Supplementary Information

Manganese(I)–CNP Complex–Catalyzed Multicomponent Synthesis of 2-Pyrazolines by Acceptorless Alcohol Dehydrogenation

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1. General Information

Alcohols, ketones and hydrazines, were all ordered from Innochem, Aladdin, TCI, Titan, Energy Chemical, or Bidepharm. Nitrogen (99.9%) were supplied by Southwest Institute of Chengdu. Unless otherwise stated, commercial reagents were used without purification. All manipulations of air- and moisture-sensitive reagents were performed under an inert atmosphere of nitrogen in either a vacuum atmosphere or using standard Schlenk techniques. All solvents were reagent grade or higher, unless otherwise noted, all operations were performed under the nitrogen balloon and all solvents were performed degassing and dehydrating treatment.

NMR spectra were recorded using the following NMR spectrometers: Bruker Avance 400 MHz (^{1}H, ^{13}C, ^{31}P,). Chemical shifts of the NMR spectra are reported relative to $CDCl_3$ (^{1}H NMR: δ = 7.26 ppm, ^{13}C NMR: δ = 77.0 ppm), and CD_3SOCD_3 (^{1}H NMR: δ = 2.50 ppm, ^{13}C NMR: δ = 39.5 ppm). Data for ^{1}H NMR spectra were reported as follows: chemical shift (ppm), peak shape (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. Data for ^{13}C, and ^{31}P NMR are reported in terms of chemical shift (ppm). Data for ^{13}C NMR are reported with chemical shift (ppm) values referenced to the residual solvent peak; data for ^{31}P NMR are reported with chemical shift (ppm) values as observed.

High resolution mass spectra (HRMS) were obtained with a Shimadzu (LCMS-IT-TOF). The data are given as mass units per charge (m/z) and intensities of signals are given in brackets. Gas chromatography and mass spectrometry (GC-MS) analysis was conducted on a Shimadzu GCMS-QP2020 (SH-Rtx-35MS, 30 m × 0.25 mm × 0.25 μm). X-ray crystallographic analyses were performed on a Bruker D8 VENTURE Metaljet diffractometer. Fourier Transform Infrared (FT-IR) spectra were obtained using a Shimadzu IRTracer-100 spectrometer. All the data have been reported in the wavenumber (cm^{-1}).

2. General Procedure for the Synthesis of 2-Pyrazolines

After Mn-CNP (0.005 mmol, 3.50 mg), KOMe (0.6 mmol, 42 mg) were added into a dried Schlenk tube equipped with a N_2 balloon, and it was subject to three cycles of vacuum and refilled with nitrogen. Alcohol (0.5 mmol), ketone (0.8 mmol), hydrazine (0.5 mmol) and anhydrous toluene (1 mL) were sequentially injected into the tube. The solution was stirred at 120 °C for 24 hours. At the end of the reaction, the mixture was cooled to room temperature and diluted with dichloromethane and filtered with Celite. The yield was calculated by GC and isolating. Isolation method: After the reaction was cooled to room temperature, the solid was removed by filtration and the filtrate was concentrated to 1 mL, subsequently it was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1/30, v/v) as eluent to obtain the corresponding pyrazoline product.

3. Synthesis and Characterization of Ligands and Manganese Complexes

3.1 Synthesis of Ligands

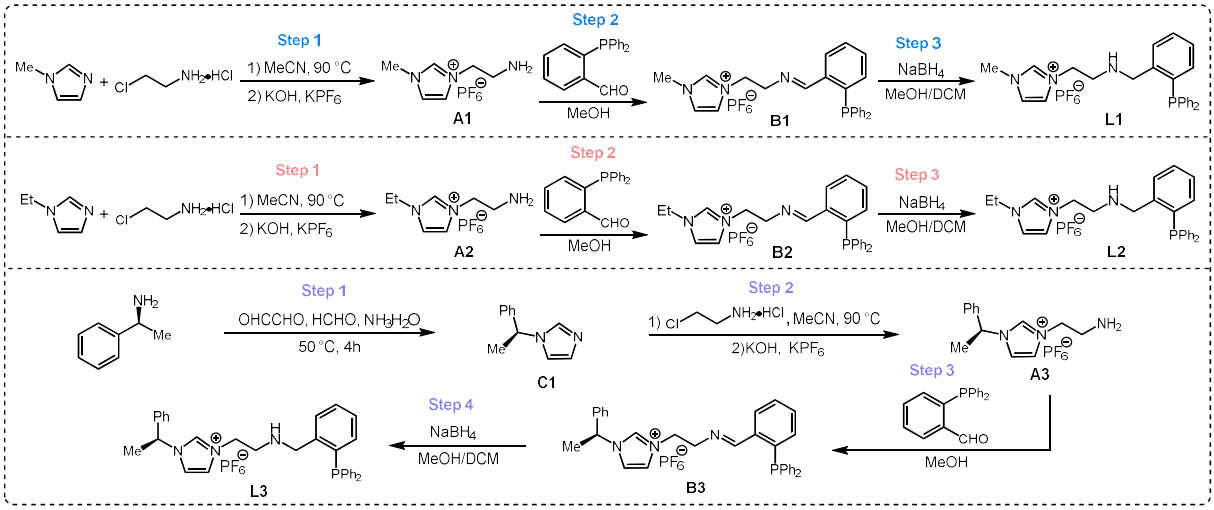


Figure S1. Synthesis of Ligands

3.1.1 Synthesis of **L1**

Setp 1:

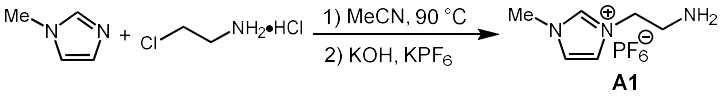


Figure S2. The Synthesis of **A1**

2-Chloroethylamine hydrochloride (2.9 g, 25 mmol) and 1-methylimidazole (4 mL, 50 mmol) were added to a mixture of acetonitrile (30 mL) in a 100 mL two-neck flask. The mixture was refluxed at 90 °C for 12 h. After cooling to room temperature, the yellow supernatant was decanted, and the solid residue was washed with acetonitrile (3 × 10 mL). The resulting white solid was dissolved in distilled water, and the pH was adjusted to 10 with KOH. To the vigorously stirred aqueous solution, KPF_6 (4.6 g, 25 mmol) was added portionwise over 1 h, yielding a pale-yellow turbid emulsion. Water was removed by vacuum distillation, and the oily residue was dissolved in THF/EtOH (25 mL, 1:1 v/v). After filtration to remove insoluble KCl, the filtrate was concentrated to afford the pale-yellow ionic liquid as a viscous oil (5.6 g, 70% yield). **^{1}H NMR** (400 MHz, CD_3SOCD_3) δ 8.64 (s, 1H), 7.27 (dt, J = 15.1, 1.9 Hz, 2H), 3.69 (t, J = 5.7 Hz, 2H), 3.45 (s, 3H), 2.50 (t, J = 5.7 Hz, 2H). **^{13}C NMR** (100 MHz, CD_3SOCD_3) δ 137.2, 123.7, 122.9, 52.5, 41.7, 36.1.

Setp 2:

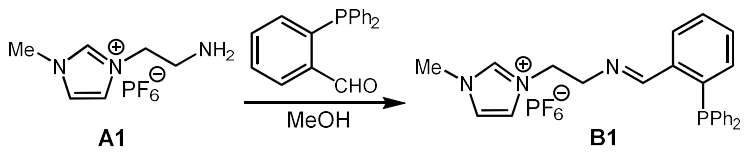


Figure S3. The Synthesis of **B1**

In a glovebox, to a 50 mL round-bottom flask were added successively the imidazolium salt (542 mg, 2 mmol), 2-(diphenylphosphino)benzaldehyde (580 mg, 2 mmol), and Na_2SO_4 (568 mg, 4 mmol). Methanol (10 mL) was added to dissolve the solids, and the mixture was stirred at room temperature for 12 h, during which a large amount of white solid precipitated. The solid was collected by filtration, dissolved in DCM, and passed through a Celite pad to remove Na_2SO_4. The resulting pale-yellow solution was subjected to recrystallization (vapor diffusion of diethyl ether into DCM) to afford the product **B1** as a white solid (923 mg, 85% yield). **^{1}H NMR** (400 MHz, CD_3SOCD_3) δ 9.04 (s, 1H), 8.78 (d, *J* = 1.6 Hz, 1H), 7.93 (ddd, *J* = 7.7, 3.9, 1.6 Hz, 1H), 7.63 (p, *J* = 1.7 Hz, 2H), 7.53 – 7.37 (m, 8H), 7.18 (dddd, *J* = 7.6, 5.8, 2.9, 1.5 Hz, 4H), 6.84 (ddd, *J* = 7.8, 4.4, 1.5 Hz, 1H), 4.37 (t, *J* = 4.6 Hz, 2H), 3.90 – 3.78 (m, 5H). **^{13}C NMR** (100 MHz, CD_3SOCD_3) δ 162.3, 162.1, 139.1, 138.9, 137.7, 137.5, 137.2, 136.8, 136.7, 134.0, 133.8, 133.7, 131.3, 129.6 (d, *J* = 6.3 Hz), 129.3 (d, *J* = 7.1 Hz), 128.9 (d, *J* = 4.1 Hz), 123.9, 122.9, 59.5, 50.1, 36.2. **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ -14.85, -131.02, -135.41, -139.81, -144.19, -148.59, -152.98, -157.37.

Setp 3:

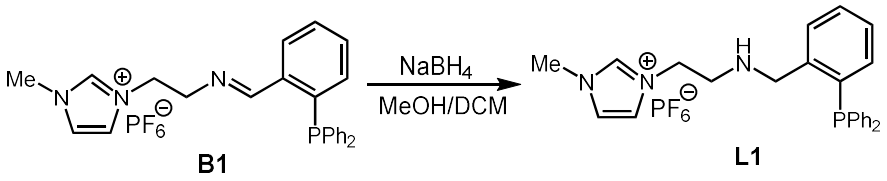


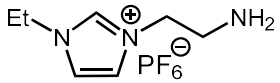
Figure S4. The Synthesis of **L1**

Under a nitrogen atmosphere, compound **B1** (1.1 g, 2 mmol) was dissolved in a mixture of MeOH and DCM (20 mL, 1:1 v/v) in a 50 mL round-bottom flask. $NaBH_4$ (152 mg, 4 mmol) was added in small portions, with immediate vigorous gas evolution. After stirring for 5 h, the reaction was quenched with distilled water and the mixture was stirred for 30 min and then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 (1 g). After filtration, the solvent was removed under reduced pressure. The residue was washed with *n*-hexane and dried to afford the product **L1** as a colorless oil (873 mg, 80% yield). **^{1}H NMR** (400 MHz, CD_3SOCD_3) δ 9.05 (s, 1H), 7.67 (dt, *J* = 6.4, 1.9 Hz, 2H), 7.50 –

7.36 (m, 8H), 7.20 (td, *J* = 6.7, 2.4 Hz, 5H), 6.84 – 6.74 (m, 1H), 5.76 (s, 1H), 4.15 (t, *J* = 5.6 Hz, 2H), 3.86 (s, 5H), 2.82 (t, *J* = 5.7 Hz, 2H). **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ -17.09, -135.35, -139.75, -144.14, -148.53, -152.92.

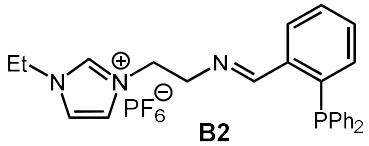
3.1.2 Synthesis of **L2**

It is worth noting that the synthesis methods for **L2** are identical to those of **L1**.



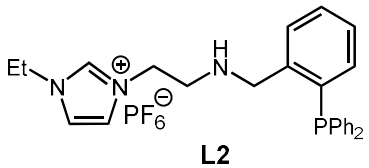
A2

^{1}H NMR (400 MHz, CD_3SOCD_3) δ 9.12 (d, *J* = 1.7 Hz, 1H), 7.75 (dt, *J* = 20.3, 1.9 Hz, 2H), 4.19 (q, *J* = 7.3 Hz, 2H), 4.14 – 4.06 (m, 2H), 2.96 – 2.88 (m, 2H), 1.43 (td, *J* = 7.3, 1.9 Hz, 3H). **^{13}C NMR** (100 MHz, CD_3SOCD_3) δ 136.4, 123.1, 122.3, 52.3, 44.6, 41.6, 15.5.



B2

^{1}H NMR (400 MHz, CD_3SOCD_3) δ 9.12 (d, *J* = 1.6 Hz, 1H), 8.75 (d, *J* = 4.5 Hz, 1H), 7.91 (ddd, *J* = 7.7, 3.9, 1.5 Hz, 1H), 7.72 (t, *J* = 1.8 Hz, 1H), 7.64 (t, *J* = 1.8 Hz, 1H), 7.48 (td, *J* = 7.4, 1.4 Hz, 1H), 7.45 – 7.34 (m, 7H), 7.21 – 7.10 (m, 4H), 6.83 (ddd, *J* = 7.8, 4.5, 1.4 Hz, 1H), 4.36 (dd, *J* = 6.7, 4.6 Hz, 2H), 4.15 (q, *J* = 7.3 Hz, 2H), 3.90 – 3.81 (m, 2H), 1.34 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, CD_3SOCD_3) δ 162.3, 162.1, 139.0, 138.8, 137.7, 137.5, 136.8, 136.7, 136.4, 134.0, 133.8, 133.7, 131.4, 129.6 (d, *J* = 5.0 Hz), 129.3 (d, *J* = 7.1 Hz), 128.9 (d, *J* = 4.4 Hz), 122.9, 122.5, 59.4, 50.1, 44.7, 15.6. **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ -14.79, -131.01, -135.40, -139.79, -144.18, -148.57, -152.96, -157.36.

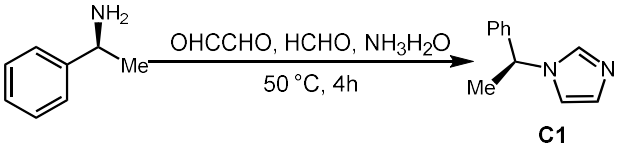


L2

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.35 – 7.29 (m, 8H), 7.25 – 7.19 (m, 6H), 7.15 (tt, *J* = 7.4, 1.7 Hz, 1H), 6.90 (ddd, *J* = 7.9, 4.6, 1.3 Hz, 1H), 5.28 (d, *J* = 1.5 Hz, 1H), 4.13 (q, *J* = 7.4 Hz, 2H), 4.01 (t, *J* = 5.4 Hz, 2H), 3.94 (d, *J* = 1.7 Hz, 2H), 2.86 (dd, *J* = 6.4, 4.2 Hz, 2H), 1.46 (td, *J* = 7.4, 1.3 Hz, 3H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ -16.28, -135.52, -139.92, -144.31, -148.71, -153.11.

3.1.3 Synthesis of **L3**

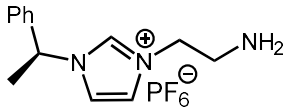
Step 1:



C1

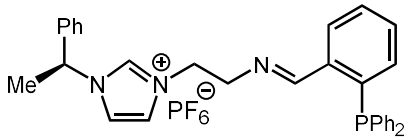
Figure S5. The Synthesis of **C1**

To a round-bottom flask was added 40% aqueous glycolaldehyde (1.5 mL, 13 mmol) and 37% aqueous formaldehyde (1.0 mL, 10 mmol). The mixture was stirred in an oil bath at 50°C for 5–10 min. A thoroughly mixed solution of L-1-Phenylethylamine (1.06 mL, 8.25 mmol) and 25% ammonia (1.6 mL, 10.6 mmol) was then added dropwise. After stirring for 4 h, the mixture was extracted with DCM (3 × 15 mL). The organic layer was concentrated and purified by column chromatography to give the product **C1** as a yellow oil (750 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.4 Hz, 1H), 7.29 (ddd, *J* = 12.1, 7.8, 6.0 Hz, 3H), 7.13 – 7.09 (m, 2H), 7.04 (q, *J* = 1.9 Hz, 1H), 6.90 (t, *J* = 1.4 Hz, 1H), 5.31 (q, *J* = 7.0 Hz, 1H), 1.81 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 135.8, 129.0, 128.7, 127.8, 125.7, 117.7, 56.3, 21.8.[1]



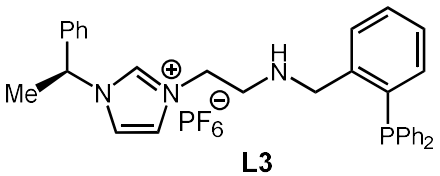
A3

^{1}H NMR (400 MHz, CD_3SOCD_3) δ 9.32 (d, *J* = 1.7 Hz, 1H), 7.84 (dt, *J* = 30.9, 1.8 Hz, 2H), 7.45 – 7.37 (m, 5H), 5.79 (q, *J* = 7.0 Hz, 1H), 4.28 – 4.18 (m, 2H), 3.09 (dd, *J* = 6.5, 5.1 Hz, 2H), 1.88 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3SOCD_3) δ 139.9, 136.2, 129.5, 129.2, 127.1, 123.6, 121.6, 59.1, 50.7, 21.0.



B3

^{1}H NMR (400 MHz, CD_3SOCD_3) δ 9.35 (s, 1H), 8.74 (d, *J* = 4.6 Hz, 1H), 7.91 – 7.64 (m, 3H), 7.52 – 7.31 (m, 10H), 7.31 – 7.24 (m, 3H), 7.16 (qt, *J* = 6.4, 3.1 Hz, 4H), 6.89 – 6.81 (m, 1H), 5.76 (q, *J* = 7.1 Hz, 1H), 4.41 (t, *J* = 5.4 Hz, 2H), 3.86 (t, *J* = 5.6 Hz, 2H), 1.82 (d, *J* = 7.0 Hz, 3H). **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ -14.73, -131.02, -135.41, -139.80, -144.19, -148.58, -152.97, -157.36.



L3

^{1}H NMR (400 MHz, CD_3SOCD_3) δ 9.31 (d, *J* = 1.7 Hz, 1H), 7.86 (t, *J* = 1.9 Hz, 1H), 7.74 (t, *J* = 1.8 Hz, 1H), 7.42 – 7.37 (m, 14H), 7.19 (dddd, *J* = 9.5, 7.4, 6.0, 1.4 Hz, 4H), 6.75 (ddd, *J* = 7.7, 4.5, 1.4 Hz, 1H), 5.80 (q, *J* = 7.0 Hz, 1H), 5.76 (1H s,), 4.16 (t, *J* = 5.7 Hz, 2H), 3.82 (d, *J* = 2.3 Hz, 2H), 2.82 (t, *J* = 5.7 Hz, 2H), 1.88 (d, *J* = 4.7 Hz, 3H). **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ -17.05, -131.02, -135.41, -139.80, -144.19, -148.58, -152.97, -157.36.

3.2 Synthesis and Characterization of Complexes

3.2.1 Synthesis and Characterization of Mn-1

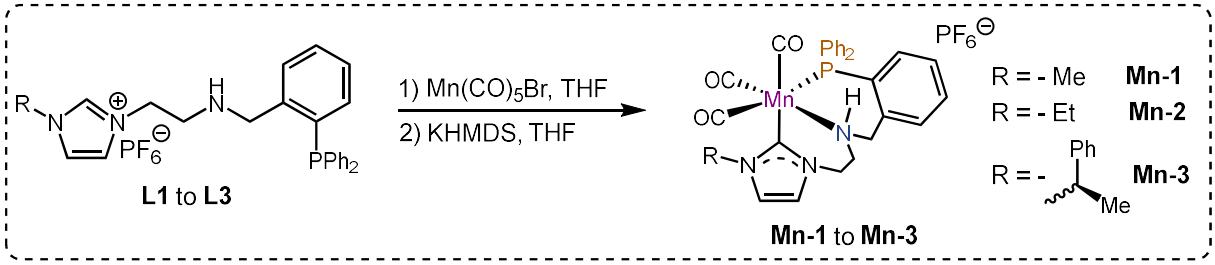


Figure S6. The Synthesis of Complexes

Add ligand **L1** (273 mg, 0.5 mmol) to an orange suspension of $[MnBr(CO)_5]$ (137.5 mg, 0.5 mmol) in THF (5 mL), and stir at 50°C for 3 h. The resulting solution was cooled to room temperature, and potassium bis(trimethylsilyl)amide (110 mg, 0.55 mmol) was added dropwise to 2 mL of THF. The mixture was stirred for 3 h and evaporated to dryness. The oily liquid was washed with n-hexane, dissolved in DCM, filtered through a Celite plug to remove inorganic salts, and evaporated to dryness. The crude product was purified by recrystallization (diffusion of diethyl ether into DCM solution) to afford yellow solid **Mn-1** in 81% yield (299 mg).[2] **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ 39.68, -135.42, -139.81, -144.20, -148.59, -152.98. HRMS (ESI^+): calculated for $C_{28}H_{26}MnN_3O_3P^+$ $[M - PF_6]^+$ 538.1092, found: 538.1085.

It is worth noting that **Mn-2** and **Mn-3** were synthesized by the same method as **Mn-1**. The Mn(I) complexes were NMR silent due to their paramagnetic nature, this results in severe line broadening, rendering the signals undetectable by solution-state ^{1}H NMR spectroscopy. However, based on the ^{31}P NMR spectroscopy, the chemical shift of the **L1** to **L3** in the ^{31}P NMR spectroscopy is less than 0 ppm, while the chemical shift of the complexes in the ^{31}P

NMR spectroscopy is more than 0 ppm. This significant change in chemical shift indicates that the ligands has coordinated with $Mn(CO)Br_5$.

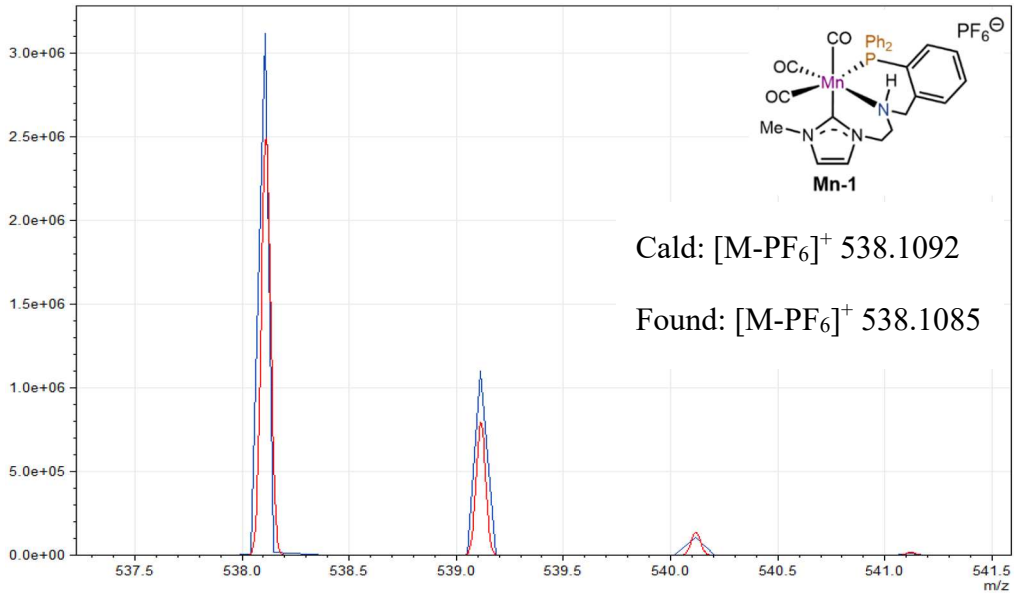


Figure S7. HRMS results of Mn-1.

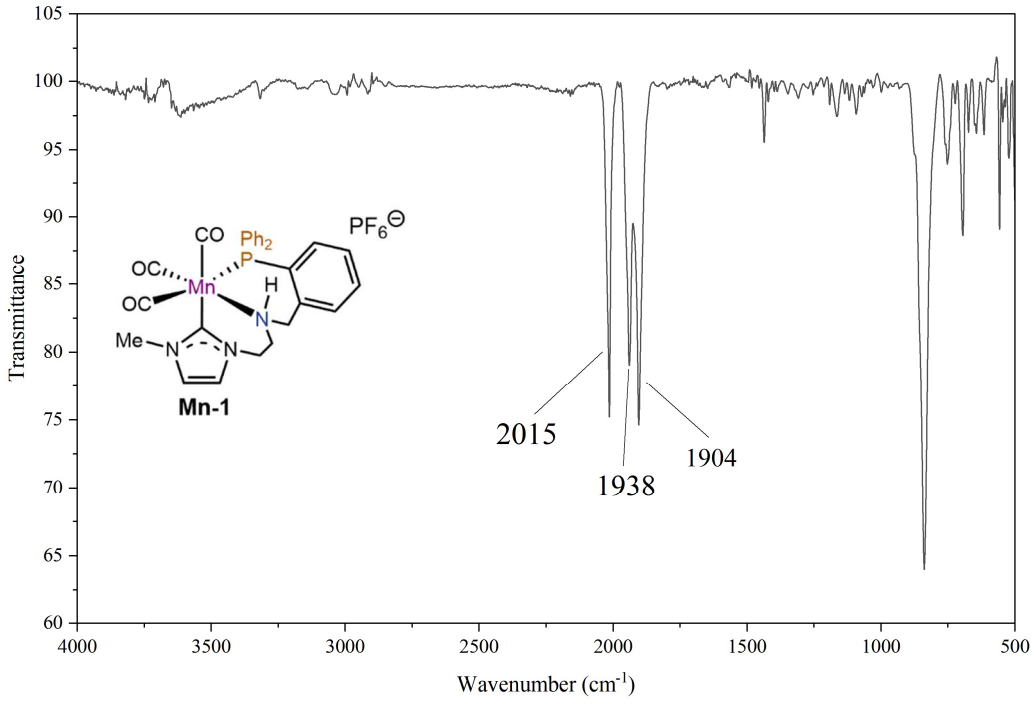


Figure S8. IR spectrum of solid complex Mn-1.

3.2.2 Synthesis and Characterization of Mn-2

Mn-2： yellow solid (yield 80%) **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ 39.09, -135.41, -139.80, -144.19, -148.58, -152.97. HRMS (ESI^+): calculated for $C_{29}H_{28}MnN_3O_3P^+$ $[M - PF_6]^+$ 552.1249, found: 552.1247.

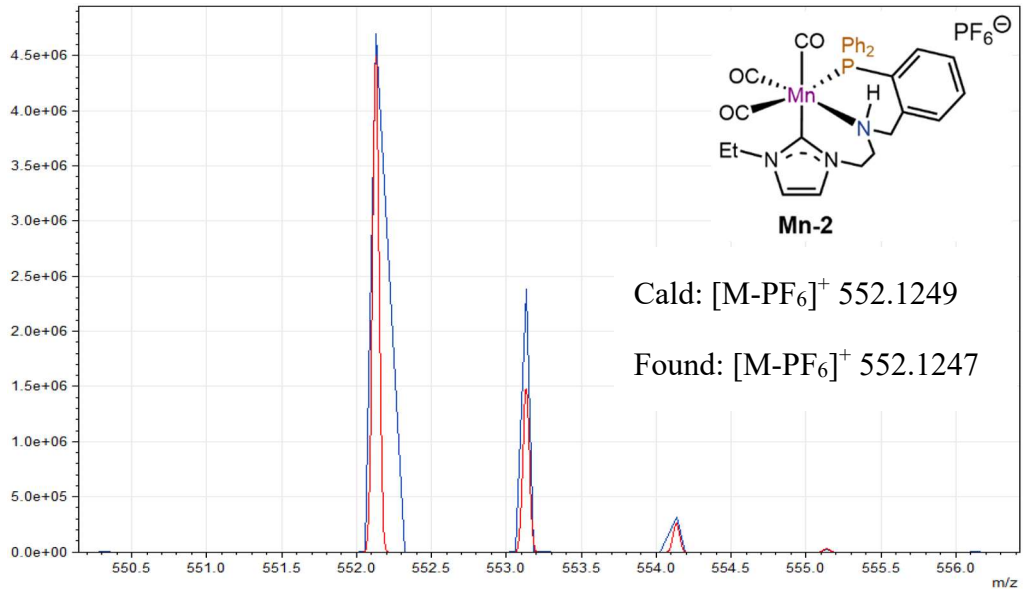


Figure S9. HRMS results of **Mn-2**

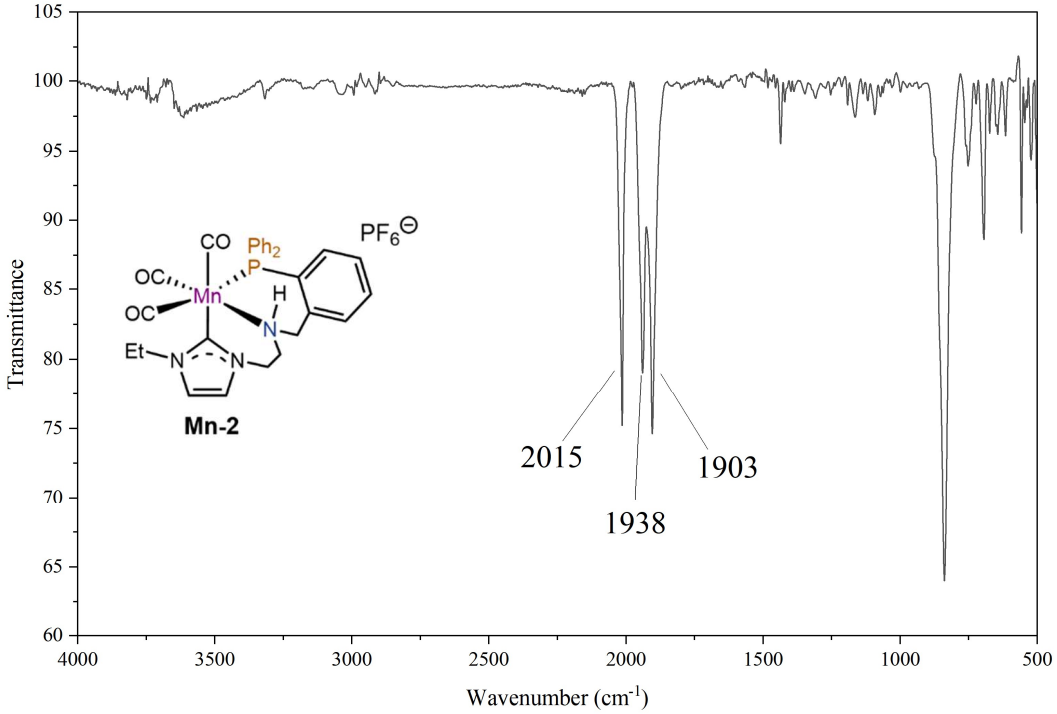


Figure S10. IR spectrum of solid complex Mn-2.

3.2.3 Synthesis and Characterization of Mn-3

Mn-3： yellow solid (yield 75%) **^{31}P NMR** (162 MHz, CD_3SOCD_3) δ 38.66, -139.80, -144.19, -148.58. HRMS (ESI^+): calculated for $C_{35}H_{32}MnN_3O_3P^+$ $[M - PF_6]^+$ 628.1562, found: 628.1961.

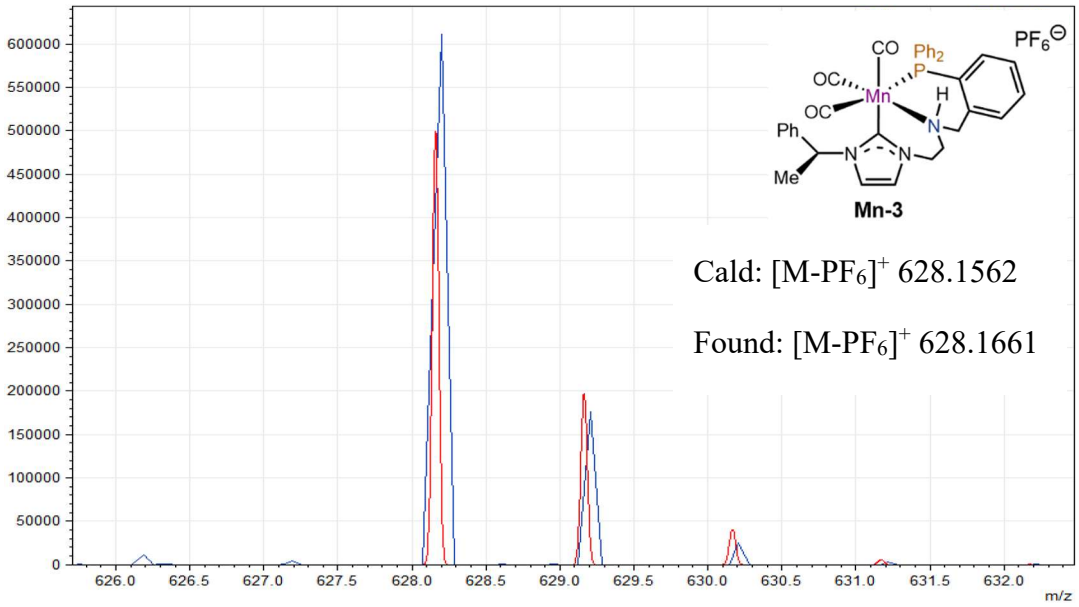


Figure S11. HRMS results of Mn-3.

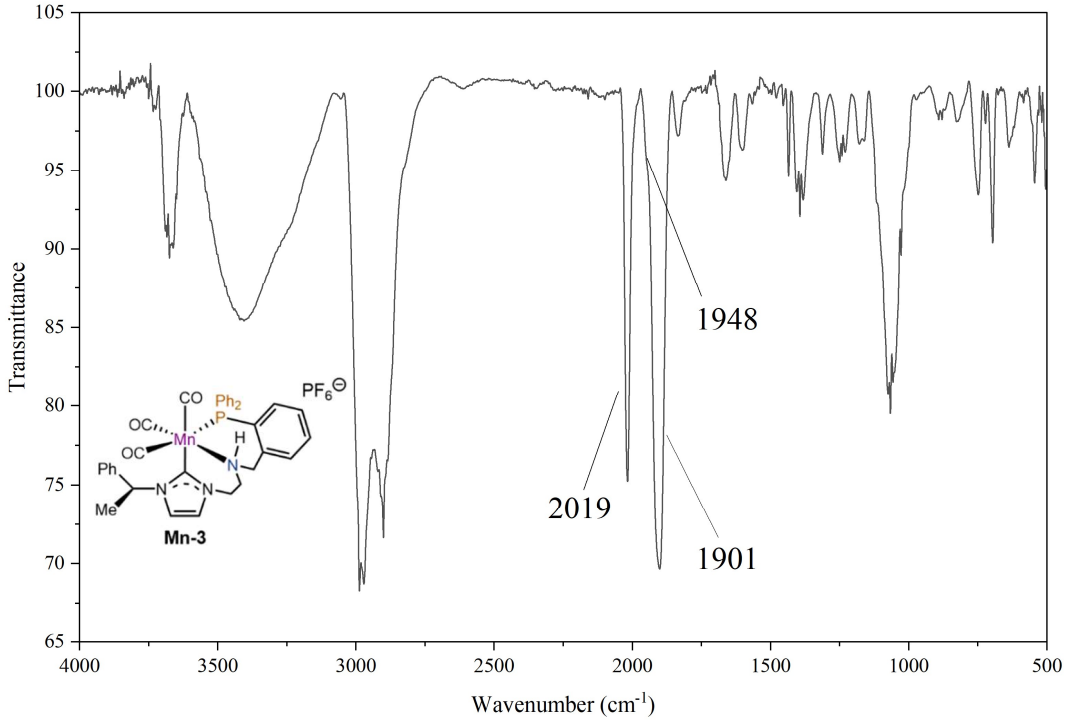


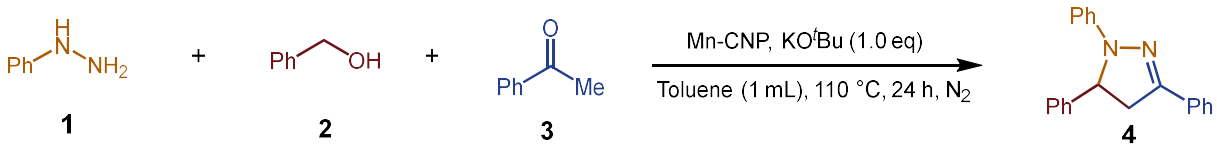
Figure S12. IR spectrum of solid complex Mn-3.

4. Optimization of Reaction Conditions for Synthesis of 2-Pyrazolines

4.1 Optimization of Reaction Conditions

Reaction procedure: After Mn-CNP, base was added into a dried Schlenk tube equipped with a N_2 balloon, and it was subject to three cycles of vacuum and refilled with nitrogen. Benzyl alcohol (0.5 mmol, 52 μL), phenylacetone, phenylhydrazine and anhydrous toluene (1 mL) were sequentially injected into the tube. The solution was stirred at a certain temperature for 24 hours. At the end of the reaction, the mixture was cooled to room temperature and diluted with dichloromethane and filtered with Celite. The yield was calculated by GC.

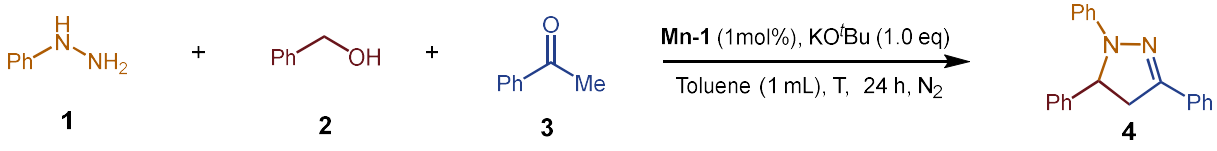
Table S1: Effect of Reaction Catalyst on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]



Entry	Catalyst (mol %)	yield of product (%)[b]
1	None	trace
2	**Mn-1** (1.0%)	57
3	**Mn-2** (1.0%)	56
4	**Mn-3** (1.0%)	29
5	**Mn-1** (0.5%)	49
6	**Mn-1** (1.5%)	57
7	**Mn-1** (2.0%)	56

[a]Reaction conditions: Phenyl hydrazine (0.5 mmol, 1 equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (0.6 mmol, 1.2 equiv.), Mn-CNP and KO^{t}Bu (0.50 mmol, 1.0 equiv.) in toluene (1 mL) at 110 °C for 24 h; [b]GC yield.

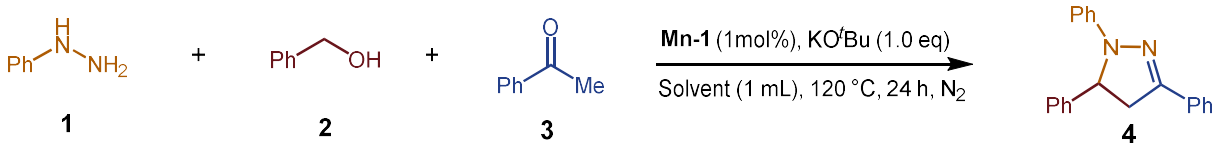
Table S2: Effect of Temperature on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]



Entry	Temperature (°C)	yield of product (%)[b]
1	110	57
2	120	62
3	130	56

[a]Reaction conditions: Phenyl hydrazine (0.5 mmol, 1 equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (0.6 mmol, 1.2 equiv.), **Mn-1** (1 mol%), and KO^{t}Bu (0.50 mmol, 1.0 equiv.) in toluene (1 mL) for 24 h; [b]GC yield.

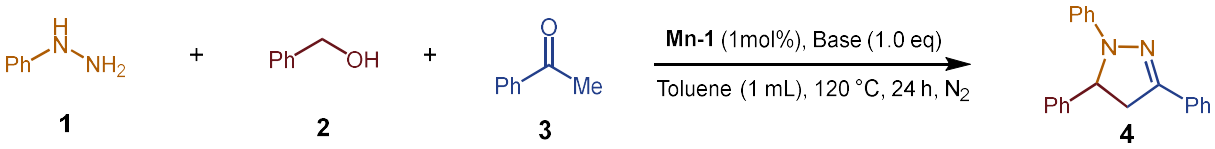
Table S3: Effect of Solvent on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]



Entry	Solvent (1 mL)	yield of product (%)[b]
1	DMSO	10
2	DMF	32
3	Chlorobenzene	56
4	Bromobenzene	53
4	*o*-xylene	53
5	Mesitylene	50
6	Toluene	62
7	*o*-dichlorobenzene	52

[a]Reaction conditions: Phenyl hydrazine (0.5 mmol, 1 equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (0.6 mmol, 1.2 equiv.), **Mn-1** (1 mol%), and KO^{t}Bu (0.50 mmol, 1.0 equiv.) in solvent (1 mL) at 120 °C for 24 h; [b]GC yield.

Table S4: Effect of Base on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]

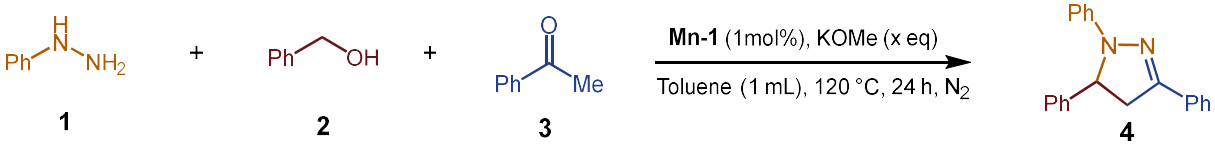


1 + 2 + 3 → 4

Entry	Base (1 equiv.)	yield of product (%)[b]
1	None	trace
2	K_3PO_4	30
3	K_2CO_3	7%
4	Cs_2CO_3	32%
5	KOMe	79%
6	NaOMe	78%
7	NaOH	56%
8	KOH	65%
9	CsOH	58%
10	KO^{t}Bu	74%
11	NaH	57%

[a]Reaction conditions: Phenyl hydrazine (0.5 mmol, 1 equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (0.6 mmol, 1.2 equiv.), **Mn-1** (1 mol%), and base (0.50 mmol, 1.0 equiv.) in toluene (1 mL) at 120 °C for 24 h; [b]GC yield.

Table S5: Effect of Base Loading on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]



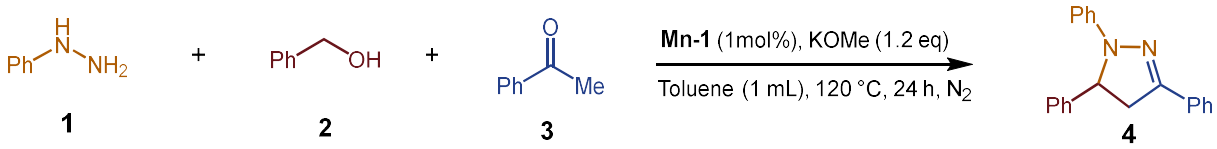
1 + 2 + 3 → 4

Entry	KOMe (x equiv.)	yield of product (%)[b]
1	0.8 equiv.	57
2	1.0 equiv.	79
3	1.2 equiv.	82
4	1.4 equiv.	75

5	1.6 equiv.	56
6	1.8 equiv.	64

[a]Reaction conditions: Phenyl hydrazine (0.5 mmol, 1 equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (0.6 mmol, 1.2 equiv.), **Mn-1** (1 mol%), and KOMe (x equiv.) in toluene (1 mL) at 120 °C for 24 h; [b]GC yield.

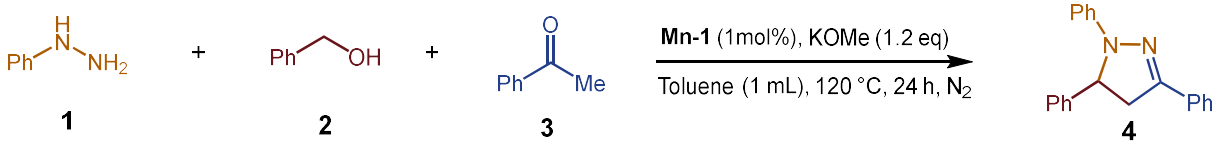
Table S6: Effect of the Amount of **3** on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]



Entry	amount of 3 (x equiv.)	yield of product (%)[b]
1	1.0	65
2	1.2	69
3	1.4	77
4	1.6	88
5	1.8	79

[a]Reaction conditions: Phenyl hydrazine (0.5 mmol, 1 equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (x equiv.), **Mn-1** (1 mol%), and KOMe (0.6 mmol, 1.2 equiv.) in toluene (1 mL) at 120 °C for 24 h; [b]GC yield.

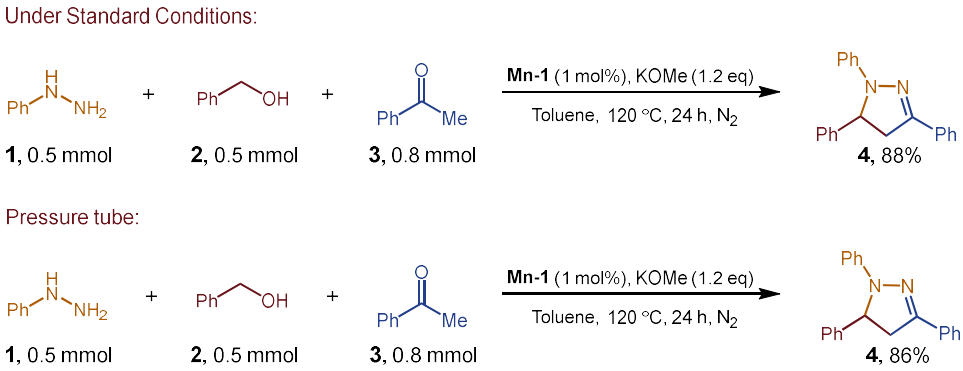
Table S7: Effect of the Amount of **1** on Acceptorless Dehydrogenative Coupling of Multicomponent Synthesis of 2-Pyrazolines[a]



Entry	amount of 1 (x equiv.)	yield of product (%)[b]
1	1.0	88%
2	1.2	79%
3	1.4	78%

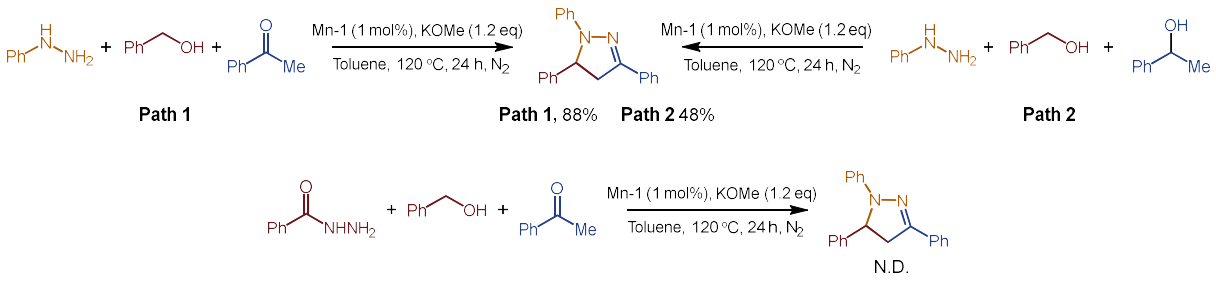
[a]Reaction conditions: Phenyl hydrazine (x equiv.), benzyl alcohol (0.5 mmol, 1 equiv.), acetophenone (0.8 mmol, 1.6 equiv.), **Mn-1** (1 mol%), and KOMe (0.6 mmol, 1.2 equiv.) in toluene (1 mL) at 120 °C for 24 h; [b]GC yield.

4.2 Optimization of the Presence of N_2 Balloon

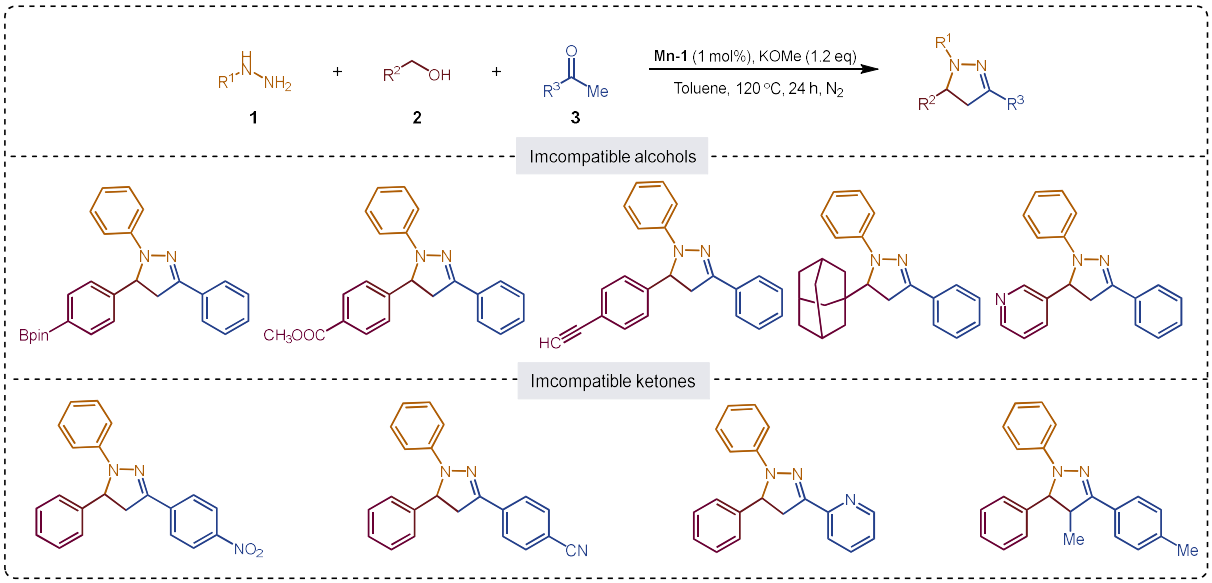


4.3 Optimization of Reaction Substrates

We also conducted reactions with secondary alcohols and found that ketones yielded better results than secondary alcohols. we have performed a reaction utilizing benzoyl hydrazine in place of phenylhydrazine and found out that benzoyl hydrazine is incompatible for current methodology and we did not observe the formation of the respective pyrazoline derivative.



At the same time, we also tested several substrates containing specific functional groups. The experimental results indicate that these substrates do not yield the expected pyrazoline derivatives. For example, substrates containing -Bpin functional groups, reducible functional groups including cyano, nitro, ester, and alkyne groups, highly sterically hindered diamanthanols and substrates containing pyridine functional groups are incompatible with the reaction.


Mn-1 (1 mol%), KOMe (1.2 eq)
Toluene, 120 °C, 24 h, N2
1
2
3
Imcompatible alcohols
Bpin
CH3OOC
HC
N
Imcompatible ketones
NO2
CN
Me
Me

5. X-ray Crystallographic Data of Catalyst Mn-1

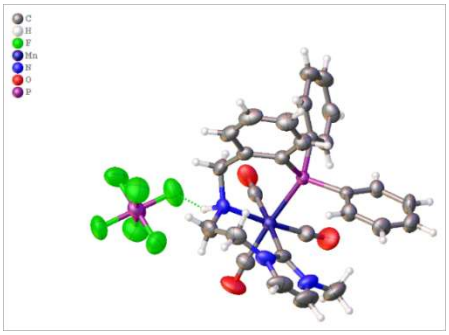


Table S7 Crystal data and structure refinement for **Mn-1** (CCDC 2472808)

Empirical formula	$C_{28}H_{26}F_6MnN_3O_3P_2$
Formula weight	683.40
Temperature/K	256.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.9741(18)
b/Å	8.5680(8)
c/Å	22.795(3)
α/°	90
β/°	93.450(4)
γ/°	90
Volume/Å^3	2919.2(6)
Z	4
ρ_{calc}g/cm^3	1.555
μ/mm^{-1}	0.636
F(000)	1392.0
Crystal size/mm^3	0.31 × 0.19 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.34 to 49.996
Index ranges	$-17 \le h \le 17$, $-10 \le k \le 10$, $-27 \le l \le 27$
Reflections collected	20735
Independent reflections	5062 [R_{int} = 0.1068, R_{sigma} = 0.0876]
Data/restraints/parameters	5062/0/389
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1468
Final R indexes [all data]	R_1 = 0.0875, wR_2 = 0.1687
Largest diff. peak/hole / e Å^{-3}	1.14/-0.41

6. Mechanistic study

6.1 Detection of the Key Active Species by the HRMS

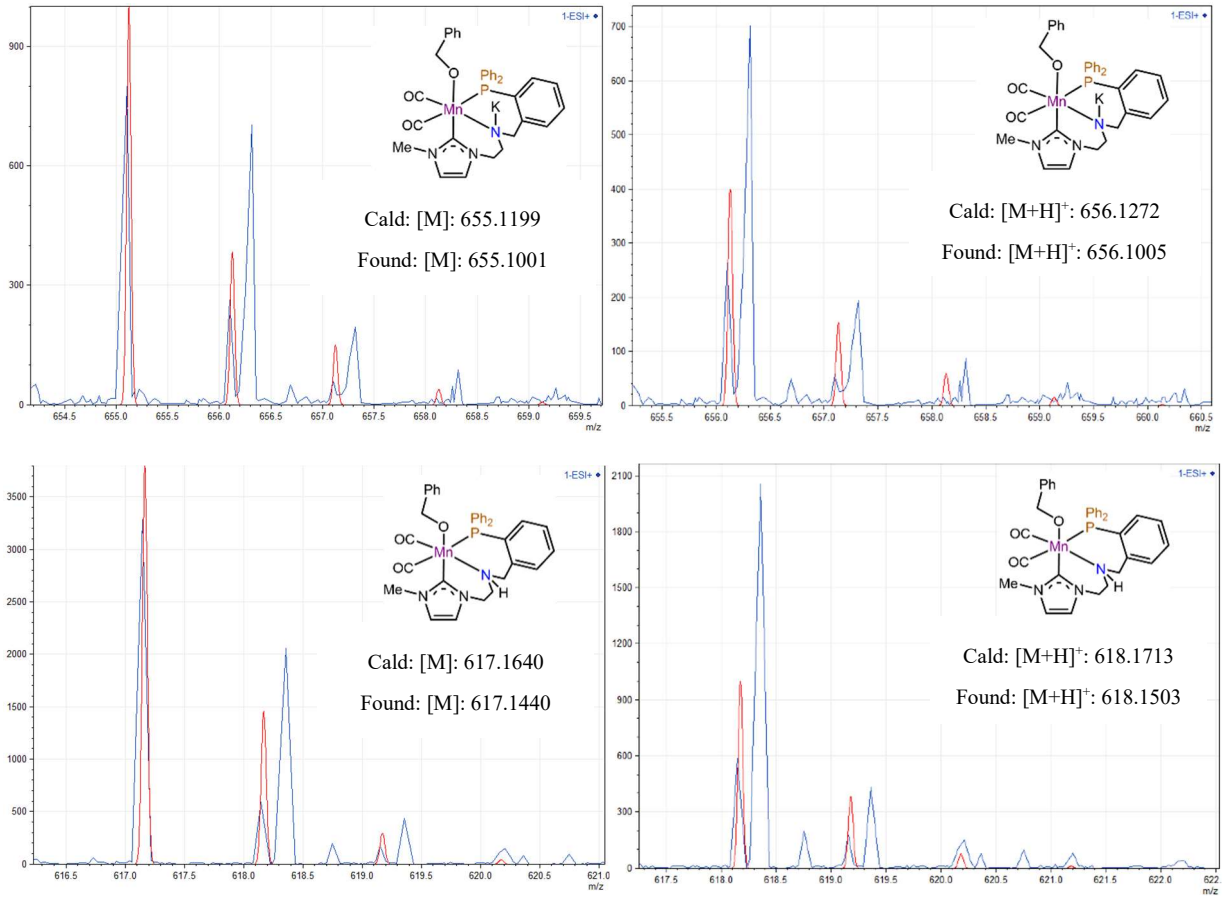
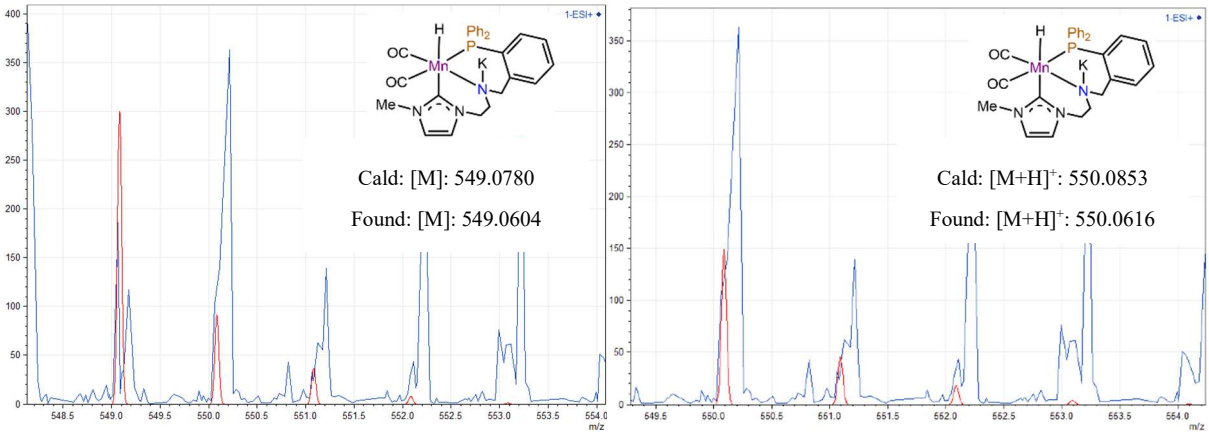


Figure S13. HRMS results of Int-1



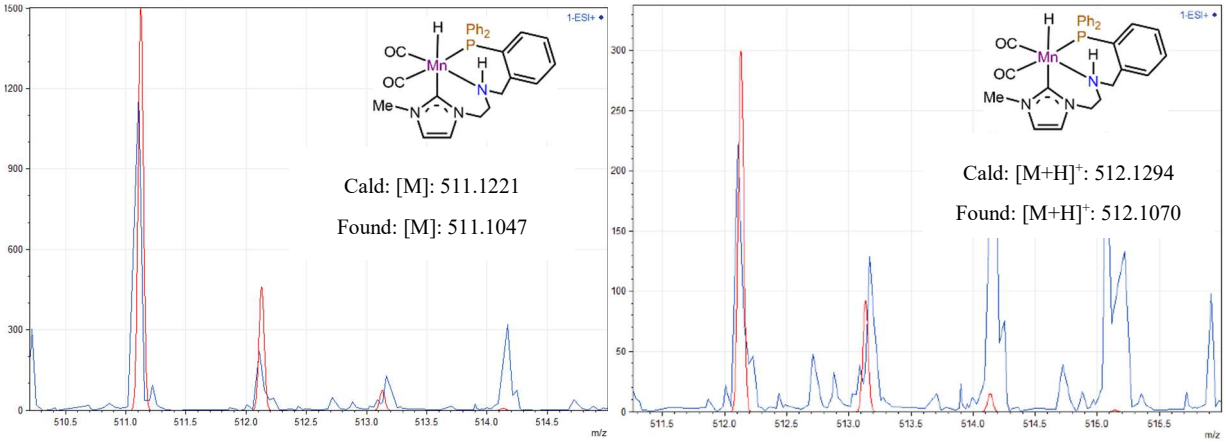


Figure S14. HRMS results of Int-2

6.2 Detection of hydrogen by GC

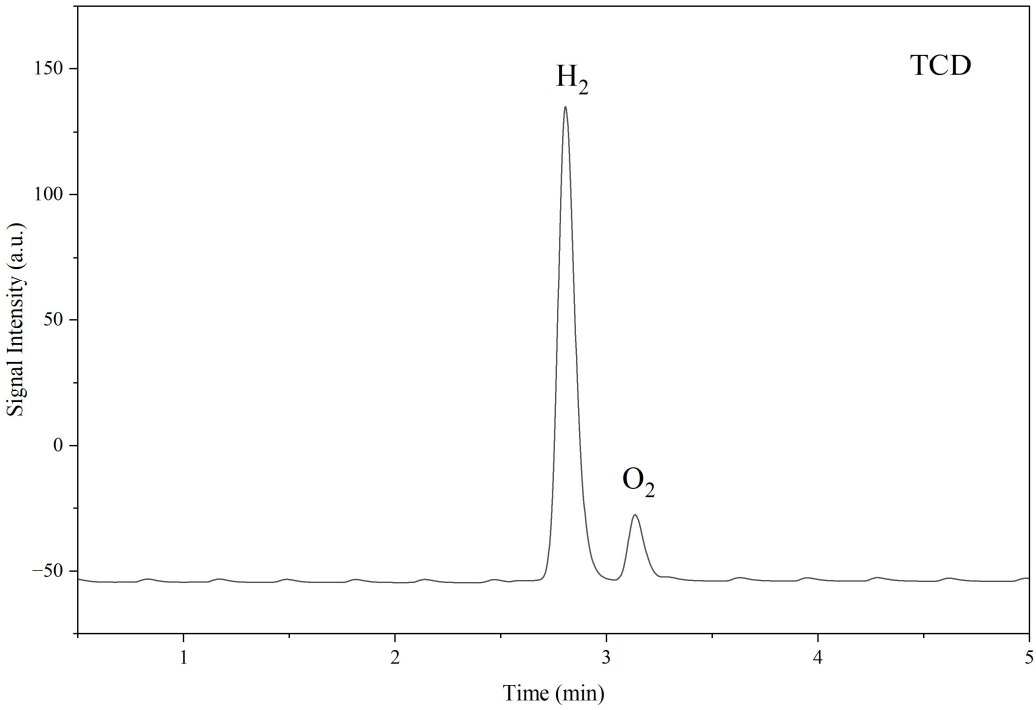
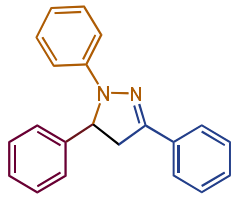


Figure S15. GC results of the detection of hydrogen

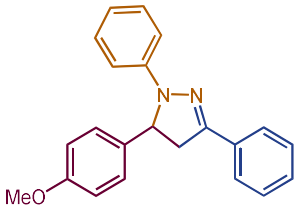
7. Characterization Data of Products



Chemical Formula: $C_{21}H_{18}N_2$
Molecular Weight: 298.3890

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

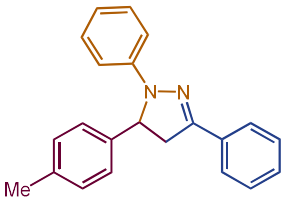
Yellow solid (131 mg, 88% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.46 – 7.27 (m, 8H), 7.26 – 7.19 (m, 2H), 7.16 – 7.08 (m, 2H), 6.82 (tdd, *J* = 6.6, 3.4, 1.4 Hz, 1H), 5.31 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.88 (AB, *J* = 17.1, 12.4 Hz, 1H), 3.18 (AB, *J* = 17.0, 7.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 144.9, 142.6, 132.8, 129.2, 128.9, 128.6, 128.6, 127.6, 125.9, 125.8, 119.1, 113.4, 64.5, 43.6. **HRMS** (ESI^+): calculated for $C_{21}H_{19}N_2^+$ $[M+H]^+$ 299.1543, found: 299.1554.



Chemical Formula: $C_{22}H_{20}N_2O$
Molecular Weight: 328.4150

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

Yellow oil (116 mg, 71% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.33 – 7.22 (m, 3H), 7.17 – 7.09 (m, 4H), 7.06 – 6.99 (m, 2H), 6.80 – 6.76 (m, 2H), 6.74 – 6.69 (m, 1H), 5.13 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.75 – 3.64 (m, 4H), 3.02 (AB, *J* = 17.1, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 146.8, 145.0, 134.7, 132.9, 129.0, 128.6, 127.1, 125.8, 119.1, 114.5, 113.5, 64.0, 55.3, 43.7. **HRMS** (ESI^+): calculated for $C_{22}H_{21}N_2O^+$ $[M+H]^+$ 329.1648, found: 329.1641.[3]

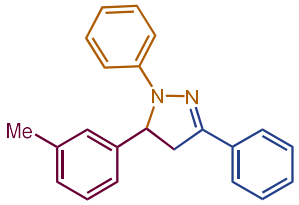


Chemical Formula: $C_{22}H_{20}N_2$
Molecular Weight: 312.4160

1,3-diphenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazole (6)

Yellow oil (137 mg, 88% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 7.21 – 7.13 (m, 1H), 7.06 (td, *J* = 7.7, 1.4 Hz, 4H), 7.02 – 6.94 (m, 4H), 6.66 (td, *J* = 7.2, 1.3 Hz, 1H), 5.07 (dd, *J* = 12.4, 7.3 Hz, 1H), 3.63 (AB, *J* = 17.0, 12.3 Hz, 1H), 2.96 (AB, *J* = 17.1, 7.2 Hz, 1H), 2.18

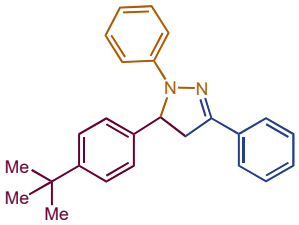
(s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 145.0, 139.8, 137.3, 132.9, 129.9, 129.0, 128.6, 125.9, 125.8, 119.1, 113.5, 64.4, 43.7, 21.2. **HRMS** (ESI^+): calculated for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1699, found: 313.1701.[4]



Chemical Formula: $C_{22}H_{20}N_2$
Molecular Weight: 312.4160

1,3-diphenyl-5-(m-tolyl)-4,5-dihydro-1H-pyrazole (7)

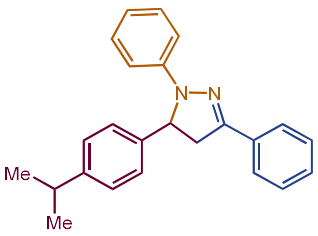
Yellow oil (132 mg, 85% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 – 7.18 (m, 8H), 6.93 (td, *J* = 7.2, 1.3 Hz, 1H), 5.37 – 5.26 (m, 1H), 3.90 (AB, *J* = 17.1, 12.4 Hz, 1H), 3.23 (AB, *J* = 17.1, 7.4 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.9, 145.1, 142.8, 139.0, 132.9, 129.1, 129.0, 128.7, 128.7, 128.5, 126.5, 125.9, 123.1, 119.2, 113.5, 64.6, 43.7, 21.6. **HRMS** (ESI^+): calculated for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1700, found: 313.1693.



Chemical Formula: $C_{25}H_{26}N_2$
Molecular Weight: 354.4970

5-(4-(tert-butyl)phenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (8)

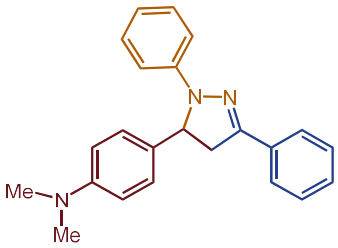
Yellow oil (138 mg, 78% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.51 – 7.35 (m, 5H), 7.35 – 7.23 (m, 4H), 7.19 (d, *J* = 7.7 Hz, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 5.31 (dd, *J* = 12.4, 7.1 Hz, 1H), 3.85 (AB, *J* = 17.1, 12.3 Hz, 1H), 3.20 (AB, *J* = 17.1, 7.1 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 146.8, 145.0, 139.6, 132.9, 129.0, 128.9, 128.6, 126.1, 125.8, 125.6, 119.1, 113.4, 64.2, 43.6, 34.6, 31.4. **HRMS** (ESI^+): calculated for $C_{25}H_{27}N_2^+$ $[M+H]^+$ 355.2169, found: 355.2170.



Chemical Formula: $C_{24}H_{24}N_2$
Molecular Weight: 340.4700

5-(4-isopropylphenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (9)

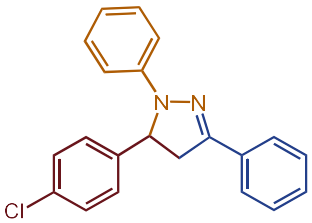
Yellow oil (137 mg, 81% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.28 – 7.15 (m, 3H), 7.14 – 7.02 (m, 6H), 7.02 – 6.96 (m, 2H), 6.72 – 6.61 (m, 1H), 5.10 (dd, *J* = 12.4, 7.1 Hz, 1H), 3.65 (AB, *J* = 17.1, 12.3 Hz, 1H), 2.99 (AB, *J* = 17.1, 7.2 Hz, 1H), 2.76 (hept, *J* = 6.7 Hz, 1H), 1.12 (d, *J* = 1.6 Hz, 3H), 1.10 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 146.8, 145.0, 140.0, 132.9, 129.0, 128.6, 127.2, 125.9, 125.8, 119.1, 113.5, 64.3, 43.7, 33.8, 24.1 (d, *J* = 1.3 Hz). **HRMS** (ESI^+): calculated for $C_{24}H_{25}N_2^+$ $[M+H]^+$ 341.2012, found: 341.2010.[5]



Chemical Formula: $C_{23}H_{23}N_3$
Molecular Weight: 341.4580

4-(1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)-N,N-dimethylaniline (10)

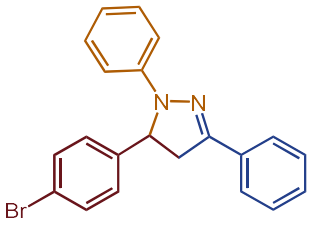
Yellow oil (143 mg, 82% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.31 – 7.20 (m, 6H), 6.87 (tt, *J* = 7.0, 1.4 Hz, 1H), 6.80 – 6.75 (m, 2H), 5.26 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.83 (AB, *J* = 17.1, 12.2 Hz, 1H), 3.20 (AB, *J* = 17.0, 7.2 Hz, 1H), 2.99 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 146.8, 145.2, 133.1, 130.3, 129.0, 128.6, 128.5, 126.8, 125.8, 119.0, 113.5, 113.0, 64.2, 43.7, 40.6. **HRMS** (ESI^+): calculated for $C_{23}H_{24}N_3^+$ $[M+H]^+$ 342.1965, found: 342.1960.



Chemical Formula: $C_{21}H_{17}ClN_2$
Molecular Weight: 332.8310

5-(4-chlorophenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (11)

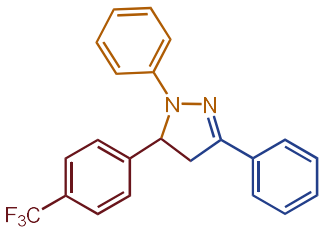
Yellow oil (121 mg, 73% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 6.2, 1.4 Hz, 2H), 7.29 – 7.15 (m, 5H), 7.14 – 7.04 (m, 4H), 6.97 – 6.90 (m, 2H), 6.69 (td, *J* = 7.3, 1.2 Hz, 1H), 5.08 (dd, *J* = 12.3, 7.1 Hz, 1H), 3.66 (AB, *J* = 17.0, 12.4 Hz, 1H), 2.94 (AB, *J* = 17.1, 7.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 144.7, 141.2, 133.4, 132.6, 129.4, 129.1, 128.8, 128.7, 127.4, 125.8, 119.4, 113.5, 63.9, 43.5. **HRMS** (ESI^+): calculated for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1154, found: 333.1160.



Chemical Formula: $C_{21}H_{17}BrN_2$
Molecular Weight: 377.2850

5-(4-bromophenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (12)

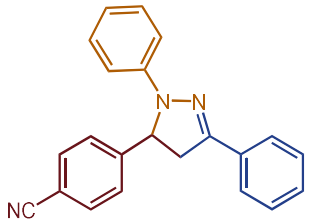
Yellow oil (122 mg, 65% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.57 – 7.42 (m, 5H), 7.30 (qd, *J* = 6.8, 2.0 Hz, 4H), 7.19 – 7.14 (m, 2H), 6.92 (td, *J* = 7.3, 1.2 Hz, 1H), 5.28 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.88 (AB, *J* = 17.0, 12.4 Hz, 1H), 3.16 (AB, *J* = 17.1, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 144.7, 141.7, 132.6, 132.4, 129.1, 128.8, 128.7, 127.8, 125.8, 121.5, 119.5, 113.5, 63.9, 43.5. **HRMS** (ESI^+): calculated for $C_{21}H_{18}BrN_2^+$ $[M+H]^+$ 377.0648, found: 377.0640.



Chemical Formula: $C_{22}H_{17}F_3N_2$
Molecular Weight: 366.3872

1,3-diphenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (13)

Yellow oil (121 mg, 66% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.36 (m, 5H), 7.27 – 7.20 (m, 2H), 7.12 – 7.04 (m, 2H), 6.90 – 6.81 (m, 1H), 5.33 (dd, *J* = 12.4, 7.1 Hz, 1H), 3.88 (AB, *J* = 17.1, 12.4 Hz, 1H), 3.13 (AB, *J* = 17.1, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 146.6, 144.6, 132.4, 129.96 (q, *J* = 32 Hz), 129.1, 128.9, 128.7, 126.4, 126.3 (q, *J* = 3.9 Hz), 125.8, 122.7, 119.6, 113.4, 64.0, 43.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.41. HRMS (ESI^+): calculated for $C_{22}H_{18}F_3N_2^+$ $[M+H]^+$ 367.1417, found: 367.1424.

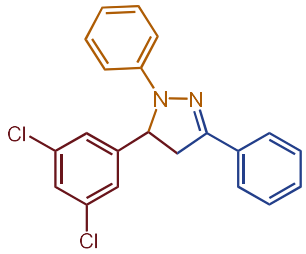


Chemical Formula: $C_{22}H_{17}N_3$
Molecular Weight: 323.3990

4-(1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)benzonitrile (14)

Yellow solid (57 mg, 35% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.20 (m, 5H), 7.15 – 6.99 (m, 4H), 6.72 (ddt, *J* = 7.2, 5.8, 1.2 Hz, 1H), 5.22 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.79

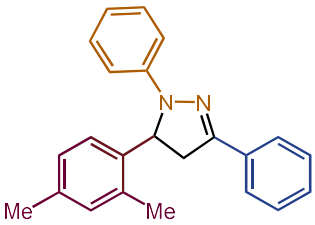
(AB, J = 17.1, 12.4 Hz, 1H), 3.09 (AB, J = 17.1, 7.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 144.9, 142.6, 132.7, 129.2, 128.9, 128.6, 128.6, 127.6, 125.9, 125.8, 119.4, 119.1, 113.4, 64.5, 43.6. **HRMS** (ESI^+): calculated for $C_{22}H_{18}N_3^+$ $[M+H]^+$ 324.1496, found: 324.1502.



Chemical Formula: $C_{21}H_{16}Cl_2N_2$
Molecular Weight: 367.2730

5-(3,5-dichlorophenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (15)

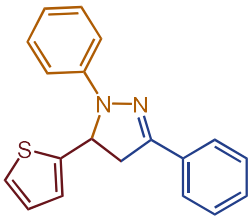
Yellow oil (99 mg, 54% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.32 – 7.21 (m, 3H), 7.19 – 7.06 (m, 5H), 6.95 (d, J = 8.1 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 5.02 (dd, J = 12.5, 7.2 Hz, 1H), 3.68 (AB, J = 17.2, 12.5 Hz, 1H), 2.96 (AB, J = 17.2, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.9, 146.3, 144.6, 135.9, 132.3, 129.2, 129.0, 128.7, 128.1, 125.9, 124.5, 119.8, 113.4, 63.7, 43.4. **HRMS** (ESI^+): calculated for $C_{21}H_{17}Cl_2N_2^+$ $[M+H]^+$ 367.0764, found: 367.0758.



Chemical Formula: $C_{23}H_{22}N_2$
Molecular Weight: 326.4430

5-(2,4-dimethylphenyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (16)

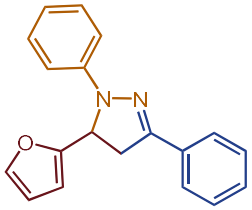
Yellow oil (112 mg, 69% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 2H), 7.46 (dd, J = 8.3, 6.4 Hz, 2H), 7.43 – 7.34 (m, 1H), 7.31 – 7.25 (m, 2H), 7.18 (d, J = 7.8 Hz, 1H), 7.16 – 7.09 (m, 3H), 7.00 (dd, J = 7.9, 1.8 Hz, 1H), 6.88 (t, J = 7.3 Hz, 1H), 5.43 (dd, J = 12.5, 7.4 Hz, 1H), 3.90 (AB, J = 16.9, 12.5 Hz, 1H), 3.06 (AB, J = 16.9, 7.4 Hz, 1H), 2.52 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 144.9, 137.2, 137.0, 133.7, 132.9, 131.8, 129.0, 128.6, 127.6, 125.8, 119.0, 113.2, 61.6, 42.1, 21.1, 19.5. **HRMS** (ESI^+): calculated for $C_{23}H_{23}N_2^+$ $[M+H]^+$ 327.1856, found: 327.1851.



Chemical Formula: $C_{19}H_{16}N_2S$
Molecular Weight: 304.4110

1,3-diphenyl-5-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (17)

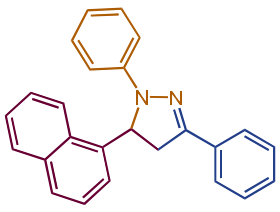
Yellow solid (96 mg, 63% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.47 – 7.36 (m, 3H), 7.27 (dd, *J* = 8.8, 6.8 Hz, 2H), 7.23 (dd, *J* = 6.7, 2.2 Hz, 3H), 7.05 (d, *J* = 3.5 Hz, 1H), 6.97 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.88 (tt, *J* = 7.0, 1.6 Hz, 1H), 5.56 (dd, *J* = 11.9, 7.0 Hz, 1H), 3.83 (AB, *J* = 17.0, 11.9 Hz, 1H), 3.31 (AB, *J* = 17.0, 7.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 146.2, 145.1, 132.6, 129.0, 128.9, 128.6, 127.1, 125.9, 125.0, 124.2, 119.7, 113.9, 60.6, 43.9. **HRMS** (ESI^+): calculated for $C_{19}H_{17}N_2S^+$ $[M+H]^+$ 305.1107, found: 305.1110.



Chemical Formula: $C_{19}H_{16}N_2O$
Molecular Weight: 288.3500 qq

5-(furan-2-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (18)

Yellow solid (86 mg, 60% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.56 – 7.35 (m, 4H), 7.33 – 7.21 (m, 4H), 6.90 (tt, *J* = 7.2, 1.3 Hz, 1H), 6.35 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 5.39 (dd, *J* = 12.1, 6.7 Hz, 1H), 3.73 (AB, *J* = 16.9, 12.2 Hz, 1H), 3.42 (AB, *J* = 16.9, 6.7 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 147.4, 145.1, 142.3, 132.6, 129.0, 128.8, 128.6, 125.9, 119.6, 113.7, 110.5, 107.1, 58.2, 40.1. **HRMS** (ESI^+): calculated for $C_{19}H_{17}N_2O^+$ $[M+H]^+$ 289.1335, found: 289.1334.

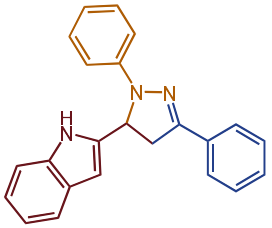


Chemical Formula: $C_{25}H_{20}N_2$
Molecular Weight: 348.4490

5-(naphthalen-1-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (19)

Yellow oil (142 mg, 82% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.05 – 8.01 (m, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.69 (dt, *J* = 23.4, 7.3 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 1H), 7.48 –

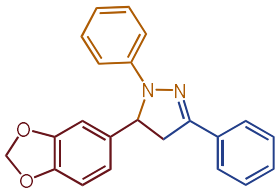
7.36 (m, 4H), 7.28 (dd, *J* = 8.7, 7.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.00 (d, *J* = 11.2 Hz, 1H), 4.07 (AB, *J* = 17.0, 12.6 Hz, 1H), 3.20 (AB, *J* = 17.4, 6.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 145.0, 136.8, 134.5, 132.8, 130.0, 129.4, 129.1, 128.7, 128.7, 128.2, 126.6, 126.1, 125.9, 125.9, 123.1, 119.2, 113.5, 60.5, 42.8. **HRMS** (ESI^+): calculated for $C_{25}H_{21}N_2^+$ $[M+H]^+$ 349.1700, found: 349.1696.[6]



Chemical Formula: $C_{23}H_{19}N_3$
Molecular Weight: 337.4260

2-(1,3-diphenyl-4,5-dihydro-1H-pyrazol-5-yl)-1H-indole (20)

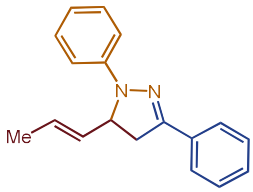
Yellow oil (86 mg, 51% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.88 – 7.76 (m, 2H), 7.68 – 7.57 (m, 1H), 7.48 – 7.37 (m, 3H), 7.31 – 7.14 (m, 7H), 6.95 – 6.83 (m, 1H), 6.61 (d, *J* = 2.1 Hz, 1H), 5.46 (dd, *J* = 12.2, 8.6 Hz, 1H), 3.86 (AB, *J* = 17.2, 12.2 Hz, 1H), 3.34 (AB, *J* = 17.2, 8.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 145.7, 138.9, 136.1, 132.3, 129.1, 128.7, 128.6, 125.9, 122.1, 120.5, 120.2, 120.1, 113.9, 111.2, 99.9, 59.7, 42.4. **HRMS** (ESI^+): calculated for $C_{23}H_{20}N_3^+$ $[M+H]^+$ 338.1652, found: 338.1650.



Chemical Formula: $C_{22}H_{18}N_2O_2$
Molecular Weight: 342.3980

5-(benzo[d][1,3]dioxol-5-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (21)

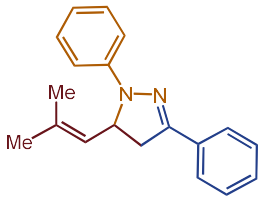
Yellow oil (138 mg, 81% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m, 1H), 7.27 (dd, *J* = 8.7, 7.1 Hz, 2H), 7.21 – 7.14 (m, 2H), 6.85 (dq, *J* = 12.1, 7.4 Hz, 4H), 5.99 – 5.92 (m, 2H), 5.22 (dd, *J* = 12.3, 7.1 Hz, 1H), 3.82 (AB, *J* = 17.1, 12.3 Hz, 1H), 3.15 (AB, *J* = 17.1, 7.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 147.1, 146.8, 144.9, 136.7, 132.8, 129.0, 128.7, 128.6, 125.8, 119.2, 119.2, 113.5, 108.7, 106.3, 101.2, 64.3, 43.6. **HRMS** (ESI^+): calculated for $C_{22}H_{19}N_2O_2^+$ $[M+H]^+$ 343.1442, found: 343.1448.



Chemical Formula: $C_{18}H_{18}N_2$
Molecular Weight: 262.3560

(E)-1,3-diphenyl-5-(prop-1-en-1-yl)-4,5-dihydro-1H-pyrazole (22)

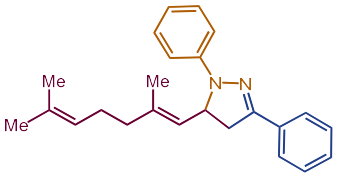
Yellow oil (26 mg, 20% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 3H), 7.29 – 7.07 (m, 4H), 6.77 (dt, *J* = 8.3, 4.2 Hz, 1H), 5.74 – 5.64 (m, 1H), 5.47 (dd, *J* = 15.5, 7.4 Hz, 1H), 4.67 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.45 (AB, *J* = 16.8, 11.7 Hz, 1H), 2.94 (AB, *J* = 16.8, 6.9 Hz, 1H), 1.64 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 145.3, 133.0, 130.8, 128.9, 128.5, 128.5, 127.9, 125.7, 119.0, 113.7, 62.7, 40.5, 17.7. **HRMS** (ESI^+): calculated for $C_{18}H_{19}N_2^+$ $[M+H]^+$ 263.1543, found: 263.1538.



Chemical Formula: $C_{19}H_{20}N_2$
Molecular Weight: 276.3830

5-(2-methylprop-1-en-1-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (23)

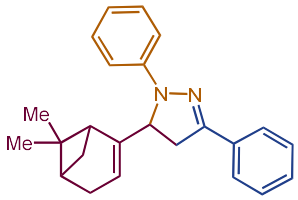
Yellow oil (76 mg, 55% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.56 – 7.21 (m, 7H), 6.91 (tt, *J* = 7.3, 1.3 Hz, 1H), 5.40 (dp, *J* = 8.9, 1.5 Hz, 1H), 4.98 (ddd, *J* = 11.6, 8.8, 7.6 Hz, 1H), 3.57 (AB, *J* = 16.7, 11.6 Hz, 1H), 2.99 (AB, *J* = 16.8, 7.6 Hz, 1H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.81 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 145.5, 134.1, 133.1, 129.0, 128.6, 128.4, 126.2, 125.7, 119.1, 113.7, 59.4, 40.4, 25.7, 18.4. **HRMS** (ESI^+): calculated for $C_{19}H_{21}N_2^+$ $[M+H]^+$ 277.1699, found: 277.1696.



Chemical Formula: $C_{24}H_{28}N_2$
Molecular Weight: 344.5020

(E)-5-(2,6-dimethylhepta-1,5-dien-1-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (24)

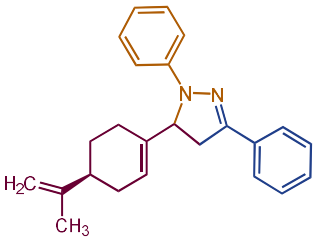
Yellow oil (79 mg, 46% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.31 (m, 3H), 7.30 – 7.23 (m, 2H), 6.92 (tt, *J* = 7.2, 1.3 Hz, 1H), 5.44 (dq, *J* = 8.8, 1.3 Hz, 1H), 5.13 (tdd, *J* = 6.8, 2.8, 1.4 Hz, 1H), 5.08 – 4.93 (m, 1H), 3.59 (AB, *J* = 16.7, 12.1 Hz, 1H), 2.99 (AB, *J* = 16.7, 7.8 Hz, 1H), 2.34 – 2.04 (m, 4H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.84 (dd, *J* = 10.6, 1.4 Hz, 1H), 1.78 – 1.72 (m, 3H), 1.68 (d, *J* = 1.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 145.5, 137.5, 133.1, 131.8, 128.9, 128.5, 128.4, 126.5, 125.7, 123.8, 119.1, 113.7, 59.4, 40.5, 39.4, 26.3, 25.8, 17.8, 16.7. **HRMS** (ESI^+): calculated for $C_{24}H_{29}N_2^+$ $[M+H]^+$ 345.2326, found: 345.2324.



Chemical Formula: $C_{24}H_{26}N_2$
Molecular Weight: 342.4860

5-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (25)

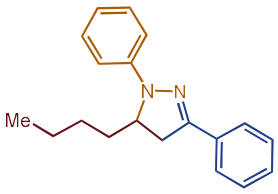
Yellow oil (148 mg, 87% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2H), 7.54 – 7.46 (m, 2H), 7.45 – 7.31 (m, 5H), 7.00 – 6.89 (m, 1H), 5.72 – 5.60 (m, 1H), 4.83 (dt, *J* = 12.4, 8.1 Hz, 1H), 3.51 (AB, *J* = 17.1, 13.9, 12.3 Hz, 1H), 3.03 (AB, *J* = 22.4, 17.1, 7.1 Hz, 1H), 2.64 – 2.31 (m, 3H), 2.29 – 2.14 (m, 2H), 1.36 (d, *J* = 6.0 Hz, 3H), 1.14 (d, *J* = 8.7 Hz, 1H), 1.04 (s, 2H), 0.78 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 147.1, 146.7, 146.4, 145.7, 145.4, 133.1, 128.9, 128.8, 128.6, 128.5, 125.7, 125.7, 119.7, 119.0, 118.9, 113.6, 113.6, 65.4, 64.5, 53.6, 42.3, 41.8, 40.9, 40.9, 38.4, 38.2, 38.0, 37.9, 32.3, 31.6, 31.3, 31.2, 26.3, 26.2, 21.7, 21.5. **HRMS** (ESI^+): calculated for $C_{24}H_{27}N_2^+$ $[M+H]^+$ 343.2169, found: 343.2163. d.r.=3:1.



Chemical Formula: $C_{24}H_{26}N_2$
Molecular Weight: 342.4860

1,3-diphenyl-5-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)-4,5-dihydro-1H-pyrazole (26)

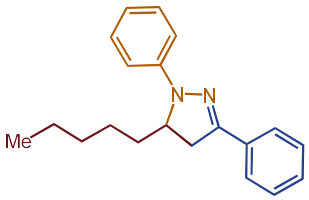
Yellow oil (107 mg, 63% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.47 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.44 – 7.26 (m, 5H), 6.94 (td, *J* = 7.1, 1.5 Hz, 1H), 5.93 – 5.85 (m, 1H), 4.86 – 4.73 (m, 3H), 3.59 (AB, *J* = 17.1, 12.4, 8.8 Hz, 1H), 3.08 (AB, *J* = 16.9, 9.5, 7.1 Hz, 1H), 2.32 – 2.07 (m, 5H), 1.95 – 1.85 (m, 1H), 1.85 – 1.79 (m, 3H), 1.65 – 1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 149.5, 147.3, 147.1, 145.4, 145.4, 137.1, 137.0, 133.0, 133.0, 129.0, 129.0, 128.6, 128.5, 125.7, 123.6, 123.2, 118.9, 118.9, 113.3, 113.1, 109.0, 109.0, 66.3, 66.2, 41.3, 40.8, 39.9, 39.7, 30.6, 30.5, 27.4, 27.3, 23.9, 23.6, 21.0, 20.9. **HRMS** (ESI^+): calculated for $C_{24}H_{27}N_2^+$ $[M+H]^+$ 343.2169, found: 343.2168. d.r.=1:1.



Chemical Formula: $C_{19}H_{22}N_2$
Molecular Weight: 278.3990

5-butyl-1,3-diphenyl-4,5-dihydro-1H-pyrazole (27)

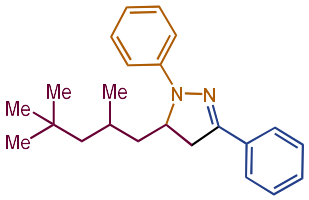
Yellow oil (65 mg, 45% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.50 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 7.25 – 7.17 (m, 2H), 6.88 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.41 (dddd, *J* = 11.6, 9.2, 5.0, 2.7 Hz, 1H), 3.45 (AB, *J* = 16.8, 11.4 Hz, 1H), 3.02 (AB, *J* = 16.8, 5.0 Hz, 1H), 1.97 – 1.83 (m, 1H), 1.68 – 1.53 (m, 1H), 1.45 – 1.32 (m, 4H), 1.01 – 0.85 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 144.4, 133.2, 129.1, 128.5, 128.4, 125.6, 118.8, 113.3, 59.8, 38.1, 32.1, 27.1, 22.7, 14.1. **HRMS**(ESI^+): calculated for $C_{19}H_{23}N_2^+$ $[M+H]^+$ 279.1856, found: 279.1851.



Chemical Formula: $C_{20}H_{24}N_2$
Molecular Weight: 292.4260

5-pentyl-1,3-diphenyl-4,5-dihydro-1H-pyrazole (28)

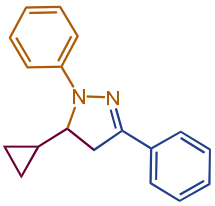
Yellow oil (64 mg, 42% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.26 (m, 3H), 7.21 – 7.14 (m, 2H), 6.84 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.38 (dddd, *J* = 11.6, 9.2, 5.0, 2.7 Hz, 1H), 3.42 (AB, *J* = 16.8, 11.4 Hz, 1H), 2.99 (AB, *J* = 16.8, 5.0 Hz, 1H), 1.93 – 1.81 (m, 1H), 1.55 (dtd, *J* = 14.0, 9.3, 3.7 Hz, 1H), 1.43 – 1.26 (m, 6H), 0.89 (td, *J* = 5.5, 2.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 144.4, 133.2, 129.1, 128.5, 128.4, 125.6, 118.8, 113.3, 59.9, 38.1, 32.3, 31.7, 24.7, 22.7, 14.1. **HRMS**(ESI^+): calculated for $C_{20}H_{25}N_2^+$ $[M+H]^+$ 293.2013, found: 293.2017.



Chemical Formula: $C_{23}H_{30}N_2$
Molecular Weight: 334.5070

1,3-diphenyl-5-(2,4,4-trimethylpentyl)-4,5-dihydro-1H-pyrazole (29)

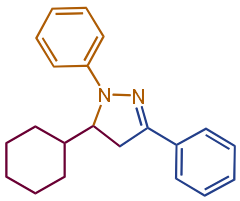
Yellow oil (63 mg, 38% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.36 (ddd, *J* = 8.9, 7.2, 3.4 Hz, 3H), 7.25 – 7.19 (m, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 4.44 (dtdd, *J* = 18.4, 11.0, 5.0, 2.4 Hz, 1H), 3.46 (AB, *J* = 16.6, 11.1 Hz, 1H), 3.05 (AB, *J* = 16.7, 5.1, 3.5 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.52 (ddt, *J* = 16.4, 6.6, 3.5 Hz, 1H), 1.40 – 1.29 (m, 1H), 1.26 – 1.17 (m, 3H), 1.05 (d, *J* = 16.5 Hz, 6H), 0.96 (s, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 147.1, 144.4, 144.3, 133.3, 129.2, 128.6, 128.5, 128.4, 125.6, 118.9, 118.8, 113.5, 113.5, 58.7, 58.5, 52.3, 50.0, 41.6, 41.4, 38.9, 38.1, 31.4, 31.1, 30.1, 30.1, 26.7, 26.4, 24.3, 21.5. **HRMS**(ESI^+): calculated for $C_{23}H_{31}N_2^+$ $[M+H]^+$ 335.2482, found: 335.2484. d.r.=1:1.



Chemical Formula: $C_{18}H_{18}N_2$
Molecular Weight: 262.3560

5-cyclopropyl-1,3-diphenyl-4,5-dihydro-1H-pyrazole (30)

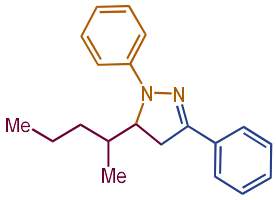
Yellow oil (69 mg, 53% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.47 – 7.30 (m, 7H), 6.91 (tt, *J* = 5.8, 2.5 Hz, 1H), 4.13 (ddd, *J* = 11.7, 6.8, 5.2 Hz, 1H), 3.49 (AB, *J* = 16.9, 11.3 Hz, 1H), 3.14 (AB, *J* = 16.8, 5.3 Hz, 1H), 1.19 (ddt, *J* = 15.1, 8.0, 5.4 Hz, 1H), 0.72 – 0.64 (m, 1H), 0.60 – 0.47 (m, 2H), 0.42 – 0.32 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 145.6, 133.1, 128.9, 128.5, 128.5, 125.7, 119.2, 114.4, 63.4, 39.4, 15.8, 5.4, 2.3. **HRMS**(ESI^+): calculated for $C_{18}H_{19}N_2^+$ $[M+H]^+$ 263.1543, found: 263.1546.



Chemical Formula: $C_{21}H_{24}N_2$
Molecular Weight: 304.4370

5-cyclohexyl-1,3-diphenyl-4,5-dihydro-1H-pyrazole (31)

Yellow oil (73 mg, 48% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.46 – 7.40 (m, 2H), 7.38 – 7.30 (m, 3H), 7.22 (dd, *J* = 8.7, 1.3 Hz, 2H), 6.87 (td, *J* = 7.2, 1.3 Hz, 1H), 4.40 (ddd, *J* = 11.9, 5.1, 3.5 Hz, 1H), 3.27 (AB, *J* = 17.2, 12.0 Hz, 1H), 3.13 (AB, *J* = 17.2, 5.1 Hz, 1H), 2.09 (tq, *J* = 12.0, 3.5 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.70 (d, *J* = 13.6 Hz, 3H), 1.58 – 1.44 (m, 1H), 1.31 (tt, *J* = 12.6, 3.4 Hz, 1H), 1.14 (tdd, *J* = 24.4, 12.2, 3.3 Hz, 3H), 0.93 (qd, *J* = 12.2, 3.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 144.6, 133.0, 129.1, 128.5, 128.3, 125.6, 118.5, 113.3, 64.1, 38.6, 33.6, 28.9, 26.5, 26.3, 25.7, 25.0. **HRMS**(ESI^+): calculated for $C_{21}H_{25}N_2^+$ $[M+H]^+$ 305.2013, found: 305.2009.

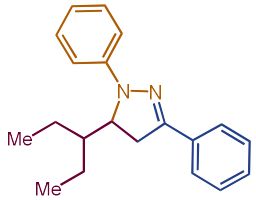


Chemical Formula: $C_{20}H_{24}N_2$
Molecular Weight: 292.4260

5-(pentan-2-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (32)

Yellow oil (60 mg, 46% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.42 (td, *J* = 7.7, 2.1 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 4.46 (m, 1H), 3.27 (AB, *J* = 17.3, 12.3, 10.3 Hz, 1H), 3.09 (AB, *J* = 17.3, 5.1 Hz, 1H), 2.42 – 1.99 (m, 1H), 1.88 – 1.42 (m, 1H),

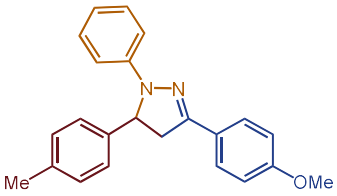
1.42 – 1.33 (m, 1H), 1.28 (dtd, *J* = 13.2, 6.5, 3.1 Hz, 1H), 1.18 – 0.99 (m, 3H), 0.99 – 0.80 (m, 1H), 0.76 (dd, *J* = 15.0, 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 147.3, 144.7, 144.5, 133.0, 129.1, 129.1, 128.5, 128.3, 128.3, 125.6, 125.6, 118.7, 118.6, 113.4, 113.3, 65.0, 63.4, 35.5, 33.4, 33.2, 32.7, 32.5, 30.8, 20.6, 20.5, 15.9, 14.5, 14.2, 12.4. **HRMS**(ESI^+): calculated for $C_{20}H_{25}N_2^+$ $[M+H]^+$ 293.2013, found: 293.2010. d.r.=1.6:1.



Chemical Formula: $C_{20}H_{24}N_2$
Molecular Weight: 292.4260

5-(pentan-3-yl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole (33)

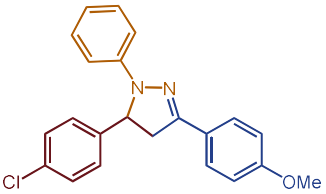
Yellow oil (61 mg, 42% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.46 – 7.40 (m, 2H), 7.40 – 7.27 (m, 3H), 7.26 – 7.20 (m, 2H), 6.87 (tt, *J* = 7.2, 1.2 Hz, 1H), 4.63 (ddd, *J* = 12.5, 6.0, 3.3 Hz, 1H), 3.28 (AB, *J* = 17.2, 12.5 Hz, 1H), 3.08 (AB, *J* = 17.2, 6.0 Hz, 1H), 2.05 – 1.93 (m, 1H), 1.69 (dqd, *J* = 14.8, 7.4, 4.7 Hz, 1H), 1.45 – 1.24 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H), 1.08 – 1.00 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 144.7, 133.1, 129.1, 128.5, 128.3, 125.6, 118.6, 113.2, 61.9, 42.0, 33.1, 23.1, 20.6, 12.3, 12.2. **HRMS**(ESI^+): calculated for $C_{20}H_{25}N_2^+$ $[M+H]^+$ 293.2013, found: 293.2009.



Chemical Formula: $C_{23}H_{22}N_2O$
Molecular Weight: 342.4420

3-(4-methoxyphenyl)-1-phenyl-5-(p-tolyl)-4,5-dihydro-1H-pyrazole (34)

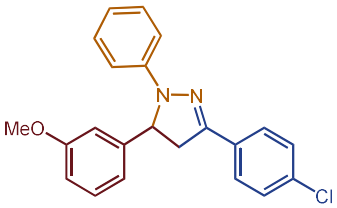
Yellow oil (154 mg, 90% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 2H), 7.30 – 7.13 (m, 8H), 7.02 – 6.94 (m, 2H), 6.84 (tt, *J* = 7.2, 1.1 Hz, 1H), 5.23 (dd, *J* = 12.2, 7.3 Hz, 1H), 3.88 (s, 3H), 3.82 (AB, *J* = 17.0, 12.3 Hz, 1H), 3.14 (AB, *J* = 17.0, 7.3 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 146.9, 145.3, 139.9, 137.2, 129.8, 128.9, 127.3, 125.9, 125.7, 118.8, 114.1, 113.3, 64.3, 55.4, 43.9, 21.2. **HRMS**(ESI^+): calculated for $C_{23}H_{23}N_2O^+$ $[M+H]^+$ 343.1805, found: 343.1804.



Chemical Formula: $C_{22}H_{19}ClN_2O$
Molecular Weight: 362.8570

5-(4-c hlorophenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (35)

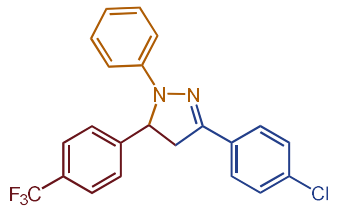
Yellow solid (150 mg, 83% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 2H), 7.39 – 7.19 (m, 6H), 7.14 – 7.05 (m, 2H), 7.00 – 6.91 (m, 2H), 6.85 (tt, *J* = 7.3, 1.2 Hz, 1H), 5.20 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.87 (s, 3H), 3.81 (AB, *J* = 17.0, 12.2 Hz, 1H), 3.09 (AB, *J* = 17.0, 7.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 146.9, 145.0, 141.3, 133.3, 129.3, 129.0, 127.4, 127.3, 125.3, 119.1, 114.1, 113.3, 63.9, 55.4, 43.7. **HRMS**(ESI^+): calculated for $C_{22}H_{20}ClN_2O^+$ $[M+H]^+$ 363.1259, found: 363.1258.



Chemical Formula: $C_{22}H_{19}ClN_2O$
Molecular Weight: 362.8570

3-(4-chlorophenyl)-5-(3-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (36)

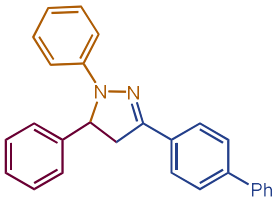
Yellow oli (132 mg, 73% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.42 – 7.35 (m, 2H), 7.33 – 7.20 (m, 3H), 7.18 – 7.09 (m, 2H), 6.95 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.91 – 6.82 (m, 3H), 5.25 (dd, *J* = 12.4, 7.4 Hz, 1H), 3.80 (s, 4H), 3.13 (AB, *J* = 17.1, 7.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.3, 145.7, 144.7, 144.2, 134.3, 131.3, 130.4, 129.0, 128.8, 126.9, 119.4, 118.1, 113.5, 112.9, 111.5, 64.7, 55.3, 43.4. **HRMS**(ESI^+): calculated for $C_{22}H_{20}ClN_2O^+$ $[M+H]^+$ 363.1259, found: 363.1268.



Chemical Formula: $C_{22}H_{16}ClF_3N_2$
Molecular Weight: 400.8292

3-(4-chlorophenyl)-1-phenyl-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole (37)

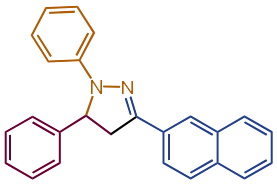
Yellow oli (128 mg, 64% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 4H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.29 – 7.22 (m, 2H), 7.10 – 7.05 (m, 2H), 6.91 – 6.84 (m, 1H), 5.35 (dd, *J* = 12.5, 7.2 Hz, 1H), 3.85 (AB, *J* = 17.1, 12.5 Hz, 1H), 3.10 (AB, *J* = 17.1, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 145.6, 144.3, 134.6, 131.0, 130.6 – 129.5 (q, *J* = 30 Hz), 129.1, 128.9, 127.0, 126.3, 125.9 – 126.2 (q, *J* = 4.3 Hz), 125.4, 119.8, 113.5, 64.1, 43.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.46. HRMS(ESI^+): calculated for $C_{22}H_{17}ClF_3N_2^+$ $[M+H]^+$ 401.1027, found: 401.1035.



Chemical Formula: $C_{27}H_{22}N_2$
Molecular Weight: 374.4870

3-([1,1'-biphenyl]-4-yl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (38)

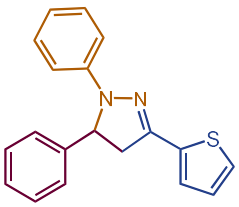
Yellow solid (132 mg, 71% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 2H), 7.57 – 7.49 (m, 4H), 7.40 – 7.34 (m, 2H), 7.35 – 7.20 (m, 5H), 7.21 – 7.14 (m, 1H), 7.13 – 7.07 (m, 2H), 7.04 – 6.97 (m, 2H), 6.71 (tt, *J* = 7.2, 1.2 Hz, 1H), 5.20 (dd, *J* = 12.3, 7.2 Hz, 1H), 3.77 (AB, *J* = 17.0, 12.4 Hz, 1H), 3.08 (AB, *J* = 17.0, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 144.8, 142.6, 141.2, 140.5, 131.7, 129.2, 129.0, 128.9, 127.6, 127.5, 127.2, 127.0, 126.2, 125.9, 119.2, 113.4, 64.5, 43.6. **HRMS**(ESI^+): calculated for $C_{27}H_{23}N_2^+$ $[M+H]^+$ 375.1856, found: 375.1863.



Chemical Formula: $C_{25}H_{20}N_2$
Molecular Weight: 348.4490

3-(naphthalen-2-yl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (39)

Yellow solid (115 mg, 66% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.78 – 7.69 (m, 4H), 7.39 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.22 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 7.07 – 7.01 (m, 2H), 6.72 (tt, *J* = 7.2, 1.3 Hz, 1H), 5.25 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.87 (AB, *J* = 16.9, 12.4 Hz, 1H), 3.19 (AB, *J* = 17.0, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 144.7, 142.6, 133.4, 133.3, 130.4, 129.2, 129.0, 128.2, 128.1, 127.8, 127.6, 126.5, 126.4, 125.9, 125.1, 123.5, 119.2, 113.5, 64.6, 43.5. **HRMS**(ESI^+): calculated for $C_{25}H_{21}N_2^+$ $[M+H]^+$ 349.1699, found: 349.1705.

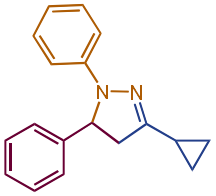


Chemical Formula: $C_{19}H_{16}N_2S$
Molecular Weight: 304.4110

1,5-diphenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazole (40)

Yellow solid (97 mg, 64% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 6H), 7.10 – 7.01 (m, 2H), 6.98 – 6.87 (m, 4H), 6.68 (tt, *J* = 7.4, 1.2 Hz, 1H), 5.13 (dd, *J* = 12.3, 7.3 Hz, 1H), 3.71 (AB, *J* = 16.9, 12.4 Hz, 1H), 3.02 (AB, *J* = 16.9, 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 142.9, 142.4, 136.7,

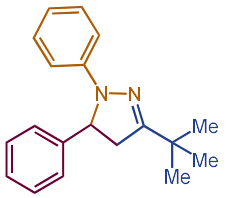
129.2, 128.9, 127.7, 127.4, 126.6, 126.0, 125.9, 119.3, 113.5, 64.7, 44.4. **HRMS**(ESI$^+$): calculated for $C_{19}H_{17}N_2S^+$ $[M+H]^+$ 305.1107, found: 305.1114.



Chemical Formula: $C_{18}H_{18}N_2$
Molecular Weight: 262.3560

3-cyclopropyl-1,5-diphenyl-4,5-dihydro-1H-pyrazole (41)

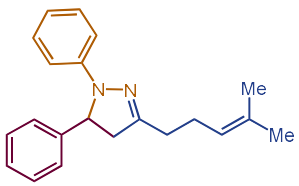
Yellow solid (81 mg, 62% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.08 (m, 5H), 7.07 – 6.98 (m, 2H), 6.86 – 6.79 (m, 2H), 6.62 (tt, *J* = 7.3, 1.2 Hz, 1H), 4.85 (dd, *J* = 11.8, 8.0 Hz, 1H), 3.14 (AB, *J* = 17.2, 11.9 Hz, 1H), 2.45 (AB, *J* = 17.2, 8.1 Hz, 1H), 1.72 (tt, *J* = 8.3, 5.1 Hz, 1H), 0.78 – 0.59 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 146.1, 143.0, 129.1, 128.9, 127.4, 126.0, 118.6, 113.2, 64.5, 44.1, 11.4, 6.3, 6.0. **HRMS**(ESI$^+$): calculated for $C_{18}H_{19}N_2^+$ $[M+H]^+$ 263.1543, found: 263.1534.



Chemical Formula: $C_{19}H_{22}N_2$
Molecular Weight: 278.3990

3-(tert-butyl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (42)

White solid (80 mg, 58% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.09 (m, 5H), 7.03 (ddt, *J* = 8.8, 7.2, 0.8 Hz, 2H), 6.90 – 6.81 (m, 2H), 6.63 (tq, *J* = 7.3, 1.0 Hz, 1H), 4.87 (dd, *J* = 11.8, 8.1 Hz, 1H), 3.34 (AB, *J* = 17.2, 11.8 Hz, 1H), 2.64 (AB, *J* = 17.2, 8.1 Hz, 1H), 1.13 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 146.5, 143.3, 129.1, 128.9, 127.4, 126.0, 118.6, 113.3, 65.2, 43.2, 33.9, 28.4. **HRMS**(ESI$^+$): calculated for $C_{19}H_{23}N_2^+$ $[M+H]^+$ 279.1856, found: 279.1850.

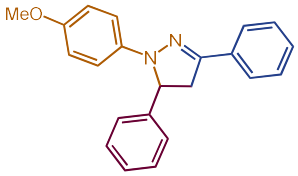


Chemical Formula: $C_{21}H_{24}N_2$
Molecular Weight: 304.4370

3-(4-methylpent-3-en-1-yl)-1,5-diphenyl-4,5-dihydro-1H-pyrazole (43)

Yellow oli (46 mg, 30% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 5H), 7.08 – 7.02 (m, 2H), 6.87 – 6.83 (m, 2H), 6.64 (tt, *J* = 7.2, 1.1 Hz, 1H), 5.06 (ddp, *J* = 7.0, 5.8, 1.5 Hz, 1H), 4.90 (dd, *J* = 11.9, 7.8 Hz, 1H), 3.30 (AB, *J* = 17.5, 12.0 Hz, 1H), 2.62 (AB, *J* = 17.3, 7.7 Hz, 1H), 2.38 – 2.31 (m, 2H),

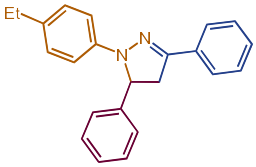
2.21 (q, J = 7.4 Hz, 2H), 1.60 (s, 3H), 1.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 146.1, 143.2, 132.7, 129.0, 128.9, 127.4, 125.9, 123.2, 118.6, 113.1, 64.5, 46.3, 30.4, 25.8, 25.5, 17.8. **HRMS**(ESI^+): calculated for $C_{21}H_{25}N_2^+$ $[M+H]^+$ 305.2013, found: 305.2004.



Chemical Formula: $C_{22}H_{20}N_2O$
Molecular Weight: 328.4150

1-(4-methoxyphenyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (44)

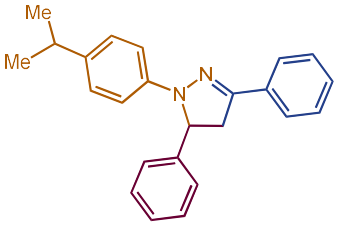
Yellow oli (126 mg, 77% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.31 – 7.04 (m, 8H), 6.91 (d, J = 8.7 Hz, 2H), 6.69 – 6.59 (m, 2H), 5.03 (dd, J = 12.3, 8.3 Hz, 1H), 3.74 – 3.62 (m, 1H), 3.60 (s, 3H), 2.99 (AB, J = 17.0, 8.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 146.3, 142.8, 139.7, 132.9, 129.2, 128.6, 128.5, 127.6, 126.2, 125.7, 114.9, 114.5, 65.7, 55.6, 43.8. **HRMS**(ESI^+): calculated for $C_{22}H_{21}N_2O^+$ $[M+H]^+$ 329.1649, found: 329.1641.



Chemical Formula: $C_{23}H_{22}N_2$
Molecular Weight: 326.4430

1-(4-ethylphenyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (45)

Yellow solid (112 mg, 69% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dt, J = 6.3, 1.4 Hz, 2H), 7.36 – 7.17 (m, 8H), 6.99 (s, 4H), 5.13 (dd, J = 12.3, 7.7 Hz, 1H), 3.71 (AB, J = 17.0, 12.4 Hz, 1H), 3.03 (AB, J = 17.0, 7.7 Hz, 1H), 2.51 (q, J = 7.6 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 143.2, 142.9, 135.1, 133.0, 129.2, 128.7, 128.6, 128.4, 127.6, 126.1, 125.8, 113.7, 65.0, 43.7, 28.1, 16.0. **HRMS**(ESI^+): calculated for $C_{23}H_{23}N_2^+$ $[M+H]^+$ 327.1856, found: 327.1849.

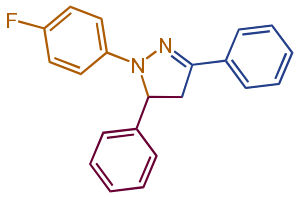


Chemical Formula: $C_{24}H_{24}N_2$
Molecular Weight: 340.4700

1-(4-isopropylphenyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (46)

Yellow oli (124 mg, 73% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 2H), 7.30 – 7.07 (m, 8H), 6.99 – 6.84 (m, 4H), 5.05 (dd, J = 12.4, 7.9 Hz, 1H), 3.63 (AB, J = 17.0, 12.4 Hz, 1H), 2.95 (AB, J = 17.0, 7.9 Hz,

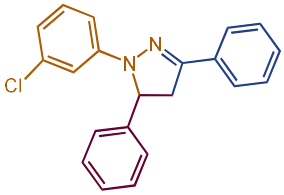
1H), 2.68 (hept, J = 6.9 Hz, 1H), 1.08 (dd, J = 7.0, 2.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 143.3, 143.0, 139.7, 133.0, 129.2, 128.6, 128.5, 127.6, 126.9, 126.1, 125.8, 113.6, 65.1, 43.7, 33.3, 24.3 (d, J = 2.1 Hz). **HRMS**(ESI^+): calculated for $C_{24}H_{25}N_2^+$ $[M+H]^+$ 341.2013, found: 341.2003.



Chemical Formula: $C_{21}H_{17}FN_2$
Molecular Weight: 316.3794

1-(4-fluorophenyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (47)

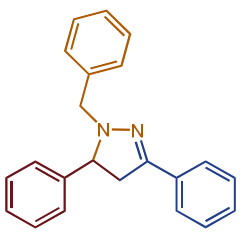
Yellow solid (98 mg, 62% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.30 – 7.11 (m, 8H), 6.92 – 6.86 (m, 2H), 6.80 – 6.69 (m, 2H), 5.04 (dd, J = 12.3, 7.8 Hz, 1H), 3.68 (dd, J = 17.0, 12.3 Hz, 1H), 3.00 (dd, J = 17.1, 7.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 155.8, 147.0, 142.4, 141.7 (d, J = 2.0 Hz), 132.7, 129.3, 128.7, 128.6, 127.8, 125.9 (d, J = 23.0 Hz), 115.5 (d, J = 22.3 Hz), 114.5 (d, J = 7.4 Hz), 65.2, 43.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.76 (tt, J = 8.5, 4.5 Hz). HRMS(ESI^+): calculated for $C_{21}H_{18}FN_2^+$ $[M+H]^+$ 317.1449, found: 317.1442.



Chemical Formula: $C_{21}H_{17}ClN_2$
Molecular Weight: 332.8310

1-(3-chlorophenyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (48)

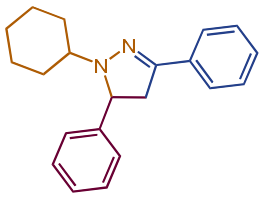
White solid (106 mg, 64% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.31 – 7.20 (m, 5H), 7.19 – 7.10 (m, 4H), 6.93 (t, J = 8.1 Hz, 1H), 6.64 (ddd, J = 14.4, 8.1, 2.1 Hz, 2H), 5.11 (dd, J = 12.3, 6.7 Hz, 1H), 3.71 (AB, J = 17.2, 12.3 Hz, 1H), 3.03 (AB, J = 17.2, 6.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 145.8, 142.0, 134.8, 132.4, 129.9, 129.3, 129.0, 128.7, 127.9, 126.0, 125.8, 118.9, 113.5, 111.2, 64.2, 43.7. **HRMS**(ESI^+): calculated for $C_{21}H_{18}ClN_2^+$ $[M+H]^+$ 333.1154, found: 333.1149.



Chemical Formula: $C_{22}H_{20}N_2$
Molecular Weight: 312.4160

1-benzyl-3,5-diphenyl-4,5-dihydro-1H-pyrazole (49)

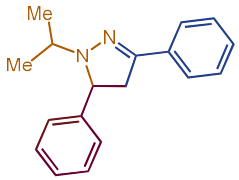
Colorless oli (95 mg, 61% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.21 (dtd, *J* = 21.7, 14.2, 7.2 Hz, 11H), 4.43 (d, *J* = 14.2 Hz, 1H), 4.15 (dd, *J* = 14.2, 10.3 Hz, 1H), 3.86 (d, *J* = 14.2 Hz, 1H), 3.23 (AB, *J* = 16.1, 10.3 Hz, 1H), 2.84 (AB, *J* = 15.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 140.7, 136.9, 133.2, 129.7, 128.8, 128.5, 128.5, 128.2, 127.9, 127.8, 127.3, 125.8, 69.1, 56.7, 43.0. **HRMS**(ESI^+): calculated for $C_{22}H_{21}N_2^+$ $[M+H]^+$ 313.1700, found: 313.1705.



Chemical Formula: $C_{21}H_{24}N_2$
Molecular Weight: 304.4370

1-cyclohexyl-3,5-diphenyl-4,5-dihydro-1H-pyrazole (50)

White solid (73 mg, 48% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 6.4, 1.4 Hz, 2H), 7.36 (dt, *J* = 6.2, 1.4 Hz, 2H), 7.29 – 7.09 (m, 6H), 4.51 (dd, *J* = 13.7, 10.8 Hz, 1H), 3.33 (AB, *J* = 16.1, 10.8 Hz, 1H), 2.78 (AB, *J* = 16.2, 13.8 Hz, 1H), 2.70 (ddt, *J* = 11.1, 7.3, 3.7 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.83 – 1.74 (m, 1H), 1.73 – 1.58 (m, 3H), 1.50 (ddd, *J* = 8.9, 4.4, 2.3 Hz, 1H), 1.23 – 0.97 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 142.7, 133.6, 128.7, 128.4, 128.0, 127.5, 127.5, 125.5, 67.2, 60.3, 43.3, 32.0, 28.9, 26.2, 26.0, 25.7. **HRMS**(ESI^+): calculated for $C_{21}H_{25}N_2^+$ $[M+H]^+$ 305.2013, found: 305.2005.

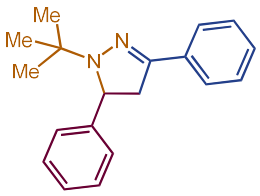


Chemical Formula: $C_{18}H_{20}N_2$
Molecular Weight: 264.3720

1-isopropyl-3,5-diphenyl-4,5-dihydro-1H-pyrazole (51)

White solid (67 mg, 51% yield, purified by flash column chromatography, PE/EA = 30/1, v/v).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.59 – 7.52 (m, 2H), 7.47 – 7.32 (m, 6H), 4.58 (dd, *J* = 13.9, 10.6 Hz, 1H), 3.52 (AB, *J* = 16.1, 10.6 Hz, 1H), 3.28 (hept, *J* = 6.6 Hz, 1H), 2.99 (AB, *J* = 16.1, 13.9 Hz, 1H), 1.40 (d, *J* = 6.7 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 142.4, 133.6, 128.7, 128.5, 128.1, 127.6, 127.5, 125.6, 67.7, 51.9, 43.2, 21.8, 17.7. **HRMS**(ESI^+): calculated for $C_{18}H_{21}N_2^+$ $[M+H]^+$ 265.1700, found: 265.1706.



Chemical Formula: $C_{19}H_{22}N_2$
Molecular Weight: 278.3990

1-(tert-butyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazole (52)

White solid (58 mg, 42% yield, purified by flash column chromatography, PE/EA = 30/1, v/v). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.52 – 7.46 (m, 2H), 7.41 – 7.23 (m, 6H), 4.70 (t, *J* = 11.9 Hz, 1H), 3.61 (AB, *J* = 16.7, 11.8 Hz, 1H), 2.93 (AB, *J* = 16.6, 11.9 Hz, 1H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 133.5, 128.9, 128.5, 128.4, 128.0, 126.9, 126.9, 125.6, 64.8, 58.0, 45.0, 27.7. **HRMS**(ESI^+): calculated for $C_{19}H_{23}N_2^+$ $[M+H]^+$ 279.1856, found: 279.1850.

8. Copies of NMR Spectra

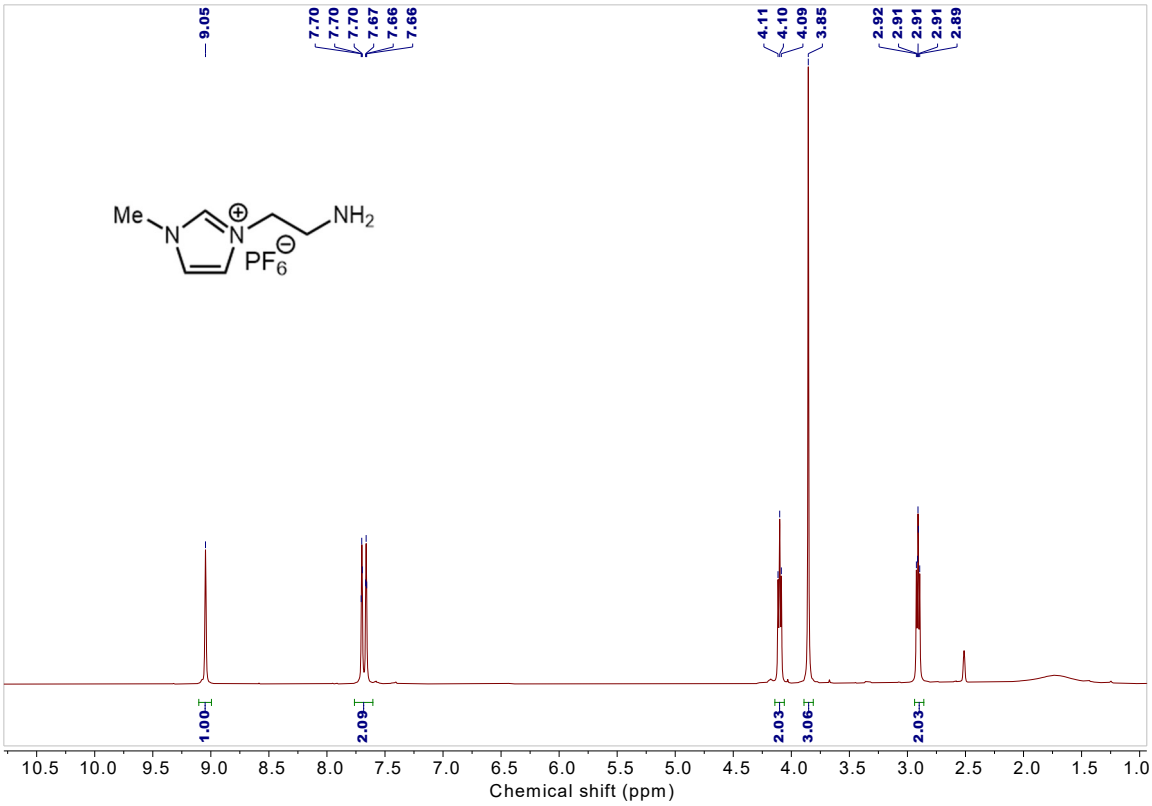


Figure S16: ^{1}H NMR spectrum of **A1** (400 MHz, CD_3SOCD_3).

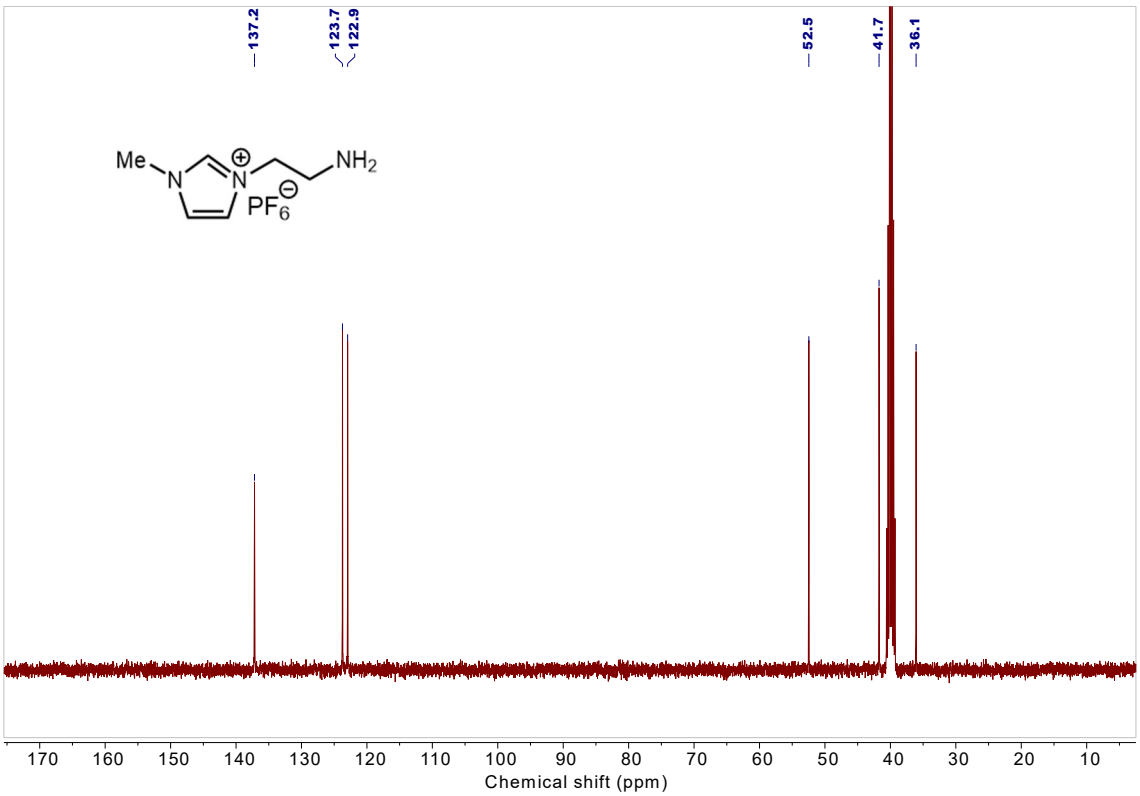


Figure S17: ^{13}C NMR spectrum of **A1** (100 MHz, CD_3SOCD_3).

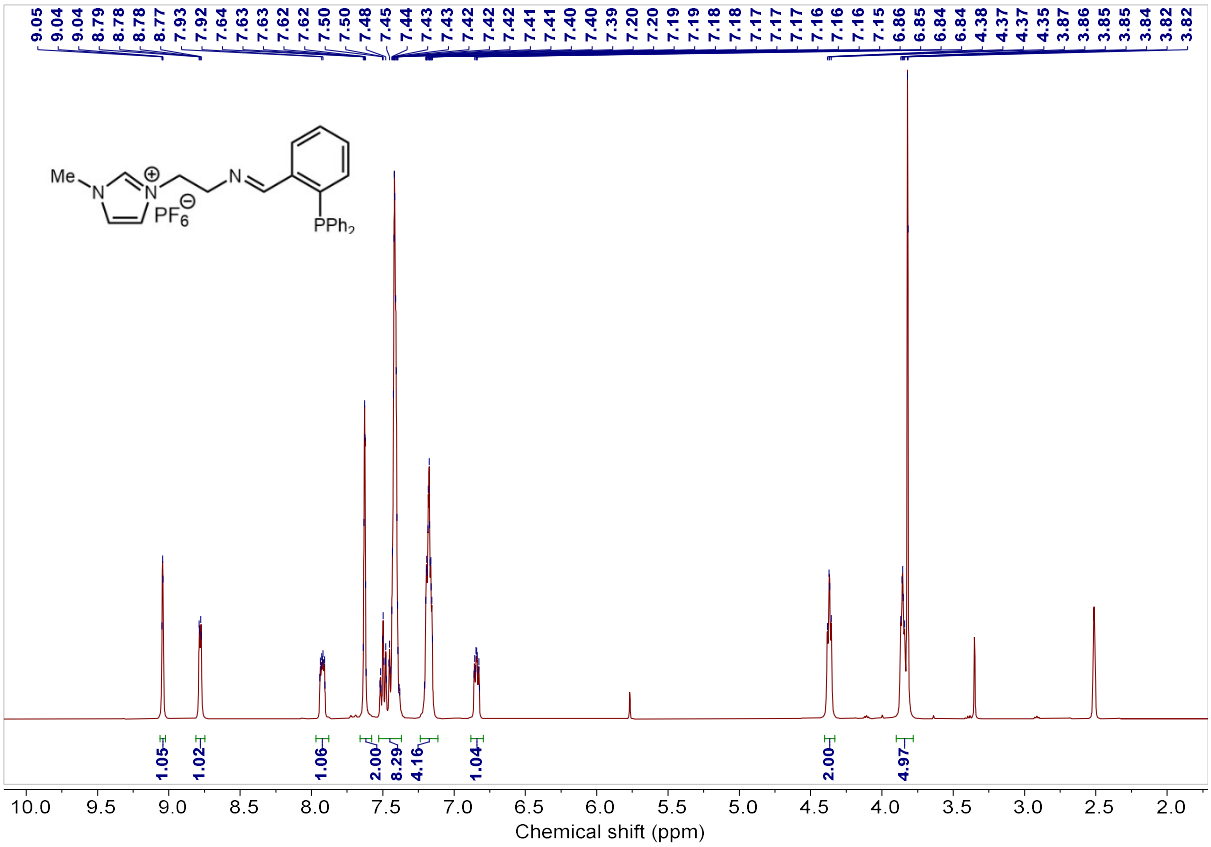


Figure S18: ^{1}H NMR spectrum of **B1** (400 MHz, CD_3SOCD_3).

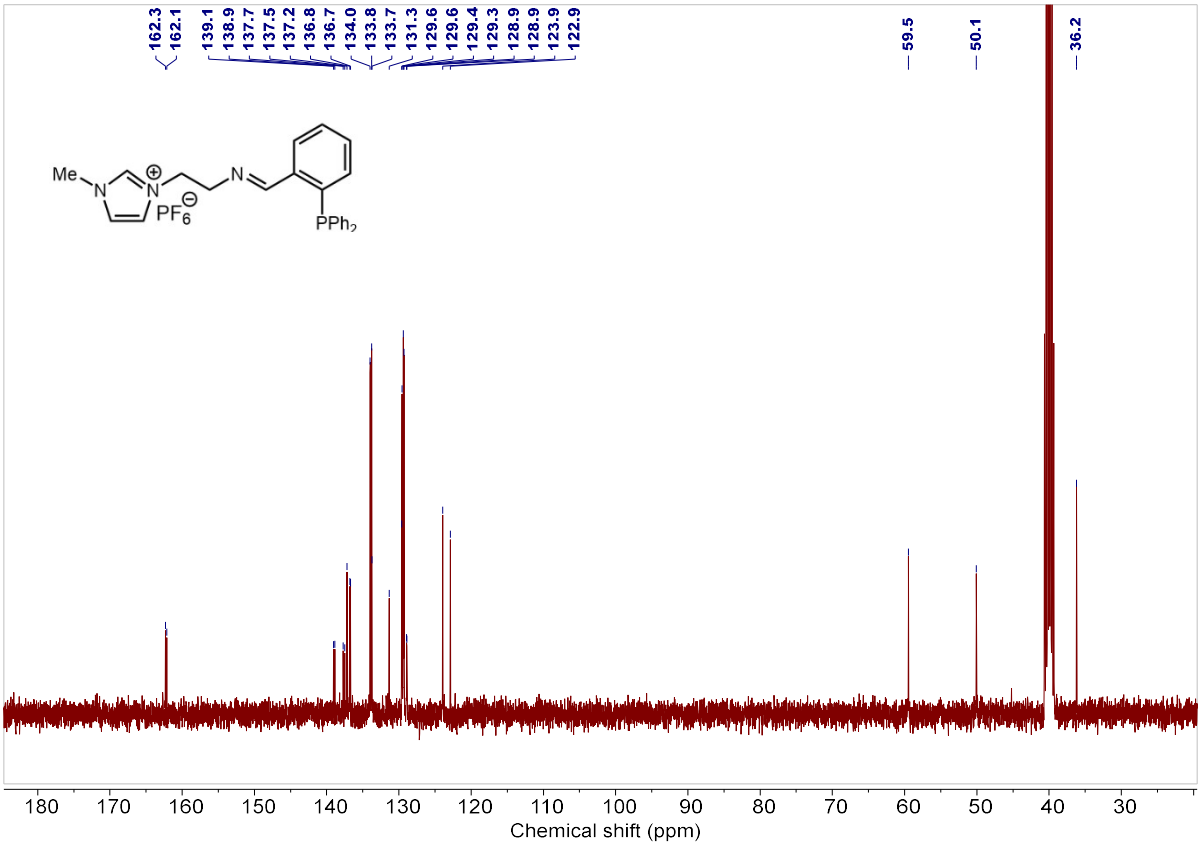


Figure S19: ^{13}C NMR spectrum of **B1** (100 MHz, CD_3SOCD_3)

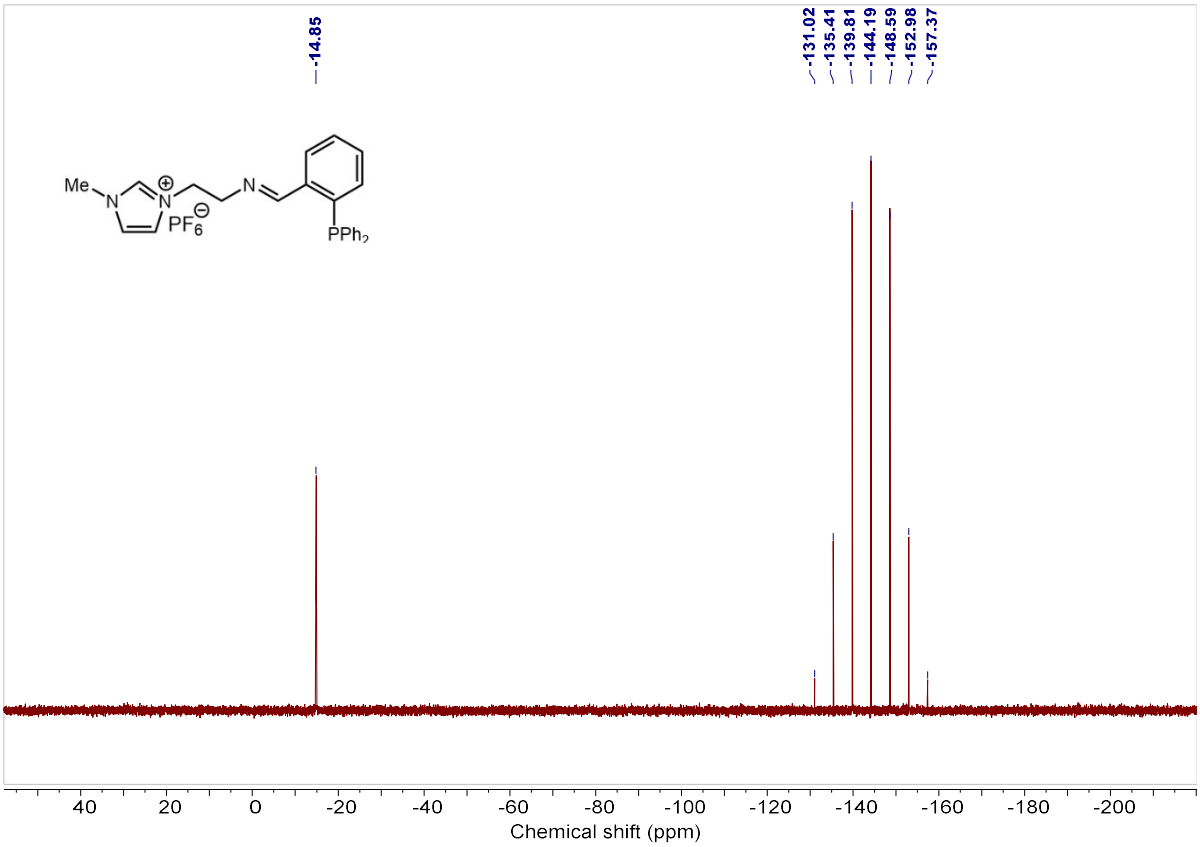


Figure S20: ^{31}P NMR spectrum of **B1** (162 MHz, CD_3SOCD_3).

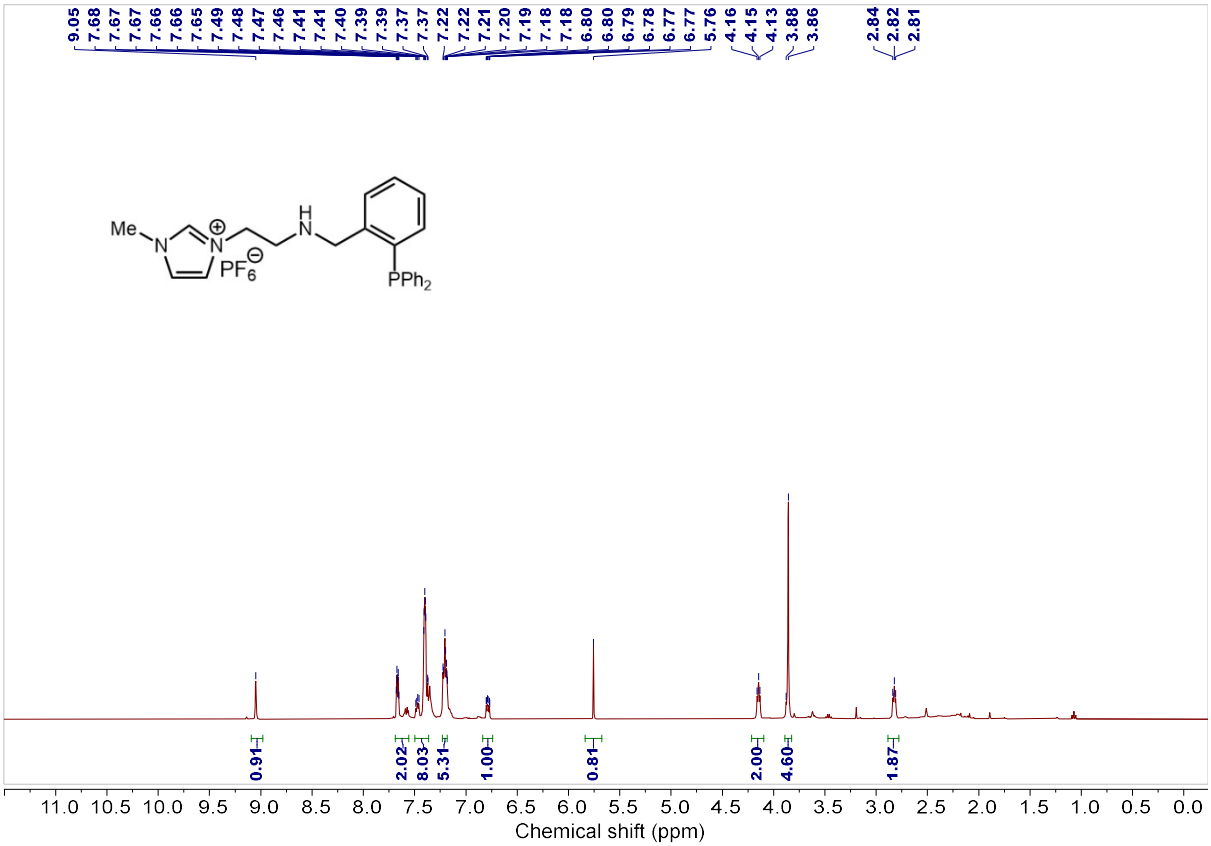


Figure S21: ^{1}H NMR spectrum of **L1** (400 MHz, CD_3SOCD_3).

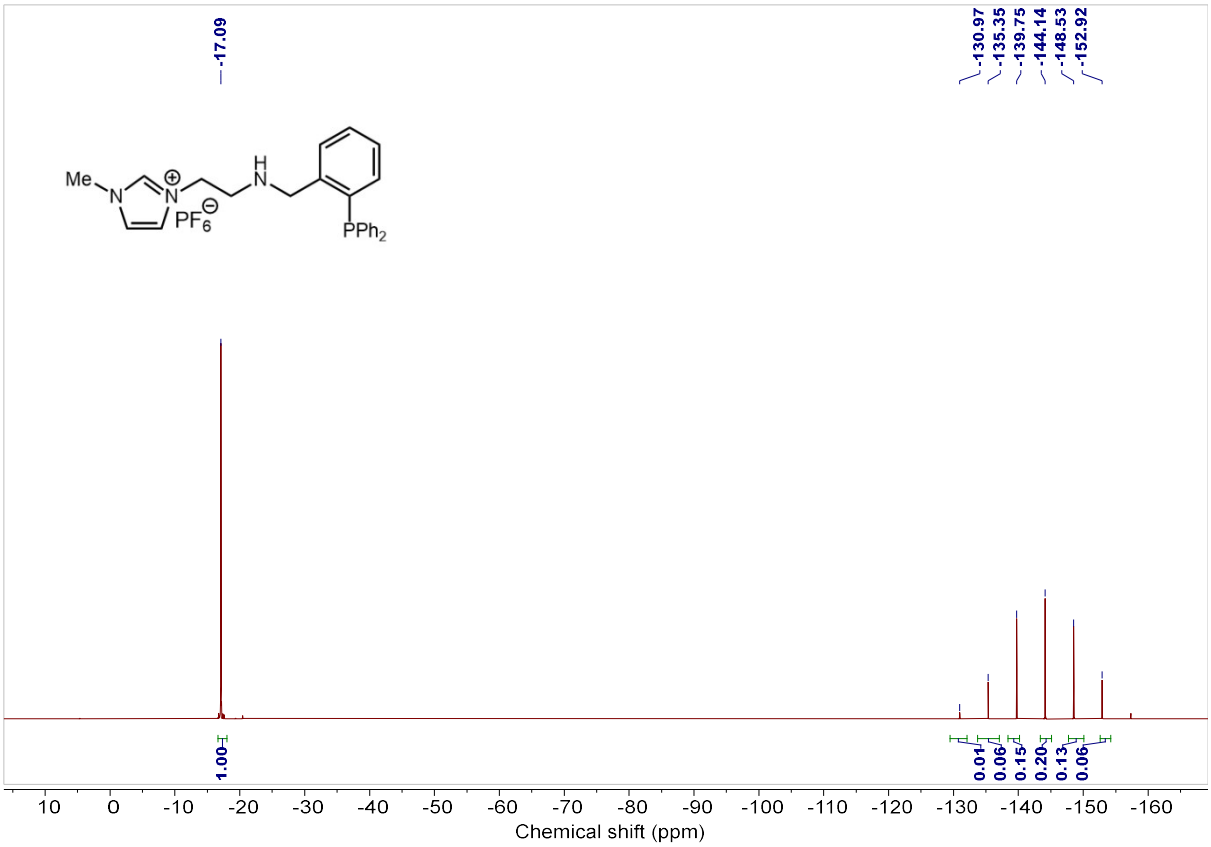


Figure S22: ^{31}P NMR spectrum of **L1** (162 MHz, CD_3SOCD_3).

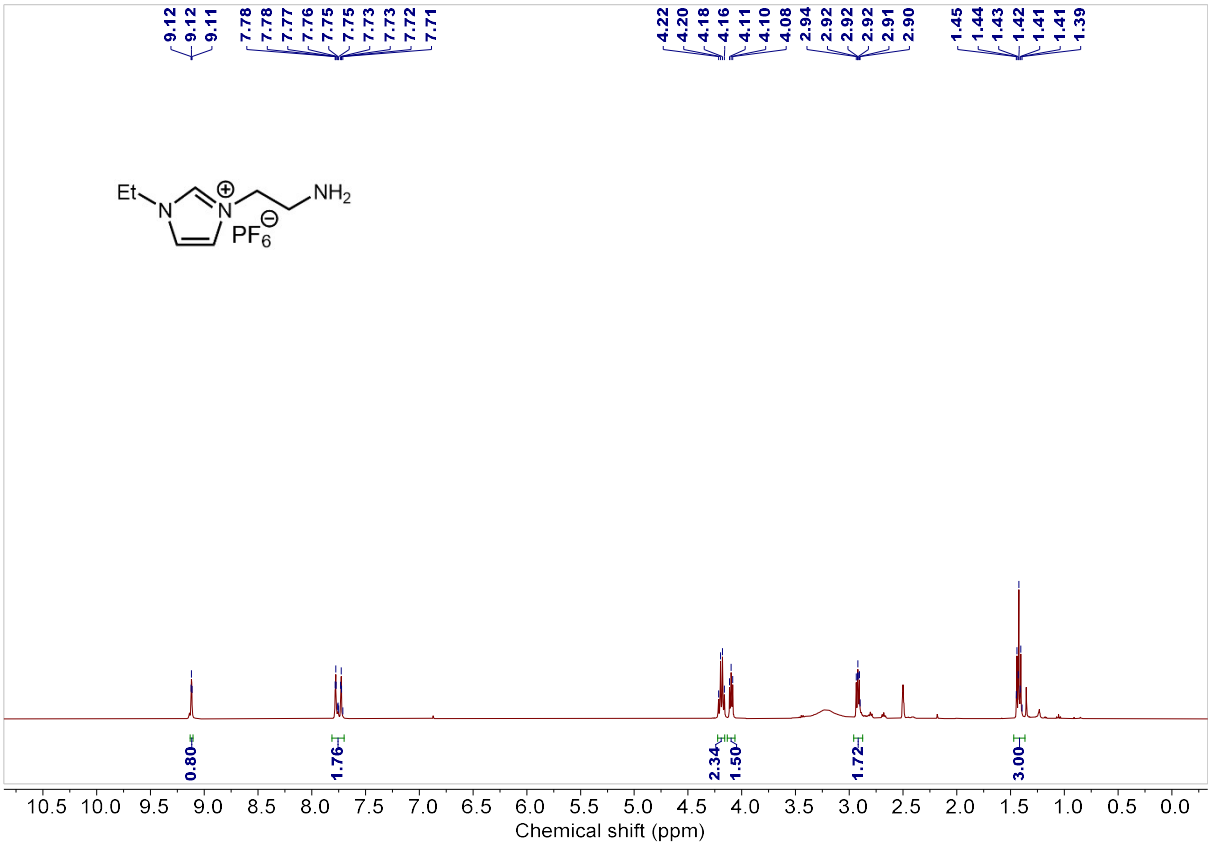


Figure S23: ^{1}H NMR spectrum of **A2** (400 MHz, CD_3SOCD_3).

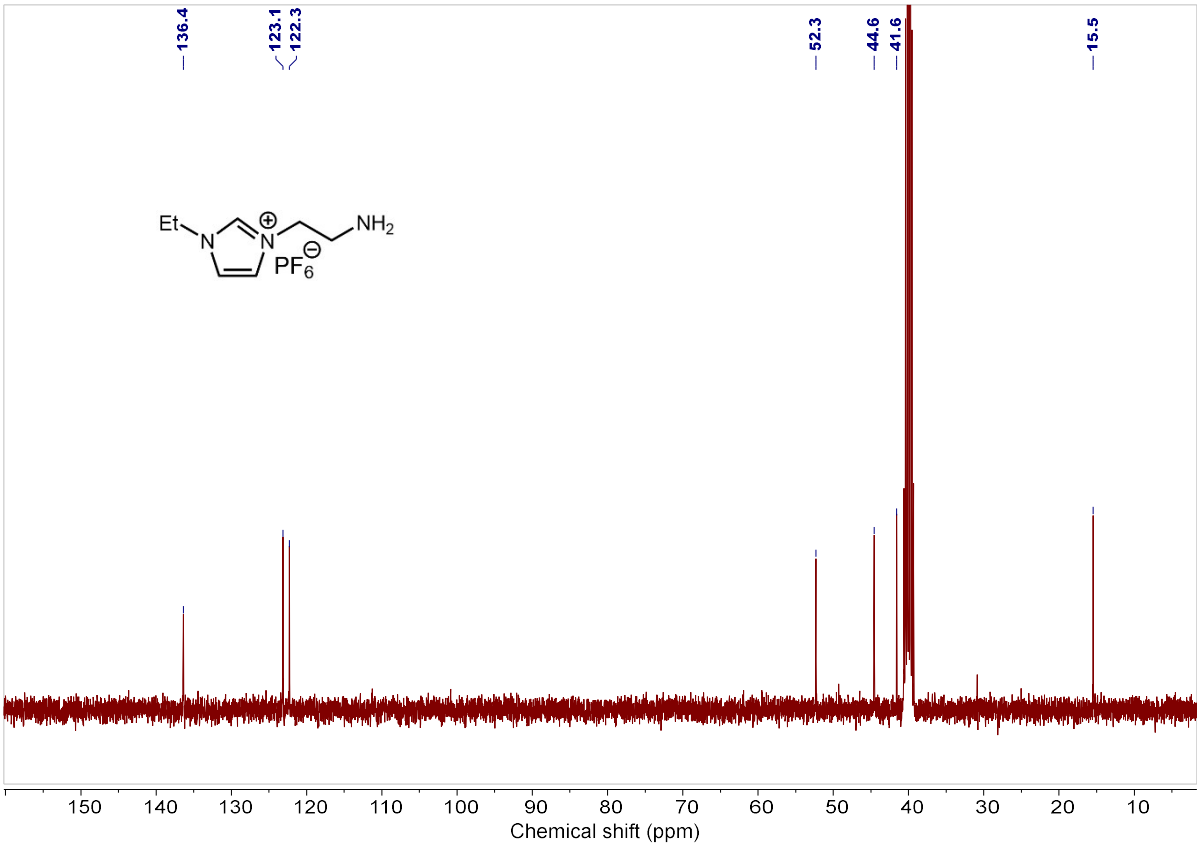


Figure S24: ^{13}C NMR spectrum of **A2** (100 MHz, CD_3SOCD_3).

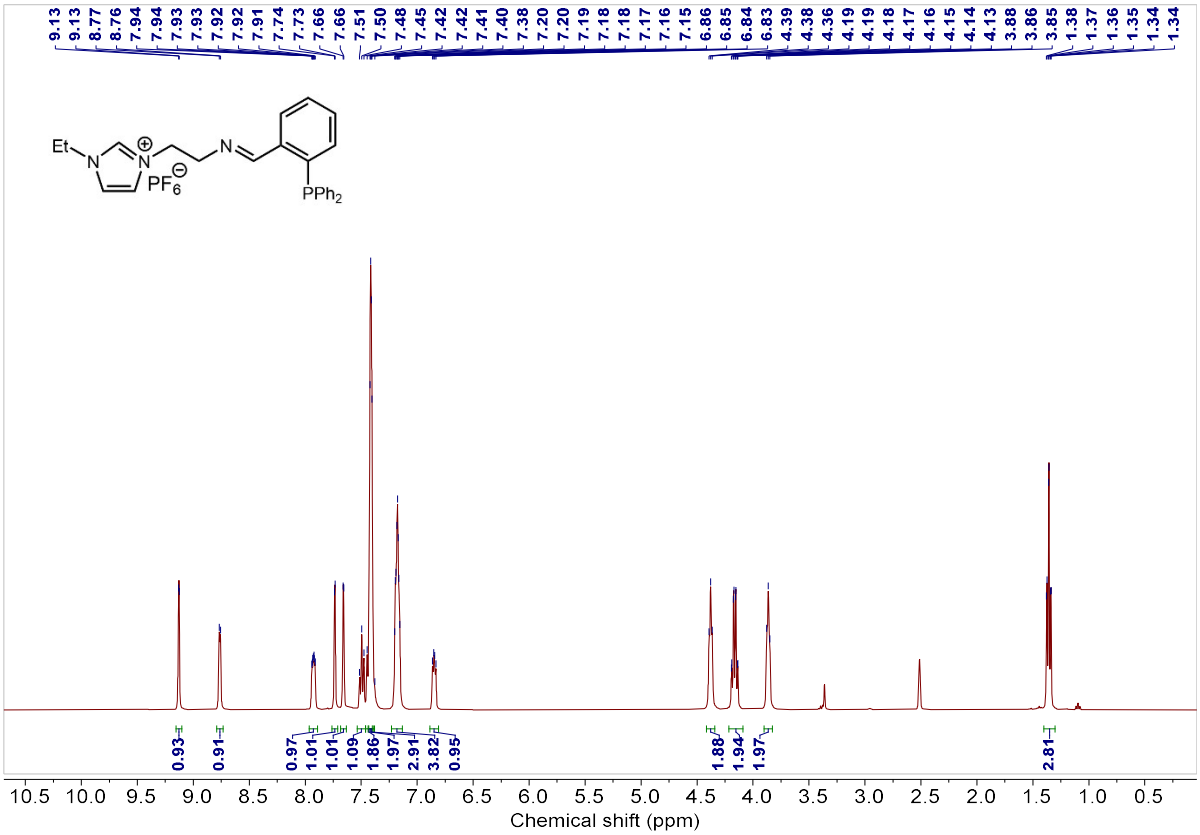


Figure S25: ^{1}H NMR spectrum of **B2** (400 MHz, CD_3SOCD_3).

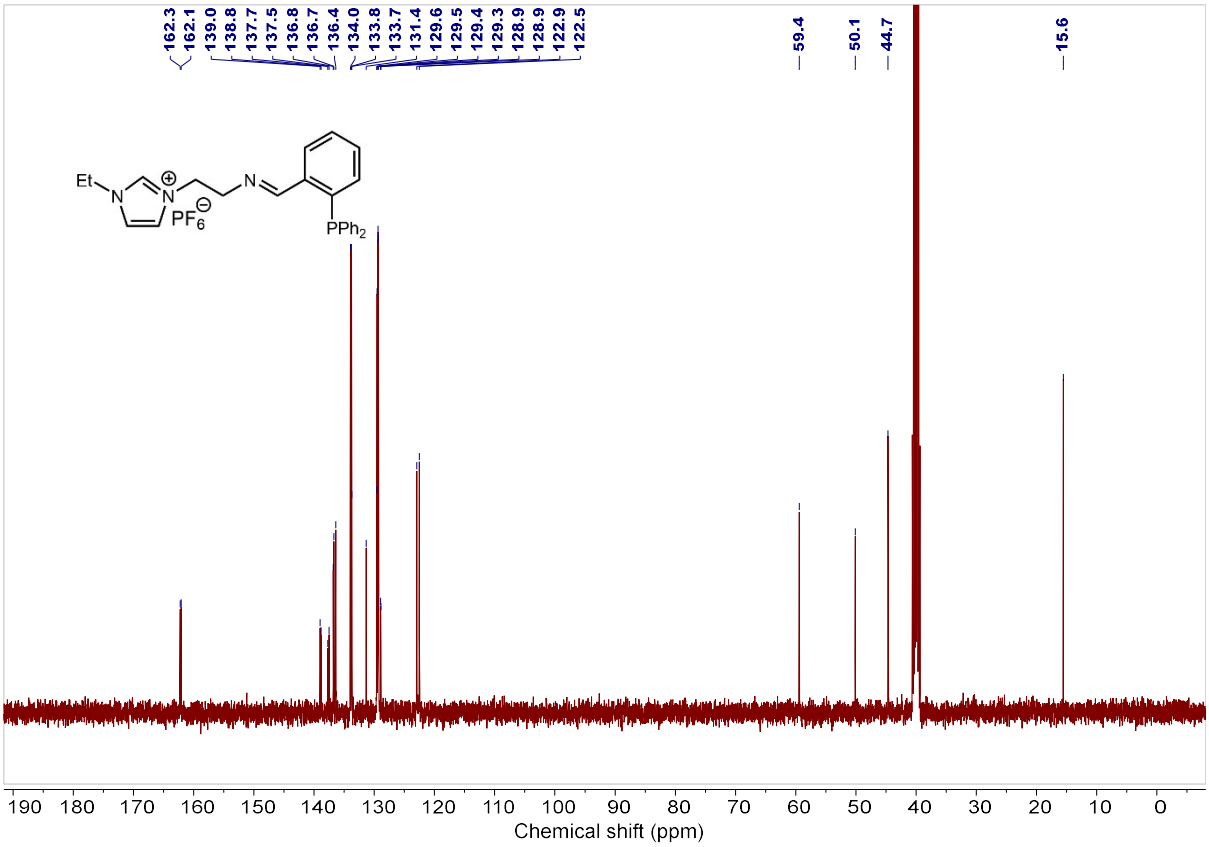


Figure S26: ^{13}C NMR spectrum of **B2** (100 MHz, CD_3SOCD_3).

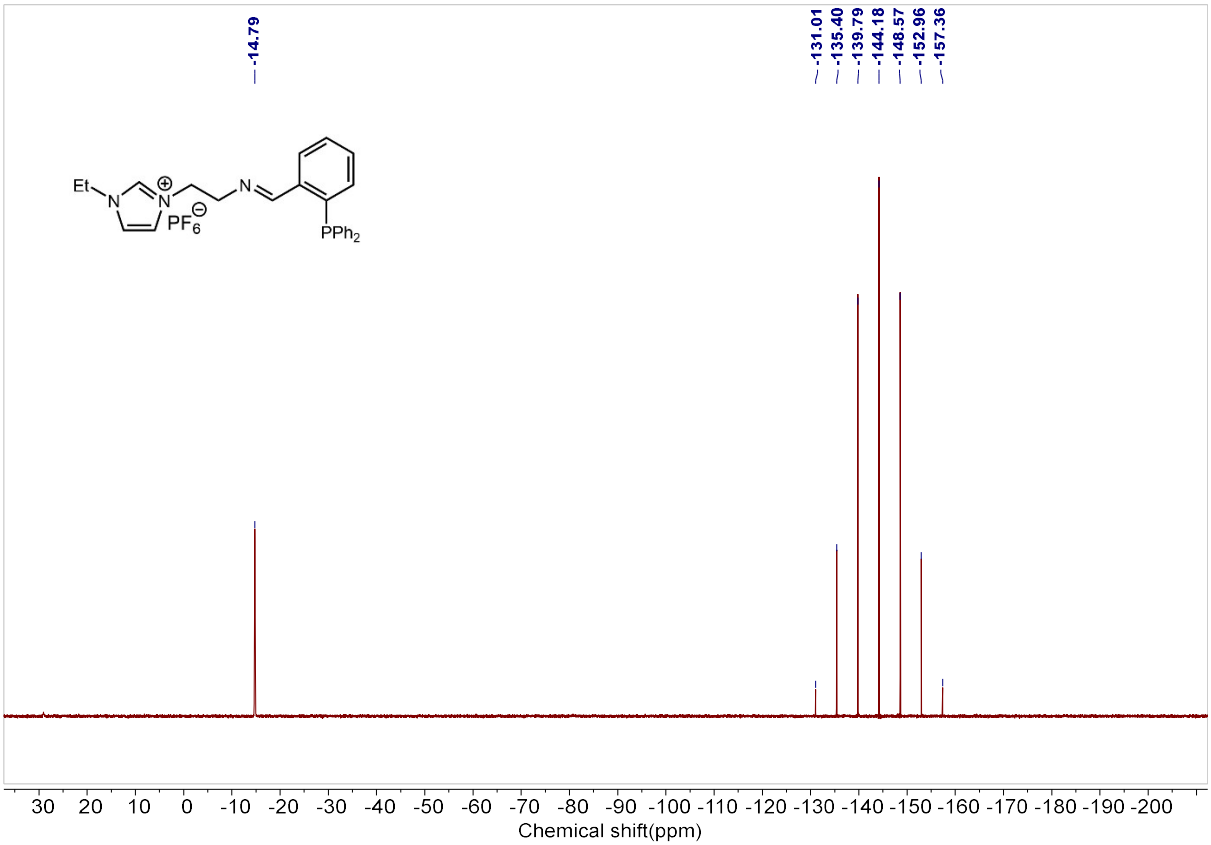


Figure S27: ^{31}P NMR spectrum of **B2** (162 MHz, CD_3SOCD_3).

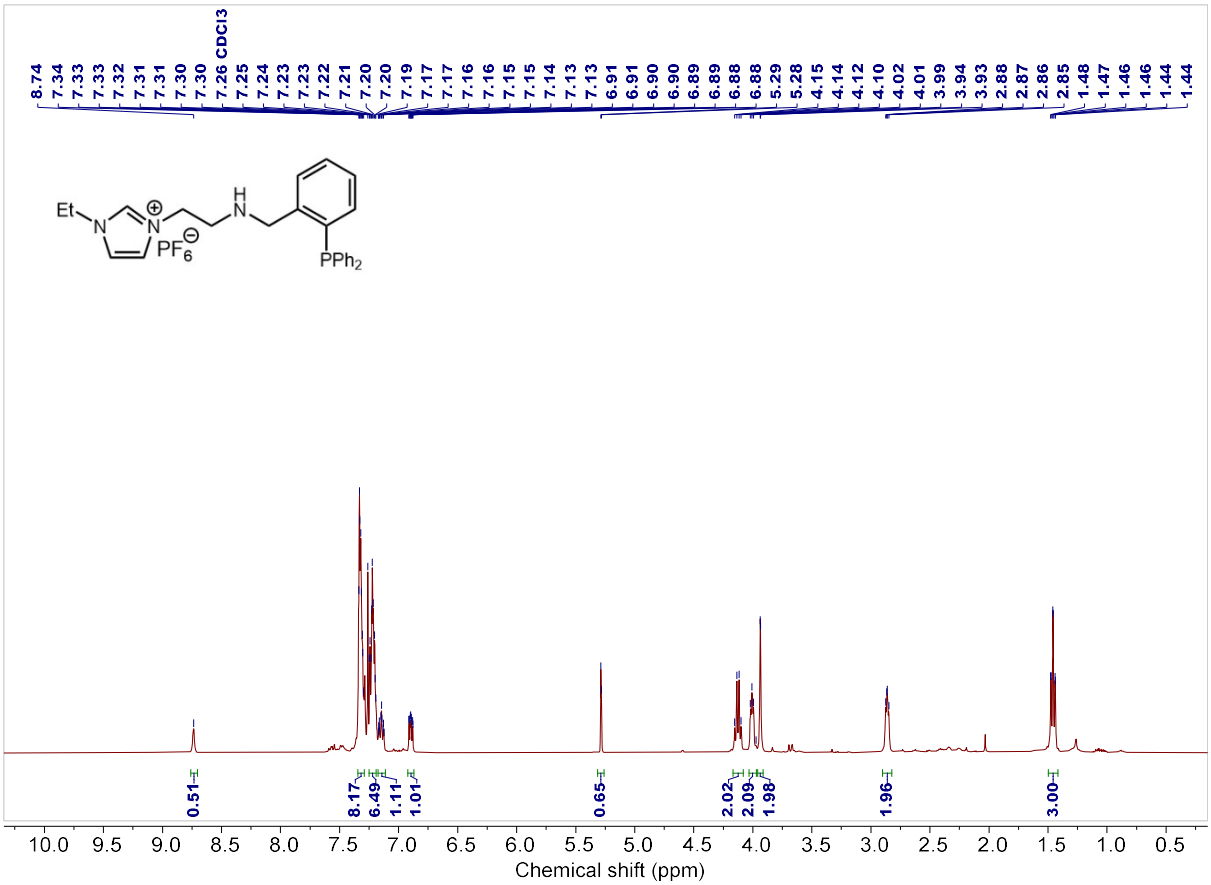


Figure S28: ^{1}H NMR spectrum of **L2** (400 MHz, $CDCl_3$).

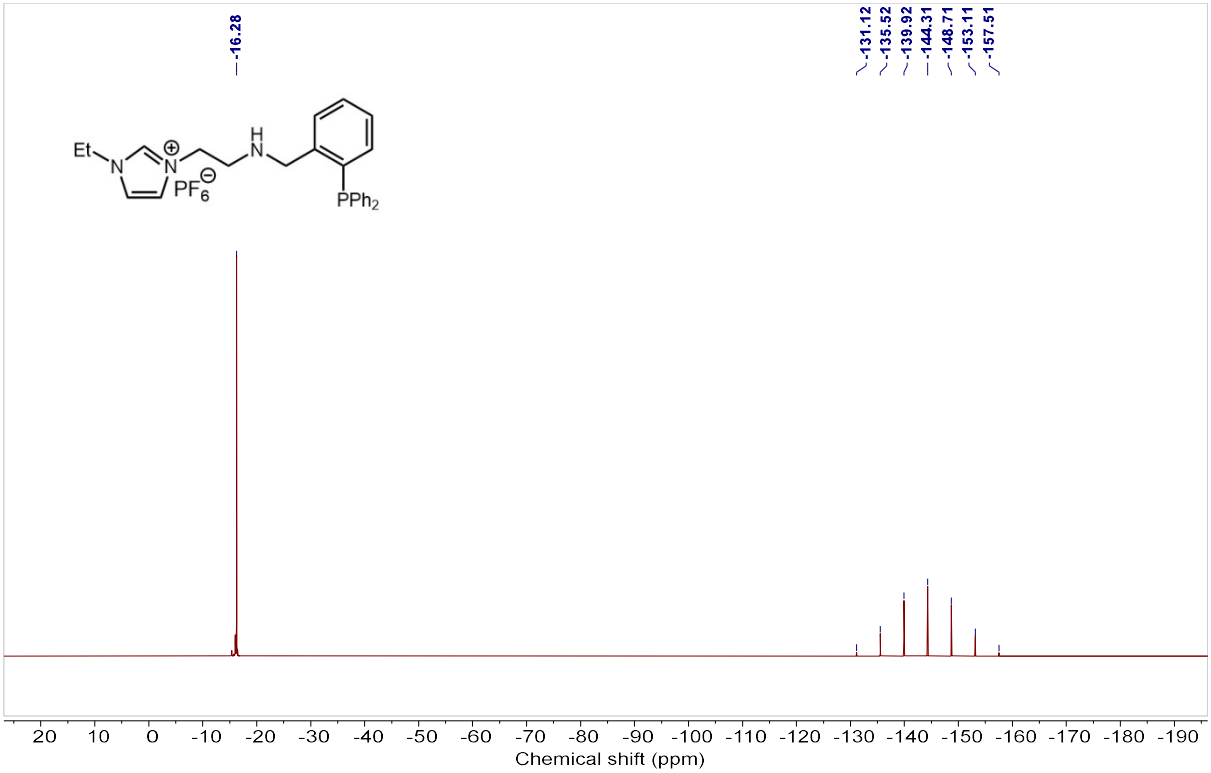


Figure S29: ^{31}P NMR spectrum of **L2** (162 MHz, $CDCl_3$).

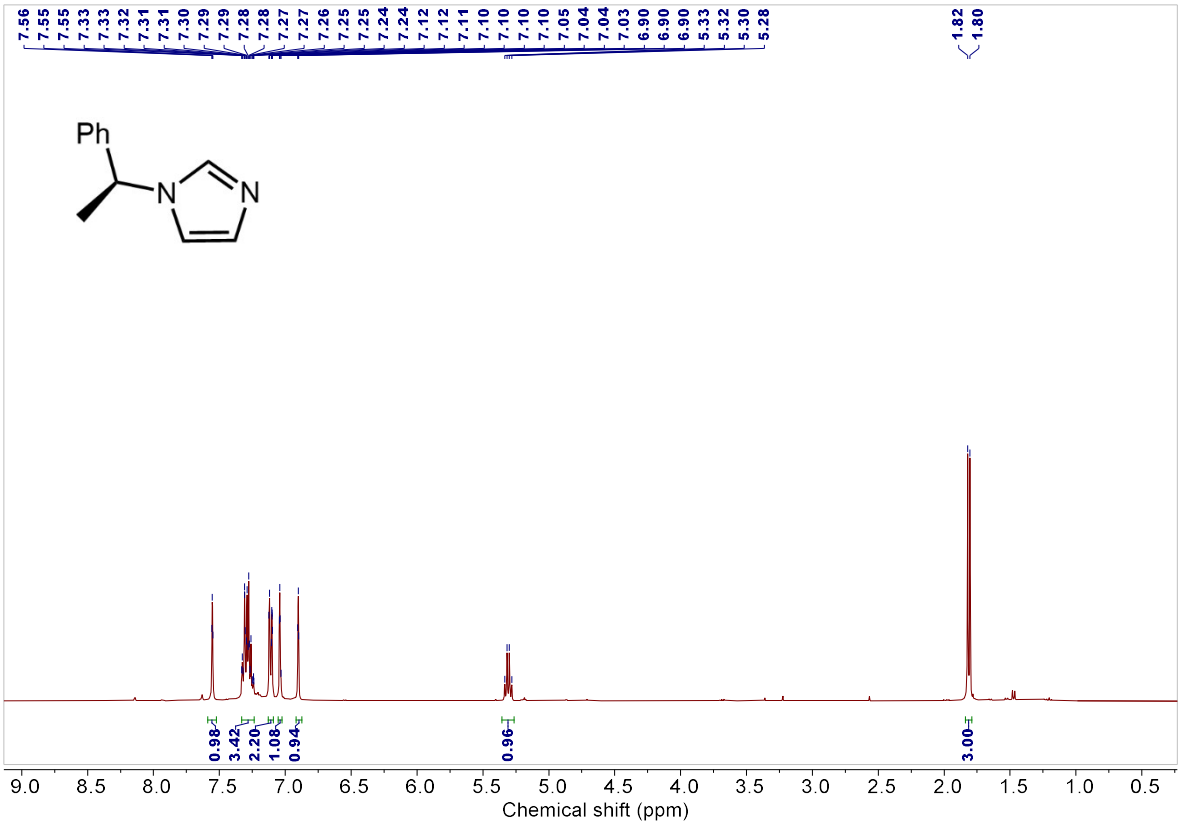


Figure S30: ^{1}H NMR spectrum of **C1** (400 MHz, $CDCl_3$).

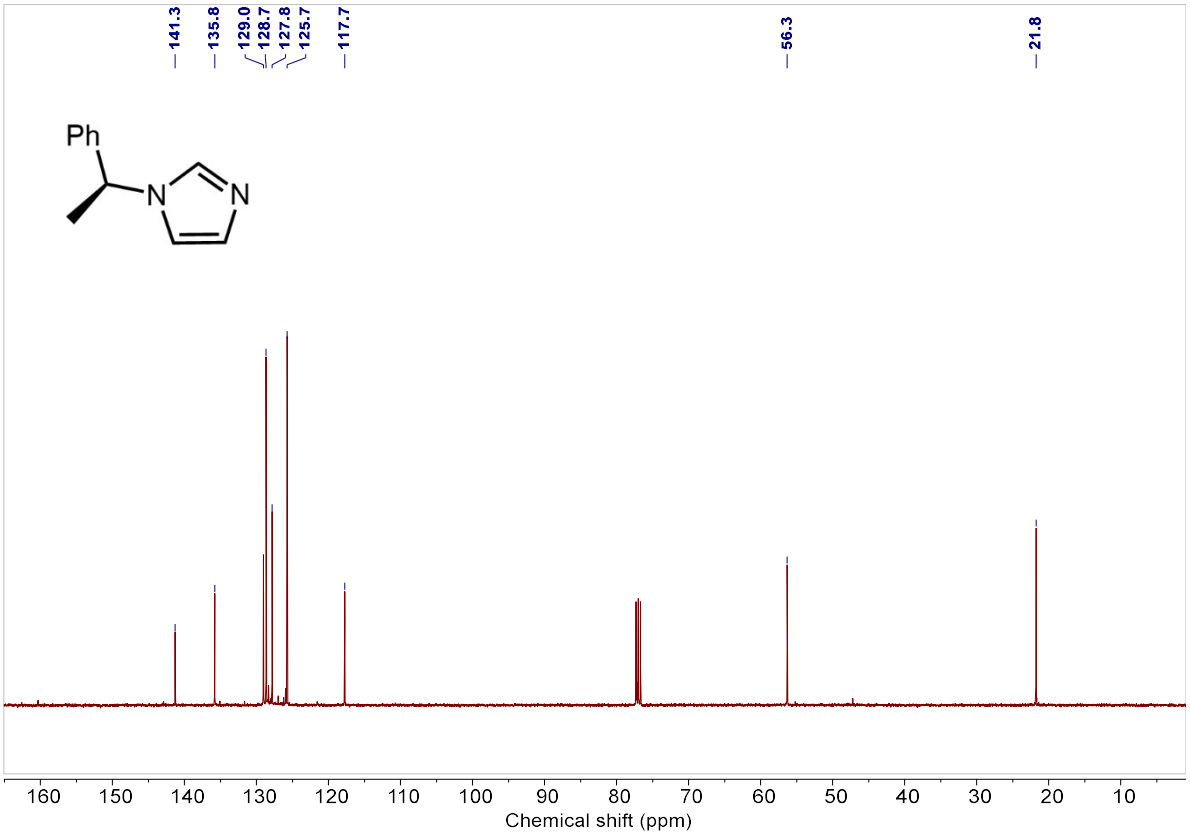


Figure S31: ^{13}C NMR spectrum of **C1** (100 MHz, $CDCl_3$)

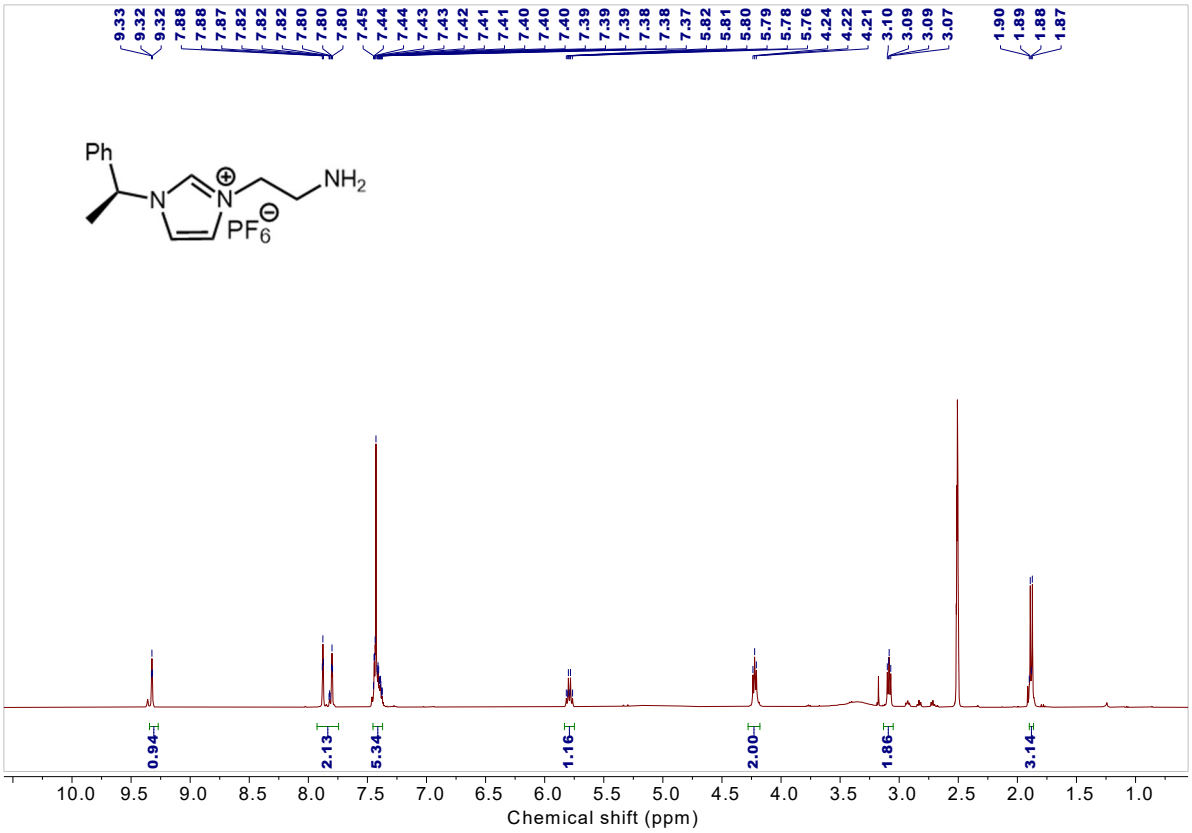


Figure S32: ^{1}H NMR spectrum of **A3** (400 MHz, CD_3SOCD_3).

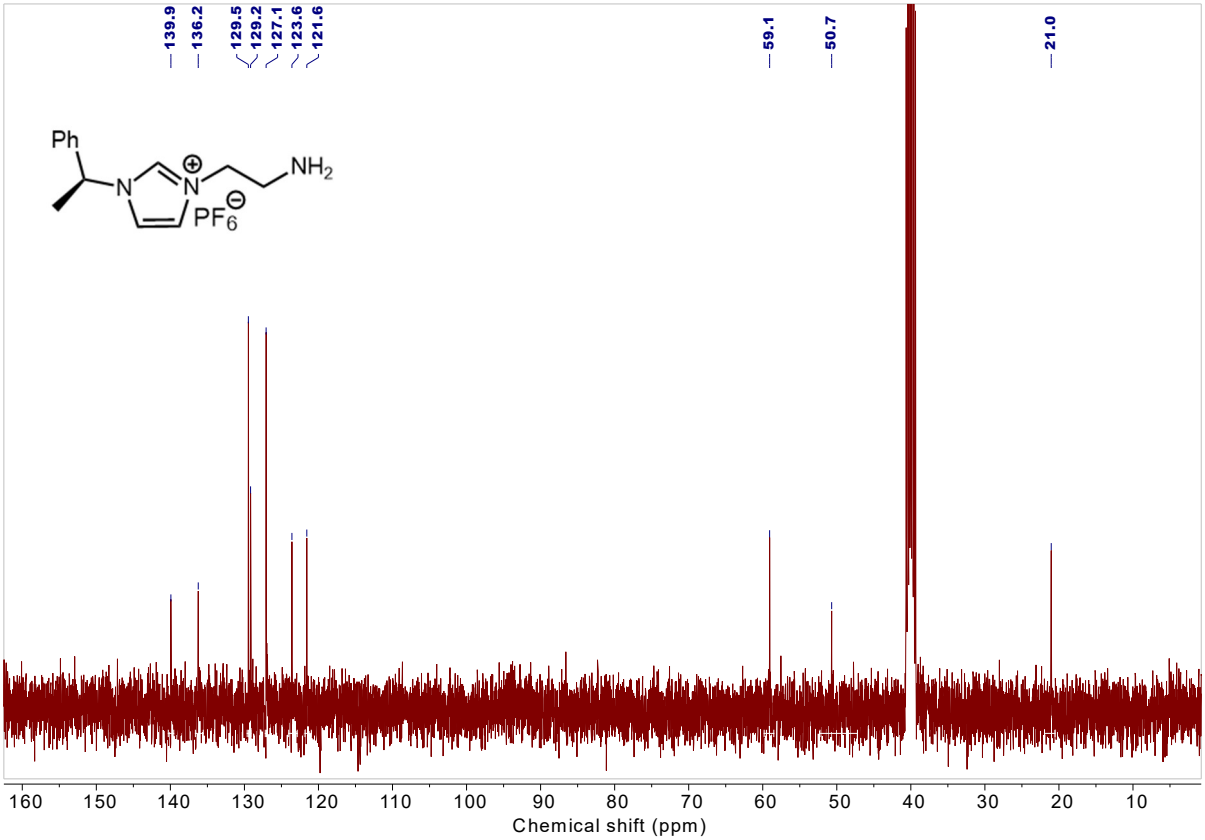


Figure S33: ^{13}C NMR spectrum of **A3** (100 MHz, CD_3SOCD_3).

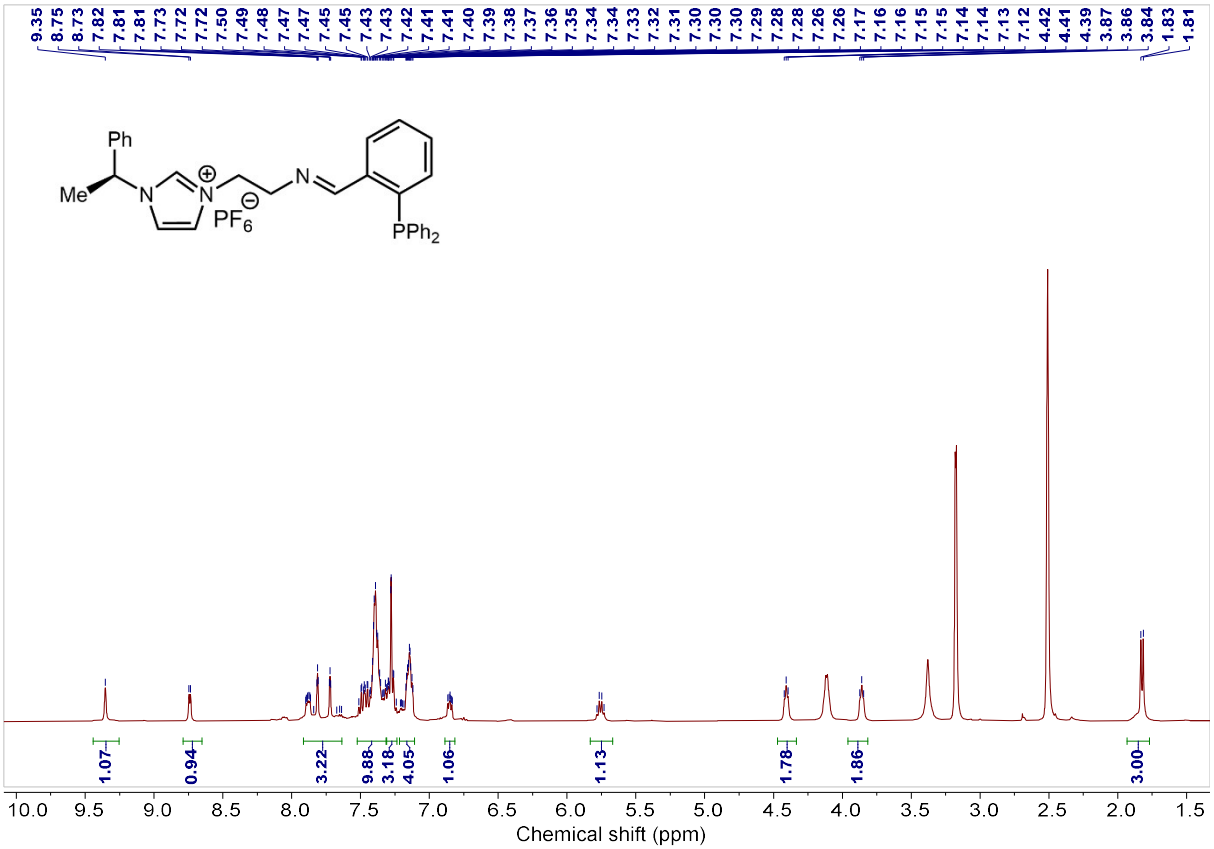


Figure S34: ^{1}H NMR spectrum of **B3** (400 MHz, CD_3SOCD_3).

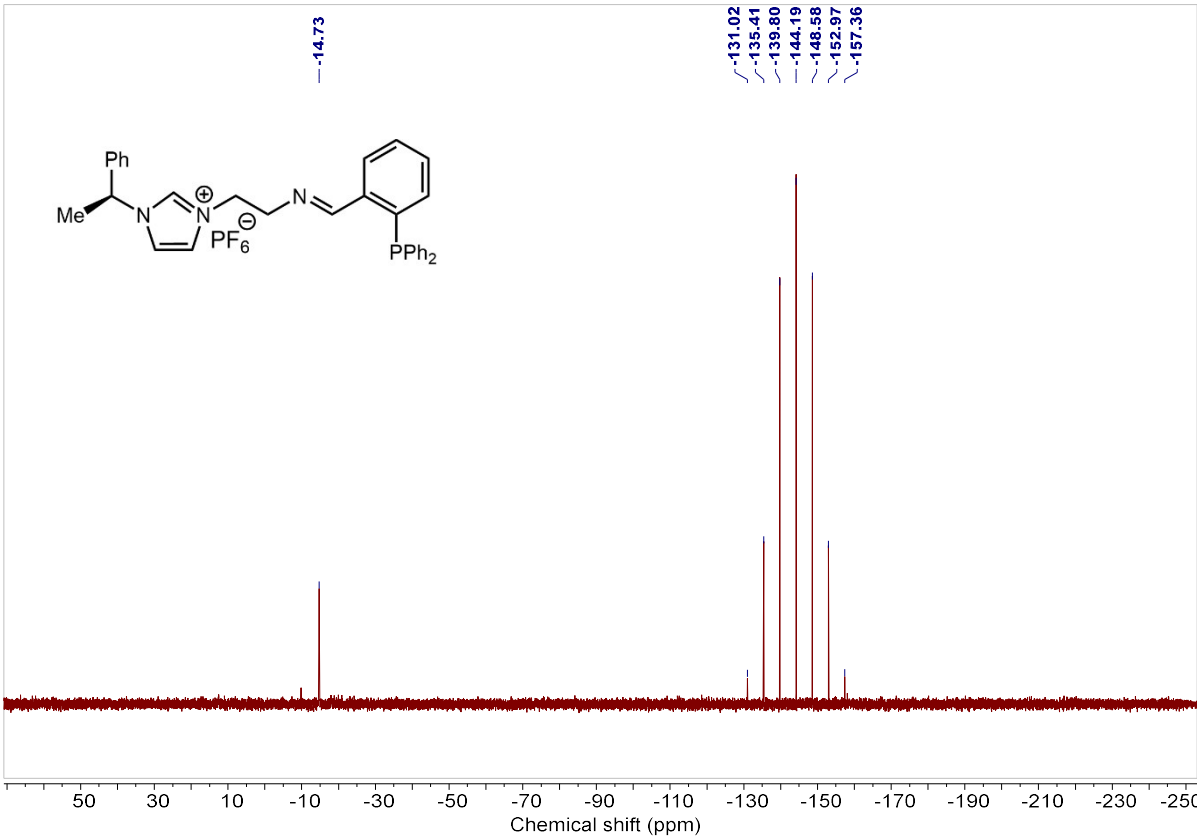


Figure S35: ^{31}P NMR spectrum of **B3** (162 MHz, CD_3SOCD_3).

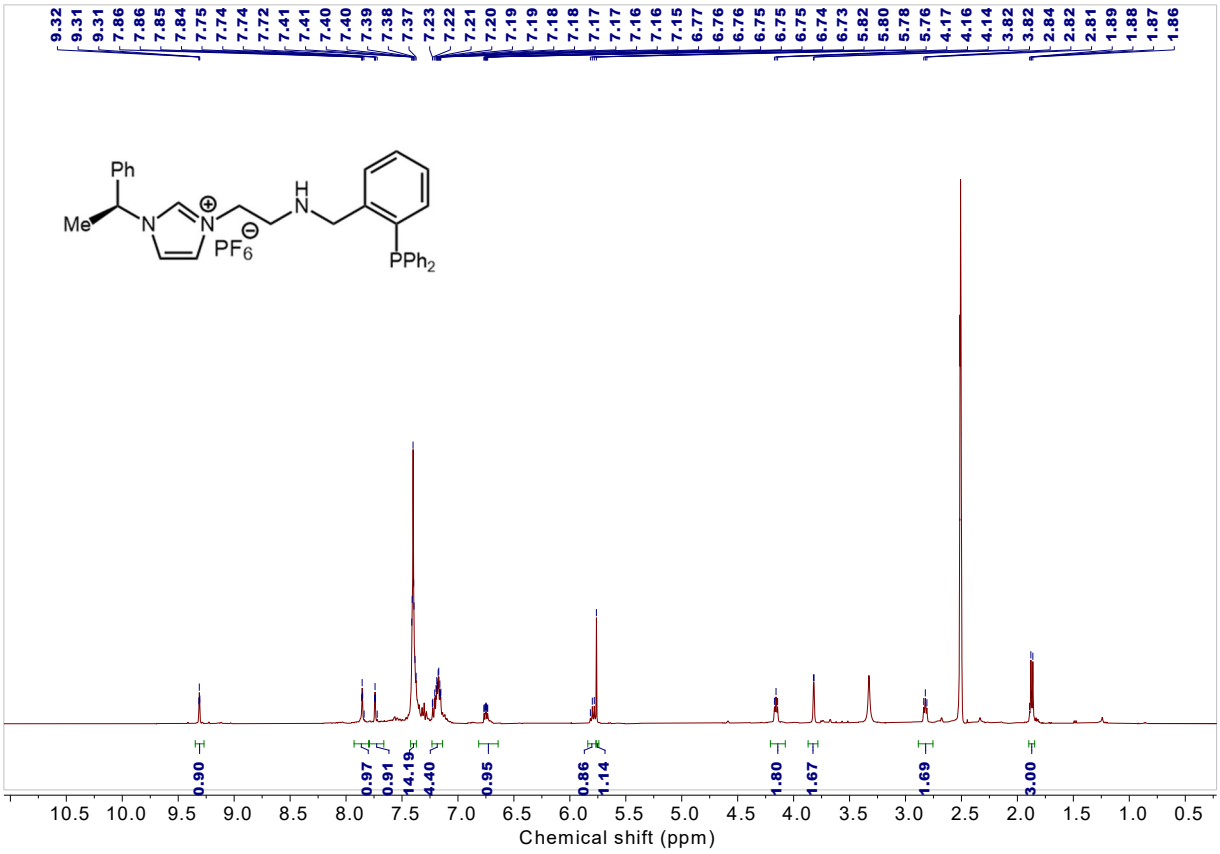


Figure S36: ^{1}H NMR spectrum of **L3** (400 MHz, CD_3SOCD_3).

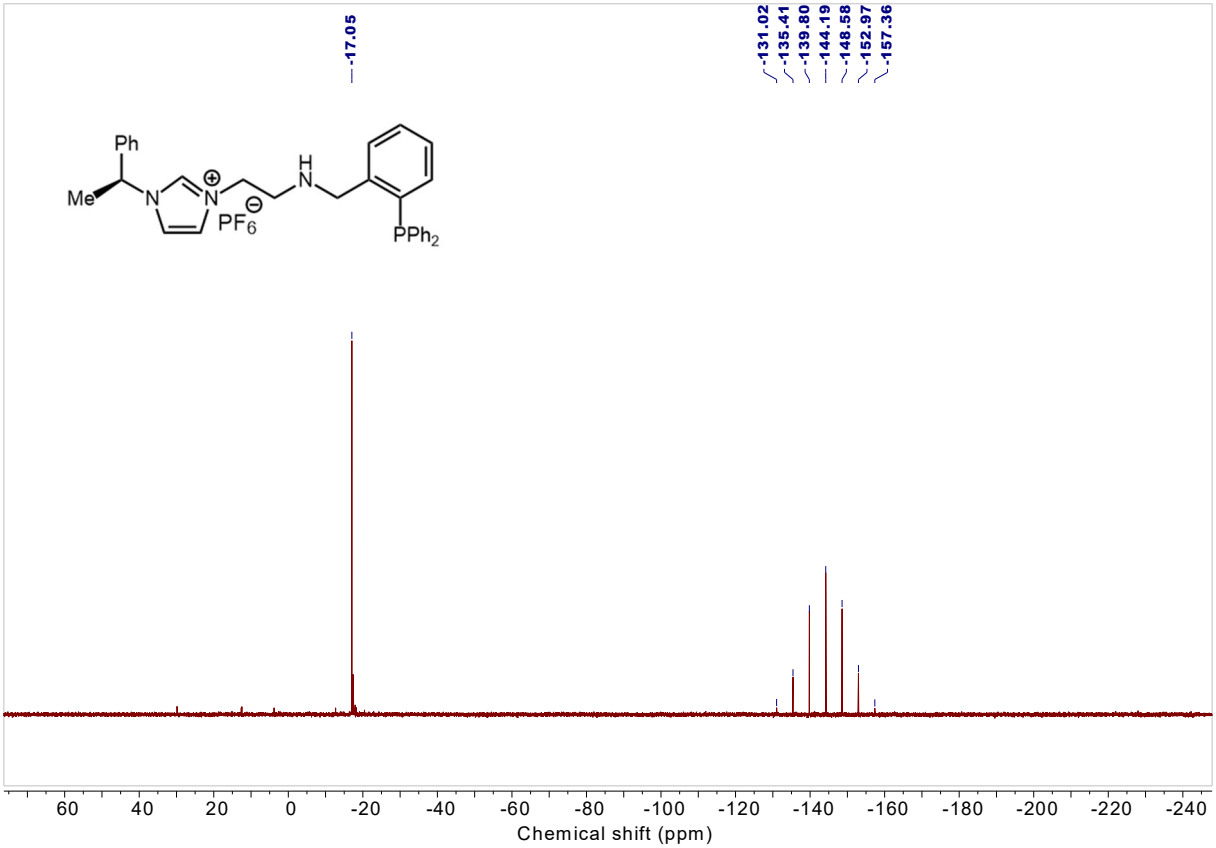


Figure S37: ^{31}P NMR spectrum of **L3** (162 MHz, CD_3SOCD_3).

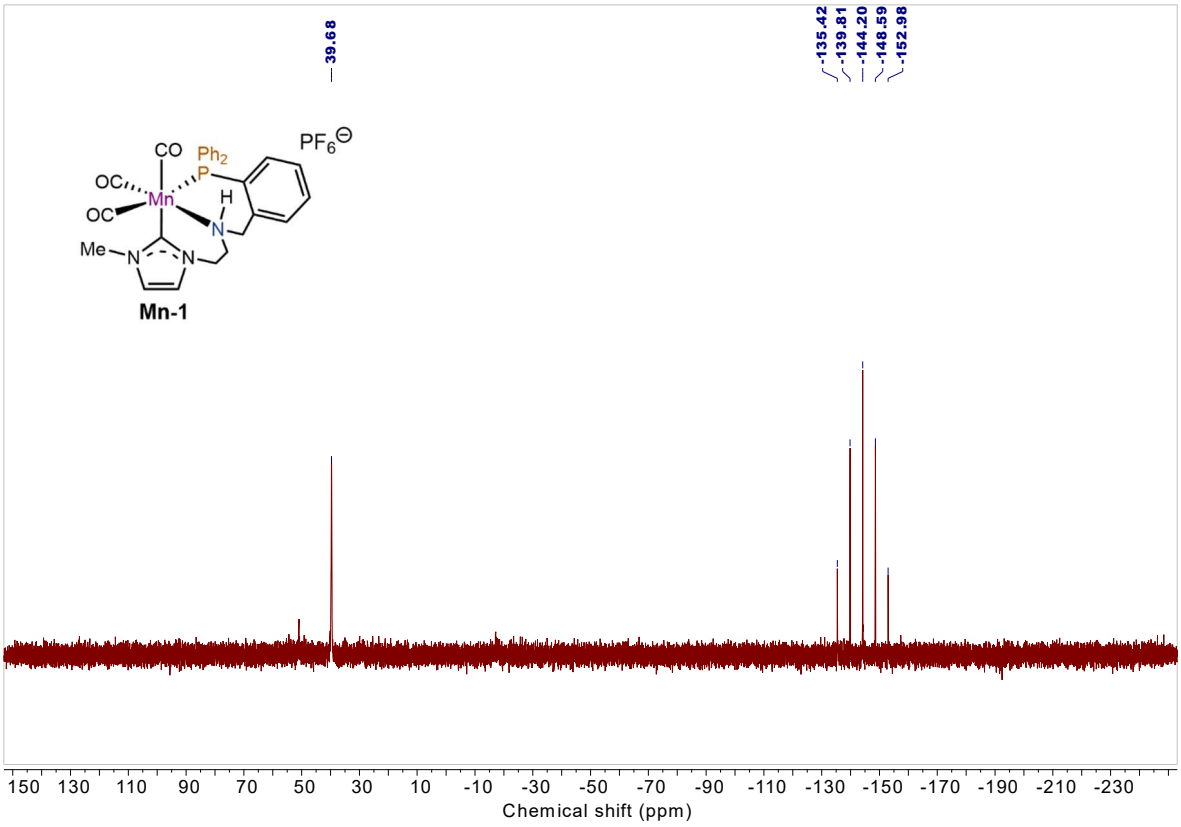


Figure S38: ^{31}P NMR spectrum of **Mn-1** (162 MHz, CD_3SOCD_3).

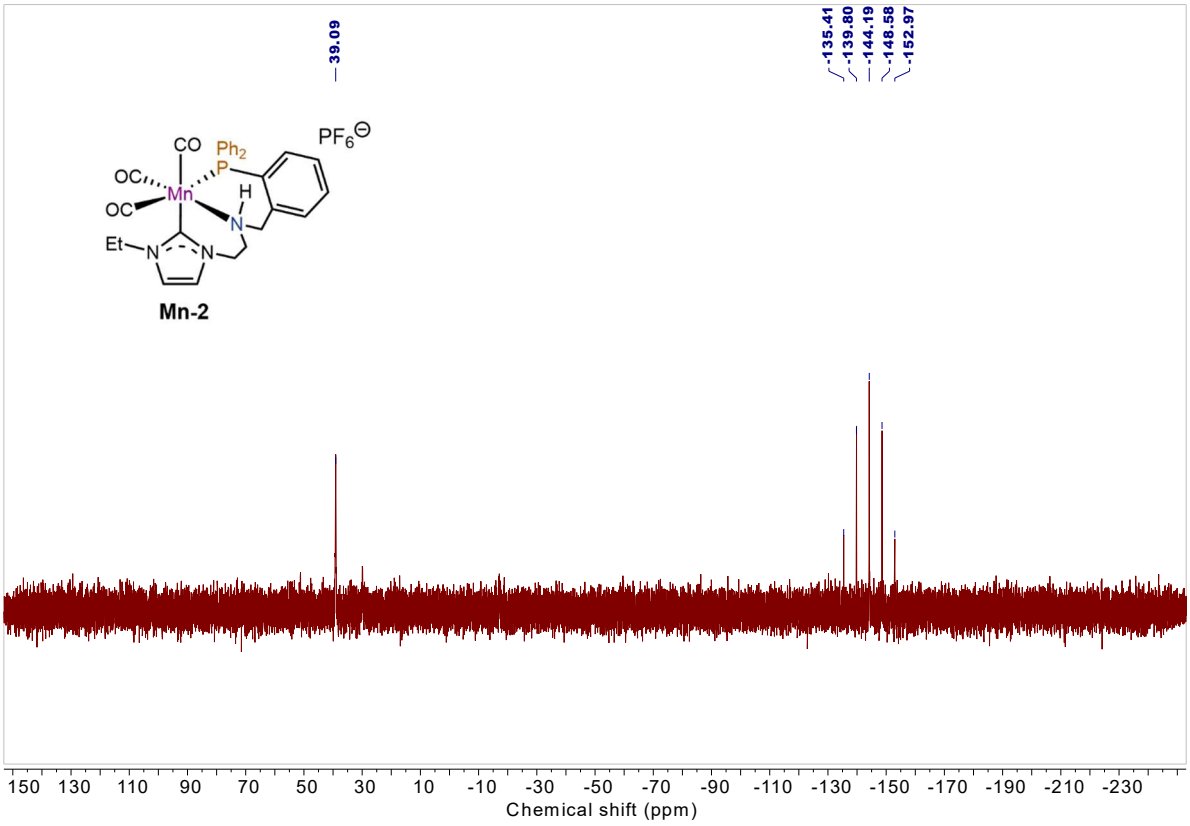


Figure S39: ^{31}P NMR spectrum of **Mn-2** (162 MHz, CD_3SOCD_3).

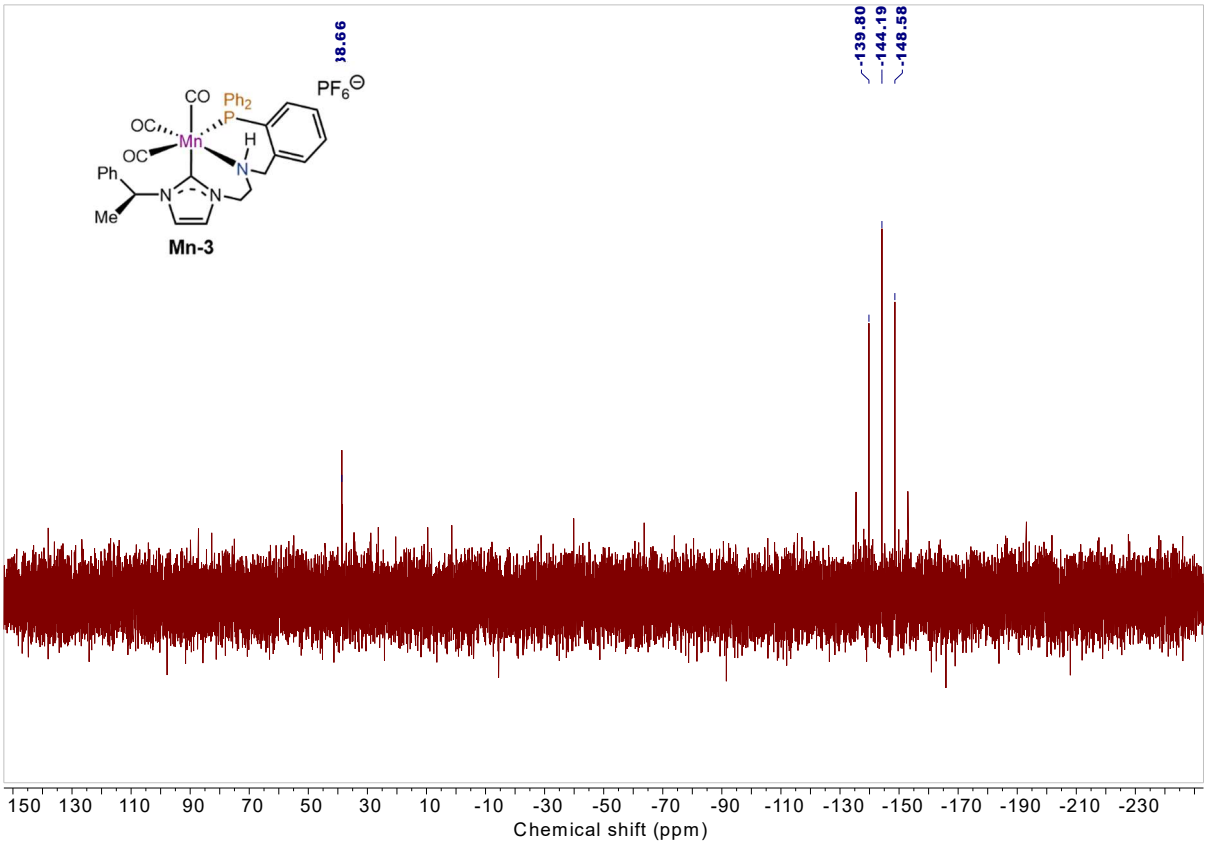


Figure S40: ^{31}P NMR spectrum of **Mn-3** (162 MHz, CD_3SOCD_3).

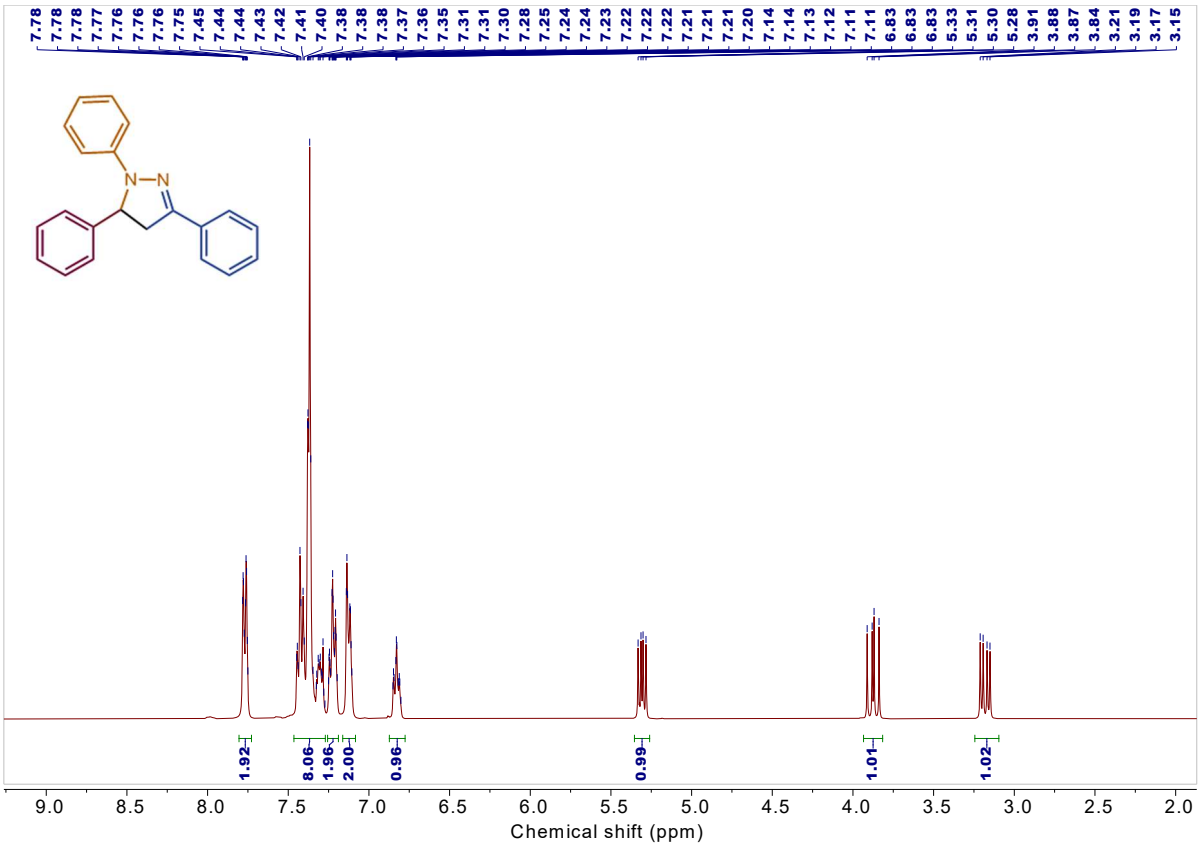


Figure S41: ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

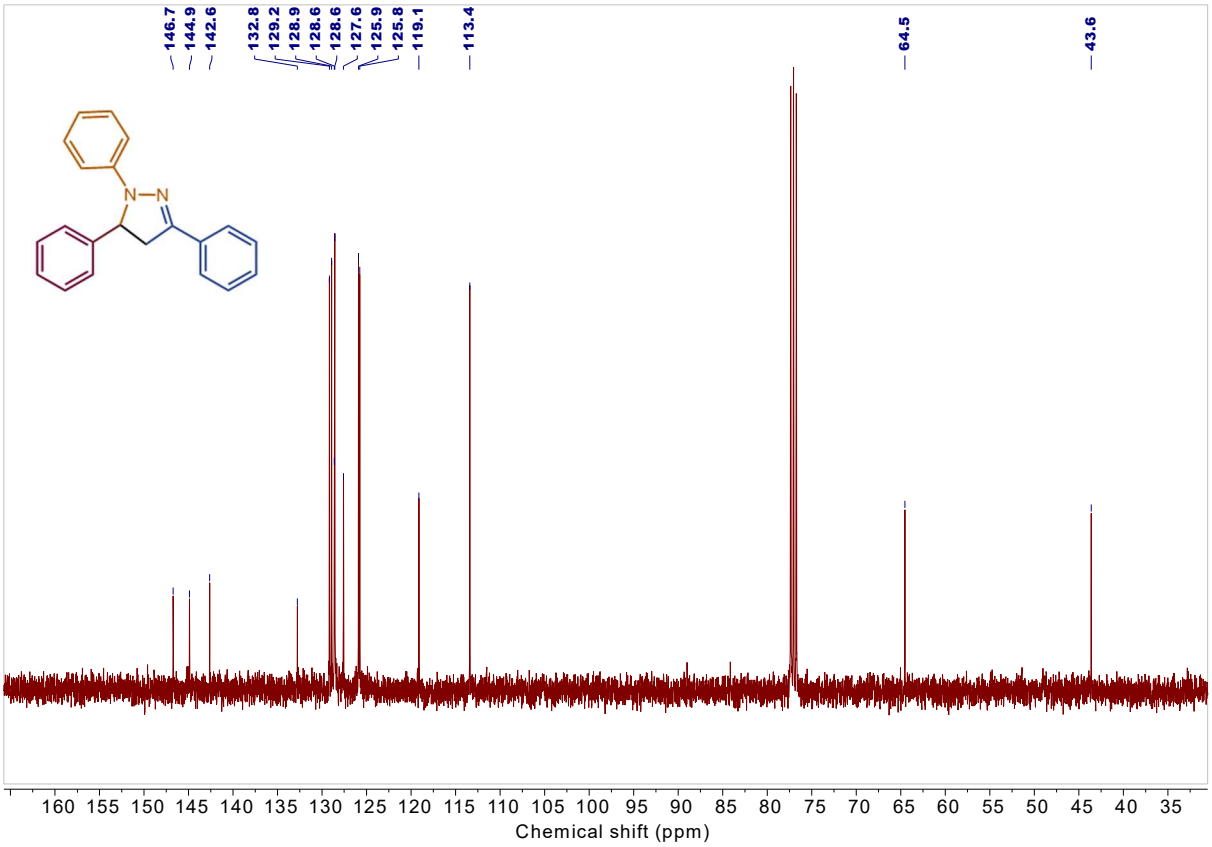


Figure S42: ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

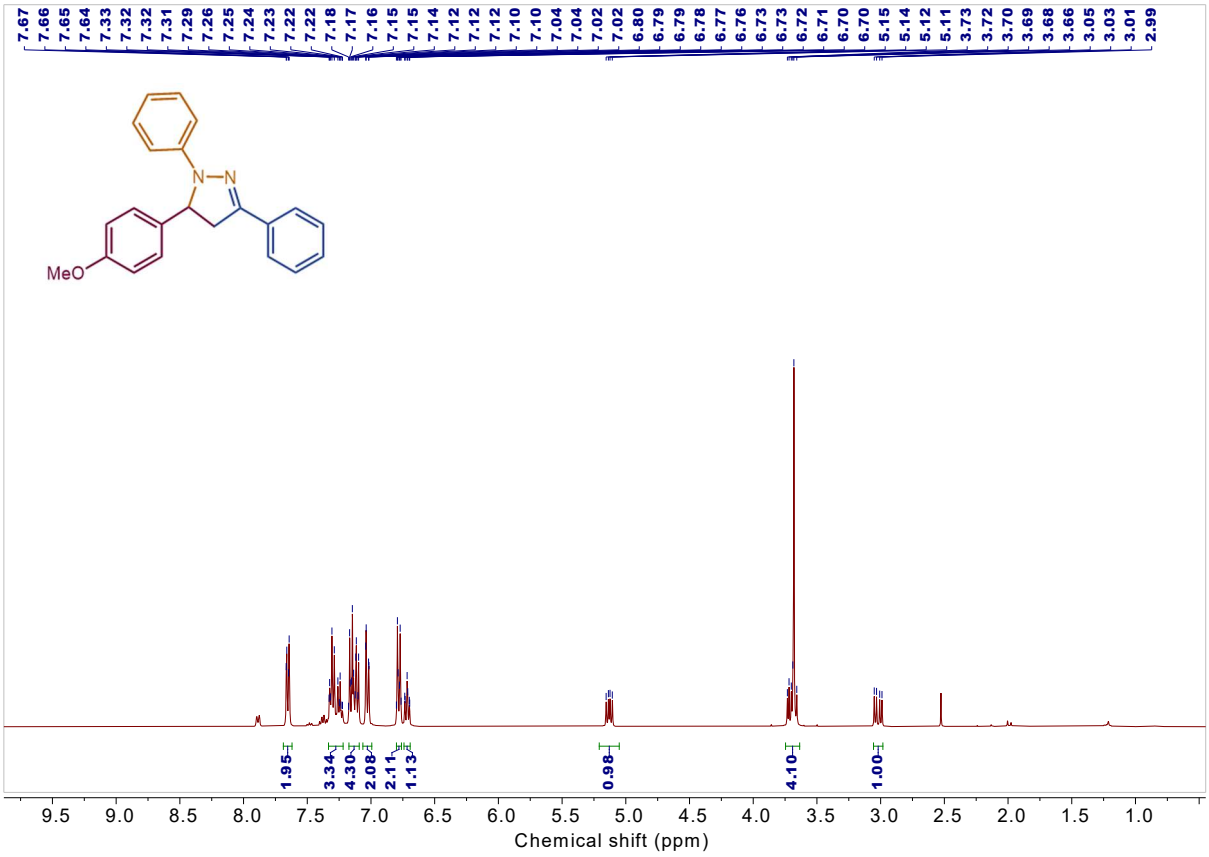


Figure S43: ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

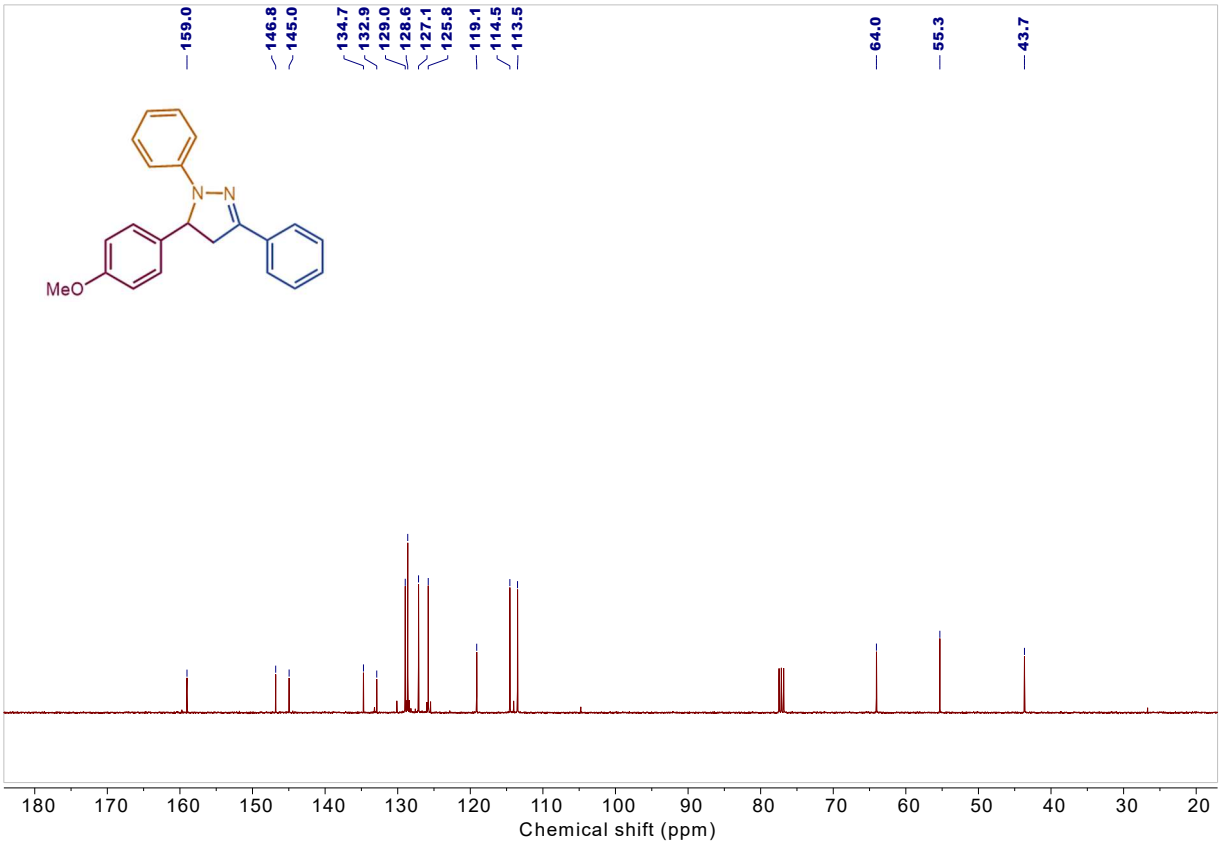


Figure S44: ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

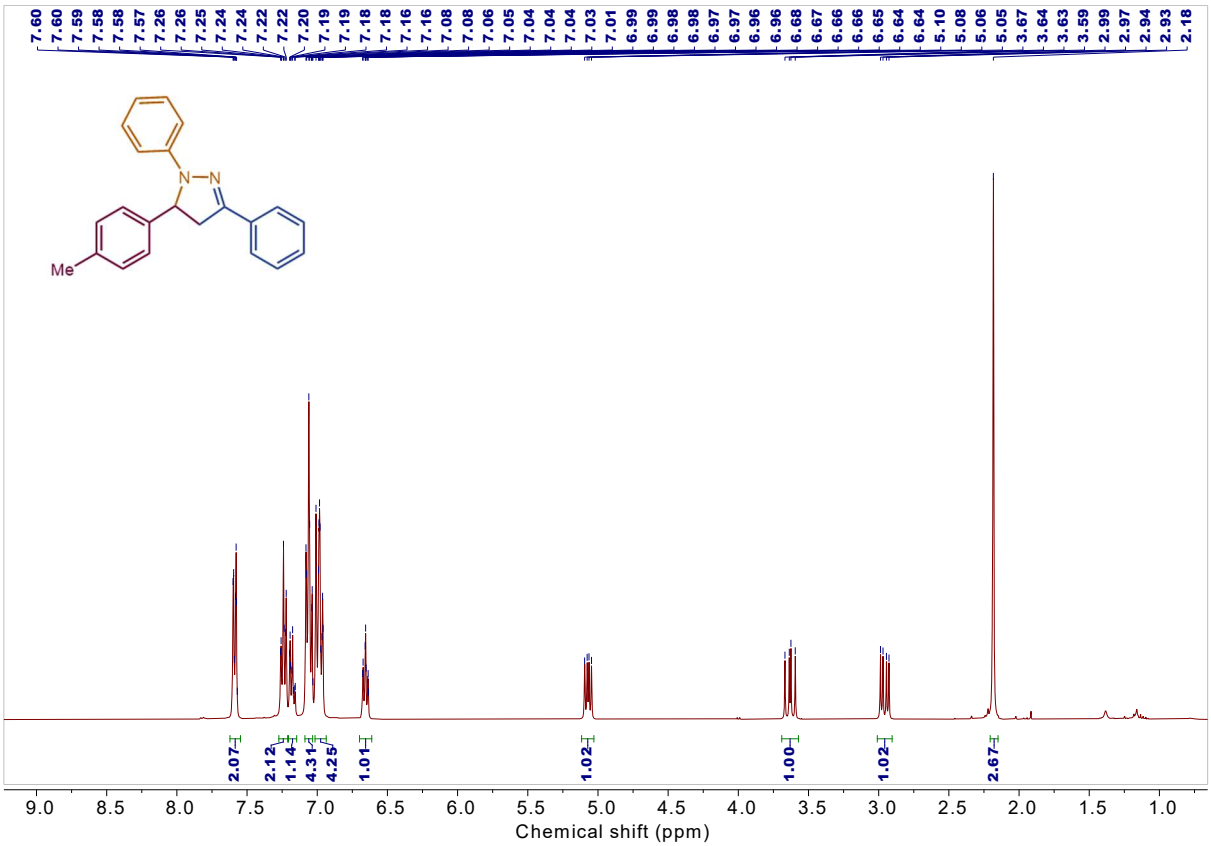


Figure S45: ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

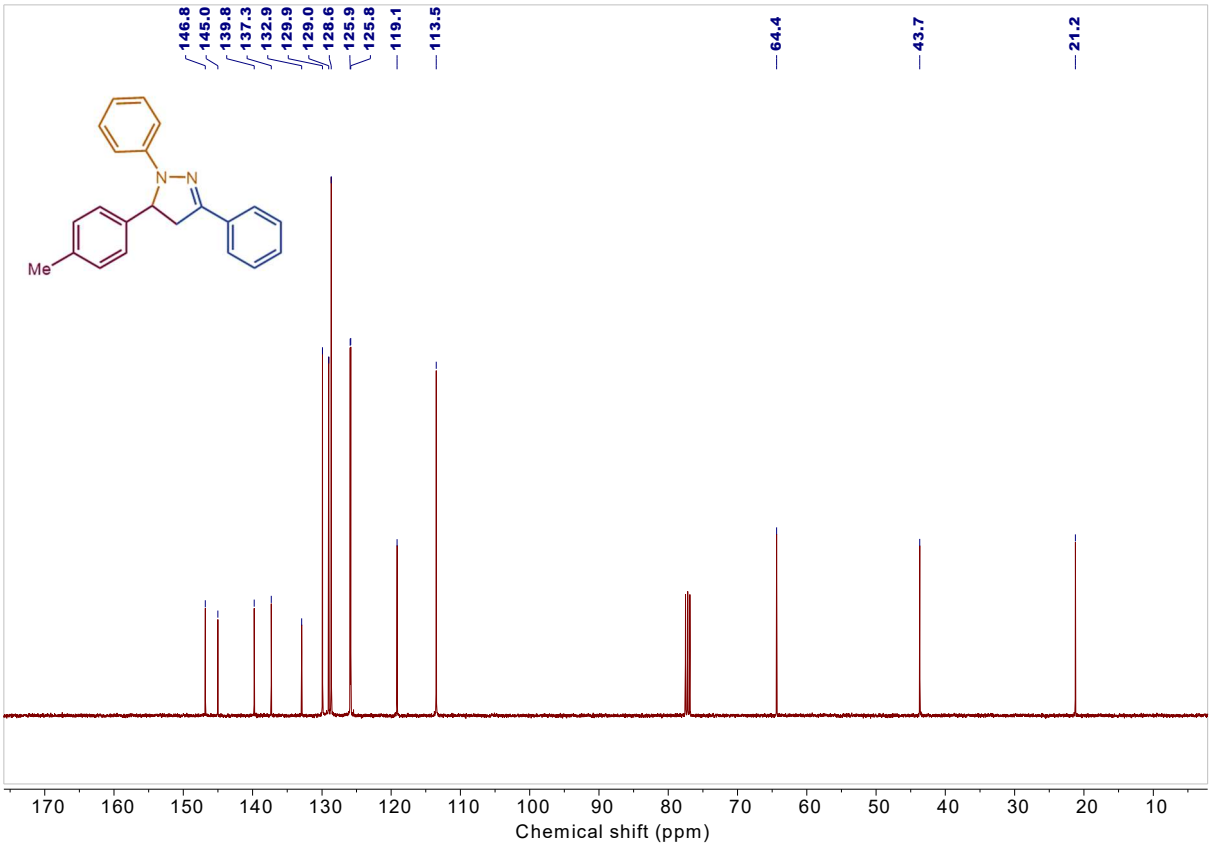


Figure S46: ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

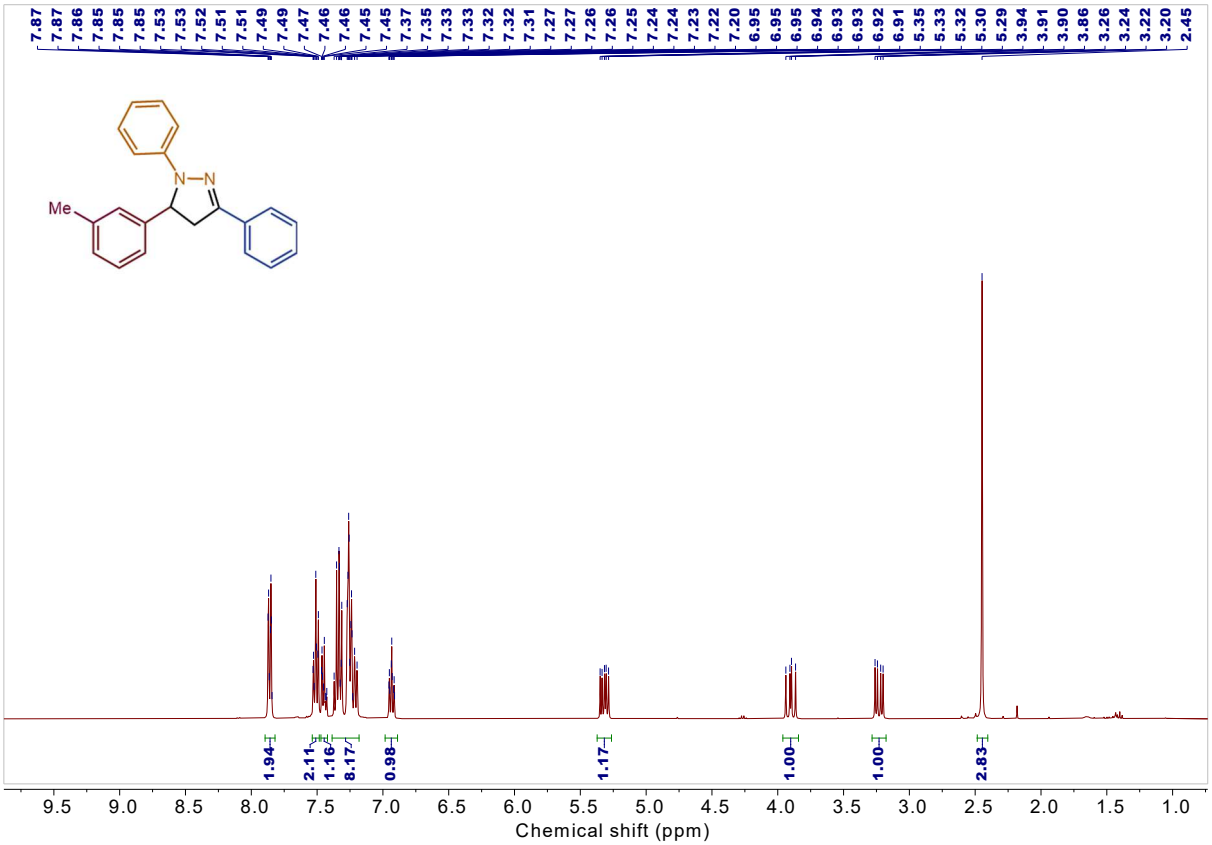


Figure S47: ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$).

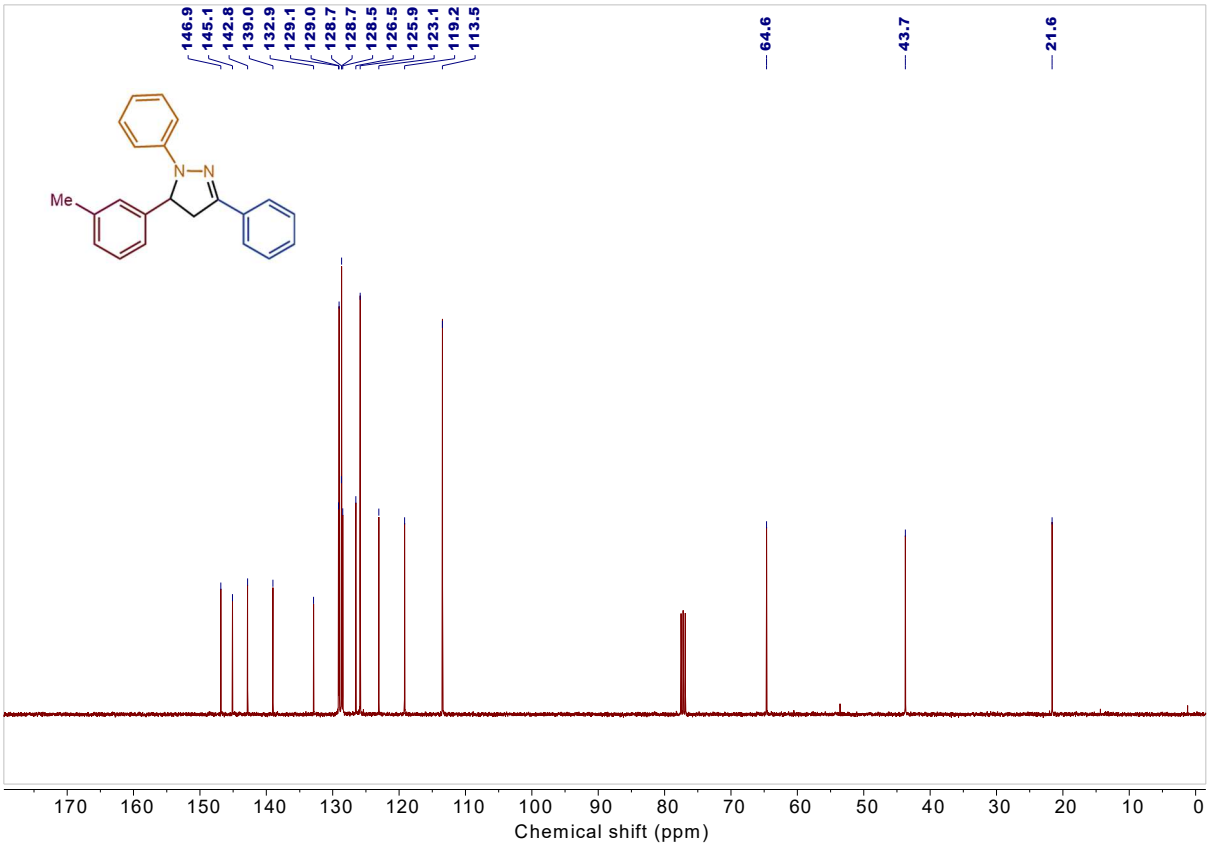


Figure S48: ^{13}C NMR spectrum of **7** (100 MHz, $CDCl_3$).

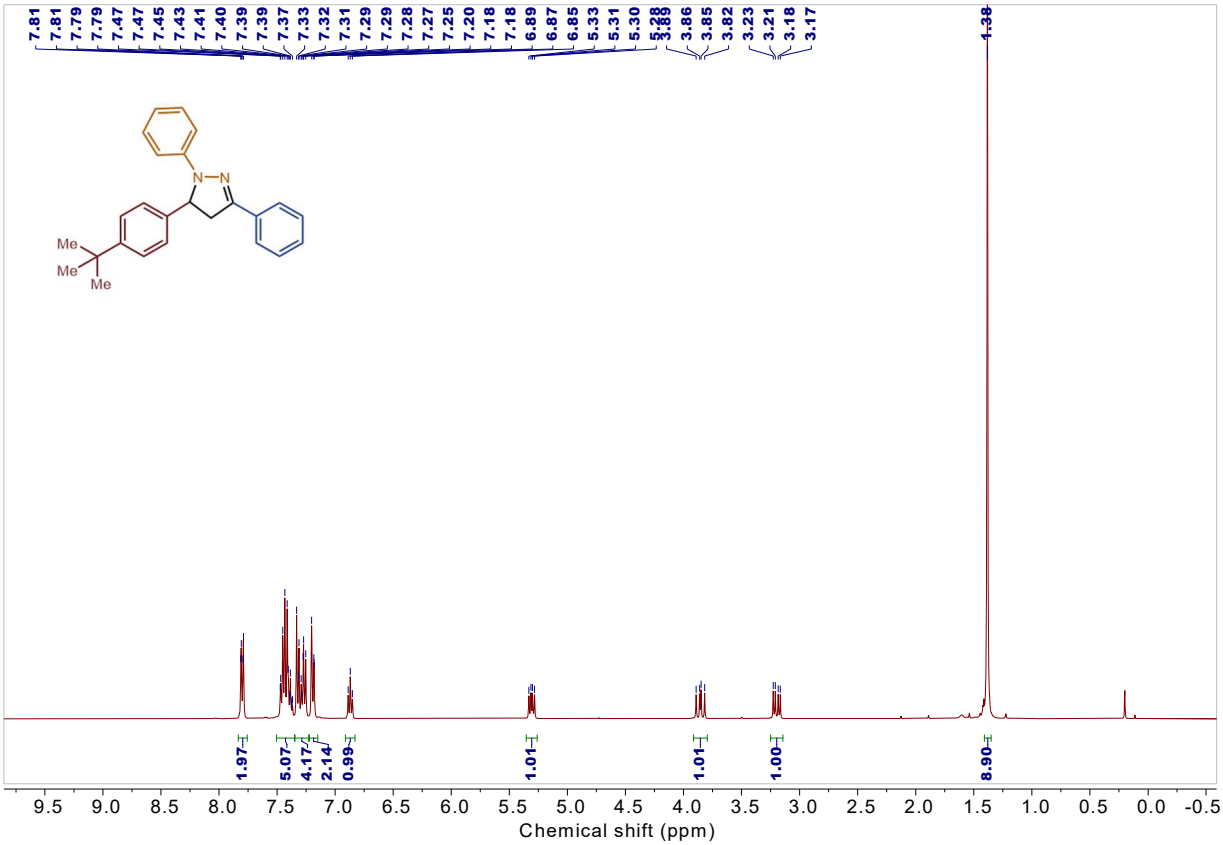


Figure S49: ^{1}H NMR spectrum of **8** (400 MHz, $CDCl_3$).

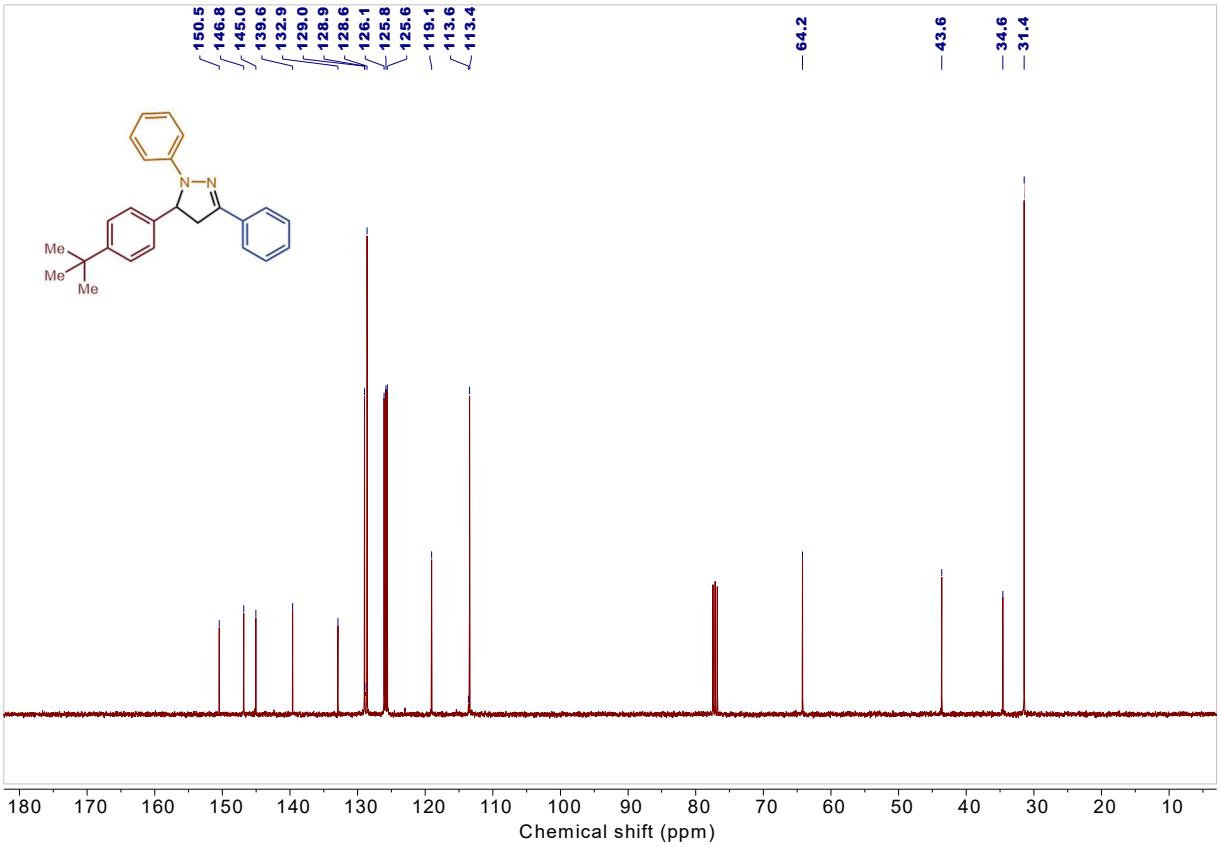


Figure S50: ^{13}C NMR spectrum of **8** (100 MHz, $CDCl_3$).

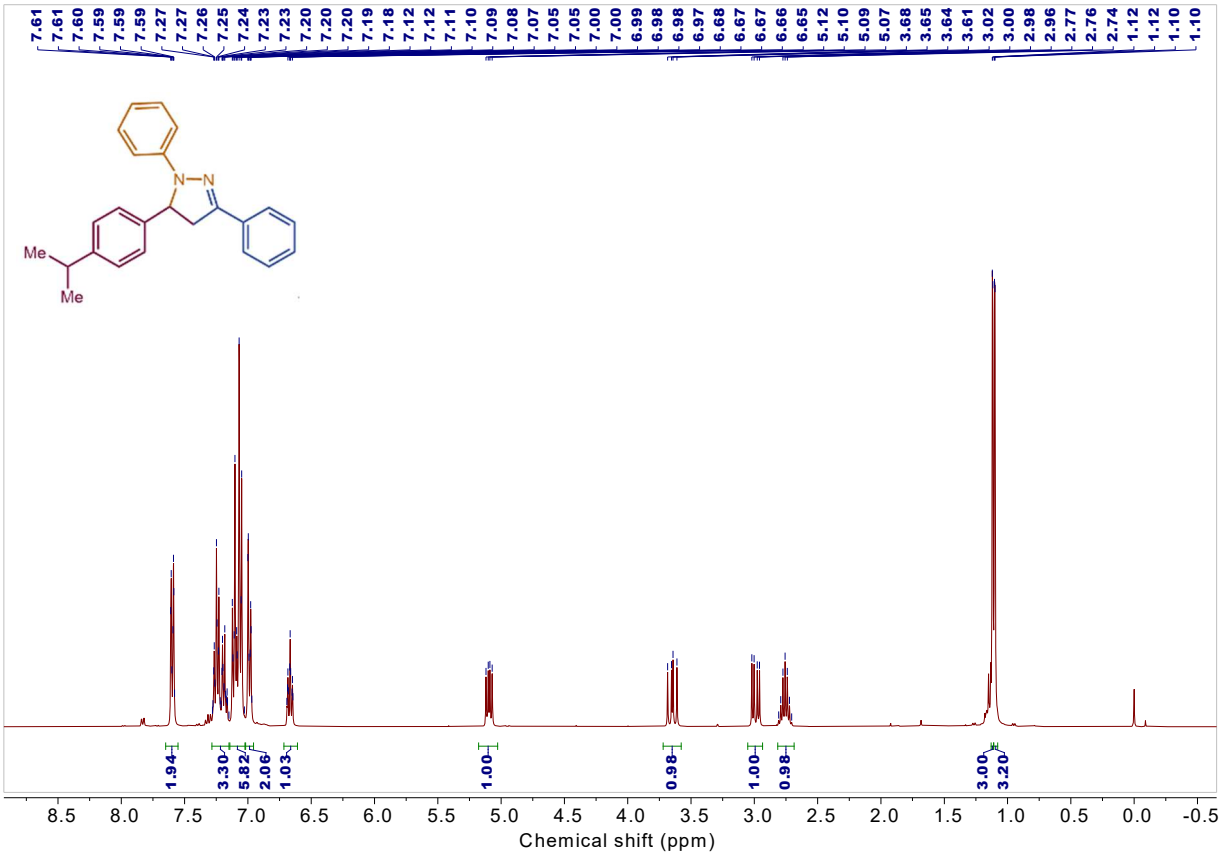


Figure S51: ^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$).

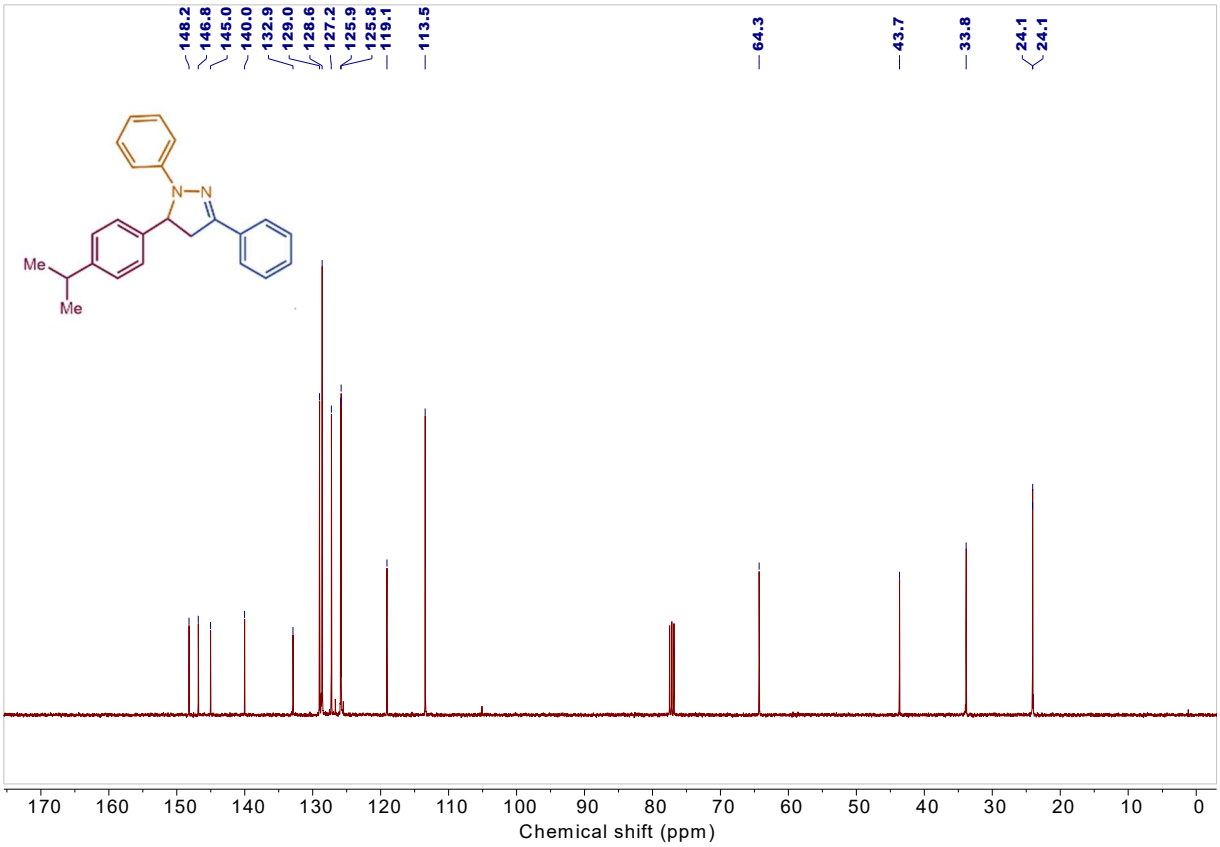


Figure S52: ^{13}C NMR spectrum of **9** (100 MHz, $CDCl_3$).

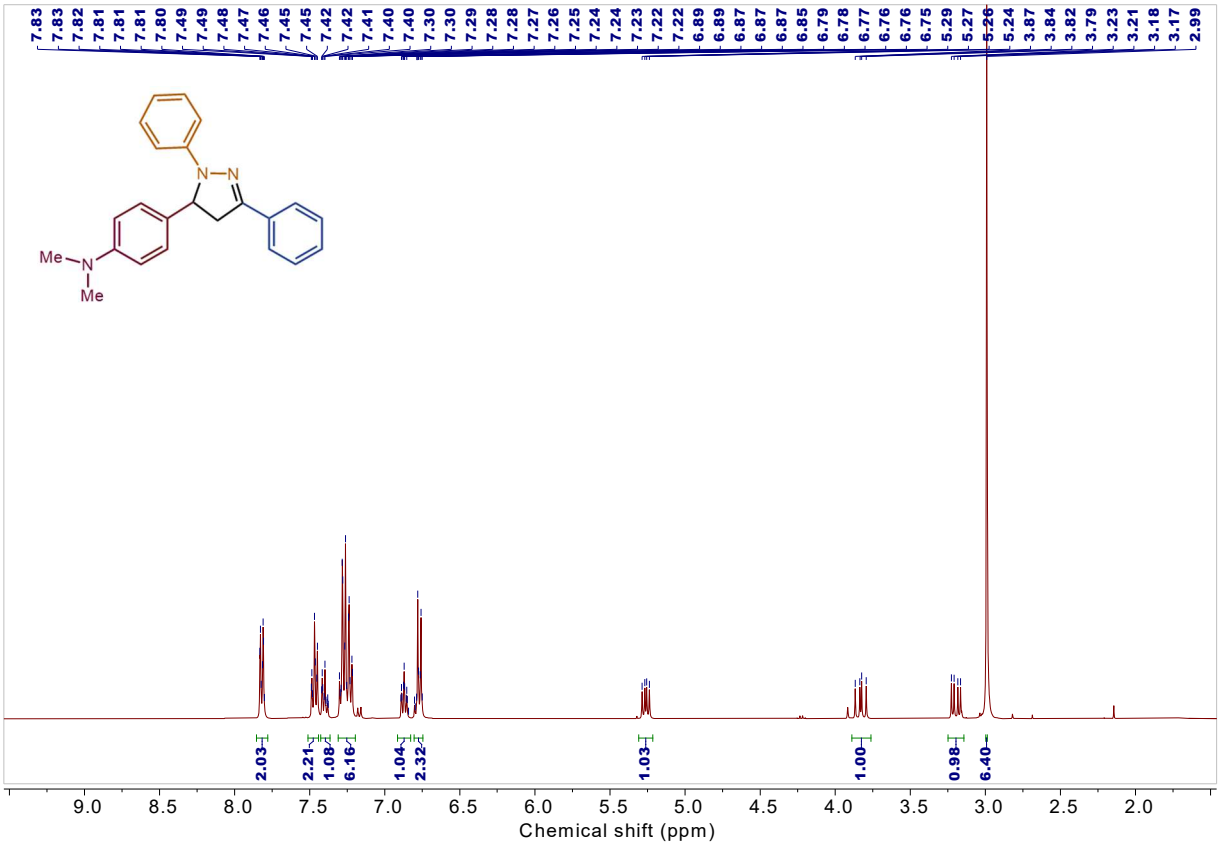


Figure S53: ^{1}H NMR spectrum of **10** (400 MHz, $CDCl_3$).

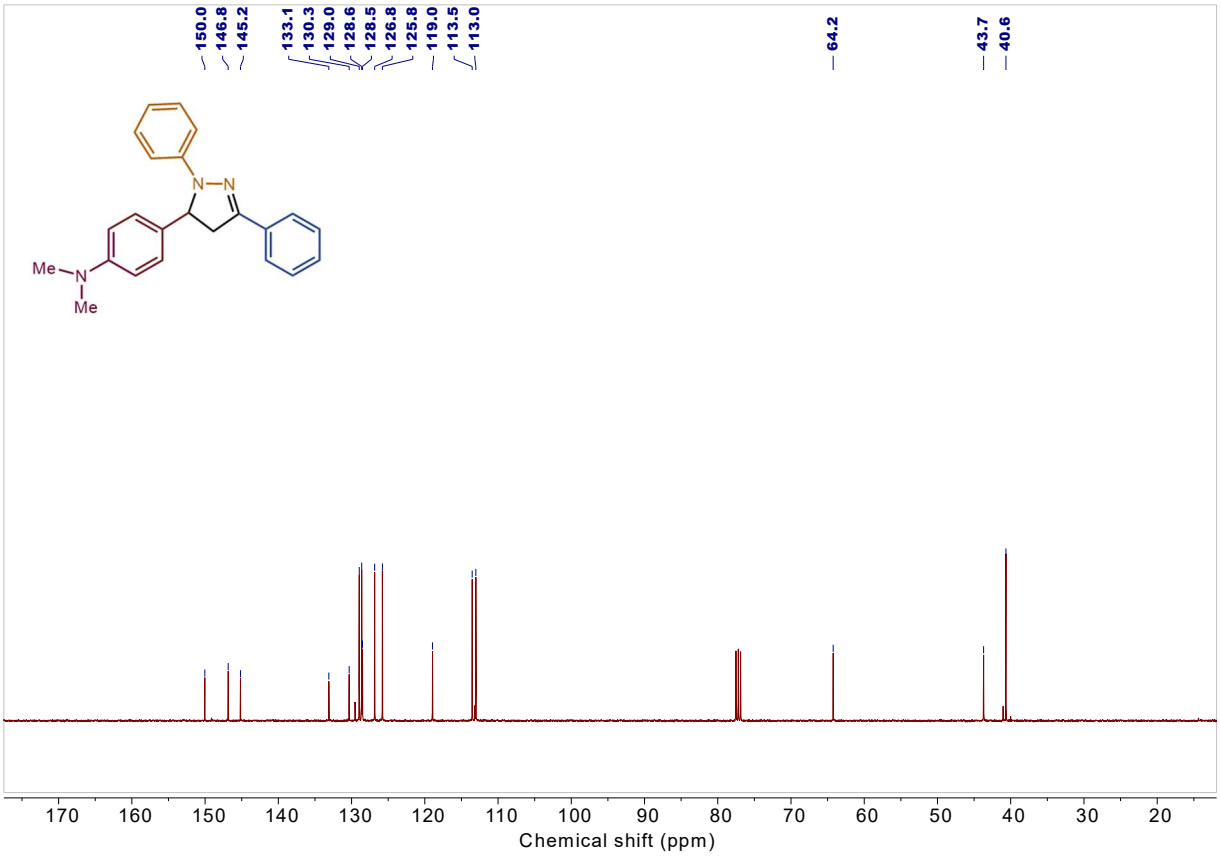


Figure S54: ^{13}C NMR spectrum of **10** (100 MHz, $CDCl_3$).

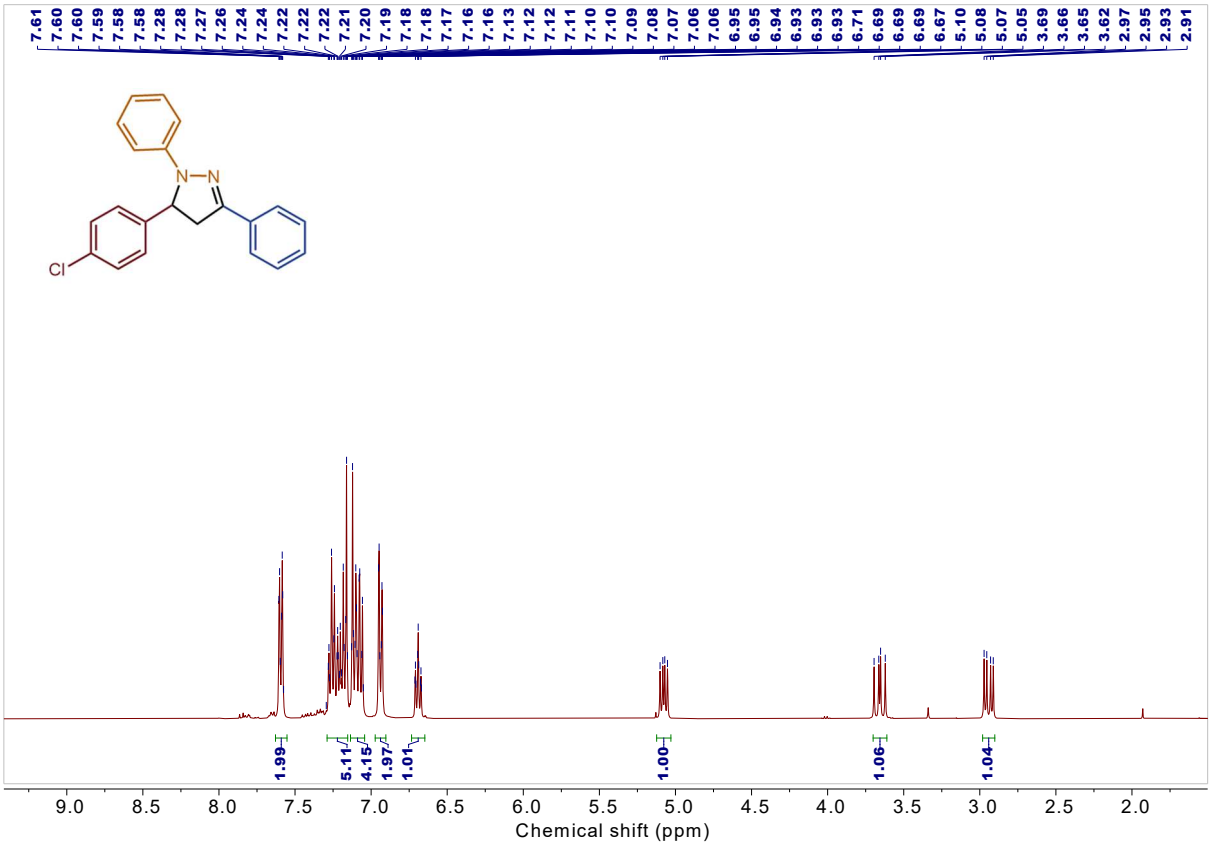


Figure S55: ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$).

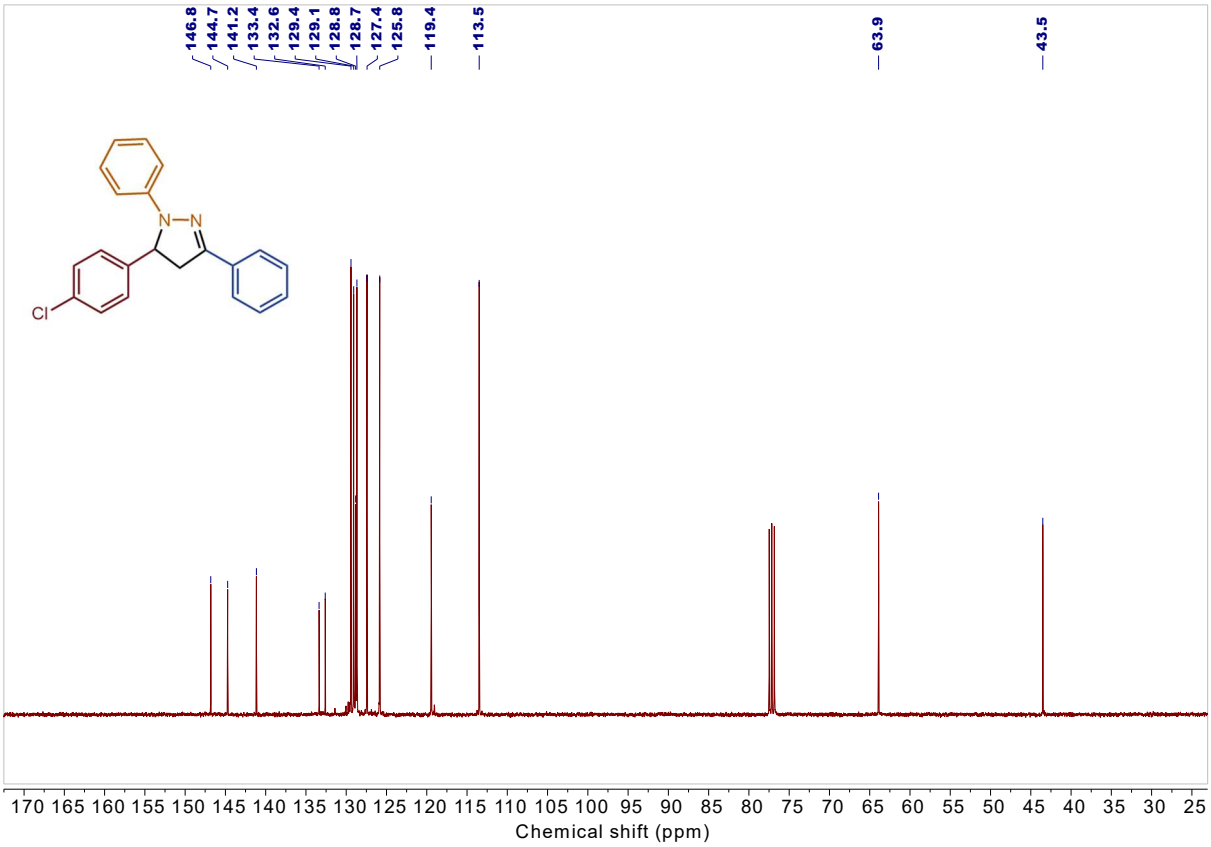


Figure S56: ^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$).

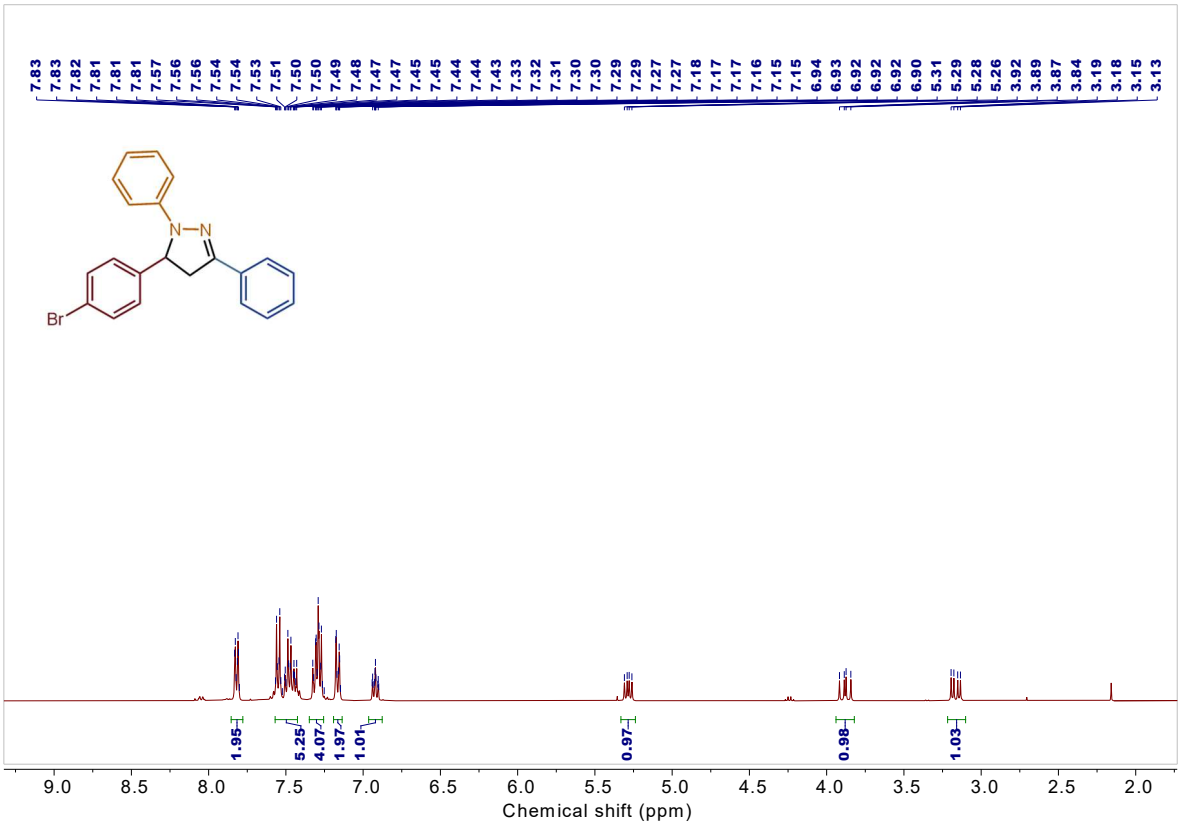


Figure S57: ^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$).

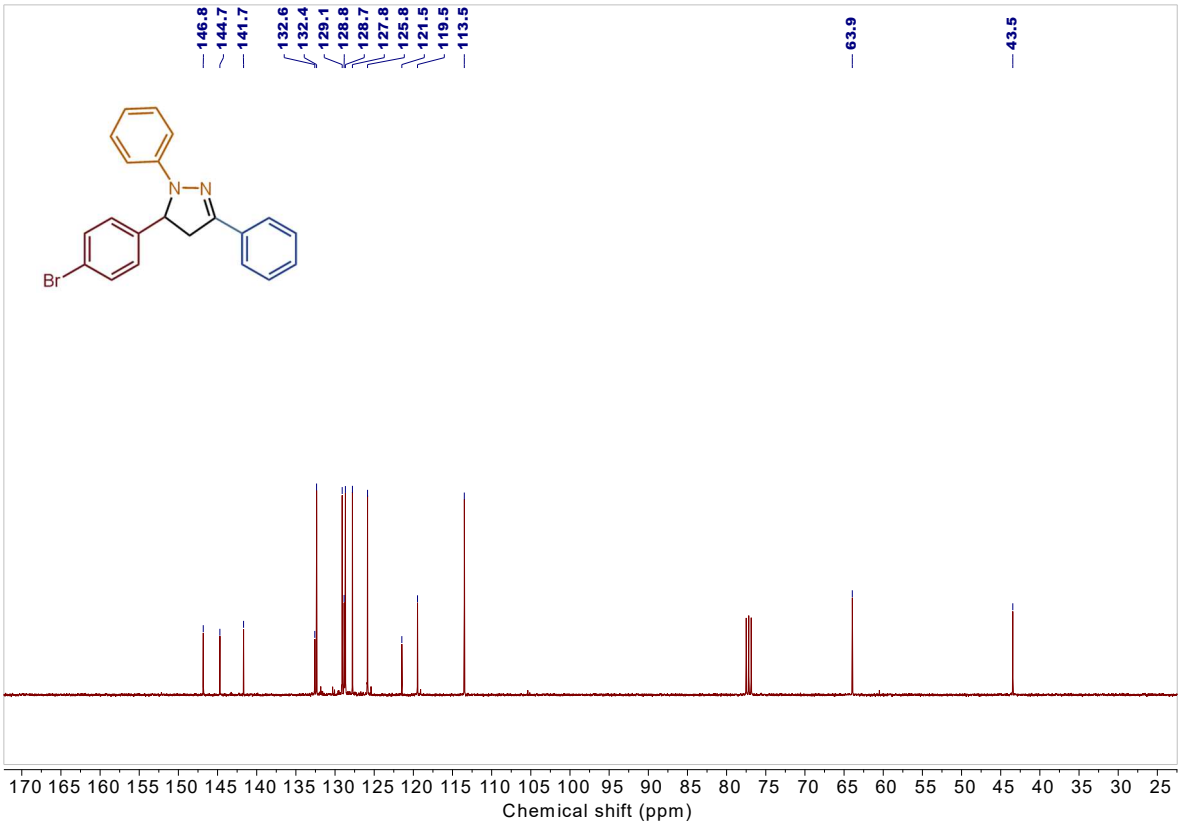


Figure S58: ^{13}C NMR spectrum of **12** (100 MHz, $CDCl_3$).

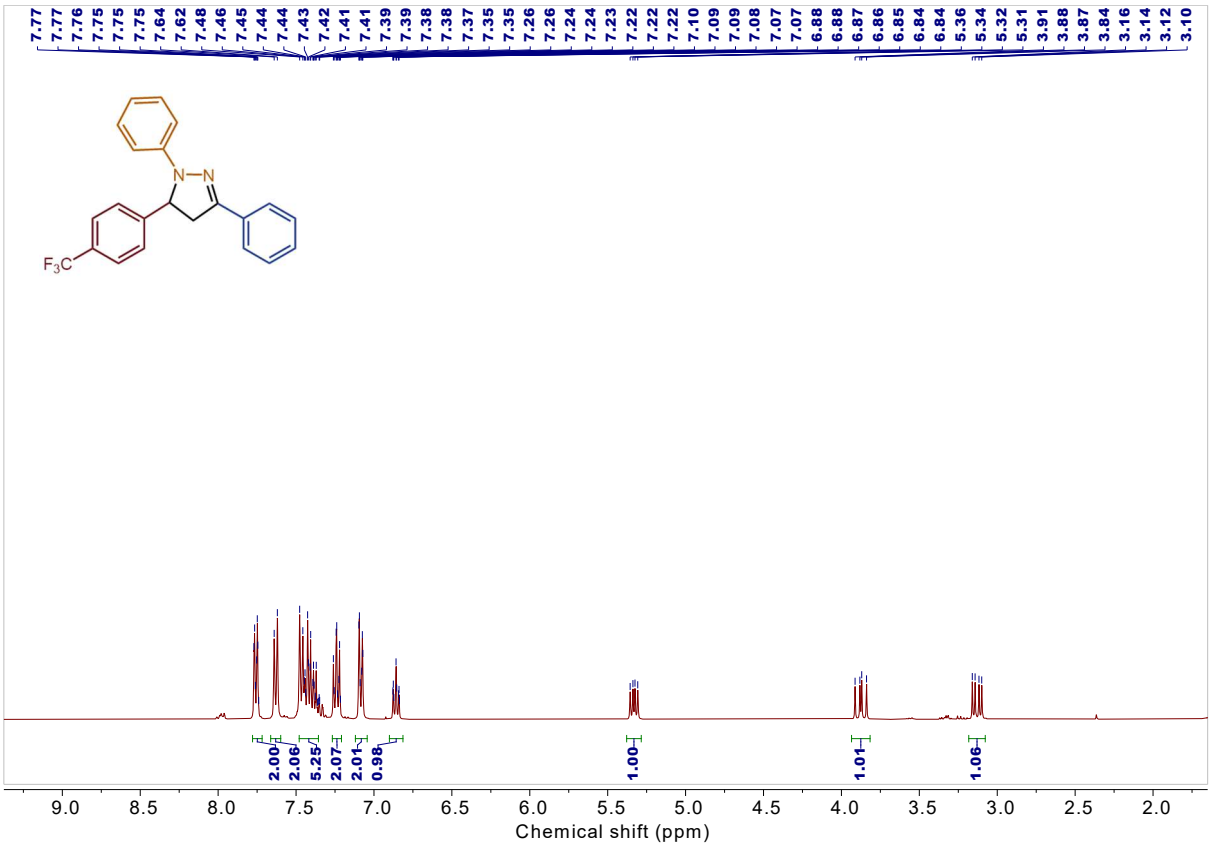


Figure S59: ^{1}H NMR spectrum of **13** (400 MHz, $CDCl_3$).

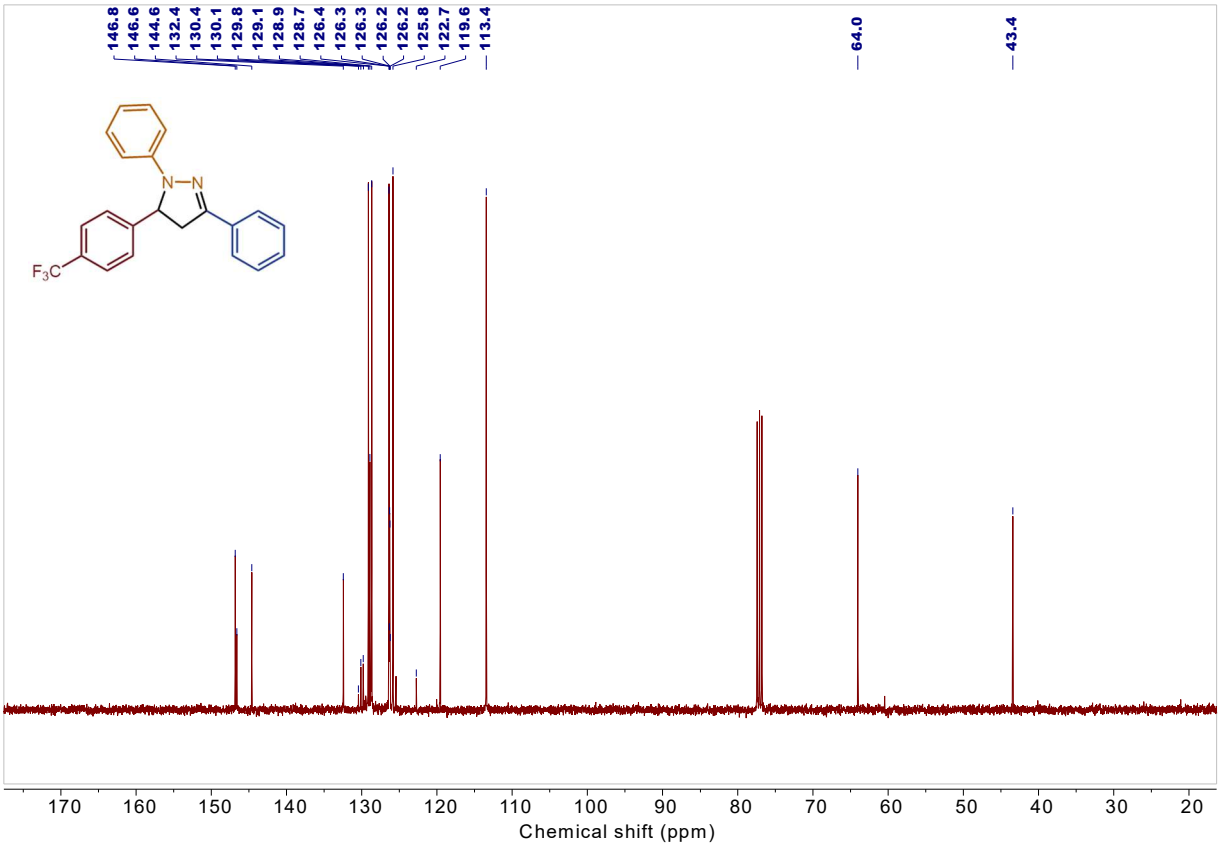


Figure S60: ^{13}C NMR spectrum of **13** (100 MHz, $CDCl_3$).

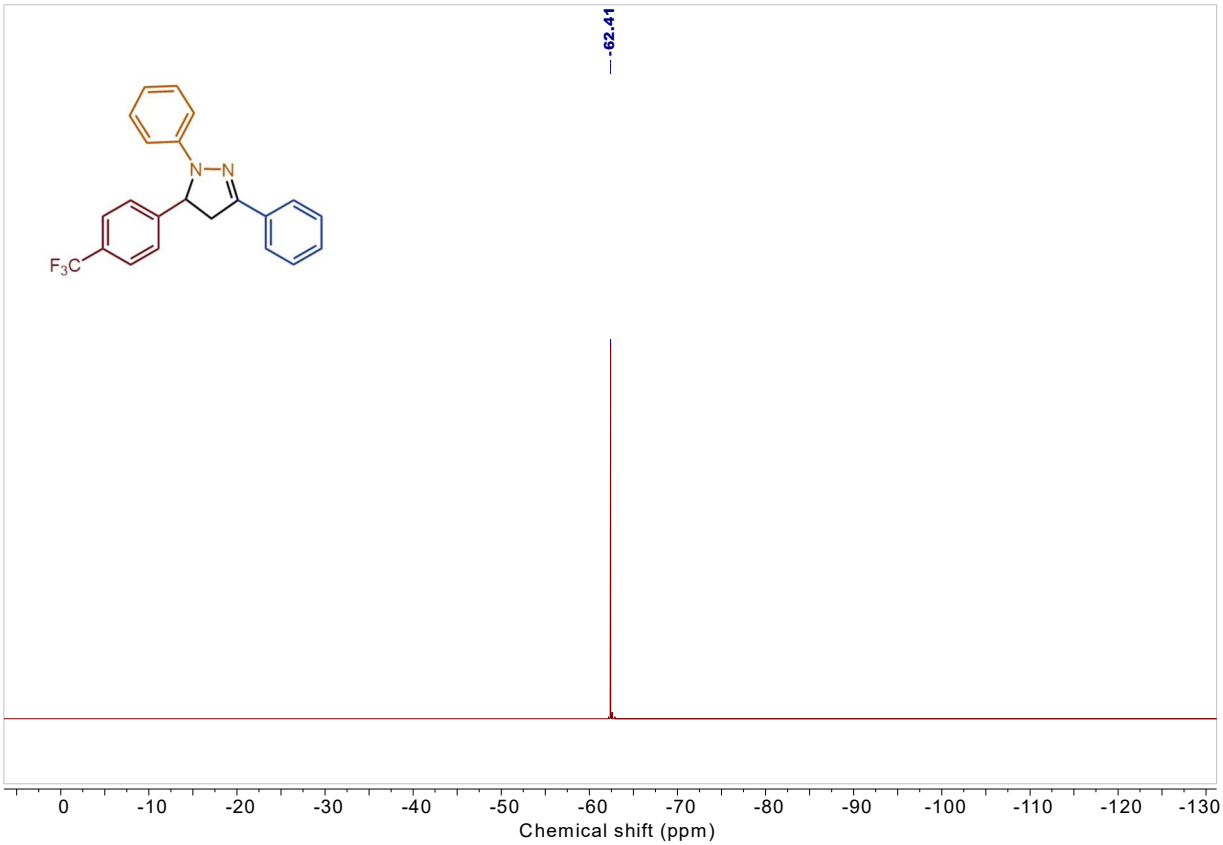


Figure S61: ^{19}F NMR spectrum of **13** (376 MHz, $CDCl_3$).

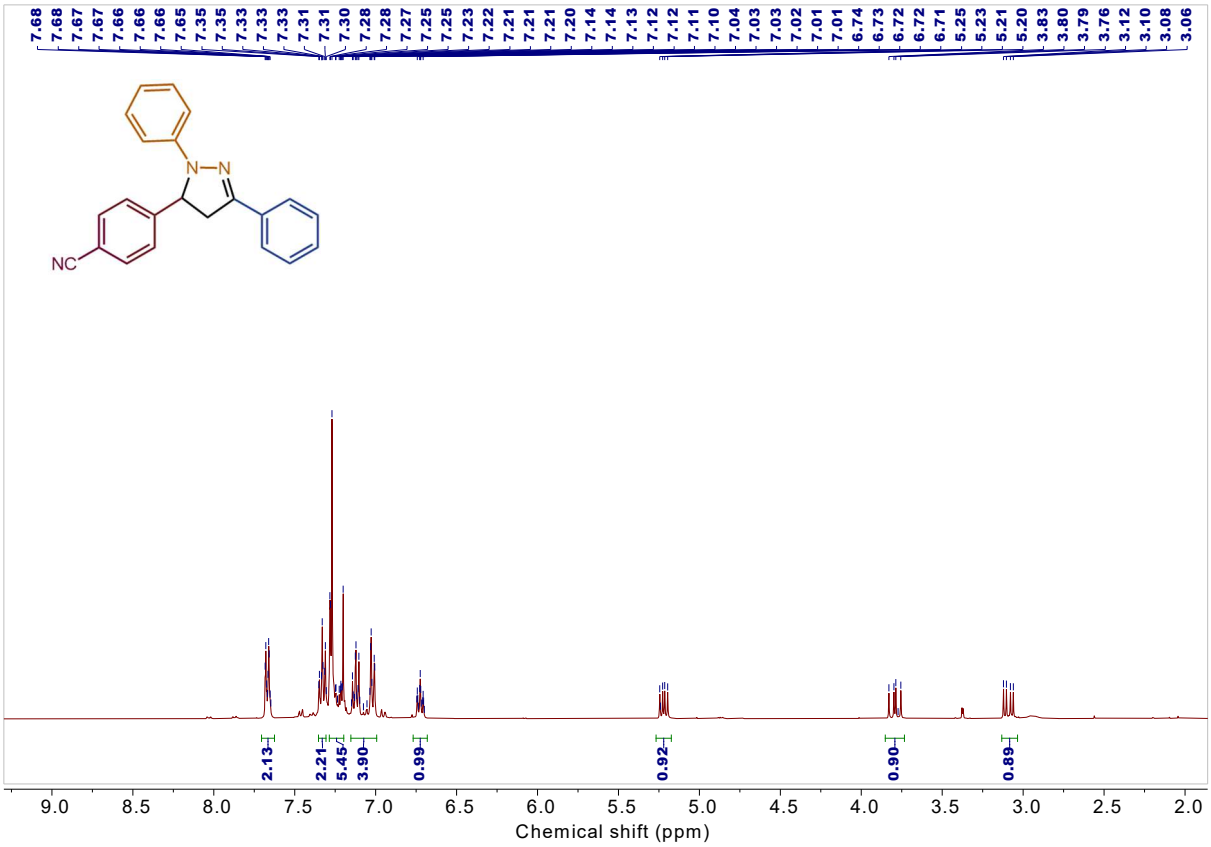


Figure S62: ^{1}H NMR spectrum of **14** (400 MHz, $CDCl_3$).

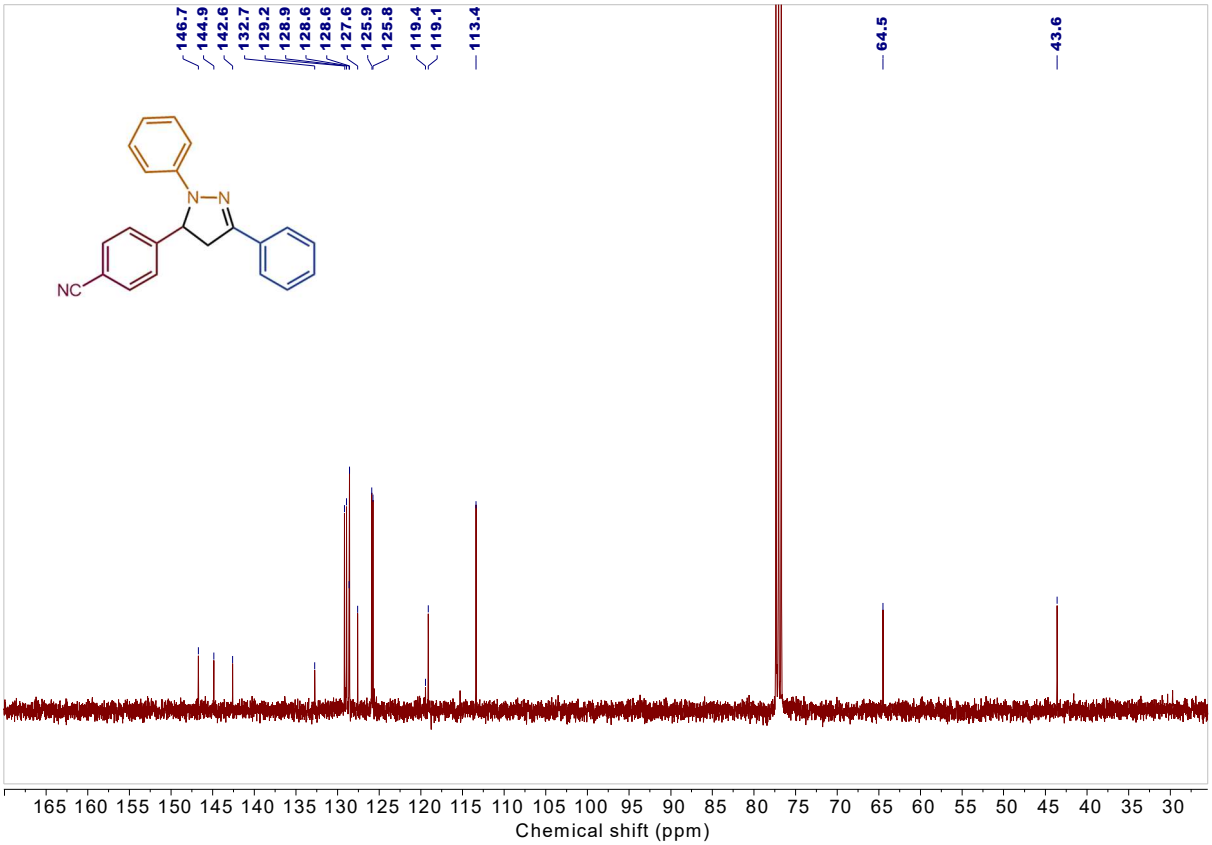


Figure S63: ^{13}C NMR spectrum of **14** (100 MHz, $CDCl_3$).

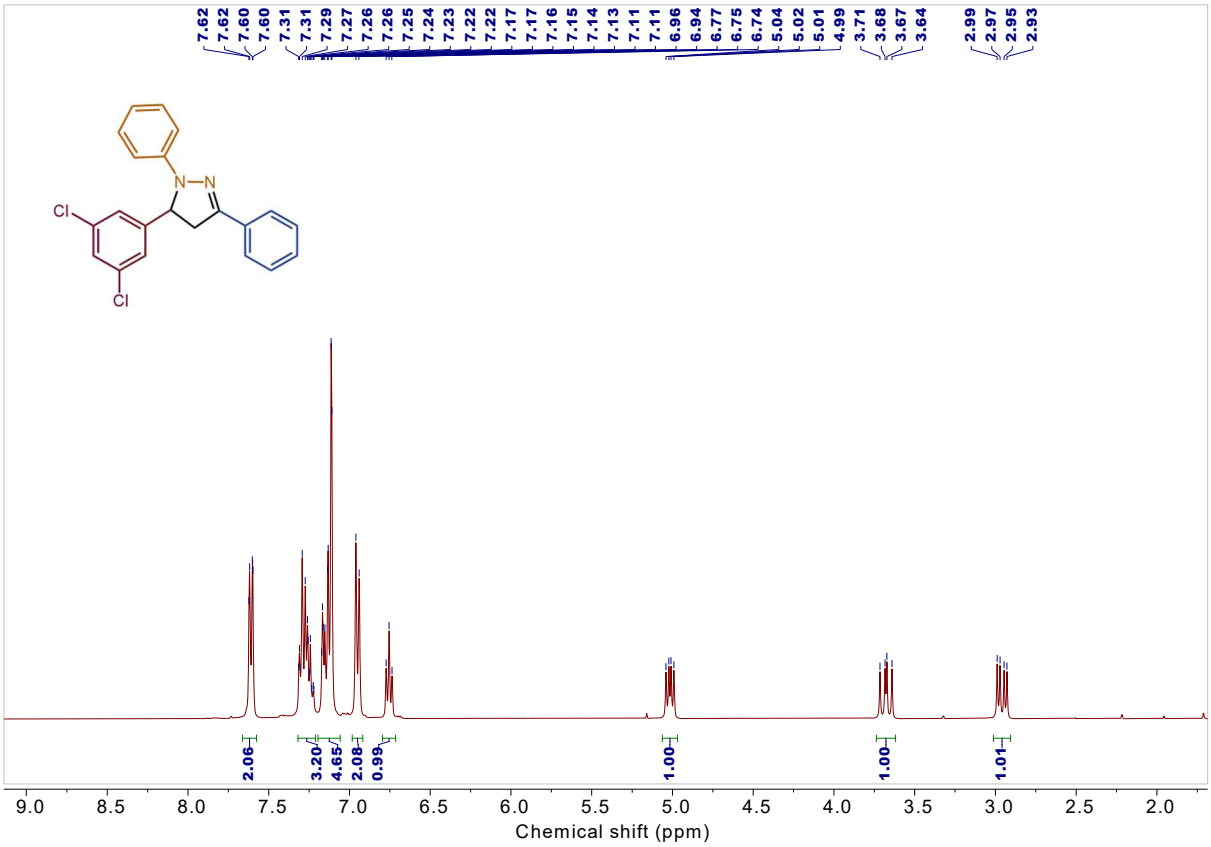


Figure S64: ^{1}H NMR spectrum of **15** (400 MHz, $CDCl_3$).

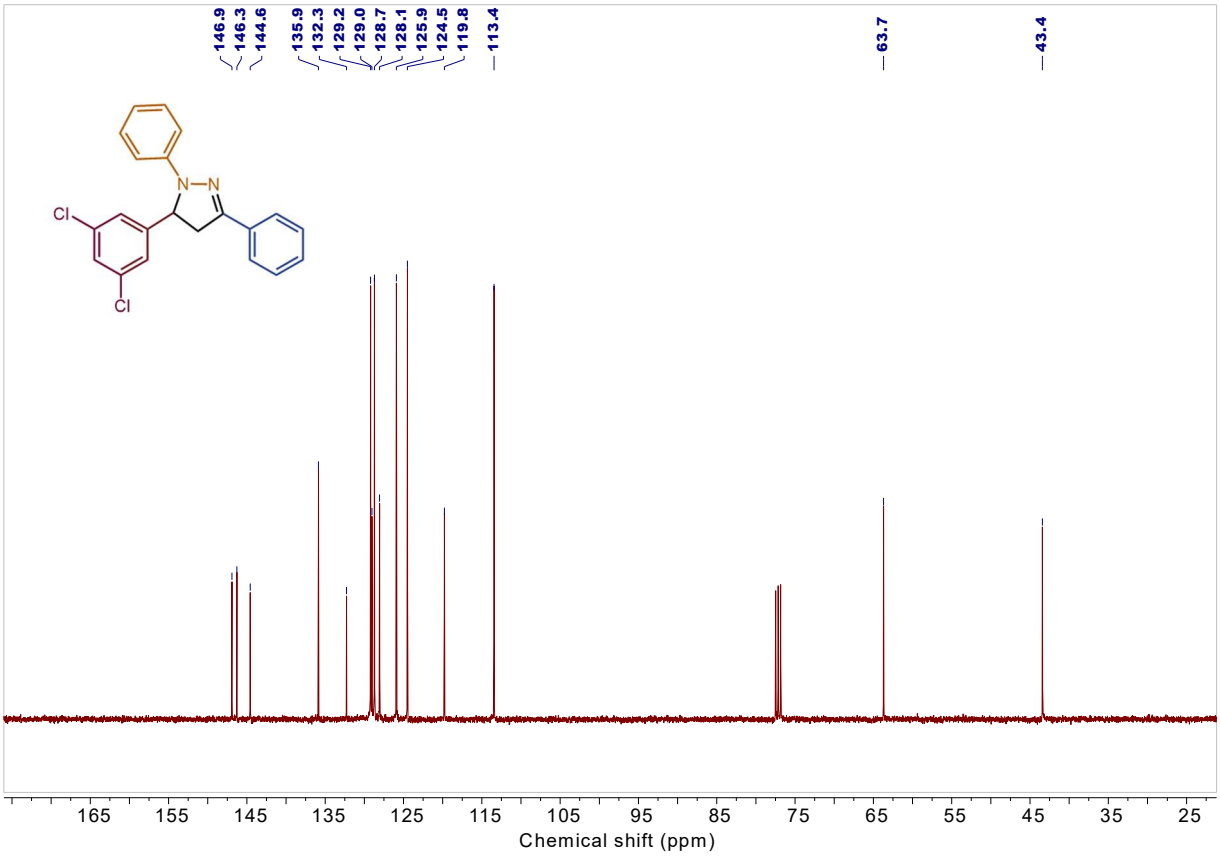


Figure S65: ^{13}C NMR spectrum of **15** (100 MHz, $CDCl_3$).

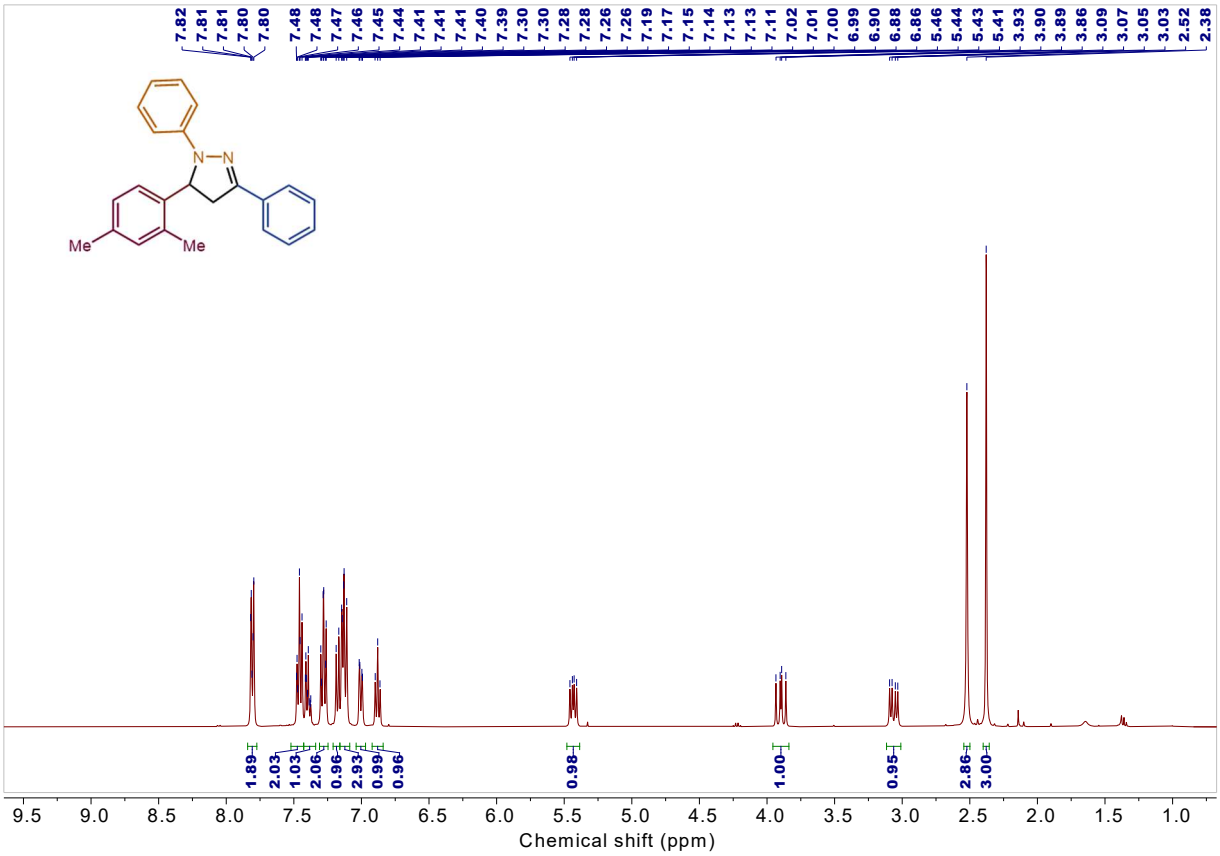


Figure S66: ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$).

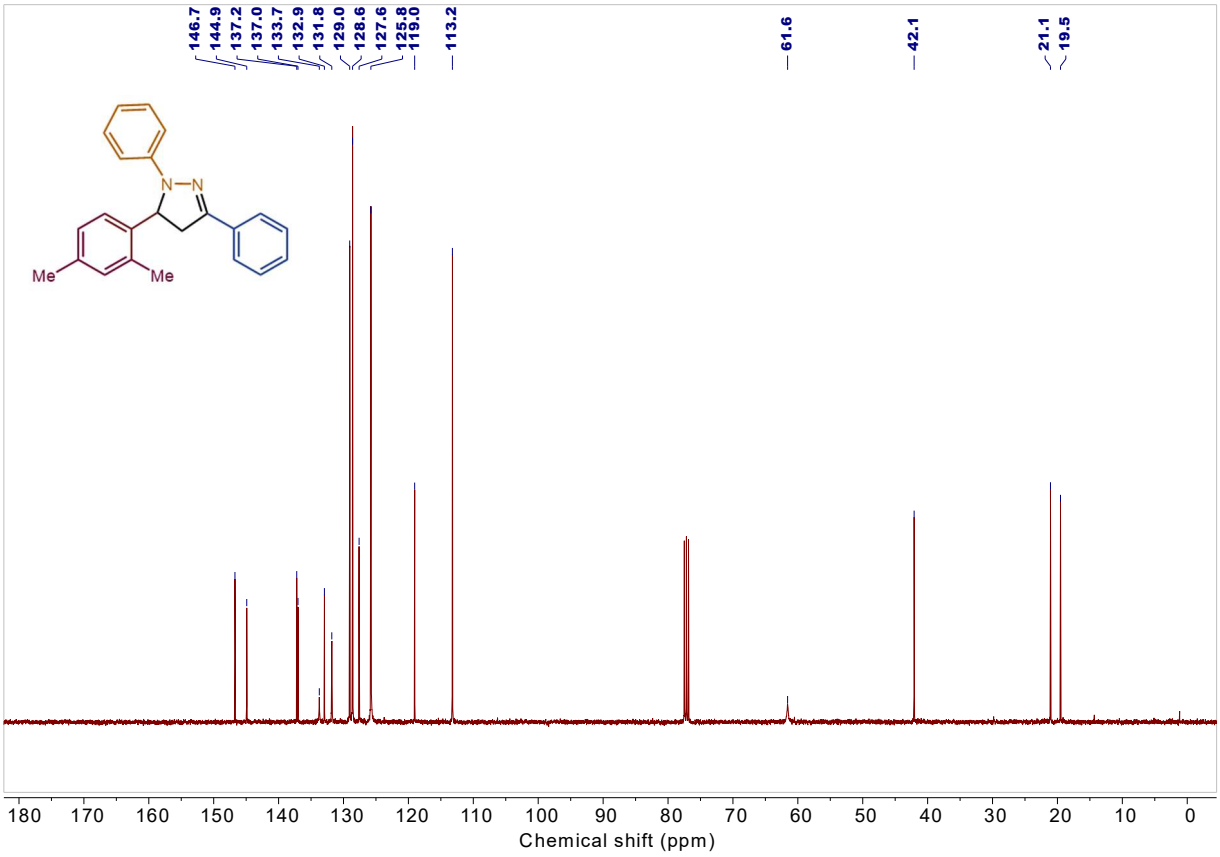


Figure S67: ^{13}C NMR spectrum of **16** (100 MHz, $CDCl_3$).

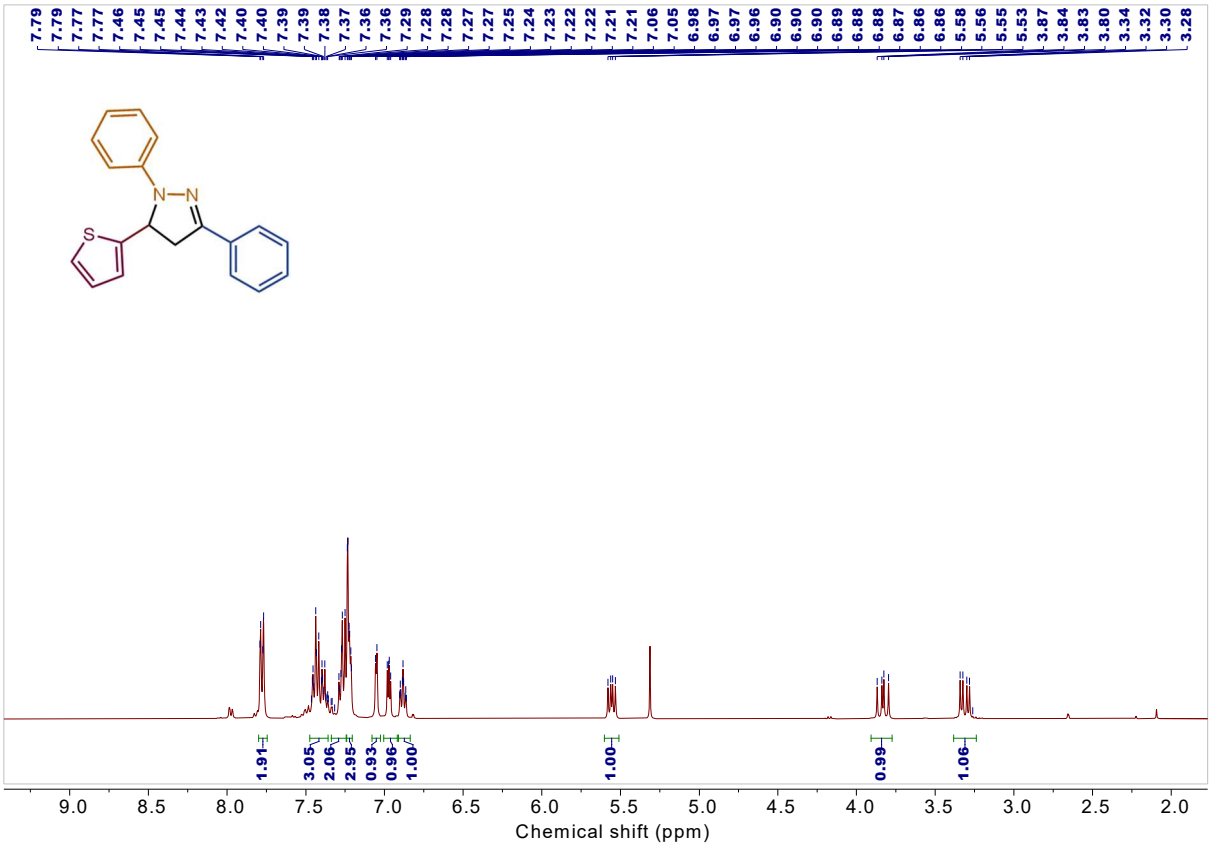


Figure S68: ^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$).

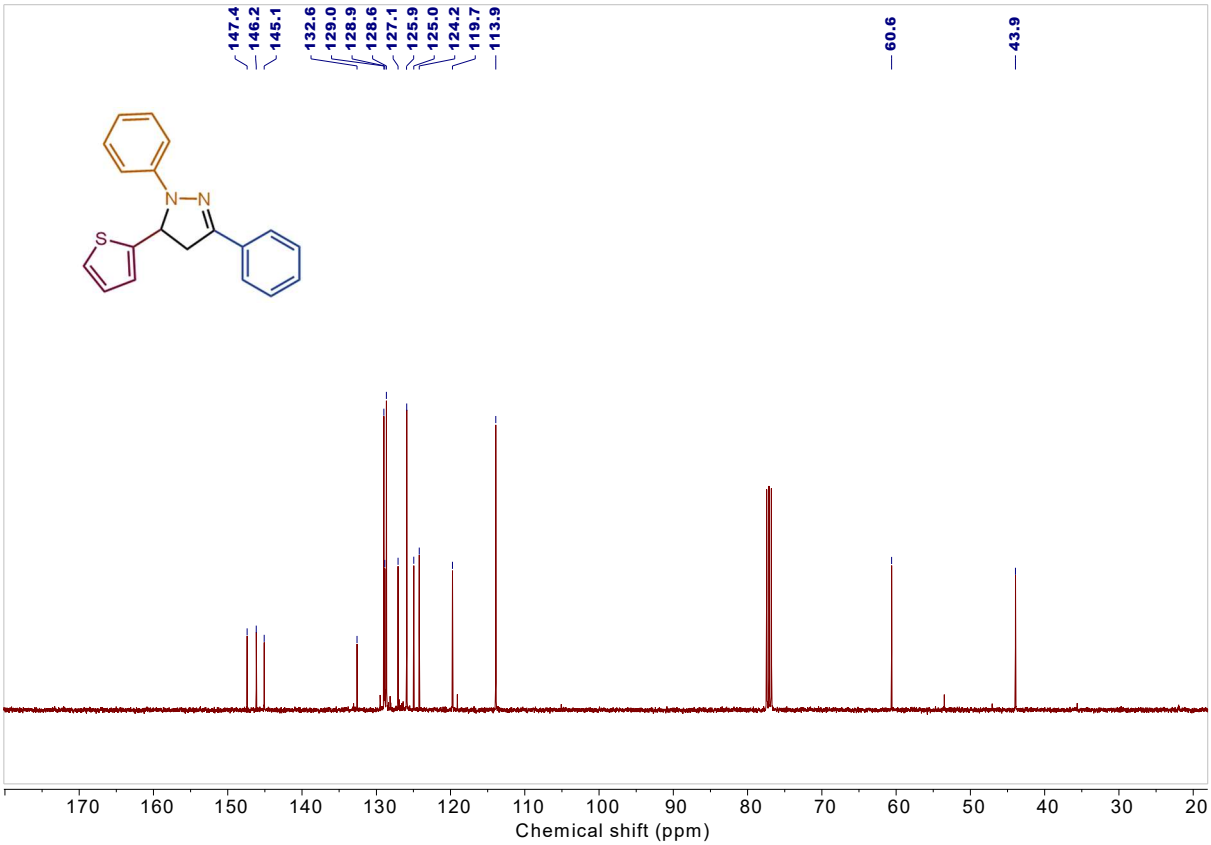


Figure S69: ^{13}C NMR spectrum of **17** (100 MHz, $CDCl_3$).

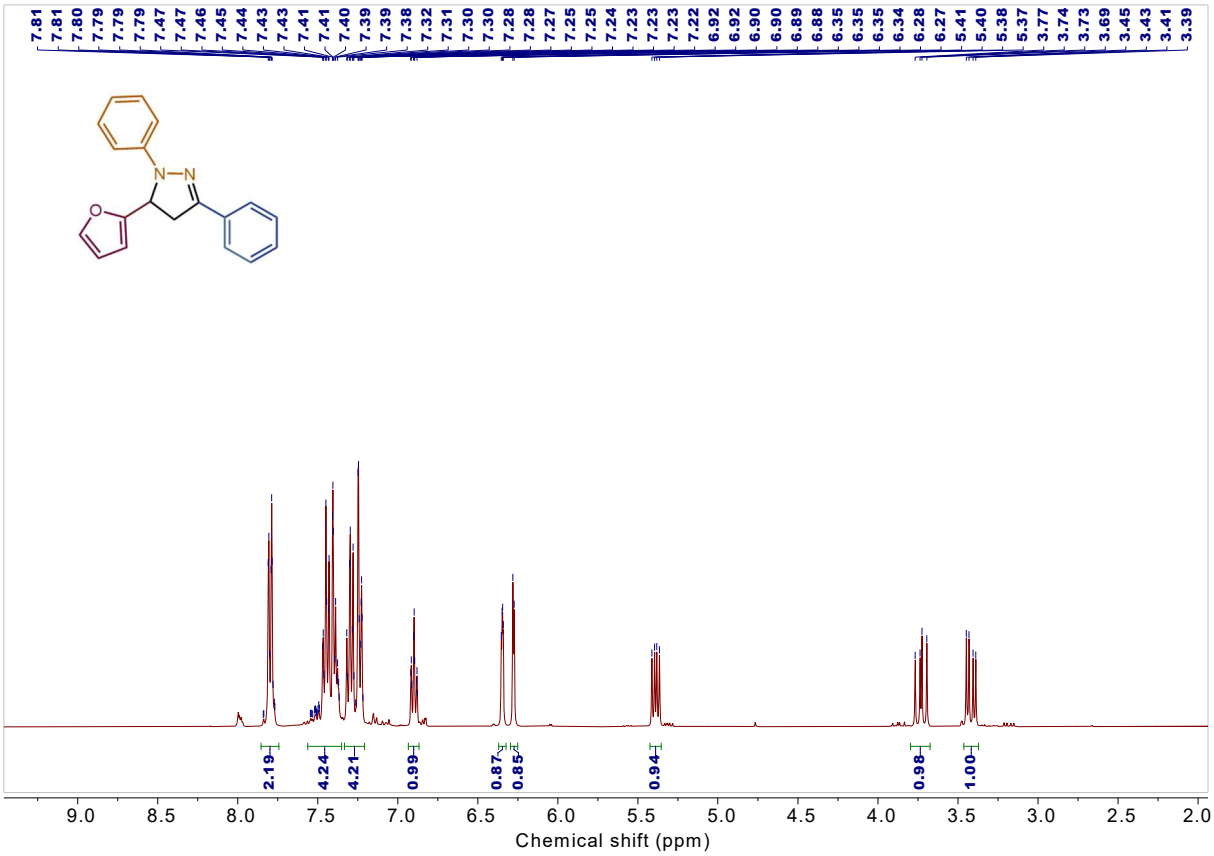


Figure S70: ^{1}H NMR spectrum of **18** (400 MHz, $CDCl_3$).

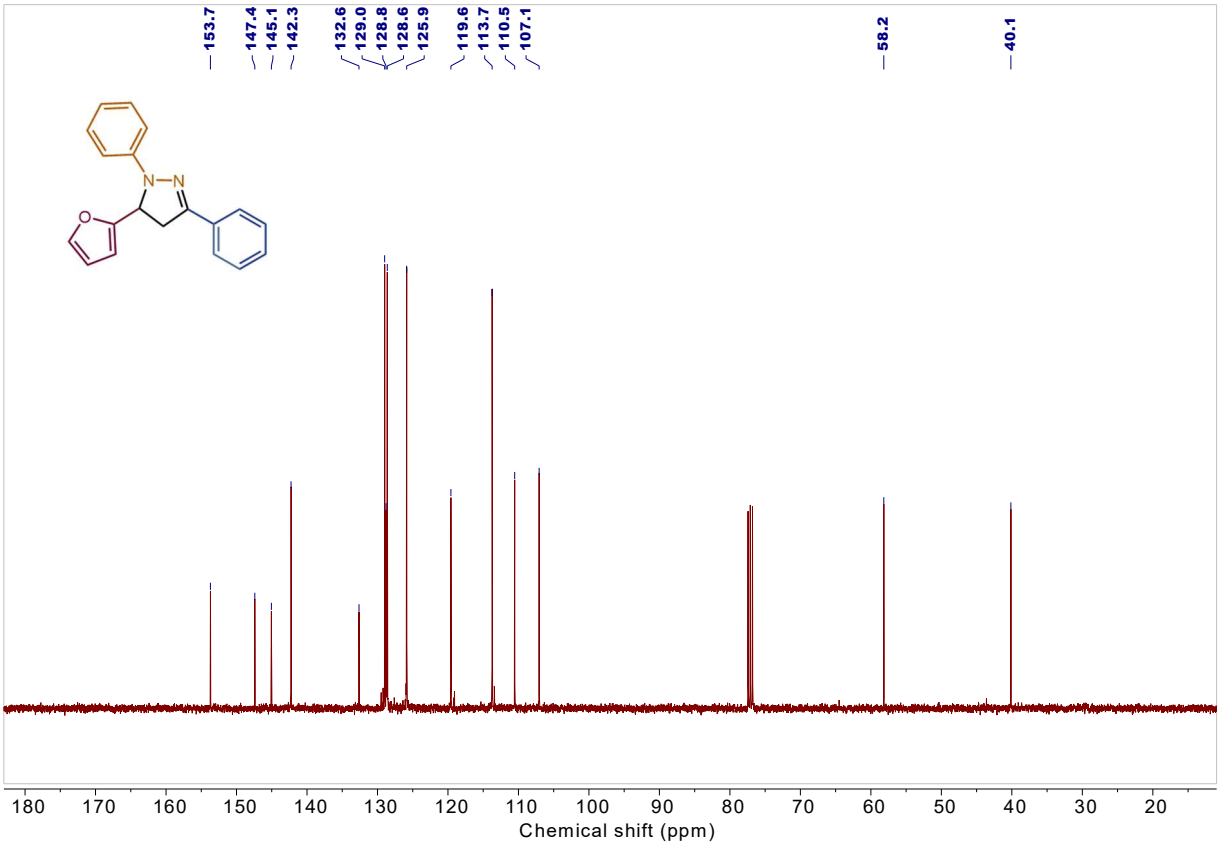


Figure S71: ^{13}C NMR spectrum of **18** (100 MHz, $CDCl_3$).

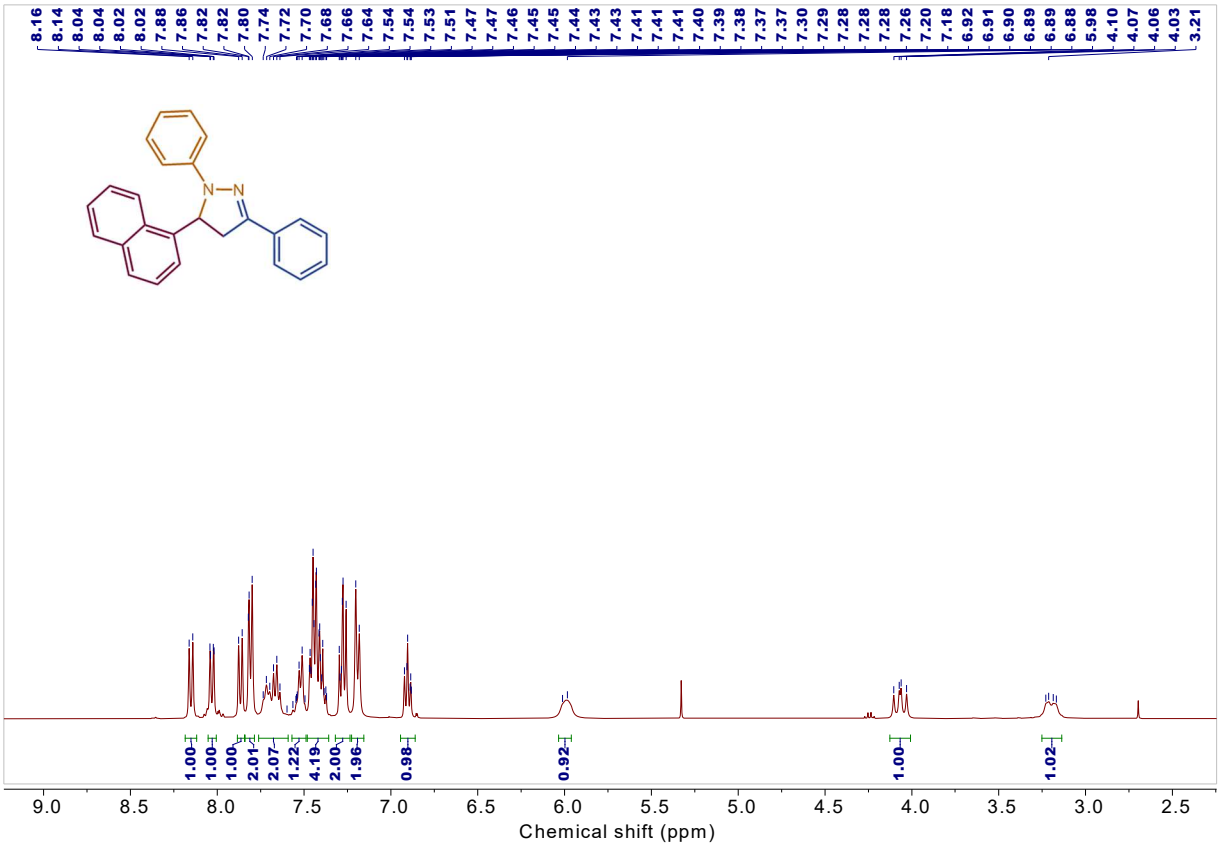


Figure S72: ^{1}H NMR spectrum of **19** (400 MHz, $CDCl_3$).

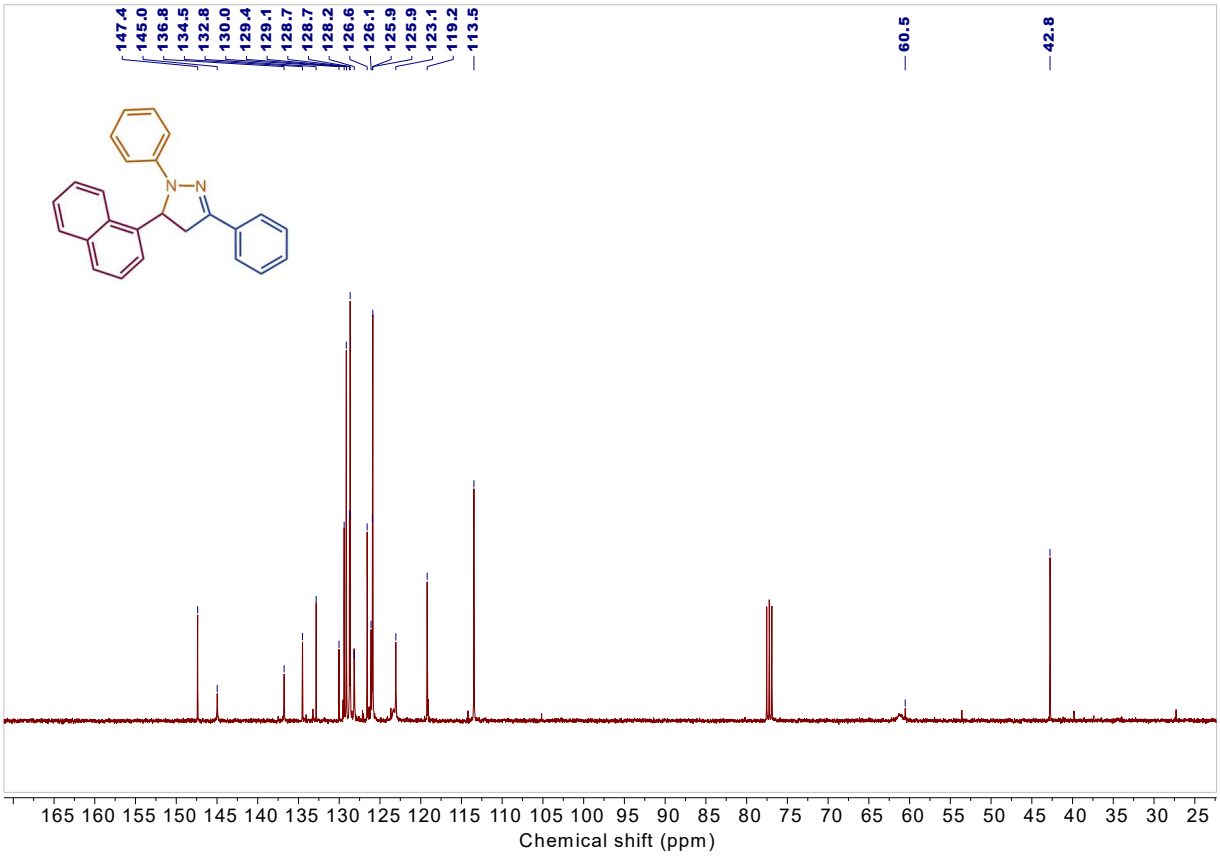


Figure S73: ^{13}C NMR spectrum of **19** (100 MHz, $CDCl_3$).

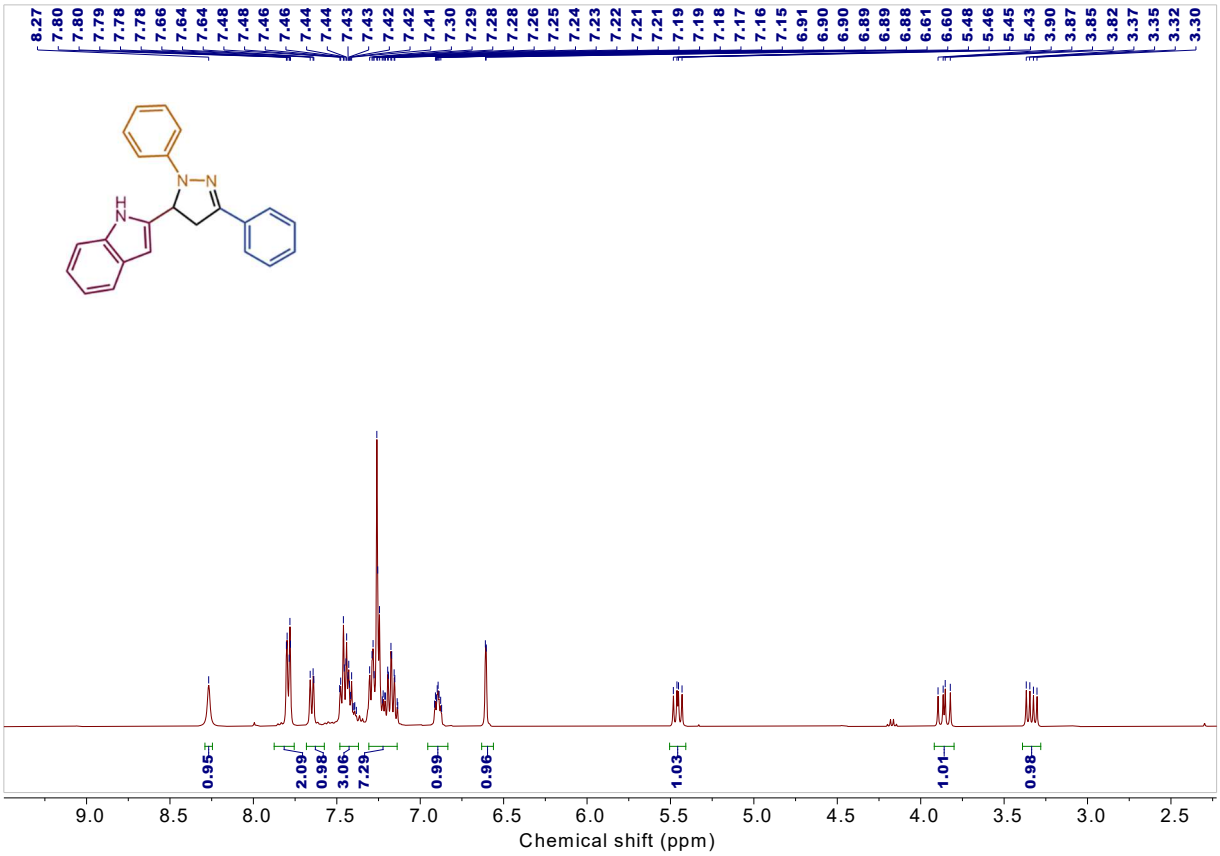


Figure S74: ^{1}H NMR spectrum of **20** (400 MHz, $CDCl_3$).

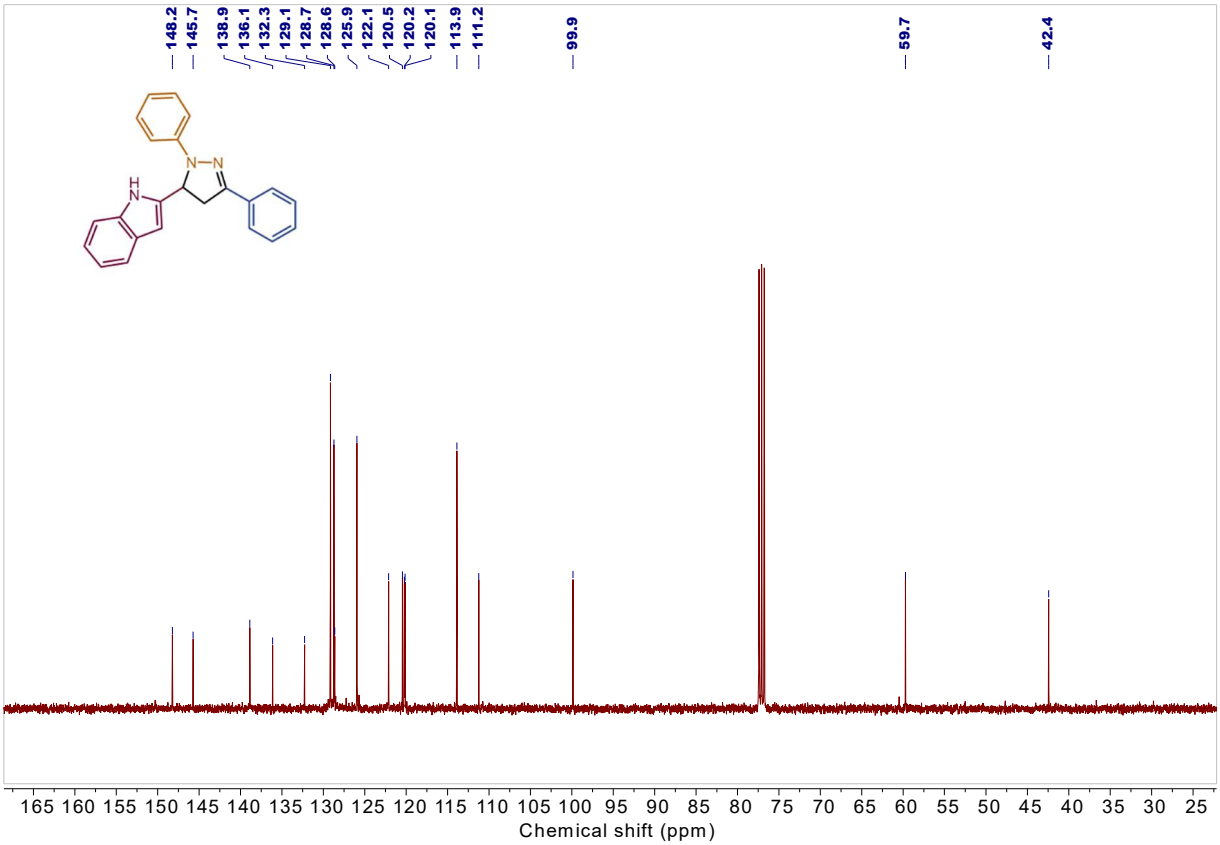


Figure S75: ^{13}C NMR spectrum of **20** (100 MHz, $CDCl_3$).

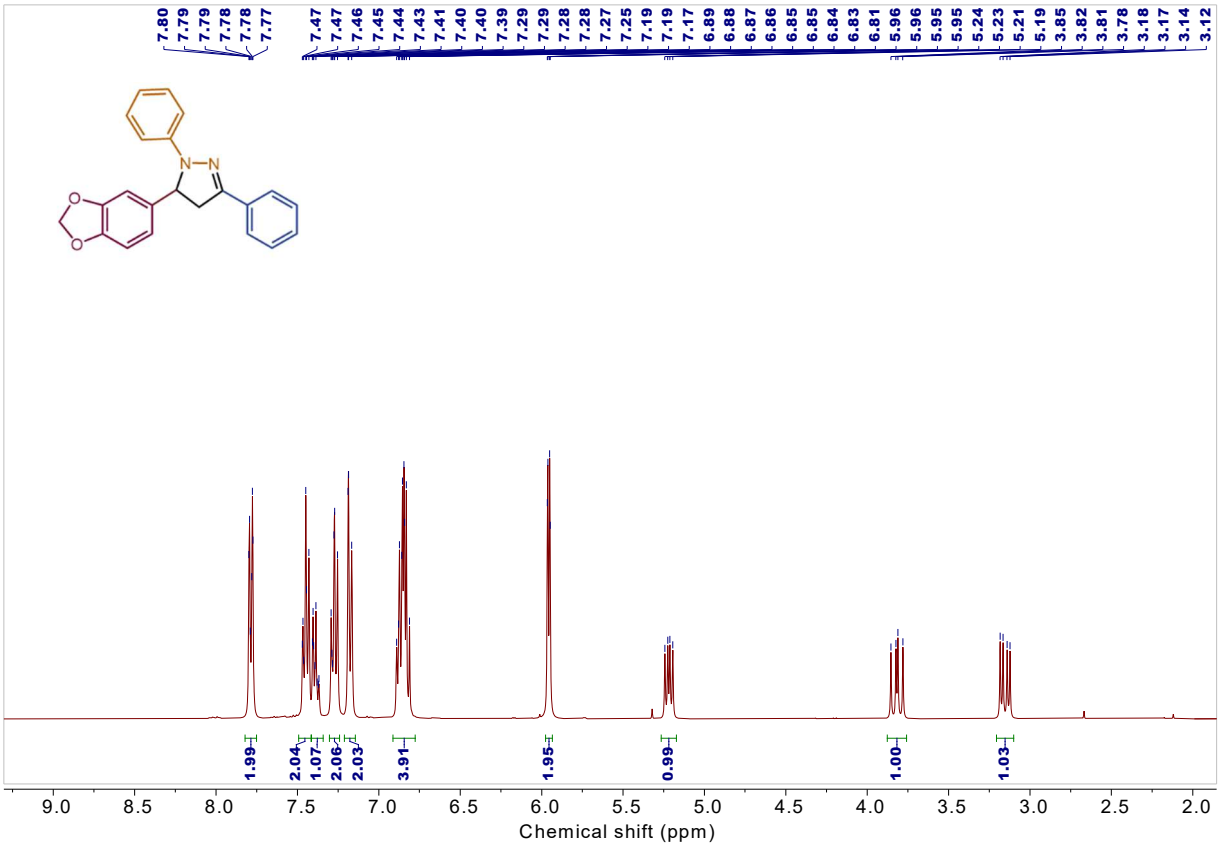


Figure S76: ^{1}H NMR spectrum of **21** (400 MHz, $CDCl_3$).

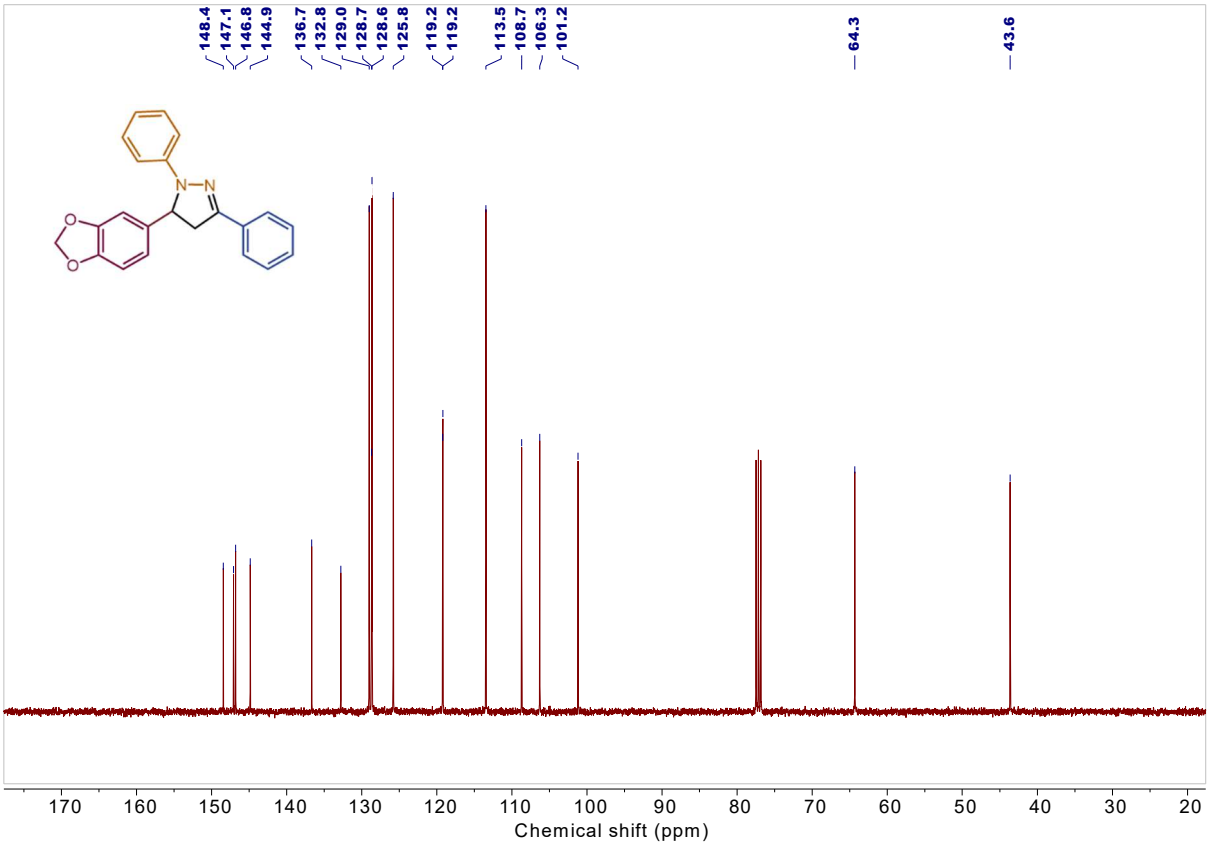


Figure S77: ^{13}C NMR spectrum of **21** (100 MHz, $CDCl_3$).

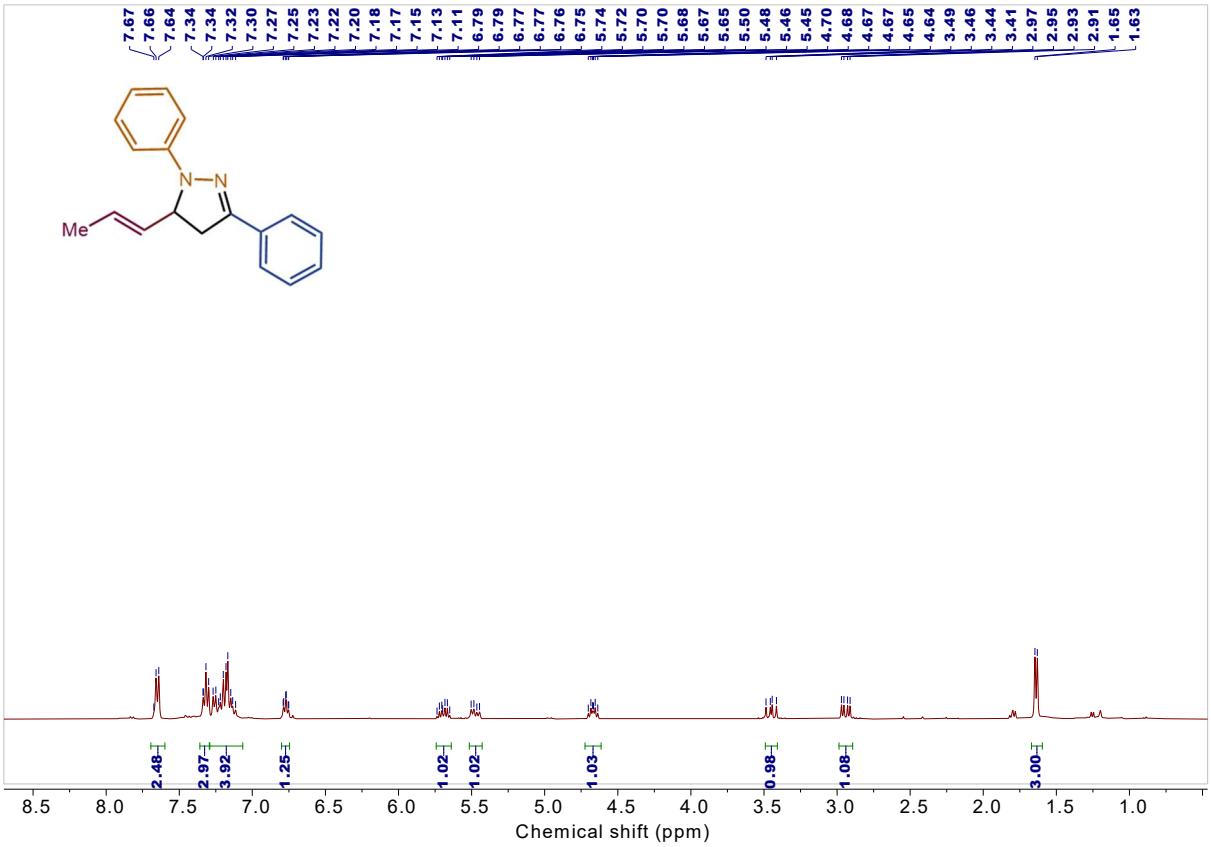


Figure S78: ^{1}H NMR spectrum of **22** (400 MHz, $CDCl_3$).

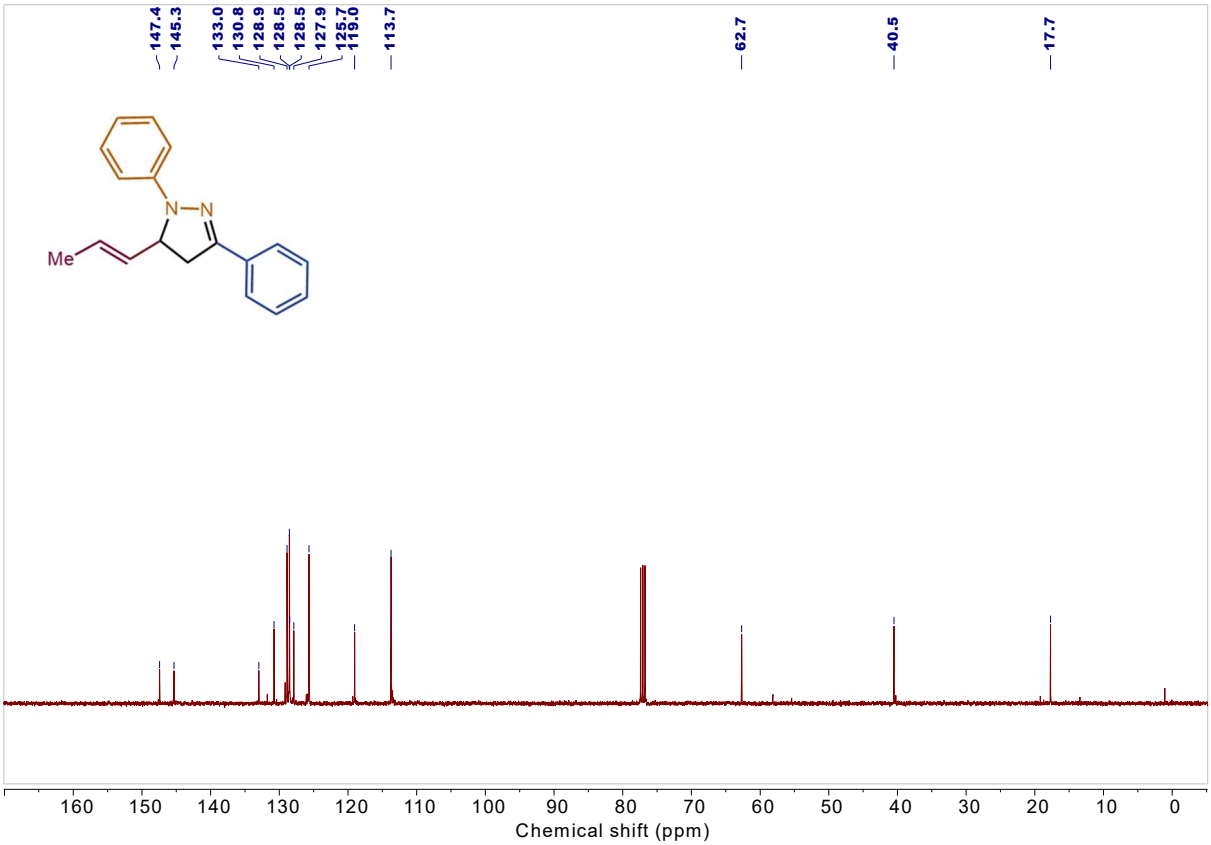


Figure S79: ^{13}C NMR spectrum of **22** (100 MHz, $CDCl_3$).

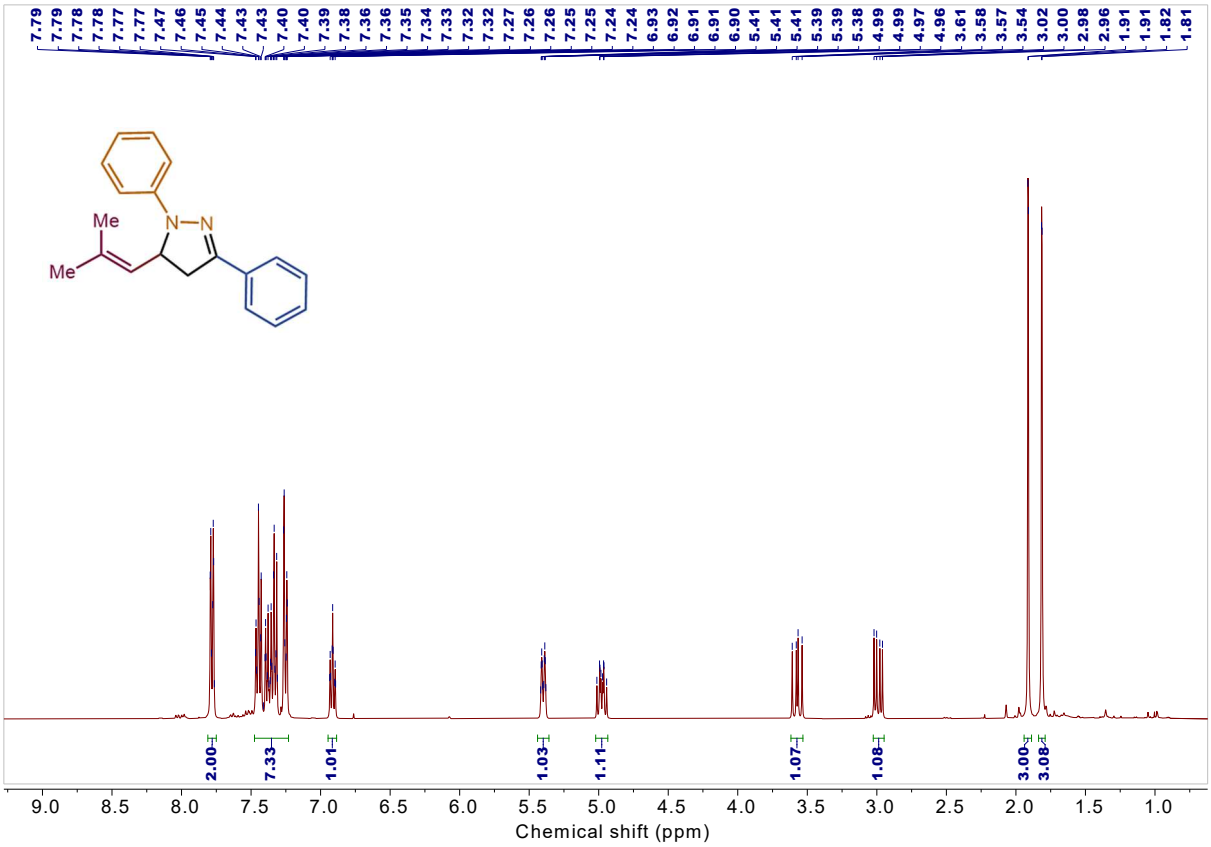


Figure S80: ^{1}H NMR spectrum of **23** (400 MHz, $CDCl_3$).

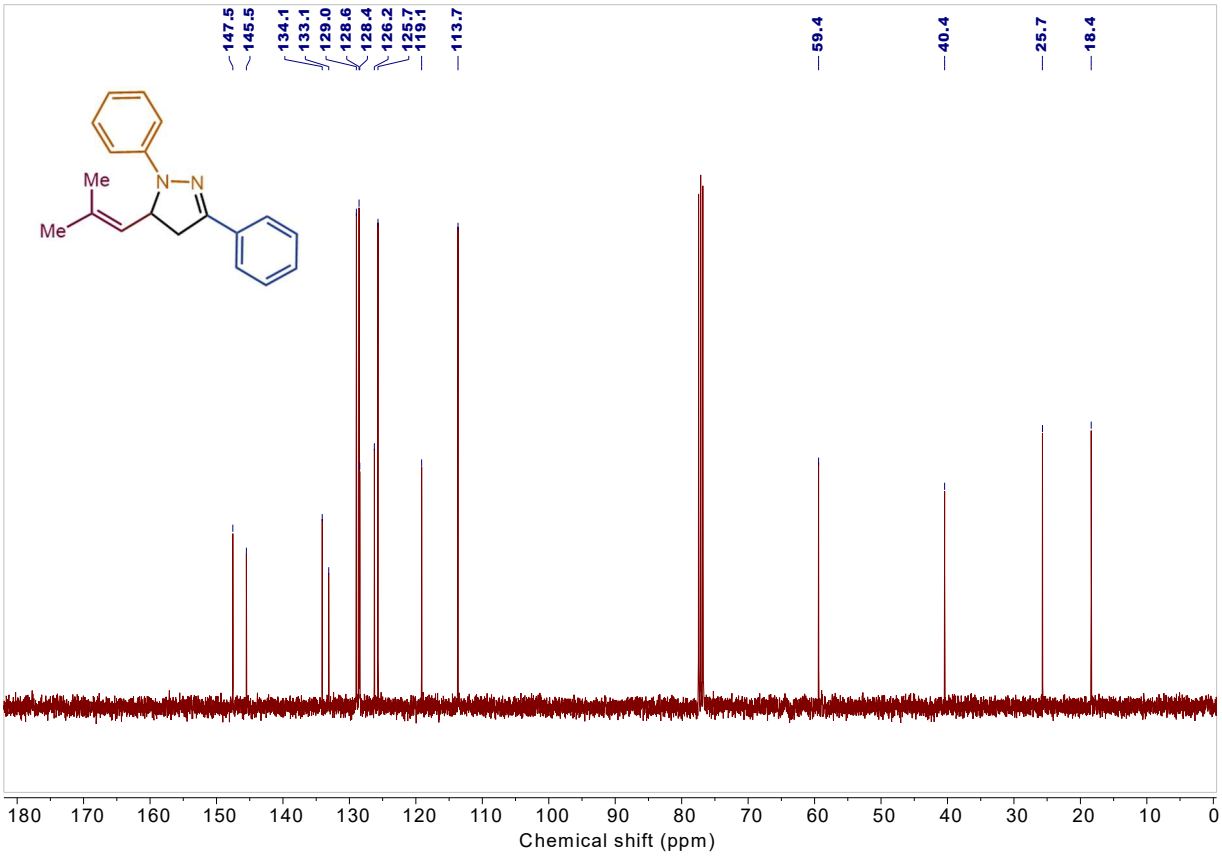


Figure S81: ^{13}C NMR spectrum of **23** (100 MHz, $CDCl_3$).

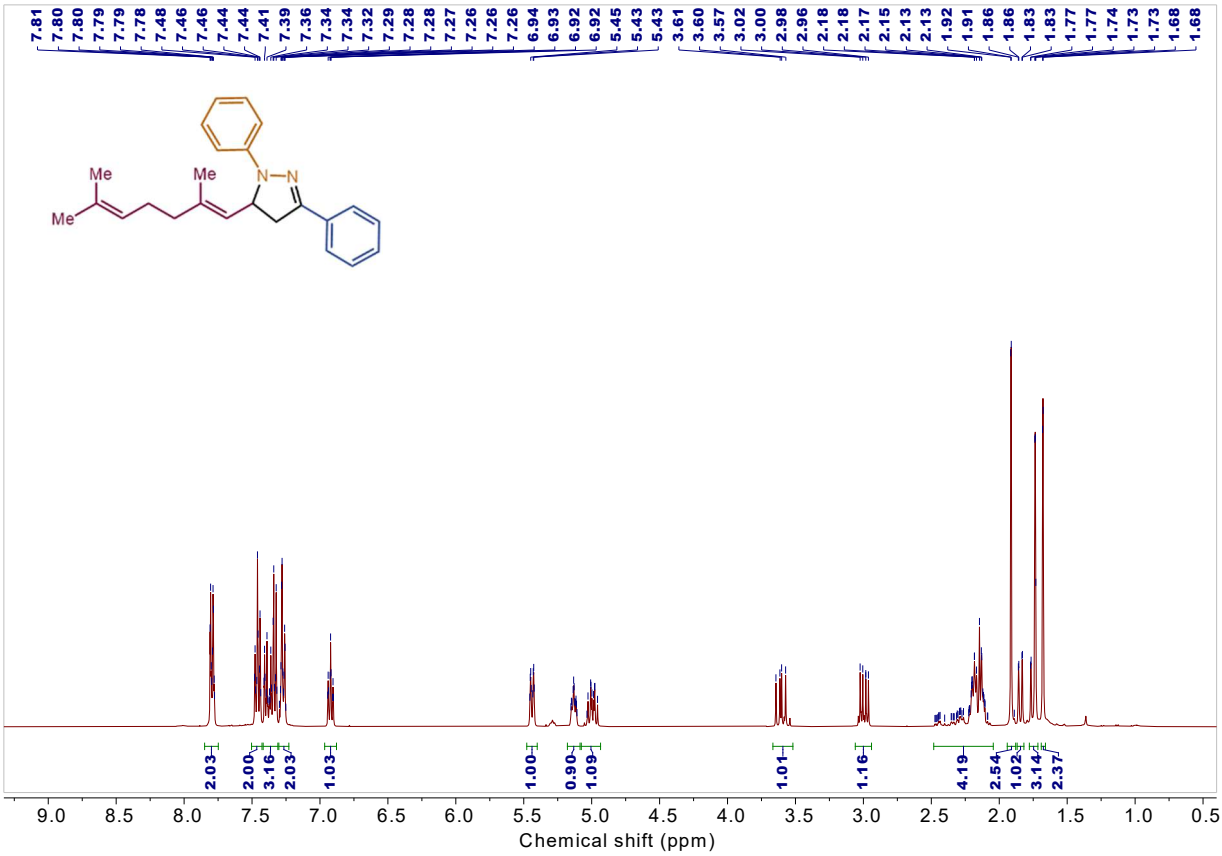


Figure S82: ^{1}H NMR spectrum of **24** (400 MHz, $CDCl_3$).

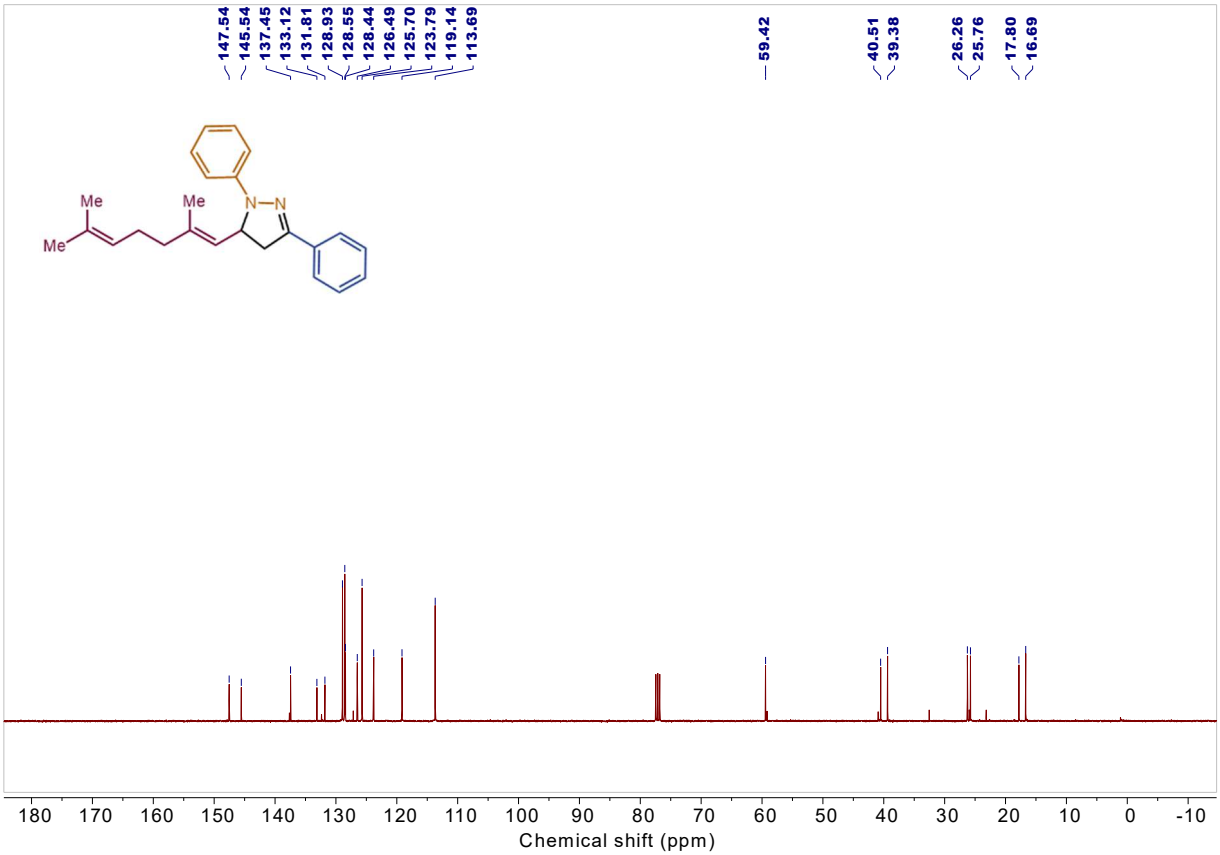


Figure S83: ^{13}C NMR spectrum of **24** (100 MHz, $CDCl_3$).

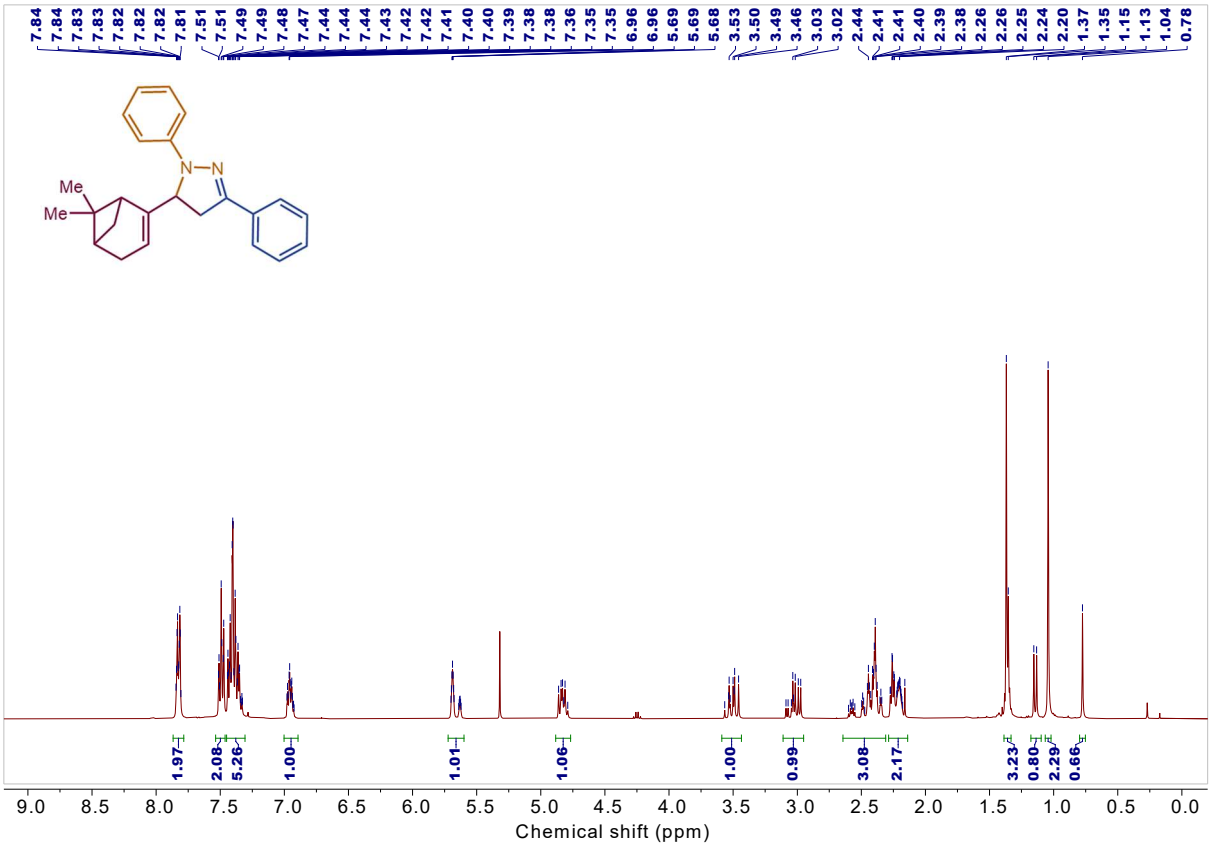


Figure S84: ^{1}H NMR spectrum of **25** (400 MHz, $CDCl_3$)**,** d.r.=3:1.

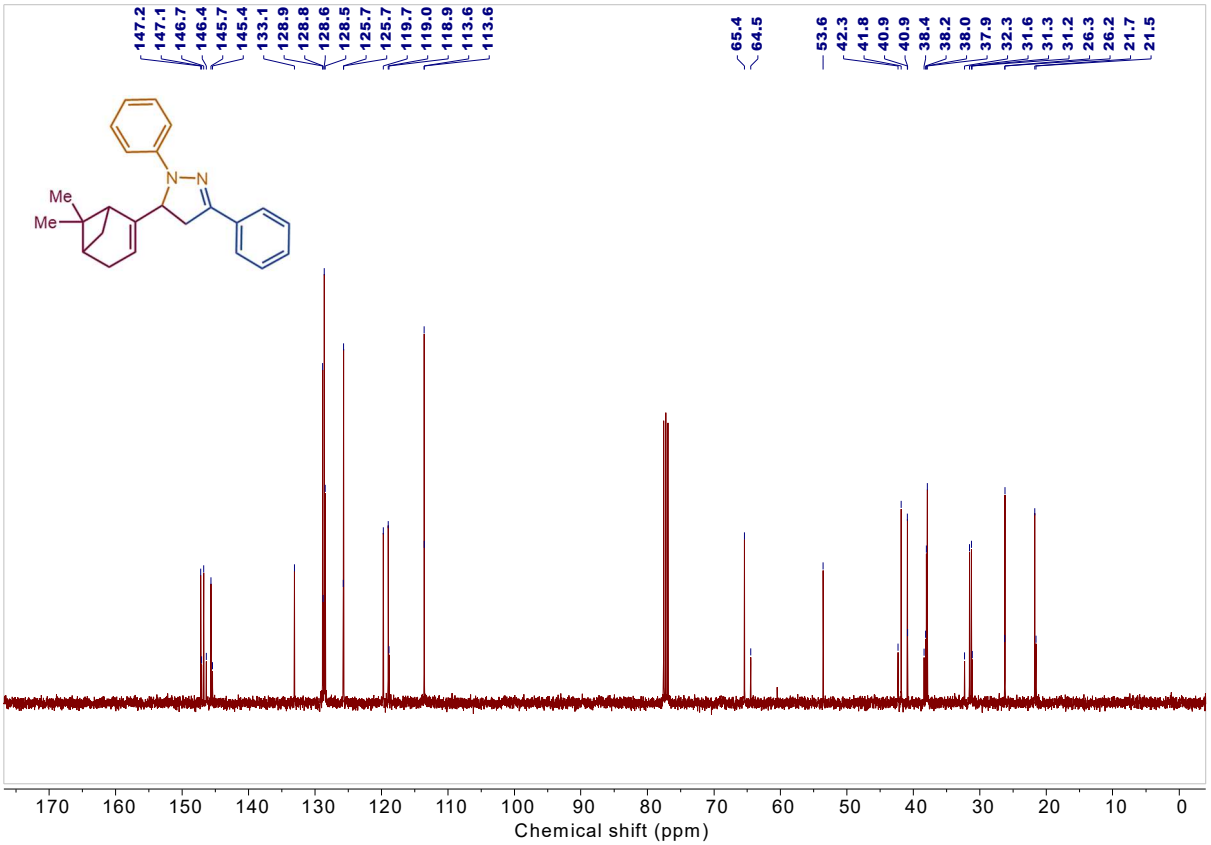


Figure S85: ^{13}C NMR spectrum of **25** (100 MHz, $CDCl_3$)**,** d.r.=3:1.

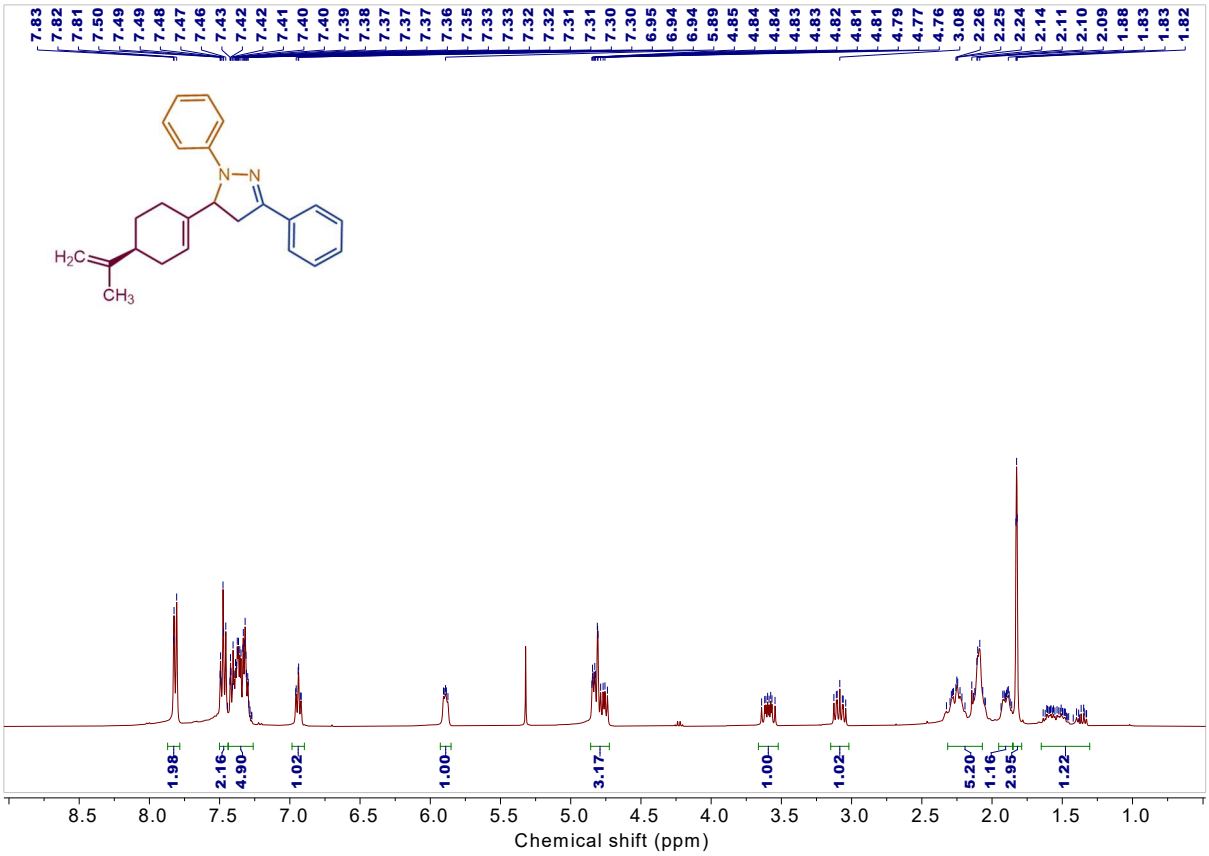


Figure S86: ^{1}H NMR spectrum of **26** (400 MHz, $CDCl_3$), d.r.=1:1

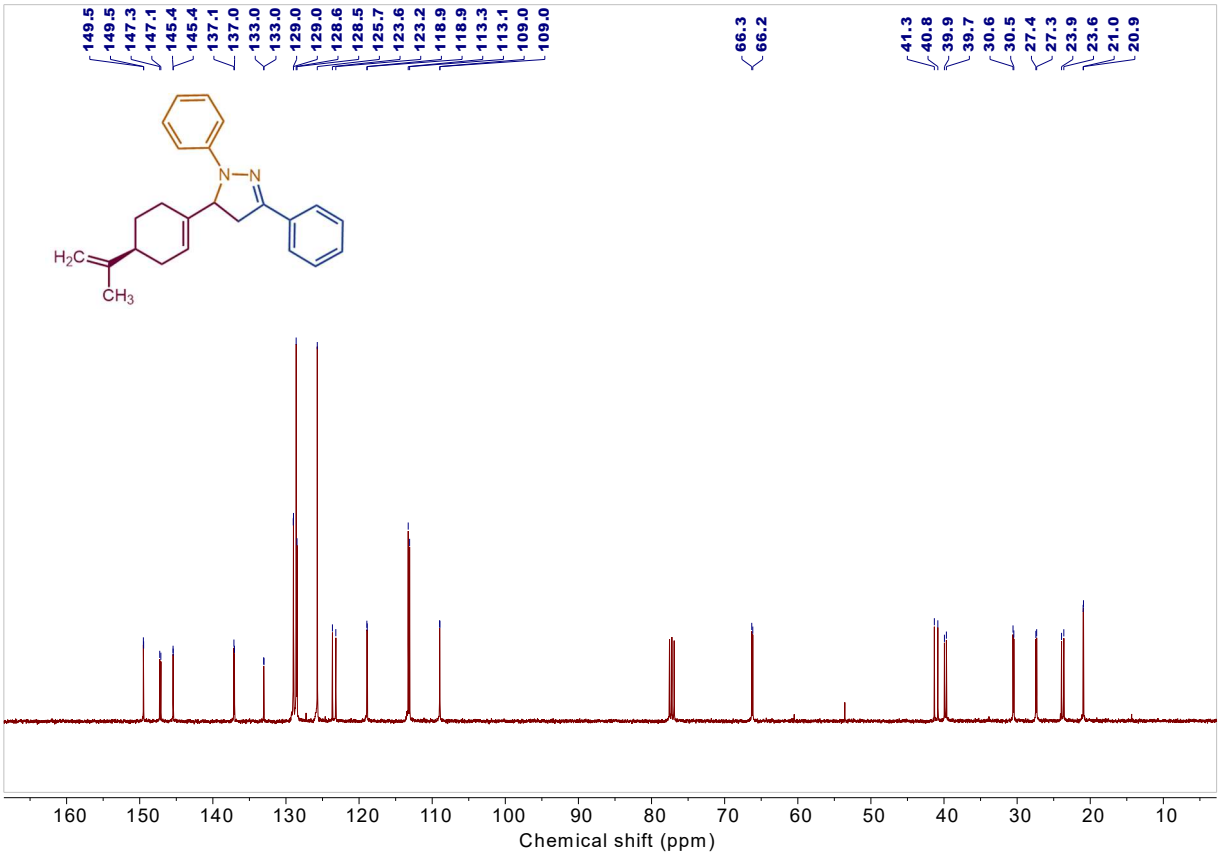


Figure S87: ^{13}C NMR spectrum of **26** (100 MHz, $CDCl_3$), d.r.=1:1

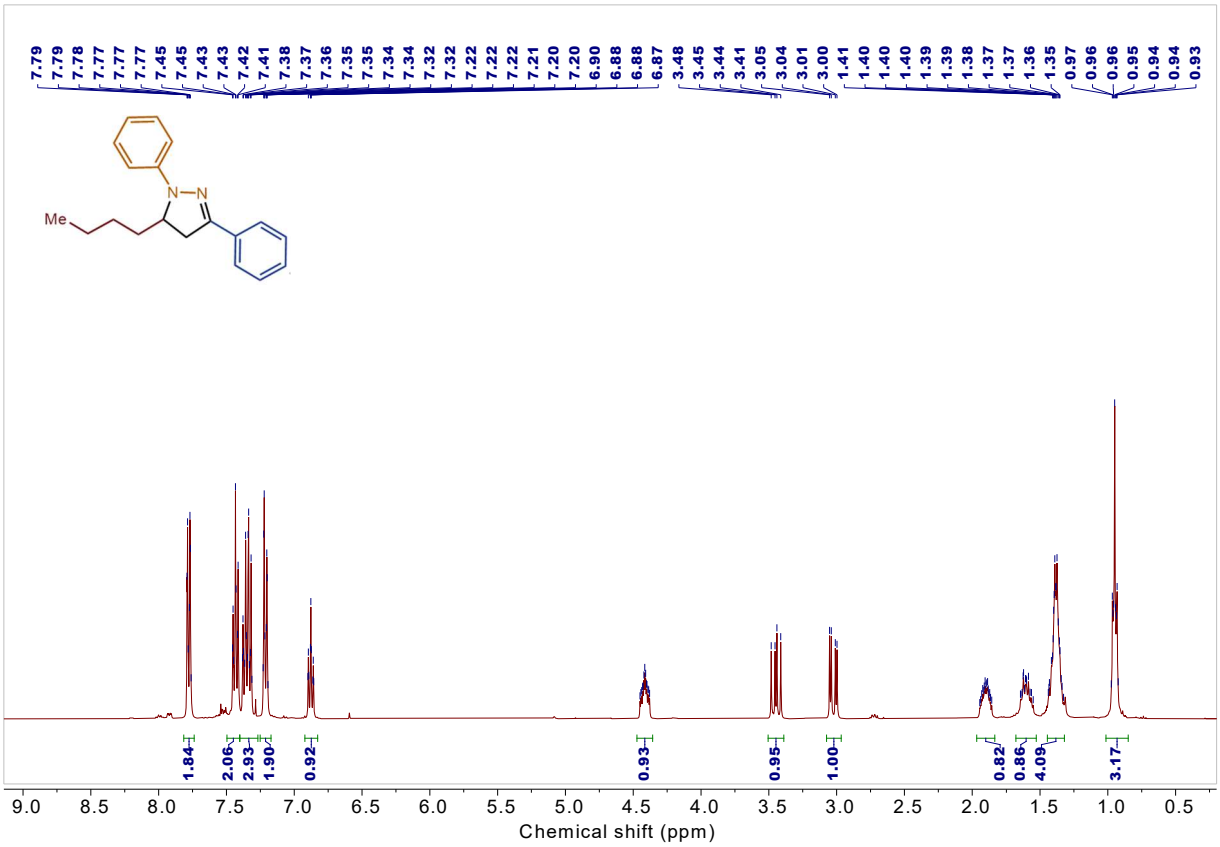


Figure S88: ^{1}H NMR spectrum of **27** (400 MHz, $CDCl_3$).

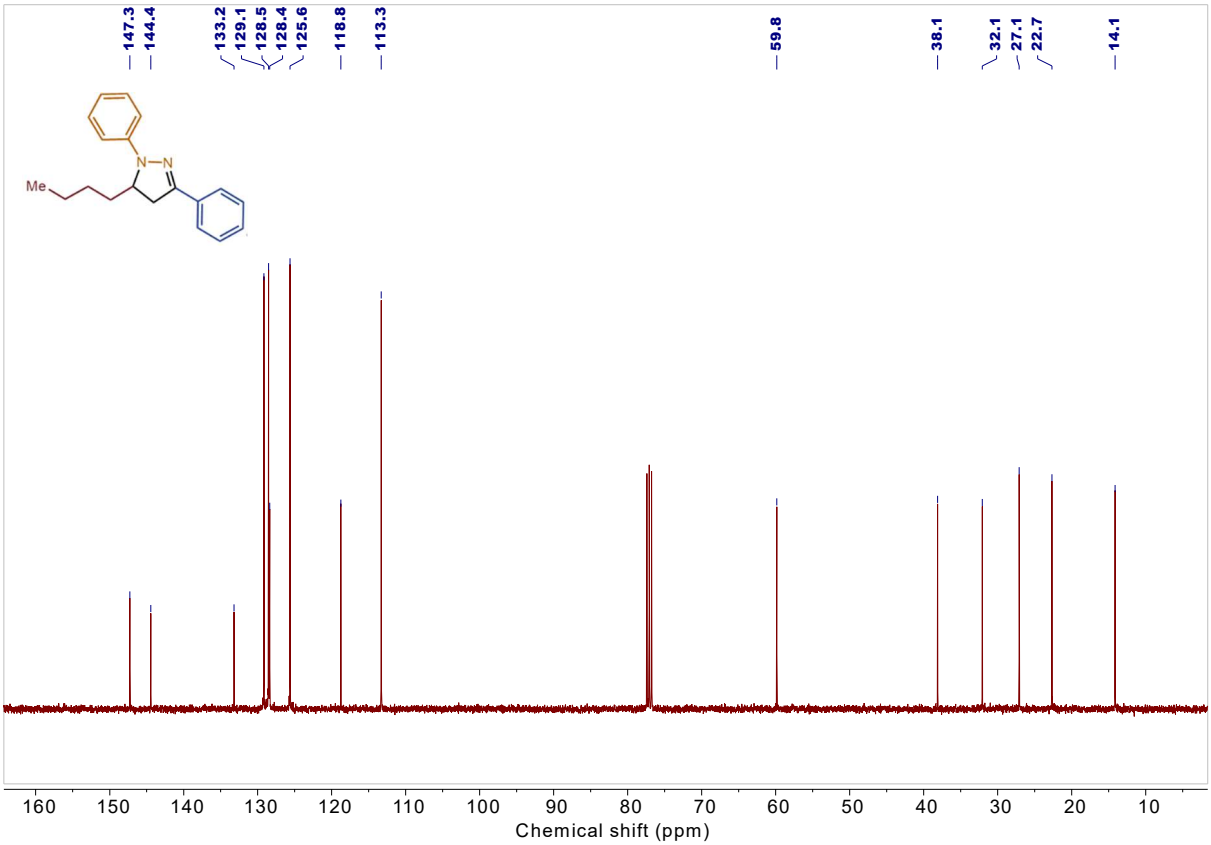


Figure S89: ^{13}C NMR spectrum of **27** (100 MHz, $CDCl_3$).

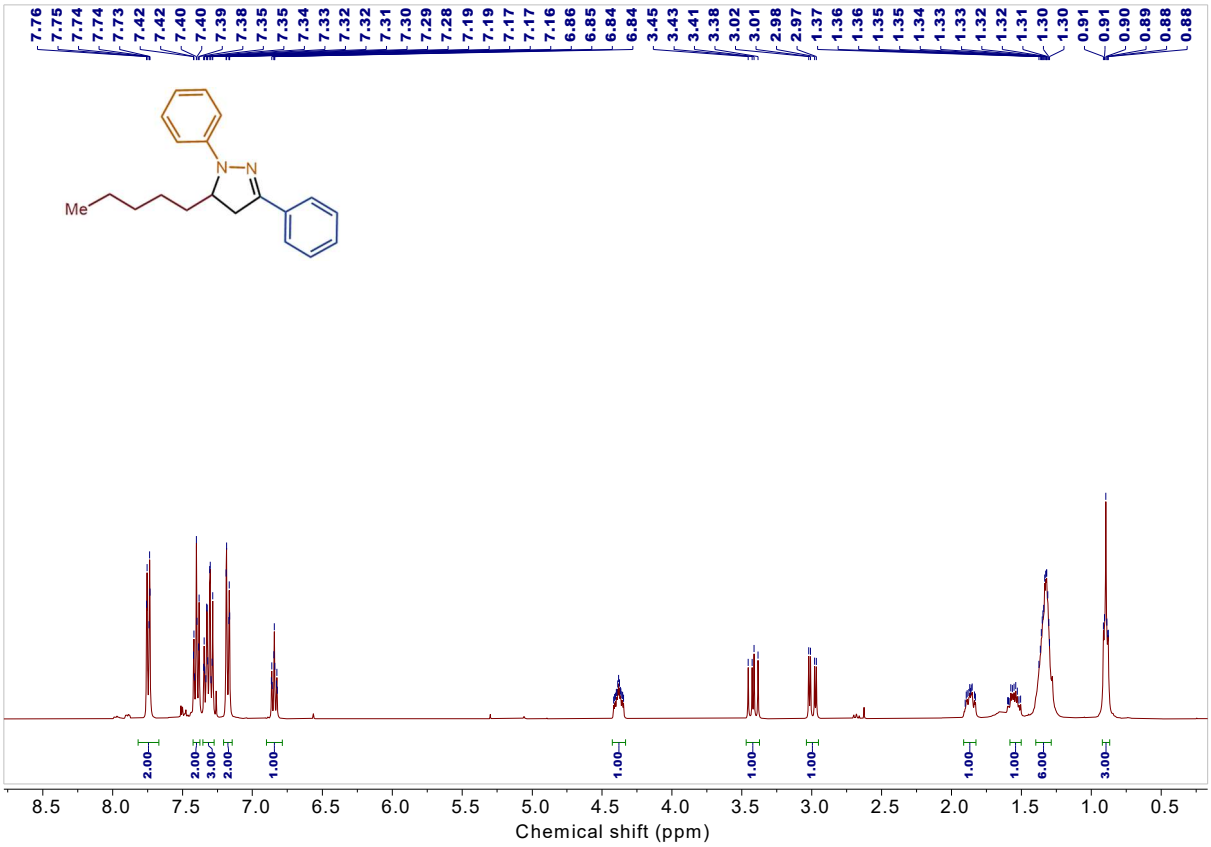


Figure S90: ^{1}H NMR spectrum of **28** (400 MHz, $CDCl_3$).

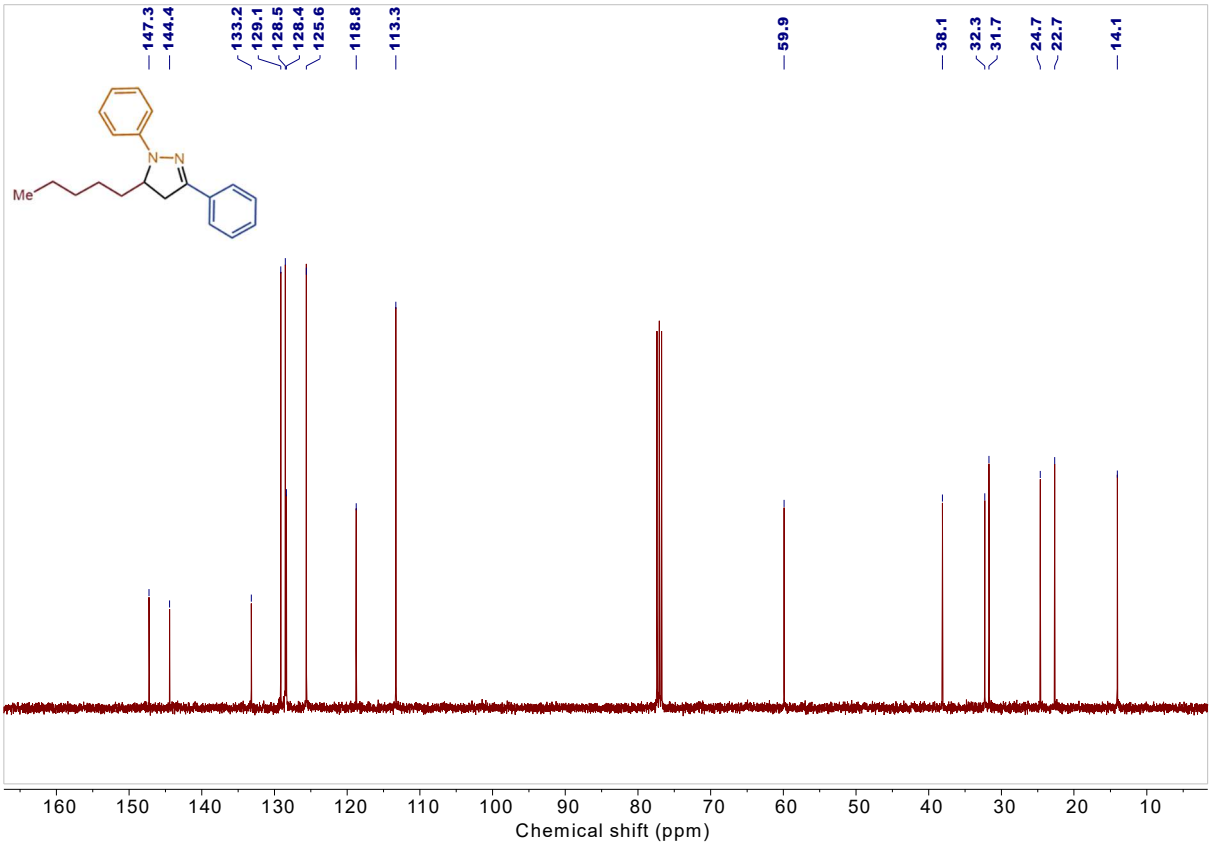


Figure S91: ^{13}C NMR spectrum of **28** (100 MHz, $CDCl_3$).

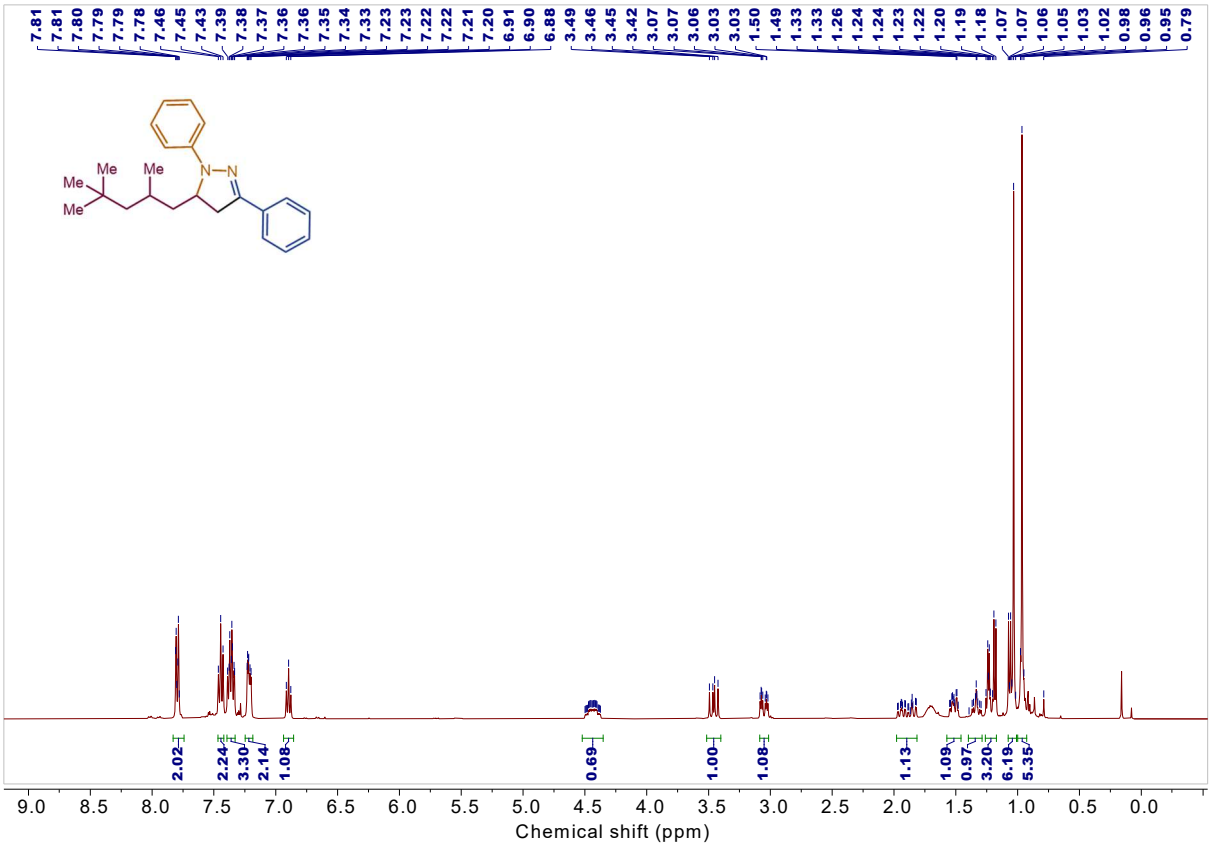


Figure S92: ^{1}H NMR spectrum of **29** (400 MHz, $CDCl_3$), d.r.=1:1.

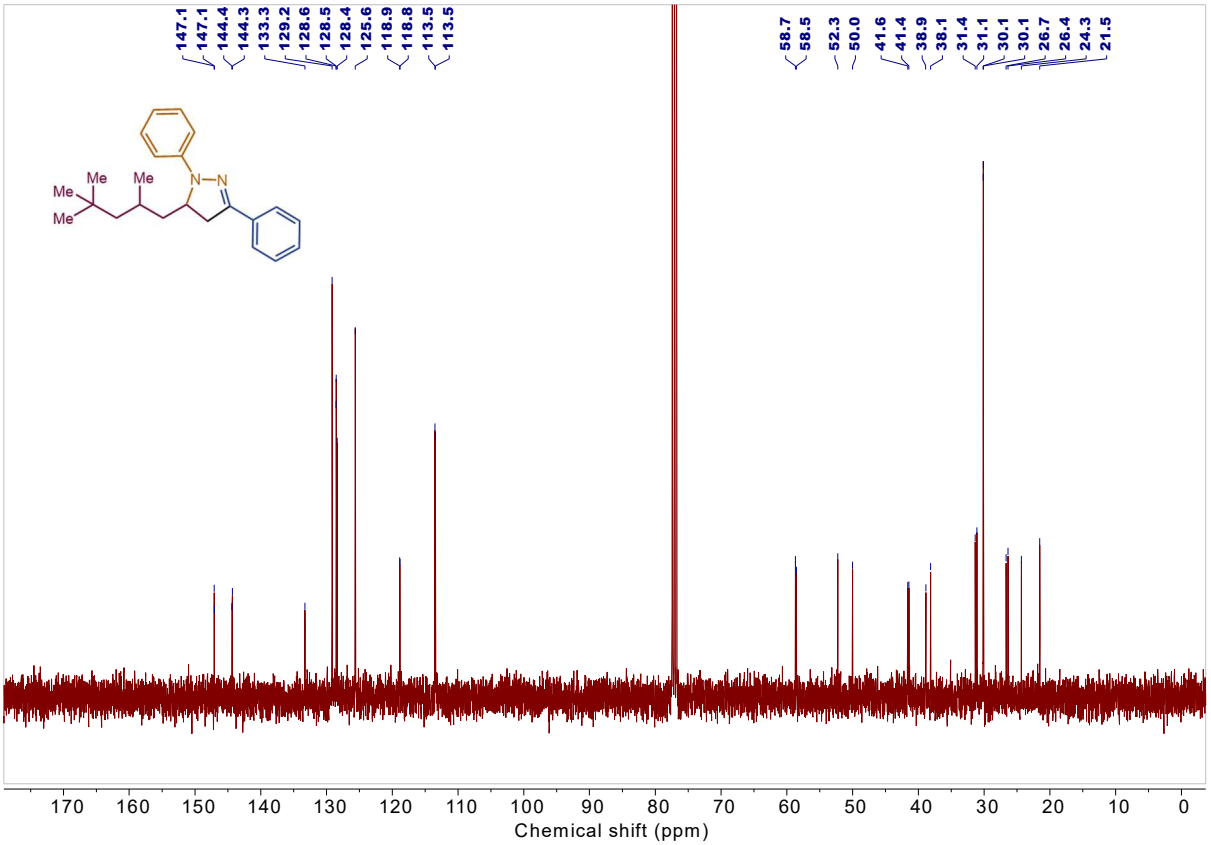


Figure S93: ^{13}C NMR spectrum of **29** (100 MHz, $CDCl_3$), d.r.=1:1.

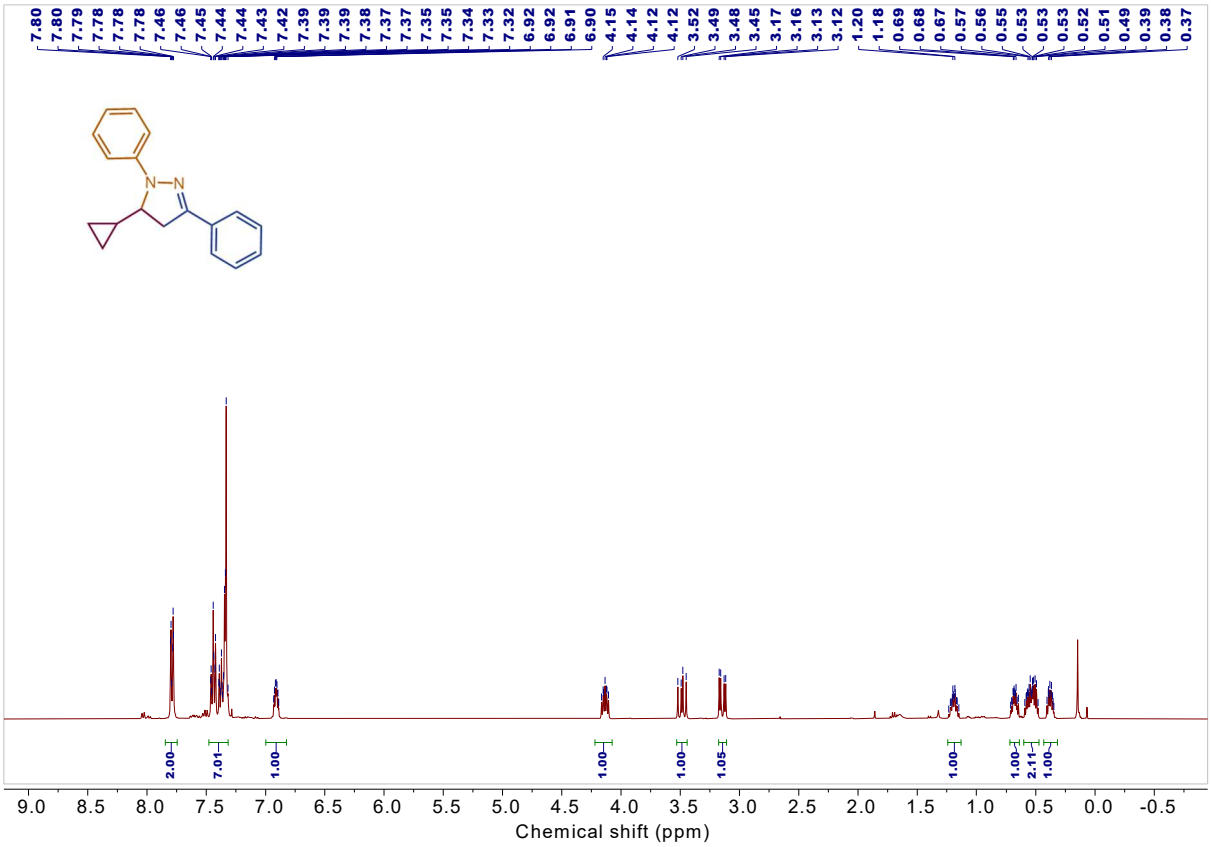


Figure S94: ^{1}H NMR spectrum of **30** (400 MHz, $CDCl_3$).

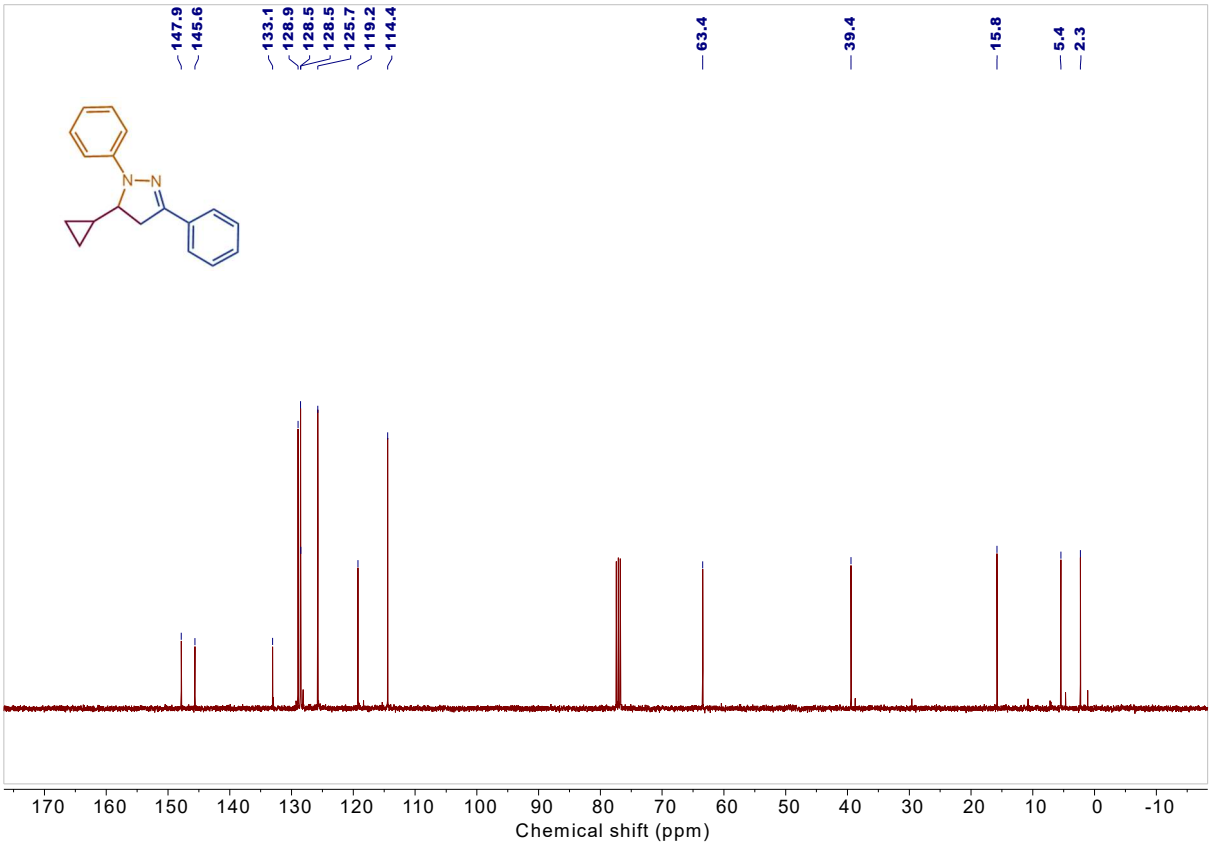


Figure S95: ^{13}C NMR spectrum of **30** (100 MHz, $CDCl_3$).

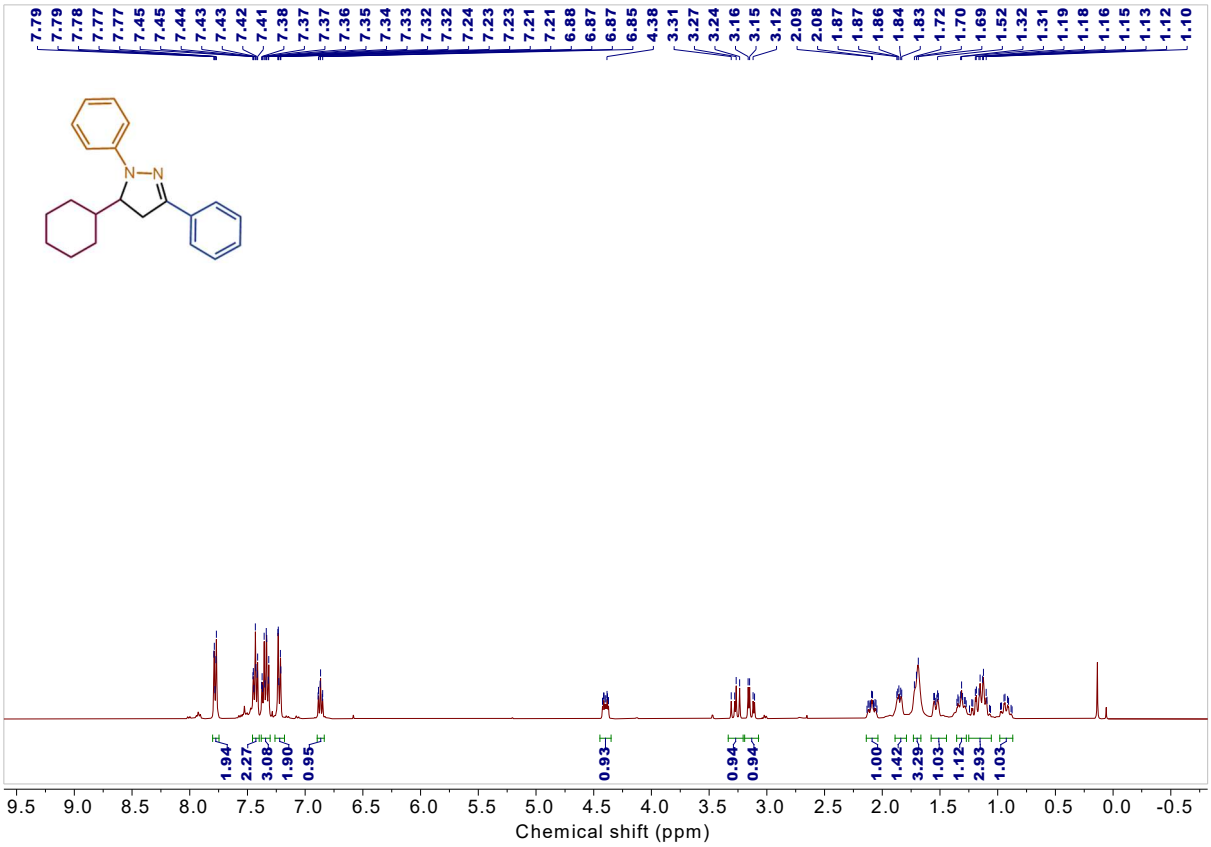


Figure S96: ^{1}H NMR spectrum of **31** (400 MHz, $CDCl_3$).

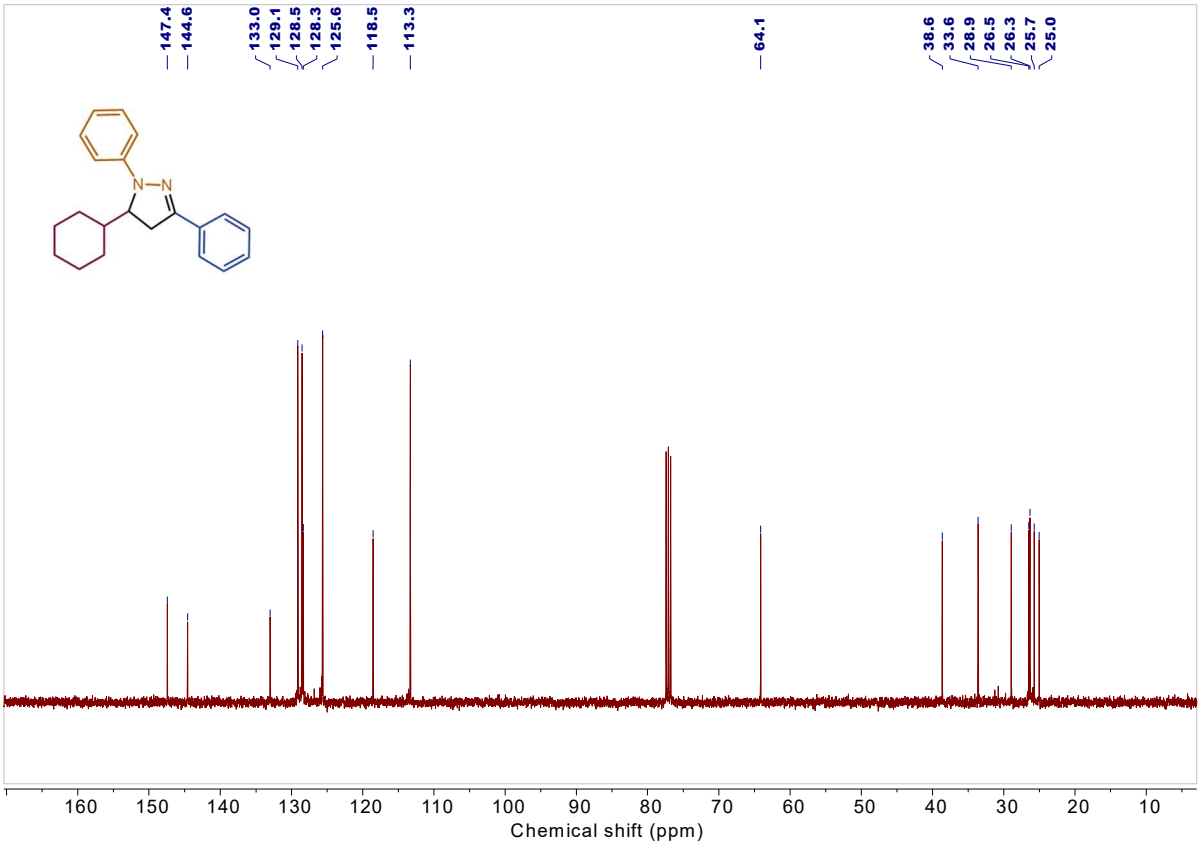


Figure S97: ^{13}C NMR spectrum of **31** (100 MHz, $CDCl_3$).

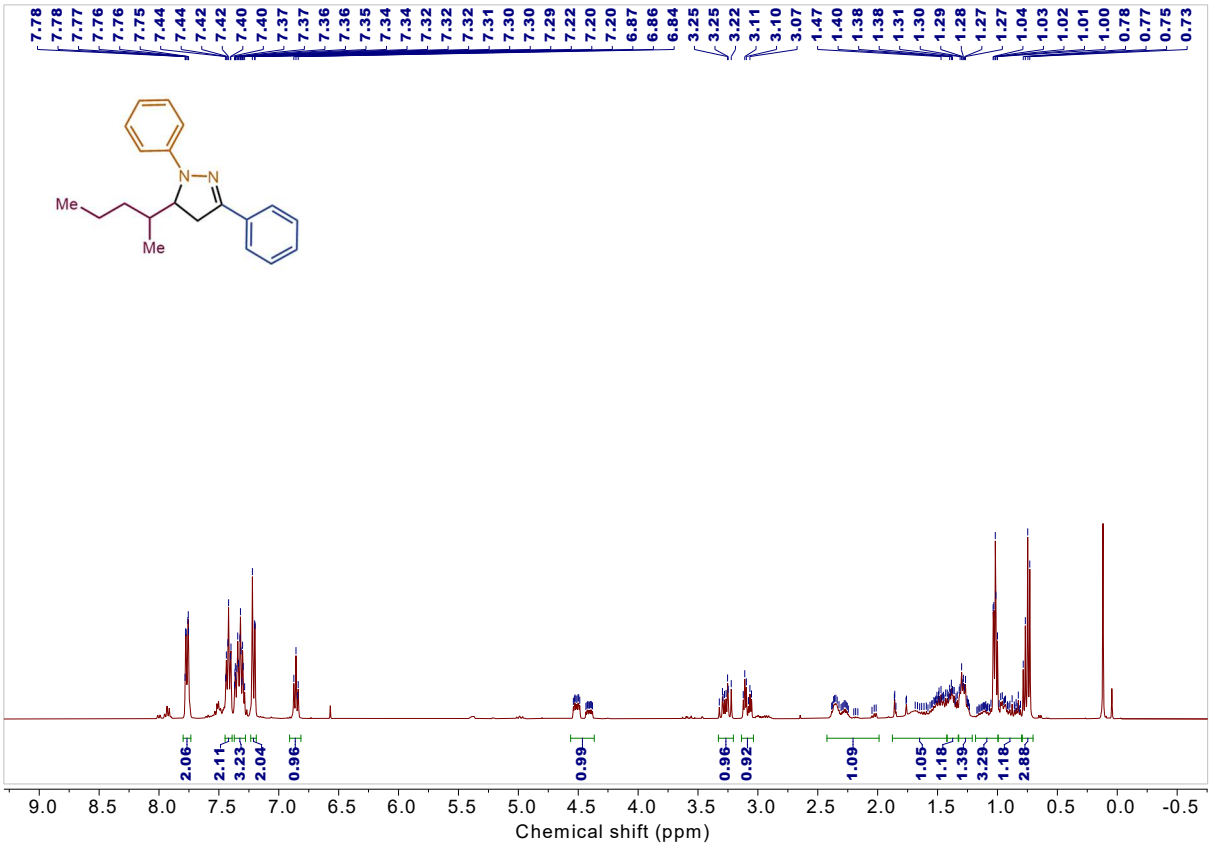


Figure S98: ^{1}H NMR spectrum of **32** (400 MHz, $CDCl_3$), d.r.=1.6:1.

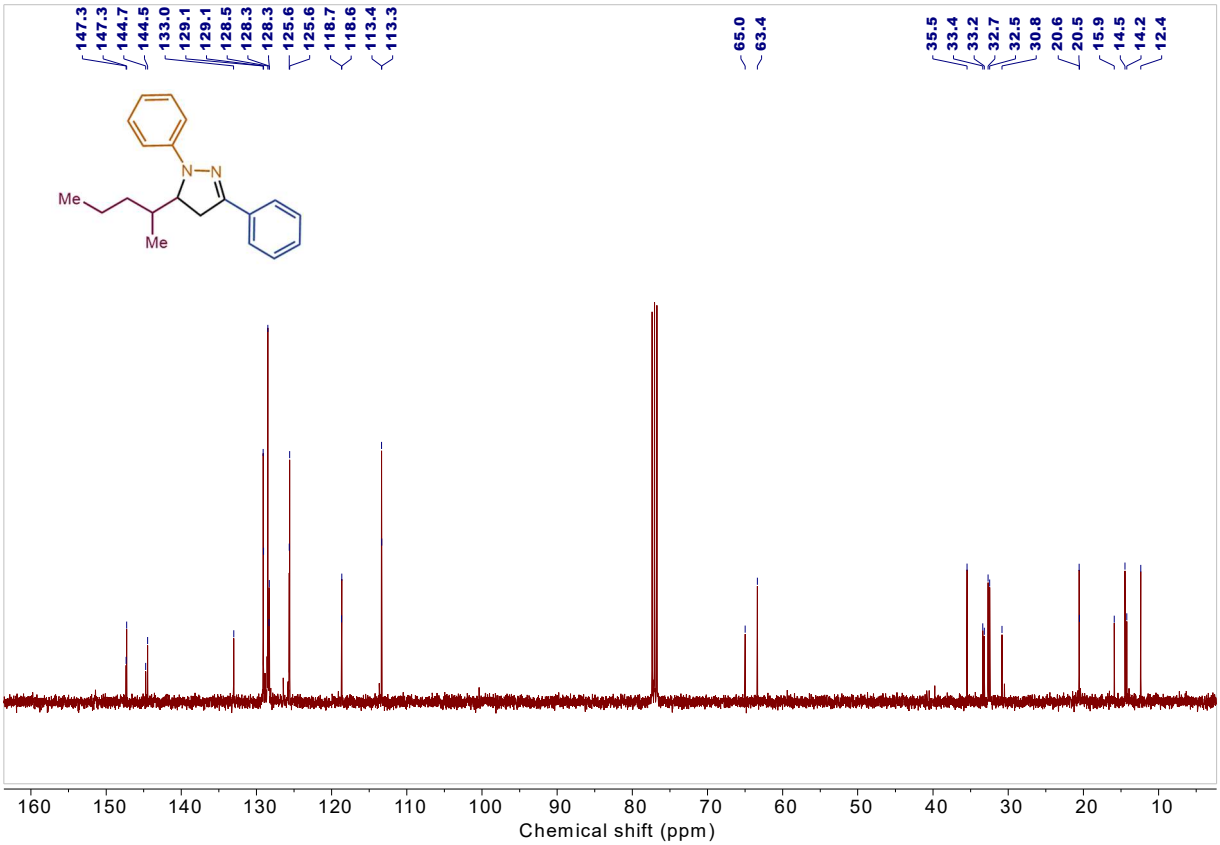


Figure S99: ^{13}C NMR spectrum of **32** (100 MHz, $CDCl_3$), d.r.=1.6:1.

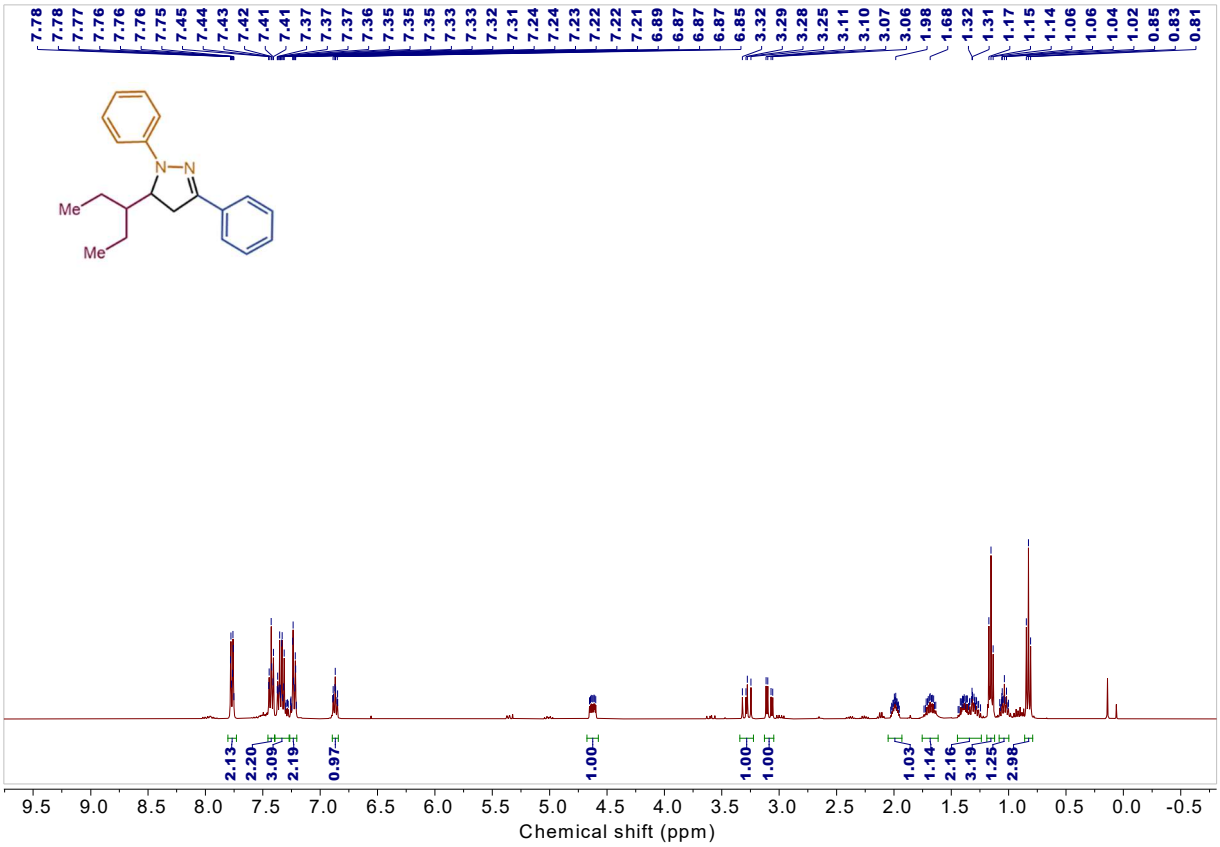


Figure S100: ^{1}H NMR spectrum of **33** (400 MHz, $CDCl_3$).

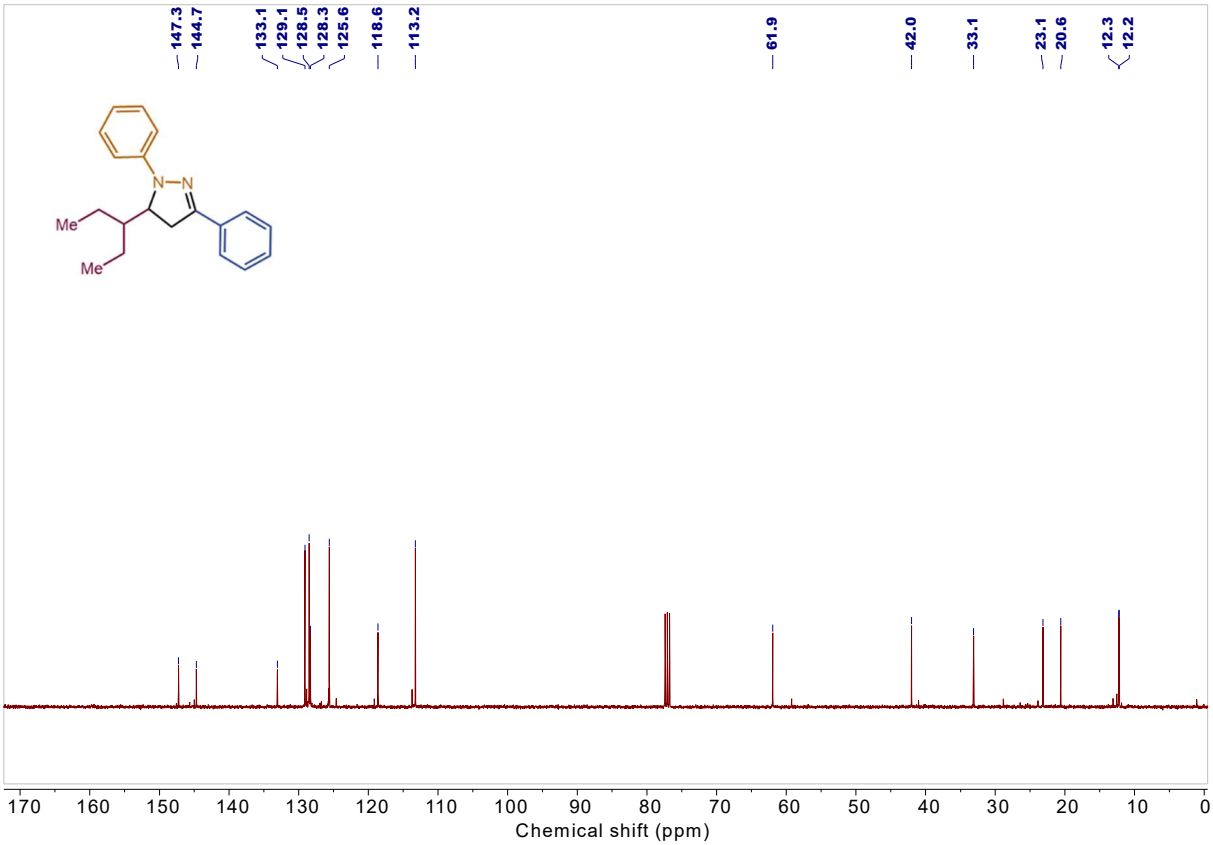


Figure S101: ^{13}C NMR spectrum of **33** (100 MHz, $CDCl_3$).

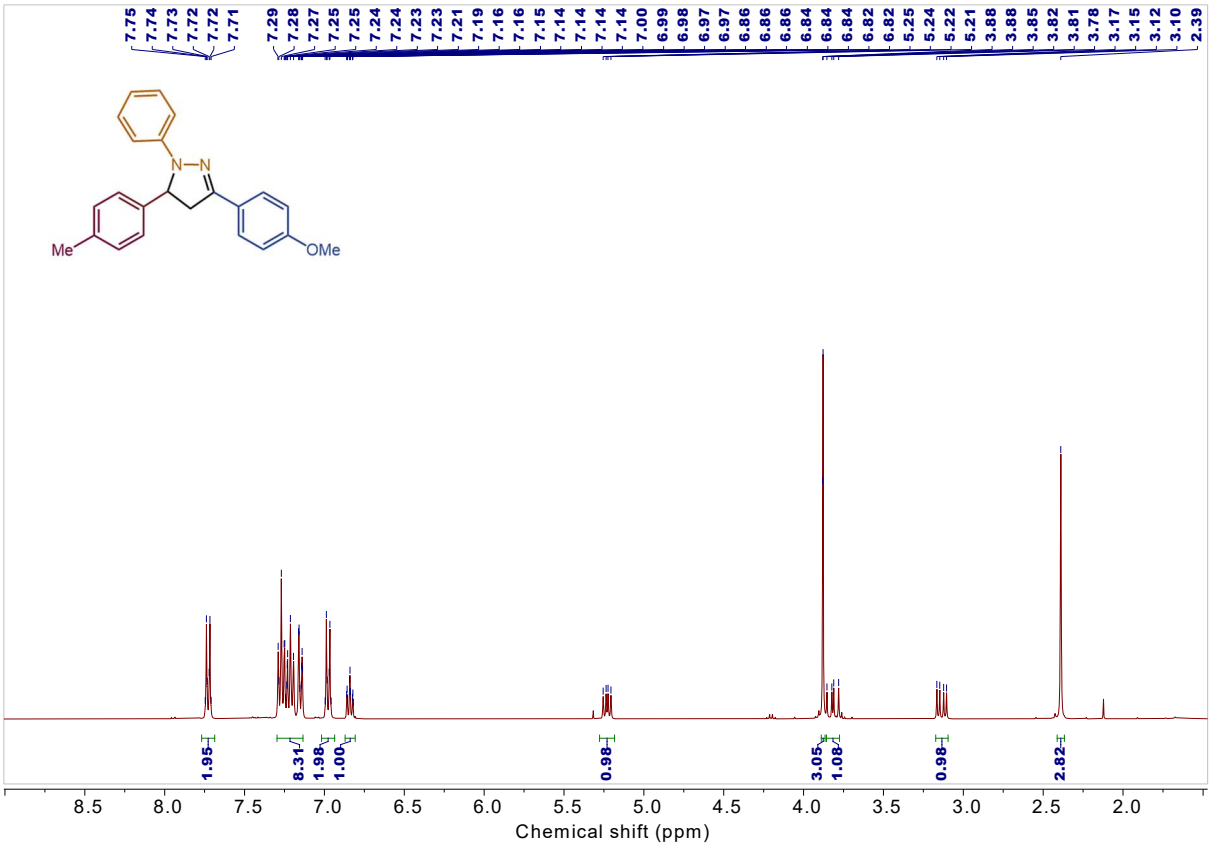


Figure S102: ^{1}H NMR spectrum of **34** (400 MHz, $CDCl_3$).

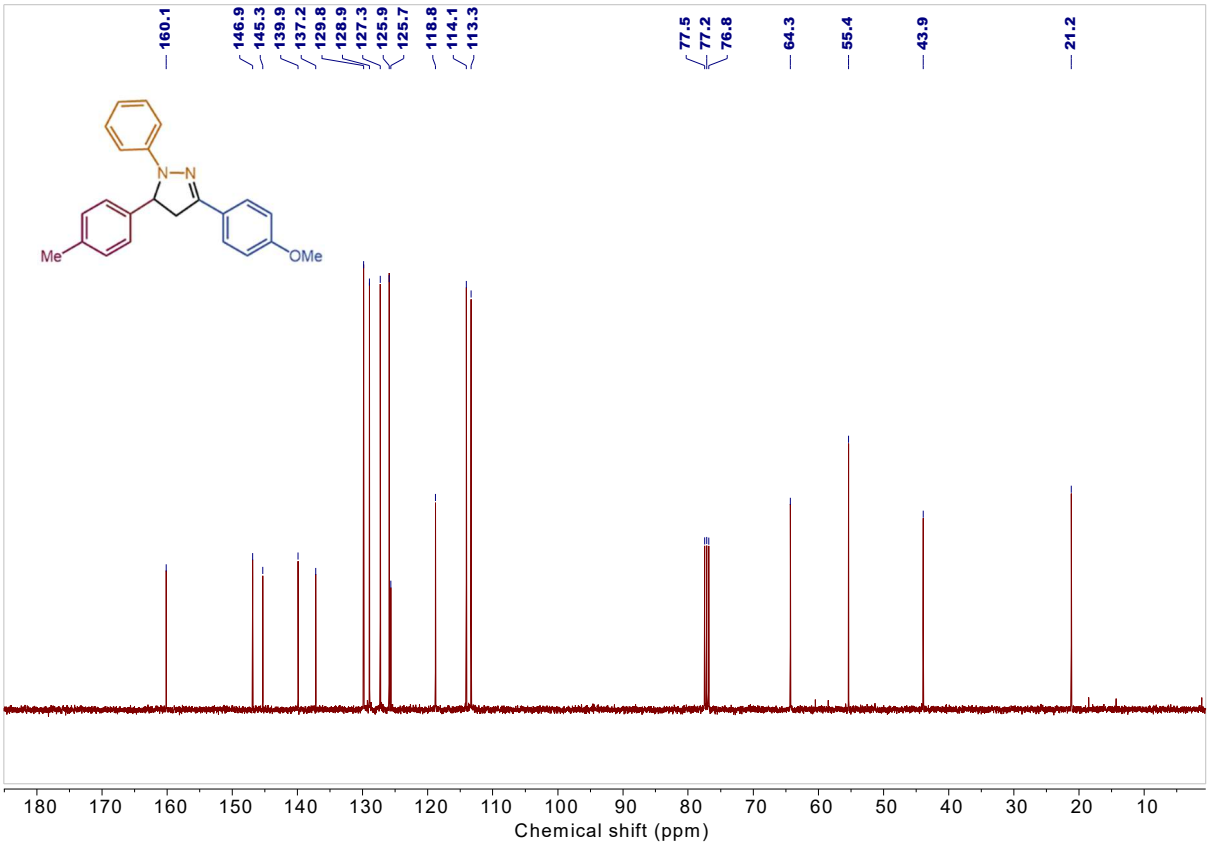


Figure S103: ^{13}C NMR spectrum of **34** (100 MHz, $CDCl_3$).

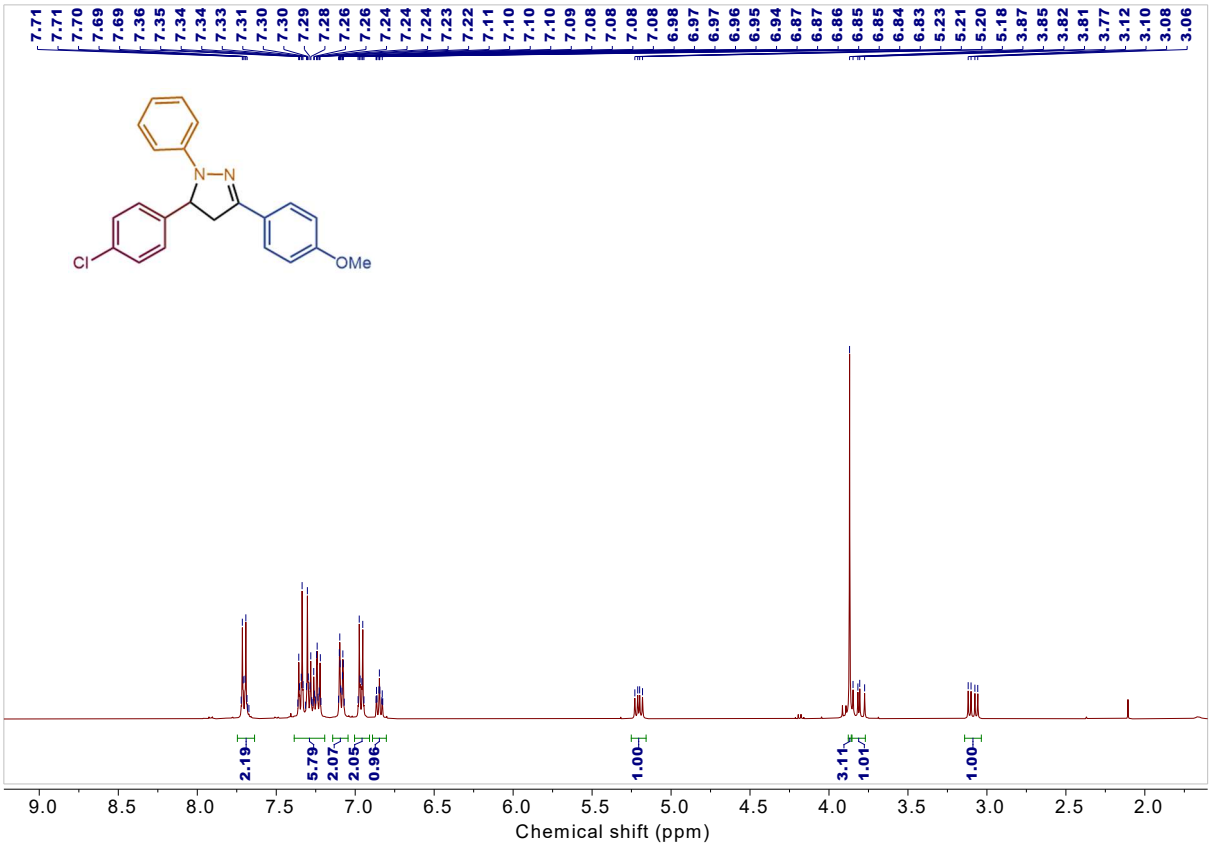


Figure S104: ^{1}H NMR spectrum of **35** (400 MHz, $CDCl_3$).

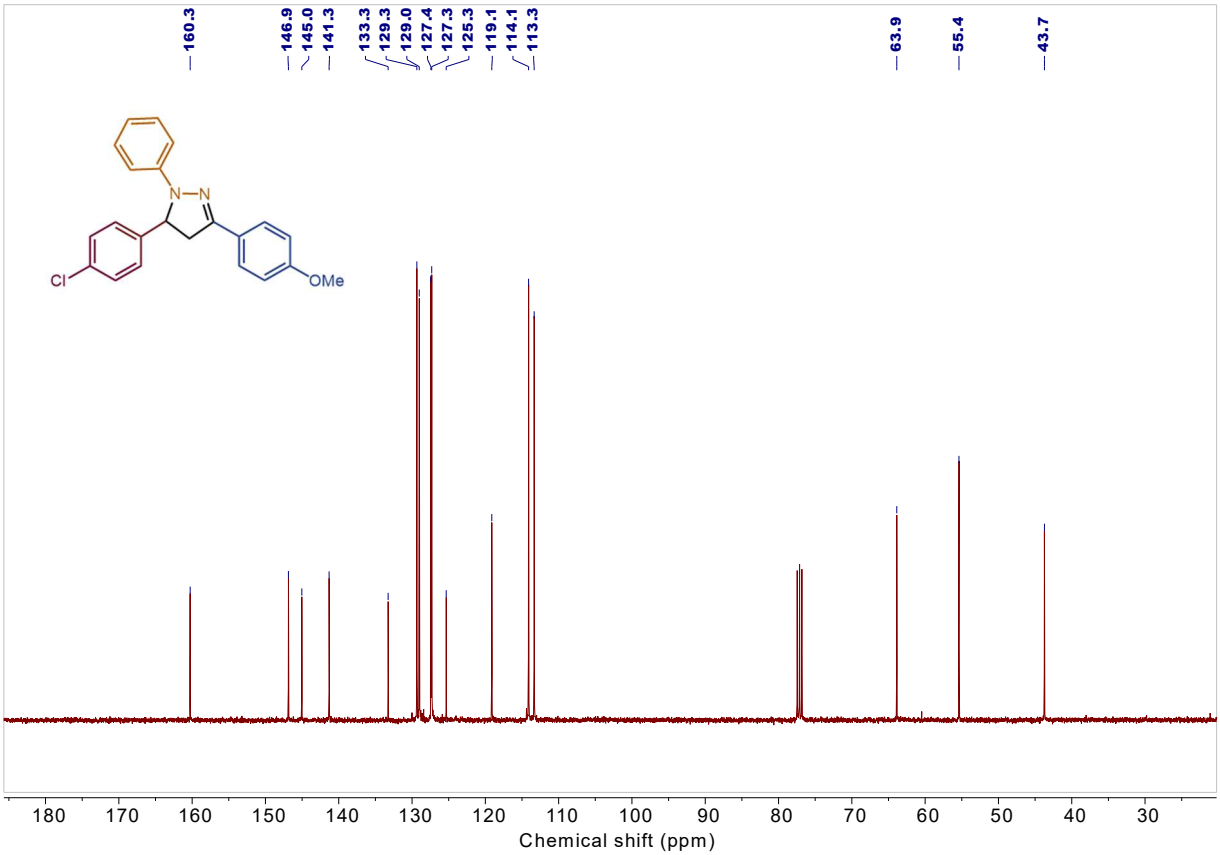


Figure S105: ^{13}C NMR spectrum of **35** (100 MHz, $CDCl_3$).

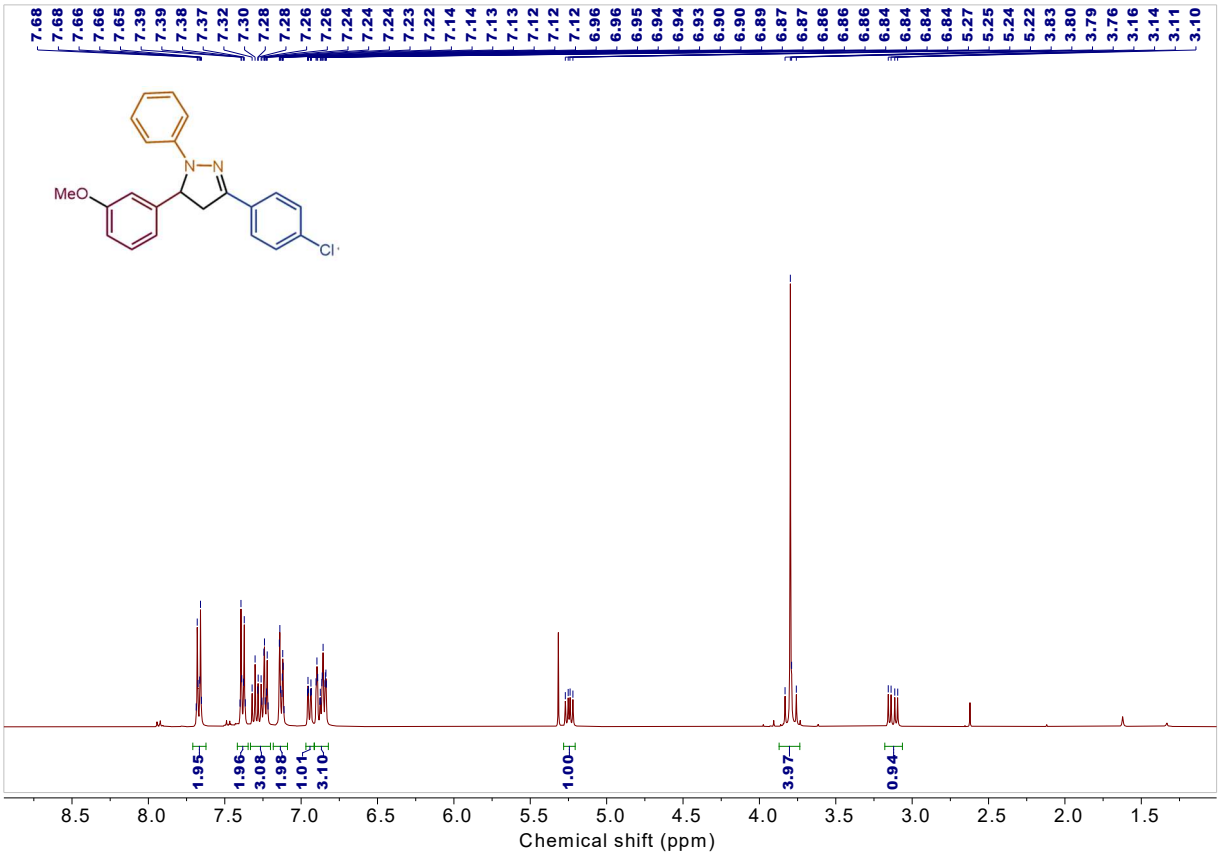


Figure S106: ^{1}H NMR spectrum of **36** (400 MHz, $CDCl_3$).

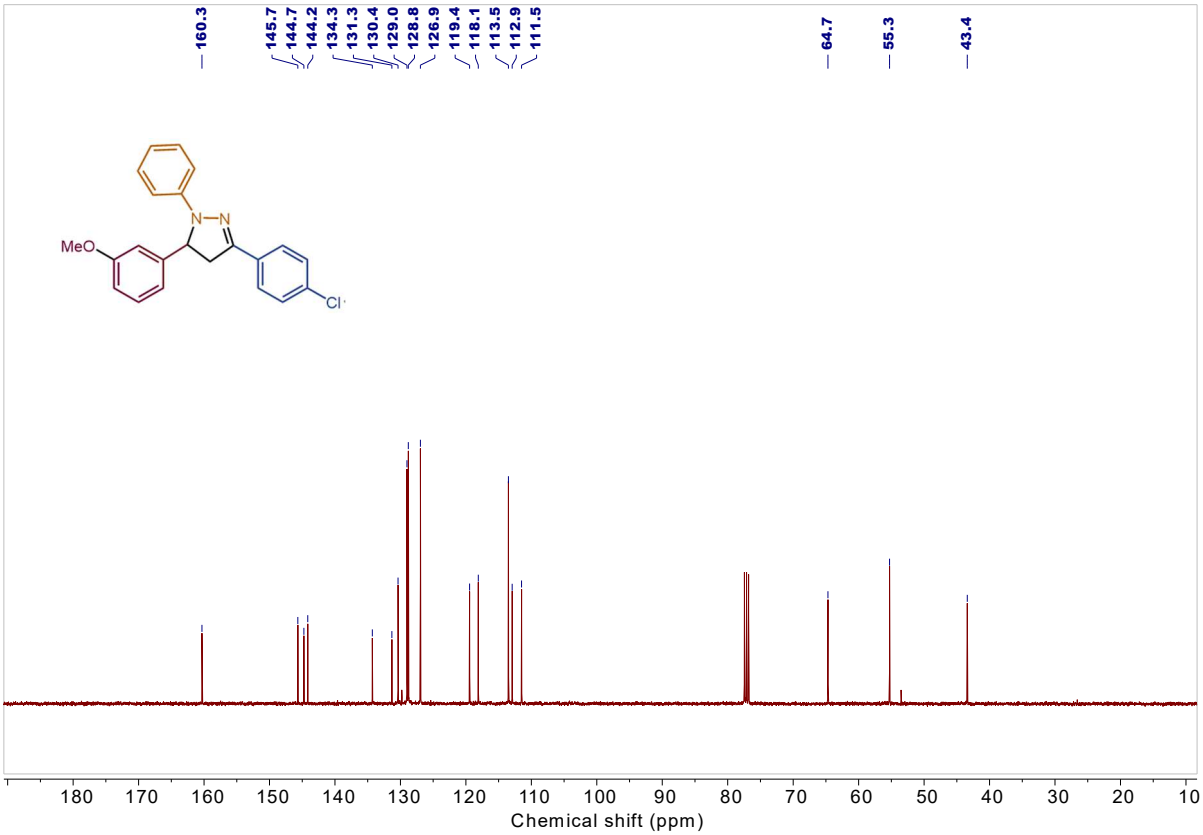


Figure S107: ^{13}C NMR spectrum of **36** (100 MHz, $CDCl_3$).

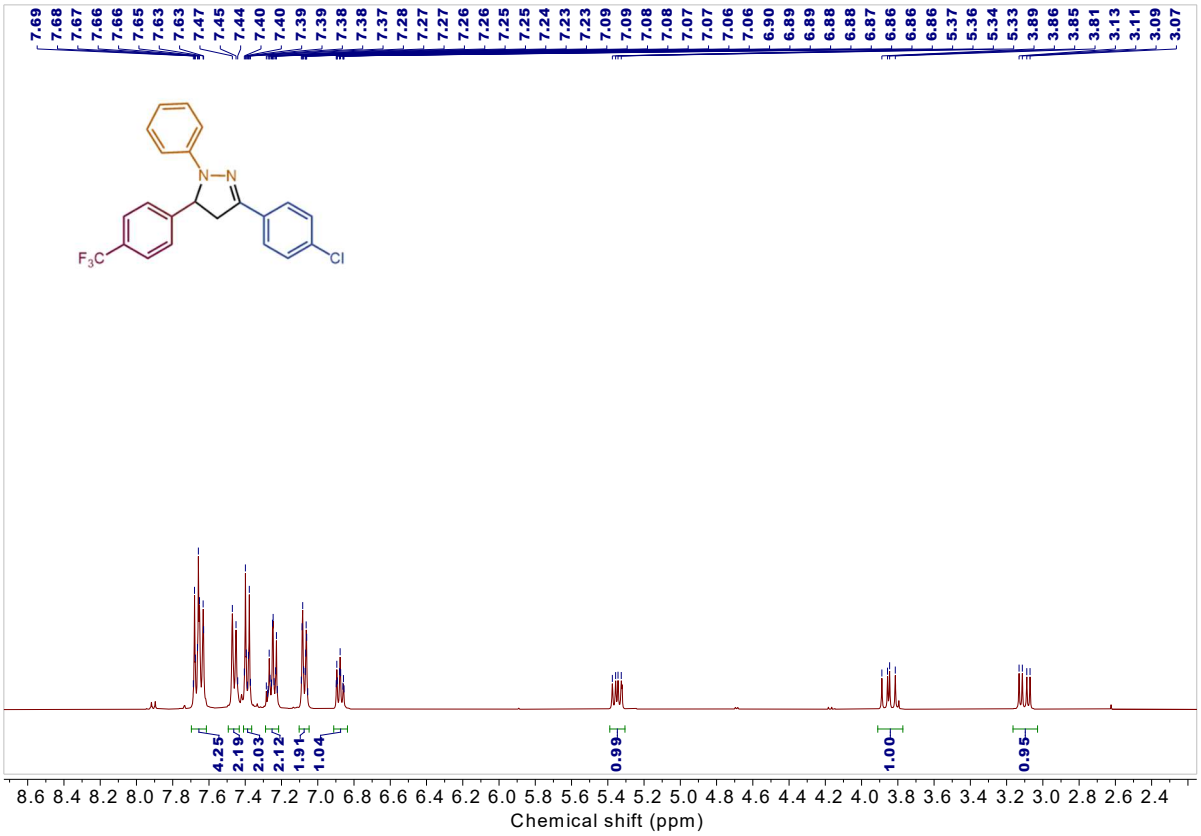


Figure S108: ^{1}H NMR spectrum of **37** (400 MHz, $CDCl_3$).

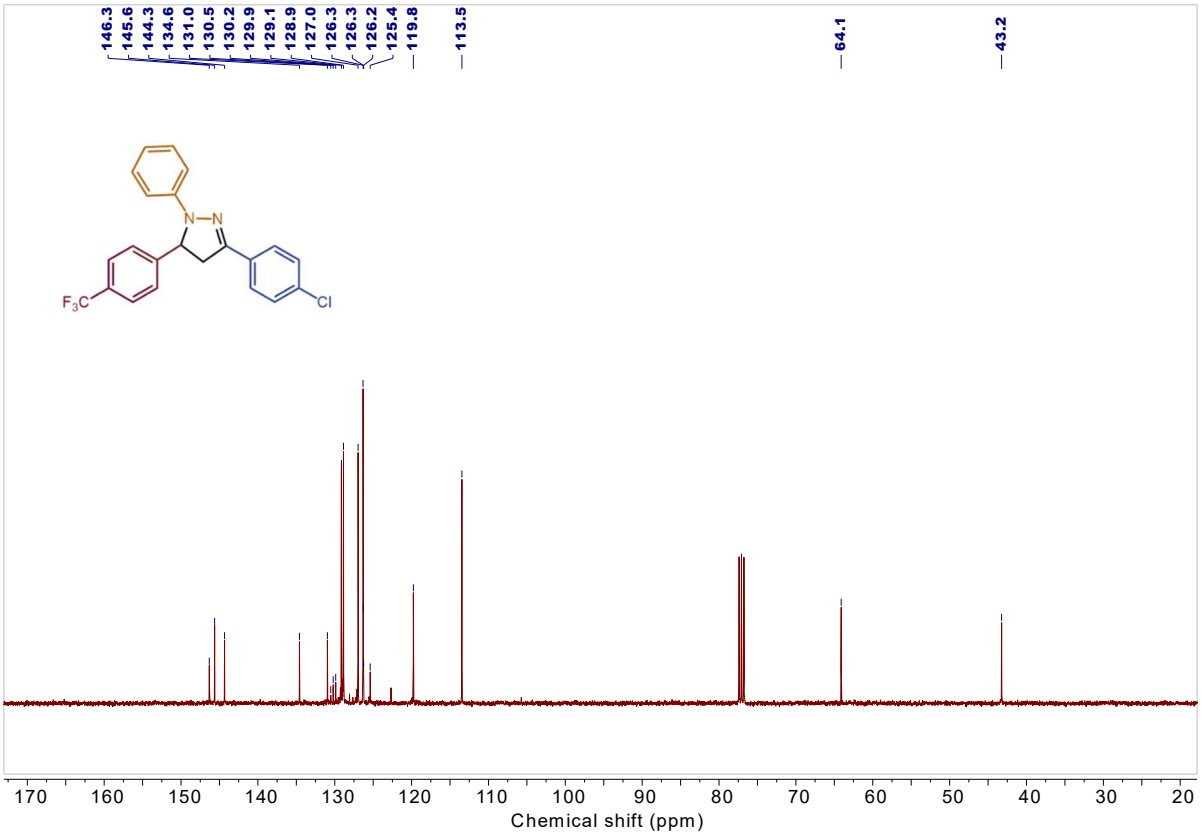


Figure S109: ^{13}C NMR spectrum of **37** (100 MHz, $CDCl_3$).

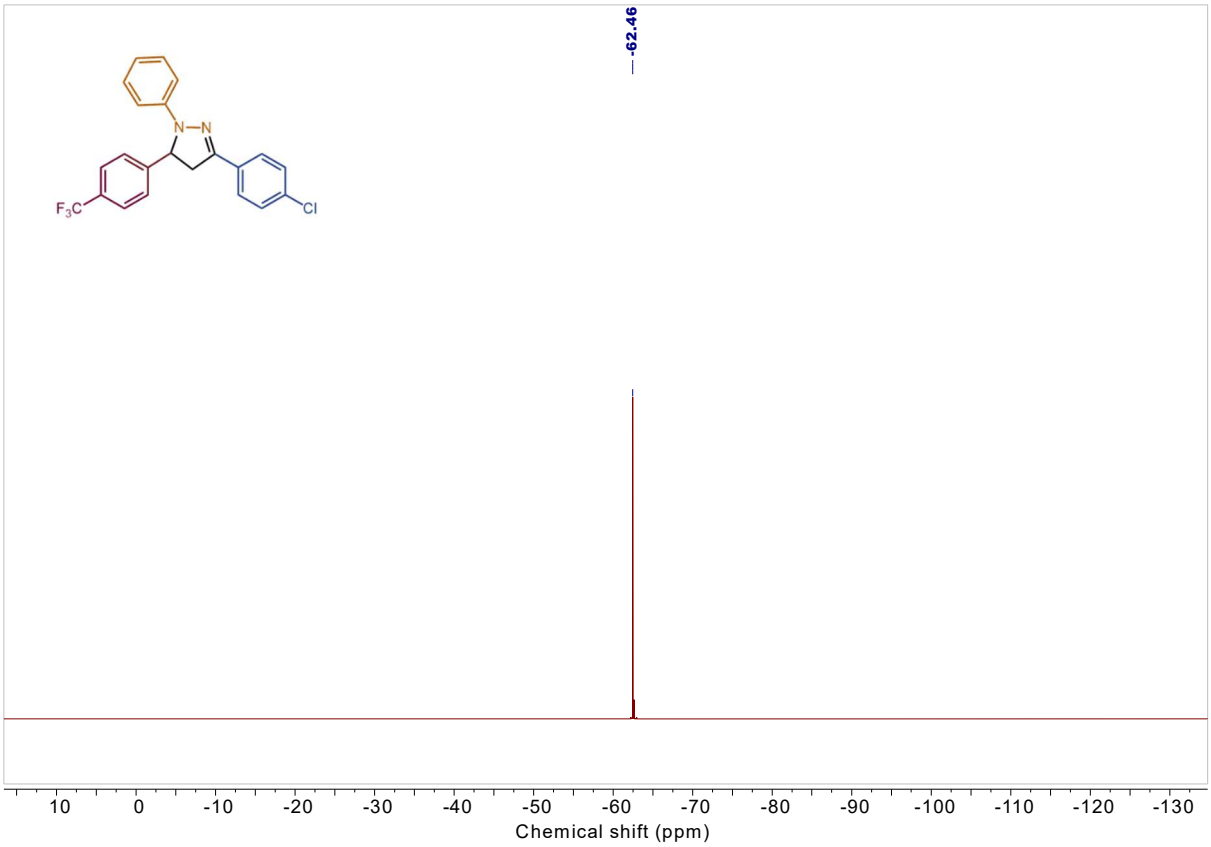


Figure S110: ^{19}F NMR spectrum of **37** (376 MHz, $CDCl_3$).

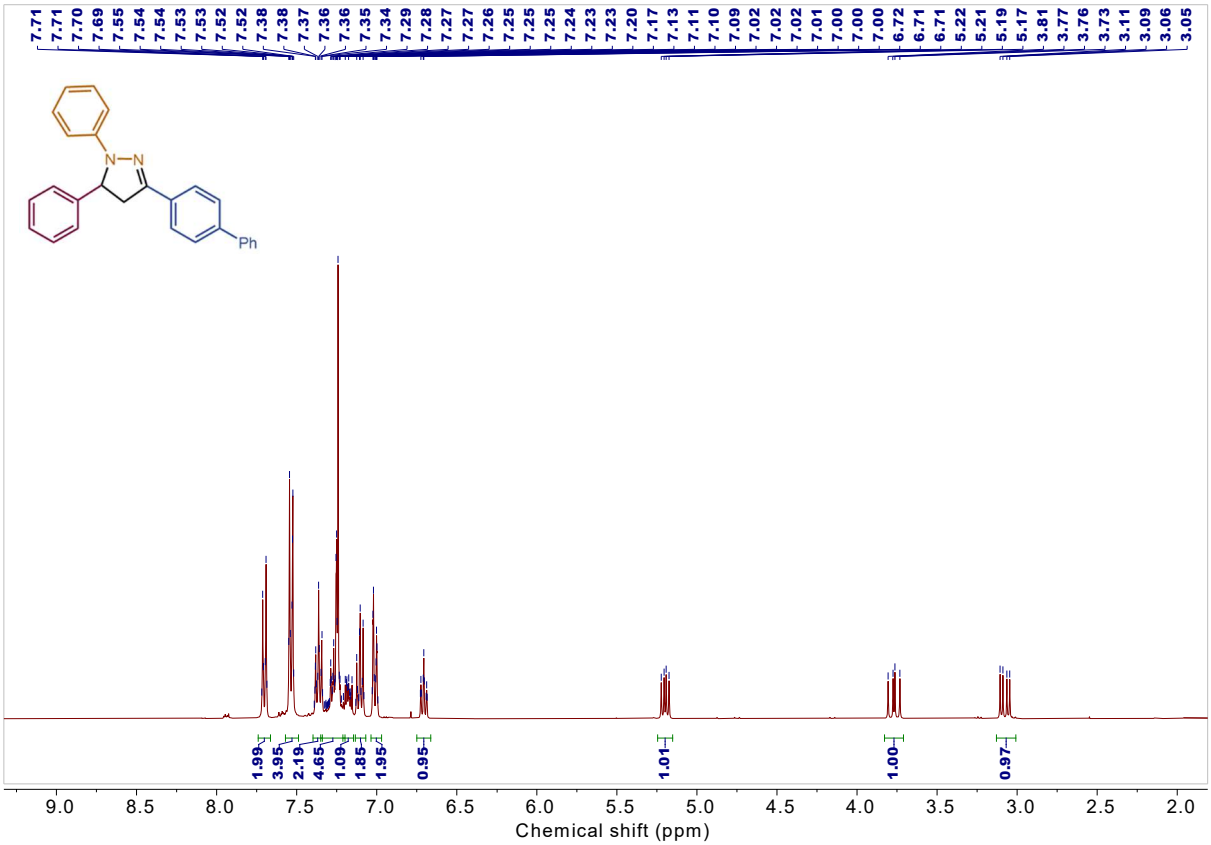


Figure S111: ^{1}H NMR spectrum of **38** (400 MHz, $CDCl_3$).

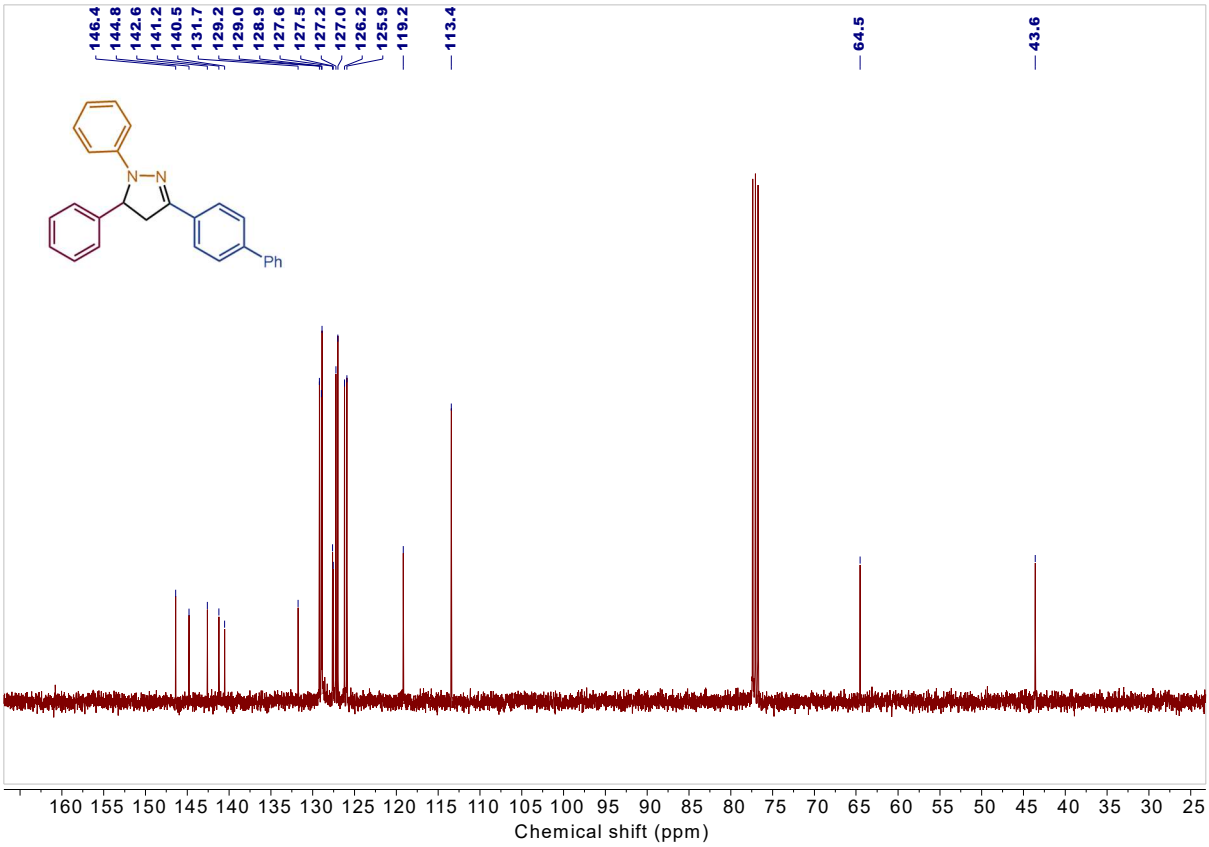


Figure S112: ^{13}C NMR spectrum of **38** (100 MHz, $CDCl_3$).

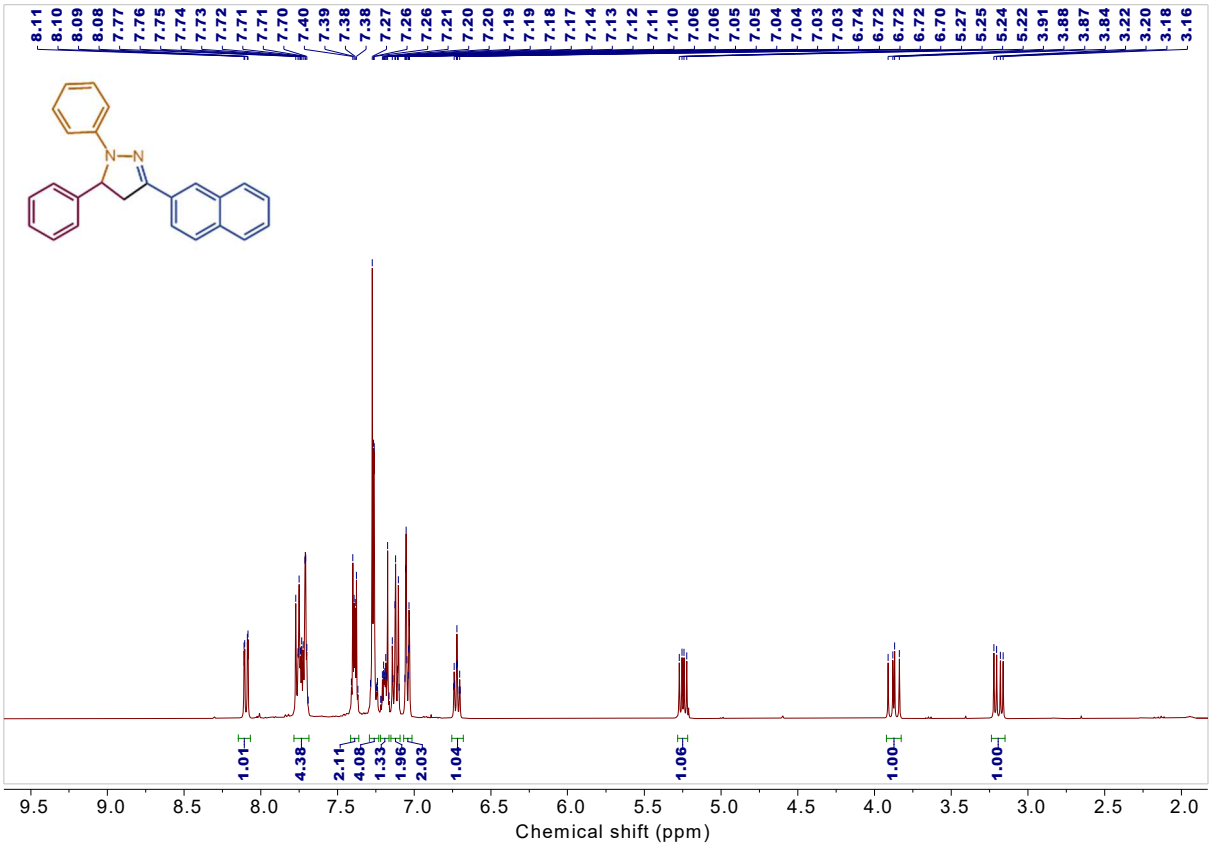


Figure S113: ^{1}H NMR spectrum of **39** (400 MHz, $CDCl_3$).

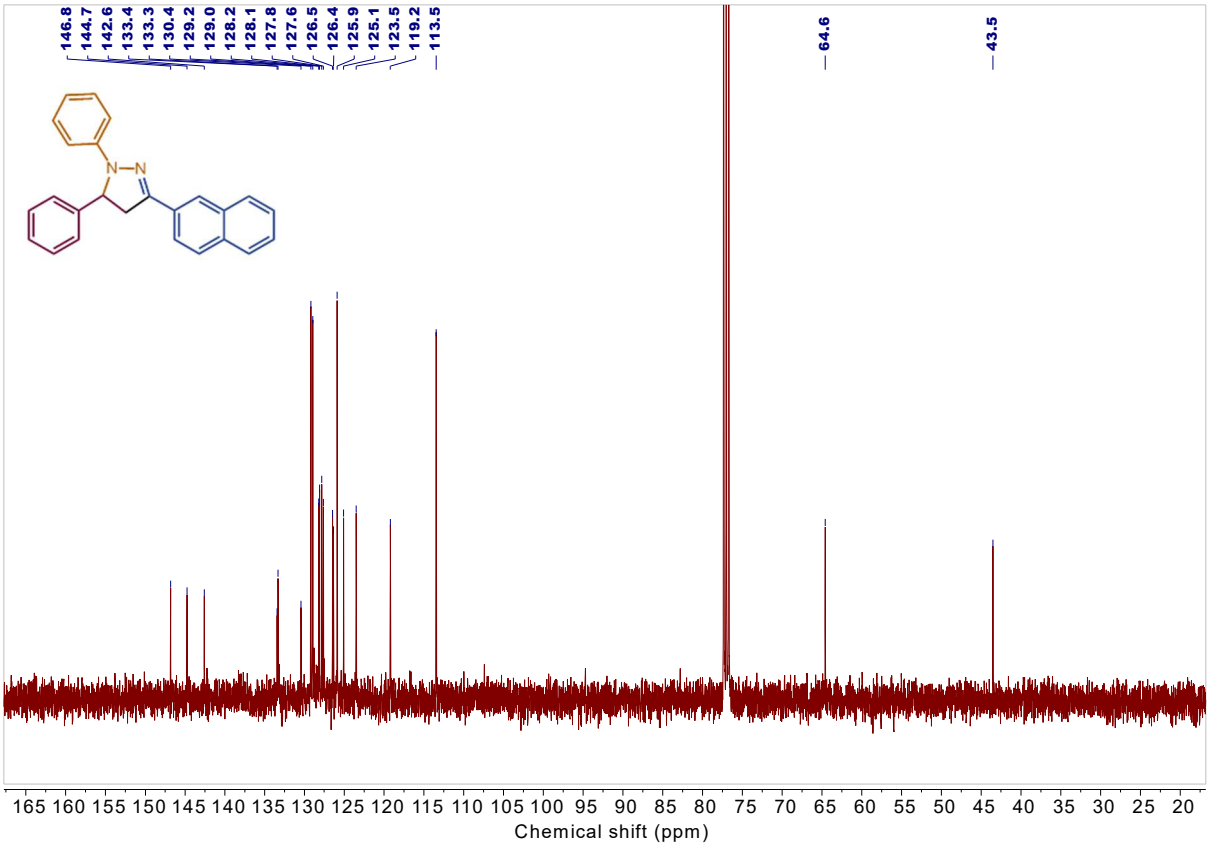


Figure S114: ^{13}C NMR spectrum of **39** (100 MHz, $CDCl_3$).

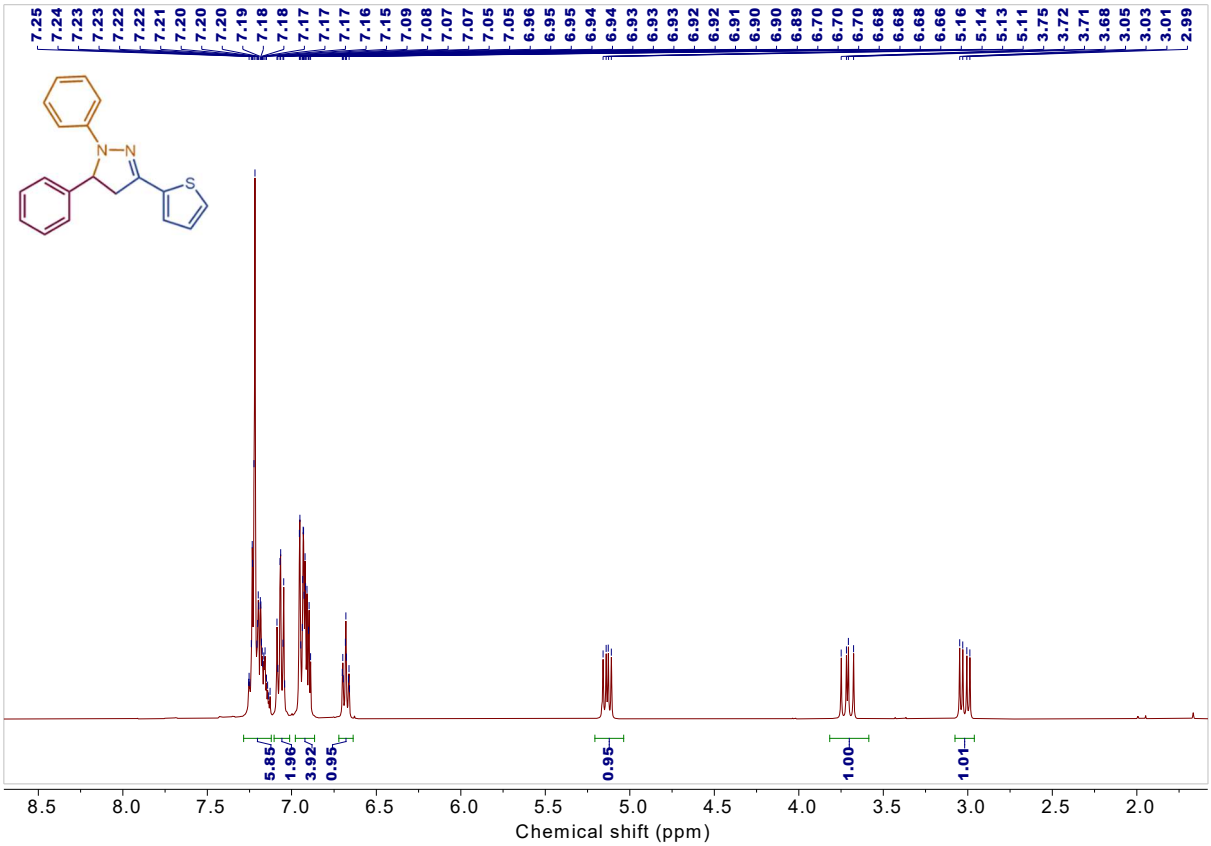


Figure S115: ^{1}H NMR spectrum of **40** (400 MHz, $CDCl_3$).

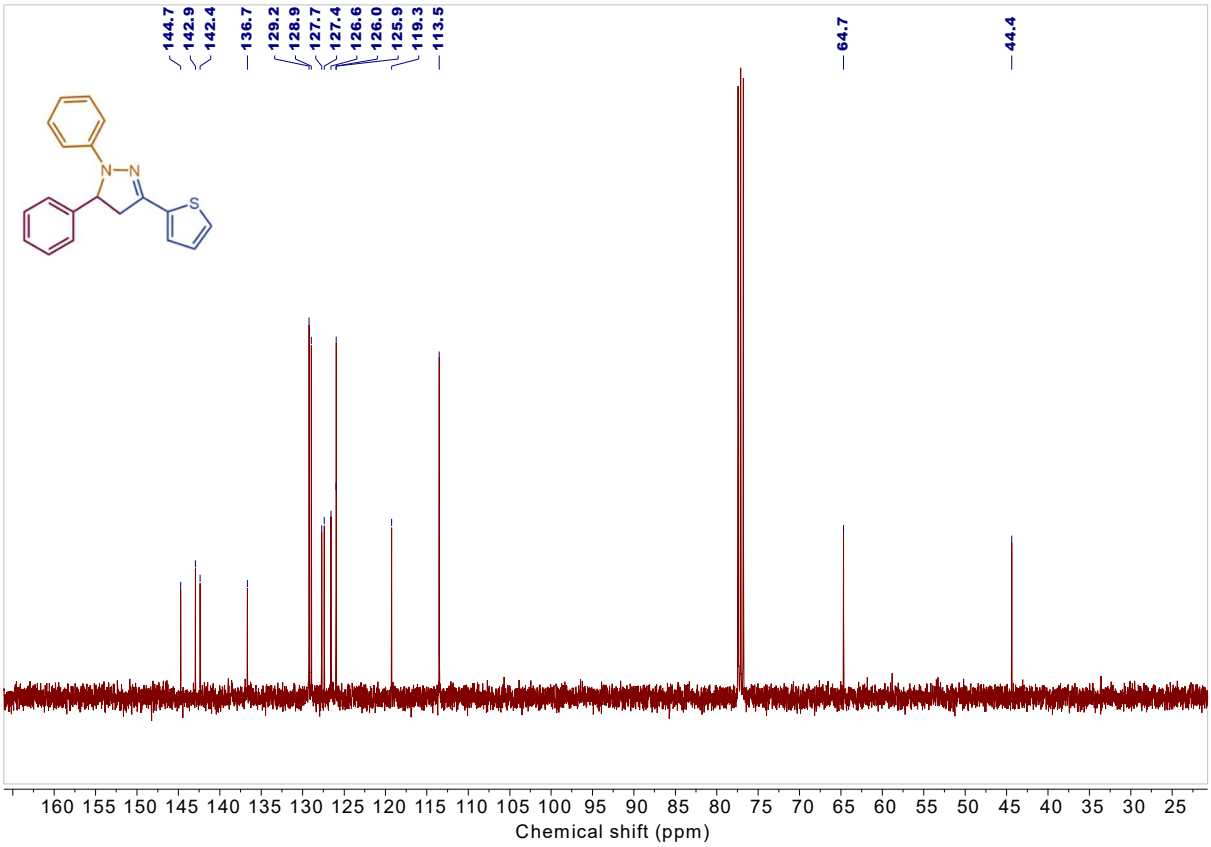


Figure S116: ^{13}C NMR spectrum of **40** (100 MHz, $CDCl_3$).

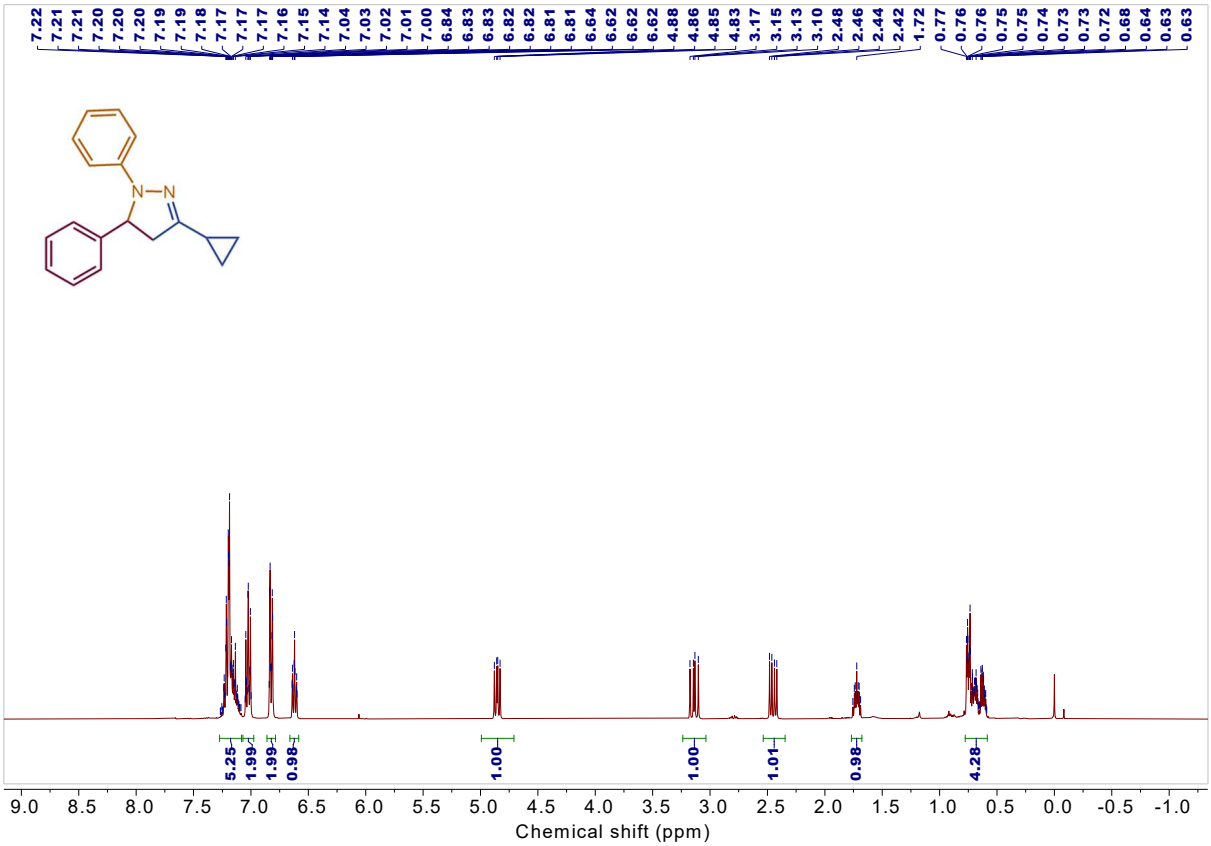


Figure S117: ^{1}H NMR spectrum of **41** (400 MHz, $CDCl_3$).

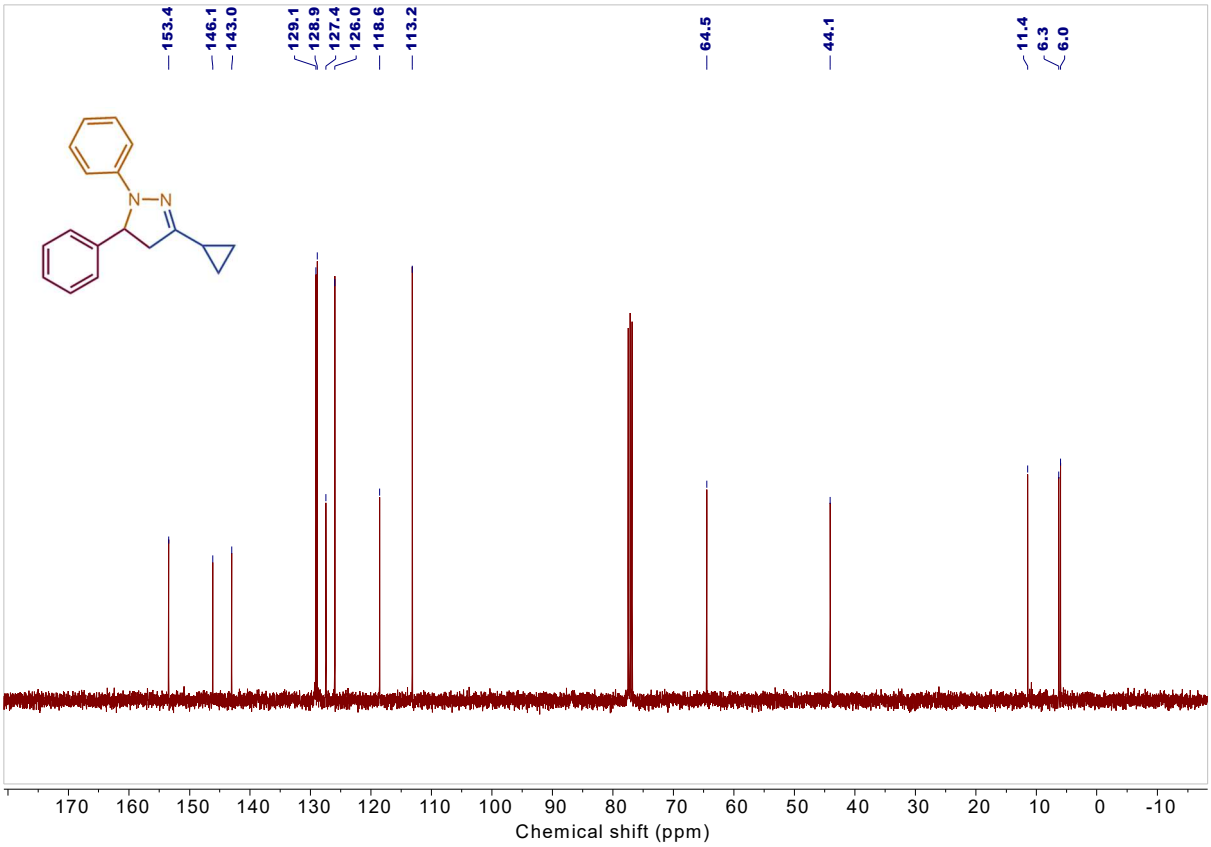


Figure S118: ^{13}C NMR spectrum of **41** (100 MHz, $CDCl_3$).

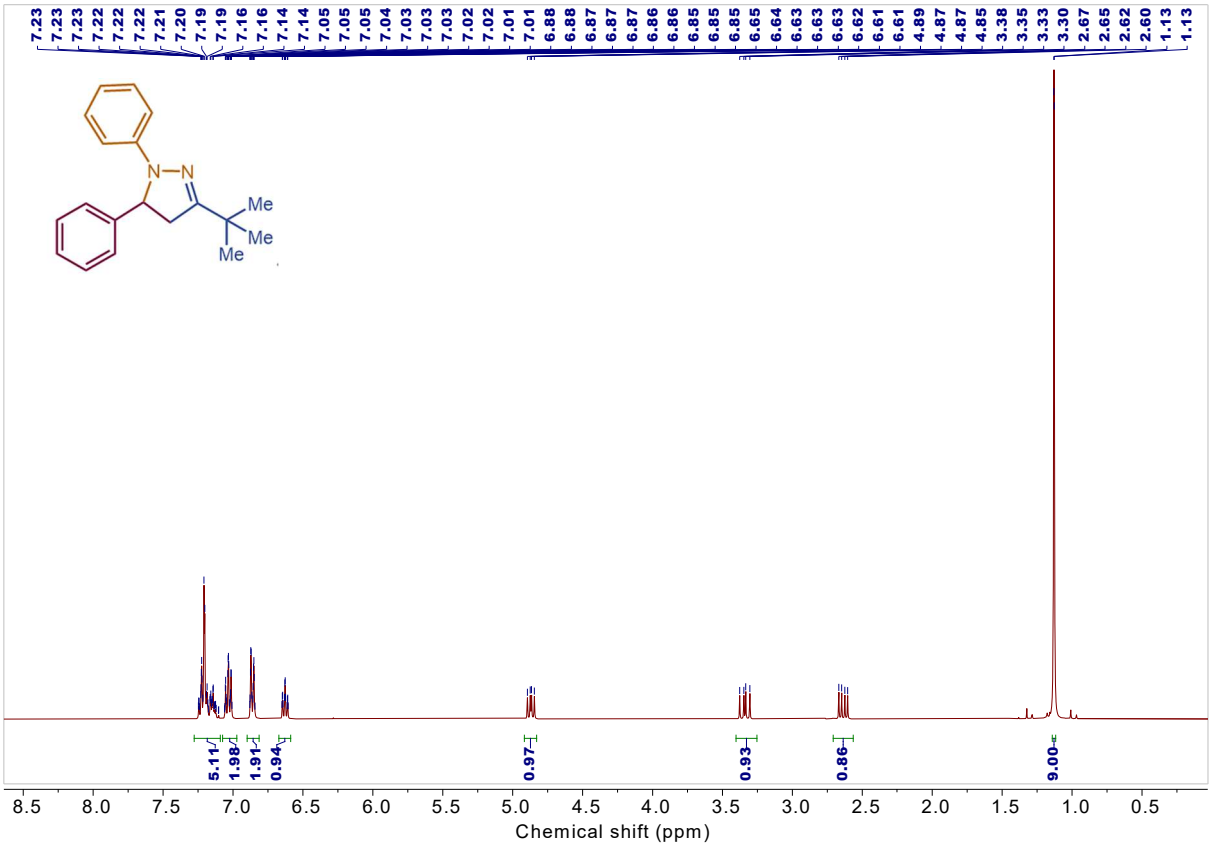


Figure S119: ^{1}H NMR spectrum of **42** (400 MHz, $CDCl_3$).

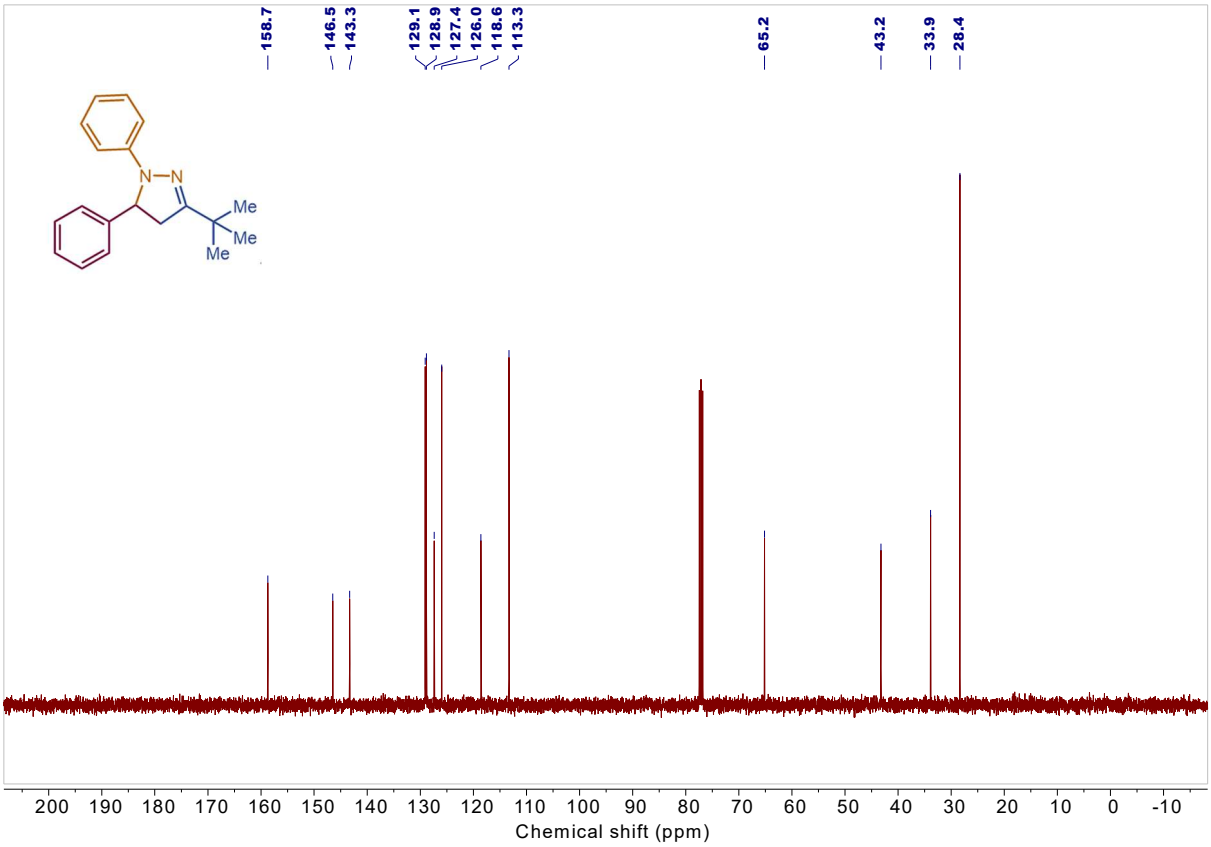


Figure S120: ^{13}C NMR spectrum of **42** (100 MHz, $CDCl_3$).

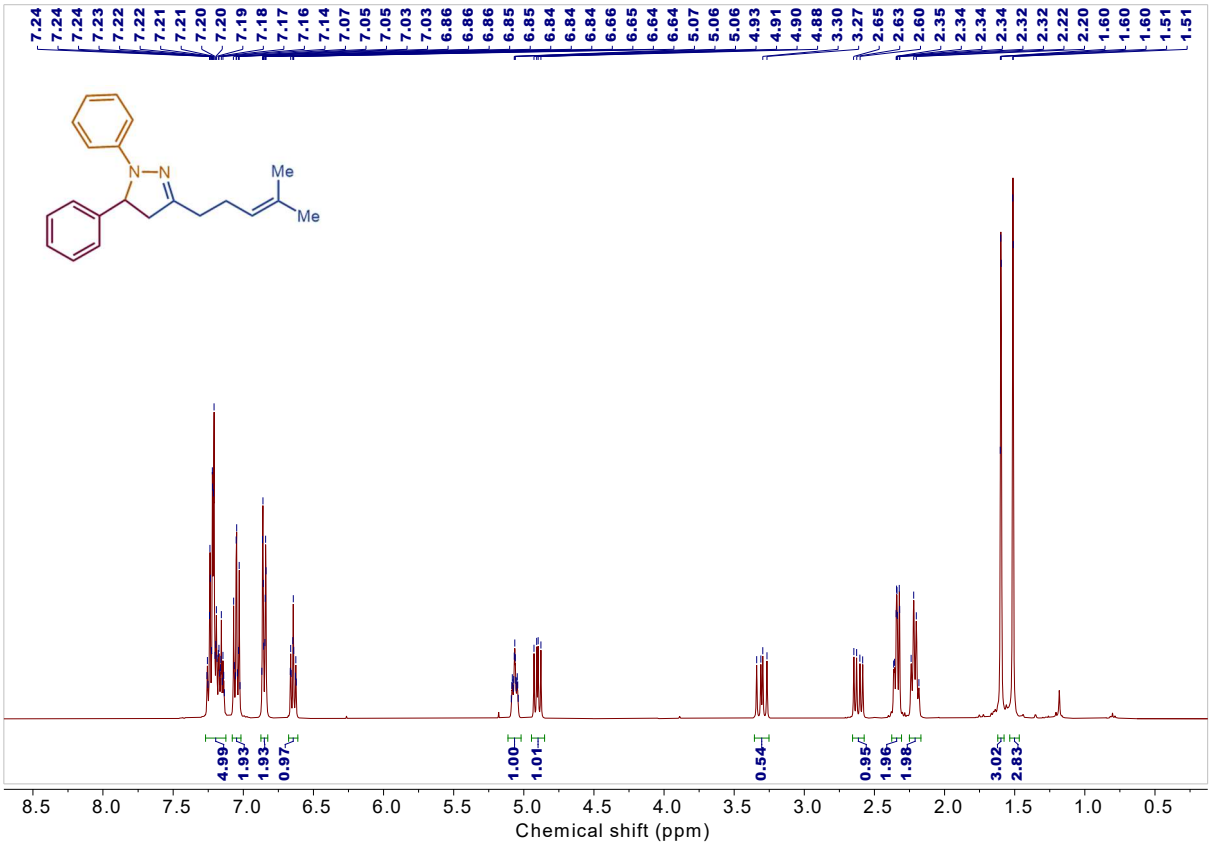


Figure S121: ^{1}H NMR spectrum of **43** (400 MHz, $CDCl_3$).

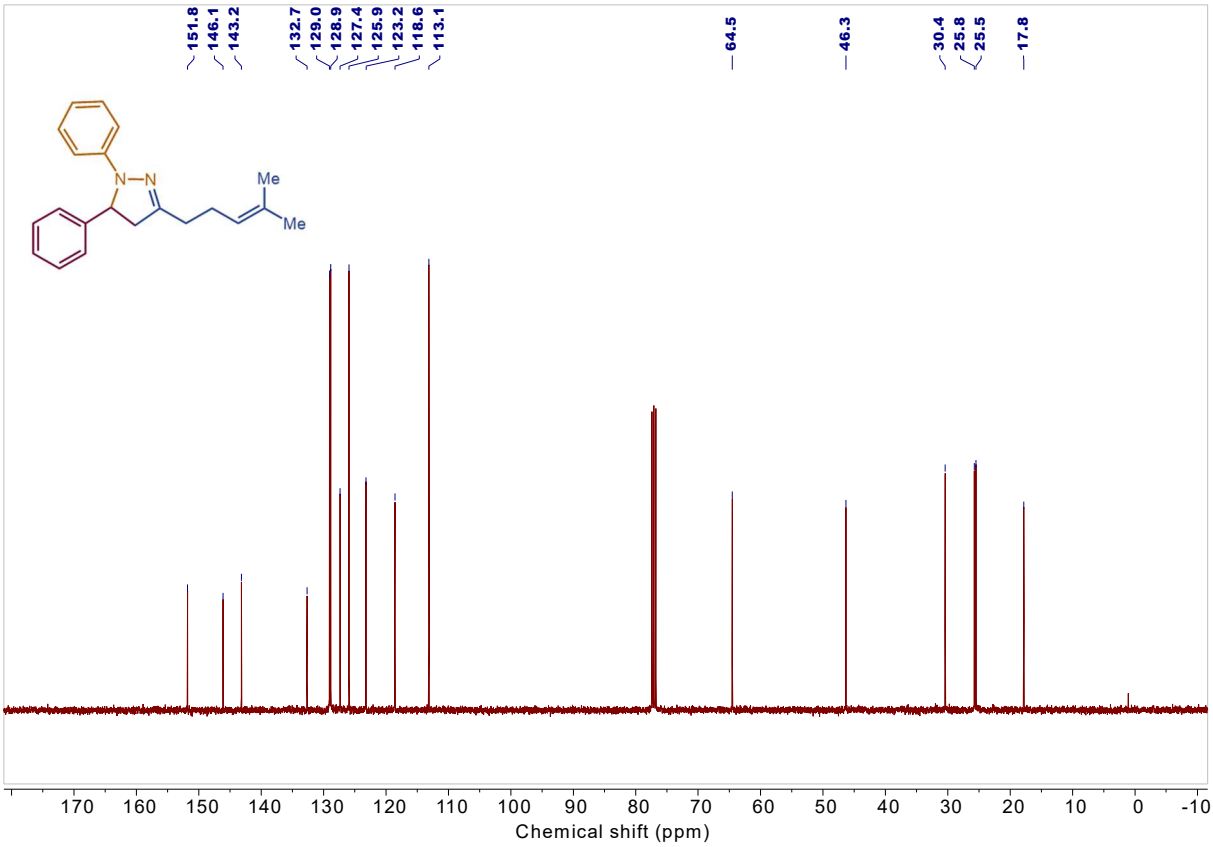


Figure S122: ^{13}C NMR spectrum of **43** (100 MHz, $CDCl_3$).

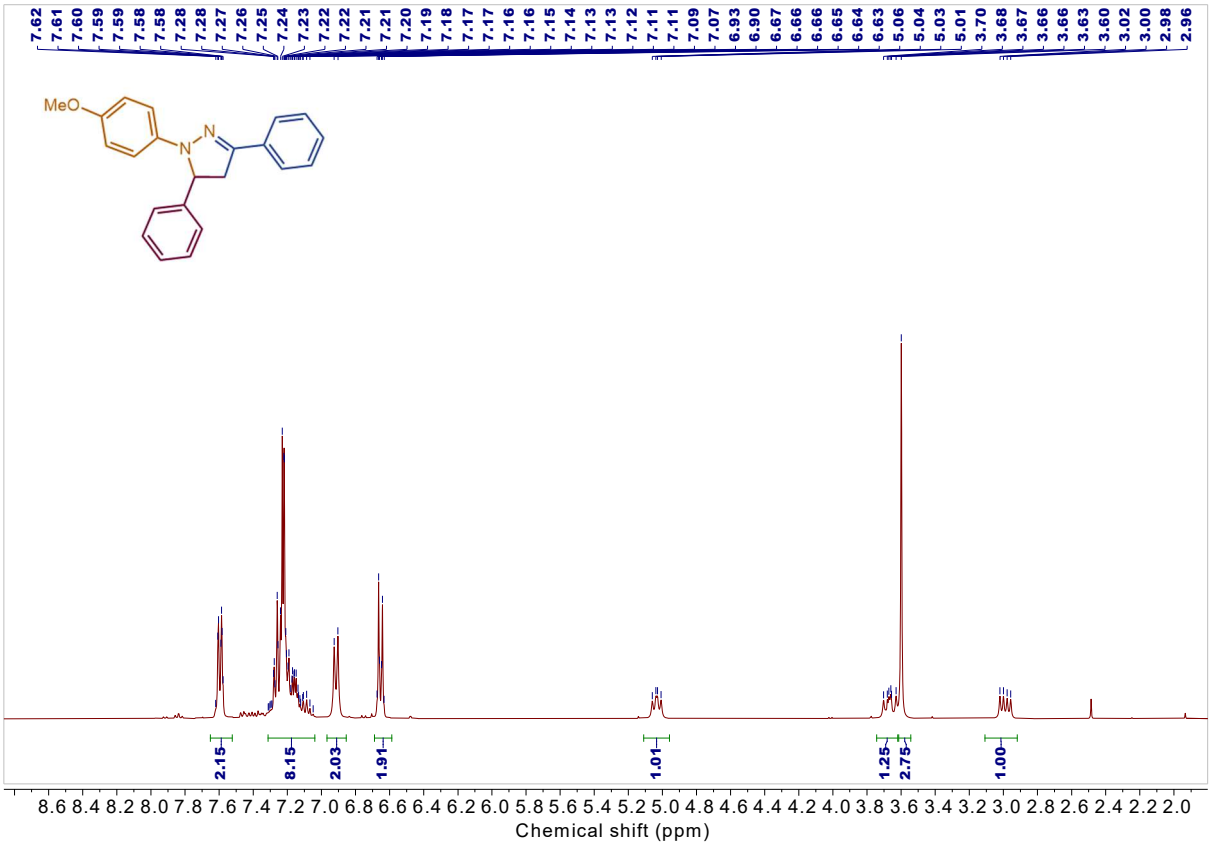


Figure S123: ^{1}H NMR spectrum of **44** (400 MHz, $CDCl_3$).

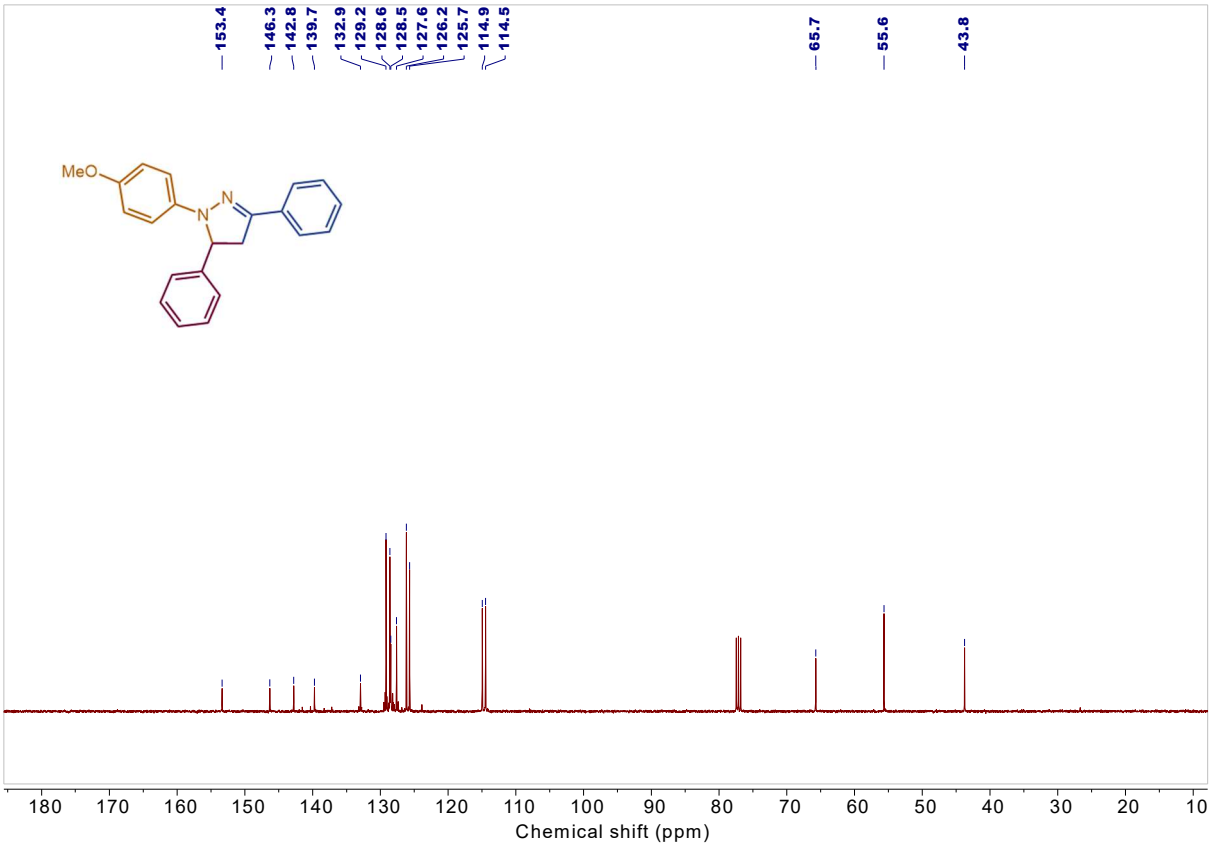


Figure S124: ^{13}C NMR spectrum of **44** (100 MHz, $CDCl_3$).

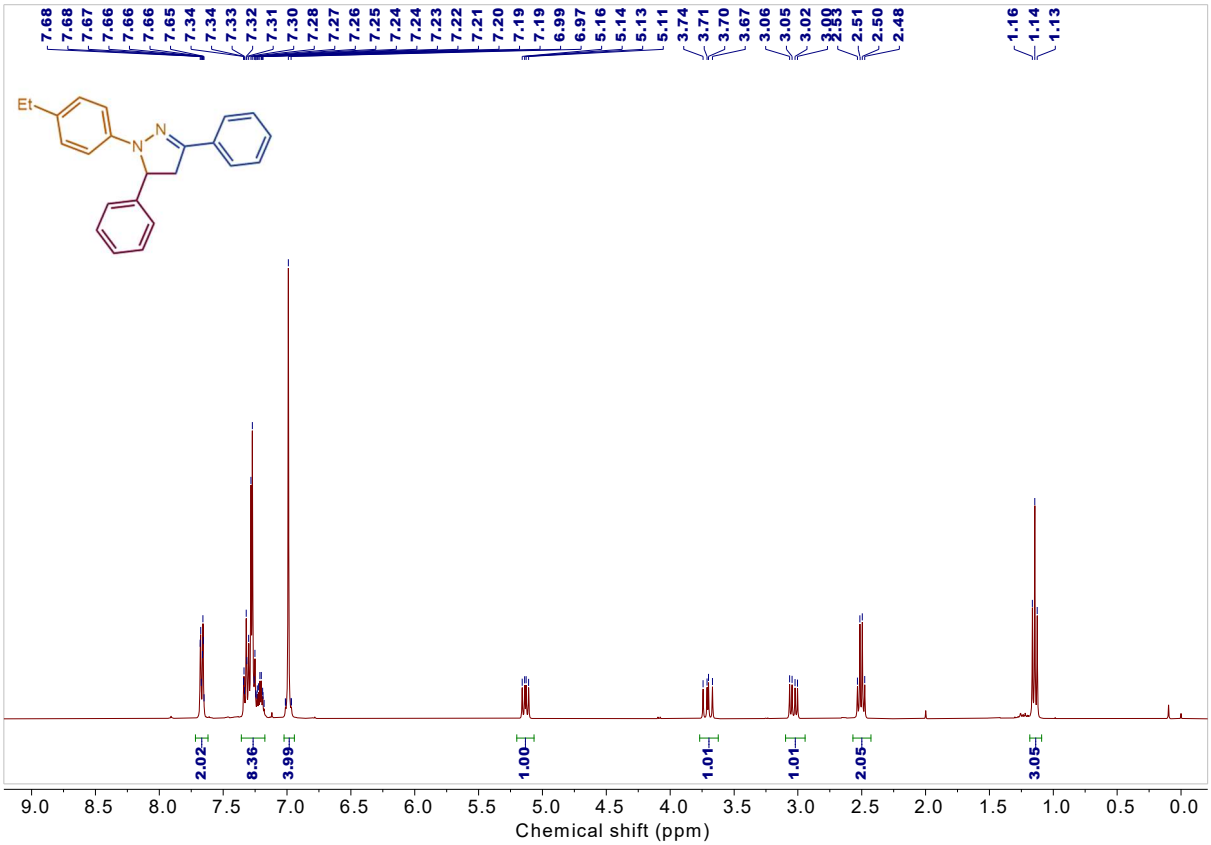


Figure S125: ^{1}H NMR spectrum of **45** (400 MHz, $CDCl_3$).

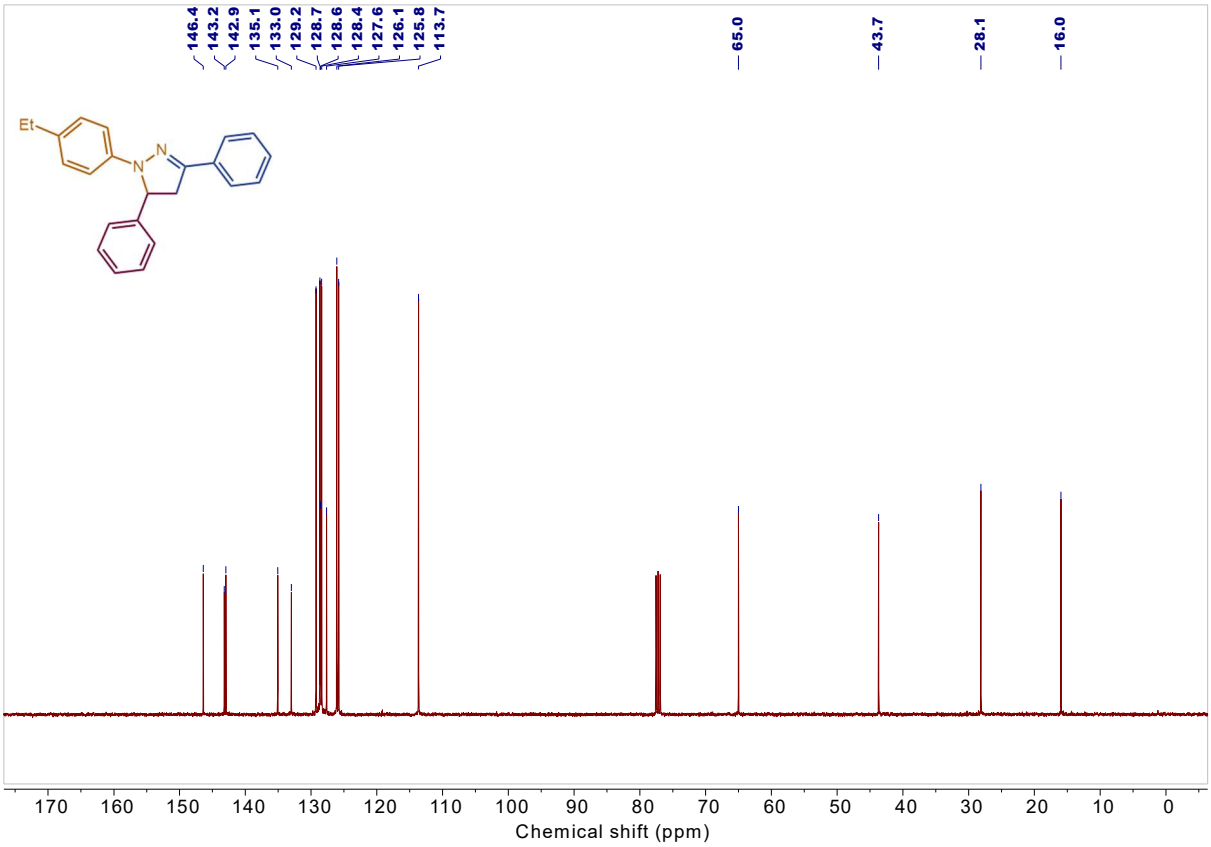


Figure S126: ^{13}C NMR spectrum of **45** (100 MHz, $CDCl_3$).

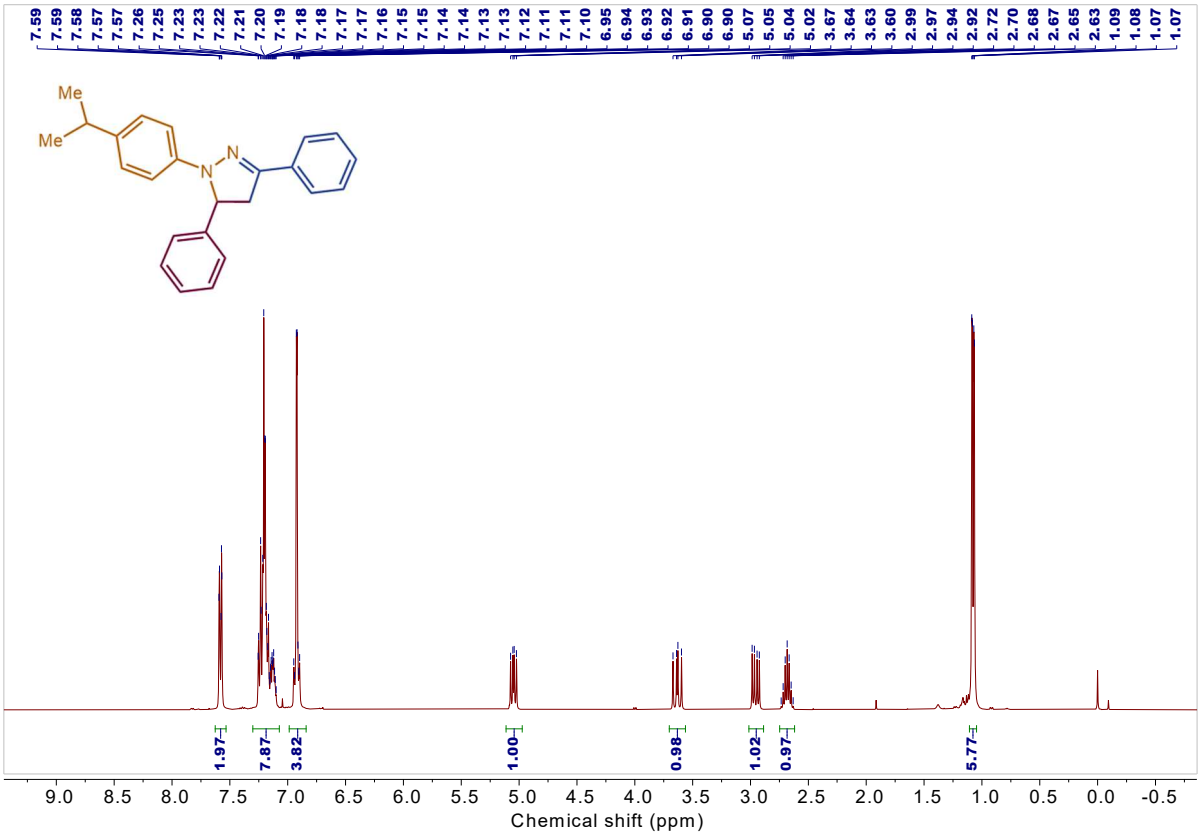


Figure S127: ^{1}H NMR spectrum of **46** (400 MHz, $CDCl_3$).

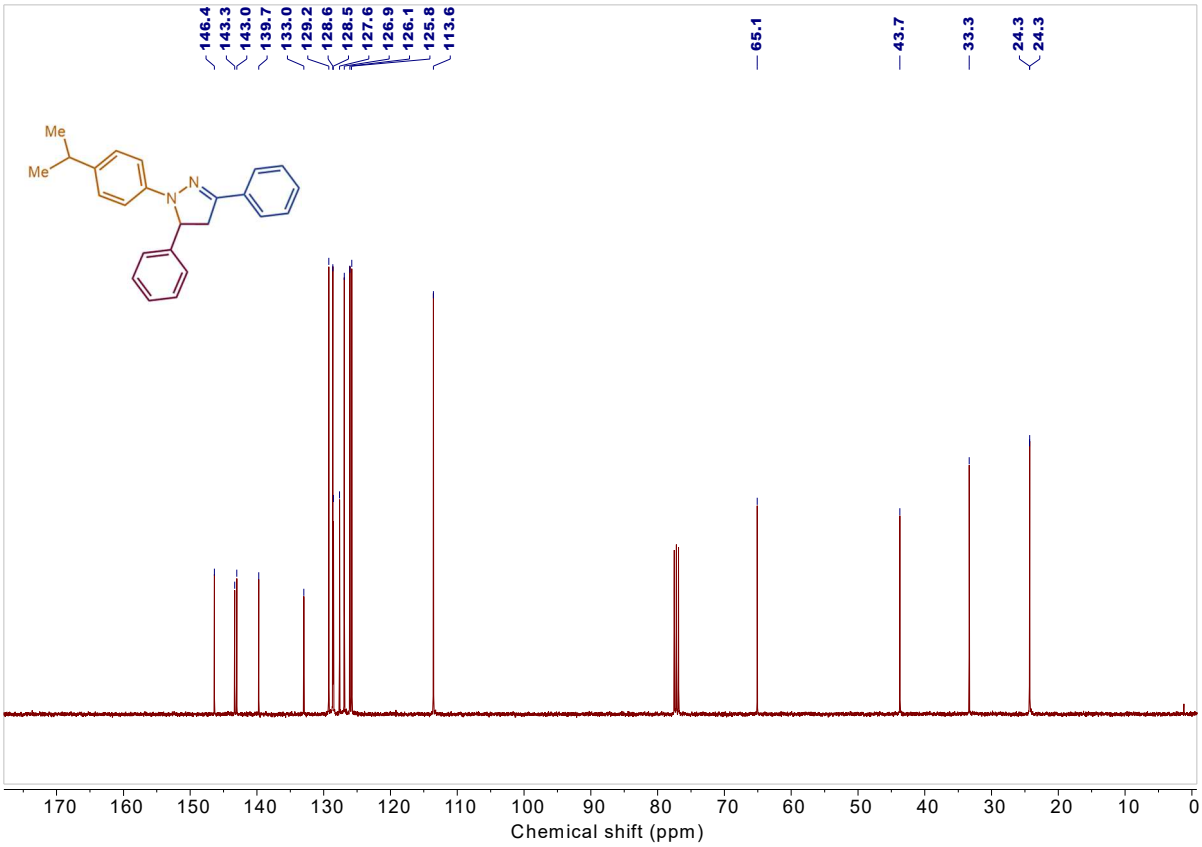


Figure S128: ^{13}C NMR spectrum of **46** (100 MHz, $CDCl_3$).

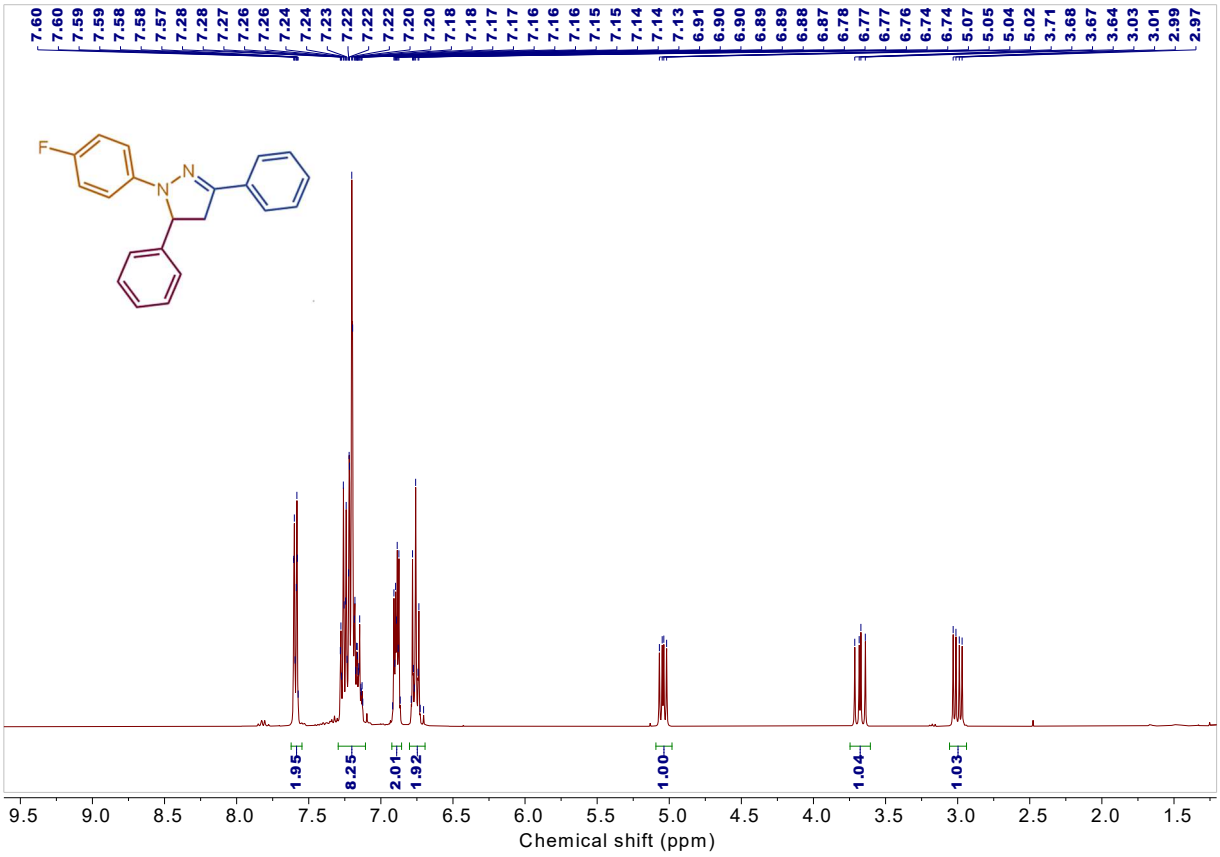


Figure S129: ^{1}H NMR spectrum of **47** (400 MHz, $CDCl_3$).

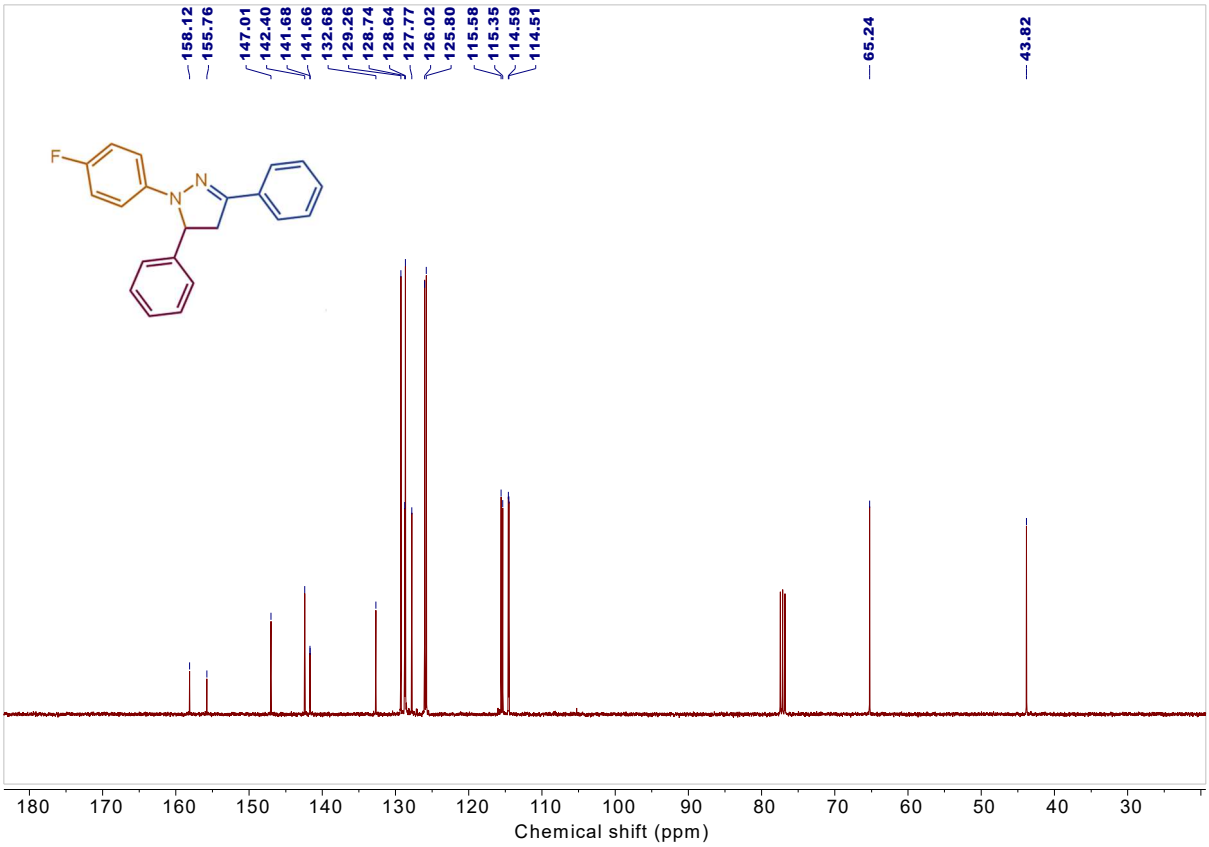


Figure S130: ^{13}C NMR spectrum of **47** (100 MHz, $CDCl_3$).

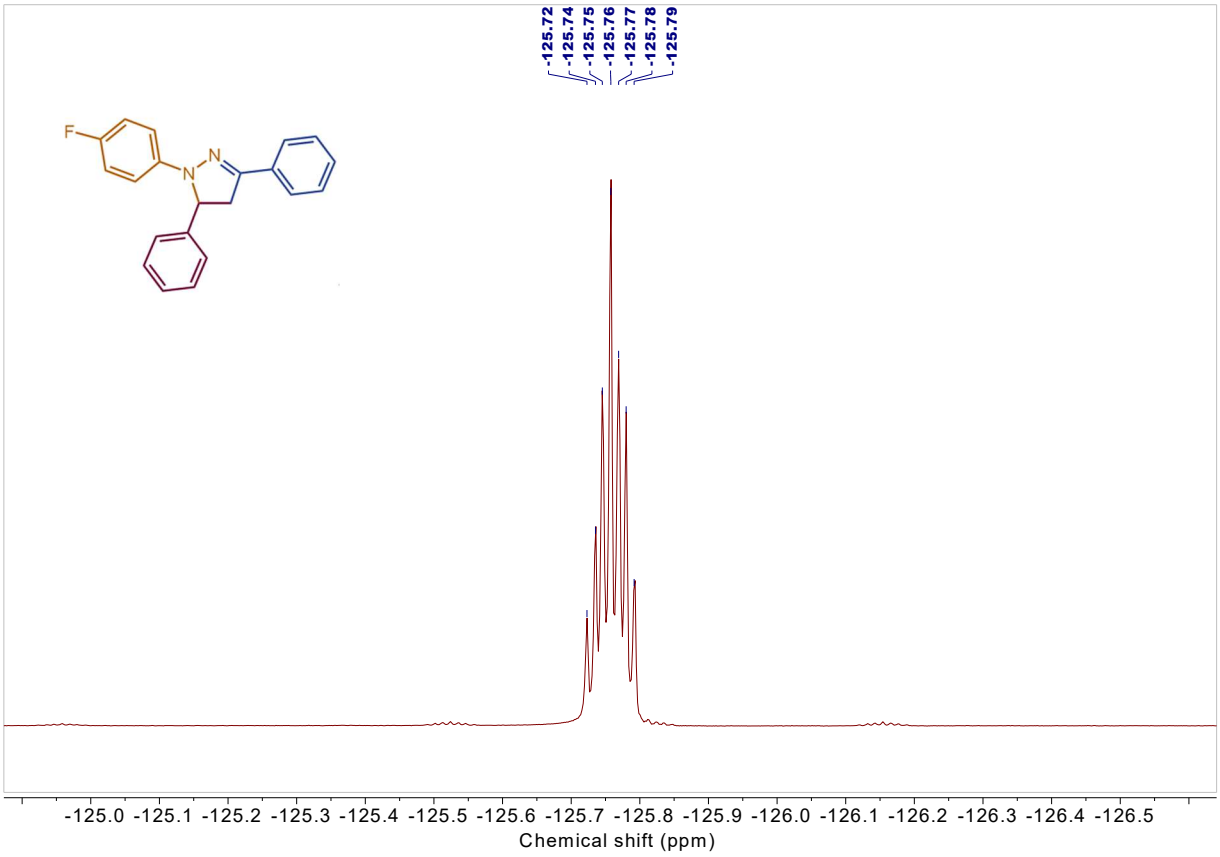


Figure S131: ^{19}F NMR spectrum of **47** (376 MHz, $CDCl_3$).

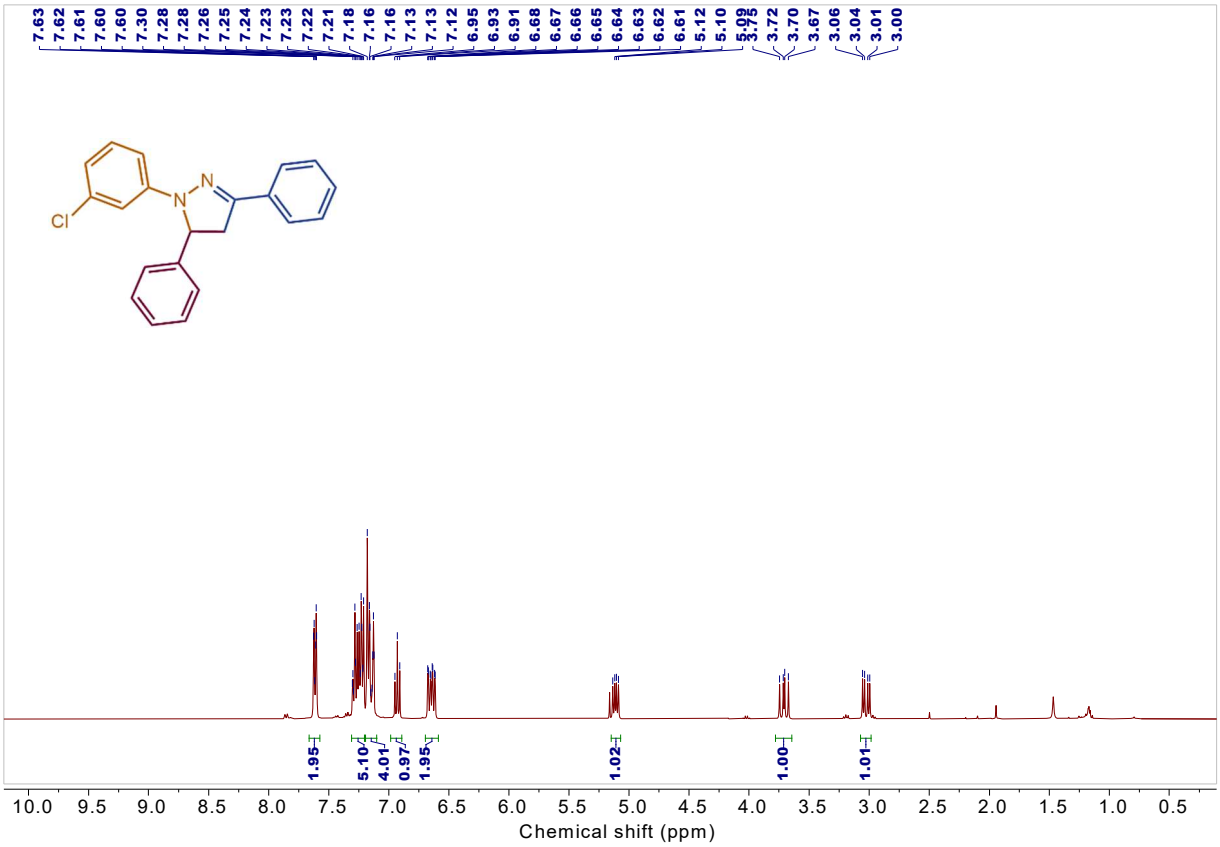


Figure S132: ^{1}H NMR spectrum of **48** (400 MHz, $CDCl_3$).

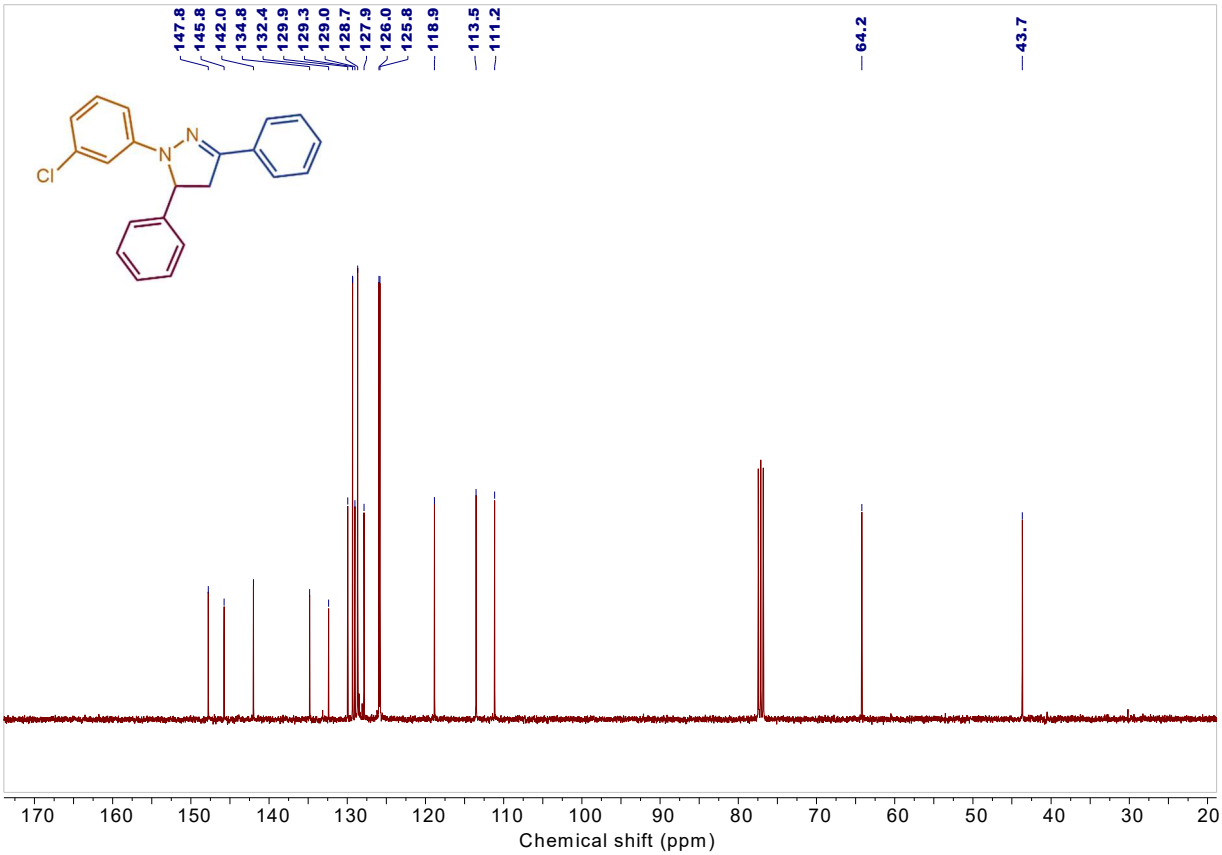


Figure S133: ^{13}C NMR spectrum of **48** (100 MHz, $CDCl_3$).

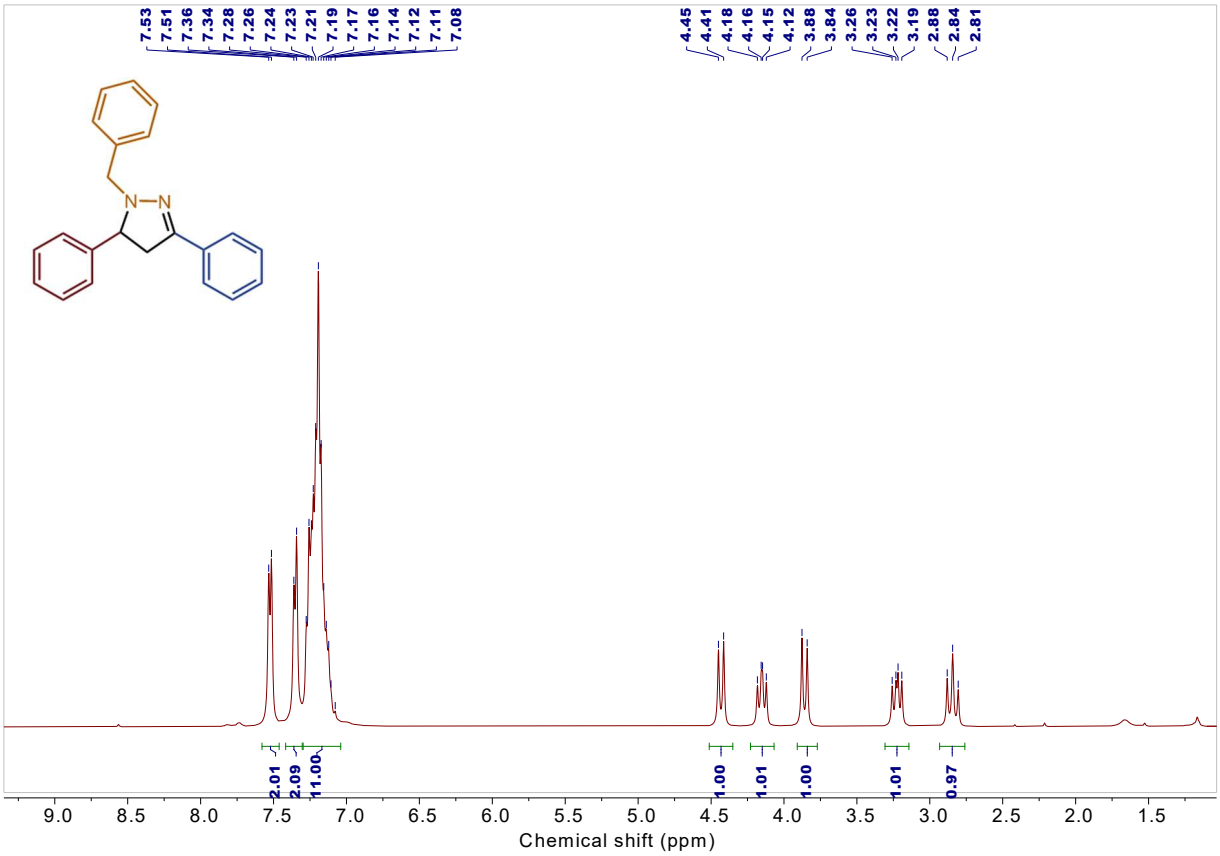


Figure S134: ^{1}H NMR spectrum of **49** (400 MHz, $CDCl_3$).

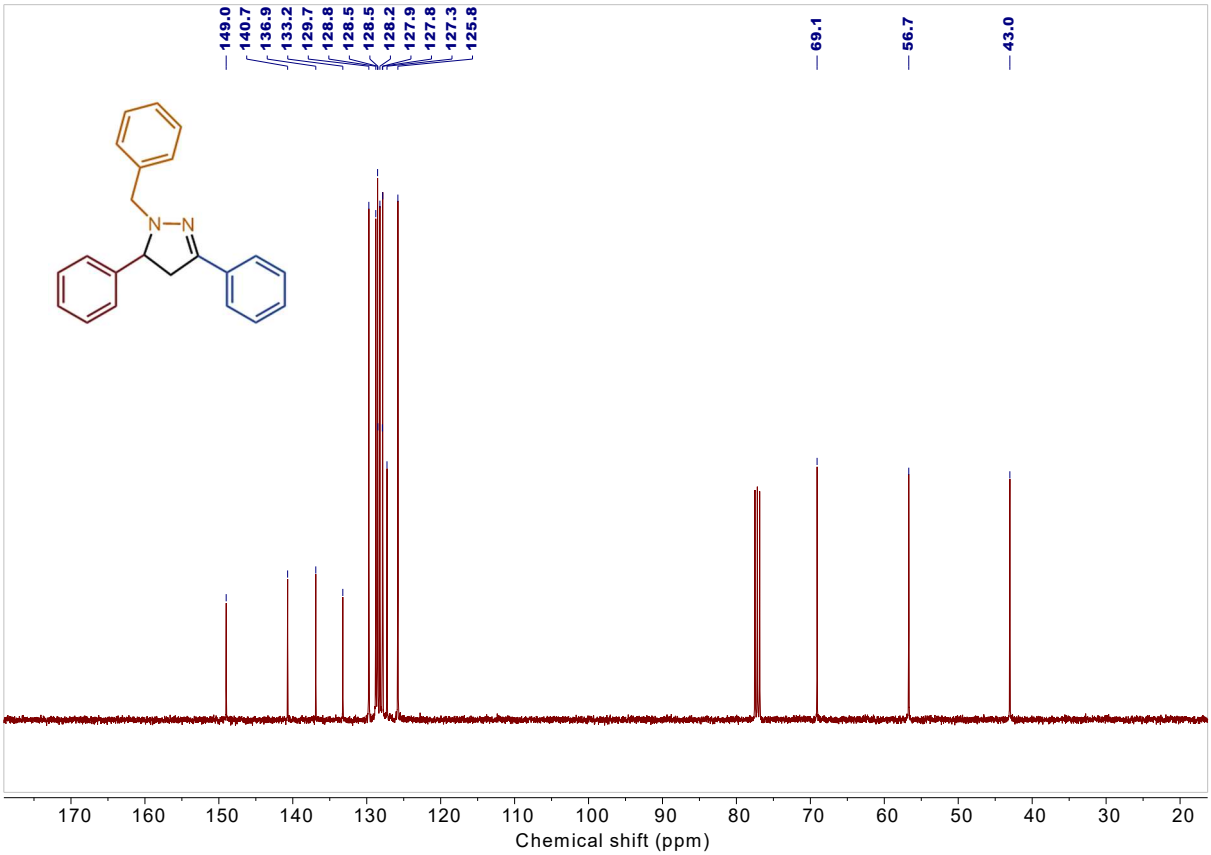


Figure S135: ^{13}C NMR spectrum of **49** (100 MHz, $CDCl_3$).

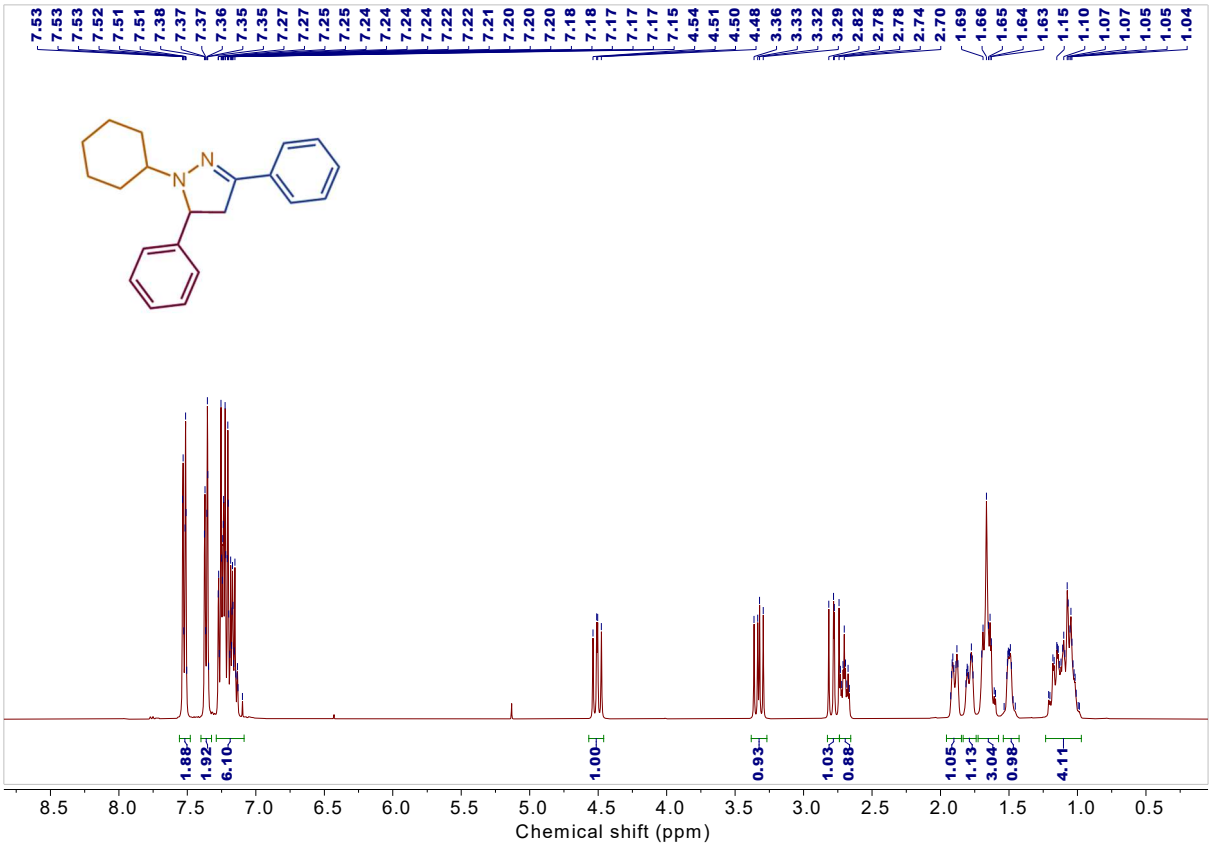


Figure S136: ^{1}H NMR spectrum of **50** (400 MHz, $CDCl_3$).

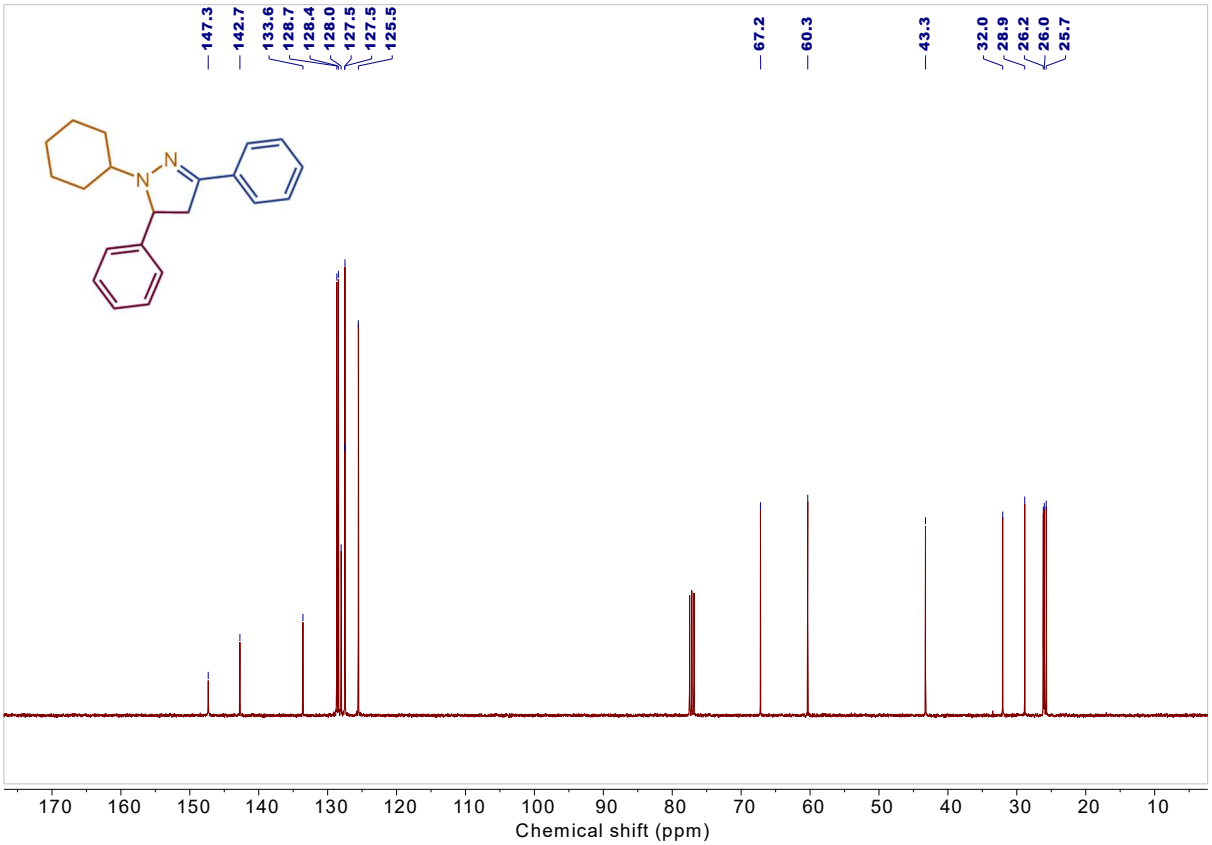


Figure S137: ^{13}C NMR spectrum of **50** (100 MHz, $CDCl_3$).

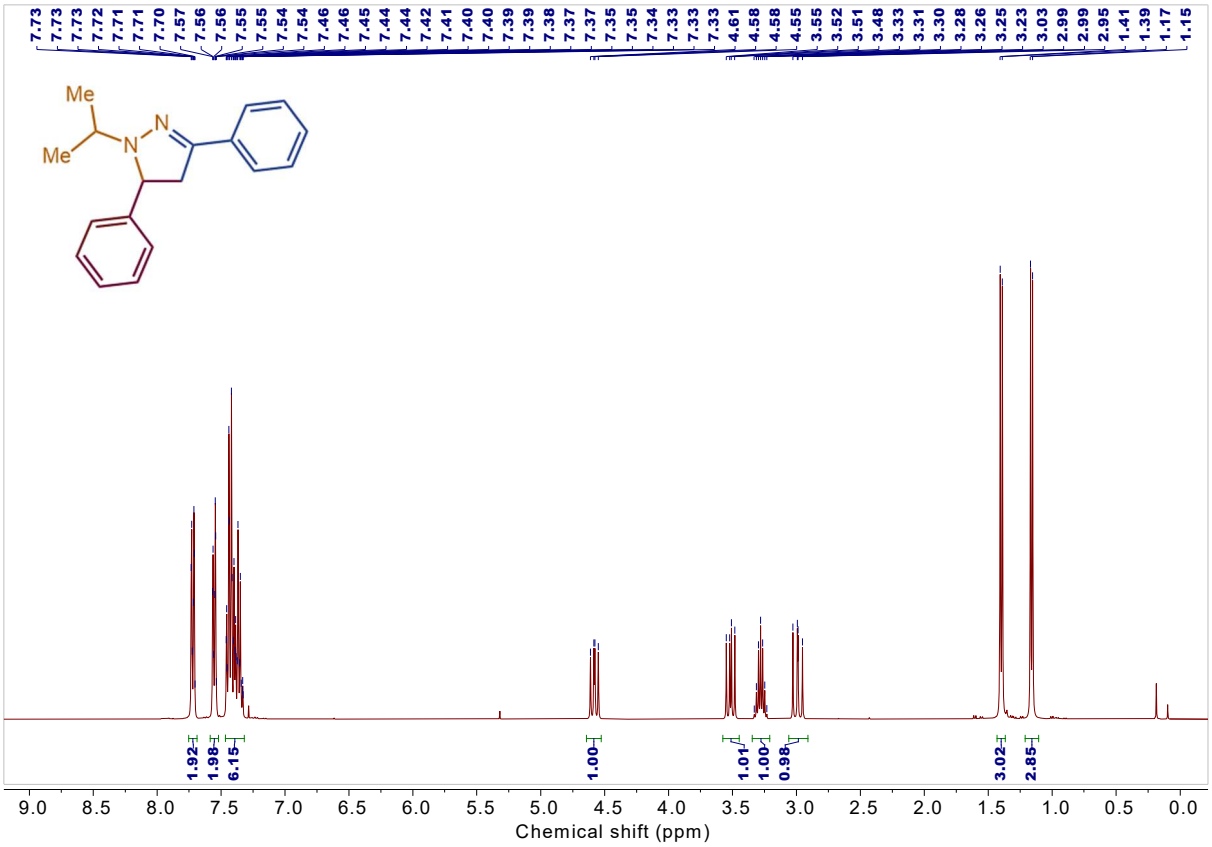


Figure S138: ^{1}H NMR spectrum of **51** (400 MHz, $CDCl_3$).

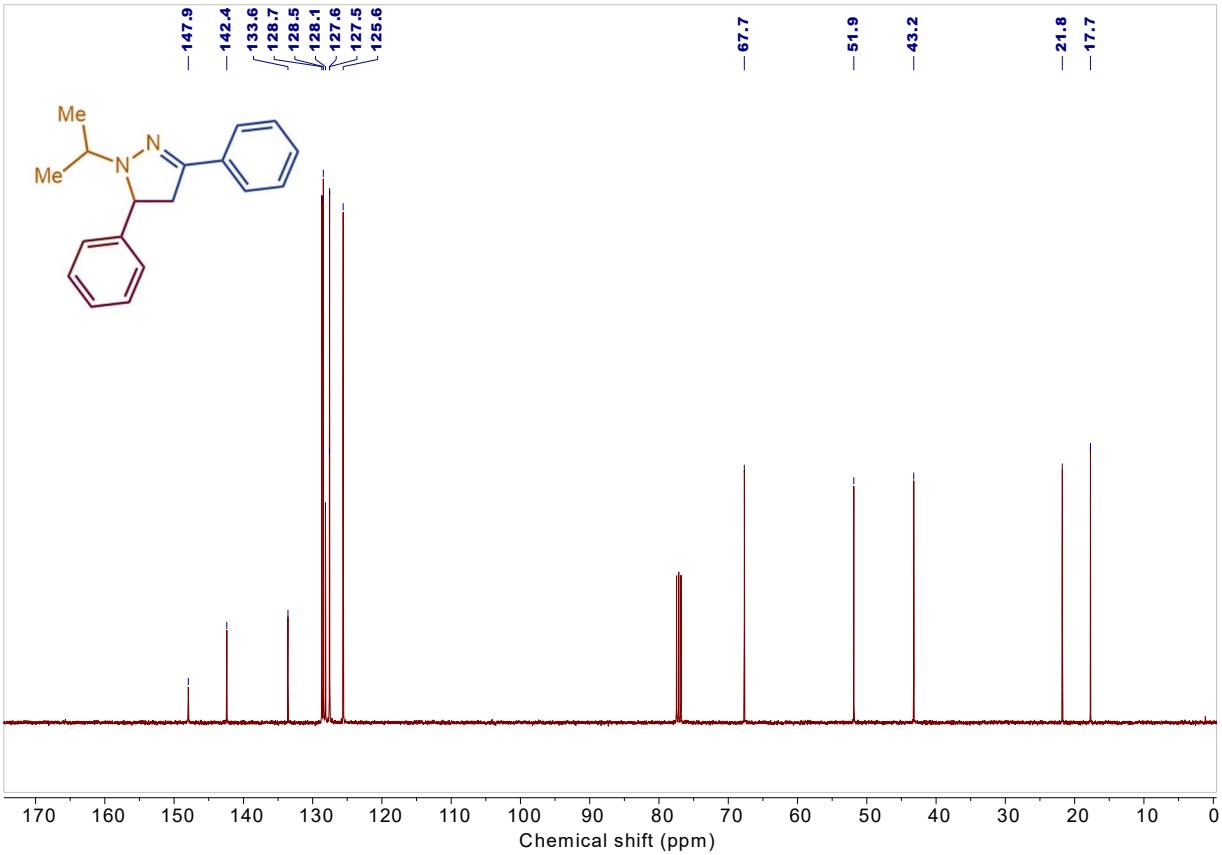


Figure S139: ^{13}C NMR spectrum of **51** (100 MHz, $CDCl_3$).

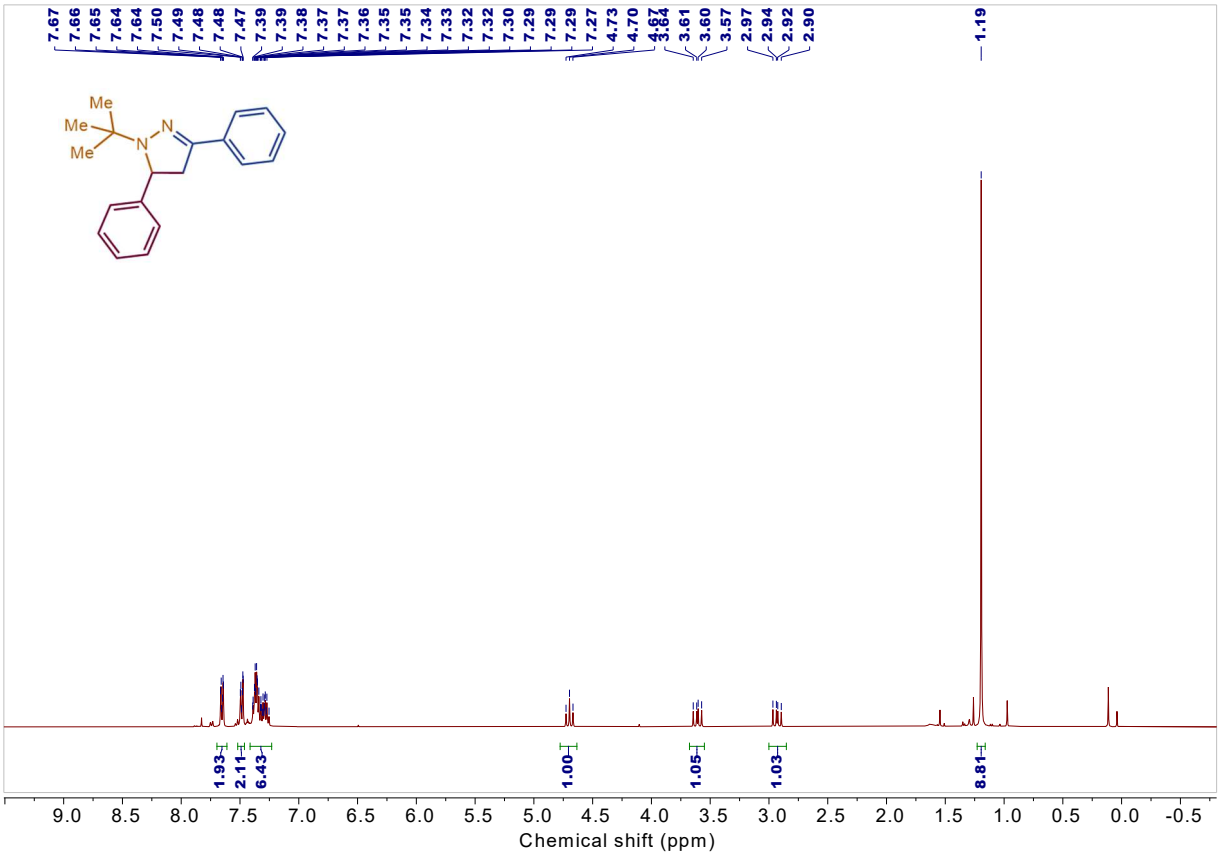


Figure S140: ^{1}H NMR spectrum of **52** (400 MHz, $CDCl_3$).

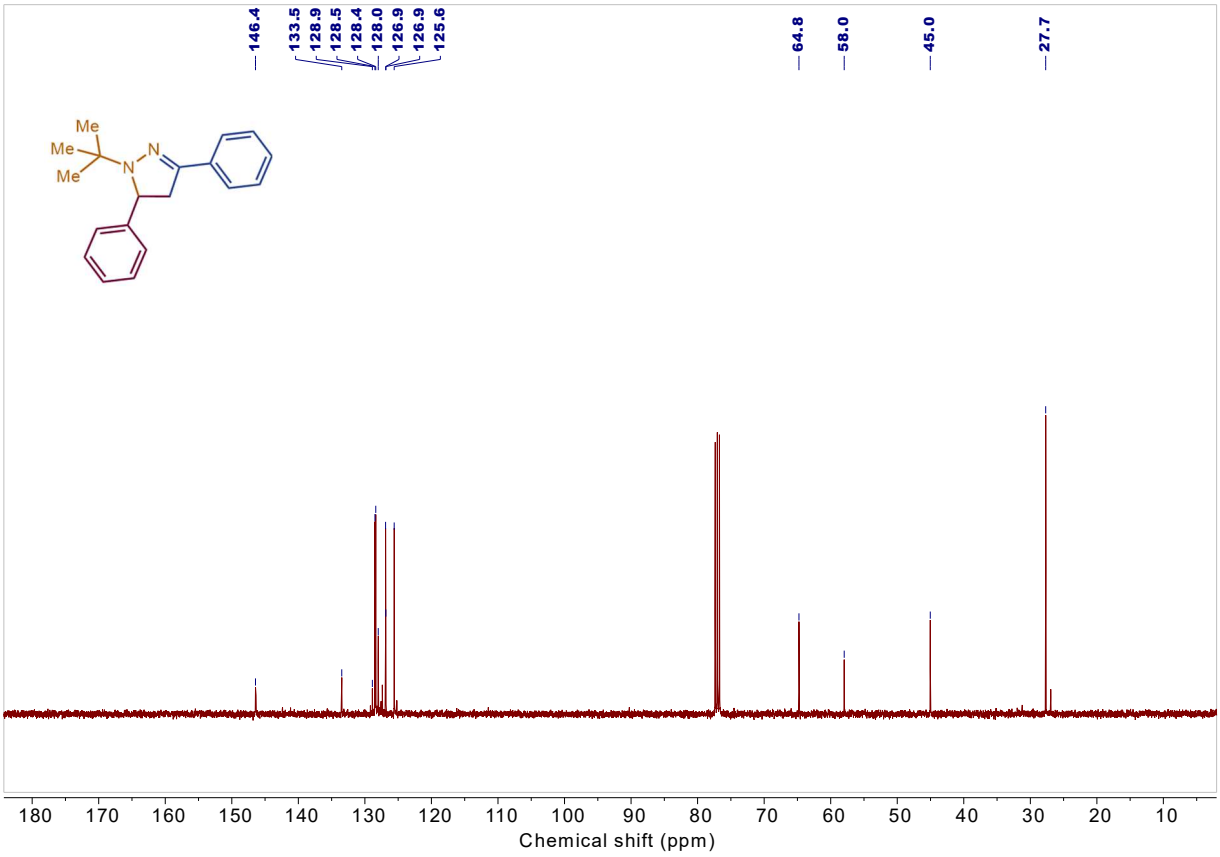


Figure S141: ^{13}C NMR spectrum of **52** (100 MHz, $CDCl_3$).

9. References

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