Supporting Information

Visible light-induced organo-photocatalyzed route to synthesize substituted pyrazoles

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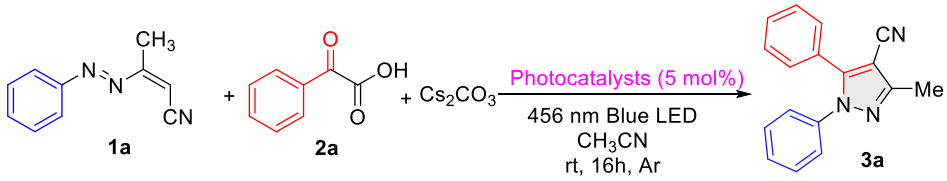
1. General Information. All solvents were dried, and commercial reagents were purified following L. L Chai and Armarego Purification of Laboratory Chemicals guidelines. All commercially available chemical reagents were obtained from commercial suppliers (Alfa Aesar, TCI, BLD pharm, Sigma-Aldrich, and Spectrochem). Unless otherwise stated, all reactions were conducted in dried glassware with magnetic stirring under an Argon atmosphere. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 and visualized under ultraviolet light, iodine stain, or $KMnO_4$ stain. Flash column chromatography was performed using silica gel (230−400 μm, Merck) using the eluent system described for each experiment. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Kessil blue LEDs, 456 nm (40 W), were used as a visible-light source. Details of the photoreaction setup are described. All NMR spectra were recorded on 500 MHz Bruker spectrometers. ^{1}H, ^{13}C, and ^{19}F NMR spectral data are reported as chemical shifts (δ) in parts per million (ppm), and coupling constants (*J*) are measured in hertz (Hz). The following abbreviations describe multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, br = broad, and m = multiplet. NMR spectra were processed in MestReNova, keeping the $CDCl_3$ residual peak at 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR. High-resolution mass spectra (HRMS, *m/z*) were recorded on a Micro-TOF spectrometer (Bruker). All fluorescence spectra were recorded in a HITACHI F7000 spectrofluorometer.

2. Optimization reaction conditions:

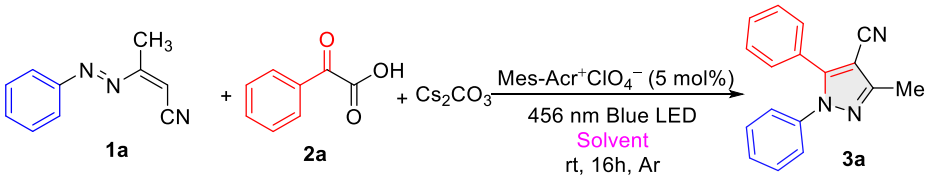
Table S1. Optimization of photocatalysts[a]:



Entry	Photocatalyst	% of 3a[b]
A.	4CzIPN	31
B.	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	35
C.	$[Ir(ppy)_2(5,5'\text{-}Me_2bpy)]PF_6$	16
D.	$[Ir(dtbbpy)(ppy)_2]PF_6$	34
E.	DCA	35
F.	$Ru(bpy)_2Cl_2$	41
G.	Mes-Acr$^{+}ClO_4^{-}$	64
H.	Eosin-Y	38
I.	T(p-Me)PPT	35

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), bases (0.1 mmol, 0.5 equiv) CH_3CN (2.0 mL), irradiation with 40 W 456 nm blue LED, 16 h, under Ar atmosphere. [b] ^{1}H NMR Yield using tetrachloroethane as an internal standard.

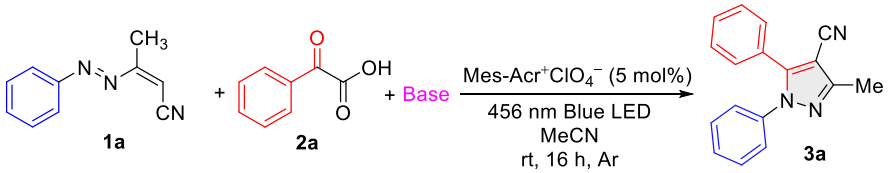
Table S2. Optimization of solvent [a]:



Entry	Solvent	% of 3a[b]
A.	DCM	51
B.	MeCN	63
C.	DCE	55
D.	$CHCl_3$	53
E.	Acetone	26
F.	MeOH	49
G.	Diethyl ether	14
H.	Chlorobenzene	15
I.	Toluene	12
J.	Dioxane	42

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), bases (0.1 mmol, 0.5 equiv) Solvent (2.0 mL), irradiation with 40 W 456 nm blue LED, 16 h, under Ar atmosphere. [b]^{1}H NMR Yield using tetrachloroethane as an internal standard.

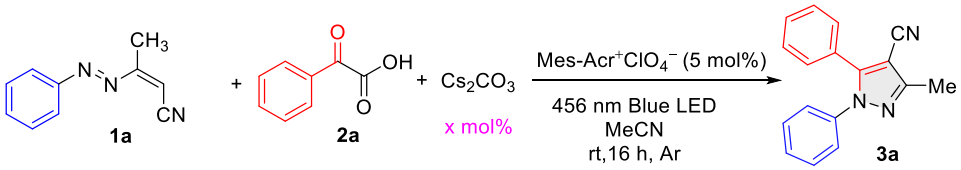
Table S3. Optimization of Bases [a]:



Entry	Base	% of 3a[b]
A.	K_2CO_3	35
B.	Cs_2CO_3	61
C.	K_3PO_4	54
D.	CsOAc	53
E.	K_2HPO_4	53
F.	DBU	46
G.	$NaHCO_3$	44
H.	^{t}BuOK	49
I.	KH_2PO_4	59
J.	Collidine	57
K.	Na_2CO_3	44
L.	-	0

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), CH_3CN (2.0 mL), irradiation with 40 W 456 nm blue LED, under Ar atmosphere. [b]^{1}H NMR Yield using tetrachloroethane as an internal standard.

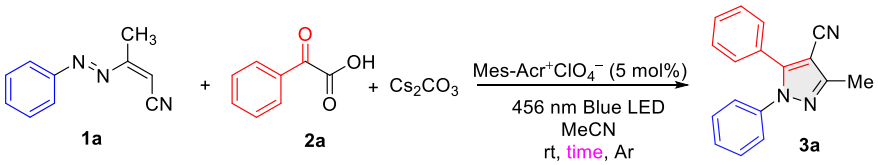
Table S4. Optimization of base amount [a]:



Entry	Amount of Cs_2CO_3	% of 3a[b]
A.	0.2 eq.	46
B.	0.5 eq.	62
C.	1 eq.	60
D.	2 eq.	58

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), CH_3CN (2.0 mL), irradiation with 40 W 456 nm blue LED, under Ar atmosphere. [b]^{1}H NMR Yield using tetrachloroethane as an internal standard.

Table S5. Optimization of reaction time [a]:



Entry	Time (h)	% of 3a[b]
A.	2	46
B.	4	60
C.	6	71
D.	8	74
E.	12	69

[a]Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.4 mmol, 2 equiv), Cs_2CO_3 (0.1 mmol, 0.5 equiv) CH_3CN (2.0 mL), irradiation with different light sources under Ar atmosphere. [b]^{1}H NMR Yield using tetrachloroethane as an internal standard.

3. General procedure and gram scale synthesis of 3a:

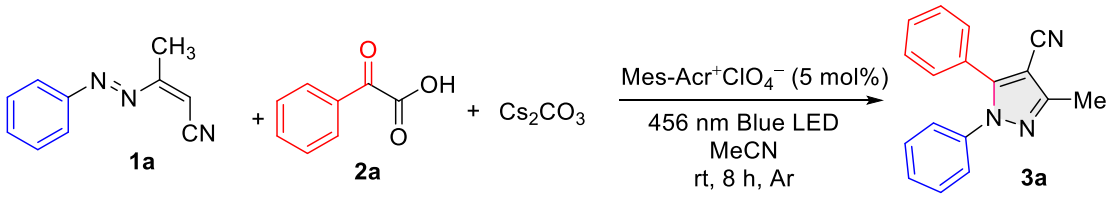
3.1 General procedure for preparation of 1,2-diaza-1,3-dienes derivatives: The starting material 3-(phenyldiazenyl)but-2-enenitrile derivatives (1a-1q) were prepared using reported method.[17]

3.2 General procedure for preparation of α-ketoacids: To a substituted methyl aryl ketones (5.0 mmol), SeO_2 (6.0 mmol), 20 mL of dry pyridine were added in a 50 mL round bottom flask. The reaction mixture was stirred at 110 ° C for 1 h in an oil bath, then the temperature was reduced to 90° C for 4 h. After completion of the reaction (monitored by TLC), the mixture was filtered, and the residue was washed with ethyl acetate (2 × 50 mL). The combined filtrate was treated with 1 M NaOH (2 × 20 mL), and the aqueous layer was separated. The aqueous layer was treated with 1 M HCl (2 × 20 ml) and washed with ethyl acetate (50 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated on a rotary evaporator. The desired products were isolated by

flash chromatography on silica gel using petroleum ether and ethyl acetate to give 2. All α-ketoacids are known compounds.

3.3 Experimental procedure for the synthesis of 3: To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar, **1** (0.2 mmol, 1 equiv.), **2** (0.3 mmol, 1.5 equiv.), Cs_2CO_3 (0.1 mmol, 0.5 equiv.) and Mes-Acr$^+$ClO$_4^-$ (5 mol%) was added. Then, the reaction tube was applied to a vacuum for 5 minutes and then backfilled with Argon, and this cycle was repeated four more times. A rubber septum was put on the top of the reaction tube tightly, with continuous Argon flow, and freshly dried CH_3CN (2 mL) was added using a syringe. Then, the reaction tube was placed on a magnetic stirrer and irradiated using a 456 nm blue LED (40 W, Kessil), keeping ~3 cm distance between them. A cooling fan was fitted approximately one foot to keep the system cool at room temperature. After 8 h, the reaction tube was removed from the setup, and the reaction mixture was diluted with 10 mL DCM in water, and the organic phase was dried over anhydrous Na_2SO_4. Then, the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (230−400 mesh) using ethyl acetate and hexane as eluent to afford product **3**.

3.4. Gram-scale reaction:

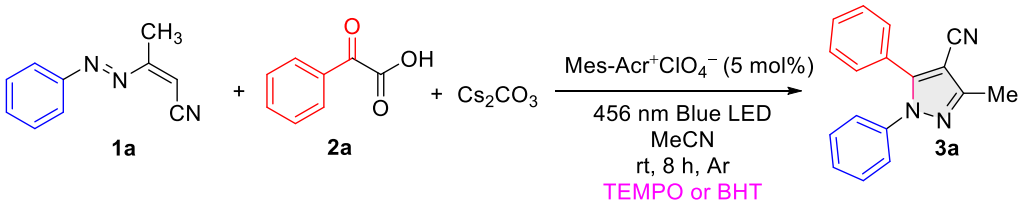


To an oven-dried 100 mL reaction tube equipped with a magnetic stir bar, **1a** (1.0 mmol, 1 equiv), **2** (1.5 mmol, 1.5 equiv), Cs_2CO_3 (0.5 mmol, 0.5 equiv) and Mes-Acr$^+$ClO$_4^-$ (5 mol%) was added. Then the reaction tube was applied to a vacuum for 5 minutes and then backfilled with argon, and this cycle was repeated another four times. A rubber septum was put on the top of the reaction tube tightly, with continuous argon flow. 20 mL of freshly dried CH_3CN and were added using a syringe. Then the reaction tube was placed on a magnetic stirrer and irradiated using a 456 nm blue LED (40 W, Kessil), keeping ~3 cm distance between them. A cooling fan was fitted approximately one foot to keep the system cool at room temperature. After 8 h, the reaction tube was removed from the setup, and the reaction mixture was diluted with 40 mL DCM in water and organic phase was dried over anhydrous Na_2SO_4. Then evaporating the solvent under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (230−400 mesh) using ethyl acetate and hexane as eluent to afford product **3a.**

4. Reaction setup for the gram-scale reaction:

5. Mechanistic investigation:

5.1 Radical trapping experiment with TEMPO or BHT:



To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar, 0.2 mmol of **1a** (1 equiv), 0.3 mmol of **2a** (1 equiv), 0.1 mmol of Cs_2CO_3 (0.5 equiv), and 0.4 mmol of TEMPO/BHT (2 equiv) were added. The reaction tube was vacuumed, backfilled with argon (3 times), and sealed with a septum. Then, 2 mL of dry MeCN were added and placed ~3 cm away from a LED setup and ~30 cm away from a cooling fan to maintain temperature. After 8 h, the reaction tube was removed from the setup, and the reaction mixture was diluted with 10 mL DCM in water and organic phase was dried over anhydrous Na_2SO_4. Then evaporating the solvent under reduced pressure. The crude product was then given for ^1H NMR with tetrachloroethane as an internal standard and found no product **3a** formed. Also the crude mixture was given for HRMS and the acyal added to quenchers detected. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{16}H_{24}NO_2$, 262.1807, found 262.1814.

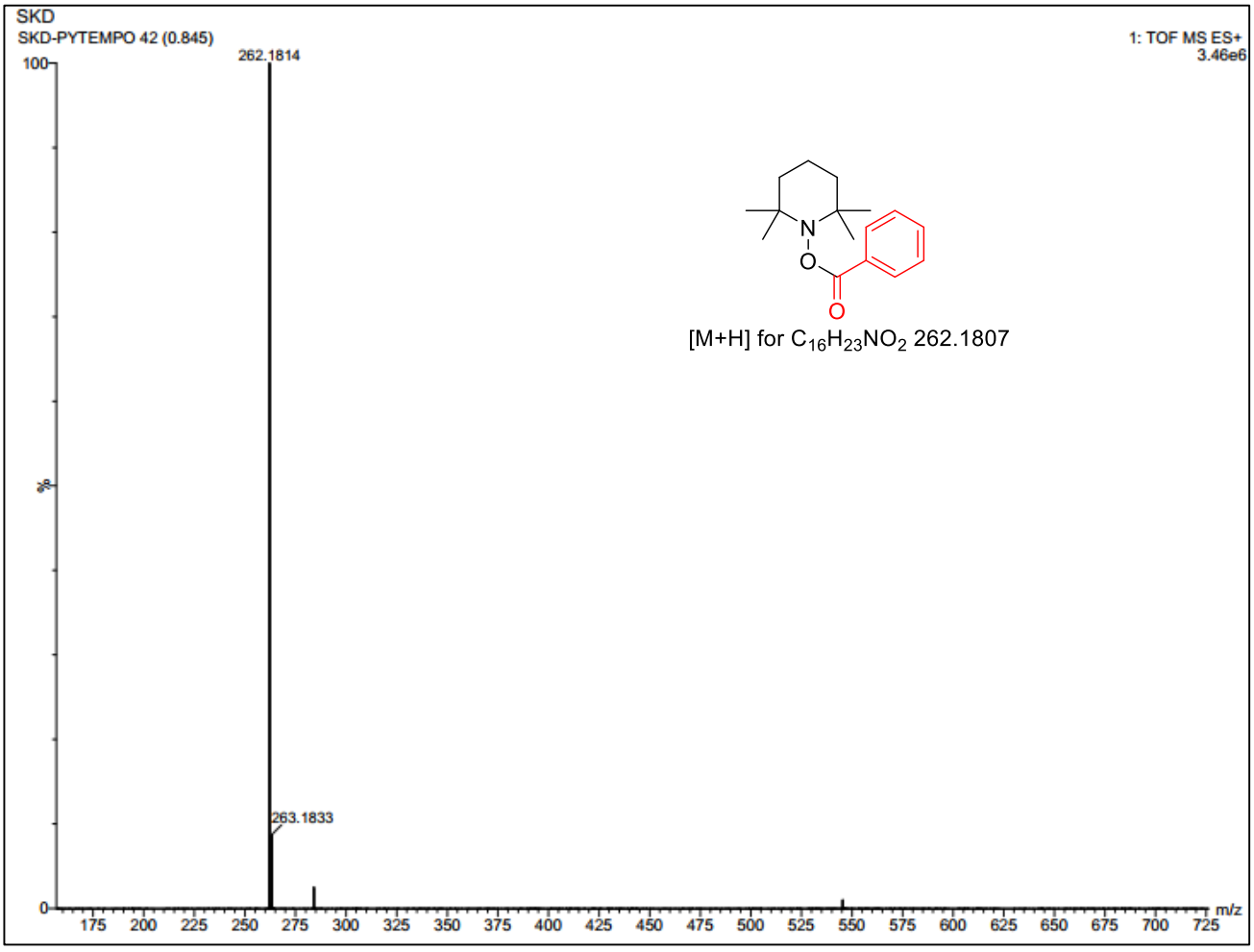
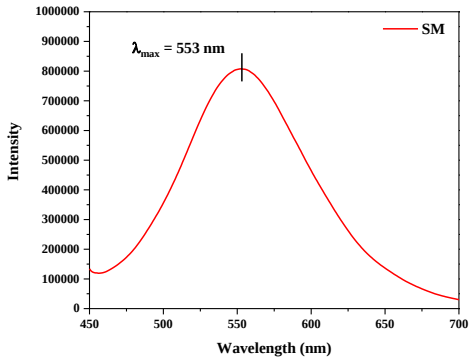
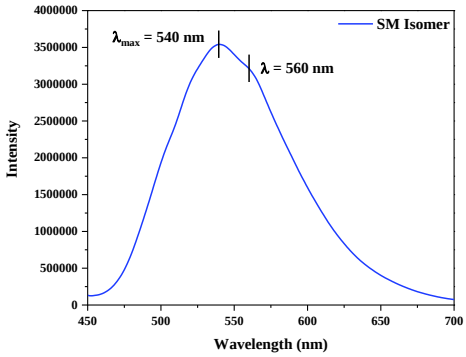


Fig: HRMS spectra of TEMPO added acyl radical

6a. Luminescence spectra of two Isomer of substrate 1a:

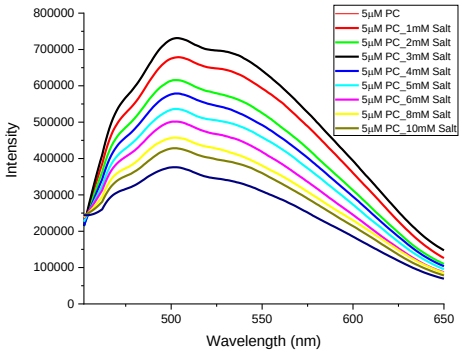




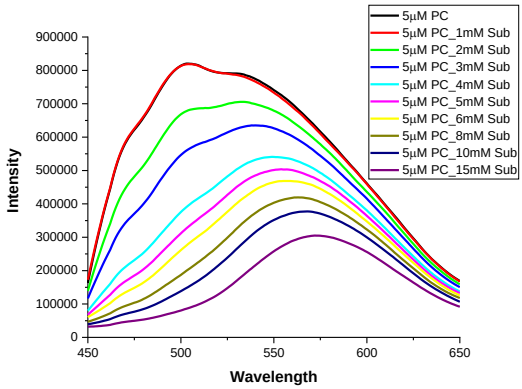
6b. Luminescence quenching studies of Acr-mes^{+}ClO$_4^{-}$ with substrate 1a and corresponding cesium salt of 2a:

To perform luminescence quenching studies of Acr-mes^{+}ClO$_4^{-}$, 5 μM of commercially available Acr-mes^{+}ClO$_4^{-}$, 1 mM of cesium salt of **2a**, and 1 mM of substrate **1a** solution in acetonitrile was prepared as a stock solution and all other solutions with different concentration were prepared by dilution.

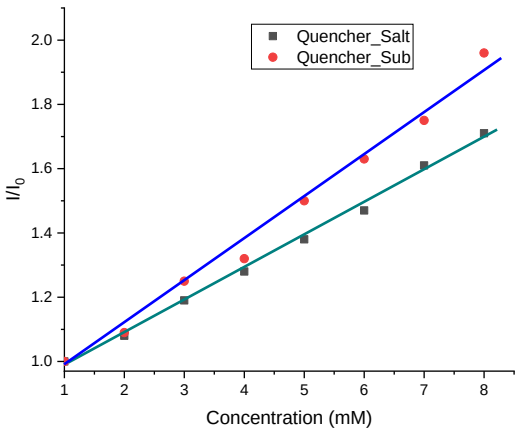
a)



b)



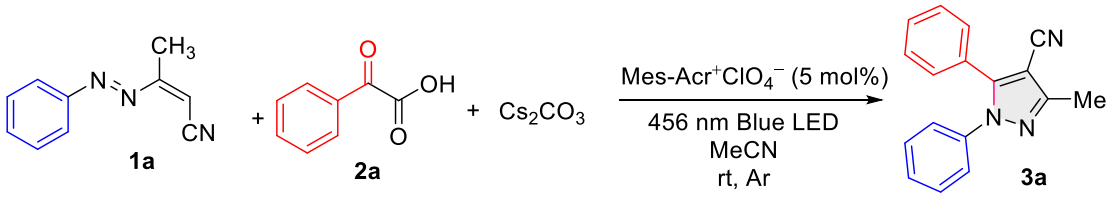
c)



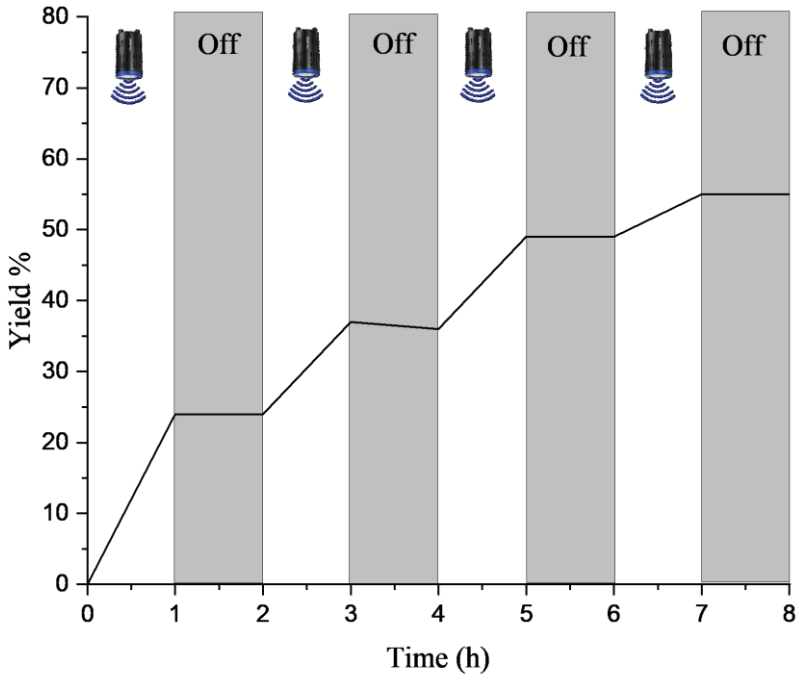
In acetonitrile solution: **a**) 5 μM Acr-mes^{+}ClO$_4^{-}$ Vs. cesium salt of **2a**, at 450 nm; b)5 μM Acr-mes^{+}ClO$_4^{-}$Vs. **1a** at 450 nm; c) Stern-Volmer plot of luminescence quenching of 5 μM Acr-mes^{+}ClO$_4^{-}$ Vs. cesium salt of **2a** and **1a.**

From the quenching experiments it is observed both the **1a** and cesium salt of **2a** are quenching. The isomerization of **1a** was observed *via* energy transfer is responsible for quenching of photocatalysts and on the other hand the *via* SET of the cesium salt of **2a** is responsible for quenching of photocatalysts.

7. Light on-off experiment:



To an oven-dried 20 mL reaction tube equipped with a magnetic stir bar, **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), Cs_2CO_3 (0.1 mmol, 0.5 equiv) and Mes-$Acr^+ClO_4^-$ (5 mol%) was added. Then the reaction tube was applied to a vacuum for 5 minutes and then backfilled with argon, and this cycle was repeated another four times. A rubber septum was put on the top of the reaction tube tightly, with continuous argon flow. 2 mL of freshly dried CH_3CN and were added using a syringe. Then the reaction tube was placed on a magnetic stirrer and irradiated using a 456 nm blue LED (40 W, Kessil), keeping ~3 cm distance between them. A cooling fan was fitted approximately one foot to keep the system cool at room temperature. After 1 h, the reaction tube was removed from the setup, and the reaction mixture was diluted with 10 mL DCM in water and organic phase was dried over anhydrous Na_2SO_4. Then, the crude ^1H NMR of resultant residue was taken using the 1, 1, 2, 2-tetrachloro ethane as an internal standard to obtain the yield of **3a** product. Thereafter, for a fresh batch of reaction was irradiated for 1 hour and then the light source was switched off with continuous stirring for the next 1 hours. After that, the crude ^1H NMR of the resultant residue was taken using the 1, 1, 2, 2-tetrachloro ethane as an internal standard to obtain the yield of **3a**. This cycle was repeated four times and the yield of **3a** with respect to time was plotted as shown below. From the experiment, we conclude that a continuous light supply is needed for the reaction and confirms that the reaction does not proceed through a chain propagation mechanism.



8.Crystal data of 1a'

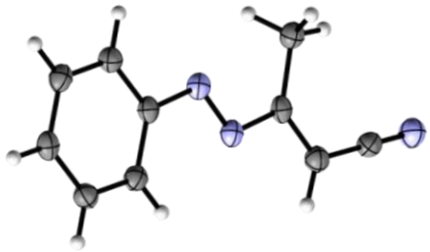
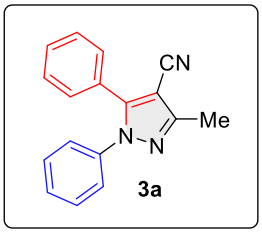


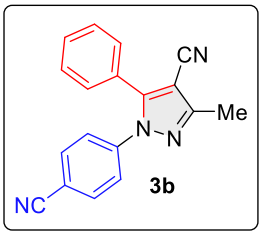
Table 1 Crystal data and structure refinement for compound 1a

Identification code	Compound 1a'
CCDC	2283220
Empirical formula	$C_{10}H_9N_3$
Formula weight	171.203
Temperature/K	107(4)
Crystal system	triclinic
Space group	P-1
a/Å	6.3402(3)
b/Å	7.4033(3)
c/Å	10.8259(4)
α/°	102.832(4)
β/°	92.959(3)
γ/°	114.223(4)
Volume/Å^3	445.98(4)
Z	13
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	0.639
F(000)	180.0
Crystal size/mm^3	0.25 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.486 to 136.2
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 8$, $-12 \le l \le 12$
Reflections collected	7820
Independent reflections	1604 [R_{int} = 0.0456, R_{sigma} = 0.0273]
Data/restraints/parameters	1604/0/119
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1274
Final R indexes [all data]	R_1 = 0.0465, wR_2 = 0.1339
Largest diff. peak/hole / e Å^{-3}	0.22/-0.27

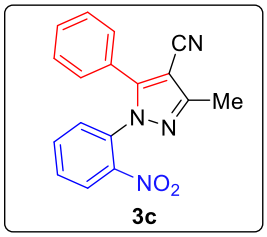
9. Characterization data for compounds 3. *3-methyl-1, 5-diphenyl-1H-pyrazole-4-carbonitrile* **(3a) [1]:** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 70% (36.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 8H), 7.25 – 7.21 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 147.8, 138.7, 129.9, 129.2, 129.0, 128.9, 128.4, 127.1, 125.2, 114.3, 93.8, 12.6.



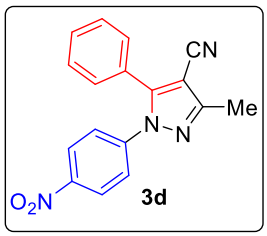
1-(4-cyanophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3b):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 63% (35.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.7 Hz, 2H), 7.45 (dt, *J* = 15.1, 7.2 Hz, 3H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 148.3, 142.0, 133.1, 130.6, 129.4, 129.0, 126.6, 125.2, 117.7, 113.6, 111.9, 12.7. HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{18}H_{13}N_4$, 285.1140, found 285.1137.



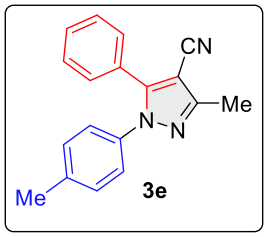
3-methyl-1-(2-nitrophenyl)-5-phenyl-1H-pyrazole-4-carbonitrile **(3c):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 61% (37.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.4 Hz, 1H), 7.65 – 7.54 (m, 2H), 7.45 – 7.36 (m, 1H), 7.39 – 7.32 (m, 2H), 7.35 – 7.29 (m, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 149.5, 145.7, 133.6, 132.3, 130.4, 130.2, 129.6, 129.2, 128.9, 126.0, 125.5, 113.9, 94.1, 12.7. HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{17}H_{13}N_4O_2$, 305.1039, found 305.1042.



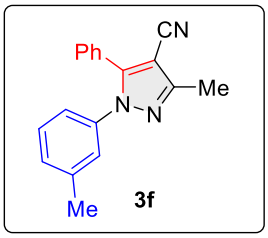
3-methyl-1-(4-nitrophenyl)-5-phenyl-1H-pyrazole-4-carbonitrile **(3d):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 63% (38.5mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.2 Hz, 2H), 7.55 – 7.39 (m, 5H), 7.32 (d, *J* = 6.9 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 148.6, 146.8, 143.5, 130.8, 129.5, 129.0, 126.6, 125.2, 124.7, 113.6, 95.9, 12.7. HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{17}H_{13}N_4O_2$, 305.1039, found 305.1042.



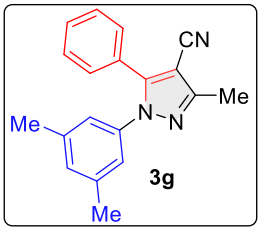
3-methyl-5-phenyl-1-(p-tolyl)-1H-pyrazole-4-carbonitrile **(3e):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 66% (36.1mg); ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 –7.34 (m, 3H), 7.31 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.18 – 7.06 (m, 4H), 2.50 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 147.8, 138.6, 136.3, 129.9, 129.8, 129.1, 128.9, 127.3, 125.1, 114.5, 93.6, 21.1, 12.7. HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{18}H_{16}N_3$, 274.1344, found 274.1341.



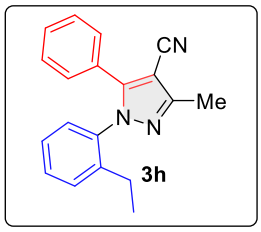
3-methyl-5-phenyl-1-(m-tolyl)-1H-pyrazole-4-carbonitrile **(3f):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 72% (39.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.32 (m, 2H), 7.20 –7.13 (m, 3H), 6.92 (d, J = 7.9 Hz, 1H), 2.50 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 147.8, 139.5, 138.7, 129.9, 129.3, 129.0, 128.9, 128.8, 127.2, 125.8, 122.3, 114.4, 93.6, 21.2, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{16}N_3$, 274.1344, found 274.1327.



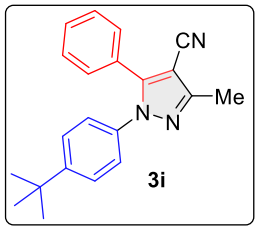
1-(3,5-dimethylphenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3g):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 74% (42.5mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 –7.33 (m, 3H), 7.35 – 7.29 (m, 2H), 7.13 (d, J = 2.3 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.83 (dd, J = 8.0, 2.3 Hz, 1H), 2.49 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 147.7, 137.9, 137.2, 136.5, 130.0, 129.8, 129.0, 128.8, 127.3, 126.2, 122.5, 114.5, 93.4, 19.7, 19.4, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{18}N_3$, 288.1501, found 288.1502.



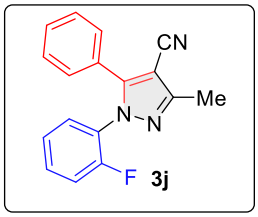
1-(2-ethylphenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3h):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 68% (39.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, J = 7.3 Hz, 2H), 7.36 (d, J = 4.9 Hz, 1H), 7.32 (d, J = 6.1 Hz, 4H), 7.25 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.9 Hz, 1H), 2.53 (s, 3H), 2.32 (q, J = 7.6 Hz, 2H), 1.01 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 149.0, 140.9, 137.4, 129.9, 129.8, 129.5, 128.8, 128.6, 128.1, 126.9, 126.7, 114.7, 92.2, 23.8, 13.8, 12.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{18}N_3$, 288.1501, found 288.1497.



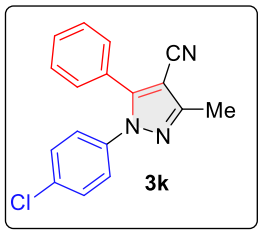
1-(4-(tert-butyl)phenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3i):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 71% (44.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 7H), 7.16 (d, J = 8.5 Hz, 2H), 2.49 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 151.7, 147.7, 136.2, 129.9, 129.1, 128.9, 127.3, 126.1, 124.7, 114.5, 93.6, 34.7, 31.2, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{22}N_3$, 316.1814 found 316.1812.



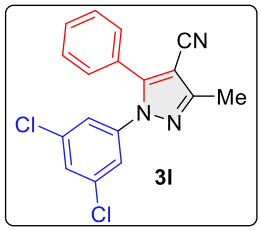
1-(2-fluorophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3j):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 63% (35 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (td, J = 7.7, 1.7 Hz, 1H), 7.42 – 7.33 (m, 4H), 7.33 – 7.30 (m, 2H), 7.23 (t, J = 7.7 Hz, 1H), 7.08 (ddd, J = 9.8, 8.3, 1.3 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4 (d, J = 253.9 Hz), 155.4, 153.3, 150.0, 131.2 (d, J = 7.8 Hz), 130.1, 128.9, 128.8, 128.3, 126.9, 126.9, 126.8, 124.9 (d, J = 4.1 Hz), 117.0, 116.8, 114.2, 93.3, 12.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{13}FN_3$, 278.1094,found 278.1080.



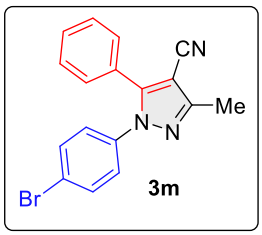
1-(4-chlorophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3k):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 65% (38.3mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 3H), 7.36 – 7.28 (m, 4H), 7.19 (d, J = 8.9 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 147.9, 137.3, 134.3, 130.2, 129.4, 129.2, 129.0, 126.9, 126.3, 114.1, 94.3, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{13}ClN_3$, 294.0798, found 294.0788.



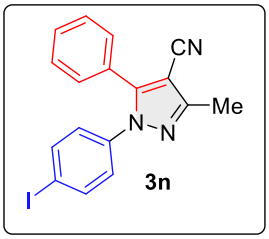
1-(3,5-dichlorophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3l):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 67% (44 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 3H), 7.33 (d, J = 7.0 Hz, 3H), 7.16 (m, 2H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 140.2, 135.5, 130.7, 129.3, 129.0, 128.5, 126.4, 123.5, 113.7, 95.0, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{12}Cl_2N_3$, 328.0408, found 328.0409.



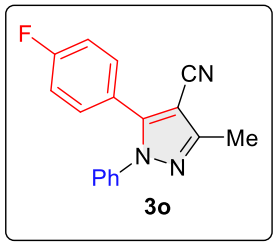
1-(4-bromophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3m):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 71% (48.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 5H), 7.31 (d, J = 9.6 Hz, 2H), 7.12 (d, J = 10.4 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 137.8, 132.4, 130.2, 129.2, 129.0, 126.9, 126.6, 122.3, 114.1, 94.4, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{13}BrN_3$, 338.0293, found 338.0280.



1-(4-iodophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carbonitrile **(3n):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 70% (53.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.9 Hz, 2H), 7.47 – 7.37 (m, 3H), 7.30 (d, J = 6.7 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 147.9, 138.4, 138.3, 130.2, 129.2, 129.0, 126.9, 126.7, 114.1, 94.4, 93.2, 12.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{13}IN_3$, 386.0154, found 386.0164.

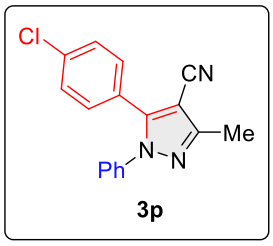


5-(4-fluorophenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3o)** [1]**:** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 62% (34.5mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 –7.34 (m, 3H), 7.30 (dd, J = 8.9, 5.3 Hz, 2H), 7.23 (d, J = 9.8 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 162.5, 152.8, 146.9, 138.6, 131.2, 131.1, 129.3, 128.7, 125.3, 123.3, 123.4, 116.4, 116.2, 114.2, 93.9, 12.6.



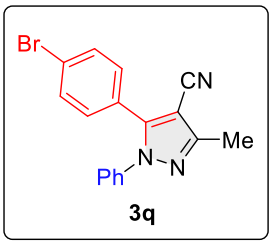
3o

5-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3p)** [1]**:** R_f = 0.5 (ethyl acetate/n-hexane, 5 : 5); white solid; yield 65% (38.2mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 4H), 7.35 (t, J = 2.1 Hz, 1H), 7.26 – 7.21 (m, 5H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 146.6, 138.5, 136.3, 130.3, 129.4, 129.1, 128.7, 125.5, 125.3, 114.1, 94.0, 12.6.



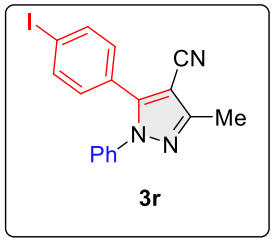
3p

5-(4-bromophenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3q)** [1]**:** R_f = 0.5 (ethyl acetate/n-hexane, 5 : 5); white solid; Yield 70% (47.5mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.27 – 7.20 (m, 2H), 7.18 (d, J = 8.5 Hz, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 146.6, 138.5, 132.3, 130.5, 129.4, 128.7, 126.0, 125.7, 124.6, 94.0, 12.6.



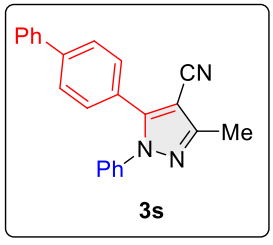
3q

5-(4-iodophenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3r):** R_f = 0.6 (ethyl acetate/n-hexane, 5 : 5); white solid; yield 71% (54.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.40 – 7.35 (m, 3H), 7.24 (t, J = 8.9 Hz, 2H), 7.04 (d, J = 8.2 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 146.8, 138.5, 138.3, 130.5, 129.4, 128.8, 126.6, 125.3, 114.1, 96.6, 93.9, 12.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{17}H_{13}IN_3$, 386.0154, found 386.0164.



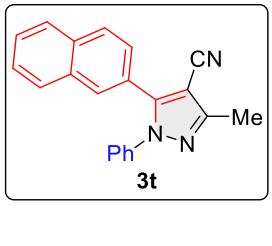
3r

5-([1,1'-biphenyl]-4-yl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3s):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 68% (45.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (t, J = 8.1 Hz, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.41 – 7.34 (m, 6H), 7.33 – 7.28 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 147.6, 142.7, 139.8, 138.9, 129.4, 129.3, 129.0, 128.6, 128.0, 127.6, 127.1, 125.9, 125.4, 114.5, 93.8, 12.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{18}N_3$, 336.1501, found 336.1511.



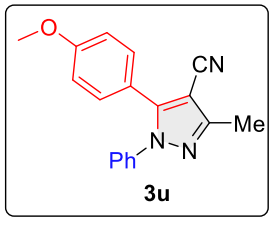
3s

3-methyl-5-(naphthalen-2-yl)-1-phenyl-1H-pyrazole-4-carbonitrile **(3t)** [1]**:** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 71% (43.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 2.1 Hz, 1H), 7.85– 7.77 (m, 3H), 7.59 – 7.49 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 5H), 7.23 (dd, J = 8.5, 1.8 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 148.0, 139.0, 133.6, 133.1, 129.4, 128.9, 128.7, 128.6, 127.9, 127.8, 127.1, 125.6, 125.4, 124.6, 114.6, 94.2, 12.84.



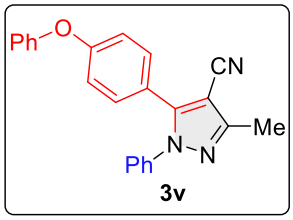
3t

5-(4-methoxyphenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3u)** [1]**:** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 74% (42.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 4.4 Hz, 3H), 7.28 – 7.21 (m, 4H), 6.88 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 152.7, 148.0, 139.1, 130.6, 129.3, 128.5, 125.4, 119.4, 114.8, 114.6, 93.4, 55.5, 12.8.

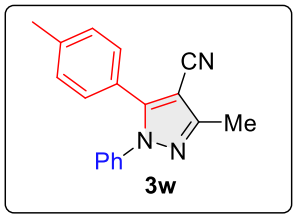


3u

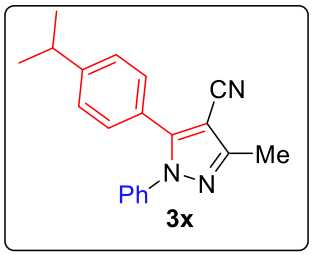
3-methyl-5-(4-phenoxyphenyl)-1-phenyl-1H-pyrazole-4-carbonitrile **(3v):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 71% (51.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (q, J = 6.5 Hz, 5H), 7.28 (m, 4H), 7.20 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 155.7, 152.7, 147.6, 138.9, 130.7, 130.0, 129.3, 128.6, 125.4, 124.5, 121.3, 120.1, 118.2, 114.5, 93.6, 12.7. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{18}N_3O$, 352.1450, found 352.1448.



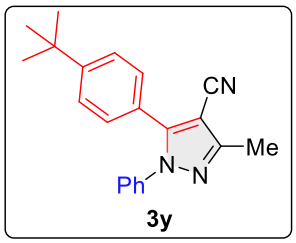
3-methyl-1-phenyl-5-(p-tolyl)-1H-pyrazole-4-carbonitrile **(3w) [1]:** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 72% (39.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.26 – 7.23 (m, 2H), 7.21 – 7.15 (m, 4H), 2.49 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 148.1, 140.3, 138.9, 129.7, 129.2, 128.9, 128.4, 125.3, 124.2, 114.6, 93.6, 21.4, 12.7.



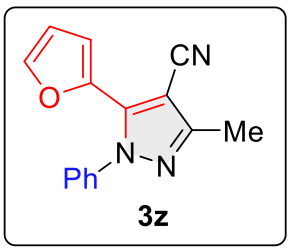
5-(4-isopropylphenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3x) [1]:** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 73% (44 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.24 (m, 6H), 2.90 (p, J = 6.9 Hz, 1H), 2.49 (s, 3H), 1.23 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 151.0, 148.1, 138.9, 129.2, 129.0, 128.4, 127.1, 125.3, 124.4, 114.6, 93.6, 34.0, 23.7, 12.7.



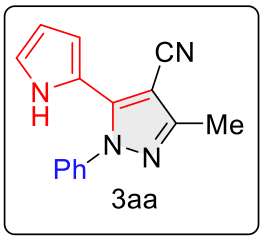
5-(4-(tert-butyl)phenyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3y):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 76% (48 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 5H), 7.28 (dd, J = 11.9, 9.2 Hz, 4H), 2.52 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 152.7, 148.0, 138.9, 129.2, 128.7, 128.4, 125.9, 125.3, 124.1, 114.6, 93.6, 34.9, 31.2, 31.1, 31.0, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{22}N_3$, 316.1814, found 316.1809.



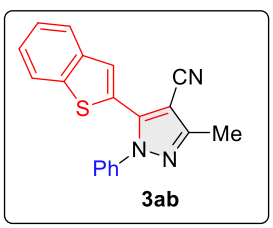
5-(furan-2-yl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3z):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); yellow solid; Yield 58% (29 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 3H), 7.46 – 7.44 (m, 1H), 7.41 – 7.33 (m, 2H), 6.44 – 6.38 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 144.3, 141.4, 139.2, 138.6, 129.4, 129.3, 125.9, 114.1, 112.5, 111.7, 91.6, 12.5. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{12}N_3O$, 250.0980, found 250.0990.



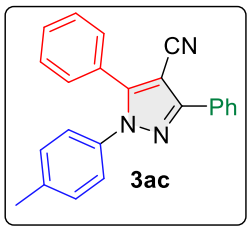
3-methyl-1-phenyl-5-(1H-pyrrol-2-yl)-1H-pyrazole-4-carbonitrile **(3aa):** R_f = 0.4 (ethyl acetate/n-hexane, 2 : 8); yellow solid; Yield 56% (27.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.53 – 7.43 (m, 2H), 7.40 (dd, J = 4.0, 2.0 Hz, 2H), 6.86 – 6.81 (m, 1H), 6.18 (t, J = 2.5 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 141.3, 139.3, 129.8, 129.7, 126.4, 121.4, 118.3, 115.5, 112.5, 110.3, 89.3, 12.6. HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}N_4$, 249.1140, found 249.1148.



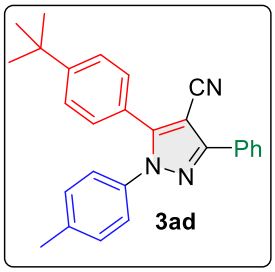
5-(benzo[b]thiophen-2-yl)-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile **(3ab):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 59% (37.3 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 9.2 Hz, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.62 (s, 1H), 7.46 (m, 3H), 7.42 (m, 2H), 7.37 (m, 2H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 142.1, 140.8, 138.7, 138.4, 129.6, 129.4, 127.2, 126.8, 126.4, 125.9, 125.0, 124.7, 122.1, 114.2, 93.9, 12.6. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{14}N_3S$, 316.0908, found 316.0907.



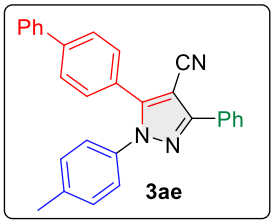
2,3,5-diphenyl-1-(p-tolyl)-1H-pyrazole-4-carbonitrile **(3ac):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 78% (52.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 7.0 Hz, 2H), 7.55 – 7.46 (m, 2H), 7.48 – 7.37 (m, 6H), 7.26 – 7.14 (m, 4H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 149.2, 138.8, 136.4, 130.7, 130.1, 129.8, 129.5, 129.3, 129.0, 128.9, 127.1, 126.9, 125.2, 115.2, 91.2, 21.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{23}H_{18}N_3$, 336.1501, found 336.1504.



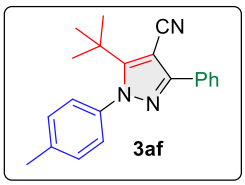
5-(4-(tert-butyl)phenyl)-3-phenyl-1-(p-tolyl)-1H-pyrazole-4-carbonitrile **(3ad):** R_f = 0.6 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 74% (58 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.02 (m, 2H), 7.54 – 7.42 (m, 3H), 7.41 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 2.39 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 153.2, 149.4, 138.7, 136.5, 130.8, 129.8, 129.4, 128.9, 128.90, 126.9, 125.9, 125.2, 124.0, 115.5, 91.0, 34.9, 31.2, 21.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{27}H_{26}N_3$, 392.2127, found 392.2129.



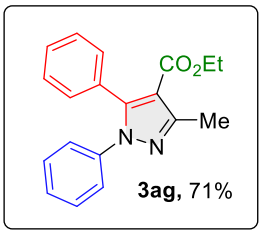
5-([1,1'-biphenyl]-4-yl)-3-phenyl-1-(p-tolyl)-1H-pyrazole-4-carbonitrile **(3ae):** R_f = 0.5 (ethyl acetate/n-hexane, 2 : 8); white solid; yield 71% (58.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 – 8.09 (m, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.51 (t, J = 7.2 Hz, 2H), 7.48 – 7.44 (m, 5H), 7.41 – 7.36 (m, 1H), 7.28 – 7.25 (m, 3H), 7.20 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 149.0, 142.8, 139.8, 138.9, 136.4, 130.6, 130.0, 129.7, 129.5, 129.0, 128.9, 128.1, 127.6, 127.2, 126.9, 125.8, 125.3, 115.4, 91.1, 21.2. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{29}H_{22}N_3$, 412.1814, found 418.1811.



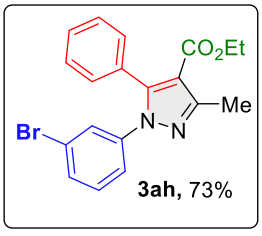
5-(tert-butyl)-3-phenyl-1-(p-tolyl)-1H-pyrazole-4-carbonitrile **(3af):** R_f = 0.4 (ethyl acetate/n-hexane, 2 : 8); yellow solid; yield 45% (28.5mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.3 Hz, 2H), 7.47 – 7.36 (m, 3H), 7.28 (m, 4H), 2.45 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 153.4, 140.3, 138.8, 130.8, 129.6, 129.2, 128.7, 128.0, 127.3, 116.6, 88.8, 34.2, 30.9, 21.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{21}H_{22}N_3$, 316.1814, found 316.1810.



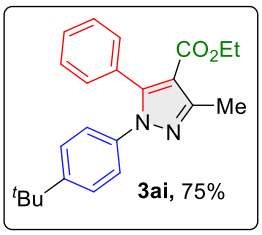
Ethyl 3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxylate **(3ag)** [2]**:** R_f = 0.3 (ethyl acetate/n-hexane, 8 : 2); yellow liquid; yield 71% (43.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.26 – 7.22 (m, 5H), 7.21 – 7.14 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 2.59 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 151.9, 146.5, 139.3, 130.6, 130.0, 129.0, 128.9, 128.0, 127.8, 125.4, 112.0, 59.9, 14.4, 14.1.



ethyl 1-(3-bromophenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carboxylate **(3ah):** R_f = 0.3 (ethyl acetate/n-hexane, 8 : 2); yellow liquid; yield 73% (56.1 mg);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 3H), 7.22 – 7.18 (m, 3H), 7.16 – 7.10 (m, 3H), 4.17 (q, J = 7.1 Hz, 2H), 2.59 (s, 3H), 1.14 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2, 151.7, 147.8, 138.3, 135.7, 130.9, 130.3, 129.6, 129.2, 128.8, 128.4, 127.7, 126.4, 110.7, 59.9, 17.7, 14.5, 14.1. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{19}H_{18}N_2O_2Br$, 385.0552, found 385.0558.



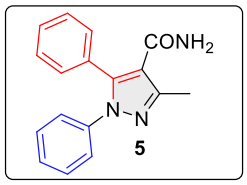
ethyl 1-(3-(tert-butyl)phenyl)-3-methyl-5-phenyl-1H-pyrazole-4-carboxylate **(3ai):** R_f = 0.4 (ethyl acetate/n-hexane, 8 : 3); yellow liquid; yield 75% (54.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3H), 7.28 – 7.23 (m, 4H), 7.09 (d, J = 9.0 Hz, 2H), 4.15 (q, J = 0.5 Hz, 2H), 2.58 (s, 3H), 1.25 (s, 9H), 1.13 (t, J = 7.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 151.8, 150.8, 146.3, 136.8, 130.6, 130.2, 128.9, 128.0, 125.8, 124.8, 111.9, 59.9, 34.7, 31.4, 14.4, 14.1. HRMS (ESI) m/z $[M + H]^+$ calcd



for $C_{23}H_{27}N_2O_2$, 363.2073, found 363.2069.

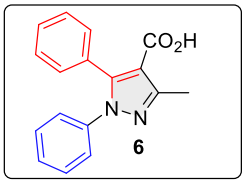
10. Experimental procedure for the synthesis of 5. To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar **3a** (0.2 mmol, 1.0 equiv.), 1 mL H_2SO_4 and 1 mL water were added, and the reaction tube was capped with a rubber septum. The reaction mixture was stirred at 110 ° C for 6 h in an oil bath. The reaction mixture was brought to room temperature, poured into 10 mL of cold water, and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (230−400 mesh) using 50% ethyl acetate in hexane as an eluent to obtain the **5** in 78% yield.

Characterization data for compounds 5. *3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxamide* **(5):** R_f = 0.4 (ethyl acetate/n-hexane, 6 : 4); white solid; yield 78% (43.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.0, 1.6 Hz, 3H), 7.25 – 7.20 (m, 5H), 7.14 (dd, *J* = 7.9, 1.9 Hz, 2H), 5.84 (s, 1H), 5.15 (s, 1H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 151.4, 142.7, 139.1, 130.3, 130.1, 129.8, 129.3, 129.3, 129.2, 128.8, 127.6, 125.2, 114.4, 13.9. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{17}H_{16}N_3O$, 278.1293, found 278.1282.



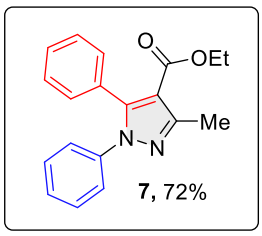
Experimental procedure for the synthesis of 6. To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar **3a** (0.2 mmol, 1.0 equiv.), NaOH (0.4 mmol, 2equiv.),1 mL H_2O, and 1 mL methanol was added, and the reaction tube was capped with a rubber septum. After stirring for 12 h at room temperature, water (10 mL) followed by EtOAc (10 mL) was added. 1 N of HCl was added to the aqueous layer, made pH = 2, and extracted with EtOAc (2×20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. Product 6 was obtained with a 76% yield.

Characterization data for compound 6. *3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxylic acid* **(6):** R_f = 0.3 (ethyl acetate/n-hexane, 8 : 2); white solid; yield 76% (43.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 3H), 7.27 – 7.22 (m, 5H), 7.17 – 7.13 (m, 2H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 152.8, 147.2, 139.0, 130.5, 129.4, 129.1, 128.8, 128.0, 127.8, 125.5, 110.7, 14.4. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{17}H_{15}N_2O_2$, 279.1134, found 279.1122.



Experimental procedure for the synthesis of 7. To an oven-dried 20 mL reaction tube equipped with a magnetic stirring bar **3a** (0.2 mmol, 1.0 equiv.), NaOH (0.4 mmol, 2 equiv.),1 mL H_2O, and 1 mL methanol was added, and the reaction tube was capped with a rubber septum. After stirring for 12 h at room temperature, water (10 mL) followed by EtOAc (10 mL) was added. 1 N of HCl was added to the aqueous layer, made pH = 2, and extracted with EtOAc (2×20 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The product was dissolved in ethanol (5 mL) and 2-3 drops of H_2SO_4 were added and refluxed for 6 h. After that the reaction was cooled to room temperature and the solvent was evaporated under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (230−400 mesh) using 10% ethyl acetate in hexane as an eluent to obtain the 7 in 72% yield.

Characterization data for compounds 7. *ethyl 3-methyl-1,5-diphenyl-1H-pyrazole-4-carboxylate* **(7)** [2]: R_f = 0.3 (ethyl acetate/n-hexane, 8 : 2); yellow liquid; yield 72% (43.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.26 – 7.22 (m, 5H), 7.21 – 7.14 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 151.9, 146.5, 139.3, 130.6, 130.0, 129.0, 128.9, 128.0, 127.8, 125.4, 112.0, 59.9, 14.4, 14.1.



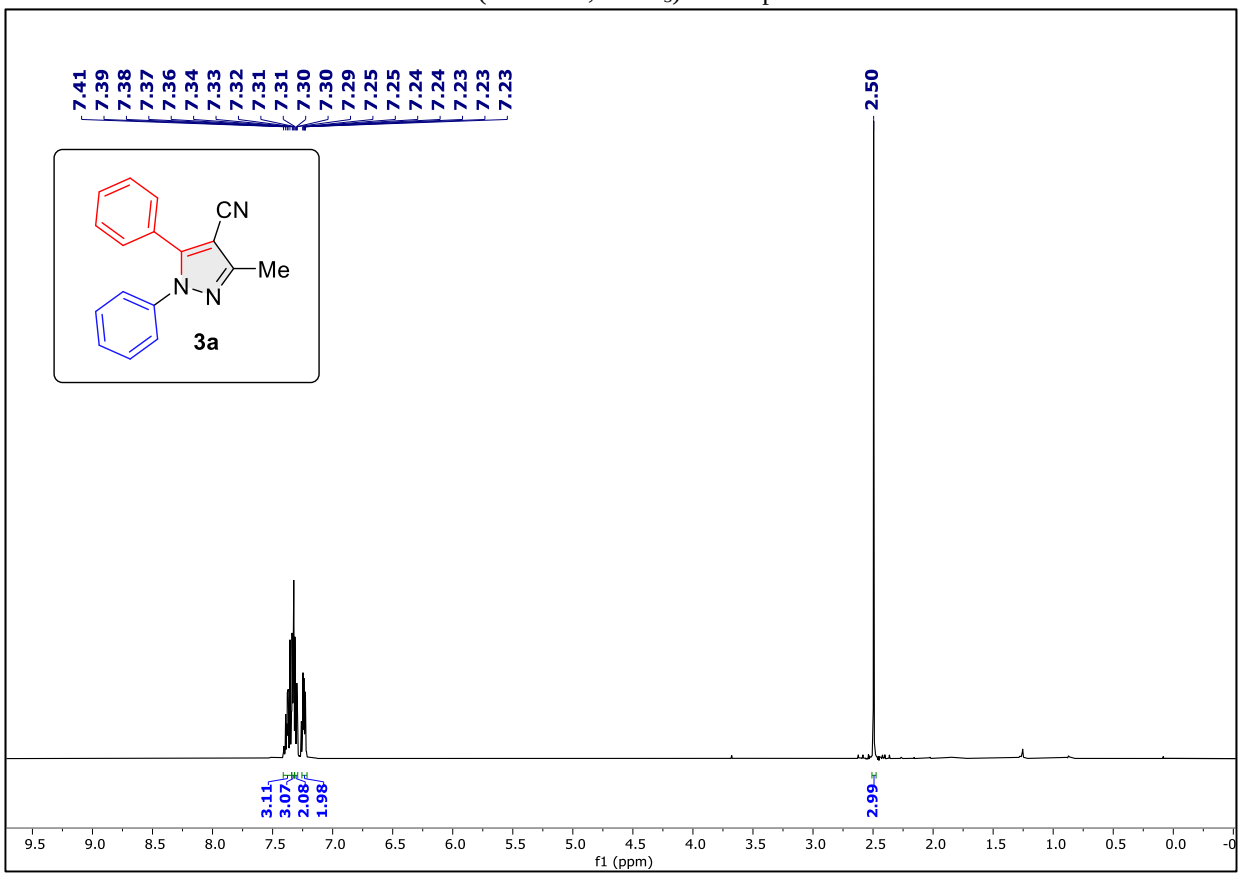
11. References:

1. S. Katiyar, A. Kumar and K. V. Sashidhara, *Chem. Commun*., 2022, **58**, 7297–7300.

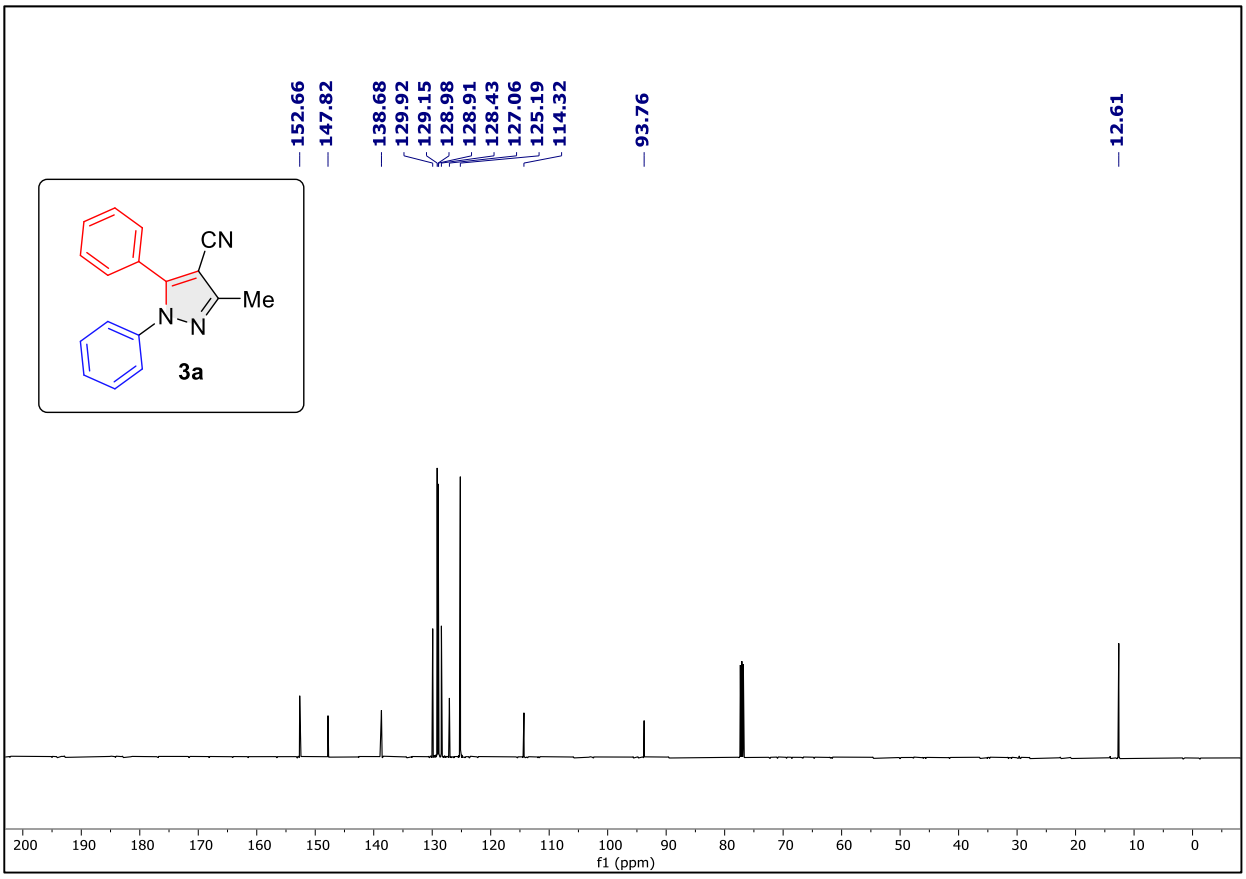
2. J. J. Neumann, M. Suri and F. Glorius, *Angew Chem Int Ed*, 2010, **49**, 7790–7794.

12. NMR spectra of the compounds 3,5,6 and 7:

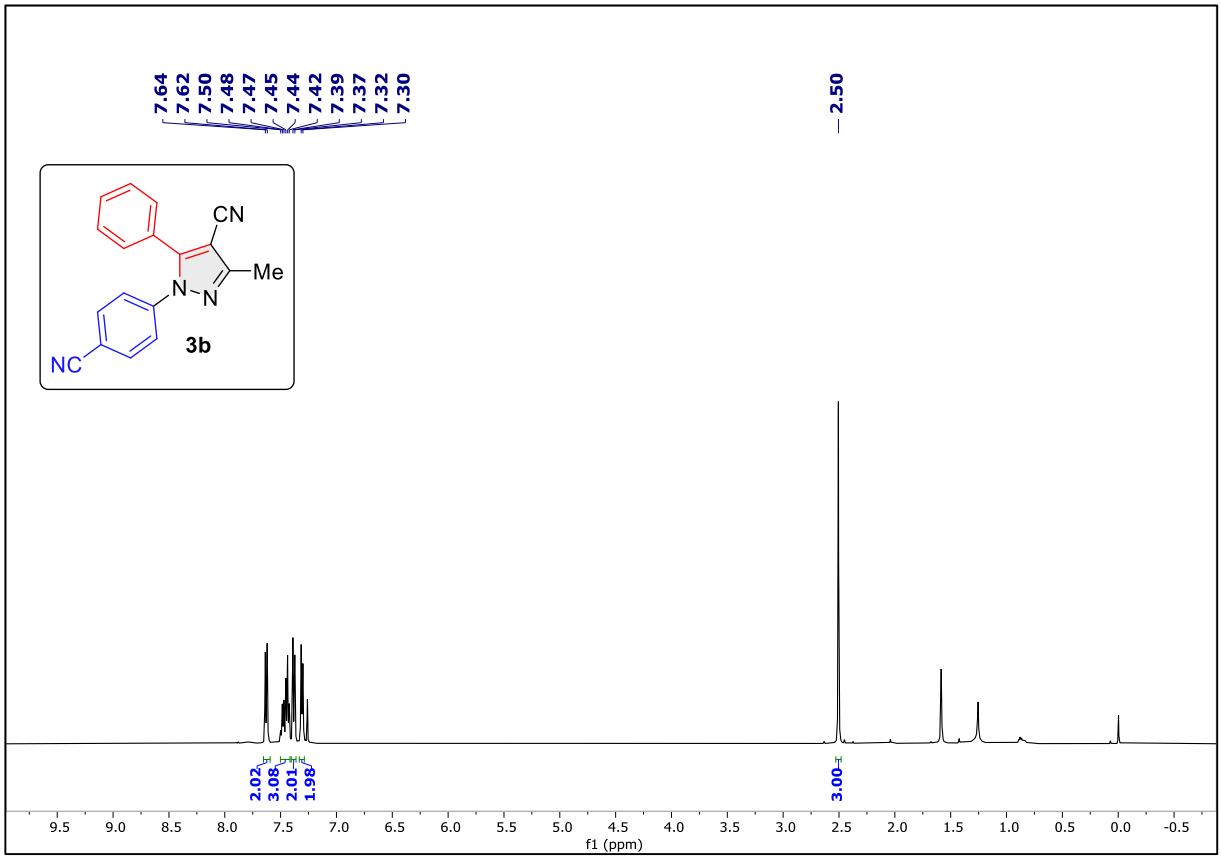
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**



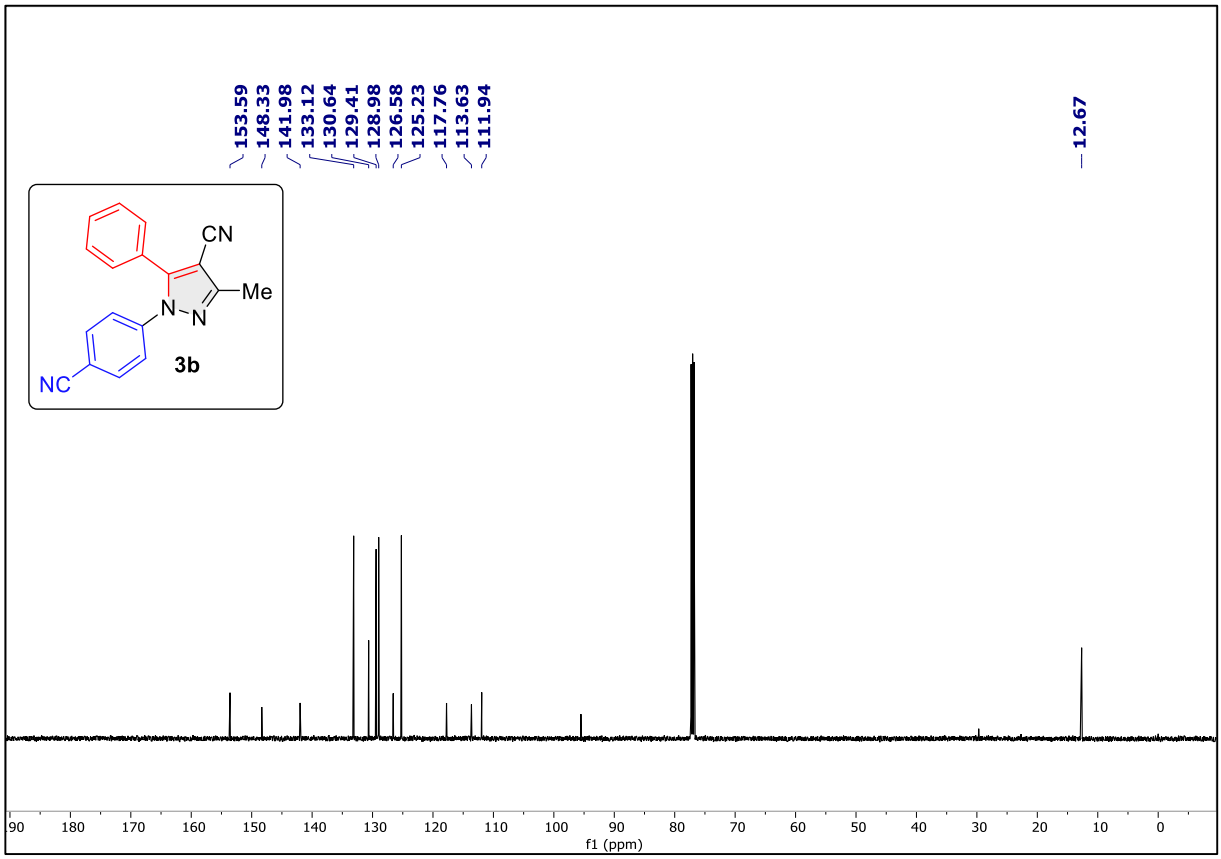
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3a**



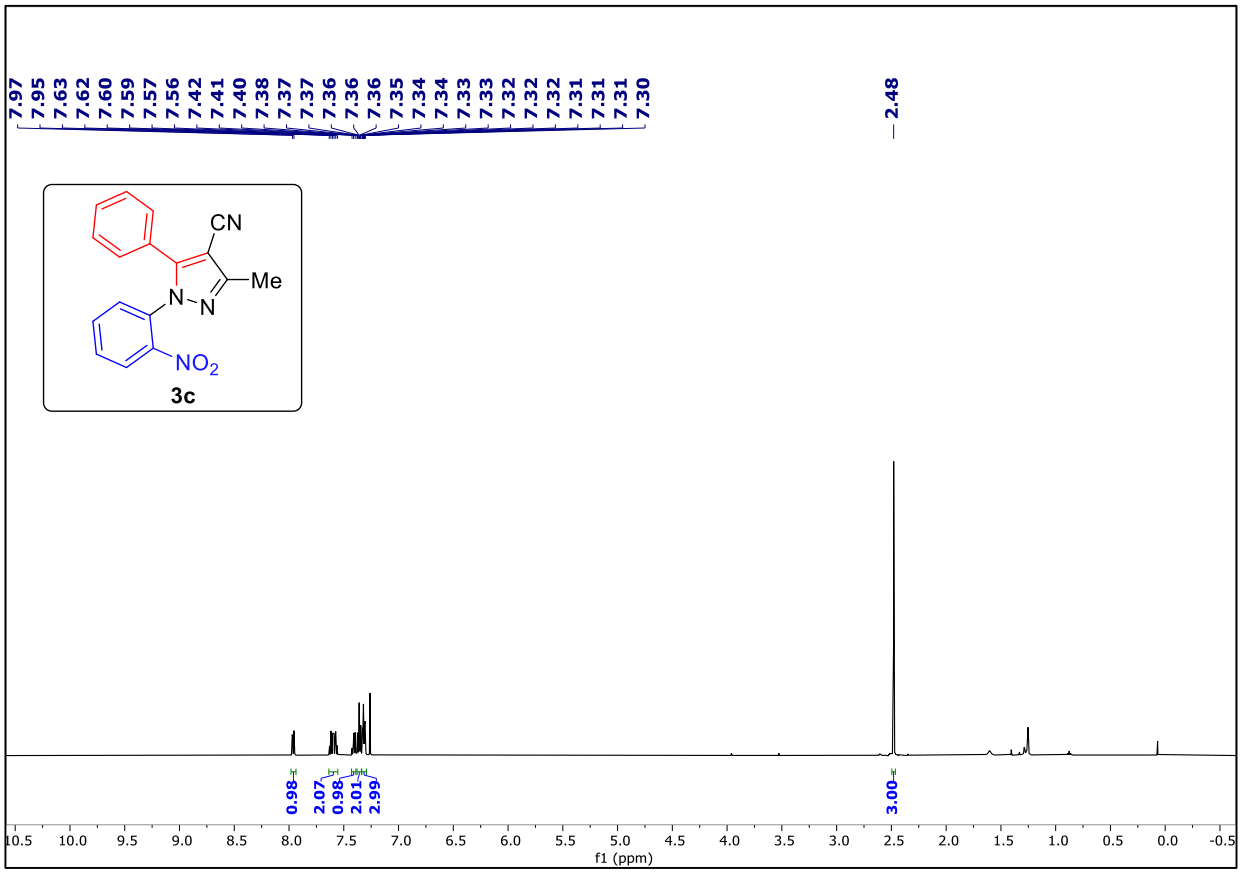
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**



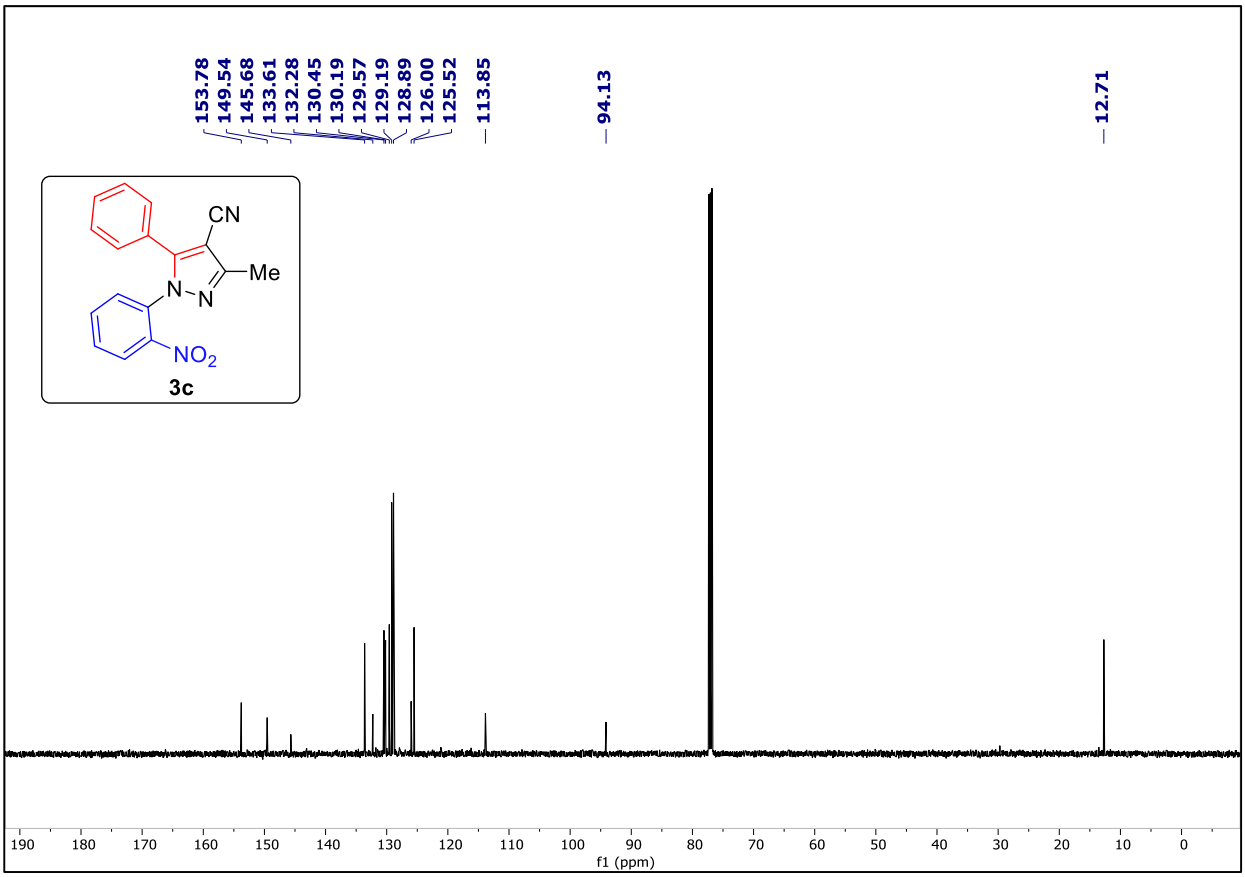
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3b**



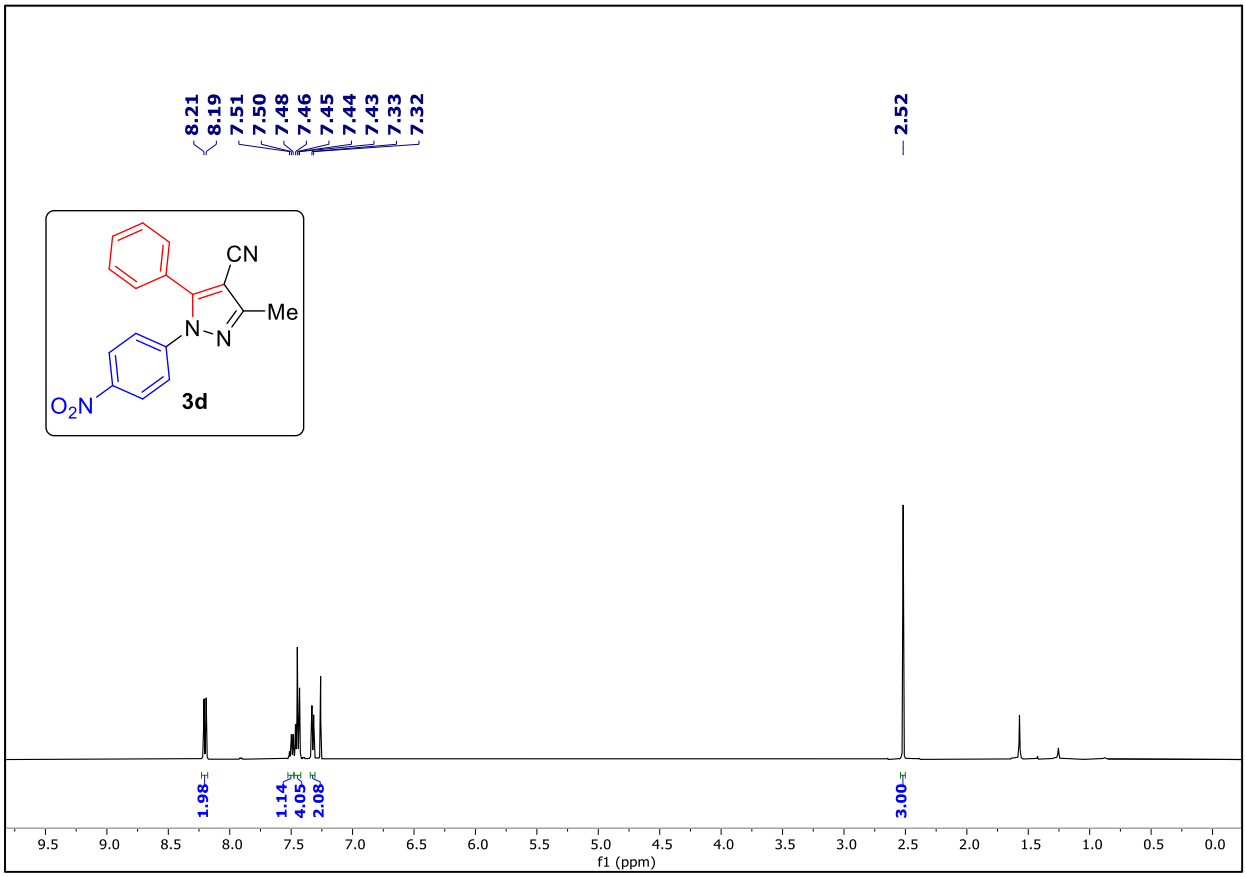
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**



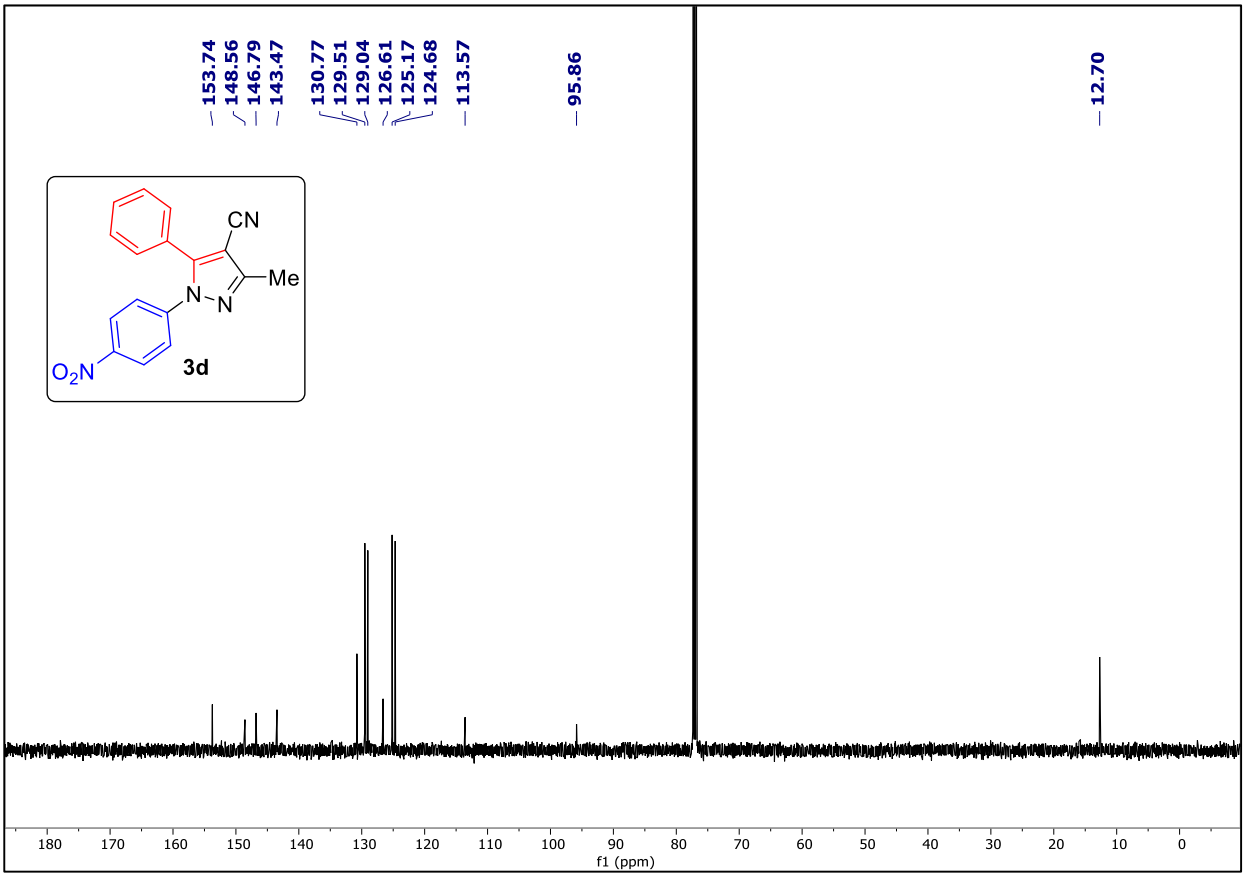
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3c**



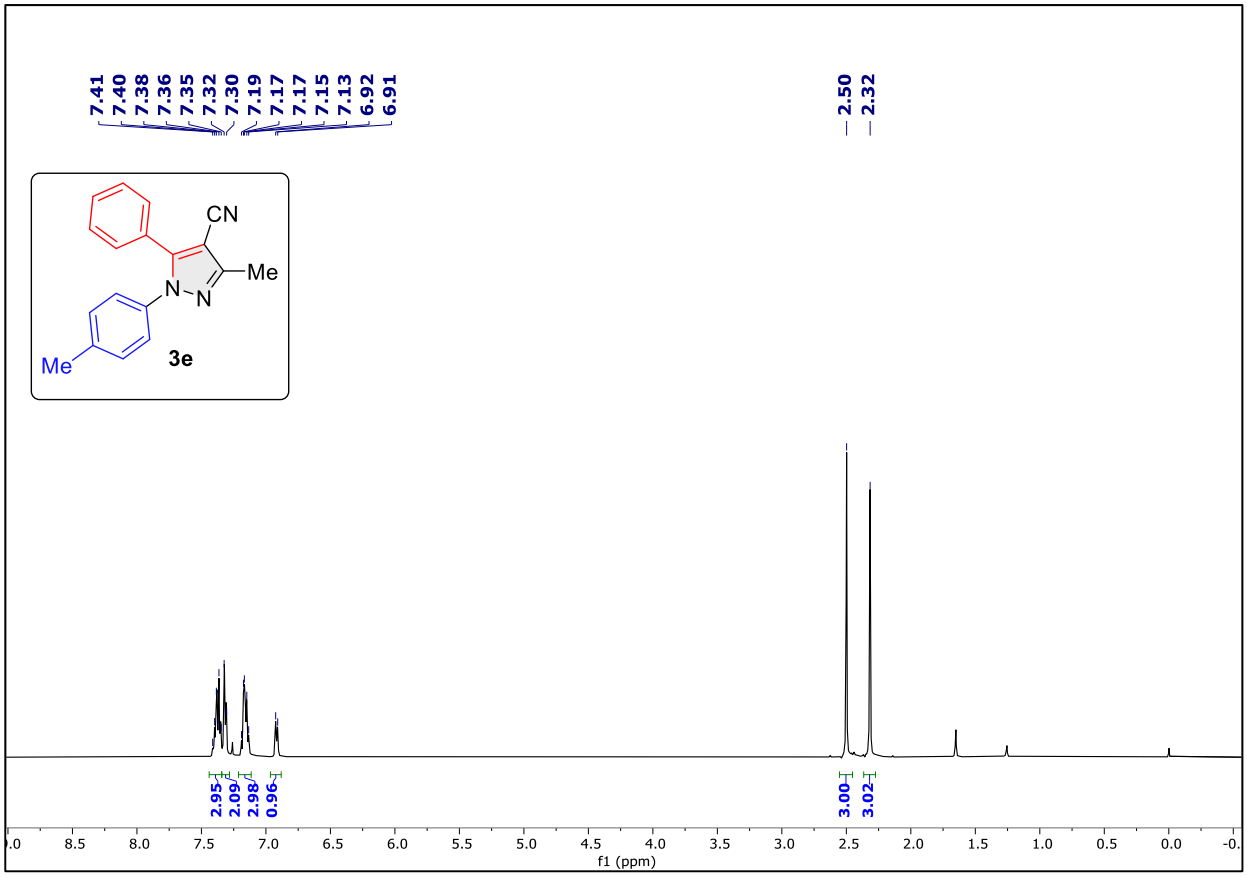
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**



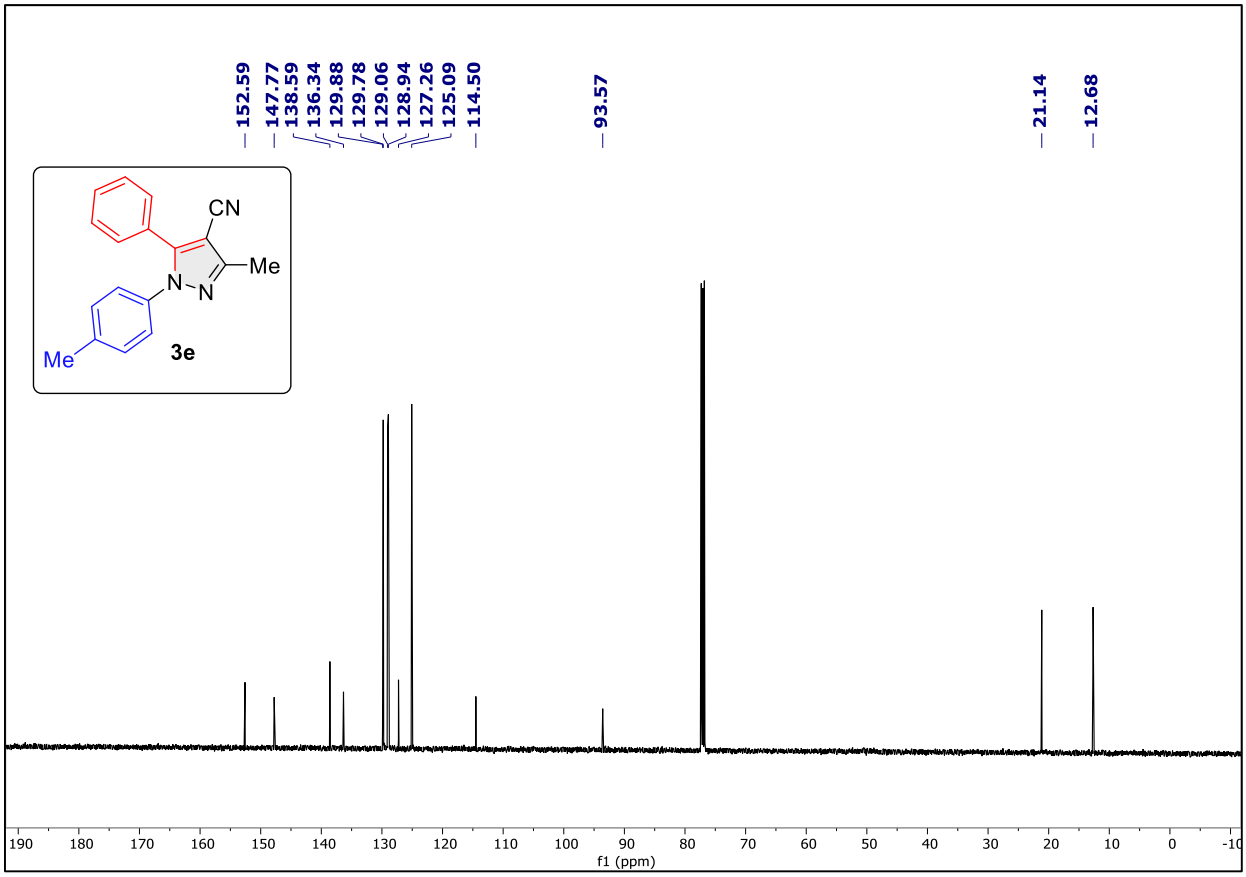
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**



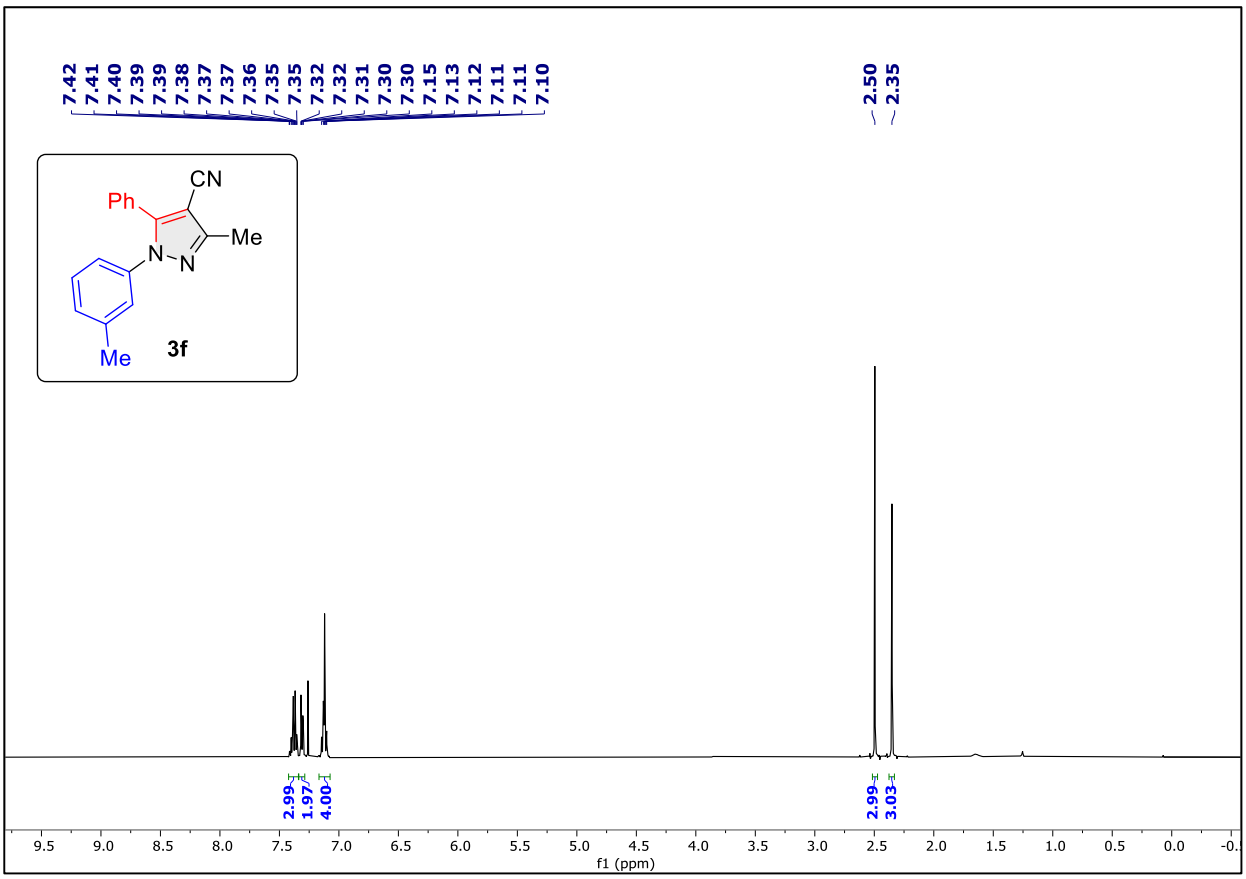
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**



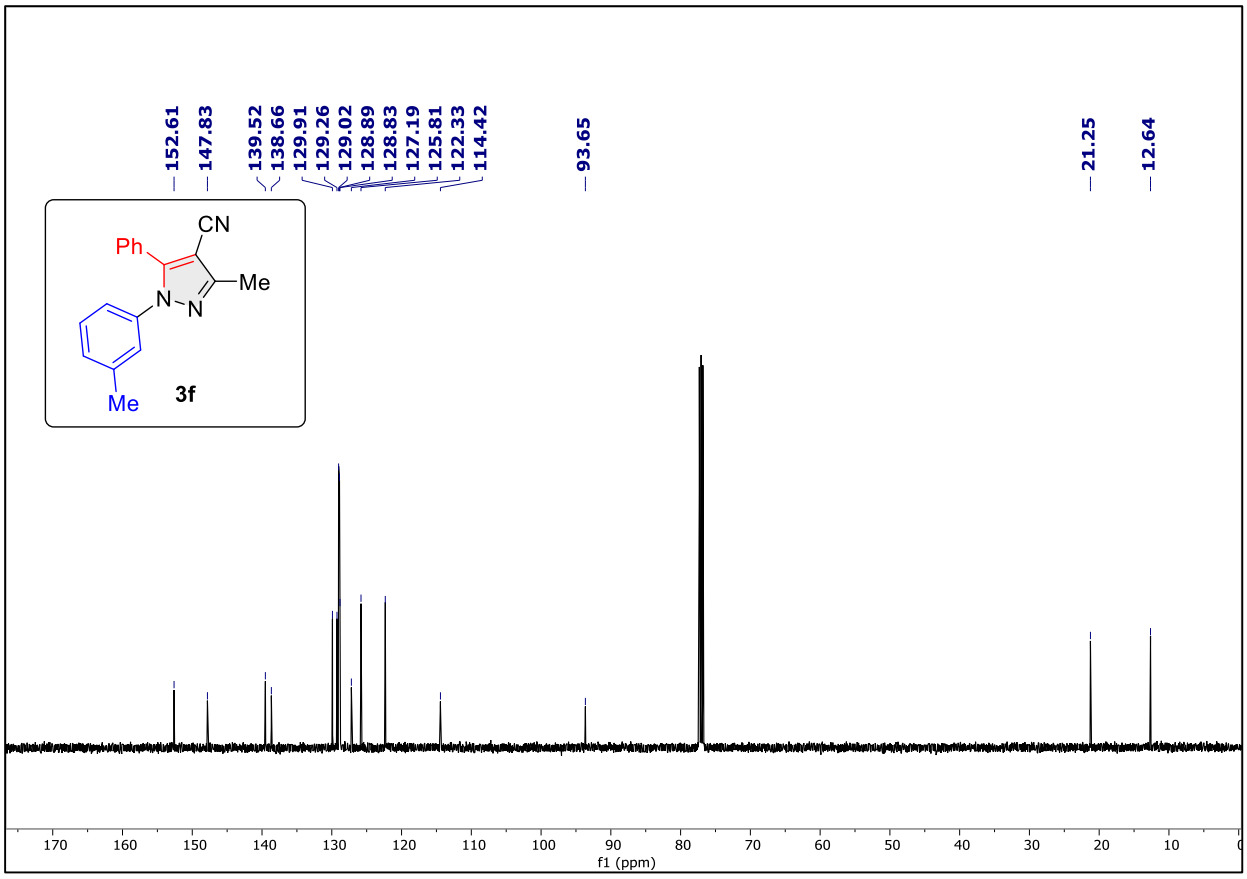
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3e**



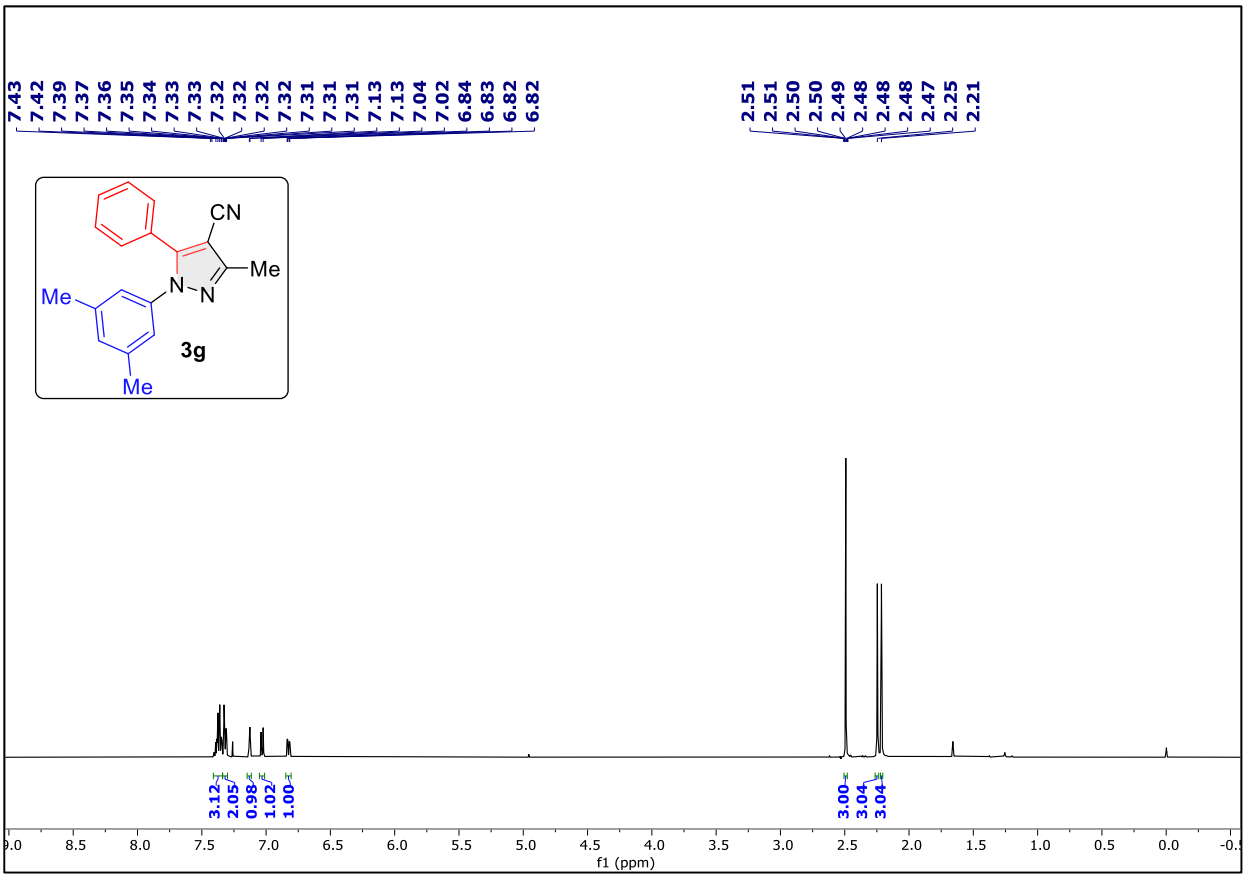
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**



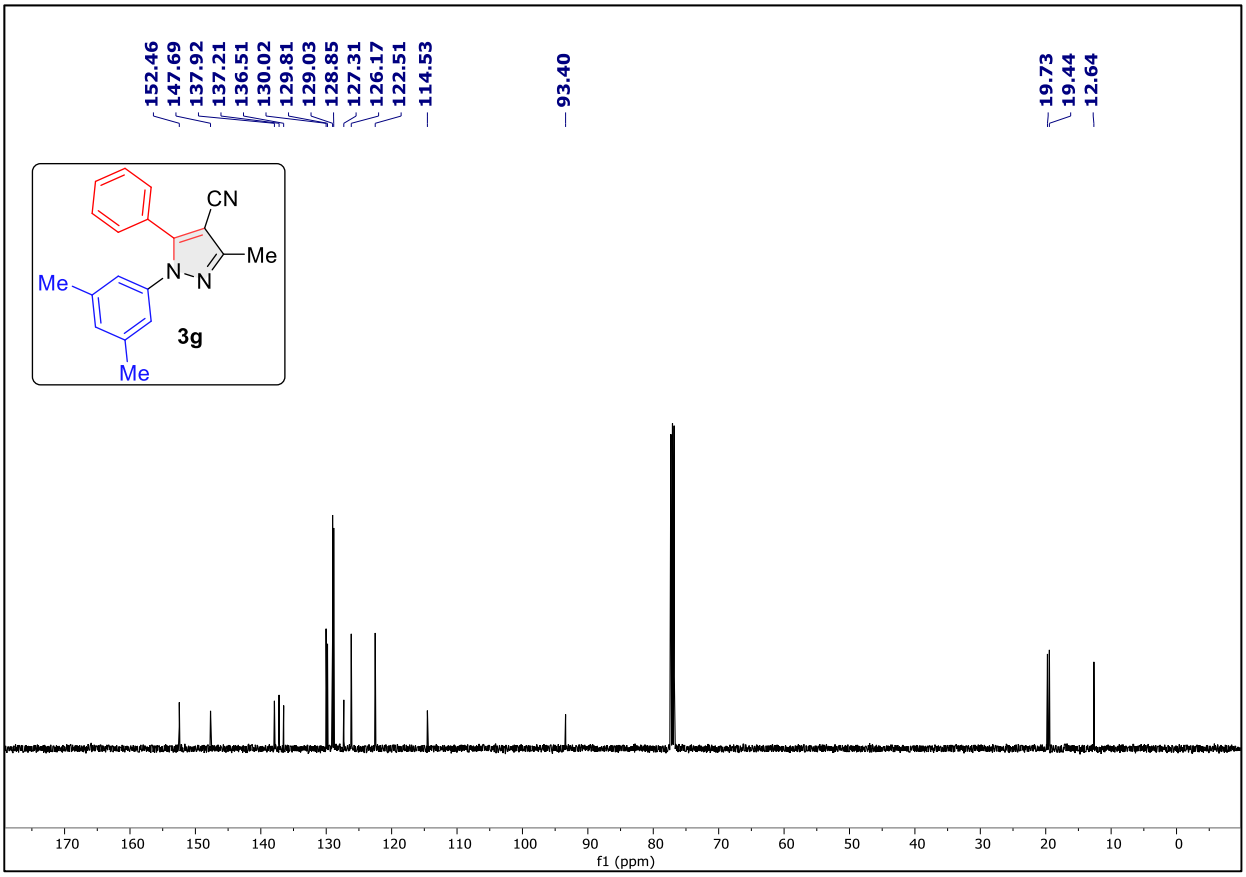
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**



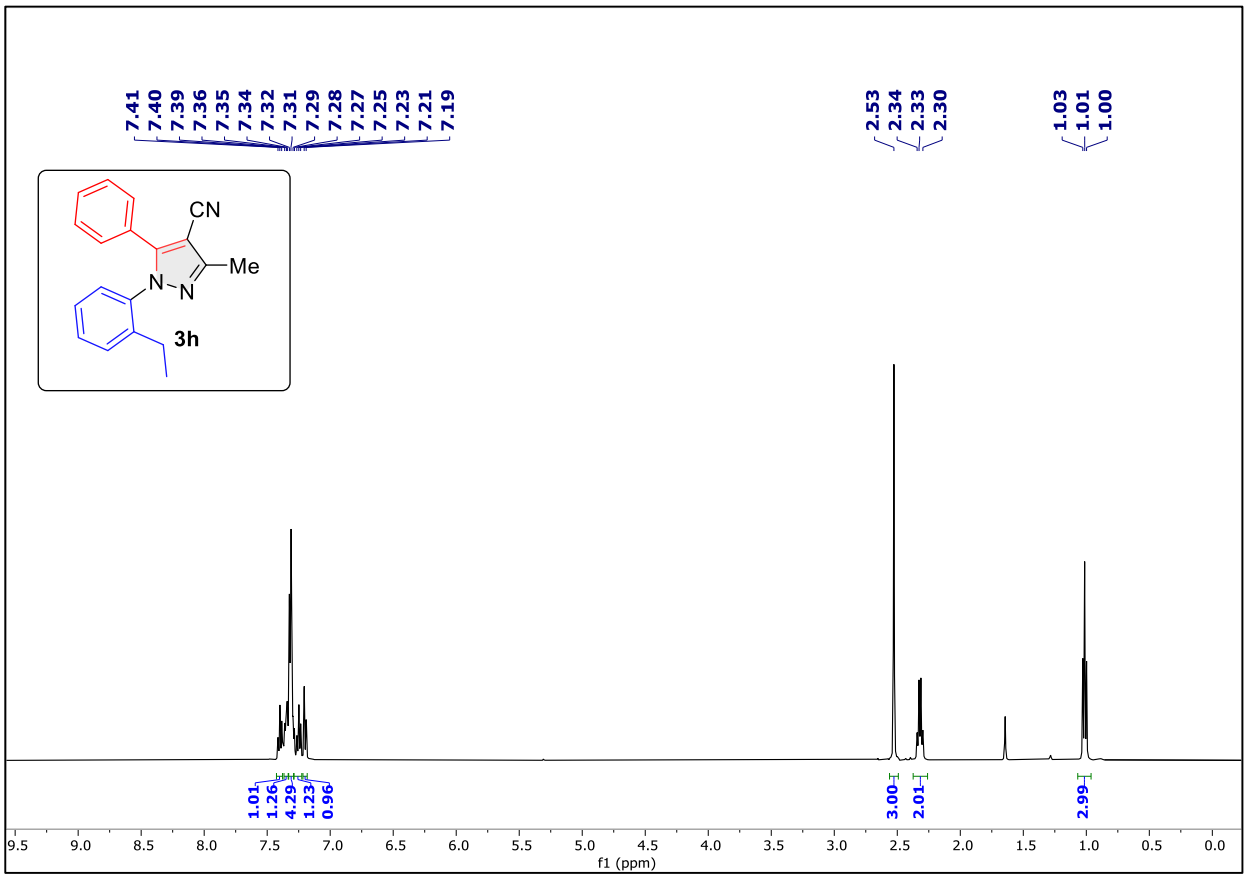
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**



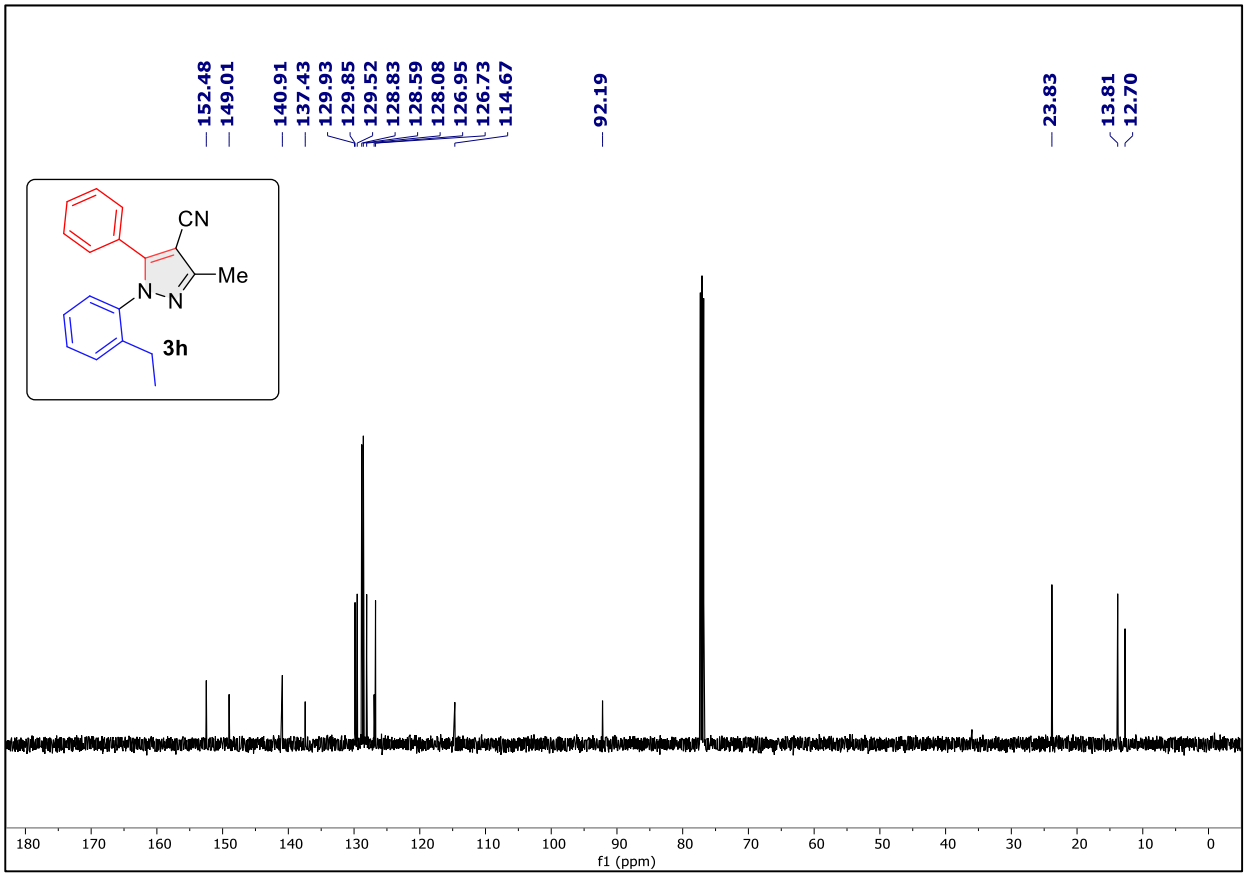
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3g**



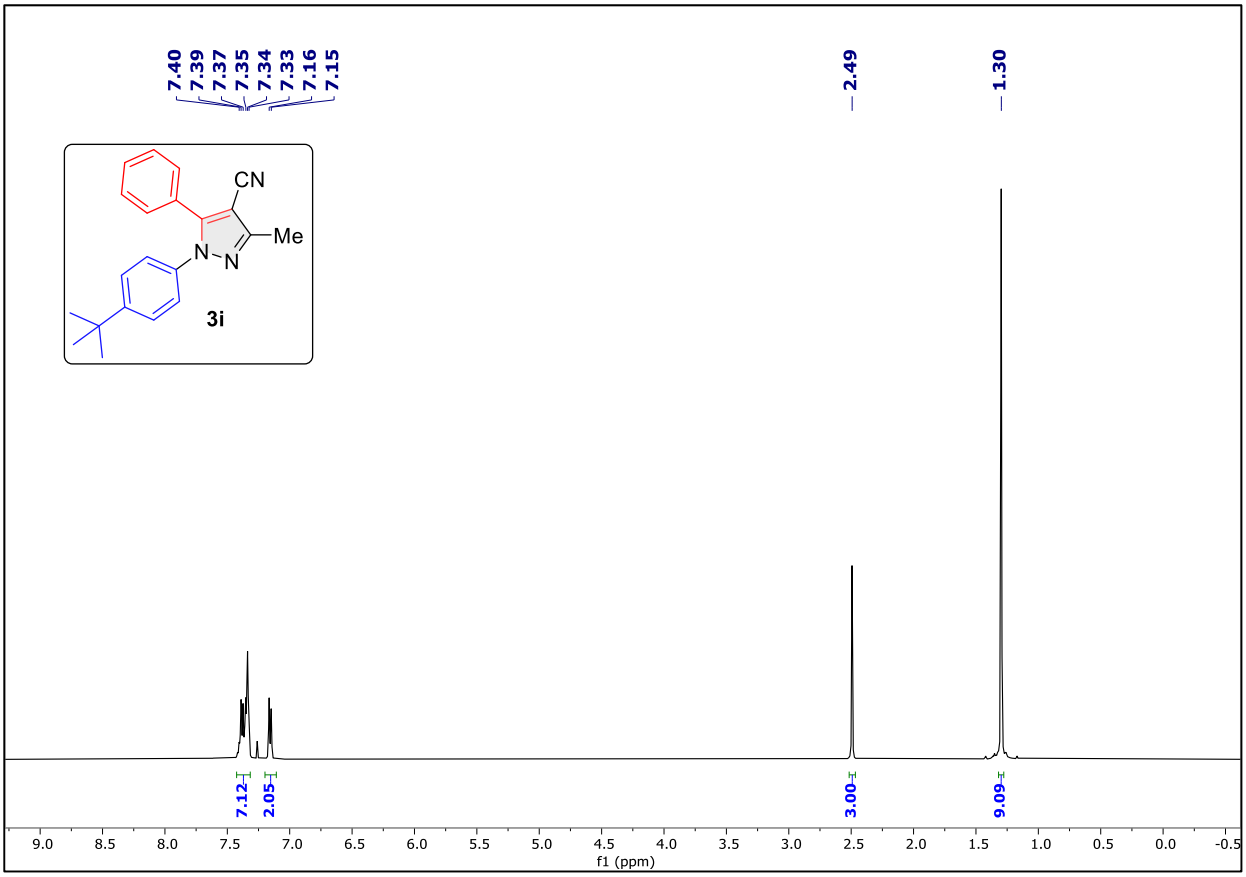
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3h**



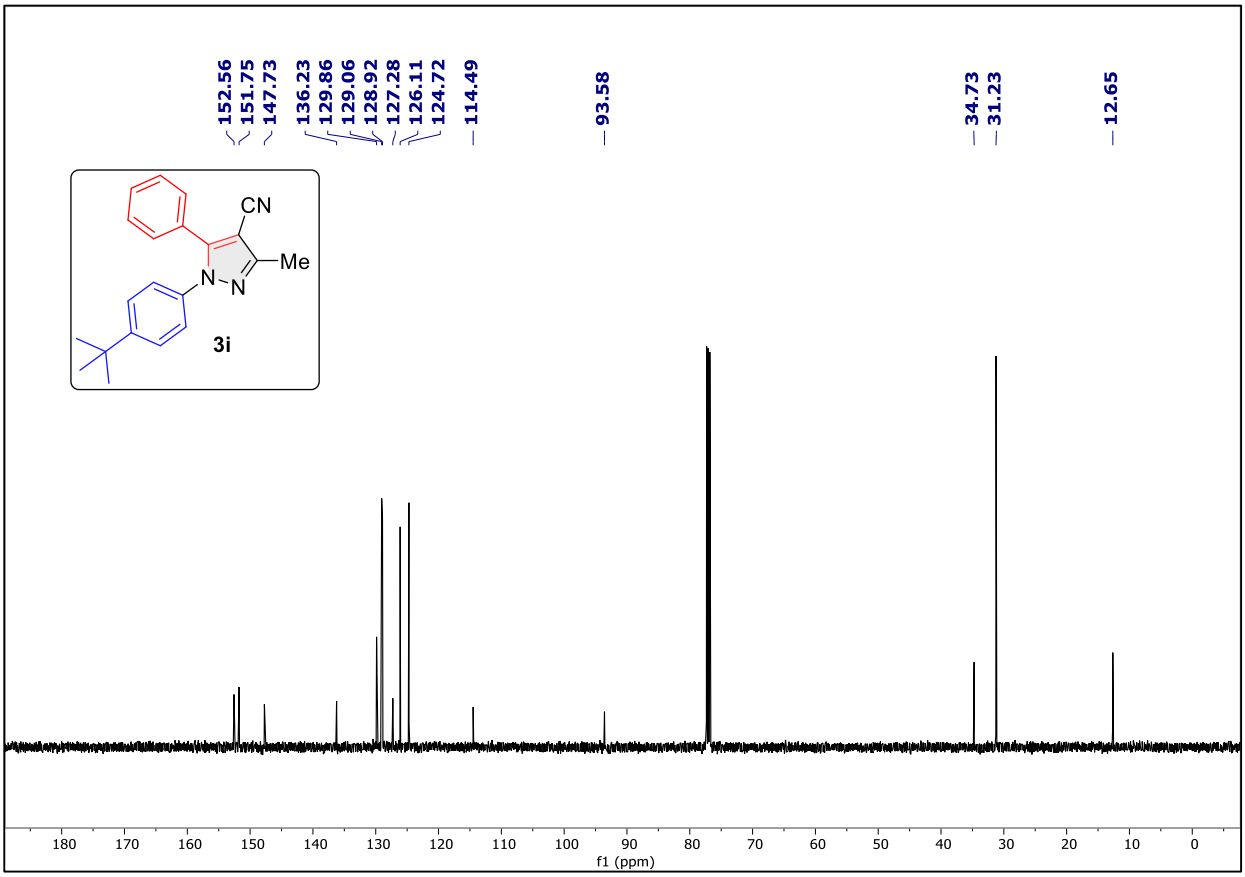
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3h**



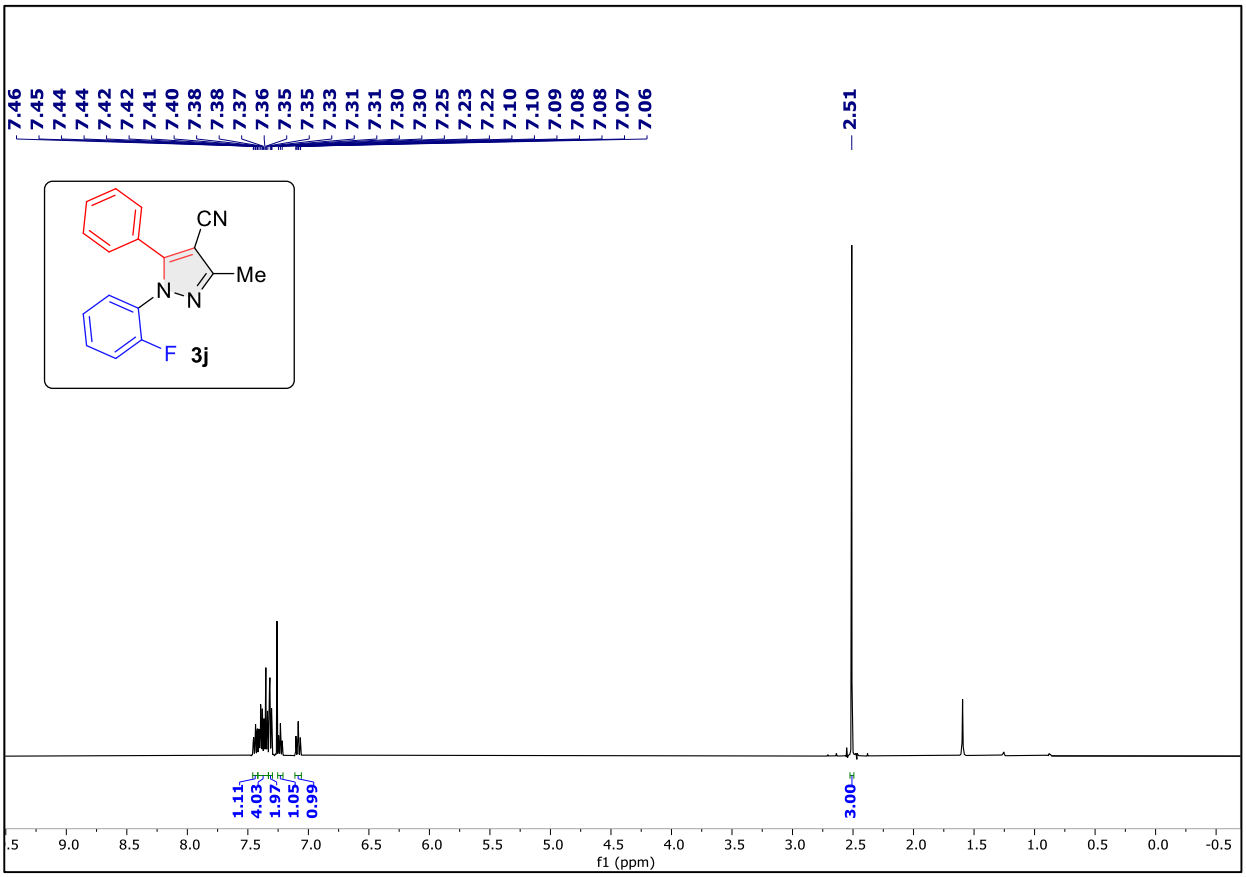
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i**



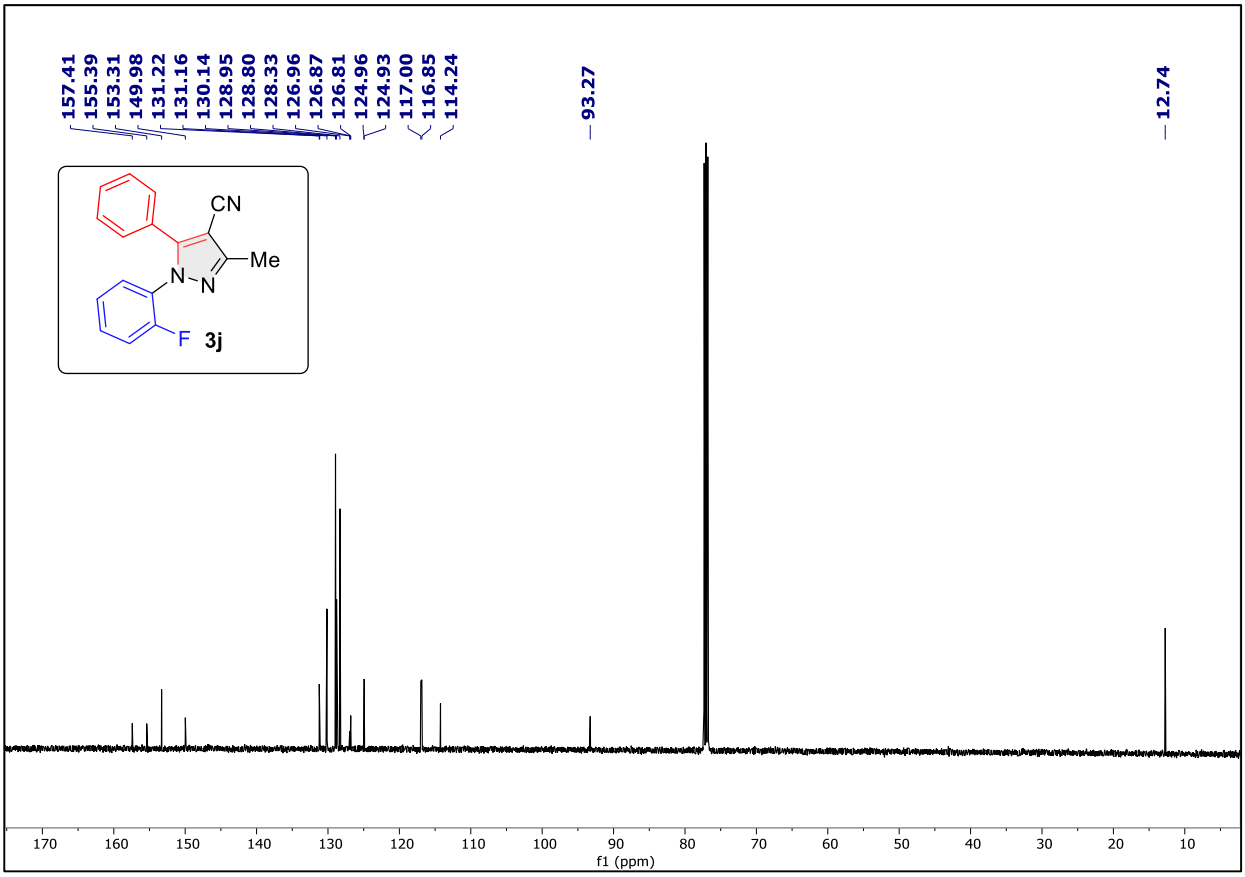
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3i**



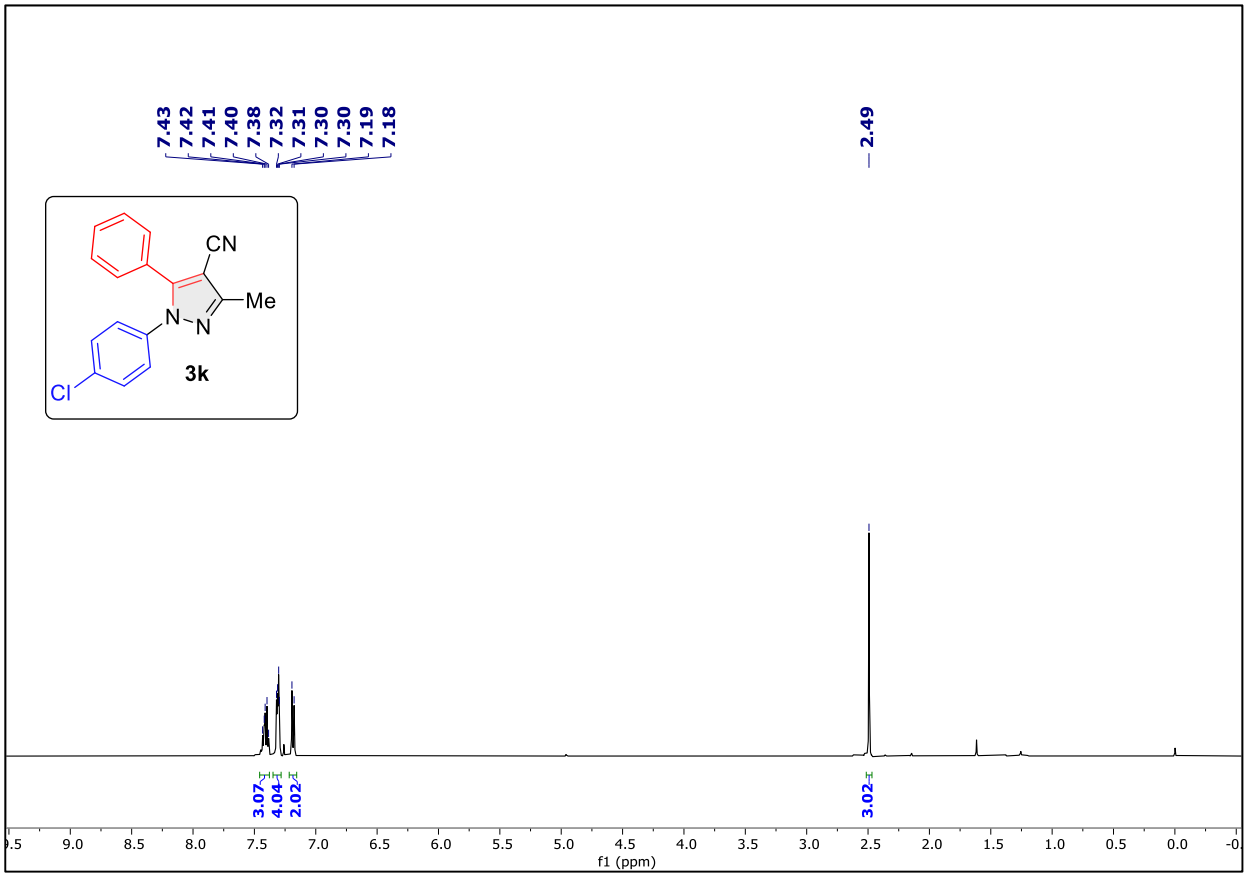
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3j**



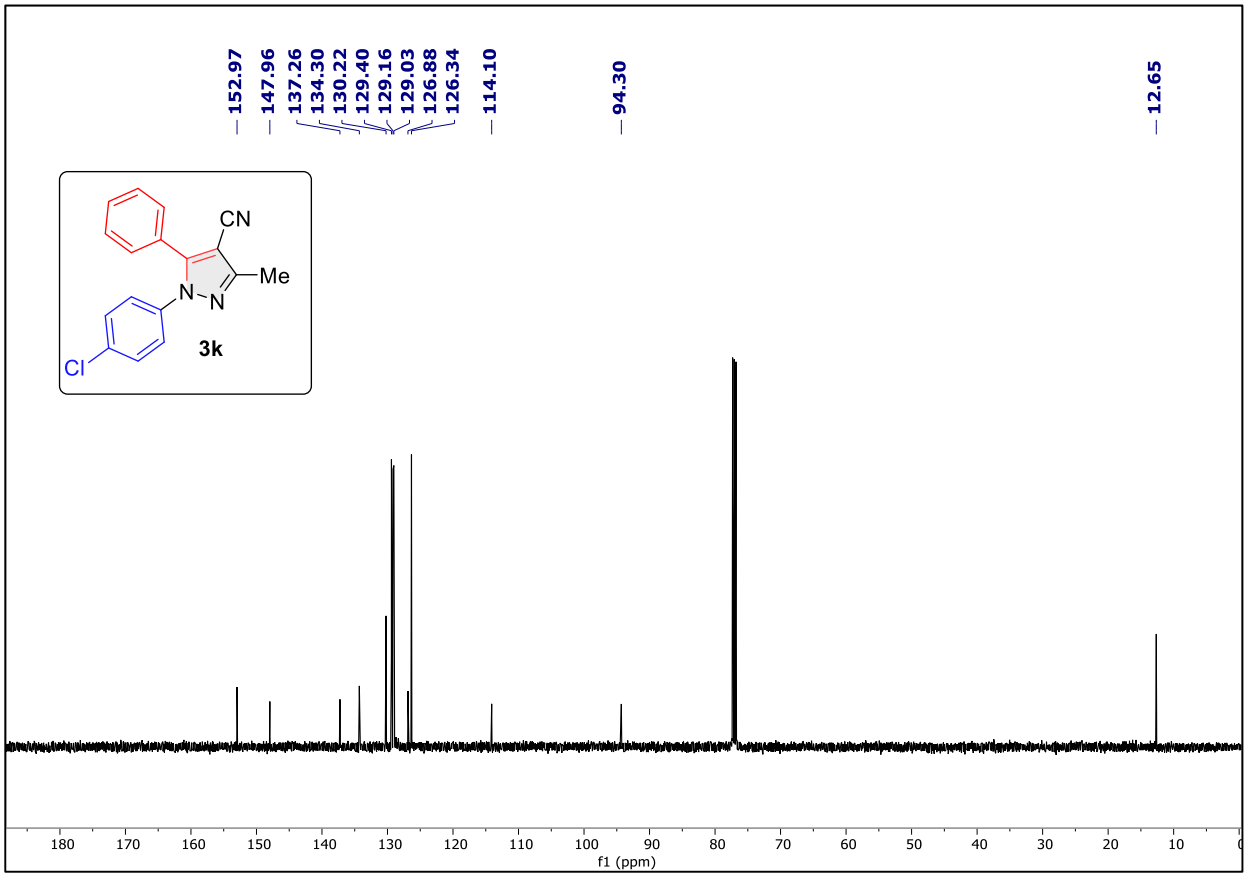
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3j**



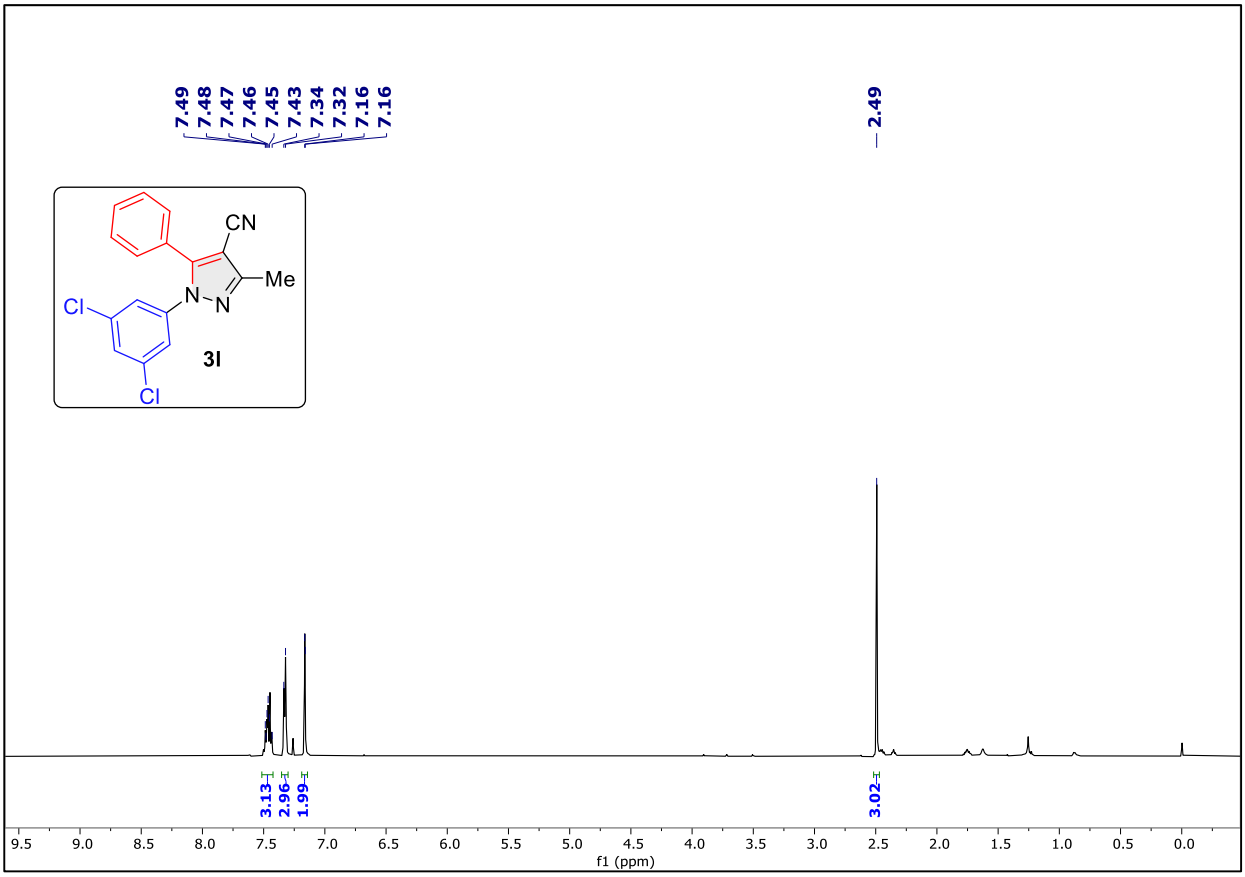
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**



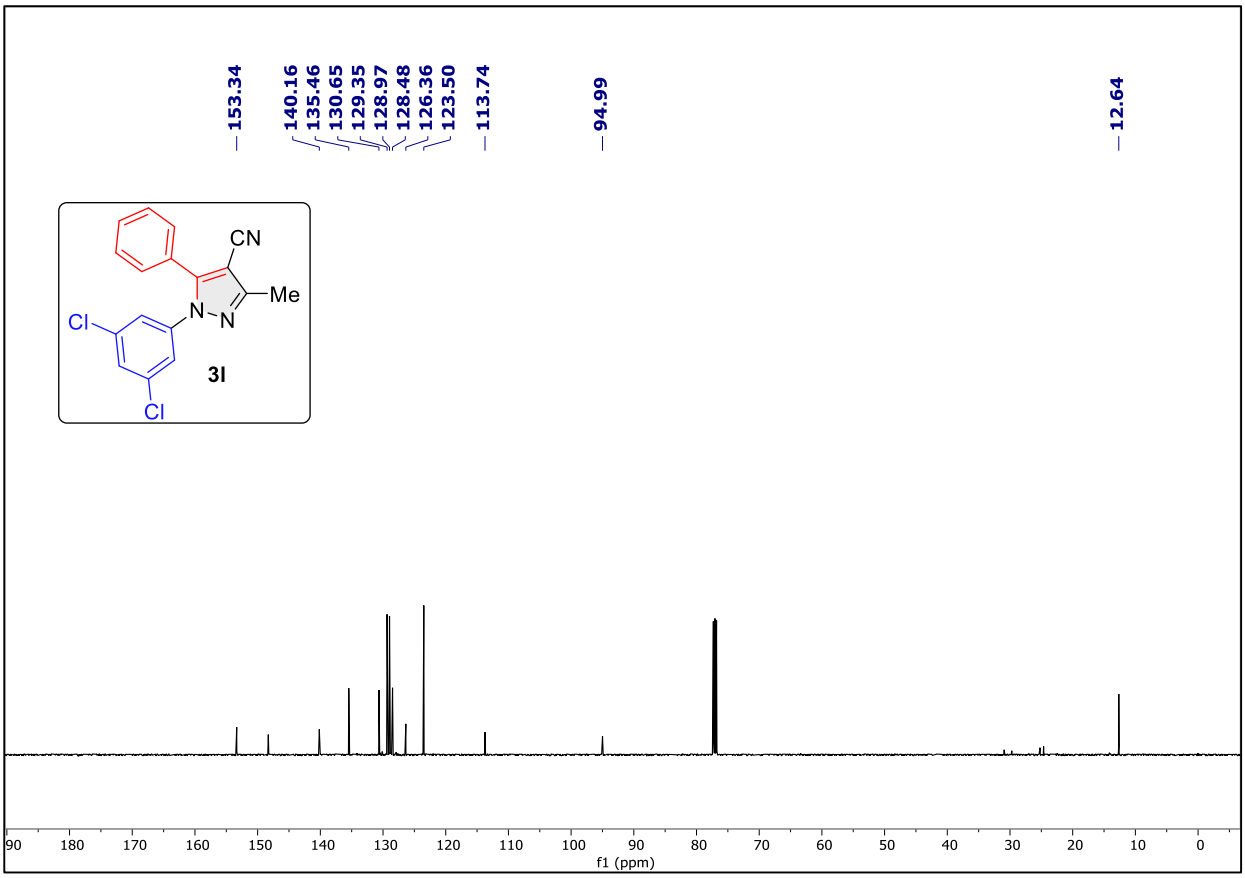
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3k**



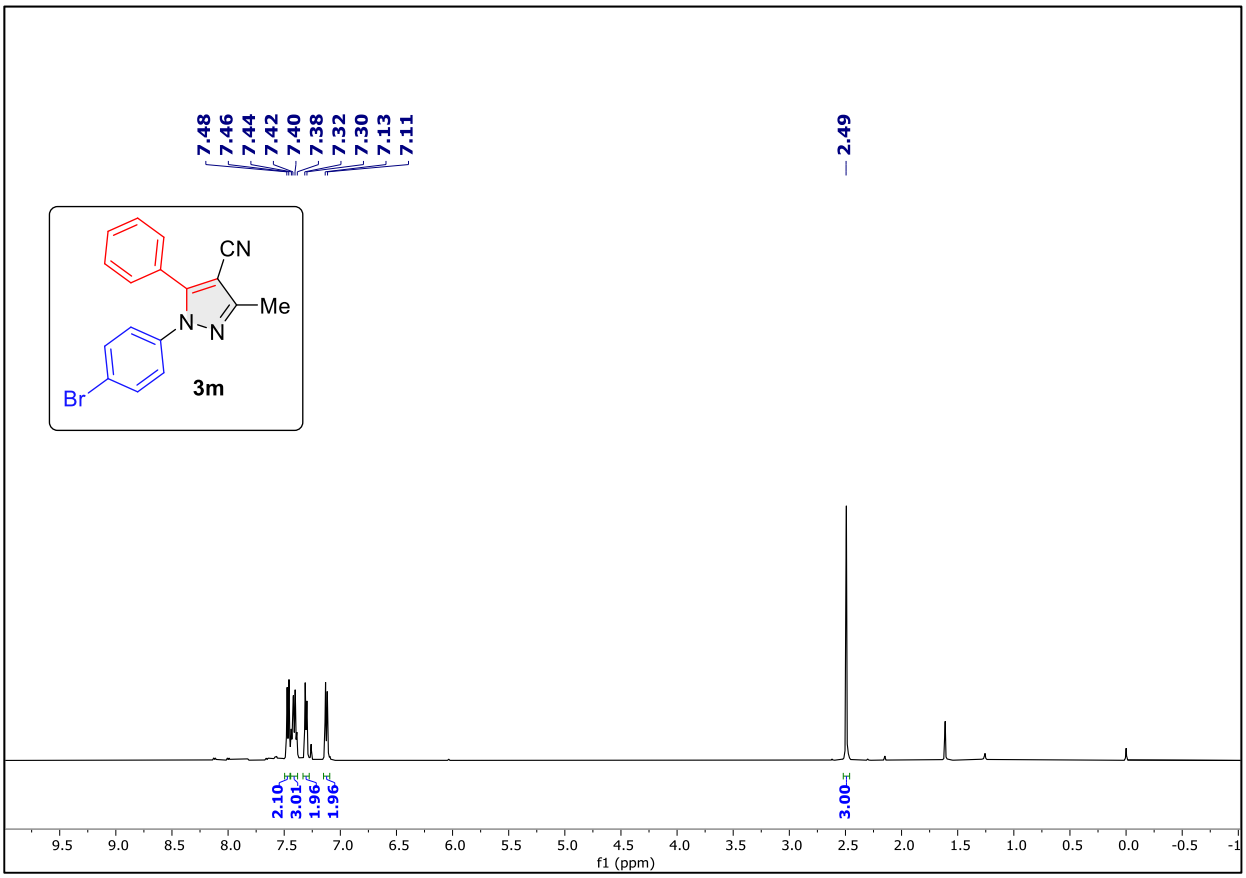
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**



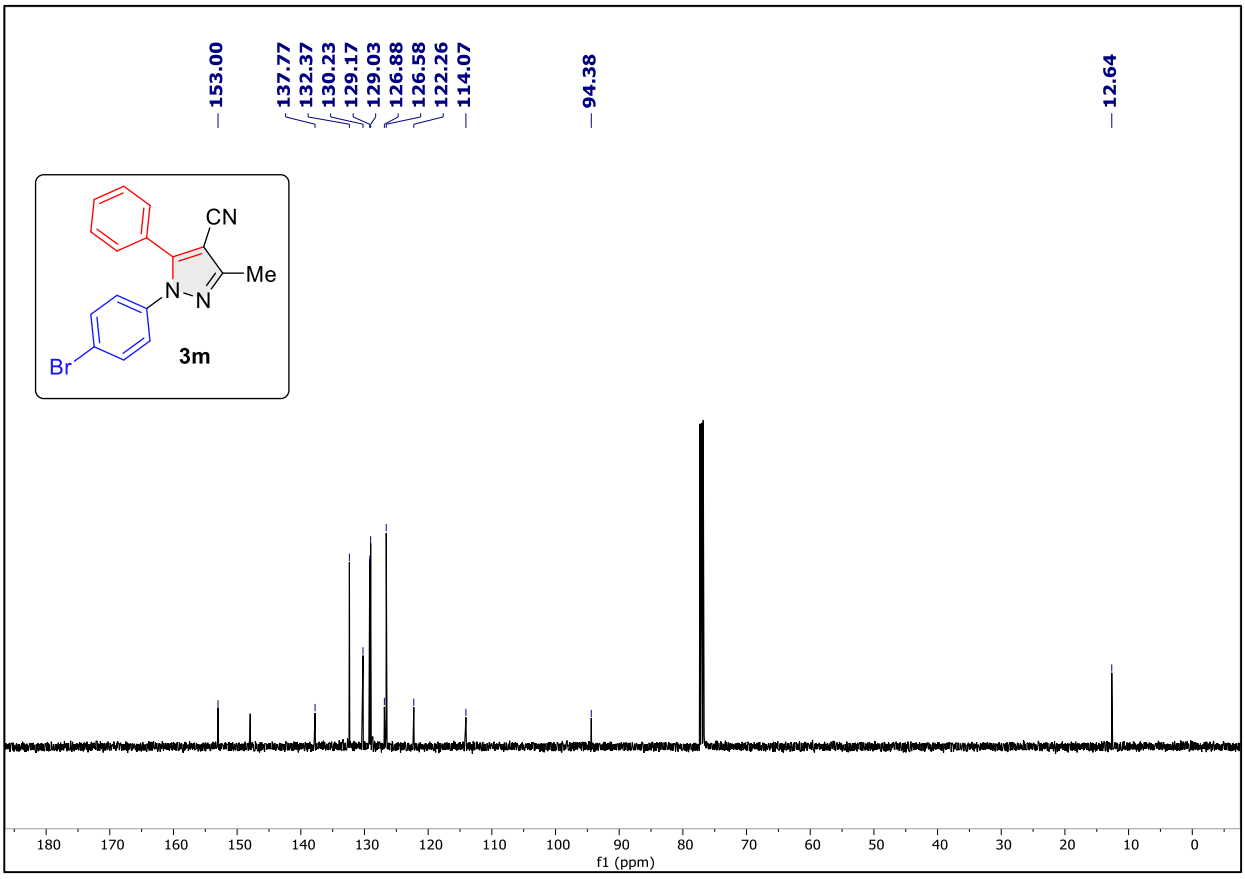
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3l**



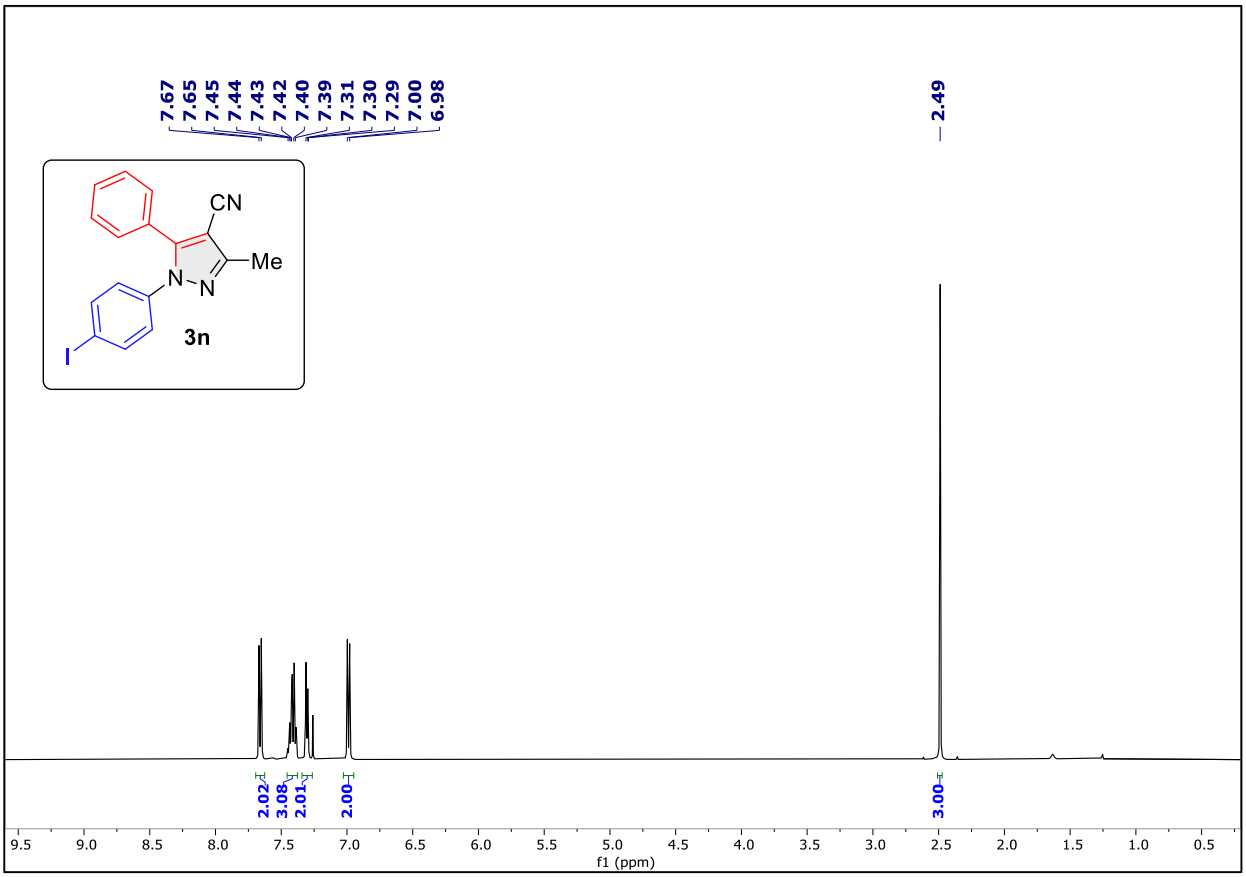
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**



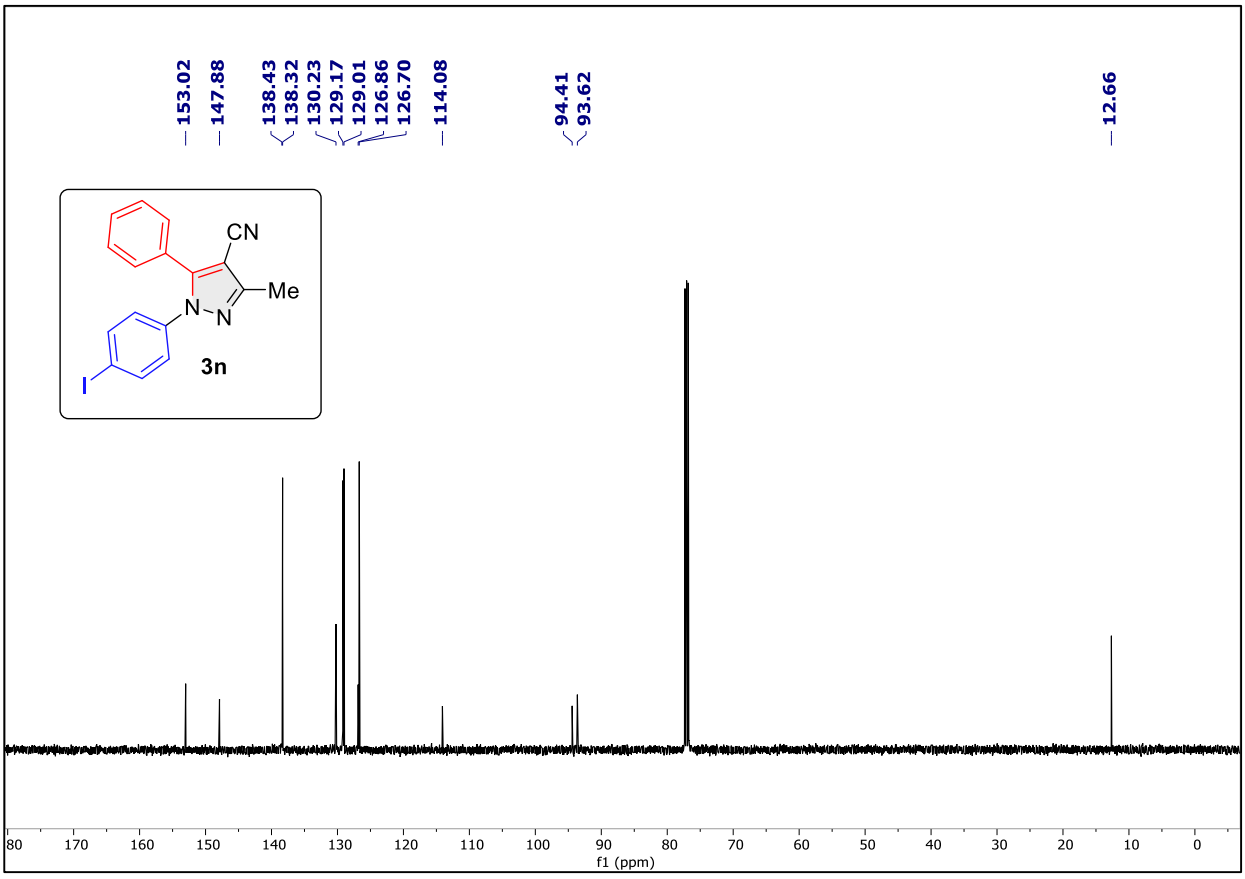
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3m**



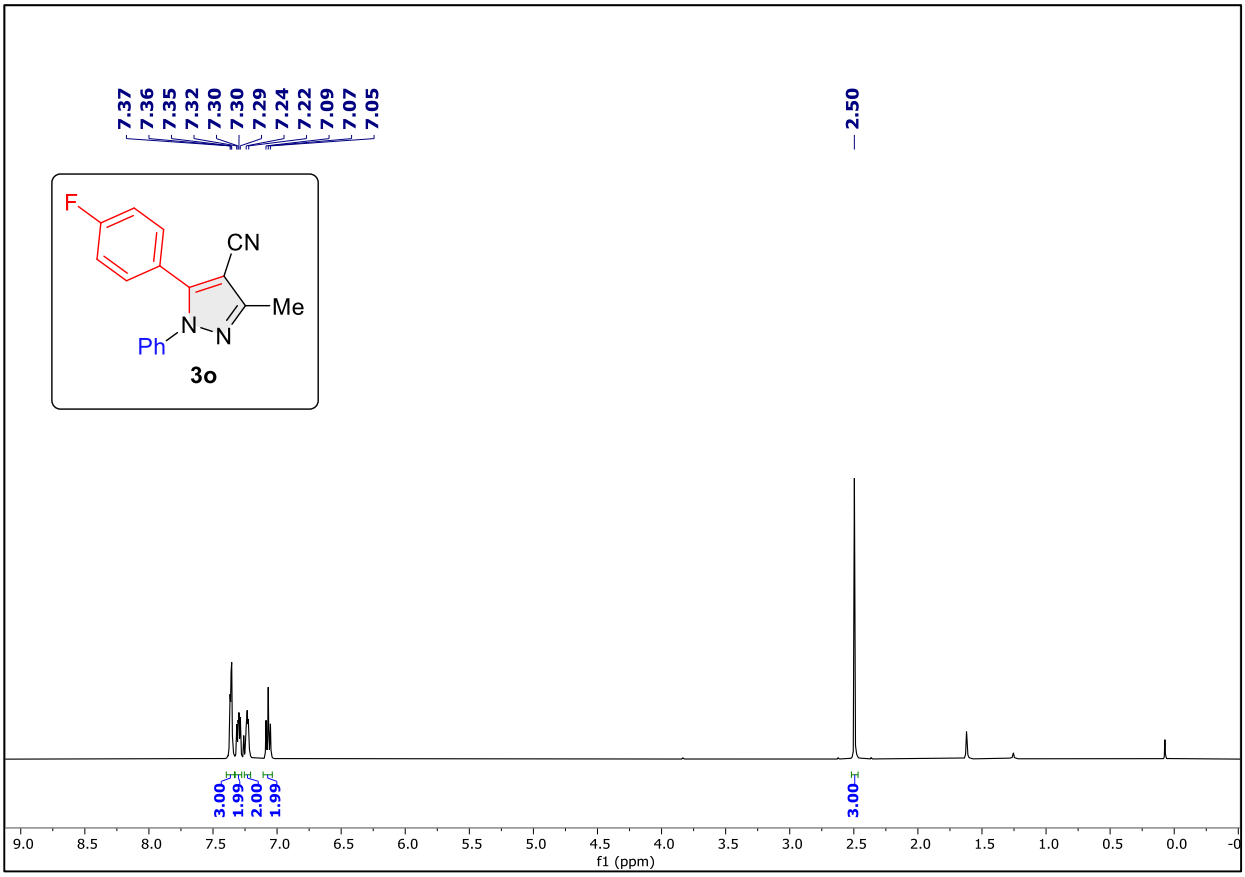
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3n**



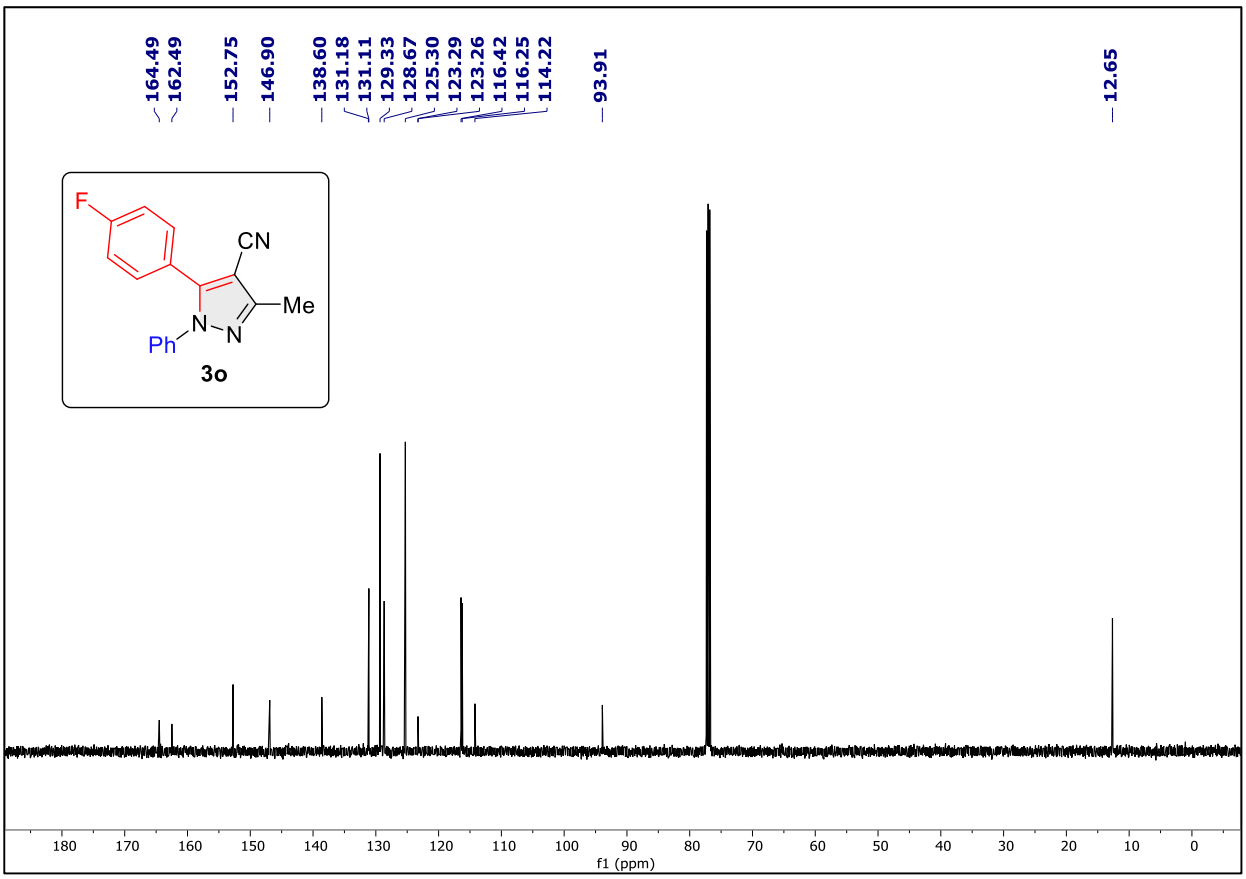
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3n**



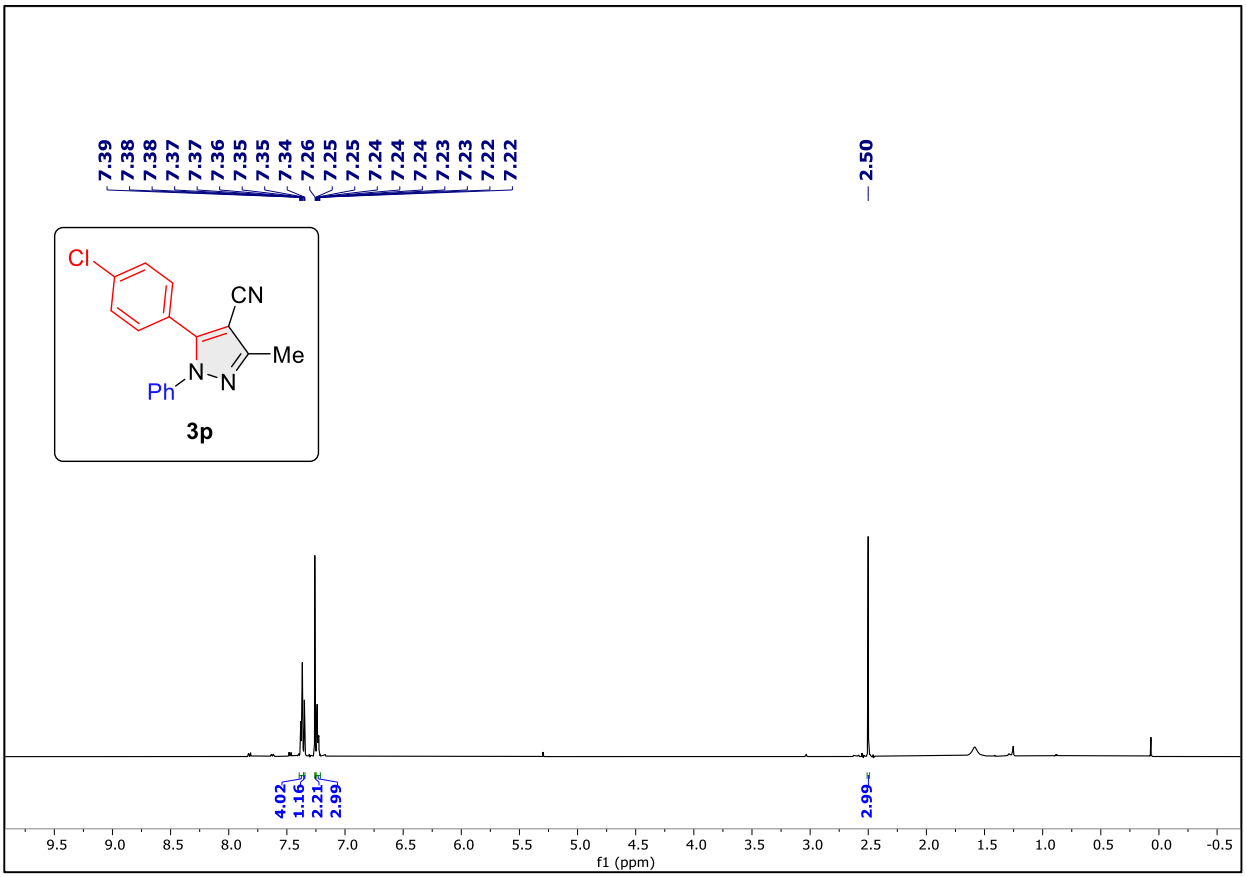
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o**



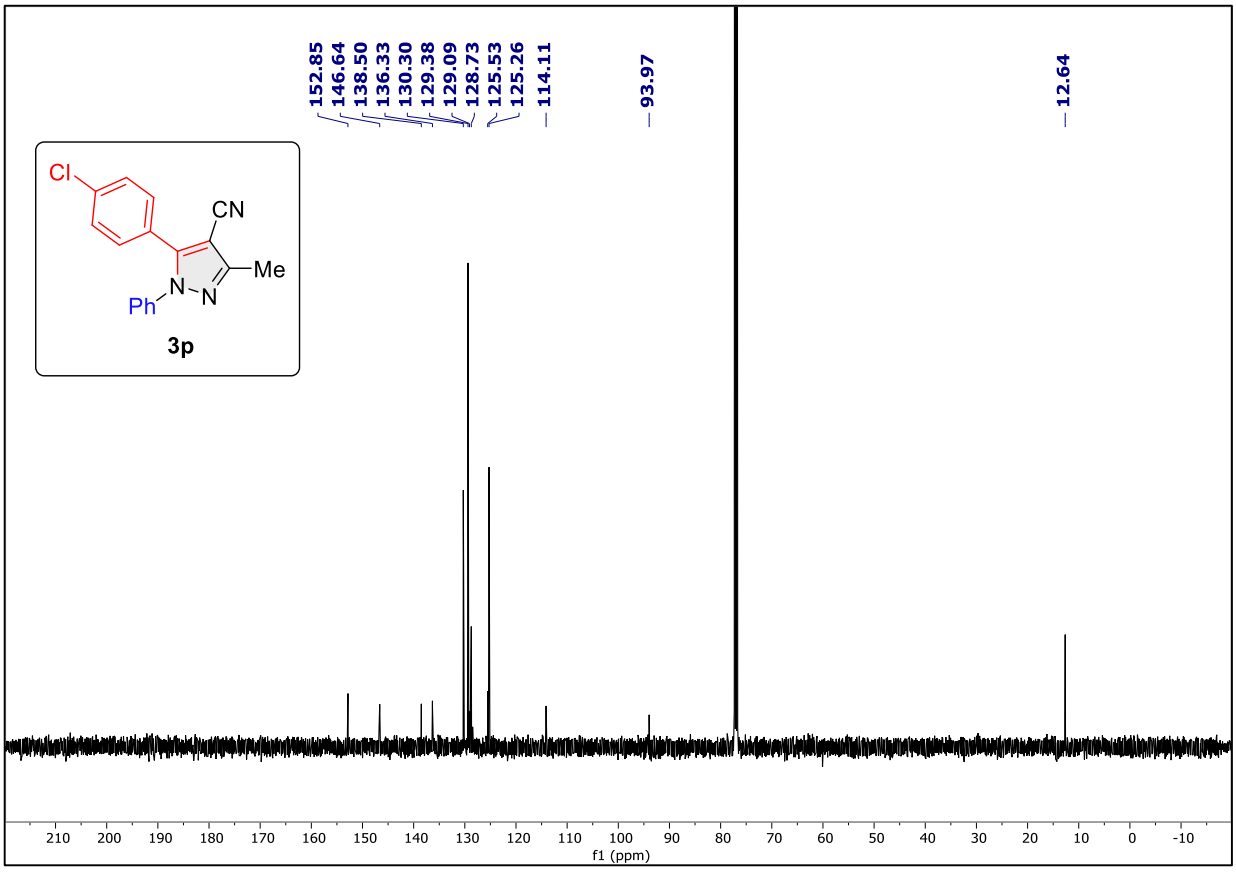
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3o**



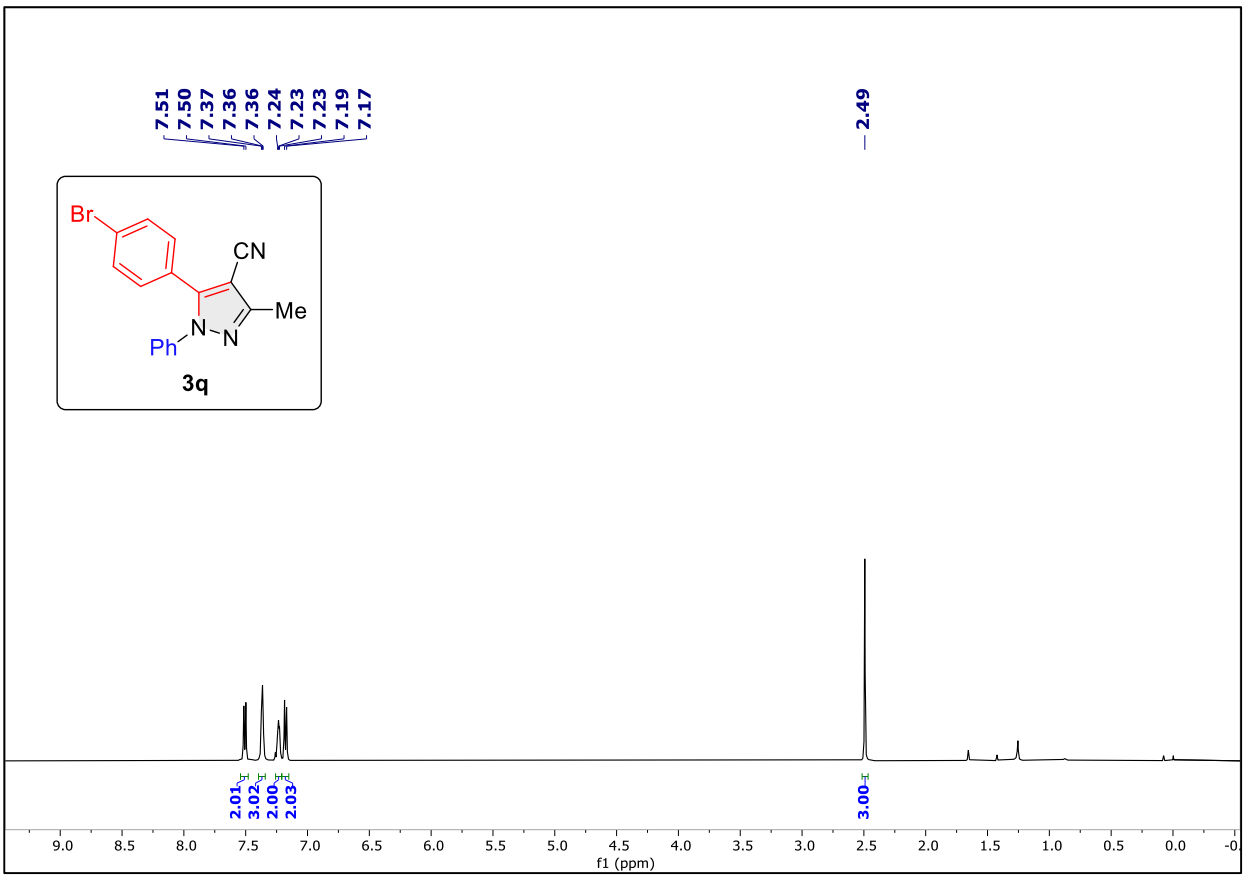
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**



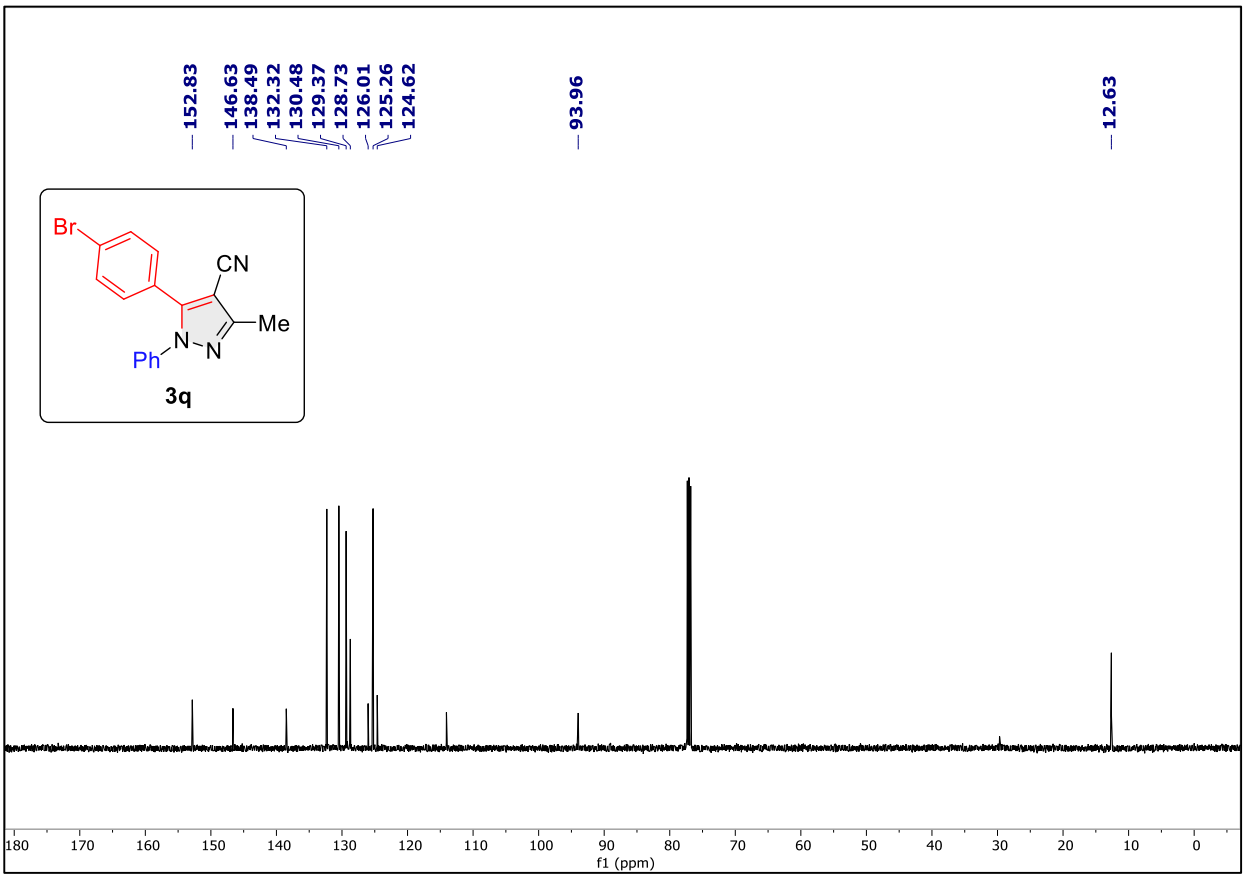
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3p**



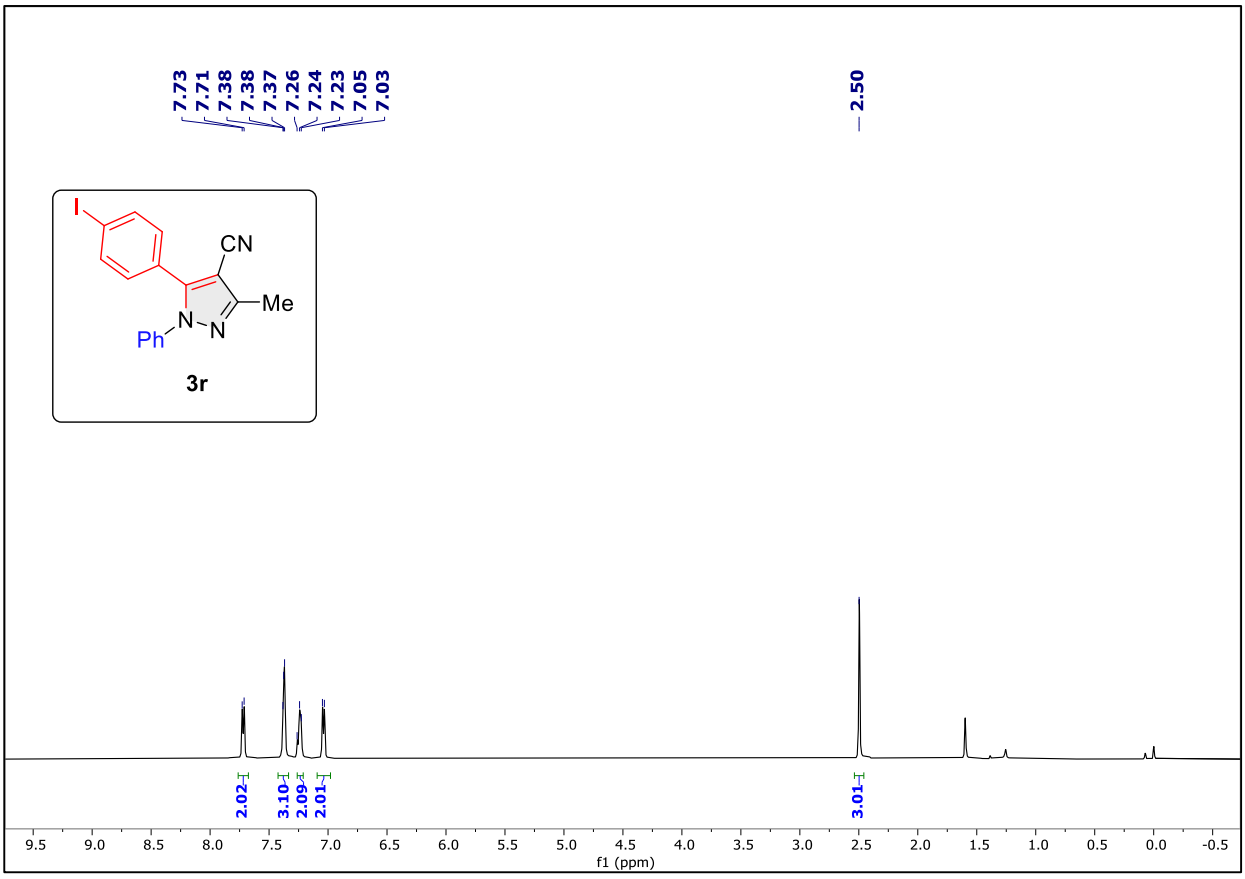
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q**



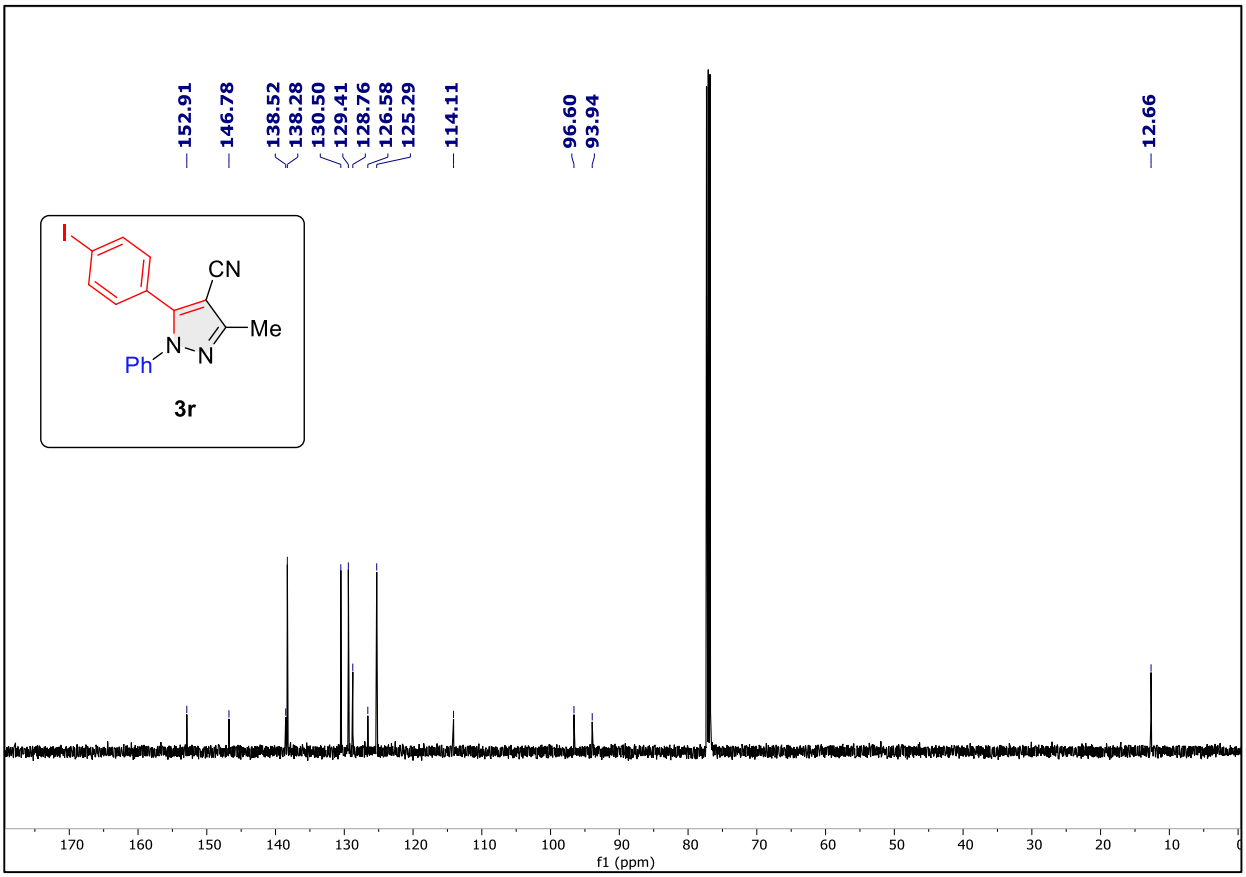
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3q**



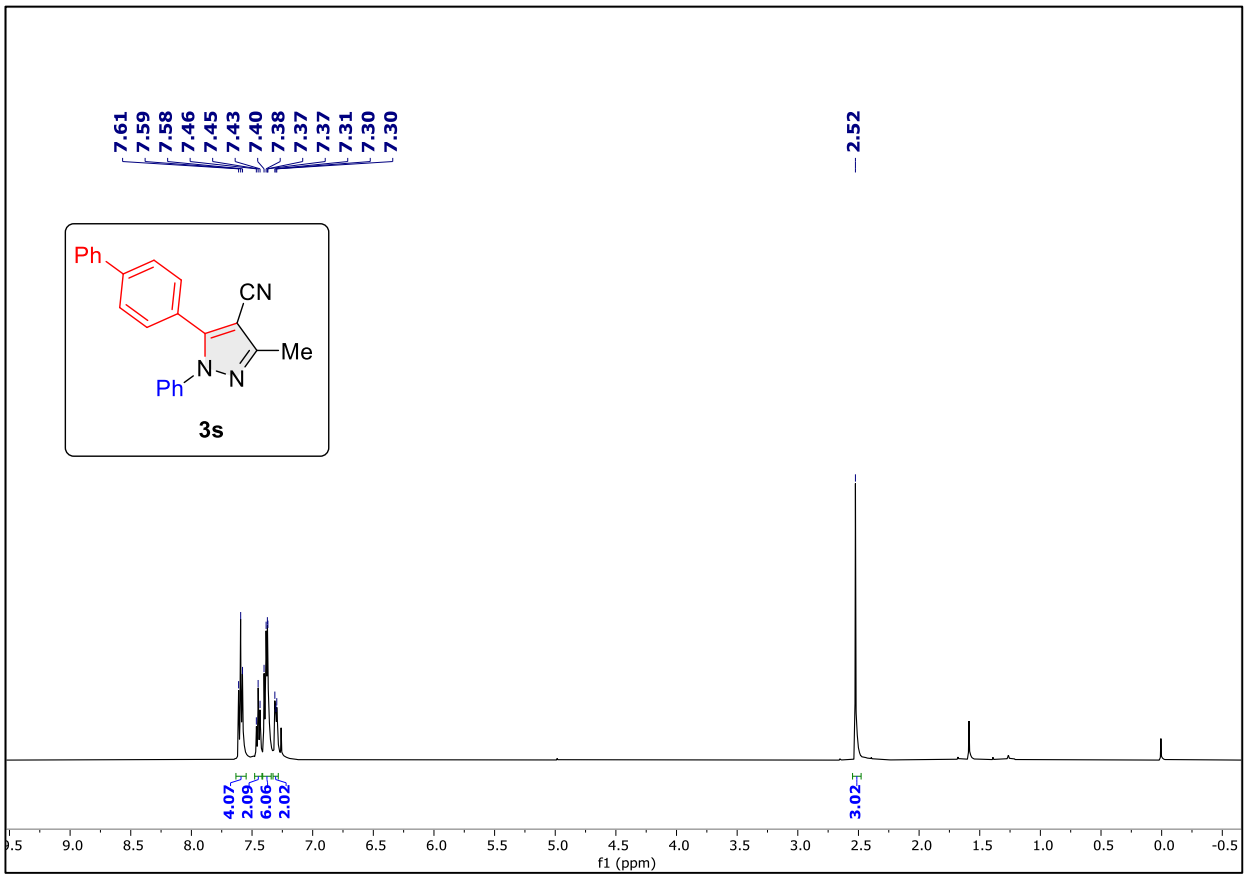
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3r**



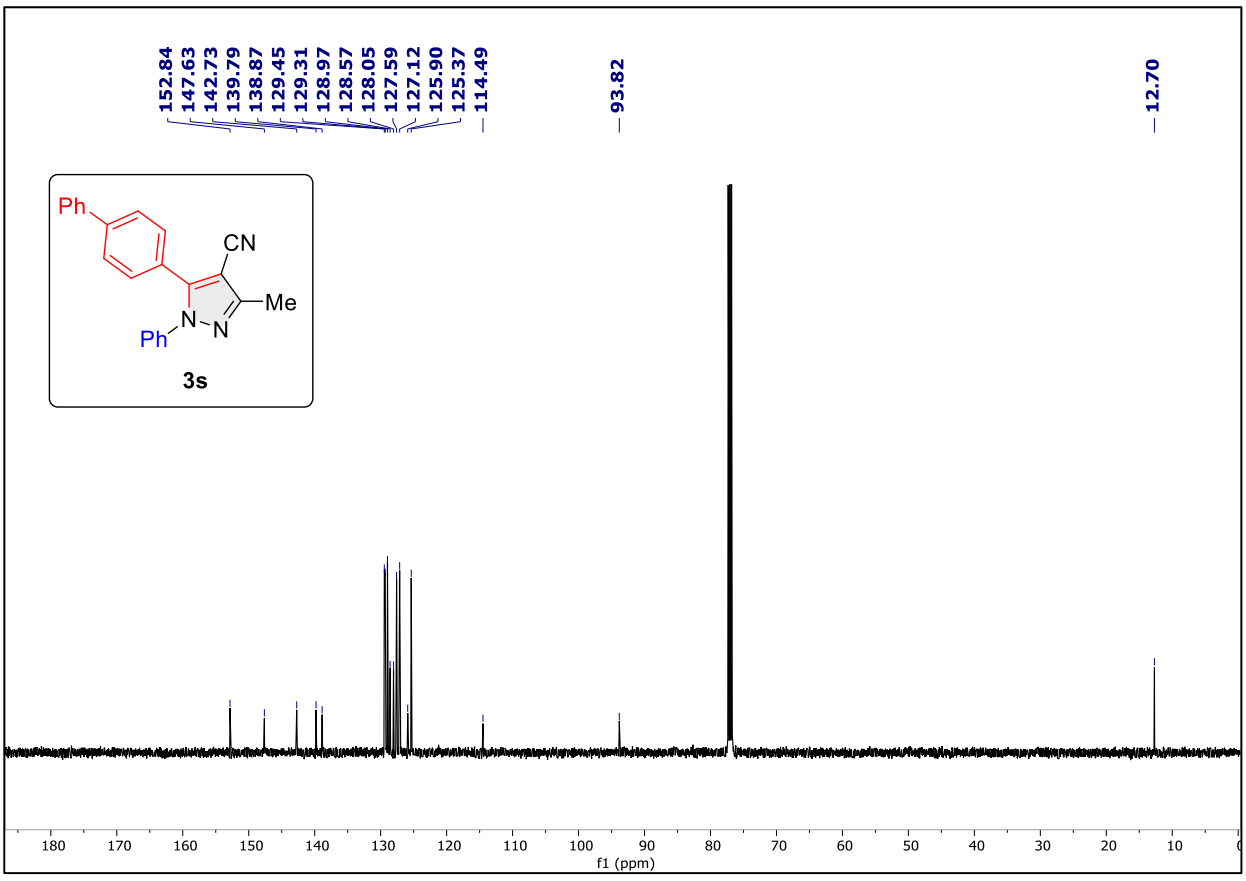
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3r**



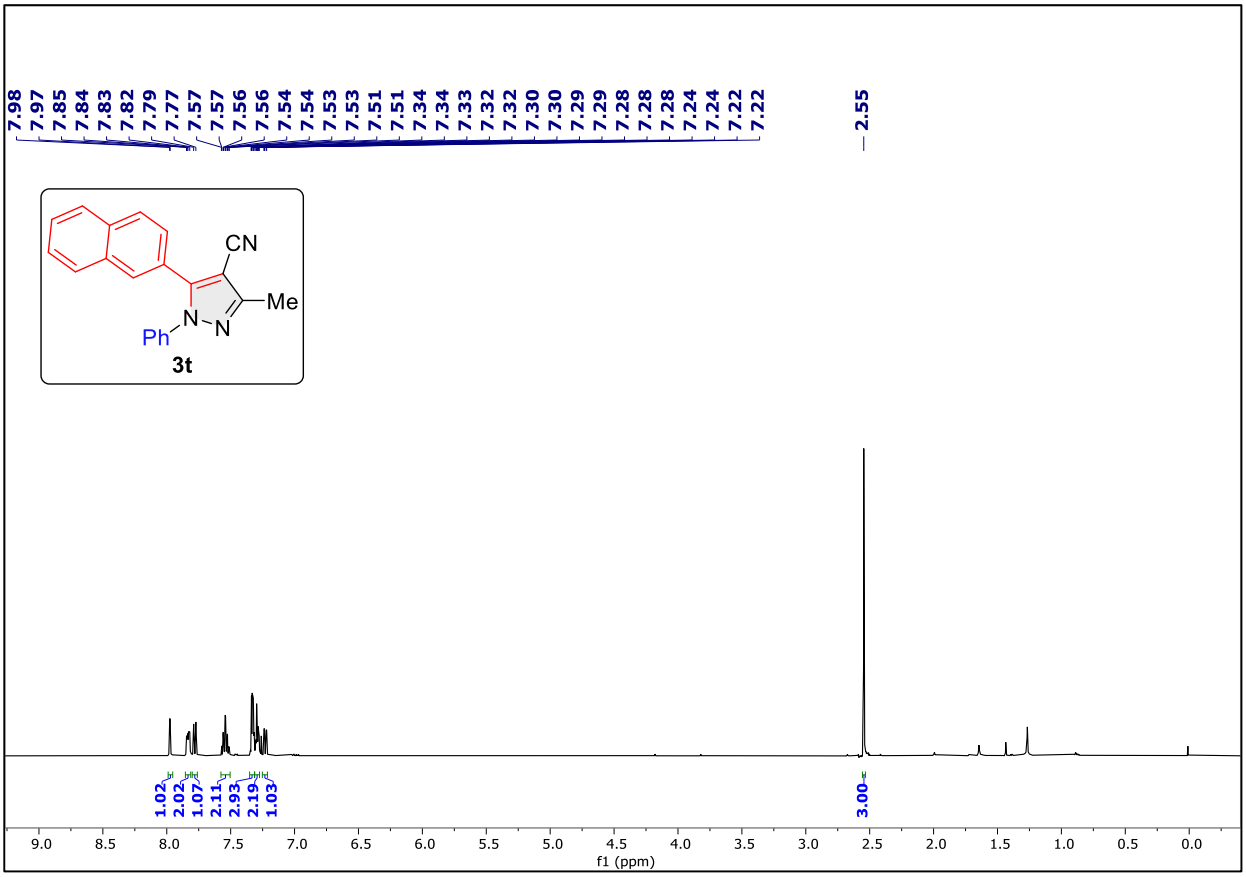
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3s**



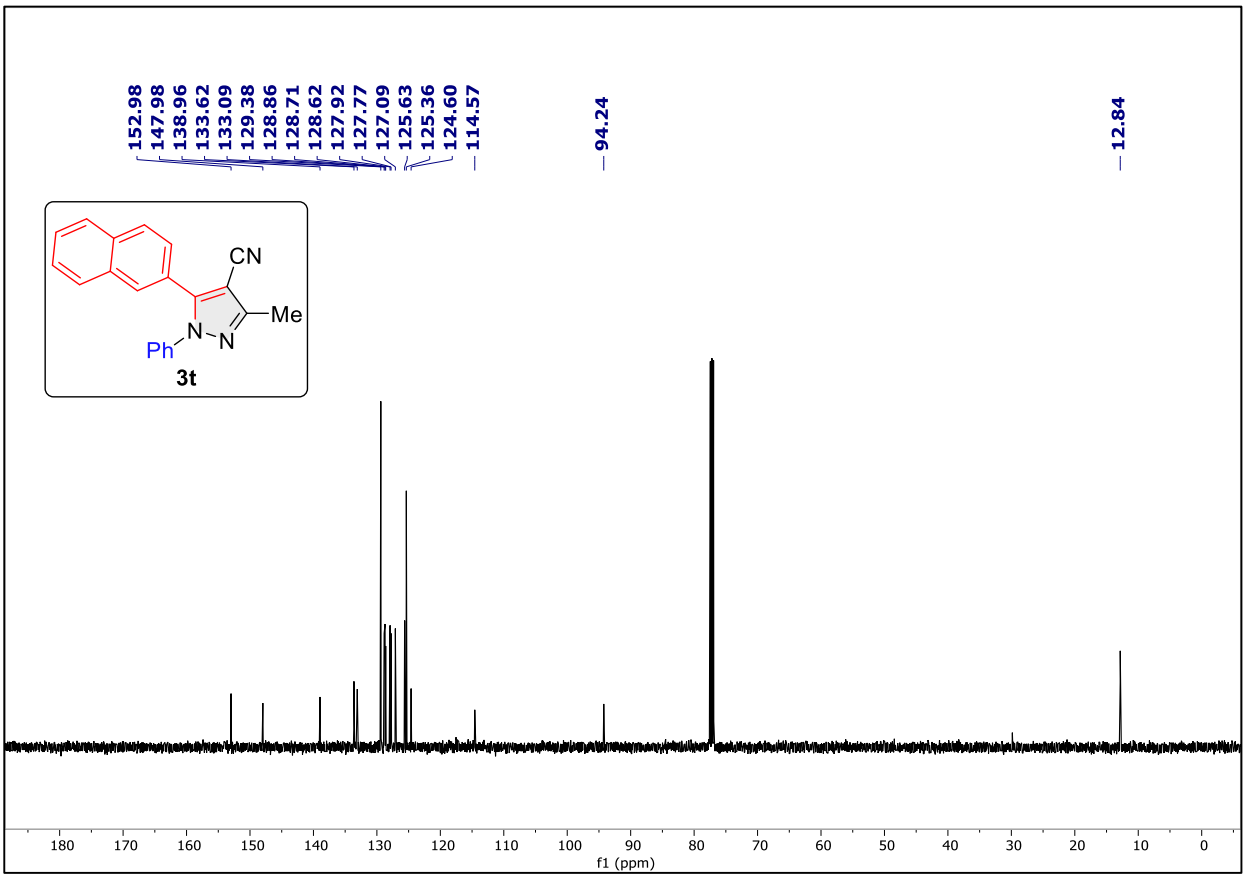
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3s**



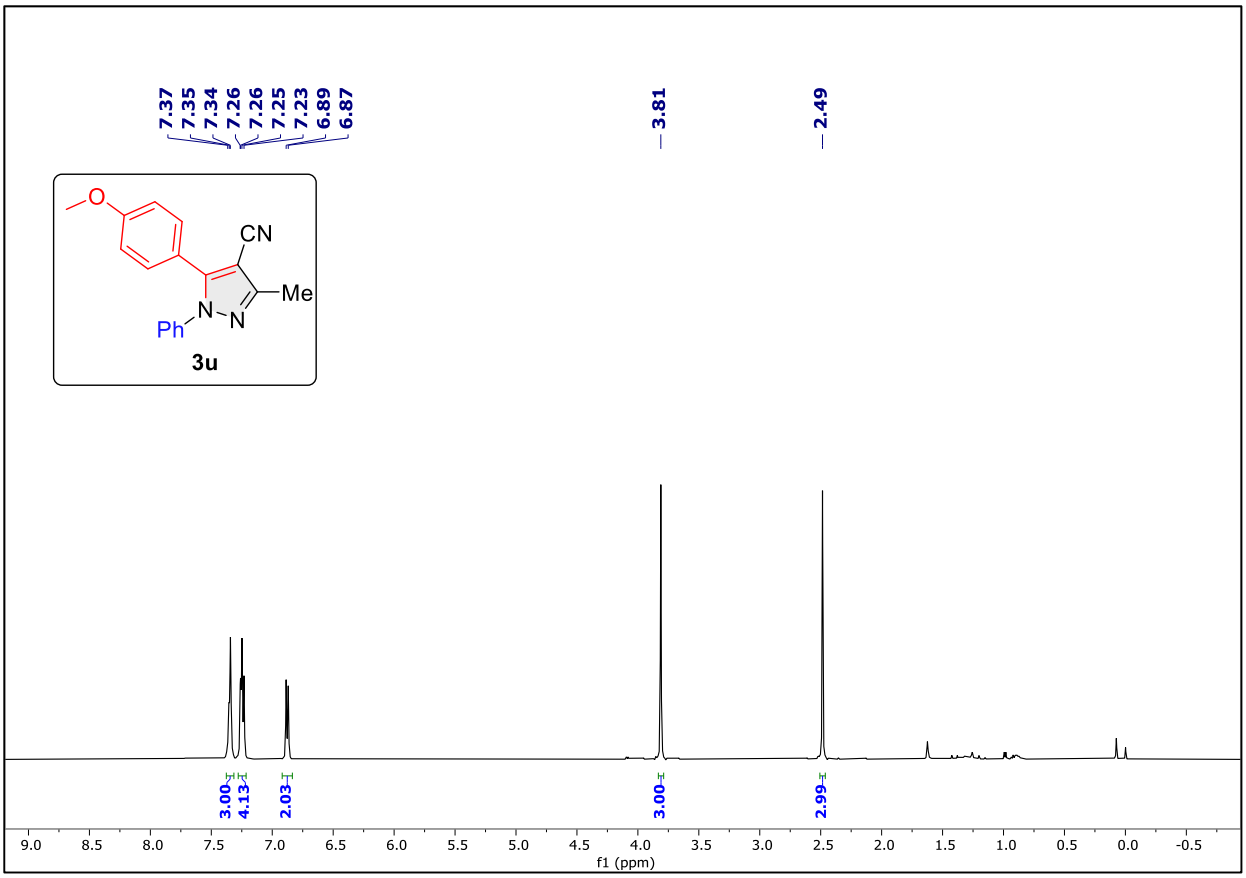
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t**



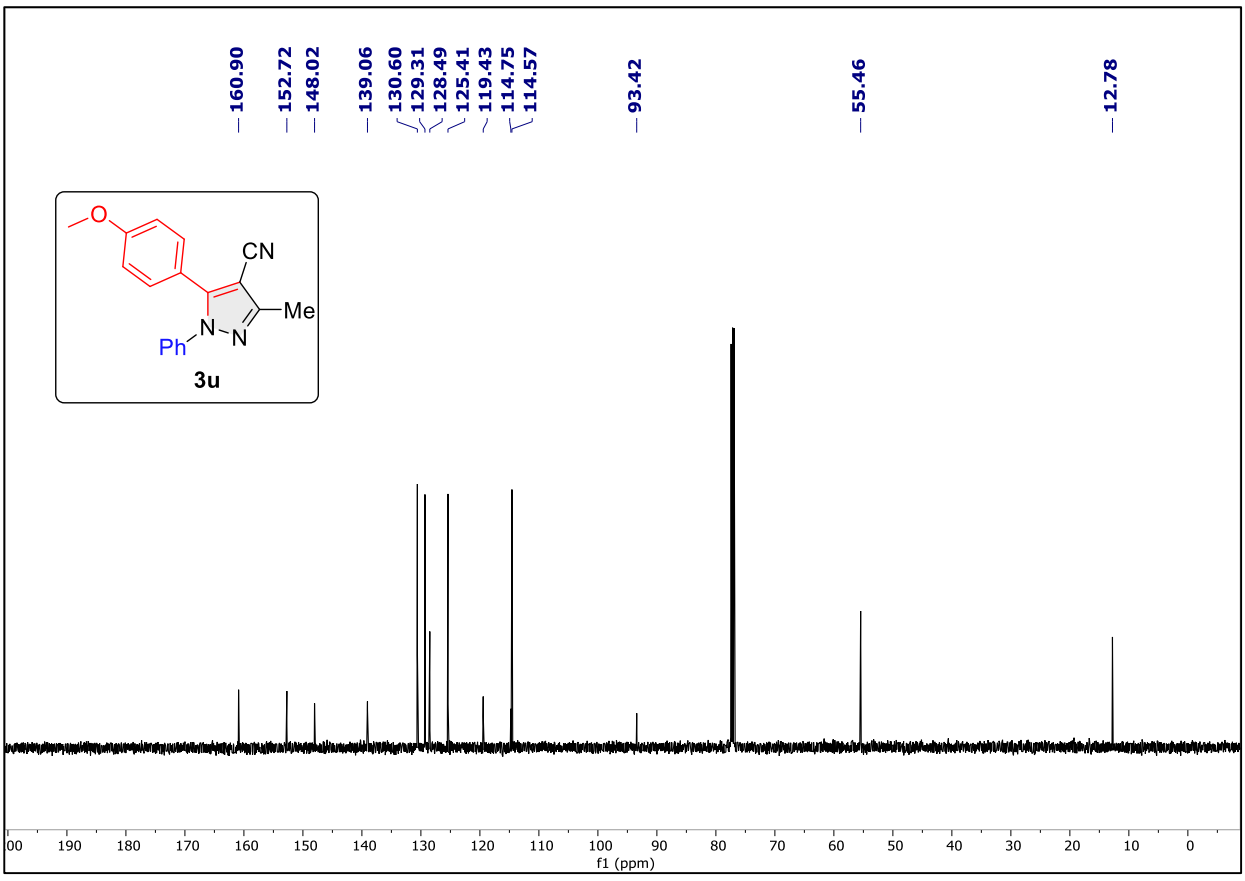
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3t**



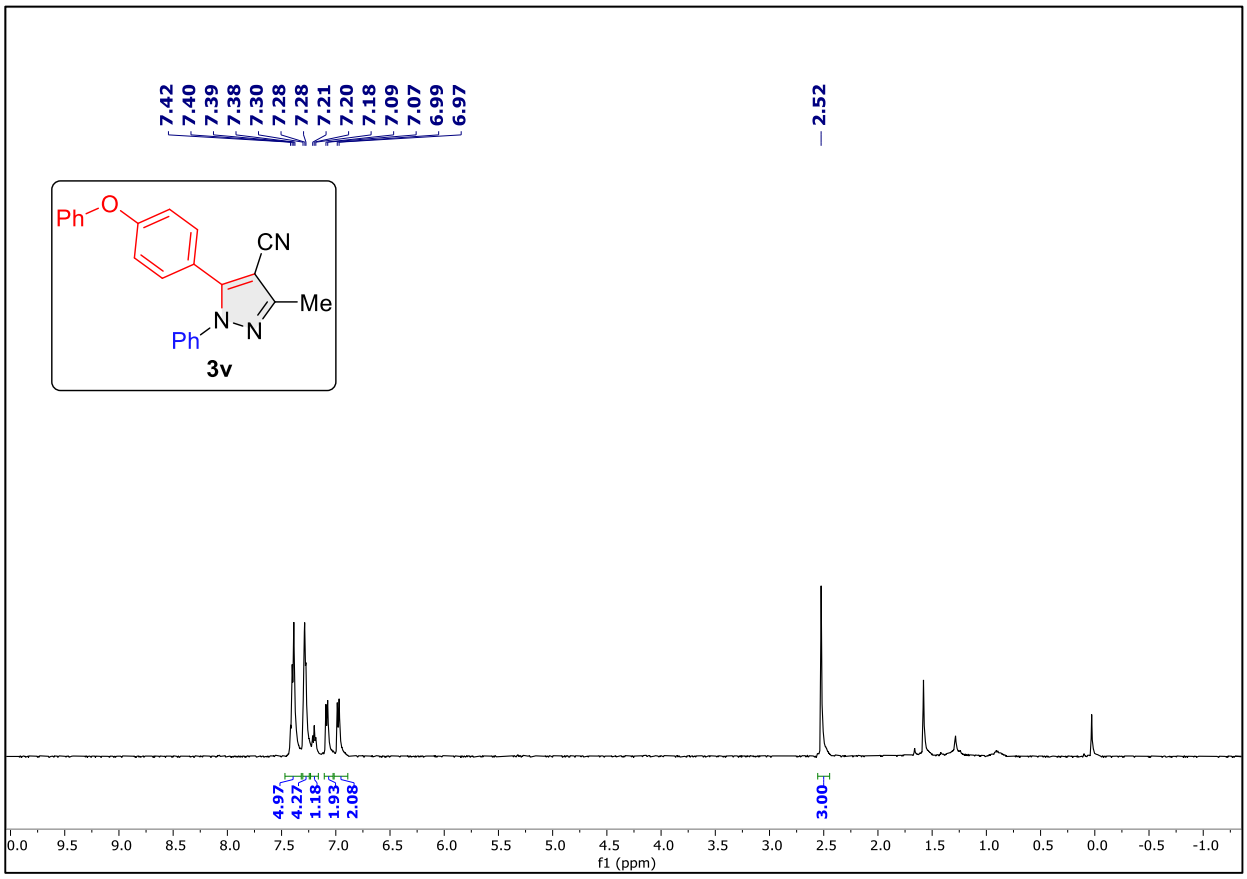
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**



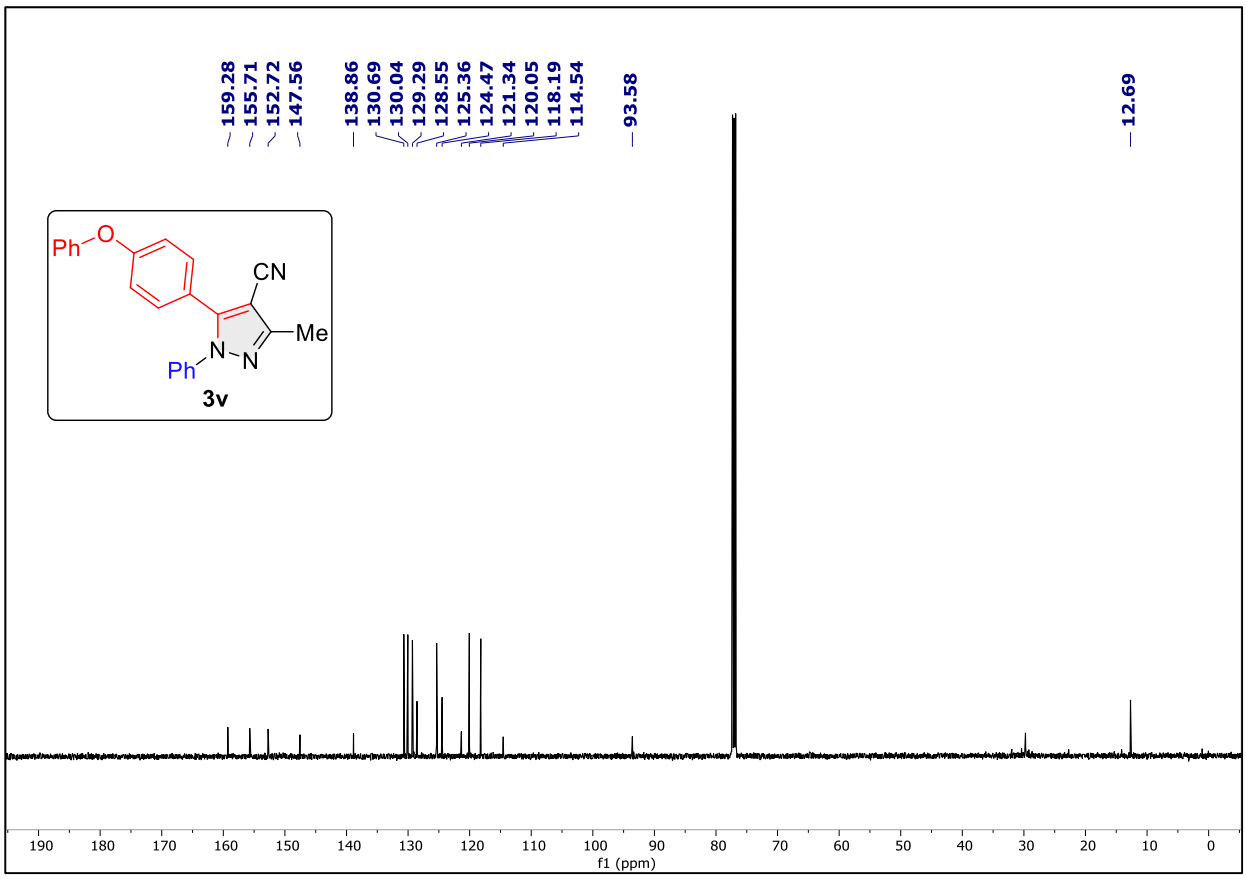
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3u**



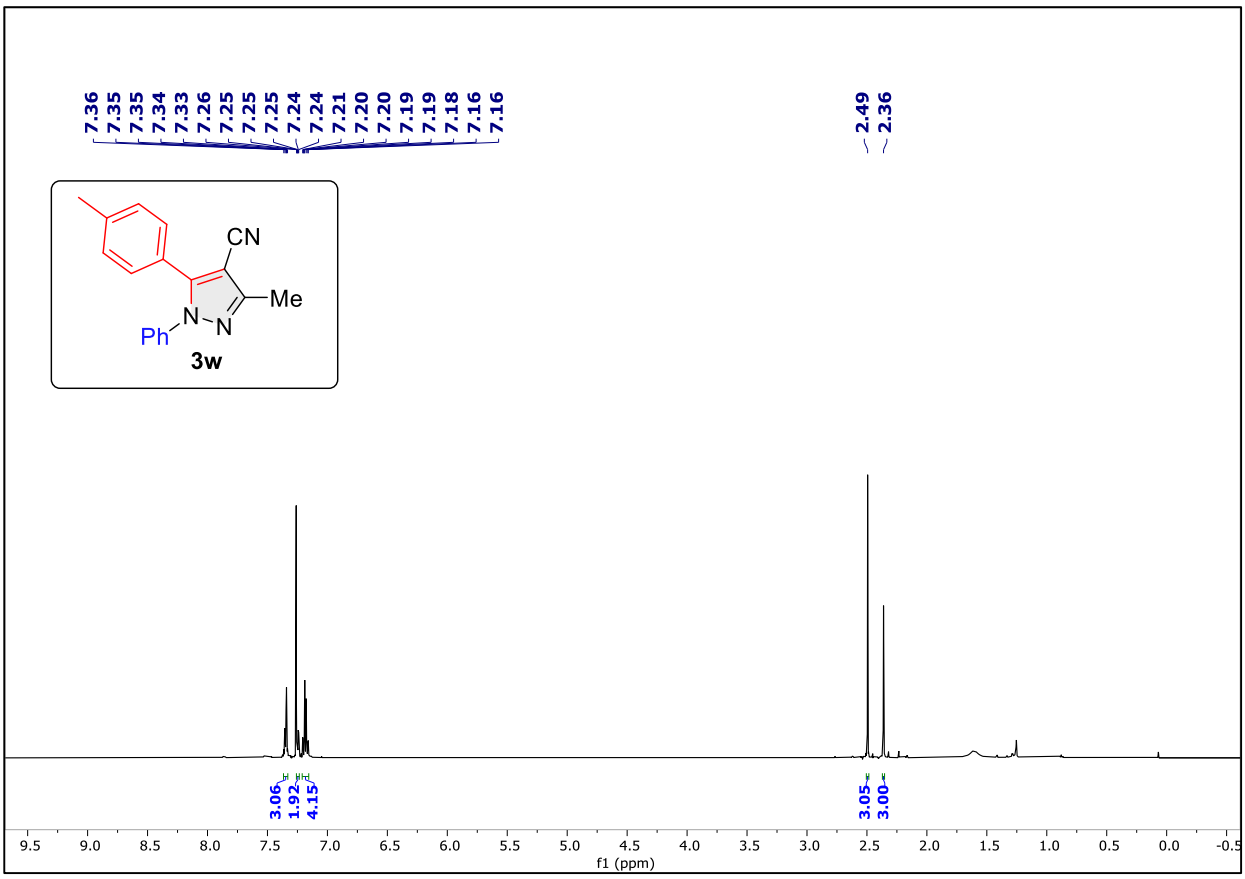
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**



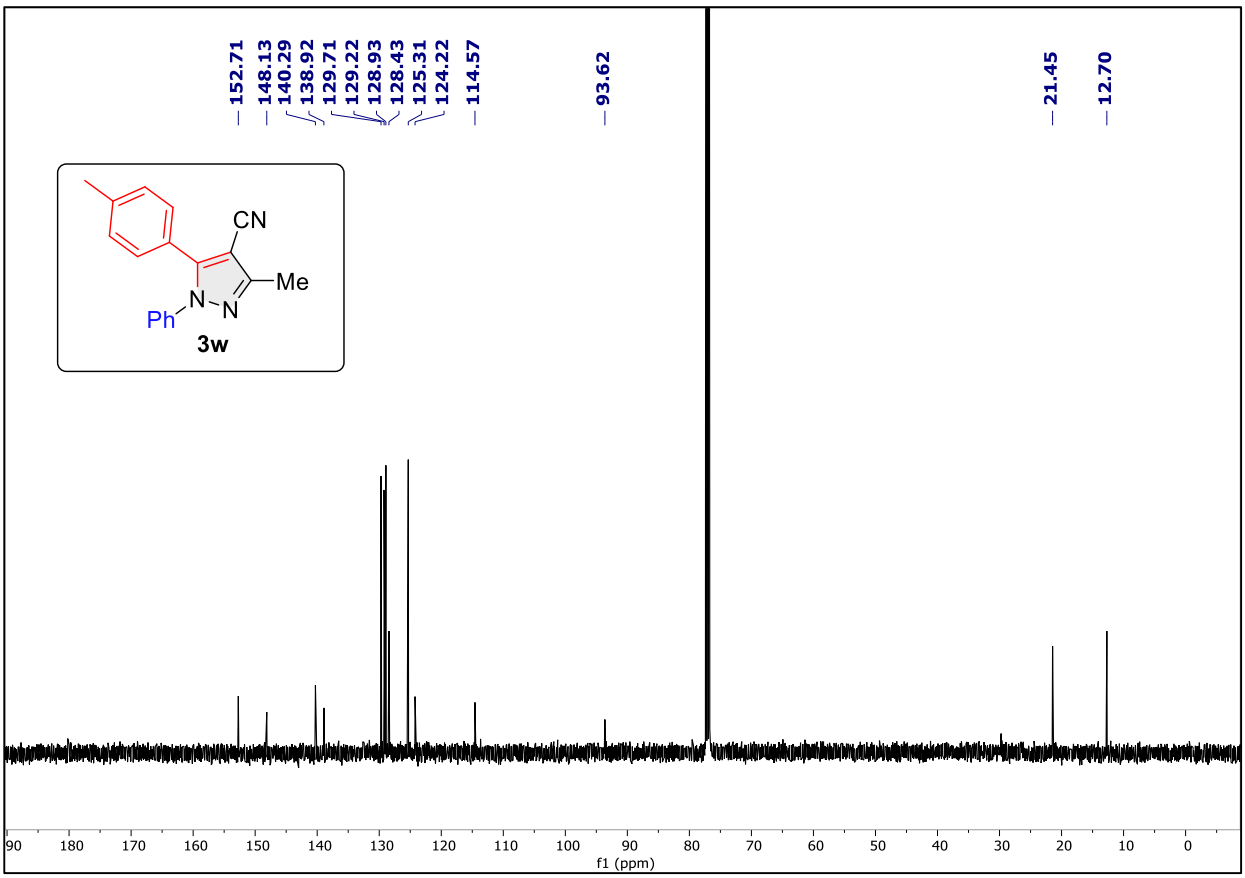
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3v**



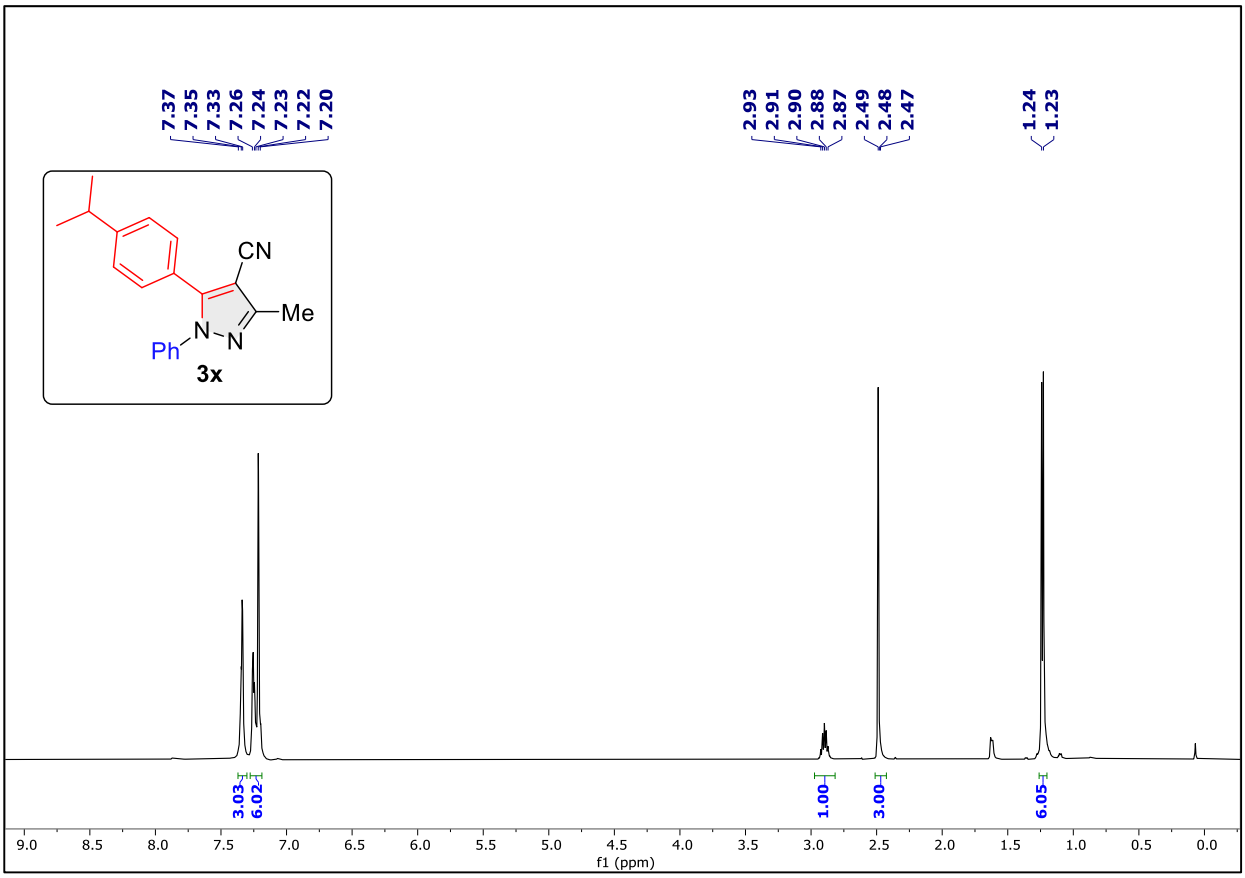
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3w**



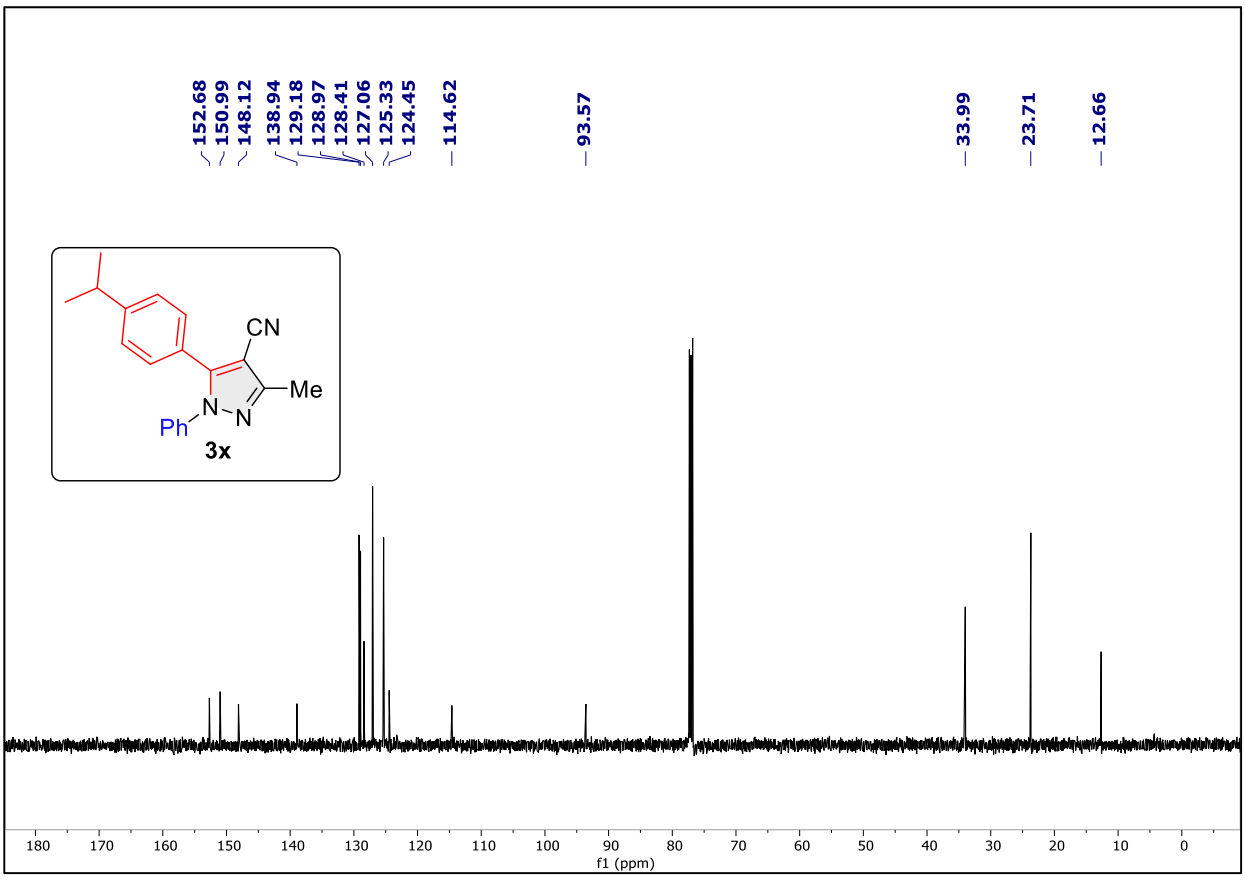
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3w**



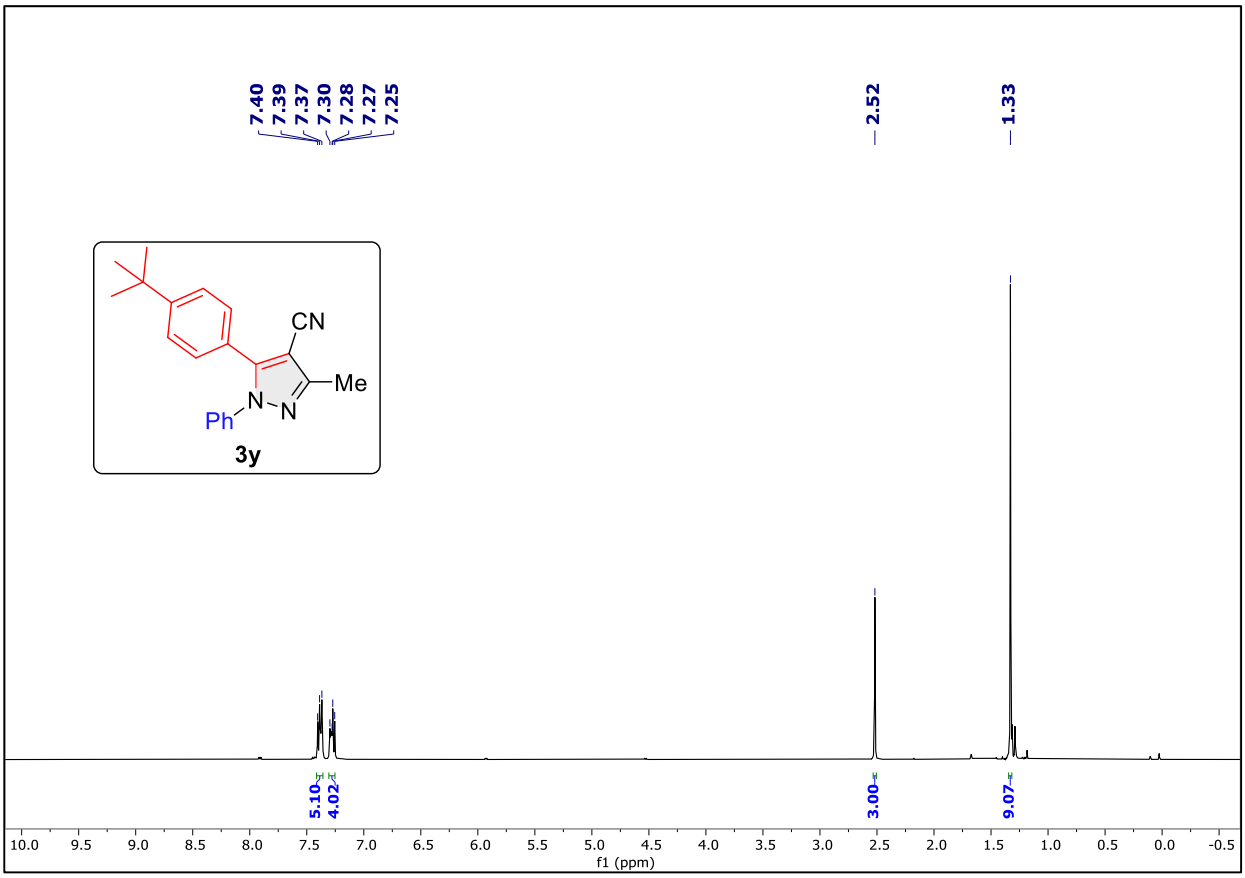
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3x**



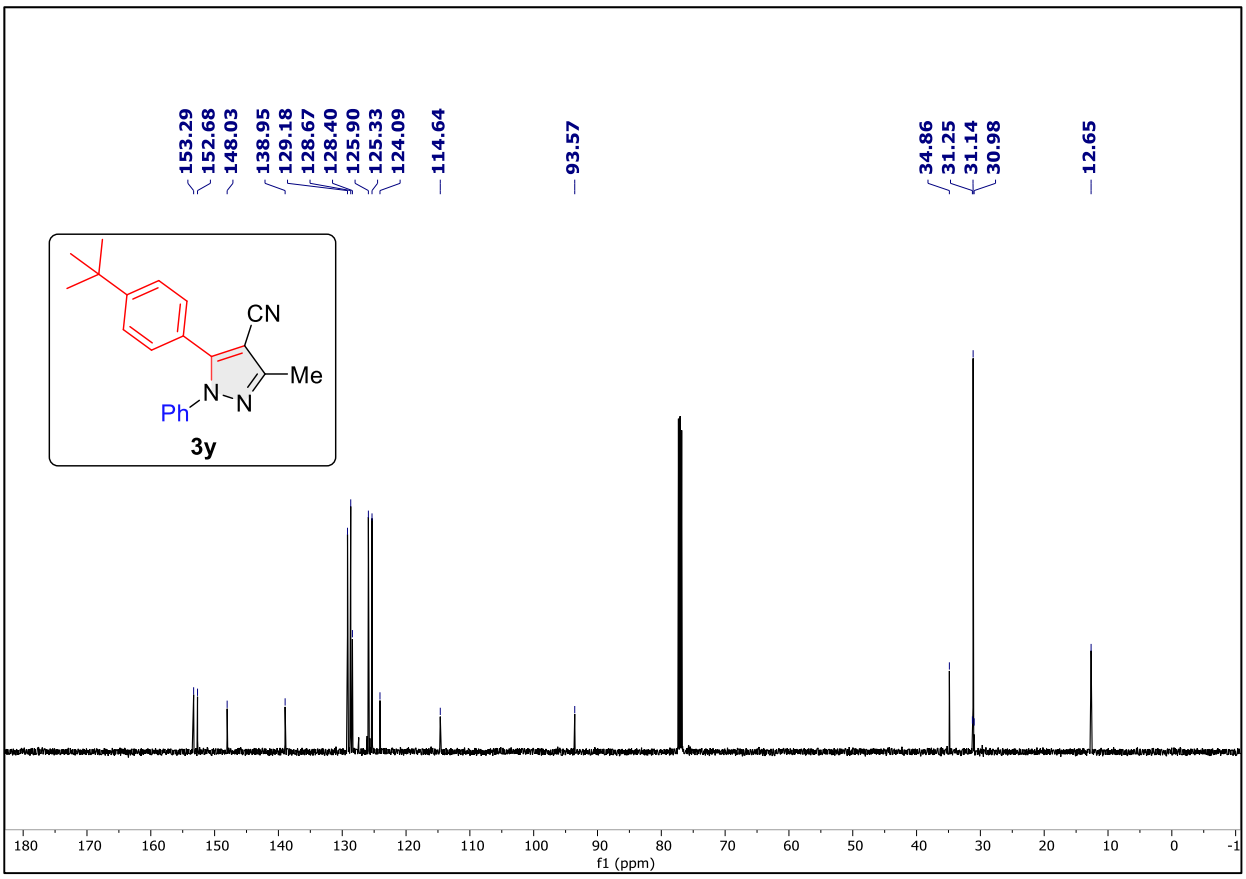
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3x**



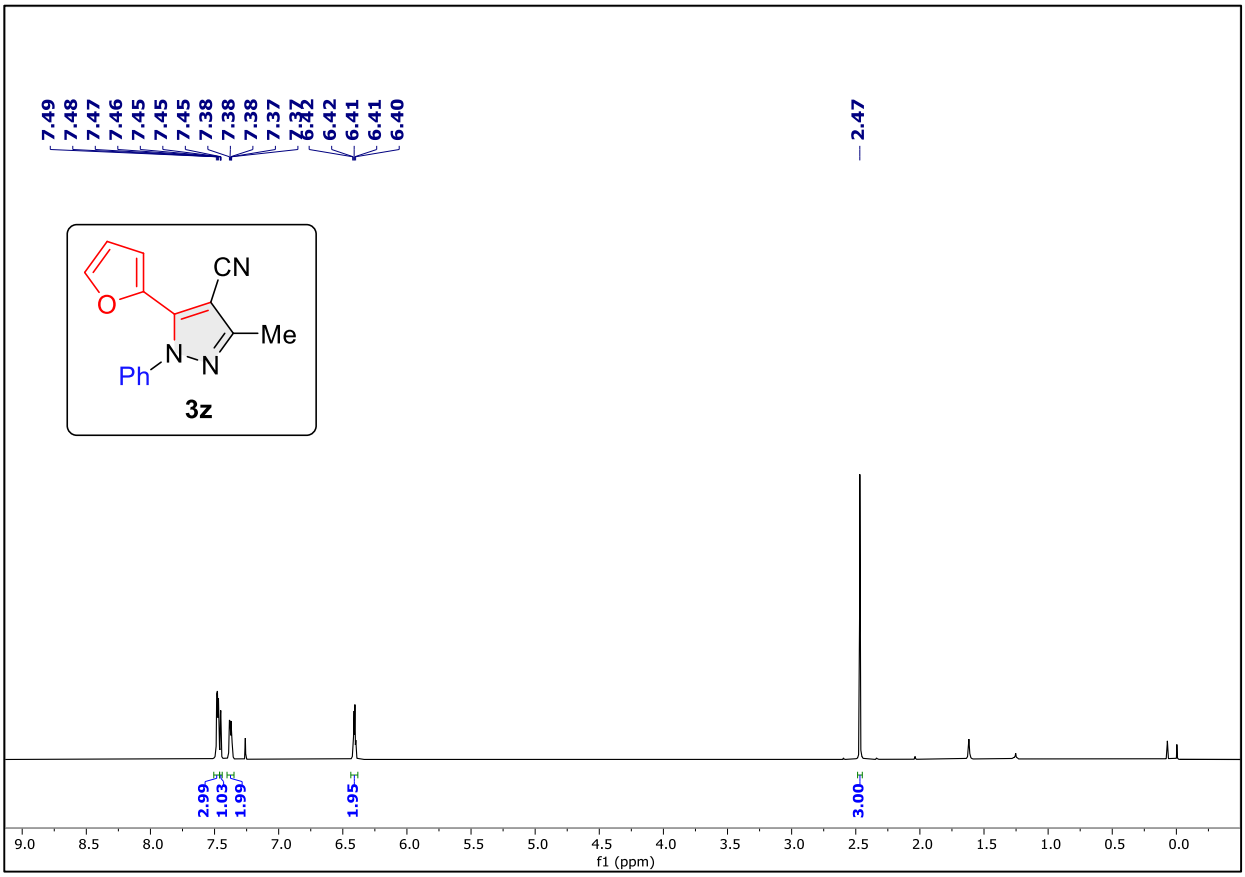
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y**



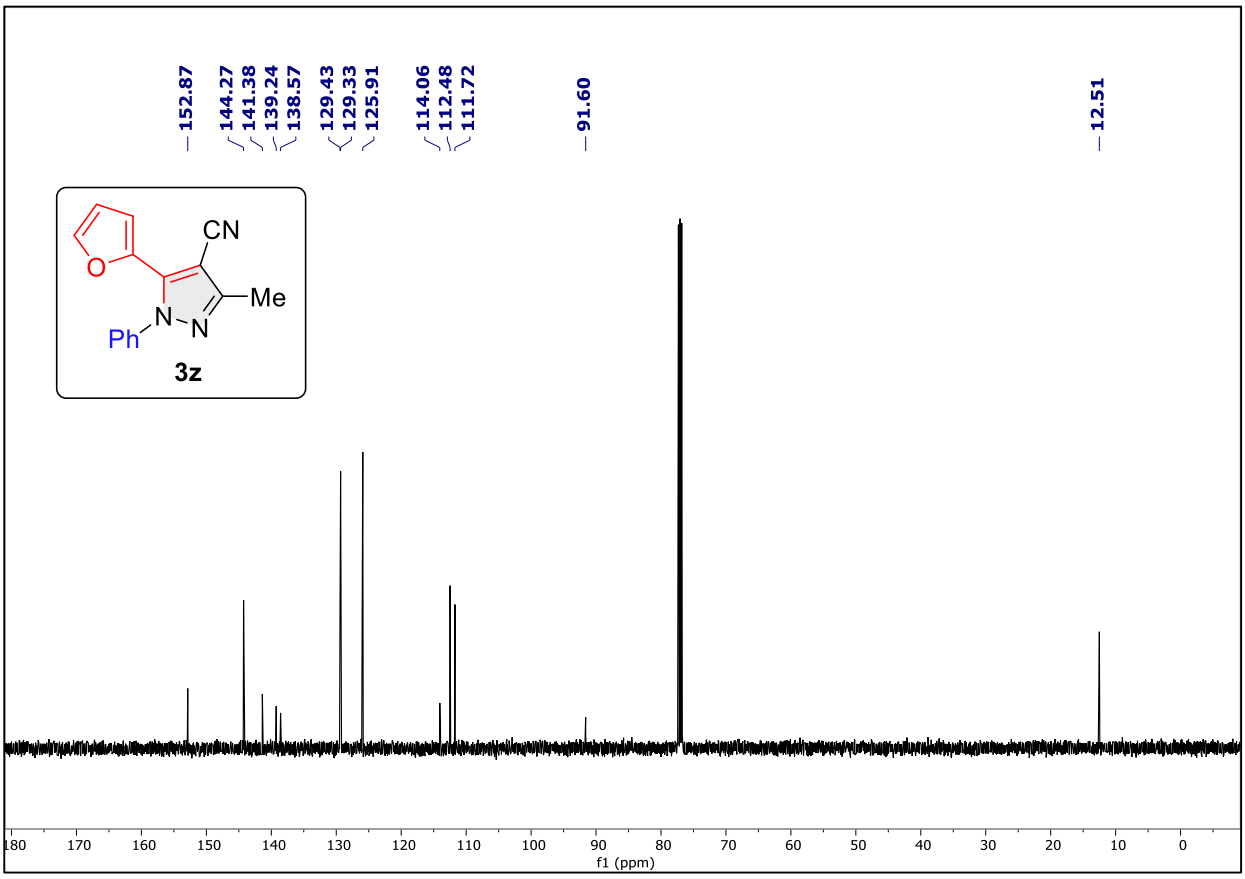
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3y**



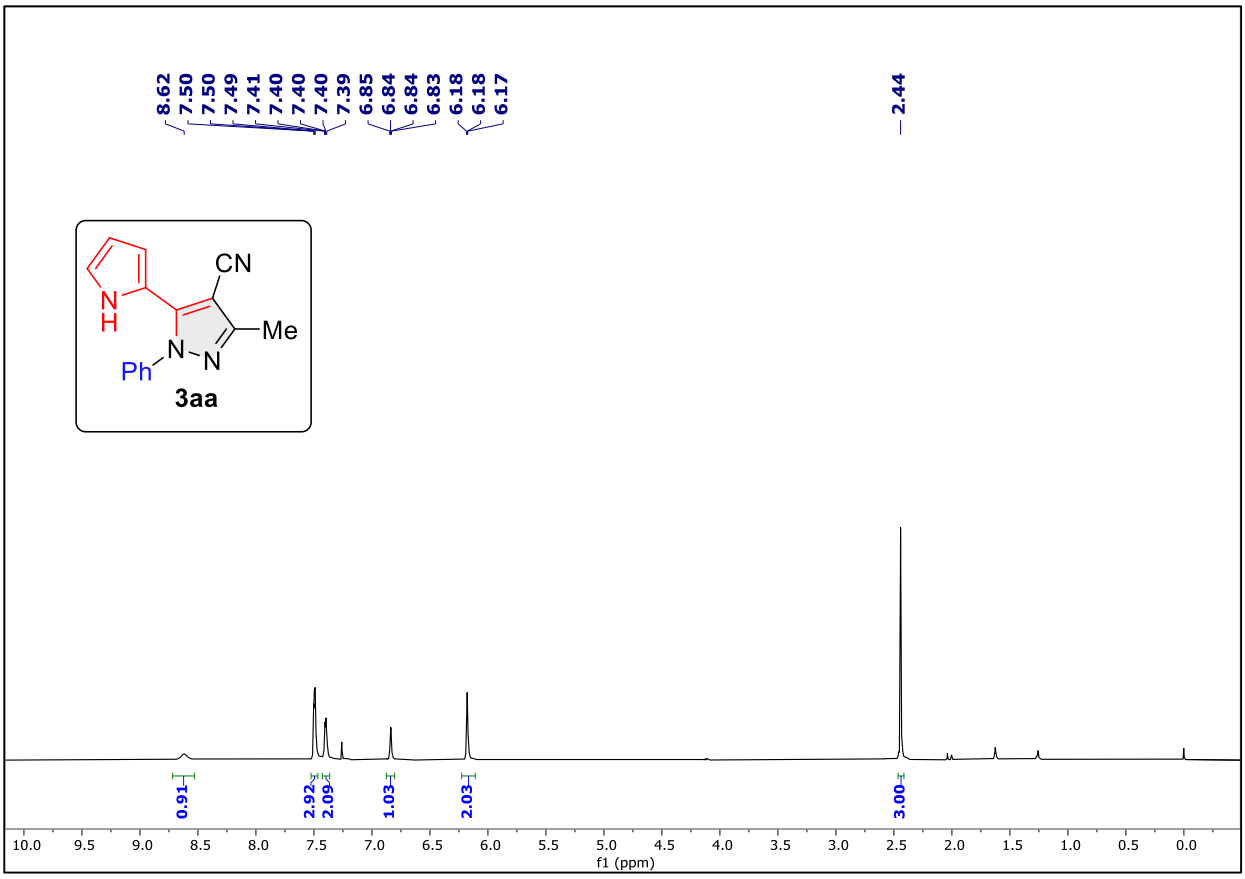
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3z**



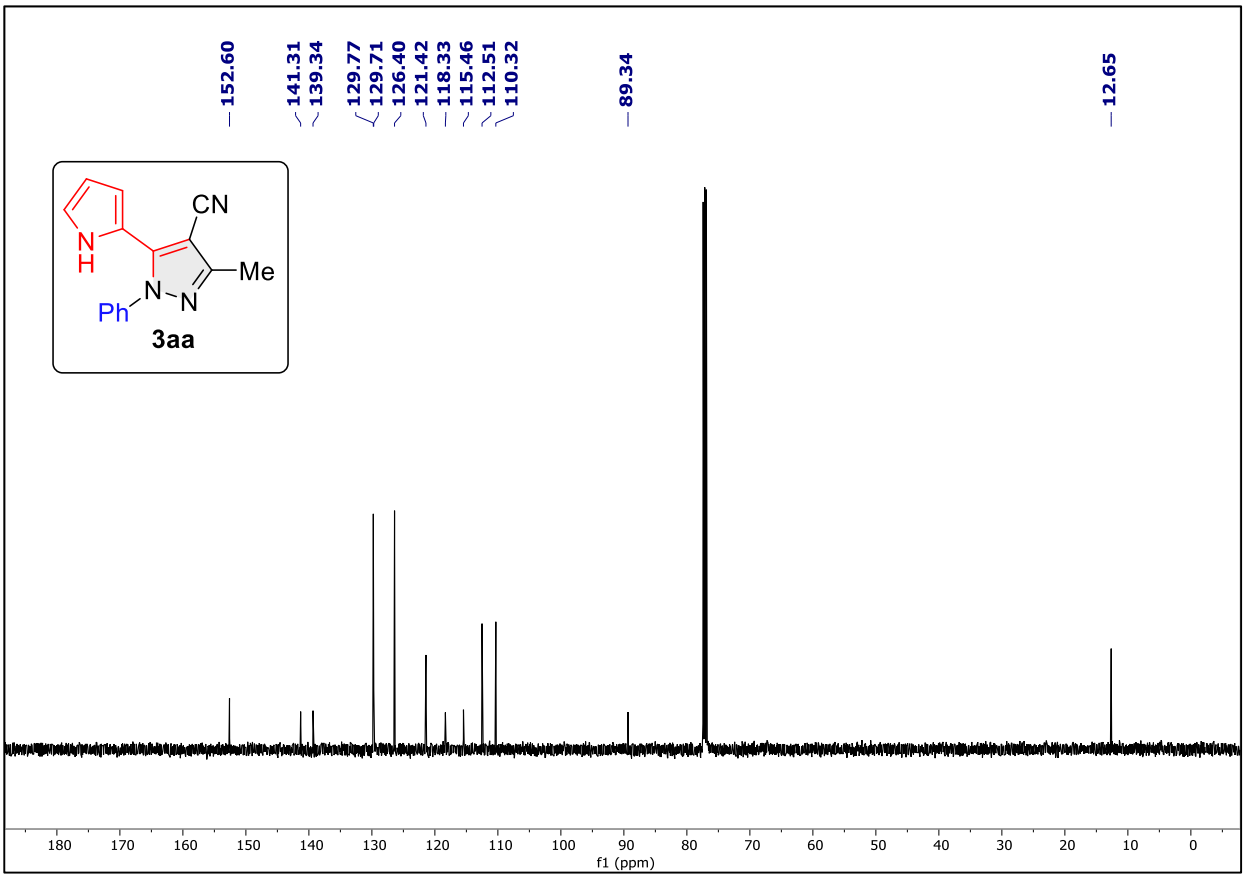
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3z**



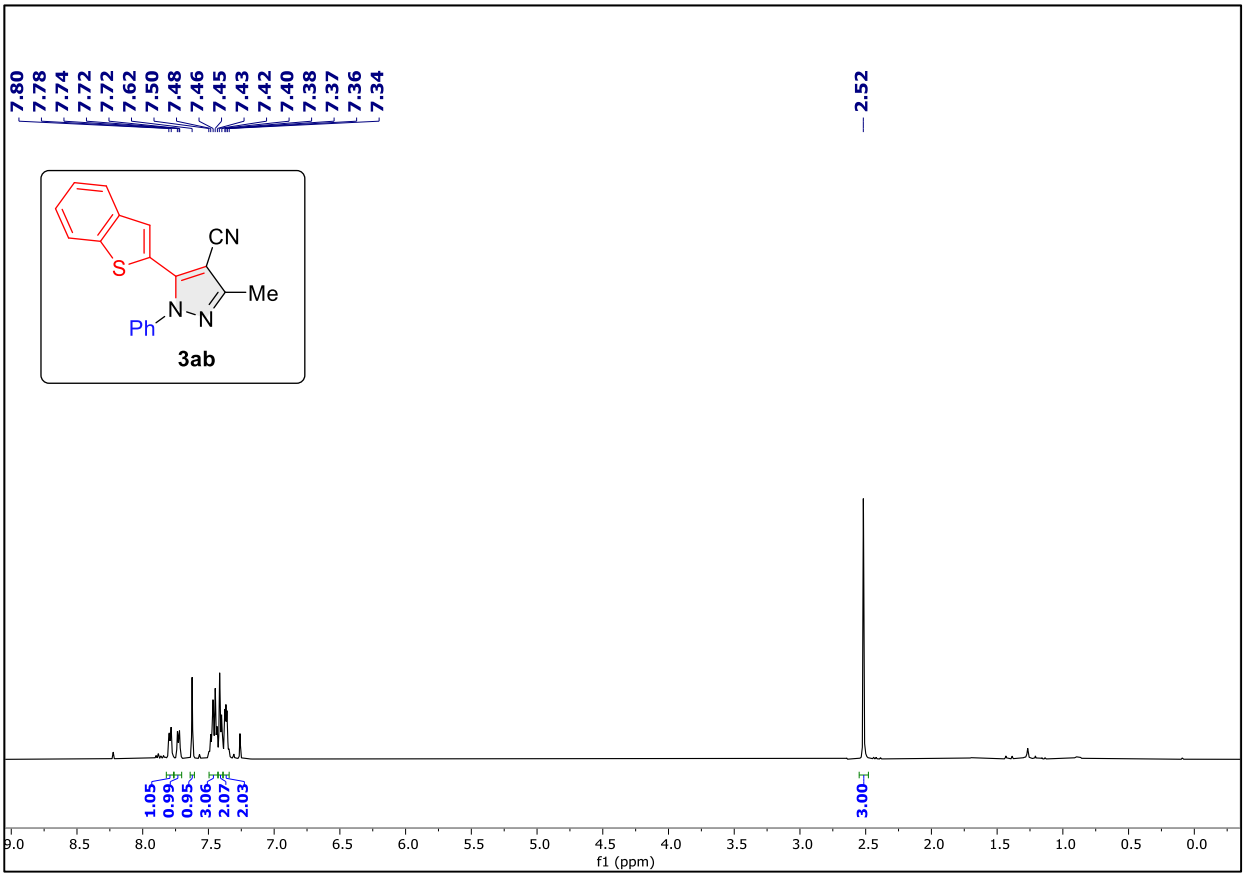
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aa**



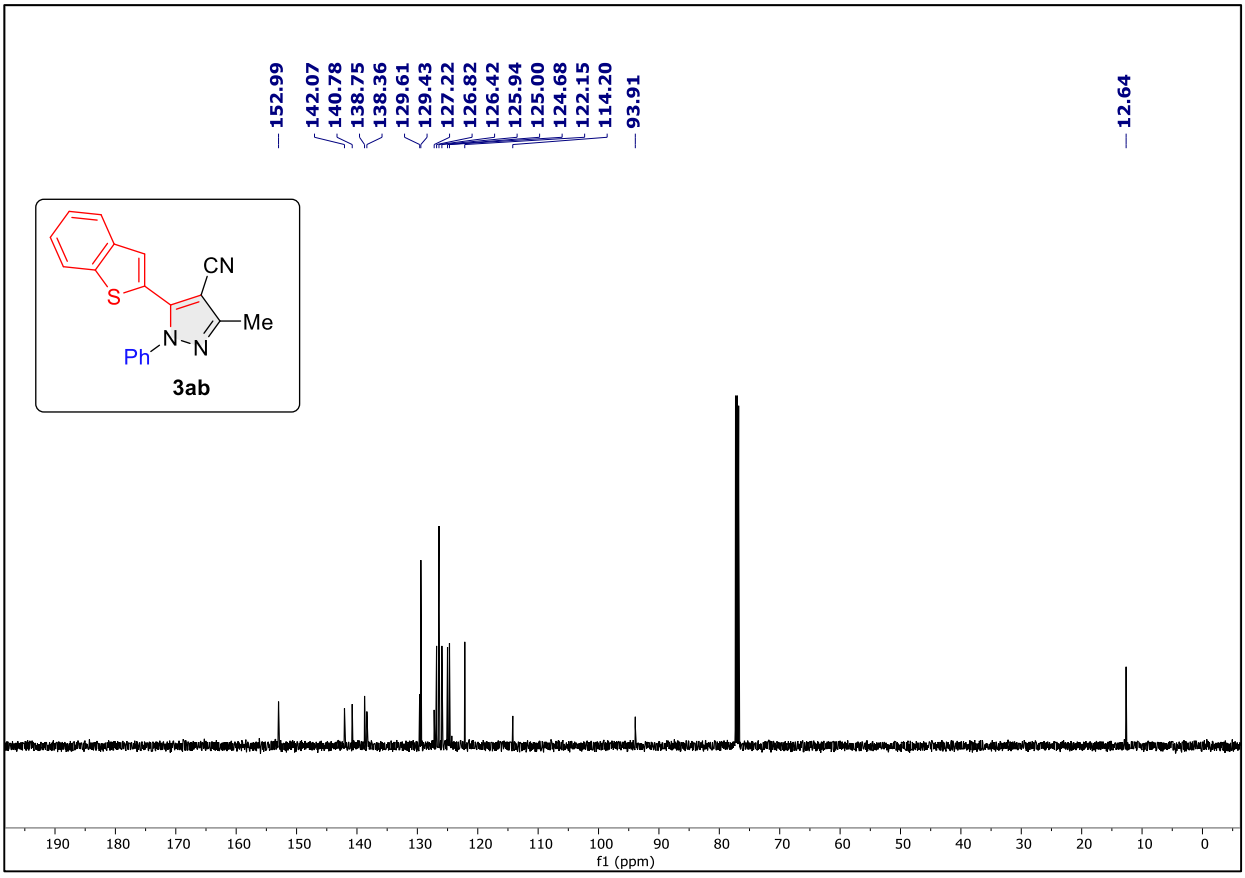
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3aa**



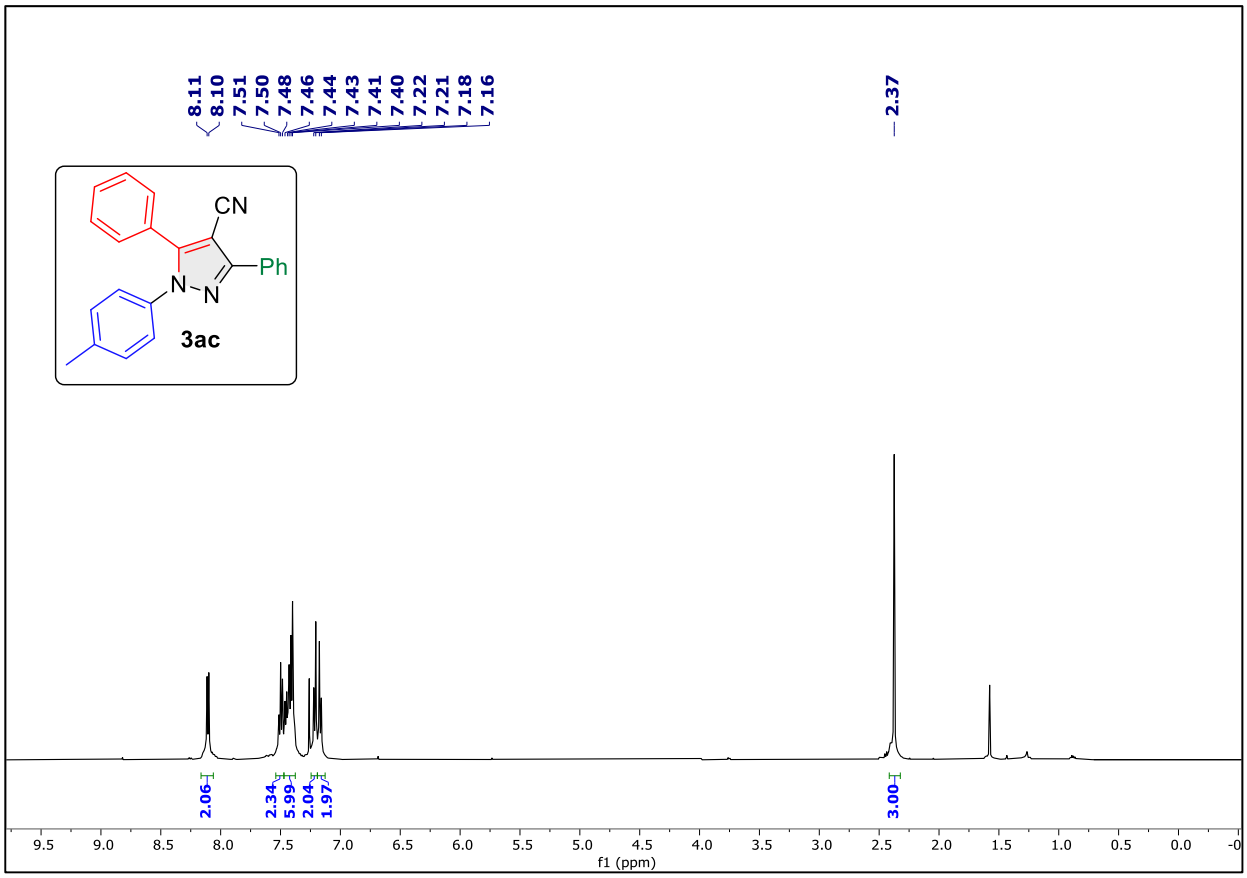
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ab**



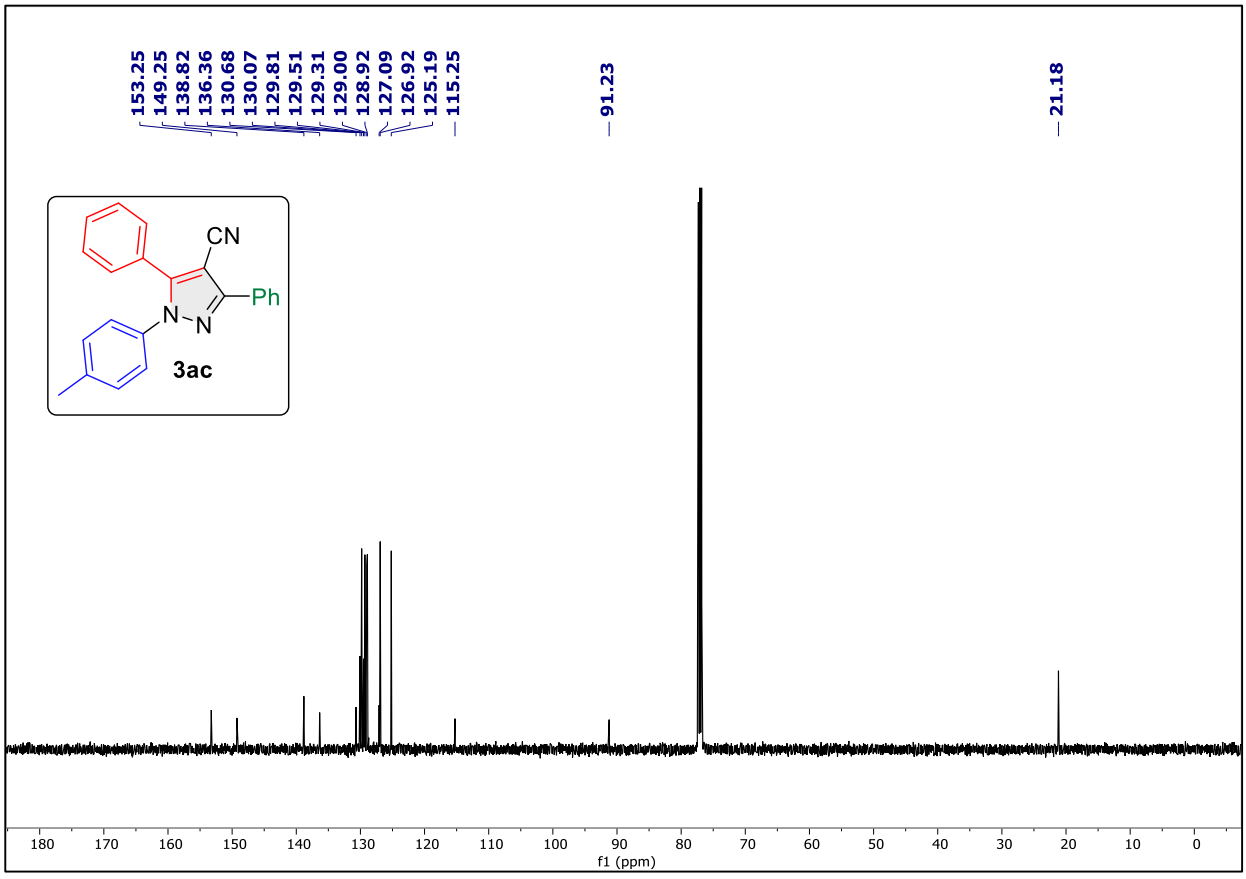
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ab**



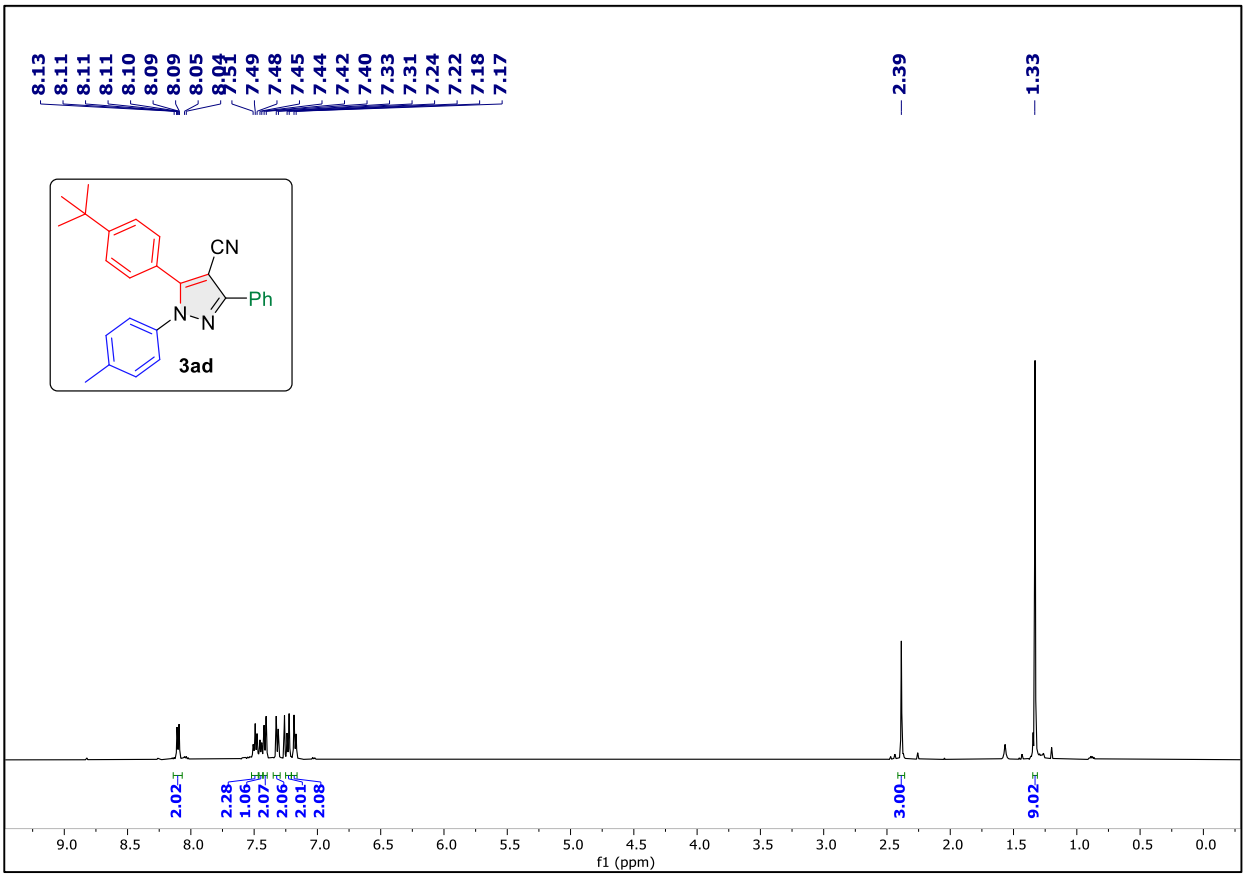
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ac**



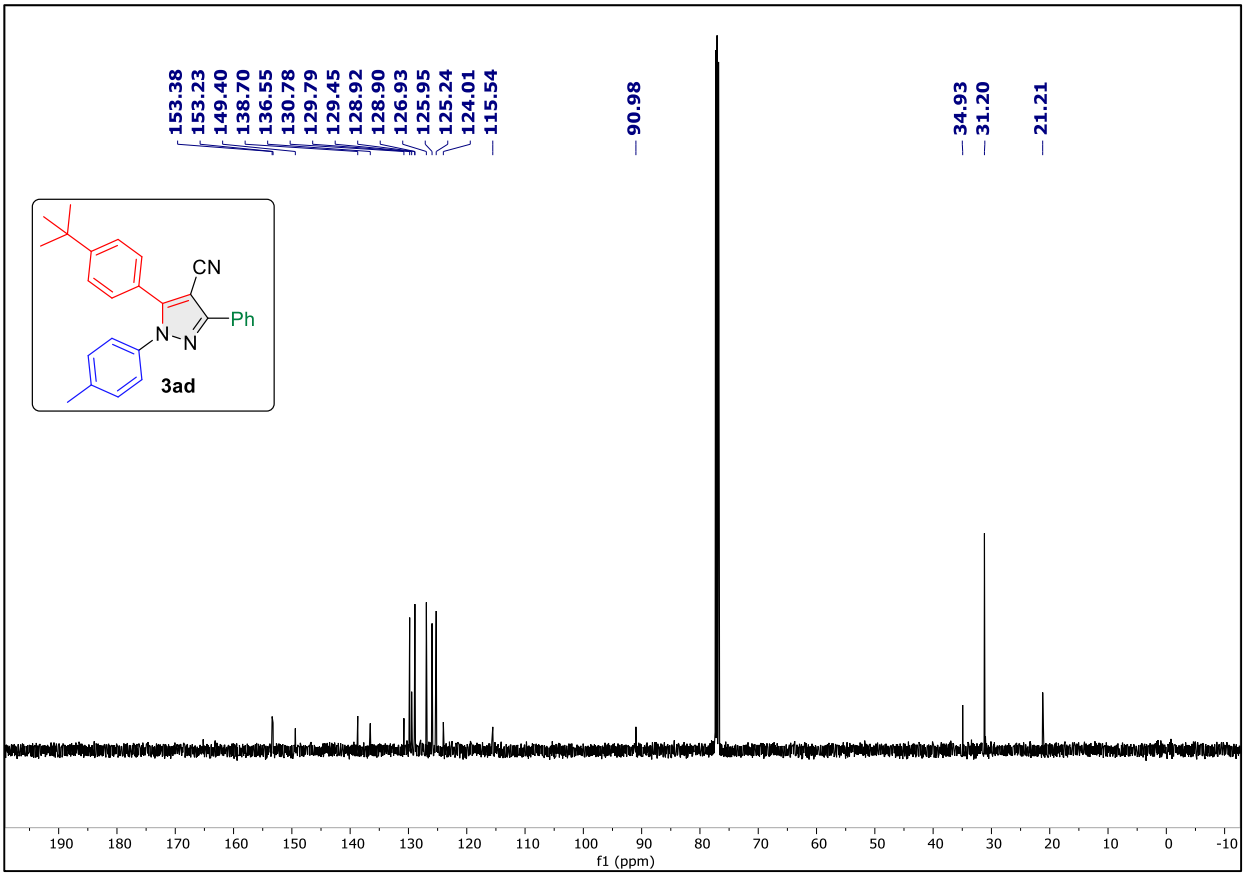
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ac**



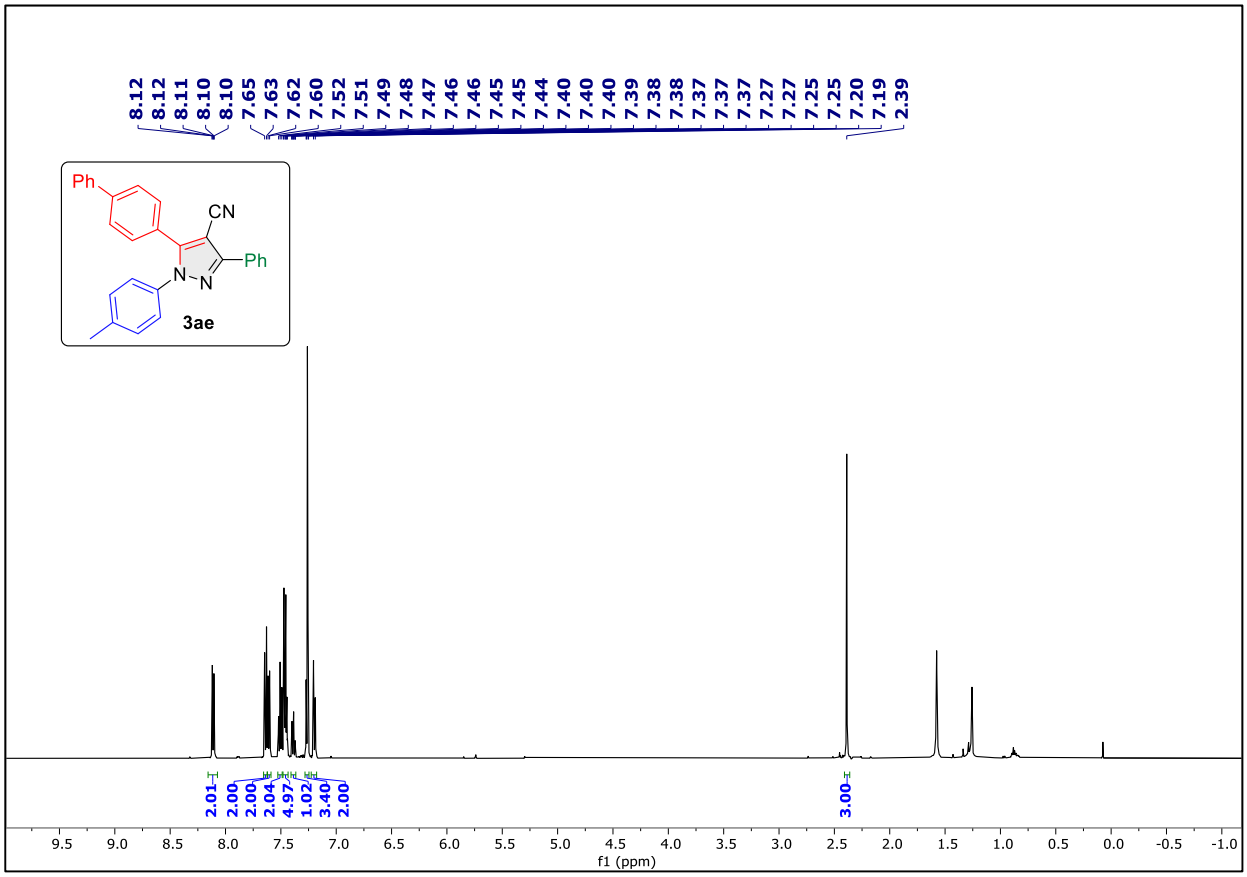
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ad**



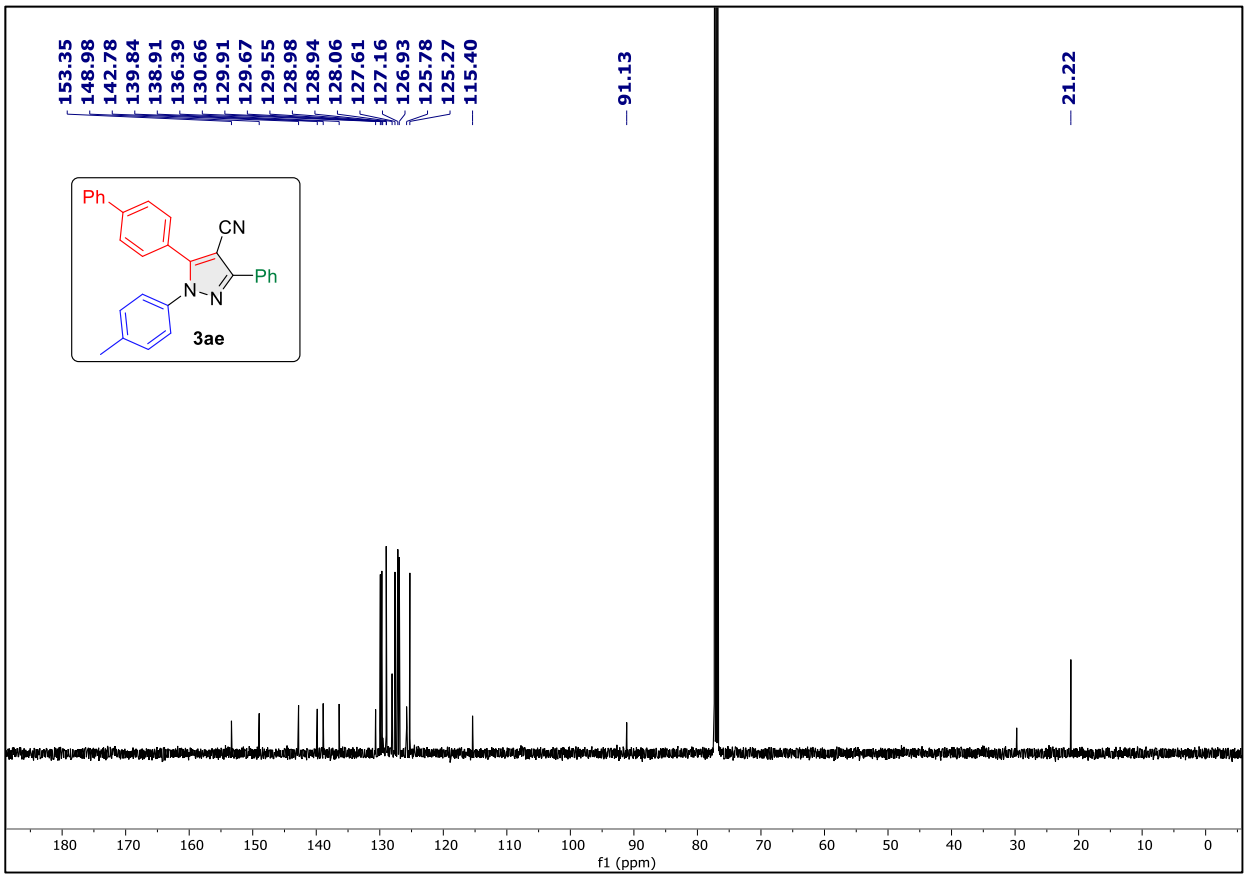
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ad**



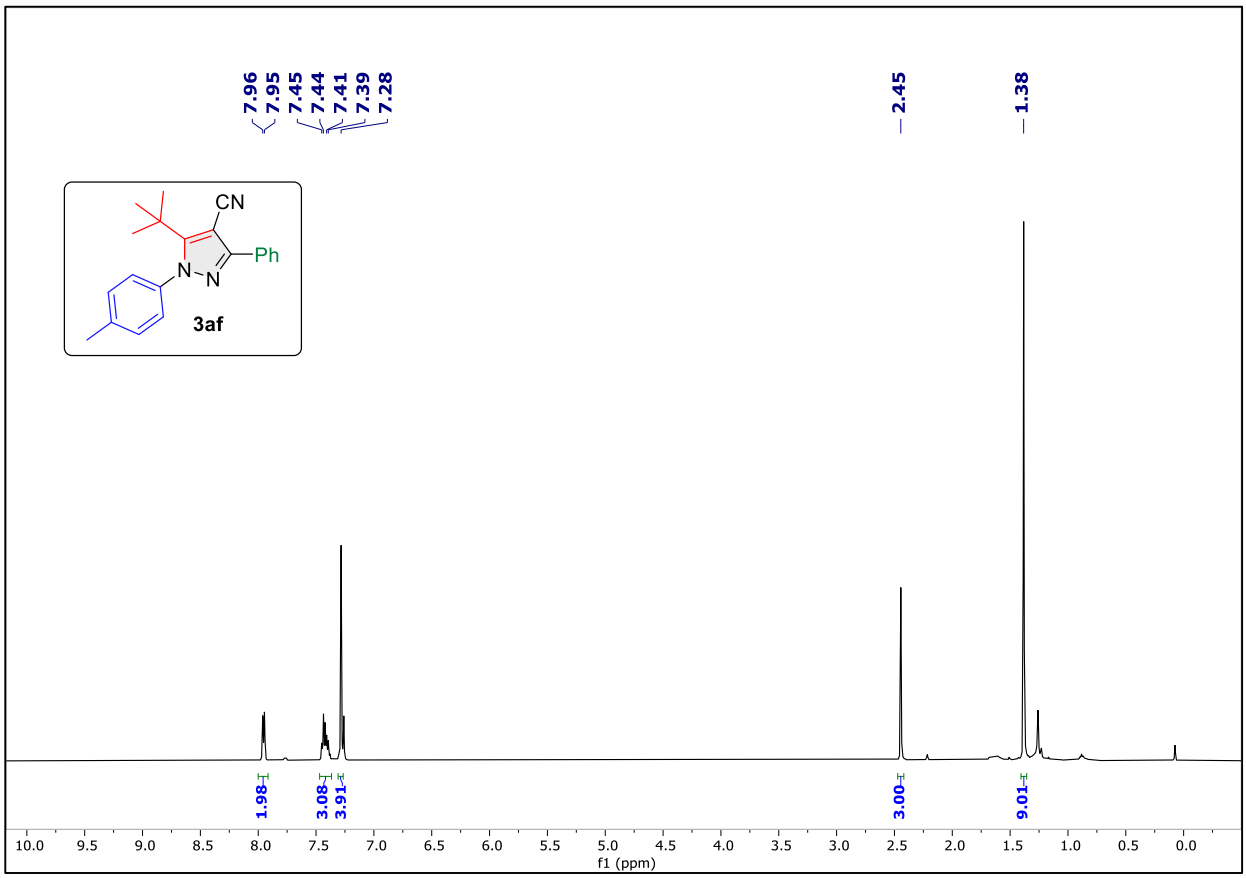
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ae**



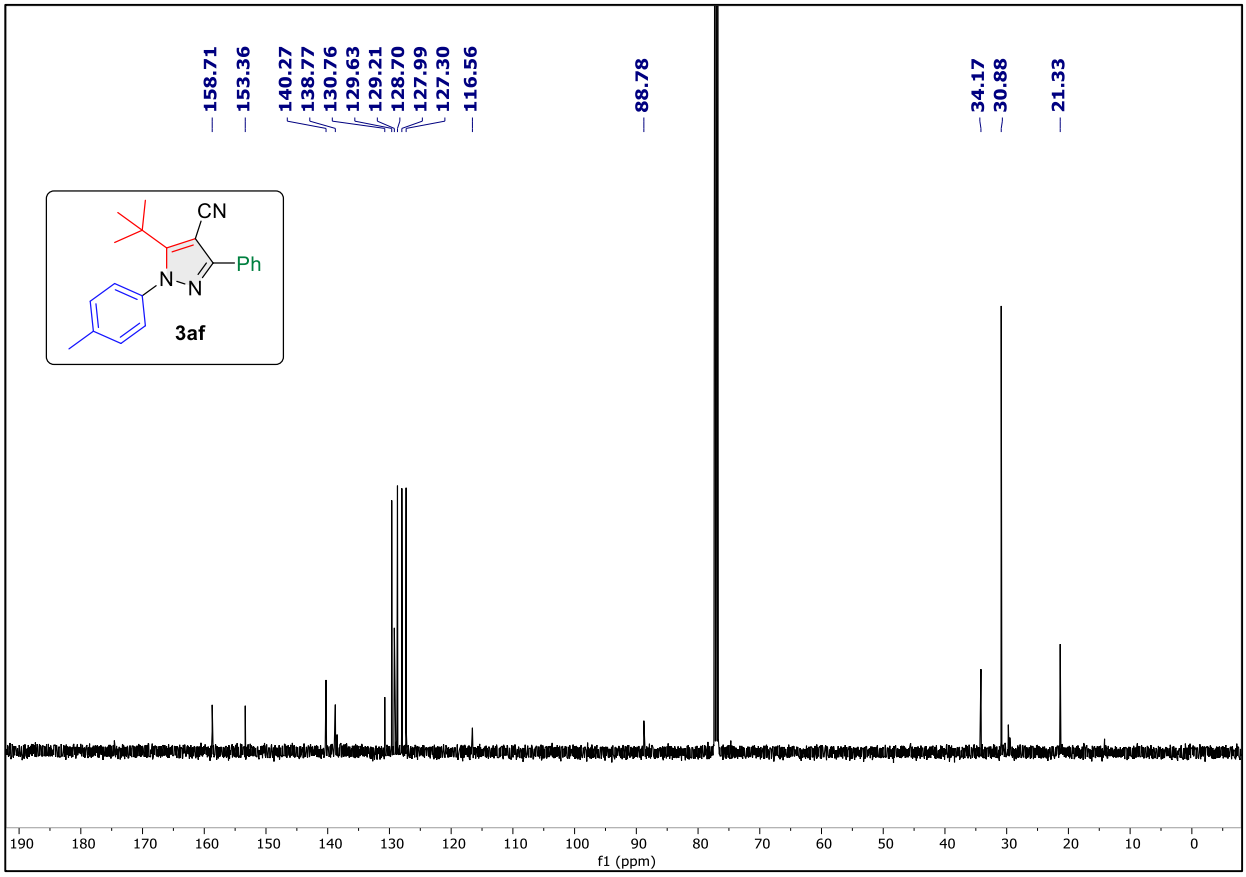
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ae**



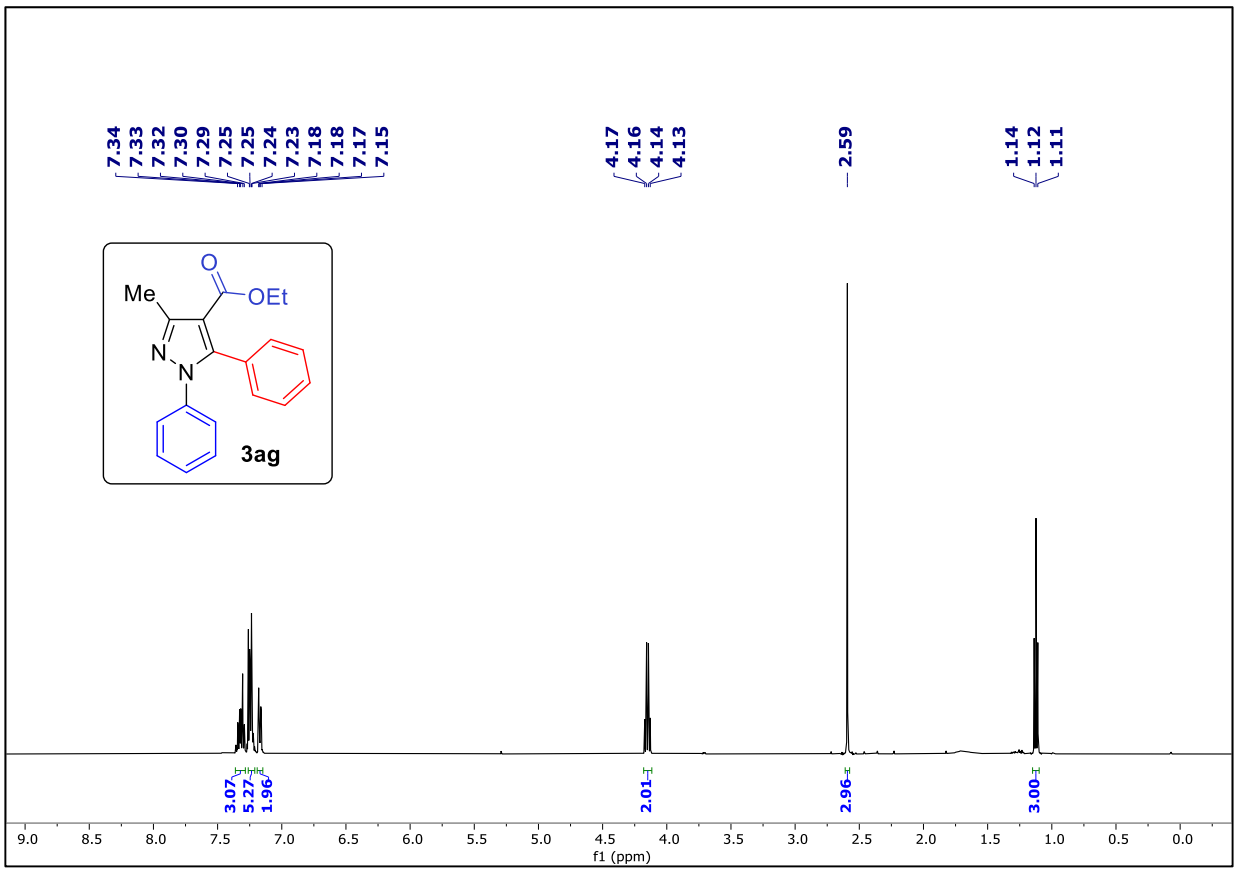
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3af**



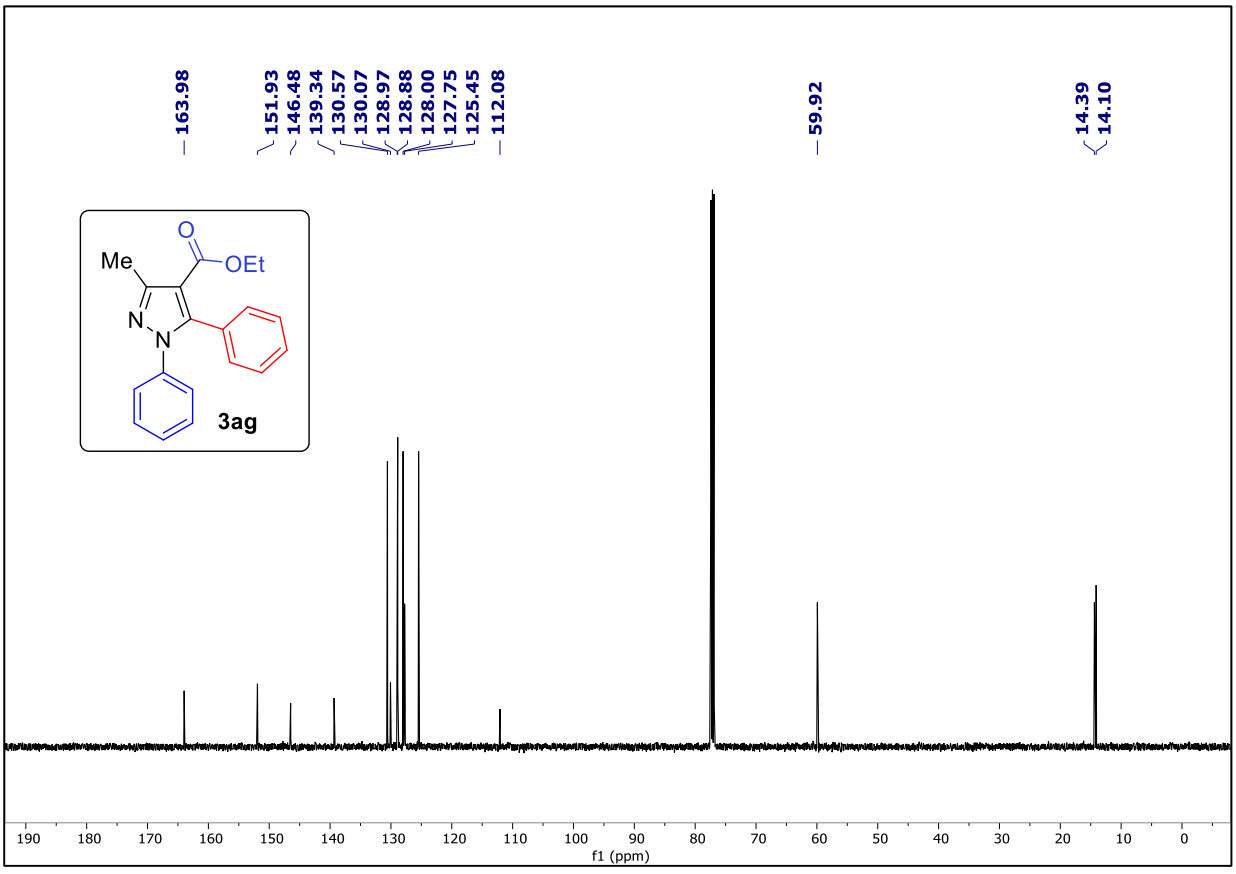
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3af**



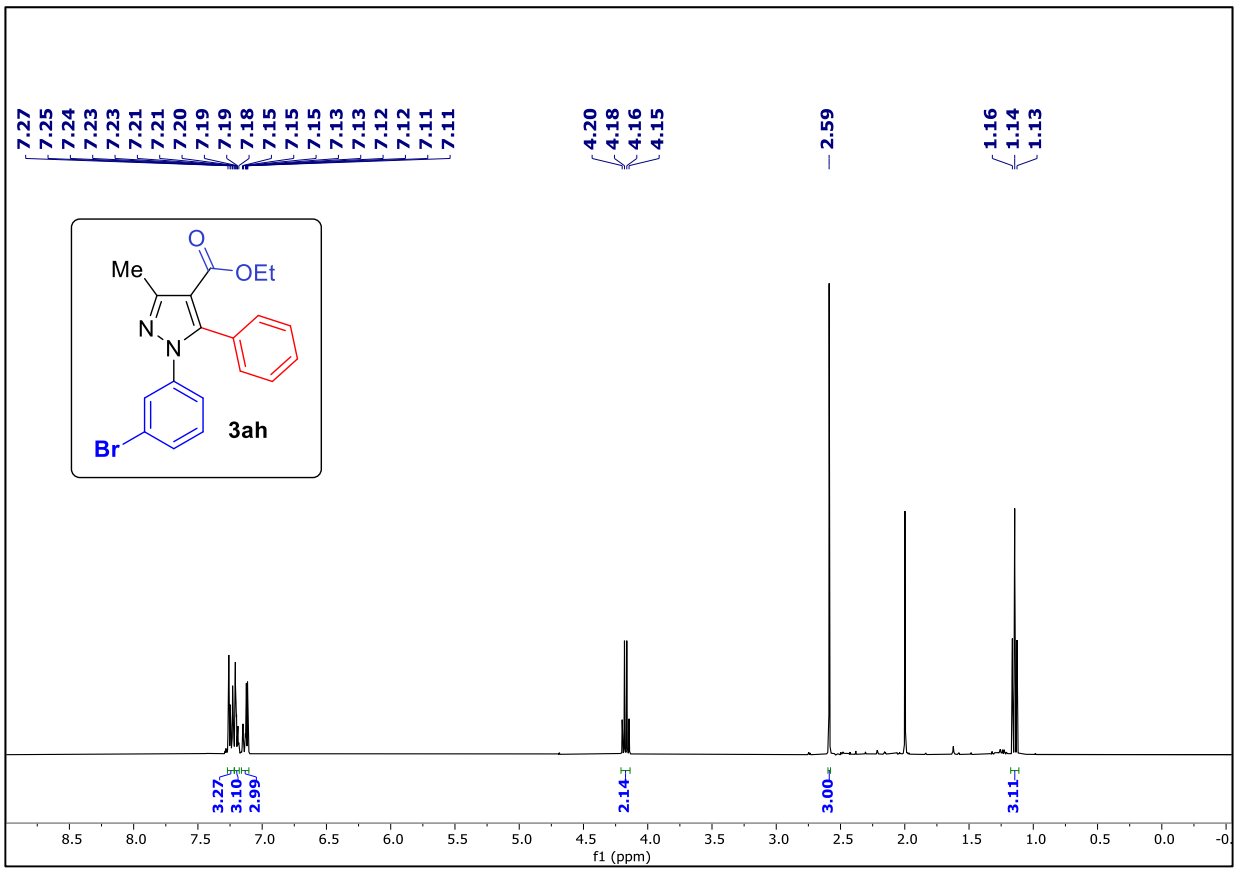
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ag**



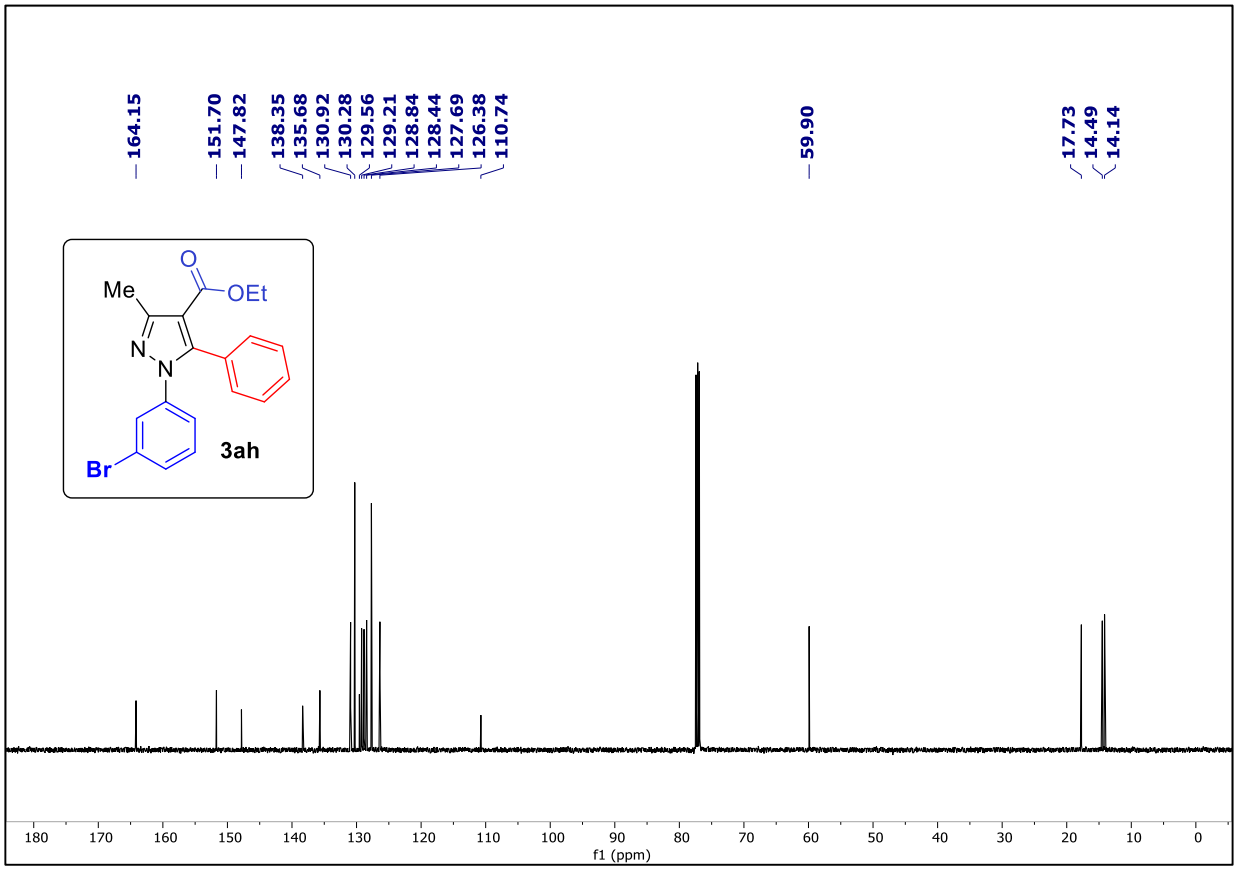
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ag**



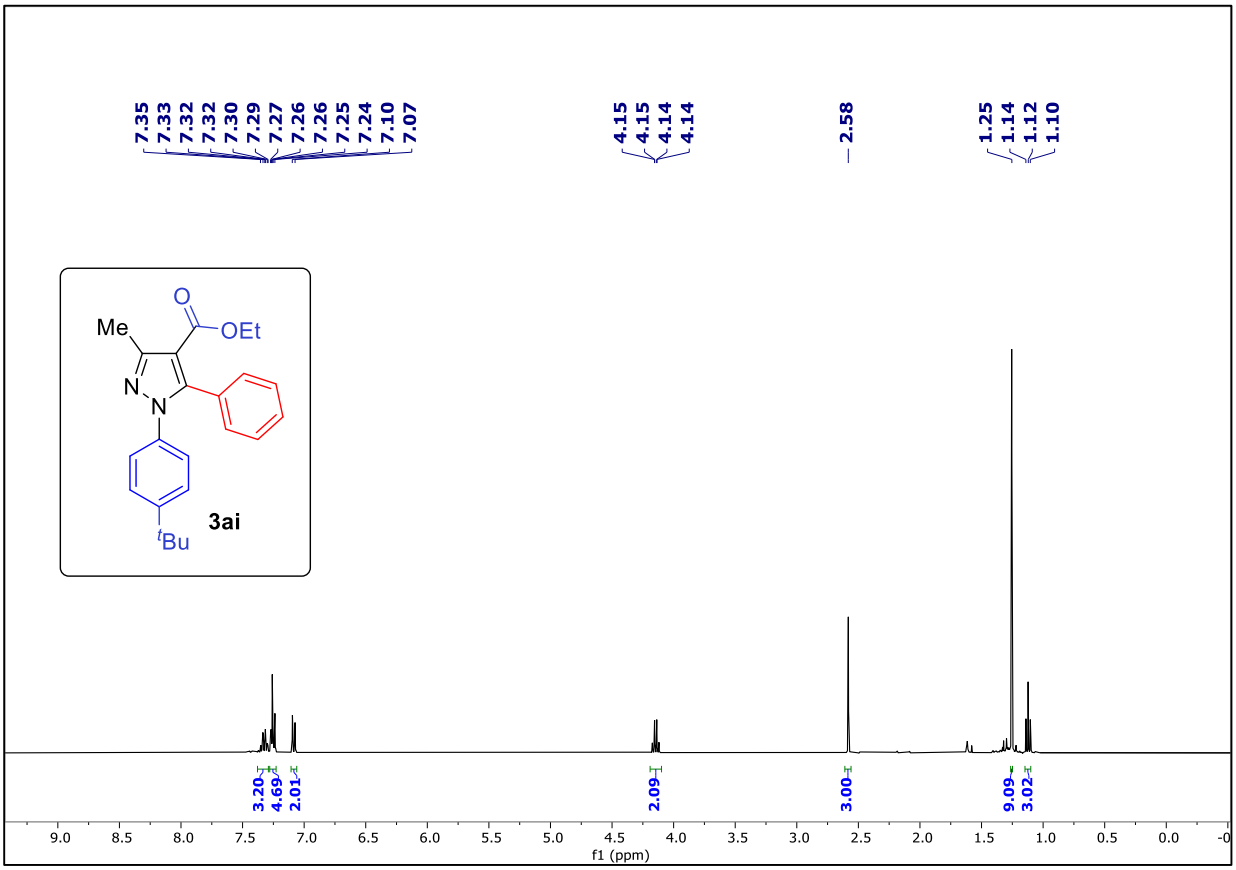
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ah**



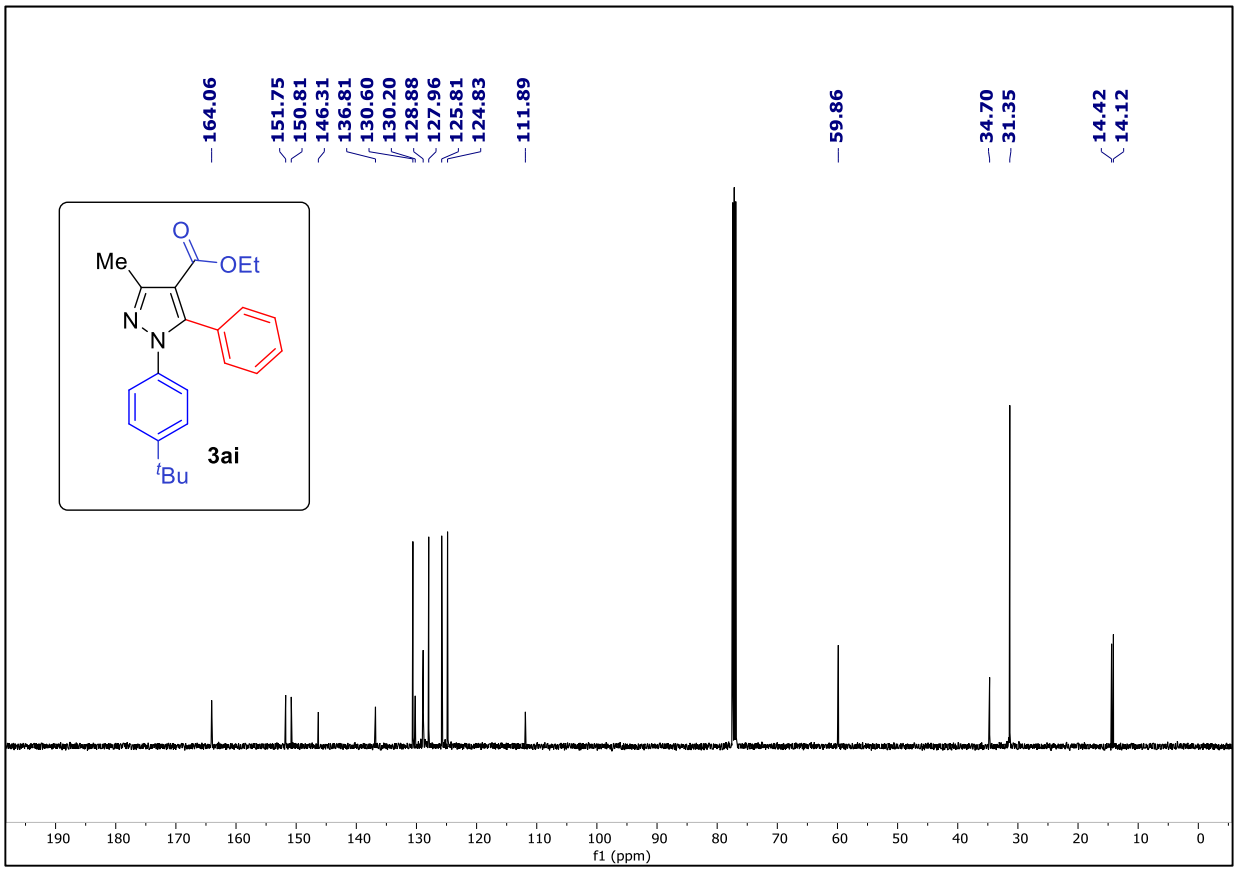
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ah**



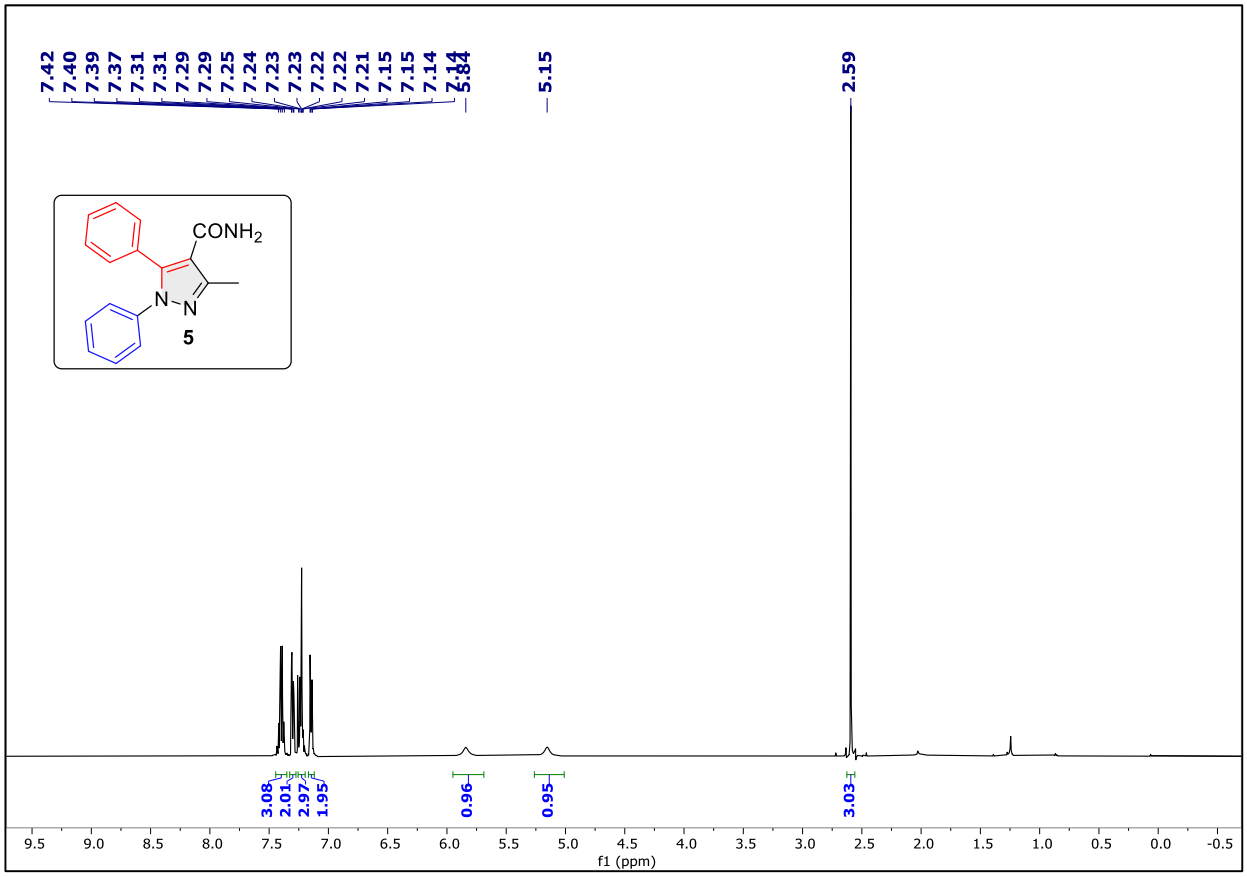
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ai**



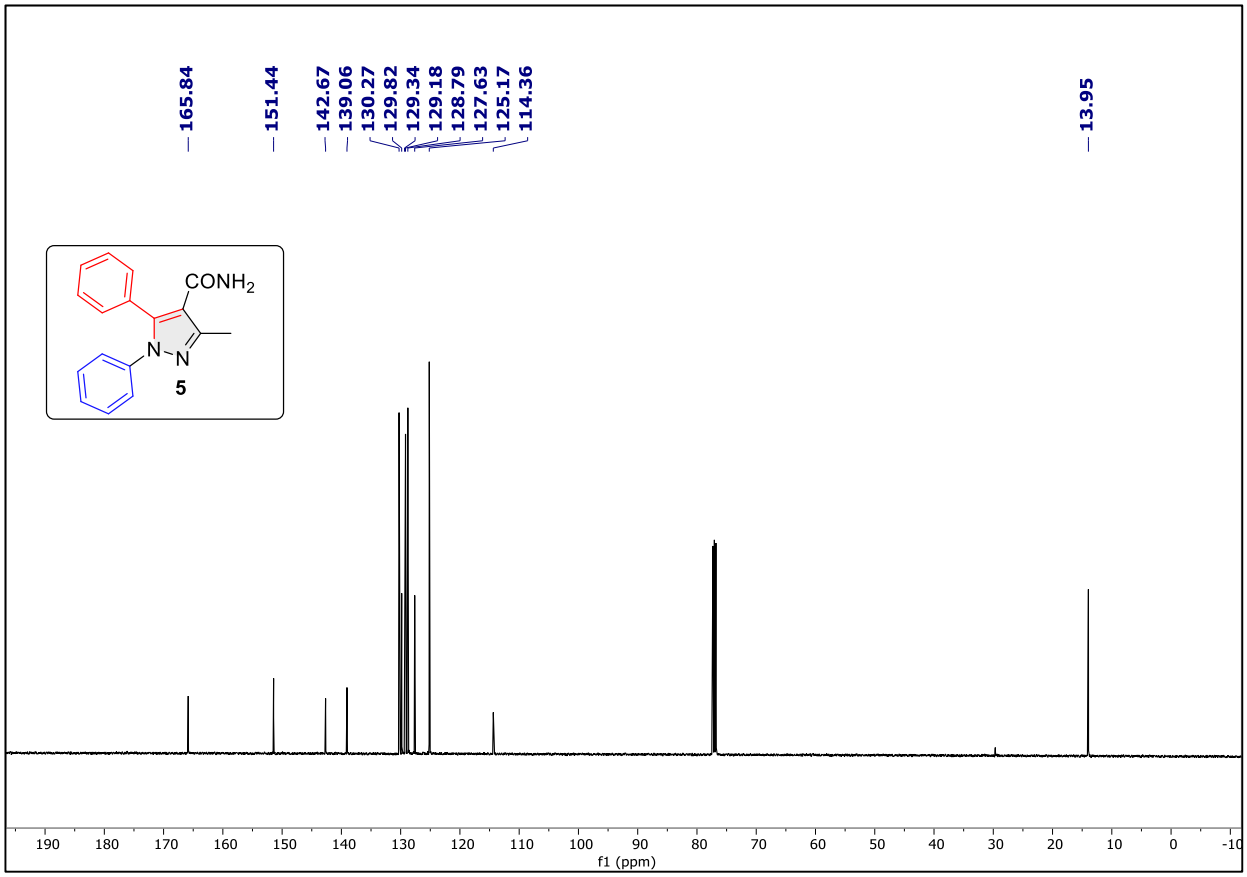
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ai**



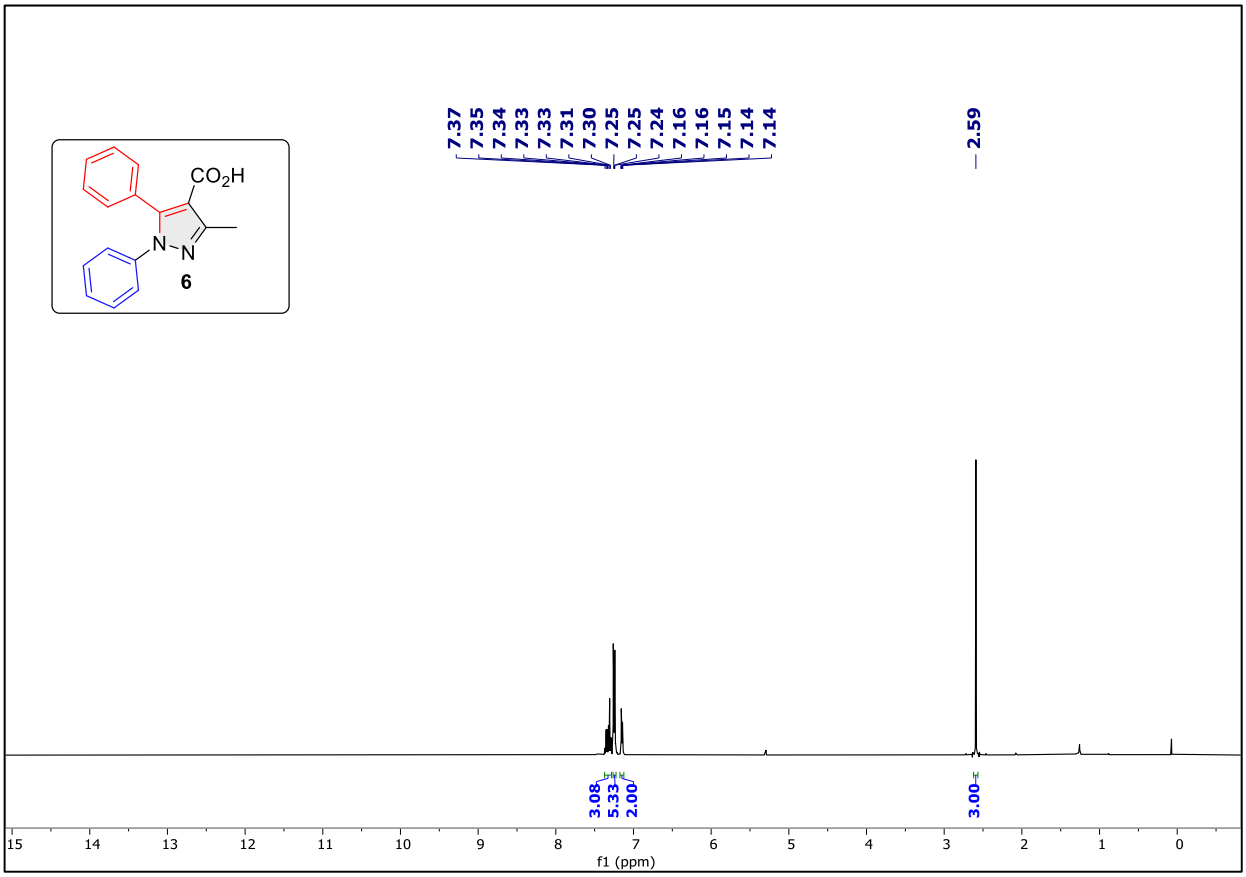
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**



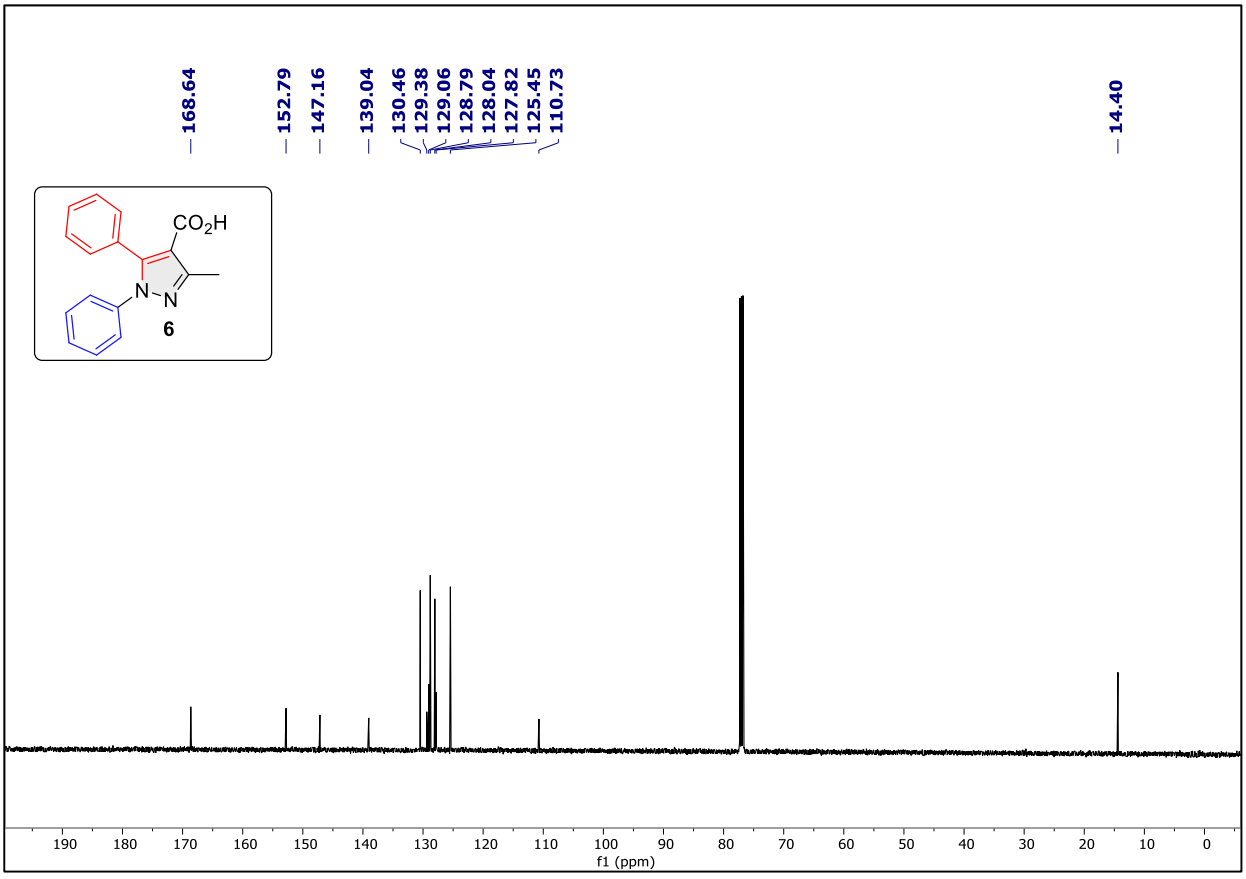
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5**



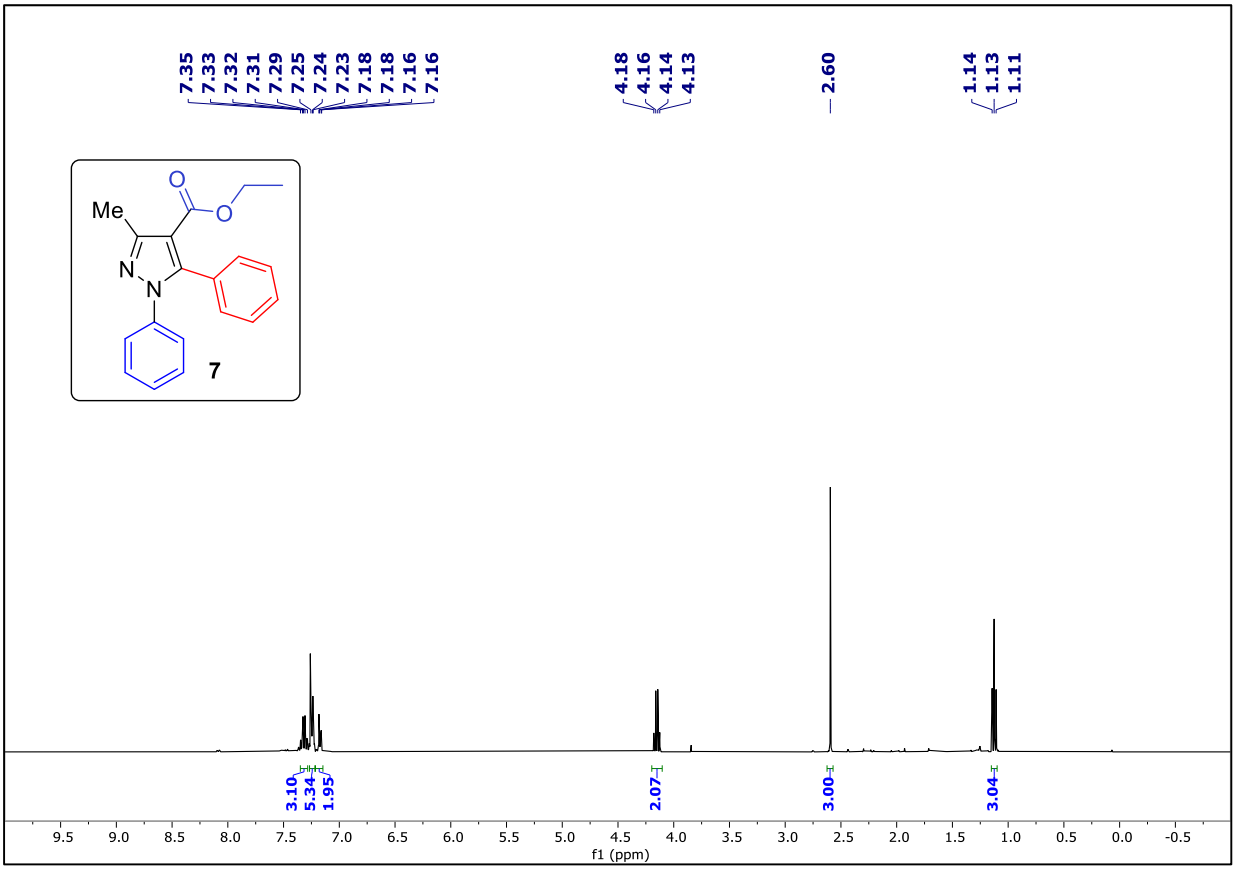
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **6**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**



^{13}CNMR (126 MHz, $CDCl_3$) of compound **7**