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Electronic Supplementary Information (ESI)

Electrochemically Enabled Oxidative Aromatization of Pyrazolines

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1. General Information

Unless otherwise stated, all chemicals were purchased and used without further purification. Anhydrous solvents were either purchased or dried over standard drying agents and freshly distilled prior to use. Reactions were monitored by TLC (Silica gel 60 F_{254}, *Merck KGaA*, Darmstadt, Germany), GC (GC-2025, *Shimadzu*, Kyoto, Japan with quartz capillary column HP-5MS, Agilent Technologies, Santa Clara, California, USA) and GC-MS (GCMS-QP2010, *Shimadzu*, Kyoto, Japan with quartz capillary column HP-5MS, *Agilent Technologies*, Santa Clara, California, USA). Flash column chromatography was performed on Silica Gel 60 M (40–63 µm, *Machery-Nagel GmbH & Co.*, Düren, Germany) with a *Büchi* Sepacore system with *Büchi* Control Unit C-620, *Büchi* UV photometer C-635, *Büchi* fraction collector C-660 and two *Büchi* Pump Modules C-605 (*Büchi-Labortechnik GmbH*, Essen, Germany) or on a pre-packed PURIFLASH C18-HP 30 UM F0080 flash column (*Interchim*, Montluçon Cedex, France) with a *Büchi* Sepacore system in the same setup as described before. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were acquired on a *Bruker* Avance III HD 300, Avance II 400, Avance III HD 400 or Avance III 600 (*Bruker*, Karlsruhe, Germany) in $CDCl_3$, DMSO-d_6, CD_2Cl_2, CD_3CN, $(CD_3)_2CO$ or CD_3OD at 25 °C with the solvent residual peaks as internal reference for ^{1}H and ^{13}C NMR spectra. Mass spectra *via* electrospray-ionization (ESI+/-) or atmospheric pressure chemical ionization (APCI+/-) mass spectrometry were recorded using an Agilent 6545 QTOF-MS (*Agilent*, Santa Clara (CA), USA).

Parameter screenings of the electrolytic conditions were performed using an IKA Screening System Package (IKA-Werke GmbH & Co. KG, Staufen, Germany, Figure S1 left and center) with electrodes the size of 70 mm × 10 mm × 3 mm. The apparatus and detailed construction information is reported in literature.[1] The electrode surfaces were cleaned prior use. Isostatic graphite (C_{gr}, Sigrafine™ V2100, SGL Carbon, Bonn, Germany) was wet-polished with sandpaper (grade 1000 + 1200, Bosch, Stuttgart, Germany), rinsed with acetone and the abrasion was wiped off with a paper towel until the latter was not stained anymore. Glassy carbon (C_{gl}, SIGRADUR™ G, HTW, Thierhaupten, Germany), DSA electrodes (DeNora, Milano, Italy) were rinsed with several solvents and wiped with a paper towel. Boron-doped diamond (BDD, DIACHEM™, 15 µm diamond layer on silicon support, CONDIAS GmbH, Itzehoe, Germany) was conditioned by electrolyzing as anode in 20% aqueous sulfuric acid (10 C/cm², 10 mA/cm²) and subsequently rinsed with water.

Constant current electrolyses for scope and scale-up experiments were carried out in beaker-type cells (SynLectro™, *Merck KGaA*, Darmstadt, Germany, Figure S1, right) using TDK-Lambda Z+ series *(TDK-Lambda UK Limited*, Devon, UK) or multichannel power supply HMP4040 (*Rohde & Schwarz*, München, Germany) as power sources.

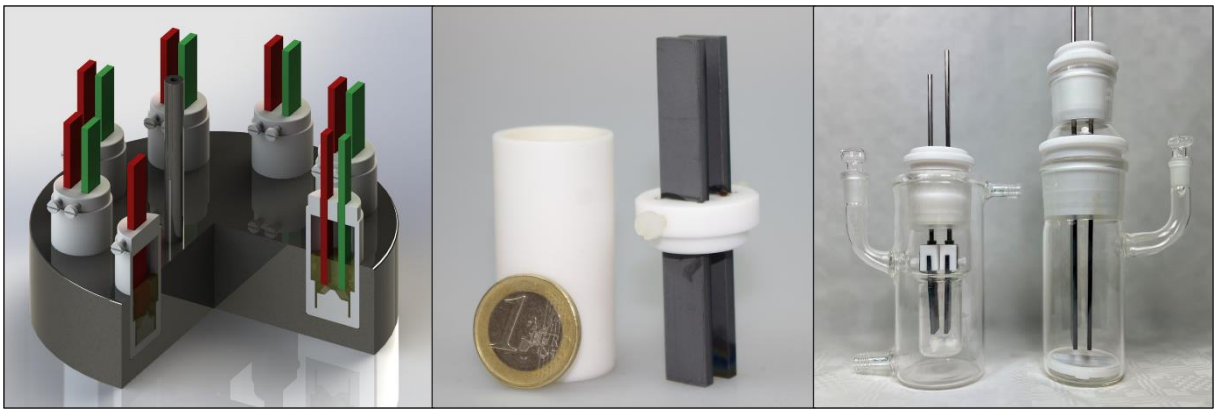


Figure S1: Schematic illustration of a screening block with undivided cells (left); Undivided teflon screening cell with BDD electrodes (center); jacketed beaker-type cell (1.5 – 3.75 mmol scale, 25 mL reaction volume) and beaker-type cell (26.25 mmol scale, 175 ml reaction volume) for scale-up (right).

2. Calibration of Gaschromatographic Yields

The evaluation of the GC yields was achieved by external calibration with 1,3,5-trimthoxybenzene as internal standard. Stock solutions of 1,3,5-trimethoxybenzene, ethyl glyoxylate phenylhydrazone (**6**), ethyl 1*H*-1,5-diphenyl-4,5-dihydro-pyrazole-3-carboxylate (**4a**) and ethyl 1*H*-1,5-diphenyl-pyrazole-3-carboxylate (**5a**) were prepared in ethyl acetate (Table S1). Different quantities of the stock solutions were transferred to GC vials (Table S2) and filled with acetonitrile (approx. 1 mL). Each vial was analysed three times and for each substance the mean value of the peak areas *A* from these three runs was used as a calibration point. The calibration factors *k* for each substance were determined according to equation (*1*) (Figure S2) and can be found in Table S3.

$$\frac{n_{\text{analyte}}}{n_{\text{standard}}} = k\,\frac{A_{\text{analyte}}}{A_{\text{standard}}} \qquad (1)$$

Table S1: Stock solutions for external calibrations using gas chromatography.

#	substance	*m* / mg	*n* / mmol	V_{solvent} / mL	*c* / mM
stock 1	1,3,5-trimethoxybenze	3000.3	17.84	100	178.4
stock 2	ethyl glyoxylate phenylhydrazone (**6**)	62.1	0.32	10	32.3
stock 3	ethyl 1*H*-1,5-diphenyl-4,5-dihydro-pyrazole-3-carboxylate (**4a**)	46.1	0.157	5	31.3
stock 4	ethyl 1*H*-1,5-diphenyl-pyrazole-3-carboxylate (**5a**)	45.5	0.156	5	31.1

Table S2: Calibration solutions for ethyl glyoxylate phenylhydrazone (**6**), ethyl 1H-1,5-diphenyl-4,5-dihydro-pyrazole-3-carboxylate (**4a**) and ethyl 1H-1,5-diphenyl -pyrazole-3-carboxylate (**5a**), internal standard: 1,3,5-trimethoxybenzene.

#	$V_{\text{Stock 1}}$ / µL	$V_{\text{Stock 2}}$ / µL	$V_{\text{Stock 3}}$ / µL	#	$V_{\text{Stock 1}}$ / µL	$V_{\text{Stock 4}}$ / µL
calibration 1	10	30	30	calibration 9	10	30
calibration 2	10	60	60	calibration 10	10	60
calibration 3	10	90	90	calibration 11	10	90
calibration 4	10	120	120	calibration 12	10	120
calibration 5	10	150	150	calibration 13	10	150
calibration 6	10	190	190	calibration 14	10	190
calibration 7	10	225	225	calibration 15	10	225
calibration 8	10	260	260	calibration 16	10	260

Table S3: Calibration factors for hydrazone **6**, pyrazoline **4a** and pyrazole **5a** used in the screening experiments.

substance	*k*
ethyl glyoxylate phenylhydrazone (**6**)	1.9299
ethyl 1*H*-1,5-diphenyl-4,5-dihydro-pyrazole-3-carboxylate (**4a**)	0.3905
ethyl 1*H*-1,5-diphenyl-pyrazole-3-carboxylate (**5a**)	0.4155

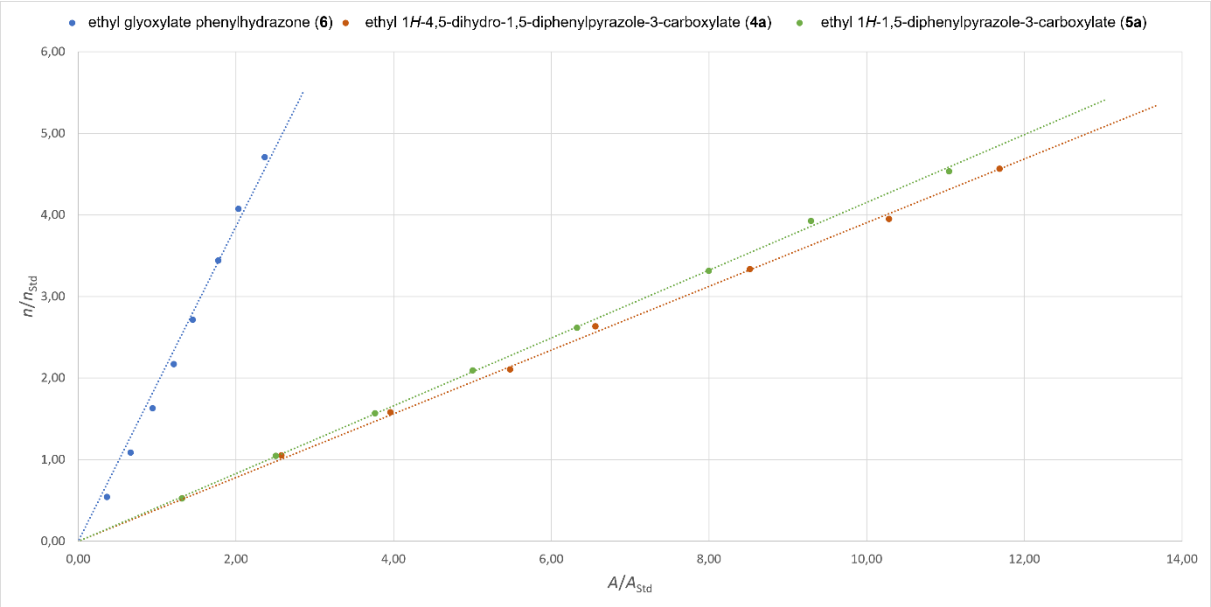


Figure S2: GC calibration for hydrazone **6**, pyrazoline **4a** and pyrazole **5a** used in the screening experiments (internal standard: 1,3,5-trimethoxybenzene).

3. Standard Operating Protocols

SOP1: Screening for Suitable Electrolytic Conditions

In 5 mL PTFE cells, the respective pyrazoline was dissolved in a mixture of organic solvent and aqueous sodium halide solution at a given temperature under vigorous stirring (magnetic stirrer set to approx. 1000 rpm). The mixture was subjected to galvanostatic electrolysis using electrodes with a relevant surface area of 1.38 cm^2 (surface: 70 mm x 10 mm, immersion depth of 1.38 cm). The biphasic mixture was allowed to cool to room temperature and transferred to a separatory funnel, the cell was rinsed with ethyl acetate. 1 mL of a solution of 1,3,5-trimethoxybenzene (3.000 g/100 mL ethyl acetate) was added as internal standard and the mixture shaken briefly. After separation of the layers, the organic fraction was dried over anhydrous magnesium sulphate and filtered. An aliquot was filtered through silica and subjected to GC analysis for quantitative analysis.

SOP2: Synthesis of Pyrazole Derivatives (Protocol A)

In a 25 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, the respective pyrazoline was dissolved in ethyl acetate (5 mL). Pyridine (0.4 eq.) and 1 M aqueous sodium chloride solution (20 mL) were added, and the reaction mixture heated to 70 °C. BDD plates (size: 60 x 20 x 3 mm) were used as anode and cathode with an immersion depth of 2.7 cm and a relevant anode surface area of 5.4 cm^2. Constant current electrolysis was carried out at 70 °C and vigorous stirring (1000 rpm), applying a current density of 15 mA/cm^2 and 3.25 F (573 C). The biphasic mixture was allowed to cool to room temperature and transferred to a separatory funnel. The layers were separated, and the aqueous layer extracted with ethyl acetate (2 x 15 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The crude product was purified by recrystallization or flash column chromatography.

SOP3: Synthesis of Pyrazole Derivatives (Protocol B)

In a 25 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, the respective pyrazoline was dissolved in ethyl acetate (5 mL). Pyridine (0.4 eq.) and 1 M aqueous sodium bromide solution were added, and the reaction mixture heated to 70 °C. BDD plates (size: 60 x 20 x 3 mm) were used as anode and cathode with an immersion depth of 2.7 cm and a relevant anode surface area of 5.4 cm^2. Constant current electrolysis was carried out at 70 °C and vigorous stirring (1000 rpm), applying a current density of 15 mA/cm^2 and 3.25 F (573 C). The biphasic mixture was allowed to cool to room temperature and transferred to a separatory funnel. The layers were separated, and the aqueous layer extracted with ethyl acetate (2 x 15 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The crude product was purified by recrystallization or flash column chromatography.

SOP4: Synthesis of Pyrazole Derivatives (Protocol C)

In a 25 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, the respective pyrazoline was dissolved in ethyl acetate (5 mL). Pyridine (0.4 eq.), 1 M aqueous sodium chloride solution (10 mL) and 1 M aqueous sodium iodide solution (10 mL) were added, and the reaction mixture heated to 70 °C. BDD plates (size: 60 x 20 x 3 mm) were used as anode and cathode with an immersion depth of 2.7 cm and a relevant anode surface area of 5.4 cm^2. Constant current electrolysis was carried out at 70 °C and vigorous stirring (1000 rpm), applying a current density of 15 mA/cm^2 and 3.25 F (573 C). The biphasic mixture was allowed to cool to room temperature and transferred to a separatory funnel. The layers were separated, and the aqueous layer extracted with ethyl acetate (2 x 15 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The crude product was purified by recrystallization or flash column chromatography.

SOP5: Synthesis of Chalcones

The synthesis was performed analogous to a previously described procedure.[2]

In a 100 mL round bottom flask, 20 mmol (1.0 eq.) of the respective acetophenone and 20 mmol (1.0 eq.) of the respective benzaldehyde were dissolved in ethanol (40 mL). The solution was cooled to 0 °C in an ice bath and 20 mmol (1.0 eq.) sodium hydroxide dissolved in water (40 mL) were added while stirring. The mixture was stirred overnight at room temperature and filtered afterwards. The solid was washed with water, dried open to air and, if necessary, recrystallized.

SOP6: Conventional Synthesis of Pyrazolines

The synthesis was performed analogous to a previously described procedure.[3]

In a 100 mL round bottom flask, 10 mmol (1.0 eq.) of the respective chalcone and 10 mmol (1.0 eq.) of the respective substituted hydrazine hydrochloride were dissolved in ethanol (30 mL) and 10 mmol glacial acetic acid (1.0 eq.) were added. The mixture was refluxed overnight. After cooling to room temperature, the product was filtered off, the solid was washed with water and dried open to air. Unless stated otherwise, the product was used for the next step without further purification.

SOP7: Electrochemical Synthesis of Pyrazolines

The synthesis was performed analogous to the recently described protocol. A fourfold scale-up was done compared to the described reaction.[4]

In a 100 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, ethyl glyoxylate phenylhydrazone (**6**, 12 mmol, 2.31 g, 1,0 eq.) and the respective alkene (32.4 mmol, 2.7 eq.) were

dissolved in ethyl acetate (20 mL). 1 M aqueous sodium iodide solution (80 mL) was added. Isostatic graphite electrodes (80 × 34 × 5 mm) with an immersion depth of 6 cm and a relevant surface area of 20.4 cm² were used. Constant current electrolysis was performed at 25 °C and 800 rpm, with a current density of 35.0 mA cm^{-2} until a charge of 5.0 *F* (5789 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with ethyl acetate (1 × 50 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography.

4. Optimization of Pyrazole Syntheses

4.1. Oxidation of Ethyl 1*H*-4,5-dihydro-1,5-diphenyl-pyrazole-3-carboxylate (4a)

4.1.1. Screening for Electrode Material, Solvent and Mediator

Screening reactions were carried out according to SOP1 using ethyl 1*H*-4,5-dihydro-1,5-diphenyl-pyrazole-3-carboxylate (**4a**, 0.34 mmol, 100 mg) as test substrate (Table S4 & Table S5). Unless stated otherwise, yields were determined using GC analysis with external calibration (internal standard: 1,3,5-trimethoxybenzene).

Table S4: Screening of halide source, solvent, and temperature. Reaction conditions: graphite electrodes, 20 mA/cm², 4 *F*.

Organic solvent	Halide source	Concentration[a]	*T* / °C	Yield[b]
EtOAc	NaI	1 M	25	0%
EtOAc	NaBr	1 M	25	0%
EtOAc	NaI / NaBr	0.5 M / 0.5 M	25	0%
EtOAc	NaI / Et_4NI	0.95 M / 0.05 M	25	0%
EtOAc	NaBr / Et_4NBr	0.95 M / 0.05 M	25	1%
EtOAc	NaBr	1 M	65	2%
EtOAc	NaCl	1 M	25	26%
EtOAc	NaCl	1 M	65	38%
EtOAc	NaCl	2.5 M	65	34%
EtOAc	NaCl / NaI	0.5 M / 0.5 M	65	0%
Toluene	NaCl / NaOH	1 M / 1 M	100	0%

[a] Concentration referring to the aqueous layer (phase ratio aqueous/organic 4:1).
[b] Determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.

Table S5: Screening of electrode materials. Reaction conditions: EtOAc/ 1 M NaCl (aq.) 1:4, 70 °C, 20 mA/cm², 4 *F*.

Anode	Cathode	Yield[a]
graphite	graphite	59%
glassy carbon	glassy carbon	0%
BDD	BDD	62%
DSA (IrO_2 on Ta)	graphite	43%
DSA (Ru-Ir mixed oxide on Ta)	graphite	57%
DSA (Ru-Ir mixed oxide on Ta)	VA1.45571	49%
DSA (Ru-Ir mixed oxide on Ti)	graphite	55%

[a] Determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.

4.1.2. Optimization via Design of Experiment (DoE)

Further reaction optimization with regards to current density, amount of charge and temperature was carried out using design of experiments (DoE). To investigate three factors, a fractional factorial design was chosen (2^{4-1} resolution of III with central point and rotatable axis points, Table S7, Figures S3 & S4) and expanded to a response surface design. Reactions were carries out according to SOP1 using ethyl

1*H*-4,5-dihydro-1,5-diphenyl-pyrazole-3-carboxylate (4a, 0.34 mmol, 100 mg) as test substrate, each data point was acquired thrice. Afterwards, a target optimization was done (Table S7).

Table S6: DoE screening for oxidation of pyrazoline 4a. Reaction conditions: BDD electrodes, EtOAc / 1 M NaCl (aq.) 1:4,

Experiment	Run	*T* / °C	*j* / mA/cm²	*Q* / *F*	Yield[a]	Conversion[a]
1	1	46	20.0	3.25	50%	95%
	2	46	20.0	3.25	50%	95%
	3	46	20.0	3.25	52%	94%
2	4	50	15.0	4.00	56%	100%
	5	50	15.0	4.00	55%	100%
	6	50	15.0	4.00	57%	93%
3	7	50	25.0	2.50	47%	91%
	8	50	25.0	2.50	45%	88%
	9	50	25.0	2.50	43%	82%
4	10	60	12.9	3.25	68%	100%
	11	60	12.9	3.25	65%	100%
	12	60	12.9	3.25	66%	100%
5	13	60	20.0	2.19	55%	84%
	14	60	20.0	2.19	50%	82%
	15	60	20.0	2.19	51%	81%
6	16	60	20.0	3.25	54%	100%
	17	60	20.0	3.25	59%	100%
	18	60	20.0	3.25	57%	100%
7	19	60	20.0	4.31	54%	100%
	20	60	20.0	4.31	55%	91%
	21	60	20.0	4.31	57%	93%
8	22	60	27.1	3.25	51%	100%
	23	60	27.1	3.25	47%	95%
	24	60	27.1	3.25	47%	96%
9	25	70	15.0	2.50	73%	100%
	26	70	15.0	2.50	70%	100%
	27	70	15.0	2.50	75%	100%
10	28	70	25.0	4.00	52%	100%
	29	70	25.0	4.00	51%	100%
	30	70	25.0	4.00	55%	100%
11	31	74	20.0	3.25	62%	100%
	32	74	20.0	3.25	62%	100%
	33	74	20.0	3.25	61%	98%

[a] Determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.

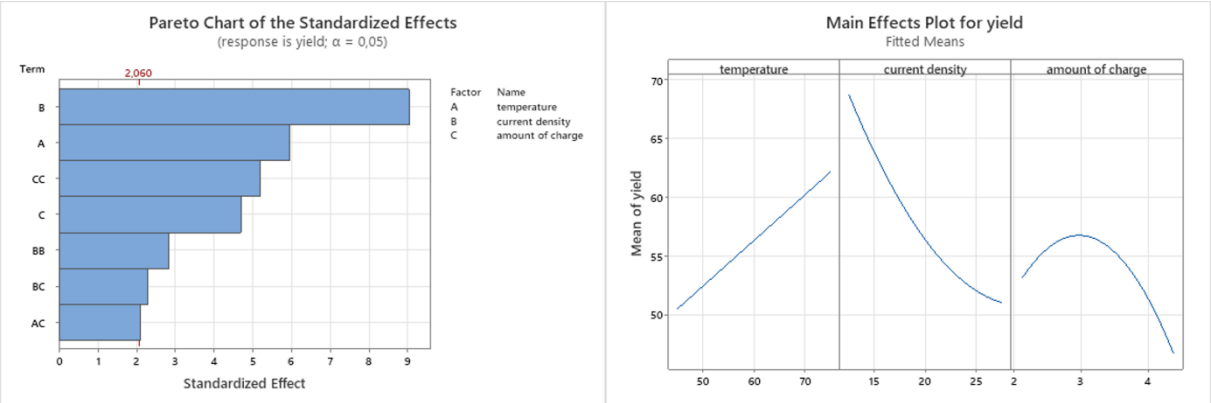


Figure S3: Pareto chart (left) and main effect plot (right) for temperature (°C), current density (mA/cm²) and amount of Charge (*F*). Yields (%) determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.

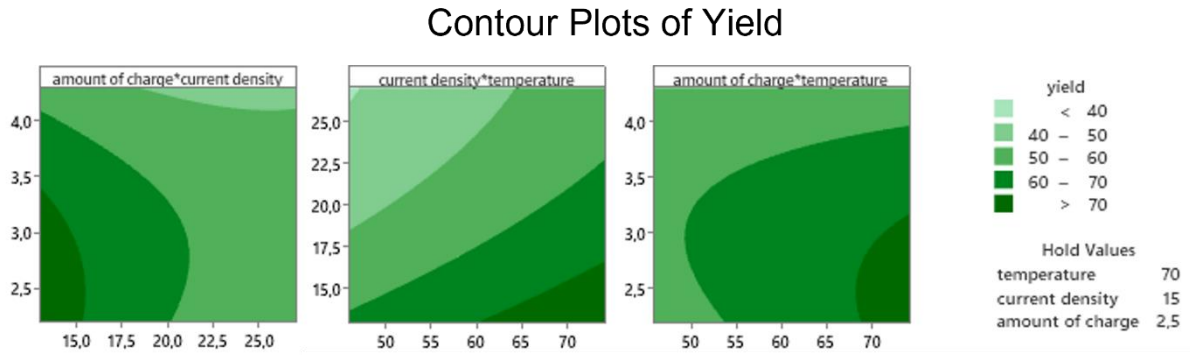


Figure S4: Contour plot for the DoE-based optimization of for temperature (°C), current density (mA/cm²) and amount of Charge (*F*). Yields (%) determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.

Table S7: Response optimization with regards to maximization of yield. Comparison of optima.

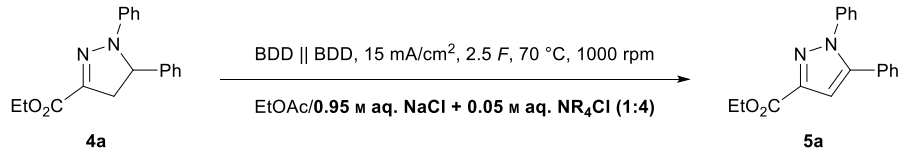
***T* / °C**	***j* / mA/cm²**	***Q* / *F***	**Yield**
74	12.9	2.21	62%[a]
70	12.9	2.32	65%[a]
70	12.9	2.50	51%[a]
70	15.0	2.50	73%[a,b]
70	15.0	3.25	69%[c]

[a] Determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.
[b] Average yield after three runs.
[c] Isolated yield; 1.70 mmol scale 5 mL EtOAc/ 1 M NaCl (aq.).

4.1.3. Further Optimization: Screening of Additives

Screening reactions were carried out according to SOP1 using ethyl 1*H*-4,5-dihydro-1,5-diphenyl-pyrazole-3-carboxylate (**4a**, 0.34 mmol, 100 mg) as test substrate and the previously determined optimized reaction conditions (Table S8). Unless stated otherwise, yields were determined using GC analysis with external calibration (internal standard: 1,3,5-trimethoxybenzene).

Table S8: Screening of quaternary ammonia salts as additives.



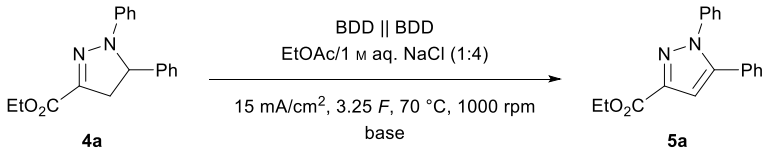
4a **5a**

Co-supporting electrolyte tetraalkylammonium chloride	Yield[a]
Me_4NCl	59%
Et_4NCl	48%
Bu_4NCl	74%
$BnEt_3NCl$	53%

[a] Determined using GC analysis with external calibration; internal standard: 1,3,5-trimethoxybenzene.

The effect of base addition was examined in 25 mL jacketed beaker-type cells. 1*H*-4,5-dihydro-1,5-diphenyl-pyrazole-3-carboxylate (**4a**, 1.70 mmol, 500 mg) was dissolved in 5 mL ethyl acetate and 20 mL 1 M sodium chloride solution was added and the reaction mixture heated to 70 °C. BDD plates (size: 60 x 20 x 3 mm) were used as anode and cathode with an immersion depth of 2.7 cm and a relevant anode surface area of 5.4 cm^2. Constant current electrolysis was carried out at 70 °C and vigorous stirring (1000 rpm), applying a current density of 15 mA/cm^2 and 3.25 F (573 C). The biphasic mixture was allowed to cool to room temperature and transferred to a separatory funnel. The layers were separated, and the aqueous layer extracted with ethyl acetate (2 x 15 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The product was obtained as light-yellow solid after flash column chromatography on silica (cyclohexane + 3% EtOAc → 5% EtOAc). The results are shown in Table S9.

Table S9: Screening of bases and base equivalents.



4a **5a**

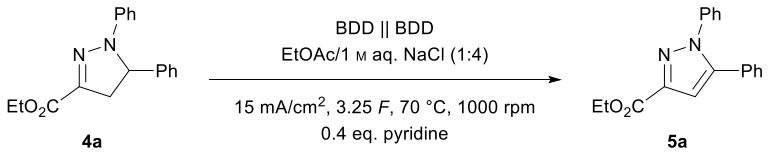
Base	Equivalents	Yield[a]
none	-	69%
Na_2CO_3	0.2	55%
triethylamine	0.2	62%
pyridine	0.2	66%
pyridine	0.4	75%
pyridine	0.5	66%
pyridine	1.0	traces[b]

[a] Isolated yield

[b] No isolation of product due to extremely poor conversion.

Screening for the optimum pyrazoline concentration was carried out according to SOP2 employing 1*H*-4,5-dihydro-1,5-diphenyl-pyrazole-3-carboxylate (**4a**) as test substrate (Table S10).

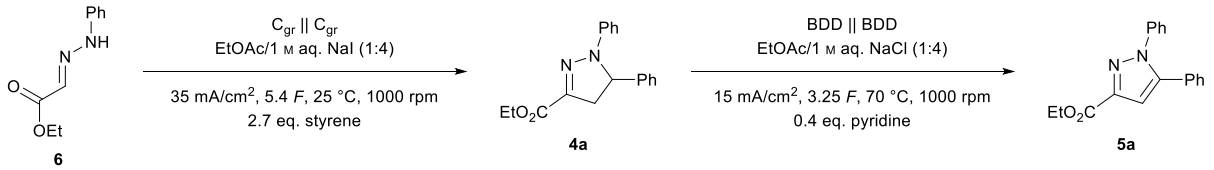
Table S10: Screening for optimum pyrazoline concentration.



***c* / mol/L** [a]	***n* / mmol**	**Yield**[b]
0.25	1.25	56%
0.34	1.70	75%
0.75	3.75	77%
1.00	5.00	55%

[a] Concentration referring to the organic layer.
[b] Isolated yield.

5. Telescoped Two-Step Synthesis of Ethyl 1*H*-1,5-diphenyl-pyrazole-3-carboxylate (5a) from Ethyl glyoxylate phenylhydrazone (6)



Step 1: Electro-synthesis of pyrazoline **4a**

According to a recently described protocol, ethyl glyoxylate phenylhydrazone (**6**, **4.5 mmol**, **865 mg**, **1 eq.**) and styrene (**12.2 mmol**, **1265 mg**, **2.7 eq.**) were placed in a 25 mL jacketed beaker-type cell. Ethyl acetate (5 mL) and 1 M sodium iodide (aq.) were added, and the reaction mixture was stirred vigorously. Constant current electrolysis was performed at 25 °C using isostatic graphite electrodes (size: 60 x 20 x 3 mm; immersion depth: 2.7 cm; relevant anode surface area: 5.4 cm^2) and a current density of 35 mA/cm^2 and an amount of charge of 5.4 *F* (2345 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The organic layer was washed with 20% aq. sodium metabisulfite (25 mL), dried over anhydrous magnesium sulphate, filtered and the solvent removed under reduced pressure. The excess styrene was removed via filtration through a pad of silica with cyclohexane and the crude pyrazoline was eluted with ethyl acetate afterwards.

Step 2: Electro-oxidation of pyrazoline **4a** to the corresponding pyrazole **5a**

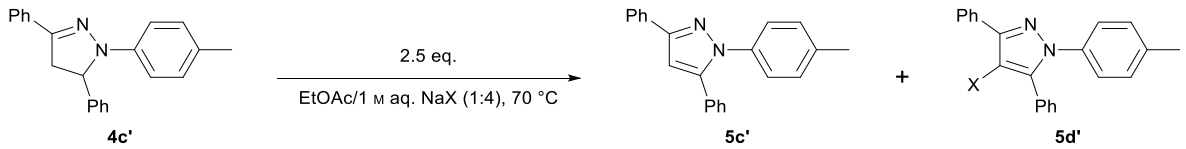
After removing the solvent under reduced pressure, the crude pyrazoline was further oxidized according to SOP2, applying an amount of charge of 5.25 *F* (1772 C). After flash column chromatography over silica with cyclohexane/ethyl acetate (3% → 5% EtOAc) the pyrazole was obtained as a yellow solid (2.67 mmol, 780 mg, 60% over two steps).

6. Further Mechanistic Investigations Employing Conventional Reactions with Elemental Halogens or Interhalogens

To determine the active species involved in oxidation and bromination of pyrazoline **4c'**, control experiments employing iodine, bromine, and iodine monochloride were performed. Reaction conditions were chosen according to the performed electrolyses in a biphasic system consisting of ethyl acetate as organic solvent and 1 M aqueous sodium halide solutions employing conventional halogens (2.5 eq. according to 2.5 *F* employed in the electrochemical reaction) as oxidants.

In a 50 mL round bottom flask, pyrazoline **4c'** (**1.5 mmol, 469 mg**) was dissolved in 5 mL ethyl acetate. 20 mL aqueous sodium halide solution (1 M, aq.) and the respective halide (2.5 eq.) were added, and the mixture heated to 70 °C under vigorous stirring. After 1.5 h, the reaction mixture was allowed to cool to room temperature and transferred to a separatory funnel. The layers were separated, the organic layer dried over anhydrous magnesium sulphate, filtered, and evaporated to dryness under reduced pressure. 1,3,5-Trimethoxybenzene (0.1 mmol, 16.8 mg) was added as internal standard, the mixture dissolved in $CDCl_3$ and an aliquot was transferred to an NMR tube. The results are shown in Table S11.

Table S11: Control experiments for oxidation of pyrazoline **4c'** with conventional halogens. *C*(pyrazoline **4c'**) = 1.5 mmol.



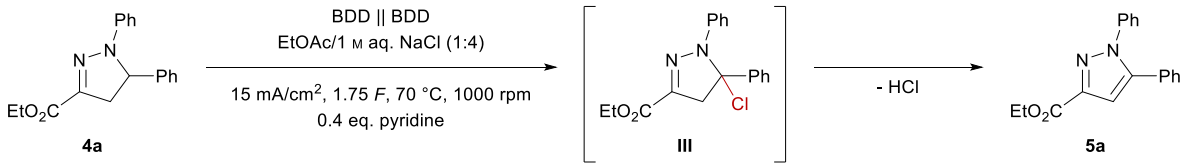
4c' **5c'** **5d'**

Halogen source (X_2)	1 M NaX (aq.)	Yield 5c'[b]	Yield 5d'[b]
I_2	NaI	57%	-
Br_2	NaBr	55%	35%
ICl	-[a]	92%	-

[a] Solely water was used.
[b] Yield determined via ^{1}H NMR, 1,3,5-trimethoxybenzene as internal standard.

7. Mechanistic Investigations: GC-MS analysis

As described in the main text, an intermediary halogenation of pyrazolines in position 5 with subsequent formation of pyrazoles via elimination of HCl was suspected in the first investigations. To determine whether this halogenation occurs during the reaction, GC-MS analysis was performed after an applied amount of charge of 1.75 *F* (Scheme S1).



4a **III** **5a**

Scheme S1: Reaction control after 1.75 *F* to investigate formation of potential intermediate **III** using GC-MS. Intermediate **III** was not observed. Reaction conditions: *c* (pyrazoline 4a) = 3.75 mmol, 25 mL batch-type electrolysis cell.

The obtained GC-MS results are summarized in Figure S5. GC-MS analysis showed only unconverted pyrazoline **4a** and product **5a**, intermediate **III** or other by-products were not observed.

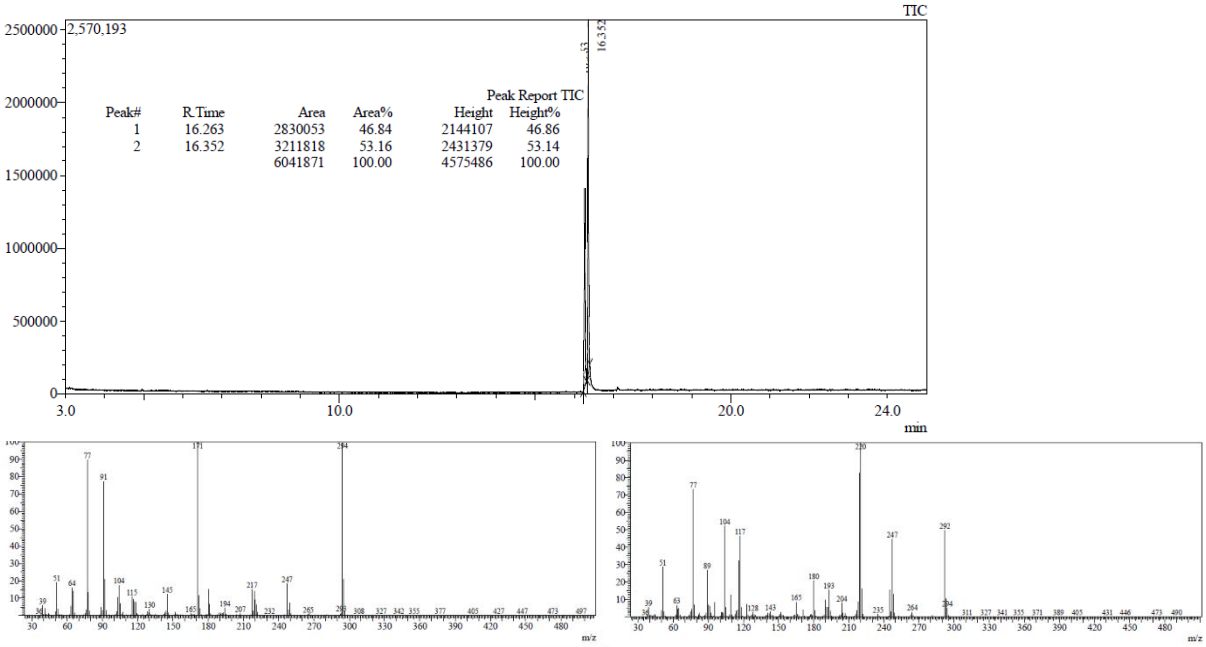
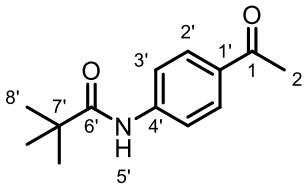


Figure S5: GC-MS analysis for reaction control. Top: gas chromatogram only two peaks; starting material (left) and product (right). Bottom: Corresponding mass spectra for starting material **4a** (left, peak at 16.263 min) and product **5a** (right, peak at 16.352 min).

8. Substrate Synthesis

4'-Pivaloylaminoacetophenone (7a)



In a 250 mL round bottom flask, 4'-aminoacetophenone (**40 mmol, 5.41 g, 1.0 eq.**) and triethylamine (**56 mmol, 5.67 g, 1.4 eq.**) were dissolved in THF (80 mL). The mixture was cooled to 0 °C in an ice bath and pivaloyl chloride (**48 mmol, 5.79 g, 1.2 eq.**) was added dropwise under vigorous stirring. The mixture was stirred overnight while warming to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue recrystallized from ethanol/water 1:1 (v/v, ca. 200 mL, reflux to -30 °C) to yield the product as pale pink flakes (**7.38 g, 33.7 mmol, 84%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.94 – 7.89 (m, 2H, *H*-2'), 7.67 – 7.62 (m, 2H, *H*-3'), 7.62 (s, 1H, *H*-5'), 2.56 (s, 3H, *H*-2), 1.32 (s, 9H, *H*-8').

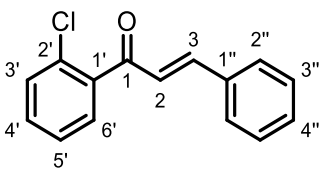
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 197.1, 177.0, 142.6, 132.9, 129.8, 119.2, 40.0, 27.7, 26.6.

HRMS (APCI+), *m/z*: calculated for $C_{13}H_{17}NO_2$ + H^+ 220.1332 $[M+H]^+$, found 220.1329.

Known compound, spectroscopic data corresponds to the literature.[5]

8.1. Synthesized Chalcones

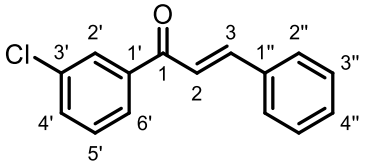
(*E*)-2'-Chlorochalcone (7b)



Chalcone synthesis was carried out according to SOP5 using 2'-chloroacetophenone (**20 mmol, 3.09 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). Instead of filtration, the mixture was evaporated to dryness under reduced pressure and the pure product was obtained after filtration through silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as a yellow oil (**4.05 g, 16.7 mmol, 83%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.60 – 7.53 (m, 2H, *H*-2''), 7.50 – 7.42 (m, 4H, *H*-3, *H*-3', *H*-4', *H*-6'), 7.42 – 7.32 (m, 4H, *H*-5', *H*-3'', *H*-4''), 7.14 (d, *J* = 16.1 Hz, 1H, *H*-2).
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 194.0, 146.4, 139.2, 134.5, 131.5, 131.4, 131.0, 130.4, 129.5, 129.1, 128.7, 127.0, 126.4.
HRMS (APCI+), *m/z*: calculated for $C_{15}H_{11}{}^{35}ClO + H^+$ 243.0571 $[M+H]^+$, found 243.0572; calculated for $C_{15}H_{11}{}^{37}ClO + H^+$ 245.0546 $[M+H]^+$, found 245.0537.
Known compound, spectroscopic data corresponds to the literature.[6]

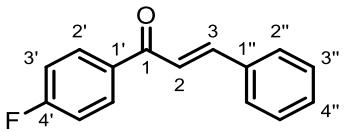
(*E*)-3'-Chlorochalcone (7c)



Chalcone synthesis was carried out according to SOP5 using 3'-chloroacetophenone (**20 mmol, 3.09 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). After recrystallization from ethanol/water 3:1(v/v, ca. 100 mL, reflux to -30 °C), the product was obtained as faint yellow needles (**3.90 g, 16.1 mmol, 80%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.99 (t, *J* = 1.9 Hz, 1H, *H*-2'), 7.89 (ddd, *J* = 7.7, 1.8, 1.1 Hz, 1H, *H*-6'), 7.83 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.69 – 7.62 (m, 2H, *H*-2''), 7.55 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1H, *H*-4'), 7.47 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.47 – 7.41 (m, 4H, *H*-5', *H*-3'', *H*-4'').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 189.2, 145.8, 139.9, 135.0, 134.7, 132.8, 131.0, 130.1, 129.1, 128.7, 126.7, 121.5.
HRMS (APCI+), *m/z*: calculated for $C_{15}H_{11}{}^{35}ClO + H^+$ 243.0571 $[M+H]^+$, found 243.0564; calculated for $C_{15}H_{11}{}^{37}ClO + H^+$ 245.0546 $[M+H]^+$, found 245.0537.
Known compound, spectroscopic data corresponds to the literature.[7]

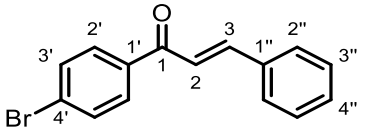
(*E*)-4'-Fluorochalcone (7d)



Chalcone synthesis was carried out according to SOP5 using 4'-fluoroacetophenone (**20 mmol, 2.76 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a colourless powder (**4.08 g, 18.0 mmol, 90%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.11 – 8.02 (m, 2H, *H*-2'), 7.82 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.70 – 7.60 (m, 2H, *H*-2''), 7.51 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.46 – 7.38 (m, 3H, *H*-3'', *H*-4''), 7.22 – 7.14 (m, 2H, *H*-3').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 189.0, 165.7 (d, *J* = 254.6 Hz), 145.2, 134.9, 134.7 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 9.2 Hz), 130.8, 129.1, 128.6, 121.7, 115.9 (d, *J* = 21.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$), δ/ppm: -106.70 (tt, *J* = 8.2, 5.4 Hz).
HRMS (APCI+), *m/z*: calculated for $C_{15}H_{11}FO + H^+$ 227.0867 $[M+H]^+$, found 227.0859.
Known compound, spectroscopic data corresponds to the literature.[8–10]

(*E*)-4'-Bromochalcone (7e)

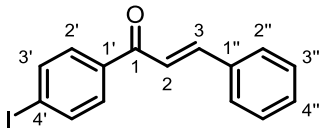


Chalcone synthesis was carried out according to SOP5 using 4'-bromoacetophenone (**20 mmol, 3.98 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). After recrystallization from ethanol/water 5:2 (v/v, ca. 100 mL, reflux to -30 °C), the product was obtained as colourless flakes (**5.00 g, 17.4 mmol, 87%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.91 – 7.87 (m, 2H, *H*-2'), 7.82 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.67 – 7.61 (m, 4H, *H*-3', *H*-2''), 7.47 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.45 – 7.40 (m, 3H, *H*-3'', *H*-4'').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 189.5, 145.5, 137.0, 134.8, 132.0, 130.9, 130.1, 129.1, 128.6, 128.0, 121.6.

HRMS (APCI+), *m/z*: calculated for $C_{15}H_{11}{}^{79}BrO + H^+$ 287.0066 [*M*+H]$^+$, found 287.0057; calculated for $C_{15}H_{11}{}^{81}BrO + H^+$ 289.0047 [*M*+H]$^+$, found 289.0039.
Known compound, spectroscopic data corresponds to the literature.[7,9,11]

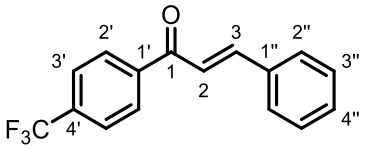
(*E*)-4'-Iodochalcone (7f)



Chalcone synthesis was carried out according to SOP5 using 4'-iodoacetophenone (**20 mmol, 4.92 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). After recrystallization from ethanol (ca. 150 mL, reflux to -30 °C), the product was obtained as orange needles (**4.75 g, 14.2 mmol, 71%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.89 – 7.85 (m, 2H, *H*-2'), 7.82 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.76 – 7.71 (m, 2H, *H*-3'), 7.67 – 7.61 (m, 2H, *H*-2''), 7.47 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.44 – 7.39 (m, 3H, *H*-3'', *H*-4'').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 189.8, 145.6, 138.1, 137.6, 134.8, 130.9, 130.1, 129.2, 128.7, 121.6, 100.8.
HRMS (APCI+), *m/z*: calculated for $C_{15}H_{11}IO + H^+$ 334.9927 [*M*+H]$^+$, found 334.9925.
Known compound, spectroscopic data corresponds to the literature.[7,9]

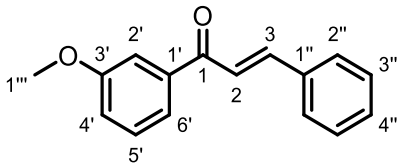
(*E*)-4'-(Trifluoromethyl)chalcone (7g)



Chalcone synthesis was carried out according to SOP5 using 4'-trifluoromethylacetophenone (**20 mmol, 3.76 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). After twofold recrystallization from ethanol/water 3:1 (v/v) and ethanol/water 2:1 (v/v, ca. 100 mL, reflux to -30 °C), the product was obtained as colourless needles (**4.76 g, 17.2 mmol, 86%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.12 – 8.08 (m, 2H, *H*-2'), 7.84 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.80 – 7.75 (m, 2H, *H*-3'), 7.68 – 7.63 (m, 2H, *H*-2''), 7.49 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.47 – 7.42 (m, 3H, *H*-3'', *H*-4'').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 189.8, 146.28, 141.2, 134.7, 134.2 (q, *J* = 32.6 Hz), 131.1, 129.2, 128.9, 128.8, 125.8 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 121.7.
^{19}F NMR (376 MHz, $CDCl_3$), *δ*/ppm: -64.16.
HRMS (APCI+), *m/z*: calculated for $C_{16}H_{11}F_3O + H^+$ 277.0835 [*M*+H]$^+$, found 277.0822.
Known compound, spectroscopic data corresponds to the literature.[7,9]

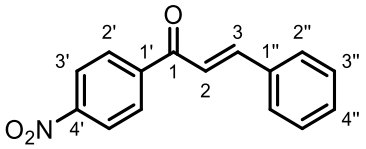
(*E*)-3'-Methoxychalcone (7h)



Chalcone synthesis was carried out according to SOP5 using 3'-methoxyacetophenone (**20 mmol, 3.00 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). Instead of filtration, the mixture was evaporated to dryness under reduced pressure. The product was obtained after filtration through silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as a yellow oil (**4.19 g, 17.6 mmol, 88%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.82 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.67 – 7.63 (m, 2H, *H*-2''), 7.61 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 1H, *H*-4'), 7.55 (dd, *J* = 2.7, 1.5 Hz, 1H, *H*-2'), 7.52 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.46 – 7.39 (m, 4H, *H*-5', *H*-3'', *H*-4''), 7.14 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H, *H*-6'), 3.89 (s, 3H, *H*-1''').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 190.4, 160.0, 145.0, 139.7, 135.0, 130.7, 129.7, 129.1, 128.6, 122.2, 121.2, 119.4, 113.0, 55.6.
HRMS (APCI+), *m/z*: calculated for $C_{16}H_{14}O_2 + H^+$ 239.1067 [*M*+H]$^+$, found 239.1063.
Known compound, spectroscopic data corresponds to the literature.[11]

(*E*)-4'-Nitrochalcone (7i)



In a 100 mL round bottom flask, 1 M aqueous sodium hydroxide solution (50 mL) was added to 4'-nitroacetophenone (**20 mmol, 3.30 g, 1.0 eq.**) and benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and stirred overnight at room temperature. The mixture was extracted with diethyl ether and the organic layer was dried over sodium sulphate and evaporated to dryness under reduced pressure. After recrystallization from acetone (ca. 100 mL, reflux to -30 °C), the product was obtained as an orange powder (**2.66 g, 10.5 mmol, 53%**).

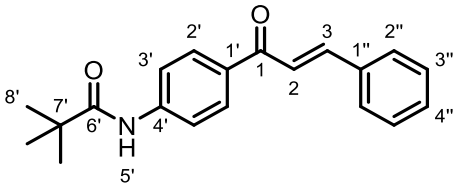
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.41 – 8.30 (m, 2H, *H*-3'), 8.22 – 8.10 (m, 2H, *H*-2'), 7.85 (d, *J* = 15.9 Hz, 1H, *H*-3), 7.70 – 7.62 (m, 2H, *H*-2''), 7.49 (d, *J* = 15.9 Hz, 1H, *H*-2), 7.46 – 7.41 (m, 3H, *H*-3'', *H*-4'').

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 189.2, 150.2, 147.0, 143.2, 134.4, 131.4, 129.5, 129.3, 128.8, 124.0, 121.4.

HRMS (APCI-), *m/z*: calculated for $C_{15}H_{11}NO_3^-$ 253.0744 $[M]^-$, found 253.0747.

Known compound, spectroscopic data corresponds to the literature.[9,12]

(*E*)-4'-(Pivaloylamino)chalcone (7j)



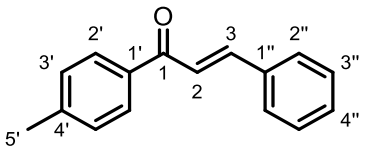
Chalcone synthesis was carried out according to SOP5 using 4'-pivaloylaminoacetophenone (**7a**, **20 mmol, 4.39 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). After recrystallization from ethanol/water 4:1 (v/v, ca. 100 mL, reflux to -30 °C), the product was obtained as dark yellow needles (**4.74 g, 15.4 mmol, 77%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.07 – 7.99 (m, 2H, *H*-2'), 7.80 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.73 – 7.69 (m, 2H, *H*-3'), 7.67 – 7.61 (m, 3H, *H*-5', *H*-2''), 7.54 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.44 – 7.38 (m, 3H, *H*-3'', *H*-4''), 1.34 (s, 9H, *H*-8').

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 189.1, 177.0, 144.6, 142.5, 135.0, 133.8, 130.6, 130.0, 129.1, 128.6, 121.9, 119.3, 40.0, 27.7.

HRMS (APCI+), *m/z*: calculated for $C_{20}H_{21}NO_2 + H^+$ 308.1645 $[M+H]^+$, found 308.1640.

(*E*)-4'-Methylchalcone (7k)



Chalcone synthesis was carried out according to SOP5 using 4'-methylacetophenone (**20 mmol, 2.68 g, 1.0 eq.**), benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a colourless powder (**3.64 g, 16.4 mmol, 82%**).

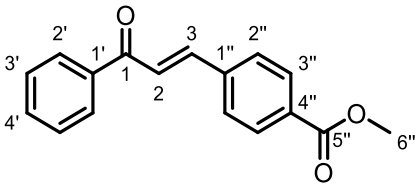
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.97 – 7.92 (m, 2H, *H*-2'), 7.81 (d, *J* = 15.7 Hz, 1H, *H*-3), 7.67 – 7.62 (m, 2H, *H*-2''), 7.54 (d, *J* = 15.7 Hz, 1H, *H*-2), 7.45 – 7.39 (m, 3H, *H*-3'', *H*-4''), 7.34 – 7.28 (m, 2H, *H*-3'), 2.44 (s, 3H, *H*-5').

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 190.2, 144.5, 143.8, 135.8, 135.1, 130.6, 129.5, 129.1, 128.8, 128.5, 122.2, 21.8.

HRMS (APCI+), *m/z*: calculated for $C_{16}H_{14}O + H^+$ 223.1117 $[M+H]^+$, found 223.1111.

Known compound, spectroscopic data corresponds to the literature.[8,11]

Methyl (*E*)-chalcone-3-carboxylate (7l)



Chalcone synthesis was carried out according to SOP5 using acetophenone (**20 mmol, 2.40 g, 1.0 eq.**), methyl 4-formylbenzoate (**20 mmol, 3.28 g, 1.0 eq.**) and sodium hydroxide (**20 mmol, 800 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a colourless solid (**4.49 g, 16.9 mmol, 84%**).

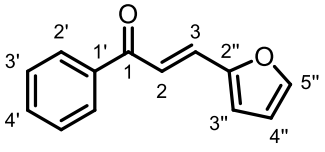
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.10 – 8.06 (m, 2H, *H*-3''), 8.05 – 8.01 (m, 2H, *H*-2'), 7.81 (d, *J* = 15.8 Hz, 1H, *H*-3), 7.72 – 7.67 (m, 2H, *H*-2''), 7.60 (d, *J* = 15.8 Hz, 1H, *H*-2), 7.63 – 7.57 (m, 1H, *H*-4'), 7.54 – 7.48 (m, 2H, *H*-3'), 3.94 (s, 3H, *H*-6'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 190.2, 166.6, 143.3, 139.2, 138.0, 133.2, 131.6, 130.3, 128.8, 128.7, 128.4, 124.2, 52.4.

HRMS (ESI+), *m/z*: calculated for $C_{13}H_{10}O$ + H^+ 267.1016 [*M*+H]$^+$, found 267.1012.

Known compound, spectroscopic data corresponds to the literature.[9]

(*E*)-2-(1-Phenylprop-2-en-1-on-3-yl)furane (7m)



In a 100 mL round bottom flask, 1 M aqueous sodium hydroxide (50 mL) was added to a mixture of acetophenone (**20 mmol, 2.40 g, 1.0 eq.**) and furfural (**20 mmol, 1,92 g, 1.0 eq.**) and stirred overnight at room temperature. The mixture was extracted with diethyl ether and the organic layer was dried over sodium sulphate and evaporated to dryness und reduced pressure. The product was obtained after filtration through silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as an orange oil (**3.33 g, 16.8 mmol, 84%**).

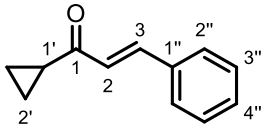
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.06 – 7.99 (m, 2H, *H*-2'), 7.60 (d, *J* = 15.3 Hz, 1H, *H*-3), 7.61 – 7.52 (m, 1H, *H*-4'), 7.55 – 7.42 (m, 3H, *H*-3', *H*-3''), 7.46 (d, *J* = 15.3 Hz, 1H, *H*-2), 6.71 (d, *J* = 3.4 Hz, 1H, *H*-5''), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H, *H*-4'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 189.9, 151.8, 145.0, 138.2, 132.9, 130.8, 128.7, 128.5, 119.4, 116.3, 112.8.

HRMS (APCI+), *m/z*: calculated for $C_{13}H_{10}O_2$ + H^+ 199.0754 [*M*+H]$^+$, found 199.0744.

Known compound, spectroscopic data corresponds to the literature.[9,12]

(*E*)-1-Cyclopropyl-3-phenylprop-2-en-1-one (7n)



In a 100 mL round bottom flask, 1 M aqueous sodium hydroxide (50 mL) was added to a mixture of acetylcyclopropane (**20 mmol, 1,68 g, 1.0 eq.**) and benzaldehyde (**20 mmol, 2.12 g, 1.0 eq.**) and stirred overnight at room temperature. The mixture was extracted with diethyl ether and the organic layer was dried over sodium sulphate and evaporated to dryness under reduced pressure. After recrystallization from ethanol/water 2:1(v/v, ca. 75 mL, reflux to -30 °C), the product was obtained as a colourless powder (**2.37 g, 13.8 mmol, 69%**).

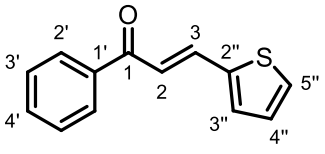
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.62 (d, *J* = 16.1 Hz, 1H, *H*-3), 7.59 – 7.54 (m, 2H, *H*-2''), 7.44 – 7.37 (m, 3H, *H*-3'', *H*-4''), 6.88 (d, *J* = 16.1 Hz, 1H, *H*-2), 2.26 (tt, *J* = 8.0, 4.6 Hz, 1H, *H*-1'), 1.16 (dt, *J* = 4.6, 3.4 Hz, 2H, *H*-2'^{a}), 0.99 (dt, *J* = 8.0, 3.4 Hz, 2H, *H*-2'^{b}).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 200.2, 142.2, 134.9, 130.5, 129.1, 128.4, 126.6, 19.8, 11.5.

HRMS (APCI+), *m/z*: calculated for $C_{12}H_{12}O$ + H^+ 173.0961 [*M*+H]$^+$, found 173.0953.

Known compound, spectroscopic data corresponds to the literature.[10]

(*E*)-2-(1-Phenylprop-2-en-1-on-3-yl)thiophene (7o)



In a 100 mL round bottom flask, 1 M aqueous sodium hydroxide (50 mL) was added to a mixture of acetophenone (**20 mmol, 2.40 g, 1.0 eq.**) and thiophene-2-carbaldehyde (**20 mmol, 2.24 g, 1.0 eq.**) and stirred at room temperature for 24 h. The mixture was extracted with diethyl ether and the organic layer was dried over sodium sulphate and evaporated to dryness under reduced pressure. The product was obtained after filtration through silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as a yellow oil (**3.94 g, 18.4 mmol, 92%**), which slowly crystallized upon standing.

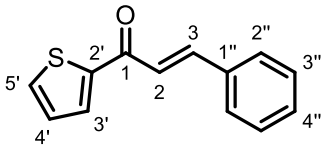
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.05 – 7.98 (m, 2H, *H*-2'), 7.95 (d, *J* = 15.3 Hz, 1H, *H*-3), 7.62 – 7.55 (m, 1H, *H*-4'), 7.53 – 7.47 (m, 2H, *H*-3'), 7.42 (dt, *J* = 5.1, 1.0 Hz, 1H, *H*-3''), 7.37 – 7.35 (m, 1H, *H*-5''), 7.34 (d, *J* = 15.3 Hz, 1H, *H*-2), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H, *H*-4'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 190.0, 140.5, 138.2, 137.3, 132.9, 132.2, 128.9, 128.7, 128.5, 128.5, 120.9.

HRMS (APCI+), *m/z*: calculated for $C_{13}H_{10}O + H^+$ 215.0525 $[M+H]^+$, found 215.0517.

Known compound, spectroscopic data corresponds to the literature.[9]

(*E*)-2-Cinnamoylthiophene (7p)



In a 100 mL round bottom flask, 1 M aqueous sodium hydroxide (50 mL) was added to a mixture of 2-acetylthiophene (4**0 mmol, 5.04 g, 1.0 eq.**) and benzaldehyde (**40 mmol, 4.25 g, 1.0 eq.**) and stirred at room temperature for 24 h. The mixture was extracted with diethyl ether and the organic layer was dried over sodium sulphate and evaporated to dryness under reduced pressure. After twofold recrystallization from ethanol/water 2:1 (v/v, ca. 150 mL, reflux to -30 °C) and ethanol/water 2:1(v/v, ca. 100 mL, reflux to -30 °C), the product was obtained as off-white crystals (**6.06 g, 28.3 mmol, 71%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.87 (dd, *J* = 3.8, 1.1 Hz, 1H, *H*-3'), 7.85 (d, *J* = 15.6 Hz, 1H, *H*-3), 7.66 (dd, *J* = 5.0, 1.1 Hz, 1H, *H*-5'), 7.65 – 7.61 (m, 2H, *H*-2''), 7.47 – 7.36 (m, 4H, *H*-2, *H*-3'', *H*-4''), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1H, *H*-4').

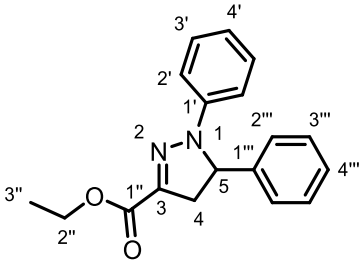
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 182.1, 145.6, 144.1, 134.7, 134.0, 131.9, 130.6, 129.0, 128.5, 128.3, 121.6.

HRMS (ESI+), *m/z*: calculated for $C_{13}H_{10}OS + H^+$ 215.0525 $[M+H]^+$, found 215.0523.

Known compound, spectroscopic data corresponds to the literature.[13]

8.2. Synthesized Pyrazolines

Ethyl 1*H*-4,5-dihydro-1,5-diphenylpyrazole-3-carboxylate (4a)



The synthesis was performed following the recently described protocol.[4] In a jacketed 300 mL beaker-type cell equipped with a magnetic stirring bar with stabilizing ring, ethyl glyoxylate phenylhydrazone (**6**, **46.8 mmol, 9.0 g, 1.0 eq.**) and styrene (**126.3 mmol, 13.16 g, 2.7 eq.**) were dissolved in ethyl acetate (60 mL). 1 M aqueous sodium iodide solution (240 mL) was added. A bipolar pack of four isostatic graphite electrodes (160 × 50 × 5 mm, spacer: 3 mm) with an immersion depth of 7 cm and a relevant surface area of 105 cm² was used. Constant current electrolysis was performed at 25 °C and 750 rpm, with a current density of 35.0 mA cm^{-2} until a charge of 5.4 *F* (24488 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with ethyl acetate (1 × 100 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 3% EtOAc) as a yellow solid (**10.6 g, 36.0 mmol, 77%**).

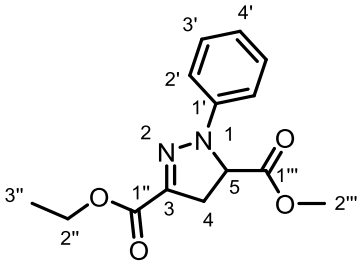
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.35 – 7.16 (m, 7H, *H*-3‘, *H*-2‘‘‘, *H*-3‘‘‘, *H*-4‘‘‘), 7.10 (dt, *J* = 7.9, 1.2 Hz, 2H, *H*-2’), 6.87 (tt, *J* = 7.2, 1.2 Hz, 1H, *H*-4‘), 5.42 (dd, *J* = 13.3, 7.0 Hz, 1H, *H*-5), 4.34 (q, *J* = 7.1 Hz, 2H, *H*-2‘‘), 3.72 (dd, *J* = 18.0, 13.3 Hz, 1H, *H*-4[a]), 3.05 (dd, *J* = 18.0, 7.0 Hz, 1H, *H*-4[b]), 1.37 (t, *J* = 7.1 Hz, 3H, *H*-3‘‘).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 162.9, 142.7, 141.3, 138.3, 129.4, 129.1, 128.1, 125.8, 121.4, 114.7, 65.5, 61.4, 42.4, 14.5.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{18}N_2O_2$ + H^+ 295.1441 [*M*+H]$^+$, found 295.1447.

Known compound, spectroscopic data corresponds to the literature.[4]

3-Ethyl, 5-methyl 1*H*-4,5-dihydro-1-phenylpyrazole-3,5-dicarboxylate (4b)



Pyrazoline synthesis was carried out according to a literature procedure using ethyl glyoxylate phenylhydrazone (**6**, **5.0 mmol, 960 mg, 1.0 eq.**) and methyl acrylate (**13.5 mmol, 1.16 g, 2.7 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as a yellow oil (**1.176 g, 4.25 mmol, 85%**).

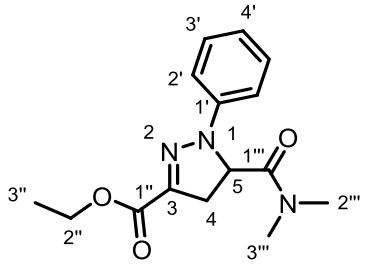
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.32 – 7.26 (m, 2H, *H*-3’), 7.12 (dt, *J* = 7.9, 1.1 Hz, 2H, *H*-2’), 6.96 (tt, *J* = 7.3, 1.1 Hz, 1H, *H*-4’), 4.93 (dd, *J* = 13.4, 6.7 Hz, 1H, *H*-5), 4.33 (qd, *J* = 7.1, 0.7 Hz, 2H, *H*-2‘‘), 3.72 (s, 3H, *H*-2‘‘‘), 3.53 (dd, *J* = 18.1, 13.4 Hz, 1H, *H*-4[a]), 3.31 (dd, *J* = 18.1, 6.7 Hz, 1H, *H*-4[b]), 1.37 (t, *J* = 7.1 Hz, 3H, *H*-3‘‘).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 170.7, 162.1, 142.5, 138.5, 129.4, 121.8, 114.0, 62.2, 61.5, 53.0, 37.3, 14.4.

HRMS (APCI+), *m/z*: calculated for $C_{14}H_{16}N_2O_4$ + H^+ 277.1183 [*M*+H]$^+$, found 277.1192.

Known compound, spectroscopic data corresponds to the literature.[4]

Ethyl 1*H*-4,5-dihydro-5-(dimethylcarbamoyl)-1-phenylpyrazole-3-carboxylate (4c)



Pyrazoline synthesis was carried out according to SOP7 using ethyl glyoxylate phenylhydrazone (**6**, **12.0 mmol, 2.31 g, 1.0 eq.**) and *N*,*N*-dimethyl acrylamide (**32.4 mmol, 3.21 g, 2.7 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 3% EtOAc) as a beige to yellow solid (**2.00 g, 8.22 mmol, 69%**).

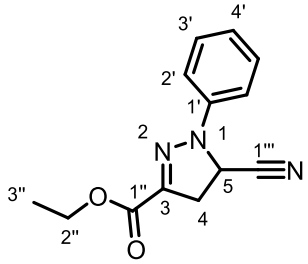
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.29 – 7.22 (m, 2H, *H*-3’), 7.08 – 7.03 (m, 2H, *H*-2’), 6.96 – 6.90 (m, 1H, *H*-4’), 5.13 (dd, *J* = 14.0, 7.9 Hz, 1H, *H*-5), 4.32 (qd, *J* = 7.1, 1.7 Hz, 2H, *H*-2’’), 3.54 (dd, *J* = 17.8, 14.0 Hz, 1H, *H*-4[a]), 3.12 (dd, *J* = 17.8, 7.9 Hz, 1H, *H*-4[b]), 3.06 (s, 3H, *H*-2’’’), 2.97 (s, 3H, *H*-3’’’), 1.35 (t, *J* = 7.1 Hz, 3H, *H*-3’’).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 168.9, 162.3, 142.6, 137.6, 129.3, 121.7, 114.0, 61.9, 61.3, 36.9, 36.9, 36.4, 14.4.

HRMS (APCI+), *m/z*: calculated for $C_{15}H_{19}N_3O_3$ + H^+ 290.1499 $[M+H]^+$, found 290.1491.

Known compound, spectroscopic data corresponds to the literature.[4]

Ethyl 1*H*-5-cyano-4,5-dihydro-1-phenylpyrazole-3-carboxylate (4d)



Pyrazoline synthesis was carried out according to SOP7 using ethyl glyoxylate phenylhydrazone (**6, 12.0 mmol, 2.31 g, 1.0 eq.**) and acryl nitrile (**32.4 mmol, 1.72 g, 2.7 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 8% EtOAc) as a yellow solid (**2.00 g, 8.22 mmol, 69%**).

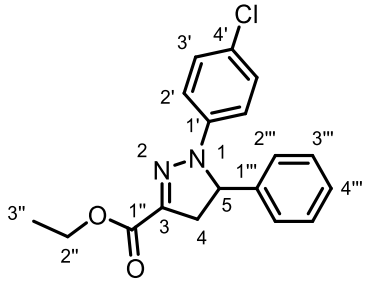
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.39 – 7.33 (m, 2H, *H*-3’), 7.24 (dt, *J* = 8.8, 1.0 Hz, 2H, *H*-2’), 7.10 – 7.04 (m, 1H, *H*-4’), 5.07 (ddd, *J* = 10.6, 8.2, 0.6 Hz, 1H, *H*-5), 4.35 (q, *J* = 7.1 Hz, 2H, *H*-2’’), 3.61 – 3.50 (m, 2H, *H*-4), 1.38 (td, *J* = 7.1, 0.6 Hz, 3H, *H*-3’’).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 161.3, 141.5, 140.0, 129.6, 123.2, 116.2, 115.0, 61.9, 50.4, 37.9, 14.3.

HRMS (ESI+), *m/z*: calculated for $C_{13}H_{13}N_3O_2$ + Na^+ 266.0900 $[M+Na]^+$, found 266.0896.

Known compound, spectroscopic data corresponds to the literature.[4]

Ethyl 1*H*-1-(4-chlorophenyl)-4,5-dihydro-5-phenylpyrazole-3-carboxylate (4e)



The synthesis was performed according to the recently described protocol.[4] In a 50 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, ethyl glyoxylate 4-chlorophenylhydrazone (**3.0 mmol, 680 mg, 1.0 eq.**) and styrene (**8.1 mmol, 844 mg, 2.7 eq.)** were dissolved in *tert*.-butyl methyl ether (5 mL). 1 M aqueous sodium iodide solution (20 mL) was added. Isostatic graphite electrodes (size: 60 × 20 × 3 mm) with an immersion depth of 2.7 cm and a relevant surface area of 5.4 cm^2 were used. Constant current electrolysis was performed at 32 °C and 800 rpm, with a current density of 32.1 mA cm^{-2} until a charge of 2.58 *F* (797 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with ethyl acetate (1 × 30 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. After flash column chromatography over silica with cyclohexane/ethyl acetate (0% → 3% EtOAc) the pyrazoline was obtained as a yellow solid (**2.65 mmol**, **872 mg**, **88%**).

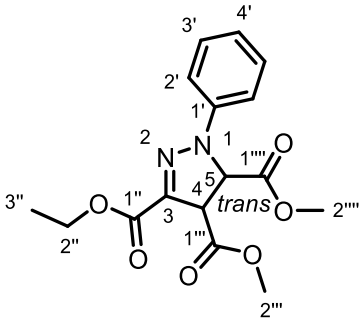
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.34 – 7.28 (m, 2H, *H*-3’’’), 7.30 – 7.20 (m, 1H, *H*-4’’’), 7.19 – 7.15 (m, 2H, *H*-2’’’), 7.12 – 7.06 (m, 2H, *H*-3’), 7.02 – 6.97 (m, 2H, *H*-2’), 5.35 (dd, *J* = 13.2, 7.0 Hz, 1H, *H*-5), 4.31 (q, *J* = 7.1 Hz, 2H, *H*-2’’), 3.70 (dd, *J* = 18.1, 13.2 Hz, 1H, *H*-4[a]), 3.03 (dd, *J* = 18.1, 7.0 Hz, 1H, *H*-4[b]), 1.34 (t, *J* = 7.1 Hz, 3H, *H*-3’’).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 162.6, 141.3, 140.8, 139.0, 129.5, 129.0, 128.2, 126.3, 125.7, 115.8, 65.5, 61.5, 42.5, 14.5.

HRMS (APCI+), *m/z*: calculated for $C_{18}H_{17}{}^{35}ClN_2O_2$ + H+ 329.1051 [*M*+H]+, found 329.1044; calculated for $C_{18}H_{17}{}^{37}ClN_2O_2$ + H+ 331.1028 [*M*+H]+, found 331.1027.

Known compound, spectroscopic data corresponds to the literature.[4,14]

3-Ethyl, 4,5-dimethyl 1*H*-4,5-*trans*-4,5-dihydro-1-phenylpyrazole-3,4,5-tricarboxylate (4f)



Pyrazoline synthesis was carried out according to SOP7 using ethyl glyoxylate phenylhydrazone (**6**, **12 mmol, 2.31 g, 1.0 eq.**) and dimethyl fumarate (**32.4 mmol, 4.67 g, 2.7 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 10% EtOAc) as a dark yellow solid (**2.51 g, 7.51 mmol, 63%**).

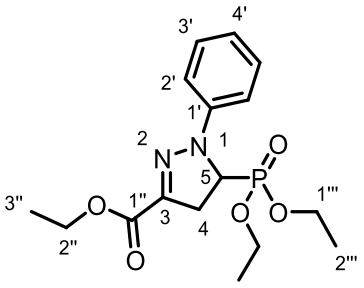
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.33 – 7.28 (m, 2H, *H*-3’), 7.18 – 7.13 (m, 2H, *H*-2’), 7.04 – 6.98 (m, 1H, *H*-4’), 5.17 (d, *J* = 5.8 Hz, 1H, *H*-5), 4.39 (d, *J* = 5.8 Hz, 1H, *H*-4), 4.44 – 4.25 (m, 2H, *H*-2’’), 3.79 (s, 3H, *H*-2’’’), 3.76 (s, 3H, *H*-2’’’’), 1.36 (t, *J* = 7.1 Hz, 3H, *H*-3’’).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 169.1, 169.0, 161.4, 141.8, 135.6, 129.4, 122.5, 114.5, 66.5, 61.7, 54.3, 53.4, 14.4.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{18}N_2O_6$ + Na^+ 357.1057 [*M*+Na]$^+$, found 357.1057.

Known compound, spectroscopic data corresponds to the literature.[4]

Ethyl 1*H*-5-(diethoxyphosphoryl)-4,5-dihydro-1-phenylpyrazole-3-carboxylate (4g)



Pyrazoline synthesis was carried out according to SOP7 using ethyl glyoxylate phenylhydrazone (**6**, **12.0 mmol, 2.31 g, 1.0 eq.**) and diethyl vinylphosphonate (**32.4 mmol, 5.32 g, 2.7 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (5% → 30% EtOAc) and flash column chromatography on C-18 silica with acetonitrile/water (25% → 60% MeCN) as a yellow oil (**970 mg, 2.74 mmol, 23%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.41 – 7.37 (m, 2H, *H*-2’), 7.31 – 7.26 (m, 2H, *H*-3’), 6.97 (tt, *J* = 7.3, 1.1 Hz, 1H, *H*-4’), 4.68 (dd, *J* = 13.7, 7.3 Hz, 1H, *H*-5), 4.33 (qd, *J* = 7.1, 0.8 Hz, 2H, *H*-2’’), 4.16 – 3.96 (m, 4H, *H*-1’’’), 3.66 – 3.38 (m, 2H, *H*-4), 1.36 (t, *J* = 7.1 Hz, 3H, *H*-3’’), 1.24 (t, *J* = 7.1 Hz, 3H, *H*-2’’’[a]), 1.22 (t, *J* = 7.1 Hz, 3H, *H*-2’’’[b]).

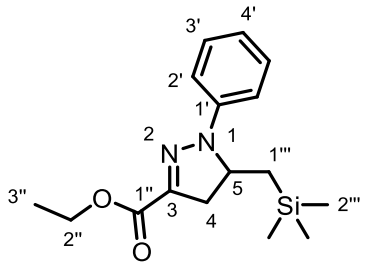
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 162.2, 143.4, 140.2 (d, *J* = 5.6 Hz), 128.9, 122.2, 115.8, 63.5 (d, *J* = 7.0 Hz), 63.0 (d, *J* = 7.0 Hz), 61.5, 58.3 (d, *J* = 163.8 Hz), 35.4 (d, *J* = 3.7 Hz), 16.5 (d, *J* = 5.3 Hz), 16.5 (d, *J* = 5.5 Hz), 14.4.

^{31}P NMR (162 MHz, $CDCl_3$), δ/ppm: 19.68.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{23}N_3O_5P$ + H^+ 355.1417 [*M*+H]$^+$, found 355.1422.

Known compound, spectroscopic data corresponds to the literature.[4]

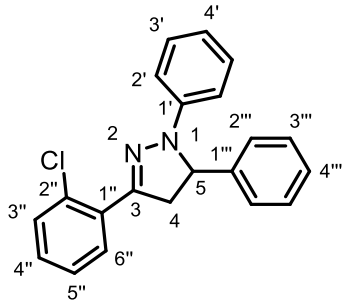
Ethyl 1*H*-4,5-dihydro-1-phenyl-5-((trimethylsilyl)methyl)pyrazole-3-carboxylate (4h)



Pyrazoline synthesis was carried out according to SOP7 using ethyl glyoxylate phenylhydrazone (**6**, **12.0 mmol, 2.31 g, 1.0 eq.**) and allyl trimethylsilane (**32.4 mmol, 3.70 g, 2.7 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 3% EtOAc) as a dark yellow oil (**896 mg, 2.94 mmol, 25%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.29 (tt, *J* = 7.3, 2.0 Hz, 2H, *H*-3'), 7.18 – 7.12 (m, 2H, *H*-2'), 6.94 (tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4'), 4.60 (dddd, *J* = 11.8, 11.7, 5.2, 1.8 Hz, 1H, *H*-5), 4.34 (qd, *J* = 7.1, 2.2 Hz, 2H, *H*-2''), 3.29 (dd, *J* = 17.4, 11.7 Hz, 1H, *H*-4^a), 2.78 (dd, *J* = 17.4, 5.2 Hz, 1H, *H*-4^b), 1.38 (t, *J* = 7.1 Hz, 3H, *H*-3''), 1.24 (dd, *J* = 14.6, 1.8 Hz, 1H, *H*-1'''^{a}), 0.90 (dd, *J* = 14.6, 11.8 Hz, 1H, *H*-1'''^{b}), 0.11 (s, 9H, *H*-2''').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 163.4, 141.9, 138.4, 129.3, 121.3, 115.1, 61.2, 58.8, 39.0, 21.2, 14.6, -0.8.
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{24}N_2O_2Si$ + H^+ 305.1680 [*M*+H]$^+$, found 305.1684.
Known compound, spectroscopic data corresponds to the literature.[4]

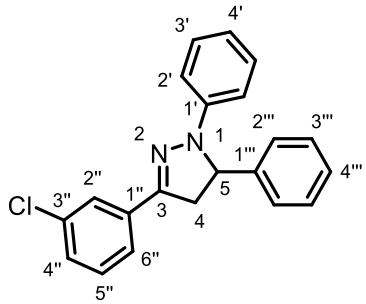
1*H*-3-(2-Chlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (4i)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-2'-chlorochalcone (**7b**, **10 mmol, 2.43 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The mixture was evaporated to dryness and the product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 1% EtOAc) as a pale-yellow solid (**1.09 g, 3.27 mmol, 33%**).

^{1}H NMR (400 MHz, $(CD_3)_2CO$), *δ*/ppm: 7.88 – 7.83 (m, 1H, *H*-3''), 7.50 – 7.46 (m, 1H, *H*-6''), 7.42 – 7.33 (m, 6H, *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 7.30 – 7.24 (m, 1H, *H*-5''), 7.18 – 7.12 (m, 2H, *H*-3'), 7.10 – 7.06 (m, 2H, *H*-2'), 6.75 (tt, *J* = 7.2, 1.3 Hz, 1H, *H*-4'), 5.49 (dd, *J* = 12.2, 6.7 Hz, 1H, *H*-5), 4.13 (dd, *J* = 17.4, 12.2 Hz, 1H, *H*-4^a), 3.31 (dd, *J* = 17.4, 6.7 Hz, 1H, *H*-4^b).
^{13}C NMR (101 MHz, $(CD_3)_2CO$), *δ*/ppm: 146.4, 145.5, 143.5, 132.5, 132.5, 131.7, 131.0, 130.5, 129.9, 129.6, 128.4, 127.9, 126.8, 120.0, 114.3, 65.1, 46.7.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}{}^{35}ClN_2$ + H^+ 333.1153 [*M*+H]$^+$, found 333.1152; calculated for $C_{21}H_{17}{}^{37}ClN_2$ + H^+ 335.1131 [*M*+H]$^+$, found 335.1126.
Known compound, spectroscopic data corresponds to the literature.[15]

1*H*-3-(3-Chlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (4j)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-3'-chlorochalcone (**7c**, **10 mmol, 2.43 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a light-yellow solid (**2.21 g, 6.64 mmol, 66%**).

^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.79 – 7.75 (m, 1H, *H*-2''), 7.57 (dt, *J* = 7.4, 1.6 Hz, 1H, *H*-6''), 7.37 – 7.25 (m, 7H, *H*-4'', *H*-5'', *H*-2''', *H*-3''', *H*-4'''), 7.21 – 7.14 (m, 2H, *H*-3'), 7.10 – 7.03 (m, 2H, *H*-2'), 6.78

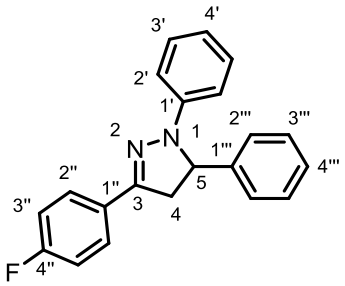
(tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4'), 5.34 (dd, *J* = 12.5, 6.8 Hz, 1H, *H*-5), 3.84 (dd, *J* = 17.2, 12.5 Hz, 1H, *H*-4^a), 3.11 (dd, *J* = 17.2, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 145.8, 144.8, 142.8, 135.2, 134.9, 130.3, 129.5, 129.3, 128.7, 128.1, 126.3, 125.9, 124.2, 119.7, 113.8, 64.8, 43.6.

HRMS (APCI+), *m/z*: calculated for $C_{21}H_{17}{}^{35}ClN_2 + H^+$ 333.1153 [*M*+H]$^+$, found 333.1122; calculated for $C_{21}H_{17}{}^{37}ClN_2 + H^+$ 335.1131 [*M*+H]$^+$, found 335.1125.

Known compound, spectroscopic data corresponds to the literature.[15]

1*H*-4,5-Dihydro-1,5-diphenyl-3-(4-fluorophenyl)pyrazole (4k)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-fluorochalcone (**7d**, **10 mmol, 2.26 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a pale-yellow solid (**1.42 g, 4.48 mmol, 45%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.76 – 7.69 (m, 2H, *H*-2''), 7.38 – 7.30 (m, 4H, *H*-2''', *H*-3'''), 7.30 – 7.23 (m, 1H, *H*-4'''), 7.19 – 7.14 (m, 2H, *H*-3'), 7.14 – 7.07 (m, 2H, *H*-3''), 7.07 – 7.03 (m, 2H, *H*-2'), 6.77 (tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4'), 5.31 (dd, *J* = 12.3, 7.1 Hz, 1H, *H*-5), 3.85 (dd, *J* = 17.1, 12.3 Hz, 1H, *H*-4^a), 3.12 (dd, *J* = 17.1, 7.1 Hz, 1H, *H*-4^b).

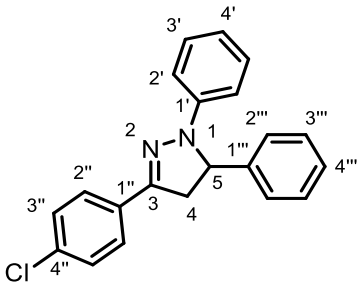
^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 163.4 (d, *J* = 248.0 Hz), 146.4, 145.2, 143.0, 129.5, 129.3, 128.0 (d, *J* = 5.5 Hz), 127.9, 126.3, 119.4, 116.0, 115.8, 113.6, 64.8, 44.0.

^{19}F NMR (376 MHz, $CDCl_3$), δ/ppm: -113.40 – -113.52 (m).

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}FN_2 + H^+$ 317.1449 [*M*+H]$^+$, found 317.1453.

Known compound, spectroscopic data corresponds to the literature.[4,16]

1*H*-3-(4-Chlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (4l)



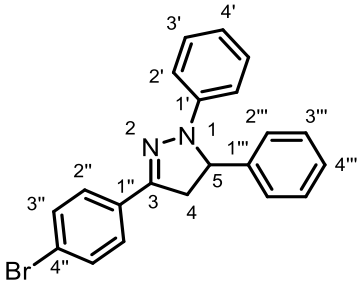
The synthesis was performed analogous to the recently described protocol[4] in fourfold scale. In a 100 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, 4-chlorobenzaldhyde phenylhydrazone (**12.8 mmol, 2.95 g, 1.0 eq.**) and styrene (**49.9 mmol, 5.20 g, 3.9 eq.**) were dissolved in *tert*.-butyl methyl ether (20 mL). 1 M aqueous sodium iodide solution (80 mL) was added. Isostatic graphite electrodes (80 × 34 × 5 mm) with an immersion depth of 6 cm and a relevant surface area of 20.4 cm^2 were used. Constant current electrolysis was performed at 32 °C and 800 rpm, with a current density of 32.1 mA cm^{-2} until a charge of 2.58 *F* (3186 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with *tert*.-butyl methyl ether (1 × 50 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 3% EtOAc) as a light orange solid (**2.71 g, 8.14 mmol, 64%**).

^{1}H NMR (400 MHz, $(CD_3)_2CO$), δ/ppm: 7.82 – 7.74 (m, 2H, *H*-2''), 7.47 – 7.37 (m, 2H, *H*-3''), 7.39 – 7.29 (m, 4H, *H*-2''', *H*-3'''), 7.32 – 7.20 (m, 1H, *H*-4'''), 7.19 – 7.09 (m, 2H, *H*-3'), 7.10 – 7.03 (m, 2H, *H*-2'), 6.73 (tt, *J* = 7.2, 1.3 Hz, 1H, *H*-4'), 5.47 (dd, *J* = 12.4, 6.8 Hz, 1H, *H*-5), 3.96 (dd, *J* = 17.4, 12.4 Hz, 1H, *H*-4^a), 3.13 (dd, *J* = 17.4, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, $(CD_3)_2CO$), δ/ppm: 206.3, 146.8, 145.5, 143.7, 134.5, 132.7, 129.9, 129.6, 129.5, 128.4, 128.1, 126.8, 119.8, 114.2, 65.0, 43.9.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}{}^{35}ClN_2 + H^+$ 333.1153 $[M+H]^+$, found 333.151; calculated for $C_{21}H_{17}{}^{37}ClN_2 + H^+$ 335.1131 $[M+H]^+$, found 335.1133.
Known compound, spectroscopic data corresponds to the literature.[4,15]

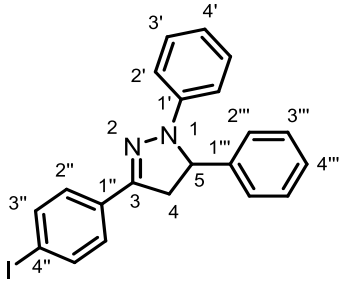
1*H*-3-(4-Bromophenyl)-4,5-dihydro-1,5-diphenylpyrazole (4m)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-bromochalcone (**7e**, **10 mmol, 2.87 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a yellow solid (**2.57 g, 6.81 mmol, 68%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.63 – 7.58 (m, 2H, *H*-2''), 7.55 – 7.50 (m, 2H, *H*-3''), 7.38 – 7.24 (m, 5H, *H*-2''', *H*-3''', *H*-4'''), 7.20 – 7.13 (m, 2H, *H*-3'), 7.08 – 7.03 (m, 2H, *H*-2'), 6.87 – 6.64 (m, 1H, *H*-4'), 5.32 (dd, *J* = 12.6, 6.9 Hz, 1H, *H*-5), 3.83 (dd, *J* = 17.2, 12.6 Hz, 1H, *H*-4^a), 3.11 (dd, *J* = 17.2, 6.9 Hz, 1H, *H*-4^b).
^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 146.2, 144.9, 142.9, 132.3, 132.0, 129.5, 129.3, 128.0, 127.6, 126.3, 122.7, 119.6, 113.7, 64.8, 43.6.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}{}^{79}BrN_2 + H^+$ 377.0648 $[M+H]^+$, found 377.0637; calculated for $C_{21}H_{17}{}^{81}BrN_2 + H^+$ 379.0628 $[M+H]^+$, found 379.0627.
Known compound, spectroscopic data corresponds to the literature.[4]

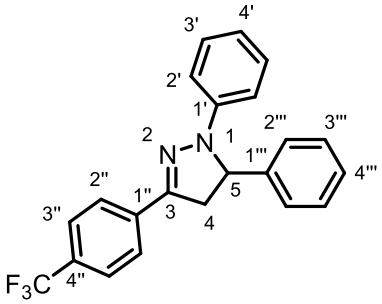
1*H*-4,5-Dihydro-1,5-diphenyl-3-(4-iodophenyl)pyrazole (4n)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-iodochalcone (**7f**, **10 mmol, 3.34 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a yellow powder (**3.71 g, 8.74 mmol, 87%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.84 – 7.73 (m, 2H, *H*-2''), 7.62 – 7.53 (m, 2H, *H*-3''), 7.37 – 7.32 (m, 4H, *H*-2''', *H*-3'''), 7.30 – 7.24 (m, 1H, *H*-4'''), 7.17 – 7.11 (m, 2H, *H*-3'), 7.09 – 7.05 (m, 2H, *H*-2'), 6.73 (tt, *J* = 7.2, 1.3 Hz, 1H, *H*-4'), 5.47 (dd, *J* = 12.4, 6.8 Hz, 1H, *H*-5), 3.95 (dd, *J* = 17.4, 12.4 Hz, 1H, *H*-4^a), 3.13 (dd, *J* = 17.4, 6.8 Hz, 1H, *H*-4^b).
^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 146.9, 145.5, 143.7, 138.5, 133.5, 129.9, 129.6, 128.4, 128.4, 126.8, 119.9, 114.2, 94.4, 65.0, 43.7.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}IN_2 + H^+$ 425.0509 $[M+H]^+$, found 425.0514.

1*H*-4,5-Dihydro-1,5-diphenyl-3-(4-(trifluoromethyl)phenyl)pyrazole (4o)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-(trifluoromethyl)chalcone (**7g**, **10 mmol, 2.76 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a yellow solid (**2.48 g, 6.77 mmol, 68%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.88 – 7.80 (m, 2H, *H*-2''), 7.69 – 7.61 (m, 2H, *H*-3''), 7.39 – 7.25 (m, 5H, *H*-2''', *H*-3''', *H*-4'''), 7.21 – 7.15 (m, 2H, *H*-3'), 7.11 – 7.05 (m, 2H, *H*-2'), 6.80 (tt, *J* = 7.2, 1.2 Hz, 1H, *H*-4'), 5.39 (dd, *J* = 12.6, 6.9 Hz, 1H, *H*-5), 3.88 (dd, *J* = 17.2, 12.6 Hz, 1H, *H*-4^a), 3.16 (dd, *J* = 17.2, 6.9 Hz, 1H, *H*-4^b).

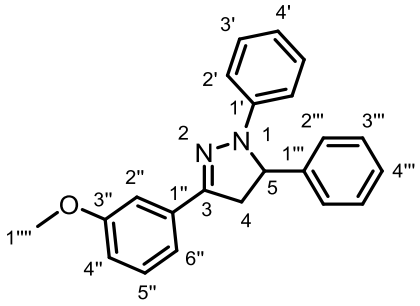
^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 145.6, 144.6, 142.7, 136.8, 123.0 (q, *J* = 32.4 Hz), 129.6, 129.3, 128.1, 126.3, 126.1, 125.8 (q, *J* = 4.0 Hz), 124.7 (q, *J* = 272.0 Hz), 119.9, 113.9, 64.9, 43.5.

^{19}F NMR (376 MHz, $CDCl_3$), δ/ppm: -63.71.

HRMS (APCI+), *m/z*: calculated for $C_{22}H_{17}F_3N_2$ + H^+ 367.1417 [*M*+H]$^+$, found 367.1418.

Known compound, spectroscopic data corresponds to the literature.[4]

1*H*-4,5-Dihydro-1,5-diphenyl-3-(3-methoxyphenyl)pyrazole (4p)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-3'-methoxychalcone (**7h**, **10 mmol, 2.38 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The mixture was evaporated to dryness. The product was obtained after recrystallization from ethanol (ca. 100 mL, reflux to room temperature) with ultra-sonification during cooling down as a pale-yellow solid (**1.94 g, 5.91 mmol, 59%**). The sonification ensured formation of small crystallites to prevent incorporation of impurities.

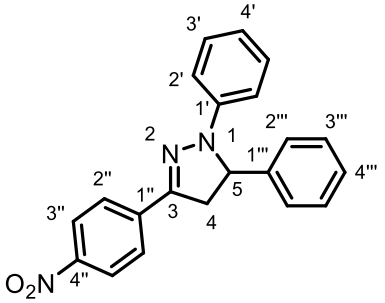
^{1}H NMR (400 MHz, $(CD_3)_2CO$), δ/ppm: 7.39 – 7.29 (m, 7H, *H*-2'', *H*-4'', *H*-6'', *H*-2''', *H*-3'''), 7.29 – 7.23 (m, 1H, *H*-4'''), 7.17 – 7.10 (m, 2H, *H*-3'), 7.10 – 7.05 (m, 2H, *H*-2'), 6.96 – 6.89 (m, 1H, *H*-5''), 6.72 (tt, *J* = 7.1, 1.3 Hz, 1H, *H*-4'), 5.43 (dd, *J* = 12.3, 6.8 Hz, 1H, *H*-5), 3.94 (dd, *J* = 17.4, 12.3 Hz, 1H, *H*-4^a), 3.84 (s, 3H, *H*-1''''), 3.13 (dd, *J* = 17.4, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, $(CD_3)_2CO$), δ/ppm: 160.8, 147.8, 145.7, 143.8, 135.1, 130.4, 129.9, 129.6, 128.3, 126.8, 119.7, 119.1, 115.4, 114.1, 111.5, 64.9, 55.6, 44.1.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{20}N_2O$ + H^+ 329.1648 [*M*+H]$^+$, found 329.1646.

Known compound, spectroscopic data corresponds to the literature.[4,15]

1*H*-4,5-Dihydro-1,5-diphenyl-3-(4-nitrophenyl)pyrazole (4q)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-nitrochalcone (**7i**, **10 mmol, 2.53 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as an intense red solid (**2.84 g, 8.27 mmol, 83%**).

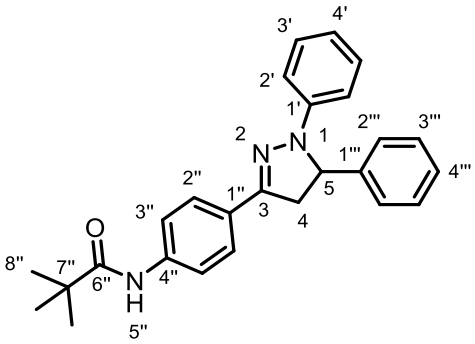
^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 8.25 – 8.19 (m, 2H, *H*-3''), 7.87 – 7.81 (m, 2H, *H*-2''), 7.40 – 7.33 (m, 2H, *H*-3'''), 7.32 – 7.26 (m, 3H, *H*-2''', *H*-4'''), 7.23 – 7.17 (m, 2H, *H*-3'), 7.14 – 7.08 (m, 2H, *H*-2'), 6.83 (tt, *J* = 7.2, 1.2 Hz, 1H, *H*-4'), 5.45 (dd, *J* = 12.7, 6.8 Hz, 1H, *H*-5), 3.89 (dd, *J* = 17.2, 12.7 Hz, 1H, *H*-4^a), 3.17 (dd, *J* = 17.2, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 147.4, 144.7, 144.0, 142.3, 139.5, 129.6, 129.4, 128.2, 126.2, 126.2, 124.3, 120.4, 114.1, 65.1, 43.2.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}N_3O_2$ + H^+ 344.1394 [*M*+H]$^+$, found 344.1394.

Known compound, spectroscopic data corresponds to the literature.[4,15]

1*H*-4,5-Dihydro-1,5-diphenyl-3-(4-pivaloylaminophenyl)pyrazole (4r)



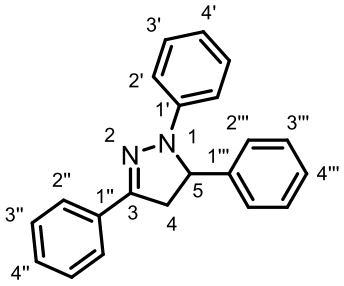
Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-(pivaloylamino)chalcone (**7j**, **10 mmol, 3.07 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a light-orange powder (**2.92 g, 7.35 mmol, 73%**).

^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.71 – 7.67 (m, 2H, *H*-2''), 7.61 – 7.56 (m, 2H, *H*-3''), 7.43 (brs, 1H, *H*-5''), 7.37 – 7.30 (m, 4H, *H*-2''', *H*-3'''), 7.29 – 7.24 (m, 1H, *H*-4'''), 7.19 – 7.12 (m, 2H, *H*-3'), 7.07 – 7.02 (m, 2H, *H*-2'), 6.75 (tt, *J* = 7.2, 1.2 Hz, 1H, *H*-4'), 5.29 (dd, *J* = 12.3, 7.1 Hz, 1H, *H*-5), 3.85 (dd, *J* = 17.1, 12.3 Hz, 1H, *H*-4^a), 3.12 (dd, *J* = 17.1, 7.1 Hz, 1H, *H*-4^b), 1.30 (s, 9H, *H*-8'').

^{13}C NMR (101 MHz, CD_2Cl_2), *δ*/ppm: 176.8, 147.0, 145.3, 143.1, 139.1, 129.4, 129.2, 128.9, 127.9, 126.7, 126.3, 120.1, 119.2, 113.6, 64.7, 43.9, 40.0, 27.7.

HRMS (APCI+), *m/z*: calculated for $C_{26}H_{27}N_3O$ + H^+ 398.2227 $[M+H]^+$, found 398.2229.

1*H*-4,5-Dihydro-1,3,5-triphenylpyrazole (4s)



The synthesis was performed following the recently described protocol.[4] In a jacketed 300 mL beaker-type cell equipped with a magnetic stirring bar with stabilizing ring, benzaldehyde phenylhydrazone (**38.2 mmol, 7.5 g, 1.0 eq.**) and styrene (**149 mmol, 15.52 g, 3.9 eq.**) were dissolved in *tert*.-butyl methyl ether (60 mL). 1 M aqueous sodium iodide solution (240 mL) was added. A bipolar pack of four isostatic graphite electrodes (160 × 50 × 5 mm, spacer: 3 mm) with an immersion depth of 7 cm and a relevant surface area of 105 cm² was used. Constant current electrolysis was performed at 32 °C and 750 rpm, with a current density of 32.1 mA cm^{-2} until a charge of 2.58 *F* (9587 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with ethyl acetate (1 × 100 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. Excess styrene was removed by vacuum distillation. The crude product was recrystallized from isopropanol (ca. 400 mL, reflux to -30 °C) to yield a yellow solid (**7.89 g, 26.4 mmol, 69%**).

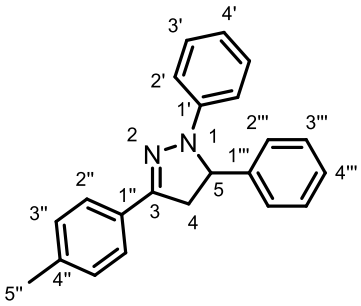
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.76 – 7.70 (m, 2H, *H*-2''), 7.42 – 7.37 (m, 2H, *H*-3''), 7.37 – 7.30 (m, 5H, *H*-4'', *H*-2''', *H*-3'''), 7.30 – 7.24 (m, 1H, *H*-4'''), 7.23 – 7.16 (m, 2H, *H*-3'), 7.11 – 7.06 (m, 2H, *H*-2'), 6.79 (tt, *J* = 7.2, 1.2 Hz, 1H, *H*-4'), 5.28 (dd, *J* = 12.4, 7.3 Hz, 1H, *H*-5), 3.85 (dd, *J* = 17.1, 12.4 Hz, 1H, *H*-4^a), 3.15 (dd, *J* = 17.1, 7.3 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 146.8, 145.0, 142.7, 132.9, 129.3, 129.0, 128.7, 128.7, 127.7, 126.0, 125.9, 119.2, 113.5, 64.6, 43.7.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{18}N_2$ + H^+ 299.1543 $[M+H]^+$, found 299.1542.

Known compound, spectroscopic data corresponds to the literature.[4,15,16]

1*H*-4,5-Dihydro-1,5-diphenyl-3-(4-methylphenyl)pyrazole (4t)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-4'-methylchalcone (**7k**, **10 mmol, 2.22 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a pale-yellow solid (**1.69 g, 5.41 mmol, 54%**).

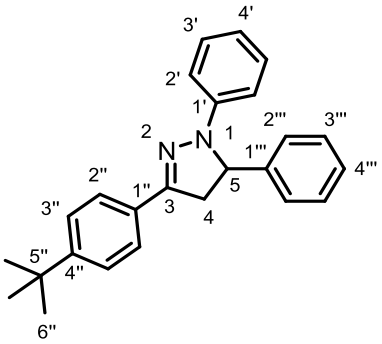
^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.65 – 7.61 (m, 2H, *H*-2''), 7.37 – 7.30 (m, 4H, *H*-2''', *H*-3'''), 7.30 – 7.24 (m, 1H, *H*-4'''), 7.24 – 7.20 (m, 2H, *H*-3''), 7.19 – 7.14 (m, 2H, *H*-3'), 7.08 – 7.02 (m, 2H, *H*-2'), 6.76 (tt, *J* = 7.2, 1.2 Hz, 1H, *H*-4'), 5.28 (dd, *J* = 12.3, 7.0 Hz, 1H, *H*-5), 3.85 (dd, *J* = 17.1, 12.3 Hz, 1H, *H*-4^a), 3.12 (dd, *J* = 17.1, 7.0 Hz, 1H, *H*-4^b), 2.38 (s, 3H, *H*-5'').

^{13}C NMR (101 MHz, CD_2Cl_2), *δ*/ppm: 147.5, 145.4, 143.2, 139.3, 130.4, 129.6, 129.4, 129.2, 127.9, 126.3, 126.0, 119.2, 113.6, 64.6, 44.0, 21.5.

HRMS (APCI+), *m/z*: calculated for $C_{22}H_{20}N_2$ + H^+ 313.1699 [*M*+H]$^+$, found 313.1692.

Known compound, spectroscopic data corresponds to the literature.[4,16]

1*H*-3-(4-*tert.*-Butylphenyl)-4,5-dihydro-1,5-diphenylpyrazole (4u)



The synthesis was performed according to the recently described protocol. In a 50 mL jacketed beaker-type cell equipped with a cross-shaped stirring bar, 4-*tert.*-butylbenzaldhyde phenylhydrazone (**3.2 mmol, 808 mg, 1.0 eq.**) and styrene (**12.5 mmol, 1302 mg, 3.9 eq.**) were dissolved in *tert*.-butyl methyl ether (5 mL). 1 M aqueous sodium iodide solution (20 mL) was added. Isostatic graphite electrodes (size: 60 × 20 × 3 mm) with an immersion depth of 2.7 cm and a relevant surface area of 5.4 cm^2 were used. Constant current electrolysis was performed at 32 °C and 800 rpm, with a current density of 32.1 mA cm^{-2} until a charge of 2.58 *F* (797 C) was applied. The reaction mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with ethyl acetate (1 × 30 mL). The combined organic fractions were dried over anhydrous magnesium sulphate, filtered and the solvent was removed under reduced pressure. After reversed phase flash column chromatography over C-18 silica with water/acetonitrile (75% → 85% MeCN) the pyrazoline was obtained as an off-white solid (**0.80 mmol**, **285 mg**, **25%**).

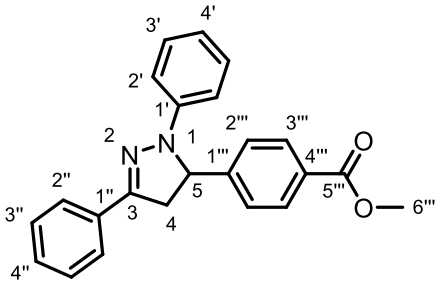
^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.63 – 7.59 (m, 2H, *H*-2''), 7.38 – 7.33 (m, 2H, *H*-3''), 7.31 – 7.22 (m, 4H, *H*-2''', *H*-3'''), 7.20 (td, *J* = 5.3, 3.0 Hz, 1H, *H*-4'''), 7.12 (tt, *J* = 7.3, 2.1 Hz, 2H, *H*-3'), 7.05 – 6.98 (m, 2H, *H*-2'), 6.71 (tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4'), 5.20 (dd, *J* = 12.3, 7.1 Hz, 1H, *H*-5), 3.78 (dd, *J* = 17.0, 12.3 Hz, 1H, *H*-4^a), 3.08 (dd, *J* = 17.0, 7.1 Hz, 1H, *H*-4^b), 1.28 (s, 9H, *H*-6'').

^{13}C NMR (101 MHz, CD_2Cl_2), *δ*/ppm: 52.0, 146.9, 145.1, 142.8, 130.1, 129.2, 129.0, 127.6, 126.0, 125.7, 125.6, 119.0, 113.4, 64.5, 43.8, 34.9, 31.4.

HRMS (ESI+), *m/z*: calculated for $C_{25}H_{26}N_2$ + H+ 355.2169 [*M*+H]$^+$, found 355.2175.

Known compound, spectroscopic data corresponds to the literature.[4]

Methyl 4-(1*H*-4,5-dihydro-1,3-diphenylpyrazol-5-yl)benzoate (4v)



Pyrazoline synthesis was carried out according to SOP6 using methyl (*E*)-chalcone-3-carboxylate (**7l**, **10 mmol, 2.66 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a faint yellow powder (**3.05 g, 8.56 mmol, 86%**).

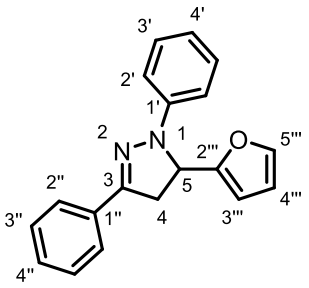
^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 8.02 – 7.96 (m, 2H, *H*-3’’’), 7.77 – 7.70 (m, 2H, *H*-2’’), 7.45 – 7.38 (m, 4H, *H*-3’’, *H*-2’’’), 7.38 – 7.32 (m, 1H, *H*-4’’), 7.20 – 7.14 (m, 2H, *H*-3’), 7.06 – 7.01 (m, 2H, *H*-2’), 6.78 (tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4’), 5.36 (dd, *J* = 12.4, 7.1 Hz, 1H, *H*-5), 3.90 (dd, *J* = 17.2, 12.4 Hz, 1H, *H*-4^a), 3.87 (s, 3H, *H*-6’’’), 3.14 (dd, *J* = 17.2, 7.1 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), *δ*/ppm: 166.9, 148.1, 147.4, 145.1, 133.0, 130.7, 130.1, 129.3, 129.1, 129.0, 126.5, 126.1, 119.6, 113.7, 64.5, 52.4, 43.7.

HRMS (APCI+), *m/z*: calculated for $C_{23}H_{20}N_2O_2$ + H^+ 357.1598 $[M+H]^+$, found 357.1596.

Known compound, spectroscopic data corresponds to the literature.[17]

1*H*-4,5-Dihydro-1,3-diphenyl-5-(furan-2-yl)pyrazole (4w)



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-2-(1-phenylprop-2-en-1-on-3-yl)furane (**7m**, **10 mmol, 1.98 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as a grey solid (**2.34 g, 8.12 mmol, 81%**).

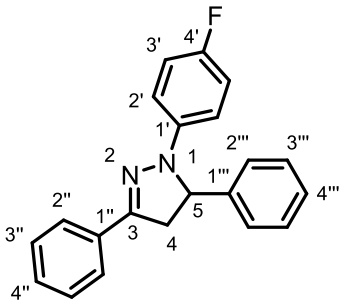
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.79 – 7.74 (m, 2H, *H*-2’’), 7.44 – 7.39 (m, 2H, *H*-3’’), 7.38 – 7.33 (m, 2H, *H*-4’’, *H*-5’’’), 7.29 – 7.23 (m, 2H, *H*-3’), 7.22 – 7.17 (m, 2H, *H*-2’), 6.86 (tt, *J* = 7.2, 1.3 Hz, 1H, *H*-4’), 6.31 (dd, *J* = 3.3, 1.8 Hz, 1H, *H*-4’’’), 6.24 (dt, *J* = 3.3, 0.7 Hz, 1H, *H*-3’’’), 5.36 (dd, *J* = 12.2, 6.7 Hz, 1H, *H*-5), 3.71 (dd, *J* = 16.9, 12.2 Hz, 1H, *H*-4^a), 3.39 (dd, *J* = 16.9, 6.7 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 153.8, 147.5, 145.1, 142.3, 132.7, 129.0, 128.9, 128.7, 125.9, 119.7, 113.8, 110.6, 107.1, 58.3, 40.2.

HRMS (APCI+), *m/z*: calculated for $C_{19}H_{16}N_2O$ + H^+ 289.1335 $[M+H]^+$, found 289.1330.

Known compound, spectroscopic data corresponds to the literature.[18]

1*H*-4,5-Dihydro-3,5-diphenyl-1-(4-fluorophenyl)pyrazole (4x)



Pyrazoline synthesis was carried out according to SOP6 using diphenyl (*E*)-chalcone (**9.60 mmol, 2.00 g, 1.0 eq.**), 4-fluorophenylhydrazine hydrochloride (**11.52 mmol, 1.87 g, 1.2 eq.**), glacial acetic acid (**9.6 mmol, 576 mg, 1.0 eq.**) and methanol as solvent. The product was obtained after filtration without further purification as light-yellow crystals (**1.69 g, 5.35 mmol, 56%**).

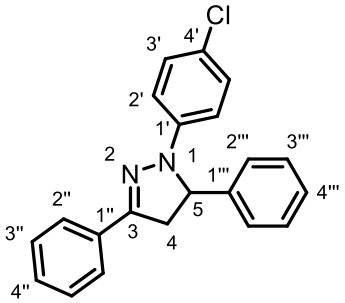
^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.76 – 7.69 (m, 2H, *H*-2’), 7.50 – 7.24 (m, 8H, *H*-3’, *H*-2’’, *H*-3’’, *H*-2’’’), 7.08 – 6.97 (m, 2H, *H*-3’’’), 6.94 – 6.84 (m, 2H, *H*-4’’, *H*-4’’’), 5.24 (dd, *J* = 12.3, 7.6 Hz, 1H, *H*-5), 3.87 (dd, *J* = 17.2, 12.3 Hz, 1H, *H*-4^a), 3.15 (dd, J = 17.2, 7.6 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 157.1 (d, *J* = 236.7 Hz), 147.6, 142.9, 142.1, 133.1, 129.5, 129.2, 129.1, 129.0, 128.9, 128.5, 128.1, 127.5 (d, *J* = 8.6 Hz), 126.4, 126.1, 116.1 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 22.4 Hz), 114.7 (d, *J* = 7.3 Hz), 105.4, 65.4, 44.1.

^{19}F NMR (282 MHz CD_2Cl_2), δ/ppm: -125.92 (tt, *J* = 8.8, 4.7 Hz).

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{17}FN_2$ + H^+ 317.1449 [*M*+H]$^+$, found 317.1448.

1*H*-1-(4-Chlorophenyl)-4,5-dihydro-3,5-diphenylpyrazole (4y)



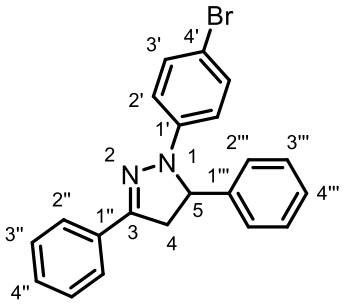
Pyrazoline synthesis was carried out according to SOP6 using diphenyl (*E*)-chalcone (**19.2 mmol, 4.00 g, 1.0 eq.**), 4-chlorophenylhydrazine hydrochloride (**23.0 mmol, 4.12 g, 1.2 eq.**), glacial acetic acid (**19.2 mmol, 1.152 g, 1.0 eq.**) and methanol as solvent. The product was obtained after filtration without further purification as light-yellow crystals (**5.99 g, 18.0 mmol, 94%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.81 – 7.73 (m, 2H, *H*-2''), 7.50 – 7.27 (m, 8H, *H*-3'', *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 7.21 – 7.13 (m, 2H, *H*-2'), 7.07 – 7.03 (m, 2H, *H*-3'), 5.32 (dd, *J* = 12.3, 6.9 Hz, 1H, *H*-5), 3.91 (dd, *J* = 17.2, 12.3 Hz, 1H, *H*-4^a), 3.20 (dd, *J* = 17.2, 6.9 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 148.0, 143.8, 142.5, 132.9, 129.5, 129.2, 129.1, 129.0, 128.1, 126.3, 126.2, 123.9, 114.8, 64.7, 44.0.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{16}{}^{35}ClN_2$ + H^+ 333.1153 [*M*+H]$^+$, found 333.1146; calculated for $C_{21}H_{16}{}^{37}ClN_2$ + H^+ 335.1131 [*M*+H]$^+$, found 335.1132.

1*H*-1-(4-Bromophenyl)-4,5-dihydro-3,5-diphenylpyrazole (4z)



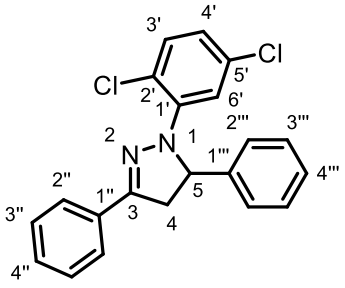
Pyrazoline synthesis was carried out according to SOP6 using diphenyl (*E*)-chalcone (**6.20 mmol, 1.29 g, 1.0 eq.**), 4-bromophenylhydrazine hydrochloride (**7.44 mmol, 1.67 g, 1.2 eq.**), glacial acetic acid (**6.20 mmol, 372 mg, 1.0 eq.**) and methanol as solvent. The product was obtained after filtration without further purification as light-yellow crystals (**2.07 g, 5.49 mmol, 88%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.82 – 7.73 (m, 2H, *H*-2''), 7.48 – 7.37 (m, 5H, *H*-3'', *H*-4'', *H*-2'''), 7.36 – 7.28 (m, 5H, *H*-3', *H*-3''', *H*-4'''), 7.05 – 6.96 (m, 2H, *H*-2'), 5.31 (dd, *J* = 12.3, 6.8 Hz, 1H, *H*-5), 3.91 (dd, *J* = 17.3, 12.3 Hz, 1H, *H*-4^a), 3.20 (dd, *J* = 17.3, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 148.10, 144.18, 142.47, 132.90, 131.97, 129.55, 129.23, 128.97, 128.11, 126.26, 126.18, 115.25, 111.15, 64.56, 44.02.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{16}{}^{79}BrN_2$ + H^+ 377.0648 [*M*+H]$^+$, found 377.0642; calculated for $C_{21}H_{16}{}^{81}BrN_2$ + H^+ 379.0630 [*M*+H]$^+$, found 379.0625.

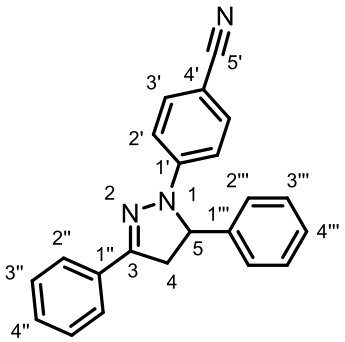
1*H*-1-(2,5-Dichlorophenylphenyl)-4,5-dihydro-3,5-diphenylpyrazole (4a')



Pyrazoline synthesis was carried out according to SOP6 using diphenyl (*E*)-chalcone (**9.60 mmol, 2.00 g, 1.0 eq.**), 2,5-dichlorphenylhydrazine hydrochloride (**11.52 mmol, 2.46 g, 1.2 eq.**), glacial acetic acid (**9.60 mmol, 576 mg, 1.0 eq.**) and methanol as solvent. The product was obtained after filtration without further purification as light-yellow crystals (**3.17 g, 8.64 mmol, 90%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.83 – 7.75 (m, 2H, *H*-2''), 7.56 (d, *J* = 2.5 Hz, 1H, *H*-6'), 7.40 (m, 1H, *H*-3'', *H*-4''), 7.24 – 7.07 (m, 6H, *H*-3', *H*-2''', *H*-3''', *H*-4'''), 6.82 (dd, *J* = 8.5, 2.5 Hz, 1H, *H*-4'), 5.95 (dd, *J* = 11.5, 4.1 Hz, 1H, *H*-5), 3.84 (dd, *J* = 17.1, 11.5 Hz, 1H, *H*-4^a), 3.40 (dd, *J* = 17.1, 4.1 Hz, 1H, *H*-4^b).
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 151.4, 144.4, 141.2, 133.0, 132.7, 131.5, 129.7, 129.0, 129.0, 128.3, 126.9, 126.5, 123.6, 123.2, 122.2, 66.3, 43.2.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{16}{}^{35}Cl^{35}ClN_2 + H^+$ 367.0763 [*M*+H]$^+$, found 367.0759; calculated for $C_{21}H_{16}{}^{35}Cl^{37}ClN_2 + H^+$ 369.0738 [*M*+H]$^+$, found 369.0731.

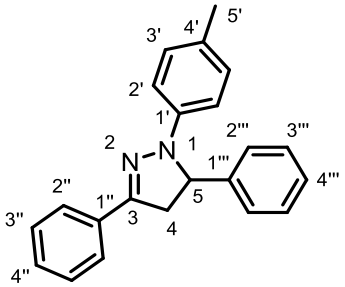
1*H*-1-(4-Cyanophenyl)-4,5-dihydro-3,5-diphenylpyrazole (4b')



Pyrazoline synthesis was carried out according to SOP6 using diphenyl (*E*)-chalcone (**10 mmol, 2.08 g, 1.0 eq.**), 4-cyanophenylhydrazine hydrochloride (**10 mmol, 1.70 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as faint yellow crystals (**2.92 g, 9.08 mmol, 91%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.78 – 7.69 (m, 2H, *H*-2''), 7.45 – 7.36 (m, 5H, *H*-3', *H*-3'', *H*-4''), 7.37 – 7.33 (m, 2H, *H*-2'''), 7.32 – 7.23 (m, 3H, *H*-3''', *H*-4'''), 7.09 – 7.01 (m, 2H, *H*-2'), 5.34 (dd, *J* = 12.2, 5.9 Hz, 1H, *H*-5), 3.91 (dd, *J* = 17.4, 12.2 Hz, 1H, *H*-4^a), 3.22 (dd, *J* = 17.4, 5.9 Hz, 1H, *H*-4^b).
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 149.9, 147.0, 141.2, 133.4, 131.9, 129.7, 129.6, 128.8, 128.2, 126.3, 125.7, 120.4, 113.1, 100.6, 63.6, 43.8.
HRMS (ESI+), *m/z*: calculated for $C_{22}H_{17}N_3 + H^+$ 324.1495 [*M*+H]$^+$, found 324.1493.

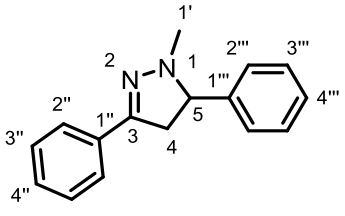
1*H*-1-4,5-Dihydro-3,5-diphenyl-(4-methylphenyl)pyrazole (4c')



Pyrazoline synthesis was carried out according to SOP6 using diphenyl (*E*)-chalcone (**9.6 mmol, 2.00 g, 1.0 eq.**), 4-methylphenylhydrazine hydrochloride (**11.52 mmol, 1.82 g, 1.0 eq.**), glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**) and methanol as solvent. The product was obtained after filtration without further purification as faint yellow crystals (**2.98 g, 9.50 mmol, 99%**).

^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.77 – 7.69 (m, 2H, *H*-2''), 7.45 – 7.23 (m, 9H, *H*-2', *H*-3', *H*-3'', *H*-4'', *H*-2'''), 7.04 – 6.94 (m, 4H, *H*-3''', 4'''), 5.28 (dd, *J* = 12.4, 7.3 Hz, 1H, *H*-5), 3.84 (dd, *J* = 17.1, 12.4 Hz, 1H, *H*-4^a), 3.13 (dd, *J* = 17.1, 7.3 Hz, 1H, *H*-4^b), 2.23 (s, 3H, *H*-5').
^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 146.8, 143.2, 143.1, 133.3, 129.7, 129.4, 128.9, 128.8, 128.7, 127.9, 126.4, 126.0, 113.7, 65.0, 43.9, 20.6.
HRMS (ESI+), *m/z*: calculated for $C_{22}H_{20}N_2 + H^+$ 313.1699 [*M*+H]$^+$, found 313.1693.

1*H*-4,5-Dihydro -3,5-diphenyl-1-methylpyrazole (4e')



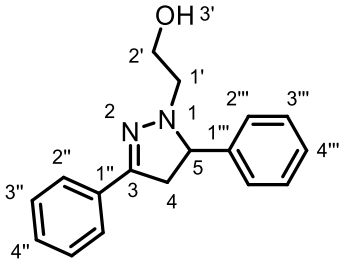
In a 100 mL round bottom flask, diphenyl (*E*)-chalcone (**10.0 mmol, 2.00 g, 1.0 eq.**) and methylhydrazine (**10.0 mmol, 0.46 g, 1.0 eq.**) were dissolved in ethanol (30 mL). The mixture was refluxed overnight. The reaction mixture was allowed to cool to room temperature and the solvent removed under reduced pressure. The pyrazoline was obtained without further purification as light-yellow solid (**2.36 g, 2.36 mmol, quant.**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.69 – 7.64 (m, 2H), 7.52 – 7.46 (m, 2H, *H*-2’’’), 7.43 – 7.30 (m, 6H, *H*-3’’, *H*-4’’, *H*-3’’’, *H*-4’’’), 4.14 (dd, *J* = 14.3, 10.0 Hz, 1H, *H*-5), 3.49 (dd, *J* = 16.1, 10.0 Hz, 1H, *H*-4^a), 3.02 (dd, *J* = 16.2, 14.3 Hz, 1H, *H*-4^b), 2.85 (s, 3H, *H*-1’).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm:

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}N_2$ + H^+ 237.1386 [*M*+H]$^+$, found 237.1387.

1*H*-4,5-Dihydro-3,5-diphenyl-1-(2-hydroxyethyl)pyrazole (4f’)



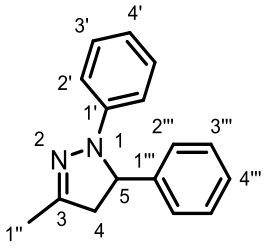
In a 100 mL round bottom flask, diphenyl (*E*)-chalcone (**10.0 mmol, 2.00 g, 1.0 eq.**) and 2-hydroxyethylhydrazine (**10.0 mmol, 0.76 g, 1.0 eq.**) were dissolved in ethanol (30 mL). The mixture was refluxed overnight. The reaction mixture was allowed to cool to room temperature and the solvent removed under reduced pressure. The pyrazoline was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a colourless solid (**2.04 g, 7.66 mmol, 76%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.66 – 7.61 (m, 2H, *H*-2’’), 7.50 – 7.45 (m, 2H, *H*-3’’), 7.43 – 7.31 (m, 6H, *H*-4’’, *H*-2’’’, *H*-3’’’, *H*-4’’’), 4.30 (dd, *J* = 14.1, 10.0 Hz, 1H, *H*-5), 4.00 (ddd, *J* = 11.6, 6.0, 4.5 Hz, 1H, *H*-2’^{a}), 3.95 – 3.85 (m, 1H, *H*-2’^{b}), 3.80 (brs, 1H, *H*-3’), 3.46 (ddd, *J* = 16.3, 10.0, 0.9 Hz, 1H, *H*-1’^{a}), 3.04 – 2.91 (m, 3H, *H*-1’^{b}, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 151.2, 140.0, 132.3, 129.3, 129.0, 128.7, 128.2, 127.7, 126.1, 72.5, 62.4, 55.6, 42.3.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{18}N_2O$ + H^+ 267.1492 [*M*+H]$^+$, found 267.1499.

1*H*-4,5-Dihydro-1,5-diphenyl -3-methylpyrazole (4g’)



In a 250 mL round bottom flask, (*E*)-benzylideneacetone (**50 mmol, 7.31 g, 1.0 eq.**) and phenylhydrazine (**50 mmol, 5.41 g, 1.0 eq.**) were dissolved in ethanol (70 mL) and 3 drops of sulfuric acid were added. The mixture was refluxed for 3 h, after which only the corresponding hydrazone was formed. The mixture was evaporated to dryness and glacial acetic acid (125 mL) was added. The solution was refluxed for 15 min and left to stand at room temperature over the weekend for crystallization. The mixture was filtered and washed with ethanol/water 1:1(v/v). The product was obtained without further purification as light-brown crystals (**3.20 g, 13.5 mmol, 27%**).

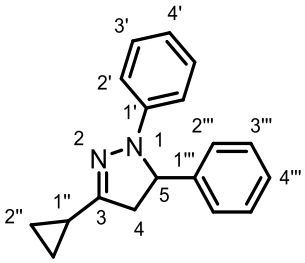
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.39 – 7.30 (m, 4H, *H*-2’’’, *H*-3’’’), 7.32 – 7.23 (m, 1H, *H*-4’’’), 7.20 – 7.12 (m, 2H, *H*-3’), 6.99 – 6.91 (m, 2H, *H*-2’), 6.76 (tt, *J* = 7.3, 1.1 Hz, 1H, *H*-4’), 5.02 (dd, *J* = 11.9, 8.1 Hz, 1H, *H*-5), 3.42 (ddq, *J* = 17.5, 11.9, 1.2 Hz, 1H, *H*-4^a), 2.73 (ddq, *J* = 17.5, 8.1, 1.2 Hz, 1H, *H*-4^b), 2.09 (dd, *J* = 1.2, 1.2 Hz, 3H, *H*-1’’).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 148.6, 146.2, 143.1, 129.1, 129.0, 127.5, 126.0, 118.7, 113.2, 64.9, 47.9, 16.0.

HRMS (APCI+), *m/z*: calculated for $C_{16}H_{16}N_2$ + H^+ 237.1386 [*M*+H]$^+$, found 237.1381.

Known compound, spectroscopic data corresponds to the literature.[4]

1*H*-3-Cyclopropyl-4,5-dihydro-1,5-diphenylpyrazole (4h')



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-1-cyclopropyl-3-phenylprop-2-en-1-one (**7n**, **10 mmol, 1.72 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as a light-yellow solid (**1.93 g, 7.36 mmol, 74%**).

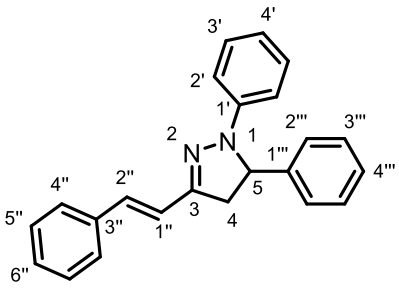
^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.38 – 7.32 (m, 2H, *H*-3'''), 7.31 – 7.24 (m, 3H, *H*-2''', *H*-4'''), 7.19 – 7.06 (m, 2H, *H*-3'), 6.95 – 6.86 (m, 2H, *H*-2'), 6.70 (tt, *J* = 7.3, 1.1 Hz, 1H, *H*-4'), 5.01 (dd, *J* = 11.8, 7.7 Hz, 1H, *H*-5), 3.30 (dd, *J* = 17.2, 11.8 Hz, 1H, *H*-4^a), 2.57 (dd, *J* = 17.2, 7.7 Hz, 1H, *H*-4^b), 1.83 (tt, *J* = 8.3, 5.1 Hz, 1H, *H*-1''), 0.92 – 0.84 (m, 2H, *H*-2''^{a}), 0.84 – 0.72 (m, 2H, *H*-2''^{b}).

^{13}C NMR (101 MHz, CD_2Cl_2), *δ*/ppm: 153.4, 146.1, 143.1, 129.0, 128.7, 127.4, 125.9, 118.2, 112.9, 64.2, 44.0, 11.2, 5.9, 5.7.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{18}N_2$ + H^+ 263.1543 $[M+H]^+$, found 263.1548.

Known compound, spectroscopic data corresponds to the literature.[4]

(*E*)-1*H*-4,5-Dihydro-1,5-diphenyl-3-(β-styryl)pyrazole (4i')



In a 50 mL round bottom flask, (1*E*,4*E*)-1,5-diphenylpenta-1,4-dien-3-one (**4.27 mmol, 1.00 g, 1.0 eq.**) and phenylhydrazine (**4.27 mmol, 462 mg, 1.0 eq.**) were dissolved in glacial acetic acid (20 mL) and refluxed for 10 min. After cooling to room temperature, the mixture was left to rest overnight. The suspension was filtered and the solid washed with cold ethanol to yield the product as a bright-yellow powder (**971 mg, 2.99 mmol, 70%**) without further purification.

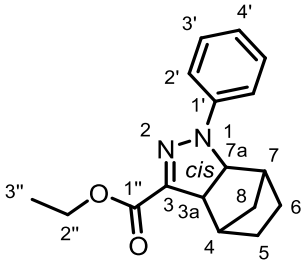
^{1}H NMR (400 MHz, CD_3CN), *δ*/ppm: 7.56 – 7.50 (m, 2H, *H*-4''), 7.40 – 7.31 (m, 4H, *H*-5'', *H*-2'''), 7.31 – 7.24 (m, 4H, *H*-6'', *H*-3''', *H*-4'''), 7.21 (d, *J* = 16.4 Hz, 1H, *H*-2''), 7.17 – 7.12 (m, 2H, *H*-3'), 7.01 – 6.95 (m, 2H, *H*-2'), 6.74 (tt, *J* = 7.3, 1.1 Hz, 1H, *H*-4'), 6.72 (d, *J* = 16.4 Hz, 1H, *H*-1''), 5.39 (dd, *J* = 12.2, 6.2 Hz, 1H, *H*-5), 3.76 (ddd, *J* = 17.1, 12.2, 0.9 Hz, 1H, *H*-4^a), 2.98 (ddd, *J* = 17.1, 6.2, 0.9 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_3CN), *δ*/ppm: 149.9, 145.1, 143.7, 137.8, 134.0, 130.1, 129.9, 129.8, 129.1, 128.6, 127.6, 126.9, 122.3, 120.0, 114.2, 64.5, 42.9.

HRMS (APCI+), *m/z*: calculated for $C_{23}H_{20}N_2$ + H^+ 325.1699 $[M+H]^+$, found 325.1717.

Known compound, spectroscopic data corresponds to the literature.[19]

Ethyl 1*H*-3a,7a-*cis*-3a,4,5,6,7,7a-hexahydro-4,7-methano-1-phenylindazole-3-carboxylate (4j')



Pyrazoline synthesis was carried out according to SOP7 using ethyl glyoxylate phenylhydrazone (**6**, **15.6 mmol, 3.00 g, 1.0 eq.**) and norbornene (**42.1 mmol, 3.96 g, 2.7 eq.**). A charge of 5.4 *F* (8128 C) was applied. The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 3% EtOAc) as a yellow solid (**3.55 g, 12.5 mmol, 80%**).

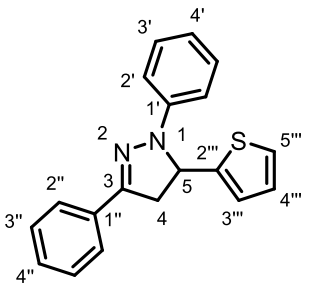
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.32 – 7.27 (m, 2H, *H*-3'), 7.23 – 7.18 (m, 2H, *H*-2'), 6.93 (tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4'), 4.39 – 4.26 (m, 2H, *H*-2''), 4.23 (d, *J* = 10.0 Hz, 1H, *H*-7a), 3.42 (d, *J* = 10.0 Hz, 1H, *H*-3a), 2.82 – 2.77 (m, 1H, *H*-7), 2.71 – 2.66 (m, 1H, *H*-4), 1.67 – 1.54 (m, 2H, *H*-5^a, *H*-6^a), 1.46 – 1.29 (m, 3H, *H*-5^b, *H*-6^b, *H*-8^a), 1.37 (t, *J* = 7.1 Hz, 3H, *H*-3''), 1.27 – 1.18 (m, 1H, *H*-8^b).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 163.1, 142.4, 141.1, 129.2, 121.0, 114.0, 69.2, 61.0, 54.3, 41.6, 40.9, 33.2, 27.7, 24.7, 14.5.

HRMS (ESI+), *m/z*: calculated for $C_{17}H_{20}N_2O_2$ + H^+ 285.1598 [*M*+H]$^+$, found 285.1599.

Known compound, spectroscopic data corresponds to the literature.[4]

1*H*-4,5-Dihydro-1,3-diphenyl-5-(thien-2-yl)pyrazole (4k')



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-2-(1-phenylprop-2-en-1-on-3-yl)thiophene (**7o**, **10 mmol, 2.14 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after filtration without further purification as an off-white solid (**2.77 g, 9.10 mmol, 91%**).

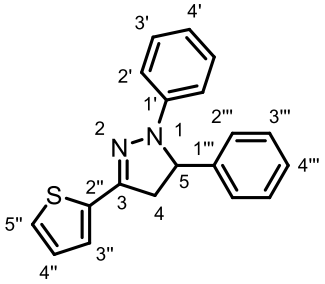
^{1}H NMR (400 MHz, CD_2Cl_2), δ/ppm: 7.80 – 7.74 (m, 2H, *H*-2''), 7.47 – 7.34 (m, 3H, *H*-3'', *H*-4''), 7.27 – 7.15 (m, 5H, *H*-2', *H*-3', *H*-5'''), 7.06 (ddd, *J* = 3.5, 1.2, 0.6 Hz, 1H, *H*-3'''), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1H, *H*-4'''), 6.84 (tt, *J* = 7.1, 1.4 Hz, 1H, *H*-4'), 5.59 (dd, *J* = 11.9, 6.8 Hz, 1H, *H*-5), 3.84 (dd, *J* = 17.0, 11.9 Hz, 1H, *H*-4^a), 3.29 (dd, *J* = 17.0, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, CD_2Cl_2), δ/ppm: 148.0, 146.5, 145.4, 133.0, 129.2, 129.2, 129.0, 127.3, 126.2, 125.3, 124.8, 119.9, 114.1, 60.8, 44.2.

HRMS (APCI+), *m/z*: calculated for $C_{19}H_{16}N_2S$ + H^+ 305.1107 [*M*+H]$^+$, found 305.1100.

Known compound, spectroscopic data corresponds to the literature.[18]

1*H*-4,5-Dihydro-1,5-diphenyl-3-(thien-2-yl)pyrazole (4l')



Pyrazoline synthesis was carried out according to SOP6 using (*E*)-2-cinnamoylthiophene (**6p**, **10 mmol, 2.14 g, 1.0 eq.**), phenylhydrazine hydrochloride (**10 mmol, 1.45 g, 1.0 eq.**) and glacial acetic acid (**10 mmol, 600 mg, 1.0 eq.**). The product was obtained after flash column chromatography on silica with cyclohexane/ethyl acetate (0% → 5% EtOAc) as a yellow powder (**1.71 g, 5.62 mmol, 56%**).

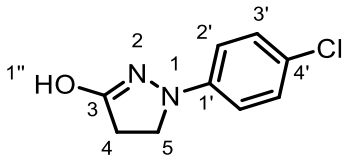
^{1}H NMR (400 MHz, $(CD_3)_2CO$), δ/ppm: 7.49 (dd, *J* = 5.1, 1.1 Hz, 1H, *H*-5''), 7.38 – 7.32 (m, 4H, *H*-2''', *H*-3'''), 7.30 – 7.24 (m, 1H, *H*-4'''), 7.20 (dd, *J* = 3.6, 1.1 Hz, 1H, *H*-3''), 7.16 – 7.10 (m, 2H, *H*-3'), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H, *H*-4''), 7.05 – 7.00 (m, 2H, *H*-2'), 6.72 (tt, *J* = 7.3, 1.2 Hz, 1H, *H*-4'), 5.43 (dd, *J* = 12.2, 6.8 Hz, 1H, *H*-5), 3.96 (dd, *J* = 17.2, 12.2 Hz, 1H, *H*-4^a), 3.14 (dd, *J* = 17.2, 6.8 Hz, 1H, *H*-4^b).

^{13}C NMR (101 MHz, $(CD_3)_2CO$), δ/ppm: 145.6, 144.3, 143.6, 137.3, 129.9, 129.6, 128.4, 128.4, 127.6, 127.6, 126.8, 119.7, 114.1, 65.0, 44.8.

HRMS (APCI+), *m/z*: calculated for $C_{19}H_{16}N_2S$ + H^+ 305.1107 [*M*+H]$^+$, found 305.1101.

Known compound, spectroscopic data corresponds to the literature.[16]

1*H*-1-(4-Chlorophenyl)-4,5-dihydropyrazol-3-ol (4m')



In a 100 mL two-necked round bottom flask, sodium (**125 mmol, 2.87 g, 5.0 eq.**) was dissolved in methanol (50 mL) under argon atmosphere. The solution was allowed to cool to 30 °C, 4-chlorophenylhydrazine hydrochloride (**25.0 mmol, 4.48 g, 1.0 eq.**) was added, and the mixture was stirred for 10 min. Methyl acrylate (**75 mmol, 6.46 g, 3.0 eq.**) was added, and the mixture was refluxed for 6 h until no hydrazine was observed anymore as by TLC analysis. The mixture was evaporated under reduced pressure, taken up in water (30 mL) and acidified to pH 6.0–6.5 with 2 M hydrochloric acid. The mixture was extracted

trice with ethyl acetate (100 mL each). The combined organic fractions were washed with 100 mL brine, dried over sodium sulphate, and evaporated under reduced pressure. The residue was recrystallized from ethyl acetate (ca. 25 mL, reflux to -30 °C) to yield the product as a light-orange solid (**1.26 g, 6.41 mmol, 26%**). The mother liquor was purified by flash column chromatography on silica with cyclohexane/ethyl acetate (10% → 90% EtOAc) to yield further product as a light-orange solid (**1.16 g, 5.90 mmol, 24%**). Overall yield: **2.42 g, 12.3 mmol, 49%**.

^{1}H NMR (600 MHz, DMSO-d_6), δ/ppm: 10.21 (brs, 1H, *H*-1''), 7.34 – 7.28 (m, 2H, *H*-2'), 7.01 – 6.96 (m, 2H, *H*-3'), 3.81 (t, *J* = 8.1 Hz, 2H, *H*-5), 2.43 (t, *J* = 8.1 Hz, 2H, *H*-4).

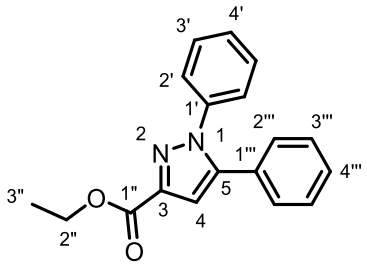
^{13}C NMR (151 MHz, DMSO-d_6), δ/ppm: 173.8, 150.6, 128.7, 124.8, 117.1, 53.4, 29.9.

HRMS (ESI-), *m/z*: calculated for $C_9H_9{}^{35}ClN_2O$ - H^+ 195.00331 [*M*-H]$^+$, found 195.0328; calculated for $C_9H_9{}^{37}ClN_2O$ - H^+ 197.0303 [*M*-H]$^+$, found 197.0309.

Known compound, spectroscopic data corresponds to the literature.[20,21]

9. Synthesized Pyrazoles

Ethyl 1*H*-1,5-diphenylpyrazole-3-carboxylate (5a)



Product synthesis was carried out according to SOP2 using ethyl 1*H*-4,5-dihydro-1,5-diphenylpyrazole-3-carboxylate (**4a**, **3.75 mmol**, **1.096 g**). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 3% → 5% EtOAc) as a light-yellow solid (**845 mg**, **2.89 mmol**, **77%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: δ 7.39 – 7.27 (m, 8H, *H*-2', *H*-3', *H*-2''', *H*-3'''), 7.24 – 7.19 (m, 2H, *H*-4', *H*-4'''), 7.05 (s, 1H, *H*-4), 4.46 (q, *J* = 7.1 Hz, 2H, *H*-2''), 1.43 (t, *J* = 7.1 Hz, 3H, *H*-3'').

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 162.6, 144.7, 144.5, 139.6, 129.7, 129.1, 128.9, 128.8, 128.7, 128.5, 125.8, 110.0, 61.3, 14.5.

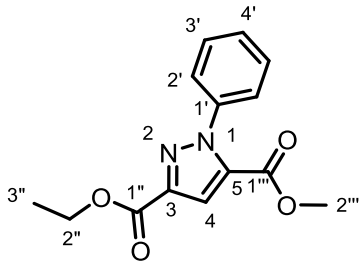
HRMS (ESI+), *m/z*: calculated for $C_{18}H_{16}N_2O_2$ + H^+ 293.1285 [*M*+H]$^+$, found 293.1288.

Known compound, spectroscopic data corresponds to the literature.[4,22,23]

Scale-up (26.25 mmol):

In a 200 mL beaker-type cell, pyrazoline **4a** (**26.25 mmol**, **7.718 g**) was dissolved in 35 mL ethyl acetate. Pyridine (**10.5 mmol**, **830 mg**, **0.4 eq.**) and 145 mL 1 M NaCl (aq.) were added, the cell immersed in an oil bath and heated to 70 °C. The reaction mixture was stirred vigorously (750 rpm) and subjected to electrolysis using BDD electrodes (size: 14 x 4 x 0.2 cm, immersion depth: 5 cm, relevant anode surface area: 20 cm^2), a current density of 15 mA/cm^2, until an amount of charge of 5.25 *F* (13296 C) was applied. The reaction mixture was allowed to cool to room temperature and transferred to a separatory funnel. The layers were separated, and the aqueous layer extracted with ethyl acetate (4 x 50 mL). The combined organic fractions were dried over anhydrous magnesium sulphate and filtered through a pad of silica. The solvent was removed under reduced pressure, the brown residue dissolved in ethanol, diluted with cyclohexane (EtOH/cyclohexane 1:9 *v*/*v*) and filtered through a frit. After removal of the solvents under reduced pressure, the pyrazole was obtained as a yellow solid (**6.818 g**, **23.34 mmol**, **89%**).

3-Ethyl, 5-methyl 1*H*-1-phenylpyrazole-3,5-dicarboxylate (5b)



Product synthesis was carried out according to SOP3 using 3-ethyl 5-methyl 1*H*-4,5-dihydro-1-phenylpyrazole-3,5-dicarboxylate (**4b**, **3.75 mmol**, **1.036 g**) applying an amount of charge of 3.75 *F* (1356 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 3% → 5% EtOAc) as a light-yellow solid (**960 mg**, **3.50 mmol**, **93%**).

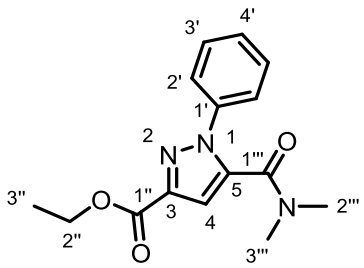
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.45 (s, 1H, *H*-4), 7.42 – 7.36 (m, 5H, *H*-2', *H*-3', *H*-4'), 4.37 (q, *J* = 7.1 Hz, 2H, *H*-2''), 3.73 (s, 3H, *H*-2'''), 1.34 (t, *J* = 7.1 Hz, 3H, *H*-3'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 161.3, 158.7, 143.7, 139.5, 134.3, 129.2, 128.5, 126.0, 114.5, 61.2, 52.2, 14.2.

HRMS (ESI+), *m/z*: calculated for $C_{14}H_{14}N_2O_4$ + H^+ 275.1026 $[M+H]^+$, found 275.1035.

Known compound, spectroscopic data corresponds to the literature.[24]

Ethyl 1*H*-4,5-dihydro-5-(dimethylcarbamoyl)-1-phenylpyrazole-3-carboxylate (5c)



Product synthesis was carried out according to SOP2 using ethyl 1*H*-4,5-dihydro-5-(dimethylcarbamoyl)-1-phenylpyrazole-3-carboxylate (**4c**, **3.75 mmol**, **1085 mg**), applying an amount of charge of 3.25 *F* (1176 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 10% → 100% EtOAc) as a light-yellow solid (**735 mg**, **2.75 mmol**, **73%**).

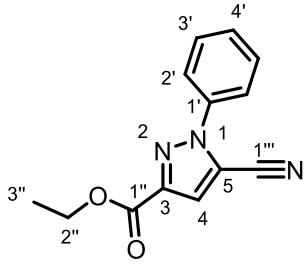
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.55 – 7.47 (m, 2H, *H*-3'), 7.45 – 7.32 (m, 4H, *H*-2', *H*-4'), 7.00 (s, 1H, *H*-4), 4.40 (q, *J* = 7.1 Hz, 2H, *H*-2''), 2.95 (s, 3H, *H*-2'''), 2.70 (s, 3H, *H*-3'''), 1.37 (t, *J* = 7.1 Hz, 3H, *H*-3'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 161.8, 161.6, 144.3, 139.2, 138.1, 129.3, 128.8, 123.5, 110.0, 61.4, 38.1, 35.0, 14.4.

HRMS (ESI+), *m/z*: calculated for $C_{15}H_{17}N_3O_3$ + H^+ 288.1343 $[M+H]^+$, found 288.1347.

Known compound, spectroscopic data corresponds to the literature.[24]

Ethyl 1*H*-5-cyano-1-phenylpyrazole-3-carboxylate (5d)



Product synthesis was carried out according to SOP2 using ethyl 1*H*-5-cyano-4,5-dihydro-1-phenylpyrazole-3-carboxylate (**4d**, **3.75 mmol**, **912 mg**), applying an amount of charge of 3.25 *F* (1176 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 3% → 10% EtOAc) as a light-yellow solid (**629 mg**, **2.61 mmol**, **70%**).

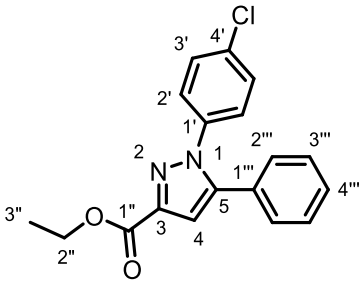
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.76 – 7.67 (m, 2H, *H*-3'), 7.59 – 7.45 (m, 4H, *H*-4, *H*-2', *H*-4'), 4.44 (q, *J* = 7.2 Hz, 2H, *H*-2''), 1.40 (t, *J* = 7.2 Hz, 3H, *H*-3'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 160.6, 145.0, 138.0, 130.0, 129.8, 123.6, 118.2, 115.7, 110.1, 61.9, 14.4.

HRMS (ESI+), *m/z*: calculated for $C_{13}H_{11}N_3O_2$ + H^+ 242.0924 $[M+H]^+$, found 242.0915.

Known compound, spectroscopic data corresponds to the literature.[24]

Ethyl 1*H*-1-(4-chlorophenyl)-5-phenylpyrazole-3-carboxylate (5e)



Product synthesis was carried out according to SOP2 using ethyl 1*H*-1-(4-chlorophenyl)-4,5-dihydro-5-phenylpyrazole-3-carboxylate (**4e**, **3.75 mmol**, **1.230 g**) applying an amount of charge of 5 *F* (1809 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 3% → 5% EtOAc) as a light-yellow solid (**997 mg**, **3.06 mmol**, **82%**).

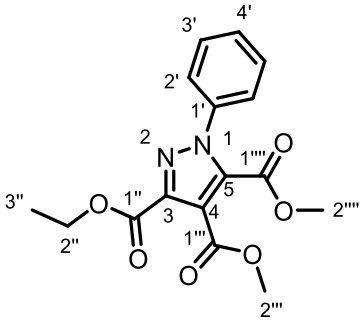
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.36 – 7.26 (m, 7H, *H*-3', *H*-2''', *H*-3''', *H*-4'''), 7.23 – 7.18 (m, 2H, *H*-2'), 7.03 (s, 1H, *H*-4), 4.45 (q, *J* = 7.1 Hz, 2H, *H*-2''), 1.42 (t, *J* = 7.1 Hz, 3H, *H*-3'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 162.2, 144.7, 144.6, 138.0, 134.1, 129.2, 129.1, 129.0, 128.9, 128.7, 126.8, 110.2, 61.2, 14.4.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{15}{}^{35}ClN_2O_2$ + H^+ 327.0895 $[M+H]^+$, found 327.0906; calculated for $C_{18}H_{15}{}^{37}ClN_2O_2$ + H^+ 329.0872 $[M+H]^+$, found 329.0880.

Known compound, spectroscopic data corresponds to the literature.[22]

3-Ethyl, 4,5-dimethyl 1*H*-1-phenylpyrazole-3,4,5-tricarboxylate (5f)



Product synthesis was carried out according to SOP2 using 3-ethyl, 4,5-dimethyl 1*H*-4,5-*trans*-4,5-dihydro-1-phenylpyrazole-3,4,5-tricarboxylate (**4f**, **3.75 mmol**, **1253 mg**), applying an amount of charge of 3.75 *F* (1357 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc as a light-brown solid (**1105 mg**, **3.33 mmol**, **89%**).

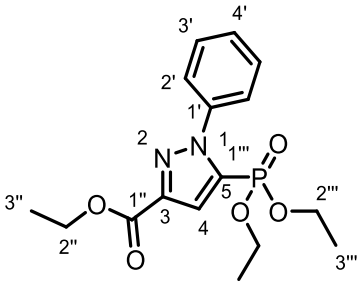
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.49 – 7.33 (m, 5H, *H*-2', *H*-3', *H*-4', *H*-5'), 4.38 (q, *J* = 7.1 Hz, 2H, *H*-2''), 3.92 (s, 3H, *H*-2'''), 3.74 (s, 3H, *H*-2''''), 1.34 (t, *J* = 7.1 Hz, 3H, *H*-3'').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 163.2, 160.5, 158.1, 141.3, 138.9, 133.3, 129.7, 128.9, 125.8, 121.0, 61.8, 52.9, 52.9, 14.1.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{16}N_2O_6$ + H^+ 333.1081 $[M+H]^+$, found 333.1076.

Known compound, spectroscopic data corresponds to the literature.[25]

Ethyl 1*H*-5-(diethoxyphosphoryl)-1-phenylpyrazole-3-carboxylate (5g)



Product synthesis was carried out according to SOP2 using ethyl 1*H*-5-(diethoxyphosphoryl)-4,5-dihydro-1-phenylpyrazole-3-carboxylate (**4g**, **2.64 mmol**, **936 mg**), applying an amount of charge of 4 *F* (1018 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 1% → 20% EtOAc) as a colourless oil (**612 mg**, **1.74 mmol**, **66%**).

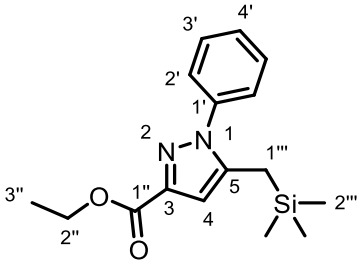
^{1}H NMR (400 MHz, CD_2Cl_2), *δ*/ppm: 7.67 – 7.63 (m, 2H, *H*-3'), 7.53 – 7.48 (m, 3H, *H*-2', *H*-4'), 7.39 (d, *J* = 2.6 Hz, 1H, *H*-4), 4.38 (q, *J* = 7.1 Hz, 2H, *H*-2''), 4.10 – 3.93 (m, 4H, *H*-2'''), 1.38 (t, *J* = 7.1 Hz, 3H, *H*-3''), 1.18 (t, *J* = 7.0 Hz, 6H, *H*-3''').

^{13}C NMR (101 MHz, CD_2Cl_2), *δ*/ppm: 161.8, 144.5 (d, *J* = 16.4 Hz), 140.5, 136.0, 133.8, 129.7, 129.2, 125.9, 119.3 (d, *J* = 17.7 Hz), 63.6 (d, *J* = 5.9 Hz), 61.6, 16.3 (d, *J* = 6.6 Hz), 14.5.

^{31}P NMR (162 MHz, $CDCl_3$), *δ*/ppm: 3.75.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{21}N_2O_5P$ + H^+ 353.1261 [*M*+H]$^+$, found 353.1257.

Ethyl 1*H*-1-phenyl-5-((trimethylsilyl)methyl)pyrazole-3-carboxylate (5h)



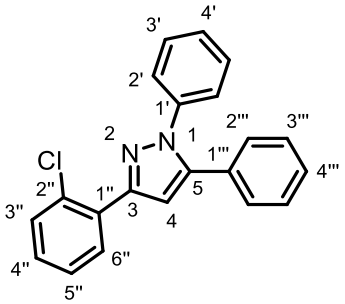
Product synthesis was carried out according to SOP2 using ethyl 1*H*-4,5-dihydro-1-phenyl-5-((trimethylsilyl)methyl)pyrazole-3-carboxylate (**4h**, **2.94 mmol**, **896 mg**), applying an amount of charge of 3.25 *F* (922 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 1% → 20% EtOAc) as a colourless oil (**448 mg**, **1.48 mmol**, **50%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.51 – 7.35 (m, 5H, *H*-2', *H*-3', *H*-4'), 6.59 (s, 1H, *H*-4), 4.39 (q, *J* = 7.1 Hz, 2H, *H*-2''), 2.10 (s, 2H, *H*-1'''), 1.38 (t, *J* = 7.1 Hz, 3H, *H*-3''), -0.08 (s, 9H, *H*-2''').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 162.9, 144.0, 143.5, 139.4, 129.2, 128.8, 126.6, 107.2, 61.0, 16.1, 14.5, -1.5.

HRMS (ESI+), *m/z*: calculated for $C_{16}H_{22}N_2O_2{}^{28}Si$ + H^+ 303.1523 [*M*+H]$^+$, found 303.1531, calculated for $C_{16}H_{22}N_2O_2{}^{29}Si$ + H^+ 304.1547 [*M*+H]$^+$, found 304.1555, calculated for $C_{16}H_{22}N_2O_2{}^{30}Si$ + H^+ 305.1529 [*M*+H]$^+$, found 305.1534.

1*H*-3-(2-Chlorophenyl)-1,5-diphenylpyrazole (5i)



Product synthesis was carried out according to SOP2 using 1*H*-3-(2-chlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4i**, **1.50 mmol**, **499 mg**), applying an amount of charge of 4 *F* (579 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 88% MeCN) as a light-yellow solid (**248 mg**, **0.75 mmol**, **50%**).

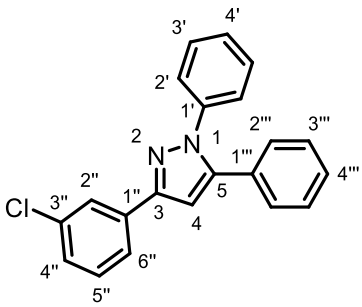
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.02 (dd, *J* = 7.7, 1.6 Hz, 1H, *H*-6''), 7.51 (dd, *J* = 7.8, 1.6 Hz, 1H, *H*-4''), 7.47 – 7.24 (m, 12H, *H*-2', *H*-3', *H*-4', *H*-3'', *H*-5'', *H*-2''', *H*-3''', *H*-4'''), 7.12 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 149.7, 143.5, 140.1, 132.4, 132.1, 130.8, 130.5, 130.4, 129.1, 129.0, 128.9, 128.6, 128.4, 127.6, 127.0, 125.4., 109.1.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}{}^{35}ClN_2$ + H^+ 331.0997 [*M*+H]$^+$, found 331.0993; calculated for $C_{21}H_{15}{}^{37}ClN_2$ + H^+ 333.0974 [*M*+H]$^+$, found 333.0970.

Known compound, spectroscopic data corresponds to the literature.[26]

1*H*-3-(3-Chlorophenyl)-1,5-diphenylpyrazole (5j)



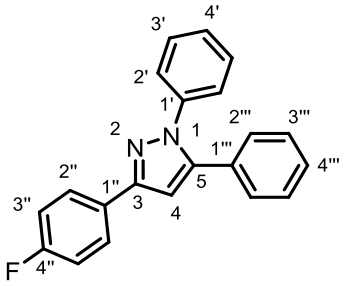
Product synthesis was carried out according to SOP2 using 1*H*-3-(3-chlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4j**, **1.50 mmol**, **499 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 85% MeCN) as a light-yellow solid (**222 mg**, **0.67 mmol**, **45%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.02 – 7.96 (m, 1H, *H*-2''), 7.86 – 7.79 (m, 1H, *H*-6''), 7.44 – 7.28 (m, 12H, *H*-2', *H*-3', *H*-4', *H*-4'', *H*-5'', *H*-2''', *H*-3''', *H*-4'''), 6.83 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 150.7, 144.7, 140.1, 135.0, 134.7, 130.4, 130.0, 129.0, 128.8, 128.6, 128.5, 128.0, 127.7, 125.9, 125.3, 124.0, 105.3.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}{}^{35}ClN_2 + H^+$ 331.0997 $[M+H]^+$, found 331.1000; calculated for $C_{21}H_{15}{}^{37}ClN_2 + H^+$ 333.0974 $[M+H]^+$, found 333.0980.
Known compound, spectroscopic data corresponds to the literature.[26]

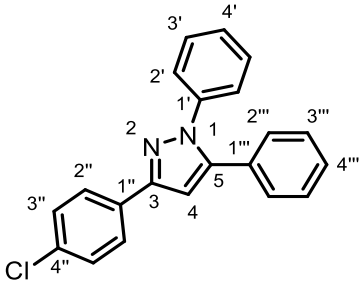
1*H*-1,5-Diphenyl-3-(4-fluorophenyl)pyrazole (5k)



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(4-fluorophenyl)pyrazole (**4k**, **1.50 mmol**, **475 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a colourless solid (**283 mg**, **0.90 mmol**, **60%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.98 – 7.88 (m, 2H, *H*-2''), 7.45 – 7.24 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 7.20 – 7.10 (m, 2H, *H*-3''), 6.80 (s, 1H, *H*-4).
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 162.8 (d, *J* = 246.6 Hz), 151.1, 144.6, 140.1, 130.5, 129.4 (d, *J* = 3.2 Hz), 129.0, 128.8, 128.6, 128.4, 127.6, 127.5 (d, *J* = 3.6 Hz), 125.3, 115.6 (d, *J* = 21.6 Hz), 105.1.
^{19}F NMR (376 MHz, $CDCl_3$), *δ*/ppm: -115.2 – -115.3 (m).
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}FN_2 + H^+$ 315.1292 $[M+H]^+$, found 315.1291.
Known compound, spectroscopic data corresponds to the literature.[23,27]

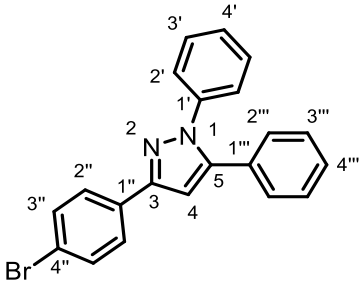
1*H*-3-(4-Chlorophenyl)-1,5-diphenylpyrazole (5l)



Product synthesis was carried out according to SOP3 using 1*H*-3-(4-chlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4l**, **1.50 mmol**, **501 mg**), applying an amount of charge of 4 *F* (579 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc and recrystallization from ethanol (ca. 20 mL, reflux to rt) as a yellow solid (**438 mg**, **1.32 mmol**, **88%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.97 – 7.89 (m, 2H, *H*-2''), 7.50 – 7.40 (m, 2H, *H*-3''), 7.39 – 7.23 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 6.83 (s, 1H, *H*-4).
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 152.4, 144.5, 138.8, 133.1, 132.9, 130.4, 129.2, 128.9, 128.8, 128.8, 128.7, 128.3, 126.4, 125.9, 105.7.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}{}^{35}ClN_2 + H^+$ 331.0997 $[M+H]^+$, found 331.0993; calculated for $C_{21}H_{15}{}^{37}ClN_2 + H^+$ 333.0974 $[M+H]^+$, found 333.0971.
Known compound, spectroscopic data corresponds to the literature.[3,23,26,27]

1*H*-3-(4-Bromophenyl)-1,5-diphenylpyrazole (5m)



Product synthesis was carried out according to SOP2 using 1*H*-3-(4-bromophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4m**, **1.50 mmol**, **566 mg**), applying an amount of charge of 4 *F* (470 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc as a yellow solid (**490 mg**, **1.30 mmol**, **87%**).

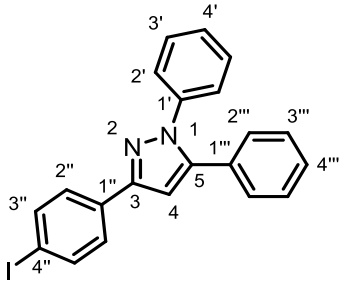
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.86 – 7.78 (m, 2H, *H*-2''), 7.61 – 7.53 (m, 2H, *H*-3''), 7.42 – 7.22 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 6.80 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 151.0, 144.7, 140.1, 132.1, 131.9, 130.5, 129.1, 128.8, 128.6, 128.5, 127.7, 127.5, 125.4, 122.0, 105.2.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}{}^{79}BrN_2 + H^+$ 375.0491 [*M*+H]$^+$, found 375.0492; calculated for $C_{21}H_{15}{}^{81}BrN_2 + H^+$ 377.0473 [*M*+H]$^+$, found 377.0476.

Known compound, spectroscopic data corresponds to the literature.[23,27]

1*H*-1,5-Diphenyl-3-(4-iodophenyl)pyrazole (5n)



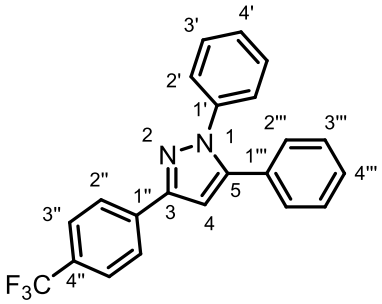
Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(4-iodophenyl)pyrazole (**4n**, **1.50 mmol**, **636 mg**), applying an amount of charge of 4.5 *F* (651 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a colourless solid (**289 mg**, **0.68 mmol**, **46%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.79 – 7.73 (m, 2H, *H*-2''), 7.71 – 7.66 (m, 2H, *H*-3''), 7.39 – 7.24 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 6.80 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 151.0, 144.7, 140.1, 137.8, 132.7, 130.4, 129.1, 128.8, 128.6, 128.5, 127.7, 127.7, 125.4, 105.2, 93.6.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}IN_2 + H^+$ 423.0353 [*M*+H]$^+$, found 423.0348.

1*H*-1,5-Diphenyl-3-(4-(trifluoromethyl)phenyl)pyrazole (5o)



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(4-(trifluoromethyl)phenyl)pyrazole (**4o**, **1.50 mmol**, **549 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after filtration through a pad of silica with cyclohexane/ethyl acetate (2:1 *v*/*v*) and recrystallization from ethanol (ca. 20 mL, reflux to rt) as a light-yellow solid (**387 mg**, **1.06 mmol**, **71%**).

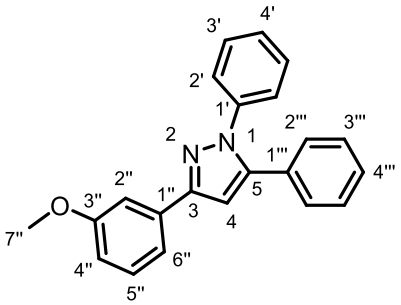
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.16 – 7.98 (m, 2H, *H*-2''), 7.81 – 7.65 (m, 2H, *H*-3''), 7.52 – 7.27 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 6.89 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 150.5, 144.8, 140.0, 136.6, 130.3, 129.8 (q, *J* = 32.4 Hz), 129.1, 128.8, 128.6, 128.6, 127.8, 126.0, 125.7 (q, *J* = 4.0 Hz), 125.4, 124.9 (q, *J* = 272.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$), δ/ppm: -63.6.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{15}F_3N_2 + H^+$ 365.1260 [*M*+H]$^+$, found 365.1264.

1*H*-1,5-Diphenyl-3-(3-methoxyphenyl)pyrazole (5p)

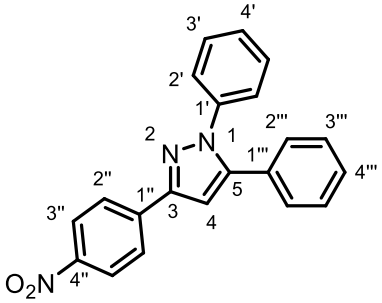


Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(3-methoxyphenyl)pyrazole (**4p**, **1.50 mmol**, **493 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 5% → 45% EtOAc) as a colourless oil (**353 mg**, **1.08 mmol**, **72%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.60 – 7.52 (m, 2H, *H*-6'', 4''), 7.48 – 7.28 (m, 11H, *H*-2', *H*-3', *H*-4', *H*-5'', *H*-2''', *H*-3''', *H*-4'''), 6.98 – 6.91 (m, 1H, *H*-2''), 6.86 (s, 1H, *H*-4), 3.90 (s, 3H, *H*-7'').

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 160.0, 151.9, 144.4, 140.2, 134.5, 130.6, 129.7, 129.0, 128.8, 128.5, 128.4, 127.5, 125.4, 118.5, 114.2, 110.9, 105.5, 55.4.
HRMS (ESI+), *m/z*: calculated for $C_{22}H_{18}N_2O$ + H^+ 327.1492 [*M*+H]$^+$, found 327.1490.
Known compound, spectroscopic data corresponds to the literature.[26,27]

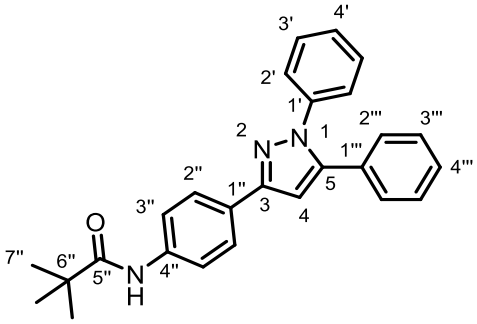
1*H*-1,5-Diphenyl-3-(4-nitrophenyl)pyrazole (5q)



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(4-nitrophenyl)pyrazole (**4q**, **1.50 mmol**, **515 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as an orange solid (**313 mg**, **0.91 mmol**, **61%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.34 – 8.25 (m, 2H, *H*-2''), 8.13 – 8.04 (m, 2H, *H*-3''), 7.47 – 7.22 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 6.91 (s, 1H, *H*-4).
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 149.7, 147.4, 145.3, 139.9, 139.5, 130.1, 129.2, 128.9, 128.8, 128.8, 128.1, 126.3, 125.4, 124.3, 106.0.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}N_3O_2$ + H^+ 342.1237 [*M*+H]$^+$, found 342.1237.
Known compound, spectroscopic data corresponds to the literature.[26]

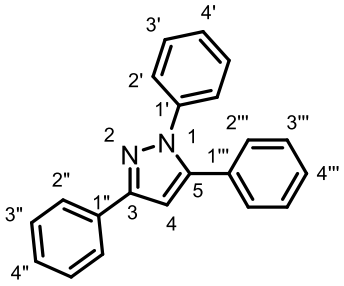
1*H*-1,5-Diphenyl-3-(4-pivaloylaminophenyl)pyrazole (4r)



Product synthesis was carried out according to SOP3 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(4-pivaloylaminophenyl)pyrazole (**4r**, **1.50 mmol**, **596 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 50% → 100% MeCN) as a colourless solid (**145 mg**, **0.37 mmol**, **24%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.93 – 7.86 (m, 2H, *H*-2''), 7.65 – 7.59 (m, 2H, *H*-3''), 7.41 – 7.27 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 6.80 (s, 1H, *H*-4), 1.34 (s, 9H, *H*-7').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 176.7, 151.6, 144.6, 143.0, 140.2, 138.0, 130.6, 129.1, 128.9, 128.6, 128.4, 127.6, 126.5, 125.5, 120.1, 105.1, 39.8, 27.8.
HRMS (ESI+), *m/z*: calculated for $C_{26}H_{25}N_3O$ + H^+ 396.2070 [*M*+H]$^+$, found 396.2072.

1*H*-1,3,5-Triphenylpyrazole (5s)

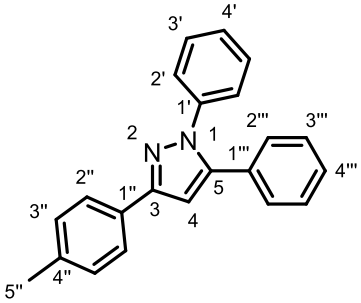


Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,3,5-triphenylpyrazole (**4s**, **3.75 mmol**, **1.118 g**). The pyrazole was obtained after filtration through a pad of silica with EtOAc as a light-yellow solid (**960 mg**, **3.31 mmol**, **88%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.02 – 7.94 (m, 2H, *H*-2''), 7.51 – 7.28 (m, 13H, *H*-2', *H*-3', *H*-4', *H*-3'', *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 6.86 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 152.1, 144.5, 140.2, 133.1, 130.7, 129.0, 128.8, 128.7, 128.6, 128.4, 128.1, 127.5, 125.9, 125.4, 105.3.
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{16}N_2 + H^+$ 297.1386 [*M*+H]$^+$, found 297.1389.
Known compound, spectroscopic data corresponds to the literature.[3,23,27–30]

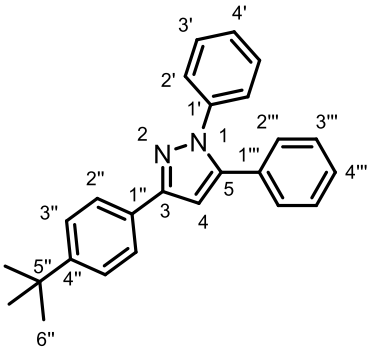
1*H*-1,5-Diphenyl-3-(4-methylphenyl)pyrazole (5t)



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(4-methylphenyl)pyrazole (**4t**, **1.50 mmol**, **469 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 0% → 10% EtOAc) as a colourless solid (**132 mg**, **0.43 mmol**, **28%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.85 – 7.78 (m, 2H, *H*-2''), 7.39 – 7.26 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 7.25 – 7.22 (m, 2H, *H*-3''), 6.79 (s, 1H, *H*-4), 2.39 (s, 3H, *H*-5'').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 152.1, 144.4, 140.3, 137.9, 130.8, 130.3, 129.5, 129.0, 128.9, 128.6, 128.4, 127.5, 125.8, 125.4, 105.2, 21.5.
HRMS (ESI+), *m/z*: calculated for $C_{22}H_{18}N_2 + H^+$ 311.1543 [*M*+H]$^+$, found 311.1543.
Known compound, spectroscopic data corresponds to the literature.[23,27]

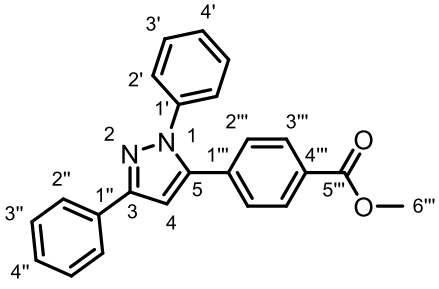
1*H*-3-(4-*tert*.-Butylphenyl)-1,5-diphenylpyrazole (5u)



Product synthesis was carried out according to SOP2 using 1*H*-3-(4-*tert.*-butylphenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4u**, **1.50 mmol**, **531 mg**), applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 85% MeCN) as a colourless solid (**217 mg**, **0.62 mmol**, **41%**).

^{1}H NMR (400 MHz, Acetone-d_6) δ/ppm: 7.94 – 7.87 (m, 2H, *H*-2''), 7.54 – 7.46 (m, 2H, *H*-3''), 7.46 – 7.28 (m, 10H, *H*-2', *H*-3', *H*-4', *H*-2''', *H*-3''', *H*-4'''), 7.00 (s, 1H, *H*-4), 1.35 (s, 9H, *H*-6'').
^{13}C NMR (101 MHz, Acetone-d_6) δ/ppm: 152.4, 151.6, 145.1, 141.4, 131.7, 131.5, 129.7, 129.6, 129.4, 129.2, 128.2, 126.3, 126.2, 126.0, 105.9, 35.2, 31.6.
HRMS (ESI+), *m/z*: calculated for $C_{25}H_{24}N_2 + H^+$ 353.2012 [*M*+H]$^+$, found 353.2020.
Known compound, spectroscopic data corresponds to the literature.[27]

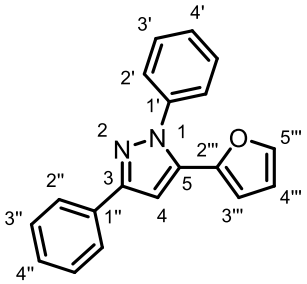
Methyl 4-(1*H*-1,3-diphenylpyrazol-5-yl)benzoate (5v)



Product synthesis was carried out according to SOP2 using methyl 4-(1*H*-4,5-dihydro-1,3-diphenylpyrazol-5-yl)benzoate (**4v**, **1.50 mmol**, **535 mg**) applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 0% → 10% EtOAc) as a light-yellow solid (**357 mg**, **1.01 mmol**, **67%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.02 – 7.97 (m, 2H, *H*-2'''), 7.96 – 7.91 (m, 2H, *H*-2''), 7.47 – 7.41 (m, 2H, *H*-3''), 7.38 – 7.32 (m, 8H, *H*-2', *H*-3', *H*-4', *H*-4'', *H*-3'''), 6.90 (s, 1H, *H*-4), 3.92 (s, 3H, *H*-6''').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 166.7, 152.3, 143.4, 140.0, 134.9, 132.8, 129.8, 129.2, 128.8, 128.7, 128.3, 127.9, 127.8, 125.9, 125.5, 105.8, 52.3.
HRMS (ESI+), *m/z*: calculated for $C_{23}H_{18}N_2O_2$ + H^+ 355.1441 [*M*+H]$^+$, found 355.1440.
Known compound, spectroscopic data corresponds to the literature.[28]

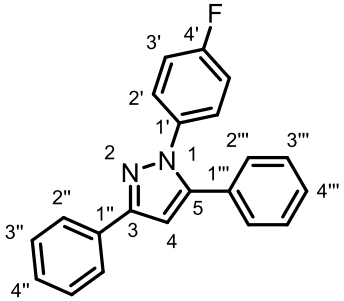
1*H*-1,3-Diphenyl-5-(furan-2-yl)pyrazole (5w)



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,3-diphenyl-5-(furan-2-yl)pyrazole (**4w**, **1.50 mmol**, **433 mg**) applying an amount of charge of 3.25 *F* (470 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 0% → 10% EtOAc) as a light-yellow solid (**131 mg**, **0.46 mmol**, **31%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.99 – 7.94 (m, 2H, *H*-2''), 7.56 – 7.42 (m, 8H, *H*-2', *H*-3', *H*-3'', *H*-4'', *H*-5'''), 7.40 – 7.35 (m, 1H, *H*-4'), 7.03 (s, 1H, *H*-4), 6.36 (dd, *J* = 3.4, 1.8 Hz, 1H, *H*-3'''), 6.02 (d, *J* = 3.4 Hz, 1H, *H*-4''').
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 152.0, 144.5, 142.6, 140.3, 135.8, 132.9, 129.2, 128.7, 128.6, 128.1, 126.1, 125.9, 111.3, 109.0, 103.4.
HRMS (ESI+), *m/z*: calculated for $C_{19}H_{14}N_2O$ + H^+ 287.1179 [*M*+H]$^+$, 287.1178.
Known compound, spectroscopic data corresponds to the literature.[29]

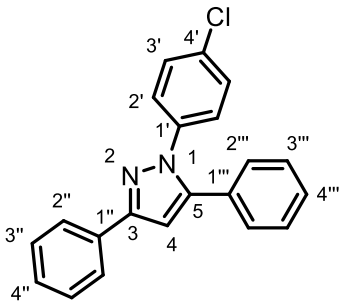
1*H*-3,5-Diphenyl-1-(4-fluorophenyl)pyrazole (5x)



Product synthesis was carried out according to SOP4 using 1*H*-4,5-dihydro-3,5-diphenyl-1-(4-fluorophenyl)pyrazole (**4x**, **1.50 mmol**, **475 mg**) applying an amount of charge of 2 *F* (289 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a light-orange solid (**260 mg**, **0.83 mmol**, **56%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 8.01 – 7.93 (m, 2H, *H*-2'), 7.53 – 7.43 (m, 2H, *H*-3'), 7.40 – 7.29 (m, 8H, *H*-2'', *H*-3'', *H*-2''', *H*-3'''), 7.12 – 7.02 (m, 2H, *H*-4'', *H*-4'''), 6.86 (s, 1H, *H*-4).
^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 161.7 (d, *J* = 247.5 Hz), 152.1, 144.5, 136.4 (d, *J* = 3.1 Hz), 133.0, 130.4, 128.8 (d, *J* = 3.1 Hz), 128.6, 128.5, 128.2, 127.1 (d, *J* = 8.5 Hz), 125.9, 116.0, 115.8, 105.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ/ppm: -114.1 (ddd, *J* = 12.9, 8.3, 4.8 Hz).
HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}FN_2$ + H^+ 315.1292 [*M*+H]$^+$, found 315.1293.
Known compound, spectroscopic data corresponds to the literature.[23]

1*H*-1-(4-Chlorophenyl)-3,5-diphenylpyrazole (5y)



Product synthesis was carried out according to SOP4 using 1*H*-1-(4-chlorophenyl)-4,5-dihydro-3,5-diphenylpyrazole (**4y**, **1.50 mmol**, **500 mg**) applying an amount of charge of 4.5 *F* (651 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc and recrystallization from ethanol (ca. 20 mL, reflux to rt) as a light-yellow solid (**447 mg**, **1.35 mmol**, **90%**).

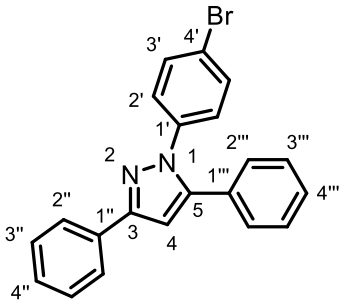
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.99 – 7.91 (m, 2H, *H*-2'), 7.50 – 7.43 (m, 2H, *H*-3'), 7.40 – 7.29 (m, 10H, *H*-2'', *H*-3'', *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 6.85 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 152.3, 144.5, 138.7, 133.1, 132.9, 130.4, 129.1, 128.8, 128.8, 128.7, 128.6, 128.2, 126.4, 125.9, 105.7.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{15}{}^{35}ClN_2 + H^+$ 331.0997 [*M*+H]$^+$, found 331.0989; calculated for calculated for $C_{22}H_{15}{}^{37}ClN_2 + H^+$ 333.0974 [*M*+H]$^+$, found 333.0967.

Known compound, spectroscopic data corresponds to the literature.[3]

1*H*-1-(4-Bromophenyl)-3,5-diphenylpyrazole (5z)



Product synthesis was carried out according to SOP4 using 1*H*-1-(4-bromophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4z**, **1.50 mmol**, **566 mg**) applying an amount of charge of 4.5 *F* (651 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc and recrystallization from ethanol (ca. 20 mL, reflux to rt) as a yellow solid (**474 mg**, **1.26 mmol**, **84%**).

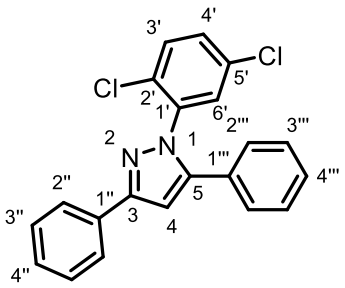
^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.97 – 7.92 (m, 2H, *H*-2'), 7.51 – 7.44 (m, 4H, *H*-3', *H*-2''), 7.41 – 7.35 (m, 4H, *H*-3'', *H*-2'''), 7.34 – 7.24 (m, 4H, *H*-4'', *H*-3''', *H*-4''), 6.85 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 152.4, 144.5, 139.2, 132.9, 132.1, 130.4, 128.9, 128.8, 128.7, 128.6, 128.3, 126.6, 125.9, 121.0, 105.8.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{15}{}^{79}BrN_2 + H^+$ 375.0491 [*M*+H]$^+$, 375.0484; calculated for $C_{21}H_{15}{}^{81}BrN_2 + H^+$ 377.0473 [*M*+H]$^+$, 377.0470.

Known compound, spectroscopic data corresponds to the literature.[3,23,30]

1*H*-1-(2,5-Dichlorophenyl)-3,5-diphenylpyrazole (5a')



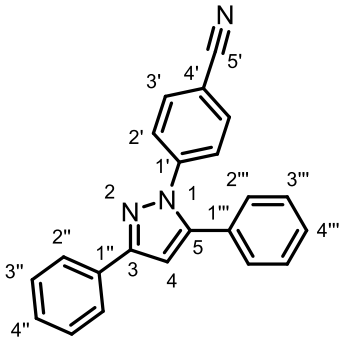
Product synthesis was carried out according to SOP3 using 1*H*-1-(2,5-dichlorophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4a'**, **1.50 mmol**, **551 mg**) applying an amount of charge of 2 *F* (289 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a light-yellow solid (**279 mg**, **0.76 mmol**, **51%**).

^{1}H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.96 – 7.88 (m, 2H, *H*-4', *H*-6'), 7.63 – 7.58 (m, 1H, *H*-3'), 7.50 – 7.41 (m, 2H, *H*-2''), 7.40 – 7.26 (m, 8H, *H*-3'', *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 6.89 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), δ/ppm: 153.0, 146.5, 139.2, 133.2, 132.8, 131.3, 130.9, 130.4, 130.3, 129.9, 128.8, 128.7, 128.7, 128.4, 128.0, 126.0, 104.1.

HRMS (ESI+), *m/z*: calculated for $C_{21}H_{14}{}^{35}Cl_2N_2 + H^+$ 365.0607 [*M*+H]$^+$, 365.0601; calculated for $C_{21}H_{14}{}^{35}Cl^{37}ClN_2 + H^+$ 367.0581 [*M*+H]$^+$, 367.0571.

1*H*-1-(4-Cyanophenyl)-3,5-diphenylpyrazole (5b')



Product synthesis was carried out according to SOP2 using 1*H*-1-(4-cyanophenyl)-4,5-dihydro-1,5-diphenylpyrazole (**4b'**, **1.50 mmol**, **485 mg**) applying an amount of charge of 4.5 *F* (651 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc as a light-yellow solid (**412 mg**, **1.28 mmol**, **85%**).

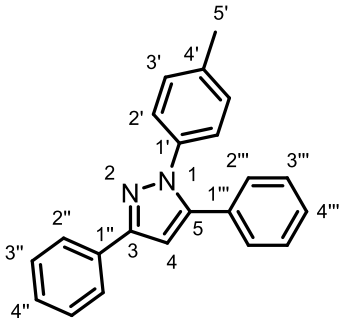
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.94 – 7.90 (m, 2H, *H*-2''), 7.65 – 7.59 (m, 2H, *H*-2'), 7.53 – 7.48 (m, 2H, *H*-3'), 7.48 – 7.27 (m, 8H, *H*-3'', *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 6.85 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 153.3, 144.9, 143.5, 133.0, 132.5, 130.3, 129.2, 129.0, 129.0, 128.9, 128.7, 126.0, 124.9, 118.5, 110.5, 107.0.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{15}N_3$ + H^+ 322.1339 $[M+H]^+$, found 322.1338.

Known compound, spectroscopic data corresponds to the literature.[30]

1*H*-3,5-Diphenyl-1-(4-methylphenyl)pyrazole (5c')



Product synthesis was carried out according to SOP3 using 1*H*-4,5-dihydro-1,5-diphenyl-1-(4-methylphenyl)pyrazole (**4c'**, **1.50 mmol**, **469 mg**) applying an amount of charge of 5 *F* (724 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a light-yellow solid (**416 mg**, **1.33 mmol**, **89%**).

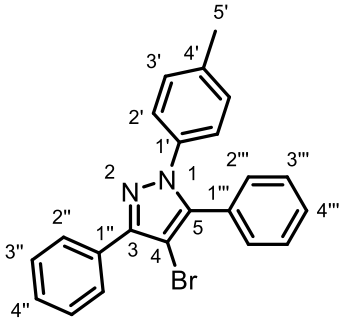
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.95 – 7.87 (m, 2H, *H*-2'), 7.46 – 7.37 (m, 2H, *H*-3'), 7.35 – 7.26 (m, 6H, *H*-2'', *H*-3'', *H*-4'', *H*-4'''), 7.26 – 7.22 (m, 2H, *H*-2'''), 7.17 – 7.09 (m, 2H, *H*-3'''), 6.80 (s, 1H, *H*-4), 2.35 (s, 3H, *H*-5').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 151.9, 144.4, 137.9, 137.5, 133.3, 130.8, 129.6, 128.9, 128.8, 128.6, 128.3, 128.0, 125.9, 125.3, 105.1, 21.2.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{18}N_2$ + H^+ 311.1543 $[M+H]^+$, found 311.1541.

Known compound, spectroscopic data corresponds to the literature.[3,23]

1*H*-4-Bromo-3,5-diphenyl-1-(4-methylphenyl)pyrazole (5d')



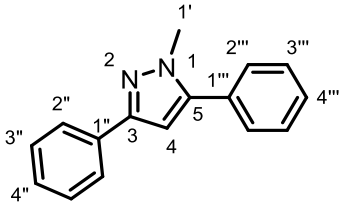
Product synthesis was carried out according to SOP4 using 1*H*-4,5-dihydro-1,5-diphenyl-1-(4-methylphenyl)pyrazole (**4c'**, **1.50 mmol**, **469 mg**) applying an amount of charge of 4.5 *F* (651 C). The pyrazole was obtained after filtration through a pad of silica with EtOAc as a yellow solid (**579 mg**, **1.48 mmol**, **99%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 8.11 – 8.03 (m, 2H, *H*-2''), 7.53 – 7.47 (m, 2H, *H*-3''), 7.47 – 7.33 (m, 6H, *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 7.23 – 7.16 (m, 2H, *H*-2'), 7.16 – 7.08 (m, 2H, *H*-3'), 2.35 (s, 3H, *H*-5').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 149.6, 142.0, 137.6, 137.5, 132.2, 130.3, 129.5, 129.2, 129.0, 128.5, 128.4, 128.1, 124.7, 94.7, 21.2.

HRMS (ESI+), *m/z*: calculated for $C_{22}H_{17}{}^{79}BrN_2 + H^+$ 389.0648 [*M*+H]$^+$, found 389.0645; calculated for $C_{22}H_{17}{}^{81}BrN_2 + H^+$ 391.0630 [*M*+H]$^+$, found 391.0629.

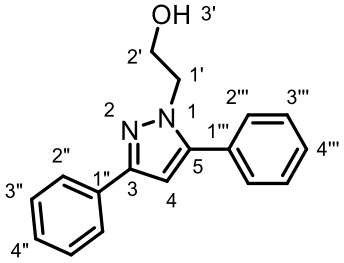
1*H*-3,5-Diphenyl-1-methylpyrazole (5e')



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-3,5-diphenyl-1-methylpyrazole (**4e'**, **3.75 mmol**, **886 mg**). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a light-yellow solid (**701 mg**, **2.99 mmol**, **80%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.90 – 7.81 (m, 2H, *H*-2''), 7.54 – 7.38 (m, 8H, *H*-3'', *H*-4'', *H*-2''', *H*-3'''), 7.37 – 7.28 (m, 1H, *H*-4'''), 6.64 (s, 1H, *H*-4), 3.94 (s, 3H, *H*-1').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 150.6, 145.1, 133.5, 130.7, 128.8, 128.8, 128.7, 128.6, 127.7, 125.6, 103.3, 37.6.
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{14}N_2 + H^+$ 235.1230 [*M*+H]$^+$, found 235.1227.
Known compound, spectroscopic data corresponds to the literature.[23]

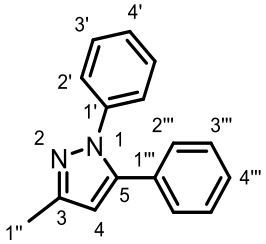
1*H*-3,5-Diphenyl-1-(2-hydroxyethyl)pyrazole (5f')



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-3,5-diphenyl-1-(2-hydroxyethyl)pyrazole (**4f'**, **3.75 mmol**, **998 mg**), applying an amount of charge of 2.5 *F* (905 C). The pyrazole was obtained after flash column chromatography on C18-silica (65% MeCN in water + 0.1 vol% formic acid, isocratic) as a colourless solid (**356 mg**, **1.35 mmol**, **36%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.89 – 7.81 (m, 2H, *H*-2''), 7.51 – 7.40 (m, 7H, *H*-3'', *H*-4'', *H*-2''', *H*-3'''), 7.36 – 7.31 (m, 1H, *H*-4'''), 4.29 – 4.23 (m, 2H, *H*-1'^{a}, *H*-2'^{a}), 4.07 – 4.02 (m, 3H, *H*-1'^{b}, *H*-2'^{b}, *H*-3').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 151.0, 145.7, 133.0, 130.3, 129.2, 128.9, 128.9, 128.8, 128.0, 125.7, 103.3, 62.2, 51.0.
HRMS (ESI+), *m/z*: calculated for $C_{17}H_{16}N_2O + H^+$ 265.1335 [*M*+H]$^+$, found 265.1331.
Known compound, spectroscopic data corresponds to the literature.[31]

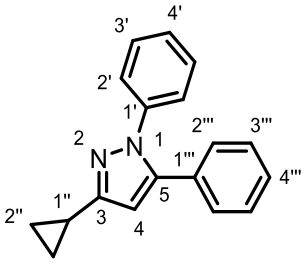
1*H*-4,5-Dihydro-1,5-diphenyl-3-methylpyrazole (5g')



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-methylpyrazole (**4g'**, **3.75 mmol**, **886 mg**) applying an amount of charge of 3.25 *F* (1176 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 3% → 5% EtOAc) as a light-yellow solid (**381 mg**, **1.63 mmol**, **43%**).

^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: δ 7.34 – 7.26 (m, 8H, *H*-2', *H*-3', *H*-2''', *H*-3'''), 7.25 – 7.21 (m, 2H, *H*-4', *H*-4'''), 6.33 (s, 1H, *H*-4), 2.41 (s, 3H, *H*-1'').
^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 149.5, 143.7, 140.2, 130.8, 128.9, 128.7, 128.5, 128.1, 127.1, 125.2, 107.8, 13.7.
HRMS (ESI+), *m/z*: calculated for $C_{16}H_{14}N_2 + H^+$ 235.1230 [*M*+H]$^+$, 235.1222.
Known compound, spectroscopic data corresponds to the literature.[30]

1*H*-3-Cyclopropyl-1,5-diphenylpyrazole (5h')



Product synthesis was carried out according to SOP2 using 1*H*-3-cyclopropyl-4,5-dihydro-1,5-diphenylpyrazole (**4h'**, **1.5 mmol**, **393 mg**) applying an amount of charge of 3 *F* (434 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a light-yellow solid (**161 mg**, **0.62 mmol**, **41%**).

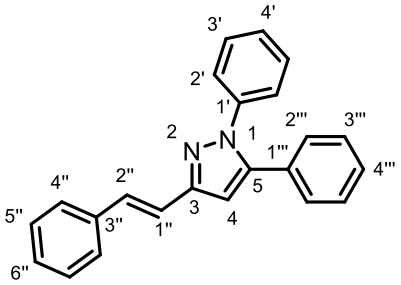
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.36 – 7.26 (m, 8H, *H*-2', *H*-3', *H*-2''', *H*-3'''), 7.26 – 7.21 (m, 2H, *H*-4', *H*-4'''), 6.19 (s, 1H, *H*-4), 2.09 (tt, J = 8.4, 5.0 Hz, 1H, *H*-1''), 1.08 – 0.93 (m, 2H, *H*-2''^{a}), 0.91 – 0.83 (m, 2H, *H*-2''^{b}).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 156.1, 143.7, 140.2, 130.9, 128.9, 128.8, 128.5, 128.2, 127.2, 125.3, 104.2, 9.3, 8.2.

HRMS (ESI+), *m/z*: calculated for $C_{18}H_{16}N_2$ + H^+ 261.1386 [*M*+H]$^+$, 261.1390.

Known compound, spectroscopic data corresponds to the literature.[4,27]

(*E*)-1*H*-1,5-Diphenyl-3-(β-styryl)pyrazole (5i')



Product synthesis was carried out according to SOP2 using (*E*)-1*H*-4,5-dihydro-1,5-diphenyl-3-(β-styryl)pyrazole (**4i'**, **1.5 mmol**, **486 mg**) applying an amount of charge of 3.75 *F* (543 C). The pyrazole was obtained after flash column chromatography on C18-silica (water/MeCN + 0.1 vol% formic acid; 70% → 80% MeCN) as a light-yellow solid (**153 mg**, **0.48 mmol**, **31%**).

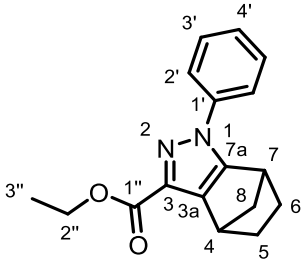
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.65 – 7.57 (m, 2H, *H*-1'', *H*-2''), 7.47 – 7.28 (m, 15H, *H*-2', *H*-3', *H*-4', *H*-2'', *H*-3'', *H*-4'', *H*-2''', *H*-3''', *H*-4'''), 6.82 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 151.3, 144.3, 140.1, 137.2, 130.8, 130.5, 129.0, 128.8, 128.8, 128.6, 128.5, 127.9, 127.5, 126.6, 125.2, 120.6, 105.1.

HRMS (ESI+), *m/z*: calculated for $C_{23}H_{18}N_2$ + H^+ 323.1543 [*M*+H]$^+$, 323.1545.

Known compound, spectroscopic data corresponds to the literature.[30]

Ethyl 1*H*-4,7-methano-1-phenyl-4,5,6,7-tetrahydroindazole-3-carboxylate (5j')



Product synthesis was carried out according to SOP2 using ethyl 1*H*-3a,7a-*cis*-3a,4,5,6,7,7a-hexahydro-4,7-methano-1-phenylindazole-3-carboxylate (**4j'**, **3.75 mmol**, **1066 mg**), applying an amount of charge of 4.5 *F* (1628 C). The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 3% → 5% EtOAc) as a light-orange solid (**159 mg**, **0.56 mmol**, **15%**).

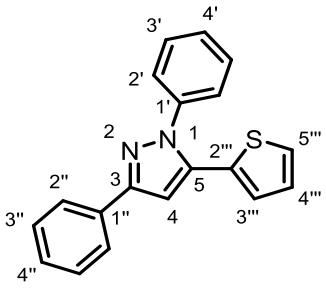
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.62 – 7.53 (m, 2H, *H*-3'), 7.36 – 7.24 (m, 2H, *H*-2'), 7.16 (m, 1H, *H*-4'), 4.27 (q, *J* = 7.1 Hz, 2H, *H*-2''), 3.59 – 3.49 (m, 2H, *H*-4, *H*-7), 2.02 – 1.93 (m, 1H, *H*-8^a), 1.89 – 1.78 (m, 2H, *H*-5^a, *H*-6^a), 1.60 – 1.52 (m, 1H, *H*-8^b), 1.27 (t, *J* = 7.1 Hz, 3H, *H*-3''), 1.13 – 1.01 (m, 2H, *H*-5^b, *H*-6^b).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 162.7, 153.0, 139.7, 136.4, 134.4, 129.2, 127.0, 120.3, 60.7, 52.3, 41.4, 38.9, 27.5, 26.6, 14.3.

HRMS (APCI+), *m/z*: calculated for $C_{17}H_{18}N_2O_2$ + H^+ 183.1441 [*M*+H]$^+$, found 283.1449.

Known compound, spectroscopic data corresponds to the literature.[32]

1*H*-1,3-Diphenyl-5-(thien-2-yl)pyrazole (5k')



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-5-(thien-2-yl)pyrazole (**4k'**, **1.50 mmol**, **457 mg**). No improvement was achieved regarding the product to substrate ratio after applying an amount of charge of 6.5 *F* (941 C) and the reaction was stopped. The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 0% → 10% EtOAc) as a yellow oil (**53 mg**, **0.18 mmol**, **12%**), **47%** of starting material (**214 mg**, **0.70 mmol**) were recovered.

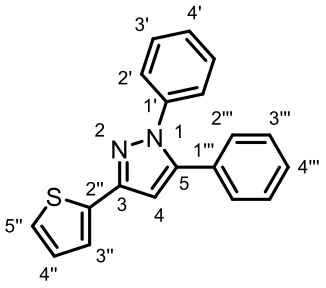
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.95 – 7.91 (m, 2H, *H*-2''), 7.51 – 7.40 (m, 7H, *H*-2', *H*-3', *H*-3'', *H*-4''), 7.39 – 7.33 (m, 1H, *H*-4'), 7.30 (dd, *J* = 5.1, 1.2 Hz, 1H, *H*-5'''), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H, *H*-4'''), 6.90 (s, 1H, *H*-4), 6.87 (dd, *J* = 3.6, 1.2 Hz, 1H, *H*-3''').

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 152.0, 140.0, 138.3, 132.9, 131.4, 129.2, 128.8, 128.4, 128.2, 127.5, 127.4, 126.6, 126.3, 125.9, 105.1.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{14}N_2S$ + H^+ 303.0950 [*M*+H]$^+$, found 303.0951.

Known compound, spectroscopic data corresponds to the literature.[29]

1*H*-1,5-Diphenyl-3-(thien-2-yl)pyrazole (5l')



Product synthesis was carried out according to SOP2 using 1*H*-4,5-dihydro-1,5-diphenyl-3-(thien-2-yl)pyrazole (**4l'**, **1.50 mmol**, **457 mg**). No improvement was achieved regarding the product to substrate ratio after applying an amount of charge of 6.5 *F* (941 C) and the reaction was stopped. The pyrazole was obtained after flash column chromatography on silica (cyclohexane/ethyl acetate; 0% → 10% EtOAc) as a yellow oil (**37 mg**, **0.12 mmol**, **8%**), **35%** of starting material (**158 mg**, **0.52 mmol**) were recovered.

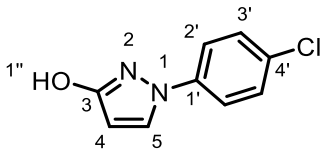
^{1}H NMR (400 MHz, $CDCl_3$), *δ*/ppm: 7.45 (dd, *J* = 3.6, 1.2 Hz, 1H, *H*-3''), 7.37 – 7.25 (m, 11H, *H*-2', *H*-3', *H*-4', *H*-5'', *H*-2''', *H*-3''', *H*-4'''), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H, *H*-4''), 6.74 (s, 1H, *H*-4).

^{13}C NMR (101 MHz, $CDCl_3$), *δ*/ppm: 147.4, 144.5, 140.0, 136.4, 130.4, 129.0, 128.9, 128.6, 128.5, 127.6, 127.6, 125.5, 125.0, 124.3, 105.3.

HRMS (ESI+), *m/z*: calculated for $C_{19}H_{14}N_2S$ + H^+ 303.0950 [*M*+H]$^+$, found 303.0952.

Known compound, spectroscopic data corresponds to the literature.[3]

1*H*-1-(4-Chlorophenyl)-3-hydroxypyrazole (5m')



Product synthesis was carried out according to SOP2 using 1-(4-chlorophenyl)-4,5-dihydropyrazol-3-ol (**4m', 3.75 mmol, 737 mg**) applying an amount of charge of 3.25 *F* (1176 C). The pyrazole was obtained after filtration through silica with ethyl acetate as a dark yellow solid (**536 mg, 2.75 mmol, 73%**).

^{1}H NMR (600 MHz, DMSO-d_6), *δ*/ppm: 10.36 (brs, 1H, *H*-1''), 8.24 (d, *J* = 2.6 Hz, 1H, *H*-5), 7.86 – 7.57 (m, 2H, *H*-2'), 7.53 – 7.38 (m, 2H, *H*-3'), 5.83 (d, *J* = 2.6 Hz, 1H, *H*-4).

^{13}C NMR (151 MHz, DMSO-d_6), *δ*/ppm: 163.0, 138.7, 129.3, 128.8, 128.5, 118.3, 95.0.

HRMS (ESI+), *m/z*: calculated for $C_9H_7{}^{35}ClN_2O$ + H^+ 195.0320 [*M*+H]$^+$, found 195.0323; calculated for $C_9H_7{}^{37}ClN_2O$ + H^+ 197.0292 [*M*+H]$^+$, found 197.0299.

Known compound, spectroscopic data corresponds to the literature.[20,21]

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11.NMR Spectra

11.1. NMR Spectra of Chalcones

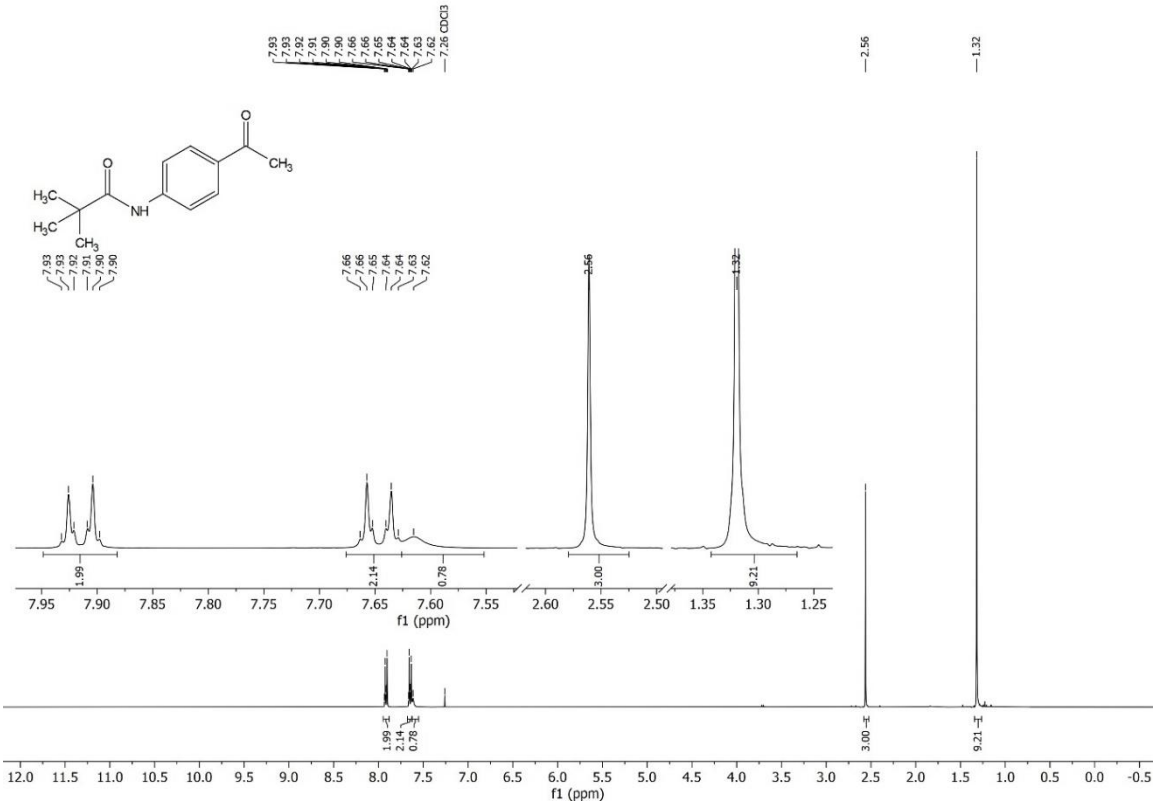

Figure S6: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a**.

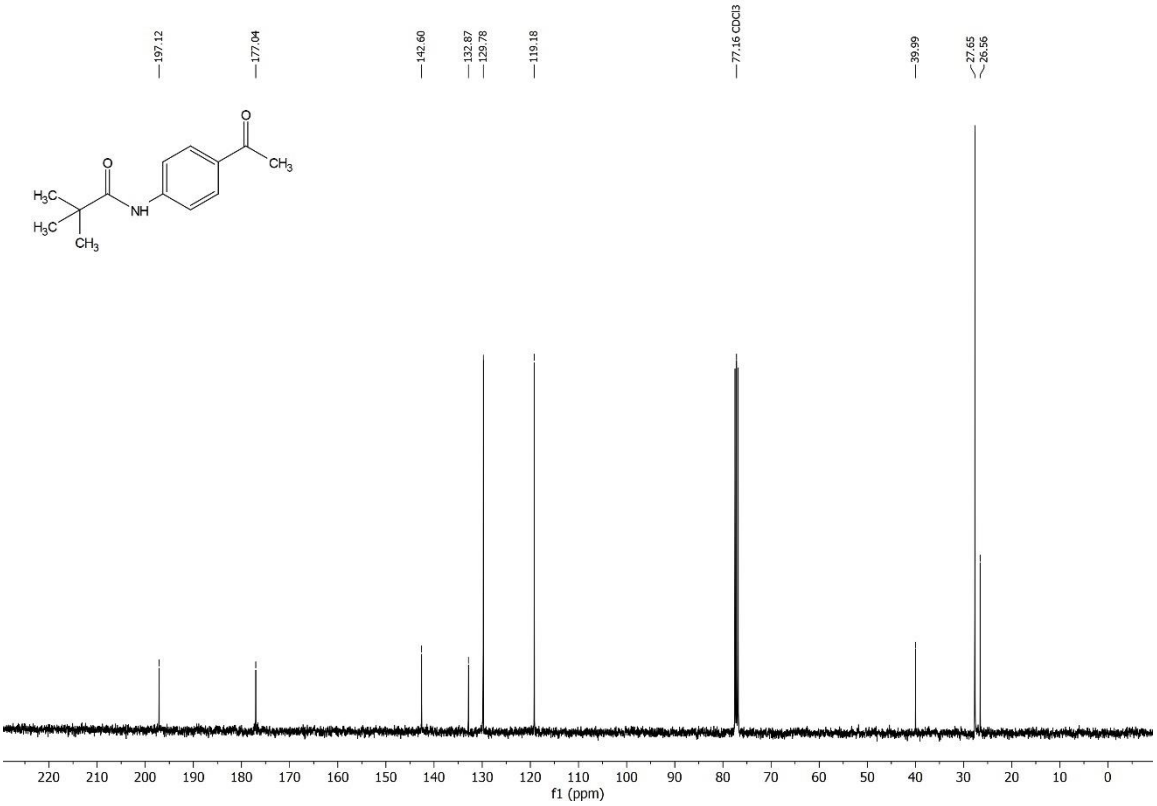

Figure S7: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7a**.

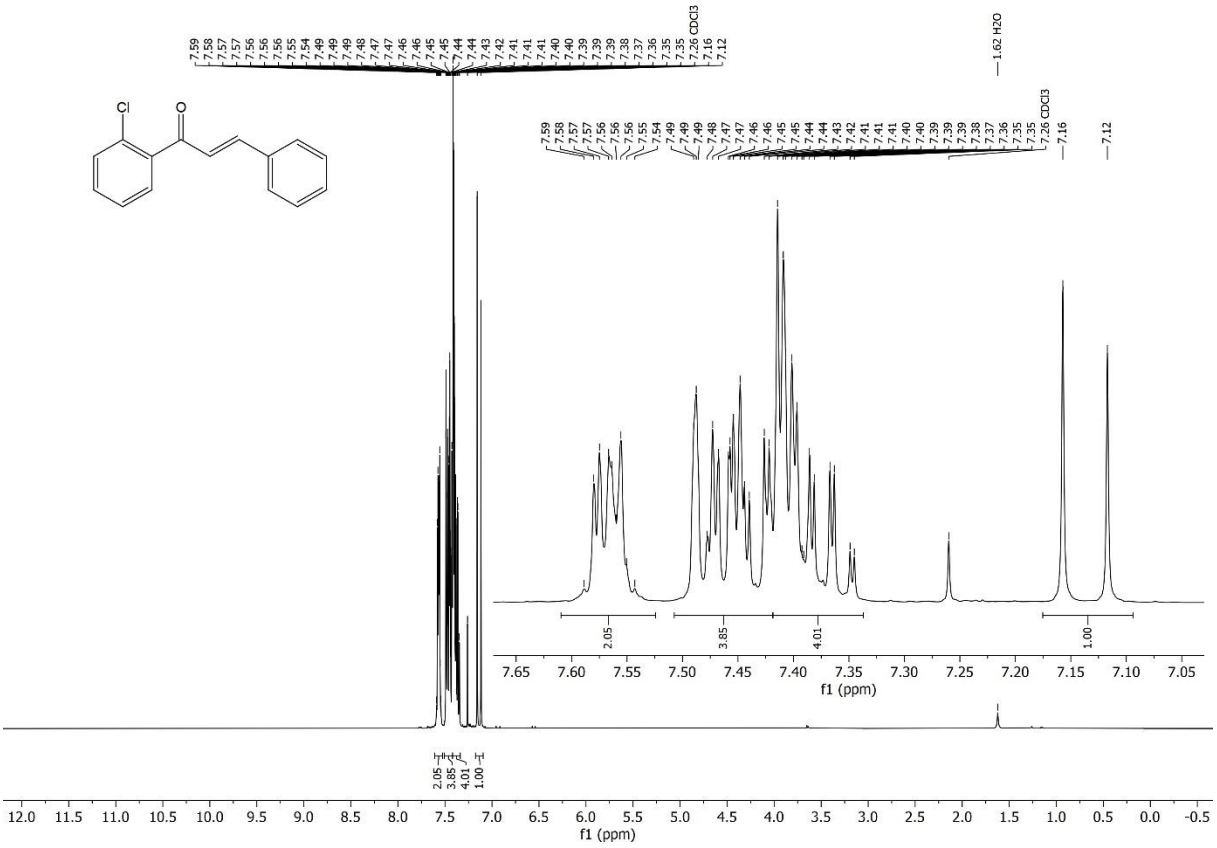

Figure S8: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7b.**

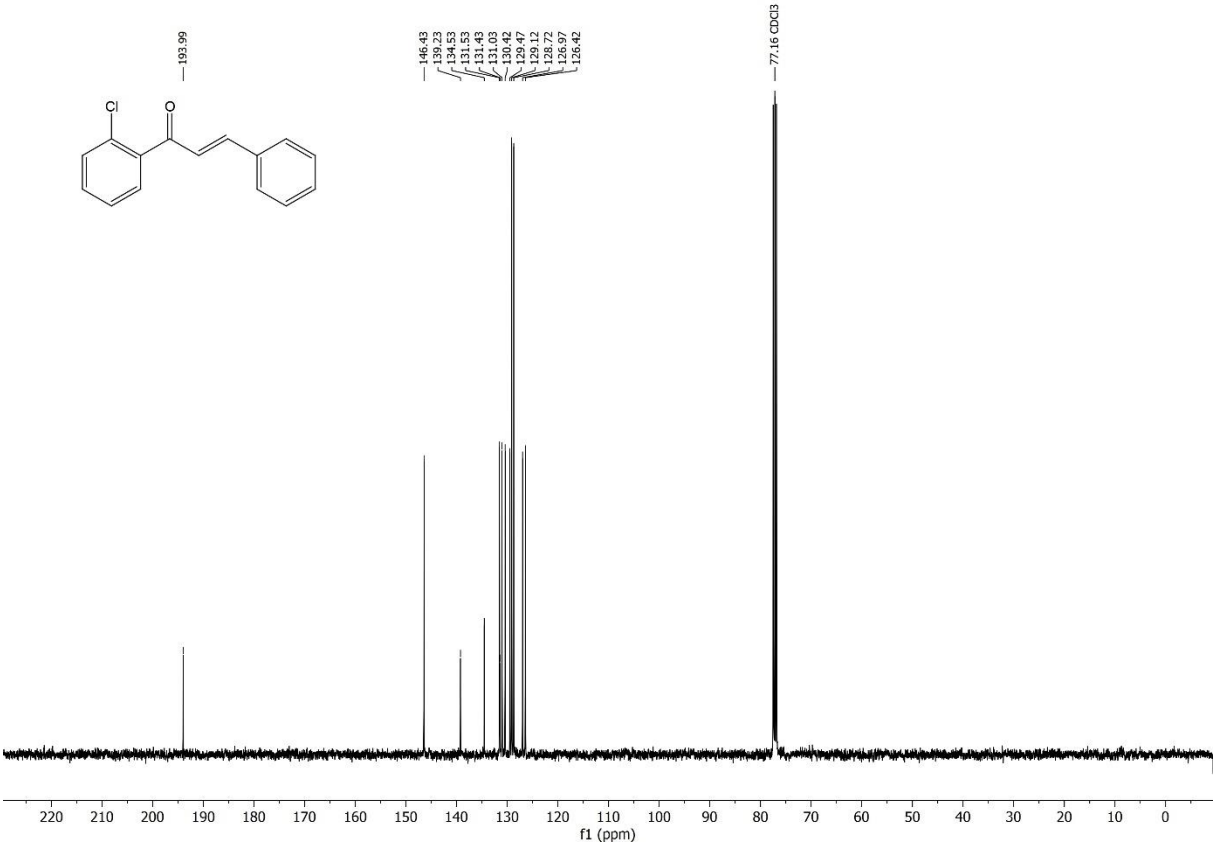

Figure S9: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7b**.

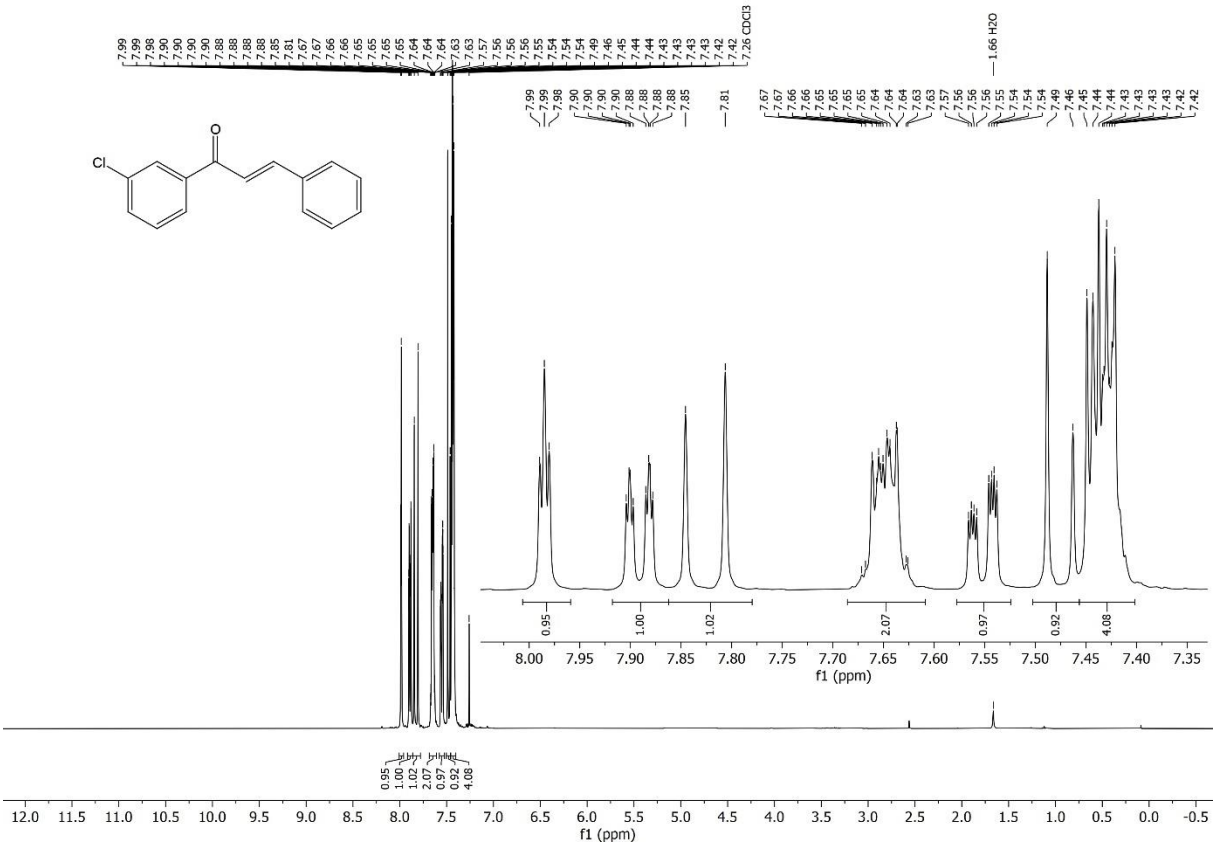

Figure S10: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7c**.

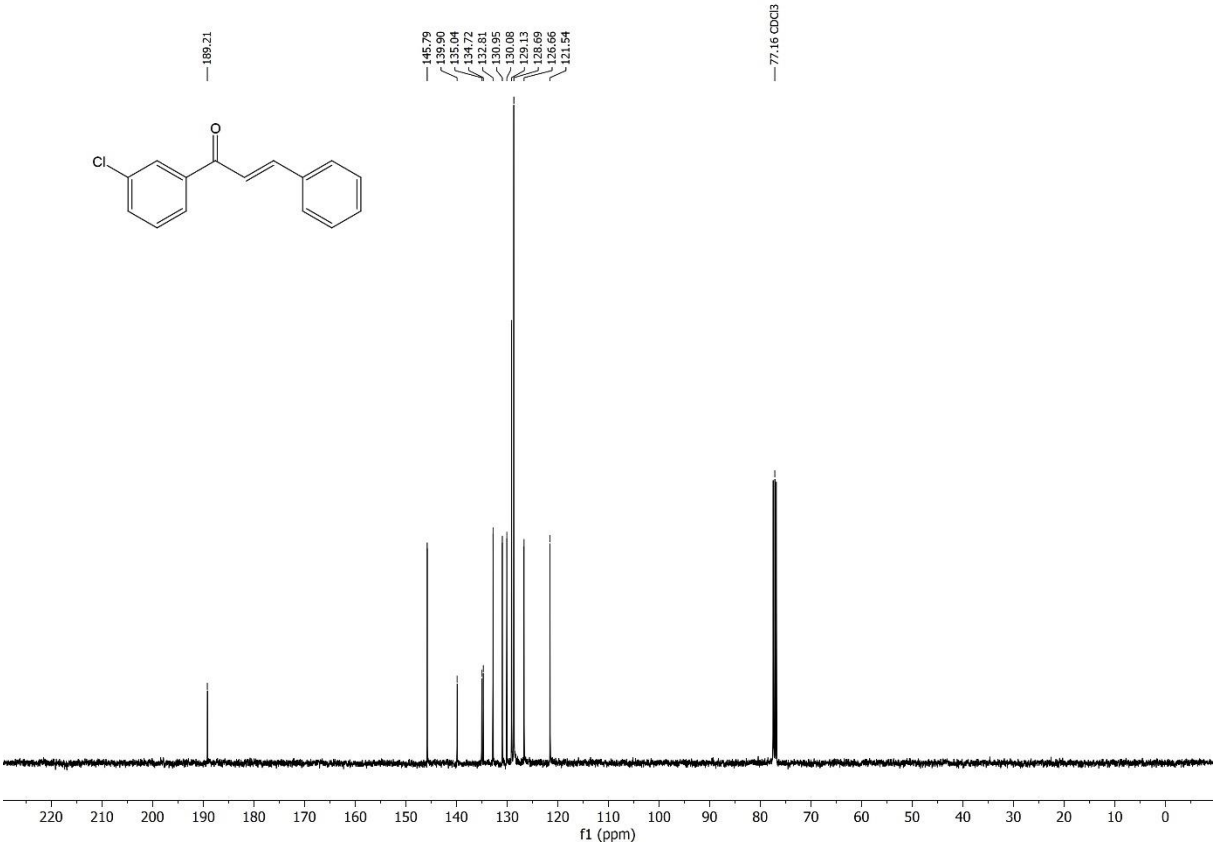

Figure S11: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7c**.

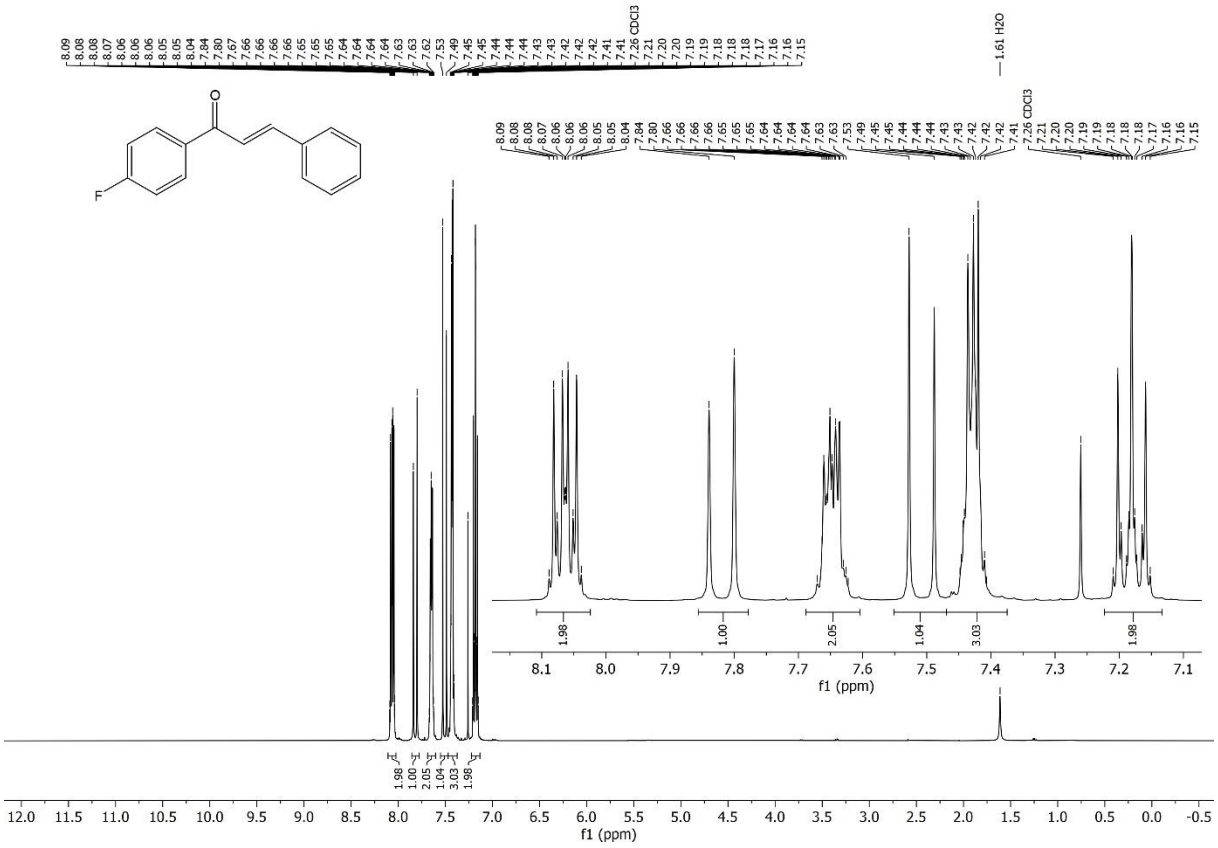

Figure S12: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7d**.

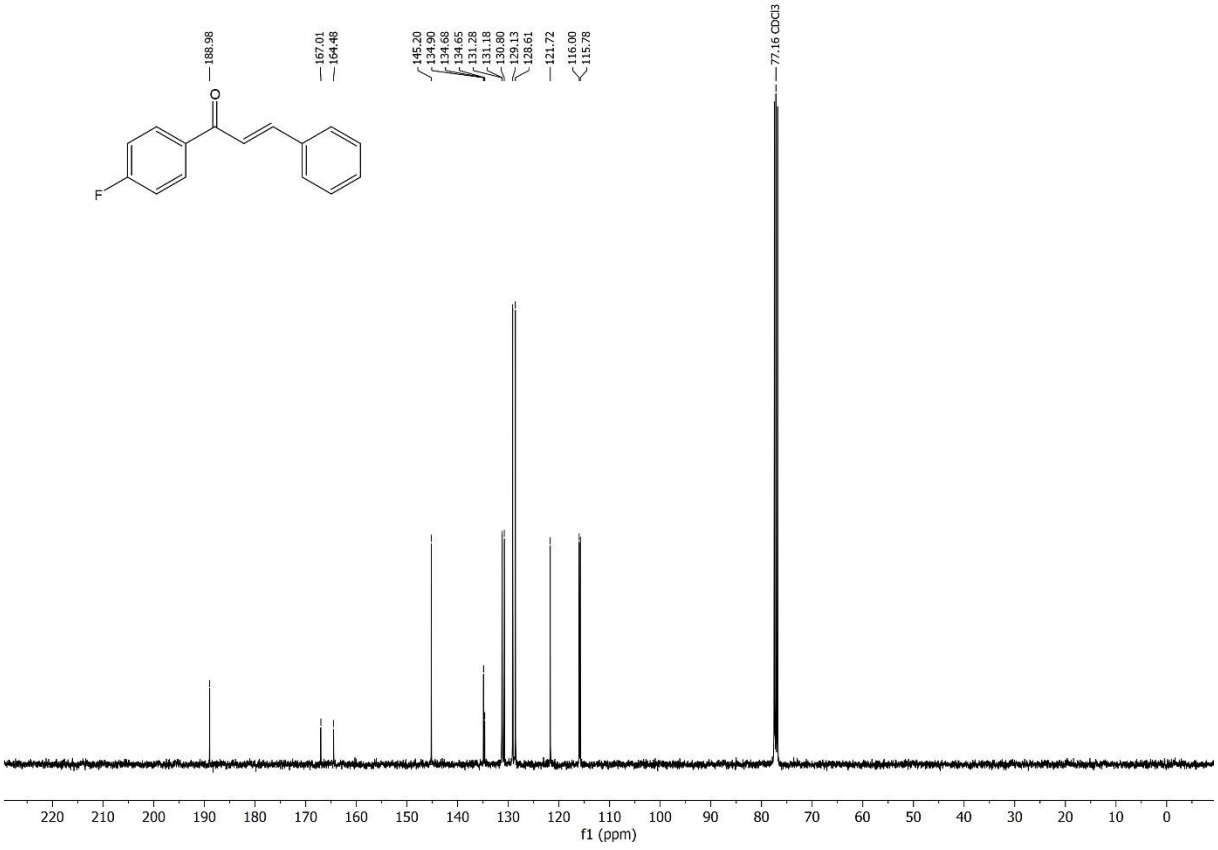

Figure S13: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7d**.

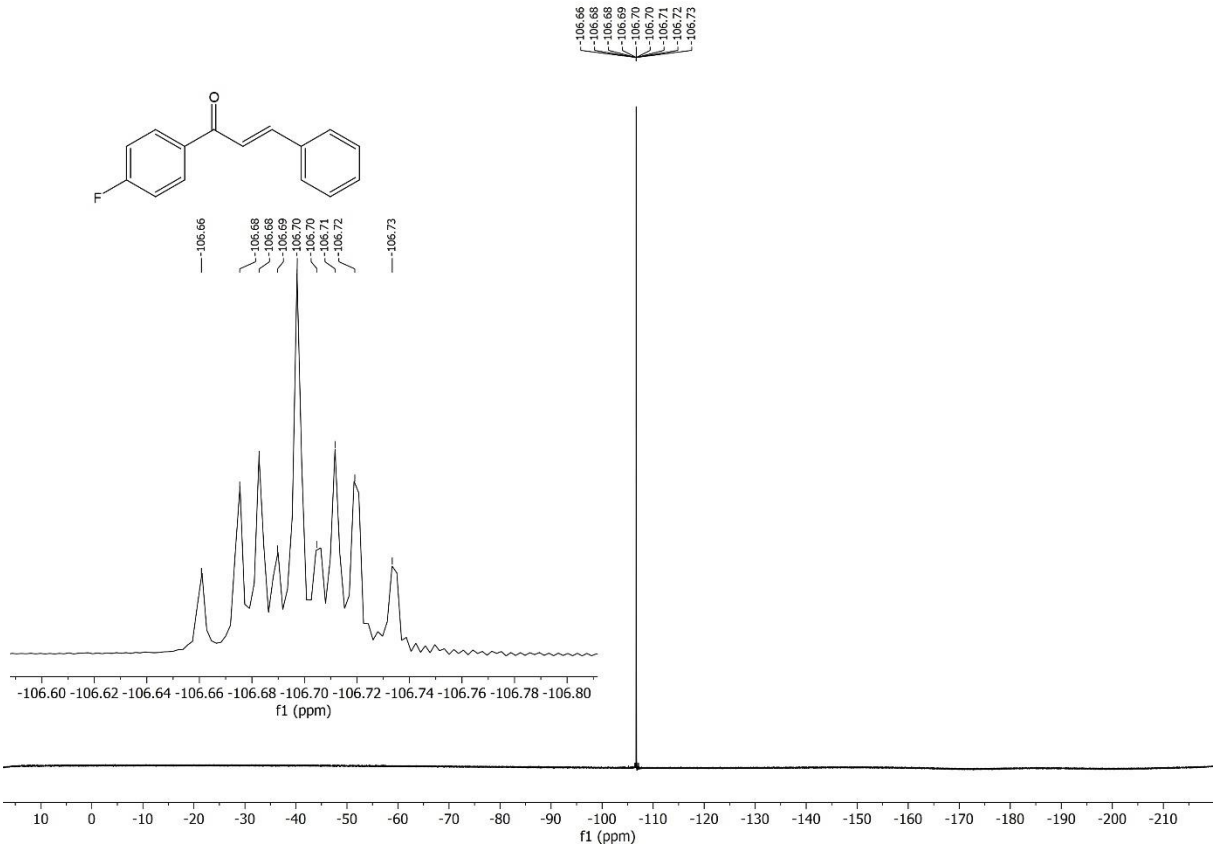

Figure S14: ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **7d**.

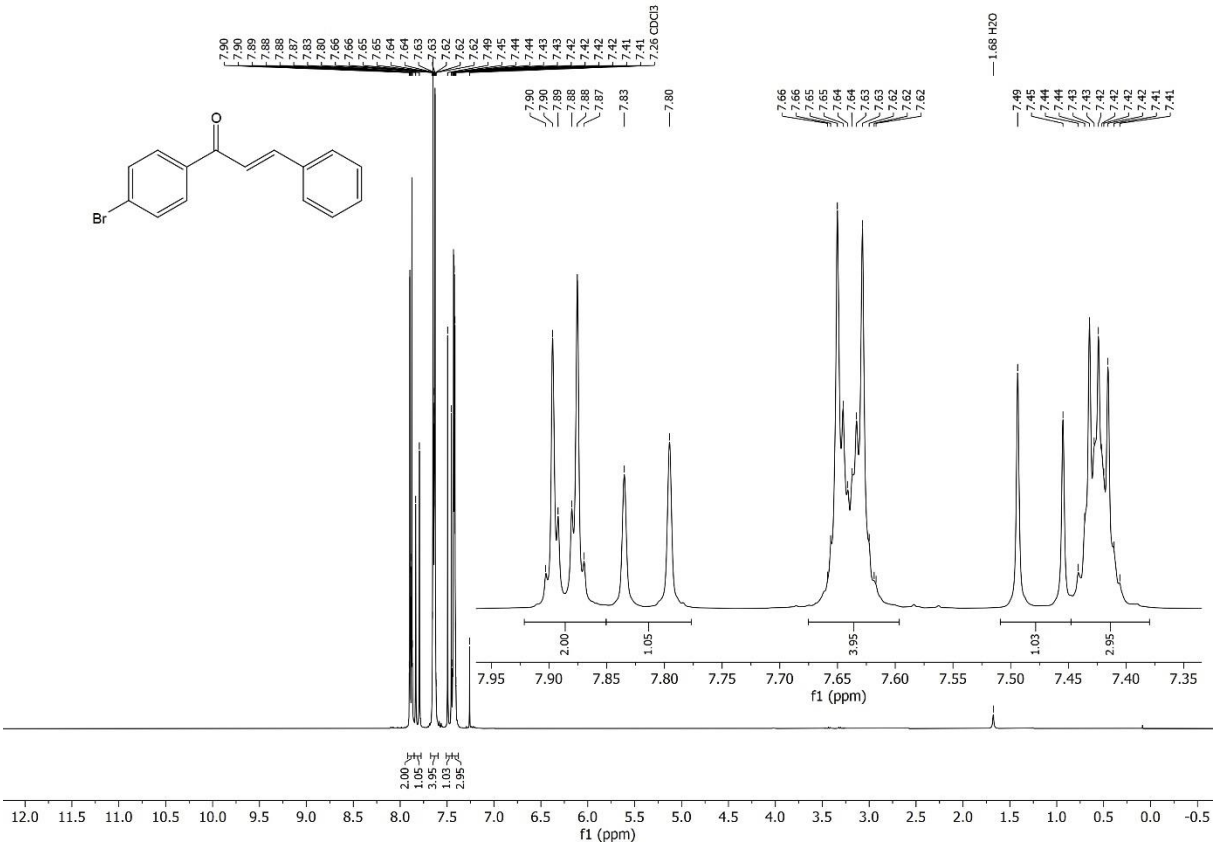

Figure S15: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7e**.

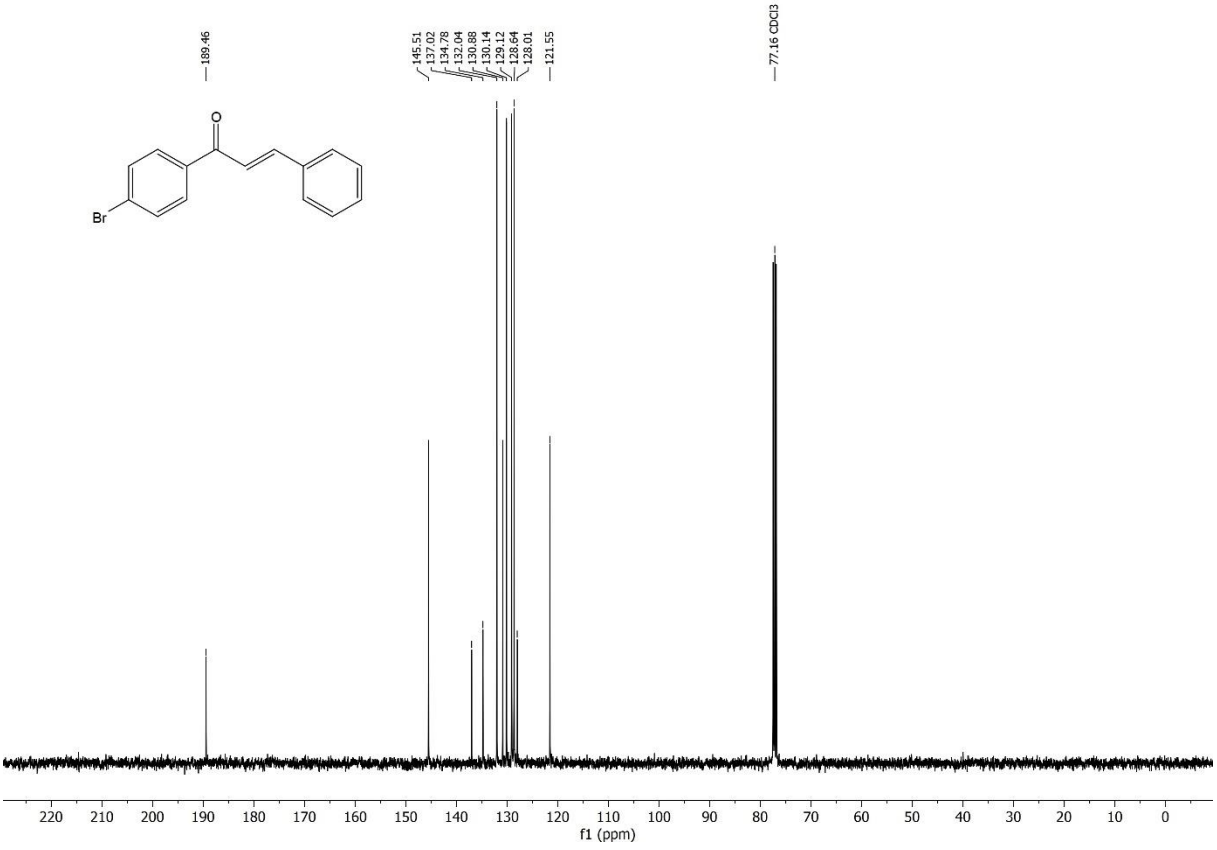

Figure S16: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7e**.

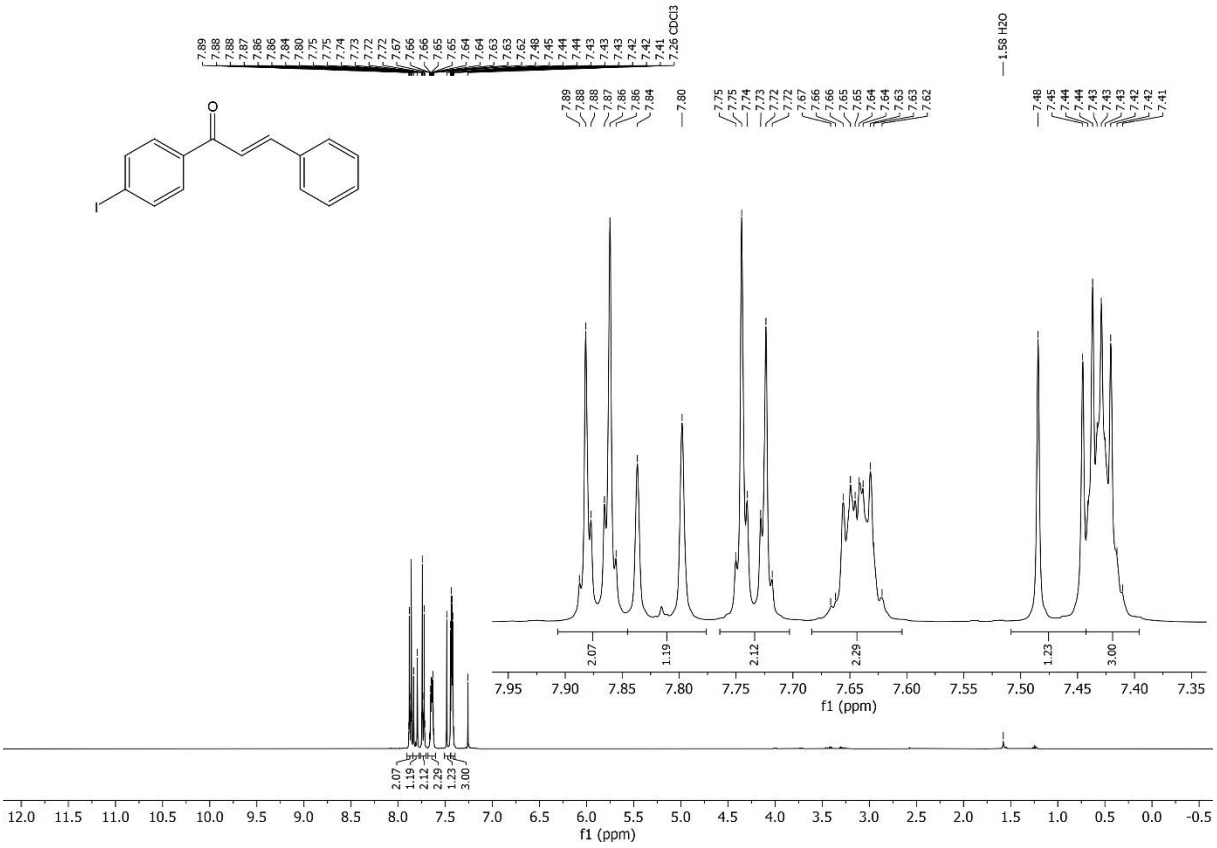

Figure S17: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7f**.

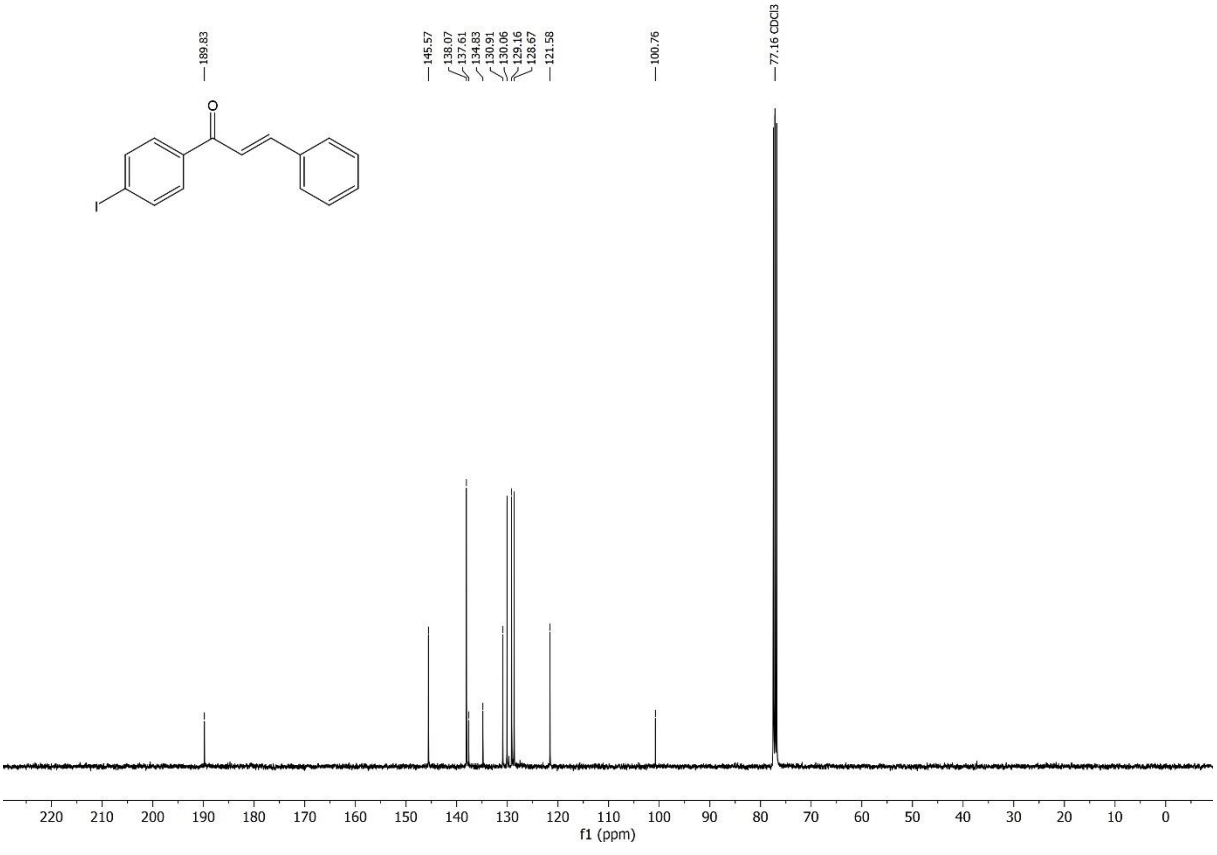

Figure S18: ^{13}C NMR spectrum (400 MHz, $CDCl_3$) of **7f**.

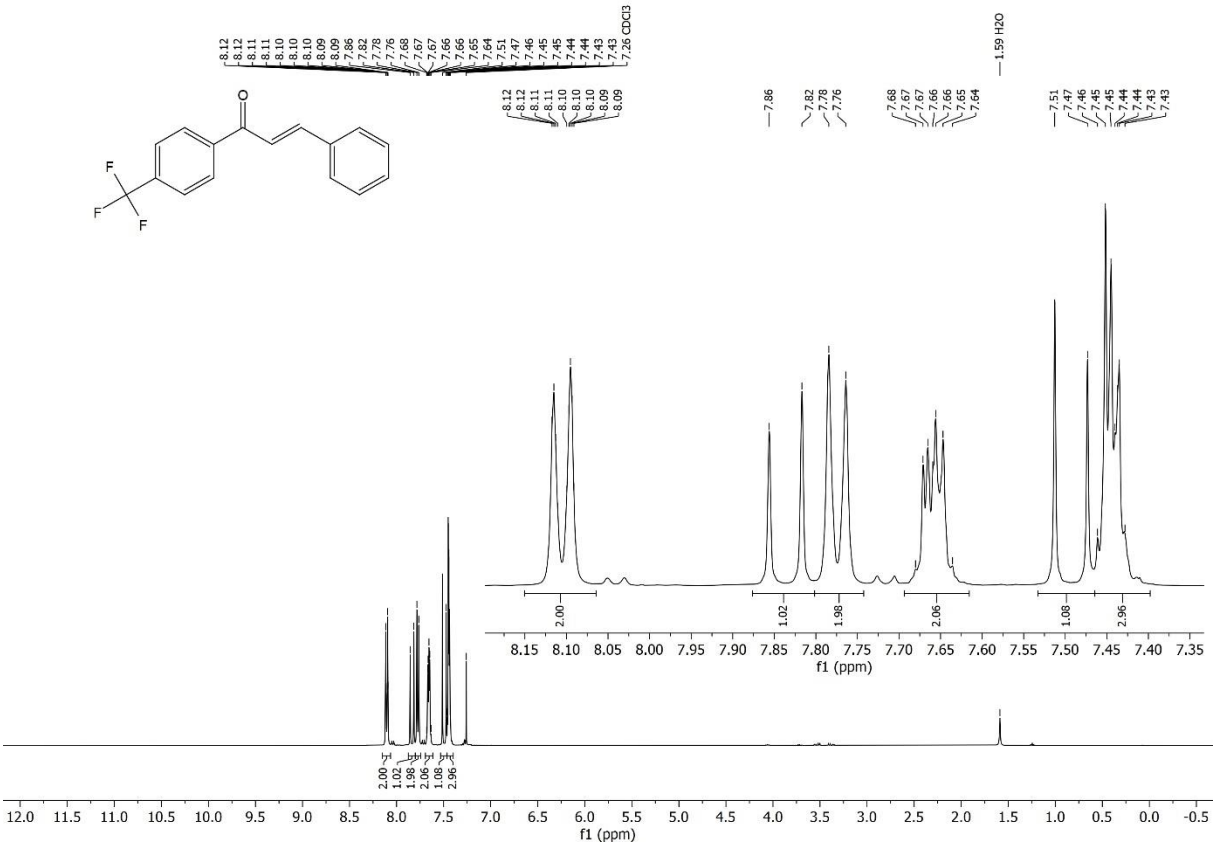

Figure S19: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7g**.

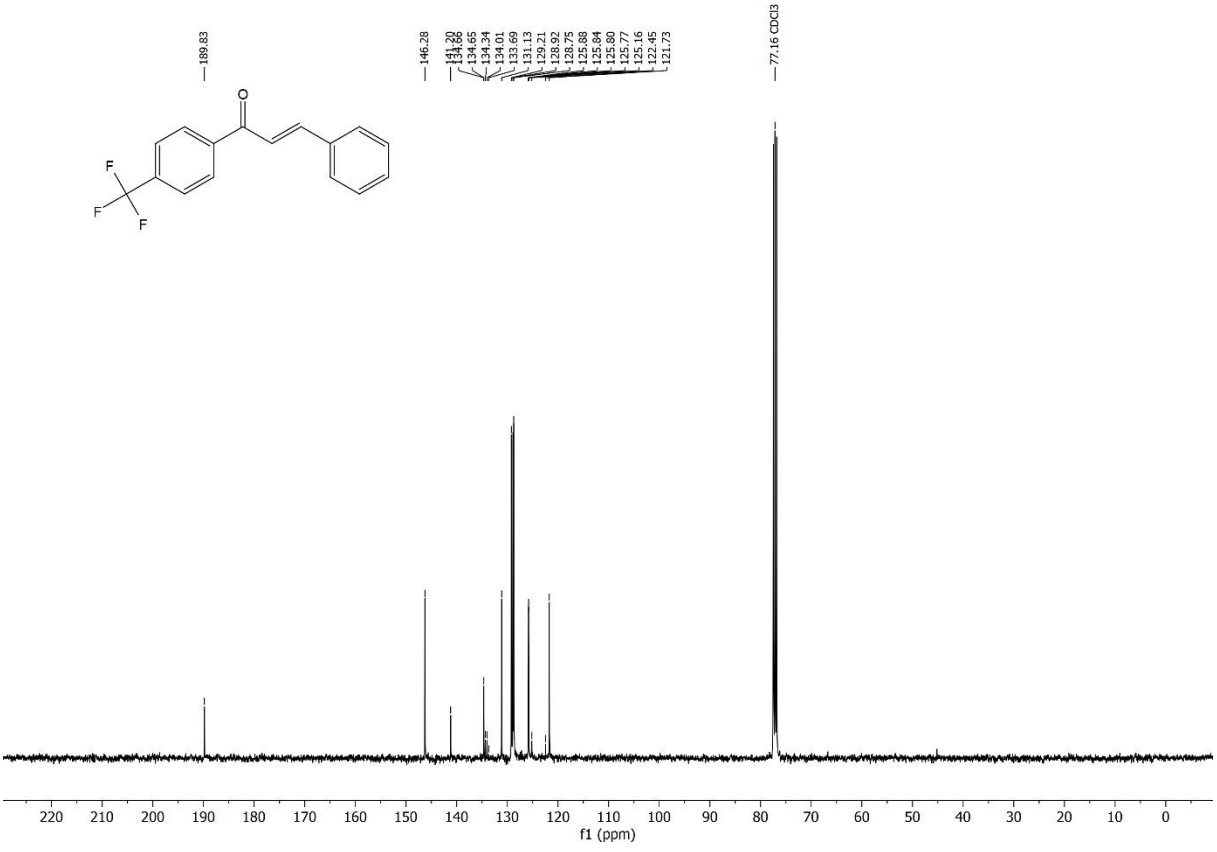

Figure S20: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7g**.

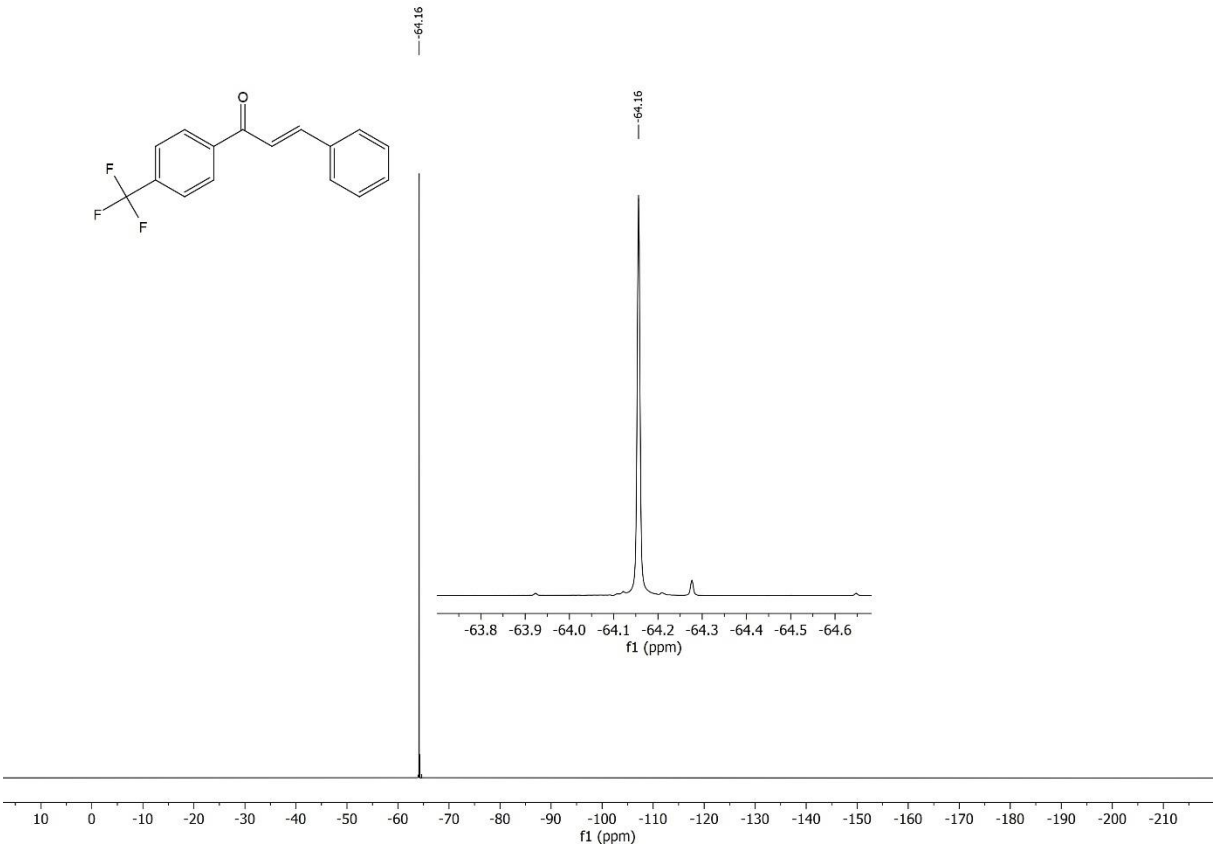

Figure S21: ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **7g**.

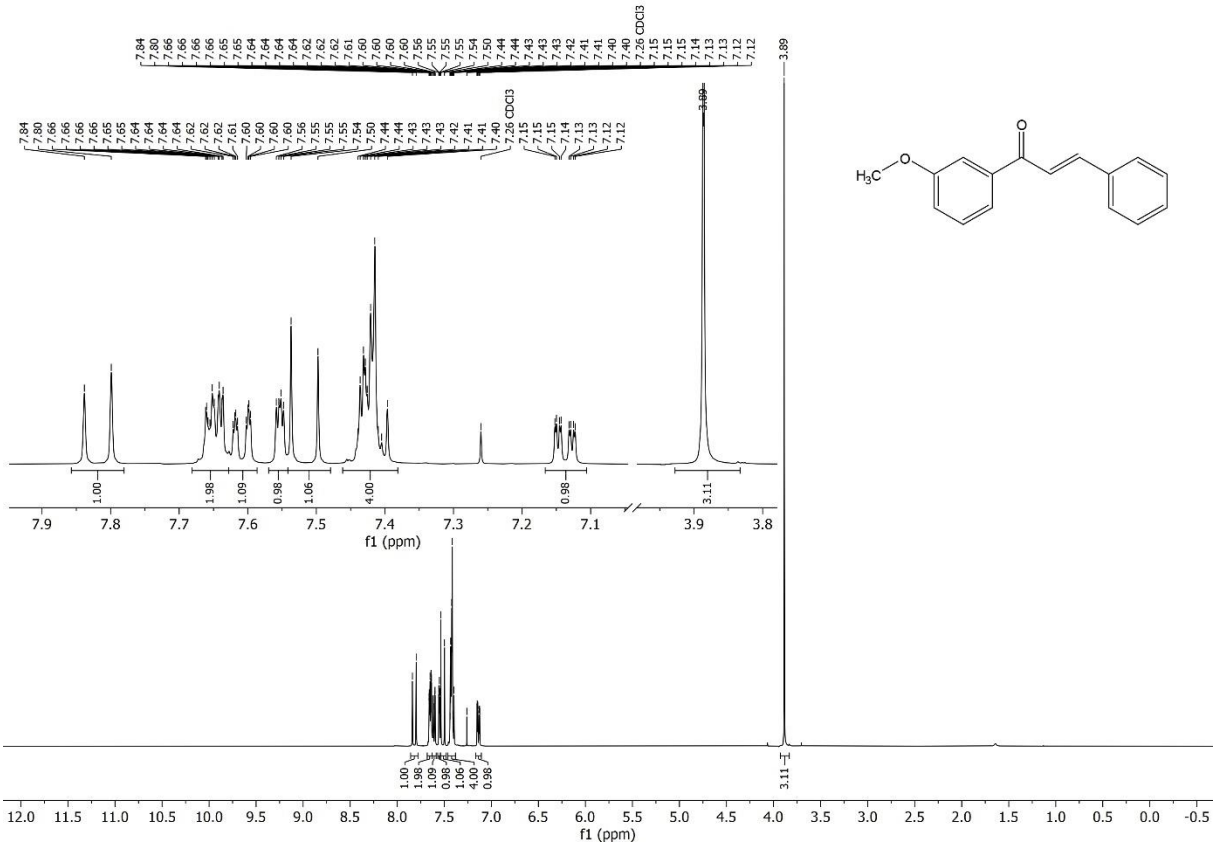

Figure S22: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7h**.

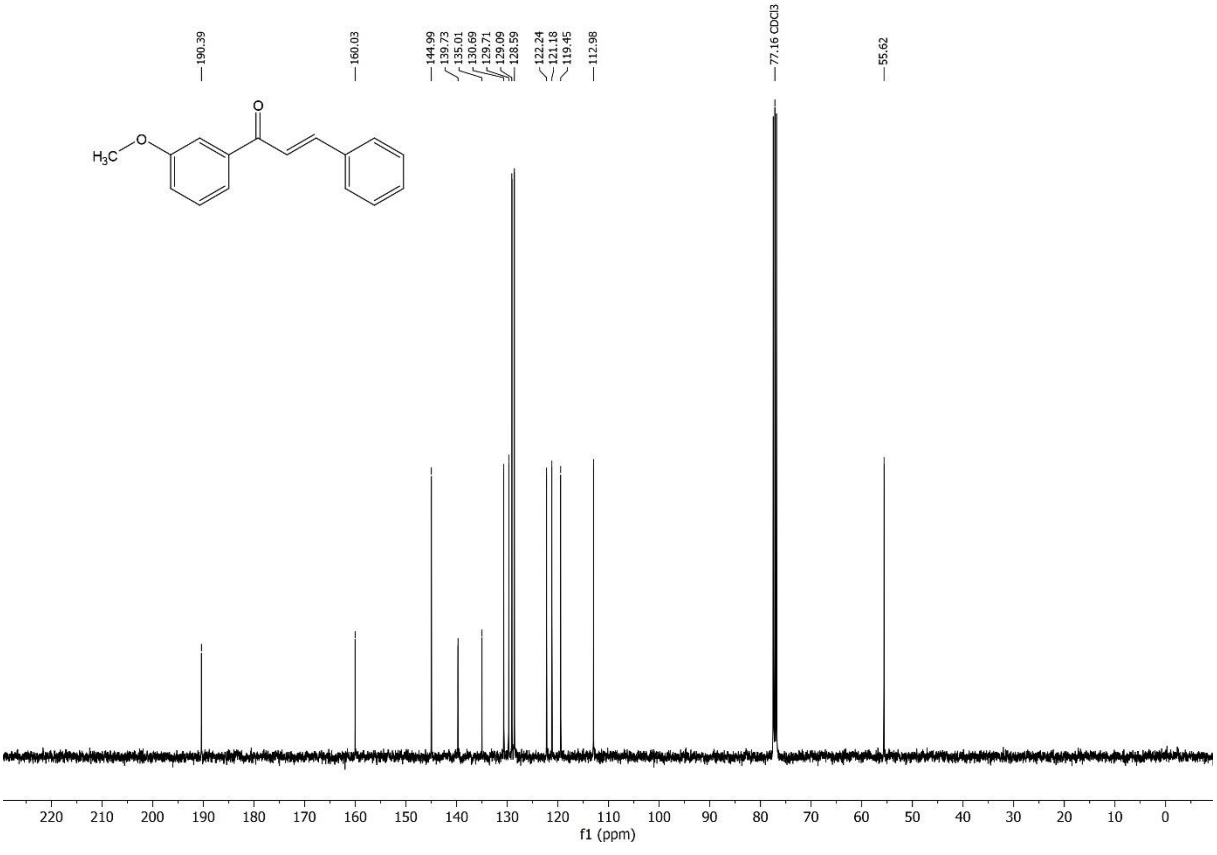

Figure S23: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7h**.

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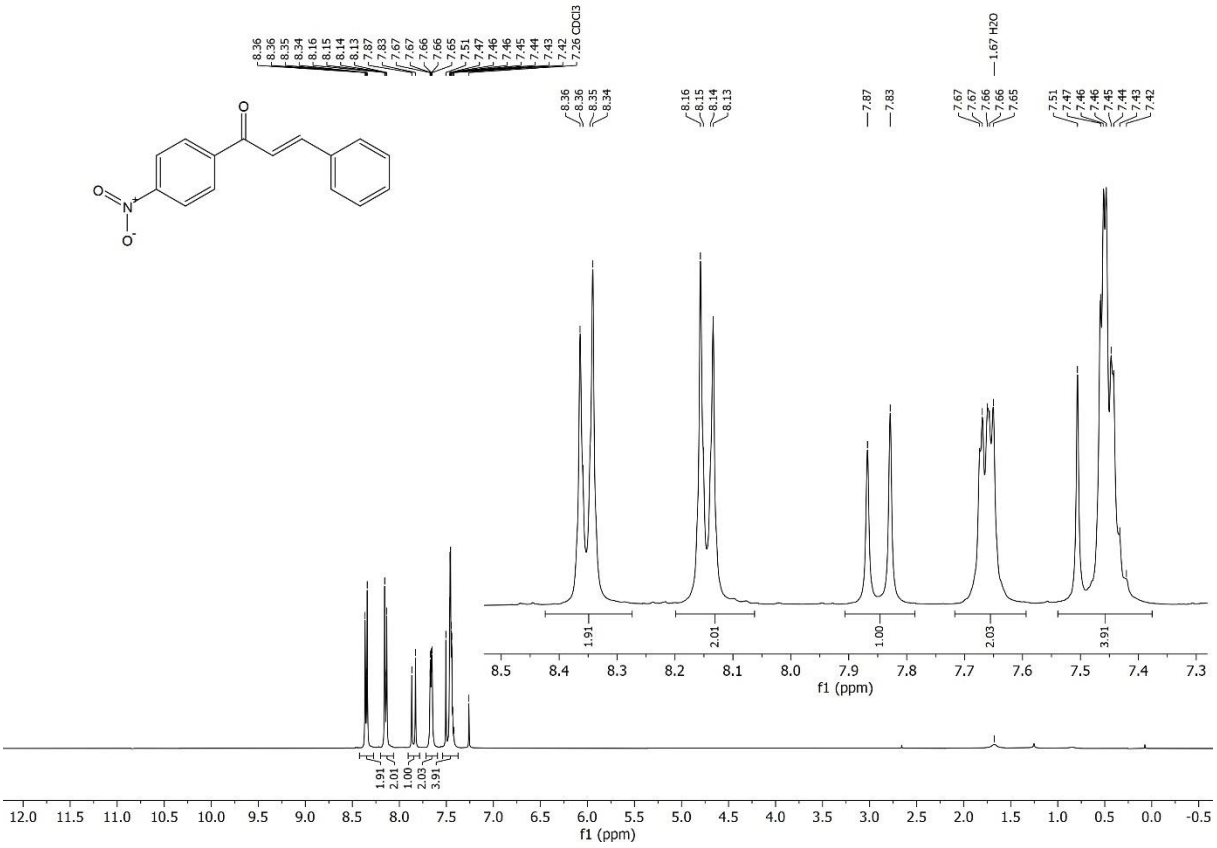

Figure S24: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7i**.

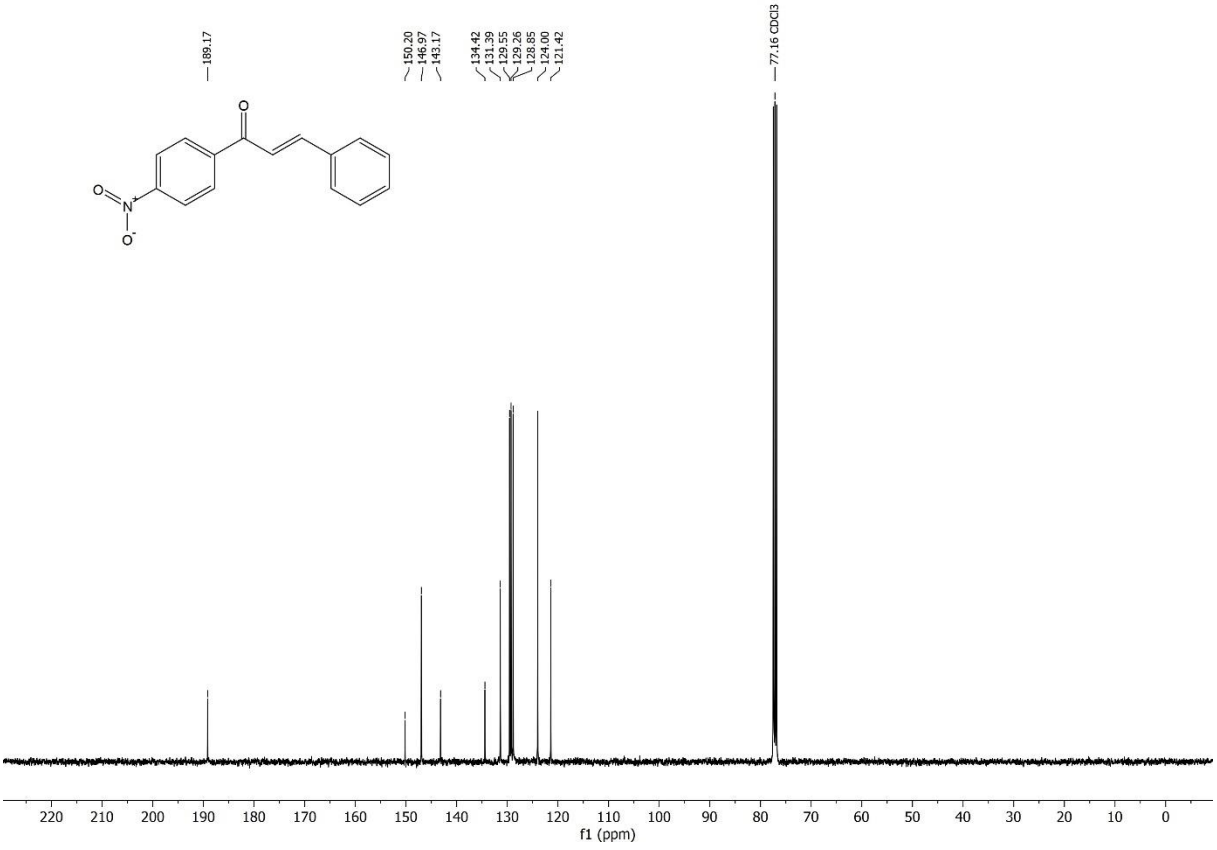

Figure S25: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7i**.

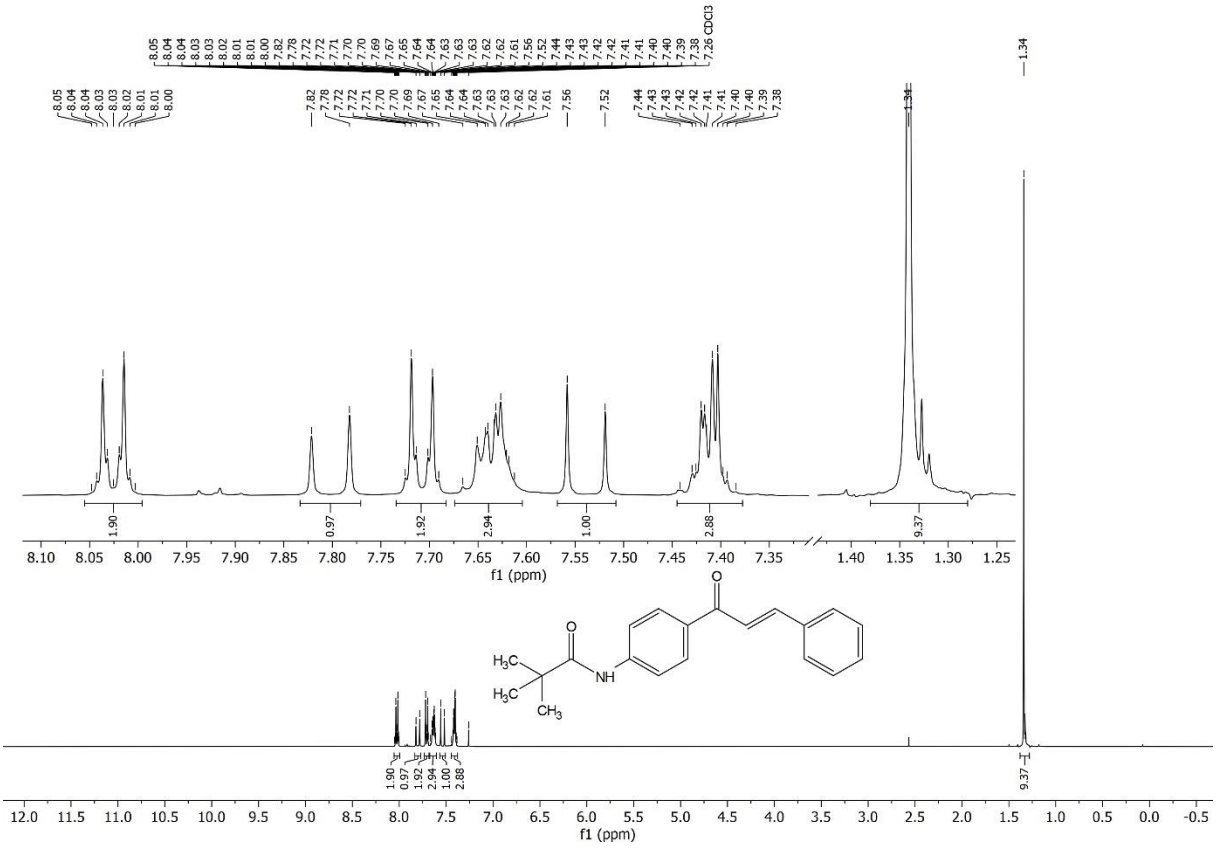

Figure S26: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7j**.

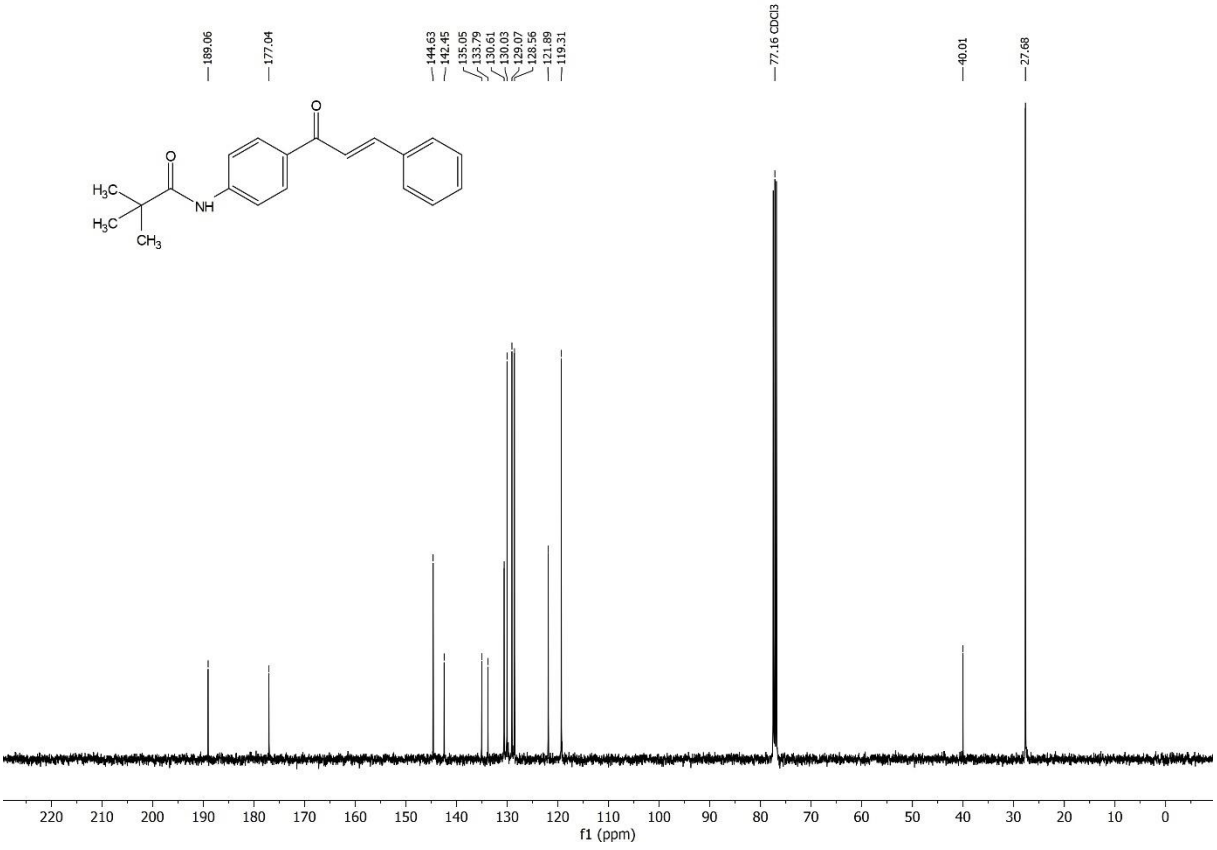

Figure S27: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7j**.

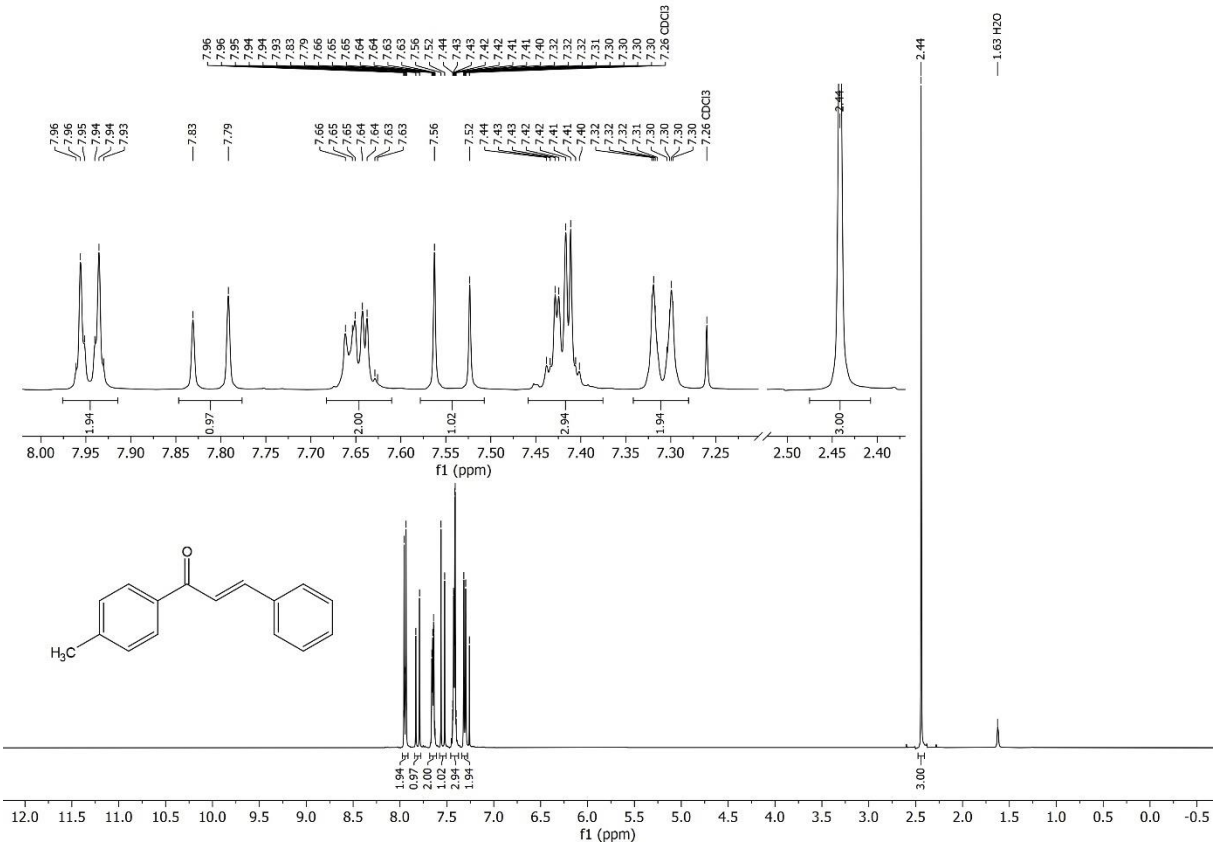

Figure S28: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7k**.

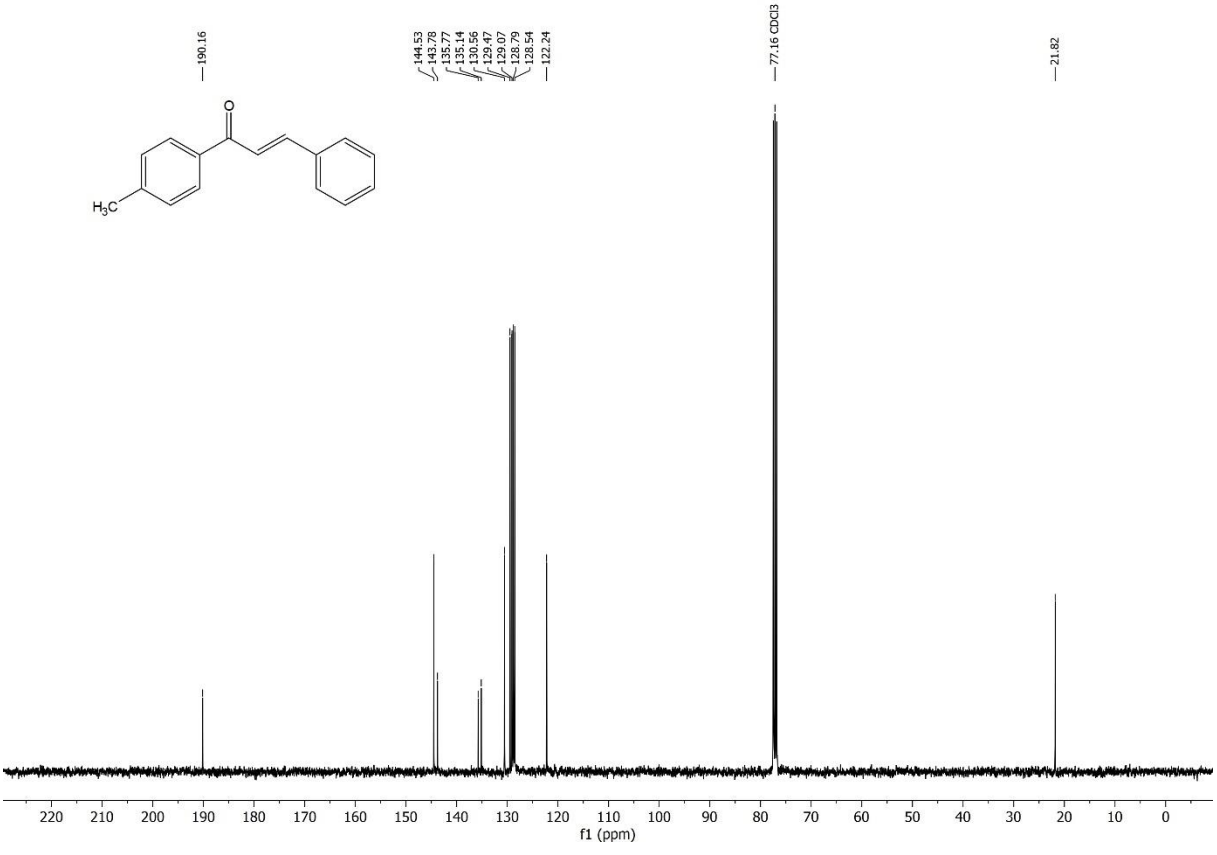

Figure S29: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7k**.

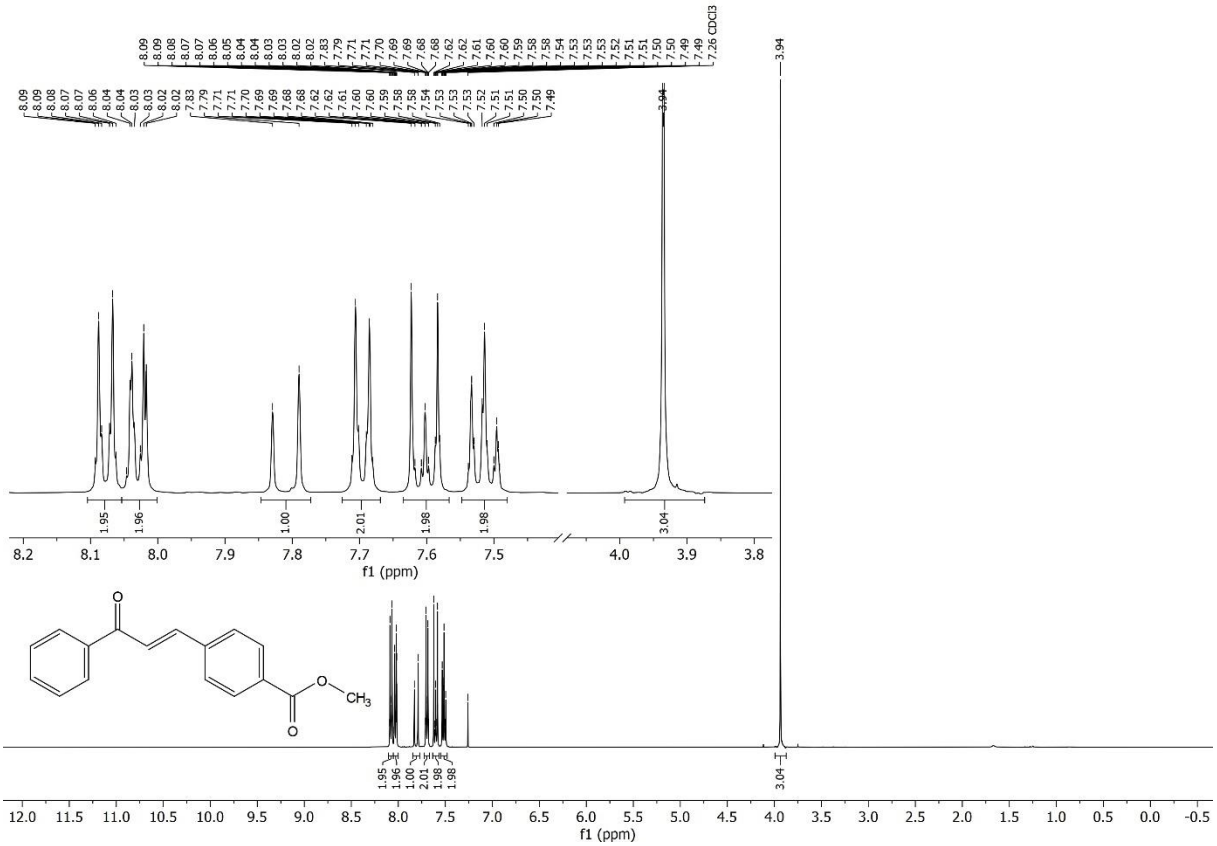

Figure S30: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7l**.

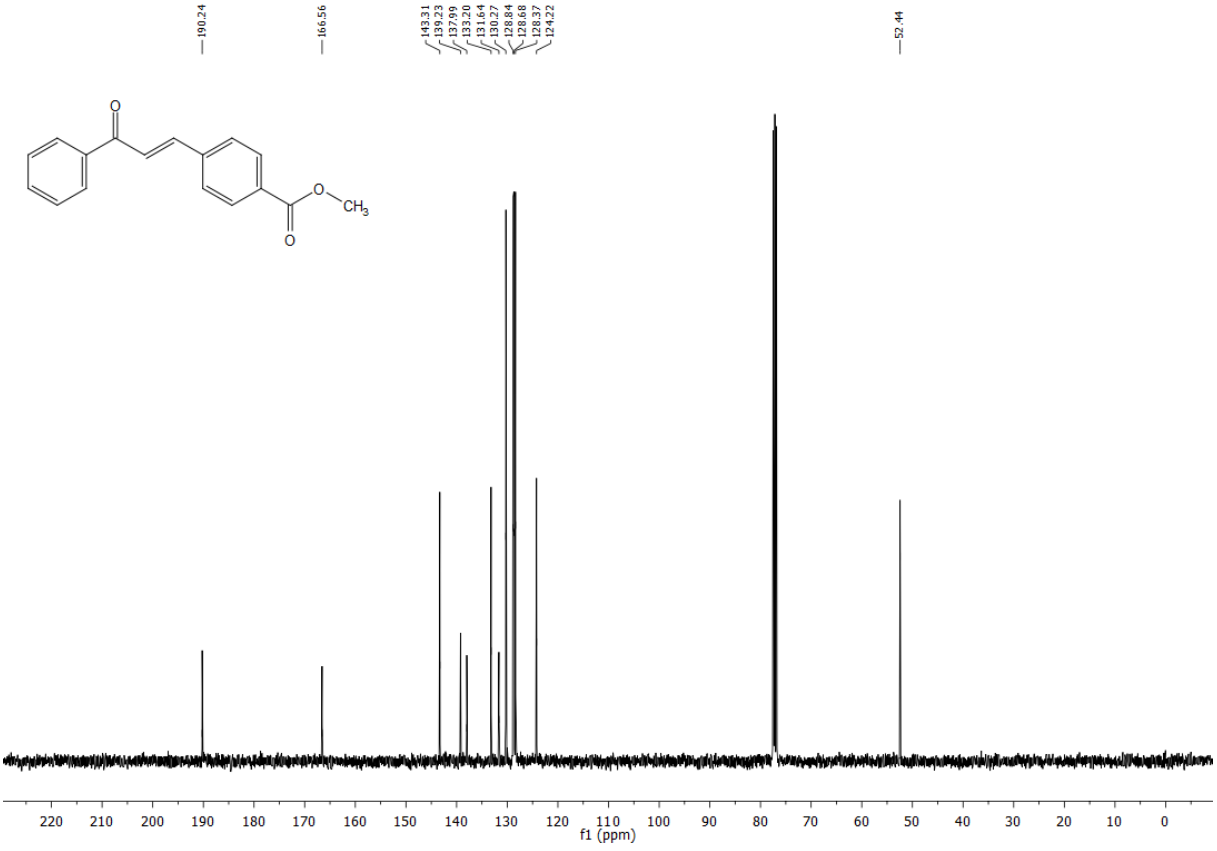

Figure S31: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7l**.

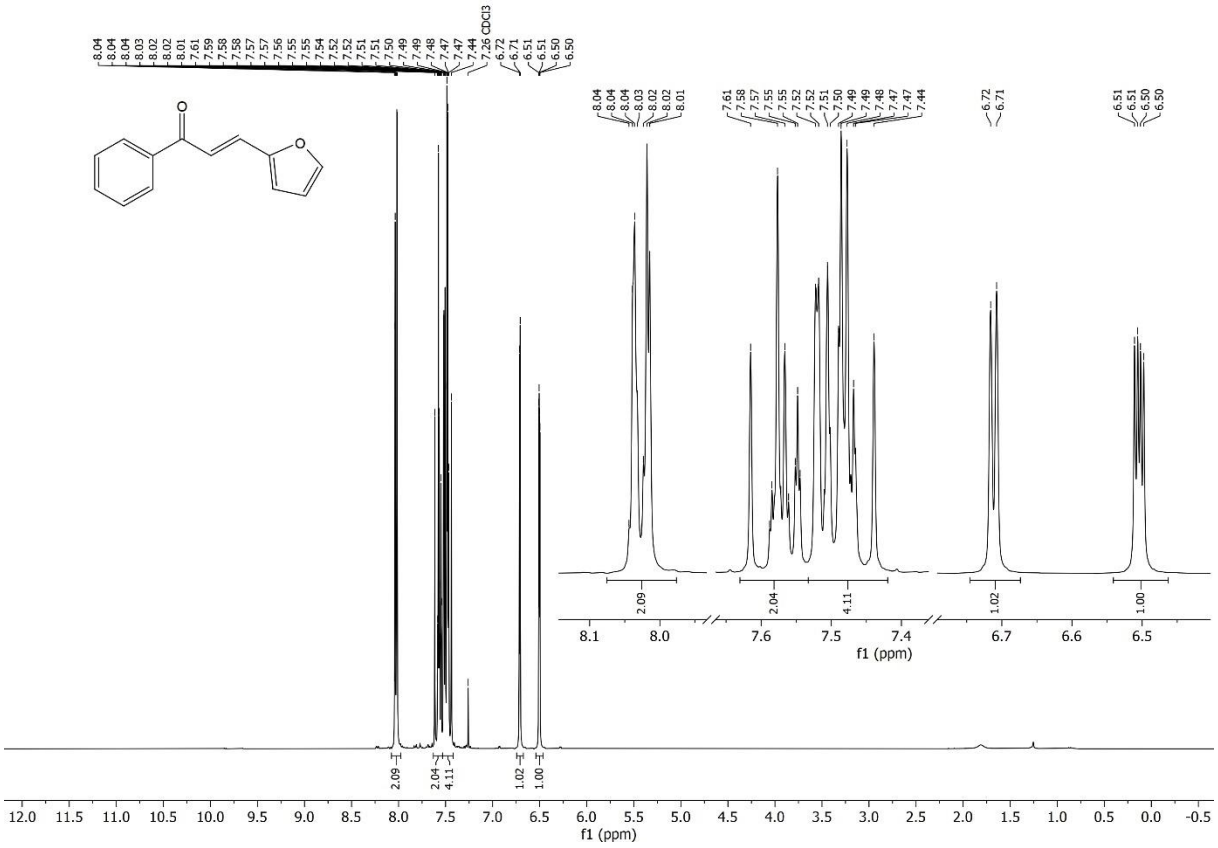

Figure S32: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7m**.

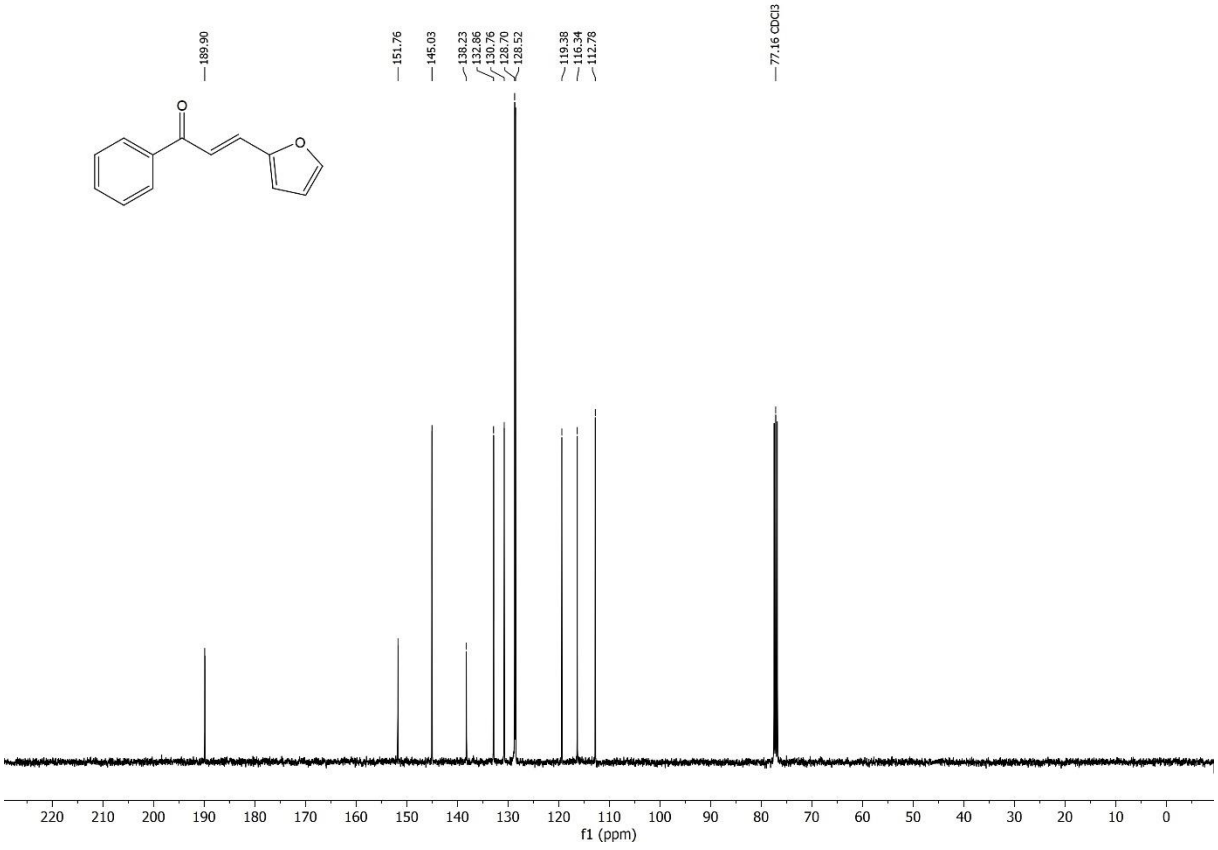

Figure S33: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7m**.

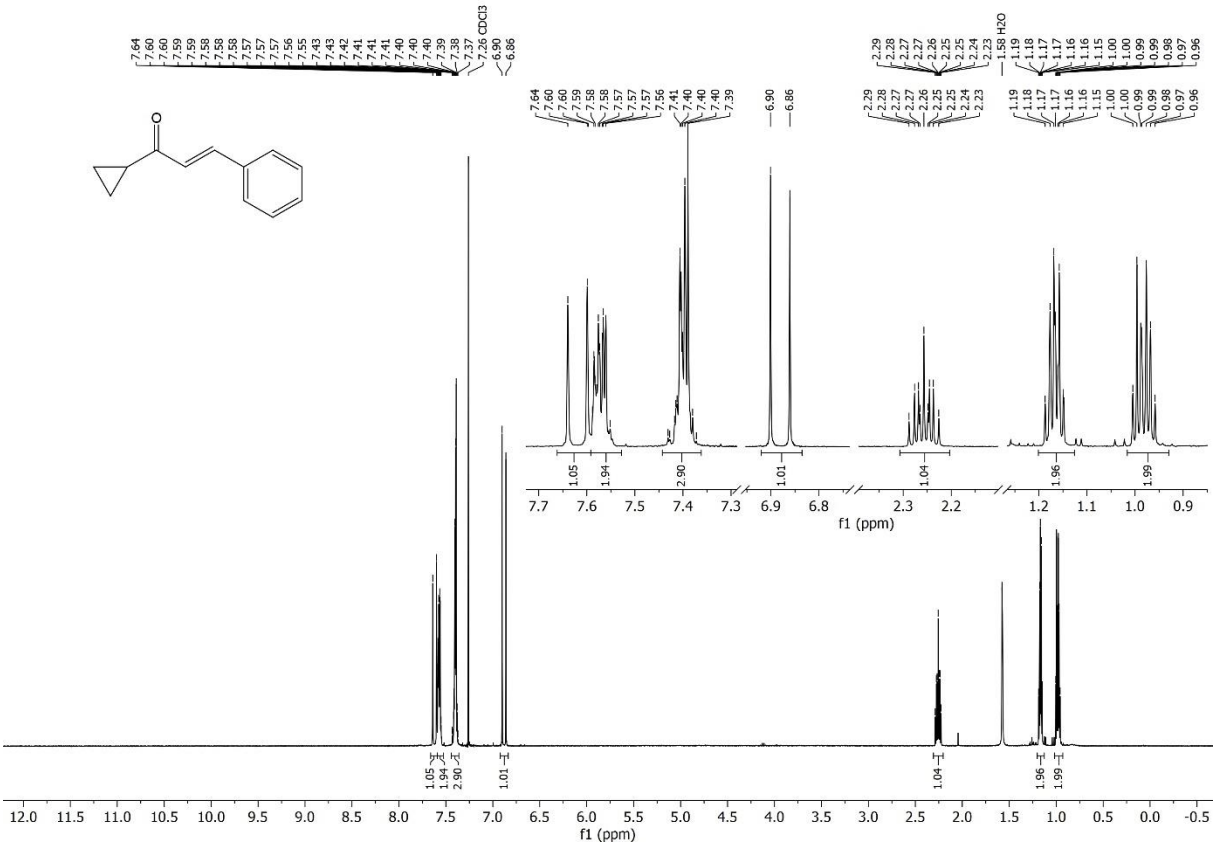

Figure S34: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7n**.

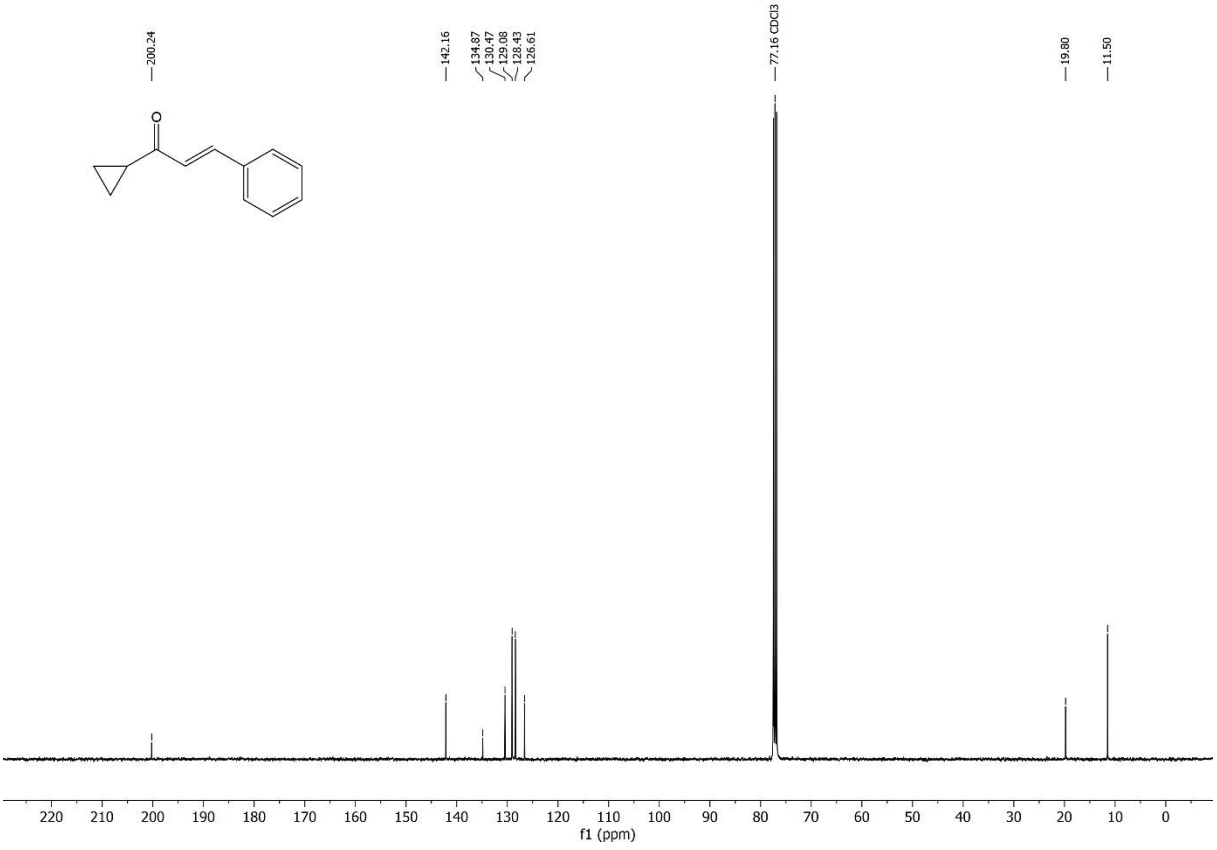

Figure S35: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7n**.

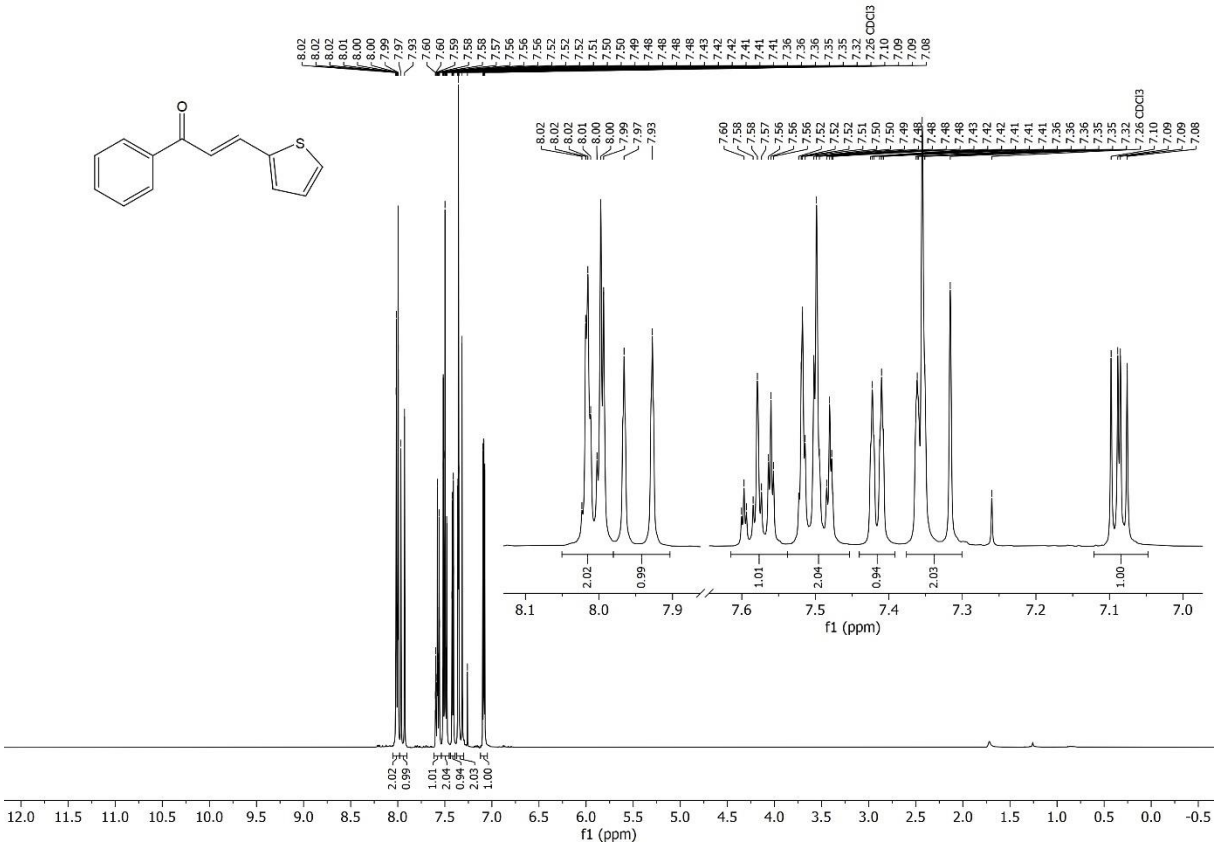

Figure S36: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7o**.

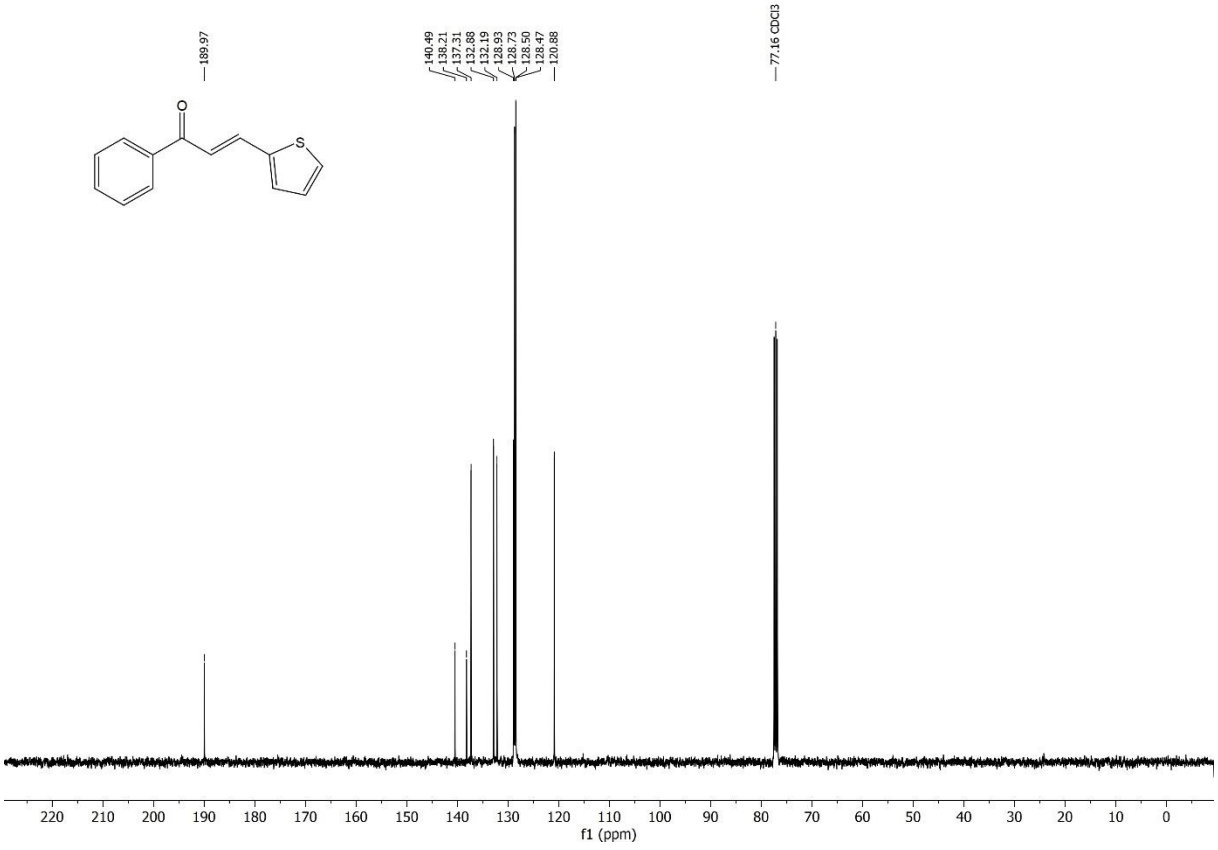

Figure S37: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7o**.

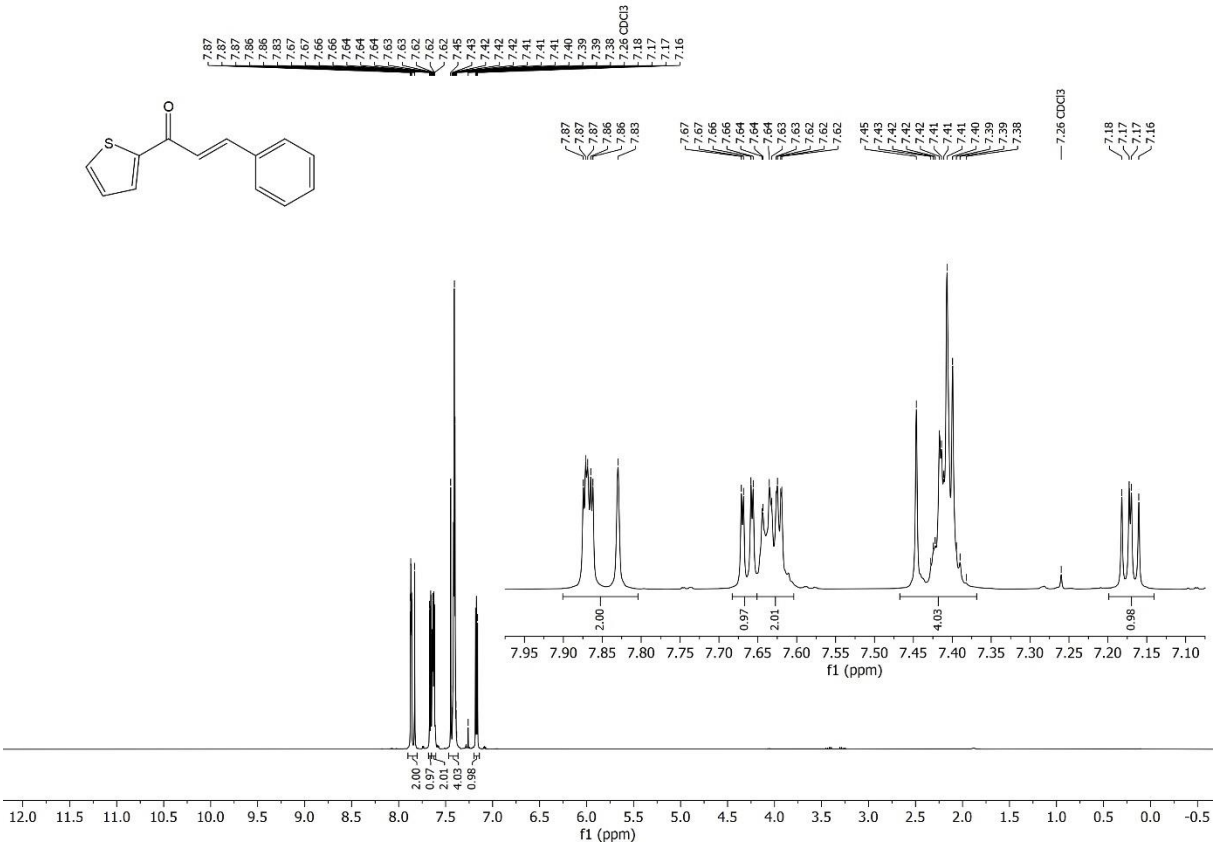

Figure S38: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7p**.

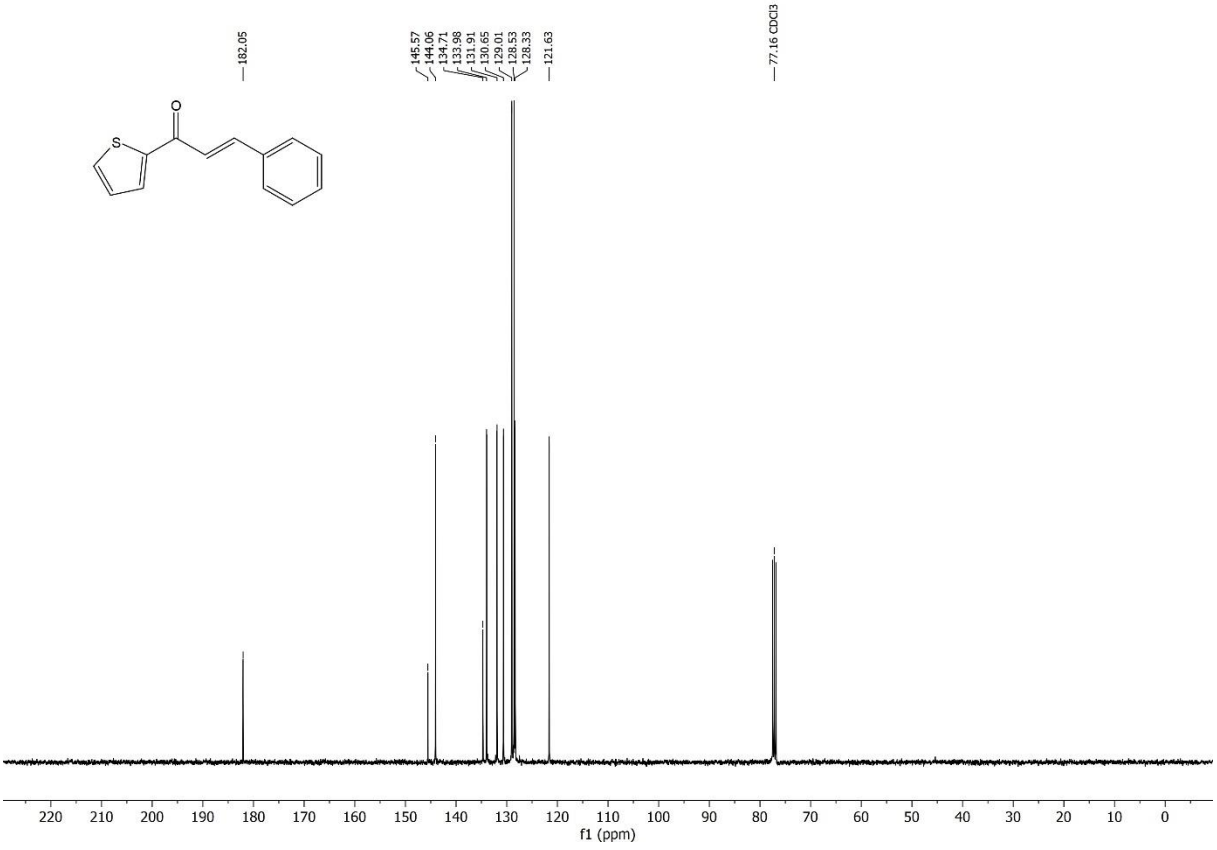

Figure S39: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7p**.

11.2. NMR Spectra of Pyrazolines

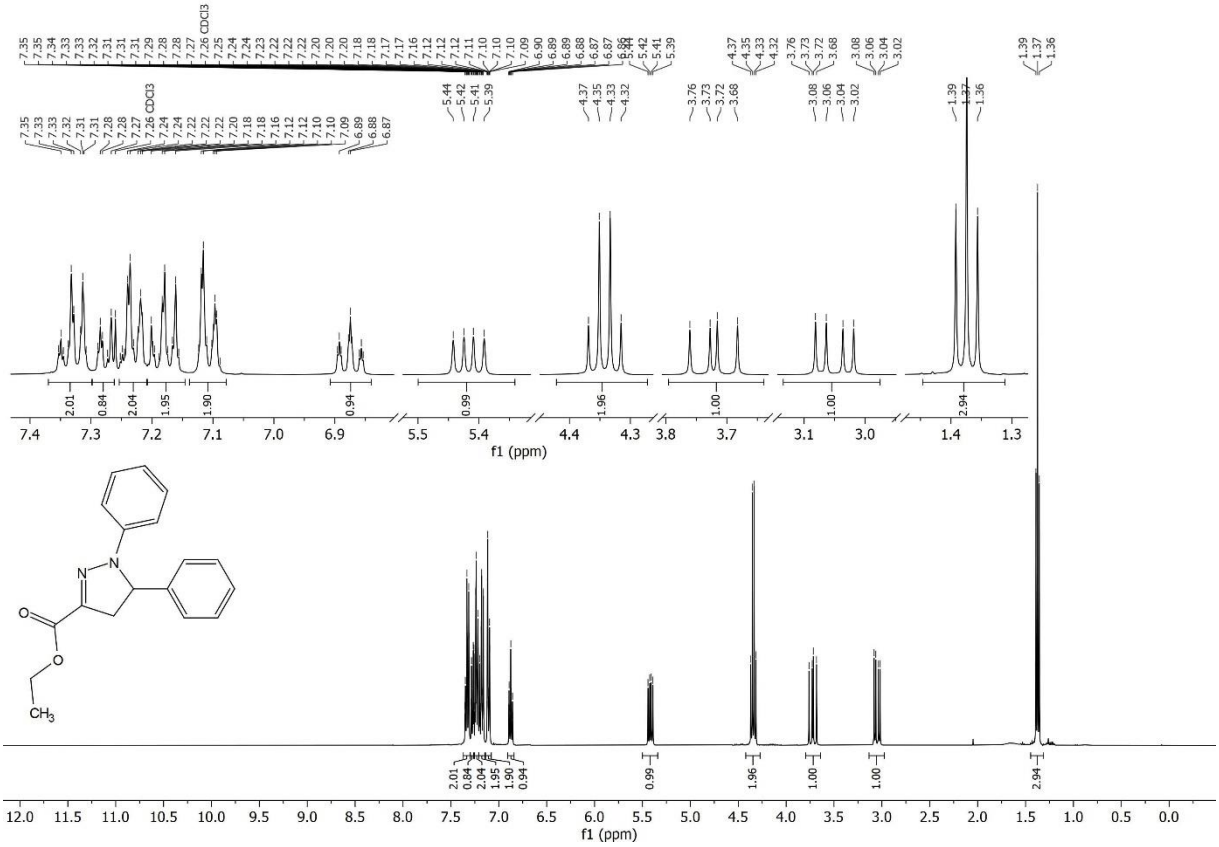

Figure S40: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**.

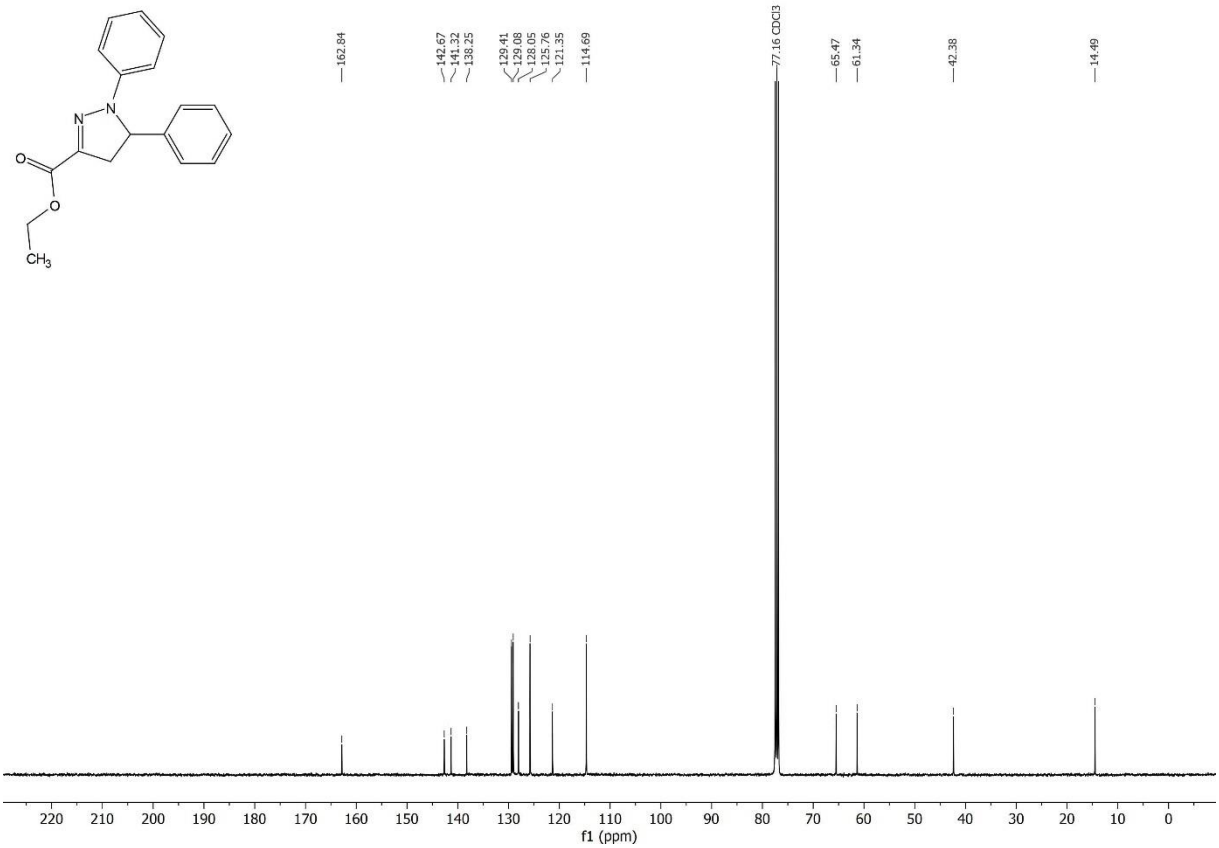

Figure S41: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4a**.

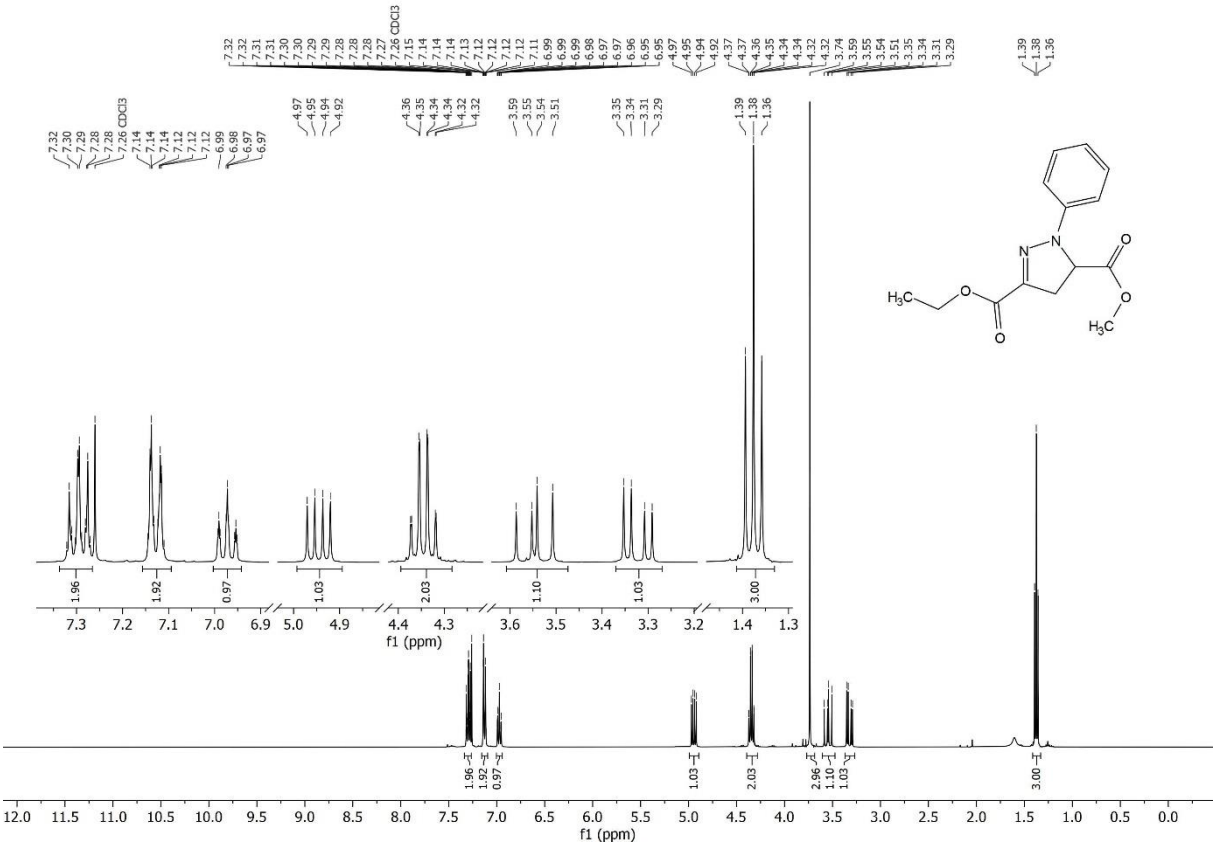

Figure S42: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**.

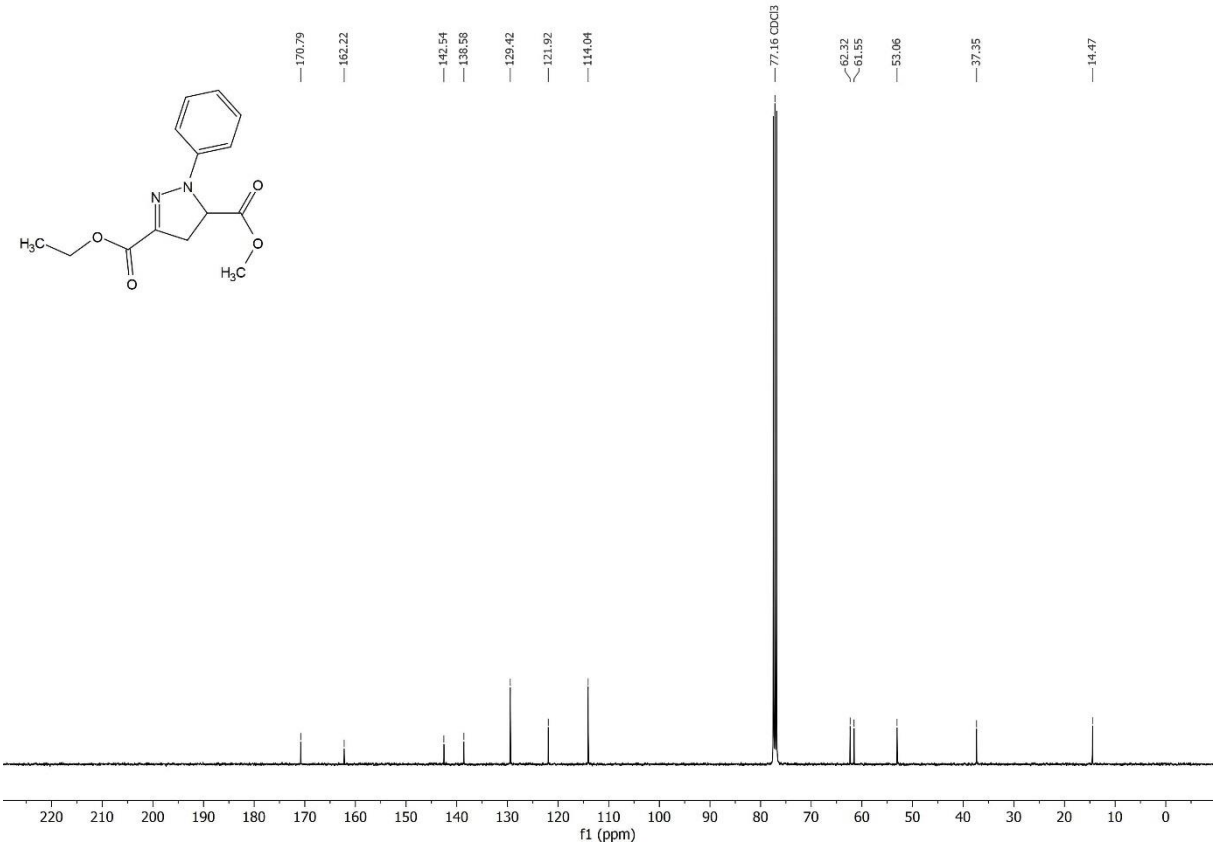

Figure S43: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4b**.

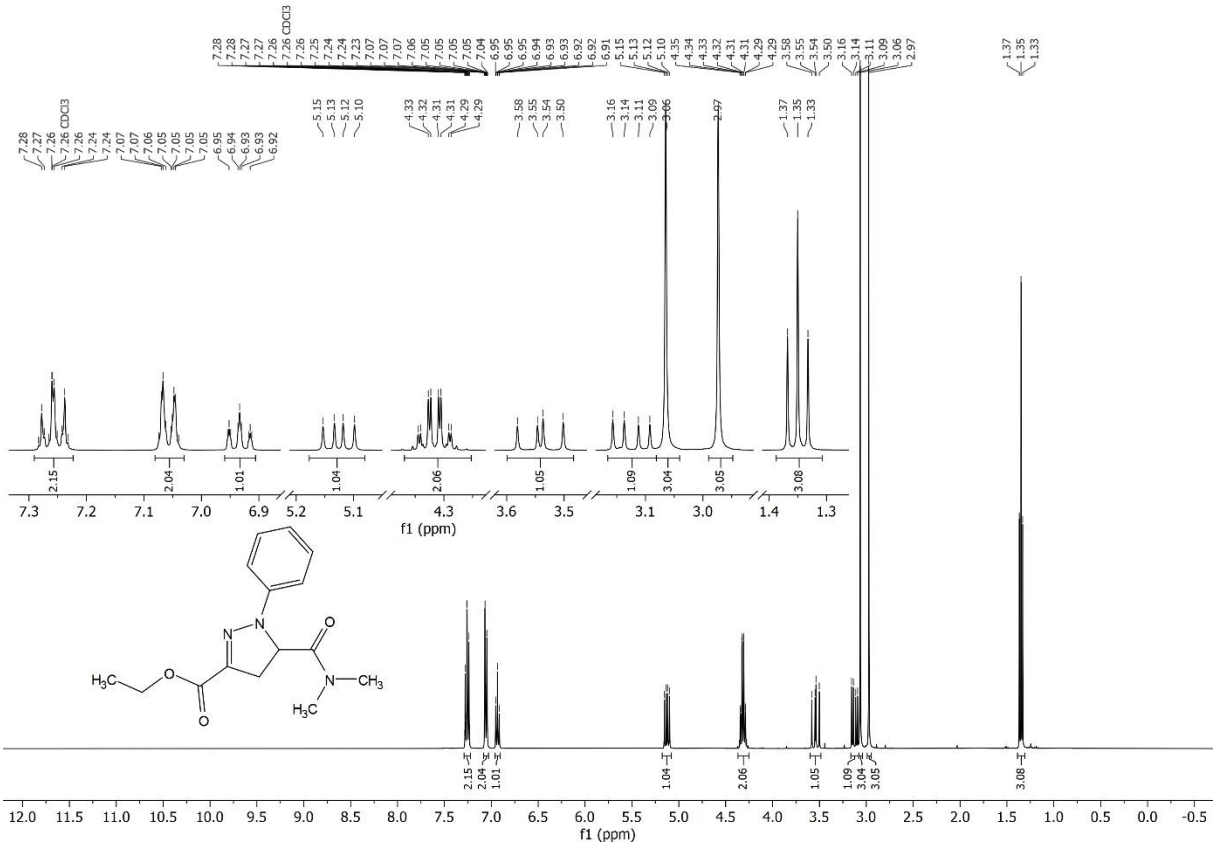

Figure S44: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4c**.

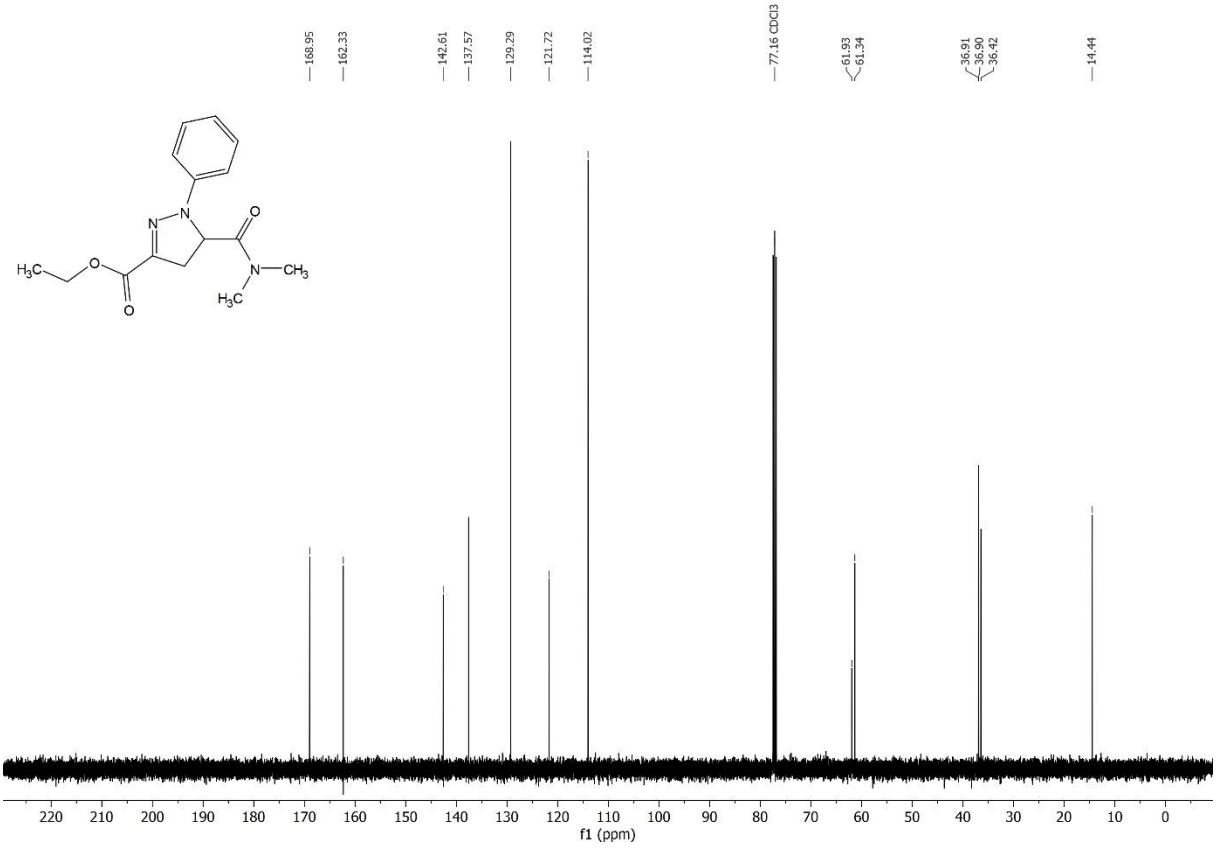

Figure S45: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4c**.

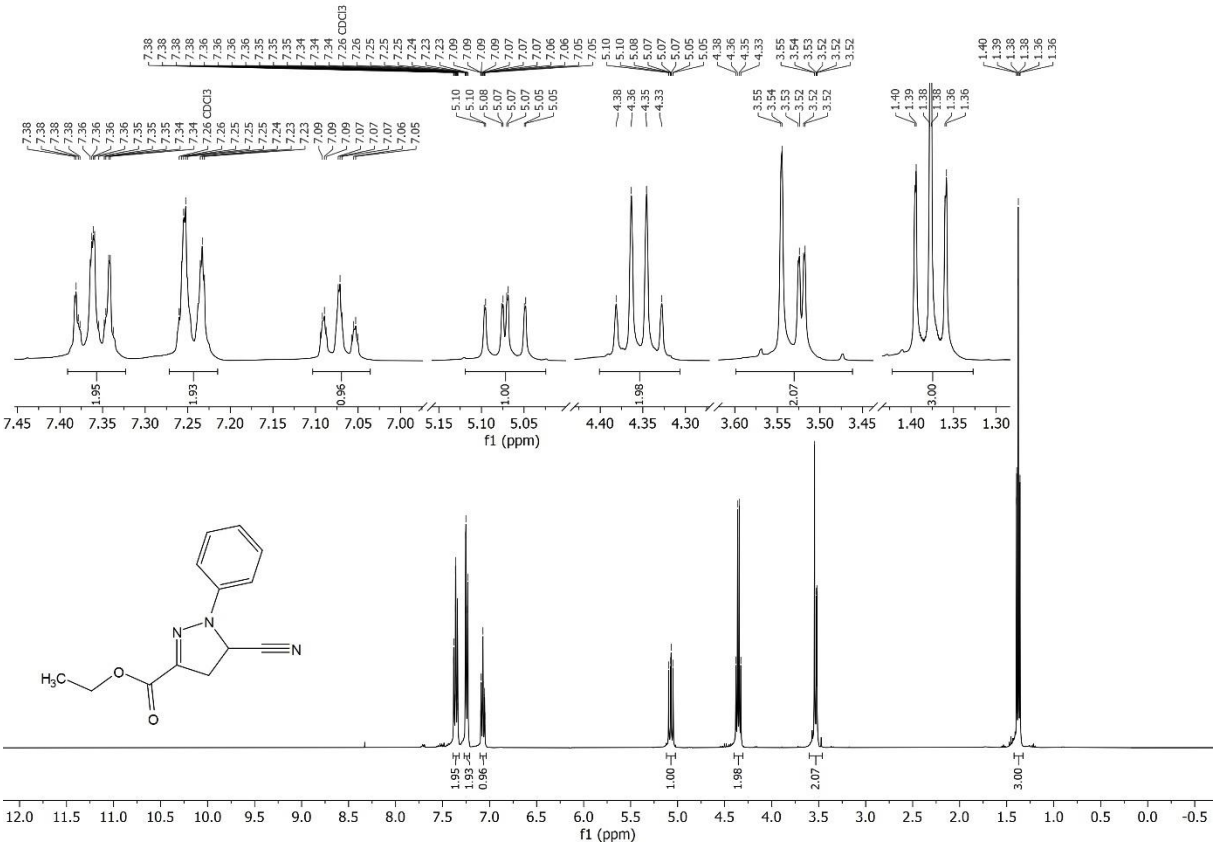

Figure S46: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4d**.

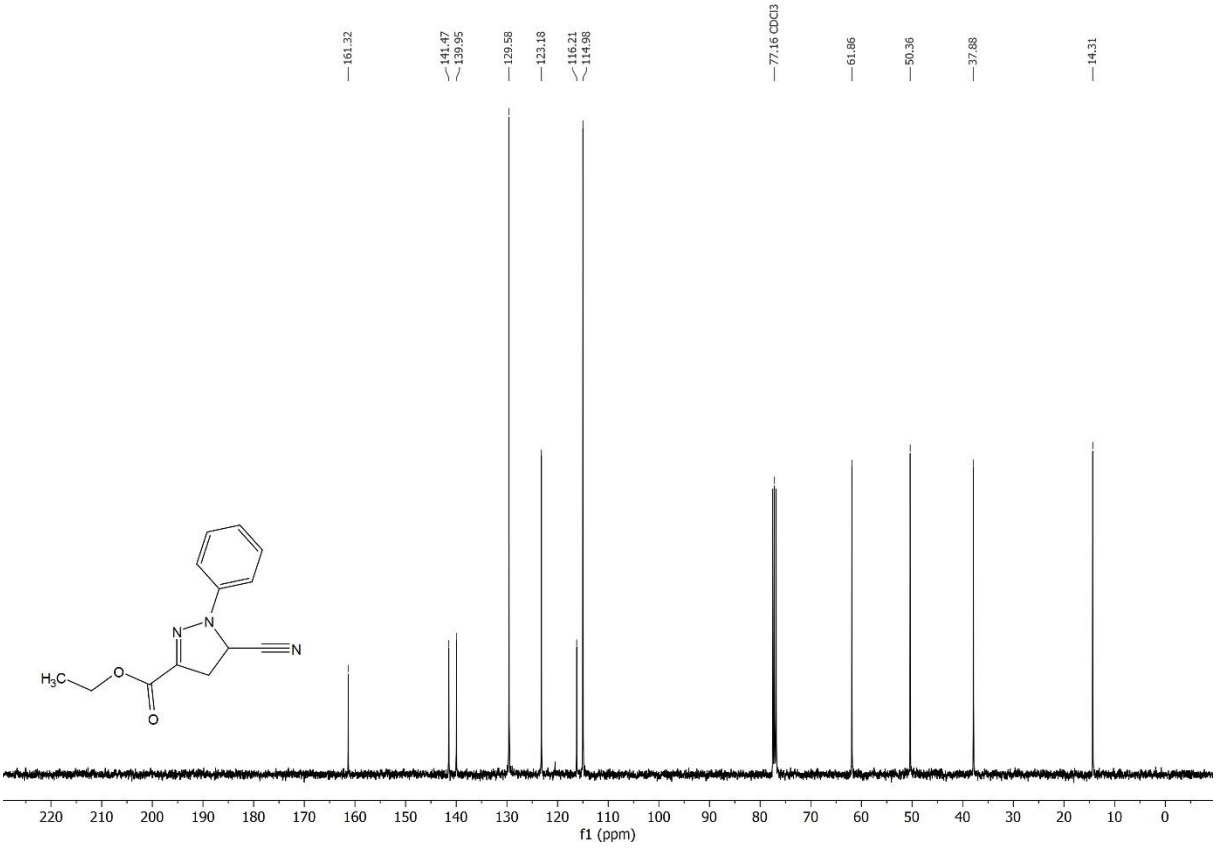

Figure S47: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4d**.

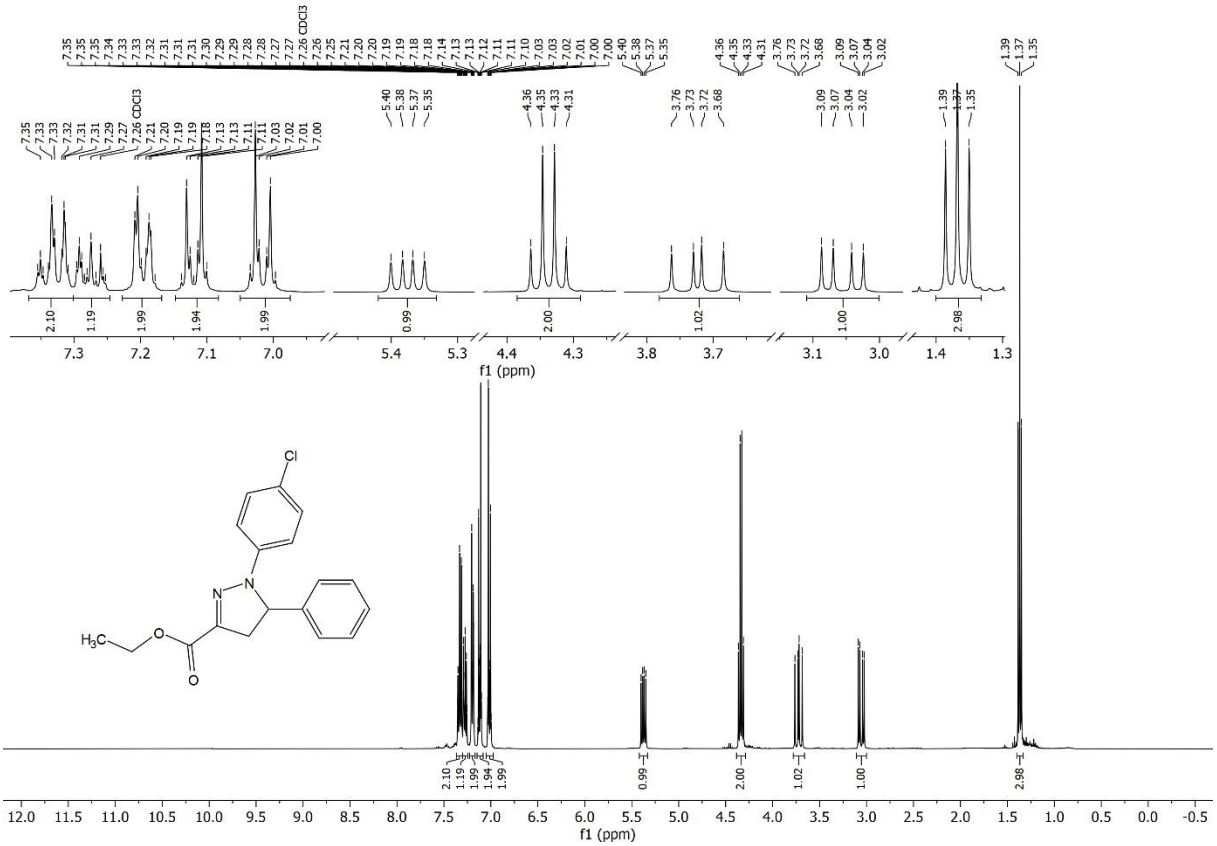

Figure S48: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4e**.

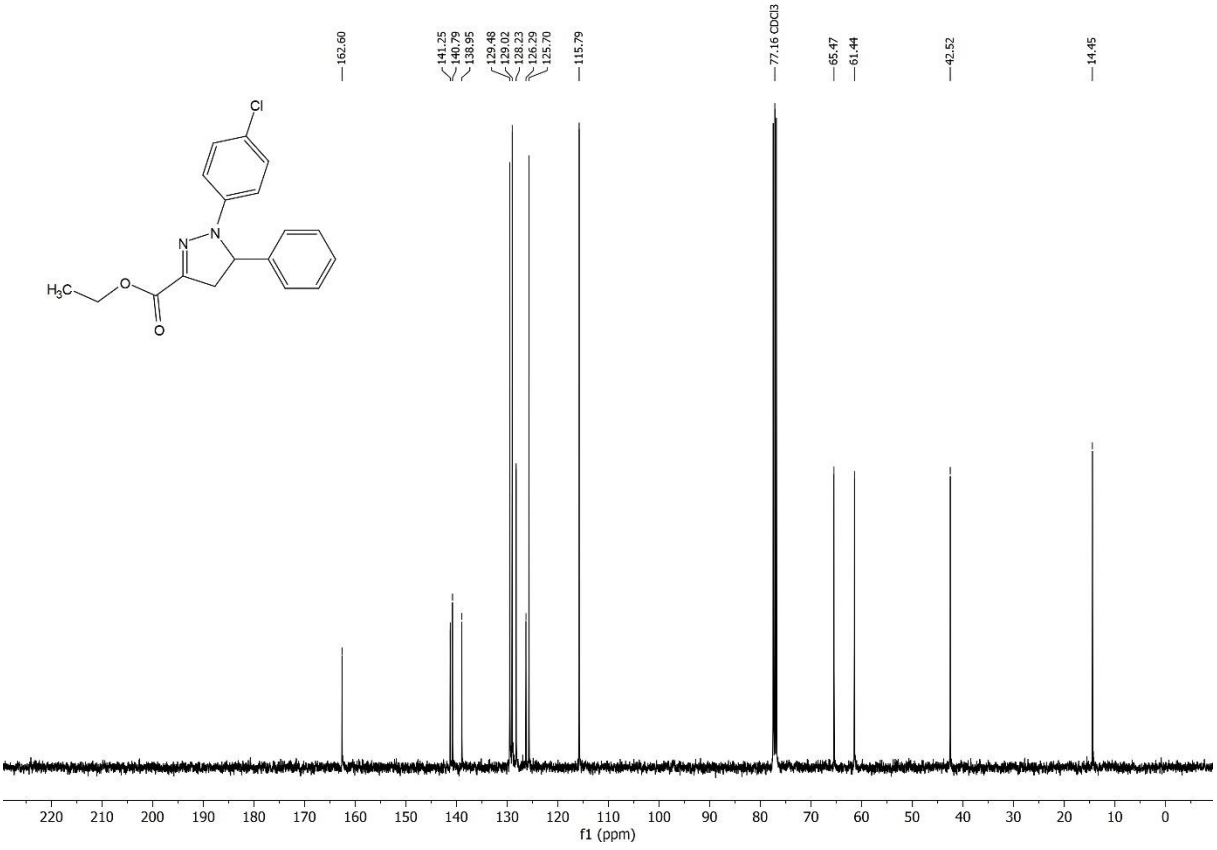

Figure S49: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4e**.

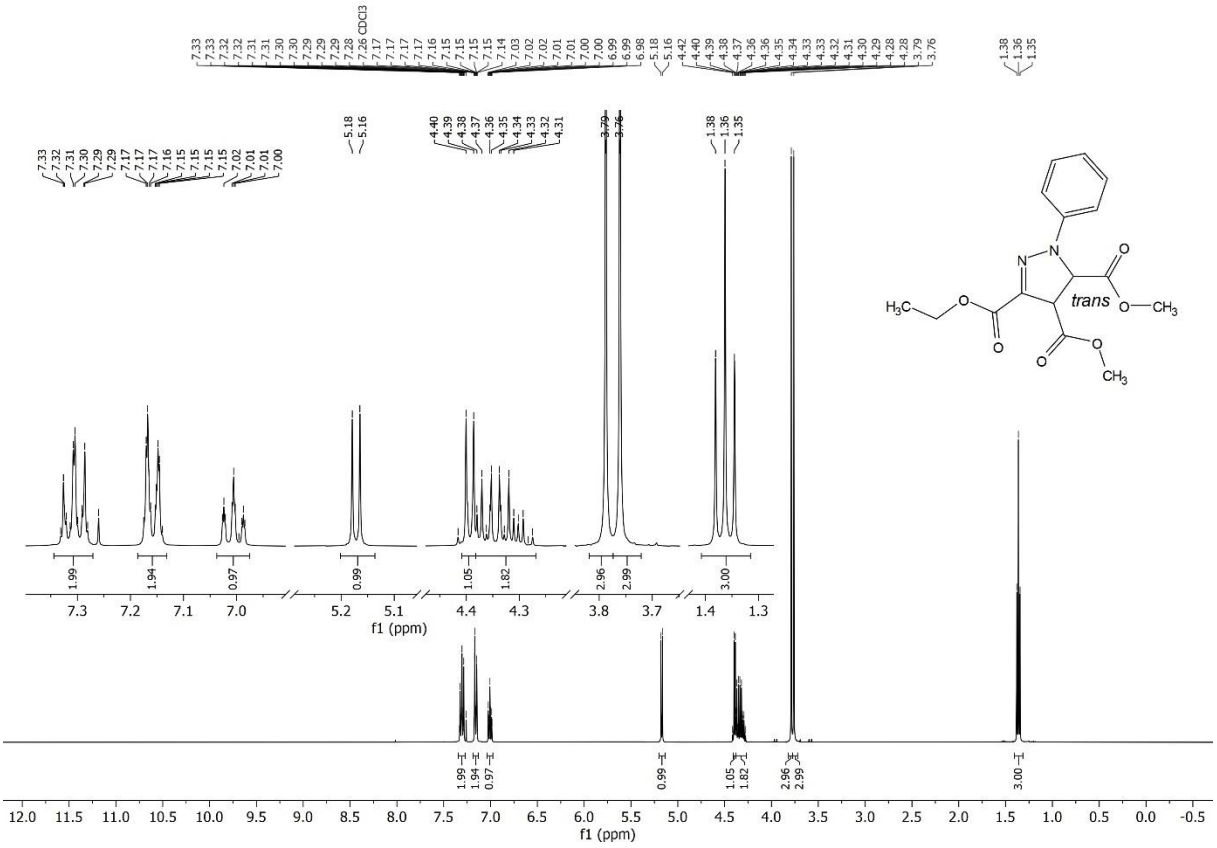

Figure S50: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4f**.

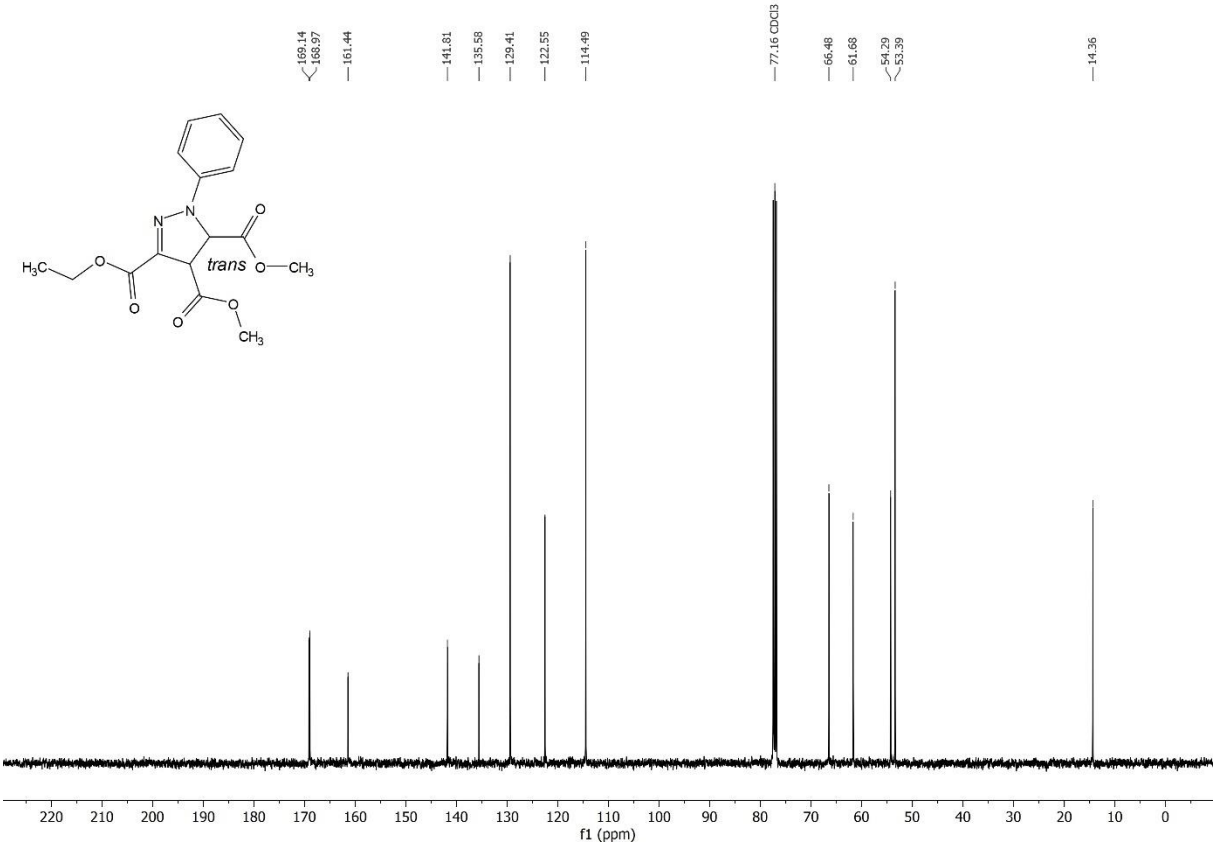

Figure S51: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4f**.

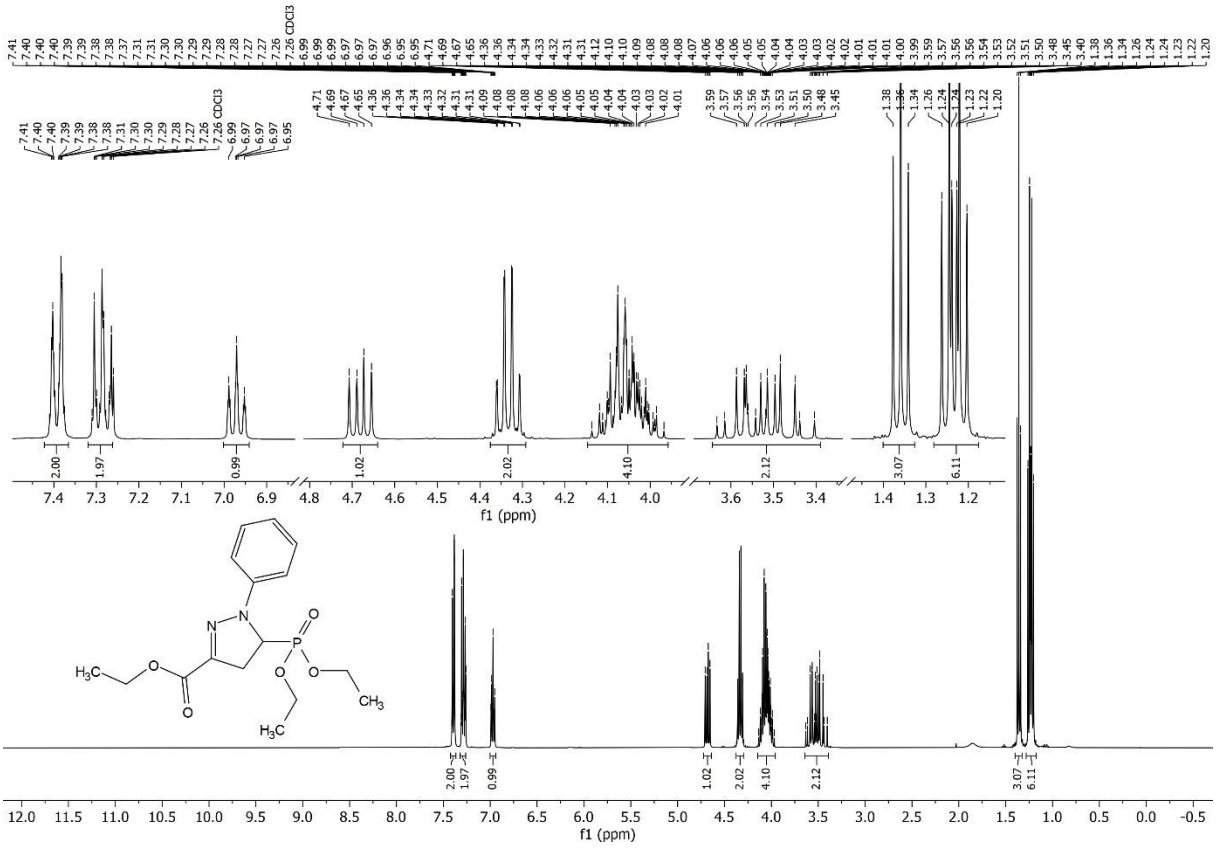

Figure S52: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4g**.

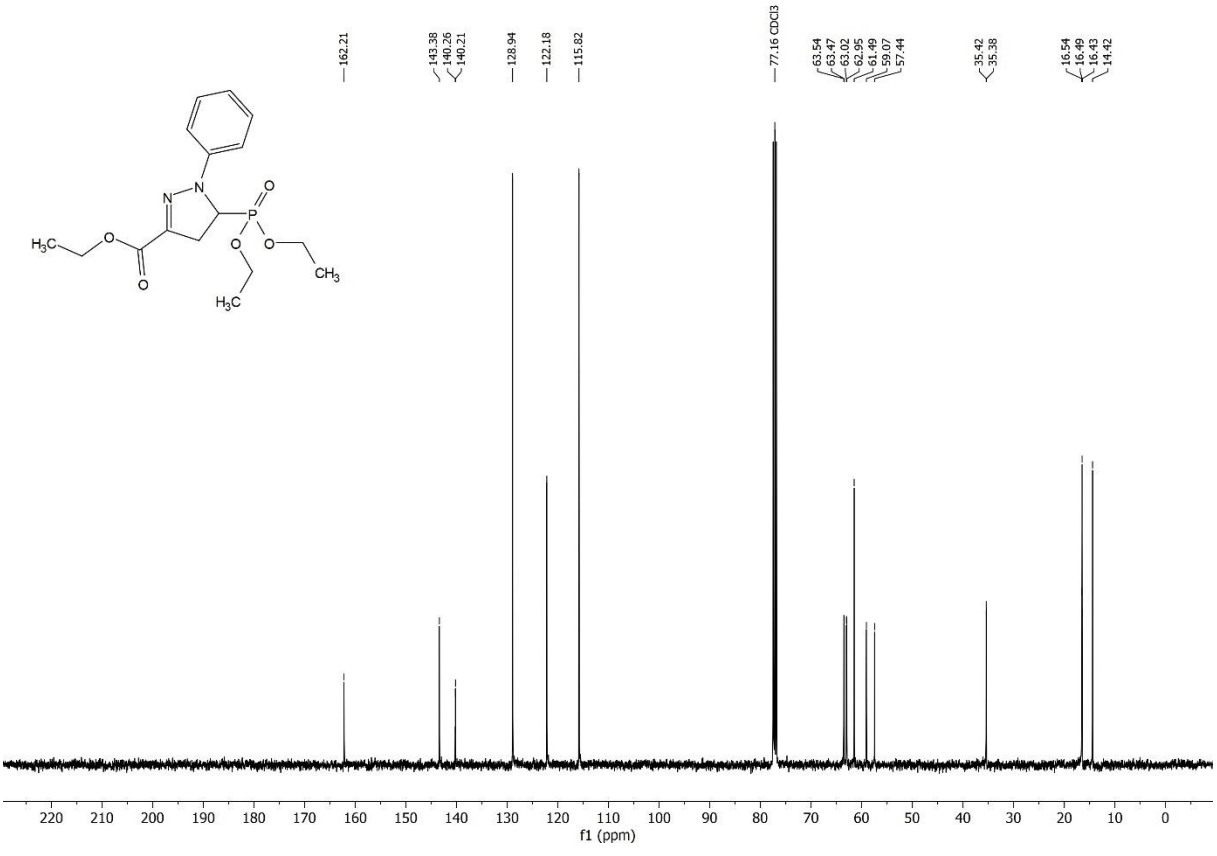

Figure S53: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4g**.

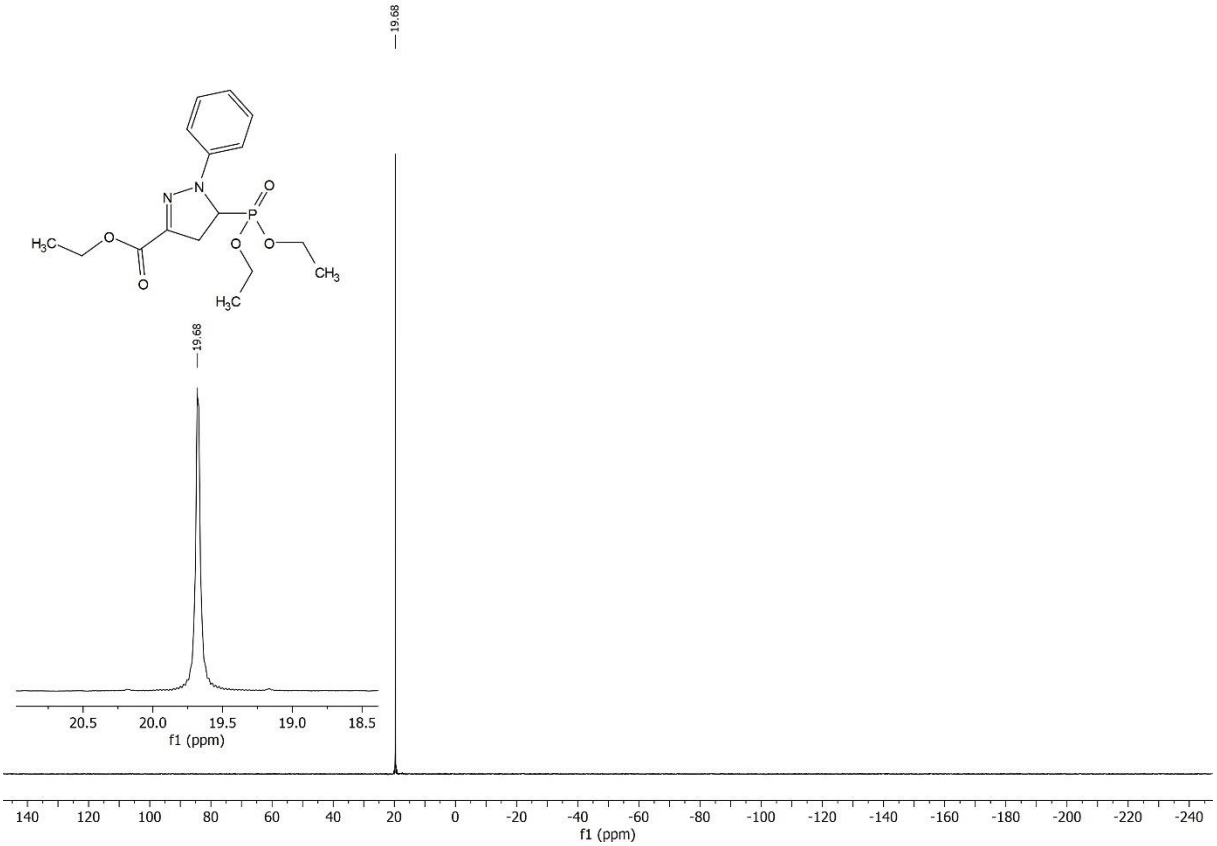

Figure S54: ^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4g**.

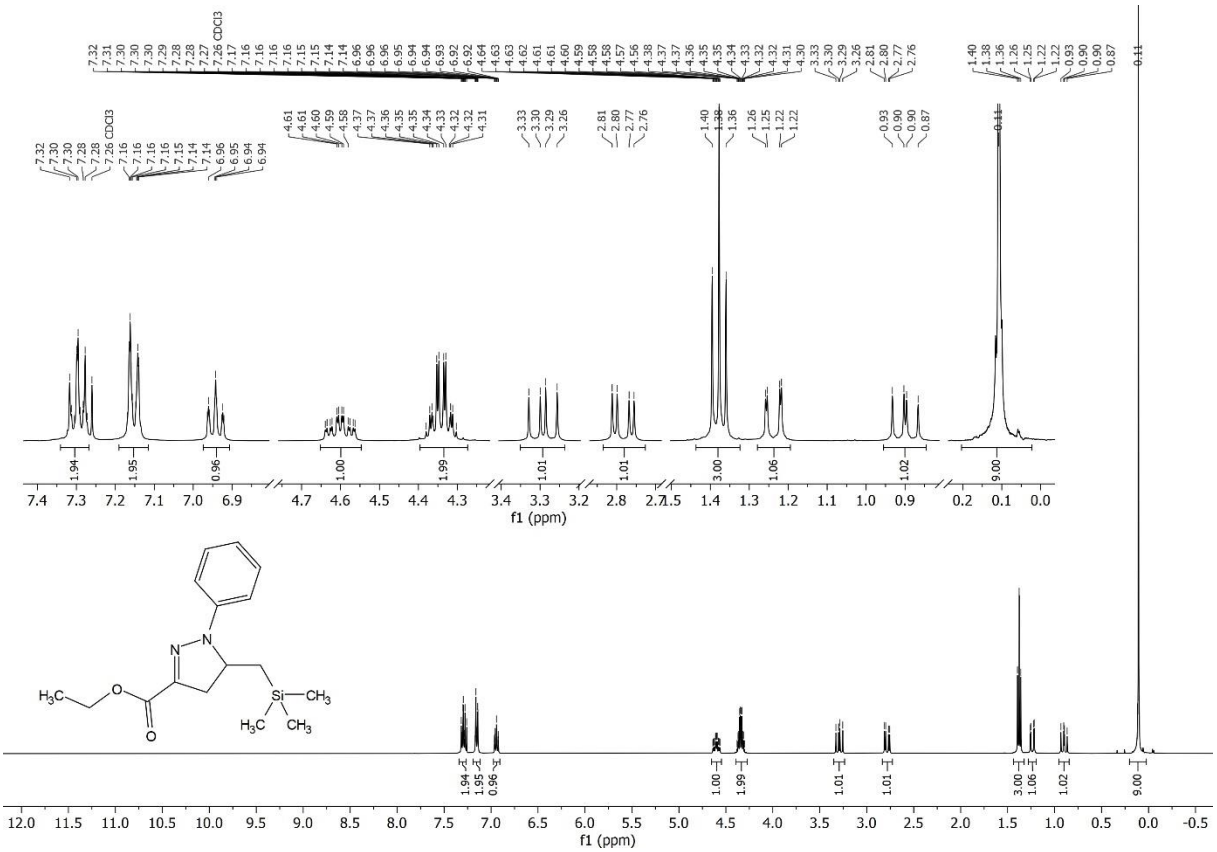

Figure S55: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4h**.

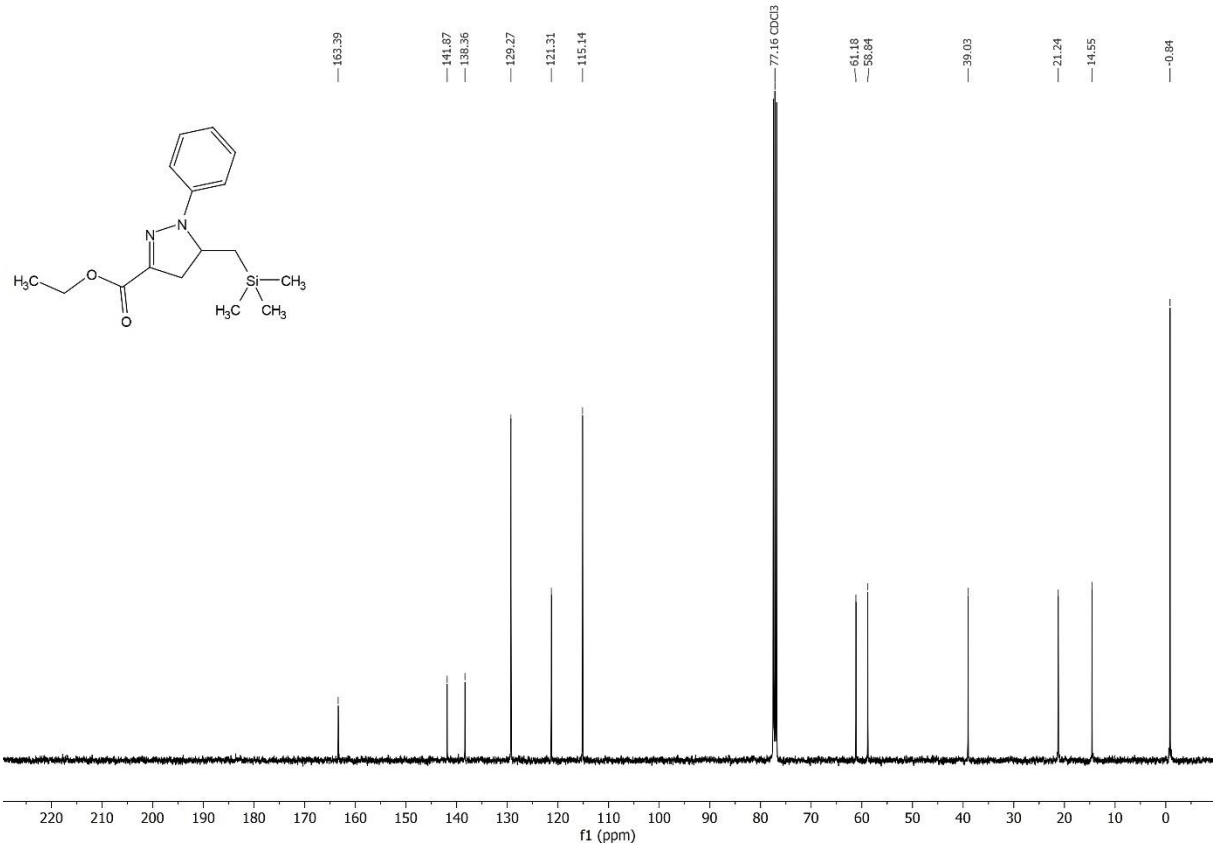

Figure S56: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4h**.

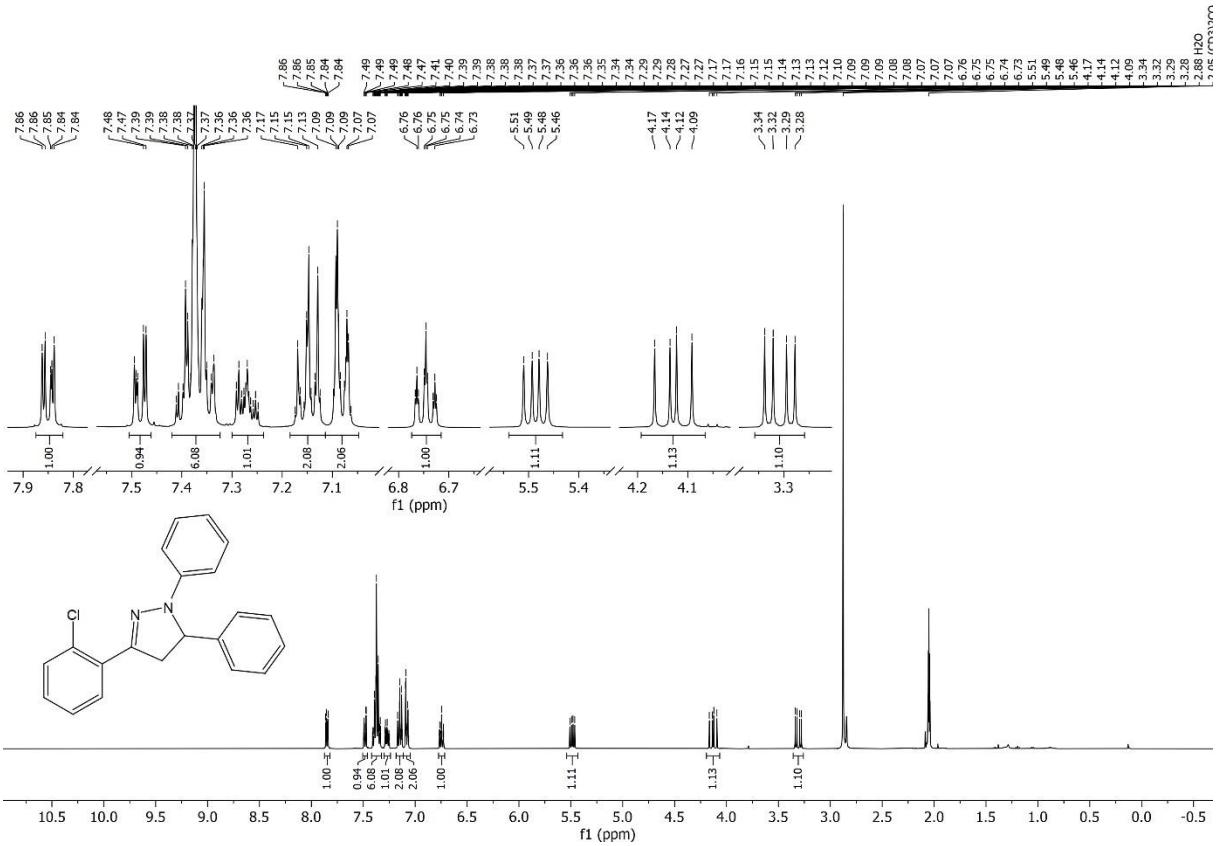

Figure S57: ^{1}H NMR spectrum (400 MHz, acetone-d_6) of **4i**.

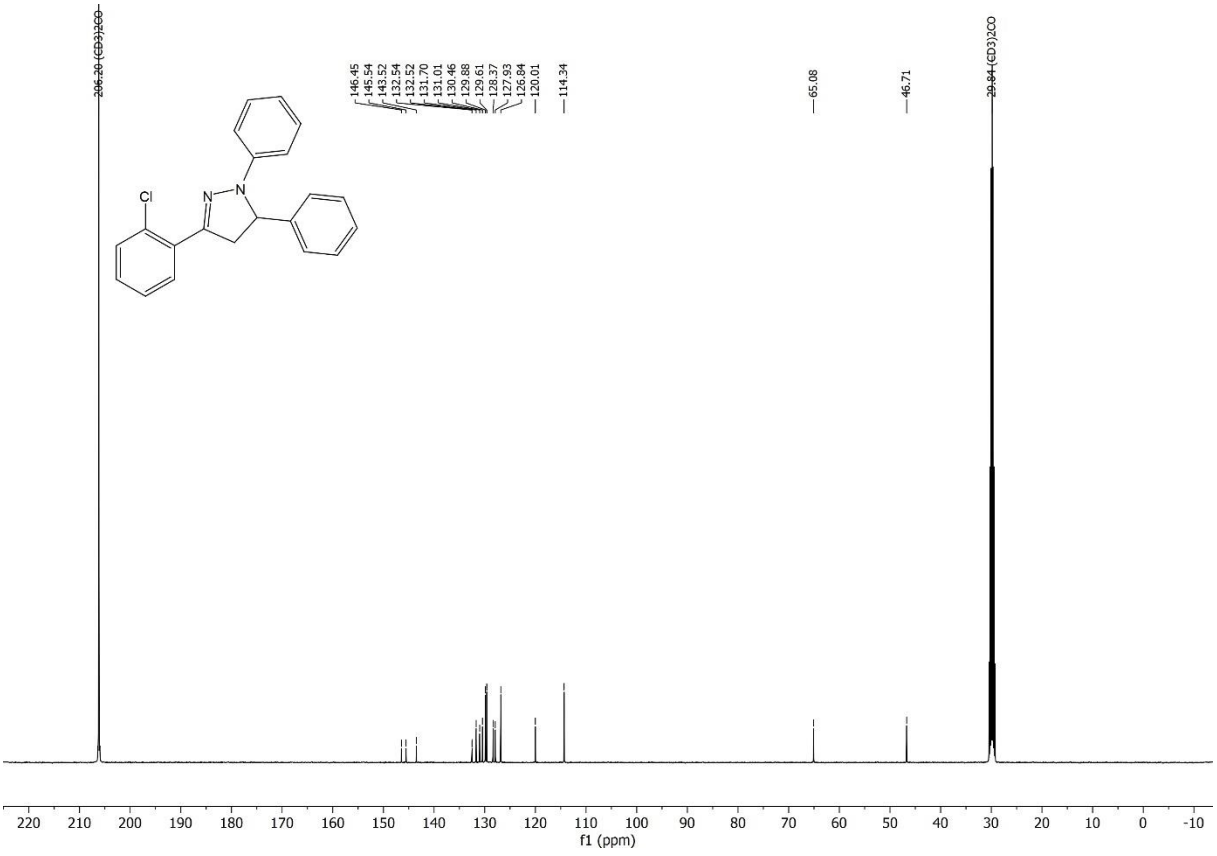

Figure S58: ^{13}C NMR spectrum (101 MHz, acetone-d_6) of **4i**.

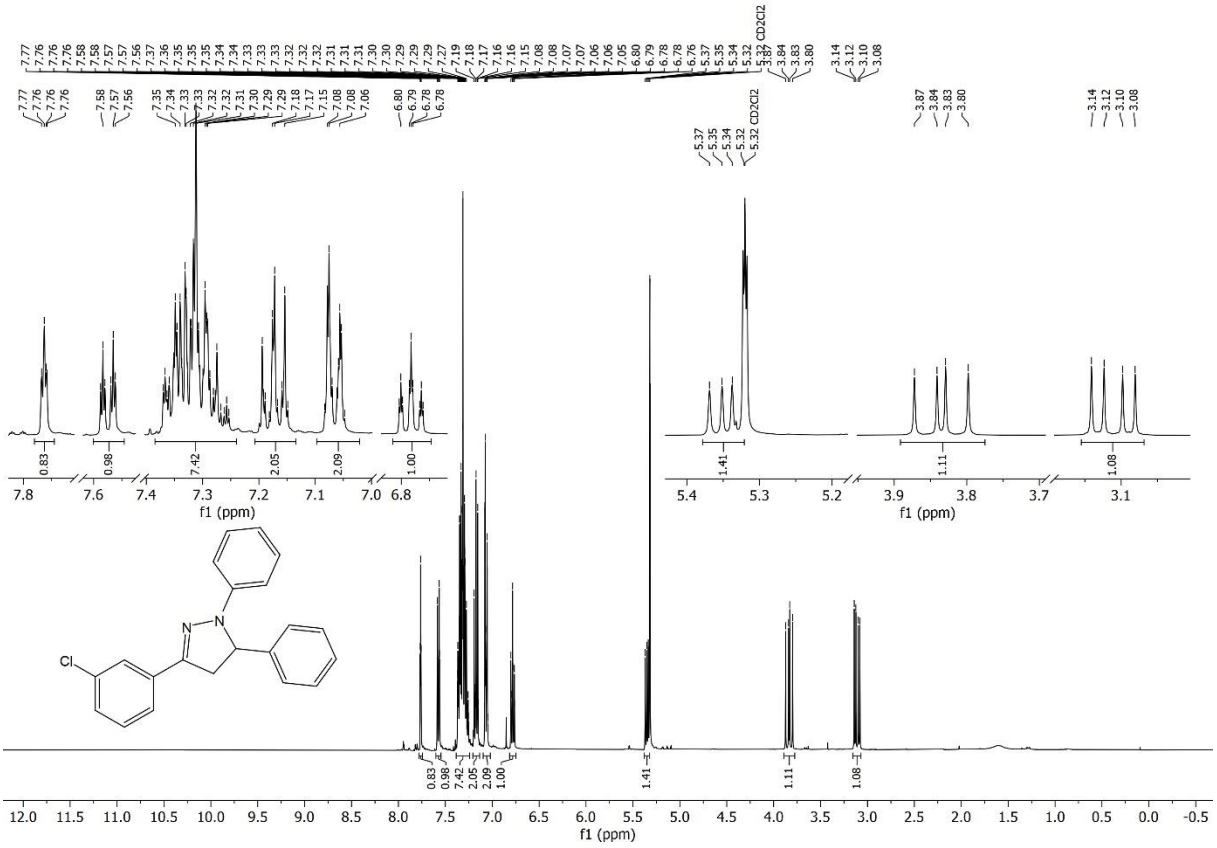

Figure S59: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4j**.

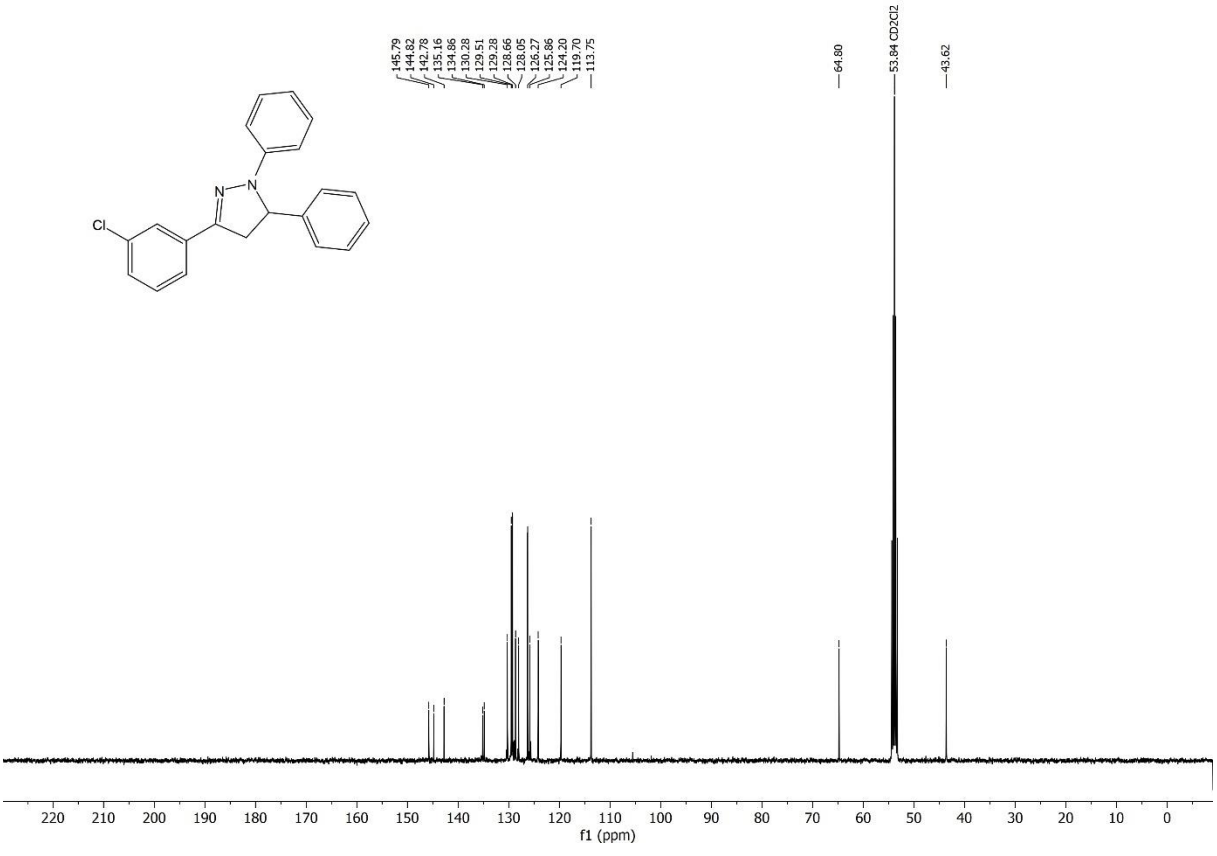

Figure S60: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4j**.

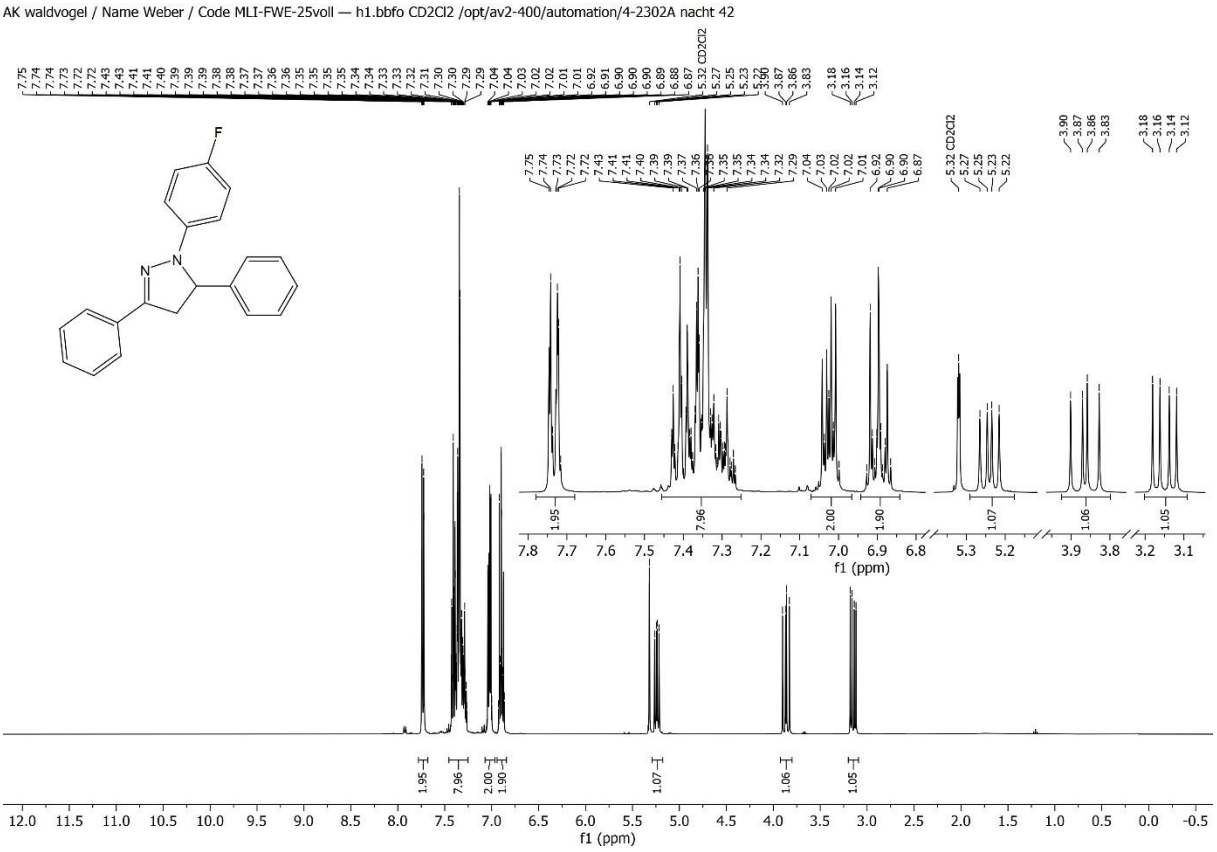

Figure S61: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4k**.

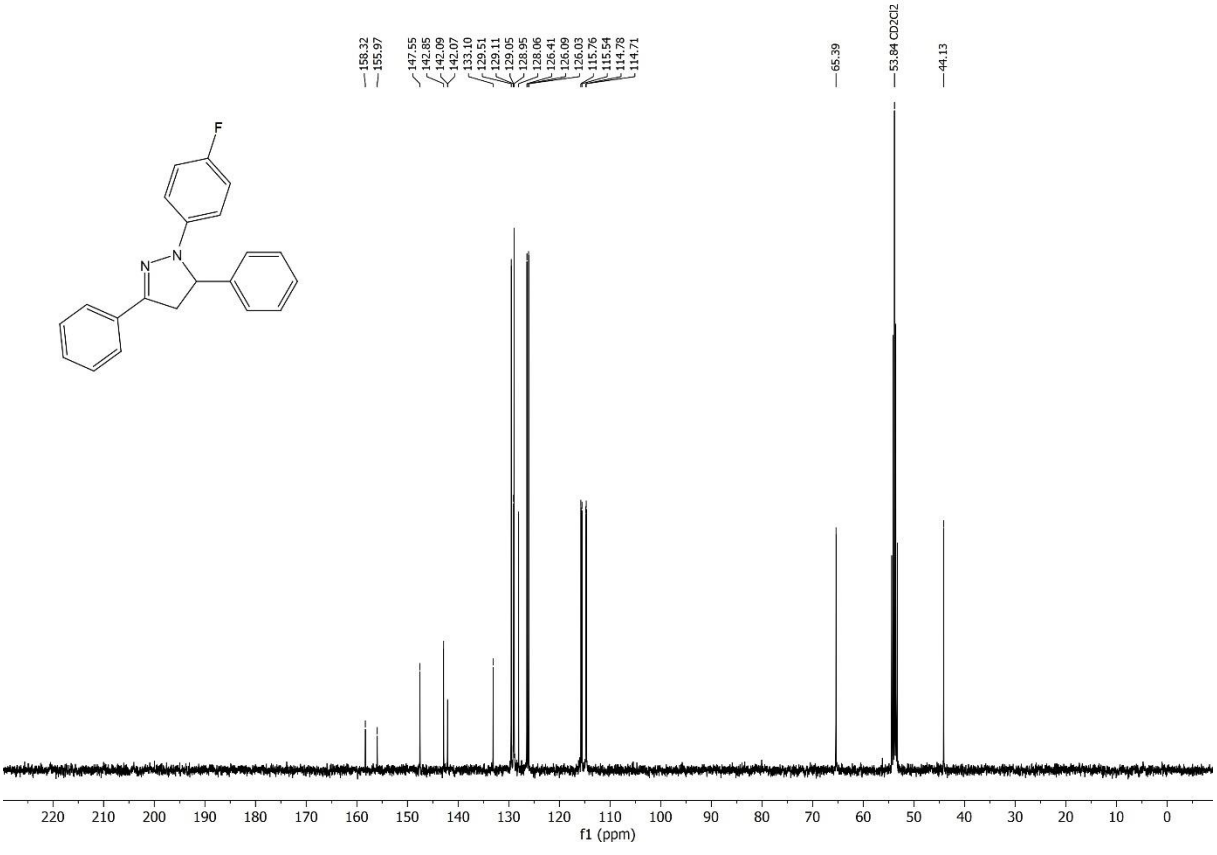

Figure S62: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4k**.

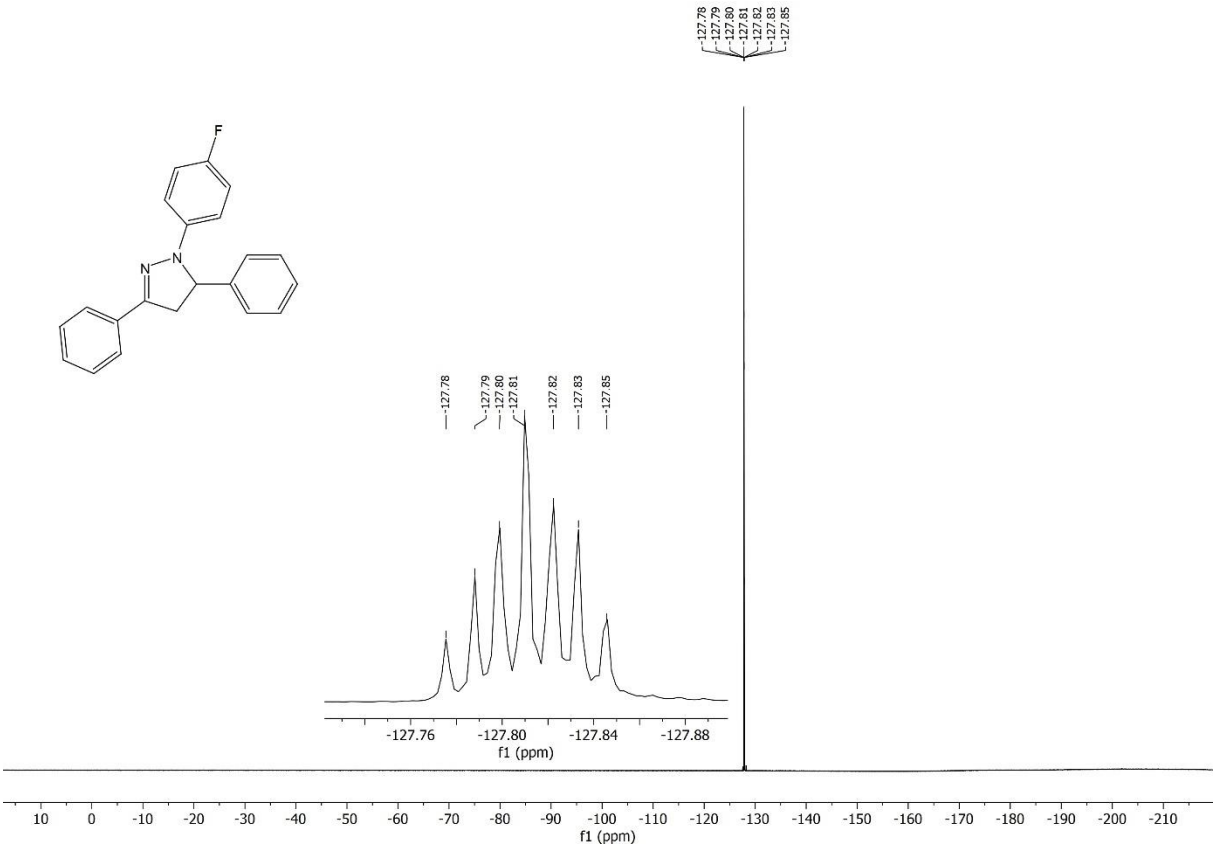

Figure S63: ^{19}F NMR spectrum (282 MHz, CD_2Cl_2) of **4k**.

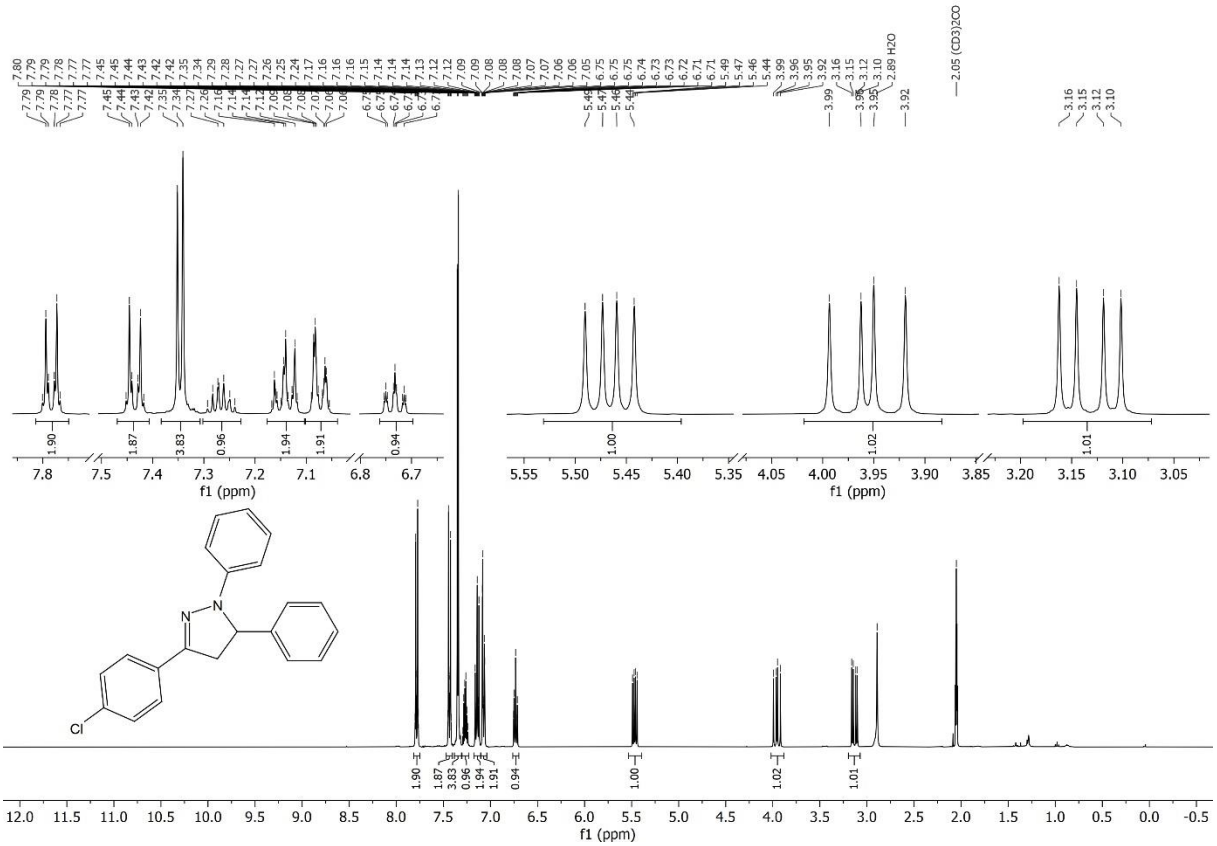

Figure S64: ^{1}H NMR spectrum (400 MHz, acetone-$_{6}$) of **4l**.

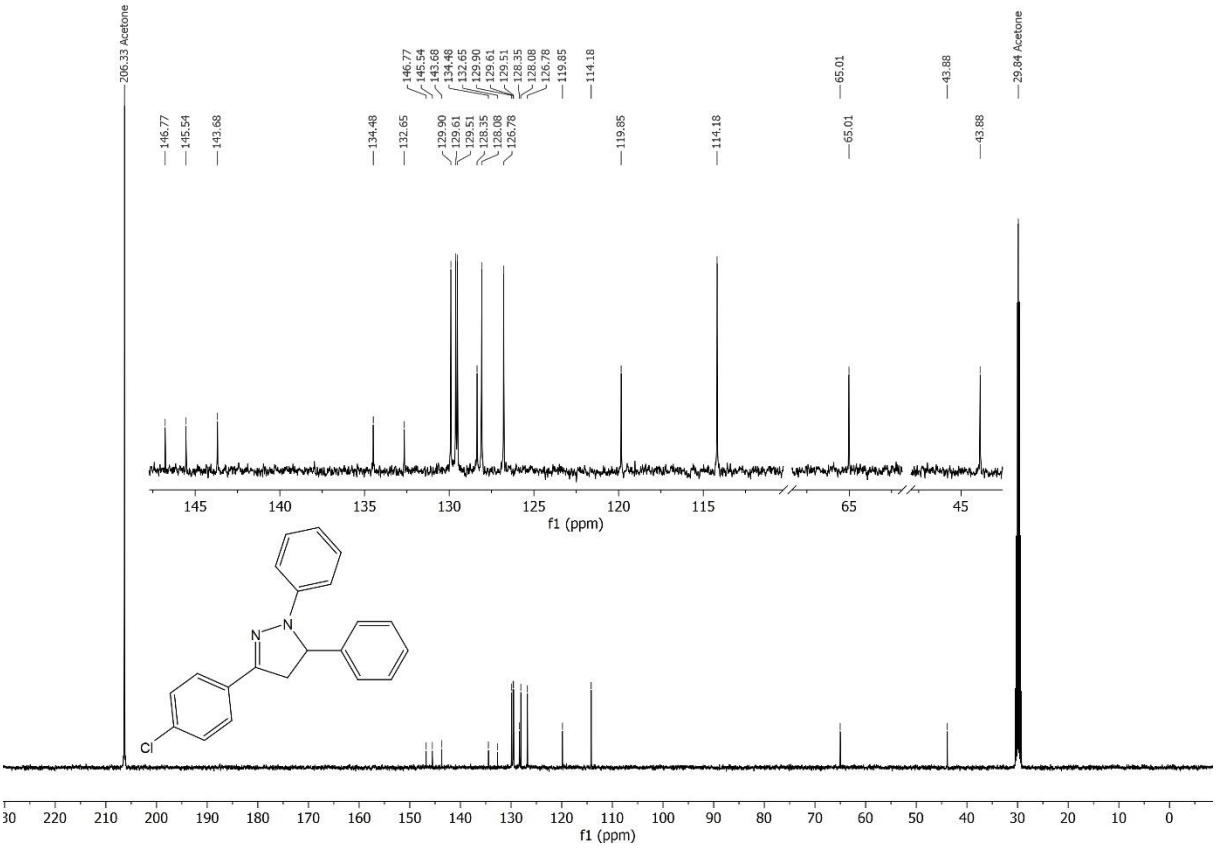

Figure S65: ^{13}C NMR spectrum (101 MHz, acetone-$_{6}$) of **4l**.

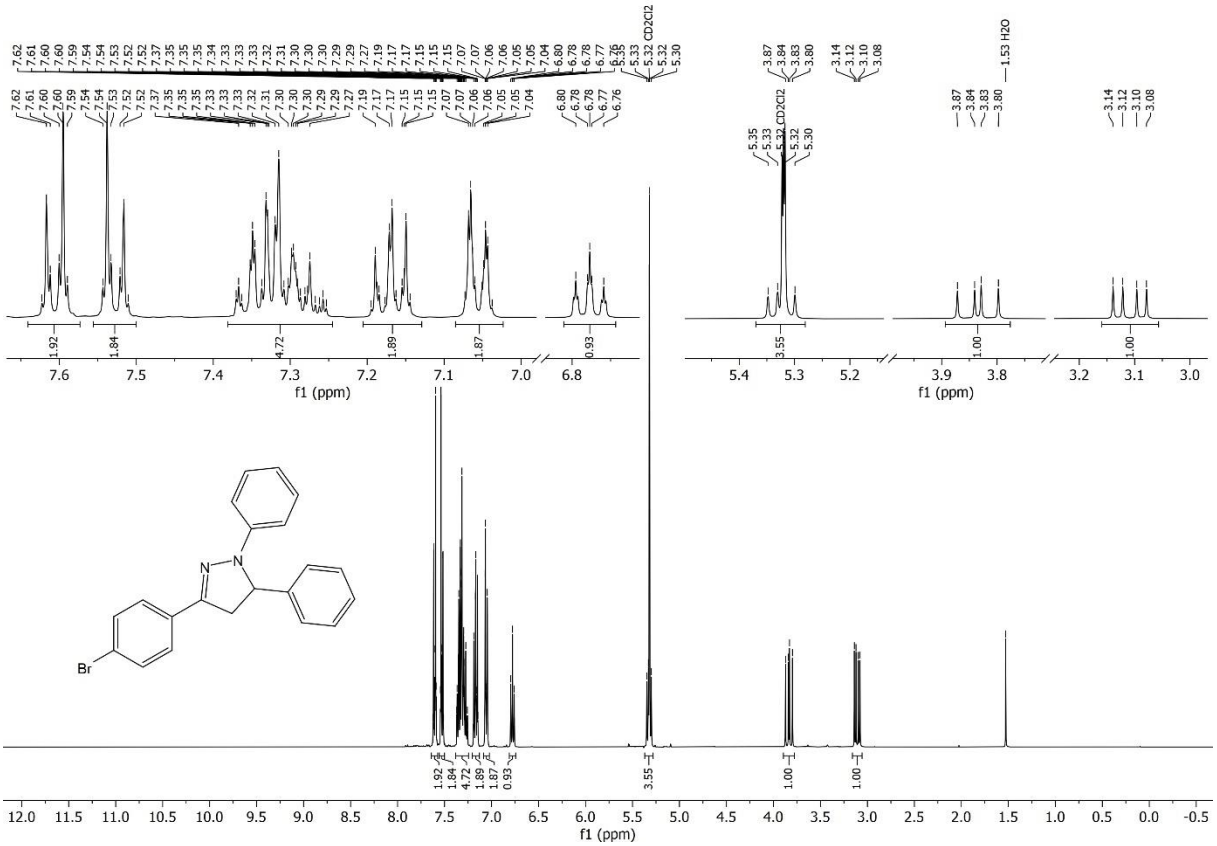

Figure S66: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4m**.

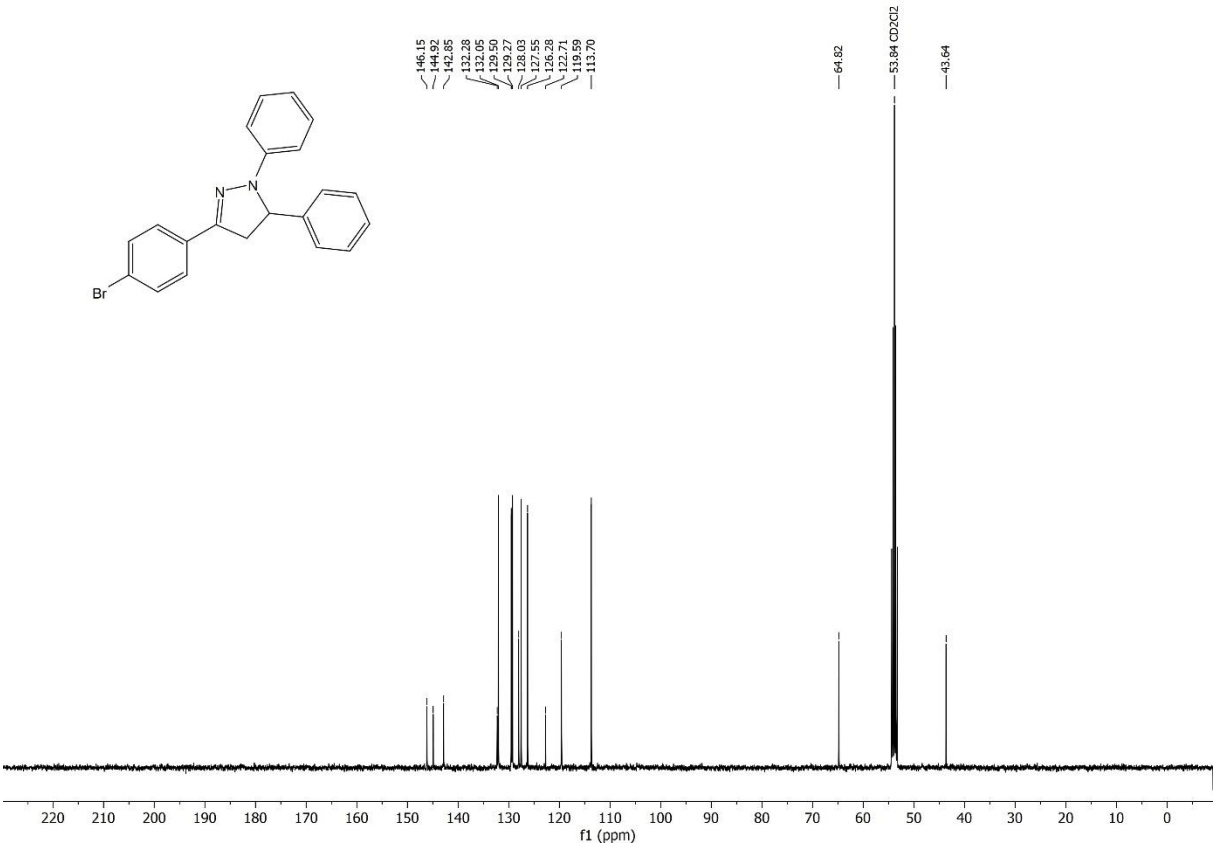

Figure S67: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4m**.

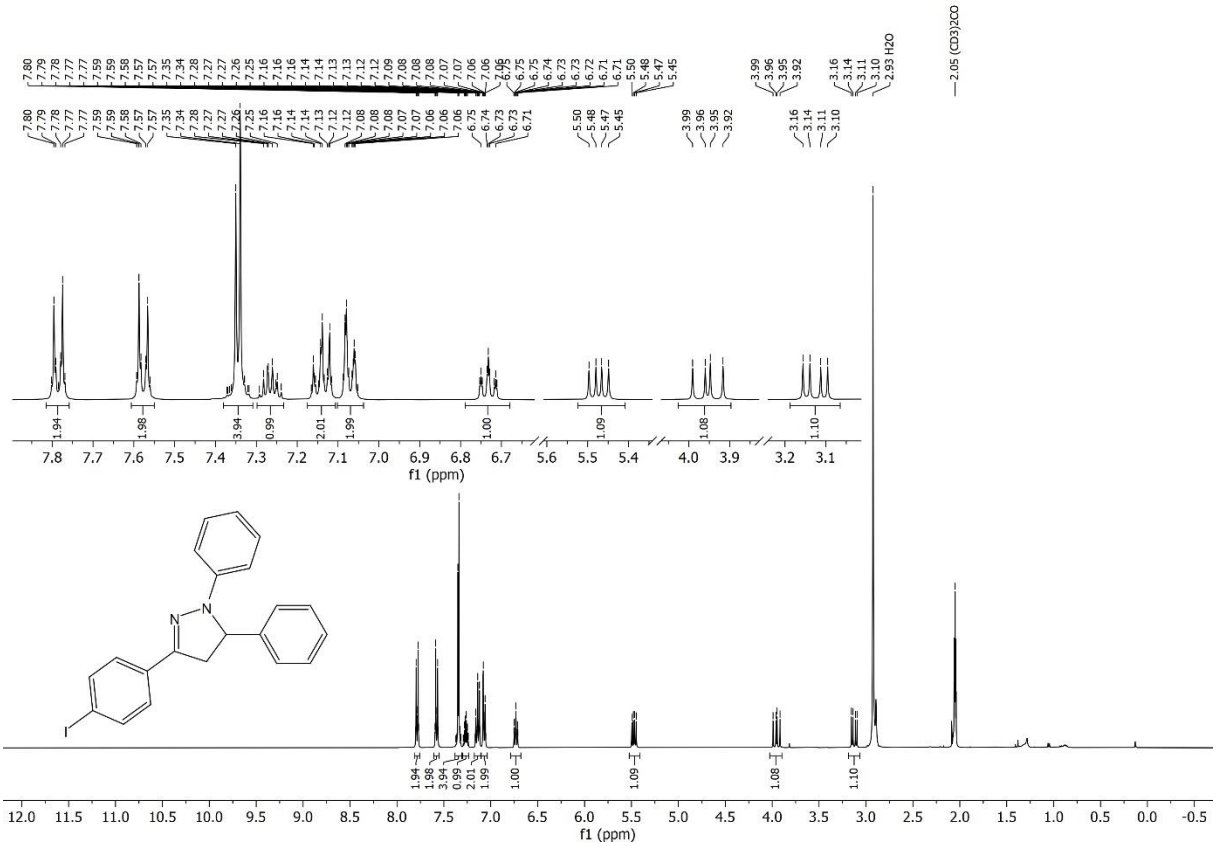

Figure S68: ^{1}H NMR spectrum (400 MHz, acetone-$_{6}$) of **4n**.

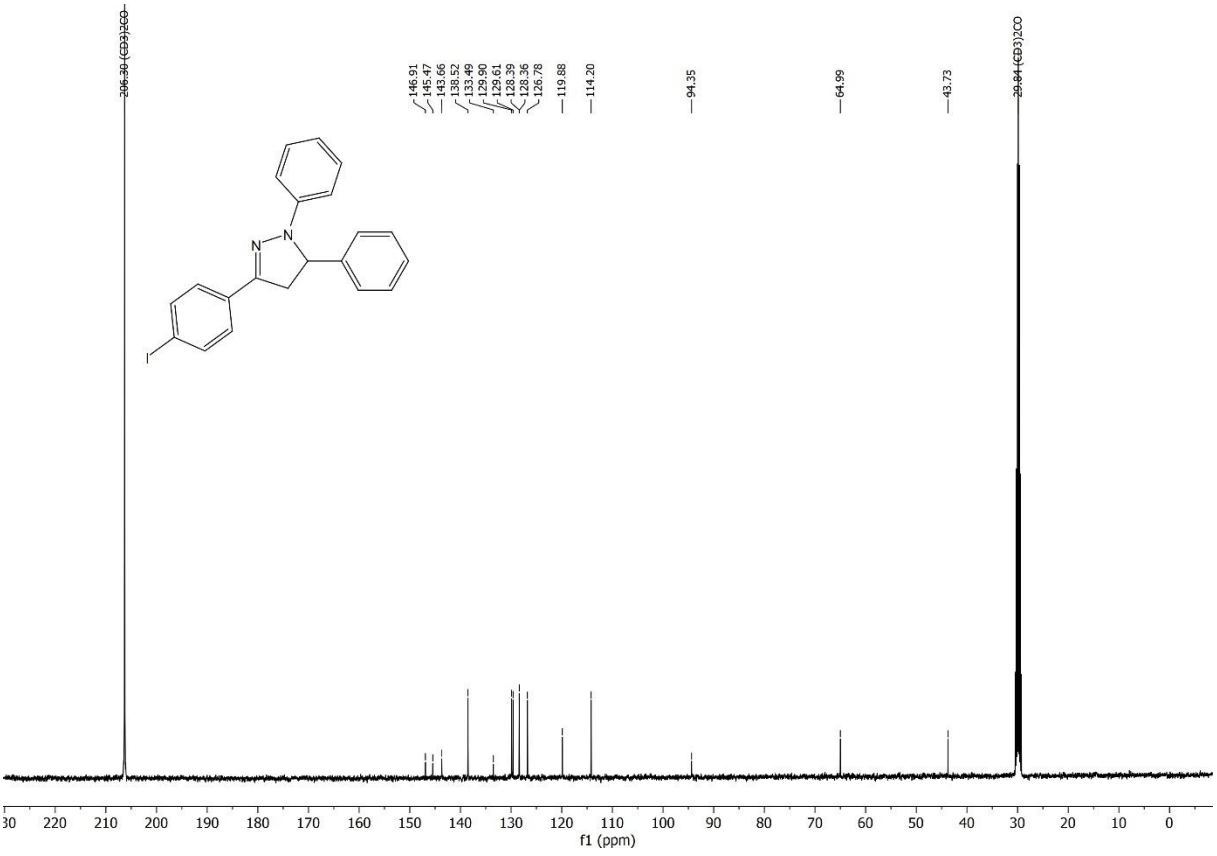

Figure S69: ^{13}C NMR spectrum (101 MHz, acetone-$_{6}$) of **4n**.

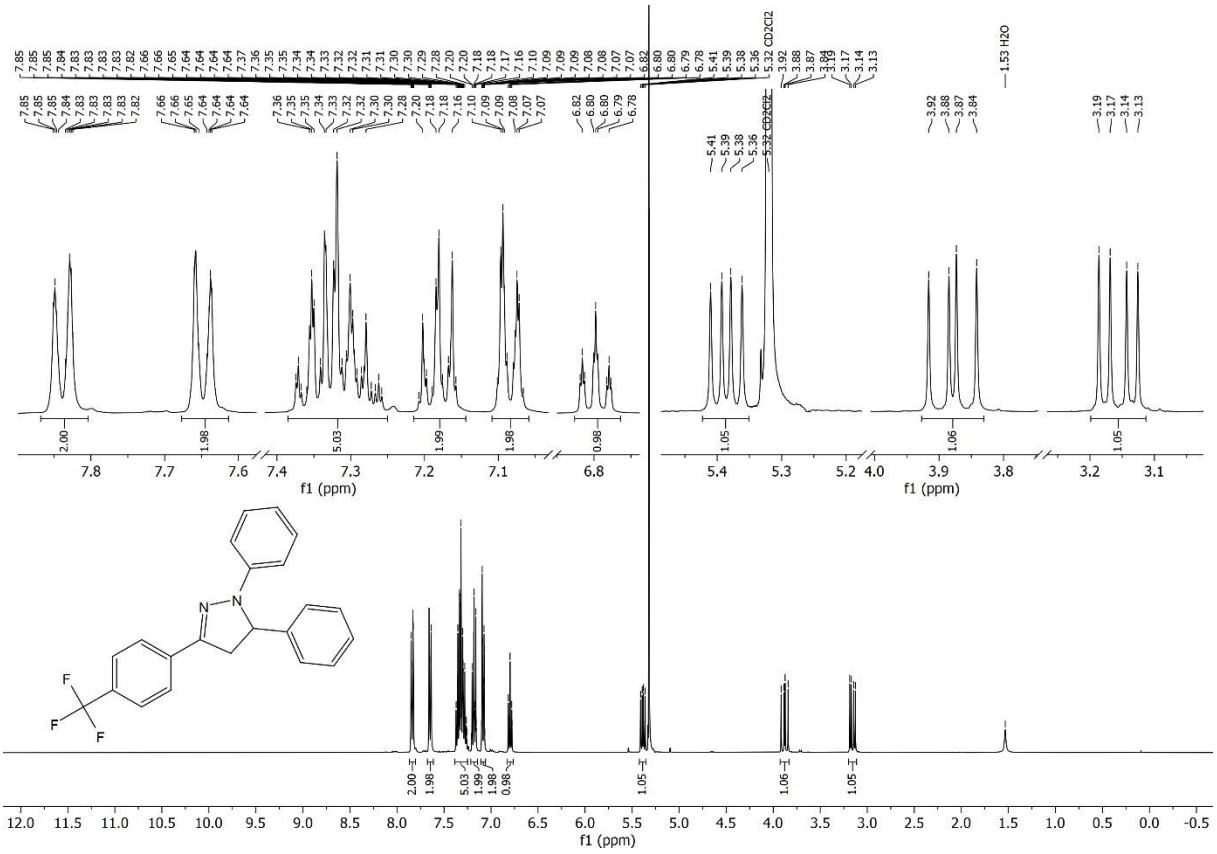

Figure S70: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4o**.

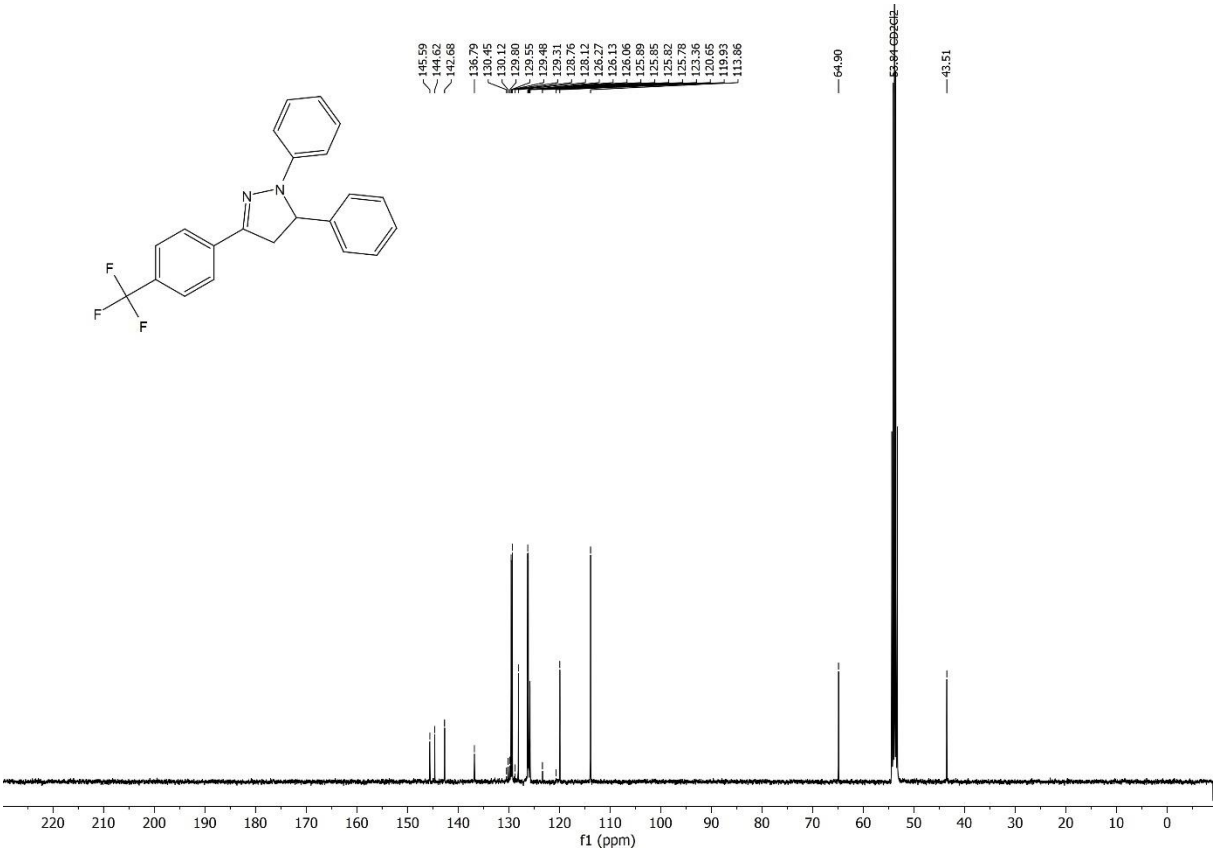

Figure S71: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4o**.

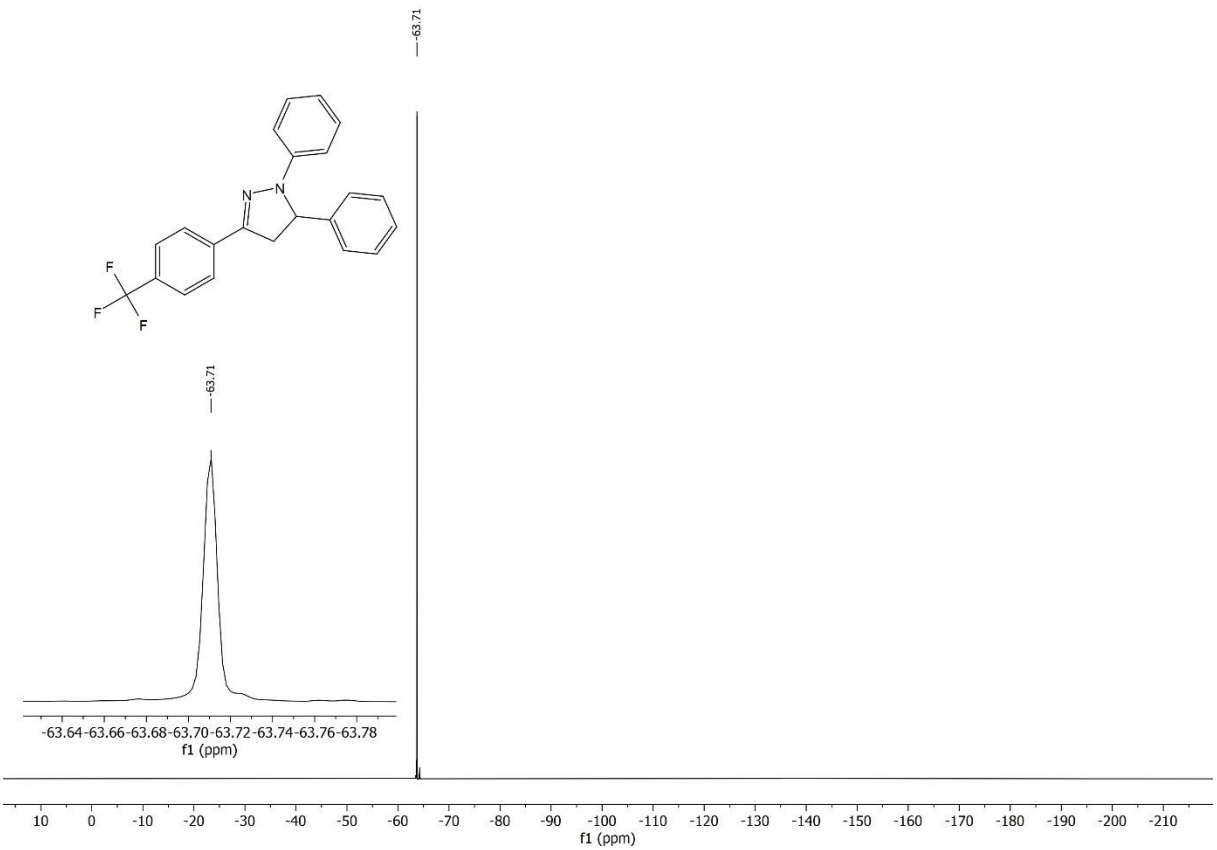

Figure S72: ^{19}F NMR spectrum (376 MHz, CD_2Cl_2) of **4m**.

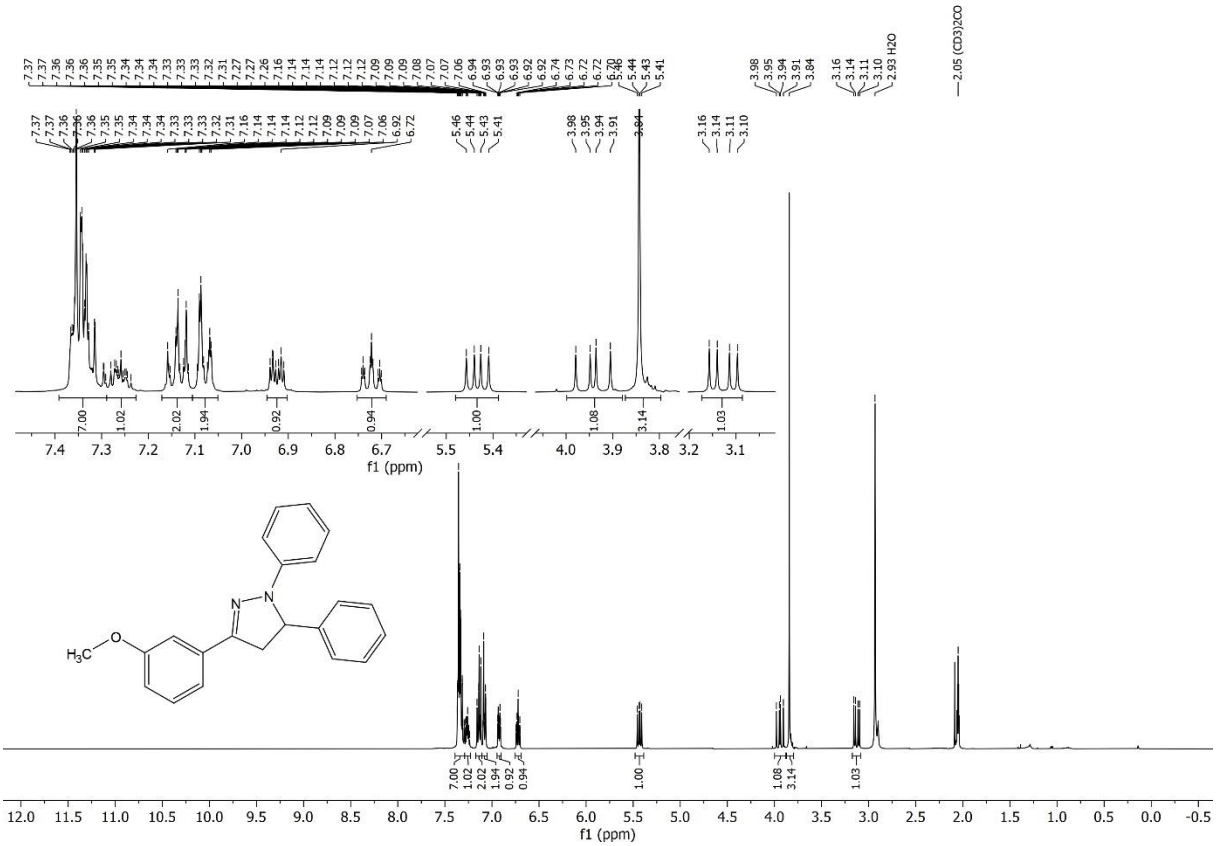

Figure S73: ^{1}H NMR spectrum (400 MHz, acetone-$_{6}$) of **4p**.

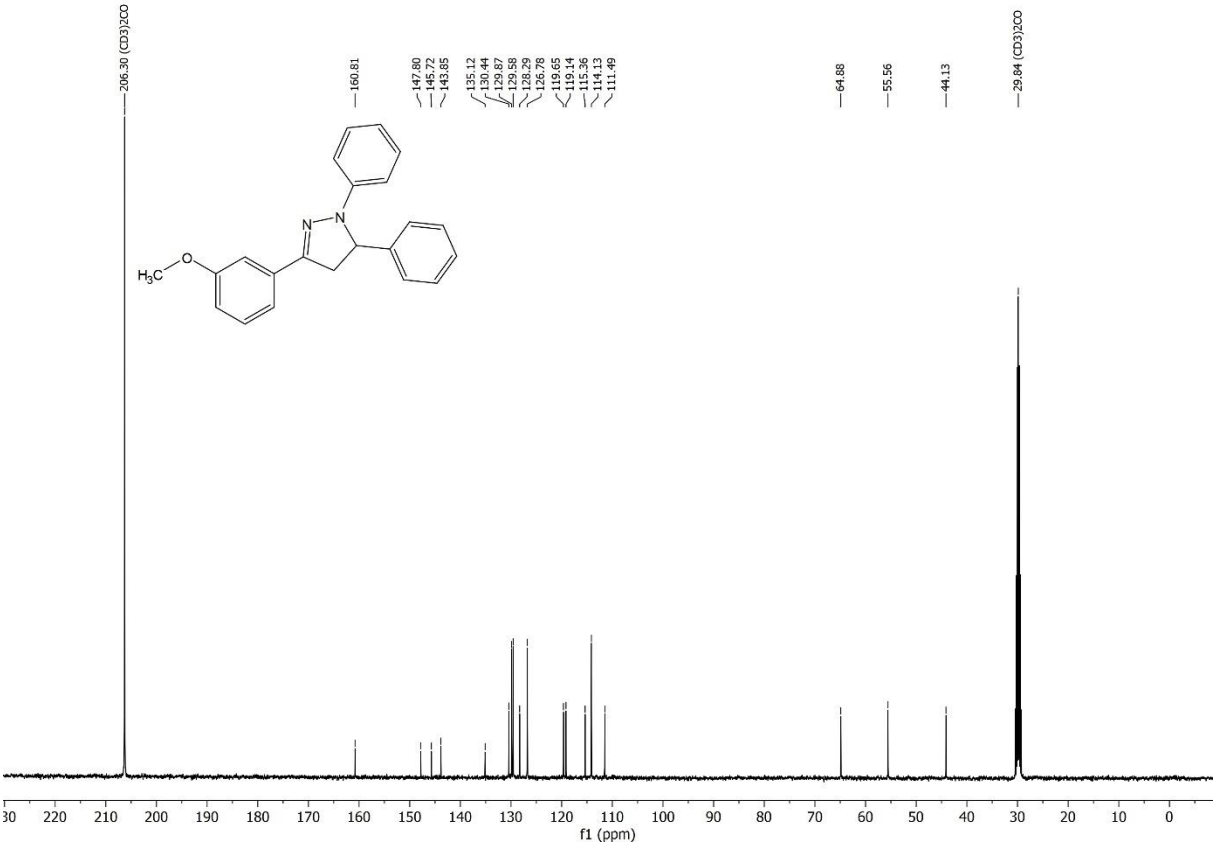

Figure S74: ^{13}C NMR spectrum (101 MHz, acetone-$_{6}$) of **4p**.

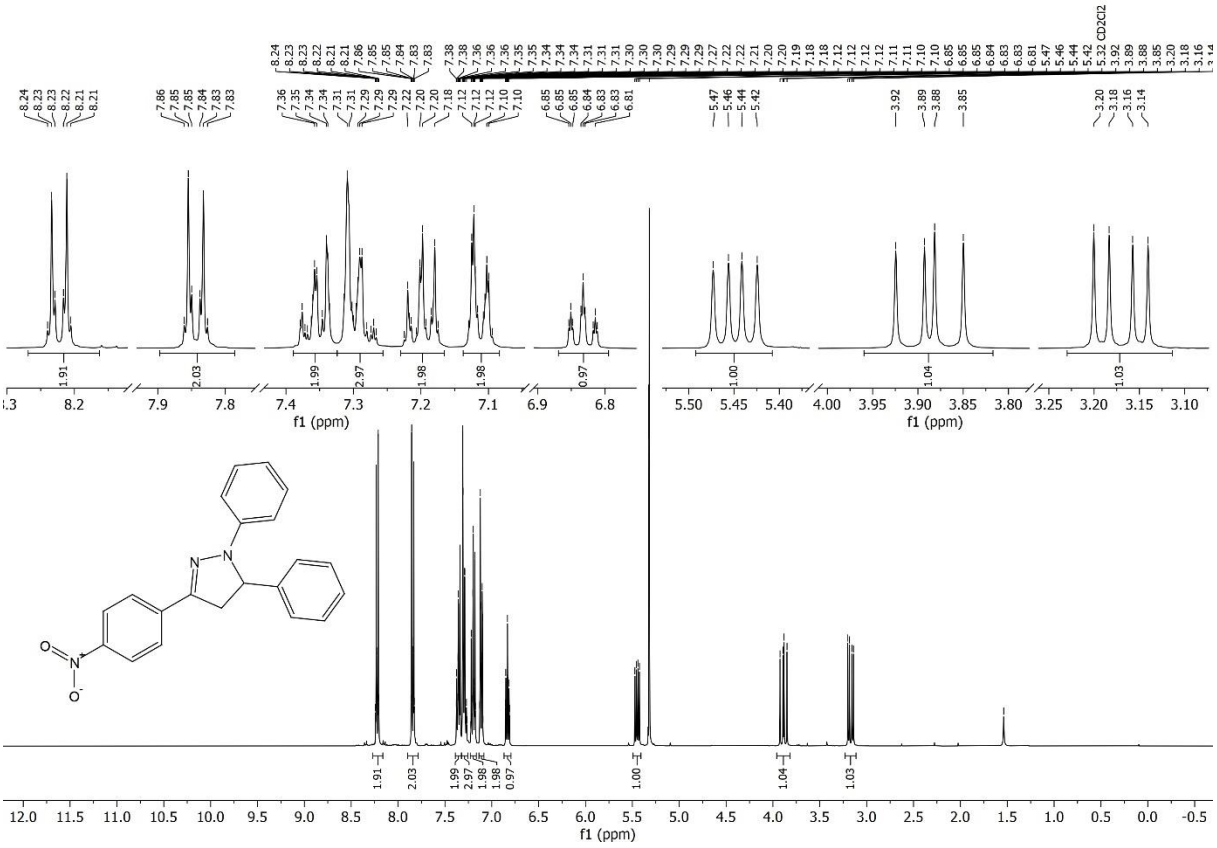

Figure S75: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4q**.

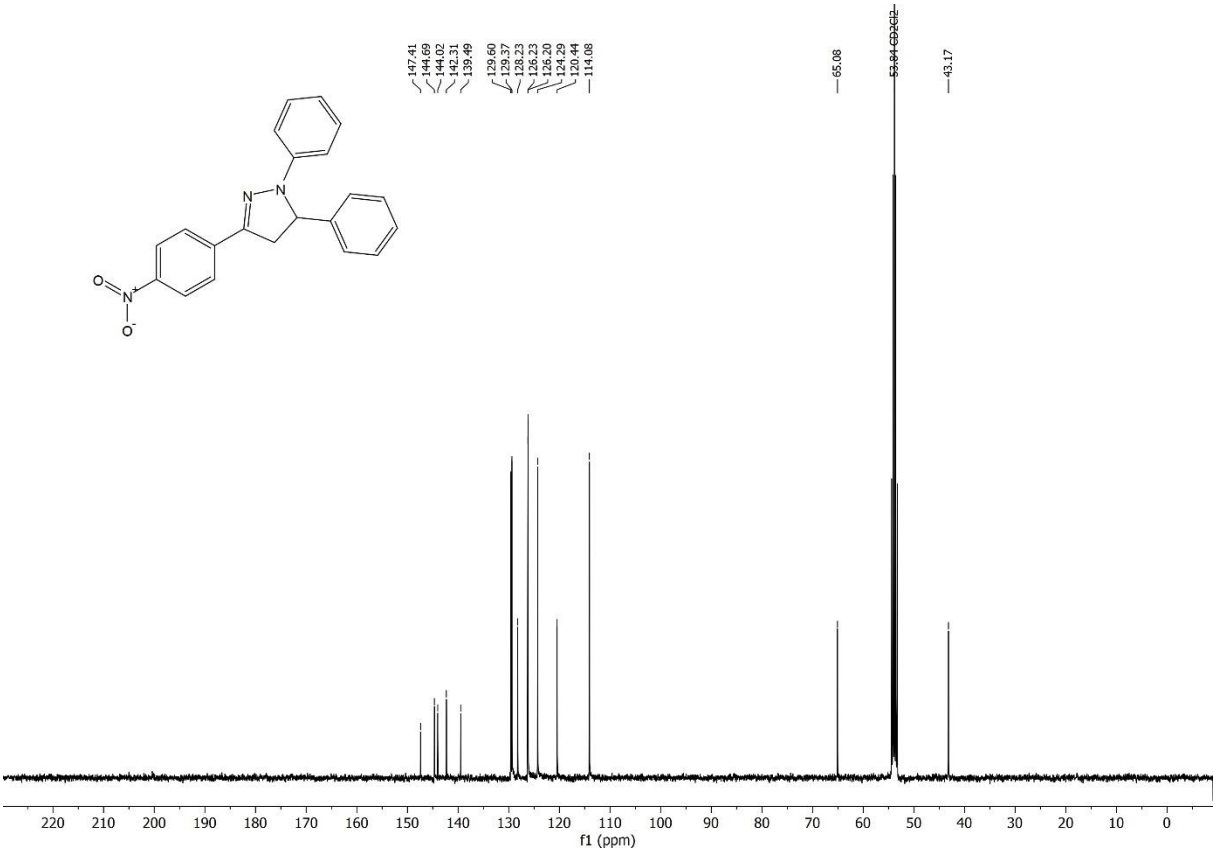

Figure S76: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4q**.

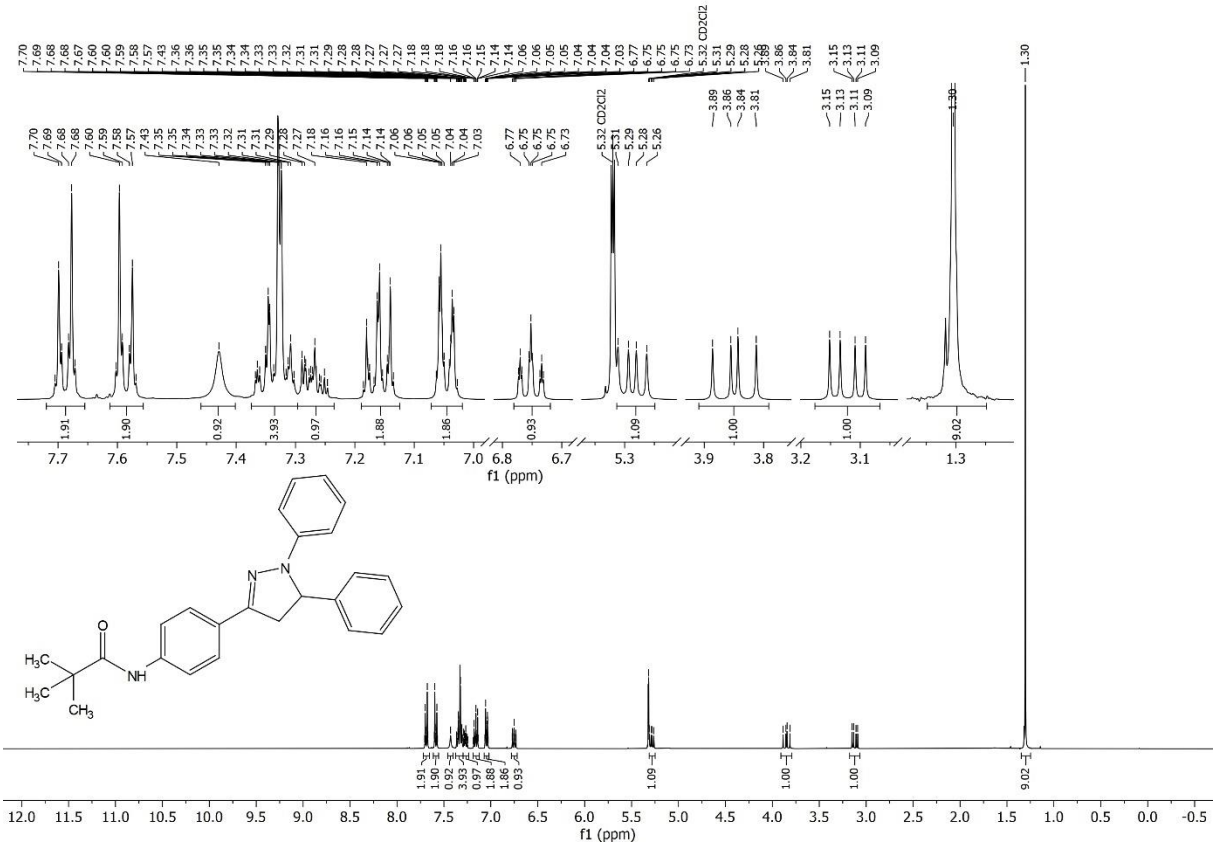

Figure S77: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4r**.

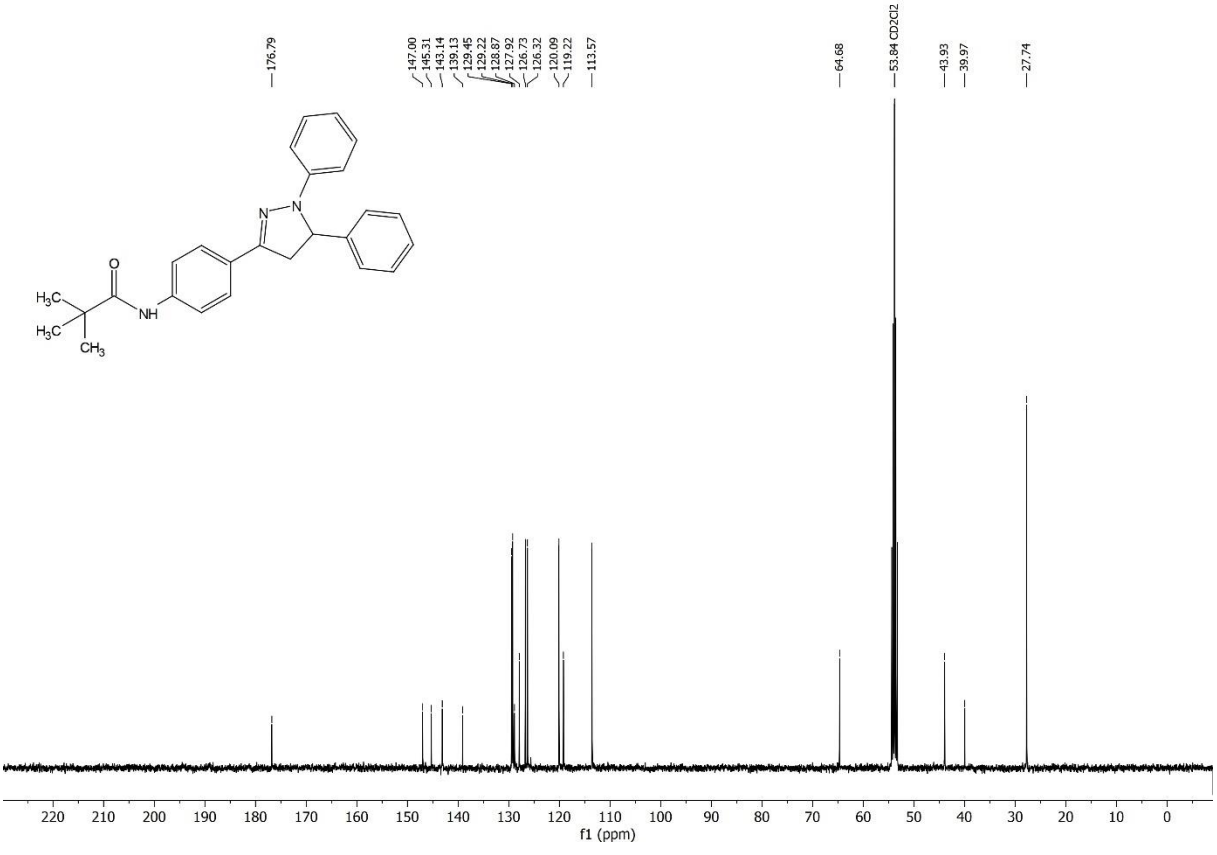

Figure S78: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4r**.

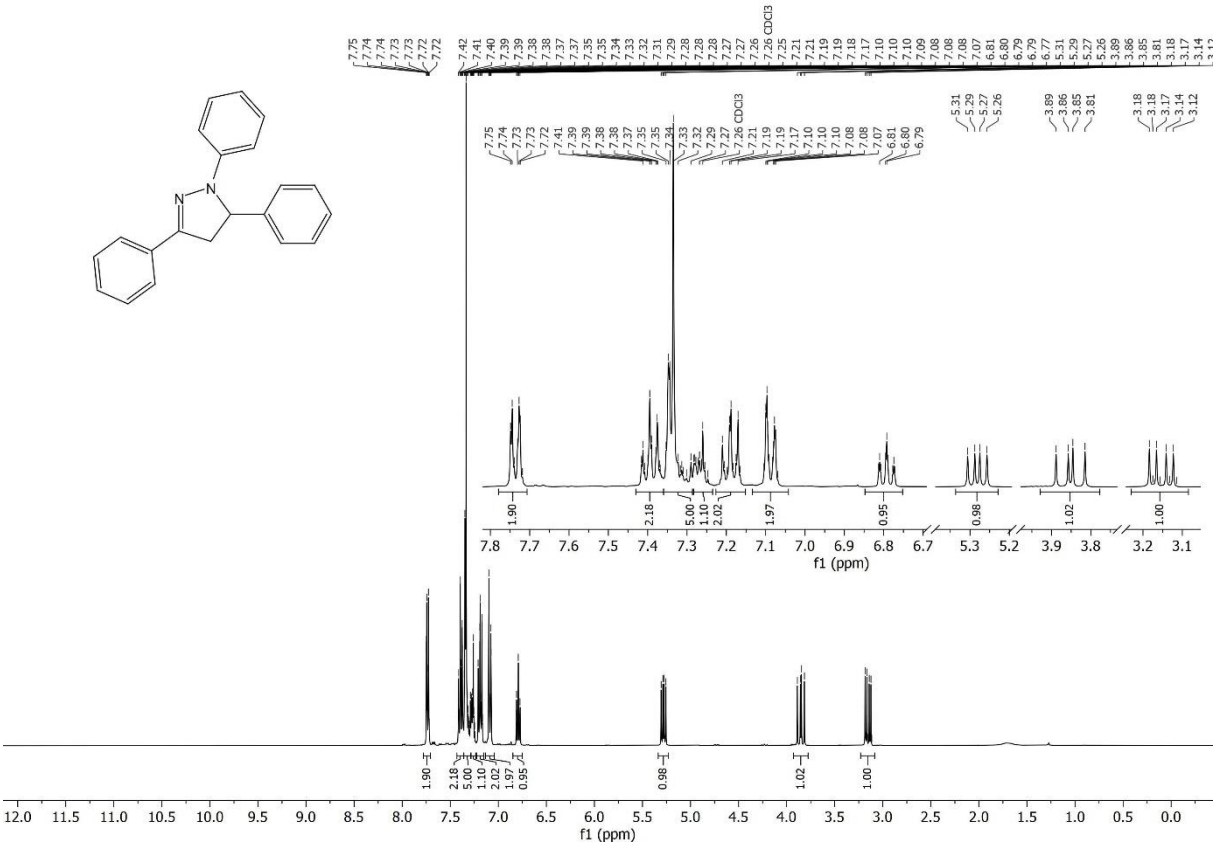

Figure S79: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4s**.

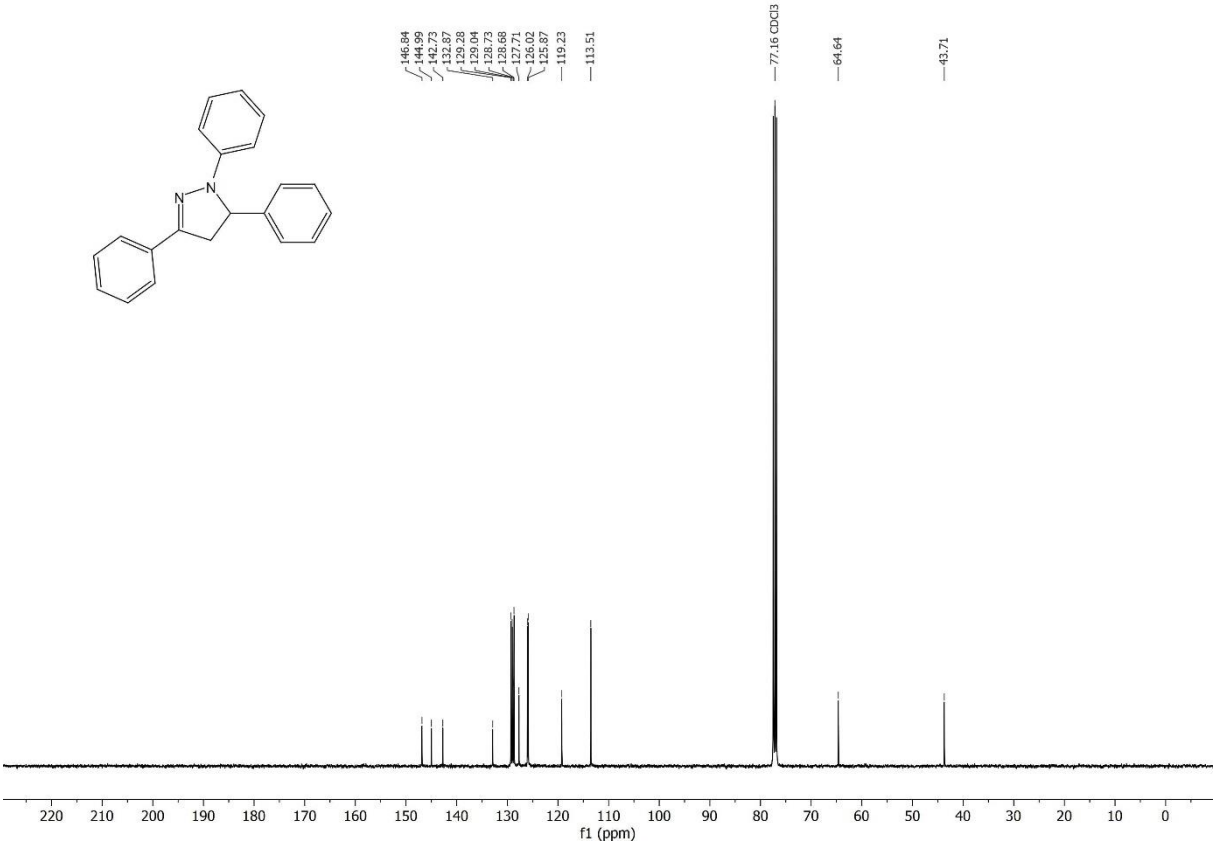

Figure S80: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4s**.

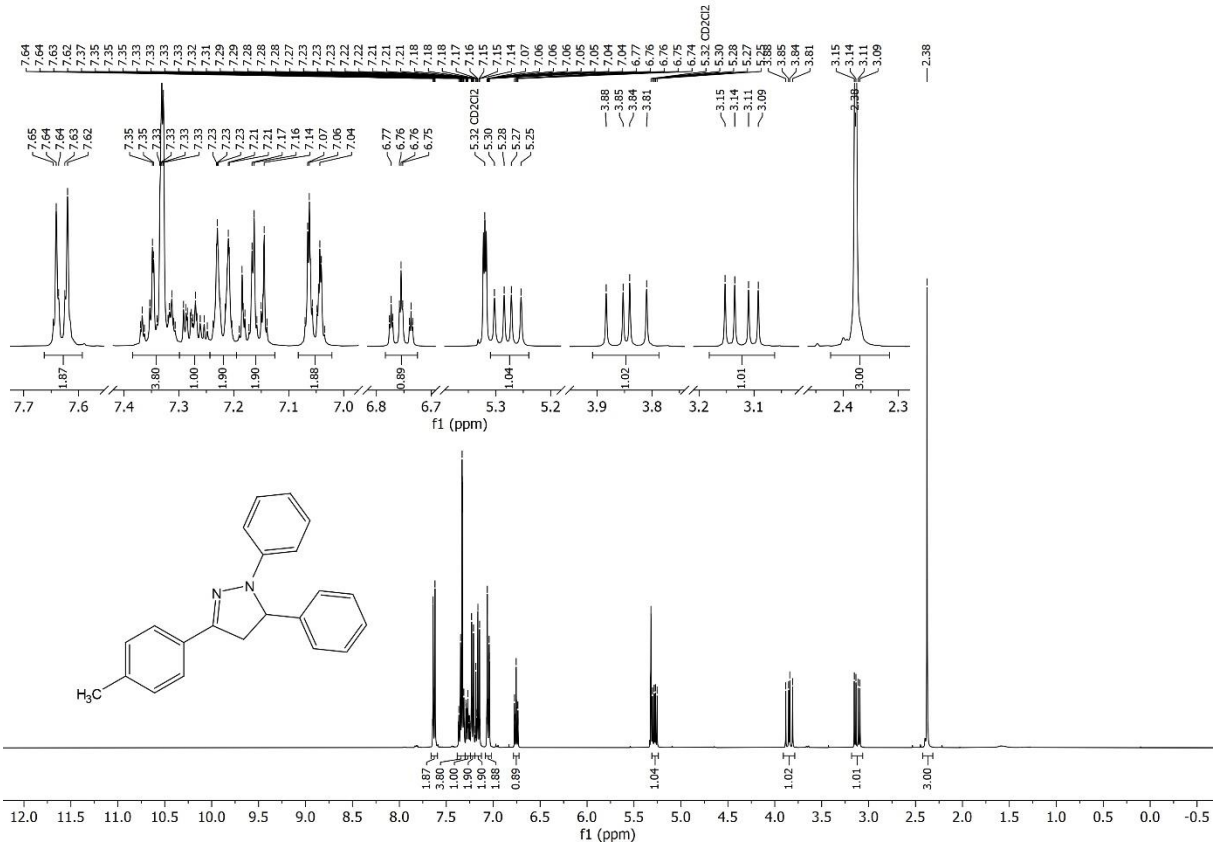

Figure S81: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4t**.

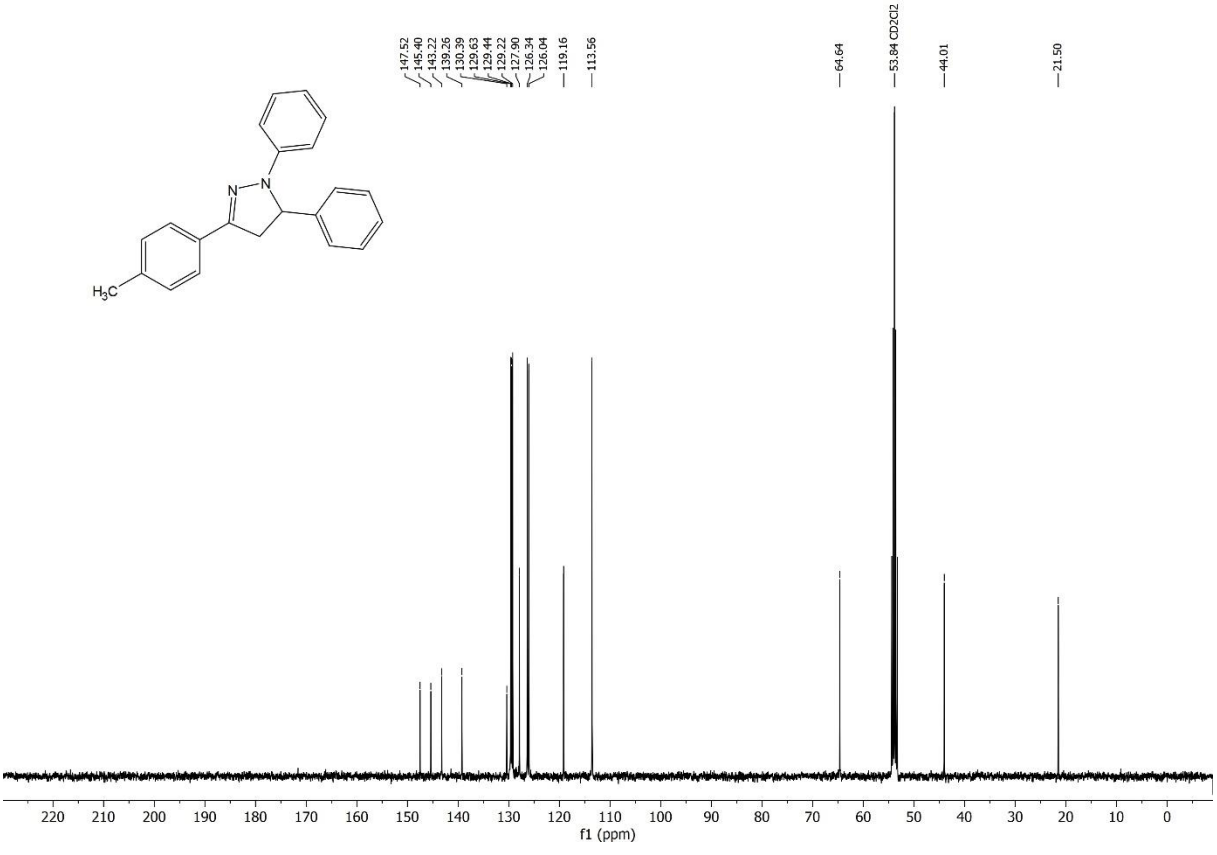

Figure S82: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4t**.

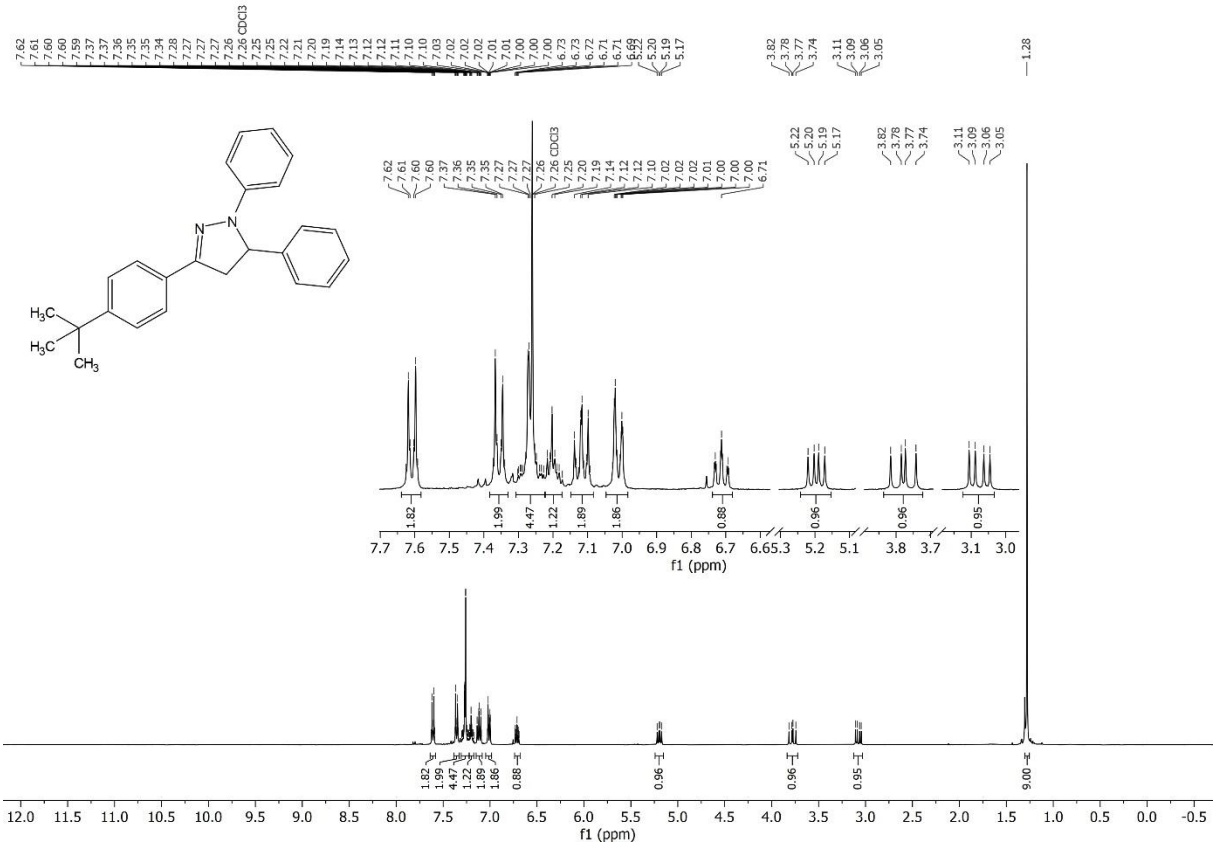

Figure S83: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4u**.

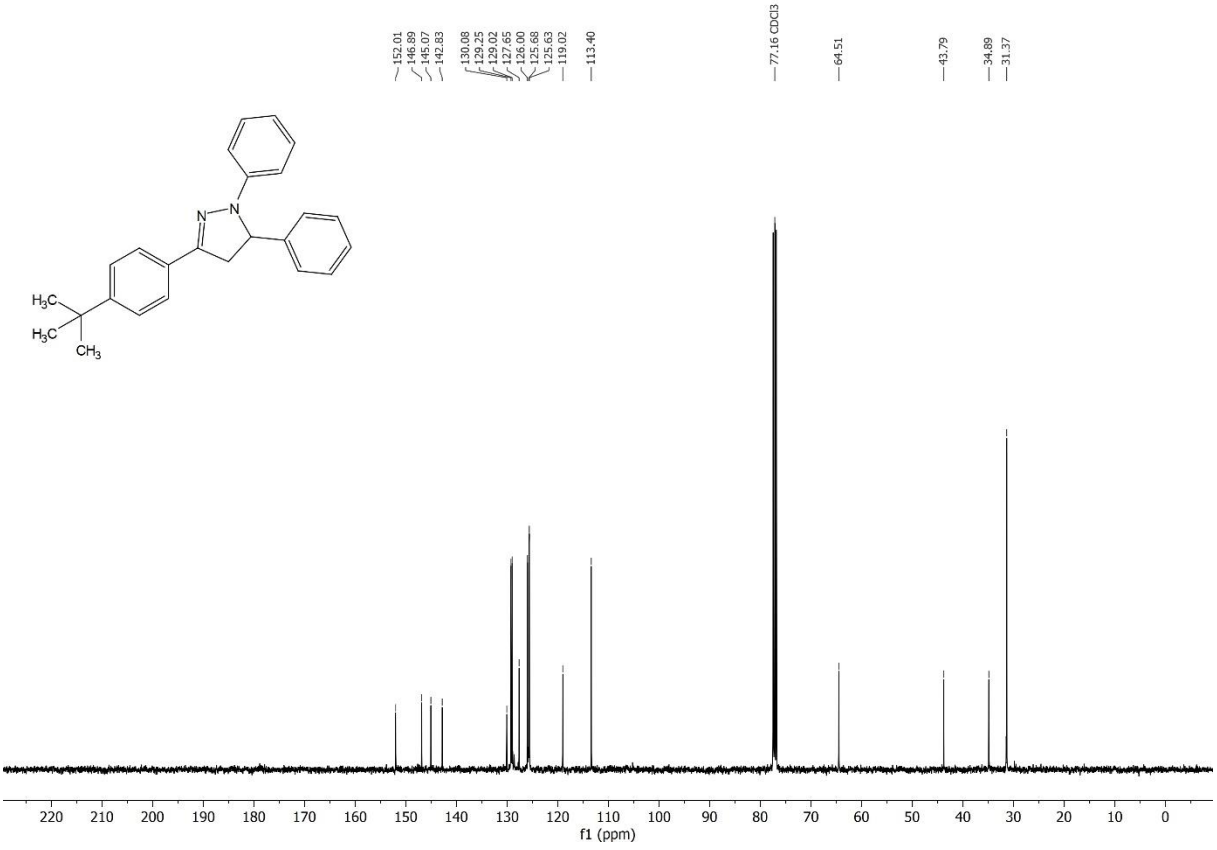

Figure S84: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4u**.

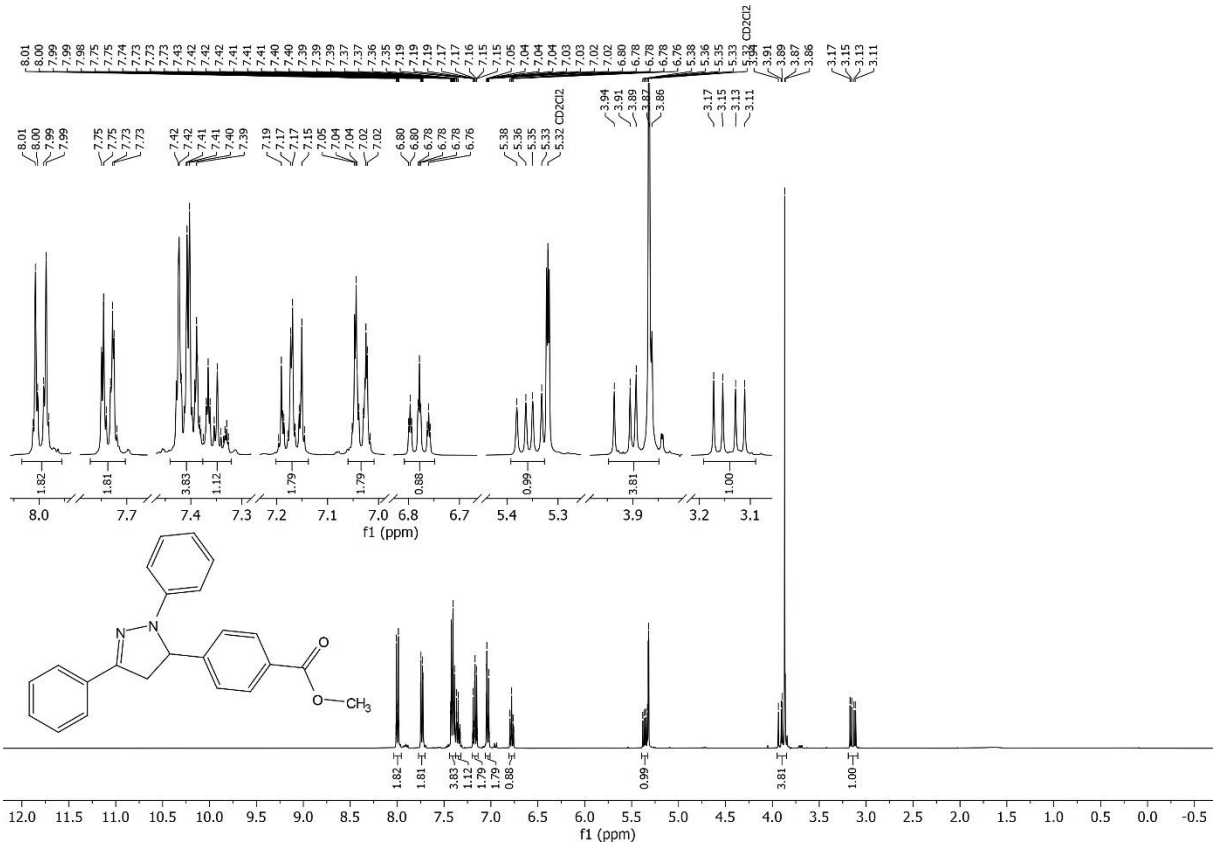

Figure S85: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4v**.

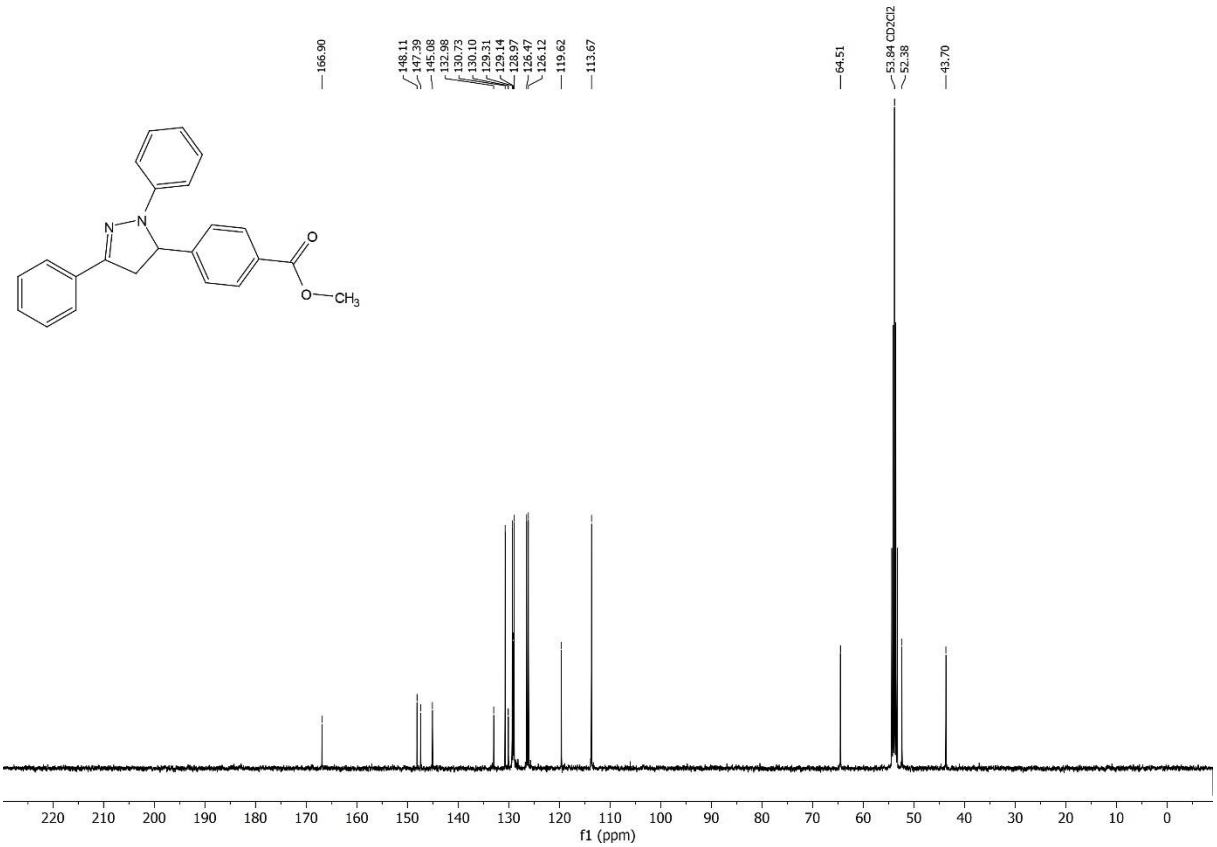

Figure S86: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4v**.

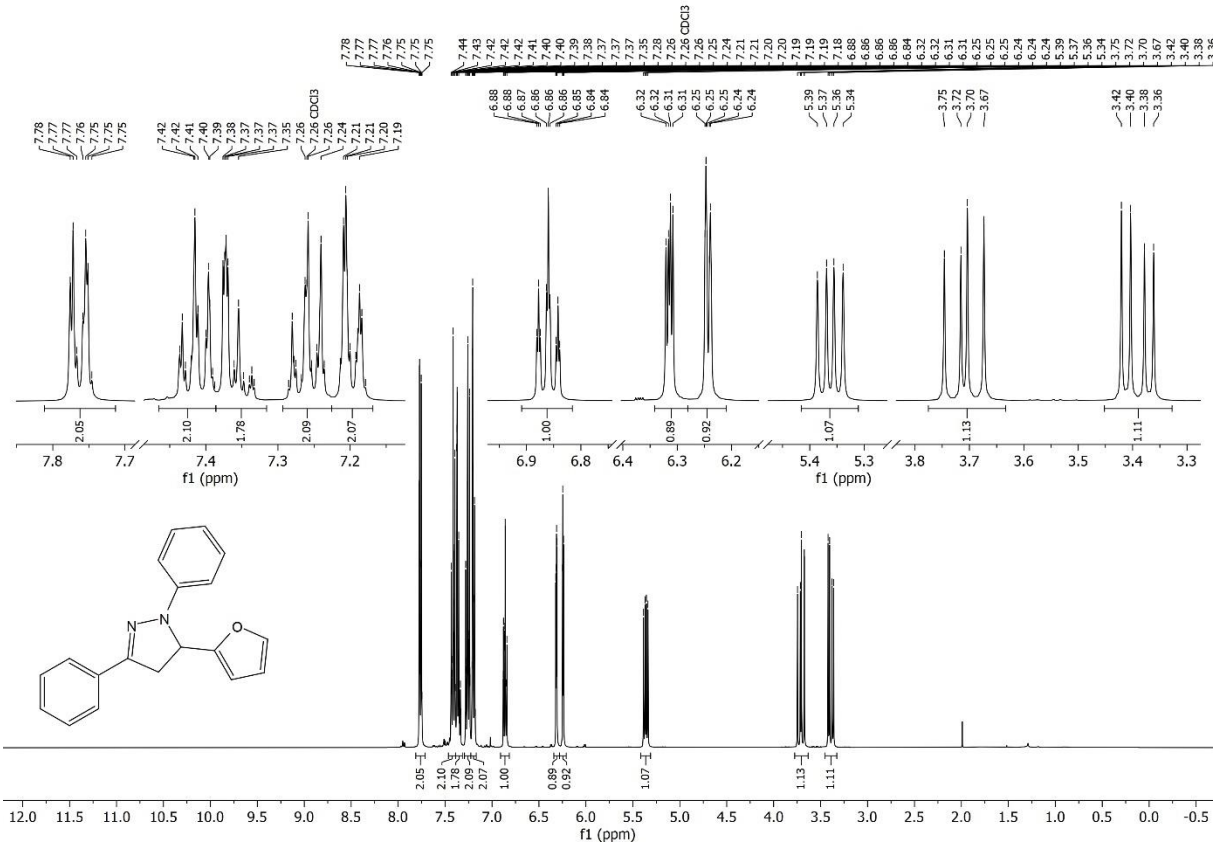

Figure S87: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4w**.

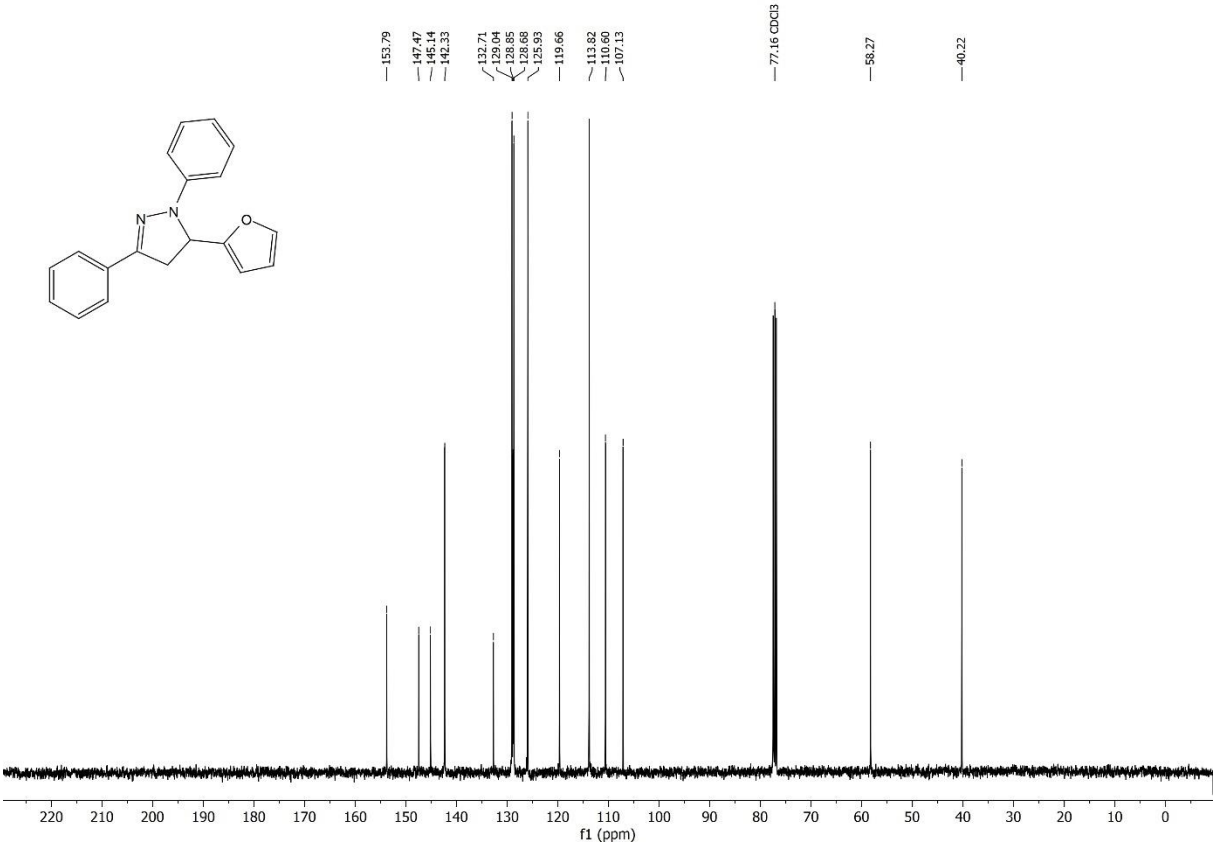

Figure S88: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4w**.

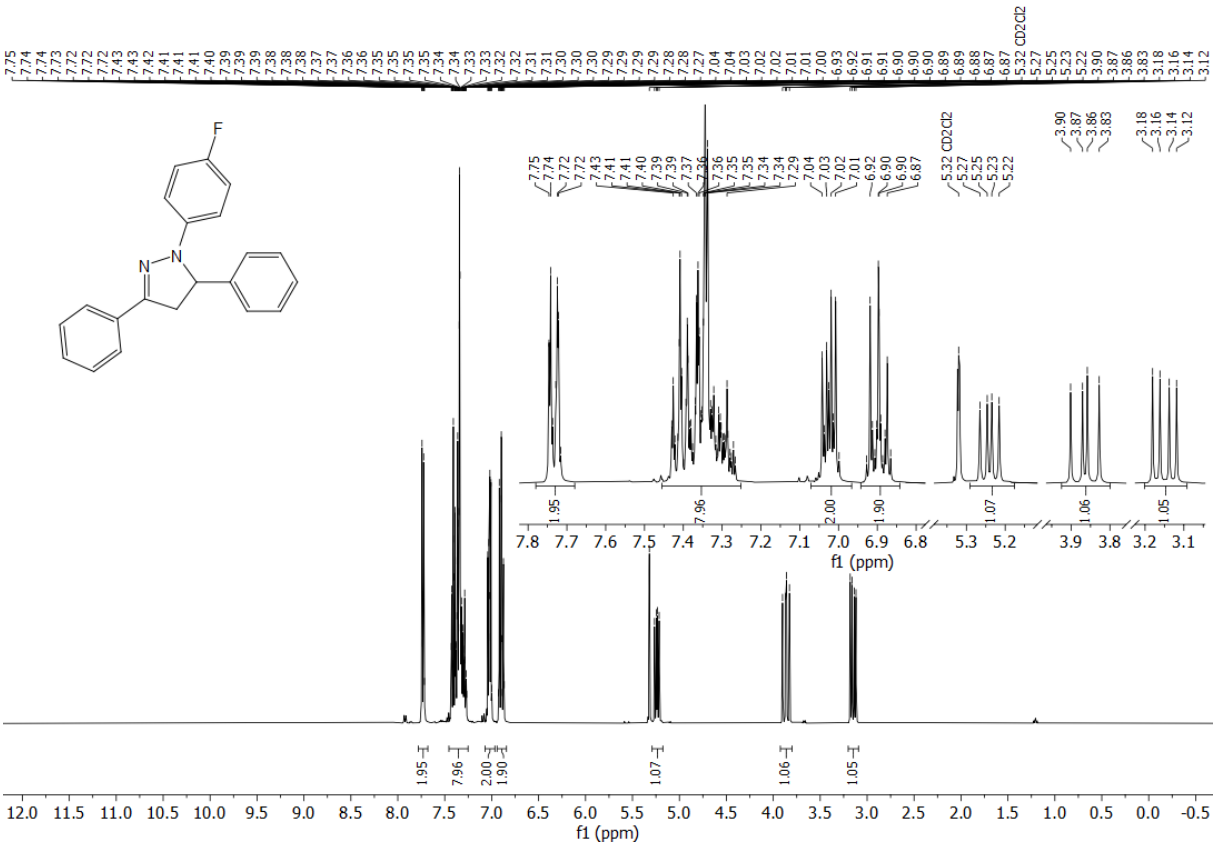

Figure S89: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4x**.

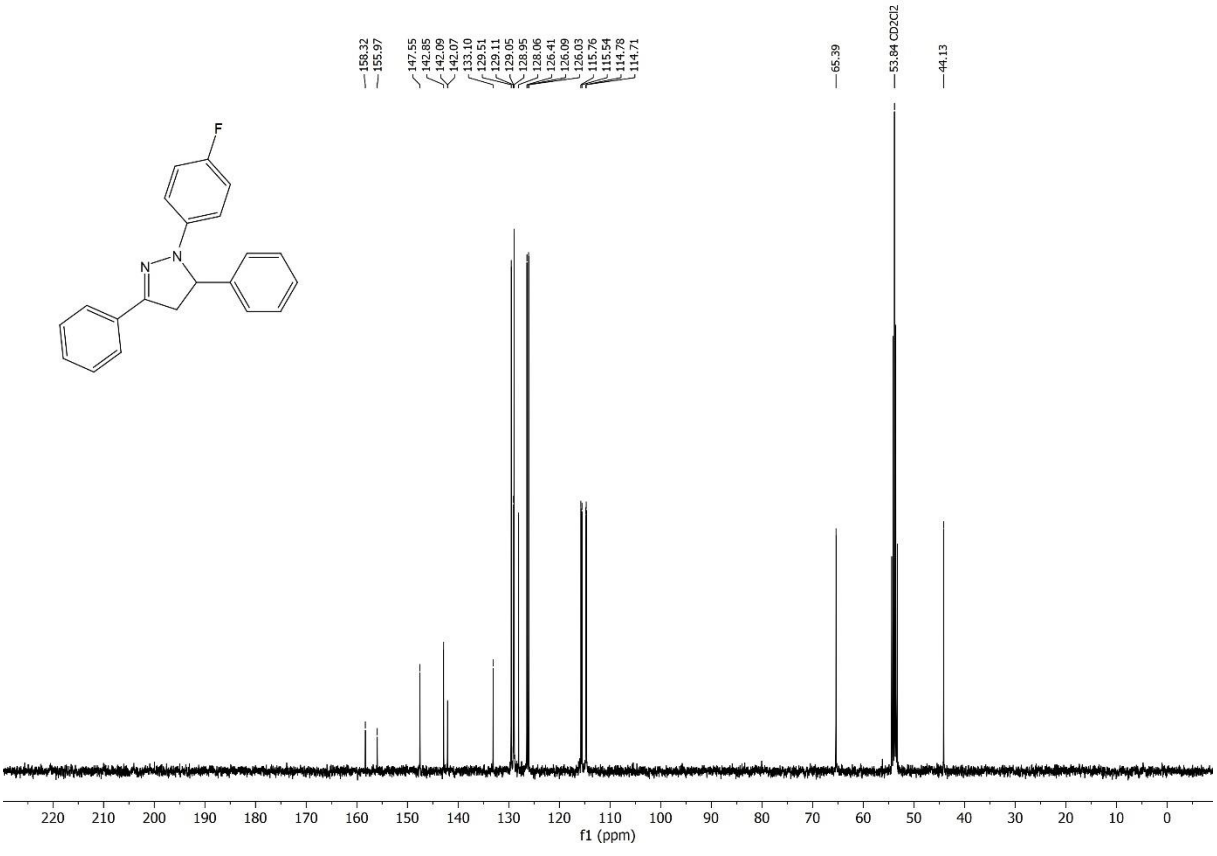

Figure S90: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4x**.

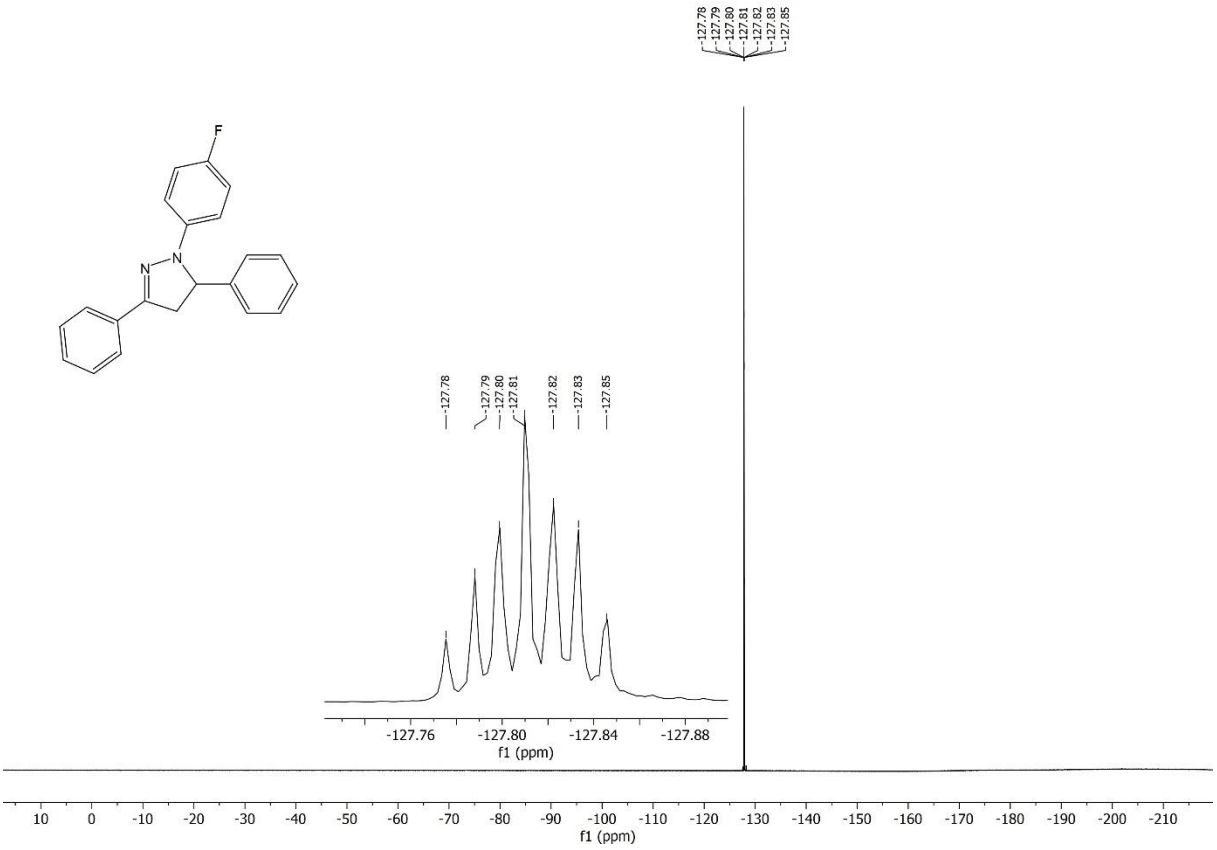

Figure S91: ^{19}F NMR spectrum (376 MHz, CD_2Cl_2) of **4x.**

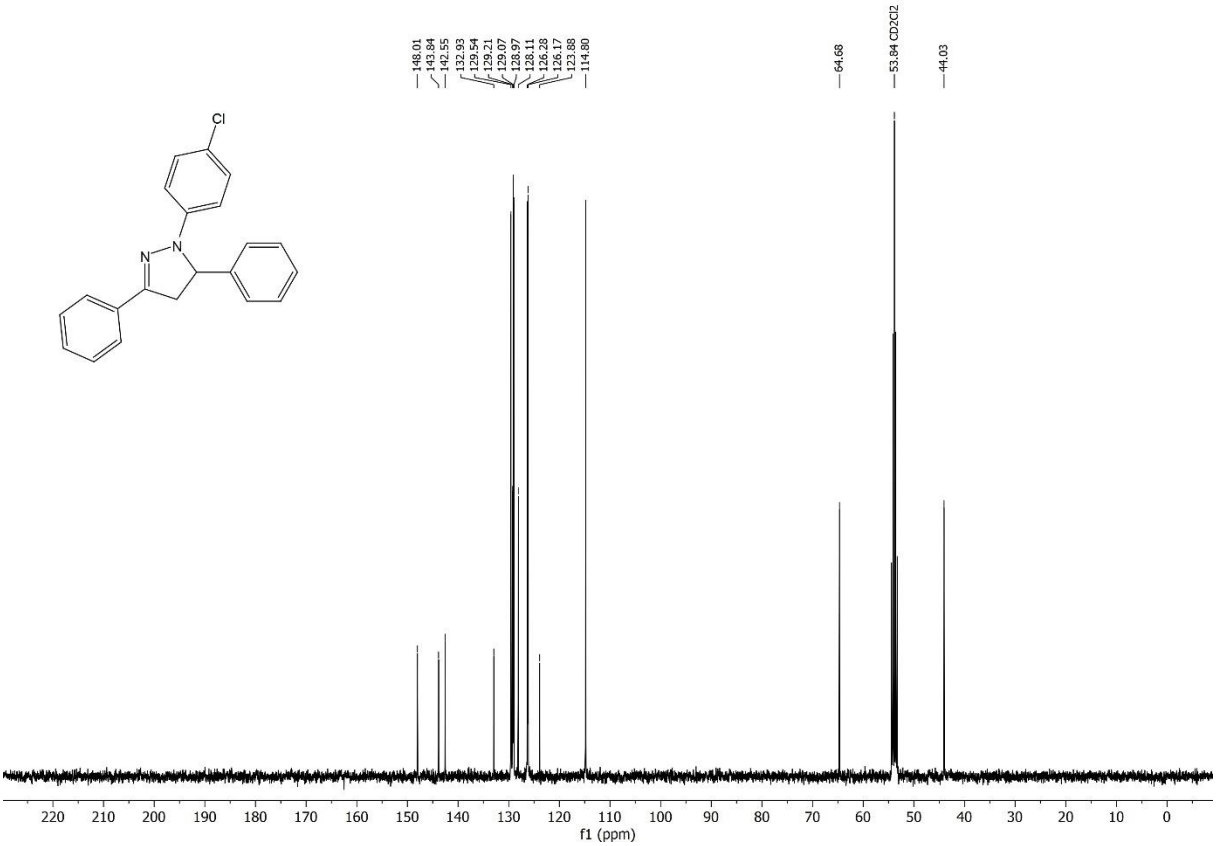

Figure S92: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4y.**

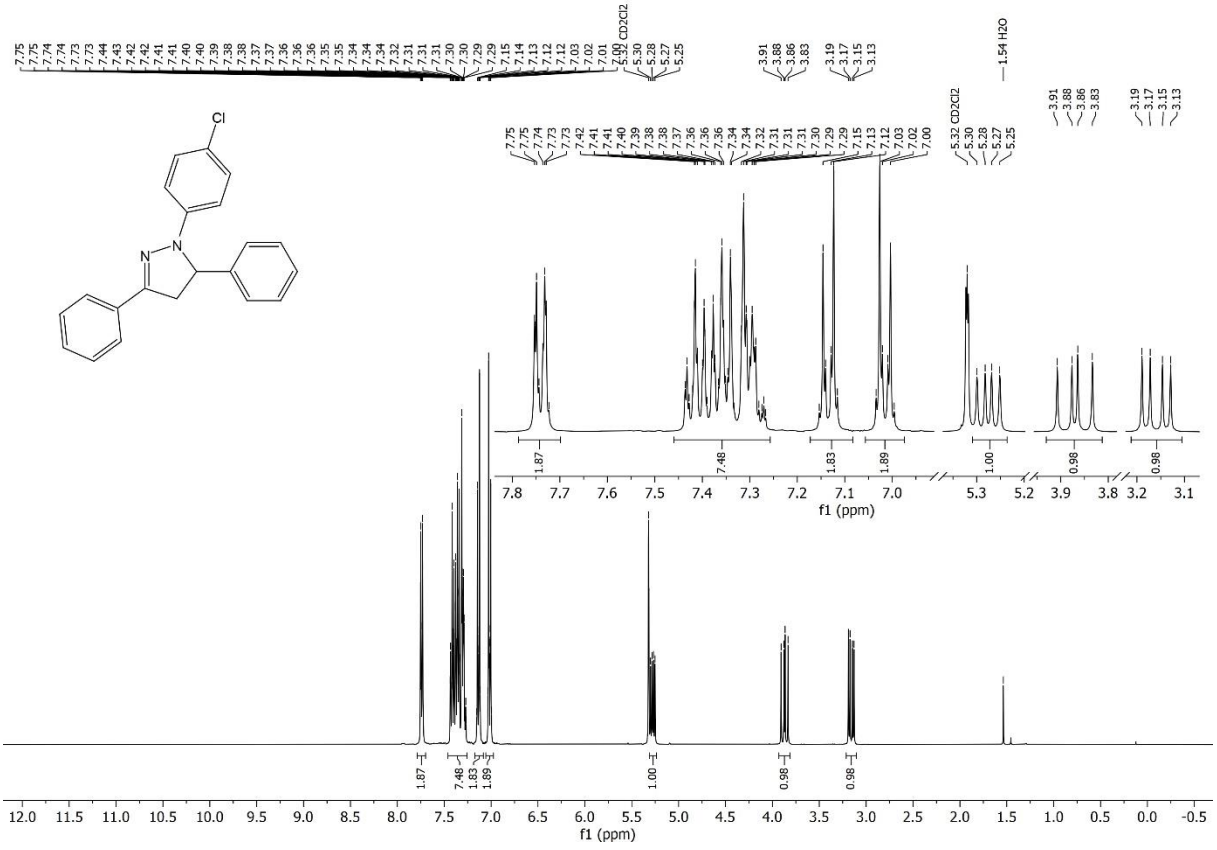

Figure S93: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4y.**

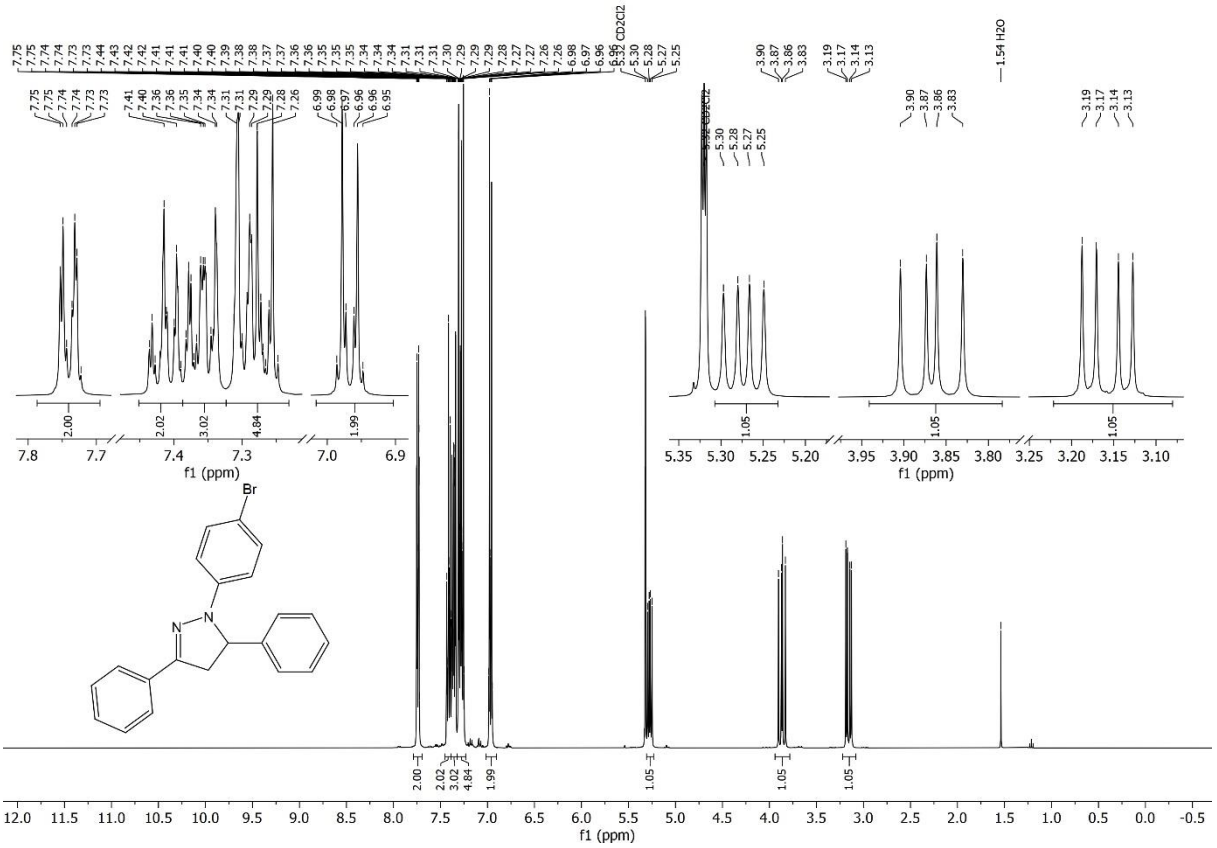

Figure S94: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4z.**

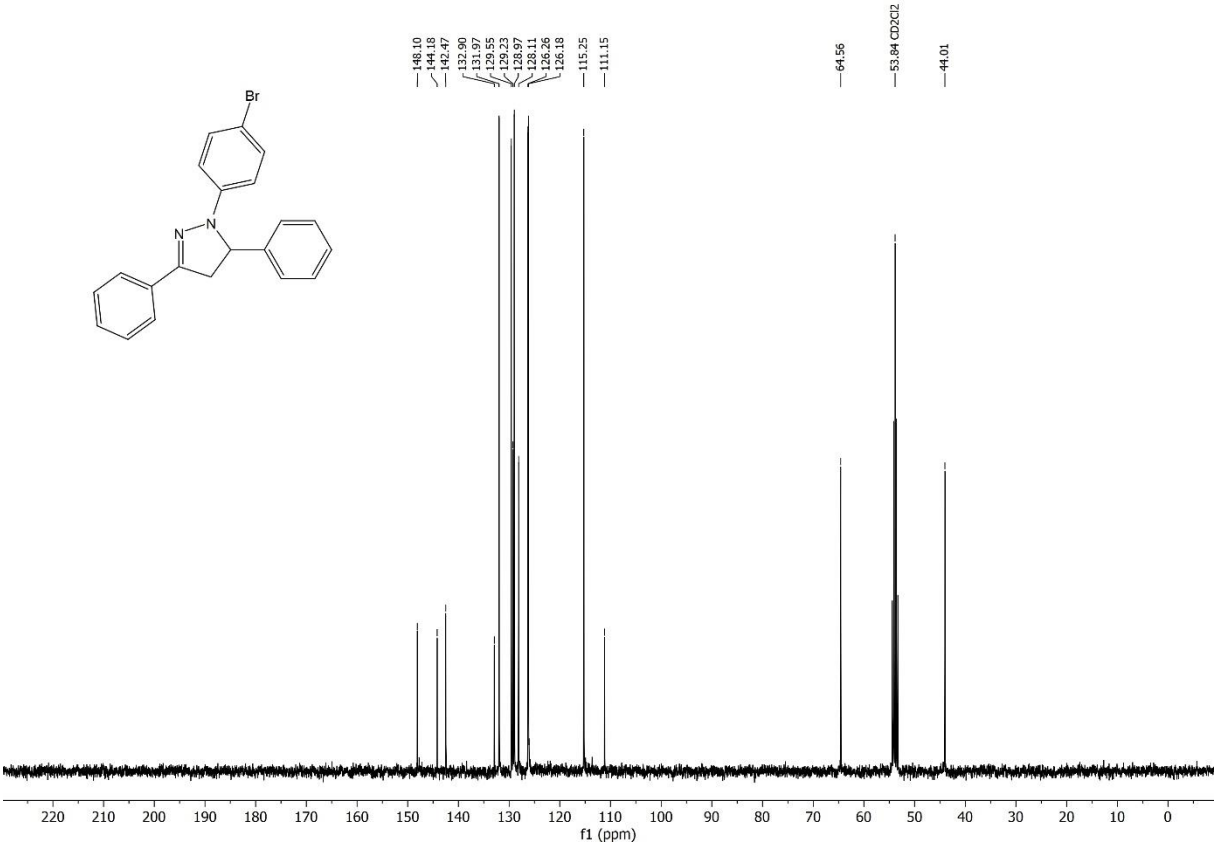

Figure S95: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4z.**

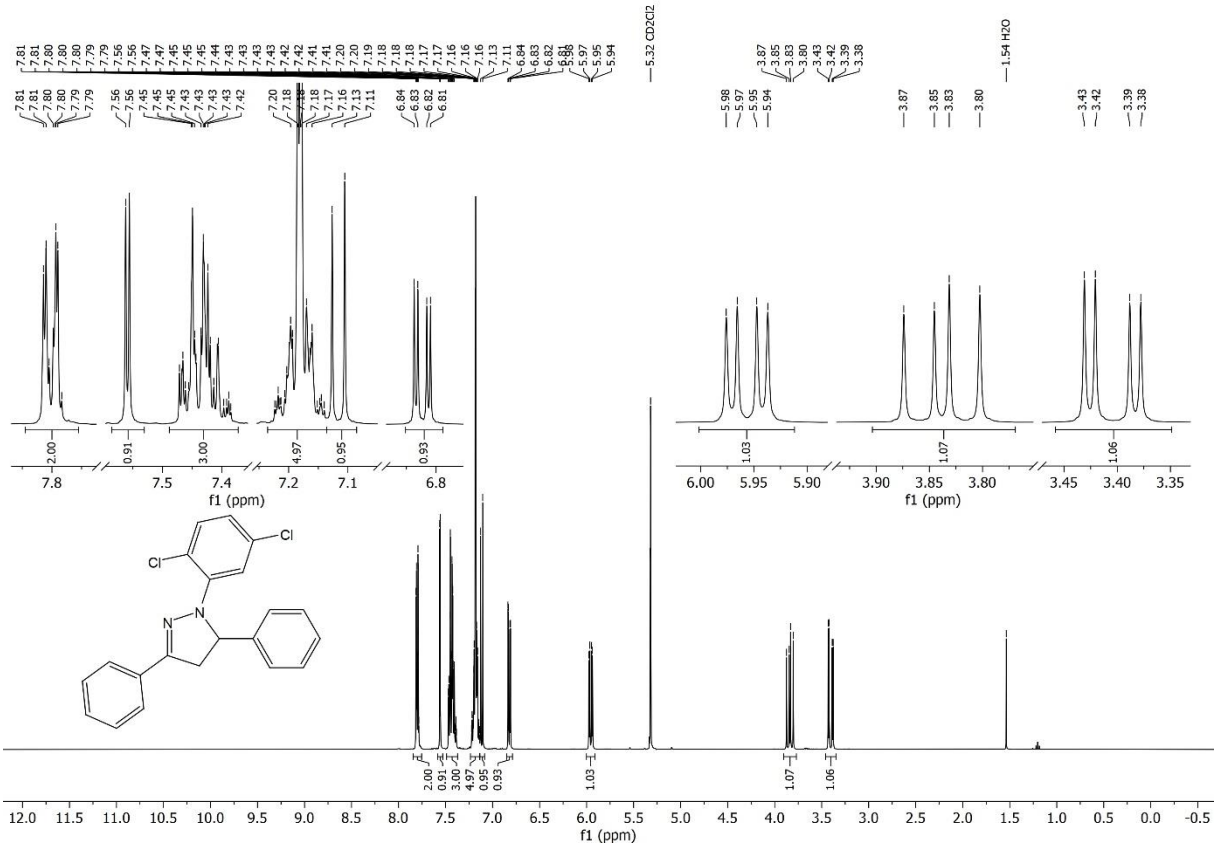

Figure S96: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4a'.**

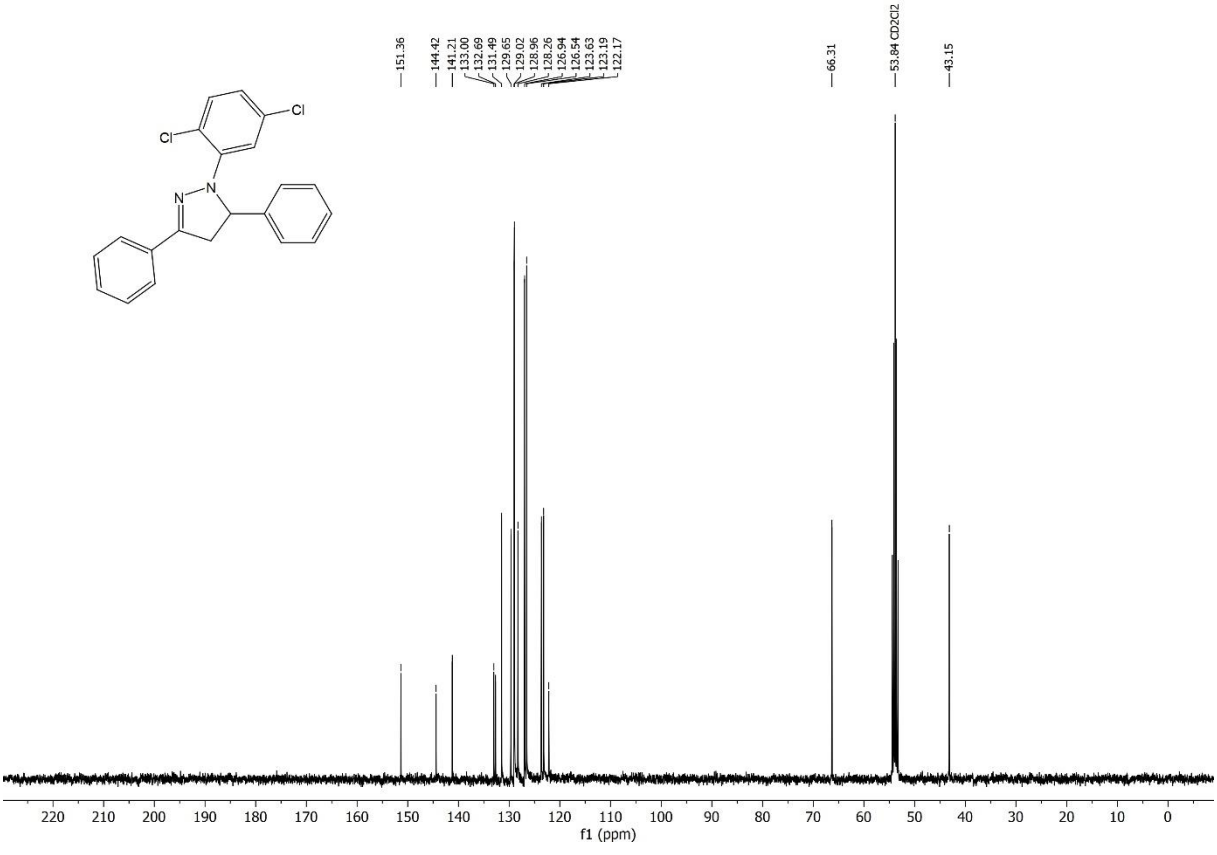

Figure S97: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4a'.**

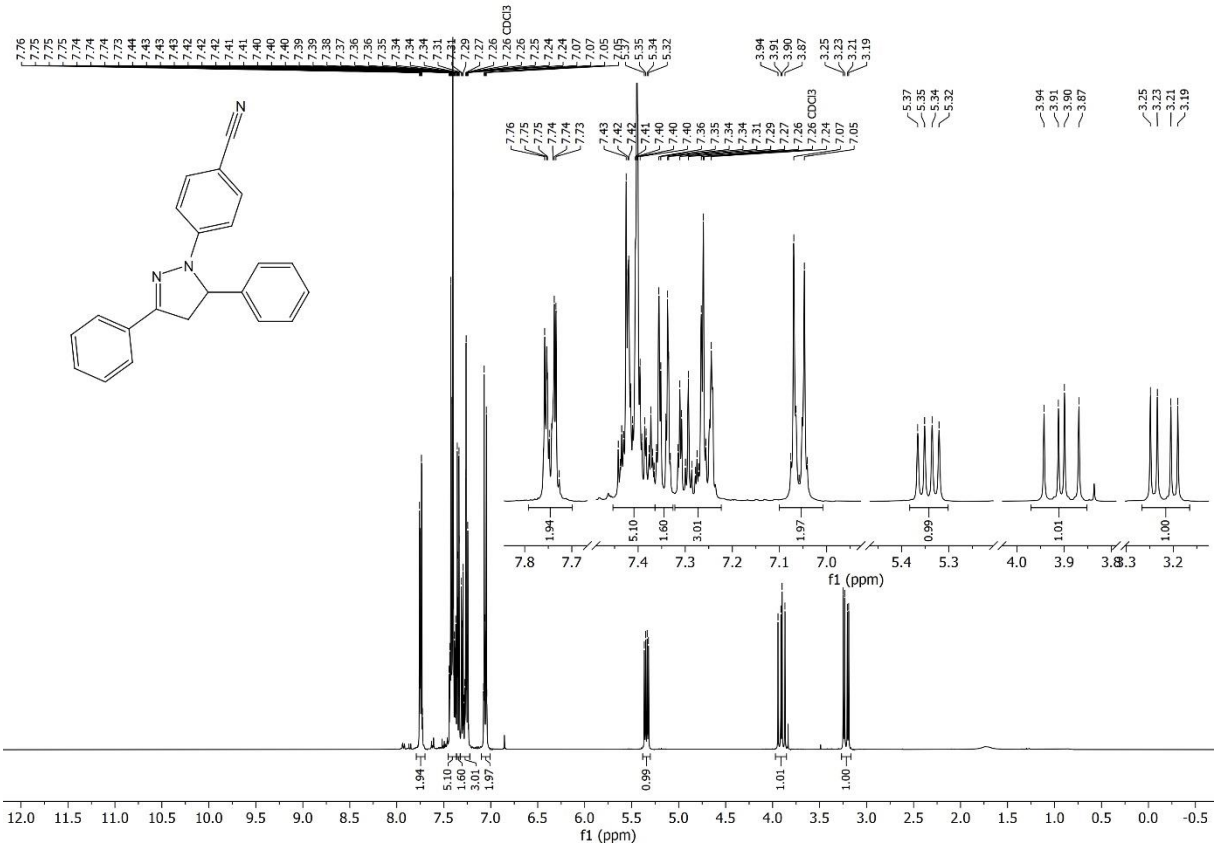

Figure S98: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b'.**

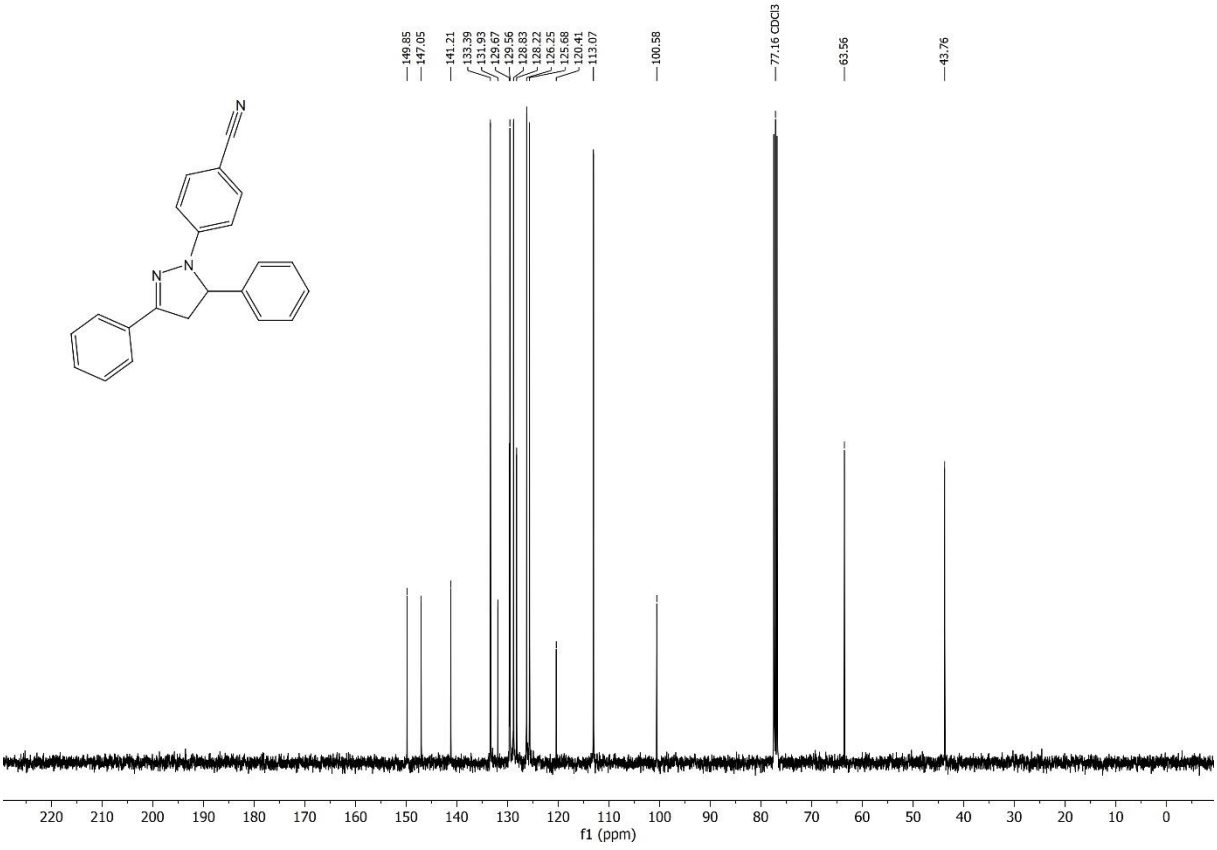

Figure S99: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4b'.**

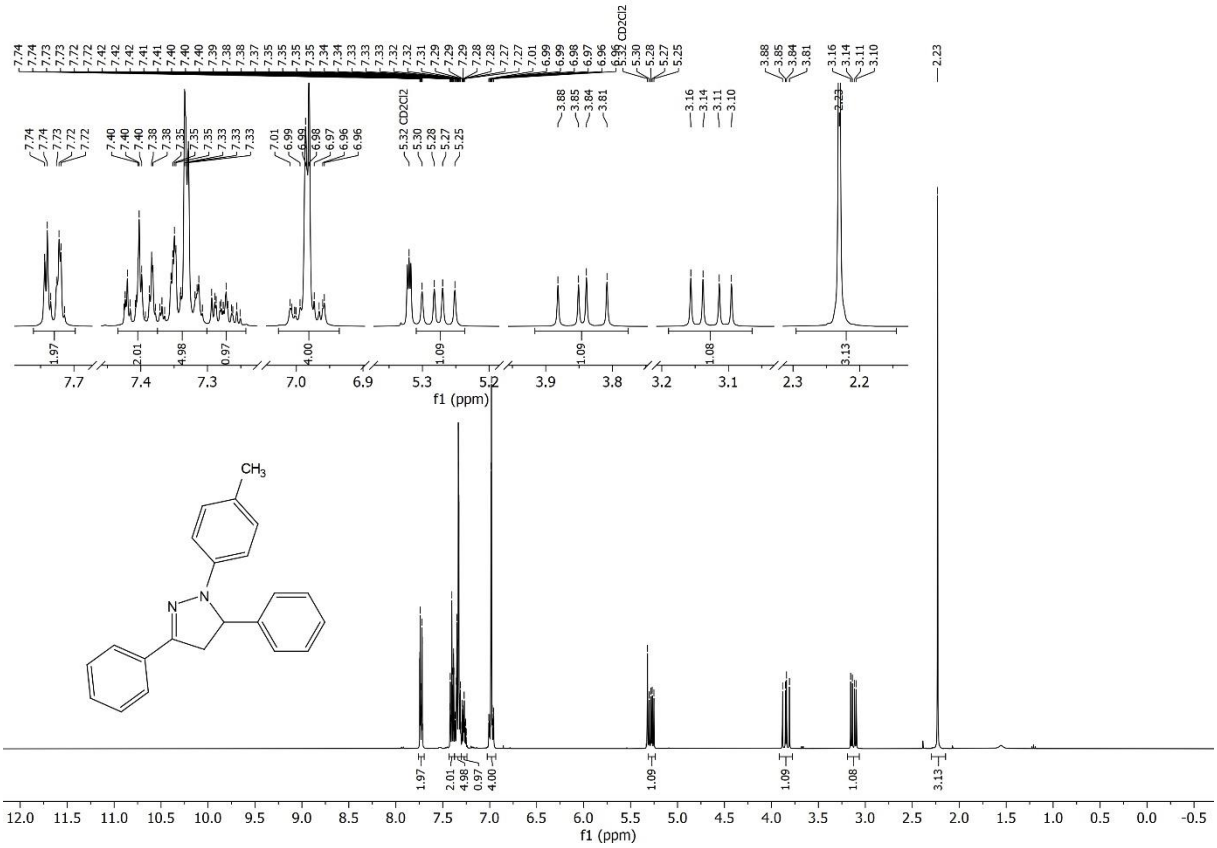

Figure S100: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4c'.**

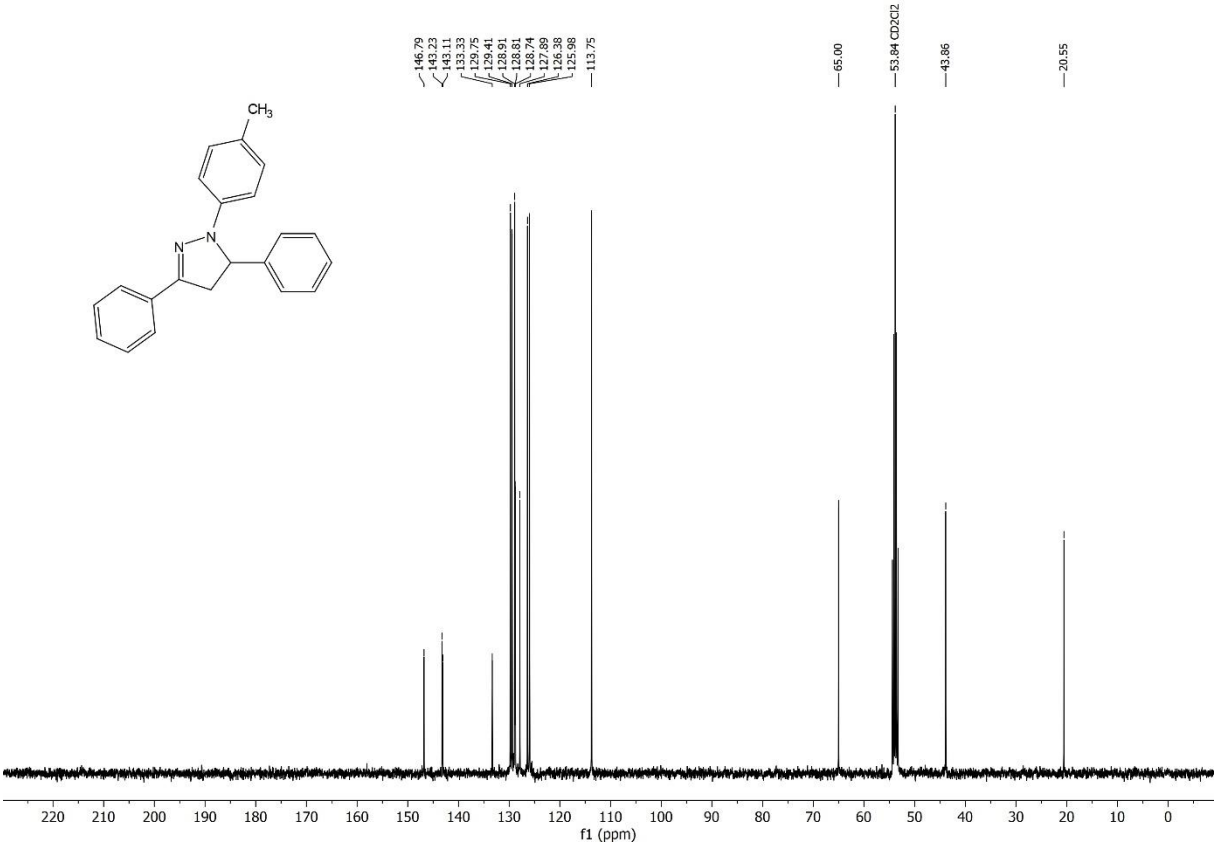

Figure S101: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4c'.**

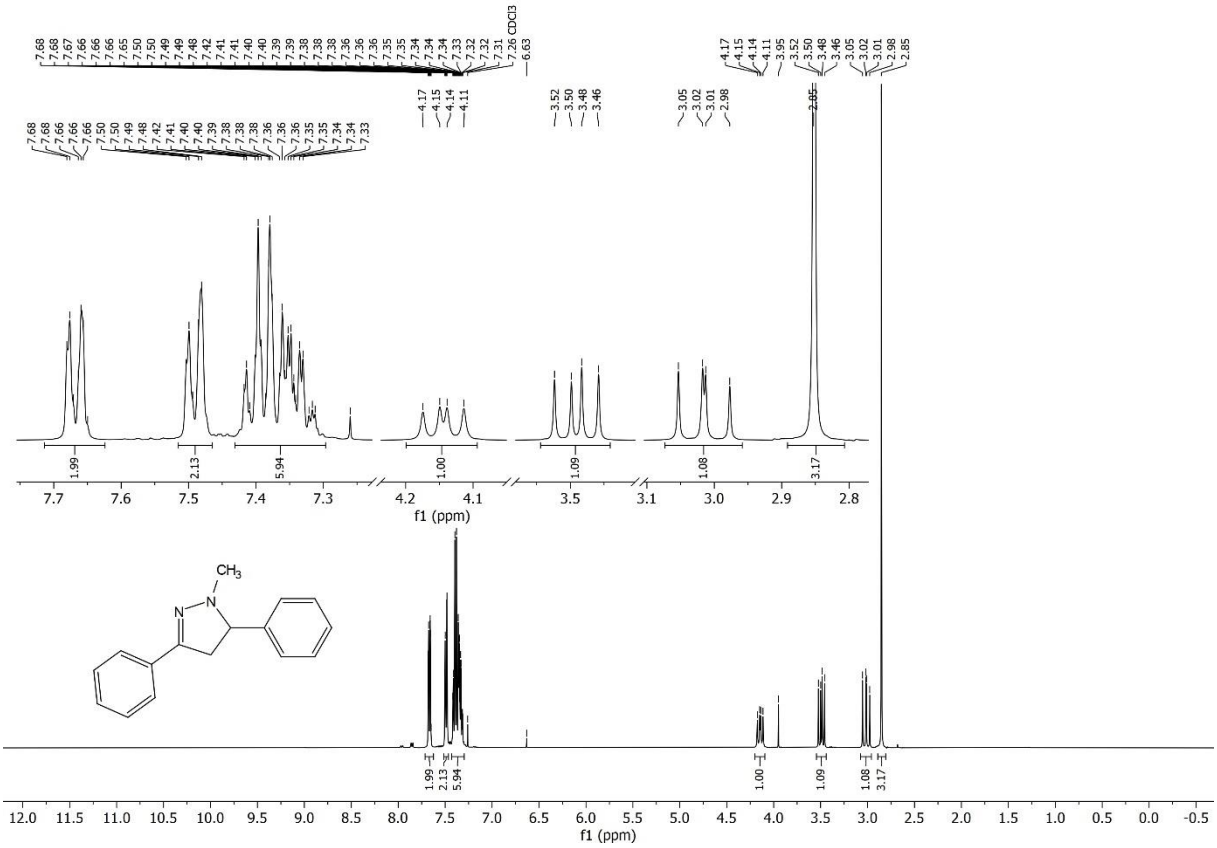

Figure S102: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4e'.**

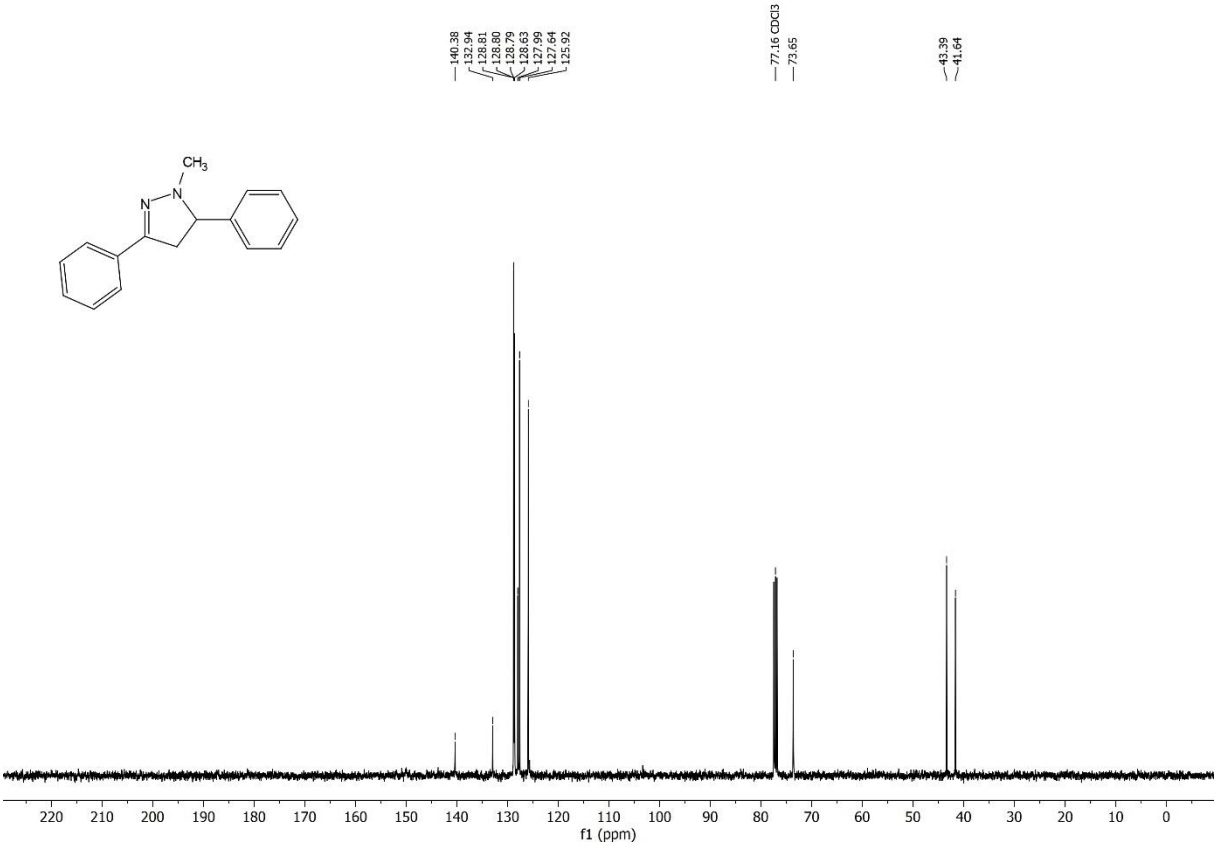

Figure S103: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4e'.**

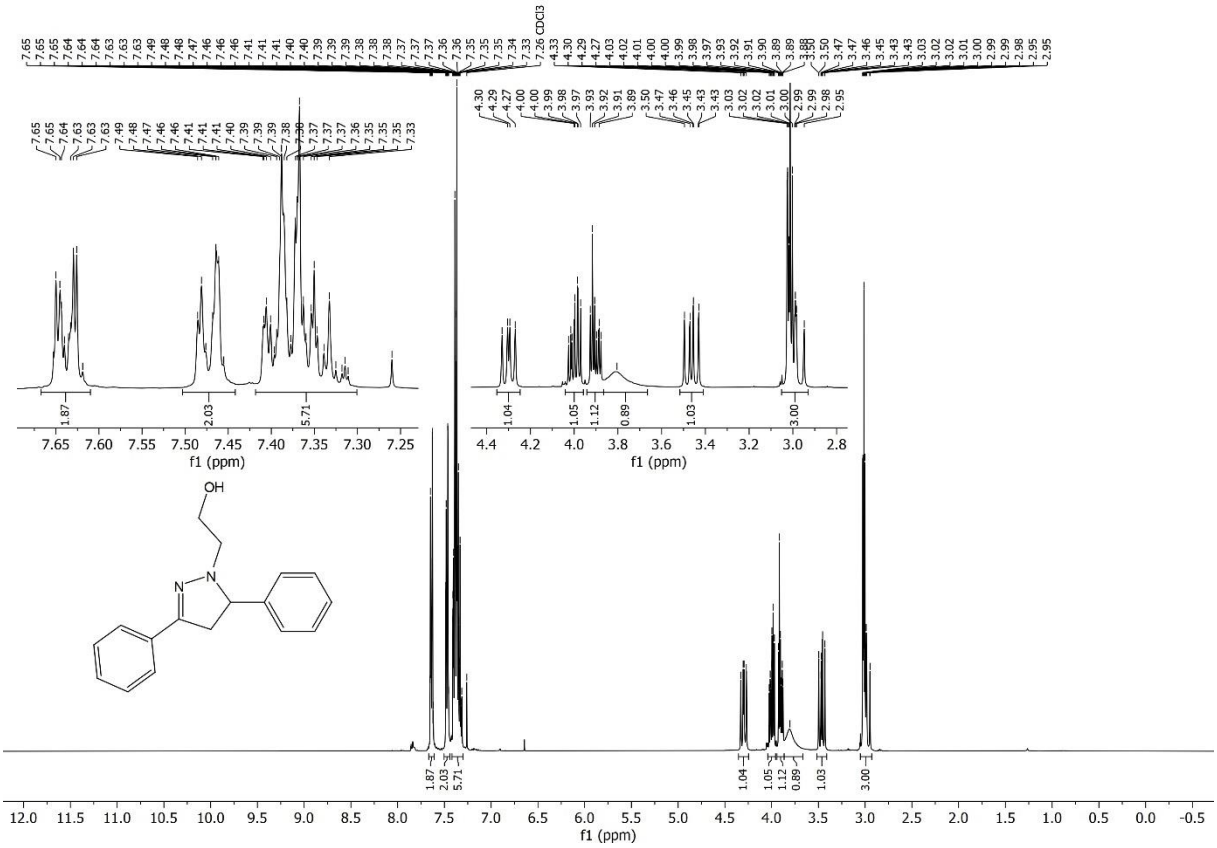

Figure S104: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4f'.**

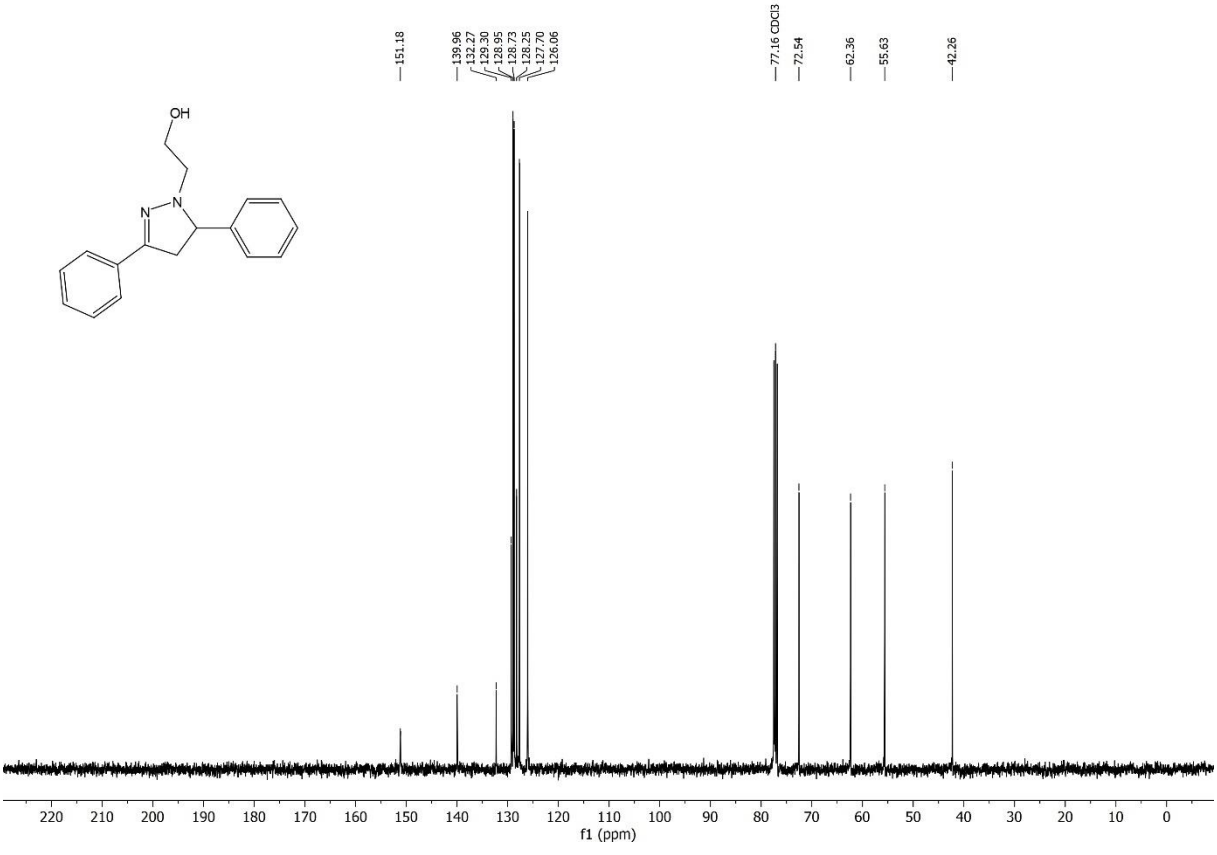

Figure S105: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4f'.**

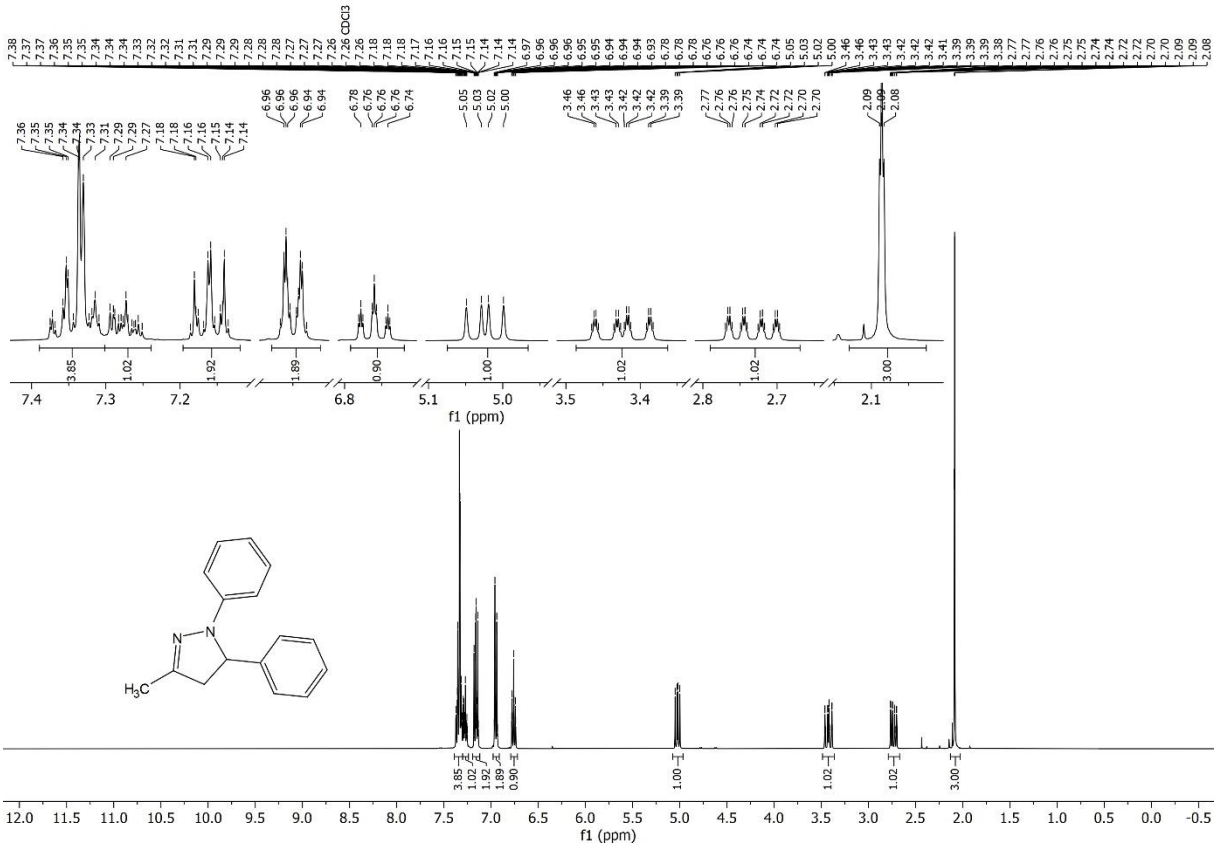

Figure S106: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4g'.**

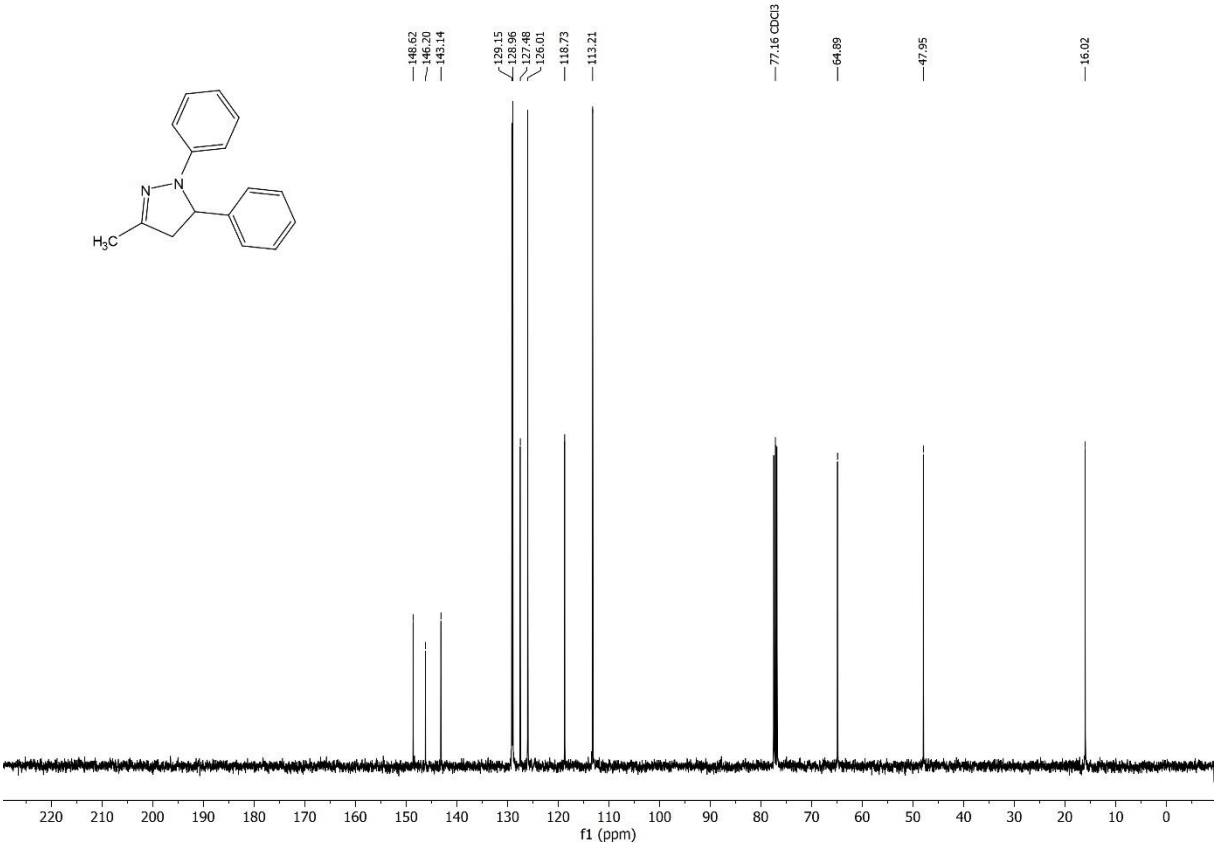

Figure S107: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4g'.**

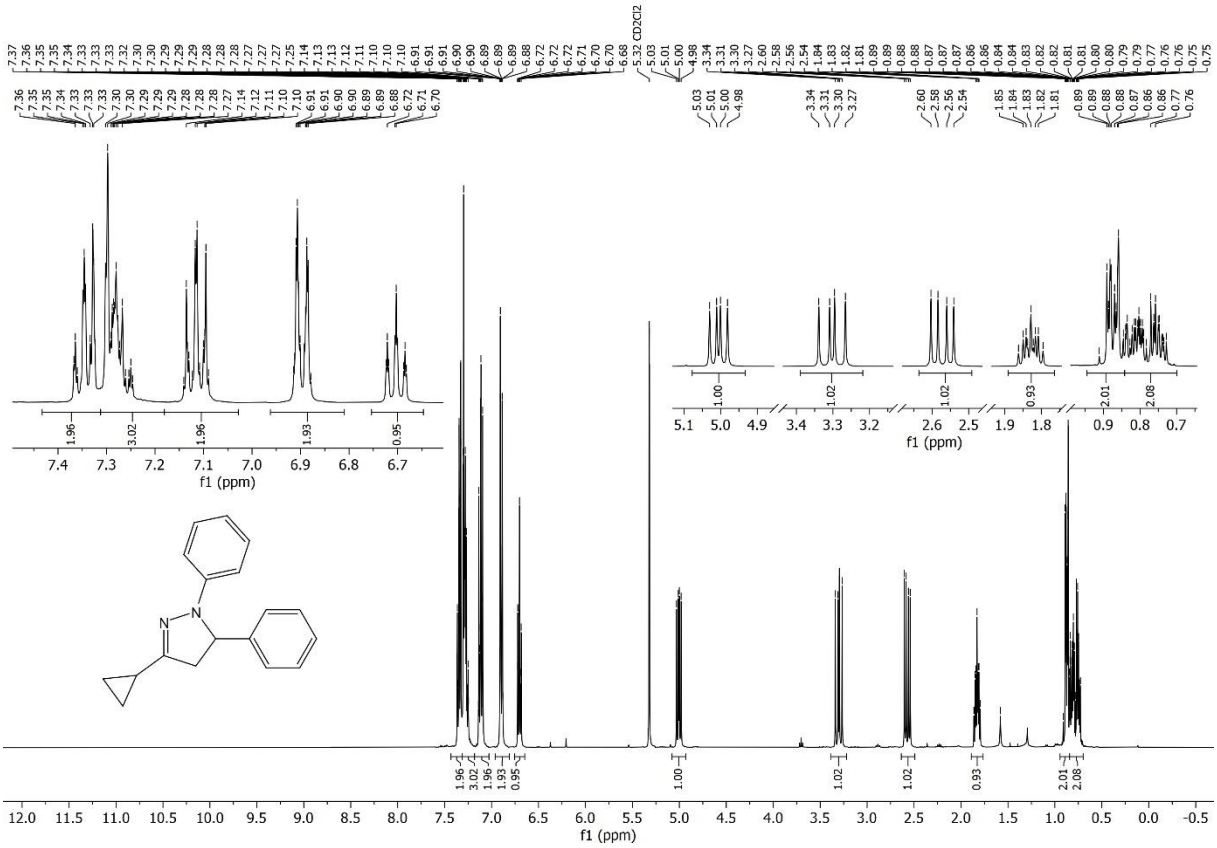

Figure S108: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4h'.**

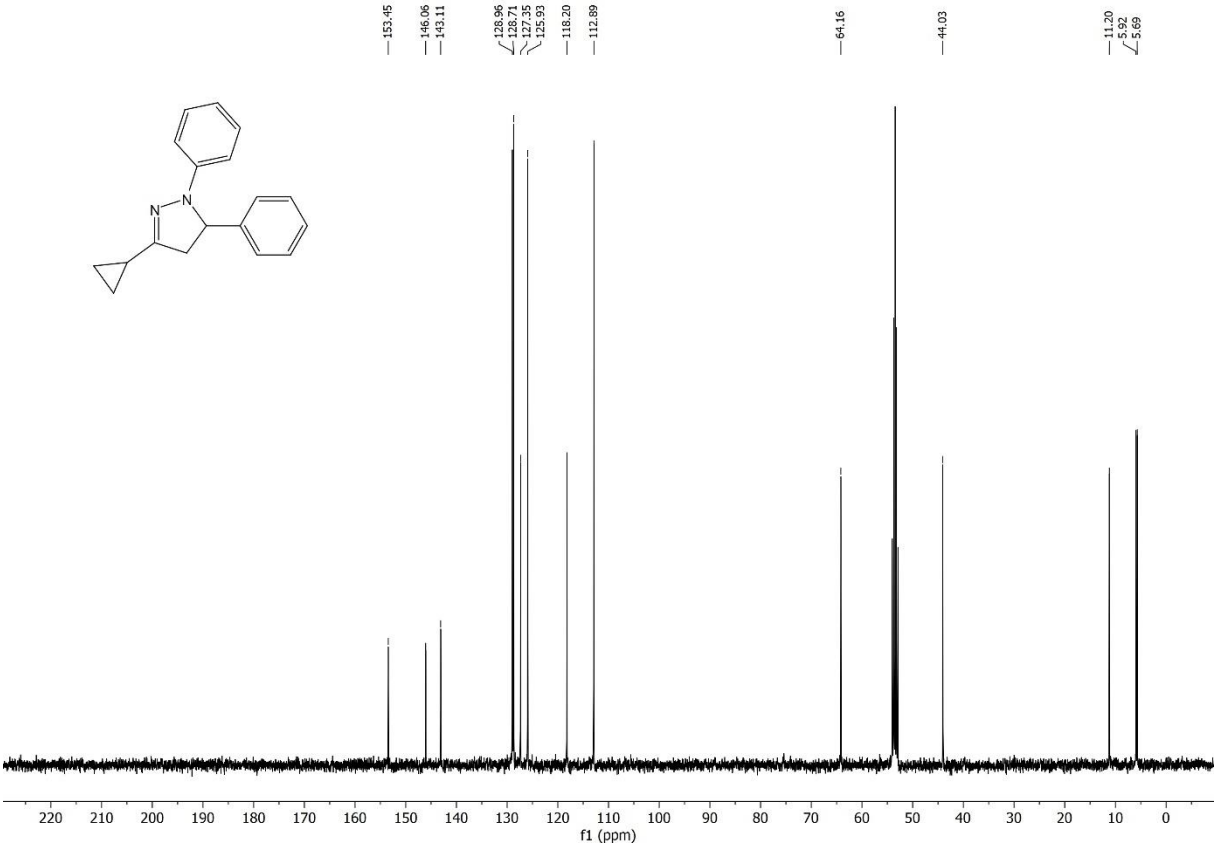

Figure S109: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4h'.**

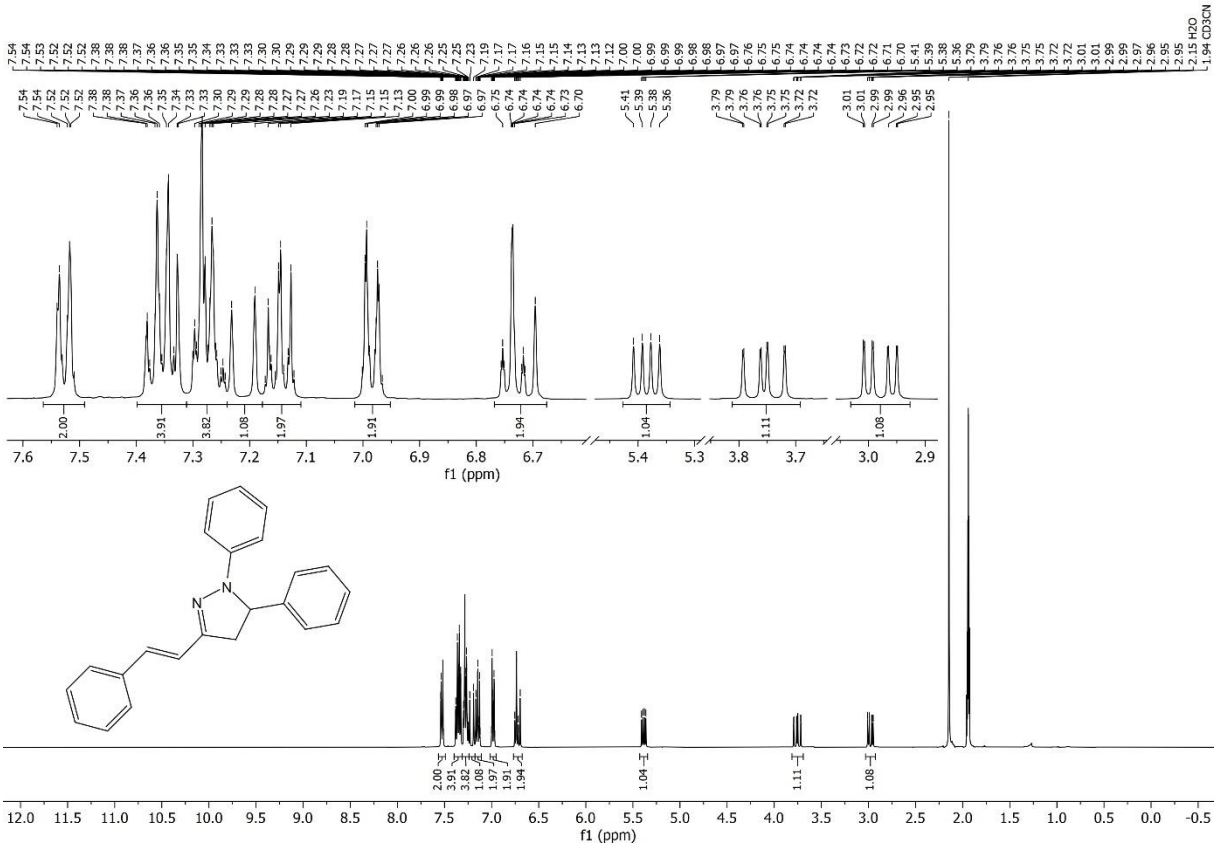

Figure S110: ^{1}H NMR spectrum (400 MHz, CD_3CN) of **4i'.**

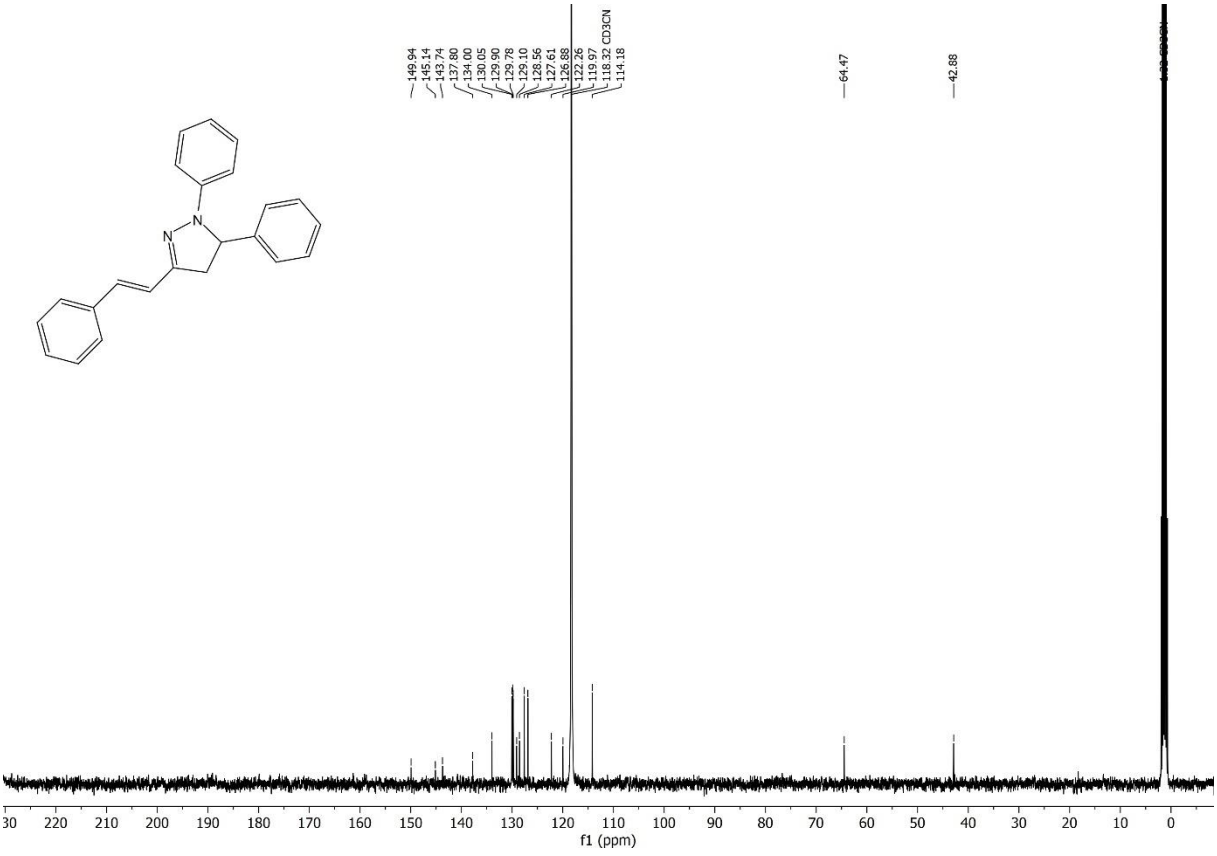

Figure S111: ^{13}C NMR spectrum (101 MHz, CD_3CN) of **4i'.**

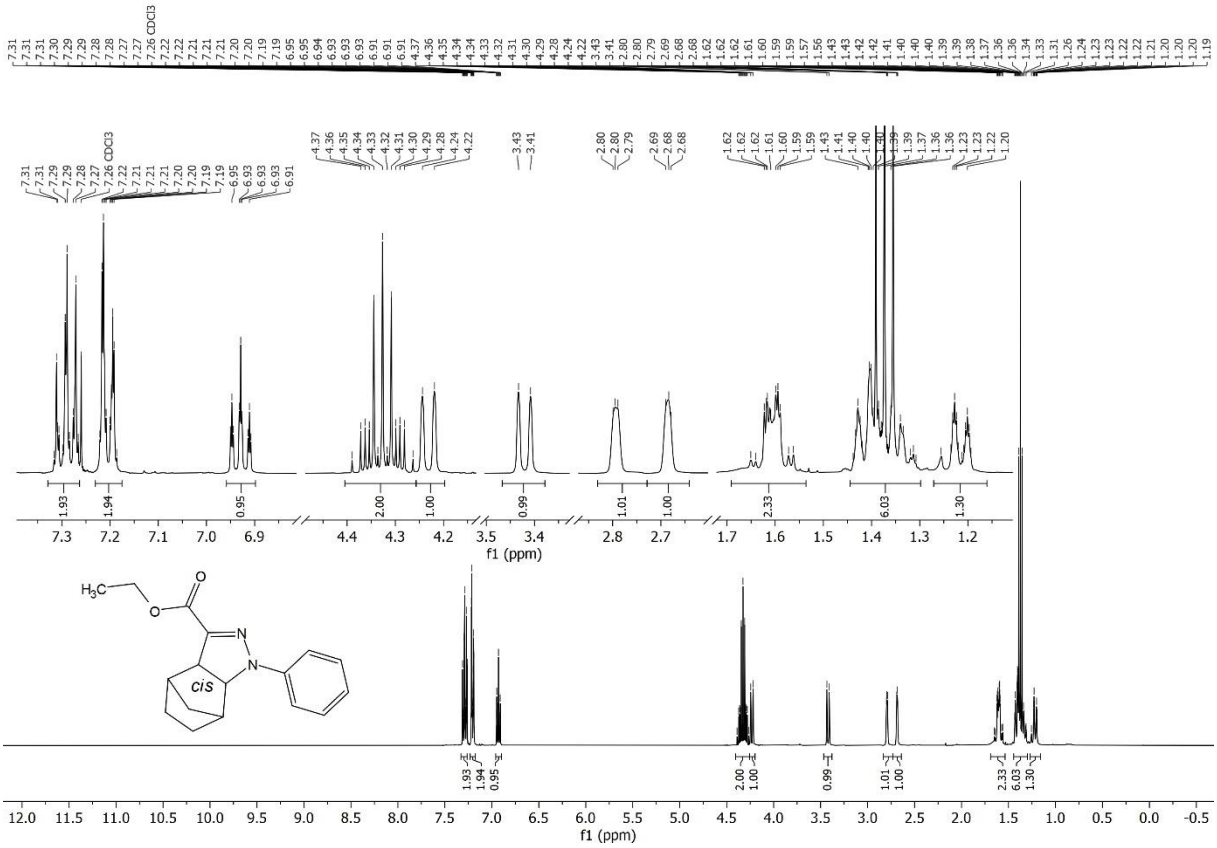

Figure S112: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4j'.**

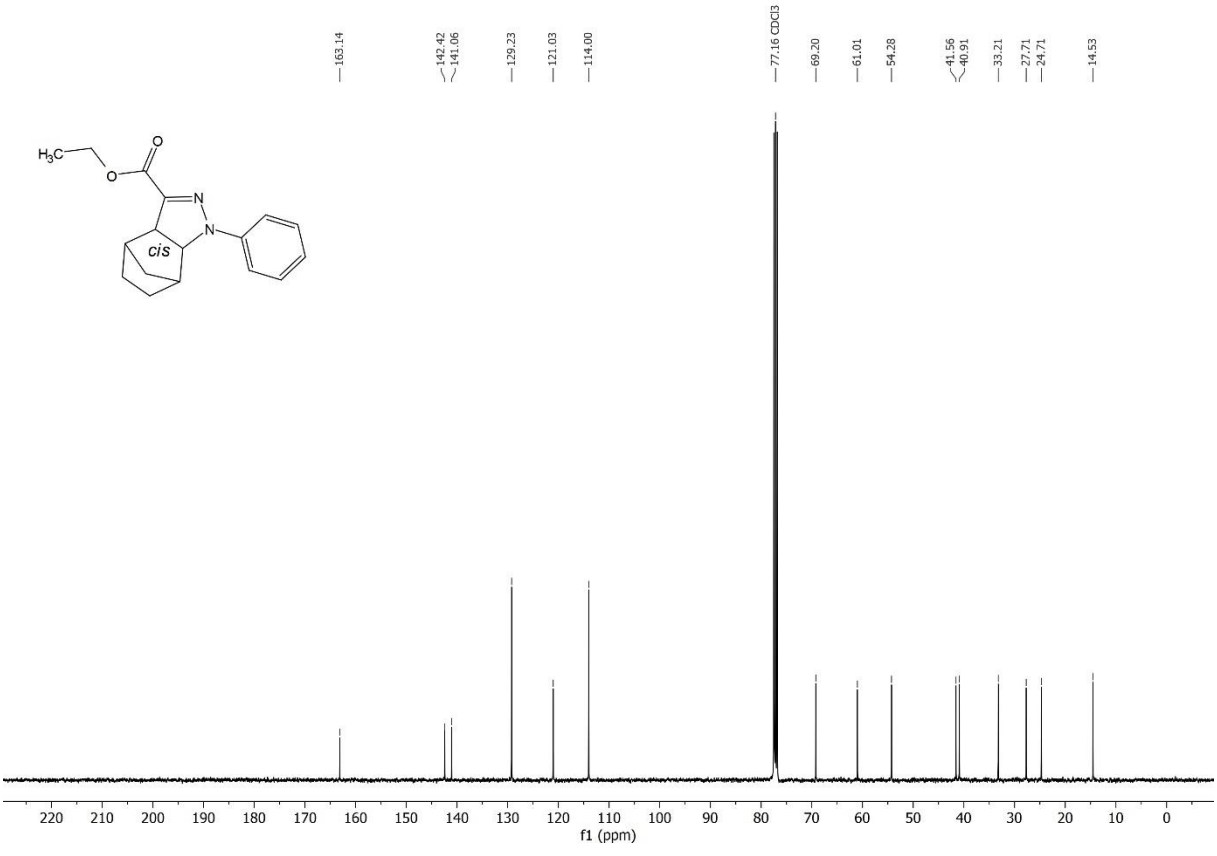

Figure S113: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4j'.**

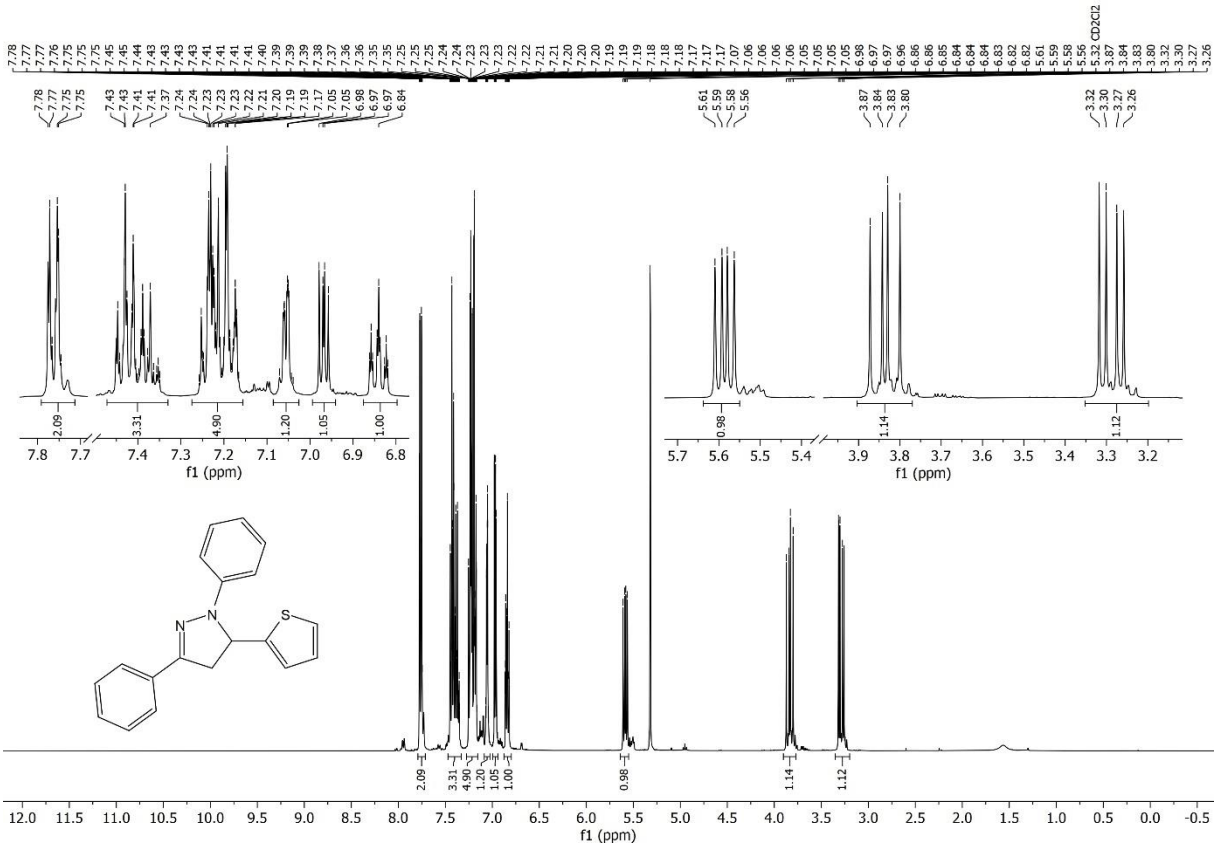

Figure S114: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4k'.**

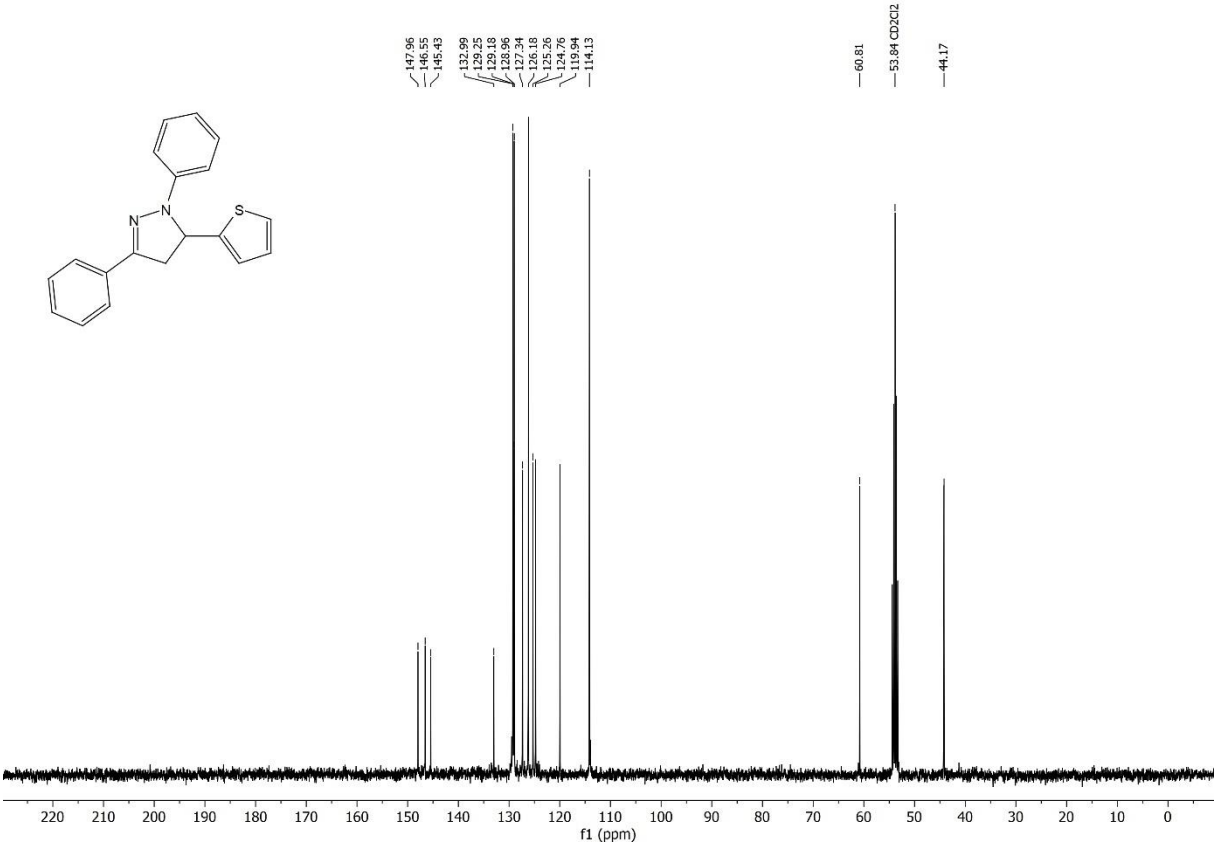

Figure S115: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **4k'.**

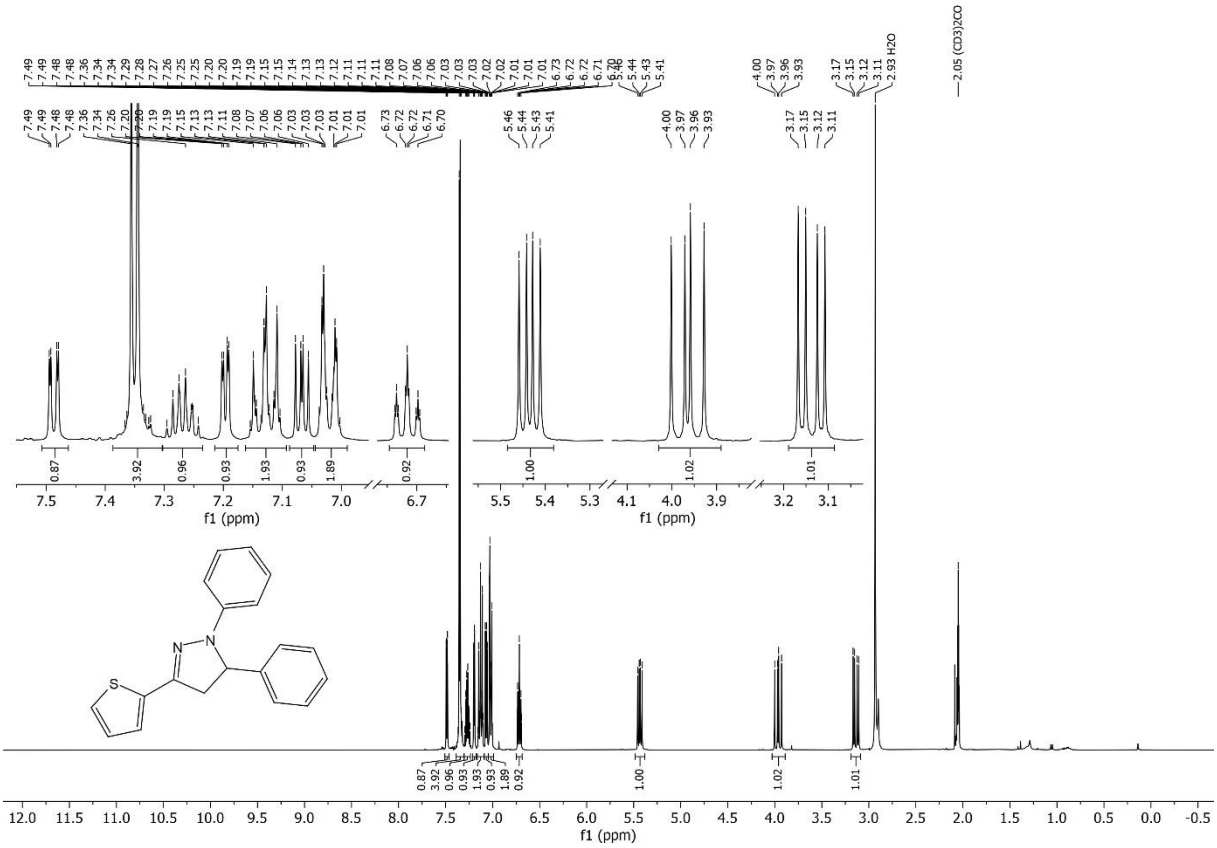

Figure S116: ^{1}H NMR spectrum (400 MHz, acetone-d_6) of **4l'.**

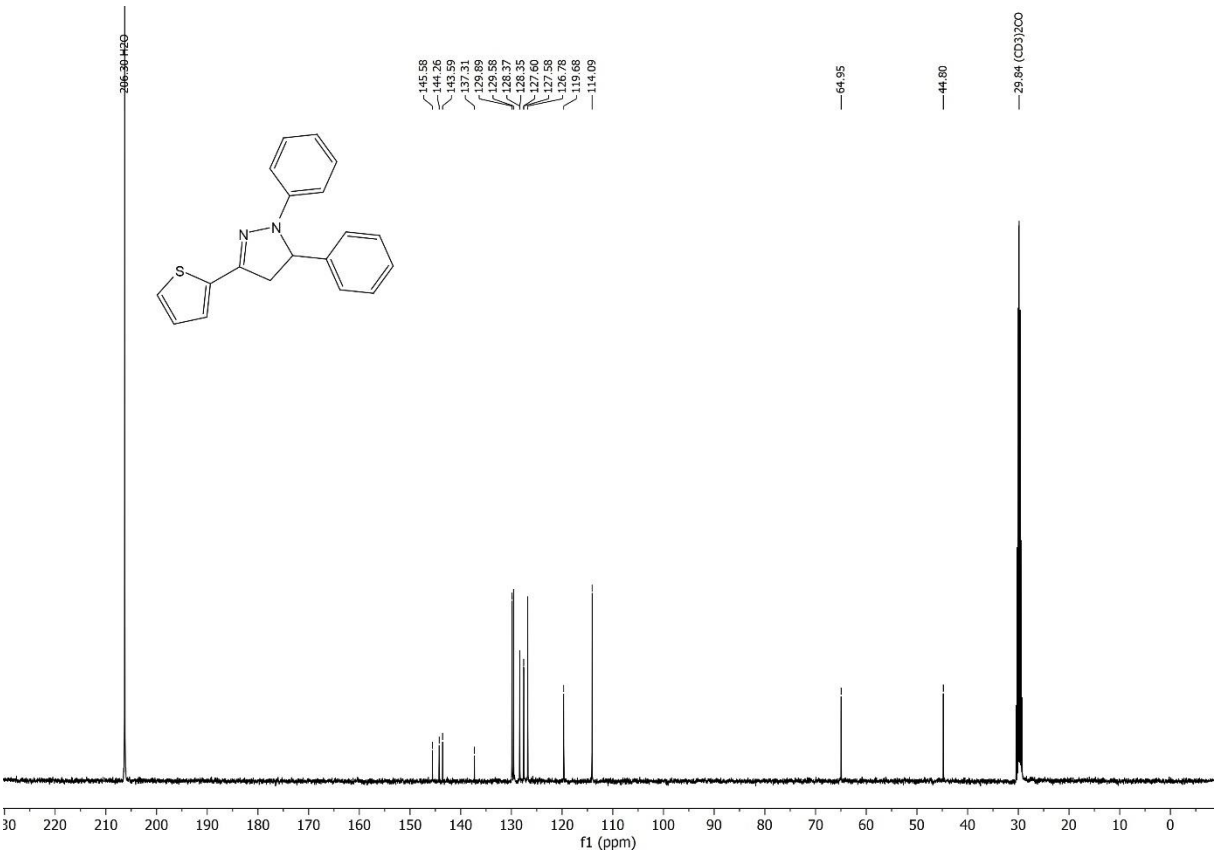

Figure S117: ^{13}C NMR spectrum (101 MHz, acetone-d_6) of **4l'.**

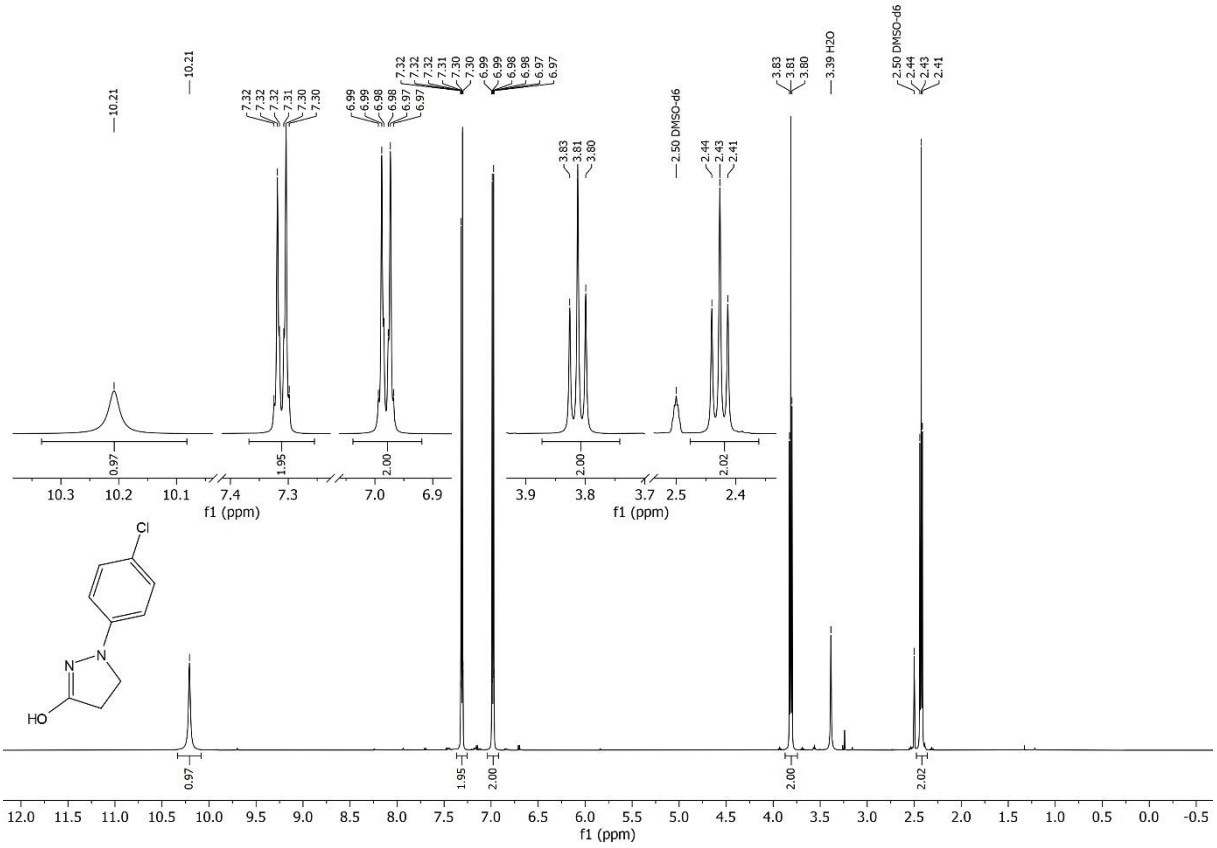

Figure S118: ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **4m'.**

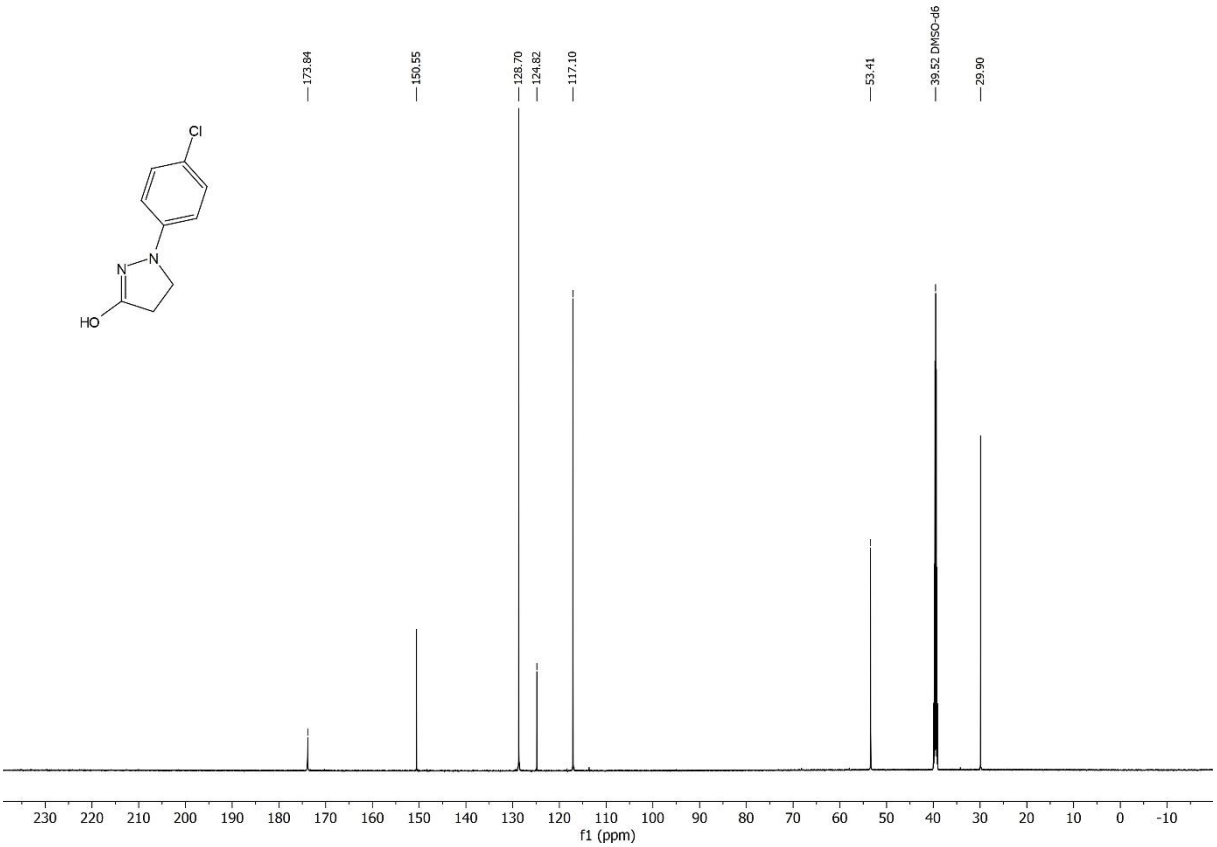

Figure S119: ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **4m'.**

11.3. NMR Spectra of Pyrazoles

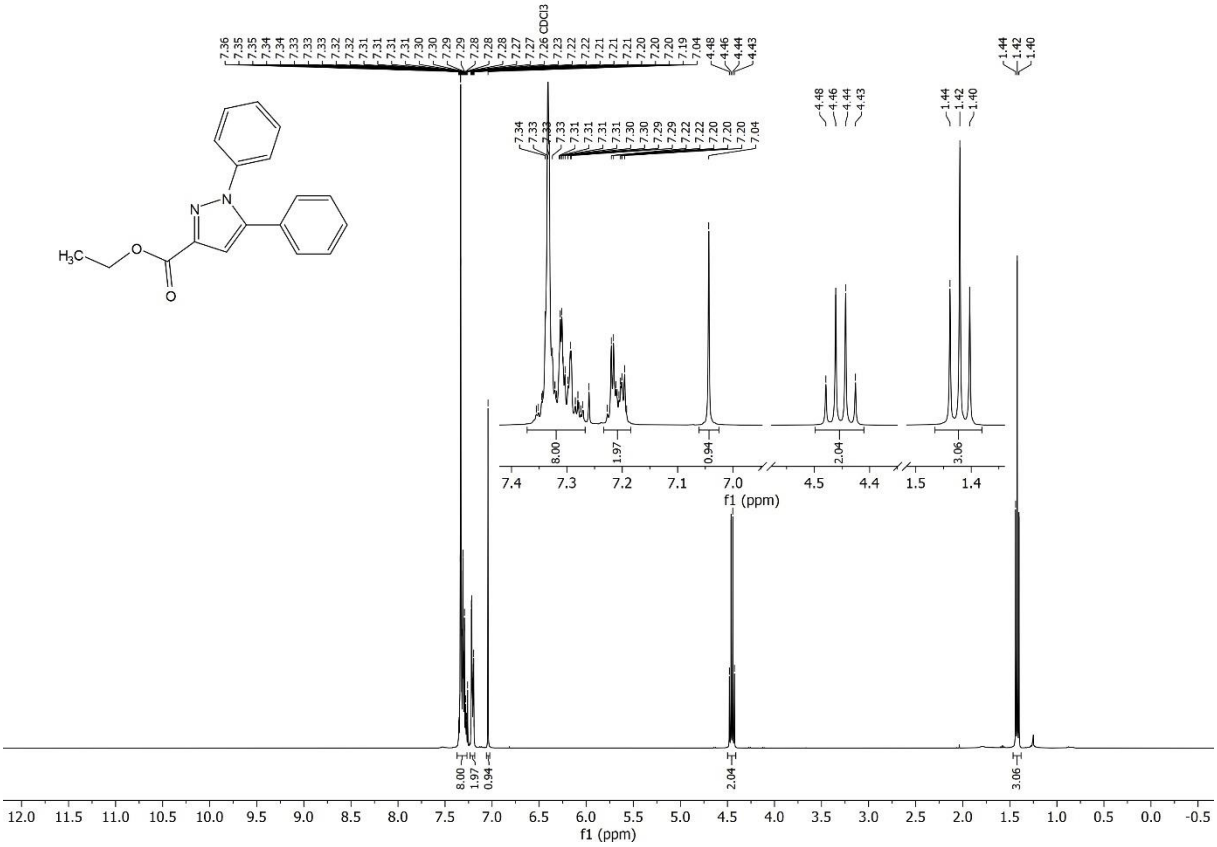

Figure S120: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a.**

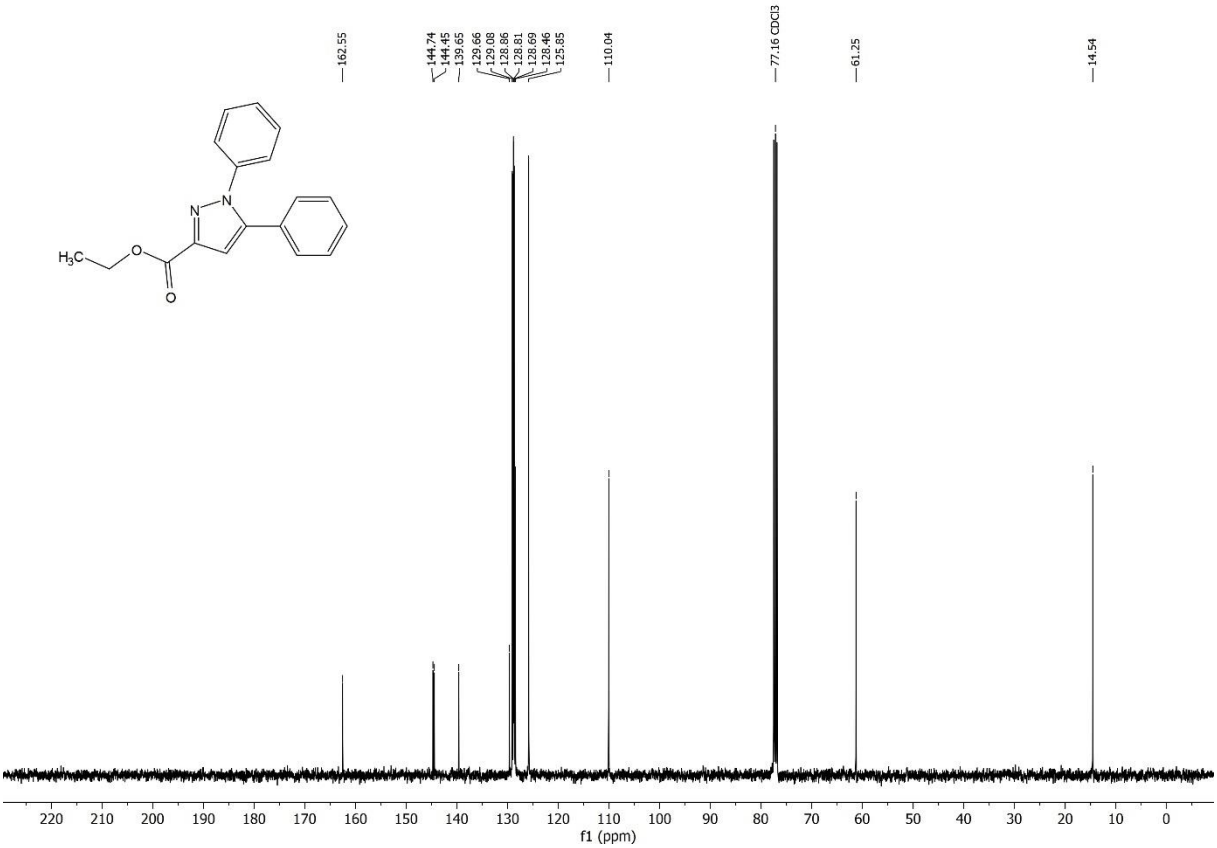

Figure S121: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5a.**

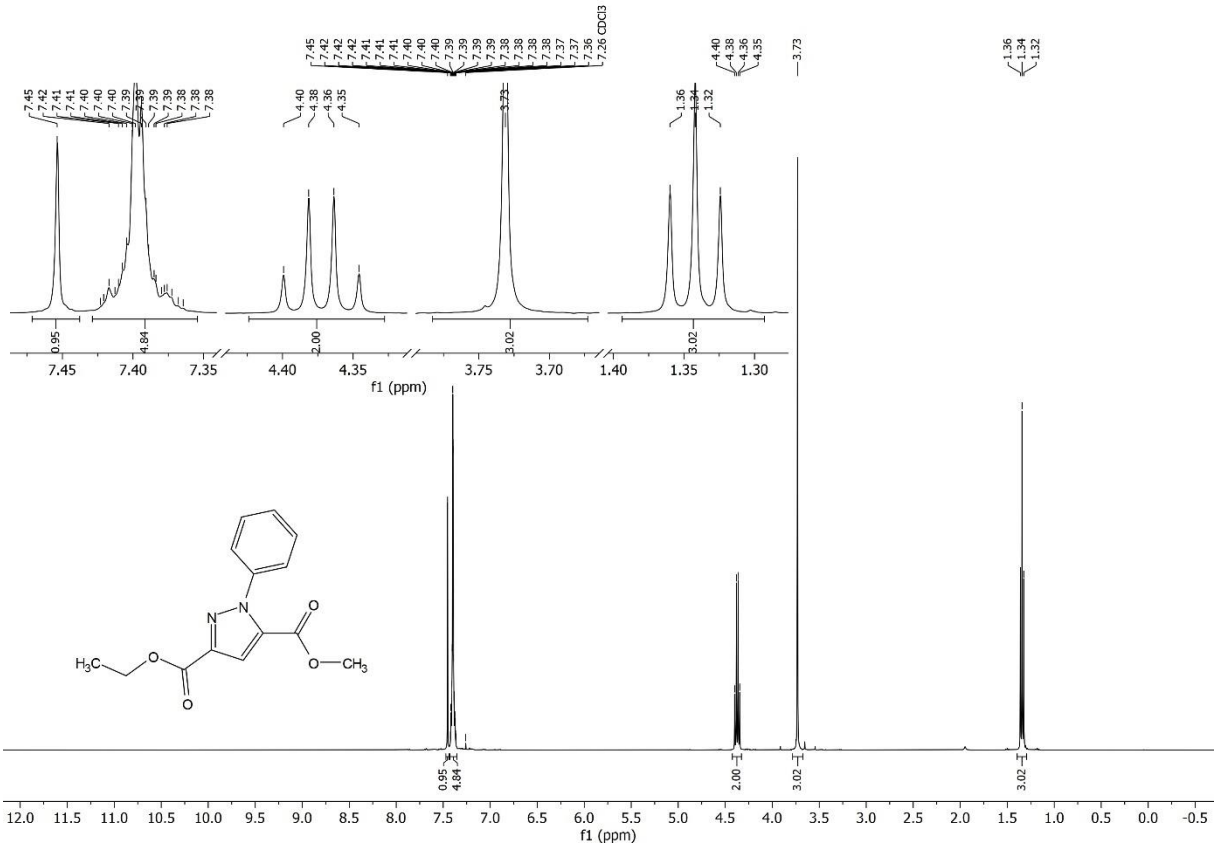

Figure S122: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b.**

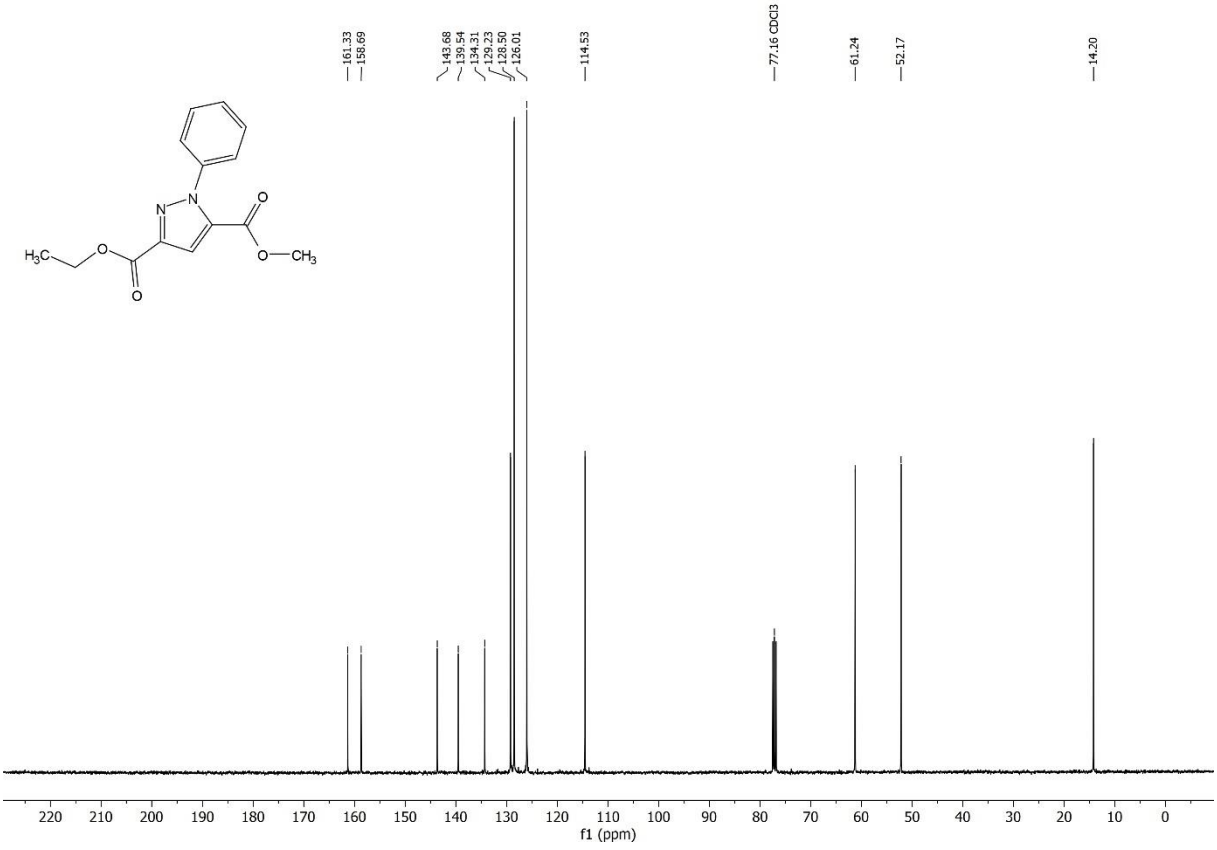

Figure S123: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5b.**

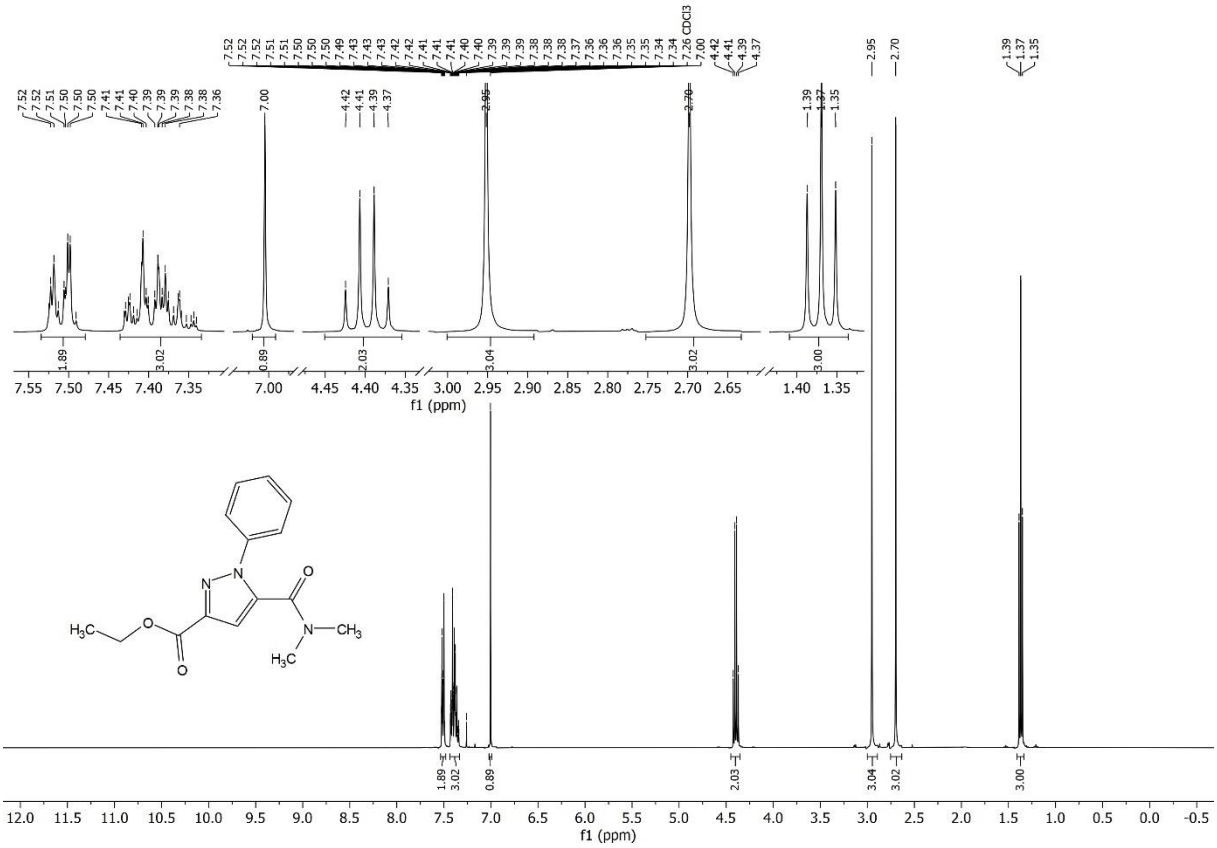

Figure S124: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c.**

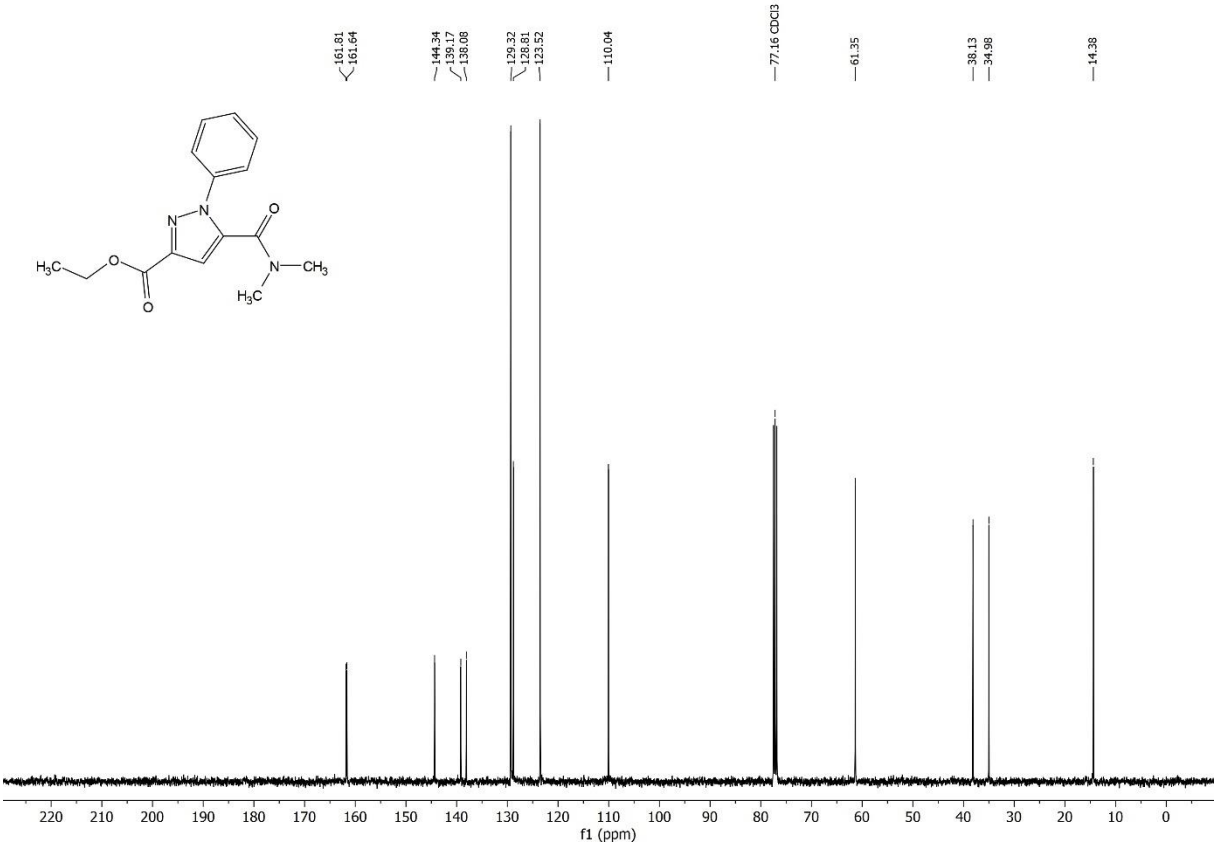

Figure S125: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5c.**

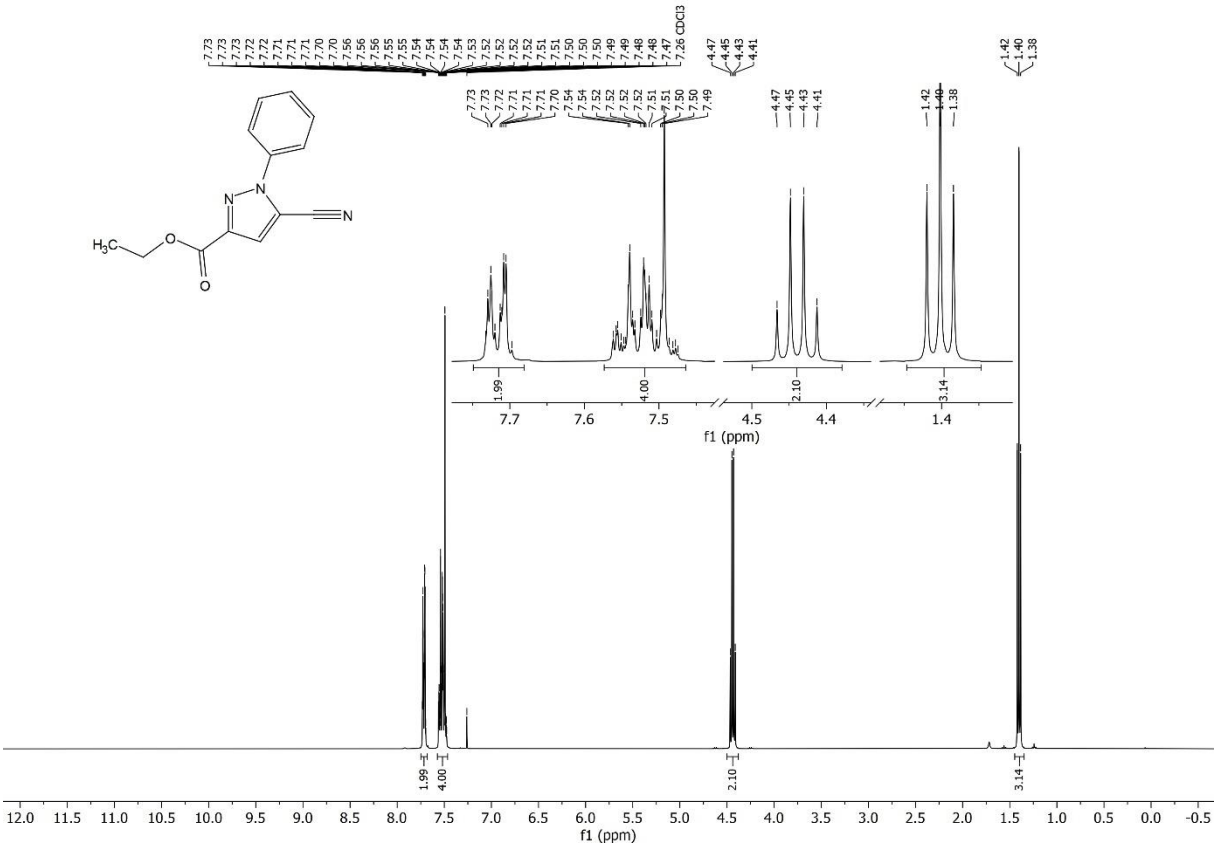

Figure S126: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5d.**

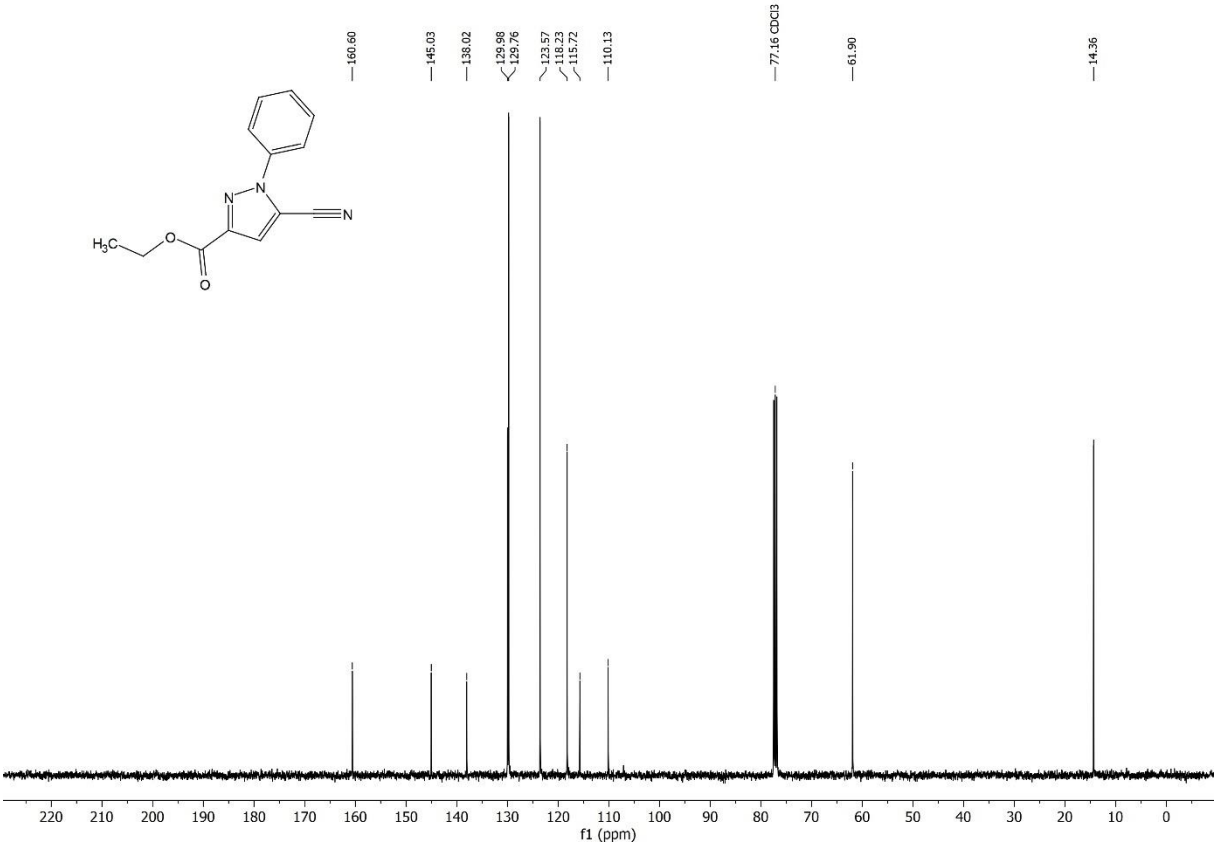

Figure S127: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5d.**

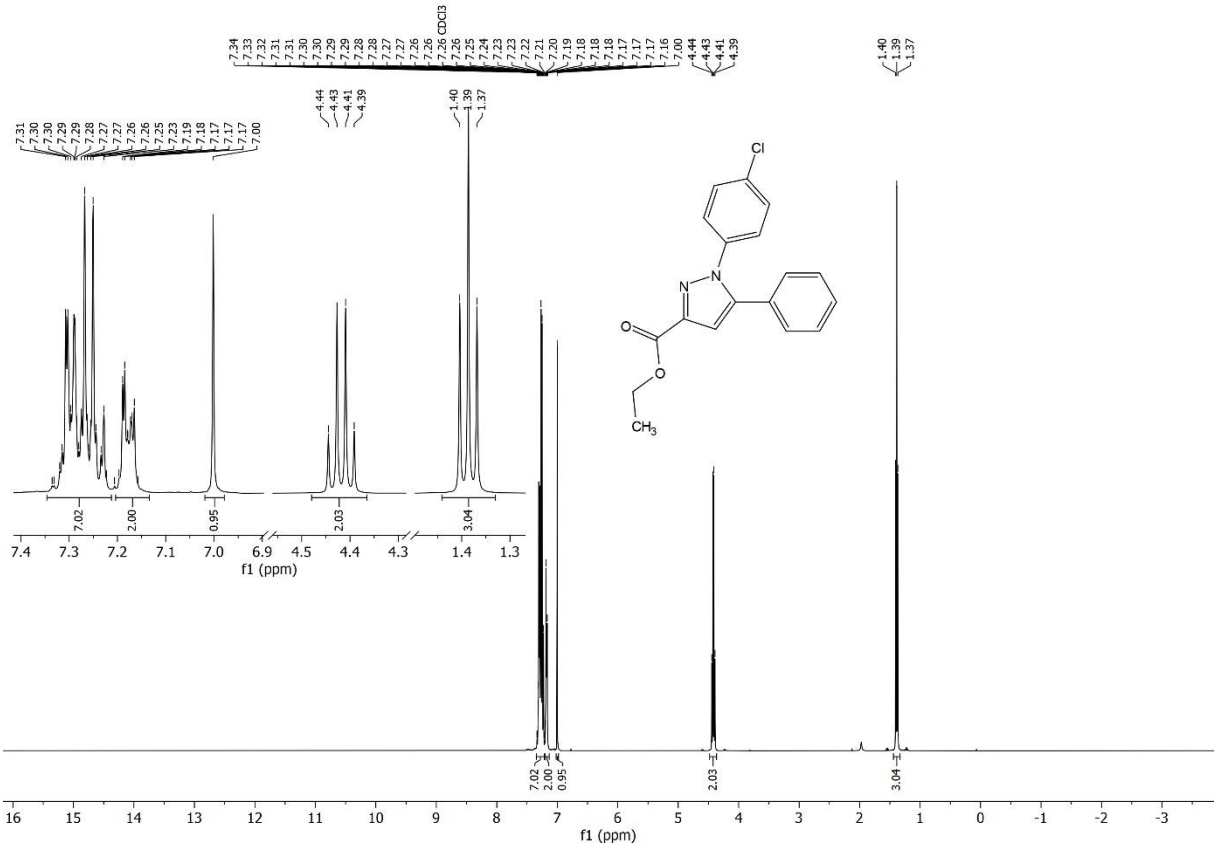

Figure S128: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5e.**

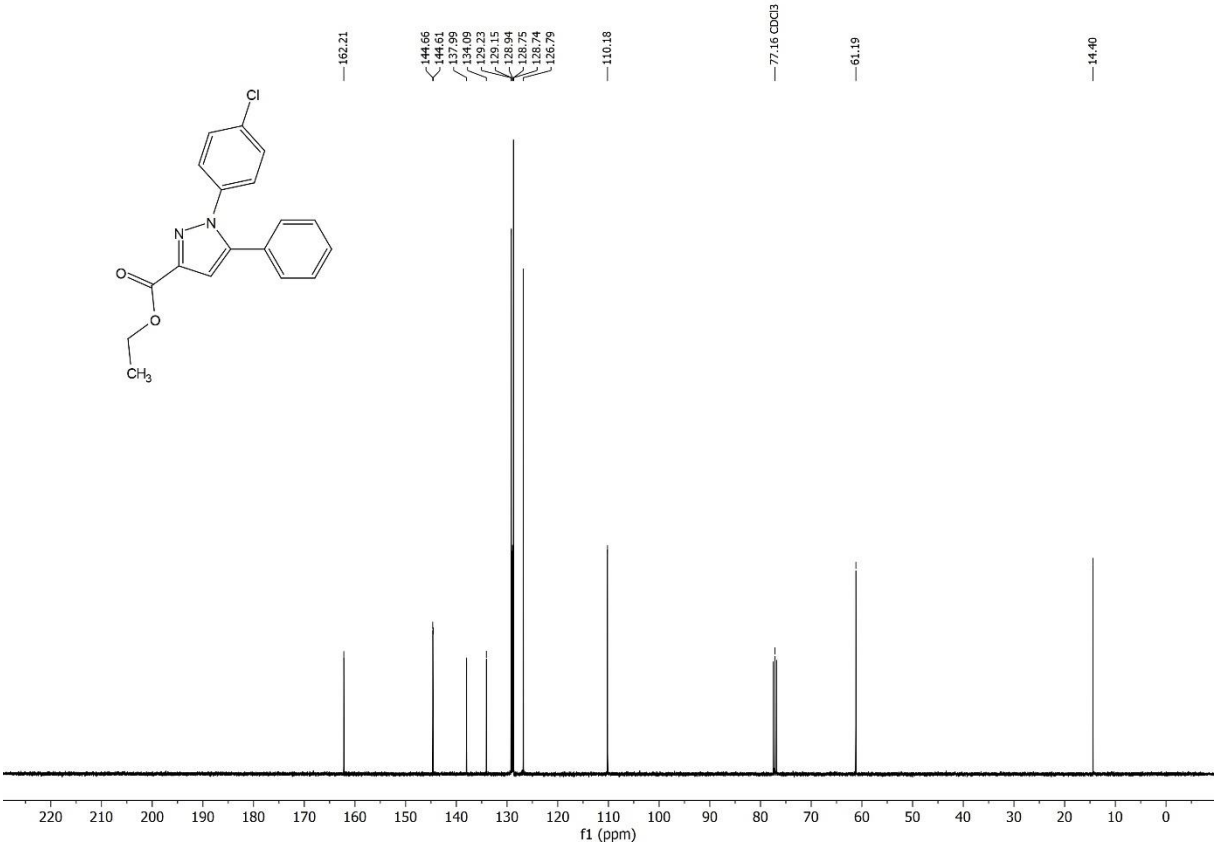

Figure S129: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5e.**

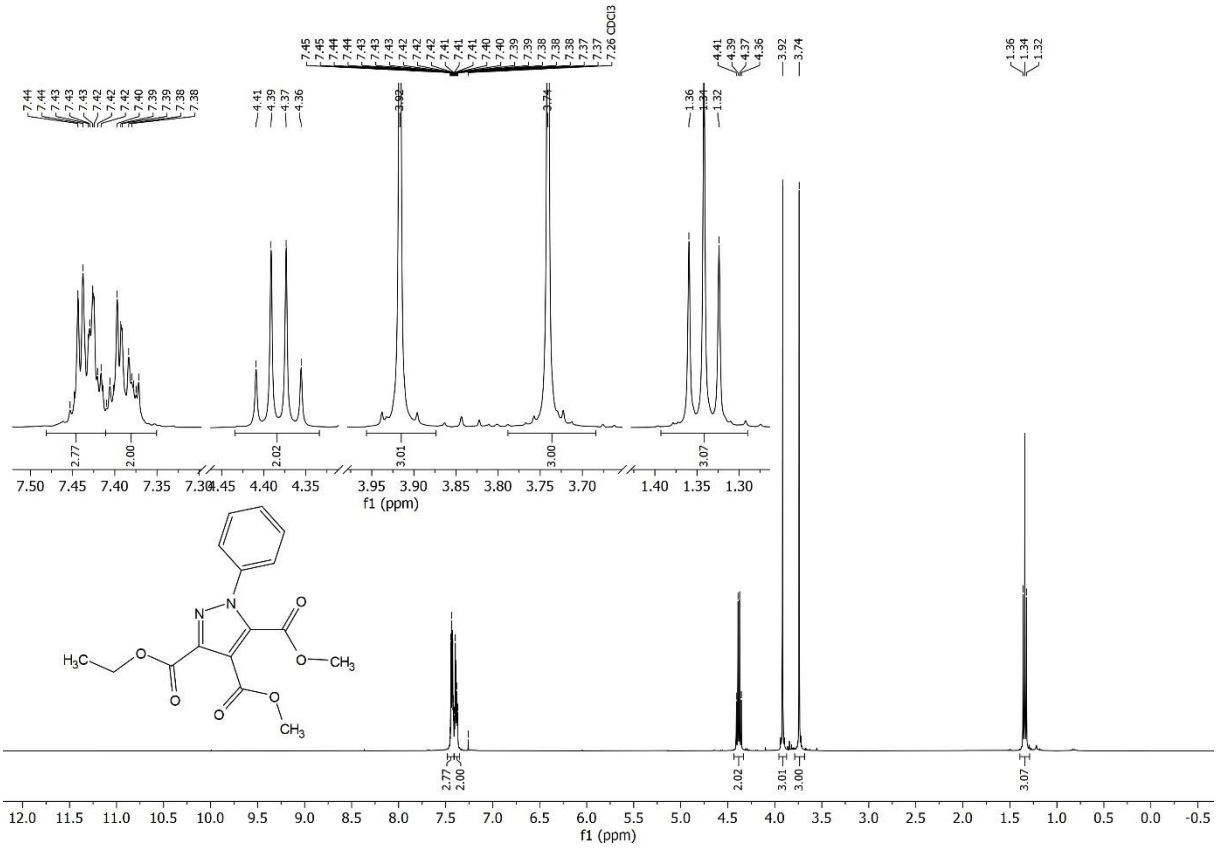

Figure S130: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5f.**

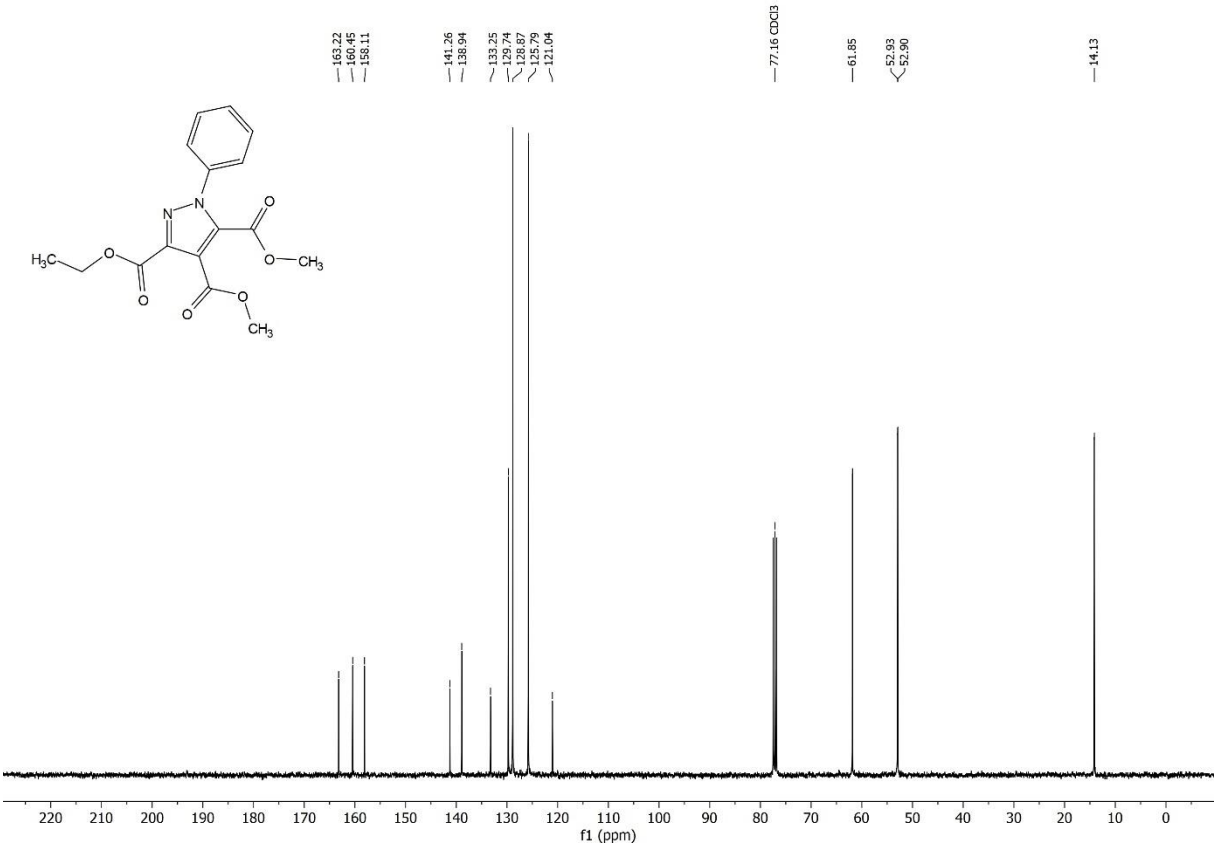

Figure S131: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5f.**

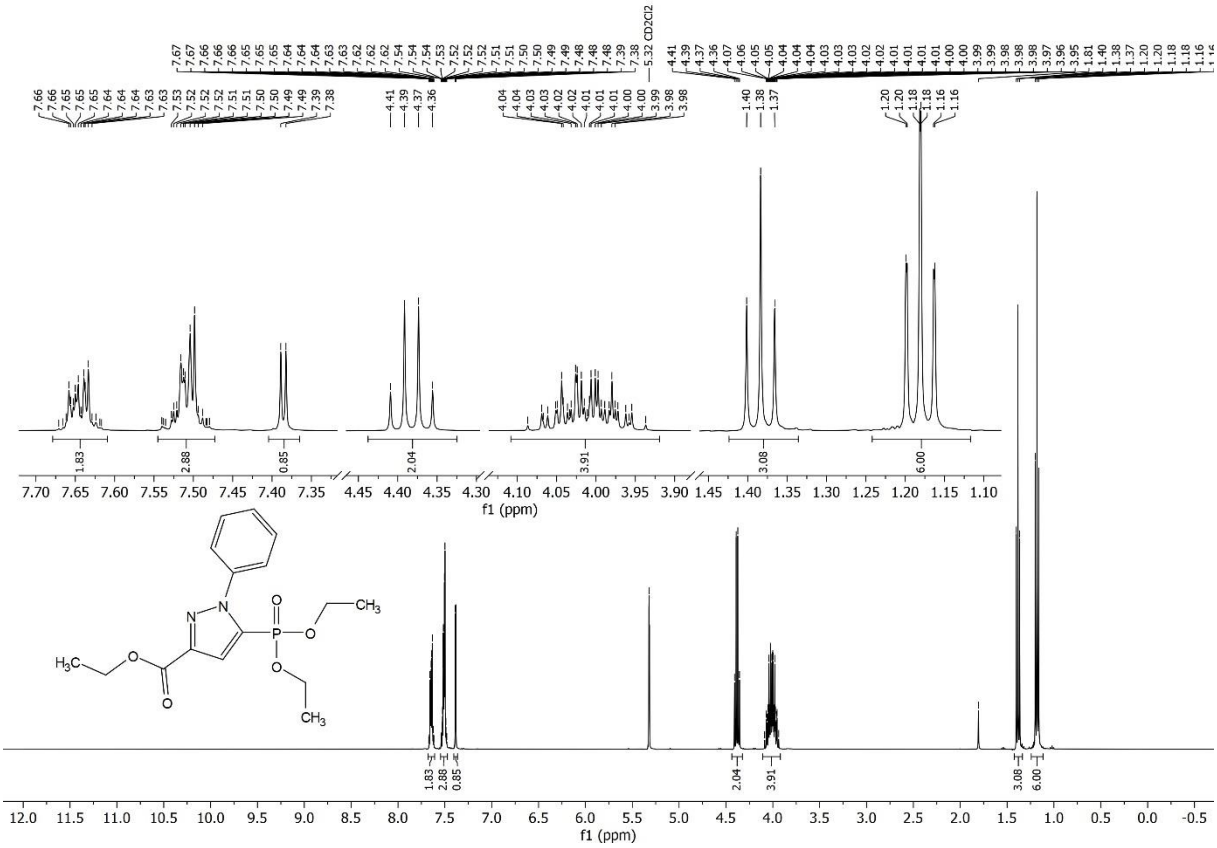

Figure S132: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5g.**

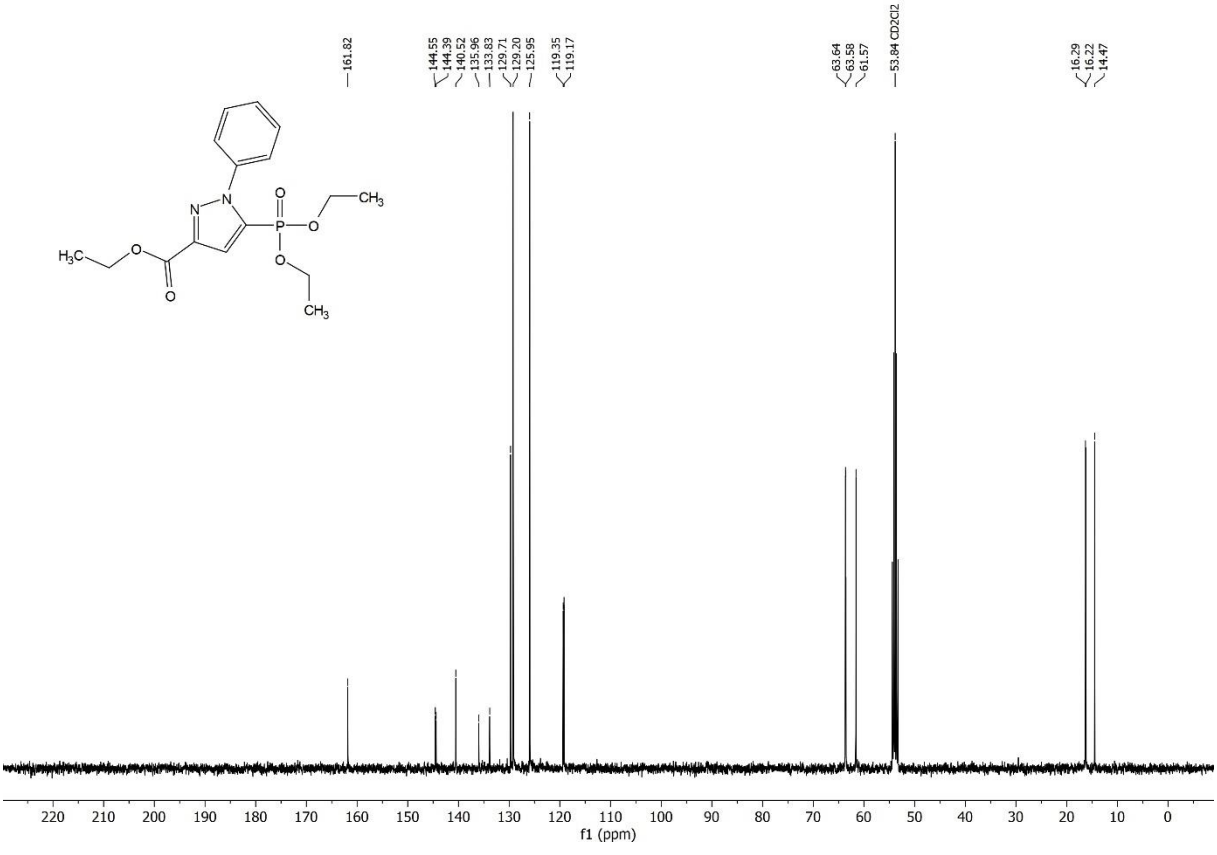

Figure S133: ^{13}C NMR spectrum (101 MHz, CD_2Cl_2) of **5g.**

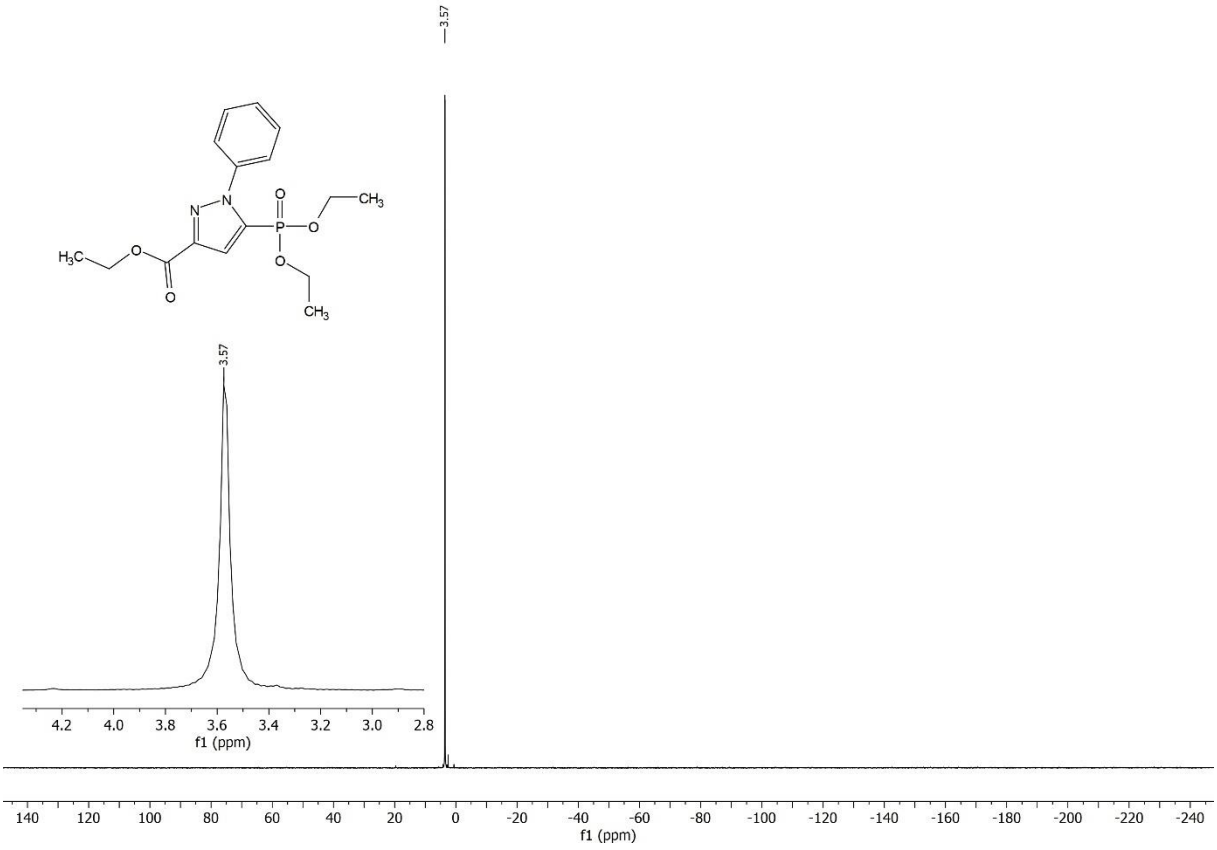

Figure S134: ^{31}P NMR spectrum (162 MHz, CD_2Cl_2) of **5g.**

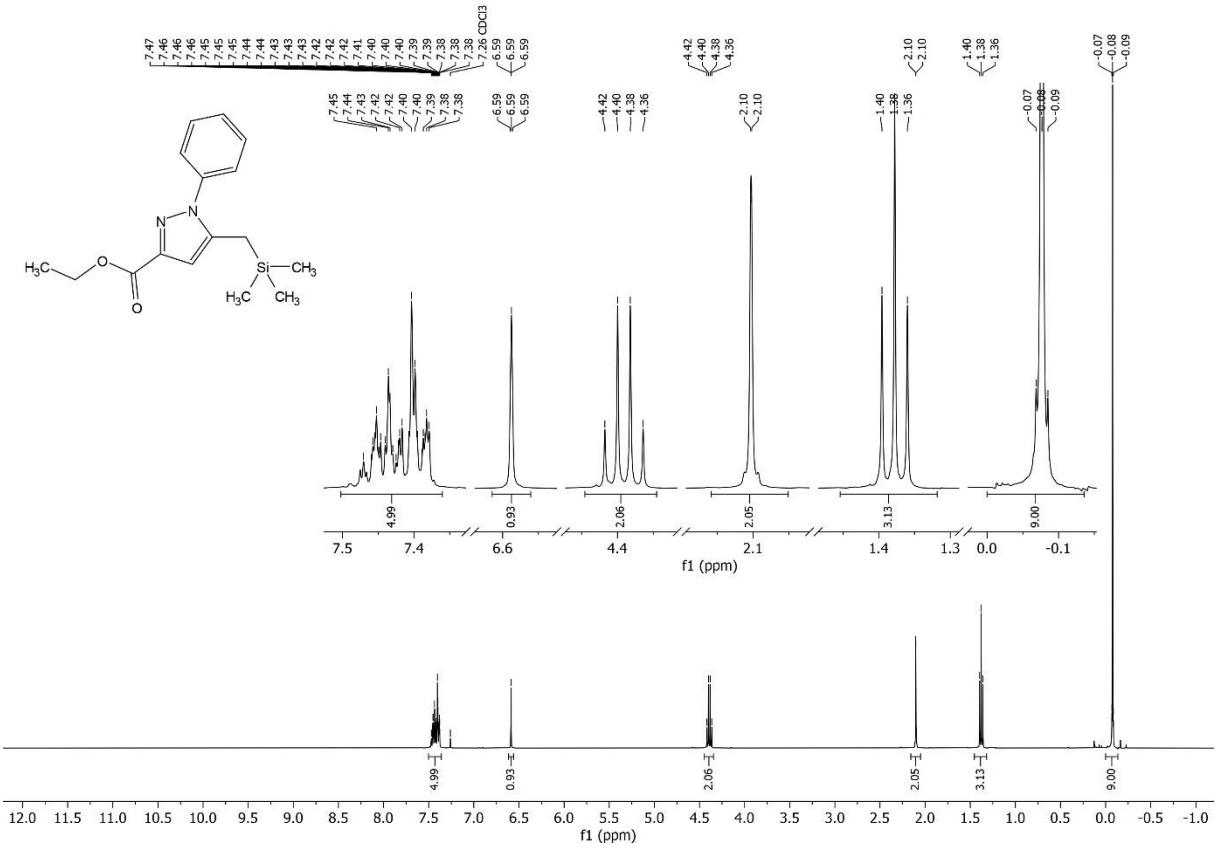

Figure S135: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5h.**

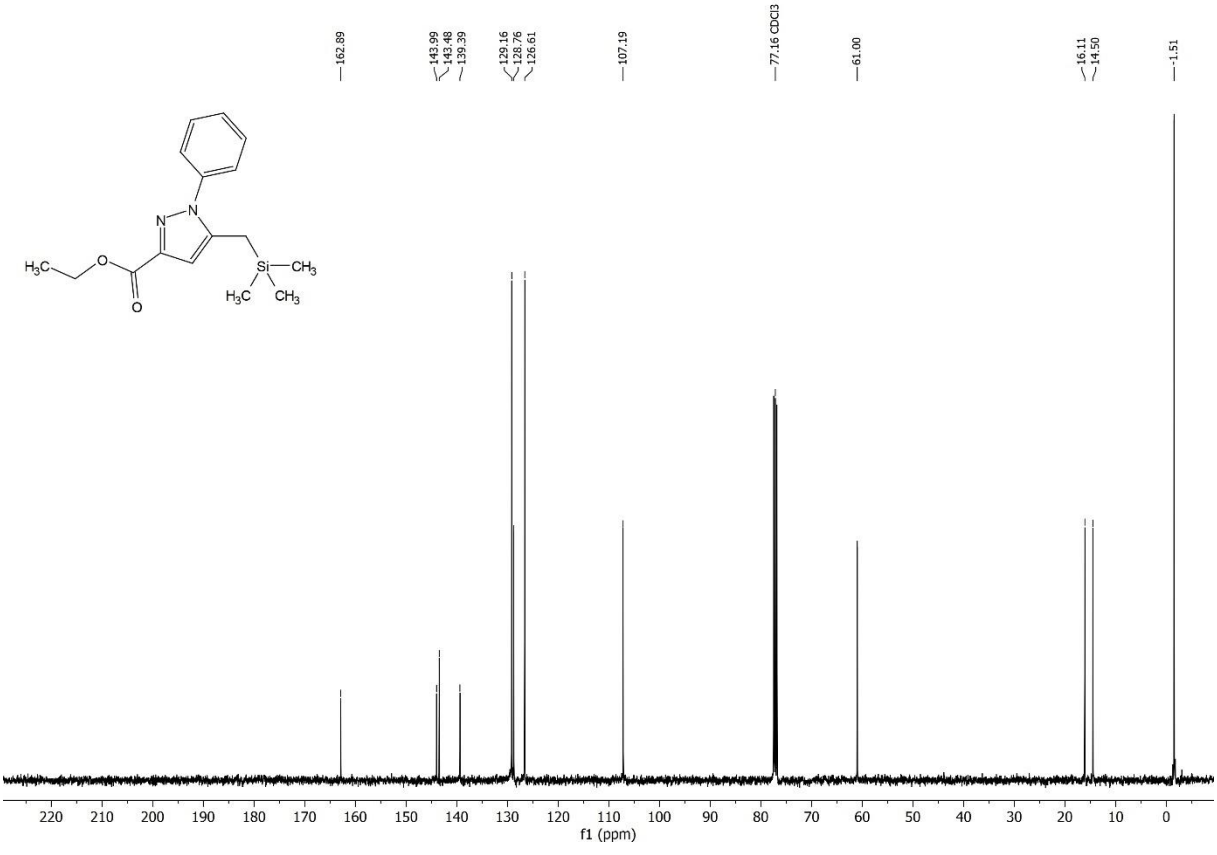

Figure S136: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5h.**

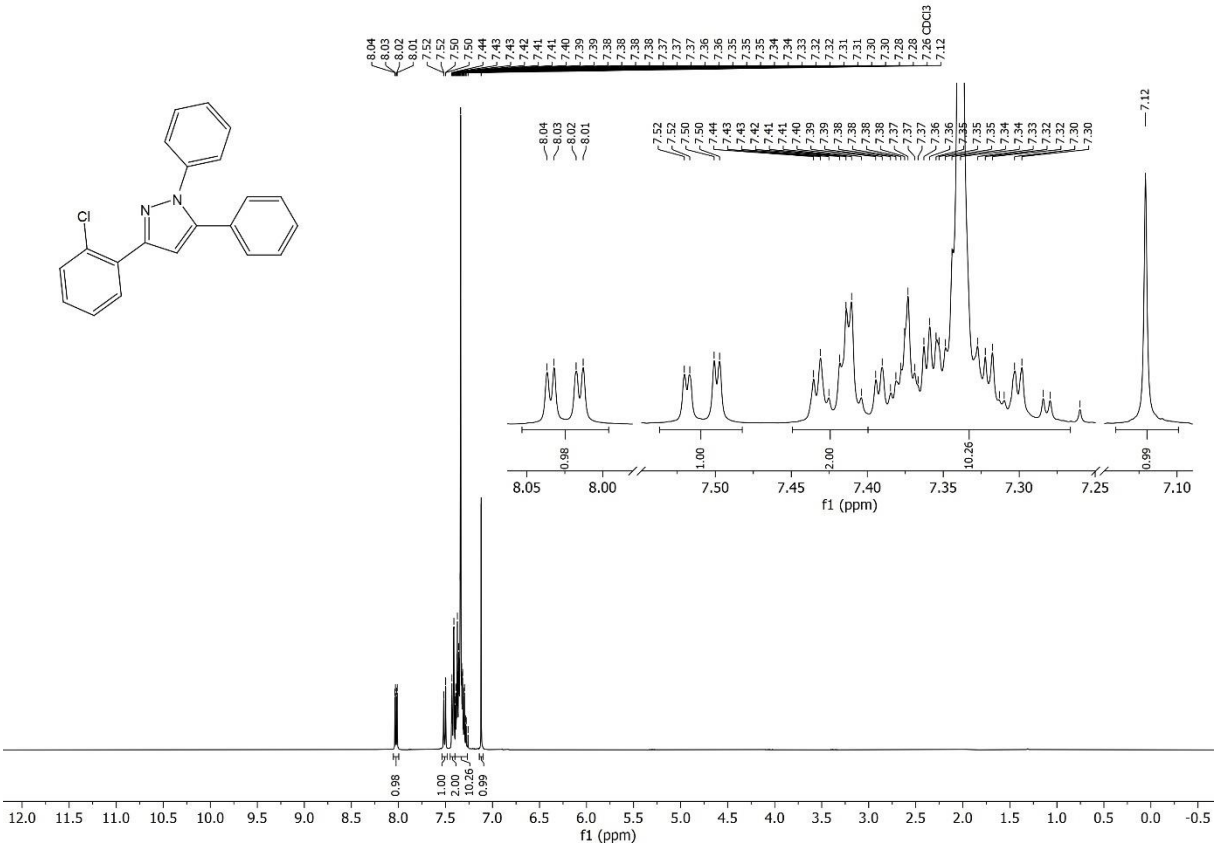

Figure S137: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5i.**

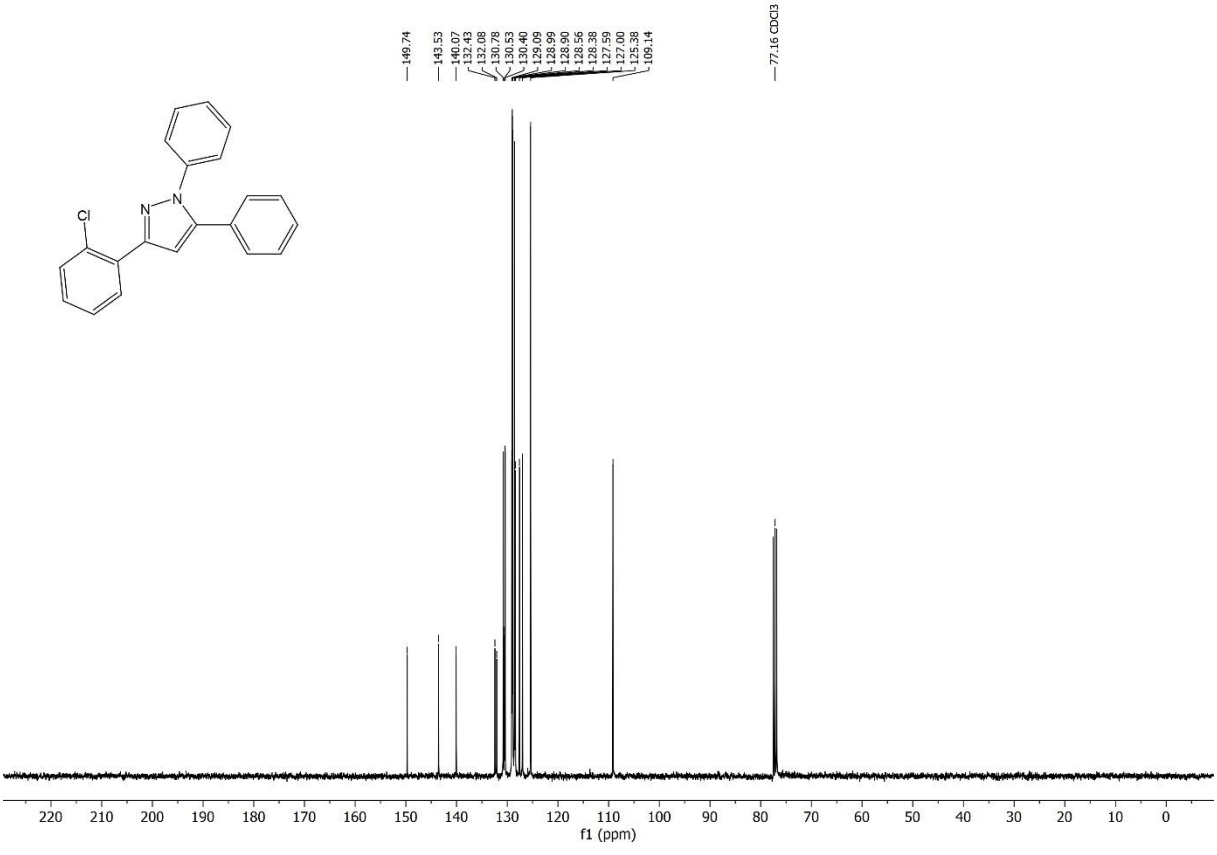

Figure S138: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5i.**

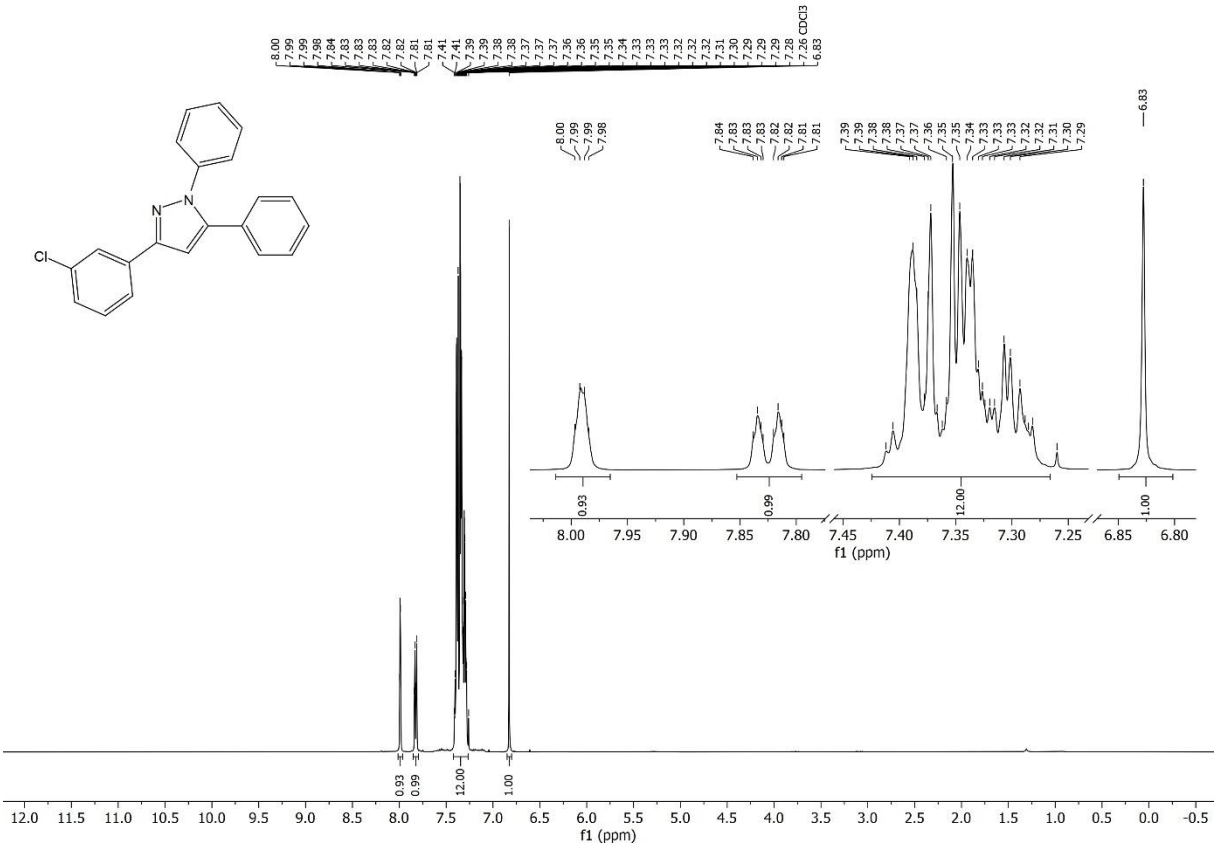

Figure S139: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5j.**

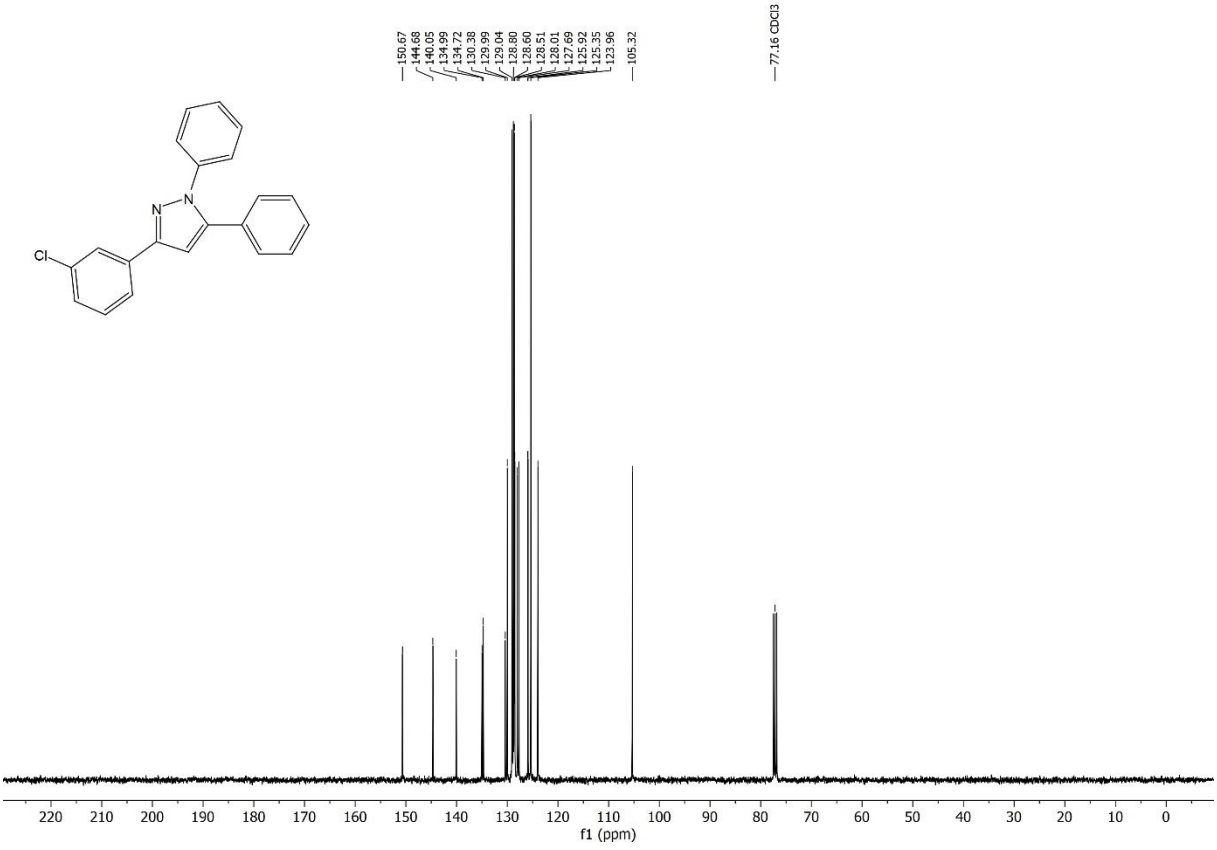

Figure S140: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5j.**

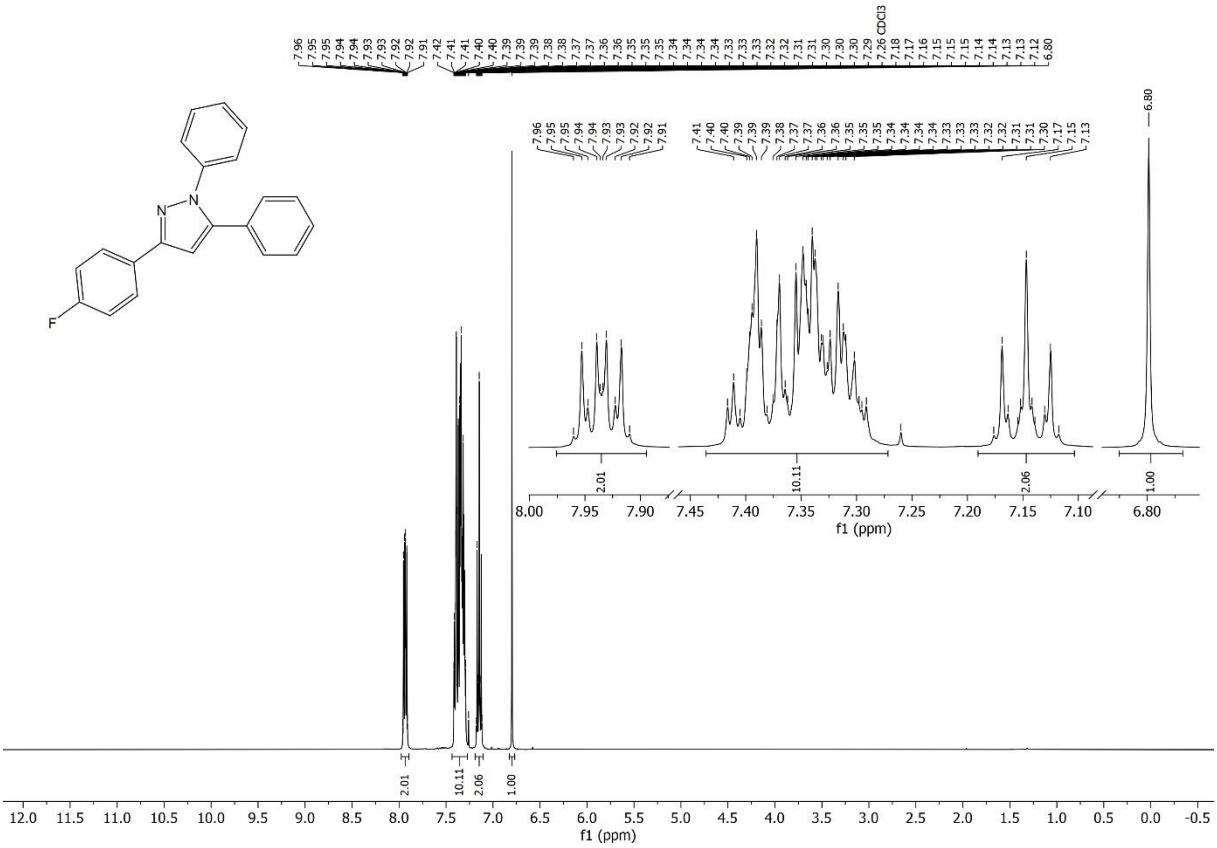

Figure S141: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5k.**

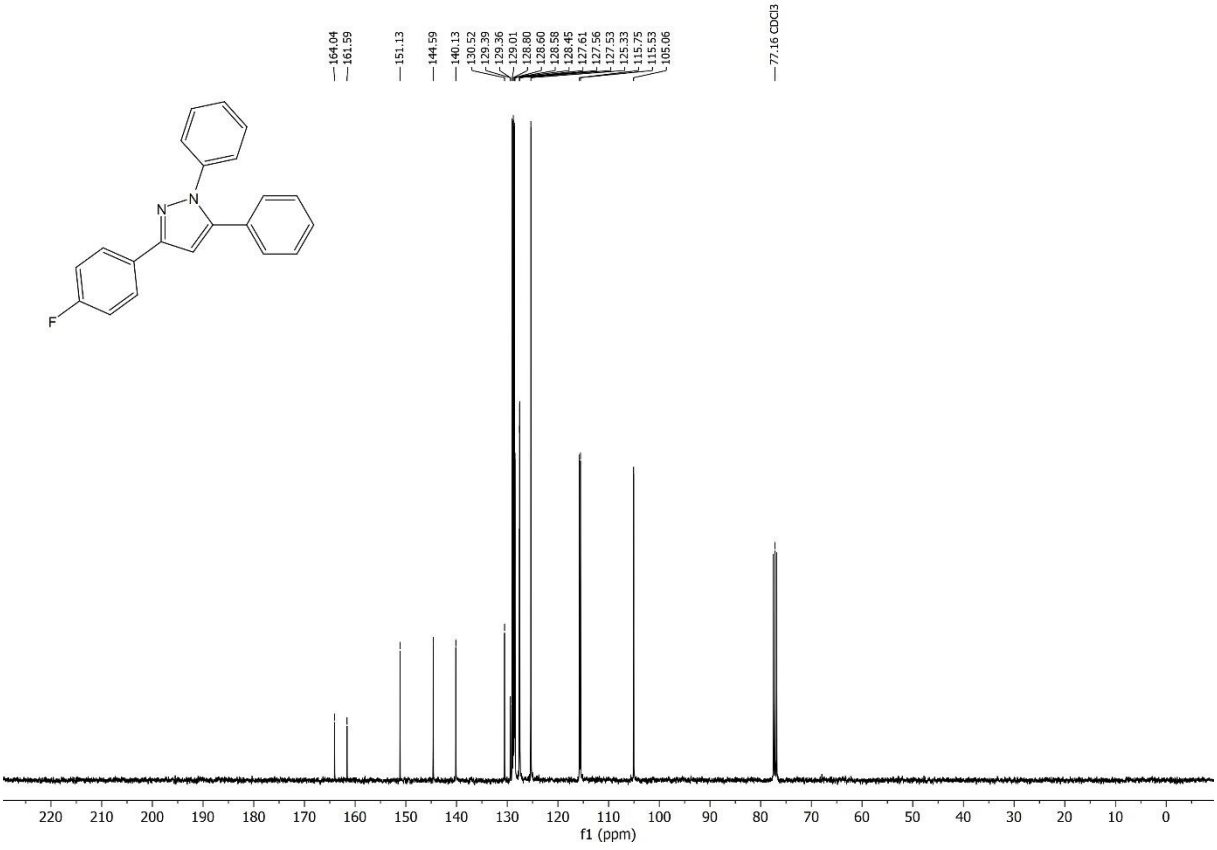

Figure S142: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5k.**

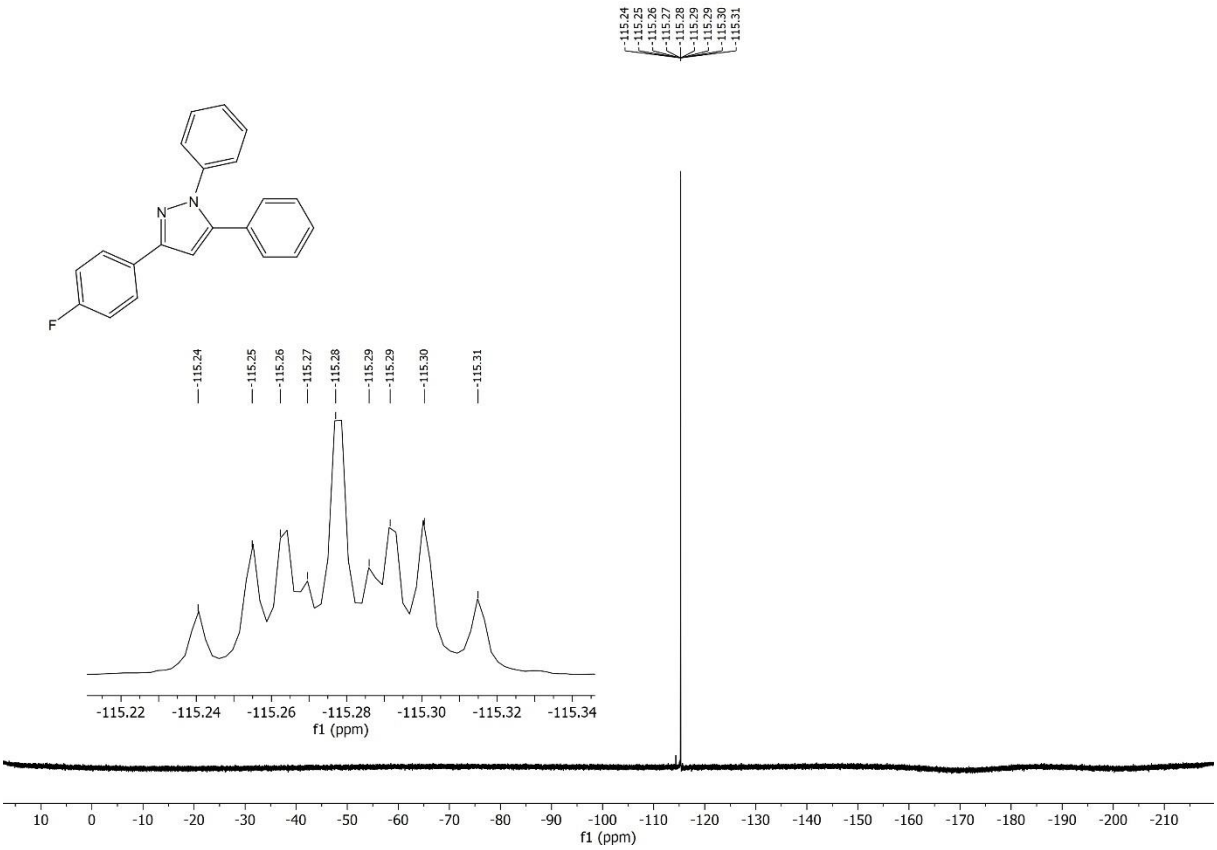

Figure S143: ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5k.**

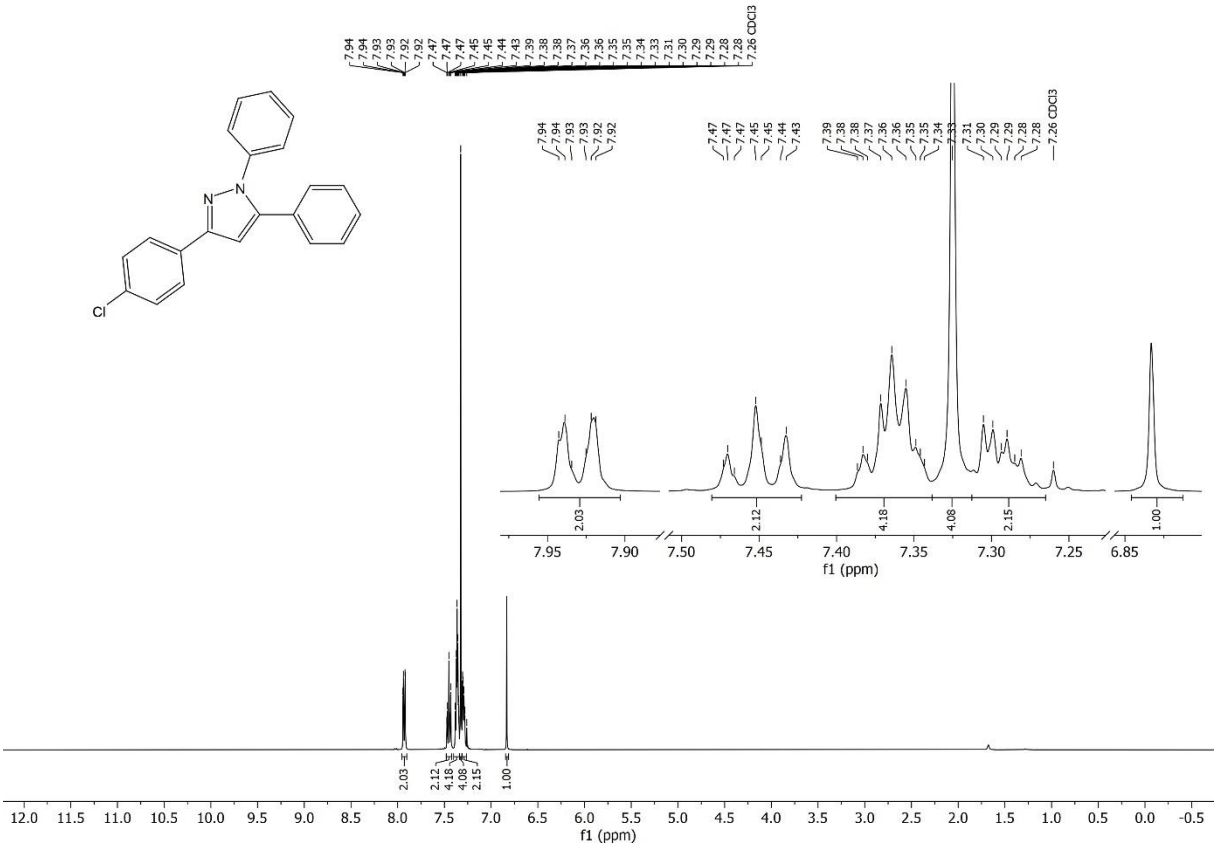

Figure S144: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5l.**

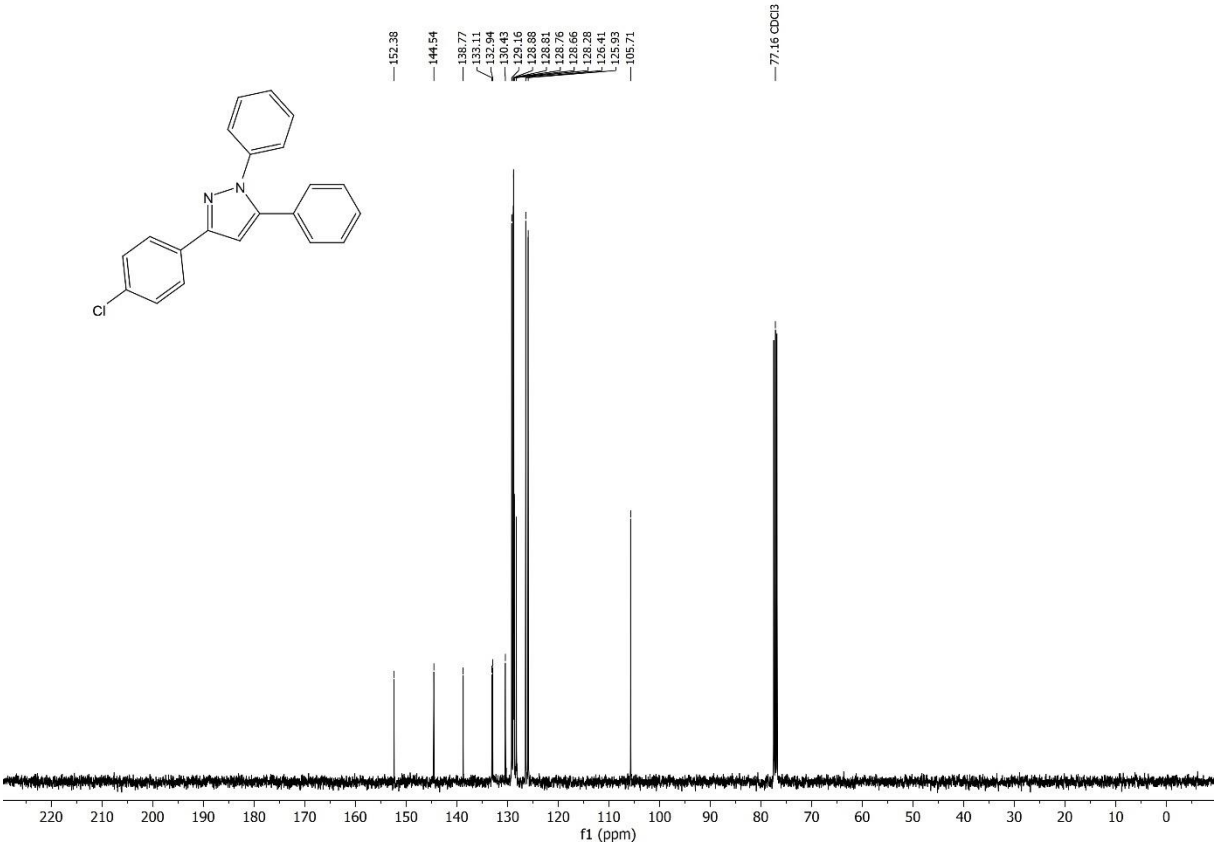

Figure S145: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5l.**

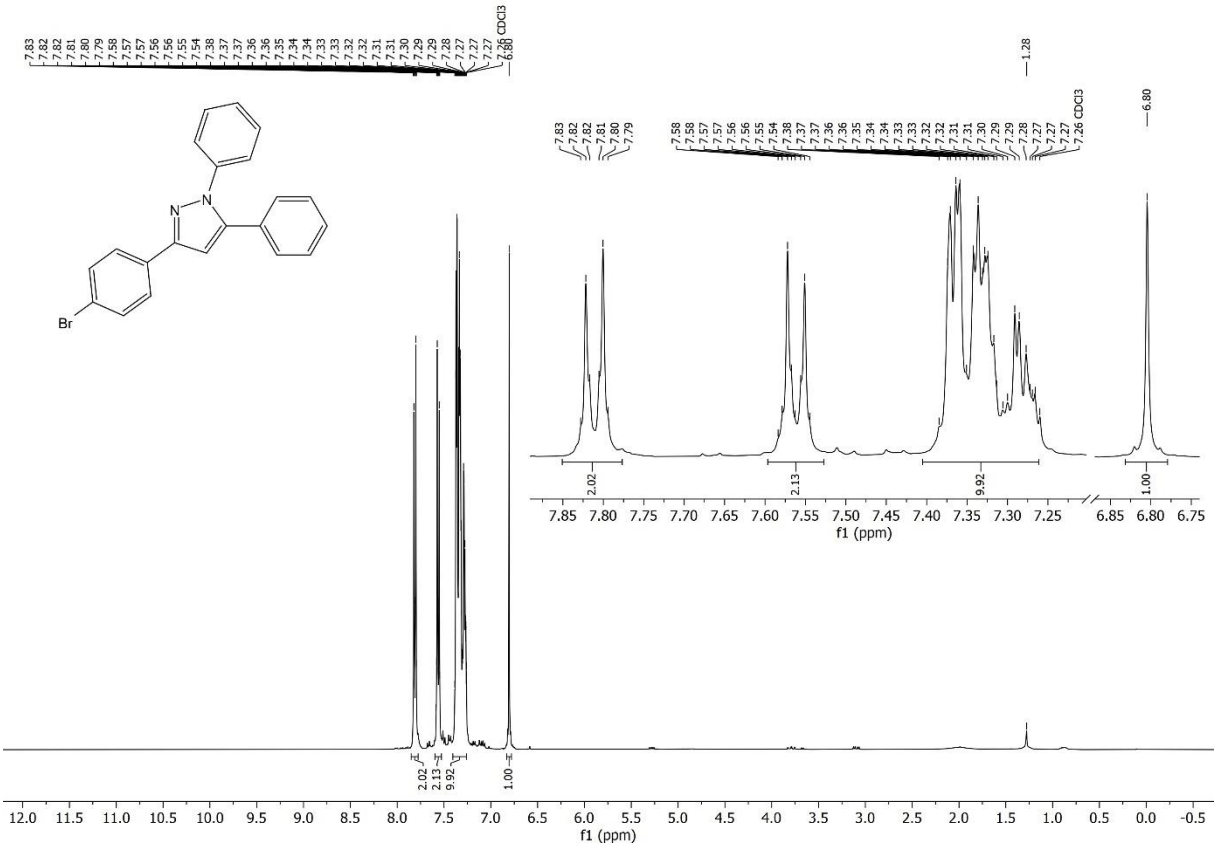

Figure S146: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5m.**

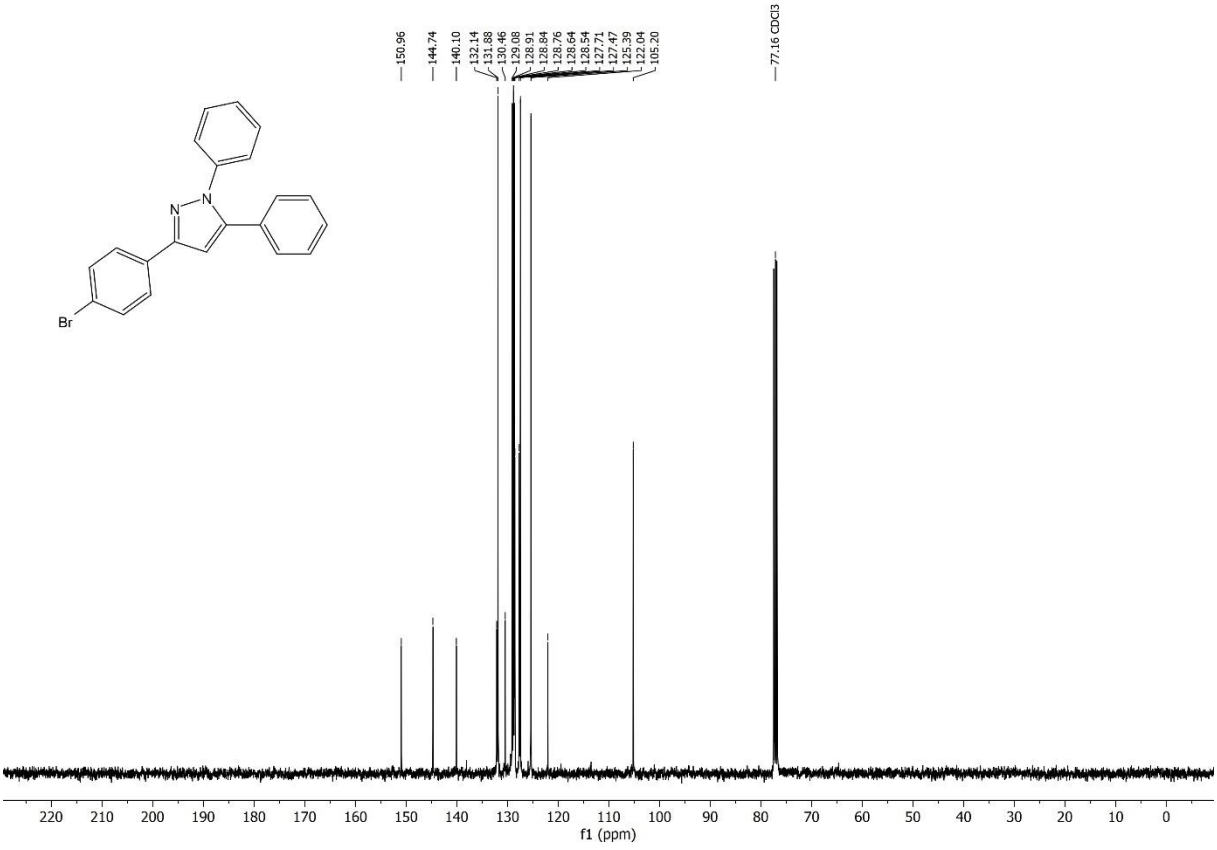

Figure S147: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5m.**

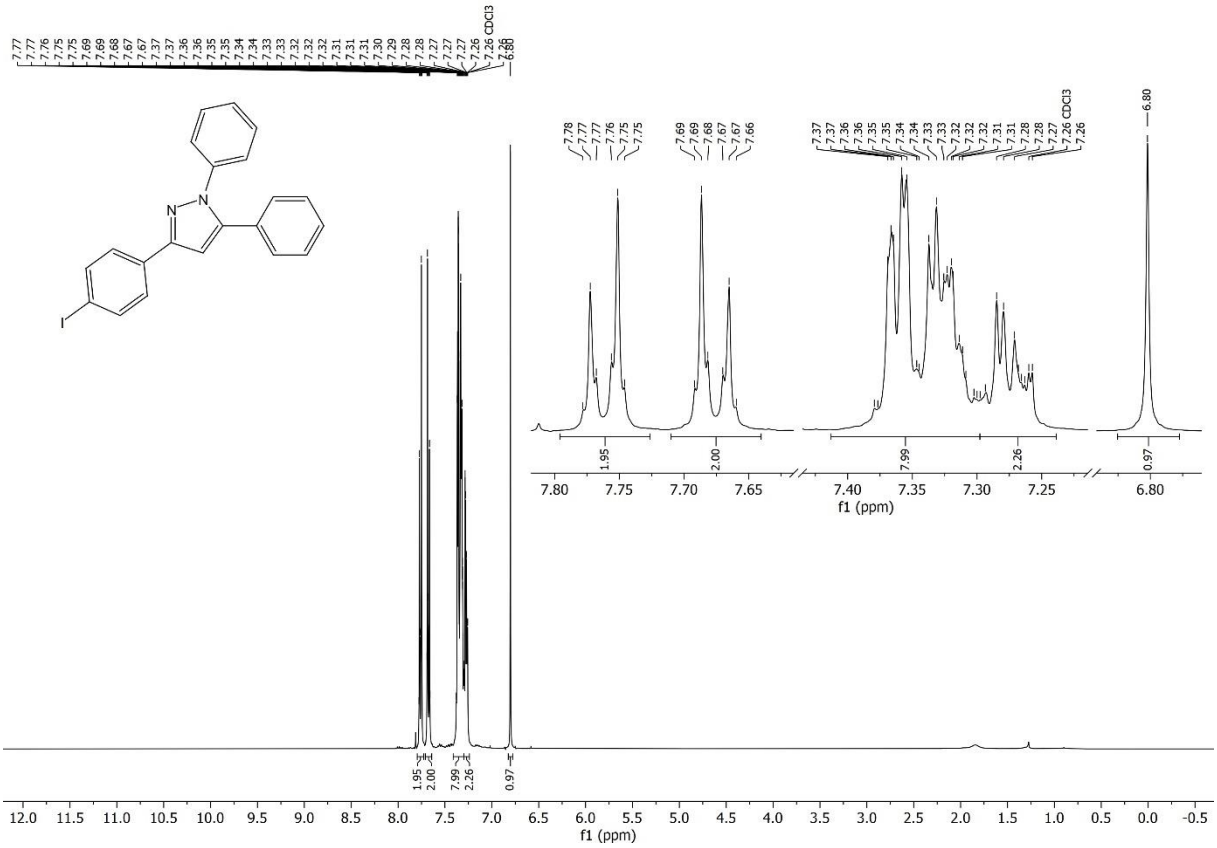

Figure S148: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5n.**

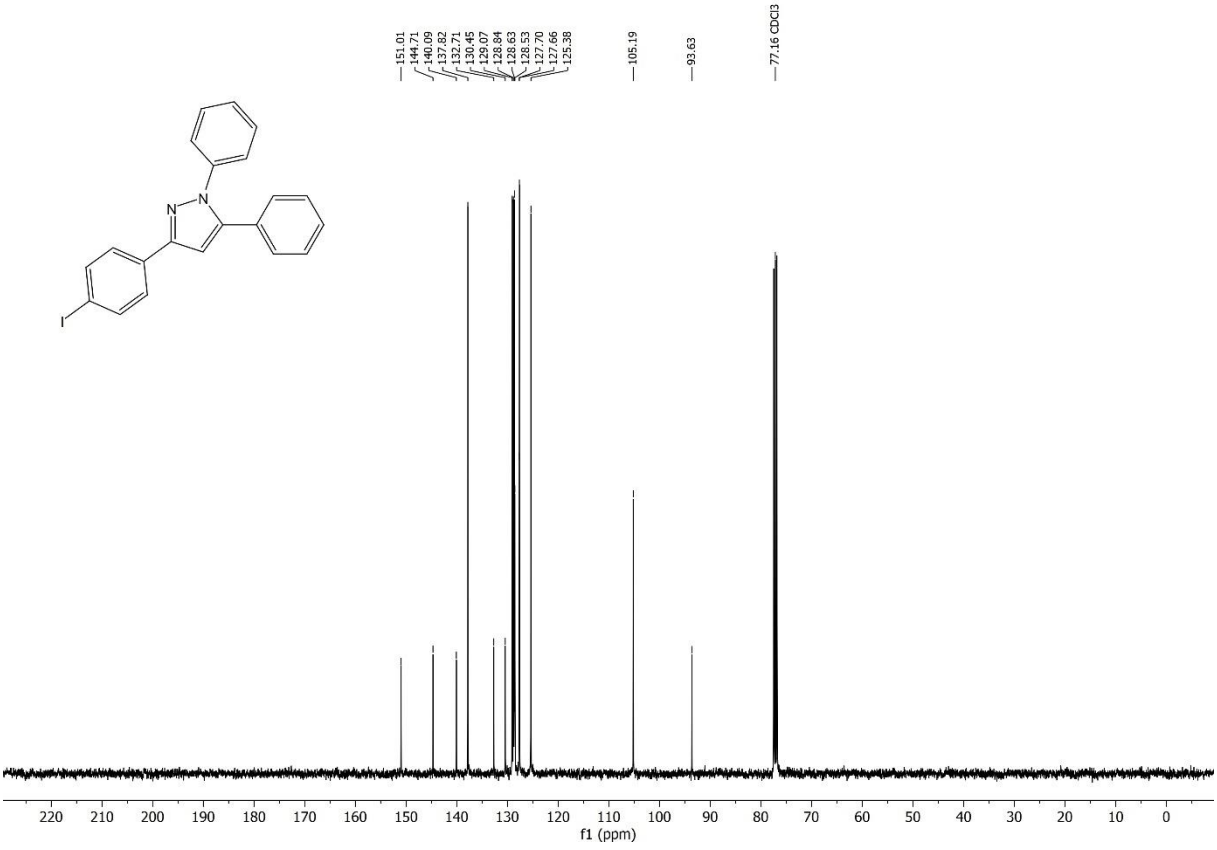

Figure S149: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5n.**

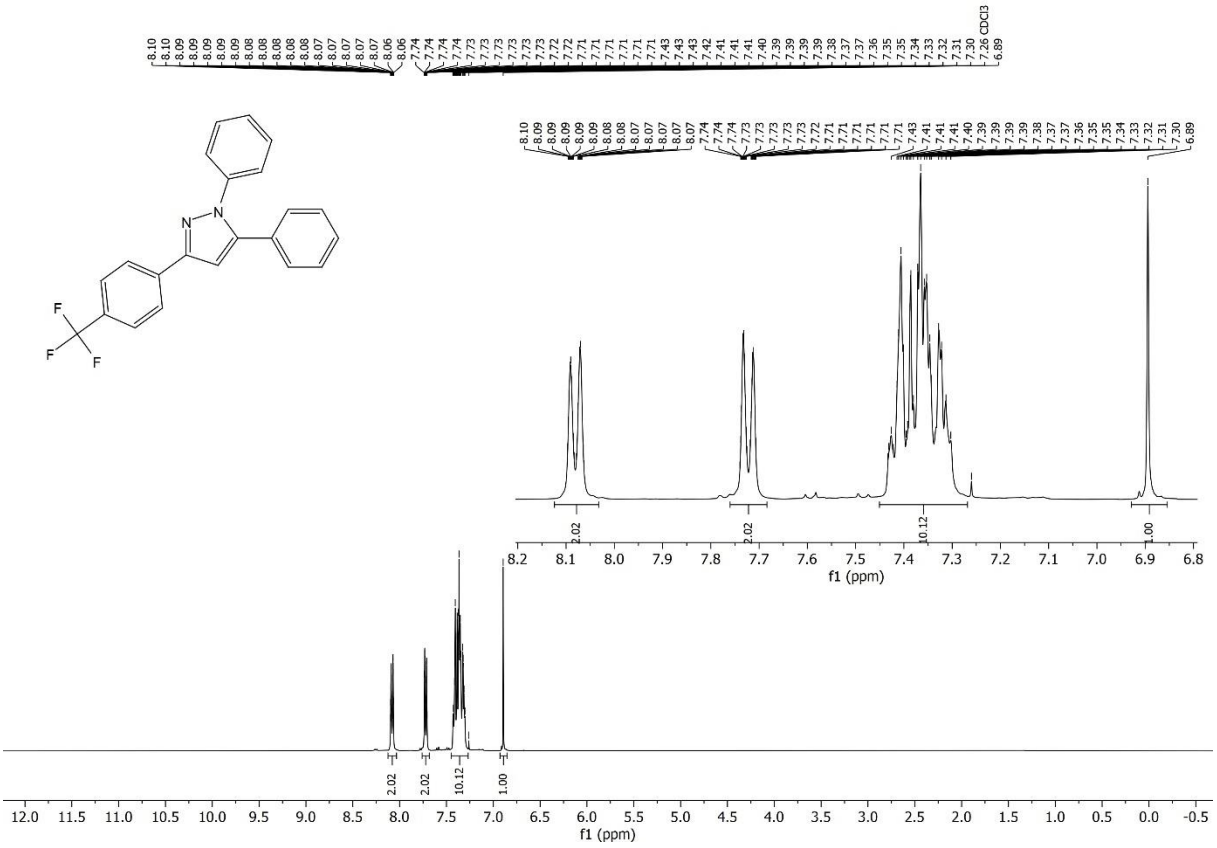

Figure S150: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5o.**

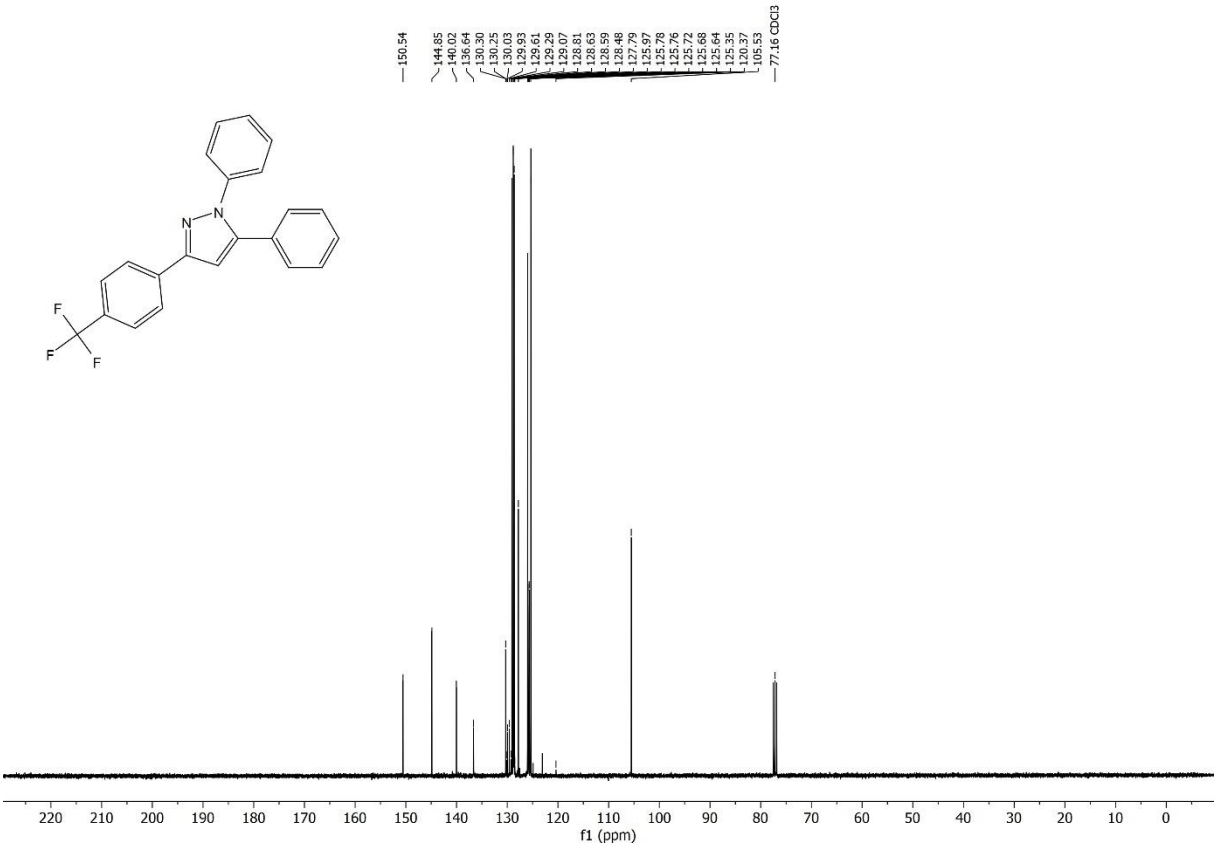

Figure S151: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5o.**

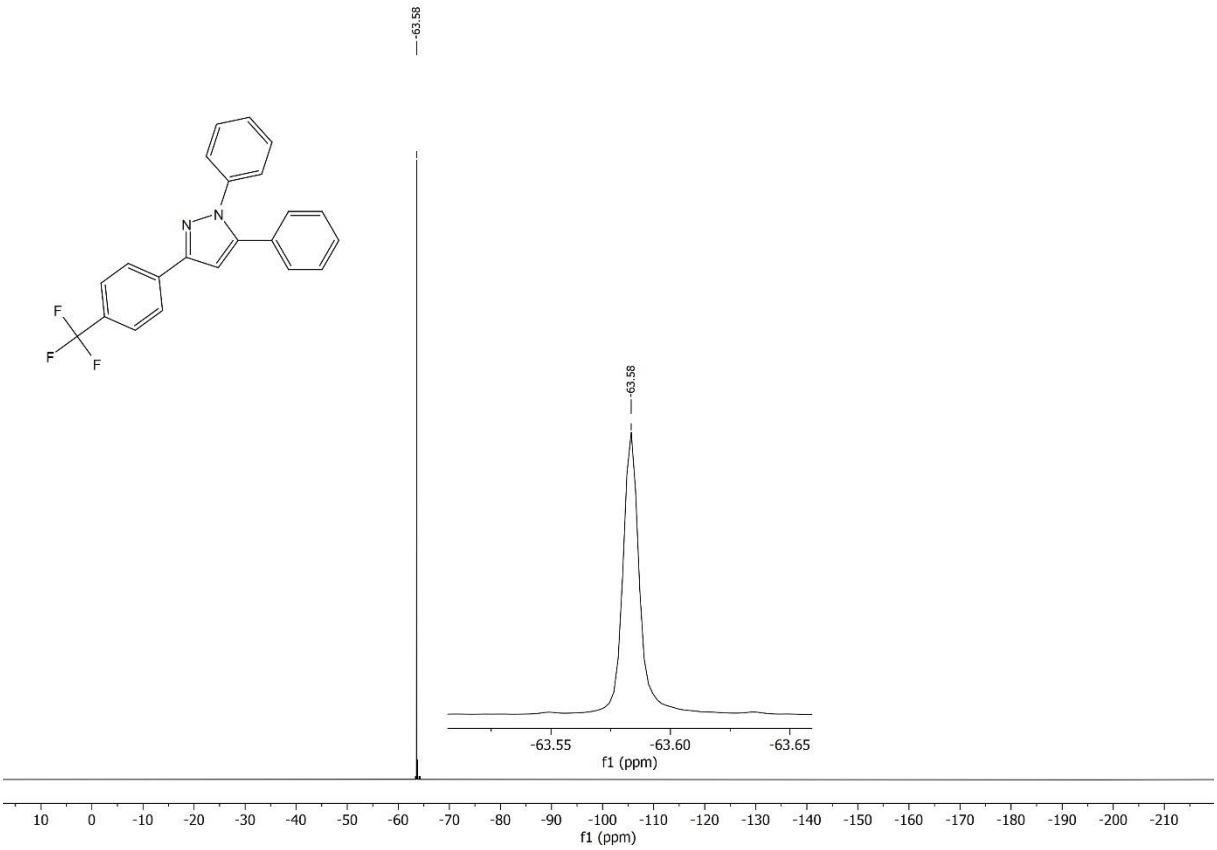

Figure S152: ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5o.**

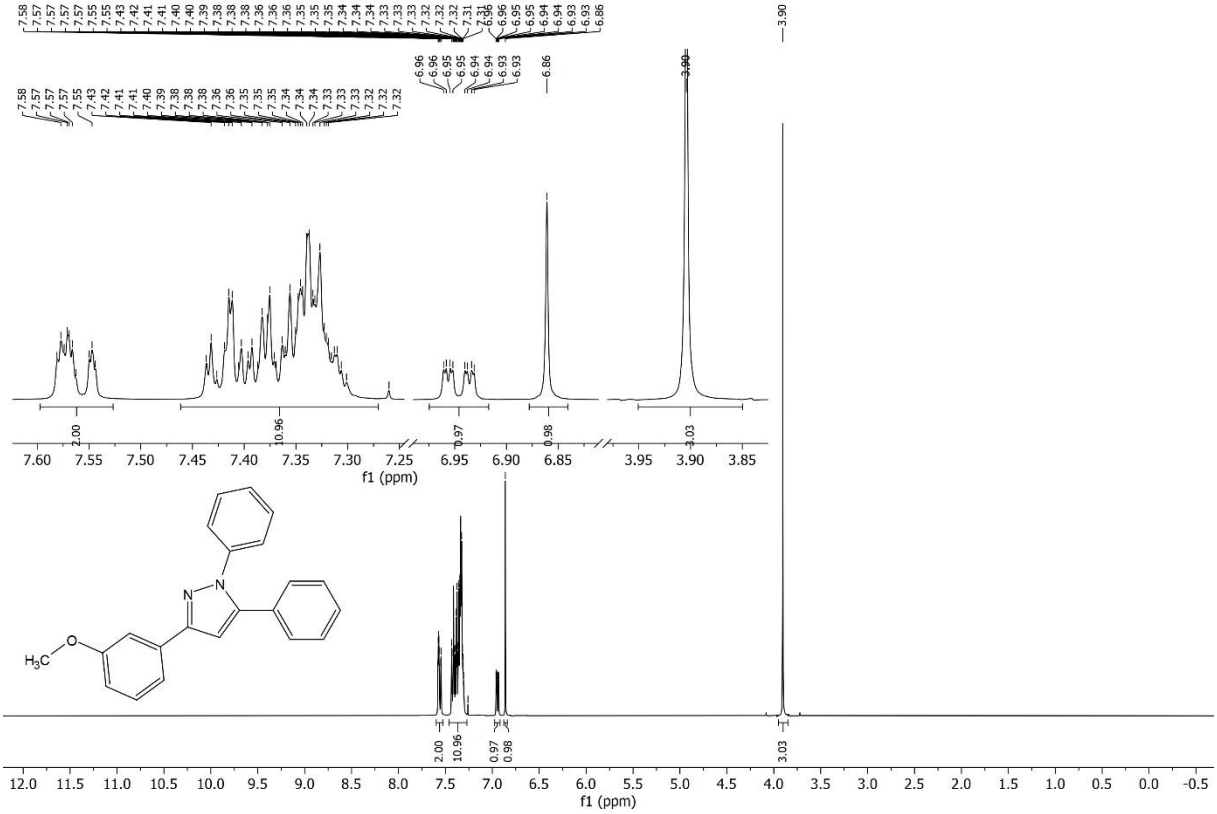

Figure S153: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5p.**

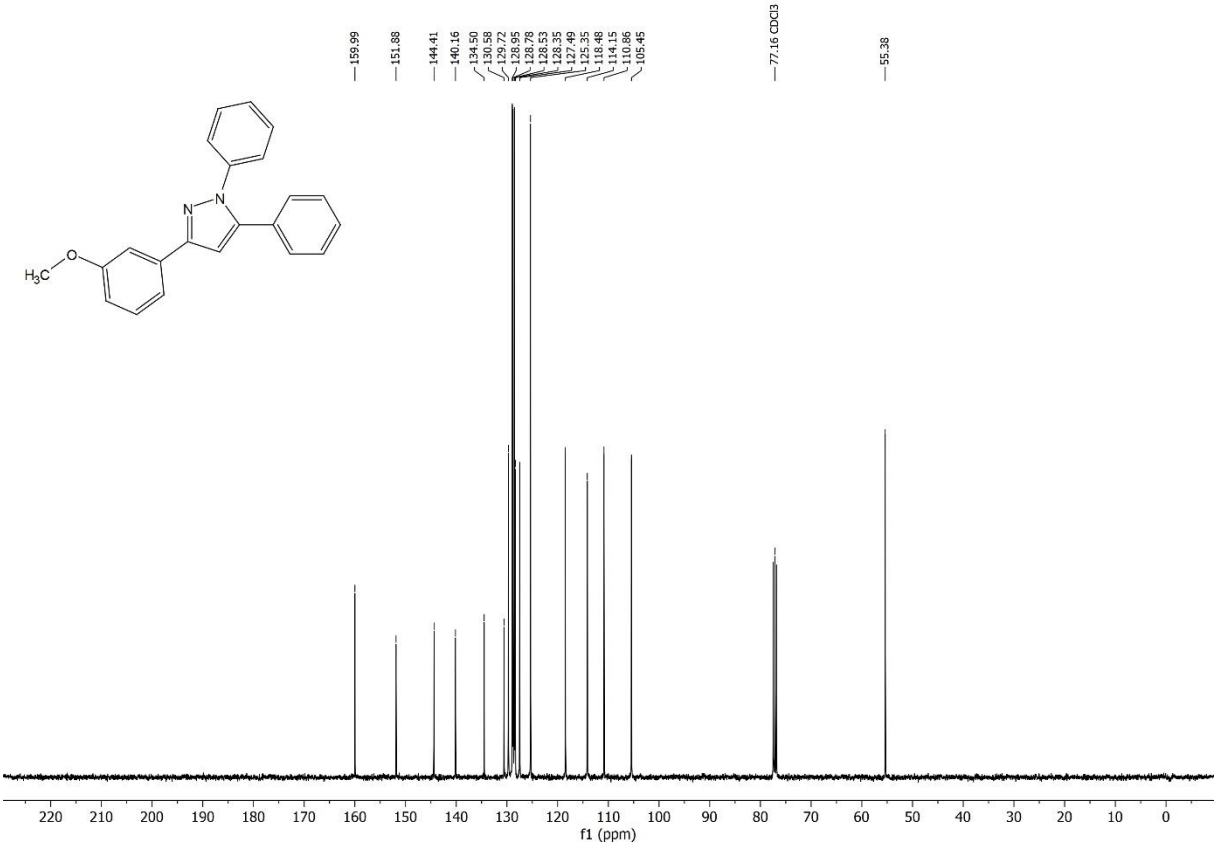

Figure S154: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5p.**

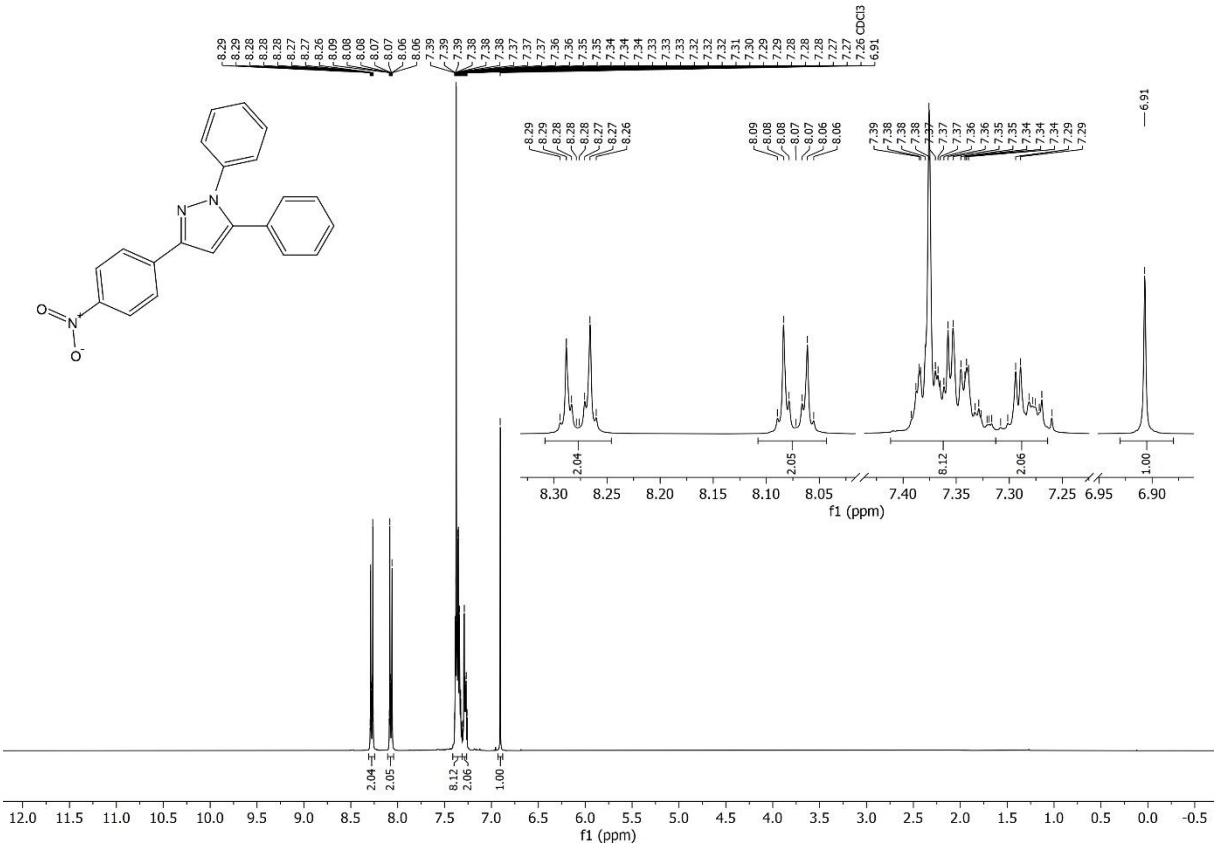

Figure S155: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5q.**

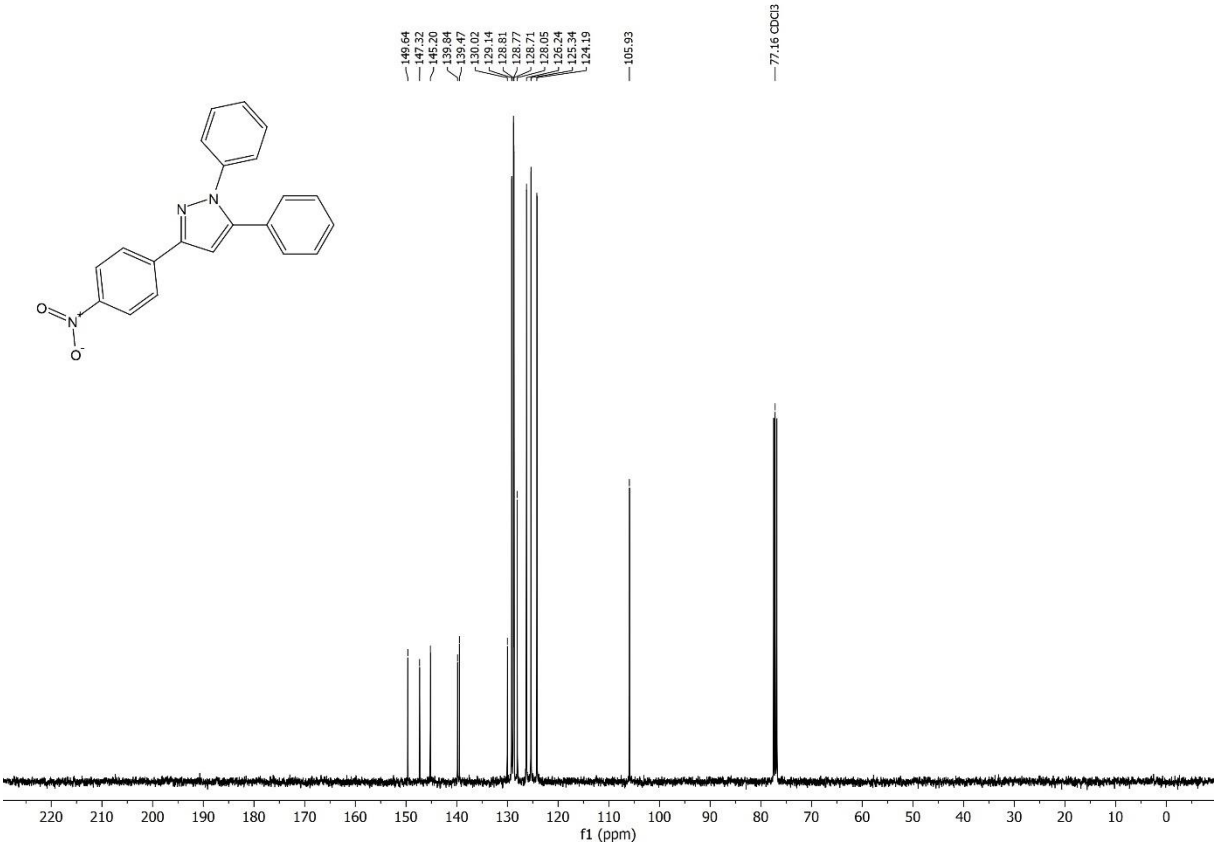

Figure S156: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5q.**

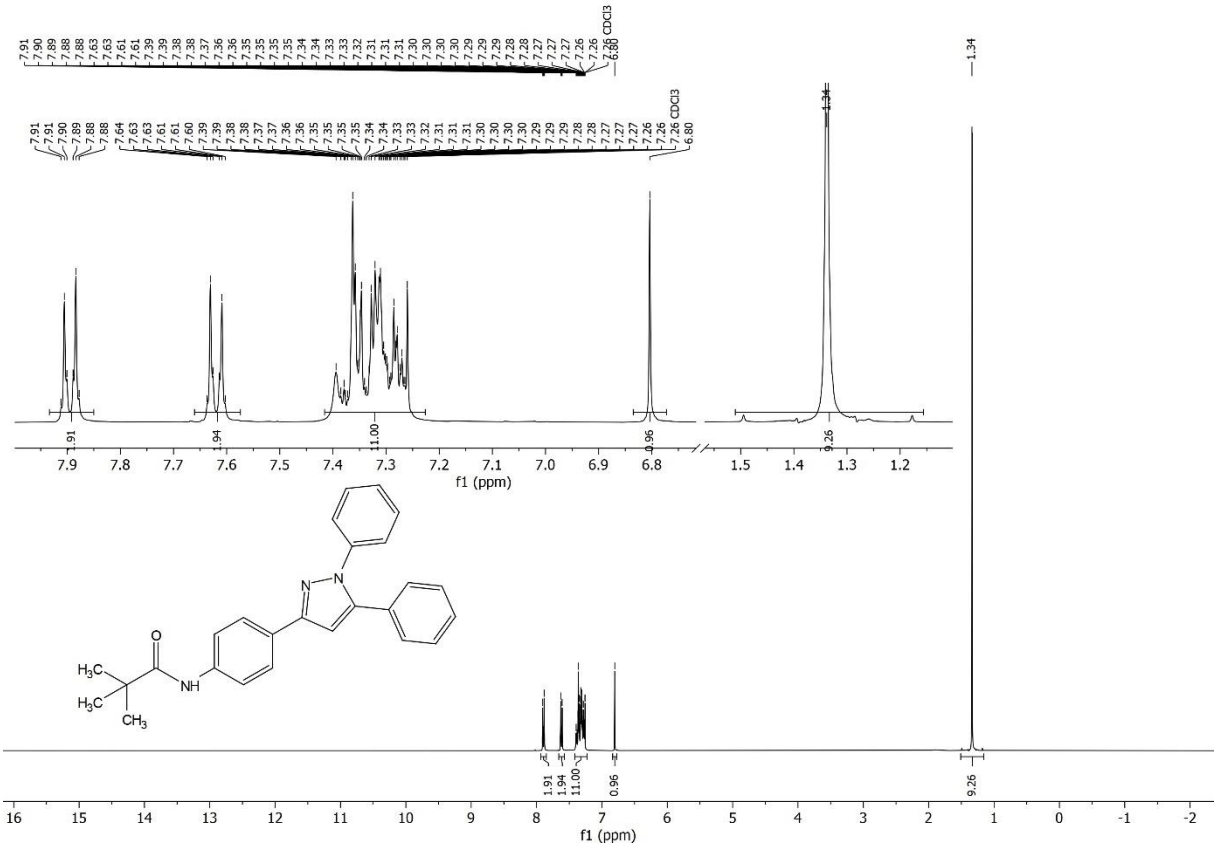

Figure S157: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5r.**

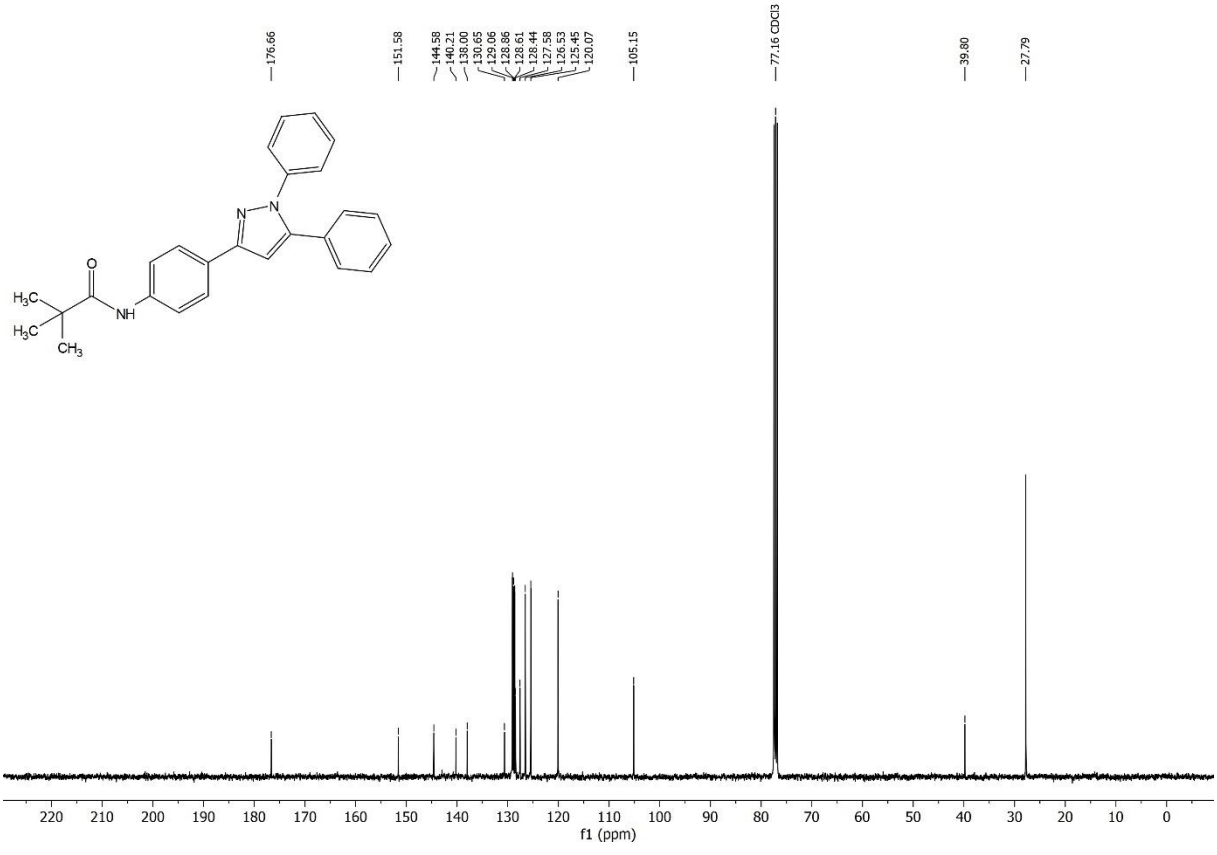

Figure S158: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5r.**

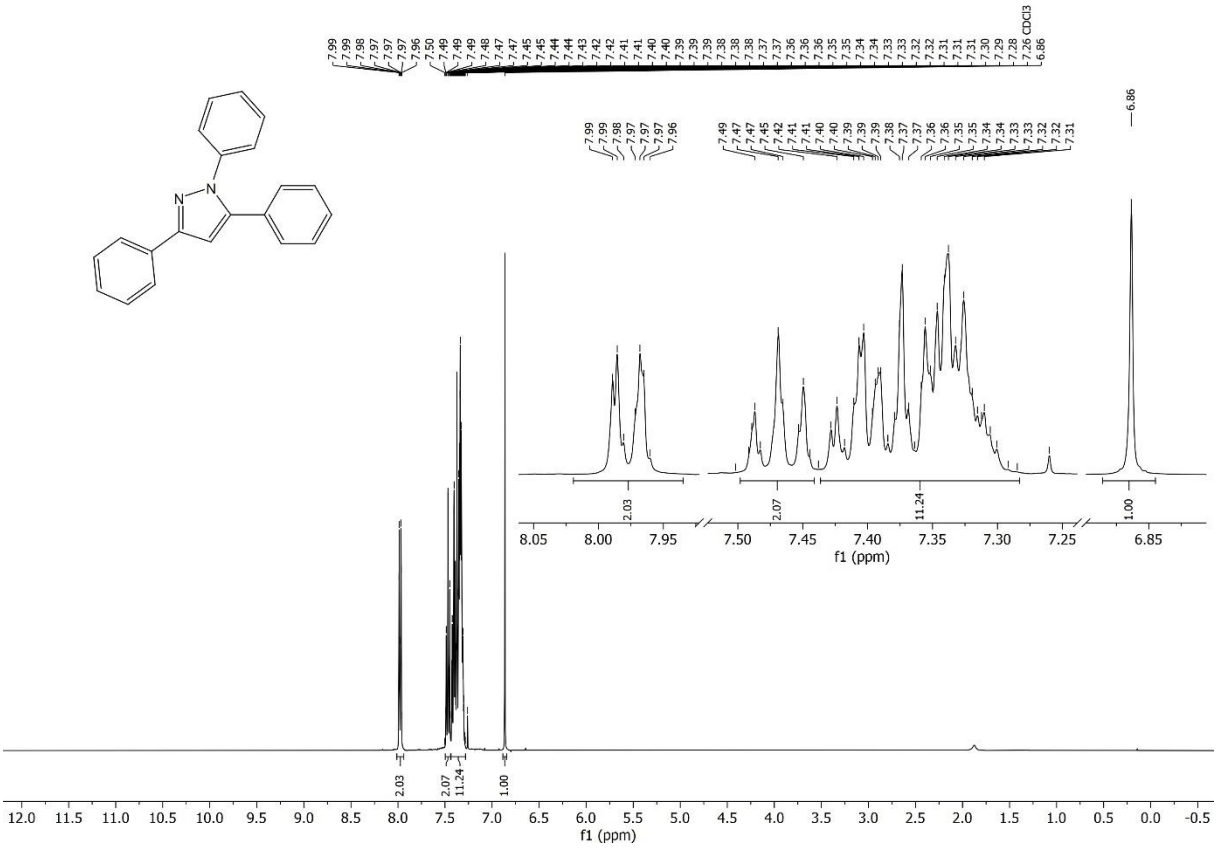

Figure S159: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5s.**

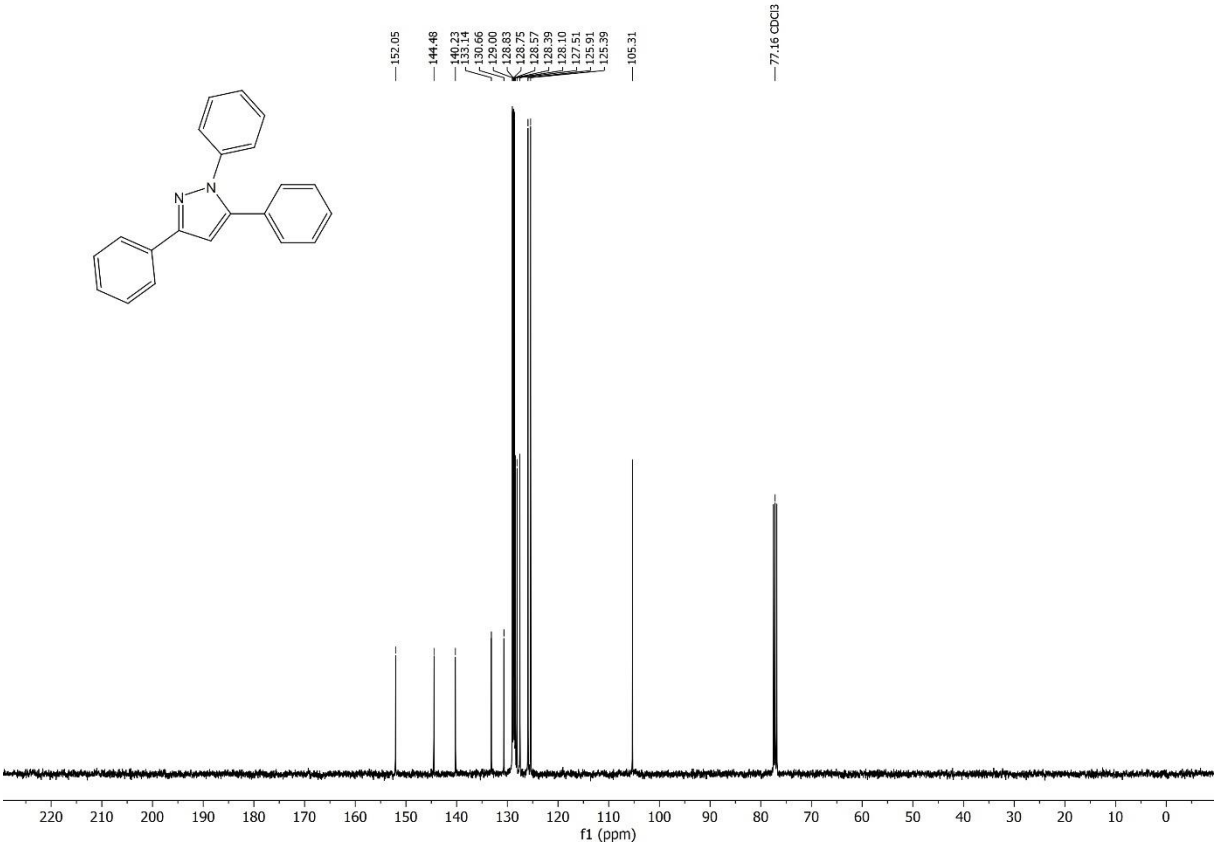

Figure S160: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5s.**

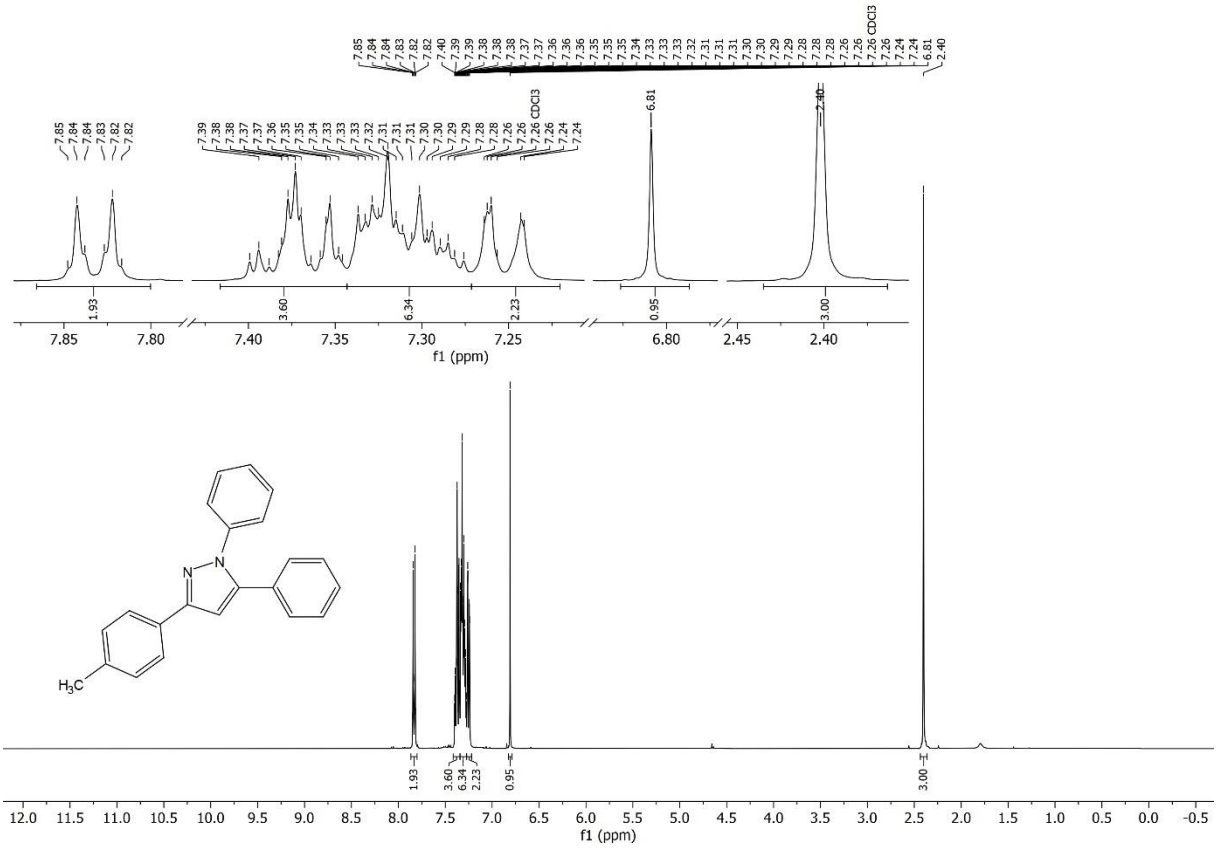

Figure S161: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5t.**

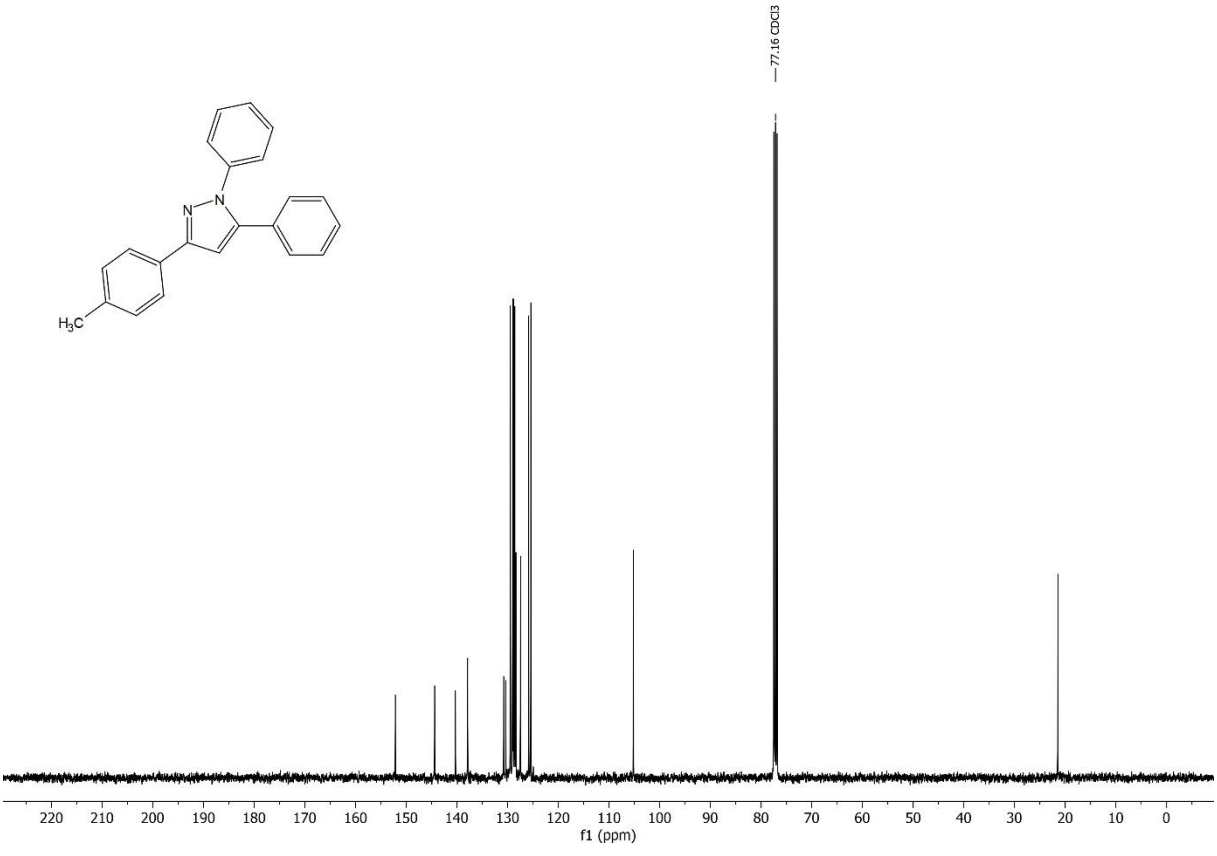

Figure S162: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5t.**

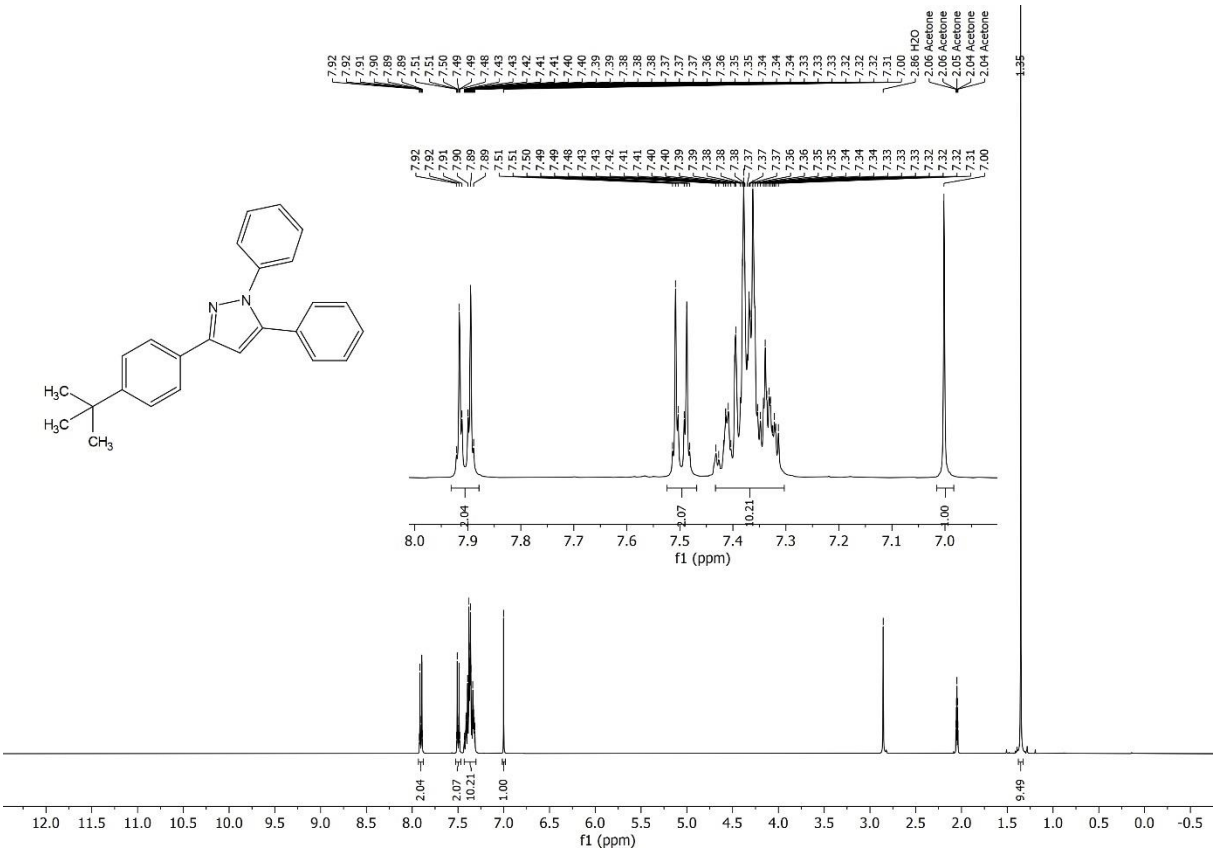

Figure S163: ^{13}C NMR spectrum (101 MHz, acetone-d_6) of **5u.**

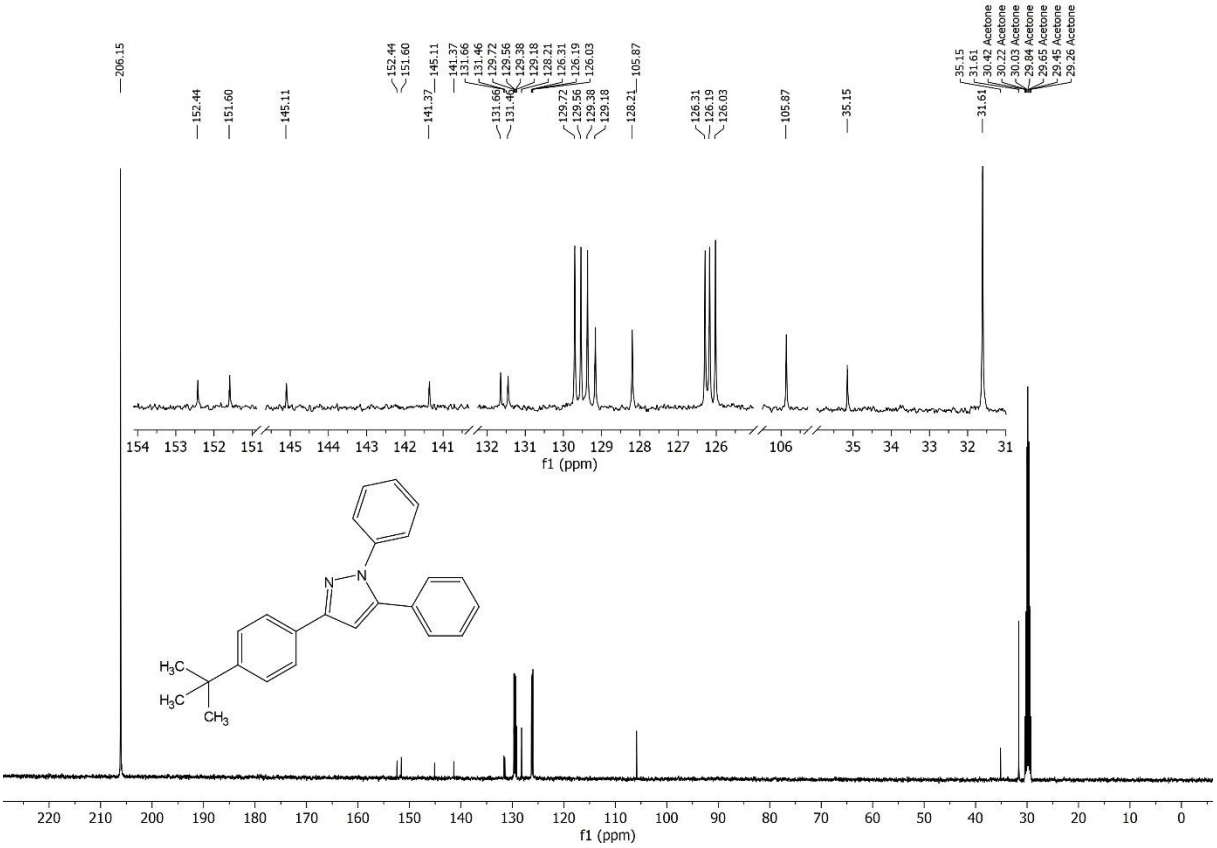

Figure S164: ^{13}C NMR spectrum (101 MHz, acetone-d_6) of **5u.**

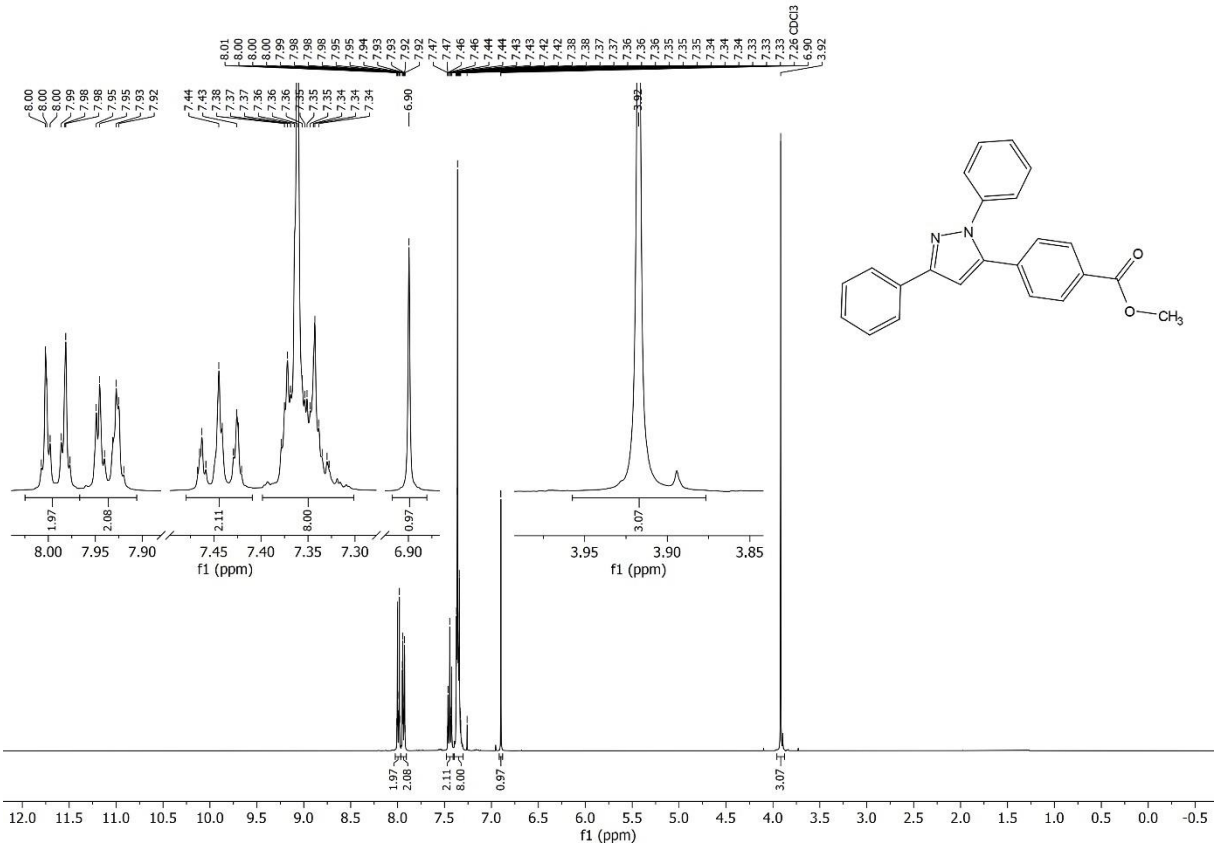

Figure S165: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5v.**

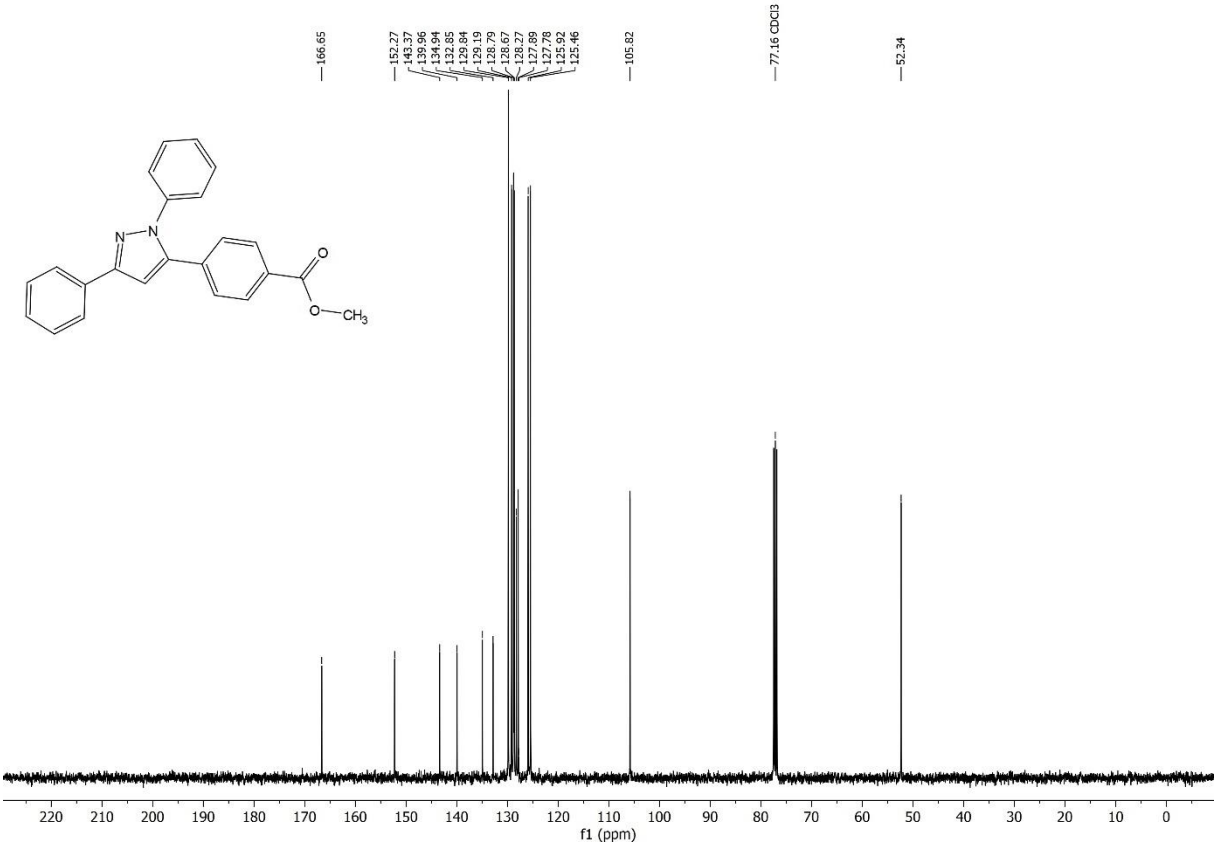

Figure S166: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5v.**

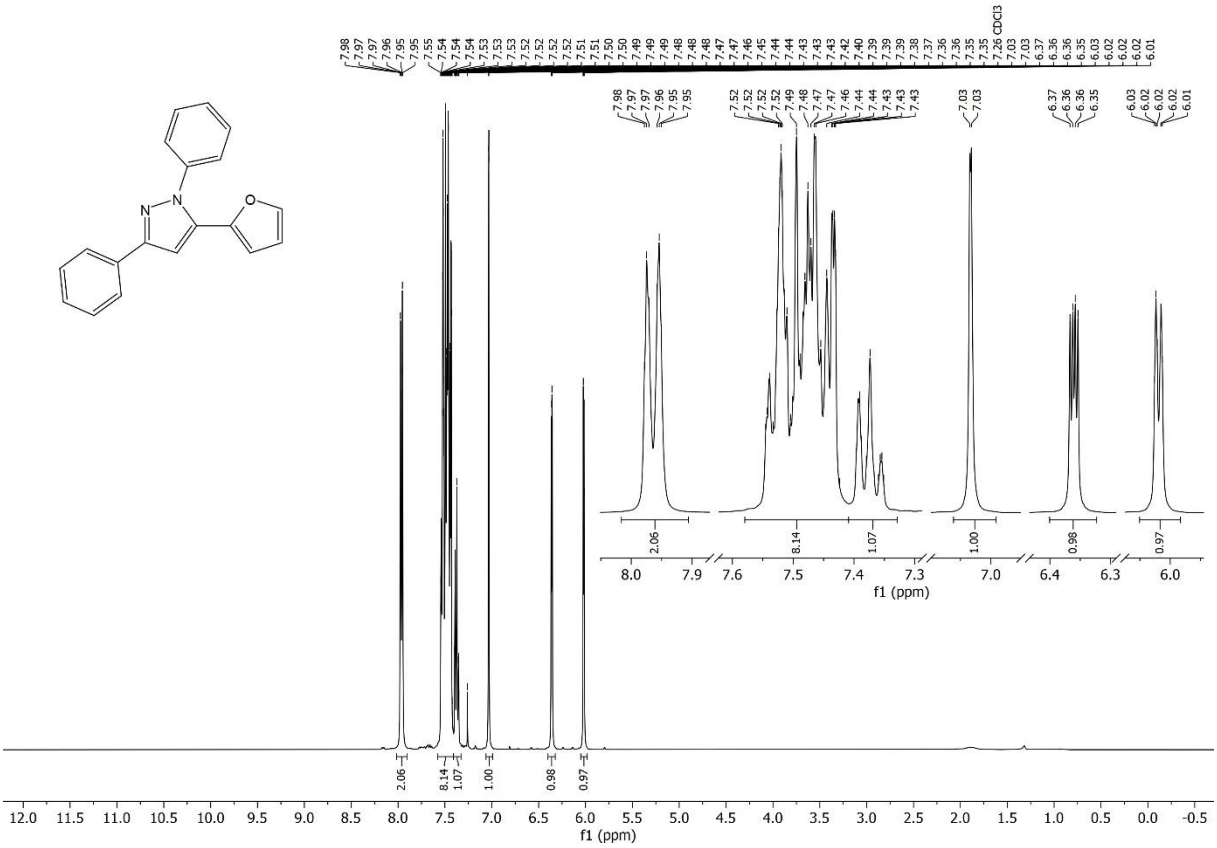

Figure S167: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5w.**

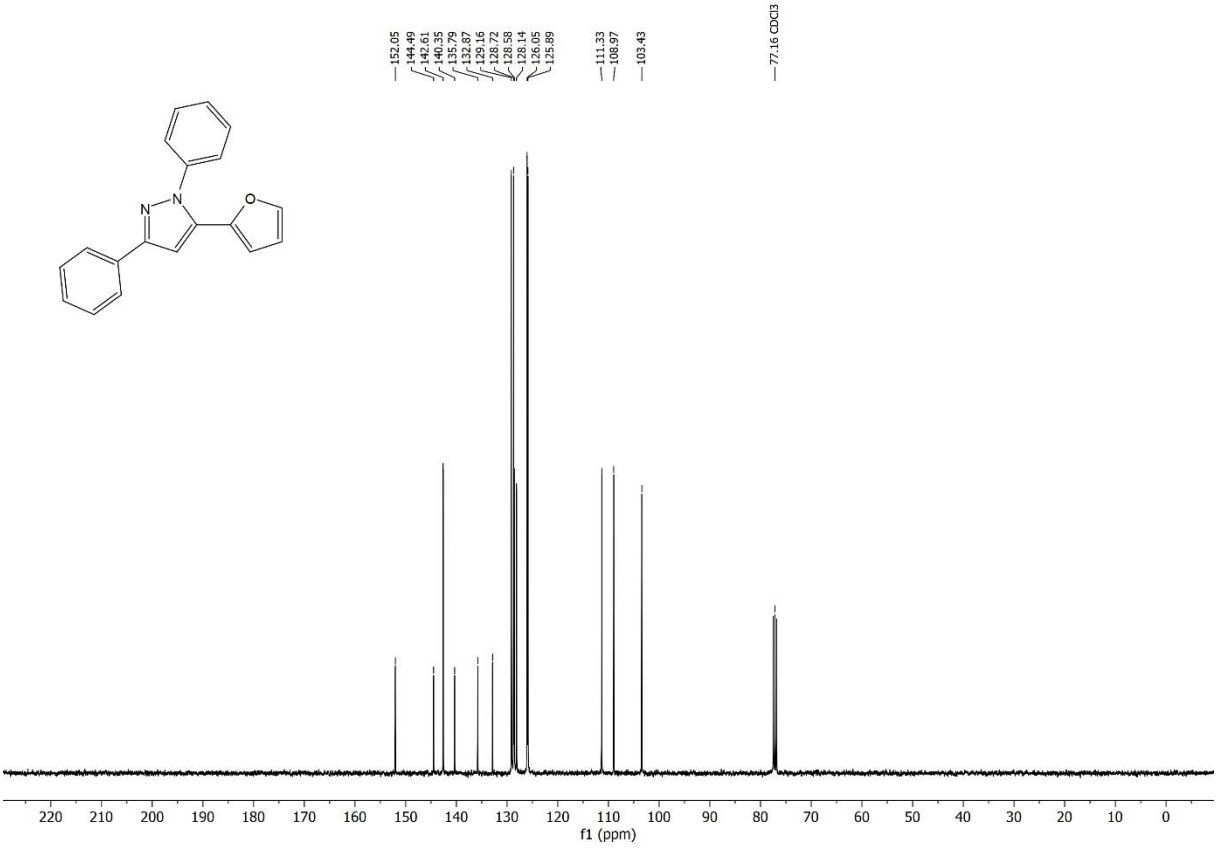

Figure S168: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5w.**

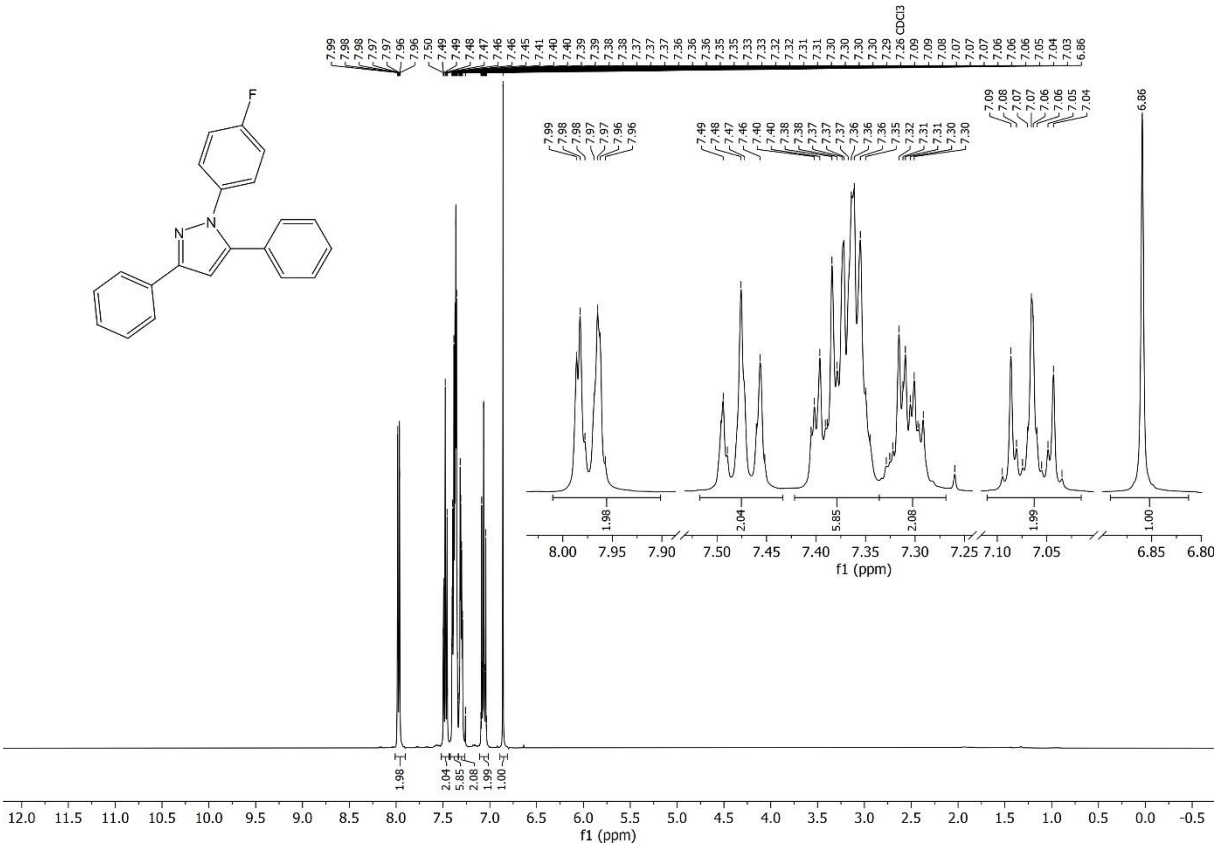

Figure S169: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5x.**

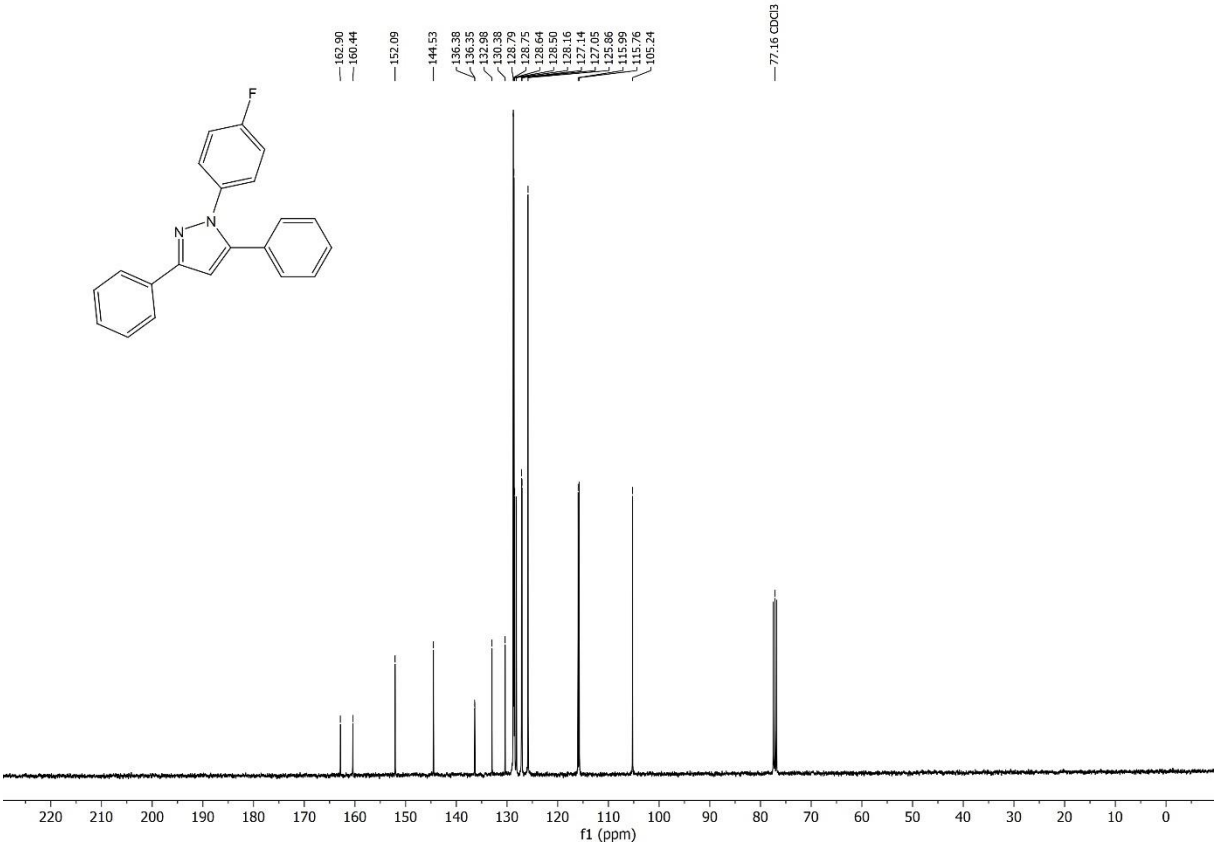

Figure S170: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5x.**

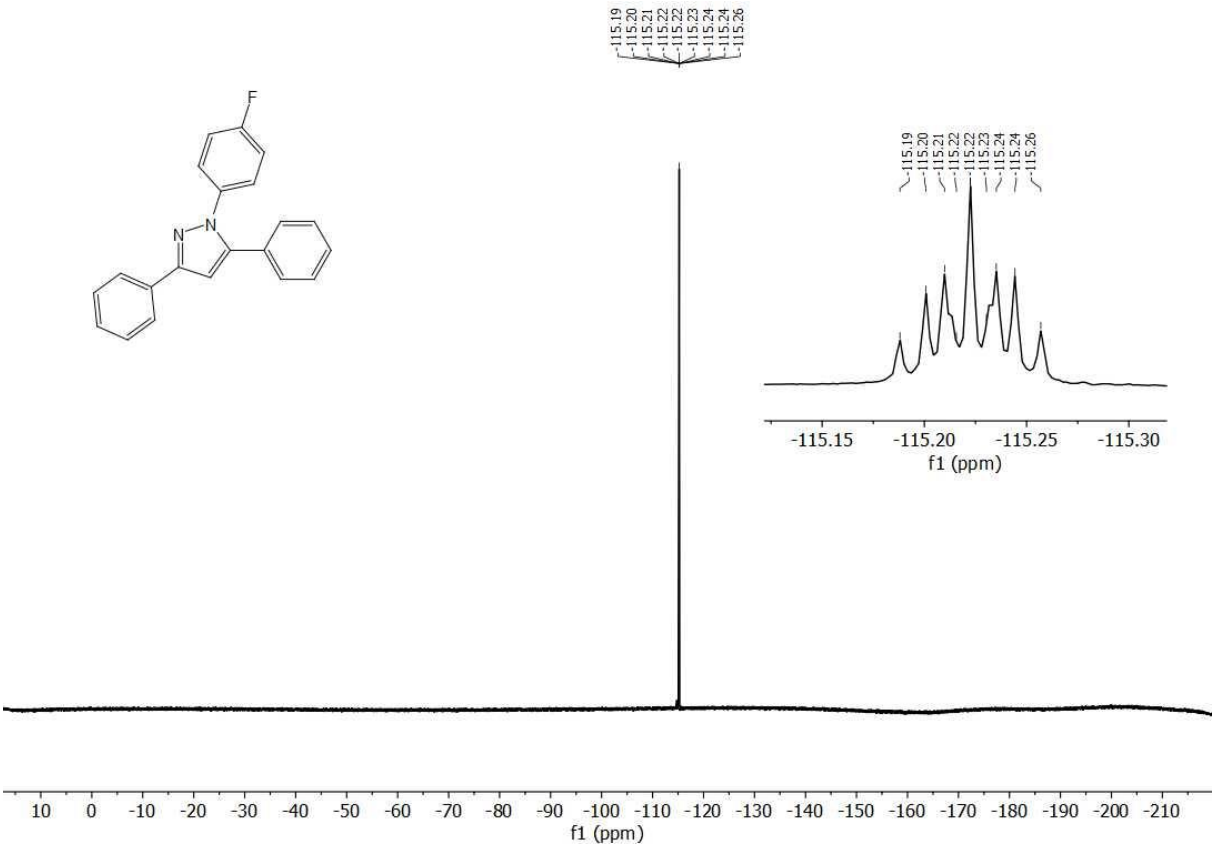

Figure S171: ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5x.**

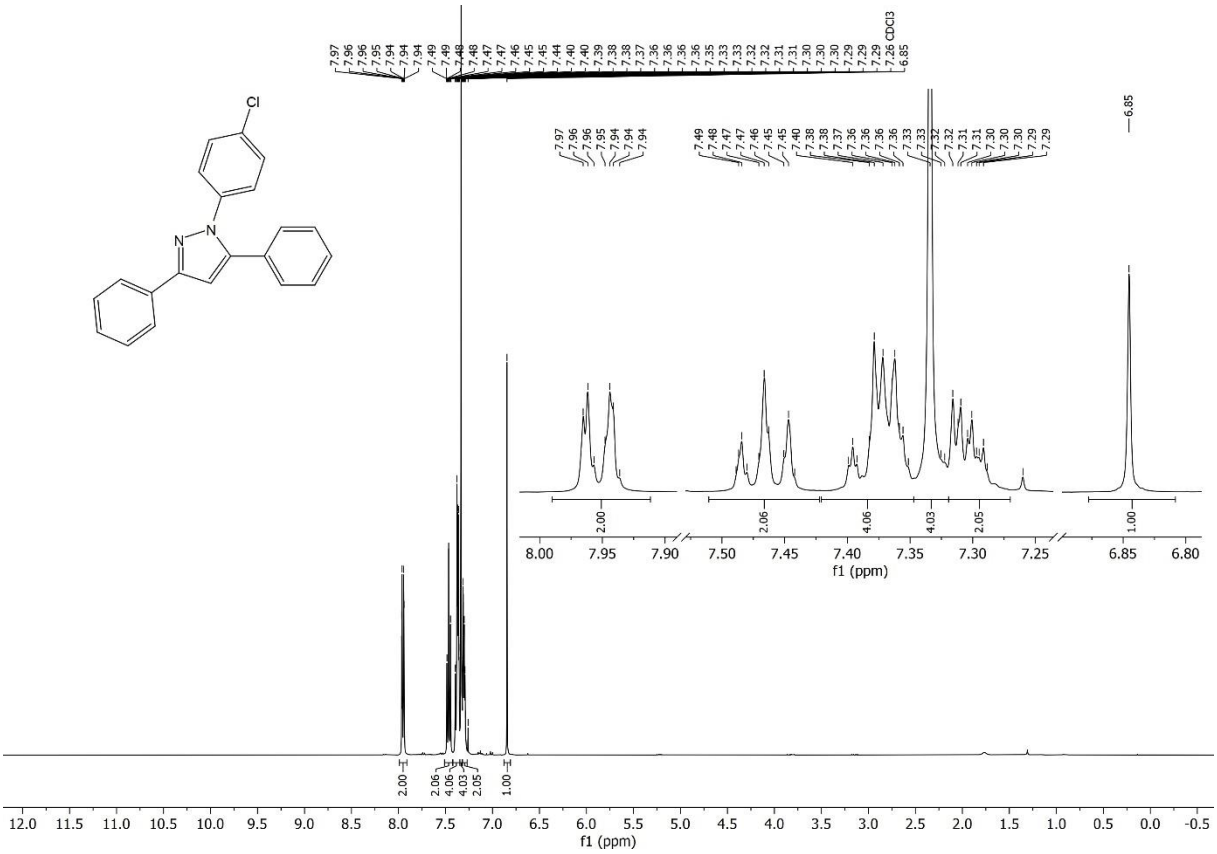

Figure S172: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5y.**

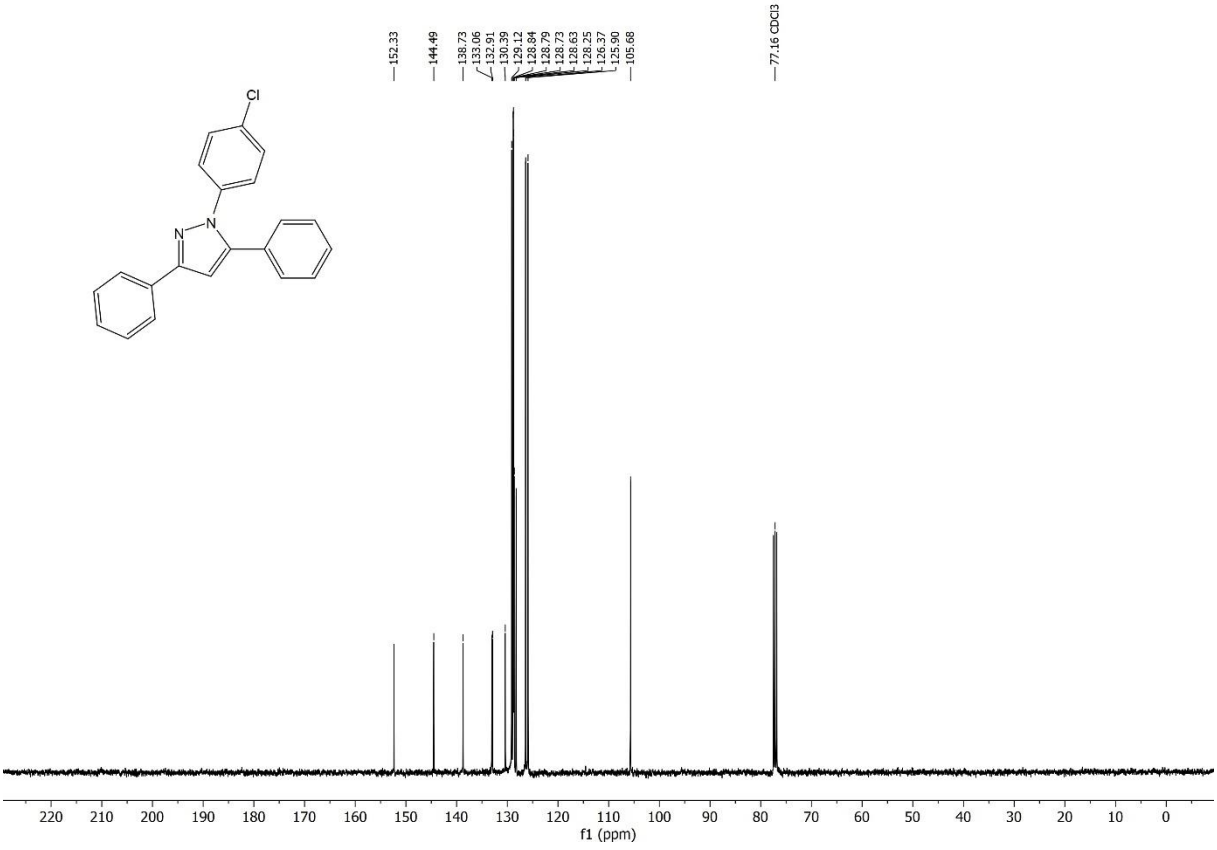

Figure S173: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5y.**

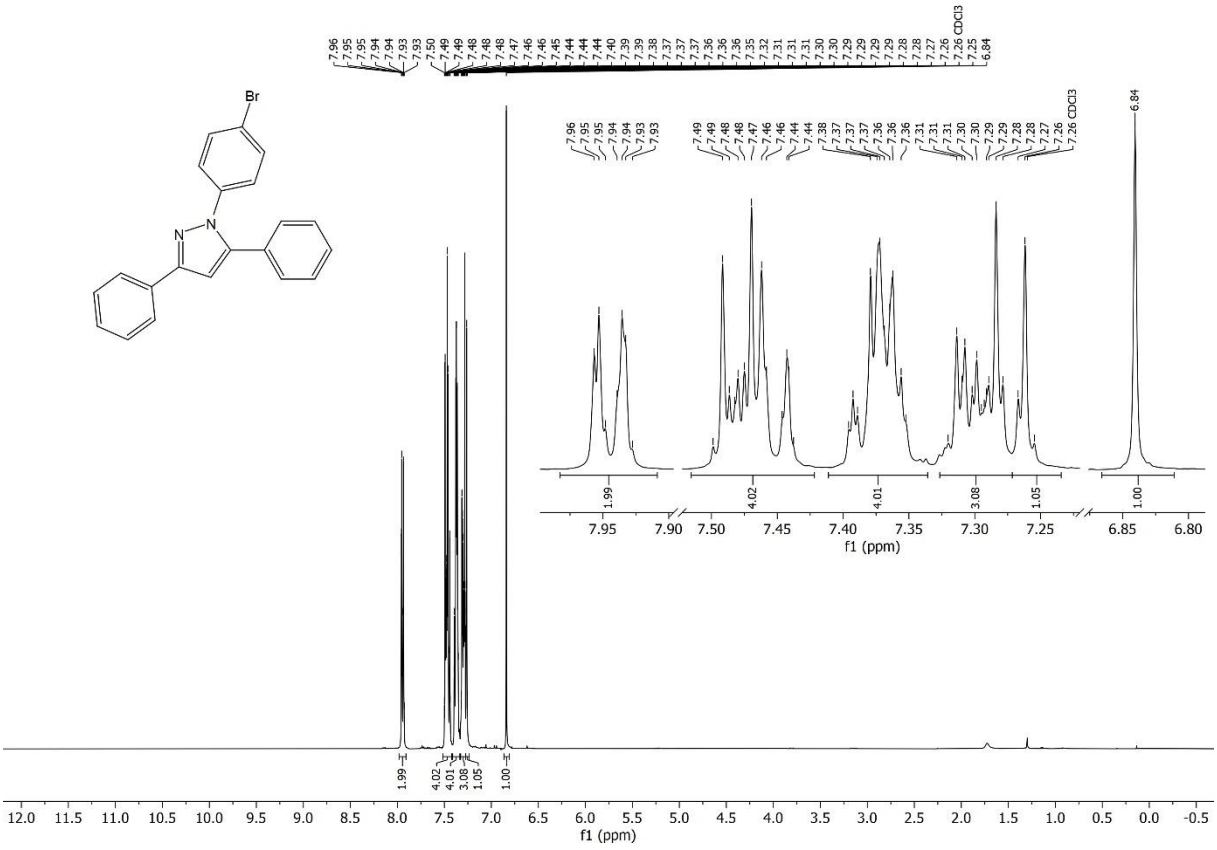

Figure S174: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5z.**

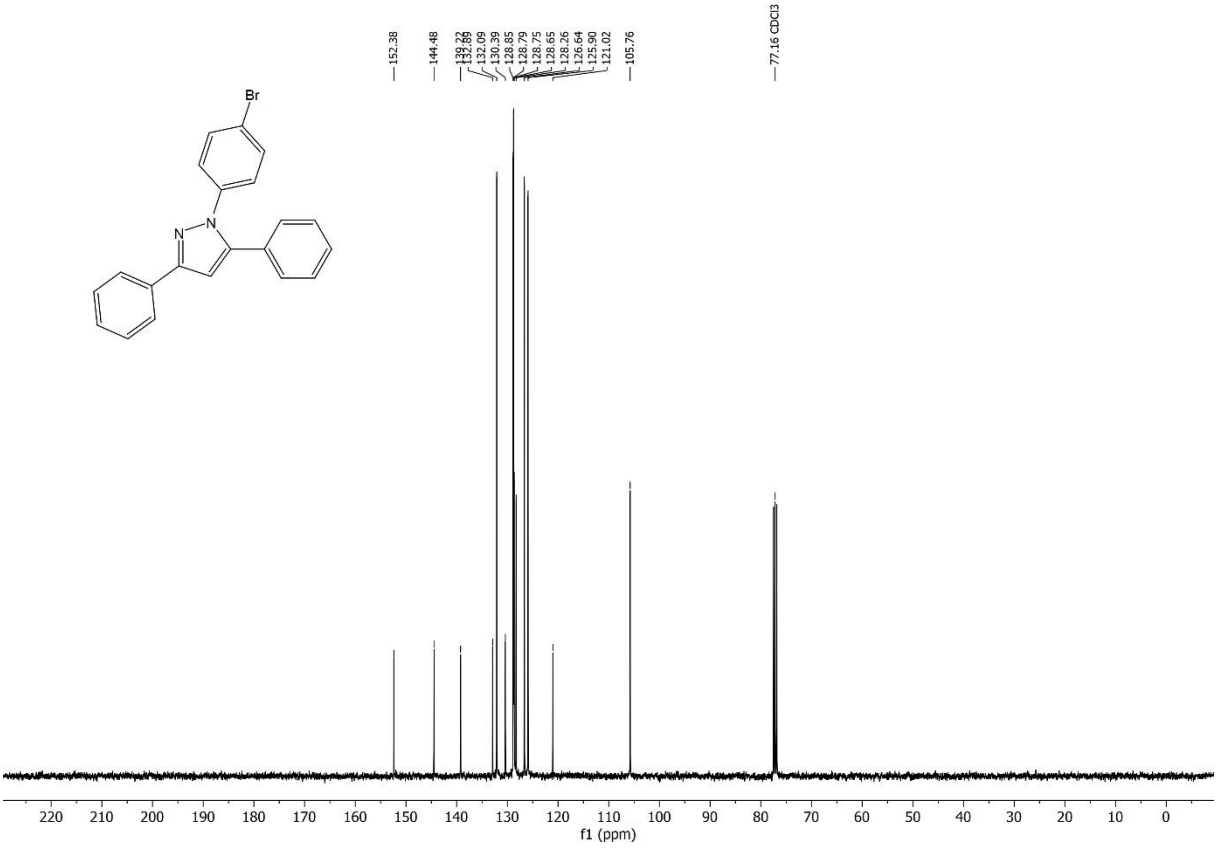

Figure S175: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5z.**

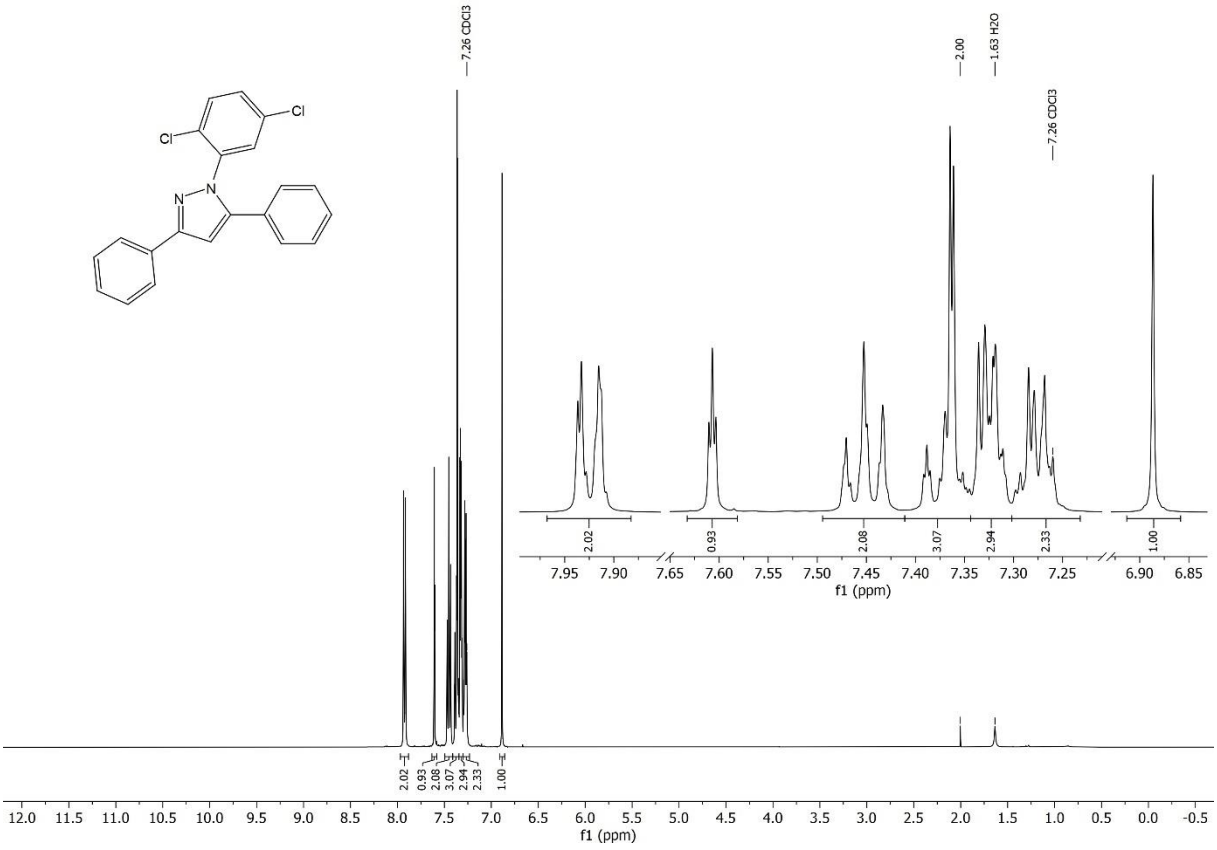

Figure S176: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5a'.**

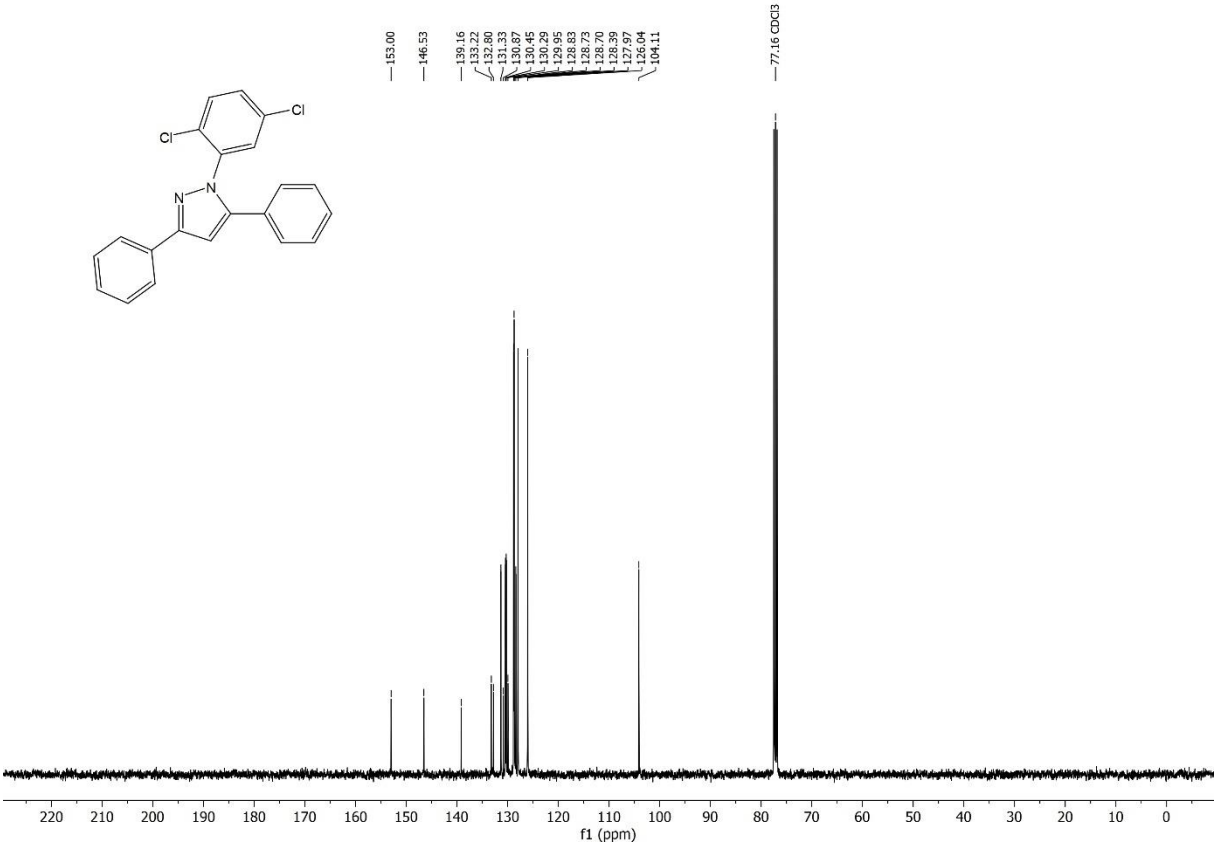

Figure S177: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5a'.**

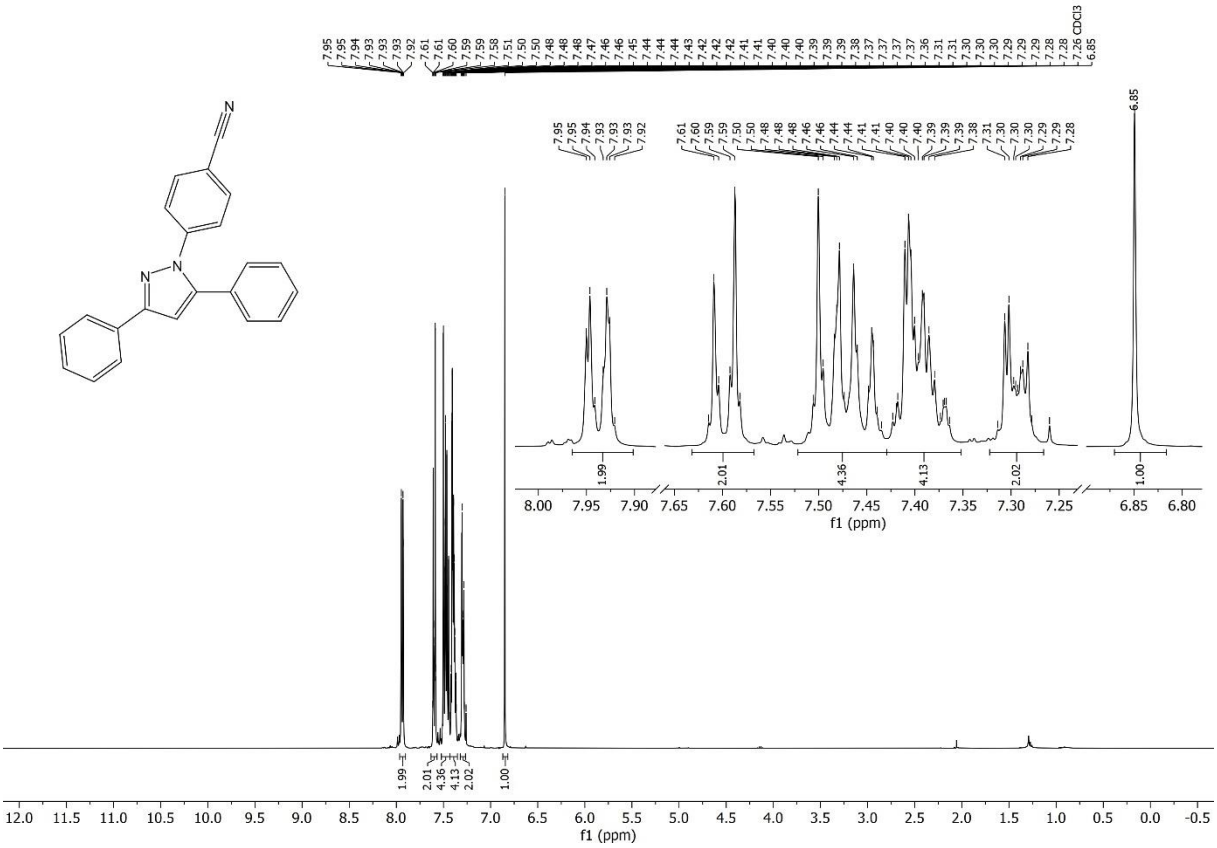

Figure S178: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b'.**

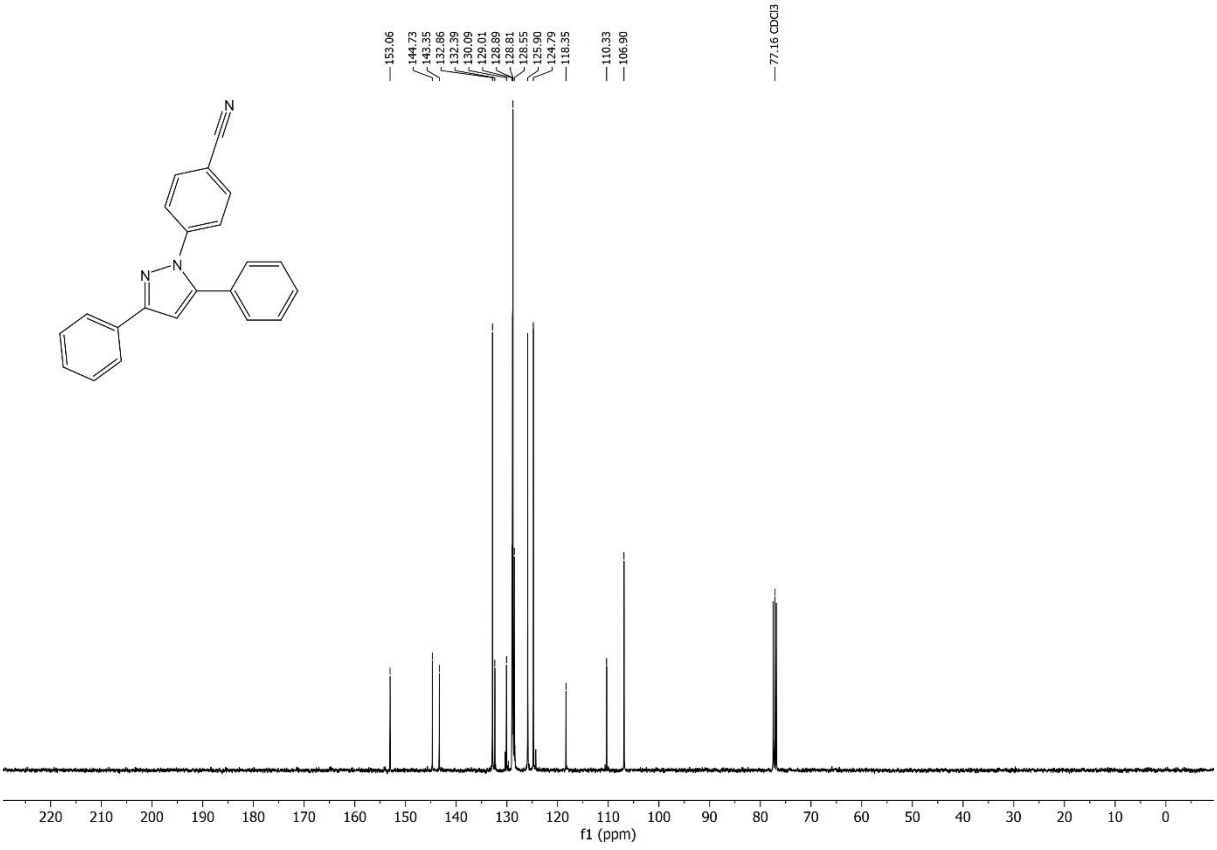

Figure S179: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5b'.**

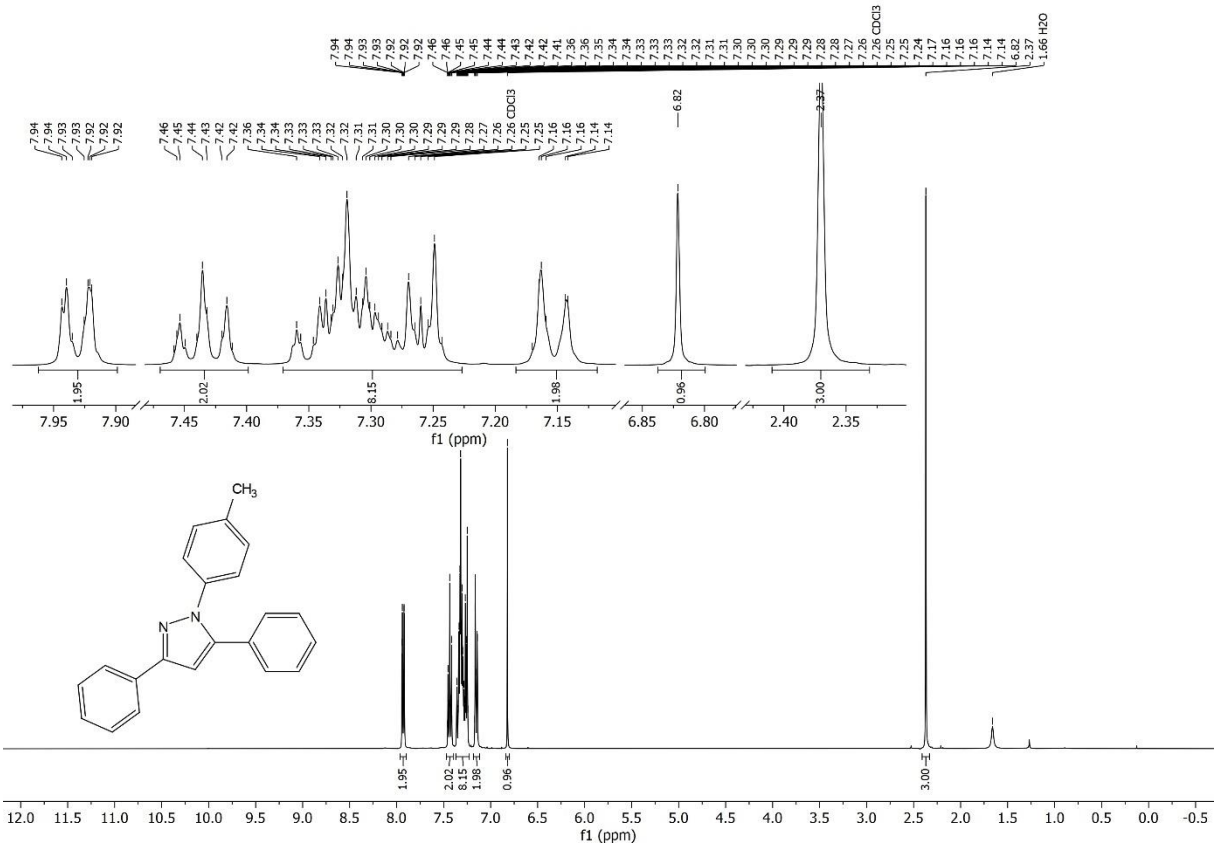

Figure S180: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c'.**

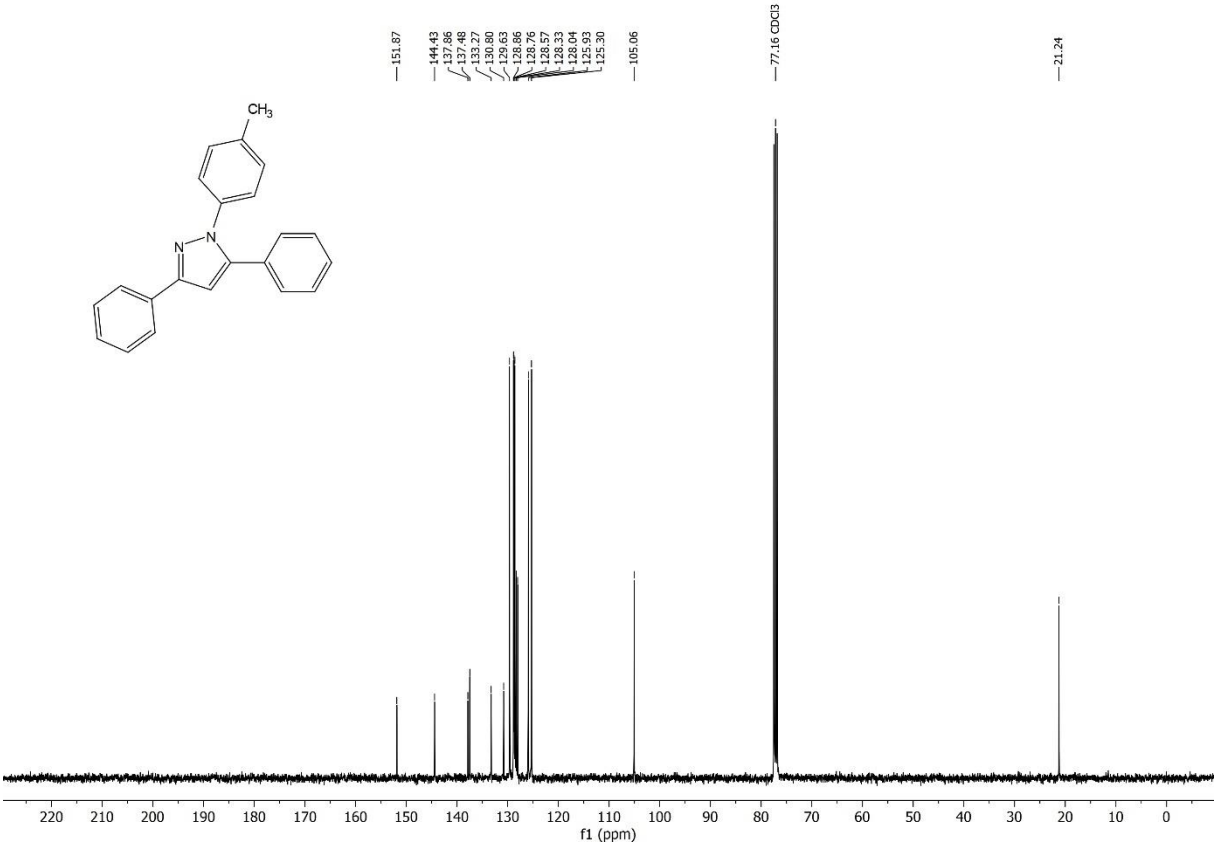

Figure S181: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5c'.**

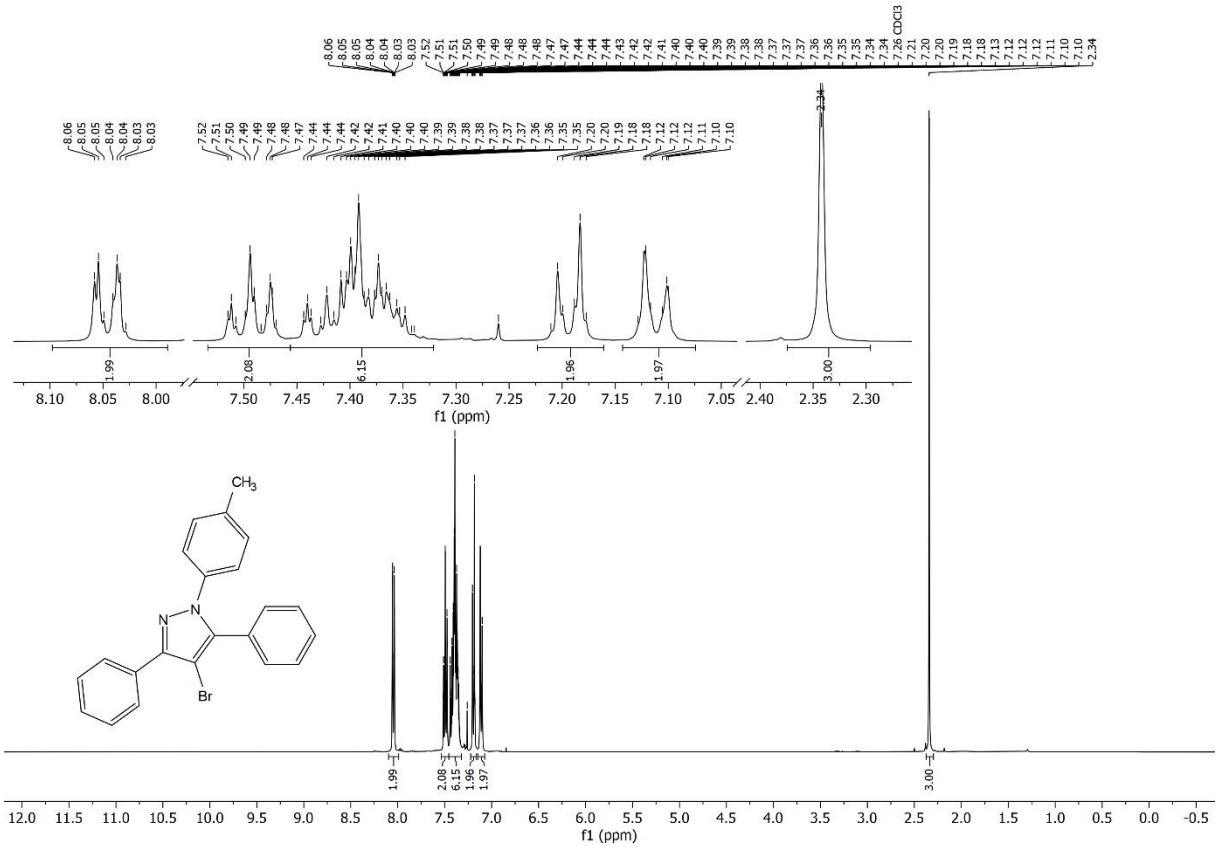

Figure S182: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5d'.**

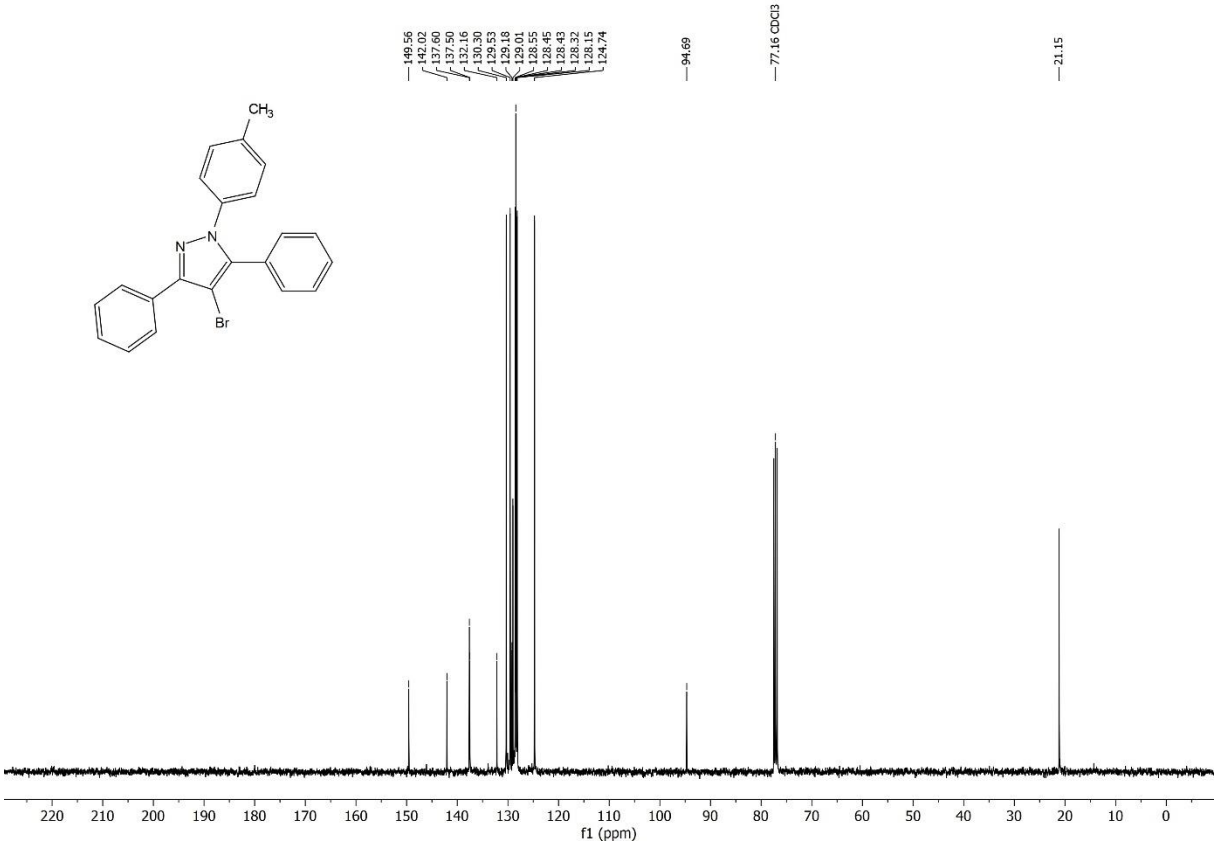

Figure S183: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5d'.**

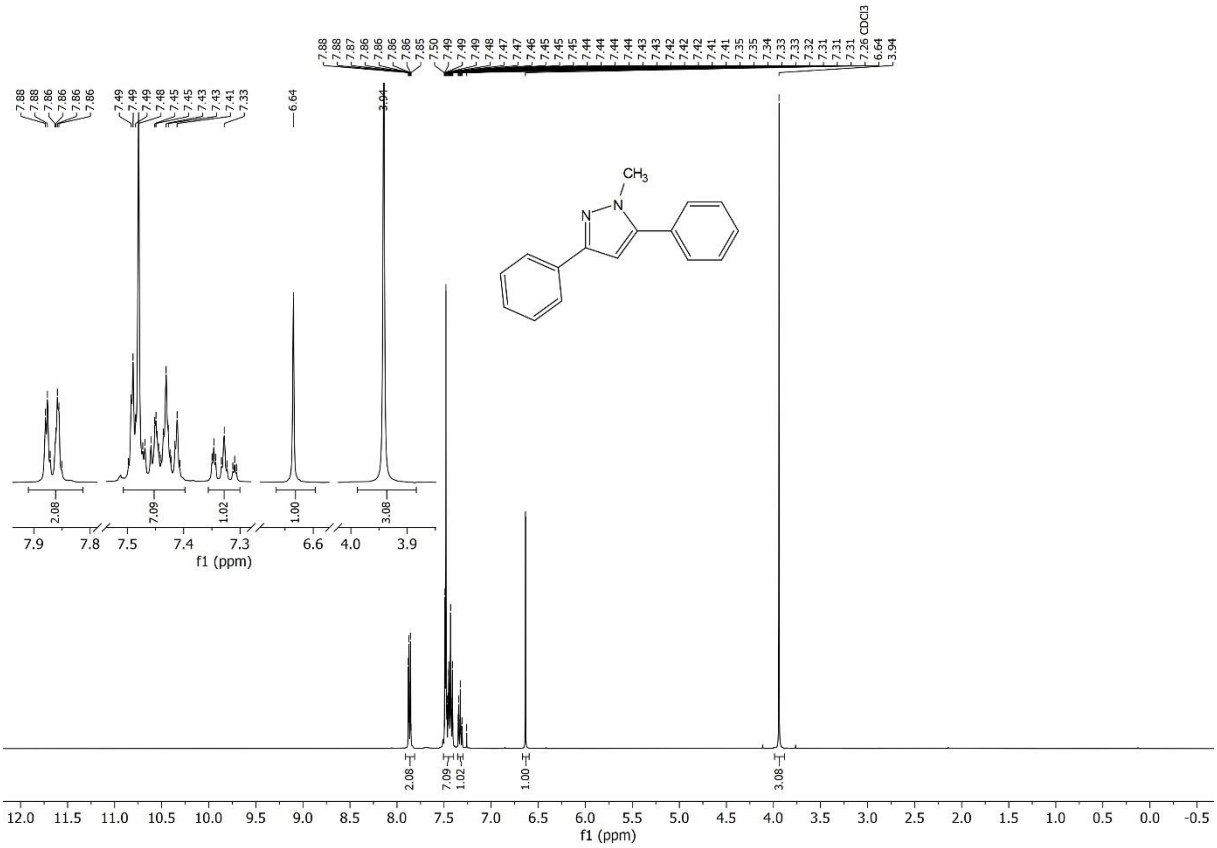

Figure S184: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5e'.**

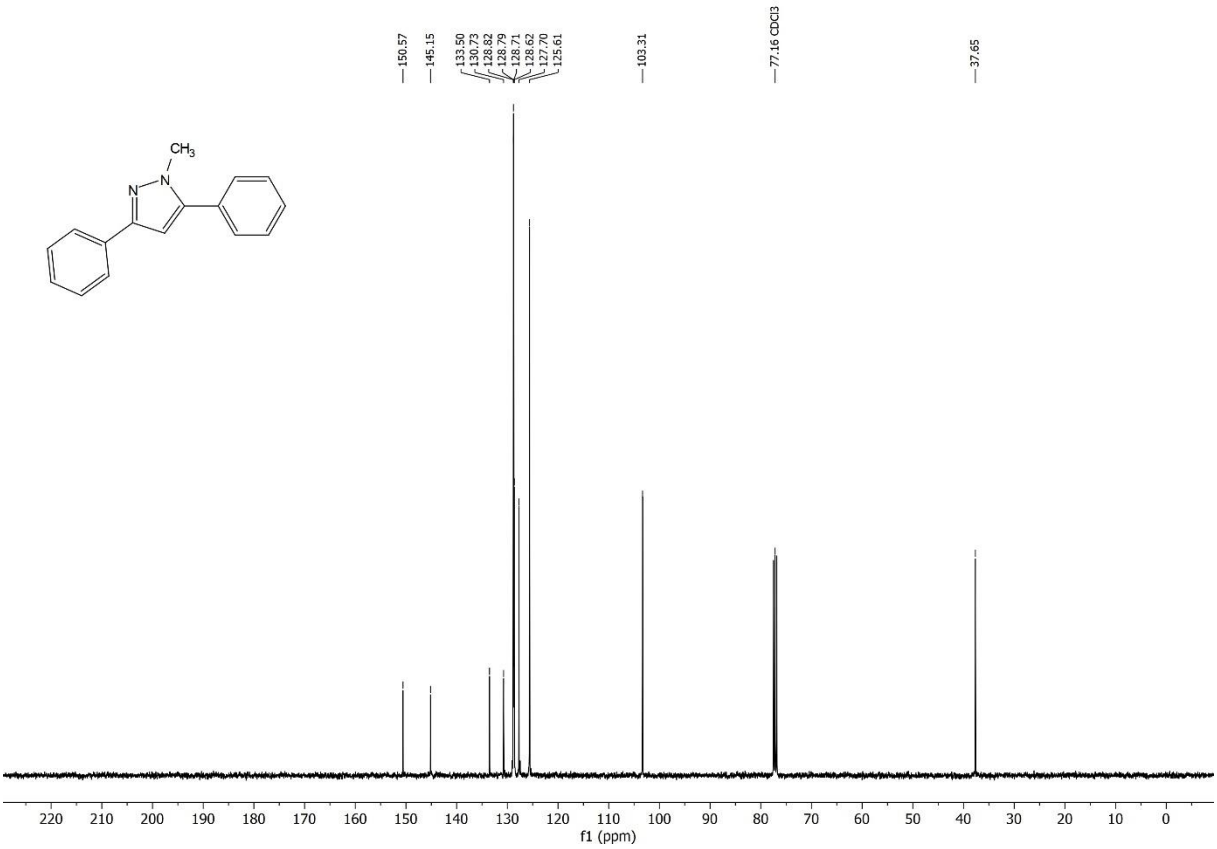

Figure S185: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5e'.**

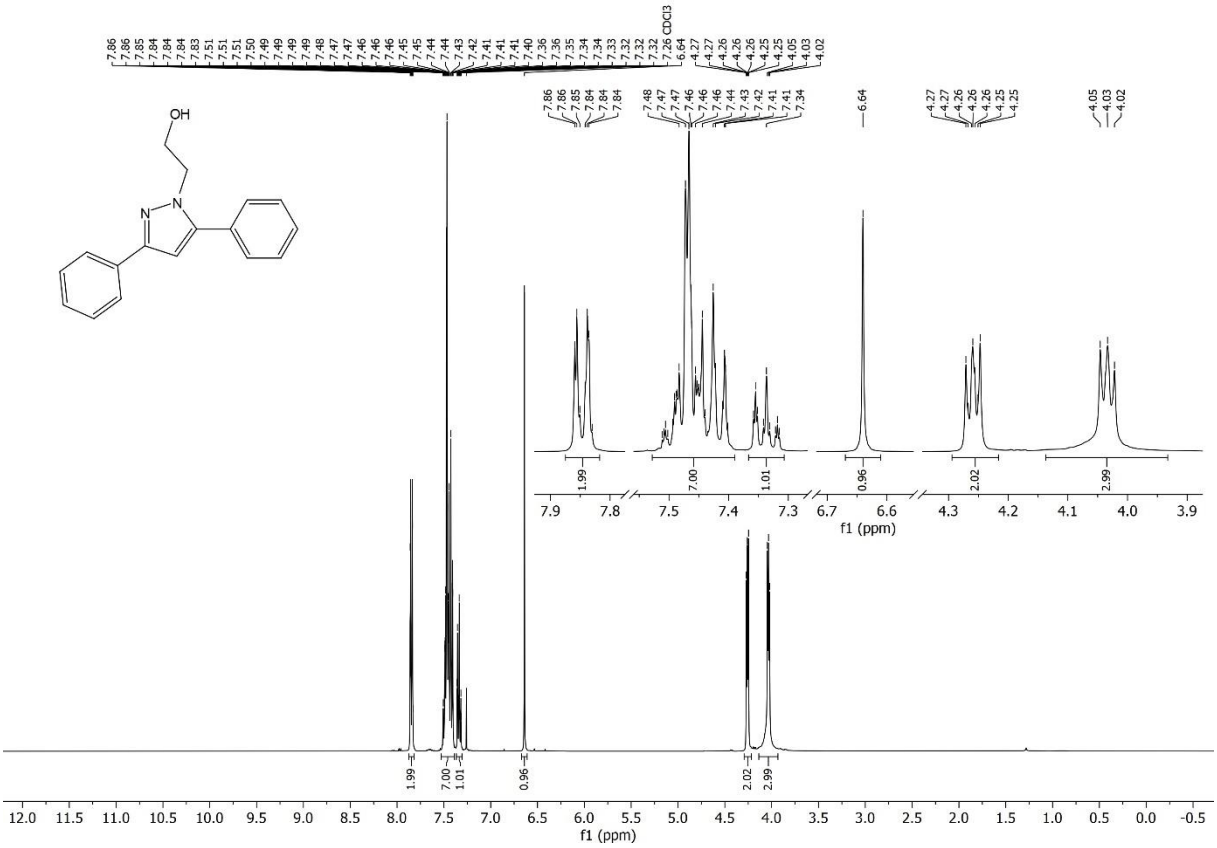

Figure S186: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5f'.**

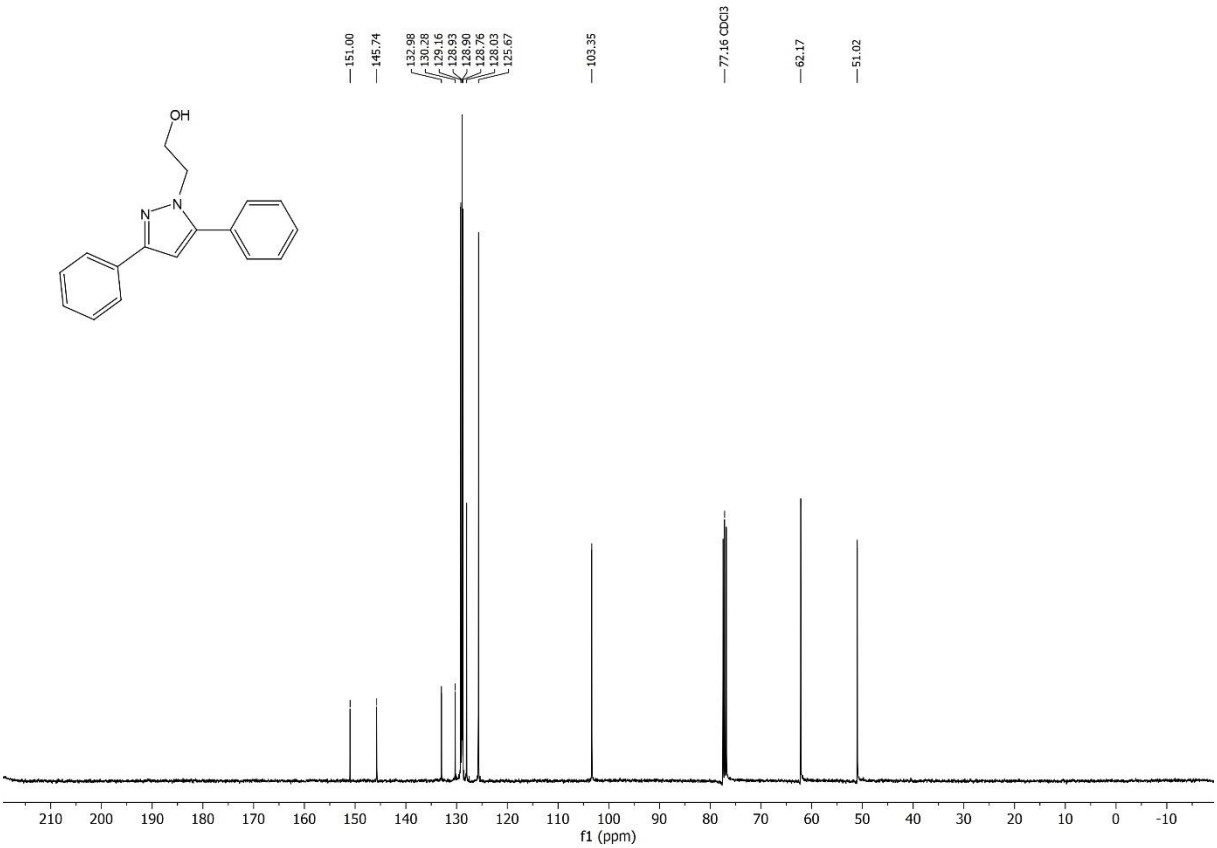

Figure S187: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5f'.**

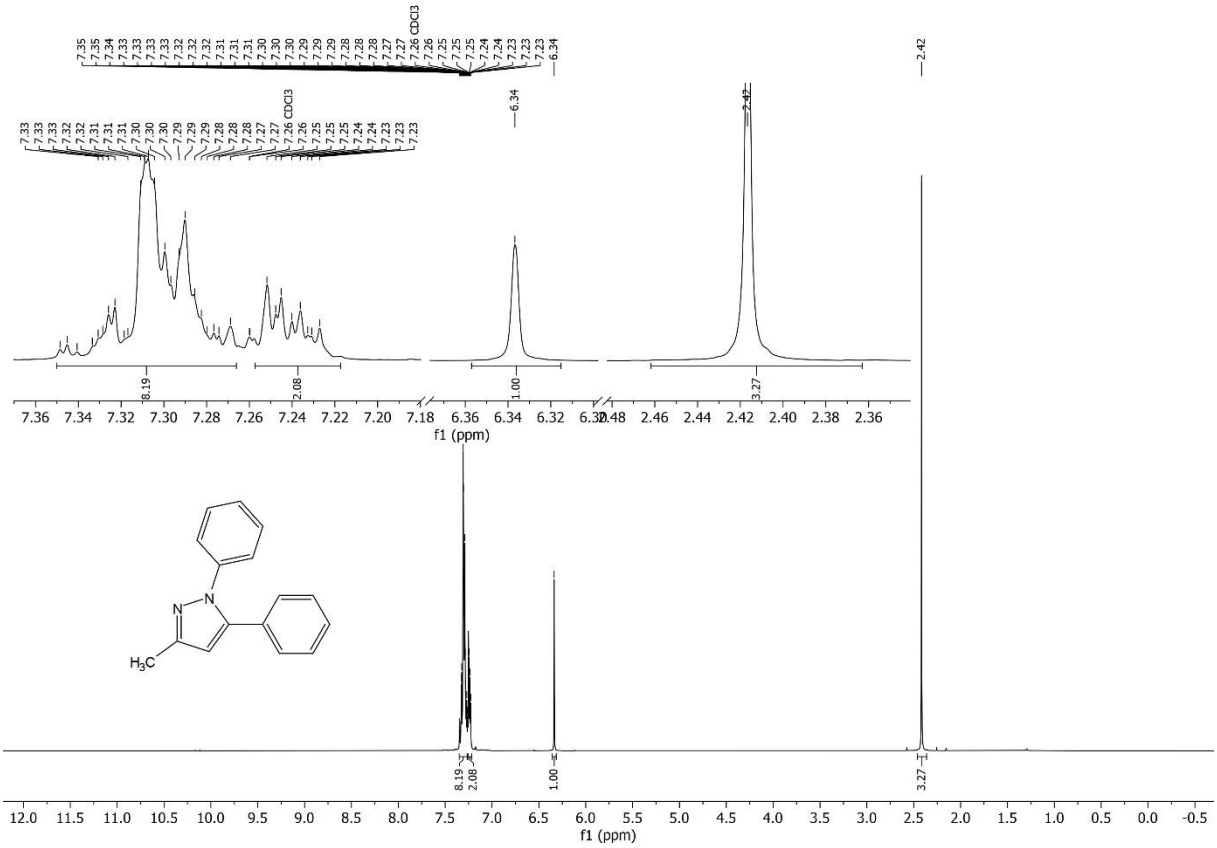

Figure S188: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5g'.**

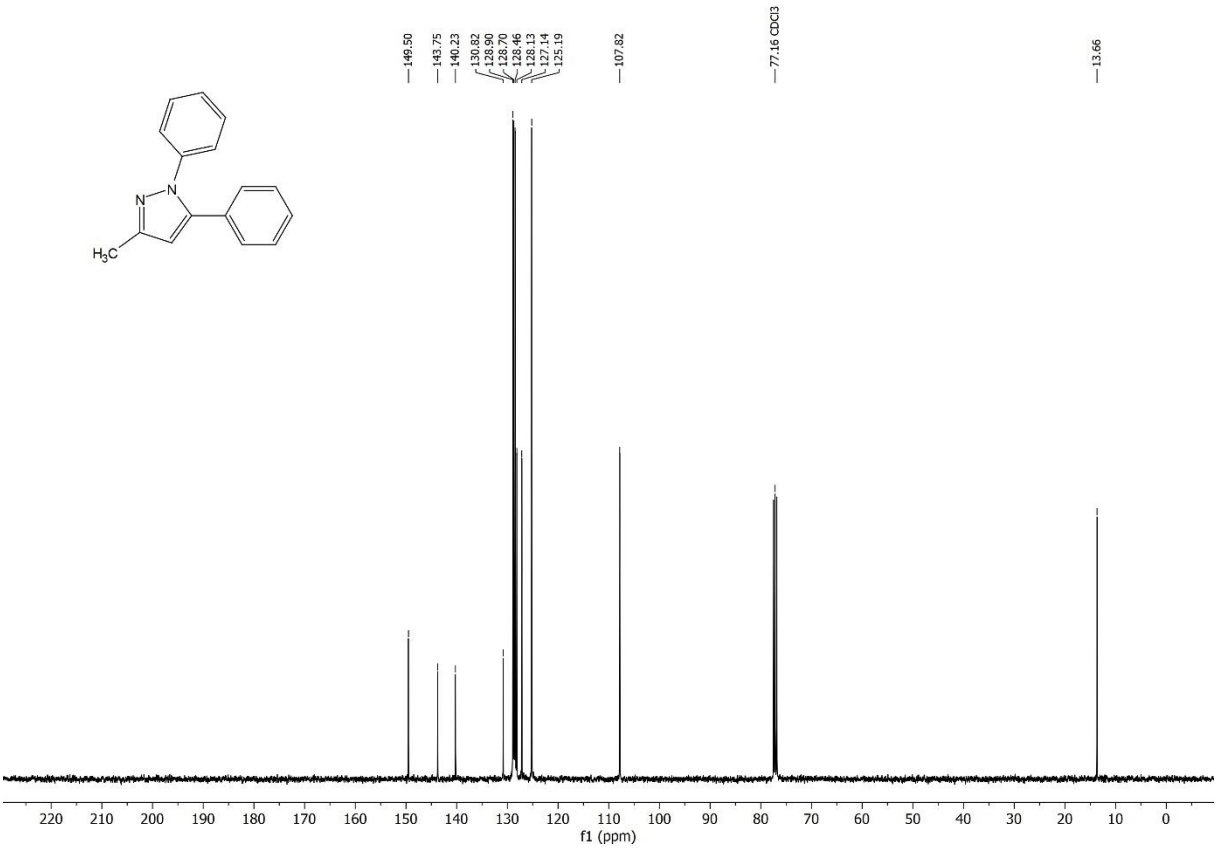

Figure S189:

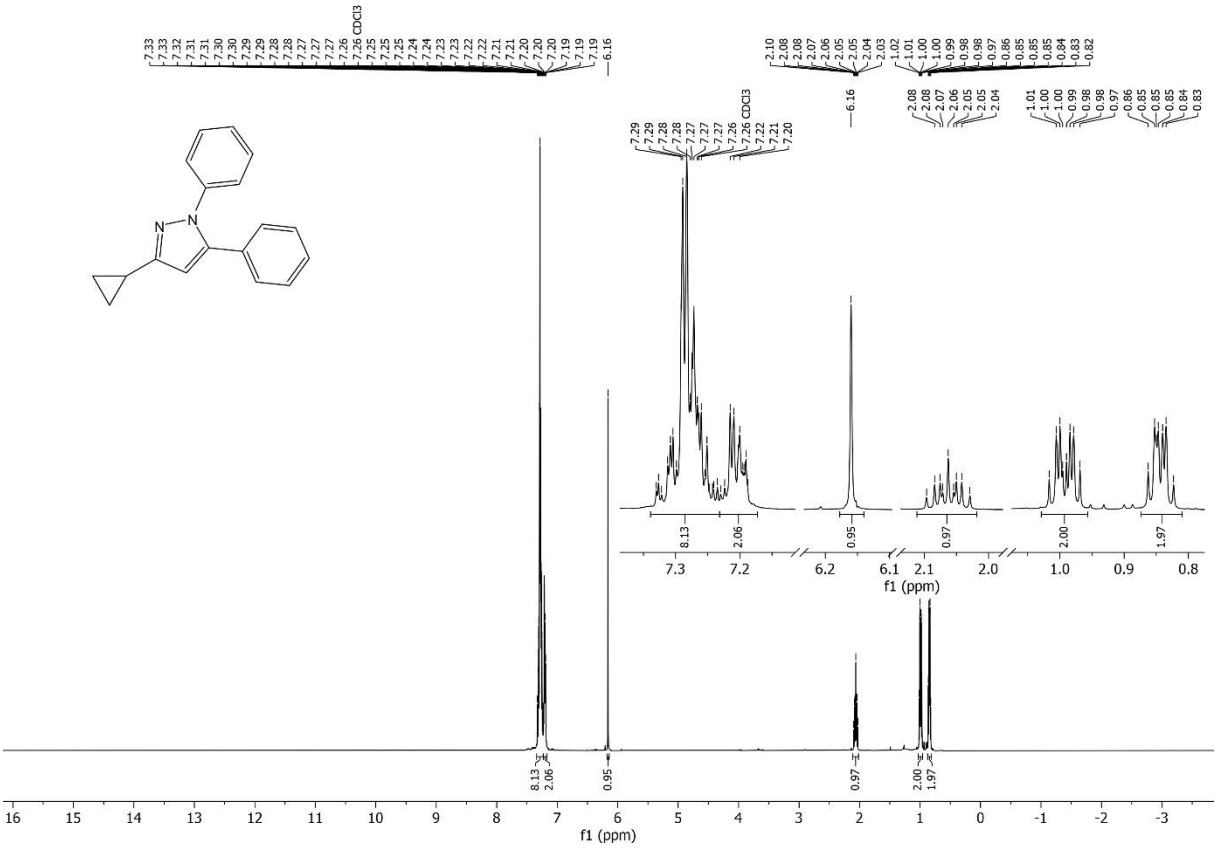

Figure S190: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5h'.**

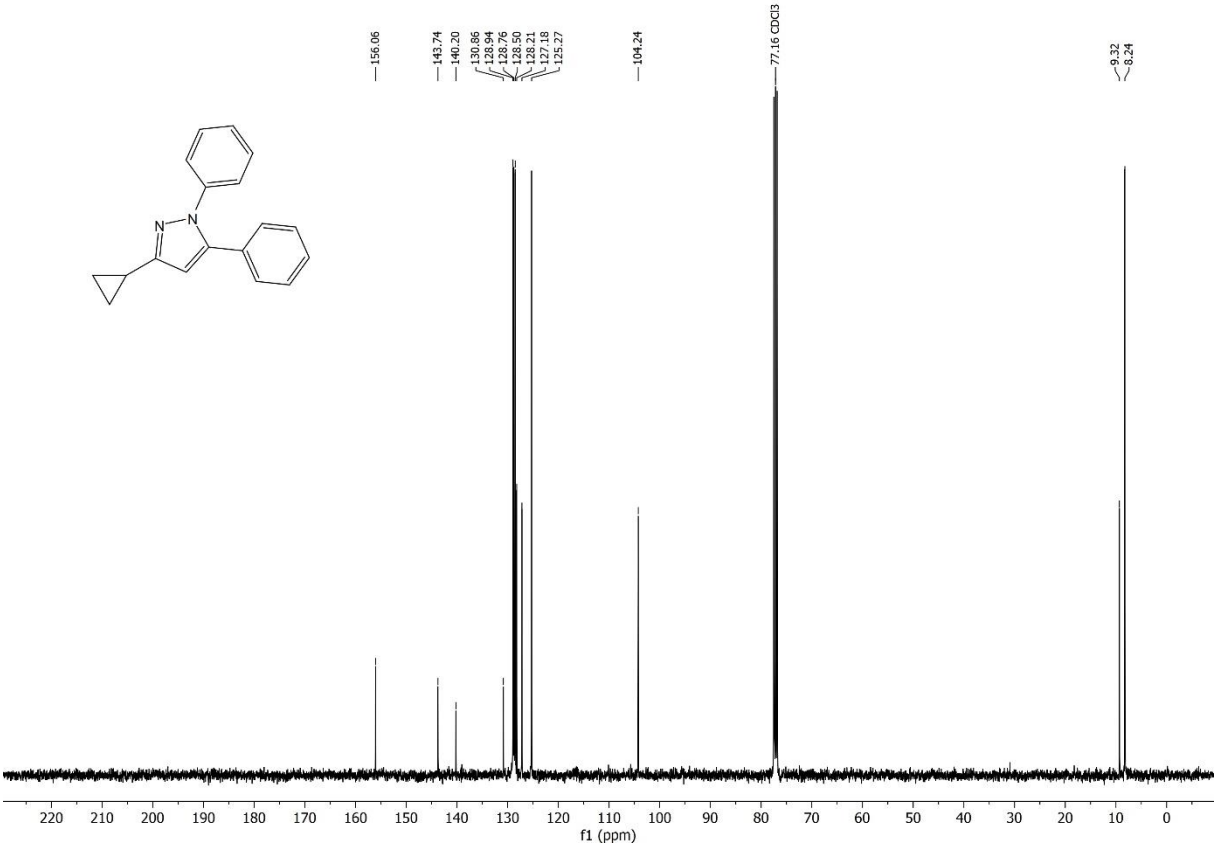

Figure S191: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5h'.**

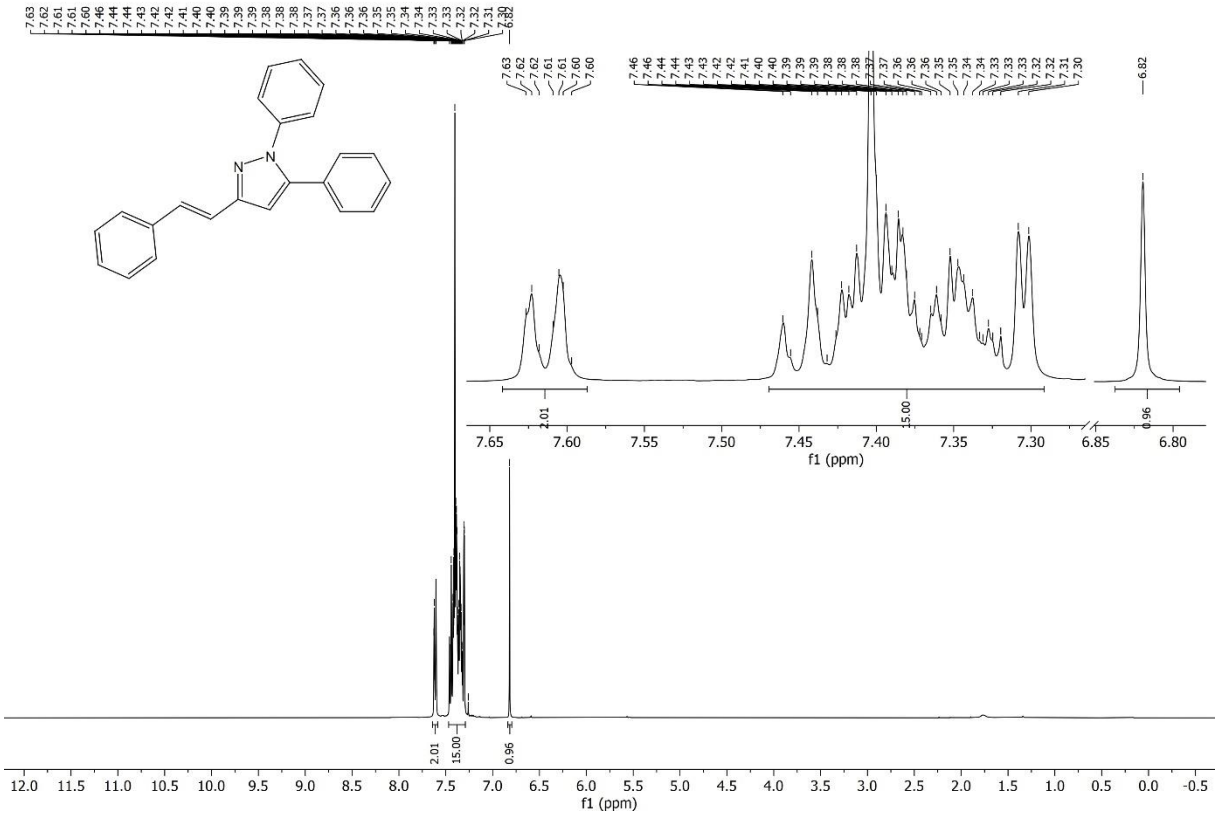

Figure S192: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5i'.**

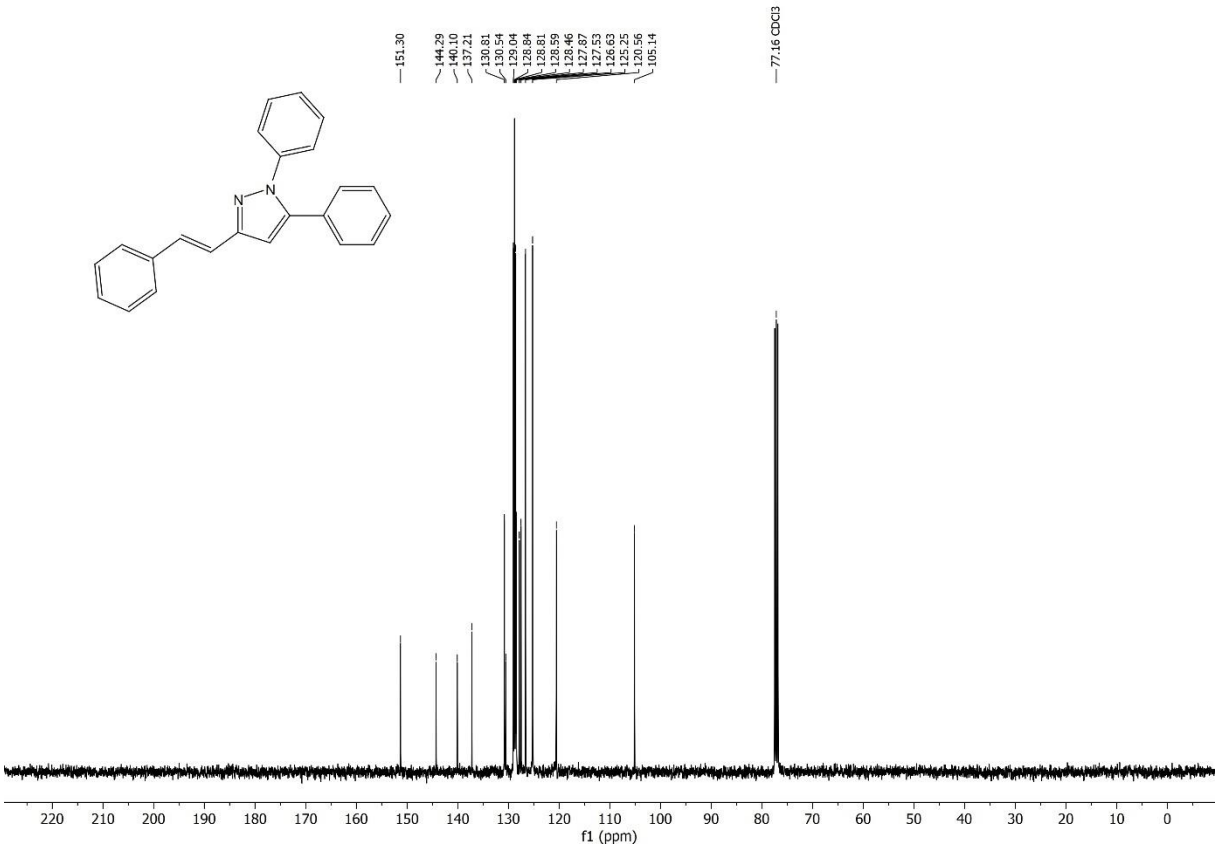

Figure S193: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5i'.**

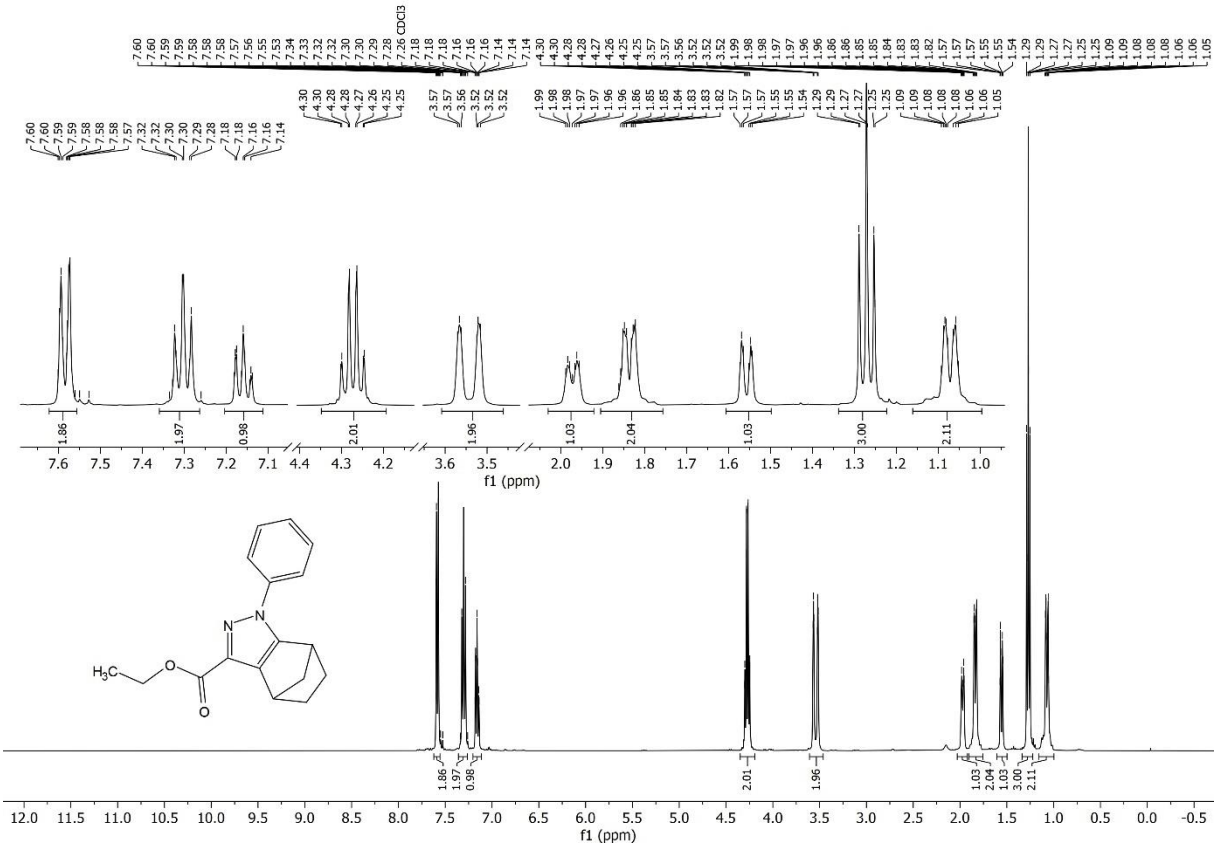

Figure S194: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5j'.**

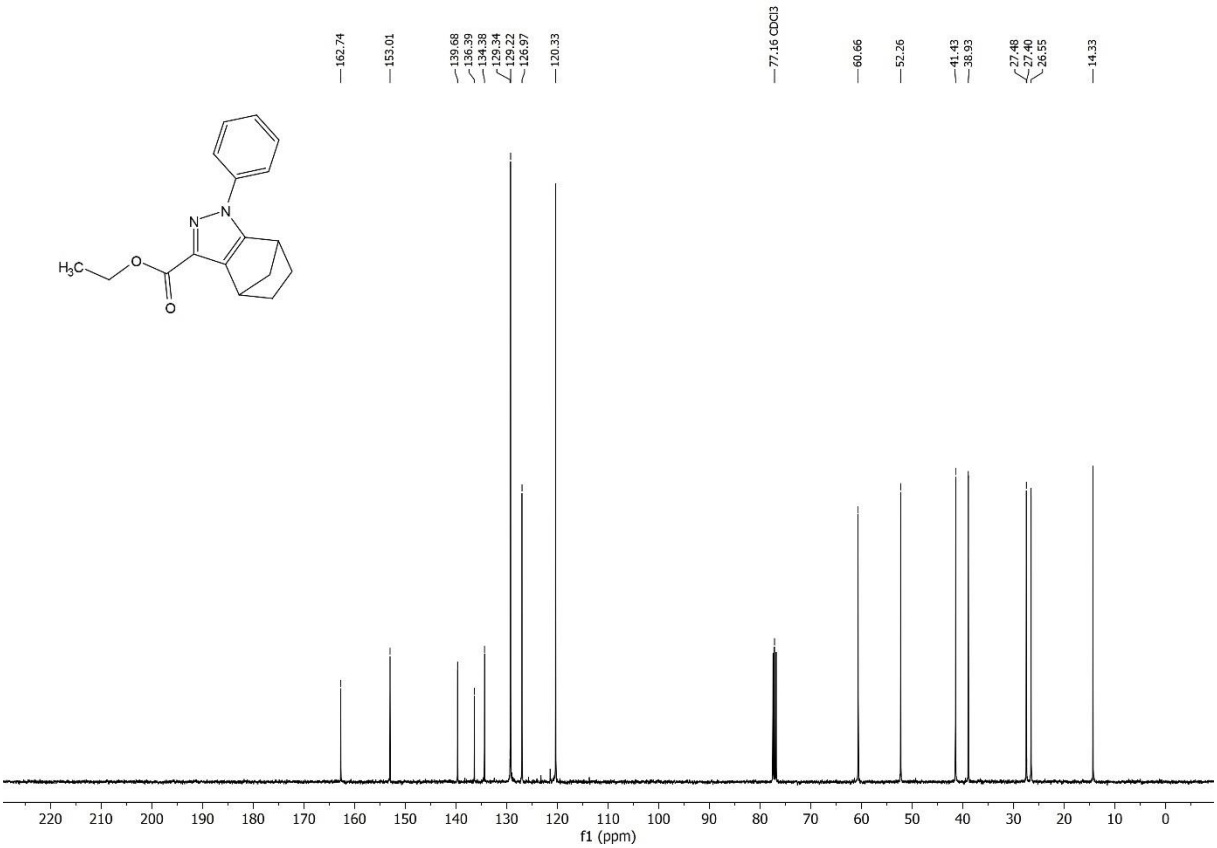

Figure S195: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5j'.**

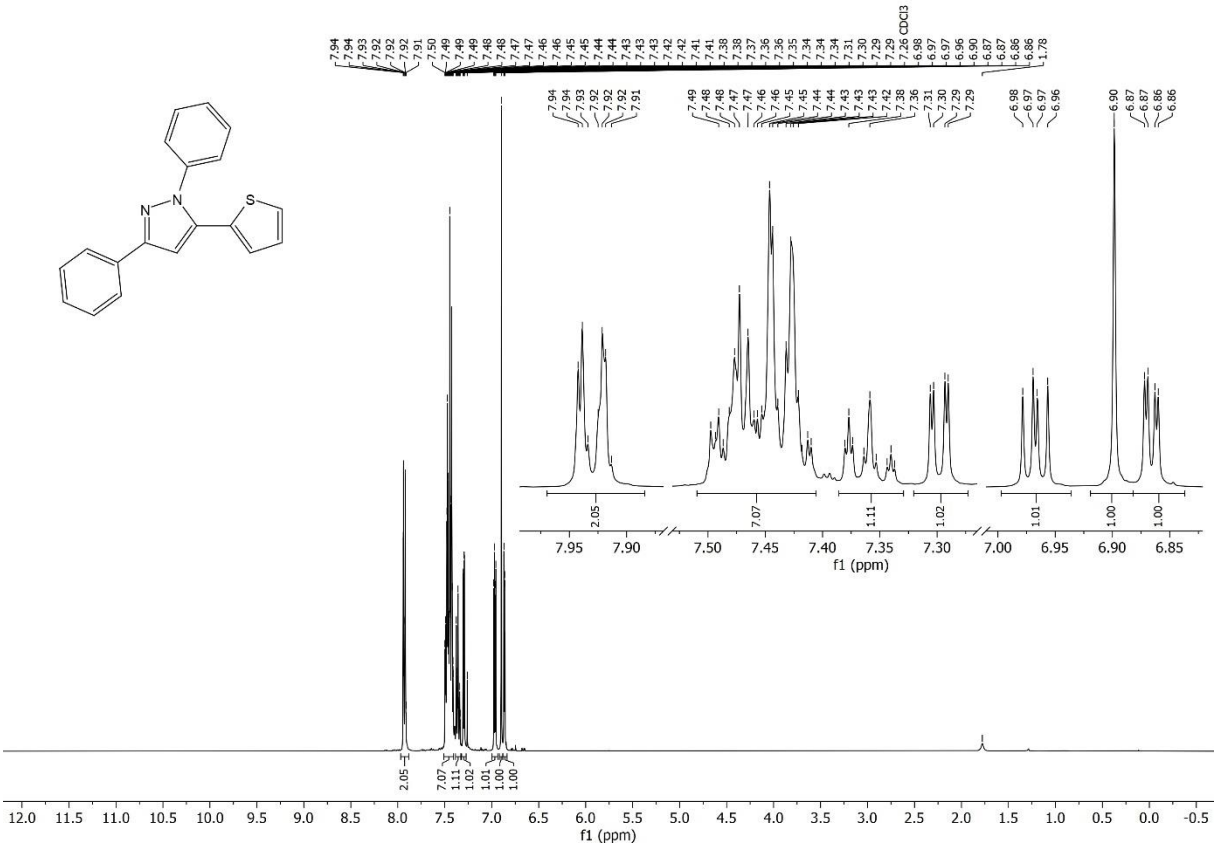

Figure S196: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5k'.**

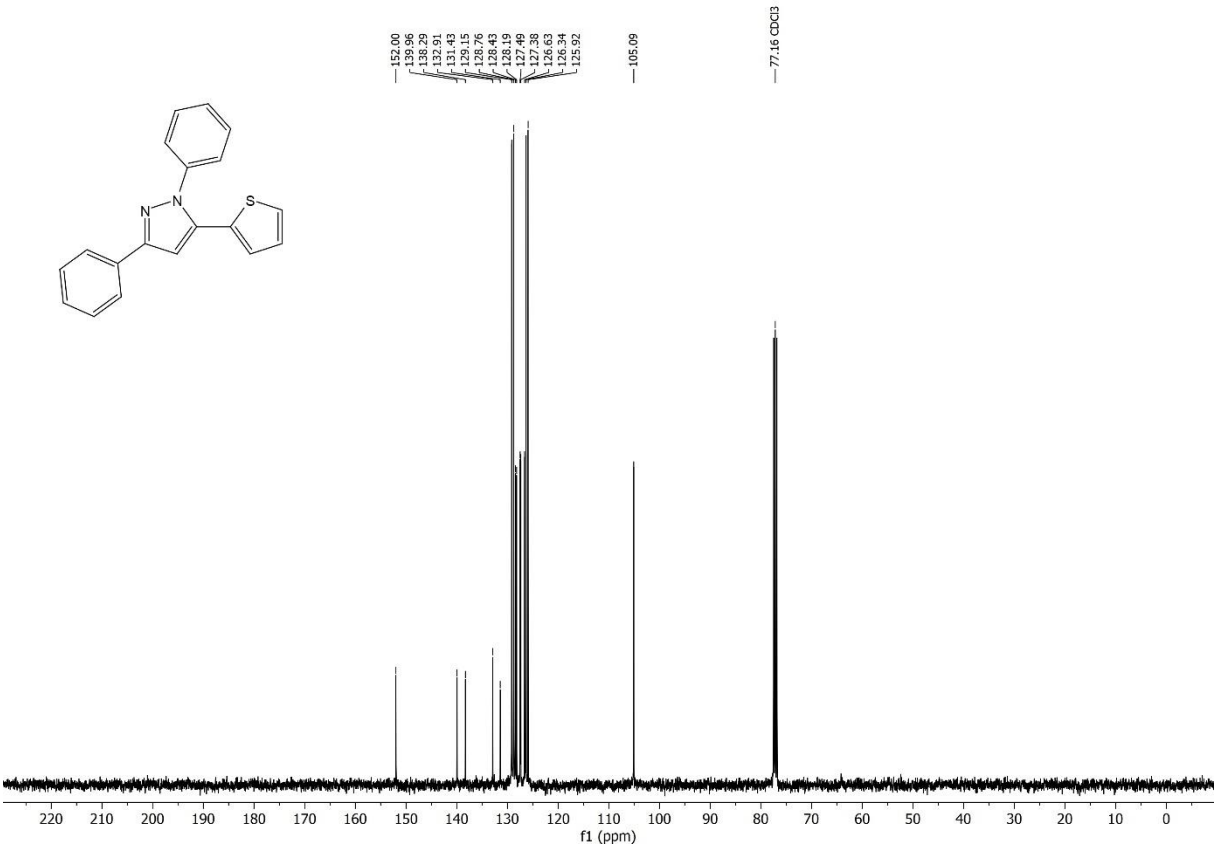

Figure S197: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5k'.**

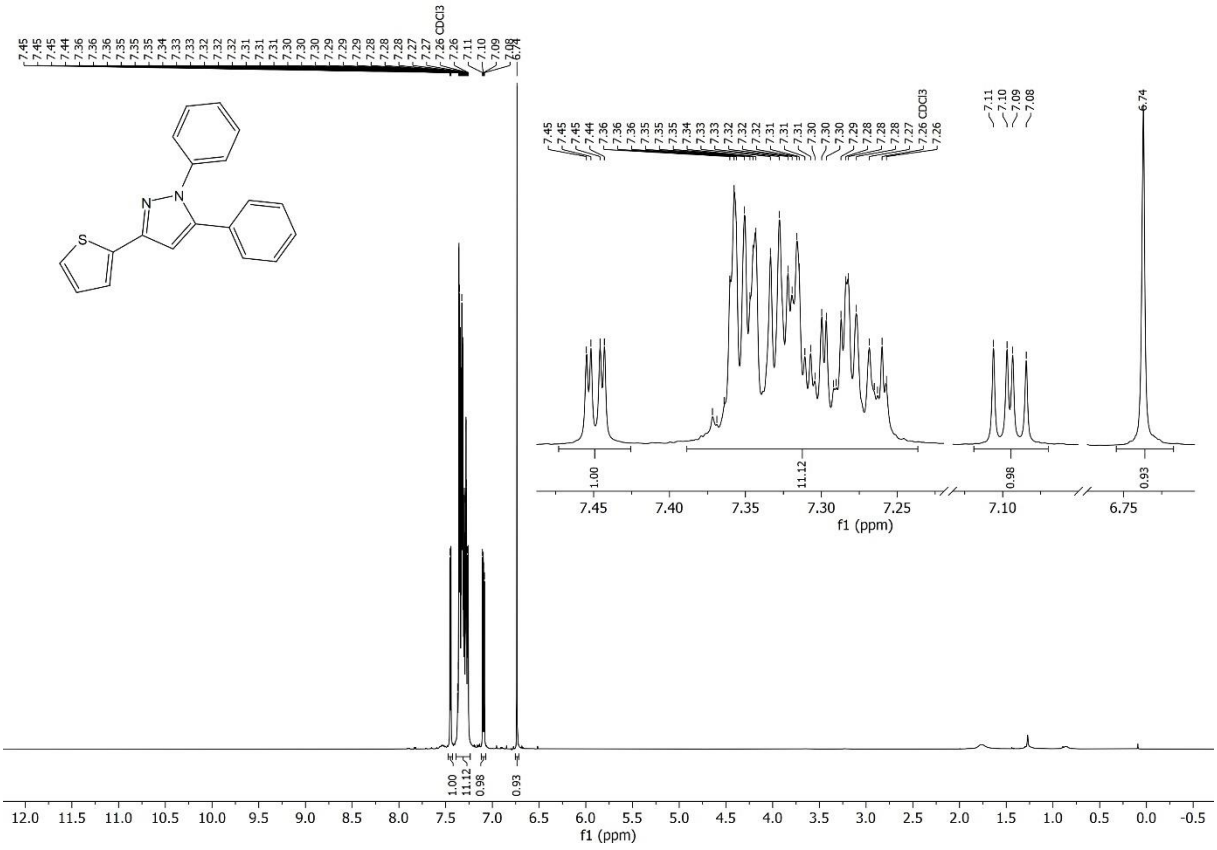

Figure S198: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5l'.**

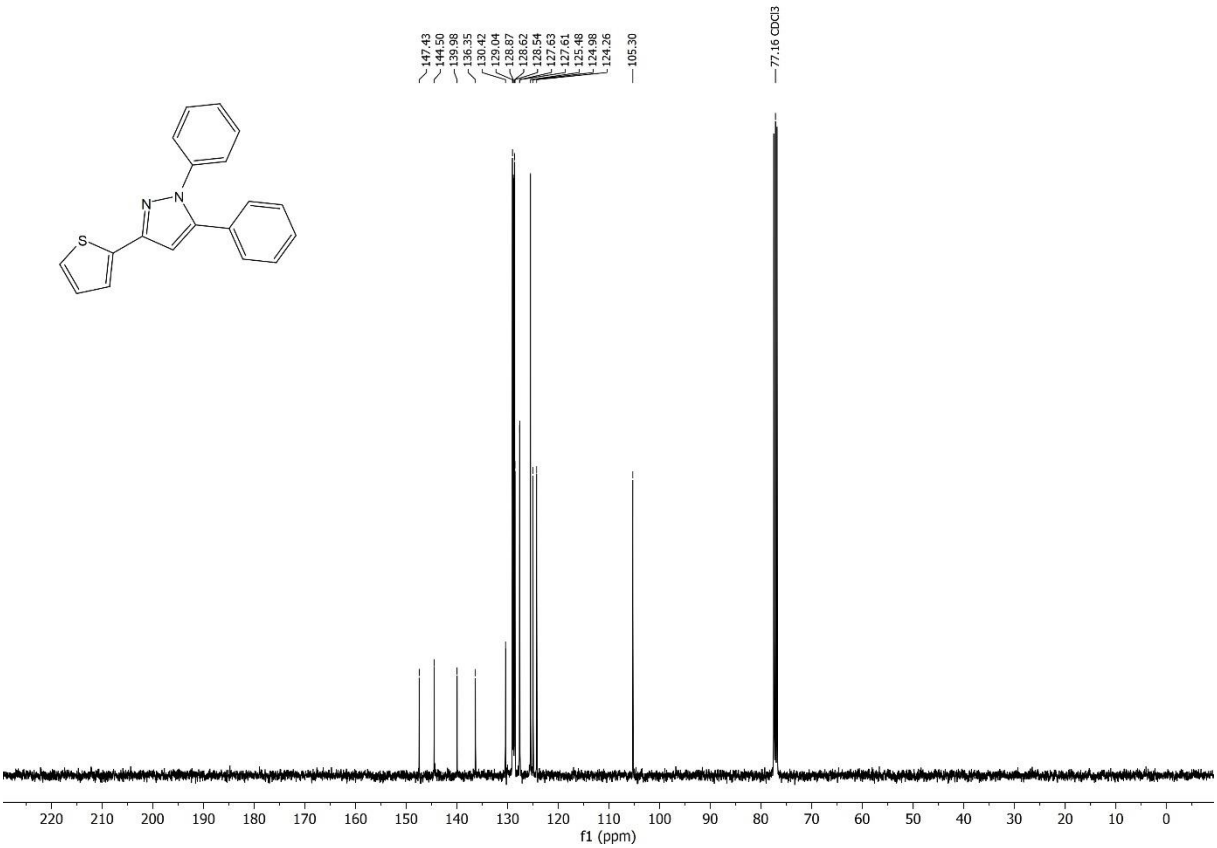

Figure S199: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5l'.**

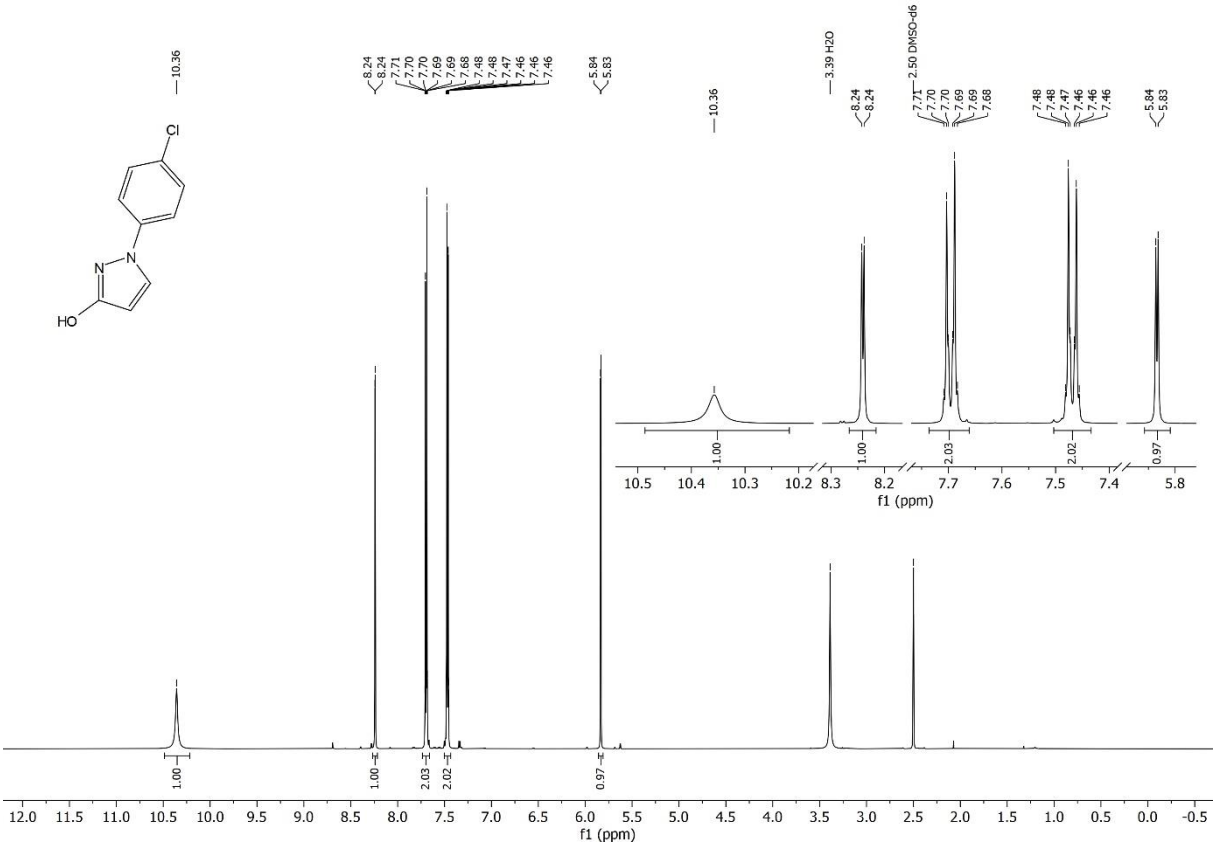

Figure S200: ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of **5m'.**

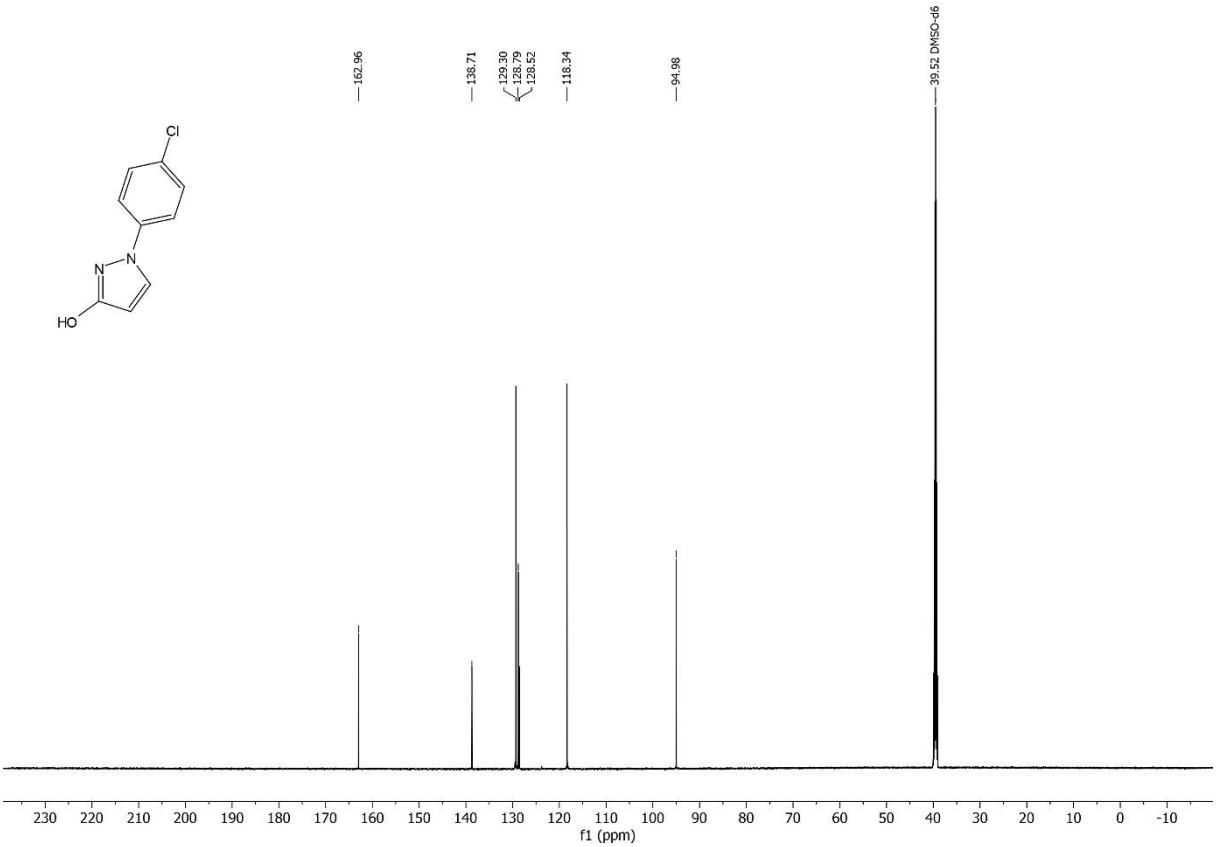

Figure S201: ^{13}C NMR spectrum (151 MHz, DMSO-d_6) of **5m'.**