Supporting Information

Photoredox-Catalyzed Arylative and Aryl Sulfonylative Radical Cascades Involving Diaryliodonium Reagents: Synthesis of Functionalized Pyrazolones

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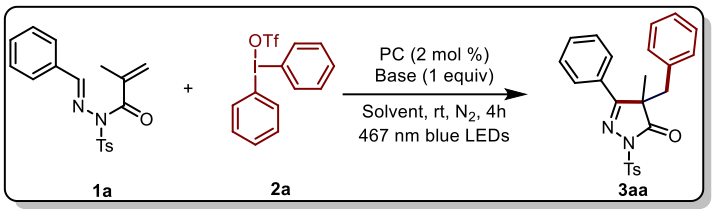
1. Optimization Table

1.1 Table-S1: Optimization Table for Arylative Cyclization

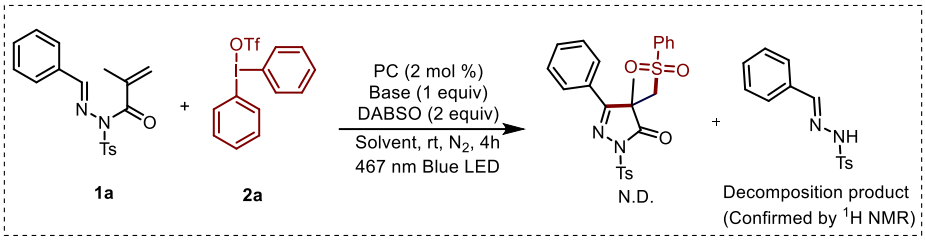


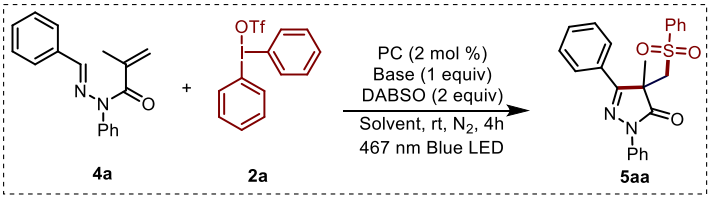
S. No.	Photocatalyst (PC)	Base	Solvent	Yield (%)[b]
1	$[Ir(dtbbpy)(ppy)_2]PF_6$ (1 mol%)	K_3PO_4	CH_3CN	56
2	Acridine Yellow G	K_3PO_4	CH_3CN	50
3	Rose Bengal	K_3PO_4	CH_3CN	21
4	Acridine Orange hemi	K_3PO_4	CH_3CN	34
5	Eosin Y	K_3PO_4	CH_3CN	19
6	4CzIPN	K_3PO_4	CH_3CN	39
7	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$**	**K_3PO_4**	**CH_3CN**	**74**
8	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	2,6-Lutidine	CH_3CN	23
9	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	Pyridine	CH_3CN	15
10	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	dtbpy	CH_3CN	21
11	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	DABCO	CH_3CN	20
12	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	DBU	CH_3CN	17
13	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	Et_3N	CH_3CN	31
14	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_2CO_3	CH_3CN	71
15	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	$KHCO_3$	CH_3CN	50
16	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	KNO_3	CH_3CN	45
17	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_2HPO_4	CH_3CN	51
18	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	$NaHCO_3$	CH_3CN	52
19	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	Na_2CO_3	CH_3CN	55
20	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	$NaH_2PO_2.H_2O$	CH_3CN	62
21	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	$NaHSO_3$	CH_3CN	51
22	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	KOH	CH_3CN	60
23	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	CsOH	CH_3CN	15
24	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	LiOH	CH_3CN	45

25	$Ru(bpy)_3Cl_2·6H_2O$	KIO_4	CH_3CN	57
26	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	Acetone	45
27	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	DCM	40
28	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	EtOAc	57
29	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	DMSO	N.D.
30	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	DCE	19
31	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	MeOH	16
32	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	THF	28
33	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	$CH_3CN:H_2O$	50
34[c]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	68
35[d]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	58
36[e]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	74
37[f]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	65
38[g]	---	K_3PO_4	CH_3CN	29
39[h]	$Ru(bpy)_3Cl_2·6H_2O$	---	CH_3CN	32
40[i]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	50
41[j]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	76
42[k]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	55
43[l]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	75
44[m]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	N.D.
45[n]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	45
46[0]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	58
47[p]	$Ru(bpy)_3Cl_2·6H_2O$	K_3PO_4	CH_3CN	65

[a]Reaction Conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2 equiv), photocatalyst (2 mol%), base (0.1 mmol, 2 equiv), solvent (1 ml) under N_2 atmosphere for 4 h at 467 nm blue LEDs. [b]isolated yield, [c]using 1.5 equiv DAIR **2a**, [d]using 0.5 equiv base, [e]using 1.5 equiv base, [f]using 1 mol% catalyst, [g]in the absence of photocatalyst, [h]in the absence of base, [i]reaction was stirred for 3 h, [j]photocatalyst (5 mol%), [k]under air, [l]using 2.5 equiv **2a**, [m]In the absence of light, [n]using 427 nm blue LEDs, [o]using 440 nm blue LEDs, [p]using 456 nm blue LEDs. N.D. = not detected.

1.2 Table S2: Optimization table for arylsulfonation





Sl.No	Photocatalyst (in mol%)	Base (1 equiv)	Solvent	Yield(%)[b]
1	**$Ru(bpy)_3Cl_2.6H_2O$**	**K_3PO_4**	**CH_3CN**	**79**
2	Eosin-Y	K_3PO_4	CH_3CN	63
3	Fluorescence	K_3PO_4	CH_3CN	40
4	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_2CO_3	CH_3CN	61
5	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	$NaH_2PO_2.H_2O$	CH_3CN	49
6	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	DIPEA	CH_3CN	35
7	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	Et_3N	CH_3CN	30
8	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_3PO_4	DCM	31
9	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_3PO_4	MeOH	65
10	$Ru(bpy)_3Cl_2.6H_2O$	---	CH_3CN	67
11	---	K_3PO_4	CH_3CN	56
12[c]	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_3PO_4	CH_3CN	72
13[d]	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_3PO_4	CH_3CN	30
14[e]	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_3PO_4	CH_3CN	N.D.
15[f]	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	K_3PO_4	CH_3CN	68

[a]Reaction Conditions: **4a** (0.1 mmol), **2a** (0.2 mmol, 2 equiv), DABSO (0.2 mmol, 2 equiv), photocatalyst (2 mol%), base (1 equiv), solvent (1 mL), 467 nm blue LEDs under N_2 atmosphere for 4 h. [b]isolated yield, [c]1.5 equiv of DABSO, [d]under air, [e]in the absence of light, [f]using 456 nm blue LEDs. N.D. = not detected.

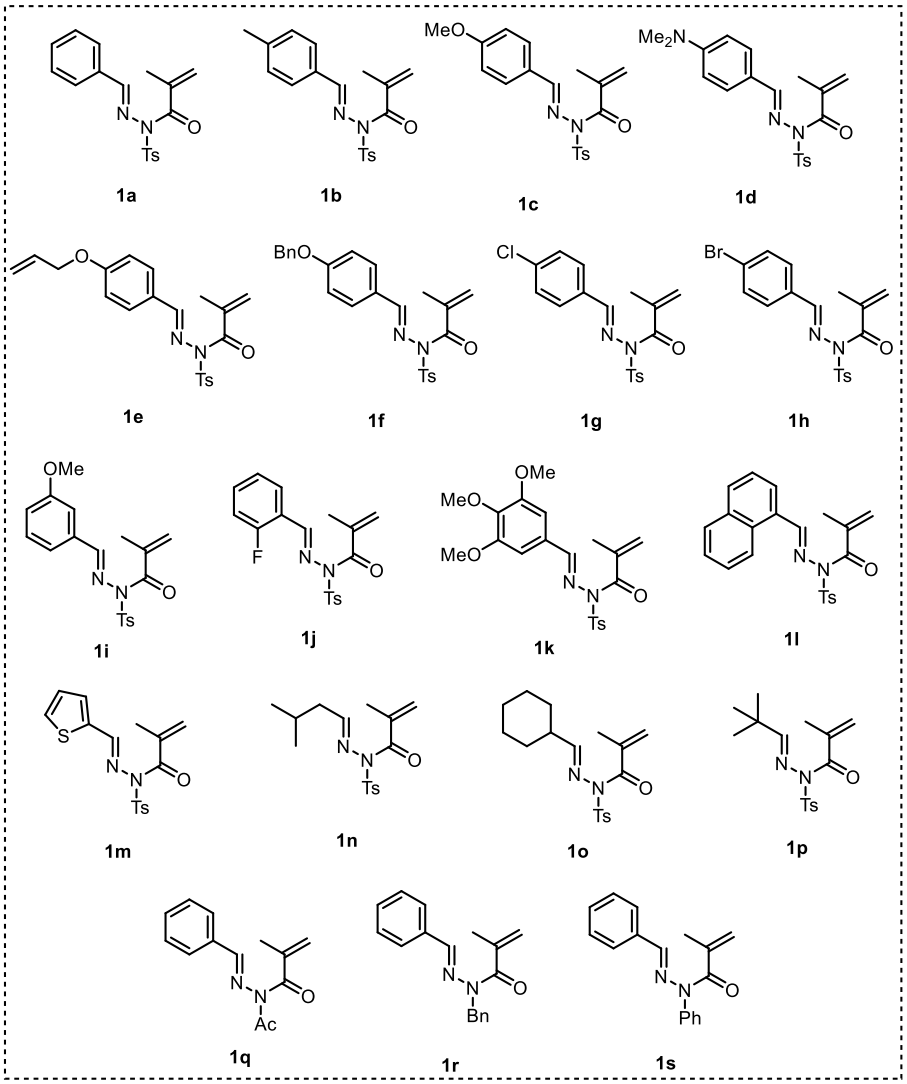
2. Experimental Section

2.1 General Information

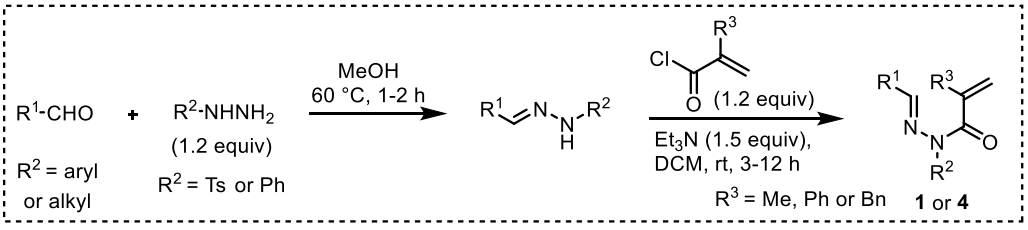
Photoredox reactions were performed under N_2 atmosphere for all the reaction sets using pre-dried glassware and standard Schlenk tubes. All the solvents were obtained from Merck (Emparta grade), dried with calcium hydride, and freshly distilled under nitrogen. The following starting materials and the reaction components such as arenes, substituted iodoarenes, *m*-CPBA, TfOH, Hydrazine, aldehyde derivatives, $Ru(bpy)_3Cl_2{\cdot}6H_2O$, K_3PO_4, triethyl amine, methacryloyl chloride, TEMPO, and ethene-1,1-diyldibenzene were obtained from commercial sources and used without further purification. Required starting materials were synthesized by the procedures mentioned below. Yields refer to isolated compounds, estimated to be >95% pure determined via ^1H NMR and ^{13}C NMR. All optimized reactions were conducted under the photo-irradiation using 40W Kessil PR160L (Linear Reflector)- 467 nm lamp (Avg. Intensity in 2×4 cm area = 137 mW/cm^2) with 2 cm from the reaction tube made up of borosilicate glass without any filter. Thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 aluminium sheets with detection under UV light at 254 nm. Chromatographic separations were carried out on Avra silica gel (100-200 mesh or 230−40 mesh. (NMR) spectroscopy was performed using Bruker 500 MHz spectrometers. Chemical shifts (δ) are provided in ppm if not otherwise specified. HRMS spectra were recorded using Agilent 6500 Q-TOF spectrometer. UV experiments were performed on LABINDIA ANALYTICAL-2000
U UV/VIS Spectrophotometer instrument.

2.2 Starting Material Preparation

The (*E*)-*N*'-benzylidene-*N*-tosylmethacrylohydrazide **1** were prepared following literature procedure and obtained characterizations data were in alignment with the literature reported data.[1]



General procedure (GP1) for the synthesis of (*E*)-*N*'-benzylidene-*N*-pheny/tosyl methacrylohydrazide derivatives (1 or 4)

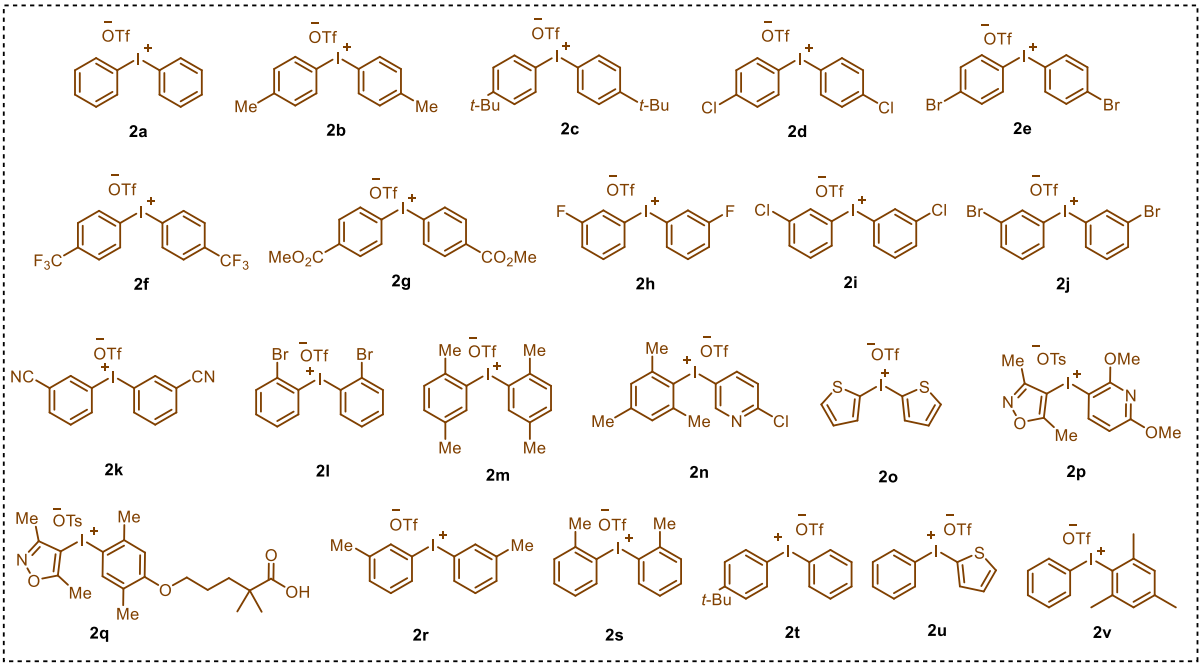


Step 1: A solution of phenyl/tosyl hydrazine (1 equiv) in methanol (0.1 M) was heated to 60 °C using an oil bath until completely dissolved. Then, respective aldehydes (1 equiv) were

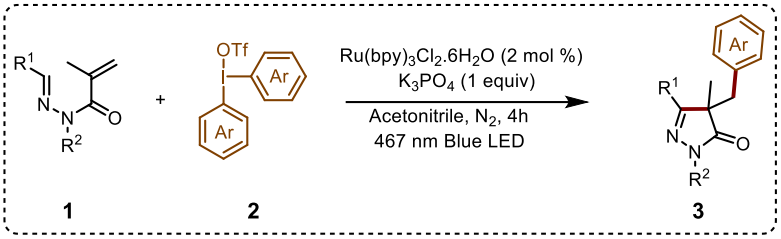
slowly added to the mixture and heating was continued for another 1-2 h. Afterward, the precipitate crude product was washed with petroleum ether and dried *in vacuo* to afford corresponding *N*-phenyl substituted hydrazones, which were directly used in the next step without further purification. Next, crude mixture of *N*-substituted hydrazones (1 equiv) in DCM, and triethyl amine (1.5 equiv) was cooled to 0 °C followed by dropwise addition of methacryloyl chloride (1.2 equiv). The resulting solution was allowed to come to room temperature and stirring was continued for 3-12 h till the completion of the reaction (confirmed by TLC). Afterward, the solvent was evaporated and the crude mixture was purified via silica gel column chromatography using 20% EtOAc in hexane as eluent to afford the corresponding products **1** or **4.**

2.3. General procedure for preparation of diaryliodonium salts (2a-v)

The diaryliodonium salts **(2a, 2b, 2c, 2d, 2e, 2f, 2p,2r, 2s),**[2] **(2g, 2h,),**[3] **(2i, 2j, 2m, 2n, 2o),**[4] **2k,**[5] **2l,**[6] **2q**[7]**, 2v**[8]**, (2t, 2u)**[9] were prepared following previous literature procedures and obtained characterization data were in alignment with the literature reported data.

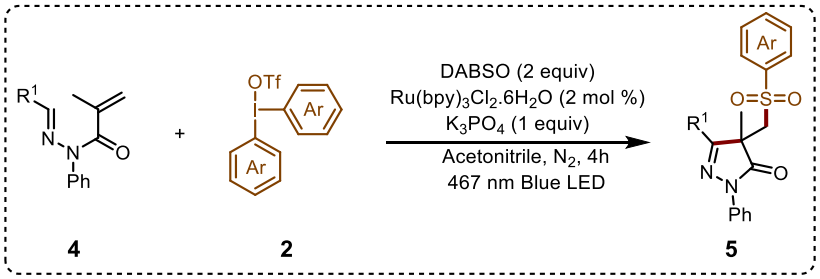


2.4. Representative general procedure (GP2) for the cascade arylation of (*E*)-*N*'-benzylidene-*N*-methacryloyl-hydrazide (3)



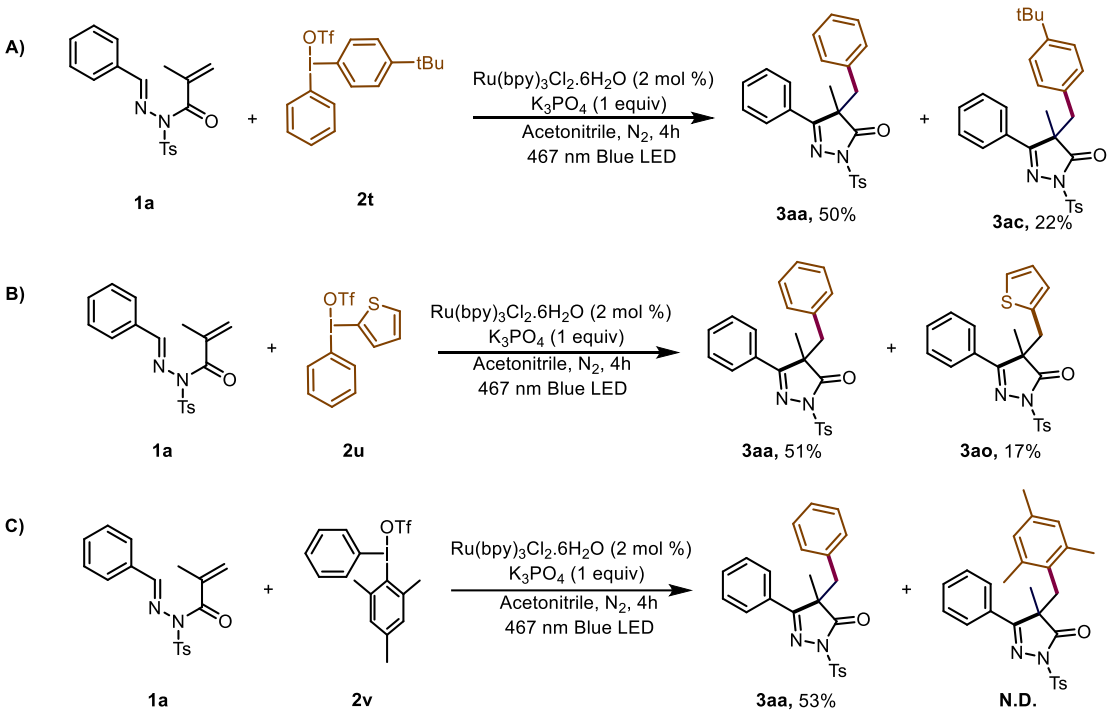
(*E*)-*N*'-benzylidene-*N*-methacryloyl-hydrazide derivative **1** (0.070 g, 0.20 mmol, 1 equiv), DIARs **2** (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), and K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv) were added in a pre-dried 10 ml Schlenk tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then, freshly distilled acetonitrile (2 mL) was added under the N_2 atmosphere. The resulting reaction mixture was allowed to stir for 4 h at room temperature under the irradiation of 40 W Kessil blue LEDs (467 nm) lamp. After completion, the reaction mixture was concentrated under vacuum and purified by silica gel column chromatography using 10-20% ethyl acetate in hexane to afford the desired product **3**.

2.5. General procedure (GP3) for the cascade arylsulfonation of (*E*)-*N*'-benzylidene-*N*-phenyl-methacrylohydrazide (5):



(E)-N'-benzylidene-*N*-phenyl-methacrylohydrazide **4** (0.20 mmol, 1 equiv), DIARs **2** (0.3 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv) and DABSO (2 equiv) were added in a pre-dried 10 ml Schlenk tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then, freshly distilled acetonitrile (2 mL) was added under the N_2 atmosphere. The resulting reaction mixture was allowed to stir for 4 h at room temperature under the irradiation of 40 W Kessil blue LEDs (467 nm) lamp. After completion, the reaction mixture was concentrated under vacuum and purified by silica gel column chromatography using 25-30 % ethyl acetate in hexane to afford the desired product **5**.

3. Chemoselective Studies for Unsymmetrical Diaryliodonium Triflate



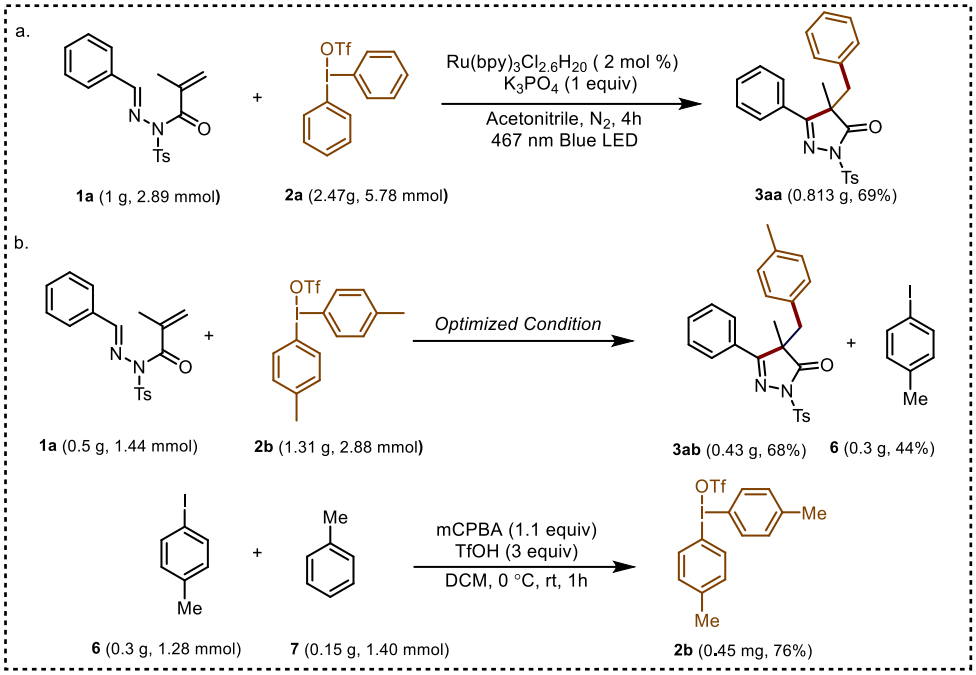
Scheme S1. Chemoselective Studies for Unsymmetrical Diaryliodonium Triflate

We synthesized a set of unsymmetrical DAIRs (**2t-2v**) and reacted those with **1a** under the established conditions to evaluate if the chemoselective transfer of one aryl moiety over the other is possible or not (Scheme S1). In case of DAIRs **2t** & **2u**, a selective transfer of electron-deficient aryl group providing corresponding compounds **3aa** (50%, Ph over 4-*t*-Bu-Ph) and **3ao** (51%, Ph over thiophene) was observed (Scheme S1, A-B). Expectedly, an exclusive transfer of sterically less demanding phenyl group was observed (**3aa**, 50%) when mesityliodonium salt **2v** was employed. The sterically hindered mesityl group served as a dummy group here (Scheme S1C).

4. Gram Scale Synthesis and Recycling of Iodoarenes

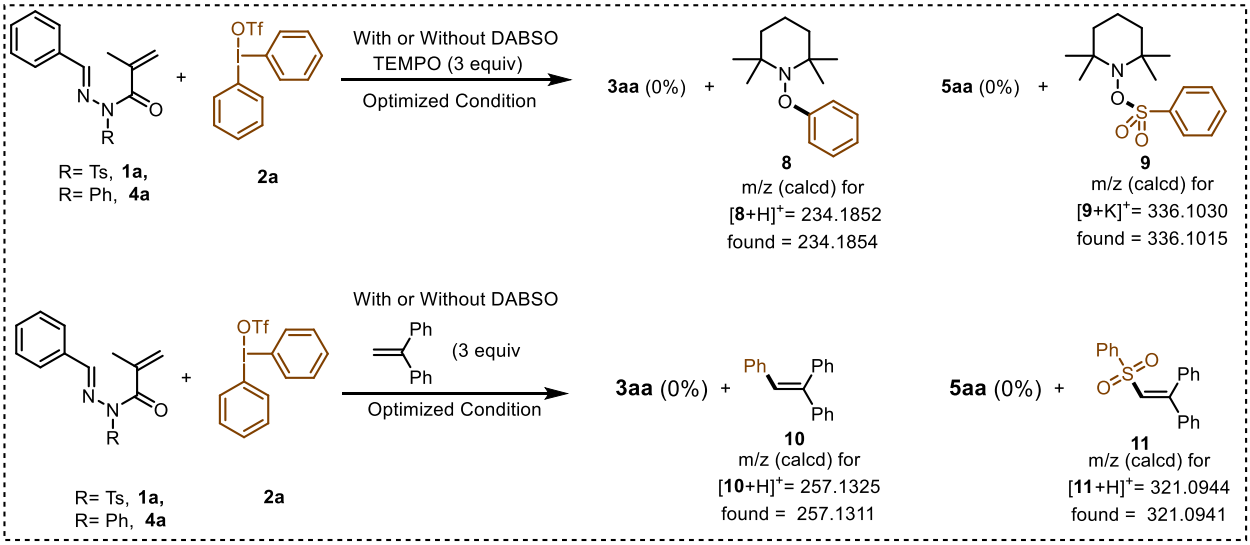
(*E*)-*N*'-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a** (1 g, 2.89 mmol, 1.0 equiv), DIARs **2a** (2.47 g, 5.78 mmol, 2 equiv), $Ru(bpy)_3Cl_2.6H_2O$ (0.043 g, 0.0574 mmol, 0.02 equiv), and K_3PO_4 (0.609 g, 2.87 mmol, 1 equiv) were added in a pre-dried 50 ml Schlenk flask under N_2 atmosphere. The flask was degassed and purged with N_2 three times. Then Acetonitrile (30 ml) was added under the N_2 atmosphere, and the resulting solution was allowed to stir for 4 h under irradiation of 40 W Kessil blue LEDs (467 nm) lamp. After completion, the reaction mixture was concentrated under vacuum and purified by silica gel column

chromatography using 10 to 20% ethyl acetate in hexane to afford the 4-benzyl-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one **3aa** (0.81 g, 69%).



Scheme S2. Gram-scale synthesis and recycling of iodoarene

5. Radical Trapping Experiment



Scheme S3. Radical trapping experiment

(a) (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a** (0.070 g, 0.20 mmol, 1 equiv) or **4a** (0.053 g, 0.2 mmol, 1 equiv), DIARs **2a** (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3 mg, 0.004 mmol, 0.02 equiv), and K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv), 2,2,6,6-Tetramethylpiperidin-1- yloxyl (TEMPO, 0.093g, 0.6 mmol, 3.0 equiv) and with or without DABSO (2 equiv) were added in a pre-dried 10 ml Schlenk tube under N_2 atmosphere.

The tube was degassed and purged with N_2 three times. Then, acetonitrile (2 ml) was added under the N_2 atmosphere. Then the mixture was allowed to stir for 4 h under irradiation of 40 W Kessil blue LED (467 nm) lamp. After completion, the reaction mixture was concentrated under vacuum, and purified by silica gel column chromatography using 10% ethyl acetate in hexane to afford the adduct. Formation of adducts were confirmed by HRMS.

(b) (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a** (0.070 g, 0.20 mmol, 1 equiv) or **4a** (0.053 g, 0.2 mmol, 1 equiv), DIAR **2a** (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), and K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv), ethene-1,1-diyldibenzene (0.108 g, 0.6 mmol, 3.0 equiv) and with or without DABSO (2 equiv) were added in a pre-dried 10 ml Schlenk tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then Acetonitrile (2 ml) was added under the N_2 atmosphere. Then the mixture was allowed to stir for 4 h under irradiation of 40 W Kessil blue LED (467 nm) lamp. After completion, the reaction mixture was concentrated under vacuum, and purified by silica gel column chromatography using 10% ethyl acetate in hexane to afford the adduct. Formation of adducts were confirmed by HRMS

6. Image of Photoreaction Setup

Front view: **Top view:**

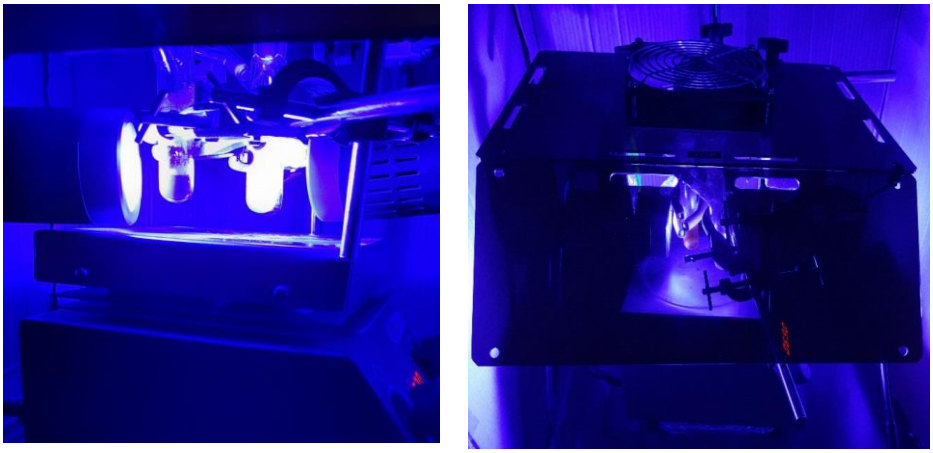


Figure S1: Representative pictures of reaction setup

7. Luminescence quenching Experiments:

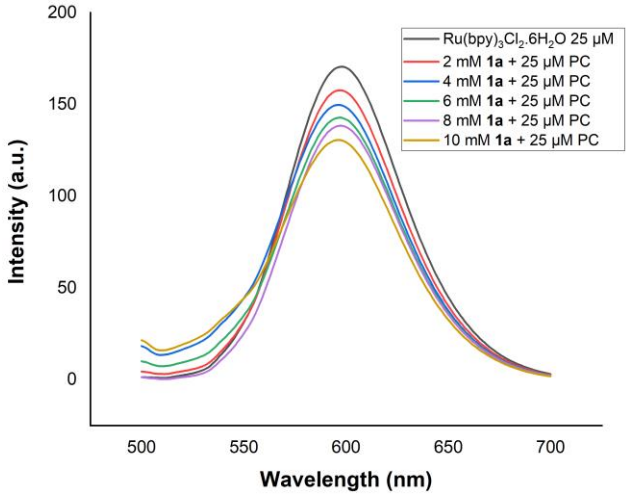
(A) Preparation of the Stock Solution:

A 0.5 mM solution of the $Ru(bpy)_3Cl_2.6H_2O$ catalyst was prepared in a sample vial by dissolving 1.87 mg of the catalyst in 5 mL of acetonitrile (spectroscopic grade, purchased from Spectrochem). The freshly prepared solution was used for the spectroscopic measurement. The required amount was taken using a micropipette from the mother solution as an aliquot and it was diluted further by dissolving in 3 mL of acetonitrile in the cuvette. Similarly, 10 mL 0.1 M solution of (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a**, diphenyliodonium trifluoromethanesulfonate **2a** were prepared by dissolving the requisite amount of each substrate in acetonitrile. Freshly prepared solutions were used for the quenching experiment.

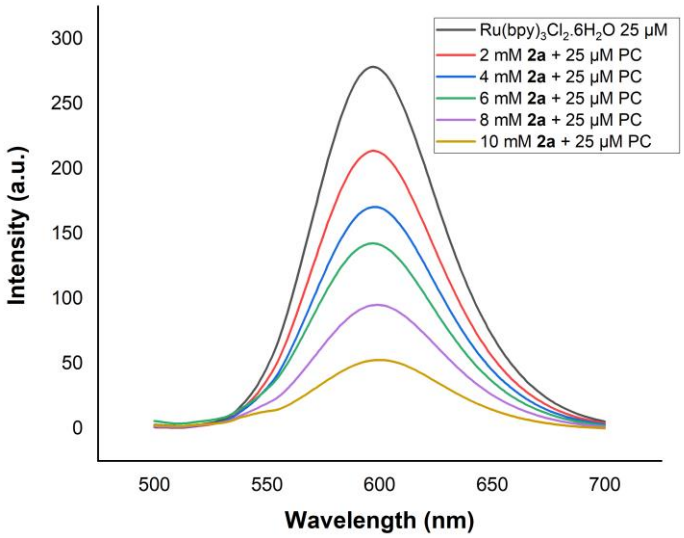
(B) Quenching studies:

Fluorescence emission spectra of the photocatalyst in the presence of different reaction components (**1a, 2a**) were recorded and analyzed in detail to estimate the light emission properties of the pure catalyst system and their distractions by external interference from the substrates. Emission intensities of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ were recorded with a "HITACHI f-7000" Scientific Spectrofluorometer using a 10.0 mm quartz cuvette. The catalyst exhibits an absorption maximum at 451 nm (confirmed from the literature). Hence, the sample solution of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ with a proper concentration of 25 **µ**M in acetonitrile was excited (degassed for 15 mins before recording the spectra) with a wavelength of 451 nm, and the emission maxima were found to be observed at 599 nm. The substrate **1a** was silent to show any emission feature in that region. To study the quenching behaviour of $Ru(bpy)_3Cl_2{\cdot}6H_2O$, different concentrations of **2a** was added to the catalyst solution and the emission spectra were measured following the aforementioned procedure. The quenching effect **2a** was quite significant on the photocatalyst; the intensity of the emission maxima decreased gradually upon increasing the concentration of **2a**. Some sets of solutions with different concentrations of the **2a** were used; the experiment was repeated and finally, the Stern-Volmer plot was depicted. On the other hand, no significant change in the emission maxima of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was observed when (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a** was used as the quencher. The corresponding Stern-Volmer plot was drawn for all the cases.

- **Luminescence spectra of $Ru(bpy)_3Cl_2.6H_2O$ (25 µM) as a function of the concentration of (*E*)-*N′*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (1a) in CH_3CN with excitation at 467 nm (Figure S2)**



- **Luminescence spectra of $Ru(bpy)_3Cl_2.6H_2O$ (25 µM) as a function of concentration of diphenyliodonium trifluoromethanesulfonate (2a) in CH_3CN with excitation at 467 nm (Figure S3)**



- **Luminescence spectra of $Ru(bpy)_3Cl_2.6H_2O$ (25 µM) as a function of concentration of Base (K_3PO_4) in CH_3CN with excitation at 467 nm (Figure S4)**

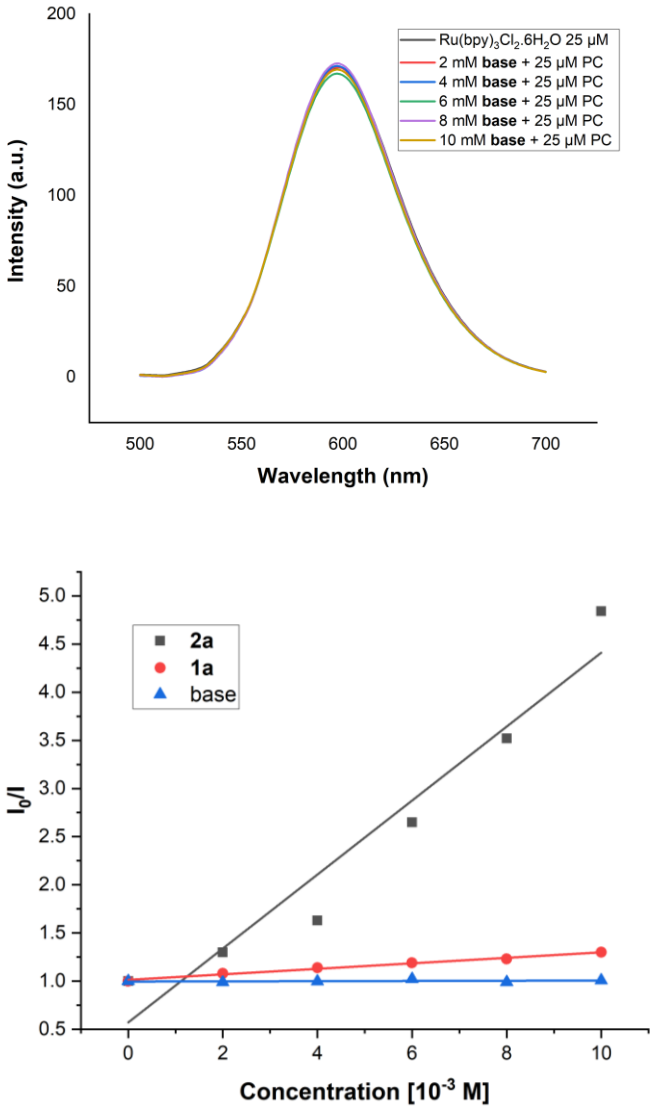


Figure S5. Stern Volmer Plot.

8. Light on-off experiment

(*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a** (0.070 g, 0.20 mmol, 1 equiv), DIARs **2a** (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), and K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv) were added in a pre-dried 10 ml Schlenk tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then Acetonitrile (2 ml) was added under the N_2 atmosphere. The mixture was irradiated using a 40 W Kessil blue LED (467 nm) lamp and the reaction was placed in light and dark in every alternative 30 min. After every time interval of 30 min, a 0.5 ml reaction aliquot was taken out by a syringe and quenched with water, organic part was taken in ethyl acetate and NMR was carried out. The NMR yield was determined using mesitylene as an internal standard.

Entry	Time (hr)	Light Source	NMR Yield
1	0.5	On	13.5
2	1	Off	13.5
3	1.5	On	31.5
4	2	Off	31.5
5	2.5	ON	45
6	3	Off	45

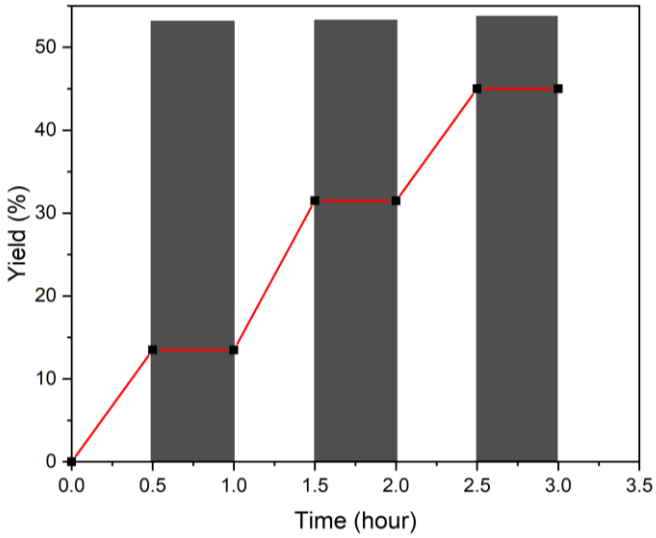


Figure S6. Light on-off Experiment.

9. Quantum Yield Calculation:[3]

(A) Determination of light intensity of the Blue LED:

0.737 g of potassium ferrioxalate trihydrate was dissolved in 10 mL H_2SO_4 (0.05 M) and stored in the dark. Then, a buffer solution was prepared by dissolving 2.5 g of sodium acetate and 0.5 mL of H_2SO_4 (95-98%) in 50 mL of distilled water.

General Protocol to assess the photon flux of the 467 nm blue LEDs: To a 10 mL Schlenk flask containing a stirring bar, 1 mL of the actinometer solution was added. Then, the solution was irradiated for 60 s. Immediately, a 100 µL aliquot was taken and added to a 10 mL volumetric flask containing 15 mg of 1, 10-phenanthroline in 3 mL of the buffer solution. The flask was filled with distilled water. The absorbance of this solution was then measured at 510 nm by UV/Vis spectrophotometry. In a similar manner, this procedure is repeated with the

actinometer solution stored in the dark. Using then the Beer's Law, the number of moles of Fe^{2+} produced by light irradiation is obtained by:

$$Fe^{2+} = \frac{v_1 v_3 \Delta A(510\ nm)}{10^3 v_2 l \varepsilon} \quad \text{.....1}$$

Where:

v_1 = Irradiated volume (1 mL)

v_2 = The aliquot of the irradiated solution taken for the estimation of Fe^{+} ions (0.100 mL)

v_3 = Final volume of the solution after complexation with 1, 10-phenanthroline (10 mL).

ε (510 nm) = Molar extinction coefficient of $[Fe(Phen)_3]^{2+}$ complex (11100 L mol^{-1} cm^{-1}).

l = Optical path-length of the cuvette (1 cm)

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

$$Fe^{2+} = \frac{1ml \times 10\ ml \times 3.486\ (510\ nm)}{10^3 \times 10^3 \times 0.1\ mL \times 1cm \times 11100\ L\ mol^{-1}\ cm^{-1}}$$

$$= 3.14 \times 10^{-8}\ mol$$

The photon flux (F) was obtained by using the following equation:

$$\phi(\lambda) = \frac{mol\ Fe^{2+}}{F(1-10^{-A\lambda})}$$

$$F = 3.14 \times 10^{-8}\ einsteins/s$$

Where: Φ (λ) = The quantum yield for Fe^{2+} formation at 467 nm is 1.

A (λ) = ferrioxalate actinometer absorbance at 467 nm, which was measured placing 1 mL of the solution in a cuvette of path length 1 cm by UV/Vis spectrophotometry. We obtained an absorbance value of 3.486. The photon flux (F) is 3.14 x 10^{-8} einsteins/s.

(B) **Quantum Yield Calculation:**

(*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide **1a** *(E)*-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1

equiv), diphenyliodonium trifluoromethanesulfonate **2a** (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.003 mg, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). were added in a pre-dried 10 ml Schlenk tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then Acetonitrile was added under the N_2 atmosphere. The mixture was irradiated using a 40 W Kessil blue LED (467 nm) lamp in the optimized condition for 1800 s and 6.75×10^{-6} moles of product were obtained. The Quantum yield was calculated using the following equations;

$$\phi\ (467\ \text{nm}) = \frac{mol\ of\ product}{F(1-10^{-A(467\ \text{nm})})t}$$

$$\phi\ (467\ \text{nm}) = \frac{6.75 \times 10^{-6}\ \text{mol}}{3.14 \times 10^{-8}\ \text{mol} \times 1 \times 1800\text{s}}$$

$$= 0.156$$

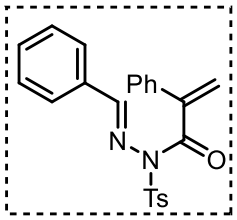
Where: A (467 nm) = is the absorbance at 467 nm of the photocatalytic reaction which was measured placing 1 mL of the solution in a cuvette of path length 1 cm by UV/Vis spectrophotometry.

t = is the reaction time i.e., 1800 s.

The quantum yield (Φ) of the reaction is **0.156**

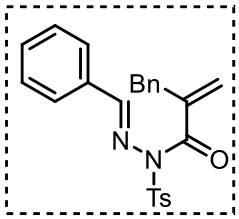
10. Report of NMR Spectral Data

***(E)-N'*-Benzylidene-4-methyl-*N*-(2-phenylacryloyl)benzenesulfonohydrazide (1t)**



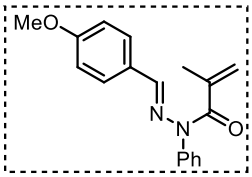
The compound was prepared according to **GP1** using benzaldehyde (0.53 g, 5 mmol, 1.0 equiv), and tosylhydrazine (1.12 g, 6 mmol, 1.2 equiv), in methanol to give corresponding *(E)-N'*-benzylidene-4-methylbenzenesulfonohydrazide, which was followed by further treatment with 2-phenylacryloyl chloride (1 g, 1.2 equiv) and Et_3N (1.1 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **1t** as a yellow solid (1.29 g, 64% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.44 (m, 3H), 7.36 (t, *J* = 8.3 Hz, 4H), 7.23 – 7.18 (m, 3H), 7.18 – 7.10 (m, 2H), 5.68 (s, 1H), 5.58 (s, 1H), 2.47 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 169.9, 167.0, 145.6, 145.3, 136.1, 135.1, 132.6, 132.3, 129.5, 128.9, 128.8, 128.7, 128.5, 128.3, 126.2, 120.3, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$ 405.1267; found 405.1275

***(E)-N*-(2-benzylacryloyl)-*N'*-benzylidene-4-methylbenzenesulfonohydrazide (1u)**



The compound was prepared according to **GP1** using benzaldehyde (0.53 g, 5 mmol, 1.0 equiv), and tosylhydrazine (1.12 g, 6 mmol, 1.2 equiv), in methanol to give corresponding *(E)-N'*-benzylidene-4-methylbenzenesulfonohydrazide, which was followed by further treatment with 2-benzylacryloyl chloride (1 g, 1.2 equiv) and Et_3N (0.76 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **1u** as a white solid (1.5 g, 73% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.67 (t, *J* = 6.8 Hz, 4H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.21 (m, 5H), 7.16 (d, *J* = 6.3 Hz, 2H), 5.70 (s, 1H), 5.51 (s, 1H), 3.69 (s, 2H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 171.0, 163.1, 144.9, 144.3, 137.4, 134.8, 132.9, 132.0, 129.5, 129.4, 128.8, 128.8, 128.6, 128.5, 126.6, 124.7, 39.2, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$ 419.1424; found 419.1436

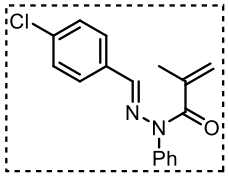
(*E*)-*N*'-(4-methoxybenzylidene)-*N*-phenylmethacrylohydrazide (4b)



The compound was prepared according to **GP1** using 4-methoxybenzaldehyde (1 g, 7.3 mmol, 1.0 equiv), and Phenylhydrazine (0.946 g, 8.76 mmol, 1.2 equiv), in methanol to give corresponding (*E*)-1-(4-methoxybenzylidene)-2-phenylhydrazine, which was followed by further treatment with methacryloyl chloride (0.9 g, 1.2 equiv) and Et_3N (1.1 g, 1.5 equiv) to

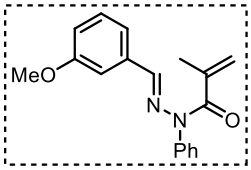
obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **4b** as a yellow solid (1.4 g, 65% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.59 – 7.53 (m, 2H), 7.51 – 7.46 (m, 3H), 7.26 – 7.21 (m, 3H), 6.90 – 6.85 (m, 2H), 5.49 (br s, 1H), 5.38 (br s, 1H), 3.82 (s, 3H), 2.19 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 172.5, 161.1, 142.23, 142.22, 141.8, 136.2, 130.2, 129.8, 128.8, 127.1, 118.7, 114.2, 55.4, 20.7. **HRMS-ESI** (*m/z*): calcd for $C_{18}H_{19}N_2O_2$ $[M+H]^+$ 295.1441; found 295.1451.

(*E*)-*N*'-(4-chlorobenzylidene)-*N*-phenylmethacrylohydrazide (4c)



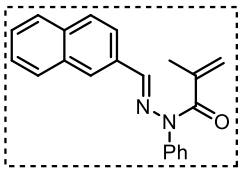
The compound was prepared according to **GP1** using 4-chlorobenzaldehyde (1 g, 7.11 mmol, 1.0 equiv), and Phenylhydrazine (0.922 g, 8.53 mmol, 1.2 equiv), in methanol to give corresponding (*E*)-1-(4-chloro-benzylidene)-2-phenylhydrazine, which was followed by further treatment with methacryloyl chloride (0.9 g, 1.2 equiv) and Et_3N (1.1 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **4c** as a yellow liquid (1.4 g, 66% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (t, *J* = 7.5 Hz, 2H), 7.51 – 7.46 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.20 (m, 3H), 5.50 (br s, 1H), 5.41 (br s, 1H), 2.19 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 172.6, 141.5, 140.8, 135.9, 135.7, 132.9, 130.3, 129.5, 129.2, 129.0, 128.4, 119.1, 20.7. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{16}ClN_2O$ $[M+H]^+$ 299.0946; found 299.0954.

(*E*)-*N*'-(3-methoxybenzylidene)-*N*-phenylmethacrylohydrazide (4d)



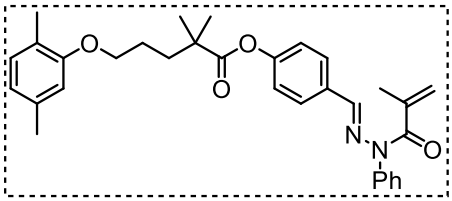
The compound was prepared according to **GP1** using 3-methoxybenzaldehyde (1 g, 7.3 mmol, 1.0 equiv), and Phenylhydrazine (0.946 g, 8.76 mmol, 1.2 equiv), in methanol to give corresponding (*E*)-1-(3-methoxybenzylidene)-2-phenylhydrazine, which was followed by further treatment with methacryloyl chloride (0.9 g, 1.2 equiv) and Et_3N (1.1 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **4d** as a white solid (1.42 g, 66% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.26 – 7.25 (m, 4H), 7.15 (s, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.52 (br s, 1H), 5.41 (br s, 1H), 3.81 (s, 3H), 2.21 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 172.6, 160.0, 142.0, 141.6, 136.0, 135.7, 130.3, 129.7, 129.4, 129.2, 120.3, 119.0, 116.0, 111.6, 55.3, 20.7. **HRMS-ESI** (*m/z*): calcd for $C_{18}H_{19}N_2O_2$ $[M+H]^+$ 295.1441; found 295.1452.

(*E*)-*N*'-(naphthalen-2-ylmethylene)-*N*-phenylmethacrylohydrazide (4e)



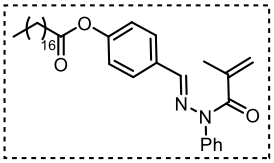
The compound was prepared according to **GP1** using 2-Bromo-benzaldehyde (1 g, 6.40 mmol, 1.0 equiv), and Phenylhydrazine (0.710 g, 6.76 mmol, 1.2 equiv), in methanol to give corresponding (*E*)-1-(naphthalen-2-ylmethylene)-2-phenylhydrazine, which was followed by further treatment with methacryloyl chloride (0.8 g, 1.2 equiv) and Et_3N (0.97 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **4e** as a white solid (1.12 g, 55% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.71 (s, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.26 – 7.23 (m, 2H), 5.54 (br s, 1H), 5.44 (br s, 1H), 2.23 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 172.8, 142.5, 141.8, 136.1, 134.2, 133.3, 132.2, 130.4, 129.5, 129.4 (2C), 128.8, 128.3, 128.0, 127.1, 126.7, 123.0, 119.1, 20.9. **HRMS-ESI** (*m/z*): calcd for $C_{21}H_{19}N_2O$ $[M+H]^+$ 315.1497; found 315.1499.

(*E*)-4-((2-Methacryloyl-2-phenylhydrazineylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (4f)



The compound was prepared according to **GP1** using 2-4-formylphenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (1 g, 2.8 mmol, 1.0 equiv), and Phenylhydrazine (0.710 g, 3.0 mmol, 1.2 equiv), in methanol to give corresponding (*E*)-4-((2-phenylhydrazineylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate, which was followed by further treatment with methacryloyl chloride (0.3 g, 1.2 equiv) and Et_3N (0.35 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **4f** as a red liquid (0.88 g, 61% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 – 7.55 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.08 – 6.98 (m, 3H), 6.72 – 6.61 (m, 2H), 5.52 (br s, 1H), 5.42 (br s, 1H), 3.99 (t, *J* = 5.2 Hz, 2H), 2.31 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H), 1.92 – 1.85 (m, 4H), 1.38 (s, 6H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 176.2, 172.7, 157.0, 152.3, 141.7, 141.2, 136.6, 136.0, 132.0, 130.5, 130.4, 129.5, 129.3, 128.4, 123.7, 122.1, 120.9, 119.0, 112.0, 67.8, 42.6, 37.2, 25.4, 25.2, 21.5, 20.8, 15.9. **HRMS-ESI** (*m/z*): calcd for $C_{32}H_{37}N_2O_4$ $[M+H]^+$ 513.2748; found 513.2761.

(*E*)-4-(2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl stearate--methane (4g)

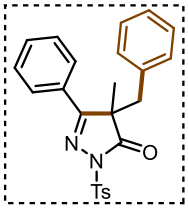


The compound was prepared according to **GP1** using 2-Bromo-benzaldehyde (1 g, 2.6 mmol, 1.0 equiv), and Phenylhydrazine (0.34 g, 3.12 mmol, 1.2 equiv), in methanol to give corresponding (*E*)-4-((2-phenylhydrazineylidene)methyl)phenyl stearate--methane, which was followed by further

treatment with methacryloyl chloride (0.3 g, 1.2 equiv) and Et_3N (0.39 g, 1.5 equiv) to obtain the desired product. Purification by column chromatography (20% ethyl acetate in hexane) gave **4g** as a white solid (0.71 g, 50% yield).

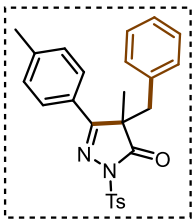
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (t, *J* = 8.4 Hz, 4H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.27 (s, 1H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 5.50 (br s, 1H), 5.40 (br s, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 1.73 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.26 (s, 28H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 172.7, 172.1, 152.0, 141.6, 141.2, 136.0, 131.9, 130.3, 129.4, 129.2, 128.3, 122.0, 119.0, 34.4, 32.0, 29.7 (4C), 29.68 (2C), 29.6, 29.5, 29.4, 29.3, 29.1, 24.9, 22.7 (2C), 20.7, 14.1. **HRMS-ESI** (*m/z*): calcd for $C_{35}H_{51}N_2O_3$ $[M+H]^+$ 547.3889; found 547.3907.

4-Benzyl-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3aa)



The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3aa** as a white solid (0.062 g, 74% yield). **^{1}H NMR (500 MHz, $CDCl_3$)**; δ 7.83 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 7.7 Hz, 2H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.25 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 13.8 Hz, 1H), 2.45 (s, 3H), 1.66 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$**; δ 175.3, 161.3, 145.1, 134.7, 134.1, 131.1, 130.5, 129.9, 129.1, 129.0, 128.2, 128.1, 127.11, 127.07, 56.0, 42.8, 22.8, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{23}N_2O_3S$ $[M+H]^+$ 419.1419; found 419.1407.

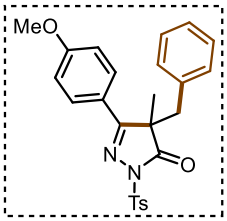
4-Benzyl-4-methyl-5-(*p*-tolyl)-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ba)



The compound was prepared according to **GP2** using (*E*)-*N*-methacryloyl-4-methyl-*N*'-(4-methylbenzylidene)benzenesulfonohydrazide (0.071 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ba** as a white solid (0.057 g, 65% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.73 (dd, *J* = 8.2, 2.6 Hz, 4H), 7.28 – 7.20 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 7.5 Hz, 2H), 3.25 (d, *J* = 13.7 Hz, 1H), 3.18 (d, *J* = 13.7 Hz, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 1.64 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 161.4, 145.7, 141.6, 134.8,

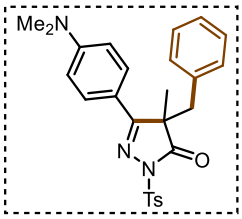
134.3, 129.84, 129.76, 129.0, 128.2, 128.1, 127.8, 127.1, 127.0, 57.0, 42.9, 22.9, 21.8, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{25}N_2O_3S$ $[M+H]^+$ 433.1580; found 433.1568.

4-Benzyl-5-(4-methoxyphenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ca)



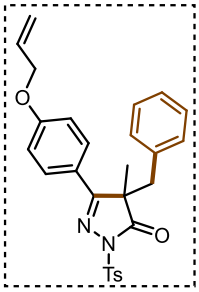
The compound was prepared according to **GP2** using (*E*)-*N*-methacryloyl-*N'*-(4-methoxybenzylidene)-4-methylbenzene-sulfonohydrazide (0.074 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ca** as a white solid (0.057 g, 63% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 – 7.77 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.99 – 6.93 (m, 3H), 6.82 (t, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.23 (d, *J* = 13.7 Hz, 1H), 3.18 (d, *J* = 13.8 Hz, 1H), 2.44 (s, 3H), 1.63 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.4, 161.7, 160.9, 145.0, 134.7, 134.2, 129.7, 128.9, 128.6, 128.1, 128.0, 127.0, 123.1, 114.3, 55.9, 55.5, 42.9, 22.9, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$ 449.1530; found 449.1510.

4-Benzyl-5-(4-(dimethylamino)phenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3da)



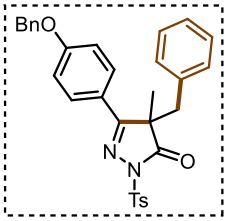
The compound was prepared according to **GP2** (*E*)-*N'*-(4-(dimethylamino)benzylidene)-*N*-methacryloyl-4-methylbenzene sulfonohydrazide (0.077 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3da** as a white solid (0.049 g, 53% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 – 7.68 (m, 4H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.72 – 6.66 (m, 4H), 3.26 (d, *J* = 13.7 Hz, 1H), 3.16 (d, *J* = 13.7 Hz, 1H), 3.05 (s, 6H), 2.43 (s, 3H), 1.61 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 161.2, 151.6, 144.6, 134.7, 134.3, 129.4, 128.8, 128.1, 127.8, 128.0, 126.6, 117.5, 111.3, 55.7, 42.7, 39.8, 22.8, 21.5. **HRMS-ESI** (*m/z*): calcd for $C_{26}H_{28}N_3O_3S$ $[M+H]^+$ 462.1846; found 462.1822.

5-(4-(Allyloxy)phenyl)-4-benzyl-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ea)



The compound was prepared according to **GP2** (*E*)-*N*'-(4-(allyloxy)benzylidene)-*N*-methacryloyl-4-methylbenzenesulfonohydrazid (0.080 g, 0.2 mmol, 1 equiv), diphenyliodoniumtrifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ea** as a white solid (0.056 g, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 6.99 – 6.93 (m, 3H), 6.81 (t, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 7.7 Hz, 2H), 6.13 – 6.02 (m, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 4.61 (d, *J* = 5.3 Hz, 2H), 3.21 (s, 1H), 3.20 (s, 1H), 2.44 (s, 3H), 1.63 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 161.1, 160.8, 145.1, 134.8, 134.3, 132.7, 129.8, 129.1, 128.8, 128.2, 128.1, 127.1, 123.3, 118.4, 115.1, 69.0, 56.0, 43.0, 23.0, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{27}H_{27}N_2O_4S$ $[M+H]^+$ 475.1686; found 475.1650.

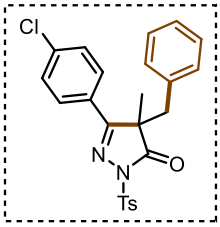
4-Benzyl-5-(4-(benzyloxy)phenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3fa)



The compound was prepared according to **GP2** using (*E*)-*N*'-(4-(benzyloxy)benzylidene)-*N*-methacryloyl-4-methylbenzene sulfonohydrazide (0.090 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20 % ethyl acetate in hexane) gave **3fa** as a white solid (0.061 g, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.39 (m, 4H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 7.6 Hz, 2H), 5.14 (s, 2H), 3.23 (d, *J* = 13.8 Hz, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 2.44 (s, 3H), 1.63 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 161.1, 161.0, 145.1, 136.4, 134.8, 134.3, 129.8, 129.0, 128.84, 128.76, 128.4, 128.2, 128.1, 127.7, 127.1, 123.4, 115.3, 70.3, 56.0, 42.9, 23.0, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{31}H_{29}N_2O_4S$ $[M+H]^+$ 525.1843; found 525.1815.

4-Benzyl-5-(4-chlorophenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ga)

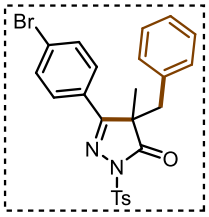


The compound was prepared according to **GP2** (*E*)-*N*'-(4-chlorobenzylidene)-*N*-methacryloyl-4-methylbenzene sulfonohydrazide (0.075 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02

equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20 % ethyl acetate in hexane) gave **3ga** as a white solid (0.065 g, 71% yield).

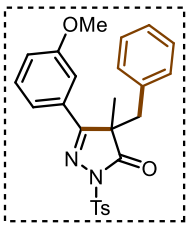
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 4H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 2H), 6.60 (d, *J* = 7.8 Hz, 2H), 3.21 (s, 1H), 3.19 (s, 1H), 2.45 (s, 3H), 1.64 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.1, 160.3, 145.3, 134.5, 133.9, 132.6, 129.8, 129.4, 128.8, 128.3, 128.2, 128.1, 127.1, 125.7, 55.9, 42.8, 22.7, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}ClN_2O_3S$ $[M+H]^+$ 453.1034; found 453.1030.

4-Benzyl-5-(4-bromophenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ha)



The compound was prepared according to **GP2** (*E*)-*N'*-(4-bromobenzylidene)-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.084 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ha** as a white solid (0.063 g, 63% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 – 7.67 (m, 4H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 2H), 6.60 (d, *J* = 7.7 Hz, 2H), 3.22 (d, *J* = 13.9 Hz, 1H), 3.18 (d, *J* = 13.9 Hz, 1H), 2.45 (s, 3H), 1.64 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.1, 160.3, 145.3, 134.6, 133.9, 132.3, 129.8, 129.4, 128.8, 128.3, 128.2, 128.1, 127.1, 125.7, 55.9, 42.8, 22.7, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}BrN_2O_3S$ $[M+H]^+$ 497.0529; found 497.0520.

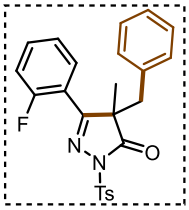
4-Benzyl-5-(3-methoxyphenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ia)



The compound was prepared according to **GP2** (*E*)-*N*-methacryloyl-*N'*-(3-methoxybenzylidene)-4-methylbenzenesulfonohydrazide (0.074 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ia** as a white liquid (0.054 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.28 (d, *J* = 5.8 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 2H), 6.67 (d, *J* = 7.5 Hz, 2H), 3.88 (s, 3H), 3.28 (d, *J* = 13.8 Hz, 1H), 3.22 (d, *J* = 13.8 Hz, 1H), 2.47 (s, 3H), 1.67 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 161.3, 160.0, 145.7, 134.7, 134.2, 131.8, 130.0, 129.9, 129.0, 128.23, 128.15,

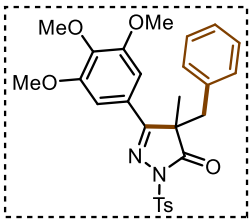
127.1, 119.5, 116.7, 112.6, 56.2, 55.6, 42.9, 23.0, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{25}N_2O_4S$ $[M+H]^+$ 449.1530; found 449.1508.

4-Benzyl-5-(2-fluorophenyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ja)



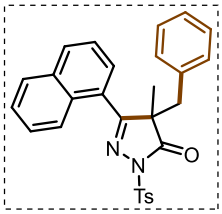
The compound was prepared according to **GP2** (*E*)-*N'*-(2-fluorobenzylidene)-*N*-methacryloyl-4-methylbenzene sulfonohydrazide (0.072 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ja** as a white solid (0.053 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.71 – 7.67 (m, 1H), 7.46 – 7.42 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 2H), 6.58 (d, *J* = 7.7 Hz, 2H), 3.17 (d, *J* = 14.0 Hz, 1H), 3.10 (d, *J* = 14.2 Hz, 1H), 2.44 (s, 3H), 1.57 (d, *J* = 1.8 Hz, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.7, 160.05 (d, *J* = 252.8 Hz), 159.72 (d, *J* = 3.0 Hz), 145.4, 134.7, 133.0, 132.9, 130.30 (d, *J* = 3.3 Hz), 130.0, 129.0, 128.23 (d, *J* = 1.9 Hz), 127.0, 124.8 (d, *J* = 3.2 Hz), 118.9, 118.8, 116.94 (d, *J* = 23.4 Hz), 56.9, 41.6 (d, *J* = 6.3 Hz), 22.1, 22.0, 21.9. **^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$)** δ -107.5. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}FN_2O_3S$ $[M+H]^+$ 437.1330; found 437.1307.

4-Benzyl-4-methyl-2-tosyl-5-(3,4,5-trimethoxyphenyl)-2,4-dihydro-3*H*-pyrazol-3-one (3ka)



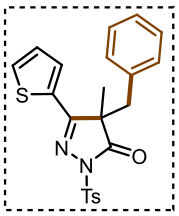
The compound was prepared according to **GP2** (*E*)-*N*-methacryloyl-4-methyl-N'-(3,4,5-trimethoxybenzylidene)benzenesulfonohydrazide (0.086 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (22% ethyl acetate in hexane) gave **3ka** as a white liquid (0.060 g, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.04 – 6.94 (m, 3H), 6.86 (t, *J* = 7.7 Hz, 2H), 6.71 – 6.64 (m, 2H), 3.92 (s, 3H), 3.90 (s, 6H), 3.21 (s, 2H), 2.45 (s, 3H), 1.63 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.8, 161.1, 153.5, 145.3, 141.0, 134.7, 134.1, 129.9, 129.1, 128.3, 128.2, 127.2, 126.0, 104.9, 61.2, 56.6, 56.0, 43.3, 23.1, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{27}H_{29}N_2O_6S$ $[M+H]^+$ 509.1741; found 509.1717.

4-Benzyl-4-methyl-5-(naphthalen-1-yl)-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3la)



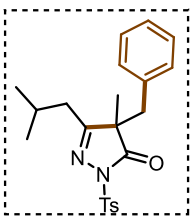
The compound was prepared according to **GP2** (*E*)-*N*-methacryloyl-4-methyl-*N*′-(naphthalen-1-ylmethylene)benzenesulfonohydrazide (0.078 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3la** as a white solid (0.052 g, 55% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.27 (m, 3H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 2H), 3.19 (d, *J* = 14.0 Hz, 1H), 3.00 (d, *J* = 14.1 Hz, 1H), 2.51 (s, 3H), 1.75 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.0, 162.2, 145.2, 134.5, 134.0, 131.2, 130.9, 129.7, 129.0, 128.9, 128.21, 128.16, 128.1, 127.5, 127.0, 126.7, 126.2, 126.1, 126.0, 124.1, 57.1, 41.8, 23.6, 21.6. **HRMS-ESI** (*m/z*): calcd for $C_{28}H_{24}N_2O_3S$ $[M+H]^+$ 469.1580; found 469.1555.

4-Benzyl-4-methyl-5-(thiophen-2-yl)-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ma)



The compound was prepared according to **GP2** (*E*)-*N*-methacryloyl-4-methyl-*N*′-(thiophen-2-ylmethylene)benzenesulfonohydrazide (0.070g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ma** as a yellow solid (0.046 g, 54% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 3.5 Hz, 1H), 7.51 (d, *J* = 4.9 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 4.1 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 3.22 (d, *J* = 13.4 Hz, 1H), 3.18 (d, *J* = 13.8 Hz, 1H), 2.45 (s, 3H), 1.62 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.0, 157.9, 145.5, 134.9, 134.3, 134.0, 130.1, 129.8, 129.3, 128.8, 128.6, 128.5, 128.2, 127.5, 56.5, 43.3, 23.0, 22.1. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{21}N_2O_3S_2$ $[M+H]^+$ 425.0988; found 425.0966.

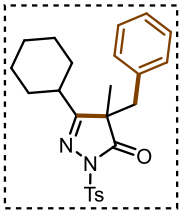
4-Benzyl-5-isobutyl-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3na)



The compound was prepared according to **GP2** (*E*)-*N*-methacryloyl-4-methyl-*N*′-(3-methylbutylidene)benzenesulfonohydrazide (0.064g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3na** as a white liquid (0.046 g, 57% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.75 (d, *J* =

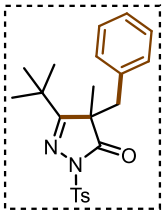
8.3 Hz, 2H), 7.25 (s, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 7.4 Hz, 2H), 3.08 (d, *J* = 14.1 Hz, 1H), 2.75 (d, *J* = 14.0 Hz, 1H), 2.45 (s, 3H), 2.17 (d, *J* = 2.7 Hz, 2H), 1.29 (s, 3H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 3H), 0.73 – 0.68 (m, 1H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.4, 166.2, 145.1, 135.0, 134.5, 129.8, 128.9, 128.5, 128.2, 127.3, 56.1, 41.7, 37.4, 25.0, 23.1, 22.4, 21.8, 21.4. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{27}N_2O_3S$ $[M+H]^+$ 399.1737; found 399.1711.

4-Benzyl-5-cyclohexyl-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3oa)



The compound was prepared according to **GP2** (*E*)-*N'*-(cyclohexylmethylene)-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3oa** as a white liquid (0.050 g, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 2H), 3.10 (d, *J* = 14.2 Hz, 1H), 2.81 (d, *J* = 14.2 Hz, 1H), 2.46 (s, 3H), 2.28 – 7.21 (m, 1H), 1.92 – 1.84 (m, 1H), 1.81 – 1.73 (m, 2H), 1.62 – 1.68 (m, 1H), 1.58 – 1.50 (m, 1H), 1.35 (s, 3H), 1.32 – 1.23 (m, 3H), 1.22 – 1.13 (m, 2H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 170.9, 145.0, 134.9, 134.7, 129.7, 128.6, 128.3, 128.0, 127.0, 56.3, 41.6, 38.5, 33.3, 29.1, 26.3, 26.0, 25.6, 22.2, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{28}N_2O_3S$ $[M+H]^+$ 425.1893; found 425.1870.

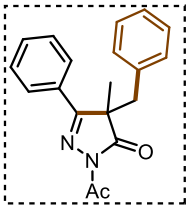
4-Benzyl-5-(*tert*-butyl)-4-methyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3pa)



The compound was prepared according to **GP2** (*E*)-*N'*-(2,2-dimethylpropylidene)-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.065g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3pa** as a white solid (0.048 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 4.4 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 2H), 6.71 (d, *J* = 7.6 Hz, 2H), 3.10 (d, *J* = 14.7 Hz, 1H), 3.06 (d, *J* = 14.8 Hz, 1H), 2.43 (s, 3H), 1.42 (s, 3H), 1.22 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.5, 172.3,

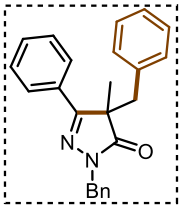
145.1, 134.8, 134.7, 129.7, 128.4, 128.2, 128.1, 127.0, 42.4, 36.9, 31.0, 29.6, 22.5, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{27}N_2O_3S$ $[M+H]^+$ 399.1737; found 399.1744.

2-Acetyl-4-benzyl-4-methyl-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3qa)



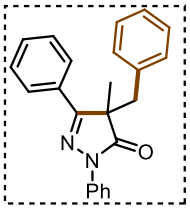
The compound was prepared according to **GP2** (*E*)-*N*-acetyl-*N*'-benzylidenemethacrylohydrazide (0.046g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3qa** as a white liquid (0.035 g, 57% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 – 7.82 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 9.2, 5.9 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.60 (s, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 3.21 (d, *J* = 13.8 Hz, 1H), 3.12 (d, *J* = 13.8 Hz, 1H), 2.45 (s, 3H), 1.69 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 177.1, 167.0, 161.2, 134.3, 131.2, 130.6, 129.1, 129.0, 128.3, 127.6, 127.1, 56.2, 43.5, 24.1, 22.3. **HRMS-ESI** (*m/z*): calcd for $C_{19}H_{19}N_2O_2$ $[M+H]^+$ 307.1441; found 307.1424.

2,4-Dibenzyl-4-methyl-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (3ra)



The compound was prepared according to **GP2** (*E*)-*N*'-(2,2-dimethylpropylidene)-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.065g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ra** as a white solid (0.033 g, 46% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 – 7.90 (m, 2H), 7.54 – 7.50 (m, 3H), 7.34 (s, 1H), 7.26 – 7.17 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.95 – 6.89 (m, 4H), 4.93 (d, *J* = 15.4 Hz, 1H), 4.73 (d, *J* = 15.4 Hz, 1H), 3.42 (d, *J* = 13.5 Hz, 1H), 3.34 (d, *J* = 13.5 Hz, 1H), 1.77 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 177.4, 160.1, 136.3, 135.4, 131.7, 130.1, 129.4, 129.0, 128.5, 128.3, 127.6, 127.3, 127.1, 126.5, 54.9, 47.8, 42.8, 22.8. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{23}N_2O$ $[M+H]^+$ 355.1805; found 355.1786.

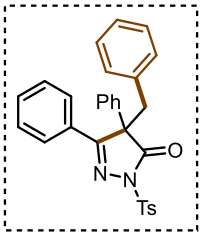
4-Benzyl-4-methyl-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (3sa)



The compound was prepared according to **GP2** (*E*)-*N*'-benzylidene-*N*-phenylmethacrylohydrazide (0.053g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv).

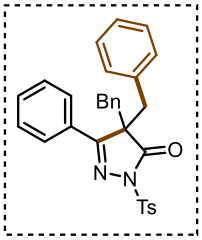
Purification by column chromatography (15% ethyl acetate in hexane) gave **3sa** as a white solid (0.035 g, 50% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 – 7.90 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 4.3 Hz, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.08 – 7.01 (m, 3H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.45 – 3.25 (m, 2H), 1.77 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 176.0, 160.0, 137.6, 134.8, 131.3, 130.2, 128.9, 128.8, 128.6, 127.9, 127.0, 126.4, 125.2, 119.4, 56.0, 43.4, 22.3. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{21}N_2O[M+H]^+$ 341.1648; found 341.1630.

4-Benzyl-4,5-diphenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ta)



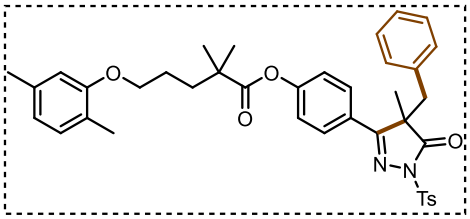
The compound was prepared according to **GP2** *(E)-N'*-benzylidene-4-methyl-*N*-(2-phenylacryloyl)benzenesulfonohydrazide (0.081 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ta** as a white solid (0.048 g, 50% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.27 (m, 7H), 7.22 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.81 (t, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 7.4 Hz, 2H), 3.89 (d, *J* = 13.1 Hz, 1H), 3.46 (d, *J* = 13.1 Hz, 1H), 2.47 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.5, 160.8, 145.3, 135.4, 134.7, 133.3, 131.0, 130.1, 129.8, 129.6, 129.3, 128.8, 128.7, 128.2, 128.1, 127.4, 127.1, 126.2, 63.3, 39.3, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{29}H_{25}N_2O_3S$ $[M+H]^+$ 481.1580 found 481.1589.

4,4-Dibenzyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ua)



The compound was prepared according to **GP2** *(E)-N*-(2-benzylacryloyl)-*N'*-benzylidene-4-methylbenzenesulfonohydrazide (0.084 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ua** as a colourless oil (0.058 g, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 6.9 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 10.0, 7.2 Hz, 3H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 2H), 6.91 (t, *J* = 7.7 Hz, 4H), 6.76 (d, *J* = 7.5 Hz, 4H), 3.47 (d, *J* = 13.7 Hz, 2H), 3.39 (d, *J* = 13.7 Hz, 2H), 2.45 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 174.4, 158.9, 144.9, 134.7, 133.6, 131.2, 131.1, 131.0, 130.4, 129.9, 129.6, 129.1, 129.0, 128.3, 128.0, 127.6, 127.2, 127.0, 62.6, 42.7, 21.7. **HRMS-ESI** (*m/z*): calcd for $C_{30}H_{27}N_2O_3S$ $[M+H]^+$ 495.1737 found 495.1742.

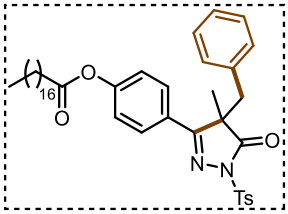
4-(4-Benzyl-4-methyl-5-oxo-1-tosyl-4,5-dihydro-1*H*-pyrazol-3-yl) phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3va)



The compound was prepared according to (*E*)-4-(2-methacryloyl-2-tosylhydrazineylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (0.118 g, 0.2 mmol, 1equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3va** as a white liquid (0.073 g, 55% yield).

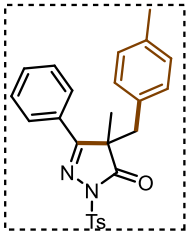
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.24 (s, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.02 – 6.95 (m, 2H), 6.83 (t, *J* = 7.7 Hz, 2H), 6.69 – 6.62 (m, 4H), 4.00 (t, *J* = 5.3 Hz, 2H), 3.22 (s, 2H), 2.45 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.94 – 1.86 (m, 4H), 1.64 (s, 3H), 1.40 (s, 6H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 176.1, 175.3, 160.6, 157.0, 153.2, 145.3, 136.7, 134.7, 134.0, 130.5, 129.9, 129.0, 128.31, 128.30, 128.8, 128.0, 127.2, 123.7, 122.3, 121.0, 112.0, 67.8, 56.1, 42.9, 42.7, 37.2, 25.4, 25.2, 22.8, 21.8, 21.5, 16.0. **HRMS-ESI** (*m/z*): calcd for $C_{39}H_{42}N_2O_6S$ $[M+H]^+$ 667.2836; found 667.2736.

4-(4-Benzyl-4-methyl-5-oxo-1-tosyl-4,5-dihydro-1*H*-pyrazole-3-yl)phenyl stearate (3wa)



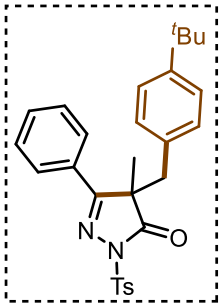
The compound was prepared according to **GP2** (*E*)-4-(2-(2-methylenebutanoyl)-2-tosylhydrazineylidene)methyl)phenyl stearatemethane (0.124 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3wa** as a white liquid (0.085 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 – 7.82 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 7.7 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 3.22 (s, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 1.80 – 1.78 (m, 2H), 1.63 (s, 3H), 1.43 – 1.38 (m, 2H), 1.26 (br s, 26H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.3, 172.0, 160.6, 152.9, 145.3, 134.7, 134.1, 129.9, 129.0, 128.3 (2C), 128.2, 128.0, 127.2, 122.3, 56.1, 42.9, 34.6, 32.1, 29.83 (5C), 29.79 (2C), 29.7, 29.6, 29.5, 29.4, 29.2, 25.0, 22.8 (2C), 21.9, 14.3. **HRMS-ESI** (*m/z*): calcd for $C_{42}H_{57}N_2O_5S$ $[M+H]^+$ 701.3983; found 701.3943.

4-Methyl-4-(4-methylbenzyl)-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ab)



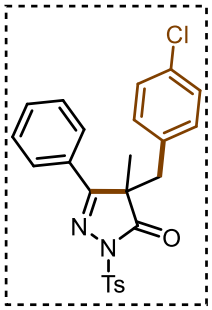
The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), di-*p*-tolyliodonium trifluoromethanesulfonate (0.183 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ab** as a white solid (0.061 g, 70% yield). **^{1}H NMR (500 MHz, $CDCl_3$);** δ 7.82 (d, *J* = 7.1 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.25 (d, *J* = 2.6 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 2H), 6.50 (d, *J* = 7.9 Hz, 2H), 3.20 (d, *J* = 13.8 Hz, 1H), 3.16 (d, *J* = 13.9 Hz, 1H), 2.45 (s, 3H), 2.13 (s, 3H), 1.64 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$);** δ 175.4, 161.4, 145.1, 136.5, 134.7, 131.1, 131.0, 130.5, 129.6, 128.9, 128.8, 128.7, 128.1, 127.0, 56.2, 42.4, 22.7, 21.8, 21.0. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{25}N_2O_3S$ $[M+H]^+$ 433.1580; found 433.1582.

4-(4-(*Tert*-butyl)benzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ac)



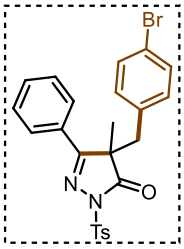
The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(4-(*tert*-butyl)phenyl)iodonium trifluoromethanesulfonate (0.216 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ac** as a white solid (0.062 g, 65% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.80 – 7.78 (m, 2H), 7.46 – 7.43 (m, 3H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 3.24 (d, *J* = 14.0 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H), 2.45 (s, 3H), 1.62 (s, 3H), 1.18 (s, 9H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.8, 161.8, 150.0, 145.4, 134.9, 131.3, 131.1, 130.6, 129.9, 128.9, 128.6, 128.4, 127.2, 125.2, 56.1, 42.5, 34.4, 31.3, 22.9, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{28}H_{31}N_2O_3S$ $[M+H]^+$ 475.2050; found 475.2053.

4-(4-Chlorobenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ad)



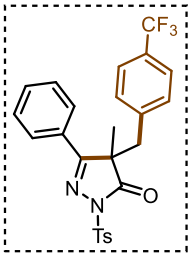
The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (0.198 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ad** as a white liquid (0.056 g, 61% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.40 (m, 3H), 7.27 – 7.21 (m, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 6.46 (d, *J* = 8.2 Hz, 2H), 3.18 (d, *J* = 13.8 Hz, 1H), 3.09 (d, *J* = 13.8 Hz, 1H), 2.45 (s, 3H), 1.65 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.0, 160.2, 145.7, 134.6, 133.1, 132.7, 131.4, 130.4, 130.3, 129.9, 129.2, 128.2, 128.0, 127.0, 56.1, 41.9, 22.8, 22.0. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}ClN_2O_3S$ $[M+H]^+$ 453.1034; found 453.1030.

4-(4-Bromobenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ae)



The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(4-bromophenyl)iodonium trifluoromethanesulfonate (0.234 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ae** as a white solid (0.059 g, 59% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 – 7.80 (m, 2H), 7.76 – 7.70 (m, 2H), 7.52 – 7.46 (m, 3H), 7.31 (t, *J* = 6.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.47 – 6.41 (m, 2H), 3.20 (d, *J* = 13.8 Hz, 1H), 3.13 (d, *J* = 13.8 Hz, 1H), 2.51 (s, 3H), 1.70 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.3, 161.2, 146.0, 134.9, 133.5, 131.6, 131.4, 131.0, 130.7, 130.2, 129.5, 128.3, 127.2, 121.6, 56.3, 42.2, 23.1, 22.3. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}BrN_2O_3S$ $[M+H]^+$ 497.0529; found 497.0514.

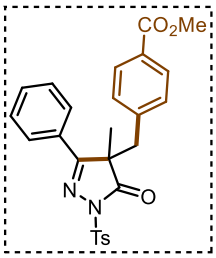
4-Methyl-5-phenyl-2-tosyl-4-(4-(trifluoromethyl)benzyl)-2,4-dihydro-3*H*-pyrazol-3-one (3af)



The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(4-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (0.226 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3af** as a white liquid (0.057 g, 58 % yield).

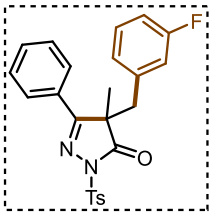
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.53 – 7.42 (m, 5H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 4.08 (d, *J* = 15.1 Hz, 1H), 4.00 (d, *J* = 15.1 Hz, 1H), 1.64 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.1, 160.9, 145.9, 138.4, 134.6, 131.6, 130.4, 129.9, 129.4 (2C), 129.2, 128.2, 126.9, 126.0 (q, *J* = 272.11 Hz), 125.1 (q, *J* = 3.7 Hz), 55.9, 42.2, 23.1, 21.7. **^{19}F{^{1}H} NMR (471 MHz)** δ -62.5. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{22}F_3N_2O_3S$ $[M+H]^+$ 487.1298; found 487.1296.

Methyl-4-((4-methyl-5-oxo-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazo 4-yl)methyl)benzoate (3ag)



The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(4-(methoxycarbonyl)phenyl)iodonium trifluoromethanesulfonate (0.218 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ag** as a white solid (0.069 g, 72% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.37–7.31 (m, 3H), 7.29 – 7.26 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H), 3.13 (d, *J* = 13.8 Hz, 1H), 3.10 (d, *J* = 13.8 Hz, 1H), 2.31 (s, 3H), 1.58 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.1, 166.6, 161.0, 145.7, 139.5, 134.5, 131.8, 130.9, 129.9, 129.5, 129.2, 129.0, 128.8, 128.1, 127.0, 55.9, 52.1, 42.5, 23.1, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{25}CO_2N_2O_3S$ $[M+H]^+$: 477.1479; found 477.1476.

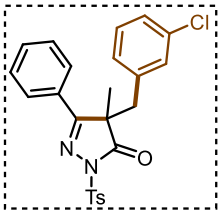
4-(3-Fluorobenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ah)



The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(3-fluorophenyl)iodonium trifluoromethanesulfonate (0.226 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ah** as a white solid (0.056 g, 64% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 – 7.80 (m, 2H), 7.79 – 7.70 (m, 2H), 7.54 – 7.44 (m, 3H), 7.28 – 7.23 (m, 2H), 6.80 – 6.74 (m, 1H), 6.66 – 6.56 (m, 1H), 6.39 (d, *J* = 7.7 Hz, 1H), 6.34 – 6.29 (m, 1H), 3.25 (d, *J* = 13.8 Hz, 1H), 3.16 (d, *J* = 13.8 Hz, 1H), 2.44 (s, 3H), 1.68 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 174.8, 161.9 (d, *J* = 218.8 Hz), 160.5, 145.2, 136.3 (d, *J* = 7.4 Hz), 134.2, 131.0, 130.1, 129.6, 129.4 (d, *J* = 8.2 Hz), 128.9, 127.7, 126.6, 124.4 (d, *J* = 2.9 Hz), 115.8 (d, *J* = 21.6 Hz), 113.8 (d, *J* = 20.9 Hz), 55.6, 41.9 (d, *J* = 1.6 Hz), 22.7, 21.5. **^{13}F{^{1}H} NMR (471**

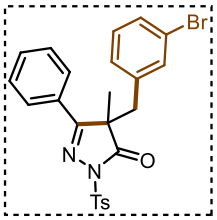
MHz $CDCl_3$) δ -112.1. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}FN_2O_3S$ $[M+H]^+$ 437.1330; found 437.1318.

4-(3-Chlorobenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-Pyrazol-3-one (3ai)



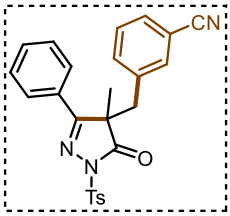
The compound was prepared according to **GP2** using (*E*)-*N*′-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(3-chlorophenyl)iodonium trifluoromethanesulfonate (0.198 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ai** as a white solid (0.055 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$);** δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.46 (m, 3H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.8 Hz, 1H), 6.60 (s, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 3.21 (d, *J* = 13.8 Hz, 1H), 3.12 (d, *J* = 13.8 Hz, 1H), 2.45 (s, 3H), 1.69 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$);** δ 174.9, 161.1, 145.3, 136.1, 134.5, 133.8, 131.3, 130.4, 129.9, 129.41, 129.37, 129.2, 127.9, 127.4, 127.1, 126.9, 55.8, 42.0, 23.0, 21.8. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}ClN_2O_3S$ $[M+H]^+$ 453.1034; found 453.1009.

4-(3-Bromobenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3aj)



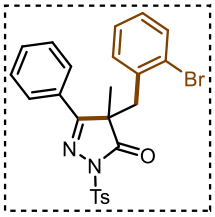
The compound was prepared according to **GP2** using (*E*)-*N*′-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(3-bromophenyl)iodonium trifluoromethanesulfonate (0.234 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3aj** as a white solid (0.061 g, 61% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.47 (m, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.75 (s, 1H), 6.66 (t, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H), 2.45 (s, 3H), 1.69 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 174.9, 161.2, 145.4, 136.4, 134.6, 132.4, 131.4, 130.4, 130.3, 130.0, 129.7, 130.0, 127.9, 127.6, 127.0, 122.1, 56.0, 42.0, 23.0, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}BrN_2O_3S$ $[M+H]^+$ 497.0529; found 497.0518.

3-(4-Methyl-5-oxo-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazol-4-yl)methyl)benzonitrile (3ak)



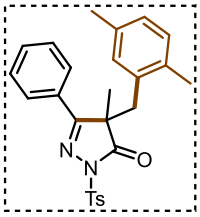
The compound was prepared according to **GP2** using (*E*)-*N*′-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(3-cyanophenyl)-iodonium trifluoromethanesulfonate (0.189 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3ak** as a white liquid (0.052 g, 58% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.97 – 6.83 (m, 3H), 3.27 (d, *J* = 13.8 Hz, 1H), 3.18 (d, *J* = 13.8 Hz, 1H), 2.48 (s, 3H), 1.71 (s, 3H). **^{3}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 174.7, 160.8, 145.7, 135.7, 134.5, 133.6, 132.7, 131.7, 131.0, 130.1 (2C), 129.4, 129.0, 128.0, 126.9, 118.2, 112.3, 55.8, 41.9, 22.9, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{22}N_3O_3S$ $[M+H]^+$ 444.1376; found 444.1354.

4-(2-Bromobenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3al)



The compound was prepared according to **GP2** using (*E*)-*N*′-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(2-bromophenyl)iodonium trifluoromethanesulfonate (0.234 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3al** as a white solid (0.060 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.43 – 7.41 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 3H), 6.89 (t, *J* = 7.7 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 3.46 (d, *J* = 15.1 Hz, 1H), 3.40 (d, *J* = 15.1 Hz, 1H), 2.45 (s, 3H), 1.63 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.3, 162.3, 145.6, 134.7, 134.2, 133.2, 131.2, 130.2, 130.0, 129.7, 128.9, 128.7, 128.3, 127.3, 127.2, 125.2, 54.5, 40.9, 23.1, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{21}BrN_2O_3S$ $[M+H]^+$ 497.0529; found 497.0528.

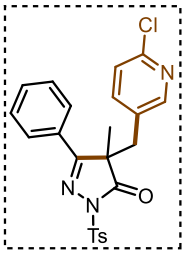
4-(2,5-Dimethylbenzyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3am)



The compound was prepared according to **GP2** using (*E*)-*N*′-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), bis(2,5-dimethylphenyl)iodonium trifluoromethanesulfonate (0.194 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **3am** as a white liquid (0.056 g, 63% yield). **^{1}H NMR (500 MHz,**

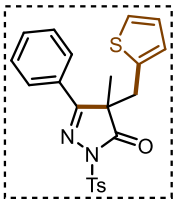
$CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 6.31 (s, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 3.06 (d, *J* = 14.4 Hz, 1H), 2.36 (s, 3H), 1.95 (s, 3H), 1.83 (s, 3H), 1.60 (s, 3H).**$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)** δ 175.6, 162.1, 145.2, 134.8, 133.7, 132.8, 132.5, 131.1, 130.9, 130.6, 129.9 (2C), 129.1, 128.0 (2C), 127.9, 55.6, 38.6, 23.2, 21.9, 20.7, 19.4. **HRMS-ESI** (*m/z*): calcd for $C_{26}H_{27}N_2O_3S$ $[M+H]^+$ 447.1737; found 447.1737.

4-((6-Chloropyridin-3-yl)methyl)-4-methyl-5-phenyl-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3an)



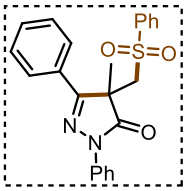
The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), (6-chloropyridin-3-yl)(mesityl)iodonium trifluoromethanesulfonate (0.202 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25% ethyl acetate in hexane) gave **3an** as a white liquid (0.050 g, 55% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 1.7 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.86 – 7.83 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 3.23 (d, *J* = 14.0 Hz, 1H), 3.13 (d, *J* = 14.0 Hz, 1H), 2.51 (s, 3H), 1.74 (s, 3H). **$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)** δ 170.2, 150.3, 146.4, 139.6, 134.2, 132.0, 131.4, 130.6, 130.3, 130.2, 129.7, 128.7, 128.2, 127.2, 123.9, 56.1, 39.0, 23.1, 22.3. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{21}ClN_3O_3S$ $[M+H]^+$ 454.0987; found 454.0998.

4-Methyl-5-phenyl-4-(thiophen-2-ylmethyl)-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one (3ao)



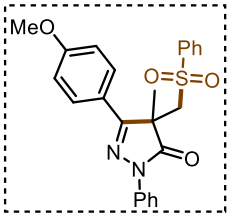
The compound was prepared according to **GP2** using (*E*)-*N'*-benzylidene-*N*-methacryloyl-4-methylbenzenesulfonohydrazide (0.070 g, 0.2 mmol, 1 equiv), di(thiophen-2-yl)-l3-iodaneyl trifluoromethanesulfonate (0.176 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20% ethyl acetate in hexane) gave **3ao** as a yellow solid (0.043 g, 50% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 3.3 Hz, 1H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.17 – 7.13 (m, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 2H), 3.33 – 3.06 (m, 2H), 2.45 (s, 3H), 1.62 (s, 3H). **$^{13}C\{^1H\}$ $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)** δ 174.7, 145.2, 134.7, 134.0, 133.8, 129.9, 129.5, 129.0, 128.5, 128.3, 128.2, 127.9, 127.8, 127.2, 56.2, 43.0, 22.8, 21.9. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{20}N_2O_3S_2$ $[M+H]^+$ 425.0988; found 425.0943.

4-Methyl-2,5-diphenyl-4-((phenylsulfonyl)methyl)-2,4-dihydro-3*H*-pyrazol-3-one (5aa)



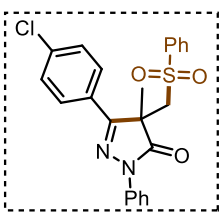
The compound was prepared according to **GP3** (*E*)-*N*'-benzylidene-N-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5aa** as a white solid (0.064 g, 79% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.81 – 7.77 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.39 (d, *J* = 5.9 Hz, 4H), 7.28 – 7.23 (m, 3H), 4.03 (d, *J* = 15.0 Hz, 1H), 3.95 (d, *J* = 15.0 Hz, 1H), 1.58 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.5, 158.4, 138.6, 138.0, 134.1, 130.7, 130.5, 129.1, 129.0, 128.9, 128.4, 126.5, 125.7, 119.4, 61.6, 50.7, 24.41. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{20}N_2O_3S$ $[M+H]^+$ 405.1273; found 405.1272.

5-(4-Methoxyphenyl)-4-methyl-2-phenyl-4-((phenylsulfonyl)methyl)-2,4-dihydro-3*H*-pyrazol-3-one (5ba)



The compound was prepared according to **GP3** (*E*)-*N*'-(4-methoxybenzylidene)-*N*-phenylmethacrylohydrazide stearate—methane (0.059 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15% ethyl acetate in hexane) gave **5ba** as a white liquid (0.052 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 3H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.02 (d, *J* = 14.9 Hz, 1H), 3.91 (d, *J* = 14.9 Hz, 1H), 3.86 (s, 3H), 1.56 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.3, 161.3, 158.1, 138.6, 138.0, 133.9, 129.0, 128.8, 128.3, 128.1, 125.4, 123.4, 119.2, 114.2, 61.5, 55.4, 50.6, 24.5. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$ 435.1379; found 435.1377.

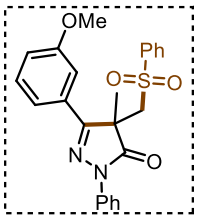
5-(4-Chlorophenyl)-4-methyl-2-phenyl-4-((phenylsulfonyl)methyl)-2,4-dihydro-3*H*-pyrazol-3-one (5ca)



The compound was prepared according to **GP3** (*E*)-*N*'-(4-chlorobenzylidene)-*N*-phenylmethacrylohydrazide (0.060 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (15%

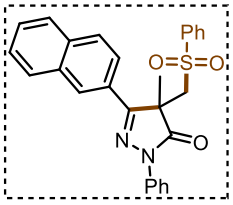
ethyl acetate in hexane) gave **5ca** as a white solid (0.062 g, 70% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.76 – 7.69 (m, 4H), 7.44 (t, *J* = 8.1 Hz, 3H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.26 (s, 1H), 4.02 (d, *J* = 14.9 Hz, 1H), 3.88 (d, *J* = 14.9 Hz, 1H), 1.56 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.3, 157.3, 138.4, 137.8, 136.5, 134.0, 129.15, 129.09, 128.9, 128.2, 127.7, 127.5, 125.7, 119.4, 61.4, 50.4, 24.2. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{20}ClN_2O_3S$ $[M+H]^+$ 439.0883; found 439.0878.

5-(3-Methoxyphenyl)-4-methyl-2-phenyl-4-((phenylsulfonyl)methyl)-2,4-dihydro-3*H*-pyrazol-3-one (5da)



The compound was prepared according to **GP3** (*E*)-*N*'-(3-methoxybenzylidene)-*N*-phenylmethacrylohydrazide (0.059 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (30 % ethyl acetate in hexane) gave **5da** as a white solid (0.055 g, 63% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.72 – 7.68 (m, 2H), 7.46 – 7.40 (m, 3H), 7.36 (d, *J* = 1.2 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.25 (d, *J* = 6.6 Hz, 2H), 6.97 – 6.93 (m, 1H), 4.01 (d, *J* = 15.0 Hz, 1H), 3.94 (d, *J* = 14.9 Hz, 1H), 3.86 (s, 3H), 1.58 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.2, 158.1, 139.2, 138.1, 137.8, 134.6, 130.5, 130.2, 128.8, 128.7, 128.55, 128.51, 126.2, 125.4, 125.3, 119.1, 61.3, 50.5, 24.2, 20.9. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{23}N_2O_4S$ $[M+H]^+$ 435.1379; found 435.1380.

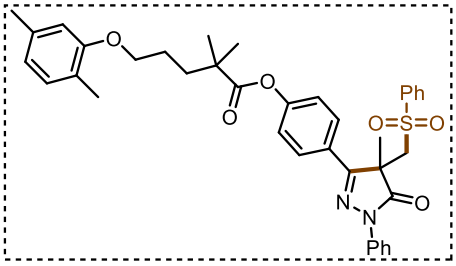
4-Benzyl-4-methyl-5-(naphthalen-1-yl)-2-tosyl-2,4-dihydro-3*H*-pyrazol-3-one--methane (5ea)



The compound was prepared according to **GP3** (*E*)-*N*'-(naphthalen-2-ylmethylene)-*N*-phenylmethacrylohydrazide (0.062 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (30 % ethyl acetate in hexane) gave **5ea** as a white solid (0.055 g, 60% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.10 – 8.05 (m, 1H), 8.01 – 7.94 (m, 3H), 7.86 – 7.81 (m, 3H), 7.70 – 7.67 (m, 2H), 7.55 – 7.50 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.28 (s, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 2H), 4.11 (s, 2H), 1.68 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.7, 158.1, 138.6, 138.0, 134.2, 133.8, 132.8, 129.1, 129.0, 128.8, 128.7, 128.28, 128.25, 127.9, 127.6, 126.9, 126.4,

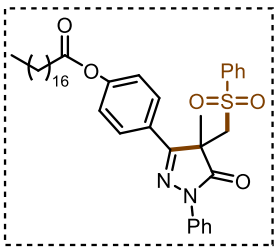
125.8, 123.4, 119.6, 61.8, 50.7, 24.6. **HRMS-ESI** (*m/z*): calcd for $C_{27}H_{23}N_2O_3S$ $[M+H]^+$ 455.1429; found 455.1437.

4-(4-Methyl-5-oxo-1-phenyl-4-((phenylsulfonyl)methyl)-4,5-dihydro-1*H*-pyrazol-3-yl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (5fa)



The compound was prepared according to **GP3** (*E*)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (0.102 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (30 % ethyl acetate in hexane) gave **5fa** as a white liquid (0.080 g, 61% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.72 – 7.66 (m, 2H), 7.47 – 7.41 (m, 3H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.71 – 6.63 (m, 2H), 4.04 – 4.00 (m, 3H), 4.01 (d, *J* = 5.5 Hz, 2H), 3.91 (d, *J* = 14.9 Hz, 1H), 2.32 (s, 3H), 2.19 (s, 3H), 1.91 (s, 4H), 1.57 (s, 3H), 1.40 (s, 6H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 175.8, 173.2, 157.3, 156.7, 152.4, 138.2, 138.0, 137.7, 136.4, 134.0, 130.3, 129.0, 128.7, 128.1, 127.4, 125.5, 123.5, 121.8, 120.0, 119.2,7 111.8, 67.6, 61.3, 50.4, 42.5, 37.0, 25.2, 25.0, 24.1, 21.3, 15.7. **HRMS-ESI** (*m/z*): calcd for $C_{38}H_{41}N_2O_6S$ $[M+H]^+$ 653.2685; found 653.2693.

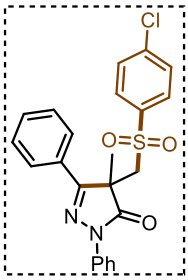
4-(4-Methyl-5-oxo-1-phenyl-4-((phenylsulfonyl)methyl)-4,5-dihydro-1*H*-pyrazol-3-yl)phenyl stearate--methane (5ga)



The compound was prepared according to **GP3** (*E*)-4-((2-methacryloyl-2-phenylhydrazineylidene)methyl)phenylstearate (0.110 g, 0.2 mmol, 1 equiv), diphenyliodonium trifluoromethanesulfonate (0.171 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (30 % ethyl acetate in hexane) gave **5ga** as a white liquid (0.087 g, 63% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.32 – 7.26 (m, 3H), 7.12 (d, *J* = 8.6 Hz, 2H), 4.04 (d, *J* = 15.0 Hz, 1H), 3.93 (d, *J* = 15.0 Hz, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.57 (s, 3H), 1.28 (br s, 28H), 0.90 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.3, 171.9, 157.4, 152.3, 138.3, 137.8, 134.1, 129.1, 129.0, 128.2,

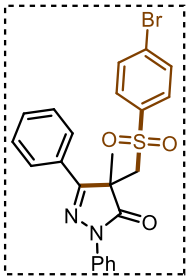
127.5, 125.7, 124.8, 122.0, 119.4, 61.5, 50.5, 34.4, 31.9, 29.7 (4C), 29.68 (2C), 29.6, 29.5, 29.4, 29.3, 29.1, 24.9, 24.2, 22.7, 14.1. **HRMS-ESI** (*m/z*): calcd for $C_{42}H_{57}N_2O_5S$ $[M+H]^+$ 687.3826; found 687.3827.

4-(4-Chlorophenyl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5ab)



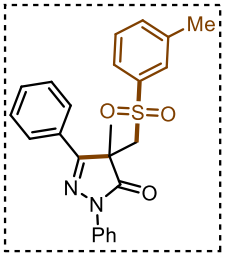
The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (0.198 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5ab** as a white solid (0.063 g, 72% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.37 (m, 5H), 7.27 (d, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 4.03 (d, *J* = 15.1 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H), 1.59 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.4, 158.1, 141.0, 137.9, 136.7, 130.6, 130.5, 129.9, 129.4, 129.1, 128.9, 126.3, 125.8, 119.3, 61.6, 50.7, 24.4. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{20}ClN_2O_3S$ $[M+H]^+$ 439.0878; found 439.0880.

4-(((4-Bromophenyl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one (5ac)



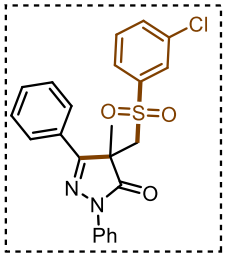
The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), bis(4-bromophenyl)iodonium trifluoromethanesulfonate (0.234 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (20-25 % ethyl acetate in hexane) gave **5ac** as a white liquid (0.067 g, 69% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 – 7.91 (m, 2H), 7.78 – 7.68 (m, 4H), 7.48 – 7.36 (m, 5H), 7.28 (d, *J* = 0.8 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 4.06 (d, *J* = 15.1 Hz, 1H), 3.98 (d, *J* = 15.1 Hz, 1H), 1.60 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.7, 158.5, 141.5, 138.3, 137.1, 131.0, 130.9, 130.3, 129.8, 129.5, 129.3, 126.8, 126.2, 119.7, 62.0, 51.1, 24.8. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{20}BrN_2O_3S$ $[M+H]^+$ 483.0373; found 483.0369.

4-Methyl-2,5-diphenyl-4-((*m*-tolylsulfonyl)methyl)-2,4-dihydro-3*H*-pyrazol-3-one (5ad)



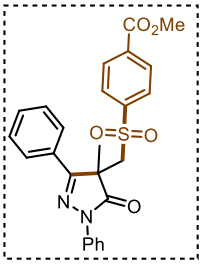
The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), bis-(4-(di-*m*-tolyl-l3-iodaneyl trifluoromethanesulfonate (0.183 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5ad** as a white solid (0.057 g, 68% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.81 – 7.77 (m, 2H), 7.54 – 7.51 (m, 1H), 7.48 – 7.37 (m, 6H), 7.26 – 7.16 (m, 3H), 4.02 (d, *J* = 15.0 Hz, 1H), 3.94 (d, *J* = 14.9 Hz, 1H), 2.15 (s, 3H), 1.58 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.4, 158.2, 139.4, 138.2, 137.9, 134.8, 130.6, 130.4, 129.0, 128.9, 128.70, 128.66, 126.4, 125.6, 125.4, 119.2, 61.5, 50.6, 24.3, 21.0. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{22}N_2O_3S$ $[M+H]^+$ 419.1424; found 419.1430.

4-(3-Chlorophenyl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5ae)



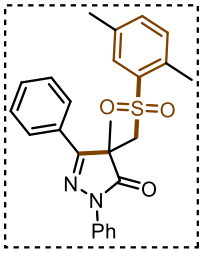
The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), bis(3-chlorophenyl)-l3-iodaneyl trifluoromethanesulfonate (0.198 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5ae** as a white solid (0.061 g, 69% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.75 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.66 (t, *J* = 1.8 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.33 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 3.96 (d, *J* = 15.0 Hz, 1H), 1.60 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.5, 157.9, 140.2, 137.9, 135.4, 134.2, 130.6, 130.5, 130.4, 129.1, 128.8, 128.56, 126.58, 126.2, 125.8, 119.4, 61.5, 50.6, 24.3. **HRMS-ESI** (*m/z*): calcd for $C_{23}H_{20}ClN_2O_3S$ $[M+H]^+$]$^+$ 439.0878; found 439.0879.

Methyl-4-(4-methyl-5-oxo-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-4-yl)methyl)sulfonyl)benzoate (5af)



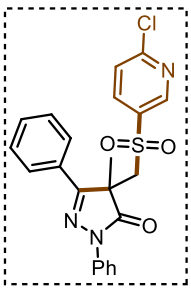
The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), bis(4-(methoxycarbonyl)phenyl)iodonium trifluoromethanesulfonate (0.218 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5af** as a white liquid (0.066 g, 71% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 – 7.85 (m, 4H), 7.75 – 7.73 (m, 4H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 1H), 4.05 (d, *J* = 15.1 Hz, 1H), 3.97 (d, *J* = 15.0 Hz, 1H), 3.91 (s, 3H), 1.59 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.4, 165.3, 158.0, 142.0, 137.9, 135.0, 130.6, 130.5, 130.2, 129.0, 128.9, 128.5, 126.4, 125.7, 119.3, 61.4, 52.7, 50.7, 24.4. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{23}N_2O_5S$ $[M+H]^+$ 463.1322; found 463.1325.

4-(((2,5-Dimethylphenyl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5ag)



The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), bis(2,5-dimethylphenyl)-l3-iodaneyl trifluoromethanesulfonate (0.194 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5ag** as a white solid (0.049 g, 56% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 – 7.86 (m, 2H), 7.83 – 7.79 (m, 2H), 7.46 (s, 1H), 7.43 – 7.37 (m, 5H), 7.25 – 7.19 (m, 1H), 7.03 (s, 2H), 4.05 (d, *J* = 14.9 Hz, 1H), 3.92 (d, *J* = 14.9 Hz, 1H), 2.60 (s, 3H), 1.98 (s, 3H), 1.59 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.3, 158.5, 138.0, 136.6, 135.9, 135.3, 135.0, 132.6, 130.9, 130.8, 130.5, 128.9, 128.8, 126.5, 125.5, 119.1, 60.2, 50.7, 24.5, 20.5, 19.9. **HRMS-ESI** (*m/z*): calcd for $C_{25}H_{25}N_2O_3S$ $[M+H]^+$ 433.1580; found 433.1582.

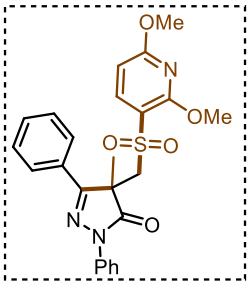
4-(6-Chloropyridin-3-yl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5ah)



The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), (6-chloropyridin-3-yl)(mesityl)-l3-iodaneyl trifluoromethanesulfonate (0.202 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2·6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5ah** as a

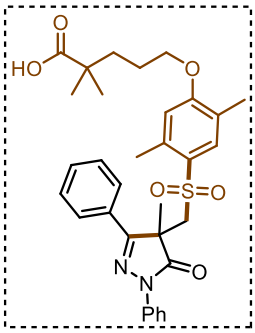
yellow liquid (0.057 g, 65% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.47 – 7.42 (m, 5H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.16 (s, 1H), 4.03 (d, *J* = 15.1 Hz, 1H), 3.96 (d, *J* = 15.1 Hz, 1H), 1.59 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 173.4, 158.1, 141.0, 137.9, 136.7, 130.6, 130.5, 129.9, 129.4 (2C), 129.0, 128.9, 126.4, 125.8, 119.3, 61.6, 50.7, 24.4. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{19}ClN_3O_3S$ $[M+H]^+$ 439.0757; found 439.0857.

4-(((2,6-dimethoxypyridin-3-yl)sulfonyl)methyl)-4-methyl-2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (5ai)



The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), (2,6-dimethoxypyridin-3-yl)(2,4-dimethyloxazol-5-yl)-l3-iodaneyl trifluoromethanesulfonate (0.204 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5ai** as a yellow solid (0.062 g, 66% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 3H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 6.02 (d, *J* = 8.5 Hz, 1H), 4.25 (d, *J* = 15.2 Hz, 1H), 4.08 (d, *J* = 15.2 Hz, 1H), 3.97 (s, 3H), 3.78 (s, 3H), 1.63 (s, 3H). **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)** δ 174.1, 167.0, 160.6, 157.8, 142.8, 138.3, 130.54, 130.48, 129.2, 128.8, 126.1, 125.9, 119.6, 111.5, 102.9, 58.8, 54.7, 54.5, 50.9, 24.4. **HRMS-ESI** (*m/z*): calcd for $C_{24}H_{24}N_3O_5S$ $[M+H]^+$ 466.1431; found 466.1437.

5-(3,6-Dimethyl-2-(4-methyl-5-oxo-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-4-yl)methyl)sulfonyl)phenoxy)-2,2-dimethylpentanoic acid (5aj)



The compound was prepared according to **GP3** (*E*)-*N'*-benzylidene-*N*-phenylmethacrylohydrazide (0.053 g, 0.2 mmol, 1 equiv), (4-((4-carboxy-4-methylpentyl)oxy)-2,5-dimethylphenyl)(3,5-dimethyl-isoxazol-4-yl)iodonium 4-methylbenzenesulfonate (0.248 g, 0.4 mmol, 2 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.003 g, 0.004 mmol, 0.02 equiv), DABSO (0.091 g, 0.2 mmol, 2 equiv), K_3PO_4 (0.042 g, 0.2 mmol, 1 equiv). Purification by column chromatography (25-30 % ethyl acetate in hexane) gave **5aj** as a white liquid (0.059 g, 51% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 – 7.85 (m, 2H), 7.82 – 7.75 (m, 2H), 7.41 – 7.39 (m, 3H), 7.37 (dd, *J* = 5.6, 2.9 Hz, 2H), 7.26 (s, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.38 (s, 1H), 4.03 (d, *J* = 15.0 Hz, 1H), 3.90 (d, *J* = 14.9 Hz, 1H), 3.86 – 3.76 (m, 2H),

2.55 (s, 3H), 1.82 (s, 3H), 1.78 –1.68 (m, 4H), 1.56 (s, 3H), 1.28 (s, 6H). **$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)** δ 183.9, 173.4, 161.2, 158.4, 138.7, 138.1, 133.0, 130.7, 130.4, 128.8, 128.6, 126.5, 126.3, 125.3, 125.0, 118.8, 113.8, 68.2, 60.4, 50.8, 42.0, 36.8, 25.15, 25.12, 25.0, 24.7, 20.5, 15.4. **HRMS-ESI** (*m/z*): calcd for $C_{32}H_{37}N_2O_6S$ $[M+H]^+$ 577.2367; found 577.2380.

11. References:

1. S. P. Panda, R. Dash, S. K. Hota, S. Murarka, *Org. Lett.* 2024, **26**, 3667–3672.

2. M. Bielawski, M. Zhu, B. Olofsson, *Adv. Synth. Catal.* 2007, **349**, 2610–2618.

3. P. K. Pramanick, Z. Zhou, Z.-L. Hou, B. Yao, *J. Org. Chem.* 2019, **84**, 5684–5694.

4. G. An, L. Wang, J. Han, *Org. Lett.* 2021, **23**, 8688-8693.

5. X. Wu, J. Han, L. Wang, *J. Org. Chem.* 2018, **83**, 49–56.

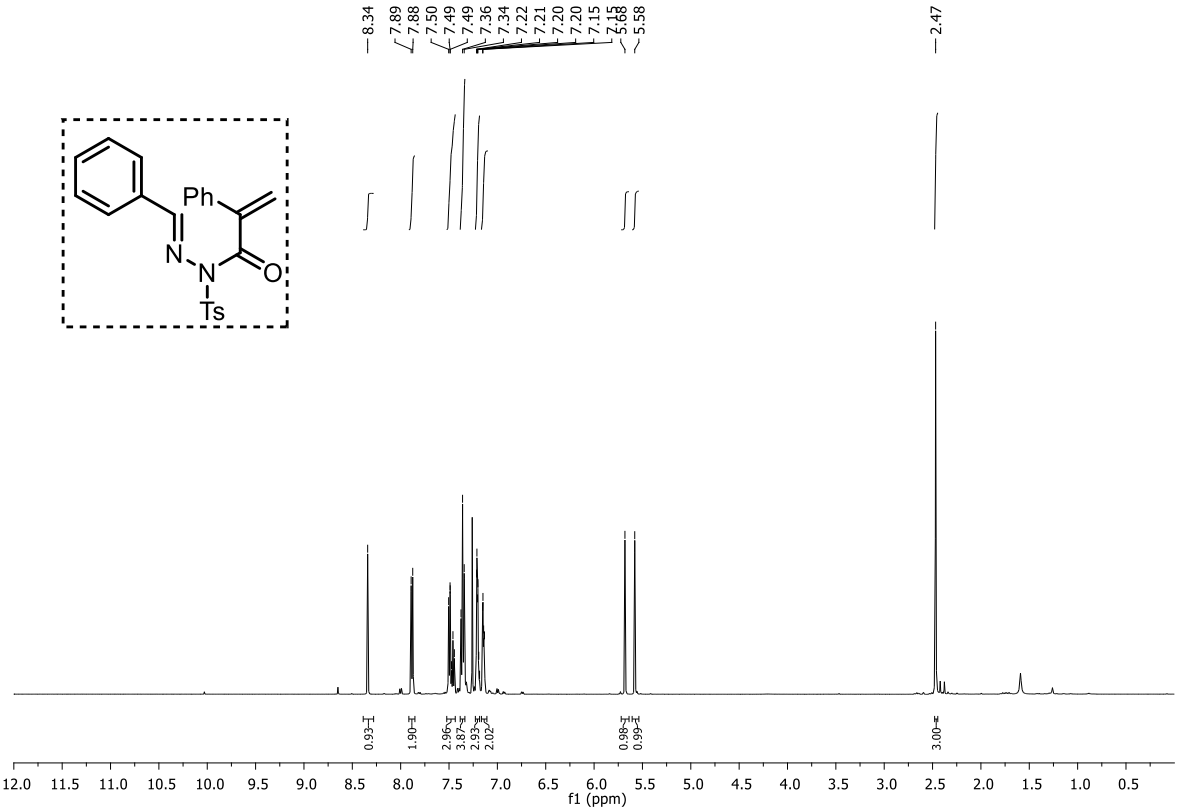
6. X. Hong, Q. Tan, B. Liu, B. Xu, *Angew. Chem. Int. Ed.* 2017, **56**, 3961–3965.

7. M. Bielawski, J. Malmgren, L. M. Pardo, Y. Wikmark, B. Olofsson, *ChemistryOpen* **2014**, *3*, 19–22.

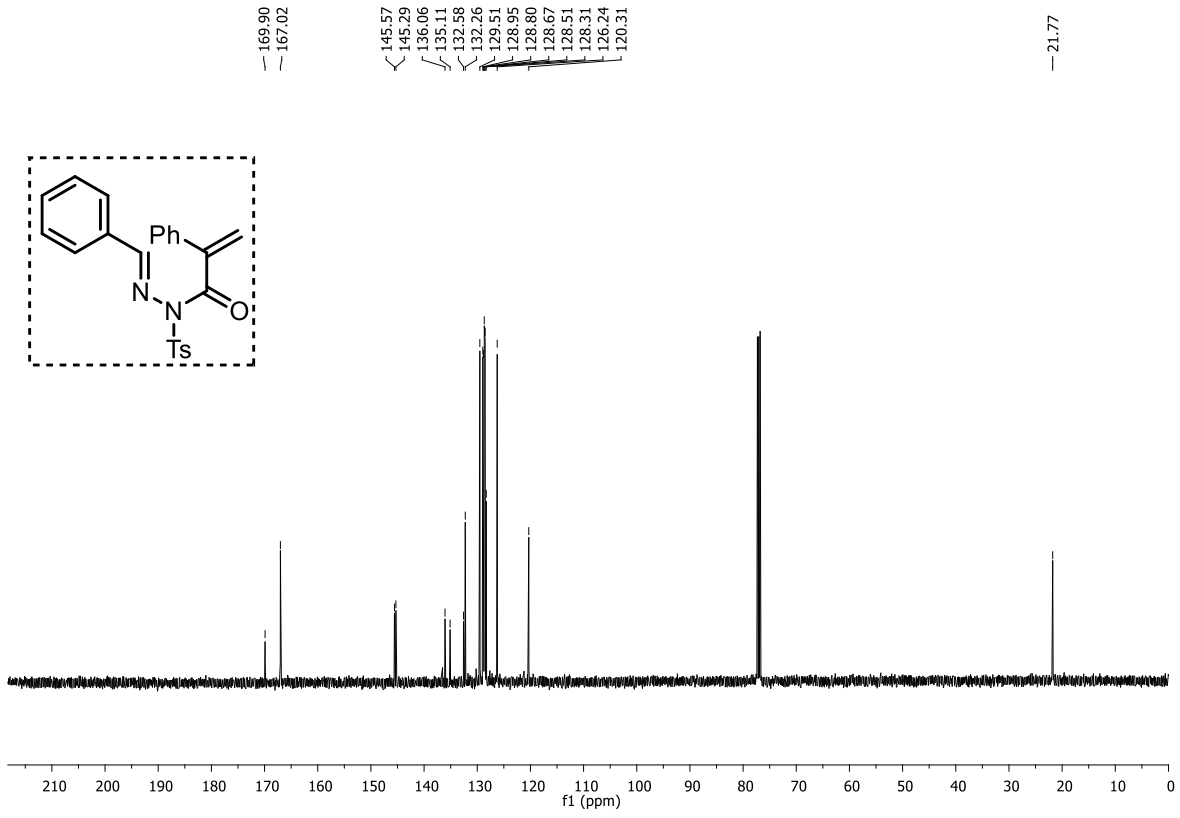
8. Y. Chen, Y. Gu, H. Meng, Q. Shao, Z. Xu, W. Bao, Y. Gu, X.-S. Xue, Y. Zhao, *Angew. Chem. Int. Ed.* 2022, **61**, e202201240.

9. N. Purkait, G. Kervefors, E. Linde, B. Olofsson, *Angew. Chem. Int. Ed.* 2018, **57**, 11427–11431.

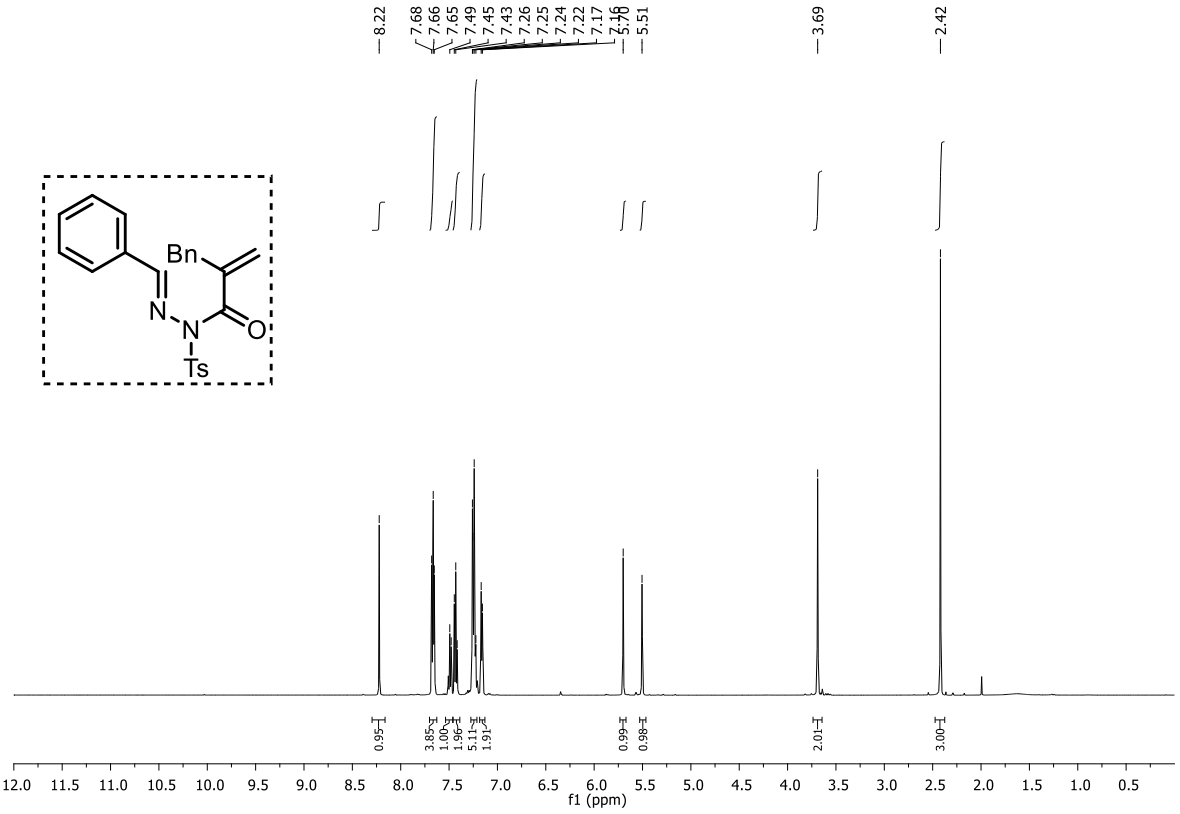
12. NMR Spectra of Compounds, ^{1}H NMR spectrum of 1t ($CDCl_3$, 500 MHz)



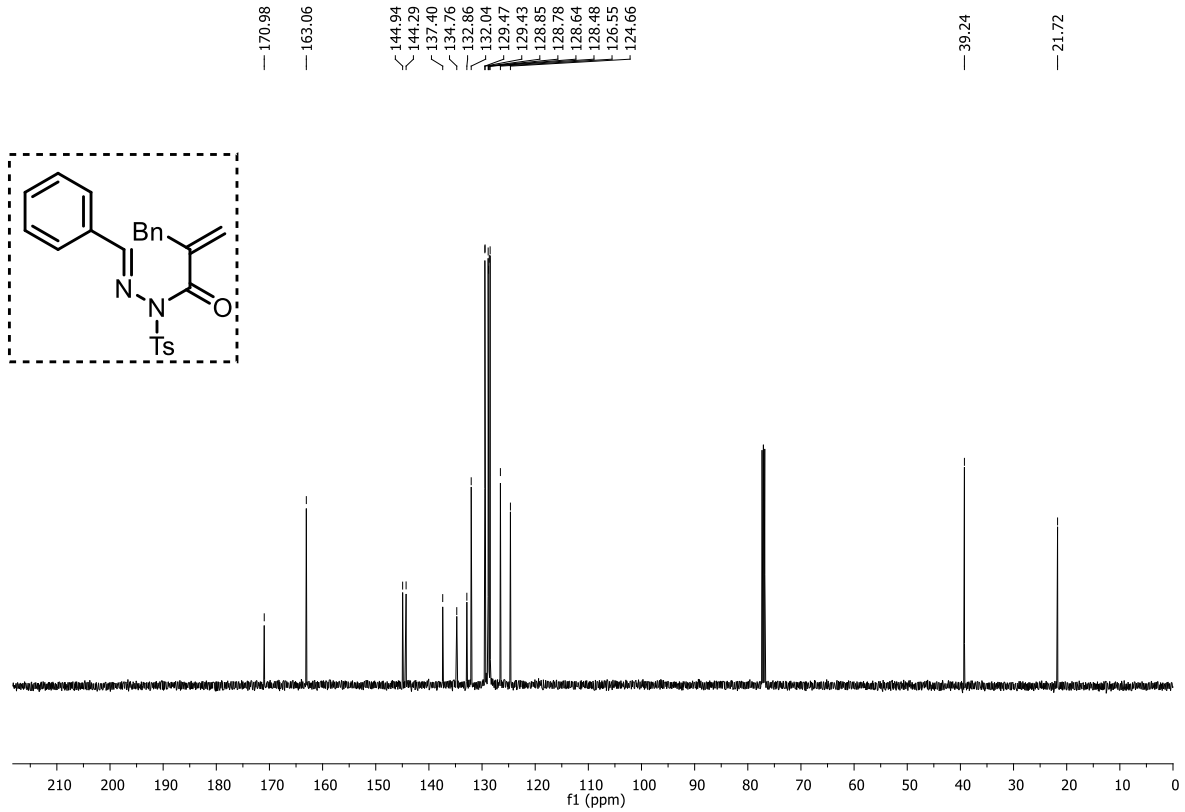
^{13}C {^{1}H} NMR spectrum of 1t ($CDCl_3$, 126 MHz)



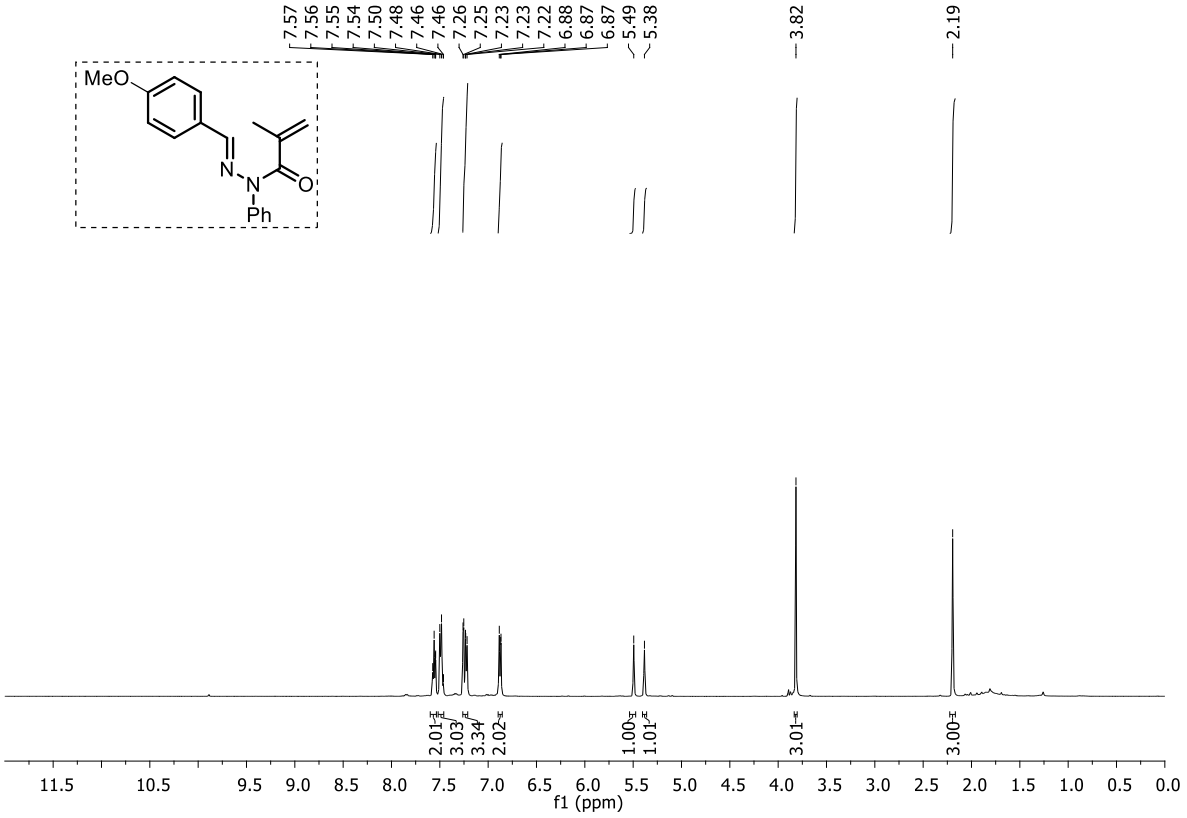
^{1}H NMR spectrum of 1u ($CDCl_3$, 500 MHz)



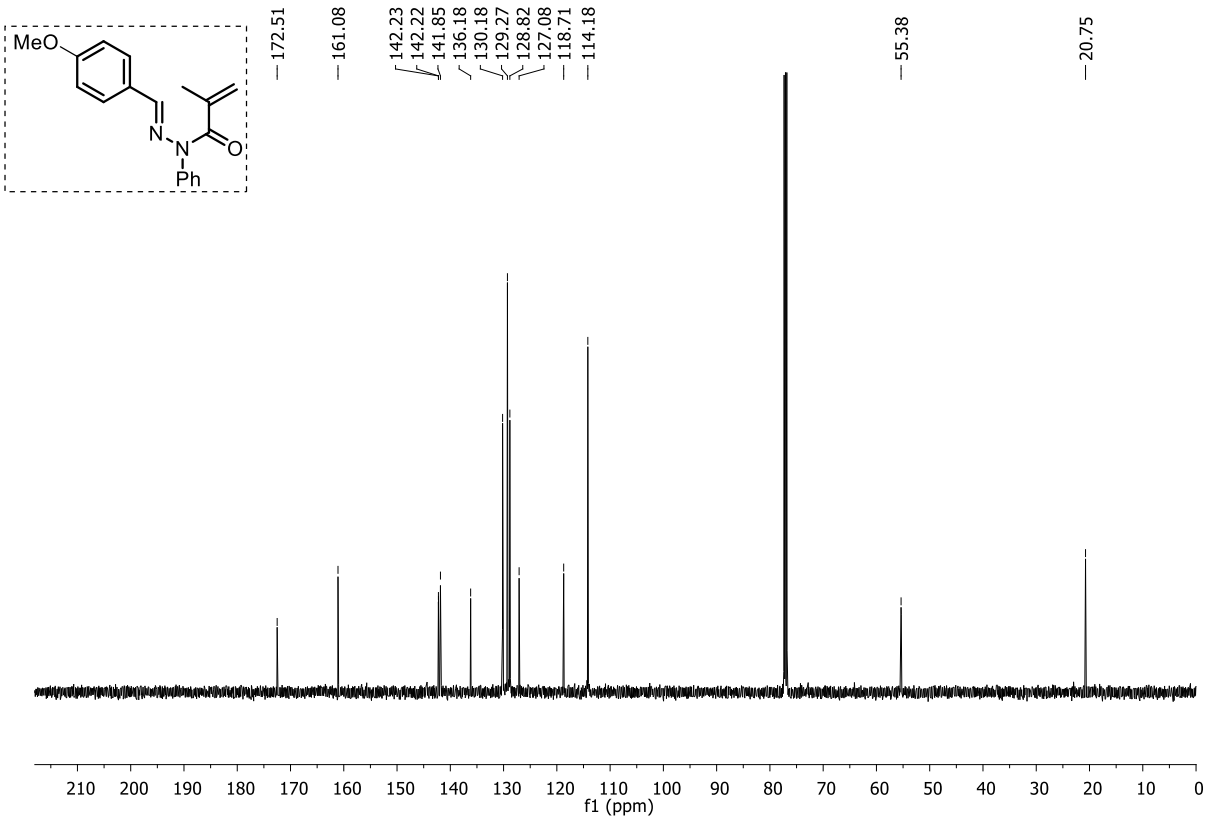
^{13}C {^{1}H} NMR spectrum of 1u ($CDCl_3$, 126 MHz)



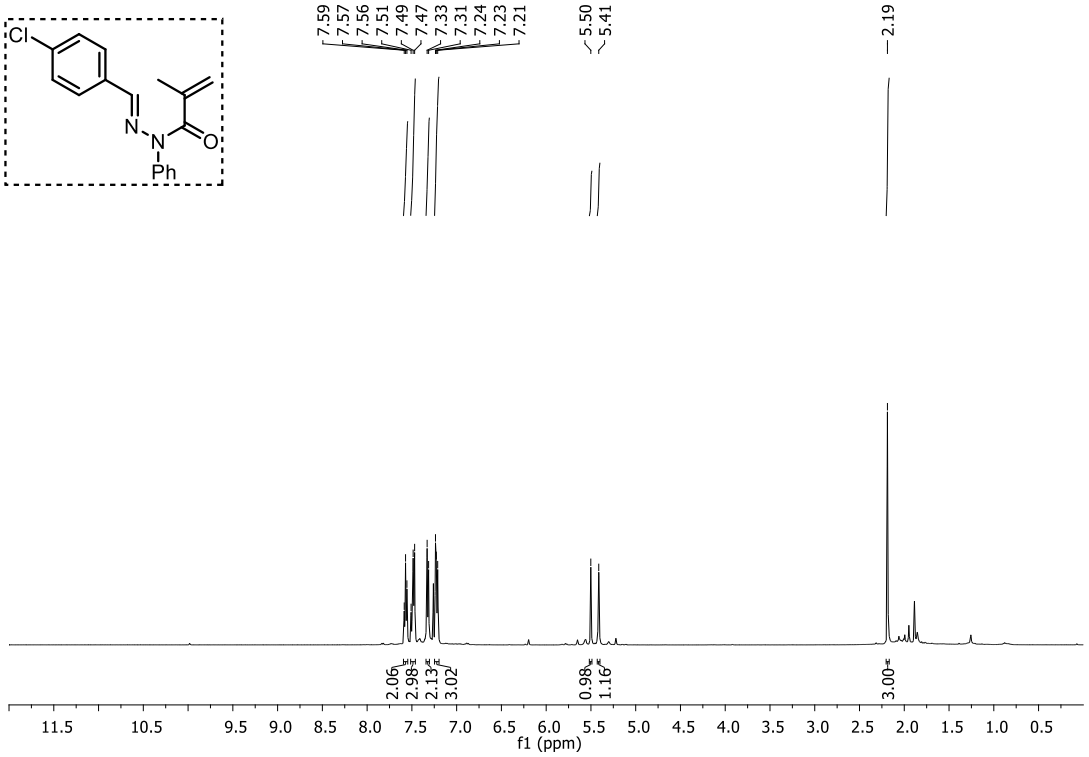
^{1}H NMR spectrum of 4b ($CDCl_3$, 500 MHz)



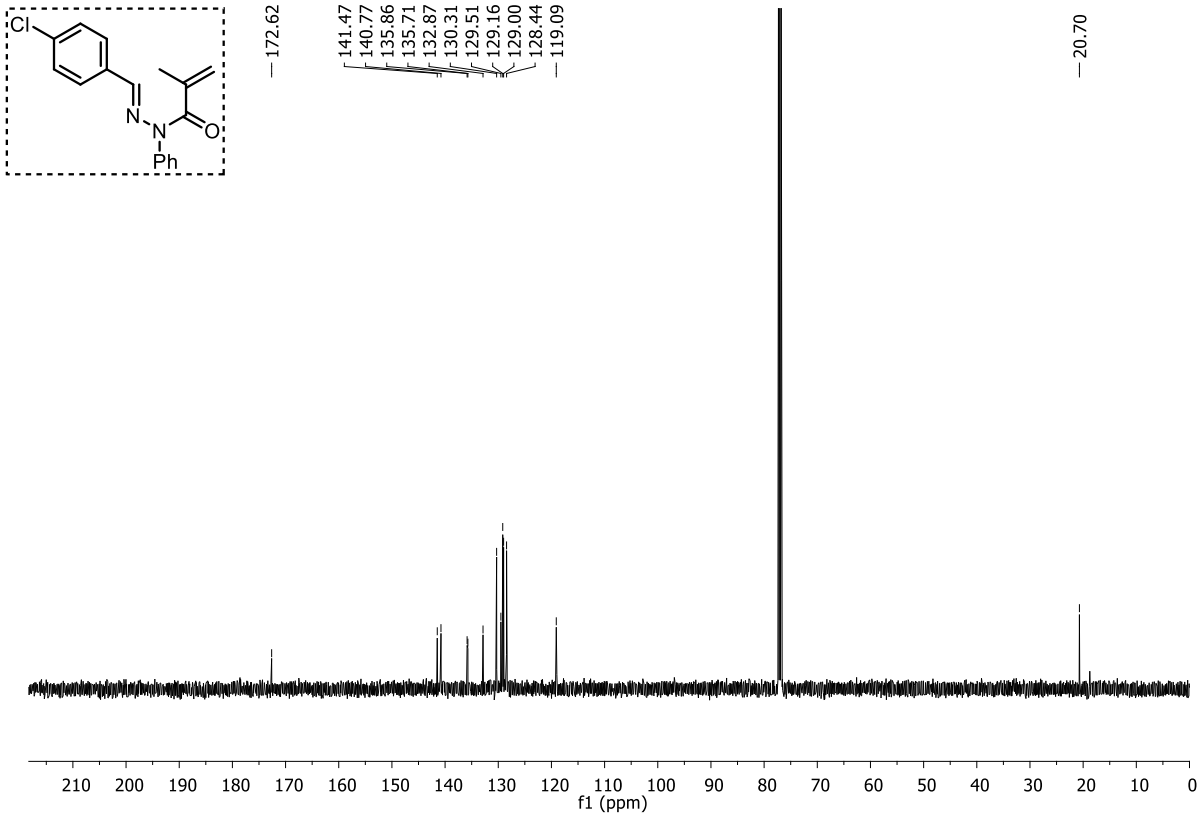
^{13}C {^{1}H} NMR spectrum of 4b ($CDCl_3$, 126 MHz)



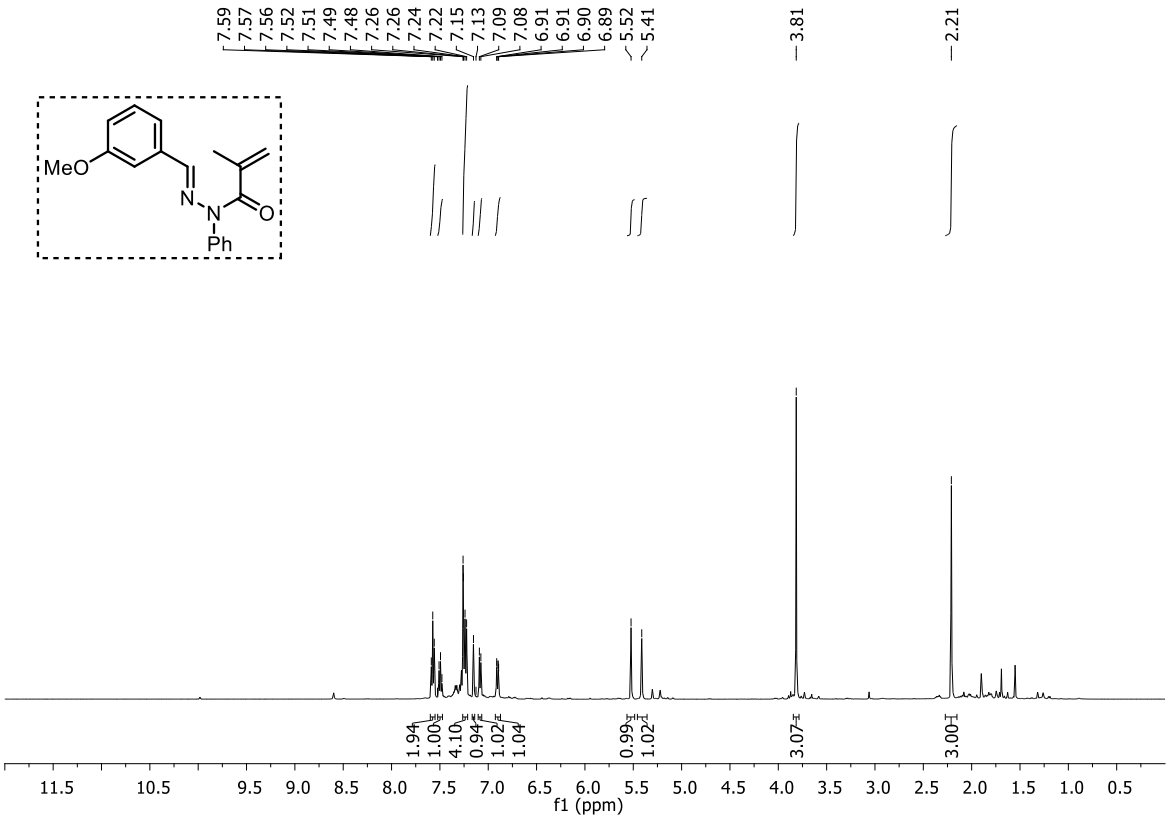
^{1}H NMR spectrum of 4c ($CDCl_3$, 500 MHz)



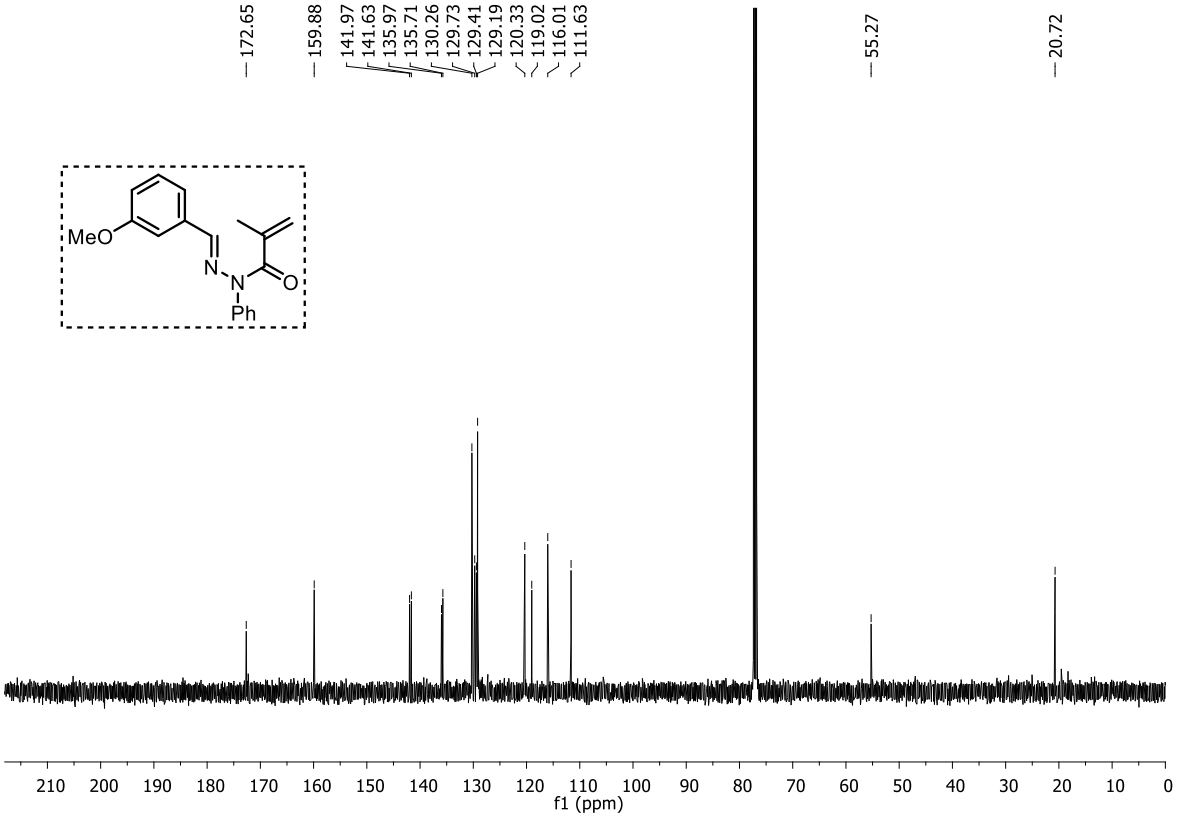
^{13}C{^{1}H} NMR spectrum of 4c ($CDCl_3$, 126 MHz)



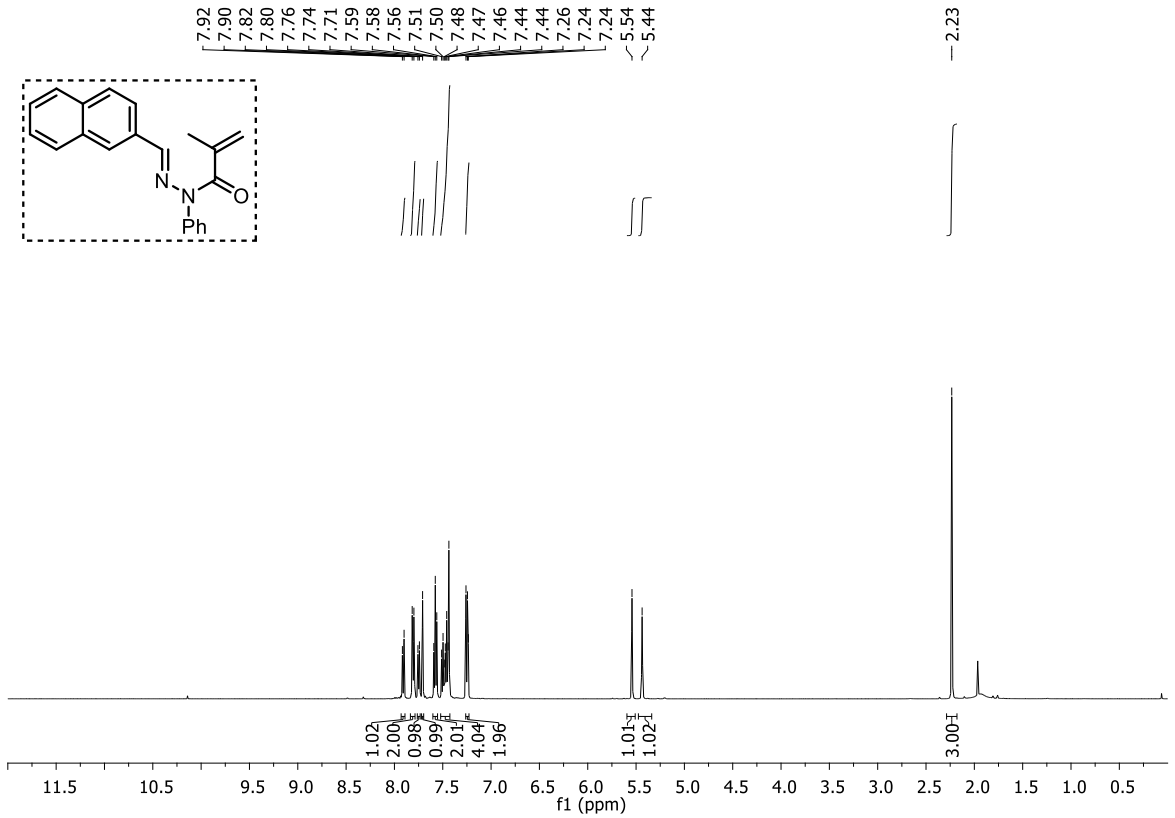
^{1}H NMR spectrum of 4d ($CDCl_3$, 500 MHz)



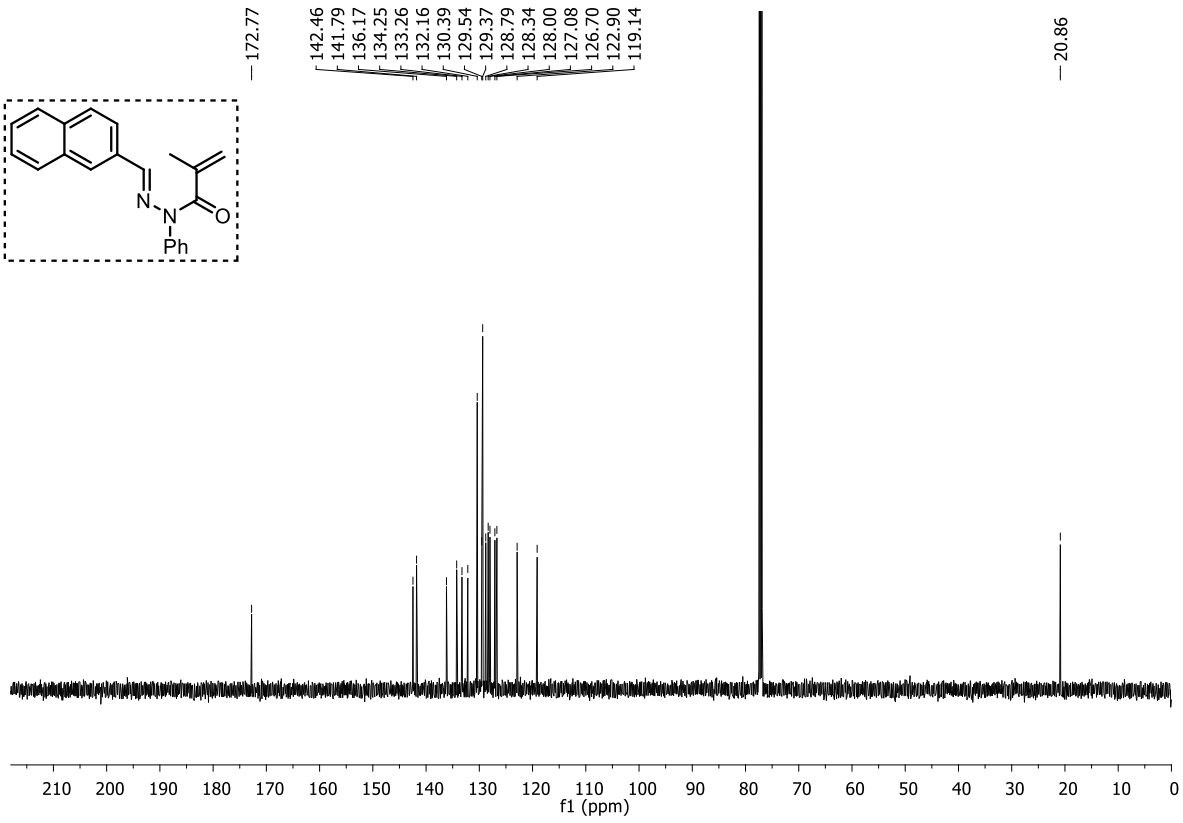
^{13}C {^{1}H} NMR spectrum of 4d ($CDCl_3$, 126 MHz)



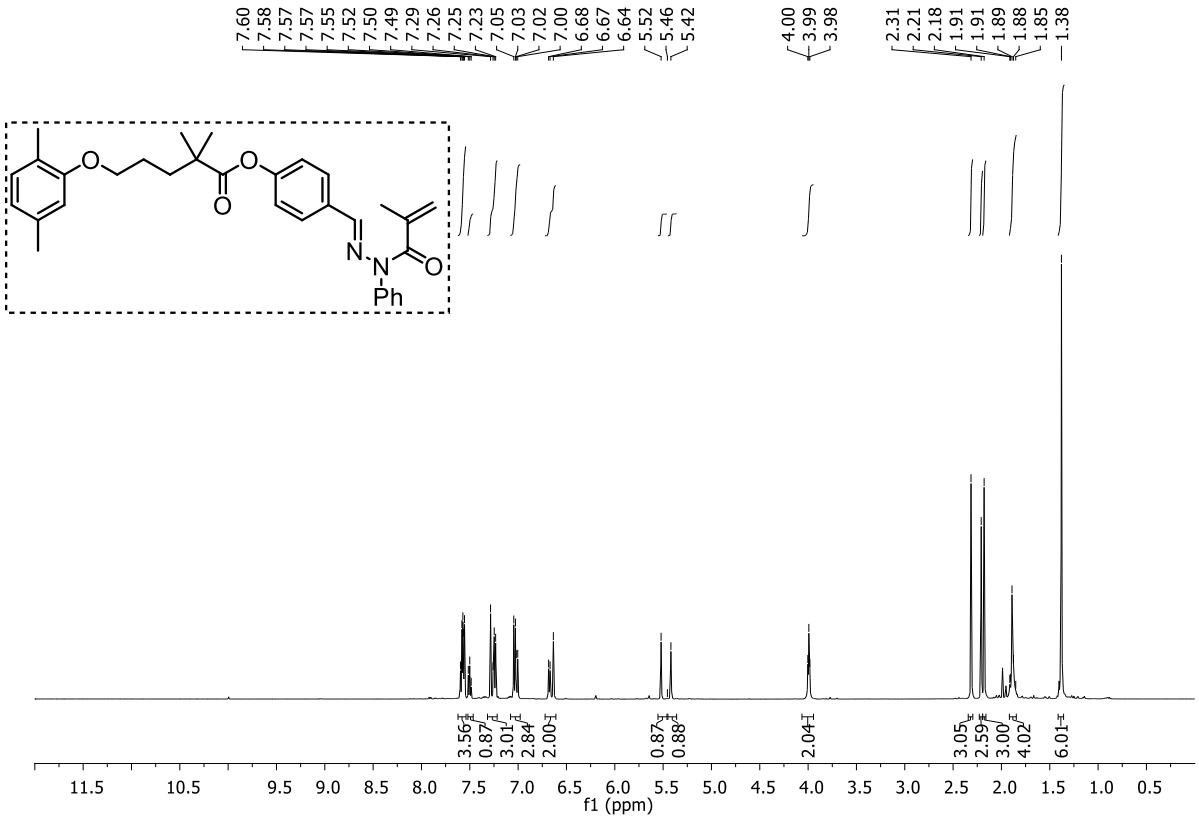
^{1}H NMR spectrum of 4e ($CDCl_3$, 500 MHz)



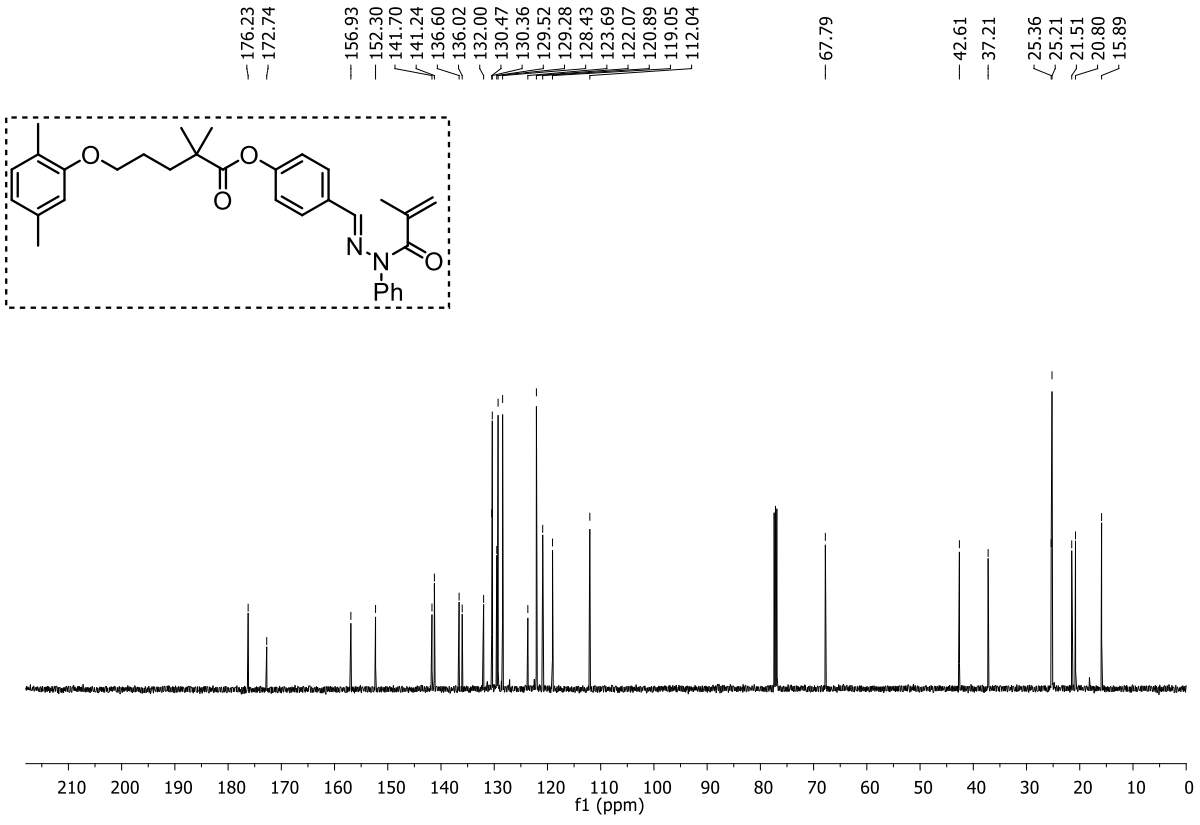
^{13}C {^{1}H} NMR spectrum of 4e ($CDCl_3$, 126 MHz)



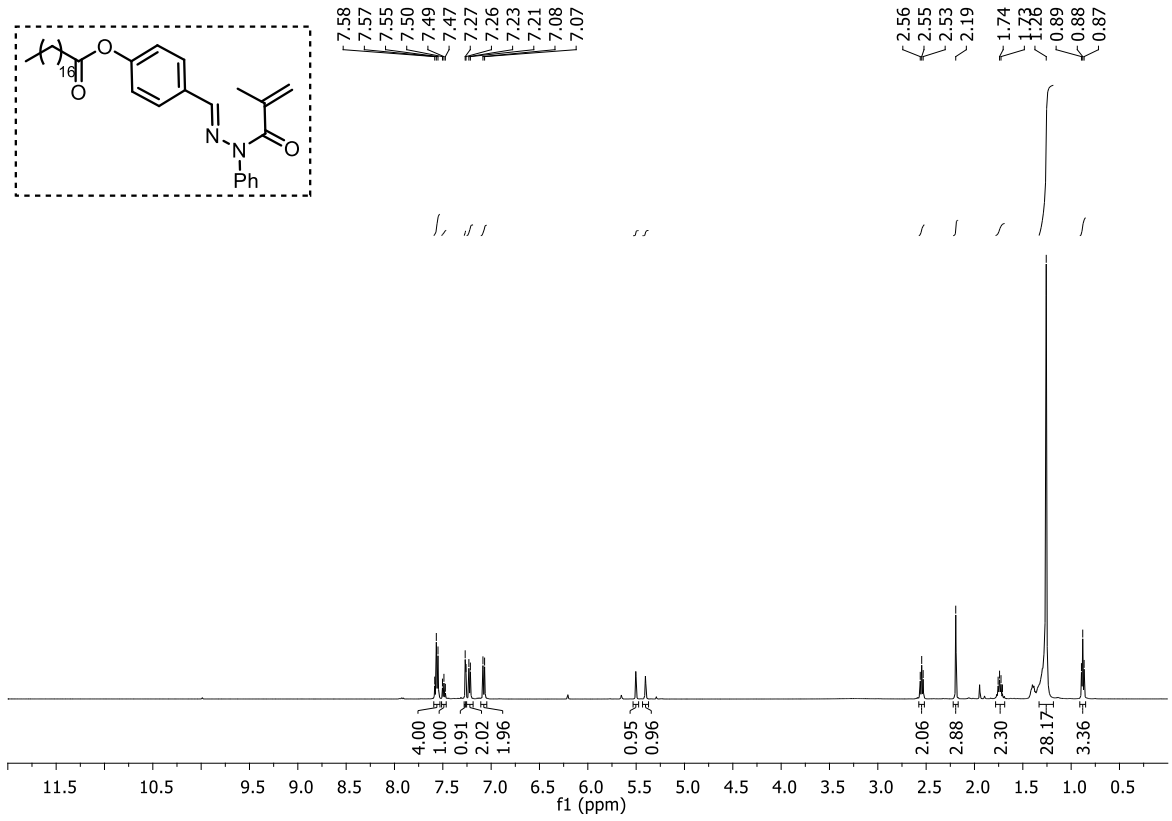
^{1}H NMR spectrum of 4f ($CDCl_3$, 500 MHz)



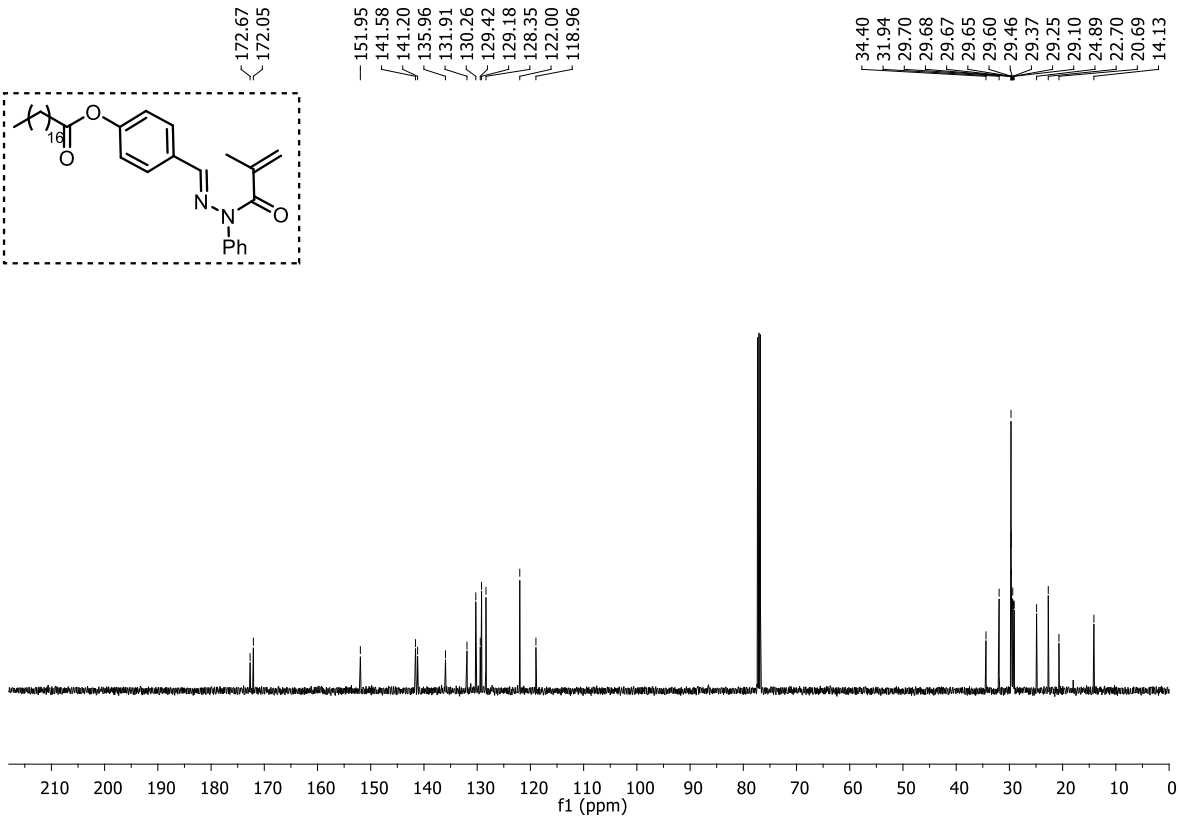
^{13}C {^{1}H} NMR spectrum of 4f ($CDCl_3$, 126 MHz)



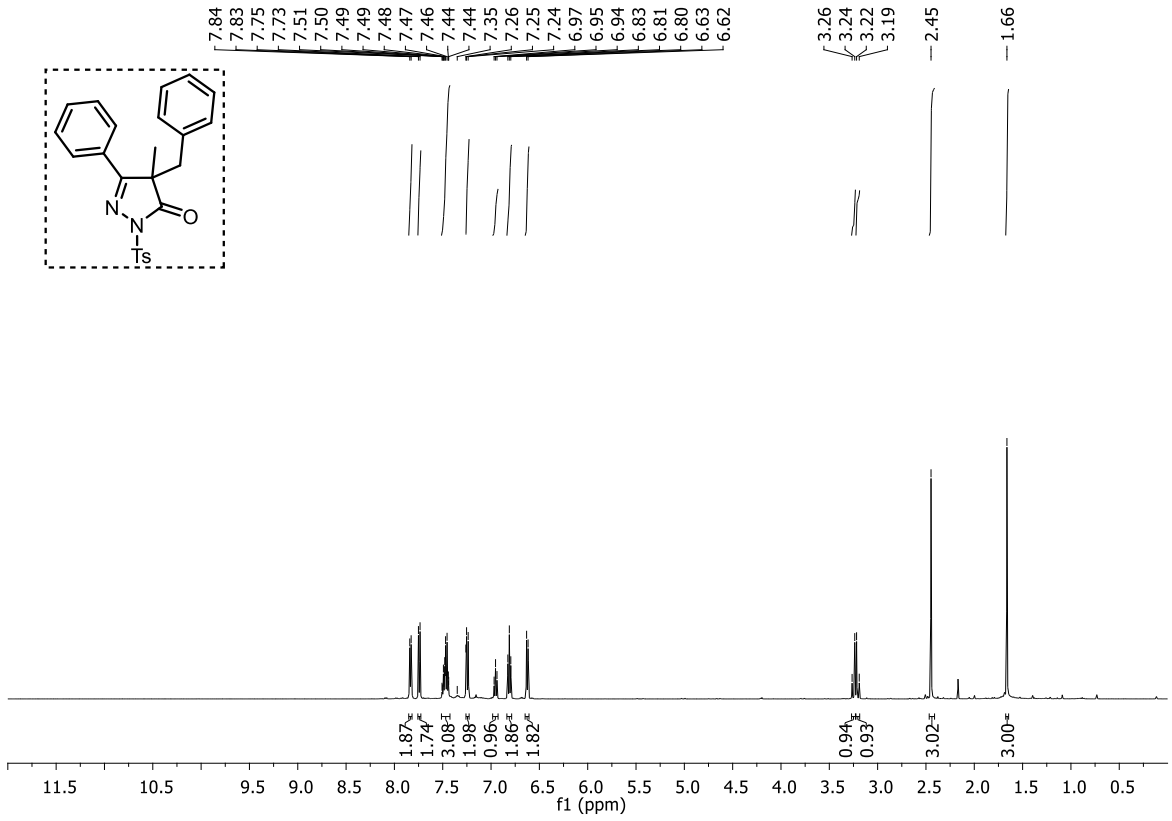
^{1}H NMR spectrum of 4g ($CDCl_3$, 500 MHz)



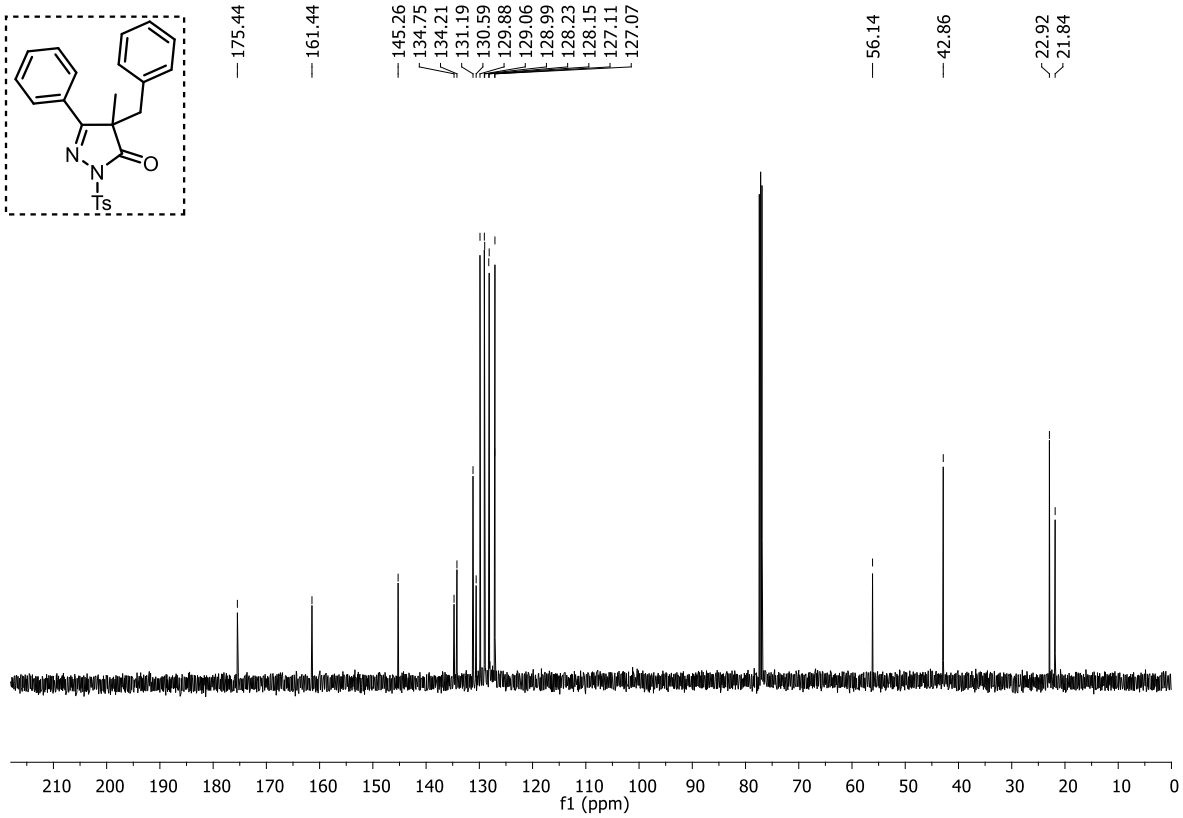
^{13}C {^{1}H} NMR spectrum of 4g ($CDCl_3$, 126 MHz)



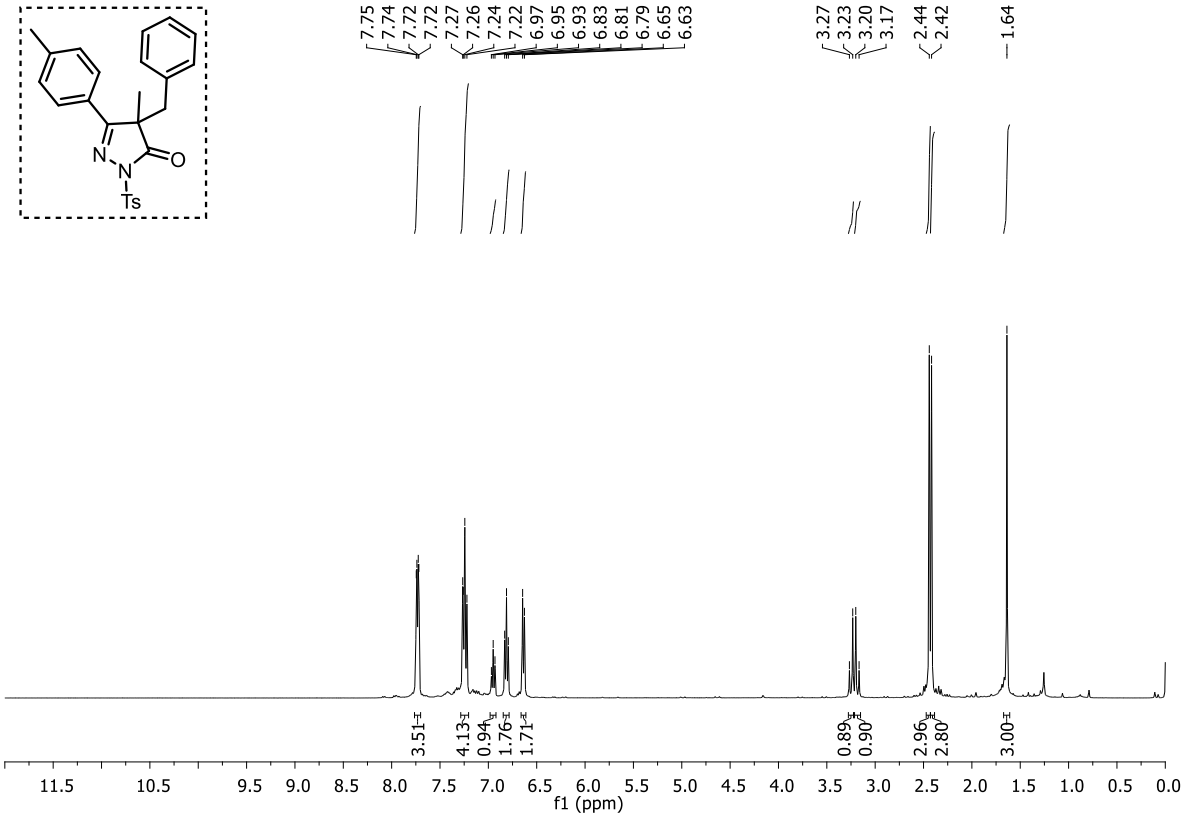
^{1}H NMR spectrum of 3aa ($CDCl_3$, 500 MHz)



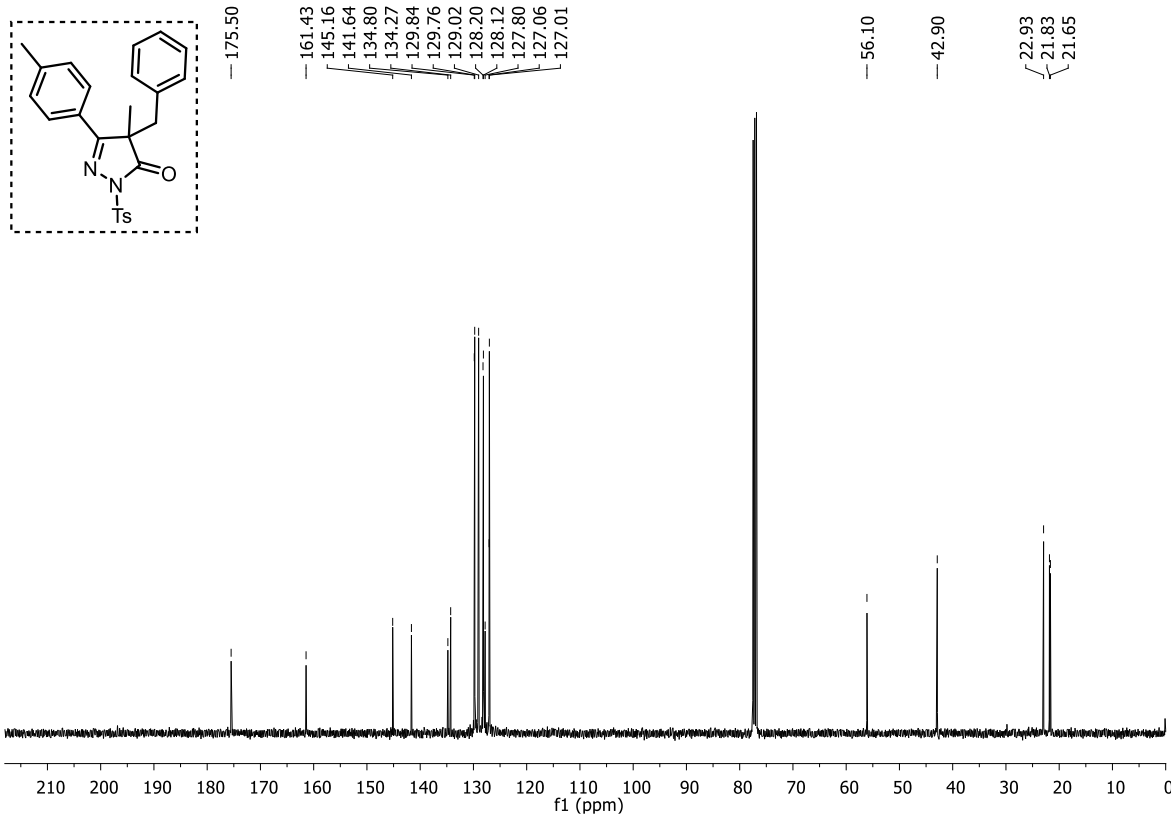
^{13}C {^{1}H} NMR spectrum of 3aa ($CDCl_3$, 126 MHz)



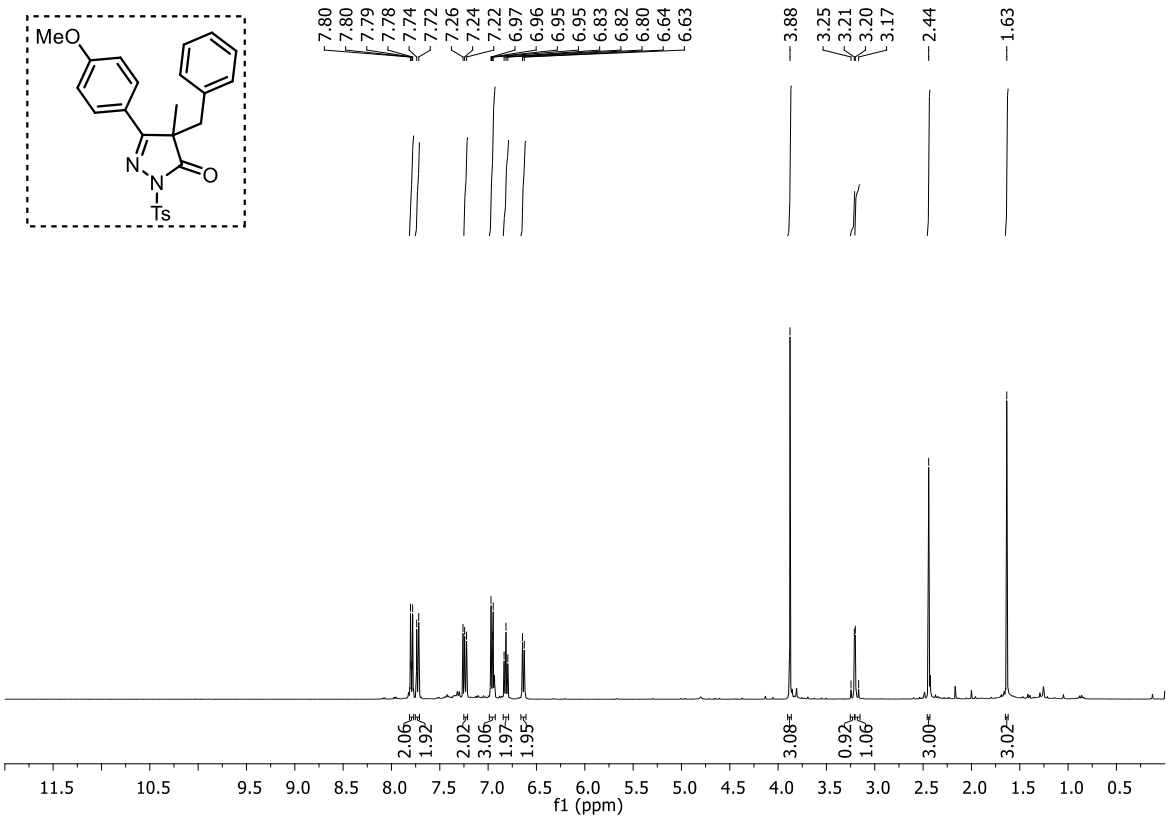
^{1}H NMR spectrum of 3ba ($CDCl_3$, 500 MHz)



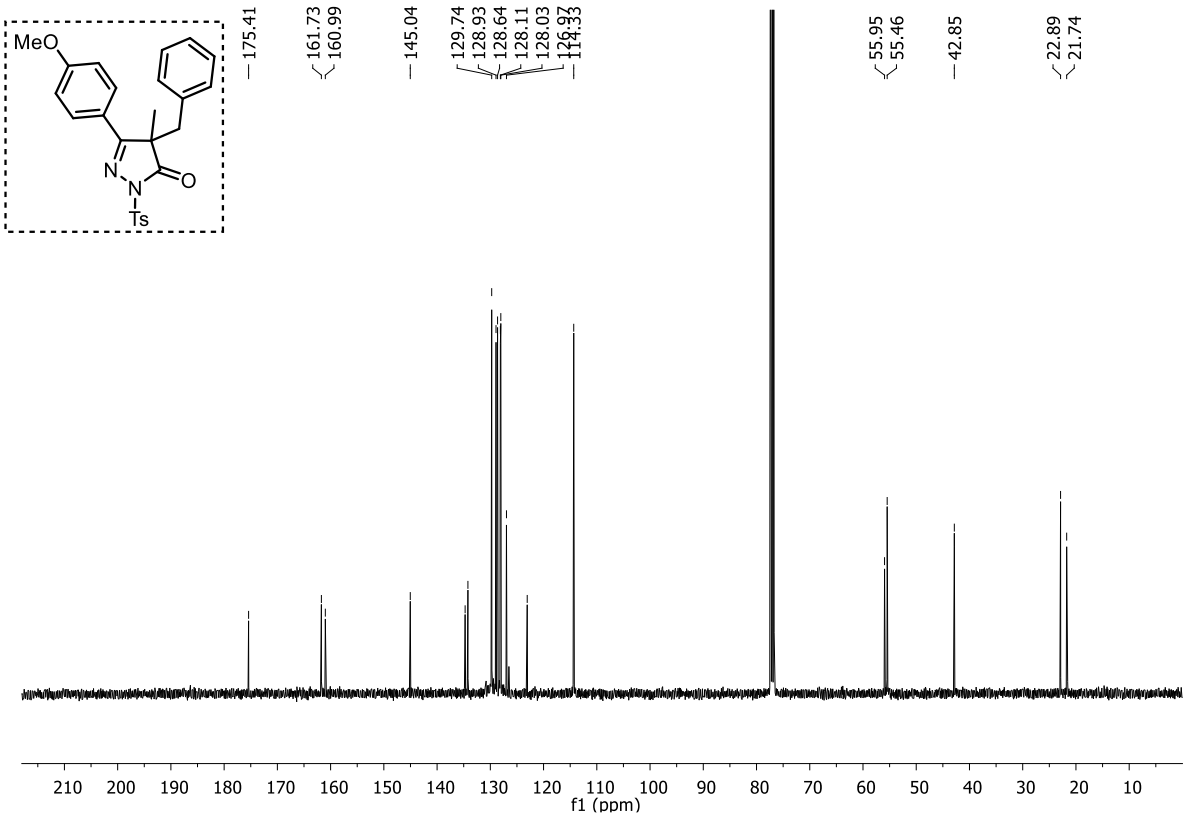
^{13}C {^{1}H} NMR spectrum of 3ba ($CDCl_3$, 126 MHz)



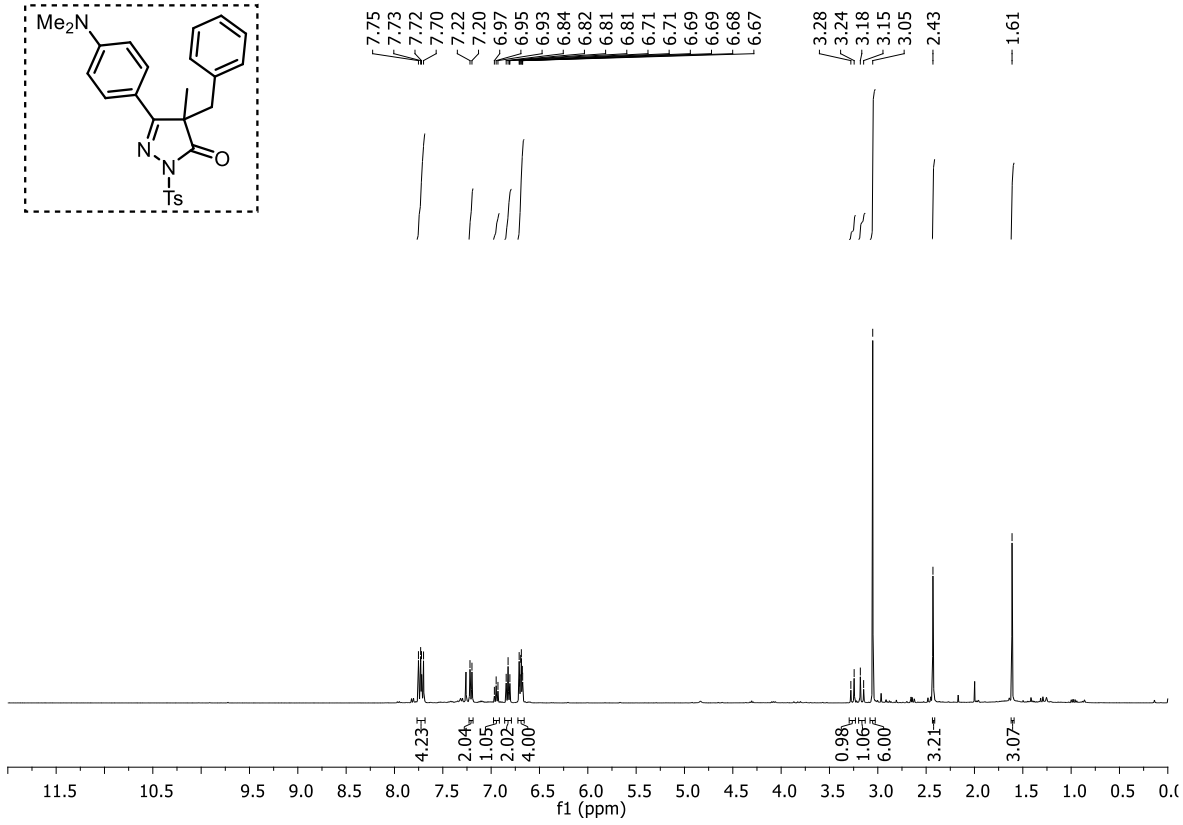
^{1}H NMR spectrum of 3ca ($CDCl_3$, 500 MHz)



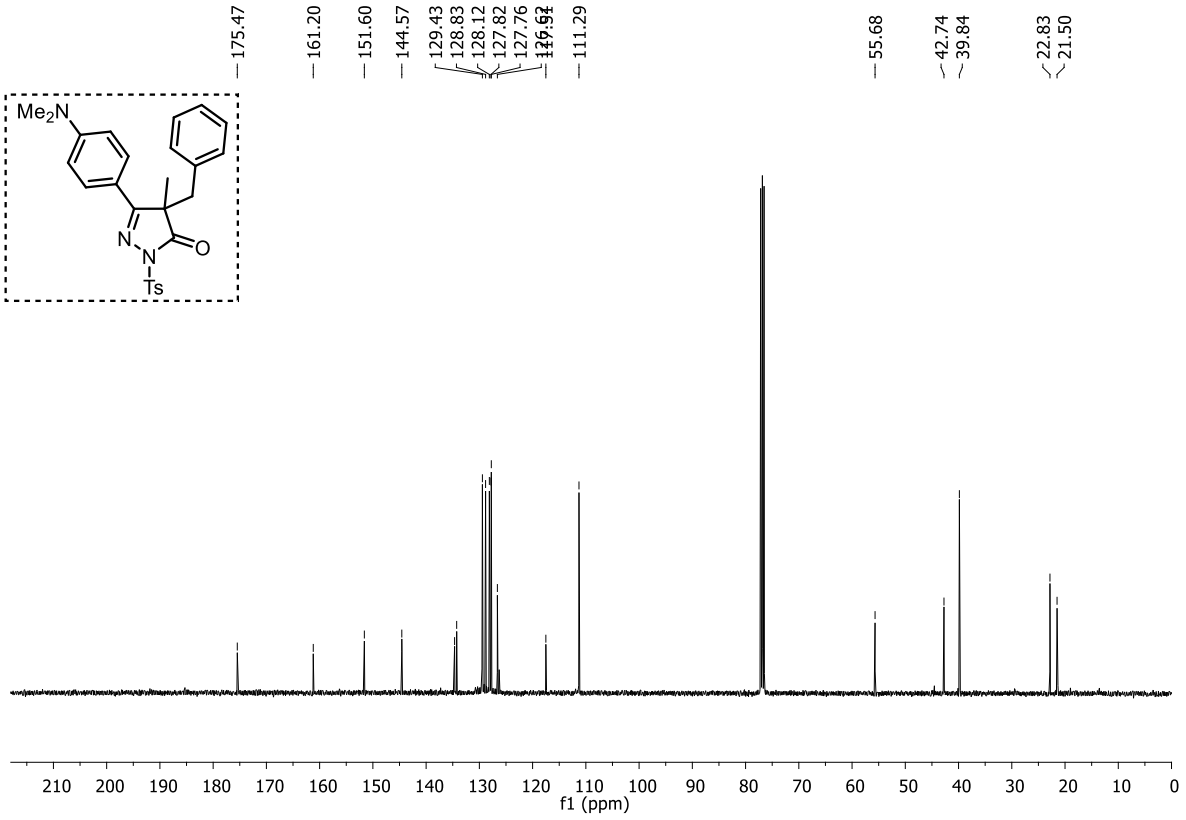
^{13}C {^{1}H} NMR spectrum of 3ca ($CDCl_3$, 126 MHz)



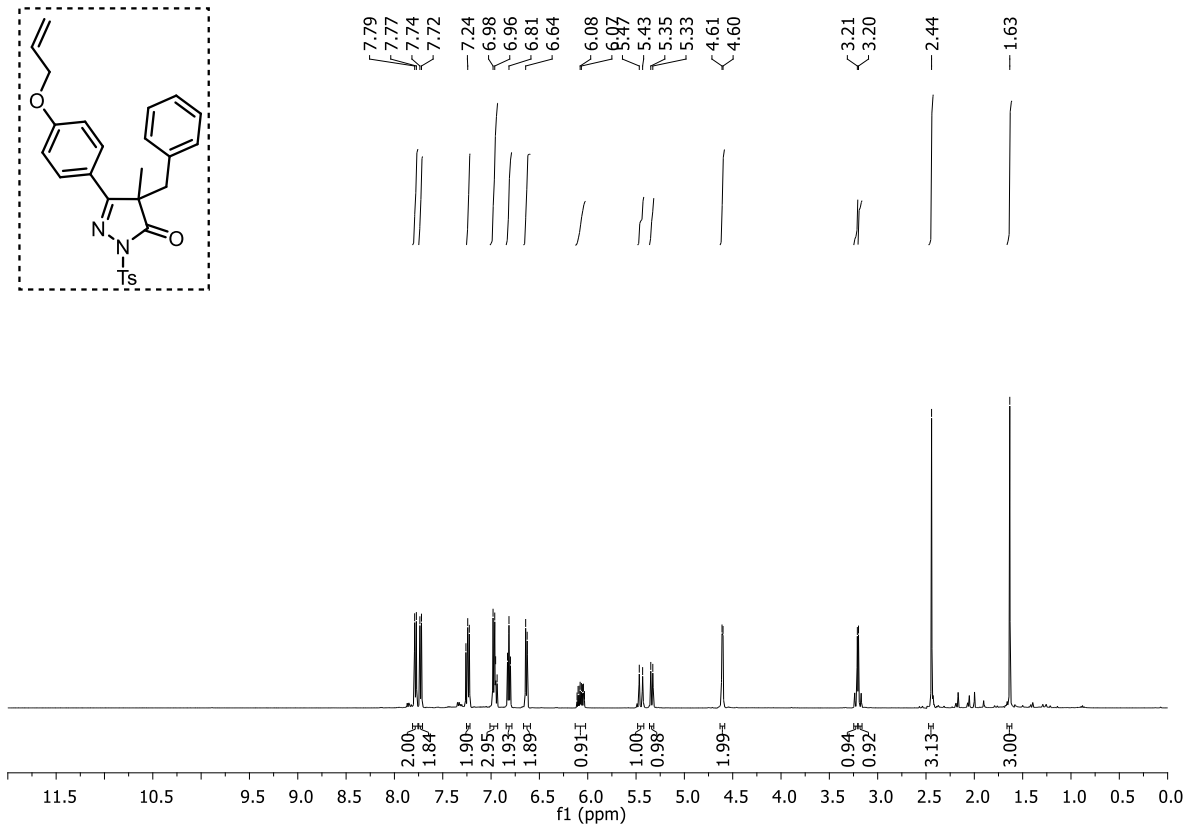
^{1}H NMR spectrum of 3da ($CDCl_3$, 500 MHz)



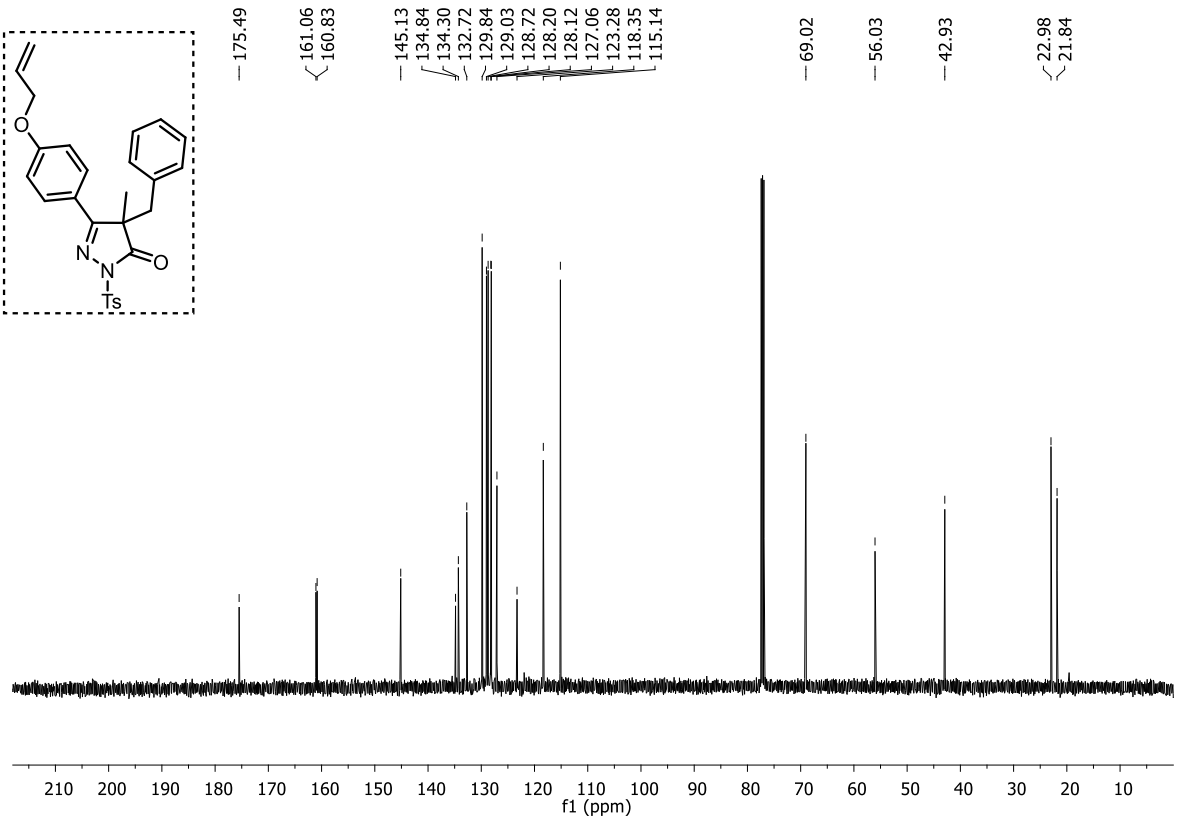
^{13}C {^{1}H} NMR spectrum of 3da ($CDCl_3$, 126 MHz)



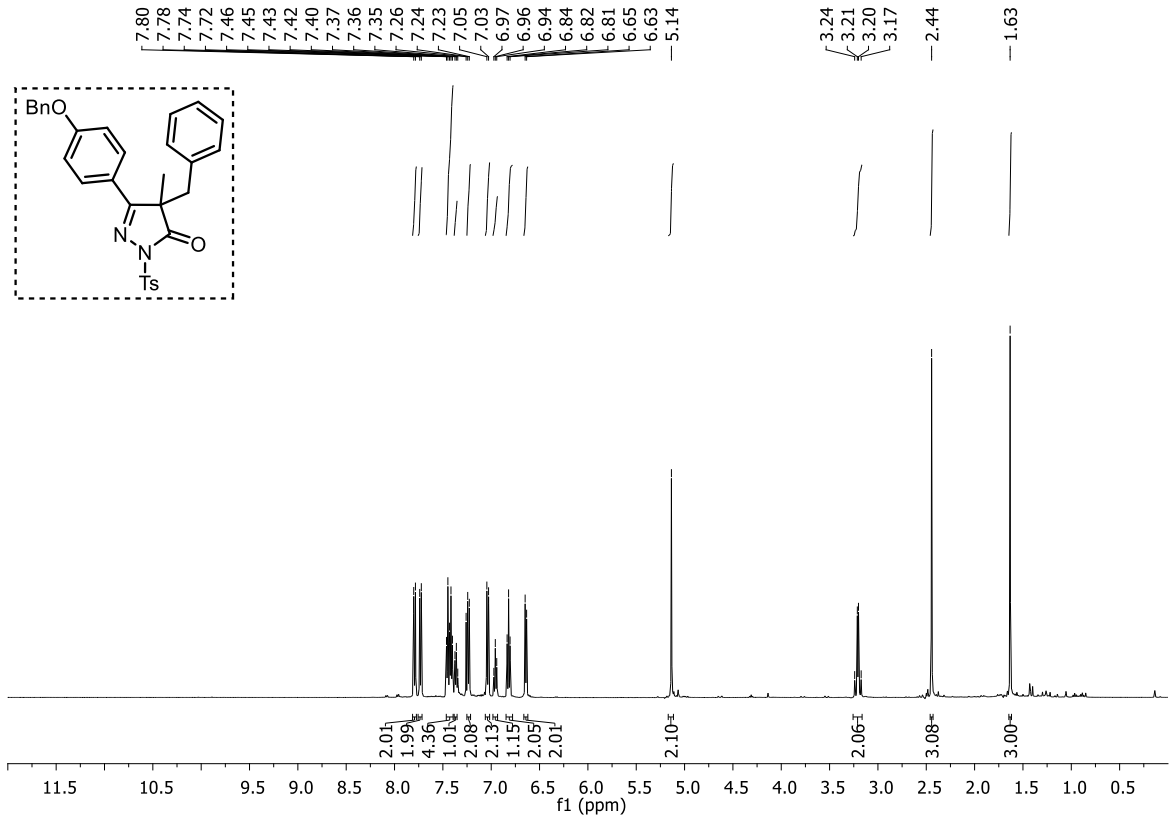
^{1}H NMR spectrum of 3ea ($CDCl_3$, 500 MHz)



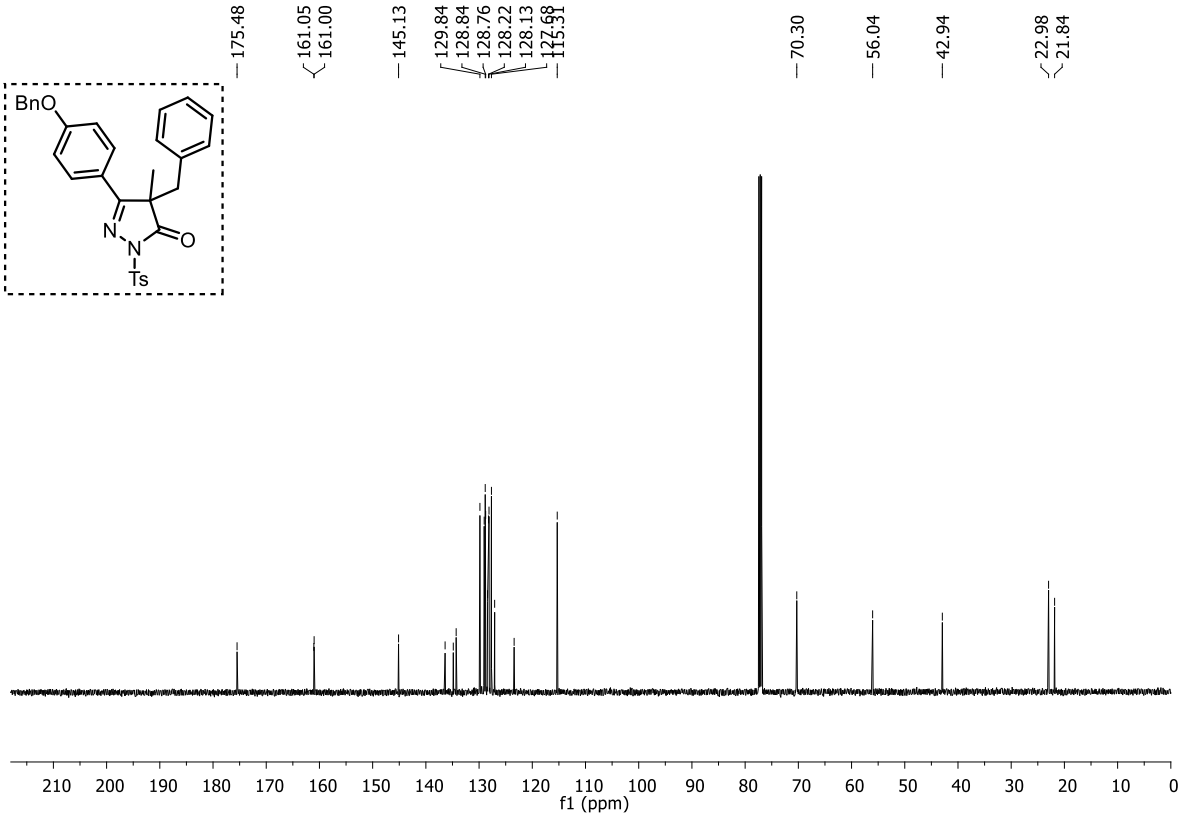
^{13}C {^{1}H} NMR spectrum of 3ea ($CDCl_3$, 126 MHz)



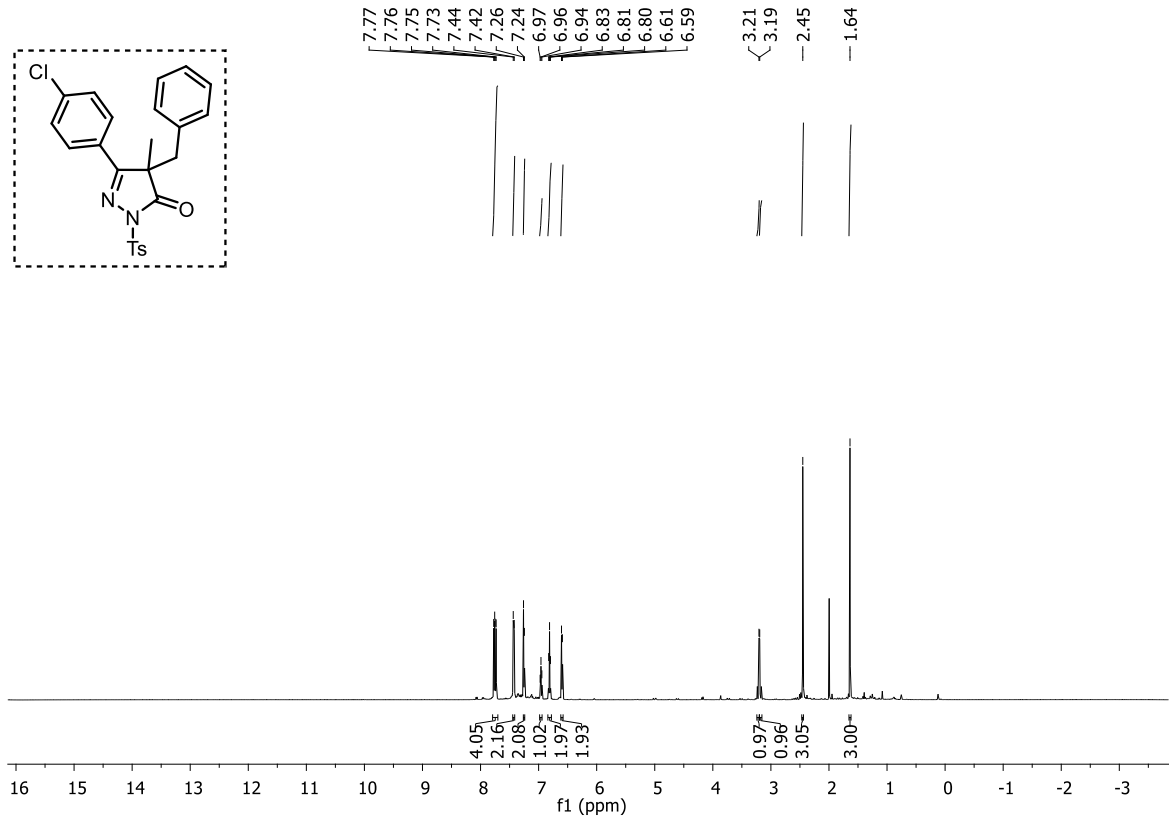
^{1}H NMR spectrum of 3fa ($CDCl_3$, 500 MHz)



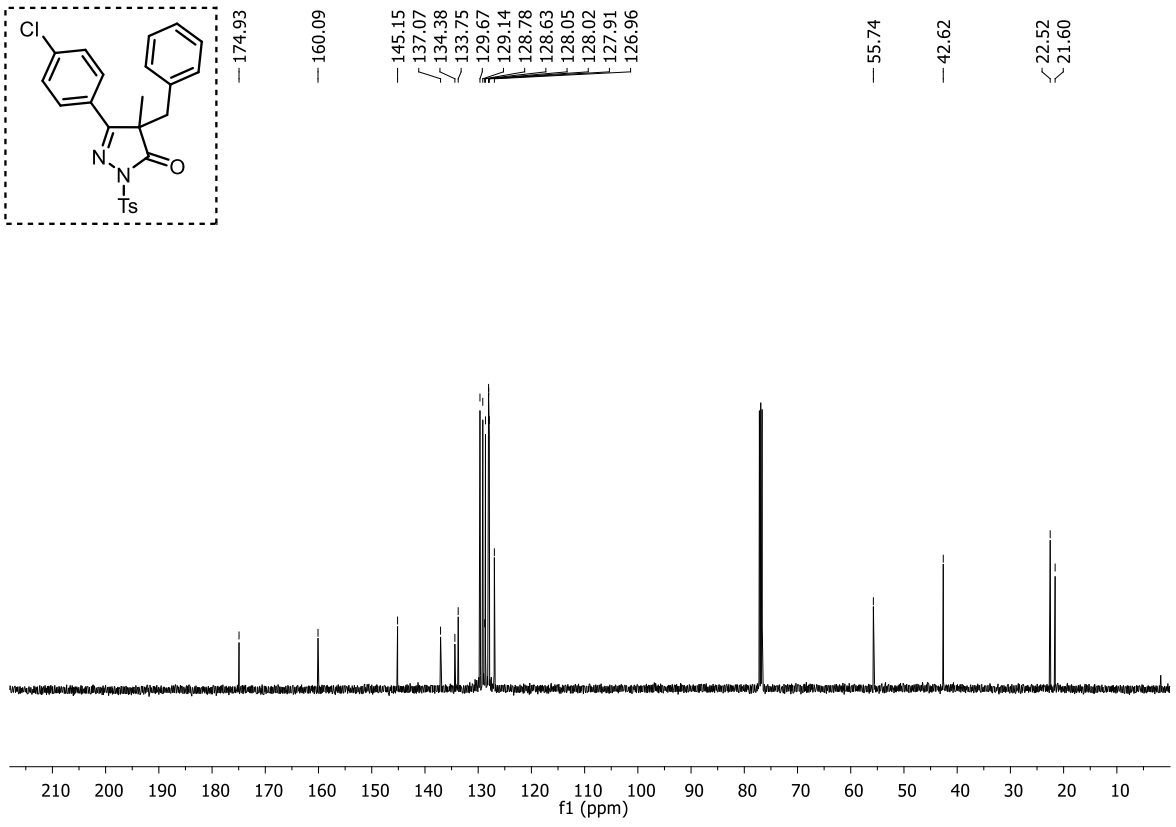
^{13}C {^{1}H} NMR spectrum of 3fa ($CDCl_3$, 126 MHz)



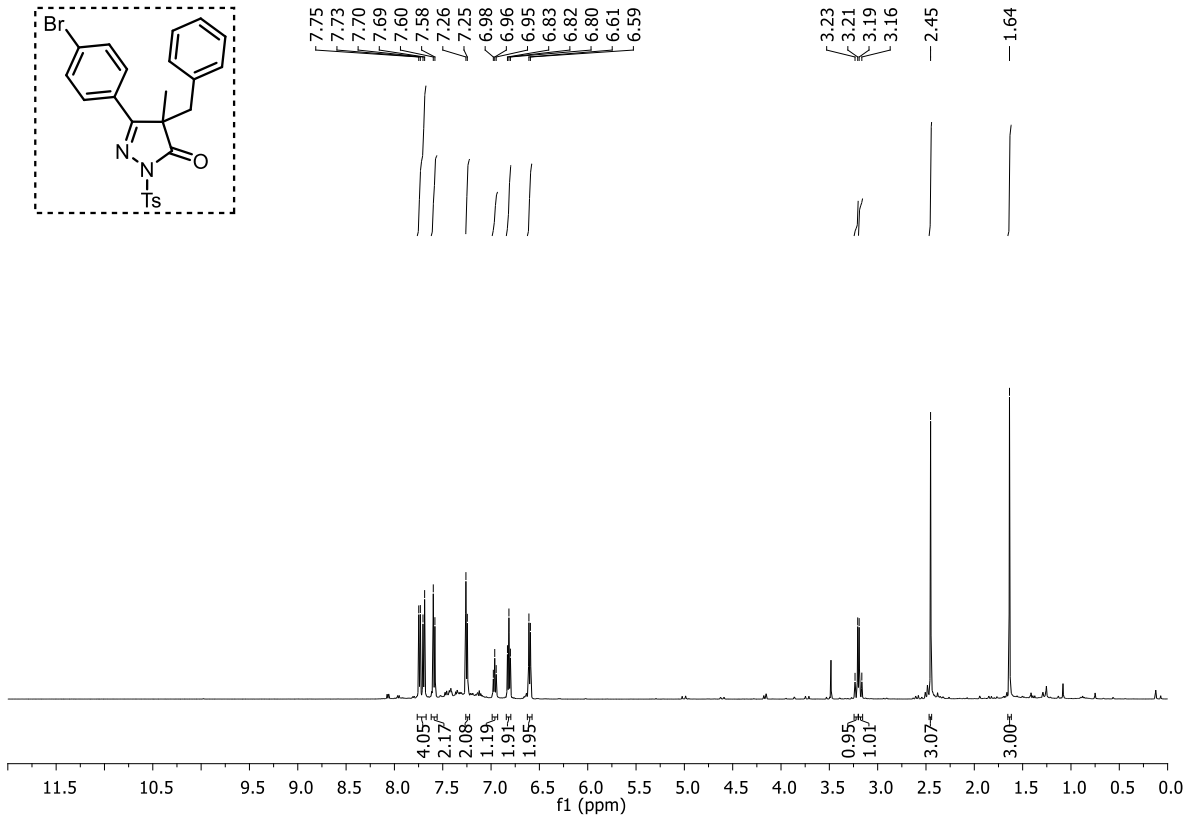
^{1}H NMR spectrum of 3ga ($CDCl_3$, 500 MHz)



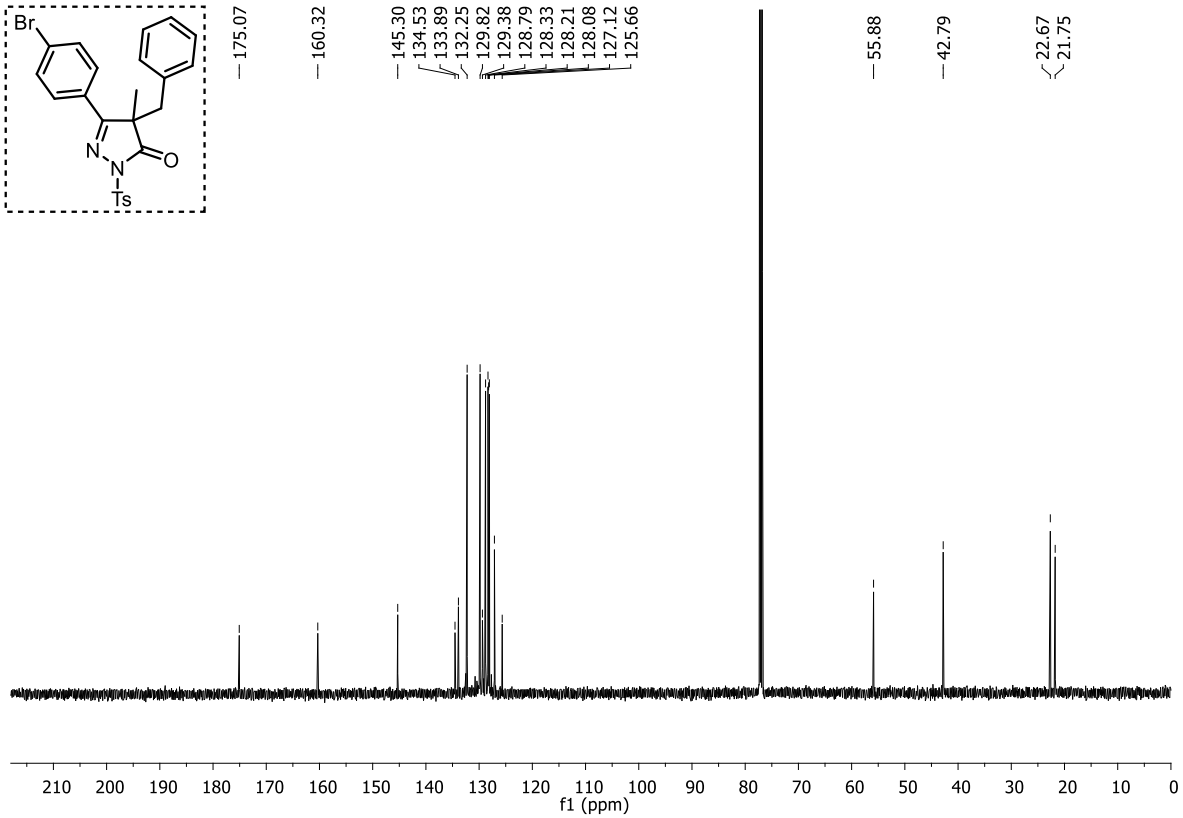
^{13}C {^{1}H} NMR spectrum of 3ga ($CDCl_3$, 126 MHz)



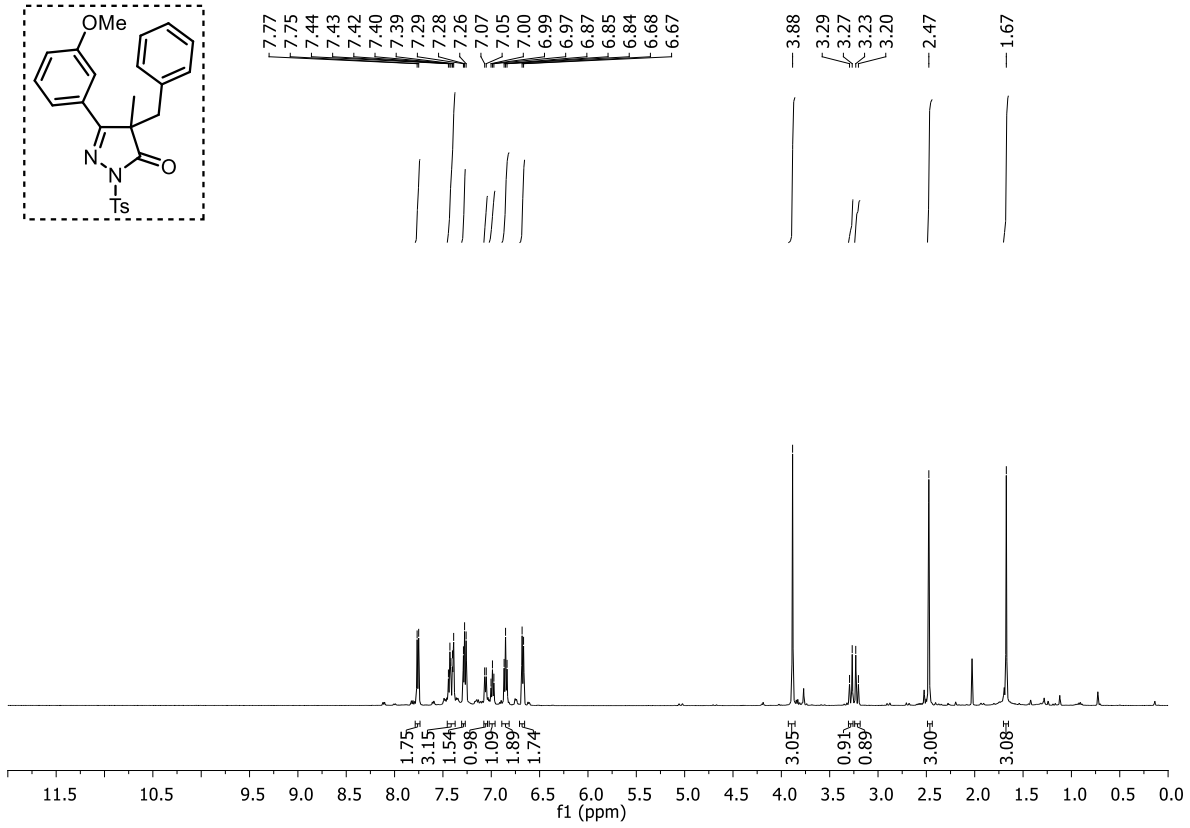
^{1}H NMR spectrum of 3ha ($CDCl_3$, 500 MHz)



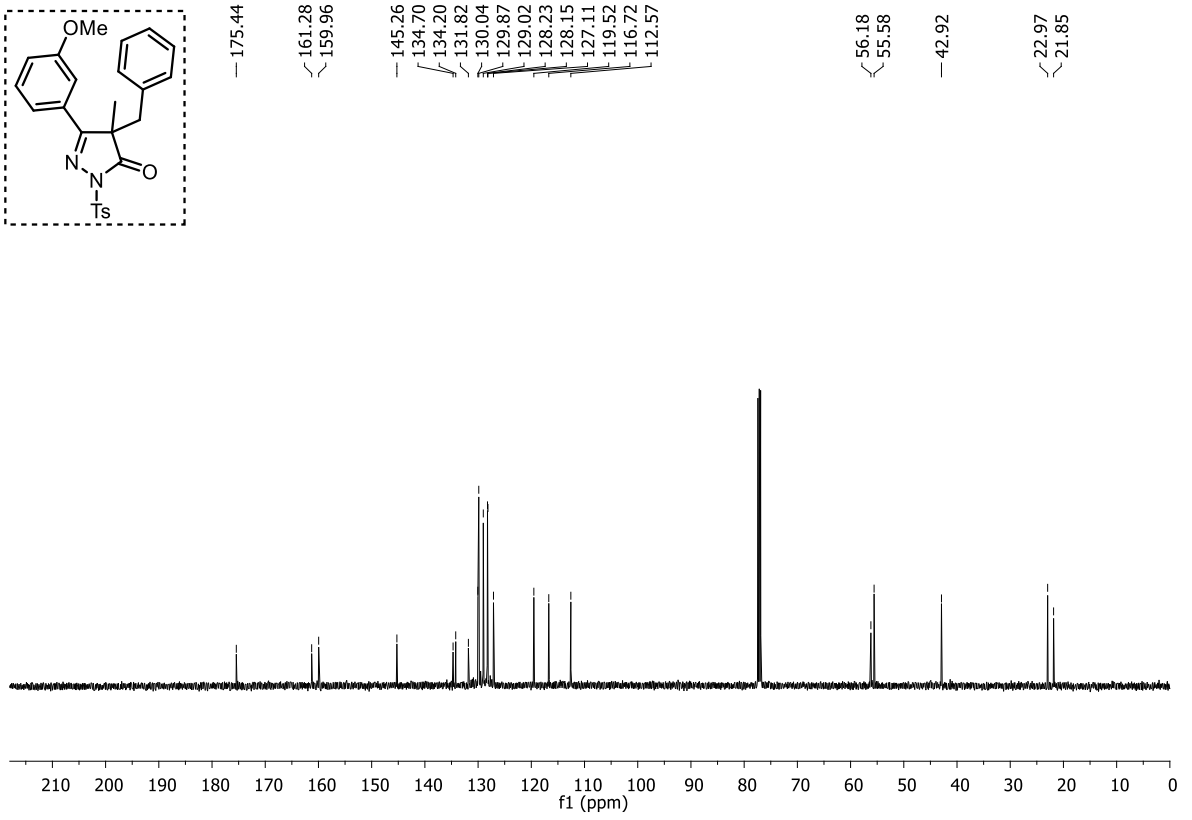
^{13}C {^{1}H} NMR spectrum of ha ($CDCl_3$, 126 MHz)



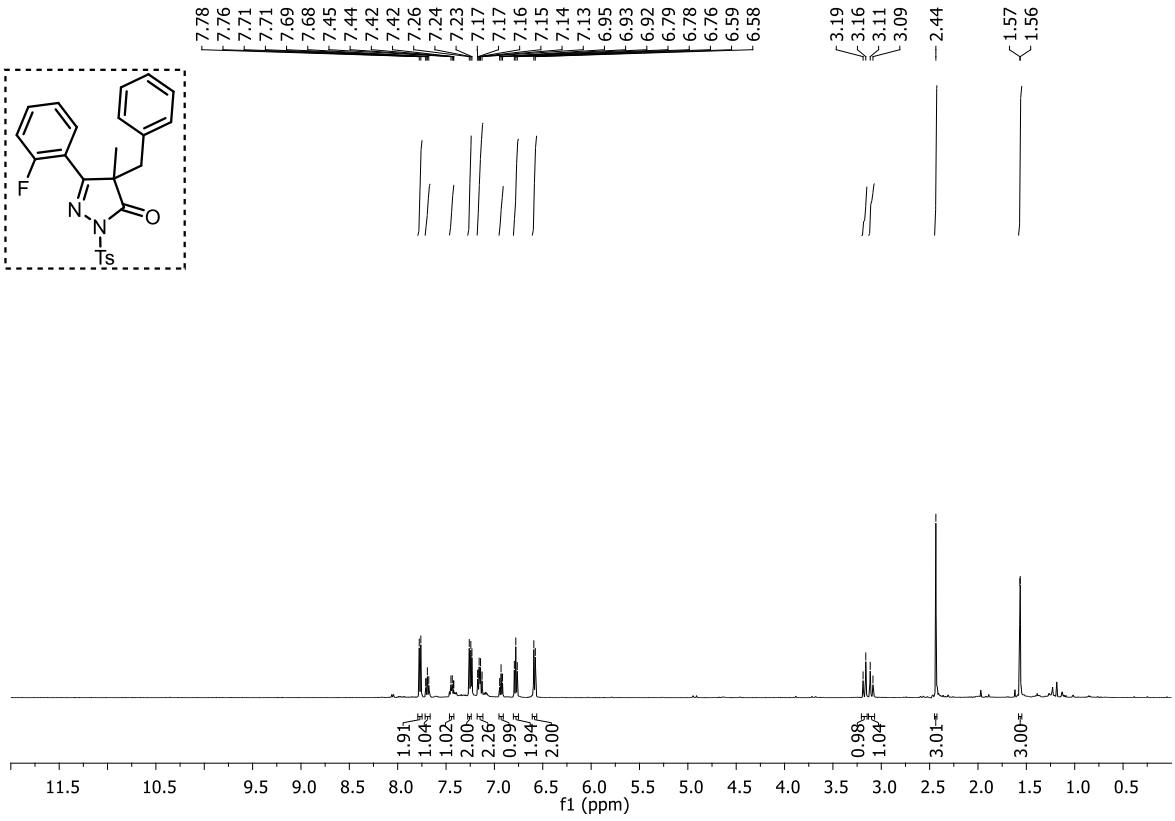
^{1}H NMR spectrum of 3ia ($CDCl_3$, 500 MHz)



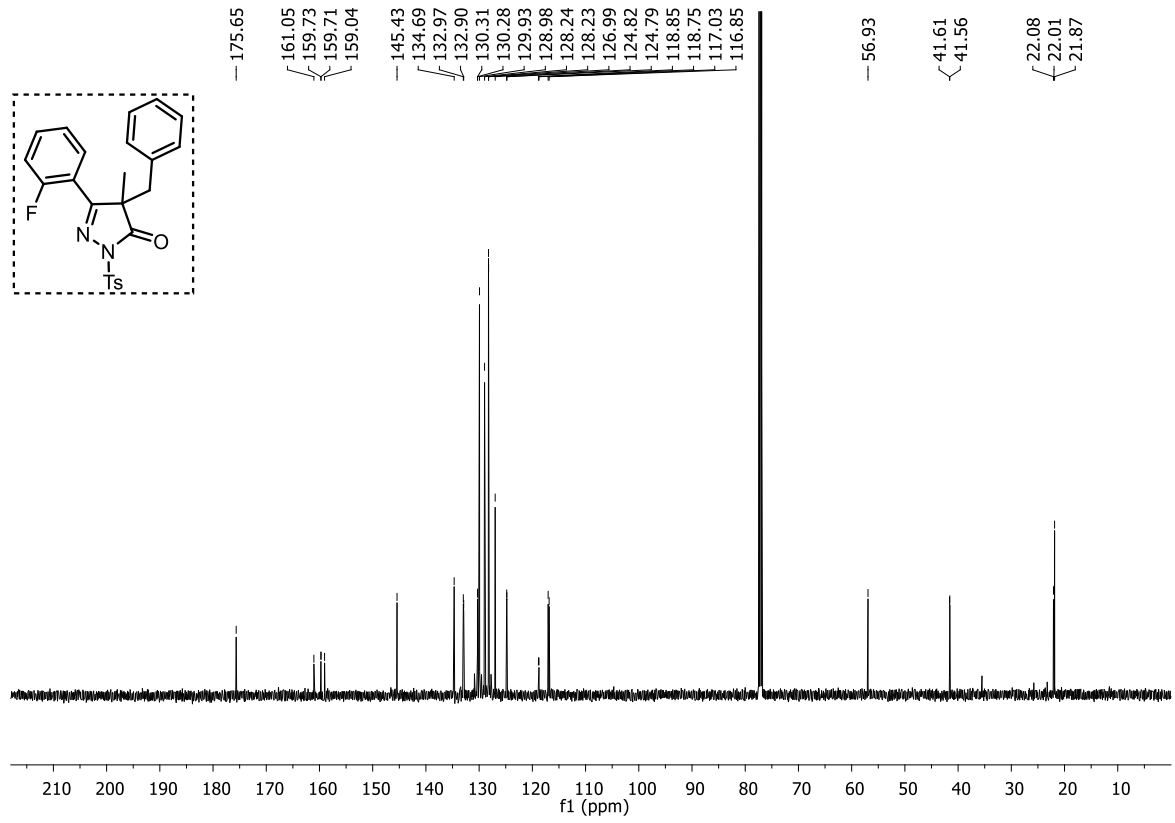
^{13}C {^{1}H} NMR spectrum of 3ia ($CDCl_3$, 126 MHz)



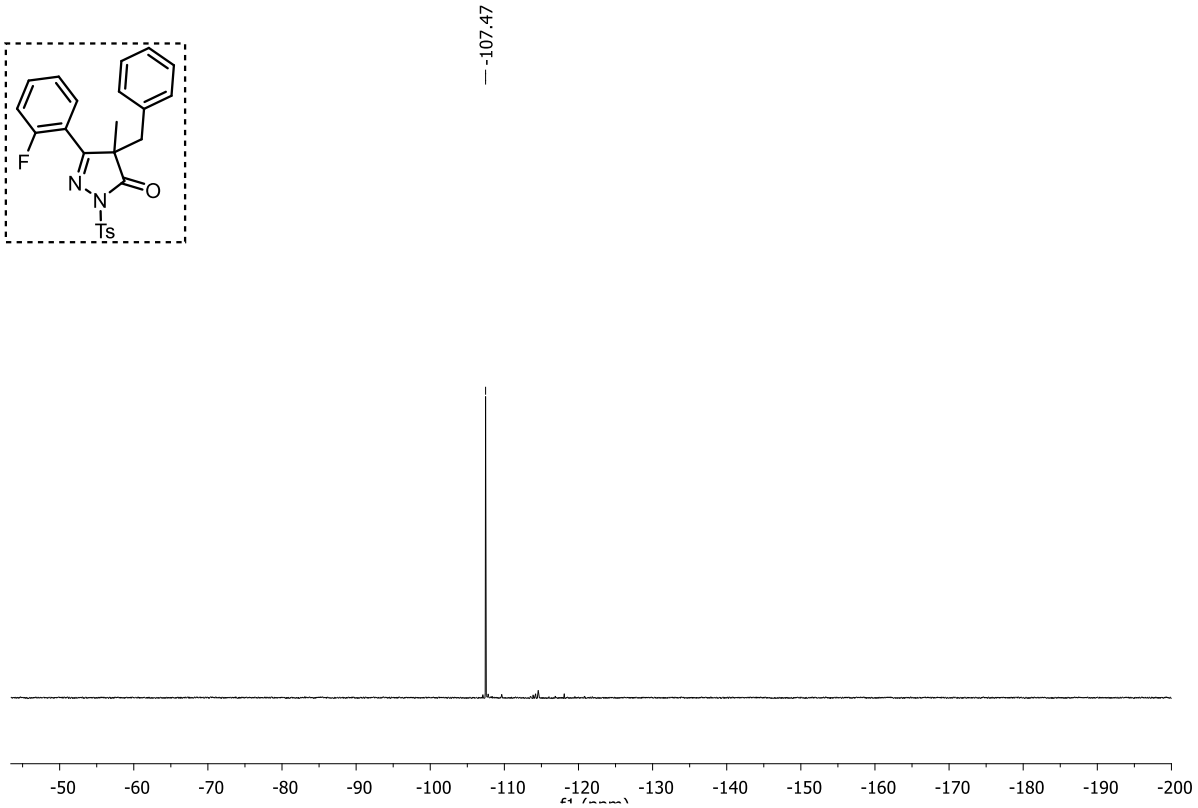
^{1}H NMR spectrum of 3ja ($CDCl_3$, 500 MHz)



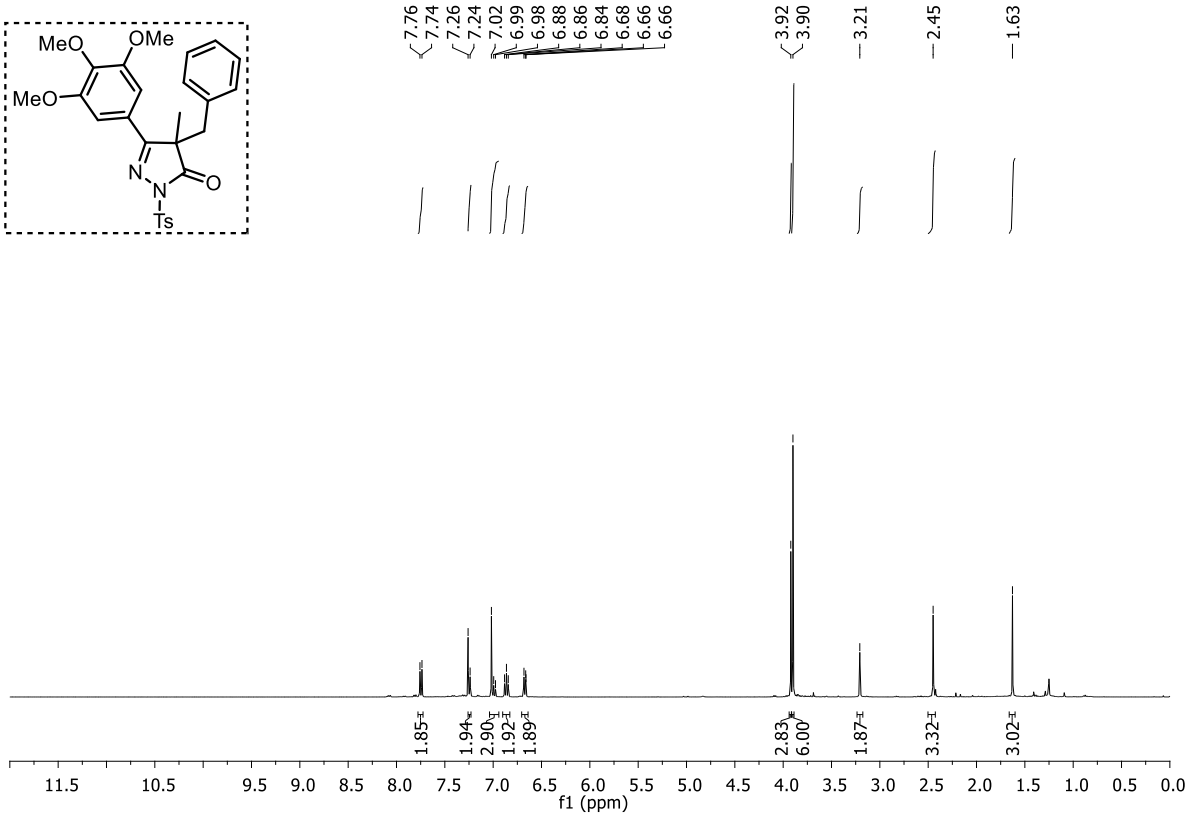
^{13}C {^{1}H} NMR spectrum of 3ja ($CDCl_3$, 126 MHz)



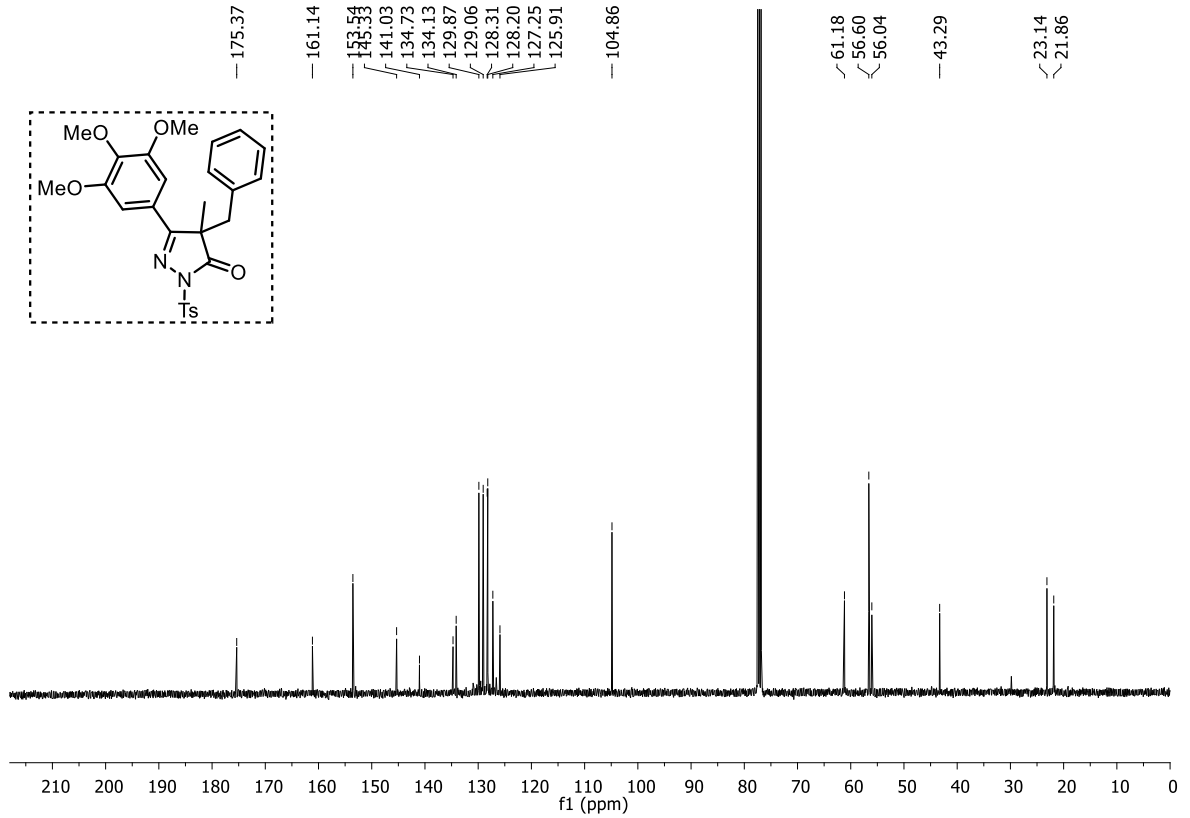
^{19}F {^{1}H} NMR spectrum of 3ja ($CDCl_3$, 471 MHz)



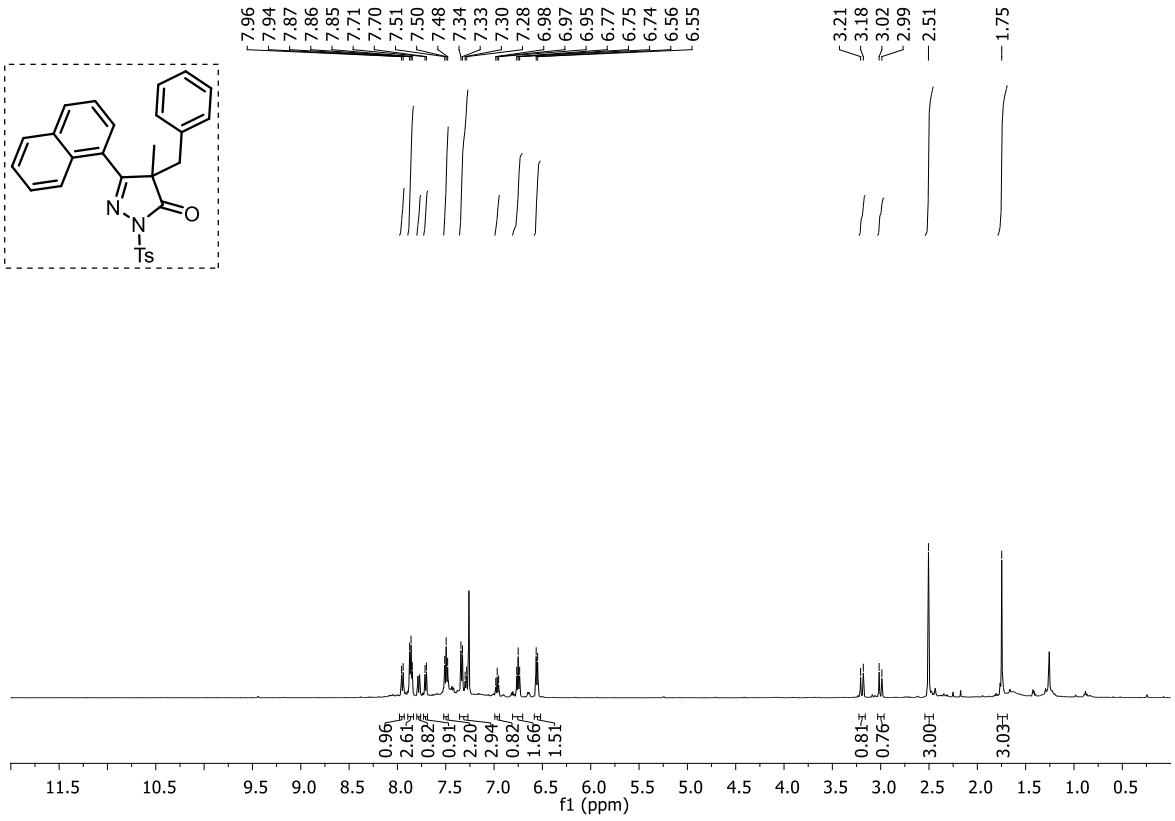
^{1}H NMR spectrum of 3ka ($CDCl_3$, 500 MHz)



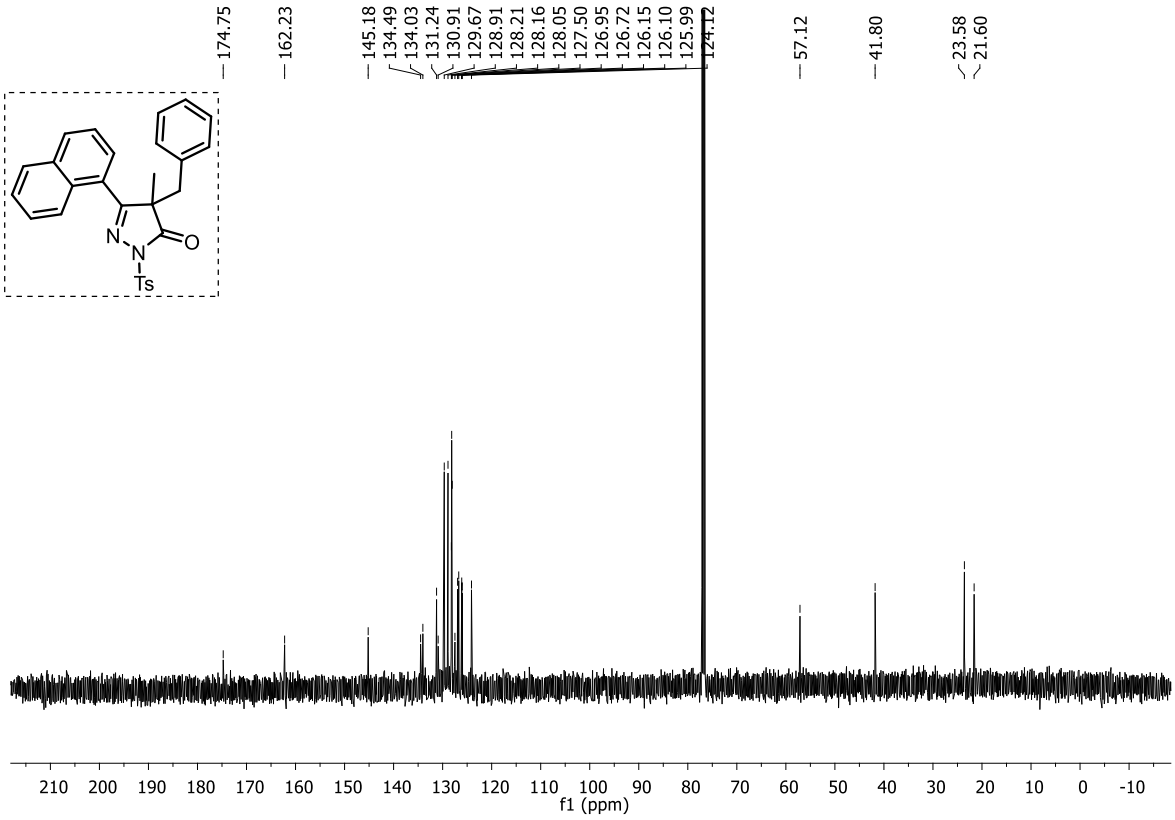
^{13}C {^{1}H} NMR spectrum of 3ka ($CDCl_3$, 126 MHz)



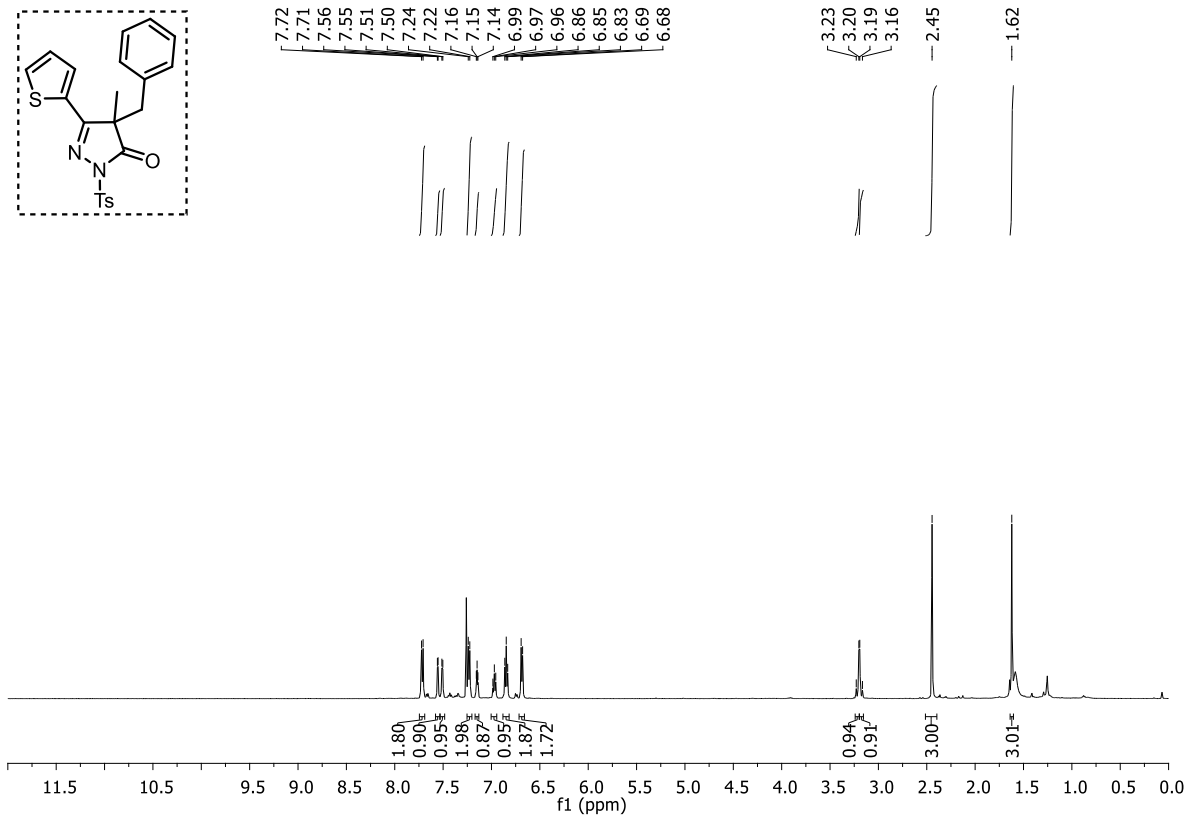
^{1}H NMR spectrum of 3la ($CDCl_3$, 500 MHz)



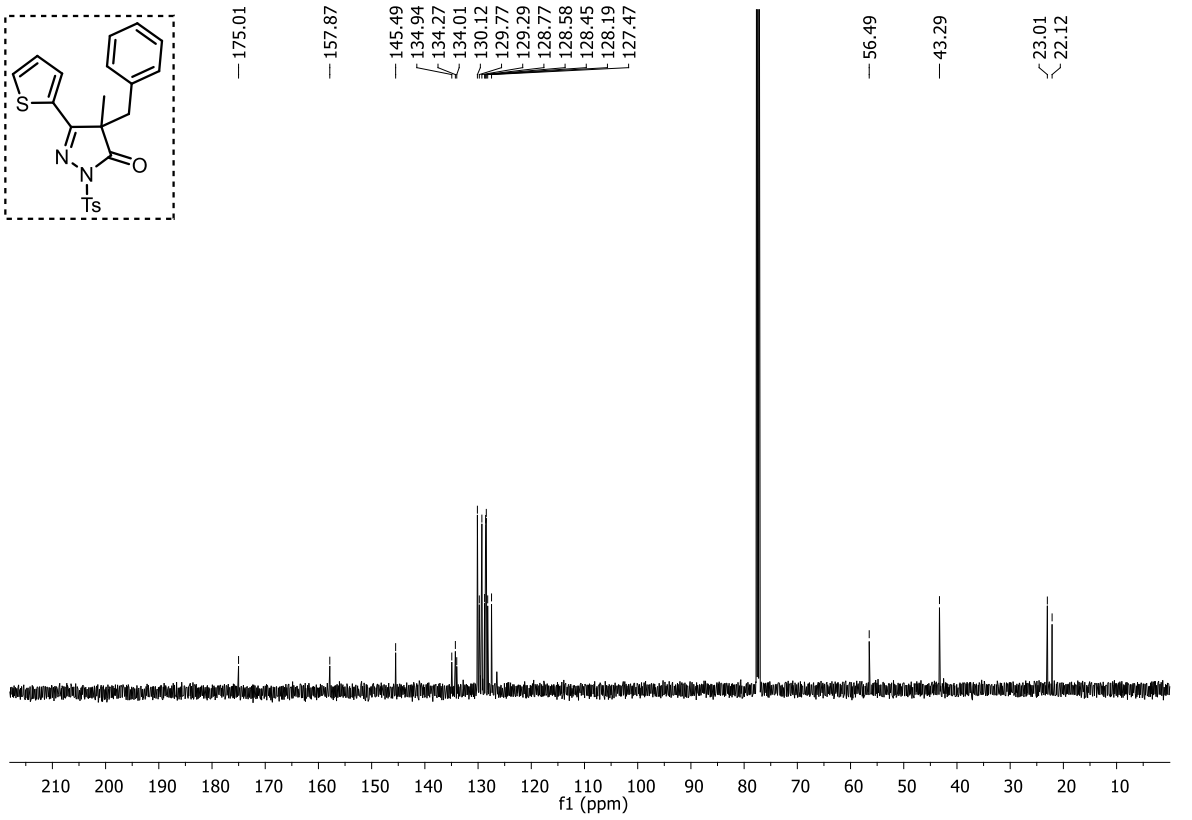
^{13}C {^{1}H} NMR spectrum of 3la ($CDCl_3$, 126 MHz)



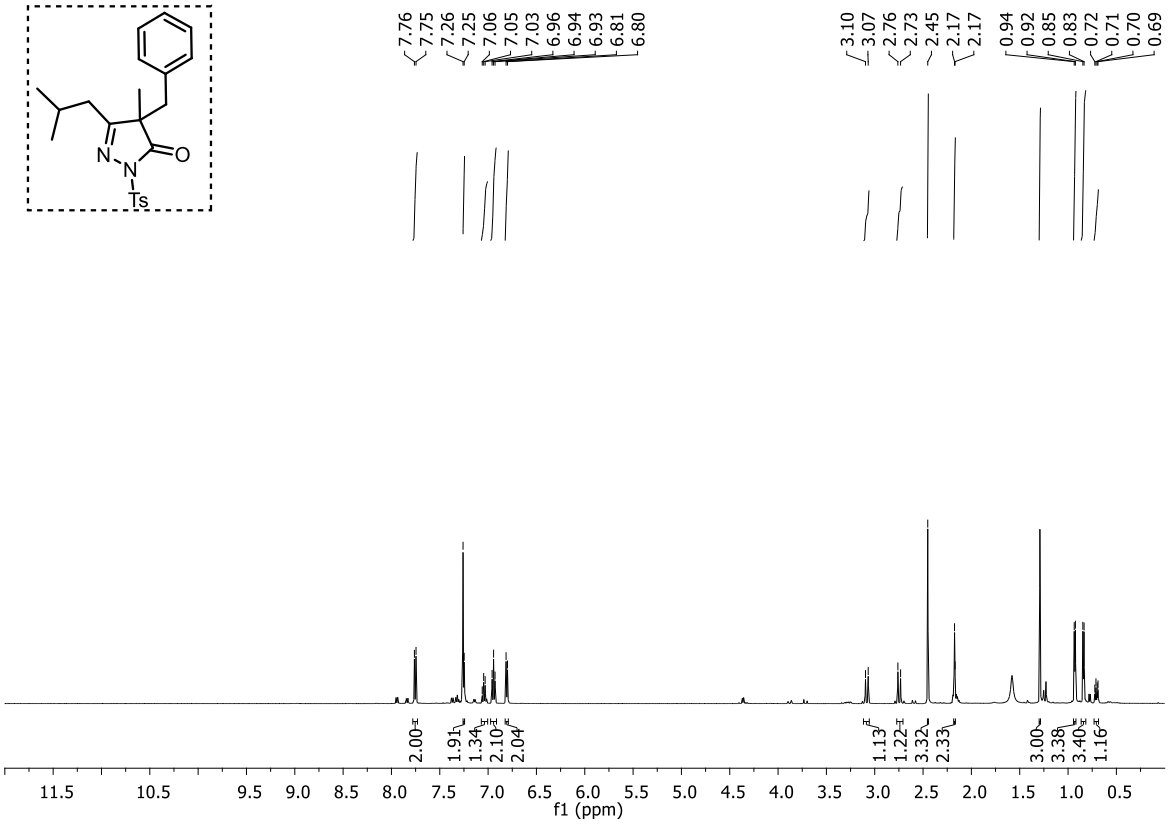
^{1}H NMR spectrum of 3ma ($CDCl_3$, 500 MHz)



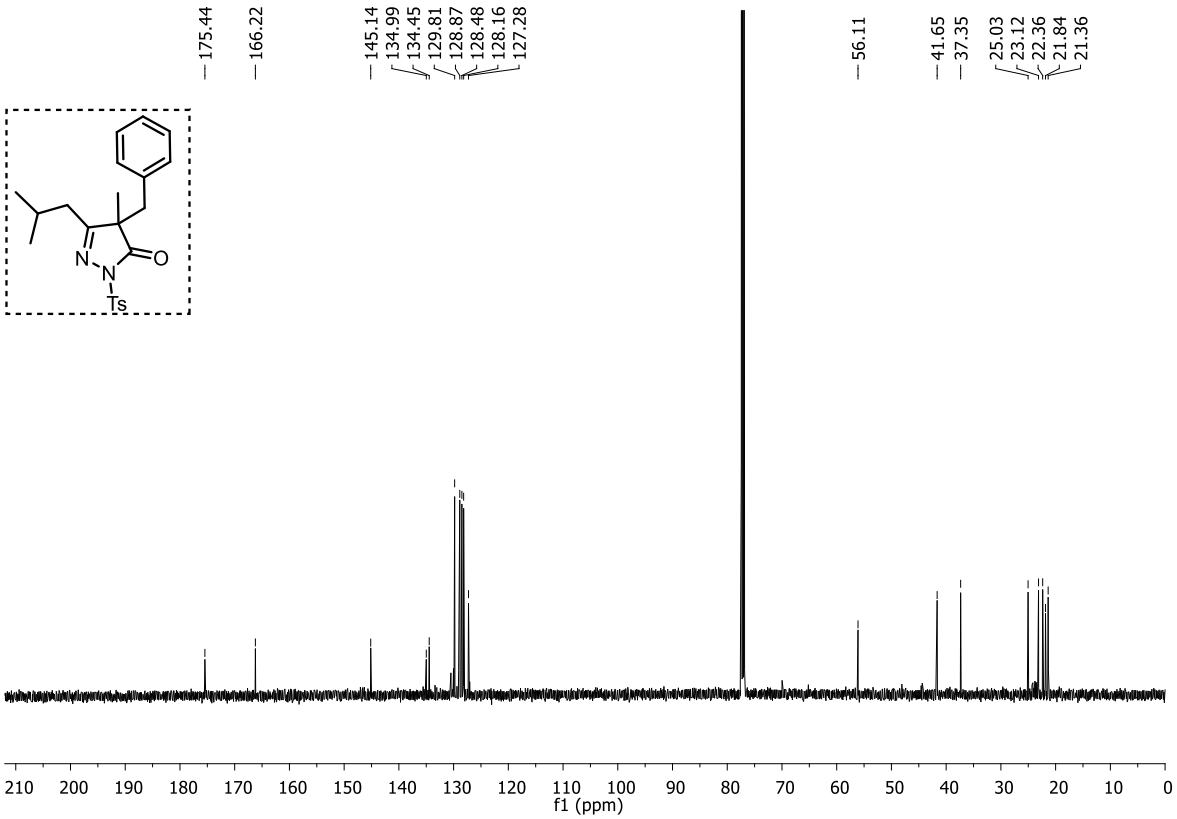
^{13}C {^{1}H} NMR spectrum of 3ma ($CDCl_3$, 126 MHz)



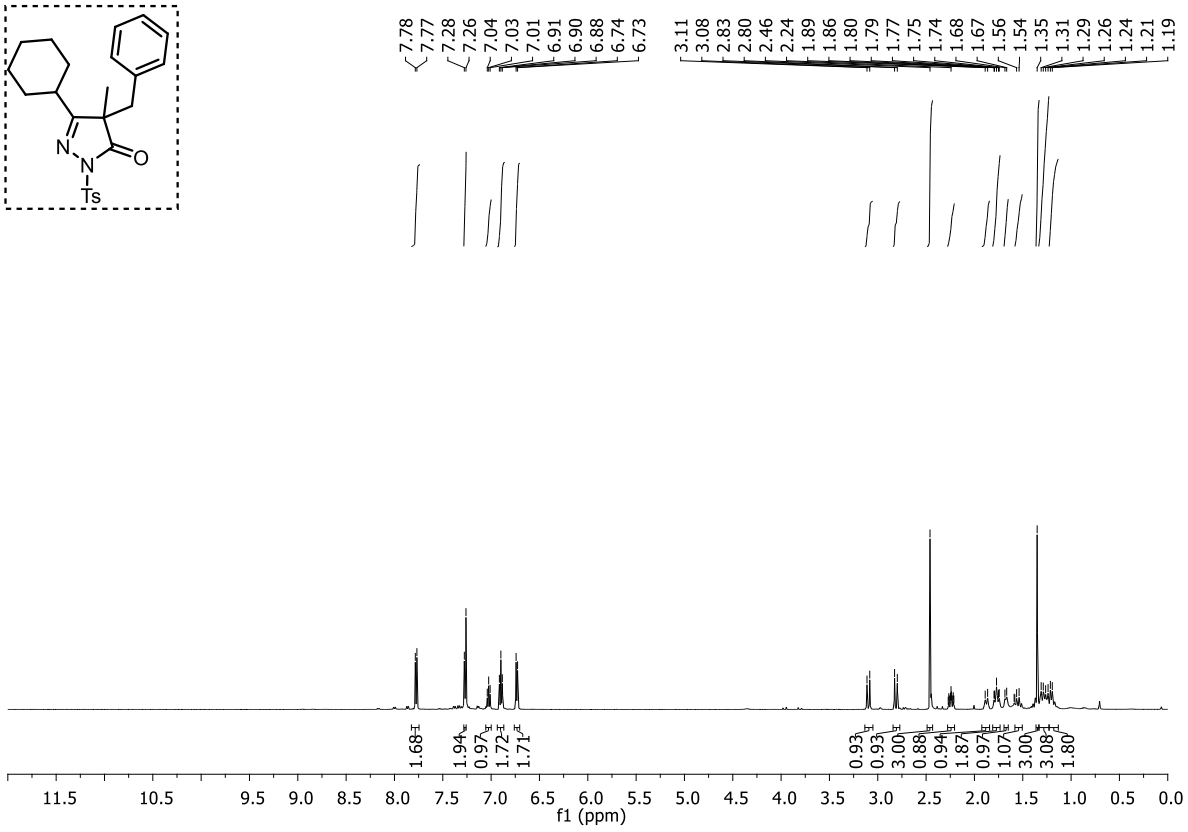
^{1}H NMR spectrum of 3na ($CDCl_3$, 500 MHz)



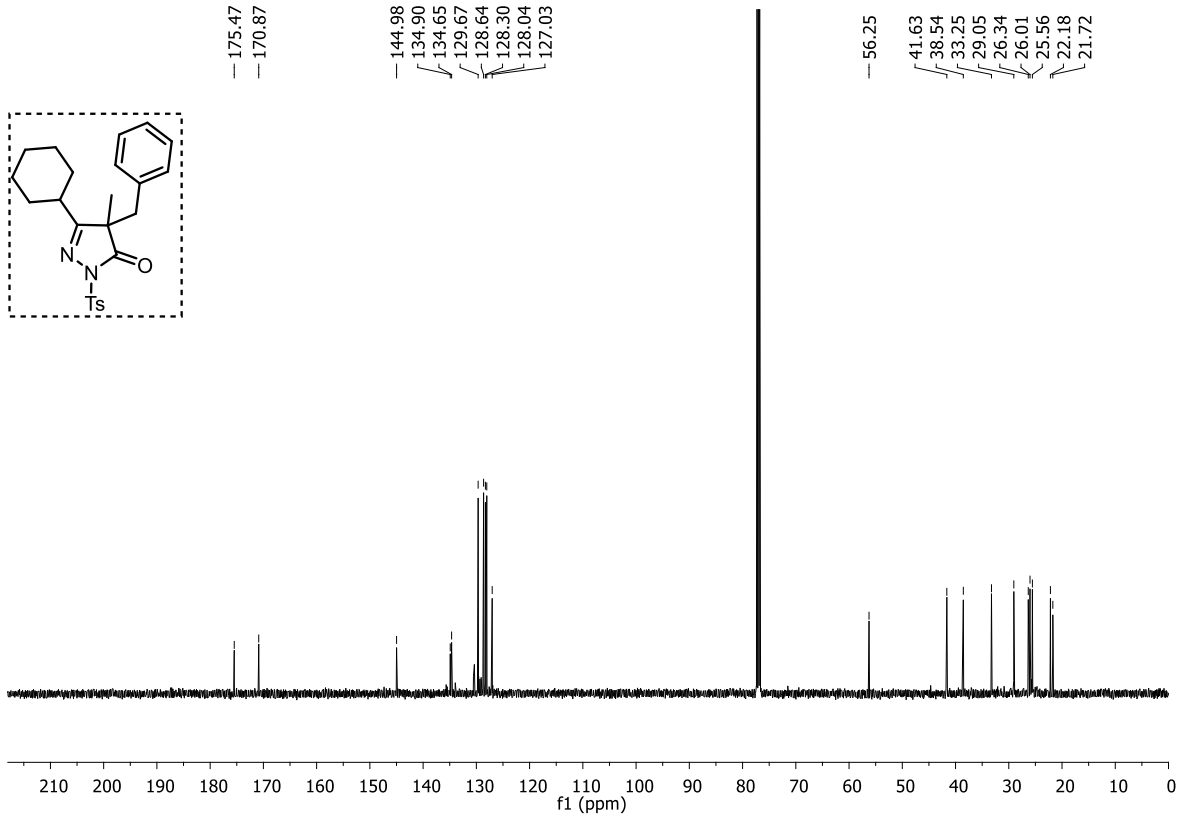
^{13}C {^{1}H} NMR spectrum of 3na ($CDCl_3$, 126 MHz)



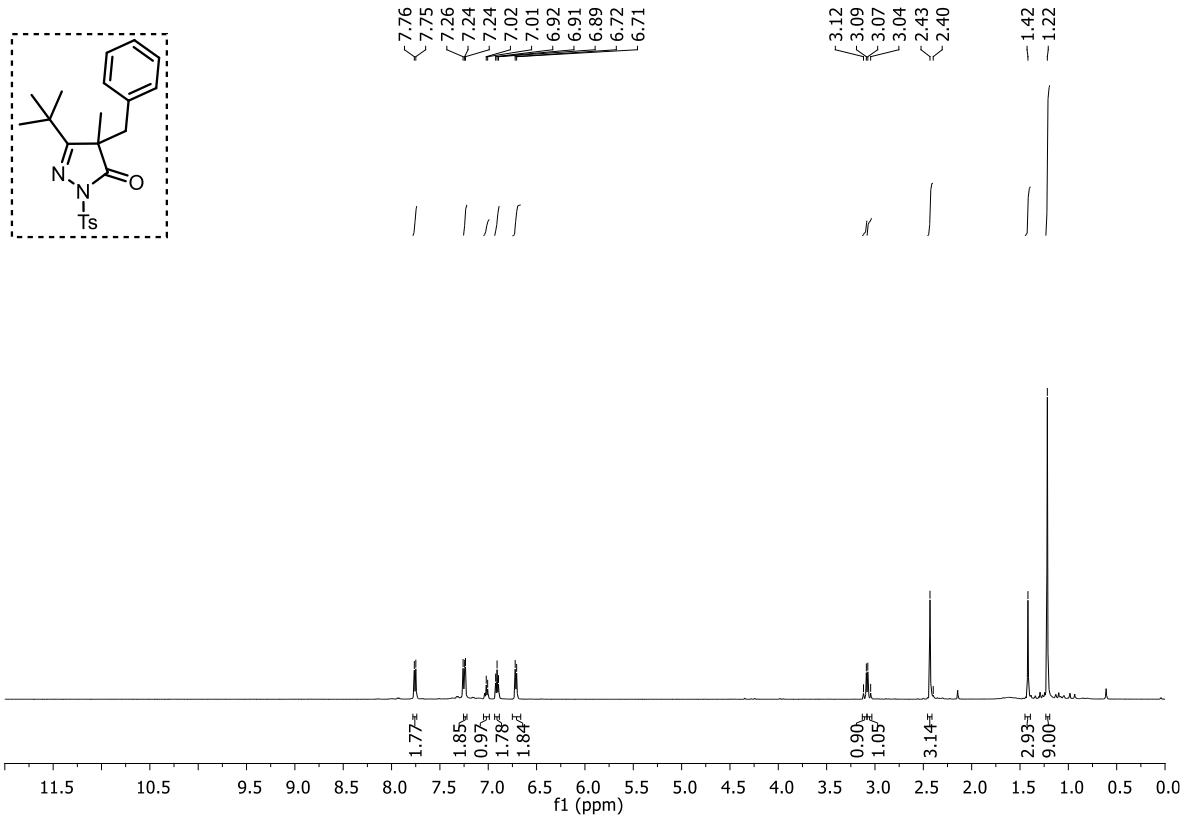
^{1}H NMR spectrum of 3oa ($CDCl_3$, 500 MHz)



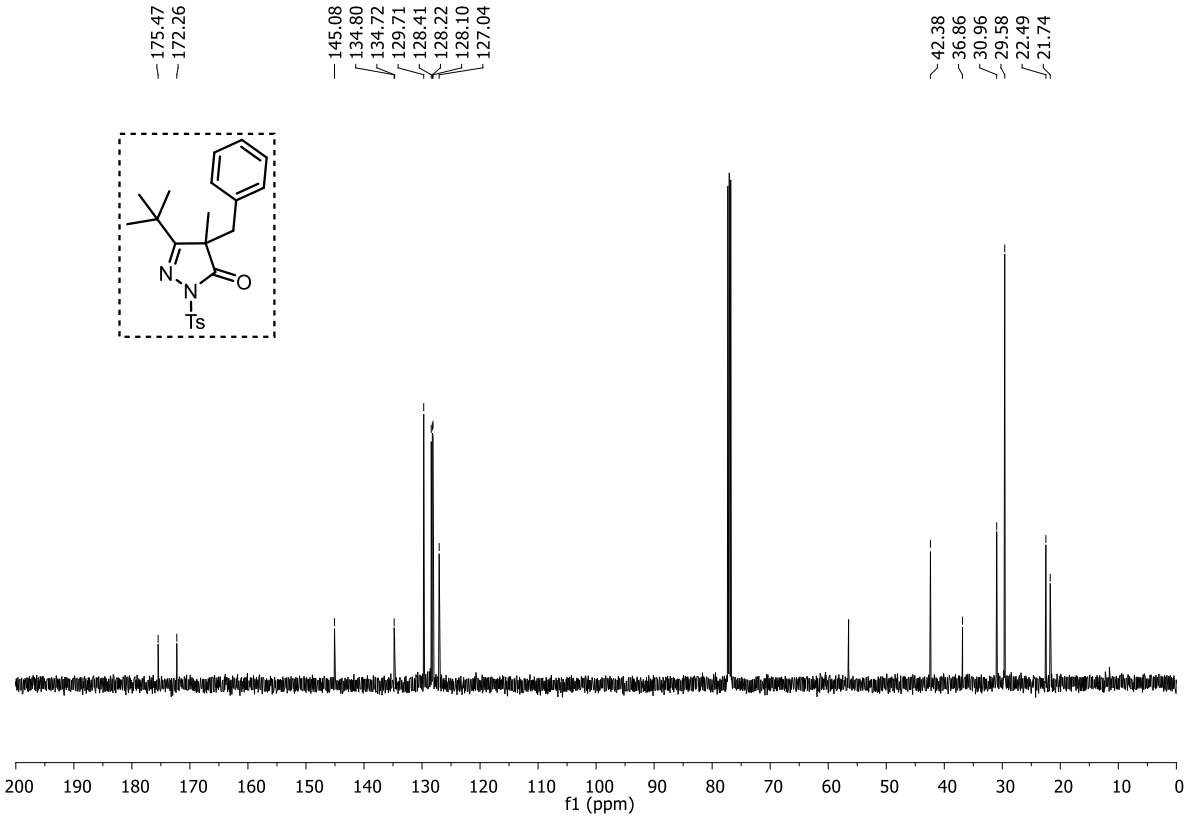
^{13}C {^{1}H} NMR spectrum of 3oa ($CDCl_3$, 126 MHz)



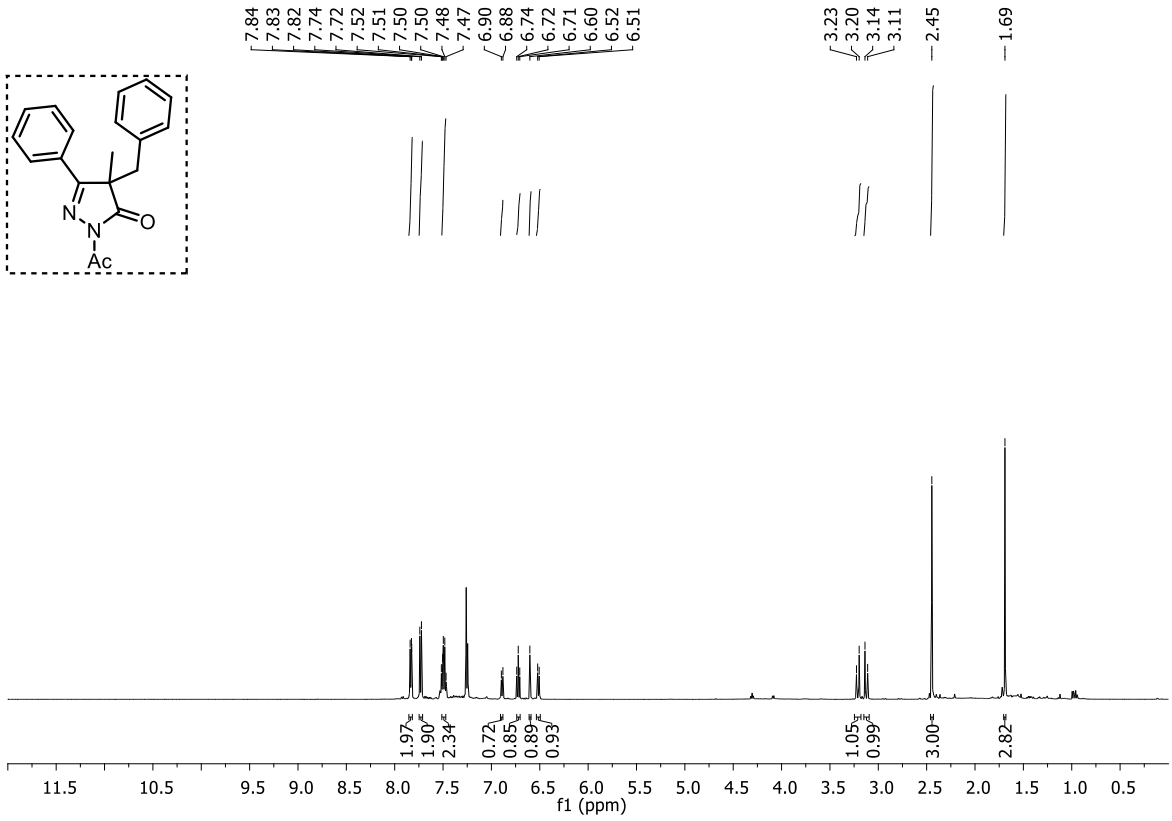
^{1}H NMR spectrum of 3pa ($CDCl_3$, 500 MHz)



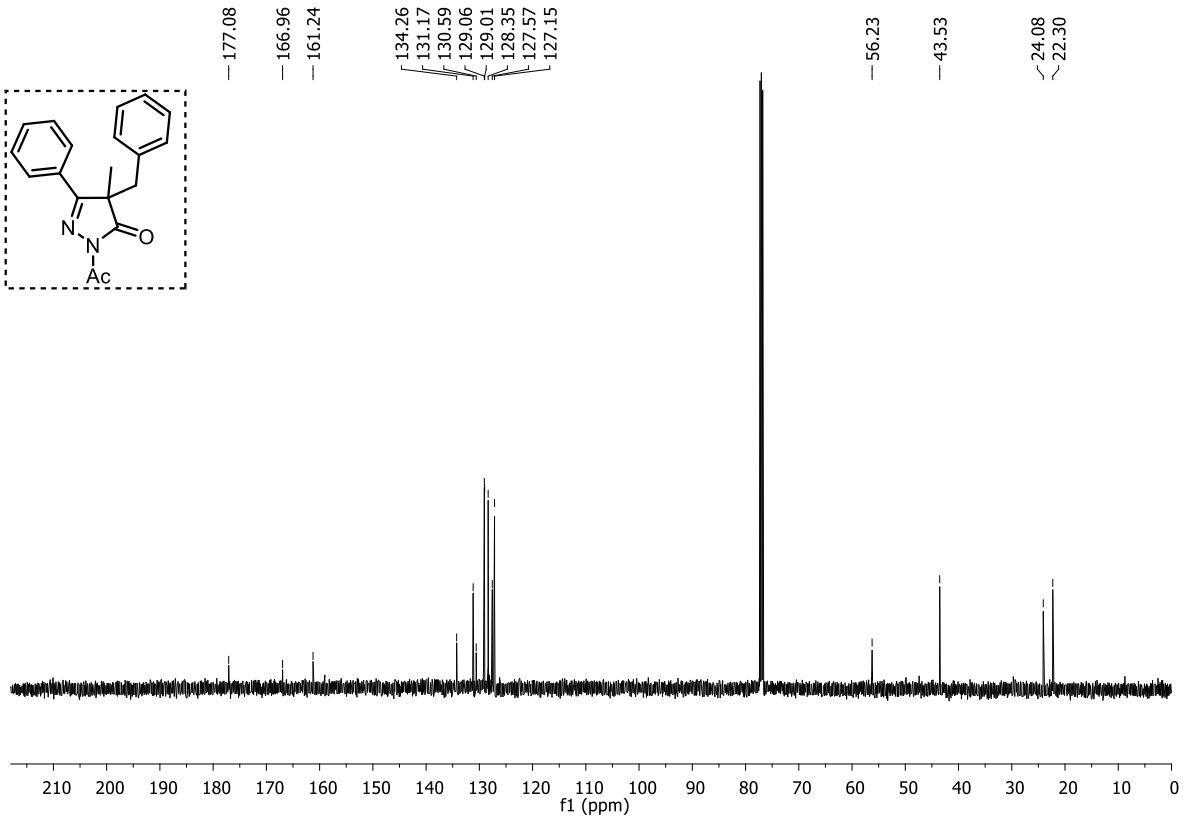
^{13}C {^{1}H} NMR spectrum of 3pa ($CDCl_3$, 126 MHz)



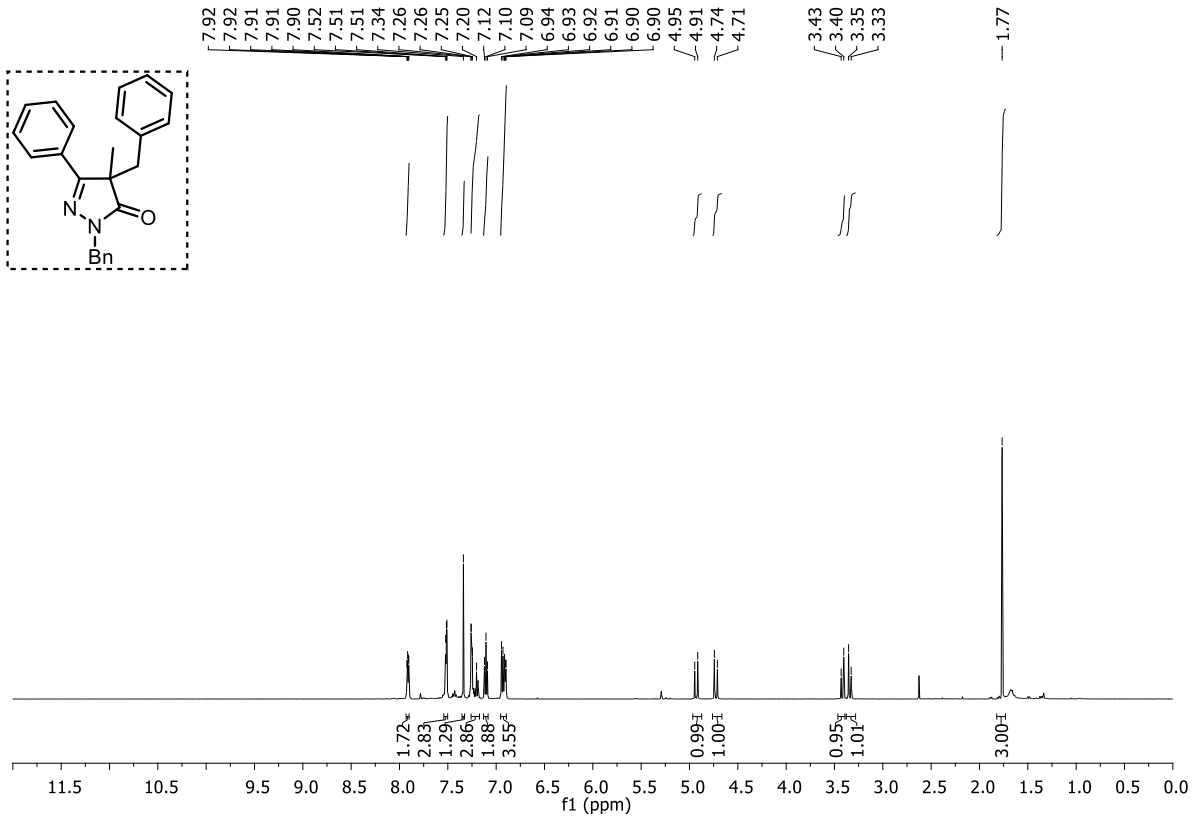
^{1}H NMR spectrum of 3qa ($CDCl_3$, 500 MHz)



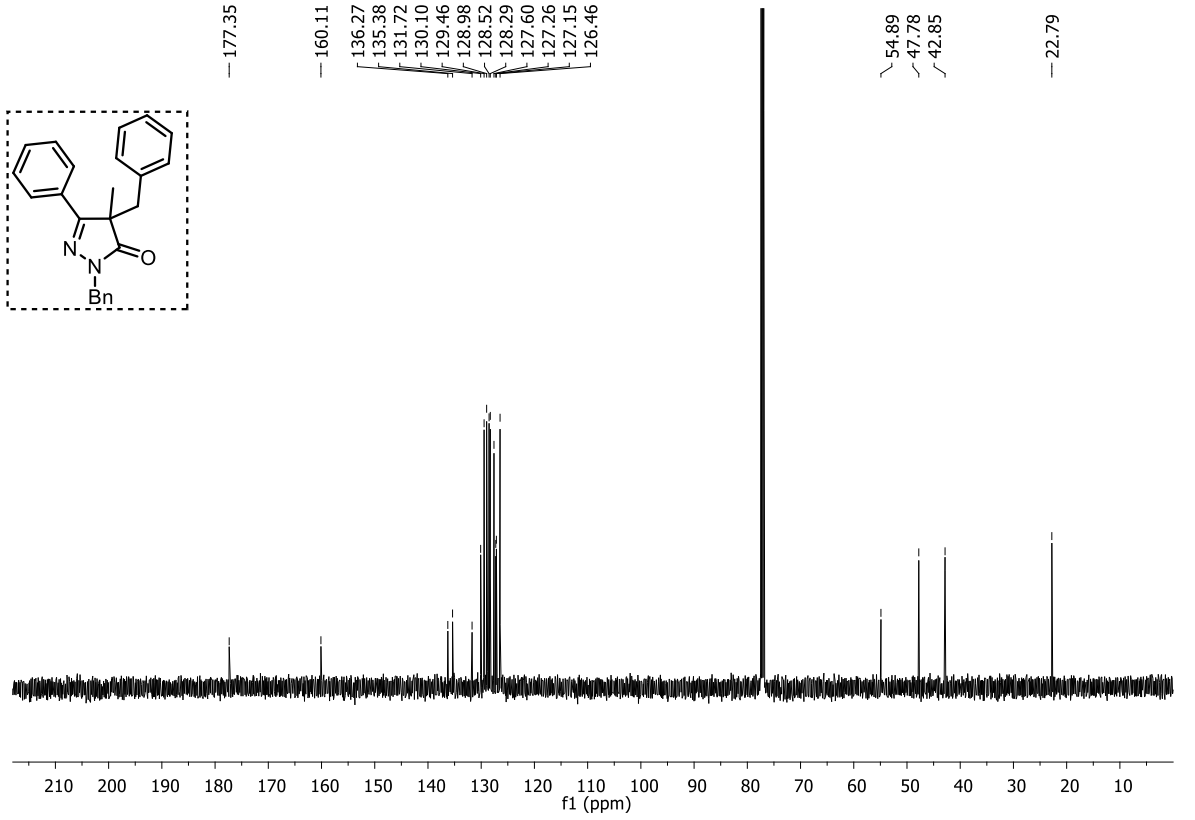
^{13}C {^{1}H} NMR spectrum of 3qa ($CDCl_3$, 126 MHz)



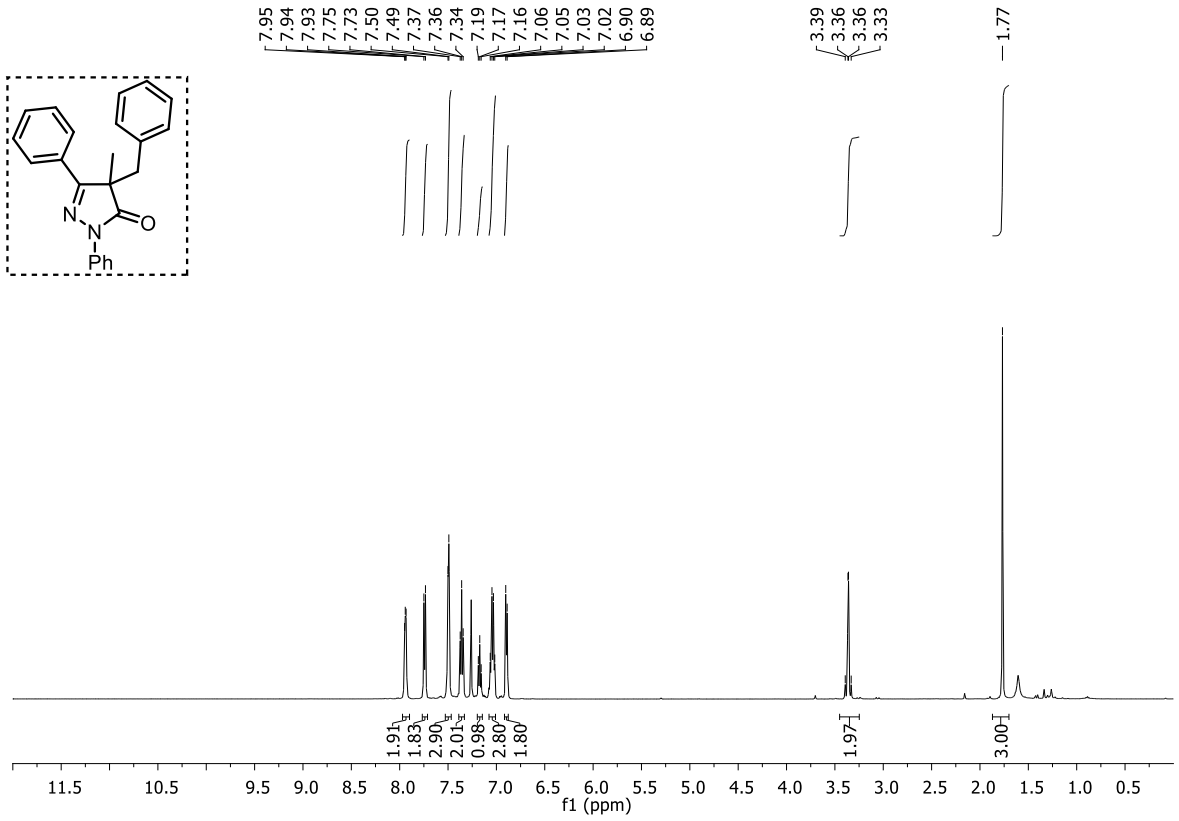
^{1}H NMR spectrum of 3ra ($CDCl_3$, 500 MHz)



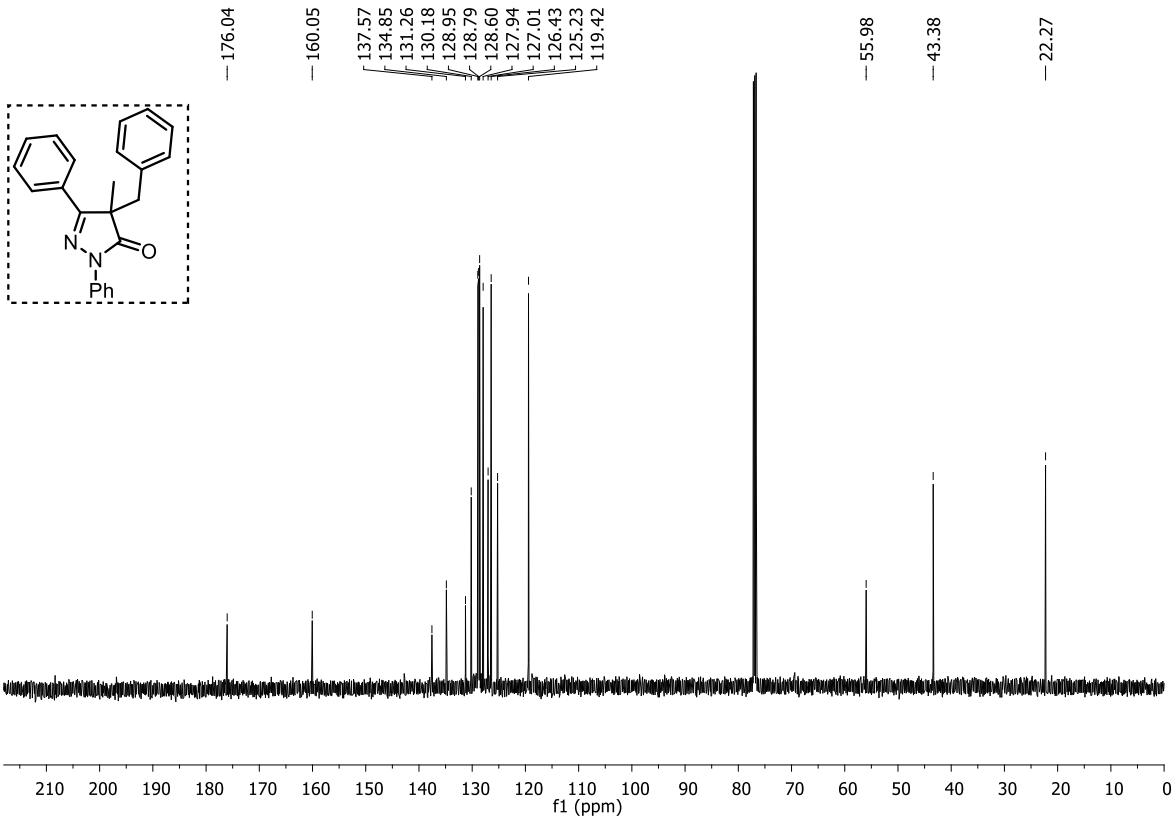
^{13}C {^{1}H} NMR spectrum of 3ra ($CDCl_3$, 126 MHz)



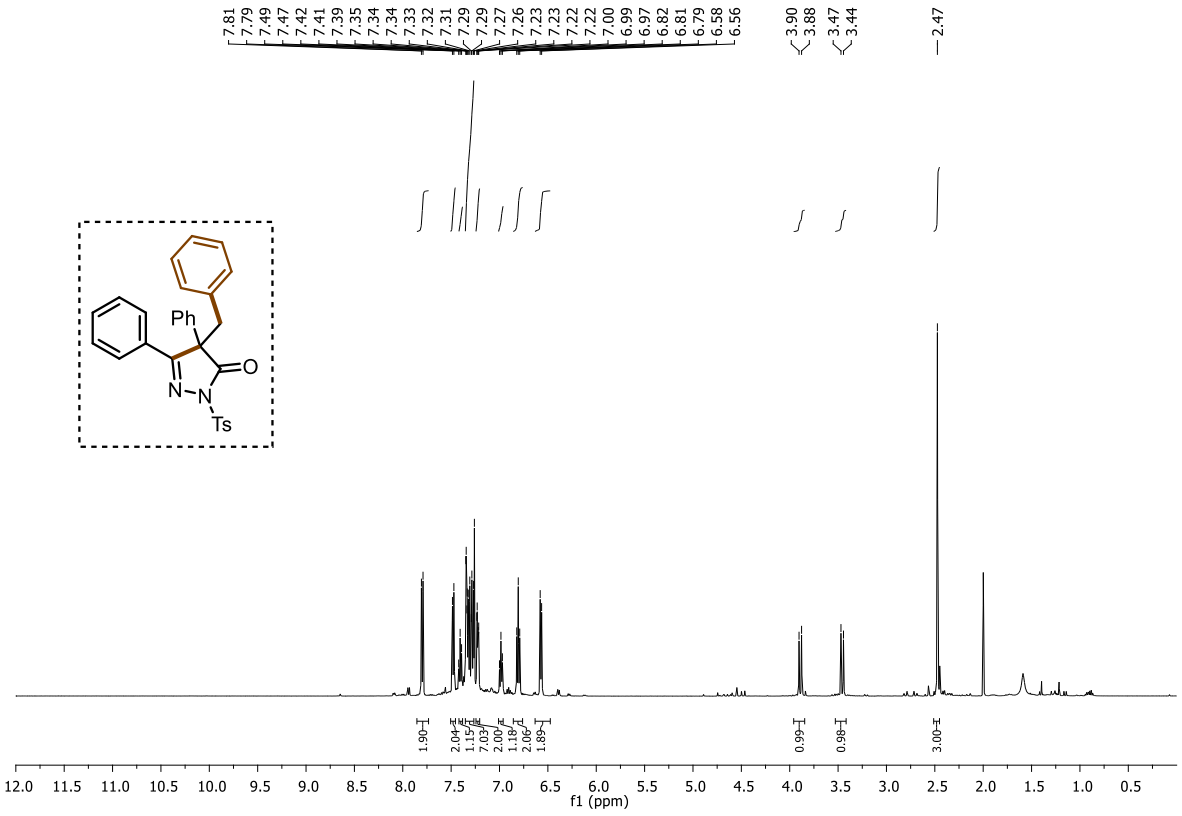
^{1}H NMR spectrum of 3sa ($CDCl_3$, 500 MHz)



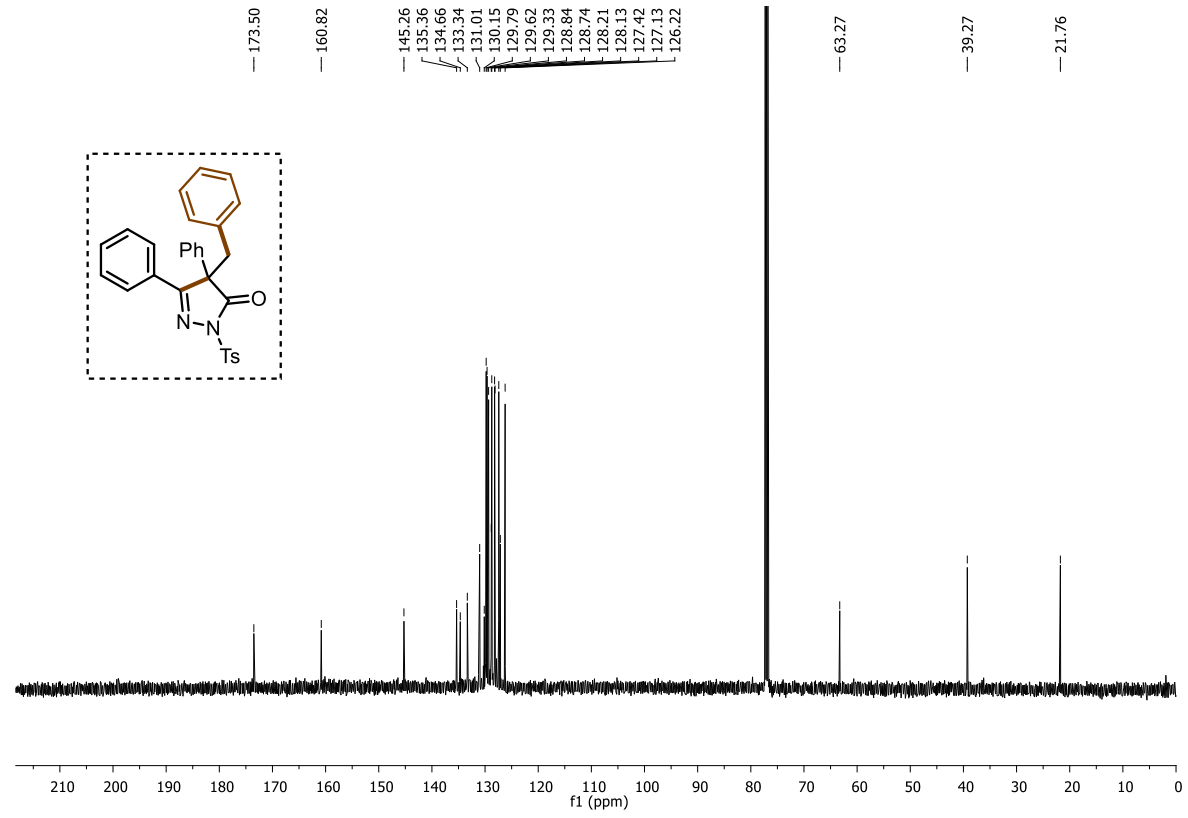
^{13}C {^{1}H} NMR spectrum of 3sa ($CDCl_3$, 126 MHz)



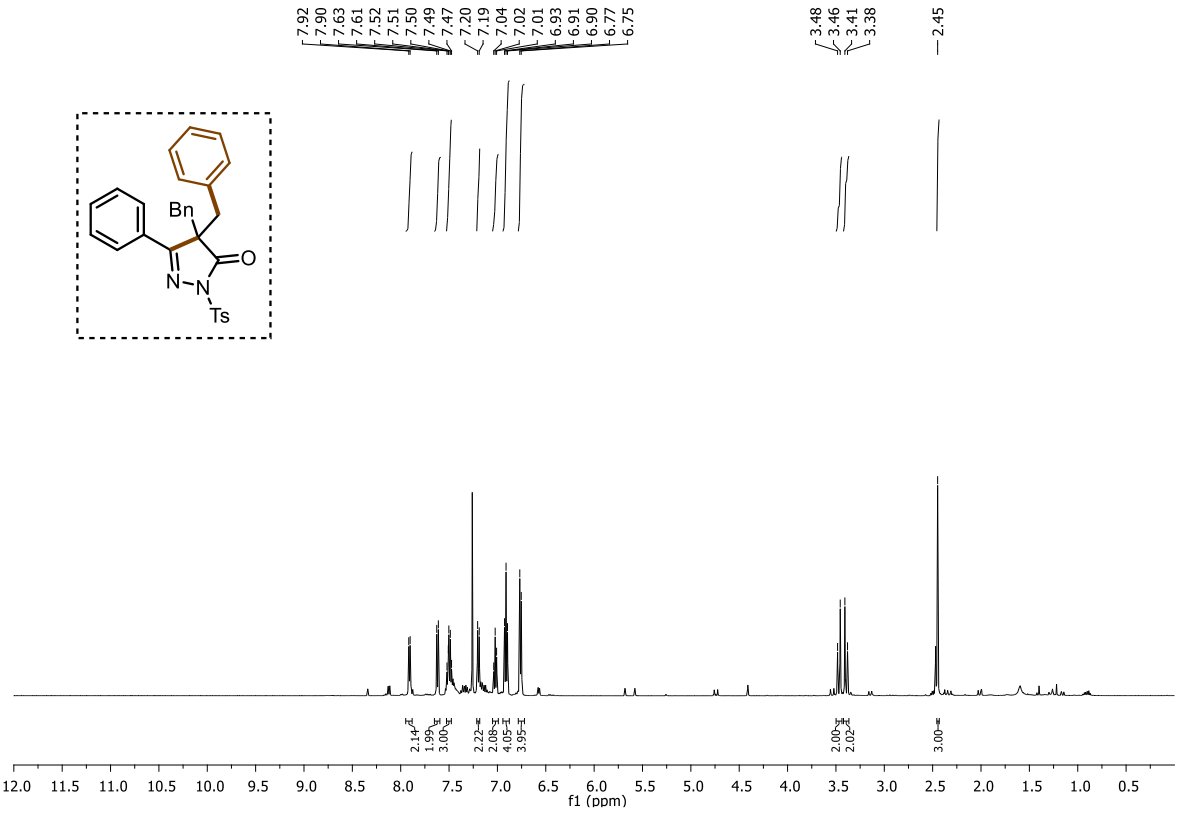
^{1}H NMR spectrum of 3ta ($CDCl_3$, 500 MHz)



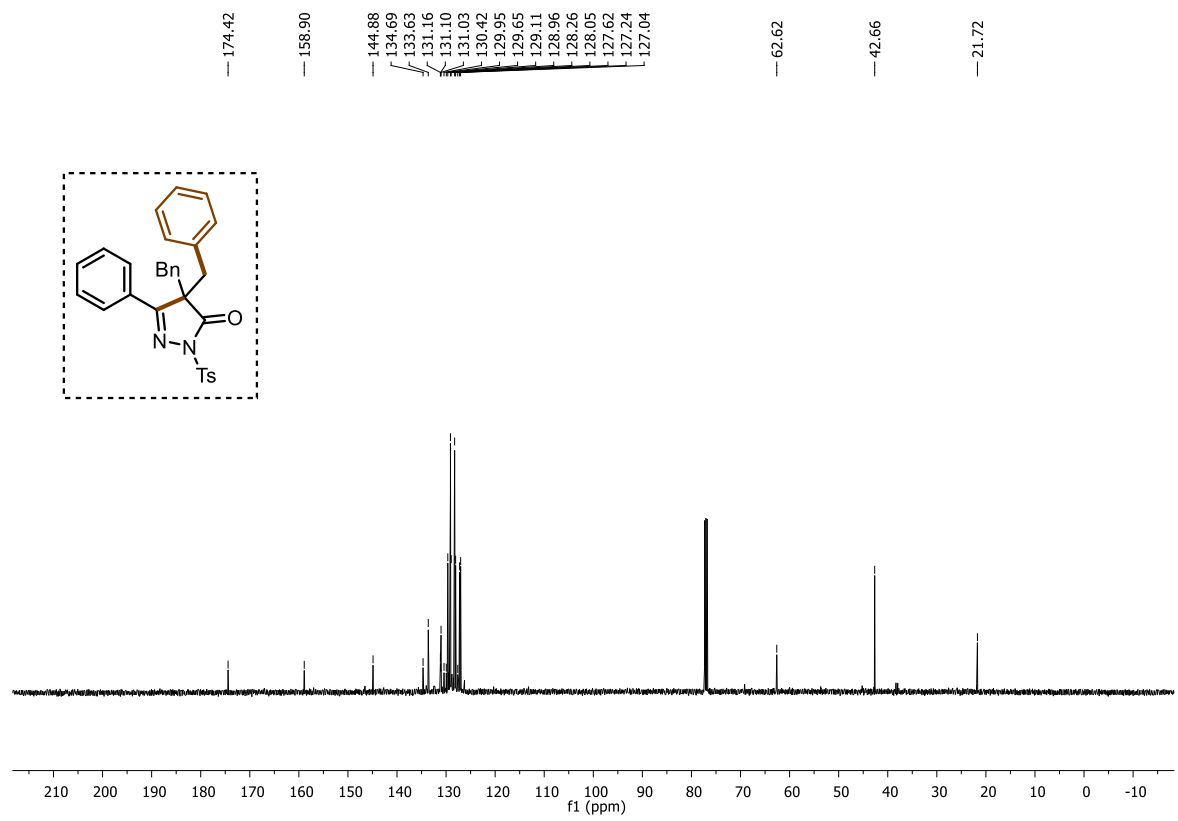
^{13}C {^{1}H} NMR spectrum of 3ta ($CDCl_3$, 126 MHz)



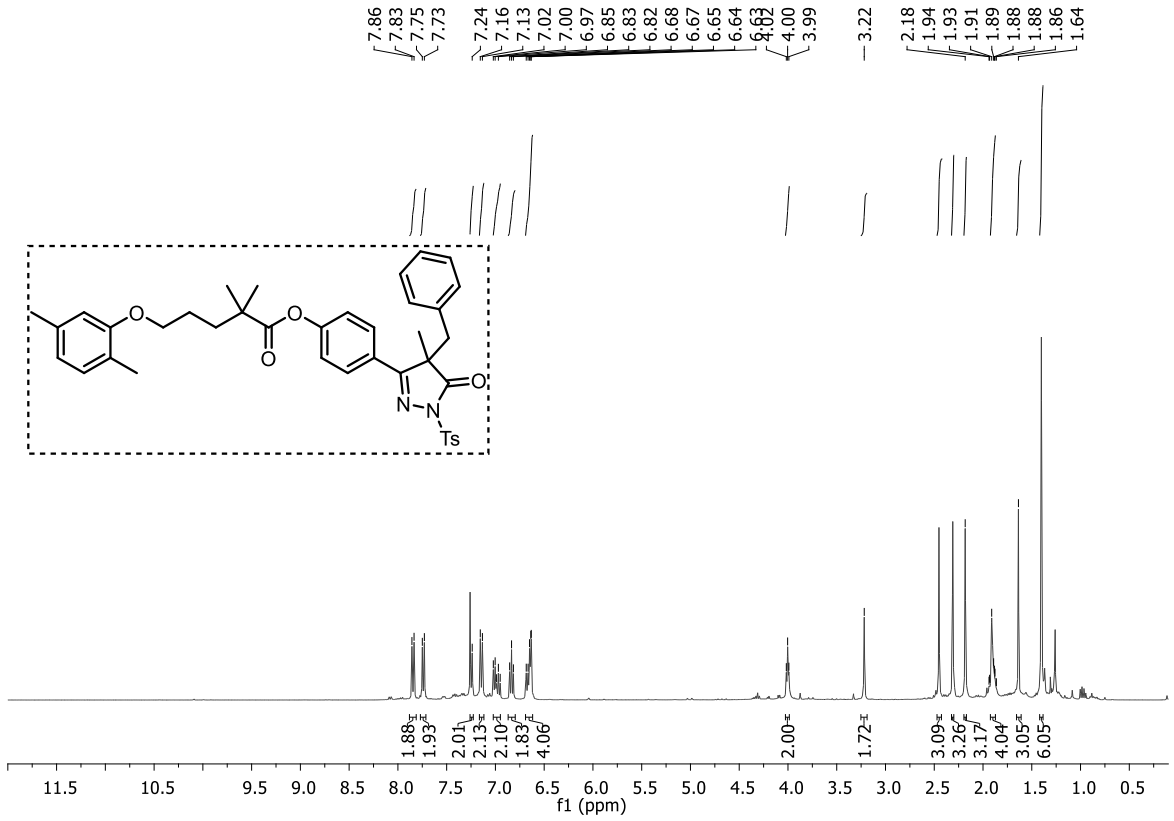
^{1}H NMR spectrum of 3ua ($CDCl_3$, 500 MHz)



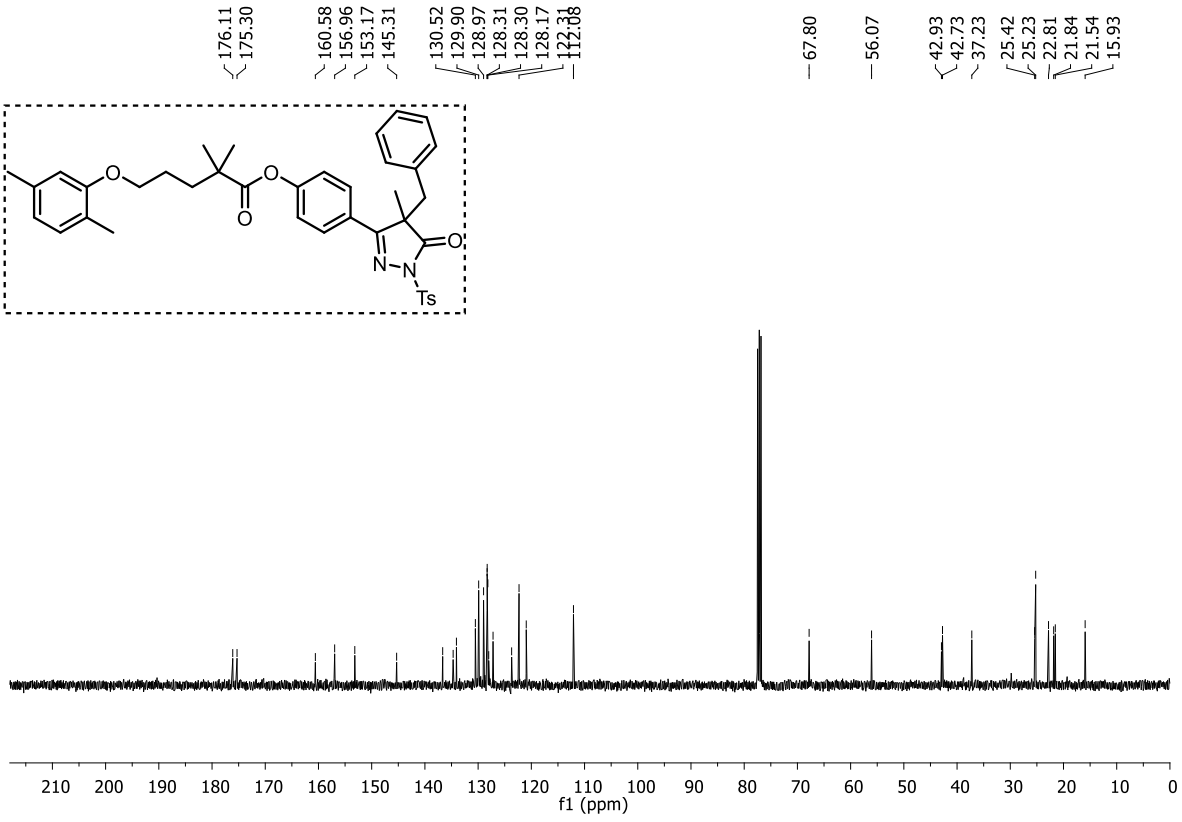
^{13}C {^{1}H} NMR spectrum of 3ua ($CDCl_3$, 126 MHz)



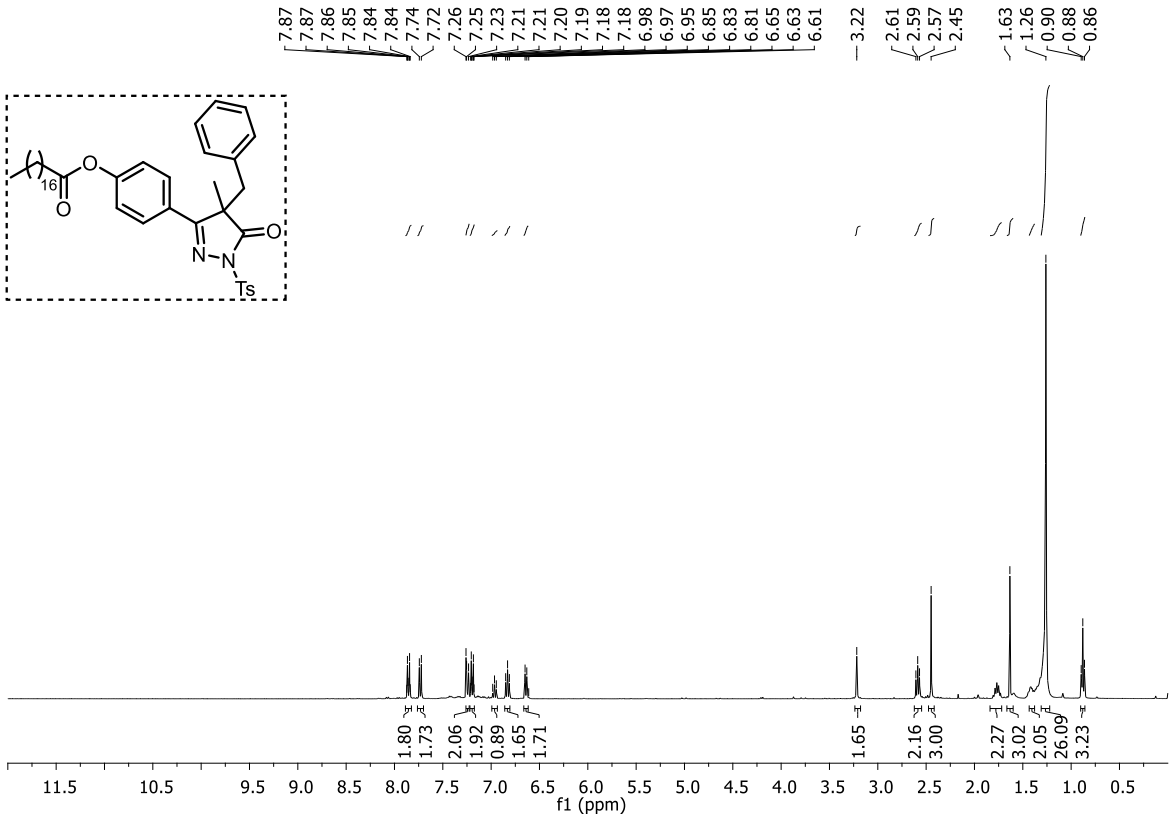
^{1}H NMR spectrum of 3va ($CDCl_3$, 500 MHz)



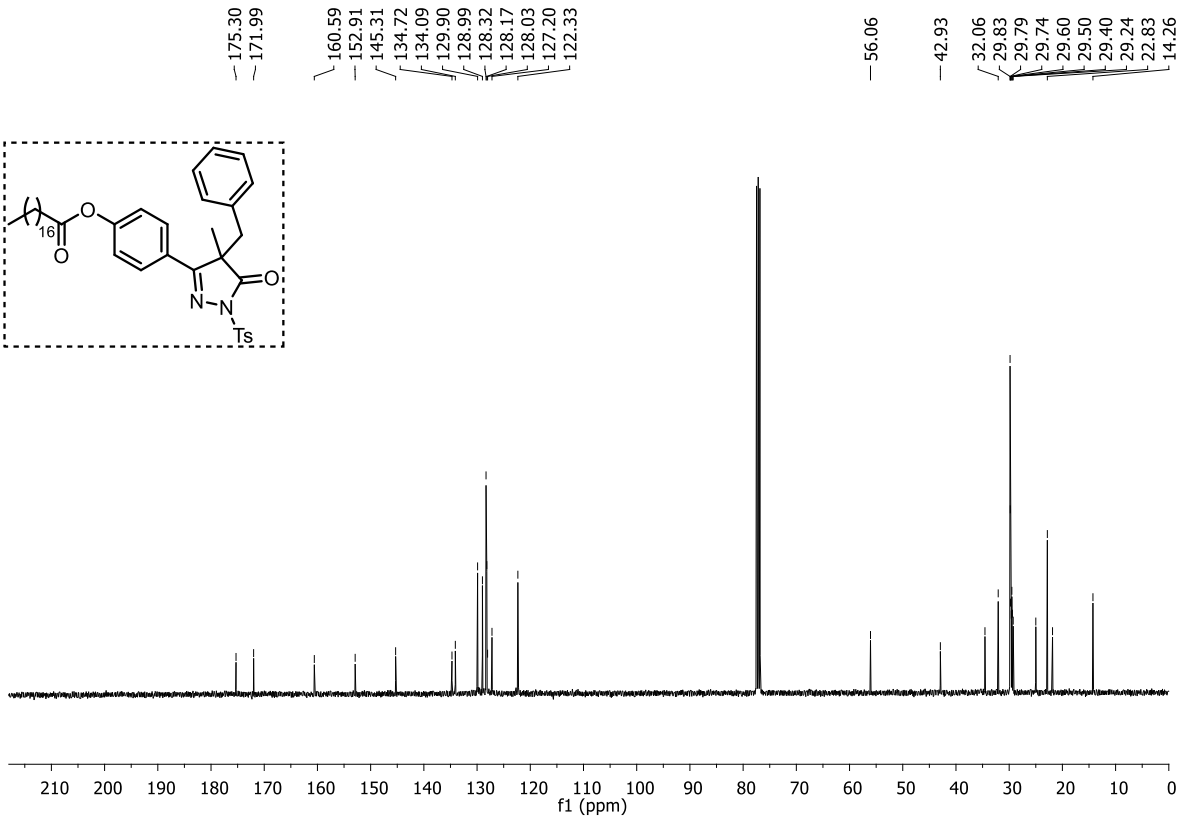
^{13}C {^{1}H} NMR spectrum of 3va ($CDCl_3$, 126 MHz)



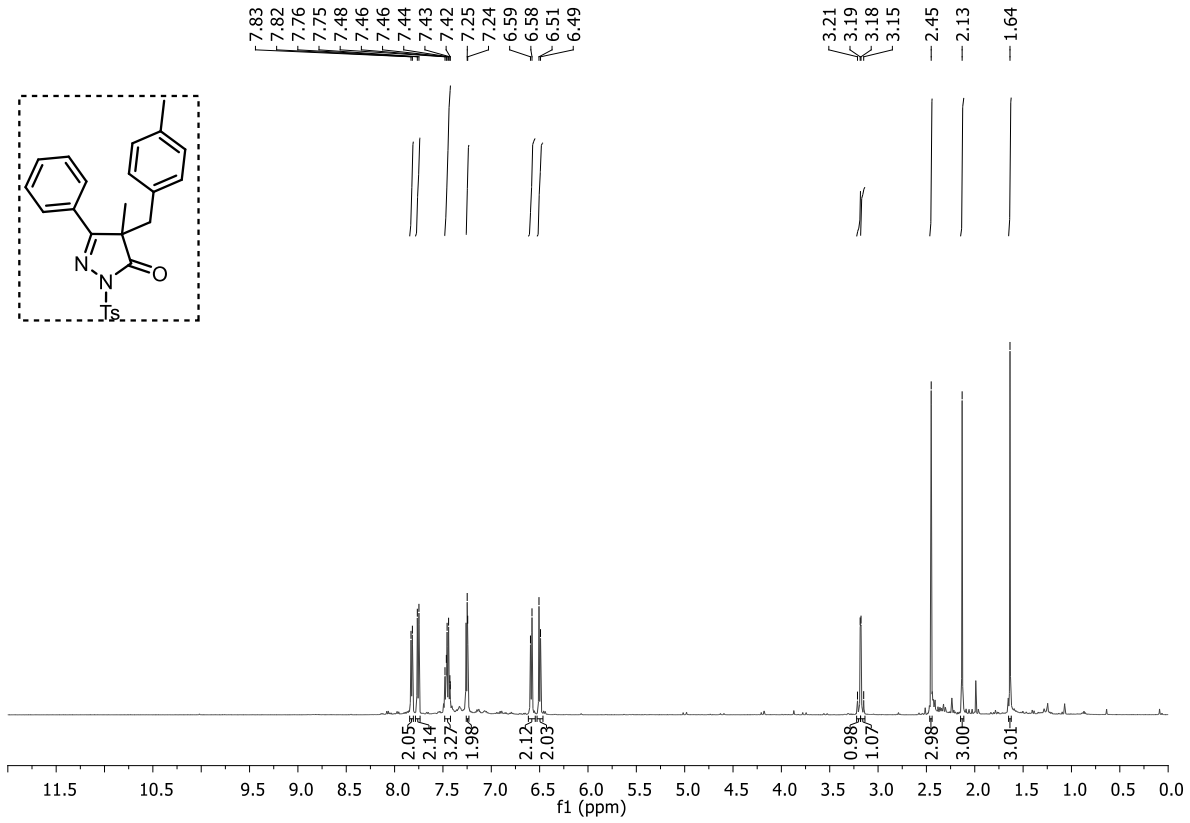
^{1}H NMR spectrum of 3wa ($CDCl_3$, 500 MHz)



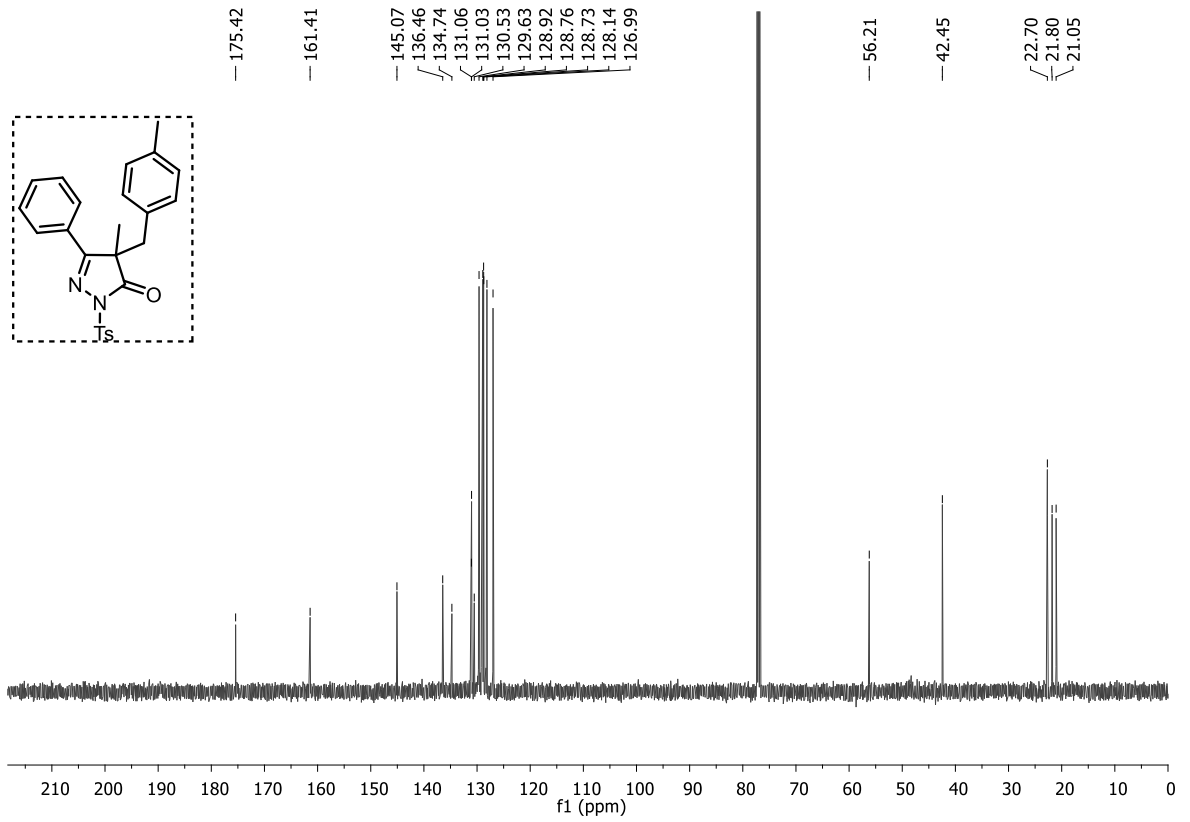
^{13}C {^{1}H} NMR spectrum of 3wa ($CDCl_3$, 126 MHz)



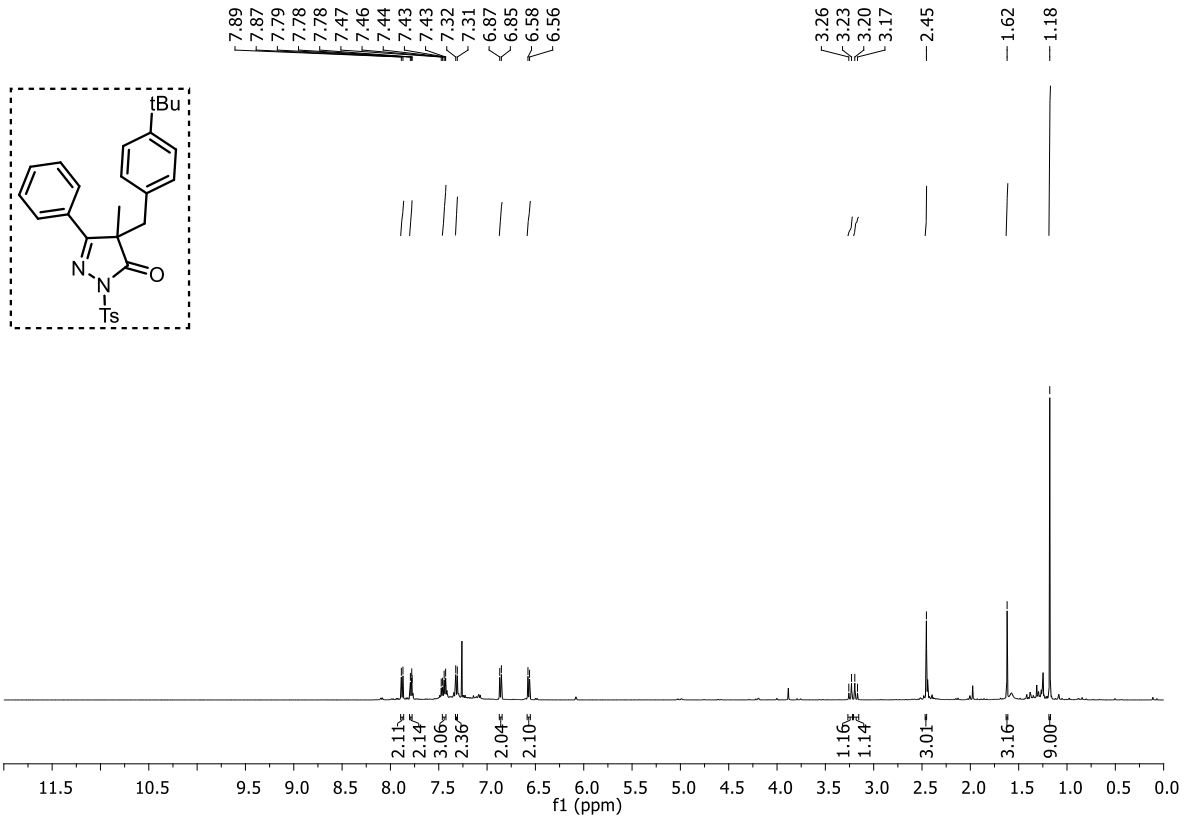
^{1}H NMR spectrum of 3ab ($CDCl_3$, 500 MHz)



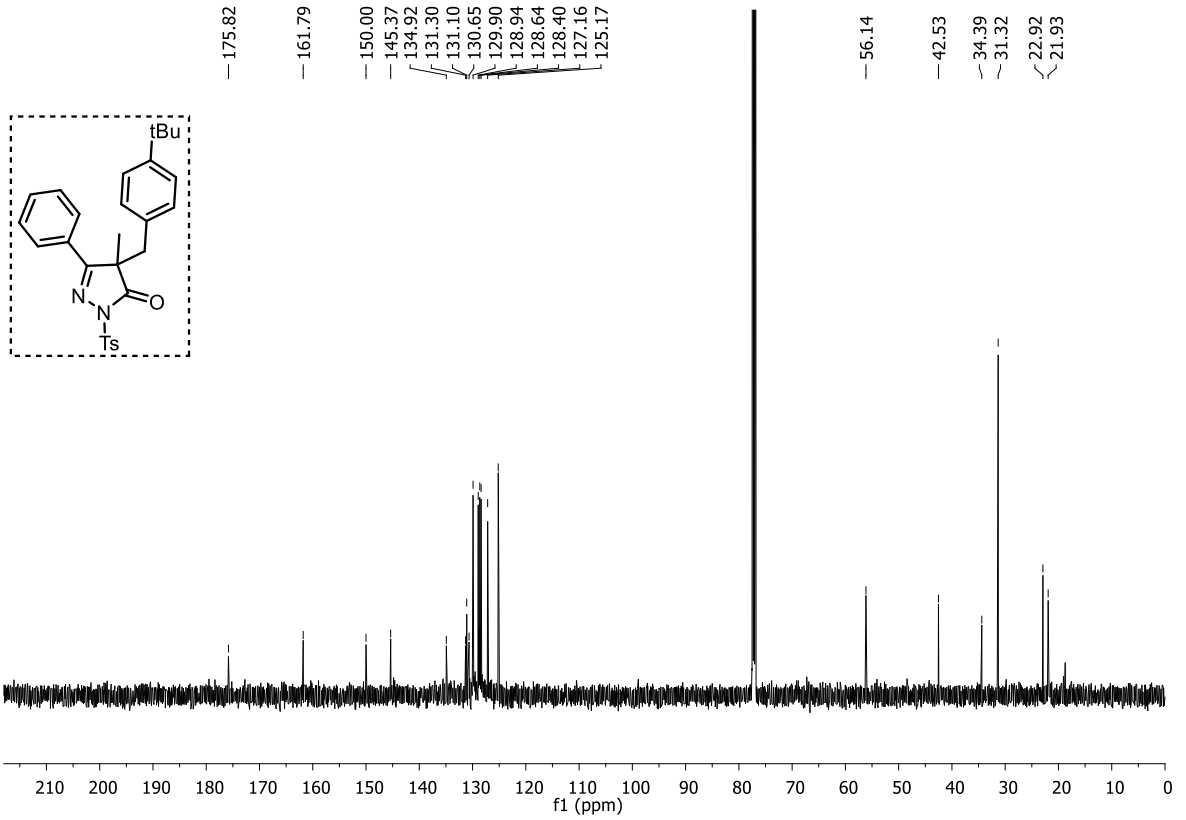
^{13}C {^{1}H} NMR spectrum of 3ab ($CDCl_3$, 126 MHz)



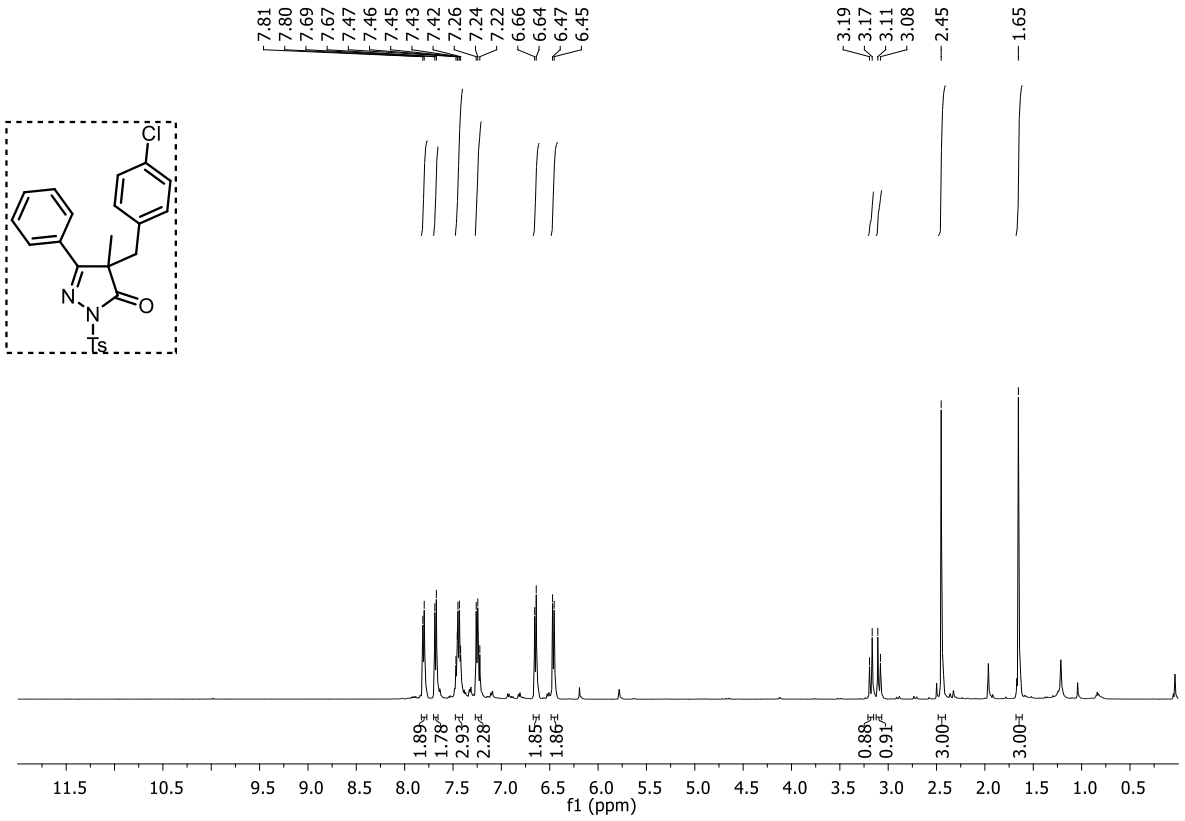
^{1}H NMR spectrum of 3ac ($CDCl_3$, 500 MHz)



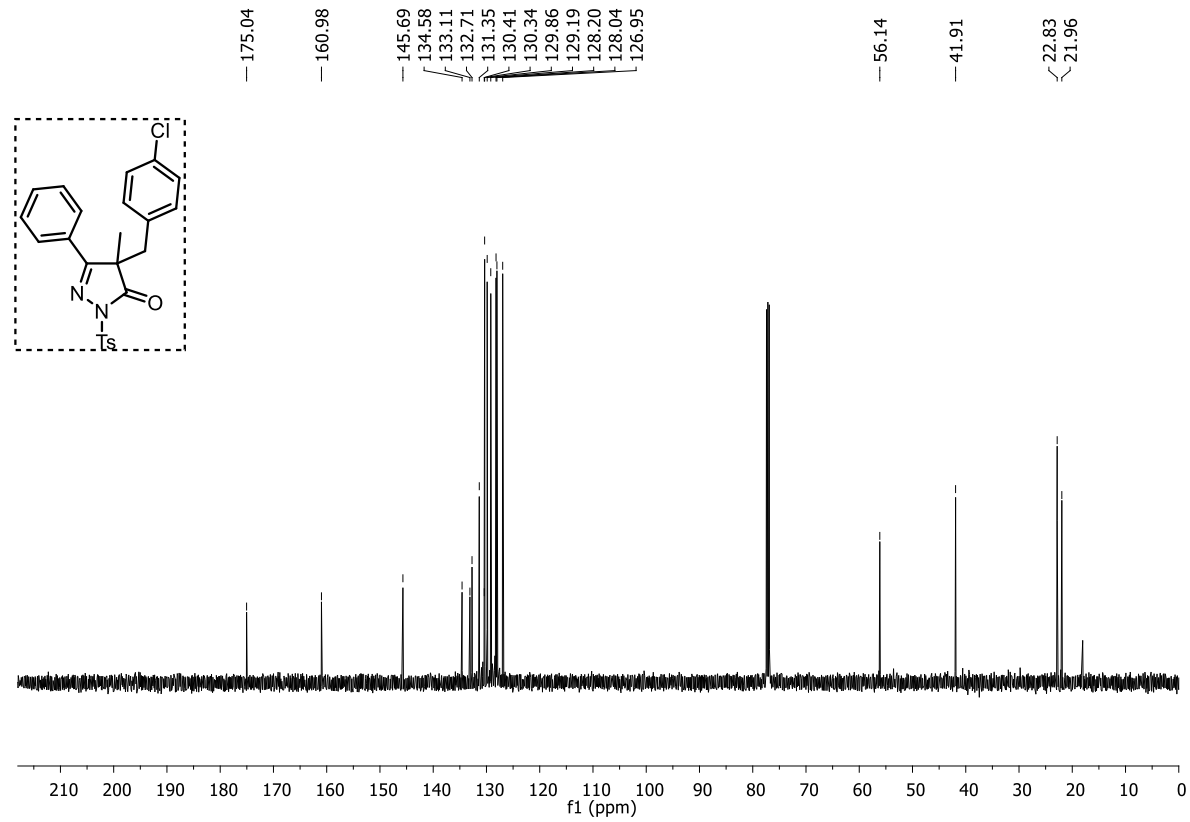
^{13}C {^{1}H} NMR spectrum of 3ac ($CDCl_3$, 126 MHz)



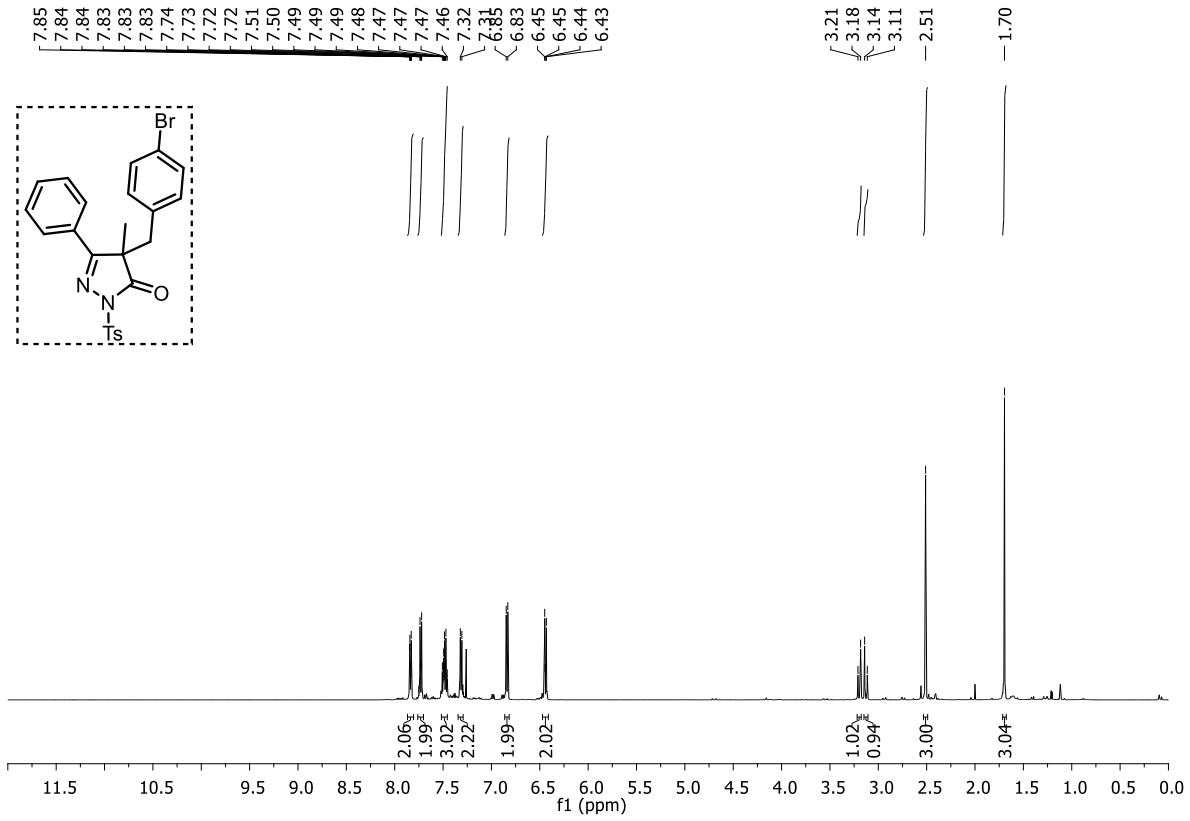
^{1}H NMR spectrum of 3ad ($CDCl_3$, 500 MHz)



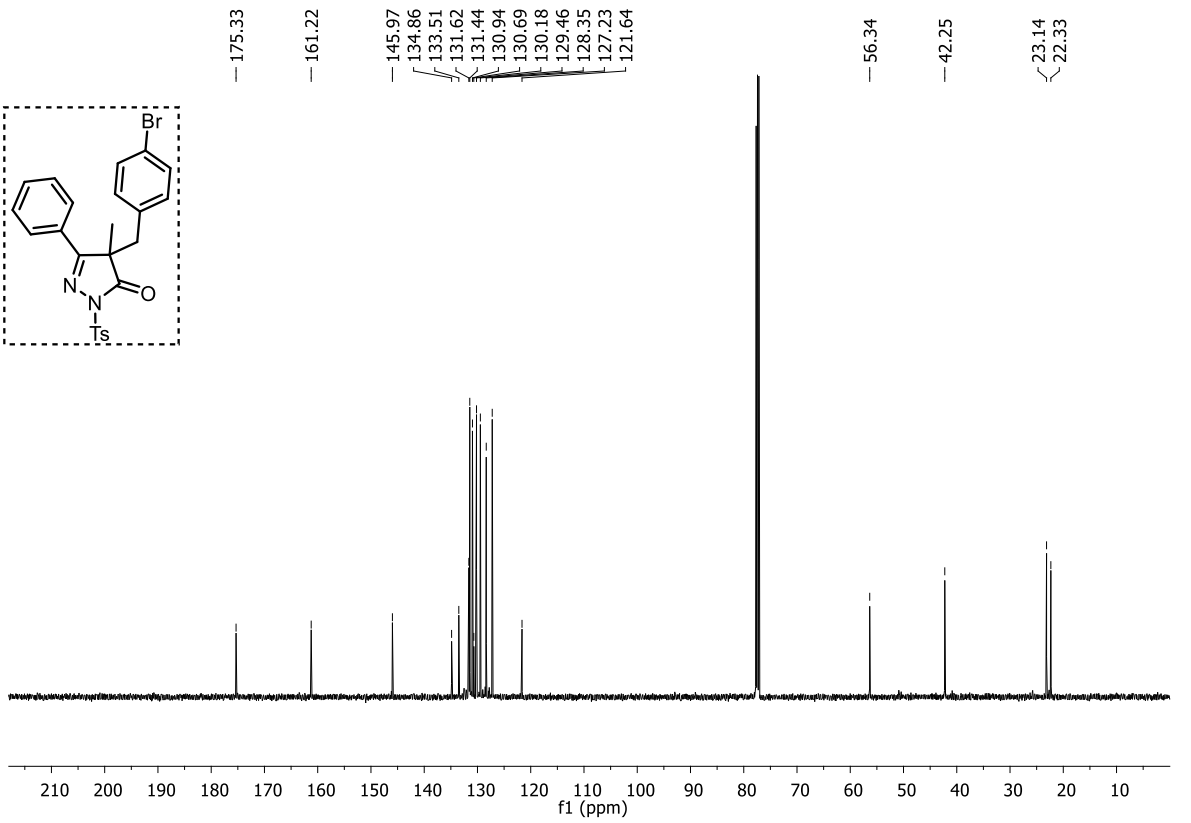
^{13}C {^{1}H} NMR spectrum of 3ad ($CDCl_3$, 126 MHz)



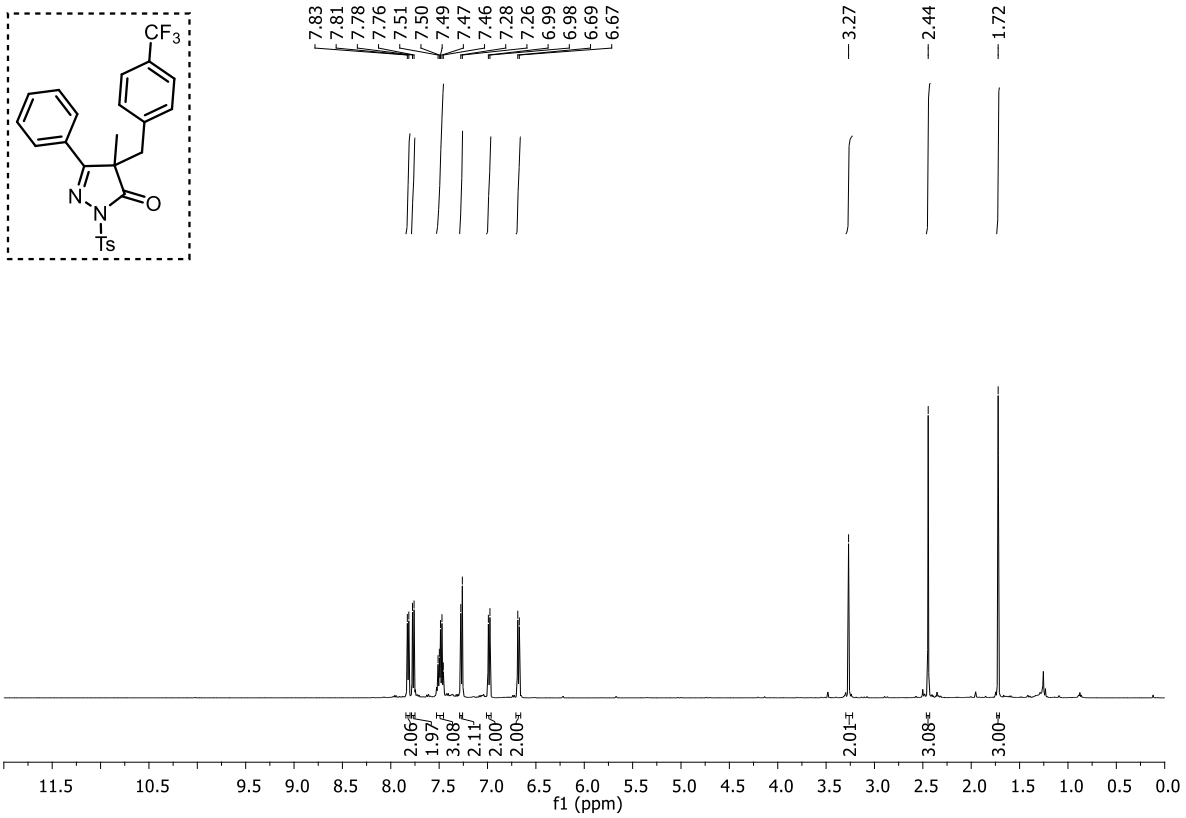
^{1}H NMR spectrum of 3ae ($CDCl_3$, 500 MHz)



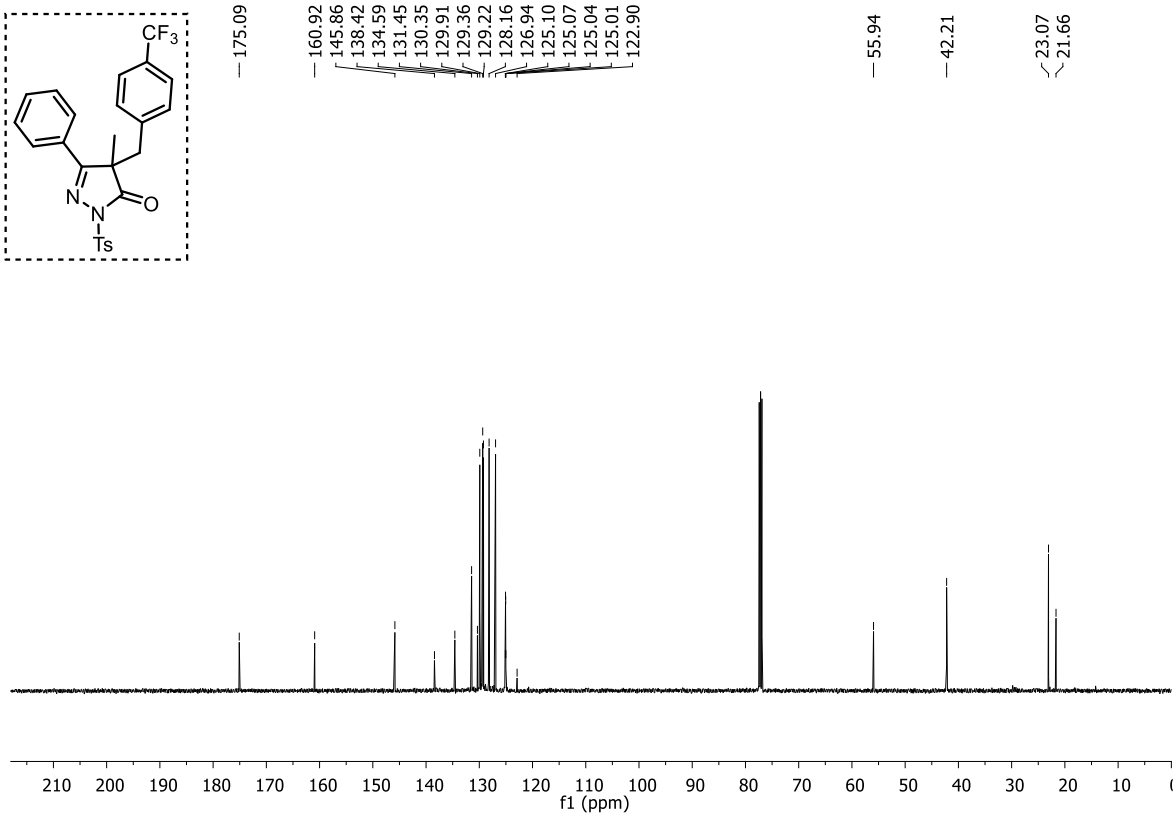
^{13}C {^{1}H} NMR spectrum of 3ae ($CDCl_3$, 126 MHz)



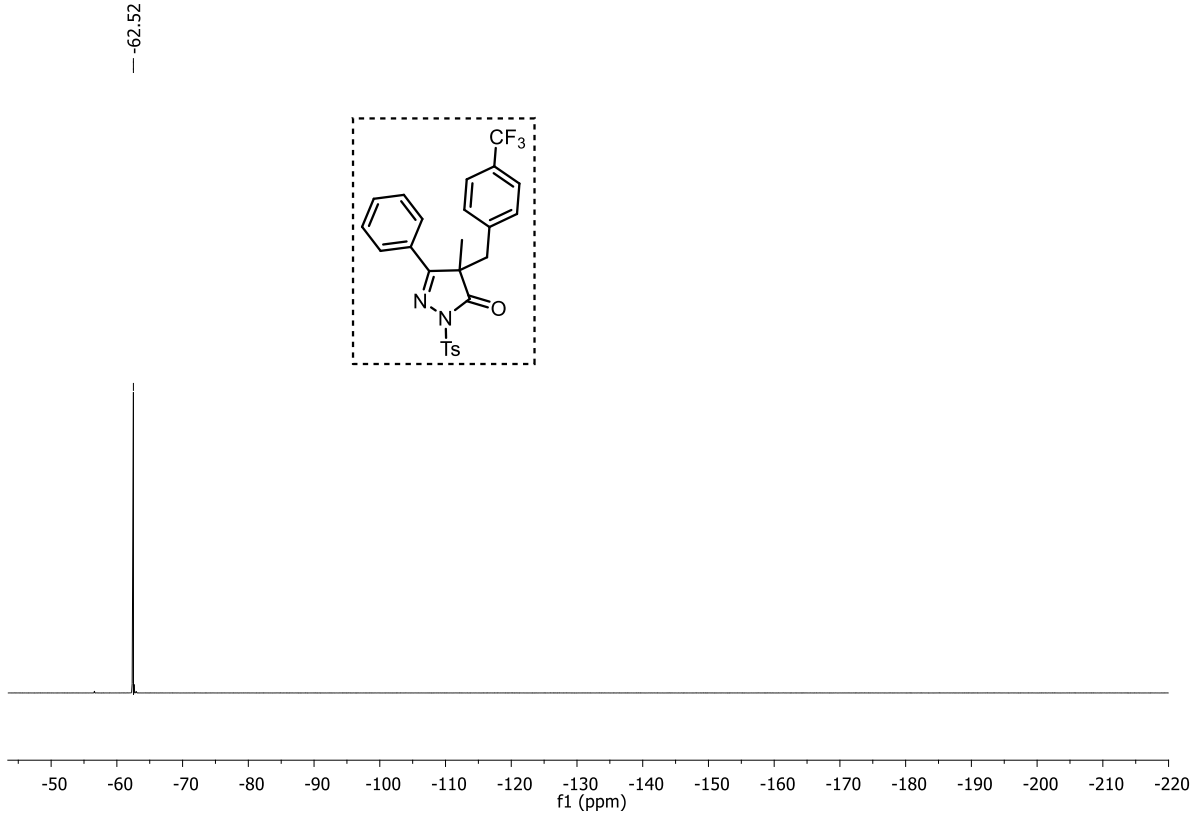
^{1}H NMR spectrum of 3af ($CDCl_3$, 500 MHz)



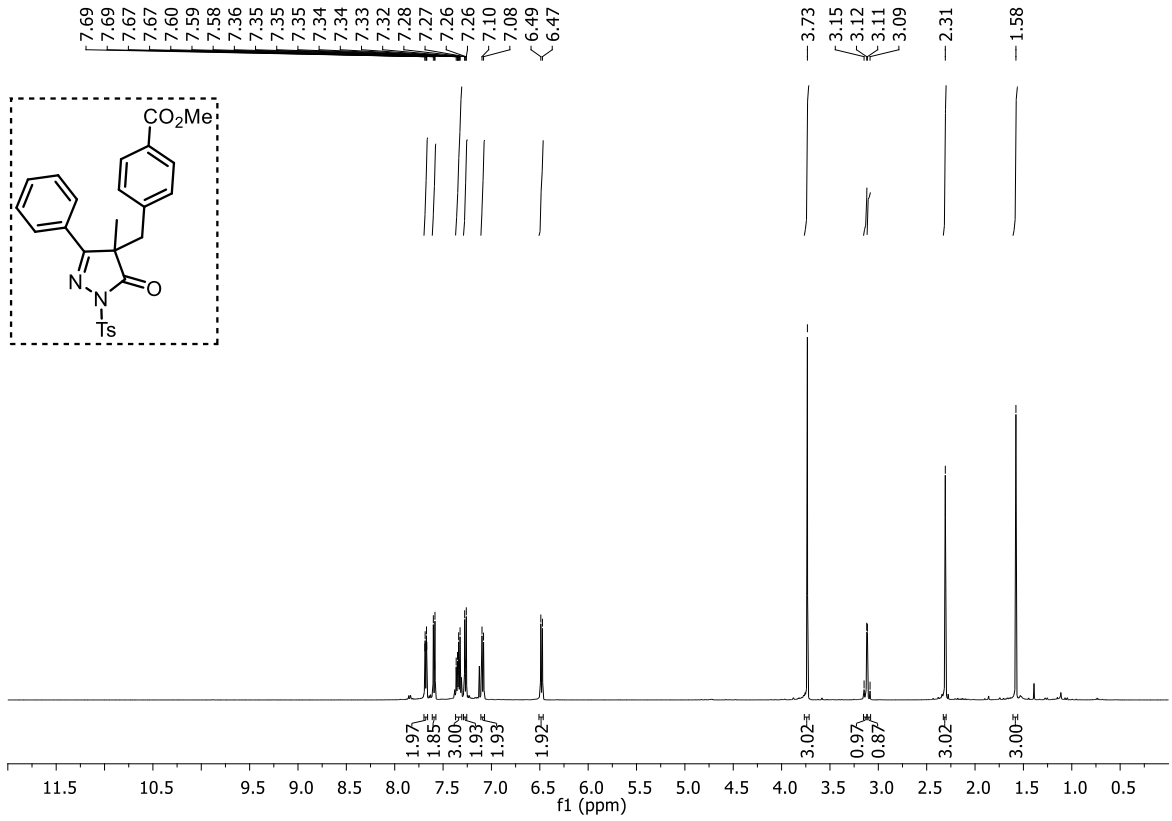
^{13}C {^{1}H} NMR spectrum of 3af ($CDCl_3$, 126 MHz)



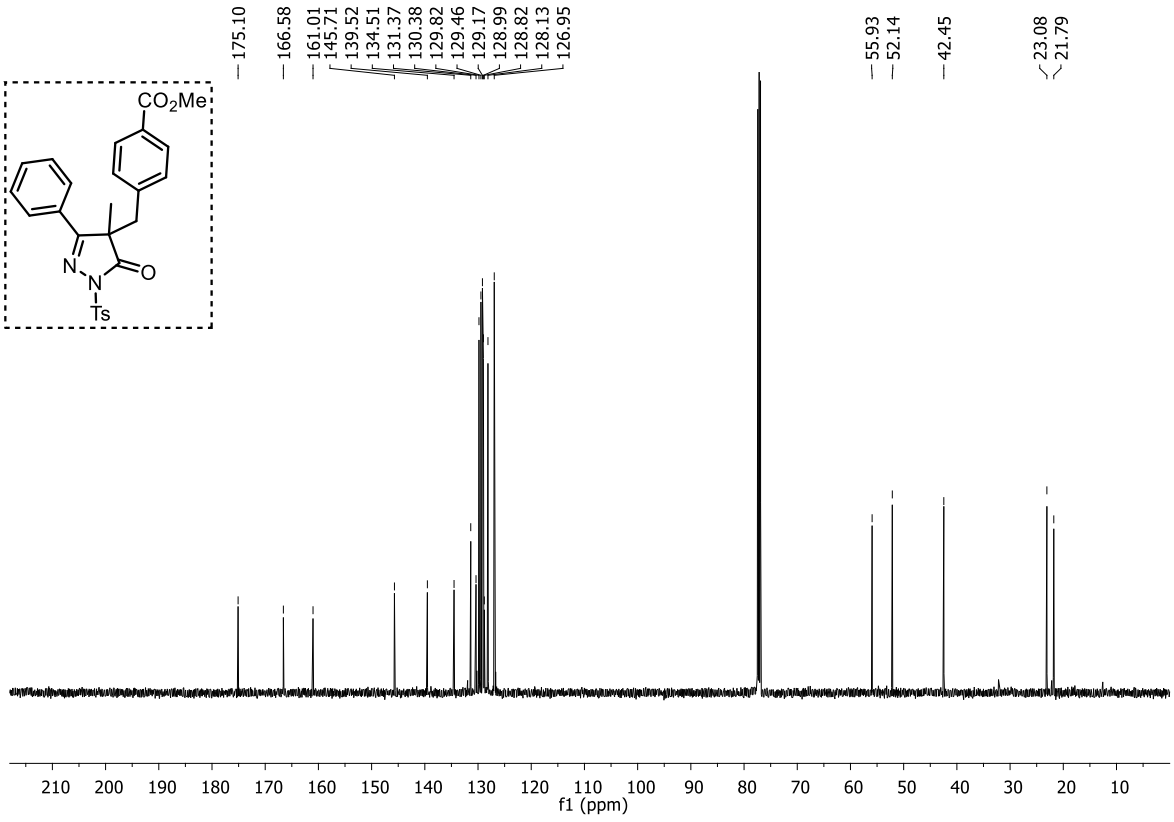
^{19}F {^{1}H} NMR spectrum of 3af ($CDCl_3$, 471 MHz)



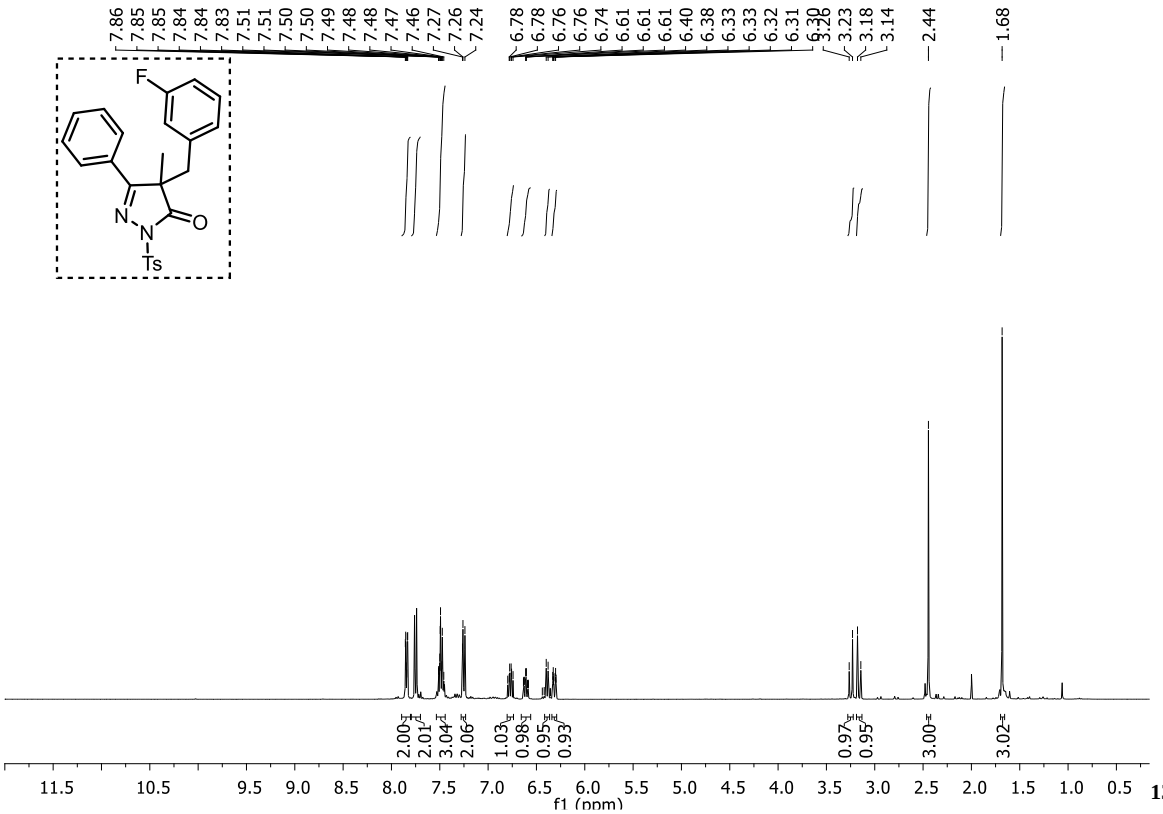
^{1}H NMR spectrum of 3ag ($CDCl_3$, 500 MHz)



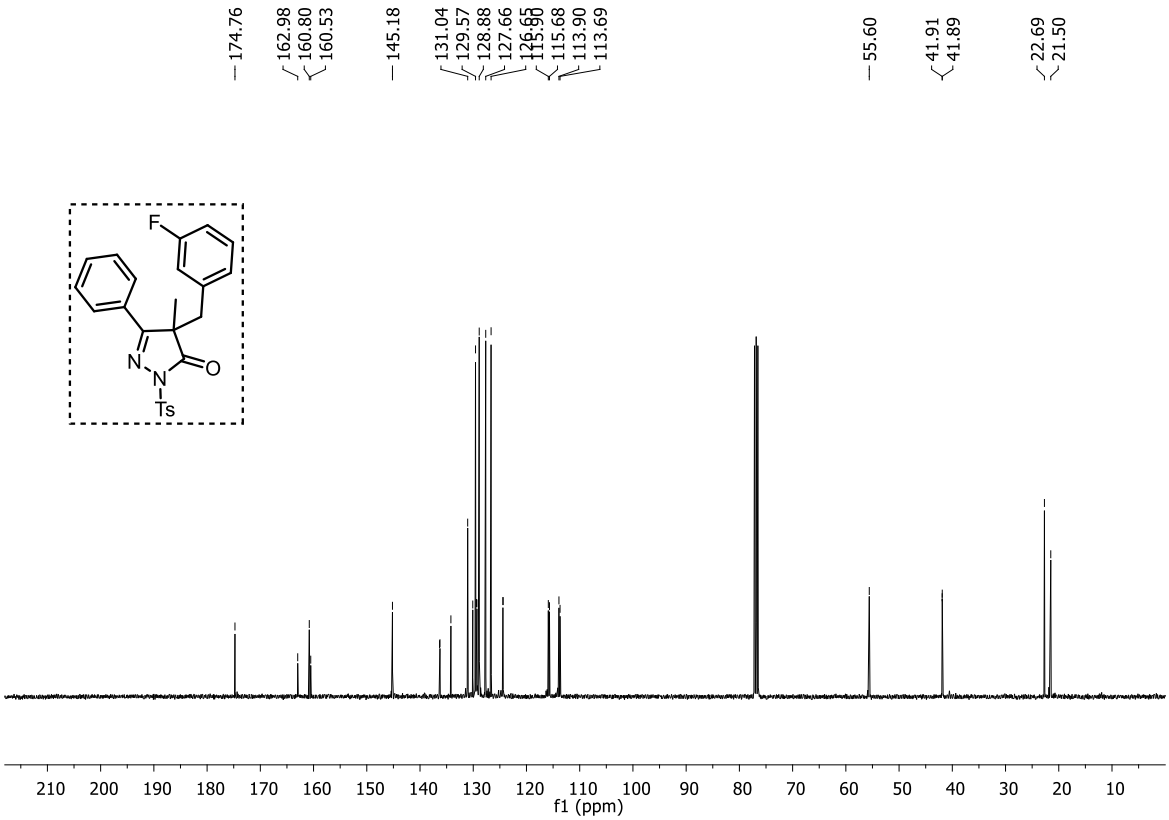
^{13}C {^{1}H} NMR spectrum of 3ag ($CDCl_3$, 126 MHz)



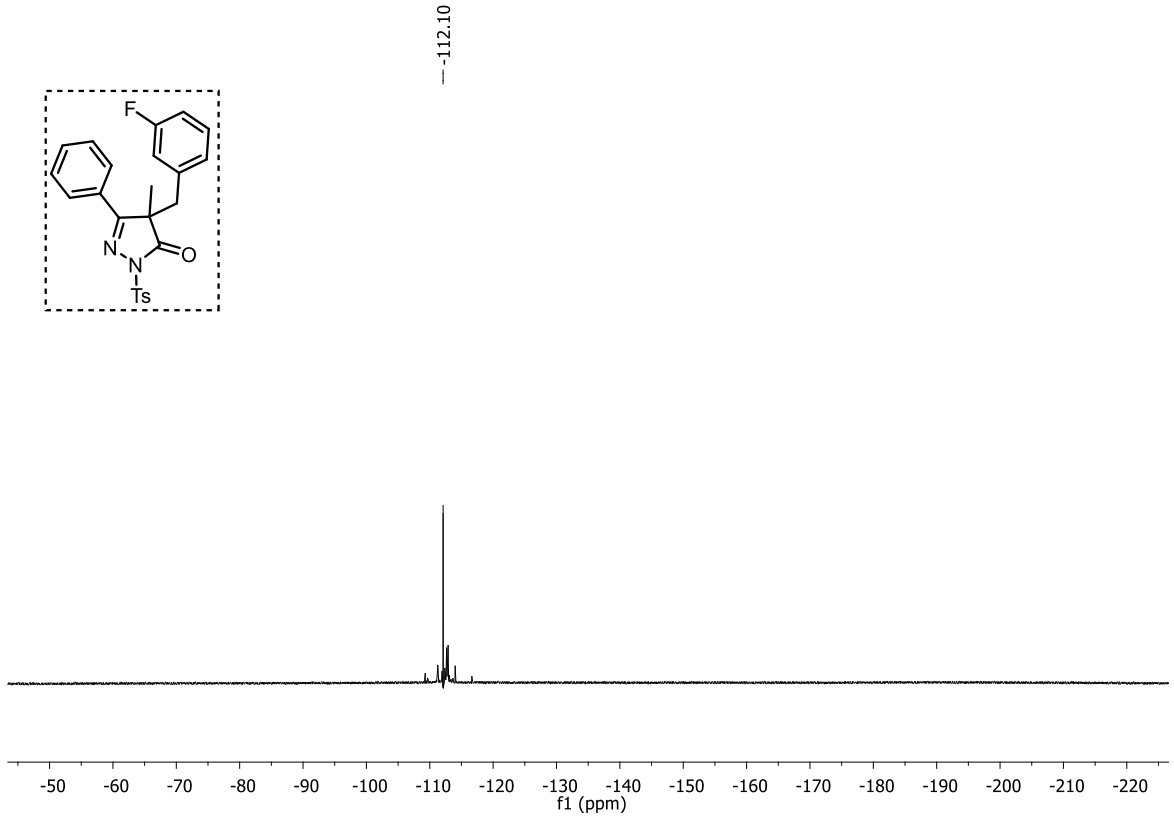
^{1}H NMR spectrum of 3ah ($CDCl_3$, 500 MHz)



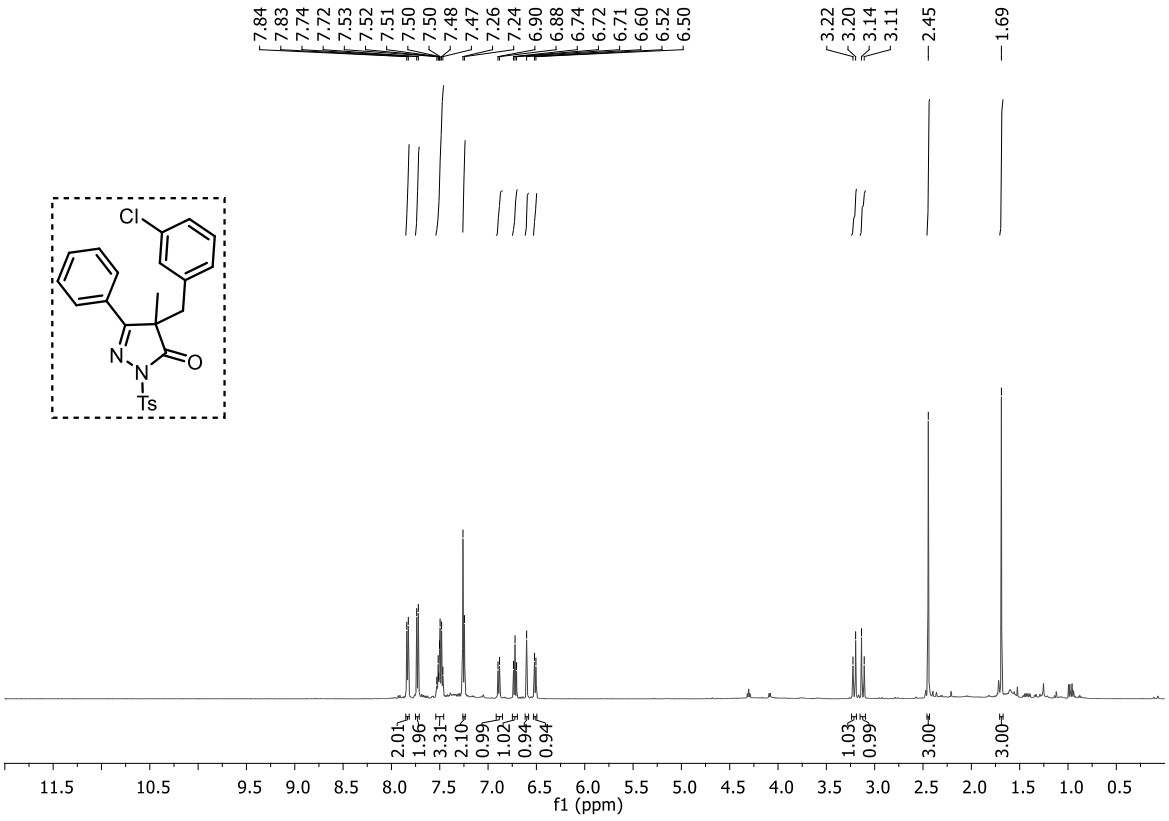
^{13}C {^{1}H} NMR spectrum of 3ah ($CDCl_3$, 126 MHz)



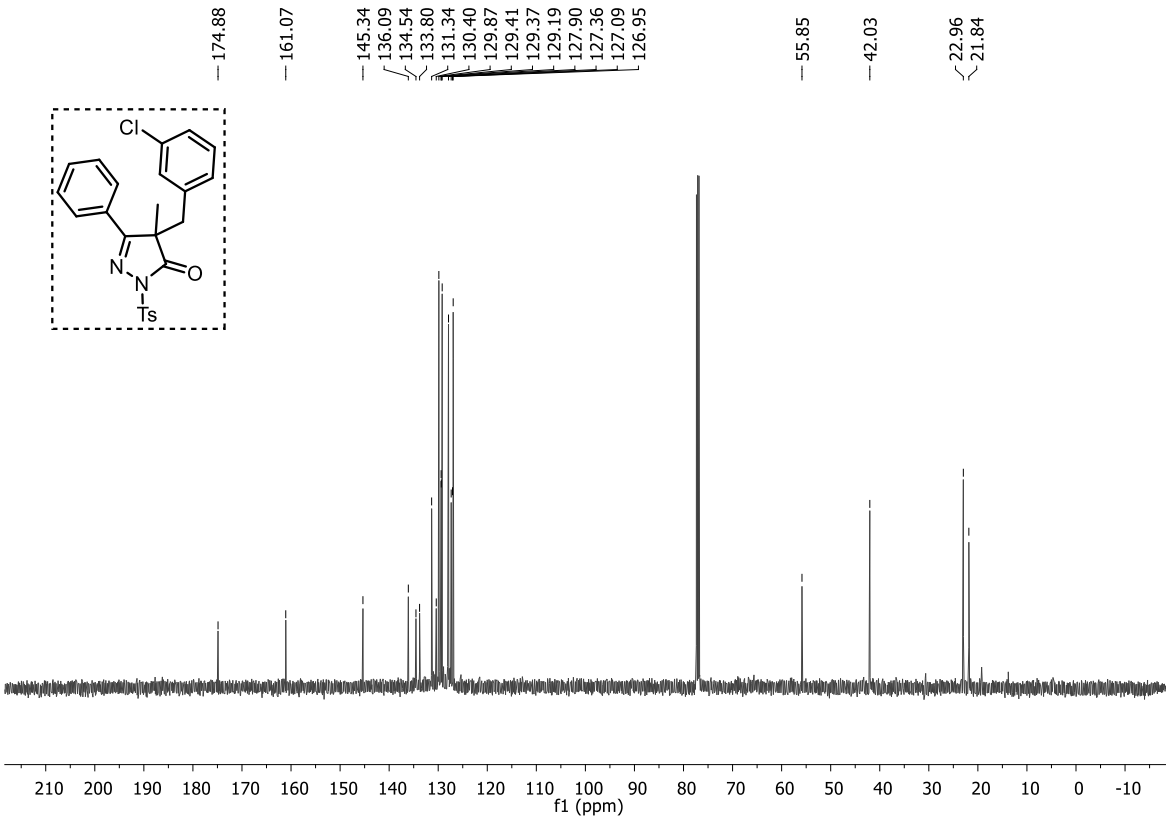
^{19}F {^{1}H} NMR spectrum of 3ah ($CDCl_3$, 471 MHz)



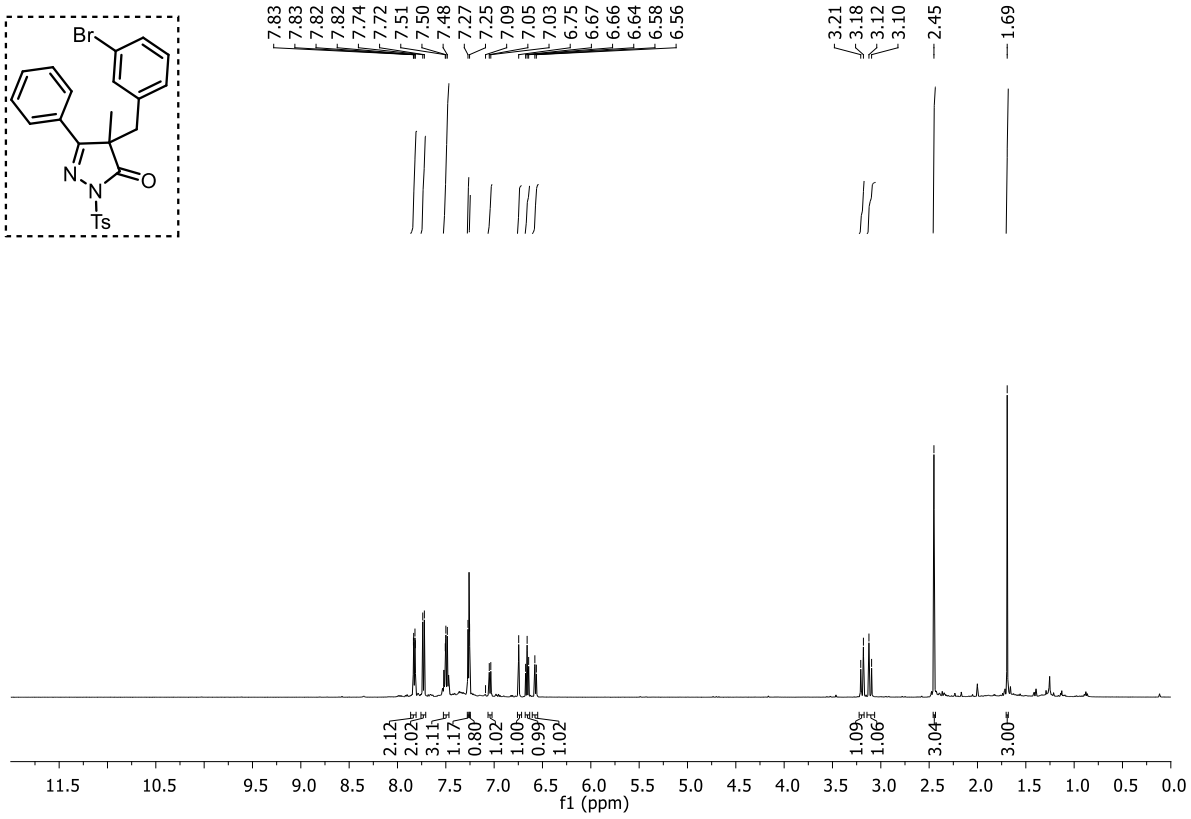
^{1}H NMR spectrum of 3ai ($CDCl_3$, 500 MHz)



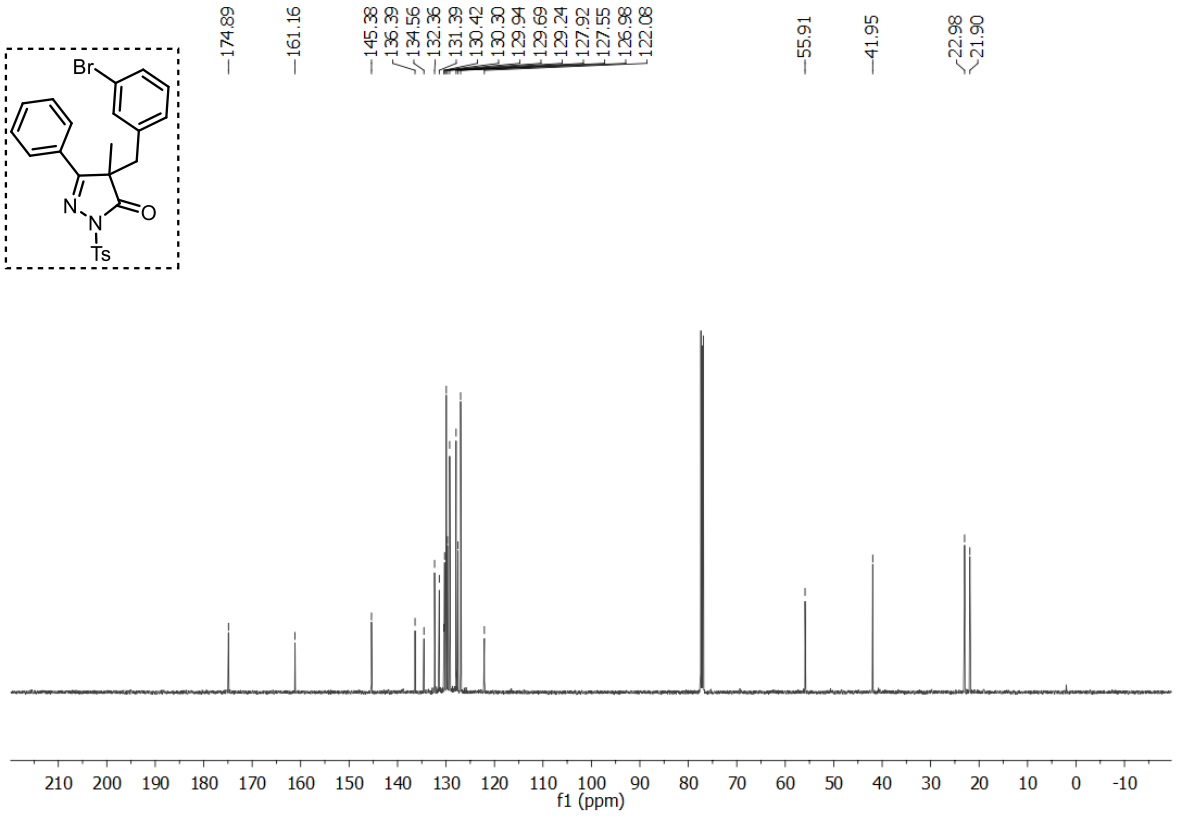
^{13}C {^{1}H} NMR spectrum of 3ai ($CDCl_3$, 126 MHz)



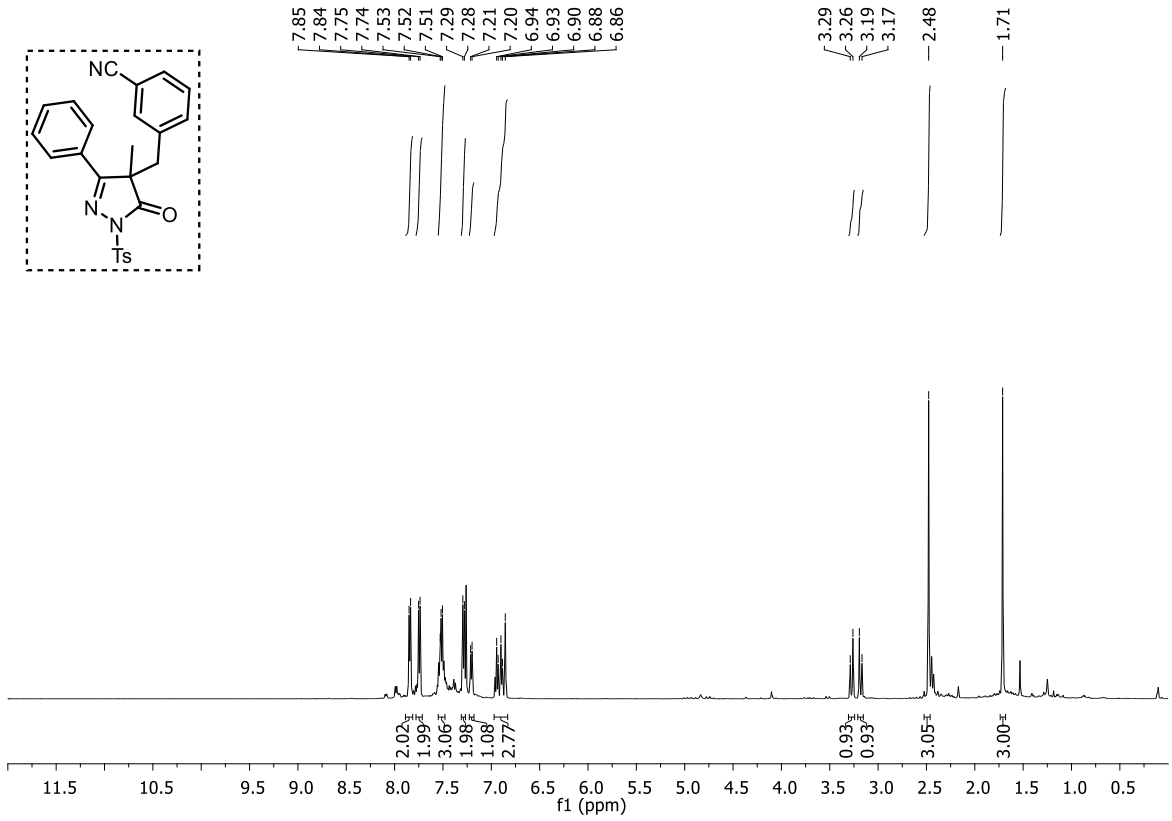
^{1}H NMR spectrum of 3aj ($CDCl_3$, 500 MHz)



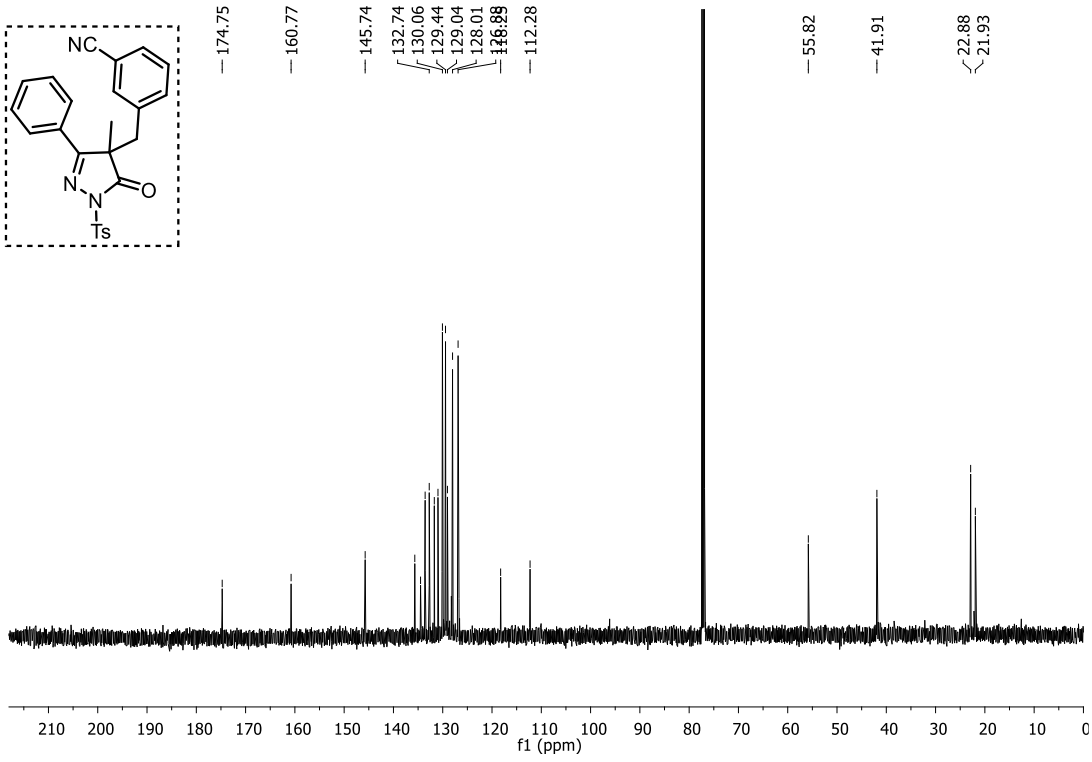
^{13}C {^{1}H} NMR spectrum of 3aj ($CDCl_3$, 126 MHz)



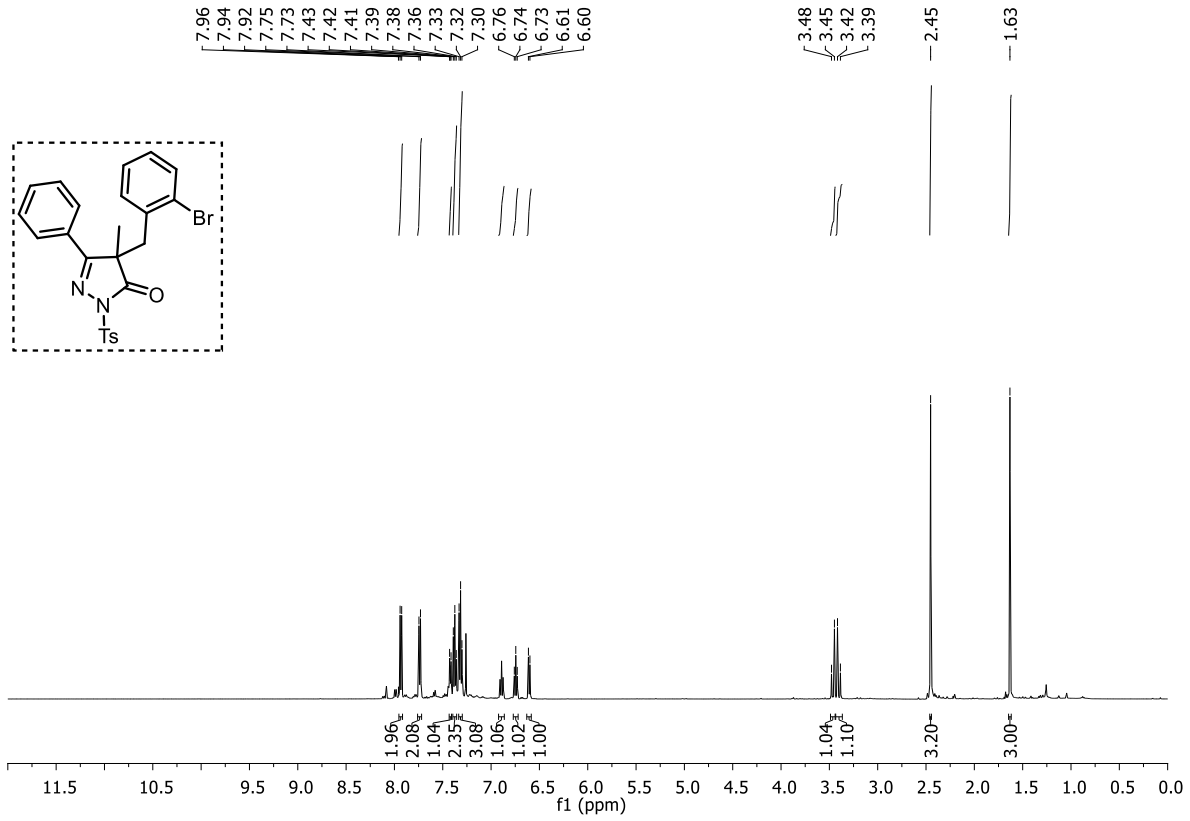
^{1}H NMR spectrum of 3ak ($CDCl_3$, 500 MHz)



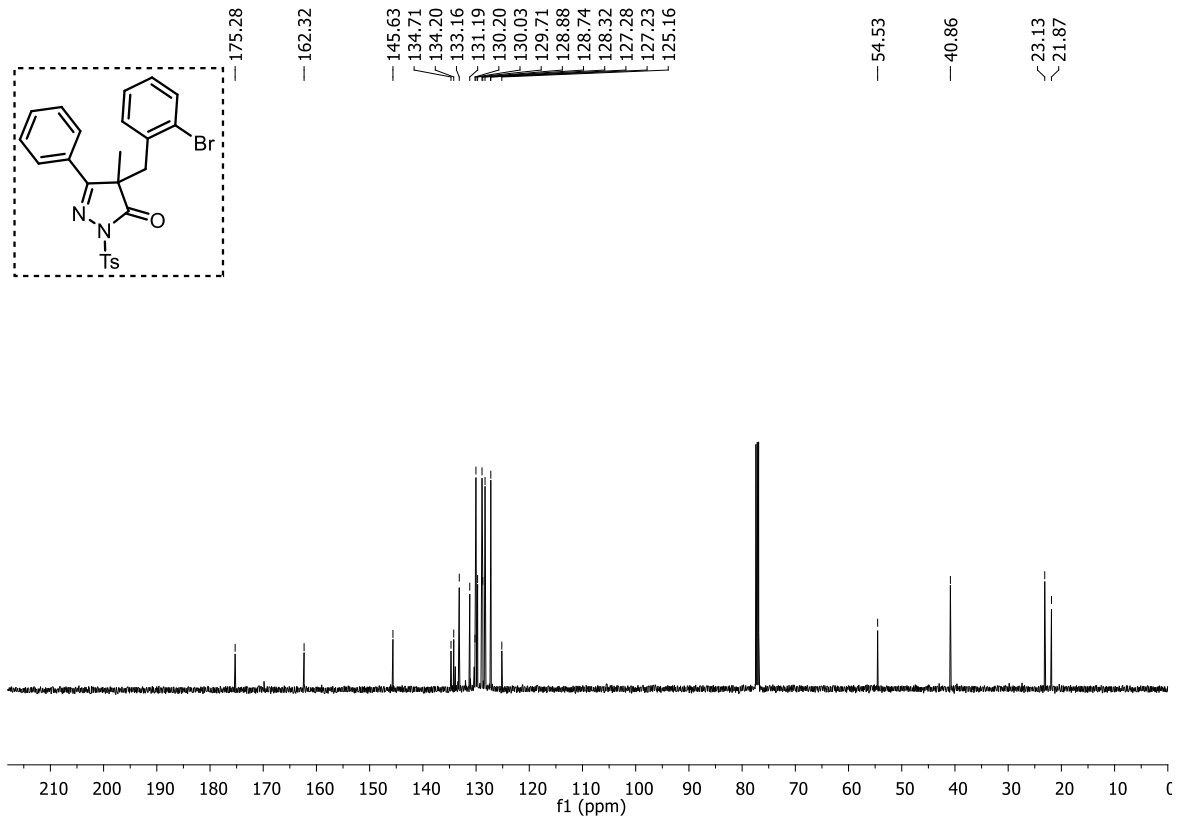
^{13}C {^{1}H} NMR spectrum of 3ak ($CDCl_3$, 126 MHz)



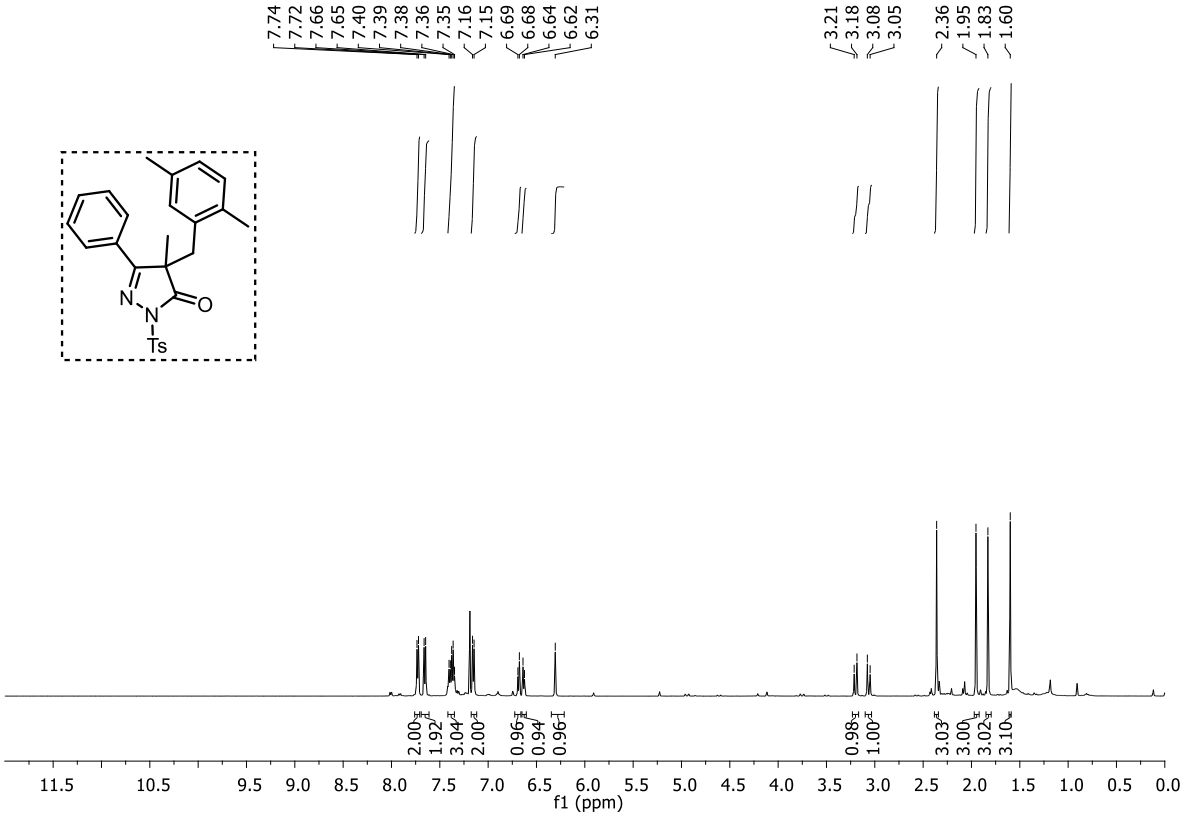
^{1}H NMR spectrum of 3al ($CDCl_3$, 500 MHz)



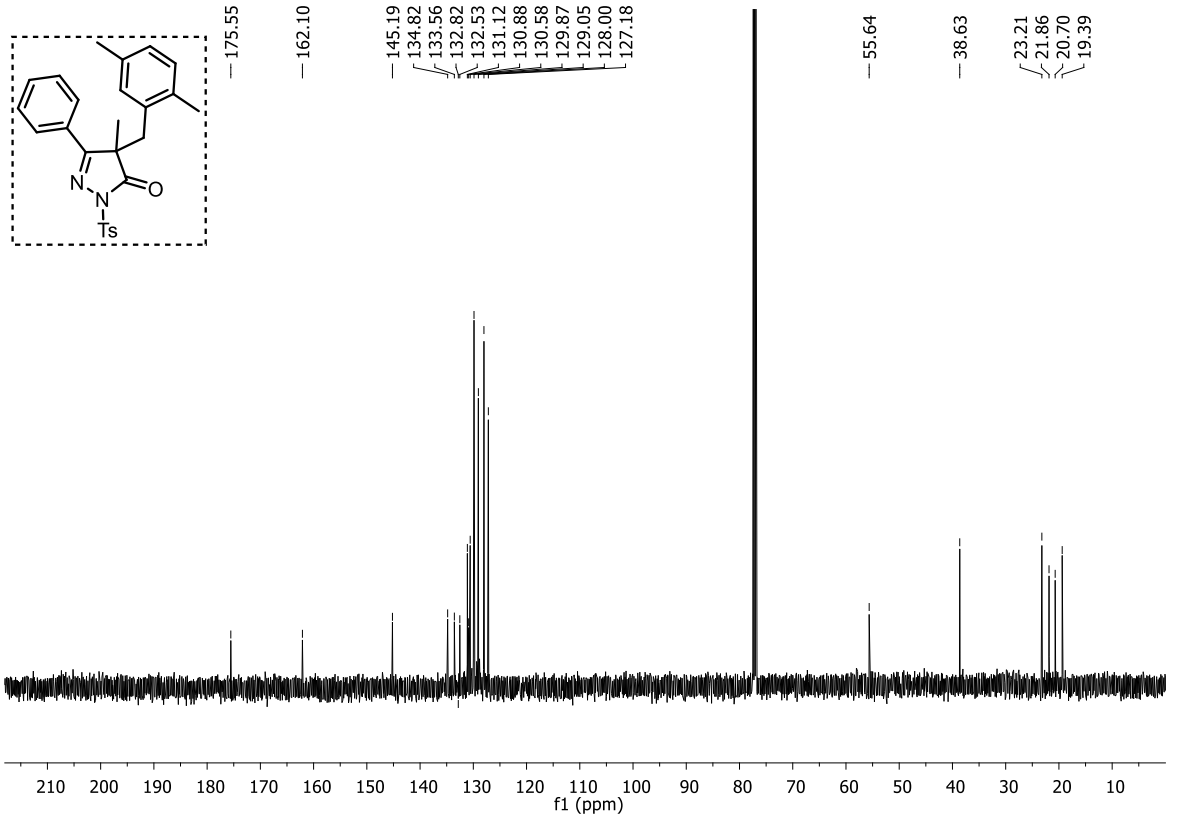
^{13}C {^{1}H} NMR spectrum of 3al ($CDCl_3$, 126 MHz)



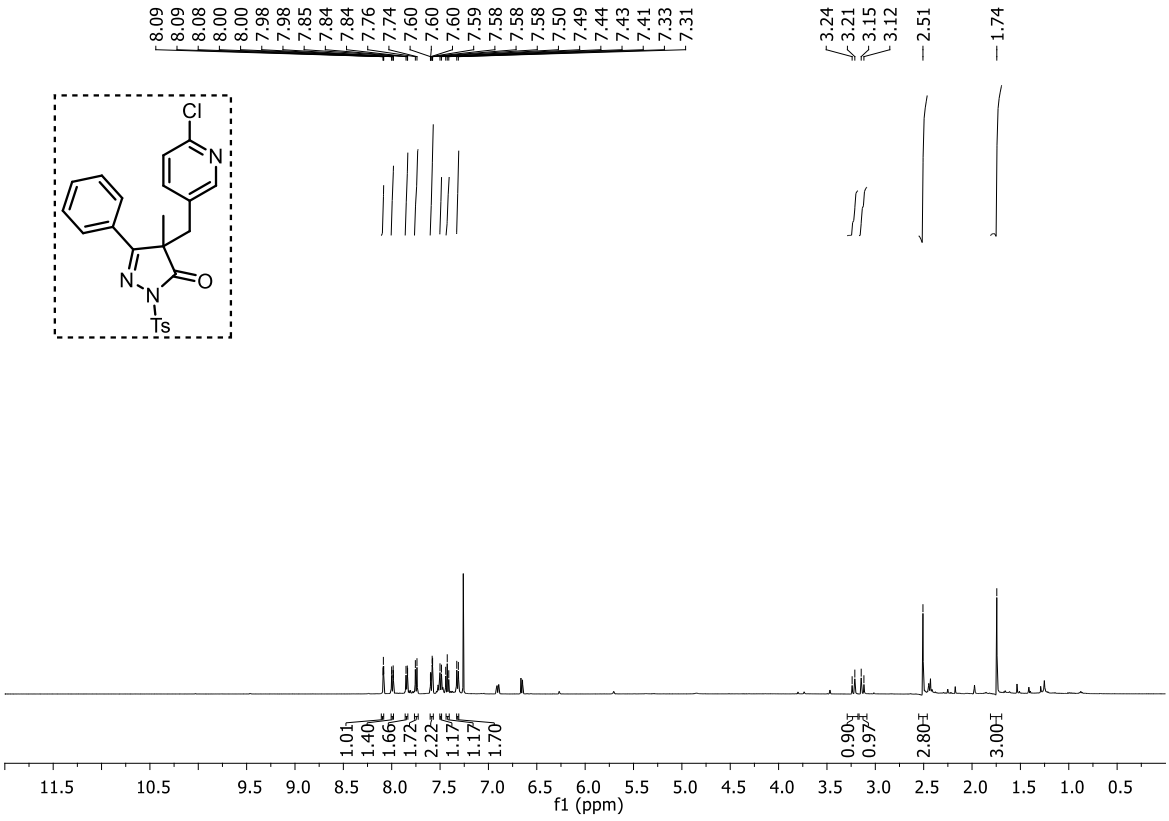
^{1}H NMR spectrum of am ($CDCl_3$, 500 MHz)



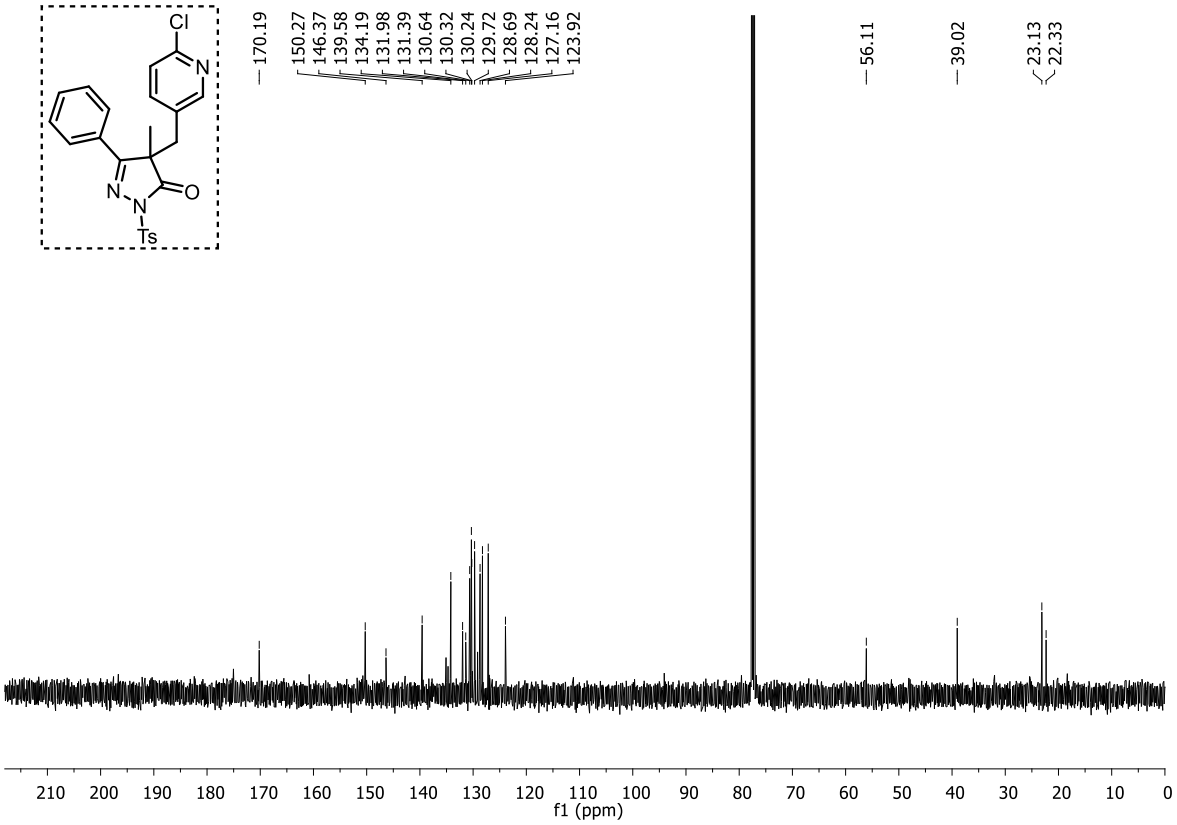
^{13}C {^{1}H} NMR spectrum of 3am ($CDCl_3$, 126 MHz)



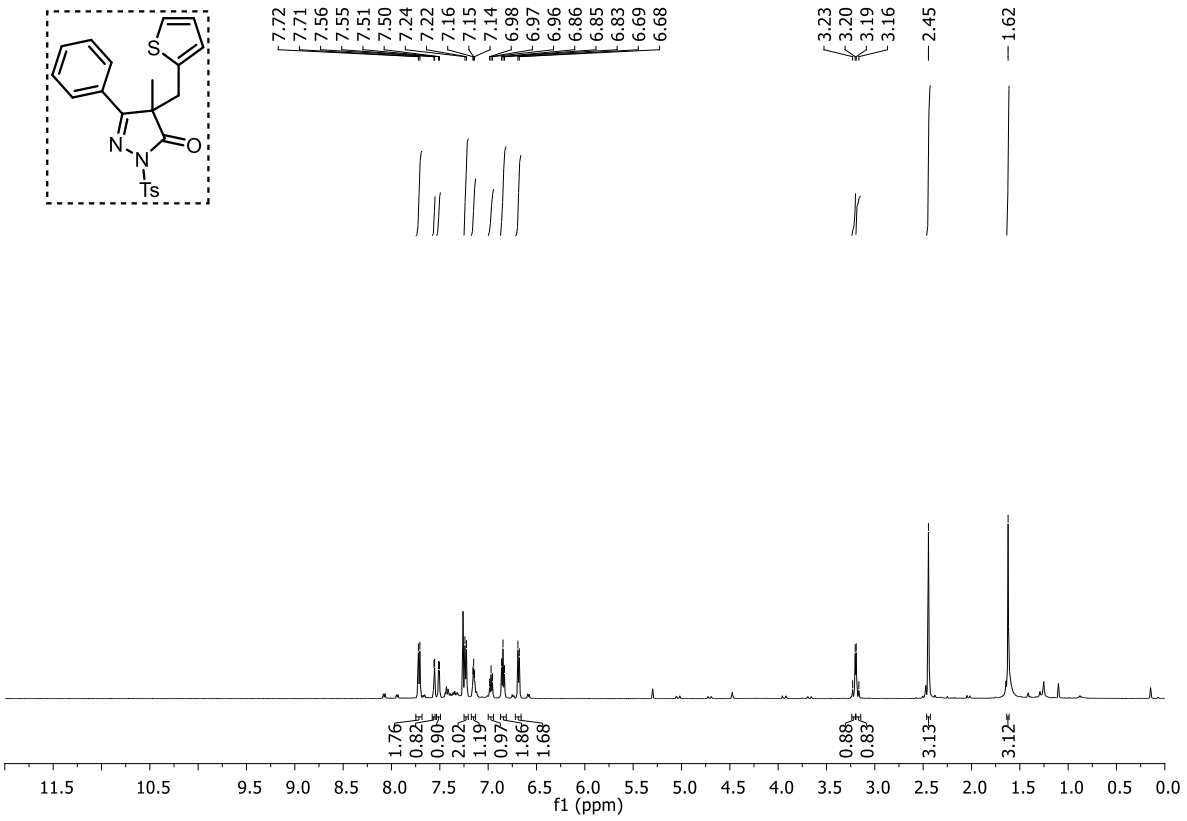
^{1}H NMR spectrum of 3an ($CDCl_3$, 500 MHz)



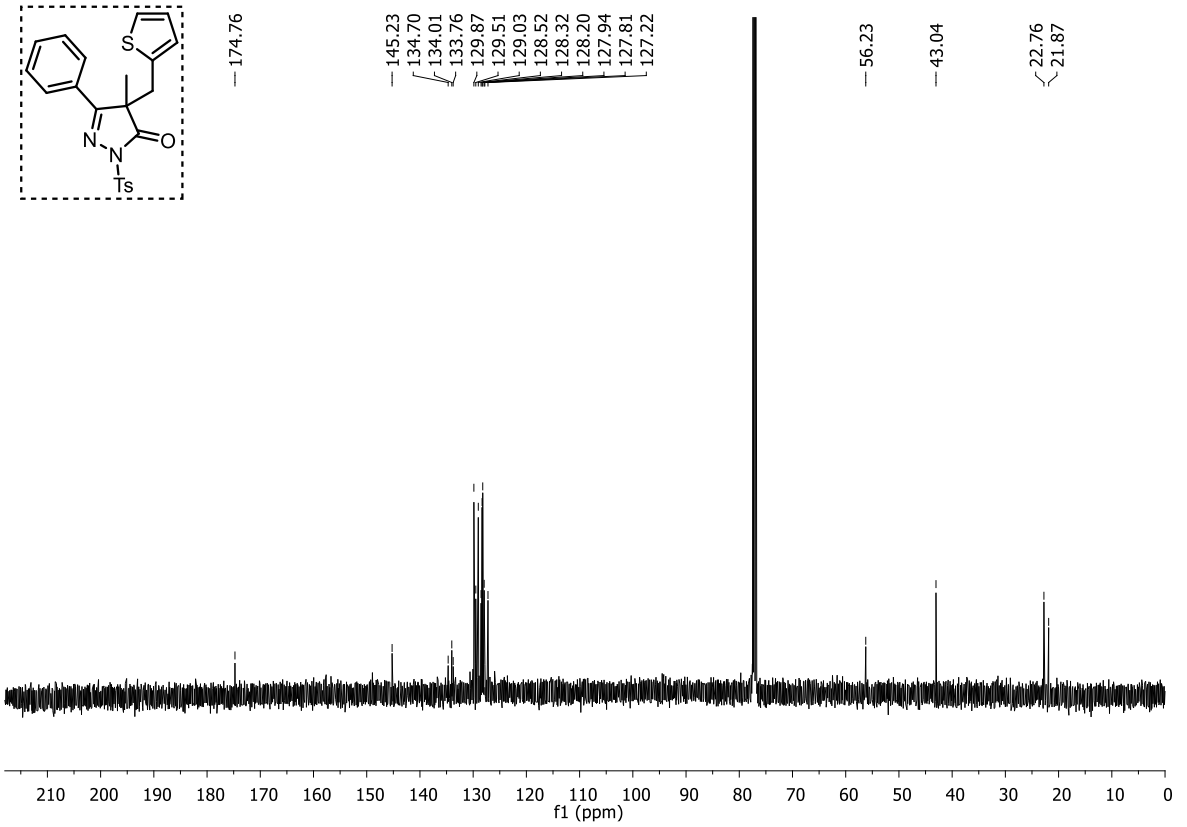
^{13}C {^{1}H} NMR spectrum of 3an ($CDCl_3$, 126 MHz)



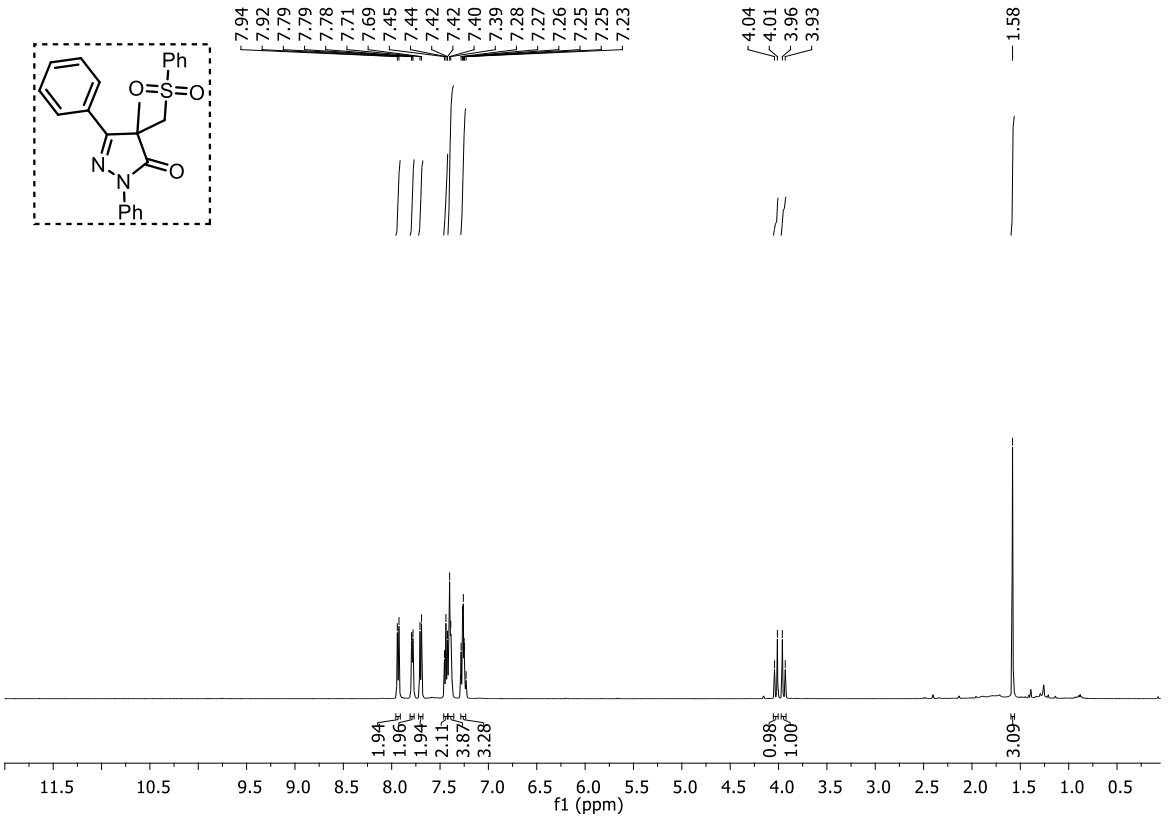
^{1}H NMR spectrum of 3ao ($CDCl_3$, 500 MHz)



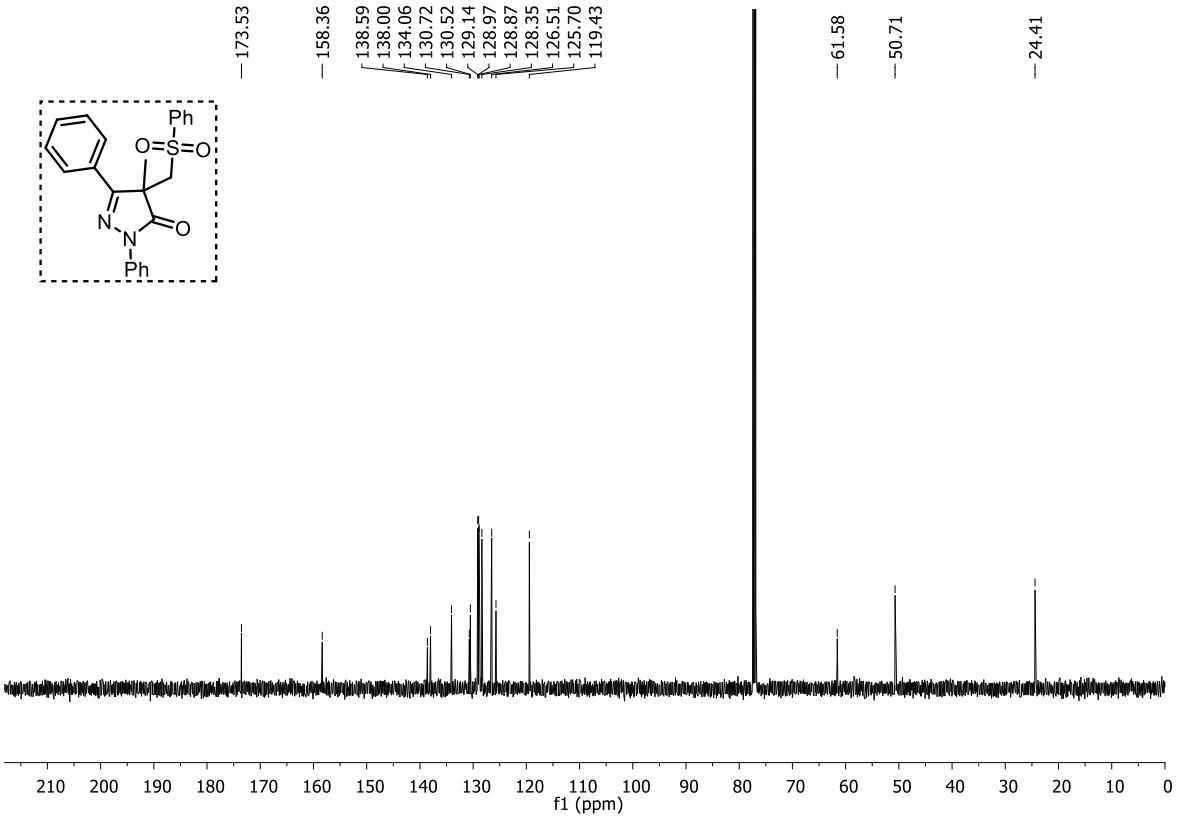
^{13}C {^{1}H} NMR spectrum of 3ao ($CDCl_3$, 126 MHz)



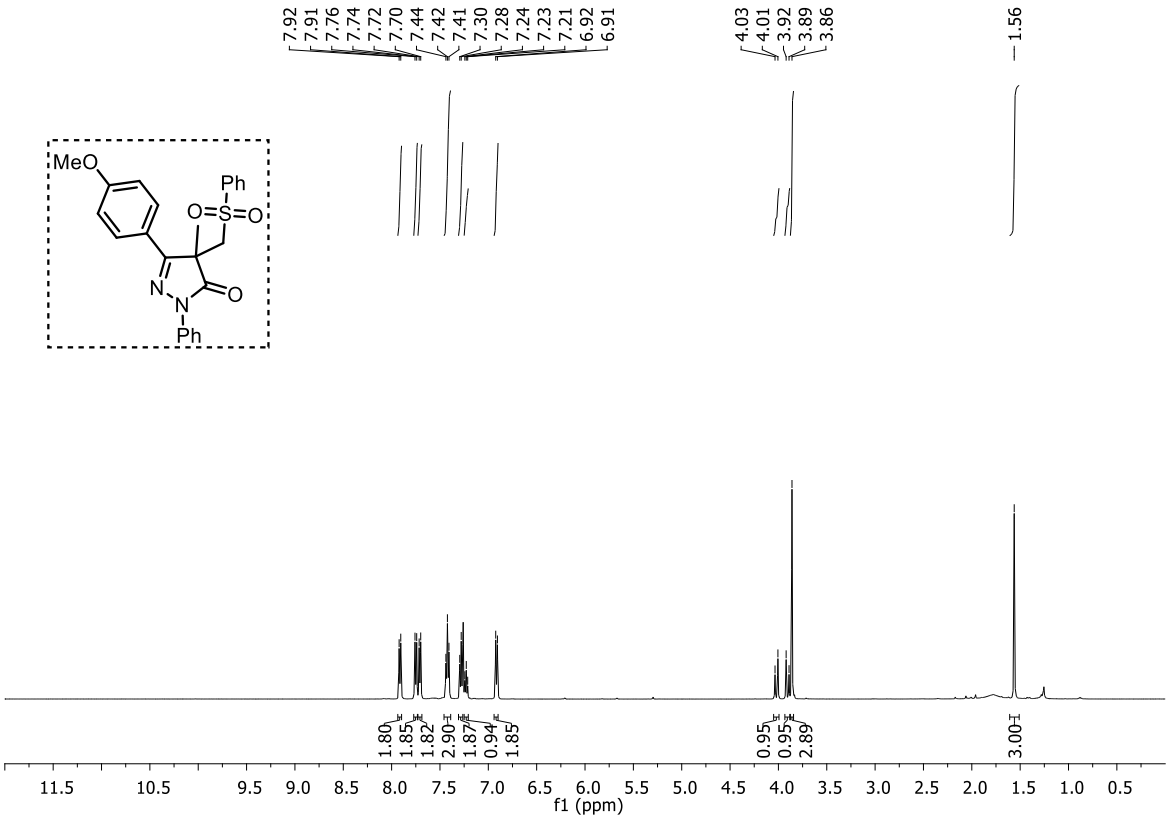
^{1}H NMR spectrum of 5aa ($CDCl_3$, 500 MHz)



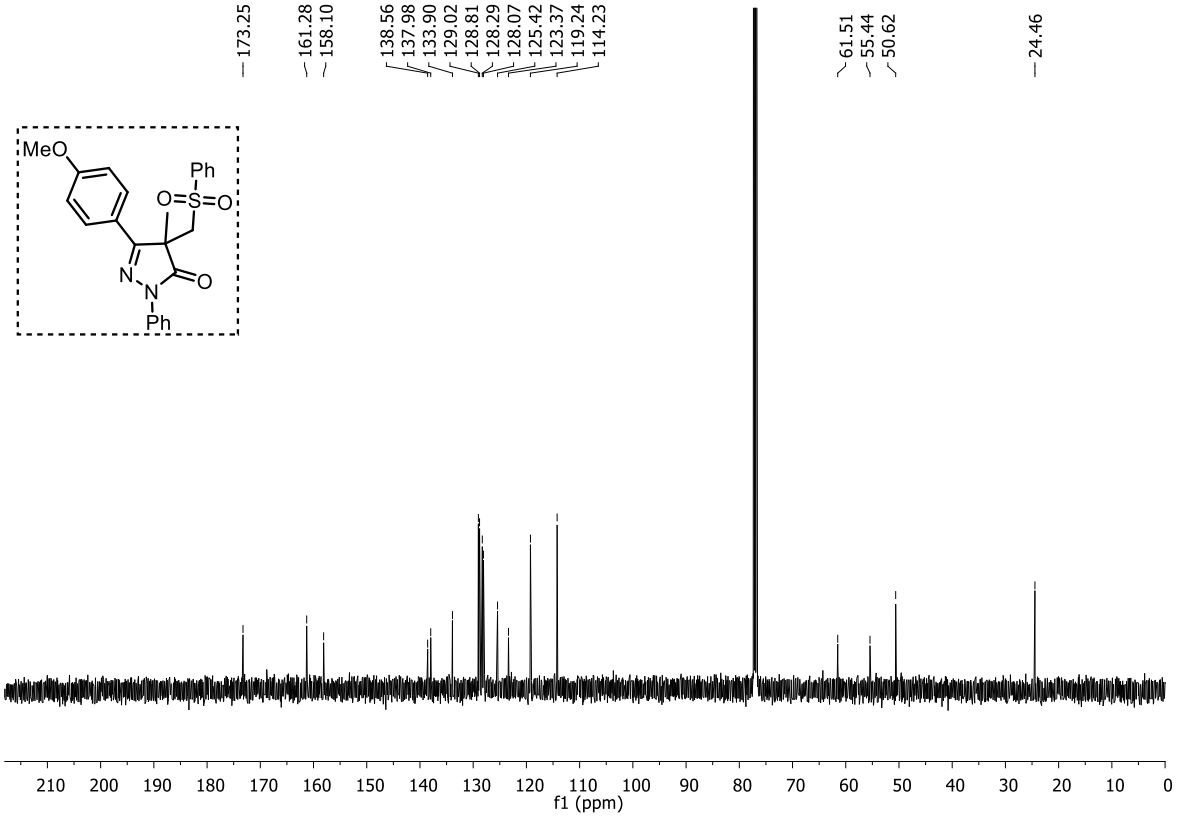
^{13}C {^{1}H} NMR spectrum of 5aa ($CDCl_3$, 126 MHz)



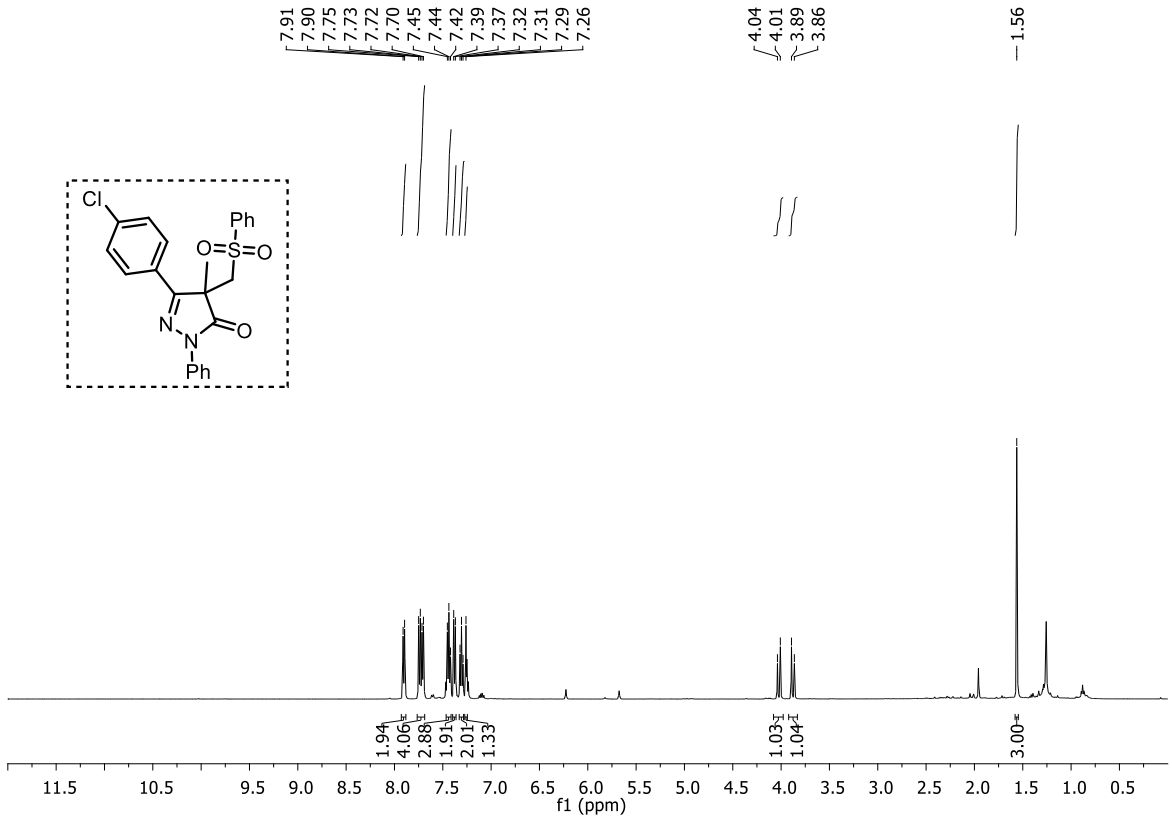
^{1}H NMR spectrum of 5ba ($CDCl_3$, 500 MHz)



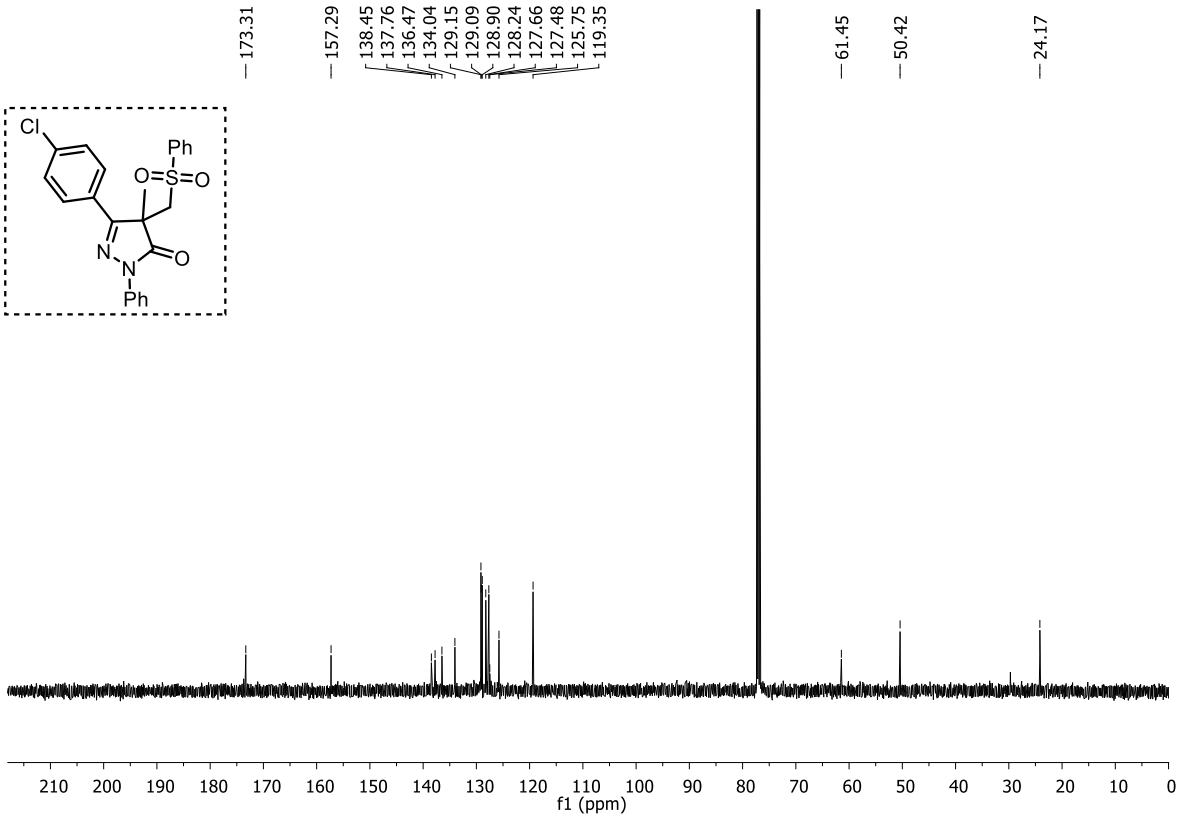
^{13}C {^{1}H} NMR spectrum of 5ba ($CDCl_3$, 126 MHz)



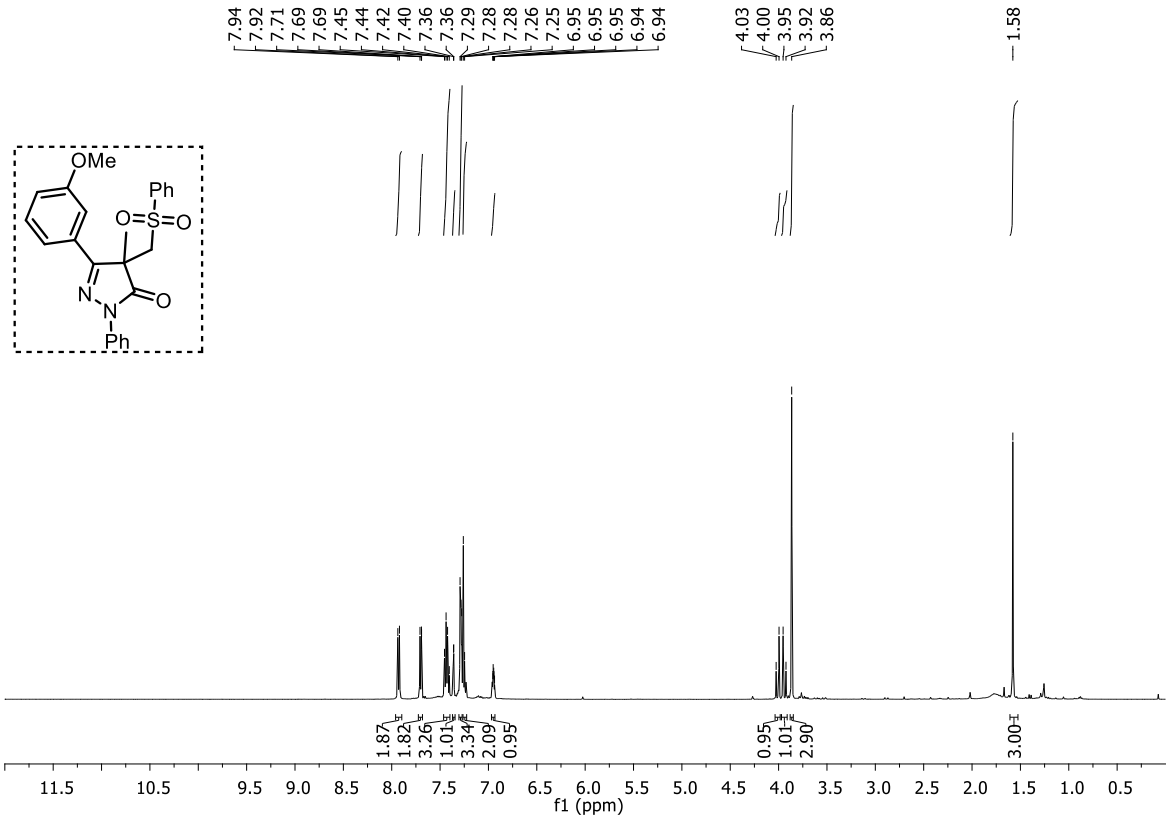
^{1}H NMR spectrum of 5ca ($CDCl_3$, 500 MHz)



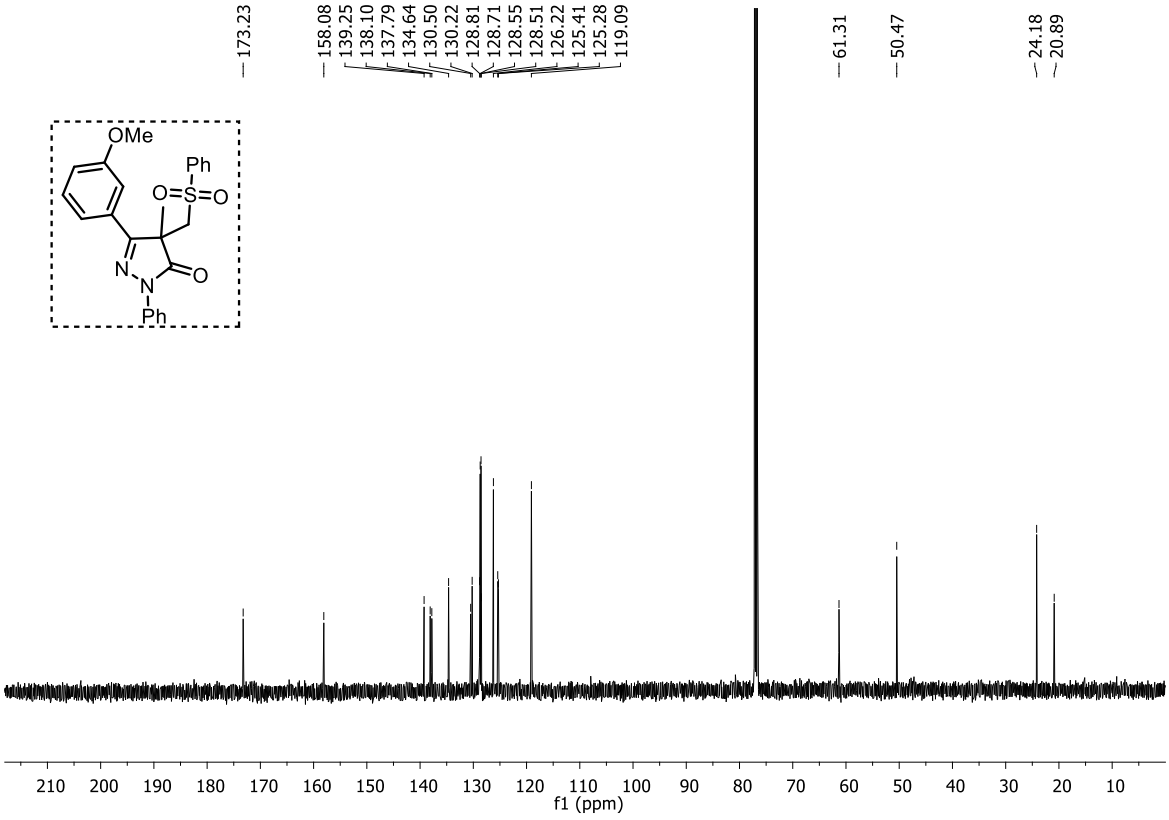
^{13}C {^{1}H} NMR spectrum of 5ca ($CDCl_3$, 126 MHz)



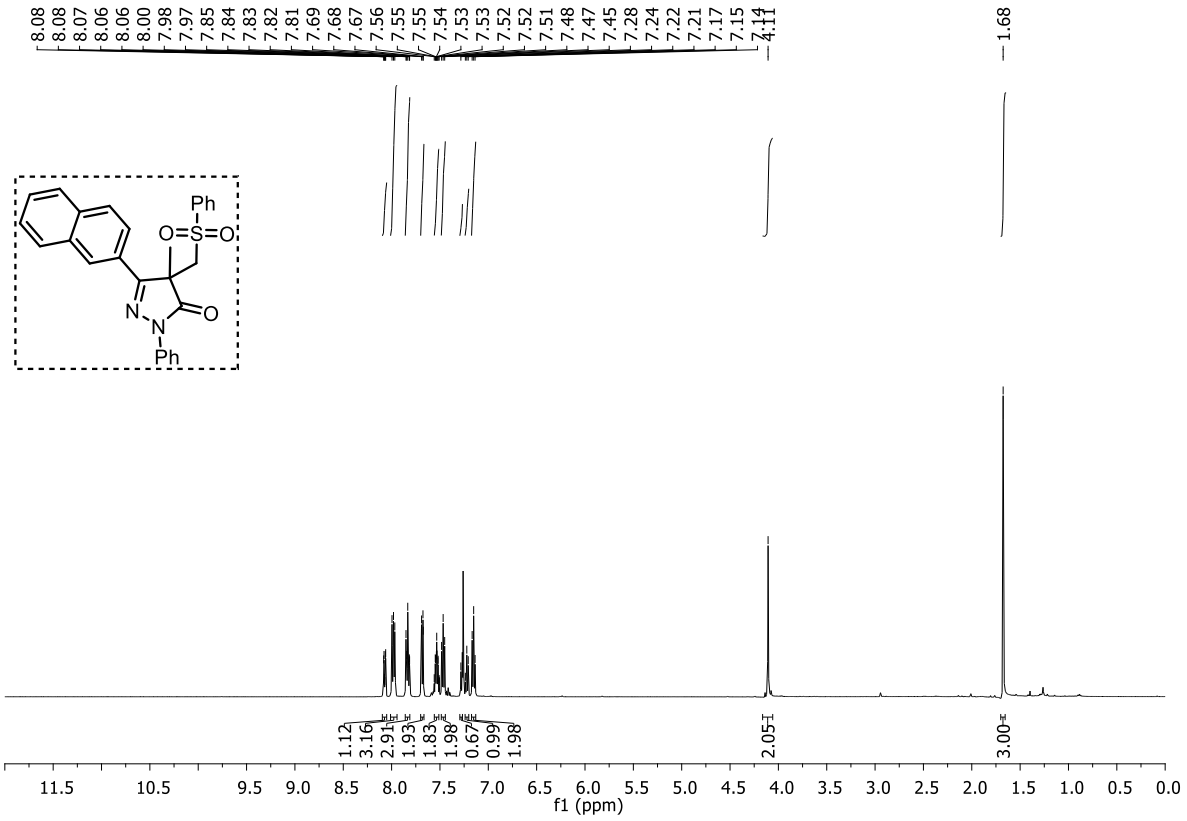
^{1}H NMR spectrum of 5da ($CDCl_3$, 500 MHz)



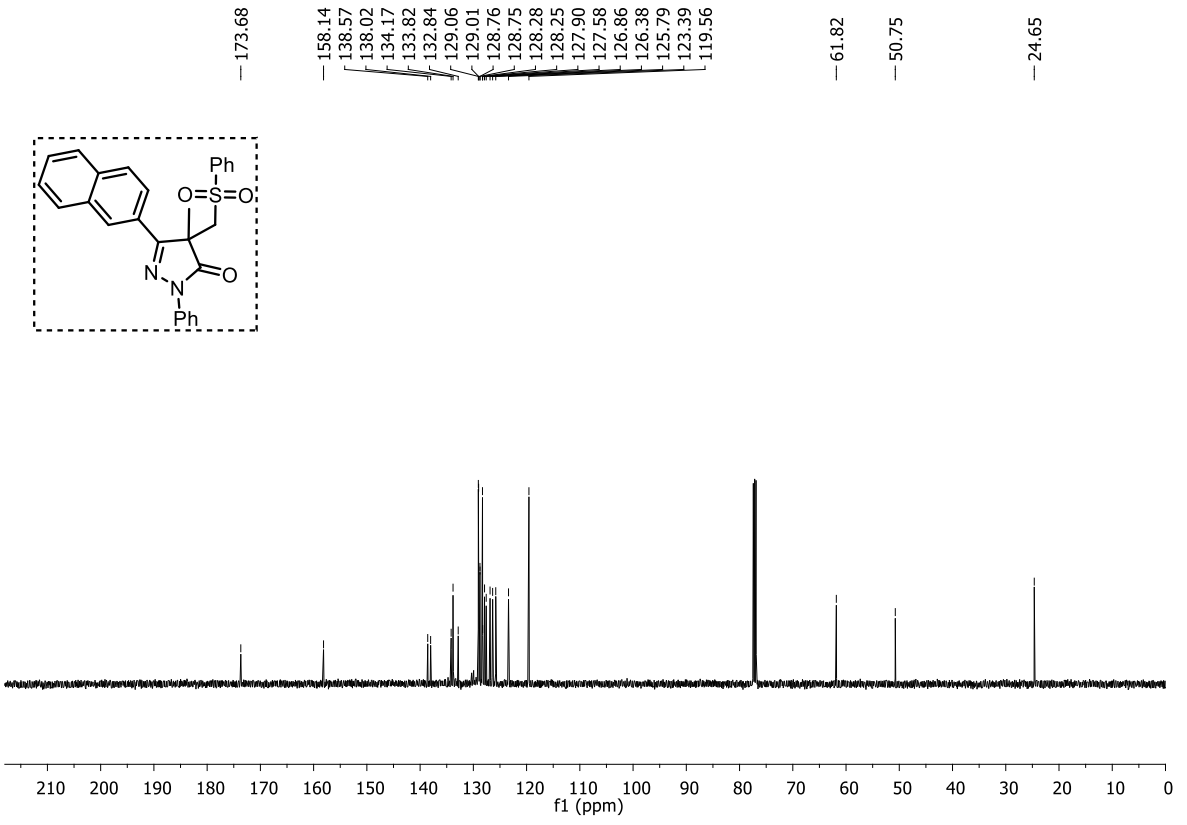
^{13}C {^{1}H} NMR spectrum of 5da ($CDCl_3$, 126 MHz)



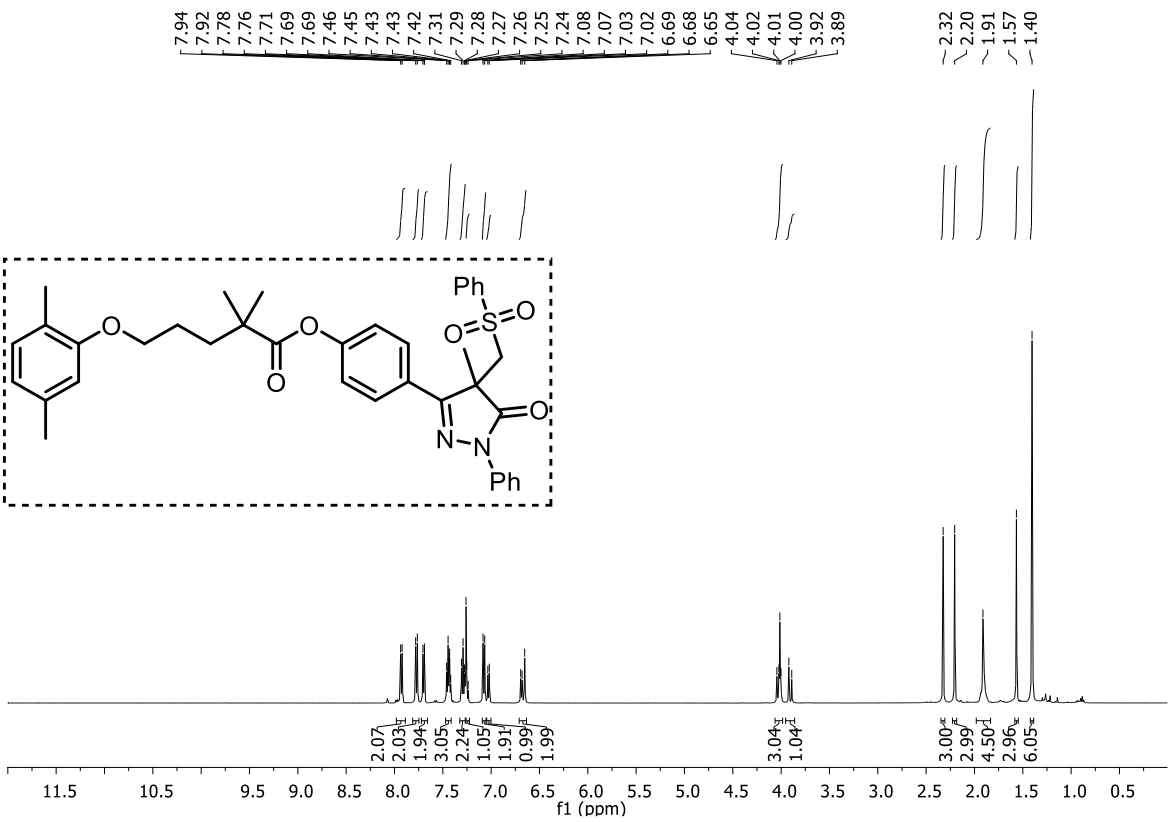
^{1}H NMR spectrum of 5ea ($CDCl_3$, 500 MHz)



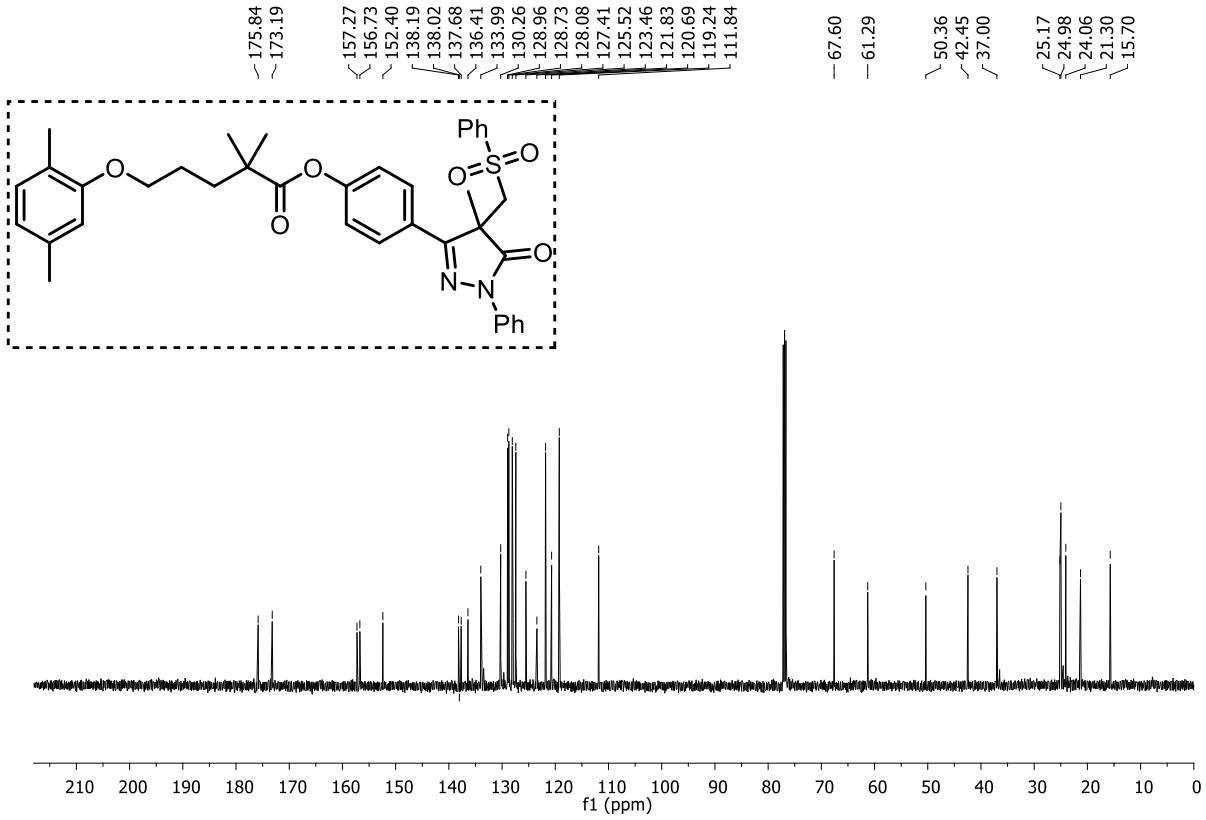
^{13}C {^{1}H} NMR spectrum of 5ea ($CDCl_3$, 126 MHz)



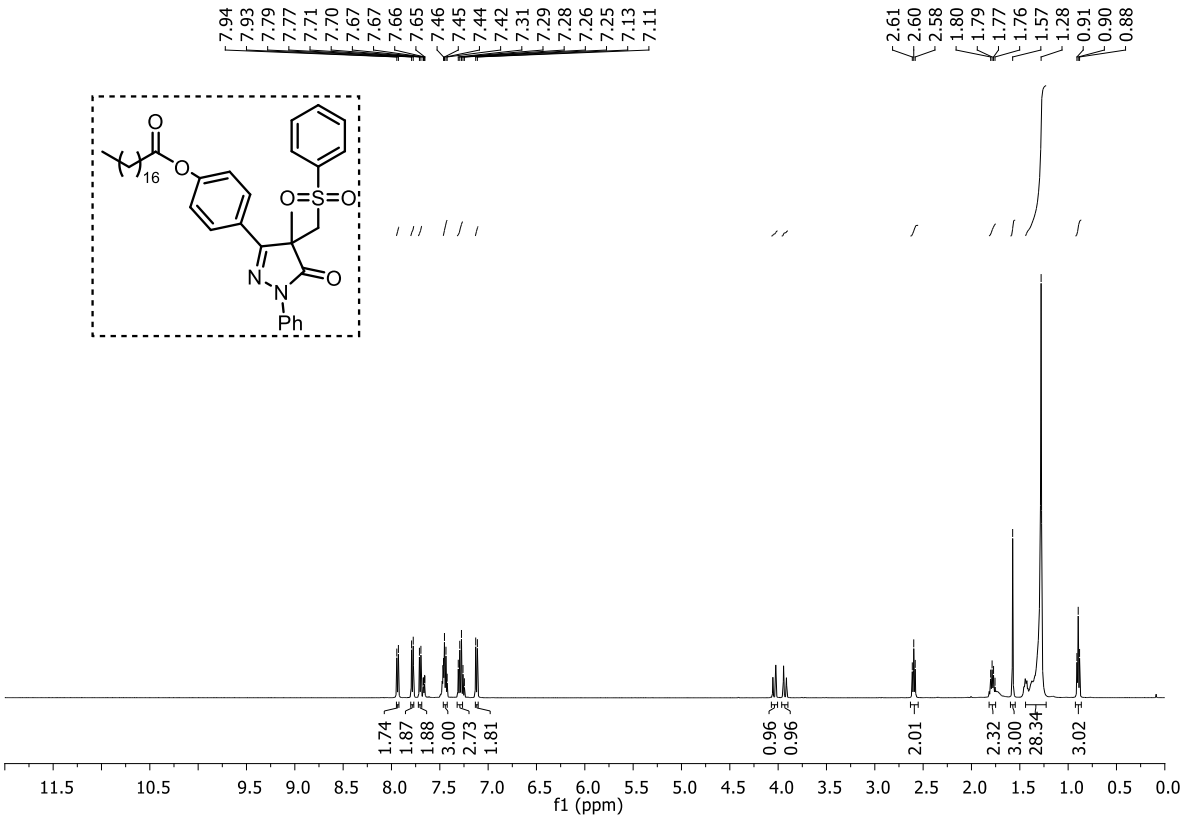
^{1}H NMR spectrum of 5fa $CDCl_3$, 500 MHz)



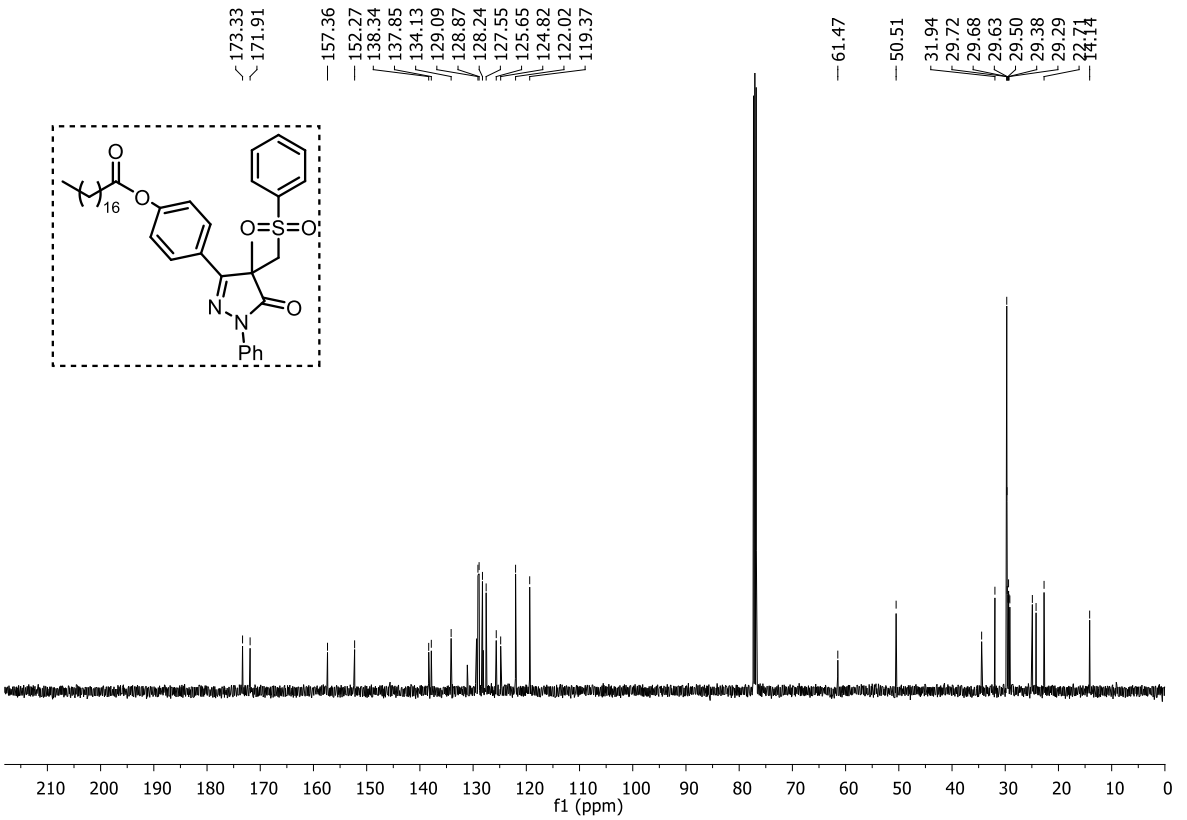
^{13}C {^{1}H} NMR spectrum of 5fa ($CDCl_3$, 126 MHz)



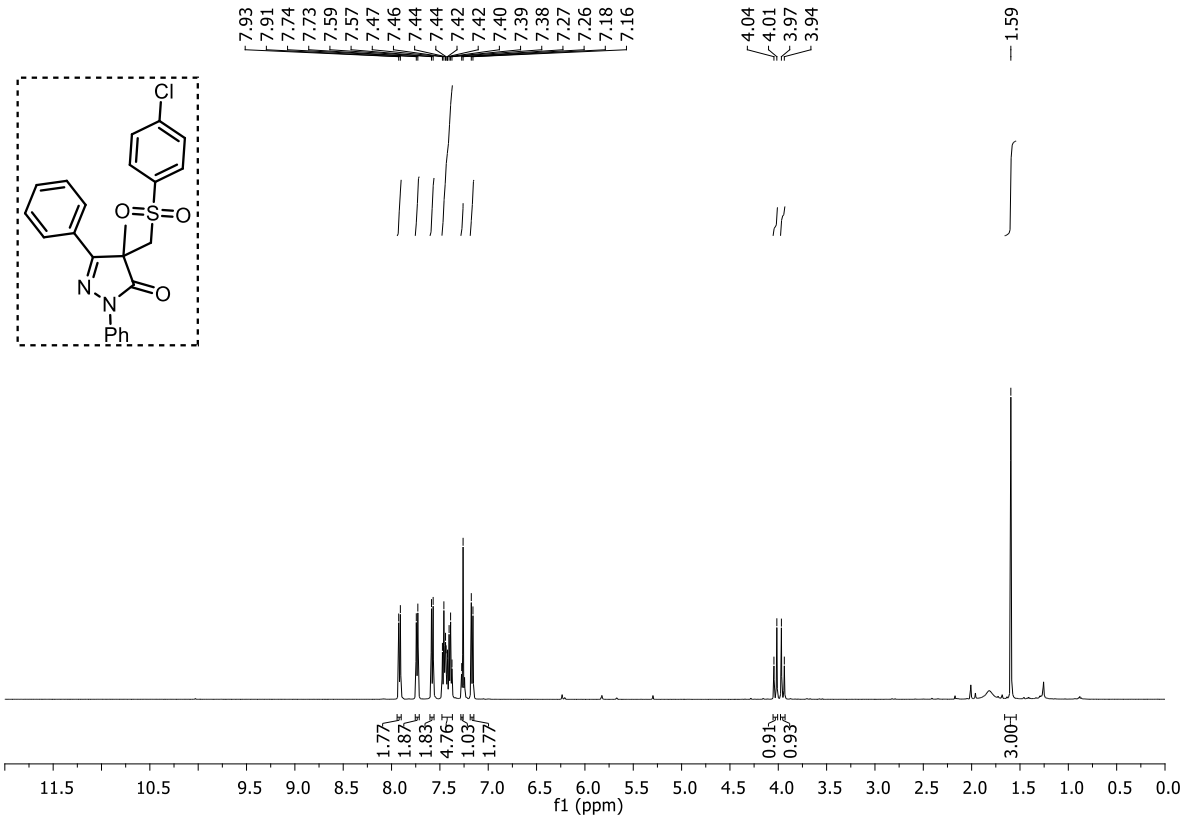
^{1}H NMR spectrum of 5ga ($CDCl_3$, 500 MHz)



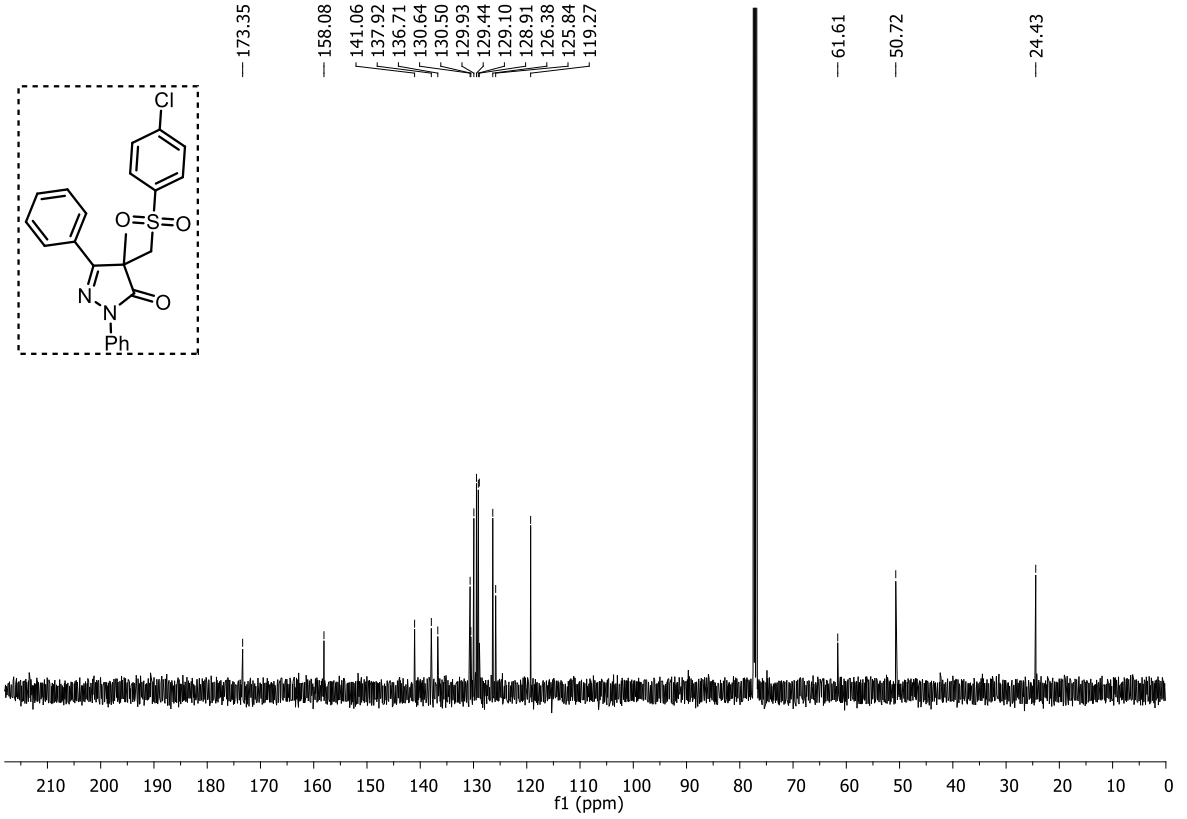
^{13}C {^{1}H} NMR spectrum of 5ga ($CDCl_3$, 126 MHz)



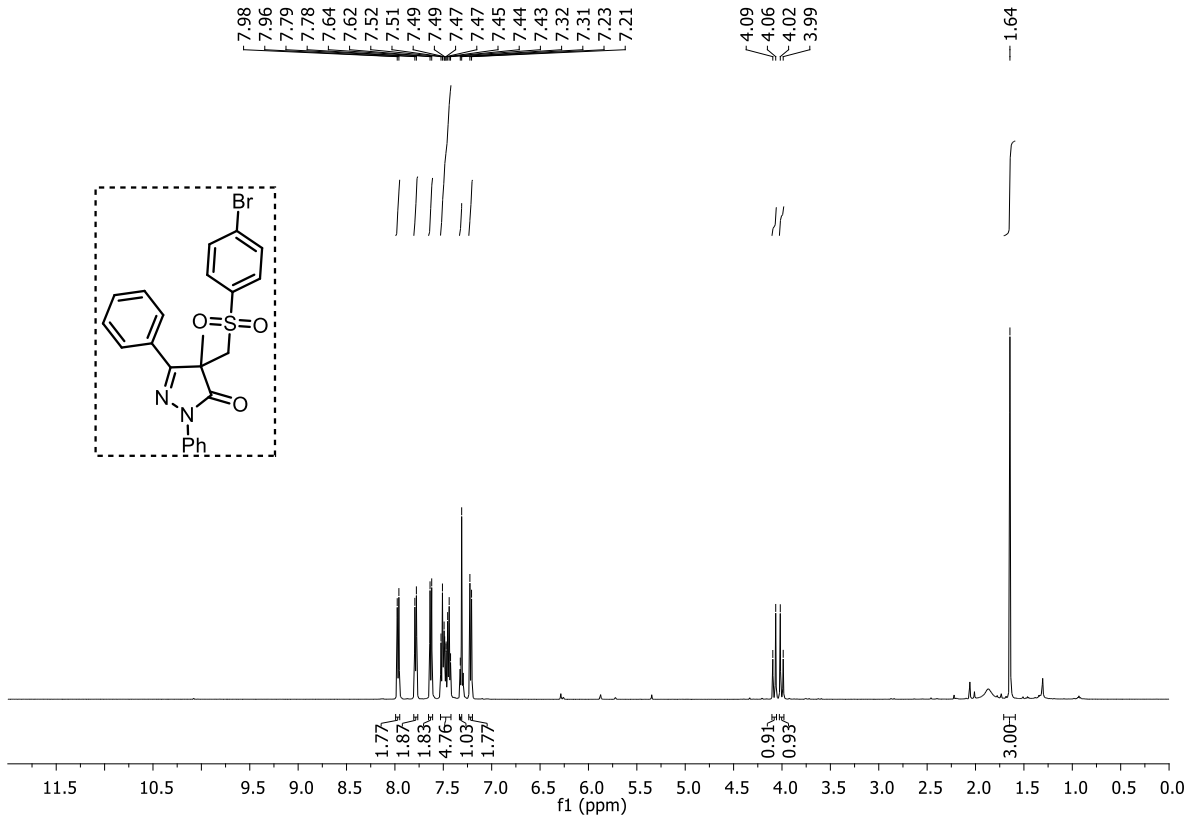
^{1}H NMR spectrum of 5ab ($CDCl_3$, 500 MHz)



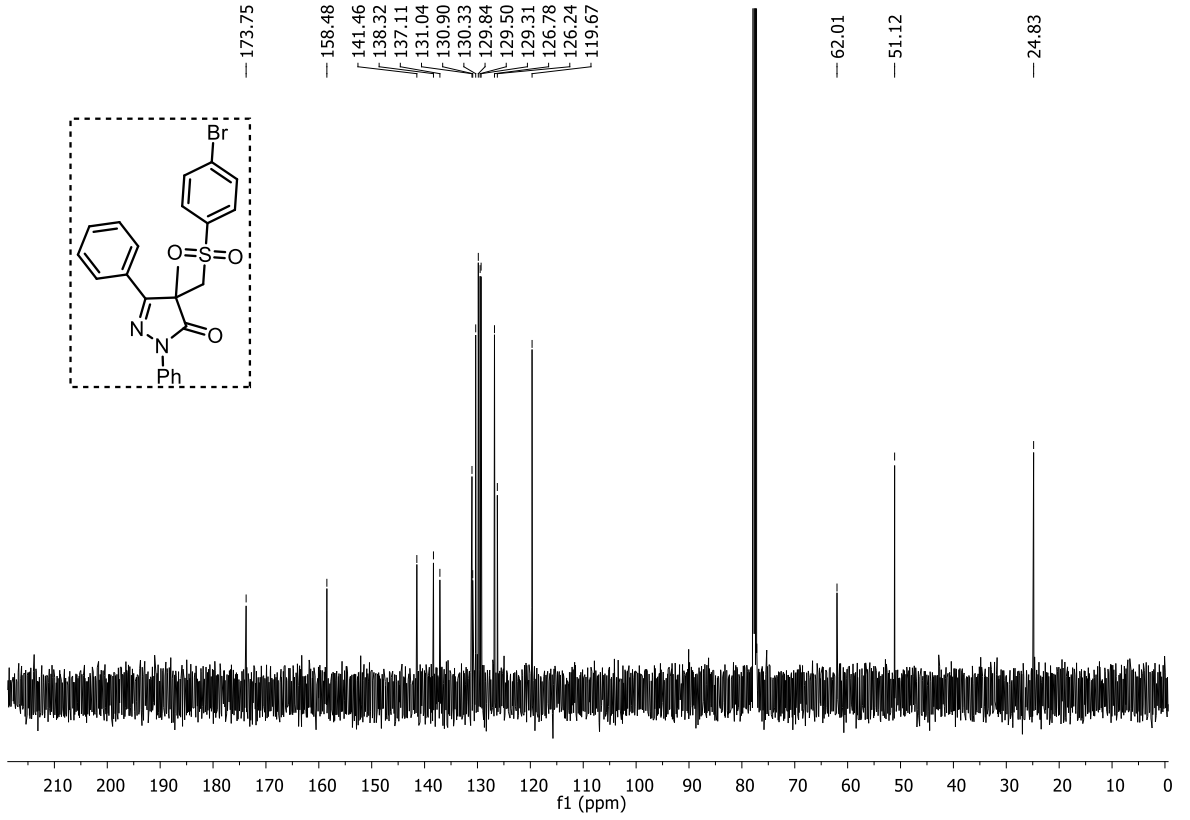
^{13}C {^{1}H} NMR spectrum of 5ab ($CDCl_3$, 126 MHz)



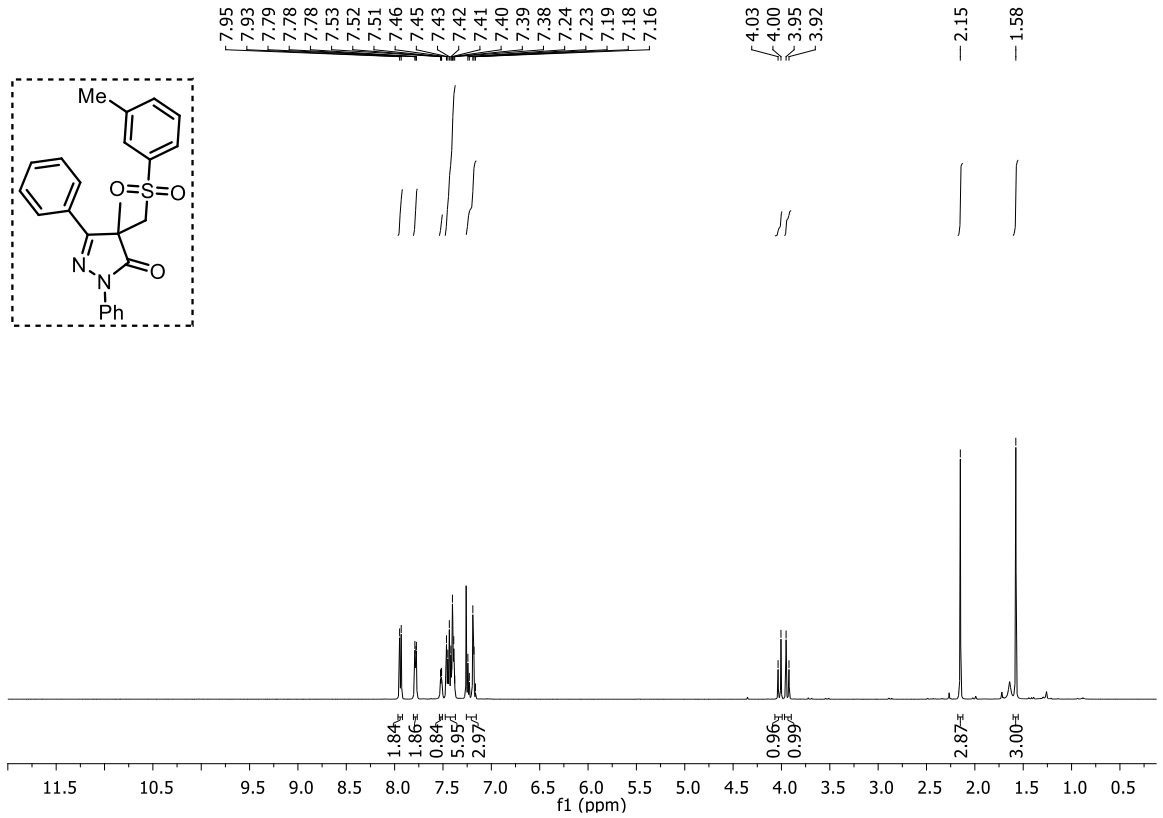
^{1}H NMR spectrum of 5ac ($CDCl_3$, 500 MHz)



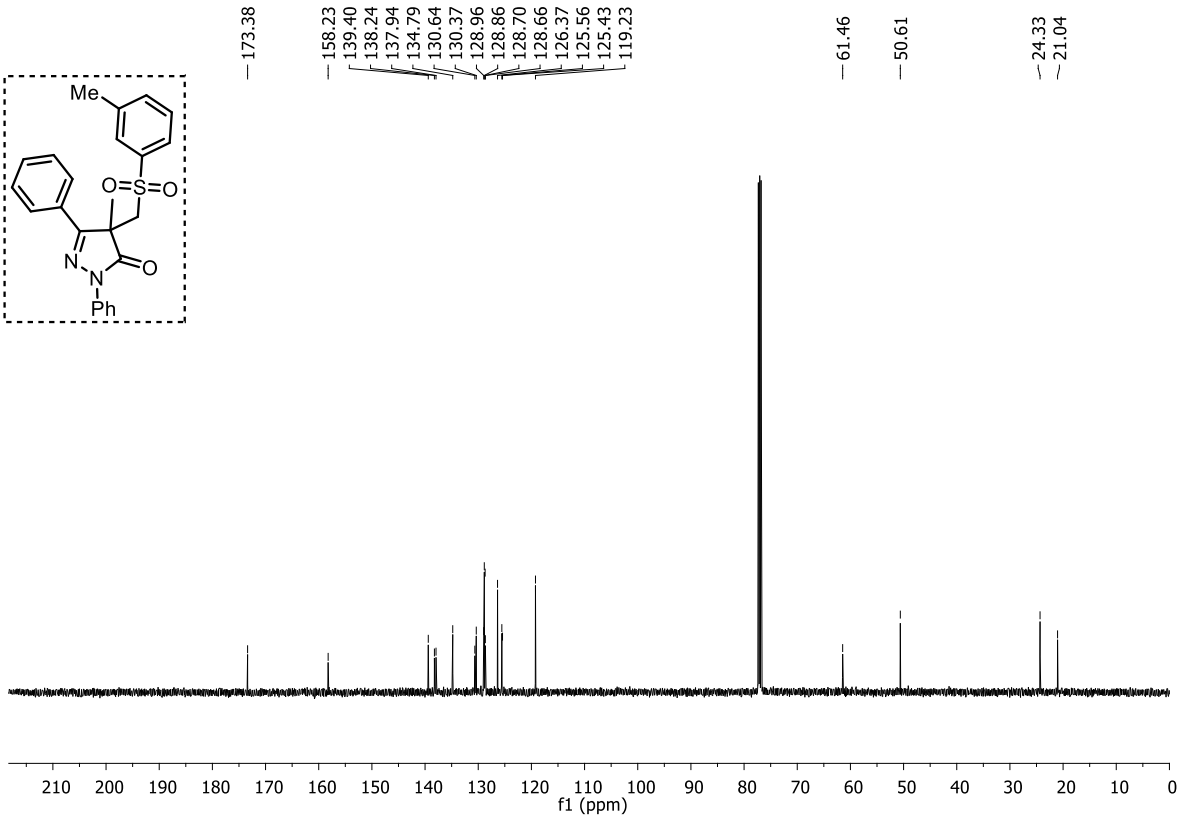
^{13}C {^{1}H} NMR spectrum of 5ac ($CDCl_3$, 126 MHz)



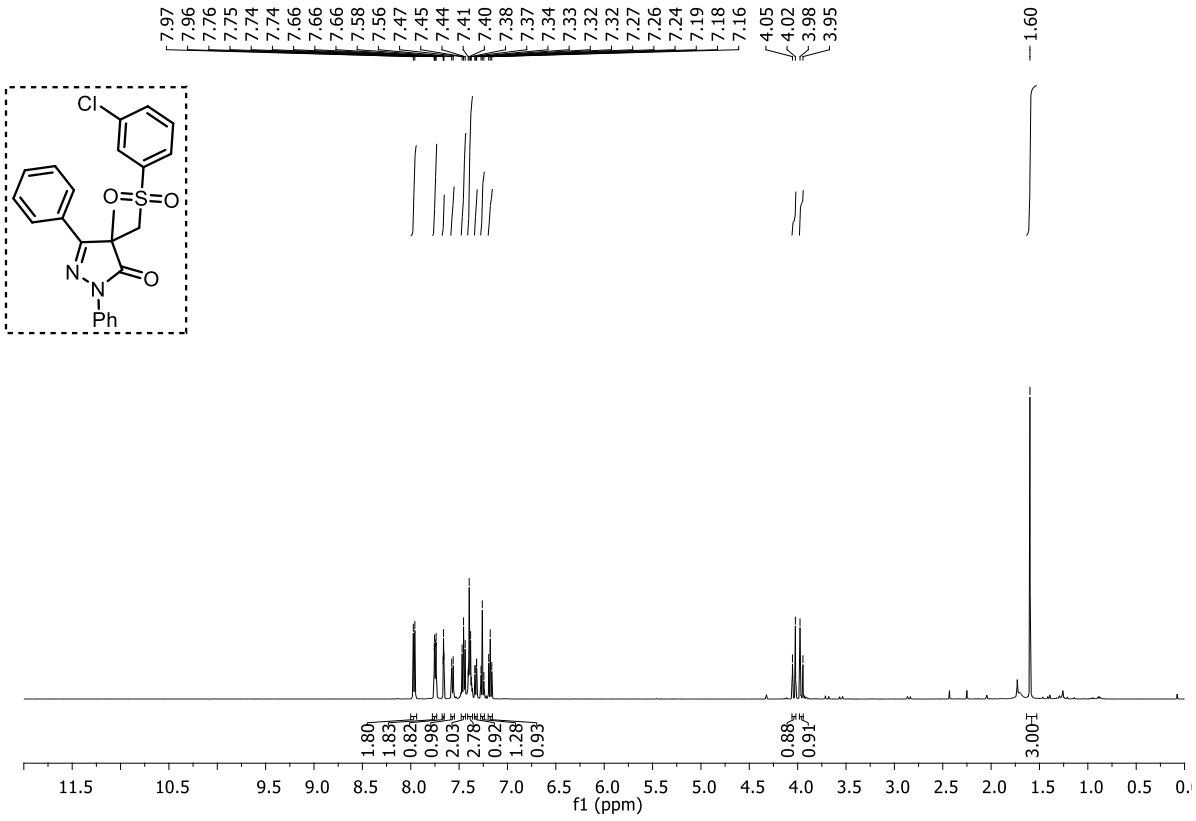
^{1}H NMR spectrum of 5ad ($CDCl_3$, 500 MHz)



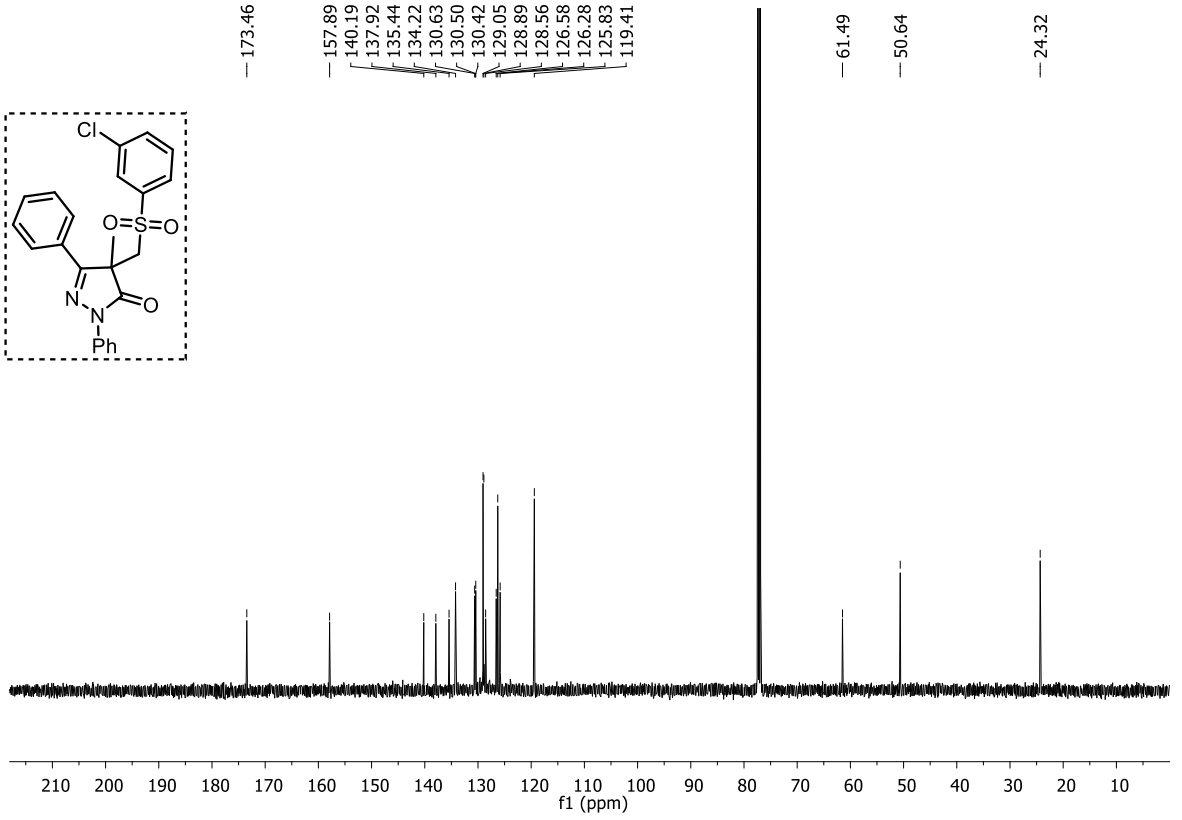
^{13}C {^{1}H} NMR spectrum of 5ad ($CDCl_3$, 126 MHz)



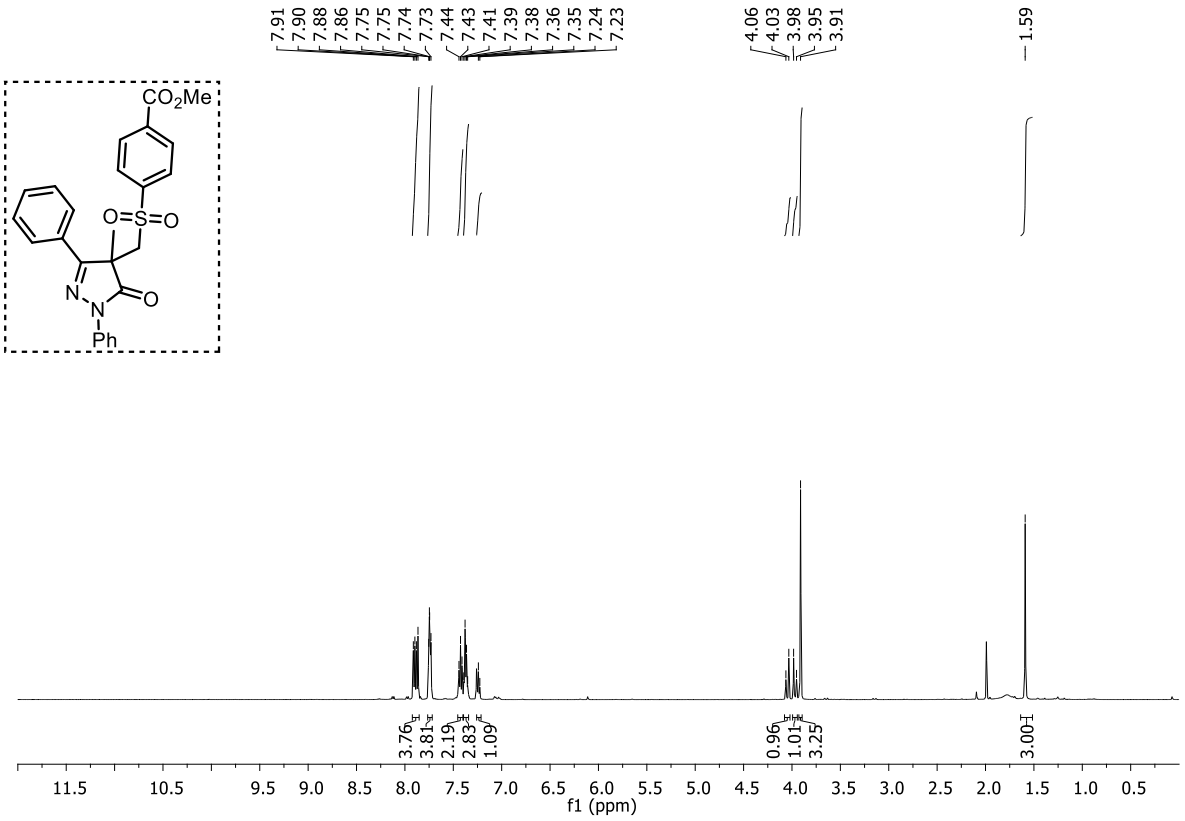
^{1}H NMR spectrum of 5ae ($CDCl_3$, 500 MHz)



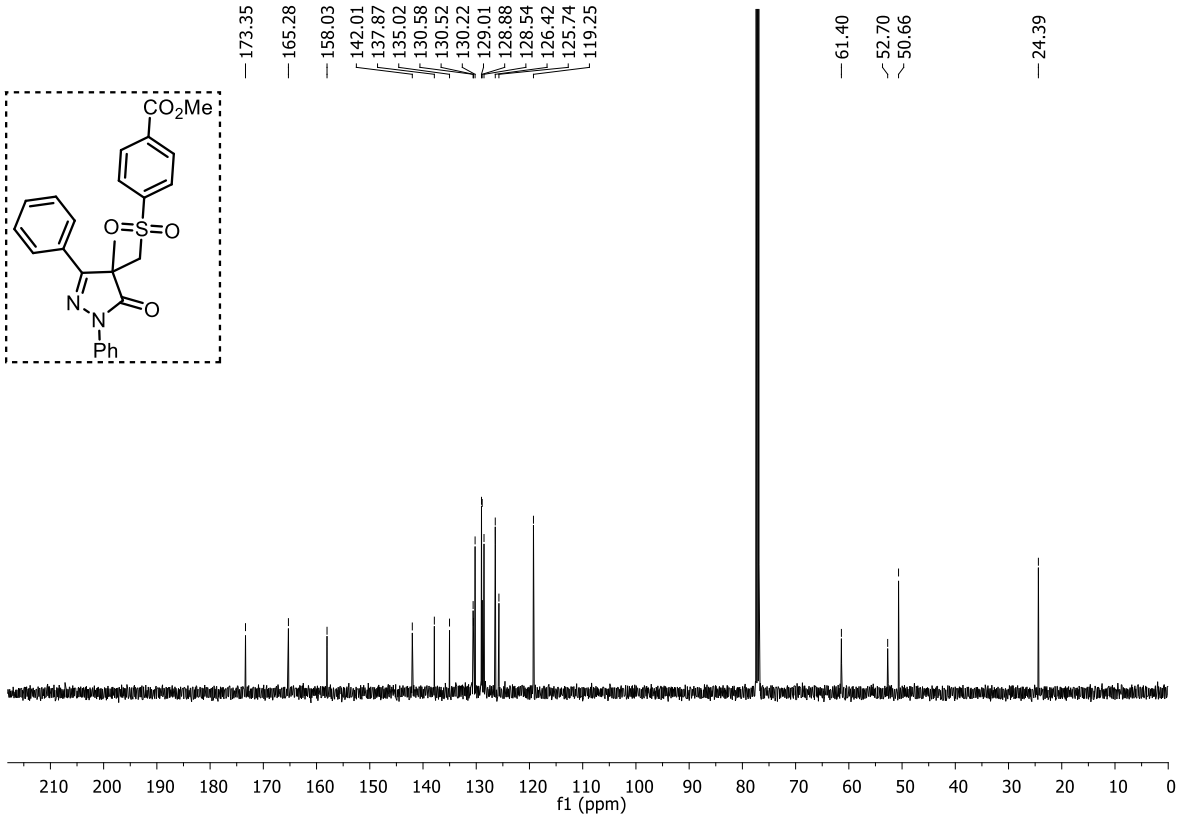
^{13}C {^{1}H} NMR spectrum of 5ae ($CDCl_3$, 126 MHz)



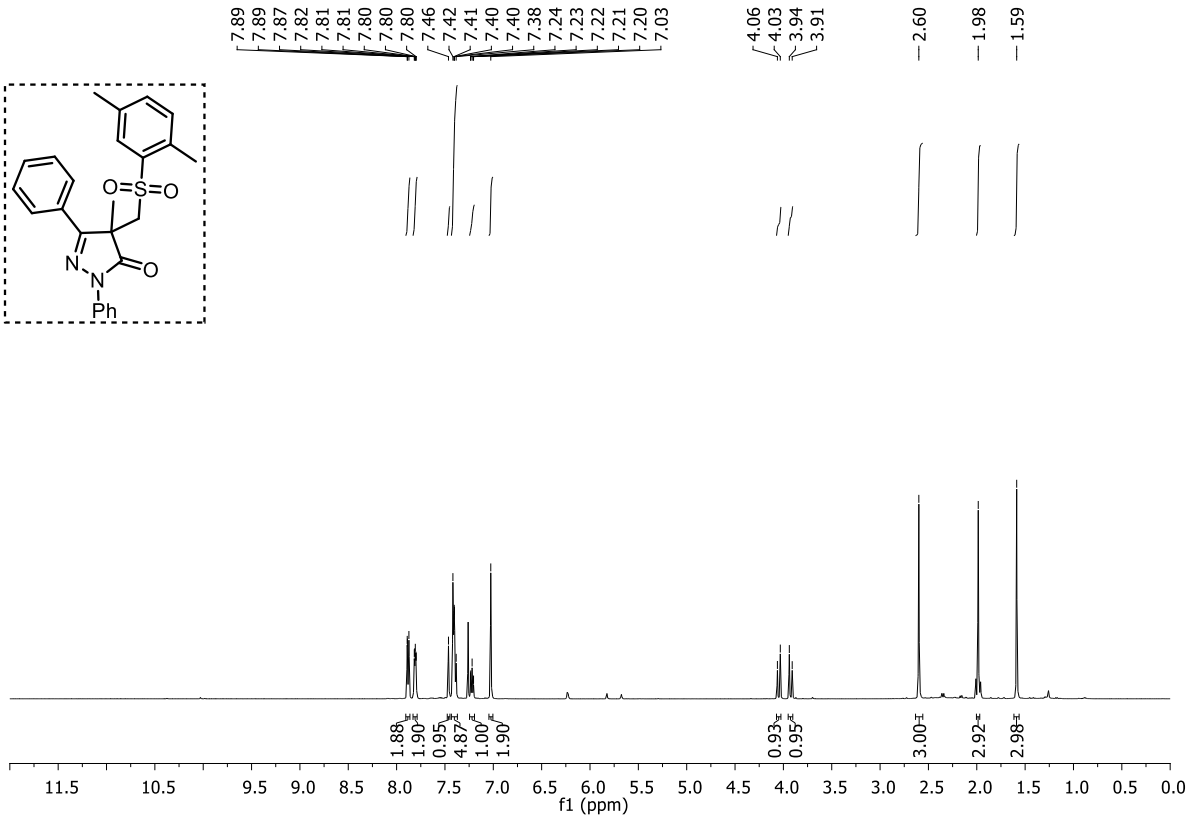
^{1}H NMR spectrum of 5af ($CDCl_3$, 500 MHz)



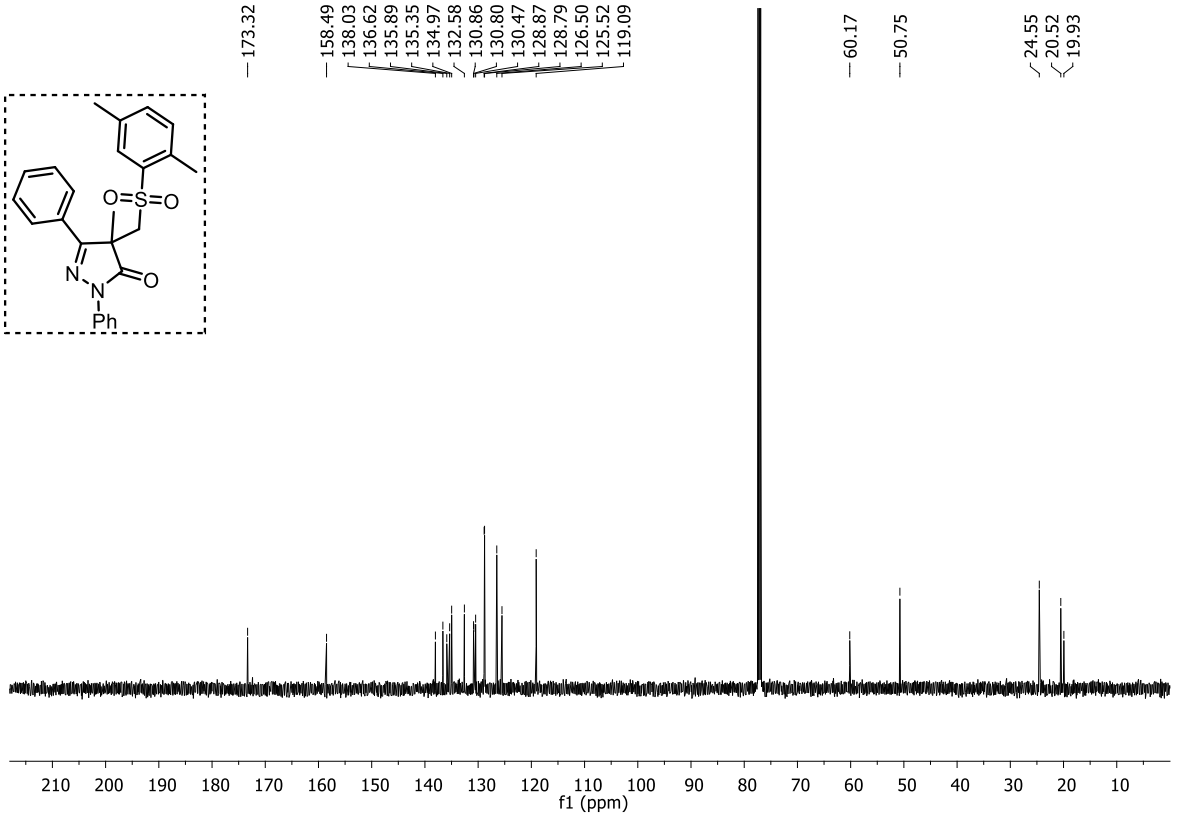
^{13}C {^{1}H} NMR spectrum of 5af ($CDCl_3$, 126 MHz)



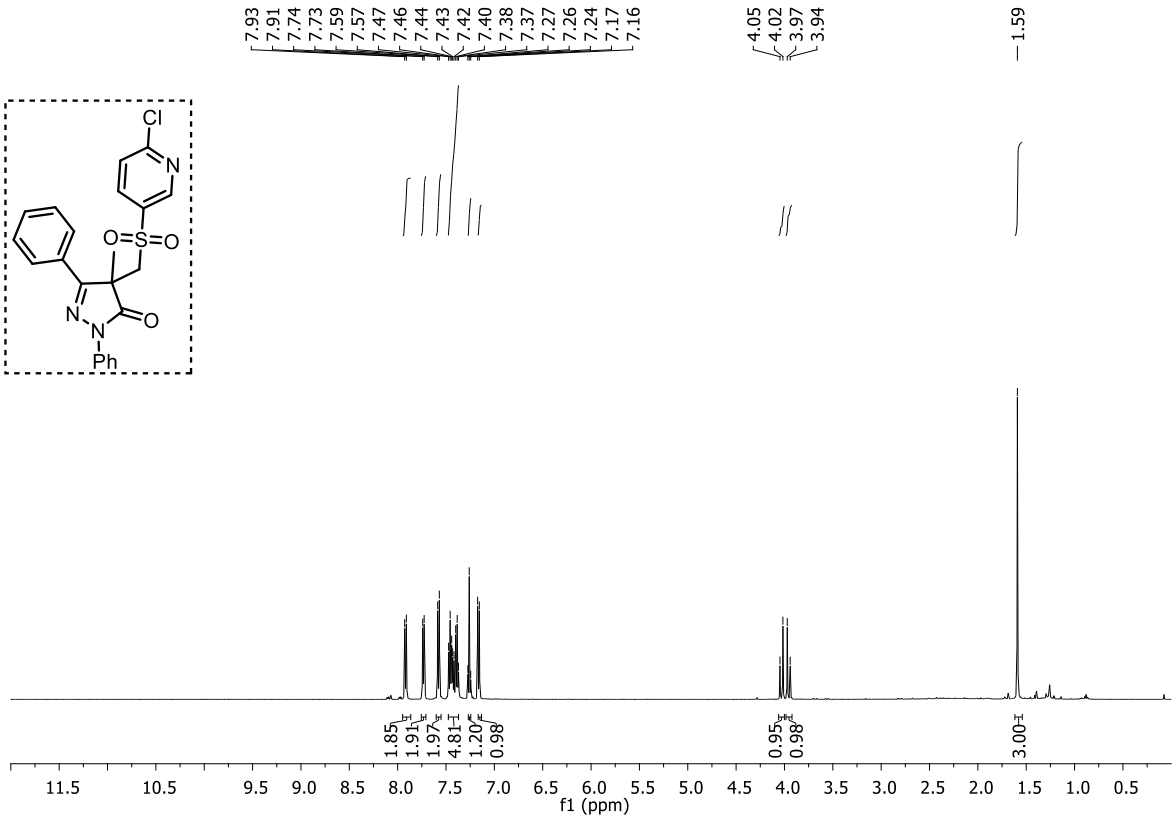
^{1}H NMR spectrum of 5ag ($CDCl_3$, 500 MHz)



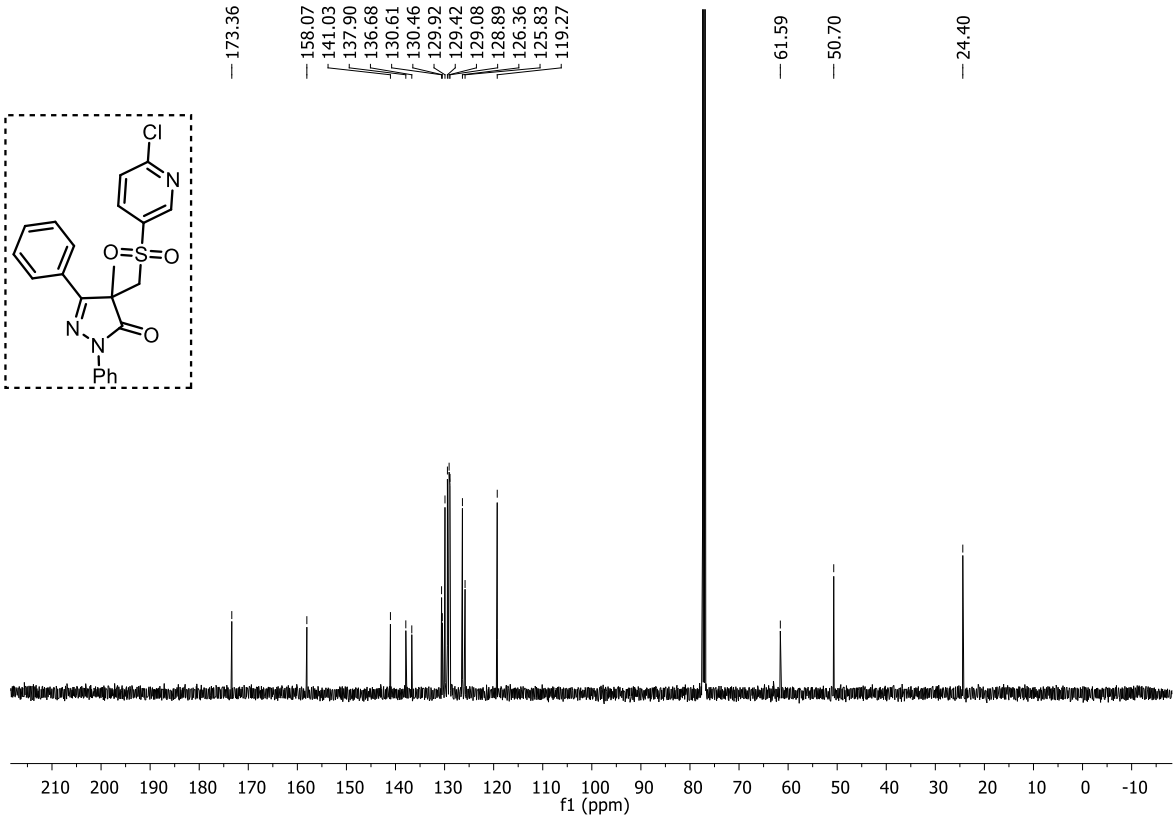
^{13}C {^{1}H} NMR spectrum of 5ag ($CDCl_3$, 126 MHz)



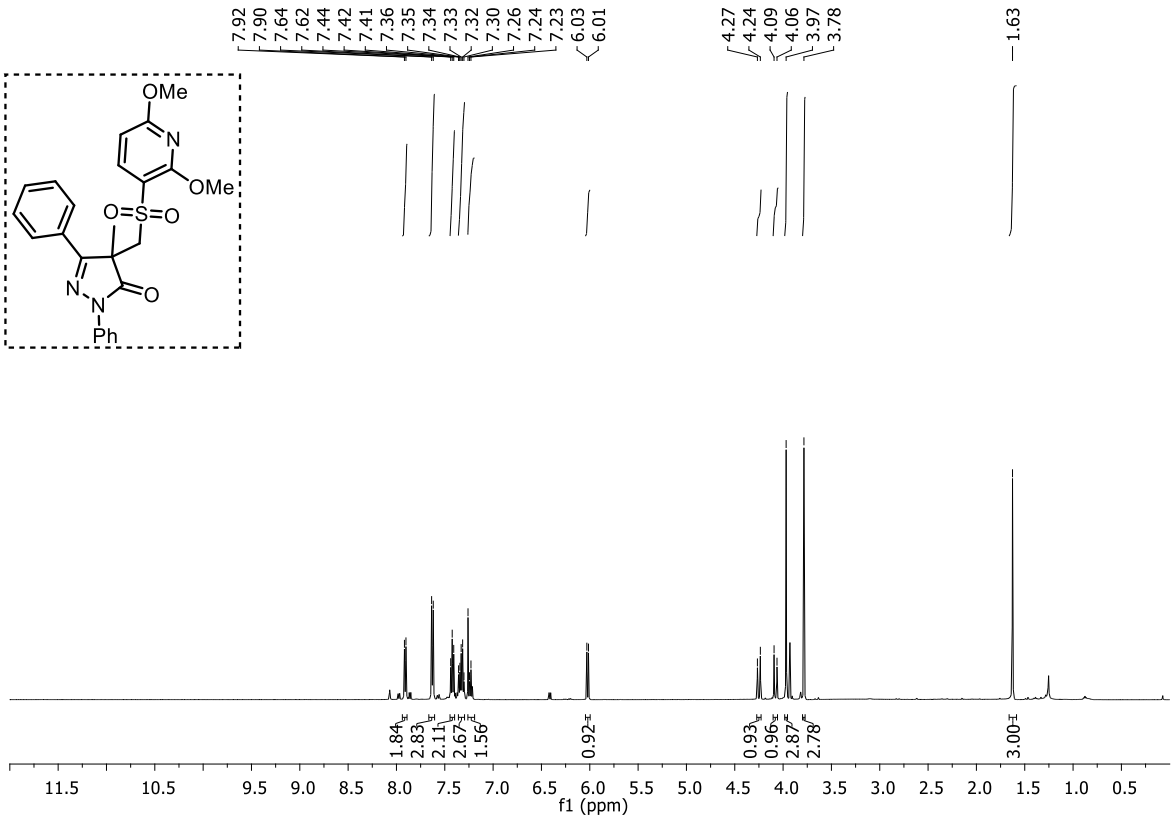
^{1}H NMR spectrum of 5ah ($CDCl_3$, 500 MHz)



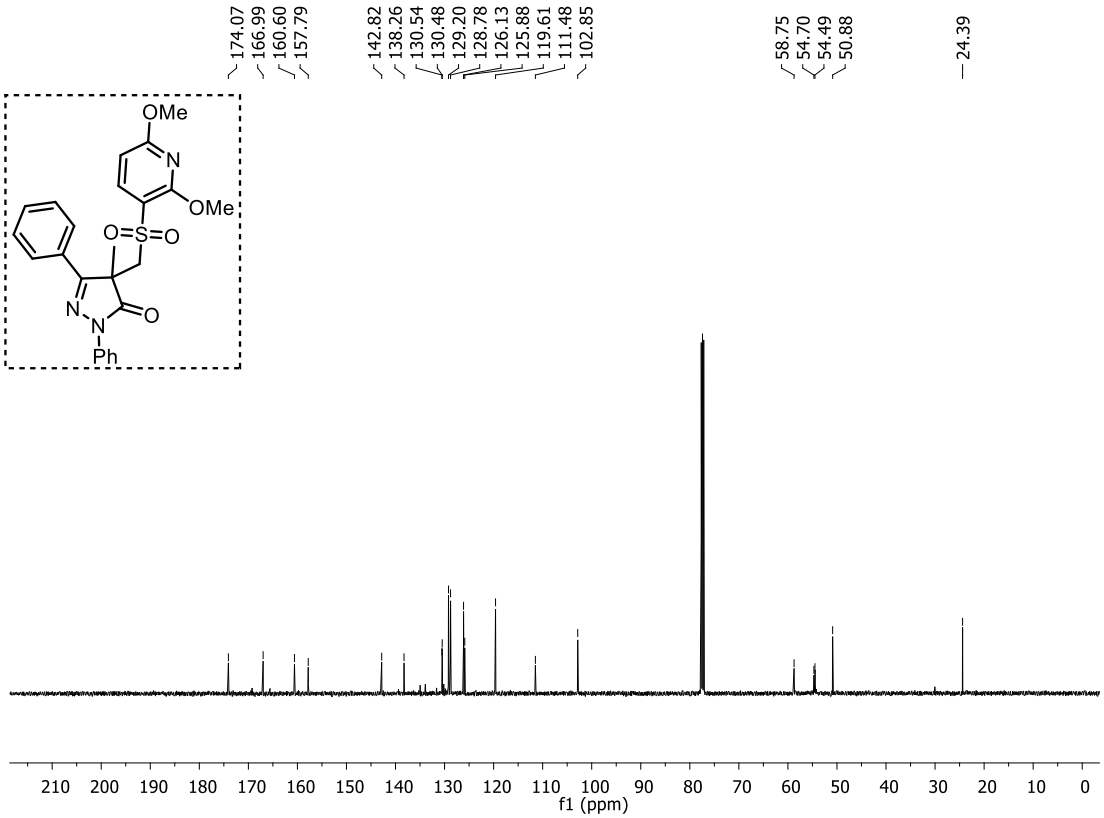
^{13}C {^{1}H} NMR spectrum of 5ah ($CDCl_3$, 126 MHz)



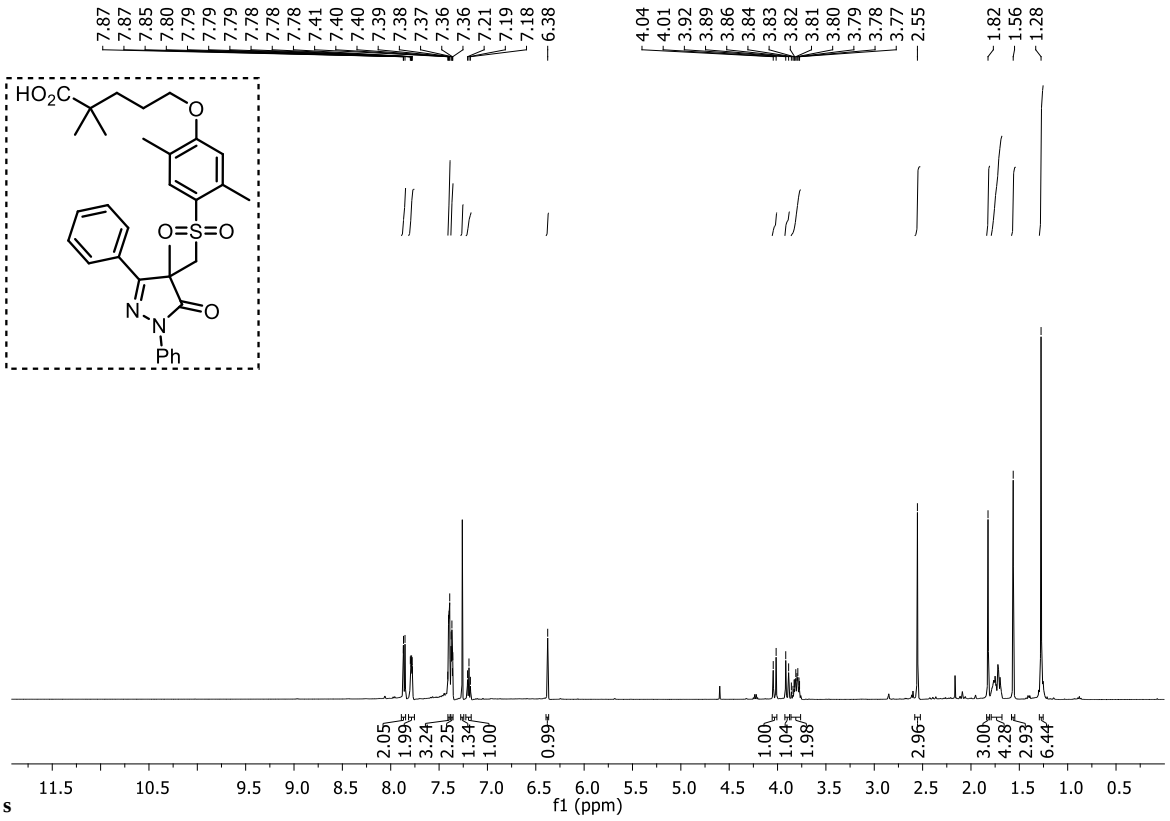
^{1}H NMR spectrum of 5ai ($CDCl_3$, 500 MHz)



^{13}C {^{1}H} NMR spectrum of 5ai ($CDCl_3$, 126 MHz)



^{1}H NMR spectrum of 5aj ($CDCl_3$, 500 MHz)



s

^{13}C {^{1}H} NMR spectrum of 5aj ($CDCl_3$, 126 MHz)