A multi-component synthetic route for 2-pyrazolines via acceptorless dehydrogenation of alcohols using homogeneous Ni(II) catalysts

Prashant Kukreti,[a#] Rahul Chauhan,[a#] Abhishek Panwar,[b] and Kaushik Ghosh[a*]

[a]Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, India.

[b]Department of Chemistry National Institute of Technology Manipur, Langol-795004, Imphal West, Manipur, India

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1. Experimental

1.1 Materials used

All the chemicals and solvents were purchased from commercially available sources such as Aldrich, Merck, TCI, SRL, and ACROS organics and used as received. Analytical grade reagents and solvents were used for whole activities and spectroscopic studies. 2,6-Bis(1-phenylhydrazinyl) pyridine was synthesized according to literature.[1] UV-Vis. Spectra were recorded using a UV-Vis Spectrophotometer (UV-2600 from Shimadzu). IR spectra were recorded on an ALPHA II compact FT-IR spectrometer with the use of KBr pellets (16 scans in cm^{-1}). NMR spectra were recorded using Bruker Avance III 500 MHz (AV 500) and Jeol 500MHz spectrometers in deuterated solvents. Chemical shift values in NMR are recorded in δ (ppm) values against TMS as internal standard. NMR coupling constants (J) are represented in hertz (Hz) values. Multiplets in the chemical shift are given as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triples), td (triplet of doublets).

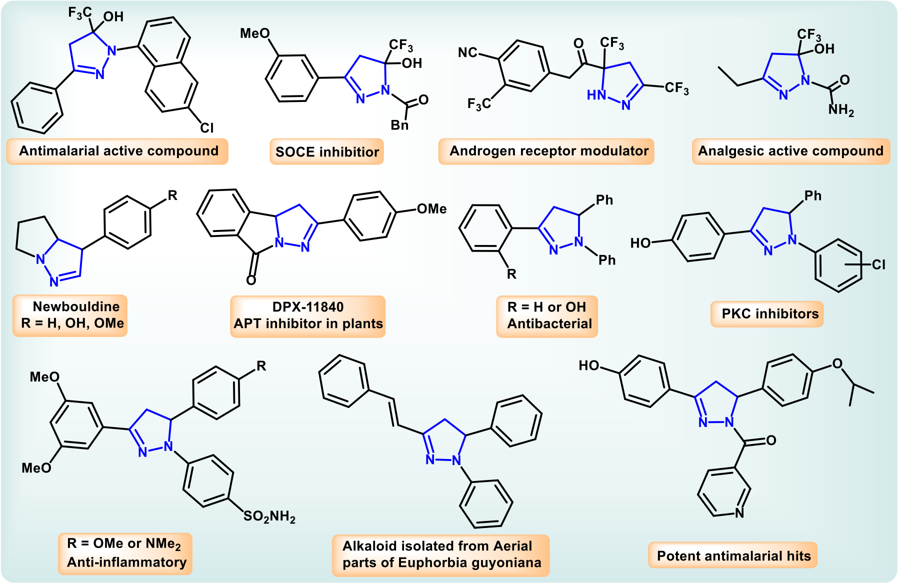
1.2 X-ray crystallography

The X-ray data collection and processing of complex 1 and complex 2 were performed on a Bruker Kappa (D8 QUEST) Apex-IV CMOS diffractometer by using graphite monochromated Mo-Kα radiation (λ = 0.71070 Å) at 119 K and 105 K, respectively. The crystal structures were solved by SIR-92 GUI control methods. The Olex[2] software was used to solve the crystal structures and refine them using ShelXT and ShelXL, respectively.[3] The bond lengths and bond angles were computed with the help of MERCURY software. Additionally, ORTEP[4] images was generated using the same MERCURY program. The hydrogen atoms were placed in geometrically determined positions and refined using the riding model. The accompanying supplementary information (SI) files contains pertinent crystallographic parameters.

1.3 Computational methods

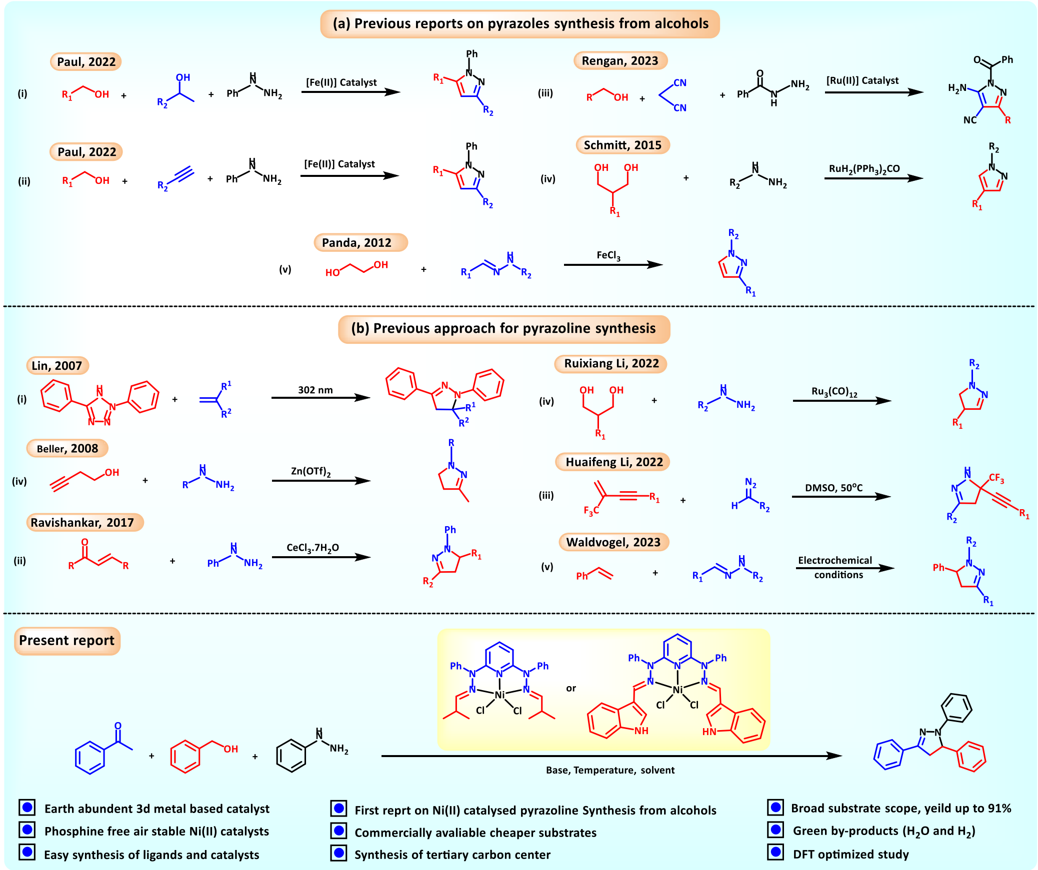
Density functional theory (DFT) calculations were performed using Gaussian 09W software. The input files for Gaussian 09 were prepared with Gauss View 5.0.8.[30] The spin-unrestricted B3LYP functional was employed alongside two basis sets: the LanL2DZ basis set for Ni and the 6-31+G(d,p) basis set for all other elements. Frequency calculations for the optimized structures were conducted at room temperature (298.15 K). All computations were carried out in toluene using the Integral Equation Formalism Polarizable Continuum Model (IEFPCM) within the self-consistent reaction field (SCRF) approach. Free energy evaluations were also performed at room temperature. The free energy change (ΔG) includes contributions from electronic energy (ΔE), zero-point vibrational energy (ΔZ0), thermal enthalpy (ΔEthermal), and entropy (−TΔS).

2.1 Biologically active molecules with pyrazoline moiety



2.2 Previous reports on transition metal catalyzed MCS of pyrazole synthesis and previous approaches for pyrazoline synthesis

Over the last few decades, many methods have been developed for the synthesis of pyrazoles and 2-pyrazolines in which the most common was the cyclization of hydrazine with various electrophiles, including 1,3-dicarbonyl compounds, α,β-unsaturated carbonyl compounds and dihalides etc.[5–10] Some of previously utilized methods for synthesis of pyrazoline are shown in Figure(2).[11–29] [13–31] Although a number of difficulties are still existed in these methods such as poor selectivity, toxicity, expensive chemicals, pre-functionalization of reactants, multi-step reactions etc.



3. Synthesis

3.1 Synthesis of L1 = 2,6-bis(2-((E)-2-methylpropylidene)-1-phenylhydrazineyl)pyridine)

To a methanolic solution of 2,6-bis(1-phenylhydrazineyl)pyridine (4 mmol, 1164mg) in 15ml methanol isobuturaldehyde (8 mmol, 576mg) was added dropwise with constant stirring. Reaction mixture was stirred for next 1 hour a white solid precipitate out. Precipitate was filtered, gently wash with cold methanol and dried. Yield - 1276 mg (80%). Selected IR data (KBr, ν_{max}/cm^{-1}): 2959 ($\nu_{sp3\ C\text{-}H}$), 1585 ($\nu_{C=N}$, imine), 1464 ($\nu_{C=C}$). UV–visible [DMF, λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$)]: 321.8 (14003.2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 4H), 7.15 (t, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 7.2 Hz, 4H), 6.56 (d, *J* = 4.9 Hz, 2H), 2.54 – 2.47 (m, 2H), 1.05 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.70, 146.03, 139.67, 138.78, 129.44, 129.11, 126.57, 99.61, 31.67, 20.13.

3.2 Synthesis of L2 = 2,6-bis(2-((E)-(1H-indol-3-yl)methylene)-1-phenylhydrazineyl)pyridine

To a methanolic solution of 2,6-bis(1-phenylhydrazineyl)pyridine (2 mmol, 582mg) in 15ml methanol a solution of indole-3-carboxaldehyde (4 mmol, 580mg) in 5ml methanol was added dropwise with constant stirring. Reaction mixture was stirred for next 4 hour a paleyellow colour solid precipitate out. Precipitate was filtered, gently wash with cold methanol and dried. Yield - 850 mg (78%). Selected IR data (KBr, ν_{max}/cm^{-1}): C2 = 1574 (C=N imine), 1436. UV–visible [DMF, λ_{max}/nm (ε/M−1cm^{-1})]: 440.18(1,881.50), 345.53(72,801.75), 281.56(32,359.37), 232.28(53,262.98). ^{1}H NMR (500 MHz,) δ 11.35 (d, J = 1.9 Hz, 2H), 8.29 (dd, J = 6.1, 2.4 Hz, 2H), 7.79 (t, J = 8.0 Hz, 1H), 7.52 (d, J = 3.1 Hz, 4H), 7.38 (dd, J = 6.2, 2.4 Hz, 2H), 7.25 (dd, J = 10.4, 4.7 Hz, 4H), 7.21 – 7.15 (m, 6H), 7.10 (d, J = 8.0 Hz, 2H), 6.96 – 6.92 (m, 4H). 13C NMR (126 MHz, DMSO) δ 156.60, 139.97, 139.51, 137.51, 136.52, 129.81, 129.66, 129.18, 127.04, 124.41, 122.89, 122.01, 120.80, 112.85, 112.27, 100.20.

3.3 Syntheses of (C1 and C2) complexes [Ni(II)(L1)Cl2] and [Ni(II)(L2)Cl2]

In a stirring solution of Ligand L1 and L2 (0.5 mmol in 10ml DCM) a solution of NiCl2.4H2O (0.5 mmol in 2 ml MeOH) was added drop wise to it. The instant colour change was observed from colourless to red orange in case of C1 and pale yellow to brown in case of C2. The reaction mixtures were stirred for next 8 hours at room temperature after that solvent was reduced under vacuum and complexes recrystalized by DCM-MeOH. Yield: C1 = 230 mg (87%), C2= 270 mg (80%). Solubility – DCM, MeOH, DMSO, DMF. Selected IR data (KBr, ν_{max}/cm^{-1}): for C1 = 2963 (sp^3 C-H), 1576 (C=N imine), 1453 and for C2 = 1571 (C=N imine), 1458. UV–visible [DMF, λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$)]: for C1 = 347.63 (42,933.36), 280.08 (44,440.26) and for C2 = 402.31 (20,972.15), 349.62 (34,188.97), 272.08 (26,371.42), 221.17 (64,067.26)

4. Characterization

4.1 Characterization of Ligand L1 (BmpPhe)

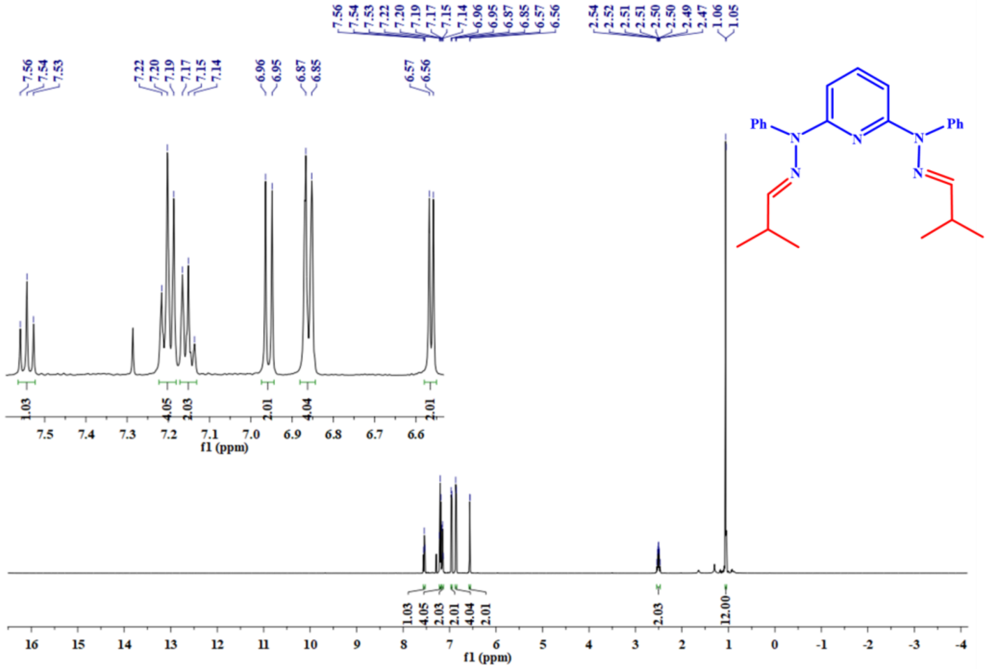


Figure S1- ^{1}H NMR spectrum of **L1**

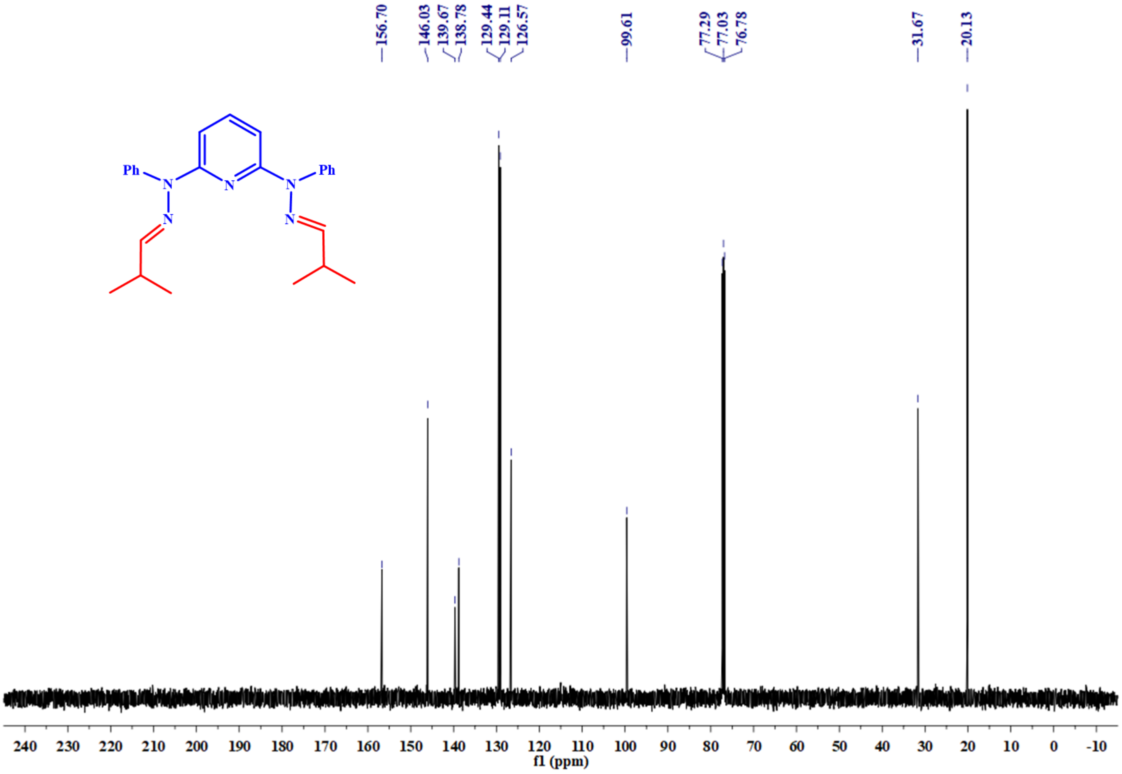


Figure S2 - ^{13}C NMR spectrum of **L1**

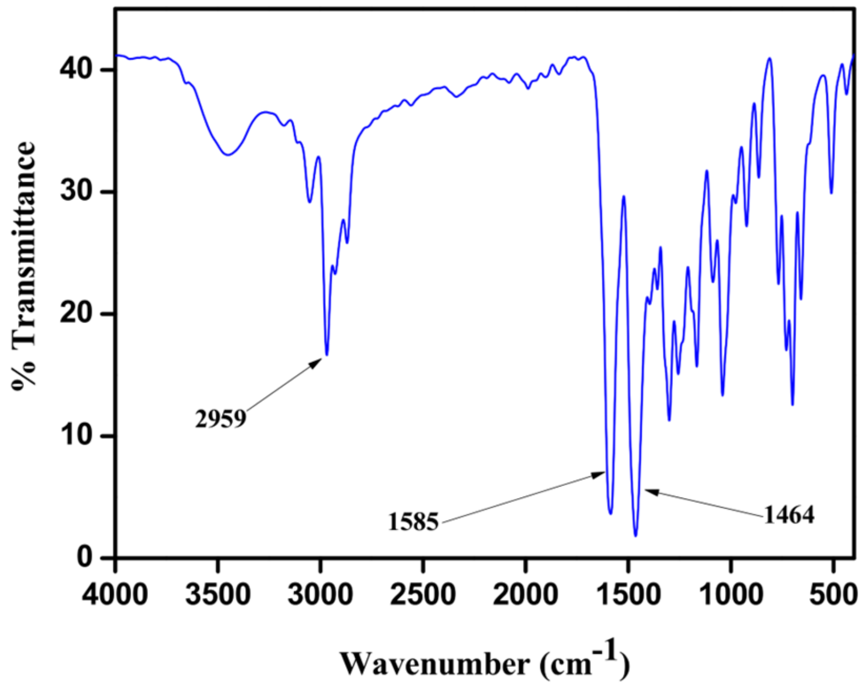


Figure S3 - IR spectrum of **L1**

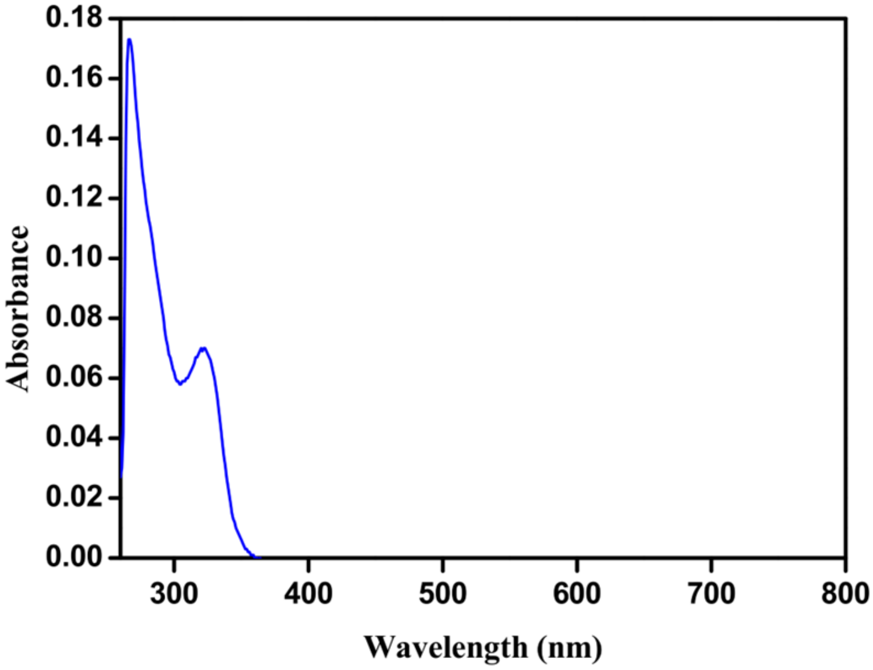
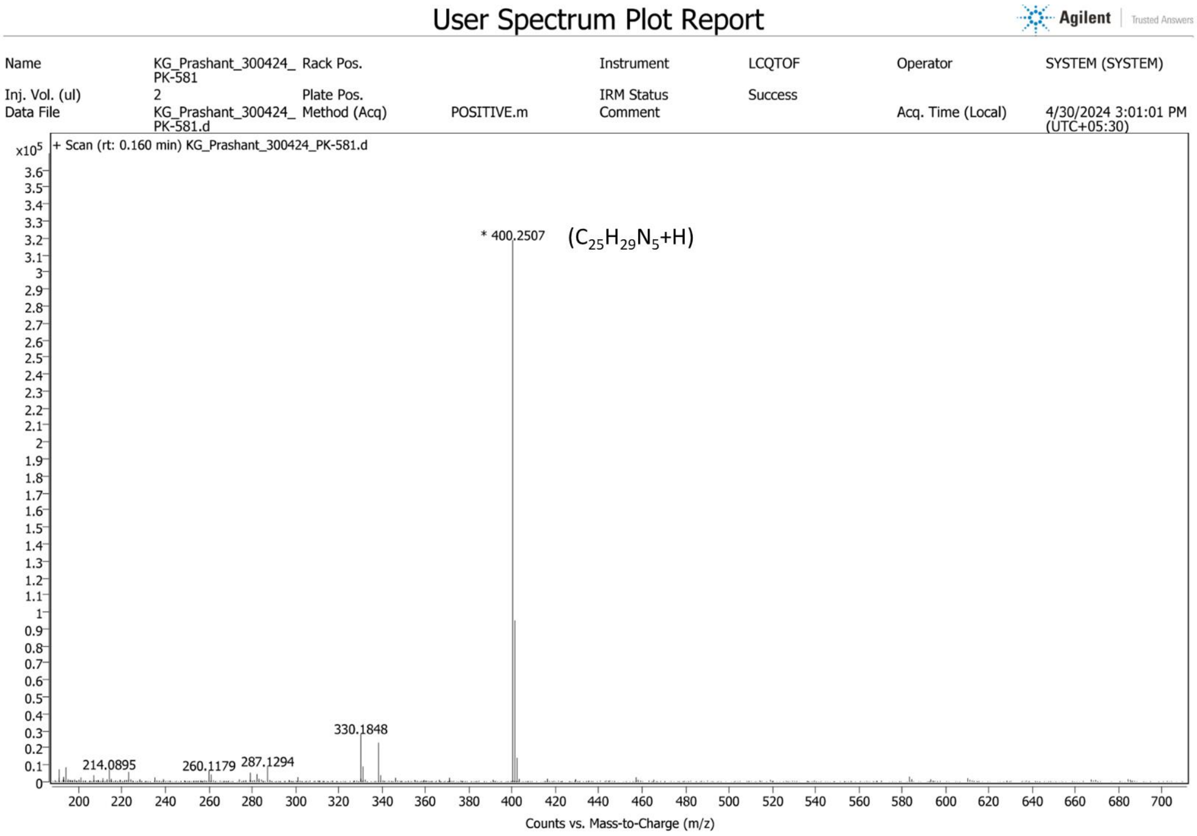


Figure S4 -UV visible spectrum of **L1**



User Spectrum Plot Report

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Figure S5 -HRMS spectrum of **L1**

4.2 Characterization of L2 (BimPhe)

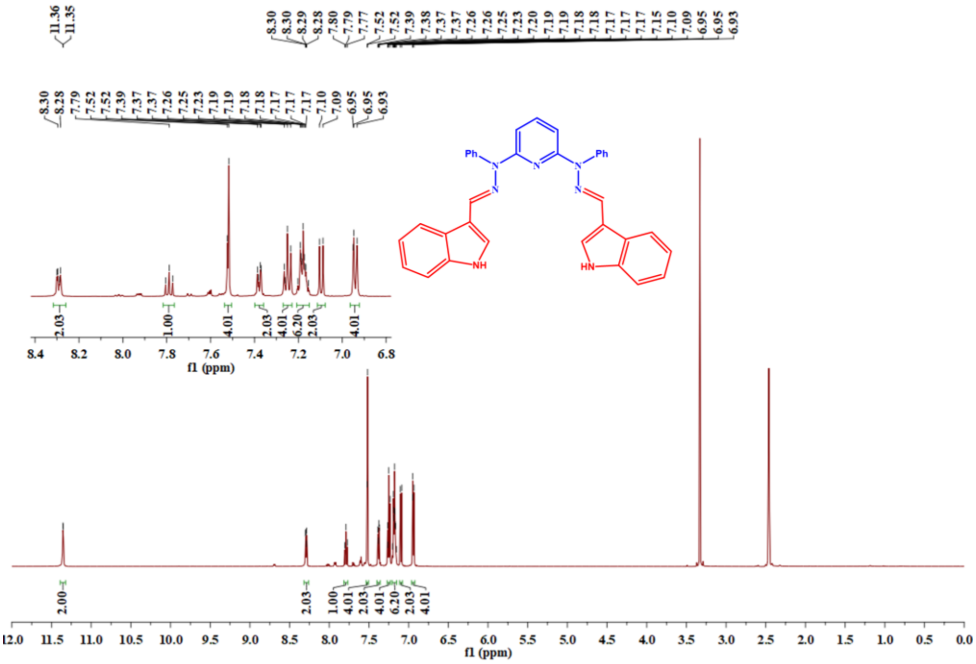


Figure S6 - ^{1}H NMR spectrum of **L2**

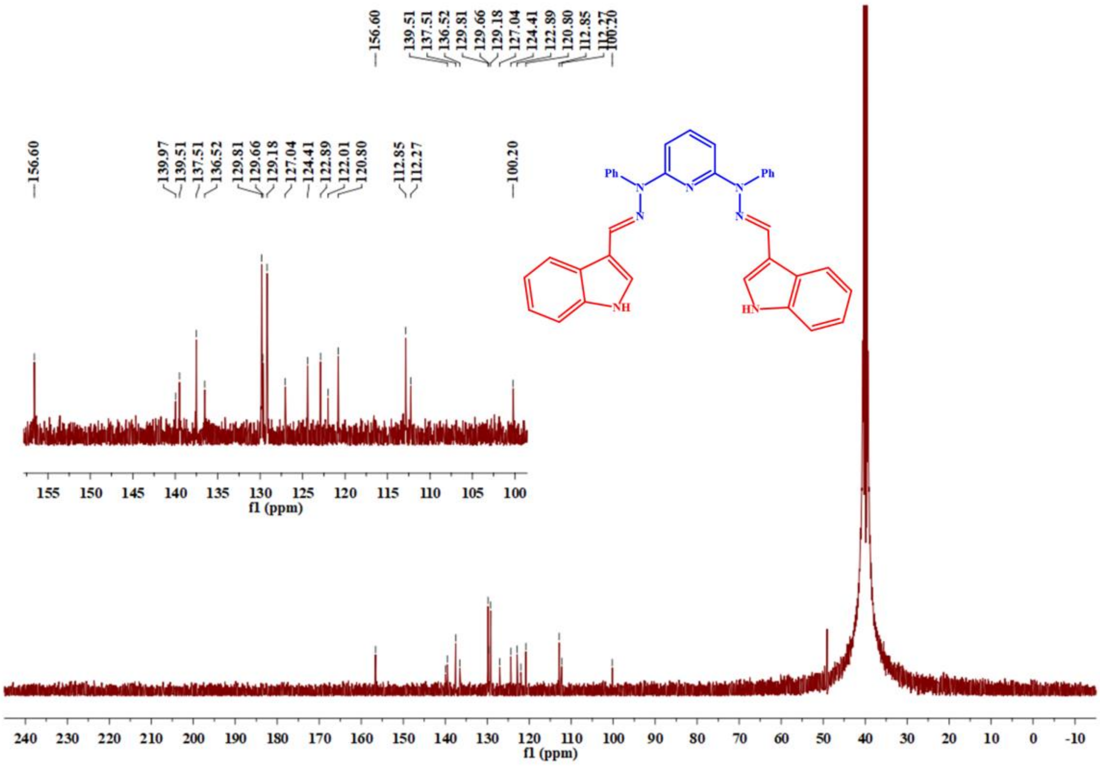


Figure S7 - ^{13}C NMR spectrum of **L2**

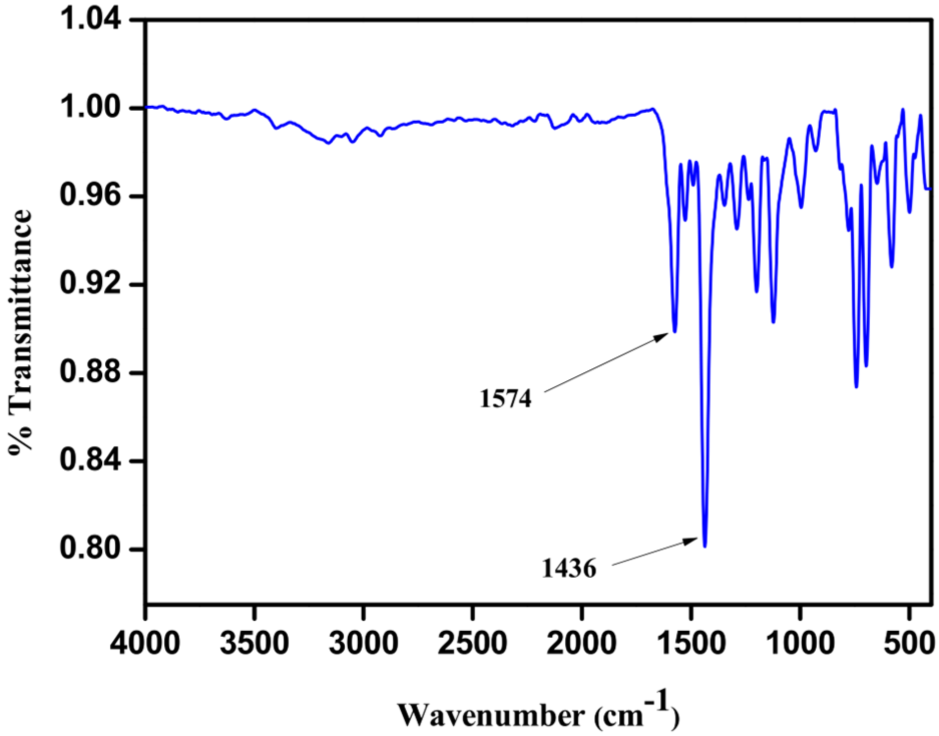
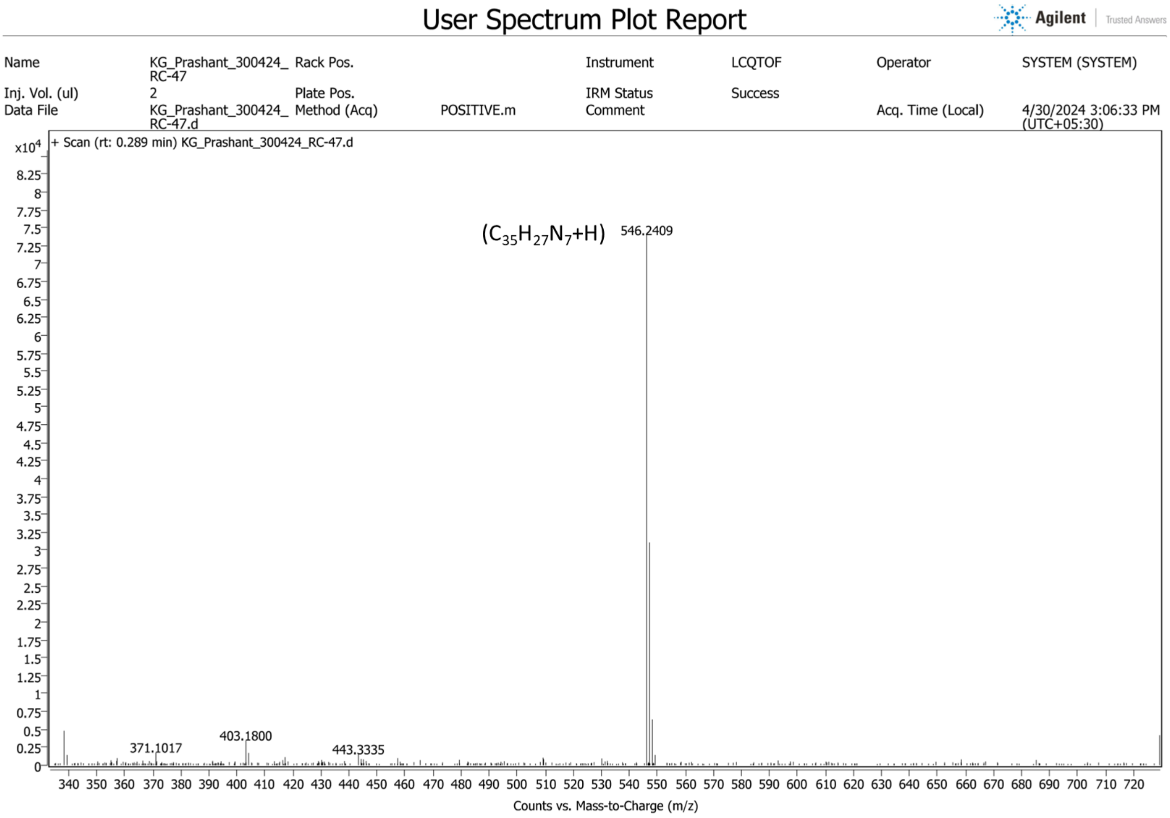


Figure S8 - IR spectrum of **L2**



User Spectrum Plot Report

Agilent Trusted Answers

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Figure S9 - HRMS spectrum of **L2**

4.3 Characterization of complexes C1 and C2

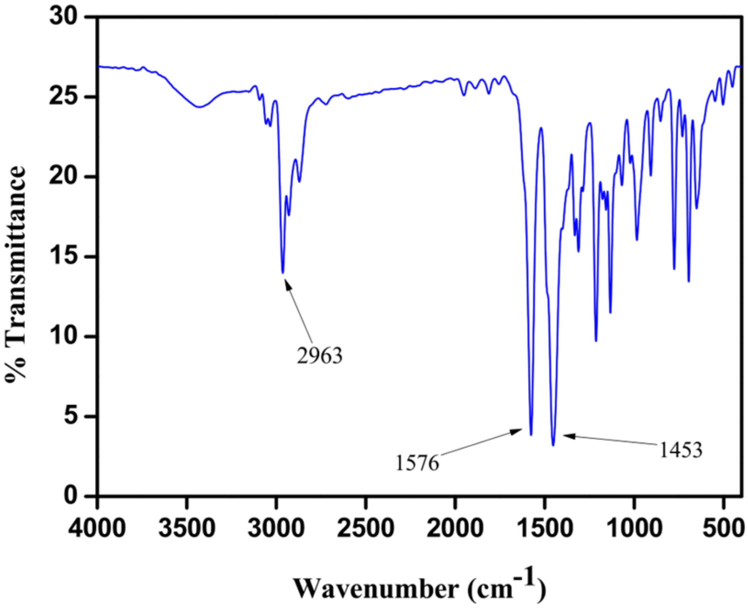


Figure S10 - IR spectrum of C1 = [Ni(II)(L1)Cl_2]

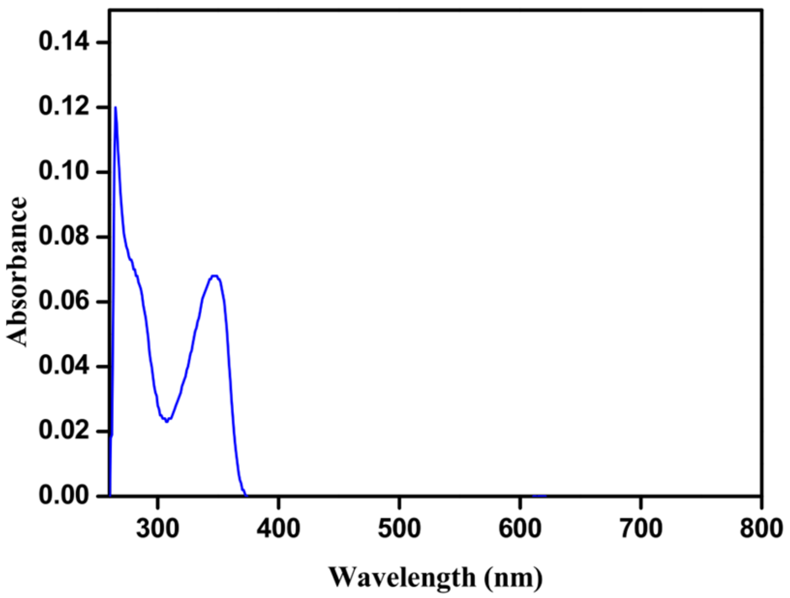
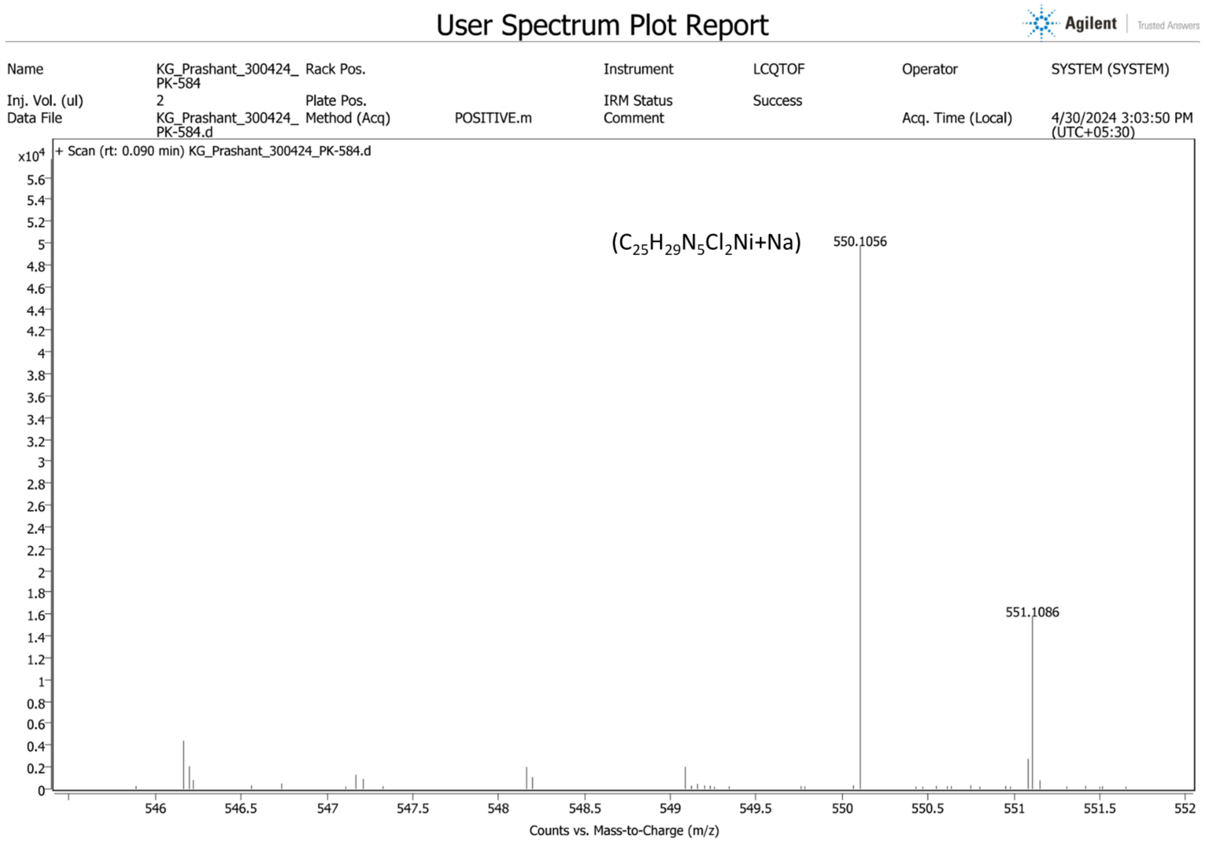


Figure S11 - UV visible spectrum of C1 = [Ni(II)(L1)Cl_2]


User Spectrum Plot Report

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($C_{25}H_{29}N_5Cl_2Ni$+Na)

Figure S12 – HRMS spectrum of C1 = [Ni(II)(L1)Cl_2]

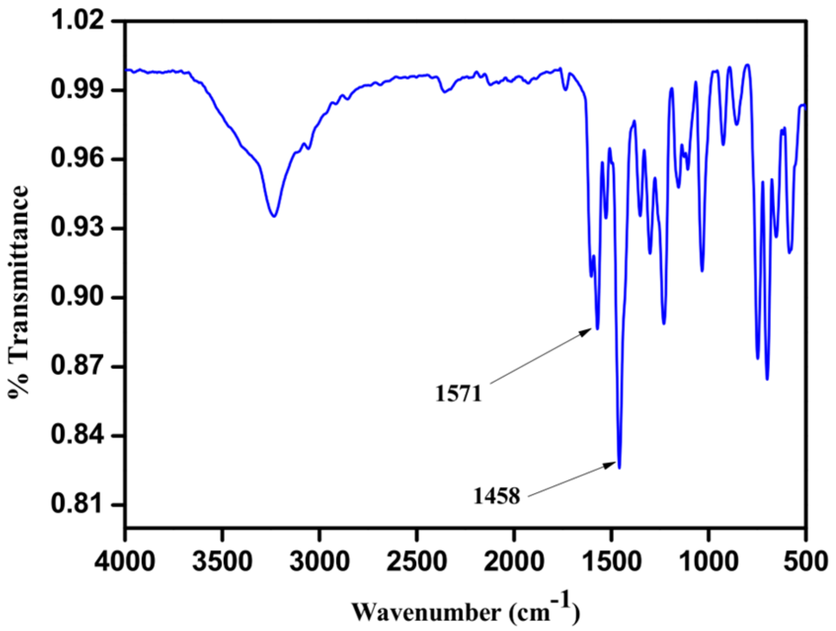


Figure S13 - IR spectrum of C2 = [Ni(II)(L2)Cl$_2$]

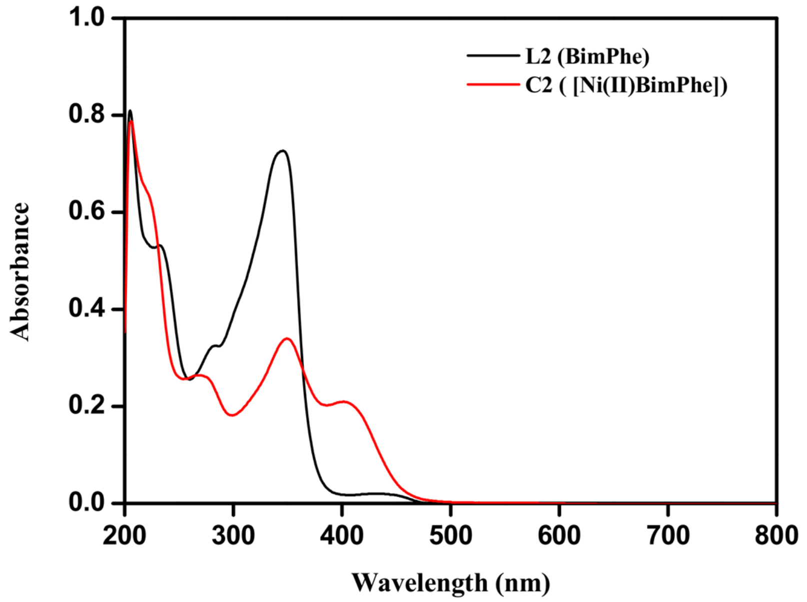


Figure S14 - UV visible spectrum of L2 and C2 = [Ni(II)(L2)Cl$_2$]

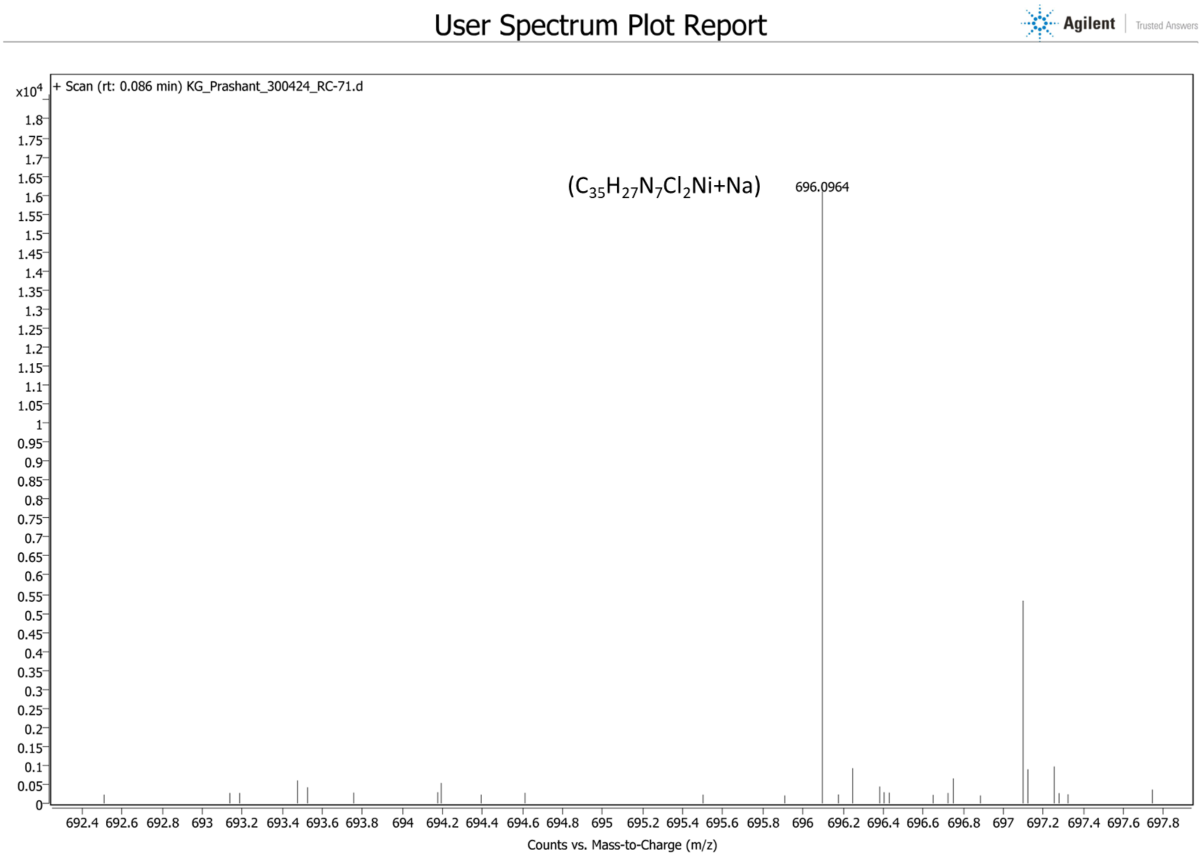


Figure S15 – HRMS spectrum of C2 = [Ni(II)(L2)Cl_2]

5. Single crystal XRD characterization

Identification	**C1 = [Ni(II)(L1)Cl_2]**	**C2 = [Ni(II)(L2)Cl_2]**
Empirical formula	$C_{25}H_{29}Cl_2N_5Ni$	$C_{35}H_{27}Cl_2N_7Ni$
Formula weight	529.14	675.24
Temperature/K	101.0	115.0
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$
a/Å	22.0346(10)	22.7783(11)
b/Å	9.1005(4)	12.1608(6)
c/Å	14.6912(6)	26.3729(12)
α/°	90	90
β/°	118.8650(10)	114.322(2)
γ/°	90	90
Volume/Å^3	2580.0(2)	6657.0(6)
Z	4	8
ρ_{calc}g/cm^3	1.362	1.347
μ/mm^{-1}	0.981	0.779

F(000)	1104.0	2784.0
Crystal size/mm^3	0.192 × 0.092 × 0.047	0.105 × 0.073 × 0.026
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.222 to 56.666	4.592 to 56.716
Index ranges	-29 ≤ h ≤ 29, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19	-30 ≤ h ≤ 30, -16 ≤ k ≤ 16, -35 ≤ l ≤ 35
Reflections collected	54268	244773
Independent reflections	3180 [R_{int} = 0.0563, R_{sigma} = 0.0233]	16576 [R_{int} = 0.0885, R_{sigma} = 0.0422]
Data/restraints/parameters	3180/0/153	16576/0/823
Goodness-of-fit on F^2	1.152	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0339, wR_2 = 0.0783	R_1 = 0.0515, wR_2 = 0.1242
Final R indexes [all data]	R_1 = 0.0355, wR_2 = 0.0791	R_1 = 0.0702, wR_2 = 0.1339
Largest diff. peak/hole / e Å^{-3}	0.61/-0.37	1.20/-0.61

Table S1 – Crystal data collections and refinement parameters for **C1 and C2**

5.1 Single crystal structure of C1 = [Ni(II)(L1)Cl$_2$]

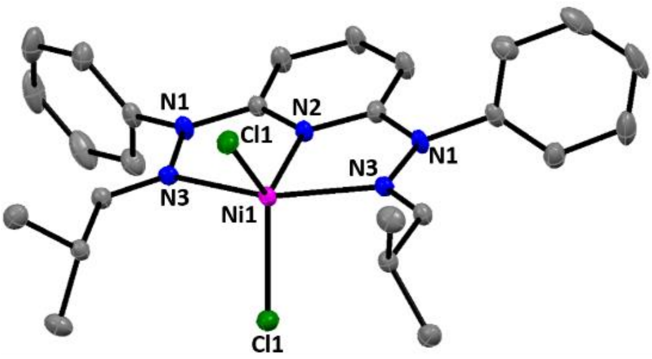


Figure S16 - ORTEP diagram (25% probability level) of C1 = [Ni(II)(L1)Cl2] hydrogen atoms connected to C atoms , anion and solvent molecule are omitted for clarity.

Bond	Bond angles (Å)	Bond	Bond length (Å)
Ni1 Cl1	2.2674(5)	N1 C1	1.439(2)
Ni1 N2	1.963(2)	N2 C7	1.341(2)
Ni1 N3	2.1590(15)	N3 C8	1.281(2)
N1 N3	1.402(2)		

Table S2 – Selected bond lengths of C1 = [Ni(II)(L1)Cl$_2$].

Bond (^{1}1-x,+y,3/2-z)	Bond angles (°)	Bond (^{1}1-x,+y,3/2-z)	Bond angles (°)
Cl1^1 Ni1 Cl1	124.72(3)	N3 Ni1 Cl1^1	94.71(4)
N2 Ni1 Cl1^1	117.640(14)	N3 Ni1 Cl1	96.81(4)
N2 Ni1 Cl1	117.639(14)	N3^1 Ni1N3	155.02(8)
N2 Ni1 N3^1	77.51(4)	C7^1 N2 Ni1	119.96(11)
N2 Ni1 N3	77.51(4)	C7 N2 Ni1	119.96(11)
N3^1 Ni1 Cl1	94.71(4)	N1 N3 Ni1	110.43(10)
N3^1 Ni1 Cl1^1	96.81(4)	C8 N3 Ni1	131.16(13)

Table S3 – Selected bond angles of C1 = [Ni(II)(L1)Cl_2].

5.2 Single crystal structure of C2 = [Ni(II)(L2)Cl2]

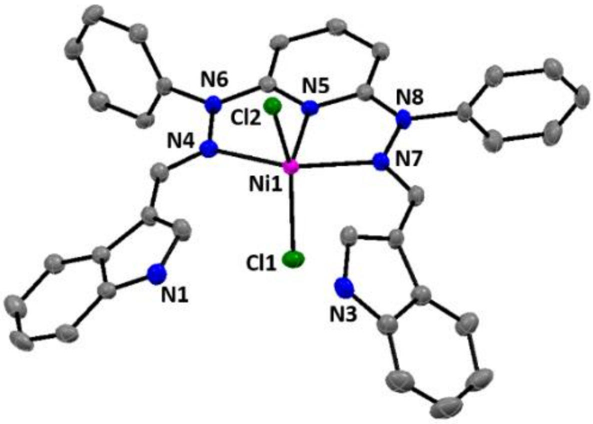


Figure S17 - ORTEP diagram (25% probability level) of C2 = [Ni(II)(L2)Cl_2] hydrogen atoms connected to C atoms , anion and solvent molecule are omitted for clarity.

Bond	Bond length (Å)	Bond	Bond length (Å)
Ni1 Cl1	2.2495(7)	N4 N6	1.400(3)
Ni1 Cl2	2.3256(7)	N4 C9	1.287(3)
Ni1 N4	2.104(2)	N7 N8	1.401(3)
Ni1 N5	1.939(2)	N7 C27	1.287(3)
Ni1 N7	2.109(2)		

Table S4 – Selected bond lengths of C2 = [Ni(II)(L2)Cl_2]

Bond	Bond angles (°)	Bond	Bond angles (°)
Cl1 Ni1 Cl2	144.74(3)	N7 Ni1 Cl1	93.34(6)
N4 Ni1 Cl1	95.38(6)	N7 Ni1 Cl2	93.72(6)

N4 Ni1 Cl2	90.88(6)	N6 N4 Ni1	109.82(15)
N4 Ni1N7	157.78(8)	C9 N4 Ni1	131.19(18)
N5 Ni1 Cl1	116.96(7)	C10 N5 Ni1	119.18(17)
N5 Ni1 Cl2	98.30(7)	C14 N5 Ni1	119.39(17)
N5 Ni1 N4	79.01(9)	N8 N7 Ni1	110.10(15)
N5 Ni1 N7	78.81(9)	C27 N7 Ni1	130.01(18)

Table S5 – Selected bond angles of C2 = [Ni(II)(L2)Cl_2]

5.3. DFT calculations

To acquire a better understanding of the electronic structure of the complexes, DFT simulations were performed. Gauss-view software was used to obtain Molecular orbital diagrams (MOs) and calculate the HOMO-LUMO energy gap for the complexes **C1** and **C2**. (shown in Figure 5). The Multwfn software was used to compute the percentage distribution of atoms to every MO.[59] The energy gap between HOMO and LUMO of complex **C1** was found to be 4.365 eV for the α-spin state, and 3.788 eV for the β-spin state, whereas, for complex **C2**, this energy gap was found to be 3.611 eV for the α-spin state and 3.081 eV for the β-spin state. In the gaseous state, the HOMO (124) of complex **C1** had (α- 0.002% and β- 0.015%) of nickel character and (α- 99.99% and β- 99.98%) ligand character. However, complex **C2** had (α- 0.37% and β- 0.73%) nickel character and (α- 99.6% and β- 99.3%) ligand character. According to the percentage contribution of several groups/ moieties in MOs. In LUMO of **C1**, the distribution is exclusively ligand (α- 98% and β- 17.7%) character, only (α- 1.54 % and β- 82.3%) character existed on the nickel centre. In the case of **C2**, the distribution is exclusively ligand (α- 98% and β- 28.4%) character, only (α- 1.97 % and β- 71.6%) character existed on the nickel centre.

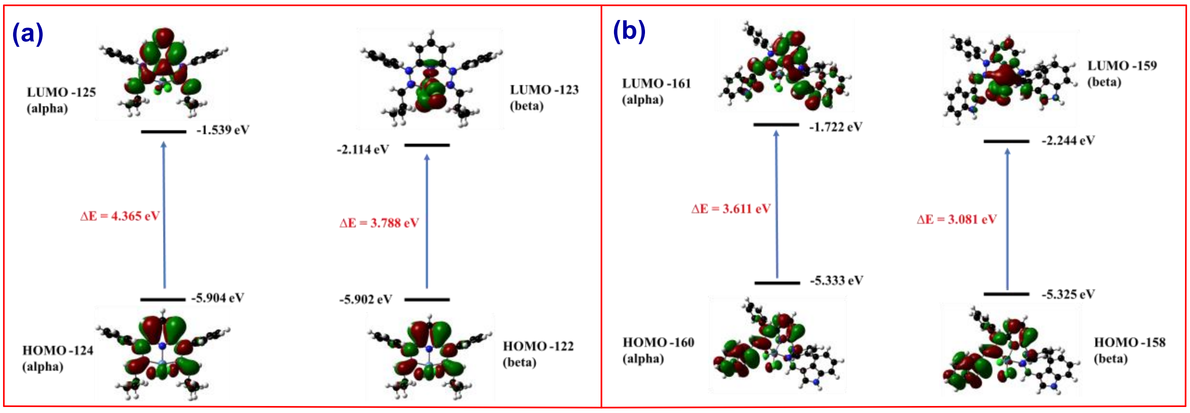
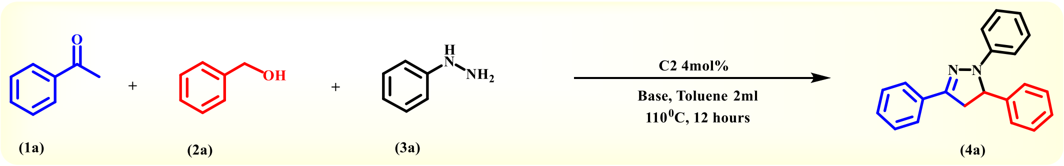


Figure S18. HOMO and LUMO energy representation of C1 (a) and C2 (b)

6. Optimization of reaction conditions

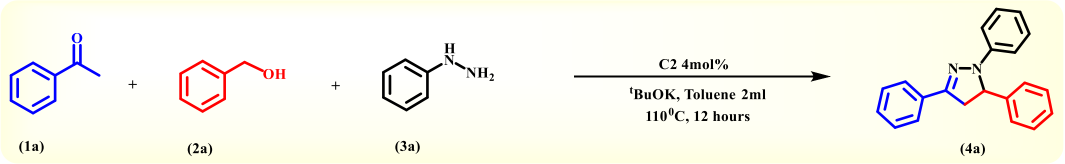
6.1. Optimization of base



Entry	Catalyst (C1 or C2) mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	-	^{t}BuOK 1.0eq	110	Toluene	12	NR
2	L1 or L2	^{t}BuOK 1eq	110	Toluene	12	NR
3	$NiCl_2.4H_2O$	^{t}BuOK 1eq	110	Toluene	12	NR
4	C1 4 mol%	^{t}BuOK 1.0eq	110	Toluene	12	82
2	C2 4 mol%	^{t}BuOK 1.0eq	110	Toluene	12	88
3	C2 4 mol%	KOH 1.0eq	110	Toluene	12	79
4	C2 4 mol%	NaOH 1.0eq	110	Toluene	12	72
5	C2 4 mol%	Cs_2CO_3 1.0eq	110	Toluene	12	66
6	C2 4 mol%	Na_2CO_3 1.0eq	110	Toluene	12	NR
7	C2 4 mol%	K_2CO_3 1.0eq	110	Toluene	12	NR
8	C2 4 mol%	$NaHCO_3$ 1.0eq	110	Toluene	12	NR

Reaction conditions and stoichiometry: benzyl alcohol (1a) (0.5 mmol), acetophenone (2a) (0.5 mmol), and phenylhydrazine (3a) (0.6 mmol); temperature 110 °C; base: 1.0 equivalent, solvent: Toluene 2ml, catalyst 4mol% and time 12 hours. Isolated yields after column chromatography.

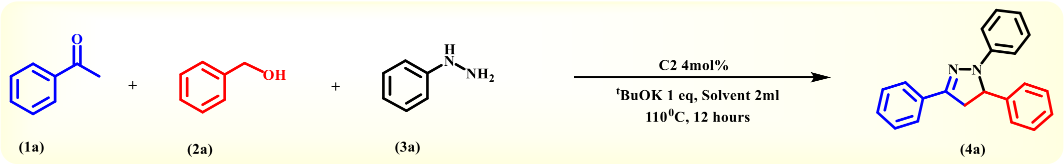
6.2. Optimization of base equivalent



Entry	Catalyst (C2) mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	4 mol%	^{t}BuOK .5eq	110	Toluene	12	55
2	4 mol%	^{t}BuOK 1eq	110	Toluene	12	88
3	4 mol%	^{t}BuOK 1.5eq	110	Toluene	12	88
4	4 mol%	^{t}BuOK 2eq	110	Toluene	12	88

Reaction conditions and stoichiometry: benzyl alcohol (1a) (0.5 mmol), acetophenone (2a) (0.5 mmol), and phenylhydrazine (3a) (0.6 mmol); temperature 110 °C; ^{t}BuOK: 0.5- 2.0 equivalent, solvent: Toluene 2ml, catalyst 4mol% and time 12 hours. Isolated yields after column chromatography.

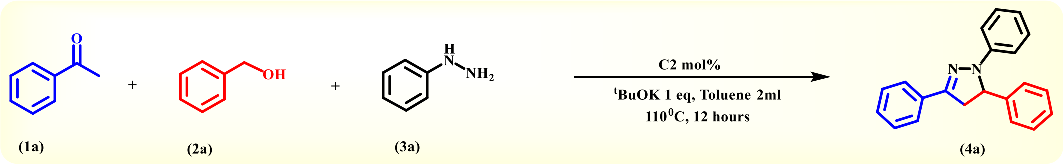
6.3. Optimization of solvent



Entry	Catalyst (C2) mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	4 mol%	^{t}BuOK 1eq	110	Toluene	12	88
2	4 mol%	^{t}BuOK 1eq	110	Xylene	12	70
3	4 mol%	^{t}BuOK 1eq	110	Benzene	12	65
4	4 mol%	^{t}BuOK 1eq	110	DMF	12	NR
5	4 mol%	^{t}BuOK 1eq	110	DMDO	12	NR
6	4 mol%	^{t}BuOK 1eq	110	t-amyl alcohol	12	NR
7	4 mol%	^{t}BuOK 1eq	110	1,4-dioxane	12	20%

Reaction conditions and stoichiometry: benzyl alcohol (1a) (0.5 mmol), acetophenone (2a) (0.5 mmol), and phenylhydrazine (3a) (0.6 mmol); temperature 110 °C; ^{t}BuOK: 1.0 equivalent, solvent 2ml, catalyst 4mol% and time 12 hours. Isolated yields after column chromatography.

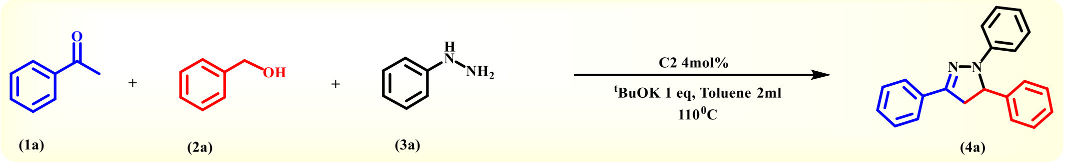
6.4. Optimization of catalyst mol%



Entry	Catalyst mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	2 mol%	^{t}BuOK 1eq	110	Toluene	12	52
2	3 mol%	^{t}BuOK 1eq	110	Toluene	12	64
3	4 mol%	^{t}BuOK 1eq	110	Toluene	12	88
4	5 mol%	^{t}BuOK 1eq	110	Toluene	12	88

Reaction conditions and stoichiometry: benzyl alcohol (1a) (0.5 mmol), acetophenone (2a) (0.5 mmol), and phenylhydrazine (3a) (0.6 mmol); temperature 110 °C; base: 1.0 equivalent, solvent: Toluene 2ml, Catalyst mol% 2-5 and time 12 hours. Isolated yields after column chromatography.

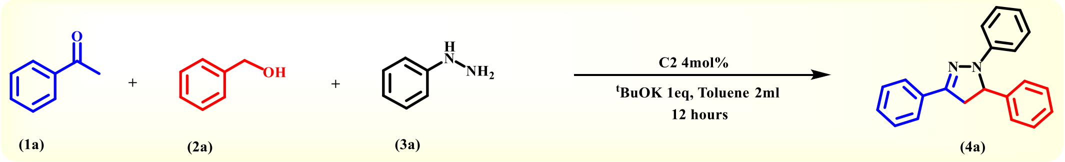
6.5. Optimization of time



Entry	Catalyst mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	4 mol%	^{t}BuOK 1eq	110	Toluene	8	61
2	4 mol%	^{t}BuOK 1eq	110	Toluene	10	75
3	4 mol%	^{t}BuOK 1eq	110	Toluene	12	88
4	4 mol%	^{t}BuOK 1eq	110	Toluene	14	88

Reaction conditions and stoichiometry: benzyl alcohol (1a) (0.5 mmol), acetophenone (2a) (0.5 mmol), and phenylhydrazine (3a) (0.6 mmol); temperature 110 °C; base: 1.0 equivalent, solvent: Toluene 2ml, Catalyst 4 mol% and time 8-12 hours. Isolated yields after column chromatography.

6.6. Optimization of temperature

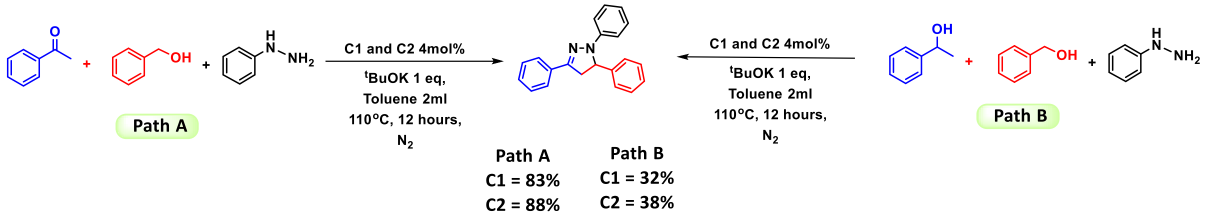


Entry	Catalyst mol%	Base	Temp. (°c)	Solvent	Time (hrs)	Yield (%)
1	4 mol%	^{t}BuOK 1eq	90	Toluene	12	68
2	4 mol%	^{t}BuOK 1eq	100	Toluene	12	76
3	4 mol%	^{t}BuOK 1eq	110	Toluene	12	88
4	4 mol%	^{t}BuOK 1eq	120	Toluene	12	88

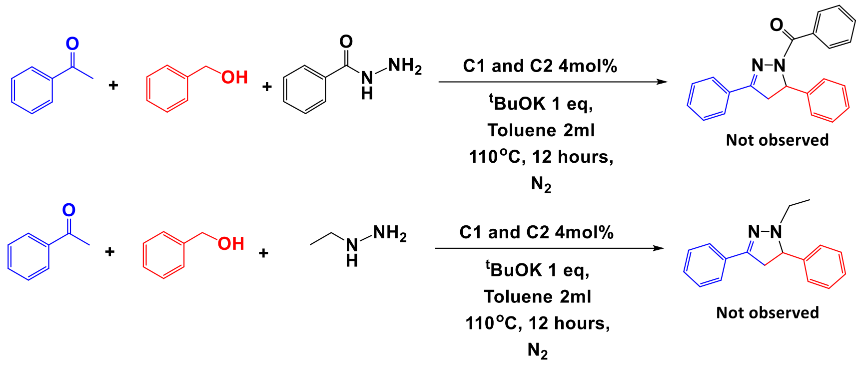
Reaction conditions and stoichiometry: benzyl alcohol (1a) (0.5 mmol), acetophenone (2a) (0.5 mmol), and phenylhydrazine (3a) (0.6 mmol); temperature 90-110 °C; base: 1.0 equivalent, solvent: Toluene 2ml, Catalyst 4 mol% and time 12 hours. Isolated yields after column chromatography.

6.7. Optimization of substrates

We have also performed reaction with secondary alcohol and it has been found out that aromatic ketones providing much better results than secondary alcohols. Utilizing 1-phenylethanol in the place of acetophenone with benzyl alcohol with phenyl hydrazine catalyst C1 provides 32% and C2 provides 38% yield of the respective pyrazoline derivative.



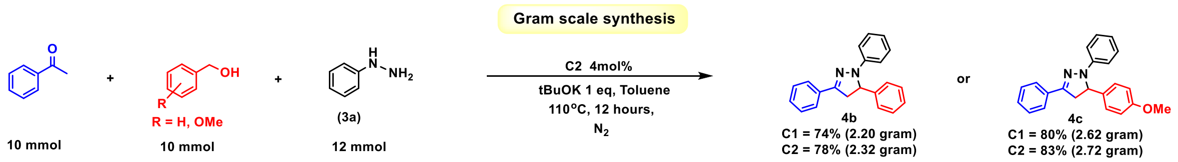
we have performed a reaction utilizing alkylhydrazines and hydarazide in place of phenylhydrazine. It has been observed that benzhydarazide is incompatible for current methodology and we did not observe the formation of the respective pyrazoline derivative.



6.7. General procedure for MCS of pyrazolines

In a clean and dried 20 ml pressure tube filled with benzyl alcohol derivative (0.5 mmol), acetophenone derivative (0.5 mmol), phenylhydrazine (0.5 mmol), ^{t}BuOK (1.0 equivalent) and catalyst (C1 or C2 4.0 mol%). The charged vial was filled with 2.0 mL of toluene and innert atmosphere was created by purging N_2 to reaction tube. The reaction mixture was heated in an oil bath at 110°C for next 12 hours. TLC was used to track the reaction's completion and ethyl acetate (4 × 5 mL) was used to extract the reaction mixture. After being dried over anhydrous Na_2SO_4, the resultant organic layer of ethyl acetate was concentrated under reduced pressure. Hexane/ethyl acetate was used as an eluent in column chromatography on silica (100–200 mesh size) to purify the resultant organic mixture. ^{1}H and ^{13}C NMR spectroscopy were used to characterize the isolated products.

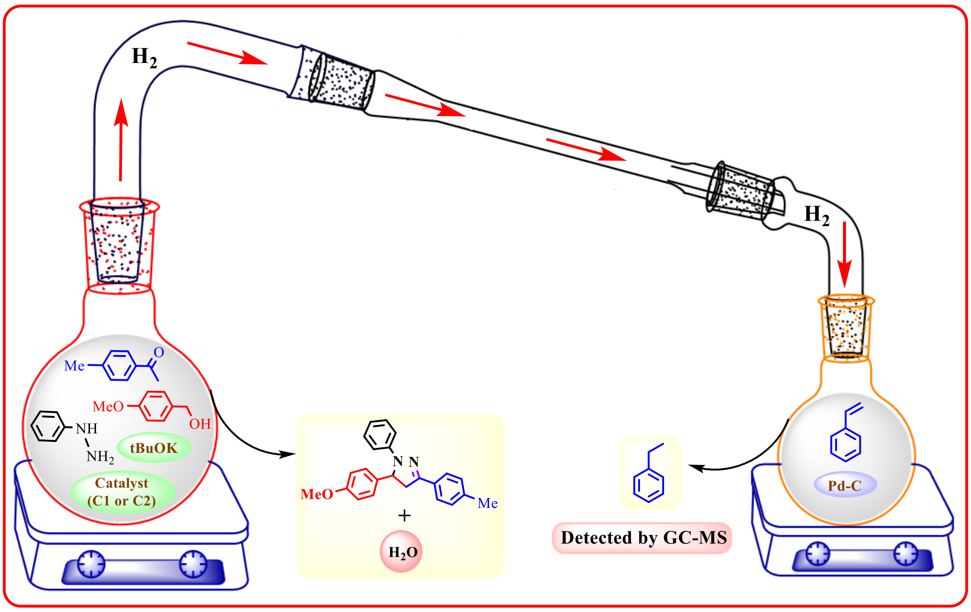
6.8. Gram Scale synthesis



In a clean and dried 20 ml pressure tube filled with benzyl alcohol derivative (10 mmol), acetophenone derivative (10 mmol), phenylhydrazine (12 mmol), ^{t}BuOK (1.0 equivalent) and catalyst (C1 or C2 4.0 mol%). The charged vial was filled with 30 mL of toluene and inert atmosphere was created by purging N_2 to reaction tube. The reaction mixture was heated in an oil bath at 110°C for next 12 hours.

7. Characterization of intermediates and side product (H_2) by GC-MS

7.1 Detection of H_2 via styrene reduction in presence of 10% Pd-C



In a round bottom 20 ml flask 4-methyl acetophenone (2.0 mmol), 4-methoxy benzyl alcohol (2.0 mmol), Phenylhydrazine (2.0 mmol), tBuOK (1.0 equivalent) and catalyst (C1 or C2, 4 mol%) were taken in 8 ml toluene. This round bottom flask then connected to another round bottom flask having styrene (2.0 mmol) with 10% Pd-C in 10 ml THF by a U-shaped glass pipeline then sealed. First round bottom flask heated at 110°c and second one is stirred at room temperature for next 12 hours. The H_2 liberated from first round bottom flask reached to second round bottom flask through U-shaped pipeline. In presence of Pd-C reduction of styrene to ethylbenzene by H_2 was detected by GC-MS confirms the formation of H_2 during catalytic cycle.

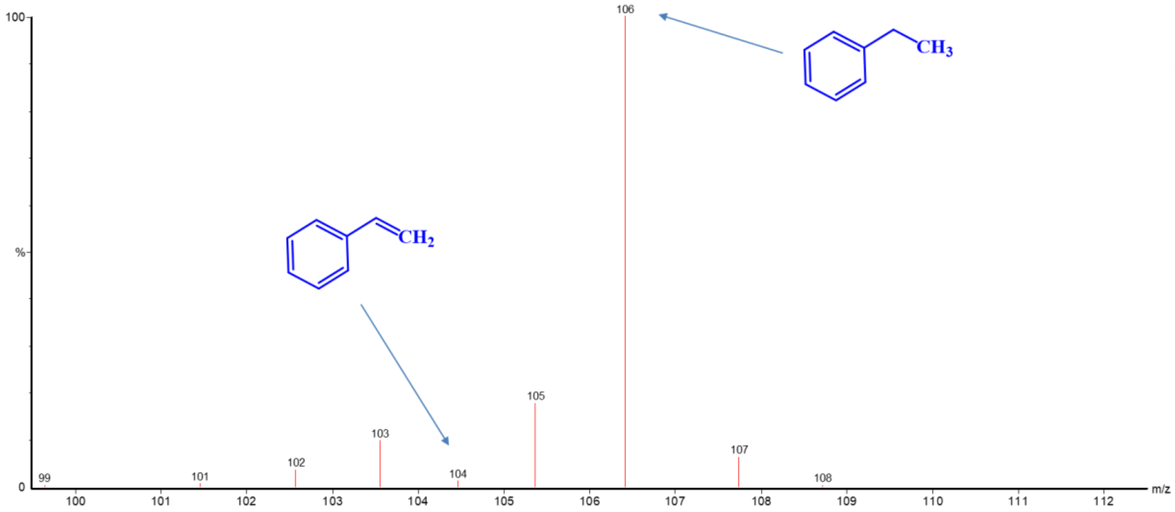


Figure S19 GC–MS spectrum of Styrene and ethyl benzene

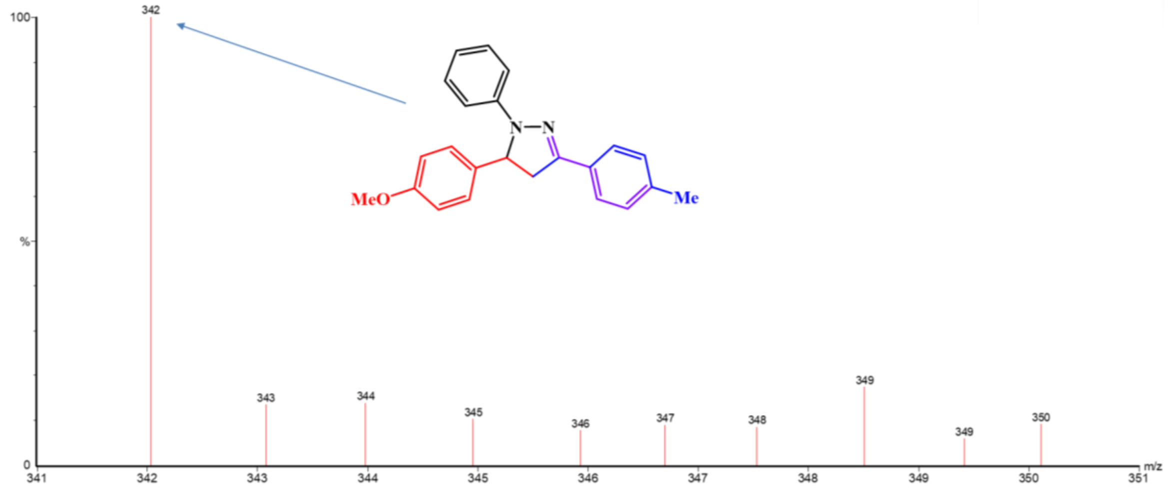


Figure S20 GC–MS spectrum of 5-(4-methoxyphenyl)-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole

7.2 Detection of in-situ formed alpha-beta unsaturated carbonyl compound

In a 10 ml pressure tube 4-methyl acetophenone (1.0 mmol), 4-methoxy benzyl alcohol (1.0 mmol), Phenylhydrazine (1.0 mmol), tBuOK (1.0 equivalent) and catalyst (C1 or C2, 4 mol%) were taken in 5 ml toluene under inert atmosphere of N_2. Tube was sealed, heated at 110^{o}c for next 4 hours after that reaction mixture was cooled at room temperature extracted with ethyl acetate and water. Formation of a-b unsaturated carbonyl compound ((E)-3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one) was then detected by GC-MS analysis.

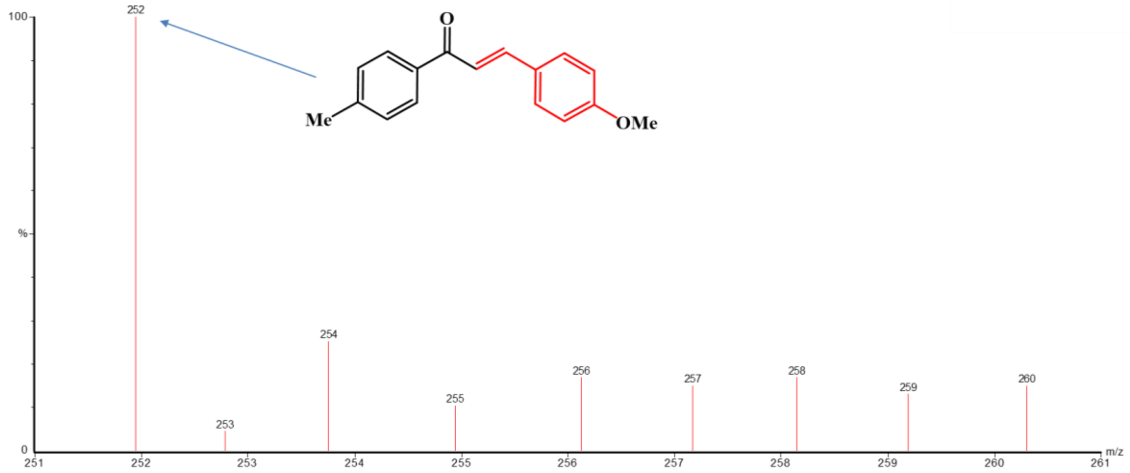


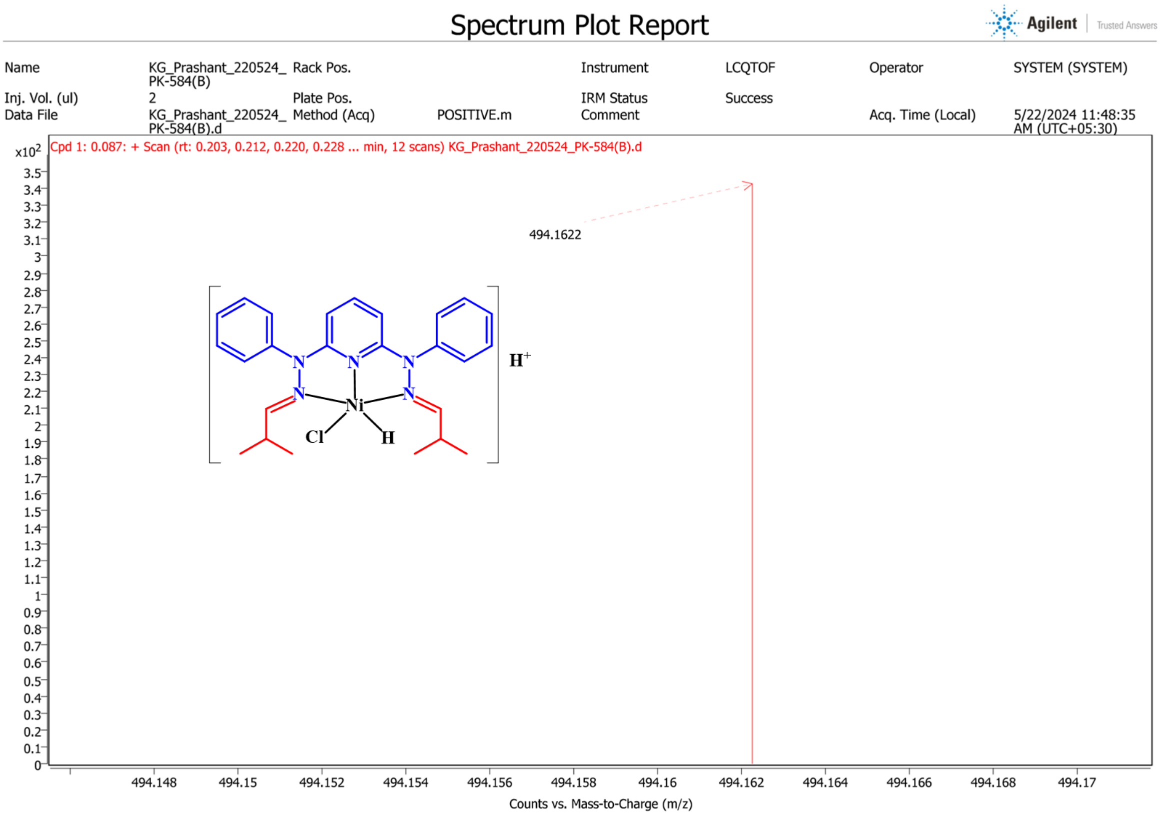
Figure S21 GC–MS spectrum of (E)-3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one

7.3 Detection of Ni-H and Ni-alkoxy intermediates during catalysis

In a 10 ml pressure tube benzyl alcohol (1.0 mmol), tBuOK (0.5 equivalent), C1 or C2 (4mol%) was taken in 2 ml dry toluene. The pressure tube was then heated at 110^o C for next 3 hours. Cool the reaction mixture at room temperature and Reaction mixture was analysed by HRMS study. All the nickel-hydride and nickel-alkoxy intermediate formed by the reaction of catalysts C1 and C2 with benzyl alcohol are detected by HRMS. All experimental and calculated m/z values are shown in the table below

Intermediates	Experimental m/z value	calculated m/z value
[(L1)Ni(Cl)(H)]+H$^+$	494.1622	494.1616
[(L1)Ni(Cl)(OCH$_2$Ph)]+H$^+$	600.2212	600.2035
[(L2)Ni(Cl)(H)]+H$^+$	640.1545	640.1521
[(L2)Ni(Cl)(OCH$_2$Ph)]	745.1914	745.1867

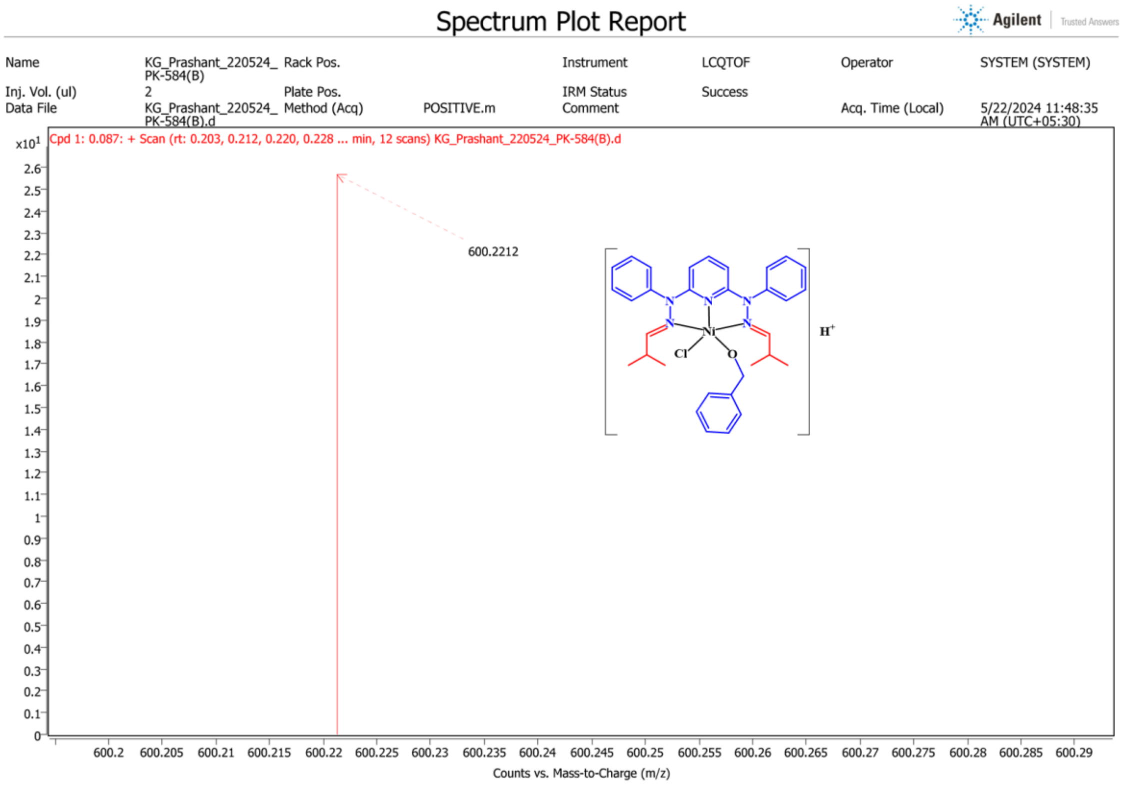
Table S6 – Experimental and calculated m/z value for the intermediates


Spectrum Plot Report

Name KG_Prashant_220524_PK-584(B)
Rack Pos.
Instrument LCQTOF
Operator SYSTEM (SYSTEM)
Inj. Vol. (ul) 2
Plate Pos.
IRM Status Success
Data File KG_Prashant_220524_PK-584(B).d
Method (Acq) POSITIVE.m
Comment
Acq. Time (Local) 5/22/2024 11:48:35 AM (UTC+05:30)

Cpd 1: 0.087: + Scan (rt: 0.203, 0.212, 0.220, 0.228 ... min, 12 scans) KG_Prashant_220524_PK-584(B).d

Figure S22 HRMS spectrum [(L1)Ni(Cl)(H)]+H$^+$



Spectrum Plot Report

Name KG_Prashant_220524_PK-584(B)
Rack Pos.
Instrument LCQTOF
Operator SYSTEM (SYSTEM)
Inj. Vol. (ul) 2
Plate Pos.
IRM Status Success
Data File KG_Prashant_220524_PK-584(B).d
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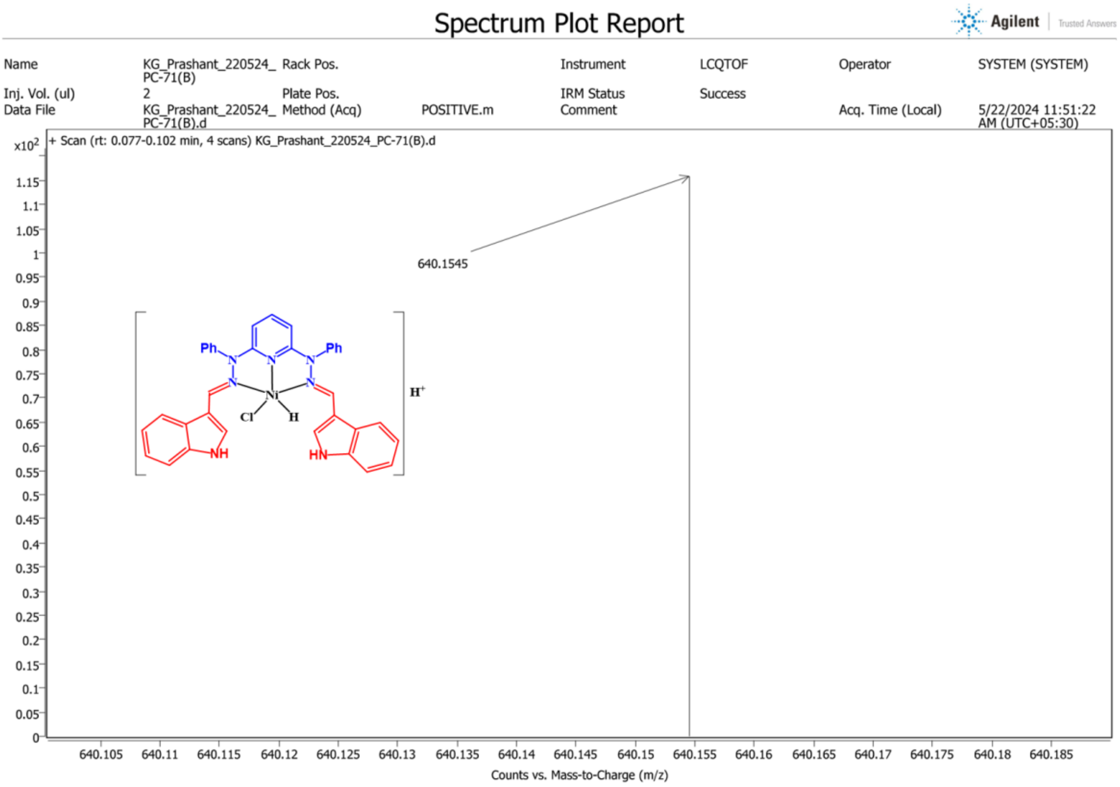
Comment
Acq. Time (Local) 5/22/2024 11:48:35 AM (UTC+05:30)

Cpd 1: 0.087: + Scan (rt: 0.203, 0.212, 0.220, 0.228 ... min, 12 scans) KG_Prashant_220524_PK-584(B).d

Figure S23 HRMS spectrum [(L1)Ni(Cl)(OCH$_2$Ph)]+H$^+$

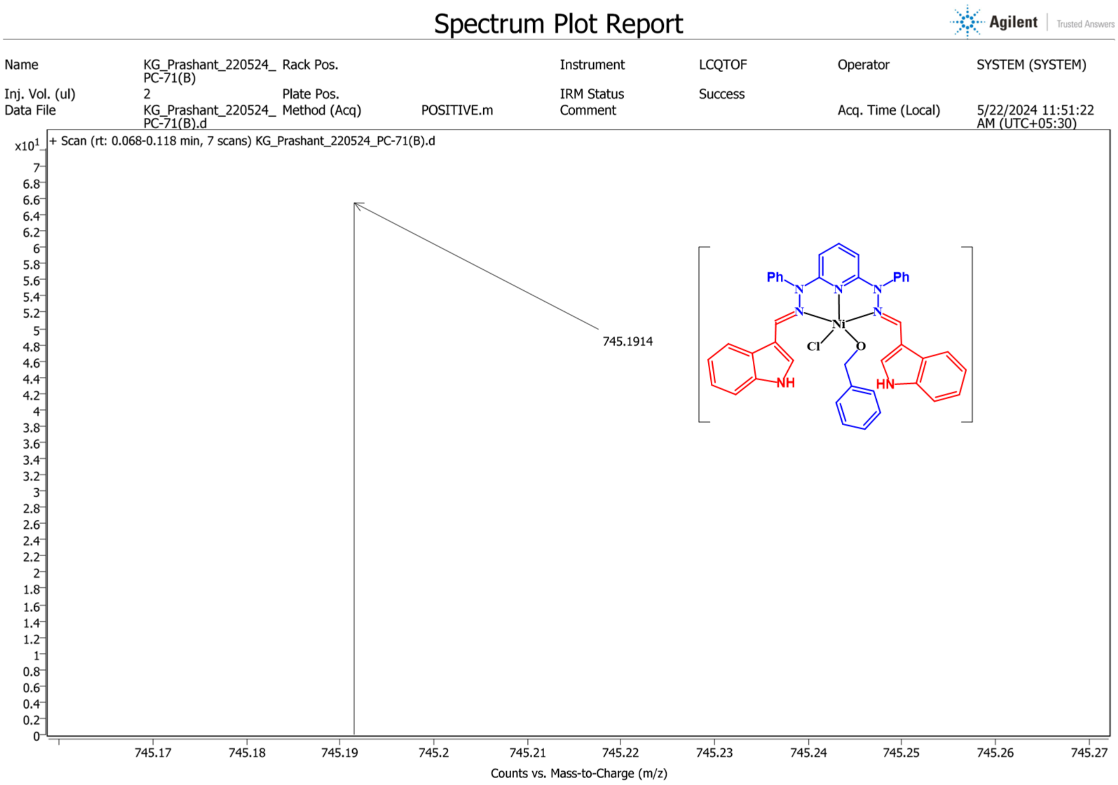


Spectrum Plot Report

Name KG_Prashant_220524_PC-71(B)
Rack Pos.
Instrument LCQTOF
Operator SYSTEM (SYSTEM)
Inj. Vol. (ul) 2
Plate Pos.
IRM Status Success
Data File KG_Prashant_220524_PC-71(B).d
Method (Acq) POSITIVE.m
Comment
Acq. Time (Local) 5/22/2024 11:51:22 AM (UTC+05:30)

+ Scan (rt: 0.077-0.102 min, 4 scans) KG_Prashant_220524_PC-71(B).d

Figure S24 HRMS spectrum [(L2)Ni(Cl)(H)]+H$^+$

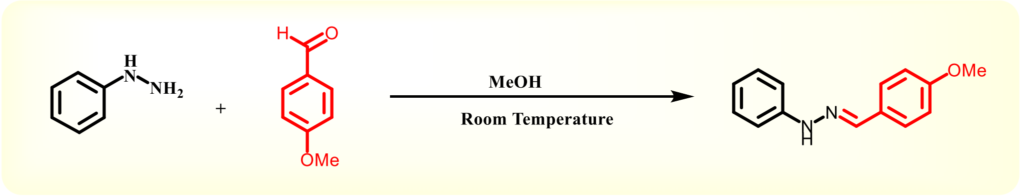


Spectrum Plot Report

Name	KG_Prashant_220524_ PC-71(B)	Rack Pos.		Instrument	LCQTOF	Operator	SYSTEM (SYSTEM)
Inj. Vol. (ul)	2	Plate Pos.		IRM Status	Success		
Data File	KG_Prashant_220524_ PC-71(B).d	Method (Acq)	POSITIVE.m	Comment		Acq. Time (Local)	5/22/2024 11:51:22 AM (UTC+05:30)

Figure S25 HRMS spectrum [(L2)Ni(Cl)(OCH_2Ph)]

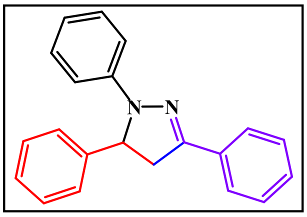
7.4 Synthesis of (E)-1-(4-methoxybenzylidene)-2-phenylhydrazine



To a methanolic solution of Phenylhydrazine (2 mmol, 216 mg) in 10 ml dry methanol 4-methoxybenzaldehyde (2 mmol, 272mg) was added dropwise with constant stirring. Reaction mixture was stirred for next 30 minute a white solid precipitate out. Precipitate was filtered, gently wash with cold methanol and dried. Yield - 389 mg (86%). ^{1}NMR (500 MHz) δ 7.61 – 7.57 (m, 2H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.12 – 7.09 (m, 2H), 6.93 – 6.87 (m, 3H), 3.82 (s, 3H). ^{13}C NMR (126 MHz) δ 160.08, 145.12, 137.62, 129.42, 128.29, 127.72, 119.86, 114.24, 112.77, 55.43.

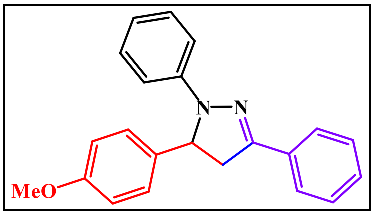
8.0. ^{1}H, ^{13}C and ^{19}F NMR characterization of products.

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



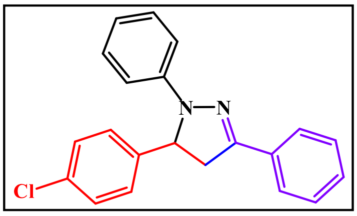
Yield: C1 = 124mg (83%) and C2 = 133mg (88%). ^{1}**NMR (500 MHz)** δ 7.72 (dt, *J* = 8.2, 1.7 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.35 – 7.30 (m, 5H), 7.26 (ddt, *J* = 7.0, 3.8, 1.7 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.07 (ddd, *J* = 4.1, 3.2, 1.7 Hz, 2H), 6.78 (tt, *J* = 7.3, 1.1 Hz, 2H), 5.27 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.84 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.14 (dd, *J* = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 146.80, 144.92, 142.67, 132.81, 129.25, 129.01, 128.70, 128.65, 127.67, 125.97, 125.83, 119.17, 113.44, 64.56, 43.66.

5-(4-methoxyphenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (4b)



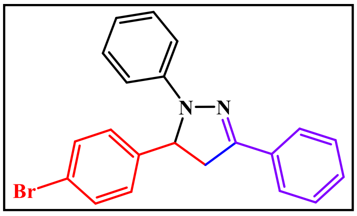
Yield: C1 = 144mg (88%), C2 = 151 mg (92%). ^{1}**NMR (500 MHz)** δ 7.75 – 7.72 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.26 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 7.12 – 7.08 (m, 2H), 6.88 – 6.85 (m, 2H), 6.81 – 6.77 (m, 1H), 5.23 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.81 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.78 (s, 3H), 3.12 (dd, *J* = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 159.06, 146.82, 144.98, 134.76, 132.92, 129.00, 128.65, 127.16, 125.82, 119.15, 114.58, 113.51, 64.09, 55.37, 43.71.

5-(4-chlorophenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (4c)



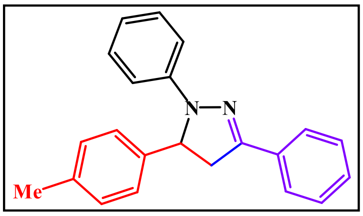
Yield: C1 = 140mg (84%), C2 = 145 mg (87%). ^{1}**NMR (500 MHz)** δ 7.72 (ddd, *J* = 4.2, 3.4, 1.8 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.32 (m, 1H), 7.32 – 7.29 (m, 2H), 7.27 – 7.24 (m, 2H), 7.22 – 7.17 (m, 2H), 7.07 – 7.03 (m, 2H), 6.83 – 6.79 (m, 1H), 5.24 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.83 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.09 (dd, *J* = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 146.82, 144.71, 141.16, 133.41, 132.61, 129.44, 129.08, 128.85, 128.69, 127.43, 125.85, 119.45, 113.47, 63.93, 43.55.

5-(4-bromophenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (4d)



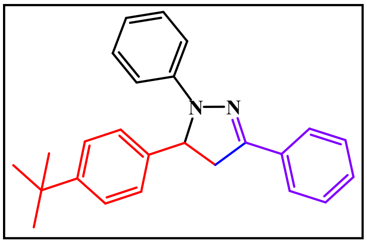
Yield: C1 = 162mg (86%), C2 = 170mg (90%). ^{1}**NMR (500 MHz)** δ 7.74 – 7.70 (m, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.22 – 7.20 (m, 1H), 7.20 – 7.17 (m, 2H), 7.08 – 7.02 (m, 2H), 6.83 – 6.79 (m, 1H), 5.22 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.82 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.09 (dd, *J* = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 146.83, 144.70, 141.69, 132.60, 132.38, 129.09, 128.86, 128.69, 127.78, 125.85, 121.50, 119.47, 113.48, 63.98, 43.50.

1,3-diphenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazole (4e)



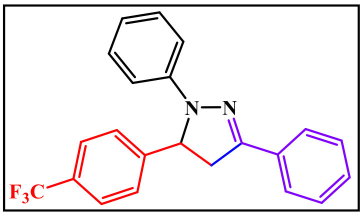
Yield: C1 = 134mg (86%), C2 = 138mg (88%). **^{1}NMR (500 MHz)** δ 7.76 – 7.71 (m, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.24 – 7.17 (m, 4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 8.8, 1.1 Hz, 2H), 6.82 – 6.77 (m, 1H), 5.24 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.82 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.13 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz) δ 146.82, 145.00, 139.75, 137.33, 132.91, 129.91, 129.00, 128.65, 125.91, 125.82, 119.13, 113.46, 64.37, 43.72, 21.23.

5-(4-(tert-butyl)phenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (4f)



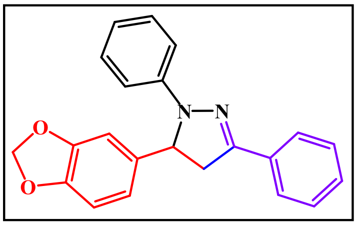
Yield: C1 = 154mg (87%), C2 = 161mg (91%). **^{1}NMR (500 MHz)** δ 7.73 (ddd, *J* = 4.1, 3.4, 1.7 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.30 (m, 3H), 7.27 – 7.24 (m, 2H), 7.22 – 7.18 (m, 2H), 7.14 – 7.09 (m, 2H), 6.83 – 6.77 (m, 1H), 5.25 (dd, *J* = 12.3, 7.1 Hz, 1H), 3.81 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.15 (dd, *J* = 17.0, 7.2 Hz, 1H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz) δ 148.48, 147.12, 146.84, 144.88, 136.71, 132.82, 129.04, 128.74, 128.68, 125.84, 119.25, 119.23, 113.48, 108.75, 106.33, 101.24, 64.36, 43.69.

1,3-diphenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (4g)



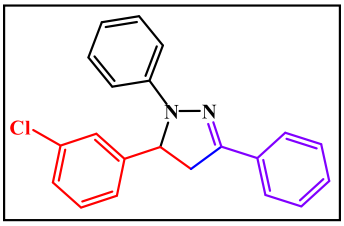
Yield: C1 = 156mg (85%), C2 = 160mg (87%). **^{1}NMR (500 MHz)** δ 7.72 (ddd, *J* = 4.5, 3.6, 1.9 Hz, 2H), 7.60 (dd, *J* = 8.8, 0.7 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.31 (m, 3H), 7.23 – 7.16 (m, 2H), 7.06 – 7.00 (m, 2H), 6.84 – 6.78 (m, 1H), 5.32 (dd, *J* = 12.8, 7.3 Hz, 1H), 3.87 (dd, *J* = 17.1, 12.4 Hz, 1H), 3.11 (dd, *J* = 17.1, 7.2 Hz, 1H) **^{13}C NMR** (126 MHz) δ 145.65, 144.42, 141.42, 134.53, 132.42, 131.88, 131.11, 130.27, 129.24, 129.10, 128.97, 128.89, 127.72, 127.15, 126.98, 125.41, 121.59, 119.68, 113.49, 105.25, 64.08, 43.33. **^{19}F NMR** (471 MHz) δ -62.38 (s), -62.57 (s).

5-(benzo[d][1,3]dioxol-5-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (4h)



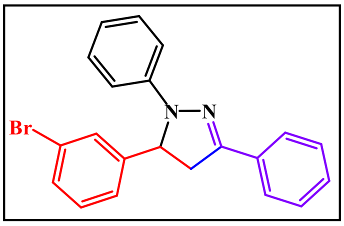
Yield: C1 = 152mg (89%), C2 = 159mg (93%). **^{1}NMR (500 MHz)** δ 7.75 – 7.72 (m, 2H), 7.42 – 7.38 (m, 2H), 7.36 – 7.32 (m, 1H), 7.24 – 7.20 (m, 2H), 7.14 – 7.10 (m, 2H), 6.84 – 6.76 (m, 4H), 5.92 (dd, *J* = 6.4, 1.4 Hz, 2H), 5.18 (dd, *J* = 12.3, 7.1 Hz, 1H), 3.78 (dd, *J* = 17.1, 12.3 Hz, 1H), 3.11 (dd, *J* = 17.1, 7.1 Hz, 1H). **^{13}C NMR** (126 MHz) 148.48, 147.12, 146.84, 144.88, 136.71, 132.82, 129.04, 128.74, 128.68, 125.84, 119.25, 119.23, 113.48, 108.75, 106.33, 101.24, 64.36, 43.69.

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



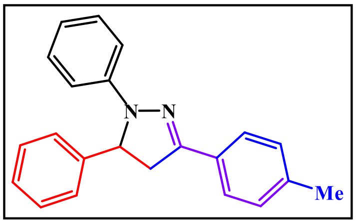
Yield: C1 = 136mg (82%), C2 = 141mg (85%). ^{1}**NMR (500 MHz)** δ 7.71 (ddd, *J* = 4.2, 3.4, 1.8 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.35 – 7.33 (m, 2H), 7.26 – 7.23 (m, 2H), 7.21 – 7.20 (m, 1H), 7.20 – 7.18 (m, 1H), 7.07 – 7.03 (m, 2H), 6.84 – 6.79 (m, 1H), 5.22 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.84 (dd, *J* = 17.1, 12.4 Hz, 1H), 3.11 (dd, *J* = 17.1, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 146.82, 144.82, 144.73, 135.09, 132.54, 130.64, 129.10, 128.88, 128.69, 127.98, 126.15, 125.87, 124.13, 119.48, 113.43, 64.06, 43.56.

5-(3-bromophenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (4j)



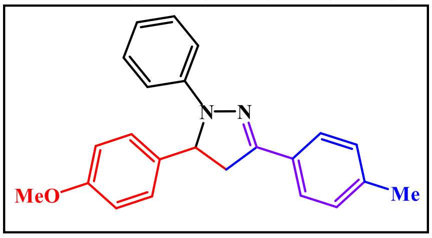
Yield: C1 = 158mg (84%), C2 = 166mg (88%). ^{1}**NMR (500 MHz)** δ 7.77 – 7.71 (m, 2H), 7.51 (t, *J* = 1.8 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.36 – 7.33 (m, 1H), 7.26 – 7.18 (m, 4H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 5.21 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.83 (dd, *J* = 17.1, 12.4 Hz, 1H), 3.11 (dd, *J* = 17.1, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 146.86, 145.12, 144.76, 132.55, 130.96, 130.93, 129.14, 129.06,128.91, 128.71, 125.90, 124.62, 123.32, 119.52, 113.47, 64.04, 43.60.

1,5-diphenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4k)



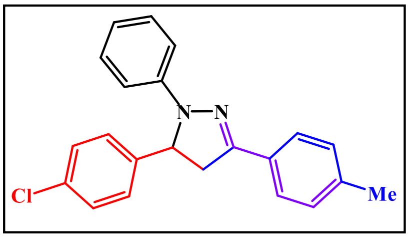
Yield: C1 = 134mg (86%), C2 = 139mg (89%). ^{1}**NMR (500 MHz)** δ 7.67 – 7.62 (m, 2H), 7.36 – 7.34 (m, 4H), 7.28 (ddt, *J* = 6.2, 4.5, 3.9 Hz, 1H), 7.23 – 7.19 (m, 4H), 7.13 – 7.09 (m, 2H), 6.81 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.24 (dd, *J* = 12.3, 7.3 Hz, 1H), 3.82 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.13 (dd, *J* = 17.0, 7.3 Hz, 1H), 2.40 (s, 3H). ^{13}**C NMR** (126 MHz) δ 147.07, 145.15, 142.85, 138.81, 130.08, 129.40, 129.25, 129.03, 127.65, 126.03, 125.86, 119.06, 113.45, 64.56, 43.81, 21.55.

5-(4-methoxyphenyl)-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4l)



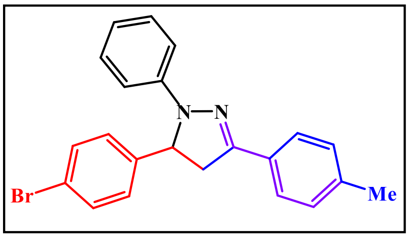
Yield: C1 = 152mg (89%), C2 = 159mg (93%). ^{1}**NMR (500 MHz)** δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.23 (t, *J* = 8.1 Hz, 4H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.93 – 6.89 (m, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 5.24 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.85 – 3.78 (m, 4H), 3.14 (dd, *J* = 17.0, 7.3 Hz, 1H), 2.43 (s, 3H). ^{13}**C NMR** (126 MHz) δ 159.00, 146.99, 145.15, 138.65, 134.85, 130.12, 129.29, 128.89, 127.12, 125.75, 118.94, 114.52, 113.44, 64.03, 55.29, 43.78, 21.42.

5-(4-chlorophenyl)-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4m)



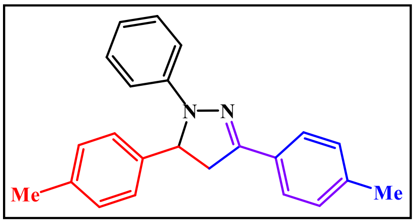
Yield: C1 = 144mg (83%), C2 = 147mg (85%). ^{1}**NMR (500 MHz)** δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 (ddd, *J* = 8.7, 4.6, 2.3 Hz, 4H), 7.07 (dt, *J* = 9.2, 1.7 Hz, 2H), 6.85 – 6.81 (m, 1H), 5.20 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.79 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.08 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (126 MHz) δ 147.09, 144.94, 141.33, 138.99, 133.37, 130.10, 129.88, 129.44, 129.10, 127.49, 125.88, 119.33, 113.48, 63.91, 43.69, 21.56.

5-(4-bromophenyl)-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4n)



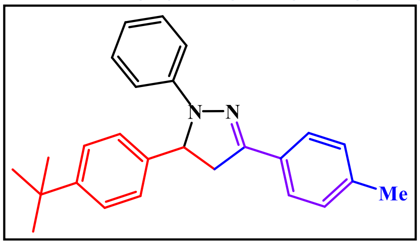
Yield: C1 = 168mg (86%), C2 = 176mg (90%). ^{1}**NMR (500 MHz)** δ 7.64 – 7.61 (m, 2H), 7.48 – 7.45 (m, 2H), 7.23 – 7.19 (m, 6H), 7.08 – 7.04 (m, 2H), 6.84 – 6.80 (m, 1H), 5.19 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.07 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz) δ 147.08, 144.89, 141.84, 139.00, 132.37, 129.83, 129.44, 129.10, 127.83, 125.87, 121.46, 119.32, 113.44, 63.94, 43.63, 21.56.

1-phenyl-3,5-di-p-tolyl-4,5-dihydro-1H-pyrazole (4o)



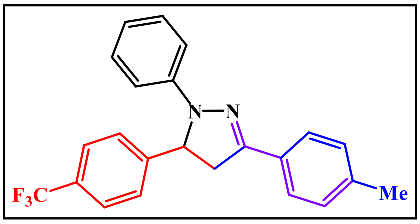
Yield: C1 = 142mg (87%), C2 = 144mg (88%). ^{1}**NMR (500 MHz)** δ 7.64 – 7.60 (m, 2H), 7.23 – 7.13 (m, 9H), 7.10 – 7.07 (m, 2H), 6.77 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.21 (dd, *J* = 12.3, 7.3 Hz, 1H), 3.80 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.10 (dd, *J* = 17.0, 7.3 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz) δ 147.03, 145.18, 139.87, 138.72, 137.26, 130.13, 129.87, 129.34, 128.96, 125.92, 125.80, 118.96, 113.41, 64.34, 43.84, 21.50, 21.20.

5-(4-(tert-butyl)phenyl)-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4p)



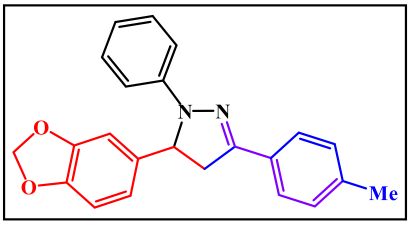
Yield: C1 = 166mg (90%), C2 = 170mg (92%). ^{1}**NMR (500 MHz)** δ 7.67 – 7.64 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.21 (m, 4H), 7.16 – 7.13 (m, 2H), 6.82 (ddt, *J* = 8.4, 7.3, 1.2 Hz, 1H), 5.24 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.80 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.14 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.41 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz) δ 150.45, 147.13, 145.26, 139.80, 138.73, 130.17, 129.39, 129.03, 126.13, 125.86, 125.68, 118.94, 113.43, 64.21, 43.80, 34.64, 31.51, 21.56.

1-phenyl-3-(p-tolyl)-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (4q)



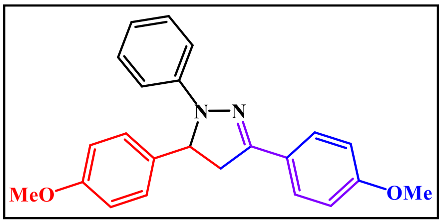
Yield: C1 = 166mg (87%), C2 = 171mg (90%). ^{1}**NMR (500 MHz)** δ 7.65 – 7.60 (m, 4H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.20 (m, 4H), 7.09 – 7.04 (m, 2H), 6.84 (tt, *J* = 7.4, 1.1 Hz, 1H), 5.28 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.84 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.10 (dd, *J* = 17.0, 7.2 Hz, 1H), 2.40 (s, 3H). ^{13}**C NMR** (126 MHz) δ 147.10, 146.79, 144.83, 139.13, 130.08, 129.91, 129.83, 129.71, 129.46, 129.16, 129.00, 126.45, 126.35, 126.32, 126.29, 126.26, 125.89, 125.25, 123.08, 119.45, 113.42, 64.03, 43.59, 21.53. ^{19}**F NMR** (471 MHz) δ -62.28 (s).

5-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole (4r)



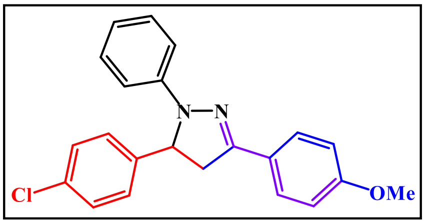
Yield: C1 = 159mg (89%), C2 = 166mg (93%). ^{1}**NMR (500 MHz)** δ 7.62 (d, J = 8.2 Hz, 2H), 7.23 – 7.18 (m, 4H), 7.10 (dd, J = 8.7, 0.9 Hz, 2H), 6.83 – 6.73 (m, 4H), 5.91 (dd, J = 6.4, 1.4 Hz, 2H), 5.15 (dd, J = 12.2, 7.2 Hz, 1H), 3.76 (dd, J = 17.0, 12.3 Hz, 1H), 3.09 (dd, J = 17.0, 7.2 Hz, 1H), 2.38 (s, 3H). ^{13}**C NMR** (126 MHz) δ 148.45, 147.07, 145.06, 138.81, 136.84, 130.04, 129.38, 129.01, 125.82, 125.37, 119.23, 119.08, 113.43, 108.72, 106.36, 101.22, 64.33, 43.81, 21.53.

3,5-bis(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (4s)



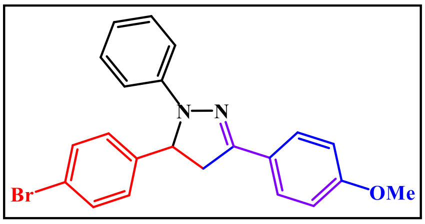
Yield: C1 = 158mg (88%), C1 = 165mg (92%). ^{1}**NMR (500 MHz)** δ 7.70 – 7.65 (m, 2H), 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 2H), 7.08 (dd, *J* = 8.7, 1.0 Hz, 2H), 6.94 – 6.90 (m, 2H), 6.88 – 6.85 (m, 2H), 6.80 – 6.76 (m, 1H), 5.17 (dd, *J* = 12.1, 7.3 Hz, 1H), 3.83 (s, 3H), 3.79 – 3.73 (m, 4H), 3.08 (dd, *J* = 17.0, 7.3 Hz, 2H). ^{13}**C NMR** (126 MHz) δ 160.17, 159.00, 146.92, 145.32, 134.93, 128.98, 127.32, 127.19, 125.68, 118.86, 114.54, 114.10, 113.38, 64.06, 55.45, 55.37, 43.95.

5-(4-chlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (4t)



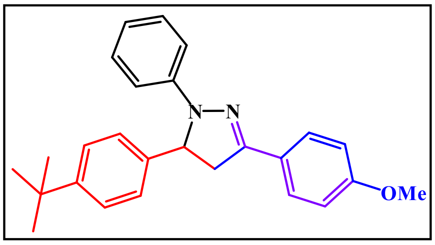
Yield: C1 = 149mg (82%), C2 = 152mg (84%). ^{1}**NMR (500 MHz)** δ 7.66 – 7.63 (m, 2H), 7.33 – 7.26 (m, 4H), 7.19 – 7.14 (m, 2H), 7.03 – 6.99 (m, 2H), 6.92 – 6.89 (m, 2H), 6.80 – 6.74 (m, 1H), 5.19 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.83 (s, 3H), 3.81 – 3.77 (m, 1H), 3.06 (dd, *J* = 17.0, 7.3 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 160.28, 146.85, 145.03, 141.32, 133.31, 129.39, 129.03, 127.45, 127.33, 125.35, 119.14, 114.11, 113.32, 63.90, 55.45, 43.78.

5-(4-bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (4u)



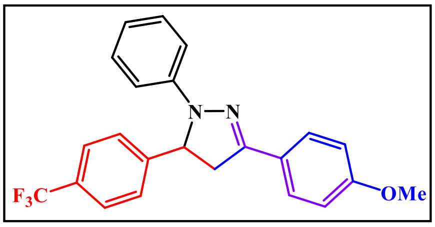
Yield: C1 = 173mg (85%), C2 = 179mg (88%). **^{1}NMR (500 MHz)** δ 7.67 – 7.63 (m, 2H), 7.48 – 7.42 (m, 2H), 7.22 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.04 – 6.99 (m, 2H), 6.93 – 6.89 (m, 2H), 6.80 – 6.76 (m, 1H), 5.17 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 14.2, 9.4 Hz, 1H), 3.06 (dd, *J* = 16.9, 7.2 Hz, 1H). **^{13}C NMR** (126 MHz) δ 160.30, 146.87, 145.02, 141.86, 132.34, 129.05, 127.81, 127.34, 125.34, 121.41, 119.17, 114.12, 113.33, 63.96, 55.46, 43.73.

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



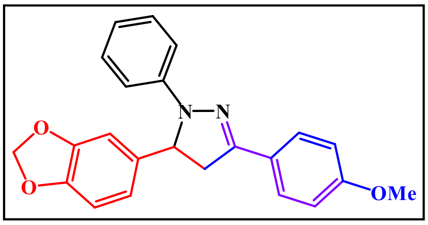
Yield: C1 = 167mg (87%), C2 = 173mg (90%). **^{1}NMR (500 MHz)** δ 7.67 – 7.64 (m, 2H), 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 2H), 7.20 – 7.15 (m, 2H), 7.08 – 7.05 (m, 2H), 6.92 – 6.88 (m, 2H), 6.76 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.19 (dd, *J* = 12.2, 7.3 Hz, 1H), 3.83 (s, 3H), 3.78 (dd, *J* = 17.0, 12.2 Hz, 1H), 3.11 (dd, *J* = 17.0, 7.3 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz) δ 160.13, 150.40, 146.92, 145.36, 139.77, 128.95, 127.29, 126.06, 125.67, 125.62, 118.75, 114.05, 113.28, 64.20, 55.43, 43.88, 34.59, 31.43.

3-(4-methoxyphenyl)-1-phenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (4w)



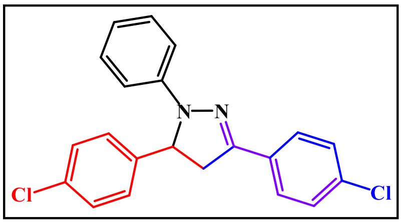
Yield: C1 = 169mg (85%), C2 = 177mg (89%). **^{1}NMR (500 MHz)** δ 7.67 – 7.64 (m. 2H), 7.59 (dd, J = 8.6, 0.5 Hz, 2H), 7.44 (dd, J = 8.0, 0.4 Hz, 2H), 7.20 – 7.16 (m, 2H), 7.03 – 6.99 (m, 2H), 6.93 – 6.89 (m, 2H), 6.81 – 6.77 (m, 1H), 5.27 (dd, J = 12.3, 7.2 Hz, 1H), 3.87 – 3.84 (m, 1H), 3.83 (s, 3H), 3.08 (dd, J = 17.0, 7.2 Hz, 1H). **^{13}C NMR** (126 MHz) δ 160.37, 146.88, 146.80, 144.95, 130.06, 129.80, 129.27, 129.10, 127.37, 126.42,126.32,126.29,126.25, 126.22, 125.49, 125.20, 123.04, 119.29, 114.14, 113.31, 64.05, 55.44, 43.70. **^{19}F NMR** (471 MHz) δ -62.58 (s).

5-(benzo[d][1,3]dioxol-5-yl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (4x)



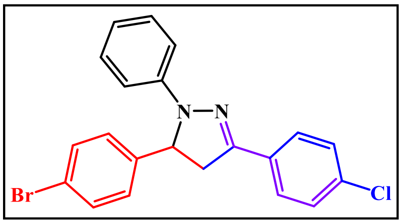
Yield: C1 = 160mg (86%), C2 = 166mg (89%). **^{1}NMR (500 MHz)** δ 7.67 – 7.63 (m, 2H), 7.20 – 7.16 (m, 2H), 7.08 – 7.04 (m, 2H), 6.92 – 6.89 (m, 2H), 6.82 – 6.74 (m, 4H), 5.92 – 5.90 (m, 2H), 5.13 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.83 (s, 3H), 3.79 – 3.73 (m, 1H), 3.07 (dd, *J* = 17.0, 7.2 Hz, 1H). **^{13}C NMR** (126 MHz) δ 160.18, 148.42, 147.03, 146.86, 145.18, 136.87, 128.97, 127.29, 125.56, 119.21, 118.93, 114.08, 113.32, 108.69, 106.35, 101.19, 64.34, 55.44, 43.92.

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



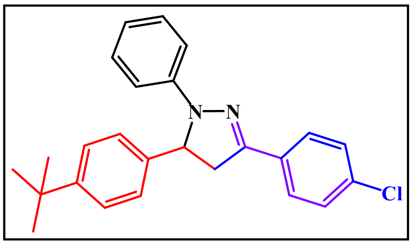
Yield: C1 = 150mg (82%), C2 = 158mg (86%). ^{1}**NMR (500 MHz)** δ 7.66 – 7.60 (m, 2H), 7.36 – 7.33 (m, 2H), 7.31 – 7.29 (m, 2H), 7.25 – 7.23 (m, 2H), 7.20 – 7.16 (m, 2H), 7.08 – 6.97 (m, 2H), 6.84 – 6.78 (m, 1H), 5.25 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.79 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.05 (dd, *J* = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 145.64, 144.44, 140.89, 134.52, 133.50, 131.13, 129.49, 129.11, 128.89, 127.38, 126.99, 119.66, 113.49, 64.02, 43.39.

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



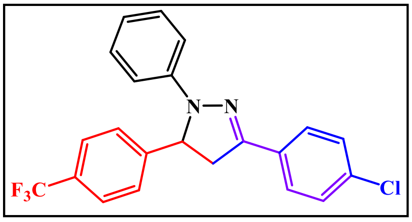
Yield: C1 = 175mg (85%), C2 = 179mg (87%). ^{1}**NMR (500 MHz)** δ 7.88 – 7.80 (m, 1H), 7.62 (dq, J = 9.3, 2.4 Hz, 2H), 7.45 (ddd, J = 6.8, 4.2, 1.9 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.20 – 7.15 (m, 3H), 7.03 – 7.00 (m, 1H), 6.82 – 6.78 (m, 1H), 5.23 (dd, J = 12.7, 7.3 Hz, 1H), 3.79 (dd, J = 17.1, 12.4 Hz, 1H), 3.05 (dd, J = 17.1, 7.3 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 146.83, 146.61, 144.62, 132.46, 129.13, 128.95, 128.70, 126.40, 126.33, 126.29, 125.86, 119.58, 113.43, 64.06, 43.47.

5-(4-(tert-butyl)phenyl)-3-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (4aa)



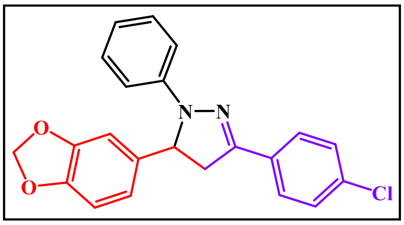
Yield: C1 = 165mg (85%), C2 = 171mg (88%). ^{1}**NMR (500 MHz)** δ 7.64 – 7.61 (m, 2H), 7.35 – 7.32 (m, 4H), 7.23 – 7.19 (m, 2H), 7.19 – 7.16 (m, 2H), 7.09 – 7.05 (m, 2H), 6.84 – 6.76 (m, 1H), 5.26 (dd, *J* = 12.4, 7.1 Hz, 1H), 3.77 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.10 (dd, *J* = 17.0, 7.2 Hz, 1H), 1.28 (s, 9H). ^{13}**C NMR** (126 MHz) δ 150.59, 145.66, 144.75, 134.26, 129.02, 128.81, 126.95, 126.15, 125.54, 119.27, 113.44, 77.37, 77.11, 76.86, 64.30, 43.47, 34.61, 32.26, 31.41.

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



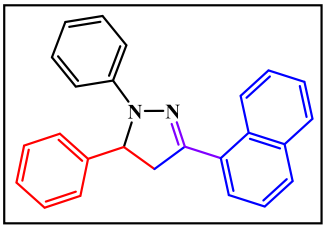
Yield: C1 = 168mg (84%), C2 = 172mg (86%). ^{1}**NMR (500 MHz)** δ 7.65 – 7.61 (m, 2H), 7.59 (t, J = 8.7 Hz, 2H), 7.42 (dd, J = 7.0, 4.2 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.36 – 7.33 (m, 2H), 7.23 – 7.15 (m, 2H), 7.03 – 7.00 (m, 1H), 6.85 – 6.80 (m, 1H), 5.33 (dd, J = 12.5, 7.2 Hz, 1H), 3.83 (dd, J = 17.0, 12.5 Hz, 1H), 3.07 (dd, J = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 152.19, 146.36, 145.67, 144.36, 139.66, 134.65, 134.09, 130.99, 130.24, 129.98, 129.32, 129.16, 129.00, 128.97, 128.91, 128.15, 127.16, 127.01, 126.36, 125.45, 119.81, 113.48, 105.75, 64.17, 43.31. ^{19}**F NMR** (471 MHz) δ -62.41 (s), -62.60 (s).

5-(benzo[d][1,3]dioxol-5-yl)-3-(4-chlorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (4ac)



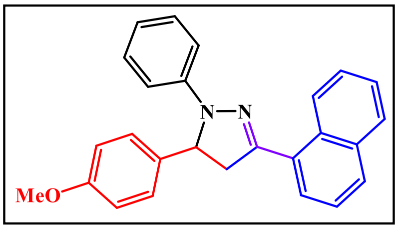
Yield: C1 = 164mg (87%), C2 = 173mg (92%). ^{1}**NMR (500 MHz)** δ 7.64 – 7.61 (m, 2H), 7.35 – 7.32 (m, 2H), 7.22 – 7.17 (m, 2H), 7.09 – 7.06 (m, 2H), 6.82 – 6.78 (m, 2H), 6.77 – 6.74 (m, 2H), 5.91 (dd, *J* = 6.1, 1.4 Hz, 2H), 5.18 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.74 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.06 (dd, *J* = 17.0, 7.2 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 148.50, 147.17, 145.63, 144.60, 136.43, 134.35, 131.34, 129.04, 128.85, 126.96, 119.46, 119.19, 113.51, 108.76, 106.25, 101.25, 64.47, 43.51.

3-(naphthalen-1-yl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (4ad)



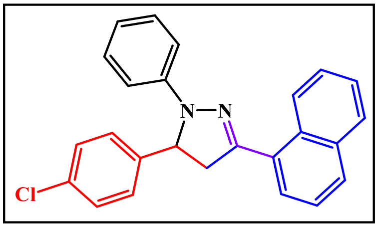
Yield: C1 = 145mg (83%), C1 = 148mg (85%). ^{1}**NMR (500 MHz)**) δ 9.56 (ddd, J = 8.7, 1.9, 0.8 Hz), 7.90 – 7.87 (m), 7.81 (dd, J = 7.4, 1.9 Hz), 7.73 – 7.66 (m), 7.56 (ddd, J = 8.1, 6.8, 1.2 Hz), 7.44 (td, J = 7.7, 4.7 Hz), 7.39 – 7.35 (m), 7.35 – 7.33 (m), 7.29 – 7.21 (m), 7.18 – 7.11 (m), 6.86 – 6.79 (m), 5.28 (dd, J = 12.3, 7.1 Hz), 4.05 (dd, J = 16.7, 12.3 Hz), 3.37 (dd, J = 16.7, 7.1 Hz). ^{13}**C NMR** (126 MHz) δ 147.35, 144.85, 142.63, 134.30, 130.69, 129.62, 129.27, 129.14, 129.09, 128.69, 127.68, 127.53, 127.41, 126.77, 126.21, 126.03, 124.95, 119.31, 113.55, 63.41, 46.19.

5-(4-methoxyphenyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole (4ae)



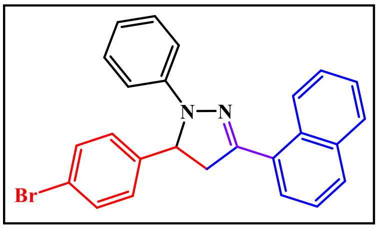
Yield: C1 = 165mg (87%), C2 = 174mg (92%). ^{1}**NMR (500 MHz)** δ 9.61 (dd, *J* = 8.7, 0.8 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.72 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.42 (m, 2H), 7.31 – 7.25 (m, 4H), 7.20 – 7.17 (m, 2H), 6.90 – 6.84 (m, 3H), 5.22 (dd, *J* = 12.2, 7.0 Hz, 1H), 3.99 (dd, *J* = 16.7, 12.2 Hz, 1H), 3.78 (s, 3H), 3.34 (dd, *J* = 16.7, 7.0 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 159.10, 147.44, 144.90, 134.69, 134.33, 130.70, 129.61, 128.75, 127.60, 127.45, 127.24, 126.83, 126.24, 125.03, 119.29, 114.63, 113.62, 62.88, 55.37, 46.21.

5-(4-chlorophenyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole (4af)



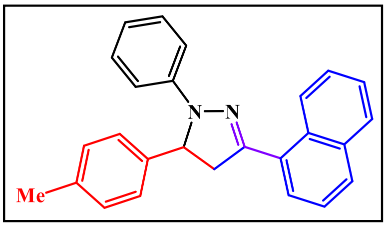
Yield: C1 = 157mg (82%), C2 = 163mg (85%). ^{1}**NMR (500 MHz)** δ 9.56 – 9.51 (m, 1H), 7.90 – 7.87 (m, 1H), 7.82 (dd, *J* = 6.2, 3.1 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.58 – 7.51 (m, 2H), 7.42 (dd, *J* = 5.2, 2.2 Hz, 2H), 7.31 (d, *J* = 0.5 Hz, 3H), 7.26 – 7.22 (m, 2H), 7.14 – 7.08 (m, 2H), 6.86 – 6.82 (m, 1H), 5.25 (dd, *J* = 12.2, 7.0 Hz, 1H), 4.04 (dd, *J* = 16.7, 12.2 Hz, 1H), 3.32 (dd, *J* = 16.7, 7.0 Hz, 1H). **^{13}C NMR** (126 MHz) δ 147.37, 144.61, 141.10, 134.29, 133.44, 130.63, 130.14, 129.80, 129.47, 129.18, 128.74, 127.48, 127.43, 126.85, 126.27, 124.95, 119.56, 113.55, 109.12, 62.74, 46.06.

5-(4-bromophenyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole (4ag)



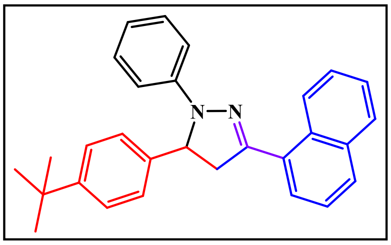
Yield: C1 = 179mg (84%), C2 = 186mg (87%). ^{1}**NMR (500 MHz)** δ 9.52 (dd, J = 8.7, 0.9 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.84 – 7.80 (m, 1H), 7.69 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.57 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.44 – 7.42 (m, 2H), 7.26 – 7.22 (m, 4H), 7.14 – 7.08 (m, 2H), 6.84 (tt, J = 7.3, 1.1 Hz, 1H), 5.24 (dd, J = 12.2, 7.0 Hz, 1H), 4.04 (dd, J = 16.7, 12.3 Hz, 1H), 3.32 (dd, J = 16.7, 7.0 Hz, 1H). **^{13}C NMR** (126 MHz) δ 147.37, 144.60, 141.64, 134.30, 132.42, 130.64, 129.81, 129.18, 128.89, 128.74, 127.83, 127.49, 127.42, 126.84, 126.27, 124.94, 121.53, 119.59, 113.56, 62.81, 46.01.

3-(naphthalen-1-yl)-1-phenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazole (4ah)



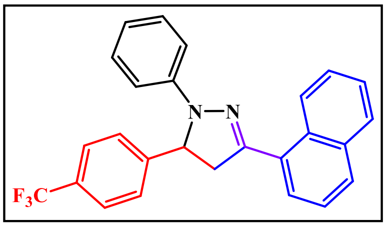
Yield: C1 = 156mg (86%), C2 = 160mg (88%). ^{1}**NMR (500 MHz)** δ 9.55 (ddd, *J* = 8.7, 1.8, 0.8 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.80 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.68 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.27 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 7.16 – 7.13 (m, 4H), 6.81 (tt, *J* = 7.3, 1.2 Hz, 1H), 5.25 (dd, *J* = 12.2, 7.1 Hz, 1H), 4.03 (dd, *J* = 16.7, 12.2 Hz, 1H), 3.35 (dd, *J* = 16.7, 7.1 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (126 MHz) δ 147.36, 144.90, 139.67, 137.34, 134.30, 130.69, 129.91, 129.56, 129.21, 129.07, 128.67, 127.55, 127.38, 126.73, 126.19, 125.95, 124.95, 119.23, 113.54, 63.20, 46.25, 21.19.

5-(4-(tert-butyl)phenyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole (4ai)



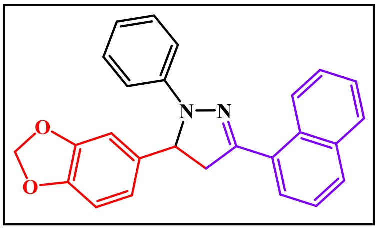
Yield: C1 = 174mg (86%), C2 = 180mg (89%). ^{1}**NMR (500 MHz)** δ 9.56 (dd, *J* = 8.6, 0.9 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.84 – 7.79 (m, 1H), 7.69 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.56 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 7.44 – 7.43 (m, 1H), 7.41 – 7.36 (m, 2H), 7.35 – 7.33 (m, 2H), 7.29 (dd, *J* = 6.2, 4.2 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.16 (ddd, *J* = 3.1, 2.5, 1.5 Hz, 2H), 6.84 – 6.80 (m, 1H), 5.26 (dd, *J* = 12.2, 7.0 Hz, 1H), 4.03 (dd, *J* = 16.7, 12.2 Hz, 1H), 3.37 (dd, *J* = 16.7, 7.0 Hz, 1H), 1.29 (s, 9H). **^{13}C NMR** (126 MHz) δ 150.51, 147.40, 144.92, 139.52, 134.28, 130.67, 129.56, 129.09, 128.68, 127.55, 127.39, 126.76, 126.19, 126.13, 125.66, 124.95, 119.16, 113.50, 108.90, 63.01, 46.16, 34.60, 31.42.

3-(naphthalen-1-yl)-1-phenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (4aj)



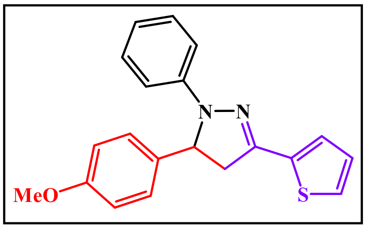
Yield: C1 = 177mg (85%), C2 = 181mg (87%). **^{1}NMR (500 MHz)** δ 9.54 (ddd, J = 8.7, 1.8, 0.8 Hz, 1H), 7.90 – 7.88 (m, 1H), 7.83 (dq, J = 7.2, 3.8 Hz, 1H), 7.70 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.58 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.44 – 7.42 (m, 2H), 7.27 – 7.23 (m, 2H), 7.14 – 7.08 (m, 2H), 6.86 (tt, J = 7.3, 1.1 Hz, 1H), 5.33 (dd, J = 12.3, 7.0 Hz, 1H), 4.11 – 4.04 (m, 1H), 3.34 (dd, J = 16.7, 7.0 Hz, 1H). **^{13}C NMR** (126 MHz) δ 147.38, 146.59, 144.53, 134.31, 130.63, 130.19, 129.91, 129.24, 129.08, 128.77, 127.54, 127.39, 126.89, 126.46, 126.38, 126.36, 126.33, 126.30, 125,48, 124.93, 123.02, 119.71, 113.53, 62.90, 45.97. **^{19}F NMR** (471 MHz) δ -62.40 (s), -62.56 (s).

5-(benzo[d][1,3]dioxol-5-yl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole (4ak)



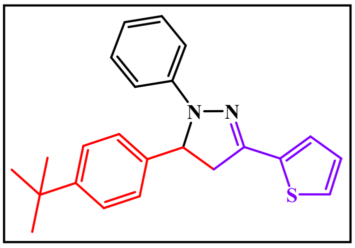
Yield: C1 = 169mg (86%), C2 = 179mg (91%). **^{1}NMR (500 MHz)** δ 9.62 – 9.52 (m, 1H), 7.89 (ddt, *J* = 8.1, 1.4, 0.5 Hz, 1H), 7.81 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.57 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.43 (q, *J* = 4.0 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.16 (m, 2H), 6.87 – 6.83 (m, 3H), 6.78 (dd, *J* = 7.9, 0.4 Hz, 1H), 5.92 (dd, *J* = 4.9, 1.4 Hz, 2H), 5.18 (dd, *J* = 12.2, 7.0 Hz, 1H), 3.98 (dd, *J* = 16.7, 12.2 Hz, 1H), 3.33 (dd, *J* = 16.7, 7.0 Hz, 1H). **^{13}C NMR** (126 MHz) δ 148.50, 147.41, 147.14, 144.78, 136.64, 134.30, 130.66, 129.66, 129.13, 129.08, 128.73, 127.54, 127.46, 126.81, 126.24, 124.98, 119.37, 119.31, 113.57, 108.78, 106.36, 101.22, 63.16, 46.19.

5-(4-methoxyphenyl)-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (4al)



Yield: C1 = 146mg (87%), C2 = 149mg (89%). **^{1}NMR (500 MHz)** δ 7.32 – 7.28 (m, 1H), 7.27 – 7.21 (m, 2H), 7.19 – 7.15 (m, 1H), 7.07 – 6.98 (m, 3H), 6.89 – 6.81 (m, 2H), 6.81 – 6.74 (m, 1H), 5.21 (dd, J = 12.5, 7.3 Hz, 1H), 3.81 (dd, J = 11.2, 5.6 Hz, 1H), 3.77 (s, 3H), 3.10 (dd, J = 16.9, 7.3 Hz, 1H). **^{13}C NMR** (126 MHz) δ 159.09, 144.78, 143.01, 136.81, 134.46, 128.97, 127.43, 127.17, 126.58, 125.96, 119.24, 114.59, 113.57, 64.24, 55.37, 44.48.

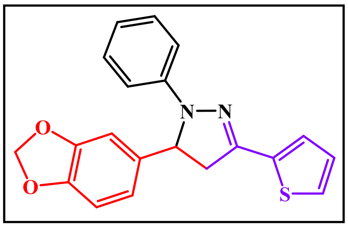
5-(4-(tert-butyl)phenyl)-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (4am)



Yield: C1 = 150mg (83%), C2 = 155mg (86%). **^{1}NMR (500 MHz)** δ 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 7.19 – 7.14 (m, 2H), 7.07 – 6.98 (m, 4H), 6.79 – 6.74 (m, 1H), 5.23 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.81 (dd, *J* = 16.9, 12.3 Hz, 1H), 3.13 (dd, *J* = 16.9, 7.2 Hz, 1H), 1.28 (s, 9H). **^{13}C NMR**

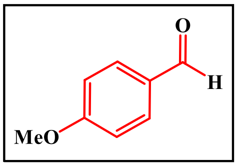
(126 MHz) δ 150.56, 144.83, 143.01, 139.32, 136.79, 128.95, 127.38, 126.54, 126.12, 125.91, 125.59, 119.13, 113.47, 64.36, 44.41, 31.41, 29.80.

5-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (4an)



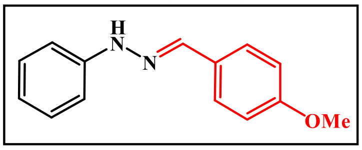
Yield: C1 = 153mg (88%), C2 = 155mg (89%). ^{1}**NMR (500 MHz)** δ 7.30 (dd, J = 5.0, 1.3 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.07 – 6.98 (m, 4H), 6.82 – 6.73 (m, 4H), 5.92 (dd, J = 6.4, 1.5 Hz, 2H), 5.16 (dd, J = 12.4, 7.3 Hz, 1H), 3.79 (dd, J = 17.0, 12.2 Hz, 1H), 3.10 (dd, J = 16.9, 7.3 Hz, 1H). ^{13}**C NMR** (126 MHz) δ 148.48, 147.16, 144.68, 142.97, 136.70, 136.41, 128.98, 127.41, 126.65, 125.97, 119.33, 119.24, 113.54, 108.73, 106.31, 101.23, 64.52, 44.45.

4-methoxybenzaldehyde (2b)



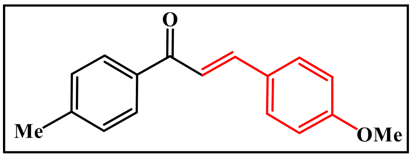
Yield: C1 = 59mg (86%), C2 = 62mg (90%). ^{1}**NMR (500 MHz)** δ 9.82 (s, 1H), 7.80 – 7.76 (m, 2H), 6.96 – 6.93 (m, 2H), 3.82 (s, 3H). ^{13}**C NMR** (126 MHz) δ 190.85, 164.61, 131.94, 129.87, 114.30, 55.52.

(E)-1-(4-methoxybenzylidene)-2-phenylhydrazine (4b)



^{1}**NMR (500 MHz)** δ 7.61 – 7.57 (m, 2H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.12 – 7.09 (m, 2H), 6.93 – 6.87 (m, 3H), 3.82 (s, 3H). ^{13}**C NMR** (126 MHz) δ 160.08, 145.12, 137.62, 129.42, 128.29, 127.72, 119.86, 114.24, 112.77, 55.43.

(E)-3-(4-methoxyphenyl)-1-(p-tolyl)prop-2-en-1-one (7b)



Yield: 111 88%. ^{1}**NMR (500 MHz)** δ 7.93 – 7.89 (m, 2H), 7.76 (d, *J* = 15.6 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.39 (d, *J* = 15.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.87 (m, 3H), 3.78 (s), 2.38 (s, 3H). ^{13}**C NMR** (126 MHz) δ 189.97, 161.68, 144.27, 143.43, 135.98, 130.26, 129.36, 128.64, 127.78, 119.78, 114.48, 55.43, 21.72.

9.0. ^{1}H, ^{13}C and ^{19}F NMR spectrums of products.

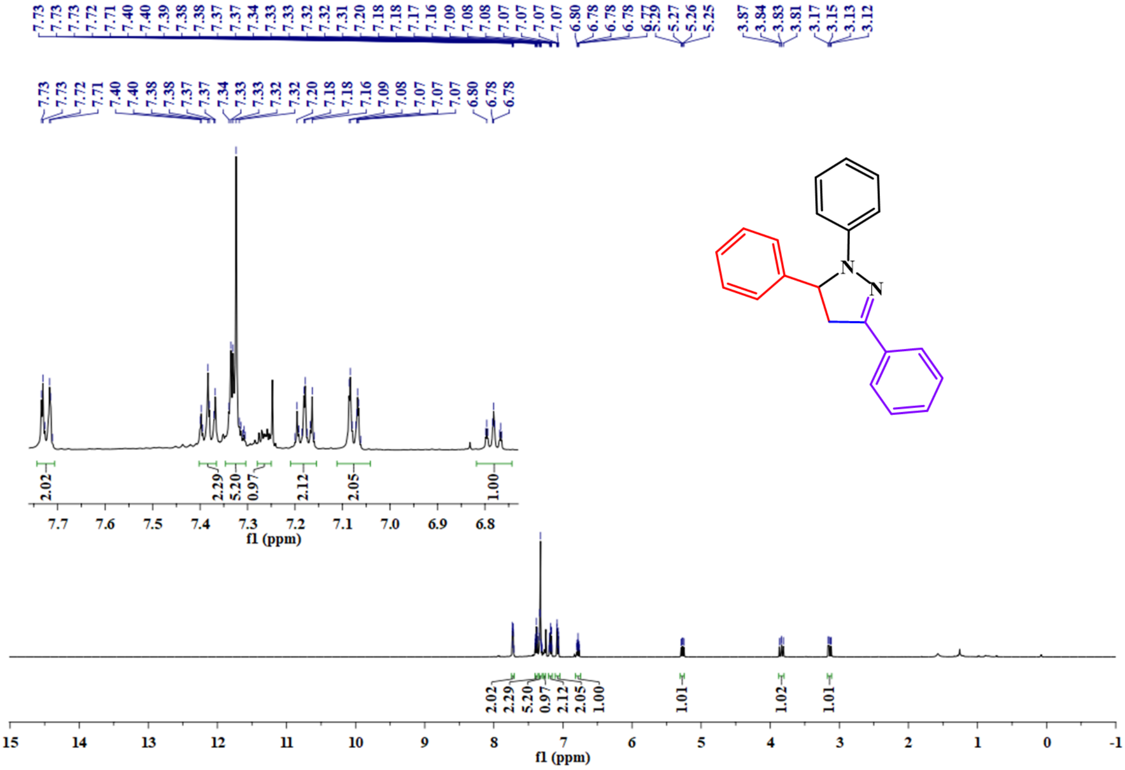


Fig. S26: ^{1}H NMR spectrum of **4a** in $CDCl_3$ at 500 MHz.

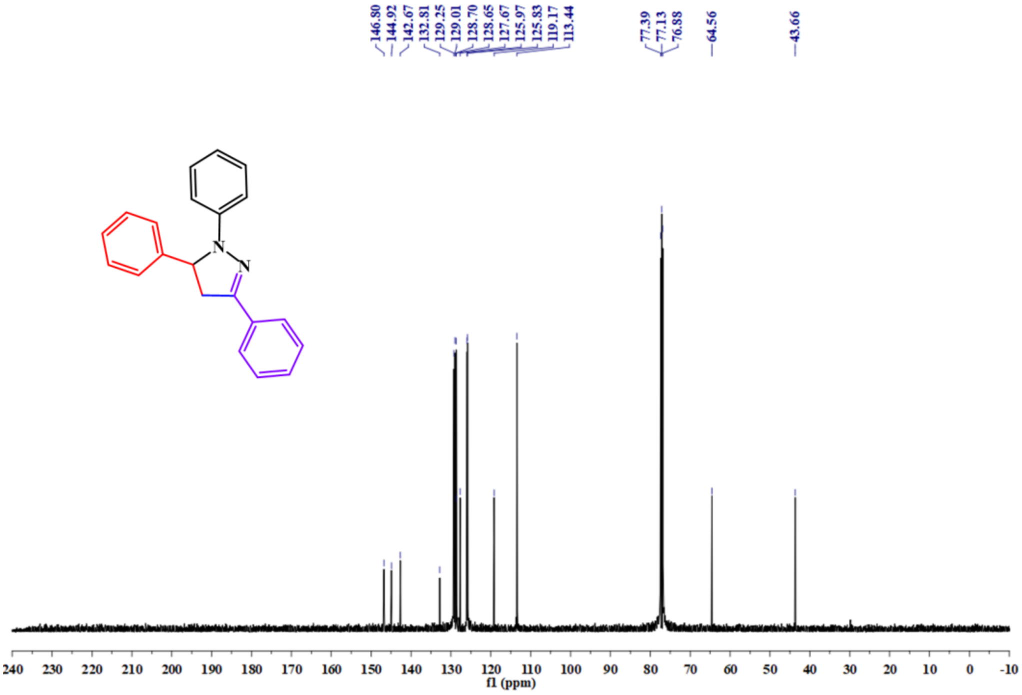


Fig. S27: ^{13}C NMR spectrum of **4a** in $CDCl_3$ at 126 MHz.

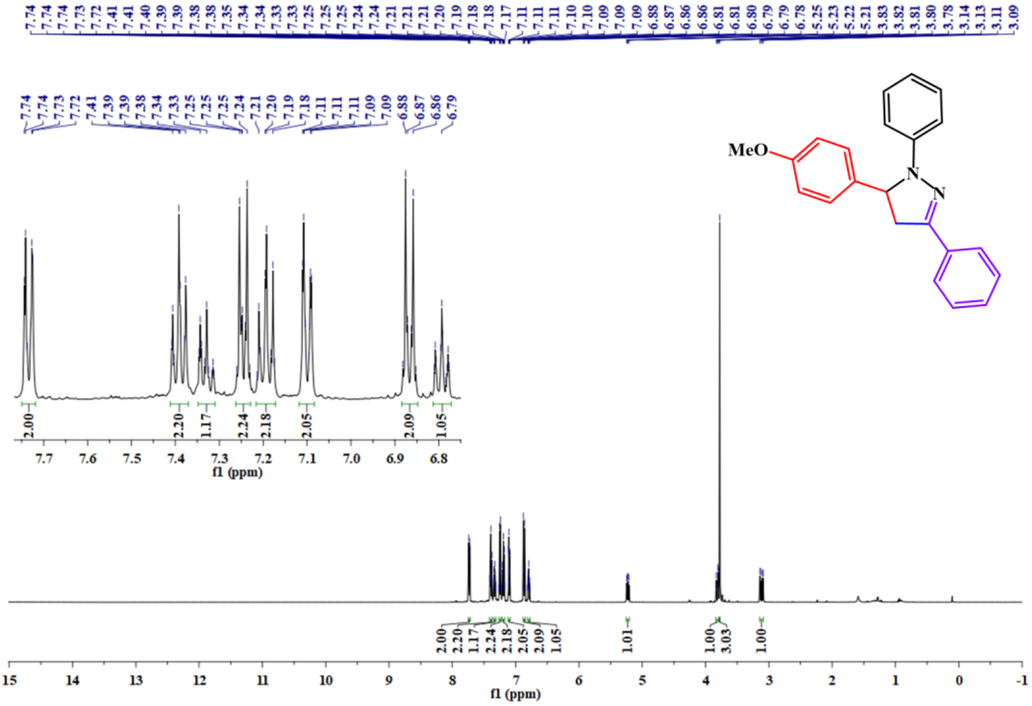


Fig. S28: ^{1}H NMR spectrum of **4b** in $CDCl_3$ at 500 MHz.

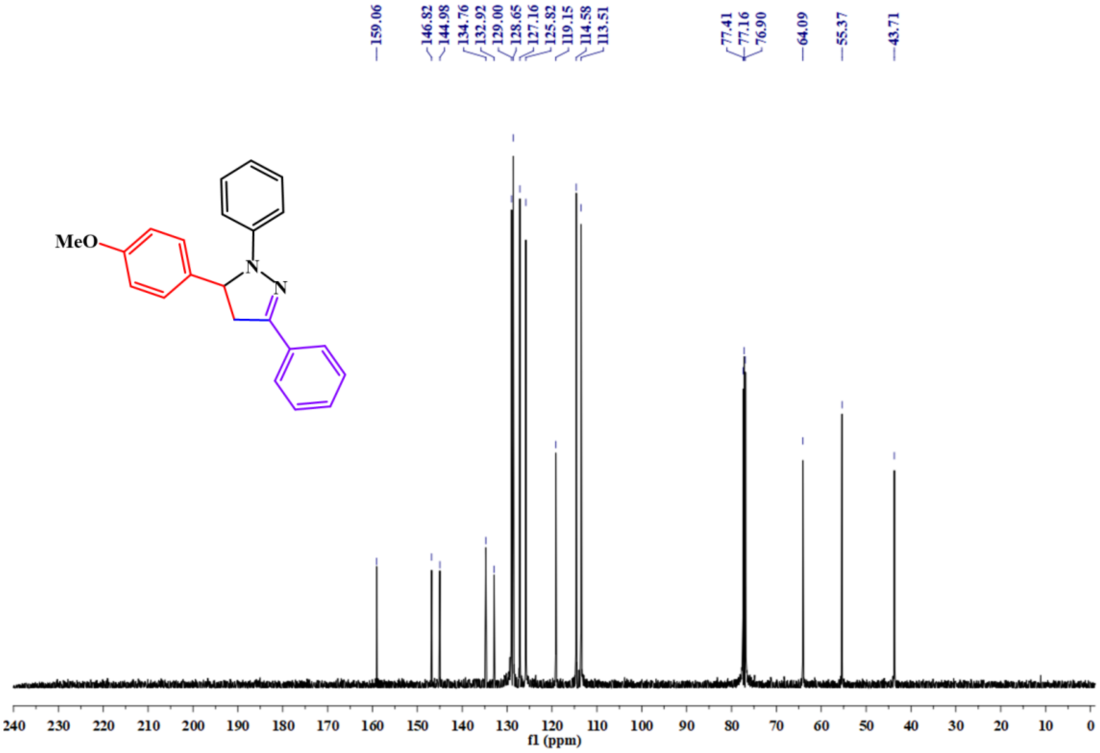


Fig. S29: ^{13}C NMR spectrum of **4b** in $CDCl_3$ at 126 MHz.

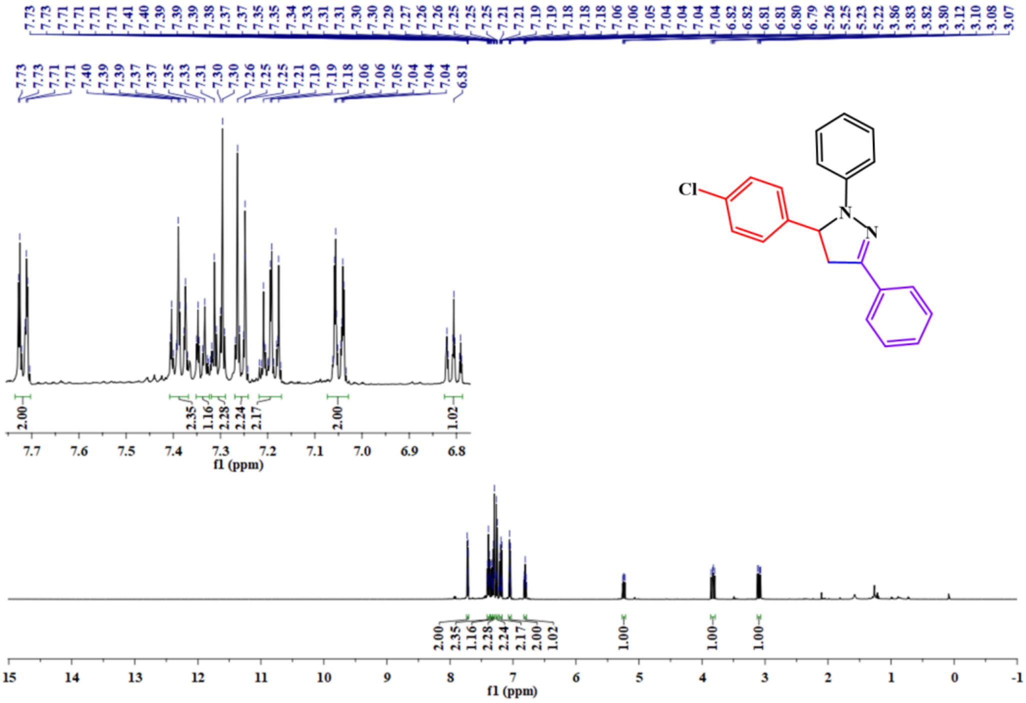


Fig. S30: ^{1}H NMR spectrum of **4c** in $CDCl_3$ at 500 MHz.

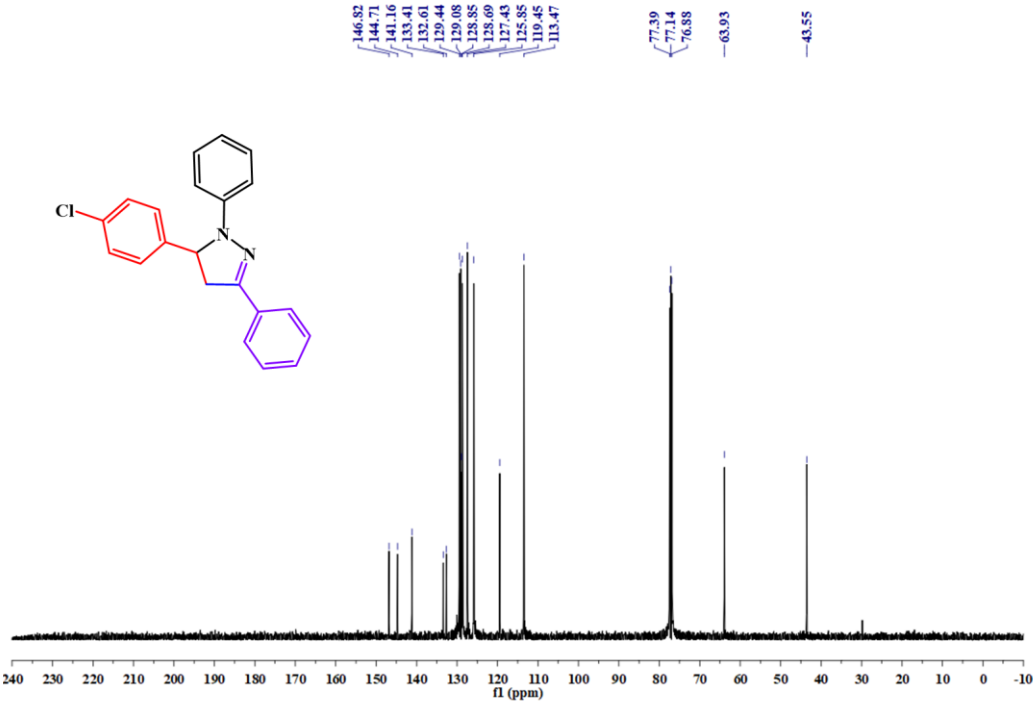


Fig. S31: ^{13}C NMR spectrum of **4c** in $CDCl_3$ at 126 MHz.

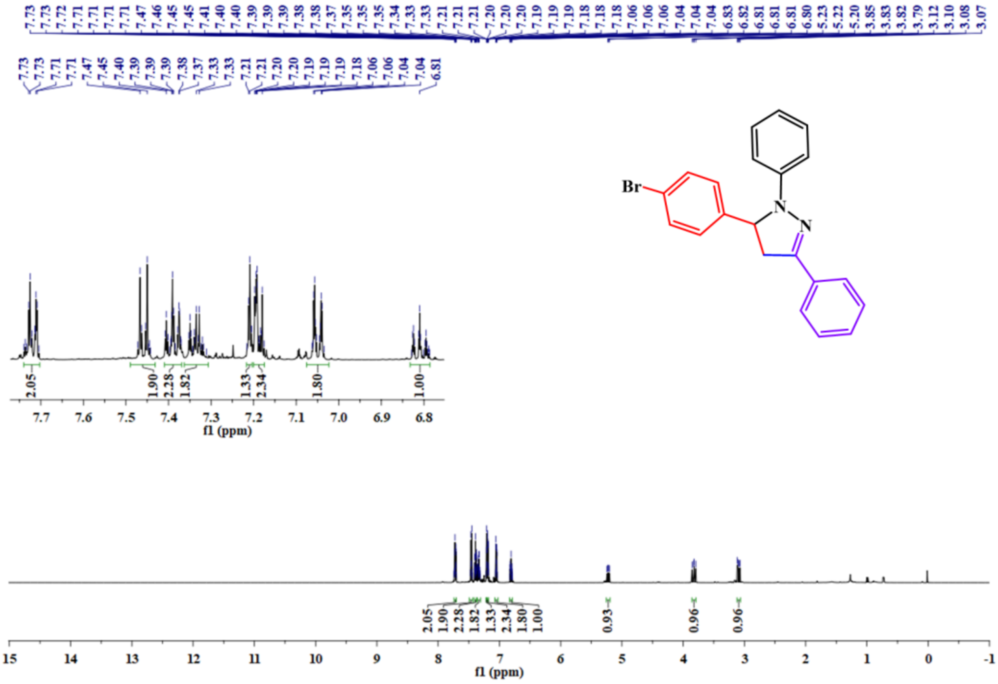


Fig. S32: ^{1}H NMR spectrum of **4d** in CDCl$_3$ at 500 MHz.

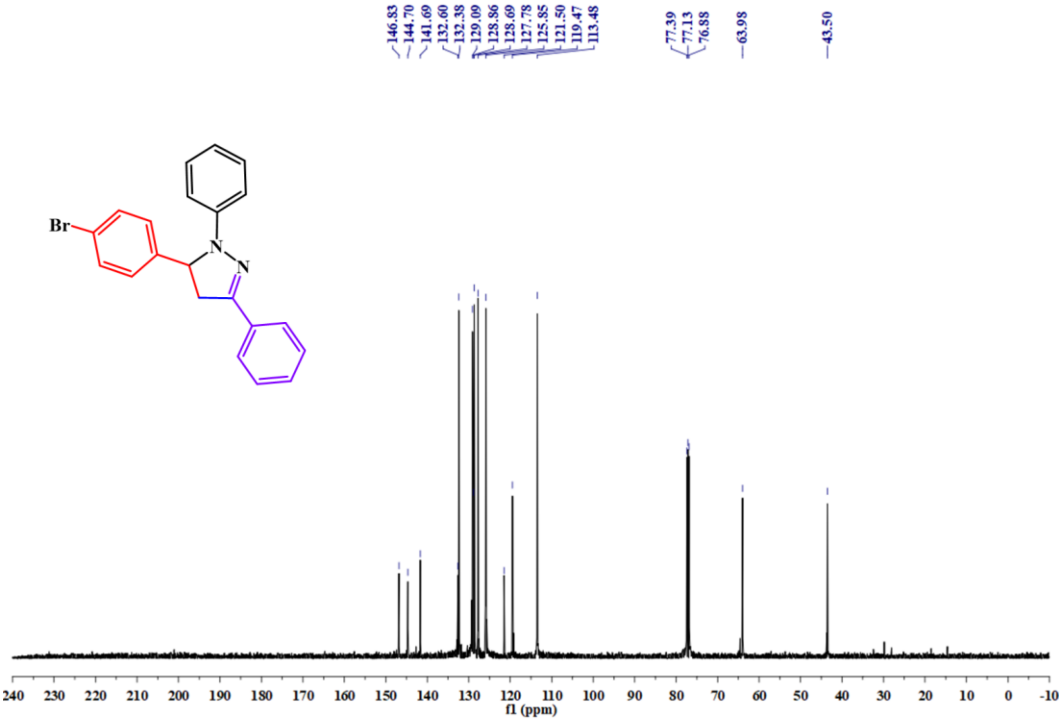


Fig. S33: ^{13}C NMR spectrum of **4d** in CDCl$_3$ at 126 MHz.

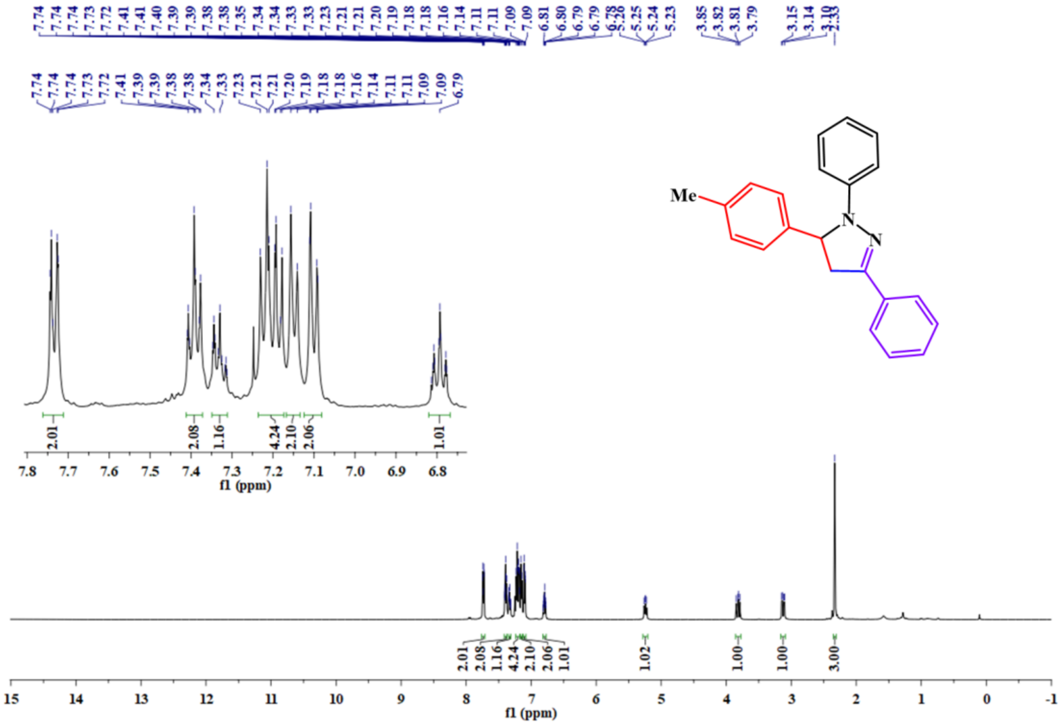


Fig. S34: ^{1}H NMR spectrum of **4e** in $CDCl_3$ at 500 MHz.

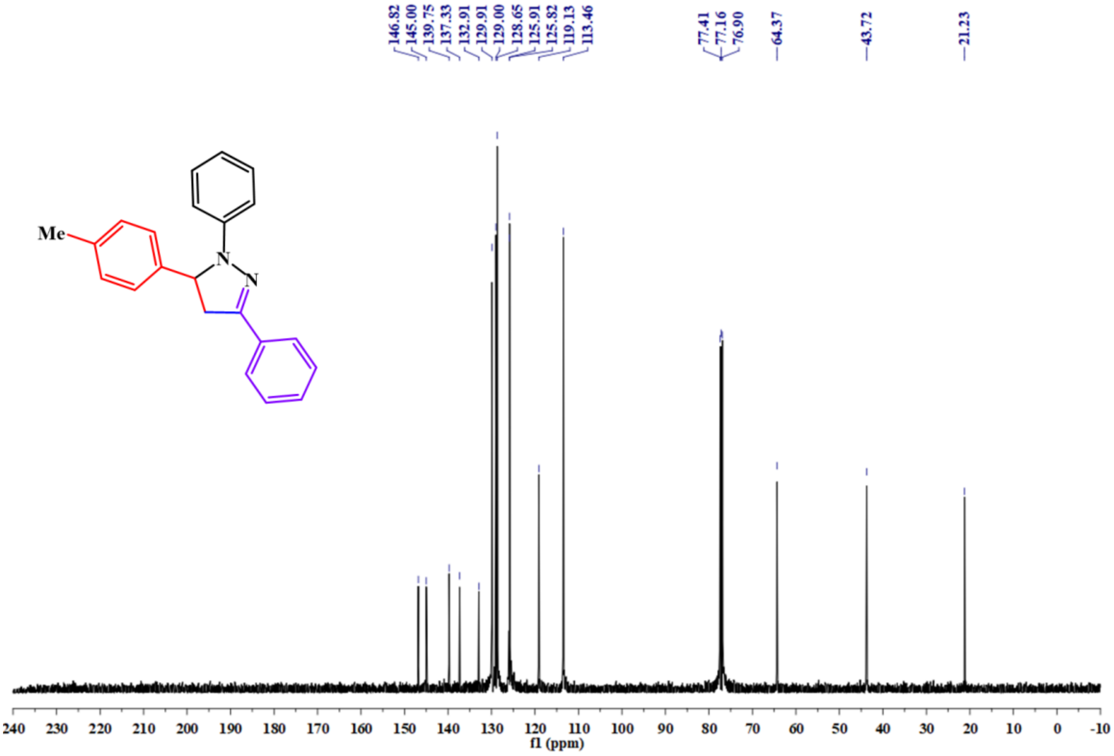


Fig. S35: ^{13}C NMR spectrum of **4e** in $CDCl_3$ at 126 MHz.

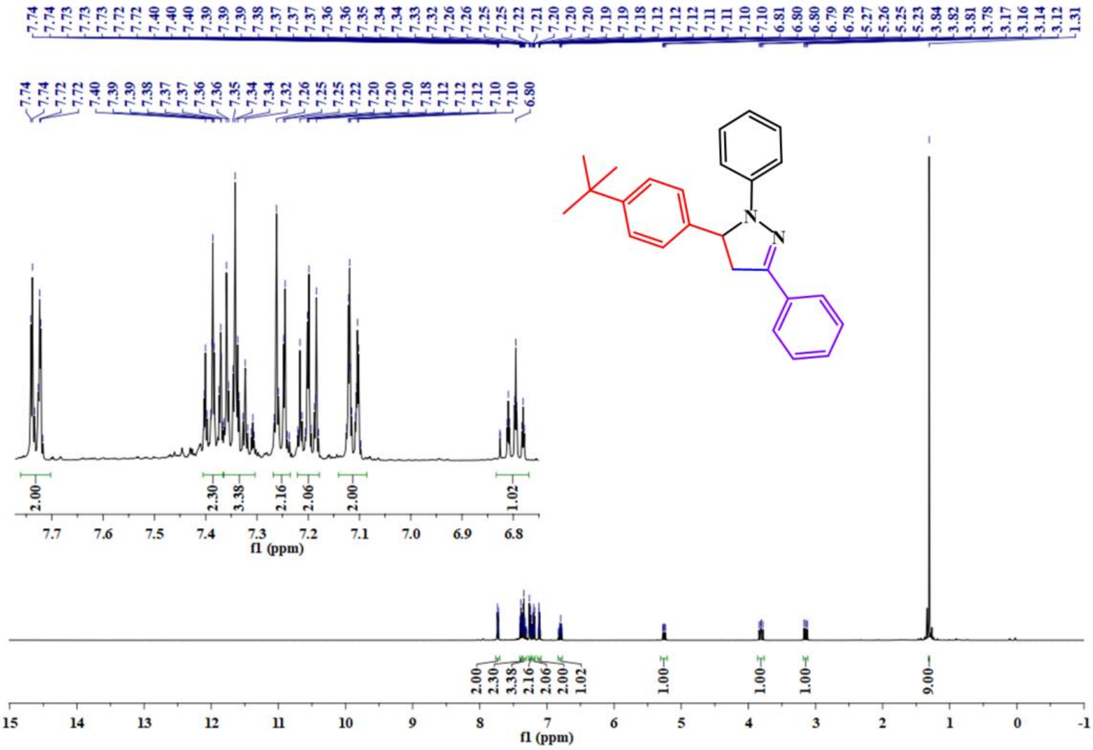


Fig. S36: ^{1}H NMR spectrum of **4f** in CDCl$_3$ at 500 MHz.

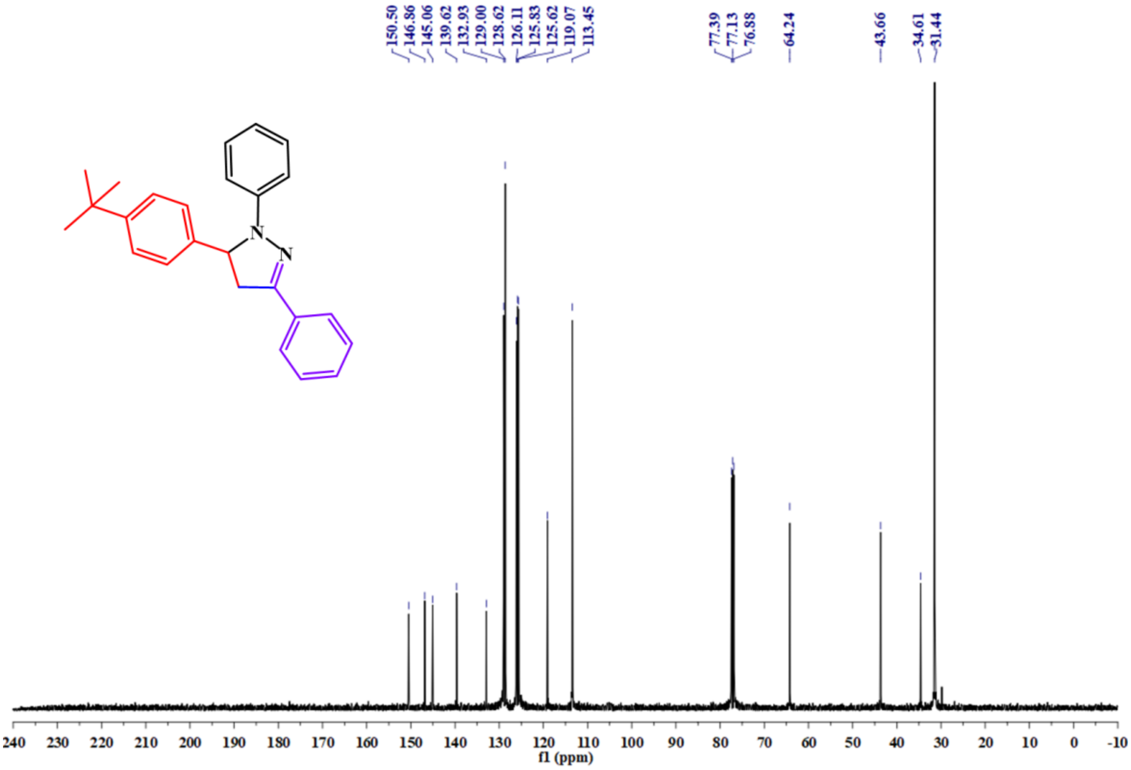


Fig. S37: ^{13}C NMR spectrum of **4f** in CDCl$_3$ at 126 MHz.

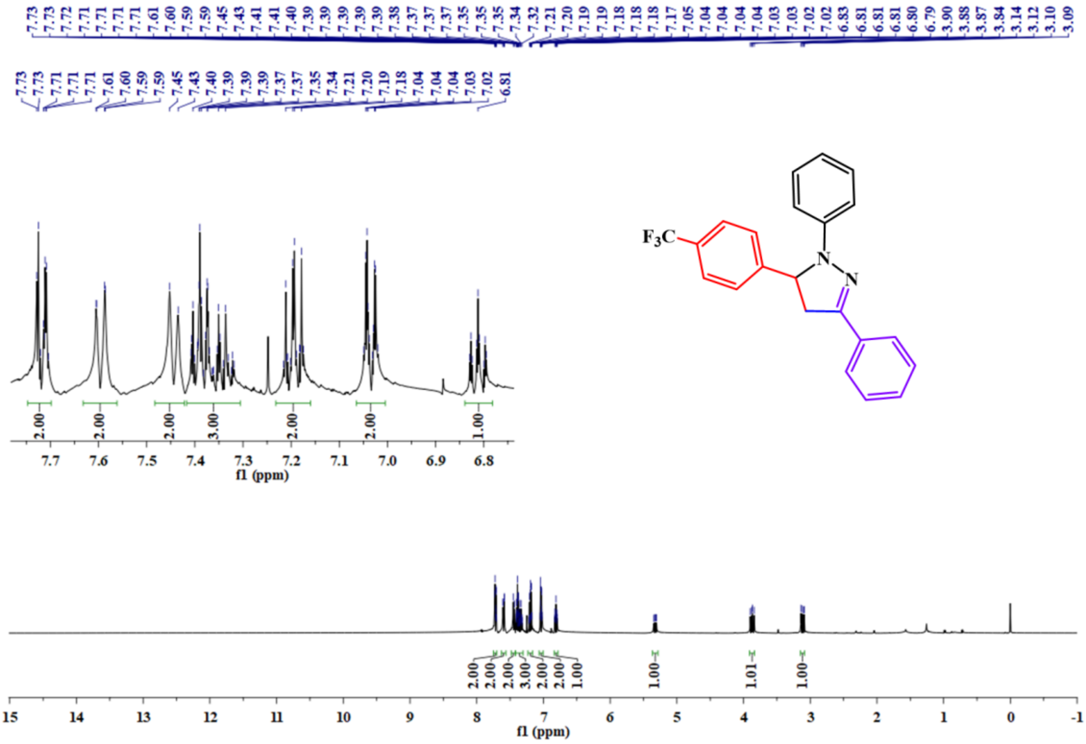


Fig. S38: ^{1}H NMR spectrum of **4g** in $CDCl_3$ at 500 MHz.

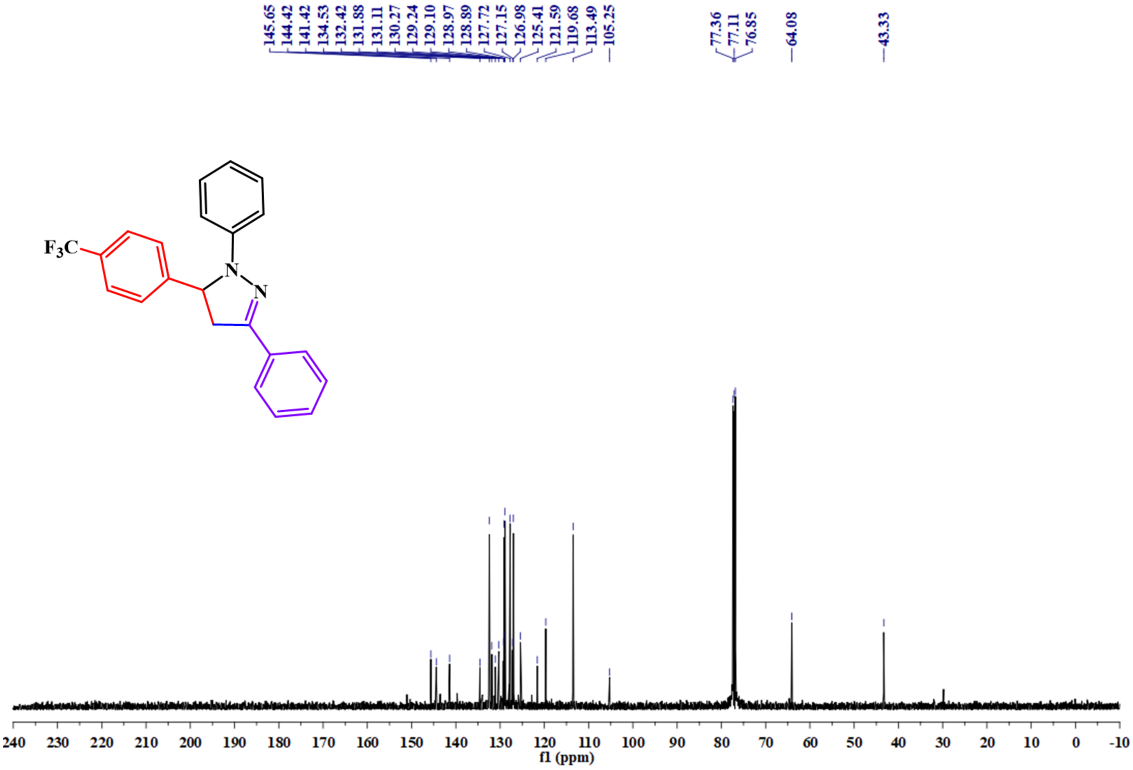


Fig. S39: ^{13}C NMR spectrum of **4g** in $CDCl_3$ at 126 MHz.

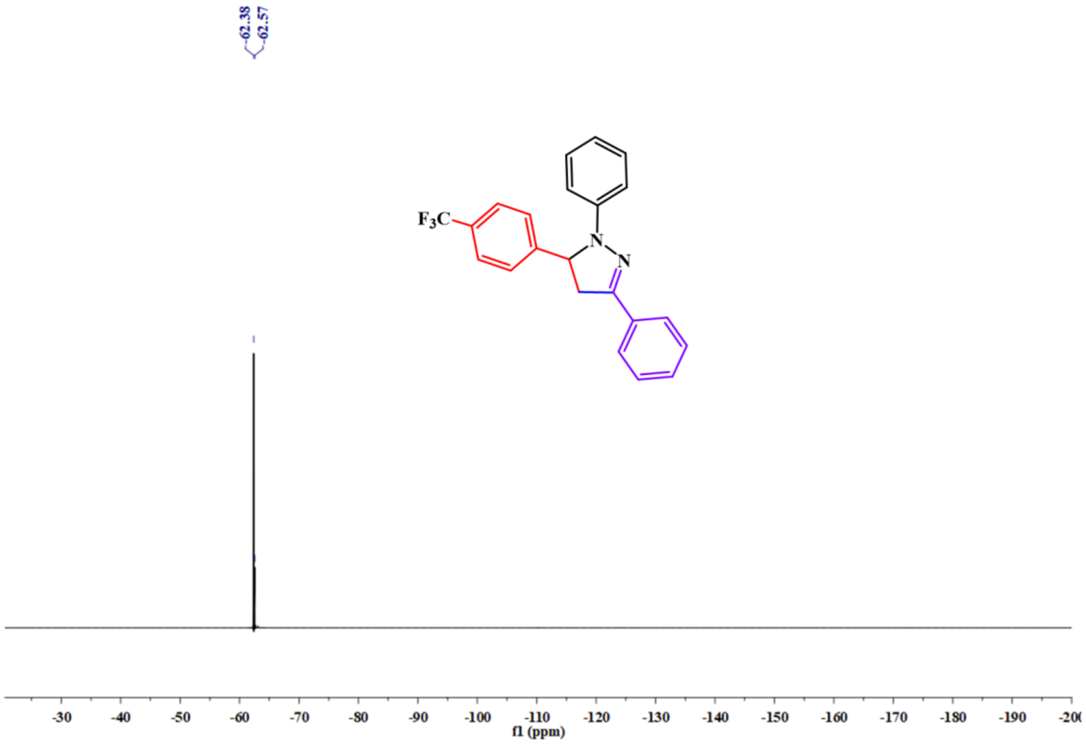


Fig. S40: ^{19}F NMR spectrum of **4g** in $CDCl_3$ at 471 MHz.

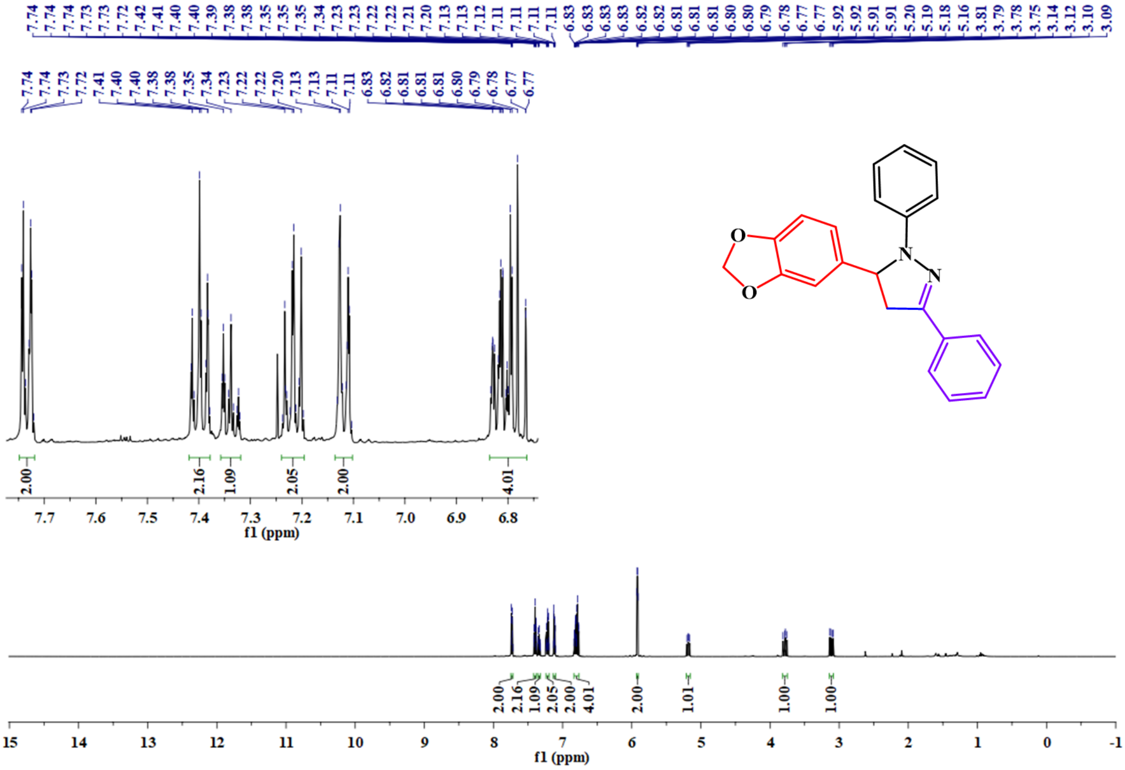


Fig. S41: ^{1}H NMR spectrum of **4h** in $CDCl_3$ at 500 MHz.

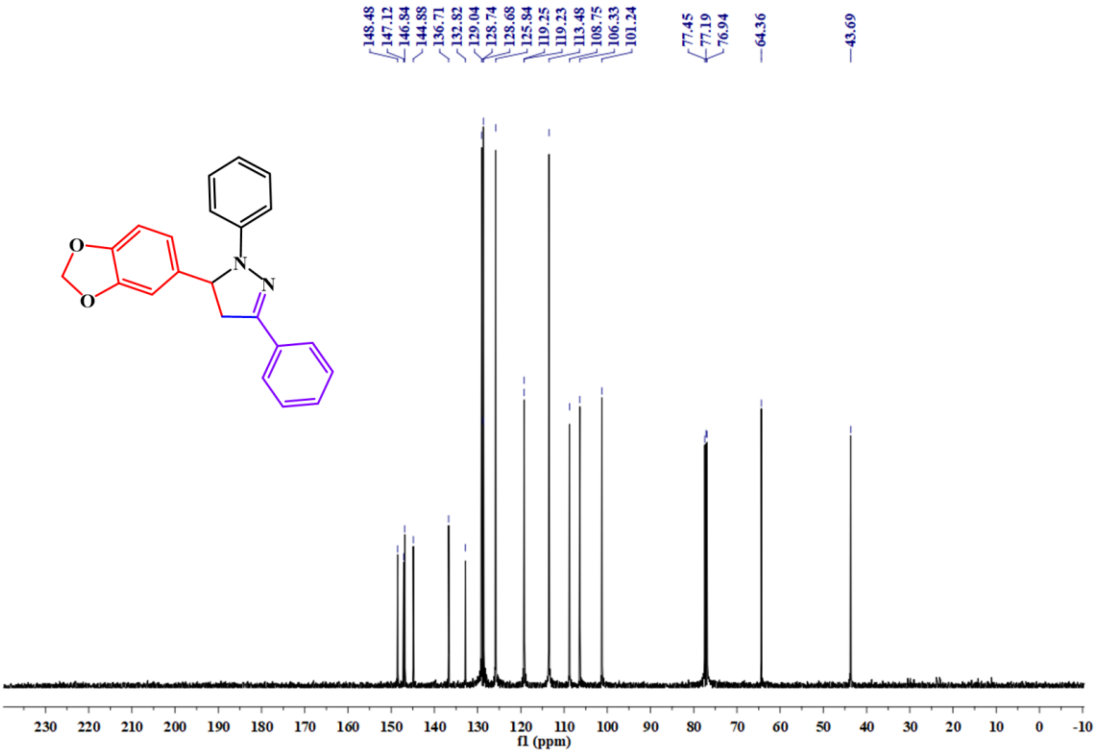


Fig. S42: ^{13}C NMR spectrum of **4h** in CDCl$_3$ at 126 MHz.

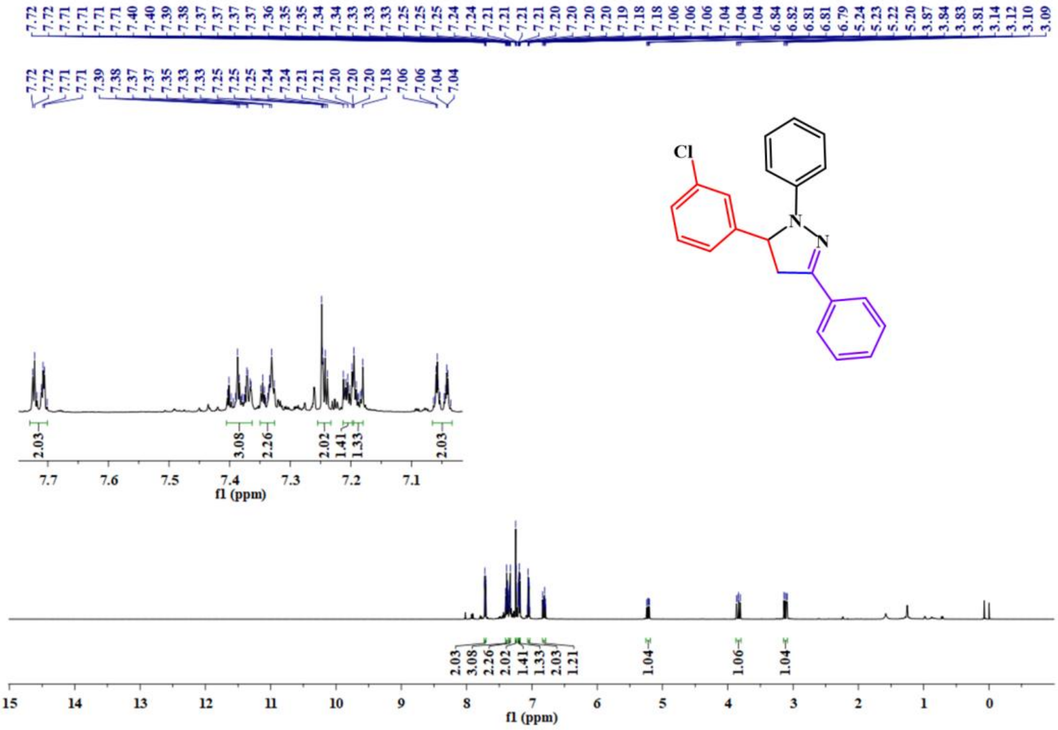


Fig. S43: ^{1}H NMR spectrum of **4i** in CDCl$_3$ at 500 MHz.

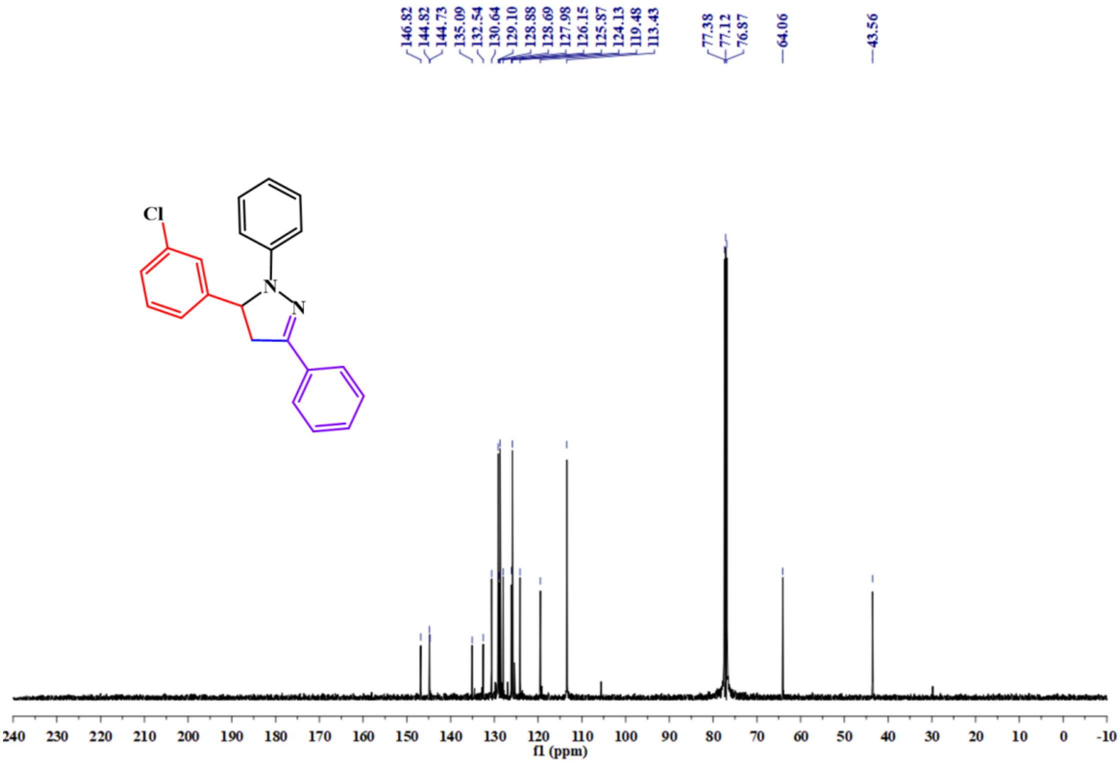


Fig. S44: ^{13}C NMR spectrum of **4i** in $CDCl_3$ at 126 MHz.

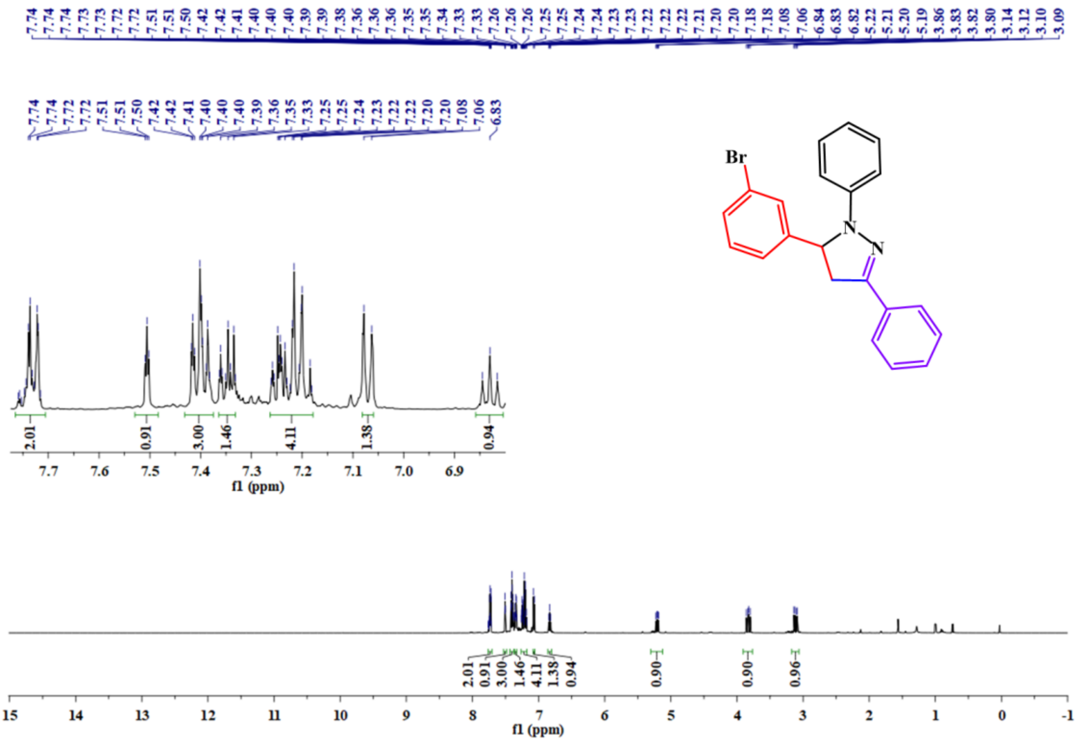


Fig. S45: ^{1}H NMR spectrum of **4j** in $CDCl_3$ at 500 MHz.

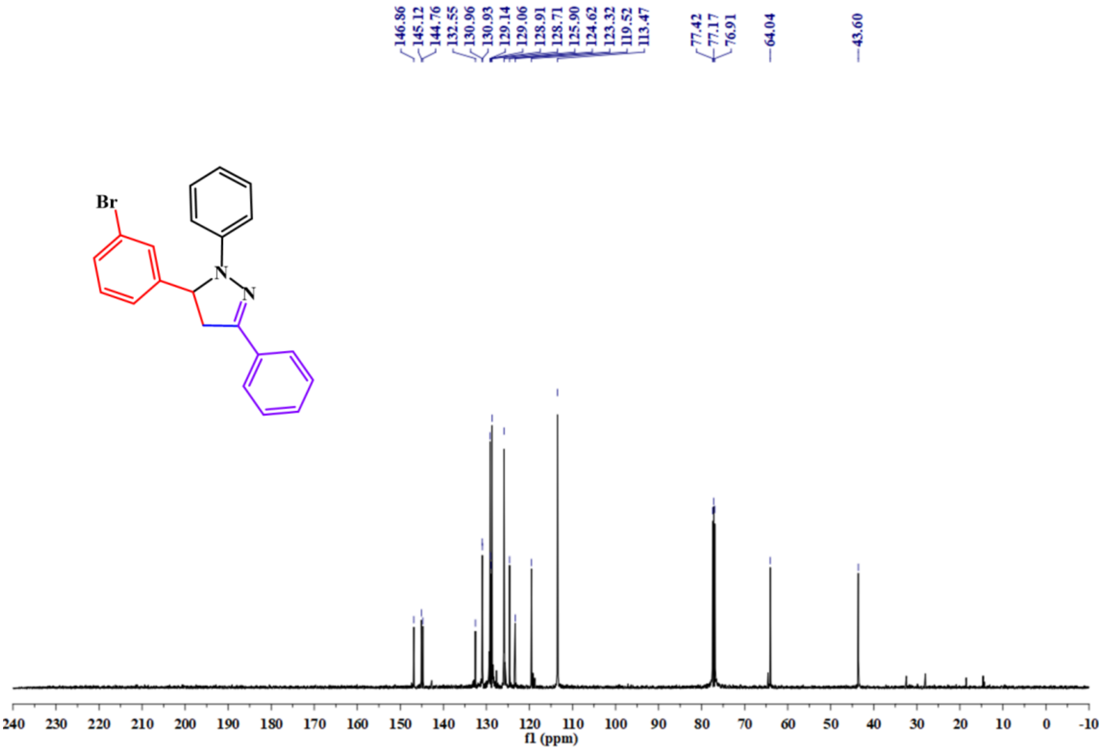


Fig. S46: ^{13}C NMR spectrum of **4j** in $CDCl_3$ at 126 MHz.

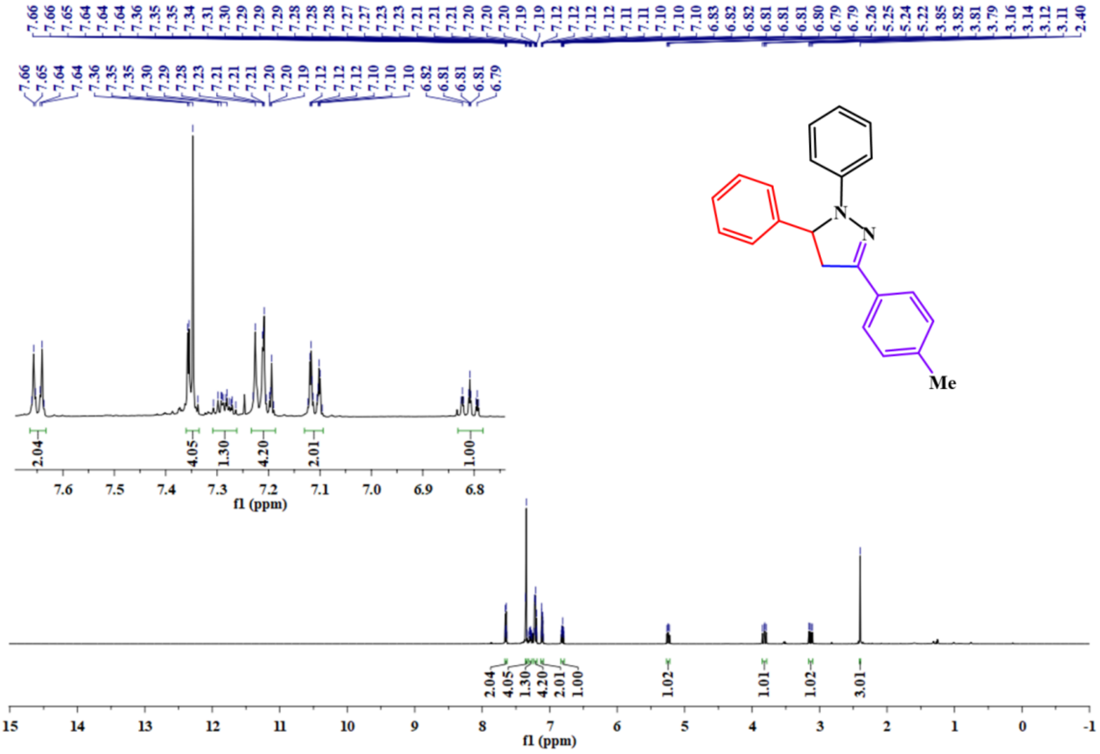


Fig. S47: ^{1}H NMR spectrum of **4k** in $CDCl_3$ at 500 MHz.

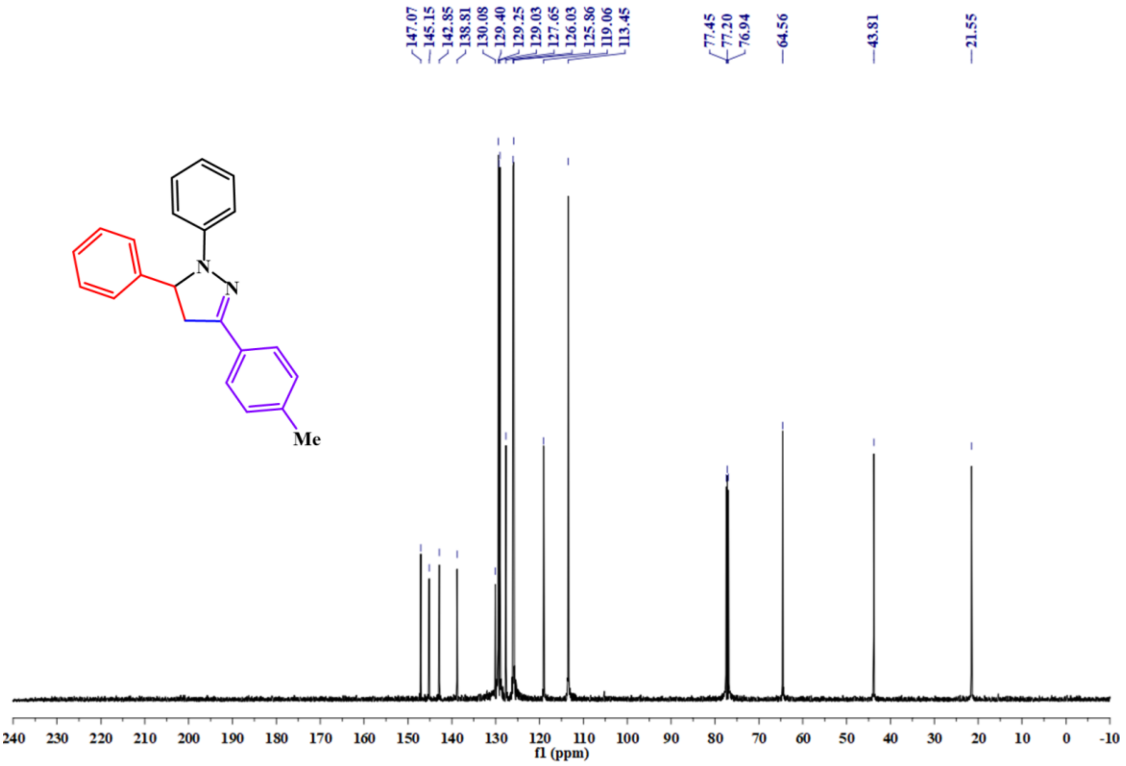


Fig. S48: ^{13}C NMR spectrum of **4k** in $CDCl_3$ at 126 MHz.

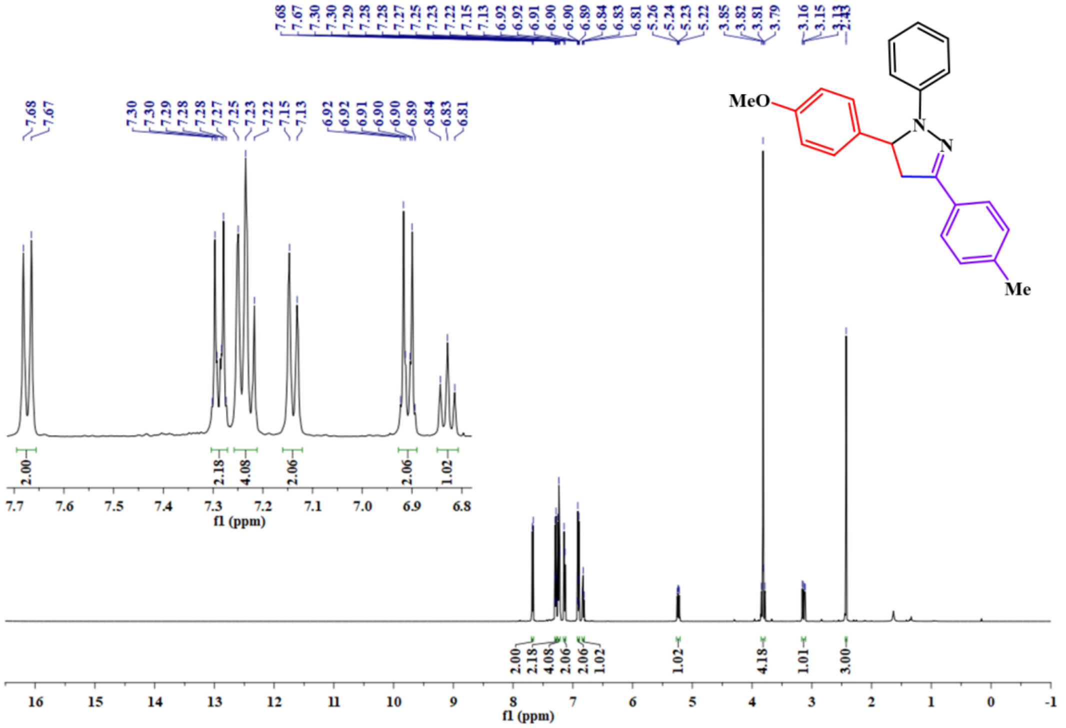


Fig. S49: ^{1}H NMR spectrum of **4l** in $CDCl_3$ at 500 MHz.

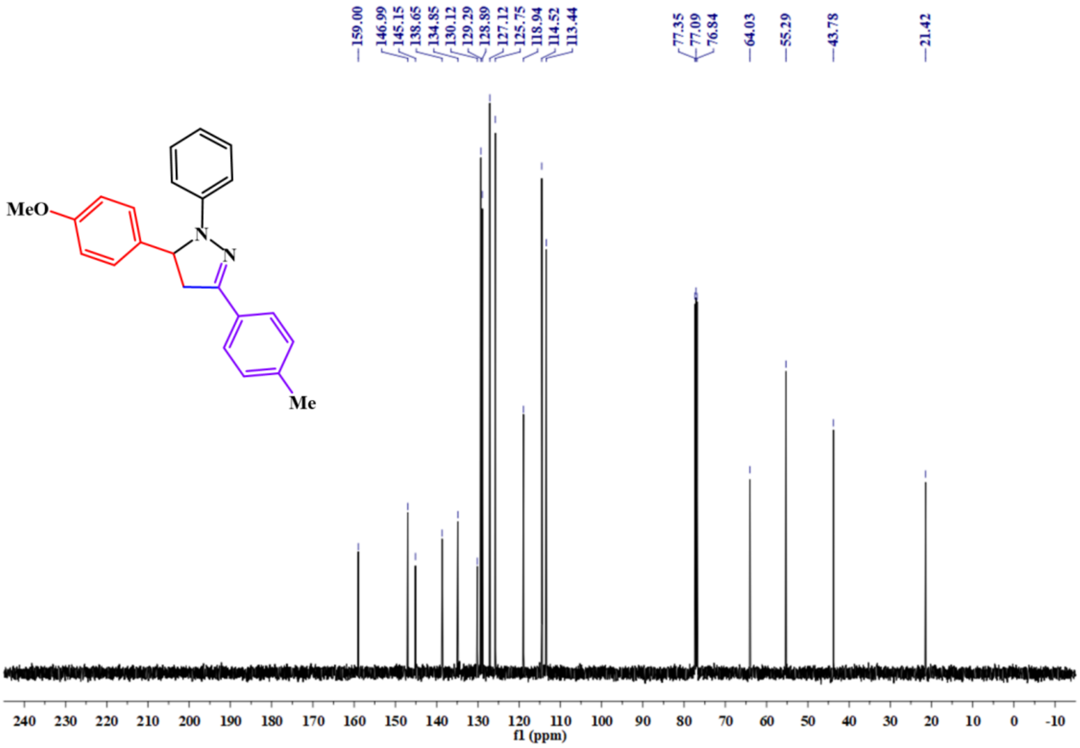


Fig. S50: ^{13}C NMR spectrum of **4l** in $CDCl_3$ at 126 MHz.

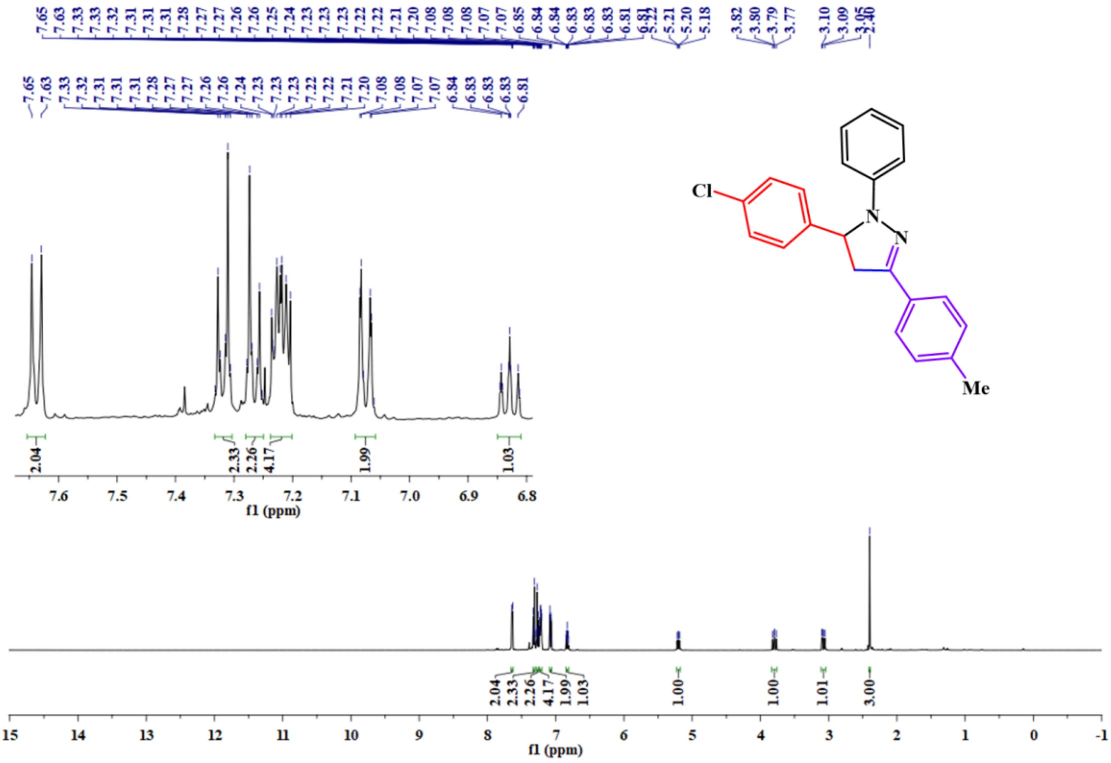


Fig. S51: ^{1}H NMR spectrum of **4m** in $CDCl_3$ at 500 MHz.

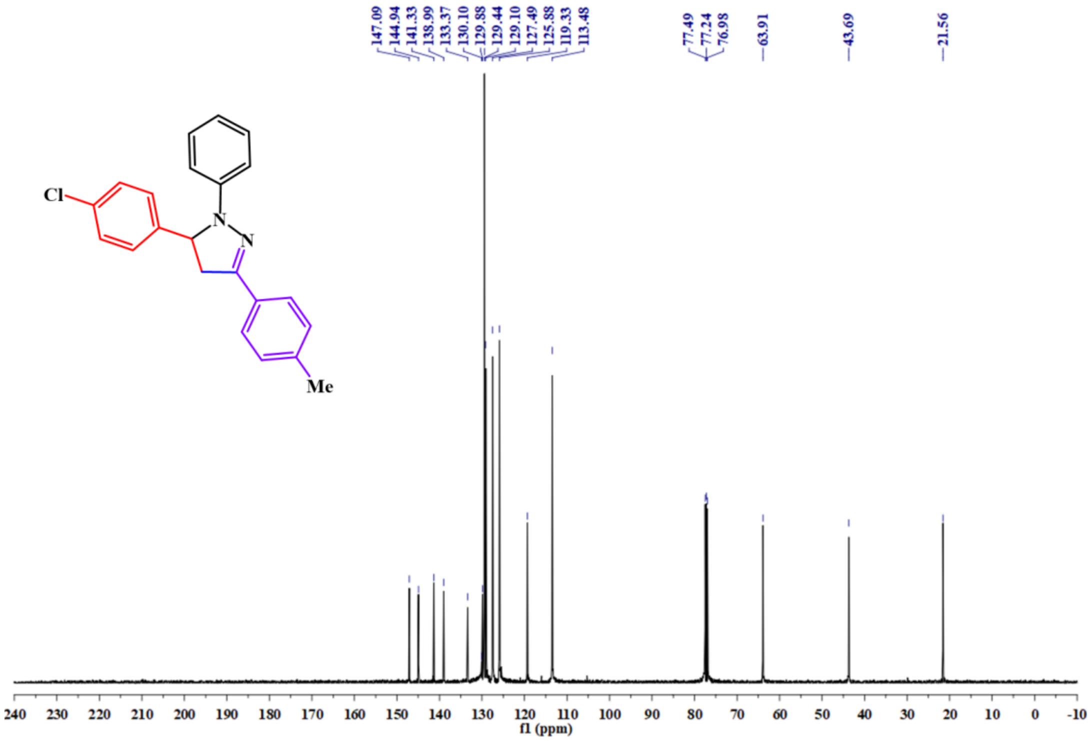


Fig. S52: ^{13}C NMR spectrum of **4m** in CDCl$_3$ at 126 MHz.

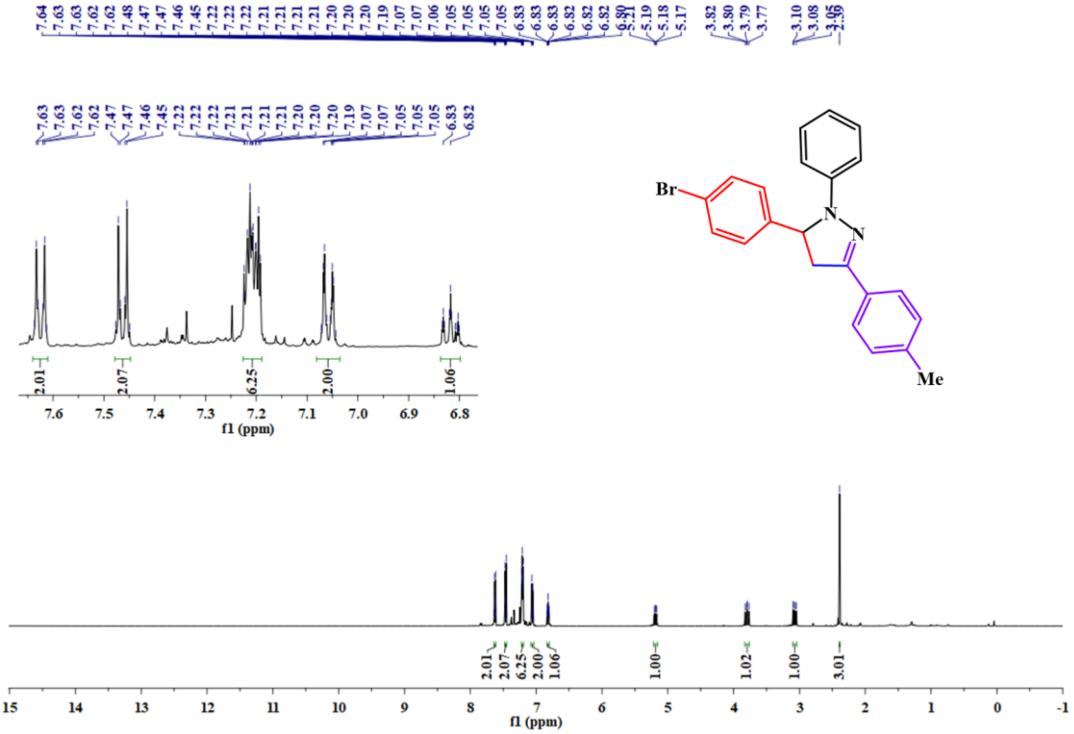


Fig. S53: ^{1}H NMR spectrum of **4n** in CDCl$_3$ at 500 MHz.

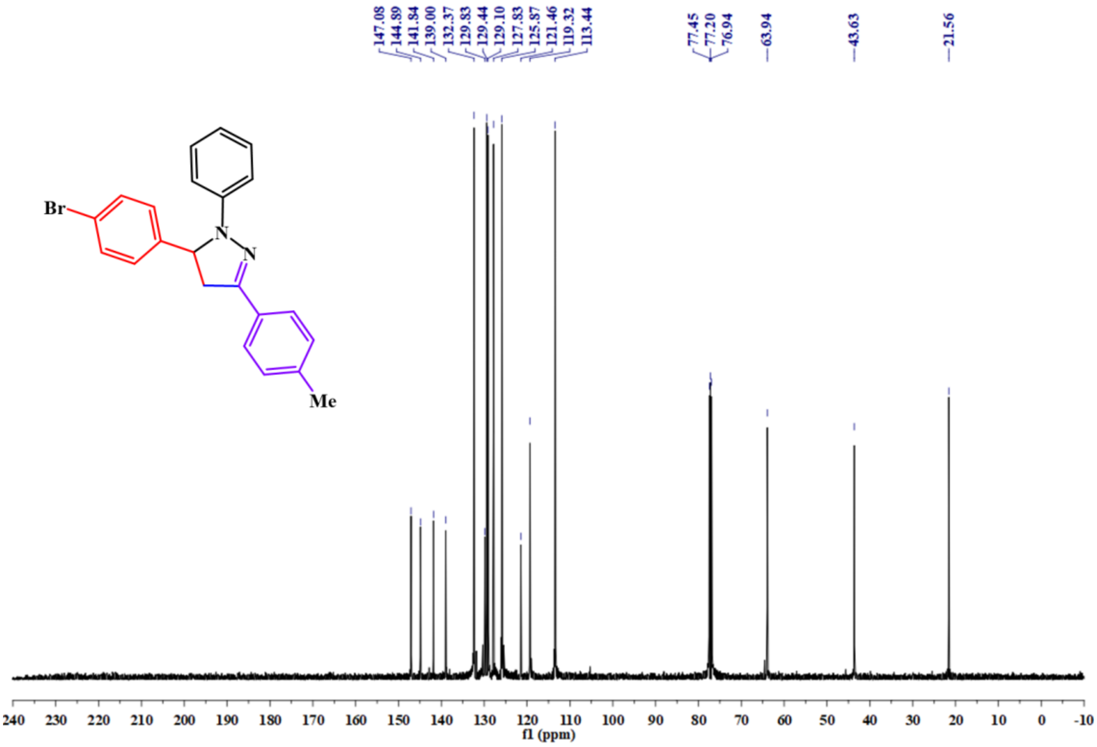


Fig. S54: ^{13}C NMR spectrum of **4n** in CDCl$_3$ at 126 MHz.

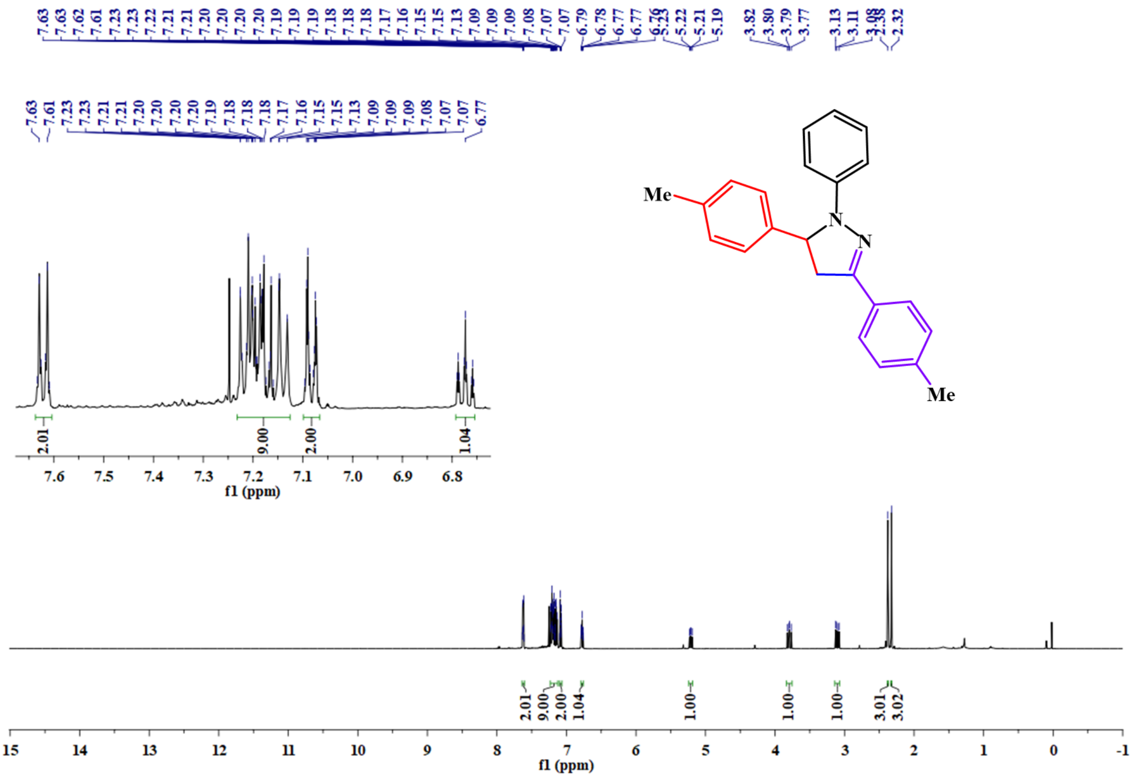


Fig. S55: ^{1}H NMR spectrum of **4o** in CDCl$_3$ at 500 MHz.

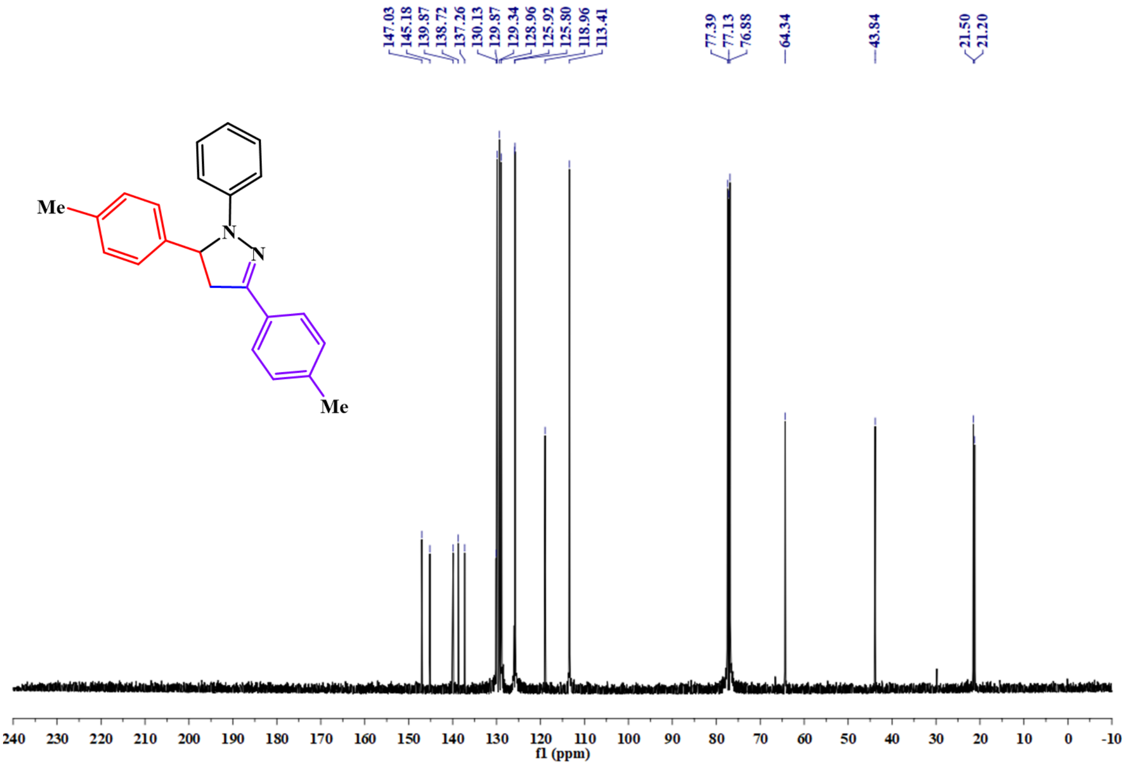


Fig. S56: ^{13}C NMR spectrum of **4o** in $CDCl_3$ at 126 MHz.

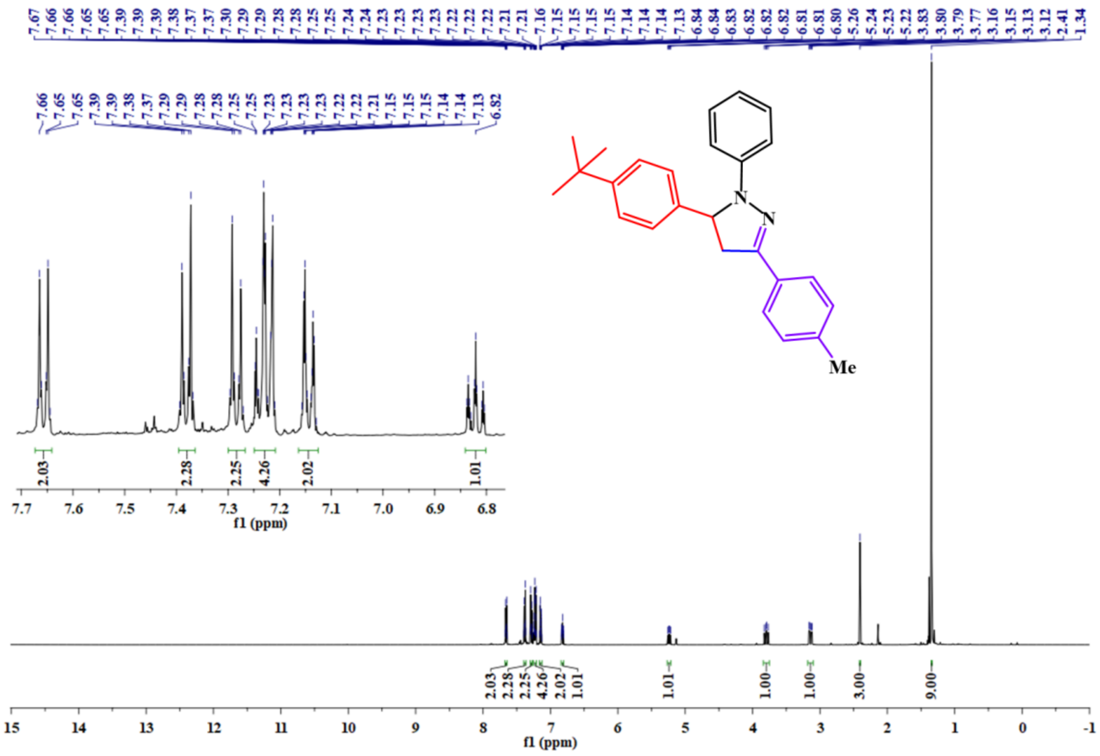


Fig. S57: ^{1}H NMR spectrum of **4p** in $CDCl_3$ at 500 MHz.

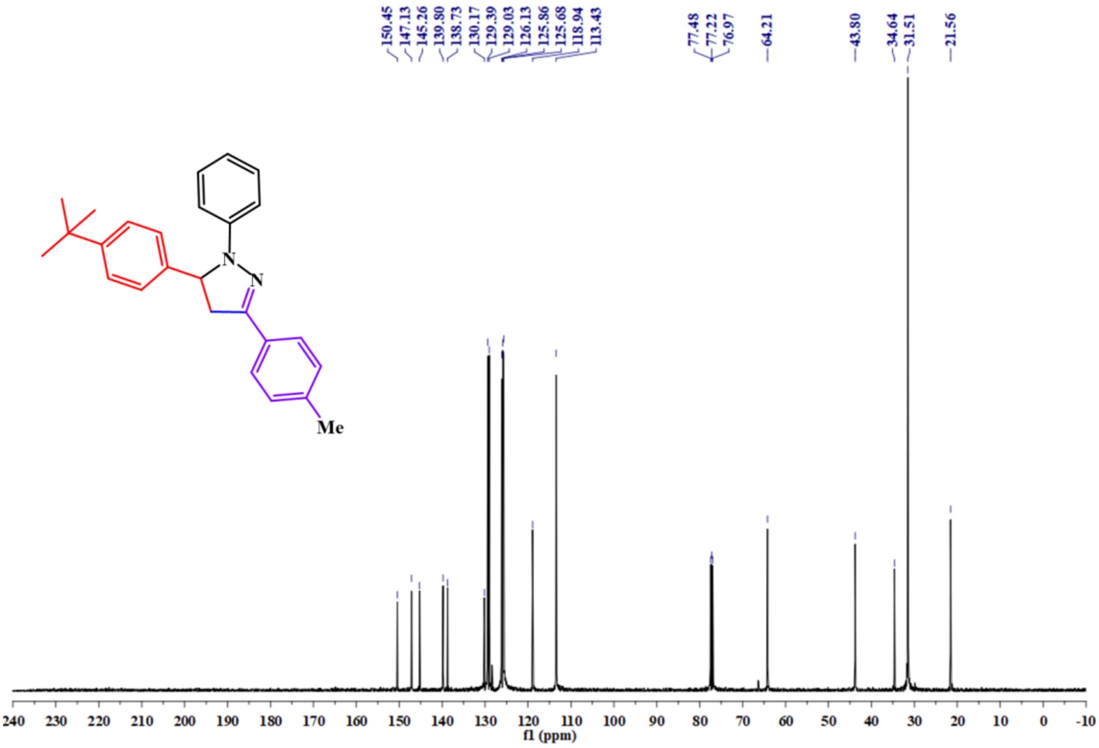


Fig. S58: ^{13}C NMR spectrum of **4p** in CDCl$_3$ at 126 MHz.

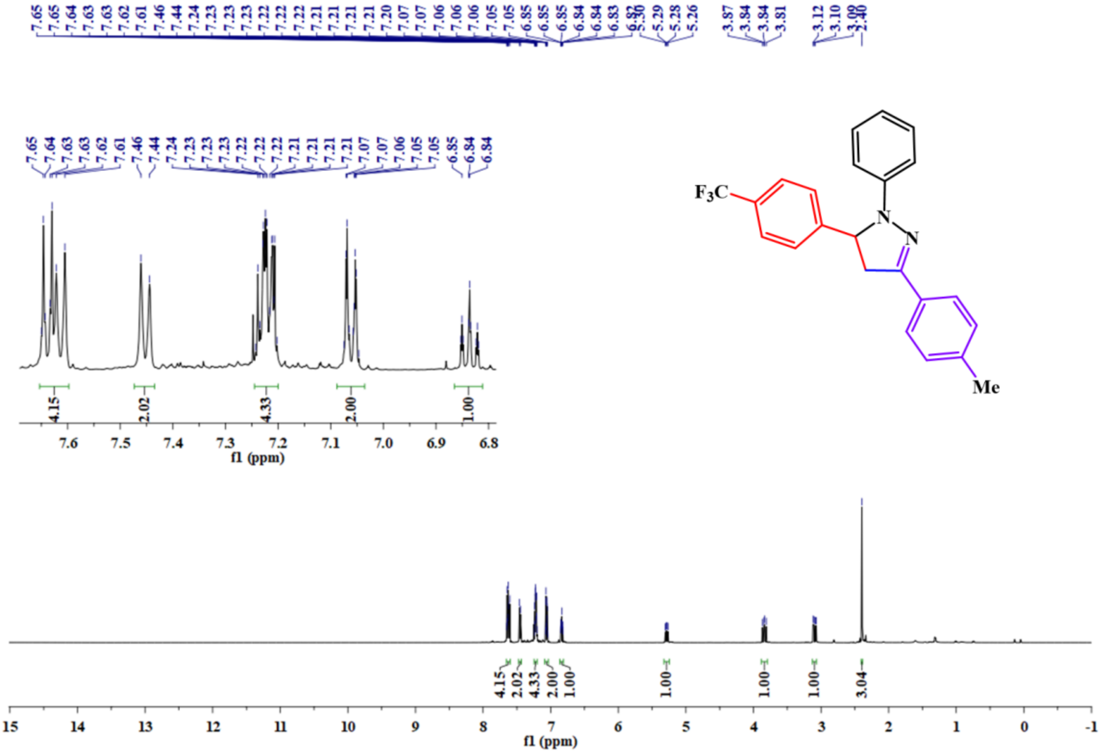


Fig. S59: ^{1}H NMR spectrum of **4q** in CDCl$_3$ at 500 MHz.

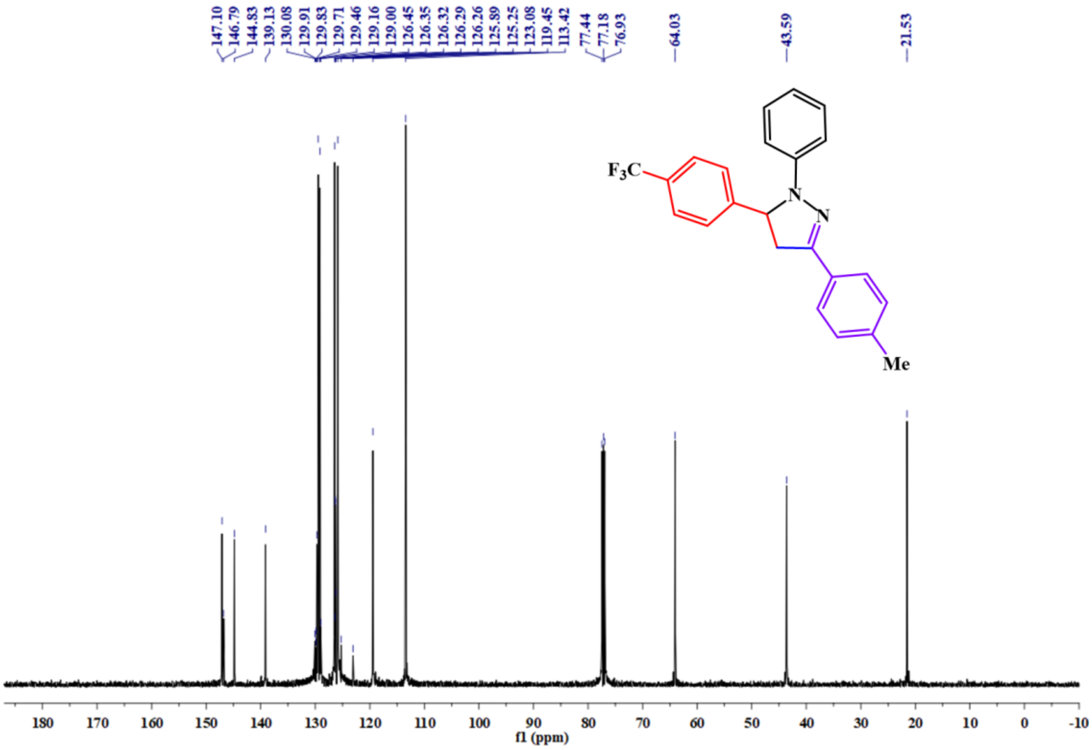


Fig. S60: ^{13}C NMR spectrum of **4q** in $CDCl_3$ at 126 MHz.

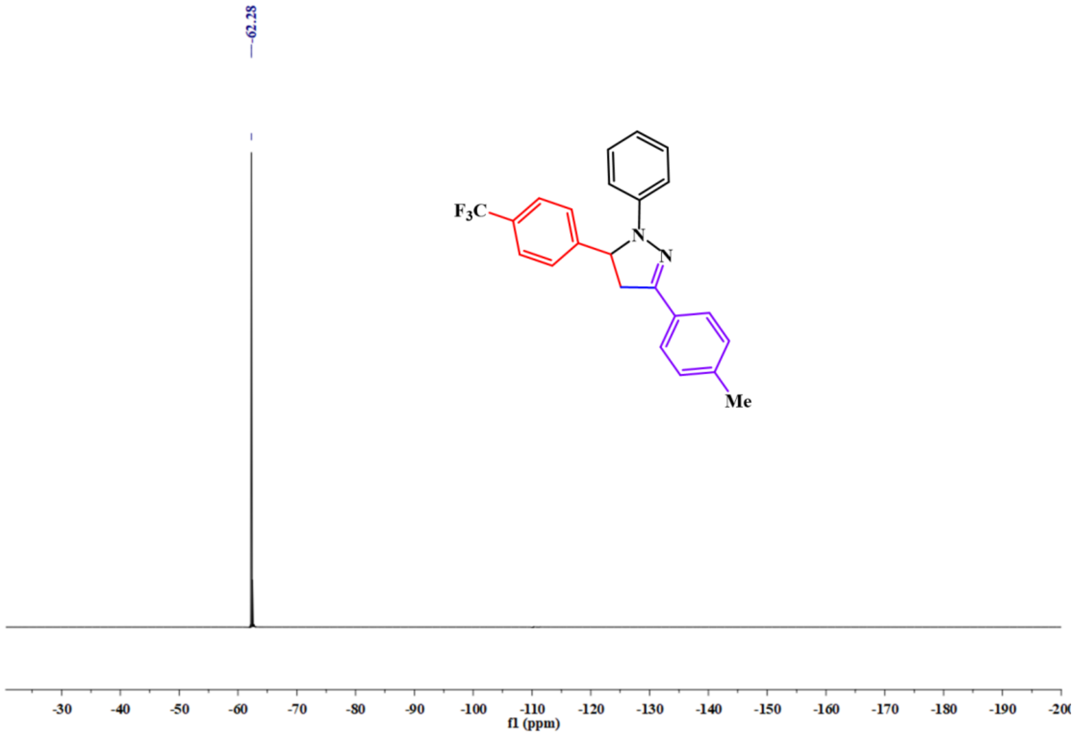


Fig. S61: ^{19}F NMR spectrum of **4q** in $CDCl_3$ at 471 MHz.

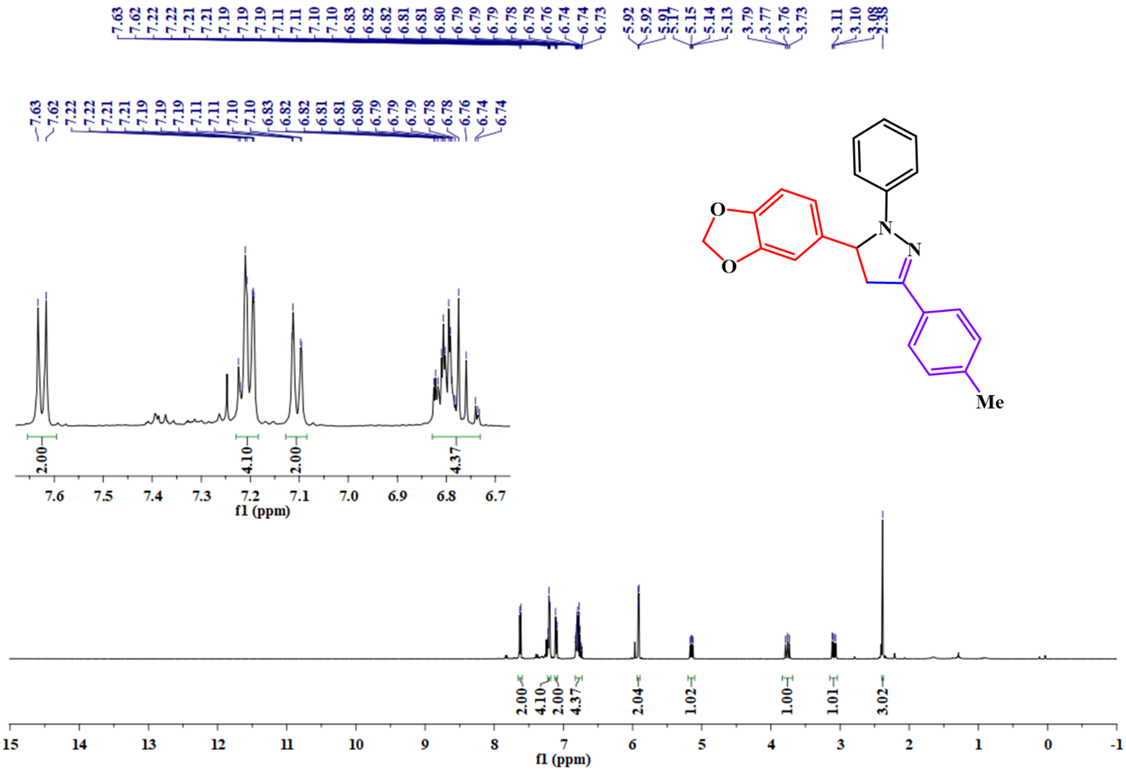


Fig. S62: ^{1}H NMR spectrum of **4r** in $CDCl_3$ at 500 MHz.

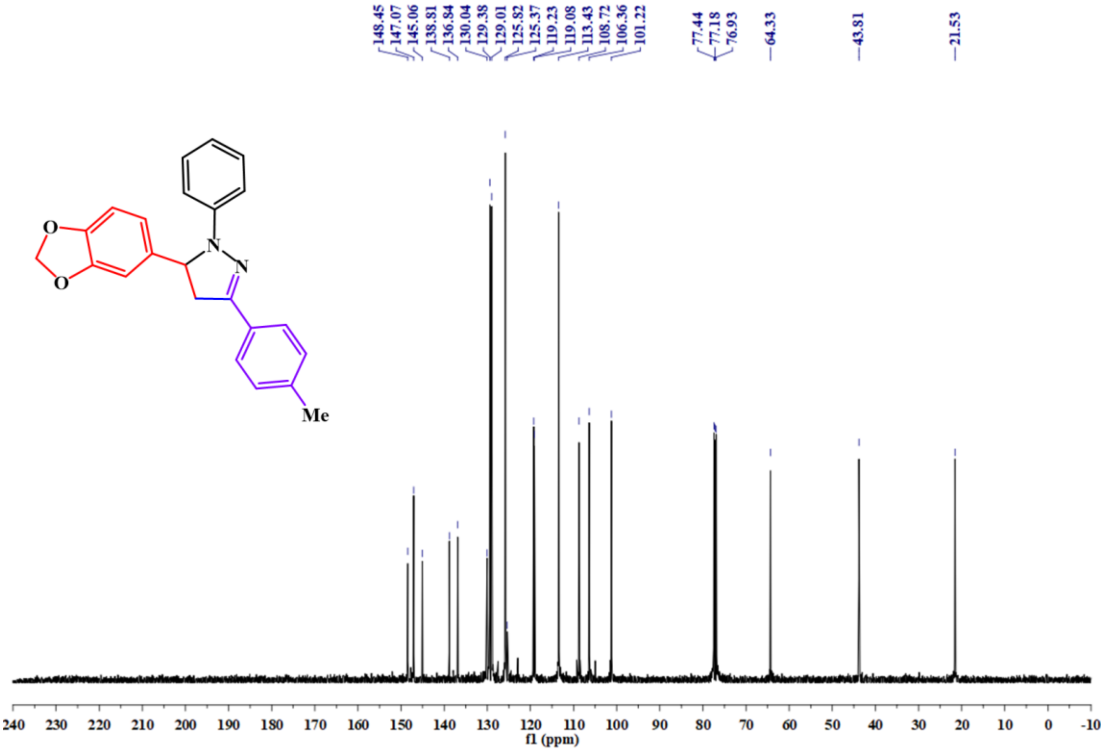


Fig. S63: ^{13}C NMR spectrum of **4r** in $CDCl_3$ at 126 MHz.

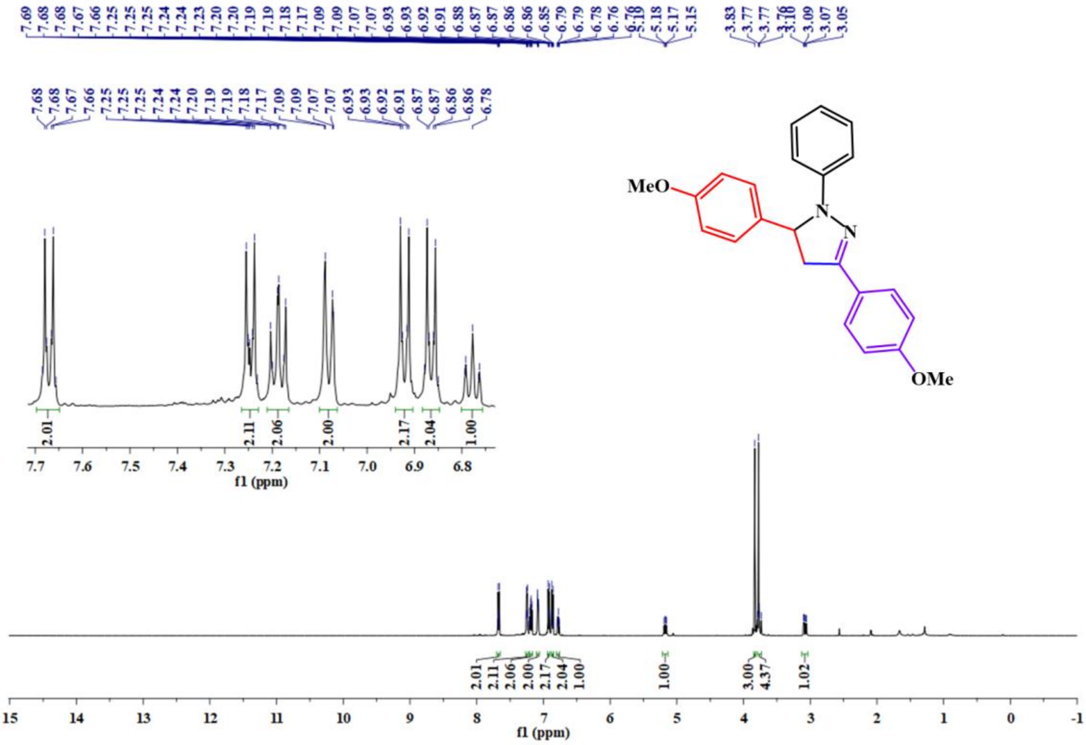


Fig. S64: ^{1}H NMR spectrum of **4s** in $CDCl_3$ at 500 MHz.

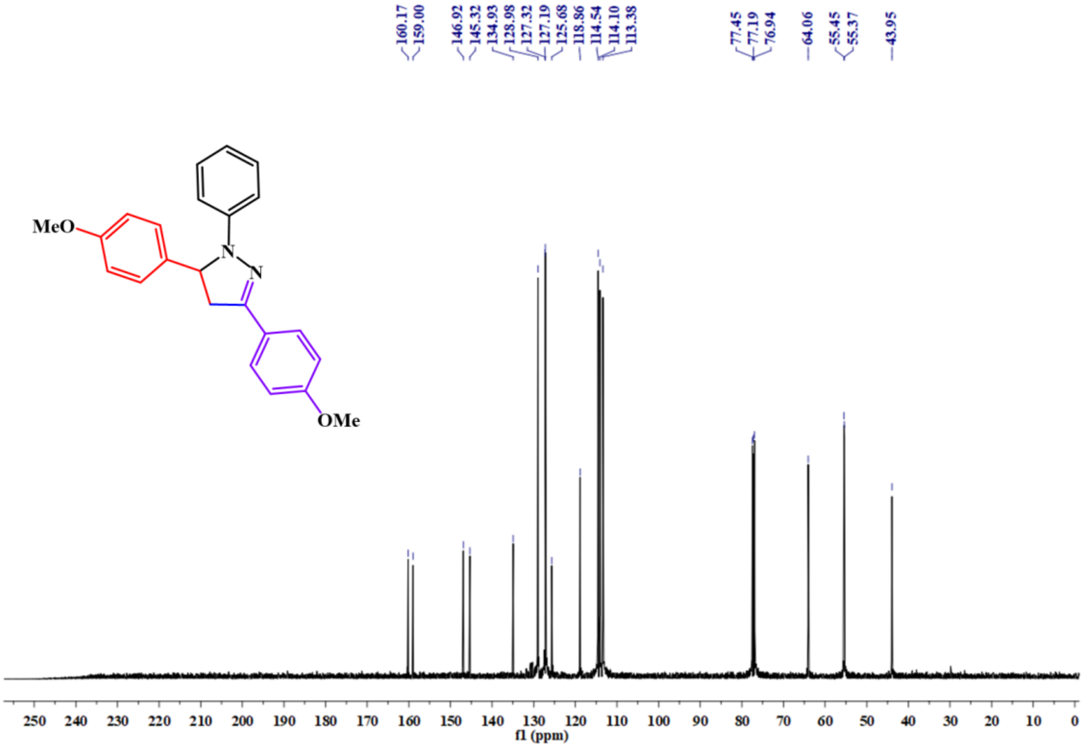


Fig. S65: ^{13}C NMR spectrum of **4s** in $CDCl_3$ at 126 MHz.

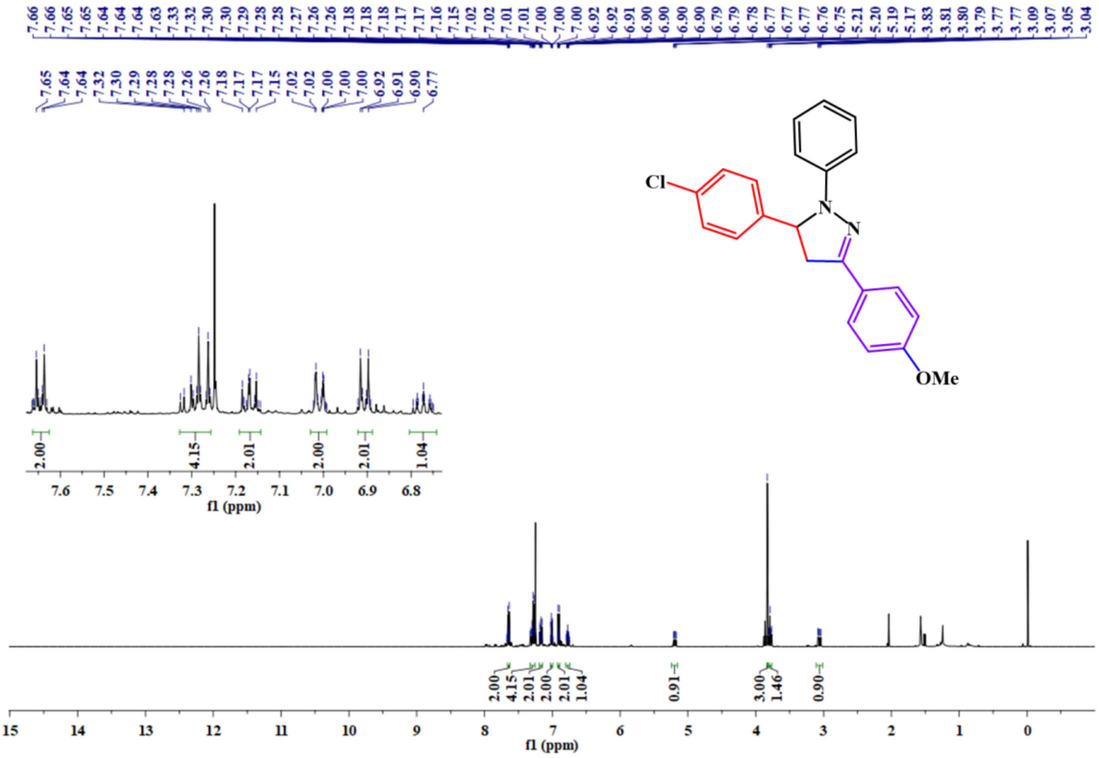


Fig. S66: ^{1}H NMR spectrum of **4t** in $CDCl_3$ at 500 MHz.

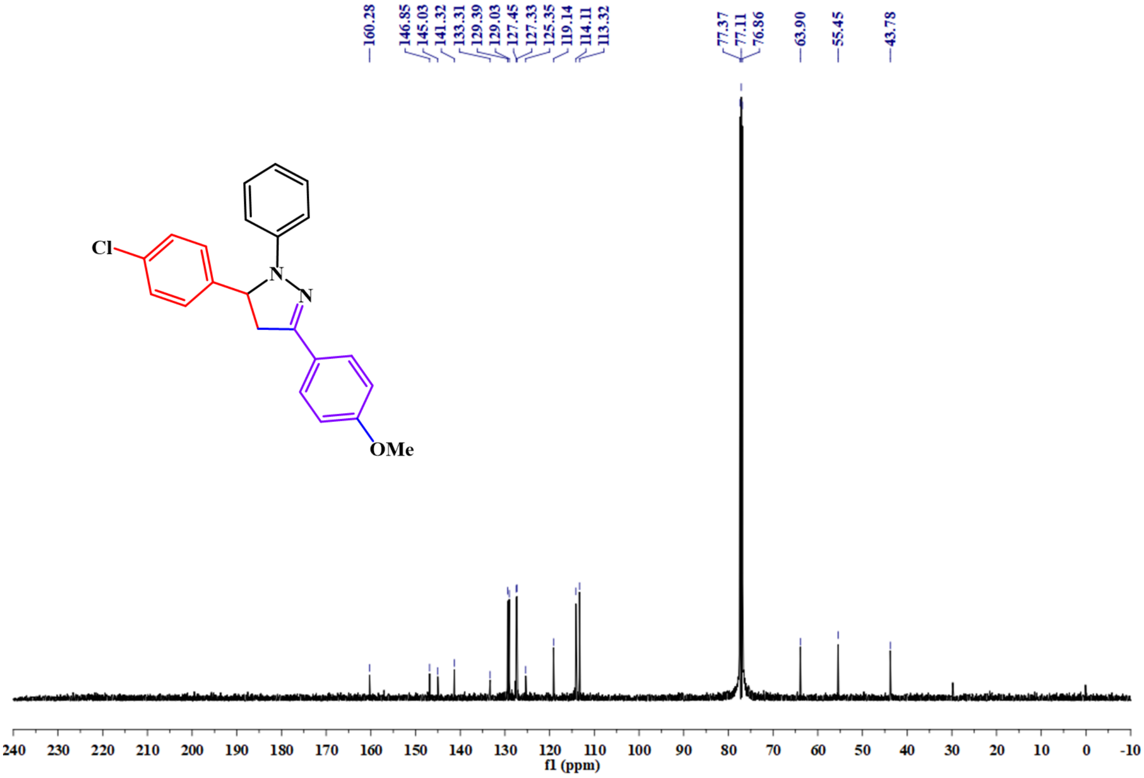


Fig. S67: ^{13}C NMR spectrum of **4t** in $CDCl_3$ at 126 MHz.

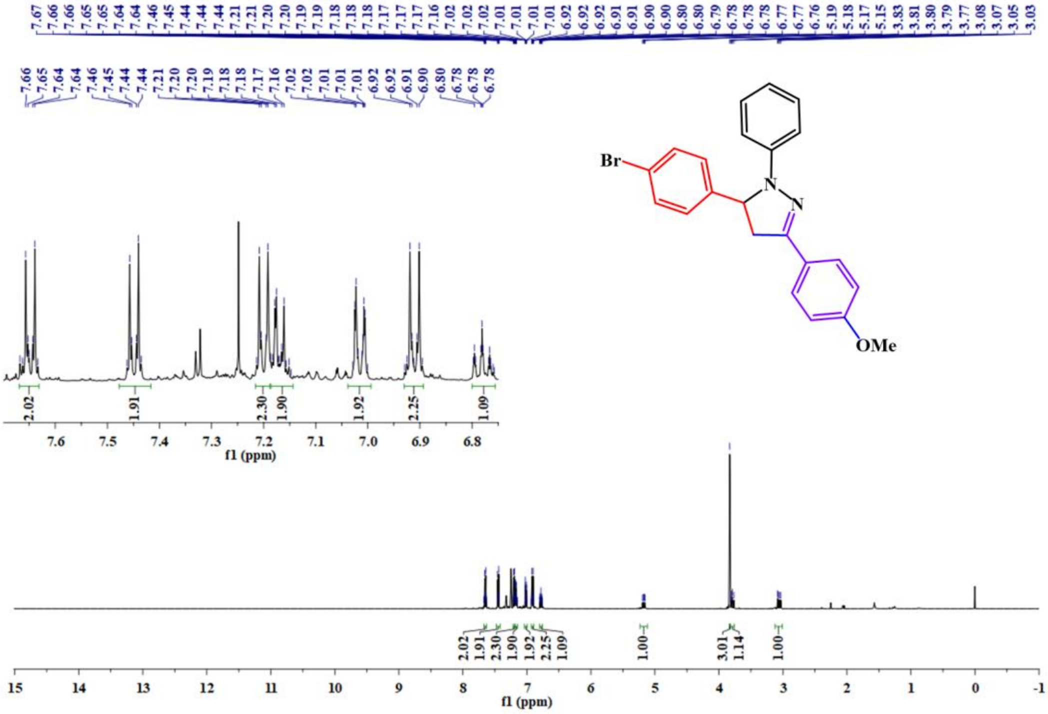


Fig. S68: ^{1}H NMR spectrum of **4u** in $CDCl_3$ at 500 MHz.

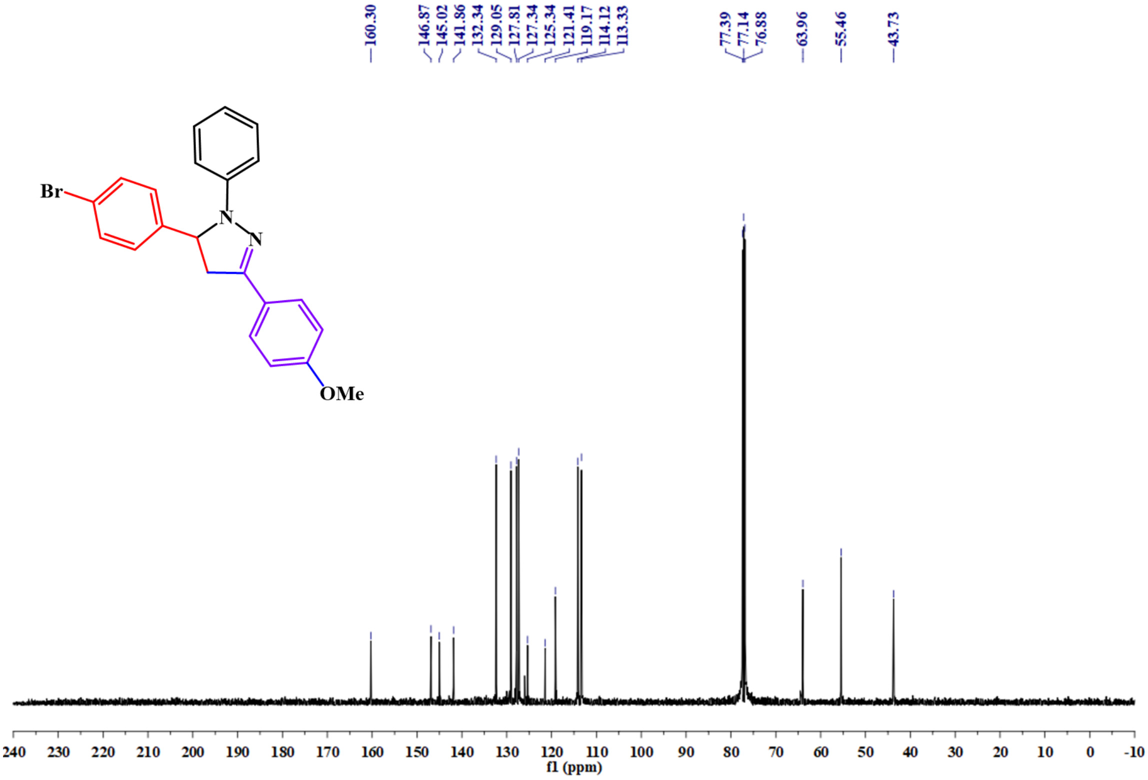


Fig. S69: ^{13}C NMR spectrum of **4u** in $CDCl_3$ at 126 MHz.

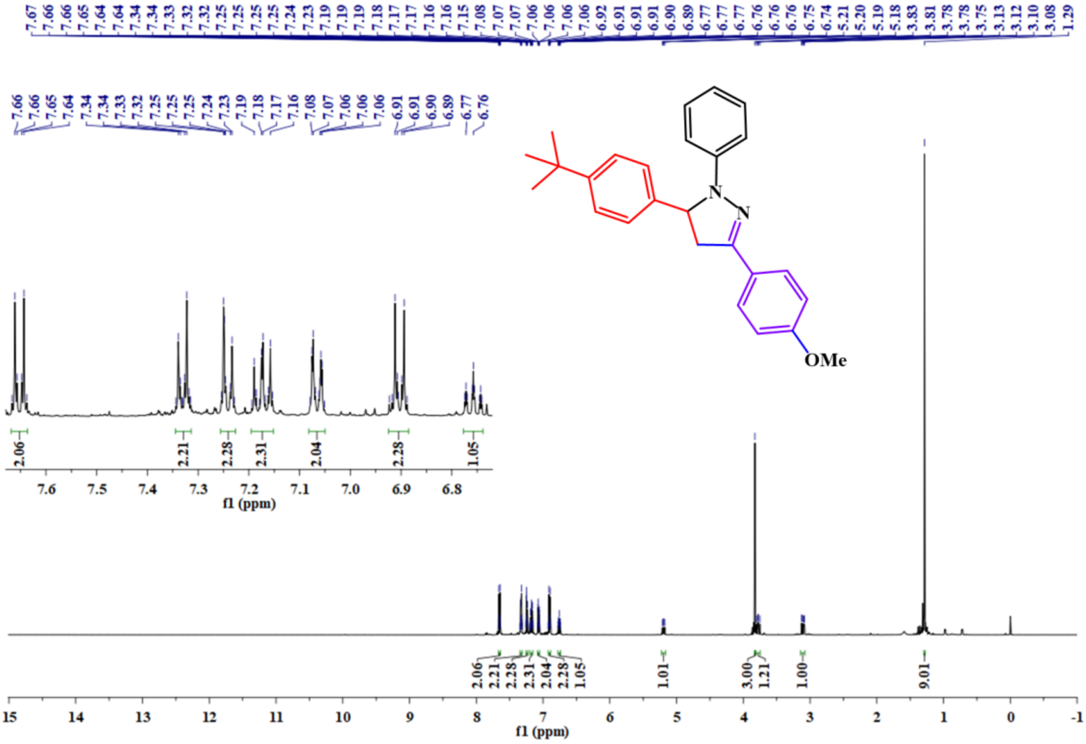


Fig. S70: ^{1}H NMR spectrum of **4v** in $CDCl_3$ at 500 MHz.

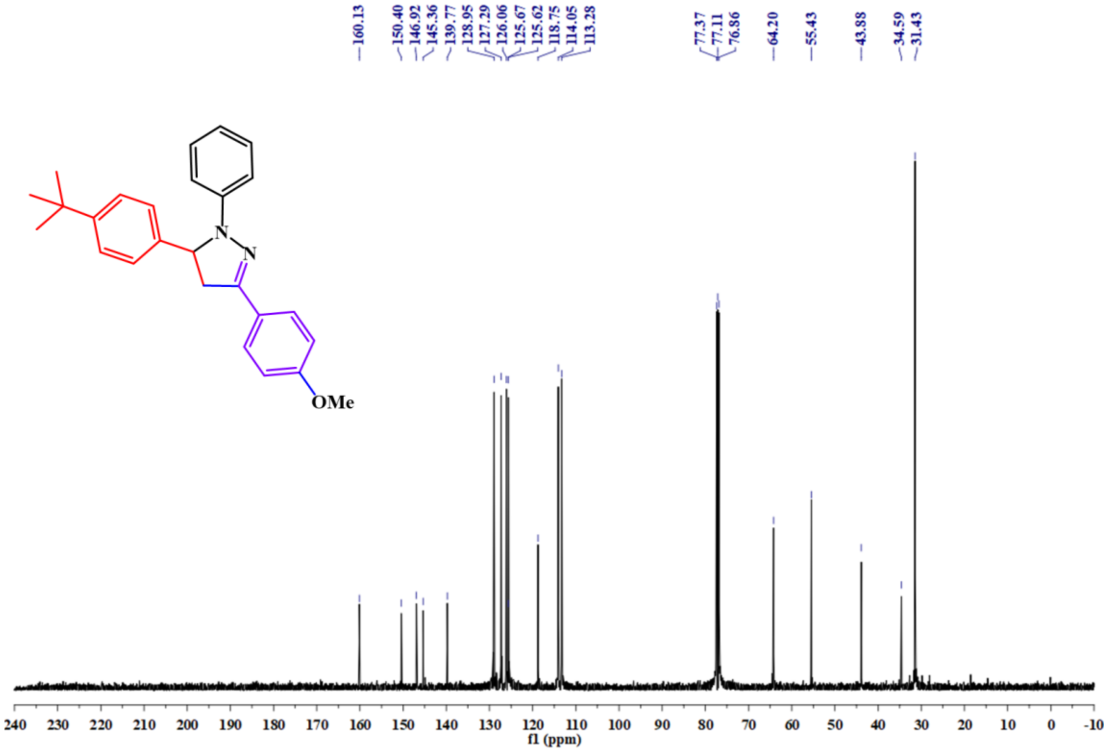


Fig. S71: ^{13}C NMR spectrum of **4v** in $CDCl_3$ at 126 MHz.

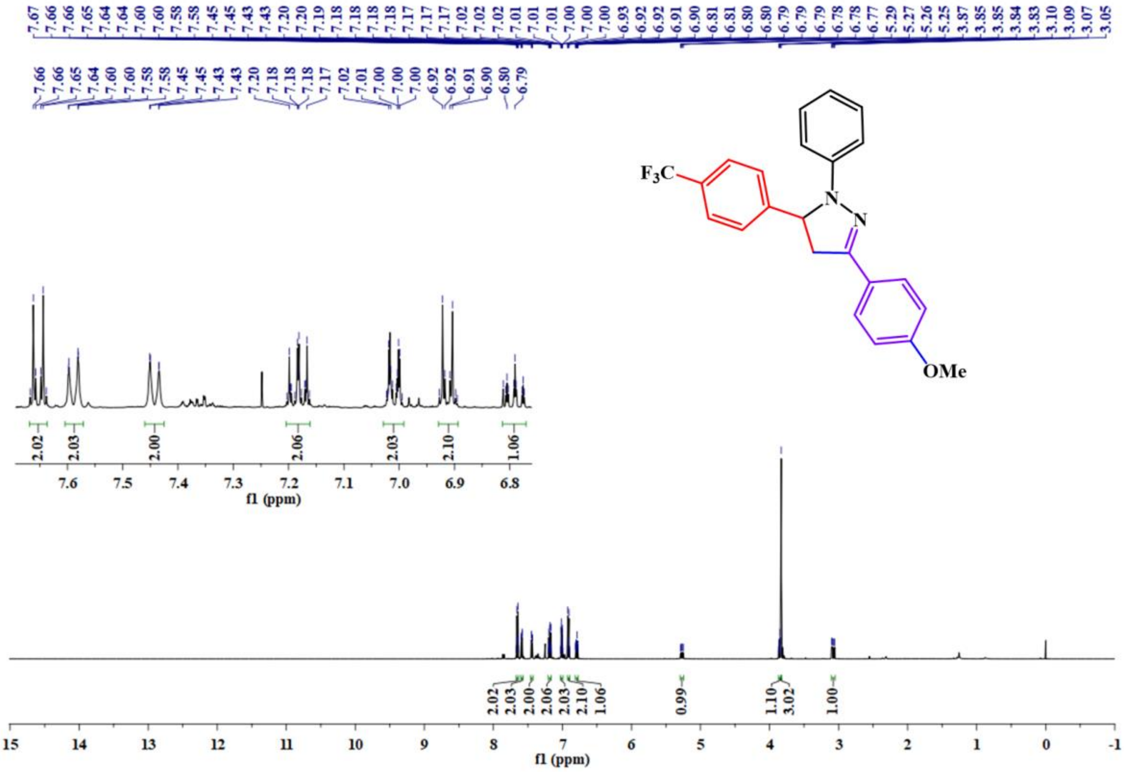


Fig. S72: ^{1}H NMR spectrum of **4w** in $CDCl_3$ at 500 MHz.

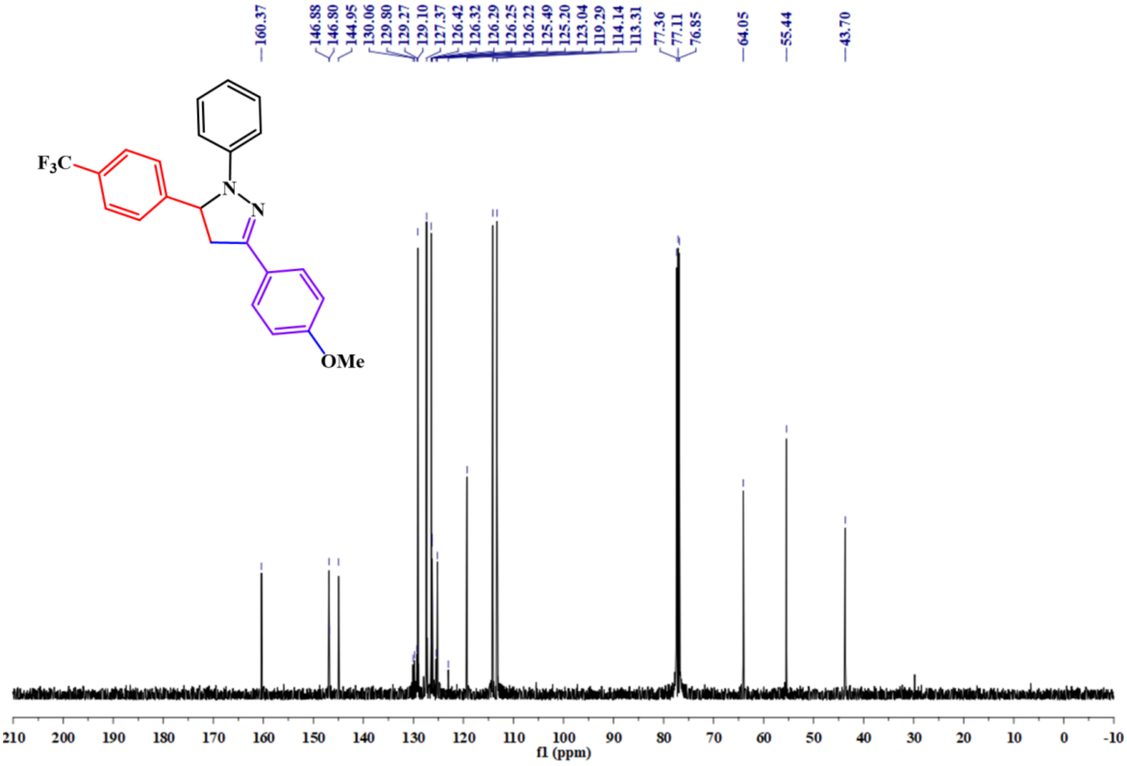


Fig. S73: ^{13}C NMR spectrum of **4w** in $CDCl_3$ at 126 MHz.

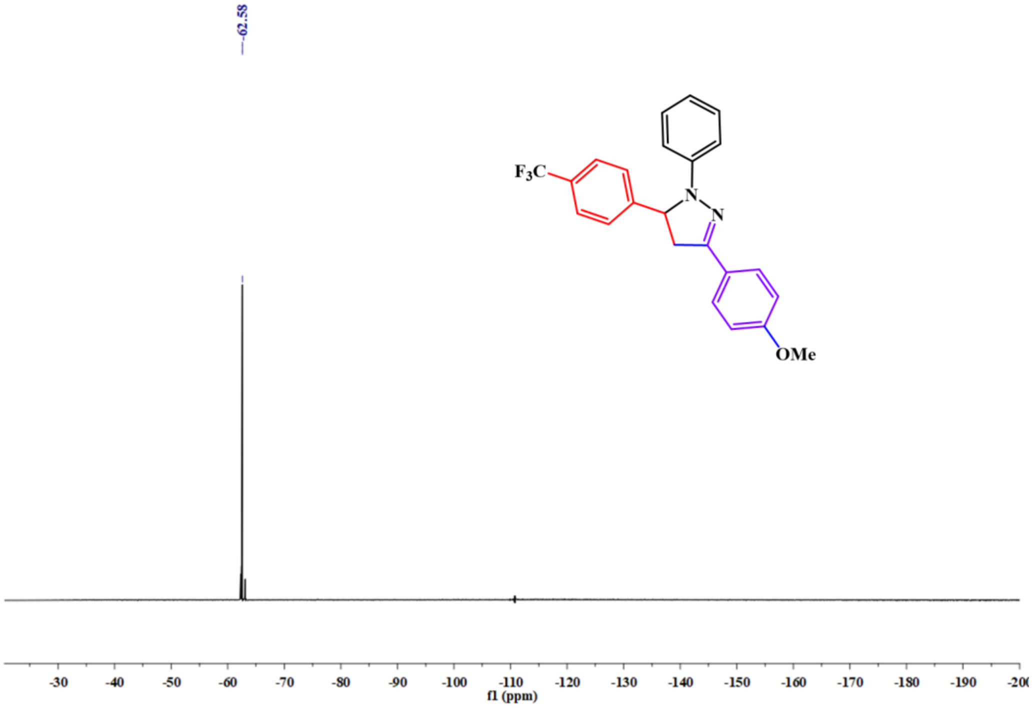


Fig. S74: ^{19}F NMR spectrum of **4w** in $CDCl_3$ at 471 MHz.

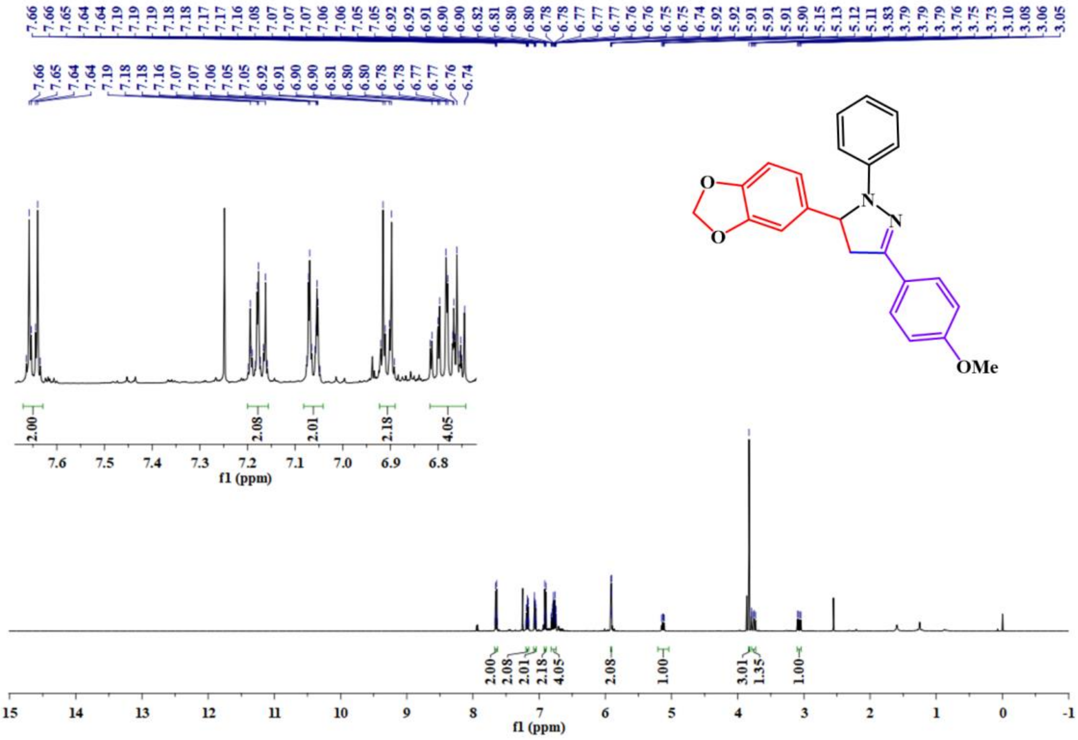


Fig. S75: ^{1}H NMR spectrum of **4x** in $CDCl_3$ at 500 MHz.

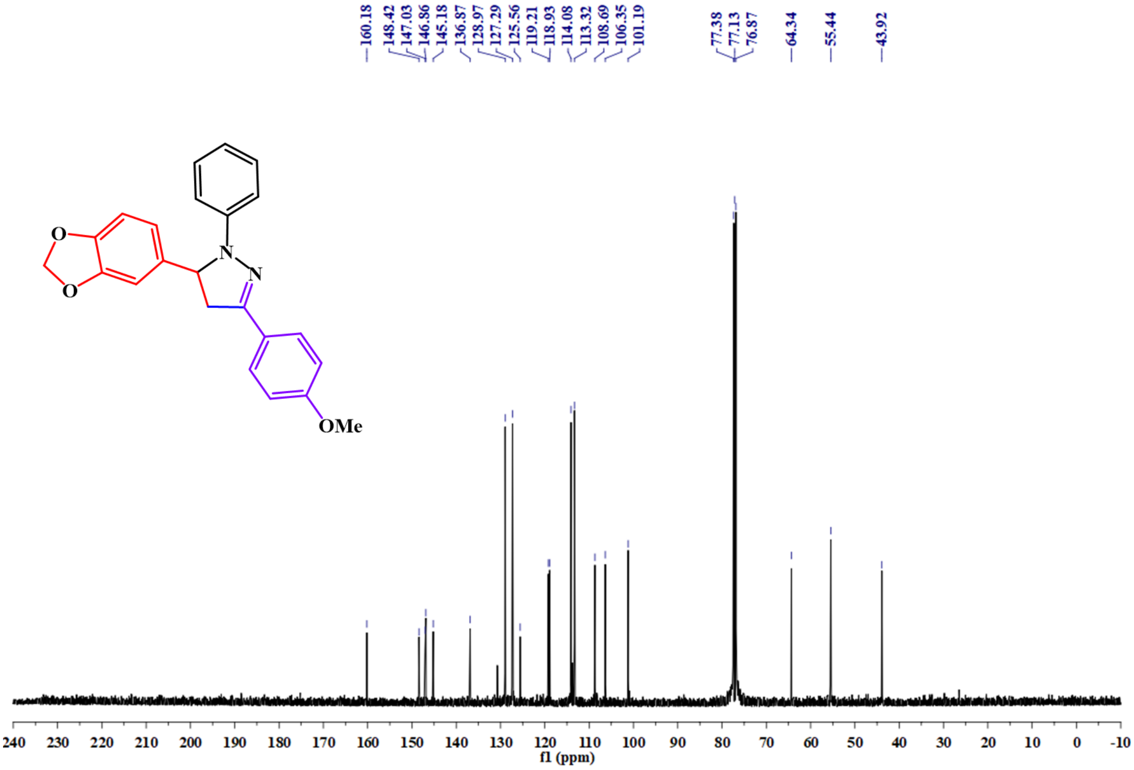


Fig. S76: ^{13}C NMR spectrum of **4x** in $CDCl_3$ at 126 MHz.

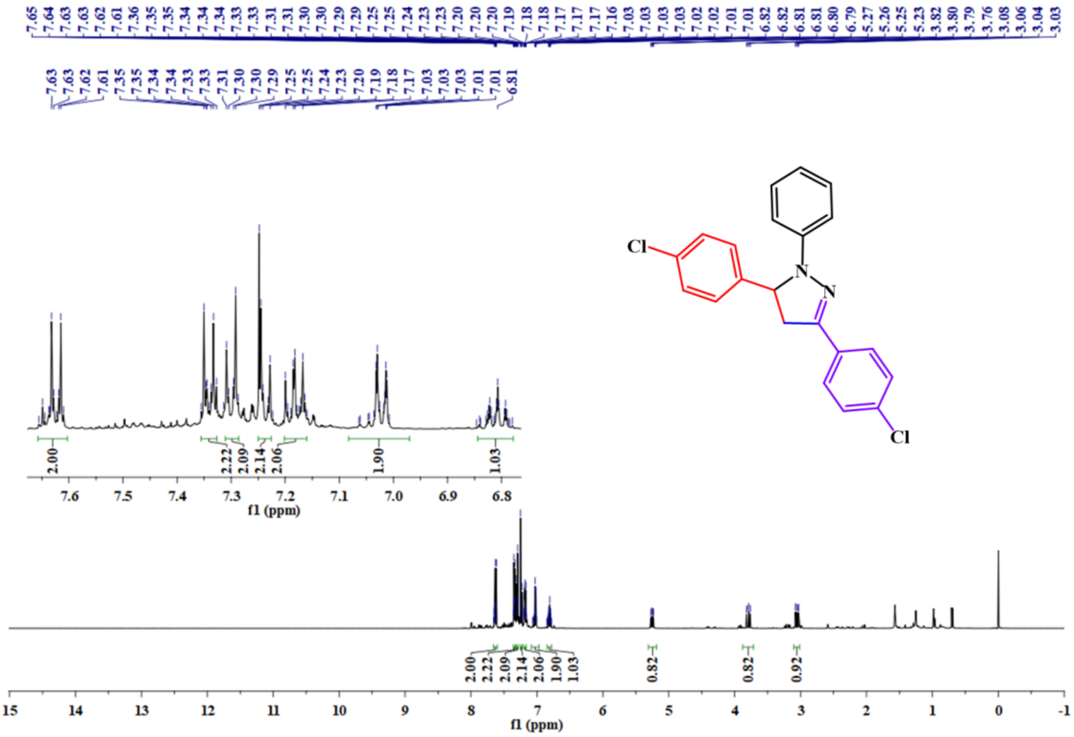


Fig. S77: ^{1}H NMR spectrum of **4y** in $CDCl_3$ at 500 MHz.

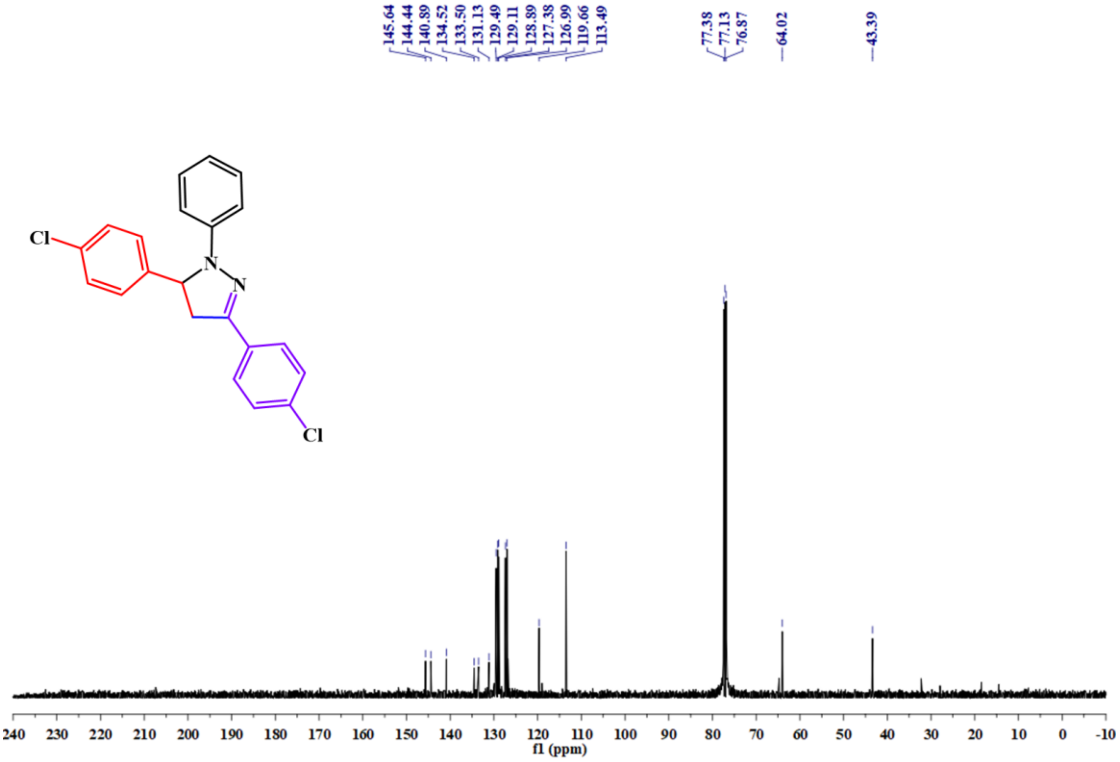


Fig. S78: ^{13}C NMR spectrum of **4y** in CDCl$_3$ at 126 MHz.

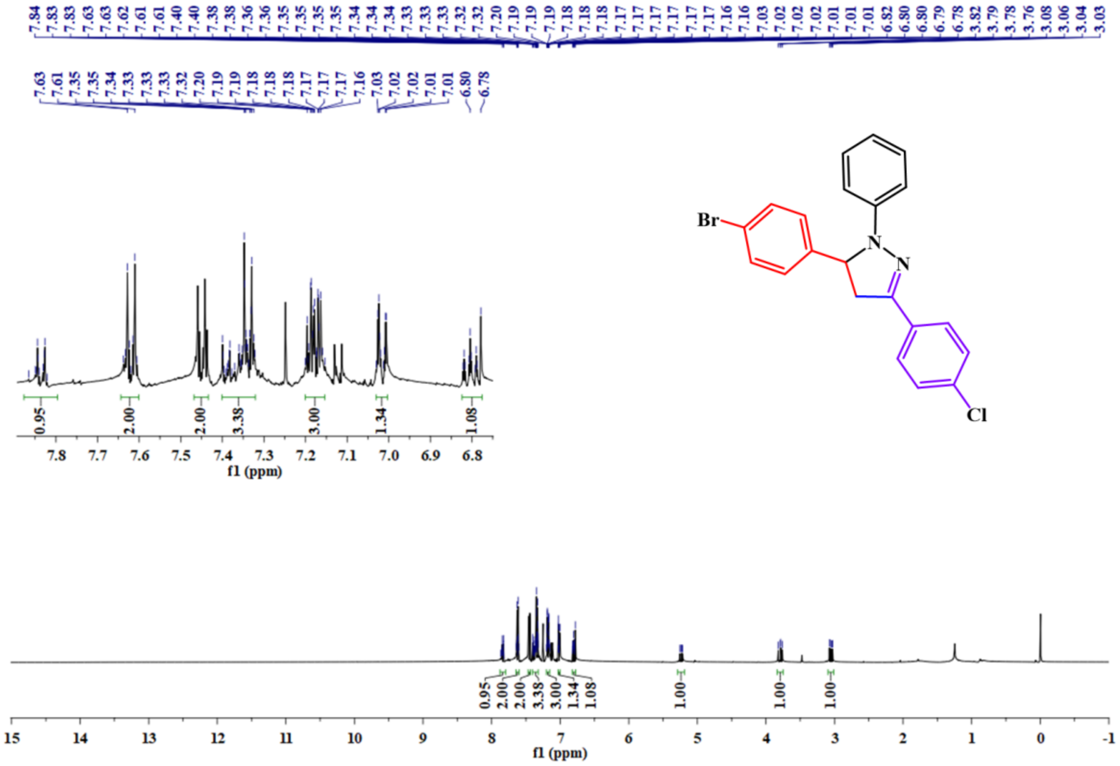


Fig. S79: ^{1}H NMR spectrum of **4z** in CDCl$_3$ at 500 MHz.

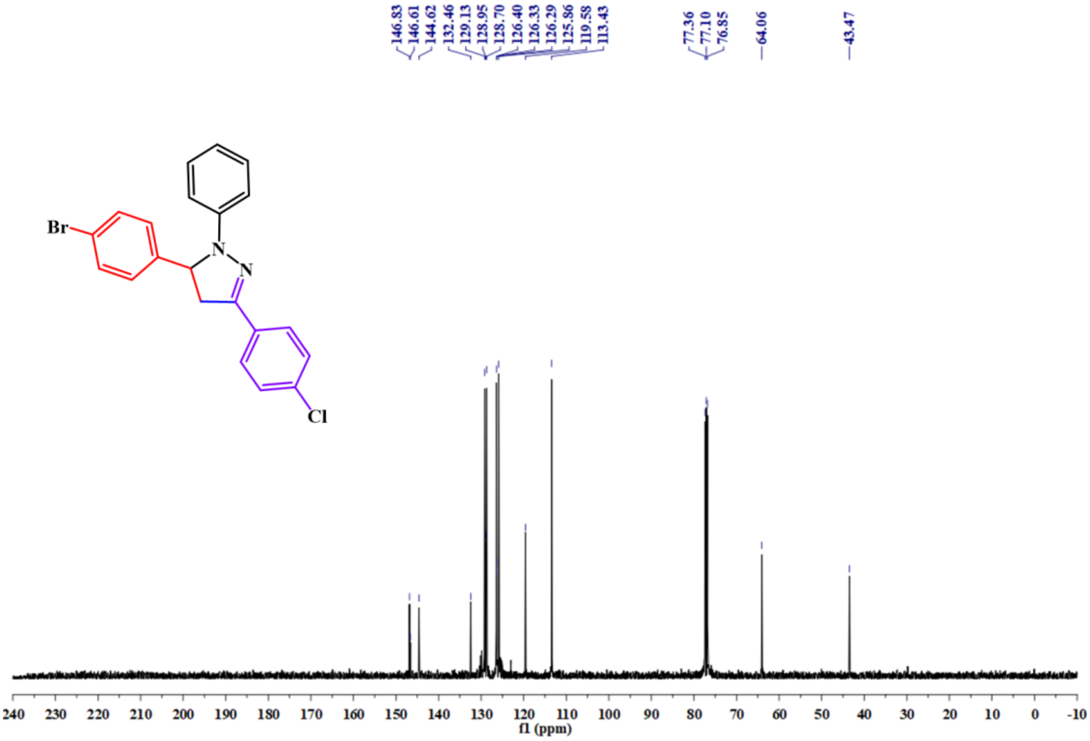


Fig. S80: ^{13}C NMR spectrum of **4z** in $CDCl_3$ at 126 MHz.

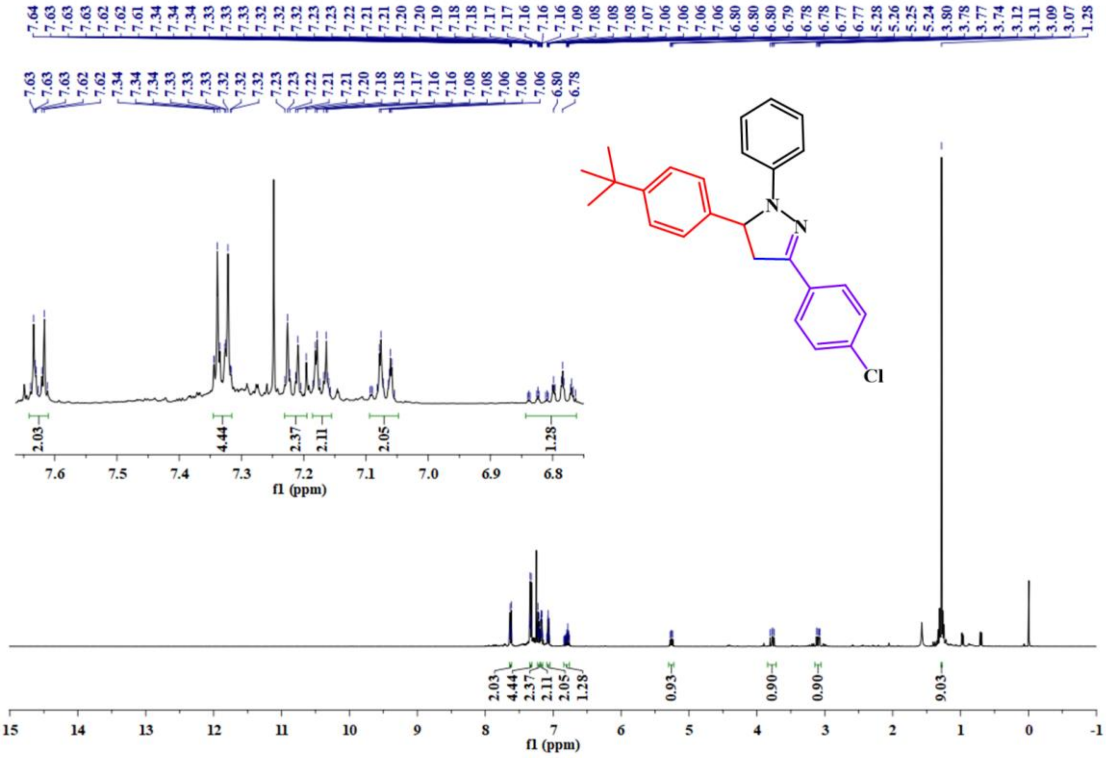


Fig. S81: ^{1}H NMR spectrum of **4aa** in $CDCl_3$ at 500 MHz.

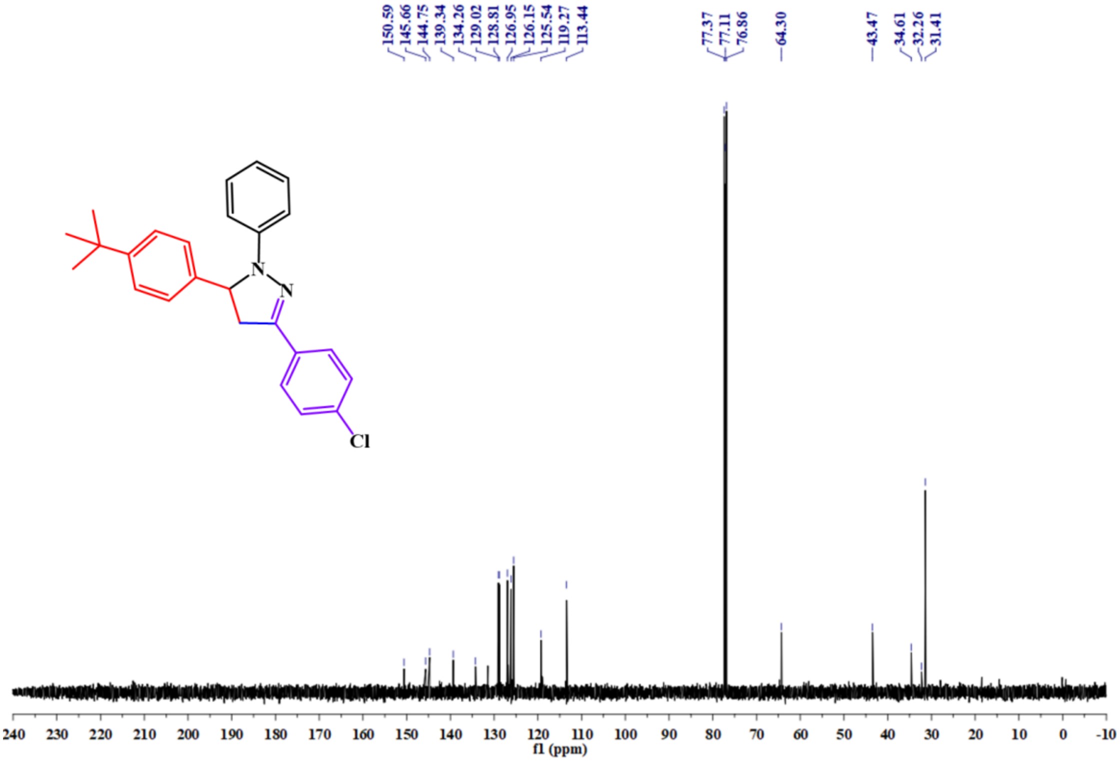


Fig. S82: ^{13}C NMR spectrum of **4aa** in CDCl$_3$ at 126 MHz.

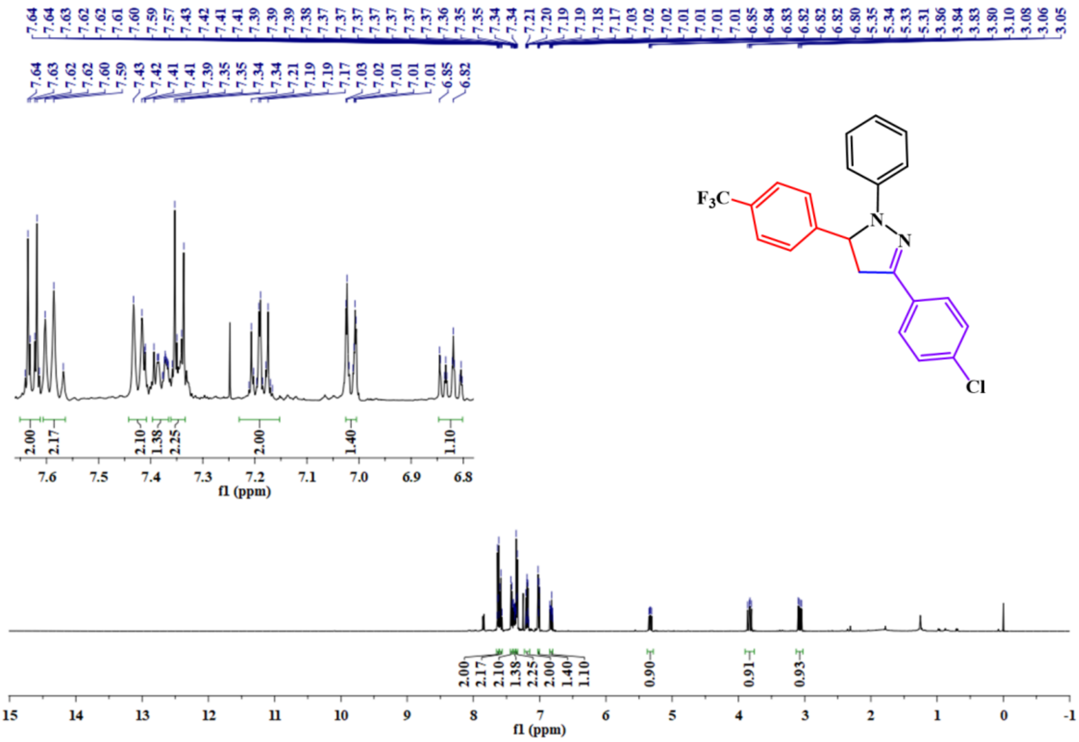


Fig. S83: ^{1}H NMR spectrum of **4ab** in CDCl$_3$ at 500 MHz.

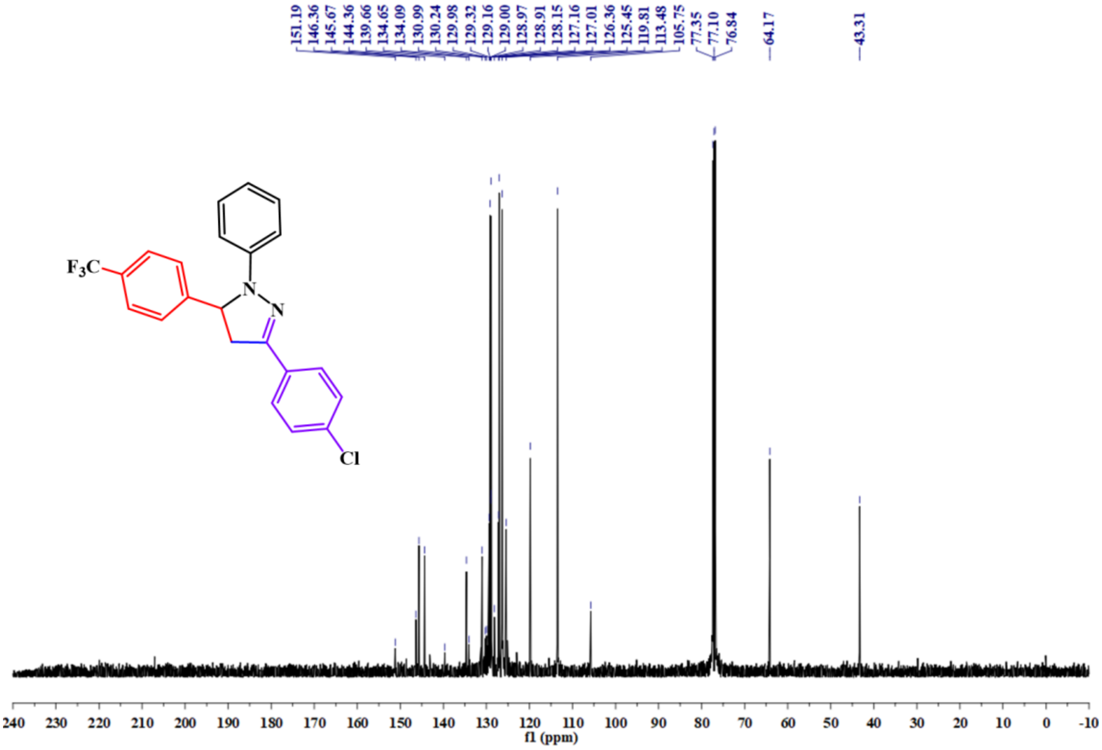


Fig. S84: ^{13}C NMR spectrum of **4ab** in CDCl$_3$ at 126 MHz.

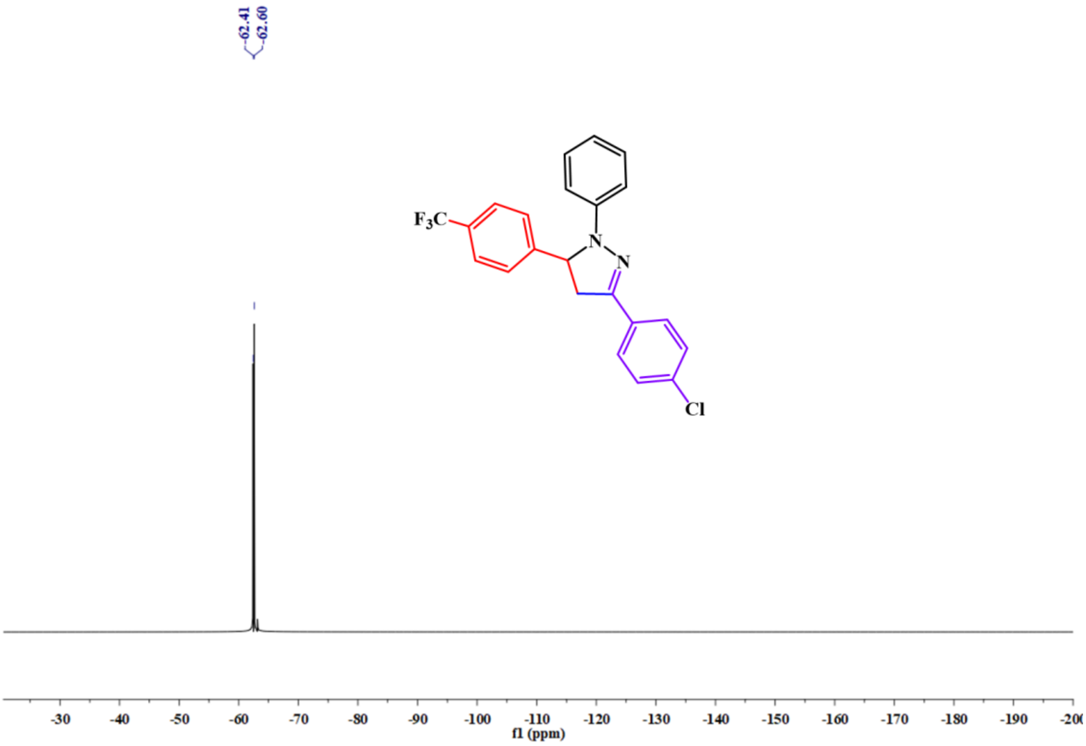


Fig. S85: ^{19}F NMR spectrum of **4ab** in CDCl$_3$ at 471 MHz.

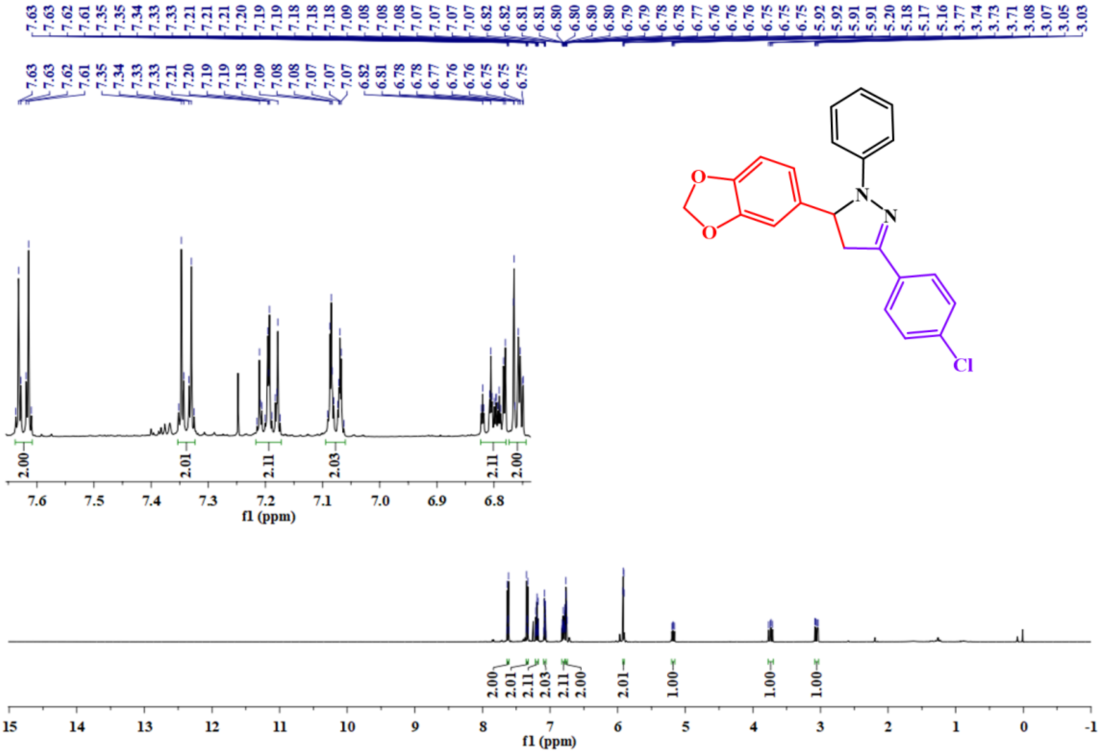


Fig. S86: ^{1}H NMR spectrum of **4ac** in $CDCl_3$ at 500 MHz.

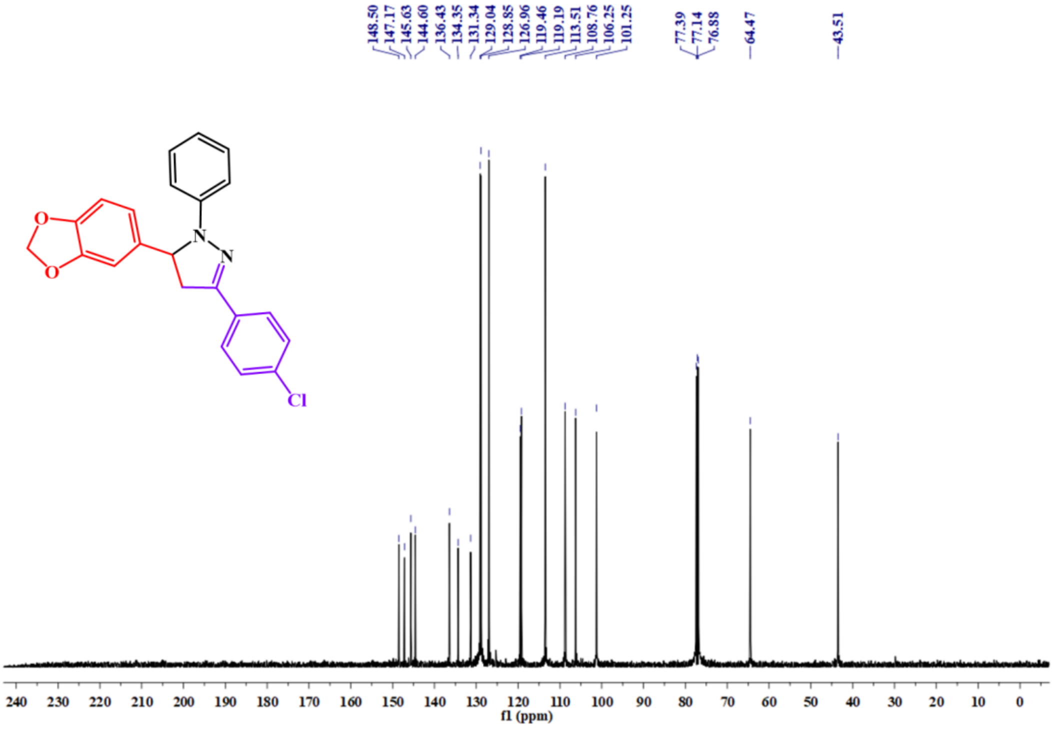


Fig. S87: ^{13}C NMR spectrum of **4ac** in $CDCl_3$ at 126 MHz.

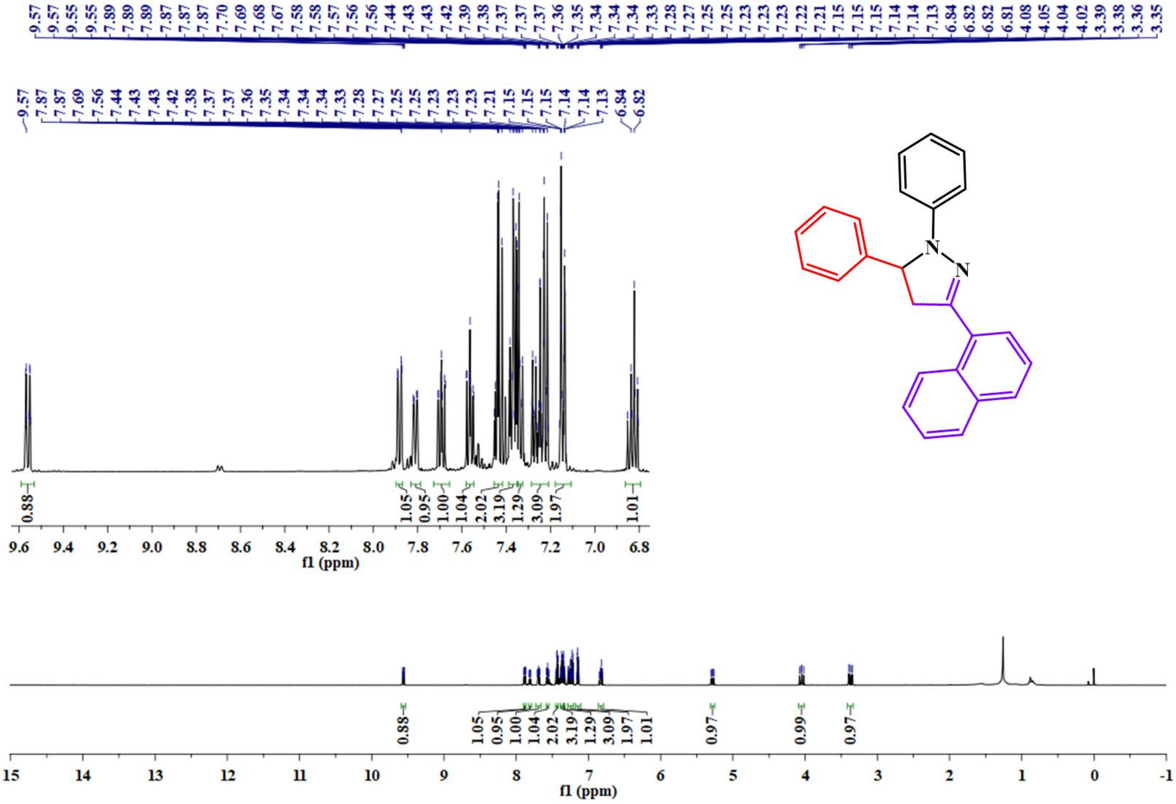


Fig. S88: ^{1}H NMR spectrum of **4ad** in $CDCl_3$ at 500 MHz.

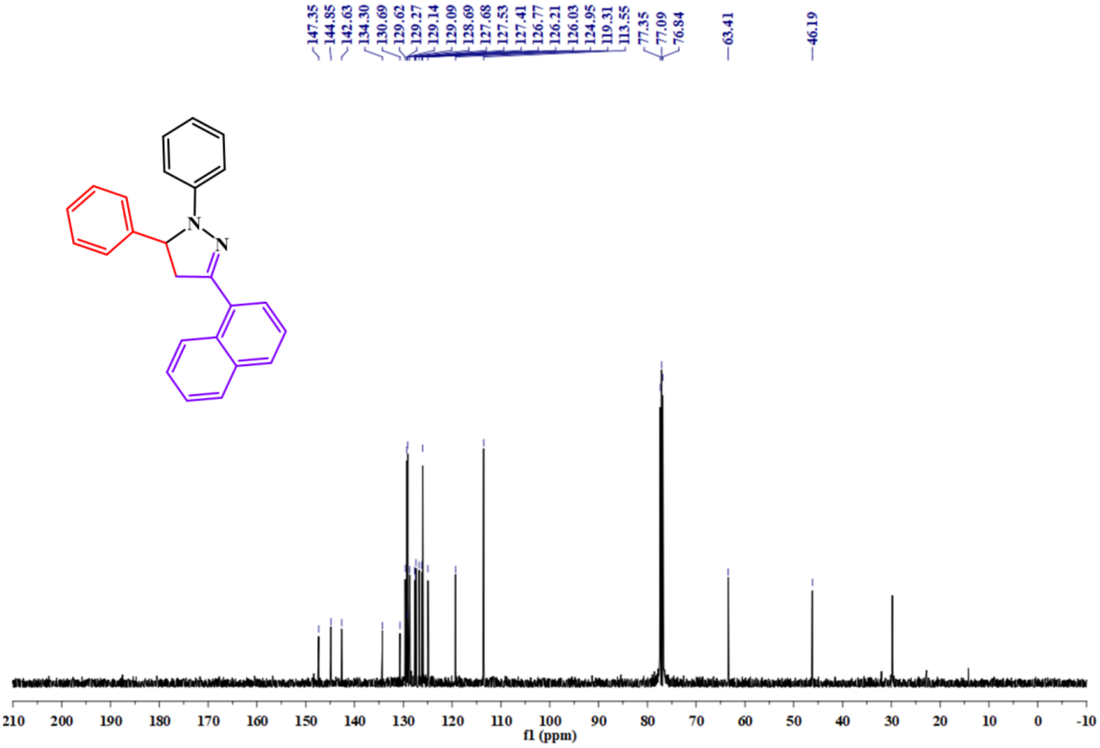


Fig. S89: ^{13}C NMR spectrum of **4ad** in CDCl$_3$ at 126 MHz.

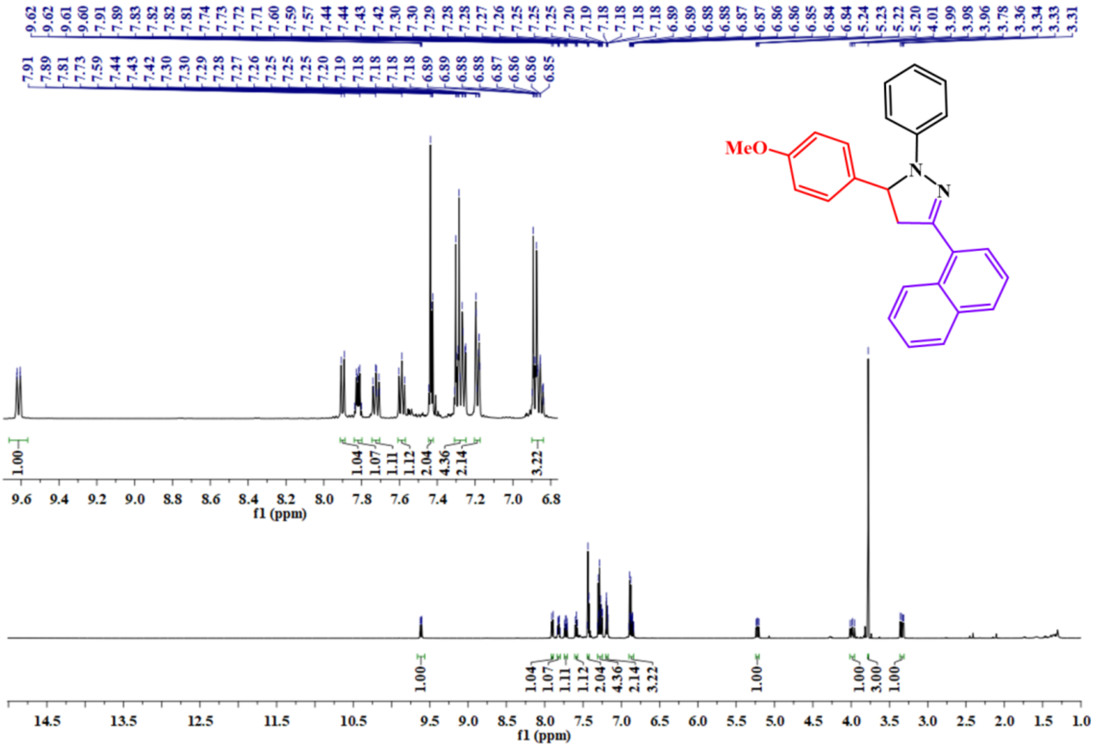


Fig. S90: ^{1}H NMR spectrum of **4ae** in CDCl$_3$ at 500 MHz.

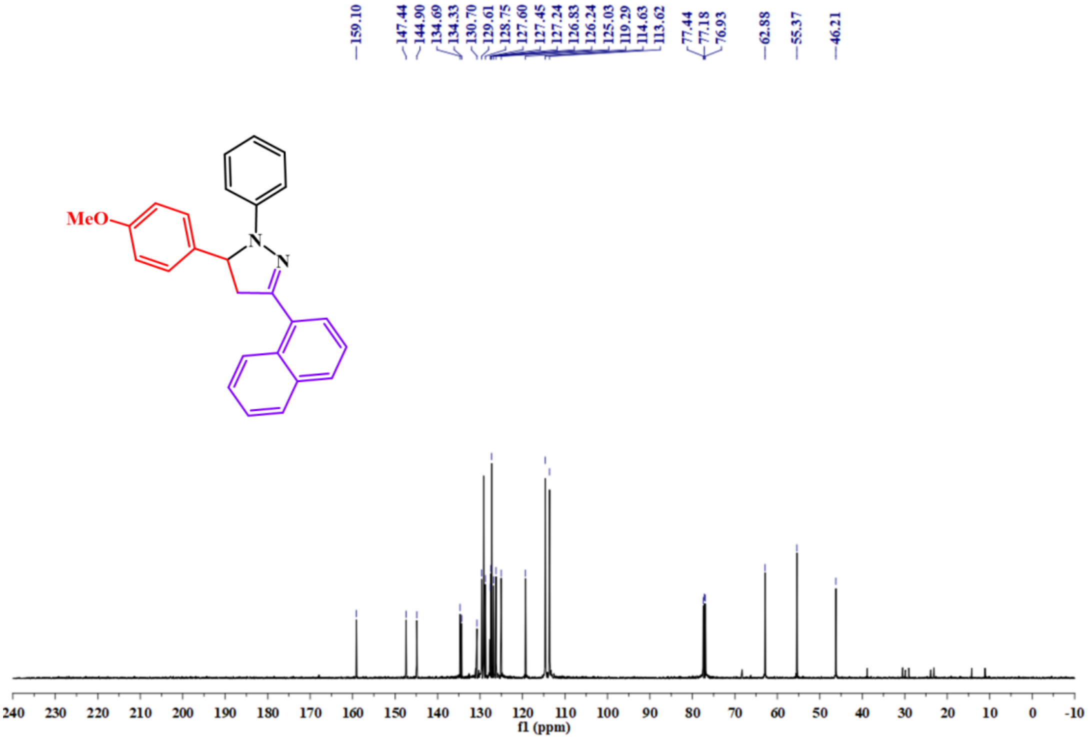


Fig. S91: ^{13}C NMR spectrum of **4ae** in $CDCl_3$ at 126 MHz.

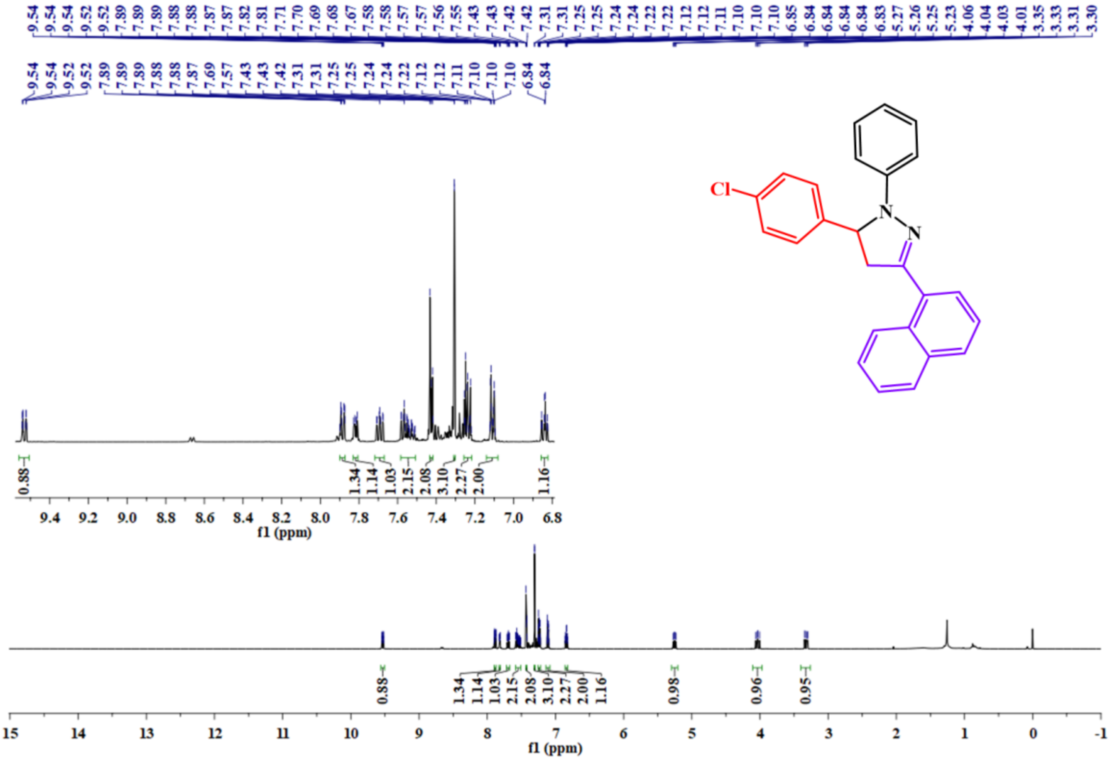


Fig. S92: ^{1}H NMR spectrum of **4af** in $CDCl_3$ at 500 MHz.

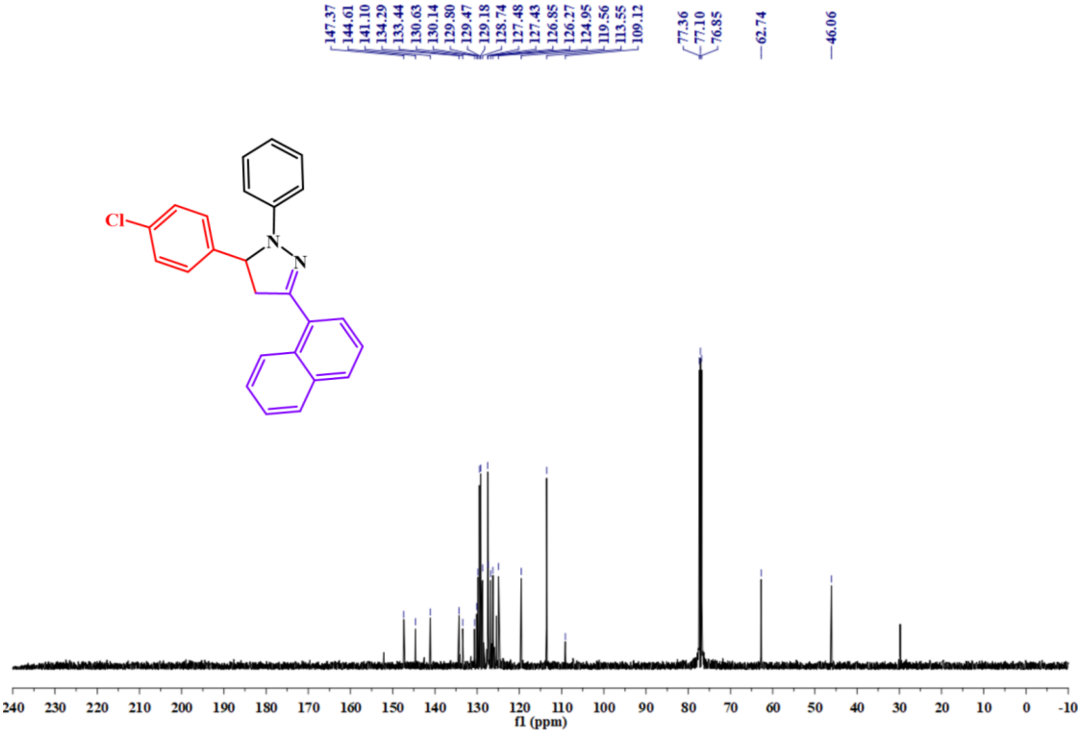


Fig. S93: ^{13}C NMR spectrum of **4af** in CDCl$_3$ at 126 MHz.

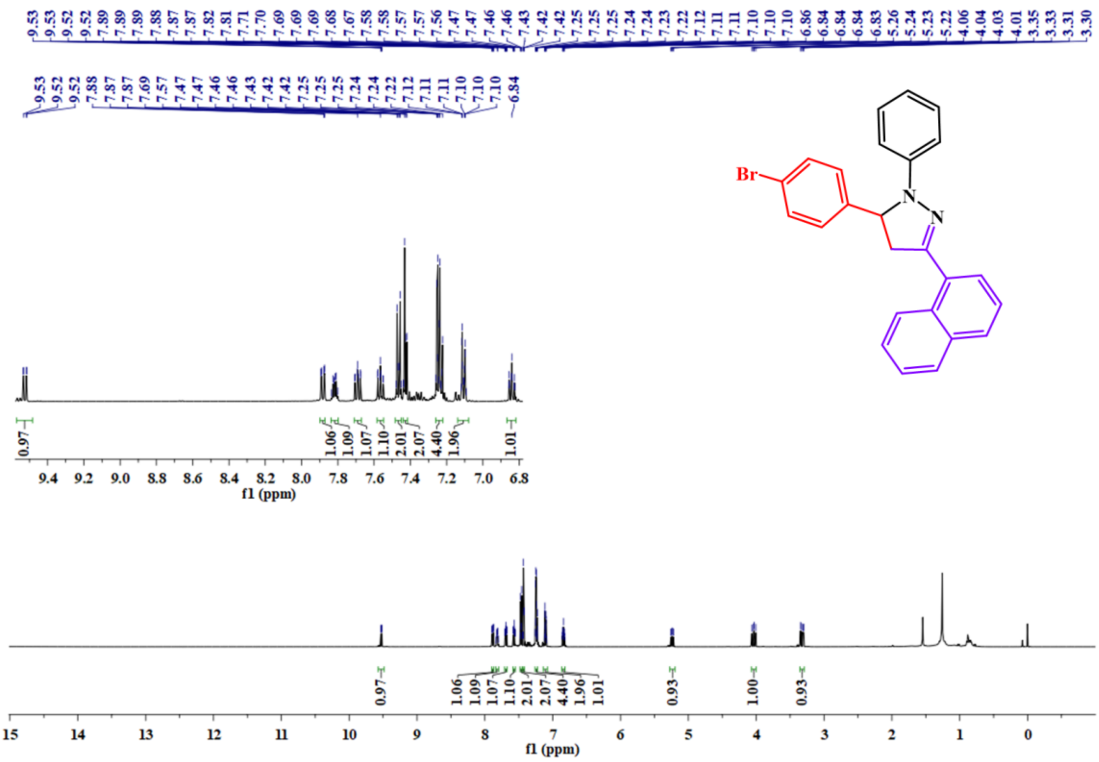


Fig. S94: ^{1}H NMR spectrum of **4ag** in CDCl$_3$ at 500 MHz.

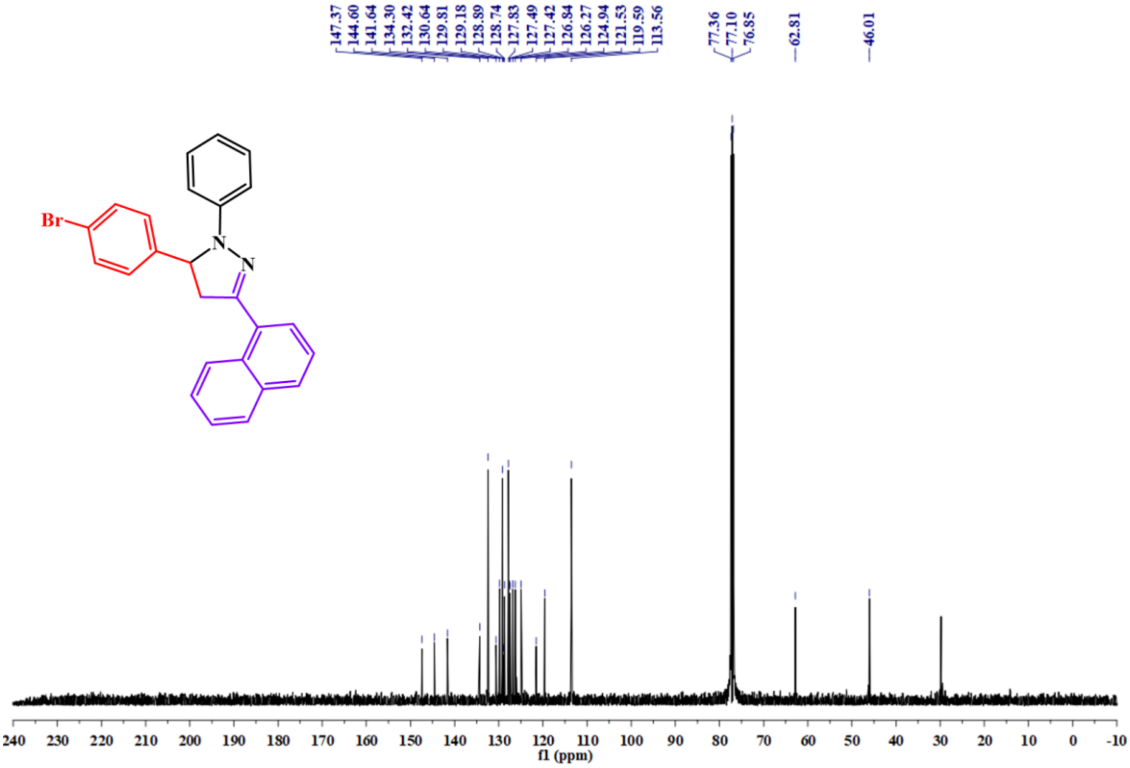


Fig. S95: ^{13}C NMR spectrum of **4ag** in $CDCl_3$ at 126 MHz.

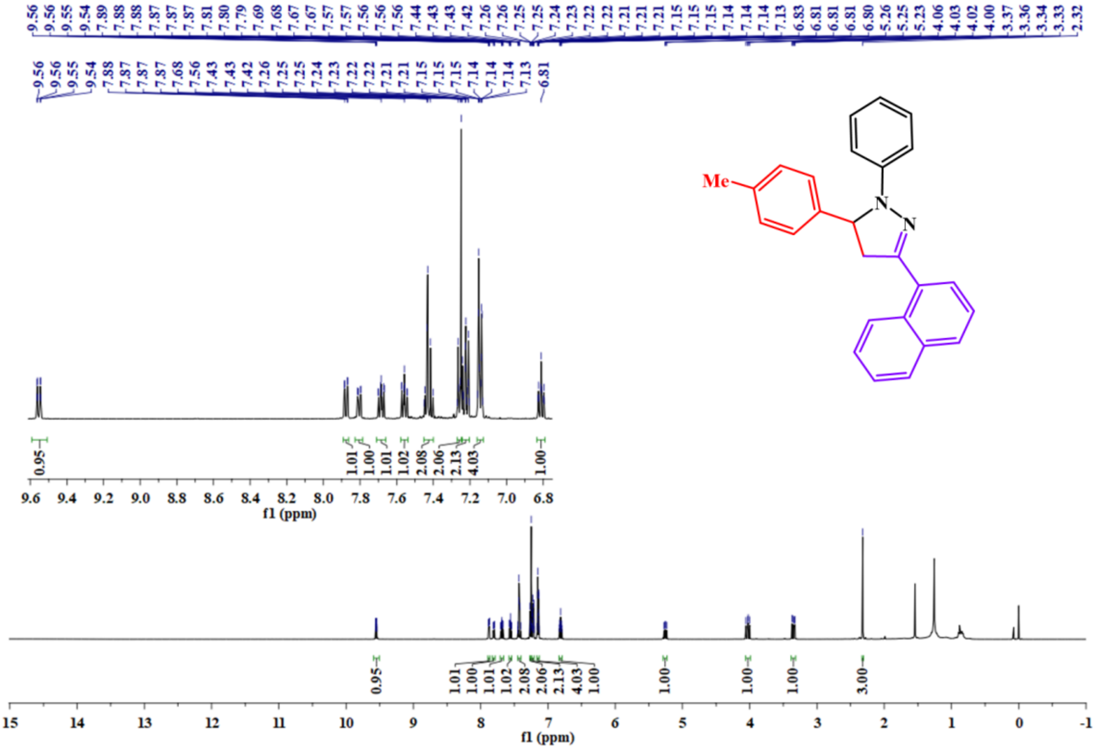


Fig. S96: ^{1}H NMR spectrum of **4ah** in $CDCl_3$ at 500 MHz.

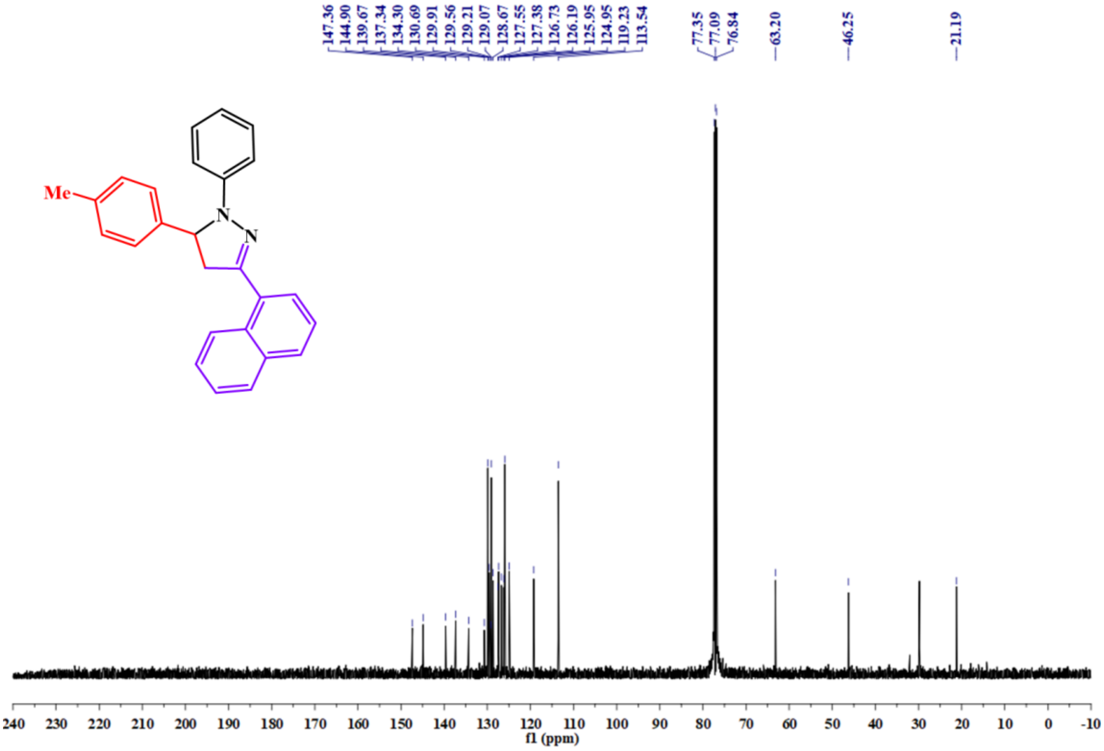


Fig. S97: ^{13}C NMR spectrum of **4ah** in CDCl$_3$ at 126 MHz.

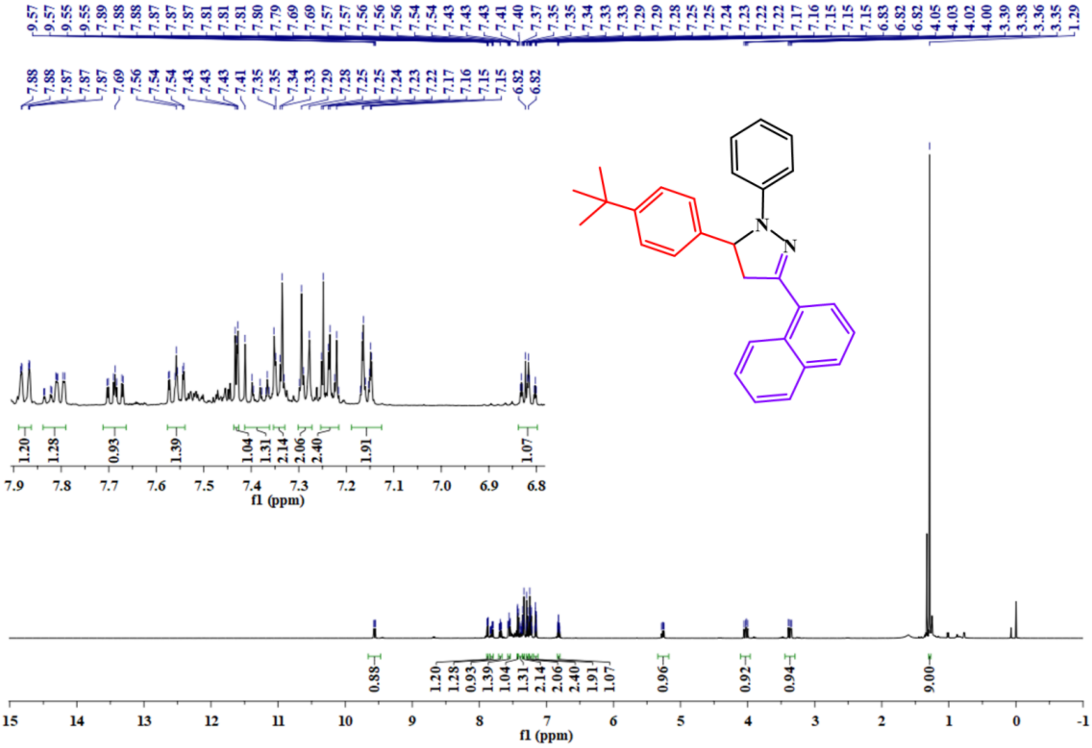


Fig. S98: ^{1}H NMR spectrum of **4ai** in CDCl$_3$ at 500 MHz.

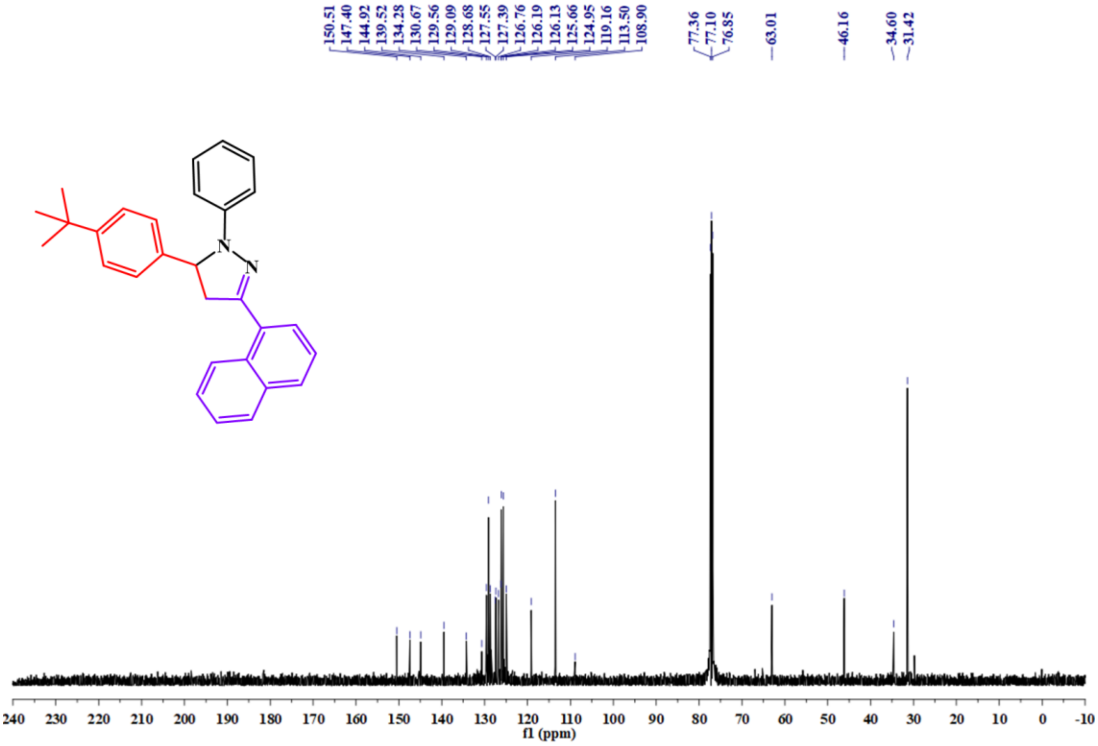


Fig. S99: ^{13}C NMR spectrum of **4ai** in $CDCl_3$ at 126 MHz.

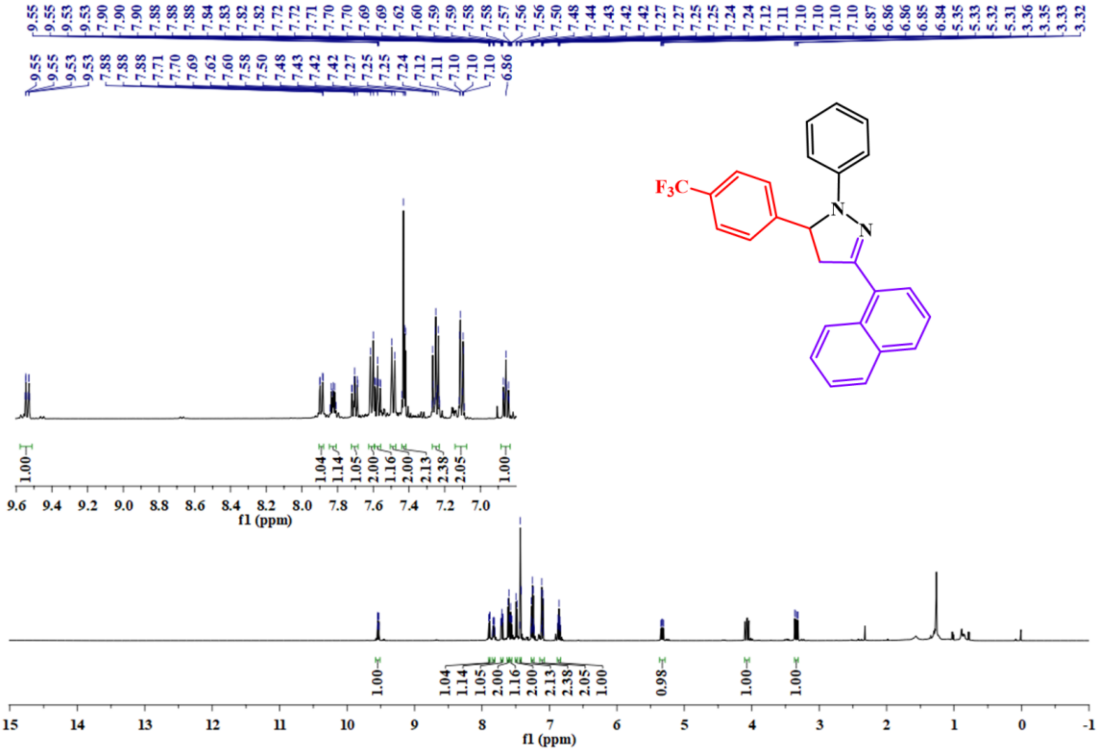


Fig. S100: ^{1}H NMR spectrum of **4aj** in $CDCl_3$ at 500 MHz.

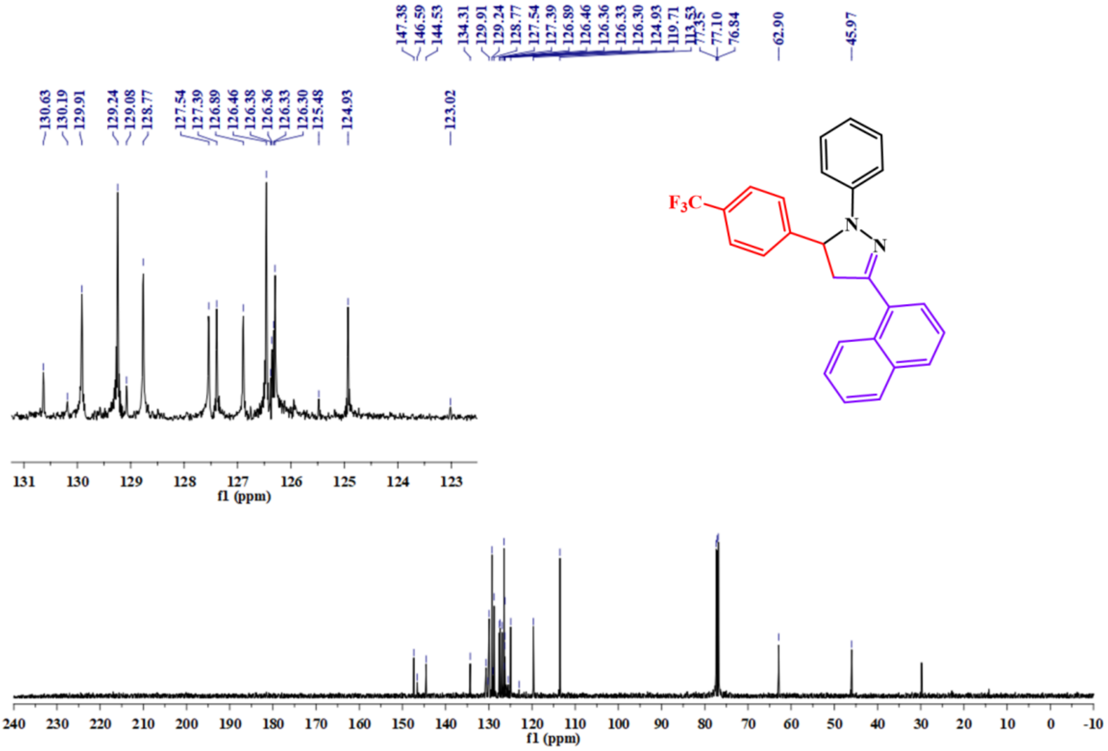


Fig. S101: ^{13}C NMR spectrum of **4aj** in CDCl$_3$ at 126 MHz.

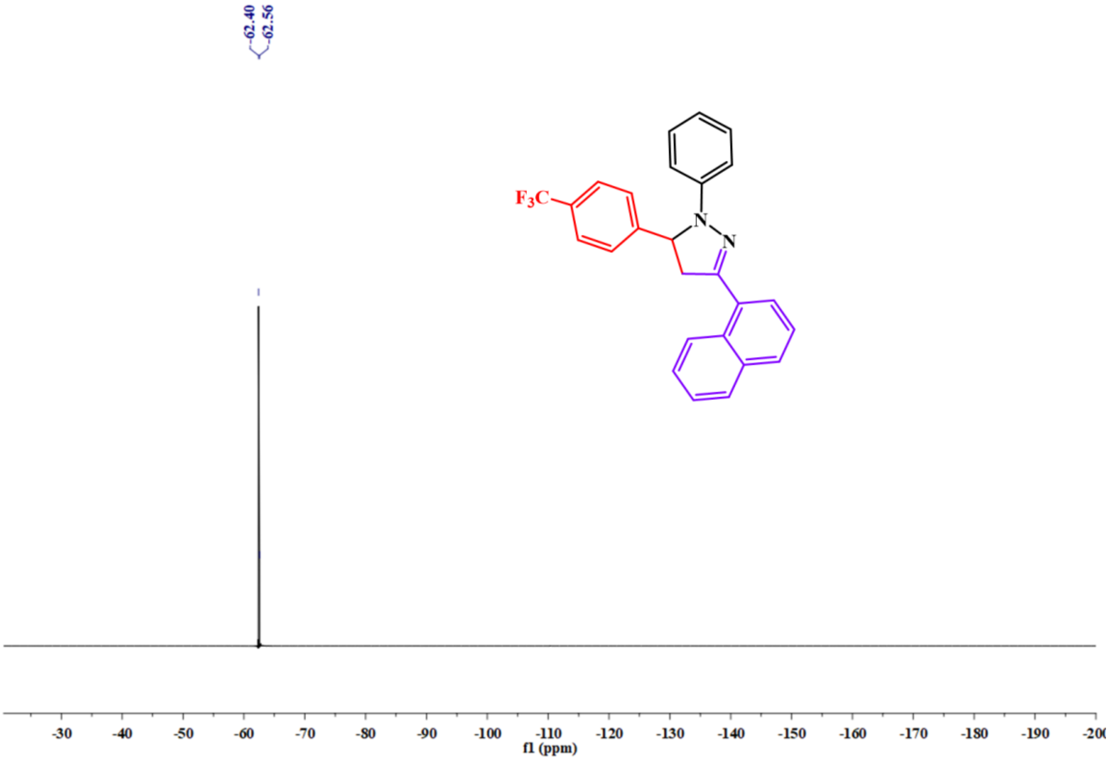


Fig. S102: ^{19}F NMR spectrum of **4ak** in CDCl$_3$ at 471 MHz.

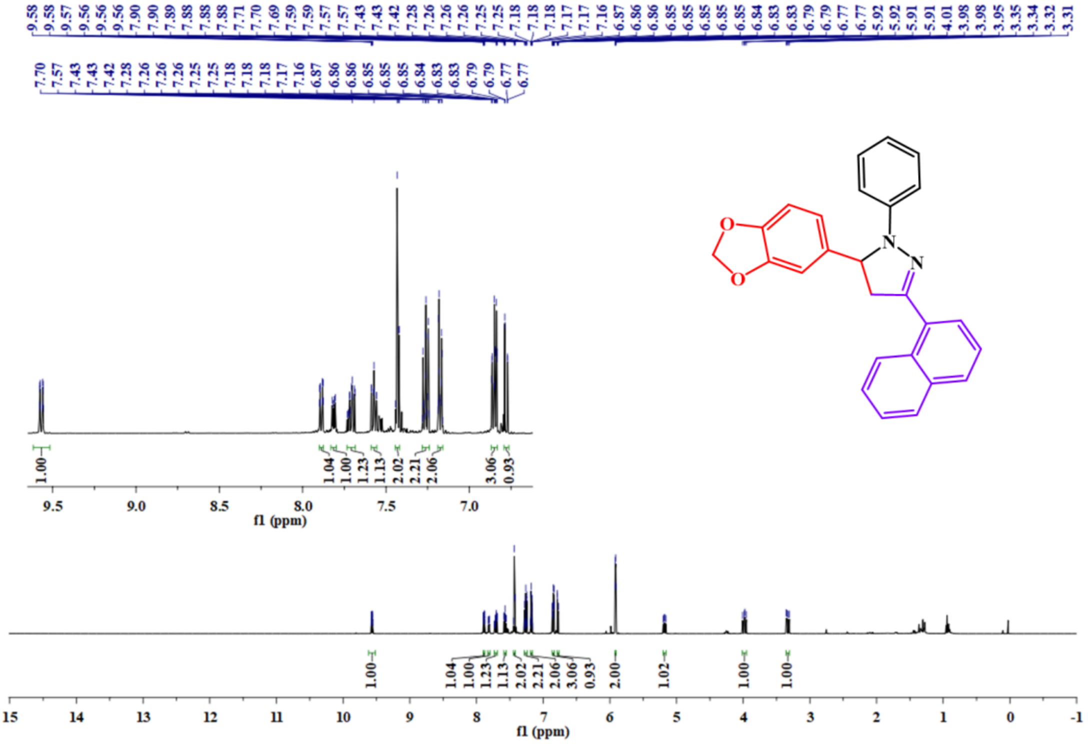


Fig. S103: ^{1}H NMR spectrum of **4ak** in CDCl$_3$ at 500 MHz.

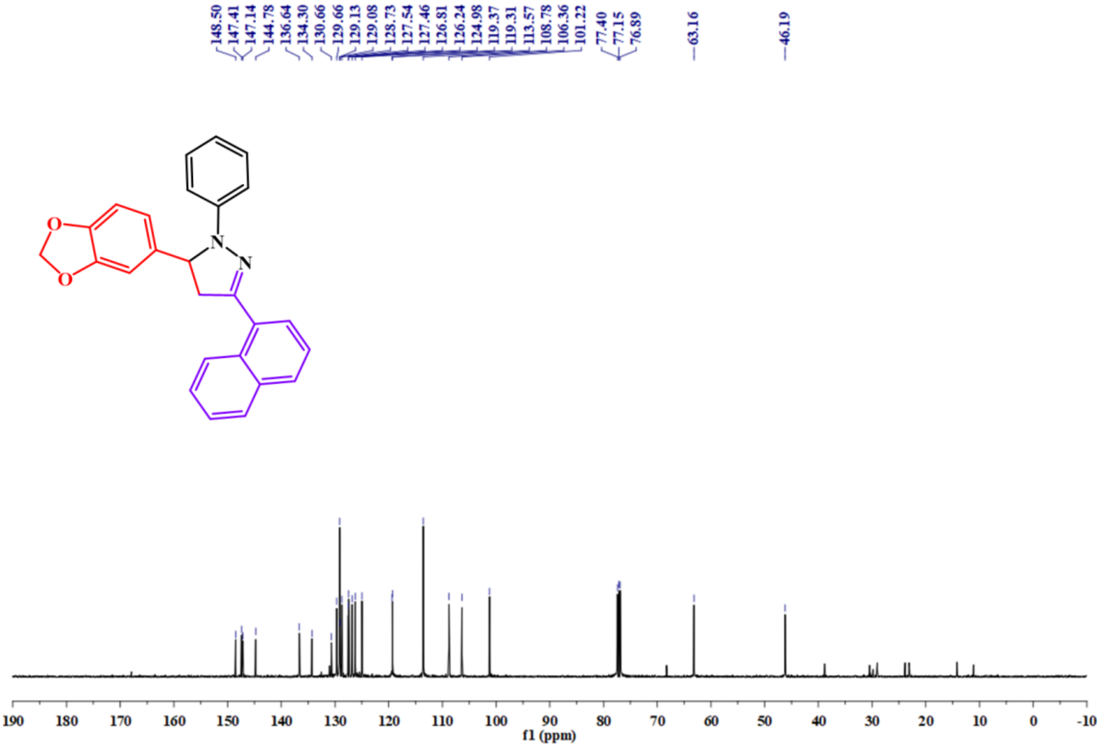


Fig. S104: ^{13}C NMR spectrum of **4ak** in CDCl$_3$ at 126 MHz.

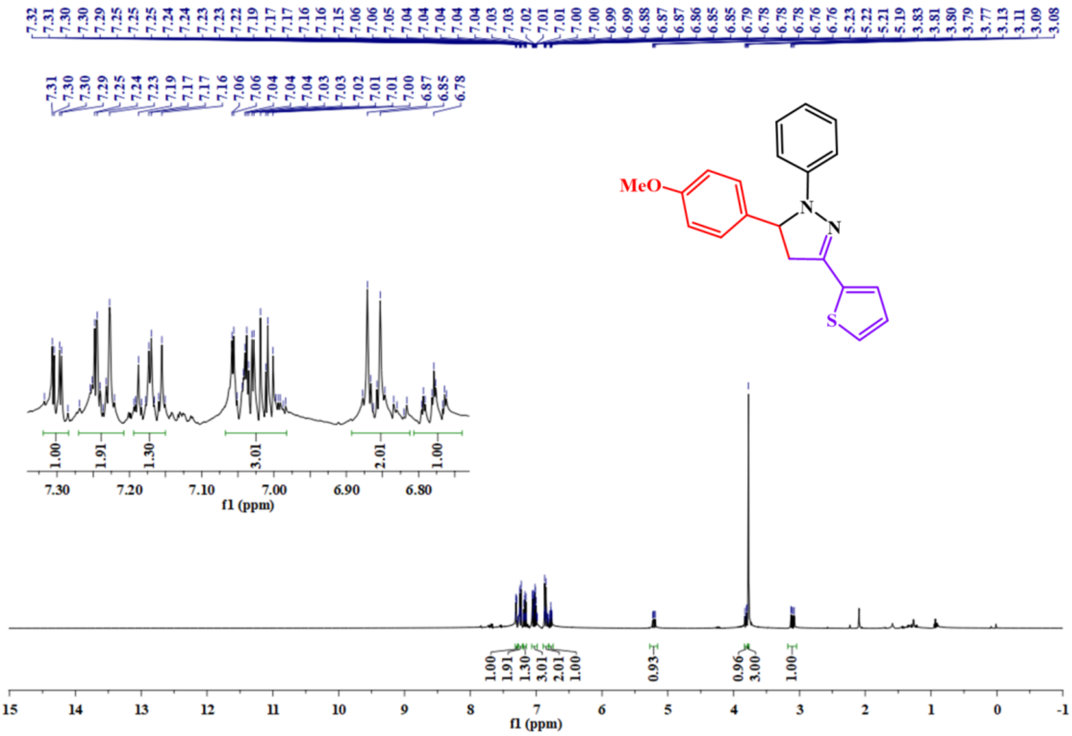


Fig. S105: ^{1}H NMR spectrum of **4al** in $CDCl_3$ at 500 MHz.

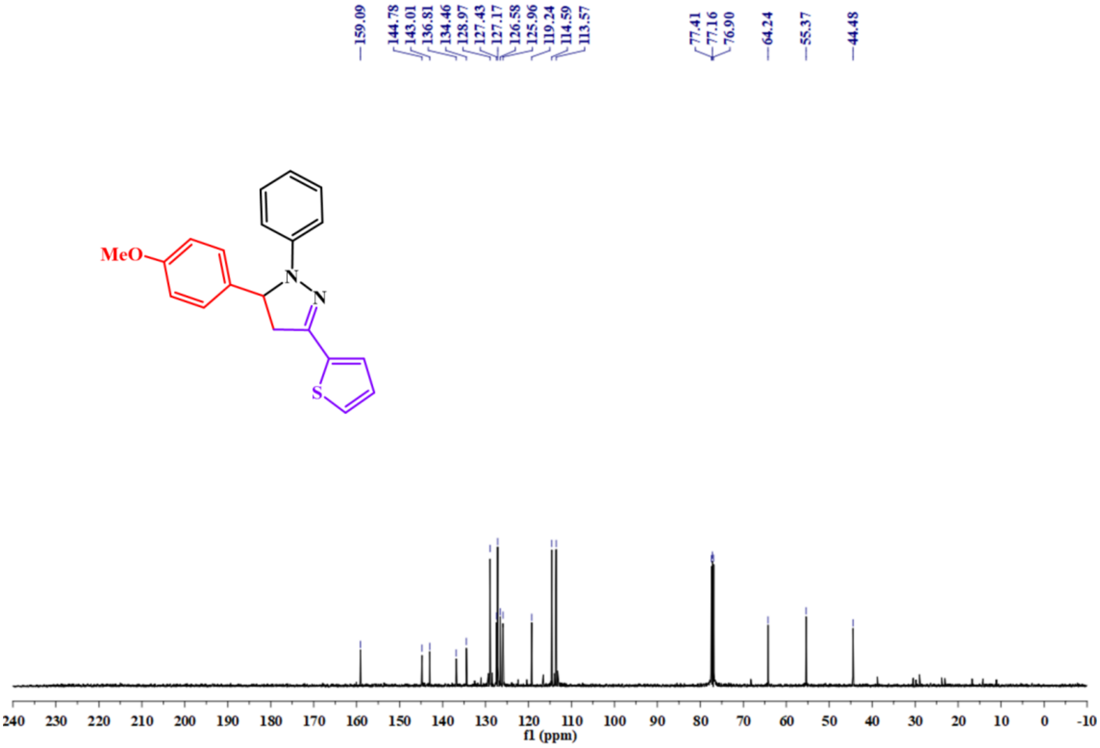


Fig. S106: ^{13}C NMR spectrum of **4al** in $CDCl_3$ at 126 MHz.

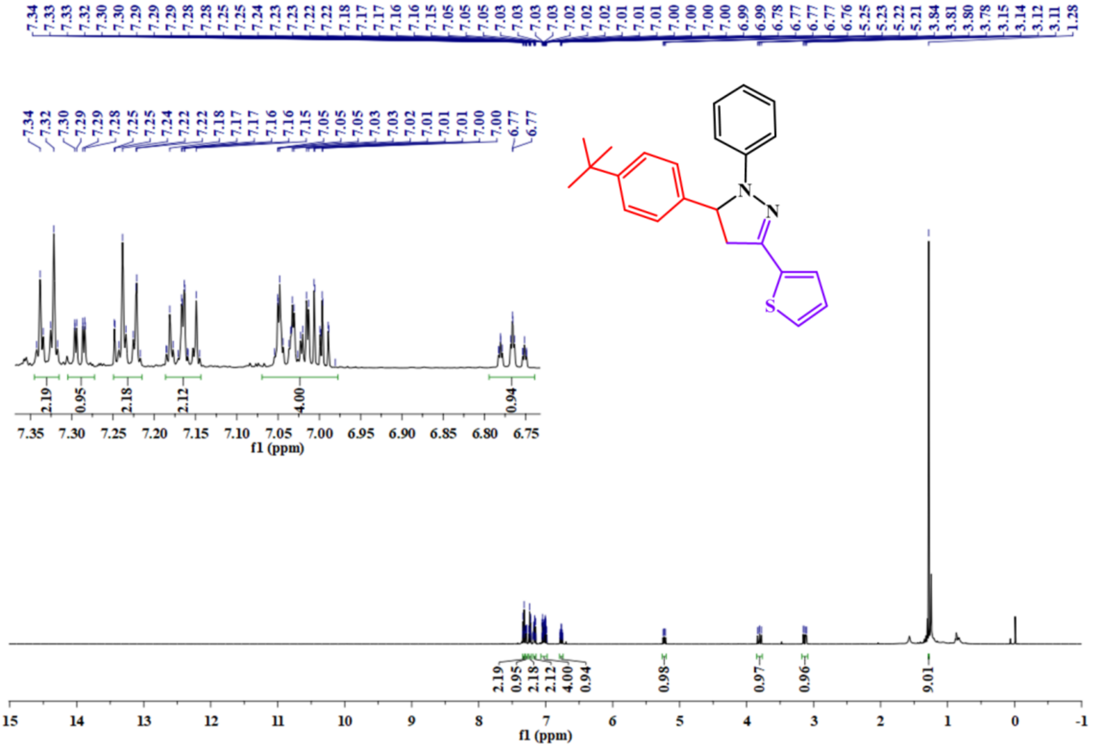


Fig. S107: ^{1}H NMR spectrum of **4am** in $CDCl_3$ at 500 MHz.

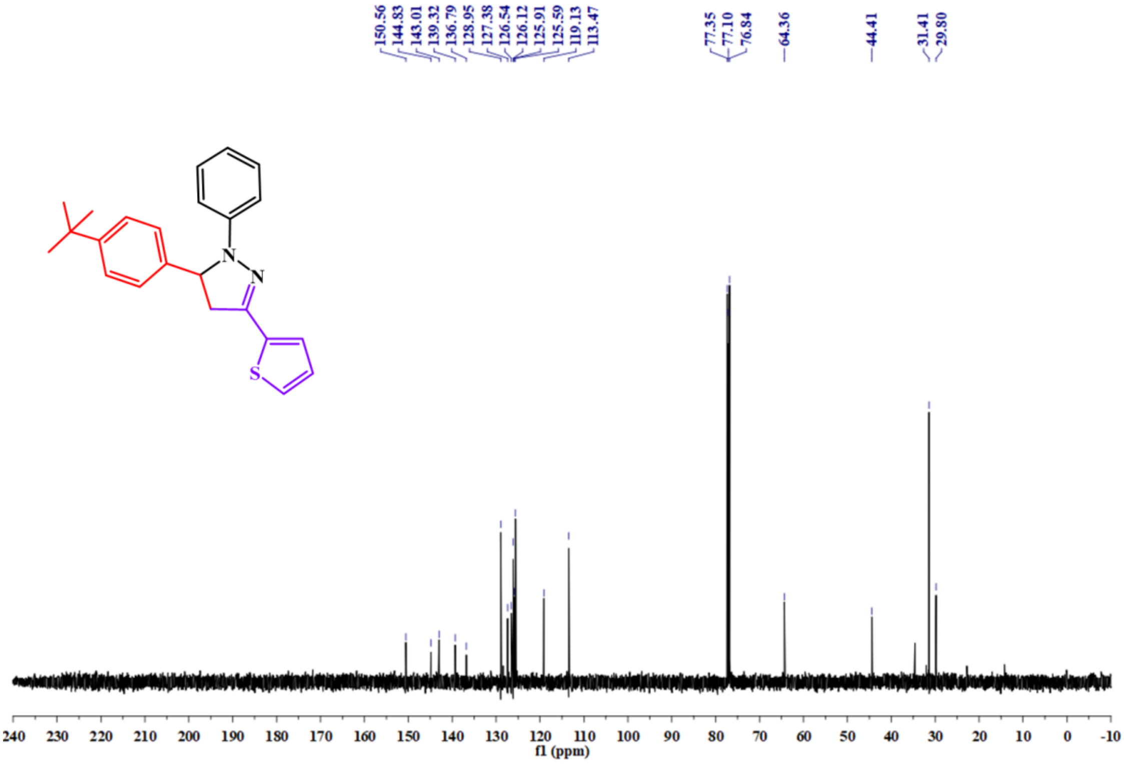


Fig. S108: ^{13}C NMR spectrum of **4am** in $CDCl_3$ at 126 MHz.

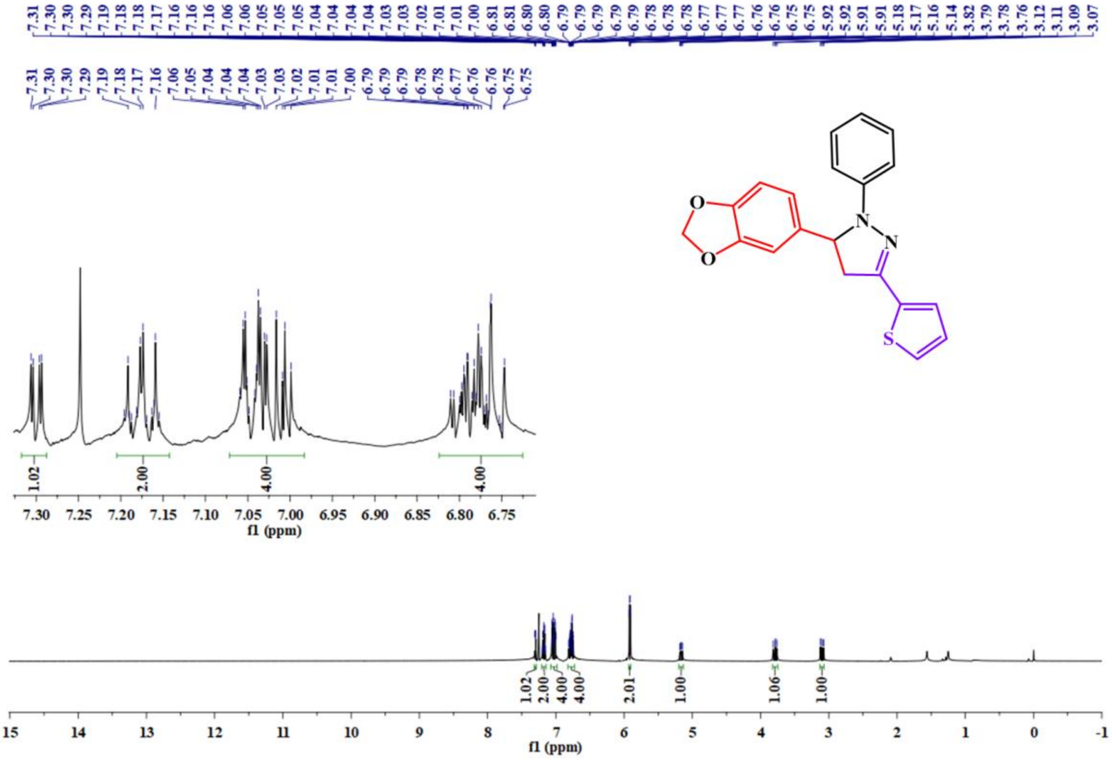


Fig. S109: ^{1}H NMR spectrum of **4an** in CDCl$_3$ at 500 MHz.

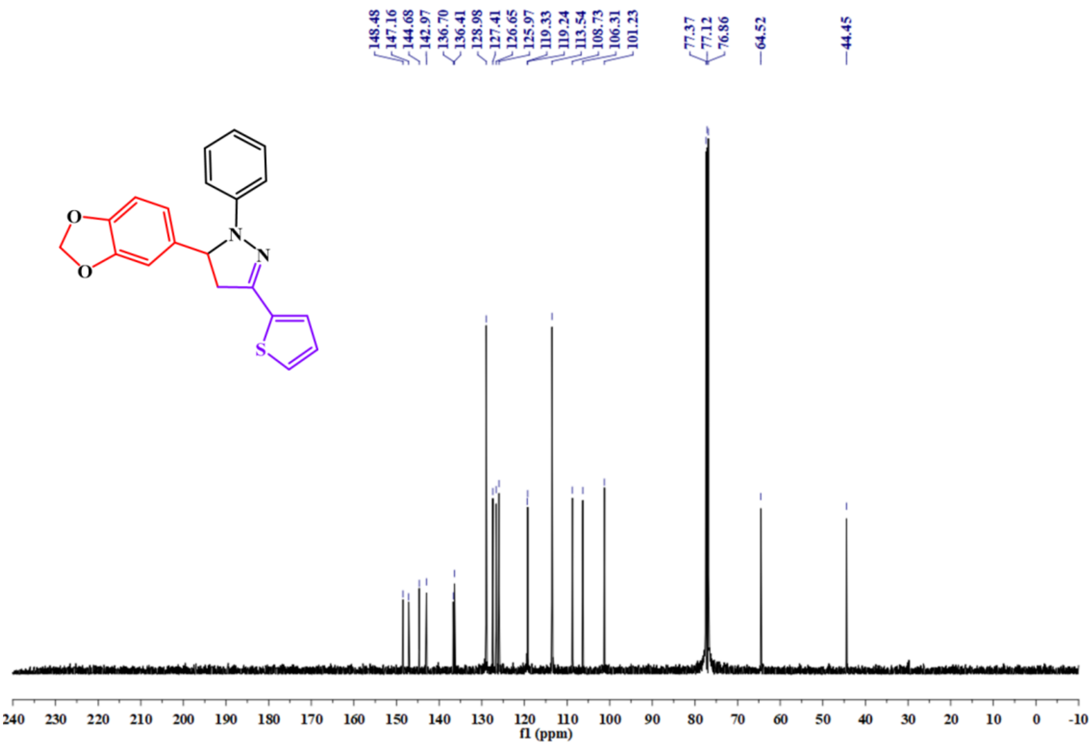


Fig. S110: ^{13}C NMR spectrum of **4an** in CDCl$_3$ at 126 MHz.

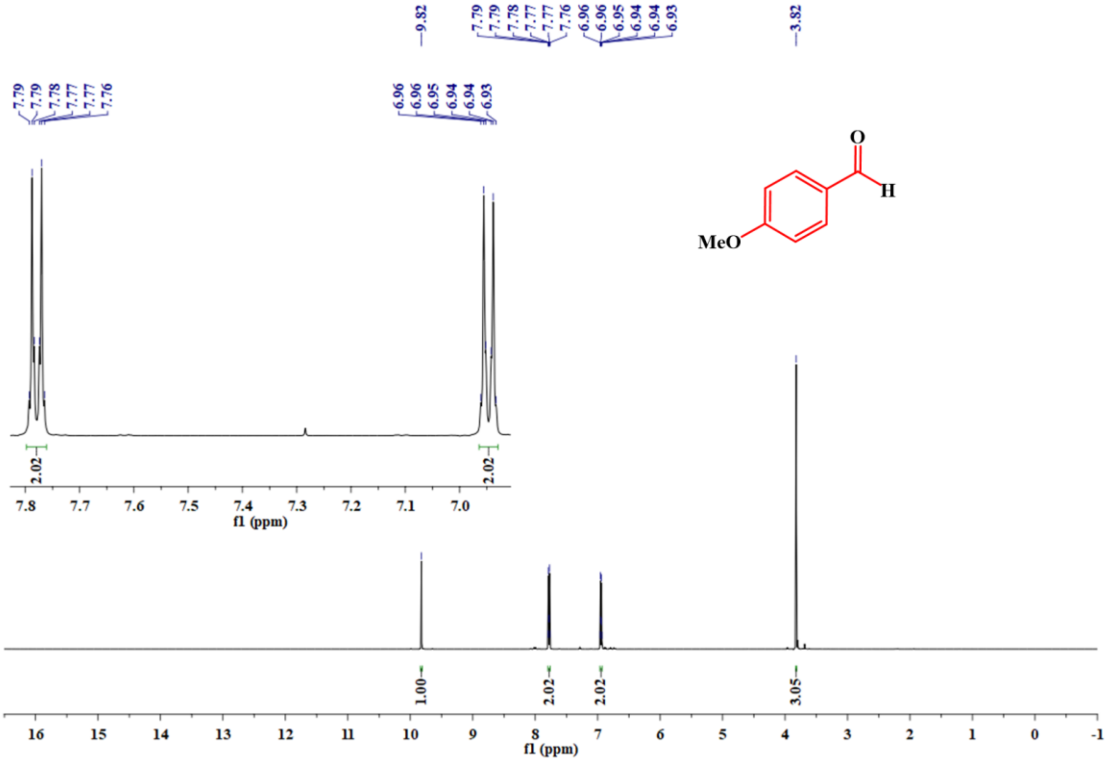


Fig. S111: ^{1}H NMR spectrum of **2b** in $CDCl_3$ at 500 MHz.

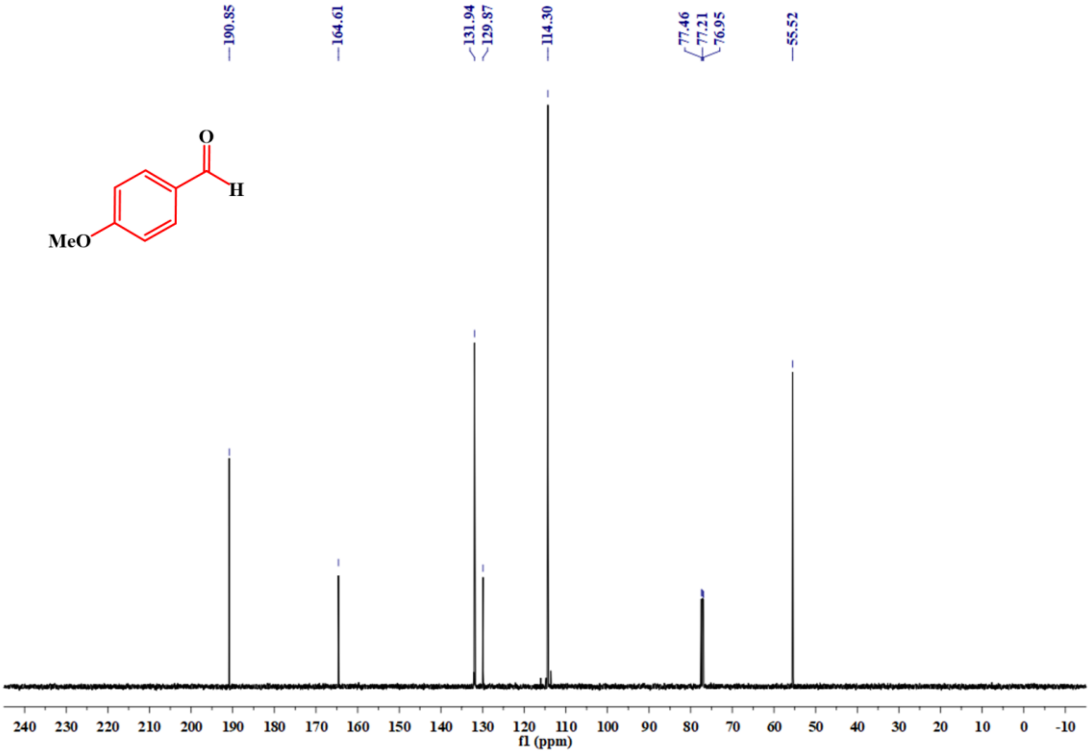


Fig. S112: ^{13}C NMR spectrum of **2b** in $CDCl_3$ at 126 MHz.

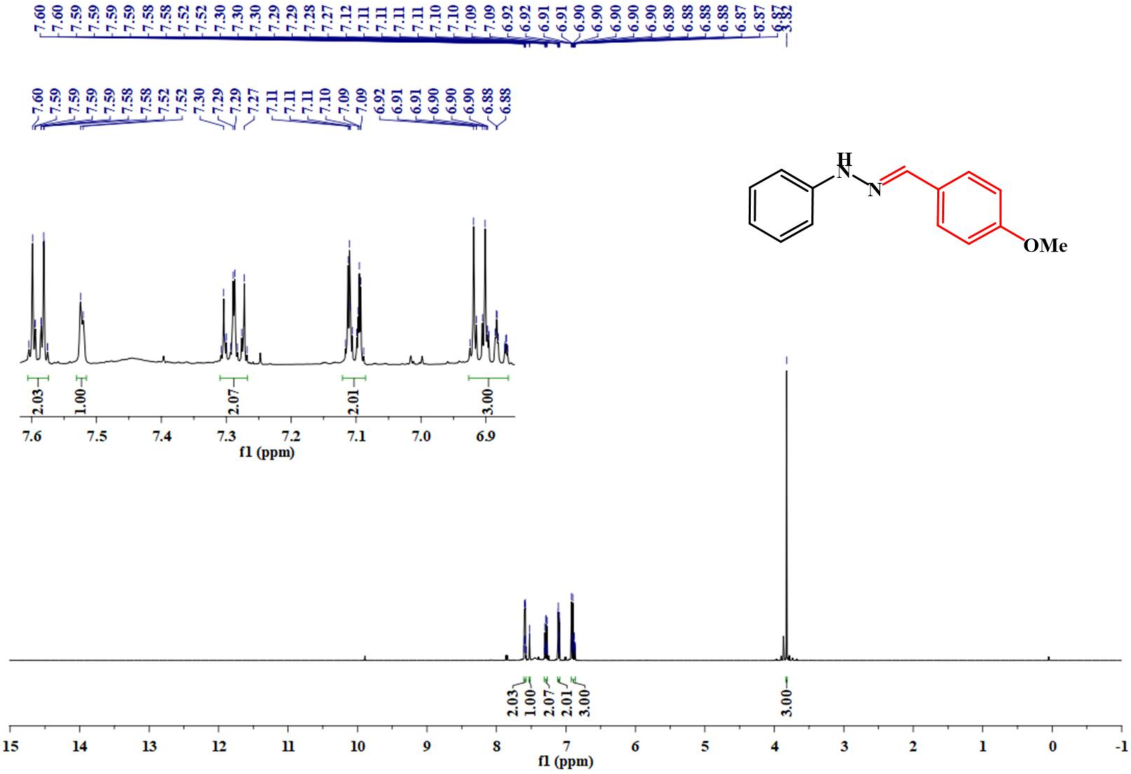


Fig. S113: ^{1}H NMR spectrum of **4b** in $CDCl_3$ at 500 MHz.

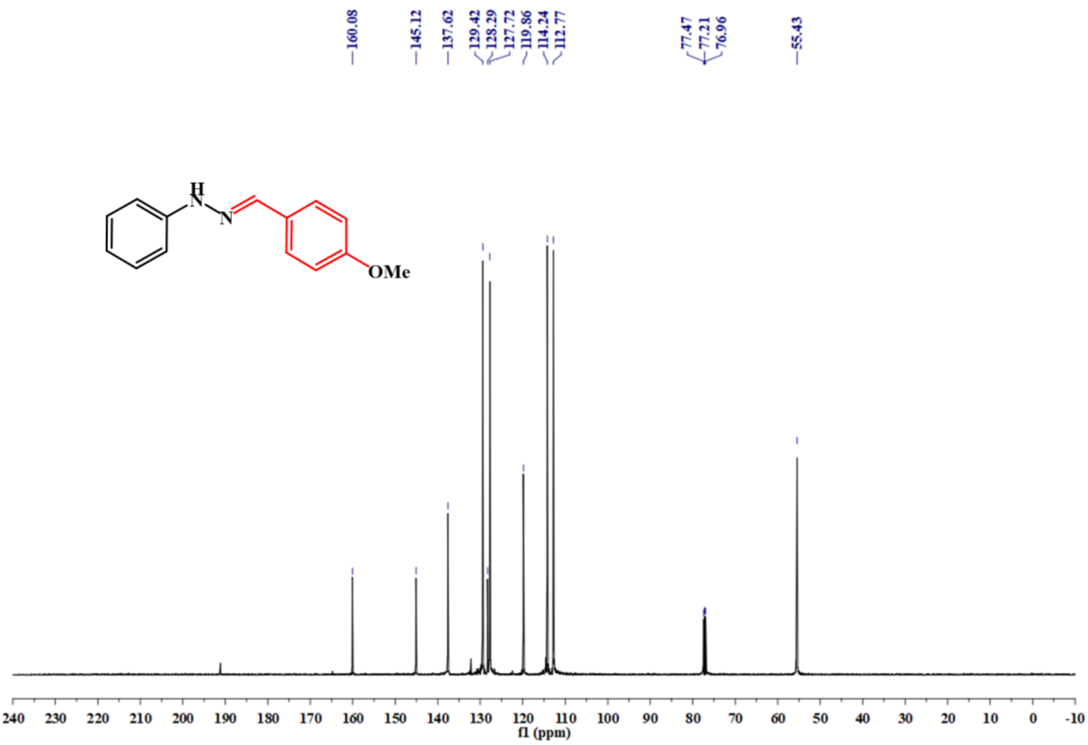


Fig. S114: ^{13}C NMR spectrum of **4b** in $CDCl_3$ at 126 MHz.

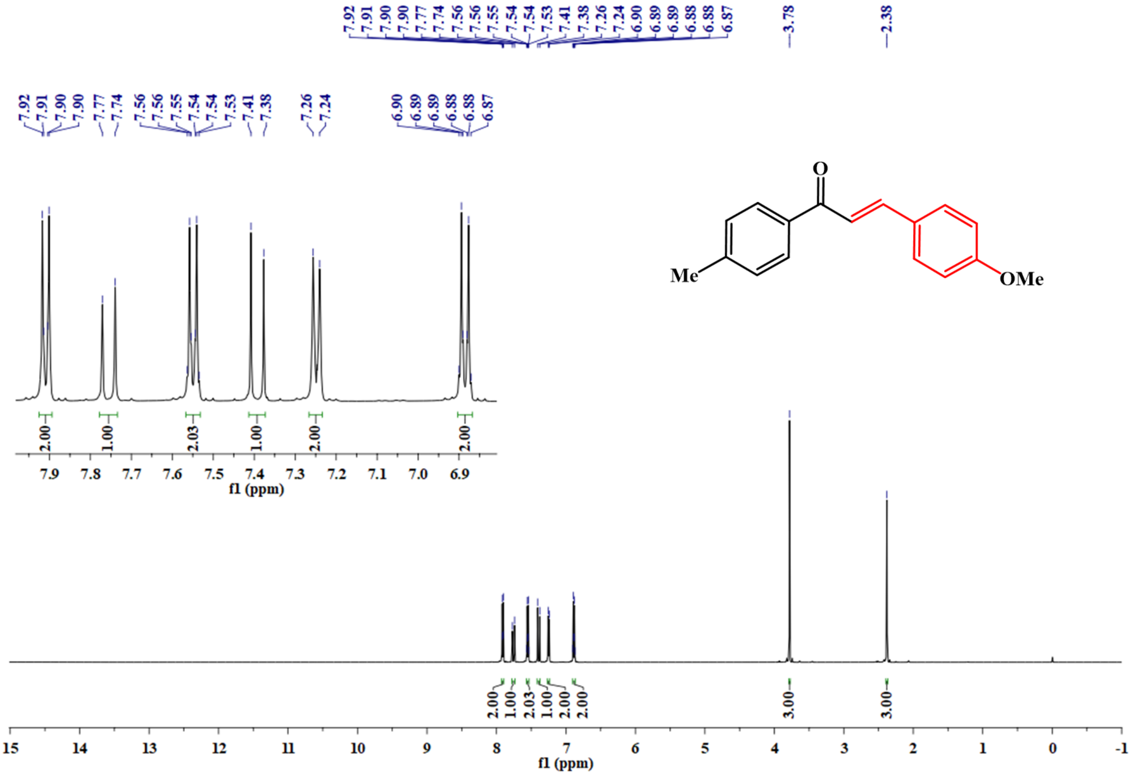


Fig. S115: ^{1}H NMR spectrum of **7b** in $CDCl_3$ at 500 MHz.

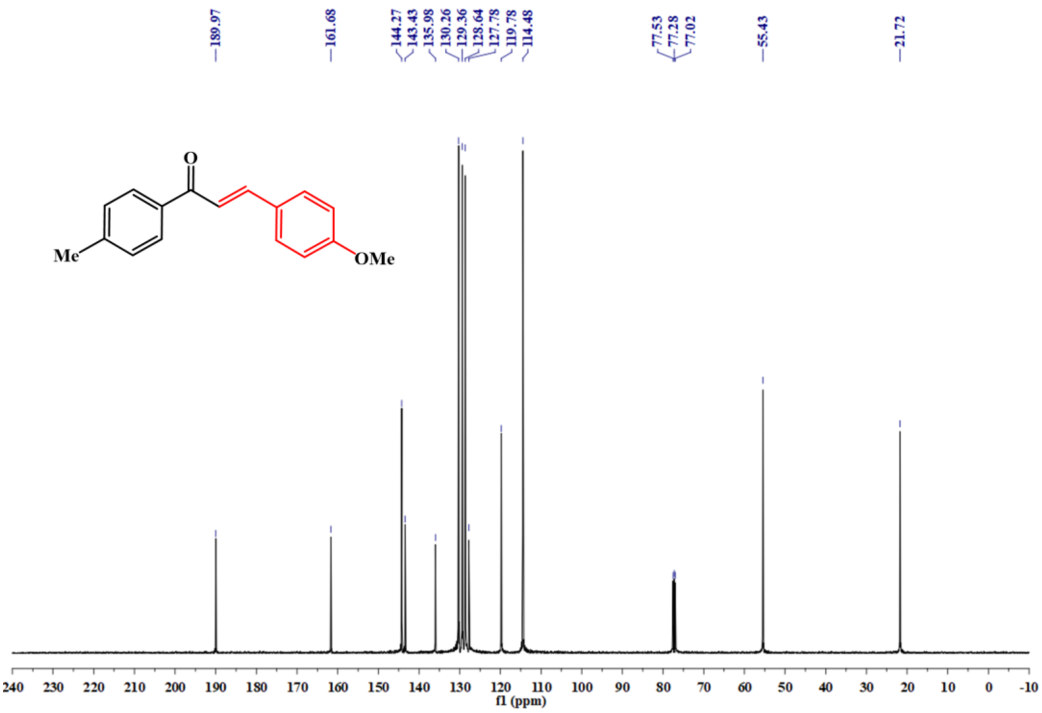


Fig. S116: ^{13}C NMR spectrum of **7b** in $CDCl_3$ at 126 MHz.

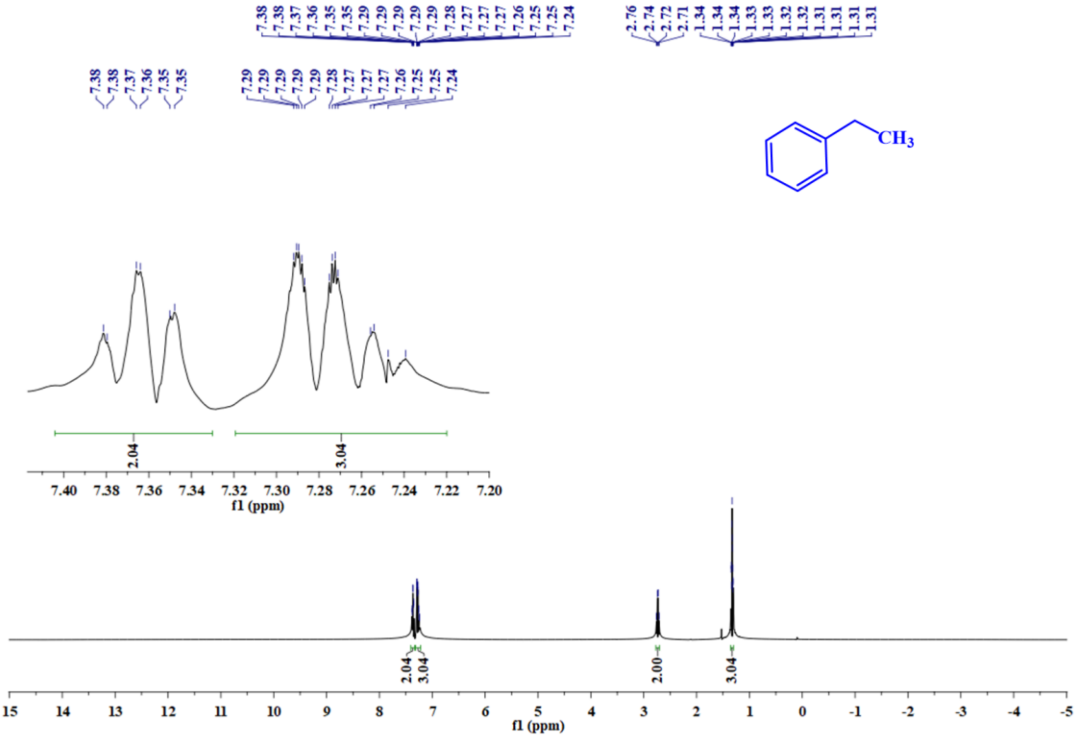


Fig. S117: ^{1}H NMR spectrum of **Ethyl benzene** in $CDCl_3$ at 500 MHz.

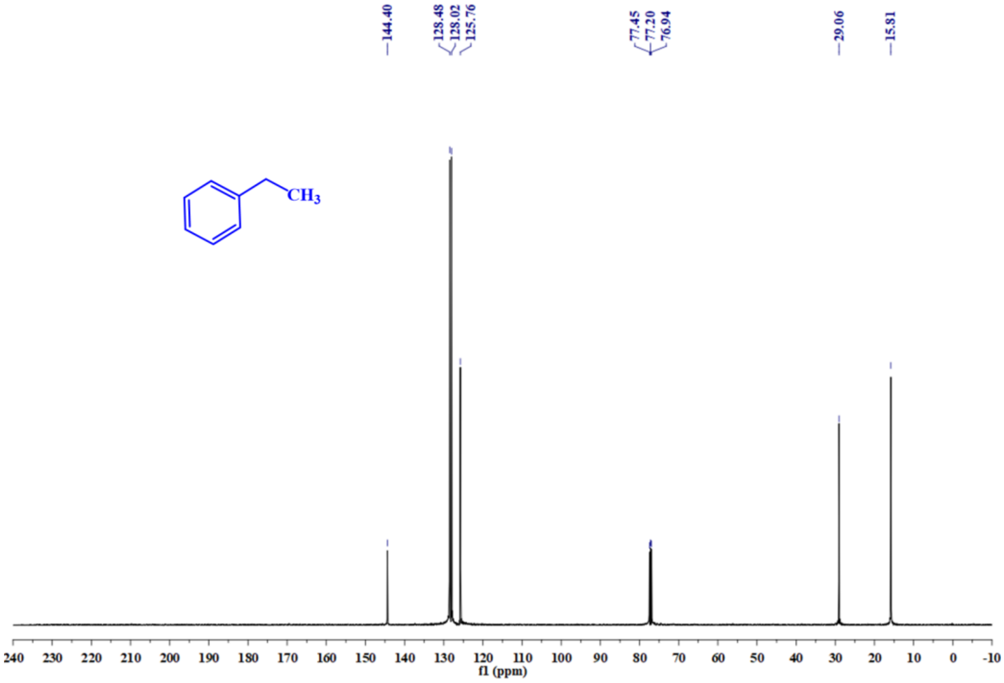
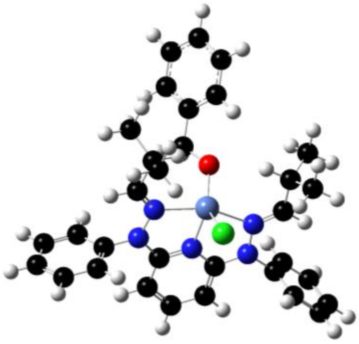


Fig. S118: ^{13}C NMR spectrum of **Ethyl benzene** in $CDCl_3$ at 126MHz.

10. Coordinates for optimized structures (atomic number, X, Y, Z)

10.1 Cartesian coordinates for C1A



C1A triplet G = -1773.602909, EZPE = -1773.525031

28	0.078849	0.162559	0.596716
17	0.282449	-0.554671	2.904897
7	2.730852	-0.864080	-0.302689
7	0.495410	-1.535738	-0.356483

7	2.232388	0.300313	0.334912
6	4.144150	-1.066967	-0.526108
6	4.922945	-1.690122	0.469039
1	4.450532	-2.018180	1.391240
6	6.300722	-1.879331	0.254252
1	6.904710	-2.361937	1.017865
6	6.894705	-1.444359	-0.948026
1	7.959119	-1.591807	-1.111841
6	6.110547	-0.817425	-1.937510
1	6.568144	-0.480980	-2.863977
6	4.732169	-0.625364	-1.727485
1	4.115079	-0.141860	-2.480361
6	1.783463	-1.826089	-0.658461
6	3.040589	1.247604	0.694645
1	4.117867	1.171277	0.524302
6	2.546370	2.495261	1.383391
1	1.452182	2.491343	1.357112
6	3.025312	2.495879	2.859568
1	2.673248	3.405218	3.363954
1	4.122805	2.477040	2.923837
1	2.625121	1.627761	3.394725
6	2.120248	-3.043811	-1.290911
1	3.146676	-3.282977	-1.535270
6	1.072772	-3.933223	-1.581753
1	1.300210	-4.878170	-2.067780
6	3.052893	3.745840	0.621274
1	2.713293	4.656508	1.130970

1	2.665065	3.764321	-0.403969
1	4.151461	3.772176	0.581894
7	-1.792114	-1.990906	-0.227007
7	-1.880632	-0.727216	0.411201
6	-2.935315	-2.868748	-0.336777
6	-3.757310	-2.806706	-1.478524
1	-3.519111	-2.104208	-2.272944
6	-4.873082	-3.659130	-1.577758
1	-5.508453	-3.617661	-2.458388
6	-5.163737	-4.564988	-0.537714
1	-6.025647	-5.222615	-0.616131
6	-4.338427	-4.619442	0.604085
1	-4.562058	-5.317570	1.406175
6	-3.222052	-3.769500	0.708321
1	-2.577005	-3.798392	1.582629
6	-0.512974	-2.399262	-0.621036
6	-3.019049	-0.303883	0.869679
1	-3.924150	-0.910618	0.783730
6	-3.154814	1.022103	1.577820
1	-2.226056	1.588177	1.442041
6	-4.333098	1.827010	0.973294
1	-4.439948	2.782563	1.500939
1	-5.280036	1.277349	1.073809
1	-4.169926	2.047352	-0.088542
6	-0.261294	-3.635859	-1.253910
1	-1.063225	-4.328703	-1.471369
6	-3.370215	0.770801	3.095658

1	-3.486784	1.730766	3.615179
1	-2.509410	0.245819	3.523102
1	-4.277788	0.176529	3.274045
6	-1.529738	3.538235	-1.487733
6	-2.394548	4.000806	-2.506479
6	-1.035411	4.462768	-0.546835
6	-2.758790	5.358156	-2.581713
1	-2.781672	3.298205	-3.244732
6	-1.398584	5.823333	-0.617394
1	-0.369145	4.094325	0.226709
6	-2.261005	6.277556	-1.634281
1	-3.424271	5.698864	-3.372604
1	-1.009279	6.525584	0.117399
1	-2.540840	7.327374	-1.690370
8	-0.210554	1.779459	-0.377826
6	-1.143886	2.058449	-1.416255
1	-0.720122	1.773941	-2.400630
1	-2.078257	1.471103	-1.307142

10.2 Cartesian coordinates for C2A

C2A triplet G = -2262.845374 EZPE = -2262.759713

28	-0.218972	-0.136711	0.500115

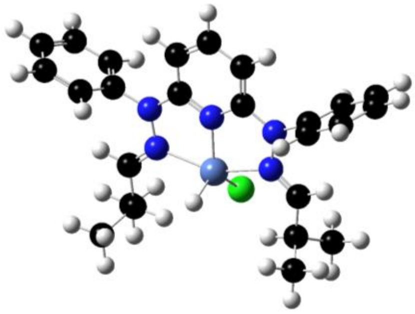
17	-0.465767	-0.968657	2.760723
7	1.884674	-0.005879	0.619572
7	-3.848582	2.580556	1.836908
1	-3.540297	3.468434	2.210961
7	-2.123126	-0.936064	-0.189609
7	0.370579	-1.761445	-0.489803
7	-1.892353	-2.129338	-0.939860
7	2.553983	-1.192518	0.181835
7	5.945591	2.448381	1.098516
1	6.665758	2.986811	1.560782
6	-5.159021	0.825613	1.218183
6	-5.160994	2.090391	1.883808
6	-6.322034	2.650212	2.444648
1	-6.303533	3.612722	2.949490
6	-7.513454	1.915680	2.330336
1	-8.432683	2.315293	2.751537
6	-7.535721	0.655047	1.674647
1	-8.474046	0.109863	1.606184
6	-6.370012	0.103091	1.120889
1	-6.408713	-0.867164	0.631253
6	-3.788548	0.578323	0.777645
6	-3.030887	1.685708	1.180139
1	-1.981044	1.888689	0.997350
6	-3.368366	-0.598986	0.060213
1	-4.175955	-1.248722	-0.278935
6	-0.570801	-2.563525	-1.043105
6	-0.204265	-3.784603	-1.656389

1	-0.944852	-4.424691	-2.116968
6	1.151219	-4.146185	-1.621339
1	1.461029	-5.083934	-2.074594
6	2.117012	-3.328205	-1.007435
1	3.157429	-3.620167	-0.967368
6	1.678009	-2.113468	-0.446231
6	-2.980713	-2.940169	-1.439734
6	-3.491431	-2.699260	-2.729956
1	-3.060309	-1.907382	-3.336734
6	-4.550093	-3.488707	-3.217117
1	-4.945300	-3.307650	-4.213084
6	-5.094669	-4.511944	-2.414990
1	-5.911813	-5.120890	-2.793096
6	-4.581166	-4.746073	-1.122937
1	-5.000559	-5.534179	-0.503444
6	-3.523690	-3.958712	-0.631094
1	-3.118728	-4.125714	0.363665
6	3.607177	-1.729451	1.047688
6	3.324524	-1.894290	2.420510
1	2.349640	-1.602377	2.806501
6	4.305252	-2.443931	3.263865
1	4.090724	-2.573619	4.321621
6	5.552284	-2.843606	2.739654
1	6.305517	-3.275342	3.394258
6	5.817546	-2.685265	1.366055
1	6.777361	-2.989125	0.955935
6	4.846119	-2.122595	0.516128

1	5.056035	-1.974606	-0.537937
6	2.550087	1.083678	0.895409
1	1.908161	1.860998	1.304446
6	3.955988	1.420742	0.708868
6	4.840073	1.154272	-0.420773
6	6.079580	1.810193	-0.140624
6	4.670118	2.235796	1.588541
1	4.352843	2.652574	2.533684
6	4.681321	0.497451	-1.663657
1	3.741312	0.017224	-1.915959
6	5.757070	0.481801	-2.563057
1	5.647778	-0.017725	-3.522658
6	6.991424	1.114630	-2.249134
1	7.806507	1.083019	-2.967980
6	7.166774	1.792913	-1.033385
1	8.102117	2.295491	-0.800326
8	-0.284249	1.620774	-0.282445
6	-0.911692	3.577311	-1.634568
6	-1.622861	4.197042	-2.687950
6	-0.168858	4.385840	-0.751226
6	-1.588781	5.593785	-2.857025
1	-2.206063	3.585791	-3.376630
6	-0.133251	5.785897	-0.915568
1	0.371743	3.895965	0.052593
6	-0.841829	6.396233	-1.968976
1	-2.141722	6.055403	-3.672778
1	0.446558	6.397195	-0.226294

1	-0.814720	7.476238	-2.097390
6	-0.947117	2.055823	-1.467990
1	-2.009045	1.737168	-1.492587
1	-0.471173	1.606439	-2.362152

10.3 Cartesian coordinates for C1B



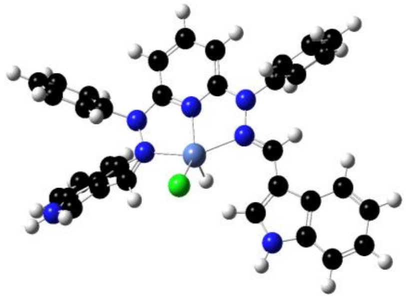
C1B triplet G = -1428.126648   EZPE = -1428.058615

28	0.000153	1.064703	0.140053
17	-0.000709	2.689223	-1.653659
7	-2.333708	-0.815168	0.007294
7	0.000071	-0.943046	0.012081
7	-2.134521	0.588713	0.090368
6	-3.654765	-1.402128	0.012188
6	-4.344674	-1.577233	-1.203414
1	-3.873563	-1.274143	-2.134764
6	-5.633149	-2.143310	-1.195488
1	-6.167748	-2.282549	-2.131258
6	-6.227509	-2.529109	0.023148
1	-7.222651	-2.966361	0.027072
6	-5.533604	-2.347439	1.236739
1	-5.991599	-2.644081	2.176512
6	-4.245441	-1.780858	1.233963

1	-3.698419	-1.633611	2.161604
6	-1.182203	-1.604141	-0.043838
6	-3.159268	1.377628	0.210118
1	-4.178030	0.981272	0.242076
6	-3.015527	2.872938	0.338066
1	-1.953498	3.127504	0.278856
6	-3.750642	3.572435	-0.833613
1	-3.670425	4.661463	-0.724191
1	-4.818534	3.310381	-0.852851
1	-3.298945	3.294459	-1.792284
6	-1.225784	-3.012511	-0.148855
1	-2.167921	-3.542303	-0.193272
6	0.000024	-3.696295	-0.198284
1	-0.000009	-4.779859	-0.280592
6	-3.578606	3.326176	1.710978
1	-3.480452	4.414741	1.809857
1	-3.029356	2.857432	2.536437
1	-4.643719	3.072345	1.811293
7	2.333821	-0.815152	0.006505
7	2.134546	0.588693	0.089411
6	3.654892	-1.402033	0.011999
6	4.245170	-1.780544	1.234027
1	3.697853	-1.633190	2.161478
6	5.533406	-2.346971	1.237367
1	5.991061	-2.643397	2.177372
6	6.227798	-2.528671	0.024068
1	7.222982	-2.965823	0.028374

6	5.633796	-2.143186	-1.194852
1	6.168732	-2.282616	-2.130402
6	4.345265	-1.577269	-1.203338
1	3.874402	-1.274408	-2.134891
6	1.182308	-1.604158	-0.044222
6	3.159203	1.377650	0.209696
1	4.177957	0.981300	0.242287
6	3.015420	2.872972	0.337451
1	1.953419	3.127557	0.277831
6	3.578001	3.326327	1.710509
1	3.479798	4.414896	1.809308
1	4.643084	3.072521	1.811231
1	3.028462	2.857631	2.535806
6	1.225846	-3.012521	-0.149378
1	2.167976	-3.542281	-0.194353
6	3.750947	3.572375	-0.834044
1	3.670774	4.661408	-0.724649
1	3.299510	3.294418	-1.792840
1	4.818818	3.310230	-0.852971
1	0.000918	1.407574	1.717075

10.4 Cartesian coordinates for C2B



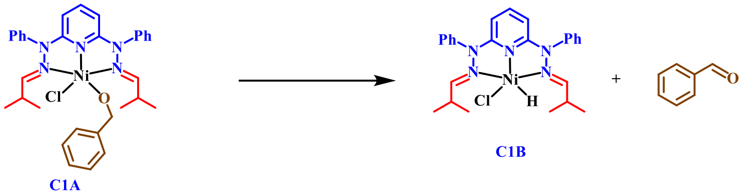
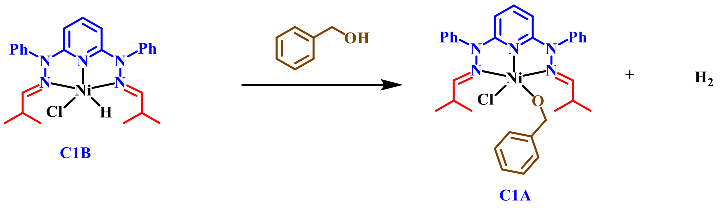
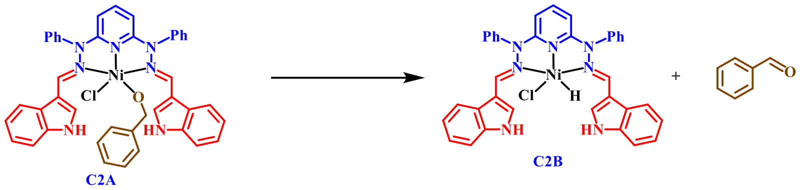
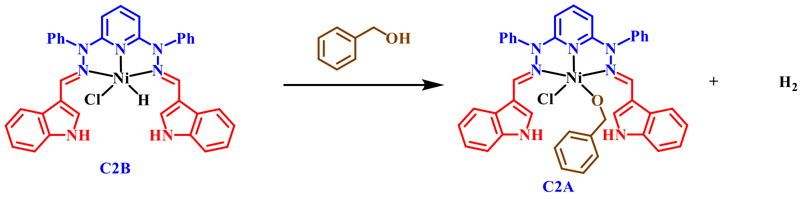
C2B triplet G = -1917.366632   EZPE = -1917.292274

28	0.296903	-0.473309	0.525882
17	0.498570	-1.812198	2.543607
7	-1.839589	-0.455326	0.639800
7	3.945630	-3.704886	0.492611
1	3.648003	-4.630678	0.771061
7	2.281590	0.406382	0.168888
7	-0.169736	1.422082	0.042473
7	2.132194	1.810660	-0.085356
7	-2.423292	0.784021	0.248309
7	-5.865757	-2.957879	0.064013
1	-6.664906	-3.523017	0.317753
6	5.219474	-1.961410	-0.225010
6	5.225313	-3.367329	0.030131
6	6.358360	-4.172614	-0.177078
1	6.341102	-5.240716	0.024345
6	7.519367	-3.543440	-0.655621
1	8.417019	-4.132156	-0.828020
6	7.537975	-2.147180	-0.918346
1	8.452262	-1.689770	-1.288945
6	6.399862	-1.352209	-0.708379
1	6.438249	-0.285728	-0.918093

6	3.879985	-1.472682	0.103303
6	3.145115	-2.583213	0.536862
1	2.130347	-2.622815	0.904210
6	3.479720	-0.098745	-0.042127
1	4.274430	0.563834	-0.386639
6	0.836390	2.316390	-0.132382
6	0.558971	3.690259	-0.334394
1	1.356089	4.408028	-0.473055
6	-0.785697	4.086070	-0.338582
1	-1.029811	5.134742	-0.485492
6	-1.826572	3.160114	-0.148704
1	-2.859414	3.477985	-0.136806
6	-1.471065	1.809049	0.043867
6	3.271899	2.675547	-0.297236
6	3.665407	3.012267	-1.607596
1	3.108975	2.614749	-2.452469
6	4.771660	3.859577	-1.806323
1	5.075389	4.123358	-2.815879
6	5.485265	4.360204	-0.698663
1	6.340743	5.012710	-0.853406
6	5.090934	4.014316	0.610094
1	5.640063	4.399904	1.464877
6	3.982466	3.171902	0.813717
1	3.666268	2.898033	1.816676
6	-3.742457	1.146102	0.756911
6	-3.990292	1.052508	2.141945
1	-3.214903	0.680104	2.805980

6	-5.241393	1.439928	2.652107
1	-5.433094	1.365464	3.719472
6	-6.237555	1.936513	1.786652
1	-7.202582	2.241011	2.184023
6	-5.977032	2.038120	0.406611
1	-6.740701	2.416841	-0.267683
6	-4.730807	1.639584	-0.111149
1	-4.532935	1.696735	-1.176318
6	-2.526132	-1.569091	0.697085
1	-1.943868	-2.367955	1.155017
6	-3.857425	-1.902658	0.203823
6	-4.455913	-1.585177	-1.087916
6	-5.715358	-2.259666	-1.140156
6	-4.743081	-2.763733	0.851363
1	-4.648577	-3.228841	1.822000
6	-4.014202	-0.866630	-2.223207
1	-3.045133	-0.376432	-2.223444
6	-4.844975	-0.810188	-3.351220
1	-4.517696	-0.264720	-4.233032
6	-6.108596	-1.463062	-3.370355
1	-6.728968	-1.400027	-4.261120
6	-6.558183	-2.202326	-2.265484
1	-7.512683	-2.721947	-2.288575
1	0.361510	-1.346628	-0.824865

Table S6. Gibbs free energy of each step.

step	hartree	kcal/mol
	0.0714	44.8
	-0.0674	-42.3
	0.0714	44.8
	-0.069	-43.8

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