% yield).

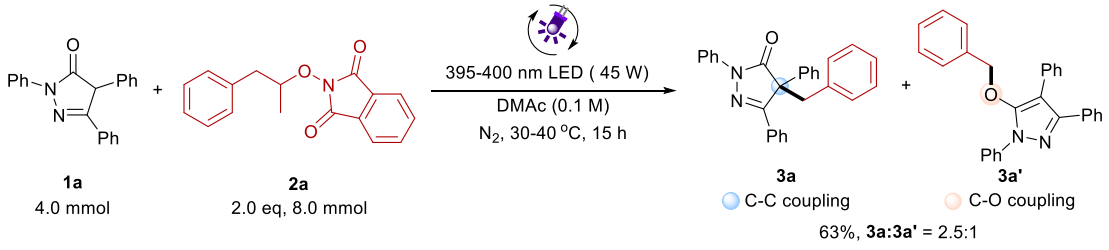
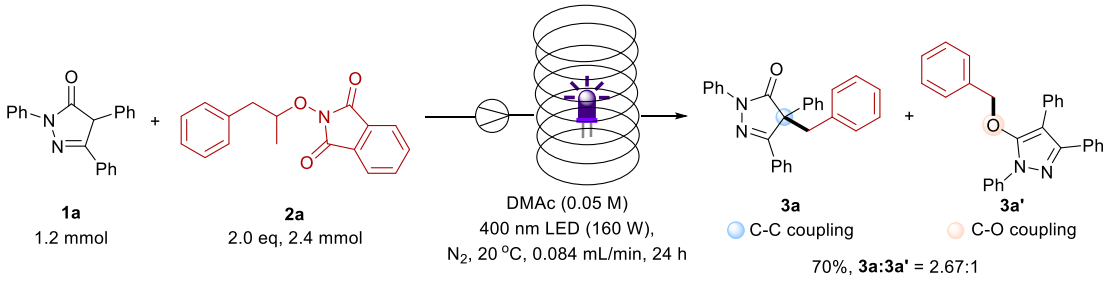


Figure S2. General procedure for gram-scale experiment.

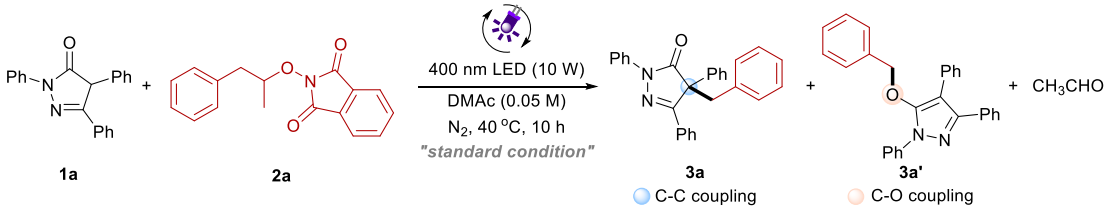
4.2 General procedure for continuous flow photoreactions

Low Flow Reactor (LFR): the total interal volume was 14.8 mL. Twelve 400 nm LED lights (Rated power per lamp 20 W) were placed perpendicular to the LFR with 2 cm distance. 5 °C circulating coolant kept on during the reaction, and the temperature of the reactors was constantly monitored during the reaction (~20 °C). An oven-dried round bottom flask (250 mL) was charged with the pyrazolone **1a** (1.250 g, 4.0 mmol) and *N*-phthalimide ethers **2a** (8.0 mmol, 2.248 g, 2 equiv.). Then, anhydrous DMAc (80 mL) was added in glove box. The round bottom flask was taken out of the glove box and LFR pipeline was degassed by N_2 sparging for 10 min. The feed solution was loaded in a flask and kept under an N_2 atmosphere. The solution was delivered to the flow reactor through a peristaltic pump (Chuang Rui-YZ1515X) set at 0.084 mL/min. The solution was irradiated with 400 nm LED (10 W x 4) at ~20 °C and collected the reaction solution. After complete consumption of pyrazolone, the mixture was diluted with water (100 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 50/1) to afford the product **3a** and **3'a** (1.119 g, 70%).



5. Mechanistic Studies

5.1 Control experiments.

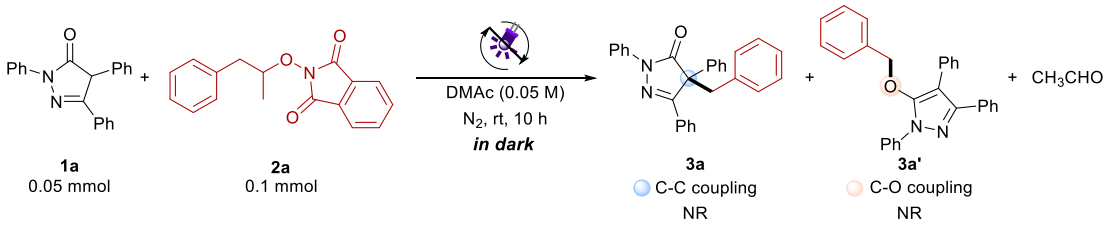


Entry	Deviation from standard conditions	Yield (%)
1	in dark	0
2	in dark 100 °C	0
3	Air instead of N_2	48 (**3a**/**3a'** > 30:1)
4	Add 5.0 eq H_2O	87 (**3a**/**3a'** > 30:1)
5	Add 2.0 eq TEMPO	0

Reaction condition: **1a** (0.05 mmol, 1.0 equiv.), **2a** (0.1 mmol, 2.0 equiv.), Additive (2.0 equiv.), DMAc (1.0 mL), 400 nm (10 W), 40 ℃, under N_2, 10-48 h, isolated yield.

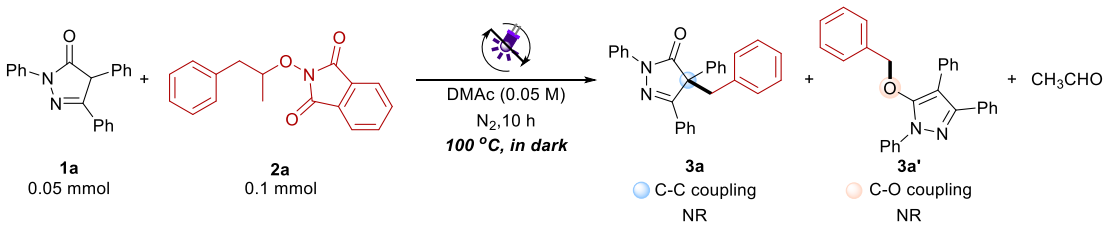
Note: *If PhthNH was contained in product, pretreatment was employed upon completion according to reported literature. After completion, mixture was diluted with Ethyl Acetate (15 mL), and then washed with K_2CO_3 (10% aq.) for three times.*[1] *Organic layer was dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was next purified by flash column chromatography.*

Reaction in dark



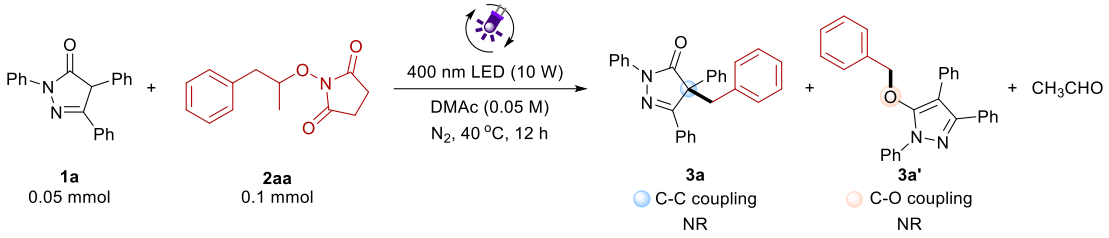
The oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.05 mmol, 1.0 equiv.) and *N*-alkoxyphthalimide derivative **2a** (0.1 mmol, 2.0 equiv.). Then, the dry DMAc (0.05 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box, and stirred in the dark for 10 h. TLC analysis revealed that no reaction occurred.

Reaction in dark at 100 ℃



An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.05 mmol, 1.0 equiv.) and *N*-alkoxyphthalimide derivative **2a** (0.1 mmol, 2.0 equiv.). Then, the dry DMAc (0.05 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box, and stirred in the dark for at 100 ℃ for 10 h. TLC analysis revealed that no reaction occurred, indicating that the reaction does not occur under thermal reaction.

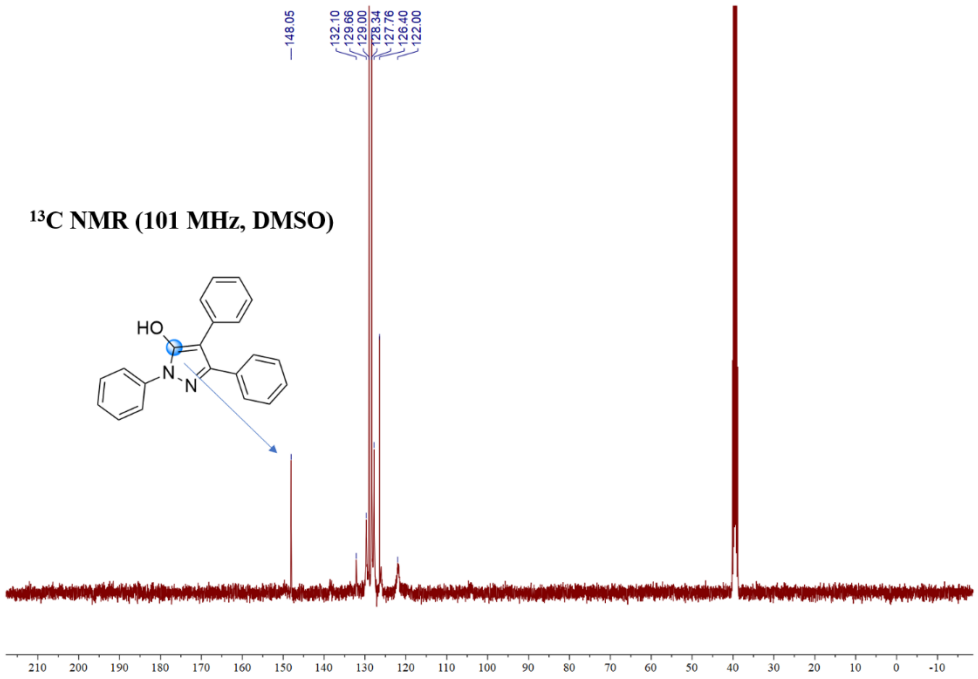
Investigated the effects of N-alkoxysuccinimide derivative 2aa without conjugated groups on the reaction

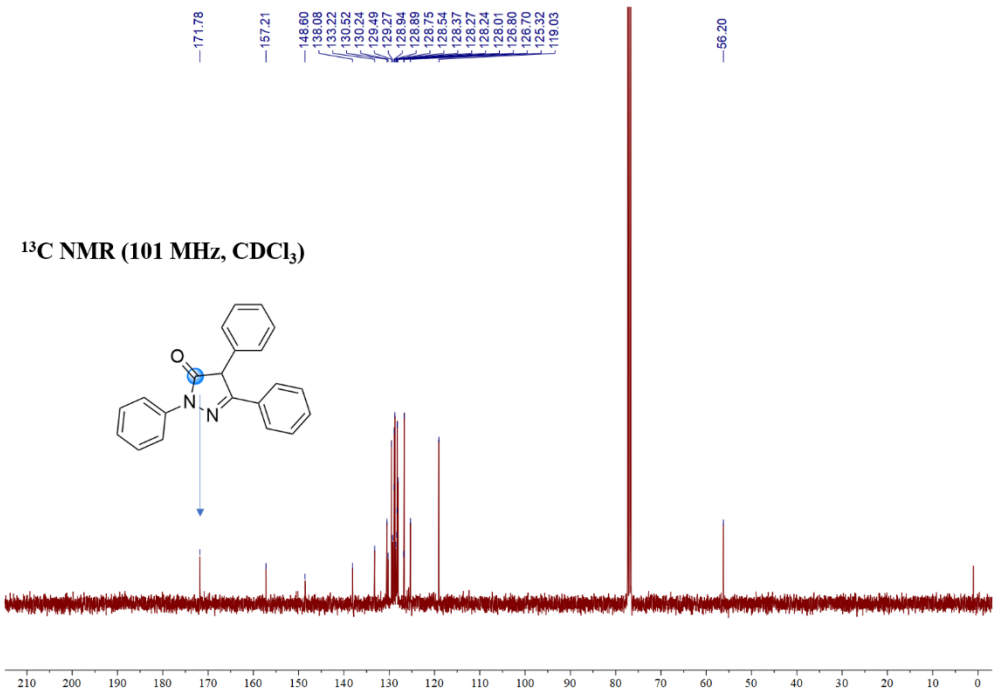


An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.05 mmol, 1.0 equiv.) and N-alkoxyphthalimide derivative **2aa** (0.1 mmol, 2.0 equiv.). Then, the dry DMAc (0.05M) was added in glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 400 nm LED lamp (10 W) at 40 °C for 12 h. TLC analysis revealed that no reaction occurred, indicating that conjugated groups with benzene rings are necessary for the reaction.

5.2 Solvent effect of pyrazolinone 1a

According to the ^{13}C-spectrum obtained from two solvents $CDCl_3$ and DMSO, in polar solvents, **1a** exhibits an enol like state.





5.3 UV-vis absorption spectrum

UV-Vis absorption spectra experiment was measured on a Thermo Scientific NanoDrop 2000C spectrophotomete. Tests were proceeded in DMAc (1×10^{-3} M). Base = TBAPhthN.

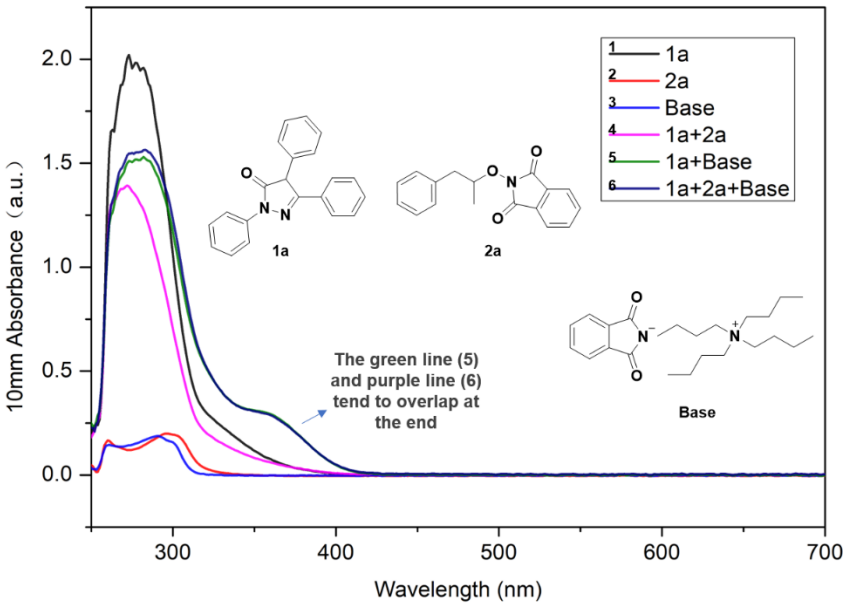


Figure S3. UV-Vis absorption spectra of pyrazolinone **1a** and *N*-alkoxyphthalimide derivative **2a** were measured with DMAc (1×10^{-3} M).

Separate test of all components demonstrated that corresponding absorption bands are all situated in ultraviolet region (below 400 nm), simply mixing two substrates came out to similar results without redshift. This indicates that there is no EDA complex between two substrates. It's worth mentioning that, there was a red shift when base was added to pyrazolinone **1a** (green line). At the

same time, the addition of substrate **2a** didn't change. These results indicated that there was no EDA complex between the three.

5.4 NMR Titration Experiments.

Solutions containing equal molar concentrations of pyrazolinone **1a** (0.2 M in DMSO) and N-alkoxyphthalimide derivative **2a** (0.2 M in DMSO) were prepared and mixed to cover **1a**/**2a** ratio from 0%, 10%, 20%, 40%, 50%, 60%, 80%, 90%, 100% **1a**.

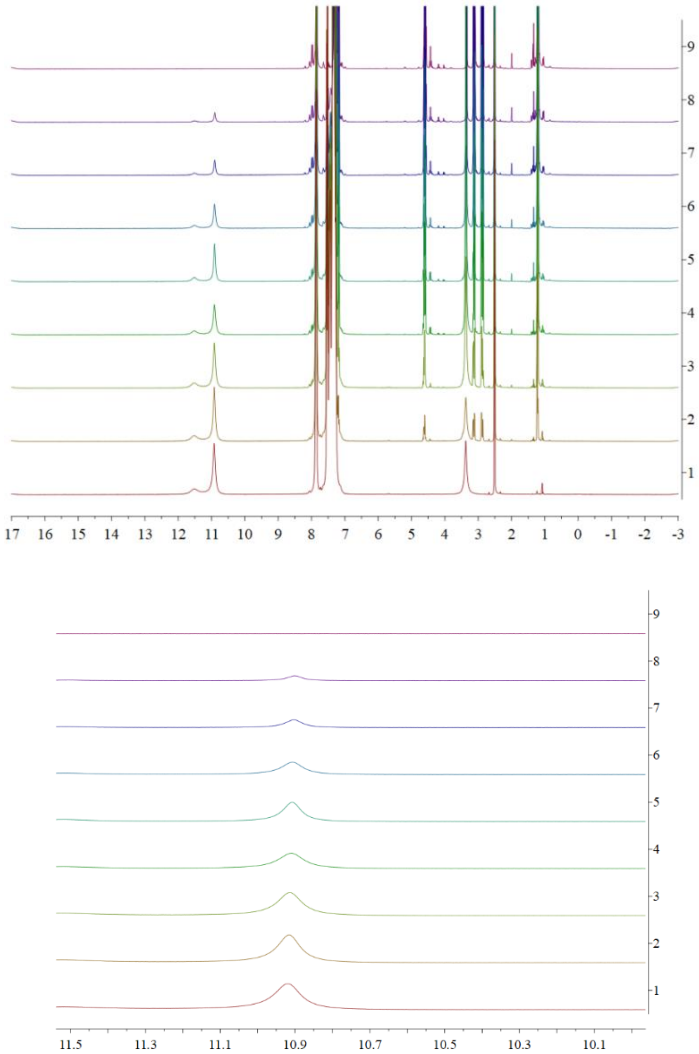


Figure S4. ^{1}H NMR titration between pyrazolinone **1a** and *N*-alkoxyphthalimide derivative **2a**.

In ^{1}H NMR titration experiments, the characteristic hydrogen did not shift significantly, which indicated that there is no interaction between **1a** and **2a**.

5.5 Fluorescence Spectra

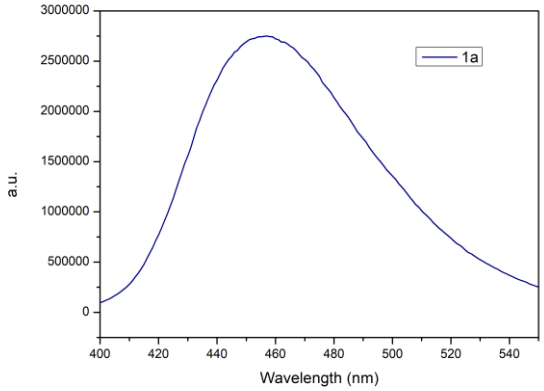


Figure S5. Fluorescence Spectra of pyrazolinone **1a** in DMAc ($c = 1 \times 10^{-4}$ M).

emission wavelength: 455 nm

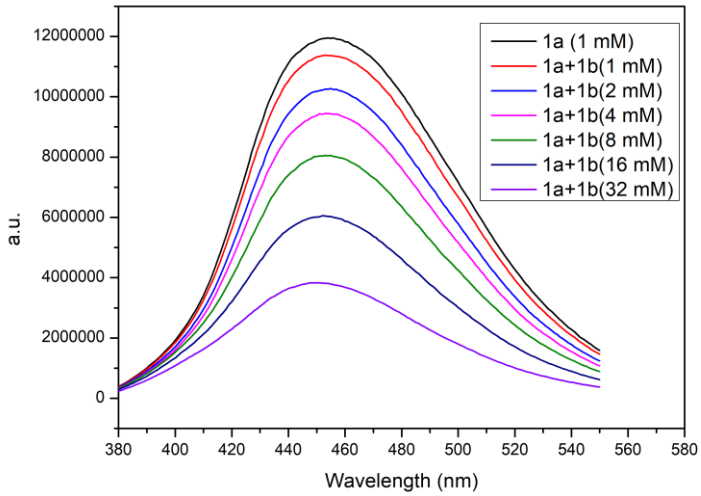


Figure S6. Fluorescence quenching of the emission of pyrazolinone **1a (**1×10^{-4} M in DMAc) in the presence of increasing amounts of **2a** at room temperature. Excitation wavelength: 360 nm.

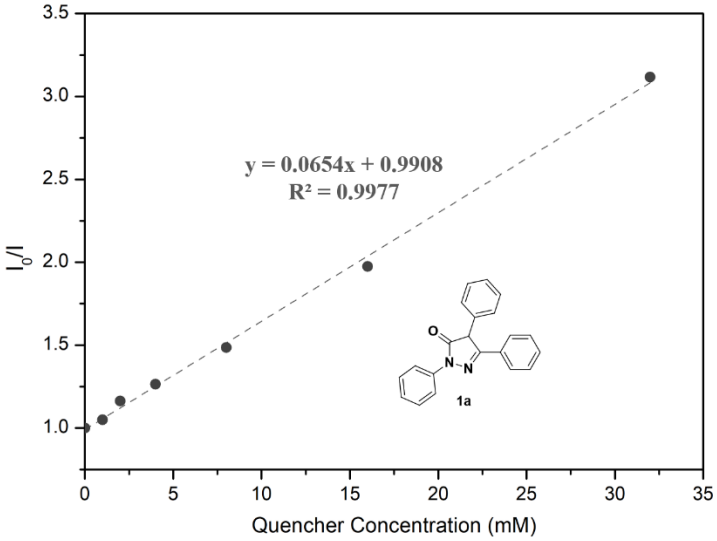


Figure S7. Stern-Volmer plots of quenching of **1a** with **1b** in DMAc at room temperature.

5.6 Cyclic voltammetry studies

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature (N_2). The working electrode was a platinum disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge.

Preparation of sample **1a**: 5 mL of DMF containing 0.1 M *n*Bu_4NPF_6 were poured into the electrochemical cell in all experiments. Concentration of a sample: 0.05 M. The scan rate is 0.1 V/s, ranging from 0 V to 2.0 V. The peak potentials vs. Ag/AgCl for used.

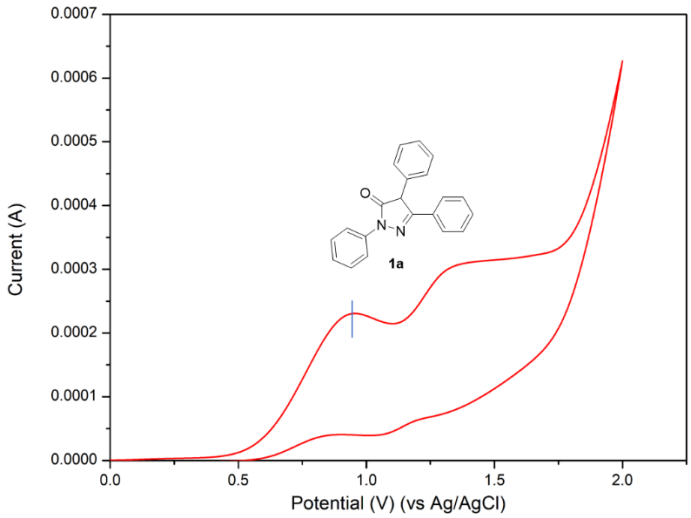


Figure S8. Cyclic voltammegram for pyrazolinone **1a** (0.05 M) in (0.1 M) $TBAPF_6$ in DMF.

Ep (**1a**) = +0.955 V vs. Ag/ AgCl in DMF

Preparation of sample **2a**: 5 mL of DMF containing 0.1 M nBu$_4$NPF$_6$ were poured into the electrochemical cell in all experiments. Concentration of a sample: 0.05 M. The scan rate is 0.1 V/s, ranging from 0 V to - 3.0 V. The peak potentials vs. Ag/AgCl for used.

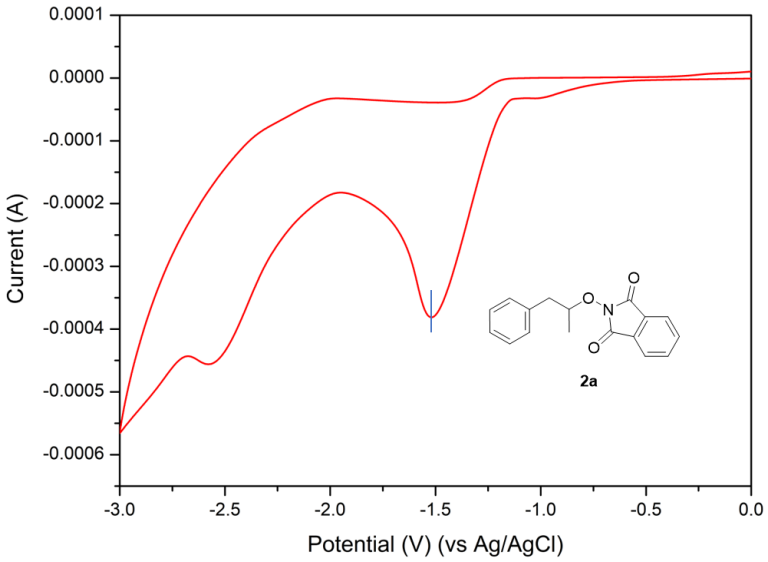


Figure S9. Cyclic voltammegram for *N*-alkoxyphthalimide **2a** (0.05 M) in (0.1 M) TBAPF$_6$ in DMAc.

E$_p$ (2a) = **-**1.5 V vs. Ag/ AgCl in DMAc

Based on the data obtained from the UV-Vis, fluorescence spectra and the cyclic voltammetry, RehmWeller equation[2] described below afforded the approximated redox potential value of the photoexcited **II***.

Rehm-Weller equation:

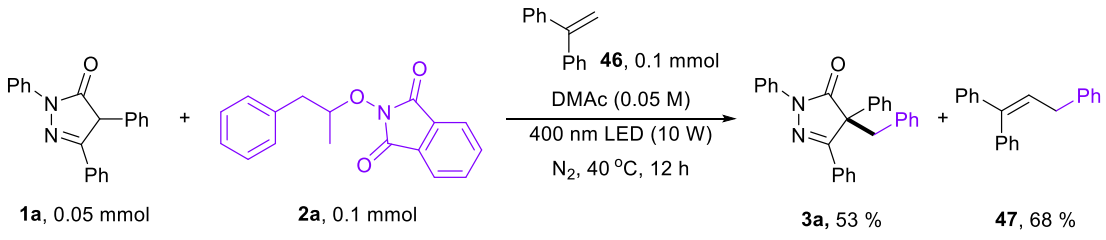
$$E\ (\mathbf{II}^{+\bullet}/\mathbf{II}^*) = E\ (\mathbf{II}^{+\bullet}/\mathbf{II}) - E_{oo}\ (\mathbf{II}^*/\mathbf{II})$$

$$E\ (\mathbf{II}^{+\bullet}/\mathbf{II}^*) = 0.955 - 2.95 = -1.995\ V \approx -2.0\ V\ (vs.\ Ag/AgCl)$$

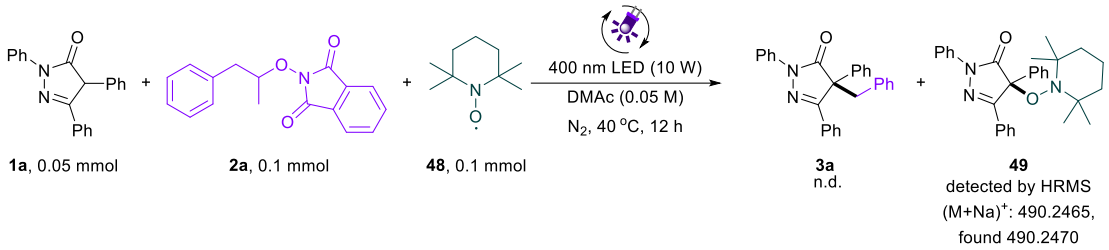
Therefore, we used an anodic half peak potential $E_{pa/2}$ (= +0.955 V vs. Ag/AgCl) as E (**II**$^{+\bullet}$/**II**). The excited state energy of **II** E_{00} (**II***/**II**), could be estimated from the tail of the wavelength tail of the UV/Vis absorption spectra (420 nm), which converted to 2.950 eV and used as E_{00} (**II**$^{+\bullet}$/**II***).

5.7 Mechanism experiment

5.7.1 Reaction in the presence of 1,1-diphenylethylene and TEMPO as the radical scavengers

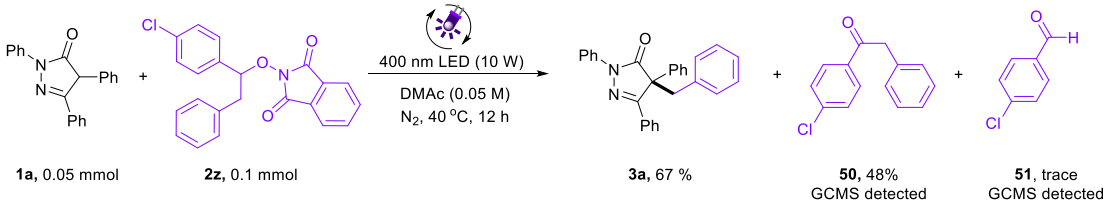


The oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.1 mmol, 1.0 equiv.) and *N*-alkoxyphthalimide **2a** (0.2 mmol, 2.0 equiv.). Then, the DMAc (0.05 M) and 1,1-diphenylethylene (0.2 mmol, 2.0 equiv.) were added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 400 nm LED lamp (10 W) for 12 h. After complete consumption of pyrazolinone, the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether, 18.4 mg, 68%) provided 1,1-diphenylethylene-trapped products **47**. Then by flash column chromatography on silica gel (petroleum ether/ethyl acetate 50:1, 21.4 mg, 53%) provided adduct **3a**.



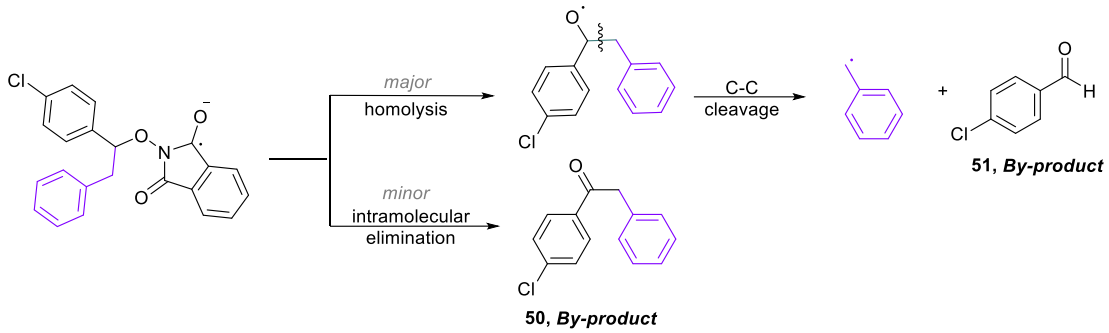
An oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.05 mmol, 1.0 equiv.) and *N*-alkoxyphthalimide **2a** (0.1 mmol, 2.0 equiv.) and TEMPO **48** (0.1 mmol, 2.0 equiv.). Then, the dry DMAc (0.05M) was added in glove box. The tube was sealed with a screw cap and took out form glove box. The reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 400 nm LED lamp (10 W) for 12 h. After complete consumption of pyrazolinone, the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. TLC analysis revealed that no radical-cross-coupling product **3a** was formed, implying that radical reactions are inhibited by radical trapping agents TEMPO.

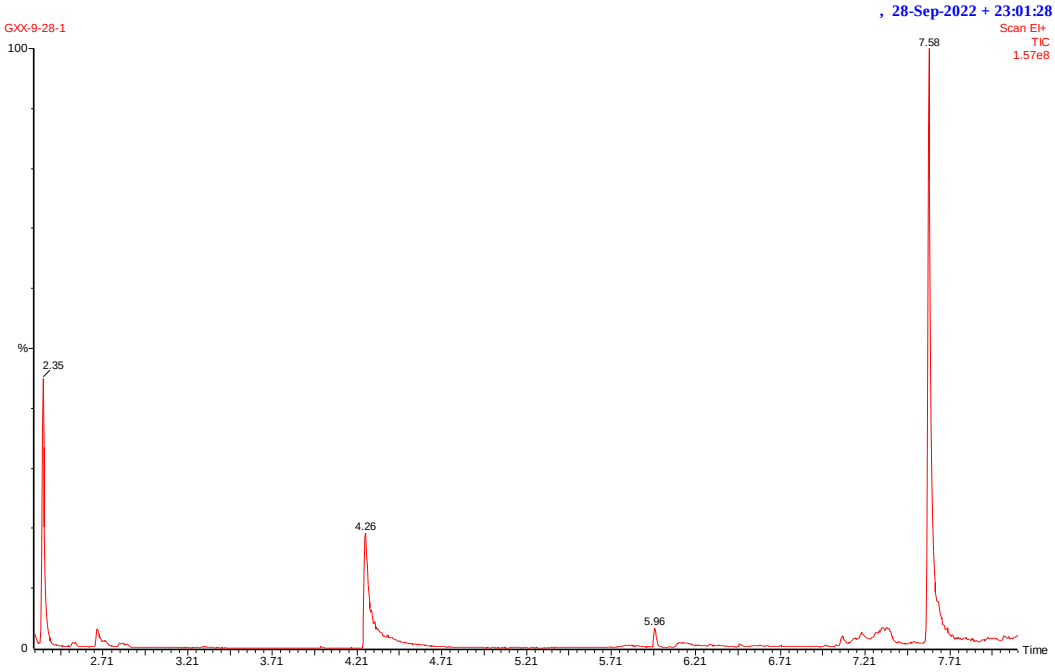
5.7.2 Verify the existence of alkoxy radicals and aldehyde removal process by capturing by-products



The oven-dried 10-mL Schlenk tube equipped with a stirrer was charged with the pyrazolinone **1a** (0.1 mmol, 1.0 equiv.) and *N*-alkoxyphthalimide **2z** (0.2 mmol, 2.0 equiv.). Then, the DMAc (0.05 M) was added in glove box. The tube was sealed with a screw cap and took out form glove box. The

reaction mixture was inserted into the PhotoSyn 3.0 reactor and irradiated using a 400 nm LED lamp (10 W) for 12 h. After complete consumption of pyrazolinone, we used GCMS to detect the reaction liquid and obtained two products **50** and **51 (As shown below)**. Then we conduct post-processing, the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification of the crude mixture by flash column chromatography on silica gel (petroleum ether, 11.1 mg, 48%) provided **50**. Then by flash column chromatography on silica gel (petroleum ether/ethyl acetate 50:1, 27.0 mg, 67%) provided adduct **3a**.





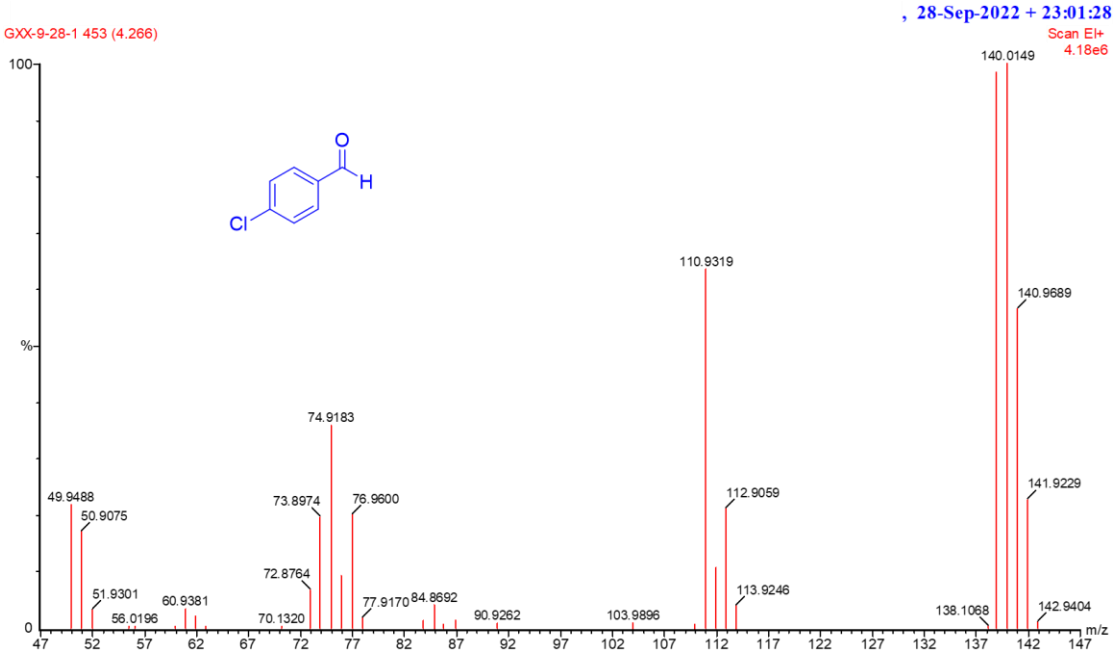


Figure S10 by-product **51**

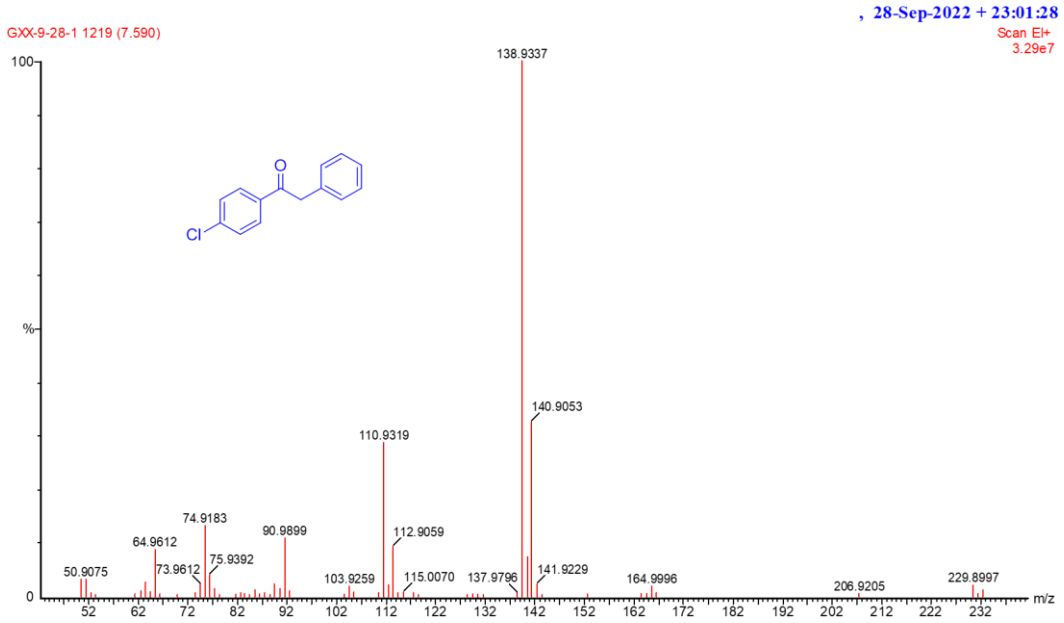
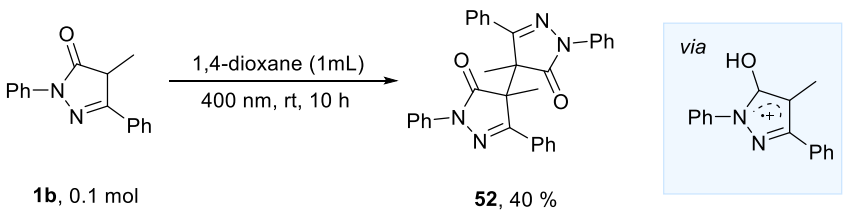


Figure S11 by-product **50**

5.7.3 Verify the presence of self-coupling products



1b, 0.1 mol

52, 40 %

The self-coupling product **52** was obtained in 40% yield when **1b** was subjected to the reaction without adding *N*-alkoxyphthalimide **2**, suggesting that the pyrazolone radical intermediate was generated in the transformation.

5.7.4 Increasing trend of yield with different time light illumination under standard conditions

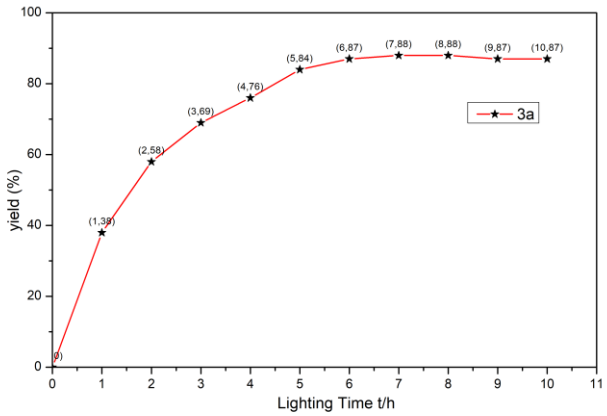


Figure S12 Reaction kinetics curve

The oven-dried 50 mL round bottom flask equipped with a stirrer was charged with the pyrazolinone **1a** (0.11 mmol, 1.0 equiv.) and *N*-alkoxyphthalimide **2a** (0.22 mmol, 2.0 equiv). Then, the dry solvent DMAc (22 mL, 0.05 M) was added in glove box. After forming a well-mixed and uniform colorless transparent liquid, take 1mL and distribute it into 20 oven-dried 10 mL Schlenk tube equipped with a stirrer, leaving 2 ml of reaction solution. The tube was sealed with a screw cap and took out from glove box. The reaction tube was inserted into the PhotoSyn 3.0 reactor and irradiated using a 400 nm LED lamp (10 W). Take 2 reactions every 1 hour. Procedure workup: the mixture was diluted with water (15 mL), then extracted with ethyl acetate (EA) for three times, the organic phase with water three times. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/EA = 50/1) to afford the product.

5.7.5 Light on/off experiments

The light on/off experiments shown that the product generation was blocked immediately when the light was turned off and resumed efficiently when turned on, indicating that constant light irradiation is essential for this transformation and the chain reaction was unlikely.

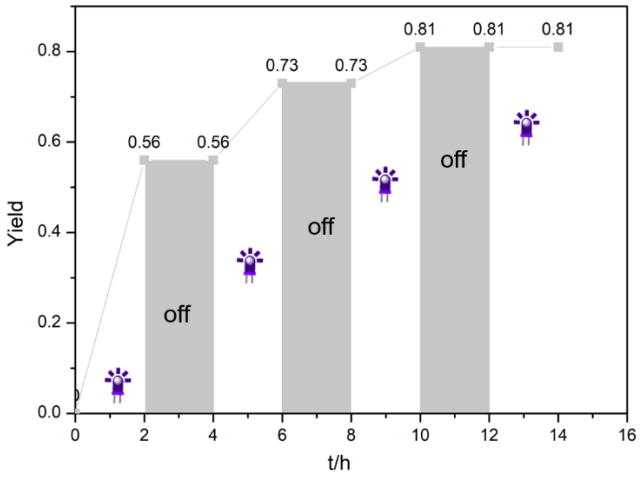


Figure S13. Light on/off experiments

5.7.6 Quantum Yield Determination

The photon flux set by the LED (λ = 400 nm, 1 W) was determined using the standard potassium ferricoxalate photometric method.

A ferrioxalate actinometer solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in the Handbook of Photochemistry.

1. Potassium ferrioxalate solution: 294.8 mg of potassium ferrioxalate and 139 μL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water.

2. Buffer solution with Phenanthroline: 20 mg 1,10-phenanthroline, 2.5 g of NaOAc and 400 μL of sulfuric acid (96%) were added to a 50 mL volumetric flask, and filled to the mark with water.

Both solutions were stored in the dark.

1.0 mL of the 0.0156 M potassium ferric oxalate solution was added to a flask containing a stirring bar. Then, the solution was irradiated for 0 s, 2 s, 5 s. Immediately after irradiation, the buffer solution with Phenanthroline (2.5 mL) was added to the cuvette and the mixture and stired in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. Take 100 uL the mixture and add water to obtain 1mL solution. The solution was transferred to a quartz cuvette (1.0 cm path length) and the absorbance at λ = 510 nm was measured by UV/Vis spectroscopy (**Figure S14**).

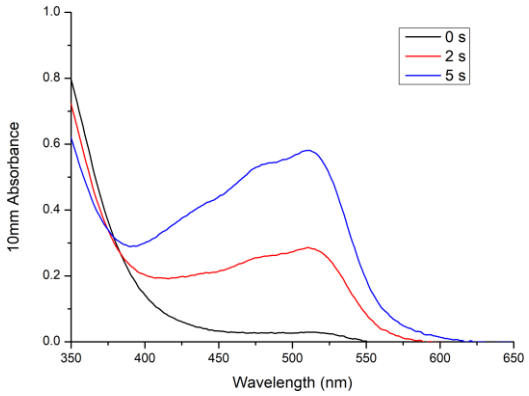


Figure S14. UV/Vis spectra of potassium ferric oxalate/1,10-phenanthroline solutions

The number of moles of Fe^{2+} produced by light irradiation was calculated using:

$$mol\ Fe^{2+} = \frac{V_1\, V_3 \Delta A\ (510\ nm)}{V_2\ l\varepsilon\ (510\ nm)}$$

Where

V_1 = the volume of potassium ferric oxalate solution irradiated (1.0×10^{-3} L).

V_2 = the volume of the solution taken for measurement of the Fe^{2+} ions (100 ul = 1.0×10^{-4} L).

V_3 = the final volume of solution after complexation with 1,10-phenanthroline (3.5×10^{-3} L).

ΔA (510 nm) = the absorbance difference at λ = 510 nm between the irradiated solution and the solution kept in dark.

l = the optical path length of the cuvette (1.0 cm).

ε (510 nm) = the molar absorption coefficient of the $Fe(phen)_3^{2+}$ complex at λ = 510 nm (1.11×10^4 L mol^{-1} cm^{-1}).

t	ΔA	$mol\ Fe^{2+}$
2s	0.257	8.18×10^{-6}
5s	0.552	1.76×10^{-5}

The moles of Fe^{2+} were plotted as a function of time (Figure. S15)

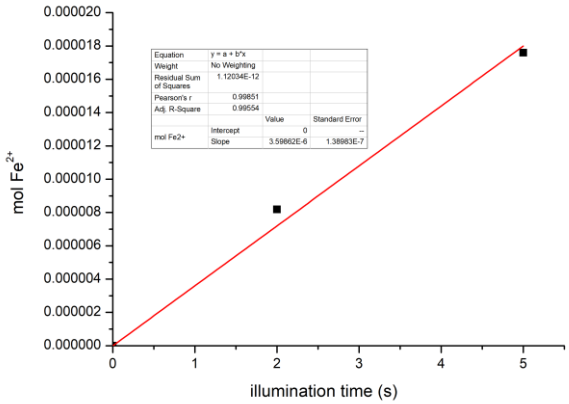


Figure S15. The molar number of Fe^{2+} as a function of time

The photon flux was then calculated using:

$$\text{photon flux} = \frac{mol\ Fe^{2+}}{\emptyset t(1-10^{-A})}$$

Where

$\emptyset$ the quantum yield of the potassium ferric oxalate in room temperature at 400 nm is 1.13.

t = the irradiated time(s).

A = the potassium ferric oxalate absorbance at 400 nm, which was measured placing 1 mL of the solutionin a cuvette which path length is 1 cm by UV/Vis spectrophotometry.

We obtained an absorbance value of 2.055.

$$\text{photon flux} = \frac{4.0 \times 10^{-6}}{1.13 \times (1-10^{-2.055})} = 3.6 \times 10^{-6}$$

The average photon flux was thus calculated to be 3.6×10^{-6} einsteins s^{-1}.

Determination of the reaction quantum yield:

To an oven-dried 10-mL Schlenk tube equipped with a stirrer bar were added pyrazolone **1a** (0.05 mmol, 15.6 mg) and N-alkoxyphthalimide **2a** (0.2 mmol, 2.0 equiv). In glove box, dry DMAc were added. Continuous circulating water was introduced to ensure that the reaction is carried out at room temperature. The reaction mixture was irradiated using 1 W LEDs (λmax = 400 nm) for 2 hours. The yield of product was determined by ^{1}H NMR, using benzyl benzoate an internal standard, 3.7% yield of product was produced.

$$\Phi = \frac{\text{Mol product}}{\text{flux} \cdot \text{t} \cdot \text{f}}$$

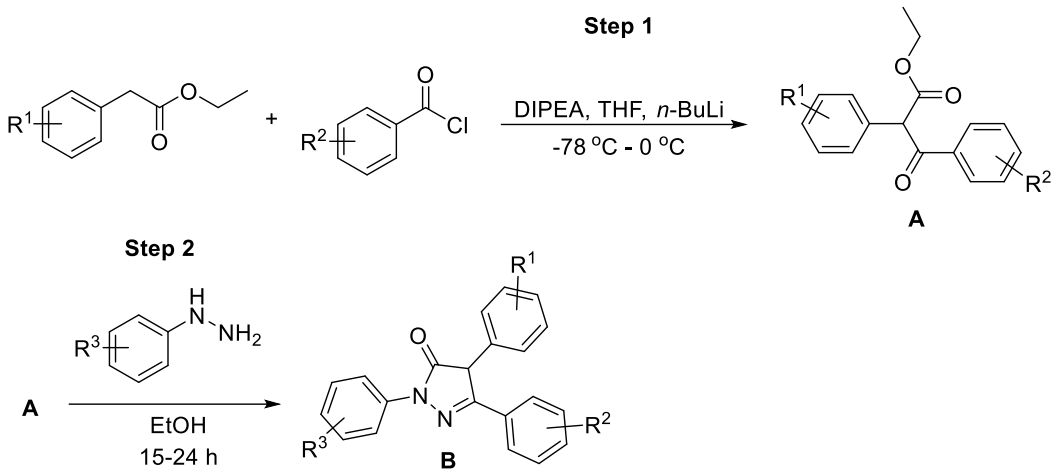
An absorption spectrum gave an A (400 nm) value of > 3, indicating that the fraction of absorbed light (f) is > 0.999.

$$\Phi = \frac{3.7 \times 10^{-6}}{3.6 \times 10^{-6} \times 2 \times 3600 \times 1} = 0.00014$$

The reaction quantum yield (Φ) was thus determined to be Φ = 0.00014.

6 Substrate Synthesis

6.1 Synthetic route to pyrazolinones[3]



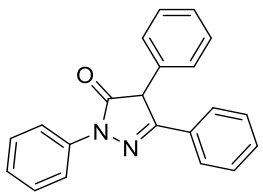
Step 1: General procedure for synthesis of dicarbonyl compounds:

To a stirred solution of diisopropylamine (10.5 mmol, 1.05 eq) in THF (30 mL) was added *n*-BuLi (2.0 M in hexanes, 1.10 eq) at 0 °C under nitrogen conditions. The reaction mixture was stirred at 0 °C for 15 min and cooled to –78 °C, then, ethyl arylacetate (10.0 mmol, 1.0 eq) was added and the reaction mixture was stirred at –78 °C for 30 min. Then, benzoyl chloride (10.5 mmol, 1.05 mmol) was added at –78 °C and the reaction was allowed to warm to room temperature and stirred for 18 h. The resulting yellow solution was quenched with saturated aq. NH_4Cl (30 mL). The aqueous phase was extracted with EtOAc (2 × 30 mL). The combined organic extracts were washed with H_2O (30 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in *vacuo* to afford a yellow oil which was purified by column chromatography (SiO_2, Hexane/EtOAc, 50:1 to 9:1) to give the target product **A**.

Step 2: General procedure for synthesis of pyrazolinones compounds:

To a stirred solution of **A** (10.0 mmol) in EtOH (1.0 M) was added aryl hydrazine (10.0 mmol, 1.0 eq) at room temperature. Stir the mixture at reflux temperature for 15-24 hours. After cooling, concentrated in *vacuo* to afford a yellow oil which was purified by column chromatography (SiO_2, Hexane/EtOAc, 50:1 to 20:1) to give the product. (Or collect the precipitated solid by filtration, recrystallize the crude solid from EtOH.

2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (1a)



white solid, eluent (PE : EA = 4 : 1)

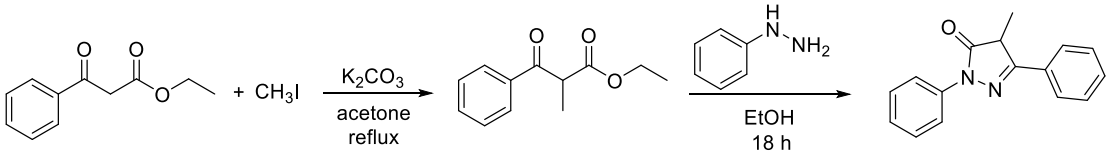
^{1}H NMR (400 MHz, DMSO) δ 10.94 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.45 (s, 2H), 7.40 – 7.23 (m, 9H).

^{13}C NMR (101 MHz, DMSO) δ 148.05, 132.10, 129.66, 129.00, 128.34, 127.76, 126.40, 122.00.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.78, 157.21, 148.60, 138.08, 133.22, 130.52, 130.24, 129.49, 129.27, 128.94, 128.89, 128.75, 128.54, 128.37, 128.27, 128.24, 128.01, 126.80, 126.70, 125.32, 119.03, 56.20.

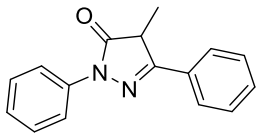
HRMS (ESI) calculated for $C_{21}H_{16}N_2O$ [M + H] $^+$ m/z: 313.1335, found: 313.1334.

Synthesis of 4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one[3b, 4]



To a stirred solution of ethyl benzoylacetate (0.866 mL, 5.00 mmol) in acetone (5 mL) was added K_2CO_3 (1.04 g, 7.50 mmol) and iodomethane (0.343 mL, 5.50 mmol). The reaction mixture was heated to 60 °C for 3 h and allowed to cool to room temperature. The resulting yellow suspension was quenched with H_2O (50 mL) and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with H_2O (3 × 50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the title compound (1.03 g, 99%) as a yellow oil; R_f 0.27 (Hexane/EtOAc, 9:1). To a stirred solution of ethyl Ethyl benzoylphenylacetate (10.0 mmol) in EtOH (1.0 M) was added phenylhidrazine (1.08 g, 10.0 mmol) at room temperature. Stir the mixture at reflux temperature for 15-24 hours. After cooling, concentrated in vacuo to afford a yellow oil which was purified by column chromatography (SiO_2, Hexane/EtOAc, 50:1 to 20:1) to give the product. (Or collect the precipitated solid by filtration, recrystallize the crude solid from EtOH.)

4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (1b)



white solid, eluent (PE : EA = 5: 1)

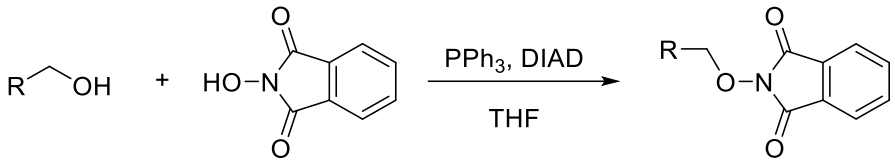
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.36 (dt, *J* = 14.7, 7.4 Hz, 2H), 6.65 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.92, 150.91, 144.91, 138.06, 132.96, 129.12, 128.57, 128.20, 127.43, 125.55, 123.24, 93.38, 20.81.

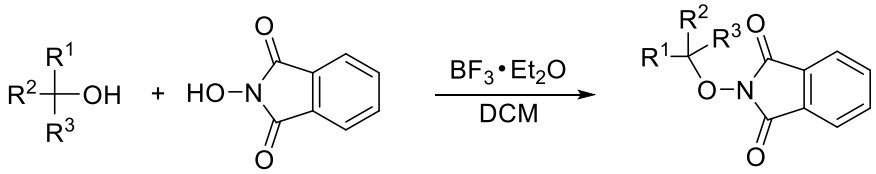
HRMS (ESI) calculated for $C_{16}H_{14}N_2O$ [M + H] $^+$ m/z: 251.1179, found: 251.1174.

6.2 Synthesis of N-Alkoxyphthalimides[5]

The N-alkoxyphthalimides were prepared using reported methods.



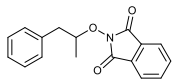
Method A: To a solution of the corresponding aliphatic alcohol (10.0 mmol), PPh_3 (3.15 g, 12.0 mmol), and N-hydroxyphthalimide (1.96 g, 12.0 mmol) in THF (30 mL) was added diisopropyl azodicarboxylate (2.4 mL, 12.0 mmol) over 10 min at 0 °C. The resulting mixture was stirred for 3-24 h, taken up in EtOAc (20 mL), and washed with saturated $NaHCO_3$ (3 x 20 mL) and brine (2 x 30 mL). The organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo, and subjected to flash chromatography to afford the targeted N-alkoxyphthalimides.



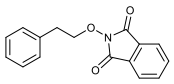
Method B: Following a literature procedure, to a solution of the corresponding tertiary alcohol (20 mmol) and N-hydroxyphthalimide (6.53 g, 40 mmol) in 70 mL wet DCM, $BF_3{\cdot}Et_2O$ (13.5 mL, 50 mmol) was added dropwise by syringe at 0 ° C. The reaction mixture was stirred for 1.5-2.0 h at room temperature. To the resulting mixture, DCM (10 mL) and saturated Na_2CO_3 solution in H_2O (50 mL) was added. The aqueous layer was extracted with DCM (20 mL x 3), the combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo, and subjected to flash chromatography to afford the targeted N-alkoxyphthalimides.

Note: *Further purification of the product can be performed by recrystallization in DCM/hexanes or Et_2O/hexanes if necessary.*

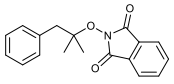
The N-alkoxyphthalimides **2a–c**, **2e–2s, 2u–2z, 2aa** were prepared using Method A. The N-alkoxyphthalimides **2d, 2t** were prepared using Method B.



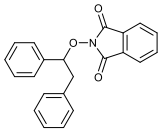
2a



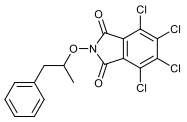
2b



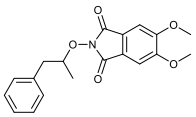
2c



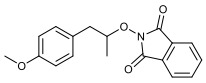
2d



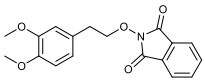
2e



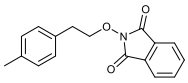
2f



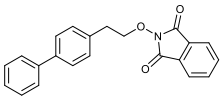
2g



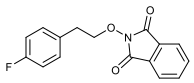
2h



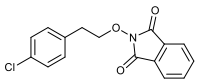
2i



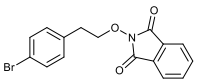
2j



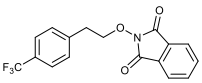
2k



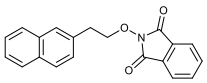
2l



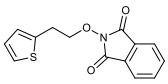
2m



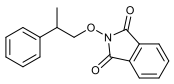
2n



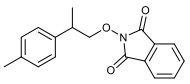
2o



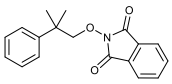
2p



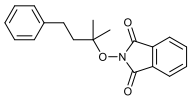
2q



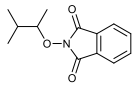
2r



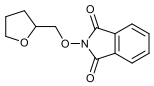
2s



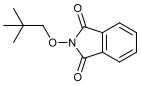
2t



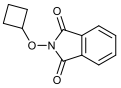
2u



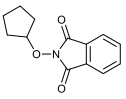
2v



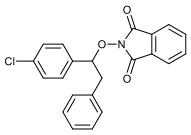
2w



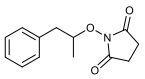
2x



2y

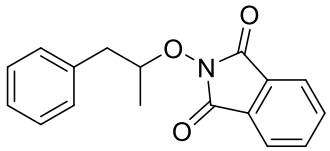


2z



2aa

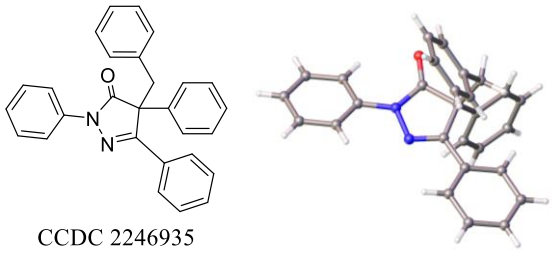
2-((1-phenylpropan-2-yl)oxy)isoindoline-1,3-dione (**2a**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.69 – 7.63 (m, 2H), 7.22 – 7.15 (m, 4H), 7.11 (ddd, *J* = 8.5, 5.1, 2.1 Hz, 1H), 4.65 – 4.54 (m, 1H), 3.16 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.81 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.21, 137.07, 134.38, 129.25, 128.88, 128.38, 126.43, 123.42, 84.63, 41.31, 18.27.

7 X-Ray Crystallographic Data



CCDC 2246935

formula	$C_{28}H_{22}N_2O$
Formula weight	402.47
crystal dimensions (mm)	
Crystal system	triclinic
space group	P -1
Hall group	-P 1
unit cell parametersa	
a (Å)	9.1228(2)
b (Å)	10.6400(2)
c (Å)	14.0872(3)
alpha (deg)	92.072(1)
beta (deg)	92.116(1)
gamma (deg)	112.202(1)
V (Å3)	1263.29(5)
Z	2
Temperature	300 K

Bond precision: C-C = 0.0026 A Wavelength=1.54178

	Calculated	Reported
Volume	1263.29(5)	1263.29(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C28 H22 N2 O[+ solvent]	C28 H22 N2 O
Sum formula	C28 H22 N2 O [+ solvent]	C28 H22 N2 O
Mr	402.48	402.47
Dx g cm-3	1.058	1.058
Z	2	2
Mu (mm-1)	0.504	0.504
F000	424.0	424.0
F000’	425.17	
h,k,lmax	10,12,16	10,12,16
Nref	4631	4558
Tmin,Tmax	0.843,0.943	0.826,0.991
Tmin’	0.763	

Correction method= # Reported T Limits: Tmin=0.826 Tmax=0.991

AbsCorr = NUMERICAL

Data completeness= 0.984

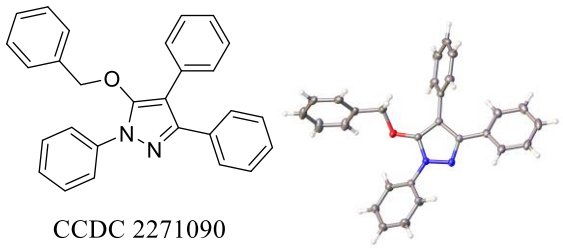
Theta(max)= 68.325

R(reflections)= 0.0458(3818)

wR2(reflections)= 0.1383(4558)

S = 1.057 Npar= 280

The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2246935. All the crystals were obtained in DCM/EA with the diffusion of n-hexane and analyzed by X-ray diffraction. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



CCDC 2271090

formula	$C_{28}H_{22}N_2O$

Formula weight	402.47
crystal dimensions (mm)	
Crystal system	triclinic
space group	P 21/n
Hall group	-P 2yn
unit cell parametersa	
a (Å)	6.2947(2)
b (Å)	19.6938 (7)
c (Å)	17.0798(6)
alpha (deg)	90
beta (deg)	98.886(1)
gamma (deg)	90
Volume	2091.91(12)
Z	4
Temperature	153 K

Bond precision: C-C = 0.0017 A Wavelength=1.54178

	Calculated	Reported
Volume	2091.91(12)	2091.91(12)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C28 H22 N2 O	C28 H22 N2 O
Sum formula	C28 H22 N2 O	C28 H22 N2 O
Mr	402.48	402.47
Dx g cm-3	1.278	1.278
Z	4	4
Mu (mm-1)	0.608	0.608
F000	848.0	848.0
F000’	850.33	
h,k,lmax	8,25,21	8,24,21
Nref	4516	4456
Tmin,Tmax	0.894, 0.926	0.842, 0.972
Tmin’	0.811	

Correction method= # Reported T Limits: Tmin=0.842 Tmax=0.972

AbsCorr = NUMERICAL

Data completeness= 0.987

Theta(max)= 79.253

R(reflections)= 0.0391(3964)

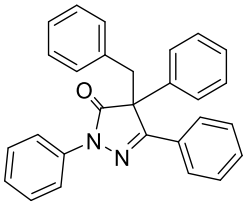
wR2(reflections)= 0.0941(4456)

S = 1.053 Npar= 280

The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2271090. All the crystals were obtained in DCM/EA with the diffusion of n-hexane and analyzed by X-ray diffraction. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

8 Characterization Data

4-benzyl-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**3a**)



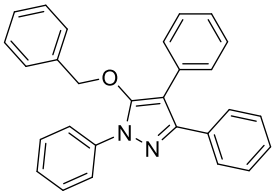
Isolated yield 87% (34.8 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.44 (dt, *J* = 7.3, 5.8 Hz, 5H), 7.41 – 7.34 (m, 5H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 4.07 (d, *J* = 12.8 Hz, 1H), 3.62 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.59, 159.53, 137.66, 136.54, 134.12, 130.87, 130.21, 129.48, 129.43, 128.67, 128.65, 128.33, 127.98, 127.22, 126.90, 126.46, 125.39, 119.62, 63.53, 39.93.

HRMS (ESI) calculated for $C_{28}H_{22}N_2O$ $[M + H]^+$ m/z: 403.1805, found: 403.1806.

5-(benzyloxy)-1,3,4-triphenyl-1H-pyrazole (**3a'**)



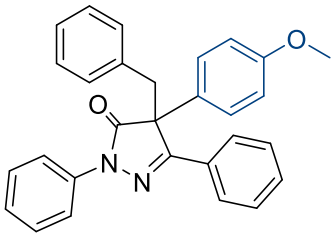
white solid, eluent (PE : EA = 30 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.60 – 7.55 (m, 2H), 7.49 – 7.20 (m, 14H), 7.06 – 7.01 (m, 2H), 4.72 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.51, 149.00, 138.57, 135.11, 133.52, 131.93, 129.90, 128.89, 128.48, 128.46, 128.29, 128.14, 128.02, 127.72, 126.89, 126.75, 122.77, 107.89, 75.94.

HRMS (ESI) calculated for $C_{28}H_{22}N_2O$ $[M + H]^+$ m/z: 403.1805, found: 403.1805.

4-benzyl-4-(4-methoxyphenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**4**)



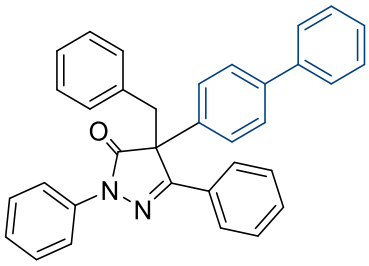
Isolated yield 56% (24.3 mg, 0.05 mmol scale×2), white solid, eluent (PE: EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, 2H), 7.60 (dd, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.32 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.05 – 6.97 (m, 4H), 6.90 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 2H), 4.00 (d, *J* = 12.7 Hz, 1H), 3.80 (s, 3H), 3.57 (d, *J* = 12.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.49, 160.27, 159.57, 137.90, 137.63, 134.06, 130.83, 130.45, 130.25, 129.50, 128.70, 128.69, 127.99, 127.24, 126.92, 125.43, 119.67, 118.76, 113.19, 112.78, 63.42, 55.28, 39.79.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O_2$ $[M + H]^+$ m/z: 433.1911, found: 433.1911.

4-([1,1'-biphenyl]-4-yl)-4-benzyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**5**)



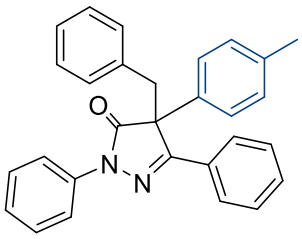
Isolated yield 79% (37.6 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.66 (dd, *J* = 7.7, 6.5 Hz, 4H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.41 – 7.35 (m, 5H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 2H), 4.09 (d, *J* = 12.8 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.59, 159.51, 141.17, 140.19, 137.64, 135.46, 134.09, 130.83, 130.31, 129.49, 128.81, 128.72, 128.11, 128.03, 127.56, 127.27, 127.05, 126.96, 126.90, 125.45, 119.63, 63.36, 40.04.

HRMS (ESI) calculated for $C_{34}H_{26}N_2O$ $[M + H]^+$ m/z: 479.2118, found: 479.2118.

4-benzyl-2,5-diphenyl-4-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (**6**)



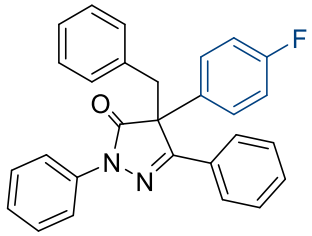
Isolated yield 73% (30.3 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.62 (dd, *J* = 7.8, 0.8 Hz, 2H), 7.42 – 7.30 (m, 7H), 7.24 – 7.15 (m, 3H), 7.12 – 7.07 (m, 1H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 2H), 4.02 (d, *J* = 12.8 Hz, 1H), 3.57 (d, *J* = 12.8 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.77, 159.64, 138.19, 137.71, 134.25, 133.52, 130.94, 130.19, 130.15, 129.48, 128.68, 128.65, 127.97, 127.18, 126.93, 126.28, 125.34, 119.60, 63.28, 39.92, 21.10.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O$ $[M + H]^+$ m/z: 417.1961, found: 417.1961.

4-benzyl-4-(4-fluorophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**7**)



Isolated yield 70% (29.3 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.34 (m, 7H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.07 (m, 3H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 4.00 (d, *J* = 12.7 Hz, 1H), 3.57 (d, *J* = 12.7 Hz, 1H).

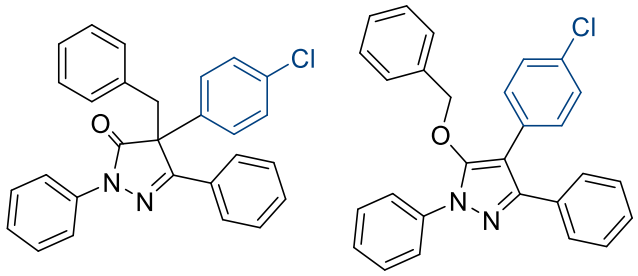
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.41, 162.48 (d, *J* = 248.2 Hz), 159.25, 137.53, 133.84, 132.38 (d, *J* = 3.3 Hz), 130.66, 130.40, 129.44, 128.70, 128.68, 128.27 (d, *J* = 8.1 Hz), 128.05, 127.35, 126.86, 125.53, 119.62, 116.38 (d, *J* = 21.7 Hz), 62.90, 40.28.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.27 (s, 1F)

HRMS (ESI) calculated for $C_{28}H_{21}FN_2O$ $[M + H]^+$ m/z: 421.1711, found: 421.1709.

4-benzyl-4-(4-chlorophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**8**)

5-(benzyloxy)-4-(4-chlorophenyl)-1,3-diphenyl-1H-pyrazole (**8'**)



Isolated yield 75% (32.8 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.61 – 7.52 (m, 2H), 7.50 – 7.31 (m, 8H), 7.29 – 7.26 (m, 1H), 7.25 – 7.16 (m, 2H), 7.15 – 7.08 (m, 1H), 7.06 – 6.99 (m, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 4.71 (s, 0.63H), 3.99 (d, *J* = 12.7 Hz, 0.69H), 3.57 (d, *J* = 12.7 Hz, 0.69H).

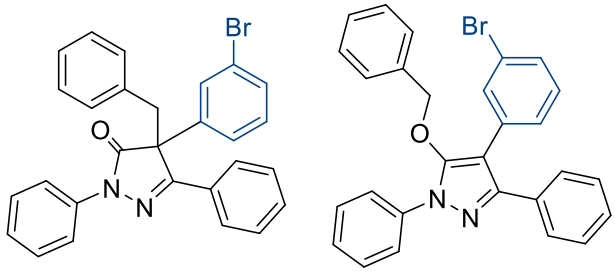
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.00, 159.00, 150.50, 148.94, 138.46, 138.38, 137.46, 135.43, 134.69, 134.23, 133.74, 133.61, 133.09, 130.63, 130.51, 130.46, 129.62, 129.51, 129.46, 129.01,

128.81, 128.75, 128.69, 128.67, 128.37, 128.29, 128.24, 128.15, 128.06, 128.03, 127.99, 127.91, 127.39, 127.00, 126.91, 126.84, 126.68, 125.61, 124.86, 122.75, 119.67, 106.90, 76.27, 63.15, 39.90.

HRMS (ESI) calculated for $C_{28}H_{21}ClN_2O$ $[M + H]^+$ m/z: 437.1415, found: 437.1415.

4-benzyl-4-(3-bromophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**9**)

5-(benzyloxy)-4-(3-bromophenyl)-1,3-diphenyl-1H-pyrazole (**9'**)



Isolated yield 76% (36.7 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 2H), 7.66 – 7.57 (m, 2H), 7.56 – 7.42 (m, 3H), 7.40 – 7.27 (m, 6H), 7.21 (m, 2H), 7.14 – 7.07 (m, 1H), 7.03 (dd, *J* = 10.1, 4.6 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 1H), 4.71 (s, 0.66H), 3.99 (d, *J* = 12.7 Hz, 0.67H), 3.57 (d, *J* = 12.7 Hz, 0.68H).

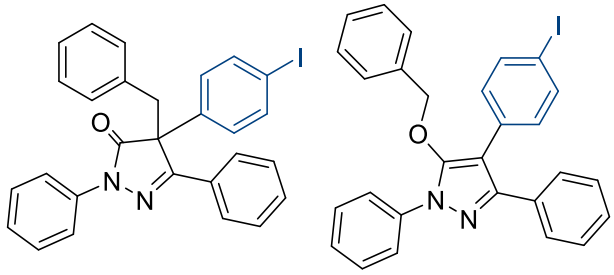
^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.98, 158.97, 150.50, 148.91, 138.69, 138.37, 137.45, 134.66, 134.02, 133.59, 133.06, 132.34, 131.63, 130.88, 130.46, 129.89, 129.79, 129.47, 129.45, 129.01, 128.82, 128.74, 128.70, 128.39, 128.34, 128.28, 128.05, 128.03, 128.00, 127.39, 127.00, 126.84, 125.60, 125.35, 123.63, 122.72, 122.44, 121.51, 119.66, 106.80, 76.28, 63.11, 44.16, 39.91.

HRMS (ESI) calculated for $C_{28}H_{21}Br^{79}N_2O$ $[M + H]^+$ m/z: 481.0910, found: 481.0910.

$C_{28}H_{21}Br^{81}N_2O$ $[M + H]^+$ m/z: 483.0890, found: 481.0910, 483.0886.

4-benzyl-4-(4-iodophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**10**)

5-(benzyloxy)-4-(4-iodophenyl)-1,3-diphenyl-1H-pyrazole (**10'**)



Isolated yield 34% (18.0 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.65 (m, 3H), 7.62 – 7.51 (m, 2H), 7.48 – 7.27 (m, 8H), 7.25 – 7.16 (m, 2H), 7.11 (dd, *J* = 16.3, 7.8 Hz, 1H), 7.03 (td, *J* = 7.9, 2.7 Hz, 2H), 6.84 (t, *J* = 8.0 Hz,

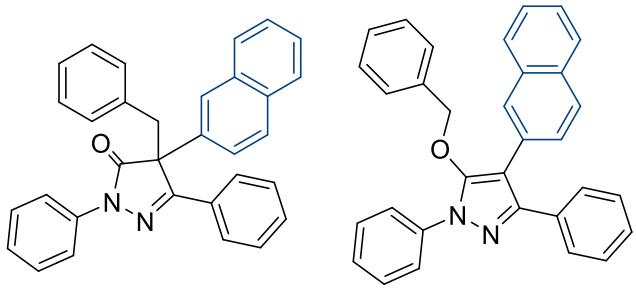
1H), 4.70 (d, *J* = 3.6 Hz, 0.74H), 4.01 (dd, *J* = 25.2, 12.7 Hz, 0.64H), 3.57 (dd, *J* = 18.8, 12.7 Hz, 0.62H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.61, 174.04, 159.56, 159.02, 150.49, 150.35, 148.99, 148.90, 138.51, 138.36, 137.64, 137.55, 137.47, 136.51, 136.33, 135.08, 134.77, 134.12, 133.70, 133.17, 131.88, 131.50, 130.85, 130.54, 130.45, 130.24, 129.88, 129.49, 129.45, 129.43, 128.98, 128.90, 128.79, 128.74, 128.70, 128.63, 128.55, 128.50, 128.45, 128.36, 128.30, 128.16, 128.06, 128.00, 127.95, 127.73, 127.37, 127.23, 126.98, 126.91, 126.84, 126.77, 126.47, 125.57, 125.42, 122.78, 119.64, 119.62, 107.88, 107.03, 94.32, 92.33, 76.17, 75.93, 63.53, 63.16, 39.94, 39.91.

HRMS (ESI) calculated for $C_{28}H_{21}IN_2O$ $[M + H]^+$ m/z: 529.0771, found: 529.0771.

4-benzyl-4-(naphthalen-2-yl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**11**)

5-(benzyloxy)-4-(naphthalen-2-yl)-1,3-diphenyl-1H-pyrazole (**11'**)



Isolated yield 52% (23.4 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 4.5:1.

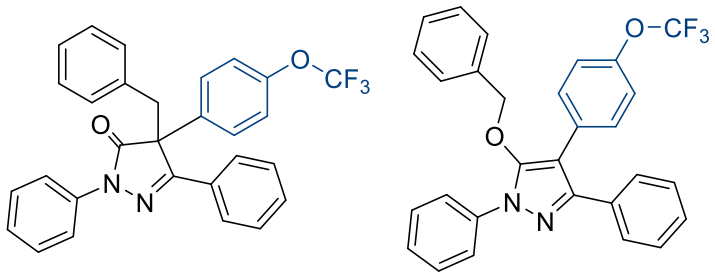
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.95 – 7.72 (m, 5H), 7.63 – 7.28 (m, 11H), 7.23 – 7.10 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 54.4, 7.3 Hz, 2H), 4.71 (s, 0.36H), 4.18 (d, *J* = 12.7 Hz, 0.81H), 3.72 (d, *J* = 12.6 Hz, 0.81H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.52, 159.62, 150.69, 149.14, 138.52, 137.64, 134.96, 134.10, 133.97, 133.64, 133.54, 133.46, 133.01, 132.29, 130.90, 130.30, 129.55, 129.38, 128.94, 128.73, 128.58, 128.52, 128.36, 128.30, 128.22, 128.09, 128.04, 127.98, 127.93, 127.82, 127.68, 127.65, 127.29, 126.89, 126.85, 126.58, 126.11, 125.88, 125.48, 124.24, 122.84, 119.67, 107.81, 76.04, 63.75, 39.92.

HRMS (ESI) calculated for $C_{32}H_{24}N_2O$ $[M + H]^+$ m/z: 453.1961, found: 453.1963.

4-benzyl-2,5-diphenyl-4-(4-(trifluoromethoxy)phenyl)-2,4-dihydro-3H-pyrazol-3-one (**12**)

5-(benzyloxy)-1,3-diphenyl-4-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (**12'**)



Isolated yield 79% (38.5 mg, 0.05 mmol scale×2), white solid, eluent (PE: EA = 20 : 1), the selectivity ratio (C4: O) is 2.5:1.

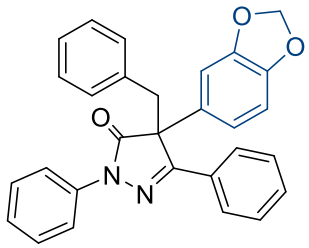
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 2H), 7.62 – 7.58 (m, 1H), 7.55 – 7.27 (m, 10H), 7.24 – 7.16 (m, 2H), 7.14 – 7.07 (m, 1H), 7.07 – 6.96 (m, 2H), 6.84 (d, *J* = 7.2 Hz, 1H), 4.74 – 4.66 (m, 0.71H), 4.08 – 3.97 (m, 0.72H), 3.63 – 3.53 (m, 0.70H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.61, 173.11, 158.56, 158.02, 149.48, 148.07, 147.93, 146.97, 137.39, 136.64, 136.44, 135.51, 134.16, 133.69, 133.12, 132.66, 132.14, 130.01, 129.84, 129.59, 129.54, 129.47, 129.23, 128.87, 128.48, 128.44, 128.43, 128.02, 127.90, 127.81, 127.74, 127.67, 127.57, 127.49, 127.42, 127.35, 127.32, 127.29, 127.15, 127.07, 127.02, 126.99, 126.95, 126.40, 126.23, 126.00, 125.91, 125.83, 125.46, 124.62, 124.41, 121.72, 120.70, 119.85, 118.64, 105.98, 75.29, 62.53, 61.95, 39.30, 38.90.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.70 (s, 0.29F), -57.73 (s, 0.71F).

HRMS (ESI) calculated for $C_{29}H_{21}F_3N_2O_2$ $[M + H]^+$ m/z: 487.1628, found: 487.1629.

4-(benzo[d][1,3]dioxol-5-yl)-4-benzyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**13**)



Isolated yield 63% (28.1 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1)

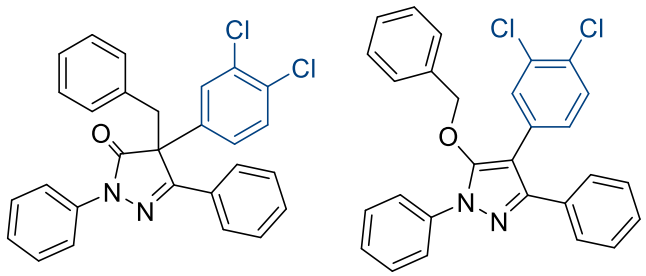
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (dd, *J* = 15.1, 7.8 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.45 – 7.33 (m, 5H), 7.21 – 7.15 (m, 1H), 7.12 – 7.07 (m, 1H), 7.05 – 6.99 (m, 2H), 6.94 – 6.88 (m, 2H), 6.84 (dd, *J* = 8.0, 6.6 Hz, 3H), 6.00 – 5.96 (m, 2H), 3.93 (d, *J* = 12.7 Hz, 1H), 3.54 (d, *J* = 12.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.71, 159.55, 148.67, 147.74, 137.70, 134.07, 130.87, 130.33, 130.17, 129.53, 128.75, 128.04, 127.30, 126.97, 125.47, 119.96, 119.68, 109.04, 107.04, 101.46, 63.15, 40.12.

HRMS (ESI) calculated for $C_{29}H_{22}N_2O_3$ $[M + H]^+$ m/z: 447.1703, found: 447.1707.

4-benzyl-4-(3,4-dichlorophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**14**)

5-(benzyloxy)-4-(3,4-dichlorophenyl)-1,3-diphenyl-1H-pyrazole (**14'**)



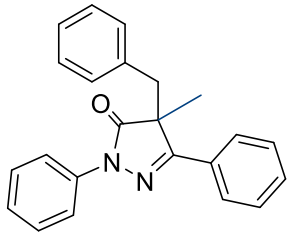
Isolated yield 67% (31.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 52.9, 8.0 Hz, 2H), 7.64 (d, *J* = 6.8 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.47 – 7.33 (m, 5H), 7.30 – 7.24 (m, 2H), 7.20 – 7.15 (m, 1H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 4.76 (s, 0.67H), 4.02 (d, *J* = 12.7 Hz, 0.67H), 3.61 (d, *J* = 12.7 Hz, 0.68H)..

^{13}C NMR (151 MHz, $CDCl_3$) δ = 173.66, 158.62, 150.42, 148.88, 138.28, 137.34, 136.68, 134.47, 133.74, 133.33, 132.87, 132.83, 132.42, 131.97, 131.29, 131.09, 130.63, 130.30, 129.42, 129.09, 128.91, 128.78, 128.73, 128.55, 128.39, 128.15, 128.11, 128.04, 127.50, 127.15, 126.79, 126.09, 125.72, 122.73, 119.65, 106.19, 76.45, 62.71, 40.09.

HRMS (ESI) calculated for $C_{28}H_{20}Cl_2N_2O$ $[M + H]^+$ m/z: 471.1025, found: 471.1024.

4-benzyl-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**15**)



Isolated yield 36.4% (12.4 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

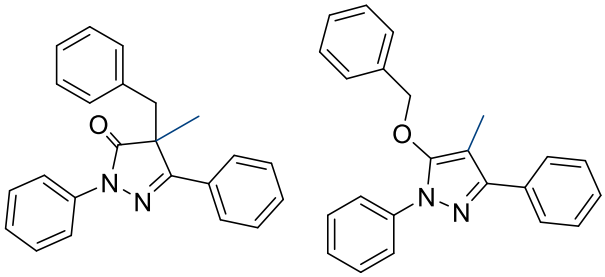
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.66 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.12 – 7.07 (m, 1H), 7.00 – 6.92 (m, 3H), 6.82 (dd, *J* = 7.7, 1.6 Hz, 2H), 3.28 (d, *J* = 2.1 Hz, 2H), 1.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.17, 160.19, 137.70, 134.98, 131.39, 130.32, 129.09, 128.92, 128.74, 128.08, 127.15, 126.57, 125.37, 119.56, 56.11, 43.52, 22.41.

HRMS (ESI) calculated for $C_{23}H_{20}N_2O$ $[M + H]^+$ m/z: 341.1648, found: 341.1649.

4-benzyl-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**15**)

5-(benzyloxy)-4-methyl-1,3-diphenyl-1H-pyrazole (**15'**)



Isolated yield 51% (17.3 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 3.0:1.

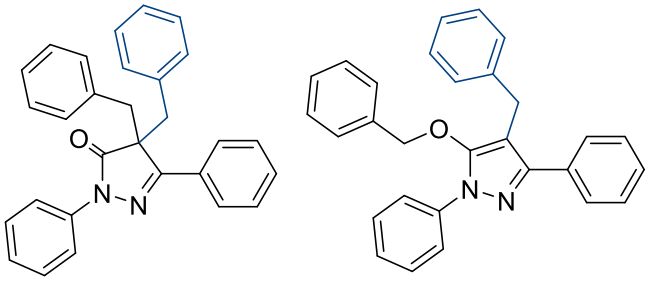
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.80 – 7.72 (m, 2H), 7.52 – 7.48 (m, 2H), 7.47 – 7.41 (m, 1H), 7.39 – 7.27 (m, 3H), 7.20 – 7.15 (m, 1H), 7.11 – 6.88 (m, 4H), 4.92 (s, 0.5H), 3.41 – 3.32 (m, 1.5H), 2.14 (s, 0.78H), 1.77 (s, 2.25H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.11, 159.13, 150.01, 148.92, 137.81, 136.64, 134.41, 133.92, 133.13, 130.33, 129.26, 128.02, 127.95, 127.86, 127.68, 127.62, 127.57, 127.48, 127.39, 127.02, 126.61, 126.33, 126.09, 125.50, 124.31, 121.42, 118.49, 100.83, 55.05, 42.45, 21.34, 7.58.

HRMS (ESI) calculated for $C_{23}H_{20}N_2O$ $[M + H]^+$ m/z: 341.1648, found: 341.1649.

4,4-dibenzyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**16**)

4-benzyl-5-(benzyloxy)-1,3-diphenyl-1H-pyrazole (**16'**)



Isolated yield 55% (23.0 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

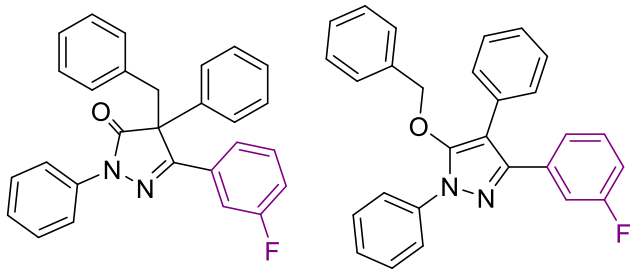
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 6.7, 3.1 Hz, 1.5H), 7.84 – 7.65 (m, 1.5H), 7.56 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.39 – 7.27 (m, 5H), 7.17 – 7.02 (m, 6H), 6.96 (dd, *J* = 7.8, 1.6 Hz, 2H), 4.72 (s, 0.72H), 3.99 (s, 0.72H), 3.56 (s, 2.59H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.03, 157.96, 151.57, 150.59, 140.60, 138.74, 137.17, 135.27, 134.65, 133.76, 132.00, 130.20, 129.21, 129.00, 128.87, 128.57, 128.48, 128.43, 128.40, 128.17, 128.06, 127.80, 127.60, 127.09, 126.73, 126.51, 126.09, 125.59, 122.59, 120.24, 104.74, 62.68, 42.58.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O$ $[M + H]^+$ m/z: 417.1961, found: 417.1961.

4-benzyl-5-(3-fluorophenyl)-2,4-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**17**)

5-(benzyloxy)-3-(3-fluorophenyl)-1,4-diphenyl-1H-pyrazole (**17'**)



Isolated yield 90% (38.0 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 4.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.33 – 7.01 (m, 11H), 6.98 – 6.81 (m, 4.4H), 6.71 (d, *J* = 7.1 Hz, 1.60H), 4.55 (s, 0.43H), 3.89 (d, *J* = 12.8 Hz, 0.78H), 3.42 (d, *J* = 12.8 Hz, 0.78H).

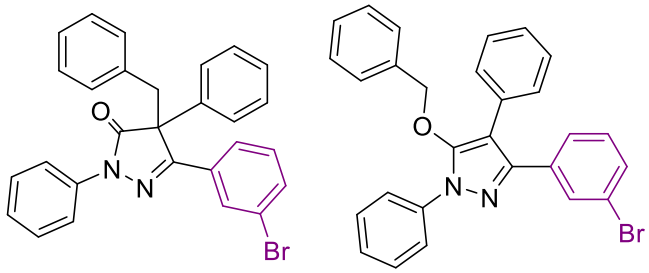
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.50, 162.74 (d, *J* = 246.7 Hz), 162.63 (d, *J* = 244.9 Hz), 158.44, 158.41, 150.54, 147.61, 138.37, 137.44, 136.08, 135.72, 135.64, 134.94, 133.88, 132.96 (d, *J* = 8.0 Hz), 131.48, 130.27 (d, *J* = 8.2 Hz), 129.99, 129.89, 129.62, 129.54, 129.36, 129.07, 128.97, 128.92, 128.72, 128.58, 128.52, 128.46, 128.29, 128.07, 127.88, 127.75, 127.35, 127.16, 126.92, 126.38, 126.21, 125.58, 123.62, 123.59, 122.76, 122.70, 122.67, 119.97, 119.61, 117.24 (d, *J* = 21.3 Hz), 114.79, 114.64, 114.56, 114.43, 113.43 (d, *J* = 23.3 Hz), 108.02, 75.94, 63.41, 39.86.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.43 (s, 0.78F), -113.23 (s, 0.21F).

HRMS (ESI) calculated for $C_{28}H_{21}FN_2O$ $[M + H]^+$ m/z: 421.1711, found: 421.1711.

4-benzyl-5-(3-bromophenyl)-2,4-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**18**)

5-(benzyloxy)-3-(3-bromophenyl)-1,4-diphenyl-1H-pyrazole (**18'**)



Isolated yield 80% (38.6 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 1H), 7.79 – 7.69 (m, 2H), 7.62 – 7.51 (m, 1H), 7.48 – 7.32 (m, 8H), 7.25 – 7.17 (m, 2.47H), 7.15 – 6.98 (m, 3.60H), 6.86 (d, *J* = 7.1 Hz, 1H), 4.71 (s, 0.64H), 4.05 (d, *J* = 12.8 Hz, 0.68H), 3.57 (d, *J* = 12.8 Hz, 0.68H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.50, 158.13, 150.50, 147.39, 138.36, 137.42, 136.01, 135.56, 134.93, 133.85, 133.13, 132.82, 131.43, 130.71, 130.66, 130.59, 130.33, 130.13, 129.86, 129.57,

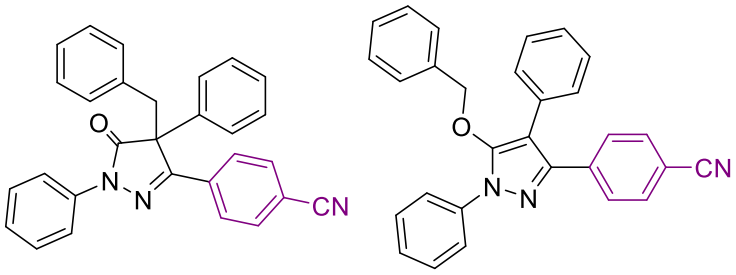
129.48, 129.38, 128.95, 128.76, 128.70, 128.60, 128.57, 128.55, 128.50, 128.32, 128.13, 128.00, 127.41, 127.18, 126.99, 126.91, 126.62, 126.40, 125.64, 125.46, 125.27, 122.98, 122.84, 122.35, 119.67, 108.03, 75.96, 63.38, 39.89.

HRMS (ESI) calculated for $C_{28}H_{21}Br^{79}N_2O$ $[M + H]^+$ m/z: 481.0910, found: 481.0907.

$C_{28}H_{21}Br^{81}N_2O$ $[M + H]^+$ m/z: 483.0890, found: 481.0889.

4-(4-benzyl-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)benzonitrile (**19**)

4-(5-(benzyloxy)-1,4-diphenyl-1H-pyrazol-3-yl)benzonitrile (**19'**)



Isolated yield 72% (30.6 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

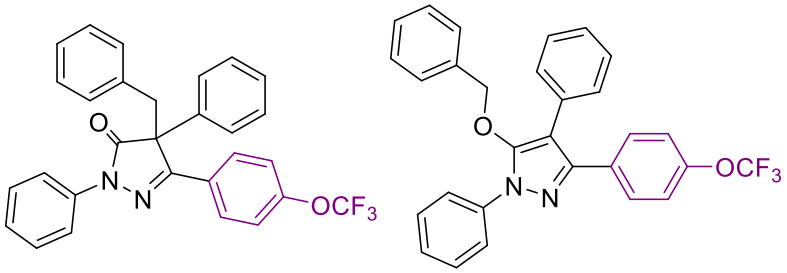
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 4H), 7.66 – 7.54 (m, 2H), 7.50 – 7.33 (m, 8H), 7.25 – 7.10 (m, 2H), 7.07 – 6.96 (m, 2H), 6.81 (d, *J* = 7.2 Hz, 1H), 4.70 (s, 0.68H), 4.07 (d, *J* = 12.9 Hz, 0.67H), 3.55 (d, *J* = 12.9 Hz, 0.67H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.46, 157.66, 150.73, 146.75, 138.19, 138.07, 137.23, 135.67, 134.87, 134.78, 133.63, 132.45, 131.98, 131.20, 130.72, 129.90, 129.71, 129.20, 129.01, 128.81, 128.77, 128.60, 128.46, 128.32, 128.19, 127.53, 127.48, 127.25, 127.10, 126.31, 125.90, 122.88, 119.71, 119.01, 118.29, 113.35, 110.98, 108.44, 76.04, 63.16, 39.92.

HRMS (ESI) calculated for $C_{29}H_{21}N_3O$ $[M + H]^+$ m/z: 428.1757, found: 428.1758.

4-benzyl-2,4-diphenyl-5-(4-(trifluoromethoxy)phenyl)-2,4-dihydro-3H-pyrazol-3-one (**20**)

5-(benzyloxy)-1,4-diphenyl-3-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (**20'**)



Isolated yield 88% (42.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.49 – 7.41 (m, 2H), 7.31 – 7.15 (m, 7H), 7.10 – 6.83 (m, 7H), 6.71 – 6.66 (m, 1H), 4.55 (s, 0.70H), 3.90 (d, *J* = 12.9 Hz, 0.64H), 3.38 (d, *J* = 12.8 Hz, 0.64H).

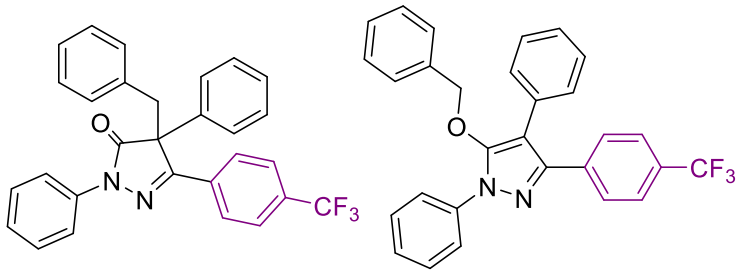
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.47, 159.56, 158.31, 150.57, 150.30, 148.78, 147.57, 138.40, 137.66, 137.49, 136.10, 134.96, 134.13, 133.89, 132.25, 131.58, 130.86, 130.22, 129.90, 129.59, 129.48, 129.44, 129.41, 129.35, 129.27, 128.94, 128.74, 128.66, 128.63, 128.56, 128.53, 128.47, 128.43, 128.31, 128.15, 128.09, 127.99, 127.91, 127.38, 127.23, 127.16, 126.93, 126.46, 126.40, 125.58, 125.40, 122.76, 121.60, 120.79, 120.57, 119.63, 119.03, 107.92, 75.96, 63.53, 63.39, 39.91, 39.85.

^{19}F NMR (377 MHz, $CDCl_3$) δ -57.58 (s, 0.64F), -57.67 (s, 0.36F).

HRMS (ESI) calculated for $C_{29}H_{21}F_3N_2O_2$ $[M + H]^+$ m/z: 487.1628, found: 487.1624.

4-benzyl-2,4-diphenyl-5-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (**21**)

5-(benzyloxy)-1,4-diphenyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole (**21'**)



Isolated yield 85% (40.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 4H), 7.64 – 7.53 (m, 1H), 7.49 – 7.32 (m, 8H), 7.24 – 7.19 (m, 2H), 7.15 – 7.10 (m, 1H), 7.08 – 6.99 (m, 2H), 6.86 – 6.81 (m, 1H), 4.72 (s, 0.71H), 4.07 (d, *J* = 12.9 Hz, 0.67H), 3.58 (d, *J* = 12.8 Hz, 0.64H).

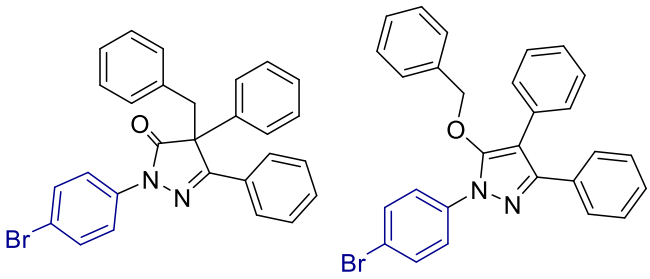
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.53, 172.78, 158.18, 150.66, 147.41, 138.34, 137.38, 137.05, 135.94, 134.92, 134.13, 133.78, 131.82, 131.44, 129.93, 129.65, 129.33, 128.99, 128.79, 128.70, 128.66, 128.58, 128.49, 128.34, 128.16, 128.03, 127.46, 127.29, 127.10, 127.01, 126.39, 125.77, 125.70, 125.67, 125.11, 122.87, 122.40, 119.74, 108.26, 76.02, 63.35, 39.88.

^{19}F NMR (377 MHz, $CDCl_3$) δ = -62.45 (s, 0.37F), -62.85 (s, 0.64F).

HRMS (ESI) calculated for $C_{29}H_{21}F_3N_2O$ $[M + H]^+$ m/z: 471.1679, found: 471.1678.

4-benzyl-2-(4-bromophenyl)-4,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (**22**)

5-(benzyloxy)-1-(4-bromophenyl)-3,4-diphenyl-1H-pyrazole (**22'**)



Isolated yield 90% (43.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 3.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.46 – 7.35 (m, 3H), 7.32 – 7.26 (m, 3H), 7.25 – 7.17 (m, 4H), 7.16 – 7.02 (m, 3H), 6.97 – 6.83 (m, 3H), 6.66 (d, *J* = 7.2 Hz, 1H), 4.55 (s, 0.53H), 3.87 (d, *J* = 12.8 Hz, 0.73H), 3.43 (d, *J* = 12.7 Hz, 0.73H).

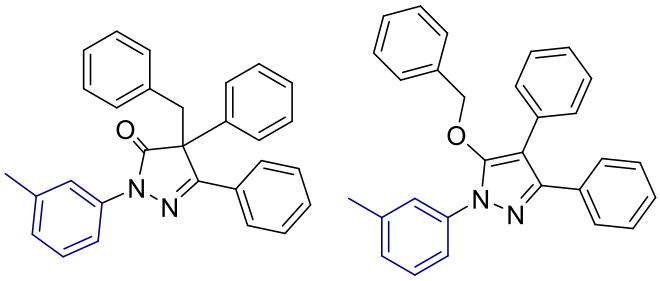
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.56, 159.84, 150.45, 149.38, 137.59, 136.69, 136.27, 134.84, 133.94, 133.23, 131.91, 131.69, 131.63, 130.60, 130.44, 129.87, 129.49, 129.41, 129.10, 128.99, 128.73, 128.66, 128.55, 128.48, 128.38, 128.29, 128.20, 128.01, 127.99, 127.90, 127.31, 127.08, 126.96, 126.46, 125.87, 123.91, 120.81, 119.99, 118.24, 108.08, 76.07, 63.64, 39.99.

HRMS (ESI) calculated for $C_{28}H_{21}Br^{79}N_2O$ $[M + H]^+$ m/z: 481.0910, found: 481.0904.

$C_{28}H_{21}Br^{81}N_2O$ $[M + H]^+$ m/z: 483.0890, found: 483.0884.

4-benzyl-4,5-diphenyl-2-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (**23**)

5-(benzyloxy)-3,4-diphenyl-1-(m-tolyl)-1H-pyrazole (**23'**)



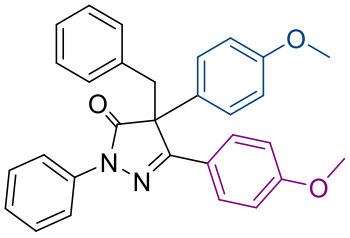
Isolated yield 88% (36.6 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 6.5:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 4H), 7.47 – 7.36 (m, 8H), 7.29 – 7.23 (m, 2H), 7.18 – 6.99 (m, 4H), 6.90 – 6.87 (m, 1H), 4.74 (s, 0.27H), 4.07 (d, *J* = 12.9 Hz, 0.86H), 3.61 (d, *J* = 12.8 Hz, 0.87H), 2.46 – 2.34 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.68, 159.57, 150.59, 148.91, 138.67, 137.65, 136.67, 135.21, 134.25, 133.51, 131.97, 131.19, 131.12, 130.98, 130.43, 130.25, 129.95, 129.57, 129.50, 128.83, 128.72, 128.59, 128.52, 128.39, 128.36, 128.21, 128.13, 128.06, 127.79, 127.70, 127.27, 126.98, 126.93, 126.52, 126.35, 125.58, 123.58, 120.37, 119.99, 119.58, 116.95, 115.07, 114.85, 107.91, 76.01, 63.58, 39.96, 29.73, 21.55.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O$ [M + H] $^+$ m/z: 416.1961, found: 416.1961.

4-benzyl-4,5-bis(4-methoxyphenyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (**24**)



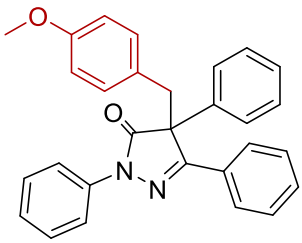
Isolated yield 50% (23.2 mg, 0.05 mmol scale×2), white solid, eluent (PE: EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.60 – 7.51 (m, 2H), 7.40 – 7.29 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.07 (m, 1H), 7.06 – 6.97 (m, 4H), 6.92 – 6.83 (m, 5H), 3.98 (d, *J* = 12.7 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.54 (d, *J* = 12.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.34, 161.07, 160.24, 159.33, 138.09, 137.72, 134.16, 130.39, 129.54, 128.65, 128.54, 127.96, 127.19, 125.26, 123.52, 119.63, 118.80, 114.08, 113.14, 112.78, 63.42, 55.30, 55.27, 39.92.

HRMS (ESI) calculated for $C_{30}H_{26}N_2O_3$ [M + H] $^+$ m/z: 463.2016, found: 463.2015.

4-(4-methoxybenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**25**)



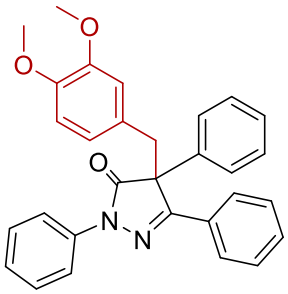
Isolated yield 84% (36.2 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.45 – 7.33 (m, 10H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.00 (d, *J* = 13.0 Hz, 1H), 3.67 (s, 3H), 3.56 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.72, 159.66, 158.60, 137.72, 136.57, 130.88, 130.55, 130.20, 129.41, 128.69, 128.66, 128.31, 126.93, 126.49, 126.08, 125.36, 119.60, 113.36, 63.69, 55.02, 39.12.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O_2$ [M + H] $^+$ m/z: 433.1911, found: 433.1910.

4-(3,4-dimethoxybenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**26**)



Isolated yield 57% (26.4 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

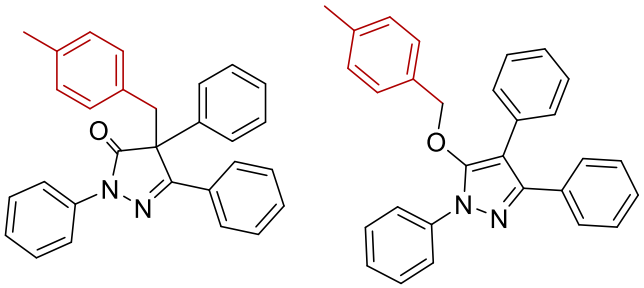
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.45 – 7.32 (m, 10H), 7.20 – 7.15 (m, 1H), 6.51 (d, *J* = 8.2 Hz, 1H), 6.42 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.28 (d, *J* = 1.9 Hz, 1H), 4.00 (d, *J* = 13.0 Hz, 1H), 3.74 (s, 3H), 3.53 (d, *J* = 12.9 Hz, 1H), 3.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.80, 159.61, 148.07, 147.90, 137.79, 136.54, 131.05, 130.18, 129.44, 128.73, 128.68, 128.36, 126.99, 126.51, 126.47, 125.34, 121.54, 119.33, 112.28, 110.55, 63.69, 55.63, 55.09, 39.80.

HRMS (ESI) calculated for $C_{30}H_{26}N_2O_3$ $[M + H]^+$ m/z: 463.2016, found: 463.2008.

4-(4-methylbenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**27**)

5-((4-methylbenzyl)oxy)-1,3,4-triphenyl-1H-pyrazole (**27'**)



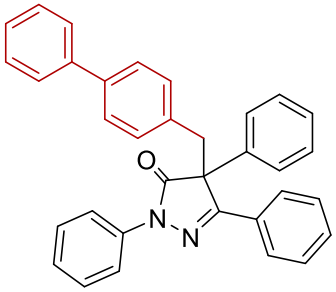
Isolated yield 74% (30.7 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 11.5:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.63 – 7.54 (m, 2H), 7.45 – 7.28 (m, 10H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 0.2H), 6.90 (d, *J* = 7.9 Hz, 0.2H), 6.84 (d, *J* = 7.9 Hz, 1.77H), 6.74 (d, *J* = 8.0 Hz, 2H), 4.67 (s, 0.16H), 4.01 (d, *J* = 12.8 Hz, 0.91H), 3.56 (d, *J* = 12.8 Hz, 0.92H), 2.25 (d, *J* = 46.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.70, 159.66, 150.56, 148.97, 138.38, 137.77, 136.74, 136.65, 133.57, 132.10, 130.99, 130.93, 130.18, 129.90, 129.42, 129.35, 128.97, 128.85, 128.71, 128.68, 128.64, 128.42, 128.31, 128.14, 128.03, 127.70, 126.96, 126.84, 126.70, 126.50, 125.35, 122.76, 119.65, 107.96, 75.92, 63.62, 39.57, 20.98.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O$ $[M + H]^+$ m/z: 417.1961, found: 417.1961.

4-([1,1'-biphenyl]-4-ylmethyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**28**)



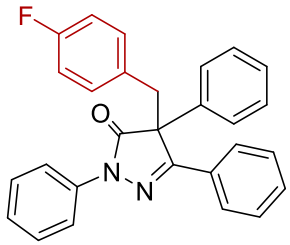
Isolated yield 63% (30.2 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.43 (m, 7H), 7.42 – 7.34 (m, 7H), 7.30 (dd, *J* = 9.7, 7.9 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.09 (d, *J* = 12.8 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.63, 159.57, 140.53, 139.89, 137.65, 136.50, 133.24, 130.85, 130.27, 129.93, 129.47, 128.71, 128.63, 128.39, 127.17, 126.96, 126.88, 126.62, 126.49, 125.48, 119.72, 63.55, 39.59.

HRMS (ESI) calculated for $C_{34}H_{26}N_2O$ $[M + H]^+$ m/z: 479.2118, found: 479.2118.

4-(4-fluorobenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**29**)



Isolated yield 74% (30.7 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.66 – 7.58 (m, 2H), 7.48 – 7.35 (m, 10H), 7.25 – 7.19 (m, 1H), 6.88 – 7.80 (m, 2H), 6.79 – 6.71 (m, 2H), 4.03 (d, *J* = 12.9 Hz, 1H), 3.59 (d, *J* = 12.9 Hz, 1H).

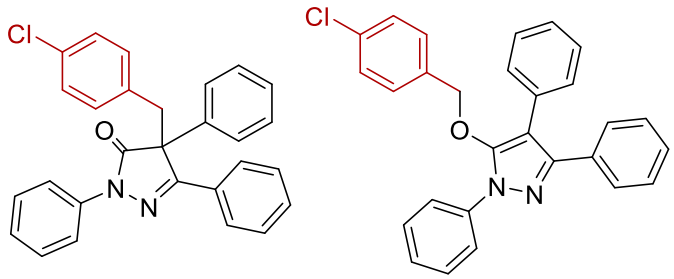
^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.50, 162.00 (d, *J* = 246.44 Hz), 159.45, 137.59, 136.32, 131.1 (d, *J* =8.08 Hz), 130.74, 130.37, 129.9 (d, *J* = 4.04 Hz), 129.50, 128.77, 128.45, 126.88, 126.43, 125.52, 119.53, 114.91 (d, *J* = 21.21 Hz), 63.54, 39.05.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.15 (s, 1F).

HRMS (ESI) calculated for $C_{28}H_{21}FN_2O$ $[M + H]^+$ m/z: 421.1711, found: 421.1712.

4-(4-chlorobenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**30**)

5-((4-chlorobenzyl)oxy)-1,3,4-triphenyl-1H-pyrazole (**30'**)



Isolated yield 73% (31.9 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 3.5:1.

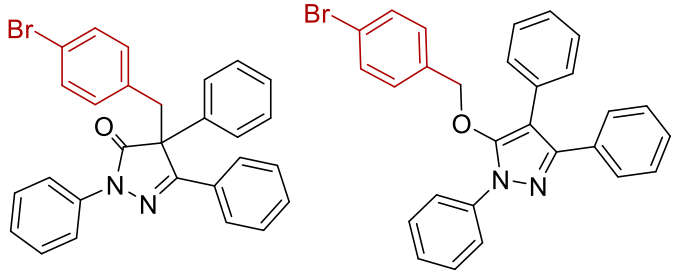
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.62 – 7.53 (m, 2H), 7.46 – 7.28 (m, 10H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 56.1, 8.4 Hz, 2H), 6.83 (dd, *J* = 53.5, 8.4 Hz, 2H), 4.66 (s, 0.44H), 4.01 (d, *J* = 12.9 Hz, 0.78H), 3.55 (d, *J* = 12.8 Hz, 0.78H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.38, 159.36, 150.16, 148.97, 138.43, 137.54, 136.49, 136.47, 136.22, 134.43, 133.47, 133.36, 133.16, 132.71, 131.77, 131.09, 130.85, 130.64, 130.42, 130.31, 129.85, 129.51, 128.93, 128.79, 128.61, 128.48, 128.43, 128.19, 127.98, 127.78, 126.95, 126.86, 126.36, 125.55, 122.78, 119.51, 108.01, 75.07, 63.36, 39.15.

HRMS (ESI) calculated for $C_{28}H_{21}ClN_2O$ $[M + H]^+$ m/z: 437.1415, found: 437.1415.

4-(4-bromobenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**31**)

5-((4-bromobenzyl)oxy)-1,3,4-triphenyl-1H-pyrazole (**31'**)



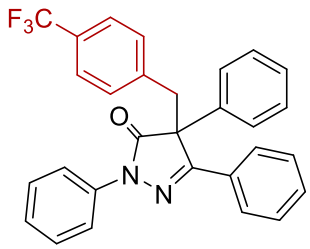
Isolated yield 73% (35.0 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 2.5:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.62 – 7.54 (m, 2H), 7.48 – 7.28 (m, 11H), 7.23 – 7.14 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 0.55H), 6.74 – 6.68 (m, 1.44H), 4.65 (s, 0.55H), 3.99 (d, *J* = 12.8 Hz, 0.72H), 3.54 (d, *J* = 12.8 Hz, 0.72H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.36, 159.34, 150.15, 148.97, 138.43, 137.54, 136.22, 133.97, 133.36, 133.23, 131.76, 131.39, 131.20, 131.13, 130.63, 130.41, 130.10, 129.83, 129.51, 128.92, 128.78, 128.48, 128.16, 127.97, 127.78, 126.95, 126.87, 126.35, 125.56, 122.79, 122.67, 121.38, 119.52, 108.00, 75.10, 63.29, 39.21.

HRMS (ESI) calculated for $C_{28}H_{21}BrN_2O$ $[M + H]^+$ m/z: 481.0910, found: 481.0910.

2,4,5-triphenyl-4-(4-(trifluoromethyl)benzyl)-2,4-dihydro-3H-pyrazol-3-one (**32**)



Isolated yield 40% (19.0 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

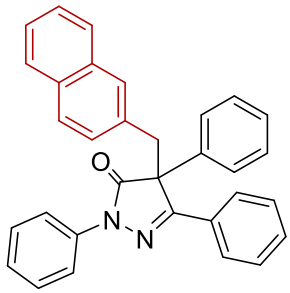
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.62 – 7.58 (m, 2H), 7.46 – 7.39 (m, 6H), 7.39 – 7.34 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 – 7.17 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.08 (d, *J* = 12.7 Hz, 1H), 3.63 (d, *J* = 12.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.24, 159.23, 138.41, 137.44, 136.09, 130.58, 130.52, 129.92, 129.58, 128.83 (d, *J* = 6.1 Hz), 128.58, 126.86, 126.36, 125.69, 124.95 (q, *J* = 4.0 Hz), 119.61, 63.26, 39.54.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.58 (s, 1F).

HRMS (ESI) calculated for $C_{29}H_{21}F_3N_2O$ $[M + H]^+$ m/z: 471.1679, found: 471.1679.

4-(naphthalen-2-ylmethyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**33**)



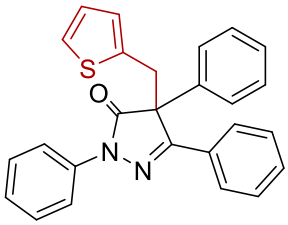
Isolated yield 57% (28.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 3H), 7.60 – 7.56 (m, 2H), 7.54 – 7.29 (m, 14H), 7.22 (s, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.22 (d, *J* = 12.8 Hz, 1H), 3.75 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.69, 159.71, 137.59, 136.57, 132.97, 132.41, 131.74, 130.98, 130.29, 129.50, 128.69, 128.65, 128.42, 127.61, 127.41, 127.03, 126.46, 125.77, 125.63, 125.40, 119.64, 63.62, 40.02.

HRMS (ESI) calculated for $C_{32}H_{24}N_2O$ $[M + H]^+$ m/z: 453.1961, found: 453.1962.

2,4,5-triphenyl-4-(thiophen-2-ylmethyl)-2,4-dihydro-3H-pyrazol-3-one (**34**)



Isolated yield 50% (20.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

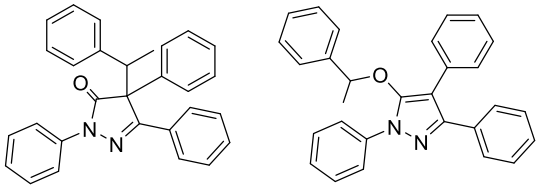
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.34 (m, 10H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.99 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.73 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.55 (d, *J* = 3.4 Hz, 1H), 4.28 (d, *J* = 14.0 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.29, 159.57, 137.81, 135.97, 135.40, 130.54, 130.32, 129.46, 128.75, 128.69, 128.45, 127.17, 126.92, 126.58, 126.34, 125.38, 124.77, 119.46, 63.38, 34.20.

HRMS (ESI) calculated for $C_{26}H_{20}N_2OS$ $[M + H]^+$ m/z: 409.1369, found: 409.1369.

2,4,5-triphenyl-4-(1-phenylethyl)-2,4-dihydro-3H-pyrazol-3-one (**35**)

1,3,4-triphenyl-5-(1-phenylethoxy)-1H-pyrazole (**35**)



Isolated yield 47% (19.7 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 1.0:1.

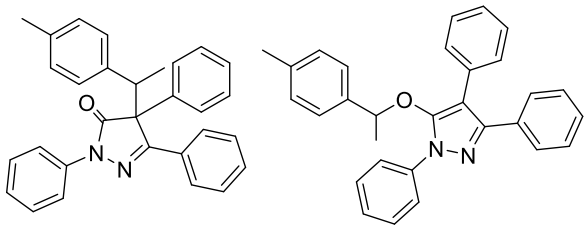
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.68 (m, 2H), 7.54 – 7.26 (m, 11H), 7.26 – 7.07 (m, 5H), 7.00 (t, *J* = 7.6 Hz, 0.67H), 6.89 – 6.85 (m, 1.44H), 4.84 – 4.76 (m, 0.5H), 4.29 – 4.09 (m, 0.5H), 1.79 (d, *J* = 7.0 Hz, 1H), 1.47 – 1.32 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.99, 160.78, 149.65, 148.79, 140.19, 138.75, 137.74, 135.99, 133.56, 132.28, 131.52, 129.95, 129.85, 129.24, 128.80, 128.75, 128.66, 128.52, 128.41, 128.19, 128.14, 128.07, 127.97, 127.85, 127.77, 127.60, 127.38, 127.23, 126.76, 126.68, 126.49, 125.45, 123.26, 119.77, 119.72, 108.09, 82.12, 65.73, 42.55, 21.96, 15.37.

HRMS (ESI) calculated for $C_{29}H_{24}N_2O$ $[M + H]^+$ m/z: 417.1961, found: 417.1962.

2,4,5-triphenyl-4-(1-(p-tolyl)ethyl)-2,4-dihydro-3H-pyrazol-3-one (**36**)

1,3,4-triphenyl-5-(1-(p-tolyl)ethoxy)-1H-pyrazole (**36'**)



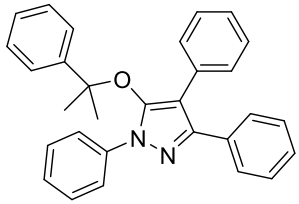
Isolated yield 47% (19.7 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1), the selectivity ratio (C4: O) is 1:3.0.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 0.50H), 7.68 – 7.57 (m, 1.45H), 7.49 – 7.30 (m, 5H), 7.27 – 7.11 (m, 8H), 6.84 – 6.78 (m, 1H), 6.74 – 6.64 (m, 3H), 4.68 (q, *J* = 6.5 Hz, 0.73H), 4.04 (q, *J* = 7.0 Hz, 0.28H), 2.17 (s, 2.2H), 2.12 (s, 0.84H), 1.68 (d, *J* = 7.0 Hz, 0.84H), 1.22 (d, *J* = 6.5 Hz, 2.2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.13, 160.92, 149.76, 148.80, 138.85, 137.98, 137.83, 137.18, 136.98, 136.12, 133.65, 132.38, 131.60, 129.99, 129.86, 129.26, 128.85, 128.77, 128.75, 128.59, 128.42, 128.22, 128.13, 128.03, 127.91, 127.64, 127.34, 126.75, 126.67, 126.56, 125.48, 123.28, 119.81, 108.23, 82.09, 65.91, 42.20, 21.87, 21.16, 21.04, 15.57.

HRMS (ESI) calculated for $C_{30}H_{26}N_2O$ $[M + H]^+$ m/z: 430.2118, found: 430.2118.

1,3,4-triphenyl-5-((2-phenylpropan-2-yl)oxy)-1H-pyrazole (37')



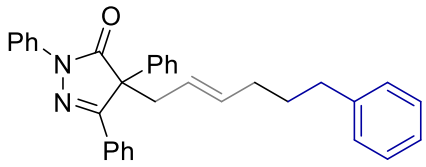
Isolated yield 29% (12.4 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 20 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.38 – 7.31 (m, 4H), 7.29 – 7.26 (m, 3H), 7.25 – 7.20 (m, 6H), 7.19 – 7.16 (m, 3H), 1.19 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.87, 146.92, 143.31, 138.39, 132.70, 131.92, 129.44, 127.66, 127.24, 127.03, 126.78, 126.51, 126.30, 125.70, 125.56, 124.10, 122.91, 110.37, 86.80, 27.06.

HRMS (ESI) calculated for $C_{30}H_{26}N_2O$ $[M + H]^+$ m/z: 431.2118, found: 431.2119.

2,4,5-triphenyl-4-(6-phenylhex-2-en-1-yl)-2,4-dihydro-3H-pyrazol-3-one (**38**)



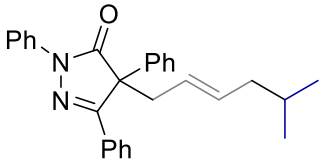
Isolated yield 36% (17.0 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.41 – 7.30 (m, 10H), 7.22 – 7.12 (m, 4H), 7.01 – 6.96 (m, 2H), 5.51 – 5.40 (m, 1H), 5.17 – 5.08 (m, 1H), 3.38 (dd, *J* = 13.0, 7.6 Hz, 1H), 3.03 (dd, *J* = 12.9, 7.1 Hz, 1H), 2.41 – 2.33 (m, 2H), 1.83 (q, *J* = 7.0 Hz, 2H), 1.46 – 1.38 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.75, 159.86, 142.24, 138.05, 136.50, 136.40, 130.49, 130.28, 129.34, 128.84, 128.66, 128.37, 128.25, 128.12, 126.82, 126.44, 125.51, 125.19, 122.12, 119.05, 62.61, 37.36, 34.77, 31.68, 30.58.

HRMS (ESI) calculated for $C_{33}H_{30}N_2O$ $[M + H]^+$ m/z: 471.2431, found: 471.2435.

4-(5-methylhex-2-en-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**39**)



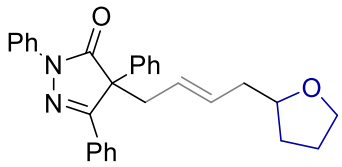
Isolated yield 40% (16.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 50 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.32 (m, 10H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.44 (dt, *J* = 14.6, 7.2 Hz, 1H), 5.10 (dt, *J* = 14.8, 7.3 Hz, 1H), 3.40 (dd, *J* = 13.0, 7.5 Hz, 1H), 3.05 (dd, *J* = 13.0, 7.2 Hz, 1H), 1.70 (t, *J* = 7.0 Hz, 2H), 1.41 – 1.31 (m, 1H), 0.67 (dd, *J* = 10.0, 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.69, 159.83, 138.11, 136.44, 135.72, 130.48, 130.20, 129.29, 128.74, 128.59, 128.18, 126.79, 126.39, 125.10, 122.50, 119.02, 62.52, 41.62, 37.44, 28.02, 21.98, 21.96.

HRMS (ESI) calculated for $C_{28}H_{28}N_2O$ $[M + H]^+$ m/z: 409.2274, found: 409.2276.

2,4,5-triphenyl-4-(4-(tetrahydrofuran-2-yl)but-2-en-1-yl)-2,4-dihydro-3H-pyrazol-3-one (**40**)



Isolated yield 48% (20.9 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 5 : 1).

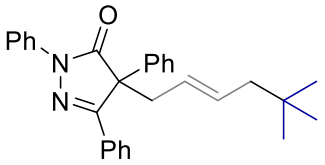
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 2H), 7.69 – 7.64 (m, 2H), 7.39 – 7.31 (m, 10H), 7.21 (t, *J* = 7.3 Hz, 1H), 5.46 (td, *J* = 15.1, 7.5 Hz, 1H), 5.17 (dt, *J* = 14.9, 7.3 Hz, 1H), 3.72 – 3.49 (m, 3H), 3.41 – 3.34 (m, 1H), 3.08 – 3.00 (m, 1H), 2.16 – 2.08 (m, 1H), 2.00 – 1.93 (m, 1H), 1.77 – 1.68 (m, 1H), 1.68 – 1.55 (m, 2H), 1.30 – 1.14 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 174.63, 159.76, 159.73, 138.09, 136.29, 132.83, 132.73, 130.38, 130.32, 130.30, 129.34, 128.81, 128.67, 128.26, 126.78, 126.40, 126.39, 125.18, 125.14, 124.16,

124.07, 119.00, 118.91, 78.45, 78.32, 67.69, 62.53, 62.44, 38.48, 38.32, 37.44, 37.32, 30.37, 30.24, 25.46.

HRMS (ESI) calculated for $C_{29}H_{28}N_2O_2$ $[M + H]^+$ m/z: 437.2224, found: 437.2224.

4-(5,5-dimethylhex-2-en-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**41**)



Isolated yield 49% (20.8 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 50 : 1).

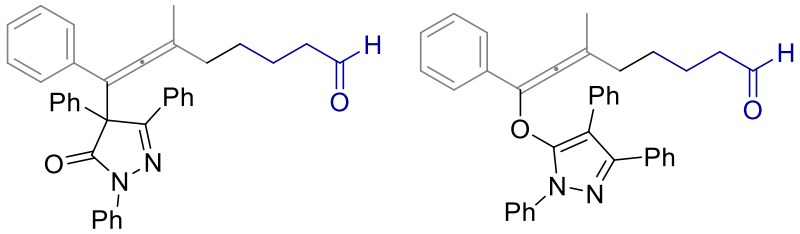
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.47– 7.31 (m, 10H), 7.23 (t, *J* = 7.4 Hz, 1H), 5.50 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.12 (dt, *J* = 14.8, 7.3 Hz, 1H), 3.45 (dd, *J* = 13.0, 7.4 Hz, 1H), 3.09 (dd, *J* = 13.0, 7.3 Hz, 1H), 1.71 (d, *J* = 7.5 Hz, 2H), 0.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.71, 159.87, 138.16, 136.48, 134.07, 130.45, 130.25, 129.32, 128.83, 128.76, 128.61, 128.22, 126.85, 126.41, 125.09, 123.66, 119.01, 62.49, 46.81, 37.67, 30.55, 28.94.

HRMS (ESI) calculated for $C_{29}H_{30}N_2O$ $[M + H]^+$ m/z: 423.2431, found: 423.2432.

6-methyl-8-(5-oxo-1,3,4-triphenyl-4,5-dihydro-1H-pyrazol-4-yl)-8-phenylocta-6,7-dienal (**42**)

6-methyl-8-phenyl-8-((1,3,4-triphenyl-1H-pyrazol-5-yl)oxy)octa-6,7-dienal (**42'**)



Isolated yield 45% (23.5 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 5 : 1), the selectivity ratio (C4: O) is 1.2:1.

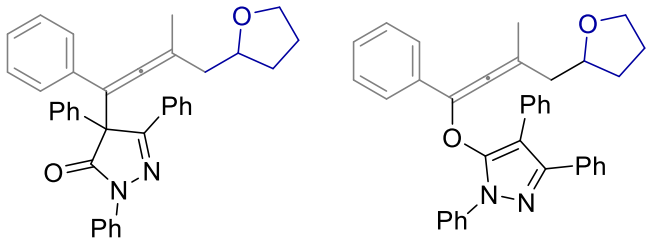
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (t, *J* = 1.7 Hz, 0.45H), 9.52 (t, *J* = 1.7 Hz, 0.55H), 8.00 – 7.87 (m, 4H), 7.58 – 7.52 (m, 2H), 7.42 – 7.35 (m, 5H), 7.31 – 7.27 (m, 3H), 7.23 – 7.18 (m, 2H), 7.17 – 7.10 (m, 4H), 2.43 – 2.37 (m, 1H), 2.16 – 2.10 (m, 1.5H), 2.01 – 1.91 (m, 1.5H), 1.74 (s, 1.65H), 1.60 (s, 1.35H), 1.57 – 1.51 (m, 1H), 1.48 – 1.39 (m, 1H), 1.34 – 1.19 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 205.24, 204.94, 202.51, 202.31, 173.62, 173.47, 159.05, 159.01, 138.03, 136.53, 136.37, 136.14, 135.78, 131.43, 130.28, 130.24, 129.19, 128.94, 128.77, 128.34, 128.29, 128.22, 128.10, 128.01, 127.82, 127.66, 127.55, 127.26, 127.22, 125.37, 125.32, 119.37, 119.26, 105.55, 105.24, 104.93, 104.89, 66.30, 66.09, 43.59, 43.40, 33.52, 33.19, 26.63, 26.56, 21.73, 21.21, 17.87, 17.53.

HRMS (ESI) calculated for $C_{36}H_{32}N_2O_2$ [M + H] $^+$ m/z: 525.2537, found: 525.2531.

4-(3-methyl-1-phenyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**43**)

5-((3-methyl-1-phenyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)oxy)-1,3,4-triphenyl-1H-pyrazole **(43')**



Isolated yield 30% (15.7 mg, 0.05 mmol scale ×2), white solid, eluent (PE : EA = 5 : 1), the selectivity ratio (C4: O) is 1.0:1.

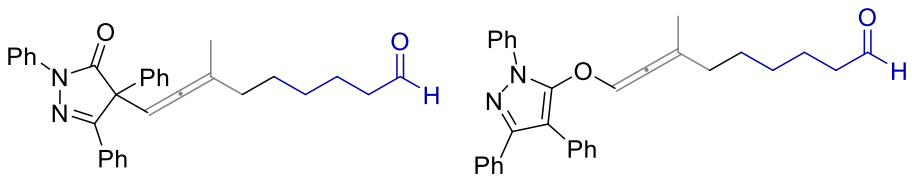
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.84 (m, 4H), 7.61 – 7.53 (m, 2H), 7.43 – 7.35 (m, 5H), 7.33 – 7.28 (m, 3H), 7.23 – 7.10 (m, 6H), 4.02 – 3.82 (m, 1H), 3.76 – 3.64 (m, 1.5H), 3.60 – 3.50 (m, 0.50H), 2.37 – 3.18 (m, 1H), 2.12 – 1.85 (m, 2H), 1.85 – 1.79 (m, 2H), 1.67 (s, *J* = 10.3 Hz, 3H), 1.51 – 1.38 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.11, 205.83, 205.79, 205.75, 173.57, 173.50, 173.44, 173.40, 158.96, 138.03, 138.02, 137.99, 136.63, 136.53, 136.49, 136.35, 136.03, 135.85, 135.54, 131.55, 131.49, 131.41, 130.26, 129.20, 129.13, 128.93, 128.75, 128.36, 128.32, 128.26, 128.23, 128.20, 128.13, 128.02, 127.95, 127.85, 127.68, 127.59, 127.55, 127.48, 127.24, 125.32, 119.38, 119.29, 105.05, 102.92, 77.84, 77.78, 77.18, 67.77, 67.69, 67.55, 67.53, 66.40, 66.25, 66.03, 65.99, 39.69, 39.49, 39.15, 39.08, 31.40, 31.34, 30.85, 30.43, 25.65, 25.55, 25.45, 18.91, 18.57, 18.17, 18.13.

HRMS (ESI) calculated for $C_{36}H_{32}N_2O_2$ [M + H] $^+$ m/z: 525.2537, found: 525.2543.

7-methyl-9-(5-oxo-1,3,4-triphenyl-4,5-dihydro-1H-pyrazol-4-yl)nona-7,8-dienal (**44**)

7-methyl-9-((1,3,4-triphenyl-1H-pyrazol-5-yl)oxy)nona-7,8-dienal (**44'**)



Isolated yield 49% (22.6 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 5 : 1), the selectivity ratio (C4: O) is 1.0:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (t, *J* = 1.7 Hz, 0.5H), 9.51 (t, *J* = 1.8 Hz, 0.5H), 7.98 (dd, *J* = 12.4, 4.4 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.37 – 7.30 (m, 5H), 7.29 – 7.21 (m, 5H), 7.16 – 7.11 (m,

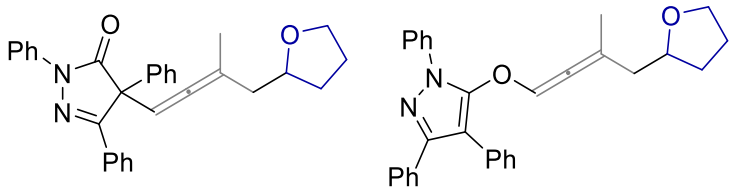
1H), 5.82 (dd, *J* = 5.7, 2.9 Hz, 0.5H), 5.67 (dd, *J* = 5.6, 2.8 Hz, 0.5H), 2.18 – 2.11 (m, 2H), 1.56 – 1.52 (m, 2H), 1.34 – 1.29 (m, 2H), 1.18 (s, 3H), 1.13 – 0.99 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.88, 202.75, 202.69, 173.89, 173.28, 160.01, 159.85, 138.36, 136.50, 136.32, 130.52, 130.12, 130.02, 129.26, 129.22, 128.95, 128.91, 128.42, 128.30, 128.23, 127.47, 127.40, 127.25, 127.11, 125.23, 125.16, 119.02, 118.97, 105.08, 105.03, 89.48, 89.44, 62.70, 62.53, 43.62, 43.56, 33.29, 33.21, 28.61, 28.53, 26.85, 26.82, 21.77, 21.74, 18.60, 18.22.

HRMS (ESI) calculated for $C_{31}H_{30}N_2O_2$ $[M + H]^+$ m/z: 462.2380, found: 462.2380.

4-(3-methyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (**45**)

5-((3-methyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)oxy)-1,3,4-triphenyl-1H-pyrazole (**45'**)



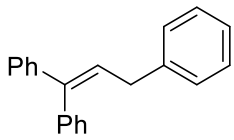
Isolated yield 37% (16.6 mg, 0.05 mmol scale×2), white solid, eluent (PE : EA = 5 : 1), the selectivity ratio (C4: O) is 1.3:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.02 (m, 2H), 7.72 – 7.64 (m, 2H), 7.46 – 7.29 (m, 10H), 7.25 – 7.19 (m, 1H), 5.96 – 5.87 (m, 0.44H), 5.82 – 5.74 (m, 0.56H), 3.81 – 3.43 (m, 3H), 2.15 – 1.81 (m, 2H), 1.81 – 1.70 (m, 2H), 1.70 – 1.64 (m, 3H), 1.34 – 1.26 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 203.54, 203.30, 173.62, 159.89, 159.73, 138.29, 136.50, 130.47, 130.10, 129.99, 129.24, 129.20, 128.99, 128.86, 128.83, 128.40, 128.26, 128.22, 127.46, 127.38, 127.15, 127.01, 125.12, 122.20, 119.00, 118.94, 102.26, 101.98, 89.15, 89.09, 88.92, 67.60, 67.53, 62.29, 39.61, 39.44, 39.20, 31.10, 29.68, 25.49, 25.44, 19.38, 19.01, 18.70, 18.25.

HRMS (ESI) calculated for $C_{30}H_{28}N_2O_2$ $[M + H]^+$ m/z: 449.2224, found: 449.2225.

prop-1-ene-1,1,3-triyltribenzene (**47**)



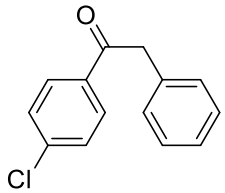
Isolated yield 40% (19.9 mg, 0.1 mmol scale ×2), colorless liquid, eluent (PE)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.07 (m, 15H), 6.18 (t, *J* = 7.6 Hz, 1H), 3.38 (d, *J* = 7.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.53, 142.49, 141.00, 139.88, 129.99, 128.54, 128.47, 128.36, 128.17, 127.82, 127.40, 127.20, 127.12, 126.06, 36.00.

HRMS (ESI) calculated for $C_{21}H_{18}$ $[M + H]^+$ m/z: 271.1481, found: 271.1481.

1-(4-chlorophenyl)-2-phenylethan-1-one (**50**)



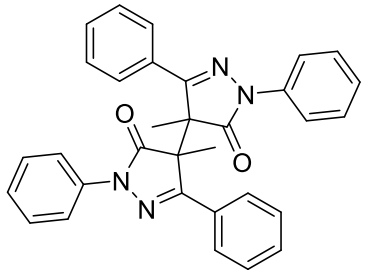
Isolated yield 48% (11.0 mg, 0.05 mmol scale ×2), colorless liquid, eluent (PE)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.37 – 7.32 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 (dt, *J* = 7.9, 4.1 Hz, 3H), 4.18 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.45, 139.65, 134.85, 134.19, 130.07, 129.40, 128.99, 128.79, 127.07, 45.56.

HRMS (ESI) calculated for $C_{14}H_{11}ClO$ $[M + H]^+$ m/z: 231.0571, found: 231.0570.

4,4'-dimethyl-2,2',5,5'-tetraphenyl-2,2',4,4'-tetrahydro-3H,3'H-[4,4'-bipyrazole]-3,3'-dione (**52**)



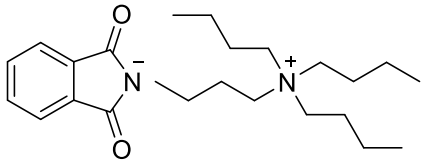
Isolated yield 40% (19.9 mg, 0.1 mmol scale), colorless liquid, eluent (PE : EA = 20 : 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.47 – 7.41 (m, 4H), 7.24-7.15 (m, 8H), 7.08 (q, *J* = 7.5 Hz, 4H), 2.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.36, 160.46, 136.84, 130.74, 130.03, 128.47, 128.11, 127.47, 125.21, 118.84, 55.07, 14.80.

HRMS (ESI) calculated for $C_{32}H_{26}N_4O_2$ $[M + H]^+$ m/z: 499.2129, found: 499.2131.

tetrabutylammonium 1,3-dioxoisoindolin-2-ide



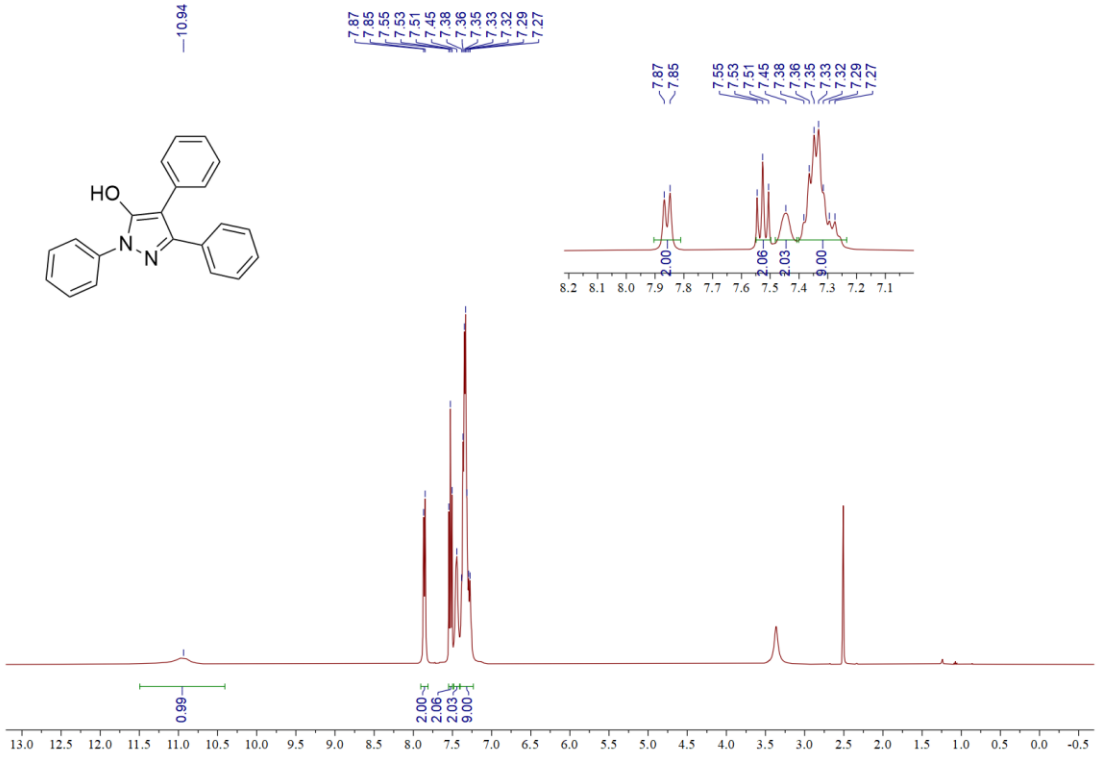
TBANPhth (base)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.36 (dd, *J* = 5.3, 3.0 Hz, 2H), 3.18 (dd, *J* = 9.9, 7.1 Hz, 8H), 1.56 – 1.46 (m, 8H), 1.35 – 1.24 (m, 8H), 0.86 (t, *J* = 7.3 Hz, 12H).

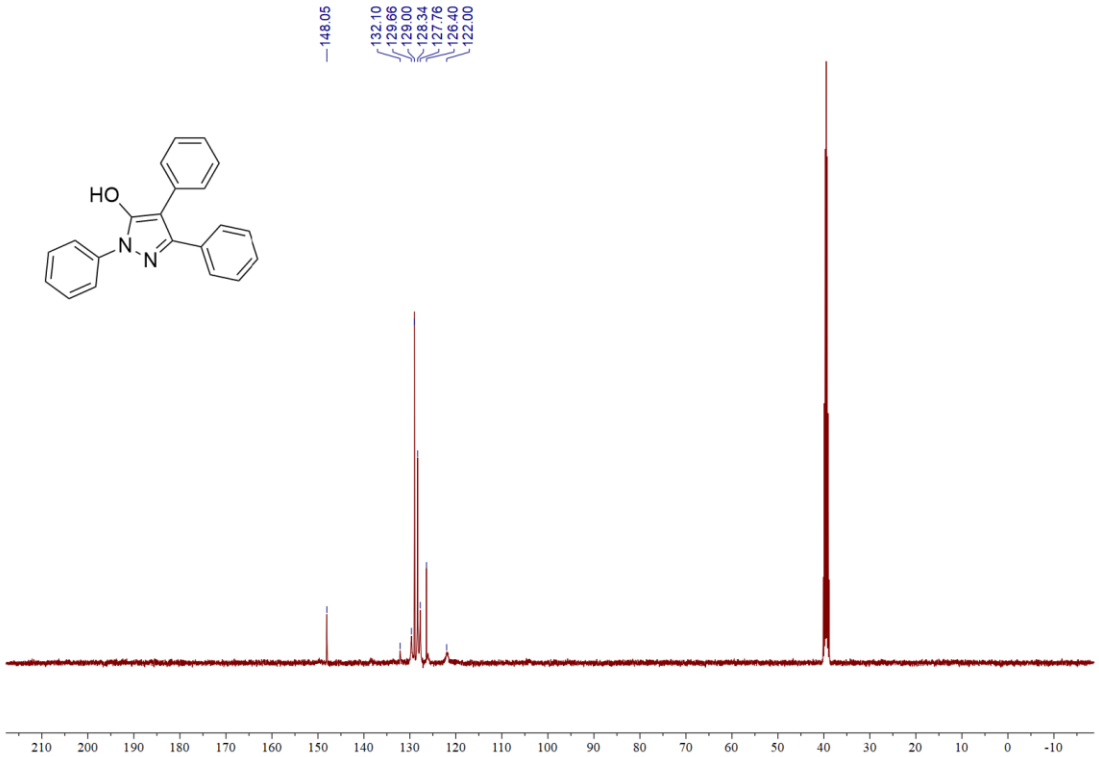
^{13}C NMR (101 MHz, $CDCl_3$) δ = 183.31, 137.53, 129.78, 119.44, 57.64, 22.92, 18.64, 12.63.

2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (1a)

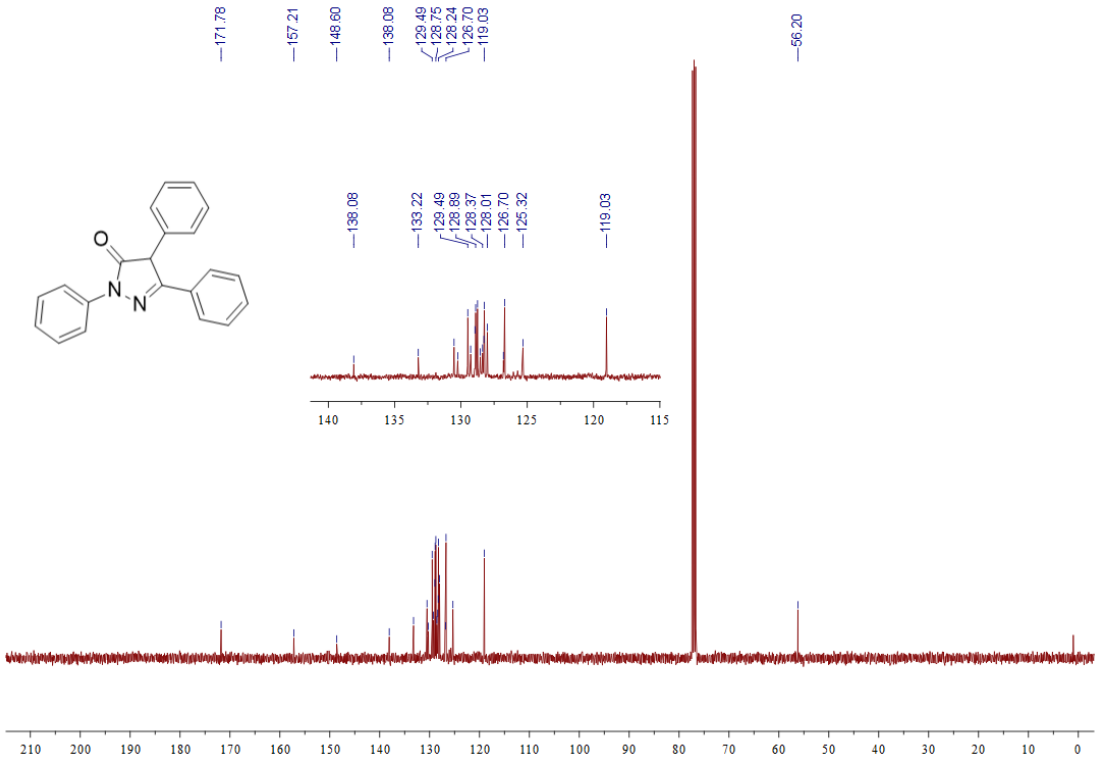
^{1}H NMR (400 MHz, DMSO)



^{13}C NMR (101 MHz, DMSO)

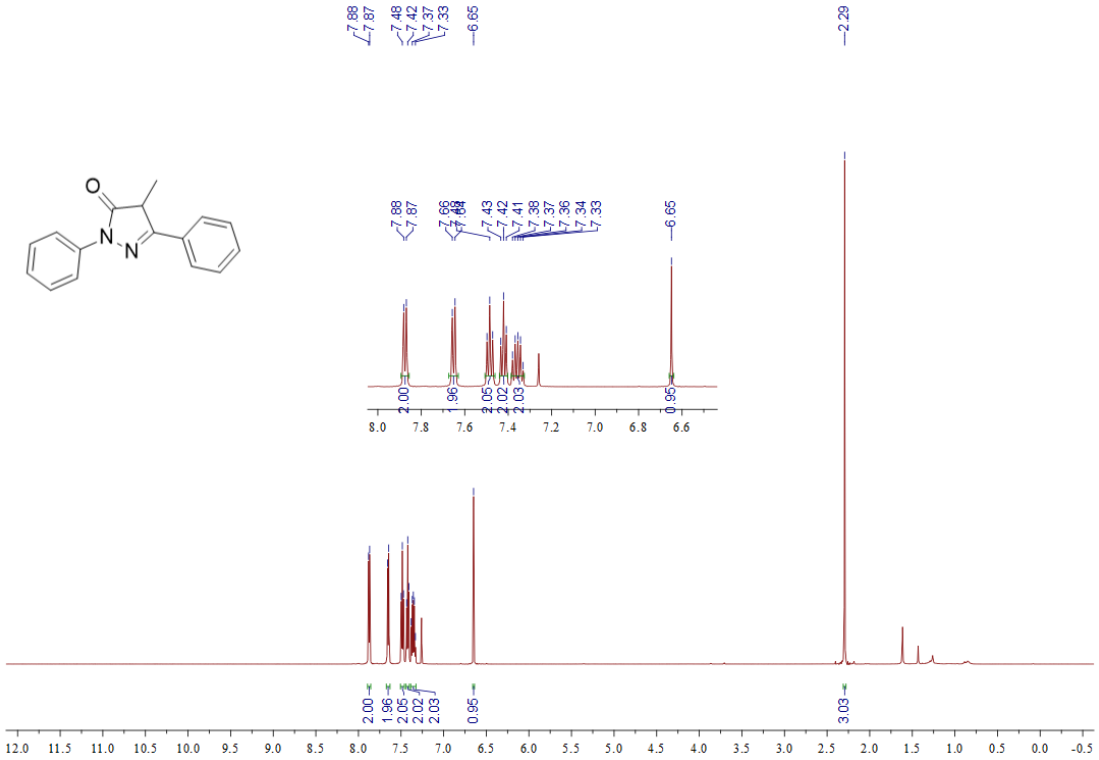


^{13}C NMR (101 MHz, $CDCl_3$)

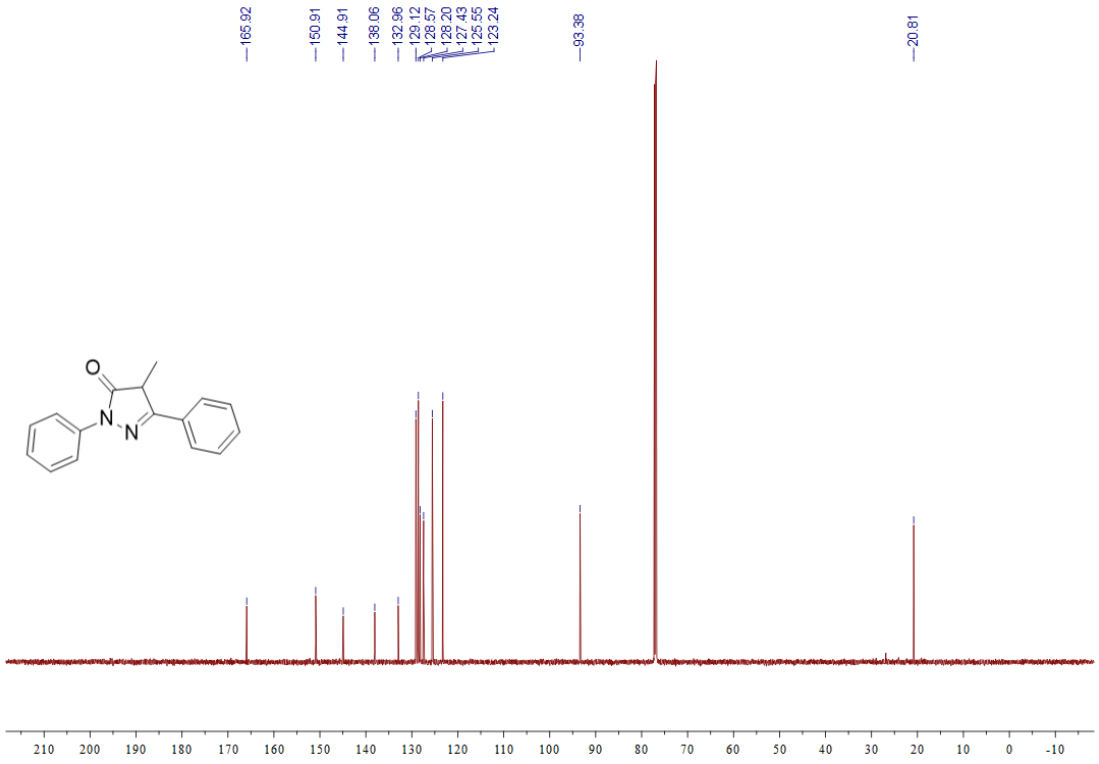


4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (1b)

^{1}H NMR (600 MHz, $CDCl_3$)

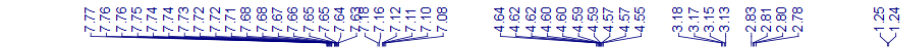


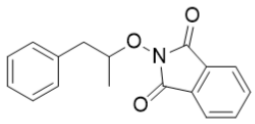
^{13}C NMR (151 MHz, $CDCl_3$)

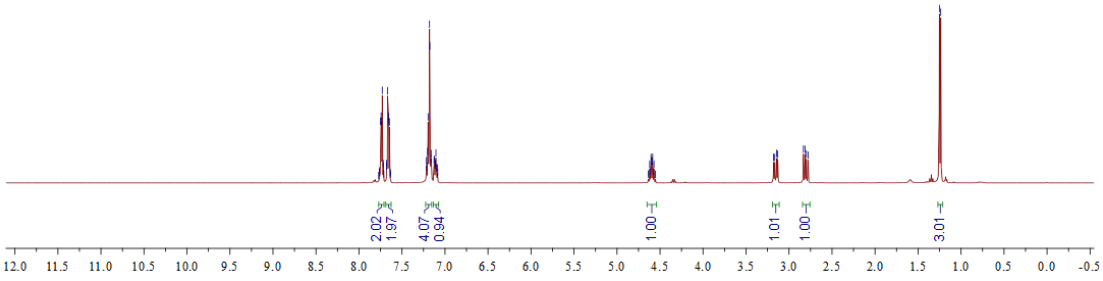


2-((1-phenylpropan-2-yl)oxy)isoindoline-1,3-dione (2a)

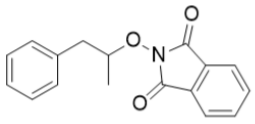
^{1}H NMR (400 MHz, $CDCl_3$)

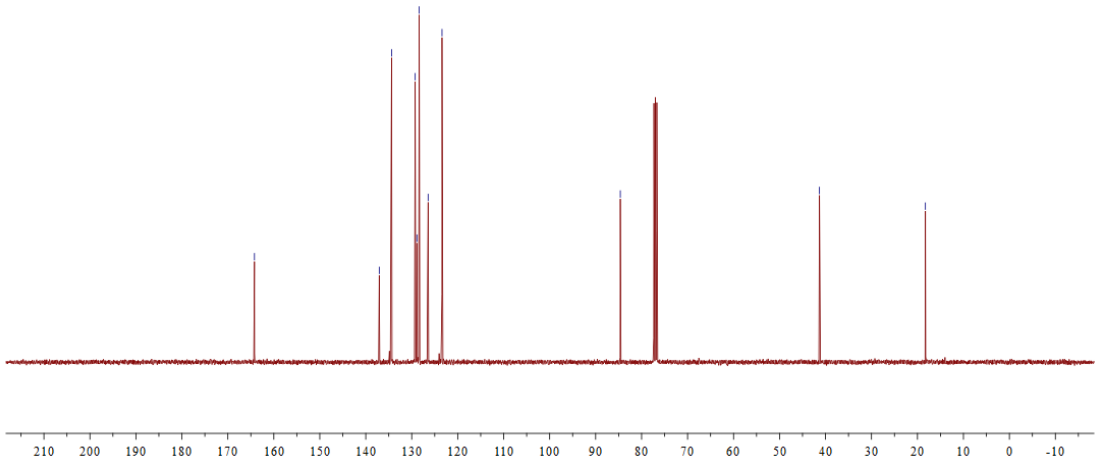






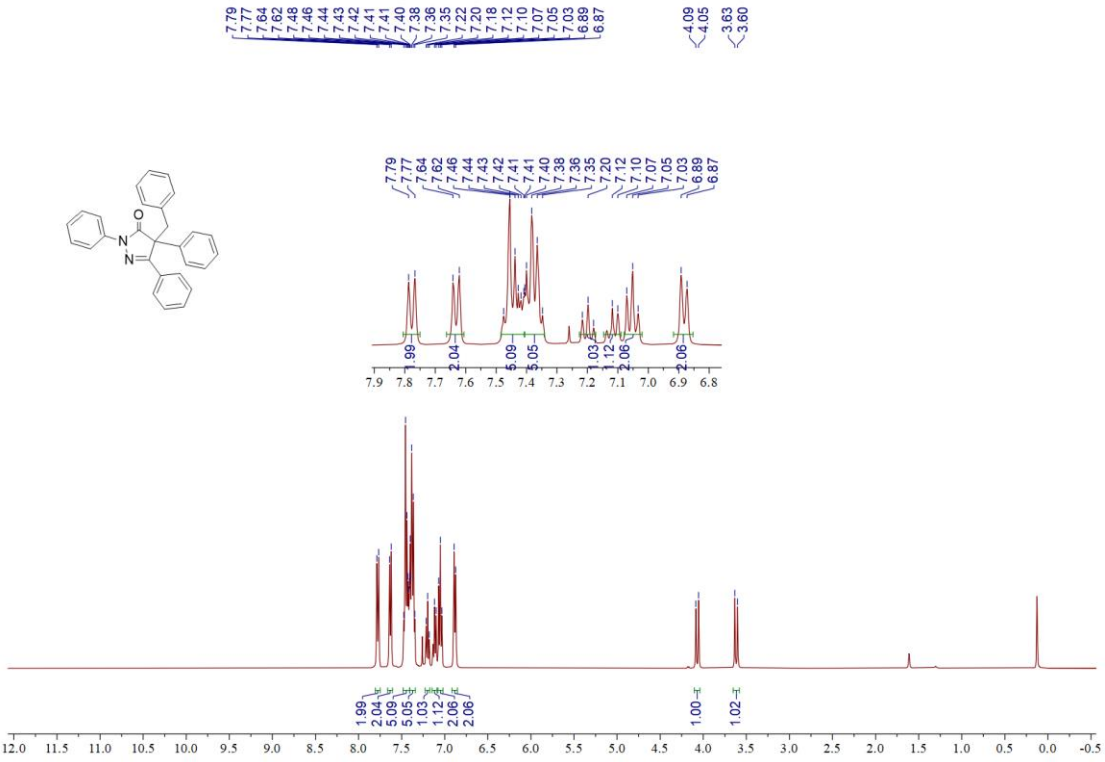
^{13}C NMR (101 MHz, $CDCl_3$)



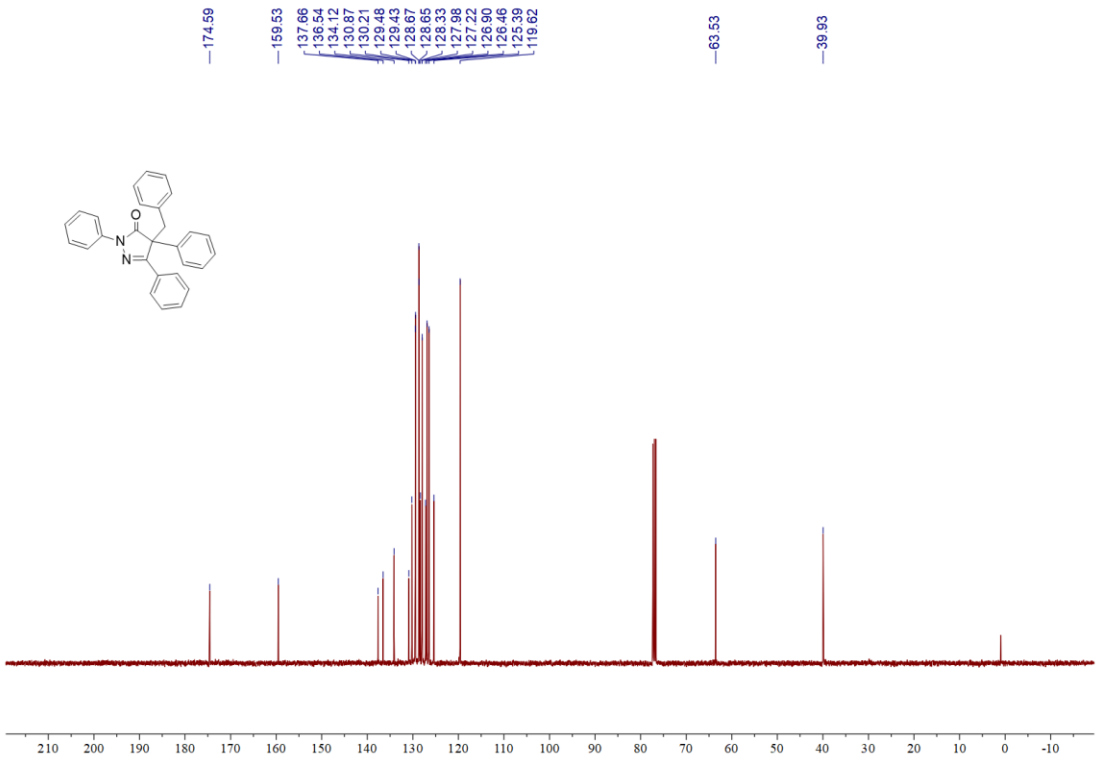


4-benzyl-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (3a)

^{1}H NMR (400 MHz, $CDCl_3$)

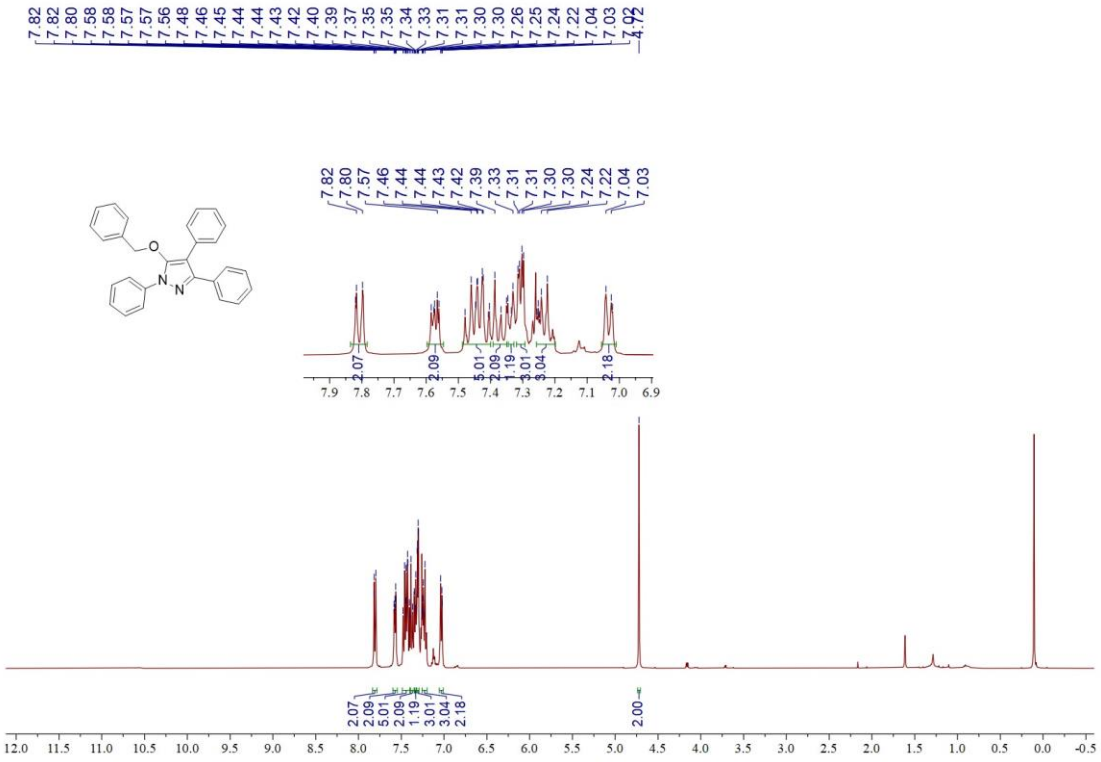


^{13}C NMR (101 MHz, $CDCl_3$)

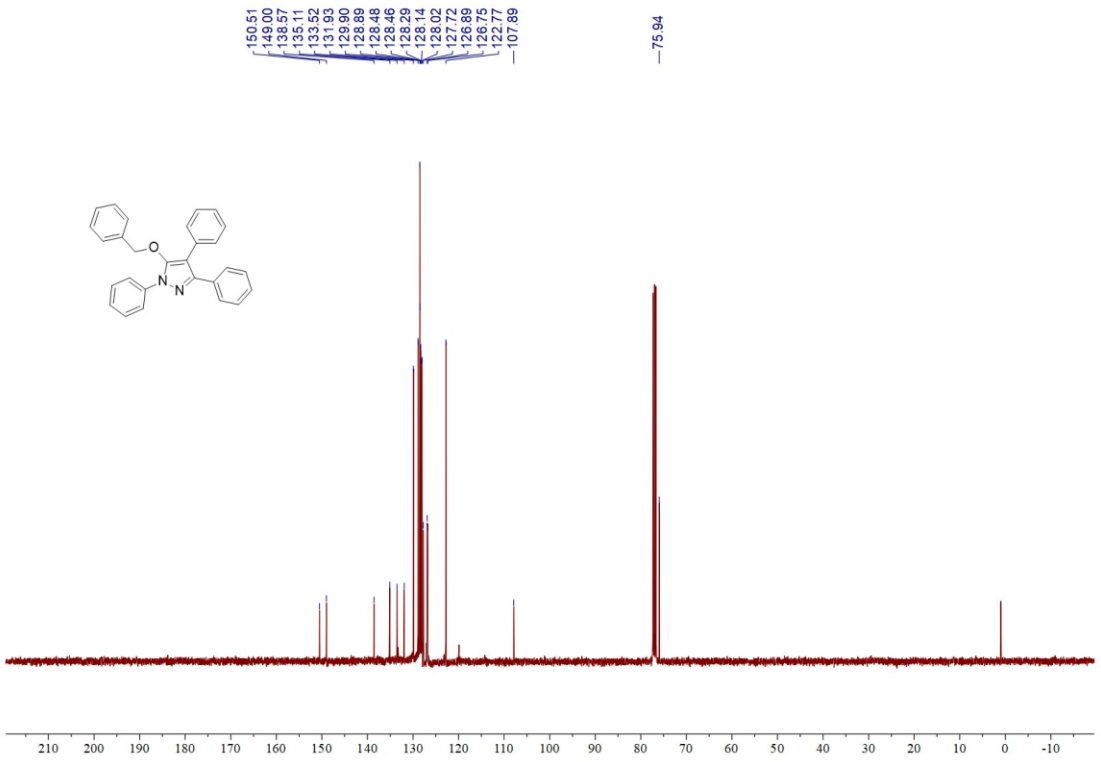


5-(benzyloxy)-1,3,4-triphenyl-1H-pyrazole (3a')

^{1}H NMR (400 MHz, $CDCl_3$)

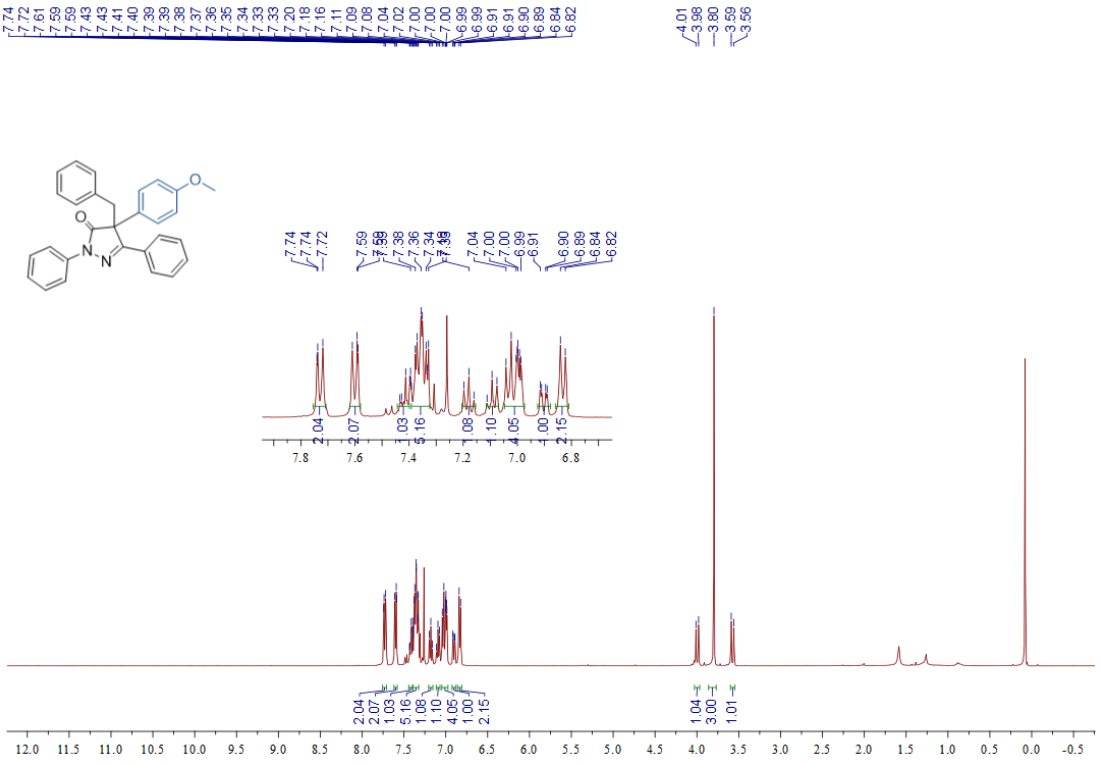


^{13}C NMR (101 MHz, $CDCl_3$)

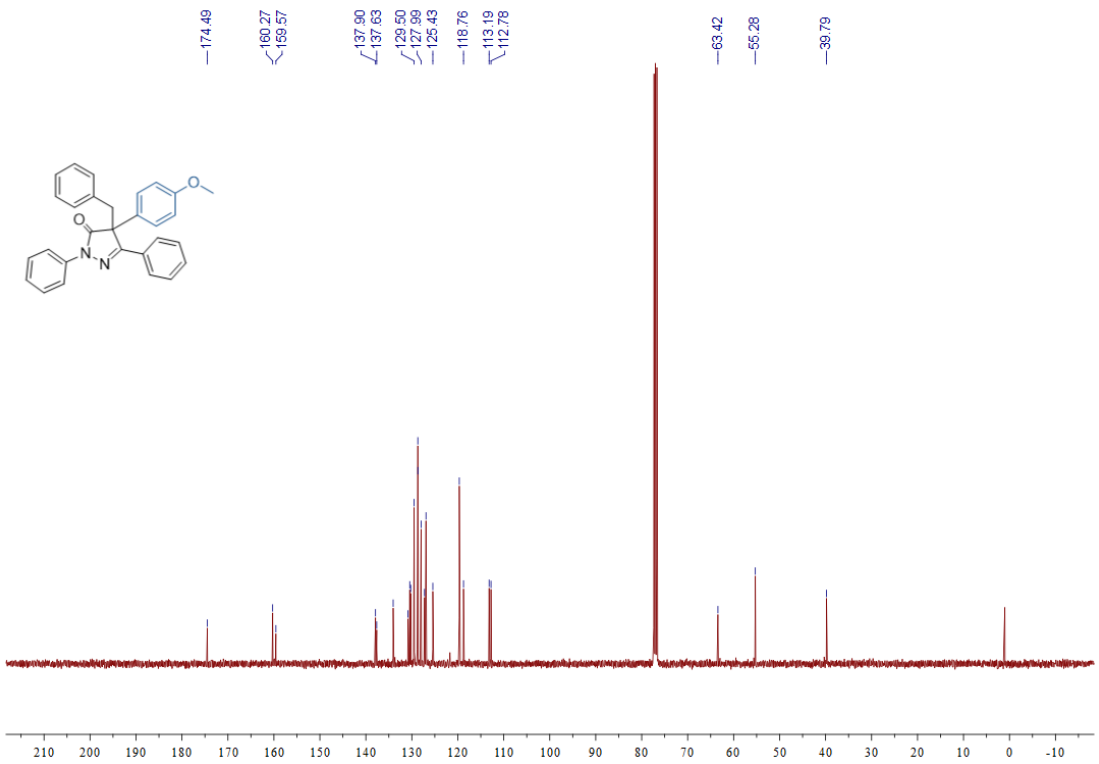


4-benzyl-4-(4-methoxyphenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (4)

^{1}H NMR (400 MHz, $CDCl_3$)

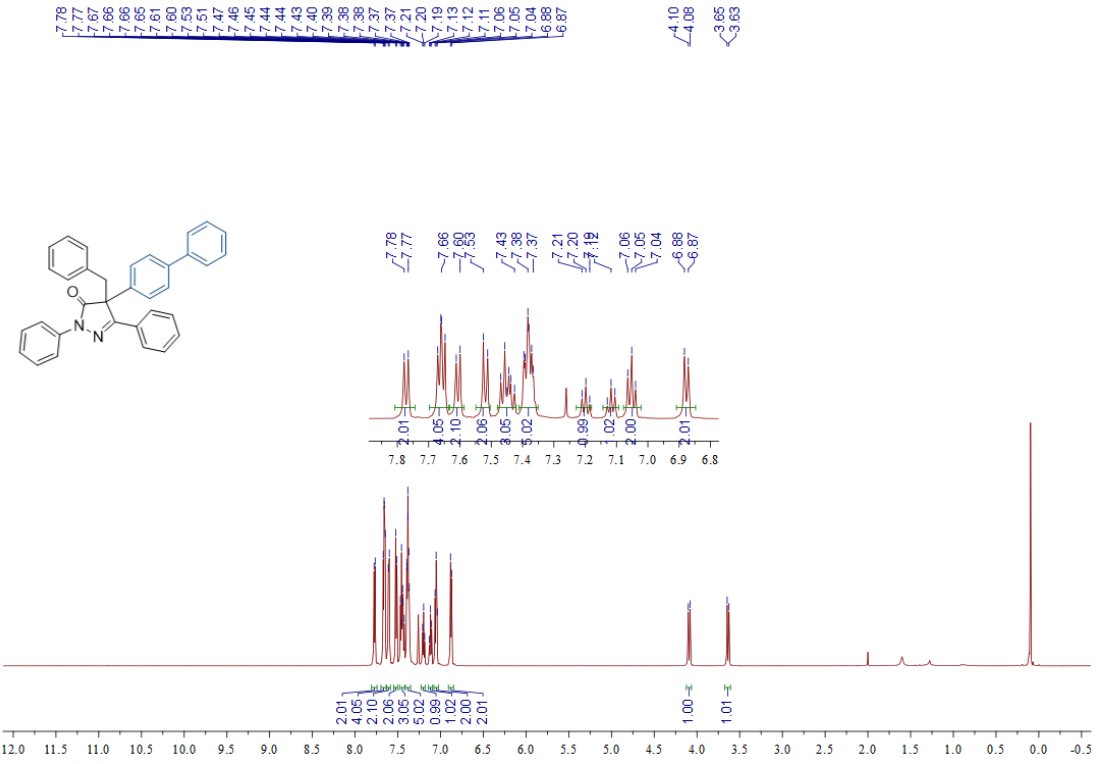


^{13}C NMR (101 MHz, $CDCl_3$)

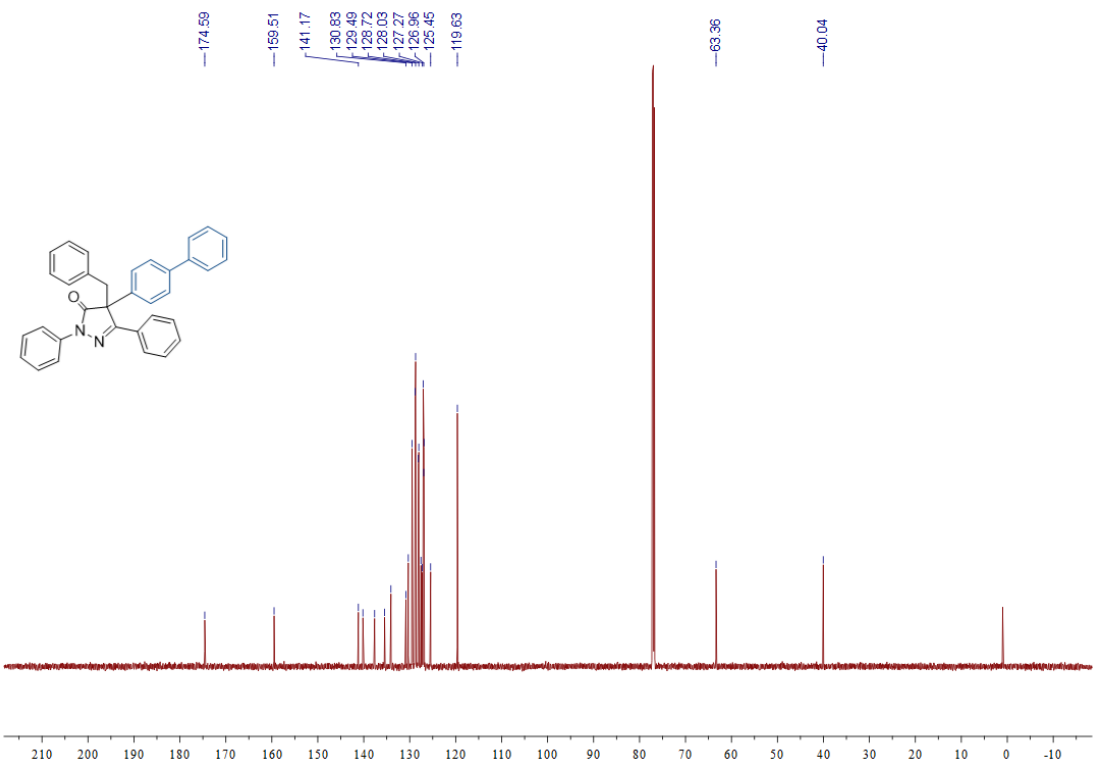


4-([1,1'-biphenyl]-4-yl)-4-benzyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (5)

^{1}H NMR (400 MHz, $CDCl_3$)

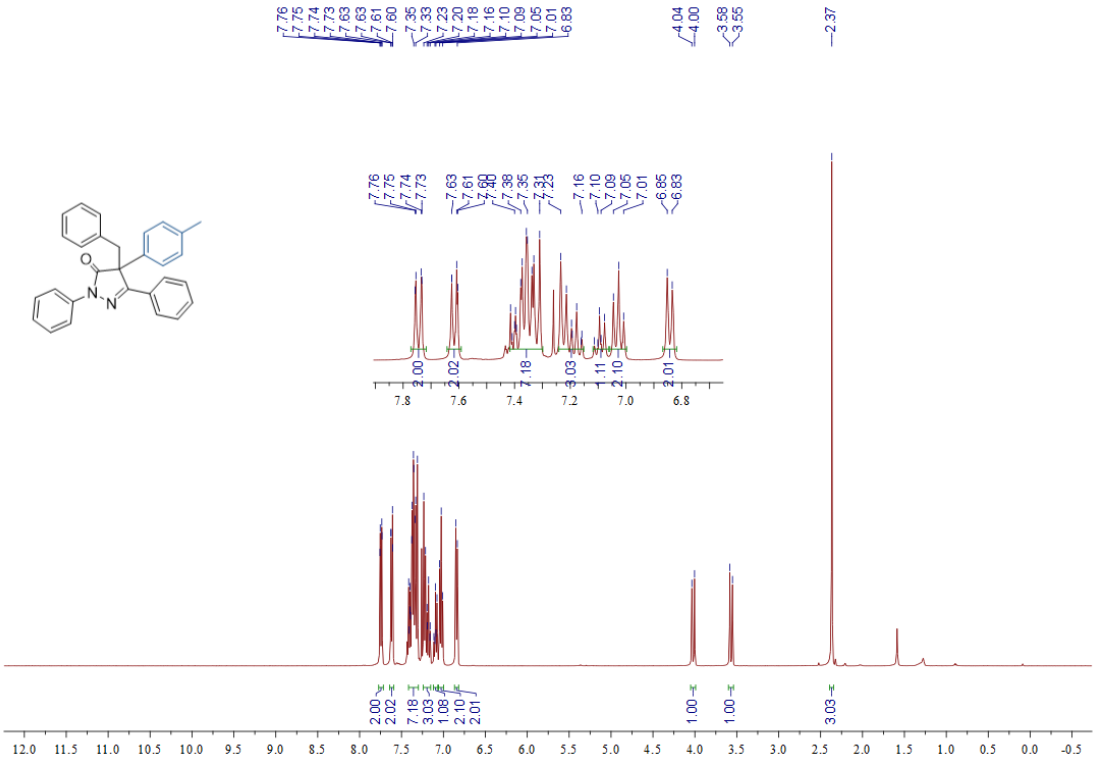


^{13}C NMR (101 MHz, $CDCl_3$)

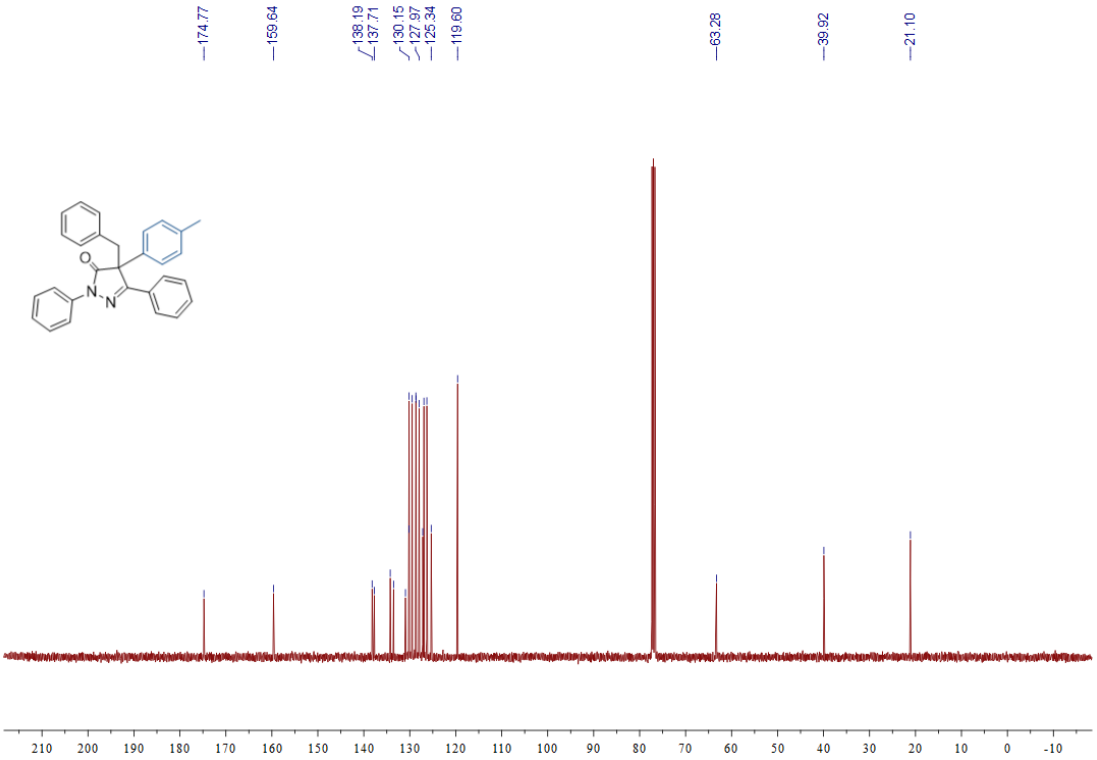


4-benzyl-2,5-diphenyl-4-(p-tolyl)-2,4-dihydro-3H-pyrazol-3-one (6)

^{1}H NMR (400 MHz, $CDCl_3$)

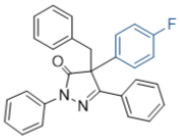


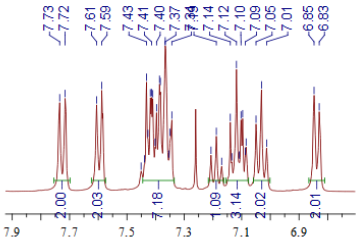
^{13}C NMR (101 MHz, $CDCl_3$)

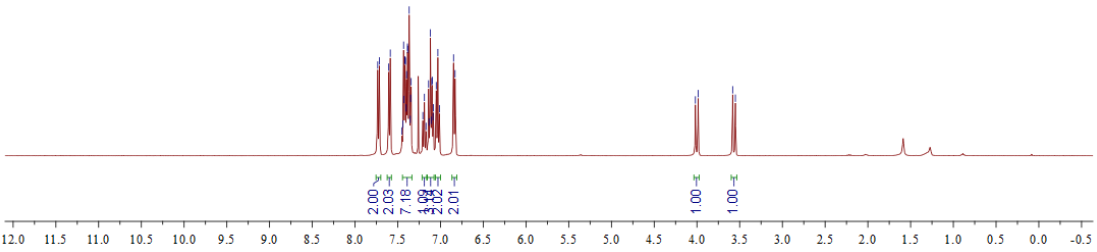


4-benzyl-4-(4-fluorophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (7)

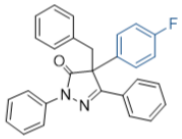
^{1}H NMR (400 MHz, $CDCl_3$)



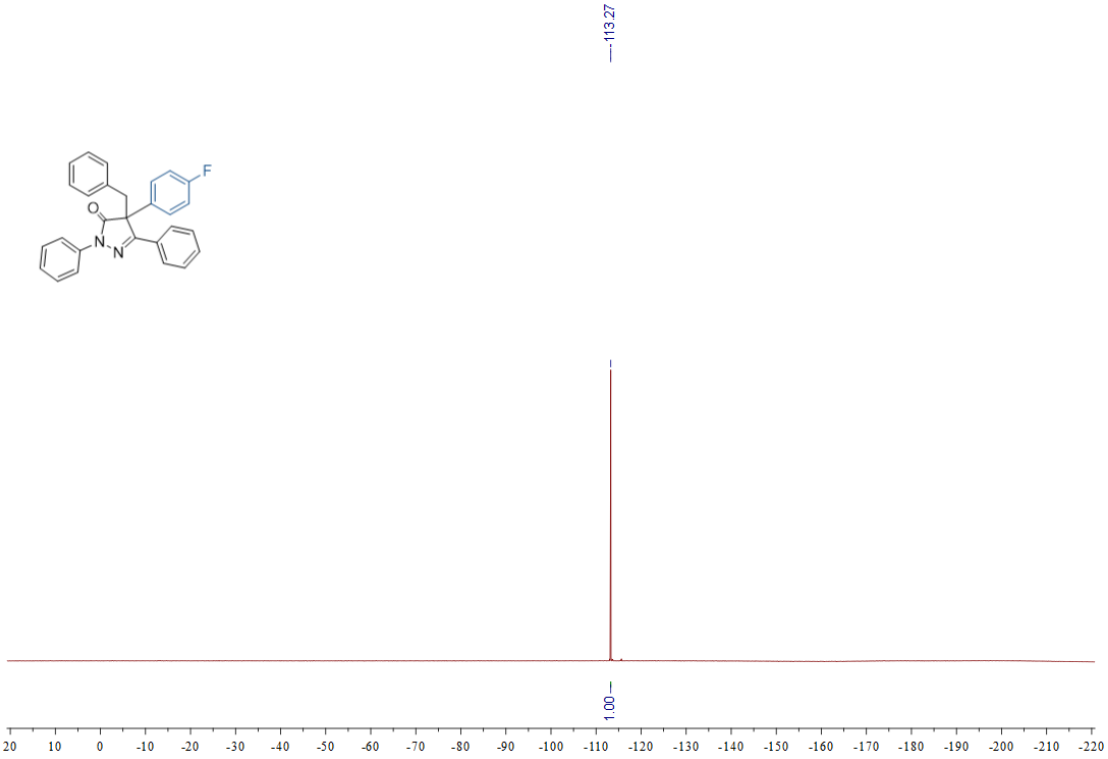




^{13}C NMR (101 MHz, $CDCl_3$)



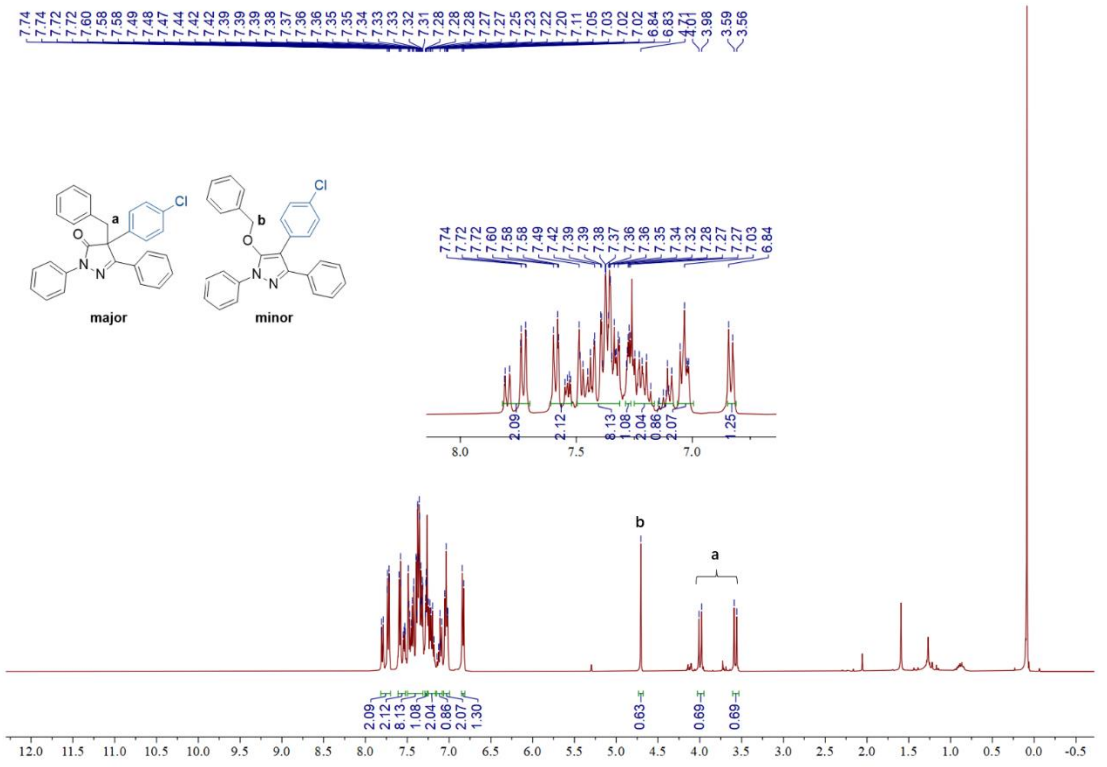
^{19}F NMR (376 MHz, $CDCl_3$)



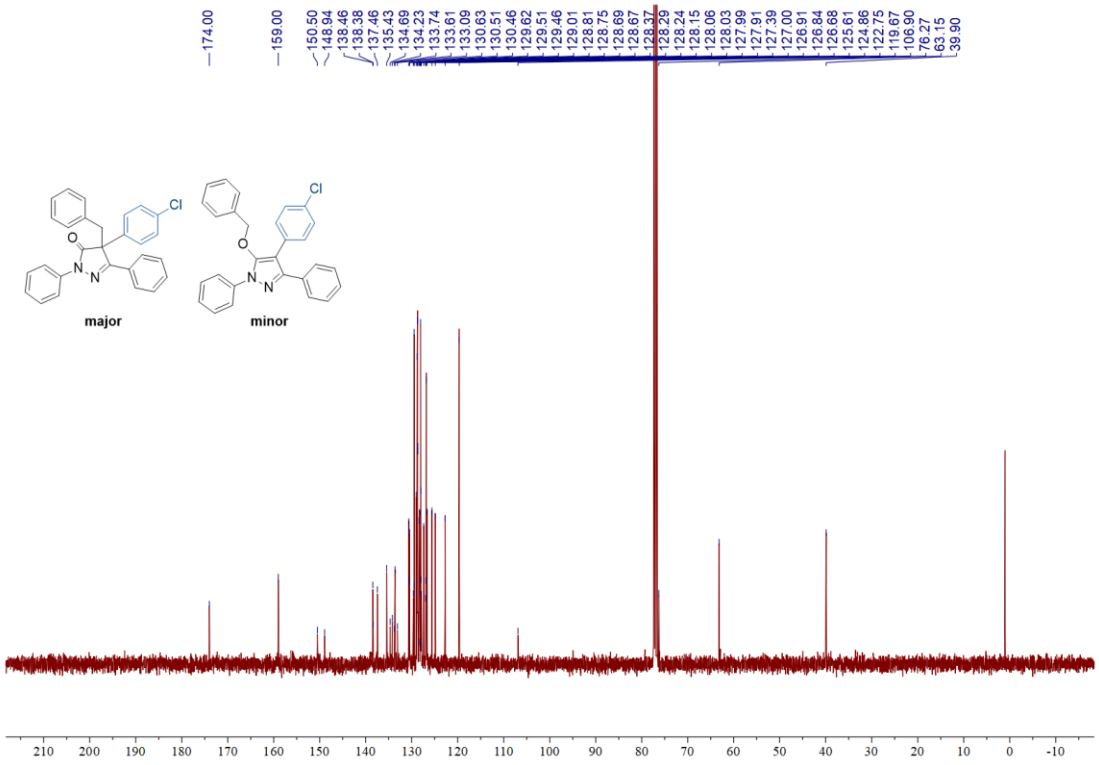
4-benzyl-4-(4-chlorophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (8)

5-(benzyloxy)-4-(4-chlorophenyl)-1,3-diphenyl-1H-pyrazole (8')

^{1}H NMR (400 MHz, $CDCl_3$)



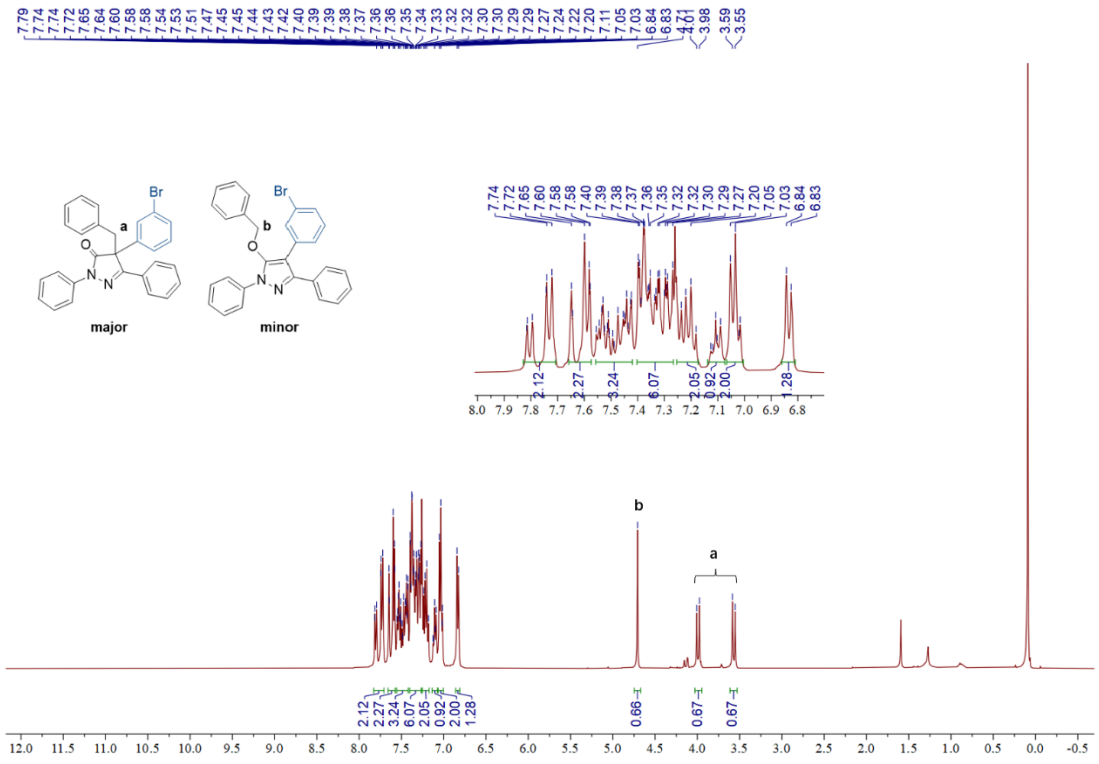
^{13}C NMR (101 MHz, $CDCl_3$)



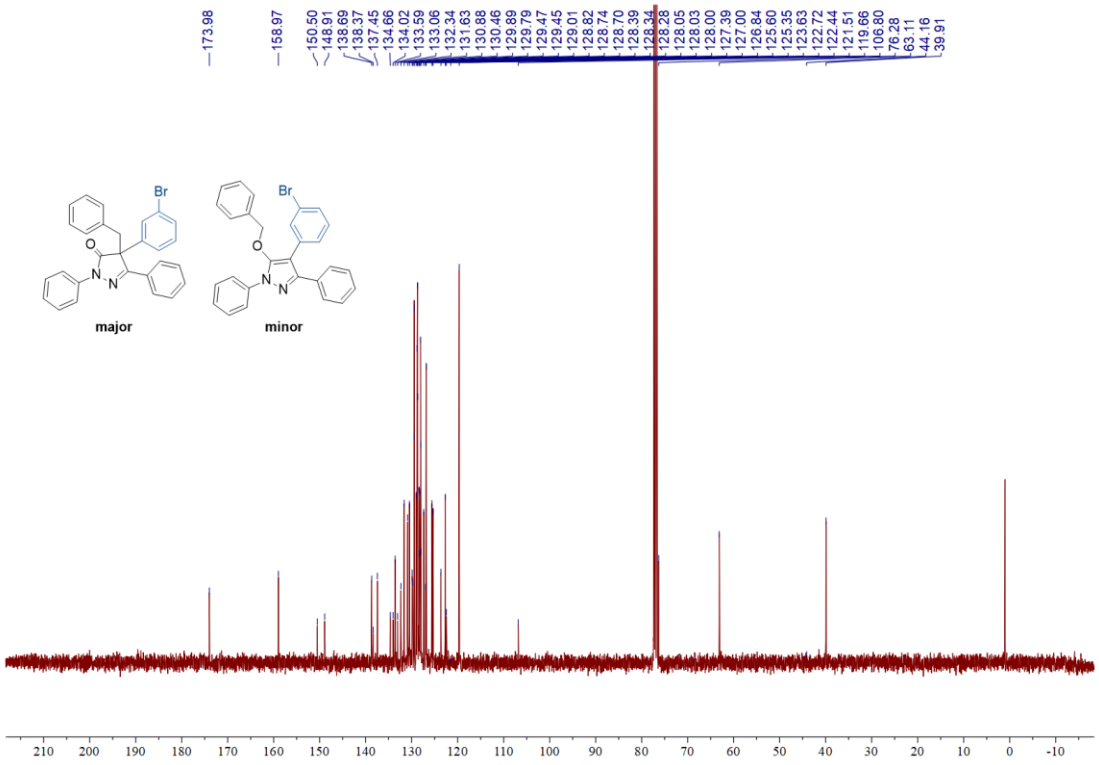
4-benzyl-4-(3-bromophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (9)

5-(benzyloxy)-4-(3-bromophenyl)-1,3-diphenyl-1H-pyrazole (9')

^{1}H NMR (400 MHz, $CDCl_3$)



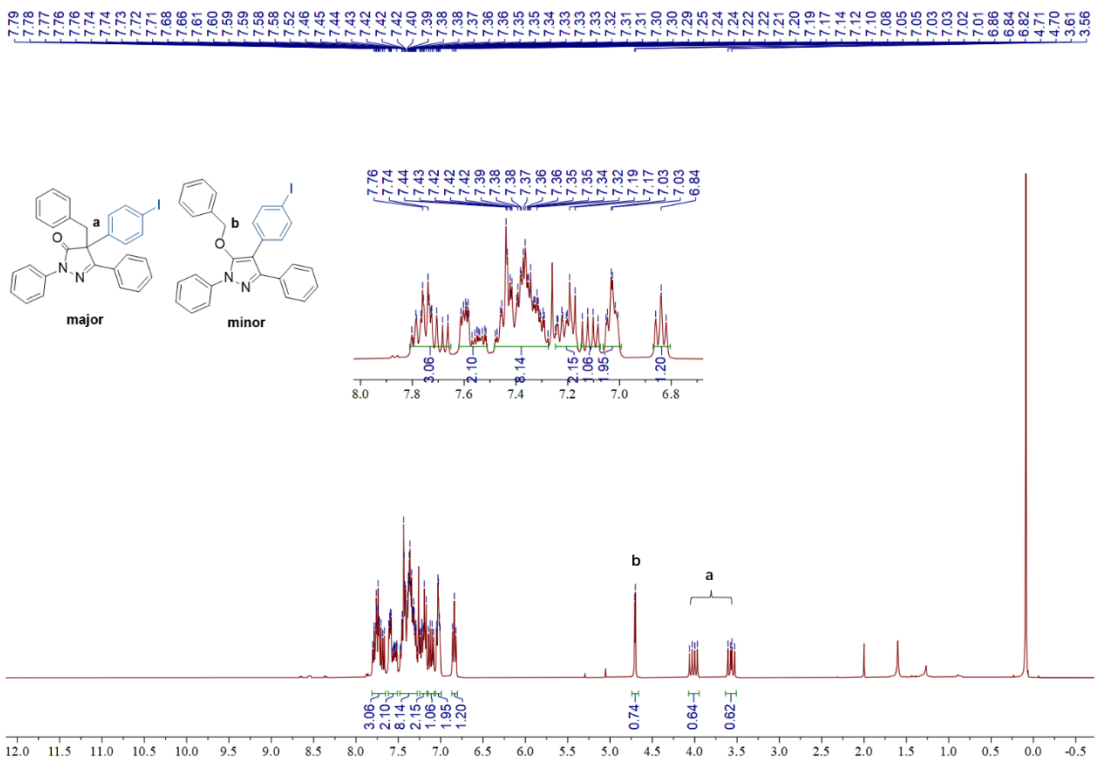
^{13}C NMR (101 MHz, $CDCl_3$)



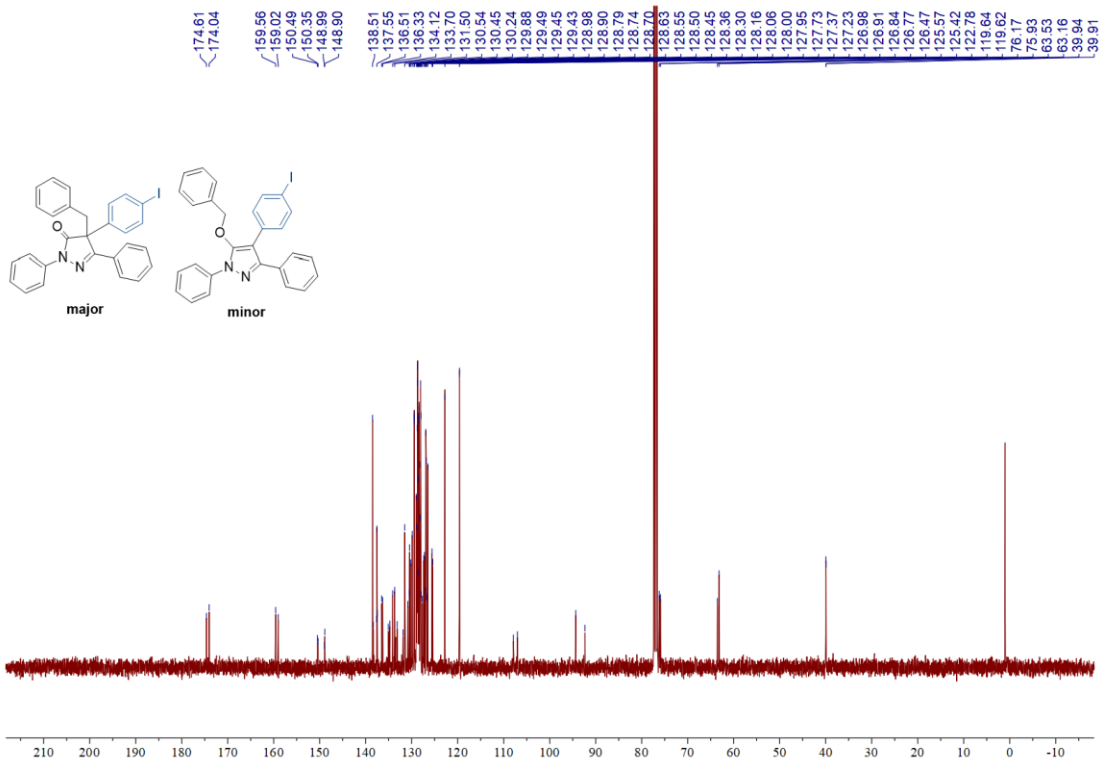
4-benzyl-4-(4-iodophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (10)

5-(benzyloxy)-4-(4-iodophenyl)-1,3-diphenyl-1H-pyrazole (10')

^{1}H NMR (400 MHz, $CDCl_3$)



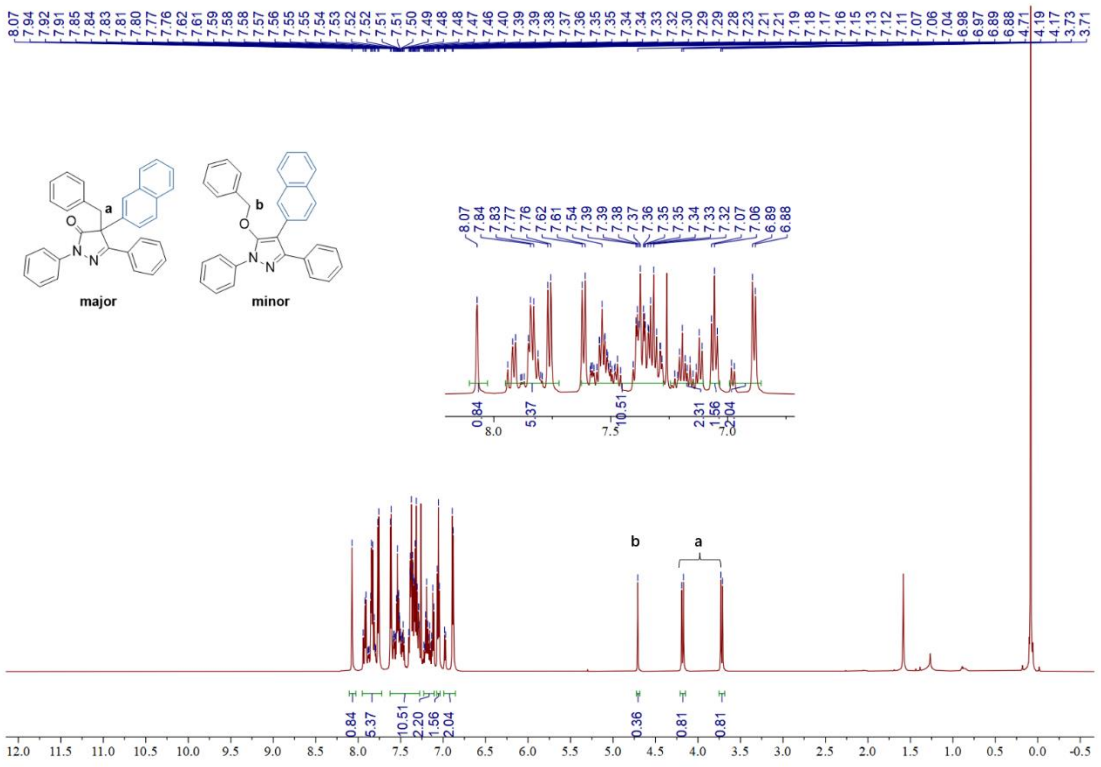
^{13}C NMR (101 MHz, $CDCl_3$)



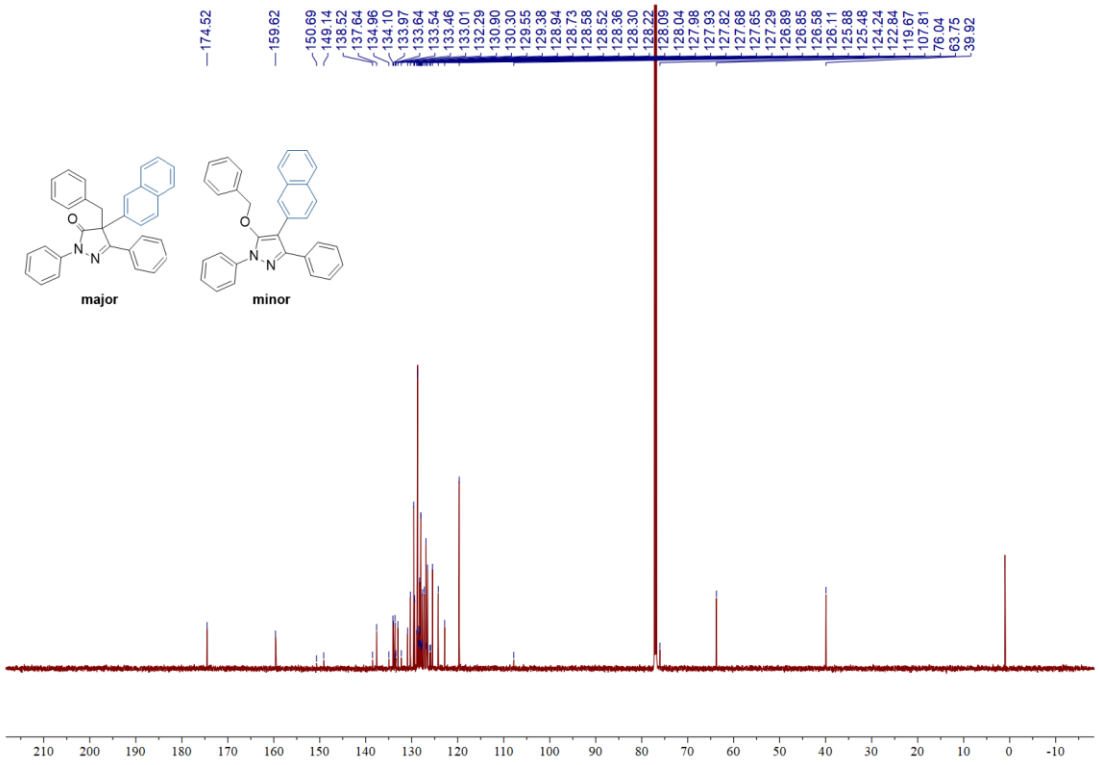
4-benzyl-4-(naphthalen-2-yl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (11)

5-(benzyloxy)-4-(naphthalen-2-yl)-1,3-diphenyl-1H-pyrazole (11')

^{1}H NMR (400 MHz, $CDCl_3$)



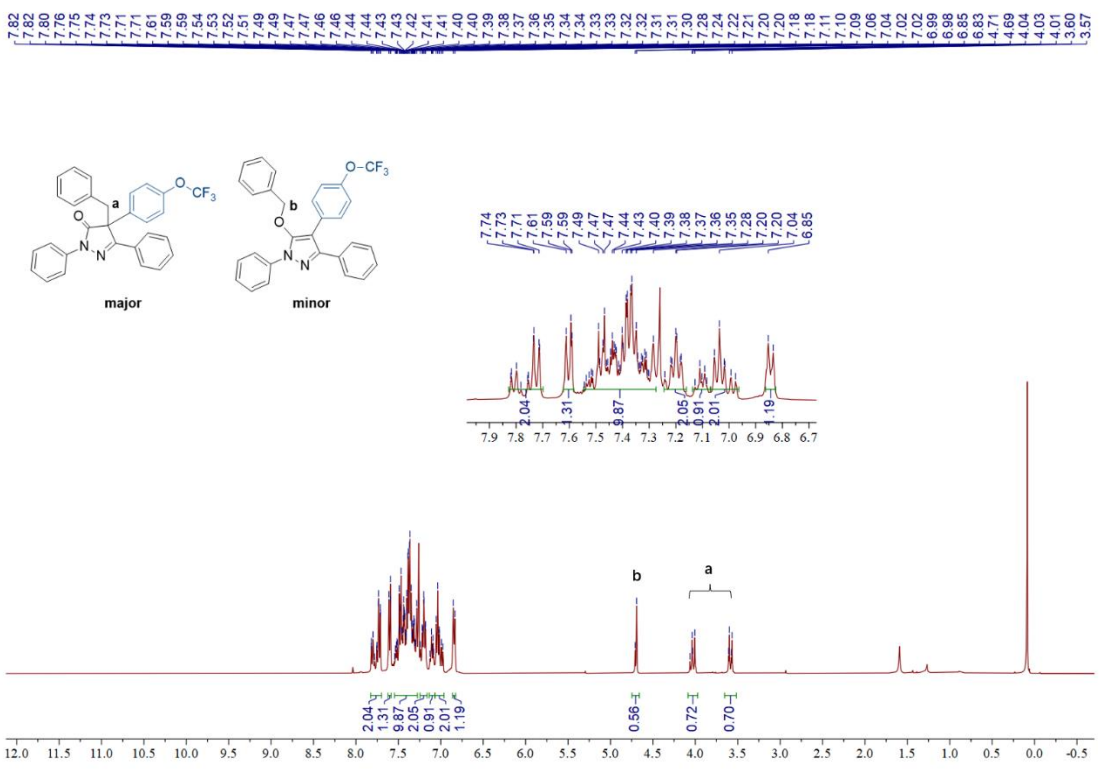
^{13}C NMR (101 MHz, $CDCl_3$)



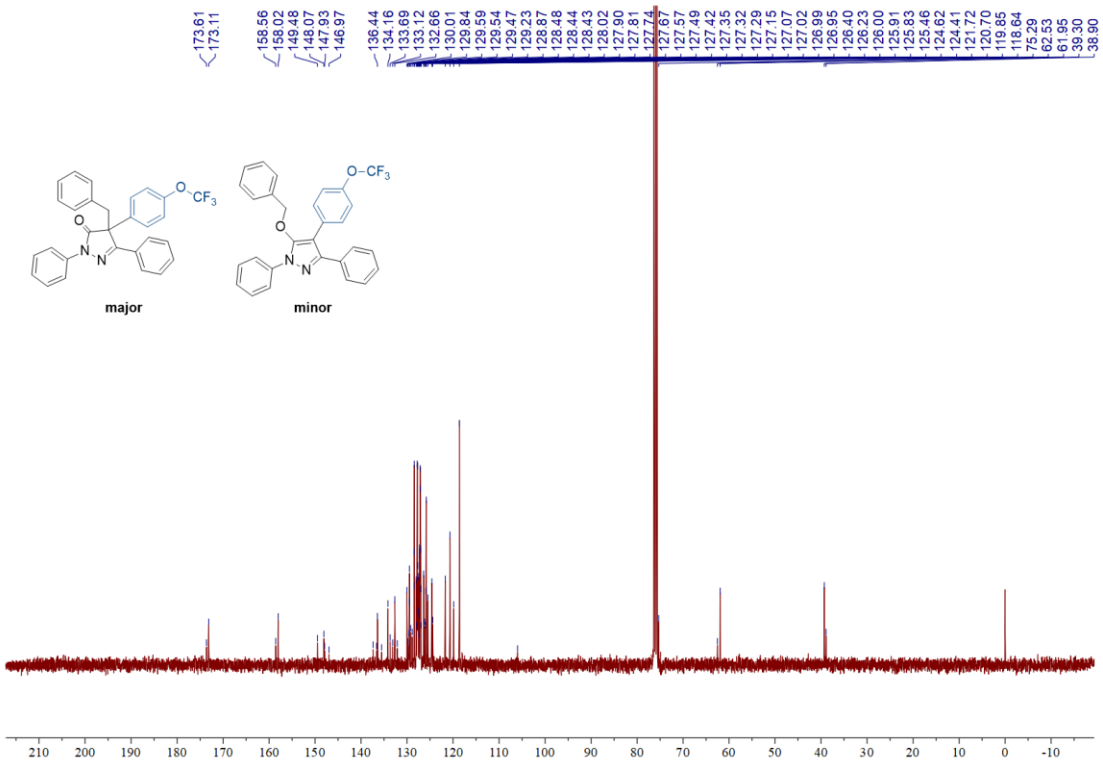
4-benzyl-2,5-diphenyl-4-(4-(trifluoromethoxy)phenyl)-2,4-dihydro-3H-pyrazol-3-one (12)

5-(benzyloxy)-1,3-diphenyl-4-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (12')

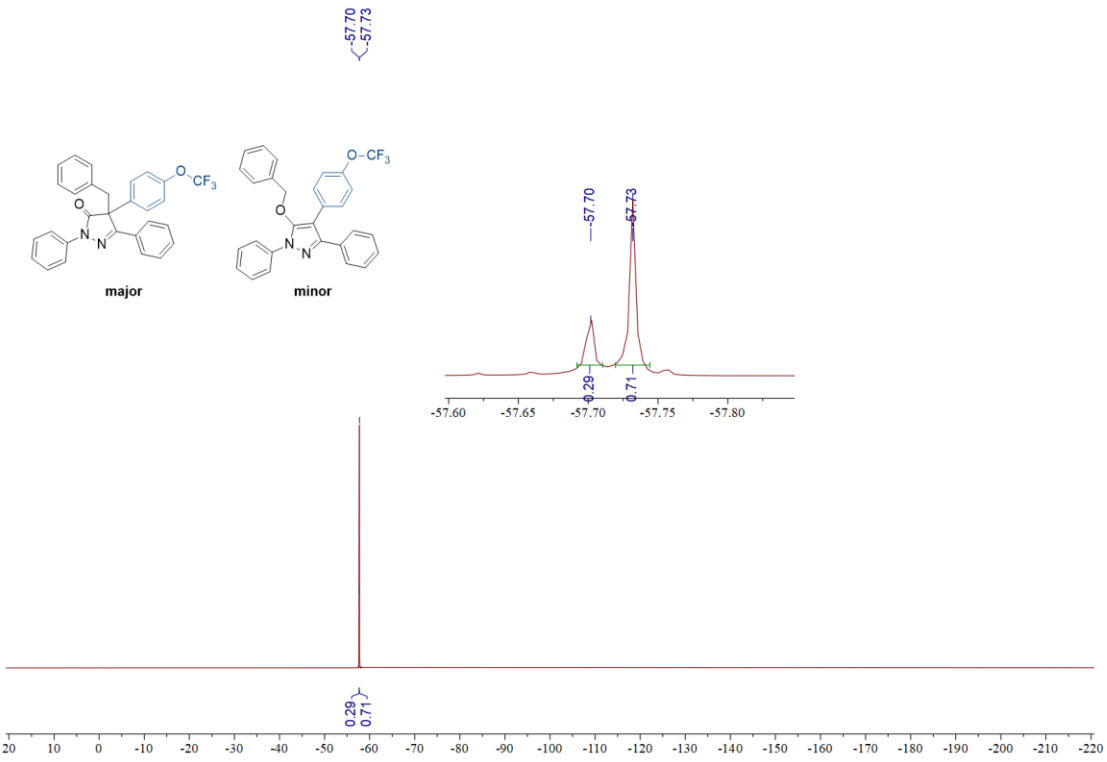
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

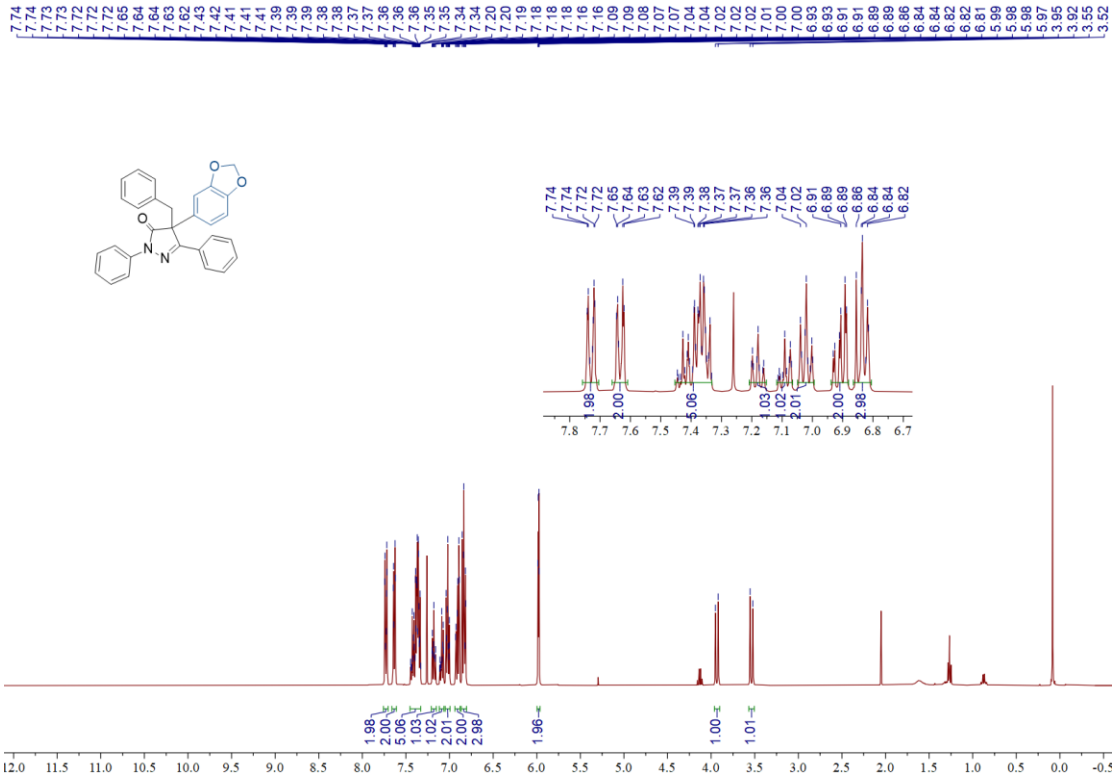


^{19}F NMR (376 MHz, $CDCl_3$)

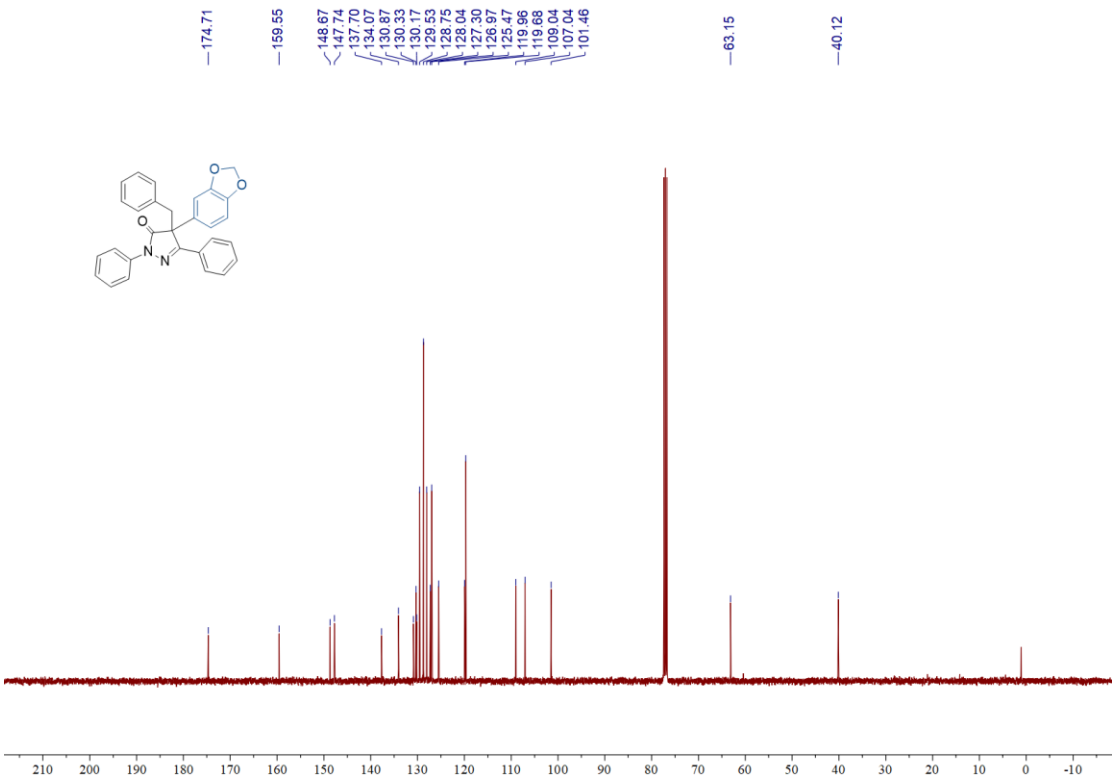


4-(benzo[d][1,3]dioxol-5-yl)-4-benzyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (13)

^{1}H NMR (400 MHz, $CDCl_3$)



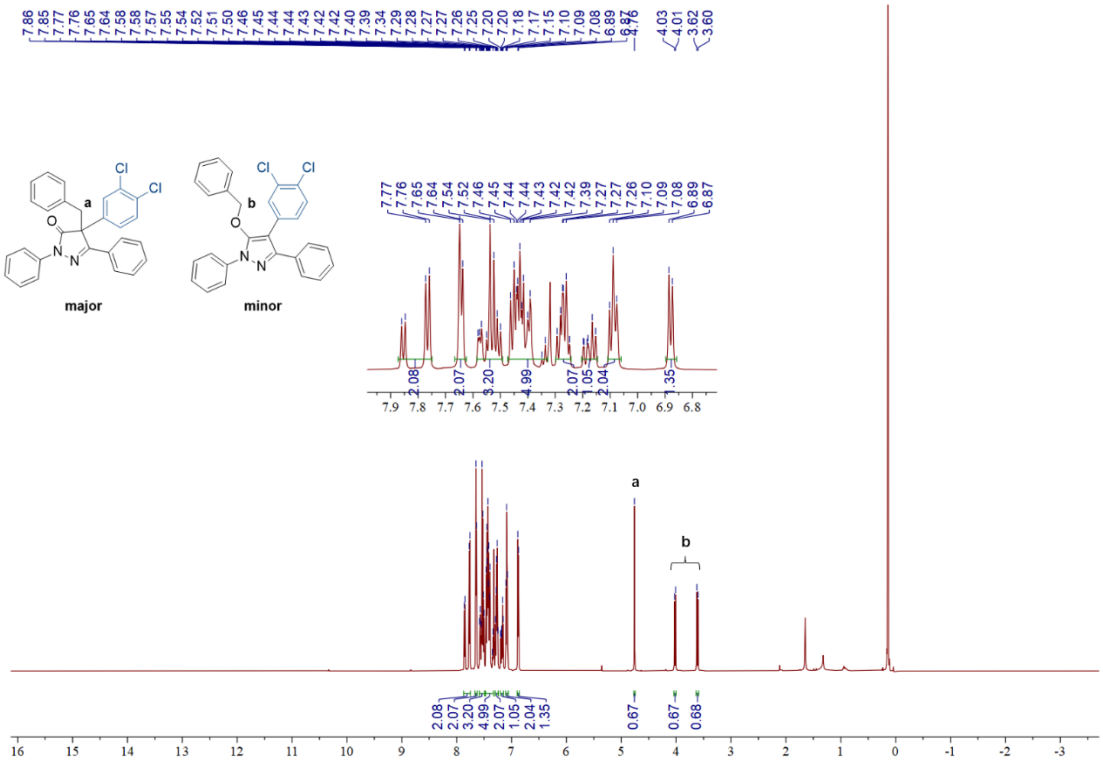
^{13}C NMR (101 MHz, $CDCl_3$)



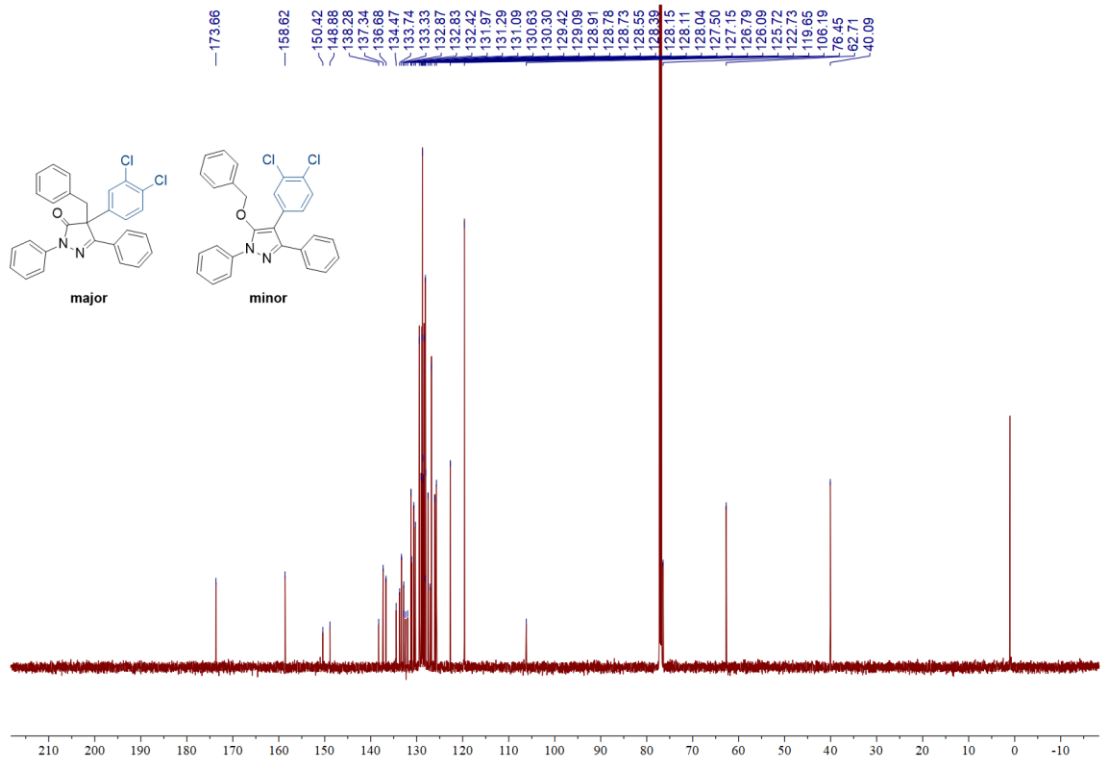
4-benzyl-4-(3,4-dichlorophenyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (14)

5-(benzyloxy)-4-(3,4-dichlorophenyl)-1,3-diphenyl-1H-pyrazole (14')

^{1}H NMR (400 MHz, $CDCl_3$)



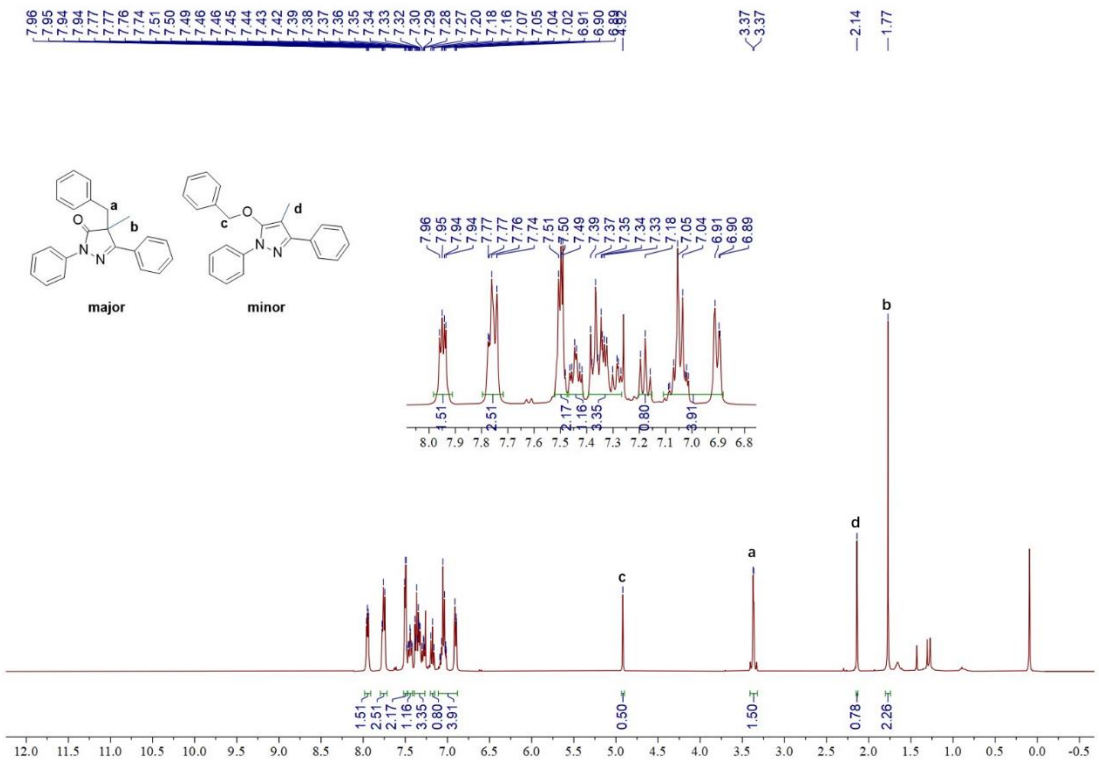
^{13}C NMR (101 MHz, $CDCl_3$)



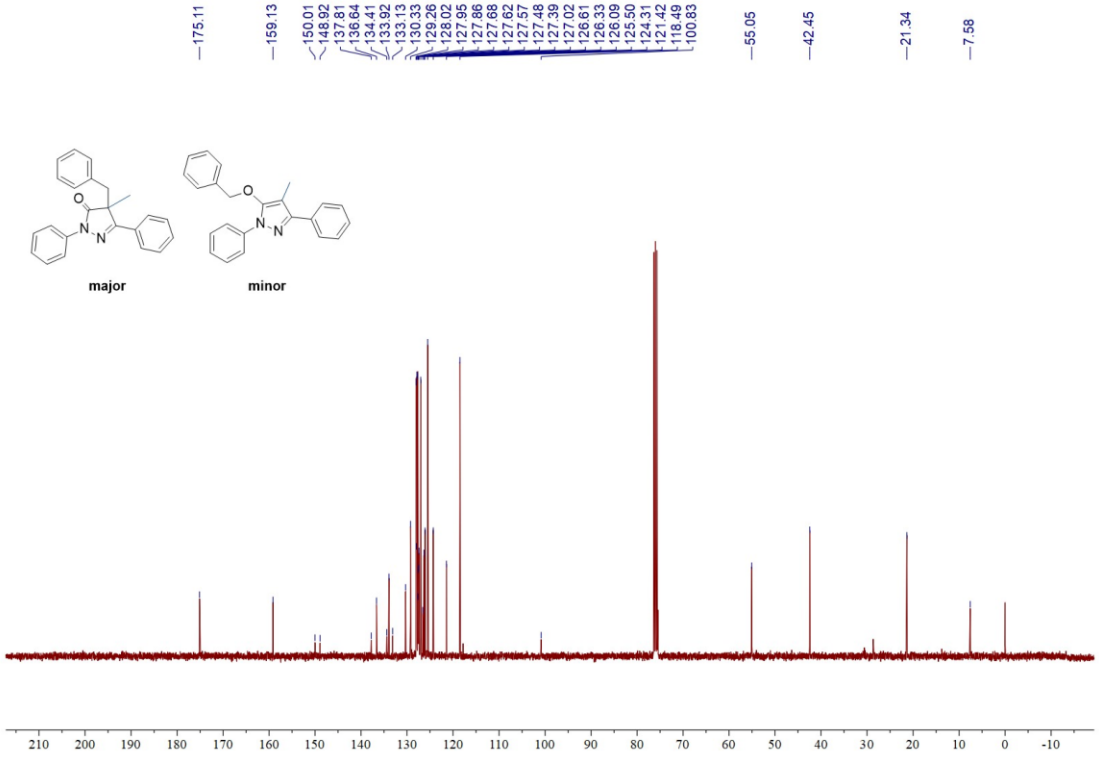
4-benzyl-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (15)

5-(benzyloxy)-4-methyl-1,3-diphenyl-1H-pyrazole (15')

^{1}H NMR (400 MHz, $CDCl_3$)



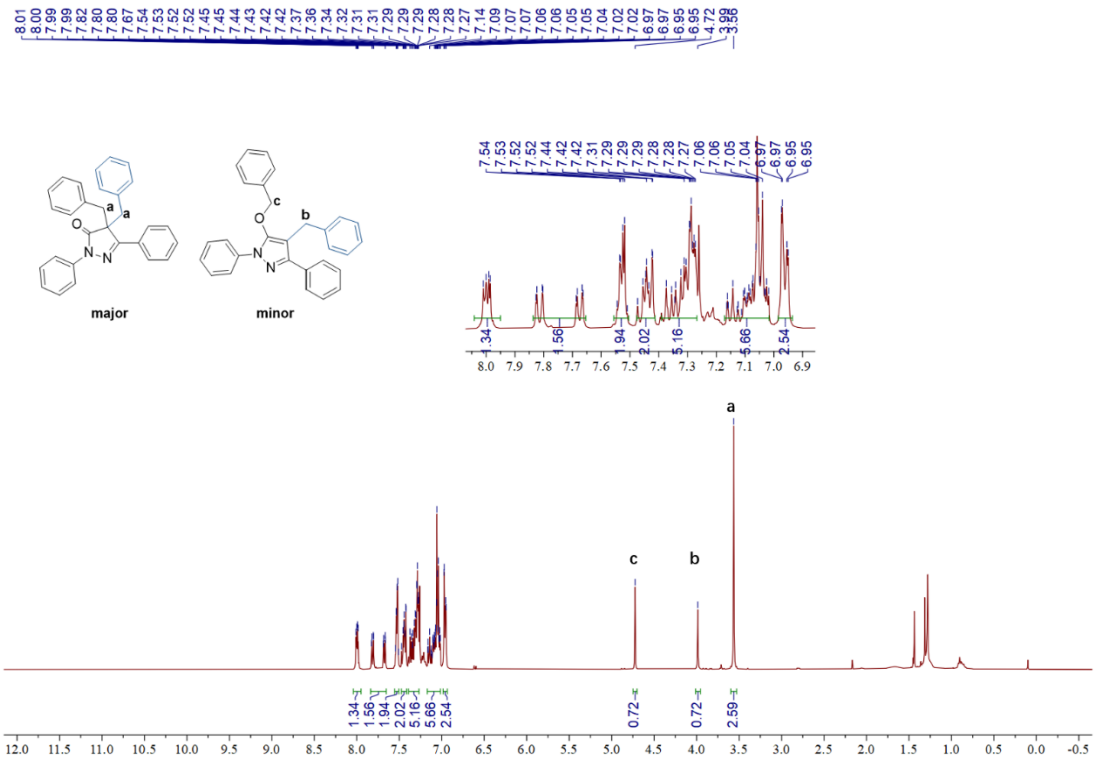
^{13}C NMR (101 MHz, $CDCl_3$)



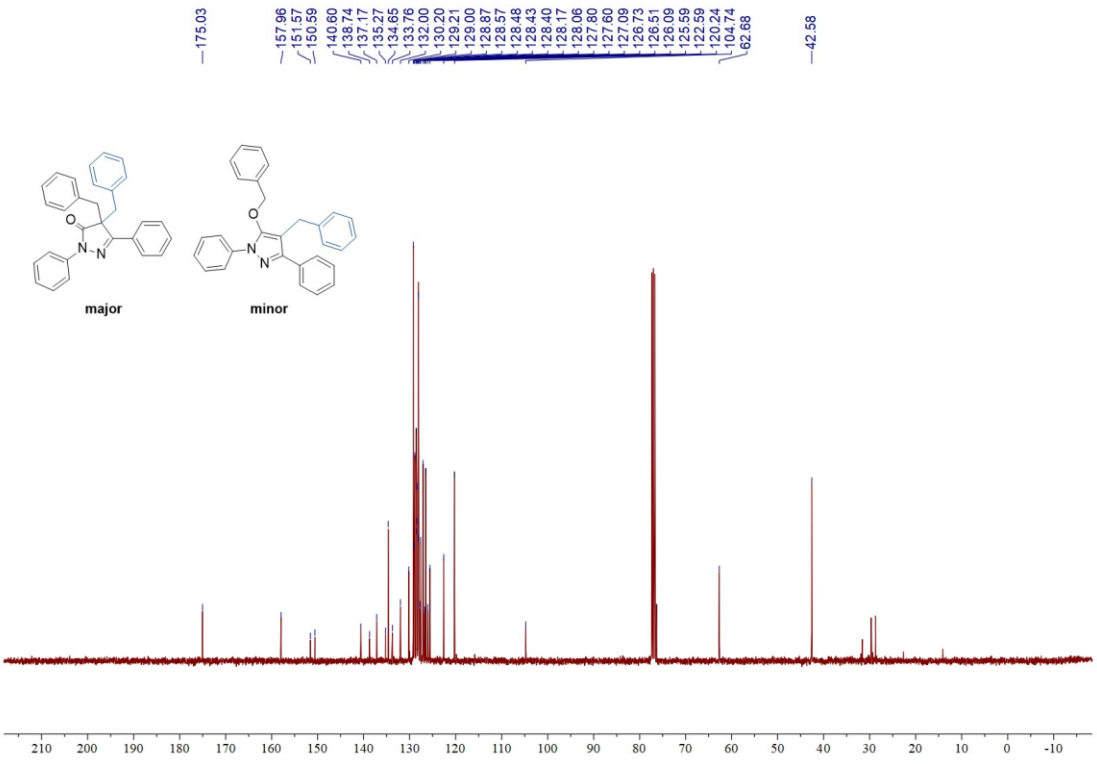
4,4-dibenzyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (16)

4-benzyl-5-(benzyloxy)-1,3-diphenyl-1H-pyrazole (16')

^{1}H NMR (400 MHz, $CDCl_3$)



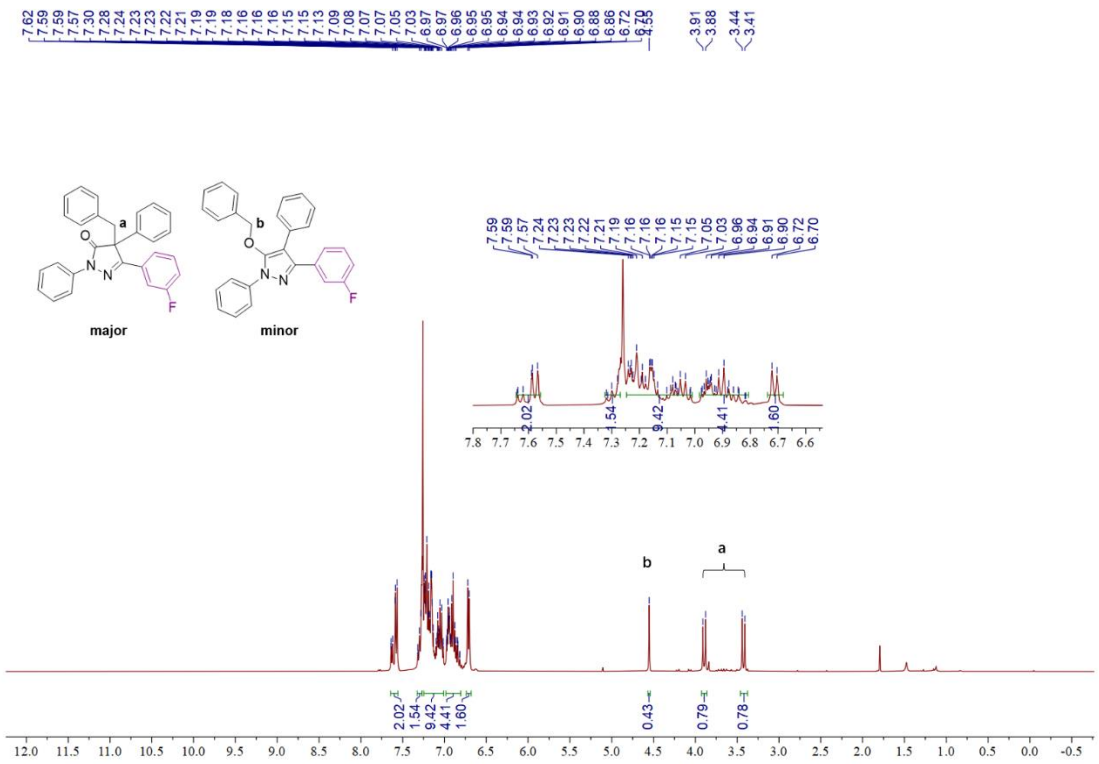
^{13}C NMR (101 MHz, $CDCl_3$)



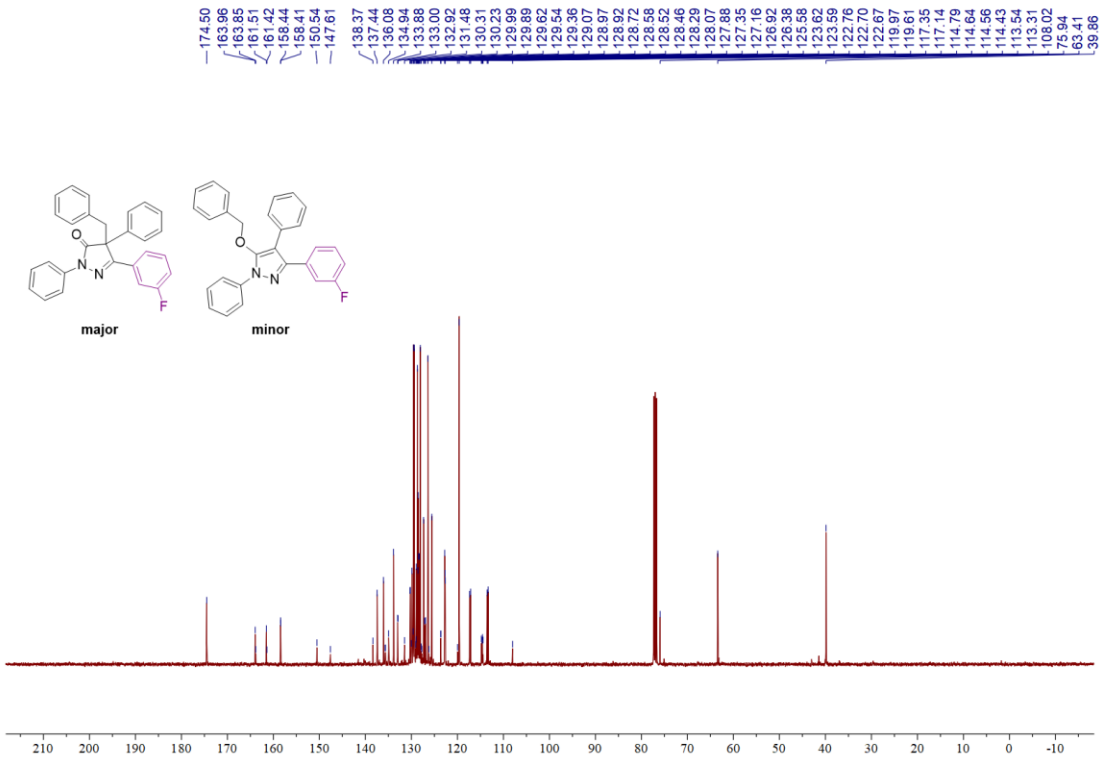
4-benzyl-5-(3-fluorophenyl)-2,4-diphenyl-2,4-dihydro-3H-pyrazol-3-one (17)

5-(benzyloxy)-3-(3-fluorophenyl)-1,4-diphenyl-1H-pyrazole (17')

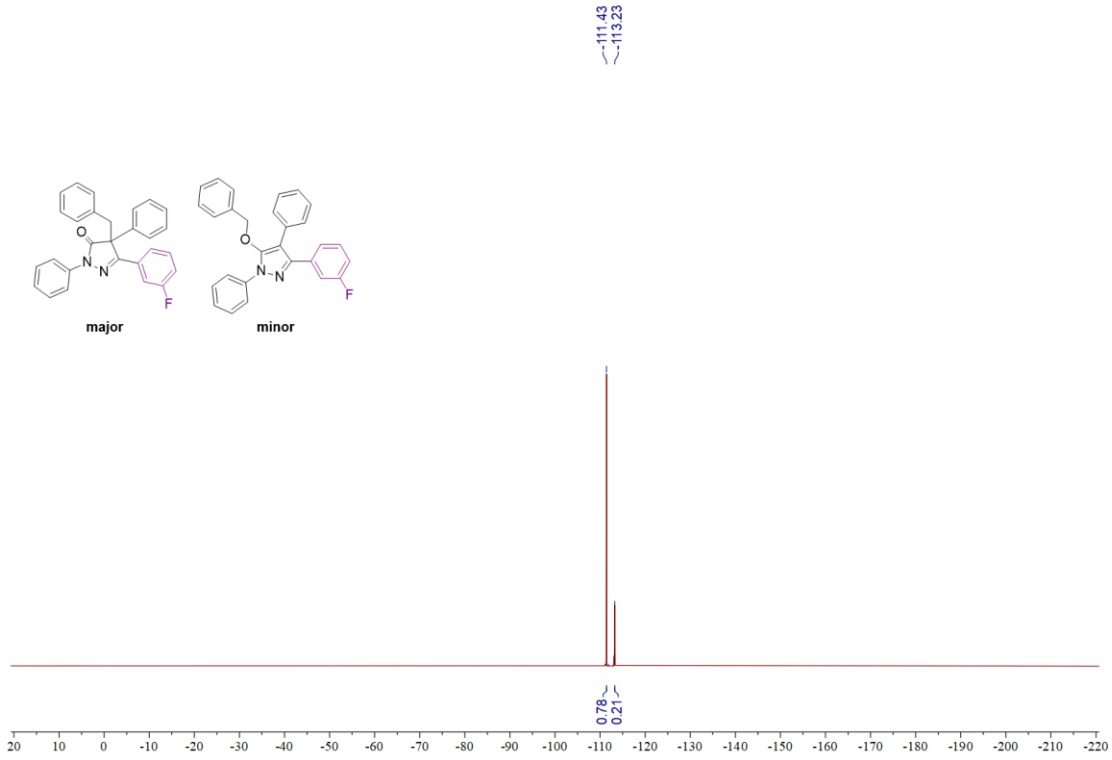
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



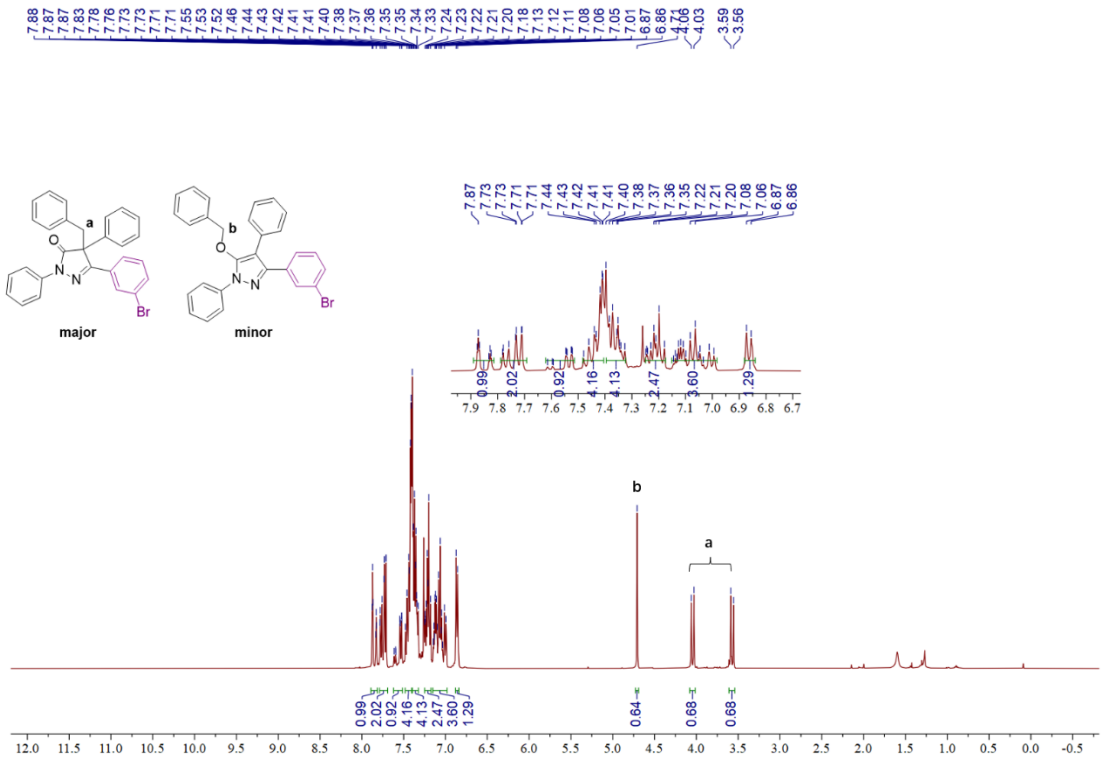
^{19}F NMR (376 MHz, $CDCl_3$)



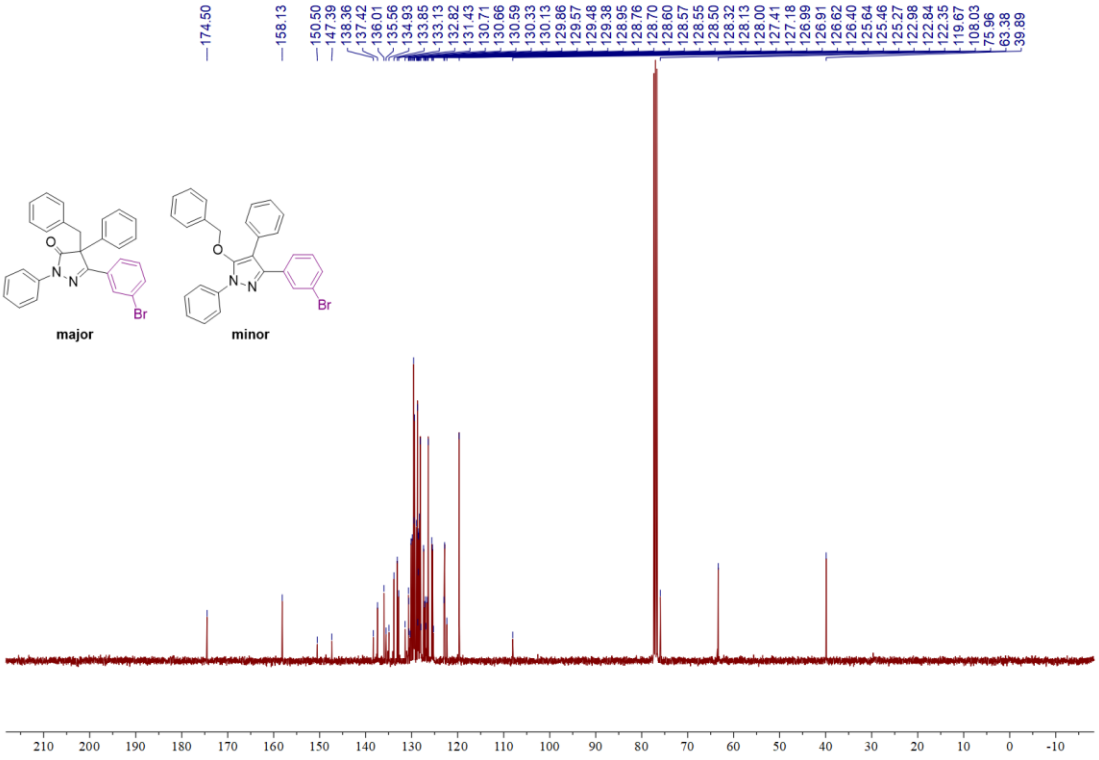
4-benzyl-5-(3-bromophenyl)-2,4-diphenyl-2,4-dihydro-3H-pyrazol-3-one (18)

5-(benzyloxy)-3-(3-bromophenyl)-1,4-diphenyl-1H-pyrazole (18')

^{1}H NMR (400 MHz, $CDCl_3$)



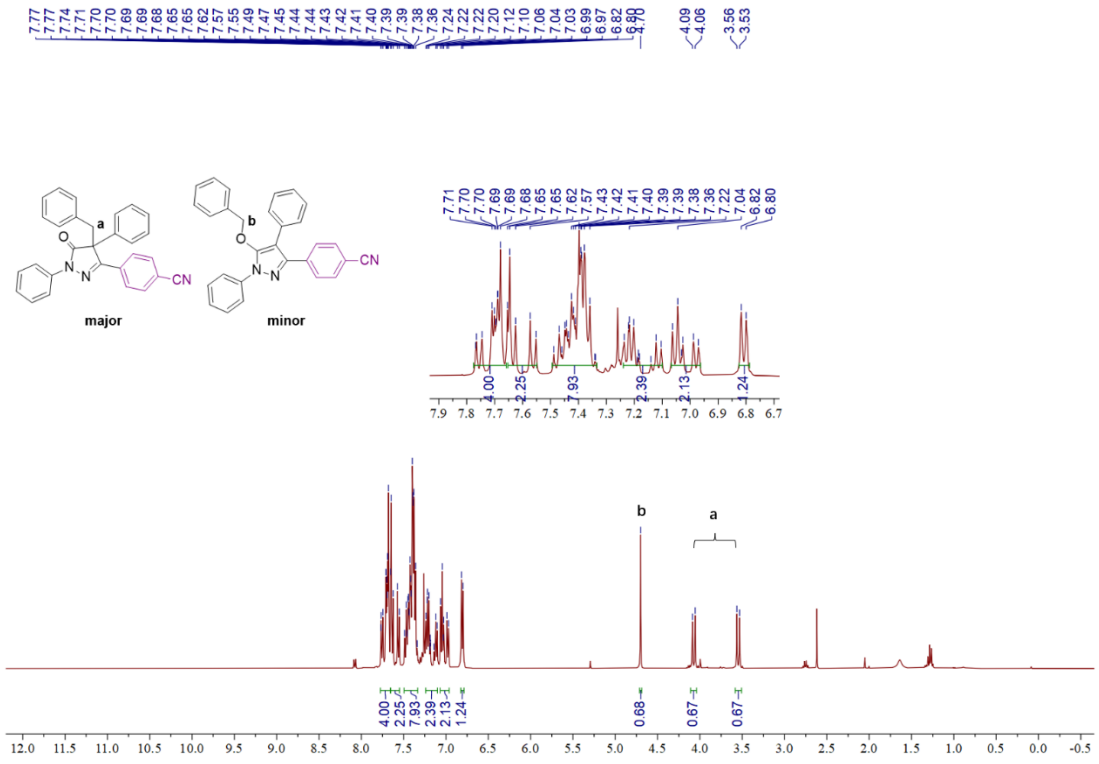
^{13}C NMR (101 MHz, $CDCl_3$)



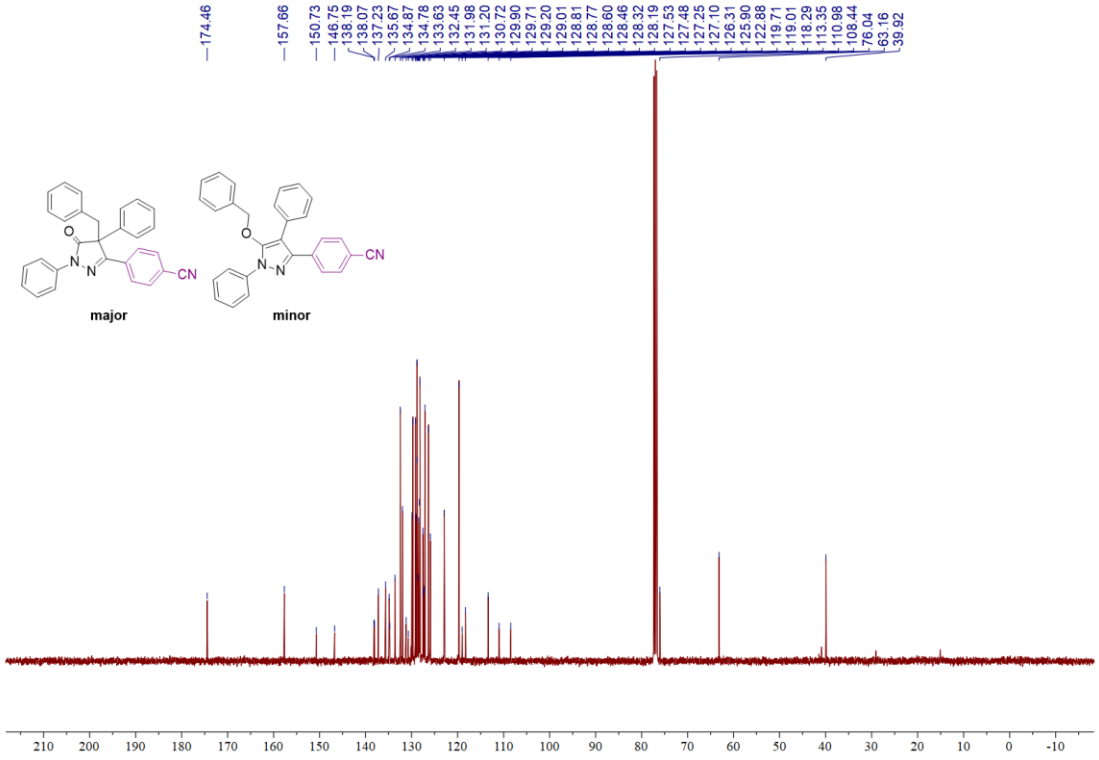
4-(4-benzyl-5-oxo-1,4-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)benzonitrile (19)

4-(5-(benzyloxy)-1,4-diphenyl-1H-pyrazol-3-yl)benzonitrile (19')

^{1}H NMR (400 MHz, $CDCl_3$)



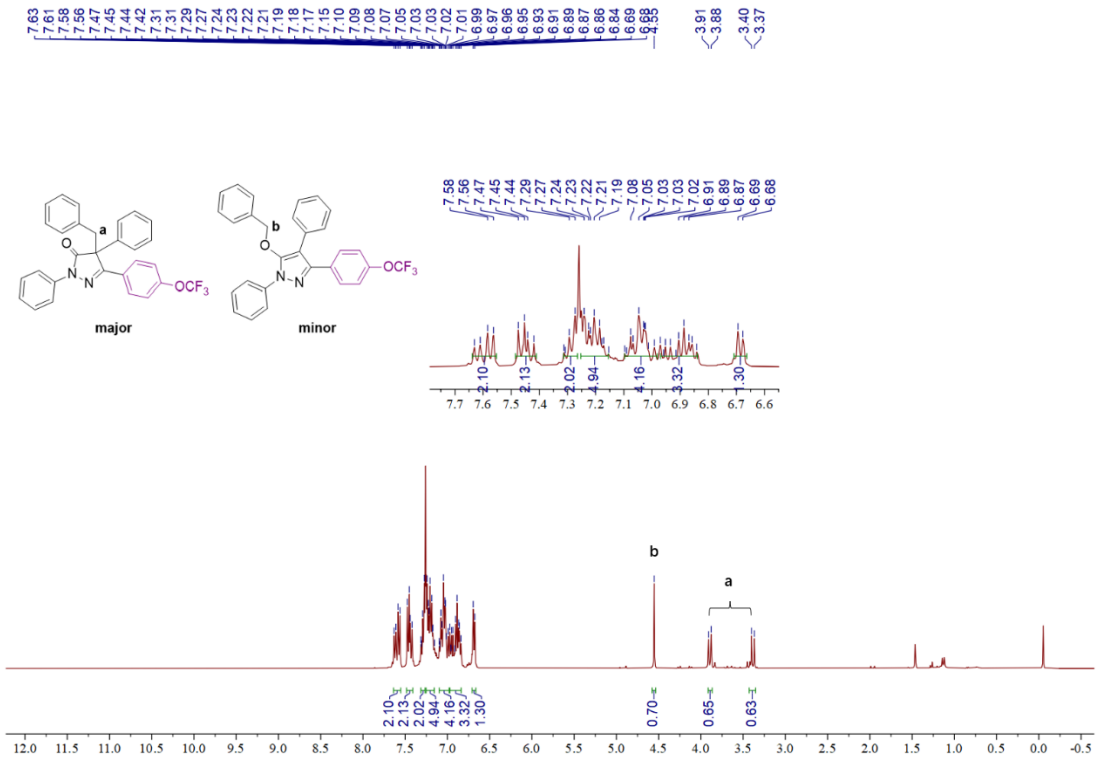
^{13}C NMR (101 MHz, $CDCl_3$)



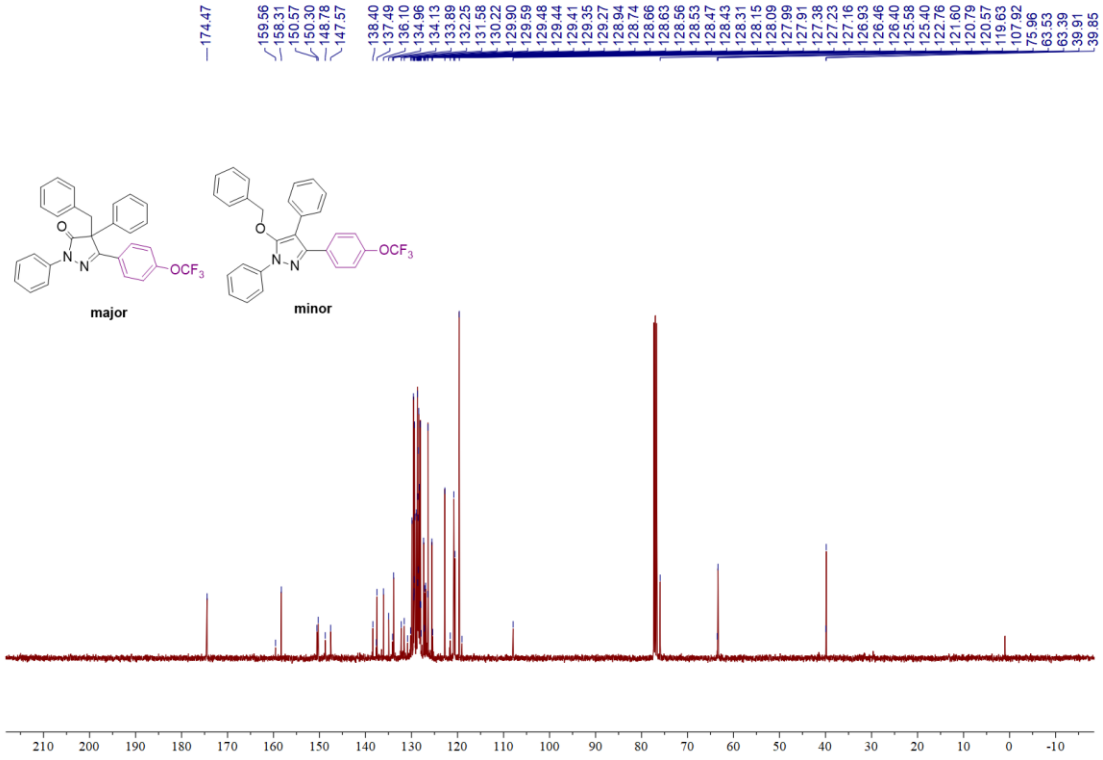
4-benzyl-2,4-diphenyl-5-(4-(trifluoromethoxy)phenyl)-2,4-dihydro-3H-pyrazol-3-one (20)

5-(benzyloxy)-1,4-diphenyl-3-(4-(trifluoromethoxy)phenyl)-1H-pyrazole (20')

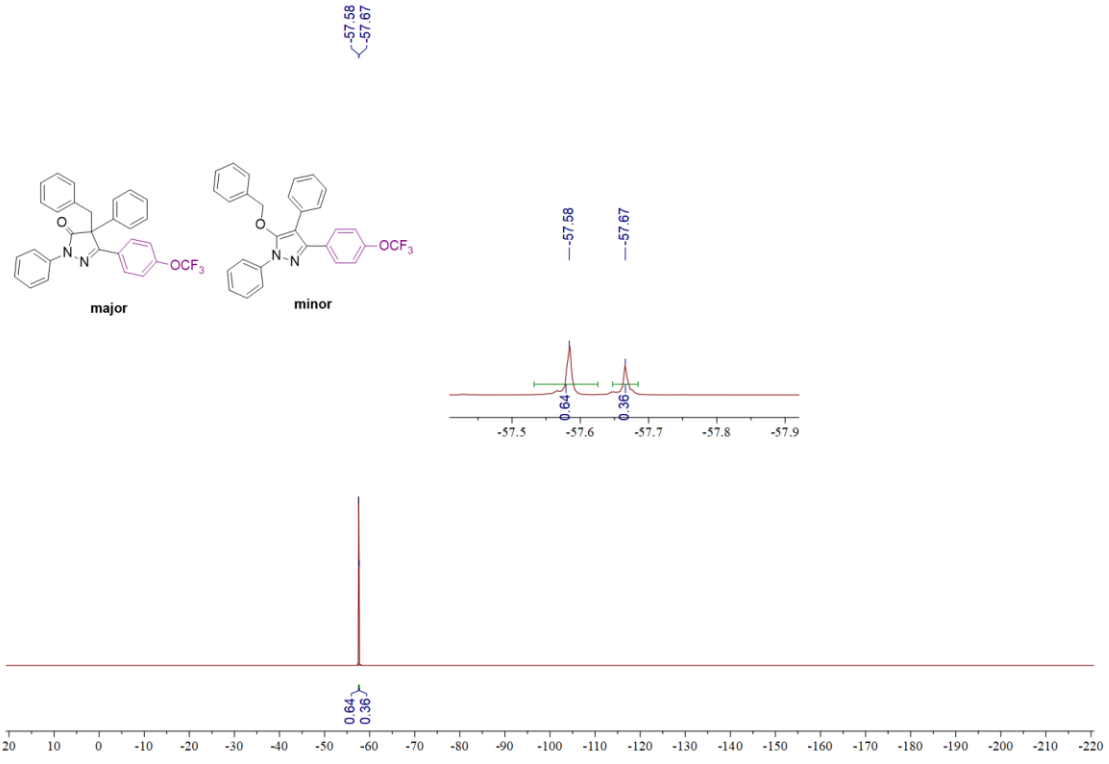
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



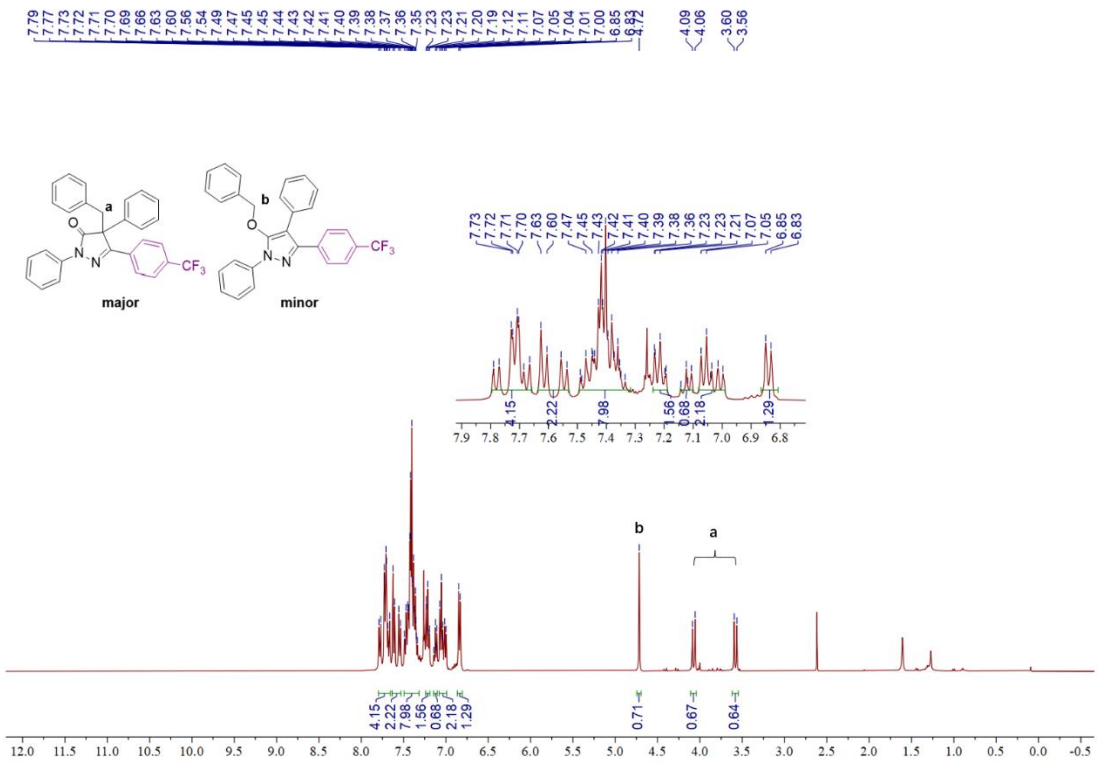
^{19}F NMR (376 MHz, $CDCl_3$)



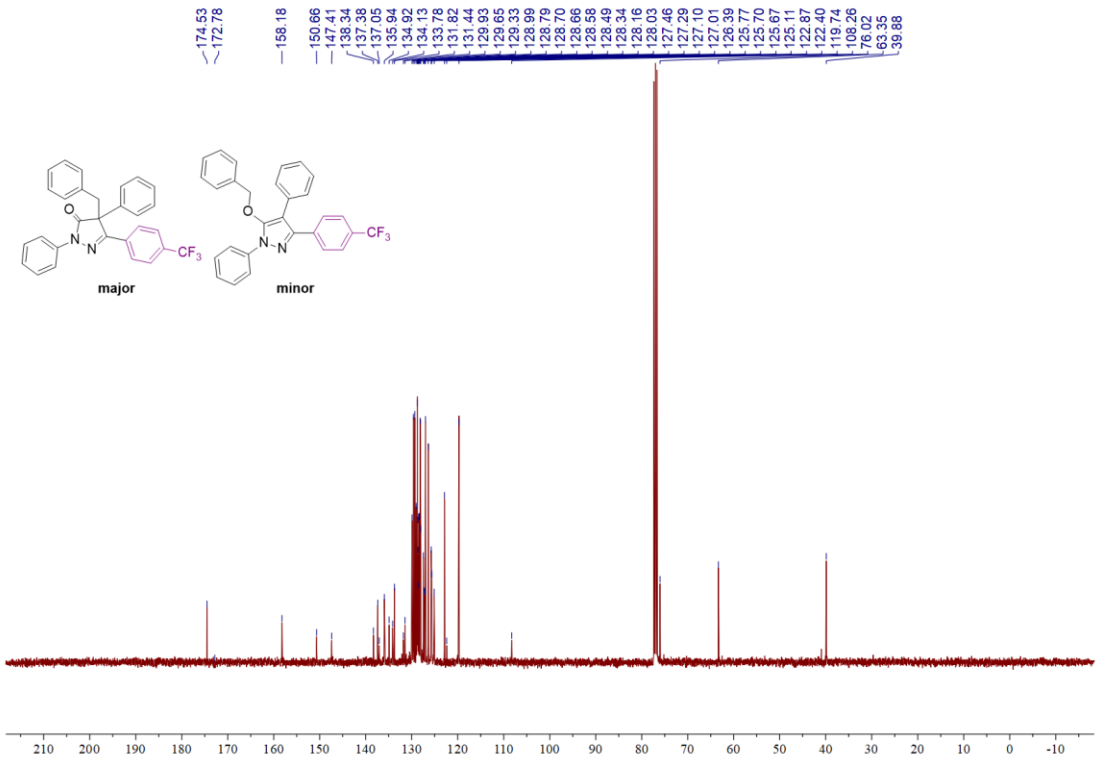
4-benzyl-2,4-diphenyl-5-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (21)

5-(benzyloxy)-1,4-diphenyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole (21')

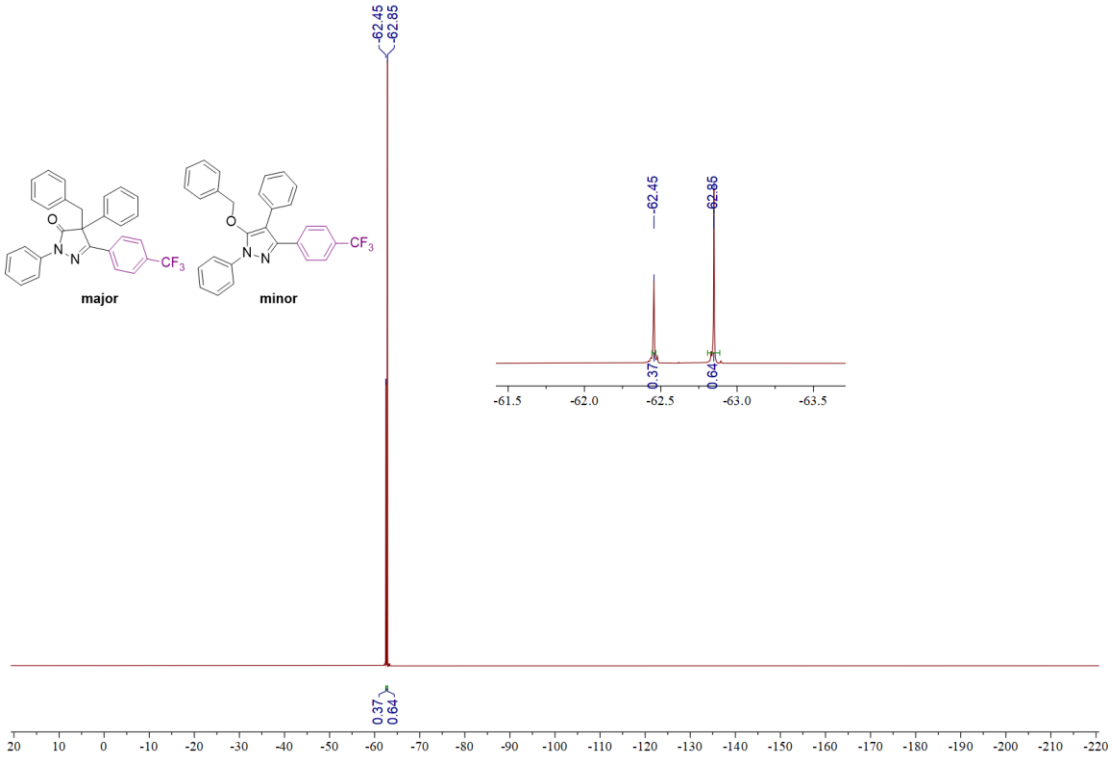
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



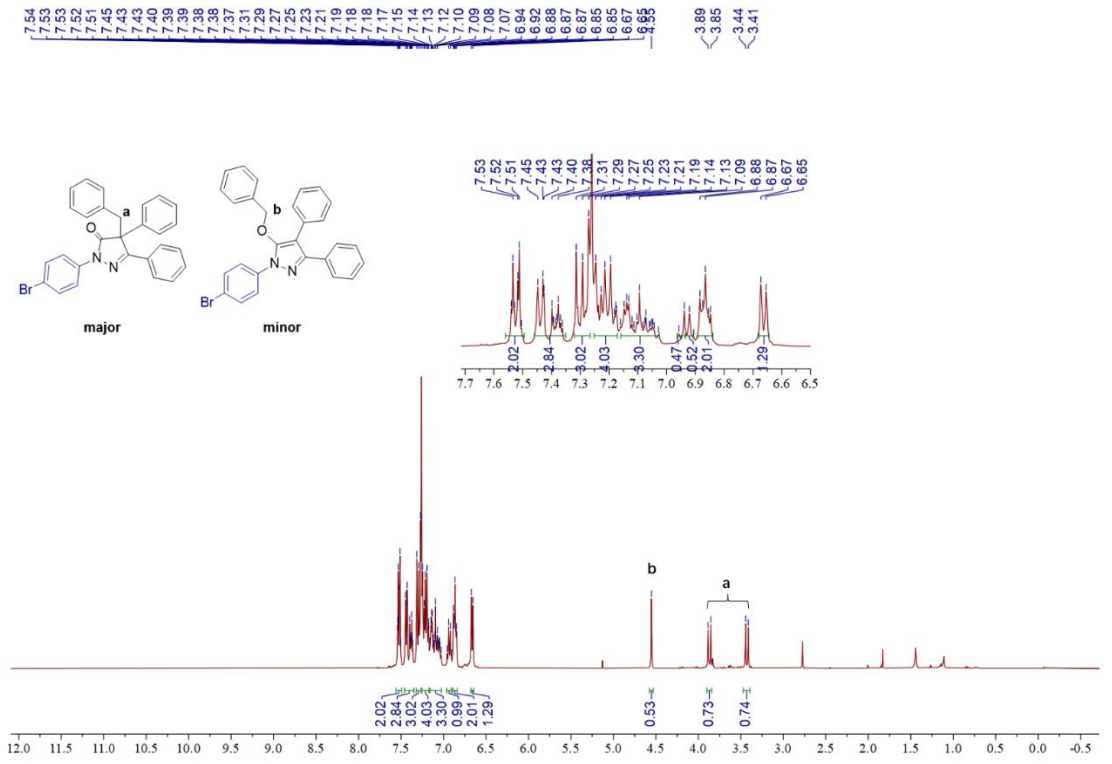
^{19}F NMR (376 MHz, $CDCl_3$)



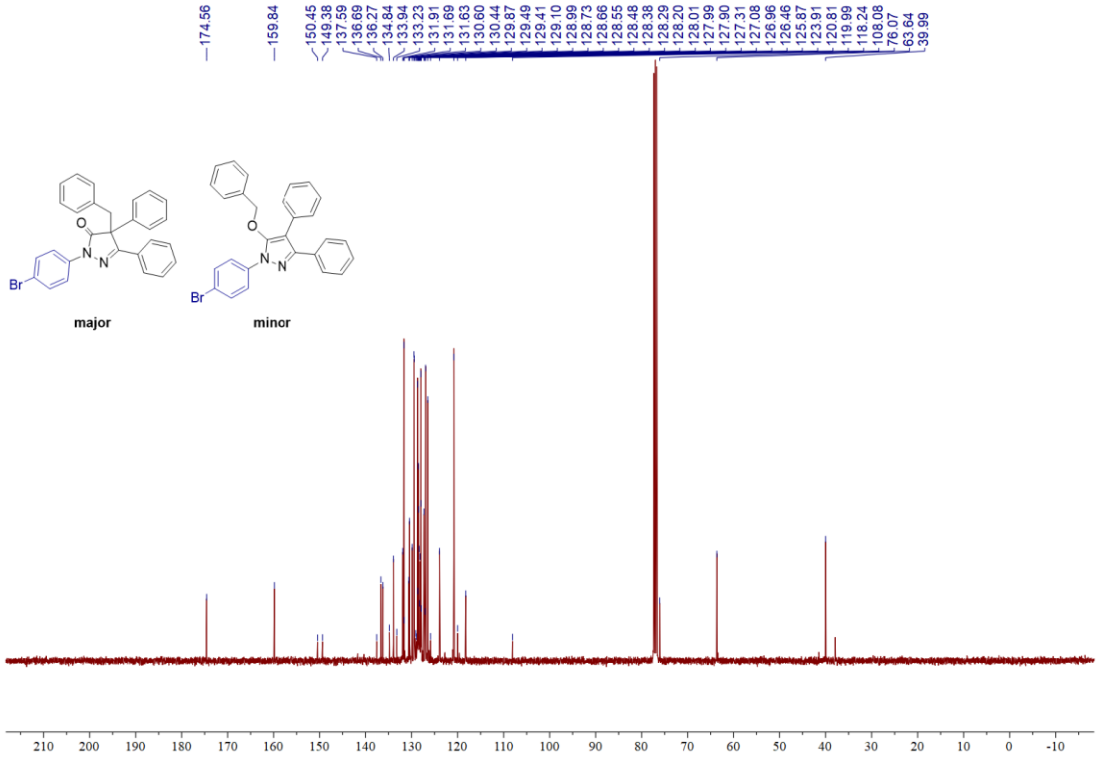
4-benzyl-2-(4-bromophenyl)-4,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (22)

5-(benzyloxy)-1-(4-bromophenyl)-3,4-diphenyl-1H-pyrazole (22')

^{1}H NMR (400 MHz, $CDCl_3$)



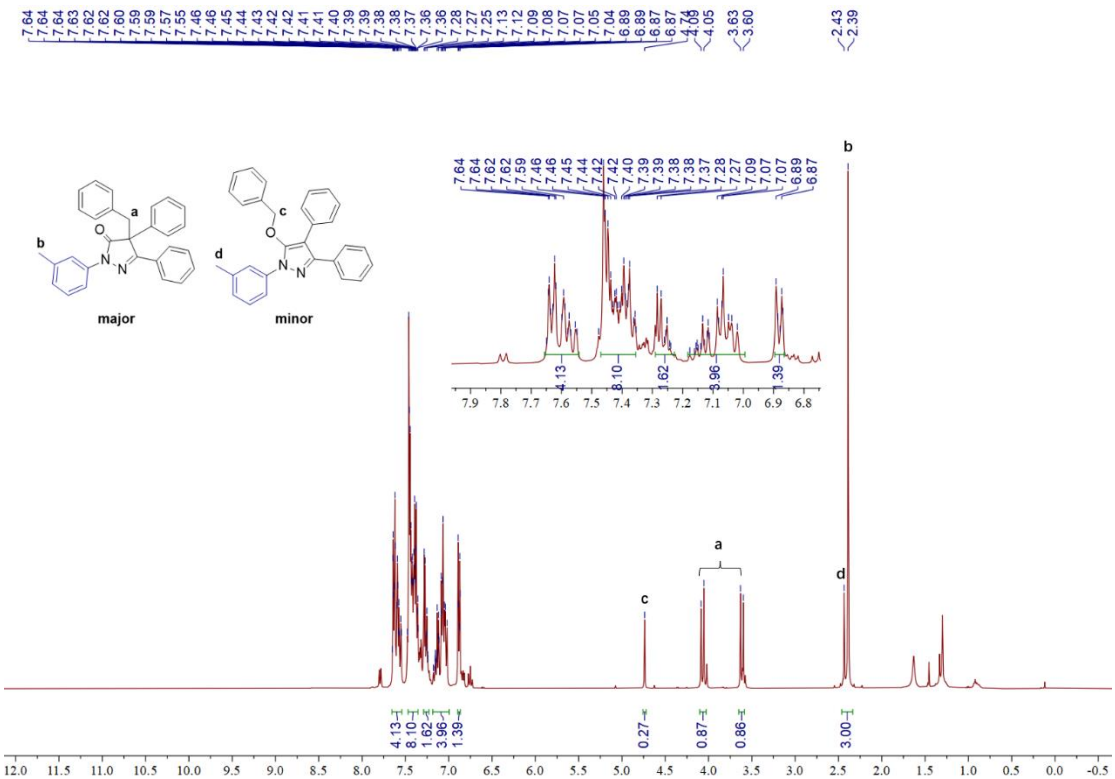
^{13}C NMR (101 MHz, $CDCl_3$)



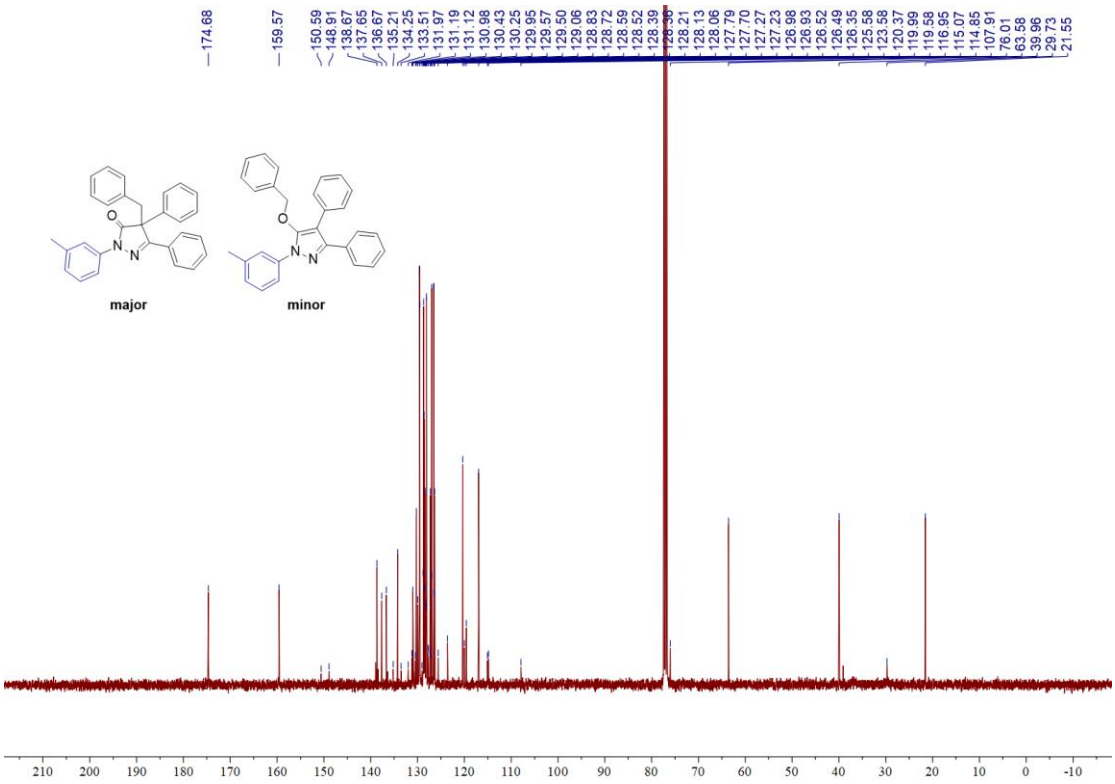
4-benzyl-4,5-diphenyl-2-(m-tolyl)-2,4-dihydro-3H-pyrazol-3-one (23)

5-(benzyloxy)-3,4-diphenyl-1-(m-tolyl)-1H-pyrazole (23')

^{1}H NMR (400 MHz, $CDCl_3$)

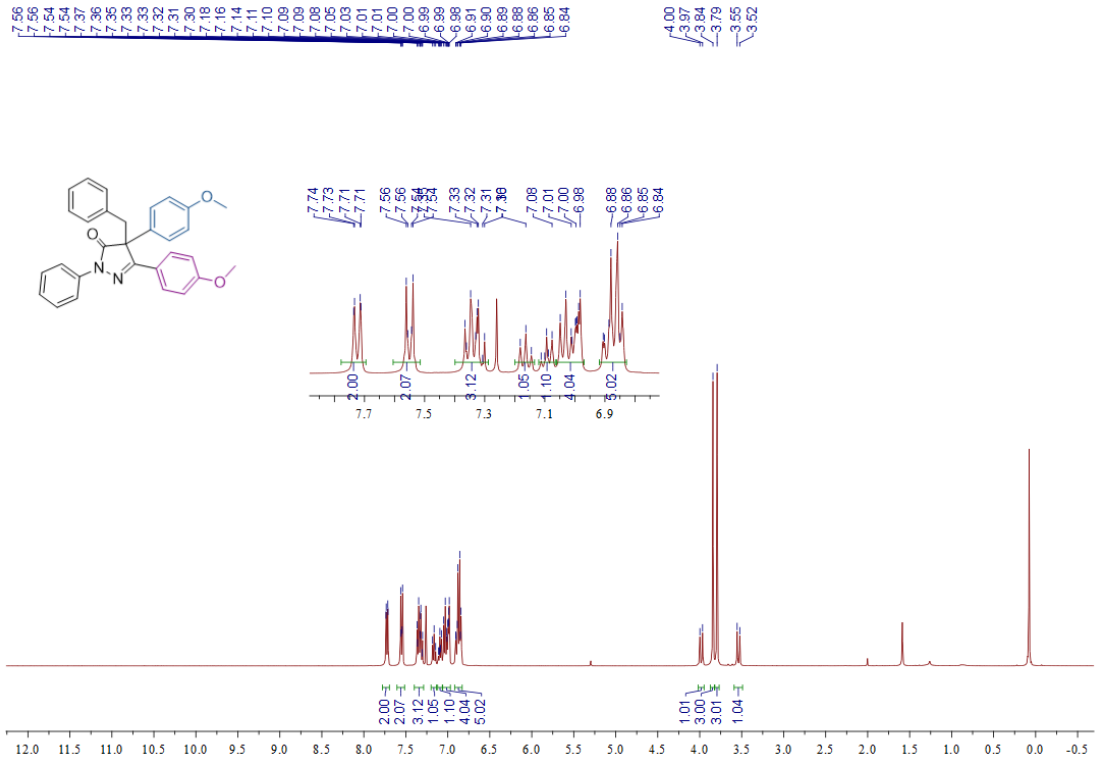


^{13}C NMR (101 MHz, $CDCl_3$)

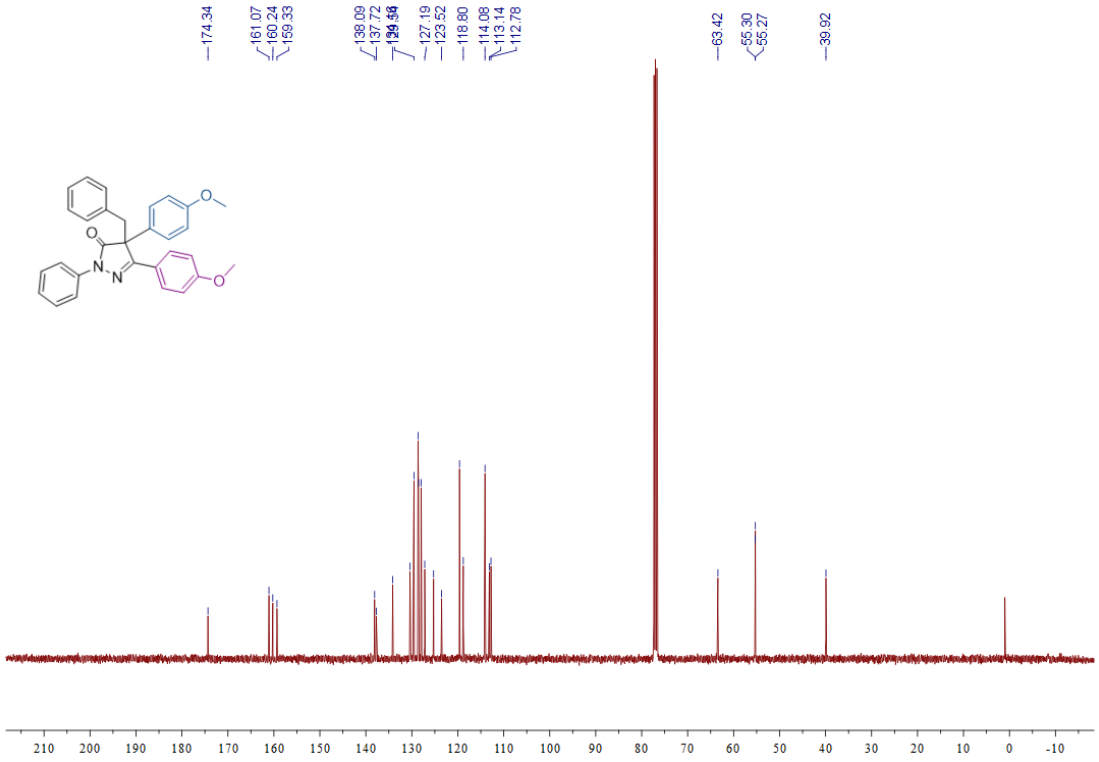


4-benzyl-4,5-bis(4-methoxyphenyl)-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (24)

^{1}H NMR (400 MHz, $CDCl_3$)

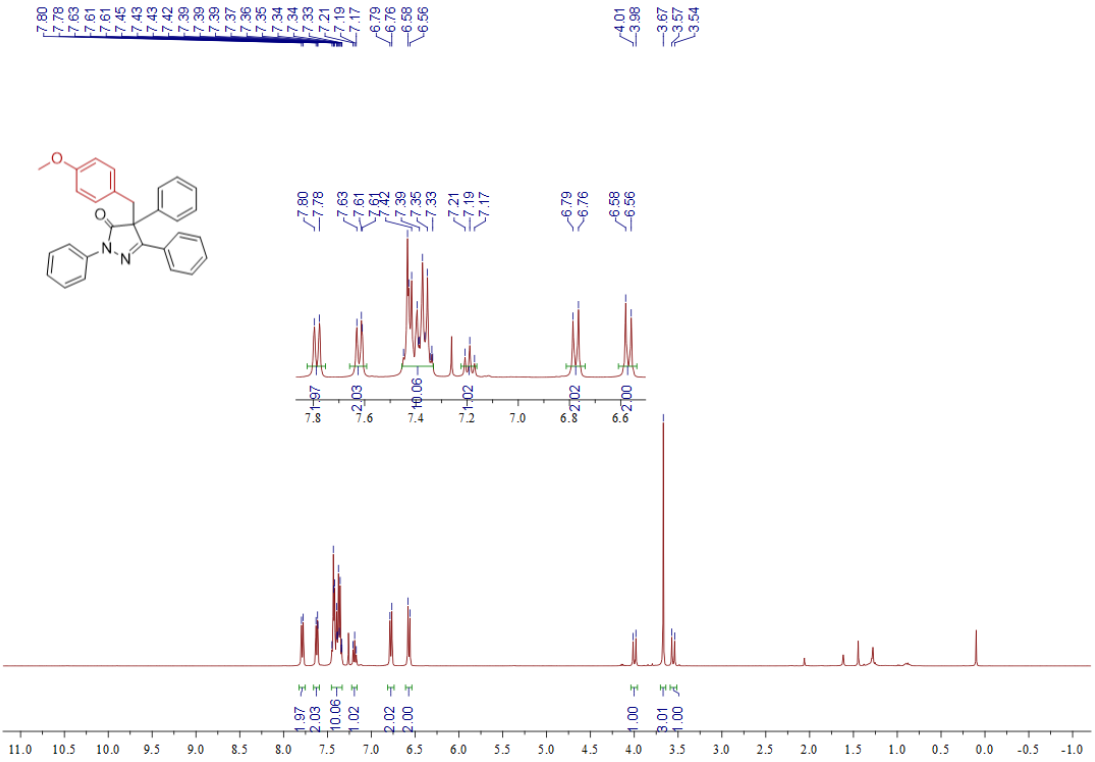


^{13}C NMR (101 MHz, $CDCl_3$)

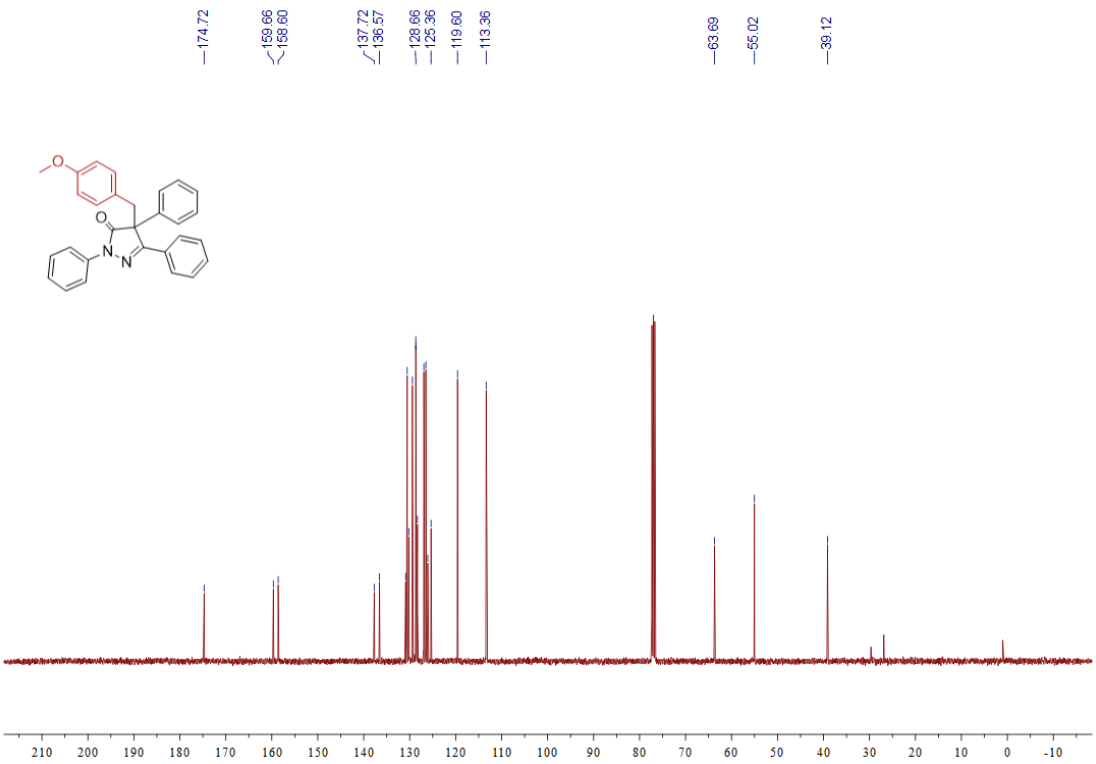

174.34
161.07
160.24
159.33
138.09
137.72
127.19
123.52
118.80
114.08
113.14
112.78
63.42
55.30
55.27
39.92
O
N
N
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

4-(4-methoxybenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (25)

^{1}H NMR (400 MHz, $CDCl_3$)

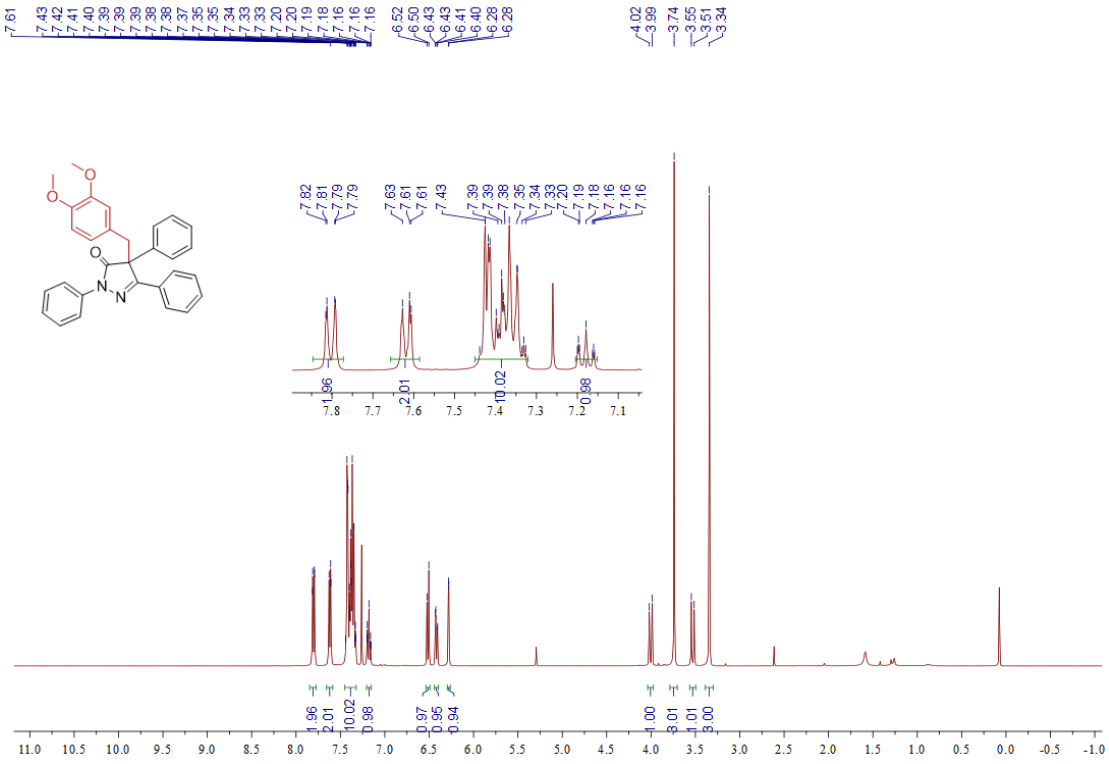


^{13}C NMR (101 MHz, $CDCl_3$)

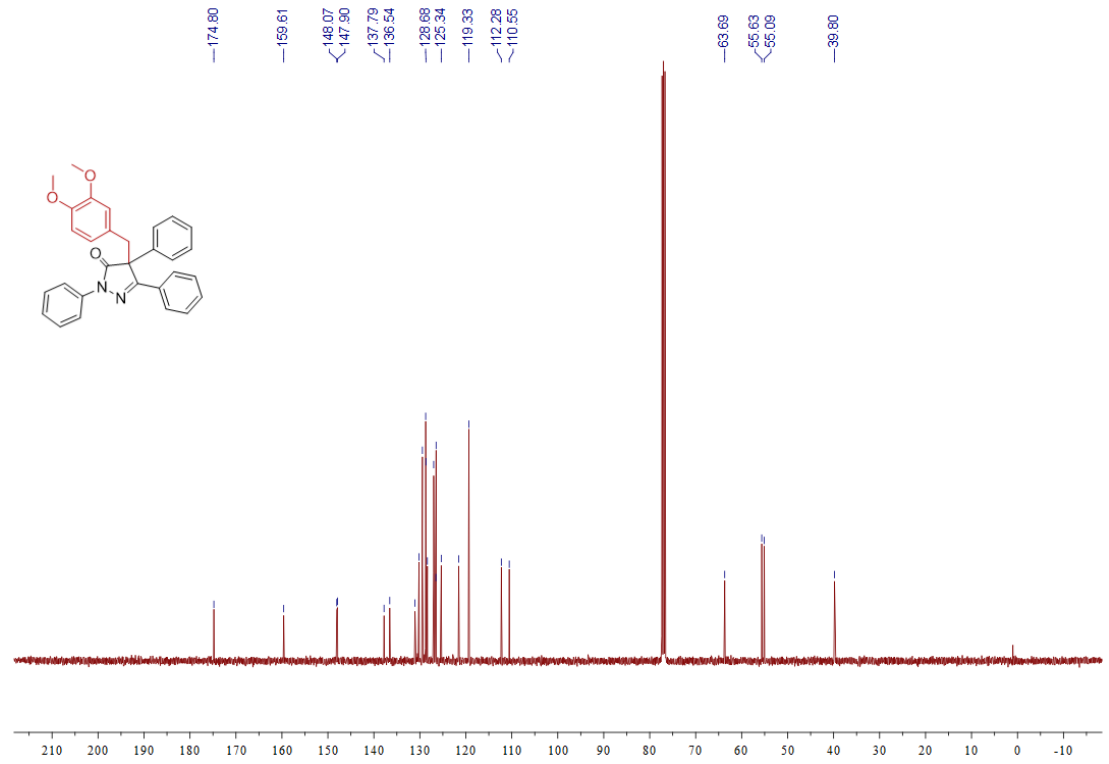


4-(3,4-dimethoxybenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (26)

^{1}H NMR (400 MHz, $CDCl_3$)



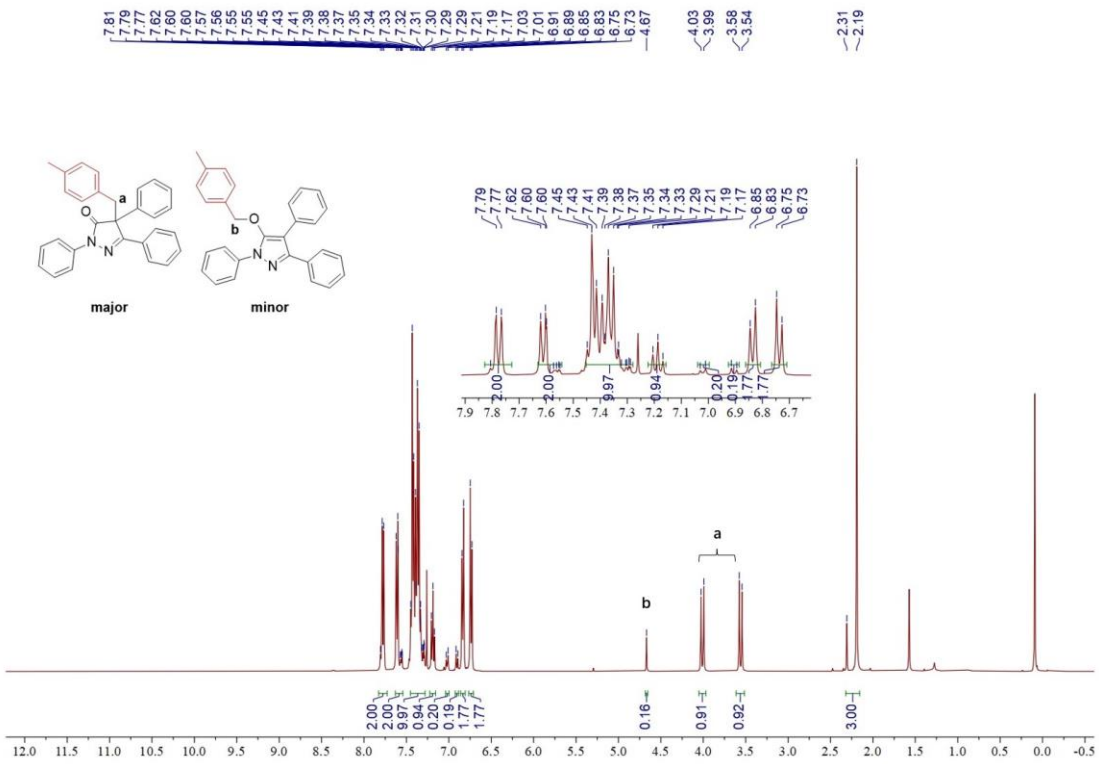
^{13}C NMR (101 MHz, $CDCl_3$)



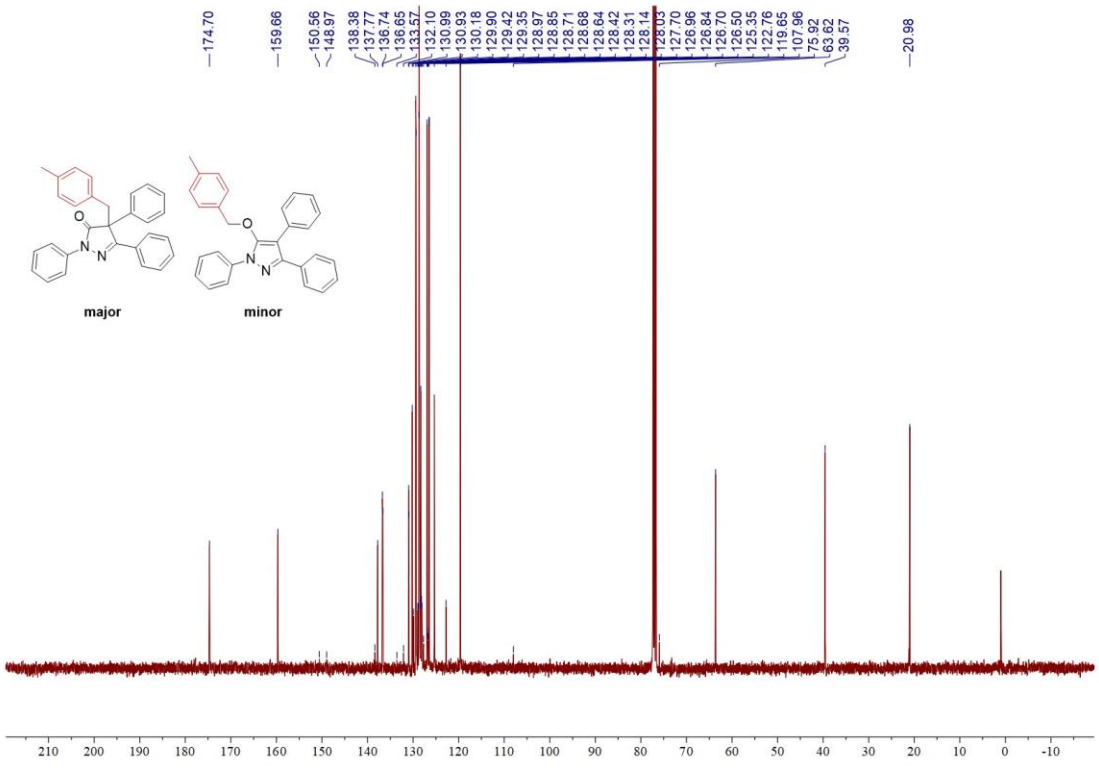
4-(4-methylbenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (27)

5-((4-methylbenzyl)oxy)-1,3,4-triphenyl-1H-pyrazole (27')

^{1}H NMR (400 MHz, $CDCl_3$)

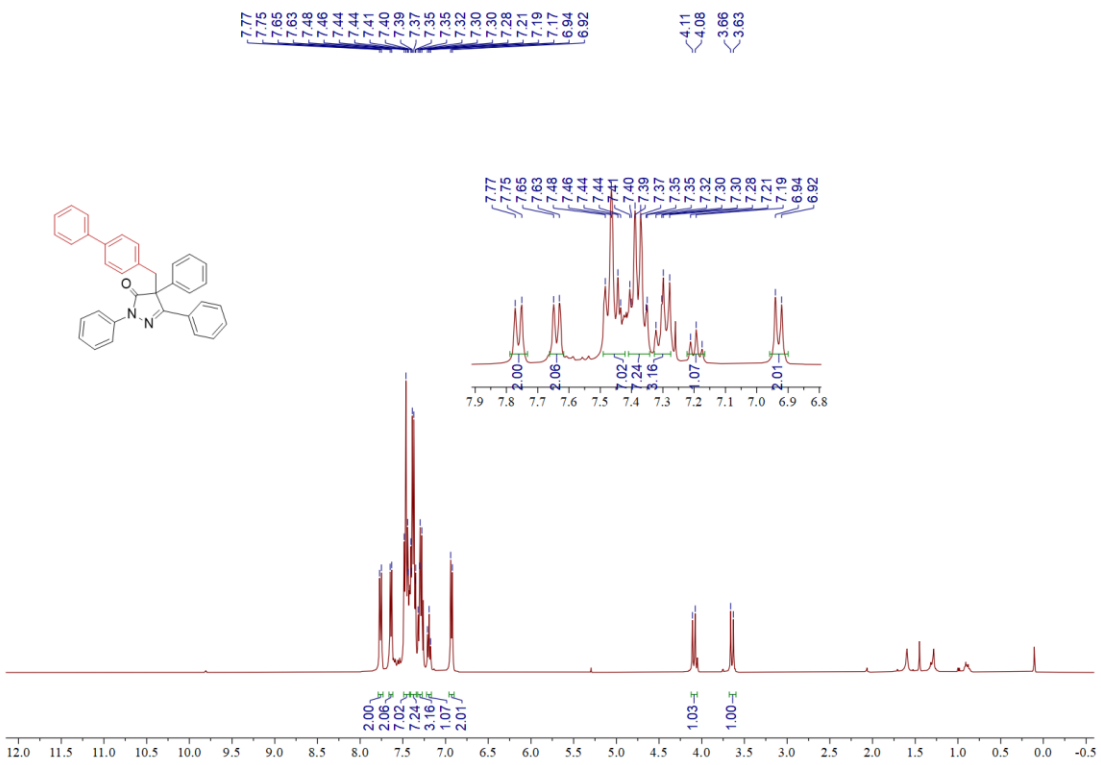


^{13}C NMR (101 MHz, $CDCl_3$)

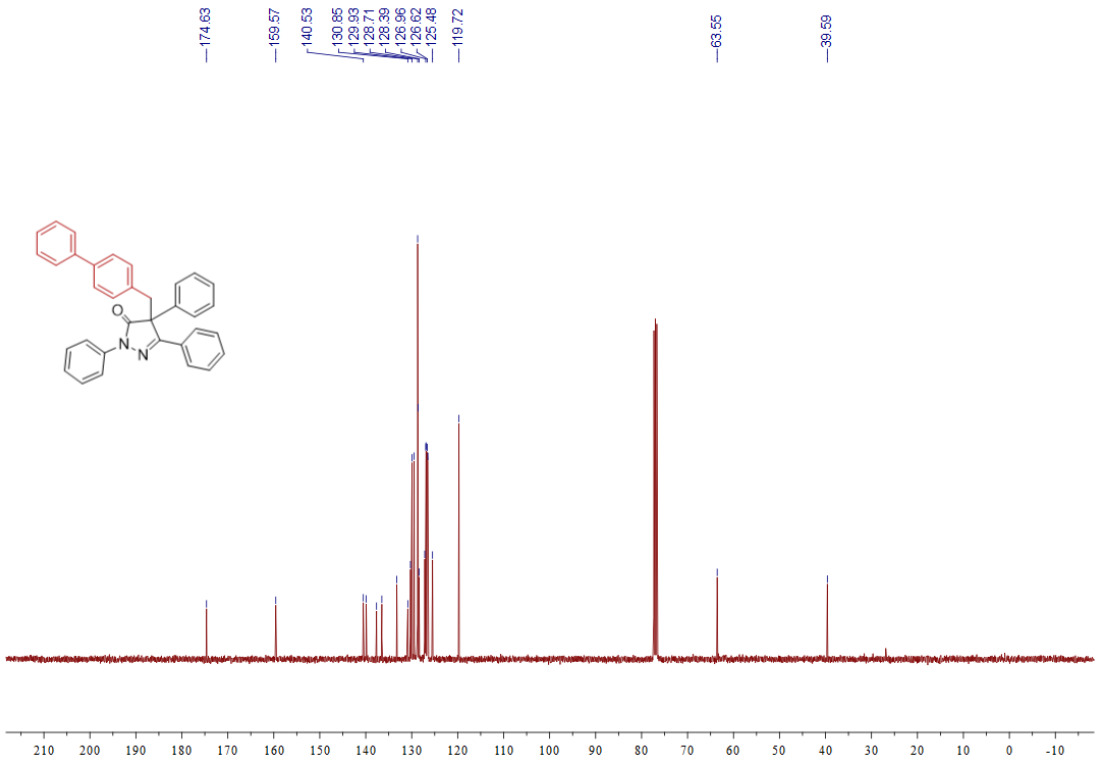


4-([1,1'-biphenyl]-4-ylmethyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (28)

^{1}H NMR (400 MHz, $CDCl_3$)

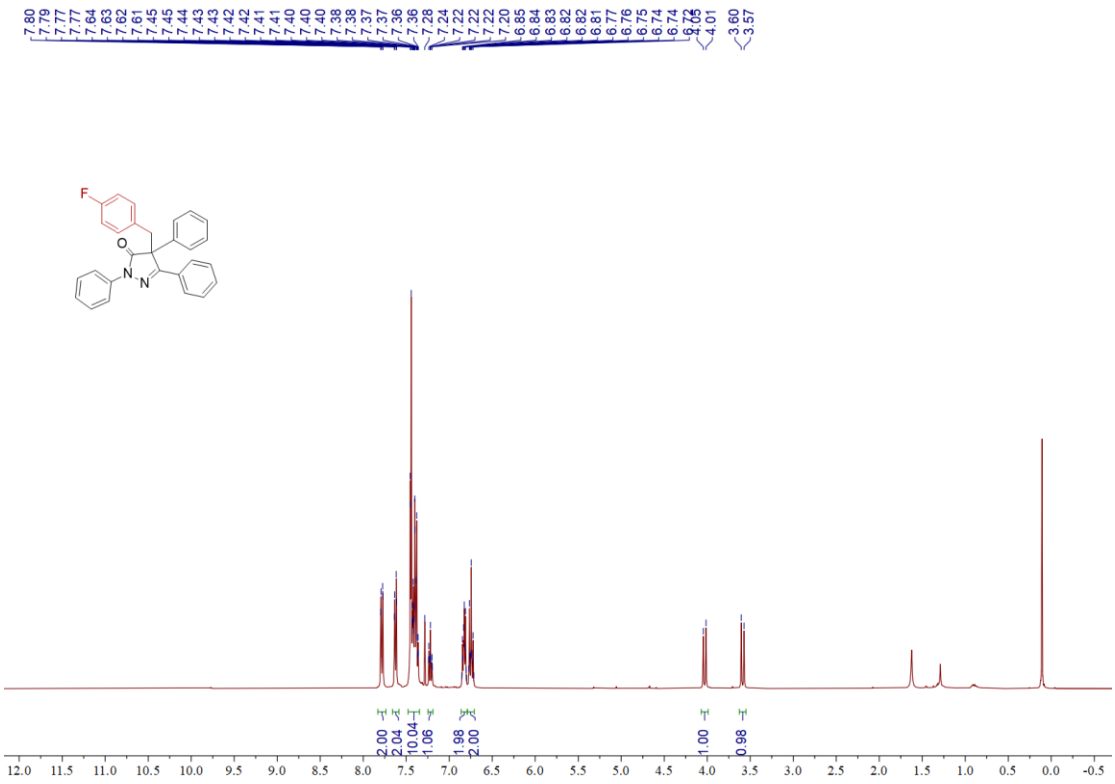


^{13}C NMR (101 MHz, $CDCl_3$)

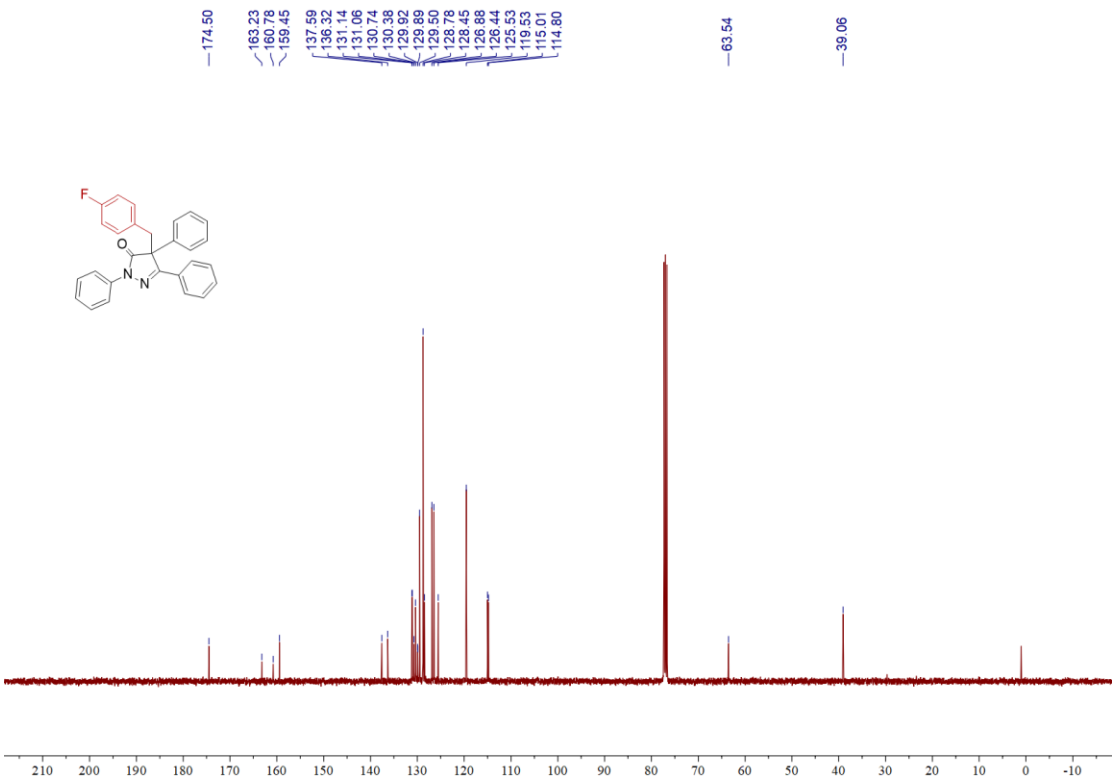


4-(4-fluorobenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (29)

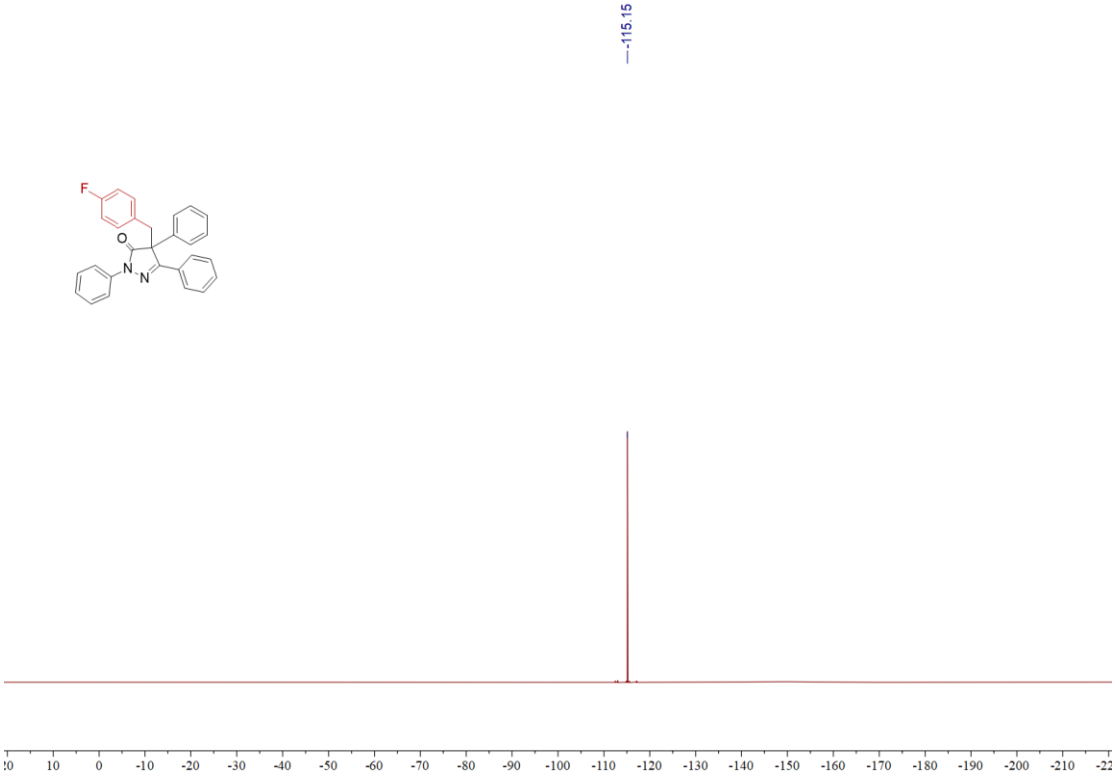
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



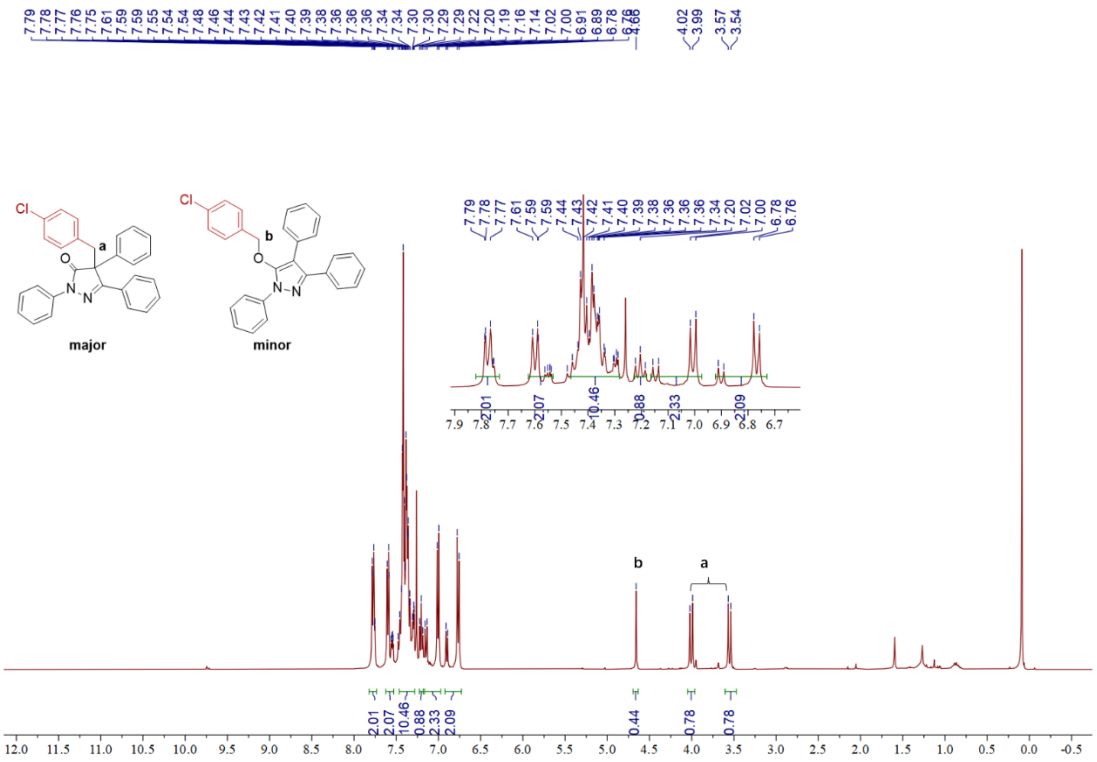
^{19}F NMR (376 MHz, $CDCl_3$)



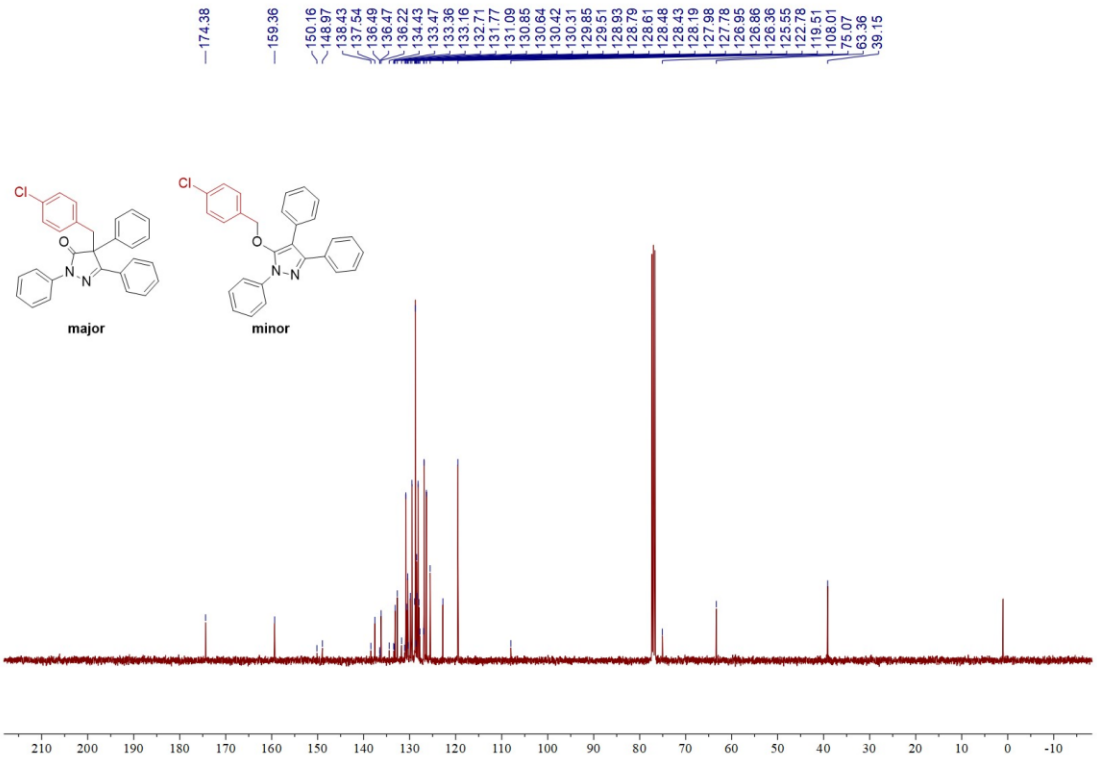
4-(4-chlorobenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (30)

5-((4-chlorobenzyl)oxy)-1,3,4-triphenyl-1H-pyrazole (30')

^{1}H NMR (400 MHz, $CDCl_3$)



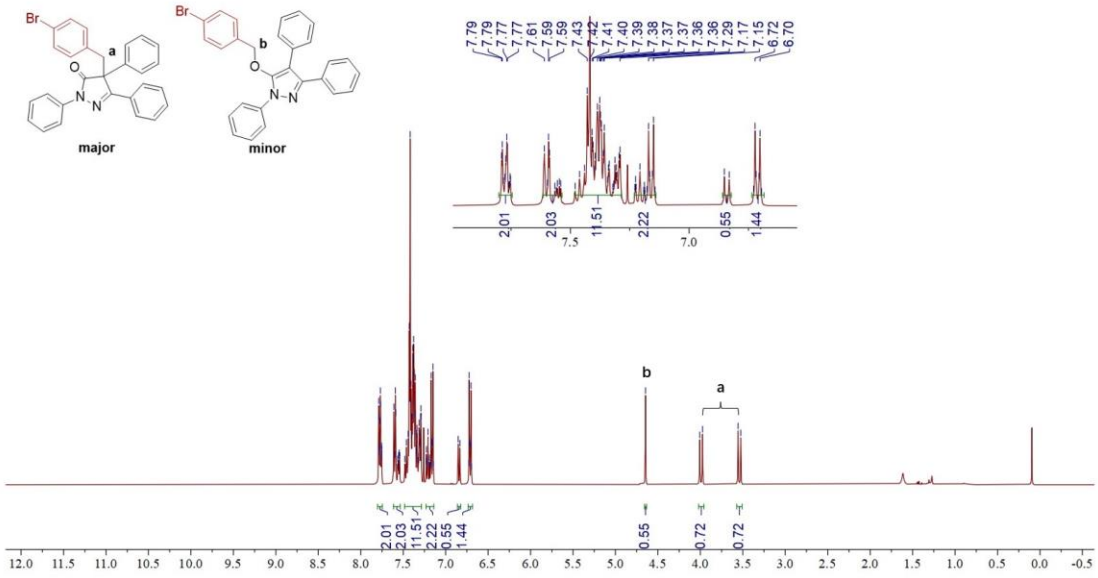
^{13}C NMR (101 MHz, $CDCl_3$)



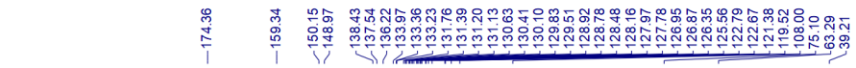
4-(4-bromobenzyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (31)

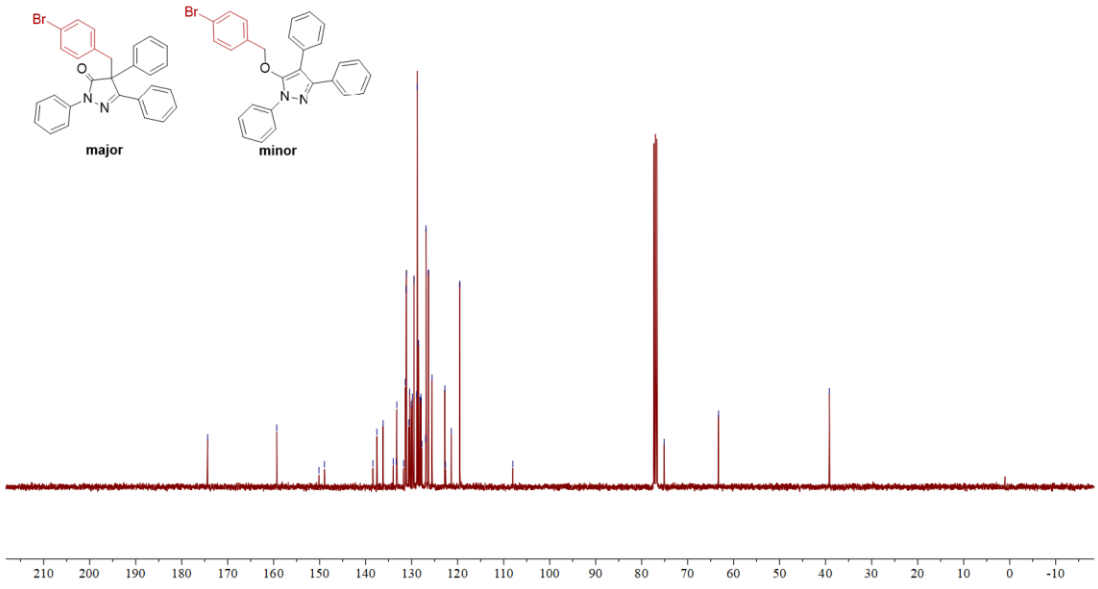
5-((4-bromobenzyl)oxy)-1,3,4-triphenyl-1H-pyrazole (31')

^{1}H NMR (400 MHz, $CDCl_3$)



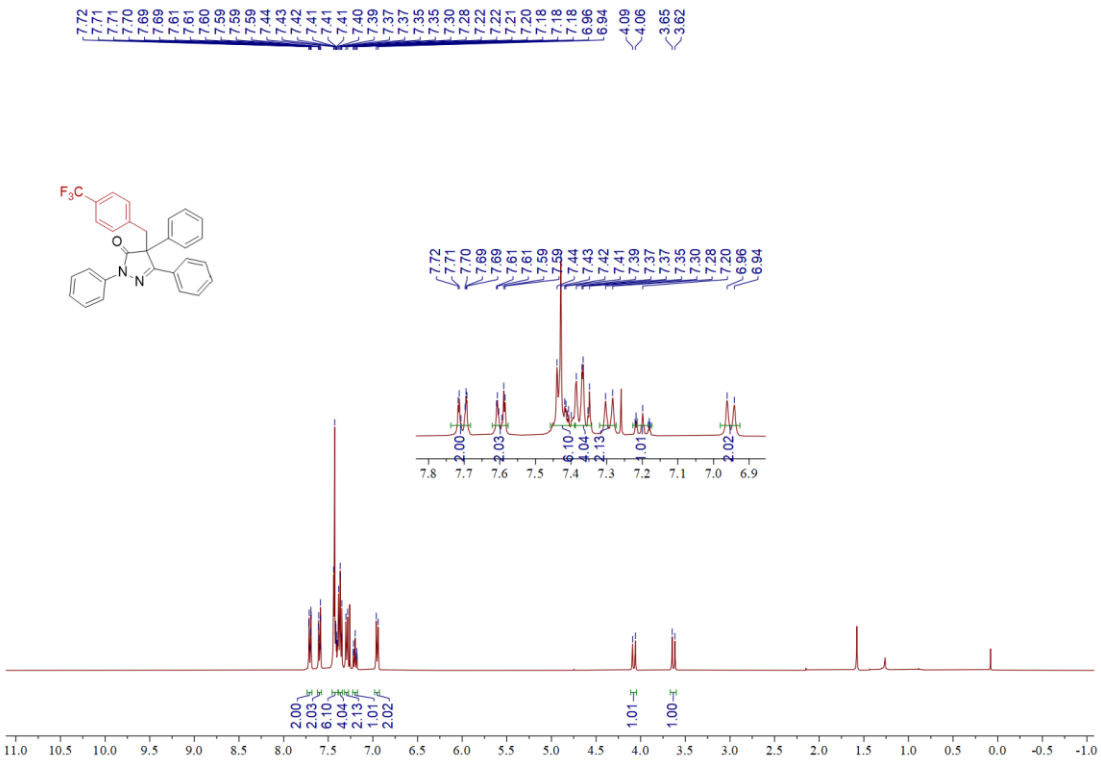
^{13}C NMR (101 MHz, $CDCl_3$)



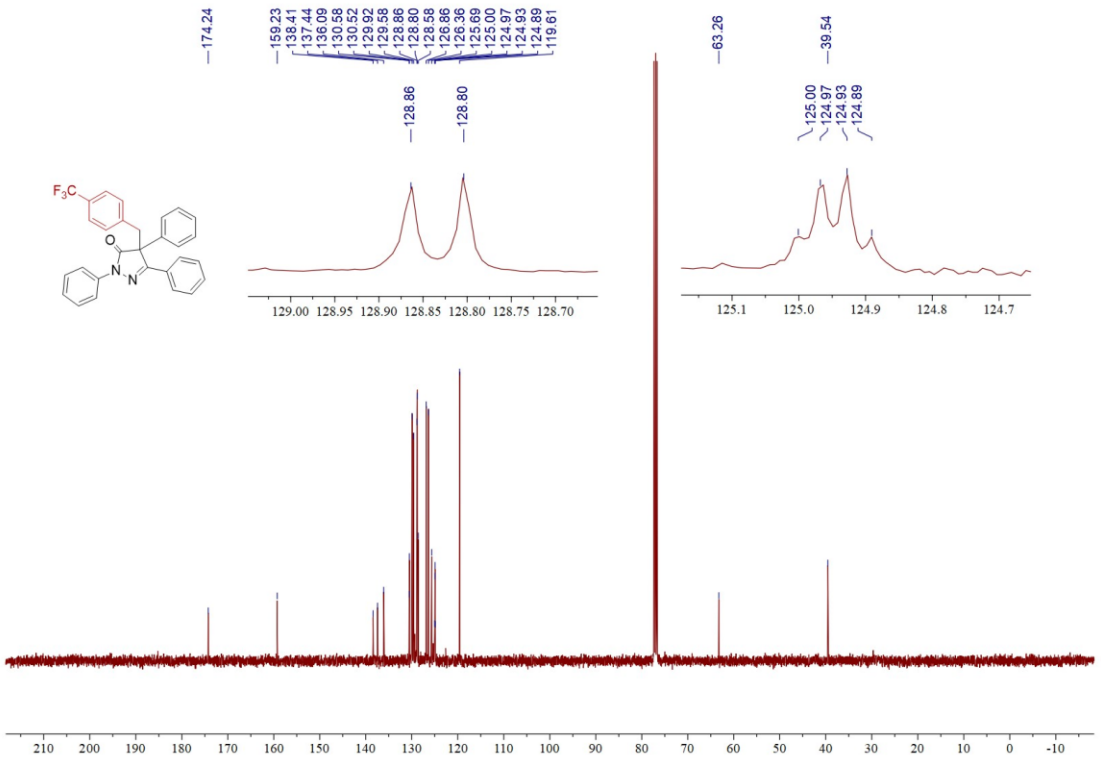


2,4,5-triphenyl-4-(4-(trifluoromethyl)benzyl)-2,4-dihydro-3H-pyrazol-3-one (32)

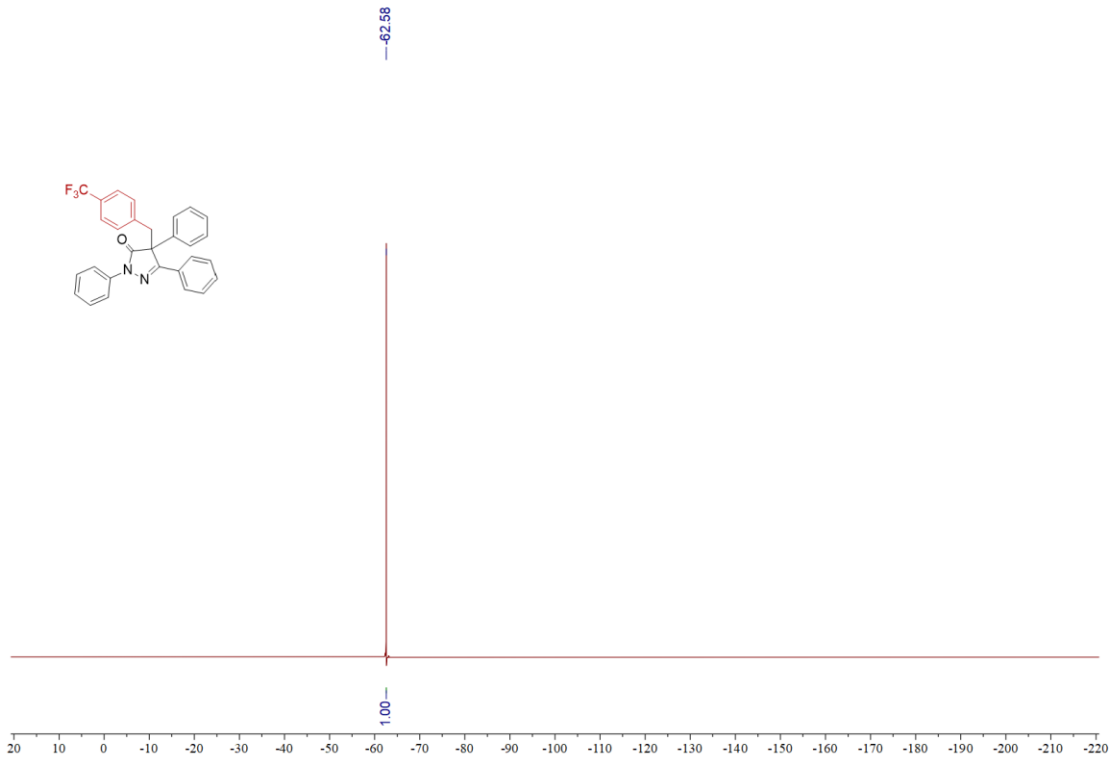
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

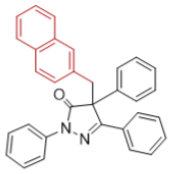


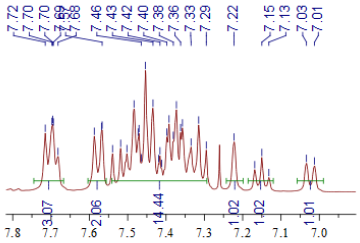
^{19}F NMR (376 MHz, $CDCl_3$)

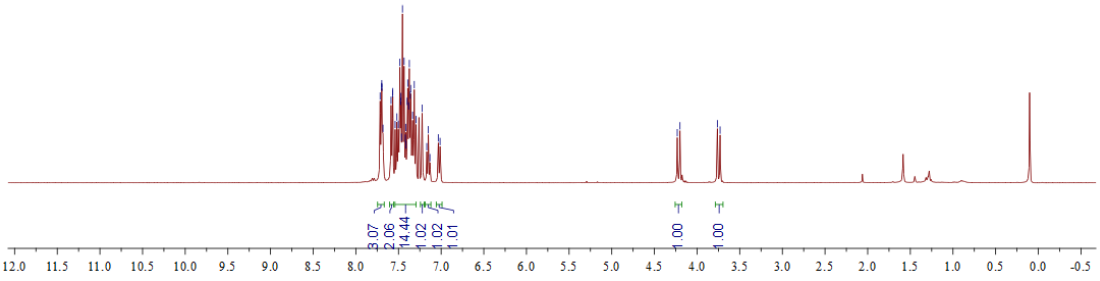

-62.58
F3C
O
N
N
1.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220

4-(naphthalen-2-ylmethyl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (33)

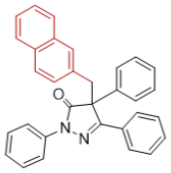
^{1}H NMR (400 MHz, $CDCl_3$)

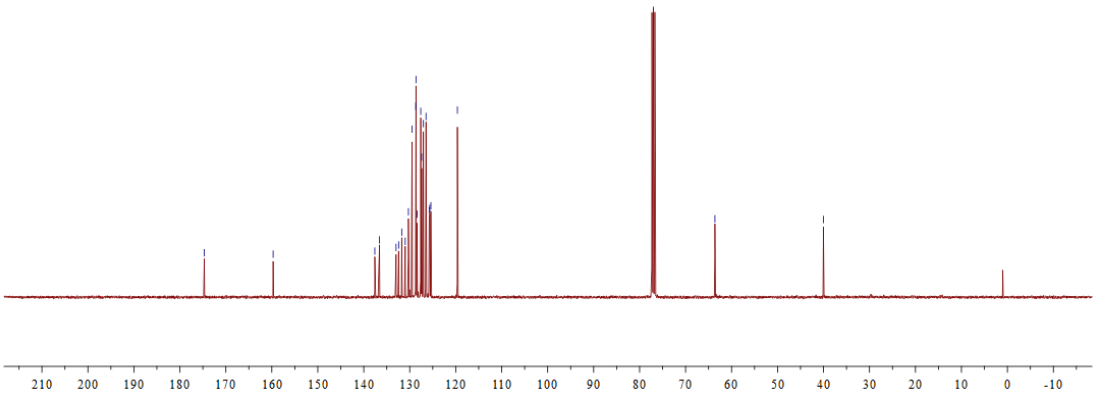






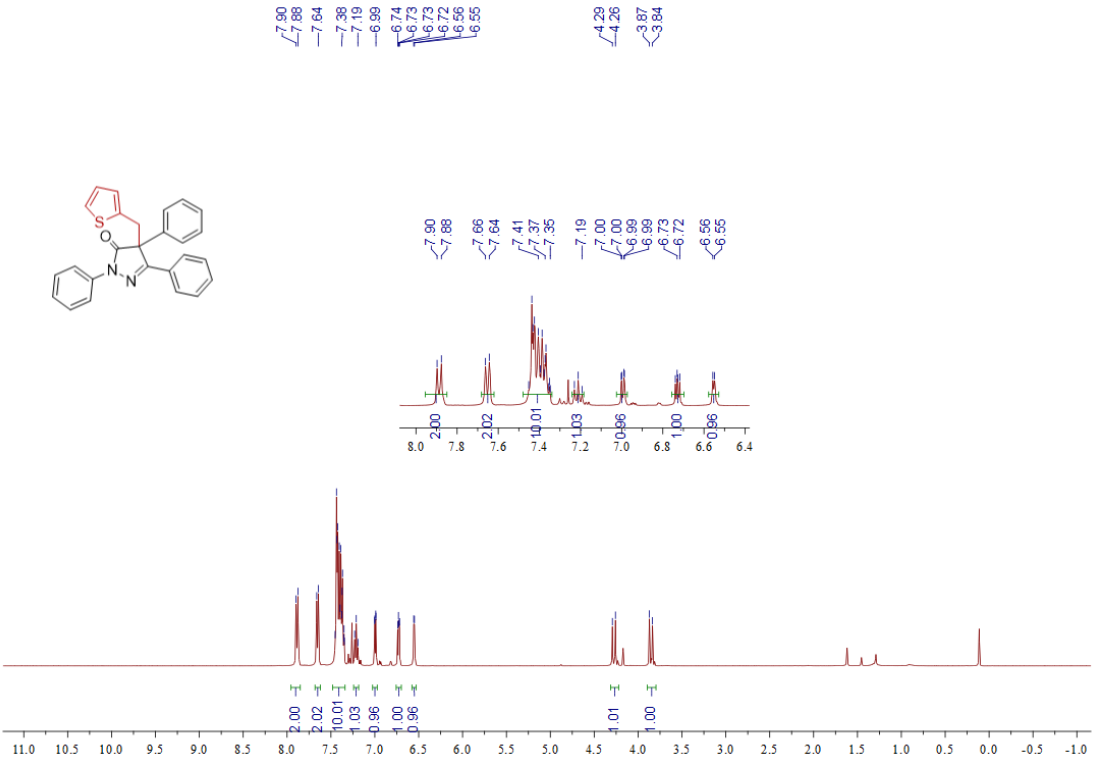
^{13}C NMR (101 MHz, $CDCl_3$)



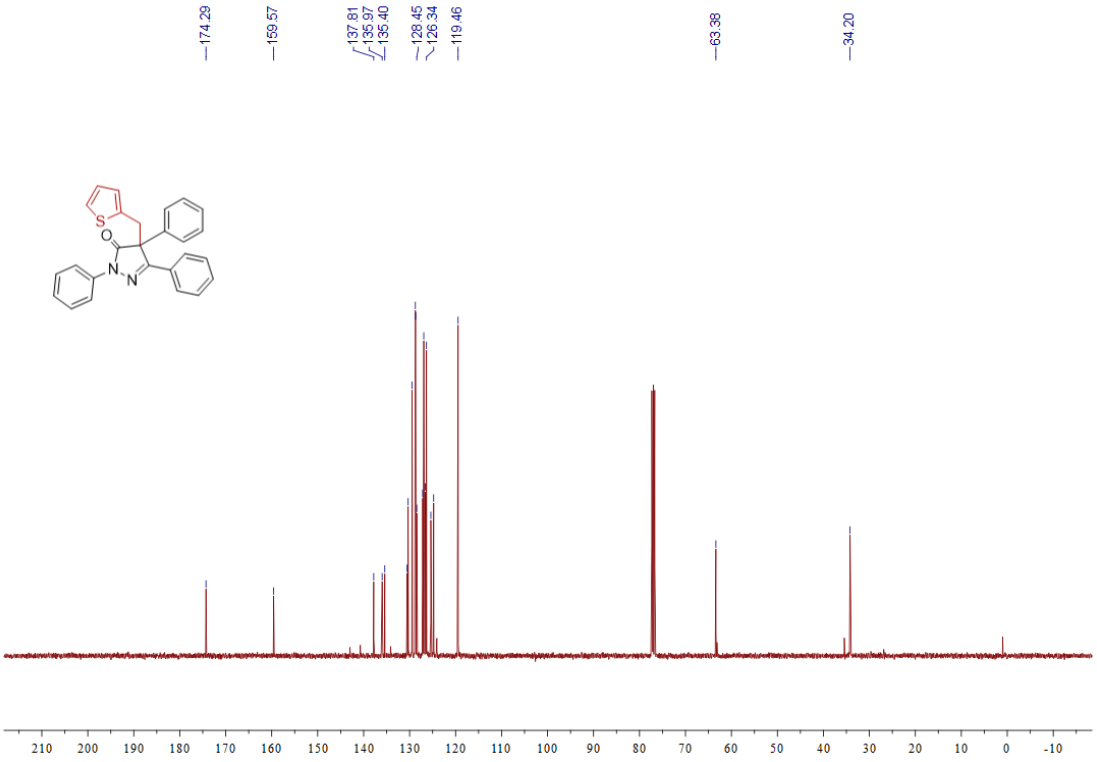


2,4,5-triphenyl-4-(thiophen-2-ylmethyl)-2,4-dihydro-3H-pyrazol-3-one (34)

^{1}H NMR (400 MHz, $CDCl_3$)



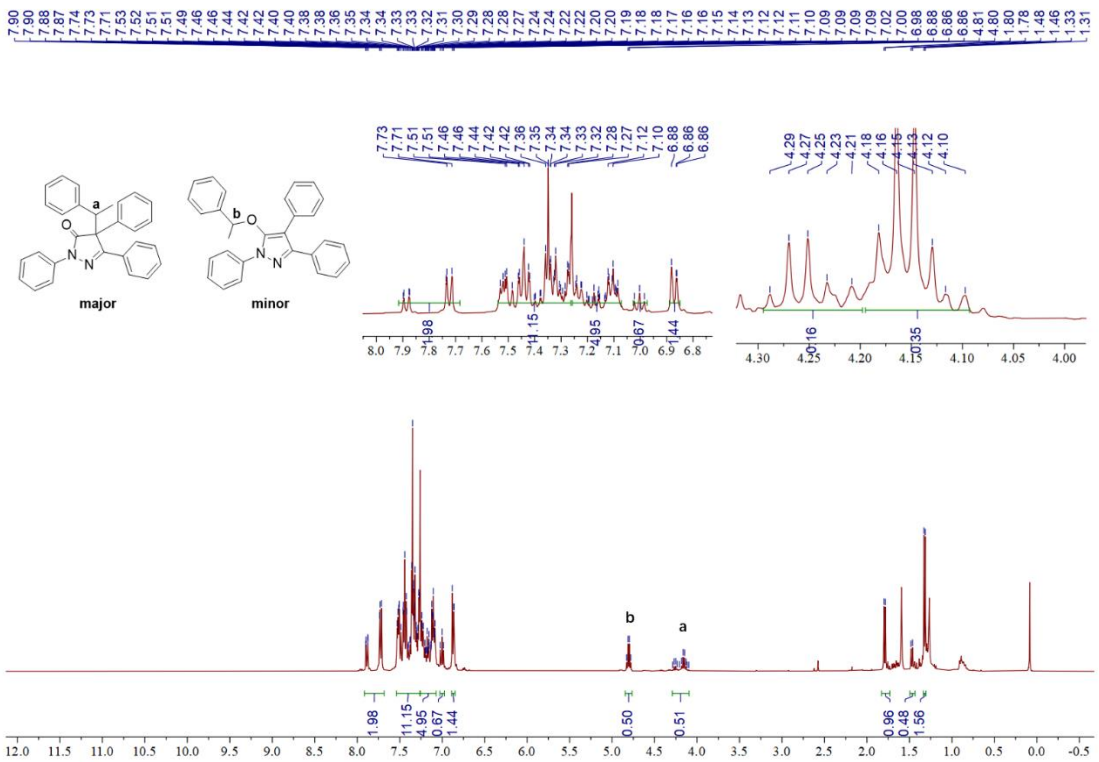
^{13}C NMR (101 MHz, $CDCl_3$)



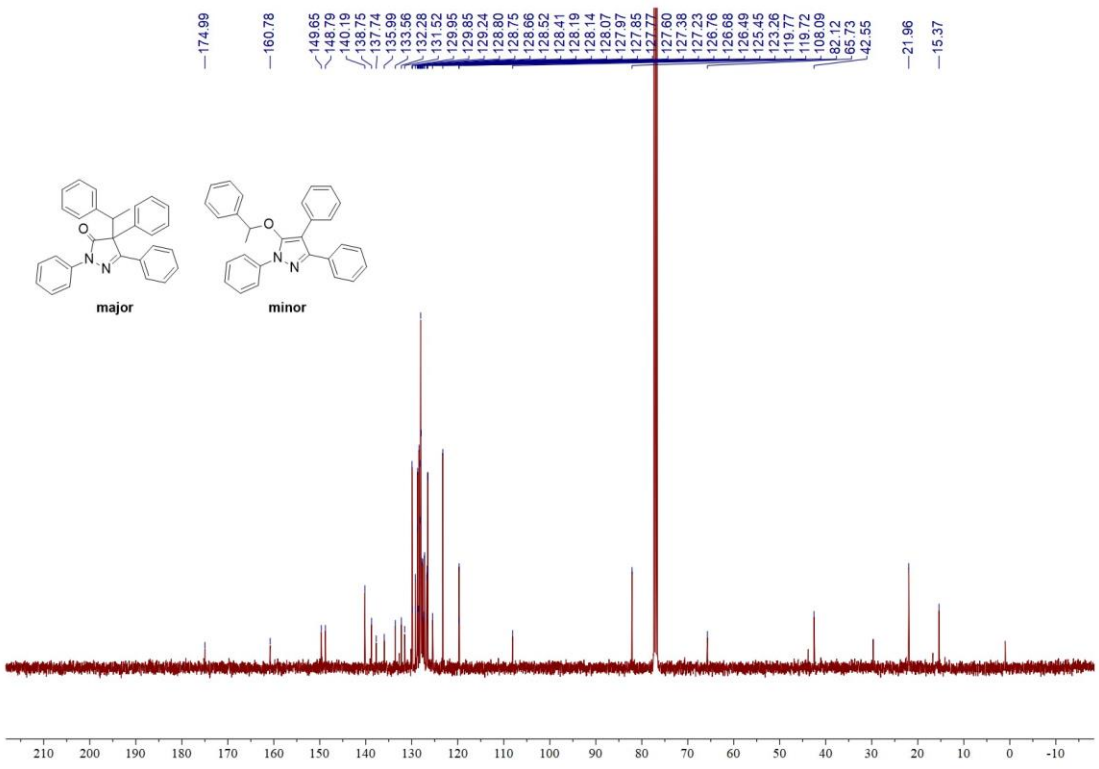
2,4,5-triphenyl-4-(1-phenylethyl)-2,4-dihydro-3H-pyrazol-3-one (35)

1,3,4-triphenyl-5-(1-phenylethoxy)-1H-pyrazole (35')

^{1}H NMR (400 MHz, $CDCl_3$)



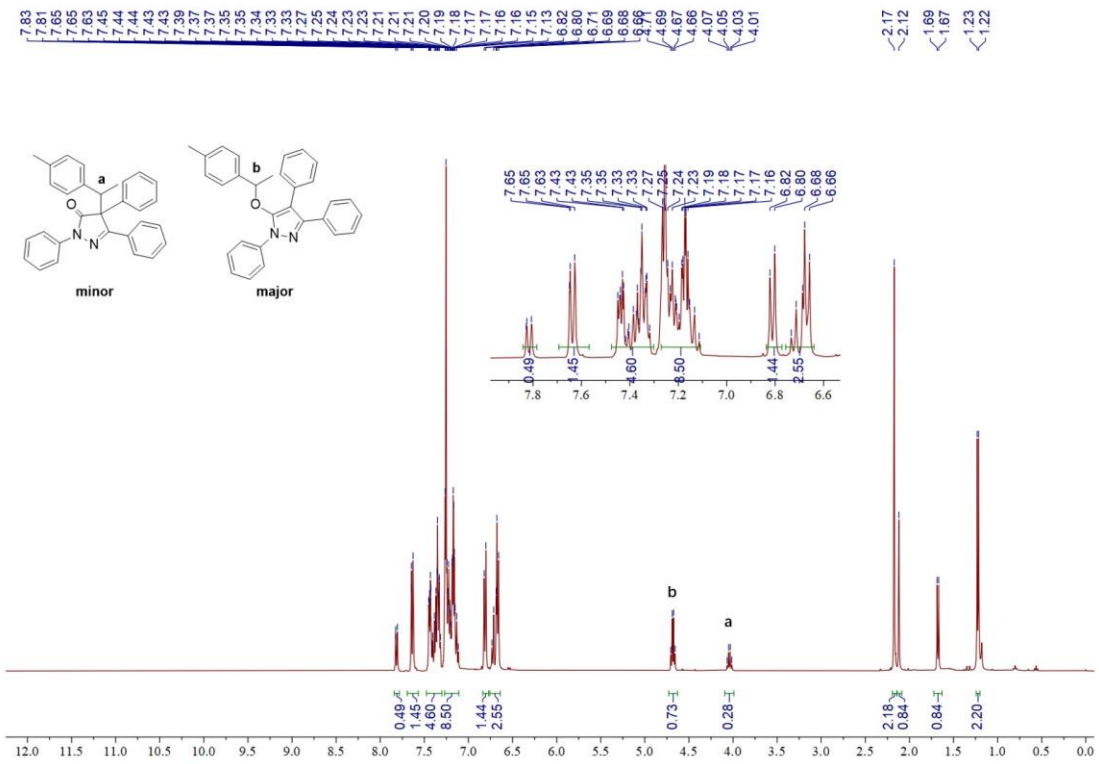
^{13}C NMR (101 MHz, $CDCl_3$)



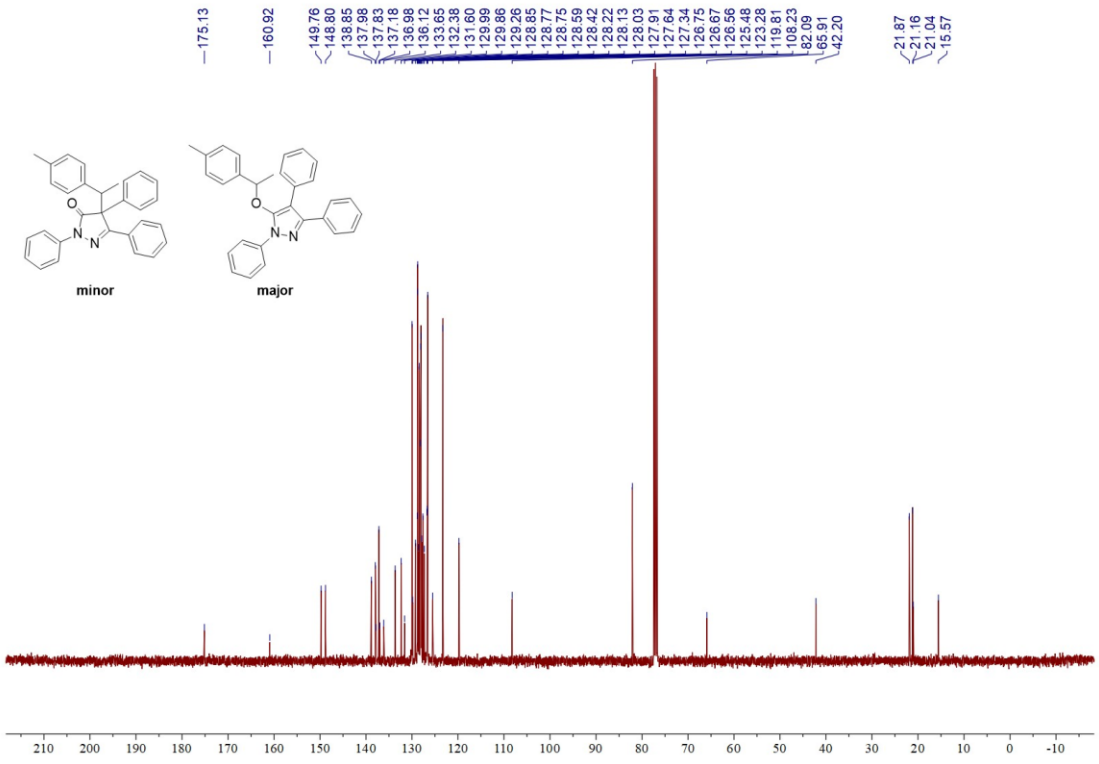
2,4,5-triphenyl-4-(1-(p-tolyl)ethyl)-2,4-dihydro-3H-pyrazol-3-one (36)

1,3,4-triphenyl-5-(1-(p-tolyl)ethoxy)-1H-pyrazole (36')

^{1}H NMR (400 MHz, $CDCl_3$)

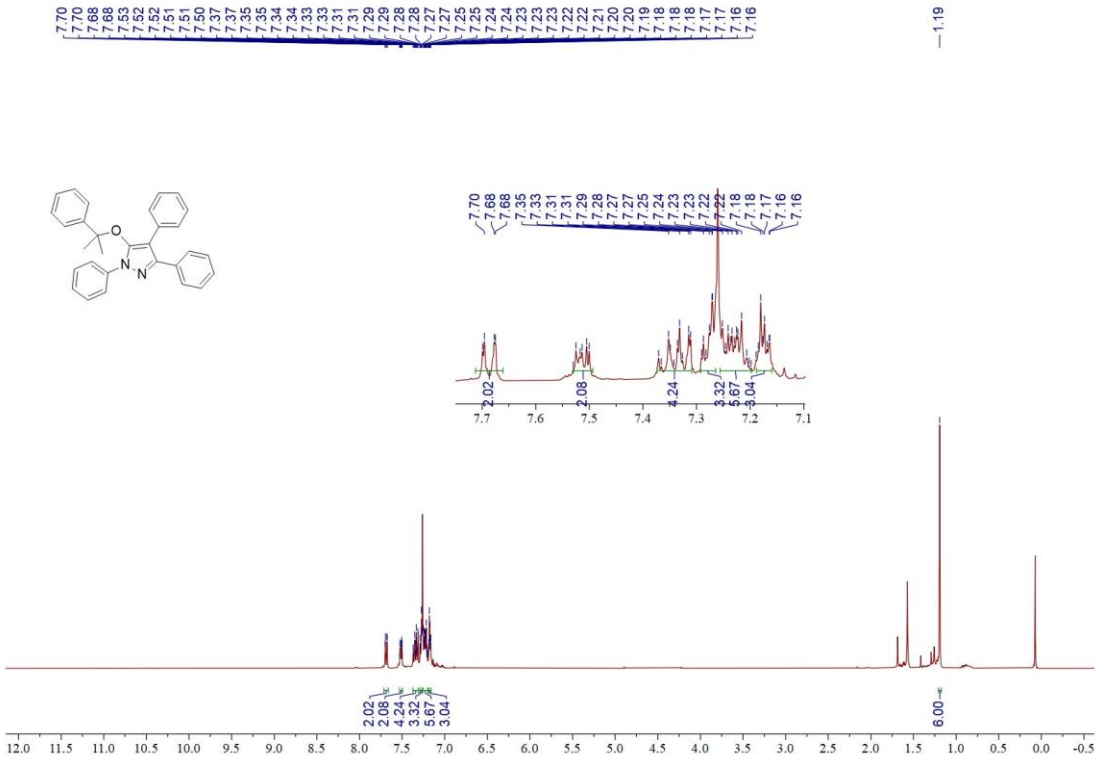


^{13}C NMR (101 MHz, $CDCl_3$)

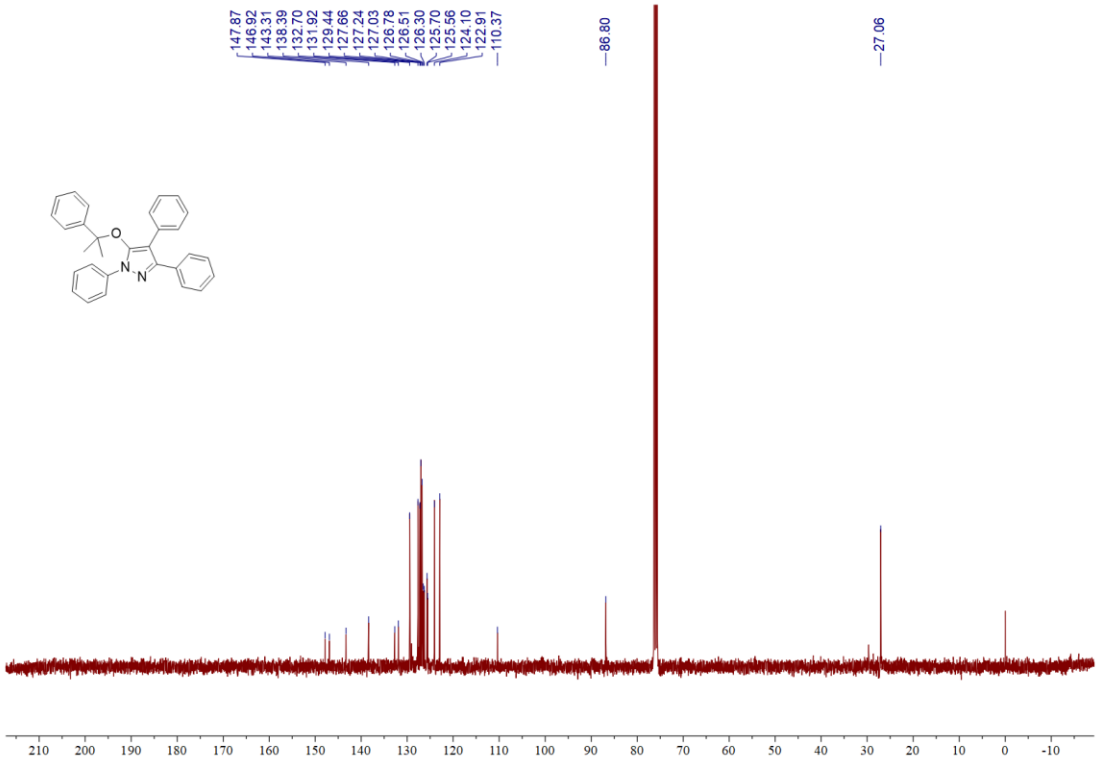


1,3,4-triphenyl-5-((2-phenylpropan-2-yl)oxy)-1H-pyrazole (37')

^{1}H NMR (400 MHz, $CDCl_3$)

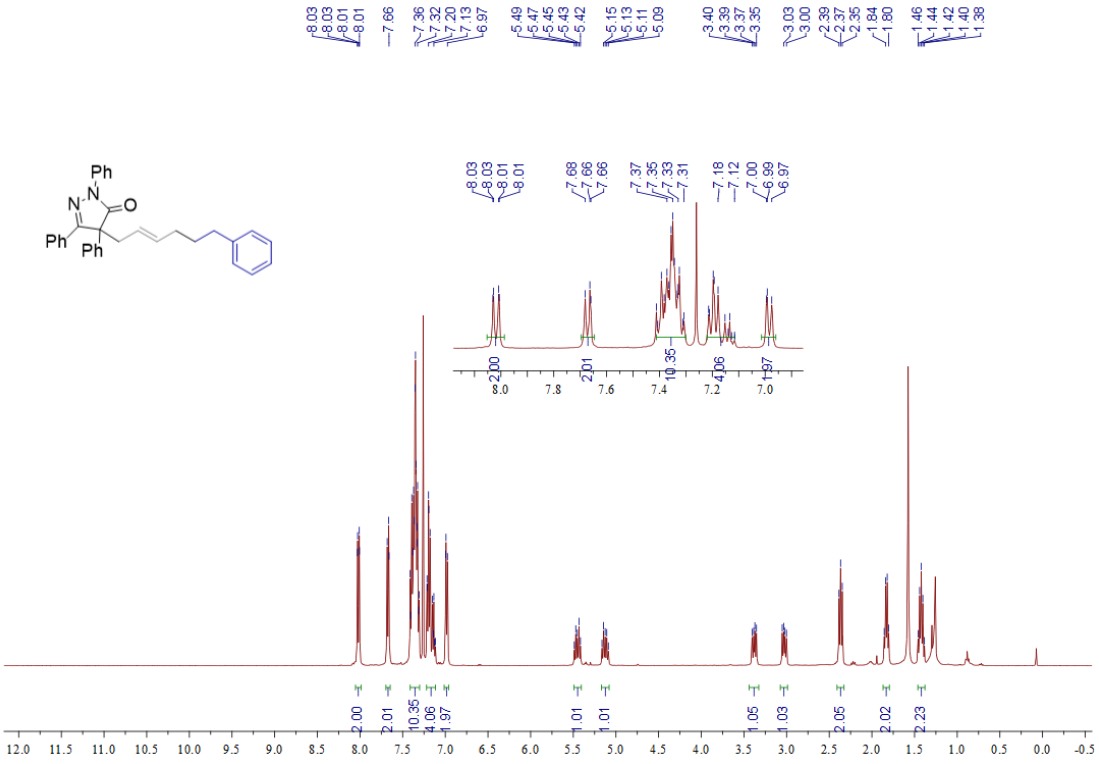


^{13}C NMR (101 MHz, $CDCl_3$)

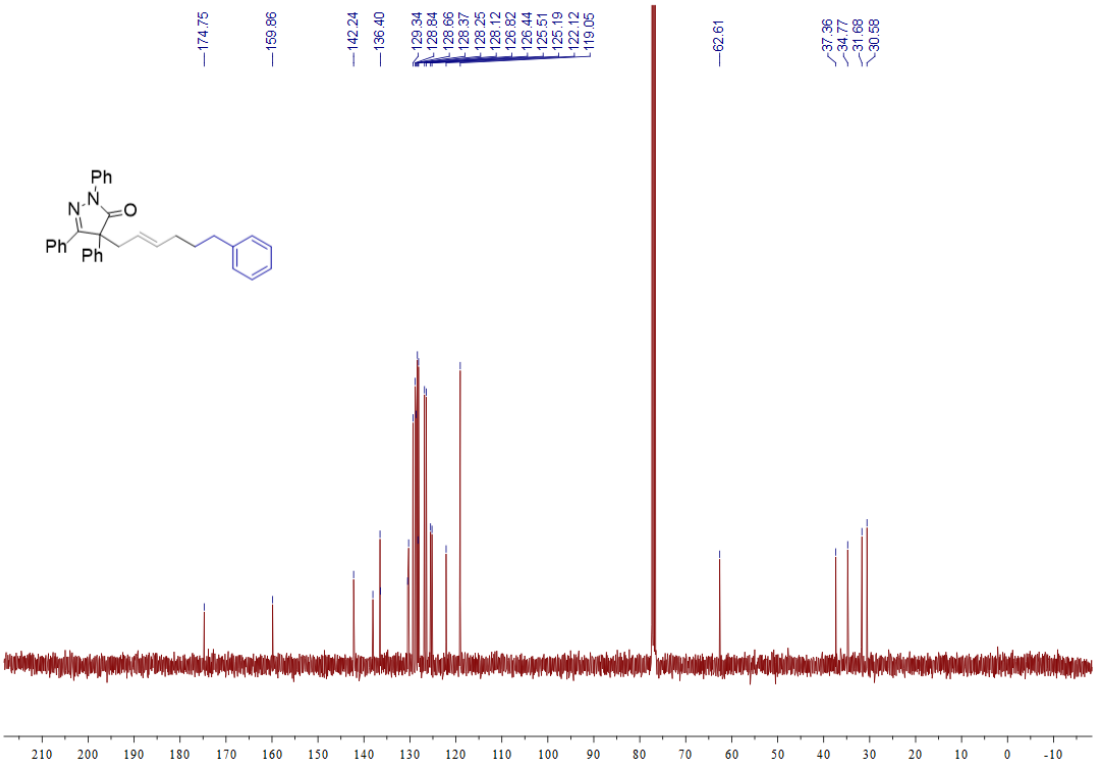


2,4,5-triphenyl-4-(6-phenylhex-2-en-1-yl)-2,4-dihydro-3H-pyrazol-3-one (38)

^{1}H NMR (400 MHz, $CDCl_3$)

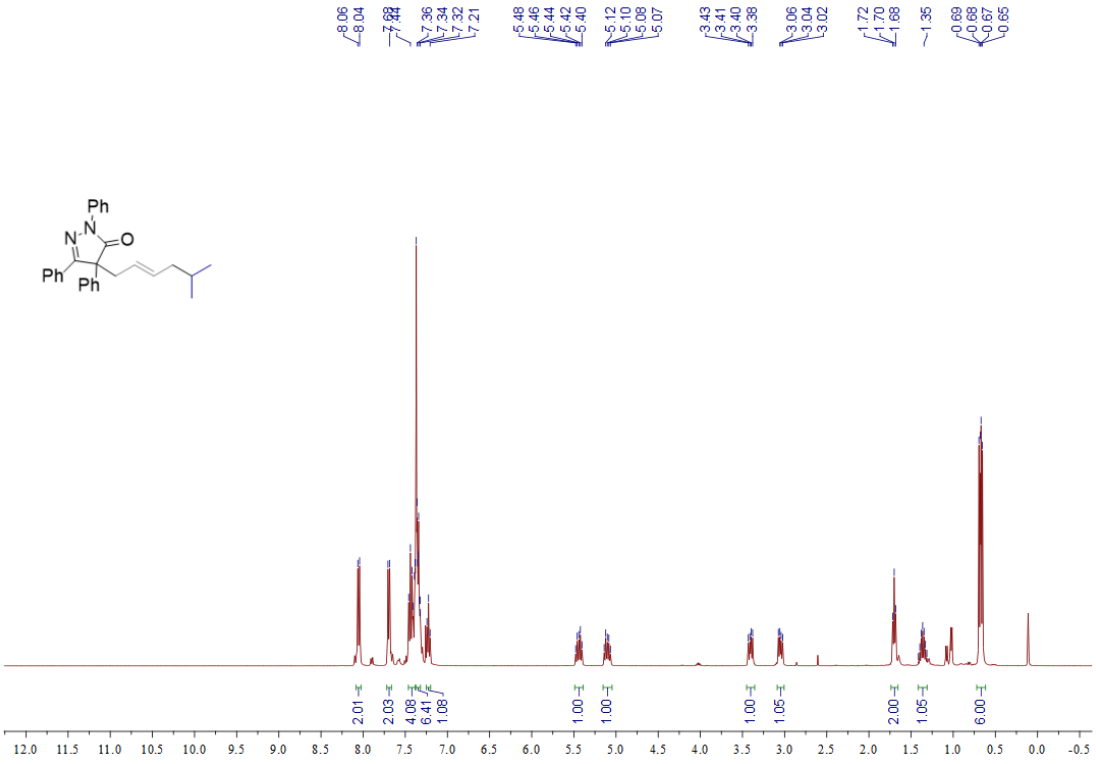


^{13}C NMR (101 MHz, $CDCl_3$)

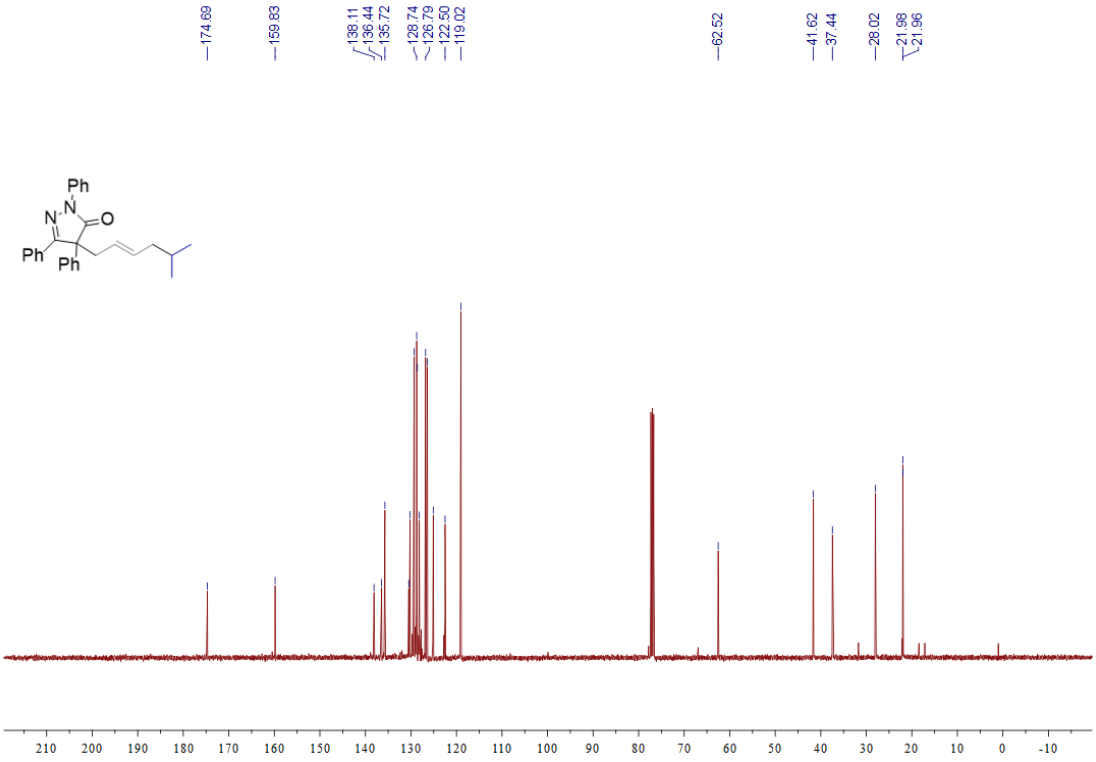


4-(5-methylhex-2-en-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (39)

^{1}H NMR (400 MHz, $CDCl_3$)

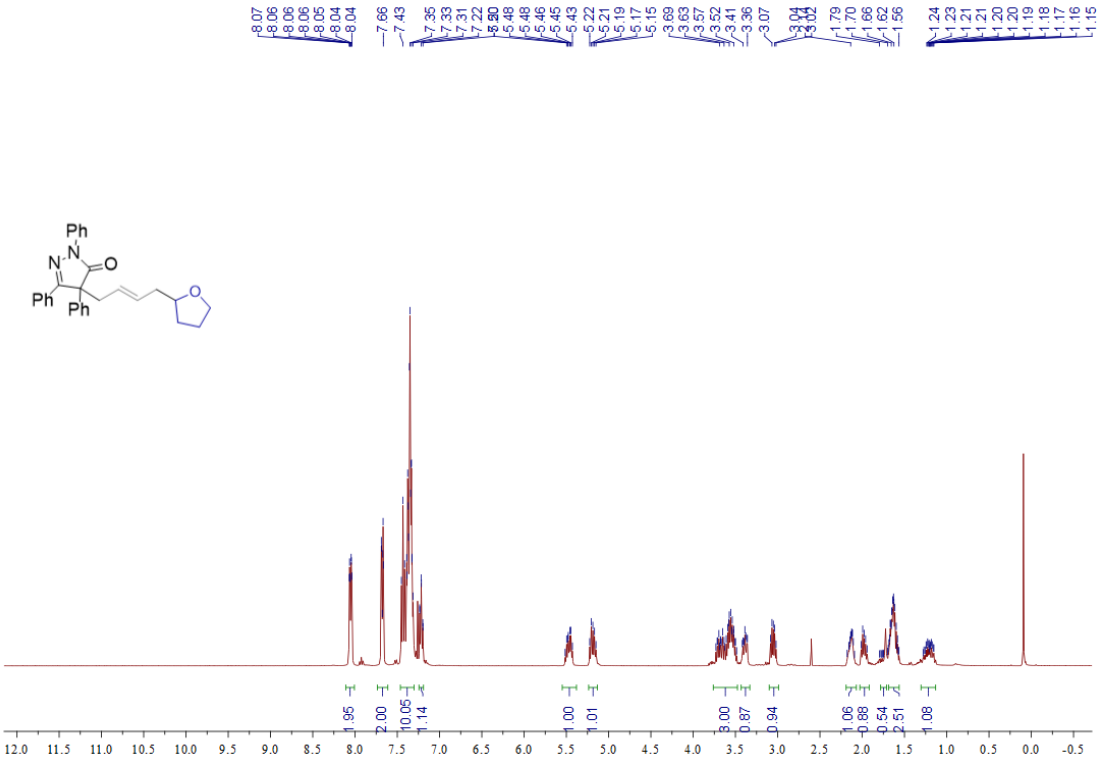


^{13}C NMR (101 MHz, $CDCl_3$)



2,4,5-triphenyl-4-(4-(tetrahydrofuran-2-yl)but-2-en-1-yl)-2,4-dihydro-3H-pyrazol-3-one (40)

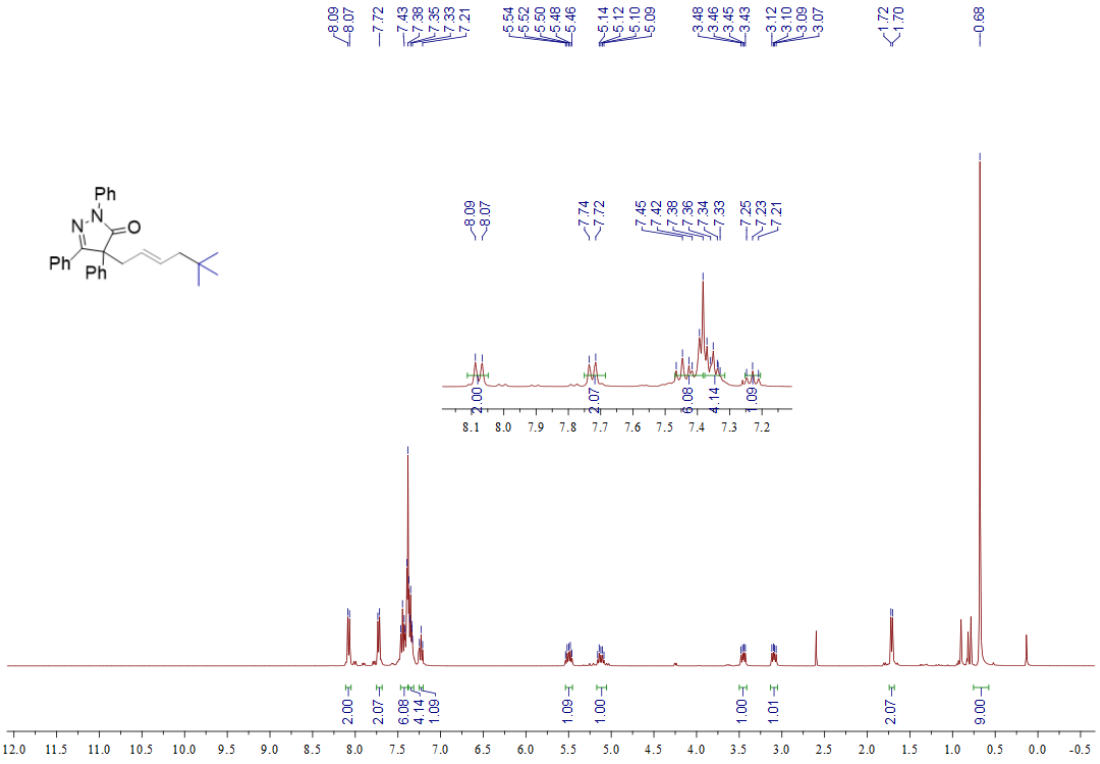
^{1}H NMR (400 MHz, $CDCl_3$)



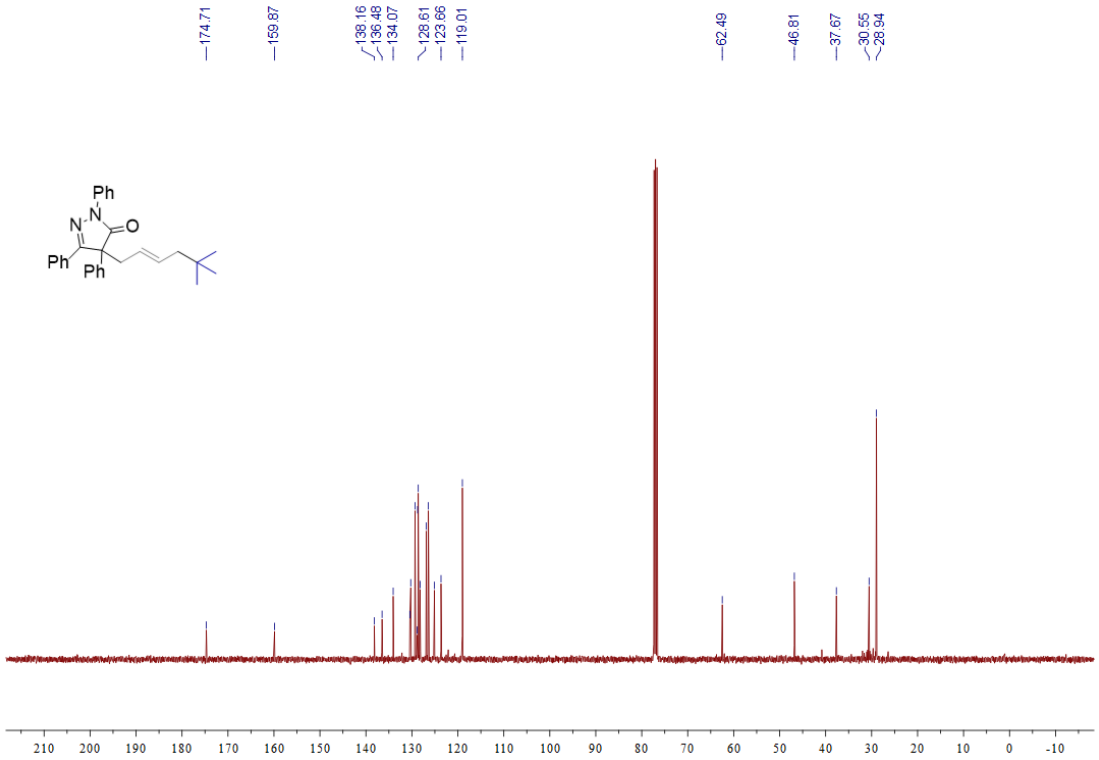
^{13}C NMR (101 MHz, $CDCl_3$)

4-(5,5-dimethylhex-2-en-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (41)

^{1}H NMR (400 MHz, $CDCl_3$)



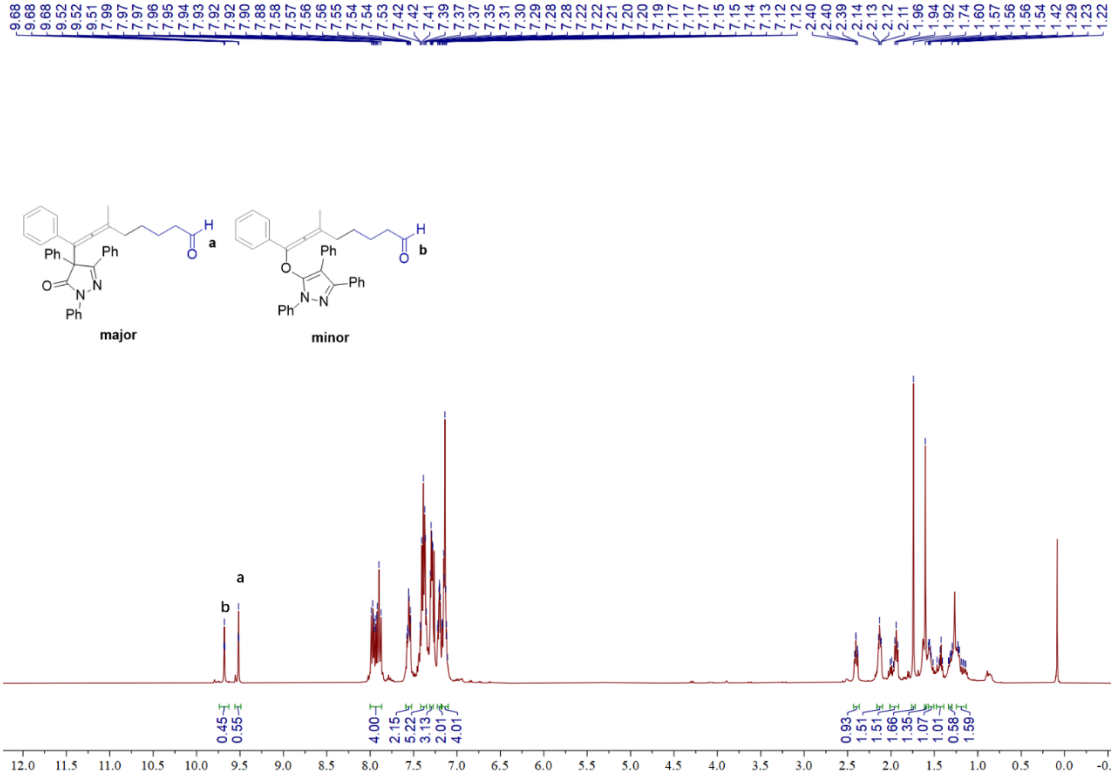
^{13}C NMR (101 MHz, $CDCl_3$)



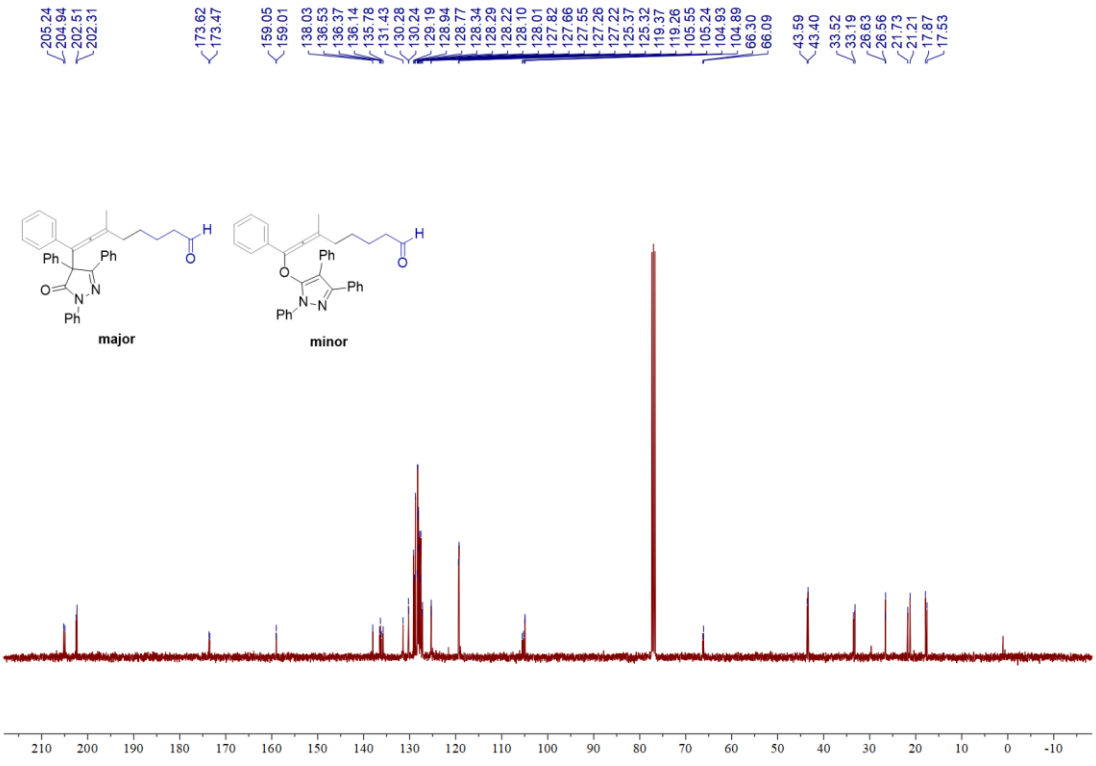
6-methyl-8-(5-oxo-1,3,4-triphenyl-4,5-dihydro-1H-pyrazol-4-yl)-8-phenylocta-6,7-dienal (42)

6-methyl-8-phenyl-8-((1,3,4-triphenyl-1H-pyrazol-5-yl)oxy)octa-6,7-dienal (42')

^{1}H NMR (400 MHz, $CDCl_3$)



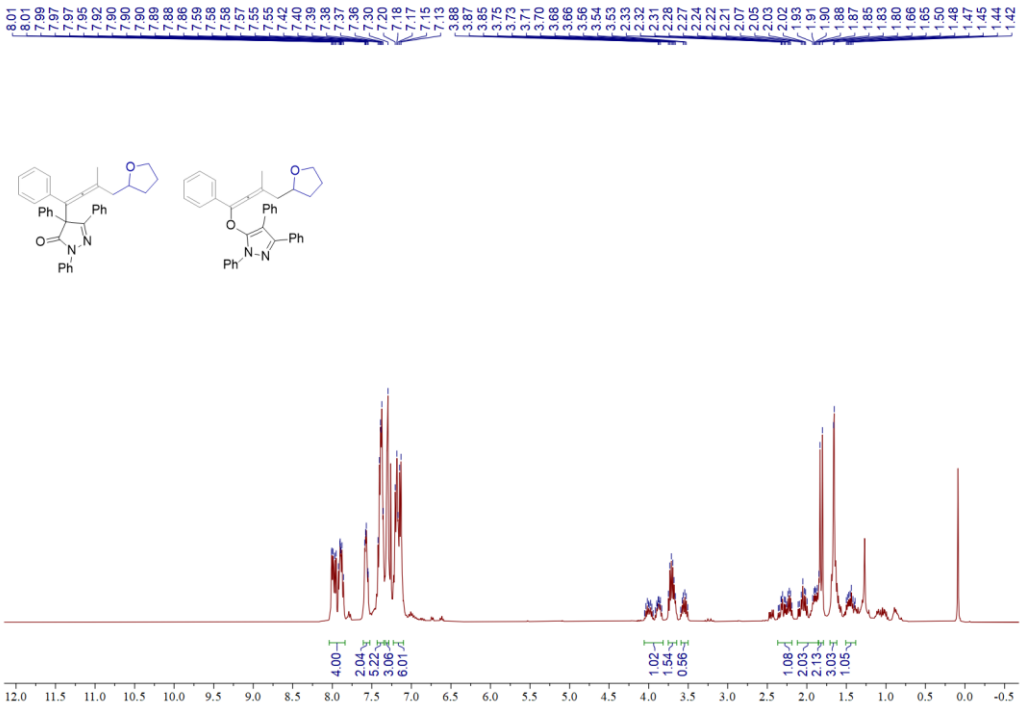
^{13}C NMR (101 MHz, $CDCl_3$)



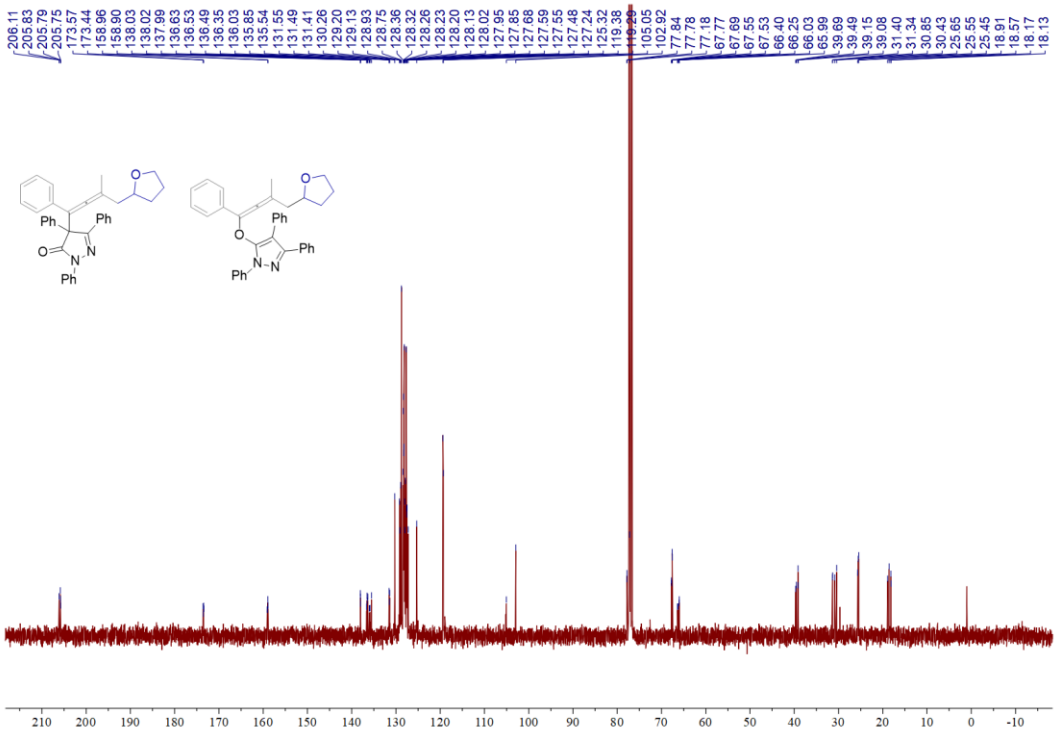
4-(3-methyl-1-phenyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (43)

5-((3-methyl-1-phenyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)oxy)-1,3,4-triphenyl-1H-pyrazole (43')

^{1}H NMR (400 MHz, $CDCl_3$)



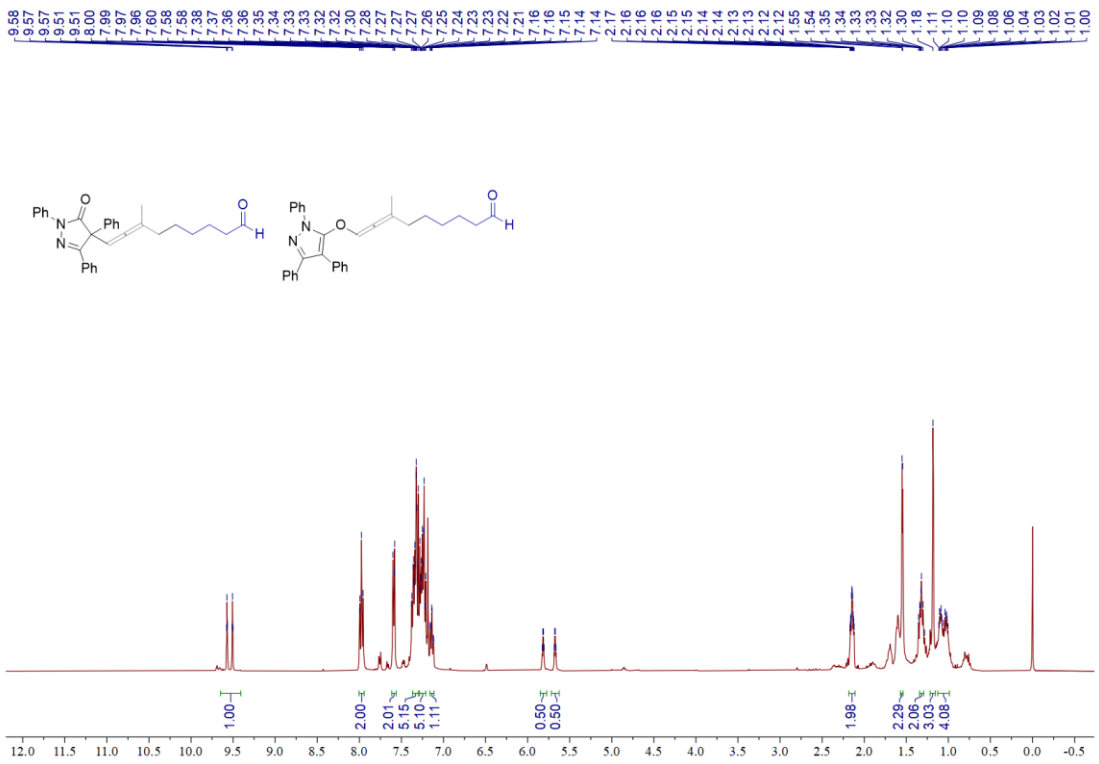
^{13}C NMR (101 MHz, $CDCl_3$)



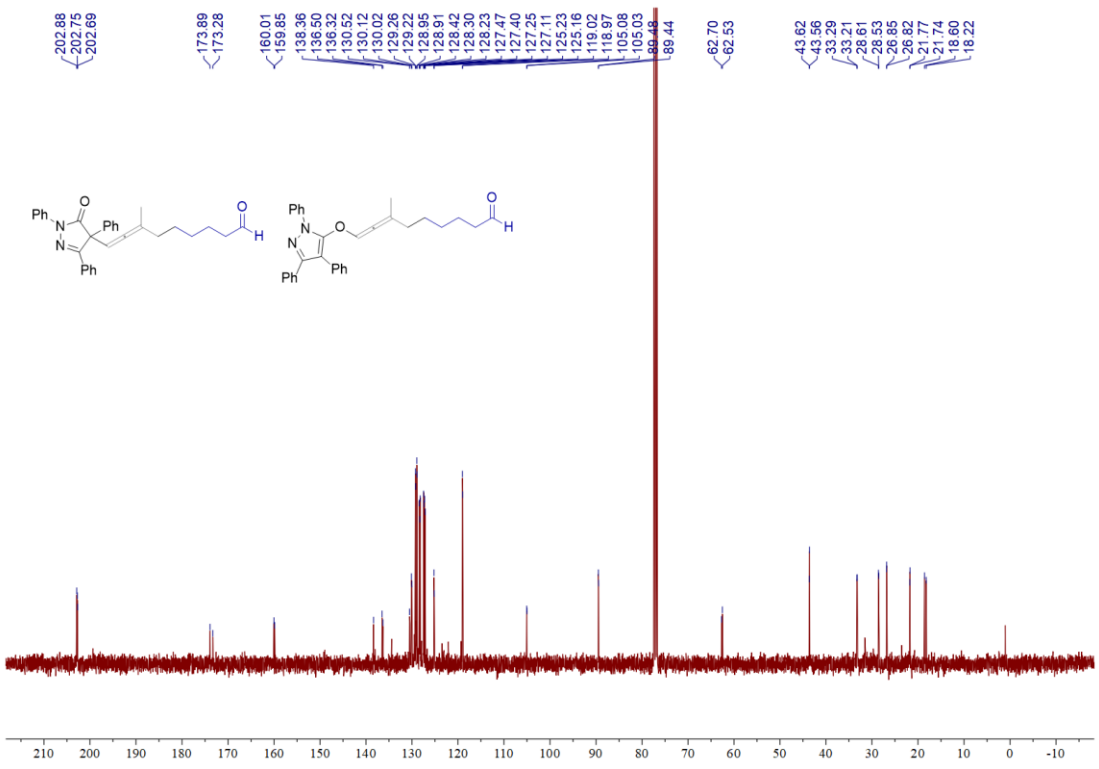
7-methyl-9-(5-oxo-1,3,4-triphenyl-4,5-dihydro-1H-pyrazol-4-yl)nona-7,8-dienal (44)

7-methyl-9-((1,3,4-triphenyl-1H-pyrazol-5-yl)oxy)nona-7,8-dienal (44')

^{1}H NMR (400 MHz, $CDCl_3$)



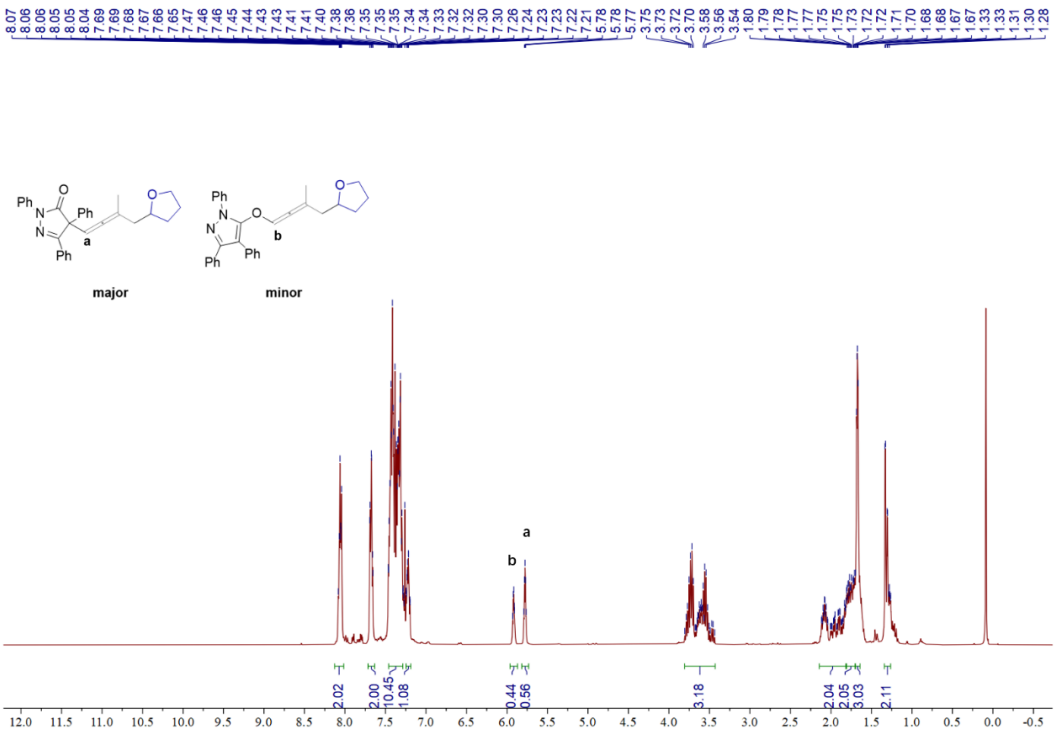
^{13}C NMR (101 MHz, $CDCl_3$)



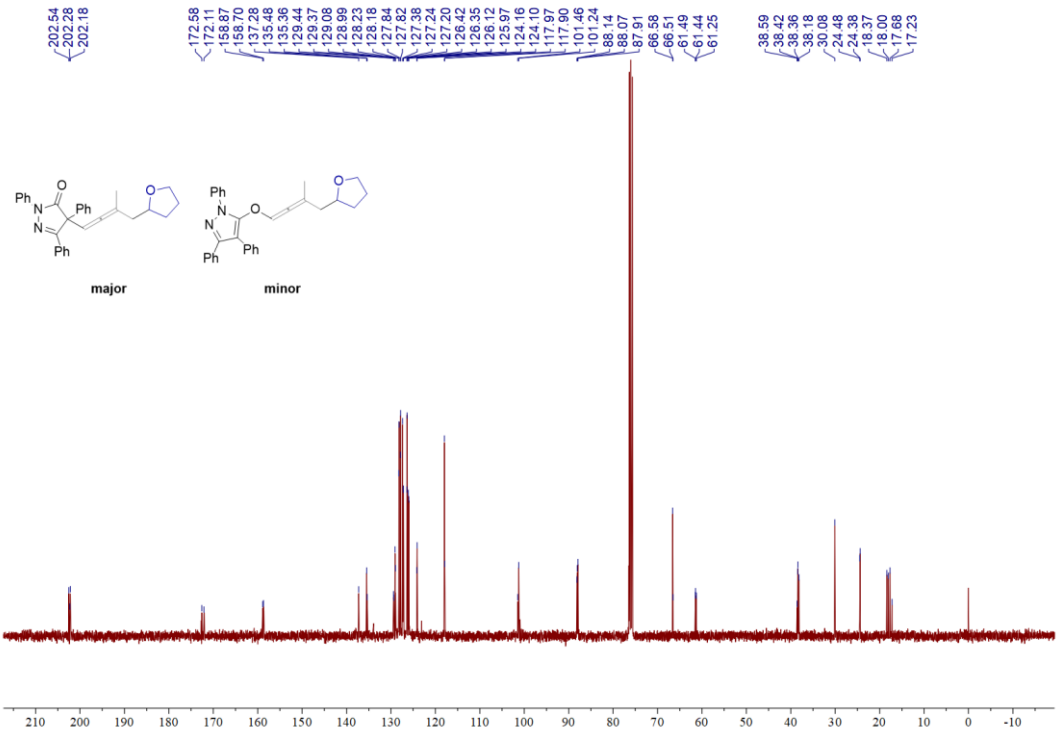
4-(3-methyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)-2,4,5-triphenyl-2,4-dihydro-3H-pyrazol-3-one (45)

5-((3-methyl-4-(tetrahydrofuran-2-yl)buta-1,2-dien-1-yl)oxy)-1,3,4-triphenyl-1H-pyrazole (45')

^{1}H NMR (400 MHz, $CDCl_3$)

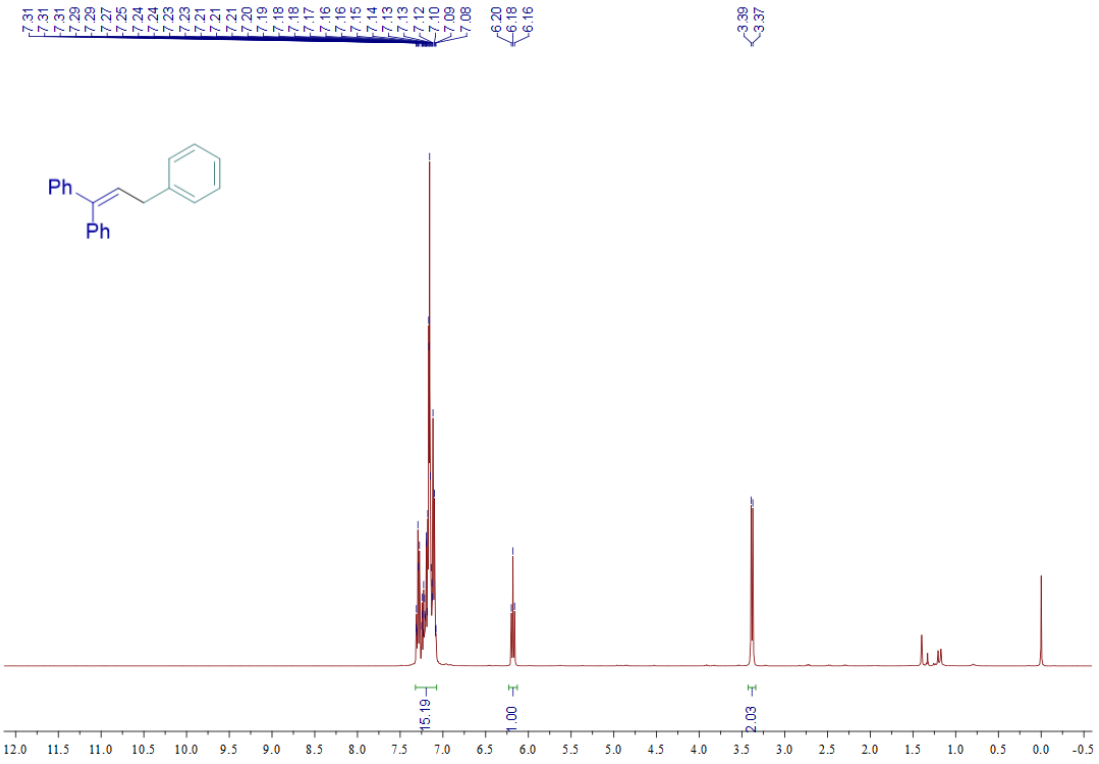


^{13}C NMR (101 MHz, $CDCl_3$)

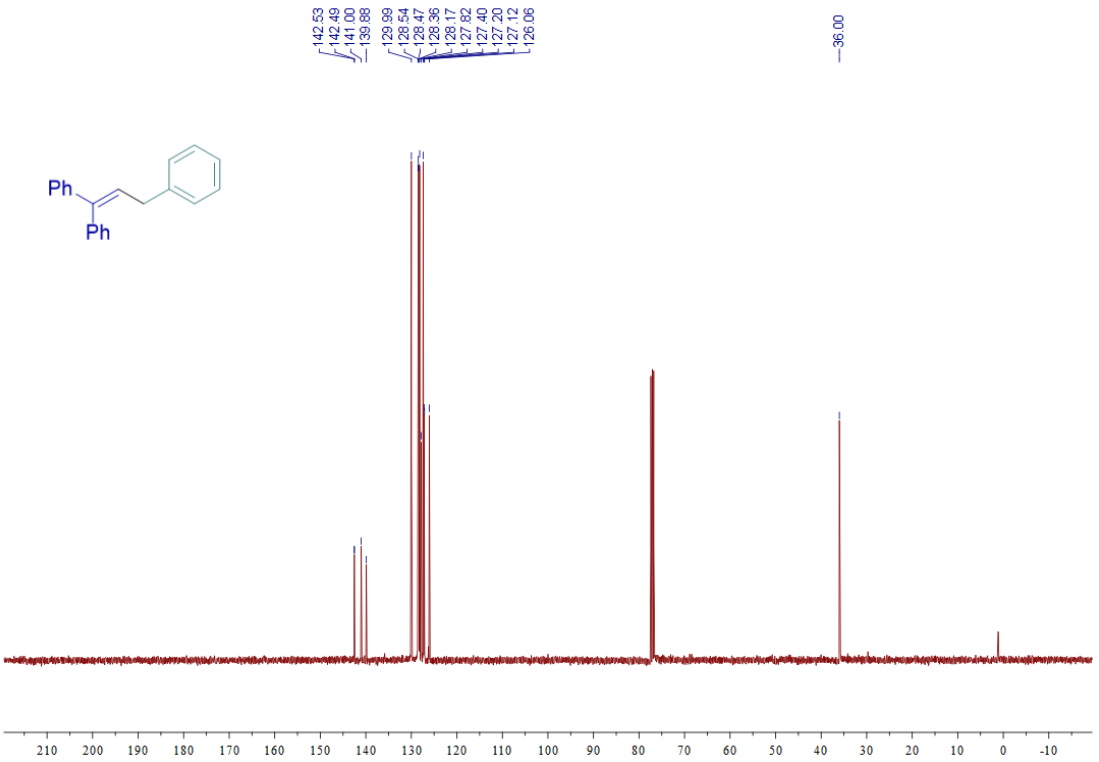


prop-1-ene-1,1,3-triyltribenzene (47)

^{1}H NMR (400 MHz, $CDCl_3$)

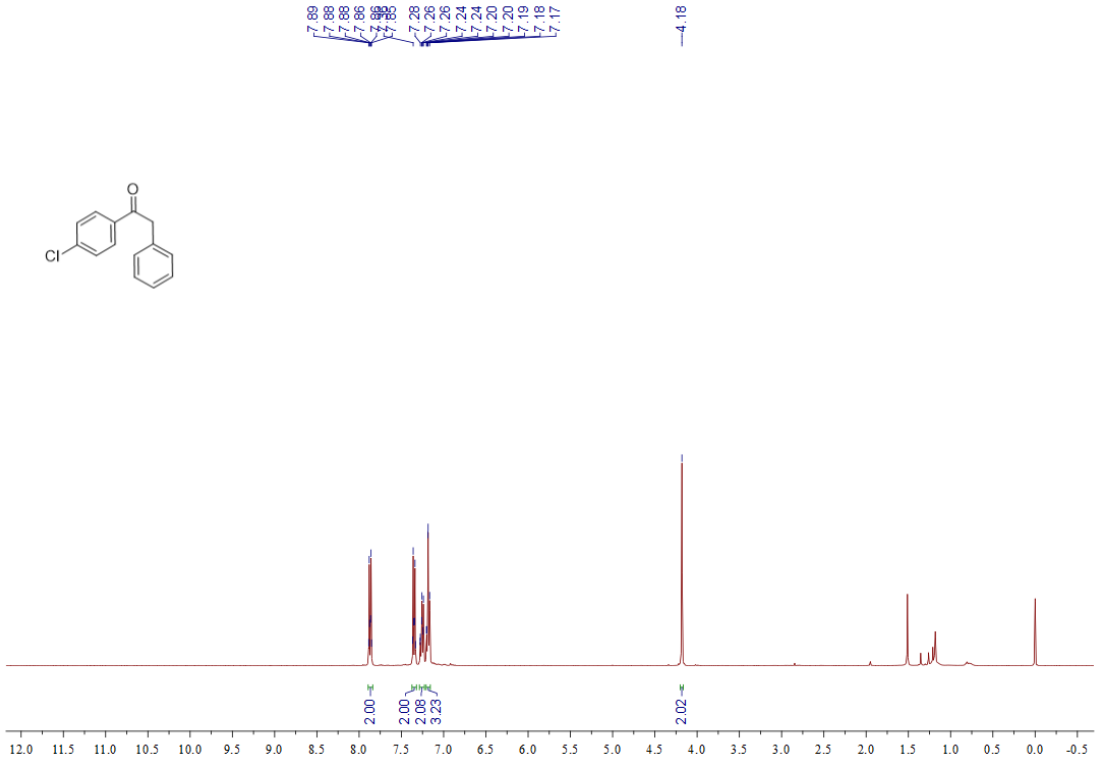


^{13}C NMR (101 MHz, $CDCl_3$)

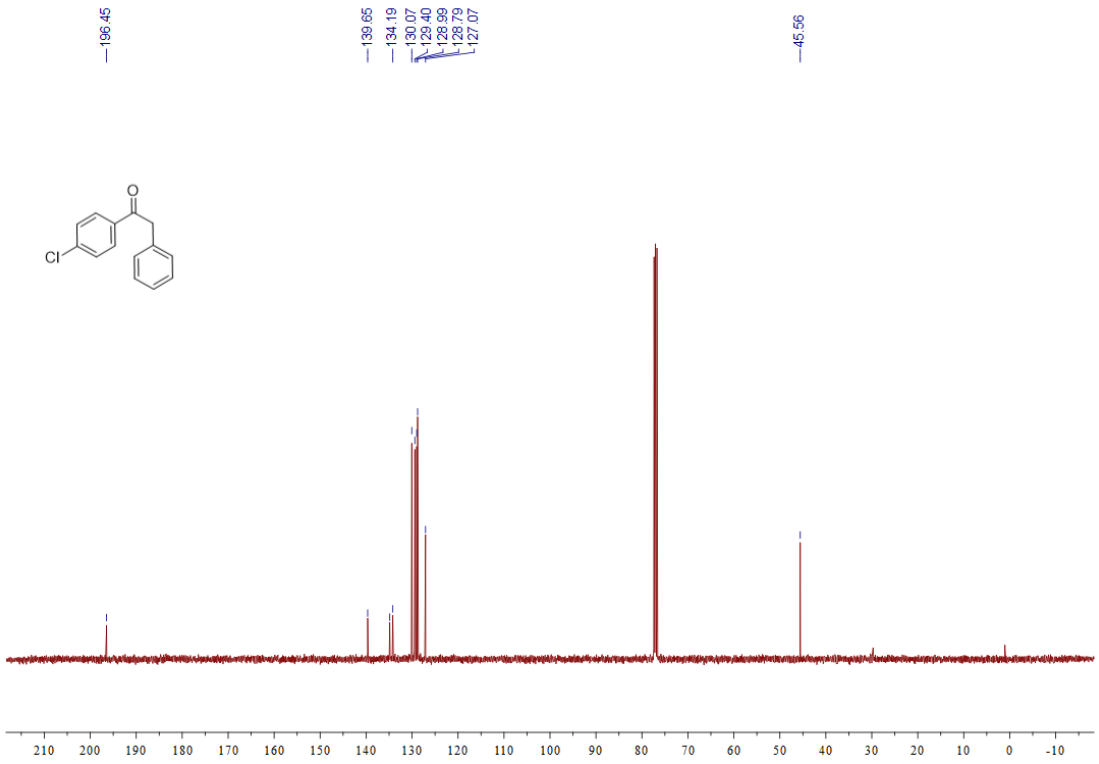


1-(4-chlorophenyl)-2-phenylethan-1-one (50)

^{1}H NMR (400 MHz, $CDCl_3$)

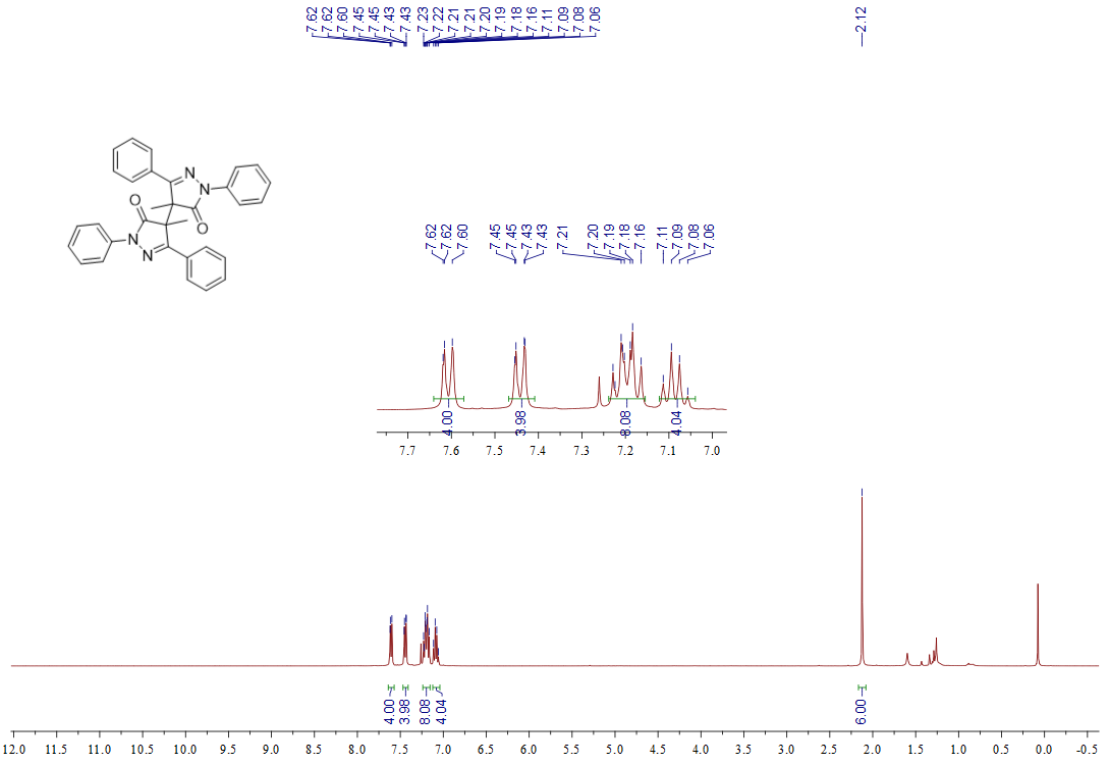


^{13}C NMR (101 MHz, $CDCl_3$)

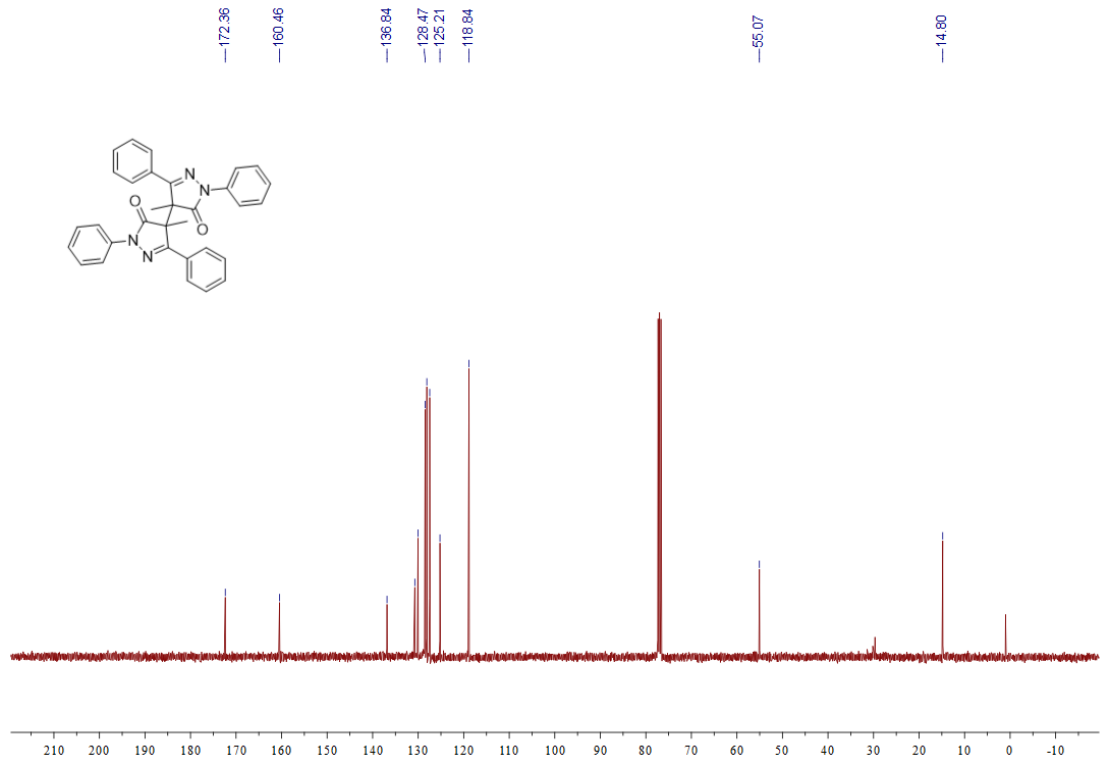


4,4'-dimethyl-2,2',5,5'-tetraphenyl-2,2',4,4'-tetrahydro-3H,3'H-[4,4'-bipyrazole]-3,3'-dione (52)

^{1}H NMR (400 MHz, $CDCl_3$)

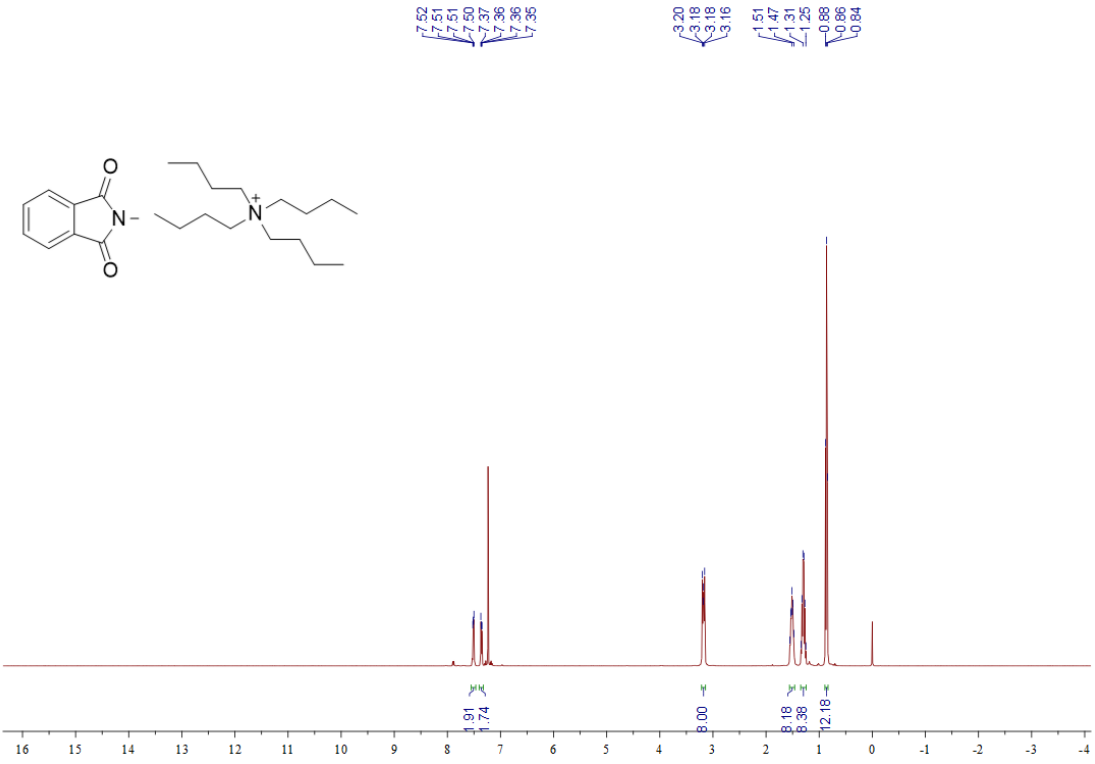


^{13}C NMR (101 MHz, $CDCl_3$)

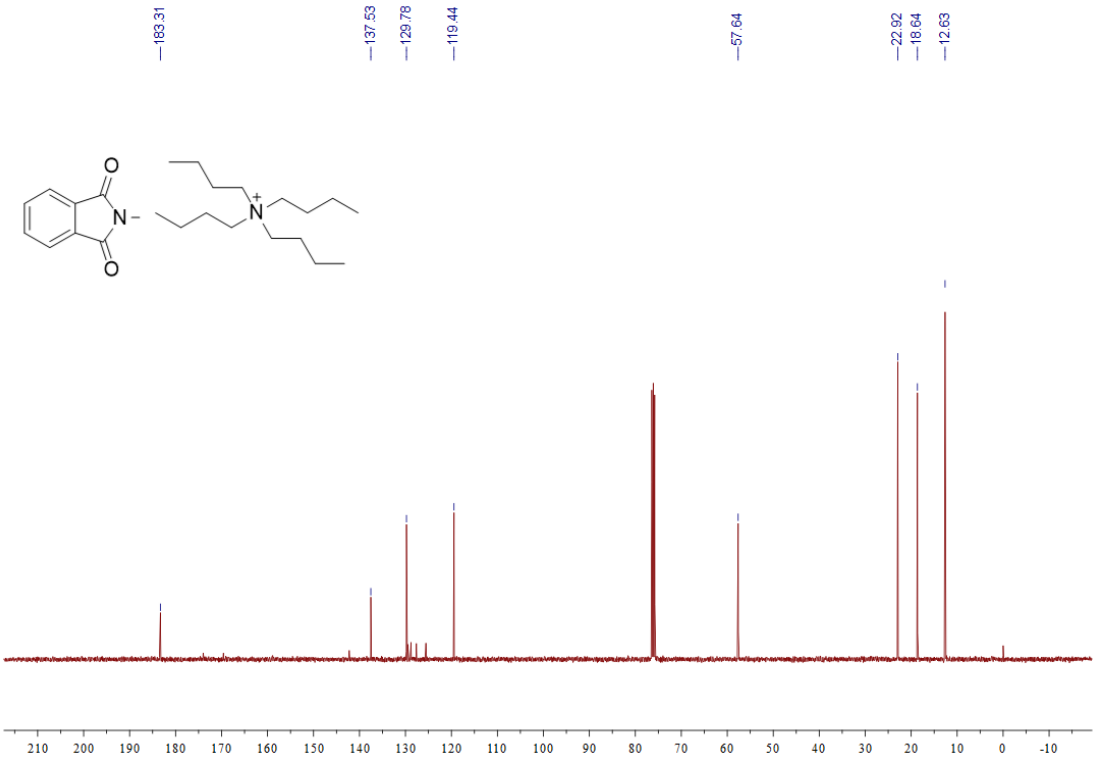


tetrabutylammonium 1,3-dioxoisoindolin-2-ide

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



9 References

1. J. Wang, M. Shang, H. Lundberg, K. S. Feu, S. J. Hecker, T. Qin, D. G. Blackmond and P. S. Baran, *ACS Catalysis.*, 2018, **8**, 9537-9542.
2. D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, 8, 259-271.
3. (a) M. J. Gomes, L. F. Pinto, P. Glória, H. S. Rzepa, S. Prabhakar and A. M. Lobo, *Chemistry Central Journal*, 2013, **7**, 94-105; (b) P. Drouhin and R. Taylor, *Eur. J. Org. Chem.*, 2015, **11**, 2333-2336; (c) M. A. Sanchez-Carmona, D. A. Contreras-Cruz and L. D. Miranda, *Org. Biomol. Chem.*, 2011, **9**, 6506-6508.
4. Z. He, H. Li and Z. Li, *J. Org. Chem.*, 2010, **75**, 4636-4639.
5. J. Zhang, Y. Li, R. Xu and Y. Chen, *Angew. Chem. Int. Ed.*, 2017, **56**, 12619-12623.