Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Blue Light Enhanced Heck Arylation at Room Temperature Applied to Allenes

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1. General

Flasks and all equipment employed for moisture-sensitive reactions and compounds were dried by electric heat gun under N_2. Analytical grade solvents were used as received. All commercially available reagents were used as received. Anhydrous solvents were purchased by Acros Organics or Sigma-Aldrich, or distilled according to the procedure reported by Armarego.[1] Triflates were prepared according to the procedure reported by Uchiyama *et al*.[2]

Products were purified by preparative column chromatography on Sigma-Aldrich silica-gel for flash chromatography, 0.04 0.063 mm/230-400 mesh. Reactions were monitored by TLC using silica-gel on TLC-PET foils Sigma Aldrich, 2 25 µm, layer thickness 0.2 mm, medium pore diameter.

Photochemical reactions were carried out in a 10 ml Schlenk-tube. A Kessil Blue Lamp was used as the irradiation source, which emission band is centred at 450 nm with about 55 nm width to half height. The irradiation source was located at 4 cm from the reaction solution surface.

NMR spectra were recorded employing a Jeol ECZR instrument. ^{1}H and ^{19}F were recorded in $CDCl_3$ or DMF-d_7 at 600 MHz. ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ or DMF-d_7 respectively at 150 MHz and 242.9 MHz. Chemical shifts were reported in ppm relative to the resonance of $CHCl_3$ (δ= 7.26) for ^{1}H NMR, to the central peak of $CDCl_3$ (δ= 77.0) for ^{13}C NMR, to H_3PO_4 85% (δ= 0.0) for ^{31}P NMR and to NaF for ^{19}F. ^{13}C NMR, ^{31}P and ^{19}F spectra were measured with complete proton decoupling. DEPT experiments were carried out with a DEPT-135 sequence.

UV–vis spectra were carried out with a Varian Cary “100 Scan” spectrophotometer. The extinctions were measured on freshly prepared and previously N_2 sparged solutions. Optical path length: 1 cm. The solutions were stable during the timescales necessary for the measurements, and the results of repeated measures were reproducible.

Fluorescence emission spectra were collected with a Cary Eclipse Fluorescence Spectrophotometer, with excitation at 415 and 450 nm. Excitation and emission slits set both at 5 nm. Spectra were taken in a fluorescence fused silica cuvette with 1 cm optical path length.

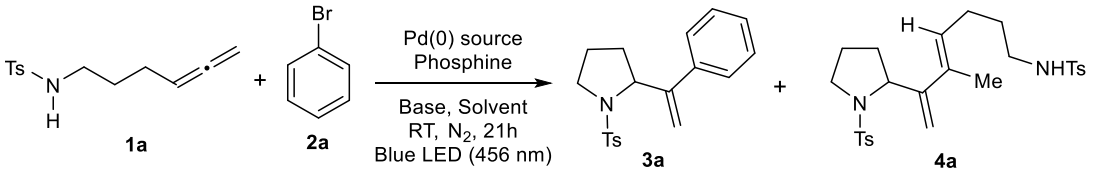
IR spectra were recorded on a BrukerVertex 70 FT-IR.

The electrochemical measurements were performed using a standard photo-electrochemical setup, composed of a computer-controlled potentiostat, AUTOLAB PGSTAT12. The electrochemical cell was a conventional three-electrode cell with a 1 mm thick fused silica window. Cyclic Voltammetry (CV) was carried out in the following conditions:

- Electrodes: Pt (W), Glassy Carbon (A), Ag/AgCl/TEACl (C)
- 0.1 M Bu_4NPF_6 in DMF solution
- Scan Rate: 100 mV s^{-1}
- Irradiation: KESSIL LAMP 1170 W m^{-2} and λ = 456 nm
- Nitrogen Atmosphere

HRMS spectra were obtained on a mass selective detector Agilent 5970 B operating at an ionizing voltage of 70 eV connected to a HP 5890 GC equipped with a HP-1 MS capillary column (25 m length, 0.25 mm I.D., 0.33 µm film thickness). The MS flow-injection analyses were run on a high resolving power hybrid mass spectrometer (HRMS) Orbitrap Fusion (Thermo Scientific, Rodano, Italy) and a Bruker Daltonics microTOF Mass Spectrometer equipped with an h-ESI ion source. The samples were analysed in methanol or acetonitrile solution using a syringe pump at a flow rate of 10 µL/min. The tuning parameters adopted for the ESI source were as follows: source voltage 3.5 kV, RF lens 60% (positive ion mode MH^+, MNa^+); source voltage 2.5 kV, RF lens 60%. The ion transfer tube was maintained at 270 °C. The mass accuracy of the recorded ions (vs the calculated ones) was <5 ppm. Analyses were run using full MS (50-500 m/z range) acquisition, at 240 000 resolution (200 m/z).

2. Screening of reaction conditions



2.1 Table S1: Thermal reactions

Entry	Pd catalyst	Phosphine	Base]	Solvent	T	1a[a] [%]	3a[a] [%]	4a[a] [%]
1	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	40°C	0	34	4
2	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	60°C	0	45	4
3	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	90°C	0	46	5

Reactions conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) anhydrous DMF (5 mL), K_2CO_3 (1.2 eq), **2a** (1.5 eq) under irradiation with 456 nm light source – blue light. [a] Determined on isolated product.

2.2 Table S2: Base and Solvent Screening

Entry	Pd catalyst	Phosphine	Base]	Solvent	1a[a] [%]	3a[a] [%]	4a[a] [%]
1	$Pd(OAc)_2$	PPh_3	**KOH**	DMF	39	22	0
2	$Pd(OAc)_2$	PPh_3	**Cs_2CO_3**	DMF	0	25	0
3	$Pd(OAc)_2$	PPh_3	**Et_3N**	DMF		0	14
4	$Pd(OAc)_2$	PPh_3	**AcOCs**	DMF		9	28
5	$Pd(OAc)_2$	PPh_3	**HCOONa**	DMF		11	28
6	$Pd(OAc)_2$	PPh_3	K_2CO_3	**DMSO**	89	2.4	0
7	$Pd(OAc)_2$	PPh_3	K_2CO_3	**DMA**	0	13	0

Reactions conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) anhydrous solvent (5 mL), base (1.2 eq), **2a** (1.5 eq) under irradiation with 456 nm light source – blue light. [a] Determined on isolated product.

2.3 Table S3: Pd Catalyst Screening

Entry	Pd catalyst	Phosphine	Base]	Solvent	1a[a] [%]	3a[a] [%]	4a[a] [%]
1	**$PdCl_2$**	PPh_3	K_2CO_3	DMF	0	4	0
2	**$PdCl_2$**	PPh_3	K_2CO_3	Toluene	46	0	0
3	**$PdCl_2$**	PPh_3	K_2CO_3	THF	26	0	0
4	**PdI_2**	PPh_3	K_2CO_3	DMF	0	traces	0
5	**$Pd(PPh_3)_4$**	PPh_3	K_2CO_3	DMF	100	0	0
6	**$Pd(dba)_2$**	PPh_3	K_2CO_3	DMF	35	0	24

Reactions conditions: **1a** (0.2 mmol), Pd source (5 mol%), PPh_3 (10 mol%) anhydrous solvent (5 mL), K_2CO_3 (1.2 eq), **2a** (1.5 eq) under irradiation with 456 nm light source – blue light. [a] Determined on isolated product.

2.4 Table S4: Phosphine Screening

Entry	Pd catalyst	Phosphine	Base]	Solvent	1a[a] [%]	3a[a] [%]	4a[a] [%]
1	$Pd(OAc)_2$	Xantphos	K_2CO_3	DMF	0	29	
2	$Pd(OAc)_2$	*Tris*-2-Furylphosphine	K_2CO_3	DMF	50	31[b], 38	
3	$Pd(OAc)_2$	*Tris-p*-Tolylphosphine	K_2CO_3	DMF	0	46	0
4	$Pd(OAc)_2$	*Tris*-cyclohexylphosphine	K_2CO_3	DMF	0	0	traces
5	$Pd(OAc)_2$	$(tBu)_3P$	K_2CO_3	DMF	17	7 + degradation	0

Reactions conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol%), Phosphine (10 mol%) anhydrous DMF (5 mL), K_2CO_3 (1.2 eq), **2a** (1.5 eq) under irradiation with 456 nm light source – blue light. [a] Determined on isolated product. [b] Calculated by NMR using CH_3NO_2 or *t*-BuOH as internal standard.

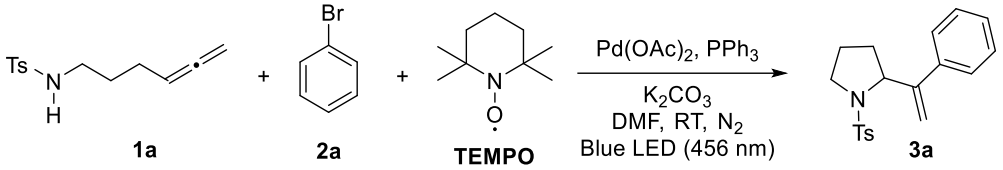
2.5 Table S5 Screening of amount of catalyst, phosphine, base and 2a

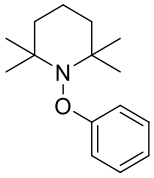
Entry	$Pd(OAc)_2$ [mol%]	PPh_3 [mol%]	2a [Eq]	K_2CO_3 [Eq]	Vol. DMF	1a[a] [%]	3a[a] [%]	4a[a] [%]
1	5 %	15%	1.5	1.2	5 ml	0	22	0
2	5 %	20%	1.5	1.2	5 ml	0	30	20
3	3 %	6%	1.5	1.2	5 ml	15	47	2
4	8 %	16%	1.5	1.2	5 ml	0	34	8
5	5 %	10%	2	1.2	5 ml	0	50	2
6	5 %	10%	3	1.2	5 ml	0	50	8
7	5 %	10%	1.1	1.2	5 ml	0	45	12
8	5 %	10%	1.5	1.5	5 ml	0	48	9
9	5 %	10%	1.5	2.4	5 ml	0	60	traces
10	5 %	16%	1.5	1.2	7 ml	0	37	2

Reactions conditions: **1a** (0.2 mmol), $Pd(OAc)_2$, PPh_3, anhydrous DMF, K_2CO_3, **2a**, under irradiation with 456 nm light source – blue light. [a] Determined on isolated product.

3. Mechanistic Investigations

3.1 Trapping Experiment with TEMPO





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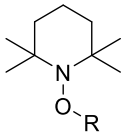


TEMPO adducts not found

In order to study the formation of radicals, two trapping experiments with TEMPO were realized. The reactions were carried out employing 1.5 Eq of TEMPO in the presence of catalytic (experiment A) or stoichiometric (experiment B) amounts of $Pd(OAc)_2$.

Experiment A, procedure: A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2, then 5 ml of dry DMF were transferred into the tube and degassed with N_2 for at least 10 minutes. Under a constant flow of N_2, $Pd(OAc)_2$ (2.24 mg, 0.01 mmol, 5 mol%) was placed in the Schlenk tube and the mixture was degassed for additional 5 minutes until the solution turned an intense yellow. Then PPh_3 (5.25 mg, 0.02 mmol, 10 mol%) was added and the solution was left under stirring under inert gas until the solution turned cherry red. Always under N_2 flow, the other reagents were added in the following order: bromobenzene **2a** (0.3 mmol, 1.5 Eq), K_2CO_3 (33 mg, 0.24 mmol, 1.2 Eq), the allene **1a** (0.2 mmol, 1 Eq) and TEMPO (0.3 mmol, 1.5 Eq). The Schlenk tube, saturated with N_2, was closed with a septum and then stirred at 4 cm from a Kessil blue lamp (456 nm) at room temperature for 21 h.
Reaction work-up: the reaction mixture was diluted with 25 ml of Et_2O and the organic phase was washed with brine (5x10 ml) and dried over Na_2SO_4. After solvent removal, the crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 7/1) to afford product **1a** in 15% yield. Around 40% of allene was recovered not reacted.
When TEMPO was added after 3 h of irradiation, product **3a** was recovered in 43% yield, with only 15% of allene **1a** not reacted.

Experiment B, procedure: the same procedure and work-up reported in experiment A was applied. The following amounts of reagents were employed:
DMF dry 5 mL
$Pd(OAc)_2$ (45 mg, 0.2 mmol, 1 Eq)
PPh_3 (105 mg, 0.4 mmol, 2 Eq)
bromobenzene **2a** (0.3 mmol, 1.5 Eq), K_2CO_3 (33 mg, 0.24 mmol, 1.2 Eq)
allene **1a** (0.2 mmol, 1 Eq)
TEMPO (0.3 mmol, 1.5 Eq).
Product **1a** was obtained in 20% yield.

3.2 Light/Dark experiment

In order to unveil the fundamental role of the light in promoting this Heck reaction at room temperature, we realised a light/dark experiment on the model reaction between allene **1a** and bromobenzene **2a**. Thus we set up a model reaction according to the general procedure reported in Section 4.2. The reaction mixture under stirring was submitted to light/dark cycles of variable time length according to Table S1.

Table 1. Results in term of yield obtained for the light/dark experiment.

Light/Dark cycle	Total reaction time [min]	Product yield [%]
Start	0	0
Light ON for 30 min	30	10
Light OFF for 30 min	60	10
Light ON for 30 min	90	15
Light OFF for 30 min	120	15
Light ON for 60 min	180	28
Light OFF for 60 min	240	28
Light ON for 60 min	300	40

For each point, 0.3 mL of crude reaction mixture were withdrawn under N_2 with a syringe. The solution was transferred in a test tube, where it was diluted with 2 mL of Et_2O and then washed with 1 mL of brine. The organic phase was dried over Na_2SO_4 and after solvent removal, the crude was analysed by ^1H NMR employing 0.8 mL of $CDCl_3$ containing *t*-BuOH (0.022 mmol) as internal standard.

3.3 ^{31}P-NMR analysis of the catalyst solution with and without illumination

A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2, then 2.8 ml of DMF-d_7 were transferred into the tube and degassed with N_2 for at least 10 minutes. Under a constant flow of N_2, $Pd(OAc)_2$ (20 mg, 0.08 mmol, 5 mol%) was placed in the Schlenk tube and the mixture was degassed for additional 5 minutes until the solution turned an intense yellow. Then PPh_3 (47 mg, 0.180 mmol, 10 mol%) was added and the solution was left under stirring under inert gas until the solution turned cherry red (catalyst solution). Starting from this solution, different NMR samples were prepared and analysed by ^{31}P-NMR. All NMR tubes employed were previously dried and placed under N_2. Each sample was provided with a small capillary containing 85% aqueous H_3PO_4 as reference.

Solution A: 0.7 mL of the catalyst solution were withdrawn with a syringe and transferred in a NMR tube.

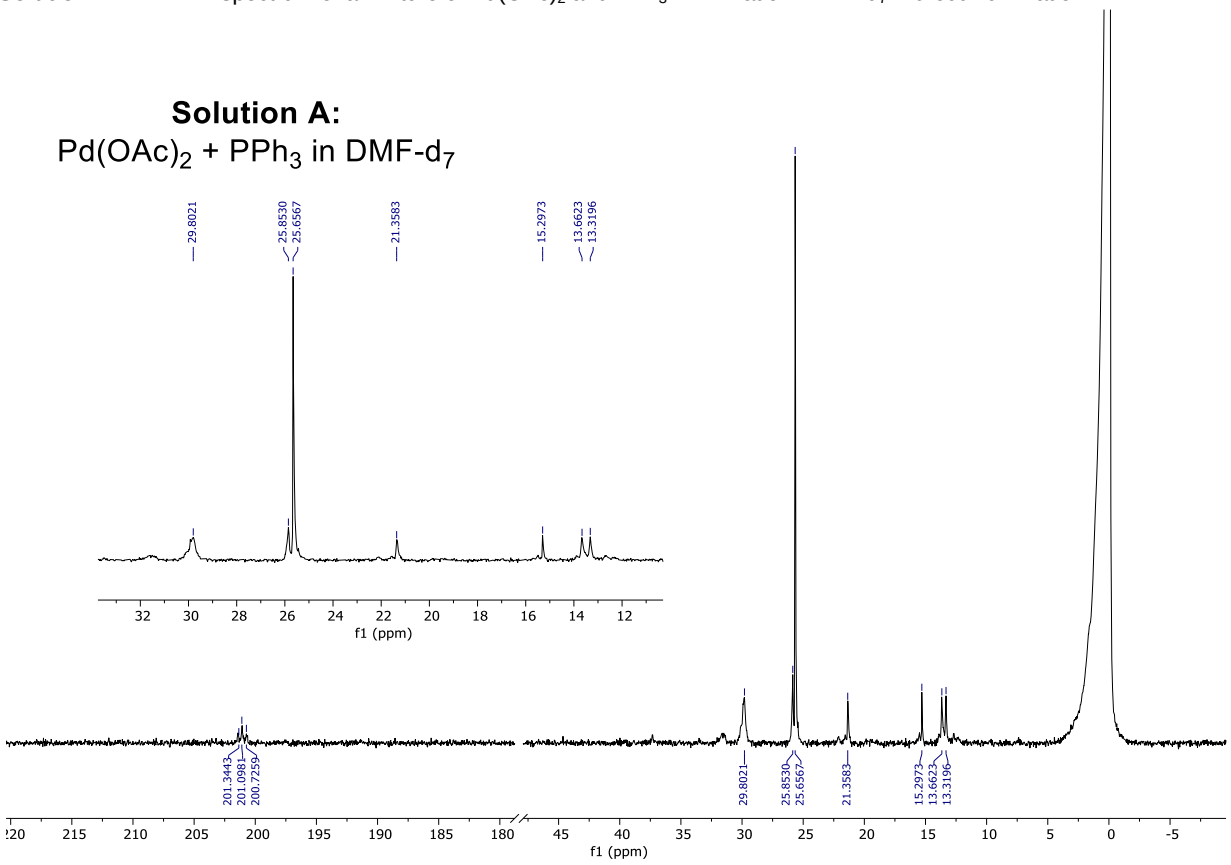
Solution B: 105 mg of bromobenzene **2a** were transferred in the NMR tube, then 0.7 mL of the catalyst solution were added to constant N_2 flow.

Solution A (hυ): 0.7 mL of the catalyst solution were withdrawn with a syringe and transferred in a NMR tube. The NMR tube was placed under the Kessil blue LED and it was irradiated for 2 h before NMR analysis.

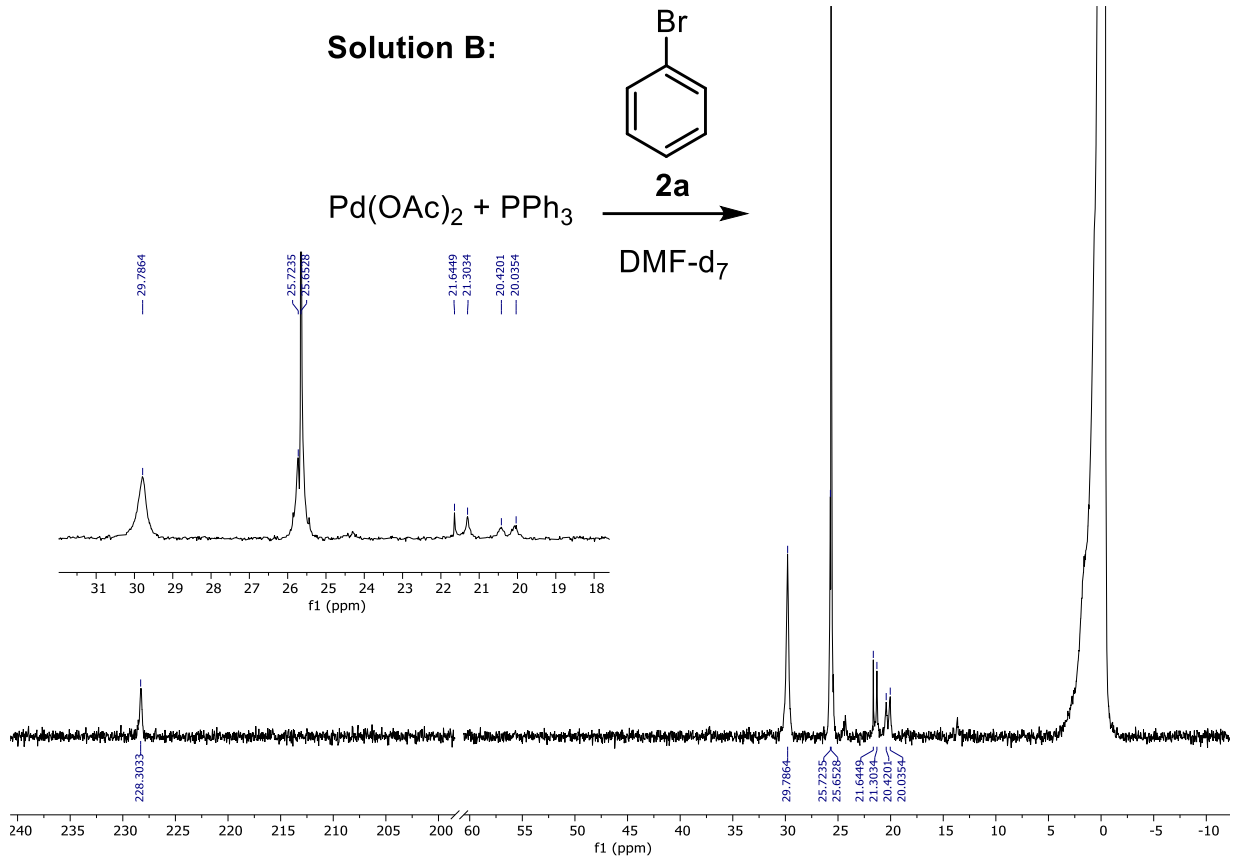
Solution B (hυ): 105 mg of bromobenzene **2a** were transferred in the NMR tube, then 0.7 mL of the catalyst solution were added to constant N_2 flow. The NMR tube was placed under the Kessil blue LED and it was irradiated for 2 h before NMR analysis.

The full spectra are shown below.

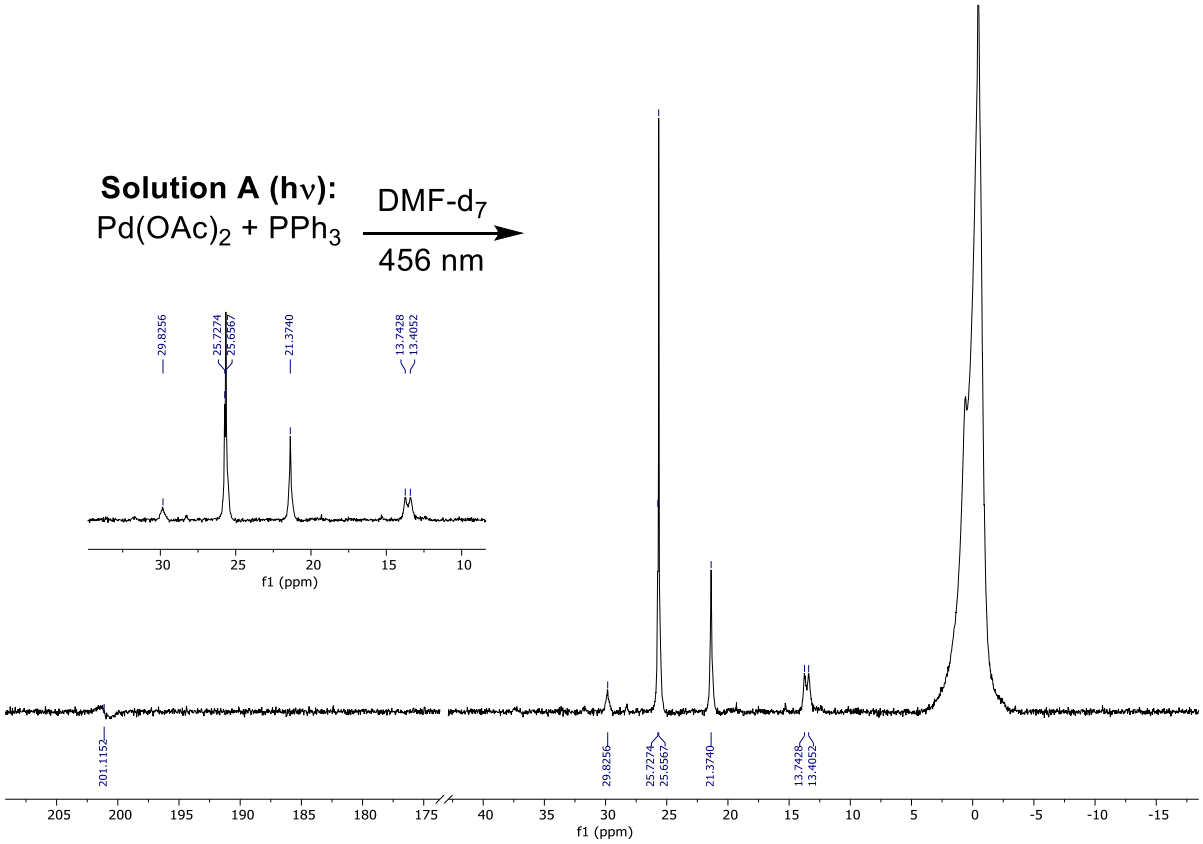
Solution A: ^{31}P-NMR spectrum of a mixture of $Pd(OAc)_2$ and PPh_3 in 1:2 ratio in DMF-d_7 without illumination



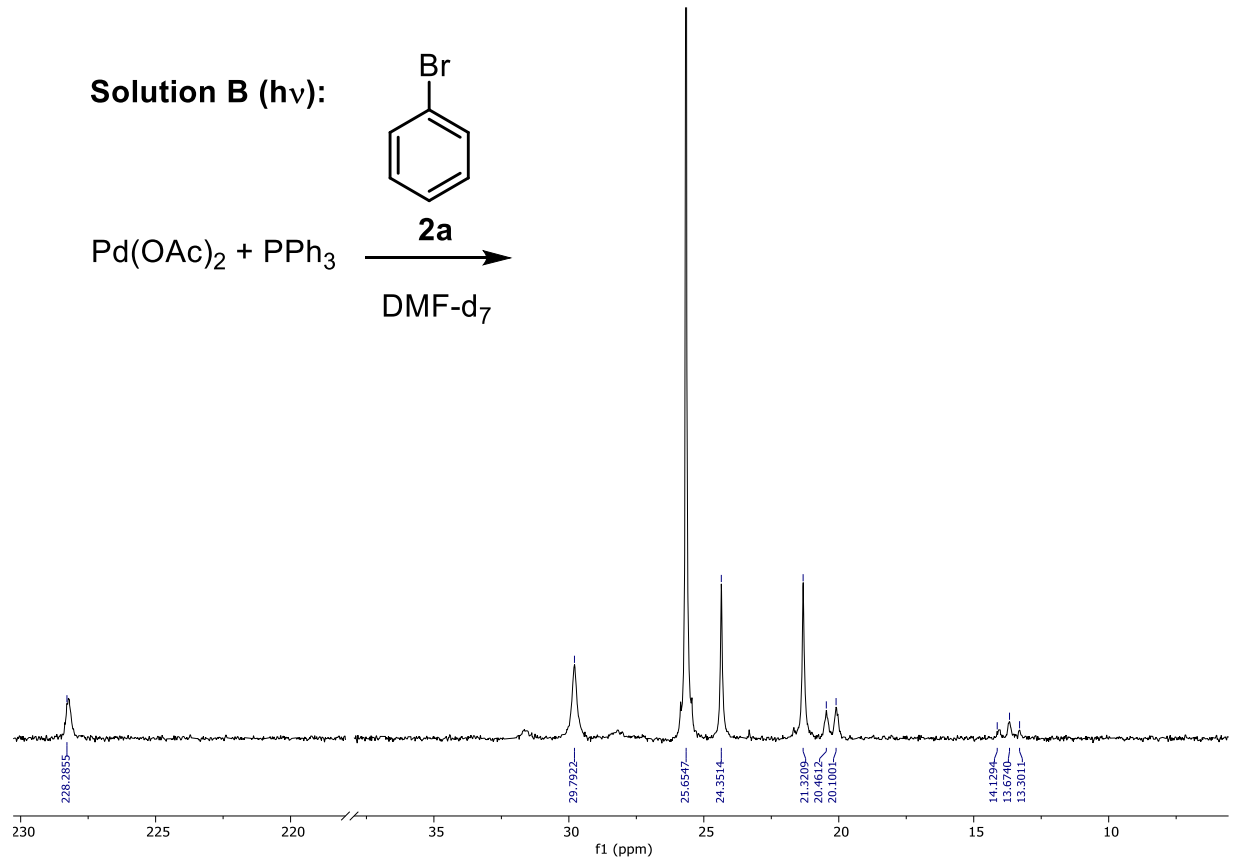
Solution B: ^{31}P-NMR spectrum of a mixture of $Pd(OAc)_2$ and PPh_3 in 1:2 ratio in DMF-d_7 after the addition of bromobenzene **2a** without illumination



Solution A (hυ): ^{31}P-NMR spectrum of a mixture of $Pd(OAc)_2$ and PPh_3 in 1:2 ratio in DMF-d_7 under illumination



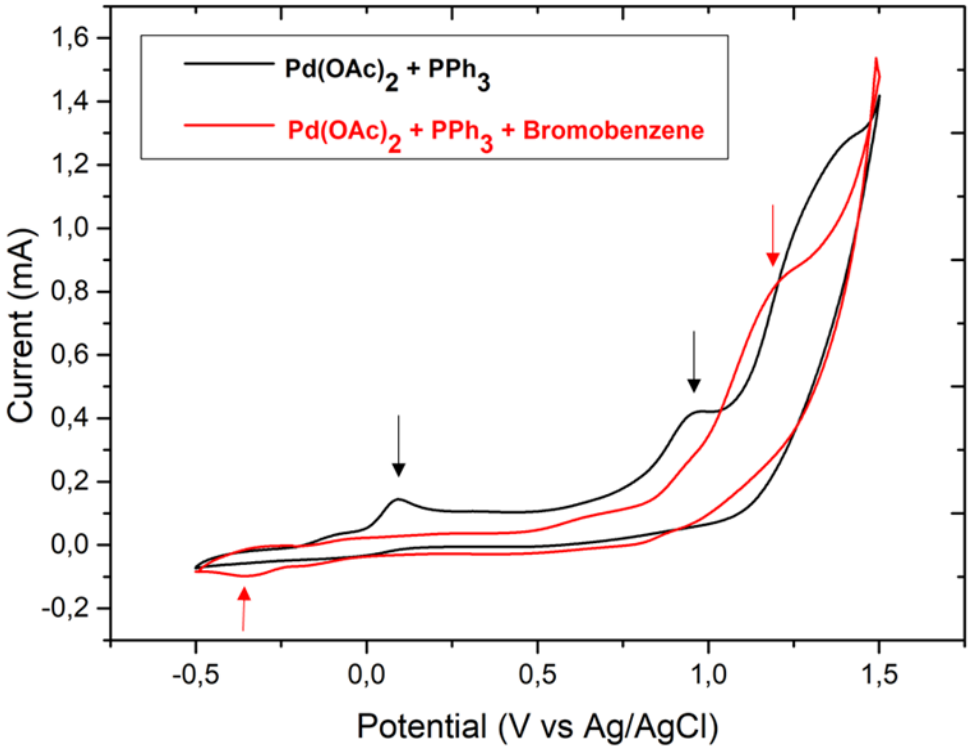
Solution B (hυ): ^{31}P-NMR spectrum of a mixture of $Pd(OAc)_2$ and PPh_3 in 1:2 ratio in DMF-d_7 after the addition of bromobenzene **2a** under illumination



3.4 Electrochemical measurements

The catalyst solution was characterised from an electrochemical point of view by cyclic voltammetry (CV) analysis. In Figure S1 are reported the CVs of a $Pd(OAc)_2$ - PPh_3 solution in a molar ratio 1:2 before and after the addition of bromobenzene **2a**.[3] As already observed by Amatore, the redox activity of this catalytic system is not so high and unstable.[3] However, two anodic peaks are clearly distinguishable at +0.10 V and +0.95 V (*vs* Ag/AgCl). Interestingly, the addition of bromobenzene **2a** in the solution influences the redox activity of the catalytic system, the peak at +0.10V disappears while a shift at +1.20V of the other one occurs. Moreover, a cathodic peak is now revealed at -0.35V. Once again, the changes of the redox behaviour of the system are consistent with the oxidative addition of bromobenzene **2a**.

Figure S1. Cyclic voltammogram analysis of a $Pd(OAc)_2$ - PPh_3 solution in a molar ratio 1:2 before and after the addition of bromobenzene **2a**.

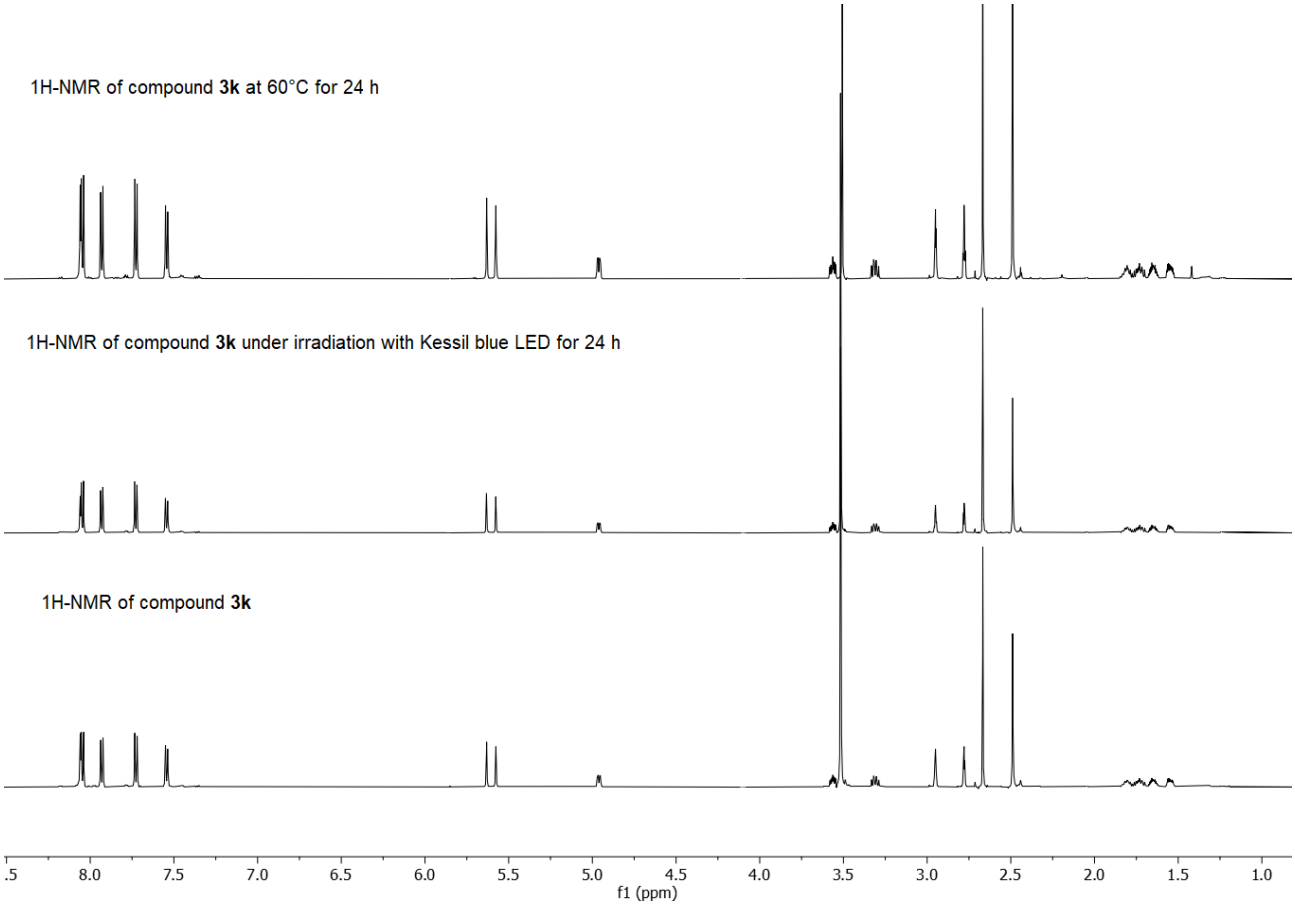


3.5 Study on the stability of product 3k

In order to assess the stability of the products derived from the photocatalysed reaction of allene with aryl halides, we studied by NMR the stability of pyrrolidine **3k** derived from 4-bromoacetophenone **2k**. The ^{1}H-NMR spectra were recorded in DMF-d_7 considering that the photocatalysed or thermal coupling reactions were realised in DMF. Figure S2 shows the comparison between the ^{1}H-NMR spectra of product **3k** in three different conditions:
pure compound **3k** after isolation by column chromatography (bottom);
compound **3k** after irradiation for 24 h with a Kessil blue lamp (middle);
compound **3k** after heating at 60°C for 24 h (top)

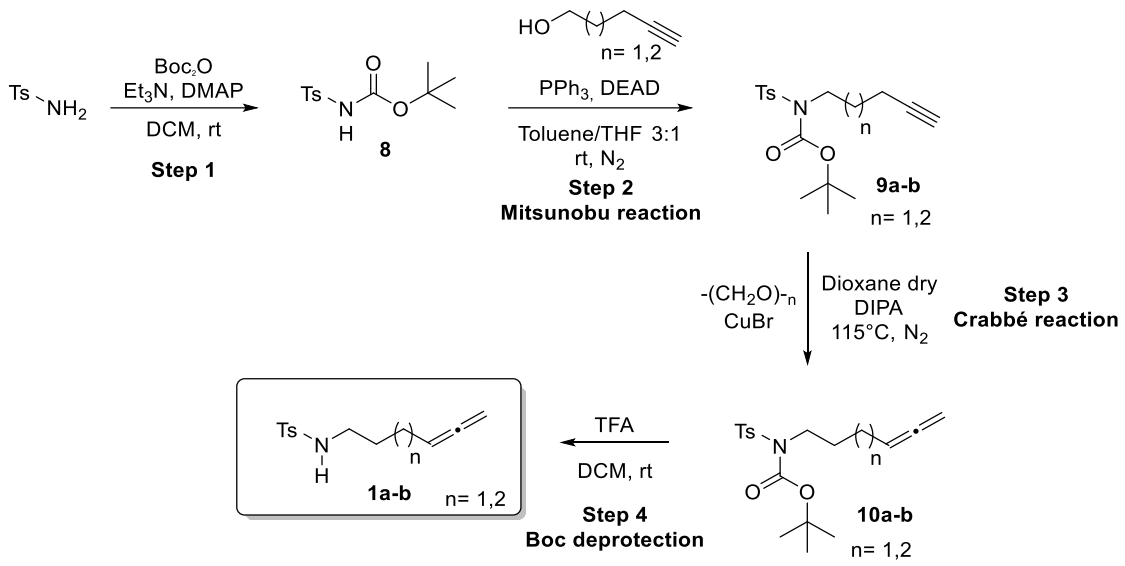
As it is possible to see in Figure S2, the ^{1}H-NMR spectra after irradiation and heating at 60°C are superimposable with the one of pure compound **3k** suggesting the stability of the pyrrolidine both under the conditions of the photocatalysed and thermal reactions. Some negligible traces of degradation can be observed under heating.

Figure S2. Comparison between the ^{1}H NMR of compound **3k** at t = 0 h (bottom); after 24 h under blue light irradiation (middle); after 24 h at 60° C (top).

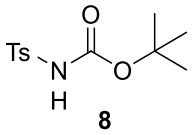


4. Experimental Procedures

4.1 General procedures for the synthesis of allenes 1a-b



Step 1: Protection of tosylamine. Synthesis of t-butyl tosylcarbamate 8[4]

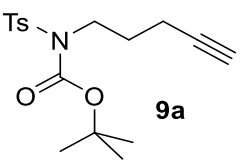


***t*-Butyl tosylcarbamate 8** was prepared according to the procedure reported in Ref. 4. White solid (yield 91%).**^{1}H-NMR** (600 MHz, $CDCl_3$): δ= 1.38 (s, 9H; C(C*H*$_3$)$_3$), 2.44 (s, 3H; Ar-C*H*$_3$), 7.33 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 7.89 (d, 2H, *J*= 8.3 Hz; Ar-*H*).

Step 2: Mitsunobu reaction[5]

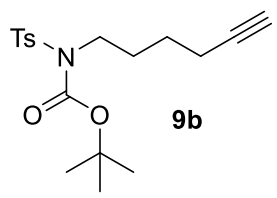
A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a constant flow of N_2, then *t*-butyl tosylcarbamate **8** (4.27 g, 15. 7 mmol, 1.05 Eq) and PPh_3 (5.11 g, 19.5 mmol, 1.30 eq) were added. The solids were then dissolved with a mixture 3/1 of dry toluene/THF.

When the solids were dissolved, the alkynol (15 mmol, 1.0 eq) was dripped into the reaction mixture. After the addition, the mixture was placed in a cooling bath in order to maintain the temperature between 0°C and -10°C. Then a solution of DEAD, 40% in THF, (8.0 g, 18 mmol, 1.2 Eq) was slowly added to the reaction mixture. The temperature was kept between 0°C and -10°C for at least 30 minutes after DEAD addition. The mixture was then allowed to warm and left under stirring at room temperature for 12 h or until the alkynol was totally consumed. Then, the solvent was removed under reduced pressure to obtain a white solid, which was purified by column chromatography on silica gel to give **9a** in 97% yield from pent-4-yn-1-ol and **9b** in 94% yield from hex-5-yn-1-ol.



***t*-Butyl pent-4-yn-1-yl(tosyl)carbamate 9a** Following the described procedure, 1.29 g (15 mmol) of pent-4-yn-1-ol were reacted with *t*-butyl tosylcarbamate **8** (4.27 g, 15. 7 mmol, 1.05 Eq) to afford 4.90 g of *t*-butyl pent-4-yn-1-yl(tosyl)carbamate **9a** as a light yellow oil (EP/EE 9/1, yield 97%).

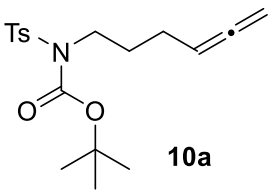
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.35 (s, 9H; C(C*H*$_3$)$_3$), 1.96-2.02 (m, 3H; CH_2-C*H*$_2$-CH_2 and CH_2-C≡C*H*), 2.28 (td, 2H, *J*= 7.1, 2.7 Hz; C*H*$_2$-C≡CH), 2.44 (s, 3H; Ar-C*H*$_3$), 3.91-3.93 (m, 2H; N-C*H*$_2$-CH_2), 7.30 (d, 2H, *J*= 8.0 Ts-*H*), 7.78 (d, 2H, *J*= 8.3 Hz; Ts-*H*).



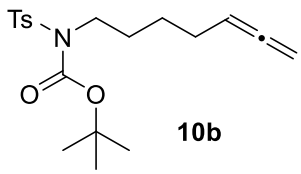
***t*-Butyl hexa-4,5-dien-1-yl(tosyl)carbamate 9b** Following the described procedure, 1.53 g (15 mmol) of hex-5-yn-1-ol were reacted with *t*-butyl tosylcarbamate **8** (4.27 g, 15. 7 mmol, 1.05 Eq) to afford 4.96 g of *t*-butyl hexa-4,5-dien-1-yl(tosyl)carbamate **9b** as a light yellow oil (EP/EE 9/1, yield 94%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.34 (s, 9H; C(CH_3)$_3$), 1.59 (quint, 2H, *J*= 7.1 Hz; CH_2-CH_2-CH_2-C≡), 1.85-1.90 (m, 2H; CH_2-CH_2-CH_2), 1.97 (t, 1H, *J*= 2.7 Hz; C≡C*H*), 2.26 (td, 2H, *J*= 7.0, 2.6 Hz; CH_2-CH_2-C≡), 2.43 (s, 3H; Ar-CH_3), 3.85 (m 2H; N-CH_2-CH_2), 7.30 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.78 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

Step 3: Crabbé reaction[6]

Compounds **10a**-**b** were obtained by a modification of the procedure reported by Yang and Li.
Four Pyrex tubes, equipped with a magnetic stirring bar, were dried and placed under a flow of N_2, then each tube was charged with alkyne **9a** or **9b** (1.41 mmol, 1.0 Eq), paraformaldehyde (85 mg, 2.8 mmol, 2.0 eq), CuBr (142 mg, 0.99 mmol, 0.7 eq) and dissolved with 15 ml of dry dioxane each. The mixture was left under stirring for 30 minutes at room temperature under inert atmosphere, then 0.4 ml of DIPA (2.82 mmol, 2 eq) were added dropwise in each tube. After saturating with N_2, each flask was closed and the reaction mixture was left under stirring for 1 h at room temperature. During this time the color of the solution turned from light blue to green. Later, the reaction mixture, under stirring, was heated at 115°C overnight. During the heating, the solution turned orange.
The reaction was monitored by TLC, when compound **9** was totally consumed, it was quenched with HCl 2 M (8 ml per mmol of DIPA). Then an aqueous solution of NH_3, (12.5%) in ratio 1/20 with compound **9**, was added. The organic and the aqueous layers were separated in a separation funnel. The blue aqueous phase was extracted with diethyl ether several times until the organic phase did not turn yellow any more.
The combined organic phases were dried over Na_2SO_4 and the solvent removed in vacuum to obtain a red oil. The residual dioxane was eliminated under high vacuum and the crude product **10a** or **10b** was used without further purification in the step 4.



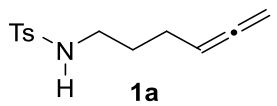
***t*-Butyl hexa-4,5-dien-1-yl(tosyl)carbamate 10a** Following the described procedure, 1.90 g (5.64 mmol) of *t*-butyl pent-4-yn-1-yl(tosyl)carbamate **9a** were reacted with paraformaldehyde (85 mg, 2.8 mmol, 2.0 eq) to afford *t*-butyl hexa-4,5-dien-1-yl(tosyl)carbamate **10a** as a red oil which was used without further purification in step 4.
^{1}H-NMR (600 MHz, $CDCl_3$): crude reaction mixture; δ= 1.33 (s, 9H; C(CH_3)$_3$), 1.88 (quint, 2H, *J*= 7.9 Hz; CH_2-CH_2-CH_2), 2.07 (tq, 2H, J= 6.9, 3.4 Hz; CH_2-CH_2-CH), 2.43 (s, 3H; Ar-CH_3), 3.70 (residue of dioxane), 3.83-3.87 (m, 2H; N-CH_2-CH_2) 4.70 (dt, 2H, *J*= 6.2, 3.1 Hz; =C=CH_2), 5.14 (quint, 1H, *J*= 6.5 Hz; CH_2-C*H*=CH_2) 7.30 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.77 (d, 2H, *J*= 8.3 Hz; Ts-*H*).



***t*-Butyl hepta-5,6-dien-1-yl(tosyl)carbamate 10b** Following the described procedure, 1.98 g (5.64 mmol) of *t*-butyl hexa-4,5-dien-1-yl(tosyl)carbamate **9b** were reacted with paraformaldehyde (85 mg, 2.8 mmol, 2.0 eq) to afford *t*-butyl hepta-5,6-dien-1-yl(tosyl)carbamate **10b** as a red oil which was used without further purification in step 4.
^{1}H-NMR (600 MHz, $CDCl_3$): crude reaction mixture; δ= 1.33 (s, 9H; C(CH_3)$_3$), 1.45-1.50 (m, 2H; CH_2-CH_2-CH_2), 1.77-1.82 (m, 2H; N-CH_2-CH_2), 2.03-2.08 (m, 2H; CH_2-CH_2-CH), 2.44 (s, 3H; Ar-CH_3), 3.70 (residue of dioxane), 3.82 (m, 2H; N-CH_2-CH_2), 4.67 (dt, 2H, *J*= 6.6, 3.3 Hz; =C=CH_2), 5.10 (quint, 1H, *J*= 6.8 Hz; CH_2-C*H*=C), 7.29 (d, 2H, *J*= 8.4 Hz; Ts-*H*), 7.77 (d, 2H, *J*= 8.4 Hz; Ts-*H*).

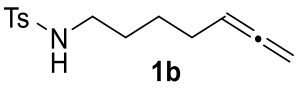
Step 4: Boc deprotection[6]

Compound **10a** or **10b** (5.1 mmol, 1 eq) was dissolved in 2.4 ml of DCM in a round bottom flask which was placed in an ice bath. Then 6 Eq of TFA (2.4 ml) were slowly added and the reaction mixture was stirred for at least 1 h. The reaction was monitored by TLC and when compound **10a-b** was totally consumed, the excess of TFA was neutralized with $NaHCO_3$.
The mixture was transferred in a separation funnel, the organic and aqueous layers were separated. The organic phase was further washed with brine (2 x 20 ml), dried over Na_2SO_4 and the solvent was removed in vacuum to obtain a yellow oil. The latter was purified by column chromatography on silica gel to give **1a** in 85% yield or **1b** in 57% yield over two steps.



1a

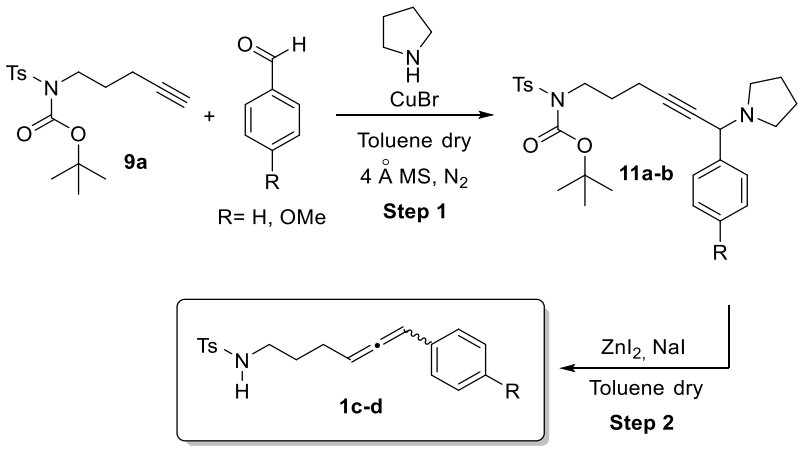
***N*-tosylhexa-4,5-dien-1-ylamine 1a** Following the described procedure, 1.80 g (5.11 mmol) of *t*-butyl hexa-4,5-dien-1-yl(tosyl)carbamate **10a** were reacted with TFA to afford 1.09 g of *N-tosylhexa-4,5-dien-1-ylamine* 1a as a yellow oil (EP/EE 9/1, yield 85%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.59 (p, 2H+H_2O, *J*= 7.1 Hz; CH_2-C*H*$_2$-CH_2), 1.99 (m, 2H; CH_2-C*H*$_2$-CH), 2.43 (s, 3H; Ar-C*H*$_3$), 2.99 (q, 2H, *J*= 7.0 Hz; NH-C*H*$_2$-CH_2), 4.30 (s broad, 1H; N*H*), 4.64 (dt, 2H, *J*= 6.7, 3.2 Hz; CH=C=C*H*$_2$), 5.02 (quint, 1H, *J*= 6.7 Hz; CH_2-C*H*=C), 7.31 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.74 (d, 2H, *J*= 8.3 Hz; Ts-*H*).



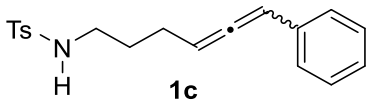
1b

***N*-tosylhepta-5,6-dien-1-ylamine 1b** Following the described procedure, 1.86 g (5.11 mmol) of *t*-butyl hepta-5,6-dien-1-yl(tosyl)carbamate **10b** were reacted with TFA to afford 0.771 mg of *N*-tosylhepta-5,6-dien-1-ylamine **1b** as a yellow oil (EP/EE 9/1, yield 57%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.39 (quint, 2H, *J*= 7.3 Hz; CH_2-C*H*$_2$-CH_2), 1.50 (quint, 2H, *J*= 7.1 Hz; NH-CH_2-C*H*$_2$-CH_2), 1.94 (m, 2H, CH_2-C*H*$_2$-CH), 2.43 (s, 3H; Ar-C*H*$_3$), 2.95 (q, 2H, J= 6.8 Hz; NH-C*H*$_2$-CH_2), 4.27 (t, 1H, *J*= 6.2 Hz; N*H*), 4.64 (dt, 2H, *J*= 6.7, 3.3 Hz; =C=C*H*$_2$), 5.02 (p, 1H, *J*= 6.7 Hz; CH_2-C*H*=C), 7.31 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.74 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

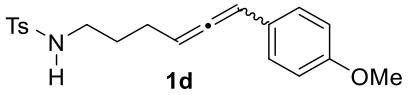
4.3 General procedure for the synthesis of internal allenes 1c-d[7]



Compounds **1c-d** were obtained by a modification of the procedure reported by Ma *et al.*[7]
A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2, then the reagents were added in the following order: CuBr (15 mg, 0.1 mmol, 0.06 Eq), 4Å molecular sieves (0.60 g), 4 ml of dry toluene, alkyne **9a** (0.56 g, 1.55 mmol, 1 Eq), 1 Eq of aldehyde and pyrrolidine (121 mg, 1.7 mmol, 1.1 Eq). The reaction mixture was left under stirring at room temperature for 12 h.
After the 12 h, the reaction was monitored by TLC and when compound **9a** was totally consumed, the solvent was removed under high vacuum. The solid residue was solved in Et_2O and the organic phase was washed with an aqueous solution of NH_3/H_2O (12%). The washings were continued until the aqueous layer remained colourless. The organic layer was additionally washed with brine twice. The crude mixture obtained was employed in the next step without any further purification. Thus, compound **11a** or **11b** was solved in dry toluene and transferred under nitrogen flow in a dried Schlenk tube, equipped with a magnetic stirring bar.
For step 2, ZnI_2 was purified by sublimation under vacuum at 300°C, while NaI was dried under vacuum at elevated temperature. After the drying process, ZnI_2 (0.247 g, 0.45 Eq) and NaI (0.129 g, 0.5 Eq) were weighted and transferred in a dried Pyrex tube. At this point, the toluene solution containing crude compound **11** was transferred with a syringe in the Pyrex tube containing ZnI_2 and NaI and the mixture was stirred at 110°C for 6 h. Then, the crude mixture was cooled, the solvent was removed under vacuum and the latter was purified by column chromatography.

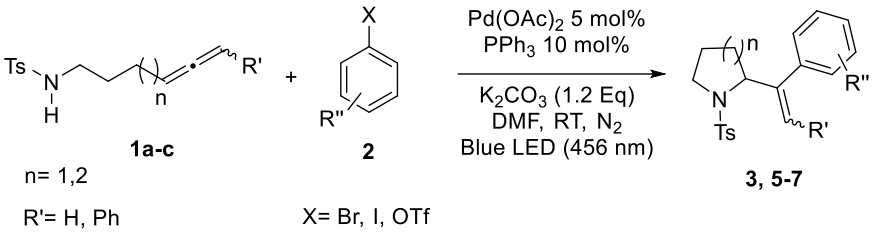


4-Methyl-*N*-(6-phenylhexa-4,5-dien-1-yl)benzenesulfonamide 1c[8] Following the described procedure, 0.56 g (1.55 mmol) of *t*-butyl pent-4-yn-1-yl(tosyl)carbamate **9a** and 164 mg of benzaldehyde were reacted to afford 304 mg of 4-methyl-*N*-(6-phenylhexa-4,5-dien-1-yl)benzenesulfonamide **1c** as a yellow oil (EP/Acetone 9/1, yield 60%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.60-1.71 (m, 2H; CH_2-C*H*$_2$-CH_2), 2.12 (m, 2H; CH_2-C*H*$_2$-CH), 2.41 (s, 3H; Ar-C*H*$_3$), 3.05 (m, 2H; NH-C*H*$_2$-CH_2), 4.31 (t, 1H, *J*= 6.2 Hz; NH), 5.51 (q, 1H, *J*= 6.5 Hz; CH_2-C*H*=C), 6.11 (dt, 1H, *J*= 6.5, 3.3 Hz; C*H*=C=CH), 7.18-7.21 (m, 1H; Ar-*H*), 7.22-7.25 (m, 2H; Ar-*H*), 7.27 (d, 2H, *J*= 8.6 Hz; Ts-*H*), 7.28-7.31 (m, 2H; Ar-*H*), 7.71 (d, 2H, *J*= 8.6 Hz; Ts-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 25.5 (CH_2), 28.8 (CH_2), 42.6 (CH_2), 93.7 (CH), 95.4 (CH), 126.6 (CH), 126.9 (CH), 127.1 (CH), 128.6 (CH), 129.7 (CH), 134.5 (Cq), 137.0 (Cq), 143.0 (Cq), 205.1 (Cq).



***N*-(6-(4-methoxyphenyl)hexa-4,5-dien-1-yl)-4-methylbenzenesulfonamide 1d**
Following the described procedure, 0.56 g (1.55 mmol) of *t*-butyl pent-4-yn-1-yl(tosyl)carbamate **9a** and 211 mg of 4-methoxybenzaldehyde were reacted to afford 221 mg of *N*-(6-(4-methoxyphenyl)hexa-4,5-dien-1-yl)-4-methylbenzenesulfonamide **1d** as a yellow oil (EP/Acetone 9/1, yield 40%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.58-1.66 (m, 2H; CH_2-C*H*$_2$-CH_2), 2.05-2.20 (m, 2H; CH_2-C*H*$_2$-CH), 2.39 (s, 3H; Ar-C*H*$_3$), 2.93-3.01 (m, 2H; NH-C*H*$_2$-CH_2), 3.78 (s, 3H; OC*H*$_3$), 4.69 (t, 1H, *J*= 6.3 Hz; N*H*), 5.46 (q, 1H, *J*= 6.5Hz; CH_2-C*H*=C), 6.05 (dt, 1H, *J*= 6.3, 3.1 Hz; C=C*H*-Ph), 6.82 (d, 2H, *J*= 8.9 Hz; Ar-*H*), 7.14 (d, 2H, *J*= 8.7 Hz; Ar-*H*), 7.25 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.71 (d, 2H, *J*= 8.3 Hz; Ts-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.4 (CH_3), 25.7 (CH_2), 28.7 (CH_2), 42.6 (CH_2), 55.3 (CH_3), 93.7 (CH), 94.7 (CH), 114.1 (CH), 126.8 (Cq), 127.0 (CH), 127.6 (CH), 129.6 (CH), 136.9 (Cq), 143.3 (Cq), 158.7 (Cq), 204.5 (Cq).
IR: 549 cm^{-1}, 662 cm^{-1}, 705 cm^{-1}, 813 cm^{-1}, 833 cm^{-1}, 878 cm^{-1}, 1030 cm^{-1}, 1092 cm^{-1}, 1155 cm^{-1}, 1243 cm^{-1}, 1302 cm^{-1}, 1322 cm^{-1}, 1440 cm^{-1}, 1509 cm^{-1}, 1605 cm^{-1}, 1679 cm^{-1}, 2934 cm^{-1}, 3276 cm^{-1}.
MS (ESI): Chemical formula $C_{20}H_{23}NO_3S$, **$[M+H]^+$** theoretical *m/z* 357.1399, found *m/z* 357.1395.

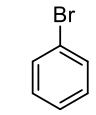
4.4 General procedure for the photocatalysed reaction of allenes 1a, 1b, 1c and 1d



A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under N_2, then 5 ml of dry DMF were transferred into the tube and degassed with N_2 for at least 10 minutes. Under a constant flow of N_2, $Pd(OAc)_2$ (2.24 mg, 0.01 mmol, 5 mol%) was added and the mixture was degassed for additional 5 minutes until the solution turned an intense yellow. Then PPh_3 (5.25 mg, 0.02 mmol, 10 mol%) was added and the solution was left under stirring until it turned cherry red (see Figure S3 left for optimal colour shade). When the colour change is not spontaneous, the reaction mixture can be gently warmed with the hands. The other reagents were added in the following order: the aromatic compound **2** (0.3 mmol, 1.5 Eq), K_2CO_3 (33 mg, 0.24 mmol, 1.2 Eq) and the allene **1** (0.2 mmol, 1 Eq). The Schlenk tube, saturated with N_2, was closed with a septum and stirred at 4 cm from a Kessil blue lamp (456 nm) at room temperature for 21 h for starting material **1a**-**b** or 48 h for internal allenes **1c**-**d**. Reaction work-up: the reaction mixture was diluted with 25 ml of Et_2O and the organic phase was washed with brine (5x10 ml) and dried over Na_2SO_4. After solvent removal, the crude mixture was purified by flash chromatography to afford product **3**, **5**-**7**.

Figure S3. Picture of the reaction set-up before and during illumination.

4.4.1 Summary of halides employed in the reaction scope



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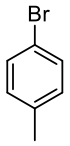

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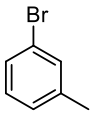

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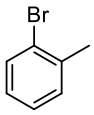

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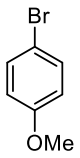

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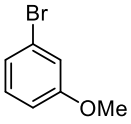

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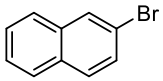

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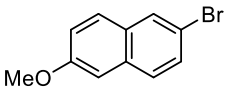

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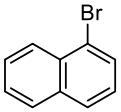

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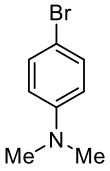

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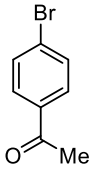

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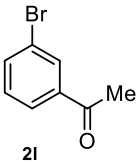

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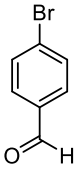

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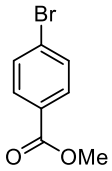

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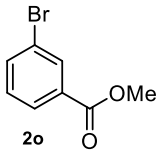

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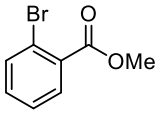

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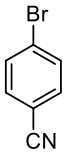

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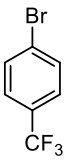
2r



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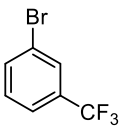

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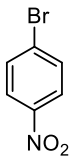
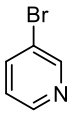
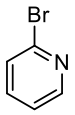


2u



2v



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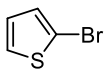
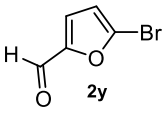
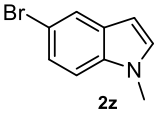


2x



2y



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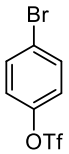

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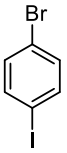
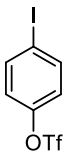
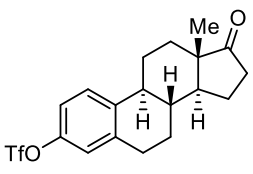


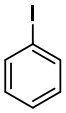
2ab



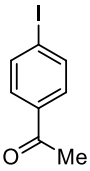
2ac



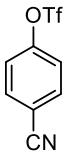
2ad



2a'

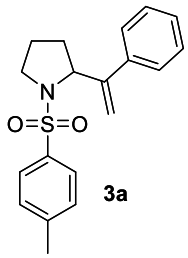


2k'



2q''

4.4.2 Characterization of vinyl pyrrolidine 3



3a

2-(1-Phenylvinyl)-1-tosylpyrrolidine 3a Following the described procedure, 47 mg (0.3 mmol) of bromobenzene **2a** (or 61 mg of iodobenzene **2a'**) and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 46 mg (21 mg from **2a'**) of 2-(1-phenylvinyl)-1-tosylpyrrolidine **3a** as a white solid (EP/AcOEt 7/1, yield 70% or 30% from **2a'**).

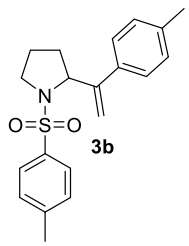
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.54-1.66 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.76-1.84 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.28 (td, 1H; *J*= 10.2, 6.4 Hz; N-C(H)*H*-CH_2), 3.54 (ddd, 1H; *J*= 10.2, 8.7, 2.5 Hz; N-C(H)*H*-CH_2), 4.75 (dd broad, 1H, *J*= 7.7, 3.2 Hz, N-C*H*-CH_2), 5.25 (s broad, 1H, C(H)*H*=C-CH), 5.39 (t narrow, 1H; *J*= 1.4 Hz; C(H)*H*=C-CH), 7.26-7.30 (m, 1H; Ar-*H*), 7.32-7.34 (m, 4H, Ar-*H*), 7.37-7.39 (m, 2H; Ar-*H*), 7.78 (d, 2H, *J*= 8.4 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 22.0 (CH_3), 23.9 (CH_2), 32.2 (CH_2), 49.4 (CH_2), 63.4 (CH), 114.3 (CH_2), 127.4 (CH), 128.0 (CH), 128.1 (CH), 128.8 (CH), 130.1 (CH), 135.6 (Cq), 140.3 (Cq), 143.8 (Cq), 149.3 (Cq).

IR: 541 cm^{-1}, 588 cm^{-1}, 656 cm^{-1}, 716 cm^{-1}, 790 cm^{-1}, 824 cm^{-1}, 857 cm^{-1}, 918 cm^{-1}, 1019 cm^{-1}, 1066 cm^{-1}, 1093 cm^{-1}, 1153 cm^{-1}, 1187 cm^{-1}, 1348 cm^{-1}, 1450 cm^{-1}, 1490 cm^{-1}, 1604 cm^{-1}, 2877 cm^{-1}, 2924 cm^{-1}, 2971 cm^{-1}

MS (ESI): Chemical formula $C_{19}H_{21}NO_2S$, **[M+H]$^+$** theoretical *m/z* 328.1366, found *m/z* 328.1365; **[M+Na]$^+$** theoretical *m/z* 350.1185, found *m/z* 350.1184.

Mp: 94.2-95.6°C



3b

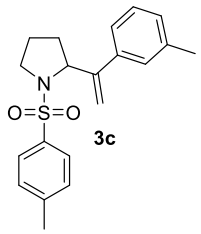
2-(1-(4-Tolyl)vinyl)-1-tosylpyrrolidine 3b Following the described procedure, 51 mg (0.3 mmol) of 4-bromotoluene **2b** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 30 mg of 2-(1-(4-tolyl)vinyl)-1-tosylpyrrolidine **3b** as a yellow/brown solid (EP/AcOEt 7/1, yield 44%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.55-1.65 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.76-1.84 (m, 1H; CH_2-C(H)*H*-CH_2), 2.35 (s, 3H; Ar-C*H*$_3$), 2.43 (s, 3H; Ar-C*H*$_3$), 3.28 (td, 1H; *J*= 9.2, 6.7 Hz; N-C(H)H-CH_2), 3.53 (ddd, 1H; *J*= 9.8, 7.3, 2.8 Hz; N-C(H)*H*-CH_2), 4.74 (dd broad, 1H; *J*= 7.7, 3.5 Hz; N-C*H*-CH_2), 5.32 (s, 1H; C(H)*H*=C-CH), 5.34 (t narrow, 1H; *J*= 1.3 Hz; C(H)*H*=C-CH), 7.14 (d, 2H; *J*= 8.3 Hz; Ar-*H*), 7.26 (d, 2H; *J*= 8.2 Hz; Ar-*H*), 7.32 (d, 2H; *J*= 7.9 Hz; Ar-*H*), 7.78 (d, 2H; *J*= 8.3 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.1 (CH_3), 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 48.9 (CH_2), 62.9 (CH), 113.1 (CH_2), 126.7 (CH), 127.5 (CH), 129.0 (CH), 129.6 (CH), 135.2 (Cq), 136.9 (Cq), 137.4 (Cq), 143.3 (Cq), 148.6 (Cq).

IR: 3025 cm^{-1}, 2930 cm^{-1}, 2856 cm^{-1}, 1586 cm^{-1}, 1448 cm^{-1}, 1332 cm^{-1}, 1152 cm^{-1}, 1089 cm^{-1}, 962 cm^{-1}, 909 cm^{-1}, 814 cm^{-1}, 739 cm^{-1}, 665 cm^{-1}, 538 cm^{-1}.

MS (ESI): Chemical formula $C_{20}H_{23}NO_2S$, **[M+H]$^+$** theoretical *m/z* 342.1522, found *m/z* 342.1525; **[M+Na]$^+$** theoretical *m/z* 364.1342, found *m/z* 364.1344. **Mp**: 91.2-92.3°C



3c

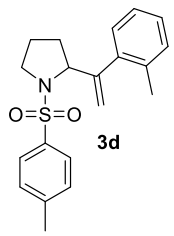
2-(1-(3-Tolyl)vinyl)-1-tosylpyrrolidine 3c Following the described procedure, 51 mg (0.3 mmol) of 3-bromotoluene **2c** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 23 mg of 2-(1-(3-tolyl)vinyl)-1-tosylpyrrolidine **3c** as a light yellow solid (EP/AcOEt 7/1, yield 33%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.56-1.66 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.76-1.85 (m, 1H; CH_2-C(H)*H*-CH_2), 2.36 (s, 3H; Ar-C*H*$_3$), 2.43 (s, 3H; Ar-C*H*$_3$), 3.28 (td broad, 1H, *J*= 9.1, 6.9 Hz; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 10.0, J_2= 7.3, 3.1 Hz; N-C(H)*H*-CH_2), 4.75 (d broad, 1H, *J*= 6.0 Hz; N-C*H*-CH_2), 5.31 (s broad, 1H; C(H)*H*=C-CH), 5.35 (t, 1H, *J*= 1.7 Hz; C(H)*H*=C-CH), 7.09 (d, 1H, *J*= 7.6 Hz), 7.13-7.17 (m, 2H; Ar-*H*), 7.21 (t, 1H, *J*= 7.6 Hz; Ar-*H*), 7.32 (d, 2H, *J*= 7.7 Hz; Ts-*H*), 7.78 (d, 2H, *J*= 8.0 Hz; Ts-*H*).

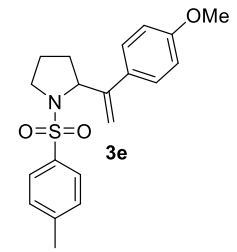
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 21.6 (CH_3), 23.6 (CH_2), 31.9 (CH_2), 48.9 (CH_2), 63.1 (CH), 113.7 (CH_2), 124.1 (CH), 127.6 (CH), 127.8 (CH), 128.3 (CH), 128.5 (CH), 129.7 (CH), 135.4 (Cq), 138.0 (Cq), 140.0 (Cq), 143.4 (Cq), 149.1 (Cq).

IR: 3041.1 cm^{-1}, 2981.9 cm^{-1}, 2951.9 cm^{-1}, 2919.0 cm^{-1}, 2874.3 cm^{-1}, 1597.2 cm^{-1}, 1492.0 cm^{-1}, 1447.4 cm^{-1}, 1332.2 cm^{-1}, 1293.7 cm^{-1}, 1186.3 cm^{-1}, 1157.0 cm^{-1}, 1118.2 cm^{-1}, 1089.6 cm^{-1}, 1070.5 cm^{-1}, 1006.8 cm^{-1}, 901.3 cm^{-1}, 852.3 cm^{-1}, 812.8 cm^{-1}, 793.9 cm^{-1}.

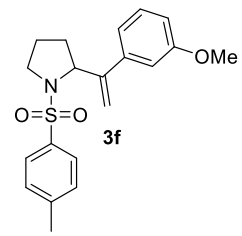
MS (ESI): Chemical formula $C_{20}H_{23}NO_2S$, **[M+H]$^+$** theoretical *m/z* 342.1522, found *m/z* 342.1526; **[M+Na]$^+$** theoretical *m/z* 364.1342, found *m/z* 364.1347. **Mp**: 73.8-75.3°C



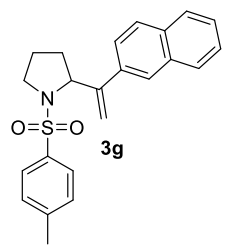
2-(1-(2-Tolyl)vinyl)-1-tosylpyrrolidine 3d Following the described procedure, 51 mg (0.3 mmol) of 2-bromotoluene **2d** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 12 mg of 2-(1-(2-tolyl)vinyl)-1-tosylpyrrolidine **3c** as a light yellow oil (EP/AcOEt 7/1, yield 18%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.31-1.37 (m, 2H; CH_2-C*H*$_2$-CH), 1.61-1.65 (m, 1H; CH_2-C(H)*H*-CH_2), 1.81-1.89 (m, 1H; CH_2-C(H)*H*-CH_2), 2.38 (s, 3H; Ar-C*H*$_3$), 2.42 (s, 3H; Ar-C*H*$_3$), 3.23 (dt broad, 1H, *J*= 9.7, 6.3 Hz; N-C(H)*H*-CH_2), 3.55 (ddd broad, 1H, *J*= 10.1, 8.7, 2.8 Hz; N-C(H)*H*-CH_2), 4.49 (bd, 1H; *J* = 8.3 Hz N-C*H*-CH_2), 5.07 (s broad, 1H; C(H)*H*=C-CH), 5.58 (t narrow, 1H, *J*= 1.6 Hz; C(H)*H*=C-CH), 7.09-7.21 (m, 4H; Ar-*H*), 7.31 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.76 (d, 2H, *J*= 8.3 Hz; Ts-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 19.8 (CH_3), 21.5 (CH_3), 23.4 (CH_2), 30.2 (CH_2), 48.9 (CH_2), 64.1 (CH), 115.4 (CH_2), 125.5 (CH), 127.3 (CH), 127.45 (CH), 129.32 (CH), 129.64 (CH), 130.2 (CH), 135.1 (Cq), 135.7 (Cq), 140.2 (Cq), 143.3 (Cq), 148.6 (Cq).
IR: 2943 cm^{-1}, 2879 cm^{-1}, 1345 cm^{-1}, 1154 cm^{-1}, 1101 cm^{-1}, 1017 cm^{-1}, 911 cm^{-1}, 827 cm^{-1}, 731 cm^{-1}, 667 cm^{-1}, 583 cm^{-1}, 540 cm^{-1}.
MS (ESI): Chemical formula $C_{20}H_{23}NO_2S$, **[M+H]$^+$** theoretical *m/z* 342.1522, found *m/z* 342.1523; **[M+Na]$^+$** theoretical *m/z* 364.1342, found *m/z* 364.1341.



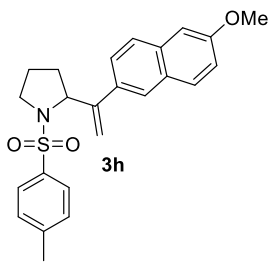
2-(1-(4-Methoxyphenyl)vinyl)-1-tosylpyrrolidine 3e Following the described procedure, 56 mg (0.3 mmol) of 4-bromoanisole **2e** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 14 mg of 2-(1-(4-methoxyphenyl)vinyl)-1-tosylpyrrolidine **3e** as a light yellow oil (EP/AcOEt 7/1, yield 20%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.58-1.64 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.75-1.84 (m, 1H; CH_2-C(H)*H*-CH_2), 2.44 (s, 3H; Ar-C*H*$_3$), 3.28 (td broad, 1H, *J*= 9.4, 6.7 Hz; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 10.3, 9.1, 3.2 Hz; N-C(H)*H*-CH_2), 3.81 (s, 3H; OC*H*$_3$), 4.71 (dbd, 1H; *J*= 8.3 Hz, N-C*H*-CH_2), 5.28 (s broad, 1H; C(H)*H*=C-CH), 5.30 (t narrow, 1H, *J*= 1.4 Hz; C(H)*H*=C-CH), 6.86 (d, 2H, *J*= 8.2 Hz; Ar-*H*), 7.30-7.33 (m, 4H; Ar-*H*), 7.77 (d, 2H, *J*= 8.2 Hz; Ar-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 48.9 (CH_2), 55.2 (OCH_3), 62.9 (CH), 112.5 (CH_2), 113.7 (CH), 127.5 (CH), 127.9 (CH), 129.6 (CH), 132.2 (Cq), 135.2 (Cq), 143.3 (Cq), 148.1 (Cq), 159.1 (Cq).
IR: 2969.8 cm^{-1}, 2925.5 cm^{-1}, 2871.6 cm^{-1}, 2836.7 cm^{-1}, 1605.9 cm^{-1}, 1510.2 cm^{-1}, 1455.5 cm^{-1}, 1336.6 cm^{-1}, 1302.1 cm^{-1}, 1243.9 cm^{-1}, 1182.7 cm^{-1}, 1155.3 cm^{-1}, 1092.1 cm^{-1}, 1029.9 cm^{-1}, 1005.8 cm^{-1}, 901.9 cm^{-1}, 833.3 cm^{-1}, 814.4 cm^{-1}.
MS (ESI): Chemical formula $C_{20}H_{23}NO_3S$, **[M+H]$^+$** theoretical *m/z* 358.1471, found *m/z* 358.1481; **[M+Na]$^+$** theoretical *m/z* 380.1296, found *m/z* 380.1306.



2-(1-(3-Methoxyphenyl)vinyl)-1-tosylpyrrolidine 3f Following the described procedure, 56 mg (0.3 mmol) of 3-bromoanisole **2f** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 25 mg of 2-(1-(3-methoxyphenyl)vinyl)-1-tosylpyrrolidine **3f** as a yellow oil (EP/AcOEt 7/1, yield 35%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.55-1.65 (m, 3H+H_2O; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.76-1.83 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.27 (td broad, 1H, *J*= 9.5, 6.4 Hz; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 9.6, 7.2, 2.7 Hz; N-C(H)*H*-CH_2), 3.82 (s, 3H; OC*H*$_3$), 4.72 (dd broad, 1H, *J*= 7.5, 3.2 Hz; N-C*H*-CH_2), 5.35 (s broad, 1H; C(H)*H*=C-CH), 5.39 (t narrow, 1H, *J*= 1.1 Hz; C(H)*H*=C-CH), 6.83 (ddd, 1H, *J*= 8.3, 2.6, 0.8 Hz; Ar-*H*), 6.90-6.91 (m, 1H; Ar-*H*), 6.95-6.96 (m, 1H; Ar-*H*), 7.23-7.24 (m, 1H; Ar-*H*), 7.32 (d, 2H, *J*= 8.5 Hz; Ts-*H*), 7.77 (d, 2H, *J*= 8.5 Hz; Ts-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 48.9 (CH_2), 55.2 (OCH_3), 62.9 (CH), 112.7 (CH), 113.0 (CH), 113.9 (CH_2), 119.4 (CH), 127.5 (CH), 129.3 (CH), 129.6 (CH), 135.1 (Cq), 141.3 (Cq), 143.3 (Cq), 148.7 (Cq), 159.5 (Cq).
IR: 2949.2 cm^{-1}, 2870.4 cm^{-1}, 2834.9 cm^{-1}, 1596.6 cm^{-1}, 1574.4 cm^{-1}, 1510.5 cm^{-1}, 1487.9 cm^{-1}, 1447.3 cm^{-1}, 1342.6 cm^{-1}, 1288.2 cm^{-1}, 1244.8 cm^{-1}, 1156.6 cm^{-1}, 1092.4 cm^{-1}, 1043.2 cm^{-1}, 1006.7 cm^{-1}, 907.5 cm^{-1}, 815.5 cm^{-1}.
MS (ESI): Chemical formula $C_{20}H_{23}NO_3S$, **[M+H]$^+$** theoretical *m/z* 358.1471, found *m/z* 358.1469; **[M+Na]$^+$** theoretical *m/z* 380.1296, found *m/z* 380.1291.



2-(1-(2-Naphtyl)vinyl)-1-tosylpyrrolidine 3g Following the described procedure, 62 mg (0.3 mmol) of 2-bromonaphthalene **2g** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 45 mg of 2-(1-(2-naphtylvinyl)-1-tosylpyrrolidine **3g** as a yellow solid (EP/AcOEt 7/1, yield 60%).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.60-1.70 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.79-1.89 (m, 1H; CH_2-C(H)*H*-CH_2), 2.44 (s, 3H; Ar-C*H*$_3$), 3.32 (td broad, 1H, *J*= 10.2, 6.4 Hz; N-C(H)*H*-CH_2), 3.57 (ddd broad, 1H, *J*= 10.5, 6.9, 2.8 Hz; N-C(H)*H*-CH_2), 4.90 (d broad, 1H, *J*= 6.9 Hz; N-C*H*-CH_2), 5.48 (s, 1H; C(H)*H*=C-CH), 5.49 (s, 1H; C(H)*H*=C-CH), 7.34 (d, 2H, *J*= 7.7 Hz; Ts-*H*), 7.48 (qd, 2H, *J*= 6.8, 1.9 Hz; Ar-*H*), 7.55 (dd, 1H, *J*= 8.6, 1.8 Hz; Ar-*H*), 7.82 (m, 6H; Ts-*H* + Ar-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.6 (CH_3), 23.6 (CH_2), 32.0 (CH_2), 49.0 (CH_2), 63.1 (CH), 114.5 (CH_2), 125.4 (CH), 125.6 (CH), 126.1 (CH), 126.4 (CH), 127.6 (CH), 128.0 (CH), 128.2 (CH), 129.8 (CH), 132.9 (Cq), 132.9 (Cq), 133.3 (Cq), 135.3 (Cq), 137.3 (Cq), 143.5 (Cq), 148.9 (Cq).
IR: 3061.8 cm^{-1}, 2979.3 cm^{-1}, 2952.2 cm^{-1}, 2916.4 cm^{-1}, 2864.1 cm^{-1}, 1625.7 cm^{-1}, 1595.7 cm^{-1}, 1490.9 cm^{-1}, 1443.8 cm^{-1}, 1338.6 cm^{-1}, 1299.7 cm^{-1}, 1185.5 cm^{-1}, 1155.9 cm^{-1}, 1116.8 cm^{-1}, 1087.9 cm^{-1}, 1061.6 cm^{-1}, 1003.8 cm^{-1}, 905.2 cm^{-1}, 884.9 cm^{-1}, 824.4 cm^{-1}, 750.5 cm^{-1}.
MS (ESI): Chemical formula $C_{23}H_{23}NO_2S$, **[M+H]$^+$** theoretical *m/z* 378.1528, found *m/z* 378.1529. **Mp**: 86.3-88.0°C



3h

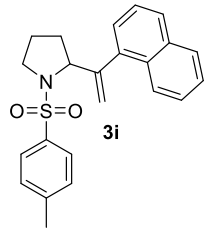
2-(1-(6-Methoxynapht-2-yl)vinyl)-1-tosylpyrrolidine 3h Following the described procedure, 71 mg (0.3 mmol) of 6-methoxy-2-bromonaphthalene **2h** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 36 mg of 2-(1-(6-methoxynapht-2-yl)vinyl)-1-tosylpyrrolidine **3h** as a yellow oil (EP/AcOEt 7/1, yield 44%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.60-1.72 (m, 3H+ H_2O; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.79-1.88 (m, 1H; CH_2-C(H)*H*-CH_2), 2.44 (s, 3H; Ar-C*H*$_3$), 3.32 (td broad, 1H, *J*= 9.6, 6.3 Hz; N-C(H)*H*-CH_2), 3.56 (ddd broad, 1H, *J*= 9.9, 7.3, 2.9 Hz; N-C(H)*H*-CH_2), 3.92 (s, 3H; -OC*H*$_3$), 4.89 (d broad, 1H, *J*= 7.7 Hz; N-C*H*-CH_2), 5.44 (s, 1H; C(H)*H*=C-CH), 5.45 (s, 1H; C(H)*H*=C-CH), 7.12-7.13 (m, 1H; Ar-*H*), 7.15 (dd, 1H, *J*= 8.8, 2.5 Hz; Ar-*H*), 7.33 (d, 2H, *J*= 7.9 Hz; Ts-*H*), 7.51 (dd, 1H, *J*= 8.4, 1.9 Hz; Ar-*H*), 7.69-7.73 (m, 3H; Ar-*H*), 7.81 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.9 (CH_2), 48.9 (CH_2), 55.3 (OCH_3), 62.9 (CH), 105.5 (CH), 113.6 (CH_2), 119.0 (CH), 125.2 (CH), 125.8 (CH), 126.8 (CH), 127.5 (CH), 128.6 (Cq), 129.55 (CH), 129.64 (CH), 133.9 (Cq), 134.9 (Cq), 135.2 (Cq), 143.3 (Cq), 148.7 (Cq), 157.8 (Cq).

IR: 2975.2 cm^{-1}, 2950.8 cm^{-1}, 2879.1 cm^{-1}, 1626.9 cm^{-1}, 1598.2 cm^{-1}, 1482.4 cm^{-1}, 1446.5 cm^{-1}, 1391.7 cm^{-1}, 1341.1 cm^{-1}, 1322.3 cm^{-1}, 1271.5 cm^{-1}, 1200.5 cm^{-1}, 1187.2 cm^{-1}, 1155.4 cm^{-1}, 1092.4 cm^{-1}, 1006.9 cm^{-1}, 909.2 cm^{-1}, 894.7 cm^{-1}, 813.4 cm^{-1}, 754.2 cm^{-1}.

MS (ESI): Chemical formula $C_{24}H_{25}NO_3S$, **[M+H]$^+$** theoretical *m/z* 408.1628, found *m/z* 408.1627; **[M+Na]$^+$** theoretical *m/z* 430.1447, found *m/z* 430.1448.



3i

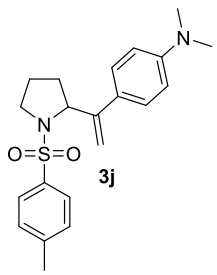
2-(1-(1-Naphtyl)vinyl)-1-tosylpyrrolidine 3i Following the described procedure, 62 mg (0.3 mmol) of 1-bromonaphthalene **2i** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 40 mg of 2-(1-(1-naphtylvinyl)-1-tosylpyrrolidine **3i** as an orange/yellow oil (EP/AcOEt 7/1, yield 53%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.25-1.33 (m, 1H; CH_2-C(H)*H*-CH), 1.57-1.67 (m, 2H+H_2O; CH_2-C(H)*H*-CH and CH_2-C(H)*H*-CH_2), 1.87-1.95 (m, 1H; CH_2-C(H)*H*-CH_2), 2.39 (s, 3H; Ar-C*H*$_3$), 3.23 (td, 1H, *J*= 9.9, 6.7 Hz; N-C(H)*H*-CH_2), 3.62 (ddd broad, 1H, *J*= 10.0, 7.2, 2.6 Hz; N-C(H)*H*-CH_2), 4.67 (d broad, 1H, *J*= 8.3 Hz; N-C*H*-CH_2), 5.30 (s broad, 1H; C(H)*H*=C-CH), 5.82 (t, 1H, *J*= 1.6 Hz; C(H)*H*=C-CH), 7.29 (d, 2H, *J*= 8.6 Hz; Ts-*H*), 7.32 (d, 1H, *J*= 7.3 Hz; Ar-*H*), 7.44 (dd, 1H, *J*= 8.3, 6.8 Hz; Ar-*H*), 7.50-7.53 (m, 1H¸ Ar-*H*), 7.56-7.60 (m, 1H; Ar-*H*), 7.77-7.82 (m, 3H; Ts-*H* and Ar-*H*), 7.87 (d, 1H, *J*= 8.3 Hz; Ar-*H*), 8.30 (d, 1H, *J*= 8.5 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.3 (CH_2), 30.7 (CH_2), 49.2 (CH_2), 64.4 (CH), 116.5 (CH_2), 125.2 (CH), 125.9 (CH), 126.29 (CH), 126.3 (CH), 127.5 (CH), 127.8 (CH), 128.2 (CH), 129.7 (CH), 131.7 (Cq), 133.6 (Cq), 134.8 (Cq), 138.6 (Cq), 143.3 (Cq), 148.2 (Cq).

IR: 3038.26 cm^{-1}, 2975.7 cm^{-1}, 2944.7 cm^{-1}, 2891.7 cm^{-1}, 2870.5 cm^{-1}, 1597.0 cm^{-1}, 1492.9 cm^{-1}, 1446.6 cm^{-1}, 1397.3 cm^{-1}, 1340.9 cm^{-1}, 1243.3 cm^{-1}, 1183.9 cm^{-1}, 1155.4 cm^{-1}, 1112.2 cm^{-1}, 1087.2 cm^{-1}, 1045.9 cm^{-1}, 992.7 cm^{-1}, 911.2 cm^{-1}, 815.7 cm^{-1}, 782.8 cm^{-1}, 754.9 cm^{-1}.

MS (ESI): Chemical formula $C_{23}H_{23}NO_2S$, **[M+H]$^+$** theoretical *m/z* 378.1528, found *m/z* 378.1530.



3j

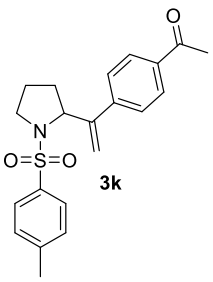
2-(1-(*N,N*-Dimethylaminophenyl)vinyl)-1-tosylpyrrolidine 3j Following the described procedure, 60 mg (0.3 mmol) of 4-bromo-*N,N*-dimethyaniline **2j** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 26 mg of 2-(1-(*N,N*-dimethylaminophenyl)vinyl)-1-tosylpyrrolidine **3j** as an amber oil (EP/AcOEt 7/1, yield 37%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.59-1.66 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.78-1.87 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 2.96 (s, 6H; N-(C*H*$_3$)$_2$), 3.27-3.32 (m, 1H; N-C(H)*H*-CH_2), 3.53 (m, 1H; N-C(H)*H*-CH_2), 4.75-4.77 (m, 1H; N-C*H*-CH_2), 5.21 (s, 1H; C(H)*H*=C-CH), 5.26 (s, 1H; C(H)*H*=C-CH), 6.68 (d broad, 2H, *J*= 8.3 Hz; Ar-*H*), 7.27 (d, 2H+$CDCl_3$, *J*= 8.7 Hz; Ts-*H*), 7.31 (d, 2H, *J*= 7.9 Hz; Ar-*H*), 7.77 (d, 2H, *J*= 8.2; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 32.0 (CH_2), 40.5 (CH_3), 48.9 (CH_2), 62.8 (CH), 110.7 (CH_2), 121.1 (CH), 127.4 (CH), 127.5 (CH), 129.6 (CH), 135.3 (Cq), 143.2 (Cq), 148.1 (Cq), 150.0 (Cq).

IR: 2873.7 cm^{-1}, 1607.8 cm^{-1}, 1520.5 cm^{-1}, 1479.8 cm^{-1}, 1444.9 cm^{-1}, 1342.5 cm^{-1}, 1303.1 cm^{-1}, 1190.0 cm^{-1}, 1156.1 cm^{-1}, 1092.5 cm^{-1}, 1060.8 cm^{-1}, 1006.8 cm^{-1}, 946.5 cm^{-1}, 895.2 cm^{-1}, 852.7 cm^{-1}, 816.2 cm^{-1}, 754.7 cm^{-1}, 709.7 cm^{-1}, 664.1 cm^{-1}, 589.6 cm^{-1}, 551.9 cm^{-1}.

MS (ESI): Chemical Formula: $C_{21}H_{26}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 393.1607, found *m/z* 393.1603.



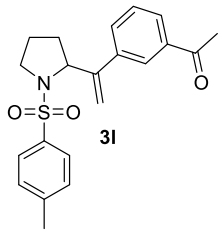
2-(1-(4-Acetylphenyl)vinyl)-1-tosylpyrrolidine 3k Following the described procedure, 60 mg (0.3 mmol) of 4-bromoacetophenone **2k** (or 74 mg of 4-iodoacetophenone **4k'**) and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 73 mg (38 mg from **4k'**) of 2-(1-(4-acetylphenyl)vinyl)-1-tosylpyrrolidine **3k** as a light yellow solid (gradient: EP/AcOEt 7/1 to 7/3, yield 85%, 52% from **4k'**).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.49-1.57 (m, 1H; CH_2-C(H)*H*-CH_2), 1.57-1.58 (m, 2H; CH_2-CH_2-CH), 1.74-1.83 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-CH_3), 2.60 (s, 3H;CO-CH_3), 3.27 (td broad, 1H, *J*= 9.4, 6.8 Hz; N-C(H)*H*-CH_2), 3.52 (ddd, 1H, *J*= 9.8, 8.5, 3.4 Hz; N-C(H)*H*-CH_2), 4.73 (dd broad, 1H, *J*= 8.5, 3.2 Hz; N-C*H*-CH_2), 5.44 (s, 1H; C(H)*H*=C-CH), 5.50 (s broad, 1H; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.47 (d, 2H, *J*= 8.5 Hz; Ar-*H*), 7.77 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.92 (d, 2H, *J*= 8.5 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 26.6 (CH_3), 31.9 (CH_2), 48.9 (CH_2), 62.7 (CH), 115.6 (CH_2), 127.1 (CH), 127.5 (CH), 128.4 (CH), 129.7 (CH), 134.9 (Cq), 136.2 (Cq), 143.5 (Cq), 144.5 (Cq), 148.1 (Cq), 197.6 (Cq).

IR: 3051.7 cm^{-1}, 3029.6 cm^{-1}, 2977.4 cm^{-1}, 2956.7 cm^{-1}, 2876.3 cm^{-1}, 1676.3 cm^{-1}, 1598.9 cm^{-1}, 1556.7 cm^{-1}, 1447.7 cm^{-1}, 1405.7 cm^{-1}, 1344.5 cm^{-1}, 1266.8 cm^{-1}, 1189.1 cm^{-1}, 1157.8 cm^{-1}, 1087.0 cm^{-1}, 1059.5 cm^{-1}, 998.6 cm^{-1}, 958.5 cm^{-1}, 905.1 cm^{-1}, 854.3 cm^{-1}, 824.9 cm^{-1}, 811.9 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{23}NO_3S$, **[M+H]$^+$** theoretical *m/z* 370.1471, found *m/z* 370.1477. **Mp**: 85.5-86.1°C



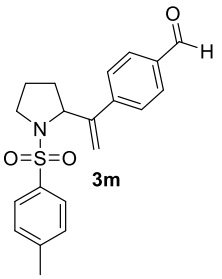
2-(1-(3-Acetylphenyl)vinyl)-1-tosylpyrrolidine 3l Following the described procedure, 60 mg (0.3 mmol) of 3-bromoacetophenone **2l** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 33 mg of 2-(1-(3-acetylphenyl)vinyl)-1-tosylpyrrolidine **3l** as a yellow oil (gradient: EP/AcOEt 7/1 to 7/3, yield 44%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.54-1.70 (m, 3H+H_2O; CH_2-CH_2-CH and CH_2-C(H)*H*-CH_2), 1.75-1.82 (m, 1H; CH_2-C(H)*H*-CH_2), 2.44 (s, 3H; Ar-CH_3), 2.62 (s, 3H; CO-CH_3), 3.28 (td, 1H, *J*= 9.5, 6.6 Hz; N-C(H)*H*-CH_2), 3.52 (ddd, 1H, *J*= 10.2, 8.1, 3.9 Hz; N-C(H)*H*-CH_2), 4.72 (m broad, 1H; N-C*H*-CH_2), 5.40 (s, 1H; C(H)*H*=C-CH), 5.47 (s broad, 1H; C(H)*H*=C-CH), 7.34 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.44 (t, 1H, *J*= 7.9 Hz; Ar-*H*), 7.60 (d, 1H, *J*= 7.6 Hz; Ar-*H*), 7.78 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.87 (d, 1H, *J*= 7.6 Hz; Ar-*H*), 7.95(s, 1H; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.6 (CH_2), 26.7 (CH_3), 31.9 (CH_2), 48.9 (CH_2), 62.9 (CH), 115.1 (CH_2), 126.7 (CH), 127.5 (CH), 127.6 (CH), 128.6 (CH), 131.6 (CH), 135.0 (Cq), 137.2 (Cq), 140.3 (Cq), 143.5 (Cq), 148.2 (Cq), 198.1 (Cq).

IR: 2973.2 cm^{-1}, 2949.6 cm^{-1}, 2872.9 cm^{-1}, 1682.4 cm^{-1}, 1596.2 cm^{-1}, 1492.9 cm^{-1}, 1446.2 cm^{-1}, 1423.5 cm^{-1}, 1343.0 cm^{-1}, 1233.7 cm^{-1}, 1190.0 cm^{-1}, 1156.4 cm^{-1}, 1092.1 cm^{-1}, 1006.8 cm^{-1}, 910.6 cm^{-1}, 813.9 cm^{-1}, 755.2 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{23}NO_3S$, **[M+H]$^+$** theoretical *m/z* 370.1471, found *m/z* 370.1475.



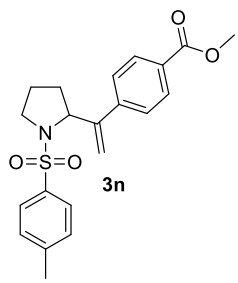
2-(1-(4-Formylphenyl)vinyl)-1-tosylpyrrolidine 3m Following the described procedure, 56 mg (0.3 mmol) of 4-bromobenzaldehyde **2m** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 48 mg of 2-(1-(4-formylphenyl)vinyl)-1-tosylpyrrolidine **3m** as a yellow solid (EP/AcOEt 6/4, yield 67%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.51-1.56 (m, 1H; CH_2-C(*H*)H-CH), 1.60-1.70 (m, 2H; CH_2-C(*H*)H-CH and CH_2-C(H)*H*-CH_2), 1.75-1.83 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-CH_3), 3.24-3.30 (m, 1H; N-C(H)*H*-CH_2), 3.49-3.55 (m, 1H; N-C(H)*H*-CH_2), 4.72 (d, 1H, *J*= 6.6 Hz; N-C*H*-CH_2), 5.47 (s, 1H; C(H)*H*=C-CH), 5.53 (s, 1H; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 8.2 Hz; Ts-*H*), 7.54 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 7.76 (d, 2H, *J*= 8.2 Hz; Ts-*H*), 7.84 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 9.99 (s, 1H; C*H*O).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.9 (CH_2), 48.9 (CH_2), 62.6 (CH), 116.1 (CH_2), 127.4 (CH), 127.5 (CH), 129.7 (CH), 129.8 (CH), 134.8 (Cq), 135.5 (Cq), 143.5 (Cq), 145.9 (Cq), 148.1 (Cq), 191.7 (CHO).

IR: 2959.5 cm^{-1}, 2877.6 cm^{-1}, 2818.7 cm^{-1}, 2734.6 cm^{-1}, 1687.9 cm^{-1}, 1602.2 cm^{-1}, 1563.6 cm^{-1}, 1447.4 cm^{-1}, 1331.3 cm^{-1}, 1259.9 cm^{-1}, 1221.1 cm^{-1}, 1088.3 cm^{-1}, 1039.2 cm^{-1}, 1003.3 cm^{-1}, 905.6 cm^{-1}, 812.3 cm^{-1}.

MS (ESI): Chemical formula $C_{20}H_{21}NO_3S$, **[M+H]$^+$** theoretical *m/z* 356.1315, found *m/z* 356.1325. **Mp**: 81.3-84.0°C



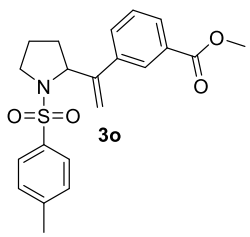
Methyl 4-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate 3n Following the described procedure, 65 mg (0.3 mmol) of methyl 4-bromobenzoate **2n** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 36 mg of methyl 4-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate **3n** as a yellow oil (EP/AcOEt 7/1, yield 47%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.51-1.55 (m, 1H; CH_2-C(*H*)-CH), 1.59-1.67 (m, 2H+H_2O; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2), 1.73-1.84 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-CH_3), 3.27 (td broad, 1H, *J*= 10.9, 7.4 Hz; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 9.1, 8.6, 3.6 Hz; N-C(H)*H*-CH_2), 3.91 (s, 3H; -OCH_3), 4.71-4.74 (dd, 1H, *J*= 8.3, 3.6 Hz; N-C*H*-CH_2), 5.43 (s, 1H; C(H)*H*=C-CH), 5.49 (t narrow, 1H, *J*= 1.4 Hz; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.44 (d, 2H, *J*= 8.6 Hz; Ar-*H*), 7.77 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.99 (d, 2H, *J*= 8.6 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.9 (CH_2), 48.9 (CH_2), 52.1 (OCH_3), 62.7 (CH), 115.5 (CH_2), 126.9 (CH), 127.5 (CH), 129.3 (Cq), 129.66 (CH), 129.71 (CH), 135.0 (Cq), 143.5 (Cq), 144.3 (Cq), 148.2 (Cq), 166.8 (Cq).

IR: 2951.9 cm^{-1}, 2874.6 cm^{-1}, 2253.3 cm^{-1}, 1716.4 cm^{-1}, 1606.8 cm^{-1}, 1434.9 cm^{-1}, 1403.5 cm^{-1}, 1344.7 cm^{-1}, 1276.2 cm^{-1}, 1188.8 cm^{-1}, 1155.8 cm^{-1}, 1092.7 cm^{-1}, 1007.2 cm^{-1}, 911.3 cm^{-1}, 863.9 cm^{-1}, 814.5 cm^{-1}, 781.8 cm^{-1}, 723.5 cm^{-1}, 665.1 cm^{-1}, 586.6 cm^{-1}.

MS (ESI): Chemical Formula: $C_{21}H_{23}NO_4S$, **[M+Na]$^+$** theoretical *m/z* 408.1240, found *m/z* 408.1236.



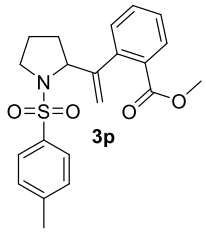
Methyl 3-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate 3o Following the described procedure, 65 mg (0.3 mmol) of methyl 3-bromobenzoate **2n** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 33 mg of methyl 3-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate **3o** as a light yellow oil (EP/AcOEt 7/1, yield 43%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.52-1.58 (m, 1H; CH_2-C(*H*)-CH), 1.59-1.68 (m, 2H; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2), 1.74-1.84 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-CH_3), 3.27 (td broad, 1H, *J*= 9.8, 7.1 Hz; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 10.0, 8.9, 3.2 Hz; N-C(H)*H*-CH_2), 3.93 (s, 3H; OCH_3), 4.74 (dd, 1H, *J*= 8.7, 3.0 Hz; N-C*H*-CH_2), 5.40 (s broad, 1H; C(H)*H*=C-CH), 5.46 (t broad, 1H, *J*= 1.3 Hz; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 7.9 Hz; Ts-*H*), 7.41 (t, 1H, *J*= 8.1; Ar-*H*), 7.59 (ddd, 1H, *J*= 7.6, 1.3, 0.8 Hz; Ts-*H*), 7.78 (d, 2H, *J*= 8.3; Ar-*H*), 7.95 (dt, 1H, *J*= 7.7, 1.2 Hz; Ar-*H*), 8.0 (t, 1H, J= 1.8 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 48.9 (CH_2), 52.2 (OCH_3), 62.8 (CH), 114.9 (CH_2), 127.5 (CH), 128.0 (CH), 128.5 (CH), 128.7 (CH), 129.7 (CH), 130.3 (Cq), 131.4 (CH), 135.0 (Cq), 140.1 (Cq), 143.4 (Cq), 148.0 (Cq), 166.9 (Cq).

IR: 2982.5 cm^{-1}, 2956.4 cm^{-1}, 2878.5 cm^{-1}, 2867.3 cm^{-1}, 1720.6 cm^{-1}, 1596.8 cm^{-1}, 1580.1 cm^{-1}, 1449.2 cm^{-1}, 1439.9 cm^{-1},1383.2 cm^{-1}, 1323.4 cm^{-1}, 1303.5 cm^{-1}, 1270.8 cm^{-1}, 1244.9 cm^{-1}, 1191.9 cm^{-1}, 1150.4 cm^{-1}, 1091.6 cm^{-1}, 1011.6 cm^{-1}, 965.3 cm^{-1}, 907.3 cm^{-1}, 850.1 cm^{-1}, 814.7 cm^{-1}, 762.6 cm^{-1}.

MS (ESI): Chemical Formula: $C_{21}H_{23}NO_4S$, **[M+Na]$^+$** theoretical *m/z* 408.1240, found *m/z* 408.1238.



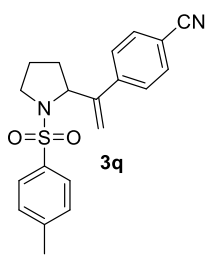
Methyl 2-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate 3p Following the described procedure, 65 mg (0.3 mmol) of methyl 2-bromobenzoate **2n** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 31 mg of methyl 2-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate **3p** as a yellow oil (EP/AcOEt 7/1, yield 40%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.31-1.38 (m, 1H; CH_2-C(*H*)-CH), 1.58-1.66 (m, 1H+H2O; CH_2-C(H)*H*-CH_2), 1.70-1.78 (m, 1H; CH_2-C(*H*)-CH), 1.80-1.88 (m, 1H; CH_2-C(H)*H*-CH_2), 2.42 (s, 3H; Ar-CH_3), 3.23 (td broad, 1H, *J*= 9.6, 7.0 Hz; N-C(H)*H*-CH_2), 3.51 (ddd broad, 1H, *J*= 10.2, 9.2, 2.8 Hz; N-C(H)*H*-CH_2), 3.87 (s, 3H; OCH_3), 4.69 (d broad, 1H, *J*= 7.4 Hz; N-C*H*-CH_2), 5.05 (s broad, 1H; C(H)*H*=C-CH), 5.47 (t narrow, 1H, *J*= 1.4 Hz; C(H)*H*=C-CH), 7.31 (d, 2H, J= 7.9 Hz; Ts-*H*), 7.32-7.37 (m, 2H; Ar-*H*), 7.46 (td, 1H, J_1= 7.5 Hz, J_2= 1.4 Hz; Ar-*H*), 7.74 (dd, 1H, *J*= 7.8, 1.4 Hz; Ar-*H*), 7.77 (d, 2H, *J*= 7.9; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.4 (CH_2), 30.3 (CH_2), 48.8 (CH_2), 52.2 (OCH_3), 64.3 (CH), 115.6 (CH_2), 127.3 (CH), 127.4 (CH), 129.62 (CH), 129.65 (CH),130.0 (CH), 131.0 (Cq), 131.1 (Cq), 135.1 (Cq), 140.8 (Cq), 143.3 (Cq), 148.1 (Cq), 168.7 (Cq).

IR: 3051.6 cm^{-1}, 3029.5 cm^{-1}, 2977.7 cm^{-1}, 2955.7 cm^{-1}, 2876.1 cm^{-1}, 1724.3 cm^{-1}, 1676.1 cm^{-1}, 1597.6 cm^{-1}, 1556.8 cm^{-1}, 1446.9 cm^{-1}, 1343.3 cm^{-1}, 1300.2 cm^{-1}, 1266.1 cm^{-1}, 1189.9 cm^{-1}, 1157.2 cm^{-1}, 1087.4 cm^{-1}, 1060.1 cm^{-1}, 998.6 cm^{-1}, 958.5 cm^{-1}, 905.1 cm^{-1}, 853.9 cm^{-1}, 811.9 cm^{-1}, 751.3 cm^{-1}.

MS (ESI): Chemical Formula: $C_{21}H_{23}NO_4S$, **[M+Na]$^+$** theoretical *m/z* 408.1240, found *m/z* 408.1241.



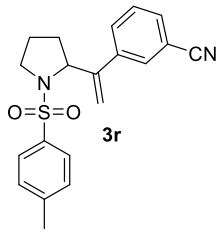
4-(1-(1-Tosylpyrrolidin-2-yl)vinyl)benzonitrile 3q Following the described procedure, 54 mg (0.3 mmol) of 4-bromobenzonitrile **2q** (or 75 mg of 4-cyanophenyl trifluoromethanesulfonate **2q''**) and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 49 mg (36 mg from **2q''**) of 4-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzonitrile **3q** as a yellow oil (gradient EP/AcOEt 7/1 to 7/3, yield 70%, 51% from **2q''**).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.50-1.54 (m, 1H; CH_2-C(*H*)H-CH), 1.58-1.71 (m, 2H+H_2O; CH_2-C(*H*)H-CH and CH_2-C(H)*H*-CH_2), 1.73-1.82 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-CH_3), 3.27 (td broad, 1H, *J*= 9.5, 7.1 Hz; N-C(H)*H*-CH_2), 3.51 (ddd, 1H, *J*= 10.0, 6.9 Hz, J_3= 3.2 Hz; N-C(H)*H*-CH_2), 4.65 (dd broad, 1H, *J*= 8.9, 3.5 Hz; N-C*H*-CH_2), 5.43 (s, 1H; C(H)*H*=C-CH), 5.54 (s, 1H; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 8.0 Hz; Ts-*H*), 7.48 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 7.62 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 7.75 (d, 2H, *J*= 8.2 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.9 (CH_2), 48.9 (CH_2), 62.9 (CH), 111.3 (Cq), 116.5 (CH_2), 118.7 (Cq), 127.4 (CH), 127.6 (CH), 129.7 (CH), 132.2 (CH), 134.7 (Cq), 143.6 (Cq), 144.4 (Cq), 147.7 (Cq).

IR: 2972.9 cm^{-1}, 2884.1 cm^{-1}, 2224.2 cm^{-1}, 1605.7 cm^{-1}, 1509.5 cm^{-1}, 1450.3 cm^{-1}, 1327.7 cm^{-1}, 1305.4 cm^{-1}, 1154.0 cm^{-1}, 1090.4 cm^{-1}, 1073.7 cm^{-1}, 1010.7 cm^{-1}, 989.5 cm^{-1}, 929.0 cm^{-1}, 847.9 cm^{-1}, 812.3 cm^{-1}, 766.3 cm^{-1}.

MS (ESI): Chemical Formula: $C_{20}H_{20}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 375.1138, found *m/z* 375.1135.



3r

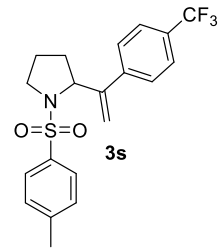
3-(1-(1-Tosylpyrrolidin-2-yl)vinyl)benzonitrile 3r Following the described procedure, 54 mg (0.3 mmol) of 3-bromobenzonitrile **2q** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 52 mg of 3-(1-(1-tosylpyrrolidin-2-yl)vinyl)benzonitrile **3r** as a white solid (gradient EP/AcOEt 7/1 to 7/3, yield 74%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ=1.49-1.54 (m, 1H; CH_2-C(*H*)-CH), 1.59-1.70 (m, 2H; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2), 1.71-1.80 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.27 (m, 1H, N-C(H)*H*-CH_2), 3.51 (ddd broad, 1H, *J*= 10.1, 6.8, 3.3 Hz; N-C(H)*H*-CH_2), 4.62 (dd broad, 1H, *J*= 7.7, 2.6 Hz; N-C*H*-CH_2), 5.39 (s, 1H; C(H)*H*=C-CH), 5.51 (s, 1H; C(H)*H*=C-CH), 7.34 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.45 (t, 1H, *J*= 8.6 Hz; Ar-*H*), 7.57 (dt, 1H, *J*= 7.8, 1.4 Hz; Ar-*H*), 7.61 (t, 1H, *J*= 1.6 Hz; Ar-*H*), 7.64 (dt, 1H, *J*= 7.8, 1.5 Hz; Ar-*H*), 7.76 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.6 (CH_2), 23.5 (CH_3), 31.8 (CH), 48.9 (CH), 62.7 (CH_2), 112.5 (Cq), 116.1 (CH_2), 118.7 (Cq), 127.4 (CH), 129.2 (CH), 129.8 (CH), 130.5 (CH), 131.1 (CH), 131.4 (CH), 134.7 (Cq), 141.0 (Cq), 143.6 (Cq), 147.2 (Cq).

IR: 2977.1 cm^{-1}, 2954.2 cm^{-1}, 2893.1 cm^{-1}, 2231.3 cm^{-1}, 1596.4 cm^{-1}, 1485.3 cm^{-1}, 1443.8 cm^{-1}, 1333.2 cm^{-1}, 1298.8 cm^{-1}, 1289.7 cm^{-1}, 1198.6 cm^{-1}, 1179.5 cm^{-1}, 1155.5 cm^{-1}, 1116.6 cm^{-1}, 1087.6 cm^{-1}, 1060.4 cm^{-1}, 1003.8 cm^{-1}, 909.6 cm^{-1}, 885.8 cm^{-1}, 850.4 cm^{-1}, 808.8 cm^{-1}.

MS (ESI): Chemical Formula: $C_{20}H_{20}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 375.1138, found *m/z* 375.1133. **Mp**: 99.0-100.8°C



3s

1-Tosyl-2-(1-(4-trifluoromethylphenyl)vinyl)pyrrolidine 3s Following the described procedure, 68 mg (0.3 mmol) of 4-bromobenzotrifluoride **2s** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 62 mg of 1-tosyl-2-(1-(4-(trifluoromethyl)phenyl)vinyl)pyrrolidine **3s** as a yellow solid (EP/AcOEt 7/1, yield 78%).

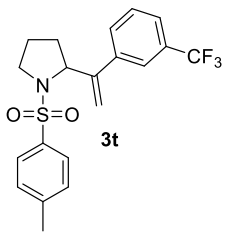
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.49-1.56 (m, 1H; CH_2-C(*H*)-CH), 1.58-1.69 (m, 2H; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2), 1.73-1.82 (m, 1H; CH_2-C(H)*H*-CH_2), 2.38-2.46 (s, 3H; At-C*H*$_3$), 3.28 (td broad, 1H, *J*= 9.7, 6.6 Hz; N-C(H)*H*-CH_2), 3.52 (ddd broad, 1H, *J*= 10.2, 7.0, 3.1 Hz; N-C(H)*H*-CH_2), 4.69 (d broad, 1H, *J*= 7.5 Hz; N-C*H*-CH_2), 5.40 (s, 1H; C(H)*H*=C-CH), 5.49 (s, 1H; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.48 (d, 2H, *J*= 8.6 Hz; Ar-*H*), 7.58 (d, 2H, *J*= 8.6 Hz; Ar-*H*), 7.77 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.8 (CH_2), 31.6 (CH_2), 48.9 (CH_2), 62.7 (CH), 115.6 (CH_2), 124.2 (Cq, $J_{C\text{-}F}$ = 271 Hz), 125.2 (CH, $J_{C\text{-}F}$ = 3.7 Hz), 127.3 (CH), 129.7 (CH), 129.6 (Cq, $J_{C\text{-}F}$ = 32.3 Hz), 134.9 (Cq), 143.5 (Cq), 143.7 (Cq), 148.1 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF): δ -62.43 (3F, s).

IR: 2976.1 cm^{-1}, 2948.7 cm^{-1}, 2871.2 cm^{-1}, 1614.9 cm^{-1}, 1597.6 cm^{-1}, 1404.9 cm^{-1}, 1374.3 cm^{-1}, 1322.5 cm^{-1}, 1244.1 cm^{-1}, 1188.4 cm^{-1}, 1092.6 cm^{-1}, 1082.3 cm^{-1}, 1062.3 cm^{-1}, 1004.5 cm^{-1}, 908.5 cm^{-1}, 851.7 cm^{-1}, 814.5 cm^{-1}.

MS (ESI): Chemical formula $C_{20}H_{20}F_3NO_2S$, **[M+H]$^+$** theoretical *m/z* 396.1240, found *m/z* 396.1245. **Mp**: 93.6-94.5°C



3t

1-Tosyl-2-(1-(3-trifluoromethylphenyl)vinyl)pyrrolidine 3t Following the described procedure, 68 mg (0.3 mmol) of 3-bromobenzotrifluoride **2t** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 56 mg of 1-tosyl-2-(1-(3-(trifluoromethyl)phenyl)vinyl)pyrrolidine **3t** as a yellow oil (EP/AcOEt 7/1, yield 71%).

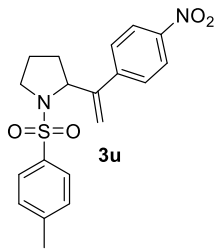
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.54-1.57 (m, 1H; CH_2-C(*H*)-CH), 1.61-1.71 (m, 2H; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2), 1.75-1.83 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.30 (m, 1H; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 9.9, 8.1, 3.5 Hz; N-C(H)*H*-CH_2), 4.70 (dd broad, 1H, *J*= 8.5, 3.8 Hz; N-C*H*-CH_2), 5.39 (s, 1H; C(H)*H*=C-CH), 5.48 (t narrow, 1H, *J*= 1.0 Hz; C(H)*H*=C-CH), 7.33 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.44-7.47 (m, 1H; Ar-*H*), 7.54-7.58 (m, 3H; Ar-*H*), 7.77 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 48.9 (CH_2), 62.8 (CH), 115.5 (CH_2), 123.7 (CH, $J_{C\text{-}F}$ = 4.1 Hz), 124.3 (CH, $J_{C\text{-}F}$ = 3.8 Hz), 124.0 (Cq, $J_{C\text{-}F}$ = 270 Hz), 127.5 (CH), 128.8 (CH), 129.7 (CH), 130.3 (CH), 130.7 (CH, $J_{C\text{-}F}$ = 32.3 Hz), 135.0 (Cq), 140.6 (Cq), 143.5 (Cq), 147.9 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF): δ -62.47 (3F, s).

IR: 2872.6 cm^{-1}, 2195.5 cm^{-1}, 2041.4 cm^{-1}, 1596.9 cm^{-1}, 1489.0 cm^{-1}, 1434.8 cm^{-1}, 1328.8 cm^{-1}, 1248.0 cm^{-1}, 1156.9 cm^{-1}, 1121.1 cm^{-1}, 1092.9 cm^{-1}, 1071.5 cm^{-1}, 1006.8 cm^{-1}, 906.6 cm^{-1},846.1 cm^{-1}, 812.5 cm^{-1}, 757.4 cm^{-1}, 738.2 cm^{-1}, 707.0 cm^{-1}, 664.6 cm^{-1}, 587.1 cm^{-1}, 548.4 cm^{-1}.

MS (ESI): Chemical formula $C_{20}H_{20}F_3NO_2S$, **[M+H]$^+$** theoretical *m/z* 396.1240, found *m/z* 396.1246.



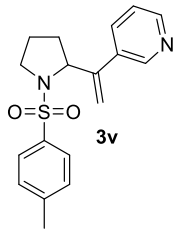
1-Tosyl-2-(1-(4-nitrophenyl)vinyl)pyrrolidine 3u Following the described procedure, 61 mg (0.3 mmol) of 1-bromo-4-nitrobenzene **2u** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 42 mg of 1-tosyl-2-(1-(4-(nitrophenylvinyl)pyrrolidine **3u** as a yellow solid (gradient EP/AcOEt 7/1 to 6/4, yield 56%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.51-1.56 (m, 1H; CH_2-C(H)*H*-CH_2), 1.62-1.83 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 2.24 (s, 3H; Ar-C*H*$_3$), 3.28 (dbd broad, 1H, *J*= 9.8, 6.7 Hz; N-C(H)*H*-CH_2), 3.53 (ddd broad, 1H, *J*= 10.3, 7.3, 3.5 Hz; N-C(H)*H*-CH_2), 4.68 (dd broad, 1H, *J*= 8.3, 3.8 Hz; N-C*H*-CH_2), 5.48 (s broad, 1H; C(H)*H*=C-CH), 5.58 (s broad, 1H; C(H)*H*=C-CH), 7.34 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.55 (d, 2H, *J*= 8.9 Hz; Ar-*H*), 7.76 (d, 2H, *J*=8.3 Hz; Ts-*H*), 8.19 (d, 2H, *J*=8.9 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.6 (CH_2), 32.0 (CH_2), 49.0 (CH_2), 62.7 (CH), 117.1 (CH_2), 123.7 (CH), 127.6 (CH), 127.8 (CH), 129.8 (CH), 134.7 (Cq), 143.7 (Cq), 146.4 (Cq), 147.2 (Cq), 147.5 (Cq).

IR: 2987.0 cm^{-1}, 2952.5 cm^{-1}, 2928.8 cm^{-1}, 2859.2 cm^{-1}, 1593.7 cm^{-1}, 1506.5 cm^{-1}, 1455.1 cm^{-1}, 1260.4 cm^{-1}, 1216.3 cm^{-1}, 1155.9 cm^{-1}, 1089.5 cm^{-1}, 1061.9 cm^{-1}, 1005.2 cm^{-1}, 931.9 cm^{-1}, 846.5 cm^{-1}, 836.1 cm^{-1}, 812.1 cm^{-1}, 768.7 cm^{-1}.

MS (ESI): Chemical formula $C_{19}H_{20}N_2O_4S$, **[M+H]$^+$** theoretical *m/z* 373.1217, found *m/z* 373.1217. **Mp**: 140.8-141.6°C



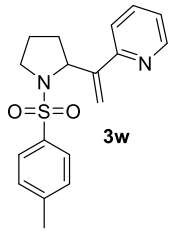
1-Tosyl-2-(1-(3-pyridyl)vinyl)pyrrolidine 3v Following the described procedure, 48 mg (0.3 mmol) of 3-bromopyridine **2v** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 31 mg of 1-tosyl-2-(1-(3-pyridyl)vinyl)pyrrolidine **3v** as a yellow oil (gradient EP/AcOEt 7/1 to 6/4, yield 46%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.50-1.58 (m, 1H; CH_2-C(H)*H*-CH_2), 1.58-1.73 (m, 2H; CH_2-C*H*$_2$-CH), 1.75-1.80 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.28 (td broad, 1H, *J*= 10.2, 6.7 Hz; N-C(H)*H*-CH_2), 3.52 (ddd broad, 1H, *J*= 10.2, 8.4, 3.7 Hz; N-C(H)*H*-CH_2), 4.64 (dd, 1H, *J*= 8.3, 3.4 Hz; N-C*H*-CH_2), 5.39 (s, 1H; C(H)*H*=C-CH), 5.50 (s, 1H; C(H)*H*=C-CH), 7.26-7.28 (m, 1H; Pyr-*H*), 7.33 (d, 2H, *J*= 8.0 Hz; Ts-*H*), 7.72-7.74 (dt, 1H, *J*= 8.6, 1.6 Hz; Pyr-*H*), 7.76 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 8.52-8.53 (dd, 1H, *J*= 4.9, 1.6 Hz; Pyr-*H*), 8.59 (d, 1H, *J*= 2.9 Hz; Pyr-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 49.0 (CH_2), 62.8 (CH), 115.8 (CH_2), 123.2 (CH), 127.5 (CH), 129.7 (CH), 134.4 (CH), 134.7 (Cq), 135.3 (Cq), 143.6 (Cq), 146.0 (Cq), 148.1 (Cq), 148.9 (Cq).

IR: 2979.6 cm^{-1}, 2953.6 cm^{-1}, 2877.2 cm^{-1}, 1710.7 cm^{-1}, 1630.9 cm^{-1}, 1596.3 cm^{-1}, 1456.8 cm^{-1}, 1335.2 cm^{-1}, 1189.8 cm^{-1}, 1155.4 cm^{-1}, 1093.0 cm^{-1}, 1063.4 cm^{-1}, 1007.6 cm^{-1}, 910.6 cm^{-1}, 848.7 cm^{-1}, 814.5 cm^{-1}, 755.9 cm^{-1}.

MS (ESI): Chemical Formula: $C_{18}H_{20}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 351.1138, found *m/z* 351.1136.



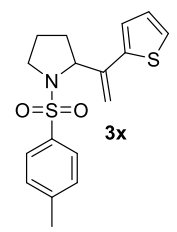
1-Tosyl-2-(1-(2-pyridyl)vinyl)pyrrolidine 3w Following the described procedure, 48 mg (0.3 mmol) of 2-bromopyridine **2w** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 7 mg of 1-tosyl-2-(1-(2-pyridyl)vinyl)pyrrolidine **3w** as a pinkish solid (gradient EP/AcOEt 7/1 to 6/4, yield 10%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.59-1.68 (m, 2H; CH_2-C*H*$_2$-CH), 1.73-1.86 (m, 2H; CH_2-C*H*$_2$-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.25 (ddd broad, 1H, *J* = 9.6 Hz, 7.2, 2.0 Hz; N-C(H)*H*-CH_2), 3.61 (ddd broad, 1H, *J*= 9.9, 8.4, 3.8 Hz; N-C(H)*H*-CH_2), 5.19 (d broad, 1H, *J*= 7.7 Hz; N-C*H*-CH_2), 5.71 (s, 1H; C(H)*H*=C-CH), 5.86 (s broad, 1H; C(H)*H*=C-CH), 7.15 (m, 1H; Pyr-*H*), 7.32 (d, 2H, *J*= 7.92 Hz; Ts-*H*), 7.54-7.57 (m, 1H; Pyr-*H*), 7.60-7.65 (m, 1H; Pyr-*H*), 7.78 (d, 2H, *J*= 8.34 Hz; Ts-*H*), 8.51-8.55 (m, 1H; Pyr-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.8 (CH_2), 32.8 (CH_2), 49.3 (CH_2), 61.4 (CH), 115.6 (CH_2), 120.8 (CH), 122.4 (CH), 127.7 (CH), 130.1 (CH), 135.0 (Cq), 136.2 (CH), 143.0 (Cq), 148.6 (CH), 157.2 (Cq).

IR: 2979.7 cm^{-1}, 2954.2 cm^{-1}, 2876.3 cm^{-1}, 1631.6 cm^{-1}, 1583.1 cm^{-1}, 1562.7 cm^{-1}, 1461.8 cm^{-1}, 1431.6 cm^{-1}, 1379.7 cm^{-1}, 1333.5 cm^{-1}, 1254.3 cm^{-1}, 1190.1 cm^{-1}, 1156.0 cm^{-1}, 1093.9 cm^{-1},1020.8 cm^{-1}, 1000.0 cm^{-1}, 989.0 cm^{-1}, 919.6 cm^{-1}, 852.9 cm^{-1}, 805.8 cm^{-1}, 757.5 cm^{-1}.

MS (ESI): Chemical Formula: $C_{18}H_{20}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 351.1138, found *m/z* 351.1139. **Mp**: 136.1-136.6°C



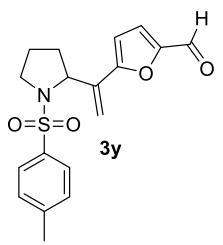
1-Tosyl-2-(1-(2-thienyl)vinyl)pyrrolidine 3x Following the described procedure, 49 mg (0.3 mmol) of 2-bromothiophene **2x** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 41 mg of 1-tosyl-2-(1-(2-thienyl)vinyl)pyrrolidine **3x** as a pale yellow solid (EP/AcOEt 7/1, yield 65%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.63-1.69 (m, 1H; CH_2-C(H)*H*-CH_2), 1.74-1.79 (m, 2H; CH_2-C*H*$_2$-CH), 1.80-1.88 (m, 1H; CH_2-C(H)*H*-CH_2), 2.44 (s, 3H; Ar-C*H*$_3$), 3.28-3.32 (m, 1H; N-C(H)*H*-CH_2), 3.54-3.58 (ddd broad, 1H, *J*= 10.1, 8.6, 3.4 Hz; N-C(H)*H*-CH_2), 4.65 (m, 1H; N-C*H*-CH_2), 5.30 (d, 1H, *J*= 1.4 Hz; C(H)*H*=C-CH), 5.51 (s, 1H; C(H)*H*=C-CH), 6.96-6.70 (m, 1H; Thio--*H*), 7.03-7.04 (dd, 1H, *J*= 3.6, 1.1 Hz; Thio--*H*), 7.18-7.20 (dd, 1H, *J*= 5.2, 1.3 Hz; Thio-*H*), 7.33 (d, 2H, *J*= 8.2 Hz; Ts-*H*), 7.76 (d, 2H, *J*= 8.2 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.7 (CH_2), 32.5 (CH_2), 49.1 (CH_2), 62.6 (CH), 112.3 (CH_2), 123.7 (CH), 124.5 (CH), 127.2 (CH), 127.5 (CH), 129.6 (CH), 134.9 (Cq), 142.0 (Cq), 142.3 (Cq), 143.4 (Cq).

IR: 3089.9 cm^{-1}, 2970.2 cm^{-1}, 2948.4 cm^{-1}, 2874.4 cm^{-1}, 1739.1 cm^{-1}, 1617.7 cm^{-1}, 1448,0 cm^{-1}, 1381.7 cm^{-1}, 1320.9 cm^{-1}, 1251.5 cm^{-1}, 1228.5 cm^{-1}, 1137.0 cm^{-1}, 1150.6 cm^{-1}, 1101.0 cm^{-1}, 1092.1 cm^{-1}, 1071.9 cm^{-1}, 1011.0 cm^{-1}, 917.3 cm^{-1}, 886.4 cm^{-1}, 853.6 cm^{-1}, 838.8 cm^{-1}, 814.6 cm^{-1}.

MS (ESI): Formula $C_{17}H_{19}NO_2S_2$, **[M+H]$^+$** theoretical *m/z* 334.0930, found *m/z* 334.0929; **[M+Na]$^+$** theoretical *m/z* 356.0749, found *m/z* 356.0748. **Mp**: 103-104.7°C



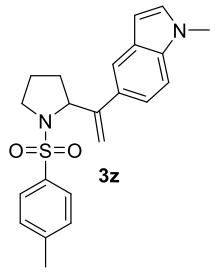
5-(1-(1-Tosylpyrrolidin-2-yl)vinyl)furan-2-carbaldehyde 3y Following the described procedure, 56 mg (0.3 mmol) of 5-bromo-2-furaldehyde **2y** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 35 mg of 5-(1-(1-tosylpyrrolidin-2-yl)vinyl)furan-2-carbaldehyde **3y** as a yellow solid (EP/AcOEt 7/1, yield 54%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.64-1.71 (m, 1H; CH_2-C(H)*H*-CH_2), 1.72-1.78 (m, 1H; CH_2-C(*H*)H-CH), 1.79-1.90 (m, 2H; CH_2-C(*H*)H-CH and CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.27-3.31 (m, 1H; N-C(H)*H*-CH_2), 3.54-3.58 (m, 1H; N-C(H)*H*-CH_2), 4.65 (dd, 1H, *J*= 7.4, 3.5 Hz; N-C*H*-CH_2), 5.61 (d, 1H, *J*= 1.4 Hz; C(H)*H*=C-CH), 5.96 (s, 1H; C(H)*H*=C-CH), 6.56 (d, 1H, *J*= 3.7 Hz; Fu-*H*), 7.22 (d, 1H, *J*= 3.7 Hz; Fu-*H*), 7.32 (d, 2H, *J*= 8.4 Hz; Ts-*H*), 7.72 (d, 2H, *J*= 8.4 Hz; Ts-*H*), 9.59 (s, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.6 (CH_2), 32.7 (CH_2), 49.0 (CH_2), 60.4 (CH), 109.0 (CH), 116.1 (CH_2), 127.4 (CH), 129.7 (CH), 134.6 (Cq), 137.8 (Cq), 143.6 (Cq), 151.7 (Cq), 157.8 (Cq), 177.3 (CHO).

IR: 3134.1 cm^{-1}, 3115.7 cm^{-1}, 2957.1 cm^{-1}, 2925.9 cm^{-1}, 2873.1 cm^{-1}, 2798.1 cm^{-1}, 1673.3 cm^{-1}, 1500,3 cm^{-1}, 1340.9 cm^{-1}, 1258.6 cm^{-1}, 1154.3 cm^{-1}, 1090.8 cm^{-1}, 1005.6 cm^{-1}, 968.9 cm^{-1}, 927.5 cm^{-1}, 907.2 cm^{-1}, 825.2 cm^{-1}, 771.8 cm^{-1}, 748.0 cm^{-1}.

MS (ESI): Chemical formula $C_{18}H_{19}NO_4S$, **[M+H]$^+$** theoretical *m/z* 346.1108, found *m/z* 346.1111. **Mp**: 118.8-119.9°C



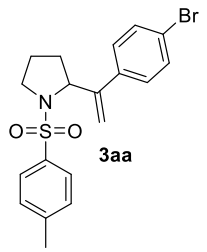
1-Methyl-5-(1-(1-tosylpyrrolidin-2-yl)vinyl)-1*H*-indole 3z Following the described procedure, 63 mg (0.3 mmol) of 5-bromo-1-methyl-1*H*-indole **2z** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 32 mg of 1-methyl-5-(1-(1-tosylpyrrolidin-2-yl)vinyl)-1*H*-indole **3z** as a yellow oil (EP/AcOEt 7/3, yield 42%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.53-1.66 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2), 1.77-1.87 (m, 1H), 2.40-2.46 (s, 3H; Ar-C*H*$_3$), 3.30 (td broad, 1H, *J*= 9.7, 6.7 Hz; N-C(H)*H*-CH_2), 3.59 (ddd broad, 1H, *J*= 10.2, 7.1, 3.2 Hz; N-C(H)*H*-CH_2), 3.79 (s, 3H, N-C*H*$_3$), 4.87 (d broad, 1H, *J*= 8.2 Hz; N-C*H*-CH_2), 5.33 (s broad, 1H; C(H)*H*=C-CH), 5.34 (s, 1H; C(H)*H*=C-CH), 6.48 (d, 1H, *J*= 3.2 Hz; Ar-*H*), 7.06 (d, 1H, *J*= 3.0 Hz; Ar-*H*), 7.28 (d, 2H, *J*= 8.2 Hz; Ts-*H*), 7.33 (d, 1H, *J*= 8.6 Hz; Ar-*H*), 7.60 (s, 1H; Ar-*H*), 7.81 (d, 2H, *J*=7.8 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_2), 23.4 (CH_3), 31.8 (CH_3), 33.1 (CH_2), 49.1 (CH), 63.8 (CH_2), 101.2 (CH), 109.1 (CH), 112.6 (CH_2), 119.2 (CH), 121.2 (CH), 127.5 (CH), 129.5 (CH), 131.5 (Cq), 135.5 (Cq), 136.3 (Cq), 143.4 (Cq), 149.7 (Cq).

IR: 2976.2 cm^{-1}, 2950.3 cm^{-1}, 2920.4 cm^{-1}, 2230.8 cm^{-1}, 1596.9 cm^{-1}, 1512.5 cm^{-1}, 1488.6 cm^{-1}, 1444.1 cm^{-1}, 1332.5 cm^{-1}, 1244.1 cm^{-1}, 1154.3 cm^{-1}, 1088.4 cm^{-1}, 1004.2 cm^{-1}, 908.7 cm^{-1}, 885.5 cm^{-1}, 849.8 cm^{-1}, 808.6 cm^{-1}.

MS (ESI): Chemical formula $C_{22}H_{24}N_2O_2S$, **[M+H]$^+$** theoretical *m/z* 381.1631, found *m/z* 381.1643.



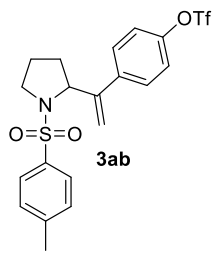
1-Tosyl-2-(1-(4-bromophenyl)vinyl)pyrrolidine 3aa Following the described procedure, 92 mg (0.3 mmol) of 4-bromophenyl trifluoromethanesulfonate **2aa** (or 85 mg of 1-bromo-4-iodobenzene **2ab**) and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 41 mg or 46 mg of 1-tosyl-2-(1-(4-bromophenyl)vinyl)pyrrolidine **3aa** from **2aa** or **2ab** respectively as a yellow oil (EP/AcOEt 7/1, yield 50% and 57% from **2aa** and **2ab** respectively).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.52-1.57 (m, 1H; CH_2-C(*H*)H-CH), 1.58-1.67 (m, 2H+H_2O; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2), 1.75-1.82 (m, 1H; CH_2-C(H)*H*-CH_2), 2.43 (s, 3H; Ar-C*H*$_3$), 3.25-3.30 (m, 1H; N-C(H)*H*-CH_2), 3.51 (ddd broad, 1H, *J*= 9.9, 8.1, 3.3 Hz; N-C(H)*H*-CH_2), 4.66 (dd broad, 1H, *J*= 8.1, 3.7 Hz; N-C*H*-CH_2), 5.33 (s, 1H; C(H)*H*=C-CH), 5.40 (t narrow, 1H, *J*= 1.3 Hz; C(H)*H*=C-CH), 7.24 (d, 2H, *J*= 8.5 Hz; Ar-*H*), 7.33 (d, 2H, *J*= 8.6 Hz; Ts-*H*), 7.45 (d, 2H, *J*= 8.0 Hz; Ar-*H*), 7.76 (d, 2H, *J*= 8.4 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.8 (CH_2), 48.9 (CH_2), 62.9 (CH), 114.5 (CH_2), 121.6 (Cq), 127.5 (CH), 128.6 (CH), 129.7 (CH), 131.4 (CH), 135.0 (Cq), 138.7 (Cq), 143.5 (Cq), 147.9 (Cq).

IR: 2975.5 cm^{-1}, 1487.7 cm^{-1}, 1343.6 cm^{-1}, 1189.1 cm^{-1}, 1154.5 cm^{-1}, 1058.0 cm^{-1}, 1005.0 cm^{-1}, 909.7 cm^{-1}, 813.4 cm^{-1}, 731.3 cm^{-1}, 707.8 cm^{-1}, 665.2 cm^{-1}, 586.5 cm^{-1}, 546.6 cm^{-1}.

MS (ESI): Chemical formula $C_{19}H_{20}BrNO_2S$, **[M+Na]$^+$** theoretical *m/z* 428.0296, 430.0275 found *m/z* 428.0291, 430.0270.



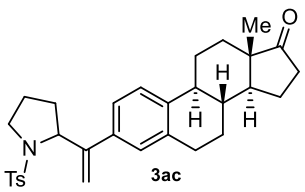
1-Tosyl-2-(1-(4-trifluoromethylsulfonylphenyl)vinyl)pyrrolidine 3ab Following the described procedure, 106 mg (0.3 mmol) of 4-iodophenyl trifluoromethanesulfonate **2ac** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 57 mg of 1-tosyl-2-(1-(4-trifluoromethylsulfonylphenyl)vinyl)pyrrolidine **3ab** as a yellow oil (EP/AcOEt 7/1, yield 59%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.53-1.56 (m, 1H; CH_2-C(*H*)H-CH_2), 1.59-1.69 (m, 2H+H_2O; CH_2-C*H*$_2$-CH), 1.74-1.81 (m, 1H; CH_2-C(H)*H*-CH_2), 2.44 (s, 3H; Ar-C*H*$_3$), 3.26-3.30 (m, 1H; N-C(H)*H*-CH_2), 3.51 (ddd broad, 1H, *J*= 10.1, 8.1, 3.5 Hz; N-C(H)*H*-CH_2), 4.64 (dd broad, 1H, *J*= 8.0, 2.2 Hz; N-C*H*-CH_2), 5.36 (s, 1H; C(H)*H*=C-CH), 5.46 (t narrow, 1H, J= 1.0 Hz; C(H)*H*=C-CH), 7.24 (d, 2H, *J*= 8.9 Hz; Ar-*H*), 7.33 (d, 2H, *J*= 7.8 Hz; Ts-*H*), 7.46 (d, 2H, *J*= 9.0 Hz; Ar-*H*), 7.76 (d, 2H, *J*= 8.0 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.5 (CH_2), 31.9 (CH_2), 49.0 (CH_2), 62.9 (CH), 115.6 (CH_2), 117.7 (Cq, J_{C-F} = 319Hz), 119.8 (Cq), 121.2 (CH), 127.5 (CH), 128.8 (CH), 129.7 (CH), 134.9 (Cq), 140.3 (Cq), 143.6 (Cq), 147.5 (Cq), 148.9 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF**):** δ -72.67 (3F, s).

IR: 2948.2 cm^{-1}, 2032.4 cm^{-1}, 1596.9 cm^{-1}, 1498.7 cm^{-1}, 1420.7 cm^{-1}, 1344.1 cm^{-1}, 1304.4 cm^{-1}, 1248.5 cm^{-1}, 1206.6 cm^{-1}, 1157.3 cm^{-1}, 1137.9 cm^{-1}, 1093.5 cm^{-1}, 1011.0 cm^{-1}, 886.2 cm^{-1}, 848.6 cm^{-1}, 816.0 cm^{-1}, 765.2 cm^{-1}, 709.1 cm^{-1}, 665.1 cm^{-1}, 607.7 cm^{-1}, 588.9 cm^{-1}, 547.9 cm^{-1}. **MS (ESI):** Chemical formula $C_{20}H_{20}F_3NO_5S_2$, **[M+Na]$^+$** theoretical *m/z* 498.0627, found *m/z* 498.0624.



3ac

(8*R*,9*S*,13*S*,14S)-13-Methyl-3-(1-(1-tosylpyrrolidin-2-yl)vinyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one 3 Following the described procedure, 121 mg (0.3 mmol) of (8*R*,9*S*,13*S*,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate **2ad** and 50 mg (0.2 mmol) of allene **1a** were reacted under the optimized conditions to afford 20 mg of (8*R*,9*S*,13*S*,14S)-13-Methyl-3-(1-(1-tosylpyrrolidin-2-yl)vinyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one **3ac** as a transparent oil (EP/AcOEt 7/1, yield 20%).

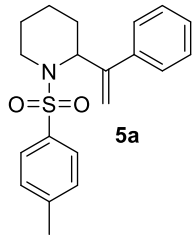
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.25 (s, 3H; CH_3), 1.52-1.43 (m, 3H), 1.57-1.68 (m, 6H), 1.81 (m, 1H), 1.94-1.98 (m, 1H), 2.05 (m, 2H), 2.15 (dt, 1H, *J*= 19, 9.1 Hz; CO-C(*H*)H-CH_2), 2.31 (td, 1H, *J*= 11, 3.9 Hz; CO-C(*H*)H-CH_2), 2.41 (m, 1H), 2.43 (s, 3H; Ar-C*H*$_3$), 2.51 (m, 1H), 2.91 (d, 1H; *J*= 4.2 Hz), 2.93 (d, 1H; *J*= 4.2 Hz), 3.29 (m, 1H; N-C(*H*)H-CH_2), 3.52 (m, 1H; N-C(*H*)H-CH_2), 4.76 (m, 1H; N-C*H*-CH_2), 5.31 (s broad, 2H; C=C*H*$_2$), 7.10 (s, 1H; Ar-*H*), 7.14 (d, 1H; *J*= 7.7 Hz; Ar-*H*), 7.25 (d, 1H; *J*= 7.7 Hz; Ar-*H*), 7.32 (d, 2H; *J*= 8.3 Hz; Ts-*H*), 7.77 (d, 2H; *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 14.1 (CH_3), 21.7 (CH_2), 21.7 (CH_2), 23.7 (CH_2), 25.8 (CH_2), 26.6 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 31.7 (CH_2), 32.0 (CH_2), 36.0 (CH_2), 38.3 (CH_3), 44.5 (CH_2), 44.5 (CH_2), 48.1 (CH), 49.0 (CH_2), 50.7 (CH), 63.0 (CH), 63.2 (CH), 77.5, 113.3 (CH_2), 124.3 (CH), 124.5 (CH), 127.7 (CH), 129.8 (CH), 135.5 (Cq), 136.6 (Cq), 137.4 (Cq), 137.5 (Cq), 139.4 (Cq), 143.4 (Cq), 148.7 (Cq), 221.1 (Cq).

IR: 2924 cm^{-1}, 1735 cm^{-1}, 1597 cm^{-1}, 1496 cm^{-1}, 1452 cm^{-1},1404 cm^{-1},1343 cm^{-1}, 1303 cm^{-1}, 1256 cm^{-1}, 1191 cm^{-1},1157 cm^{-1}, 1091 cm^{-1}, 1051 cm^{-1}, 1006 cm^{-1}, 906 cm^{-1}, 815 cm^{-1}, 729 cm^{-1}, 659 cm^{-1}, 588 cm^{-1}.

MS (ESI): Chemical formula $C_{31}H_{37}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 526.2392, found *m/z* 526.2390.

4.4.3 Characterization of vinyl piperidines 5



5a

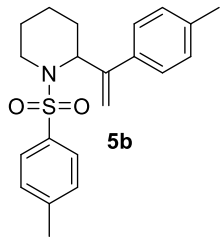
2-(1-Phenylvinyl)-1-tosylpiperidine 5a Following the described procedure, 47 mg (0.3 mmol) of bromobenzene **2a** (or 61 mg iodobenzene **2a'**) and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 30 mg (22 mg from **2a'**) of 2-(1-phenylvinyl)-1-tosylpiperidine **5a** as a light yellow solid (EP/AcOEt 7/1, yield 44%, 32% from **2a'**).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.27-1.34 (m, 1H; CH_2-C(*H*)-CH_2), 1.35-1.42 (m, 2H; N-CH_2-C(*H*)H and CH_2-C(*H*)-CH_2), 1.43-1.52 (m, 2H; CH-C(*H*)-CH_2 and N-CH_2-C(*H*)H), 1.67-1.74 (m, 1H; CH-C(*H*)-CH_2), 2.41 (s, 3H; Ar-CH_3), 3.17 (td broad, 1H, *J*= 13.7, 3.5 Hz; N-C(*H*)H-CH_2), 3.69 (dd broad, 1H, *J*= 12.6, 3.1 Hz; N-C(*H*)H-CH_2), 5.19 (d narrow, 1H, *J*= 1.3 Hz; C(*H*)H=C), 5.25-5.29 (m, 2H; C(*H*)H=C- and N-C*H*-CH_2), 7.24 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.27-7.33 (m, 5H; Ar-*H*), 7.66 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.8 (CH_2), 21.5 (CH_3), 24.5 (CH_2), 26.9 (CH_2), 41.5 (CH_2), 55.4 (CH), 116.2 (CH_2), 127.09 (CH), 127.12 (CH), 127.4 (CH), 128.3 (CH), 129.5 (CH), 138.3 (Cq), 141.1 (Cq), 142.9 (Cq), 146.8 (Cq).

IR: 2940.1 cm^{-1} 2867.5 cm^{-1}, 1597.2 cm^{-1}, 1501.0 cm^{-1}, 1459.2 cm^{-1}, 1332.4 cm^{-1}, 1152.5 cm^{-1}, 1109.0 cm^{-1}, 972.2 cm^{-1}, 909.5 cm^{-1}, 813.2 cm^{-1}, 782.8 cm^{-1}, 749.6 cm^{-1}, 665.4 cm^{-1}, 570.1 cm^{-1}, 548.6 cm^{-1}.

MS (ESI): Chemical formula $C_{20}H_{23}NO_2S$, **[M+H]$^+$** theoretical *m/z* 342.1522, found *m/z* 324.1523; **[M+Na]$^+$** theoretical *m/z* 364.1342, found *m/z* 364.1342. **Mp**: 116.8-119.0°C



5b

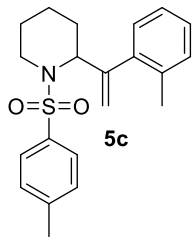
2-(1-(4-Tolyl)vinyl)-1-tosylpiperidine 5b Following the described procedure, 52 mg (0.3 mmol) of 4-bromotoluene **2b** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 30 mg of 2-(1-(4-tolyl)vinyl)-1-tosylpiperidine **5b** as a light yellow oil (EP/AcOEt 7/1, yield 42%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.20-1.40 (m, 2H; CH_2-CH_2-CH_2), 1.43-1.54 (m, 3H; CH-CH_2-CH_2 and N-CH_2-C(*H*)H), 1.68-1.74 (m, 1H; N-CH_2-C(*H*)H), 2.34 (s, 3H; Ar-CH_3), 2.40 (s, 3H; Ar-CH_3), 3.17 (ddd, 1H, *J*= 13.8, 12.4, 3.32 Hz; N-C(*H*)H-CH_2), 3.65-3.73 (m, 1H; N-C(*H*)H-CH_2), 5.15 (d, 1H, *J*= 1.3 Hz; C(*H*)H=C), 5.22-5.26 (m, 2H; C(*H*)H=C- and N-C*H*-CH_2), 7.12 (d, 2H, *J*= 7.7 Hz; Ar-*H*), 7.18 (d, 2H, *J*= 8.2 Hz; Ar-*H*), 7.24 (d, 2H, *J*= 7.9; Ts-*H*), 7.64 (d, 2H, *J*= 8.3 Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.8 (CH_2), 21.1 (CH_3), 25.5 (CH3), 24.6 (CH_2), 26.9 (CH_2), 41.6 (CH_2), 55.5 (CH), 115.7 (CH_2), 127.0 (CH), 127.1 (CH), 129.0 (CH), 129.5 (CH), 137.2 (Cq), 138.2 (Cq), 138.4 (Cq), 142.8 (Cq), 146.6 (Cq).

IR: 2951.9 cm^{-1}, 2867.3 cm^{-1}, 1459.5 cm^{-1}, 1343.2 cm^{-1}, 1163.4 cm^{-1}, 1089.9 cm^{-1}, 962.7 cm^{-1}, 909.0 cm^{-1}, 813.3 cm^{-1}, 718.8 cm^{-1}, 655.1 cm^{-1}, 538.6 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{25}NO_2S$ Exact Mass: 355.1606, **[M+H]$^+$** theoretical *m/z* 356.1679, found *m/z* 356.1683.



5c

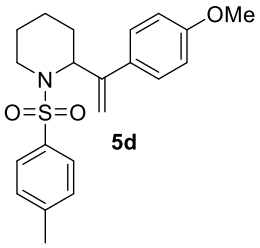
2-(1-(2-Tolyl)vinyl)-1-tosylpiperidine 5c Following the described procedure, 52 mg (0.3 mmol) of 2-bromotoluene **2d** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 20 mg of 2-(1-(2-tolyl)vinyl)-1-tosylpiperidine **5c** as a yellow oil (EP/AcOEt 7/1, yield 28%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.23-1.32 (m, 1H; N-CH_2-C(*H*)H), 1.33-1.41 (m, 1H; CH-C(*H*)H-CH_2), 1.41-1.47 (m, 2H; CH_2-CH_2-CH_2), 1.47-1.52 (m, 1H; N-CH_2-C(*H*)H), 1.52-1.61 (m, 1H; CH-C(*H*)H-CH_2), 2.33 (s, 3H; Ar-CH_3), 2.41 (s, 3H; Ar-CH_3), 3.23 (td broad, 1H, *J*= 13.5, 2.9 Hz; N-C(*H*)H-CH_2), 3.75 (dd broad, 1H, *J*= 14.2, 2.8 Hz; N-C(*H*)H-CH_2), 5.02-5.09 (m, 1H; N-C*H*-CH_2), 5.13 (s broad, 1H; C(*H*)H=C), 5.39 (s broad, 1H; C(*H*)H=C), 7.05-7.20 (m, 4H; Ar-*H*), 7.24 (d, 2H, *J*= 8.2 Hz; Ts-*H*), 7.65 (d, 2H, J= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ=19.2 (CH_2), 19.7 (CH_3), 21.4 (CH_3), 24.5 (CH_2), 26.4 (CH_2), 41.6 (CH_2), 56.0 (CH), 116.8 (CH_2), 125.5 (CH), 127.0 (CH), 127.1 (CH), 128.7 (CH), 129.5 (CH), 130.2 (CH), 135.2 (Cq), 138.4 (Cq), 140.7 (Cq), 142.8 (Cq), 146.5 (Cq).

IR: 3037.1 cm^{-1}, 2924.3 cm^{-1}, 2868.4 cm^{-1}, 1597.1 cm^{-1}, 1511.1 cm^{-1}, 1446.4 cm^{-1}, 1398.5 cm^{-1}, 1333.1 cm^{-1}, 1210.6 cm^{-1}, 1183.3 cm^{-1}, 1153.4 cm^{-1}, 1111.2 cm^{-1}, 1090.2 cm^{-1}, 992.6 cm^{-1}, 959.2 cm^{-1}, 927.9 cm^{-1}, 910.9 cm^{-1}, 869.4 cm^{-1}, 815.5 cm^{-1}, 782.8 cm^{-1}, 755.1 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{25}NO_2S$ Exact Mass: 355.1606, **[M+H]$^+$** theoretical *m/z* 356.1679, found *m/z* 356.1675.



5d

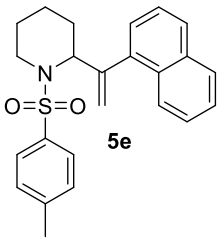
2-(1-(4-Methoxyphenyl)vinyl)-1-tosylpiperidine 5d Following the described procedure, 56 mg (0.3 mmol) of 4-bromoanisole **2e** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 28 mg of 2-(1-(4-methoxyphenyl)vinyl)-1-tosylpiperidine **5d** as a transparent oil (EP/AcOEt 7/3, yield 38%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.25-1.41 (m, 3H; CH_2-C(*H*)H-CH_2 and N-CH_2-C*H*$_2$), 1.42-1.51 (m, 2H; CH-C(*H*)H-CH_2 and CH_2-C(*H*)H-CH_2), 1.72-1.75 (m, 1H; CH-C(*H*)H-CH_2), 3.18 (ddd, 1H, *J*= 14.6, 13.9, 3.3 Hz; N-C(*H*)H-CH_2), 3.69 (bd broad, 1H, *J*= 11.8 Hz; N-C(*H*)H-CH_2), 3.81 (s, 3H; OCH_3), 5.12 (s, 1H; C(*H*)H=C), 5.22 (s broad, 2H; C(*H*)H=C and N-C*H*-CH_2), 6.84 (d, 2H, *J*= 8.7 Hz; Ar-*H*), 7.22 (d, 2H, *J*= 8.6 Hz; Ar-*H*),), 7.24 (d, 2H, *J*= 8.3 Hz; Ts-*H*),), 7.67 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.7 (CH_2), 21.5 (CH_3), 24.5 (CH_2), 26.9 (CH_2), 41.6 (CH_2), 55.2 (OCH_3), 55.5 (CH), 113.6 (CH), 115.3 (CH_2), 127.1 (CH), 128.2 (CH), 129.5 (CH), 133.5 (Cq), 138.4 (Cq), 142.8 (Cq), 146.2 (Cq), 159.0 (Cq).

IR: 2936.3 cm^{-1}, 2856.9 cm^{-1}, 1606.5 cm^{-1}, 1509.7 cm^{-1}, 1443.9 cm^{-1}, 1334.6 cm^{-1}, 1303.6 cm^{-1}, 1244.0 cm^{-1}, 1180.9 cm^{-1}, 1153.3 cm^{-1}, 1112.7 cm^{-1}, 1092.3 cm^{-1}, 1029.4 cm^{-1}, 958.8 cm^{-1}, 930.3 cm^{-1}, 908.1 cm^{-1}, 868.8 cm^{-1}, 836.4 cm^{-1}, 815.6 cm^{-1}, 769.9 cm^{-1}, 714.1 cm^{-1}, 699.5 cm^{-1}, 658.5 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{25}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 371.1555, found *m/z* 371.1557.



5e

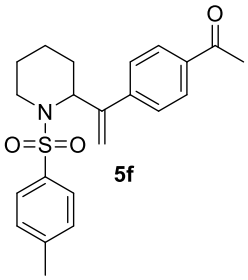
2-(1-(1-Naphtyl)vinyl)-1-tosylpiperidine 5e Following the described procedure, 62 mg (0.3 mmol) of 1-bromonaphthalene **2i** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 30 mg of 2-(1-(1-naphtyl)vinyl)-1-tosylpiperidine **5e** as a yellow oil (EP/AcOEt 7/1, yield 38%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.22-1.53 (m, 6H; CH-C*H*$_2$-CH_2, CH_2-C*H*$_2$-CH_2 and N-CH_2-C*H*$_2$), 2.39 (s, 3H; Ar-C*H*$_3$), 3.37 (td, 1H, *J*= 13.4, 4.5 Hz; N-C(*H*)H-CH_2), 3.84 (dd, 1H, *J*= 14.1, 4.5 Hz; N-C(*H*)H-CH_2), 5.22 (d narrow, 1H, *J*= 4.4 Hz; N-C*H*-CH_2), 5.35 (s, 1H; C(*H*)H=C),), 5.66 (s, 1H; C(*H*)H=C), 7.22 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.26-7.33 (m, 1H, Ar-*H*), 7.42 (t, 1H, *J*= 7.1 Hz; Ar-*H*), 7.45-7.53 (m, 2H; Ar-*H*), 7.69 (d, 2H, *J*= 8.5 Hz; Ts-*H*), 7.77 (d, 1H, *J*= 8.3 Hz; Ar-*H*), 7.84 (d, 1H, *J*= 9.6 Hz; Ar-*H*), 8.08 (d, 1H, *J*= 8.0 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 19.2 (CH_2), 21.4 (CH_3), 24.6 (CH_2), 26.6 (CH_2), 41.7 (CH_2), 56.9 (CH), 118.1 (CH_2), 125.2 (CH), 125.5 (CH), 125.8 (CH), 126.2 (CH), 126.9 (CH), 127.6 (CH), 128.3 (CH), 129.5 (CH), 131.4 (Cq), 133.7 (Cq), 138.4 (Cq), 138.9 (Cq), 142.8.

IR: 2937.0 cm^{-1}, 2857.7 cm^{-1}, 1636.8 cm^{-1}, 1596.2 cm^{-1}, 1444.6 cm^{-1}, 1334.4 cm^{-1}, 1303.3 cm^{-1}, 1178.8 cm^{-1}, 1153.4 cm^{-1}, 1109.1 cm^{-1}, 1092.4 cm^{-1}, 1055.2 cm^{-1}, 957.8 cm^{-1}, 931.2 cm^{-1}, 913.1 cm^{-1}, 803.0 cm^{-1}, 780.8 cm^{-1}, 731.6 cm^{-1}, 694.9 cm^{-1}, 658.1 cm^{-1}, 575.2 cm^{-1}.

MS (ESI): Chemical formula $C_{24}H_{25}NO_2S$, **[M+Na]$^+$** theoretical *m/z* 414.1498, found *m/z* 414.1495.



5f

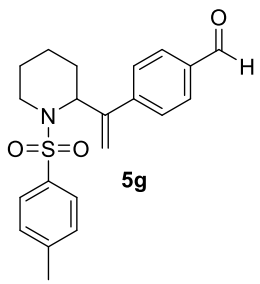
1-(4-(1-(1-Tosylpiperidin-2-yl)vinyl)phenyl)ethan-1-one 5f Following the described procedure, 60 mg (0.3 mmol) of 4-bromoacetophenone **2k** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 46 mg of 1-(4-(1-(1-tosylpiperidin-2-yl)vinyl)phenyl)ethan-1-one **5f** as a yellow oil (EP/AcOEt 7/3, yield 60%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.21-1.32 (m, 1H; N-CH_2-C(*H*)H), 1.32-1.42 (m, 2H; CH_2-C(*H*)H-CH_2 and N-CH_2-C(*H*)H), 1.44-1.53 (m, 2H; CH-C(*H*)H-CH_2 and CH_2-C(*H*)H-CH_2), 1.66-1.72 (m, 1H; CH-C(*H*)H-CH_2), 2.39 (s, 3H; Ar-C*H*$_3$), 2.59 (s, 3H; COC*H*$_3$), 3.13 (td, 1H, *J*= 13.4, 3.2 Hz; N-C(*H*)H-CH_2), 3.65-3.69 (m, 1H; N-C(*H*)H-CH_2), 5.26 (bd, 1H, *J*= 5.9 Hz; N-C*H*-CH_2), 5.31 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 5.35 (d, 1H, J= 2.2 Hz; C(*H*)H=C), 7.23 (d, 2H, *J*= 8.0 Hz, Ts-*H*), 7.38 (d, 2H, *J*= 8.4 Hz; Ar-*H*), 7.66 (d, 2H, *J*= 8.0 Hz, Ts-*H*), 7.89 (d, 2H, *J*= 8.4 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.6 (CH_2), 21.4 (CH_3), 24.3 (CH_2), 26.6 (CH_3), 26.7 (CH_2), 41.6 (CH_2), 55.2 (CH), 117.6 (CH_2), 127.0 (CH), 127.3 (CH), 128.4 (CH), 129.5 (CH), 136.1 (Cq), 138.2 (Cq), 143.0 (Cq), 145.5 (Cq), 146.1 (Cq), 197.6 (CO).

IR: 2940.4 cm^{-1}, 2859.4 cm^{-1}, 1679.9 cm^{-1}, 1602.9 cm^{-1}, 1446.8 cm^{-1}, 1335.3 cm^{-1}, 1264.4 cm^{-1}, 1215.3 cm^{-1}, 1183.3 cm^{-1}, 1152.6 cm^{-1}, 1109.8 cm^{-1}, 1091.5 cm^{-1}, 957.0 cm^{-1}, 908.7 cm^{-1}, 845.4 cm^{-1}, 814.7 cm^{-1}, 728.2 cm^{-1}, 683.3 cm^{-1}, 651.9 cm^{-1}, 567.1 cm^{-1}.

MS (ESI): Chemical formula $C_{22}H_{25}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 406.1447, found *m/z* 406.1448.



5g

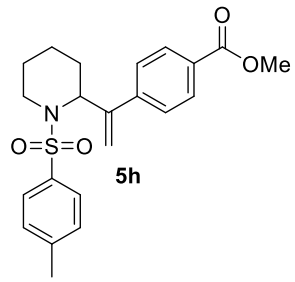
4-(1-(1-Tosylpiperidin-2-yl)vinyl)benzaldehyde 5g Following the described procedure, 55 mg (0.3 mmol) of 4-bromobenzaldehyde **2m** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 56 mg of 4-(1-(1-tosylpiperidin-2-yl)vinyl)benzaldehyde **5g** as a transparent oil (EP/AcOEt 6/4, yield 75%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.23-1.32 (m, 1H; N-CH_2-C(*H*)H), 1.34-1.44 (m, 2H; CH_2-C*H*$_2$-CH_2), 1.45-1.49 (m, 1H; N-CH_2-C(*H*)H), 1.49-1.56 (m, 1H; CH-C(*H*)H-CH_2), 1.63-1.71 (m, 1H; CH-C(*H*)H-CH_2), 2.39 (s, 3H; Ar-C*H*$_3$), 3.13 (td, 1H, *J*= 13.4, 3.2 Hz; N-C(*H*)H-CH_2), 3.68 (dd broad, 1H, *J*= 15.1, 4.7 Hz; N-C(*H*)H-CH_2), 5.28 (d broad, 1H, *J*= 3.5 Hz; N-C*H*-CH_2), 5.34 (d narrow, 1H, *J*= 2.3 Hz; C(*H*)H=C), 5.38 (d narrow, 1H, J= 2.3 Hz; C(*H*)H=C), 7.24 (d, 2H; *J*= 8.0 Hz; Ts-*H*), 7.46 (d, 2H; *J*= 8.1 Hz; Ar-*H*), 7.65 (d, 2H; *J*= 8.2 Hz; Ts-*H*), 7.82 (d, 2H; *J*= 8.0 Hz; Ar-*H*), 9.99 s, 1H; C*H*O).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.7 (CH_2), 21.4 (CH_3), 24.3 (CH_2), 26.7 (CH_2), 41.6 (CH_2), 55.2 (CH), 118.1 (CH_2), 127.0 (CH), 127.8 (CH), 129.6 (CH), 129.8 (CH), 135.5 (Cq), 138.2 (Cq), 143.1 (Cq), 146.2 (Cq), 147.3 (Cq), 191.7 (CHO).

IR: 2940.7 cm^{-1}, 2858.0 cm^{-1}, 1697.5 cm^{-1}, 1603.3 cm^{-1}, 1562.5 cm^{-1}, 1434.5 cm^{-1}, 1334.7 cm^{-1}, 1304.5 cm^{-1}, 1209.9 cm^{-1}, 1183.7 cm^{-1}, 1153.5 cm^{-1}, 1092.4 cm^{-1}, 1055.4 cm^{-1}, 958.2 cm^{-1}, 908.0 cm^{-1}, 834.4 cm^{-1}, 814.1 cm^{-1}, 724.5 cm^{-1}, 707.0 cm^{-1}, 664.6 cm^{-1}, 569.8 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{23}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 392.1290, found *m/z* 392.1281.



5h

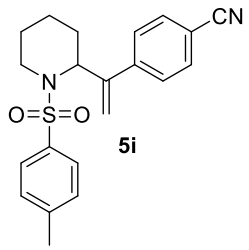
Methyl 4-(1-(1-tosylpiperidin-2-yl)vinyl)benzoate 5h Following the described procedure, 64 mg (0.3 mmol) of methyl 4-bromobenzoate **2n** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 42 mg of methyl 4-(1-(1-tosylpiperidin-2-yl)vinyl)benzoate **5h** as a yellow oil (EP/AcOEt 7/1, yield 52%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.23-1.35 (m, 1H; CH_2-C(*H*)H-CH_2), 1.36-1.42 (m, 2H; N-CH_2-C*H*$_2$), 1.43-1.49 (m, 1H; CH-C(*H*)H-CH_2), 1.49-1.55 (m, 1H; CH_2-C(*H*)H-CH_2), 1.64-1.69 (m, 1H; CH-C(*H*)H-CH_2), 2.39 (s, 3H; Ar-C*H*$_3$), 3.14 (td, 1H, *J*= 13.1, 3.2 Hz; N-C(*H*)H-CH_2), 3.65-3.73 (m, 1H; N-C(*H*)H-CH_2), 3.91 (s, 3H; CO_2CH_3), 5.26 (d broad, 1H, *J*= 5.9 Hz; N-C*H*-CH_2), 5.30 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 5.34 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 7.24 (d, 2H, *J*= 8.4 Hz; Ts-*H*), 7.35 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 7.66 (d, 2H, *J*= 8.4 Hz; Ts-*H*), 7.97 (d, 2H, *J*= 8.3 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.7 (CH_2), 21.4 (CH_3), 24.4 (CH_2), 26.7 (CH_2), 41.6 (CH_2), 52.1 (OCH_3), 55.3 (CH), 117.5 (CH_2), 127.0 (CH), 127.1 (CH), 129.2 (Cq), 129.5 (CH), 129.6 (Cq), 138.2 (Cq), 143.0 (Cq), 145.7 (Cq), 146.2 (Cq), 166.8 (*C*O_2CH_3).

IR: 2945.4 cm^{-1}, 2859.1 cm^{-1}, 1717.3 cm^{-1}, 1607.2 cm^{-1}, 1436.1 cm^{-1}, 1334.1 cm^{-1}, 1277.7 cm^{-1}, 1182.7 cm^{-1}, 1153.1 cm^{-1}, 1110.3 cm^{-1}, 1092.2 cm^{-1}, 1017.9 cm^{-1}, 956.4 cm^{-1}, 921.9 cm^{-1}, 871.2 cm^{-1}, 815.2 cm^{-1}, 778.4 cm^{-1}, 718.5 cm^{-1}, 669.9 cm^{-1}, 640.1 cm-1, 568.1 cm^{-1}.

MS (ESI): Chemical formula $C_{22}H_{25}NO_4S$, **[M+Na]$^+$** theoretical *m/z* 422.1396, found *m/z* 422.1393.



5i

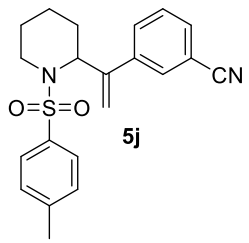
4-(1-(1-Tosylpiperidin-2-yl)vinyl)benzonitrile 5i Following the described procedure, 55 mg (0.3 mmol) of 4-bromobenzonitrile **2q** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 46 mg of 4-(1-(1-tosylpiperidin-2-yl)vinyl)benzonitrile **5i** as a transparent oil (EP/AcOEt 7/1, yield 62%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.22-1.33 (m, 1H; CH_2-C(*H*)H-CH_2), 1.33-1.49 (m, 3H; CH_2-C(*H*)H-CH_2 and N-CH_2-C(*H*)H), 1.50-1.58 (m, 1H; CH-C(*H*)H-CH_2), 1.65-1.70 (m, 1H; CH-C(*H*)H-CH_2), 2.41 (s, 3H; Ts-C*H*$_3$), 3.08 (td, 1H, J_1= 13.4 Hz, J_2= 3.1 Hz; N-C(*H*)H-CH_2), 3.61-3.68 (m,1H; N-C(*H*)H-CH_2), 5.23 (d, 1H, J= 3.4 Hz; N-C*H*-CH_2), 5.35 (s, 1H; C(*H*)H=C), 5.36 (s, 1H; C(*H*)H=C), 7.25 (d, 2H, J= 8.4 Hz; Ts-*H*), 7.40 (d, 2H, J= 8.4 Hz; Ar-*H*), 7.59 (d, 2H, J= 8.4 Hz; Ar-*H*), 7.64 (d, 2H, J= 8.4 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.6 (CH_2), 21.5 (CH_3), 24.2 (CH_2), 26.5 (CH_2), 41.7 (CH_2), 55.0 (CH), 11.2 (Cq), 118.5 (CH_2), 118.7 (Cq), 127.0 (CH), 127.9 (CH), 129.6 (CH), 132.1 (CH), 138.1 (Cq), 143.2 (Cq), 145.7 (Cq), 145.8 (Cq).

IR: 2940.9 cm^{-1}, 2859.7 cm^{-1}, 2226.7 cm^{-1}, 1604.3 cm^{-1}, 1503.7 cm^{-1}, 1449.7 cm^{-1}, 1335.2 cm^{-1}, 1212.6 cm^{-1}, 1184.0 cm^{-1}, 1152.8 cm^{-1}, 1109.4 cm^{-1}, 1091.5 cm^{-1}, 957.6 cm^{-1}, 910.1 cm^{-1}, 846.8 cm^{-1}, 814.9 cm^{-1}, 730.3 cm^{-1}, 710.5 cm^{-1}, 687.8 cm^{-1}, 652.9 cm^{-1}, 574.0 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{22}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 389.1294, found *m/z* 389.1297.



5j

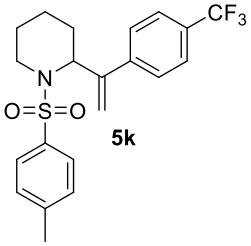
3-(1-(1-Tosylpiperidin-2-yl)vinyl)benzonitrile 5j Following the described procedure, 55 mg (0.3 mmol) of 3-bromobenzonitrile **2r** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 56 mg of 3-(1-(1-tosylpiperidin-2-yl)vinyl)benzonitrile **5j** as a yellow oil (EP/AcOEt 7/1, yield 75%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.21-1.30 (m, 1H; N-CH_2-C(*H*)H), 1.32-1.42 (m, 2H; CH_2-C(*H*)H-CH_2 and N-CH_2-C(*H*)H), 1.43-1.54 (m, 2H; CH-C(*H*)H-CH_2 and CH_2-C(*H*)H-CH_2), 1.62-1.67 (m, 1H; CH-C(*H*)H-CH_2), 2.39 (s, 3H; Ar-C*H*$_3$), 3.08 (td, 1H, *J*= 13.4, 3.2 Hz; N-C(*H*)H-CH_2), 3.66 (m, 1H; N-C(*H*)H-CH_2), 5.18 (d, 1H, *J*= 3.6 Hz; N-C*H*-CH_2), 5.32 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 5.33 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 7.24 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.41 (m, 1H; Ar-*H*), 7.51-7.56 (m, 3H; Ar-*H*), 7.64 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.8 (CH_2), 21.6 (CH_3), 24.3 (CH_2), 26.6 (CH_2), 41.8 (CH_2), 55.2 (CH), 112.6 (CH), 118.4 (CH_2), 118.7 (Cq), 127.1 (CH), 129.3 (CH), 129.8 (CH), 130.9 (CH), 131.1 (CH), 131.7 (CH), 138.2 (Cq), 142.4 (Cq), 143.3 (Cq), 145.4 (Cq).

IR: 2940.7 cm^{-1}, 2858.2 cm^{-1}, 2229.0 cm^{-1}, 1734.4 cm^{-1}, 1597.0 cm^{-1}, 1575.9 cm^{-1}, 1451.5 cm^{-1}, 1335.7 cm^{-1}, 1241.2 cm^{-1}, 1187.8 cm^{-1}, 1152.6 cm^{-1}, 1111.3 cm^{-1}, 1091.6 cm^{-1}, 1045.0 cm^{-1}, 958.7 cm^{-1}, 910.4 cm^{-1}, 856.3 cm^{-1}, 810.9 cm^{-1}, 763.5 cm^{-1}, 710.8 cm^{-1}, 699.9 cm^{-1}, 648.8 cm^{-1}, 607.7 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{22}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 389.1294, found *m/z* 389.1292.



5k

1-Tosyl-2-(1-(4-(trifluoromethyl)phenyl)vinyl)piperidine 5k Following the described procedure, 68 mg (0.3 mmol) of 4-bromobenzotrifluoride **2s** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 55 mg of 1-tosyl-2-(1-(4-(trifluoromethyl)phenyl)vinyl)piperidine **5k** as a yellow oil (EP/AcOEt 7/1, yield 75%).

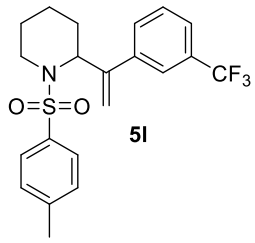
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.28-1.45 (m, 3H; CH_2-C(*H*)H-CH_2 and N-CH_2-C*H*$_2$), 1.46-1.51 (m, 1H; CH_2-C(*H*)H-CH_2), 1.52-1.61 (m, 1H; CH-C(*H*)H-CH_2), 1.70-1.73 (m, 1H; CH-C(*H*)H-CH_2), 2.40 (s, 3H; Ar-C*H*$_3$), 3.11 (td, 1H, *J*= 12.6, 3.3 Hz; N-C(*H*)H-CH_2), 3.63-3.69 (m, 1H; N-C(*H*)H-CH_2), 5.26 (d, 1H, *J*= 5.9 Hz; N-C*H*-CH_2), 5.32 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 5.34 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 7.23 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.40 (d, 2H, *J*= 8.1 Hz; Ar-*H*), 7.55 (d, 2H, *J*= 8.1 Hz; Ar-*H*), 7.62 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.7 (CH_2), 21.4 (CH_3), 24.3 (CH_2), 26.6 (CH_2), 41.6 (CH_2), 55.2 (CH), 117.8 (CH_2), 124.3 (Cq, $J_{C\text{-}F}$ = 271 Hz), 125.3 (CH, $J_{C\text{-}F}$ = 4.1 Hz), 127.0 (CH), 127.5 (CH), 129.5 (Cq), 129.6 (Cq, $J_{C\text{-}F}$ = 32.3 Hz), 138.1 (Cq), 143.1 (Cq), 144.8 (Cq), 146.0 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF): δ -62.35 (3F, s).

IR: 2940.4 cm^{-1}, 2860.4 cm^{-1}, 1615.0 cm^{-1}, 1448.0 cm^{-1}, 1403.5 cm^{-1}, 1322.5 cm^{-1}, 1213.2 cm^{-1}, 1154.5 cm^{-1}, 1115.1 cm^{-1}, 1090.9 cm^{-1}, 1064.3 cm^{-1}, 1016.0 cm^{-1}, 959.1 cm^{-1}, 932.2 cm^{-1}, 869.4 cm^{-1}, 849.2 cm^{-1}, 815.1 cm^{-1}, 728.0 cm^{-1}, 670.4 cm^{-1}, 567.9 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{22}F_3NO_2S$, **[M+Na]$^+$** theoretical *m/z* 432.1215, found *m/z* 432.1214.



5l

1-Tosyl-2-(1-(3-(trifluoromethyl)phenyl)vinyl)piperidine 5l Following the described procedure, 68 mg (0.3 mmol) of 3-bromobenzotrifluoride **2t** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 40 mg of 1-tosyl-2-(1-(3-(trifluoromethyl)phenyl)vinyl)piperidine **5l** as a transparent oil (EP/AcOEt 7/1, yield 50%).

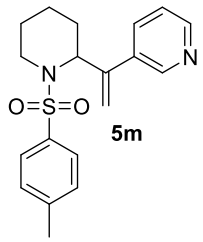
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.24-1.45 (m, 3H; CH_2-C(*H*)H-CH_2 and N-CH_2-C(*H*)H), 1.46-1.50 (m, 1H; CH_2-C(*H*)H-CH_2), 1.51-1.57 (m, 1H; CH-C(*H*)H-CH_2), 1.65-1.72 (m, 1H; CH-C(*H*)H-CH_2), 2.41 (s, 3H; Ar-C*H*$_3$), 3.14 (td, 1H, *J*= 13.7, 3.4 Hz; N-C(*H*)H-CH_2), 3.65-3.71 (m, 1H; N-C(*H*)H-CH_2), 5.27 (d, 1H, *J*= 5.8 Hz; N-C*H*-CH_2), 5.32 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 5.34 (d, 1H, *J*= 2.2 Hz; C(*H*)H=C), 7.25 (d, 2H, *J*= 8.5 Hz; Ts-*H*), 7.44 (t, 1H, *J*= 7.6 Hz; Ar-*H*), 7.50 (d, 1H, *J*= 7.9 Hz; Ar-*H*), 7.52-7.57 (m, 2H; Ar-*H*), 7.66 (d, 2H, *J*= 8.3 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.7 (CH_2), 21.4 (CH_3), 24.3 (CH_2), 26.7 (CH_2), 41.6 (CH_2), 55.2 (CH), 117.8 (CH_2), 123.9 (CH, $J_{C\text{-}F}$ = 3.9 Hz), 124.0 (Cq, $J_{C\text{-}F}$ = 270 Hz), 124.3 (CH, $J_{C\text{-}F}$ = 3.7 Hz), 127.0 (CH), 128.8 (CH), 129.6 (CH), 130.4 (CH), 130.7 (Cq, $J_{C\text{-}F}$ = 31.9 Hz), 138.2 (Cq), 141.8 (Cq), 143.0 (Cq), 145.8 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF): δ -62.43 (3F, s).

IR: 2941.6 cm^{-1}, 2861.0 cm^{-1}, 2229.2 cm^{-1}, 1597.2 cm^{-1}, 1444.8 cm^{-1}, 1399.5 cm^{-1}, 1330.8 cm^{-1}, 1253.2 cm^{-1}, 1215.5 cm^{-1}, 1153.6 cm^{-1}, 1122.8 cm^{-1}, 1092.3 cm^{-1}, 1071.4 cm^{-1}, 958.7 cm^{-1}, 907.7 cm^{-1}, 811.9 cm^{-1}, 765.0 cm^{-1}, 729.4 cm^{-1}, 654.7 cm^{-1}, 613.3 cm^{-1}.

MS (ESI): Chemical formula $C_{21}H_{22}F_3NO_2S$, **[M+Na]$^+$** theoretical *m/z* 432.1215, found *m/z* 432.1217.



5m

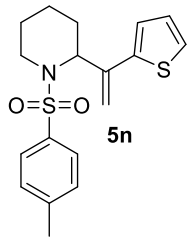
3-(1-(1-Tosylpiperidin-2-yl)vinyl)pyridine 5m Following the described procedure, 48 mg (0.3 mmol) of 3-bromopyridine **2v** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 38 mg of 3-(1-(1-tosylpiperidin-2-yl)vinyl)pyridine **5m** as an amber oil (EP/AcOEt 6/4, yield 56%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.24-1.31 (m, 1H; N-CH_2-C(*H*)H), 1.33-1.42 (m, 2H; CH_2-C*H*$_2$-CH_2), 1.42-1.53 (m, 2H; CH-C(*H*)H-CH_2 and N-CH_2-C(*H*)H), 1.67-1.70 (m, 1H; CH-C(*H*)H-CH_2), 2.39 (s, 3H; Ar-CH_3), 3.10 (td, 1H, *J*= 12.8, 3.3 Hz; N-C(*H*)H-CH_2), 3.66 (m, 1H; N-C(*H*)H-CH_2), 5.20 (d broad, 1H, *J*= 10.7 Hz; N-C*H*-CH_2), 5.33 (d narrow, 1H, *J*= 2.2 Hz; C(*H*)H=C), 5.34 (d narrow, 1H, *J*= 2.2 Hz; C(*H*)H=C), 7.24 (m, 3H, Ts-*H,* Ar-*H,*), 7.63 (dt, 1H, *J*= 7.9, 1.7 Hz; Ar-*H*), 7.65 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 8.48-8.57 (m, 2H; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.6 (CH_2), 21.5 (CH_3), 24.2 (CH_2), 26.5 (CH_2), 41.6 (CH_2), 55.1 (CH), 118.1 (CH_2), 123.0 (CH), 127.0 (CH), 129.6 (CH), 134.4 (CH), 136.5 (Cq), 138.1 (Cq), 143.1 (Cq), 143.8 (Cq), 148.2 (CH), 148.8 (CH).

IR: 2945.3 cm^{-1}, 2870.4 cm^{-1}, 1480.3 cm^{-1}, 1371.6 cm^{-1}, 1334.1 cm^{-1}, 1287.0 cm^{-1}, 1202.4 cm^{-1}, 1182.7 cm^{-1}, 1153.0 cm^{-1}, 1111.8 cm^{-1}, 1090.6 cm^{-1}, 1024.5 cm^{-1}, 952.9 cm^{-1}, 922.6 cm^{-1}, 902.8 cm^{-1}, 874.9 cm^{-1}, 816.7 cm^{-1}, 746.5 cm^{-1}, 715.2 cm^{-1}, 692.3 cm^{-1}, 665.0 cm^{-1}, 640.5 cm^{-1}, 600.1 cm^{-1}, 564.5 cm^{-1}.

MS (ESI): Chemical formula $C_{19}H_{22}N_2O_2S$, **[M+H]$^+$** theoretical *m/z* 343.1480, found *m/z* 343.1472; **[M+Na]$^+$** theoretical *m/z* 365.1294, found *m/z* 365.1294.



5n

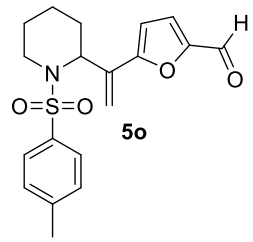
2-(1-(Thiophen-2-yl)vinyl)-1-tosylpiperidine 5n Following the described procedure, 49 mg (0.3 mmol) of 2-bromothiophene **2x** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 44 mg of 2-(1-(thiophen-2-yl)vinyl)-1-tosylpiperidine **5n** as a light yellow solid (EP/AcOEt 7/1, yield 63%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.28-1.37 (m, 1H; N-CH_2-C(*H*)H), 1.39-1.45 (m, 2H; CH_2-C*H*$_2$-CH_2), 1.49-1.53 (m, 1H; N-CH_2-C(*H*)H), 1.54-1.61 (m, 1H; CH-C(*H*)H-CH_2), 1.90-1.95 (m,1H; CH-C(*H*)H-CH_2), 2.41 (s,3H; Ar-C*H*$_3$), 3.21 (ddd, 1H, *J*=13.4, 12.4, 3.4 Hz; N-C(*H*)H-CH_2), 3.71-3.75 (m, 1H; N-C(*H*)H-CH_2), 5.12 (d, 1H, *J*= 2.1 Hz; C(*H*)H=C), 5.14-5.16 (m broad, 1H; N-C*H*-CH_2), 5.45 (d, 1H, *J*= 2.1 Hz; C(*H*)H=C), 7.70 (d, 2H, *J*= 8.3 Hz; Ts-*H*), 7.26 (d, 2H, *J*= 7.8 Hz; Ts-*H*), 6.97 (dd, 1H, *J*= 5.1, 3.6 Hz; Ar-*H*). 7.02 (dd, 1H, *J*= 3.6, 1.2 Hz; Ar-*H*), 7.17 (dd, 1H, *J*= 5.1, 1.2 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.8 (CH_2), 21.5 (CH_3), 24.4 (CH_2), 27.4 (CH_2), 42.1 (CH_2), 55.7 (CH), 115.8 (CH_2), 124.1 (CH), 124.4 (CH), 127.1 (CH), 127.2 (CH), 129.5 (CH), 138.1 (Cq), 140.0 (Cq), 142.87 (Cq), 142.95 (Cq).

IR: 2922.25 cm^{-1}, 2858.3 cm^{-1}, 1445.0 cm^{-1}, 1386.3 cm^{-1}, 1353.1 cm^{-1}, 1334.9 cm^{-1}, 1304.6 cm^{-1}, 1221.2 cm^{-1}, 1178.0 cm^{-1}, 1153.1 cm^{-1}, 1109.9 cm^{-1}, 1092.6 cm^{-1}, 1052.5 cm^{-1}, 1034.2 cm^{-1}, 959.4 cm^{-1}, 931.2 cm^{-1}, 912.2 cm^{-1}, 897.0 cm^{-1}, 850.9 cm^{-1}, 837.7 cm^{-1}, 814.9 cm^{-1}, 767.6 cm^{-1}, 721.2 cm^{-1}, 709.2 cm^{-1}, 688.3 cm^{-1}, 654.4 cm^{-1}, 602.1 cm^{-1}, 572.6 cm^{-1}.

MS (ESI): Chemical formula $C_{18}H_{21}NO_2S_2$, **[M+Na]$^+$** theoretical *m/z* 370.0905, found *m/z* 370.0904. **Mp**: 108.7-109.3°C



5o

5-(1-(1-Tosylpiperidin-2-yl)vinyl)furan-2-carbaldehyde 5o Following the described procedure, 52 mg (0.3 mmol) of 5-bromo-2-furaldehyde **2y** and 53 mg (0.2 mmol) of allene **1b** were reacted under the optimized conditions to afford 31 mg of 5-(1-(1-tosylpiperidin-2-yl)vinyl)furan-2-carbaldehyde **5o** as an orange oil (gradient EP/AcOEt from 7/1 to 7/3, yield 42%).

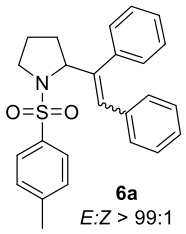
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.23-1.32 (m, 1H; N-CH_2-C(*H*)H), 1.43-1.51 (m, 3H; CH_2-C*H*$_2$-CH_2 and N-CH_2-C(*H*)H), 1.62-1.68 (m, 1H; CH-C(*H*)H-CH_2), 1.87-1.90 (m, 1H; CH-C(*H*)H-CH_2), 2.41 (s, 3H; Ar-C*H*$_3$), 3.19 (td, 1H, *J*= 12.2, 3.1 Hz; N-C(*H*)H-CH_2), 3.69 (dt, 1H, *J*= 13.9, 4.5 Hz; N-C(*H*)H-CH_2), 5.08 (d broad, 1H, *J*= 4.0 Hz; N-C*H*-CH_2), 5.40 (d narrow, 1H, *J*= 2.0 Hz; C(*H*)H=C), 5.96 (s, 1H; C(*H*)H=C), 6.72 (d, 1H, *J*= 3.8 Hz; Ar-*H*), 7.22 (d, 1H, *J*= 3.8 Hz; Ar-*H*), 7.27 (d, 2H, *J*= 7.9 Hz; Ts-*H*), 7.70 (d, 2H, *J*= 8.1 Hz; Ts-*H*), 9.58 (s, 1H; C*H*O).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 18.9 (CH_2), 21.4 (CH_3), 23.9 (CH_2), 27.4 (CH_2), 42.5 (CH_2), 53.7 (CH), 110.0 (CH), 118.5 (CH_2), 122.9 (CH), 127.1 (CH), 129.6 (CH), 135.8 (Cq), 137.7 (Cq), 143.3 (Cq), 151.6 (Cq), 158.1 (Cq), 177.3 (CHO).

IR: 2940.96 cm^{-1}, 2860.2 cm^{-1}, 1671.4 cm^{-1}, 1596.8 cm^{-1}, 1498.5 cm^{-1}, 1445.9 cm^{-1}, 1396.7 cm^{-1}, 1335.2 cm^{-1}, 1287.3 cm^{-1}, 1261.0 cm^{-1}, 1183.9 cm^{-1}, 1153.8 cm^{-1}, 1111.6 cm^{-1}, 1092.0 cm^{-1}, 1028.4 cm^{-1}, 962.6 cm^{-1}, 949.7 cm^{-1}, 915.7 cm^{-1}, 813.9 cm^{-1}, 755.1 cm^{-1}, 731.5 cm^{-1}, 709.3 cm^{-1}, 690.5 cm^{-1}, 659.4 cm^{-1}, 593.4 cm^{-1}.

MS (ESI): Chemical formula $C_{19}H_{21}NO_4S$, **[M+Na]$^+$** theoretical *m/z* 382.1083, found *m/z* 382.1081.

4.4.4 Characterization of pyrrolidines 6-7



6a
E:*Z* > 99:1

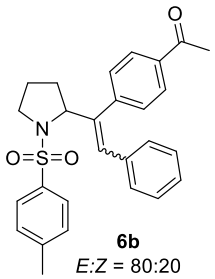
2-(1,2-Diphenylvinyl)-1-tosylpyrrolidine 6a Following the described procedure, 47 mg (0.3 mmol) of bromobenzene **2a** and 65 mg (0.2 mmol) of allene **1c** were reacted under the optimized conditions to afford 41 mg of 2-(1,2-Diphenylvinyl)-1-tosylpyrrolidine **6a** as a yellow oil (EP/AcOEt 7/1, yield 50%).

^{1}H-NMR (600 MHz, $CDCl_3$) (*E* isomer): δ= 1.54-1.59 (m, 1H; CH_2-C(H)*H*-CH_2), 1.64-1.68 (m, 1H; CH_2-C(H)*H*-CH_2), 1.69-1.76 (m, 2H; CH_2-C*H*$_2$-CH), 2.40 (s, 3H; Ar-C*H*$_3$), 3.32-3.36 (m,1H; N-C(H)*H*-CH_2), 3.46-3.49 (m, 1H; N-C(H)*H*-CH_2), 4.56 (dd, 1H, *J*= 8.0, 2.0 Hz; N-C*H*-CH_2), 6.62 (s, 1H; C=C*H*-Ph), 6.86-6.89 (m, 2H; Ar-*H*), 7.03-7.10 (m, 3H; Ar-*H*), 7.20-7.22 (m, 2H; Ar-*H*), 7.28-7.35 (m, 5H; Ar-*H* and Ts-*H*), 7.79 (d, 2H, *J*= 8.34; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$) (*E* isomer): δ= 21.4 (CH_3), 23.7 (CH_2), 31.4 (CH_2), 49.3 (CH_2), 66.5 (CH), 126.5 (CH), 127.3 (CH), 127.5 (CH), 127.7 (CH), 128.7 (CH), 129.2 (CH), 129.4 (CH), 129.6 (CH), 135.3 (Cq), 136.4 (Cq), 139.0 (Cq), 142.0 (Cq), 143.3 (Cq).

IR: 3022.7 cm^{-1}, 2973.6 cm^{-1}, 1597.3 cm^{-1}, 1492.4 cm^{-1}, 1445.0 cm^{-1}, 1342.1 cm^{-1}, 1303.6 cm^{-1}, 1260.2 cm^{-1}, 1205.7 cm^{-1}, 1182.9 cm^{-1}, 1153.9 cm^{-1}, 1090.4 cm^{-1}, 1037.4 cm^{-1}, 989.0 cm^{-1}, 917.7 cm^{-1}, 814.2 cm^{-1}, 757.5 cm^{-1}, 736.7 cm^{-1}, 695.2 cm^{-1}, 679.3 cm^{-1}, 659.2 cm^{-1}, 594.2 cm^{-1}, 581.7 cm^{-1}, 547.2 cm^{-1}.

MS (ESI): Chemical formula $C_{25}H_{25}NO_2S$, **[M+Na]$^+$** theoretical *m/z* 426.1498, found *m/z* 426.1497.



6b
E:*Z* = 80:20

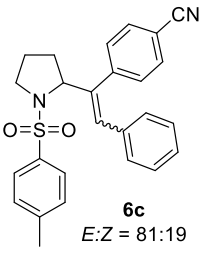
(*E* and Z)-1-(4-(2-Phenyl-1-(1-tosylpyrrolidin-2-yl)vinyl)phenyl)ethan-1-one 6b Following the described procedure, 60 mg (0.3 mmol) of 4-bromobenzophenone **2k** and 65 mg (0.2 mmol) of allene **1c** were reacted under the optimized conditions to afford 65 mg of 1-(*E* and Z)-(4-(2-phenyl-1-(1-tosylpyrrolidin-2-yl)vinyl)phenyl)ethan-1-one **6b** as a yellow oil (gradient EP/AcOEt 7/1 to 7/3, yield 73%).

^{1}H-NMR (600 MHz, $CDCl_3$); mixture of *E*/*Z* isomers in ratio 80/20: δ= 1.13-1.20 (m, 1H; CH_2-C(H)*H*-CH_2 minor isomer), 1.34-1.40 (m, 1H; CH_2-C(H)*H*-CH_2 minor isomer), 1.52-1.59 (m, 1H; CH_2-C(H)*H*-CH_2 major isomer), 1.61-1.73 (m, 3H; CH_2-C*H*$_2$-CH and CH_2-C(H)*H*-CH_2 major isomer), 1.75-1.80 (m, 1H; CH_2-C(*H*)H-CH minor isomer), 1.85-1.93 (m, 1H; CH_2-C(*H*)H-CH minor isomer), 2.35 (s, 1H; Ar-C*H*$_3$ minor isomer), 2.40 (s, 3H; Ar-C*H*$_3$ major isomer), 2.60 (s, 3H; COC*H*$_3$ major isomer); 2.63 (s, 1H; COC*H*$_3$ major isomer), 3.18-3.22 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.23-3.27 (m, 1H; N-C(H)*H*-CH_2 minor isomer); 3.31-3.35 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.42-3.46 (m, 1H; N-C(H)*H*-CH_2 major isomer), 4.53-4.55 (m, 1H; N-C*H*-CH_2 major isomer), 4.66 (m, 1H; N-C*H*-CH_2 minor isomer), 6.68 (s, 1H; C=C*H*-Ph major isomer), 6.70 (s, 1H; C=C*H*-Ph minor isomer), 6.86-6.87 (m, 2H; Ar-*H* major isomer), 7.03 (d, 1H, *J*= 8.6; Ts-*H* minor isomer), 7.06-7.09 (m, 3H; Ar-*H* major isomer), 7.10 (d, 1H, *J*= 8.3 Hz; Ar-*H* minor isomer), 7.30 (d, 2H, *J*= 7.7 Hz; Ts-*H* major isomer), 7.33 (m, 2H; Ar-*H* major isomer), 7.41-7.46 (m, 1H; Ar-*H* minor isomer), 7.73 (d, 1H, *J*= 8.5 Hz; Ar-*H* minor isomer), 7.78 (d, 2H, *J*= 8.3 Hz; Ts-*H* major isomer), 7.92 (d, 2H, *J*= 8.5 Hz; Ar-*H* major isomer), 7.96 (d, 1H, *J*= 8.5 Hz; Ar-*H* minor isomer).

^{13}C-NMR (150 MHz, $CDCl_3$) mixture of *E*/*Z* isomers in ratio 80/20: δ= 21.40 (CH_3 minor isomer), 21.43 (CH_3 major isomer), 23.8 (CH_2 major isomer), 24.3 (CH_2 minor isomer), 26.58 (CH_3 major isomer), 26.60 (CH_3 minor isomer), 31.5 (CH_2 major isomer), 32.6 (CH_2 minor isomer), 49.3 (CH_2 major isomer), 50.3 (CH_2 minor isomer), 58.3 (CH minor isomer), 66.2 (CH major isomer), 126.9 (CH major isomer), 127.1 (CH minor isomer), 127.4 (CH minor isomer), 127.46 (CH major isomer), 127.48 (CH minor isomer), 127.8 (CH major isomer), 128.3 (CH minor isomer), 128.5 (CH minor isomer), 128.6 (CH major isomer), 128.9 (CH minor isomer), 129.2 (CH major isomer), 129.4 (CH minor isomer), 129.7 (CH major isomer), 129.8 (CH major isomer), 130.1 (CH major isomer), 131.9 (CH minor isomer), 133.1 (Cq minor isomer), 135.1 (Cq major isomer), 135.92 (Cq major isomer), 135.97 (Cq major isomer), 136.8 (Cq minor isomer), 141.1 (Cq major isomer), 142.4 (Cq minor isomer), 143.1 (Cq minor isomer), 143.5 (Cq major isomer), 144.3 (Cq major isomer), 145.9 (Cq minor isomer), 197.8 (C=O major isomer), 198.0 (C=O minor isomer).

IR: 2968.5 cm^{-1}, 2870.4 cm^{-1}, 1736.2 cm^{-1}, 1679.8 cm^{-1}, 1600.7 cm^{-1}, 1557.3 cm^{-1}, 1492.2 cm^{-1}, 1445.8 cm^{-1}, 1400.5 cm^{-1}, 1343.2 cm^{-1}, 1304.3 cm^{-1}, 1264.4 cm^{-1}, 1205.6 cm^{-1}, 1182.1 cm^{-1}, 1157.2 cm^{-1}, 1091.1 cm^{-1}, 1032.2 cm^{-1}, 991.6 cm^{-1}, 957.4 cm^{-1}, 915.5 cm^{-1}, 815.6 cm^{-1}, 752.1 cm^{-1}, 732.8 cm^{-1}, 696.2 cm^{-1}, 663.7 cm^{-1}, 588.9 cm^{-1}, 551.7 cm^{-1}.

MS (ESI): Chemical formula $C_{27}H_{27}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 468.1603, found *m/z* 468.1607.



6c
E:*Z* = 81:19

(*E* and Z)-4-(2-phenyl-1-(1-tosylpyrrolidin-2-yl)vinyl)benzonitrile 6c Following the described procedure, 55 mg (0.3 mmol) of 4-bromobenzonitrile **2q** and 65 mg (0.2 mmol) of allene **1c** were reacted under the optimized conditions to afford 69 mg of (*E* and Z)-4-(2-phenyl-1-(1-tosylpyrrolidin-2-yl)vinyl)benzonitrile **6c** as a yellow oil (gradient EP/AcOEt 7/1 to 7/3, yield 80%).

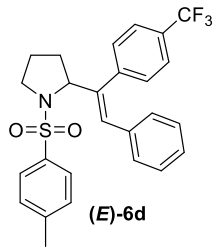
^{1}H-NMR (600 MHz, $CDCl_3$) mixture of *E*/*Z* isomers in ratio 81/19: δ= 1.17-1.22 (m, 1H; CH_2-C(H)*H*-CH_2 minor isomer),1.36-1.40 (m, 1H; CH_2-C(H)*H*-CH_2 minor isomer), 1.53-1.57 (m, 1H; CH_2-C(H)*H*-CH_2 major isomer), 1.63-1.66 (m, 3H; (m, 1H; CH_2-C(*H*)-CH and CH_2-C(H)*H*-CH_2 major isomer), 1.72-1.79 (m, 1H; CH_2-C(*H*)H-CH minor isomer and CH_2-C(*H*)H-CH major isomer), 1.88-1.95 (m, 1H; CH_2-C(*H*)H-CH minor isomer), 2.36 (s, 1H; Ar-C*H*$_3$ minor isomer), 2.41 (s, 3H; Ar-C*H*$_3$ major isomer), 3.19-3.22 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.22-3.26 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.31-3.35 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.40-3.44 3.31-3.35 (m, 1H; N-C(H)*H*-CH_2 major isomer), 4.49 (dd, 1H, *J*= 7.9; 3.5 Hz; N-C*H*-CH_2 major isomer), 4.63 (t, 1H, *J*= 7.0 Hz; N-C*H*-CH_2 minor isomer), 6.70 (s, 1H; C=C*H*-Ph major isomer), 6.81-6.85 (m, 2H; C=C*H*-Ph minor isomer and Ar-*H*), 7.03 (d, 1H, *J*= 8.3 Hz; Ar-*H* minor isomer), 7.06-7.14 (m, 4H; Ar-*H* mixture of isomers), 7.31 (m, 3H; Ar-*H* mixture of isomers), 7.37 (d, 2H, *J*= 8.5 Hz; Ar-*H* minor isomer), 7.43-7.47 (m, 1H; Ar-*H* minor isomer), 7.61 (d, 2H, *J*= 8.4; Ar-*H* major isomer), 7.66 (d, 1H, *J*= 8.3 Hz; Ar-*H* minor isomer), 7.75-7.63 (m, 3H; Ar-*H* mixture of isomers).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.3 (CH_3 minor isomer), 21.3 (CH_3 major isomer), 23.6 (CH_2 major isomer), 24.1 (CH_2 minor isomer), 31.5 (CH_2 major isomer), 32.5 (CH_2 minor isomer), 49.2 (CH_2 major isomer), 50.1 (CH_2 minor isomer), 57.9 (CH minor isomer), 65.9

(CH major isomer), 110.9 (Cq minor isomer), 111.0 (Cq major isomer), 118.5 (Cq major isomer), 118.7 (Cq minor isomer), 126.9 (CH major isomer), 127.1 (CH minor isomer), 127.37 (CH major isomer), 127.31 (CH minor isomer), 127.8 (CH major isomer), 128.2 (CH), 128.9 (CH minor isomer), 128.95 (CH major isomer), 129.1 (CH major isomer), 129.2 (CH minor isomer), 129.5 (CH major isomer), 130.4 (CH major isomer), 130.5 (CH minor isomer), 131.4 (CH major isomer), 132.2 (CH major isomer), 132.4 (CH minor isomer), 132.6 (Cq major isomer), 134.7 (Cq), 135.4 (Cq major isomer), 136.3 (Cq minor isomer), 140.3 (Cq major isomer), 141.6 (Cq minor isomer), 143.1 (Cq minor isomer), 143.4 (Cq major isomer), 143.9 (Cq major isomer), 145.5 (Cq minor isomer).

IR: 3021.7 cm^{-1}, 2974.3 cm^{-1}, 2226.6 cm^{-1}, 2096.0 $^{-1}$, 1732.4 cm^{-1}, 1597.4 cm^{-1}, 1492.3 cm^{-1}, 1446.1 cm^{-1}, 1398.9 cm^{-1}, 1343.1 cm^{-1}, 1304.2 cm^{-1}, 1258.6 cm^{-1}, 1207.0 cm^{-1}, 1184.3 cm^{-1}, 1157.0 cm^{-1}, 1091.0 cm^{-1}, 1033.7 cm^{-1}, 992.1 cm^{-1}, 914.6 cm^{-1}, 815.5 cm^{-1}, 752.9 cm^{-1}, 696.0 cm^{-1}, 663.8 cm^{-1}, 606.9 cm^{-1}, 591.9 cm^{-1}, 562.2 cm^{-1}, 550.4 cm^{-1}.

MS (ESI): Chemical formula $C_{26}H_{24}N_2O_2S$, **[M+Na]$^+$** theoretical *m/z* 451.1450, found *m/z* 451.1447.



(***E***)-6d

(*E*)-2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)vinyl)-1-tosylpyrrolidine 6d Following the described procedure, 67 mg (0.3 mmol) of 4-bromobenzotrifluoride **2s** and 65 mg (0.2 mmol) of allene **1c** were reacted under the optimized conditions to afford 44 mg of (*E*)-2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)vinyl)-1-tosylpyrrolidine **(*E*)-6d** as a yellow oil (EP/AcOEt 7/1, yield 47%).

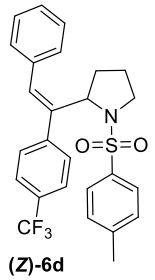
^{1}H-NMR (600 MHz, $CDCl_3$); *E* isomer: δ= 1.54-1.58 (m, 1H; CH_2-C(H)*H*-CH_2), 1.64-1.74 (m, 3H; CH_2-C(*H)H*-CH and CH_2-C(H)*H*-CH_2), 2.41 (s, 3H; Ar-CH_3), 3.32-3.36 (m, 1H; N-C(H)*H*-CH_2), 4.52 (ddd, 1H, *J*= 7.8, 4.1, 1.1 Hz; N-C*H*-CH_2), 6.69 (s, 1H; C=C*H*-Ph), 6.85 (dd, 2H; *J*= 6.4,1.7 Hz; Ar-*H*), 7.08-7.10 (m, 3H; Ar-*H*), 7.31 (d, 2H, *J*= 7.7 Hz; Ts-*H*), 7.36 (d, 2H, *J*= 8.4 Hz; Ar-*H*), 7.59 (d, 2H, *J*= 7.8 Hz; Ar-*H*), 7.78 (d, 2H, *J*= 8.4 Hz; Ts-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 23.8 (CH_2), 31.6 (CH_2), 49.4 (CH_2), 66.3 (CH), 124.3 (Cq, $J_{C\text{-}F}$ = 271 Hz), 125.0 (Cq), 125.6 (CH, $J_{C\text{-}F}$ = 3.6 Hz), 126.9 (CH), 127.5 (CH), 127.9 (CH), 128.8 (CH), 129.5 (Cq, $J_{C\text{-}F}$ =32.3 Hz), 129.7 (CH), 130.0 (CH), 135.1 (Cq), 135.9 (Cq), 140.8 (Cq), 142.9 (Cq), 143.5 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF): δ -62.31 (3F, s).

IR: 2981.1 cm^{-1}, 1615.7 cm^{-1}, 1598.7 cm^{-1}, 1447.0 cm^{-1}, 1340.3 cm^{-1}, 1321.8 cm^{-1}, 1183.5 cm^{-1}, 1158.6 cm^{-1}, 1107.3 cm^{-1}, 1090.3 cm^{-1}, 1065.6 cm^{-1}, 1016.3 cm^{-1}, 985.3 cm^{-1}, 913.0 cm^{-1}, 886.9 cm^{-1}, 855.2 cm^{-1}, 835.6 cm^{-1}, 816.0 cm^{-1}, 751.0 cm^{-1}, 725.2 cm^{-1}, 710.6 cm^{-1}, 694.8 cm^{-1}, 679.2 cm^{-1}, 662.2 cm^{-1}, 626.8 cm^{-1}, 607.7 cm^{-1}, 584.5 cm^{-1}, 552.0 cm^{-1}.

MS (ESI): Chemical formula $C_{26}H_{24}F_3NO_2S$, **[M+Na]$^+$** theoretical *m/z* 494.1372, found *m/z* 494.1371.



(***Z***)-6d

(*Z*)-2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)vinyl)-1-tosylpyrrolidine 6d' Following the described procedure, 67 mg (0.3 mmol) of 4-bromobenzotrifluoride **2s** and 65 mg (0.2 mmol) of allene **1c** were reacted under the optimized conditions to afford 8 mg of (*Z*)-2-(2-phenyl-1-(4-(trifluoromethyl)phenyl)vinyl)-1-tosylpyrrolidine **(*Z*)-6d** as a yellow oil (EP/AcOEt 7/1, yield 8%).

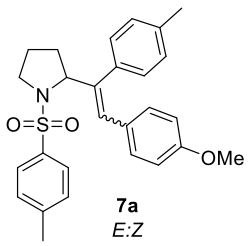
^{1}H-NMR (600 MHz, $CDCl_3$); *Z* isomer: δ= 1.14-1.21 (m, 1H; CH_2-C(H)*H*-CH_2), 1.34-1.41 (m, 1H; CH_2-C(H)*H*-CH_2), 1.75-1.80 (m, 1H; CH_2-C(*H)H*-CH), 1.87-1.93 (m, 1H; CH_2-C(*H)H*-CH), 2.34 (s, 3H; Ar-CH_3), 3.17-3.21 (m, 1H; N-C(H)*H*-CH_2), 3.24-3.28 (m, 1H; N-C(H)*H*-CH_2), 4.65 (t, 1H, *J*= 6.8 Hz; N-C*H*-CH_2), 6.69 (s, 1H; C=C*H*-Ph), 7.04 (d, 2H; *J*= 8.5 Hz; Ts-*H*), 7.10 (d, 2H; *J*= 8.5 Hz; Ts-*H*), 7.33 (d, 2H, *J*= 7.9 Hz; Ar-*H*), 7.41-7.47 (m, 3H; Ar-*H*), 7.62 (d, 2H, *J*= 7.9 Hz; Ar-*H*), 7.75 (d, 2H, *J*= 7.9 Hz; Ar-*H*).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3), 24.4 (CH_2), 32.6 (CH_2), 50.4 (CH_2), 58.3 (CH), 124.8 (CH, $J_{C\text{-}F}$ = 3.3 Hz), 125.7 (Cq, $J_{C\text{-}F}$ = 269 Hz), 127.2 (CH), 127.6 (CH), 128.4 (CH), 129.2 (CH), 129.4 (CH), 129.6 (Cq, $J_{C\text{-}F}$ = 32.7 Hz), 130.3 (CH), 132.2 (CH), 133.2 (Cq), 136.8 (Cq), 142.2 (Cq), 143.2 (Cq), 144.5 (Cq).

^{19}F-NMR (600 MHz; $CDCl_3$, NaF**):** δ -62.27 (3F, s).

IR: 2921.6 cm^{-1}, 2860.8 cm^{-1}, 1613.9 cm^{-1}, 1595.8 cm^{-1}, 1492.0 cm^{-1}, 1406.6 cm^{-1}, 1347.5 cm^{-1}, 1317.7 cm^{-1}, 1260.5 cm^{-1}, 1184.5 cm^{-1}, 1157.5 cm^{-1}, 1105.3 cm^{-1}, 1063.2 cm^{-1}, 1017.7 cm^{-1}, 999.8 cm^{-1}, 974.4 cm^{-1}, 923.2 cm^{-1}, 862.2 cm^{-1}, 826.9 cm^{-1}, 817.6 cm^{-1}, 755.6 cm^{-1}, 744.1 cm^{-1}, 709.0 cm^{-1}, 698.7 cm^{-1}, 664.7 cm^{-1}, 638.4 cm^{-1}, 623.7 cm^{-1}, 615.5 cm^{-1}, 581.9 cm^{-1}, 551.3 cm^{-1}.

MS (ESI): Chemical formula $C_{26}H_{24}F_3NO_2S$, **[M+Na]$^+$** theoretical *m/z* 494.1372, found *m/z* 494.1373.



7a
E:Z

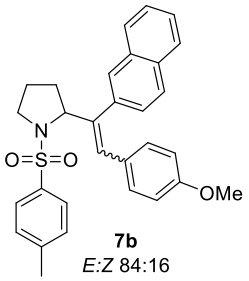
(*E* and *Z*)-2-(2-(4-Methoxyphenyl)-1-(p-tolyl)vinyl)-1-tosylpyrrolidine 7a Following the described procedure, 51 mg (0.3 mmol) of 4-bromotoluene **2b** and 72 mg (0.2 mmol) of allene **1d** were reacted under the optimized conditions to afford 41 mg of (*E* and *Z*)-2-(2-(4-methoxyphenyl)-1-(p-tolyl)vinyl)-1-tosylpyrrolidine **7a** as a yellow oil (EP/AcOEt 7/1, yield 45%).

^{1}H-NMR (600 MHz, $CDCl_3$) mixture of *E*/*Z* isomers in ratio 64/36: δ= 1.51-1.57 (m, 2H; CH_2-C*H*$_2$-CH_2 major isomer), 1.58-1.74 (m, 5H; CH_2-C*H*$_2$-CH mixture of isomers), 1.74-1.83 (m, 1H; CH_2-C*H*$_2$-CH_2 minor isomer), 2.36 (s, 3H; Ar-C*H*$_3$), 2.39 (s, 3H; Ar-C*H*$_3$), 3.25-3.34 (m, 2H; N-C(H)*H*-CH_2 mixture of isomers), 3.43-3.48 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.49-3.54 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.72 (s, 3H; OC*H*$_3$), 4.52 (dd, 1H, *J*= 7.6, 2.8 Hz; N-C*H*-CH_2 major isomer), 4.64 (m, 1H; N-C*H*-CH_2 minor isomer), 6.51 (s, 1H; C=C*H* major isomer), 6.65 (d, 2H, *J*= 9.0 Hz; Ar-*H* major isomer), 6.81 (d, 2H, *J*= 9.0 Hz; Ar-*H* major isomer), 7.08 (d, 2H, *J*= 8.3 Hz; Ar-*H* major isomer), 7.14 (d, 2H, *J*= 7.9 Hz; Ar-*H* major isomer), 7.24 (d, 1H, *J*= 8.6 Hz; Ar-*H* minor isomer), 7.28 (m, 2H; Ar-*H* mixture of isomers), 7.34 (d, 1H, *J*= 8.3 Hz; Ar-*H* minor isomer), 7.46 (d, 1H, *J*= 9.0 Hz; Ar-*H* minor isomer), 7.73-7.80 (m, 3H; Ar-*H* mixture of isomers).

^{13}C-NMR (150 MHz, $CDCl_3$) mixture of *E*/*Z* isomers in ratio 64/36: δ= 21.2 (CH_3 major isomer), 21.47 (CH_3 major isomer), 21.52 (minor isomer), 23.5 (CH_2 minor isomer), 23.7 (CH_2 major isomer), 31.4 (CH_2 major isomer), 31.9 (CH_2 minor isomer), 49.0 (CH_2 minor isomer), 49.2 (CH_2 major isomer), 55.1 (OCH_3 major isomer), 62.9 (OCH_3 minor isomer), 66.7 (CH major isomer), 67.2 (CH minor isomer), 113.3 (CH major isomer), 115.6 (CH minor isomer), 121.4 (CH major isomer), 126.8 (CH minor isomer), 127.46 (CH minor isomer), 127.5 (CH major isomer), 128.2 (CH minor isomer), 128.5 (CH minor isomer), 128.8 (CH minor isomer), 129.0 (CH), 129.26 (CH minor isomer), 129.3 (CH major isomer), 129.5 (CH major isomer), 129.6 (CH major isomer), 129.7 (CH minor isomer), 129.8 (CH major isomer), 130.4 (CH minor isomer), 134.9(Cq minor isomer), 135.5 (Cq major isomer), 136.2 (Cq major isomer), 136.8 (Cq major isomer), 139.9 (Cq major isomer), 140.3 (Cq minor isomer), 143.2 (Cq major isomer), 143.6 (Cq minor isomer), 147.5 (Cq minor isomer), 148.9 (Cq minor isomer), 158.2 (Cq major isomer).

IR: 2922.3 cm^{-1}, 1604.3 cm^{-1}, 1507.9 cm^{-1}, 1421.1 cm^{-1}, 1342.9 cm^{-1}, 1302.3 cm^{-1}, 1248.7 cm^{-1}, 1209.2 cm^{-1}, 1177.4 cm^{-1}, 1157.3 cm^{-1}, 1092.1 cm^{-1}, 1033.9 cm^{-1}, 887.9 cm^{-1}, 815.5 cm^{-1}, 756.5 cm^{-1}, 732.8 cm^{-1}, 664.0 cm^{-1}, 591.6 cm^{-1}.

MS (ESI): Chemical formula $C_{27}H_{29}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 470.1760, found *m/z* 470.1761.



7b
E:Z 84:16

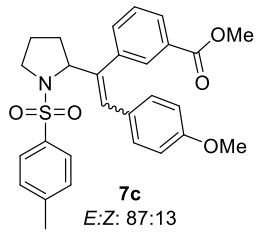
***(E* and *Z*)-2-(2-(4-Methoxyphenyl)-1-(1-naphtyl)vinyl)-1-tosylpyrrolidine 7b** Following the described procedure, 62 mg (0.3 mmol) of 1-bromonaphthalene **2i** and 72 mg (0.2 mmol) of allene **1d** were reacted under the optimized conditions to afford 30 mg of *(E* and *Z*)-2-(2-(4-Methoxyphenyl)-1-(1-naphtyl)vinyl)-1-tosylpyrrolidine **7b** as a white solid (EP/AcOEt 7/1, yield 31%).

^{1}H-NMR (600 MHz, $CDCl_3$), mixture of *E*/*Z* isomers in ratio 84/16: δ= 0.80-0.95 (m, 1H; CH_2-C(H)*H*-CH_2 minor isomer), 1.15-1.36 (m, 2H; CH_2-C(H)*H*-CH_2 and CH_2-C(*H*)H-CH minor isomer), 1.53-1.59 (m, 1H; CH_2-C(H)*H*-CH_2 major isomer), 1.62-1.73 (m, 2H; CH_2-C(H)*H*-CH_2 and CH_2-C(*H*)H-CH major isomer), 1.74-1.95 (m, 1H; CH_2-C(*H*)H-CH major isomer), 1.83-1.95 (m, 1H; CH_2-C(*H*)H-CH minor isomer), 2.37 (s, 3H, Ar-C*H*$_3$ minor isomer), 2.340 (s, 3H, Ar-C*H*$_3$ major isomer), 3.15-3.24 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.27-3.33 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.34-3.39 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.43-3.49 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.68 (s, 3H; OC*H*$_3$ major isomer), 3.92 (s, 3H; OC*H*$_3$ minor isomer), 4.66 (dd, 1H, *J*= 7.4, 3.4 Hz; N-C*H*-CH_2 major isomer), 4.79 (t broad, 1H, *J*= 6.9 Hz; N-C*H*-CH_2 minor isomer), 6.57 (d, 2H, *J*= 9.0 Hz; *p*-OC*H*$_3$-Ar-*H* major isomer), 6.65 (s, 1H; C=C*H* major isomer), 6.72 (s, 1H; C=C*H* minor isomer), 6.83 (d, 2H, *J*= 8.8 Hz; *p*-OC*H*$_3$-Ar-*H* major isomer), 7.0 6.57 (d, 1H, *J*= 8.7 Hz; Ar-*H* minor isomer), 7.07 (d, 1H, *J*= 8.0 Hz; *p*-OC*H*$_3$-Ar-*H* minor isomer), 7.20 (d, 1H, *J*= 8.0 Hz; *p*-OC*H*$_3$-Ar-*H* minor isomer), 7.28-7.31 (m, 4H; Ts-*H* mixture of isomers), 7.46-7.50 (m, 3H; Ts-*H* mixture of isomers), 7.69 (s, 1H; Ar-*H* major isomer), 7.77-7.88 (m, 6H, Ar-*H* mixture of isomers), 7.98 (s, 1H; Ar-*H* minor isomer).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3 major isomer), 23.8 (CH_2 major isomer), 24.5 (CH_2 minor isomer), 31.5 (CH_2 major isomer), 32.7 (CH_2 minor isomer), 49.2 (CH_2 major isomer), 50.4 (CH_2 minor isomer), 55.0 (CH_3 major isomer), 55.4 (CH_3 minor isomer), 58.5 (CH minor isomer), 66.8 (CH major isomer), 113.3 (CH major isomer), 113.7 (CH minor isomer), 125.7 (CH minor isomer), 125.9 (CH minor isomer), 125.9 (CH major isomer), 126.0 (CH major isomer), 127.1 (CH minor isomer), 127.5 (CH major isomer), 127.53 (CH major isomer), 127.6 (CH minor isomer), 127.0 (CH major isomer), 127.98 (CH major isomer), 128.04 (CH major isomer), 128.08 (CH major isomer), 128.1 (CH major isomer), 128.4 (CH major isomer), 128.7 (Cq minor isomer), 129.0 (Cq minor isomer), 129.3 (CH minor isomer), 129.6 (CH major isomer), 129.8 (Cq minor isomer), 130.5 (CH major isomer), 131.3 (CH major isomer), 132.5 (Cq), 133.1 (Cq minor isomer), 133.6 (Cq major isomer), 133.7 (Cq minor isomer), 135.5 (Cq major isomer), 136.9 (Cq major isomer), 138.8 (Cq minor isomer), 139.6 (Cq major isomer), 142.4 (Cq minor isomer), 143.0 (Cq minor isomer), 143.3 (Cq major isomer), 158.3 (Cq major isomer), 158.7 (Cq minor isomer).

IR: 2955.4 cm^{-1}, 1605.1 cm^{-1}, 1509.1 cm^{-1}, 1455.2 cm^{-1}, 1341.7 cm^{-1}, 1301.8 cm^{-1}, 1249.2 cm^{-1}, 1196.2 cm^{-1}, 1176.8 cm^{-1}, 1155.8 cm^{-1}, 1090.9 cm^{-1}, 1031.3 cm^{-1}, 994.1 cm^{-1}, 900.1 cm^{-1}, 862.1 cm^{-1}, 815.6 cm^{-1}, 749.5 cm^{-1}, 708.4 cm^{-1}, 662.6 cm^{-1}, 587.4 cm^{-1}.

MS (ESI): Chemical formula $C_{30}H_{29}NO_3S$, **[M+Na]$^+$** theoretical *m/z* 506.1760, found *m/z* 506.1763. **Mp:** 71.0-72.3°C



7c
E:Z: 87:13

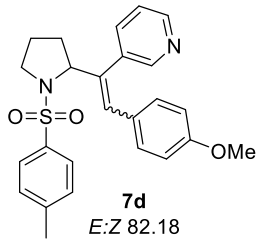
***(E* and *Z)*-Methyl 3-(2-(4-methoxyphenyl)-1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate 7c** Following the described procedure, 65 mg (0.3 mmol) of methyl 3-bromobenzoate **2o** and 72 mg (0.2 mmol) of allene **1d** were reacted under the optimized conditions to afford 52 mg of *(E* and *Z)*-Methyl 3-(2-(4-methoxyphenyl)-1-(1-tosylpyrrolidin-2-yl)vinyl)benzoate **7c** as a transparent oil (EP/AcOEt 7/1, yield 53%).

^{1}H-NMR (600 MHz, $CDCl_3$), mixture of *E*/*Z* isomers in ratio 87/13: δ= 1.14-1.33 (m, 2H+H_2O; CH_2-C(H)*H*-CH_2 minor isomer), 1.36 (ep, 1H, *J*= 6.3 Hz; CH_2-C(H)*H*-CH_2 minor isomer), 1.52-1.59 (m, 1H; CH_2-C(H)*H*-CH_2 major isomer), 1.60-1.73 (m, 3H; CH_2-C(H)*H*-CH_2 and CH_2-C*H*$_2$-CH major isomer), 1.77-1.83 (m, 1H; CH_2-C(*H*)H-CH minor isomer), 1.86-1.92 (m, 1H; CH_2-C(*H*)H-CH minor isomer), 2.36 (s, 3H; Ar-C*H*$_3$), 2.39 (s, 3H; Ar-C*H*$_3$), 3.16-3.20 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.25-3.29 (m, 1H; N-C(H)*H*-CH_2 minor isomer), 3.29-3.35 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.39-3.44 (m, 1H; N-C(H)*H*-CH_2 major isomer), 3.71 (s, 3H; OC*H*$_3$ major isomer), 3.89 (s, 3H; CO_2C*H*$_3$ major isomer), 3.90 (s, 3H; OC*H*$_3$ minor isomer), 3.92 (s, 3H; CO_2C*H*$_3$ minor isomer), 4.53 8(dd, 1H, *J*= 7.3, 3.8 Hz; N-C*H*-CH_2 major isomer), 4.68 (dd broad, 1H, *J*= 6.8 Hz; N-C*H*-CH_2 minor isomer), 6.59-6.64 (m, 3H; C=C*H* and Ar-*H* major isomer), 6.64 (s, 1H; C=C*H* minor isomer), 6.76 (d, 2H, *J*= 9 Hz; Ar-*H* major isomer), 6.97 (d, 1H, *J*= 8.7 Hz; Ar-*H* minor isomer), 7.05 (d, 2H, *J*= 8.5 Hz; Ts-*H* minor isomer), 7.16 (d, 2H, *J*= 8.5 Hz; Ts-*H* minor isomer), 7.25 (d, 1H, *J*= 9.6 Hz; Ar-*H* minor isomer), 7.29 (d, 2H, *J*= 7.8 Hz; Ts-*H* major isomer), 7.40-7.46 (m,3H; *m*-CO_2Me-Ar-*H* major isomer), 7.78 (d, 2H, *J*= 7.8 Hz; Ts-*H* major isomer), 7.85 (t broad, 1H, *J*= 1.14 Hz; *m*-CO_2Me-Ar-*H* major isomer), 7.98 (dt, 1H, *J*= 7.2, 1.7 Hz; *m*-CO_2Me-Ar-*H* major isomer), 7.99-8.00 (m, 1H, Ar-*H* minor isomer), 8.09 (t, 1H, *J*= 1.8 Hz, *m*-CO_2Me-Ar-*H* minor isomer).

^{13}C-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_3 major isomer), 23.8 (CH_2 major isomer), 24.4 (CH_2 minor isomer), 31.5 (CH_2 major isomer), 32.6 (CH_2 minor isomer), 49.2 (CH_2 major isomer), 50.3 (CH_3 minor isomer), 52.1 (CH_3 major isomer), 55.1 (CH_3 major isomer), 55.4 (CH_3 minor isomer), 58.3 (CH minor isomer), 66.4 (CH major isomer), 67.1 (CH_2 minor isomer), 113.3 (CH major isomer), 113.7 (CH minor isomer), 125.3 (CH), 127.55 (CH major isomer), 127.62 (CH minor isomer), 128.2 (CH minor isomer), 128.4 (CH minor isomer), 128.5 (CH major isomer), 128.6 (Cq major isomer), 128.96 (CH major isomer), 129.01 (CH minor isomer), 129.4 (CH minor isomer), 129.5 (Cq minor isomer), 129.65 (CH), 129.7 (Cq), 130.42 (CH major isomer), 130.47 (CH major isomer), 130.67 (Cq), 131.6 (CH), 133.5 (CH), 134.60 (CH major isomer), 134.63 (CH), 138.8 (Cq major isomer), 139.6 (Cq major isomer), 140.3 (Cq), 141.2 (Cq minor isomer), 141.5 (Cq minor isomer), 143.1 (Cq minor isomer), 143.4 (Cq major isomer), 158.4 (Cq major isomer), 158.8 (Cq minor isomer), 166.9 (Cq major isomer), 167.2 (Cq minor isomer).

IR: 2950.5 cm^{-1}, 1718.9 cm^{-1}, 1605.2 cm^{-1}, 1509.5 cm^{-1}, 1439.3 cm^{-1}, 1343.4 cm^{-1}, 1285.5 cm^{-1}, 1247.7 cm^{-1}, 1204.3 cm^{-1}, 1177.0 cm^{-1}, 1155.6 cm^{-1}, 1089.4 cm^{-1}, 1031.3 cm^{-1}, 998.3 cm^{-1}, 814.9 cm^{-1}, 750.4 cm^{-1}, 658.1 cm^{-1}, 582.5 cm^{-1}, 547.2 cm^{-1}.

MS (ESI): Chemical formula $C_{28}H_{29}NO_5S$, **[M+Na]$^+$** theoretical *m/z* 514.1659, found *m/z* 514.1660.



7d
E:Z 82.18

***(E* and *Z)*-3-(2-(4-methoxyphenyl)-1-(1-tosylpyrrolidin-2-yl)vinyl)pyridine 7d** Following the described procedure, 47 mg (0.3 mmol) of 3-bromopyridine **2w** and 72 mg (0.2 mmol) of allene **1d** were reacted under the optimized conditions to afford 15 mg of *(E* and *Z)*-3-(2-(4-methoxyphenyl)-1-(1-tosylpyrrolidin-2-yl)vinyl)pyridine **7d** as a transparent oil (EP/AcOEt 6/4, yield 17%).

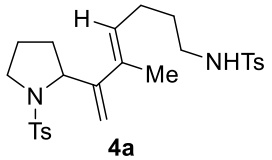
^{1}H-NMR (600 MHz, $CDCl_3$), mixture of *E*/*Z* isomers in ratio 82/18: δ= 1.17-1.28 (m, 2H; CH_2-C(*H*)H-CH_2 major isomer and CH_2-C(*H*)H-CH_2 minor isomer), 1.38 (m, 1H; CH_2-C(*H*)H-CH_2 minor isomer), 1.49-1.55 (m, 1H; CH-C(*H*)H-CH_2 major isomer), 1.66-1.71 (m, 1H;), 1.72-1.80 (m, 2H; CH_2-*C(H)*H-CH of both isomers), 1.87-1.95 (m, 1H; CH_2-*C(H)*H-CH minor isomer), 2.37 (s, 3H; Ar-C*H*$_3$), 2.41 (s, 3H; Ar-C*H*$_3$), 3.18-3.23 (m, 1H; N-C(*H*)H-CH_2 minor isomer), 3.25-3.28 (m,1H; N-C(*H*)H-CH_2 minor isomer), 3.31-3.35 (m, 1H; N-C(*H*)H-CH_2 major isomer), 3.37-3.41 (m, 1H; N-C(*H*)H-CH_2 major isomer), 3.72 (s, 3H; OC*H*$_3$), 3.91 (s, 3H; OC*H*$_3$), 4.47 (dd, 1H, *J*= 7.8, 4.0 Hz; N-C*H*-CH_2 major isomer), 4.67 (t broad, 1H, *J*= 7.6 Hz; N-C*H*-CH_2 minor isomer), 6.63 (s, 1H; C=C*H* minor isomer); 6.64 (d, 2H, *J*= 2.2 Hz; Ar-*H* mixture of isomers), 6.67 (s, 1H; C=C*H* major isomer), 6.79 (d, 2H, *J*= 9.0 Hz; Ar-*H* major isomer), 6.98 (d, 2H, *J*= 8.8 Hz; Ar-*H* minor isomer), 7.06 (d, 2H, *J*= 7.8 Hz; Ar-*H* minor isomer), 7.16 (d, 2H, *J*= 8.3 Hz; Ar-*H* minor isomer), 7.24 (d, 2H, *J*= 8.1 Hz; Ar-*H* minor isomer), 7.27-7.32 (m, 5H; mixture of isomers), 7.65 (dt, 1H, *J*= 8.1, 1.8 Hz; Ar-*H* major isomer), 7.77 (d, 2H, *J*= 8.2 Hz; Ar-*H* major isomer), 8.15 (dt, 1H, *J*= 7.8, 1.7 Hz; Ar-*H* minor isomer), 8.37 (d, 1H, *J*= 2.2 Hz; Ar-*H* major isomer), 8.54 (dd, 1H, *J*= 5.2,1.7 Hz; Ar-*H* major isomer), 8.57 (d, 1H, *J*= 3.7 Hz; Ar-*H* minor isomer), 8.63 (s, 1H, Ar-*H* minor isomer).

^{13}C-NMR (150 MHz, $CDCl_3$) mixture of *E*/*Z* isomers in ratio 82/18: δ= 17.7 (CH_3), 21.5 (CH_3), 23.3 (CH_2), 23.9 (CH_2), 24.5 (CH_2), 31.8 (CH_2), 34.4 (CH_2), 34.43 (CH_2), 49.5 (CH_2), 55.1 (OCH_3), 55.2 (OCH_3), 62.0 (CH), 66.4 (CH), 113.5 (CH), 113.8 (CH), 123.9 (CH), 126.8 (CH), 127.4 (CH), 127.6 (CH), 127.7 (CH), 128.2 (Cq), 129.5 (CH), 129.7 (CH), 129.8 (CH), 130.5 (CH), 134.9 (Cq), 135.2 (Cq), 136.2 (Cq), 138.5 (CH), 143.57 (Cq), 143.6 (Cq), 147.8 (Cq), 149.7 (CH), 158.7 (CH), 159.3 (Cq).

IR: 2954.6 cm^{-1}, 1605.2 cm^{-1}, 1508.8 cm^{-1}, 1455.7 cm^{-1}, 1407.3 cm^{-1}, 1343.4 cm^{-1}, 1301.6 cm^{-1}, 1247.8 cm^{-1}, 1176.2 cm^{-1}, 1156.0 cm^{-1}, 1089.5 cm^{-1}, 1027.2 cm^{-1}, 990.6 cm^{-1}, 811.8 cm^{-1}, 755.8 cm^{-1}, 719.7 cm^{-1}, 661.2 cm^{-1}, 580.9 cm^{-1}.

MS (ESI): Chemical formula $C_{25}H_{26}N_2O_3S$, **[M+Na]$^+$** theoretical *m/z* 457.1562, found *m/z* 457.1567.

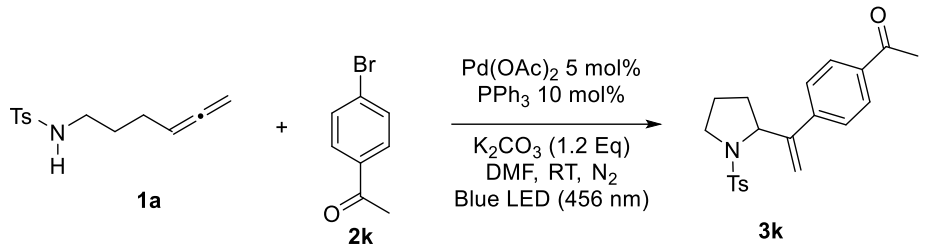
4.5 Characterization of dimer 4a



4a

(*E*)-4-methyl-N-(5-methyl-6-(1-tosylpyrrolidin-2-yl)hepta-4,6-dien-1-yl)benzenesulfonamide 4a
Following the described procedure for **3a**, employing AcONa as the base (20 mg 1,2 eq, 0,24 mmol), (*E*)-4-methyl-N-(5-methyl-6-(1-tosylpyrrolidin-2-yl)hepta-4,6-dien-1-yl)benzenesulfonamide **4a** was obtained in 66% yield as a transparent oil (gradient EP/AcOEt 8/2 to 6/4, 33 mg).
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.54-1.64 (m, 6H; CH_2-C*H*$_2$-CH_2, CH_2-C*H*$_2$-CH and CH_2-C*H*$_2$-CH_2), 1.74 (s, 3H; C*H*$_3$-C=CH), 2.11 (q, 2H, *J*= 7.4 Hz; CH-C*H*$_2$-CH_2), 2.41 (s, 3H; Ar-C*H*$_3$), 2.43 (s, 3H; Ar-*CH*$_3$), 2.94 (q, 2H, *J*= 7.5 Hz; CH_2-C*H*$_2$-NH), 3.20 (dt, 1H, *J*= 10.2, 9.5 Hz; N-C(H)*H*-CH_2), 3.49 (ddd, 1H, *J*= 10.1, 7.5, 2.9 Hz; N-C(H)*H*-CH_2), 4.51 (t, 1H, *J*= 6.3 Hz; N*H*), 4.58 (d, 1H, *J*= 7.7 Hz; N-C*H*-CH_2), 5.12 (s, 1H; C(H)*H*=C-CH), 5.21 (s, 1H; C(H)*H*=C-CH), 5.37 (t, 1H, *J*= 7.2 Hz; C=C*H*-CH_2), 7.29 (d, 2H; *J*= 8.1, Ts-*H*), 7.31 (d, 2H; *J*= 8.6, Ts-*H*), 7.73 (d, 2H; *J*= 8.1, Ts-*H*), 7.74 (d, 2H; *J*= 8.2, Ts-*H*).
^{13}C-NMR (150 MHz, $CDCl_3$): δ= 15.0 (CH_3), 21.5 (CH_3), 23.6 (CH_2), 25.4 (CH_2), 29.5 (CH_2), 32.4 (CH_2), 42.8 (CH_2), 48.7 (CH_2), 61.0 (CH), 111.3 (CH_2), 125.9 (CH), 127.0 (CH), 127.4 (CH), 129.6 (CH), 129.7 (CH), 134.4 (Cq), 135.0 (Cq), 136.8 (Cq), 143.3 (Cq), 143.4 (Cq), 149.2 (Cq).
IR: 3276.35 cm^{-1}, 2976.53 cm^{-1}, 2948.43 cm^{-1}, 2870.98 cm^{-1}, 1737.81 cm^{-1}, 1598.03 cm^{-1}, 1447.82 cm^{-1}, 1324.16 cm^{-1}, 1188.82 cm^{-1}, 1154.67 cm^{-1}, 1092.46 cm^{-1}, 1063.31 cm^{-1}, 1005.28 cm^{-1}, 908.03 cm^{-1}, 851.39 cm^{-1}, 814.00 cm^{-1}.
MS (ESI): Chemical formula $C_{26}H_{34}N2O_4S_2$, **$[M+H]^+$** theoretical *m/z* 503.2033, found *m/z* 503.2028.

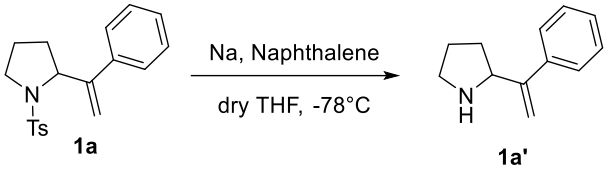
4.6 Synthesis of compound 3k in 1 mmol scale



A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2, then 25 ml of dry DMF were transferred into the tube and degassed with N_2 for at least 10 minutes. Under a constant flow of N_2, $Pd(OAc)_2$ (11 mg, 0.05 mmol, 5 mol%) was placed in the Schlenk tube and the mixture was degassed for additional 5 minutes until the solution turned an intense yellow. Then PPh_3 (26 mg, 0.1 mmol, 10 mol%) was added and the solution was left under stirring under inert gas until the solution turned cherry red. The other reagents were added in the following order: *p*-bromo acetophenone **2k** (300 mg, 1.5 mmol, 1.5 Eq), K_2CO_3 (166 mg, 1.2 mmol, 1.2 Eq) and the allene **1a** (251 mg, 1 mmol, 1 Eq). The Schlenk tube, saturated with N_2, was closed with a septum and then stirred at 4 cm from a Kessil blue lamp (456 nm) at room temperature for 21 h.

Reaction work-up: the reaction mixture was diluted with 50 ml of Et_2O and the organic phase was washed with brine (5x20 ml) and dried over Na_2SO_4. After solvent removal, the crude mixture was purified by flash chromatography on silica gel (gradient: EP/AcOEt 7/1 to 7/3,) to afford product **3k** in 63% yield.

4.7 Procedure for the synthesis of compound 1a'



1a **1a'**

Naphthalene (207 mg (0,21 g), 1.65 mmol, 6 Eq) in dry THF (6 mL) was treated with Na (38 mg, 1.65 mmol, 6 Eq) at room temperature. The solution was stirred at this temperature under N_2 until it turned green. In the meantime, a Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2, then compound **1a** (90 mg, 0.275 mmol, 1 Eq) was transferred in the tube and dissolved with 6 mL of dry THF. The mixture was cooled to –78 °C and the solution of Na/naphthalene was slowly added via a syringe. The addition was continued until the green colour was maintained. The reaction mixture was stirred at –78 °C until compound **1a** was totally consumed. Then, it was allowed to warm to RT and carefully quenched with aq. NH_4Cl solution (concentrazione, 4 mL). The phases were separated and the aqueous phase was extracted with DCM (3 × 5.0 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, DCM/MeOH from 10/1 to 3/2) to give the title product **1a'** in 40% yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.83-1.89 (m, 1H; CH-C(H)*H*-CH_2), 1.96-2.01 (m, 1H; CH_2-C(H)*H*-CH_2), 2.01-2.09 (m, 1H; CH_2-C(H)*H*-CH_2), 2.21-2.26 (m, 1H; CH-C(H)*H*-CH_2), 3.35-3.39 (m, 1H; N-C(H)*H*-CH_2), 3.49-3.53 (m, 1H; N-C(H)*H*-CH_2), 4.57 (t, 1H, J= 7.7 Hz; N-C*H*-CH_2), 5.49 (s, 1H; C(H)*H*=C-CH), 5.65 (s, 1H; C(H)*H*=C-CH), 7.28-7.34 (m, 3H; ; Ar-*H*), 7.38 (d, 2H, J= 6.8 Hz; ; Ar-*H*). **^{13}C-NMR** (150 MHz, $CDCl_3$): δ= 23.0 (CH_2), 31.1 (CH_2), 45.2 (CH_2), 61.5 (CH), 115.5 (CH_2), 126.7 (CH), 128.4 (CH), 128.7 (CH), 138.8 (Cq), 143.5 (Cq). **IR:** 2920.8 cm^{-1}, 2851.4 cm^{-1}, 1722.5 cm^{-1}, 1574.0 cm^{-1}, 1495.6 cm^{-1}, 1375.7 cm^{-1}, 1309.3 cm^{-1}, 1159.5 cm^{-1}, 1074.8 cm^{-1}, 1026.4 cm^{-1} 912.3 cm^{-1}, 777.6 cm^{-1}, 704.5 $^{-1}$, 565.2 cm^{-1}. **MS (ESI):** Chemical formula $C_{12}H_{15}N$, **$[M+H]^+$** theoretical *m/z*

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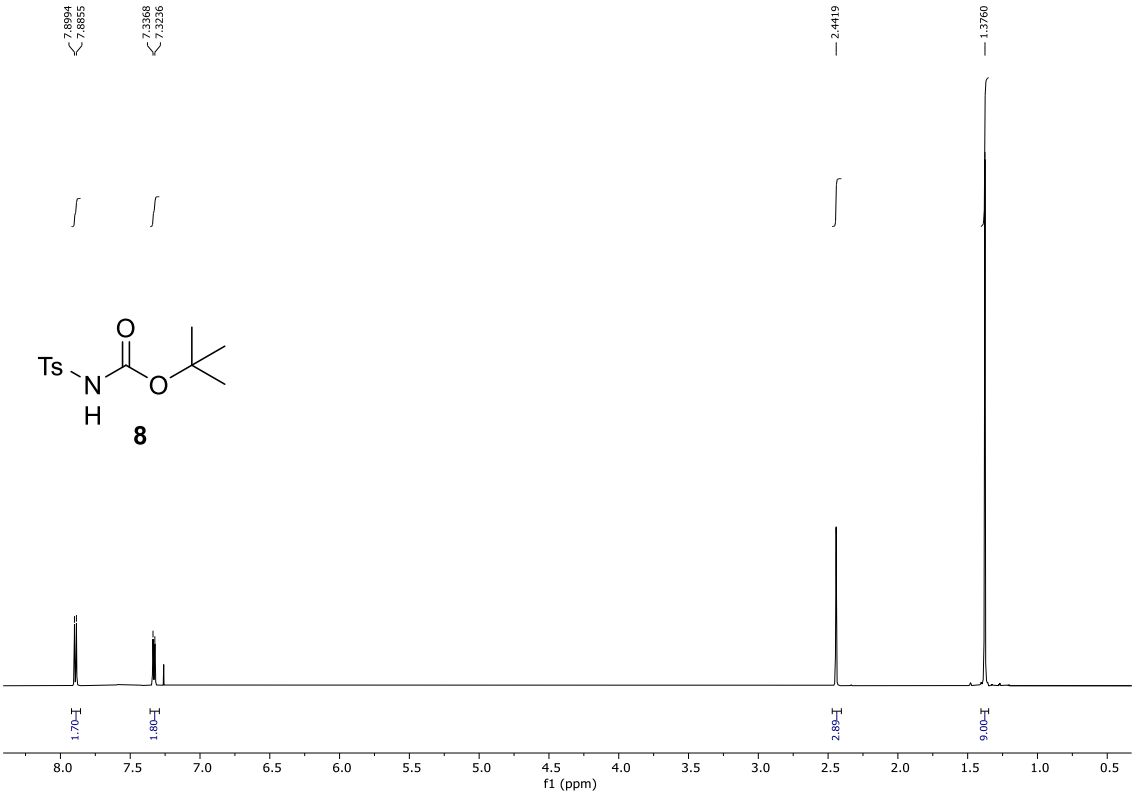
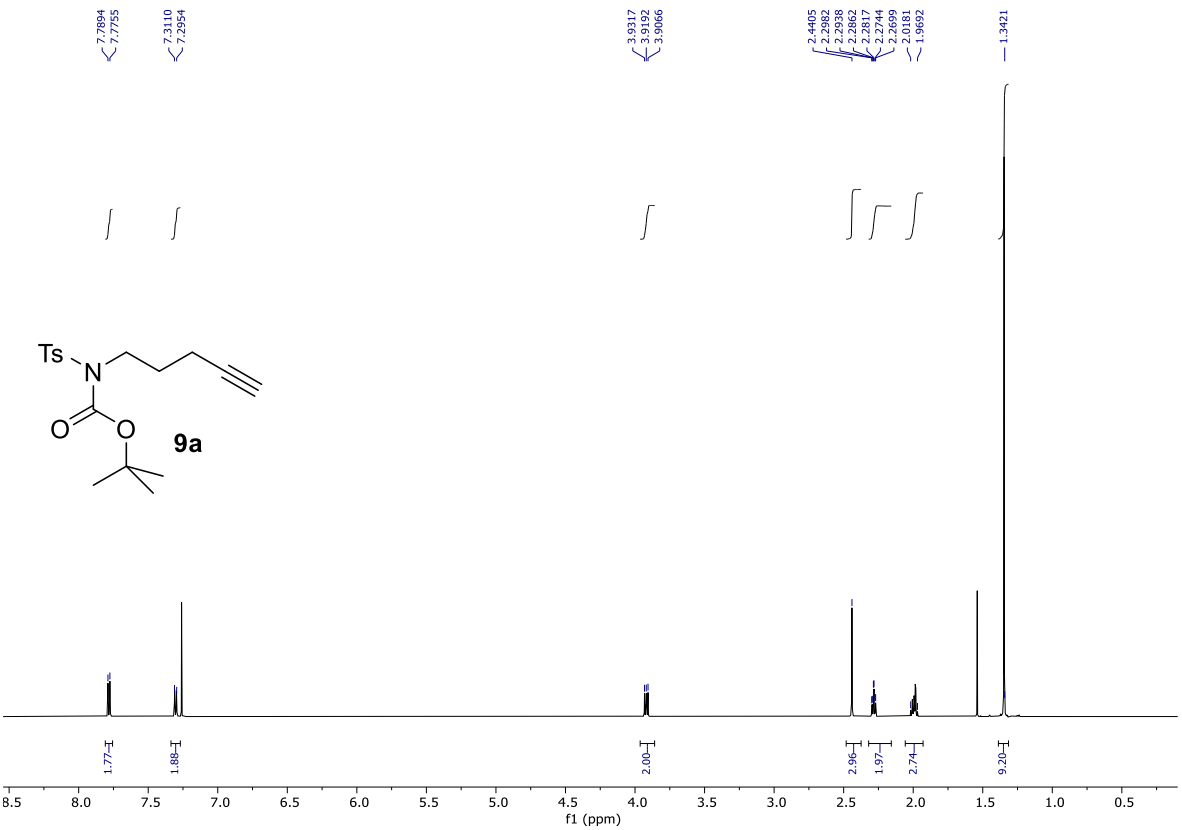
Copies of NMR spectra of starting materials and products

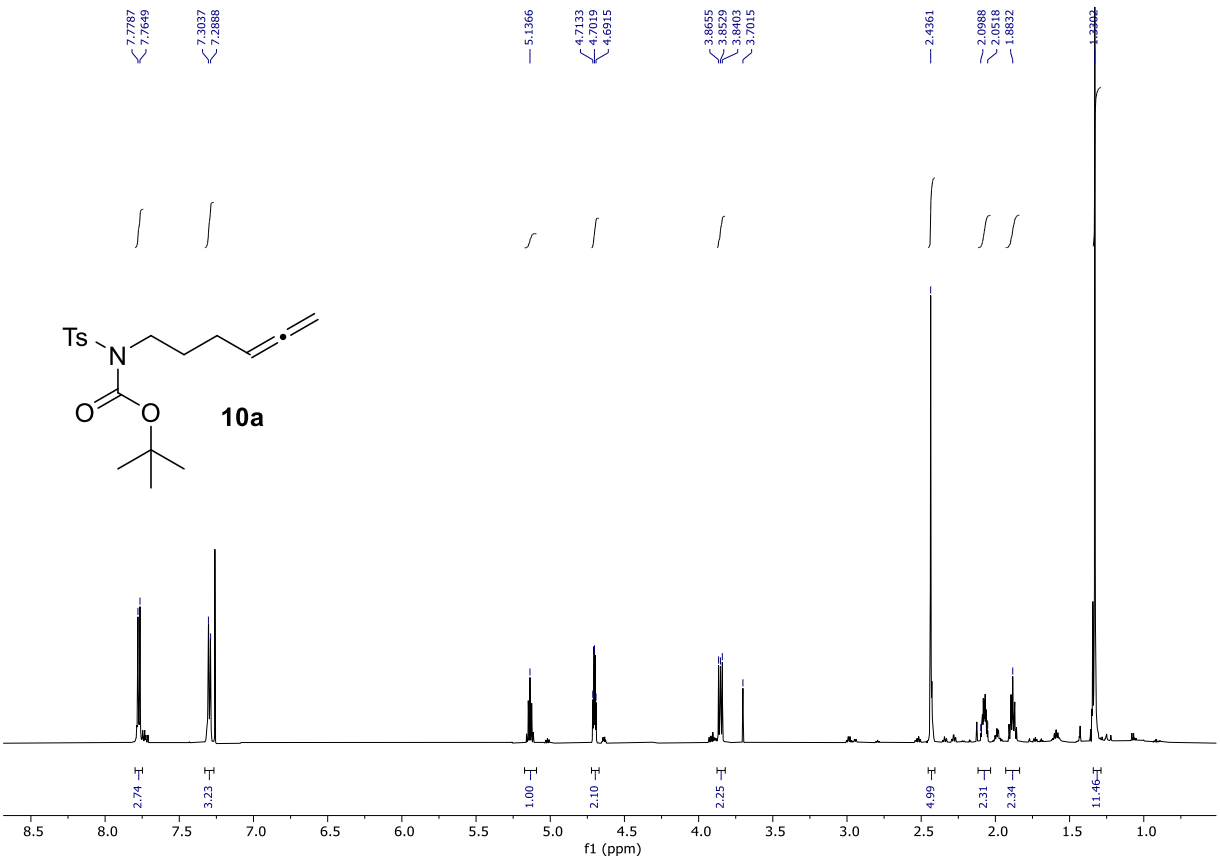
^{1}H-NMR of compound 8 (600 MHz, $CDCl_3$)



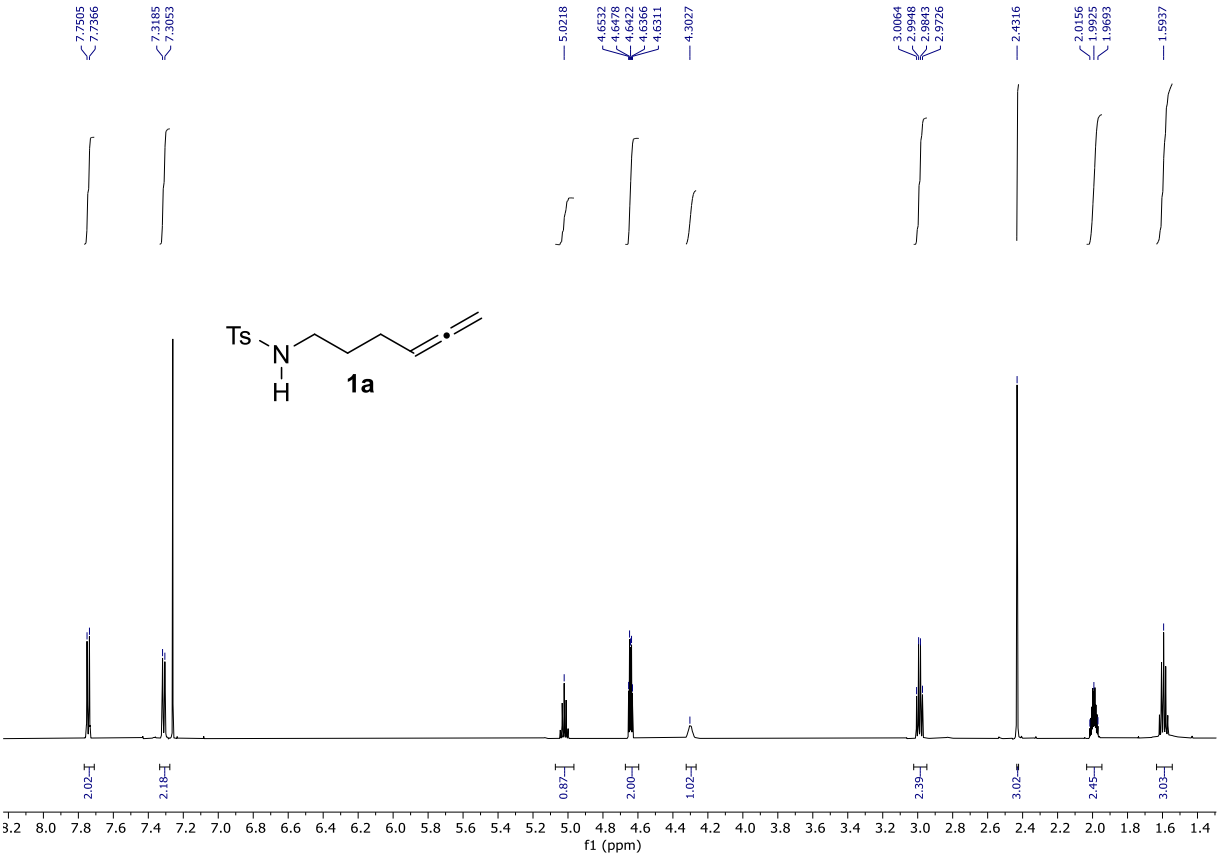
^{1}H-NMR of compound 9a (600 MHz, $CDCl_3$)



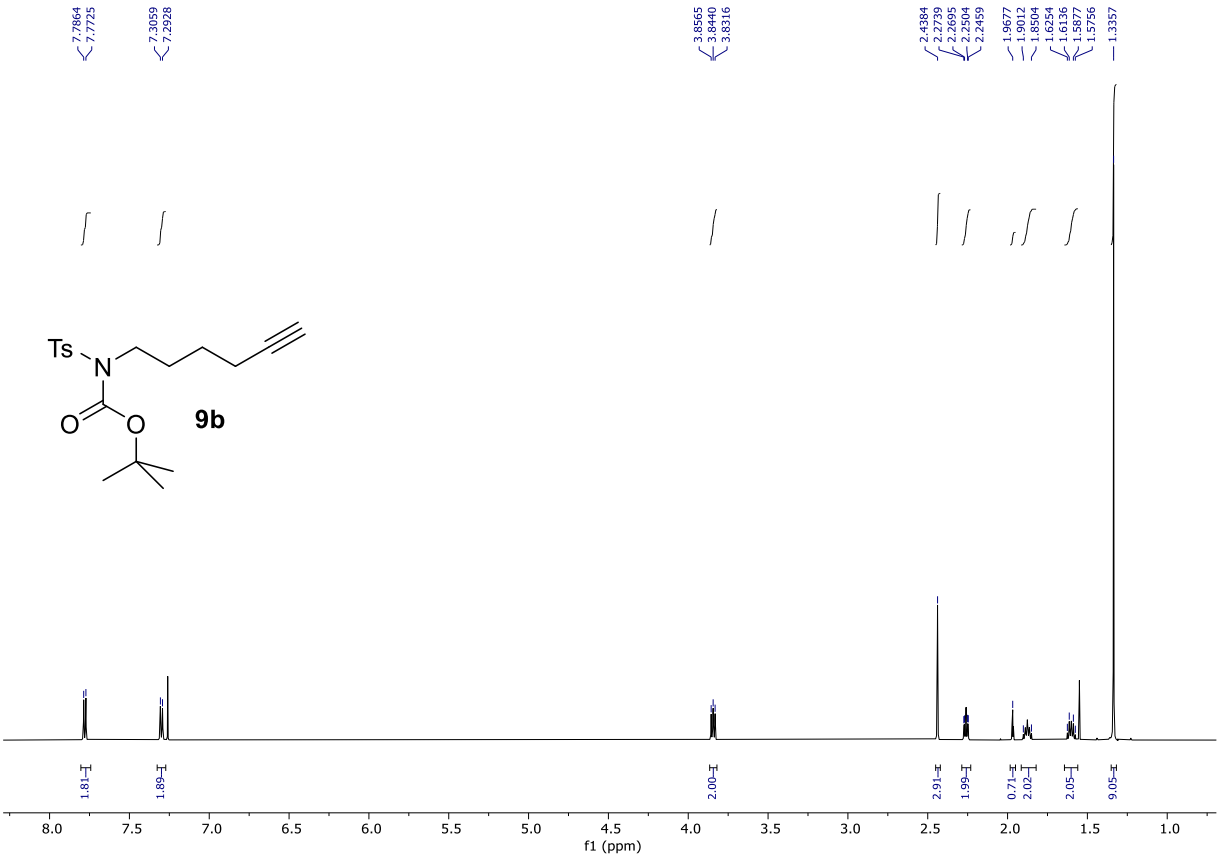
^{1}H-NMR of compound 10a crude (600 MHz, $CDCl_3$)



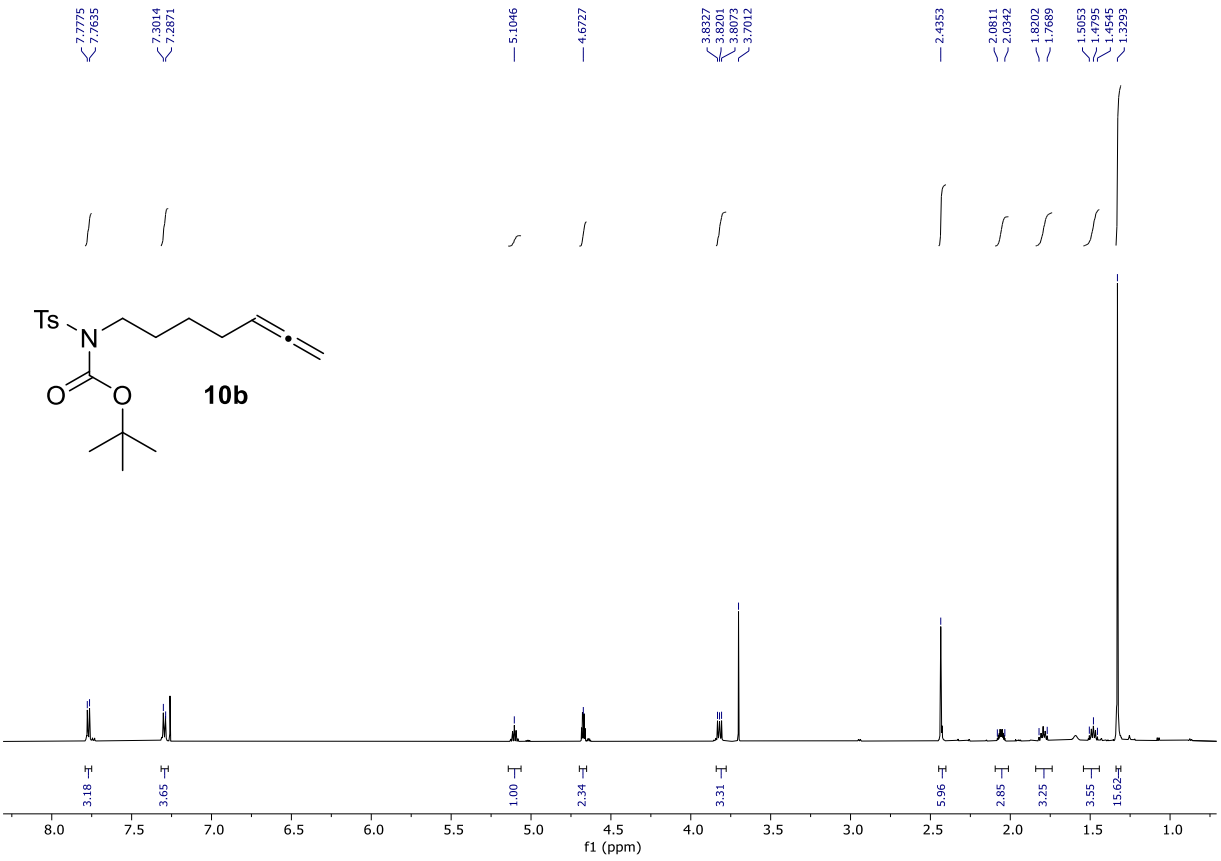
^{1}H-NMR of compound 1a (600 MHz, $CDCl_3$)



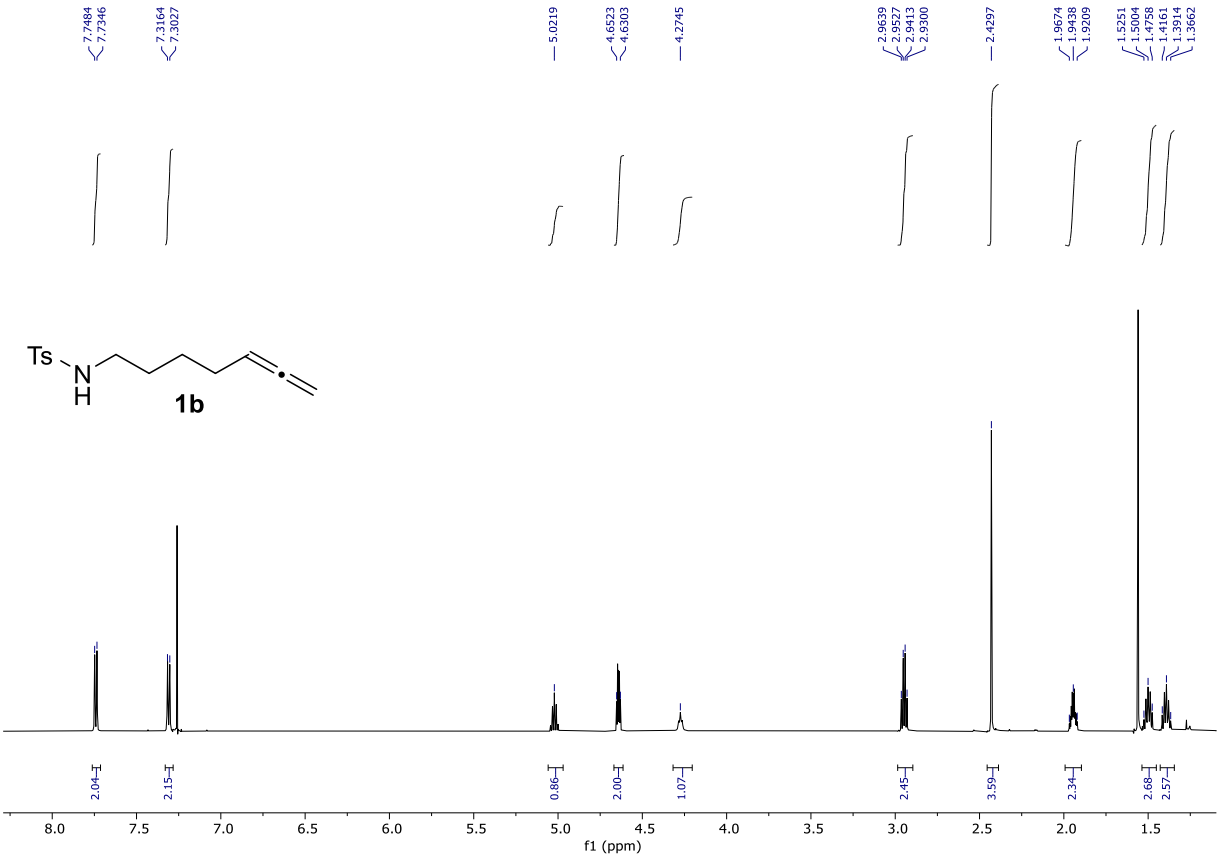
^{1}H-NMR of compound 9b (600 MHz, $CDCl_3$)



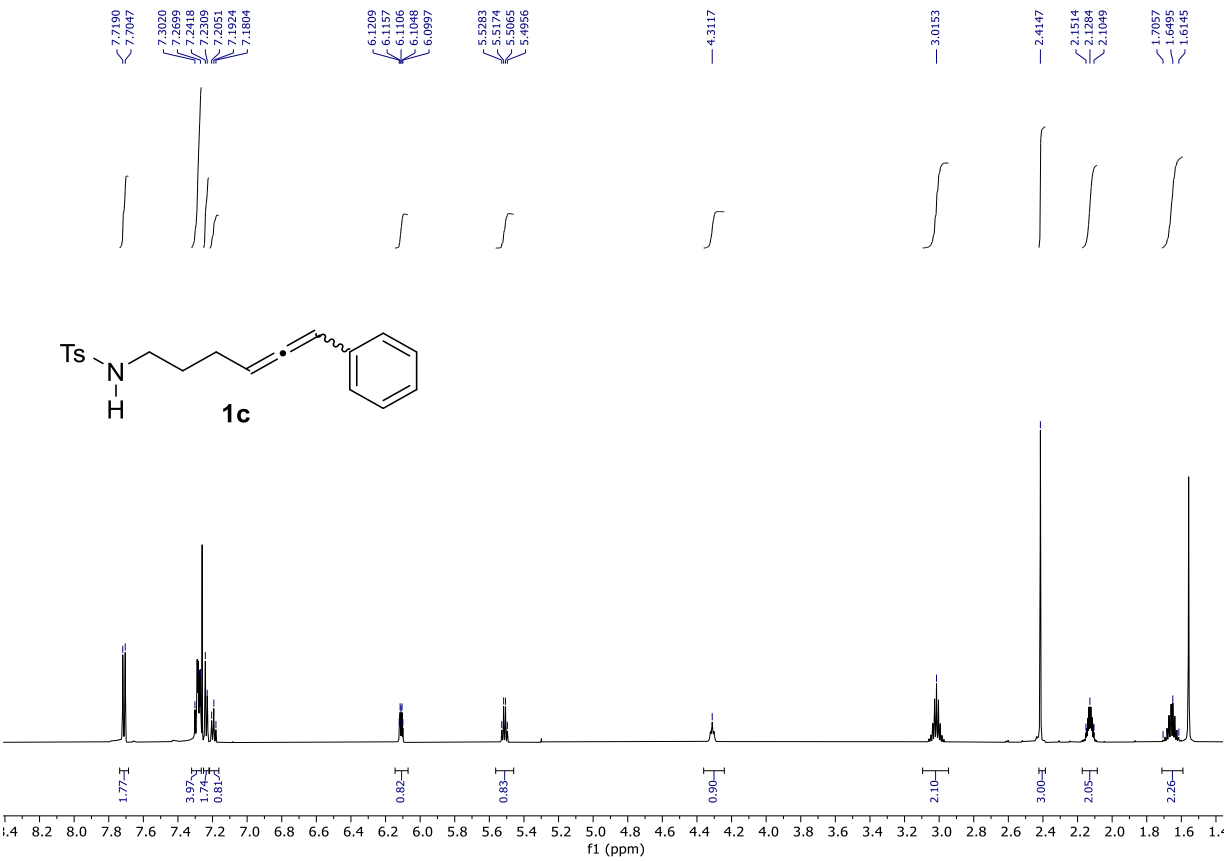
^{1}H-NMR of compound 10b (600 MHz, $CDCl_3$)



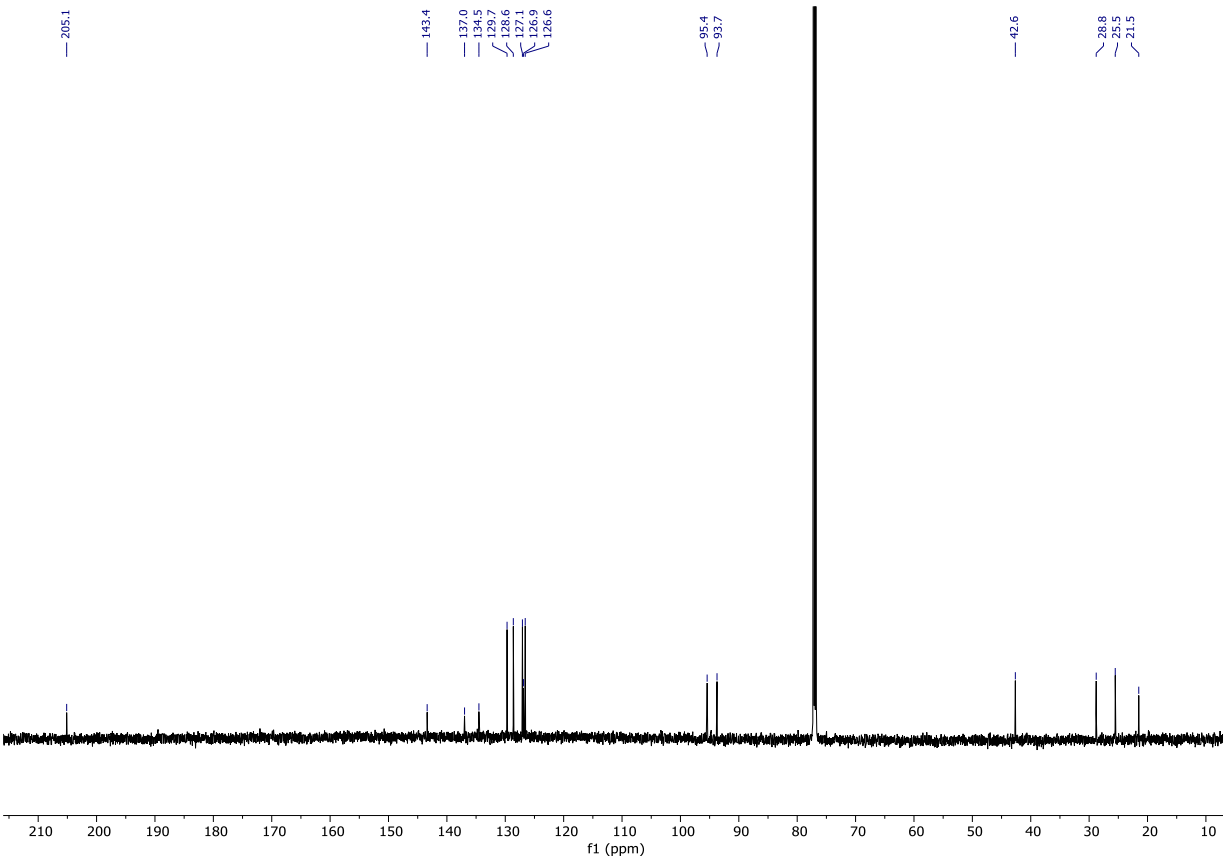
^{1}H-NMR of compound 1b (600 MHz, $CDCl_3$)



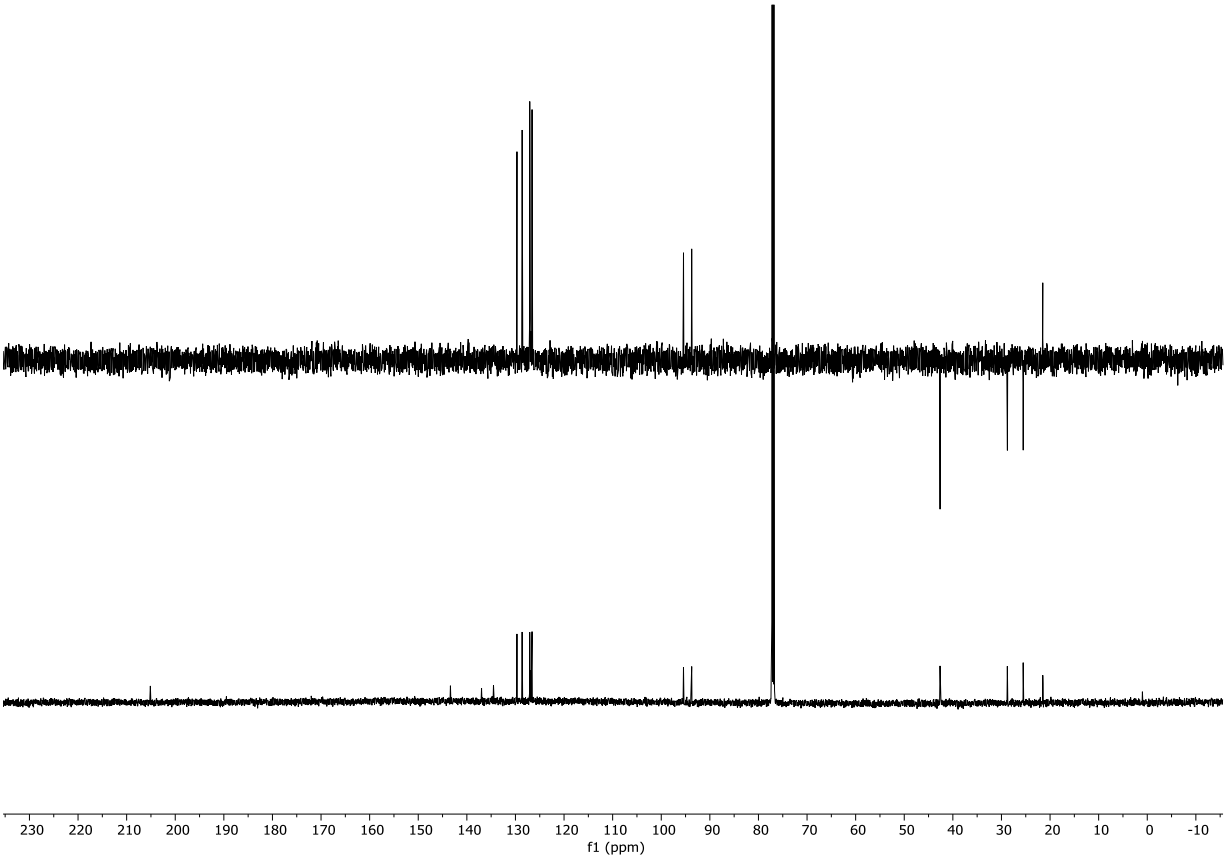
^{1}H-NMR of compound 1c (600 MHz, $CDCl_3$)



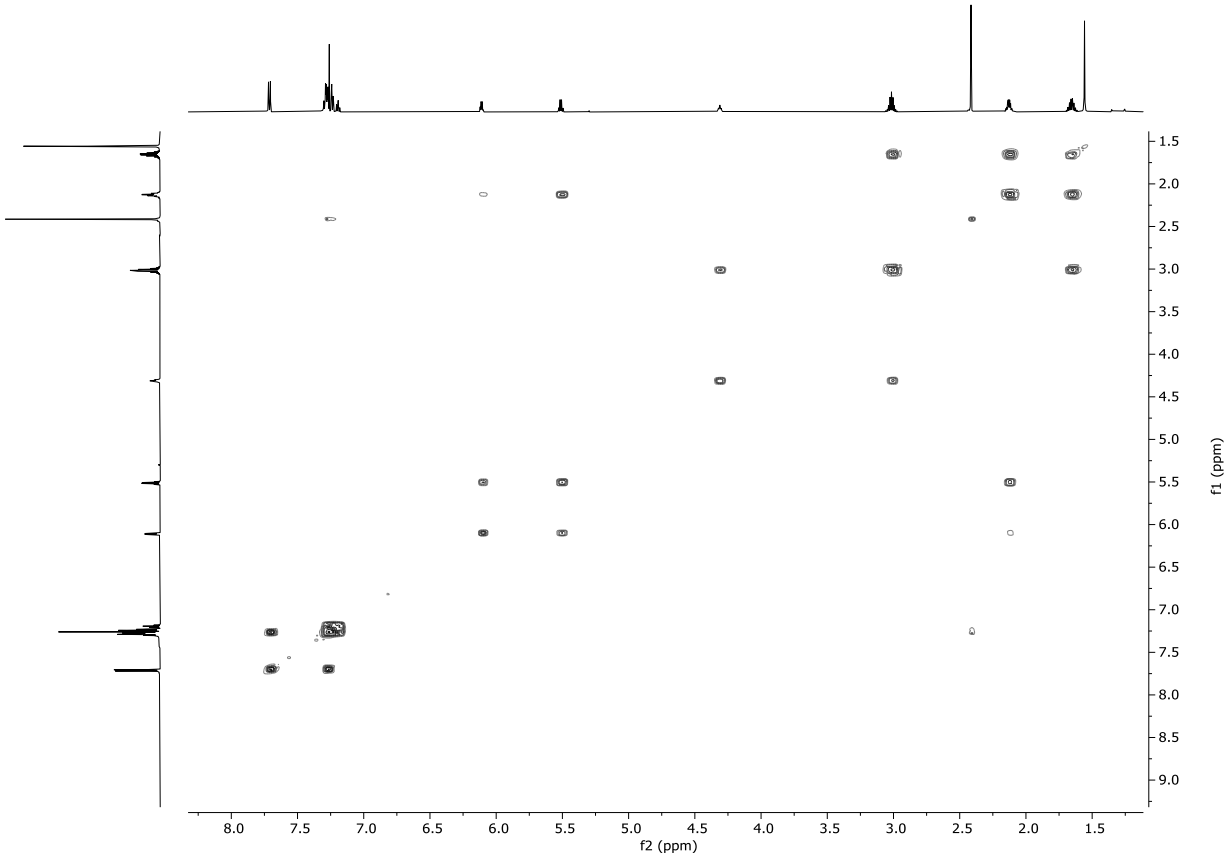
^{13}C-NMR of compound 1c (150 MHz, $CDCl_3$)



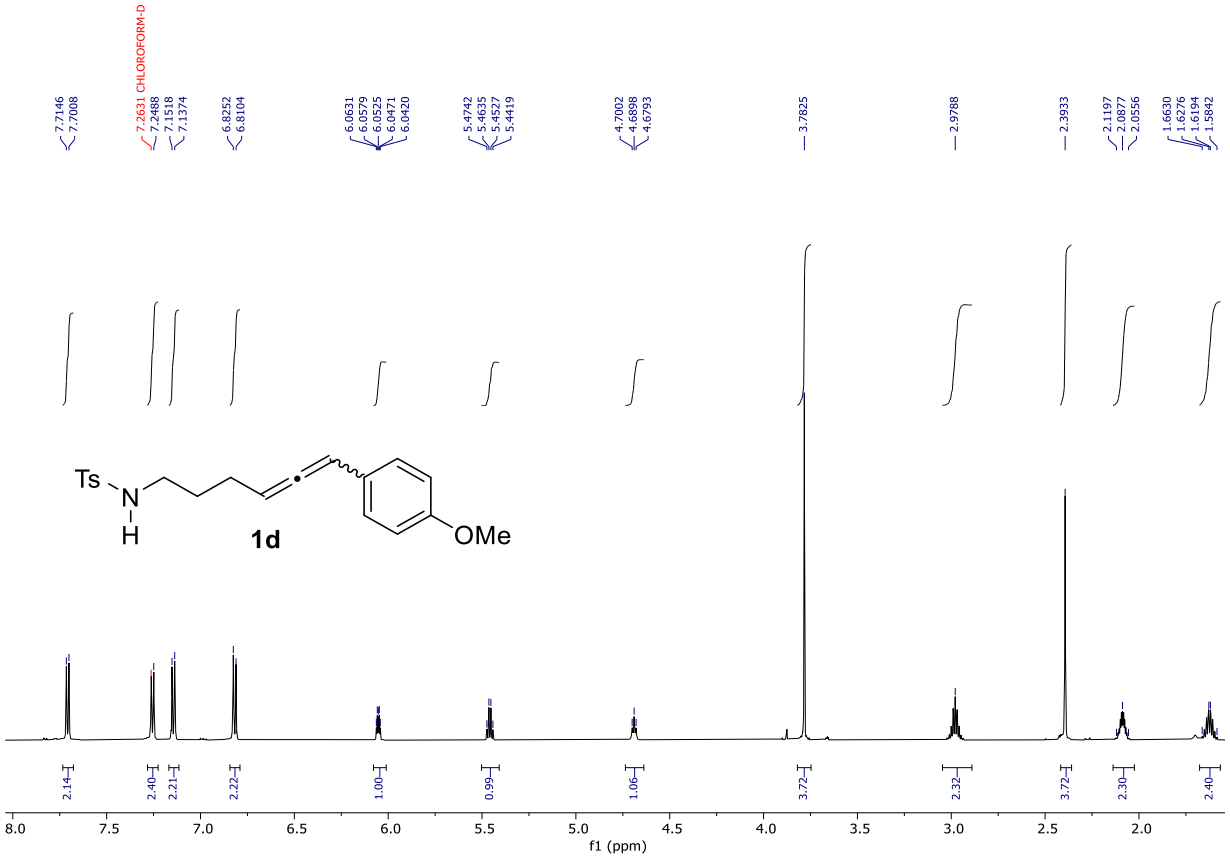
Comparison between DEPT-135 and ^{13}C-NMR of compound 1c (150 MHz, $CDCl_3$)



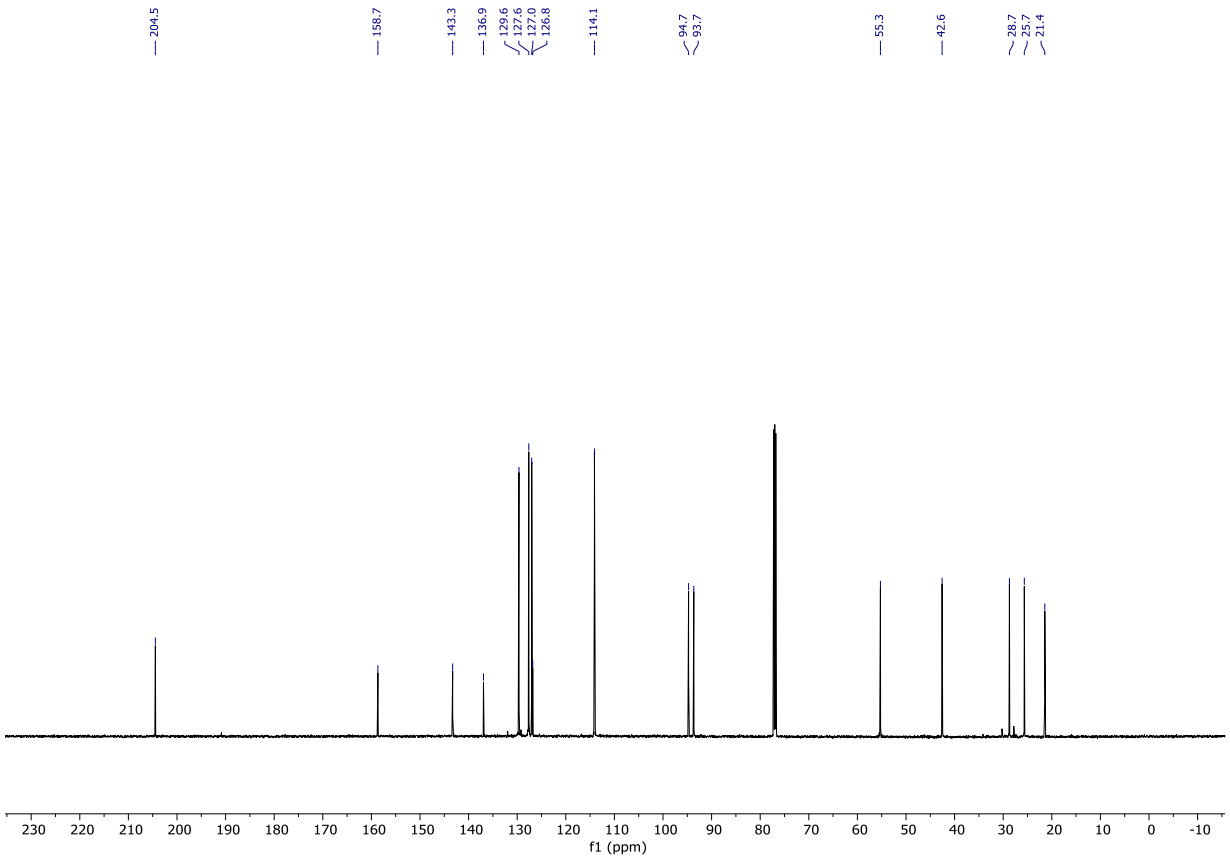
COSY-NMR of compound 1c (600 MHz, $CDCl_3$)


f2 (ppm)
f1 (ppm)

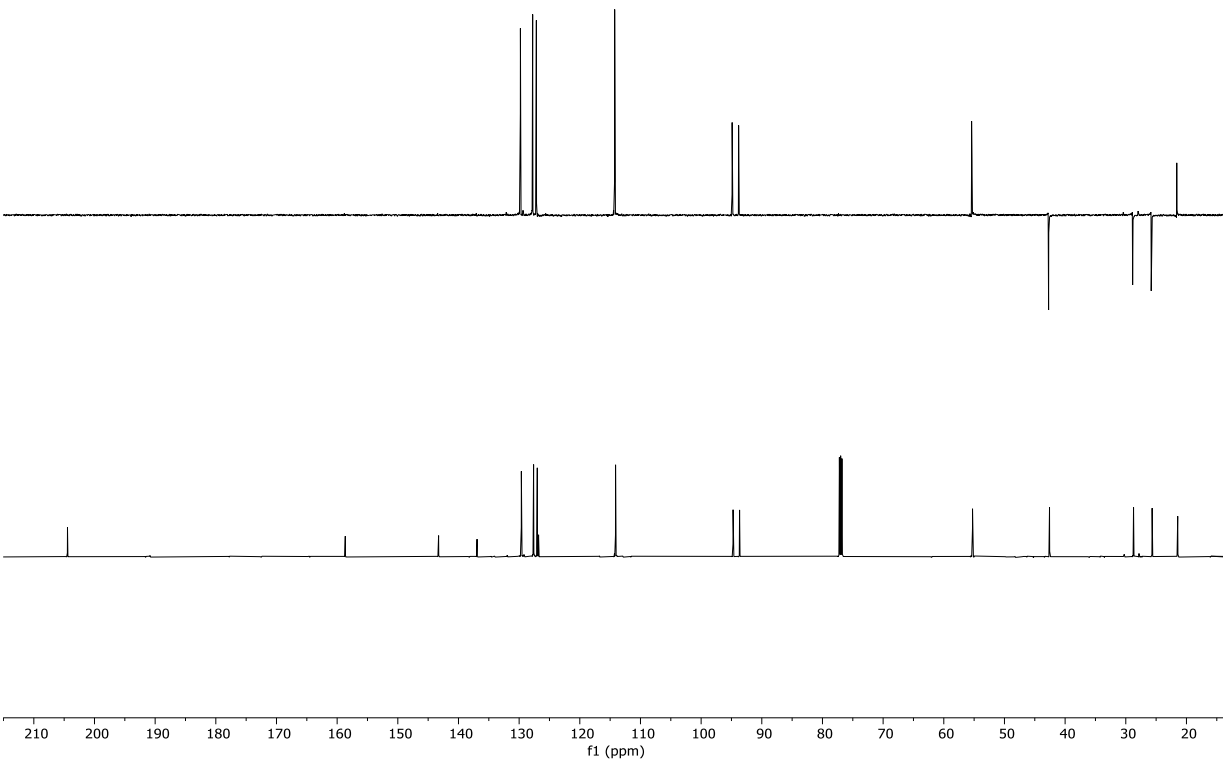
^{1}H-NMR of compound 1d (600 MHz, $CDCl_3$)



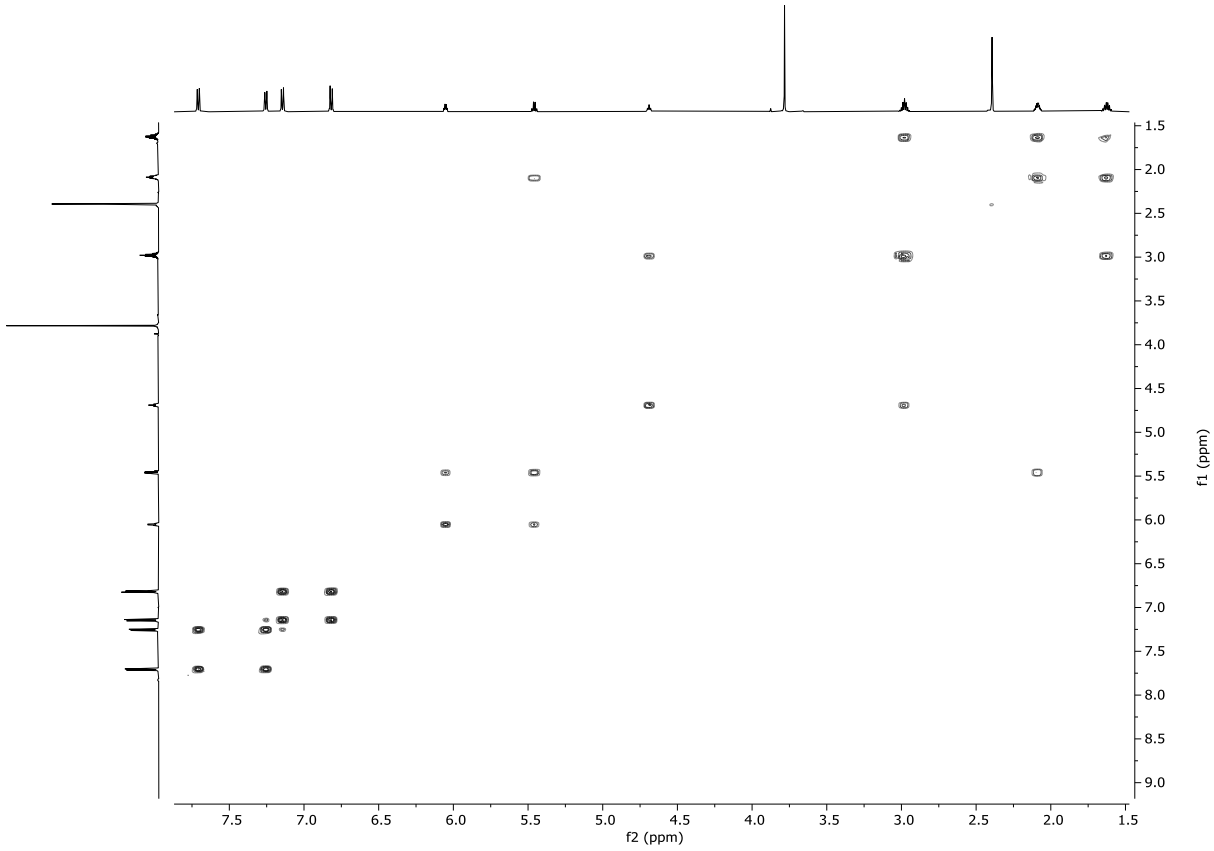
^{13}C-NMR of compound 1d (150 MHz, $CDCl_3$)



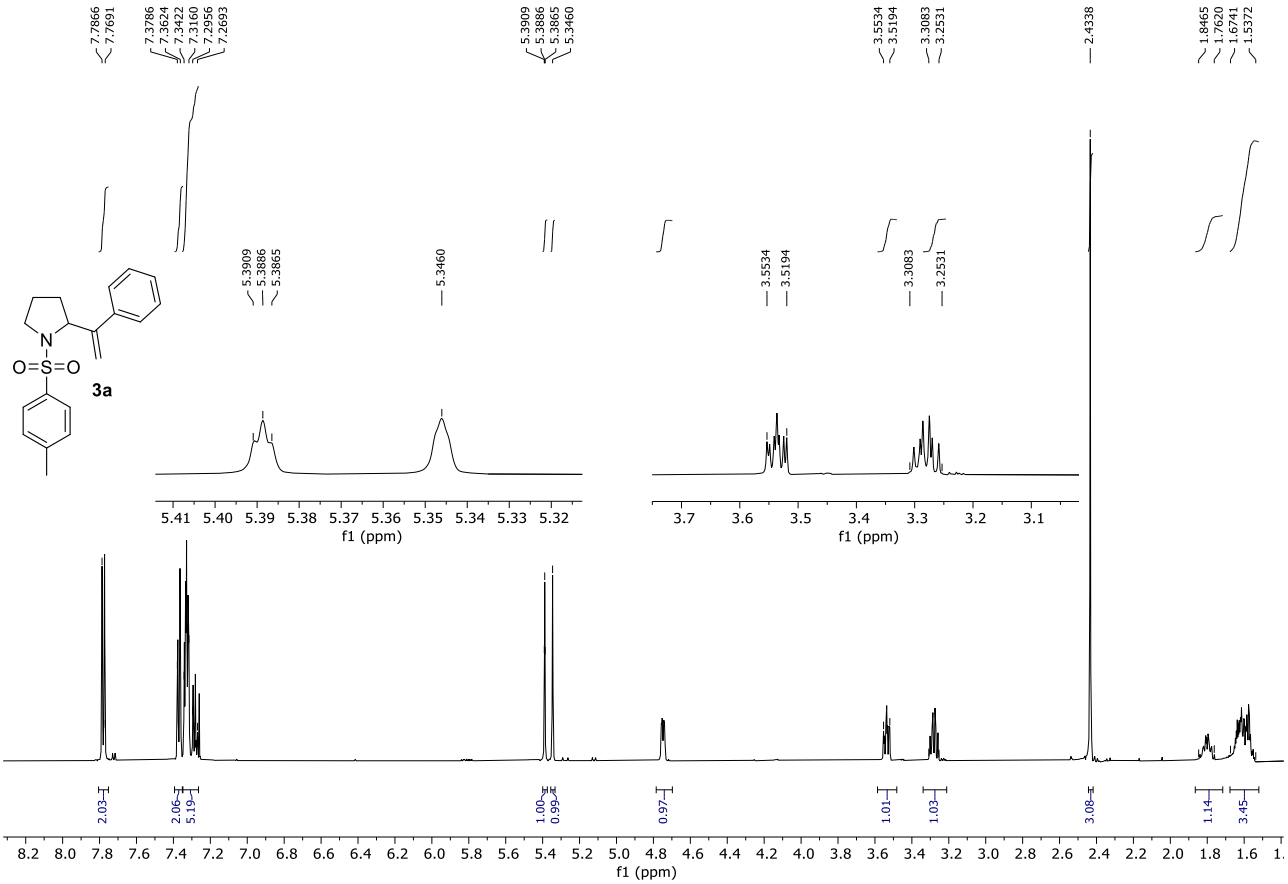
Comparison between DEPT-135 and ^{13}C-NMR of compound 1d (150 MHz, $CDCl_3$)



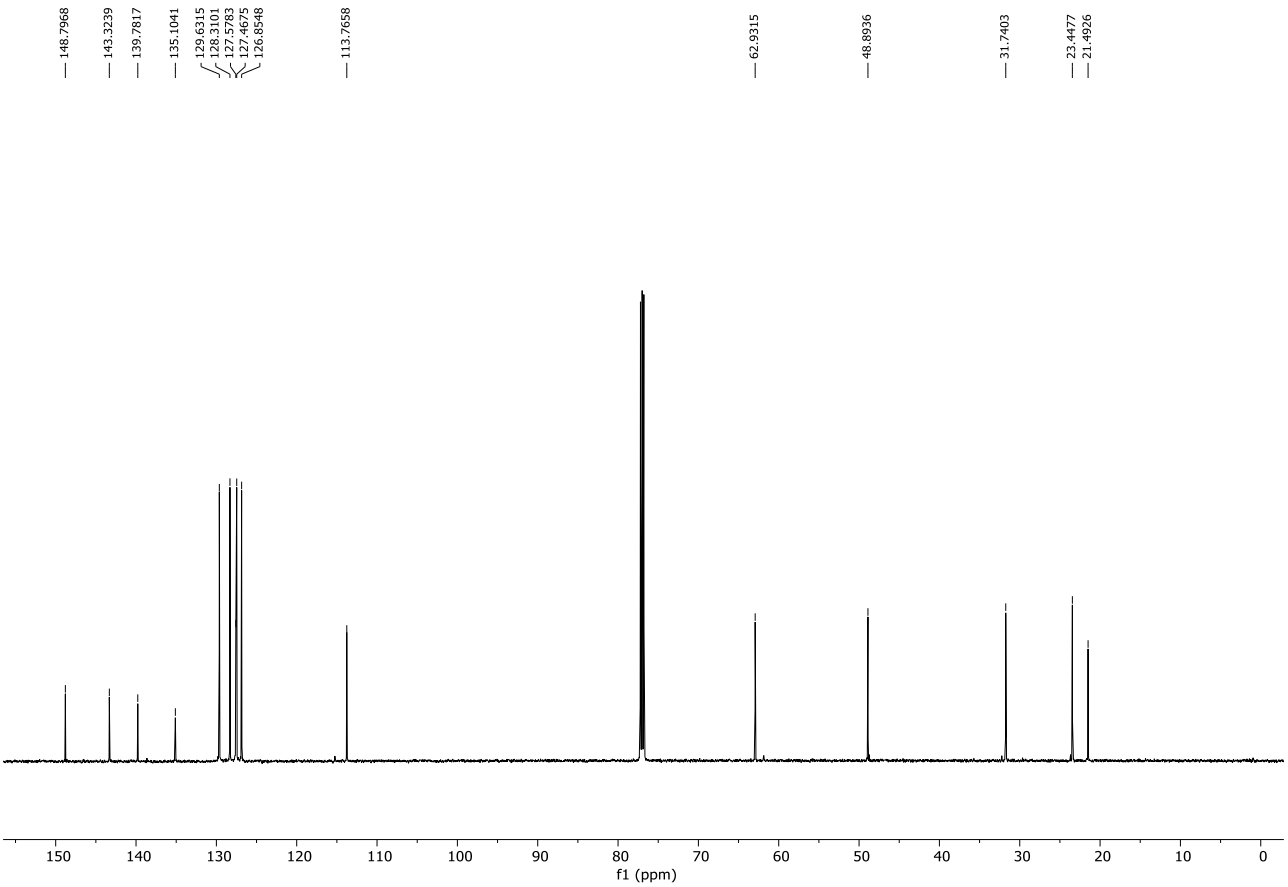
COSY-NMR of compound 1d (600 MHz, $CDCl_3$)



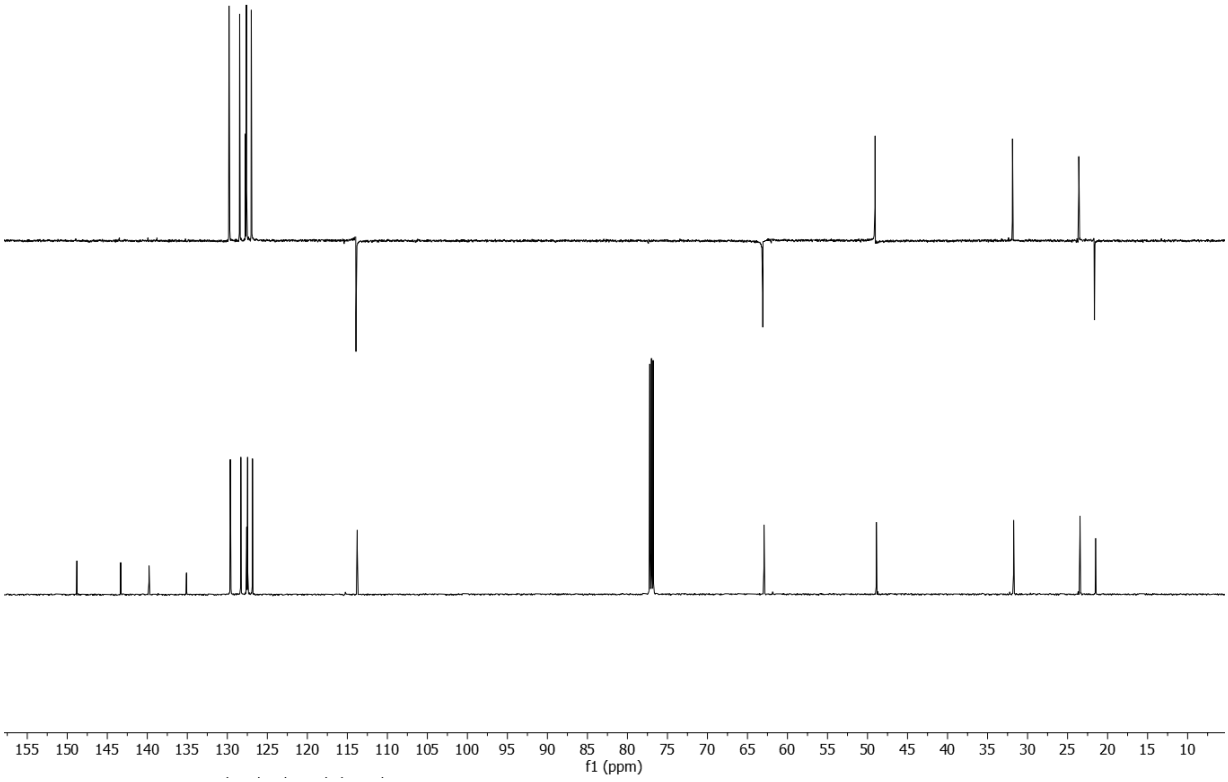
^{1}H-NMR of compound 3a (600 MHz, $CDCl_3$)



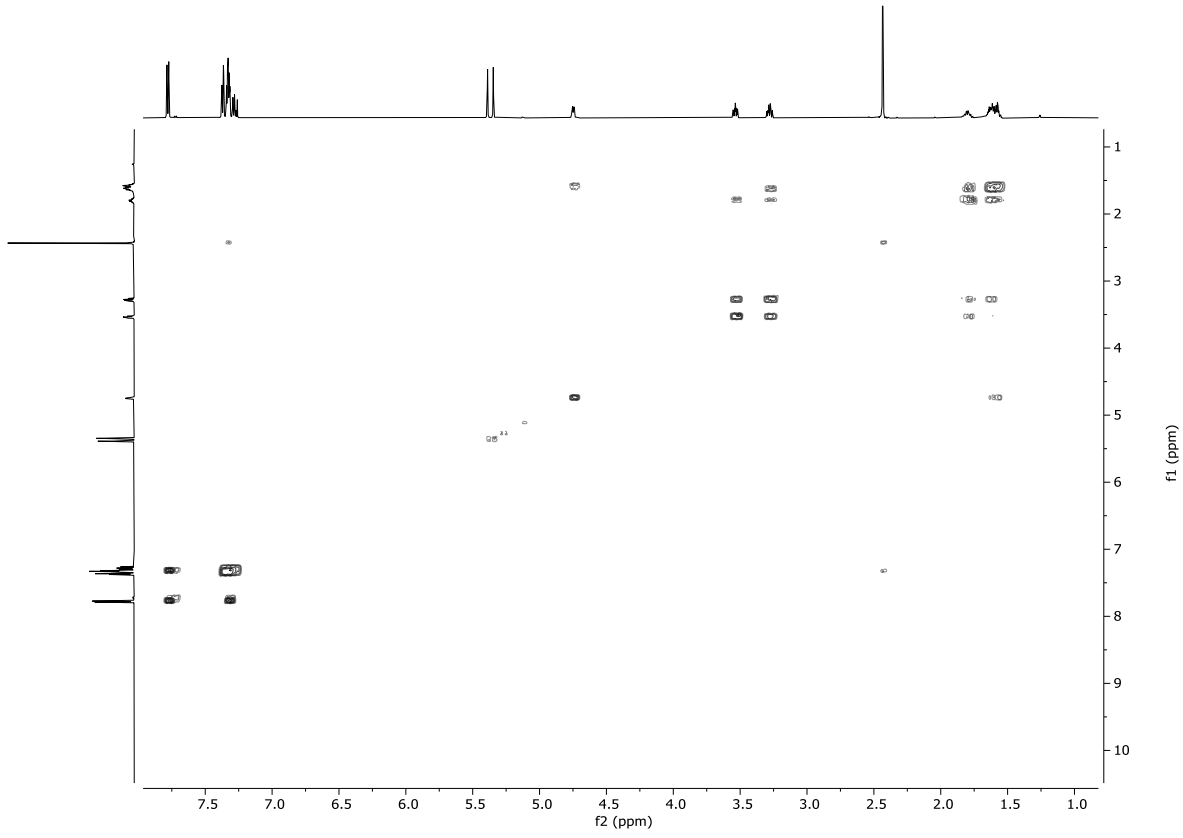
^{13}C-^{13}C-NMR of compound 3a (150 MHz, $CDCl_3$)



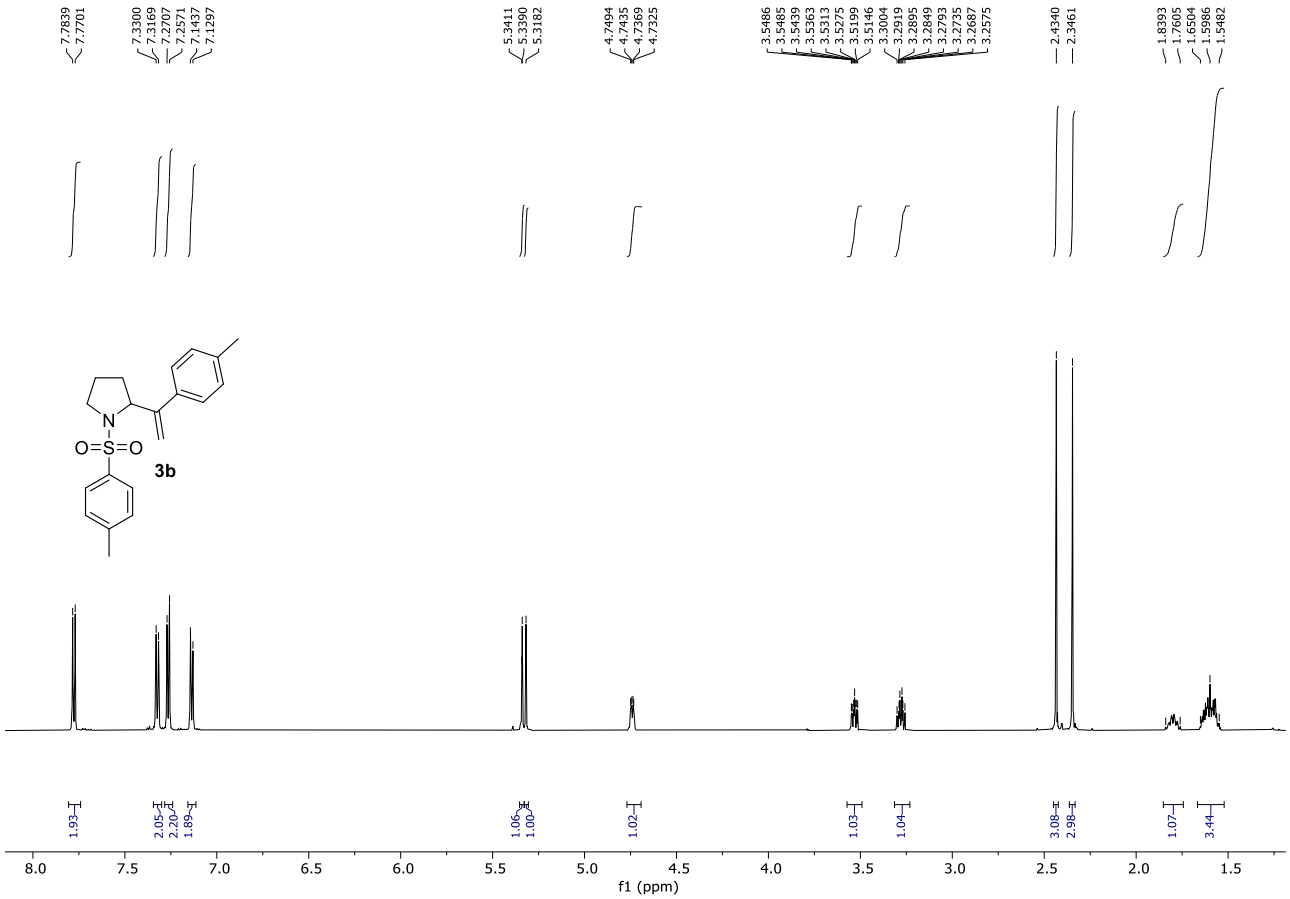
Comparison between DEPT-135 and ^{13}C-NMR of compound 3a (150 MHz, $CDCl_3$)



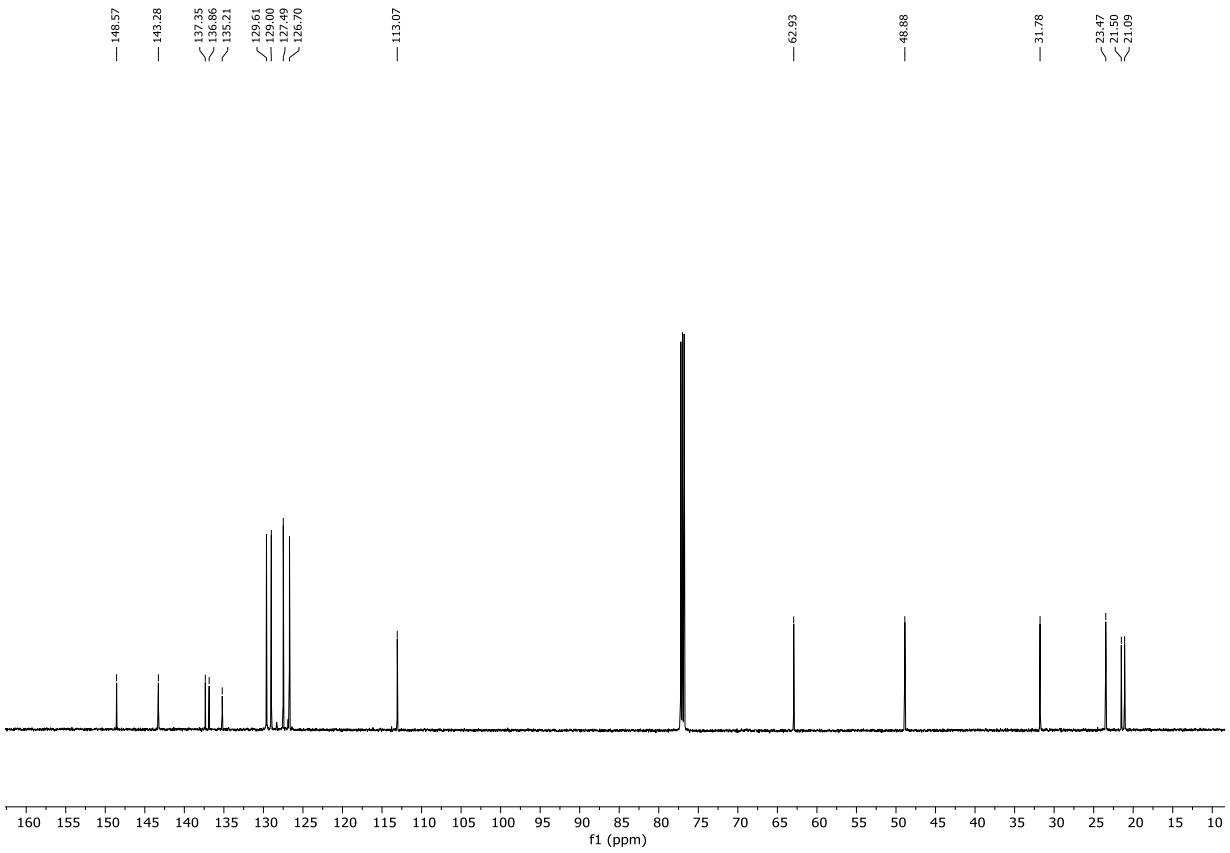
COSY-NMR of compound 3a (600 MHz, $CDCl_3$)



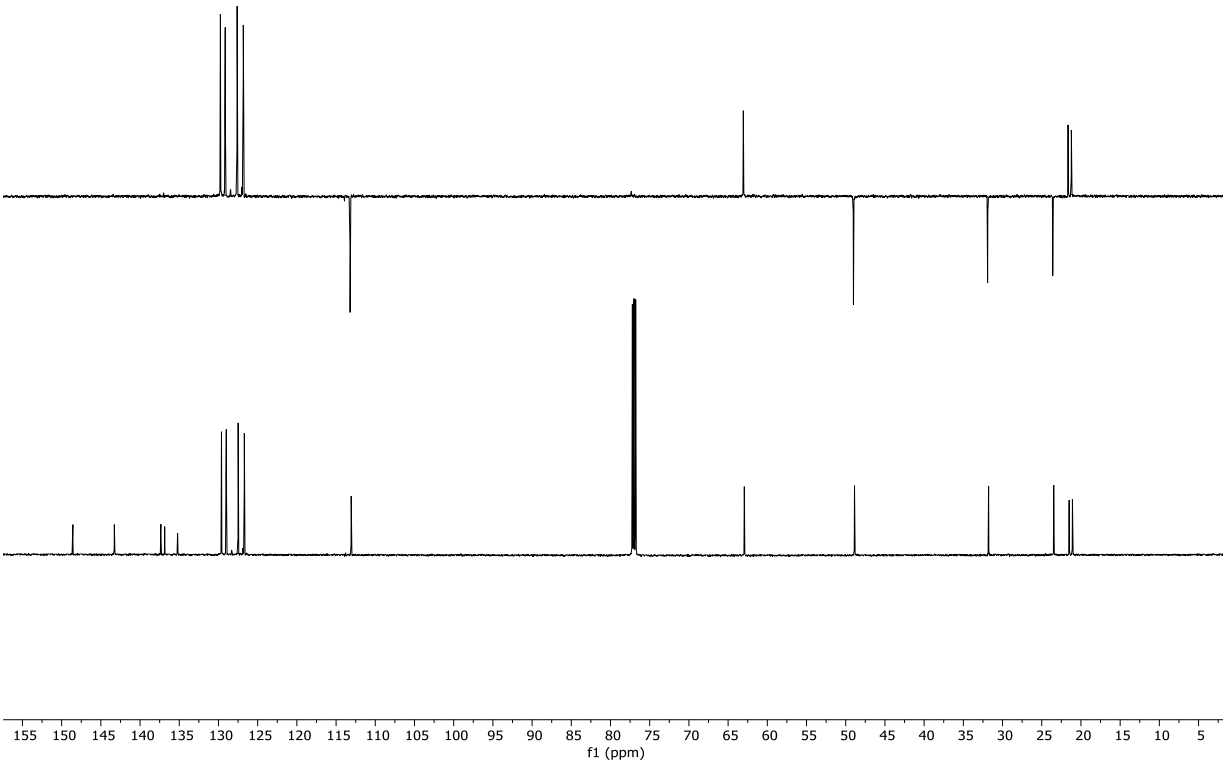
^{1}H-NMR of compound 3b (600 MHz, $CDCl_3$)



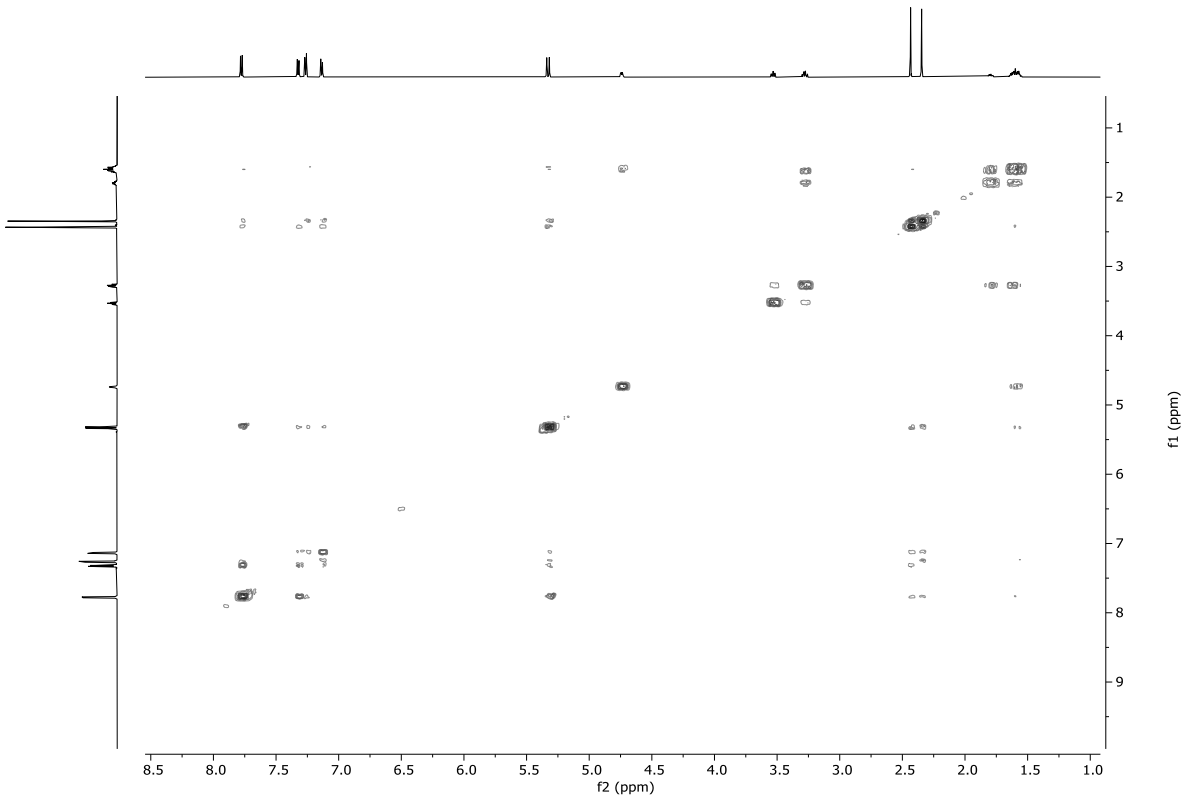
^{13}C-NMR of compound 3b (150 MHz, $CDCl_3$)



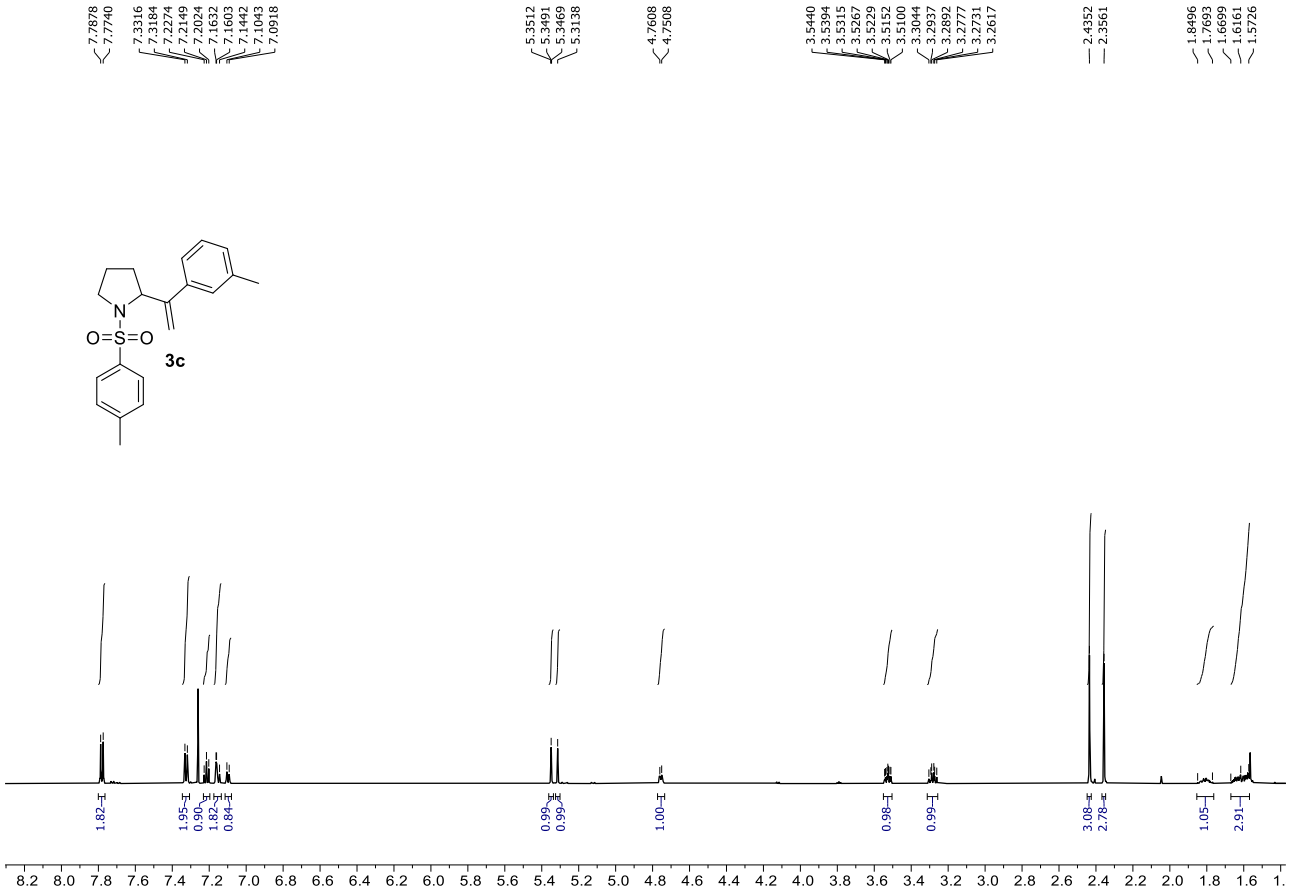
Comparison between DEPT-135 and ^{13}C-NMR of compound 3b (150 MHz, $CDCl_3$)



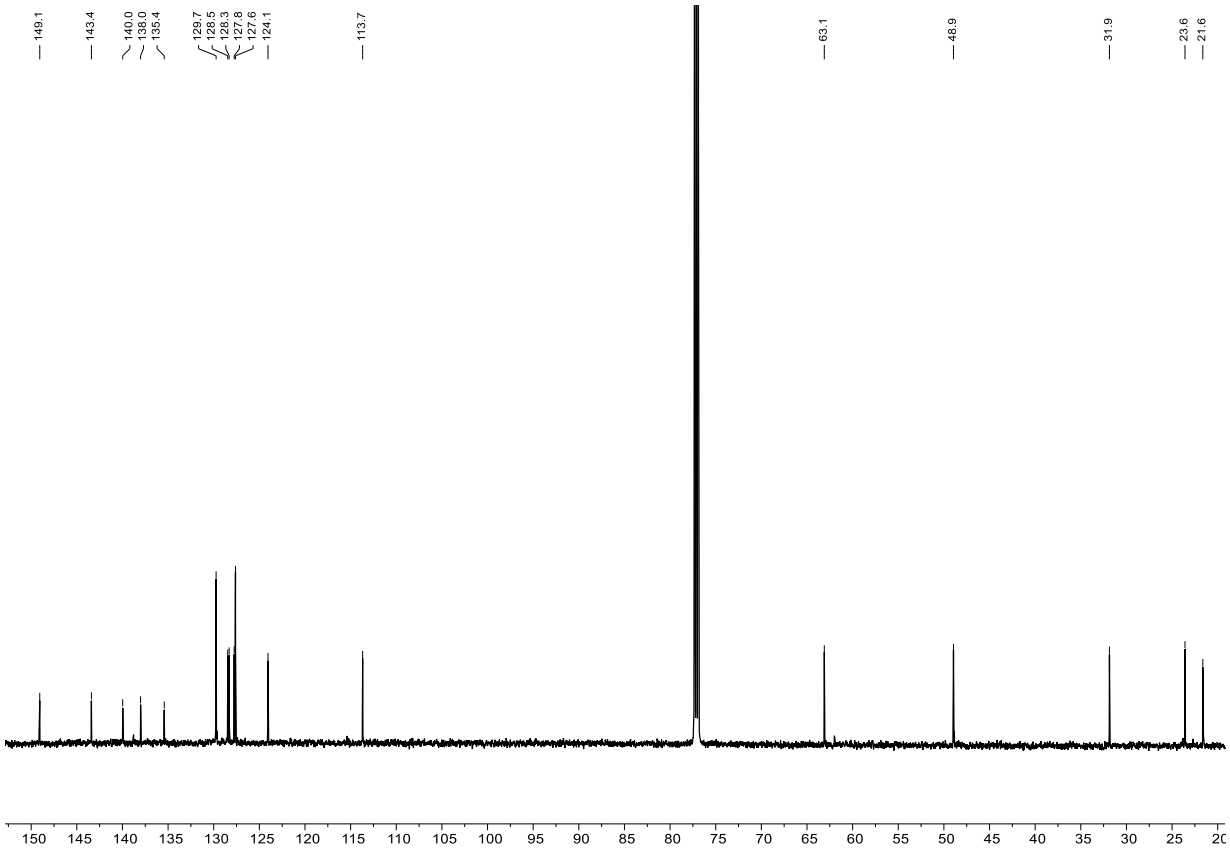
COSY-NMR of compound 3b (600 MHz, $CDCl_3$)



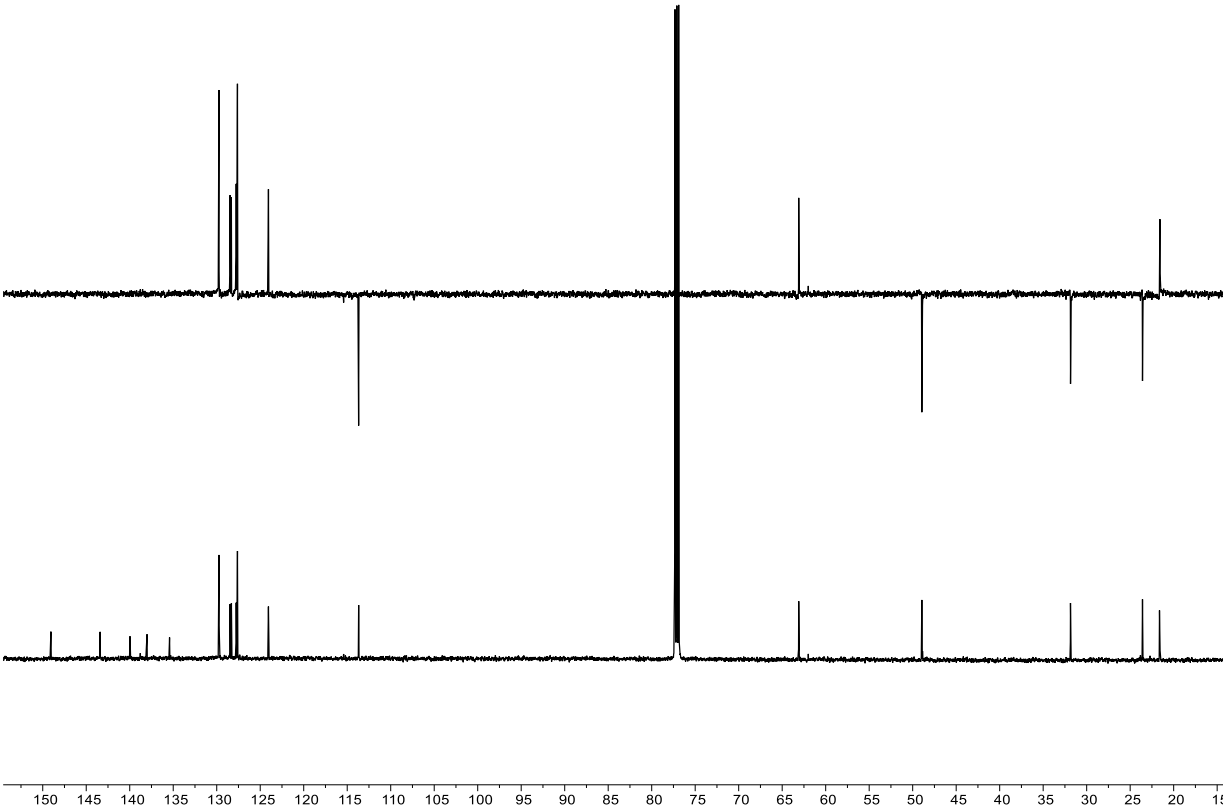
^{1}H-NMR of compound 3c (600 MHz, $CDCl_3$)



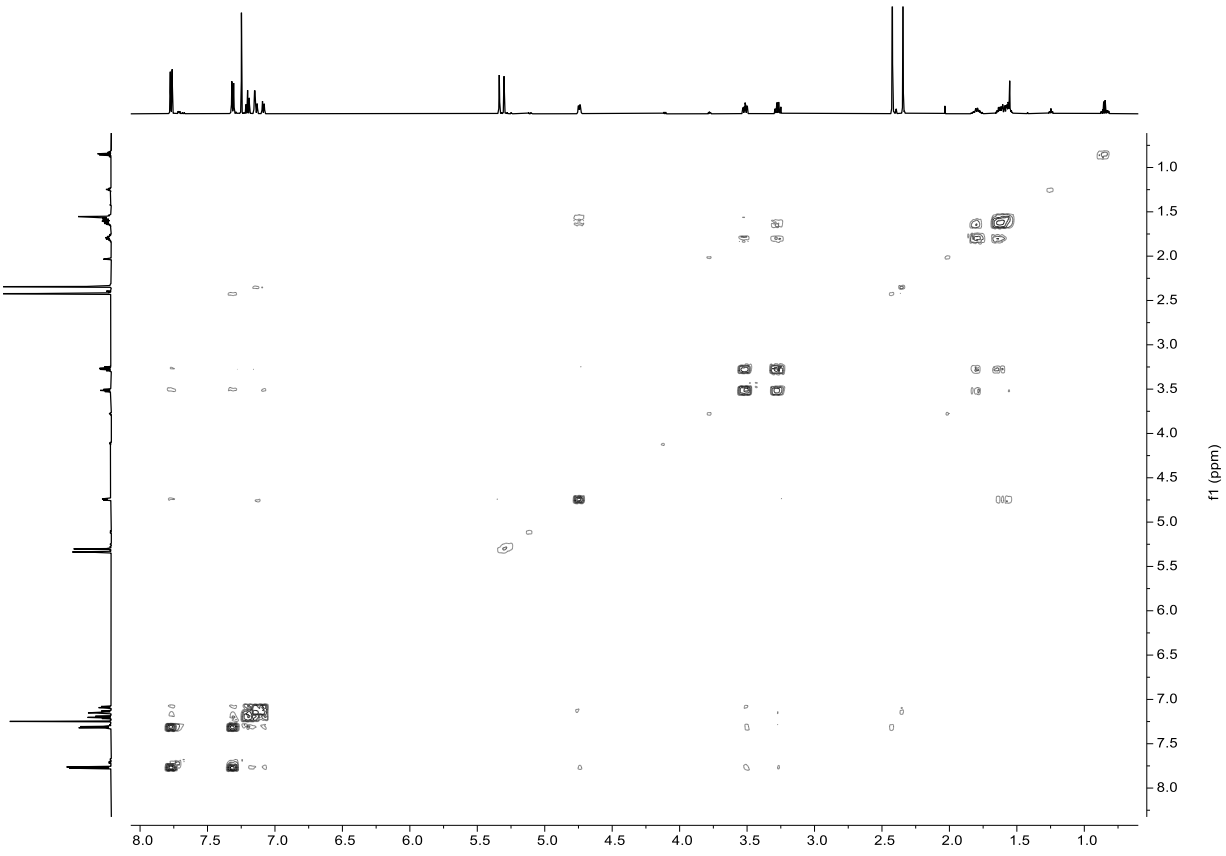
^{13}C-NMR of compound 3c (150 MHz, $CDCl_3$)



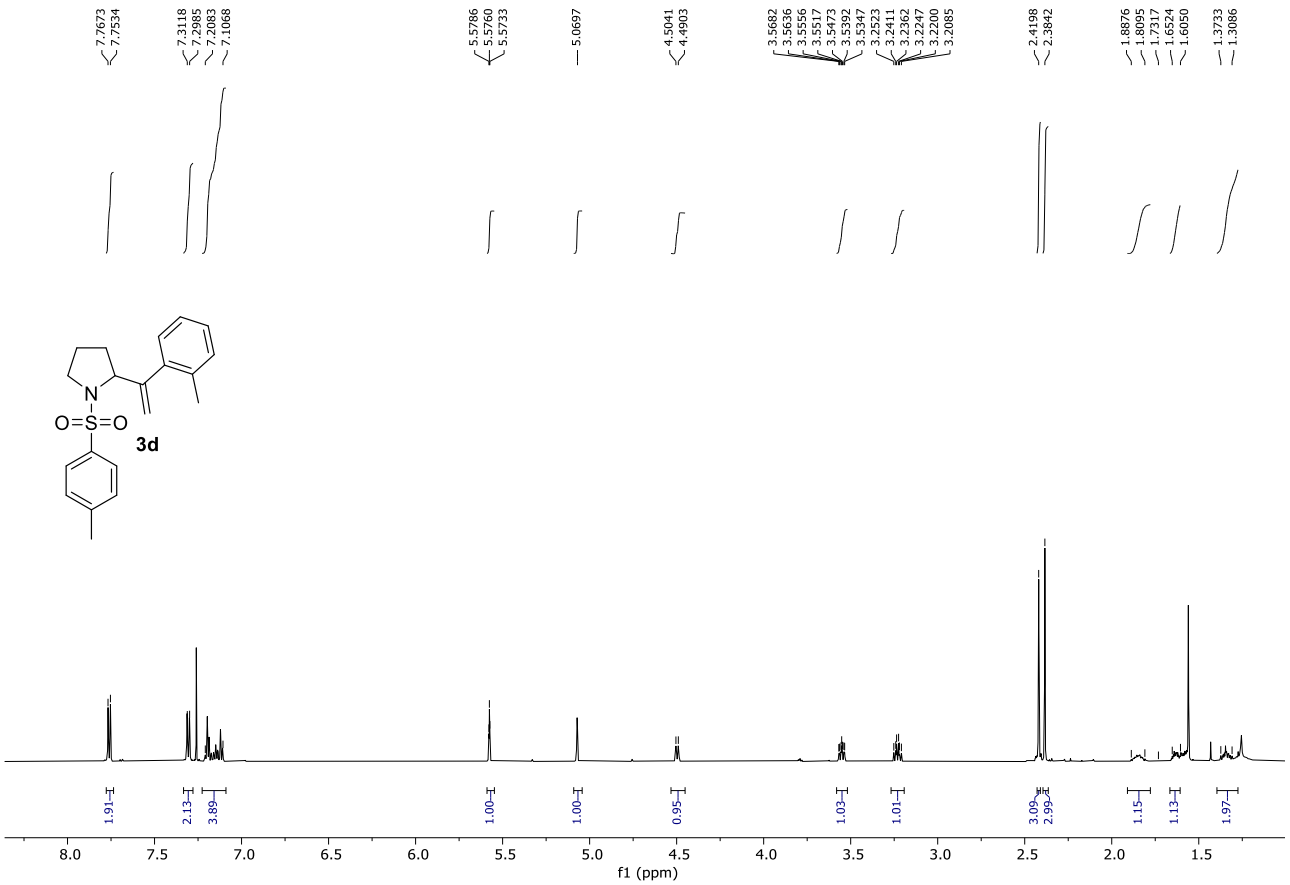
Comparison between DEPT-135 and ^{13}C-NMR of compound 3c (150 MHz, $CDCl_3$)



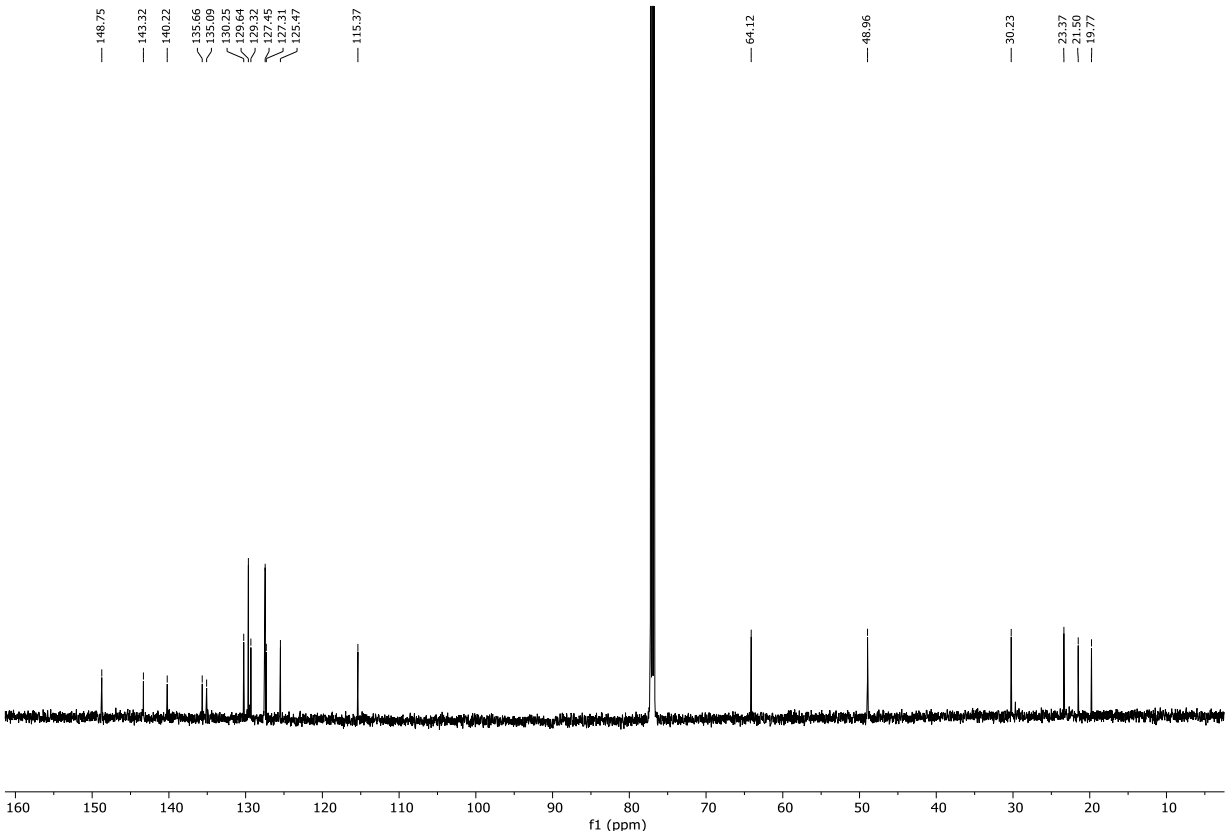
COSY-NMR of compound 3c (600 MHz, $CDCl_3$)



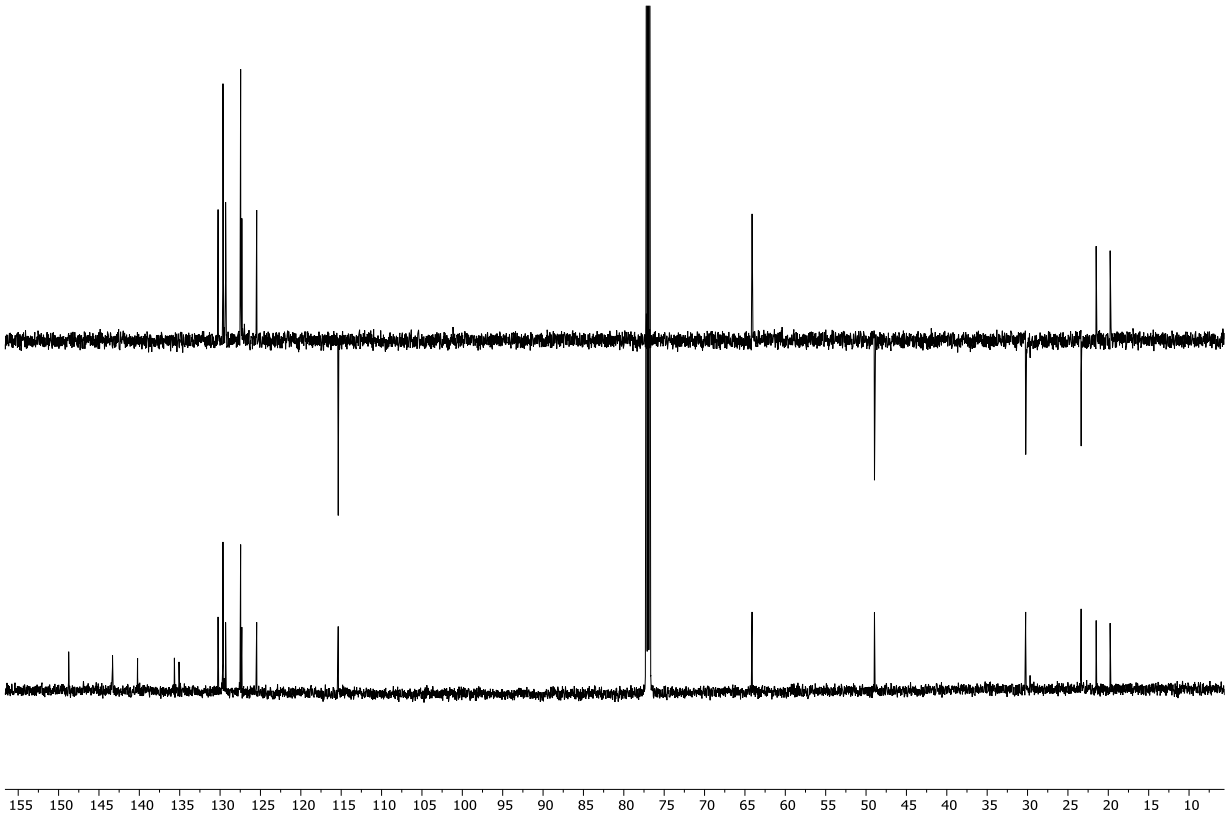
^{1}H-NMR of compound 3d (600 MHz, $CDCl_3$)



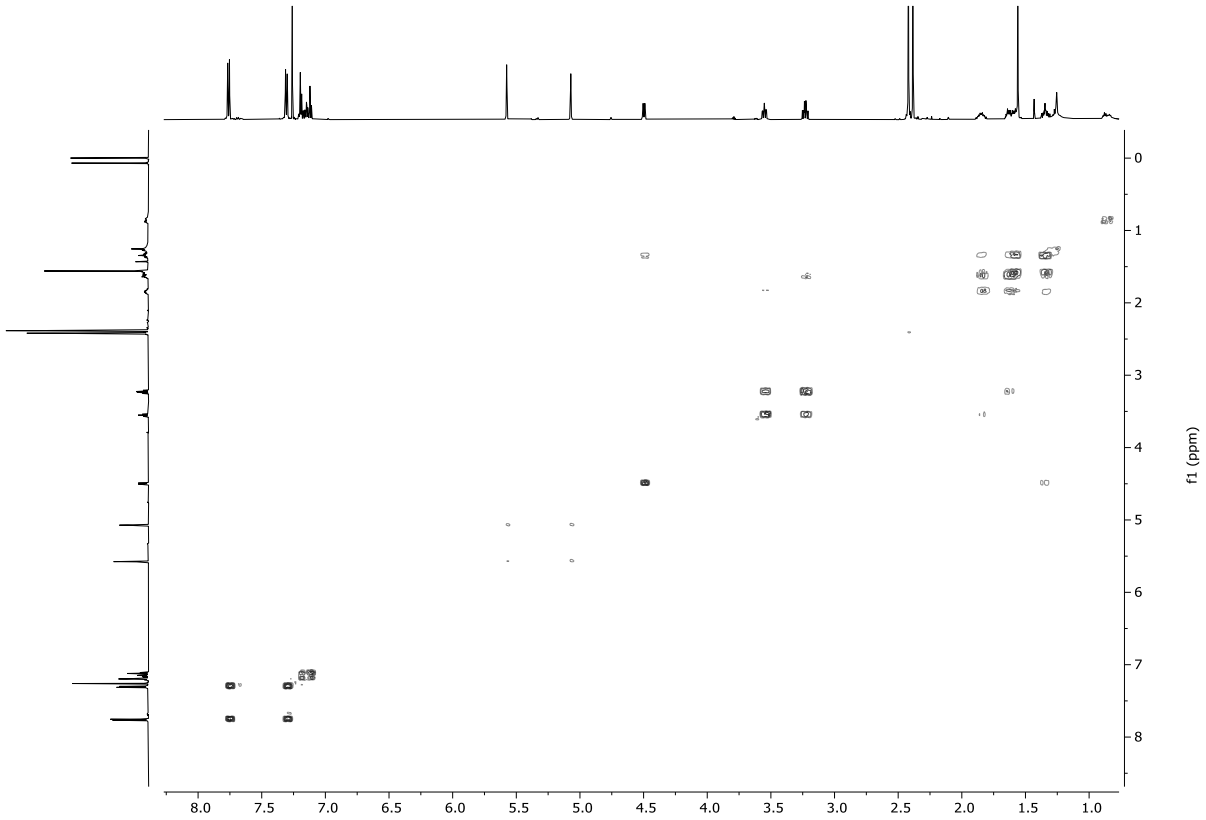
^{13}C-NMR of compound 3c (150 MHz, $CDCl_3$)



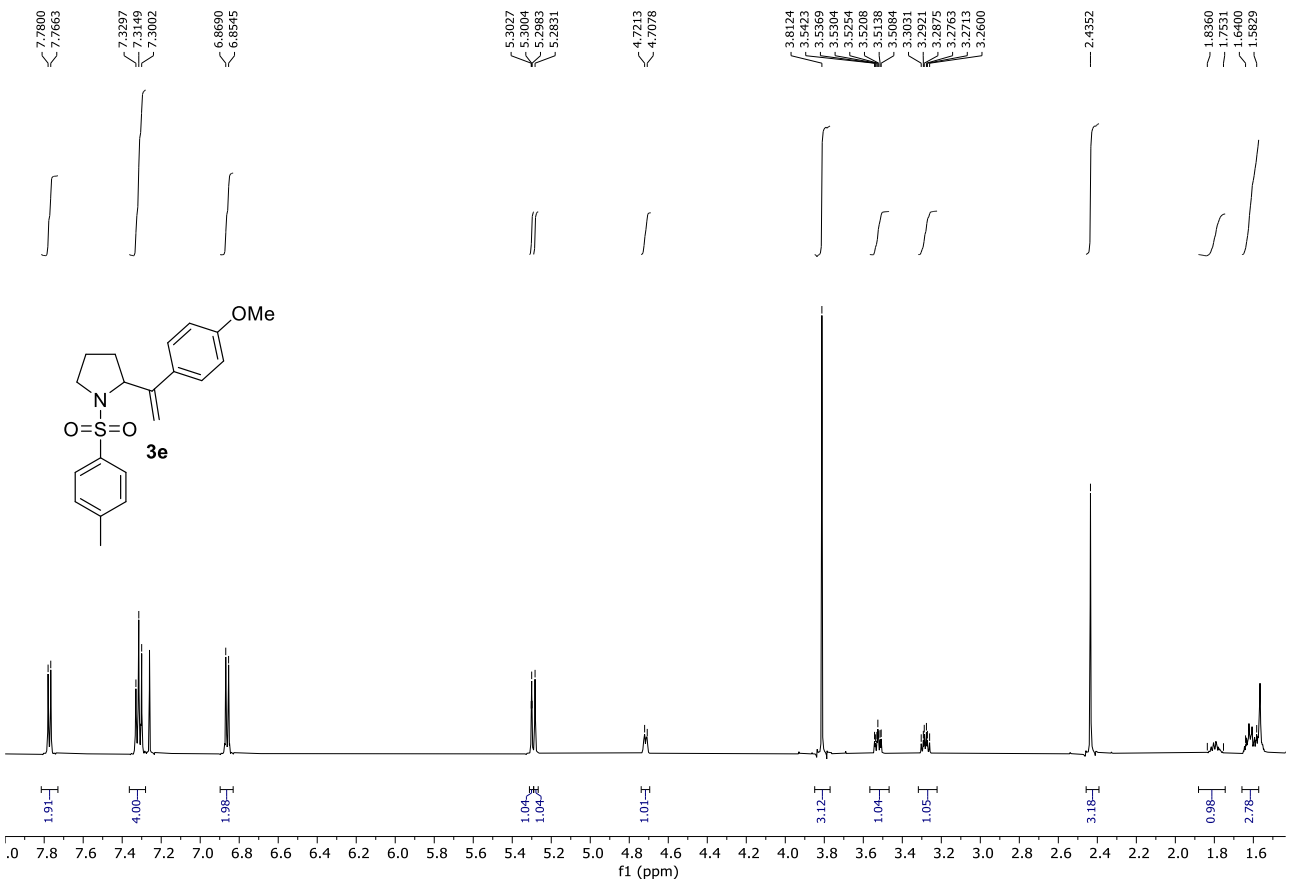
Comparison between DEPT-135 and ^{13}C-NMR of compound 3d (150 MHz, $CDCl_3$)



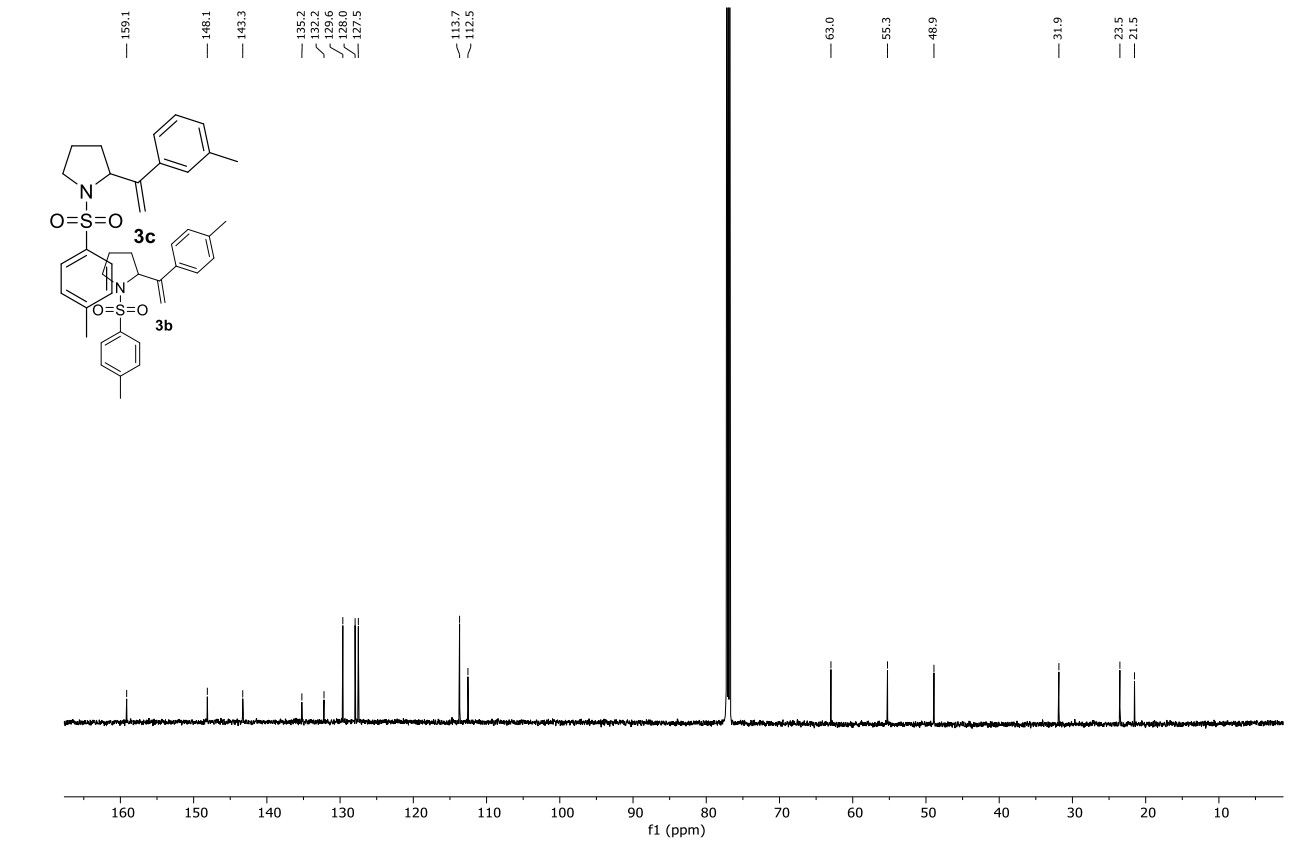
COSY-NMR of compound 3d (600 MHz, $CDCl_3$)



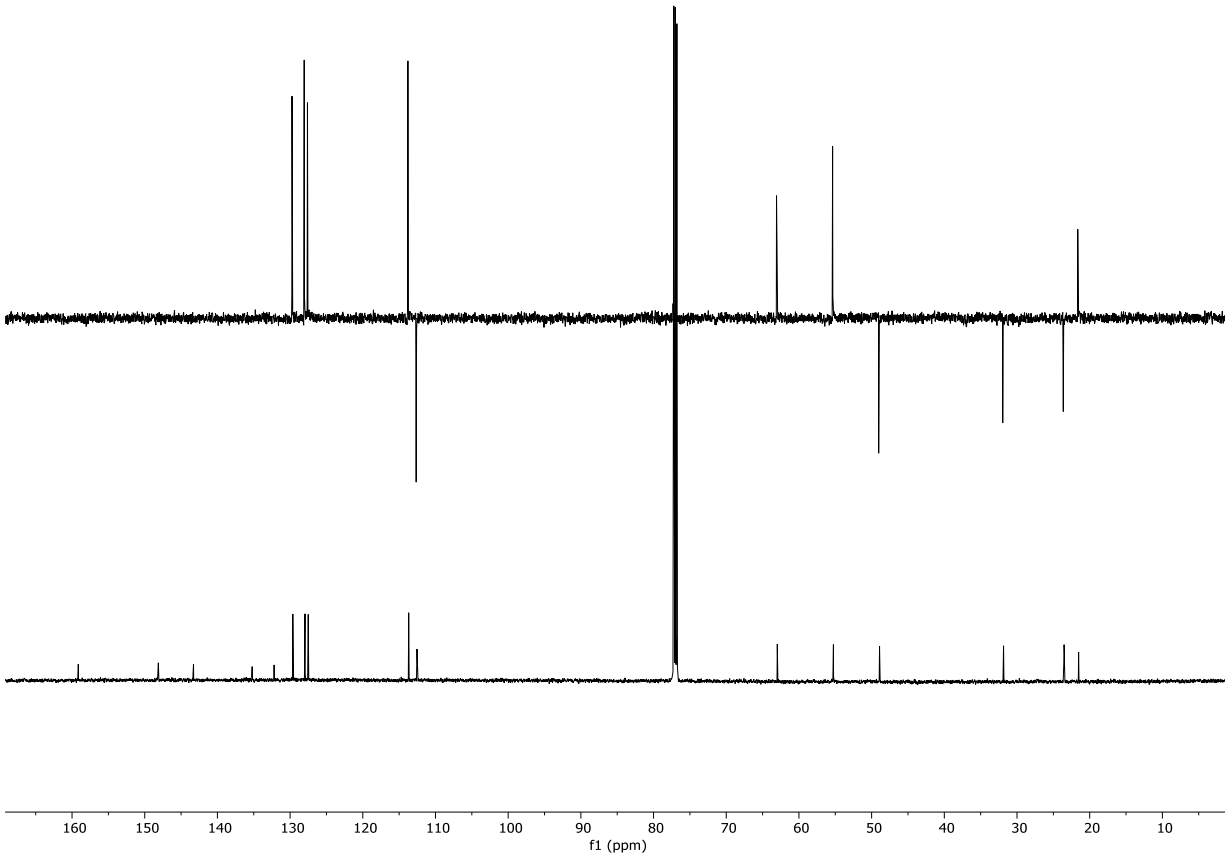
^{1}H-NMR of compound 3e (600 MHz, $CDCl_3$)



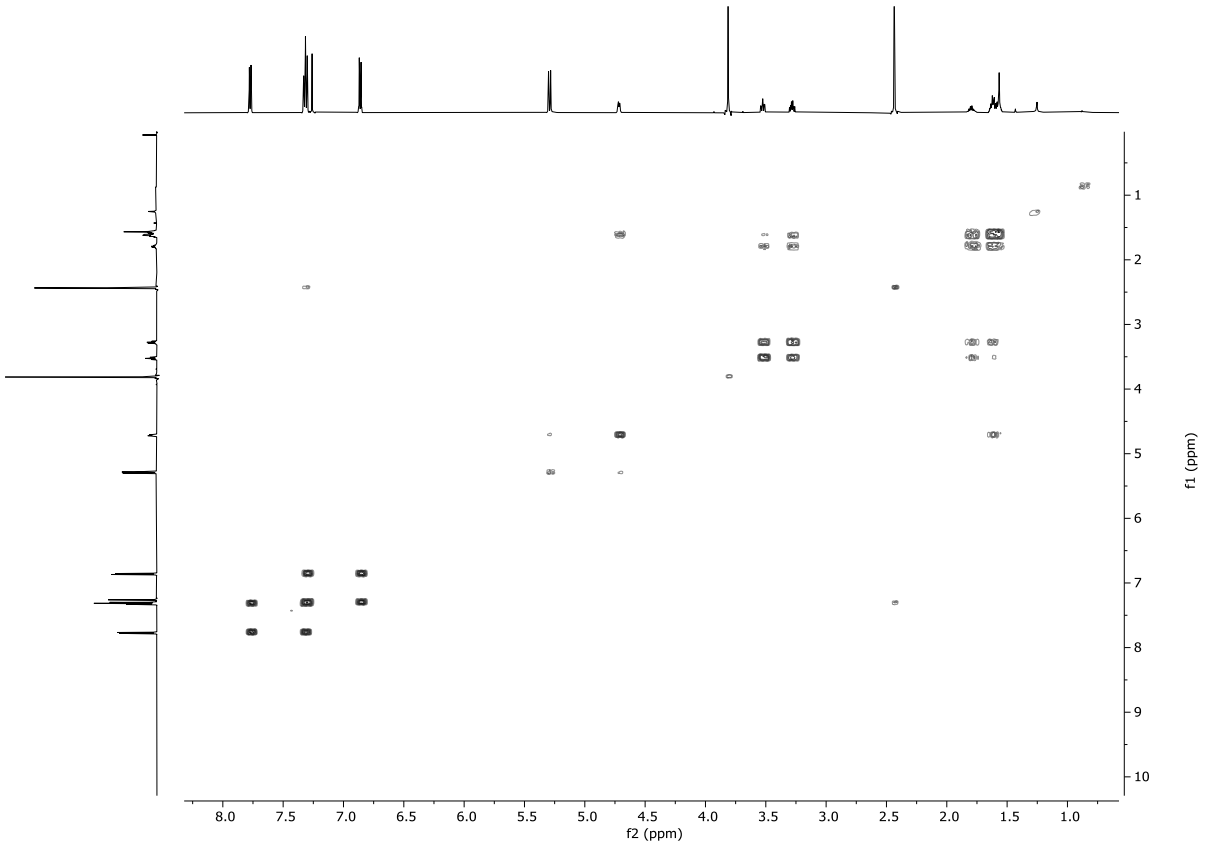
^{13}C-NMR of compound 3e (150 MHz, $CDCl_3$)



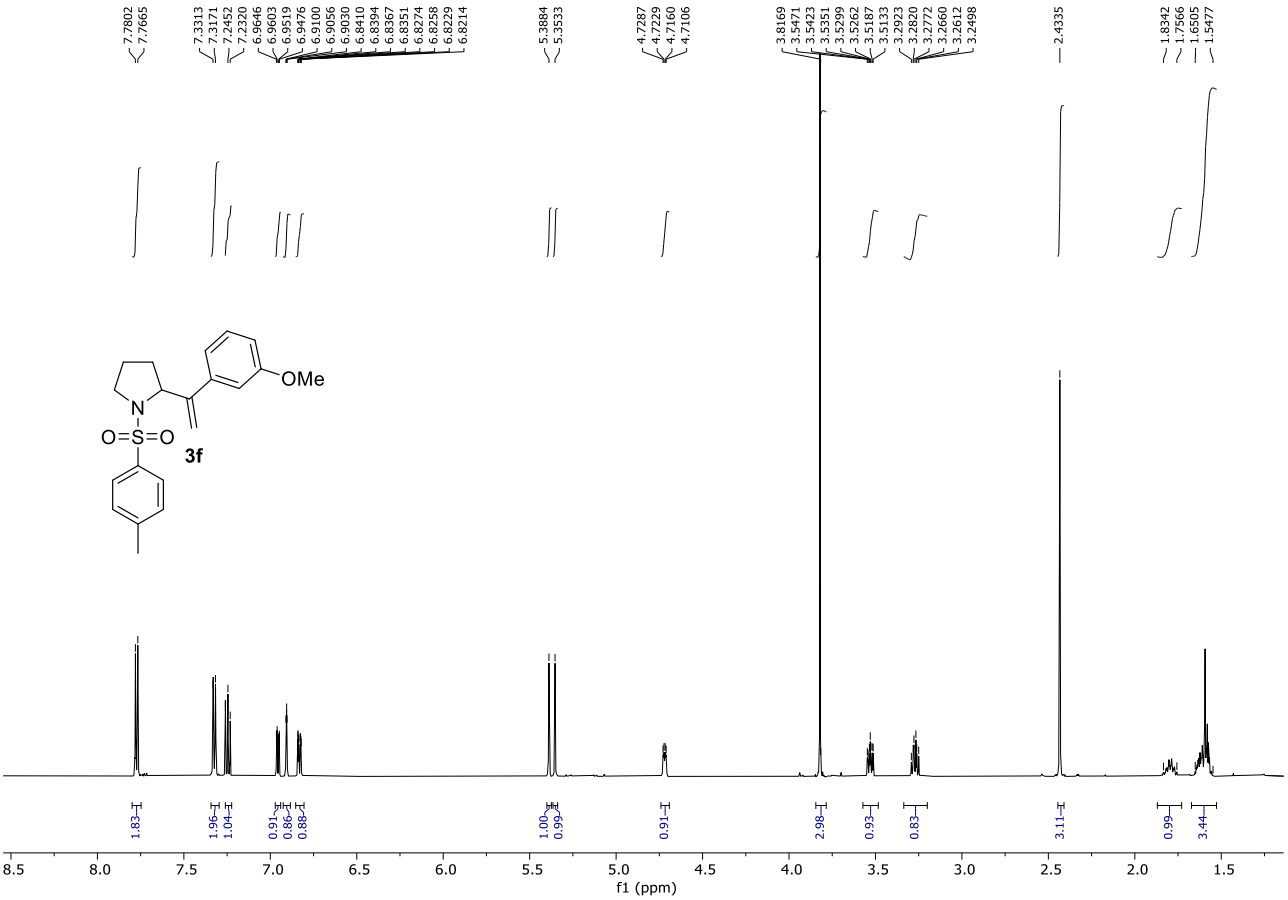
Comparison between DEPT-135 and ^{13}C-NMR of compound 3e (150 MHz, $CDCl_3$)



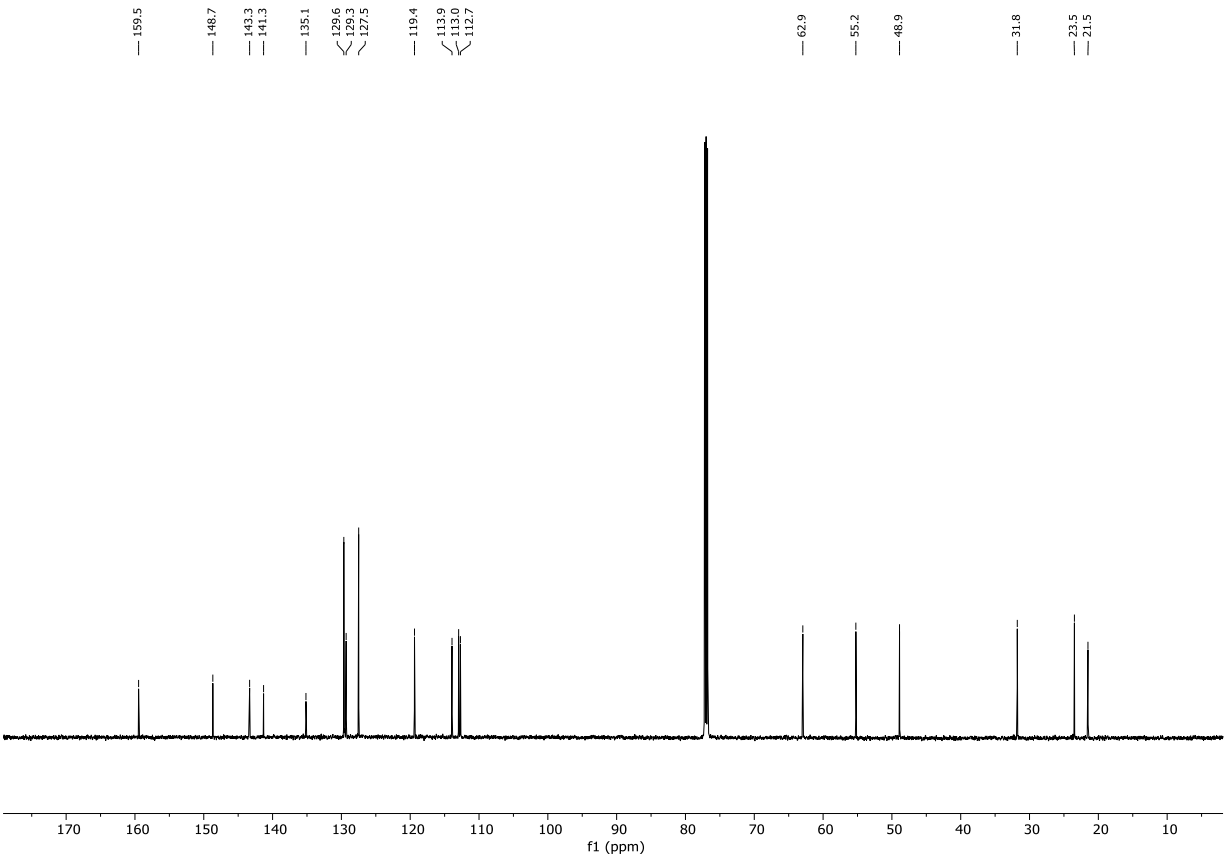
COSY-NMR of compound 3e (600 MHz, $CDCl_3$)



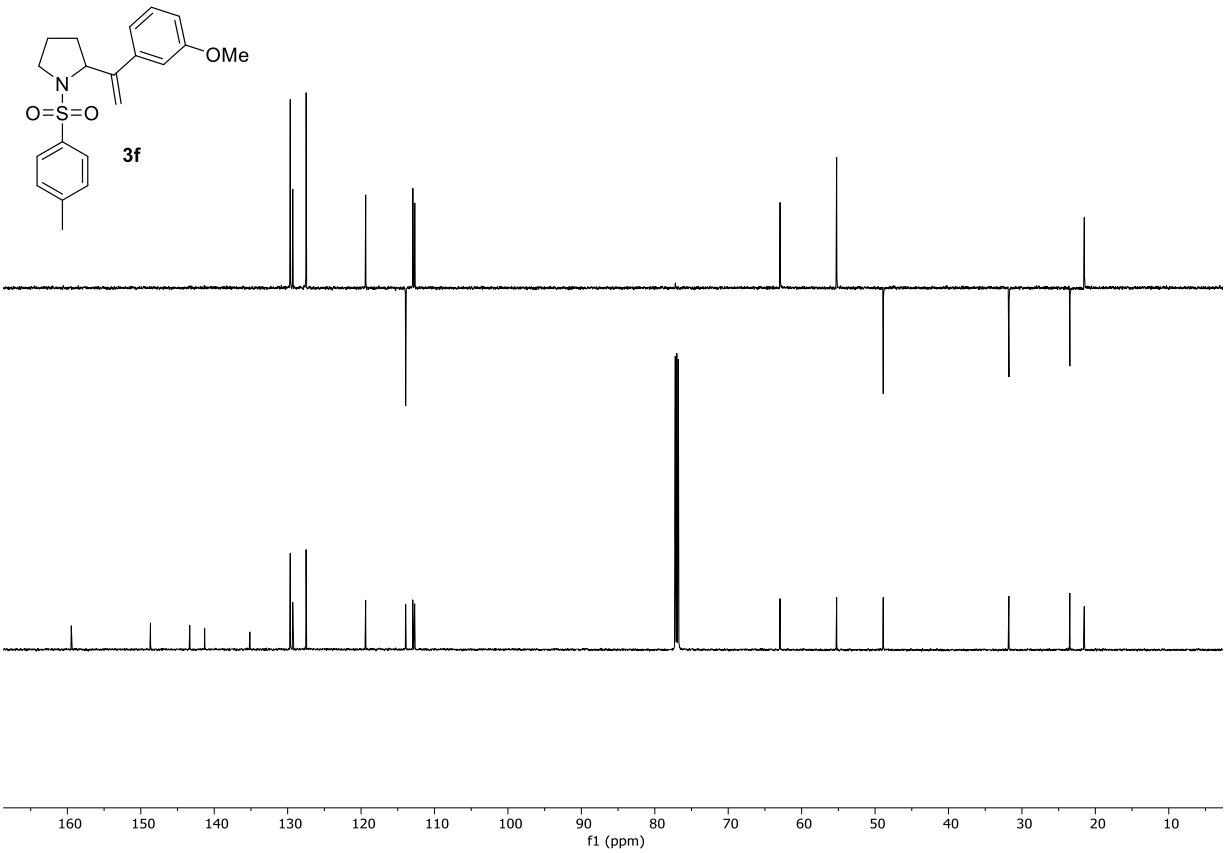
^{1}H-NMR of compound 3f (600 MHz, $CDCl_3$)



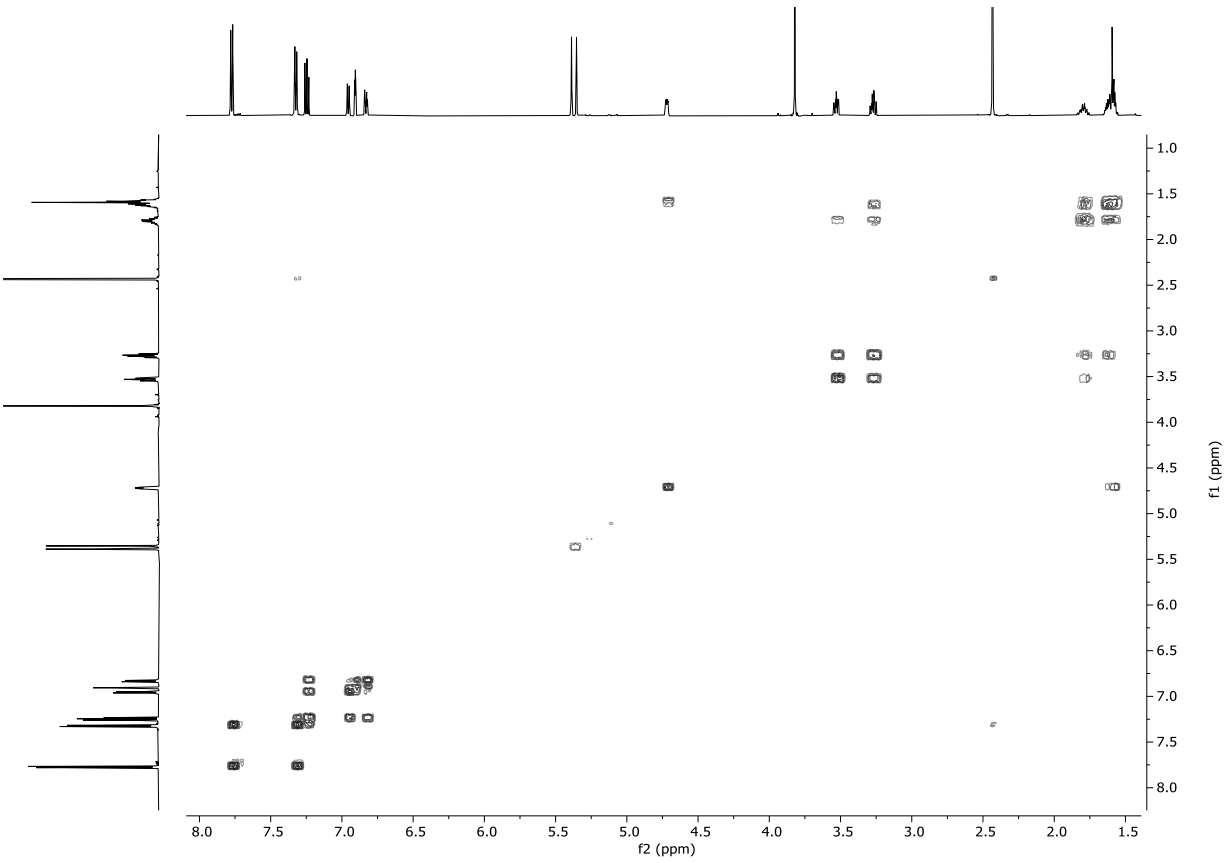
^{13}C-NMR of compound 3f (150 MHz, $CDCl_3$)



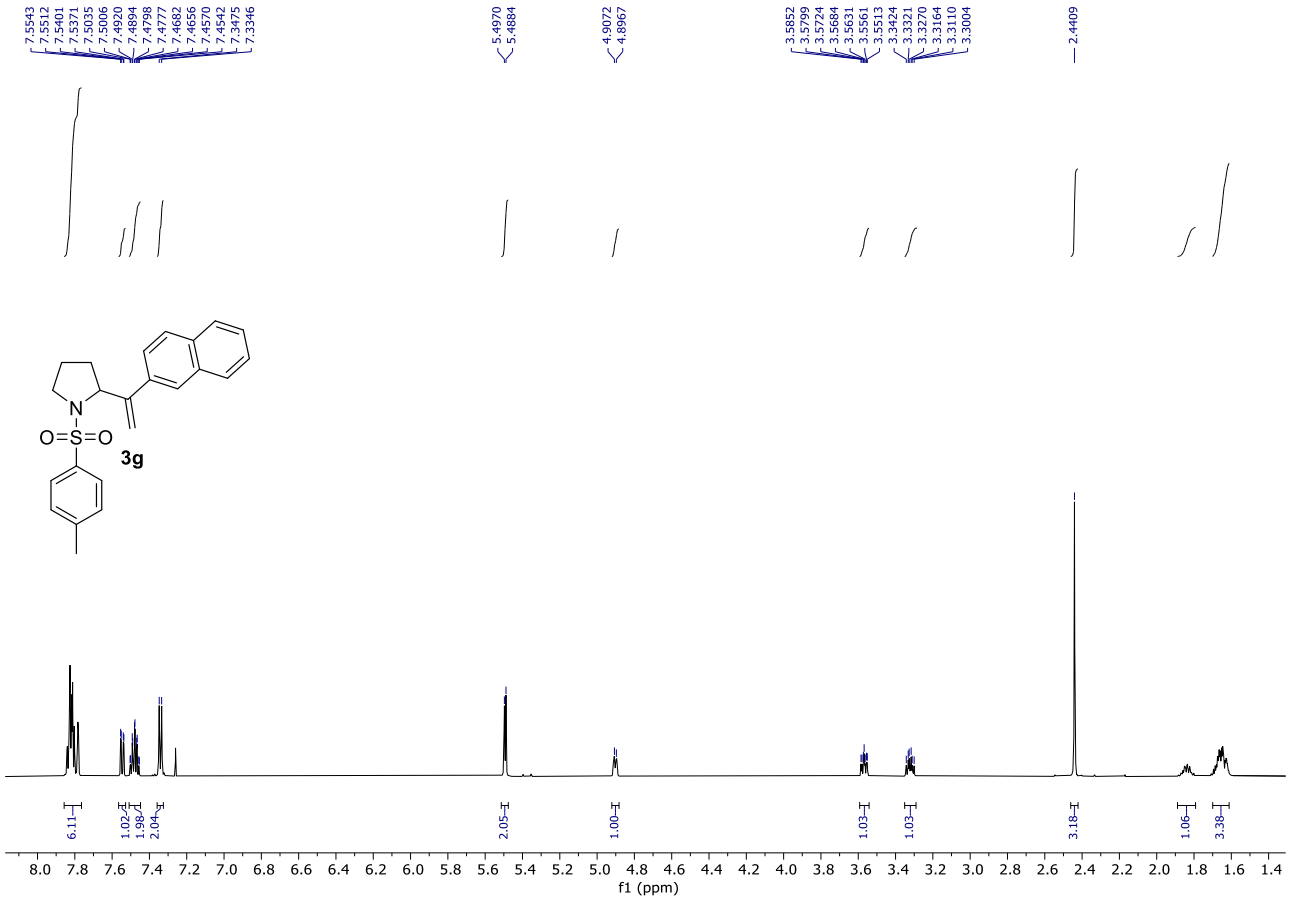
Comparison between DEPT-135 and ^{13}C-NMR of compound 3f (150 MHz, $CDCl_3$)



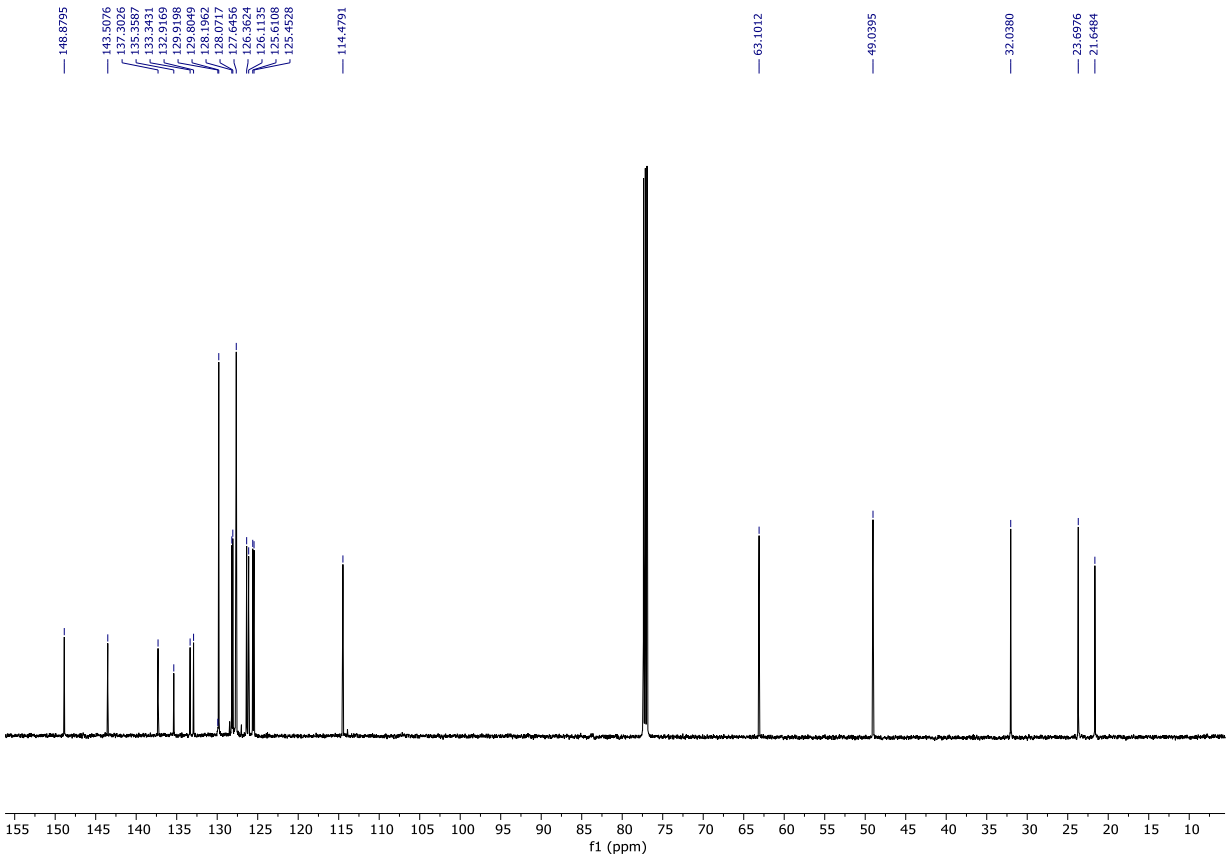
COSY-NMR of compound 3f (600 MHz, $CDCl_3$)



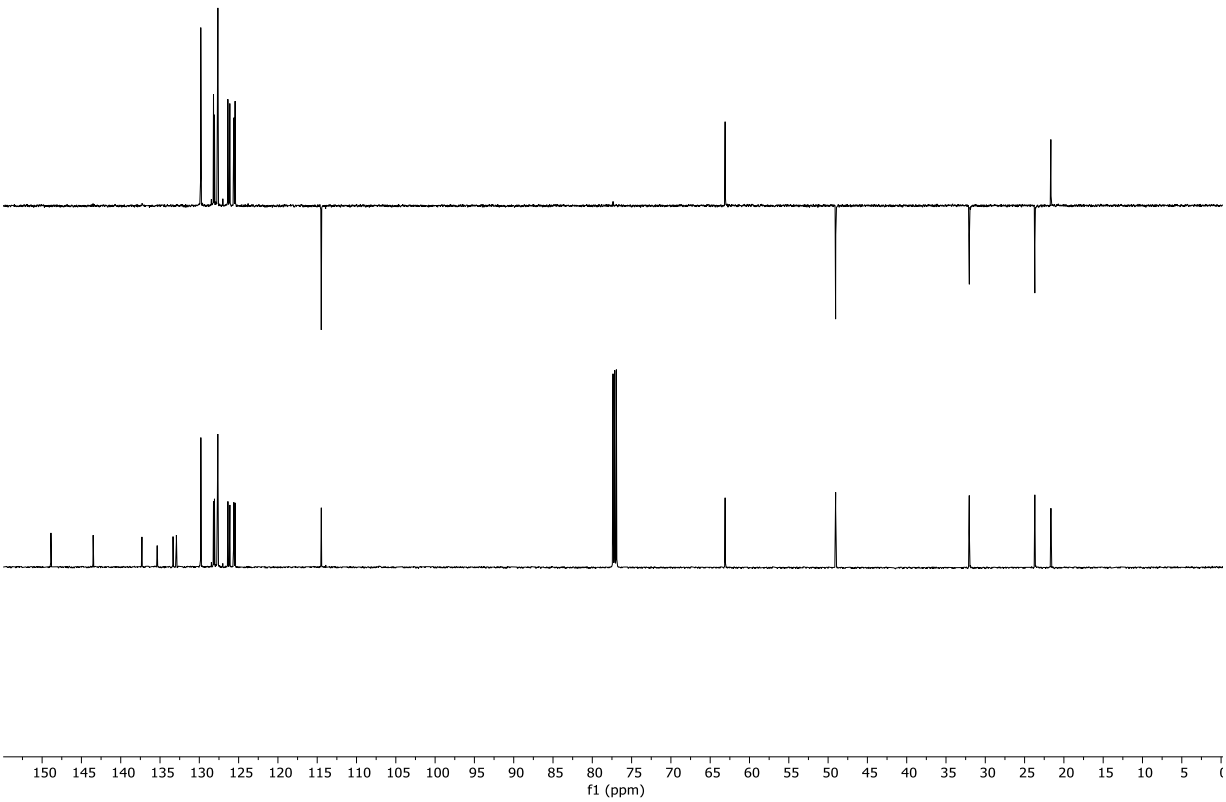
^{1}H-NMR of compound 3g (600 MHz, $CDCl_3$)



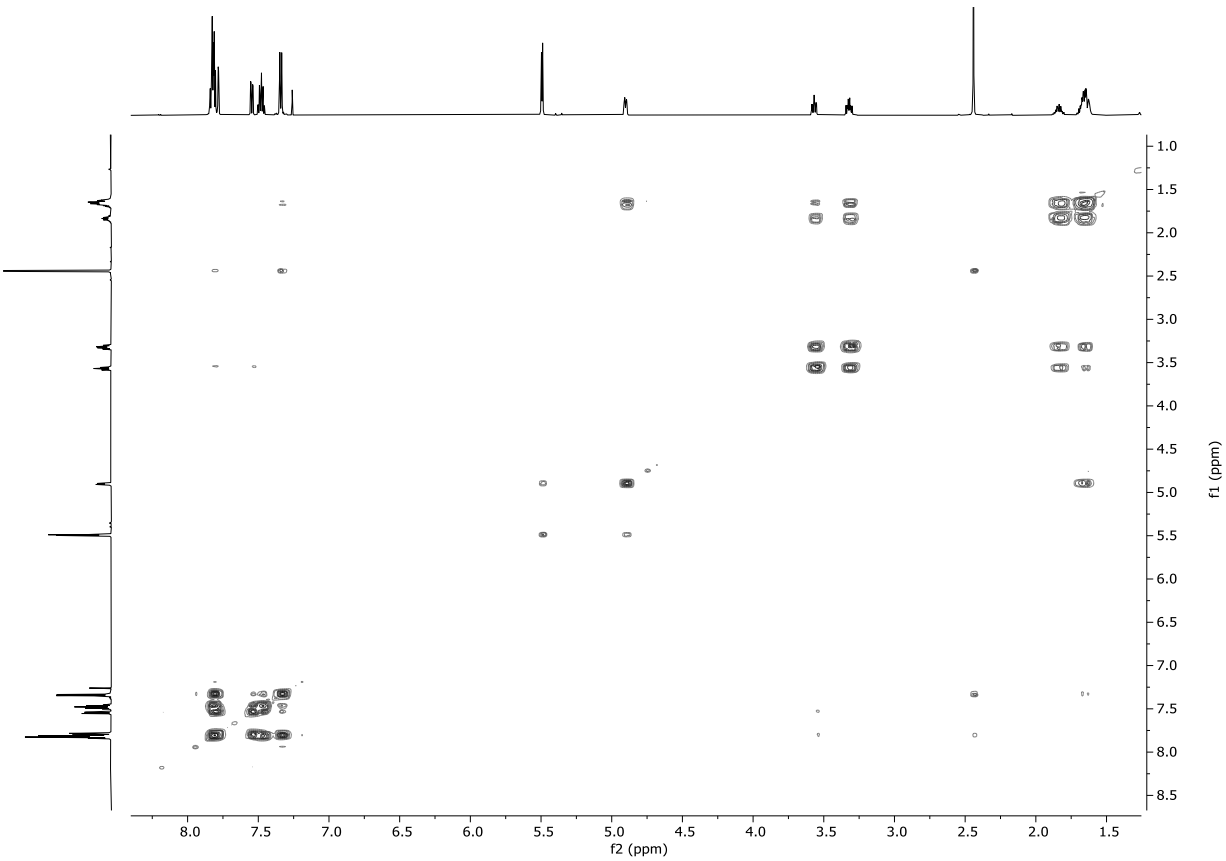
^{13}C-NMR of compound 3g (150 MHz, $CDCl_3$)



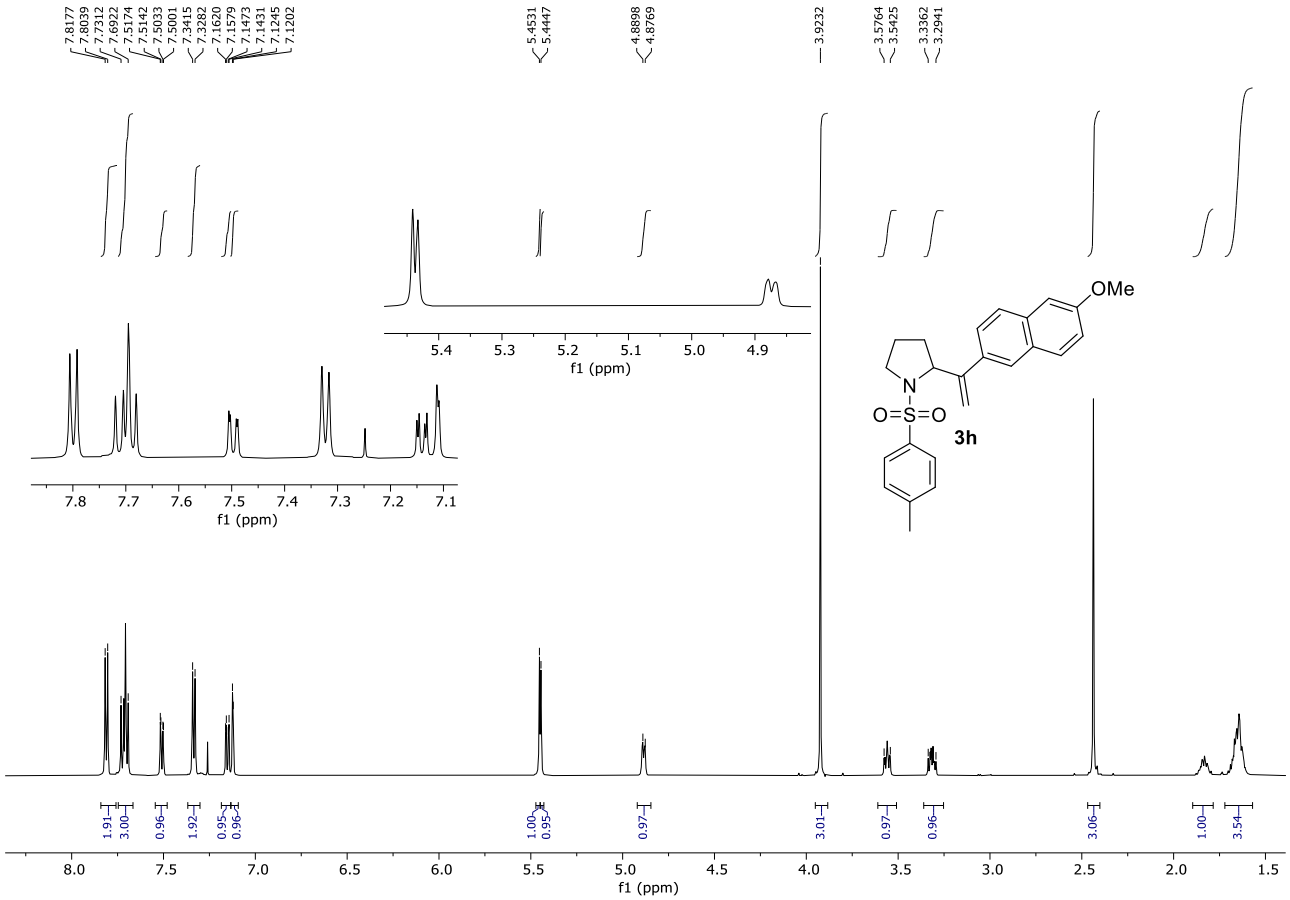
Comparison between DEPT-135 and ^{13}C-NMR of compound 3g (150 MHz, $CDCl_3$)



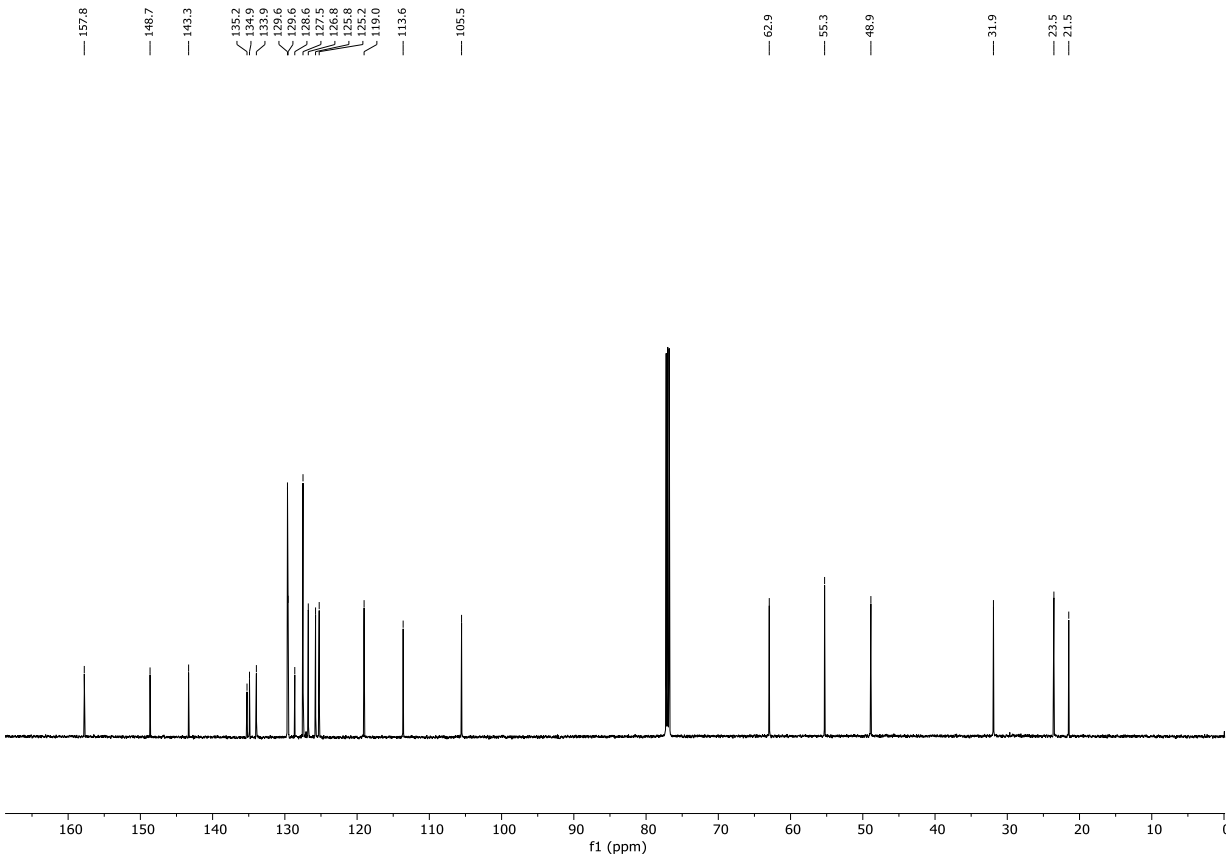
COSY-NMR of compound 3g (600 MHz, $CDCl_3$)



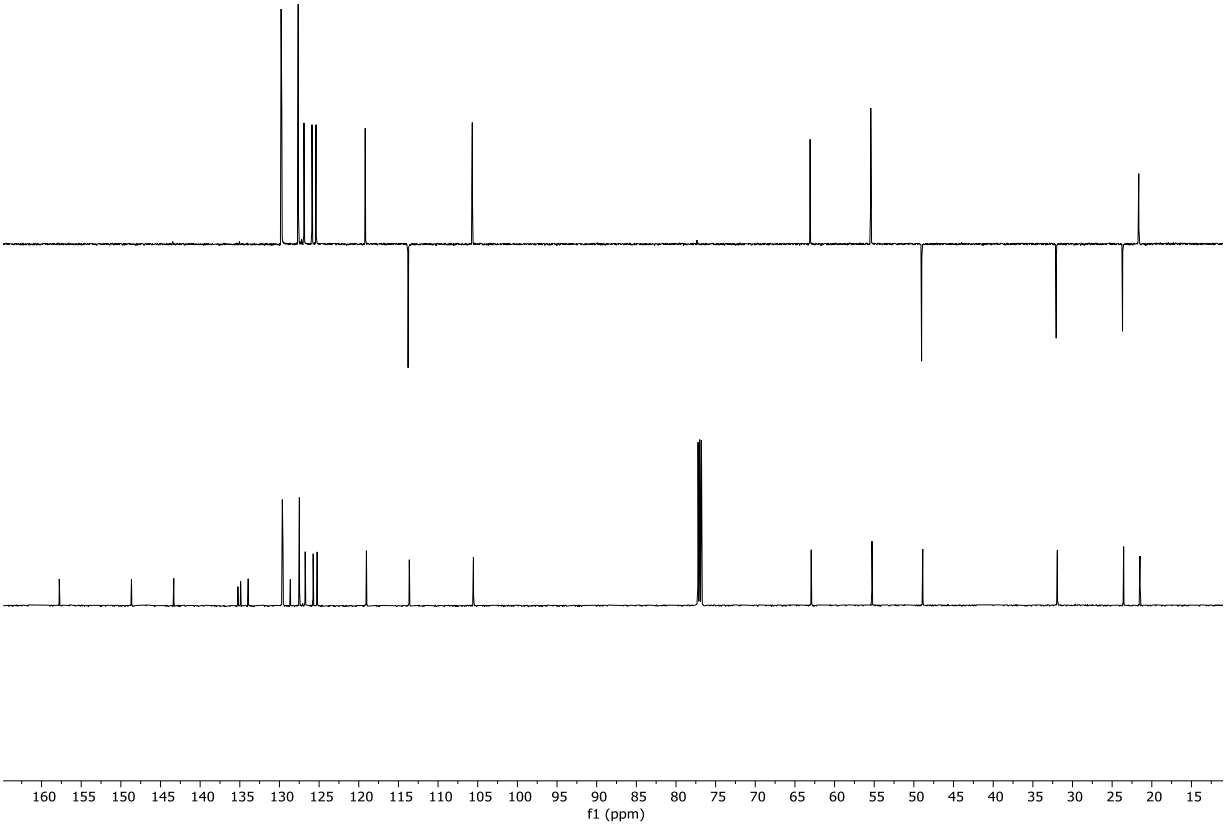
^{1}H-NMR of compound 3h (600 MHz, $CDCl_3$)



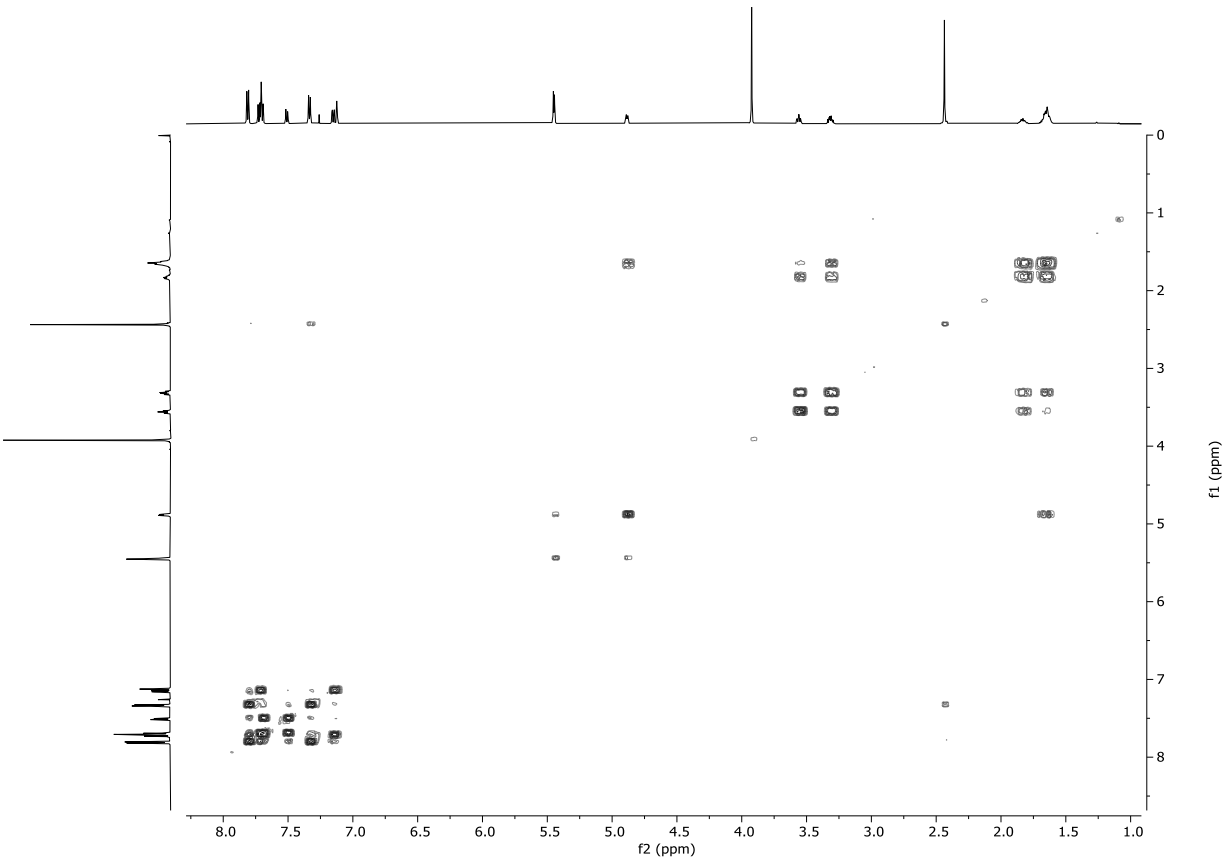
^{13}C-NMR of compound 3h (150 MHz, $CDCl_3$)



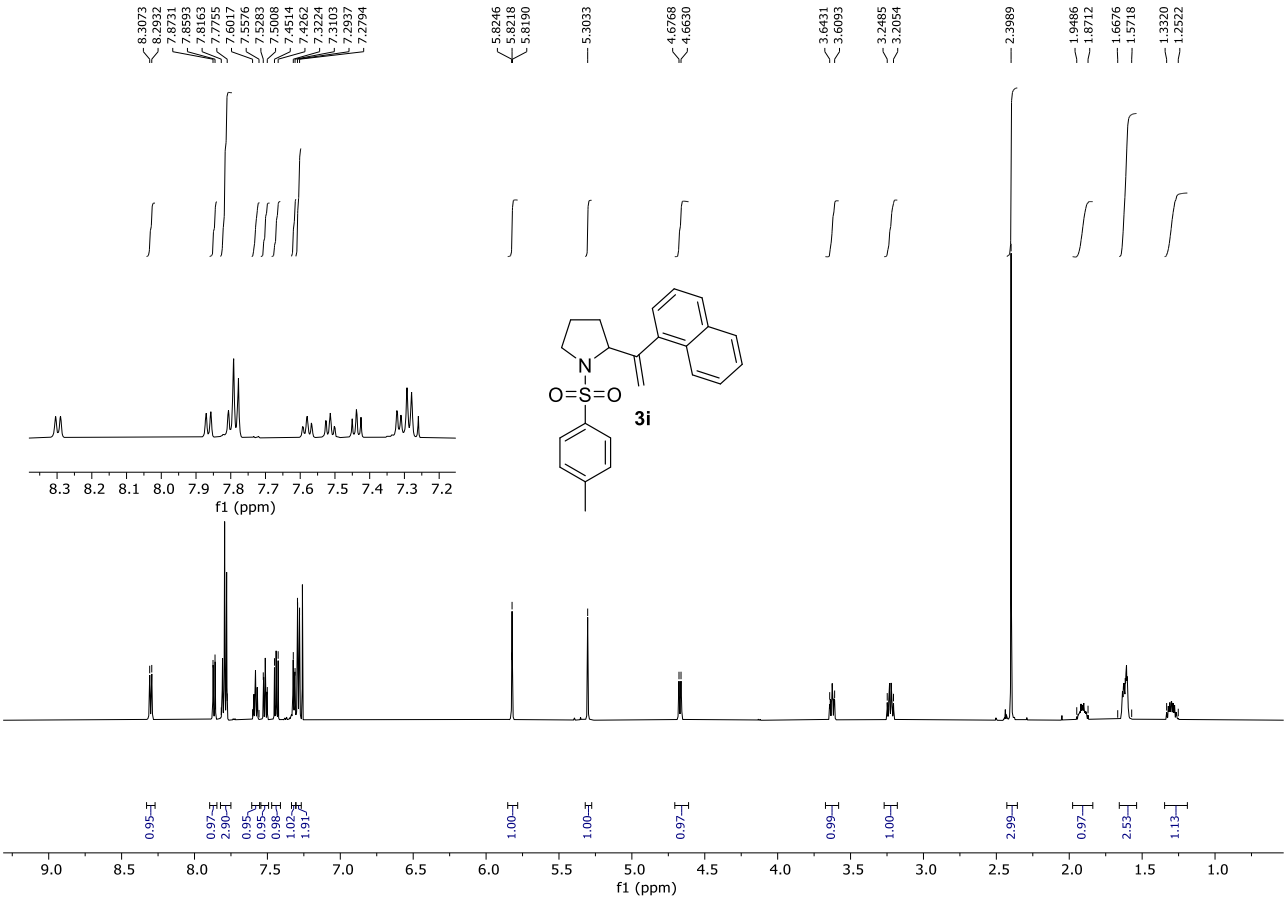
Comparison between DEPT-135 and ^{13}C-NMR of compound 3h (150 MHz, $CDCl_3$)



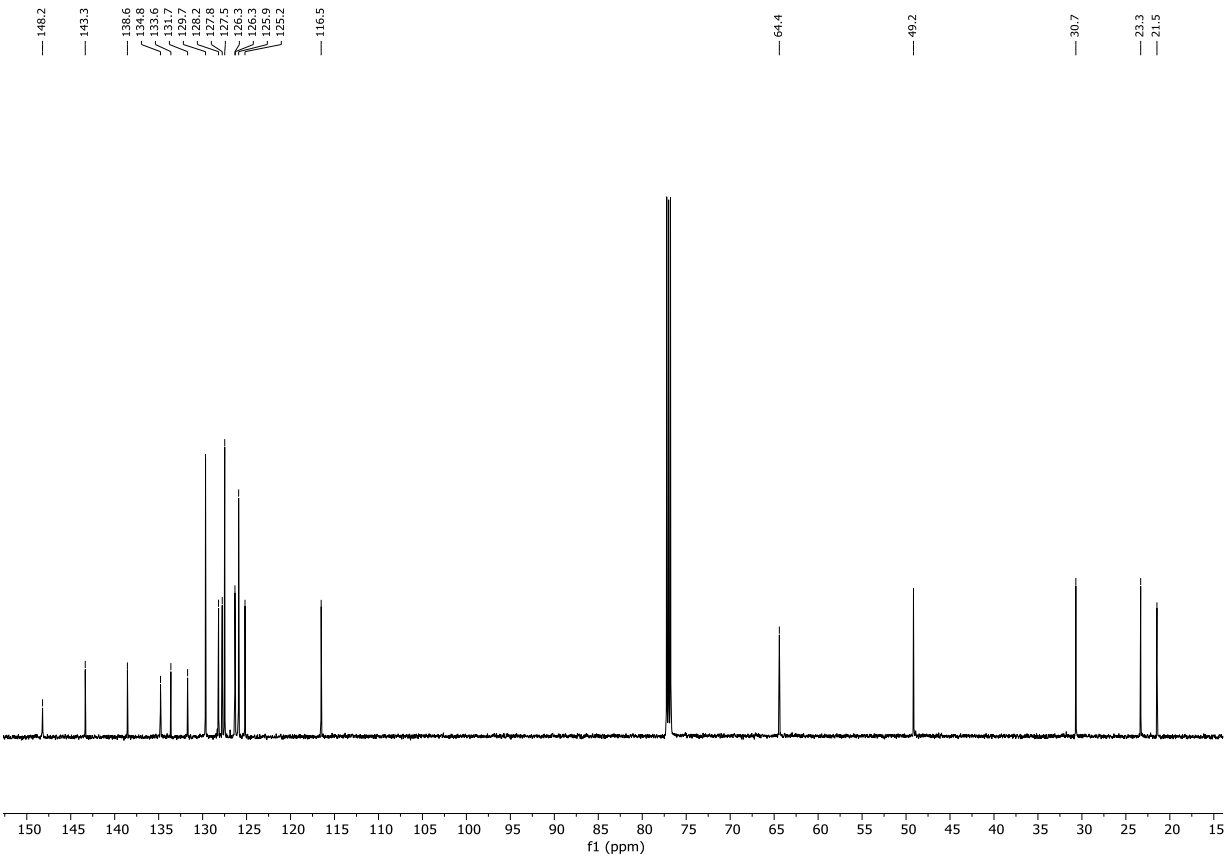
COSY-NMR of compound 3h (600 MHz, $CDCl_3$)



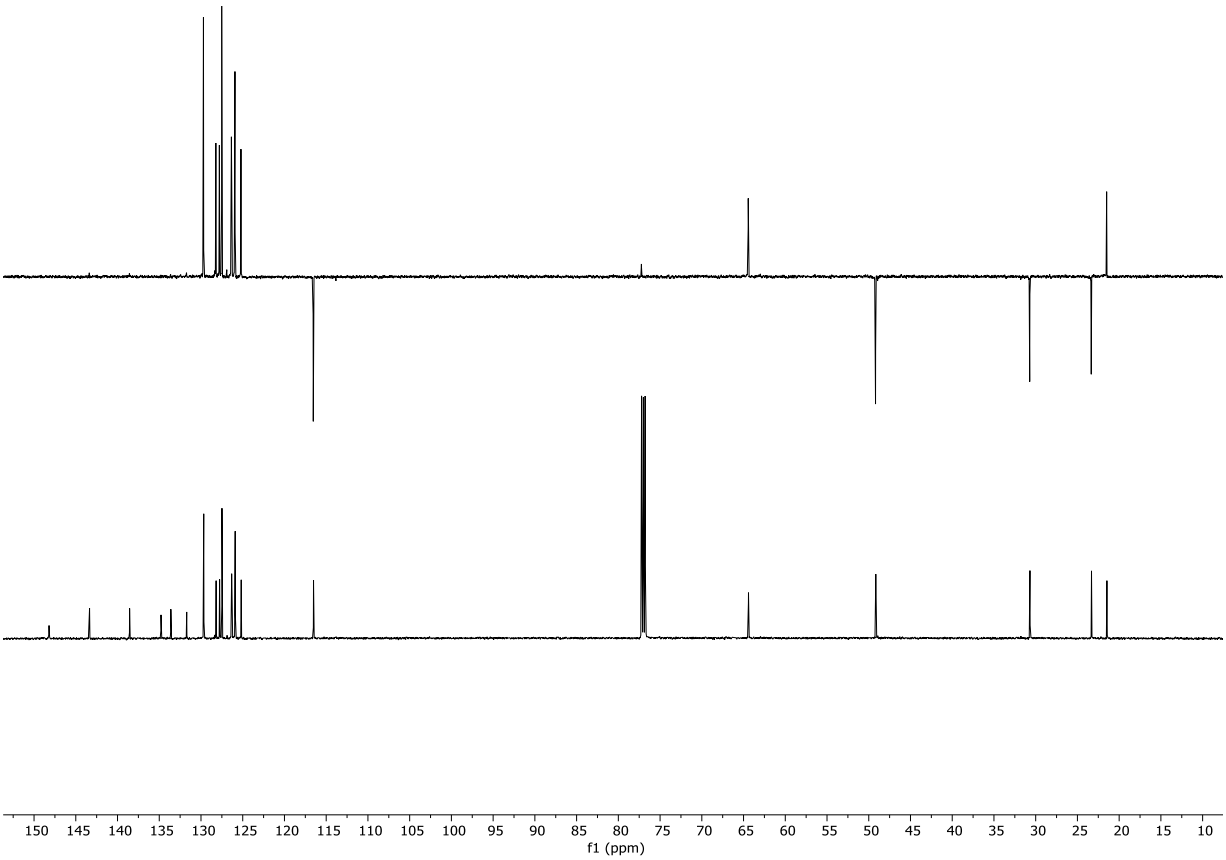
^{1}H-NMR of compound 3i (600 MHz, $CDCl_3$)



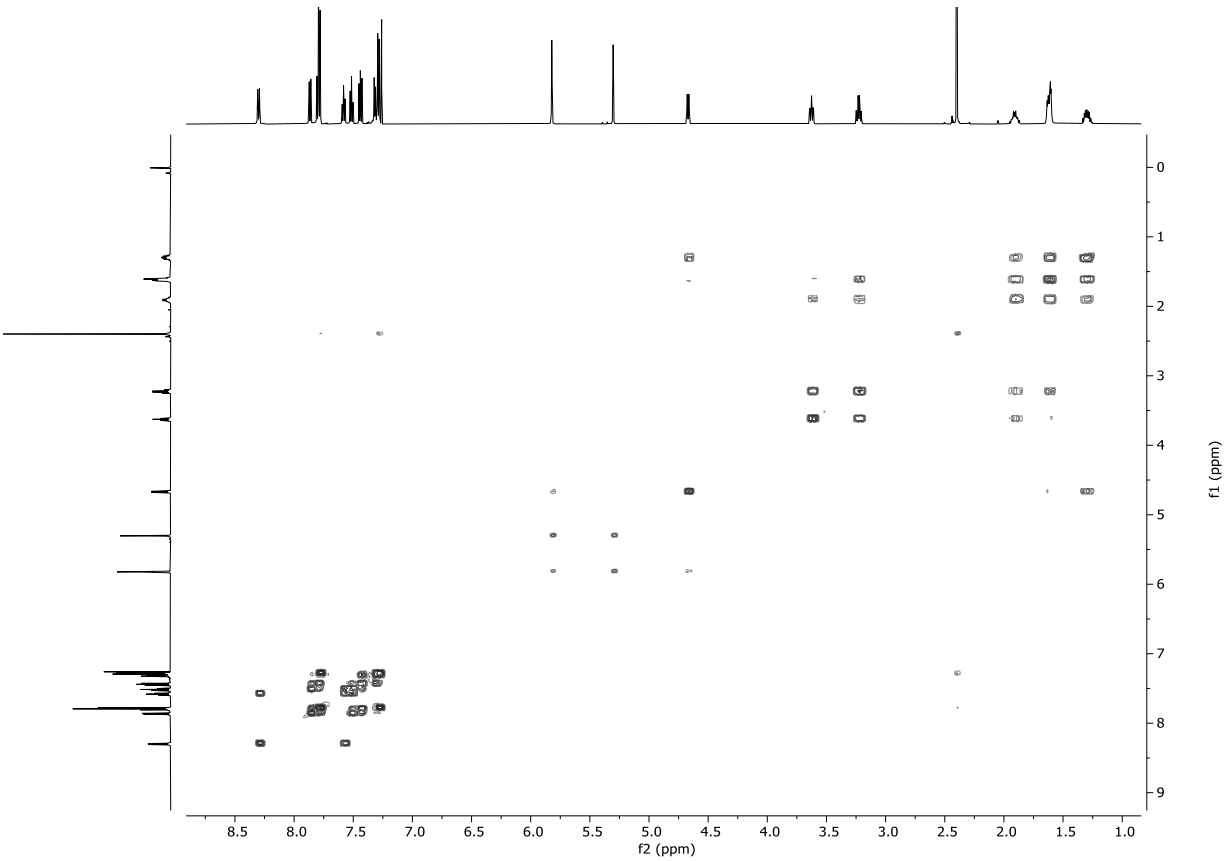
^{13}C-NMR of compound 3i (150 MHz, $CDCl_3$)



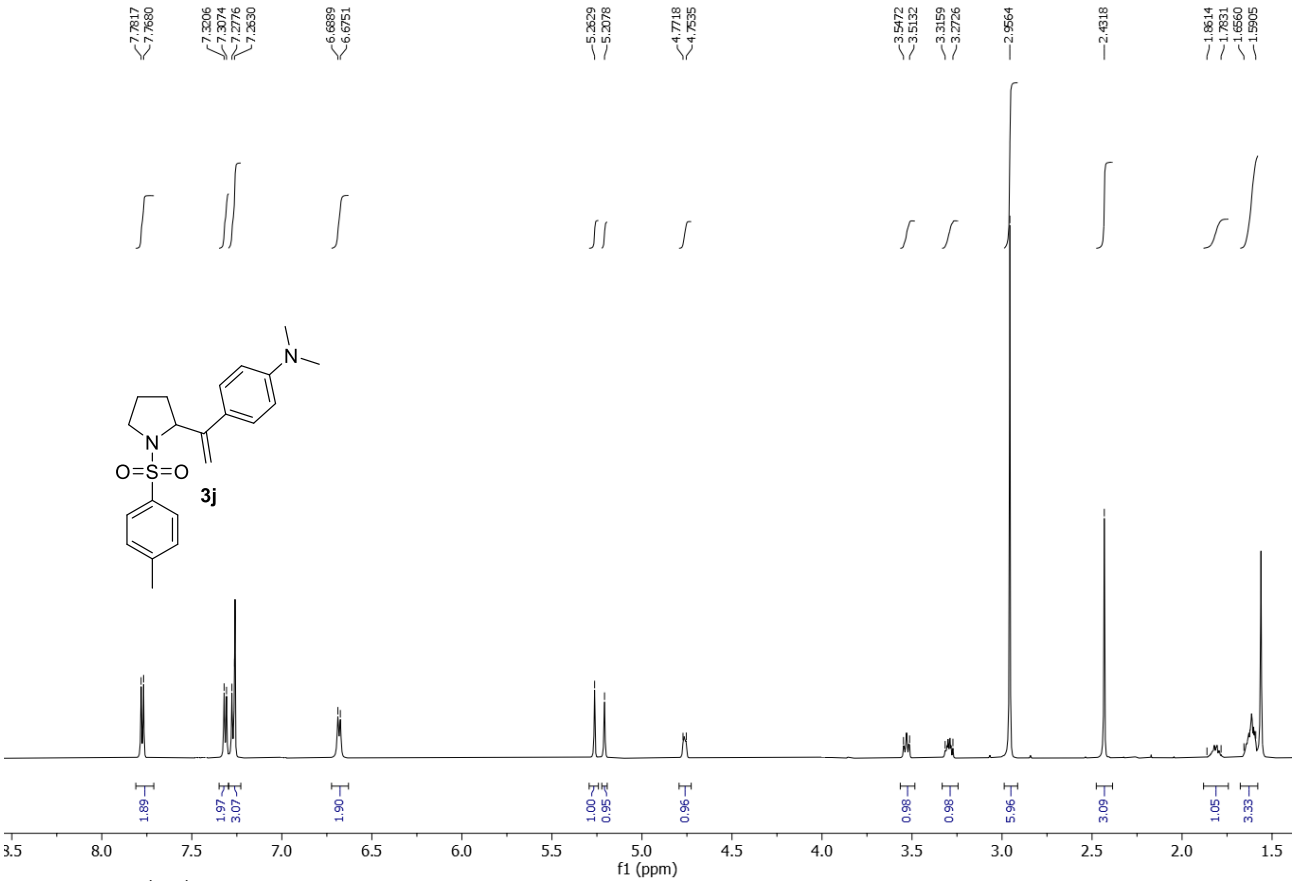
Comparison between DEPT-135 and ^{13}C-NMR of compound 3i (150 MHz, $CDCl_3$)



COSY-NMR of compound 3i (600 MHz, $CDCl_3$)

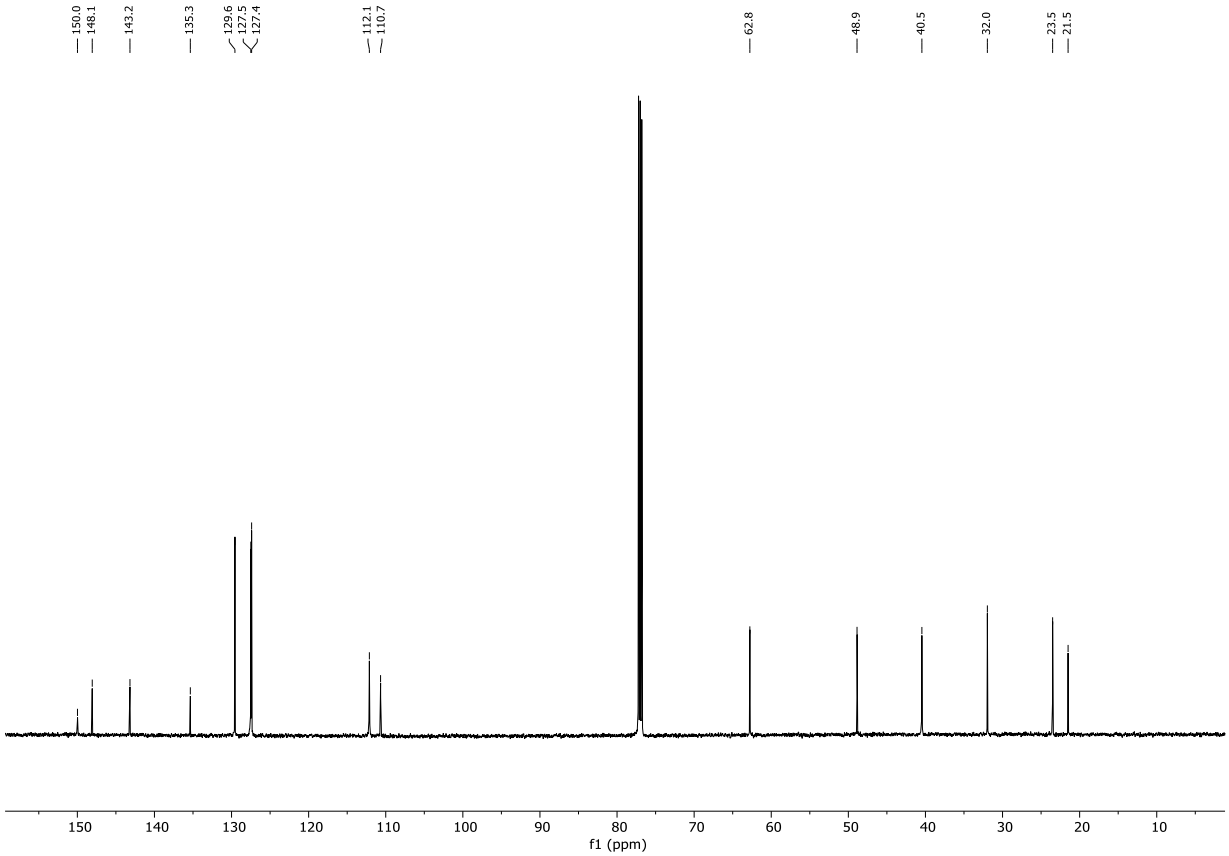


^{1}H-NMR of compound 3j (600 MHz, $CDCl_3$)

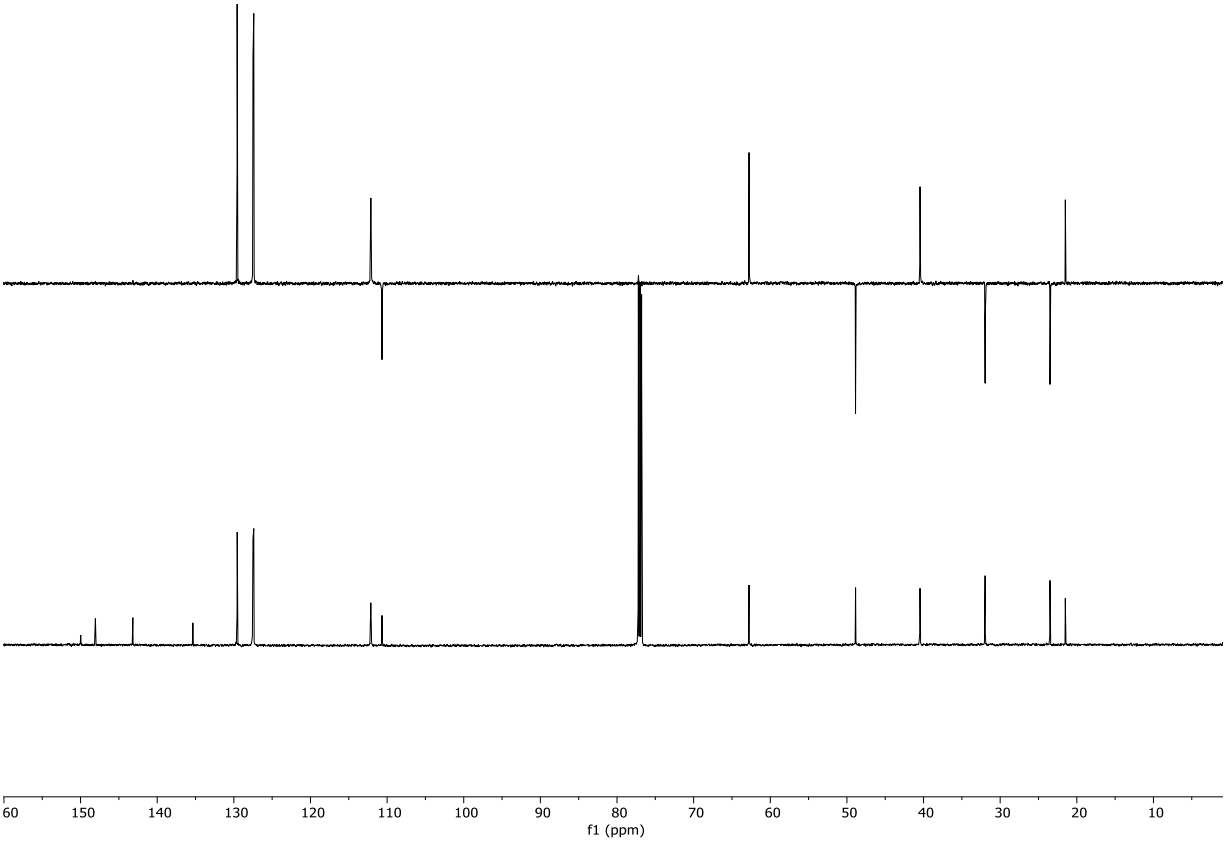


3j

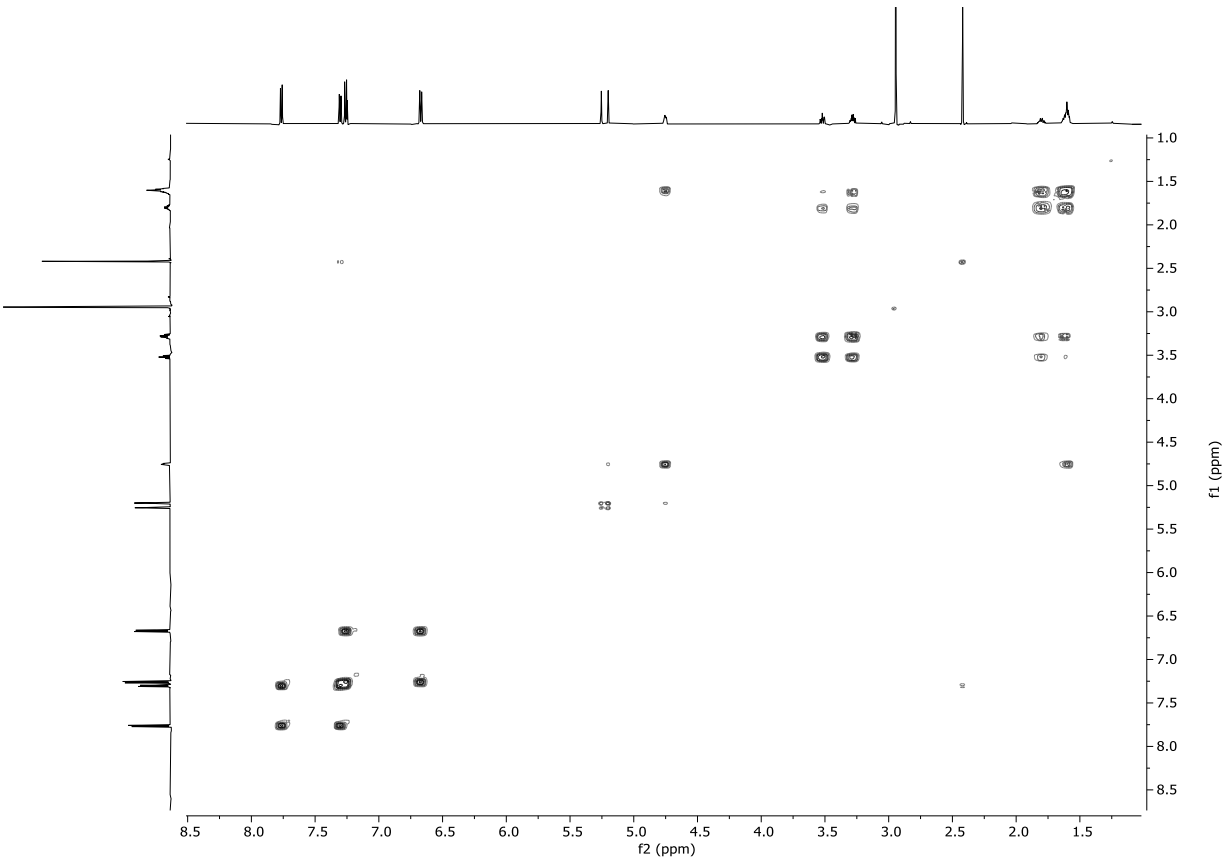
^{13}C-NMR of compound 3j (150 MHz, $CDCl_3$)



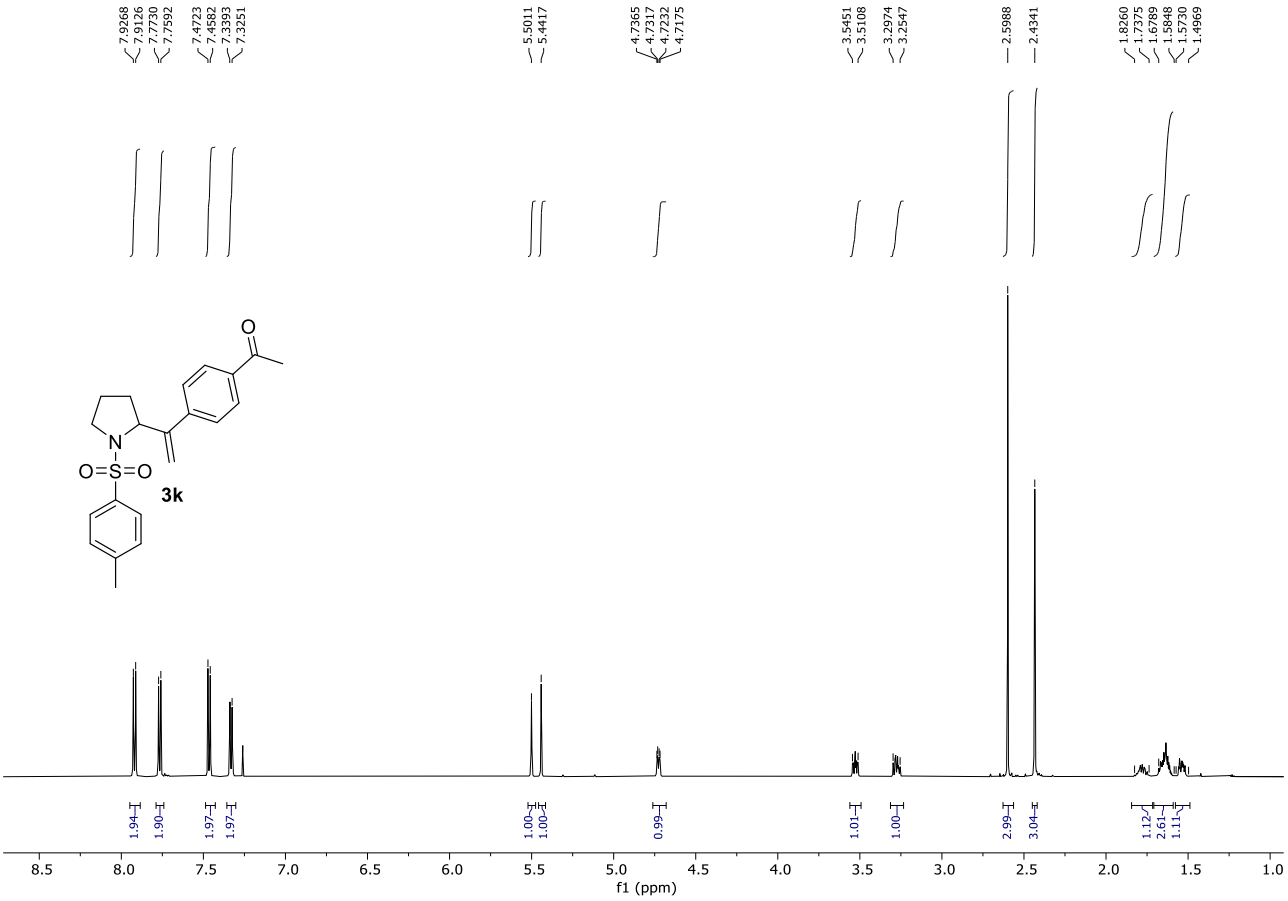
Comparison between DEPT-135 and ^{13}C-NMR of compound 3j (150 MHz, $CDCl_3$)



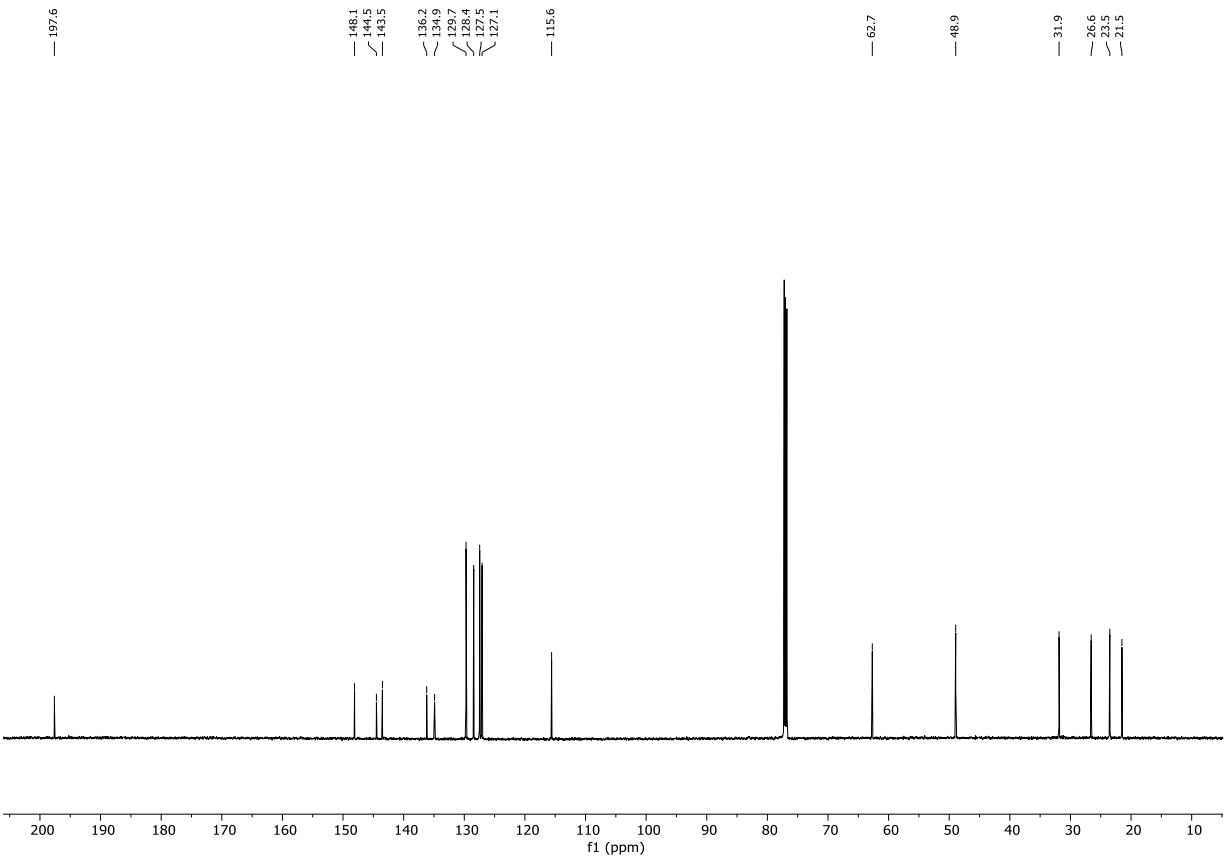
COSY-NMR of compound 3j (600 MHz, $CDCl_3$)



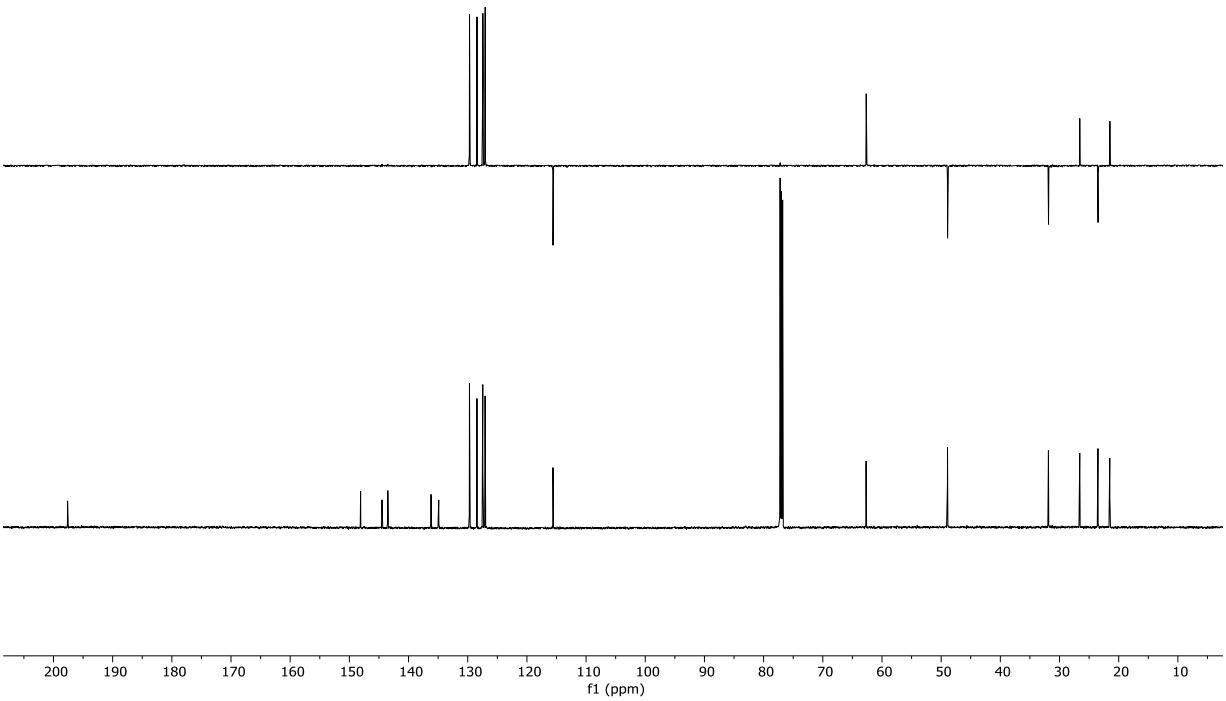
^{1}H-NMR of compound 3k (600 MHz, $CDCl_3$)



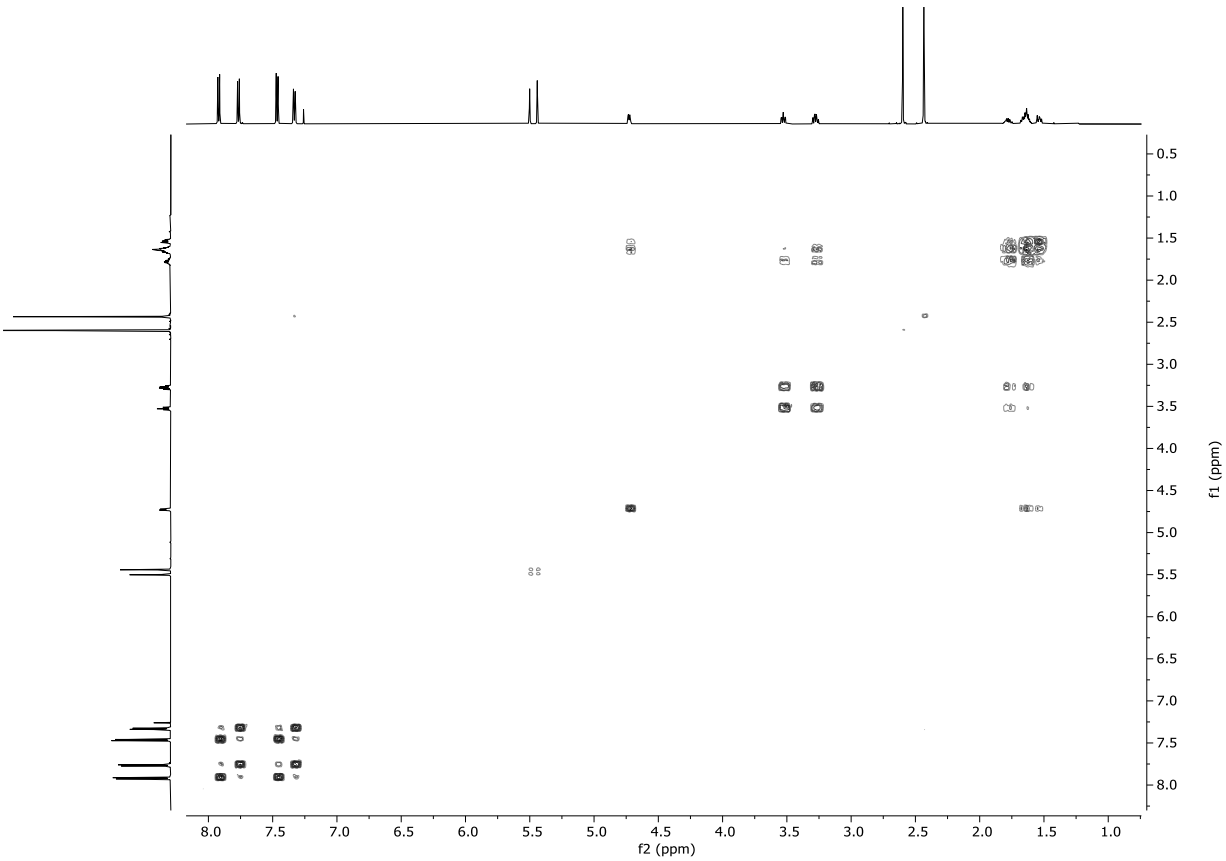
^{13}C-NMR of compound 3k (150 MHz, $CDCl_3$)



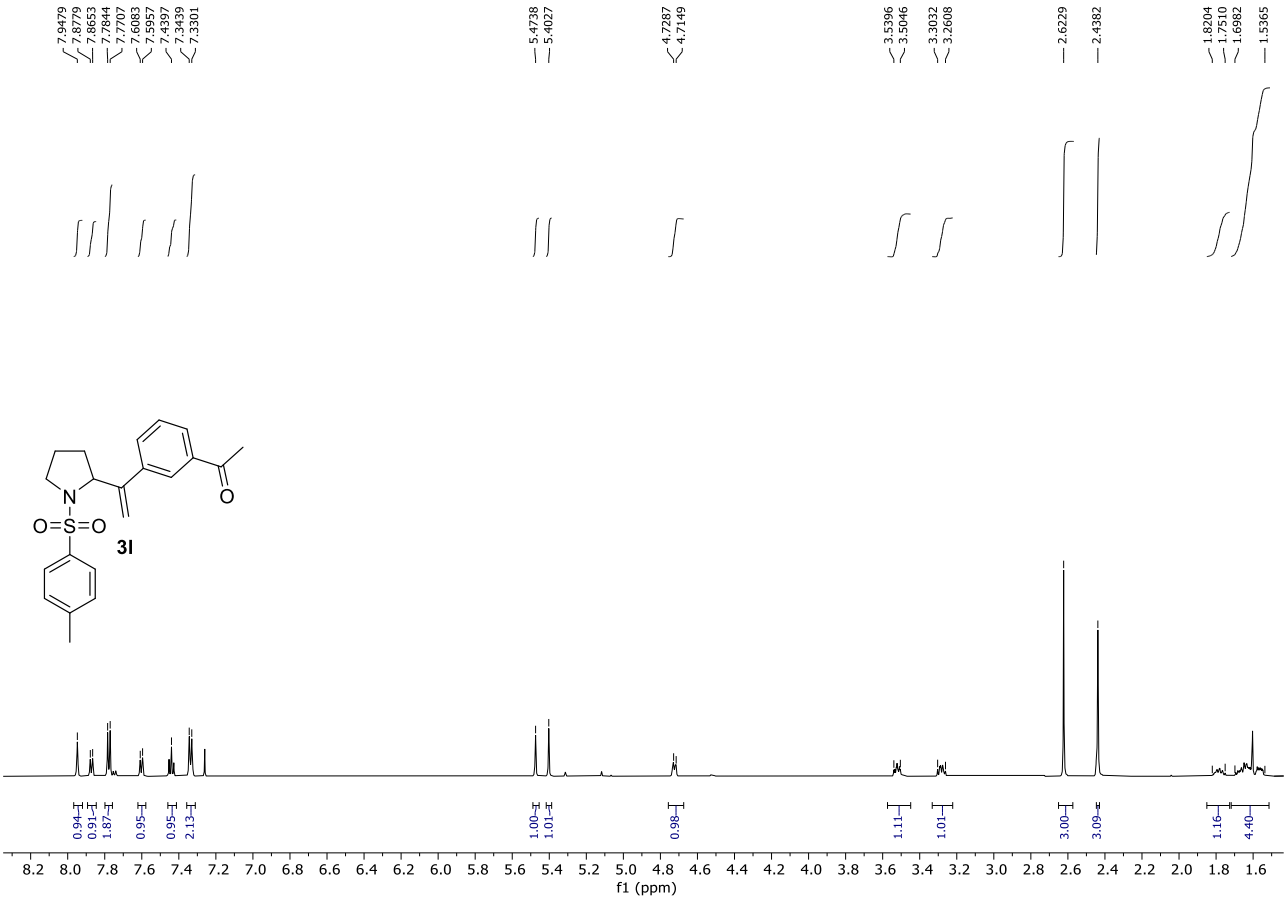
Comparison between DEPT-135 and ^{13}C-NMR of compound 3k (150 MHz, $CDCl_3$)



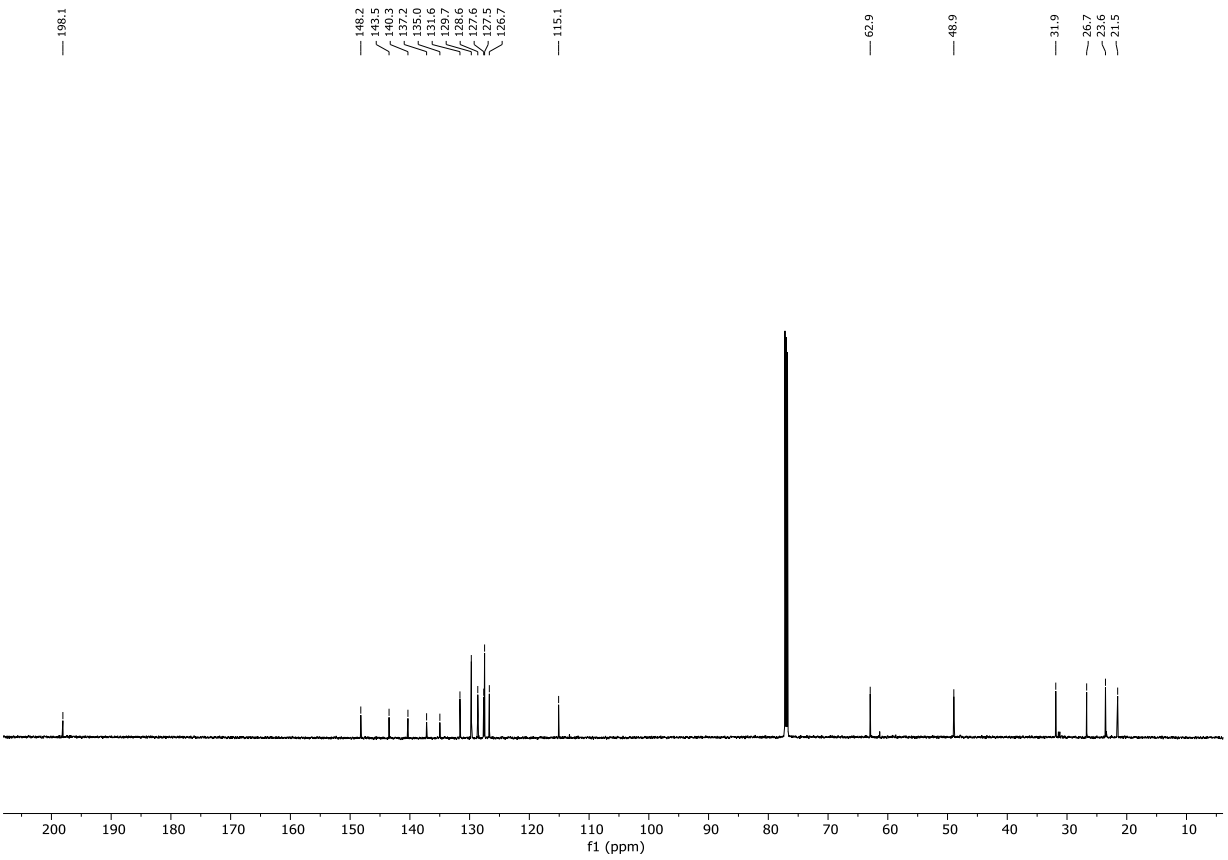
COSY-NMR of compound 3k (600 MHz, $CDCl_3$)



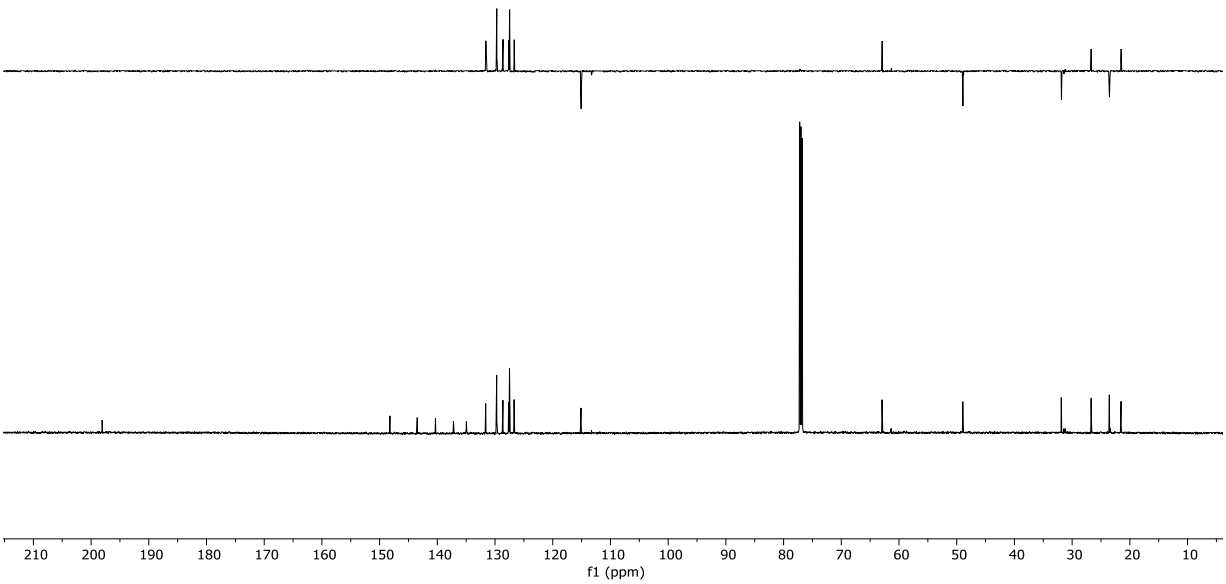
^{1}H-NMR of compound 3l (600 MHz, $CDCl_3$)



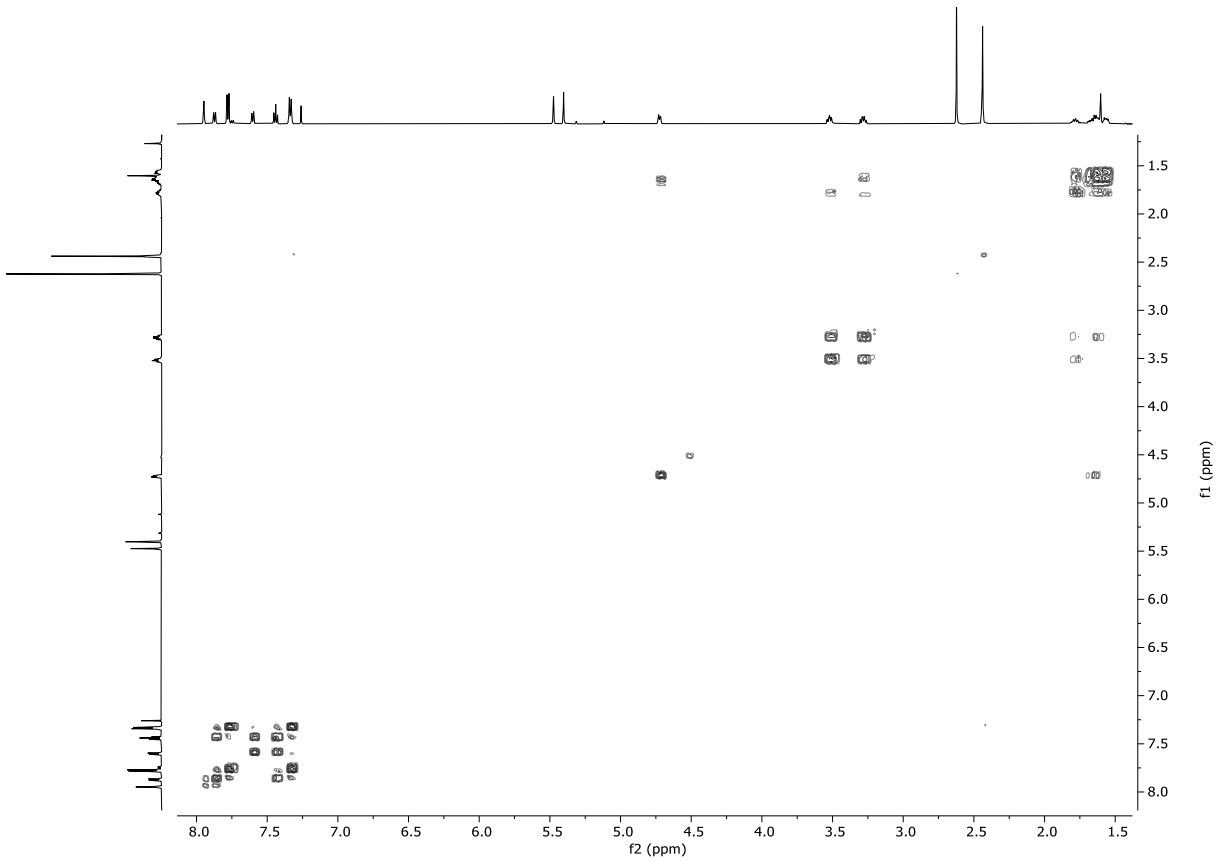
^{13}C-NMR of compound 3l (150 MHz, $CDCl_3$)



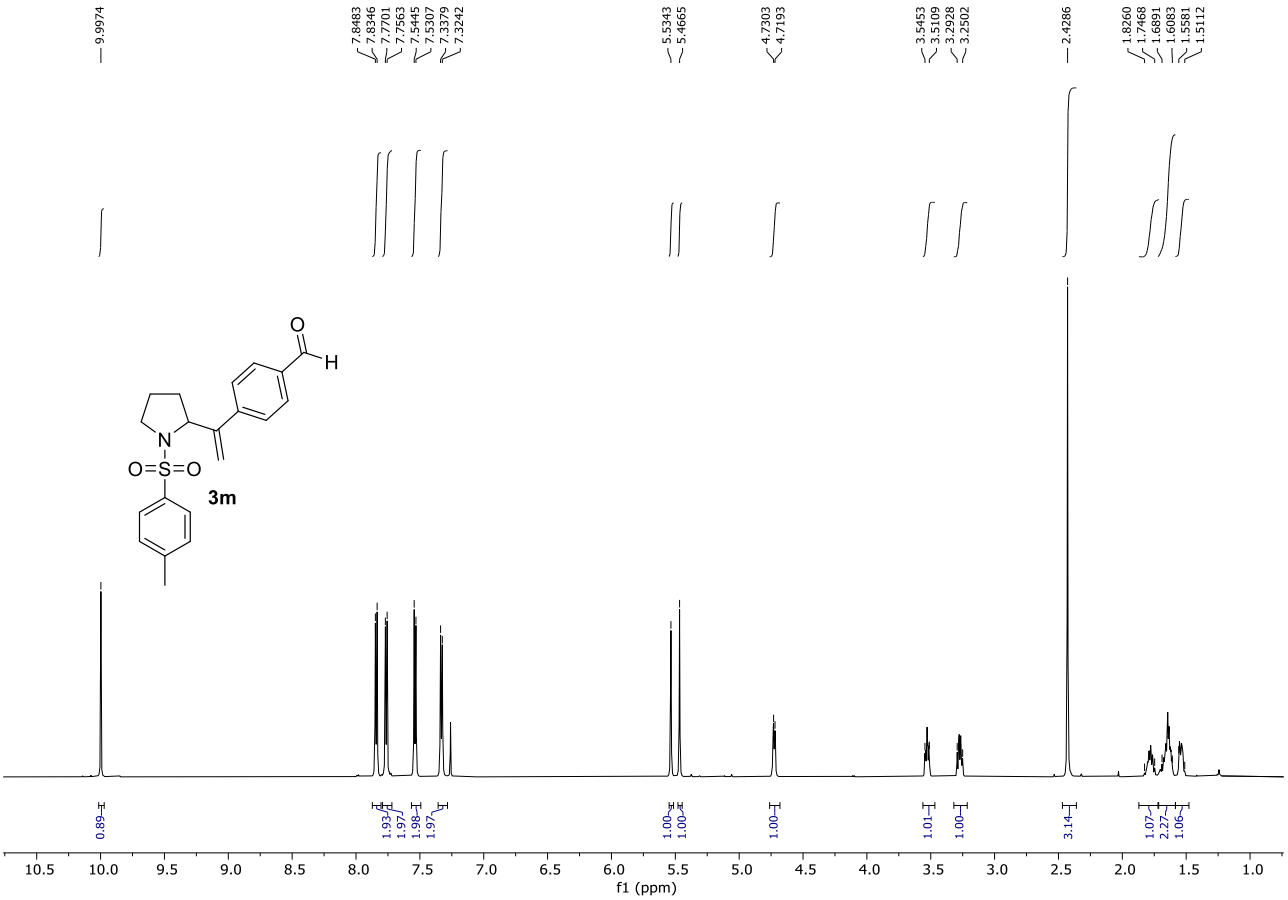
Comparison between DEPT-135 and ^{13}C-NMR of compound 3l (150 MHz, $CDCl_3$)



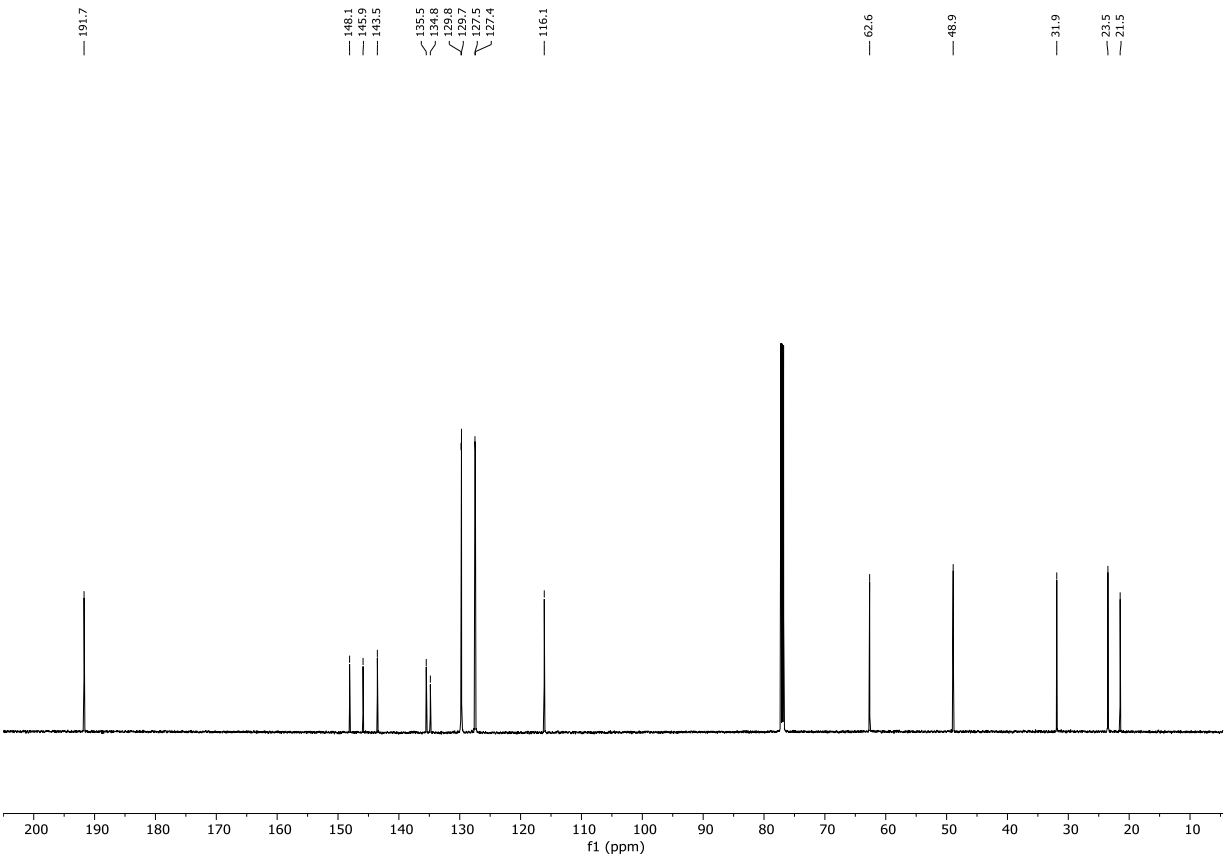
COSY-NMR of compound 3l (600 MHz, $CDCl_3$)



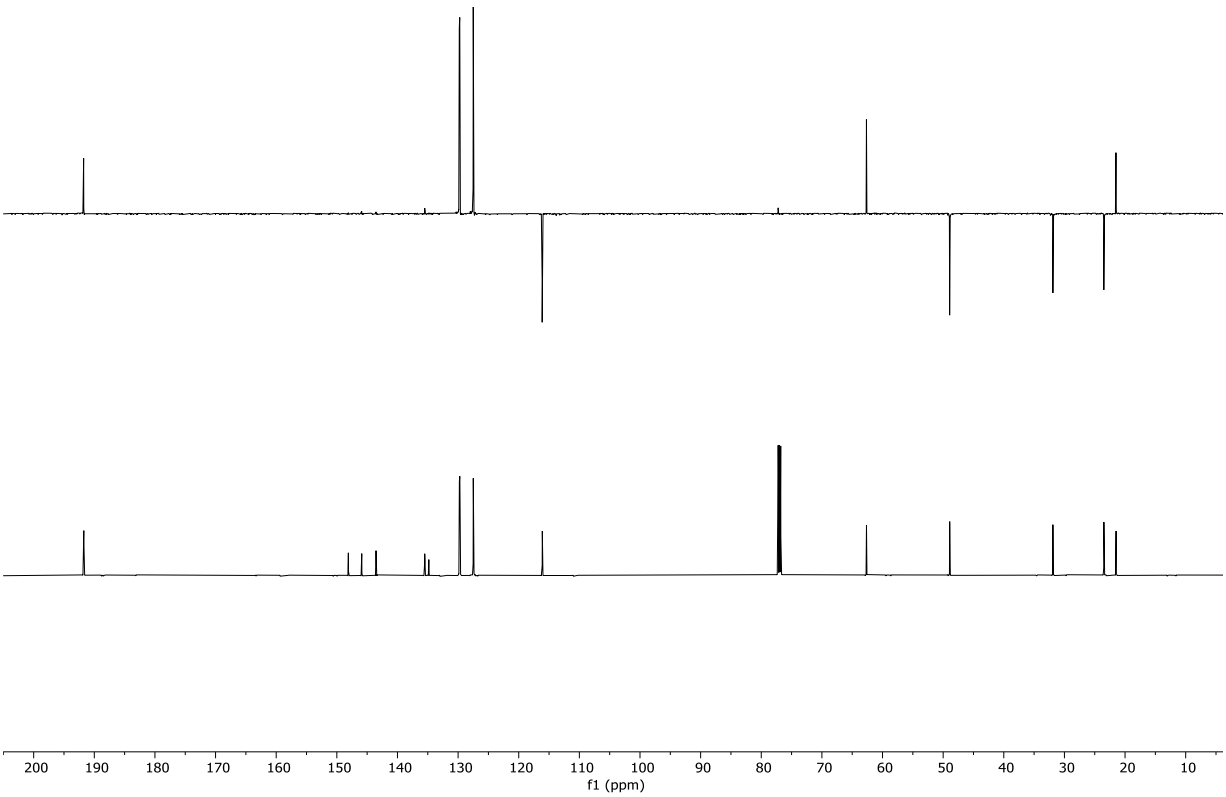
^{1}H-NMR of compound 3m (600 MHz, $CDCl_3$)



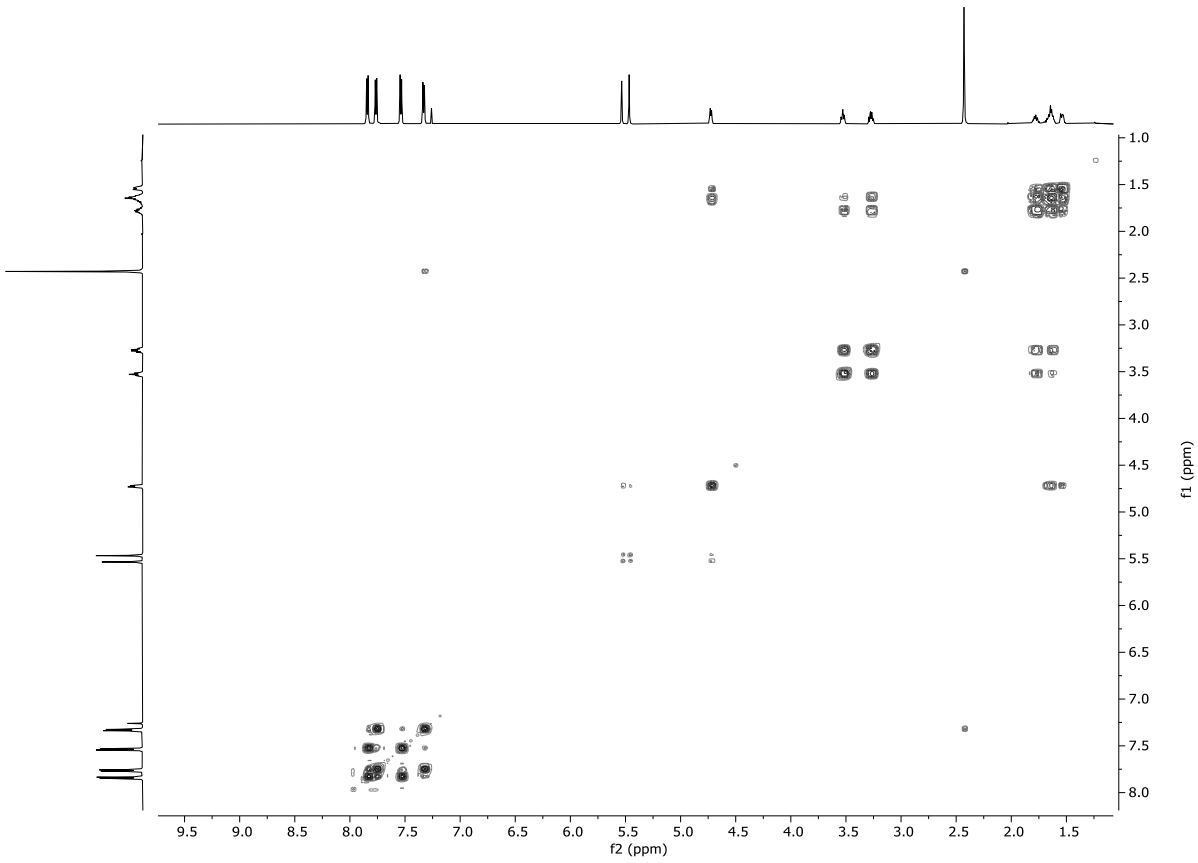
^{13}C-NMR of compound 3m (150 MHz, $CDCl_3$)



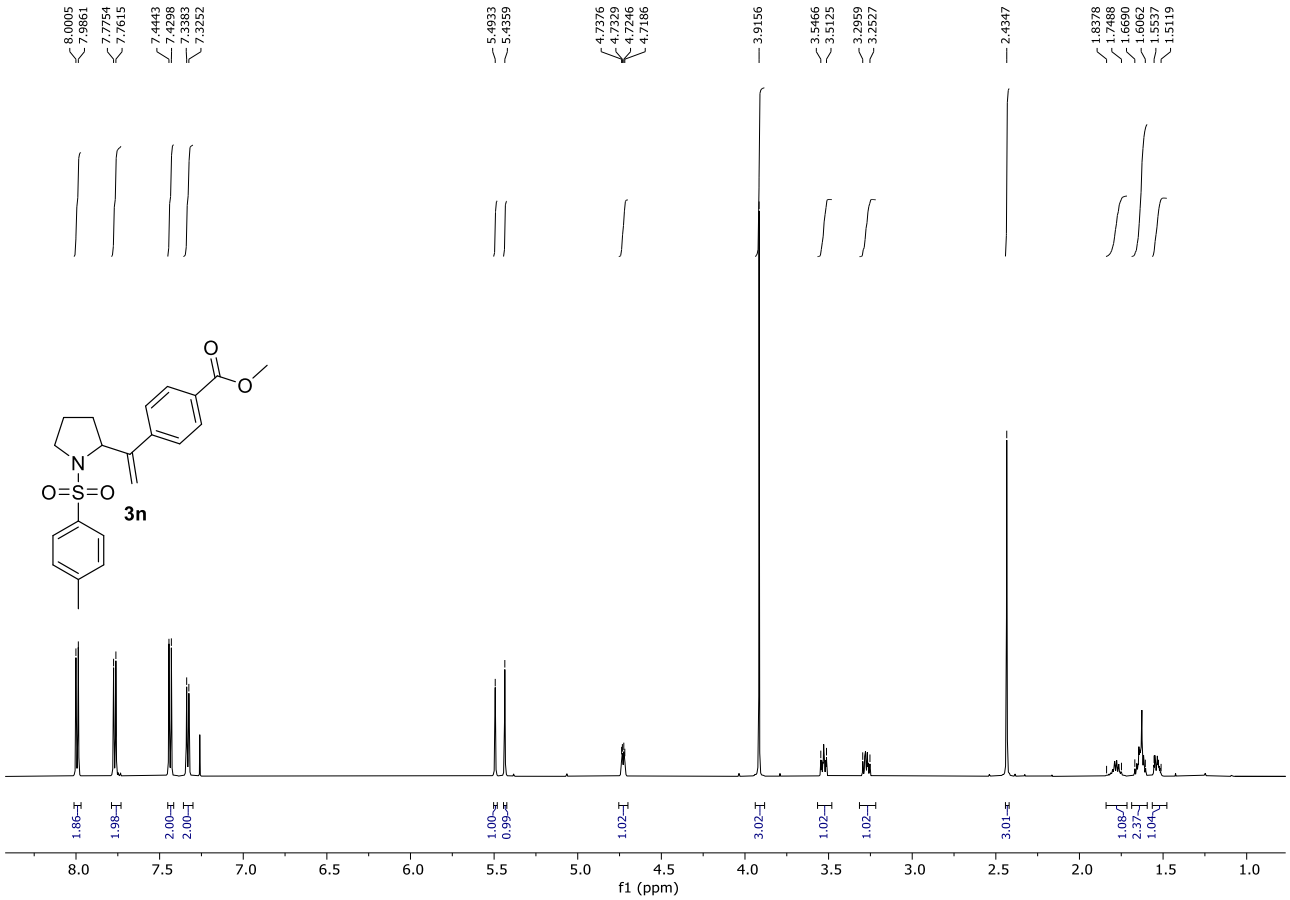
Comparison between DEPT-135 and ^{13}C-NMR of compound 3m (150 MHz, $CDCl_3$)



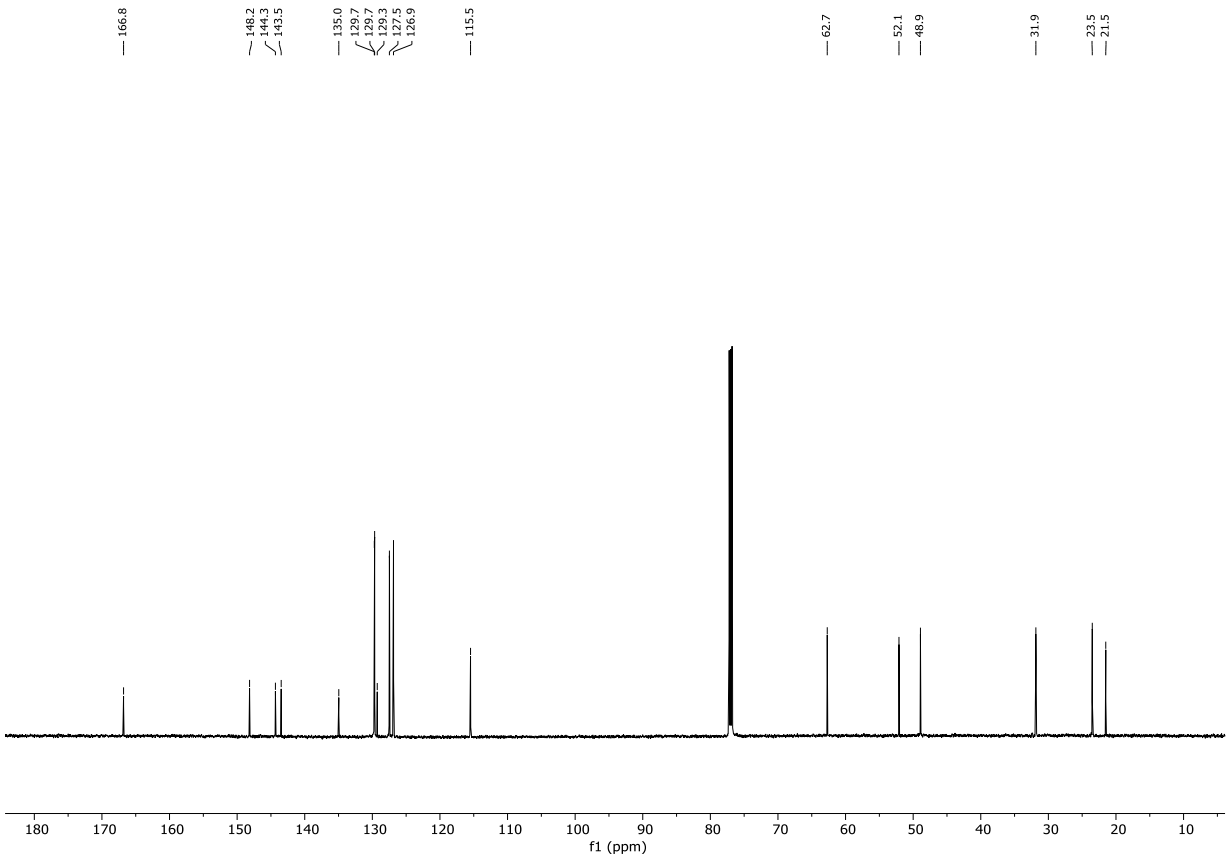
COSY-NMR of compound 3m (600 MHz, $CDCl_3$)



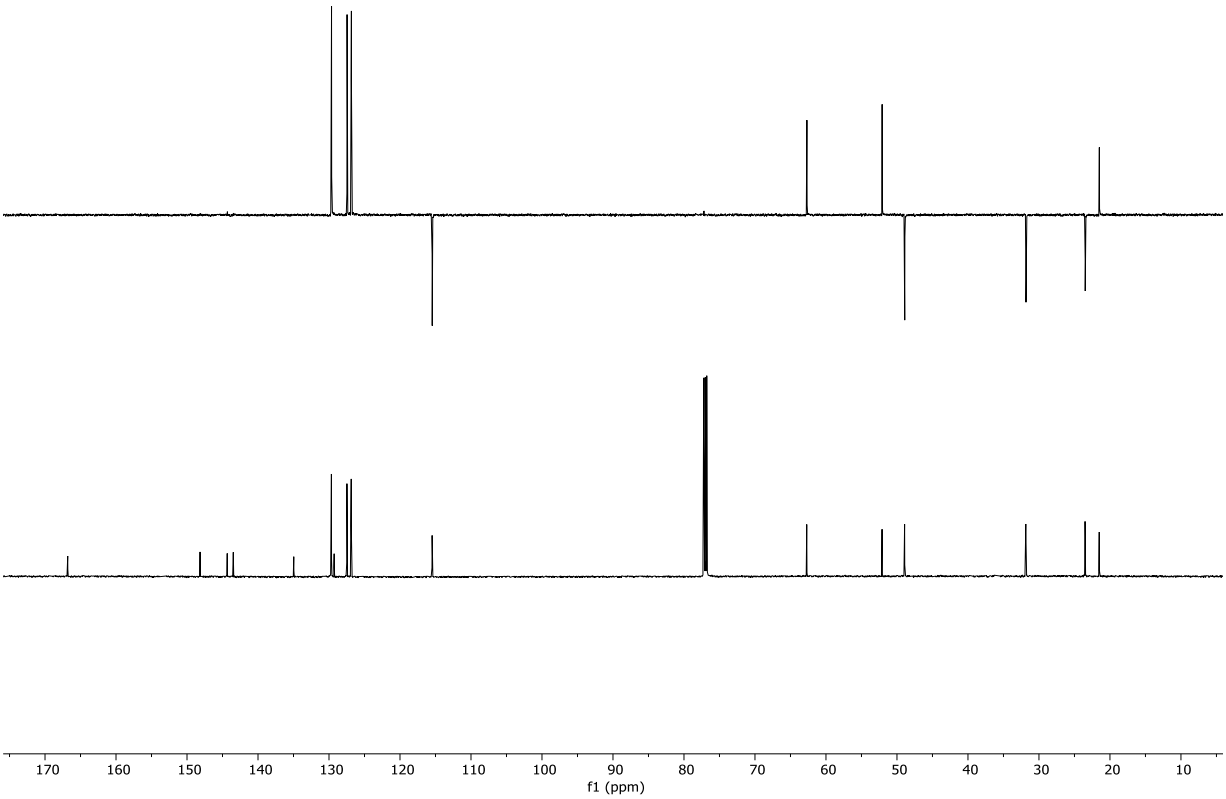
^{1}H-NMR of compound 3n (600 MHz, $CDCl_3$)



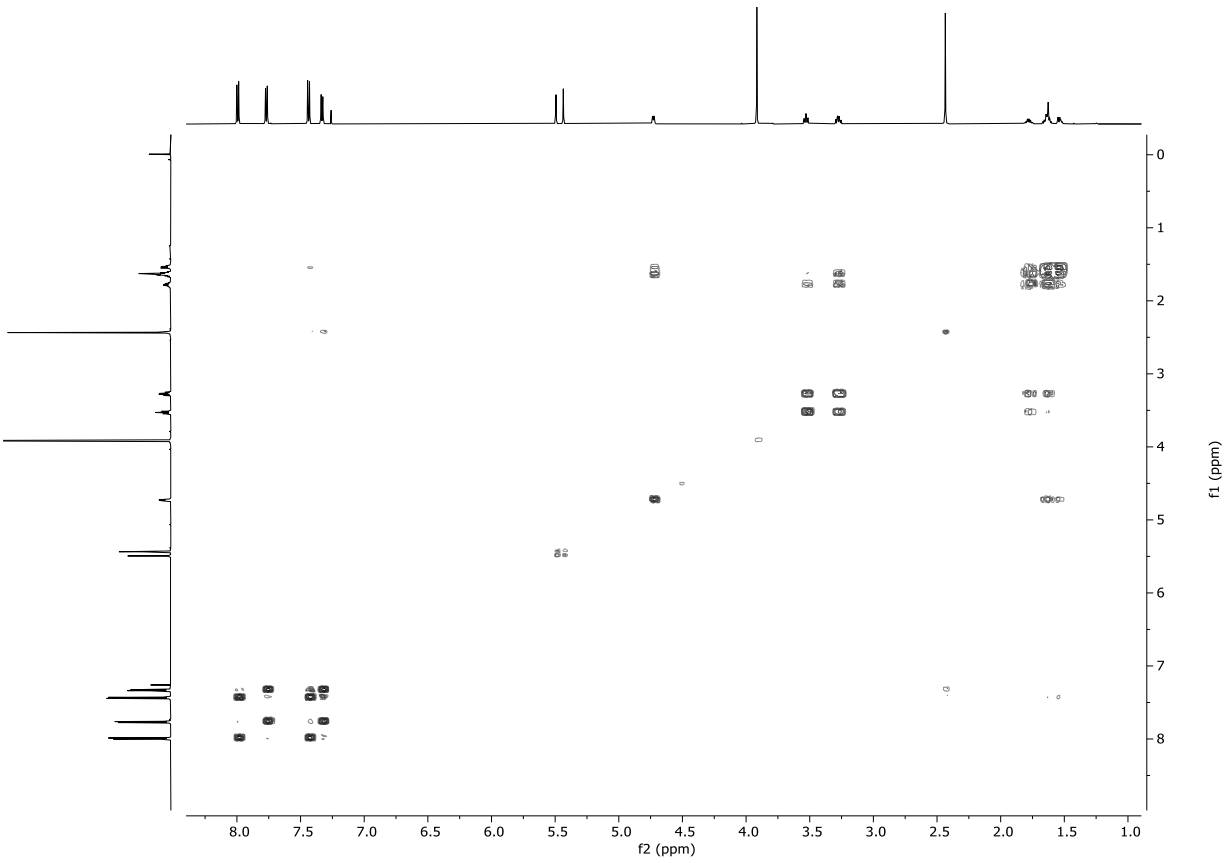
^{13}C-NMR of compound 3n (150 MHz, $CDCl_3$)



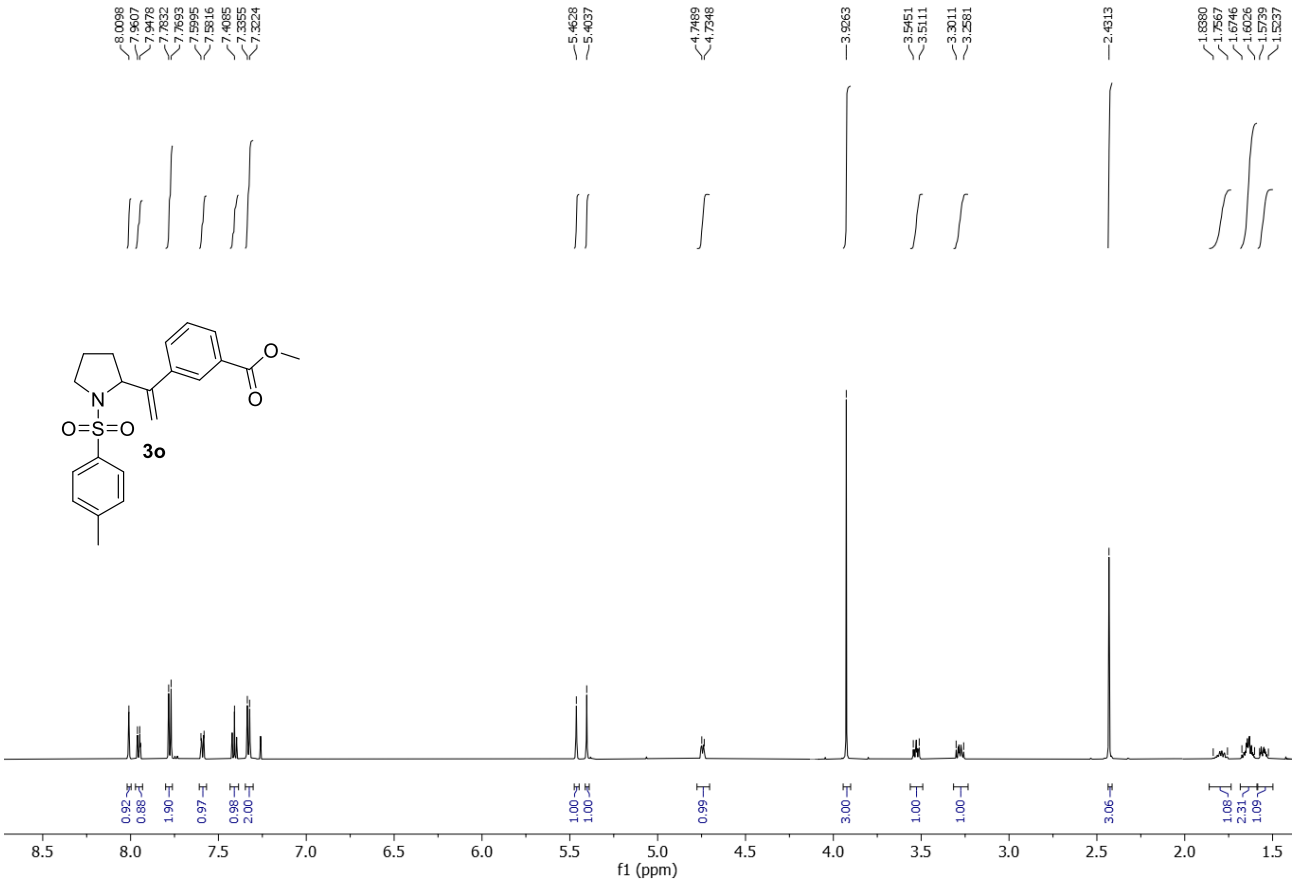
Comparison between DEPT-135 and ^{13}C-NMR of compound 3n (150 MHz, $CDCl_3$)



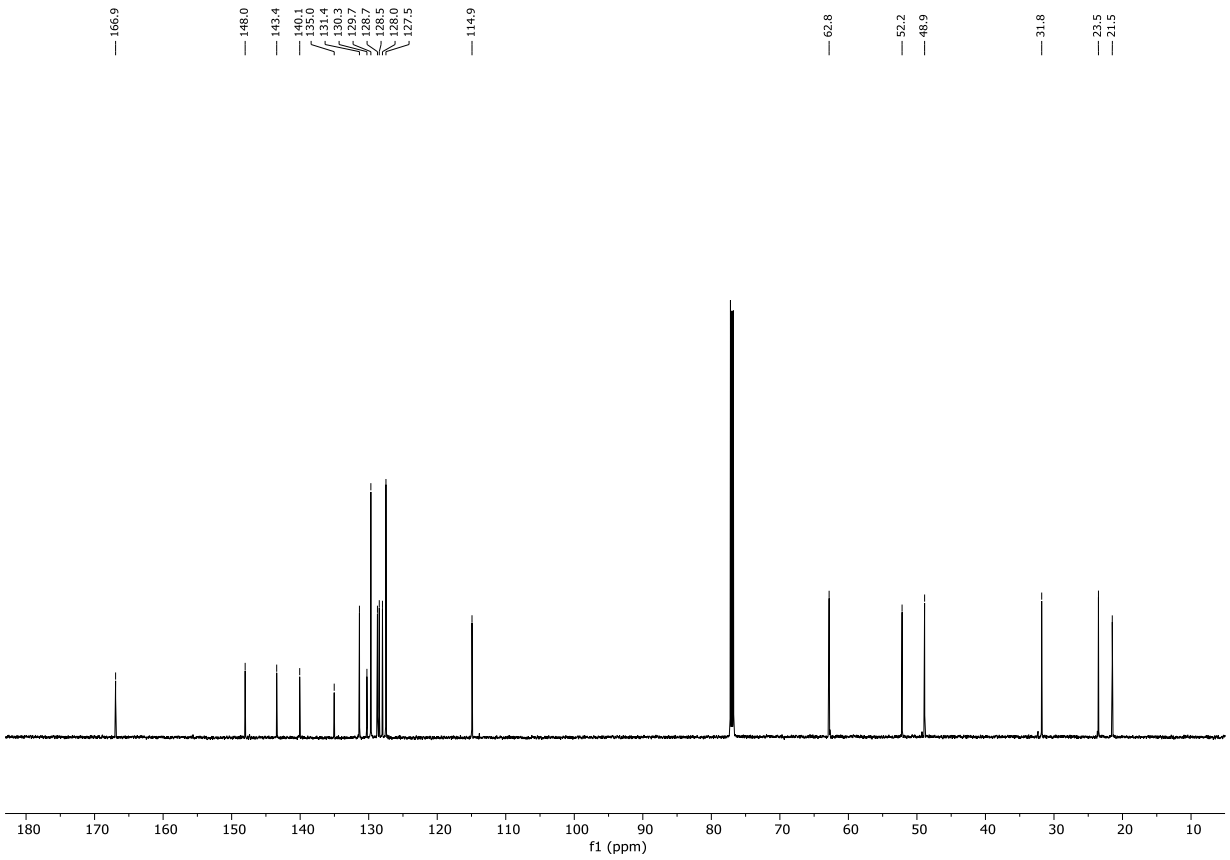
COSY-NMR of compound 3n (600 MHz, $CDCl_3$)



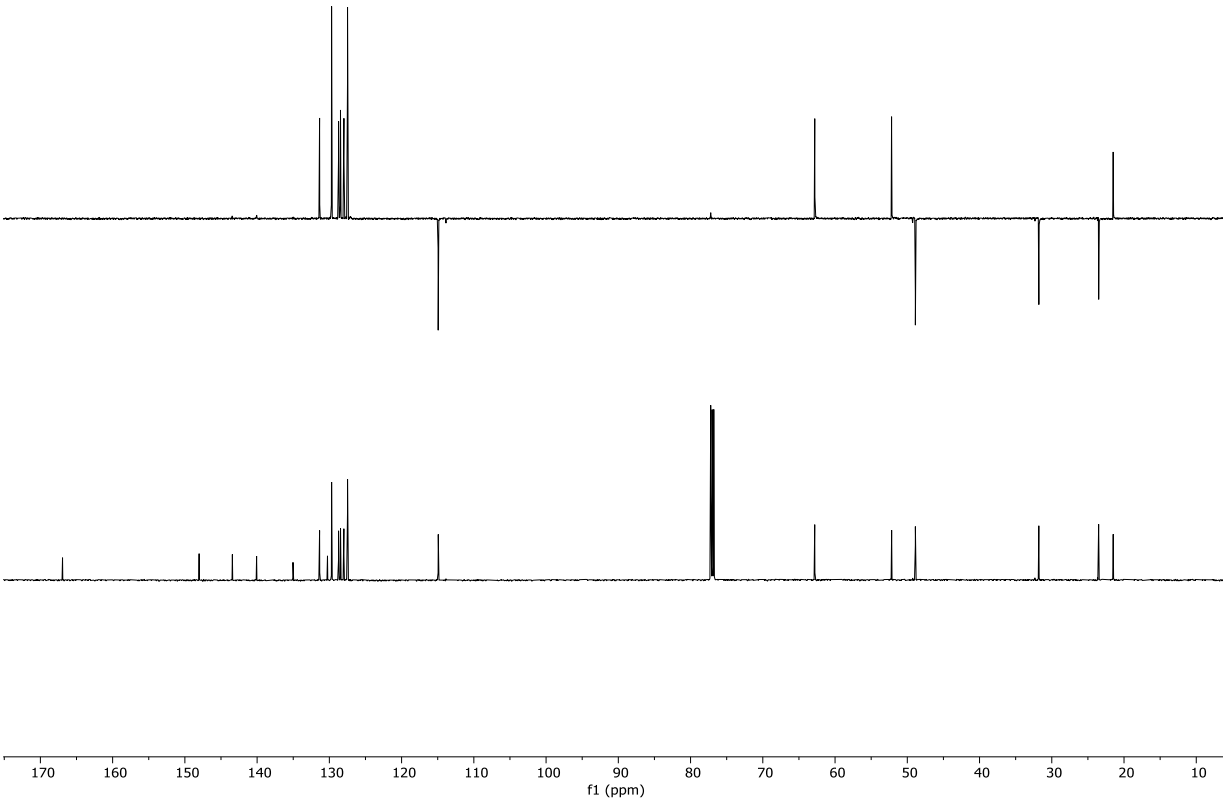
^{1}H-NMR of compound 3o (600 MHz, $CDCl_3$)



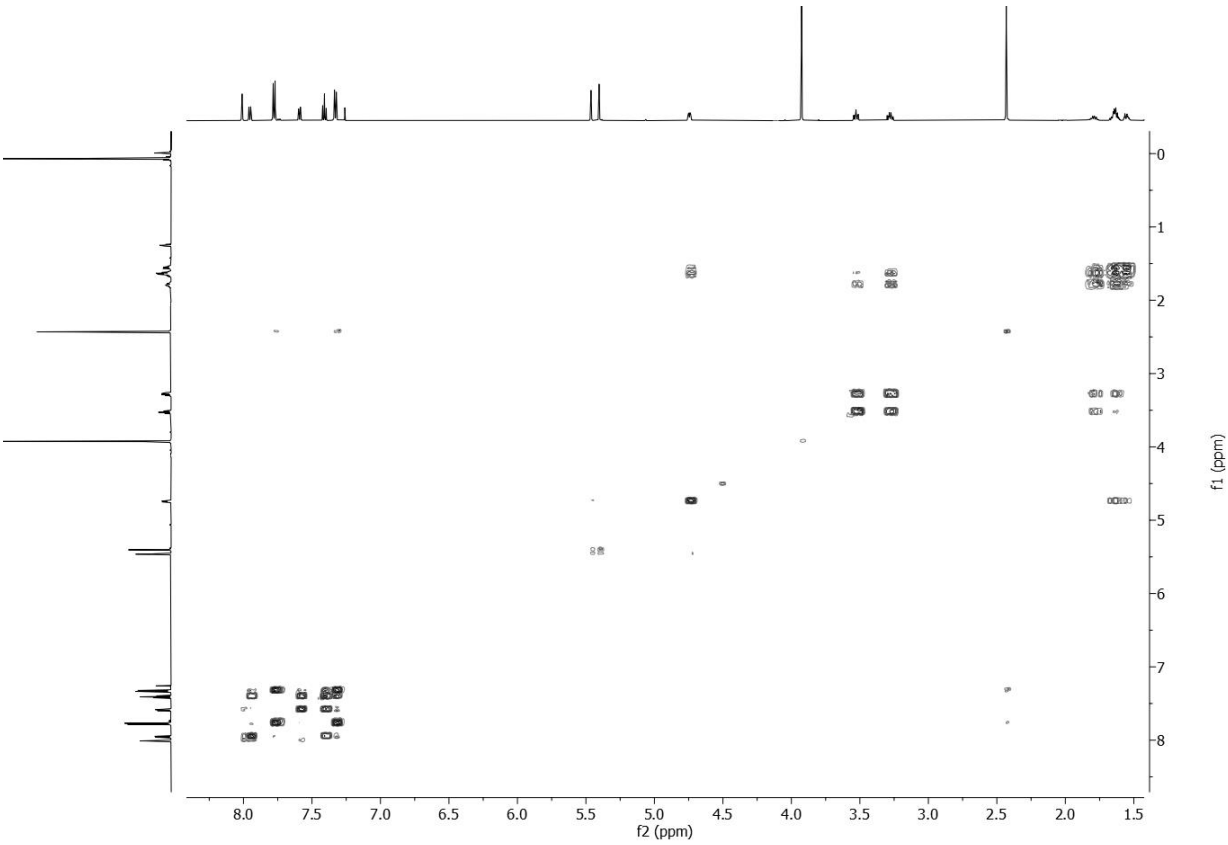
^{13}C-NMR of compound 3o (150 MHz, $CDCl_3$)



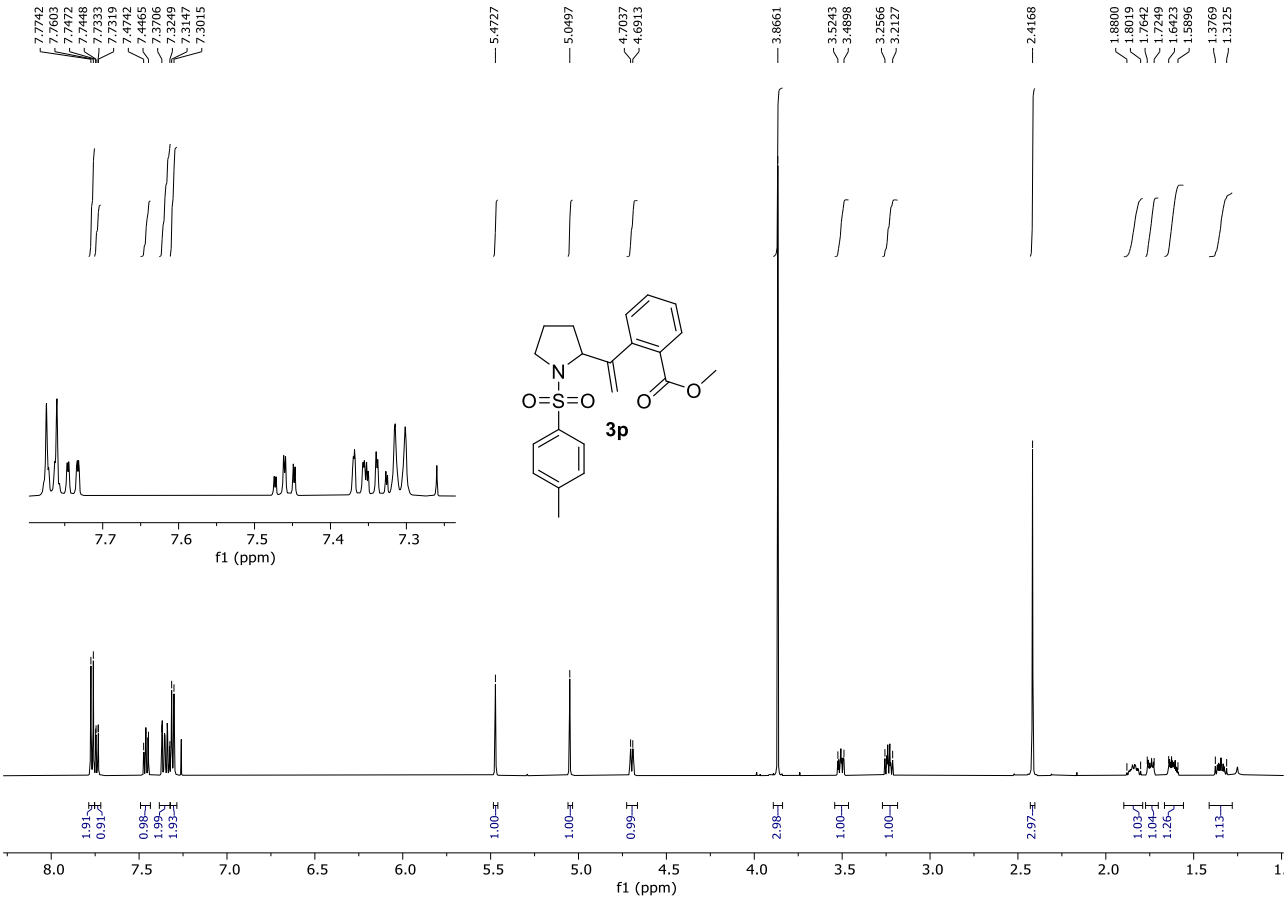
Comparison between DEPT-135 and ^{13}C-NMR of compound 3o (150 MHz, $CDCl_3$)



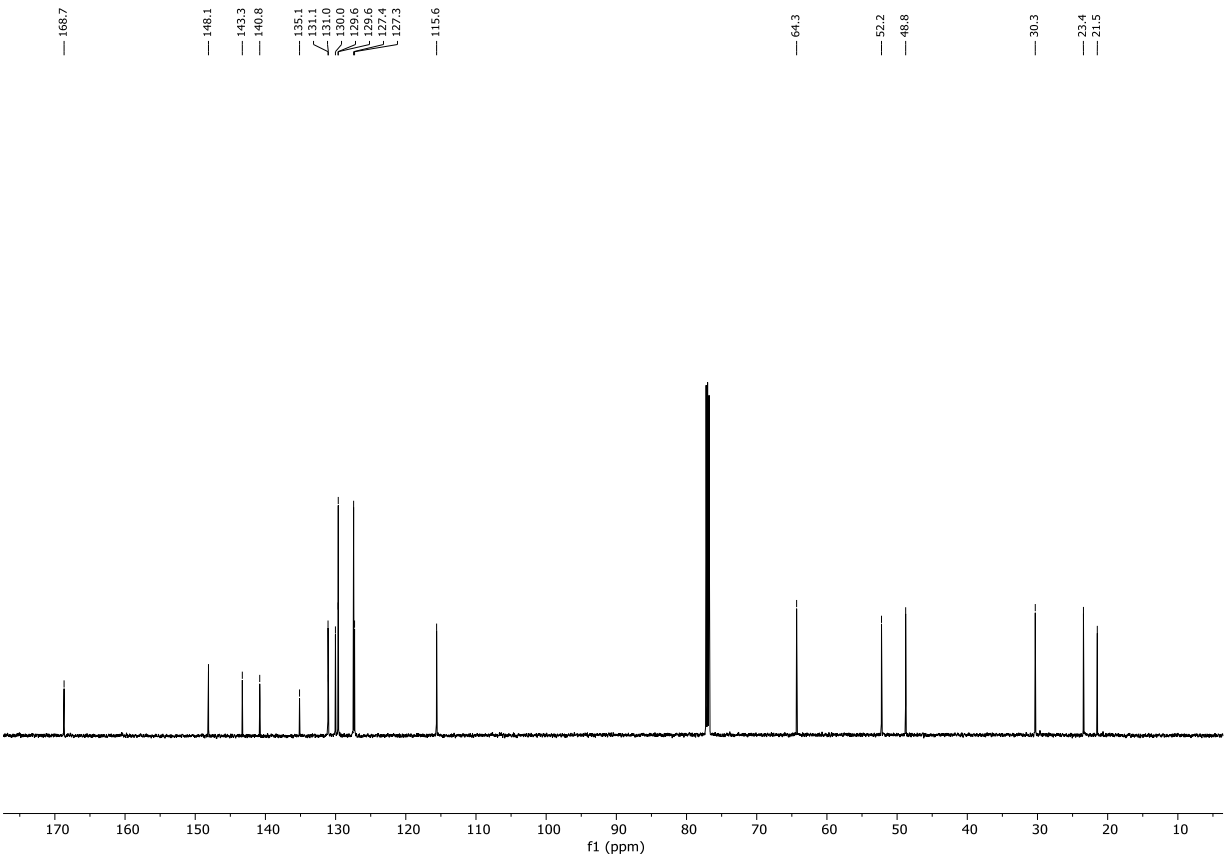
COSY-NMR of compound 3o (600 MHz, $CDCl_3$)



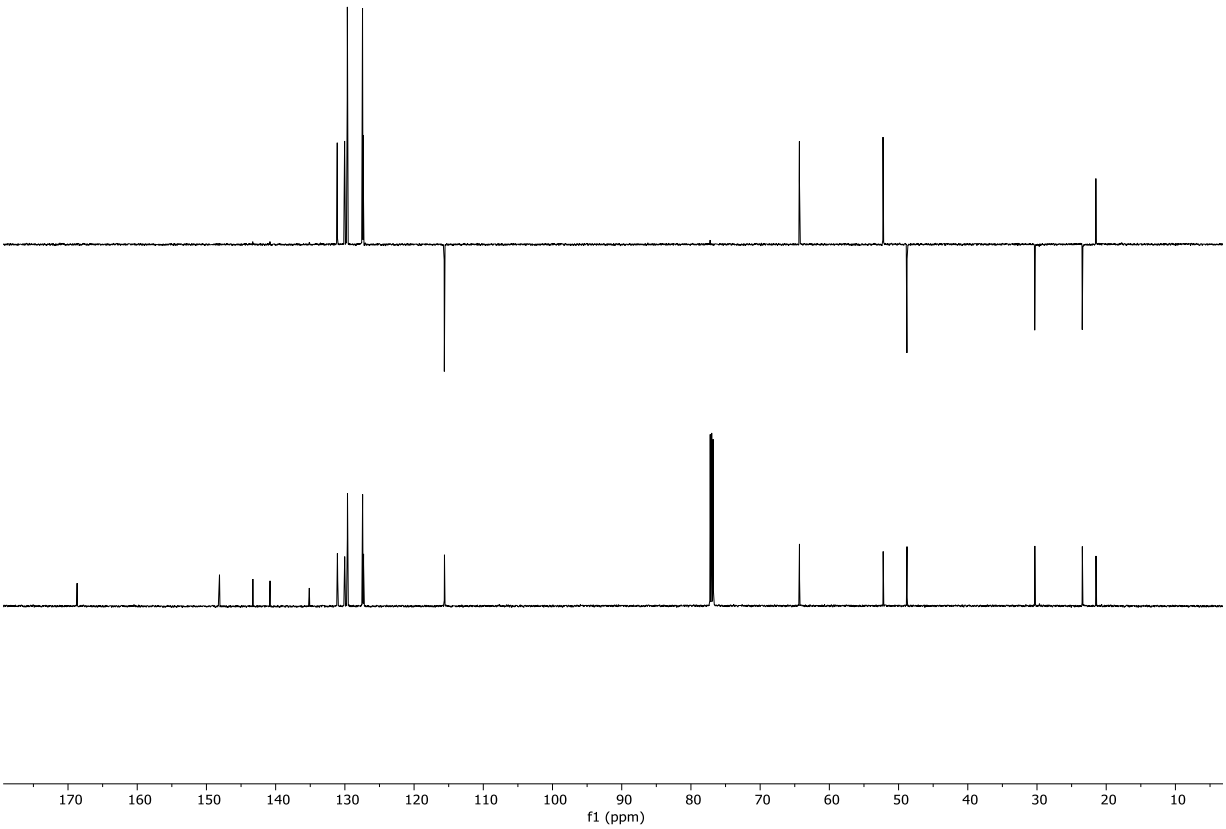
^{1}H-NMR of compound 3p (600 MHz, $CDCl_3$)



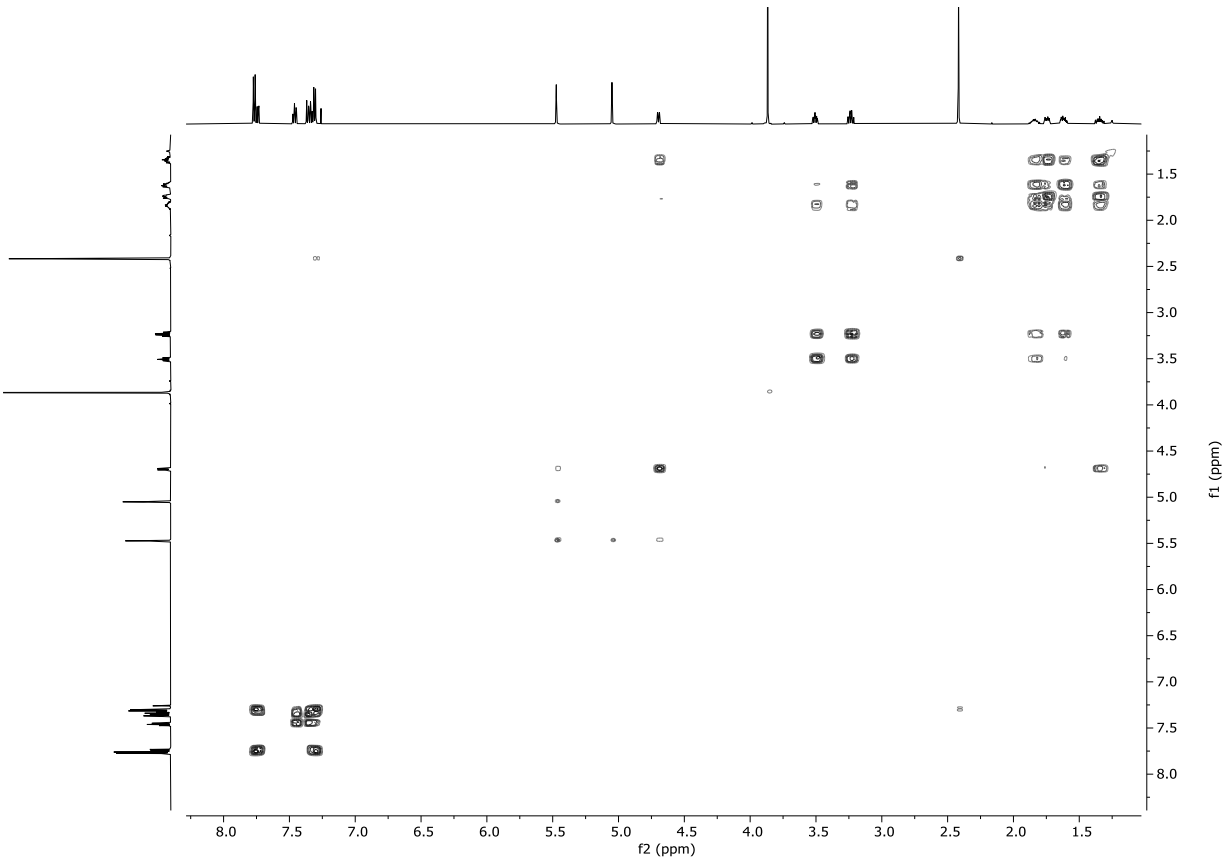
^{13}C-NMR of compound 3p (150 MHz, $CDCl_3$)



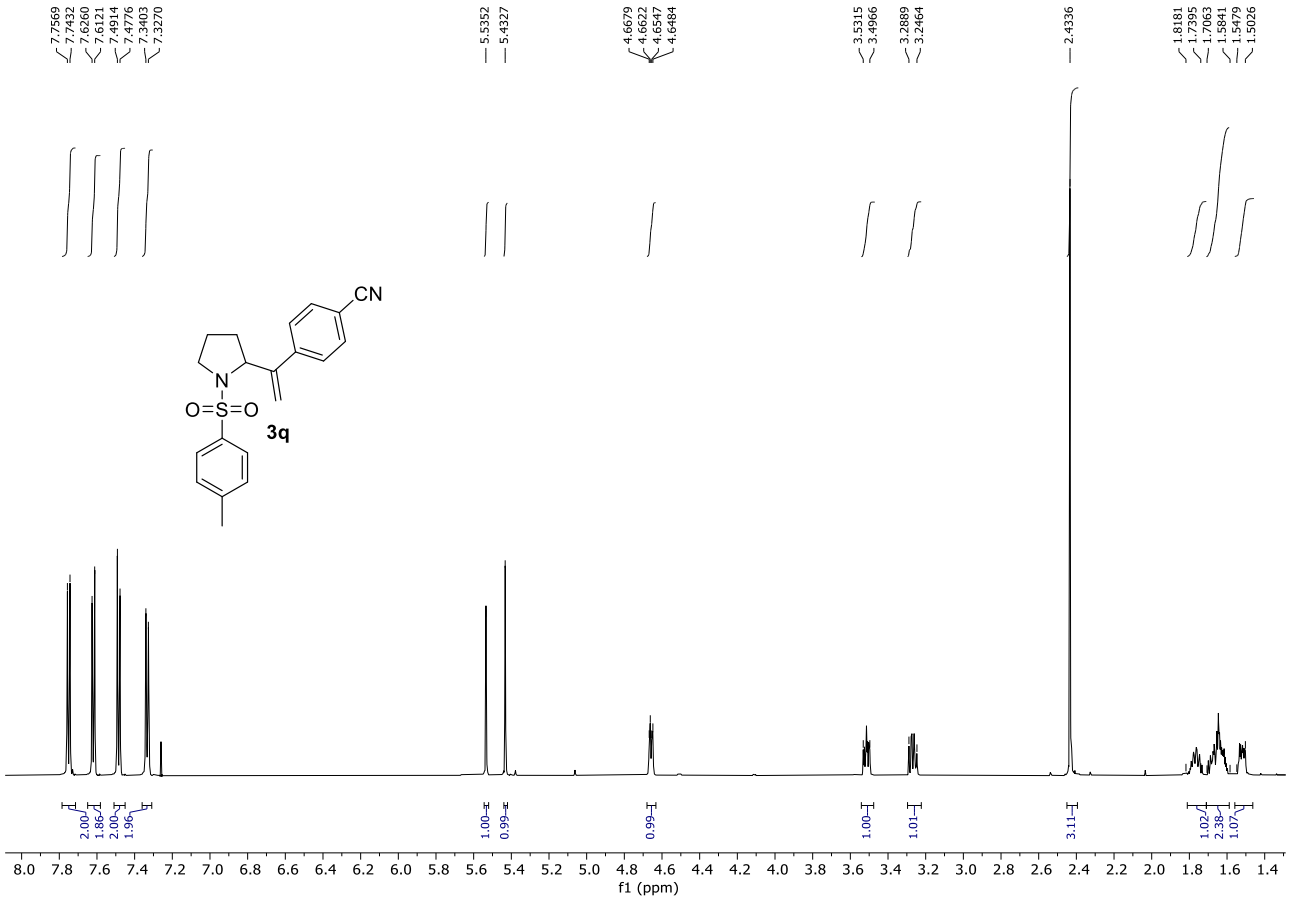
Comparison between DEPT-135 and ^{13}C-NMR of compound 3p (150 MHz, $CDCl_3$)



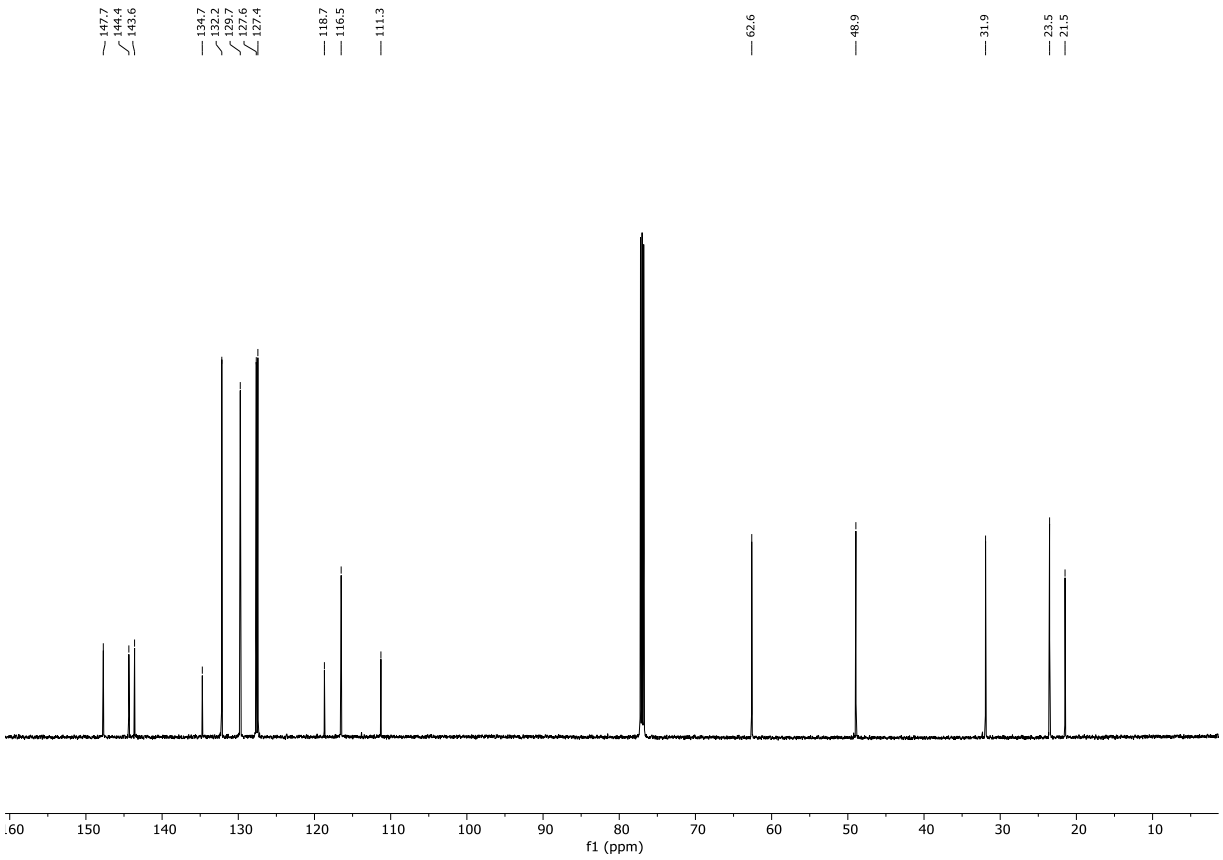
COSY-NMR of compound 3p (600 MHz, $CDCl_3$)



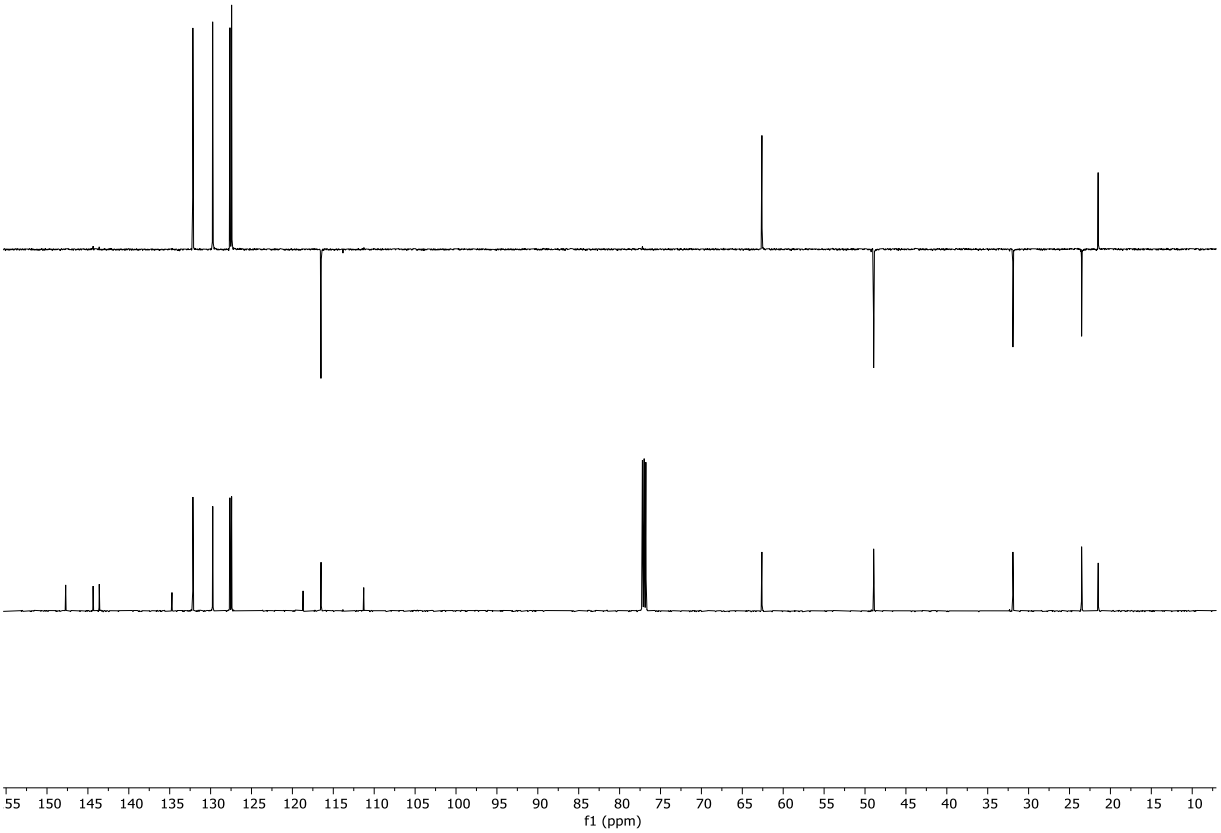
^{1}H-NMR of compound 3q (600 MHz, $CDCl_3$)



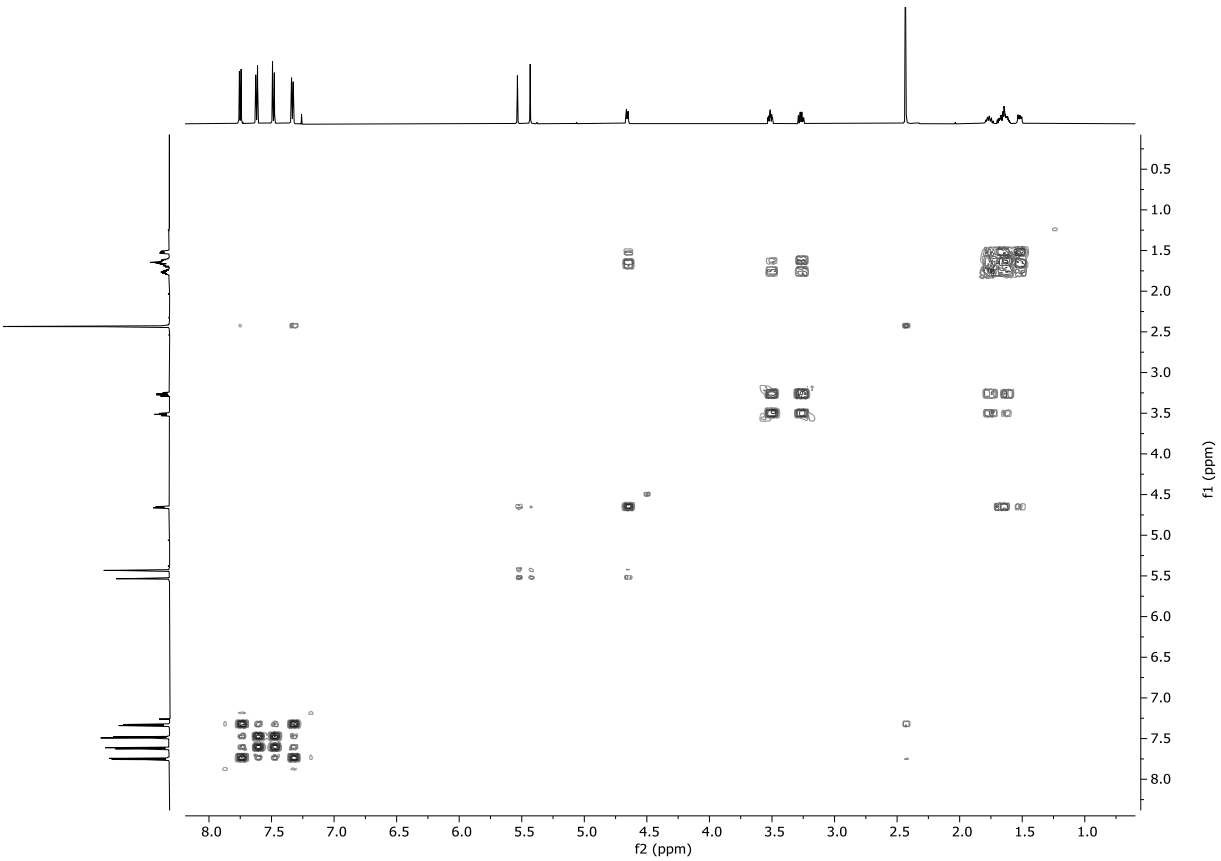
^{13}C-NMR of compound 3q (150 MHz, $CDCl_3$)



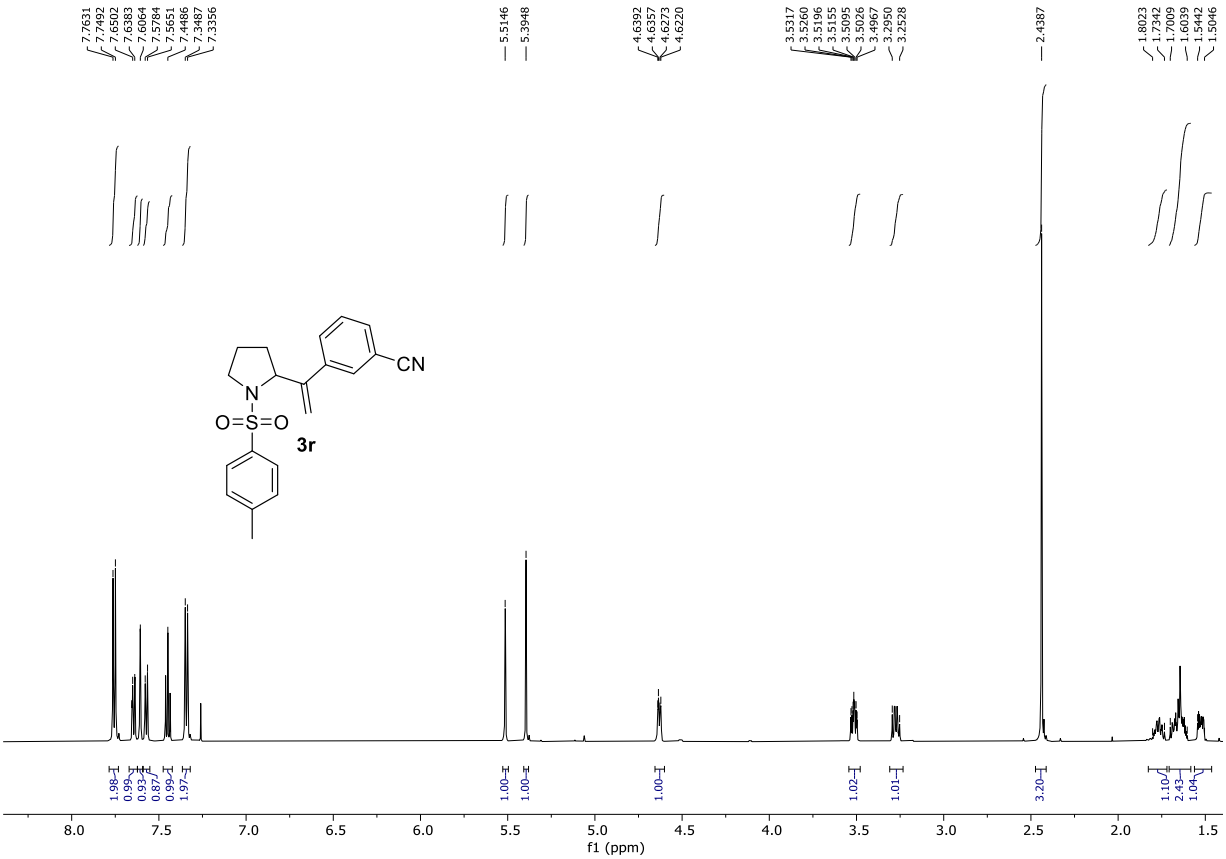
Comparison between DEPT-135 and ^{13}C-NMR of compound 3q (150 MHz, $CDCl_3$)



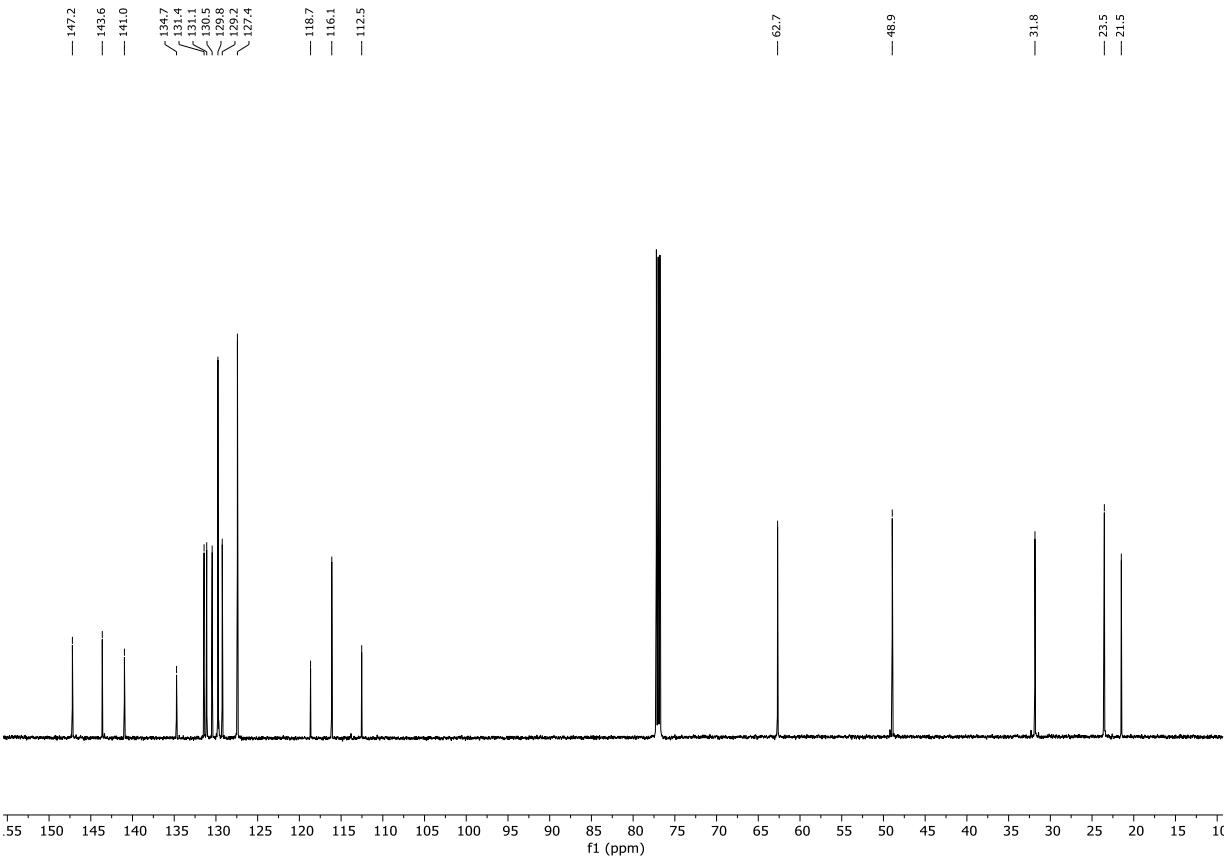
COSY-NMR of compound 3q (600 MHz, $CDCl_3$)



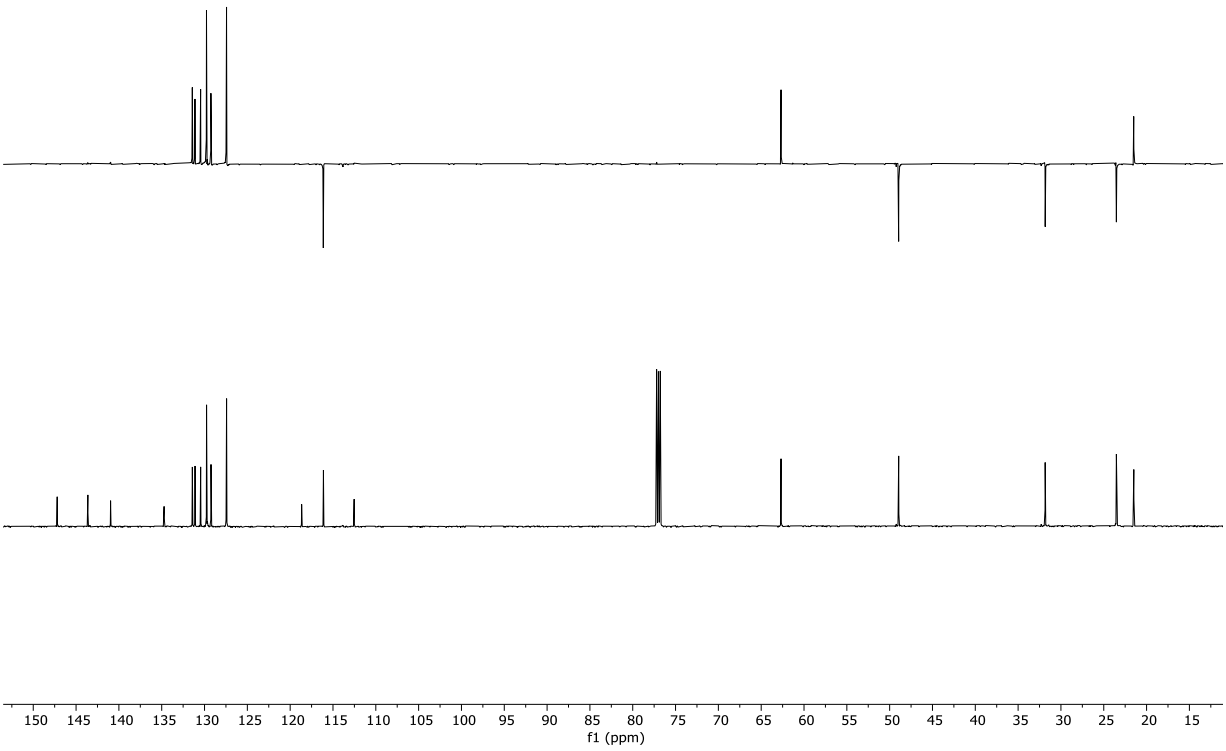
^{1}H-NMR of compound 3r (600 MHz,$CDCl_3$)



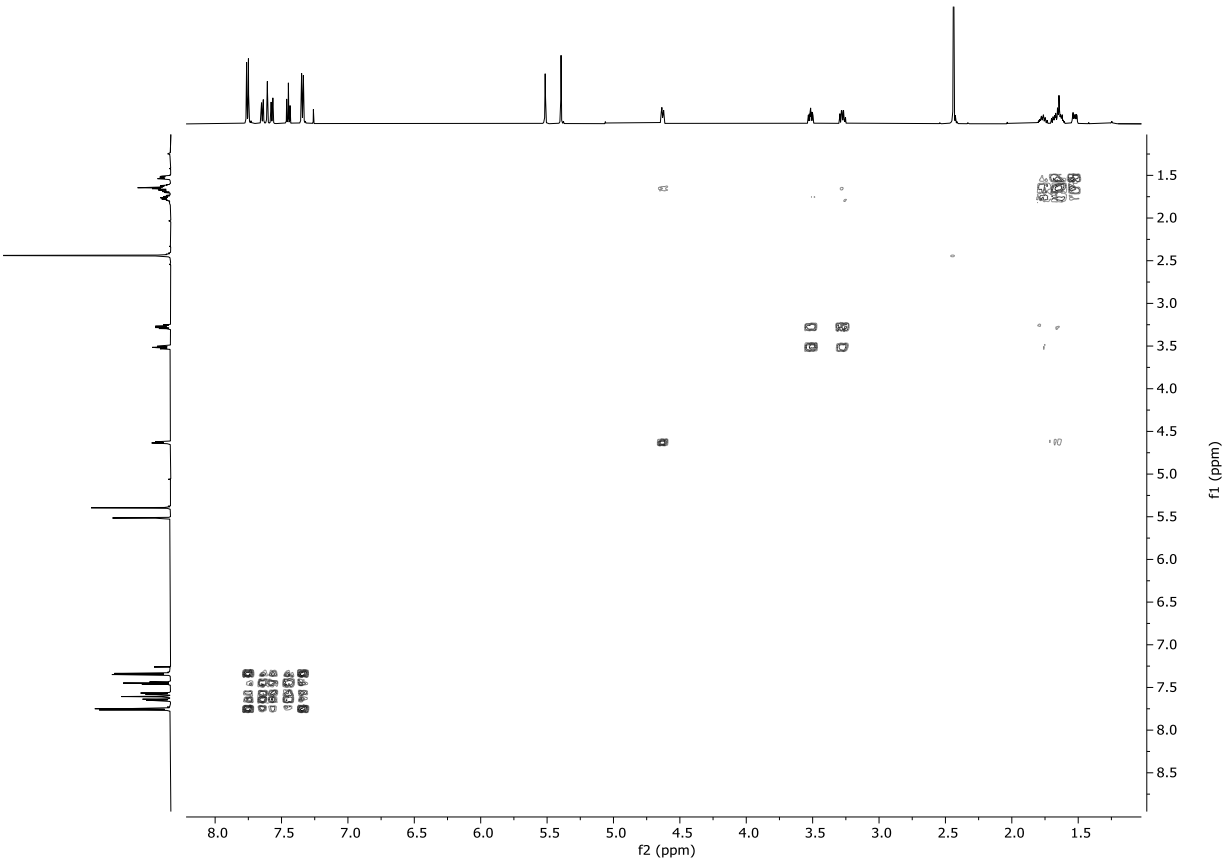
^{13}C-NMR of compound 3r (150 MHz, $CDCl_3$)



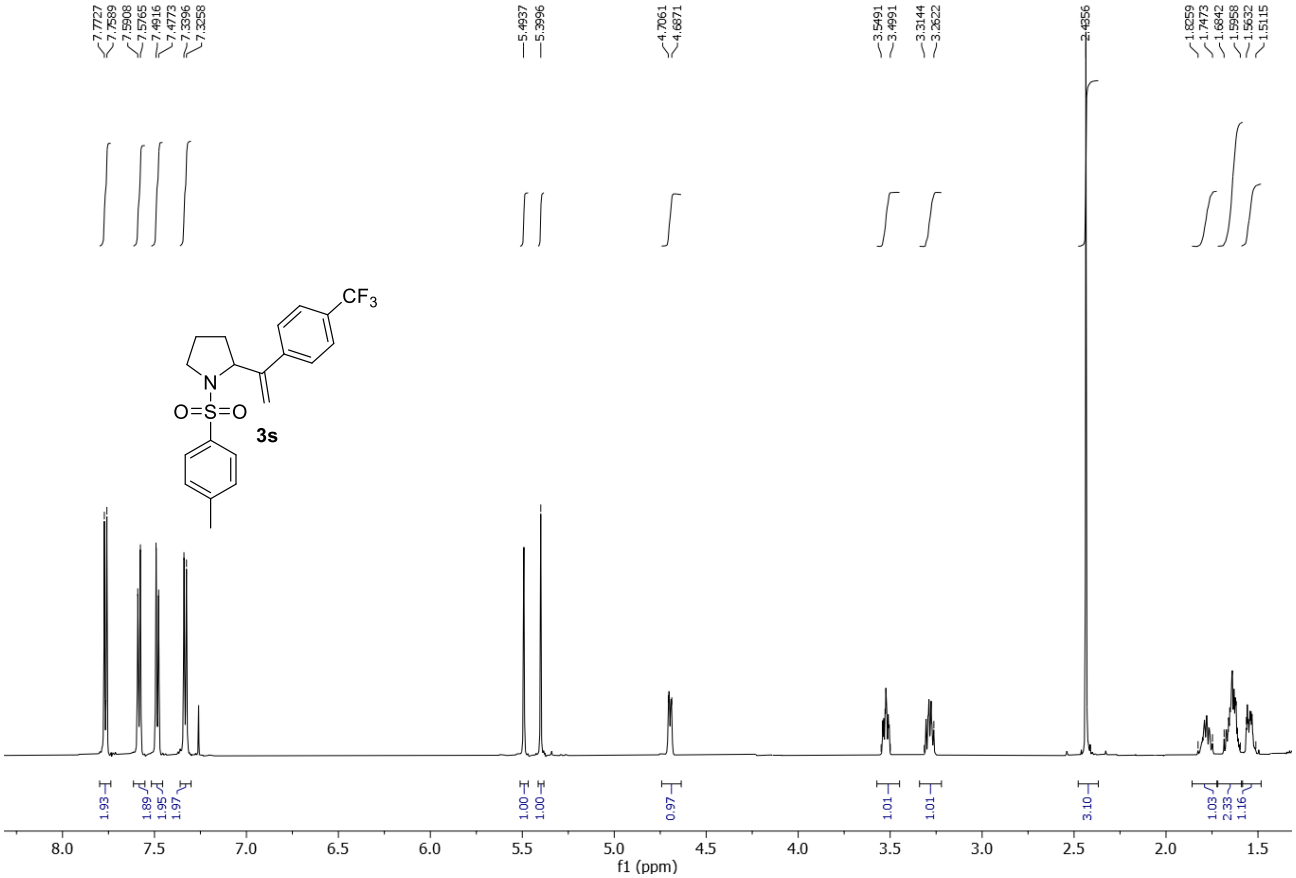
Comparison between DEPT-135 and ^{13}C-NMR of compound 3r (150 MHz, $CDCl_3$)



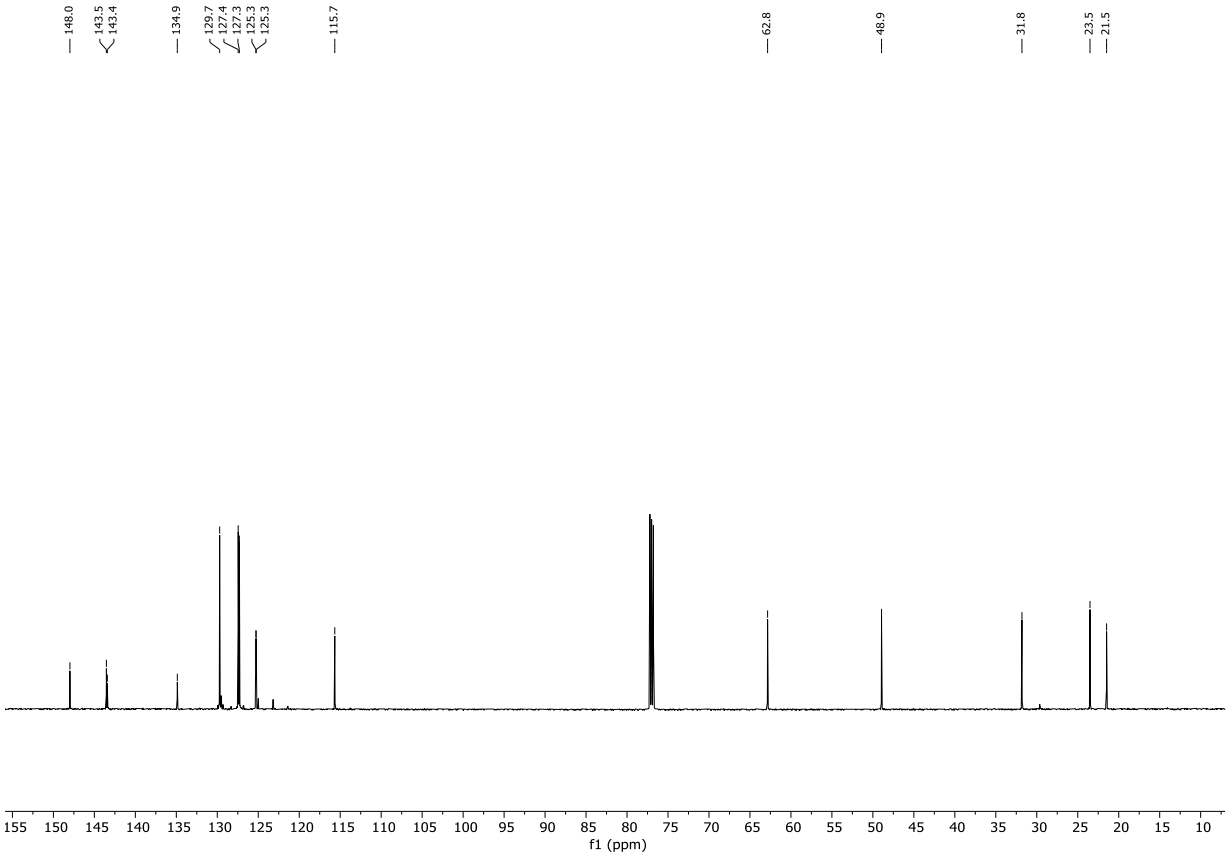
COSY-NMR of compound 3r (600 MHz,$CDCl_3$)



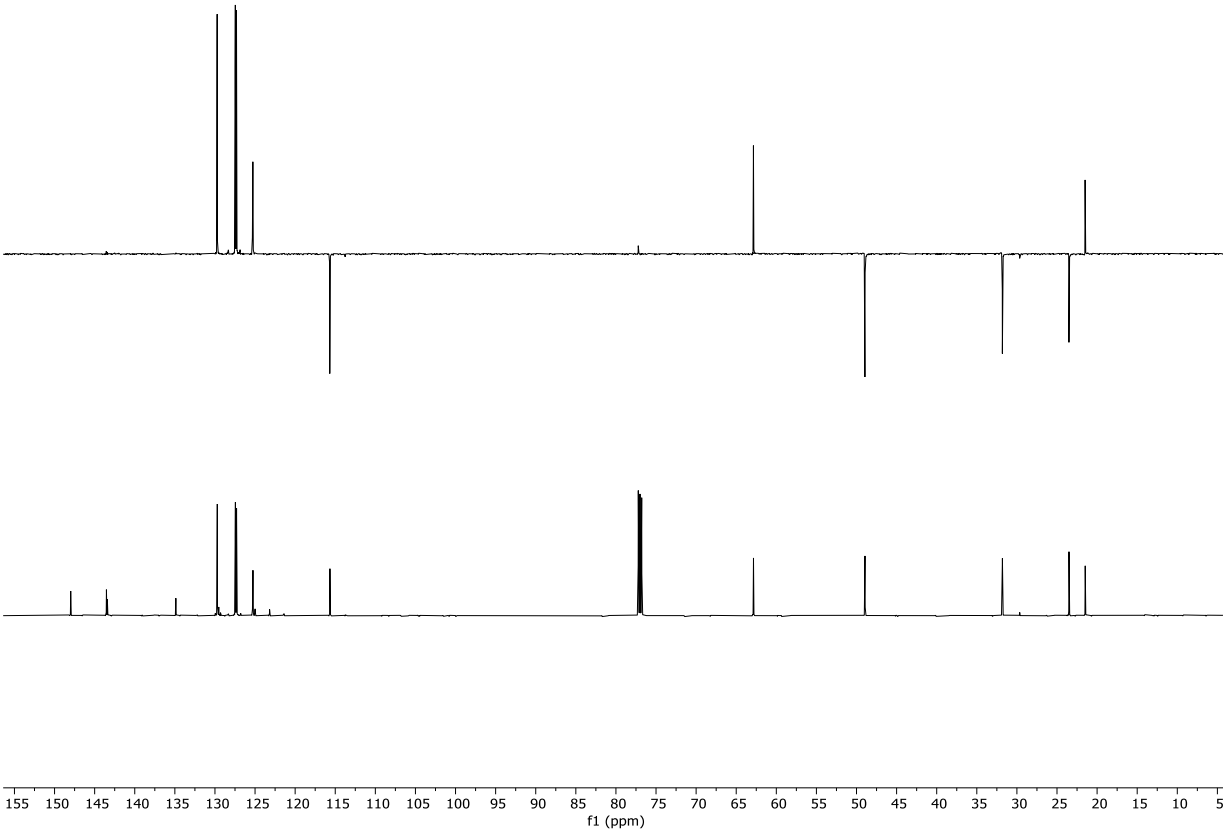
^{1}H-NMR of compound 3s (600 MHz, $CDCl_3$)



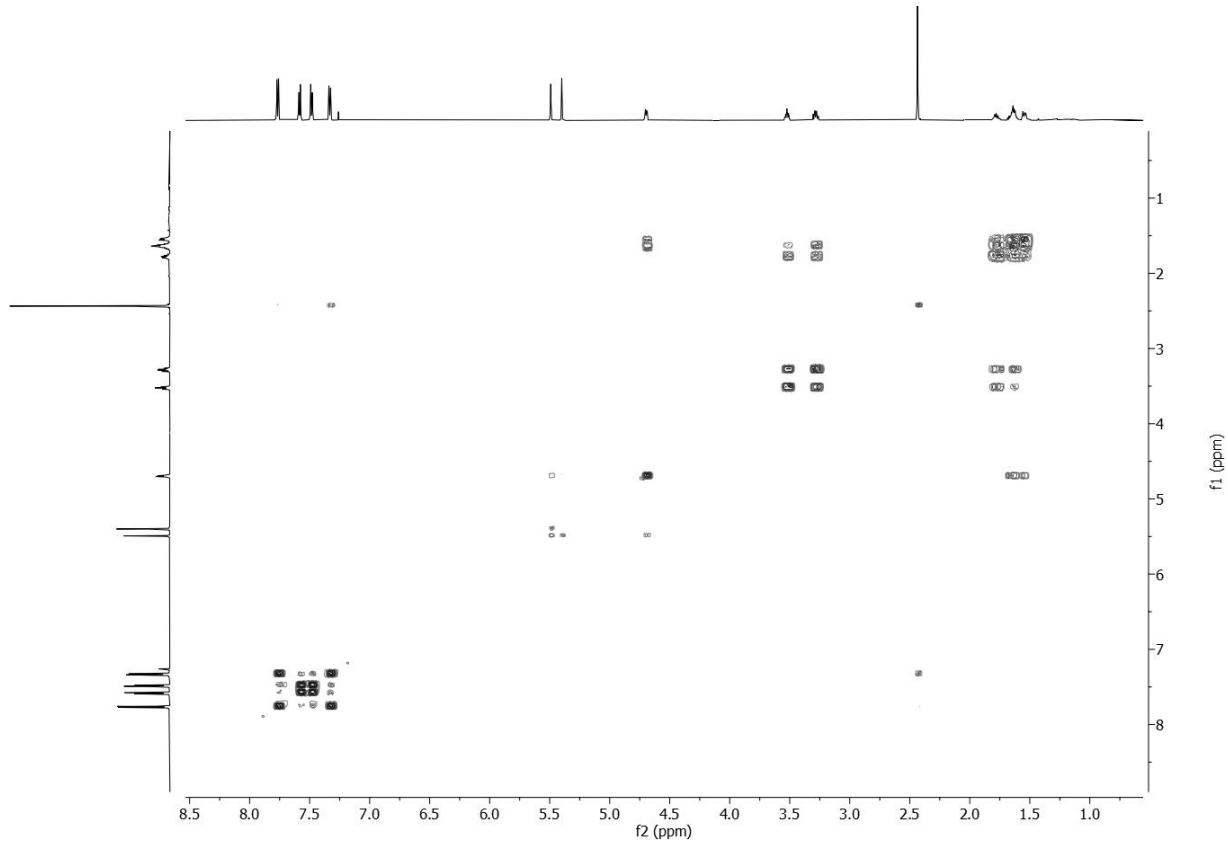
^{13}C-NMR of compound 3s (150 MHz, $CDCl_3$)



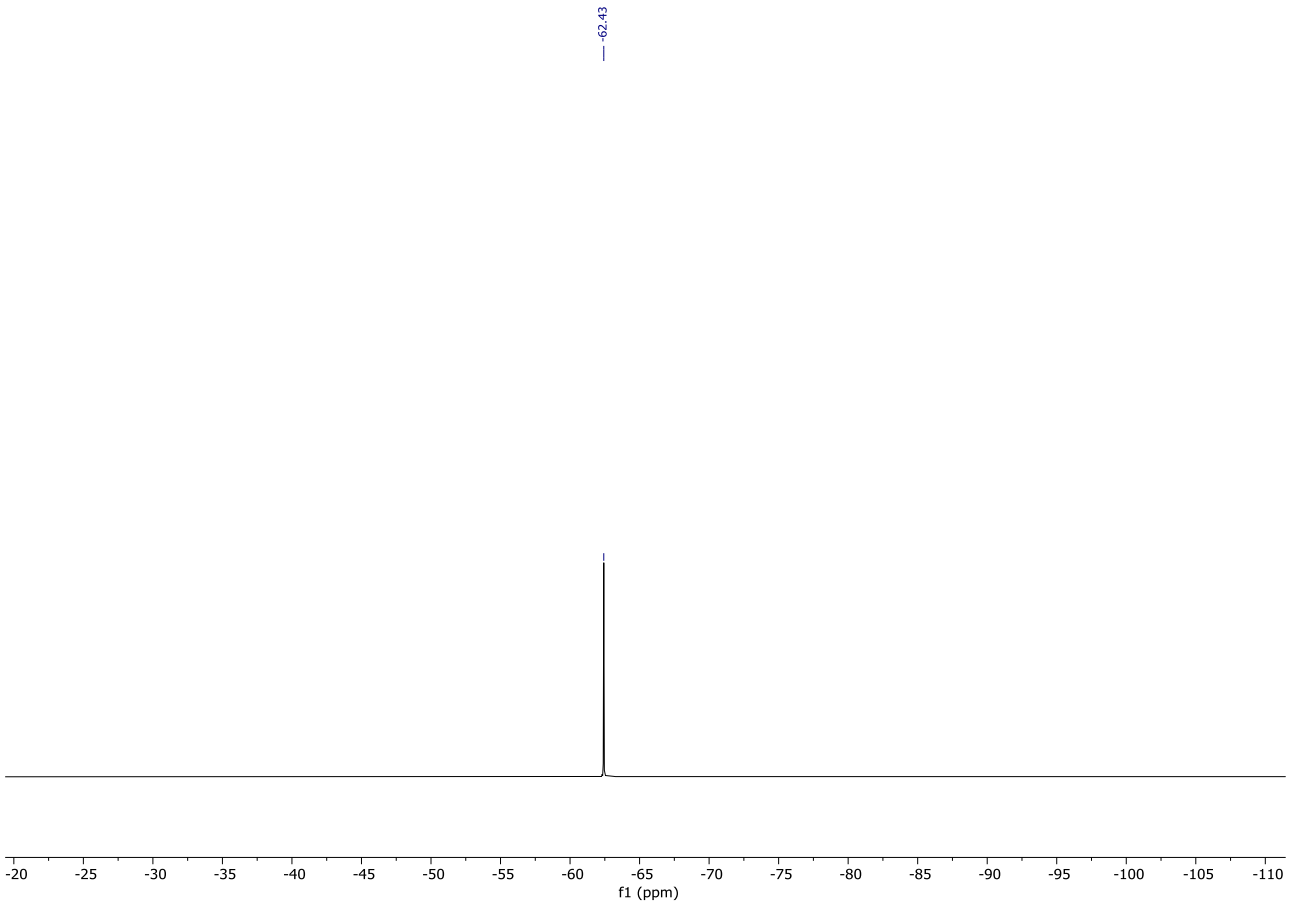
Comparison between DEPT-135 and ^{13}C-NMR of compound 3s (150 MHz, $CDCl_3$)



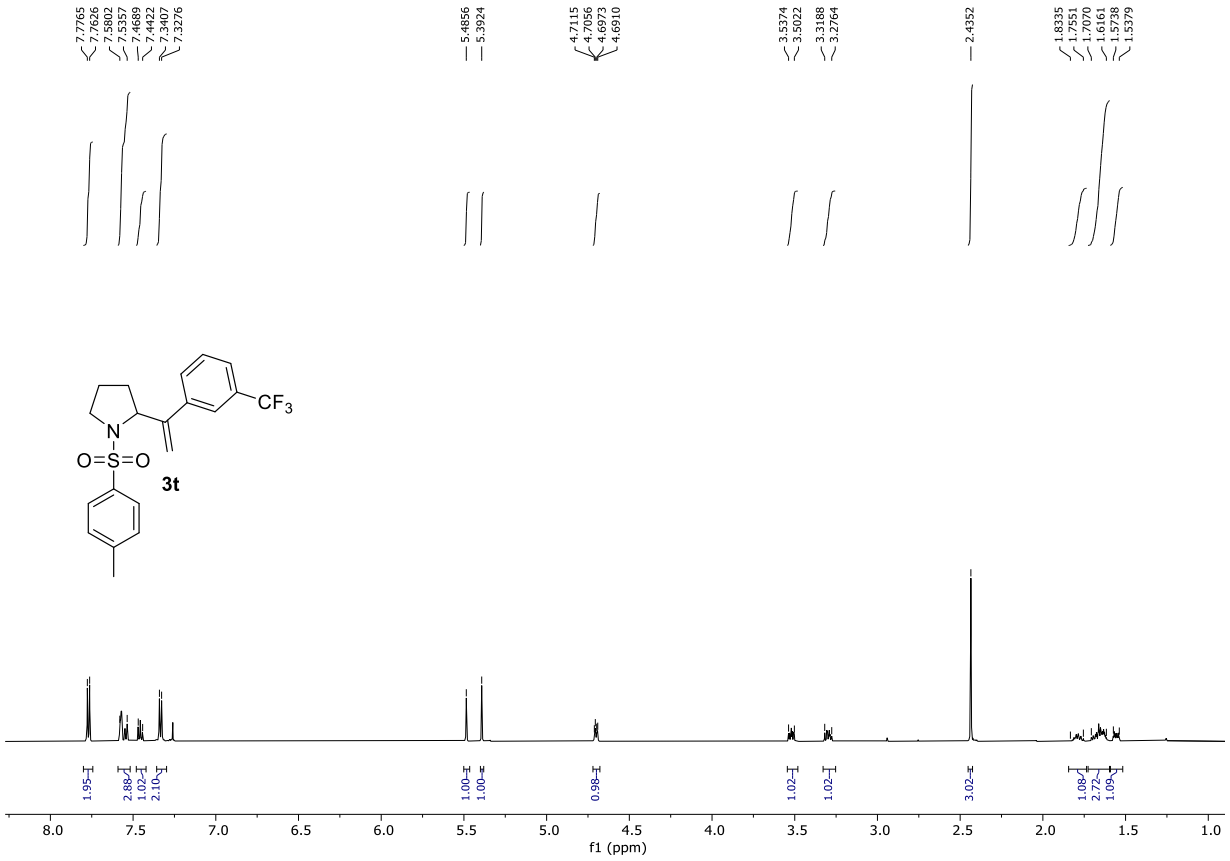
COSY-NMR of compound 3s (600 MHz, $CDCl_3$)



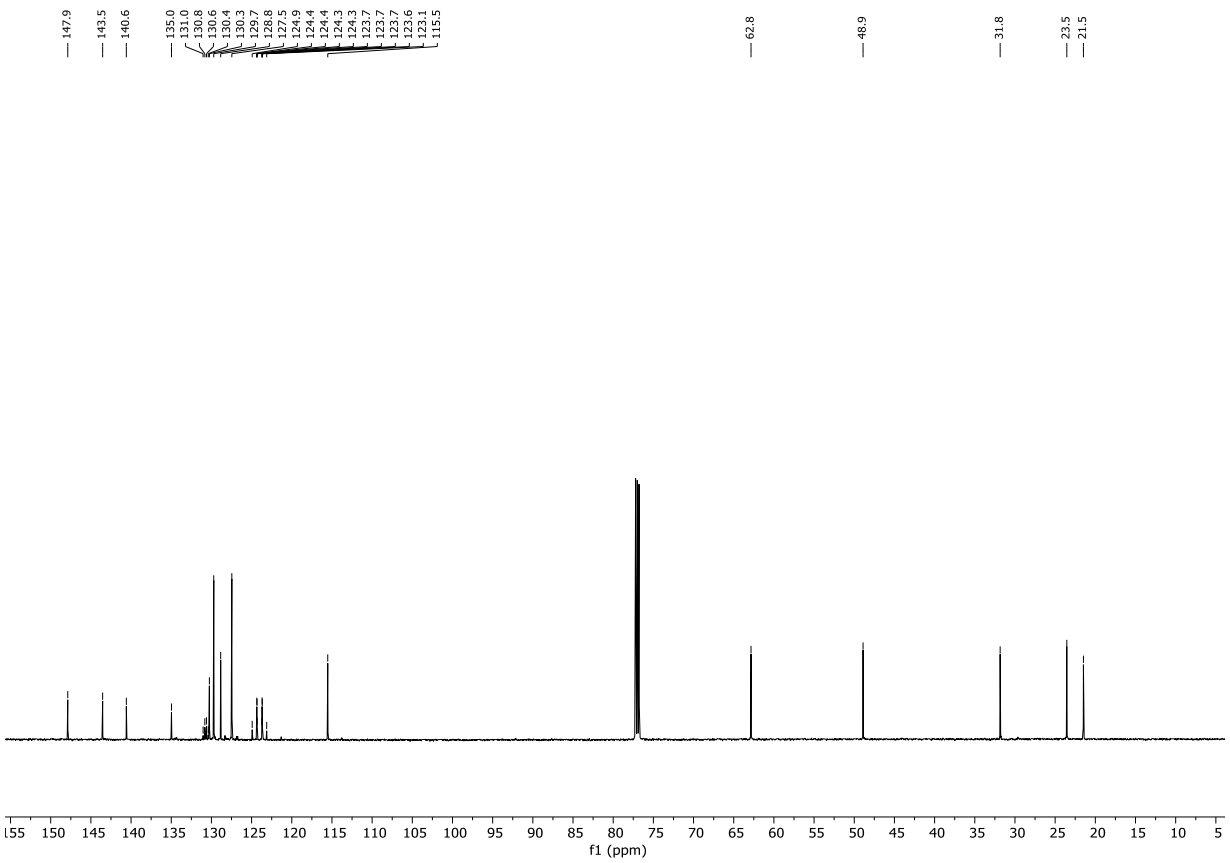
^{19}F-NMR of compound 3s (600 MHz, $CDCl_3$)



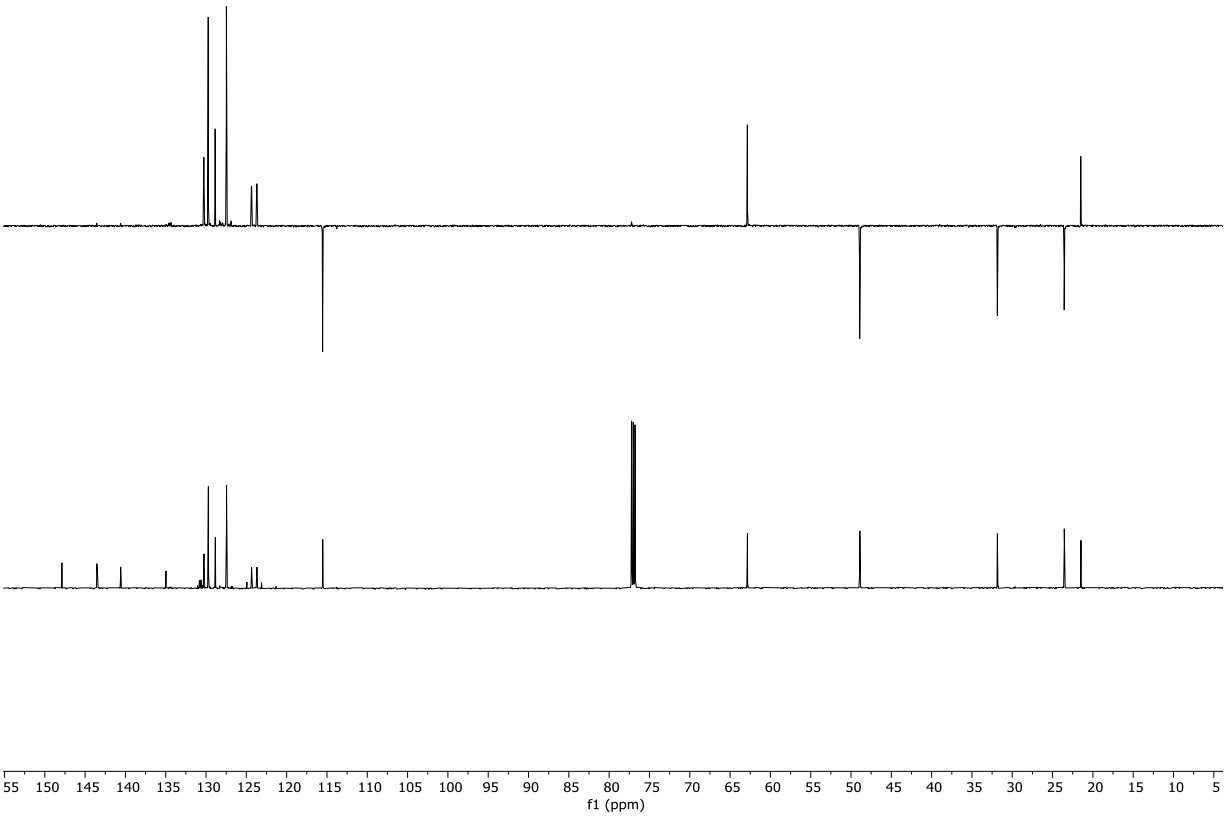
^{1}H-NMR of compound 3t (600 MHz, $CDCl_3$)



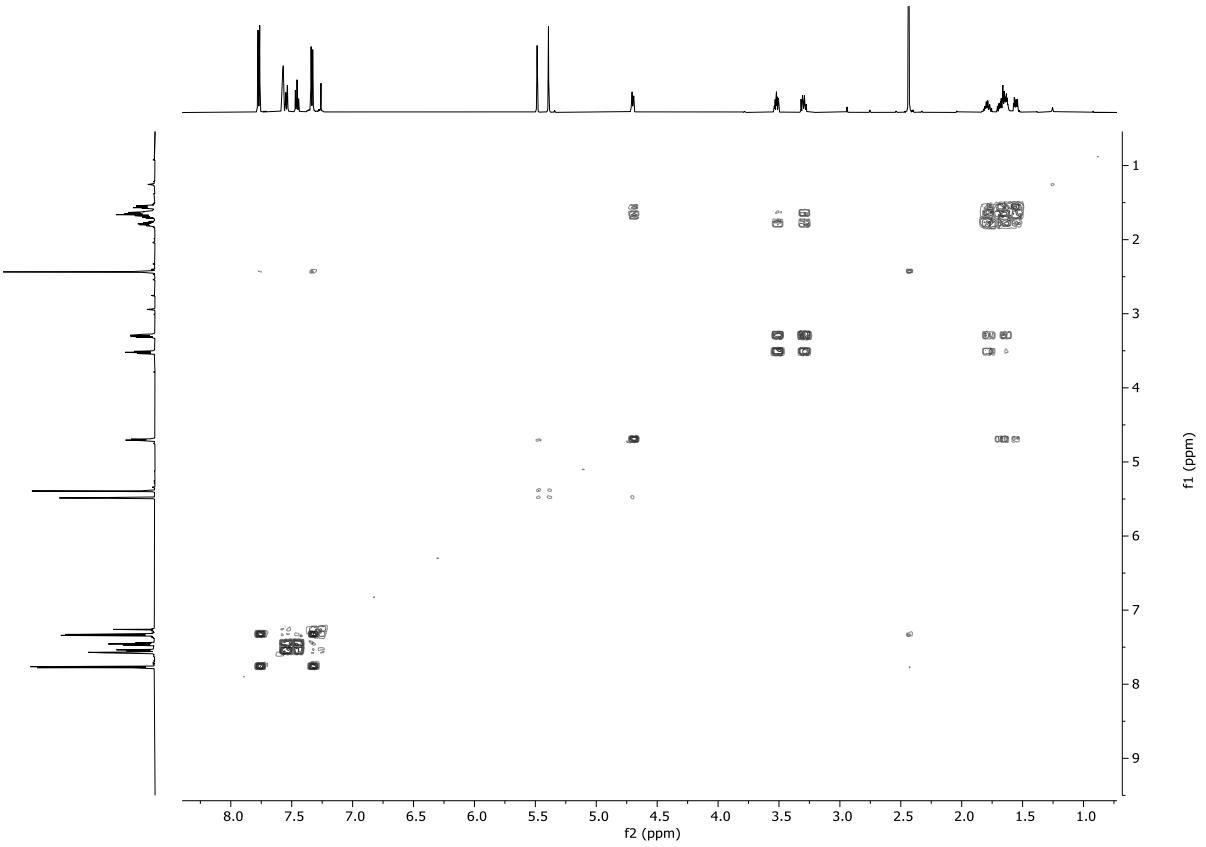
^{13}C-NMR of compound 3t (150 MHz, $CDCl_3$)



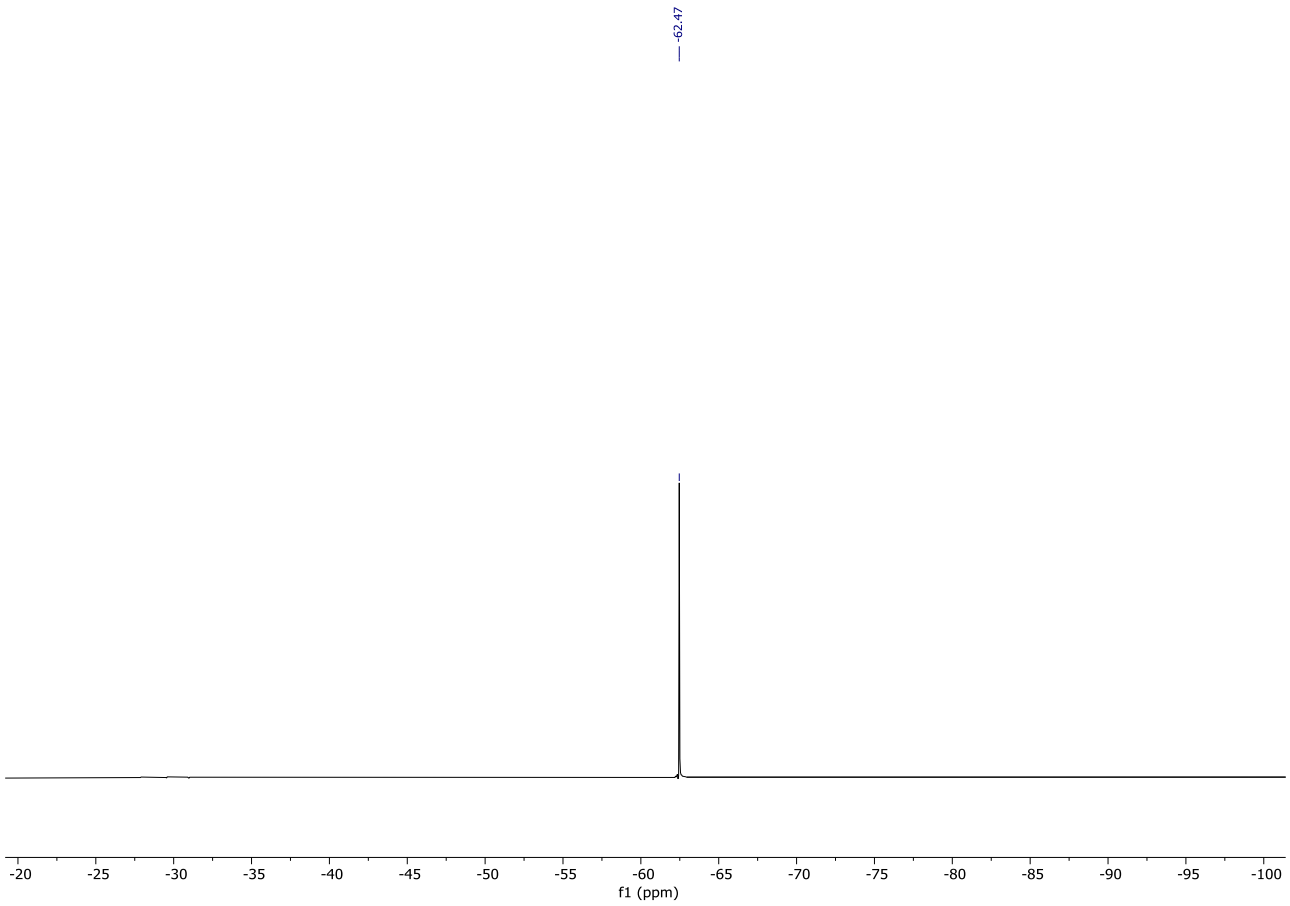
Comparison between DEPT-135 and ^{13}C-NMR of compound 3t (150 MHz, $CDCl_3$)



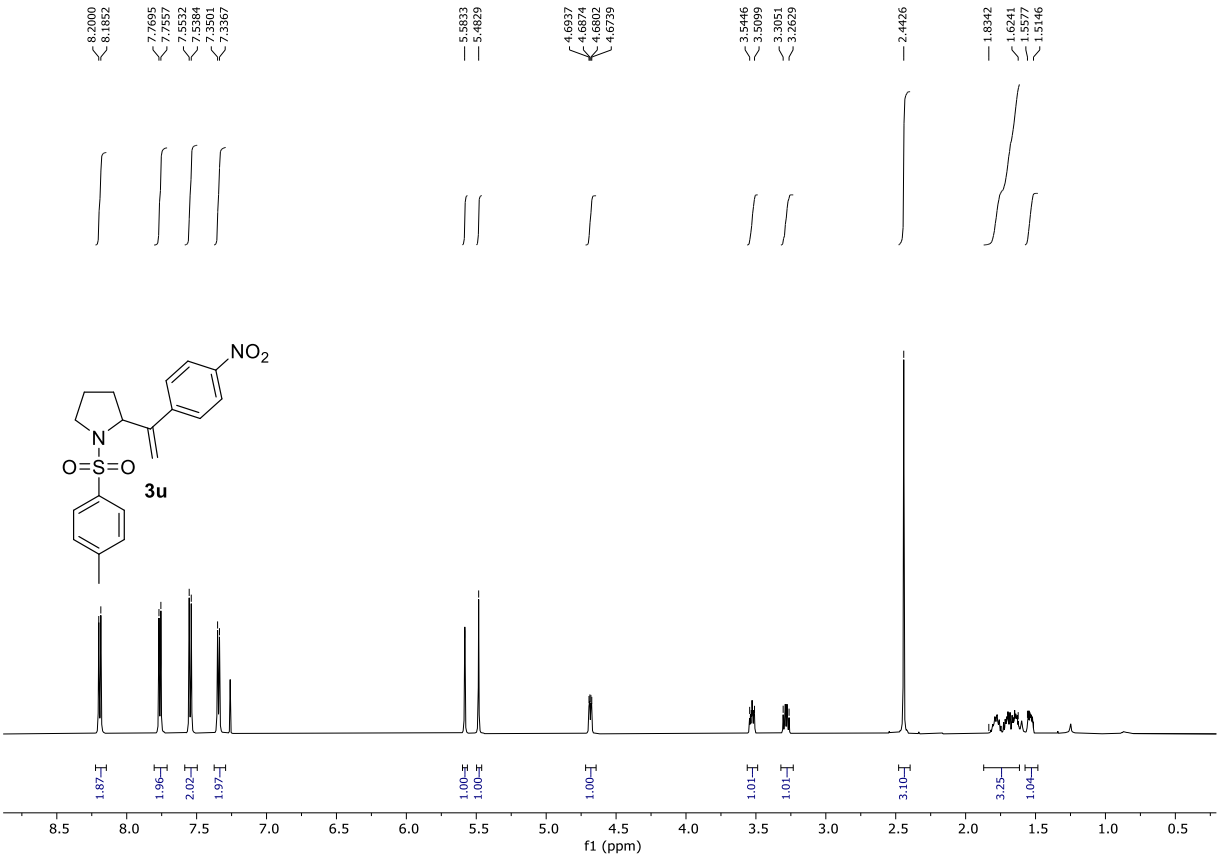
COSY-NMR of compound 3t (600 MHz, $CDCl_3$)



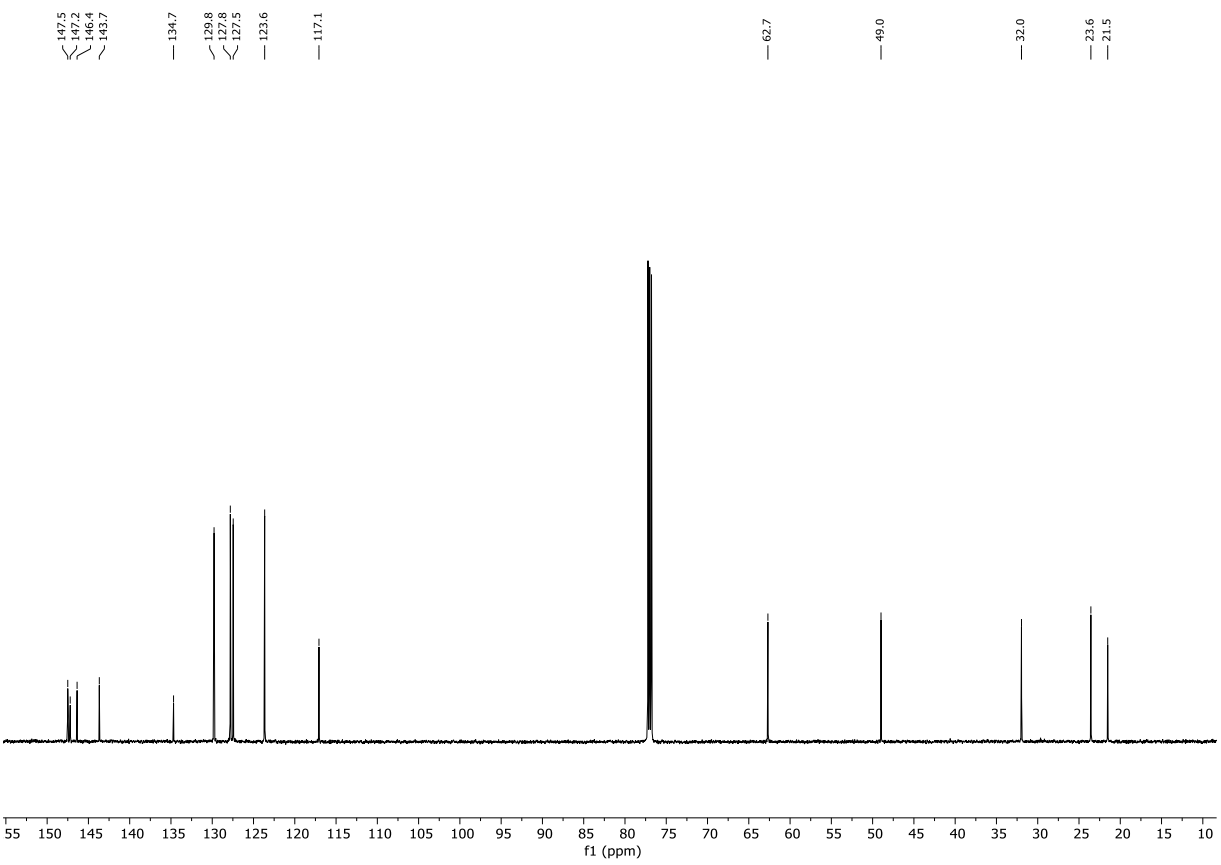
^{19}F-NMR of compound 3t (600 MHz, $CDCl_3$)



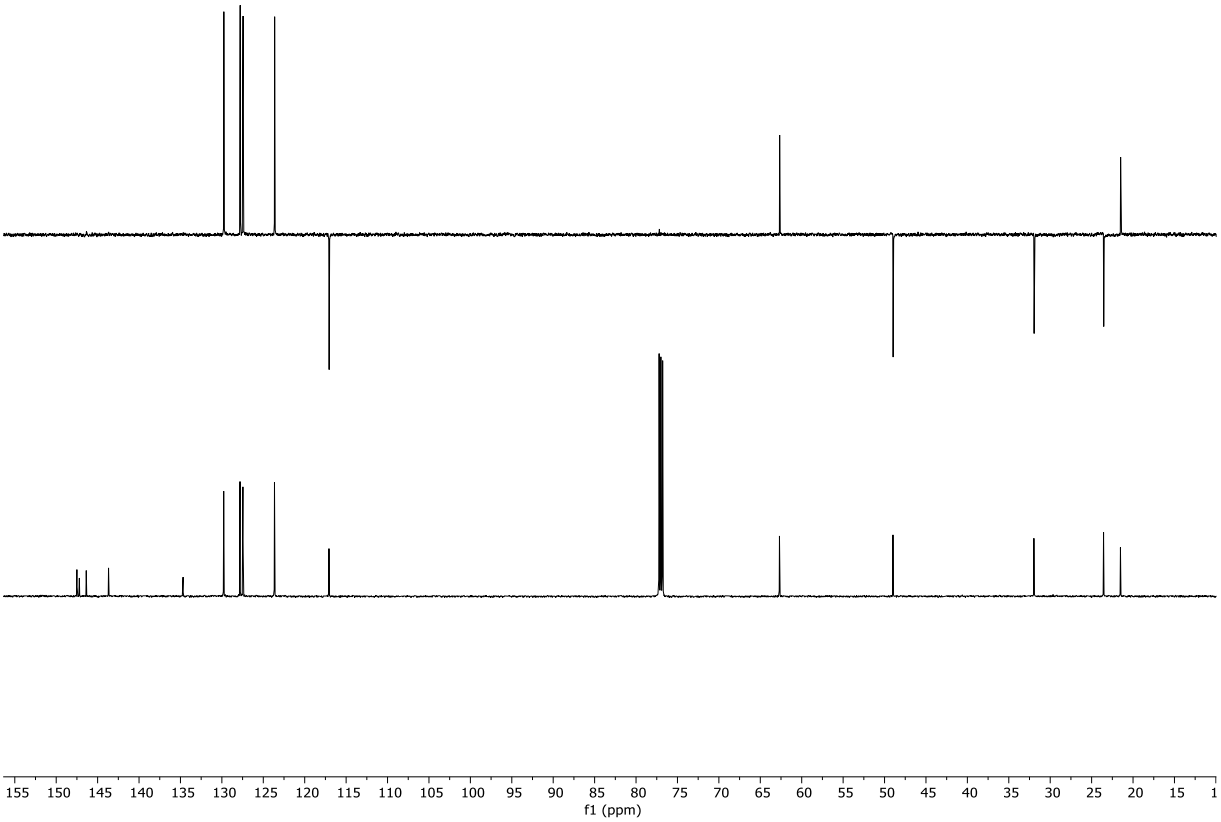
^{1}H-NMR of compound 3u (600 MHz, $CDCl_3$)



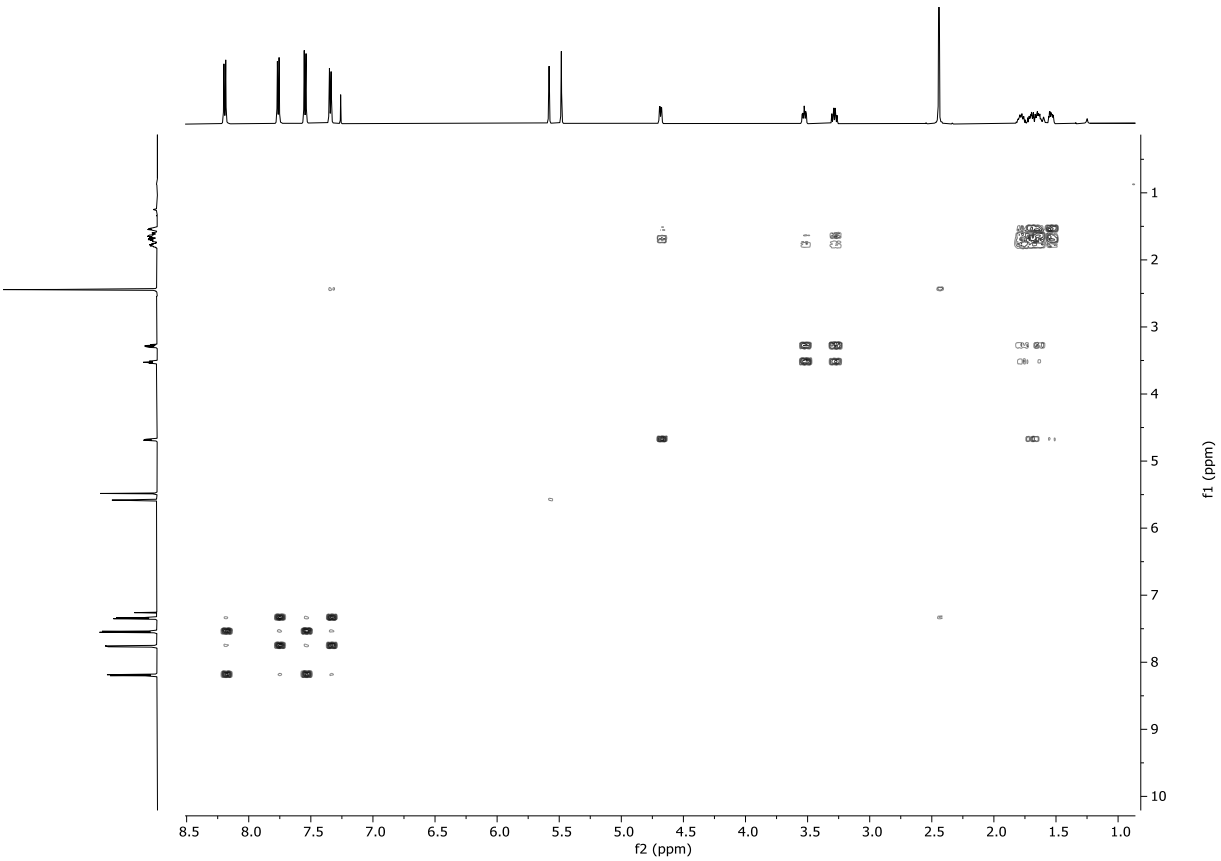
^{13}C-NMR of compound 3u (150 MHz, $CDCl_3$)



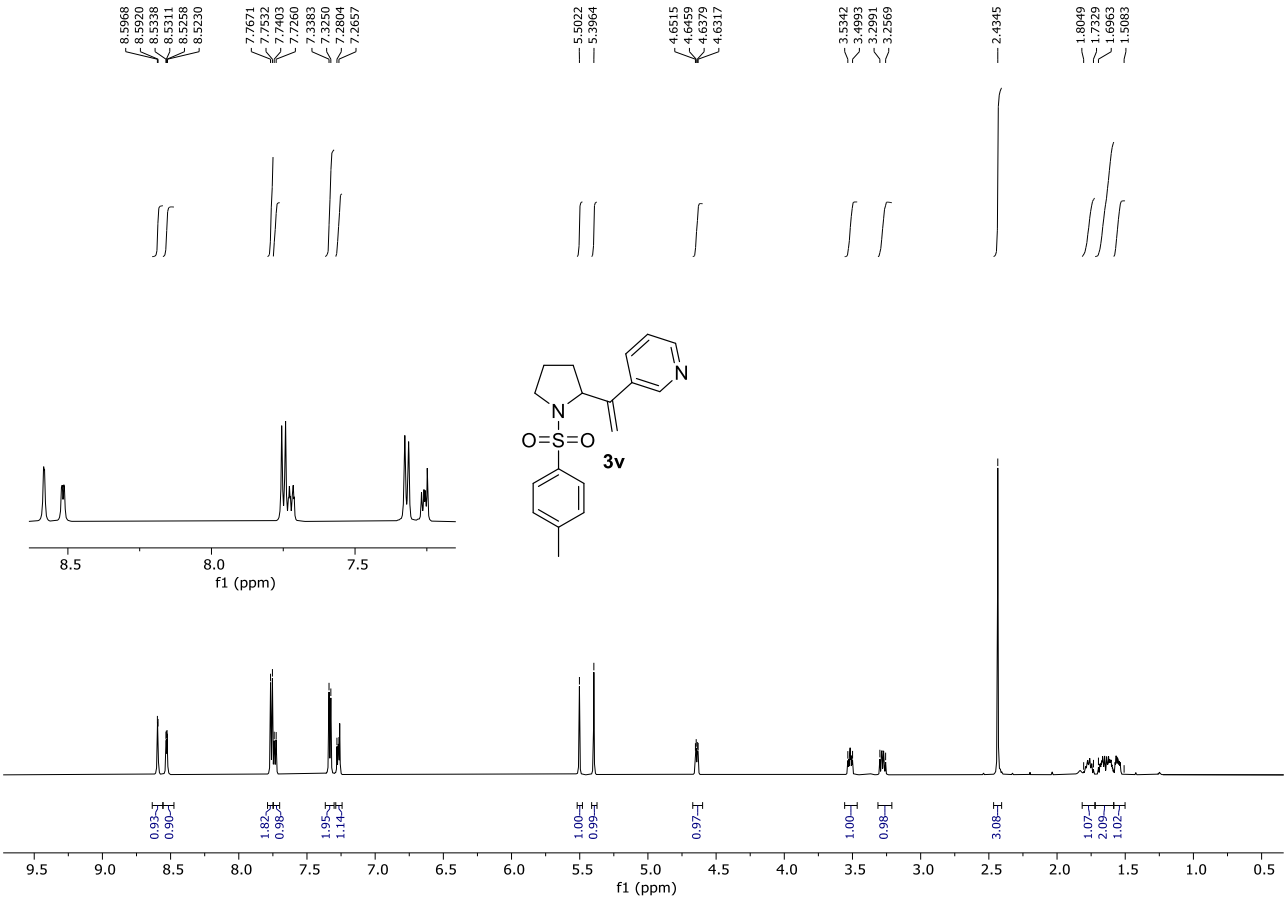
Comparison between DEPT-135 and ^{13}C-NMR of compound 3u (150 MHz, $CDCl_3$)



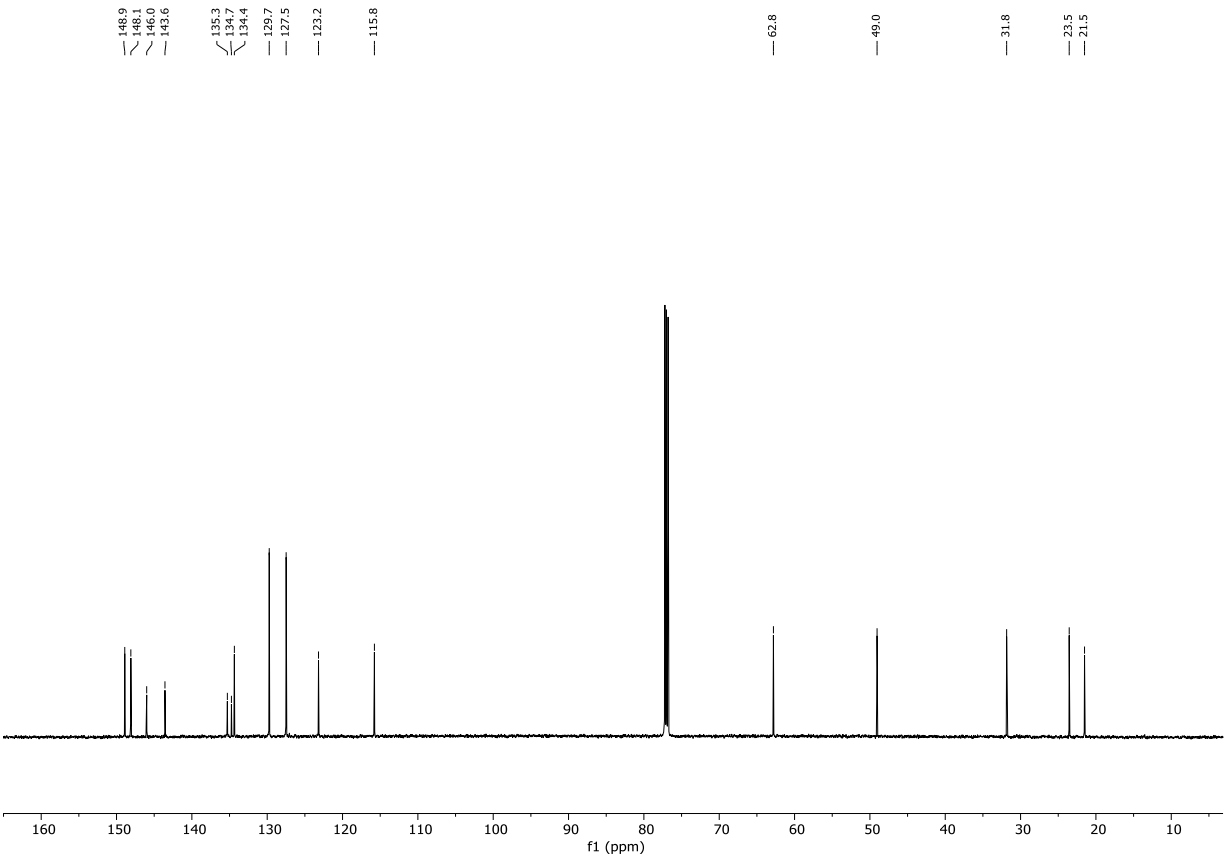
COSY-NMR of compound 3u (600 MHz, $CDCl_3$)



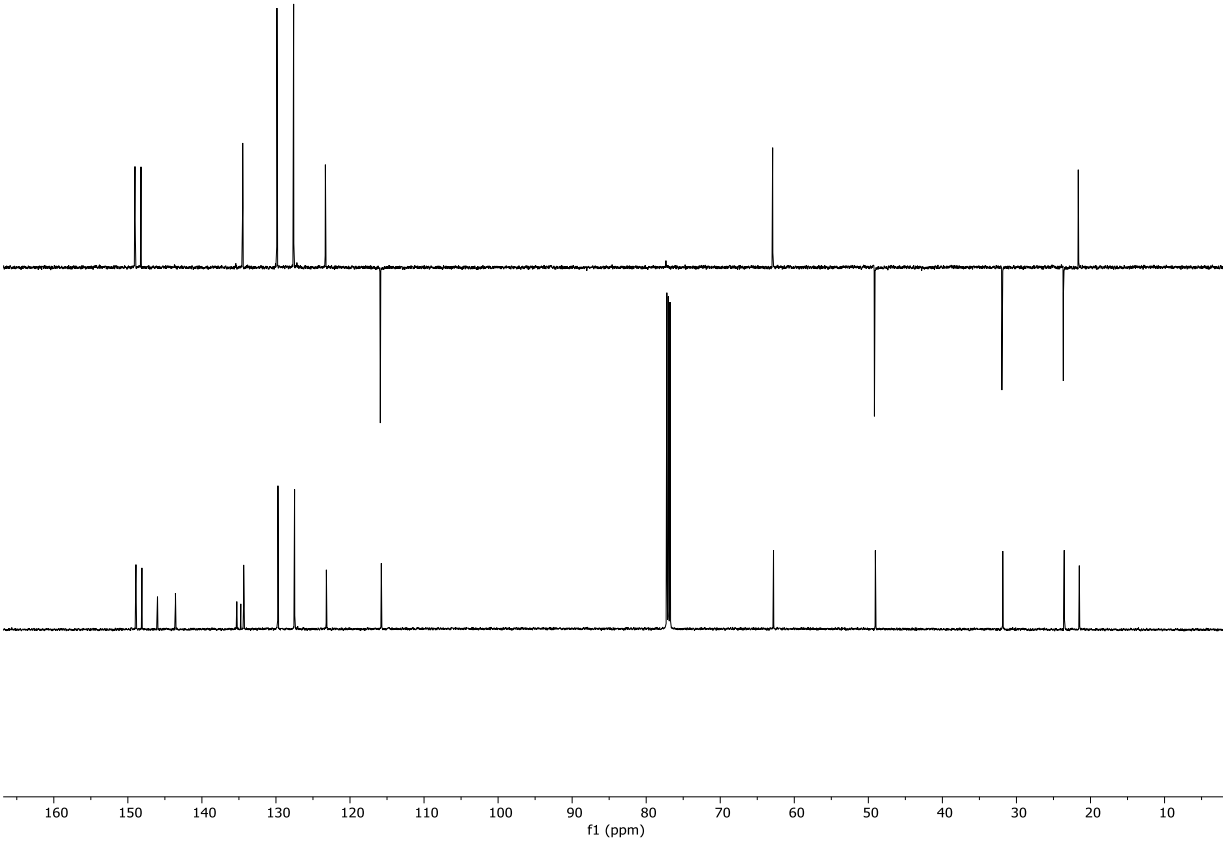
^{1}H-NMR of compound 3v (600 MHz, $CDCl_3$)



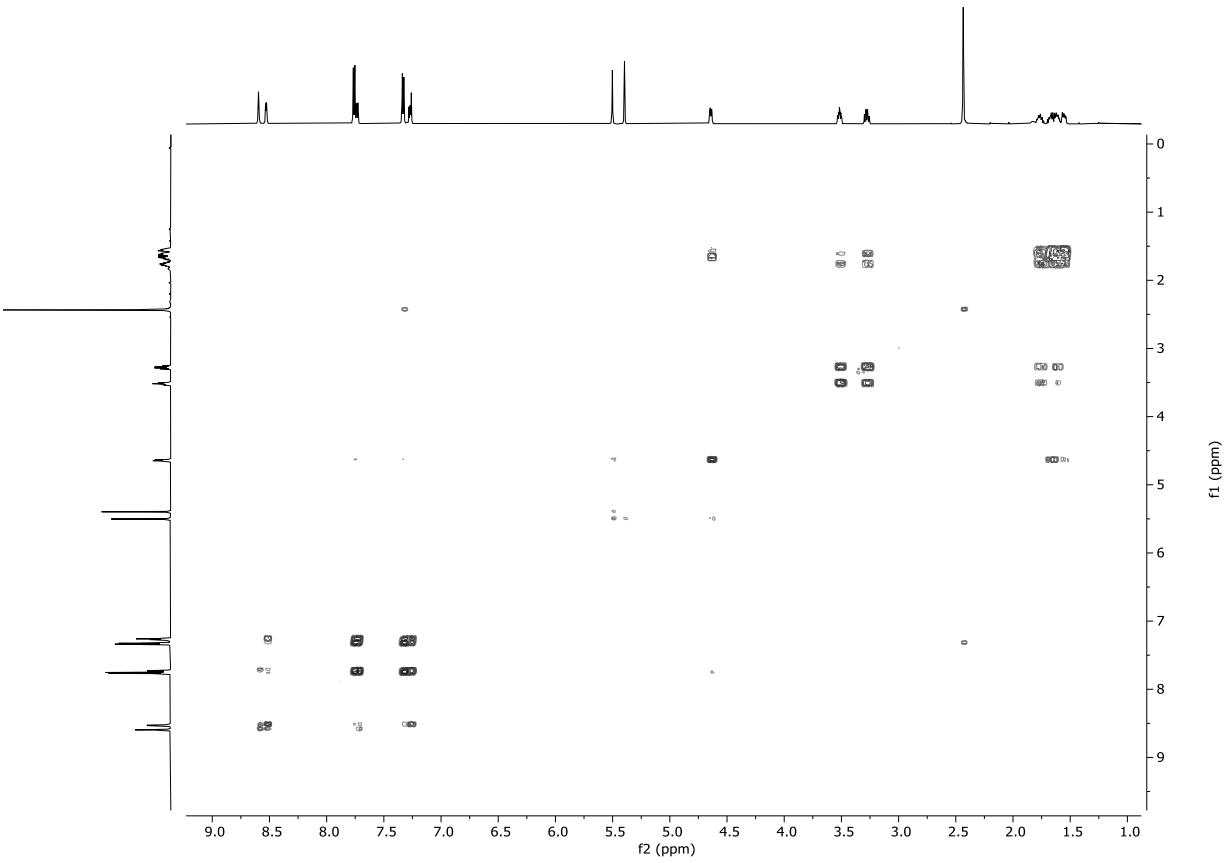
^{13}C-NMR of compound 3v (150 MHz, $CDCl_3$)



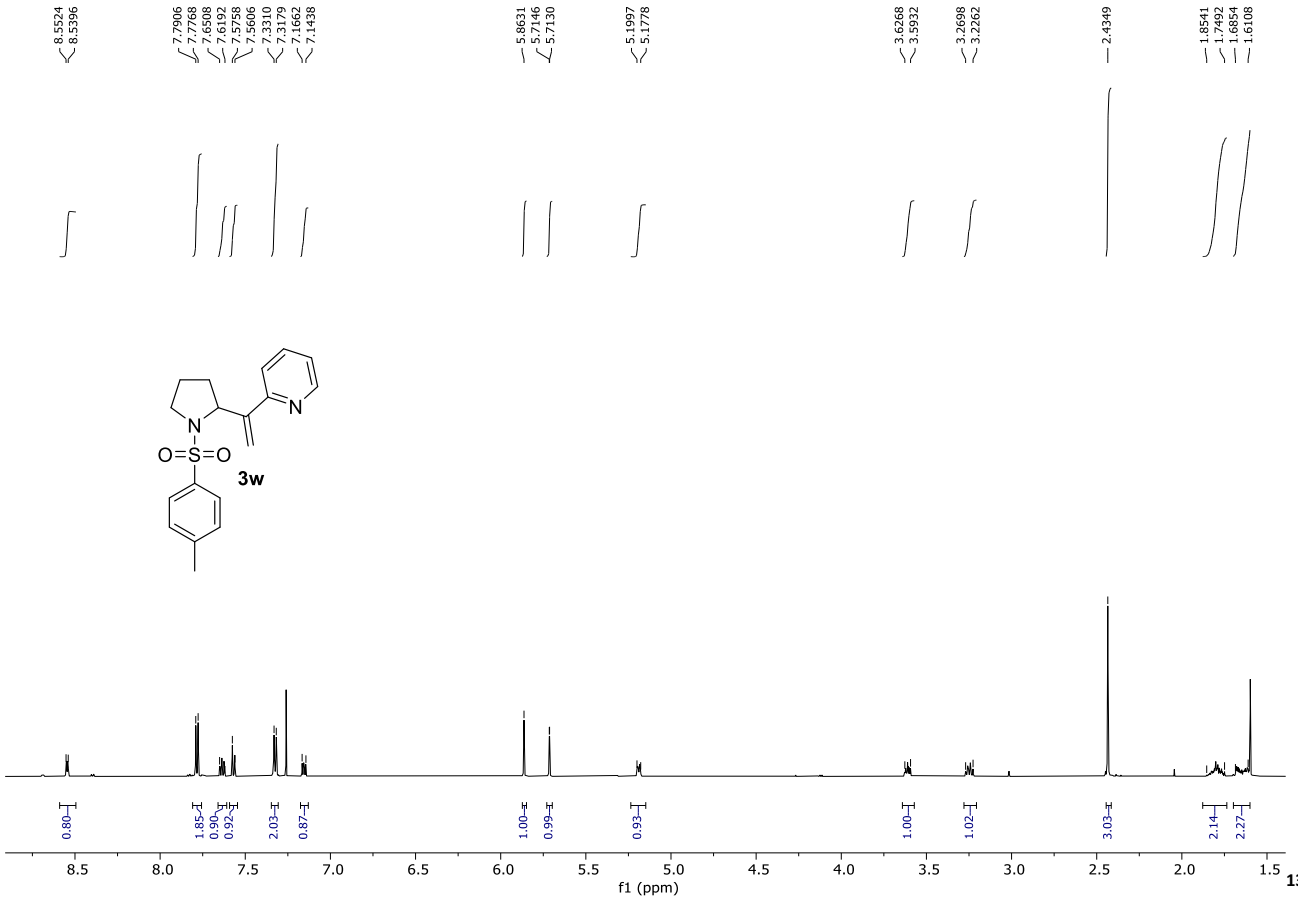
Comparison between DEPT-135 and ^{13}C-NMR of compound 3v (150 MHz, $CDCl_3$)



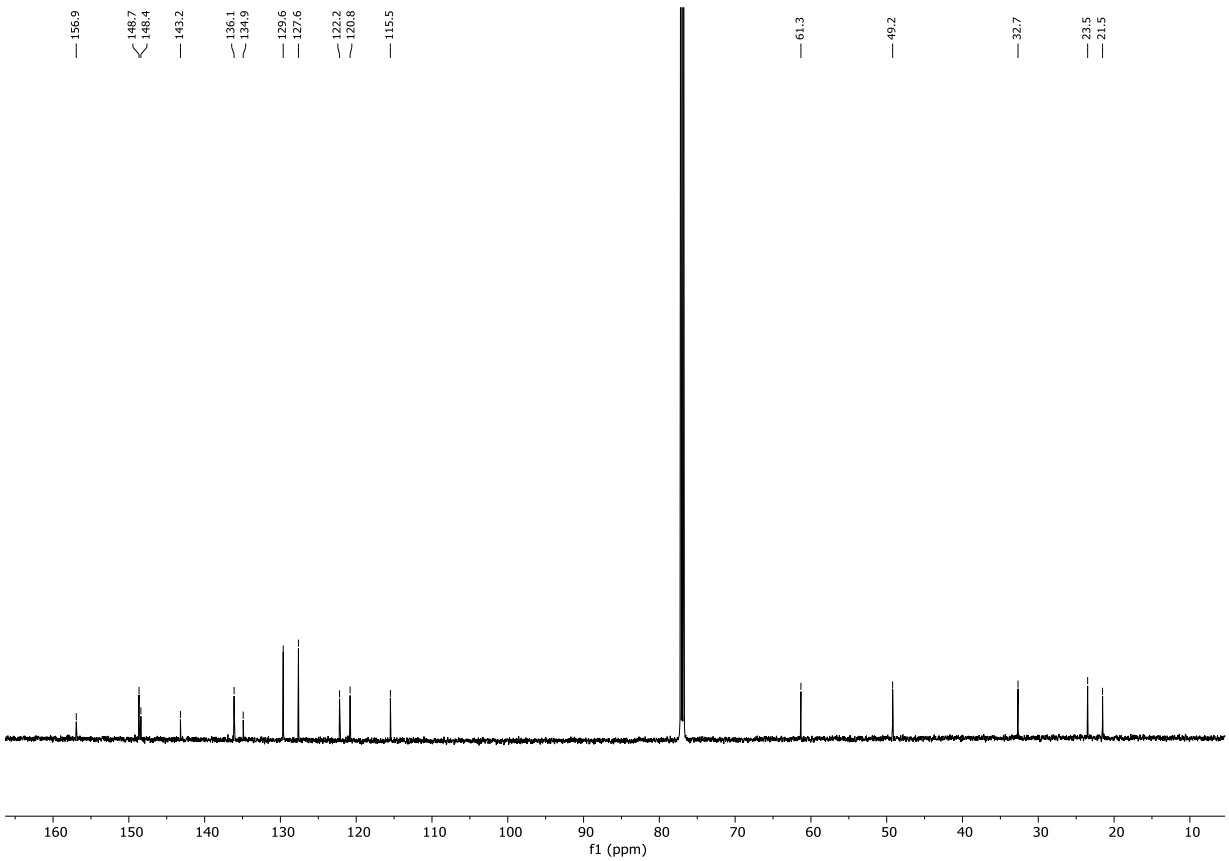
COSY-NMR of compound 3v (600 MHz, $CDCl_3$)



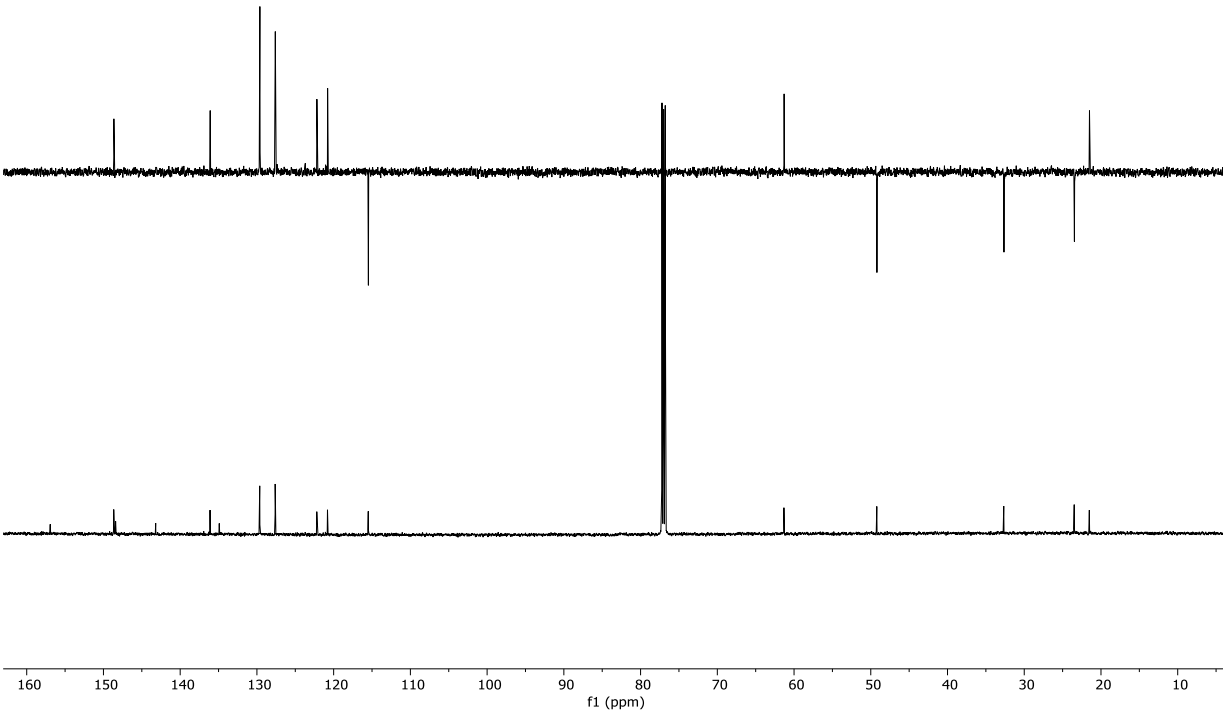
^{1}H-NMR of compound 3w (600 MHz, $CDCl_3$)



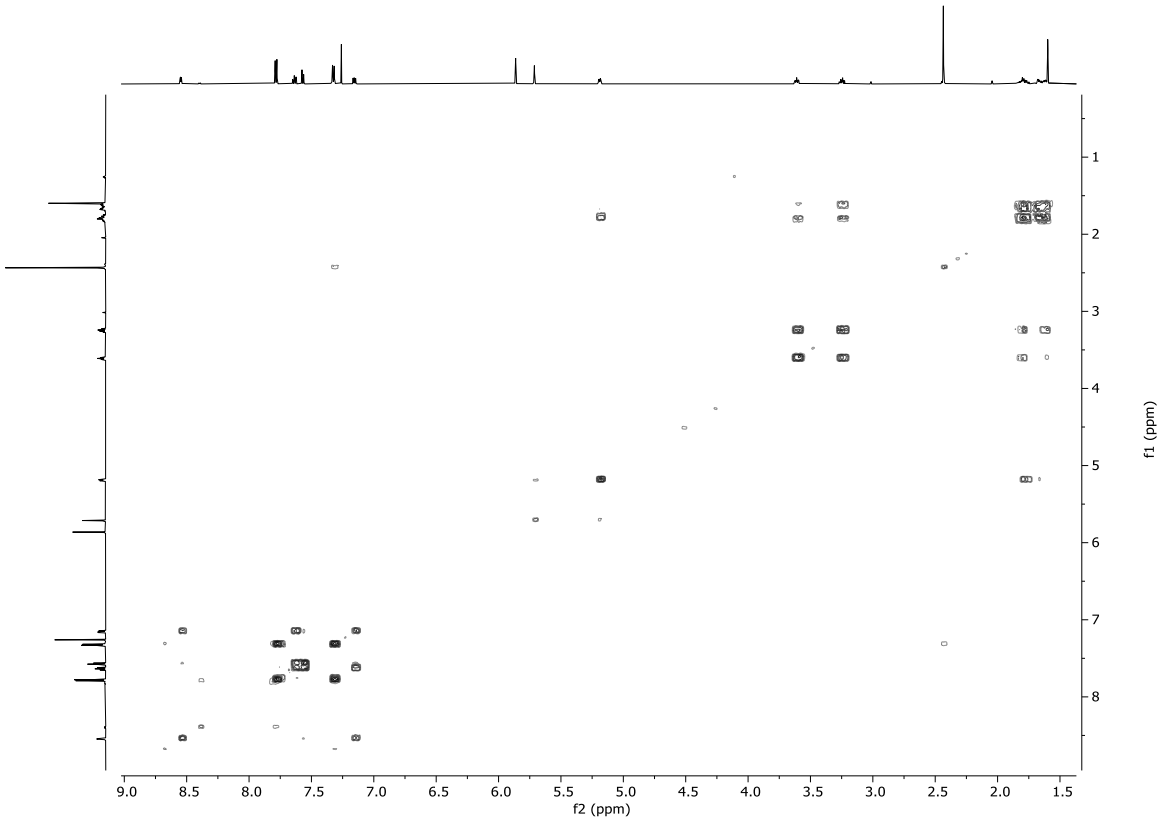
^{13}C-NMR of compound 3w (150 MHz, $CDCl_3$)



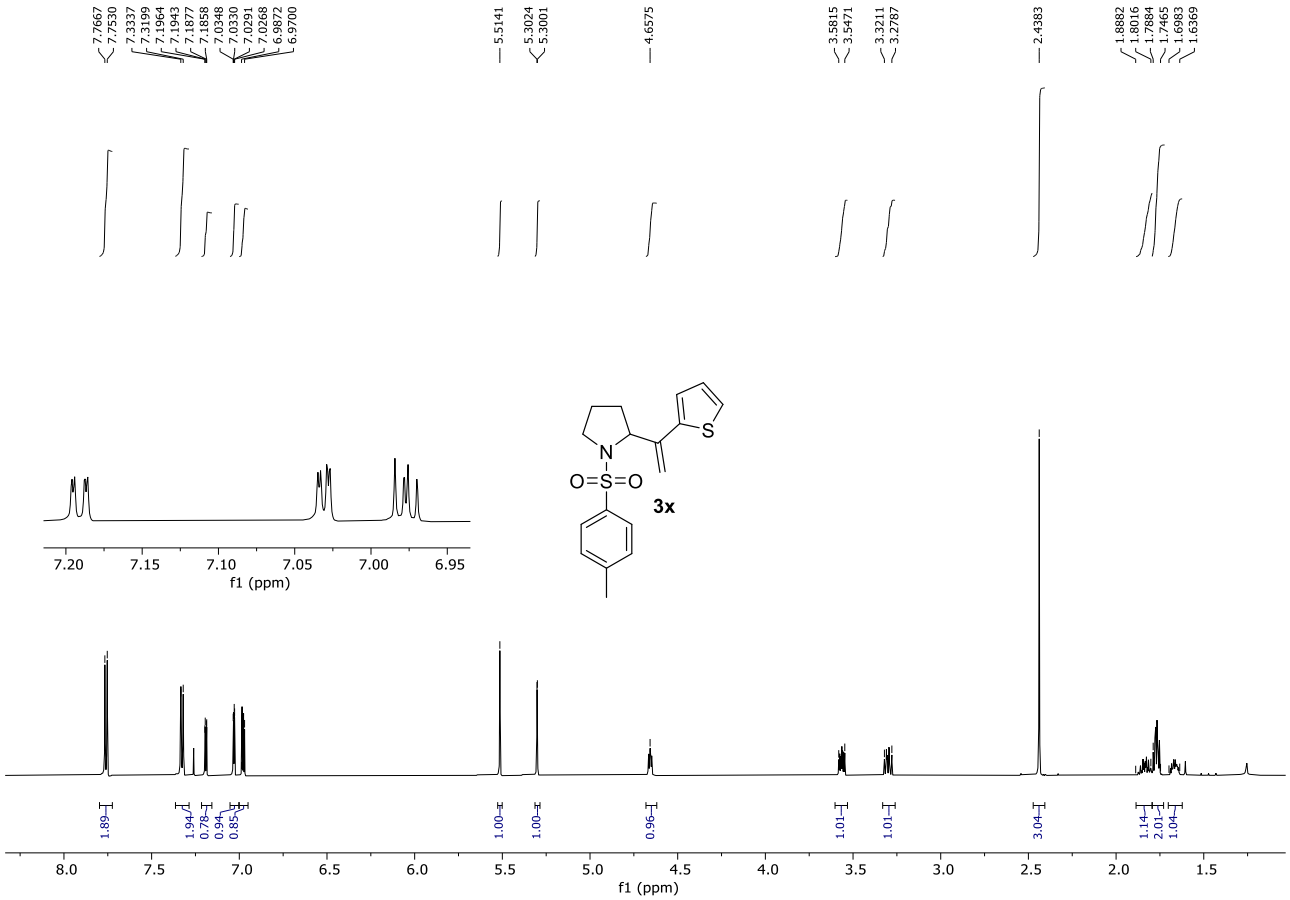
Comparison between DEPT-135 and ^{13}C-NMR of compound 3w (150 MHz, $CDCl_3$)



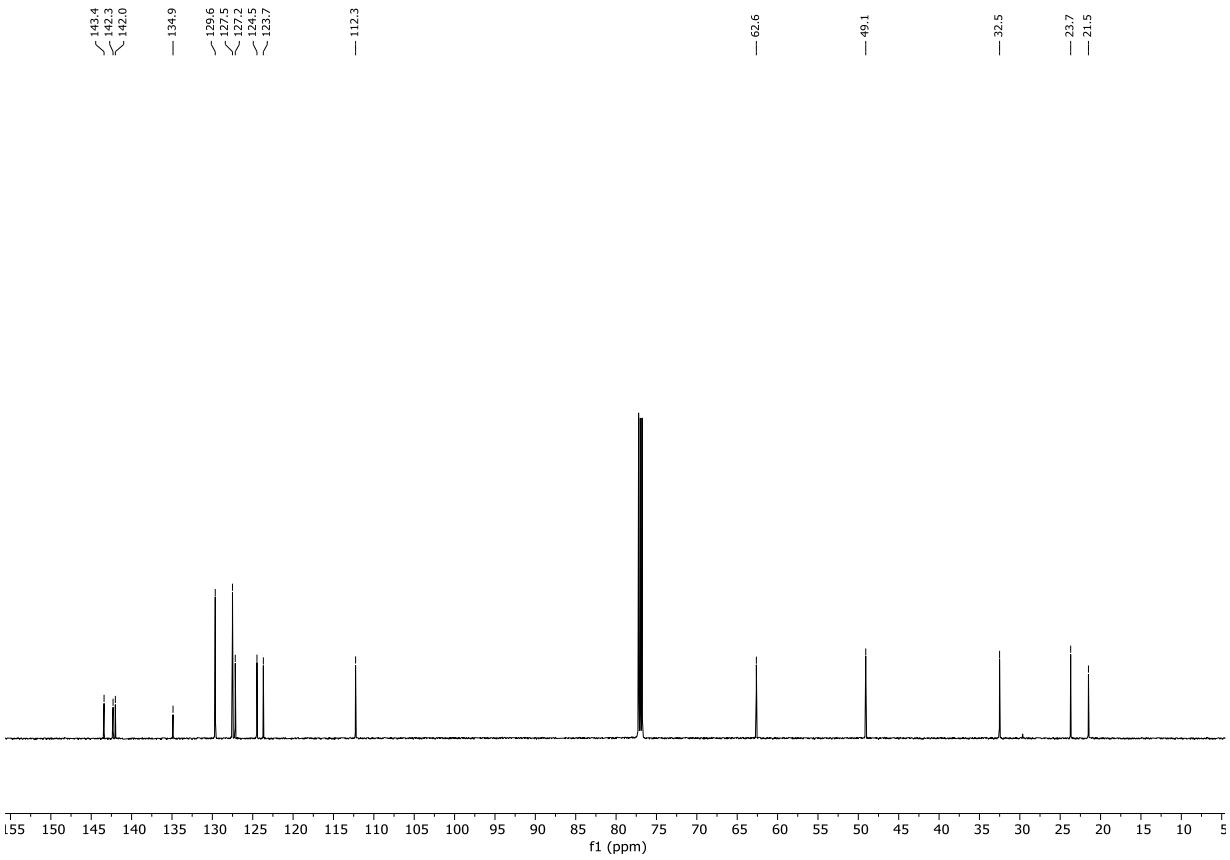
COSY-NMR of compound 3w (600 MHz, $CDCl_3$)



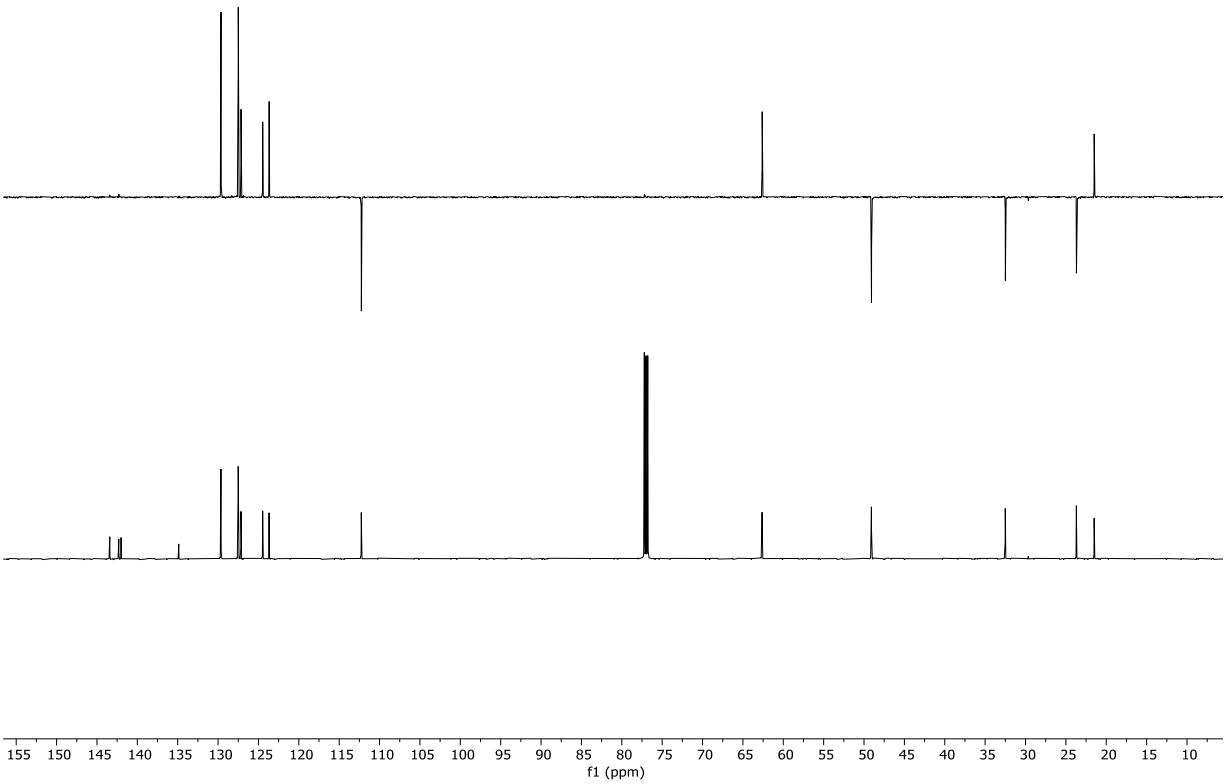
^{1}H-NMR of compound 3x (600 MHz, $CDCl_3$)



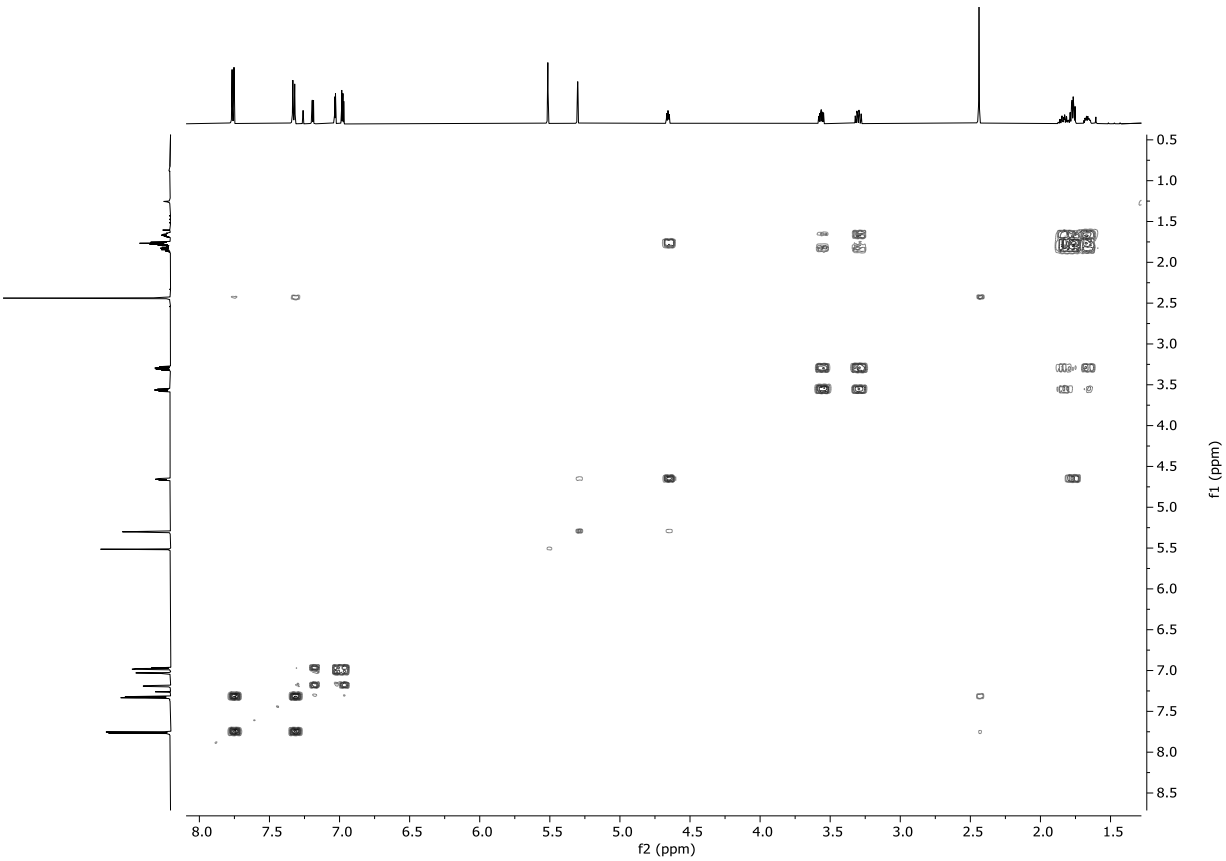
^{13}C-NMR of compound 3x (150 MHz, $CDCl_3$)



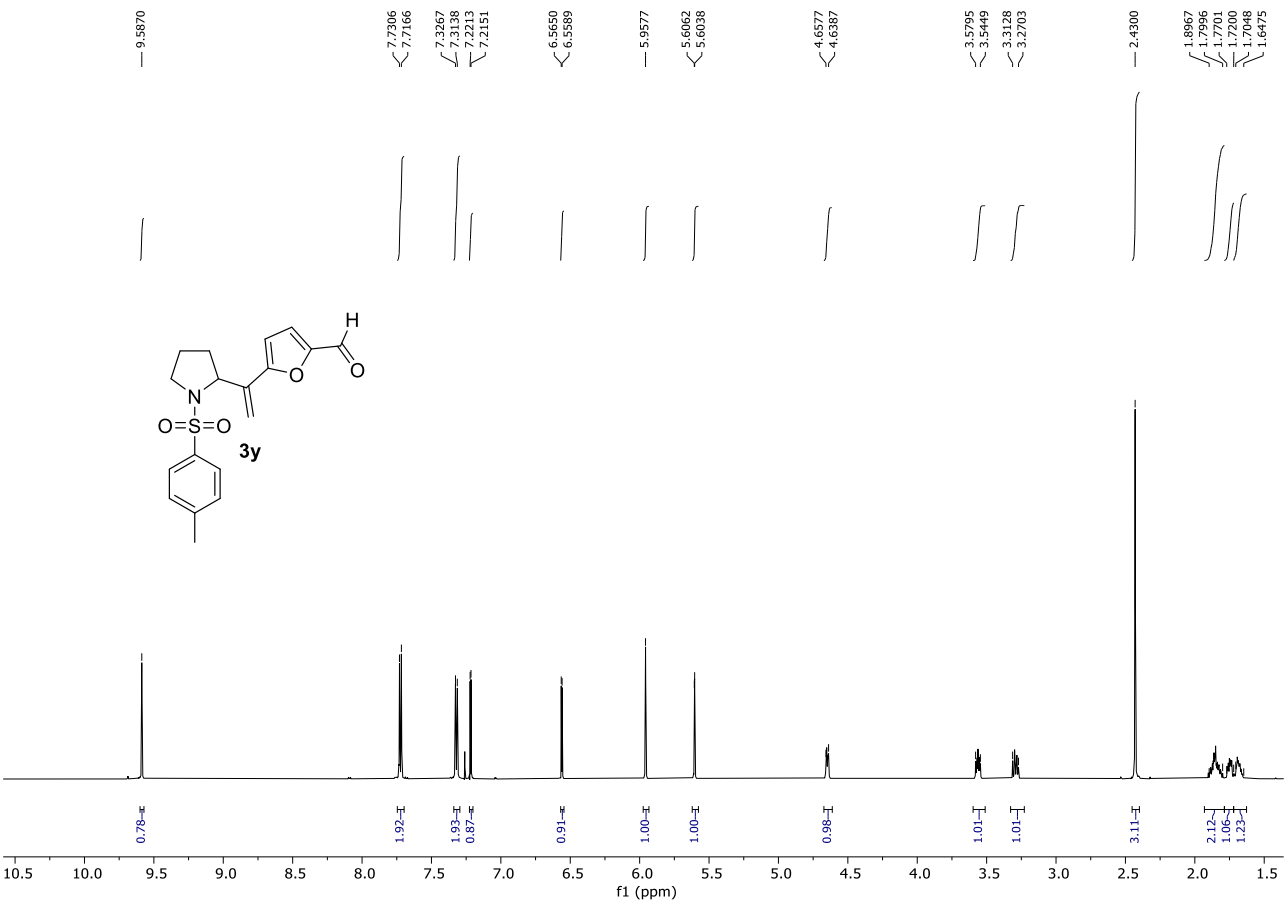
Comparison between DEPT-135 and ^{13}C-NMR of compound 3x (150 MHz, $CDCl_3$)



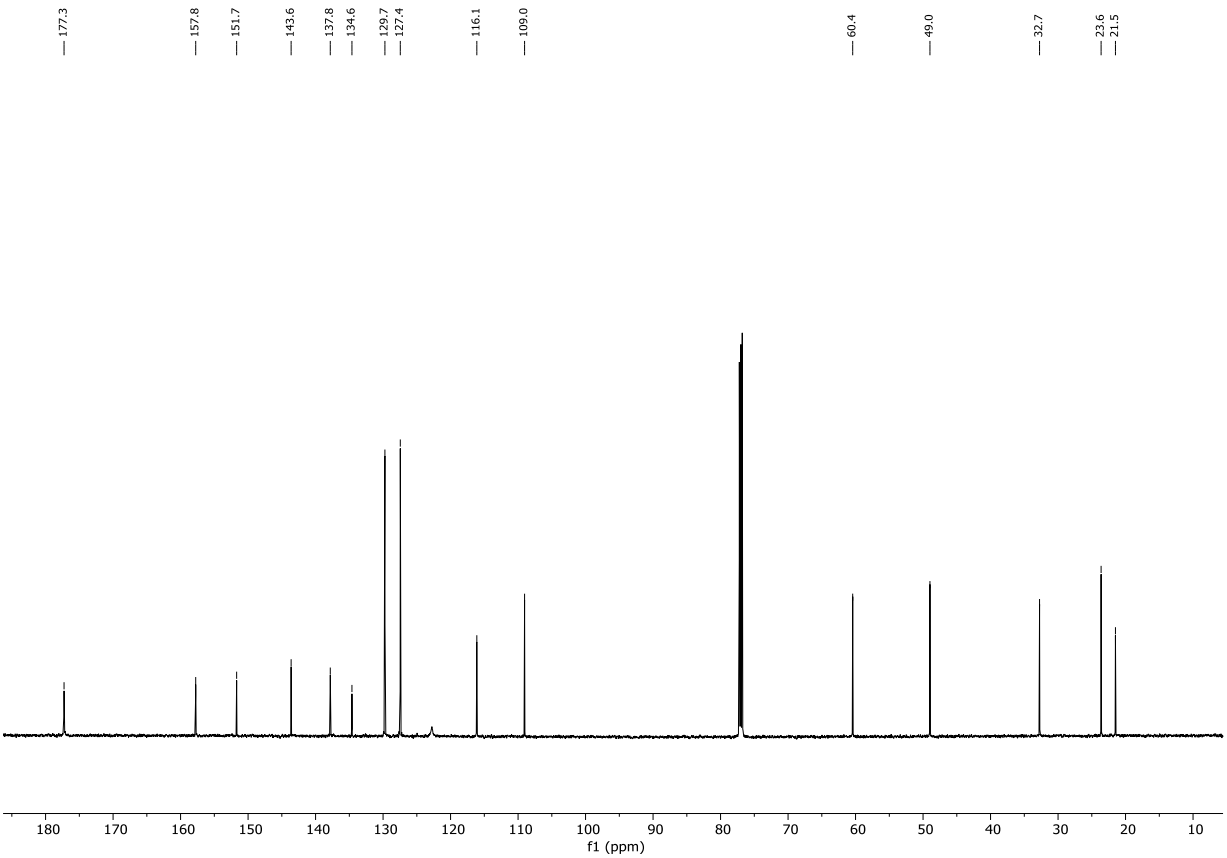
COSY-NMR of compound 3x (600 MHz, $CDCl_3$)



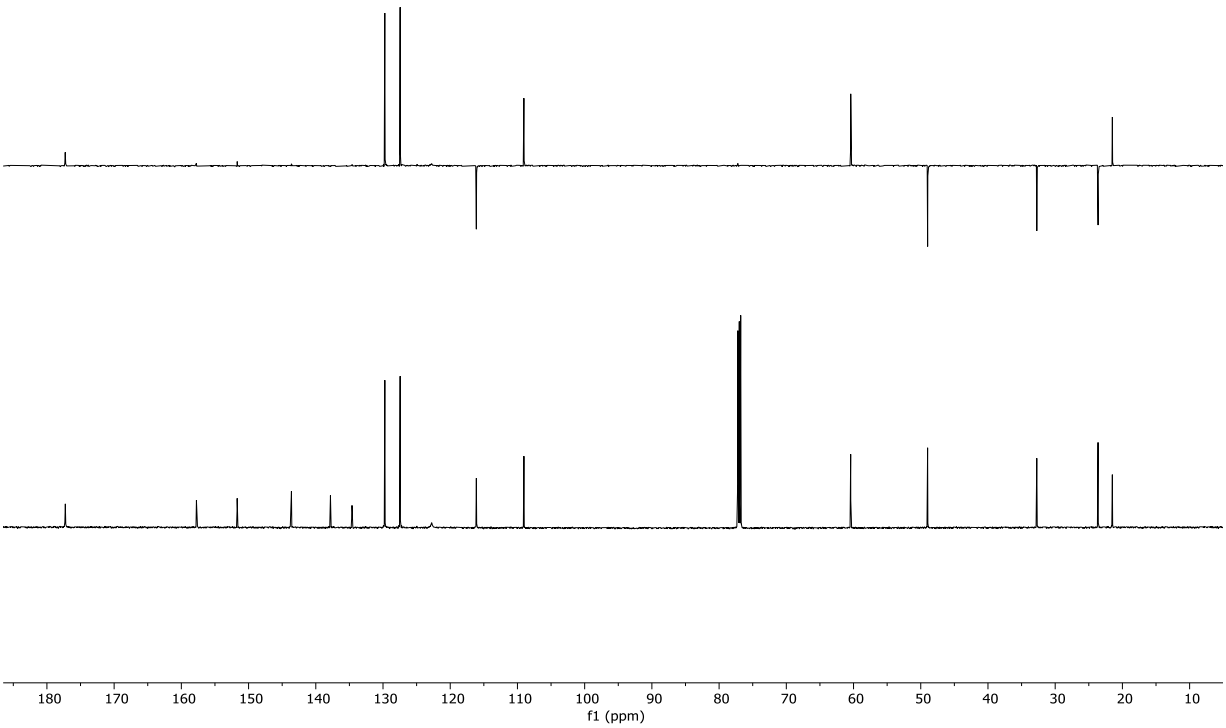
^{1}H-NMR of compound 3y (600 MHz, $CDCl_3$)



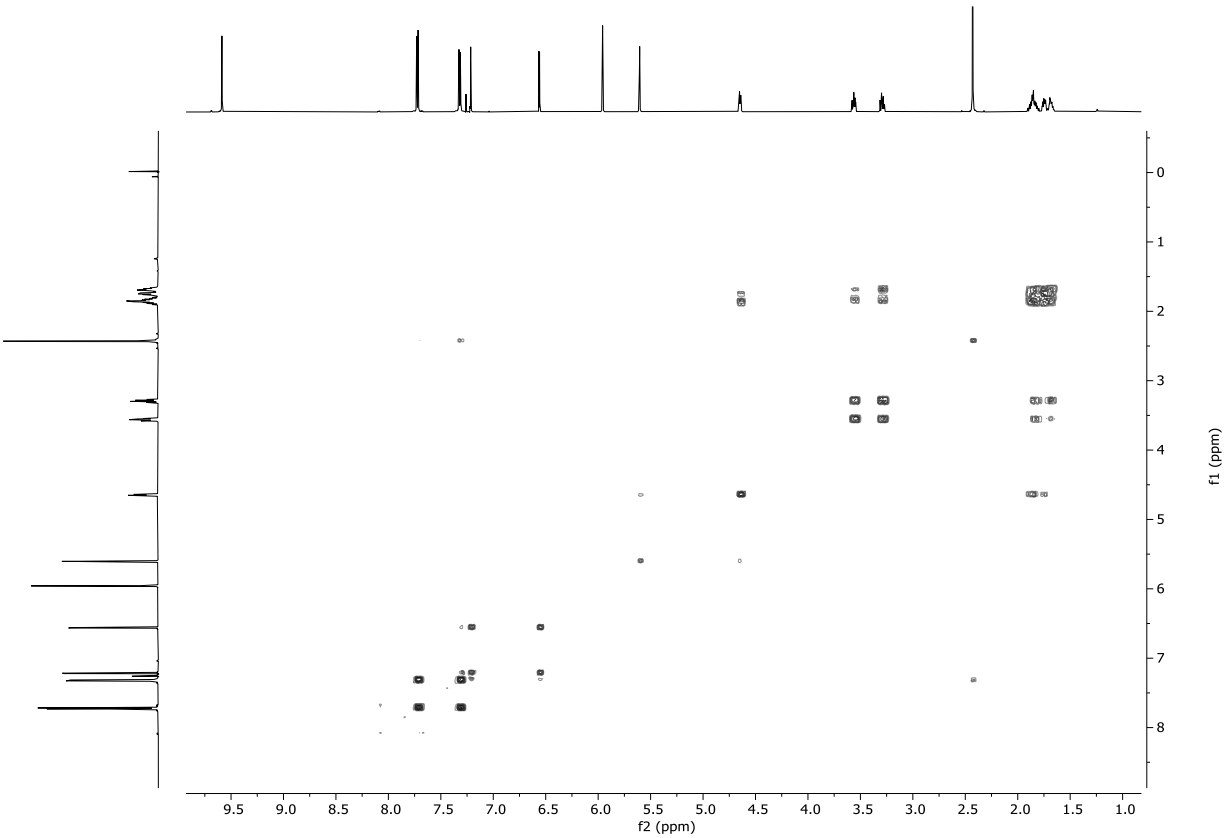
^{13}C-NMR of compound 3y (150 MHz, $CDCl_3$)



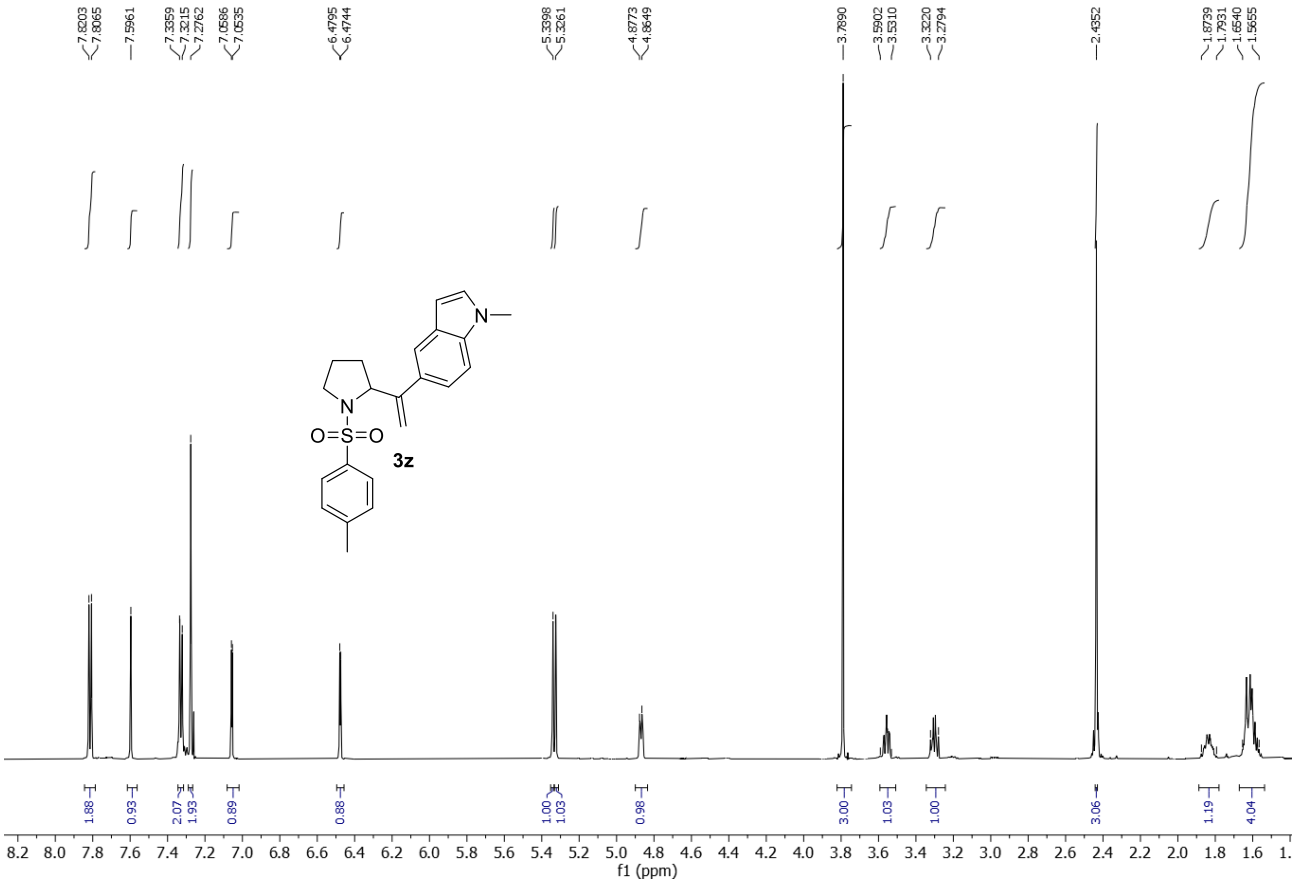
Comparison between DEPT-135 and ^{13}C-NMR of compound 3y (150 MHz, $CDCl_3$)



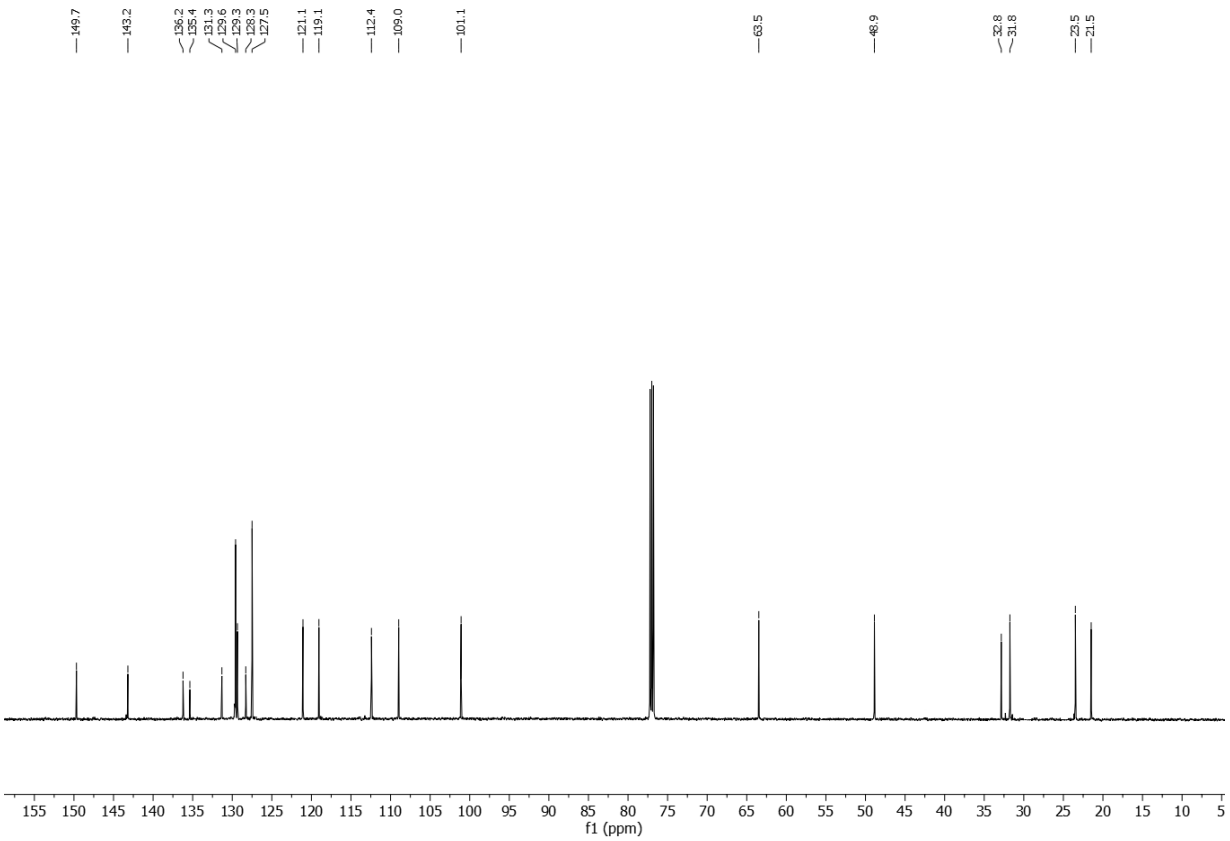
COSY-NMR of compound 3y (600 MHz, $CDCl_3$)



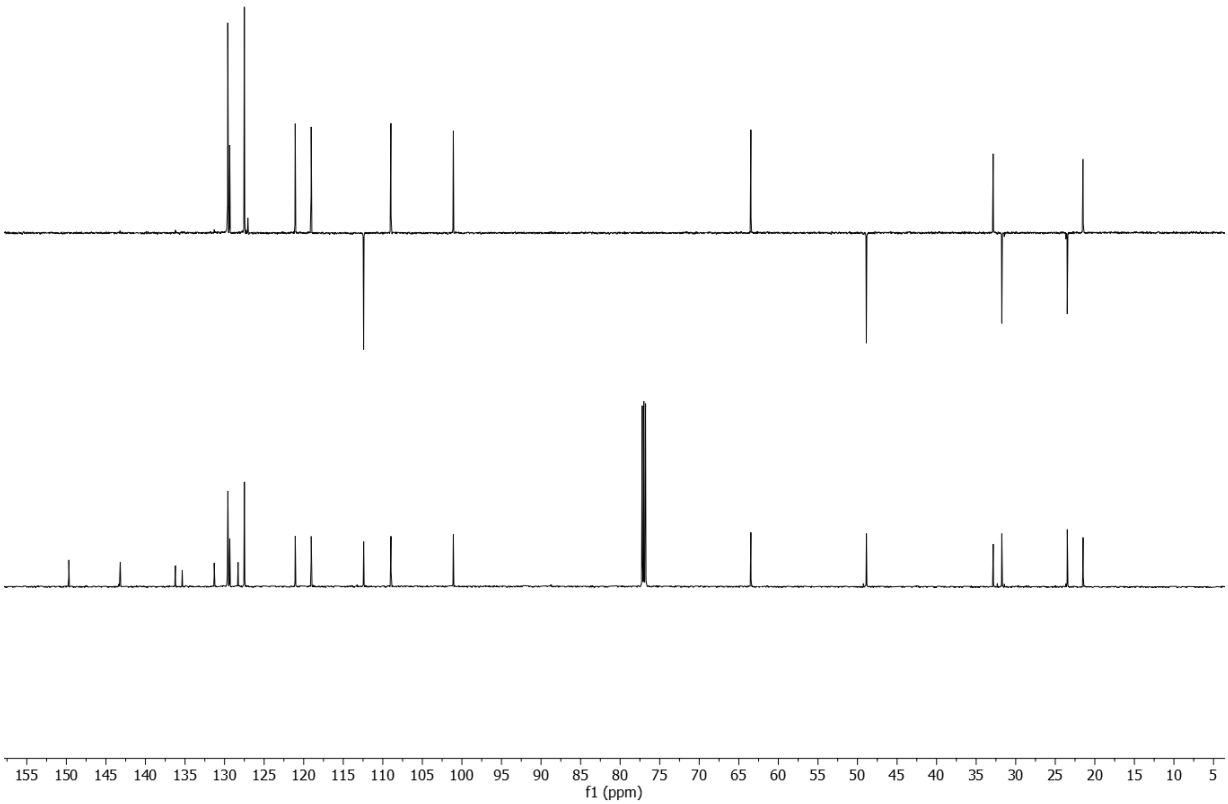
^{1}H-NMR of compound 3z (600 MHz, $CDCl_3$)



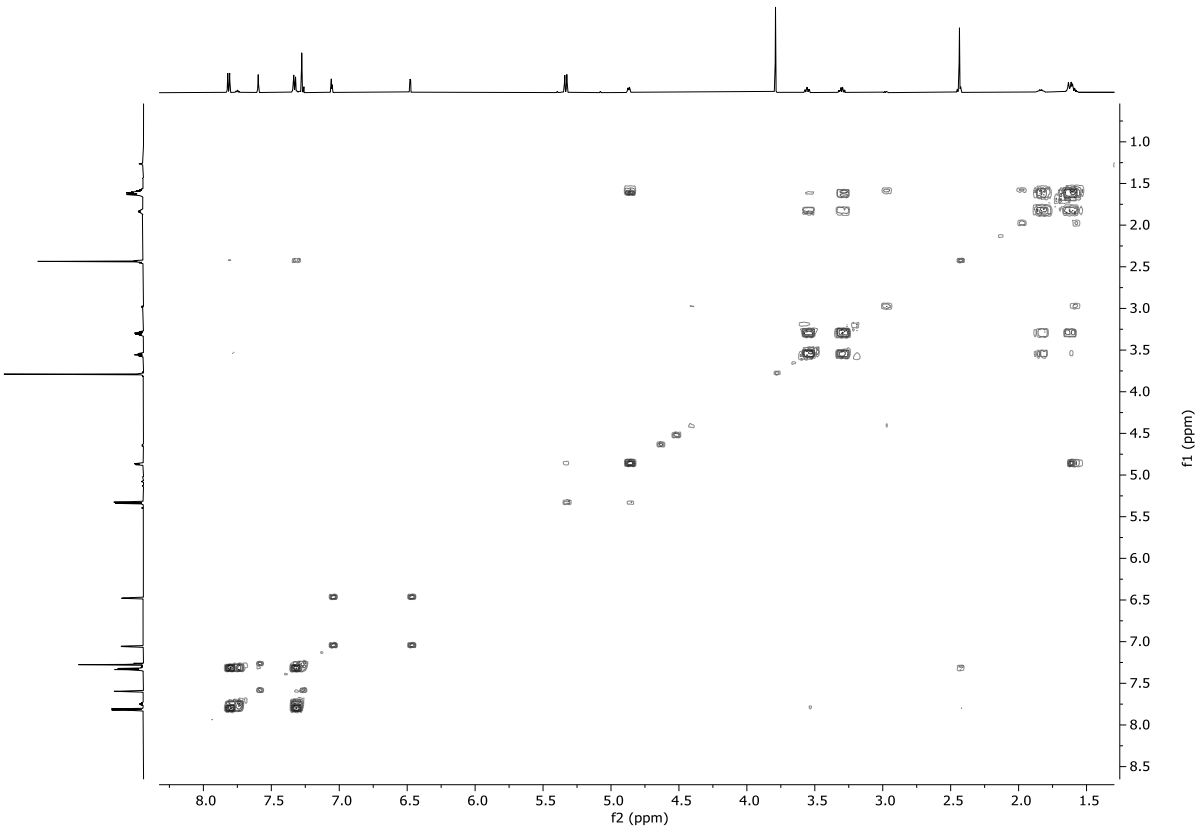
^{13}C-NMR of compound 3z (150 MHz, $CDCl_3$)



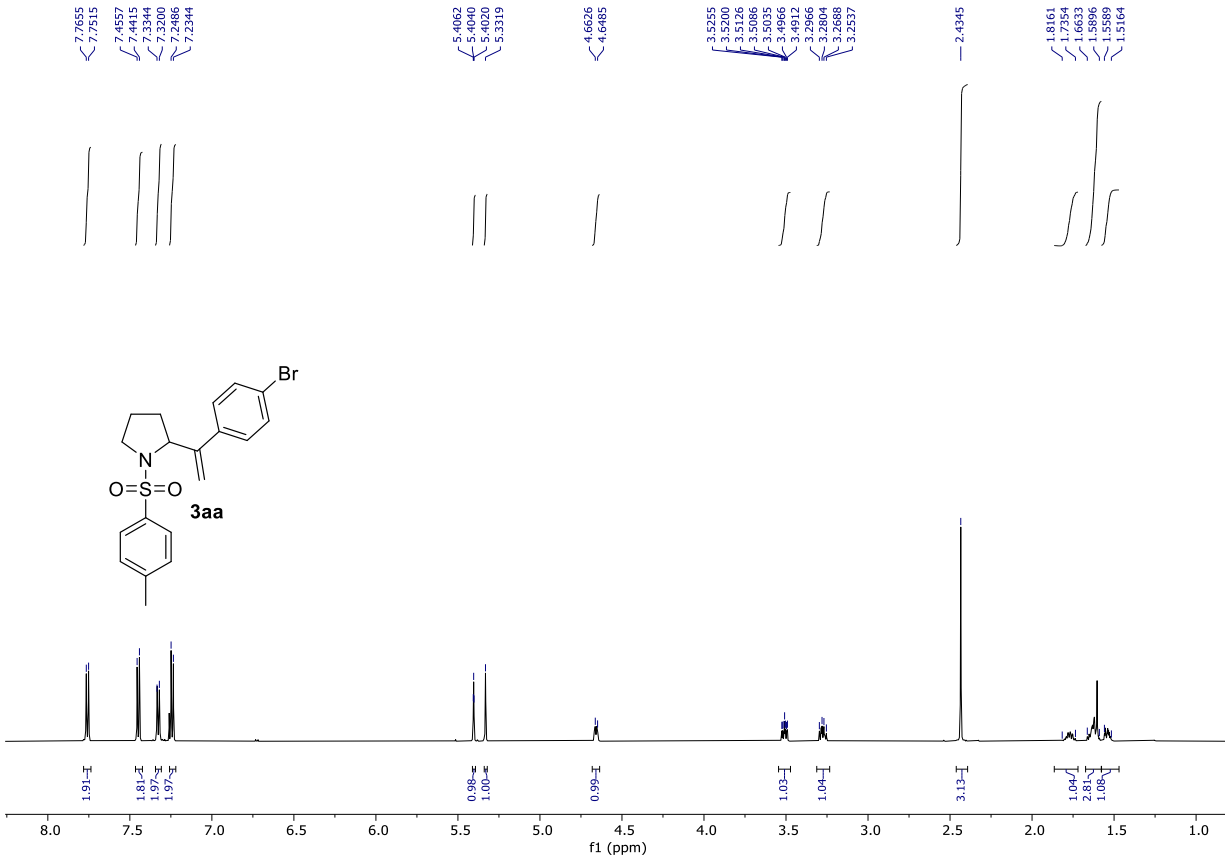
Comparison between DEPT-135 and ^{13}C-NMR of compound 3z (150 MHz, $CDCl_3$)



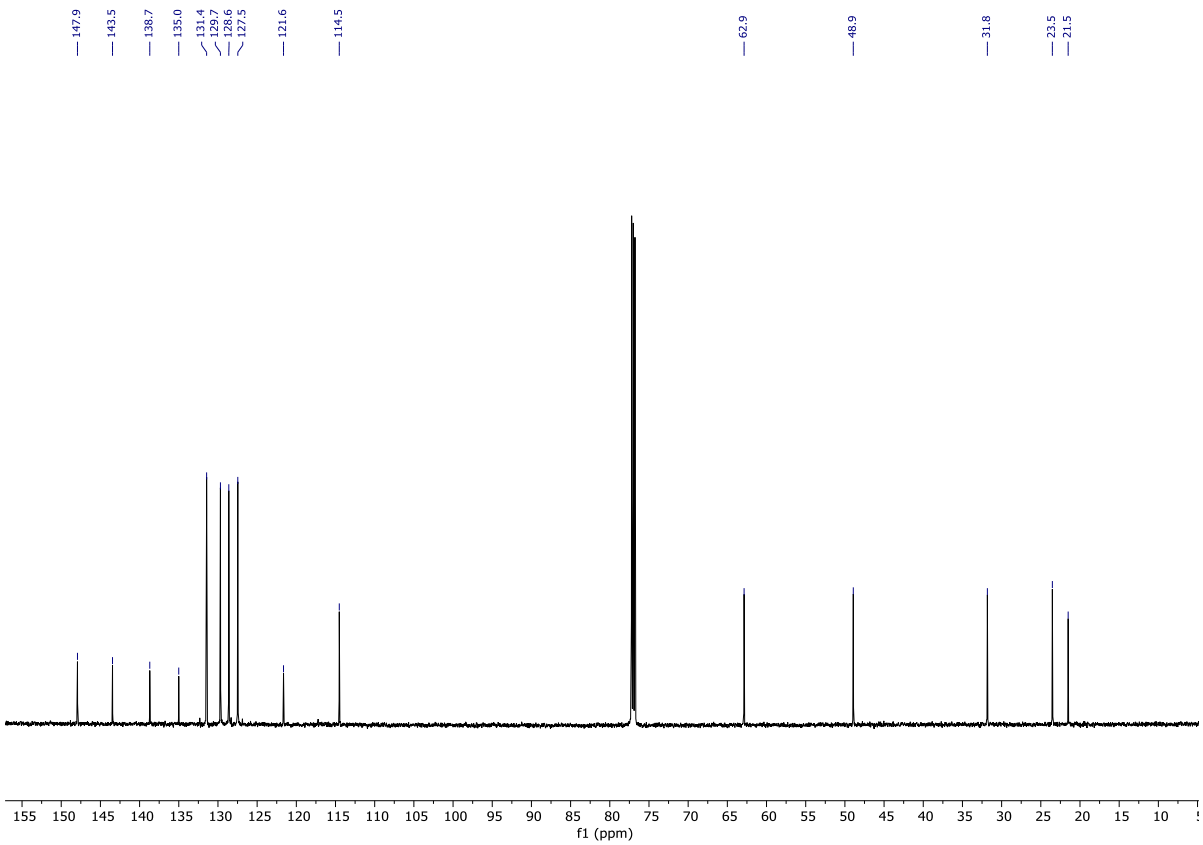
COSY-NMR of compound 3z (600 MHz, $CDCl_3$)



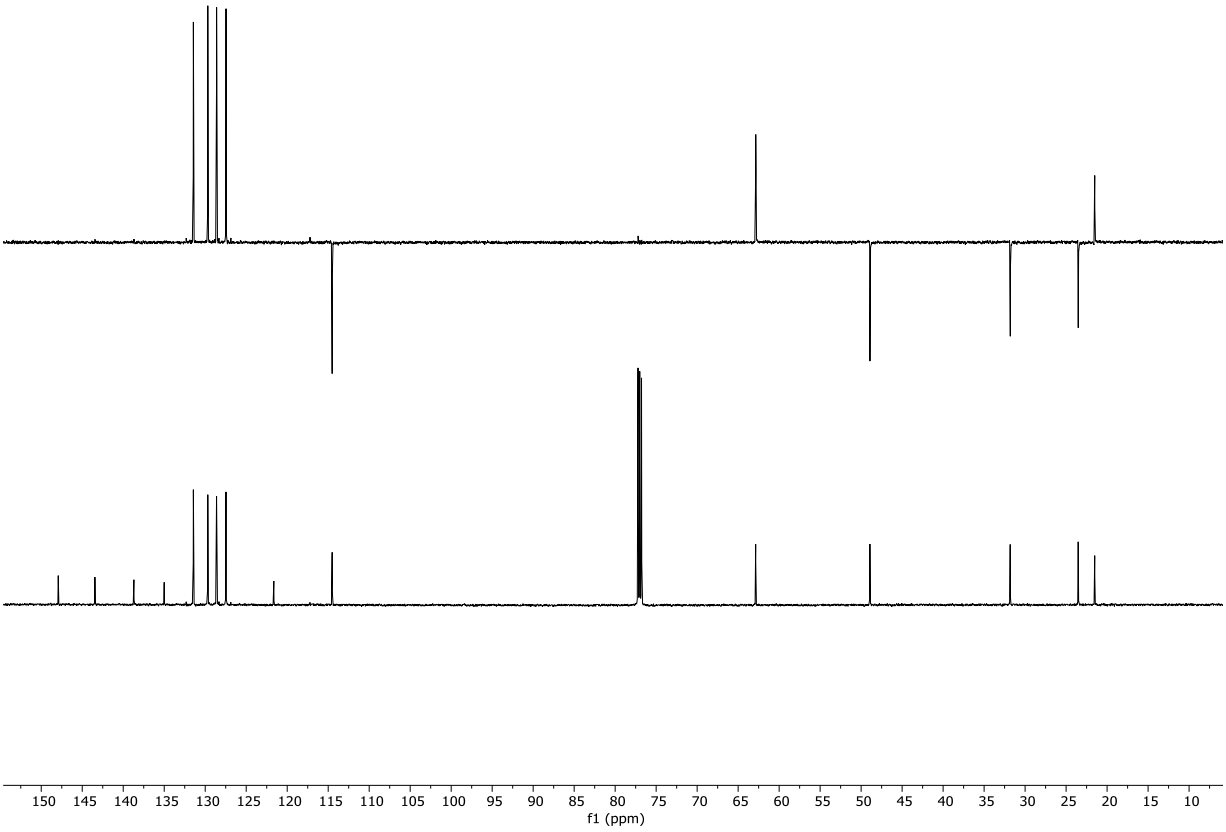
^{1}H-NMR of compound 3aa (600 MHz, $CDCl_3$)



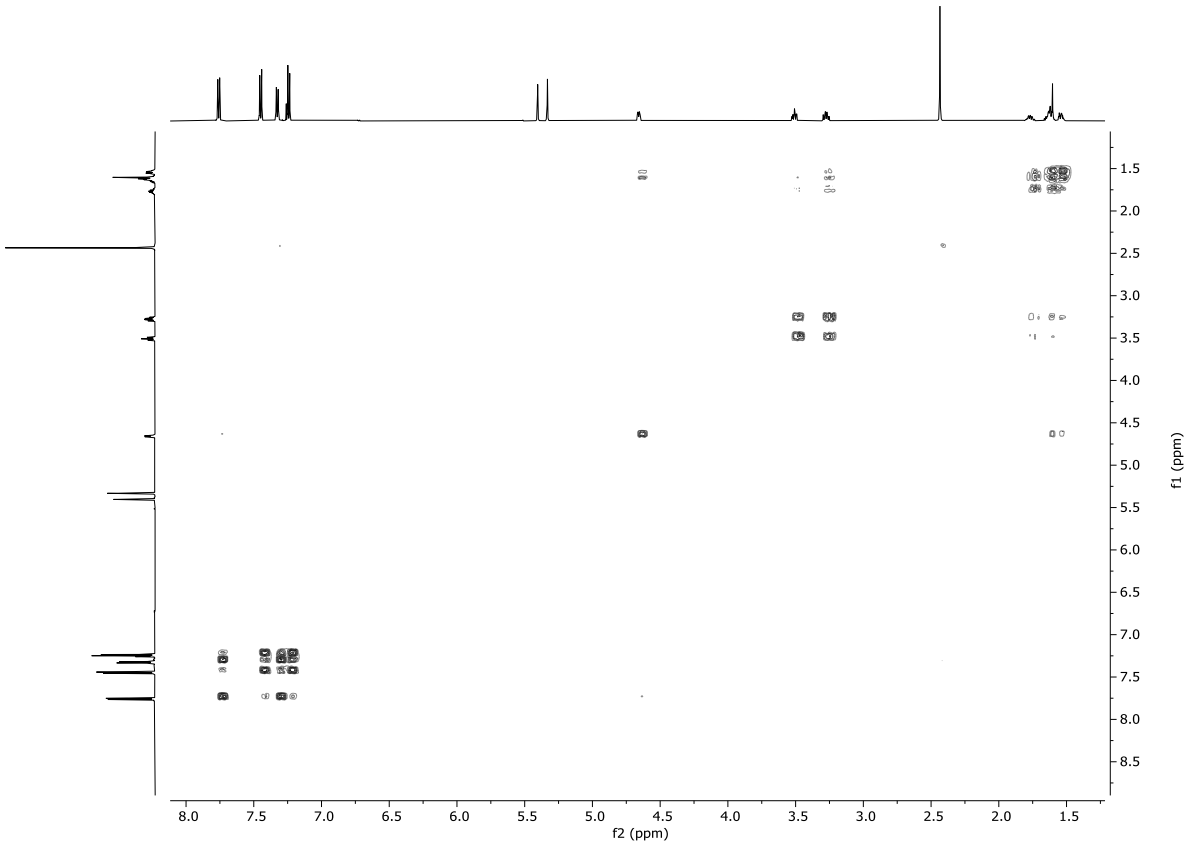
^{13}C-NMR of compound 3aa (150 MHz, $CDCl_3$)



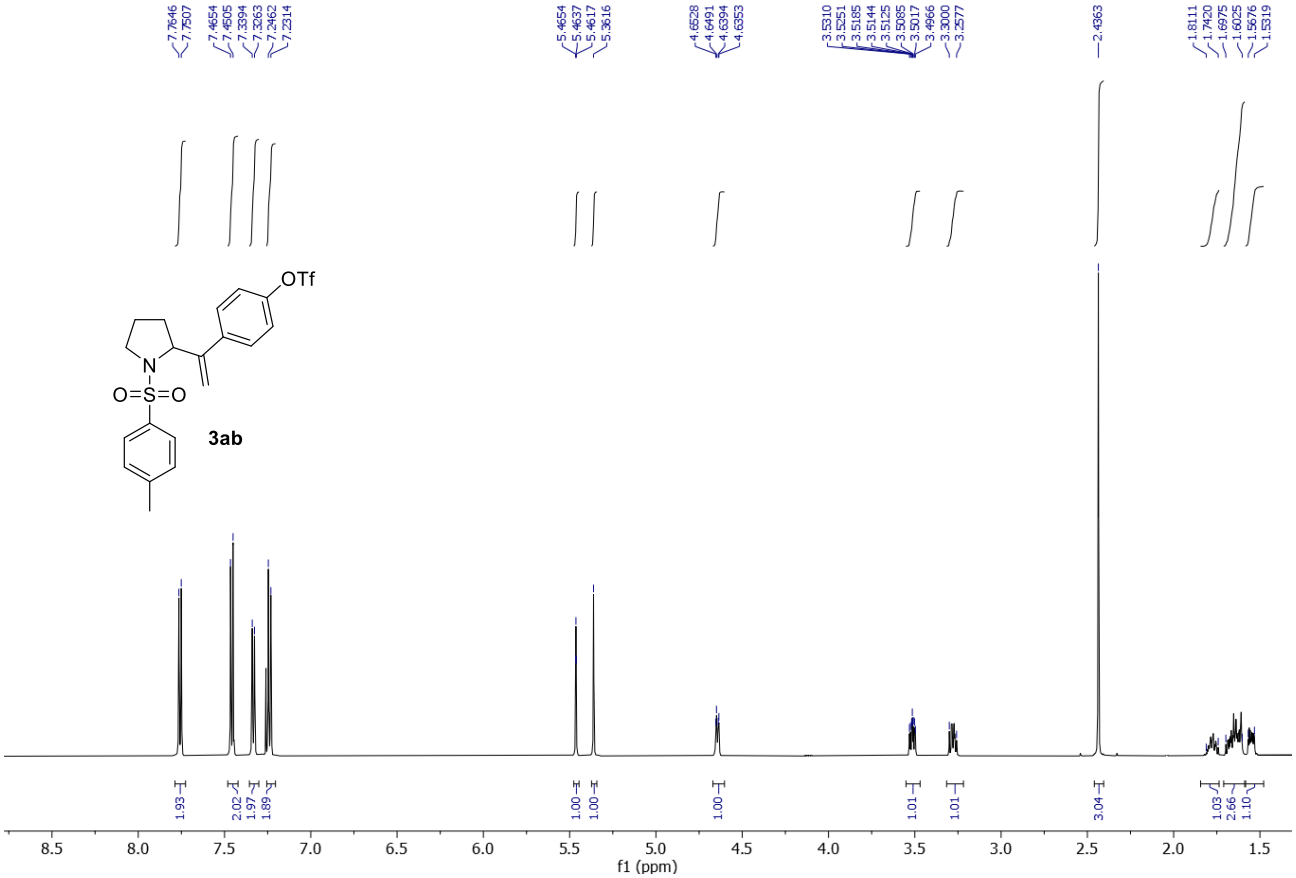
Comparison between DEPT-135 and ^{13}C-NMR of compound 3aa (150 MHz, $CDCl_3$)



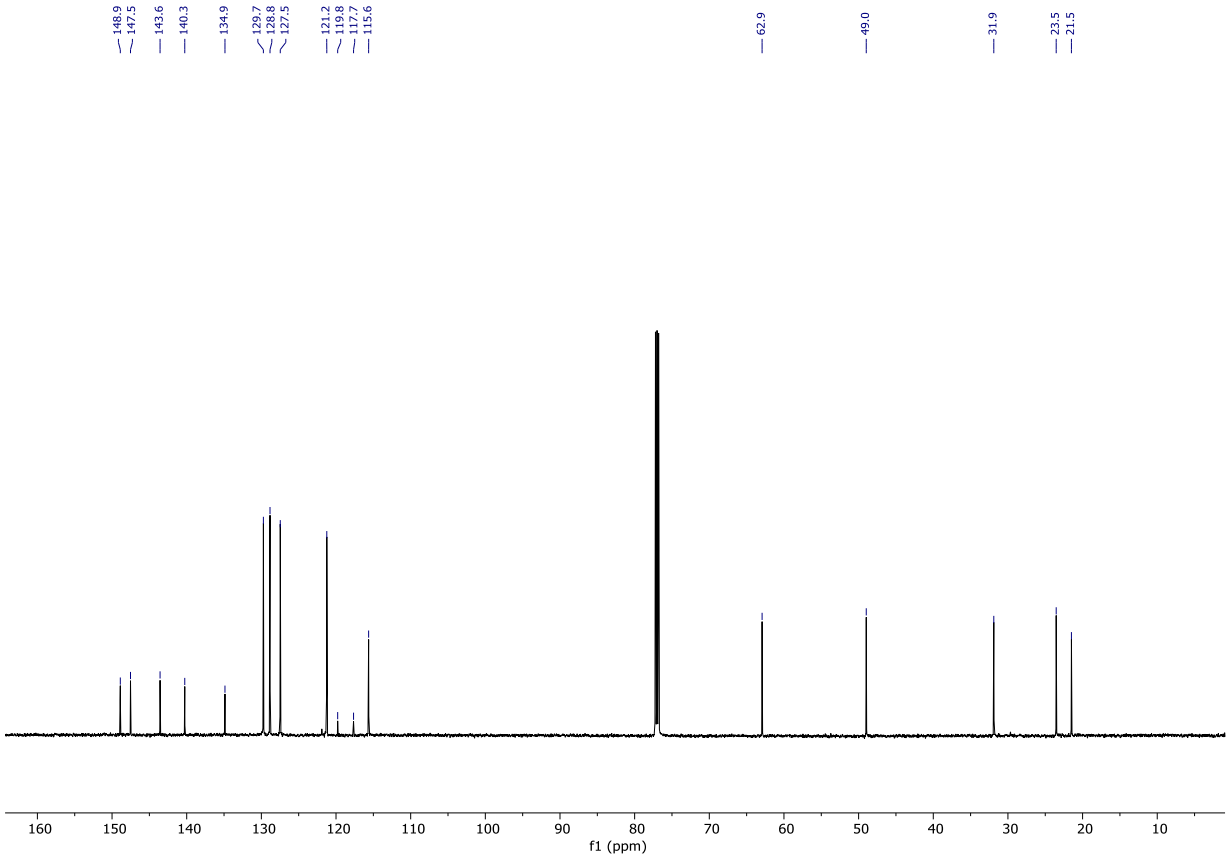
COSY-NMR of compound 3aa (600 MHz, $CDCl_3$)



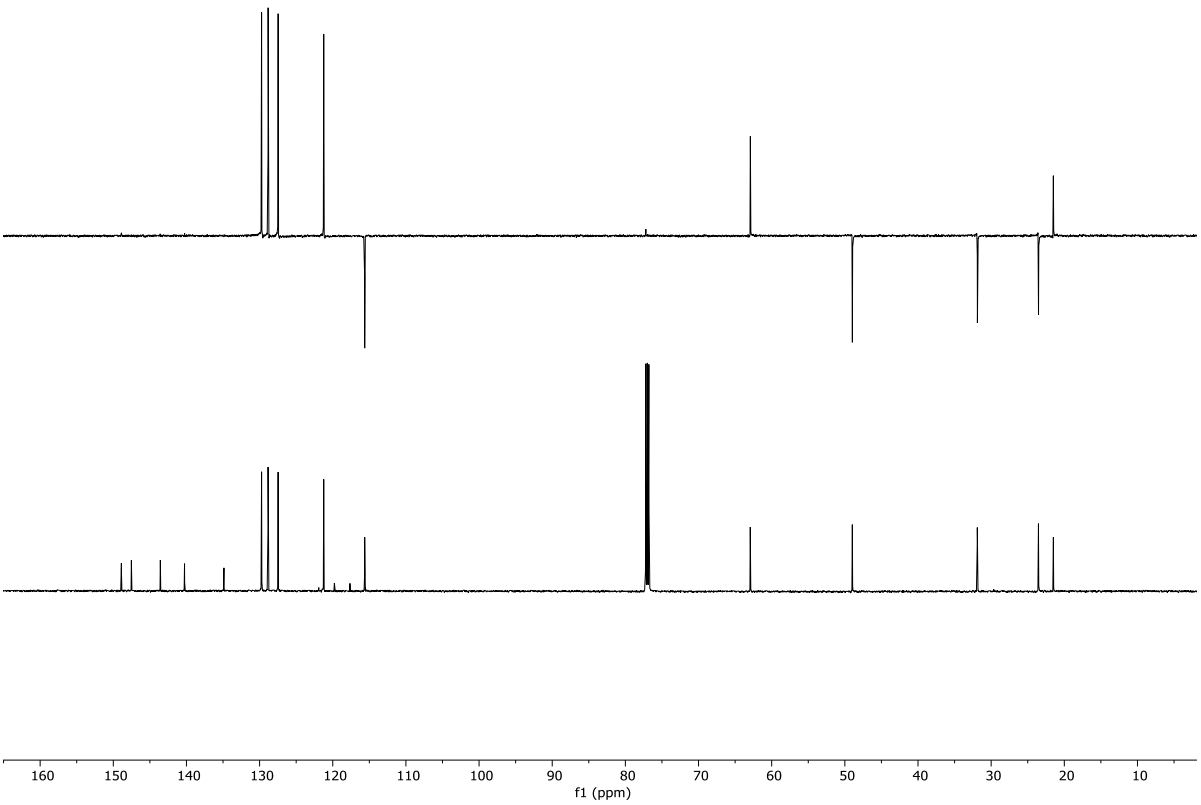
^{1}H-NMR of compound 3ab (600 MHz, $CDCl_3$)



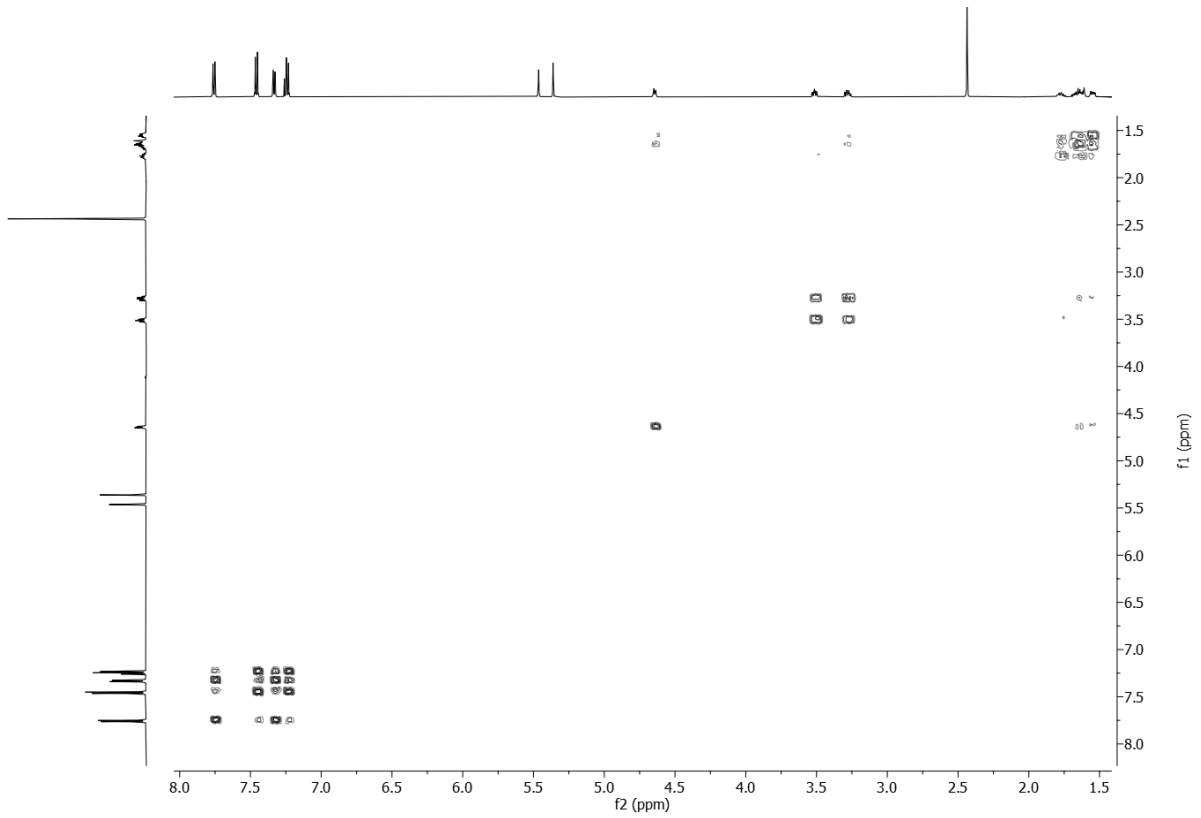
^{13}C-NMR of compound 3ab (150 MHz, $CDCl_3$)



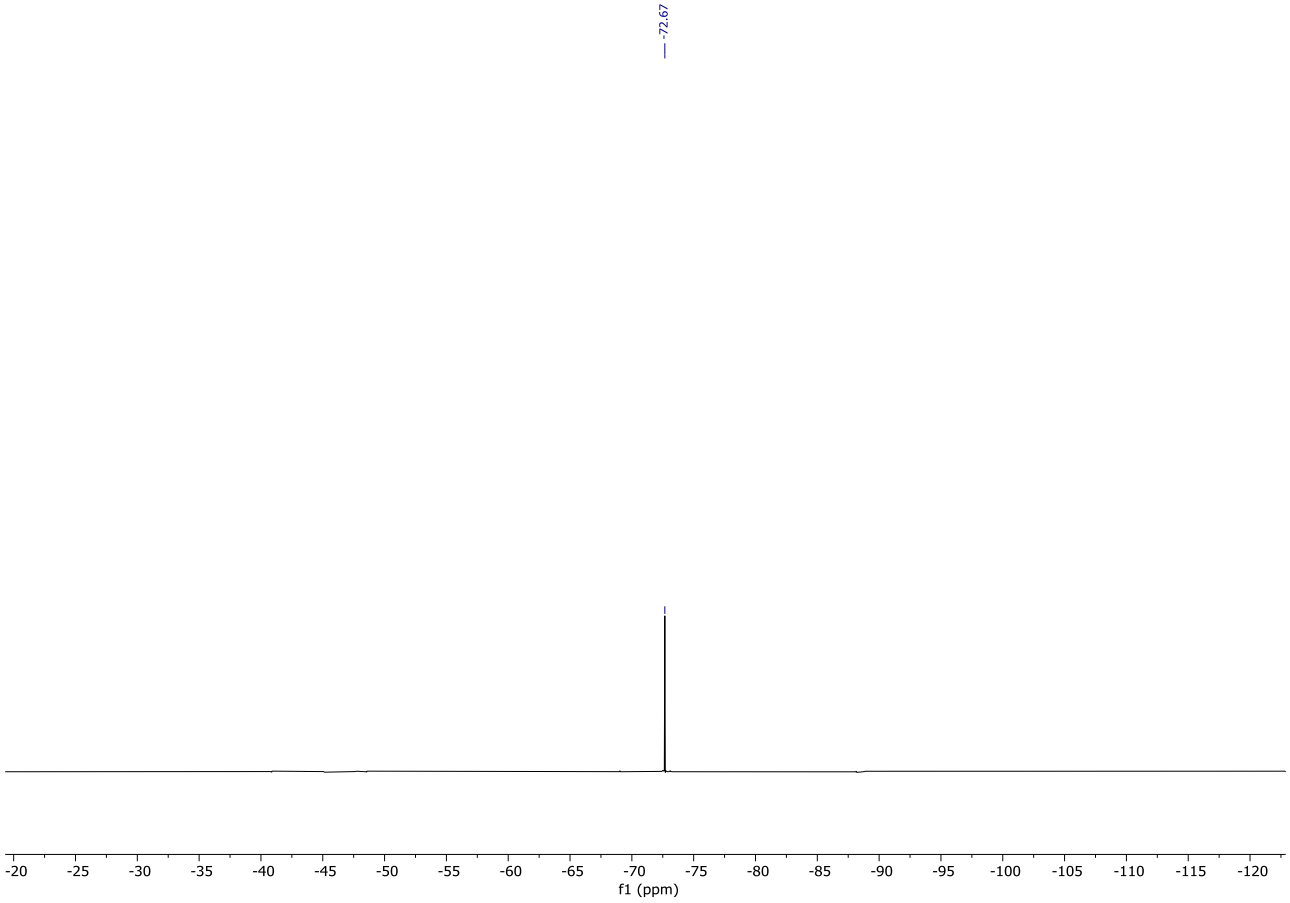
Comparison between DEPT-135 and ^{13}C-NMR of compound 3ab (150 MHz, $CDCl_3$)



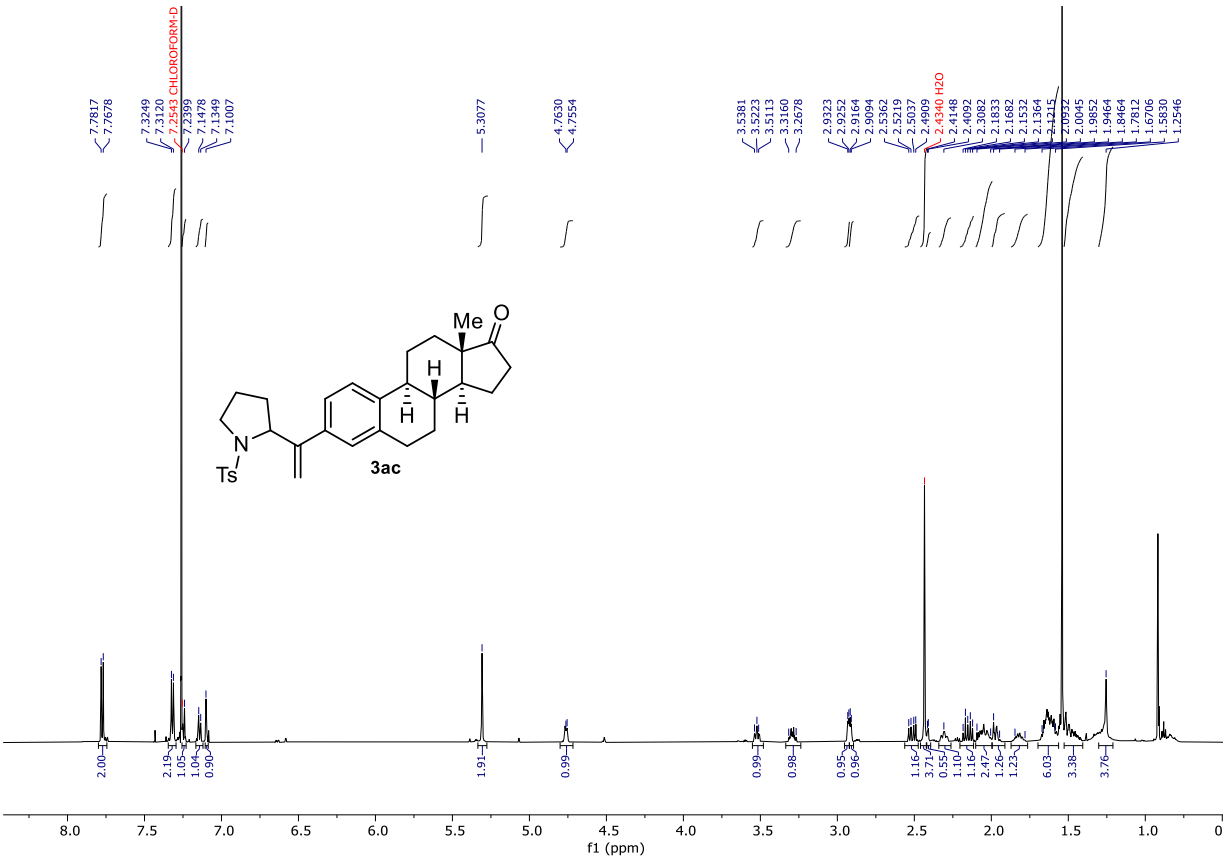
COSY-NMR of compound 3ab (600 MHz, $CDCl_3$)



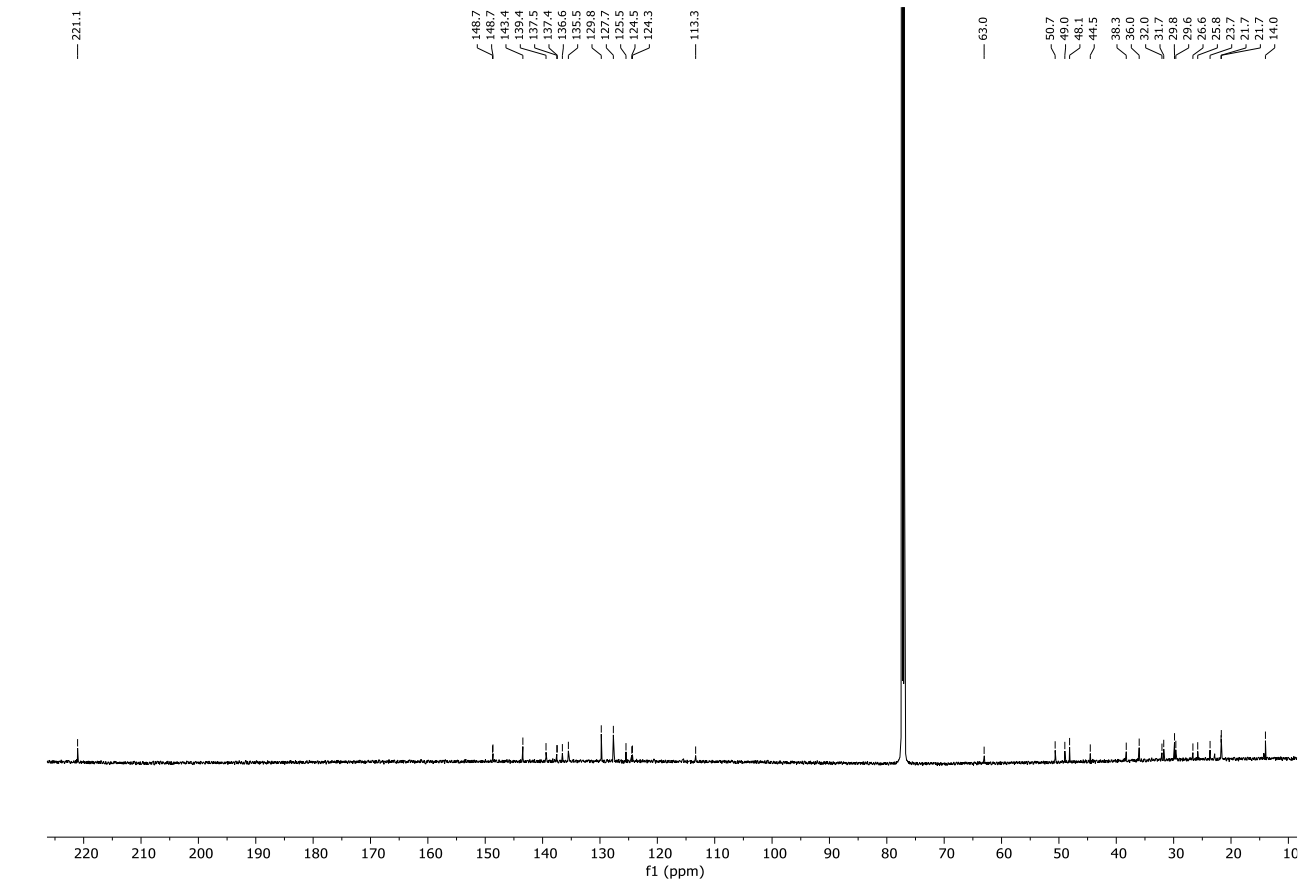
^{19}H-NMR of compound 3ab (600 MHz, $CDCl_3$)



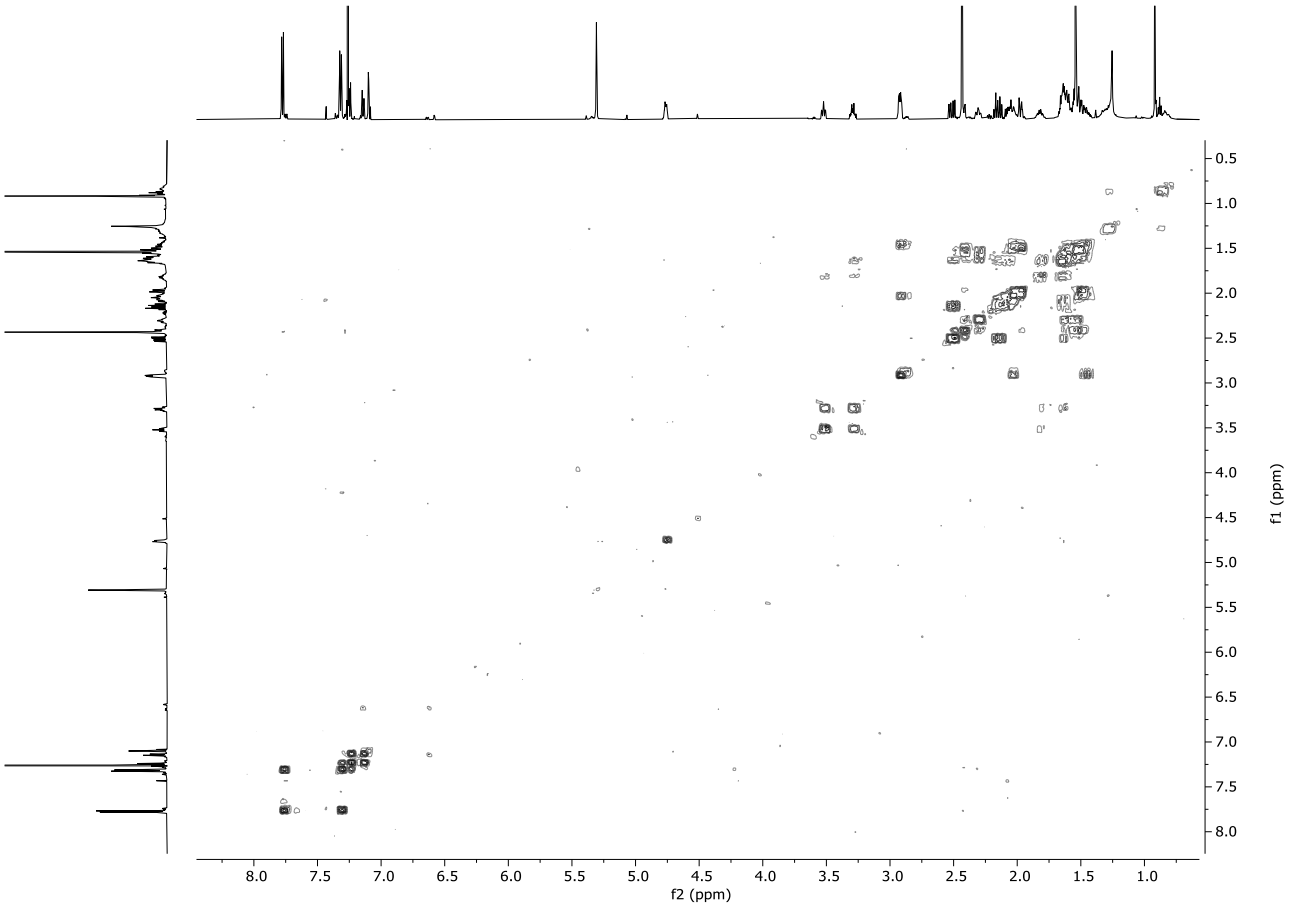
^{1}H-NMR of compound 3ac (600 MHz, $CDCl_3$)



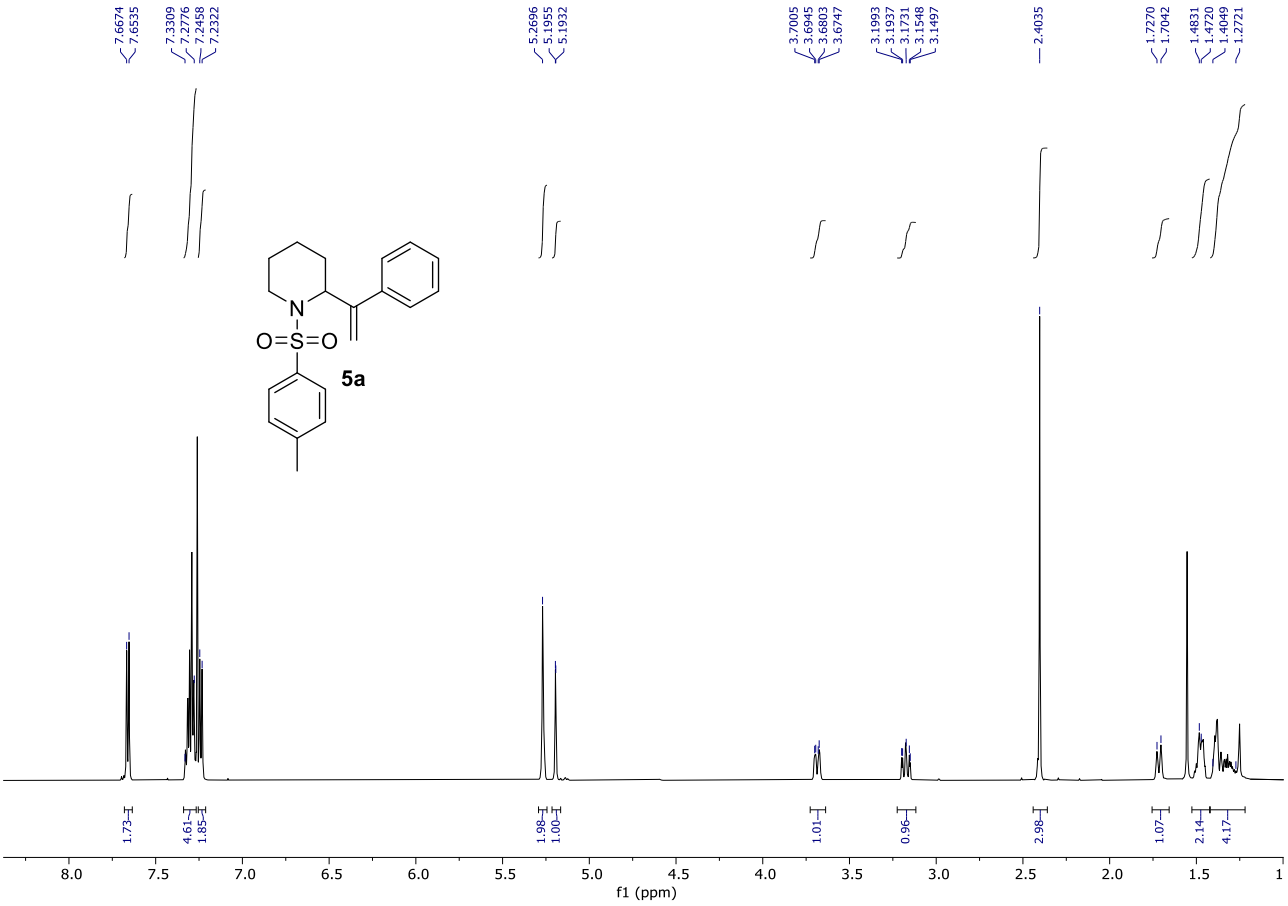
^{13}C-NMR of compound 3ac (150 MHz, $CDCl_3$)



COSY-NMR of compound 3ac (600 MHz, $CDCl_3$)

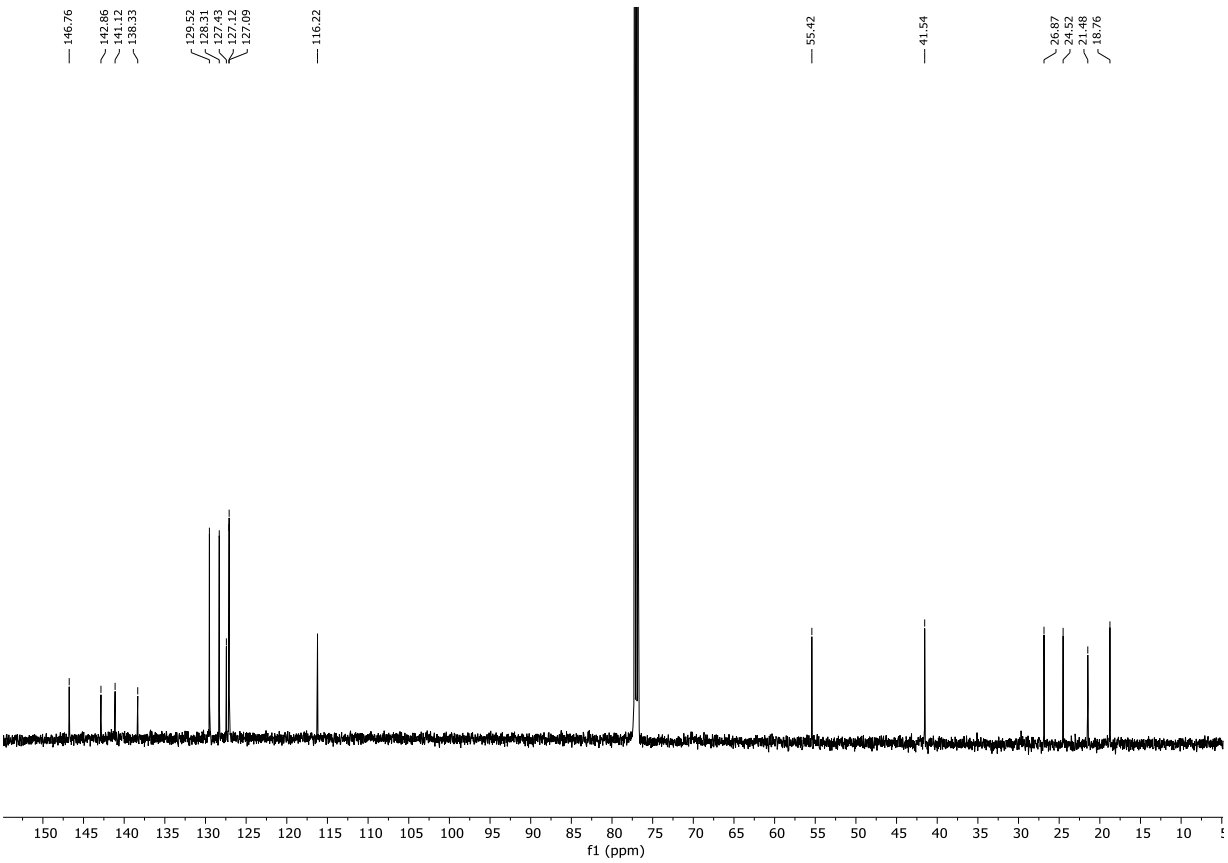


^{1}H-NMR of compound 5a (600 MHz, $CDCl_3$)

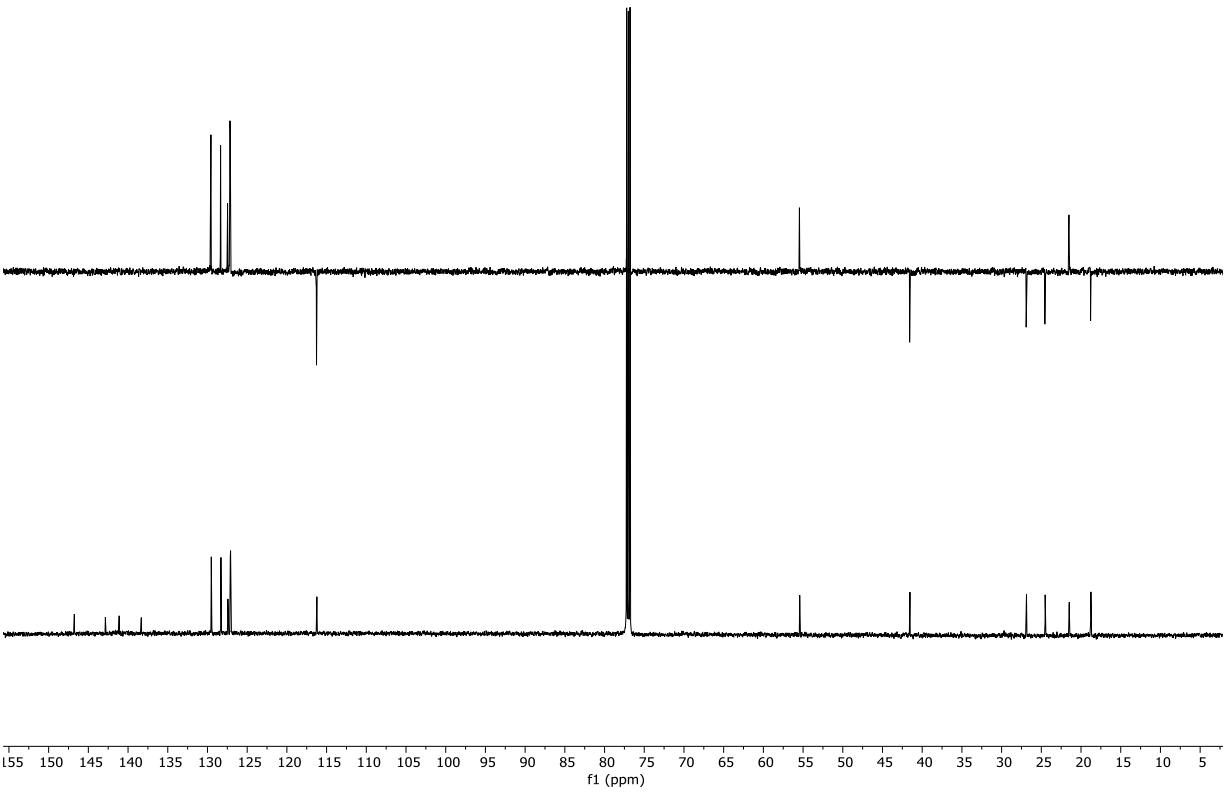


5a

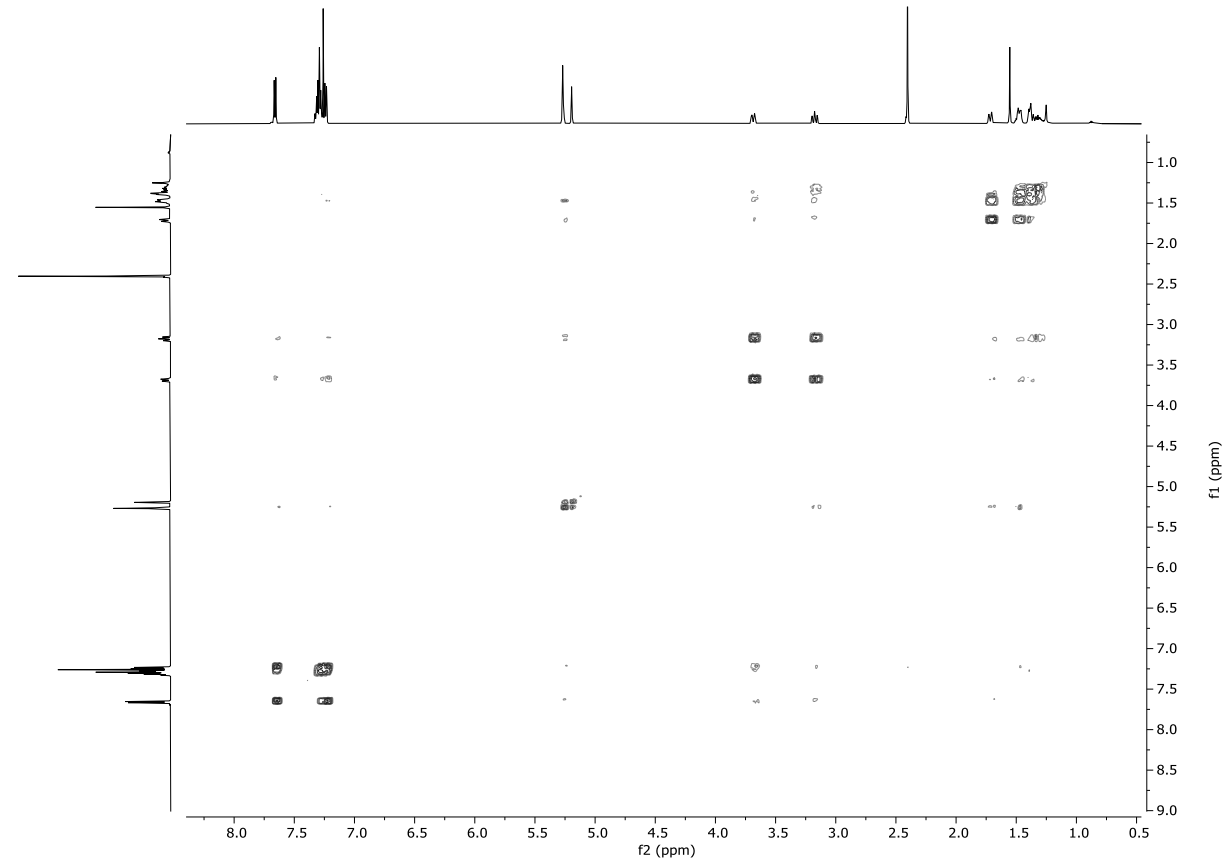
^{13}C-NMR of compound 5a (150 MHz, $CDCl_3$)



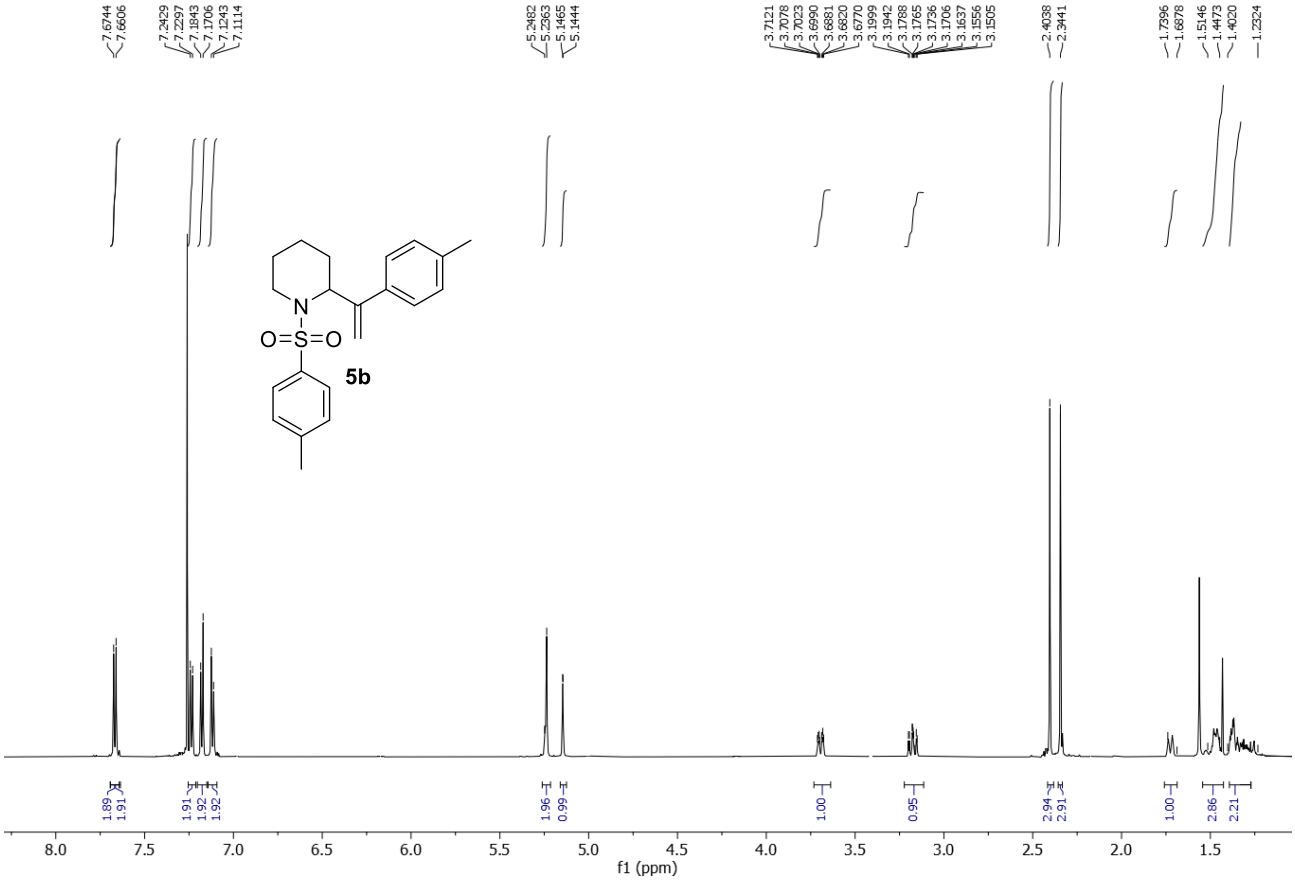
Comparison between DEPT-135 and ^{13}C-NMR of compound 5a (150 MHz, $CDCl_3$)



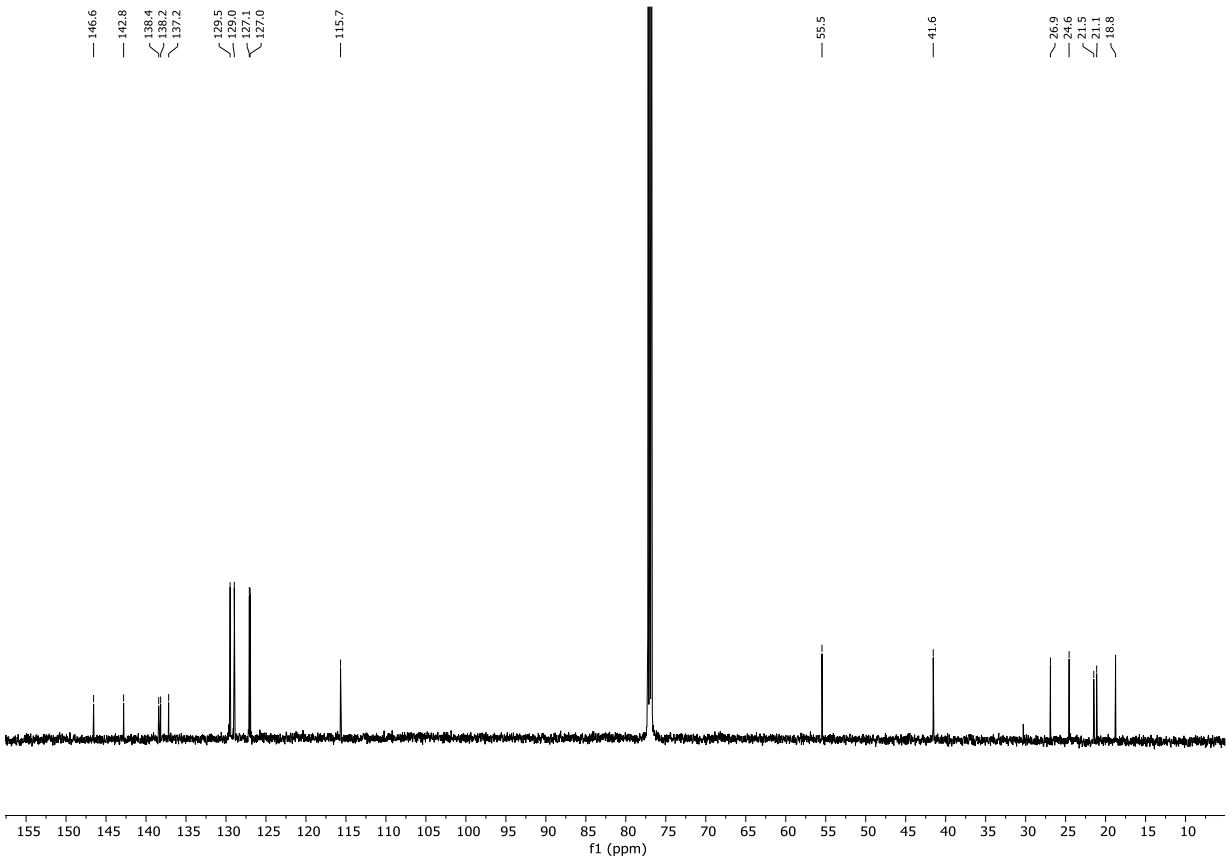
COSY-NMR of compound 5a (600 MHz, $CDCl_3$)



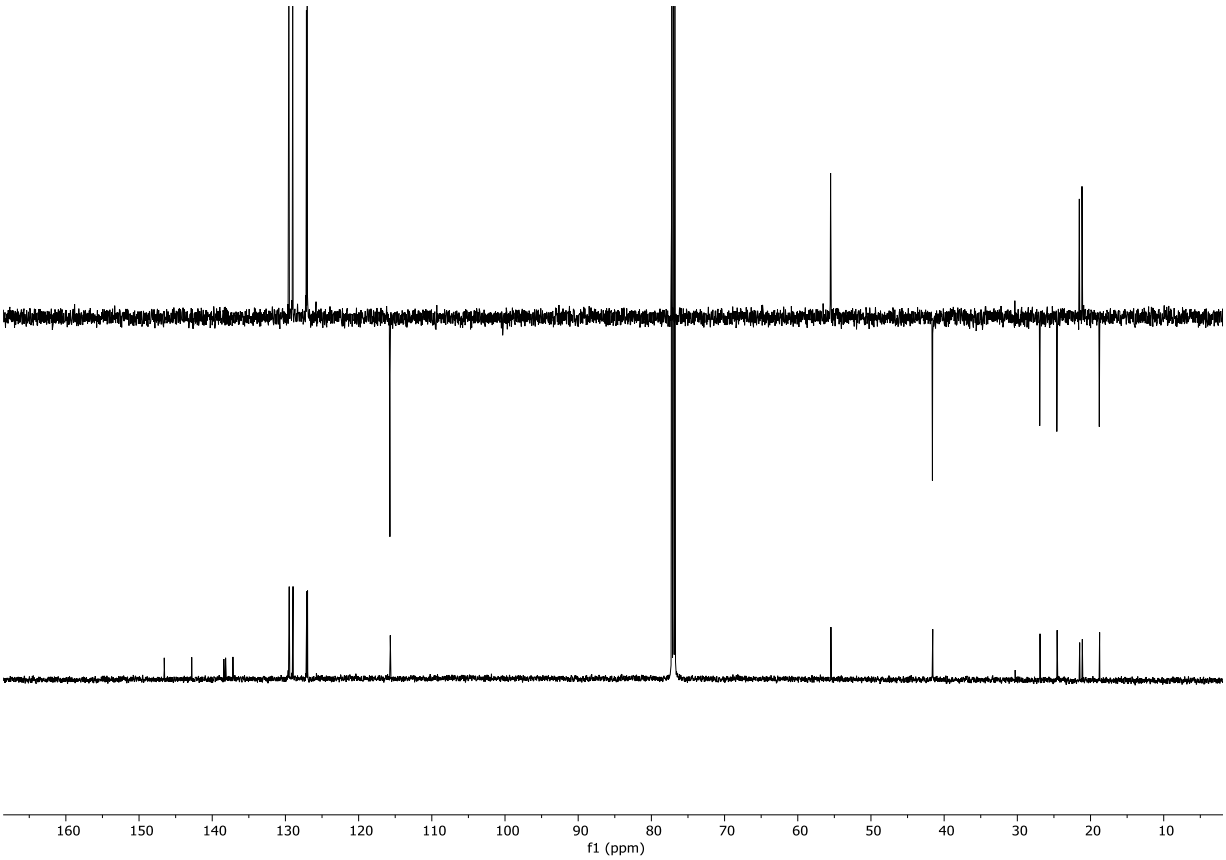
^{1}H-NMR of compound 5b (600 MHz, $CDCl_3$)



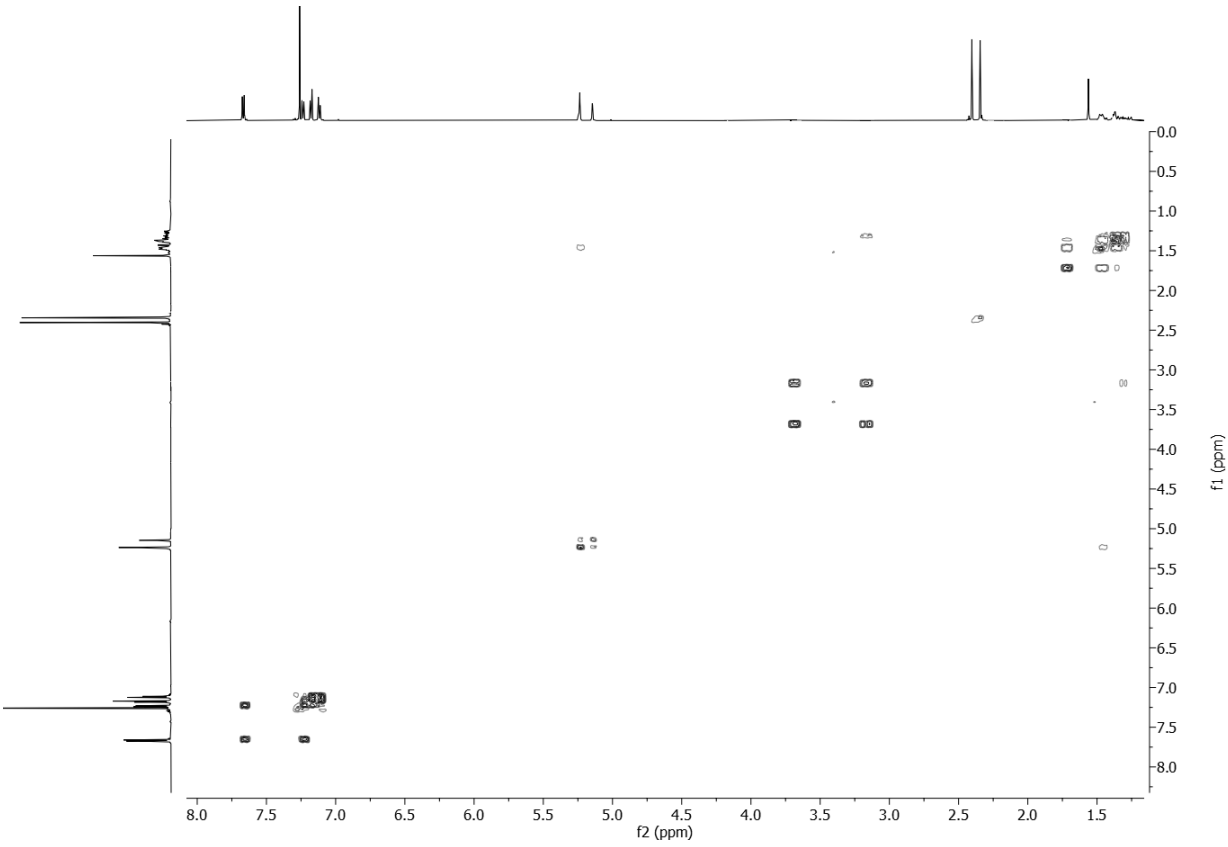
^{13}C-NMR of compound 5b (150 MHz, $CDCl_3$)



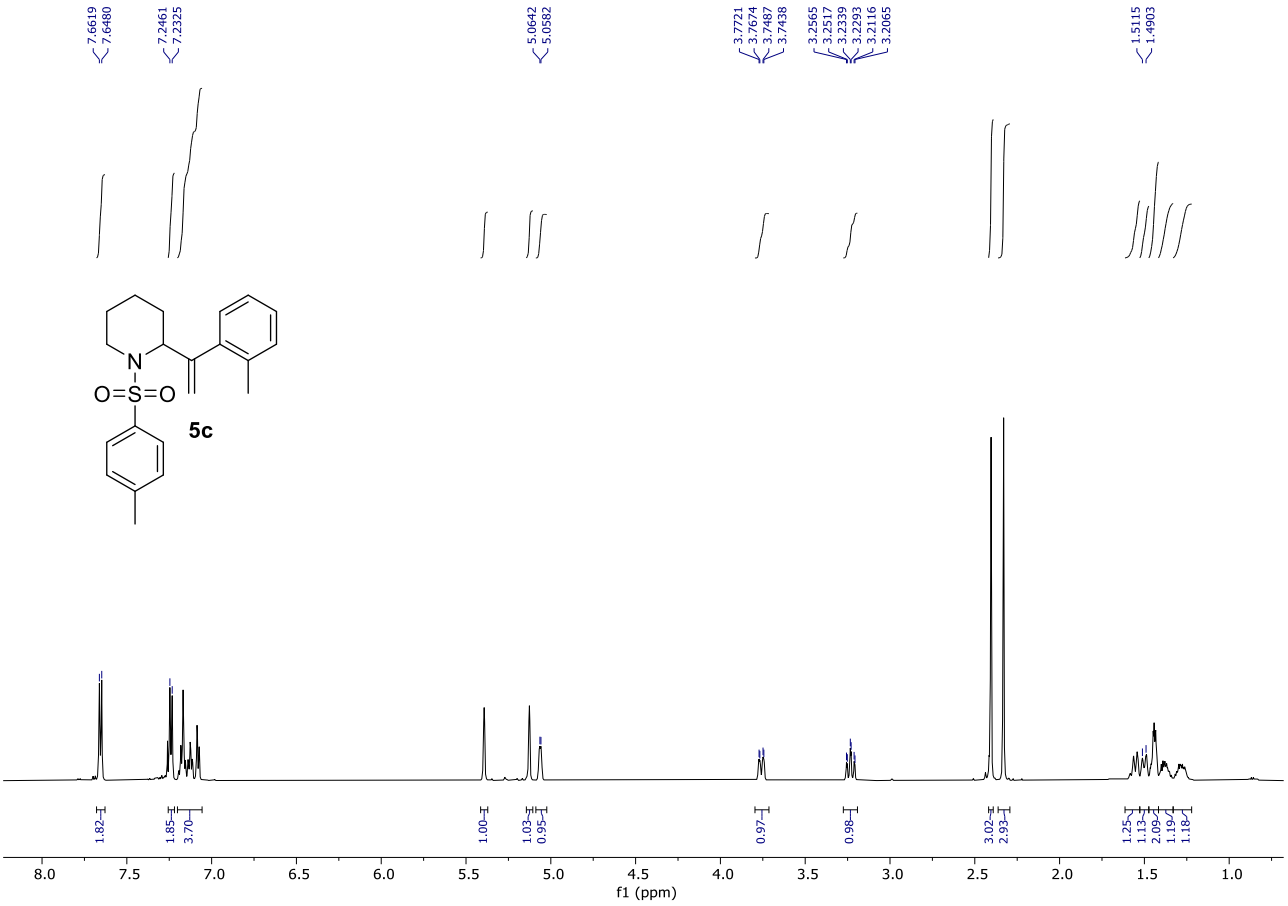
Comparison between DEPT-135 and ^{13}C-NMR of compound 5b (150 MHz, $CDCl_3$)



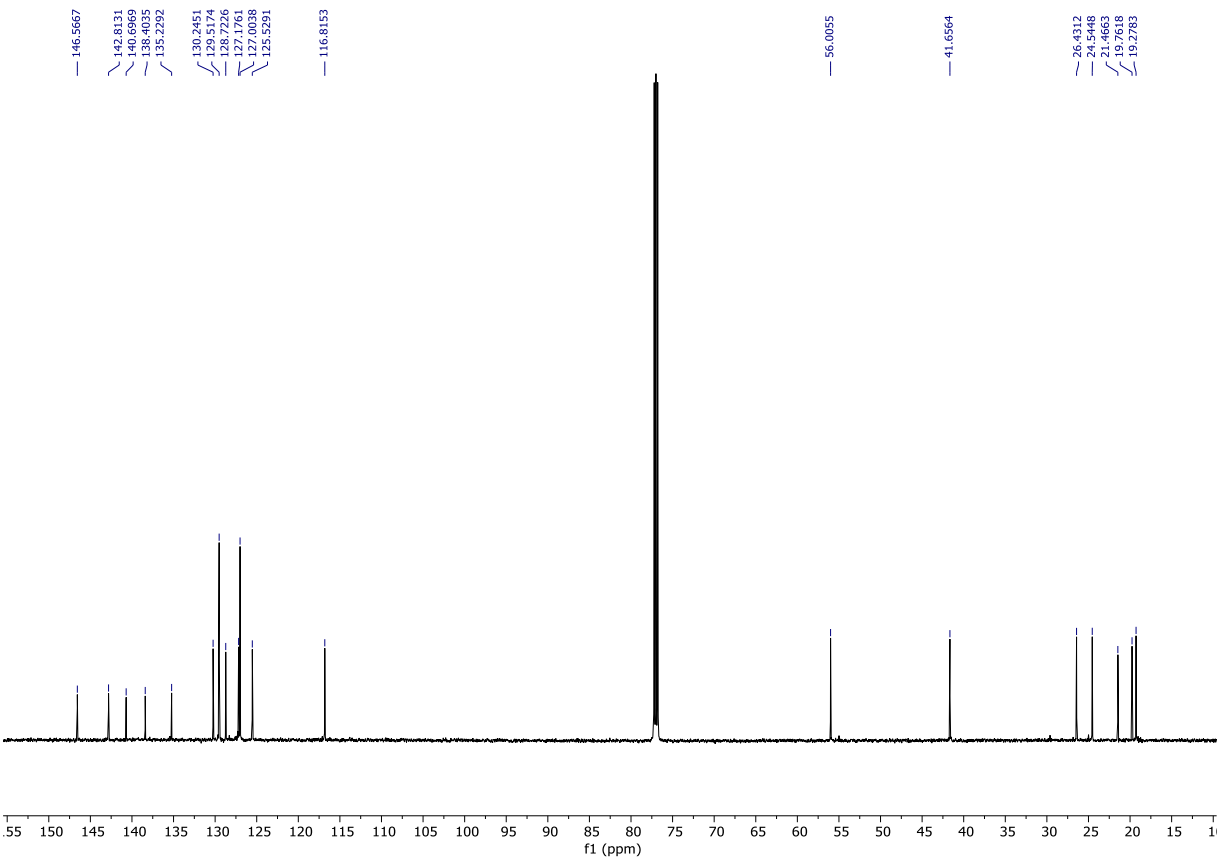
COSY-NMR of compound 5b (600 MHz, $CDCl_3$)



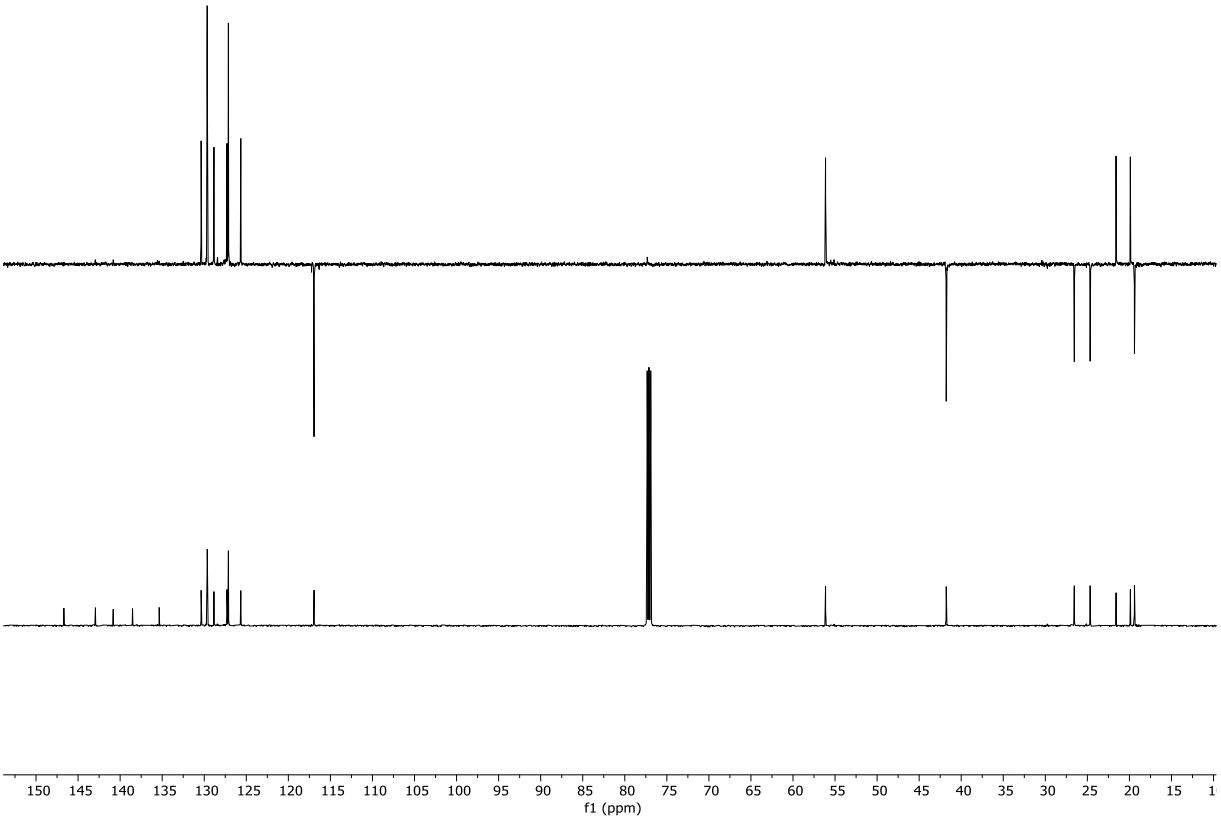
^{1}H-NMR of compound 5c (600 MHz, $CDCl_3$)



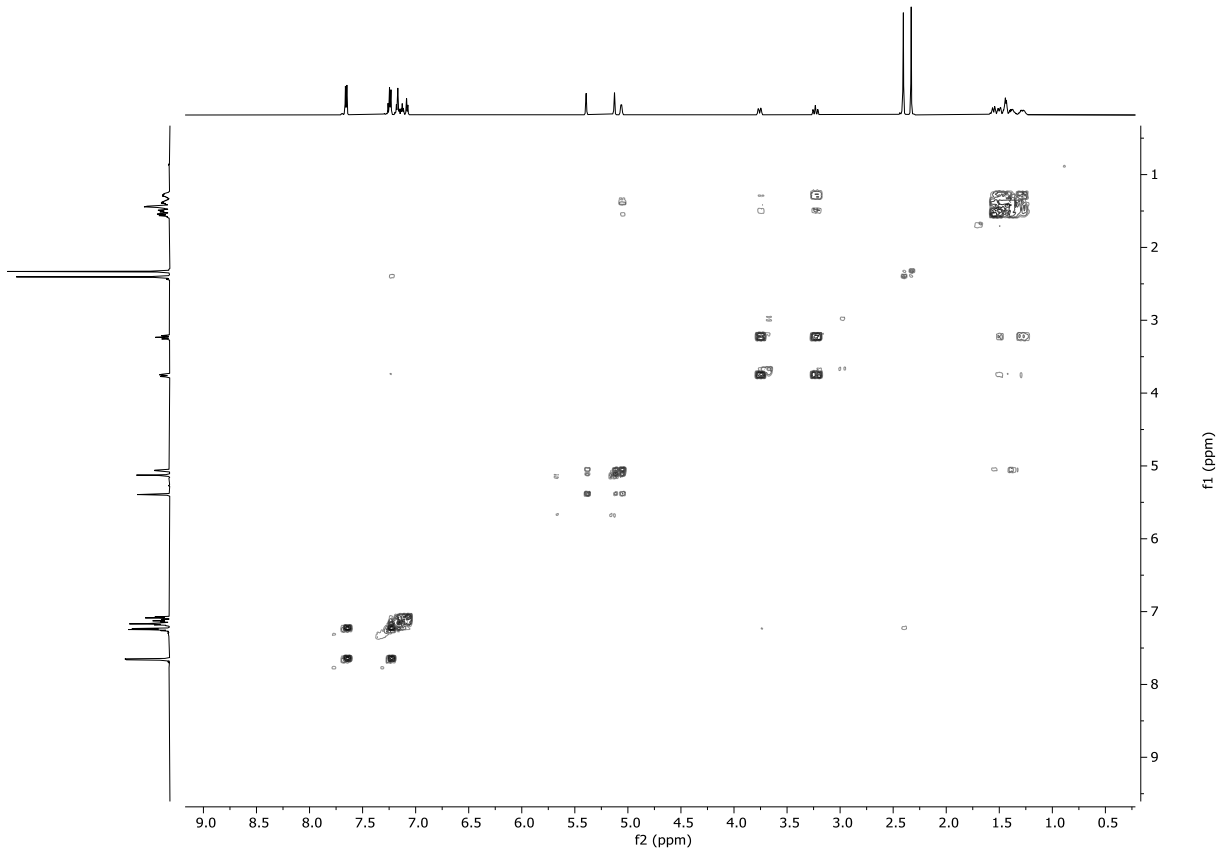
^{13}C-NMR of compound 5c (150 MHz, $CDCl_3$)



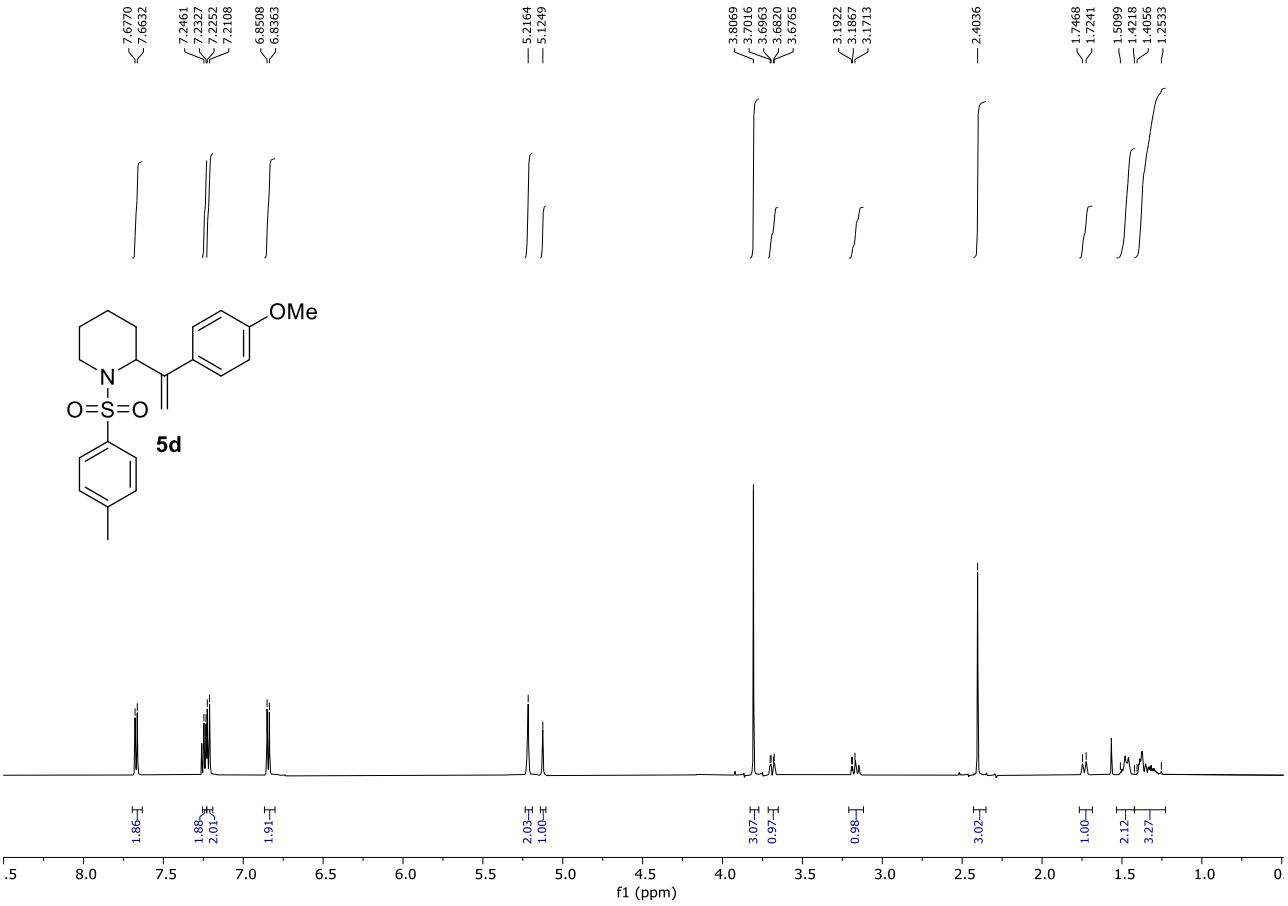
Comparison between DEPT-135 and ^{13}C-NMR of compound 5c (150 MHz, $CDCl_3$)



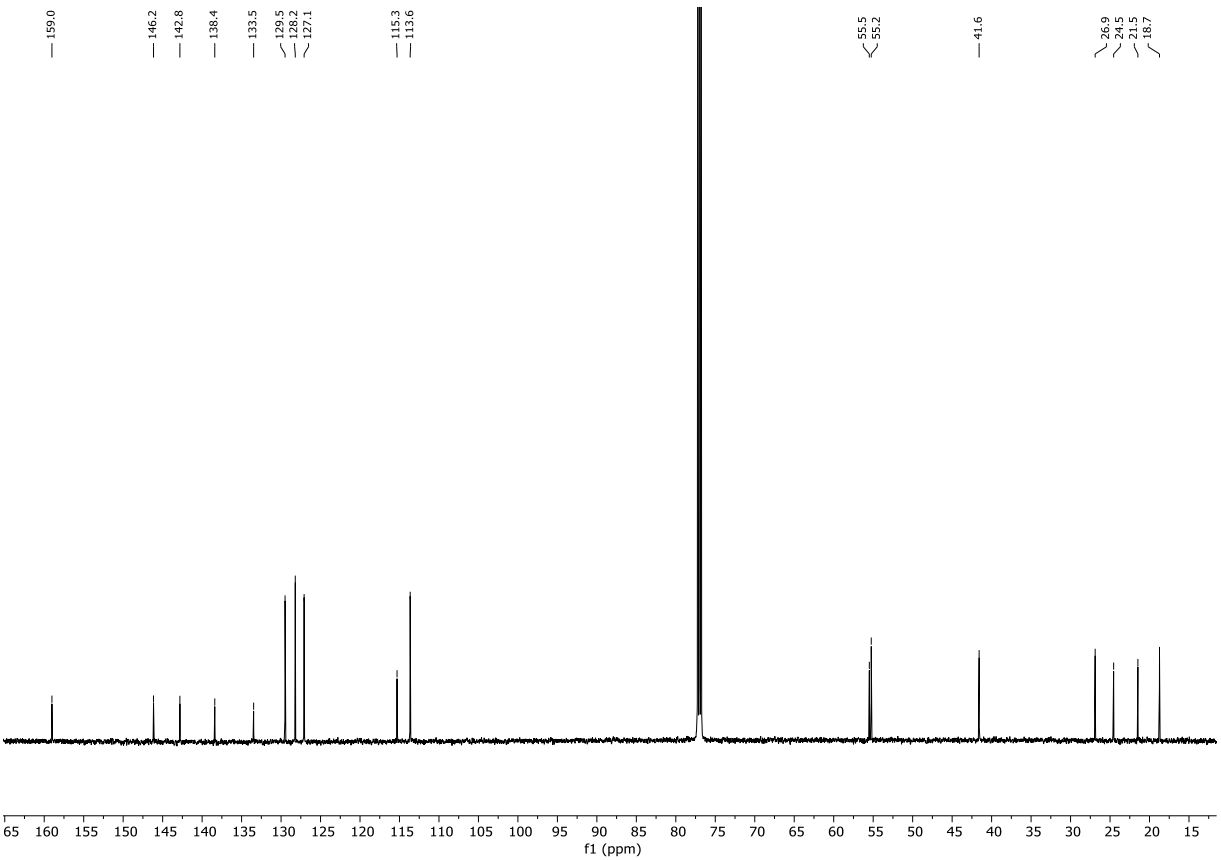
COSY-NMR of compound 5c (600 MHz, $CDCl_3$)



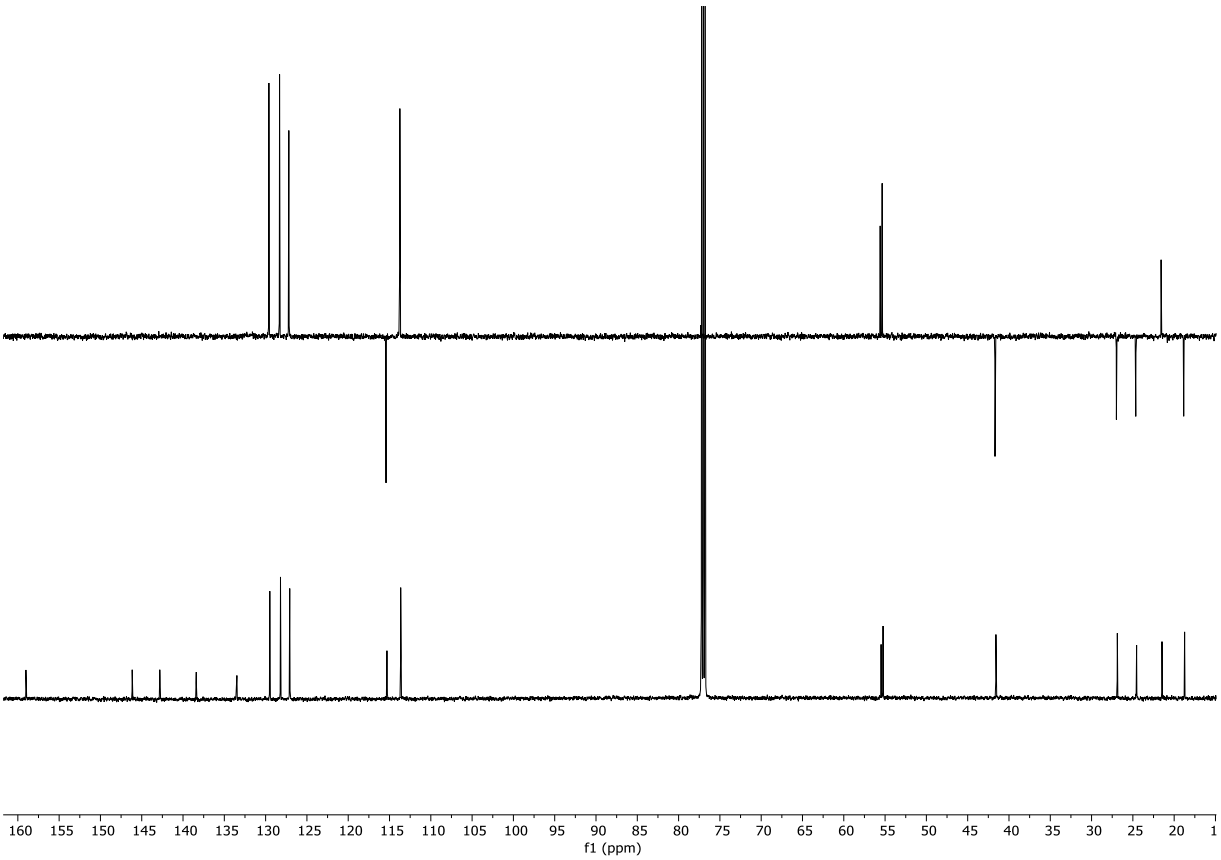
^{1}H-NMR of compound 5d (600 MHz, $CDCl_3$)



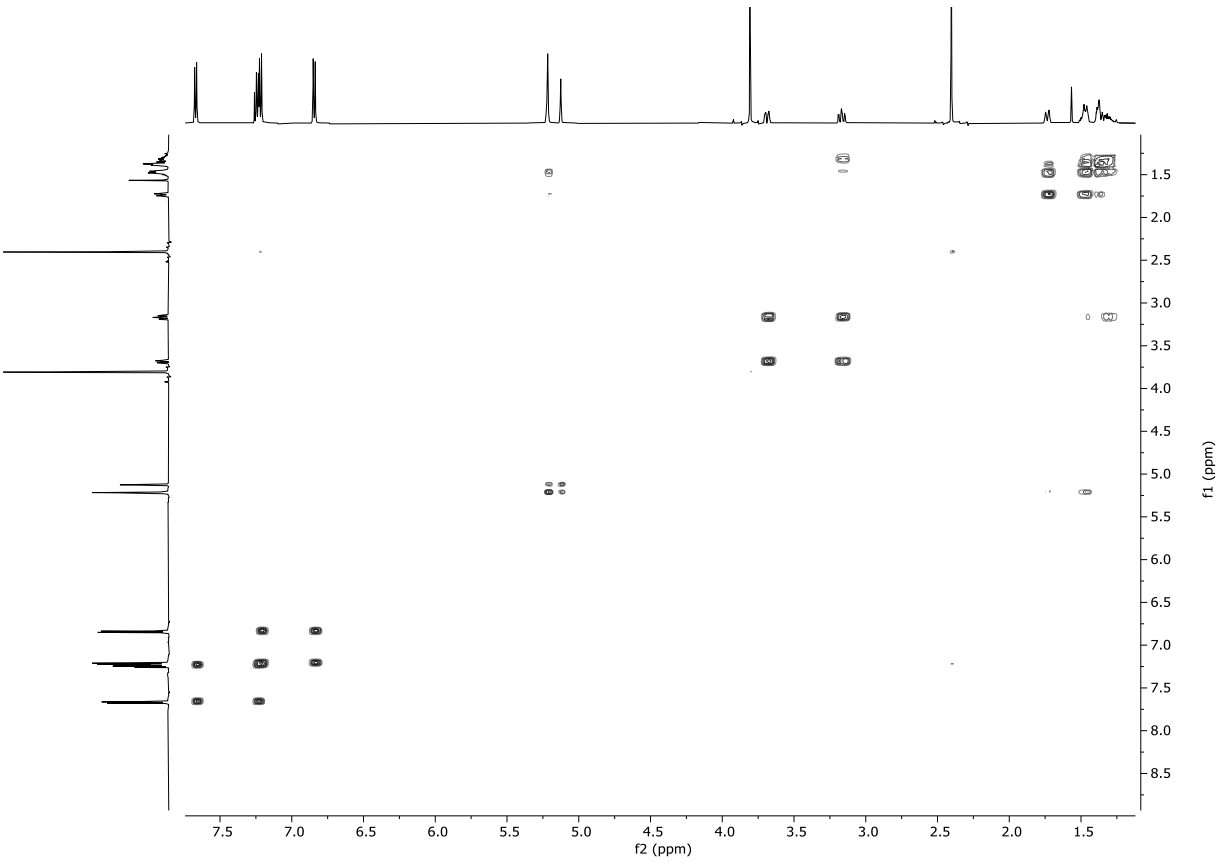
^{13}C-NMR of compound 5d (150 MHz, $CDCl_3$)



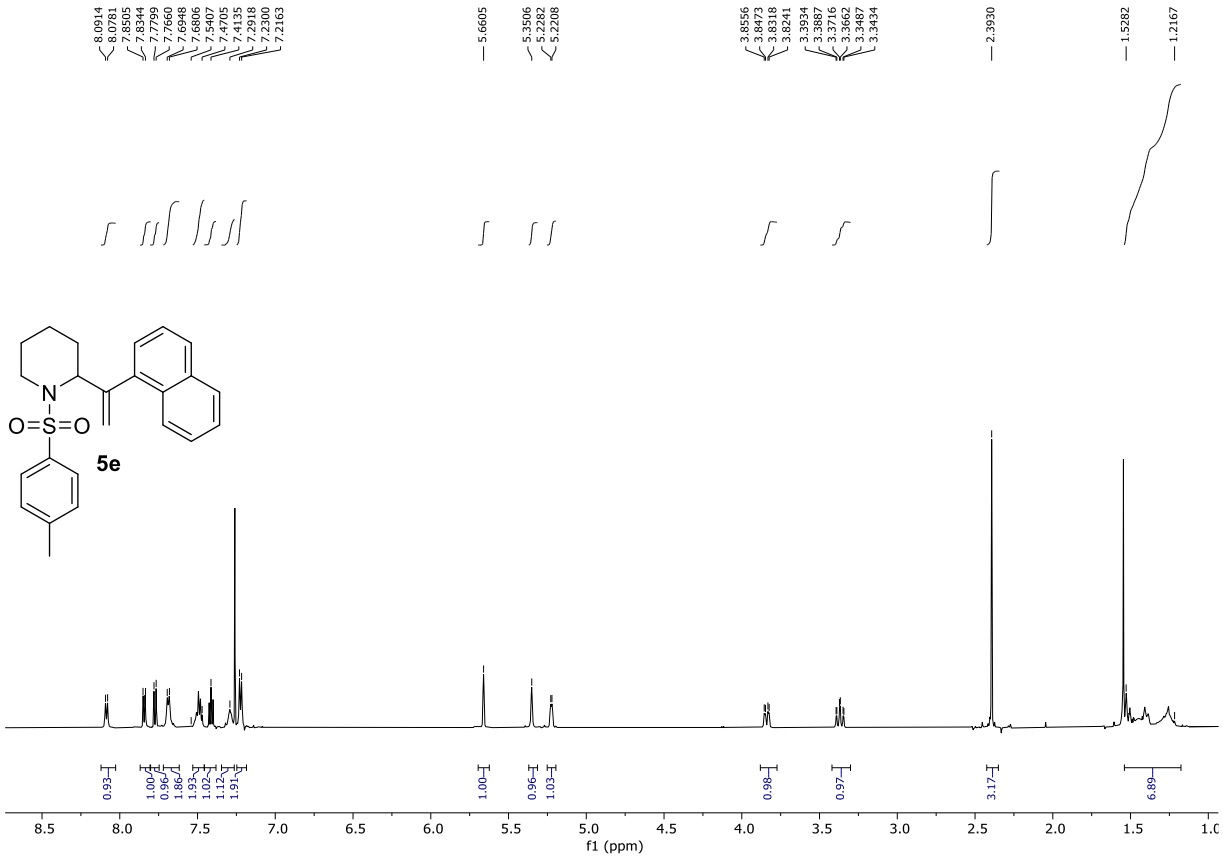
Comparison between DEPT-135 and ^{13}C-NMR of compound 5d (150 MHz, $CDCl_3$)



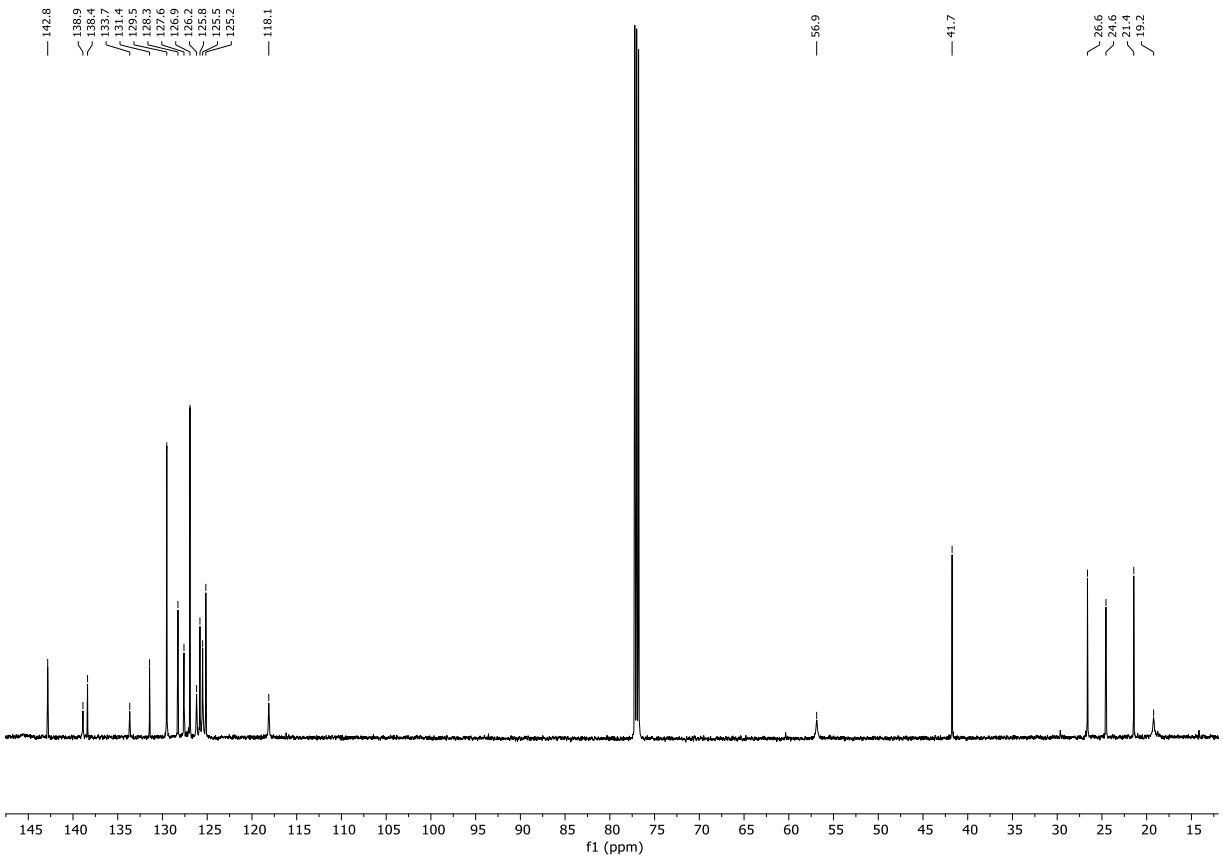
COSY-NMR of compound 5d (600 MHz, $CDCl_3$)



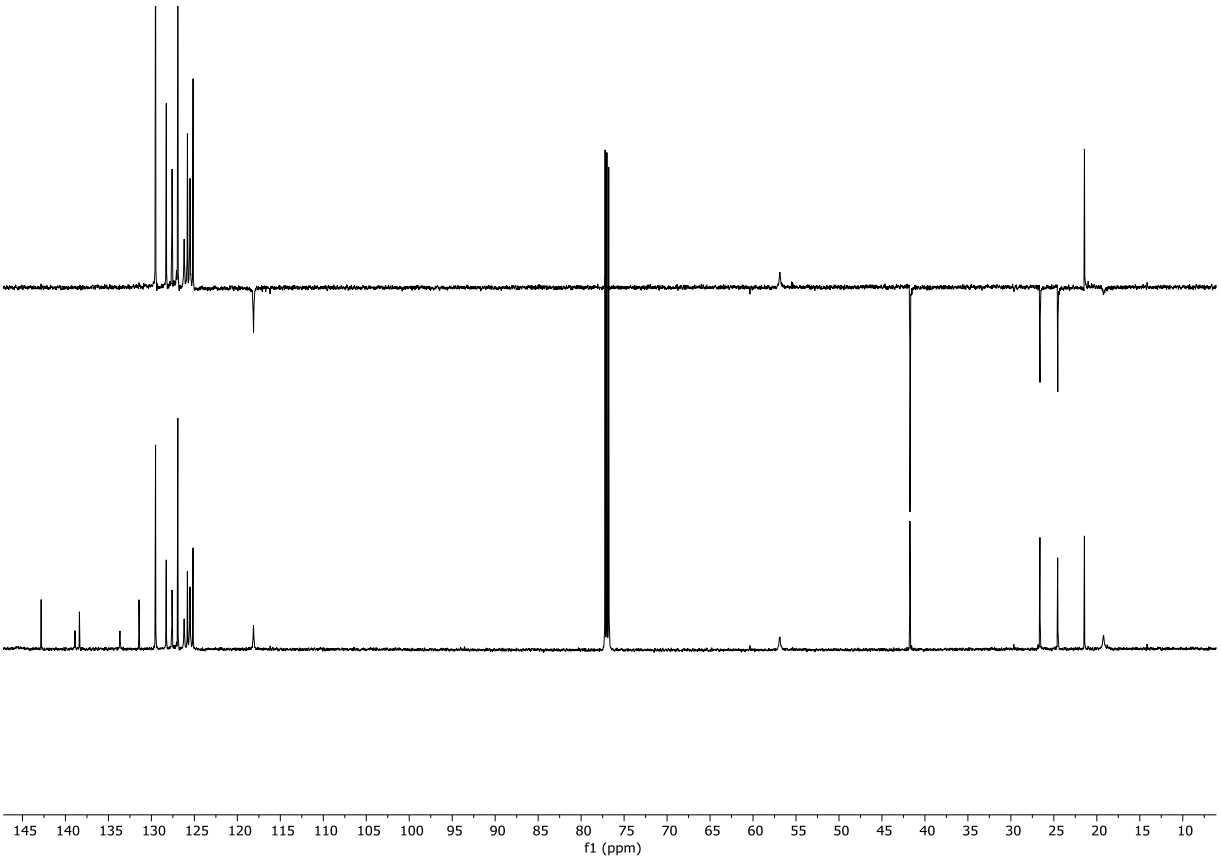
^{1}H-NMR of compound 5e (600 MHz, $CDCl_3$)



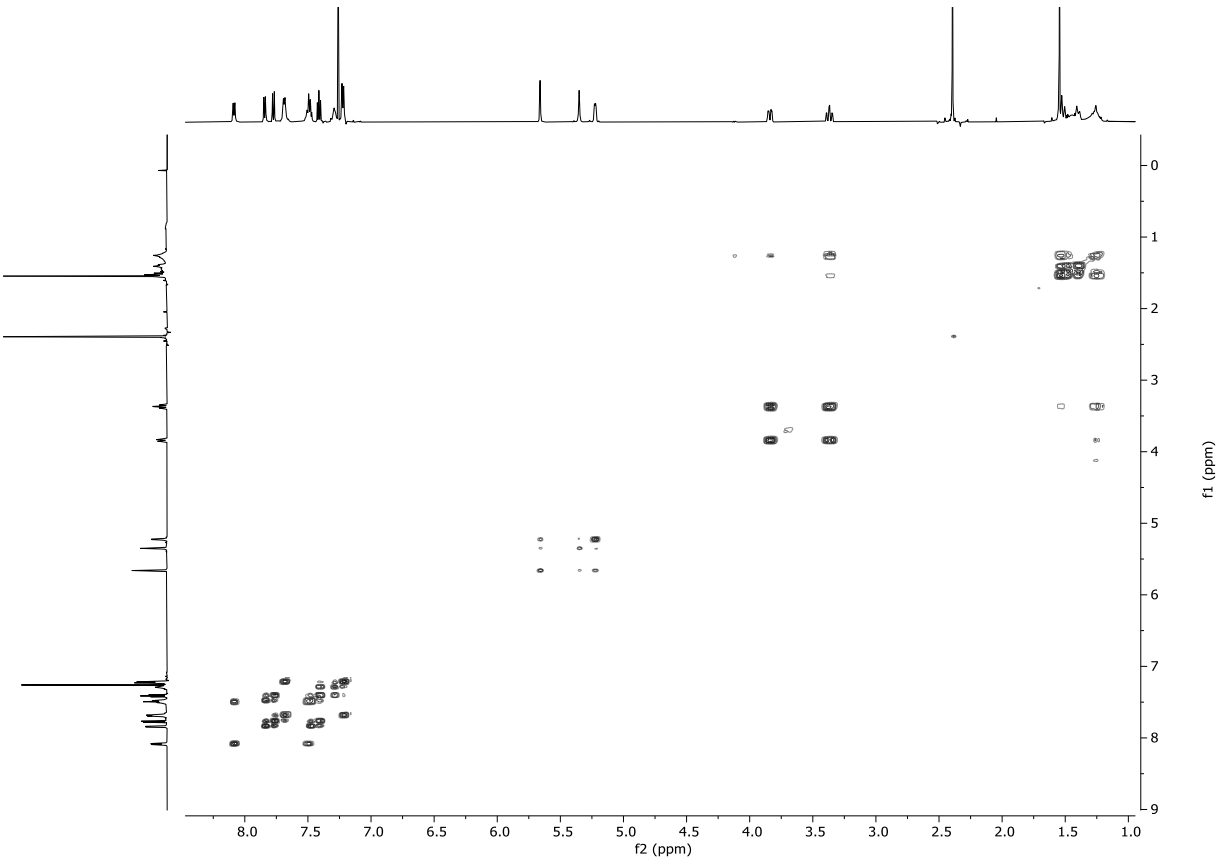
^{13}C-NMR of compound 5e (150 MHz, $CDCl_3$)



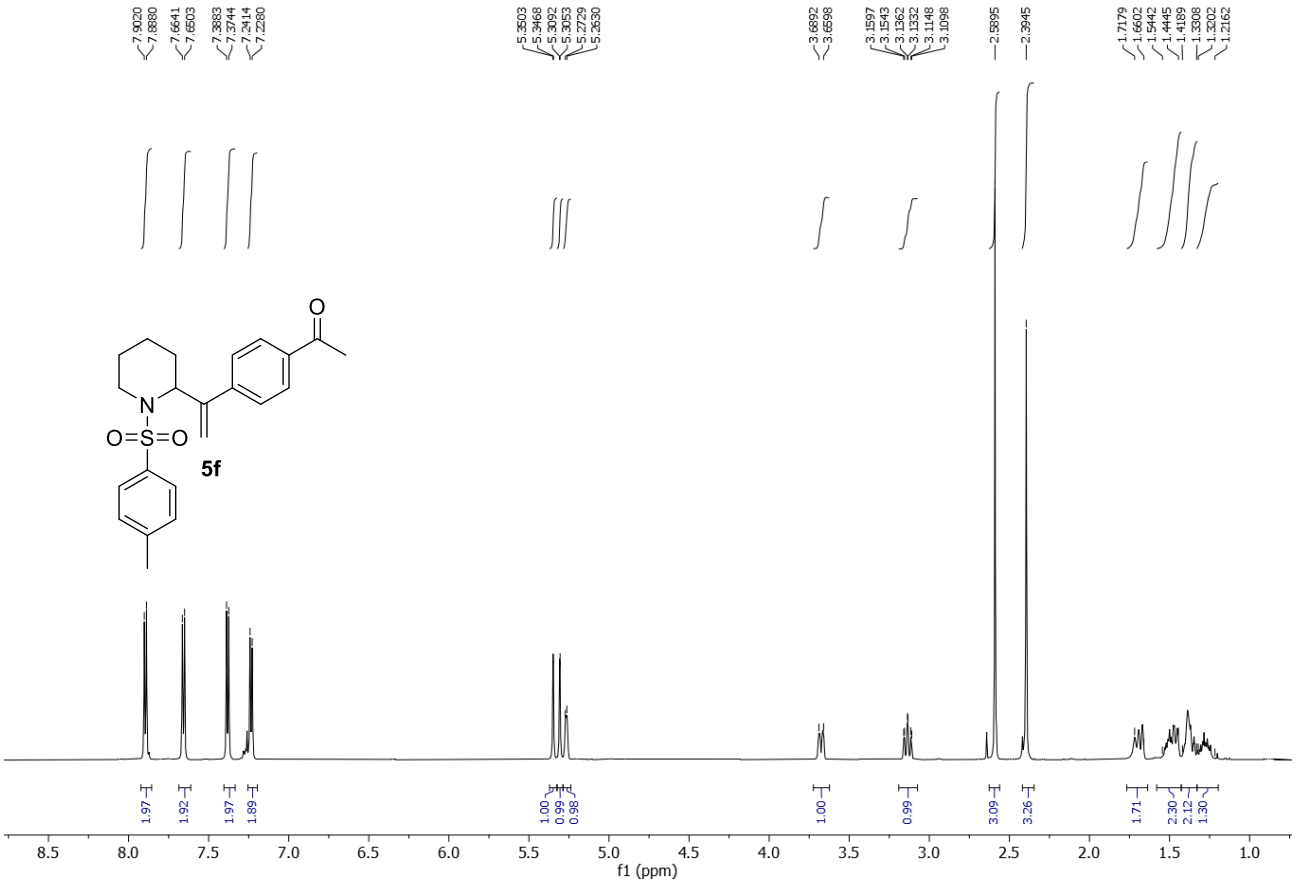
Comparison between DEPT-135 and ^{13}C-NMR of compound 5e (150 MHz, $CDCl_3$)



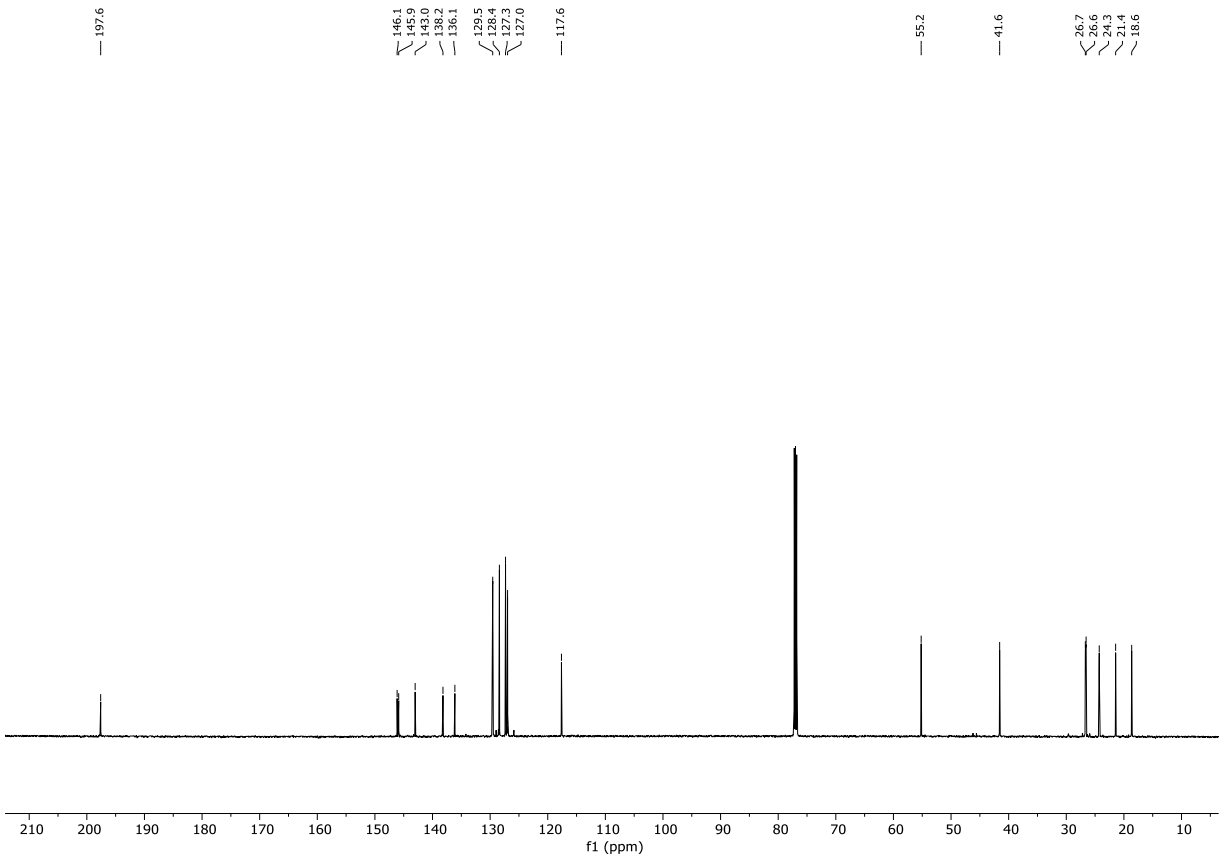
COSY-NMR of compound 5e (600 MHz, $CDCl_3$)



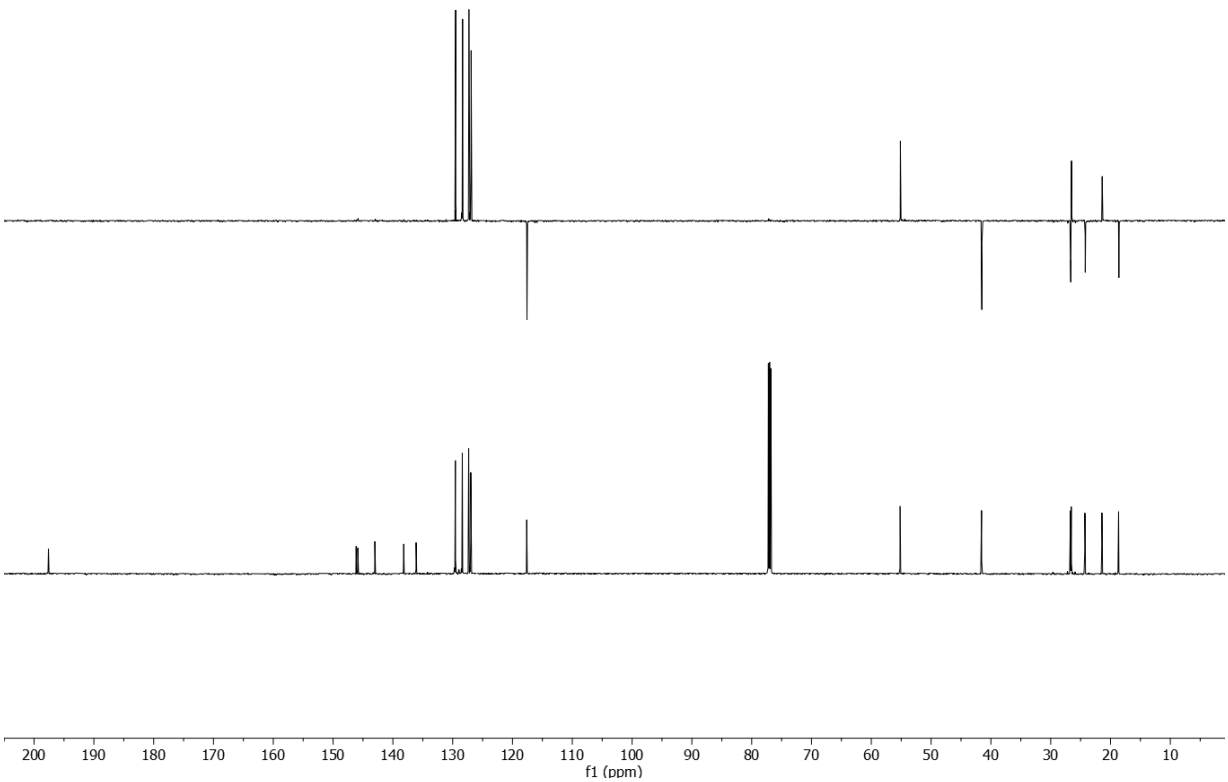
^{1}H-NMR of compound 5f (600 MHz, $CDCl_3$)



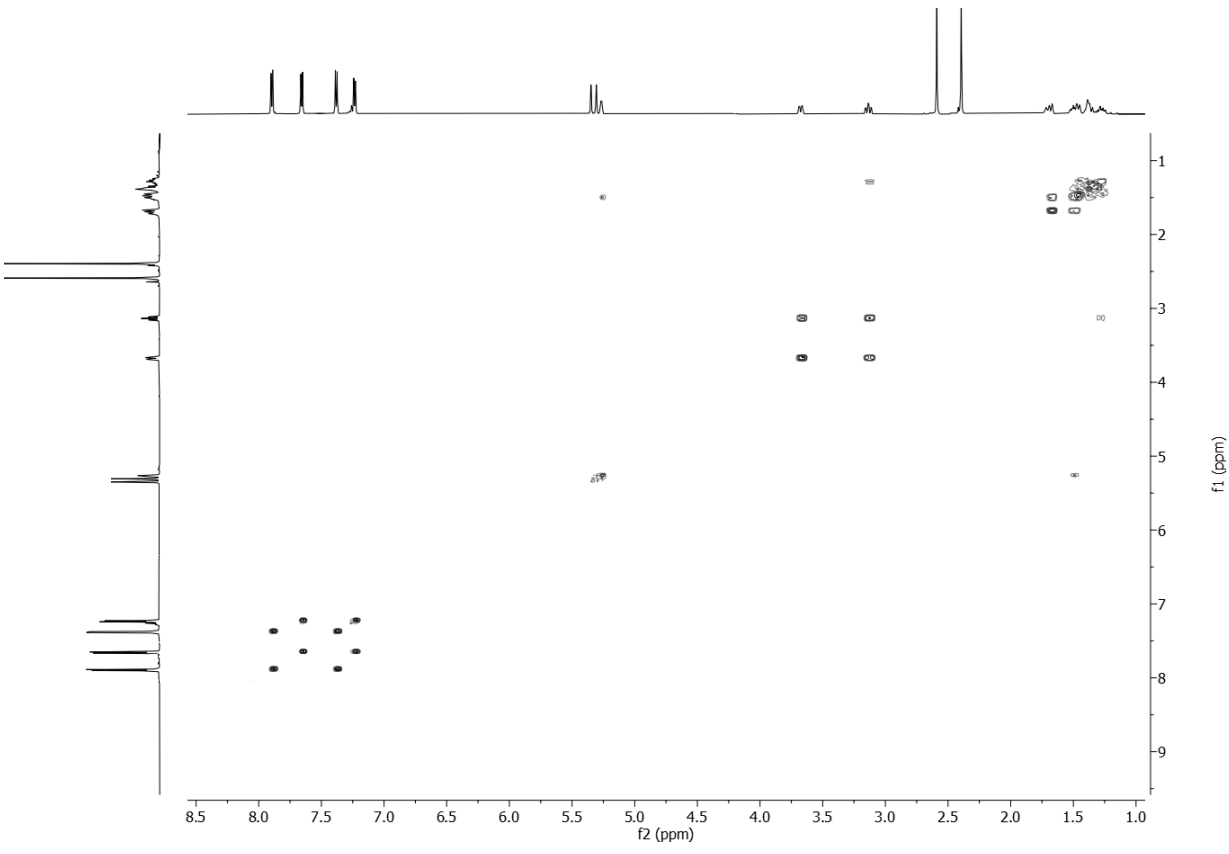
^{13}C-NMR of compound 5f (150 MHz, $CDCl_3$)



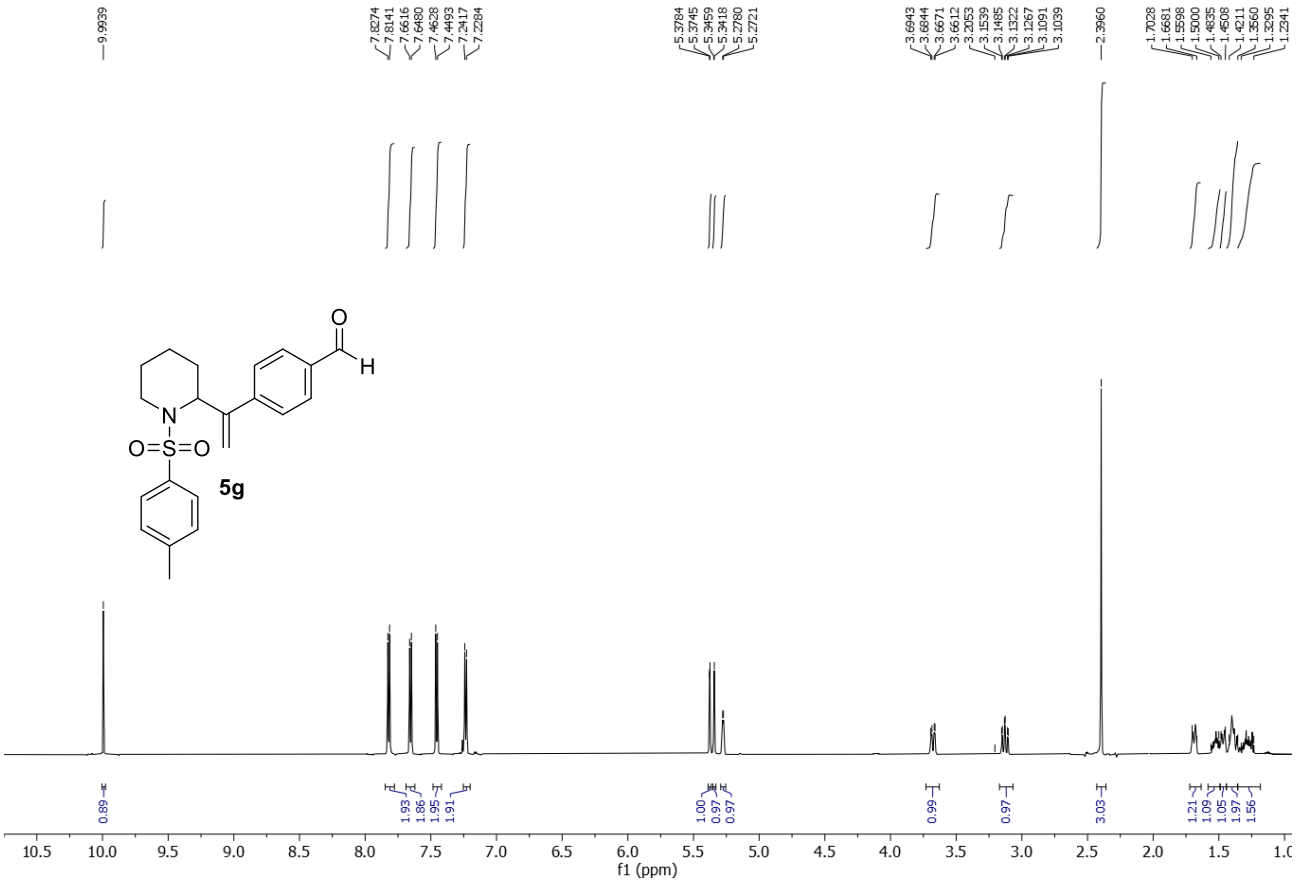
Comparison between DEPT-135 and ^{13}C-NMR of compound 5f (150 MHz, $CDCl_3$)



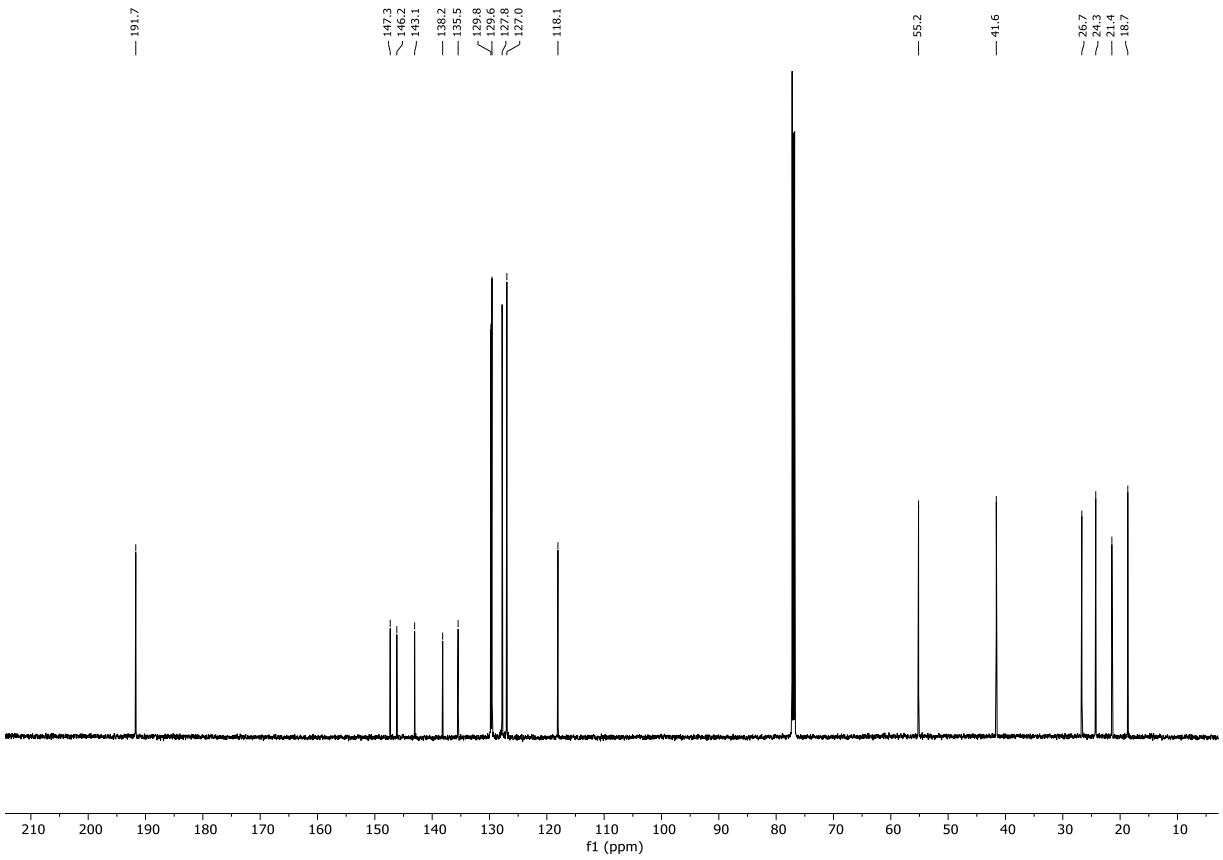
COSY-NMR of compound 5f (600 MHz, $CDCl_3$)



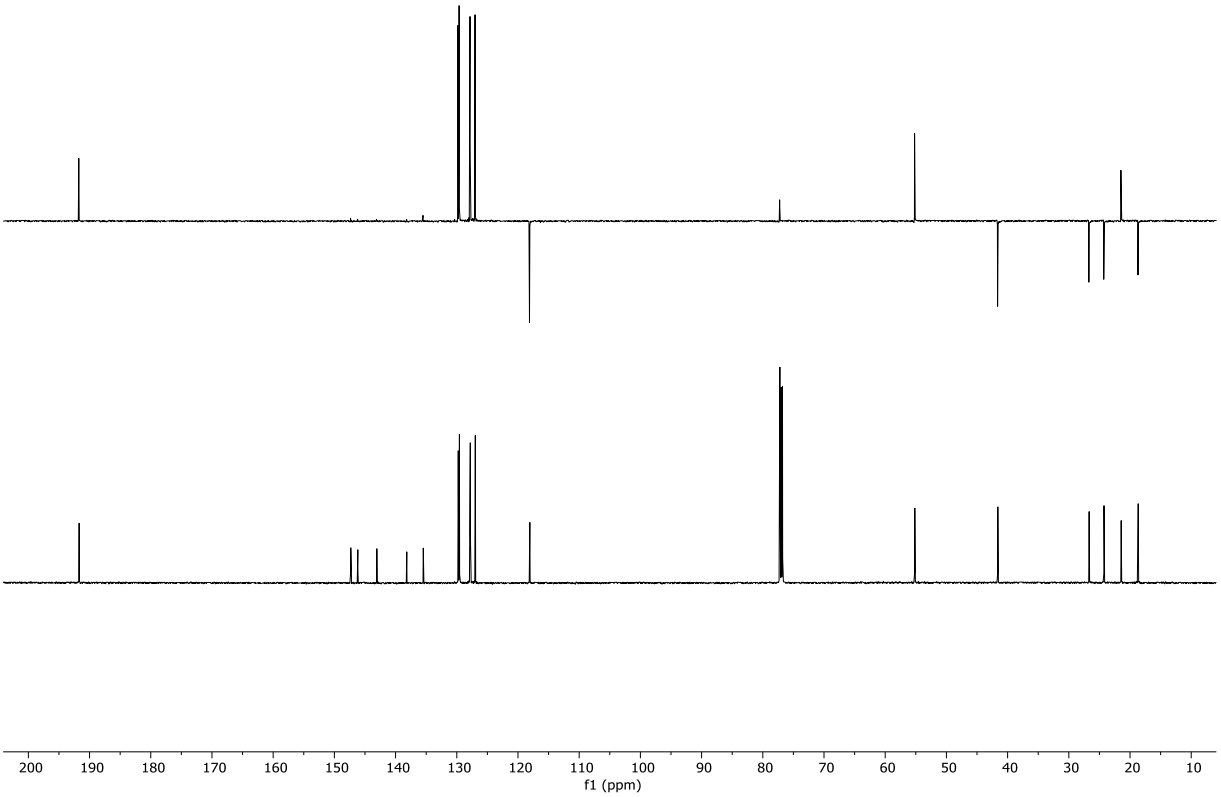
^{1}H-NMR of compound 5g (600 MHz, $CDCl_3$)



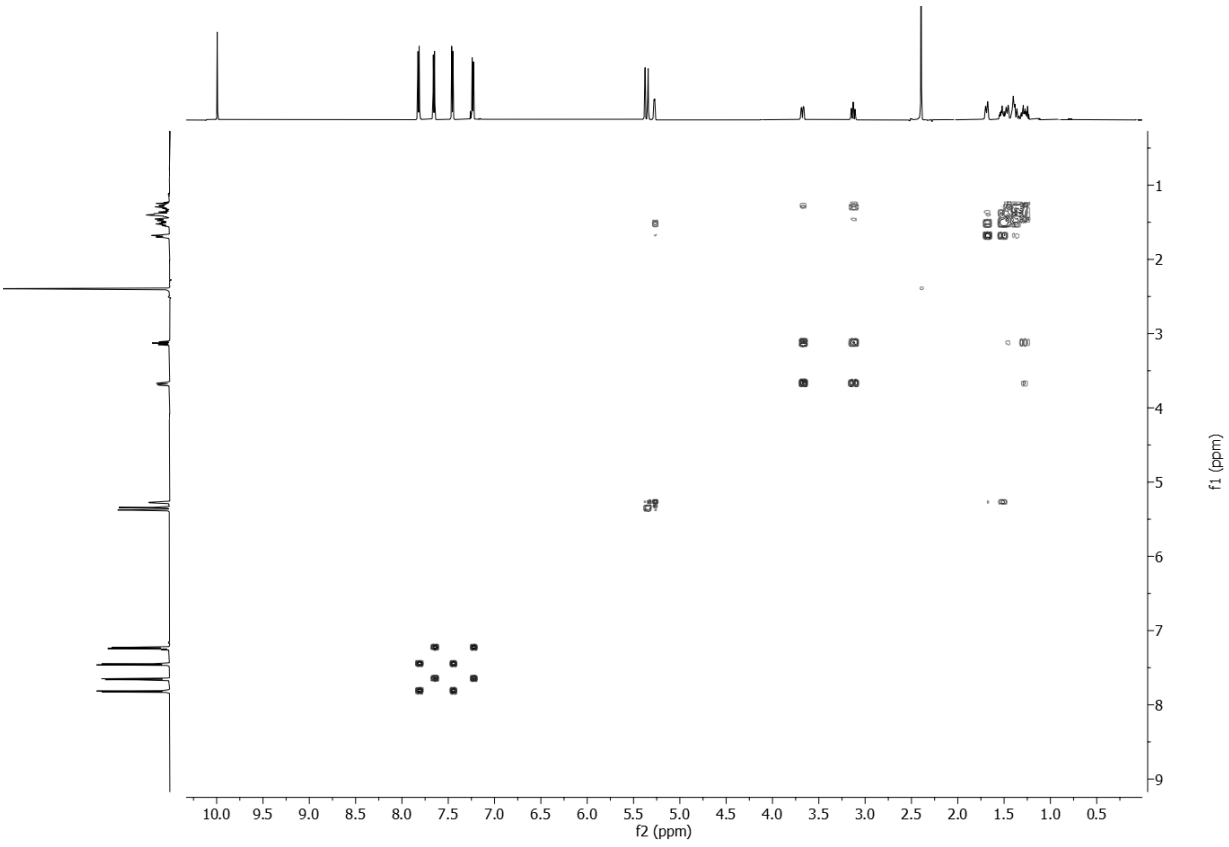
^{13}C-NMR of compound 5g (150 MHz, $CDCl_3$)



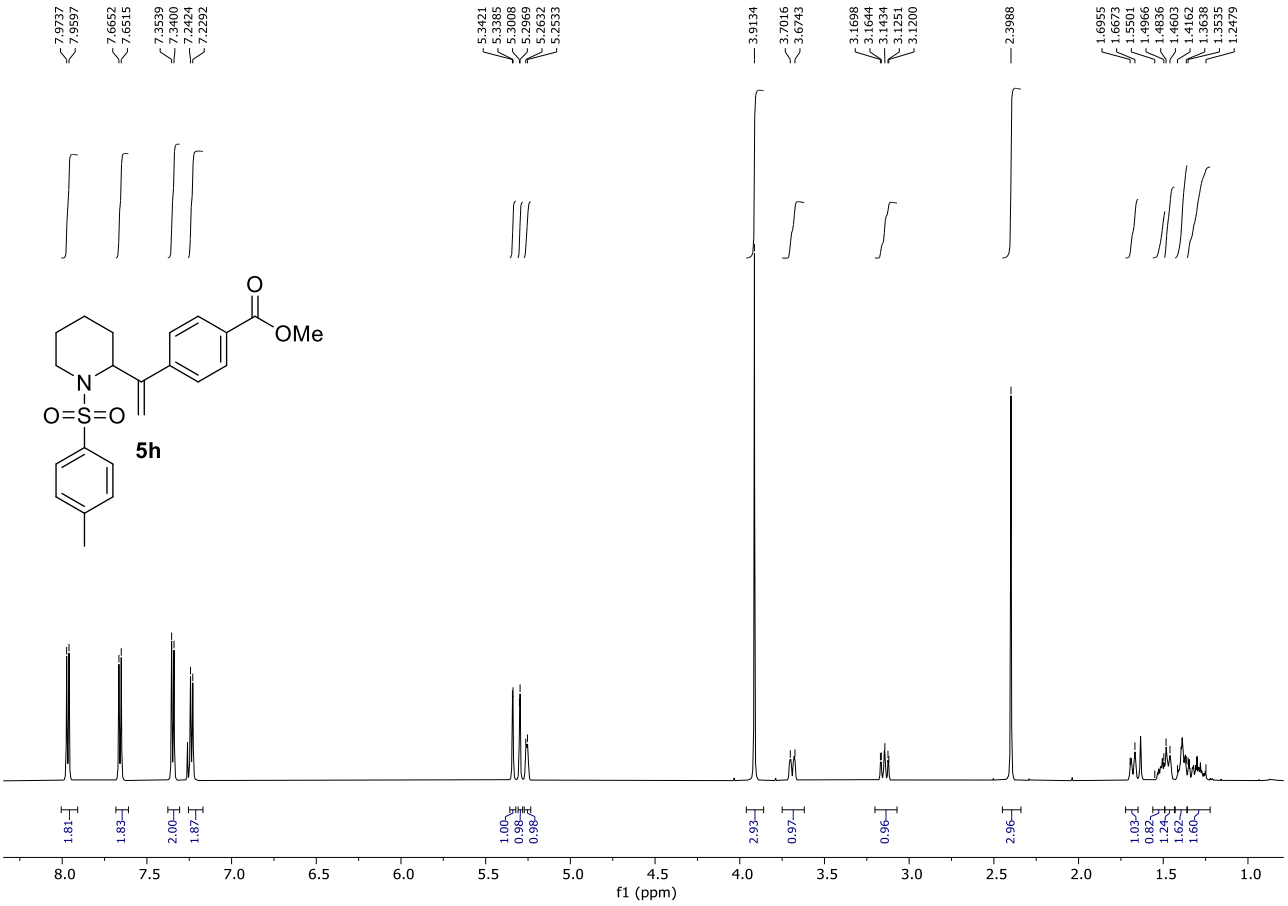
Comparison between DEPT-135 and ^{13}C-NMR of compound 5g (150 MHz, $CDCl_3$)



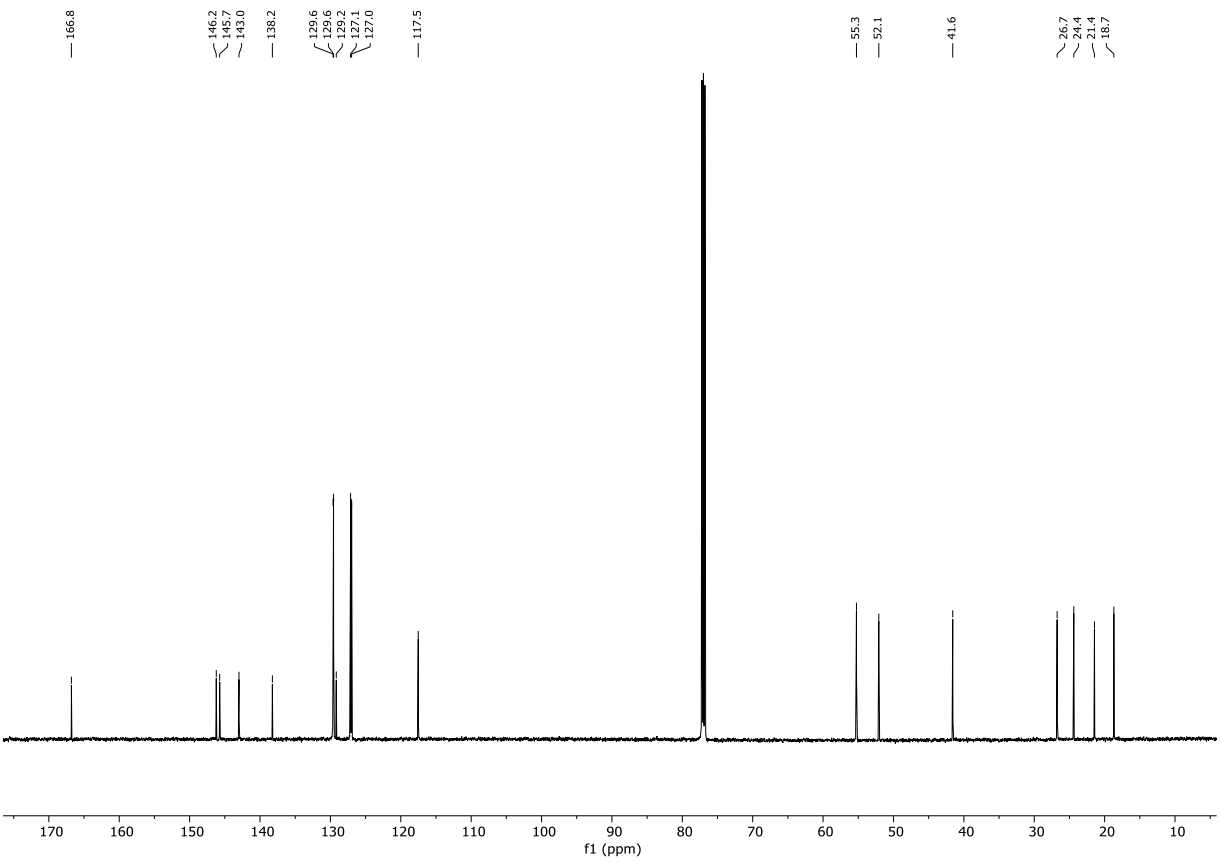
COSY-NMR of compound 5g (600 MHz, $CDCl_3$)



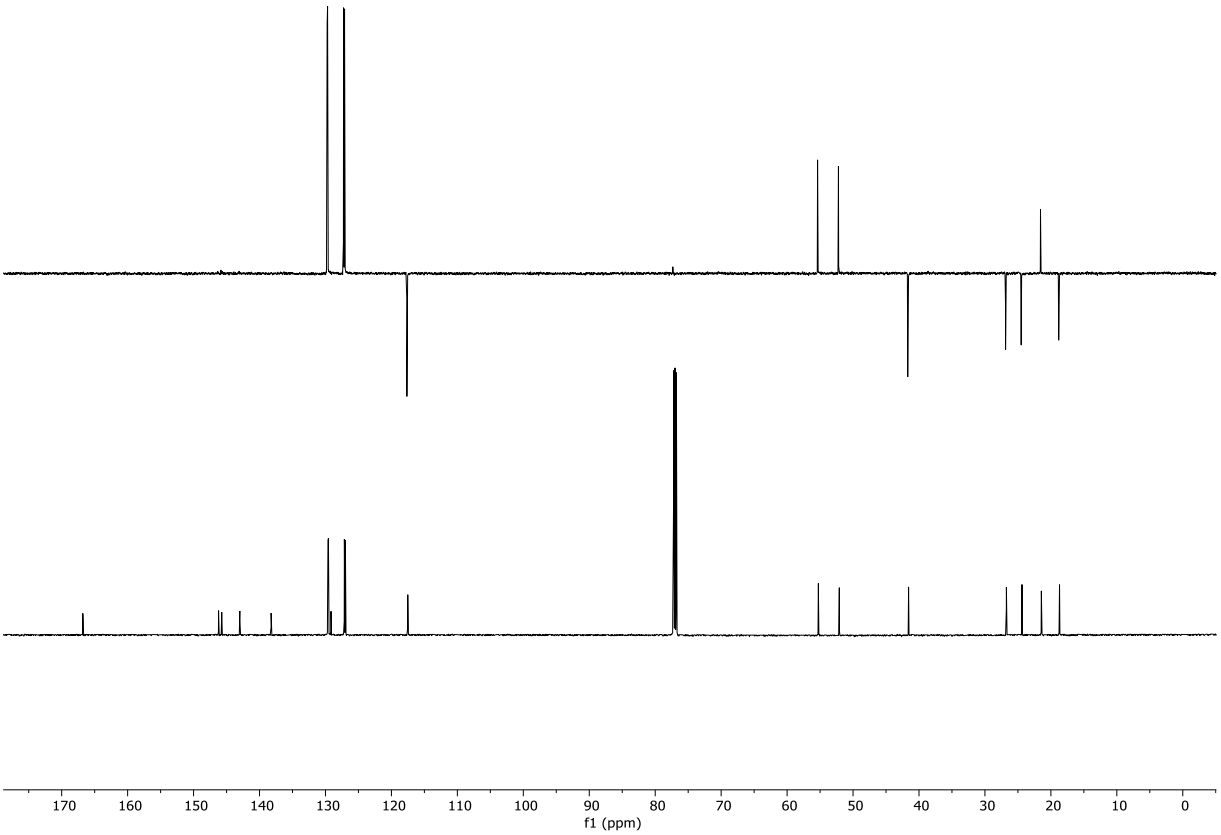
^{1}H-NMR of compound 5h (600 MHz, $CDCl_3$)



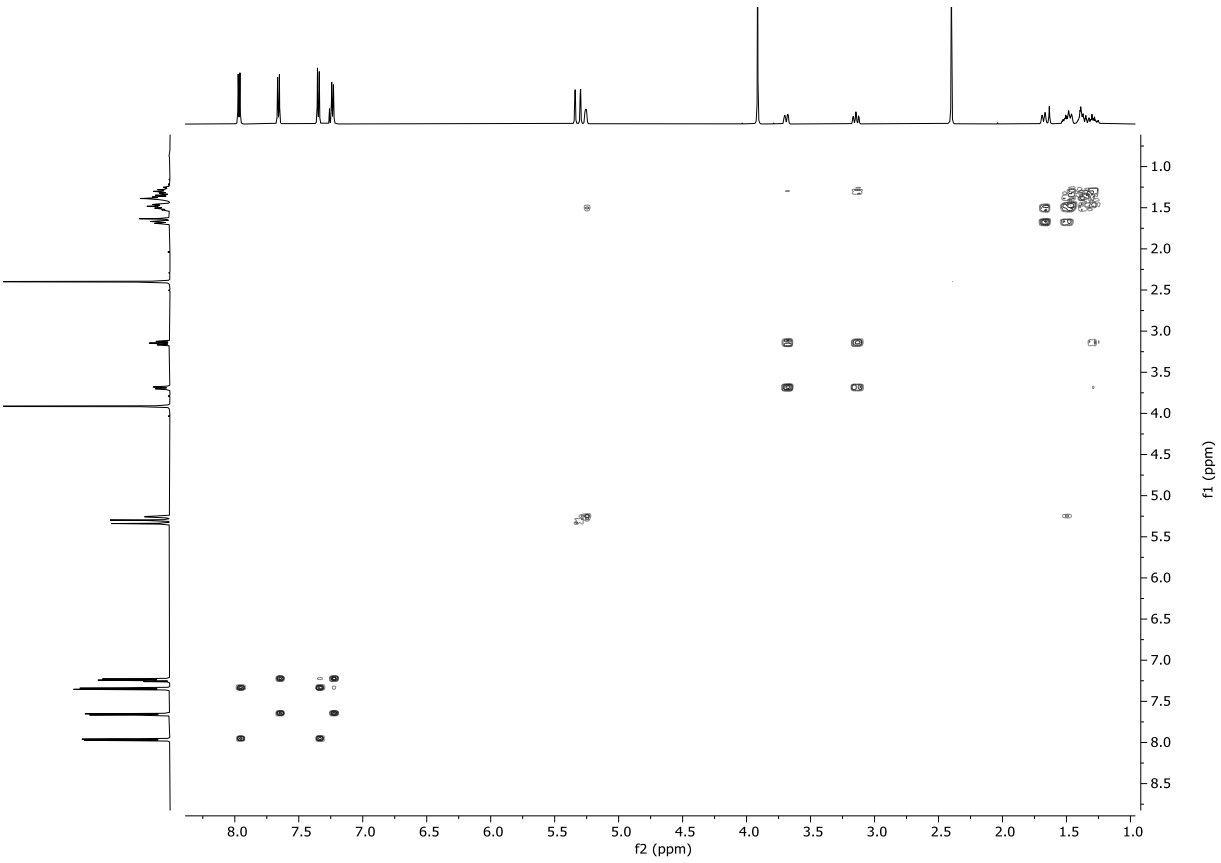
^{13}C-NMR of compound 5h (150 MHz, $CDCl_3$)



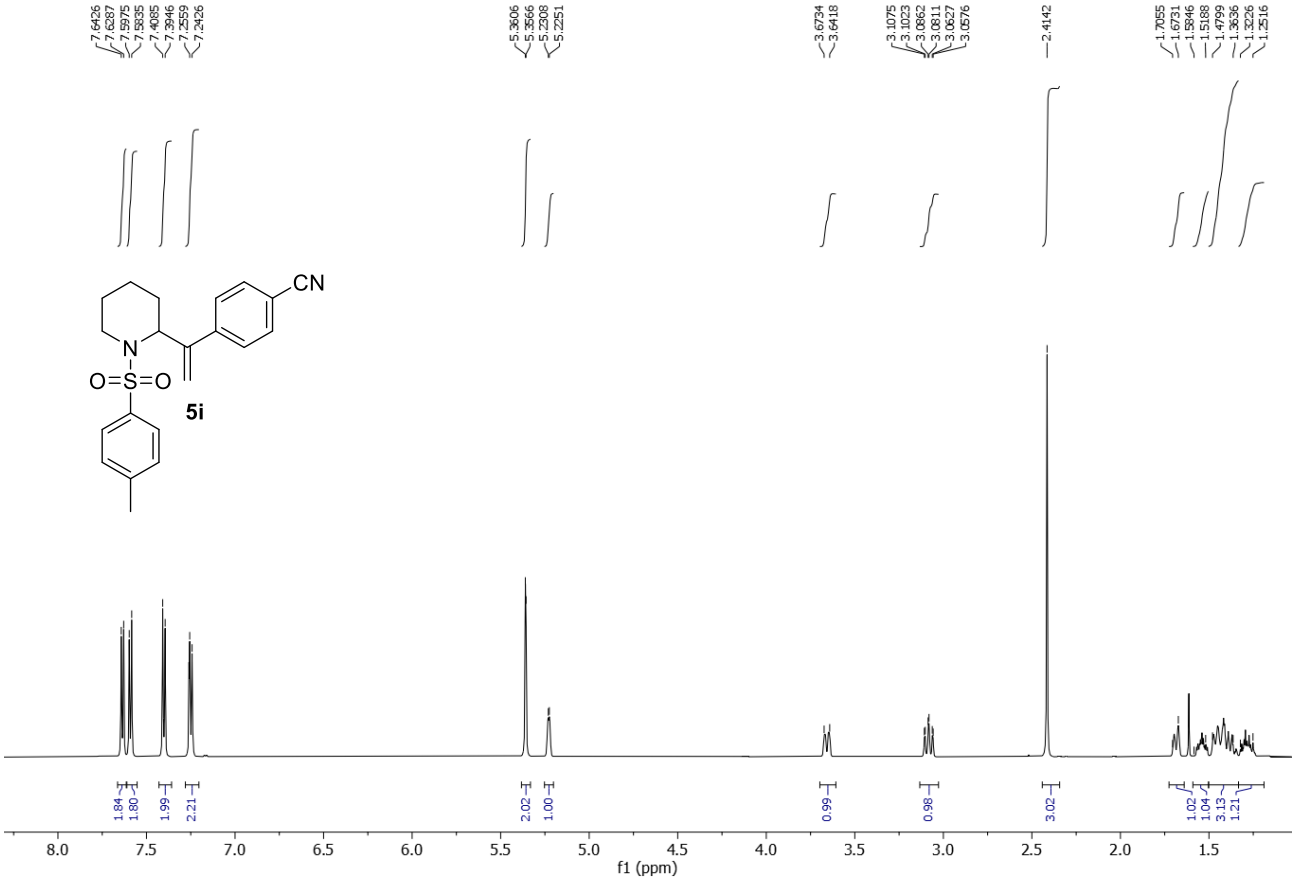
Comparison between DEPT-135 and ^{13}C-NMR of compound 5h (150 MHz, $CDCl_3$)



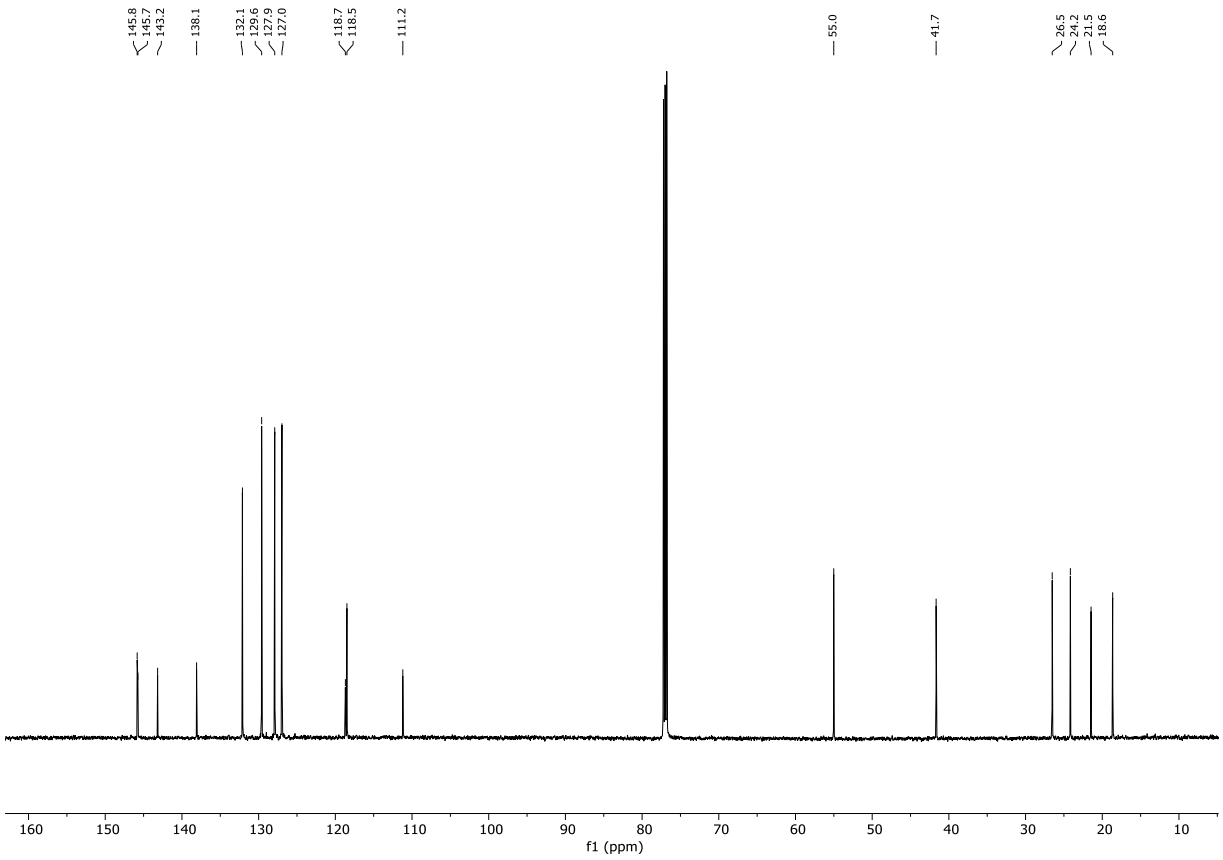
COSY-NMR of compound 5h (600 MHz, $CDCl_3$)



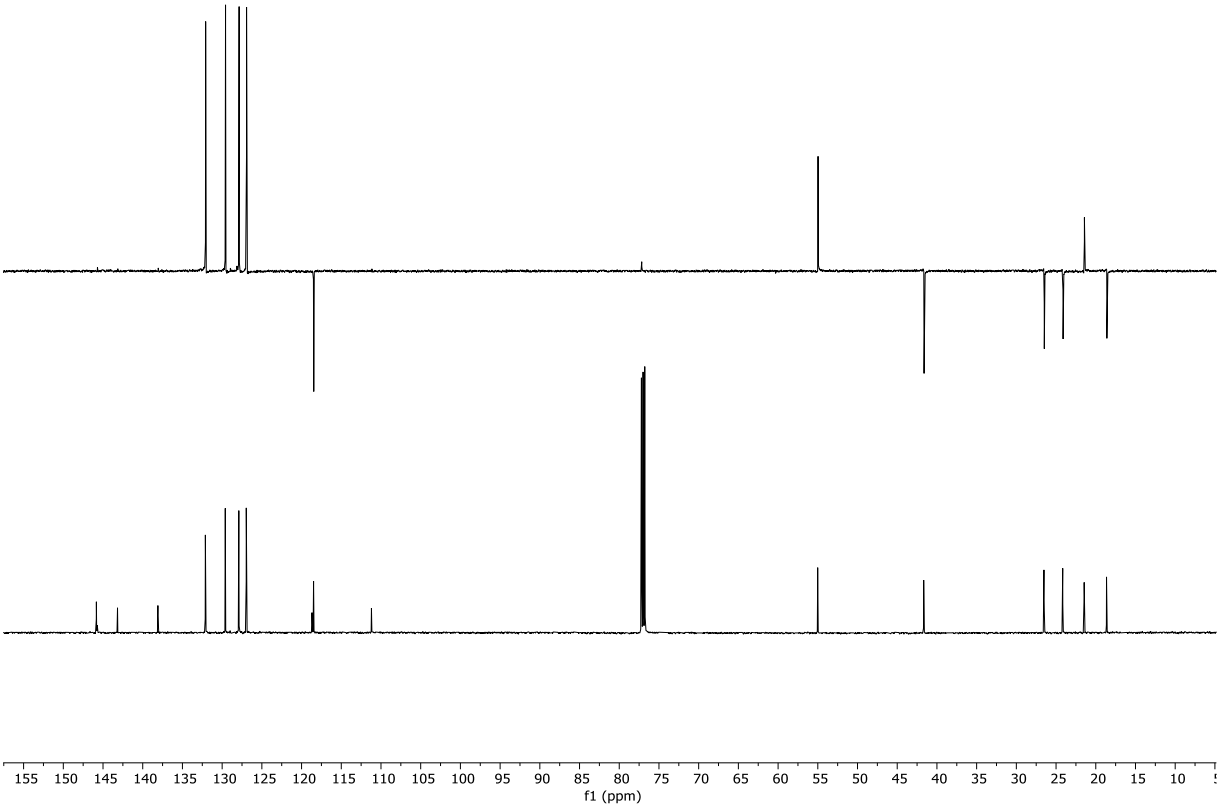
^{1}H-NMR of compound 5i (600 MHz, $CDCl_3$)



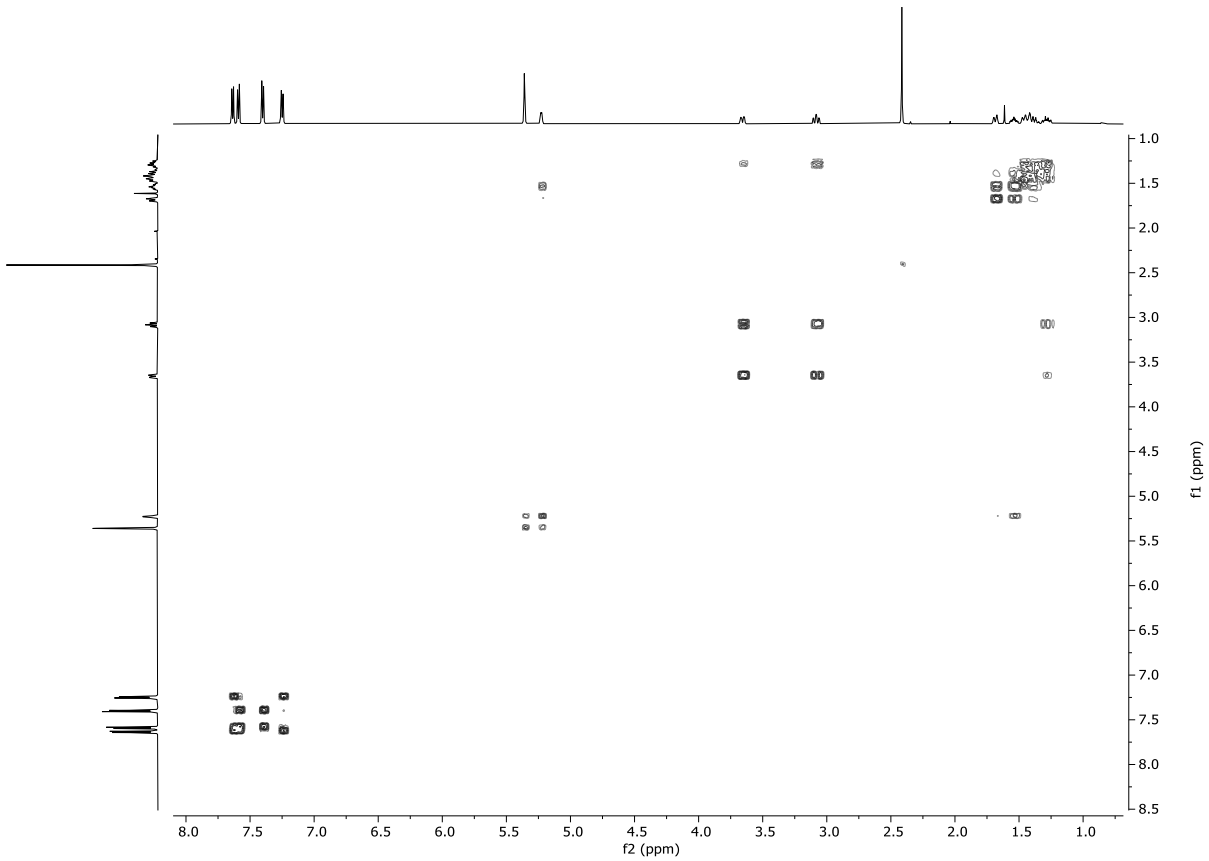
^{13}C-NMR of compound 5i (150 MHz, $CDCl_3$)



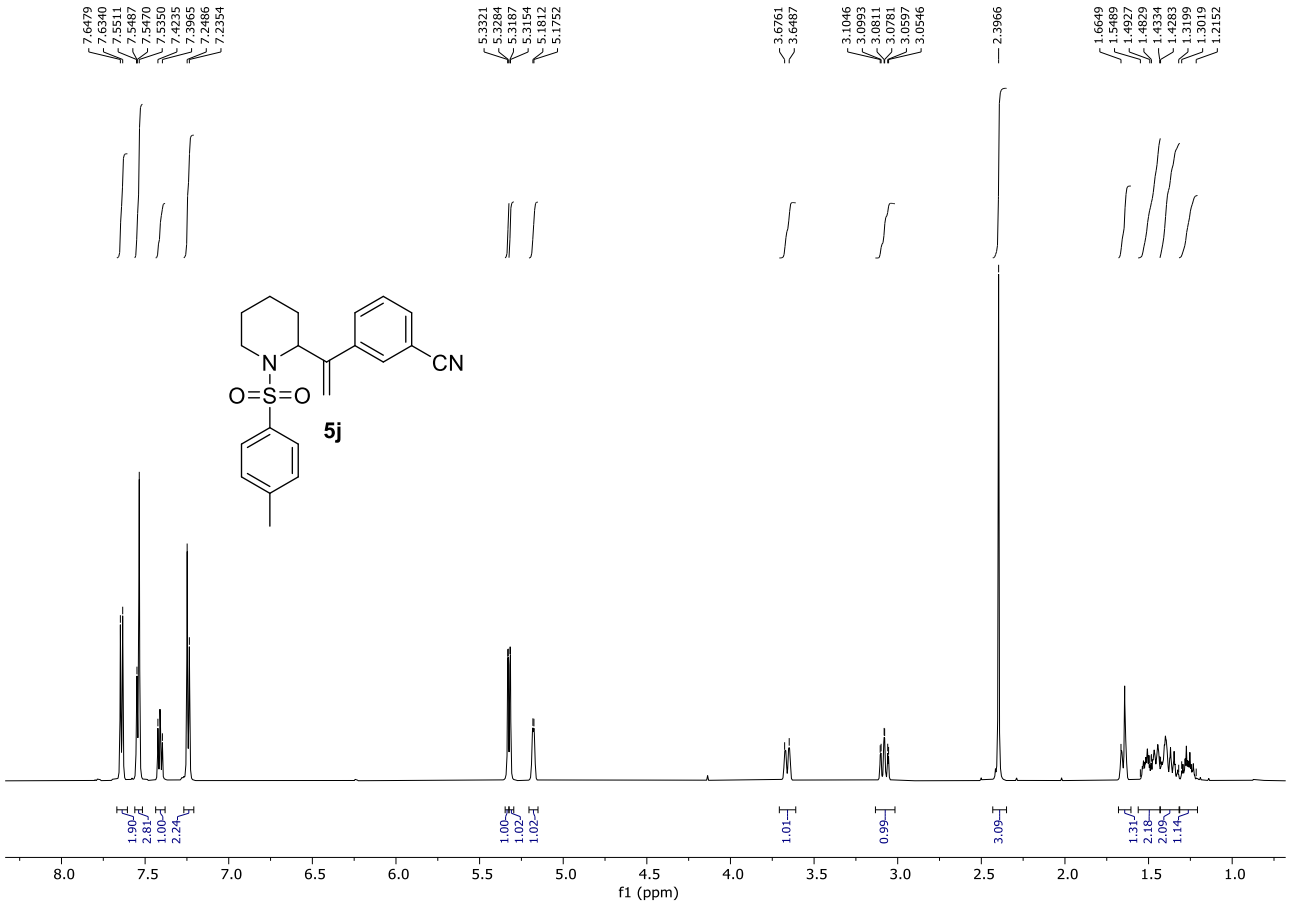
Comparison between DEPT-135 and ^{13}C-NMR of compound 5i (150 MHz, $CDCl_3$)



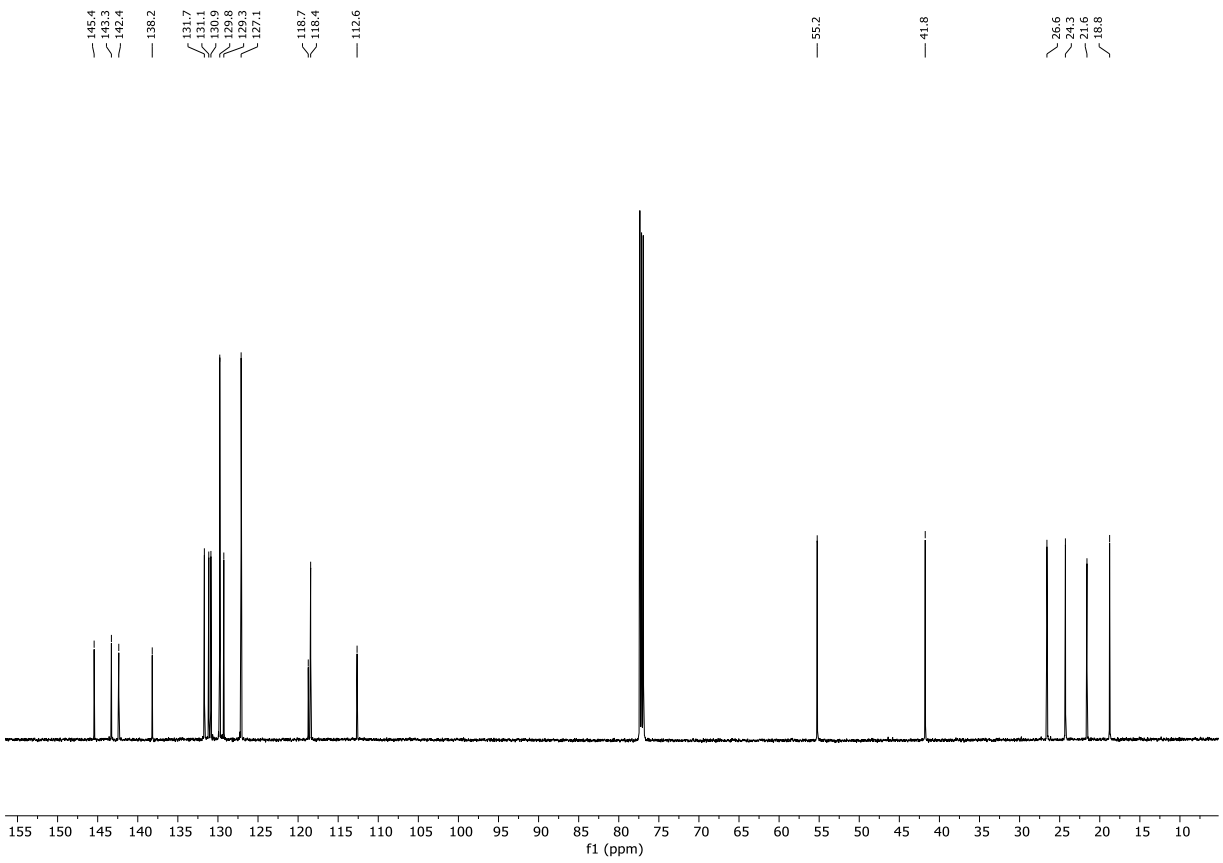
COSY-NMR of compound 5i (600 MHz, $CDCl_3$)



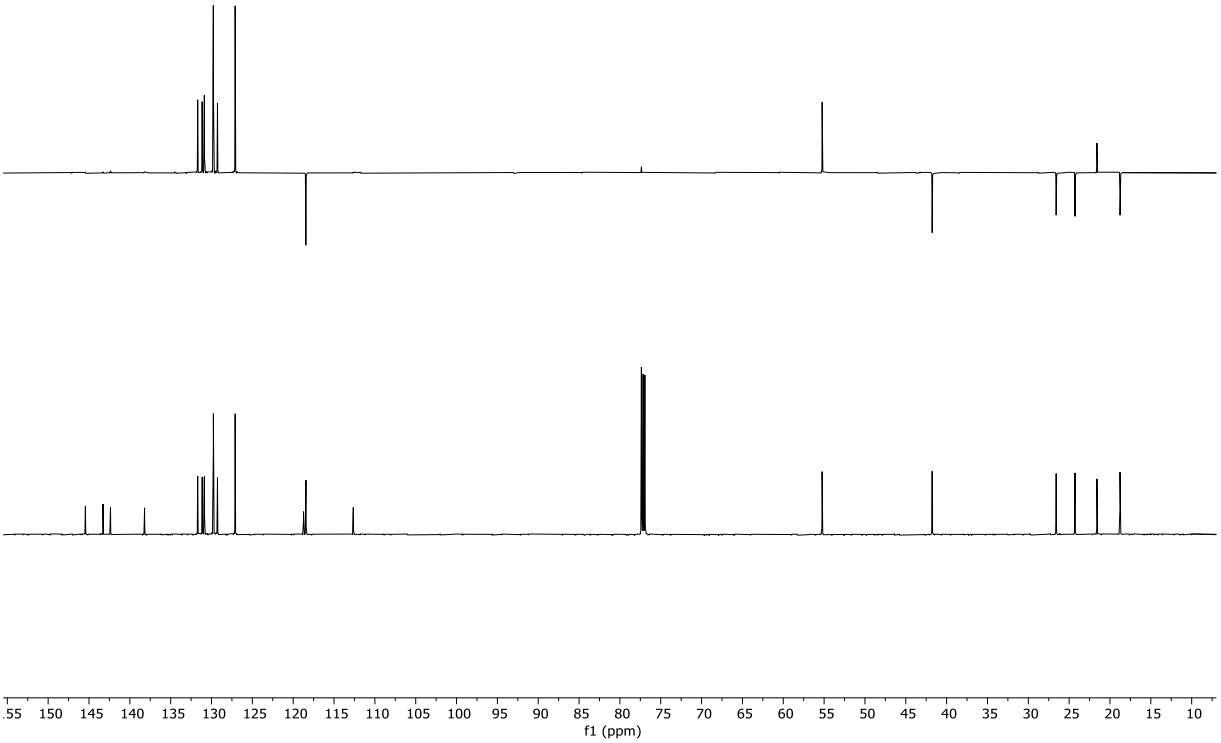
^{1}H-NMR of compound 5j (600 MHz, $CDCl_3$)



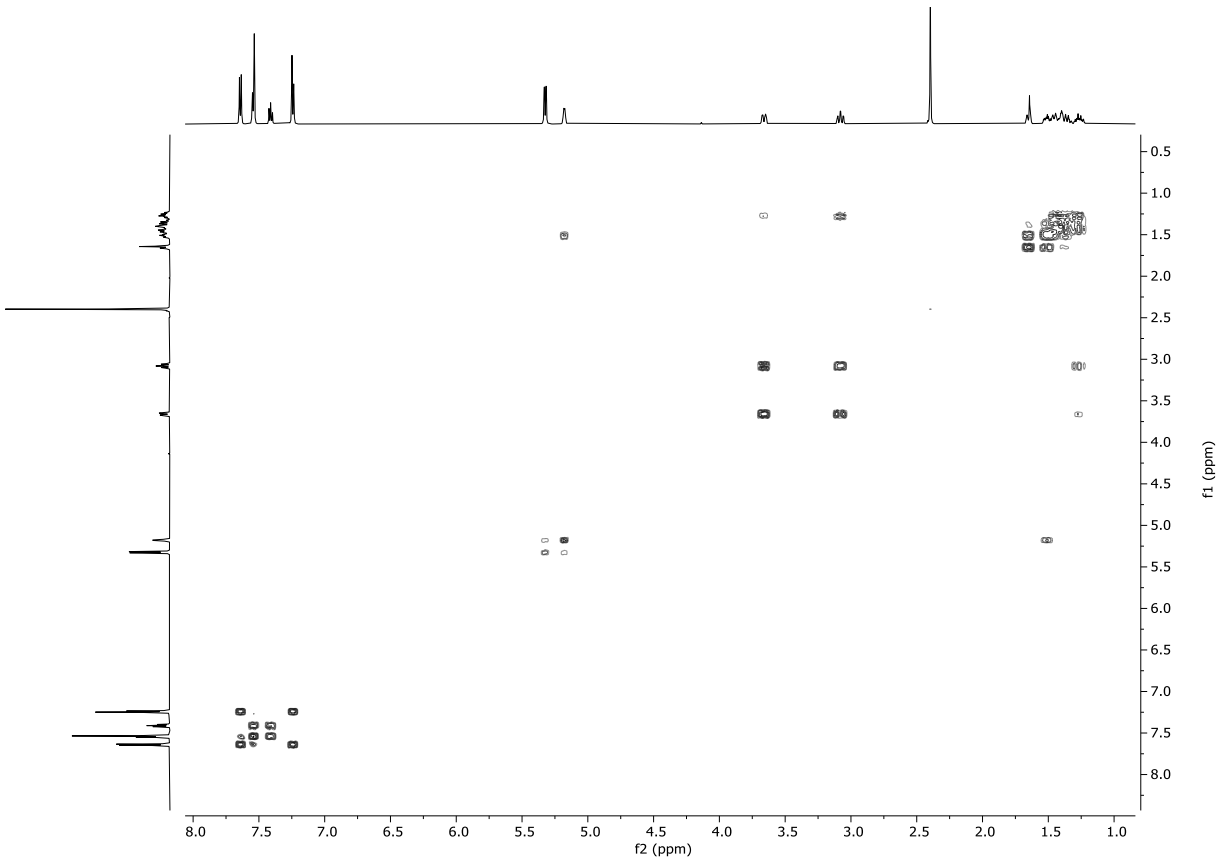
^{13}C-NMR of compound 5j (150 MHz, $CDCl_3$)



Comparison between DEPT-135 and ^{13}C-NMR of compound 5j (150 MHz, $CDCl_3$)

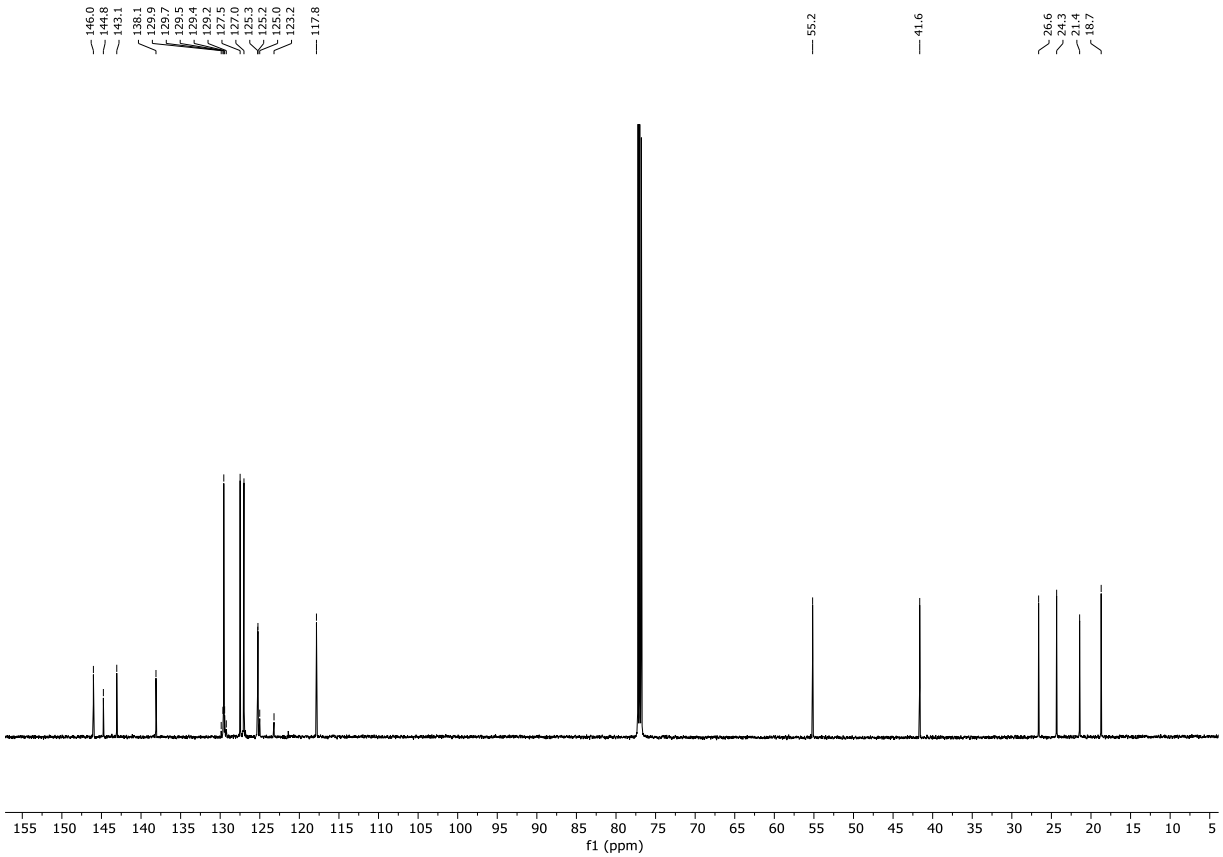


COSY-NMR of compound 5j (600 MHz, $CDCl_3$)

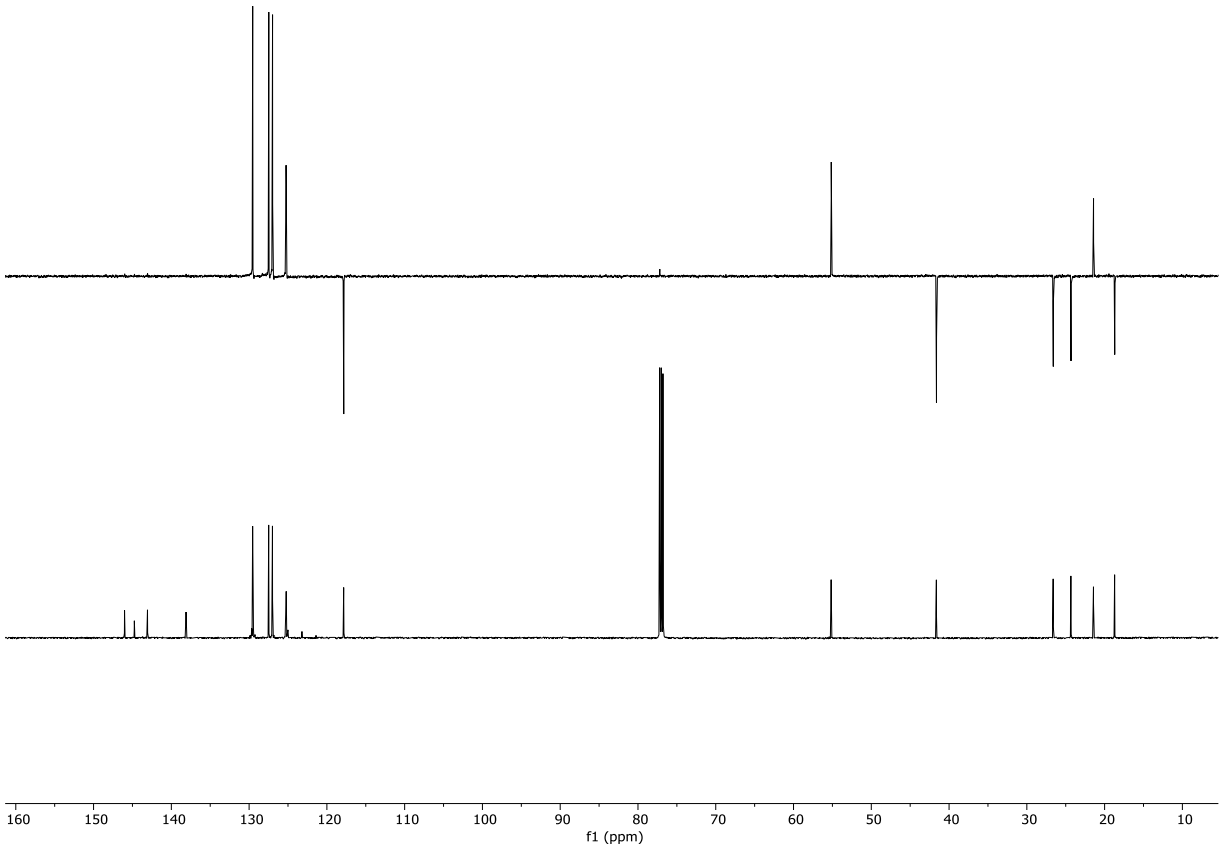


^{1}H-NMR of compound 5k (600 MHz, $CDCl_3$)

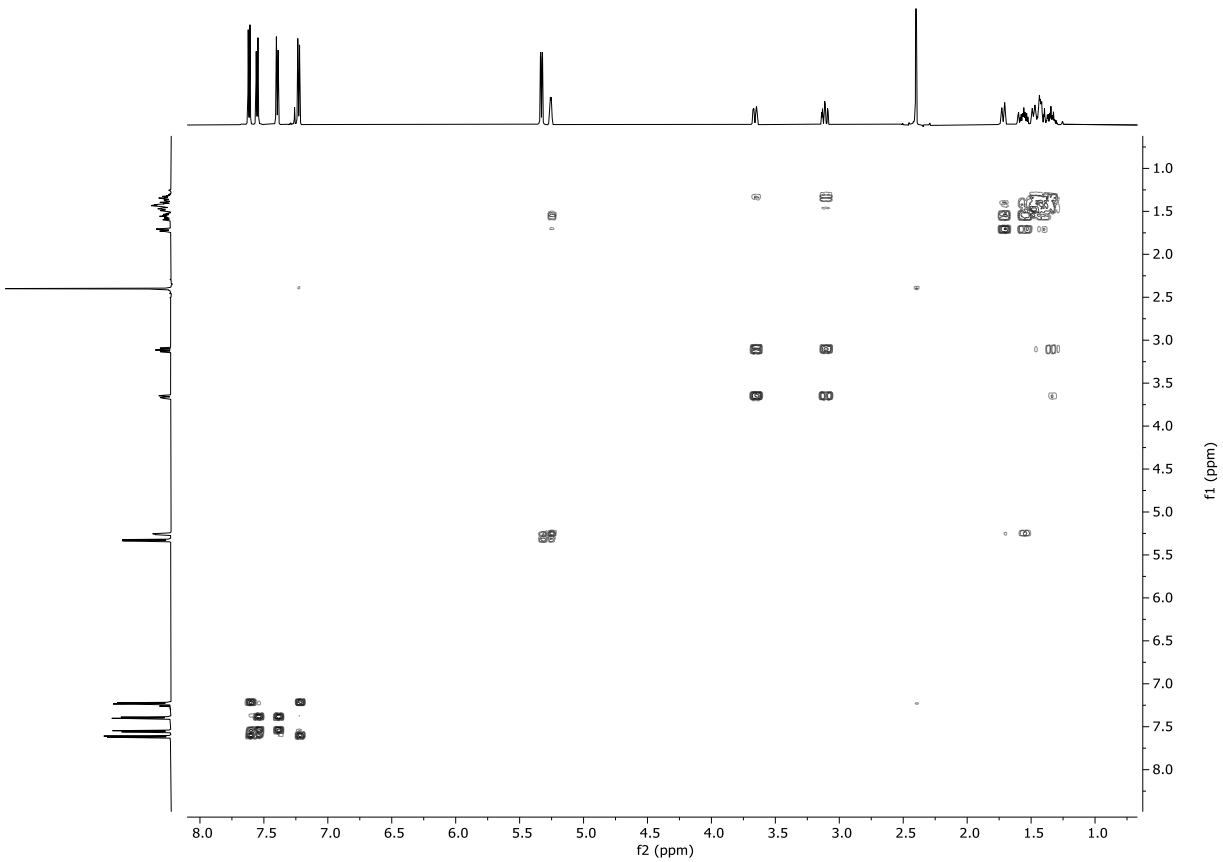
^{13}C-NMR of compound 5k (150 MHz, $CDCl_3$)



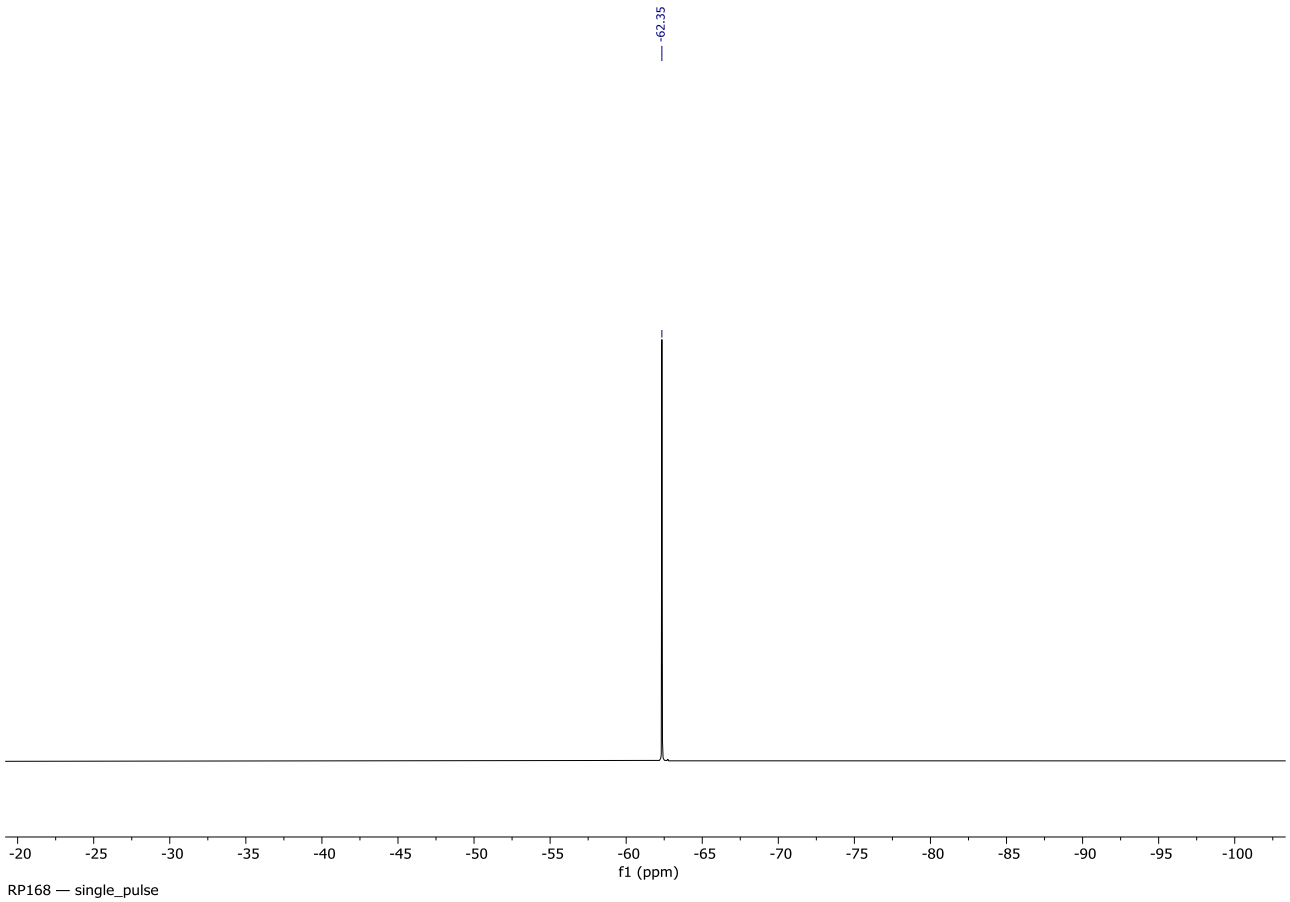
Comparison between DEPT-135 and ^{13}C-NMR of compound 5k (150 MHz, $CDCl_3$)



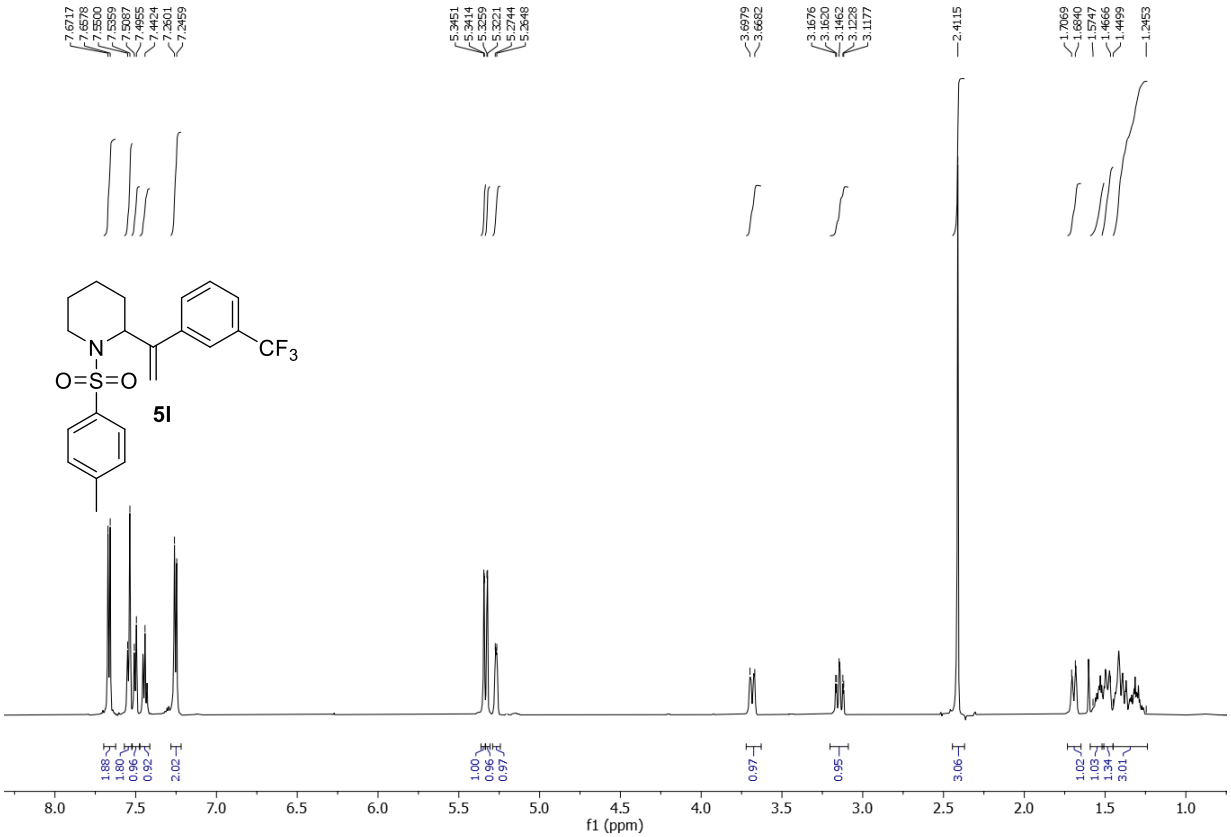
COSY-NMR of compound 5k (600 MHz, $CDCl_3$)



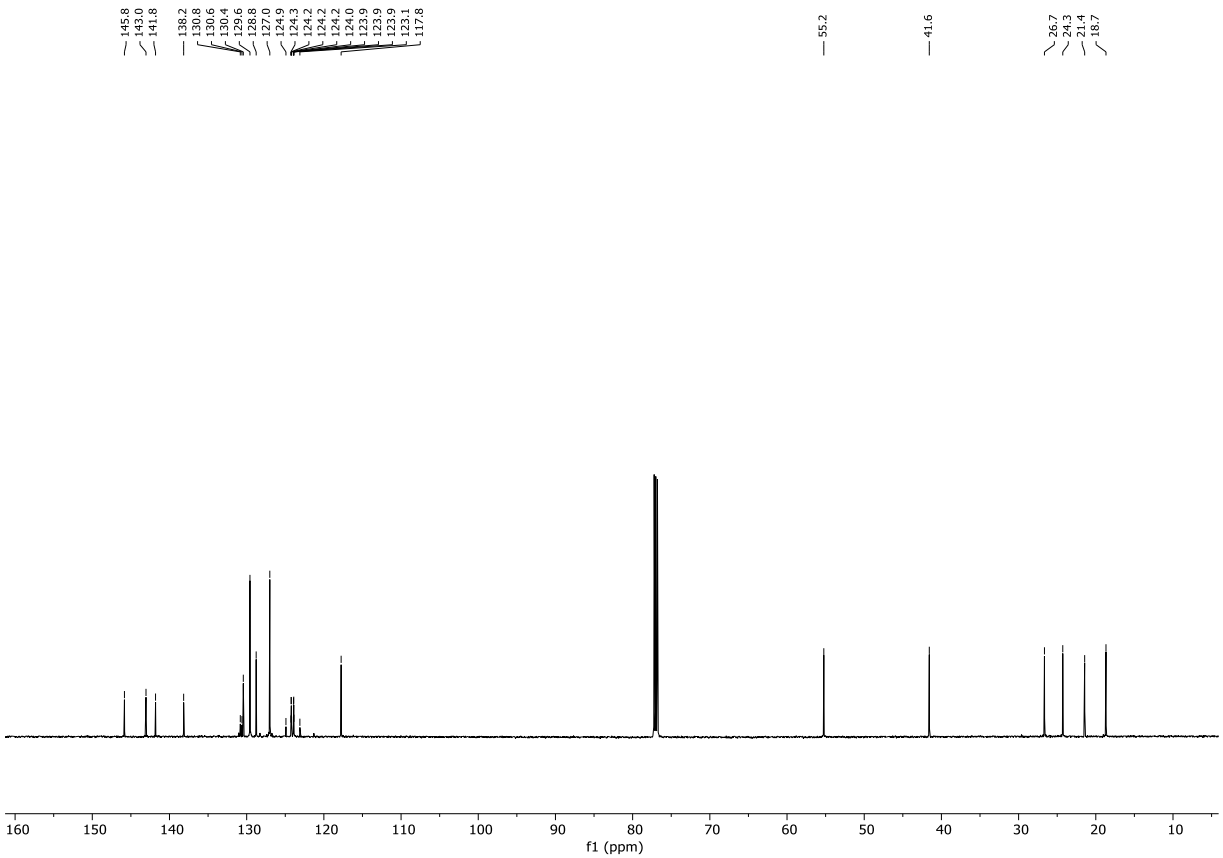
^{19}F-NMR of compound 5k (600 MHz, $CDCl_3$)



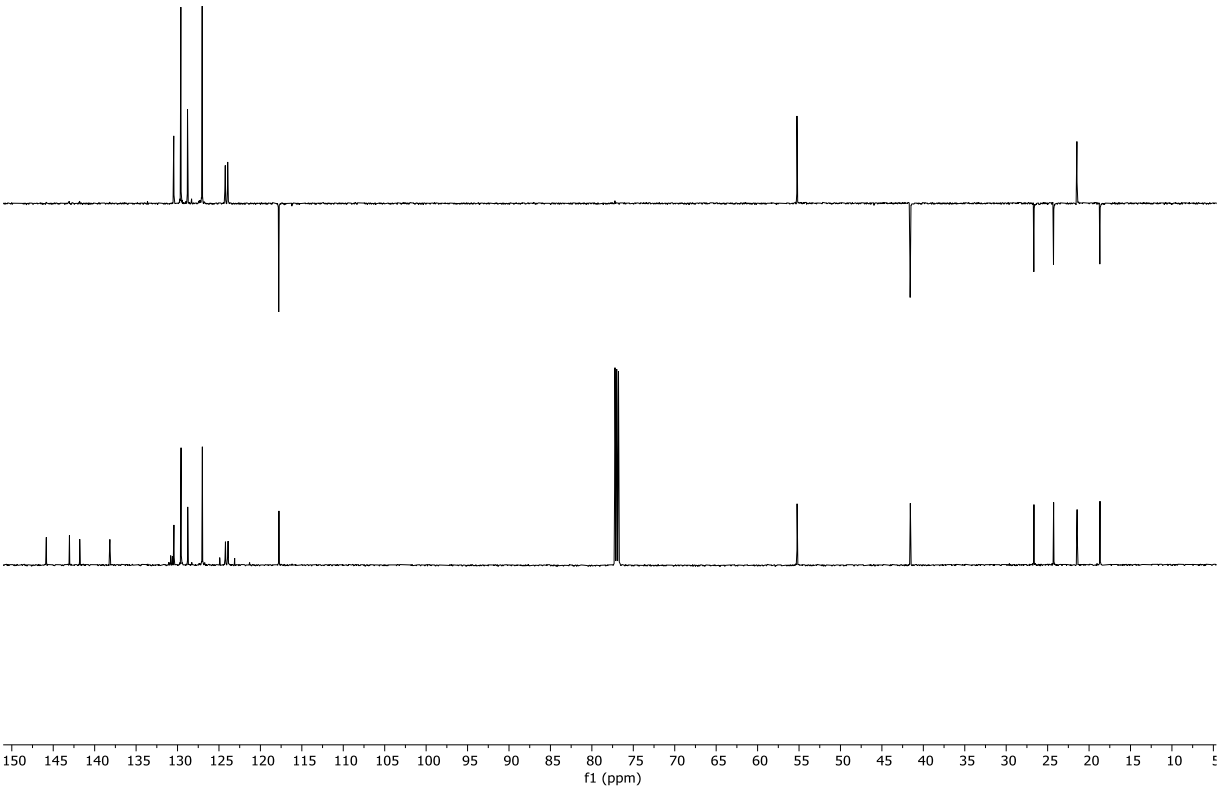
^{1}H-NMR of compound 5l (600 MHz, $CDCl_3$)



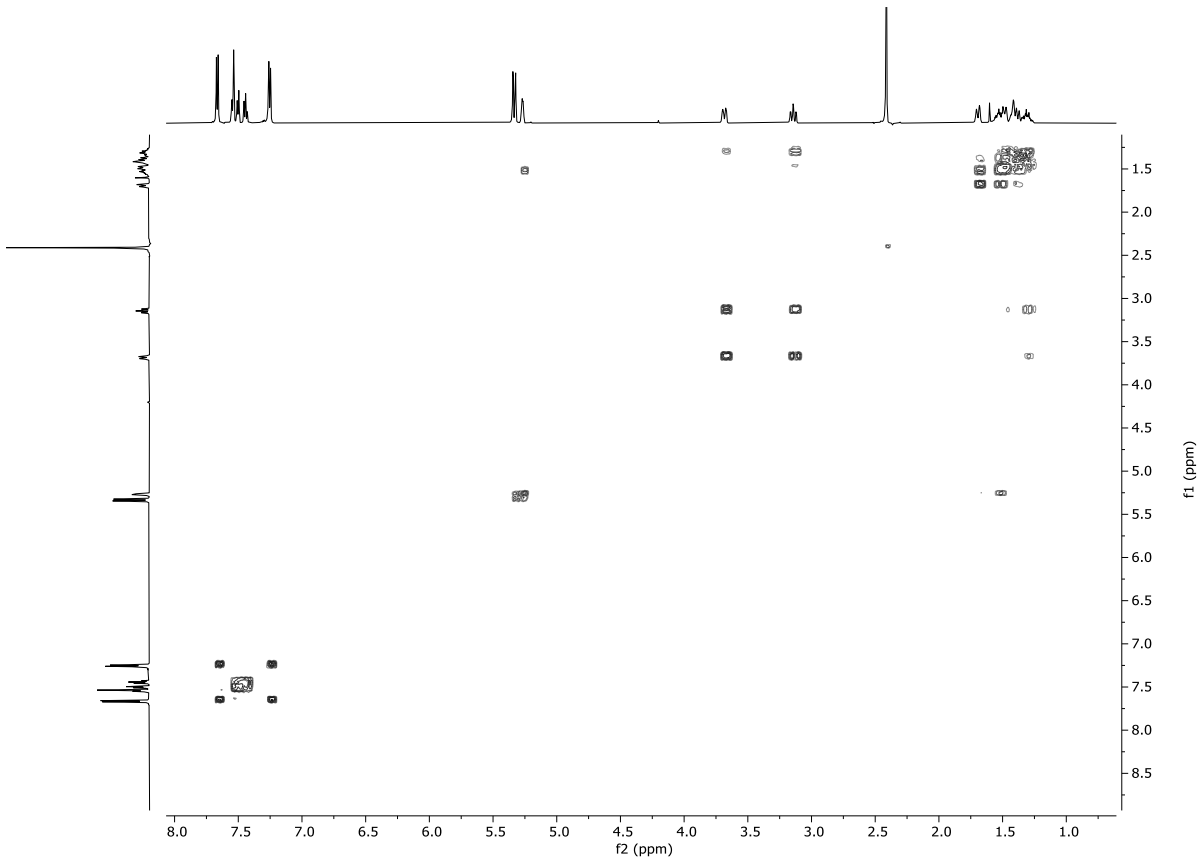
^{13}C-NMR of compound 5l (150 MHz, $CDCl_3$)



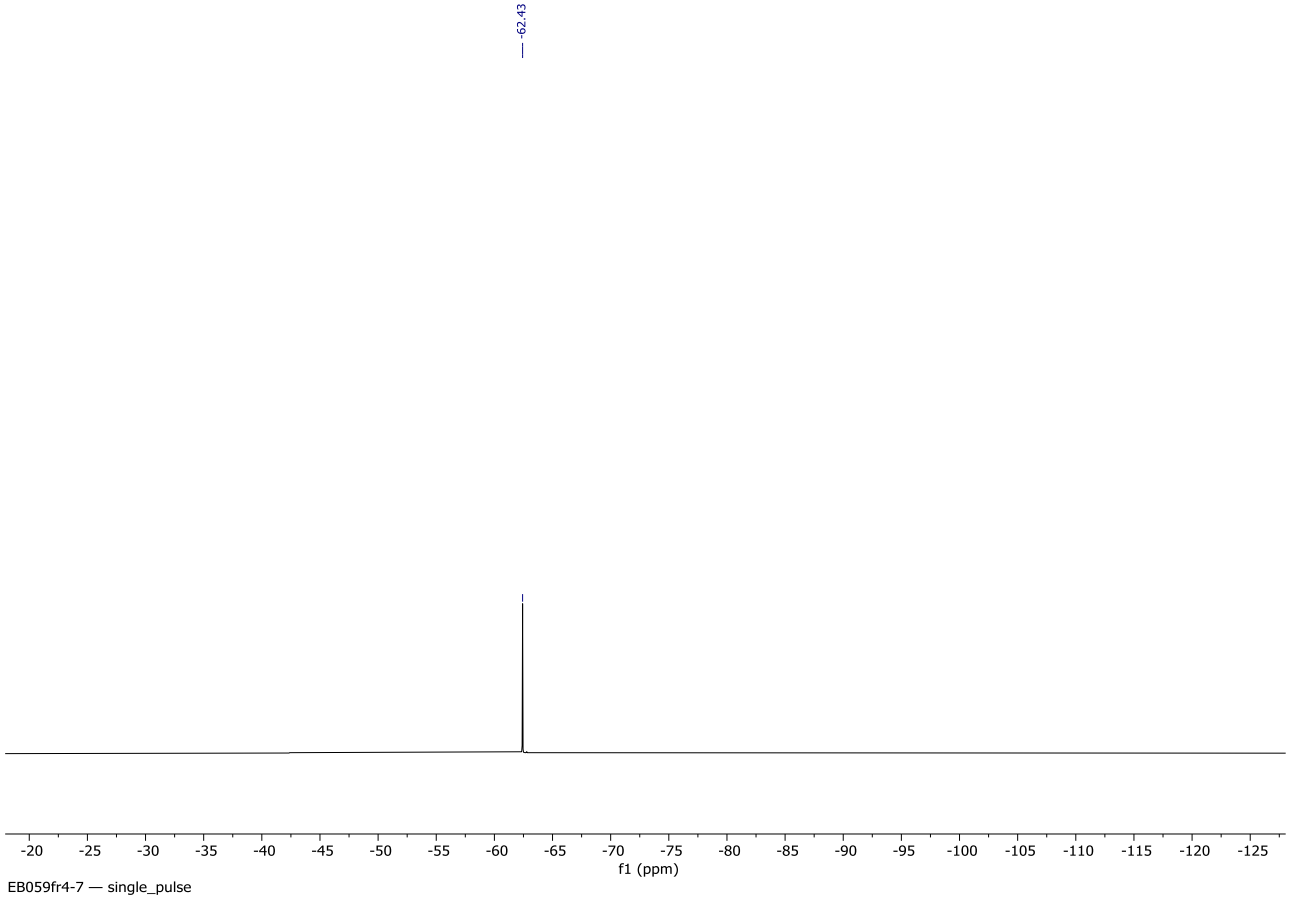
Comparison between DEPT-135 and ^{13}C-NMR of compound 5l (150 MHz, $CDCl_3$)



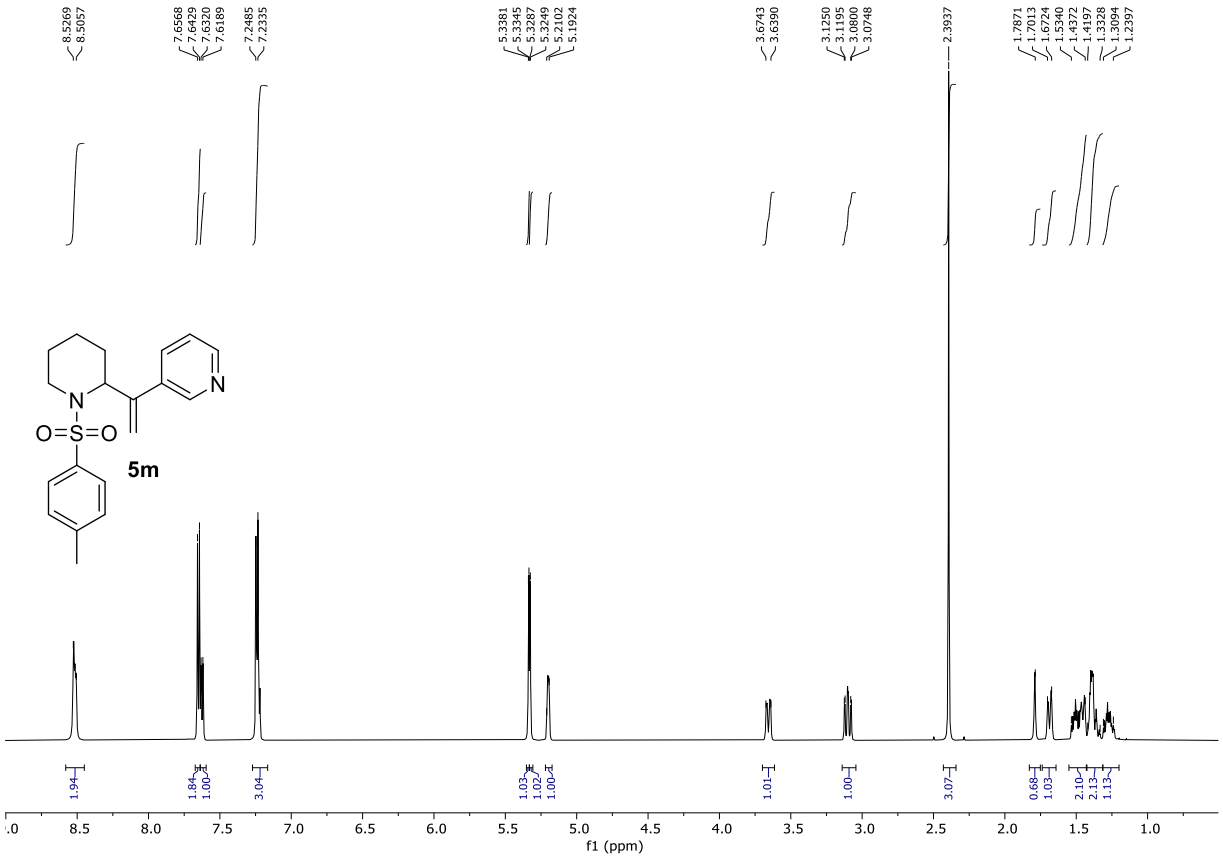
COSY-NMR of compound 5l (600 MHz, $CDCl_3$)



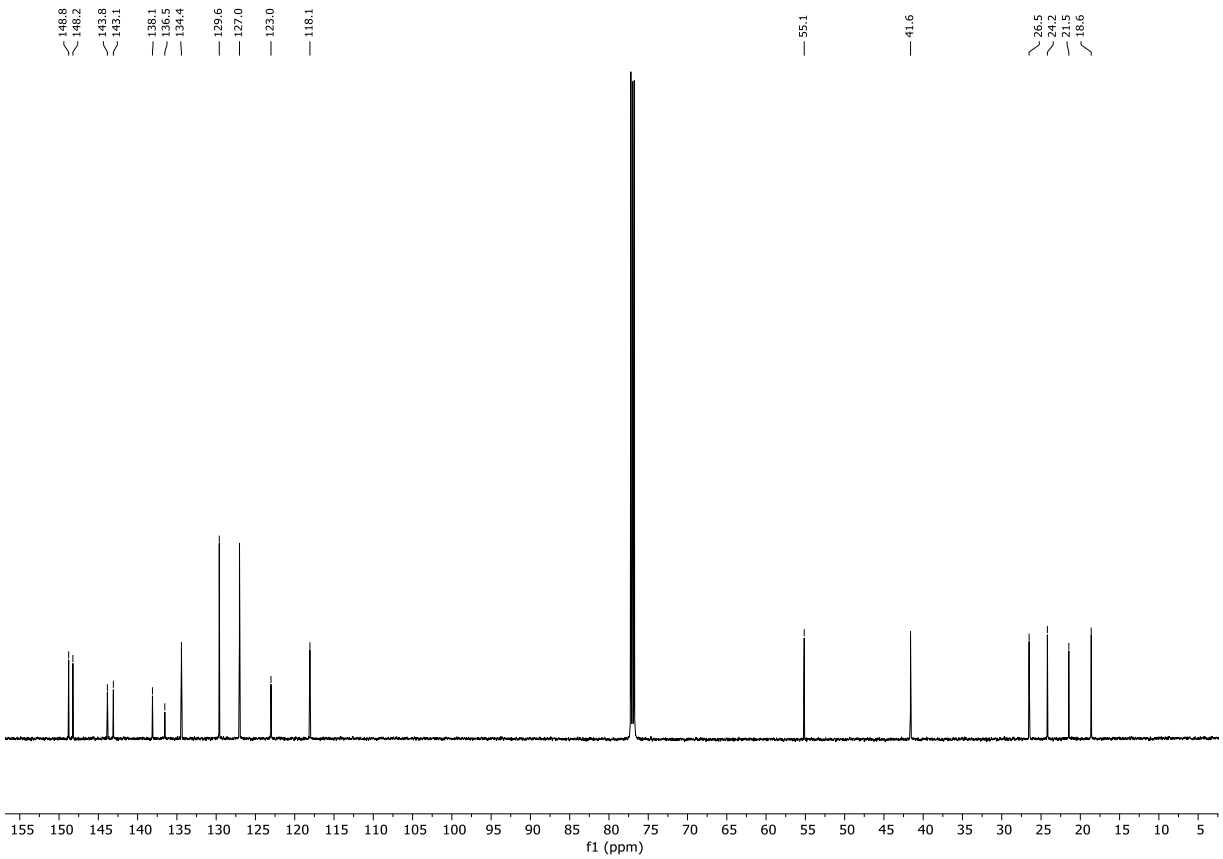
^{19}F-NMR of compound 5l (600 MHz, $CDCl_3$)



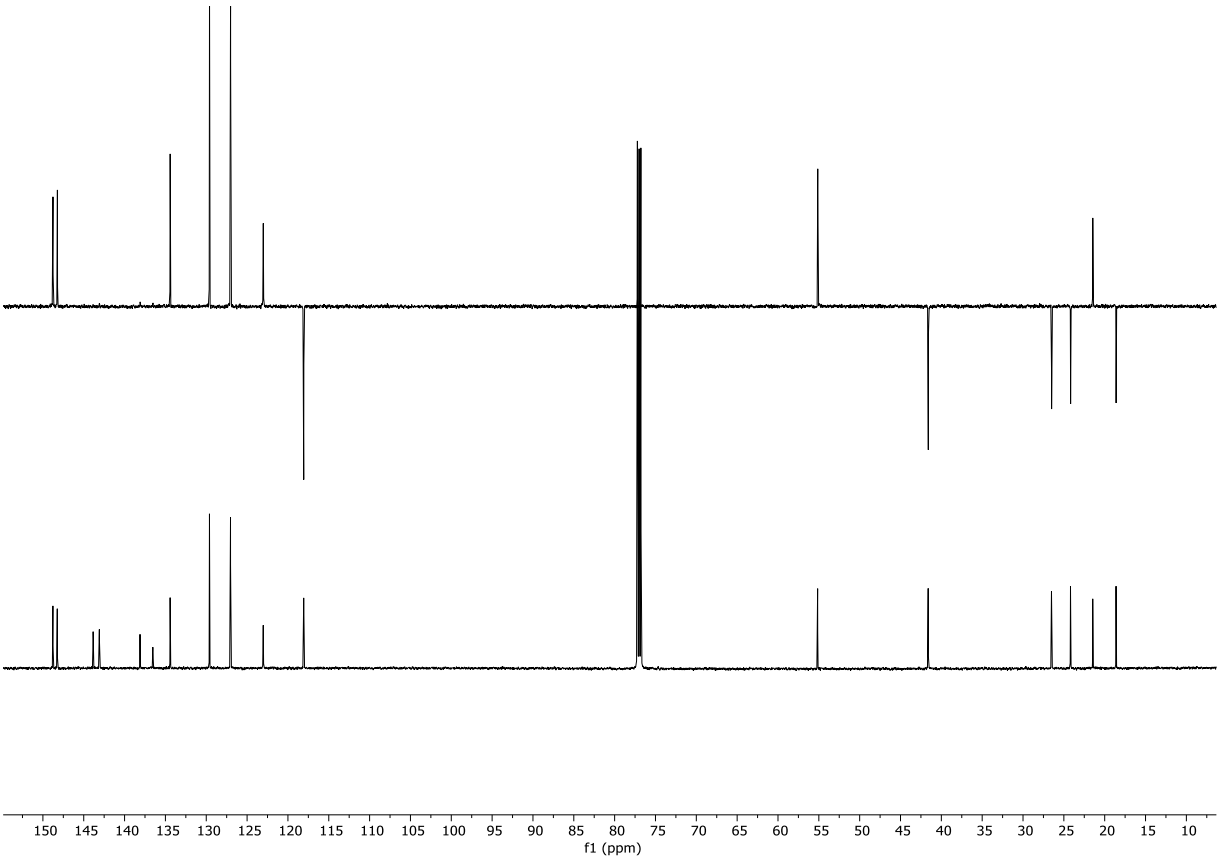
^{1}H-NMR of compound 5m (600 MHz, $CDCl_3$)



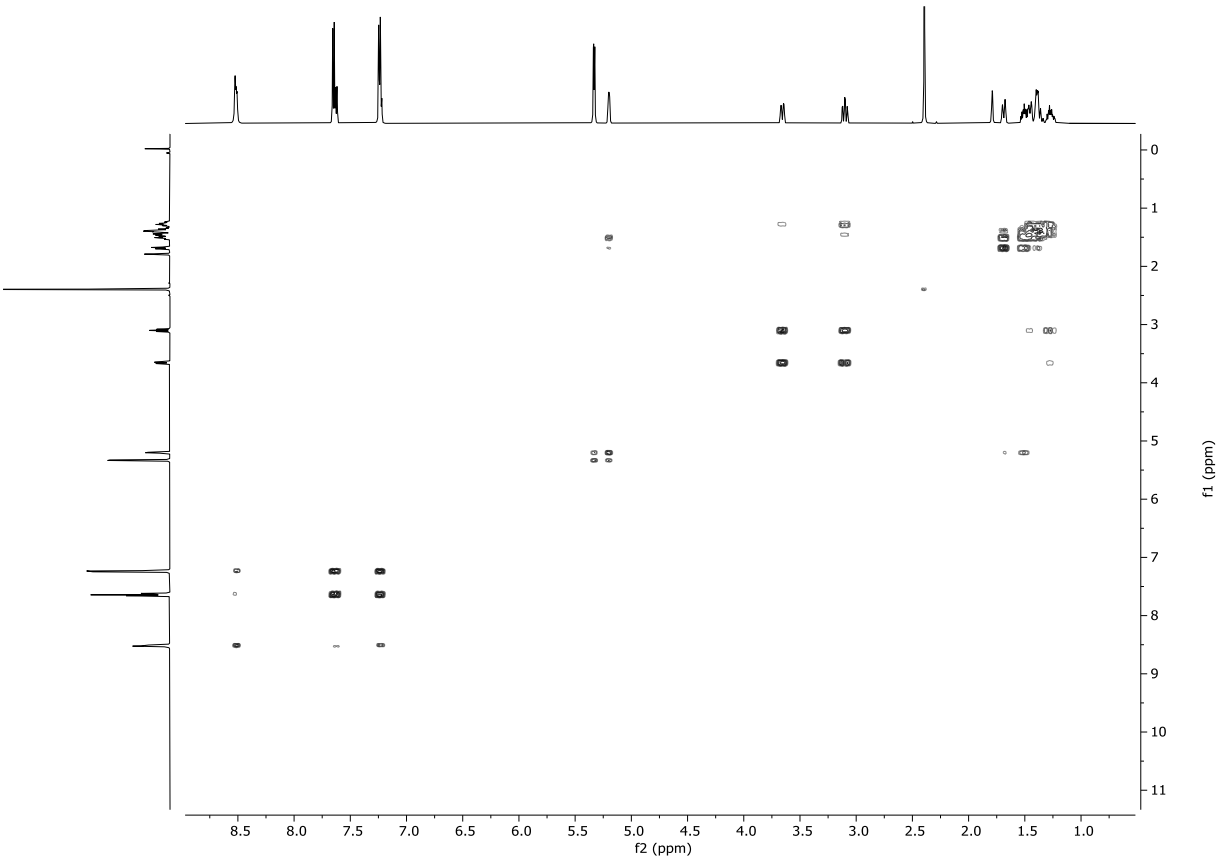
^{13}C-NMR of compound 5m (150 MHz, $CDCl_3$)



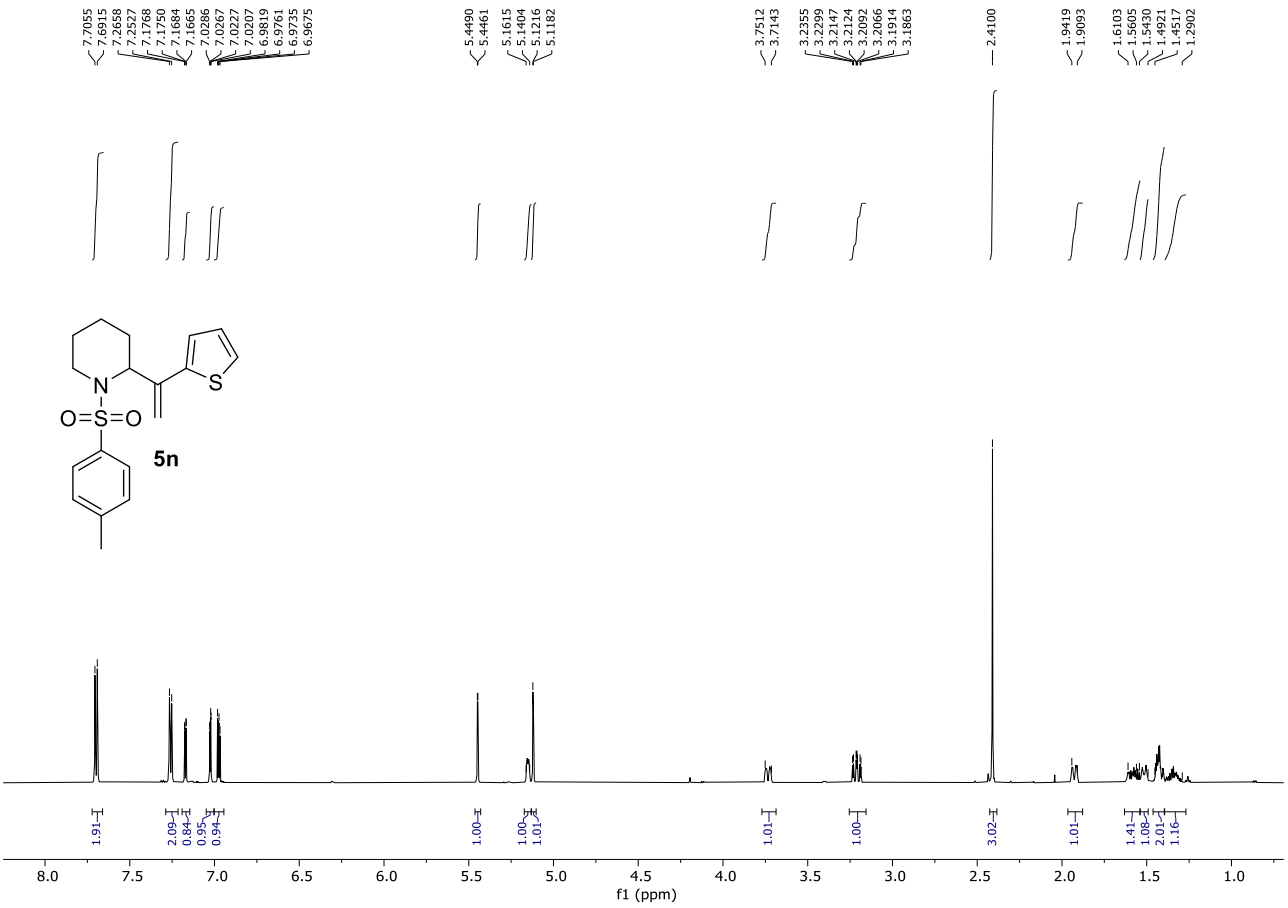
Comparison between DEPT-135 and ^{13}C-NMR of compound 5m (150 MHz, $CDCl_3$)



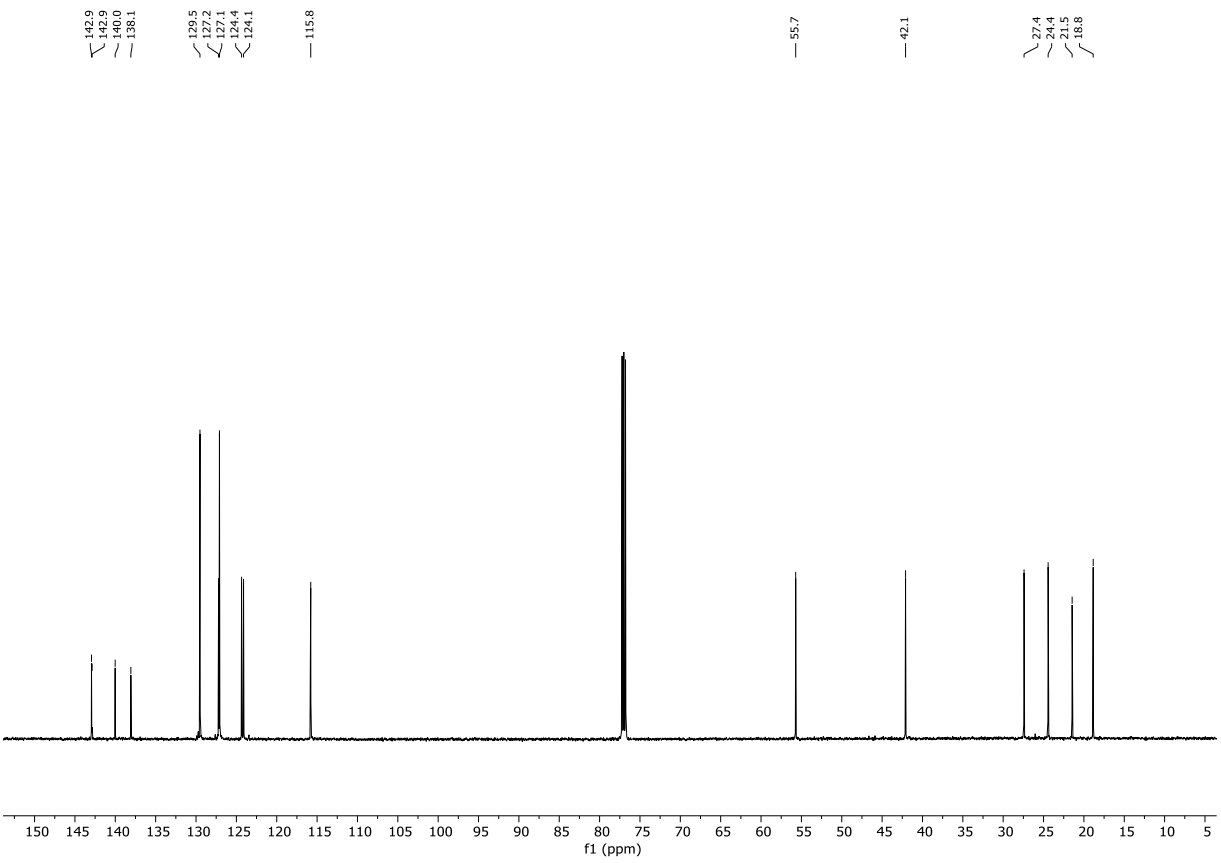
COSY-NMR of compound 5m (600 MHz, $CDCl_3$)



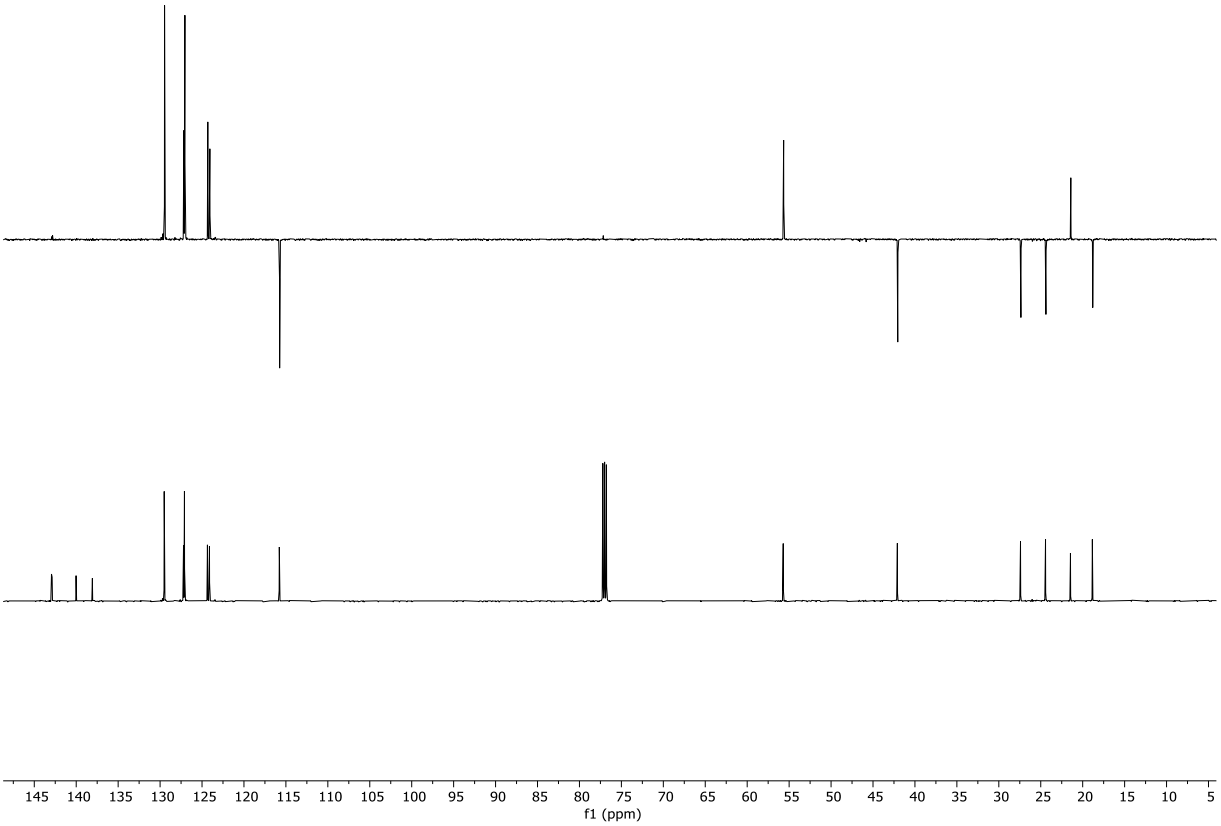
^{1}H-NMR of compound 5n (600 MHz, $CDCl_3$)



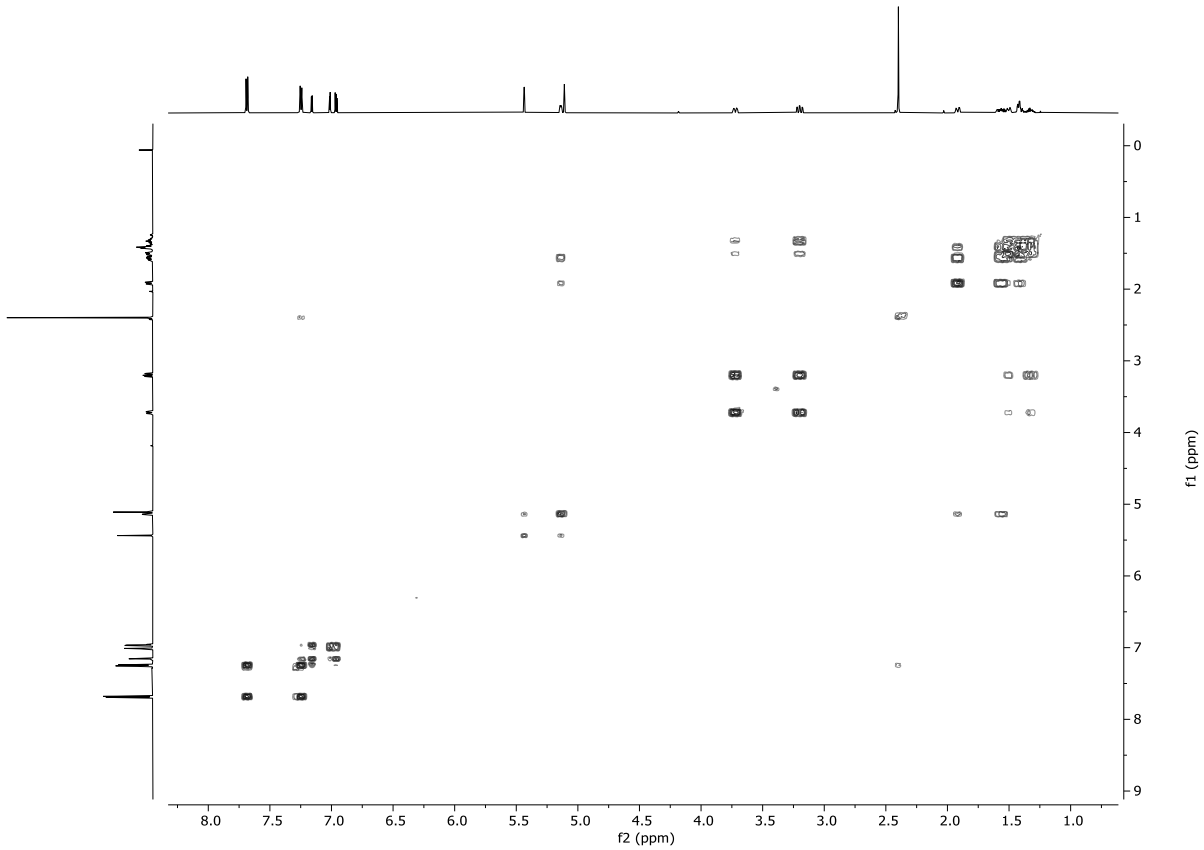
^{13}C-NMR of compound 5n (150 MHz, $CDCl_3$)



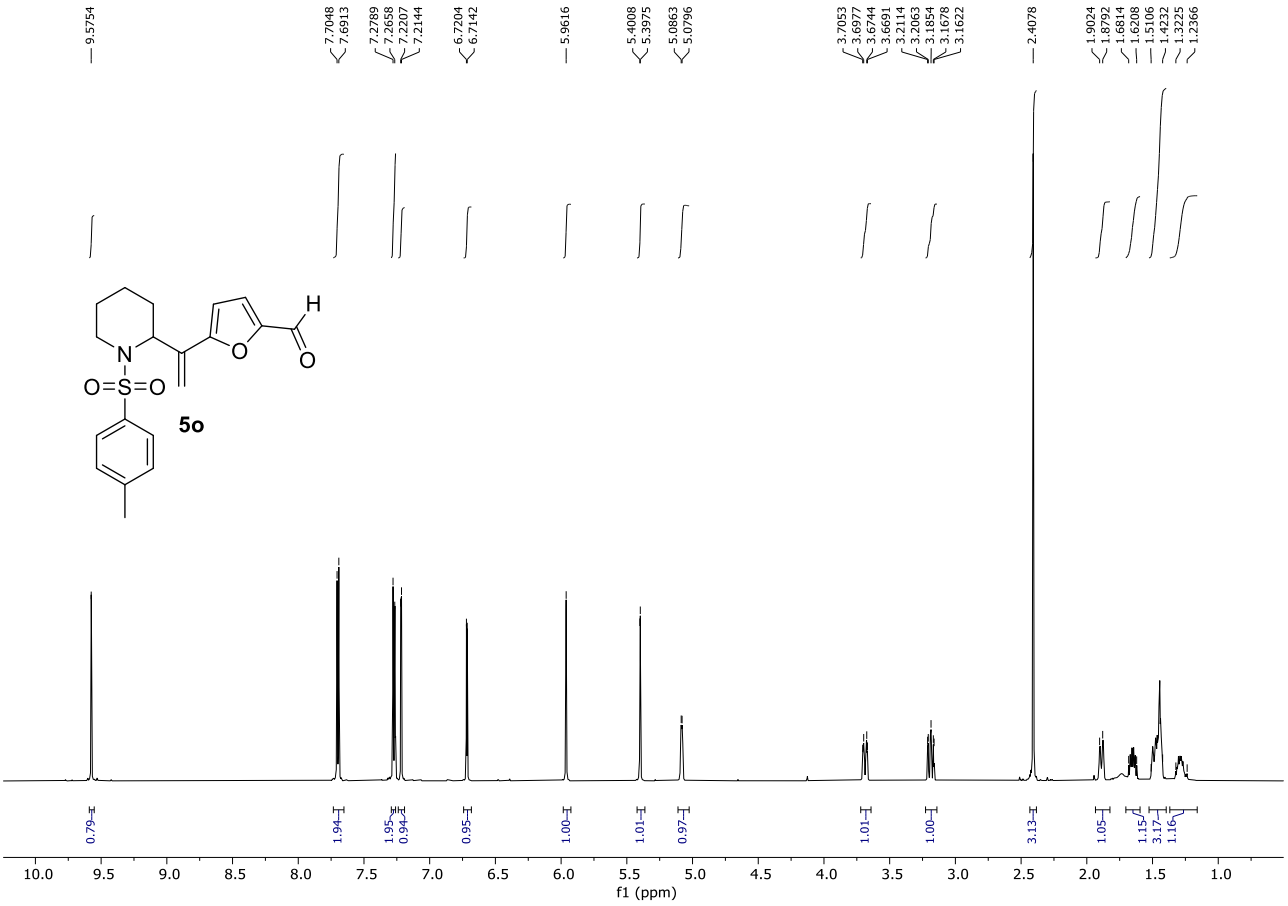
Comparison between DEPT-135 and ^{13}C-NMR of compound 5n (150 MHz, $CDCl_3$)



COSY-NMR of compound 5n (600 MHz, $CDCl_3$)

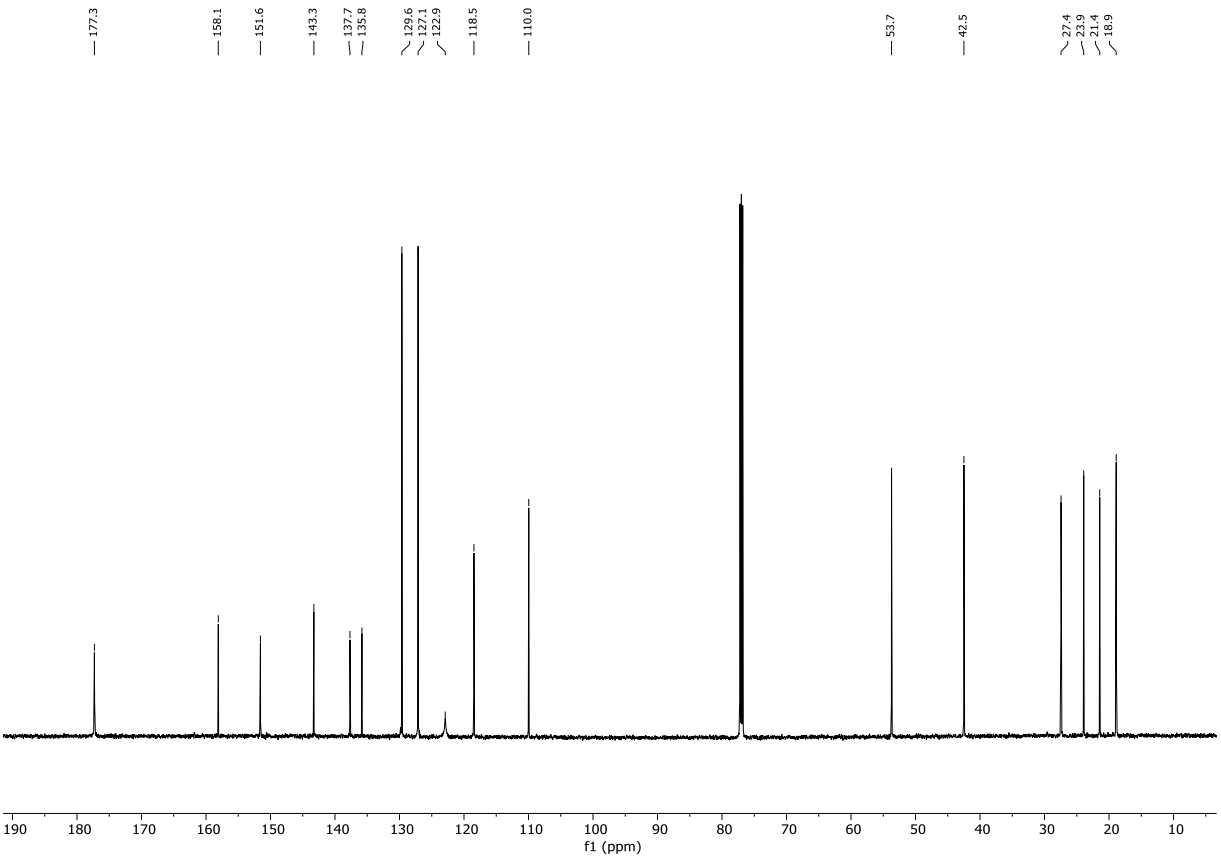


^{1}H-NMR of compound 5o (600 MHz, $CDCl_3$)

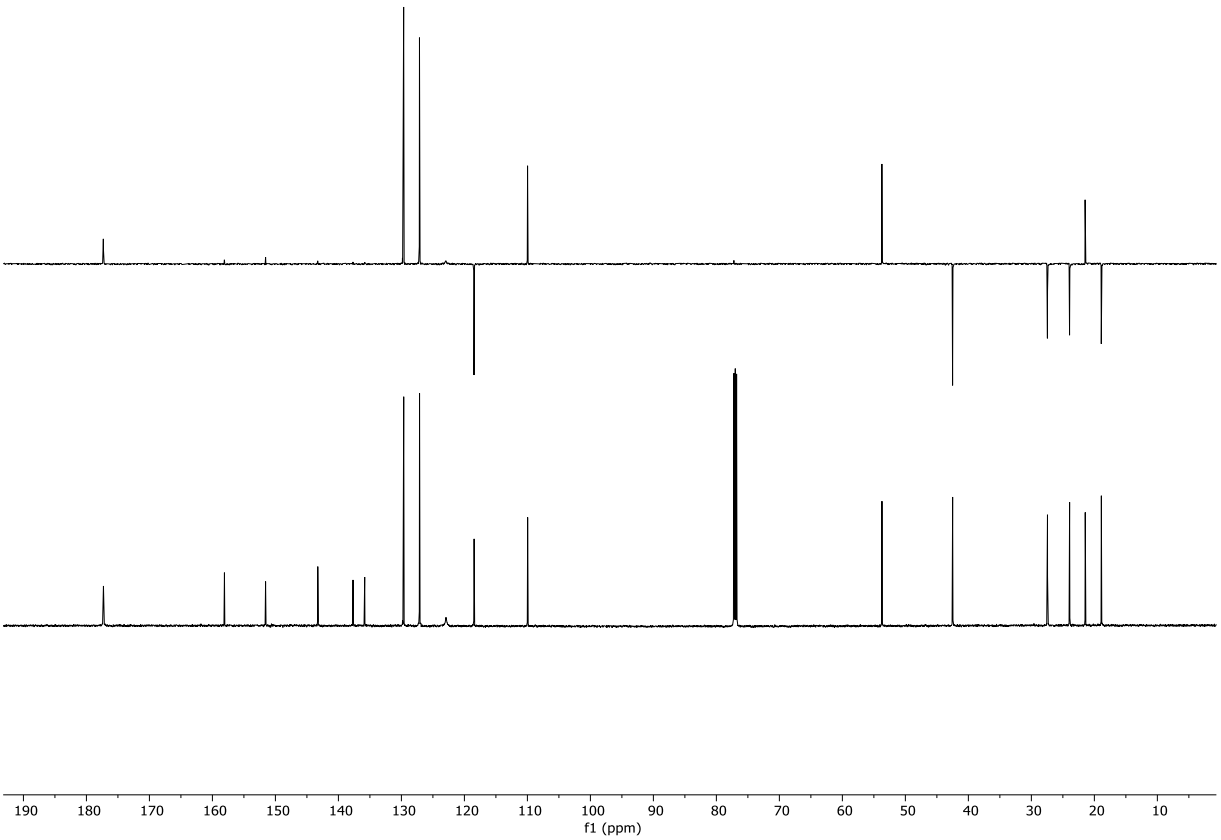


5o

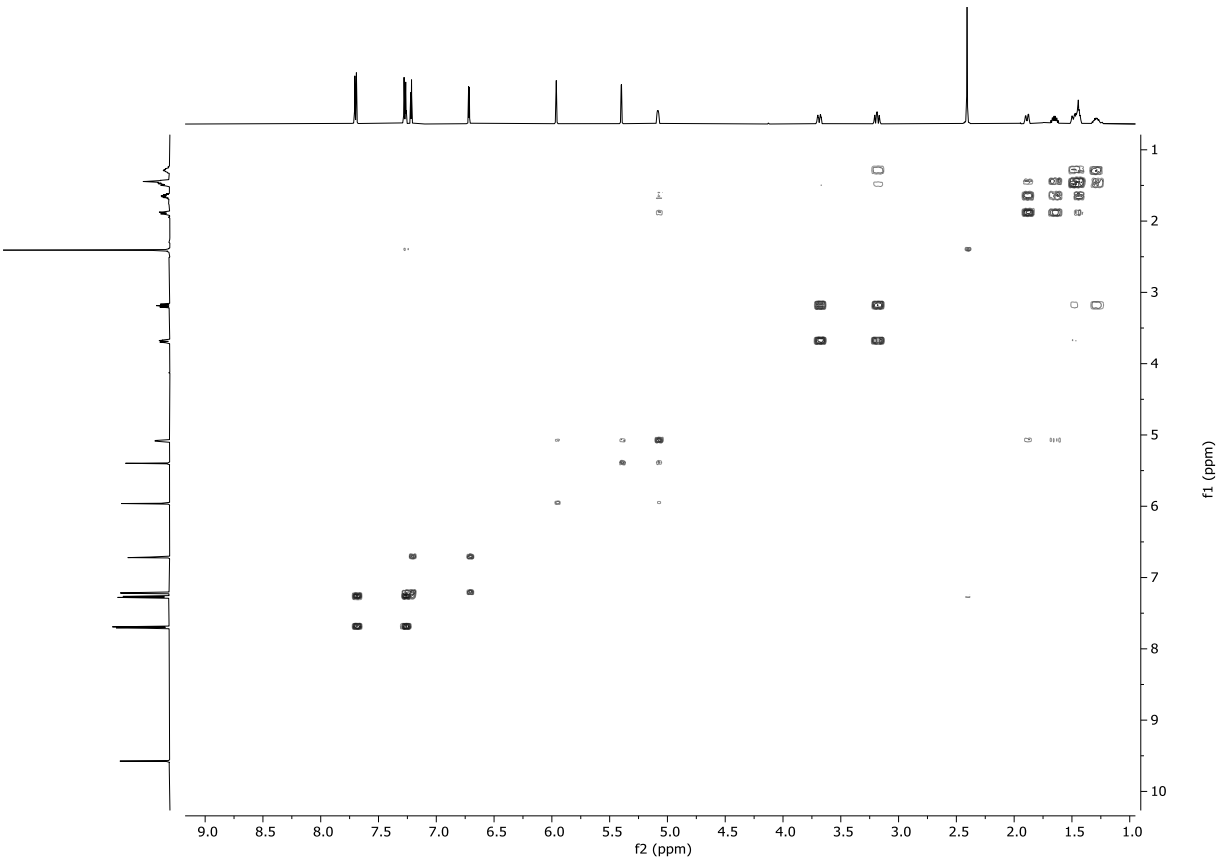
^{13}C-NMR of compound 5o (150 MHz, $CDCl_3$)



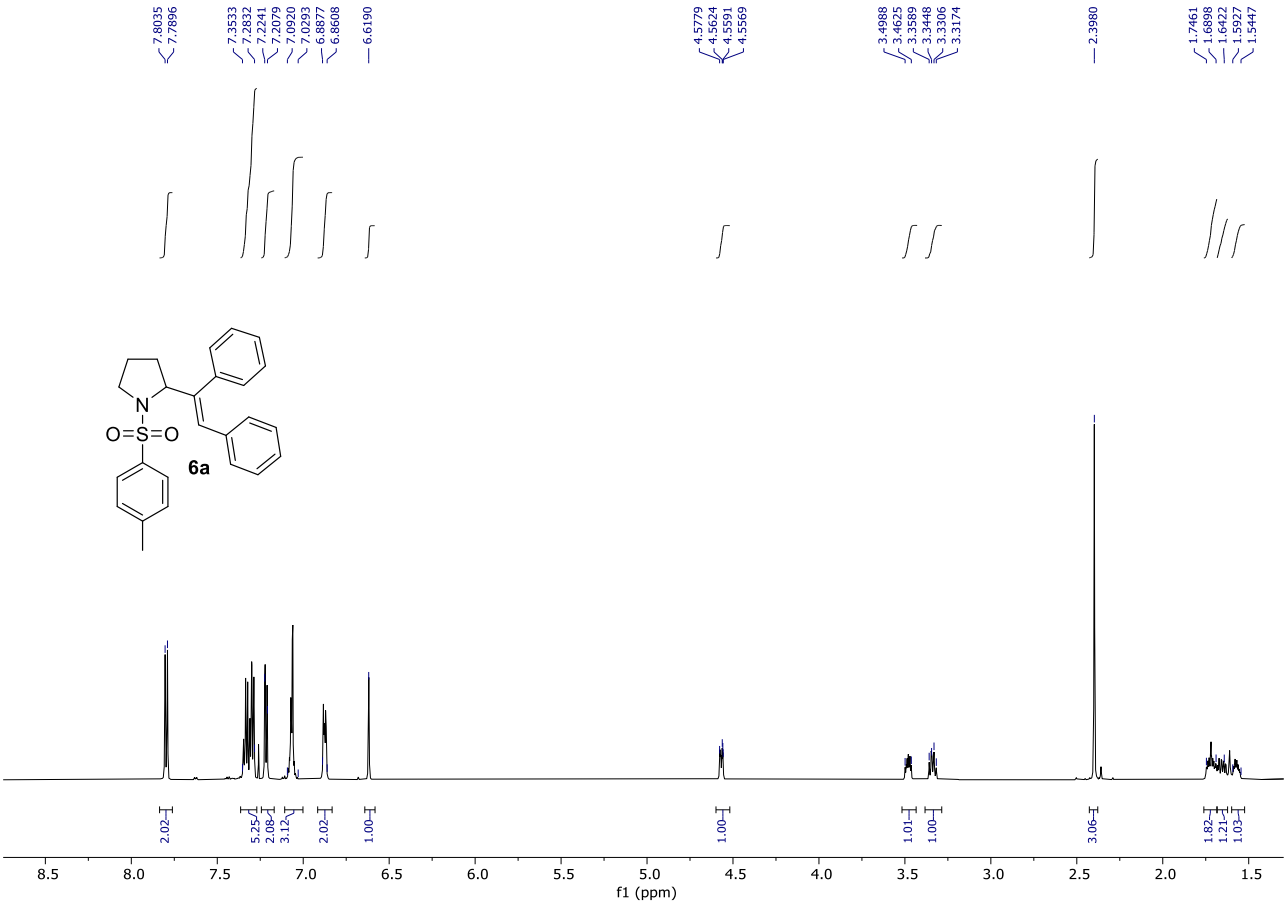
Comparison between DEPT-135 and ^{13}C-NMR of compound 5o (150 MHz, $CDCl_3$)



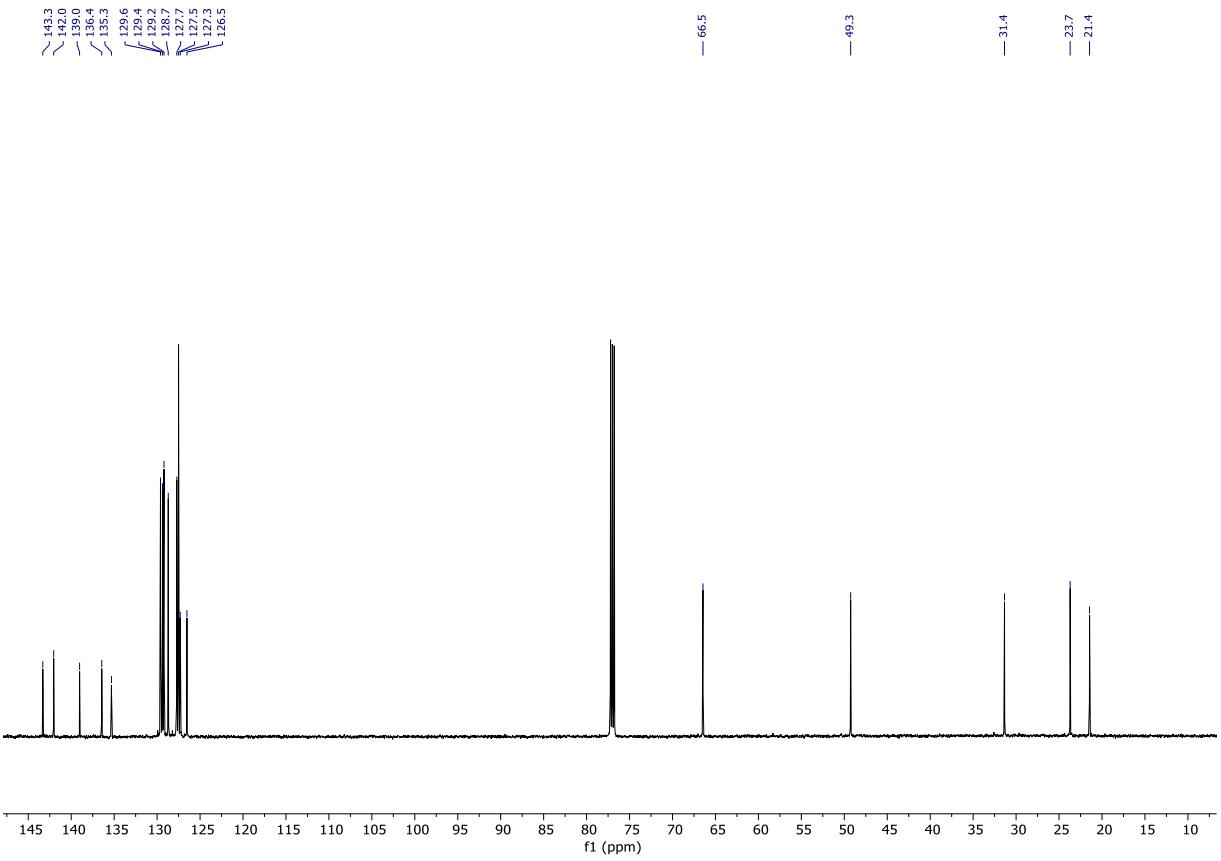
COSY-NMR of compound 5o (600 MHz, $CDCl_3$)



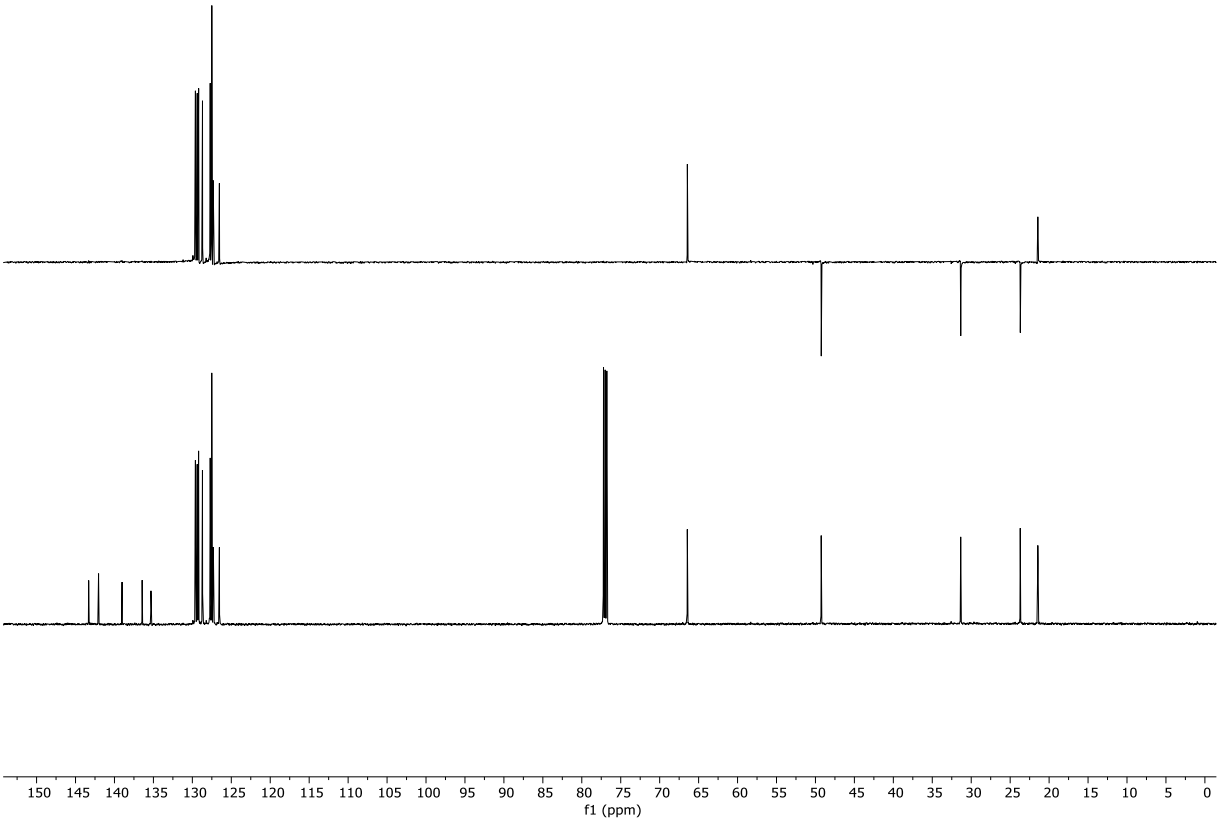
^{1}H-NMR of compound 6a (600 MHz, $CDCl_3$)



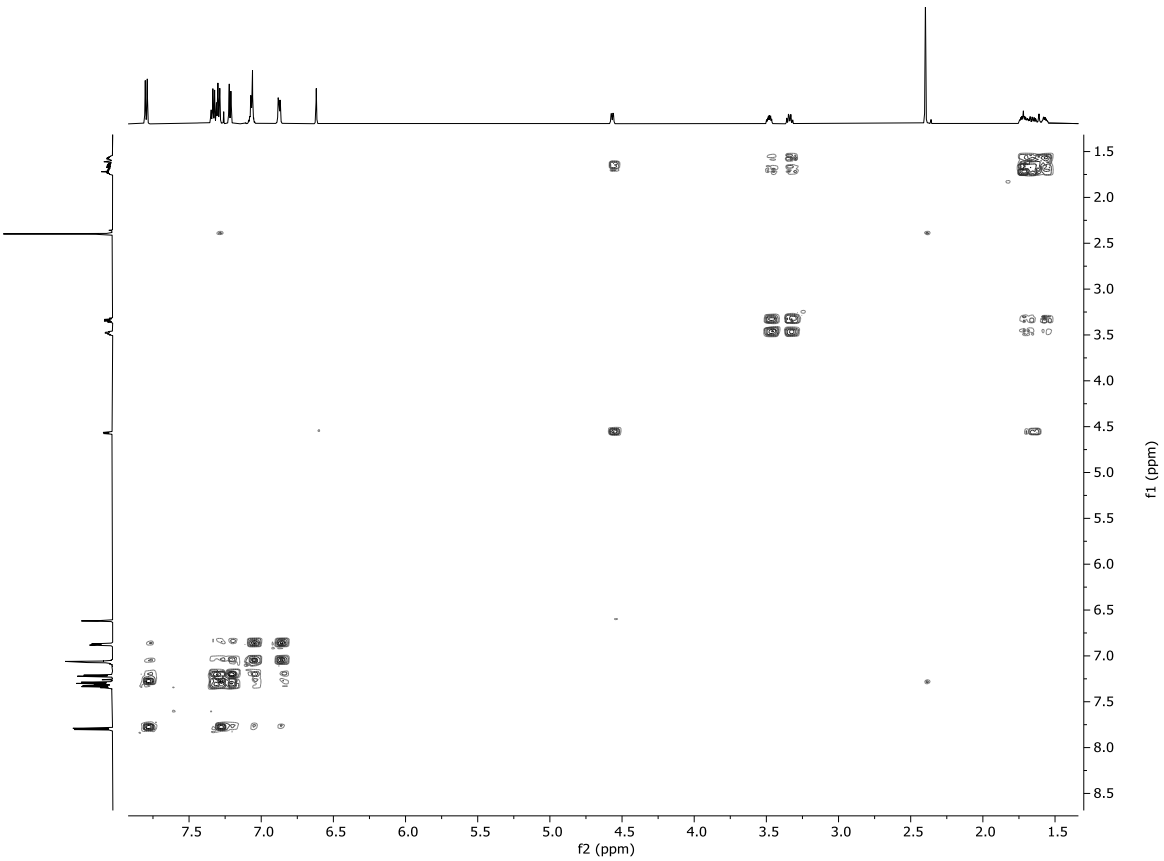
^{13}C-NMR of compound 6a (150 MHz, $CDCl_3$)



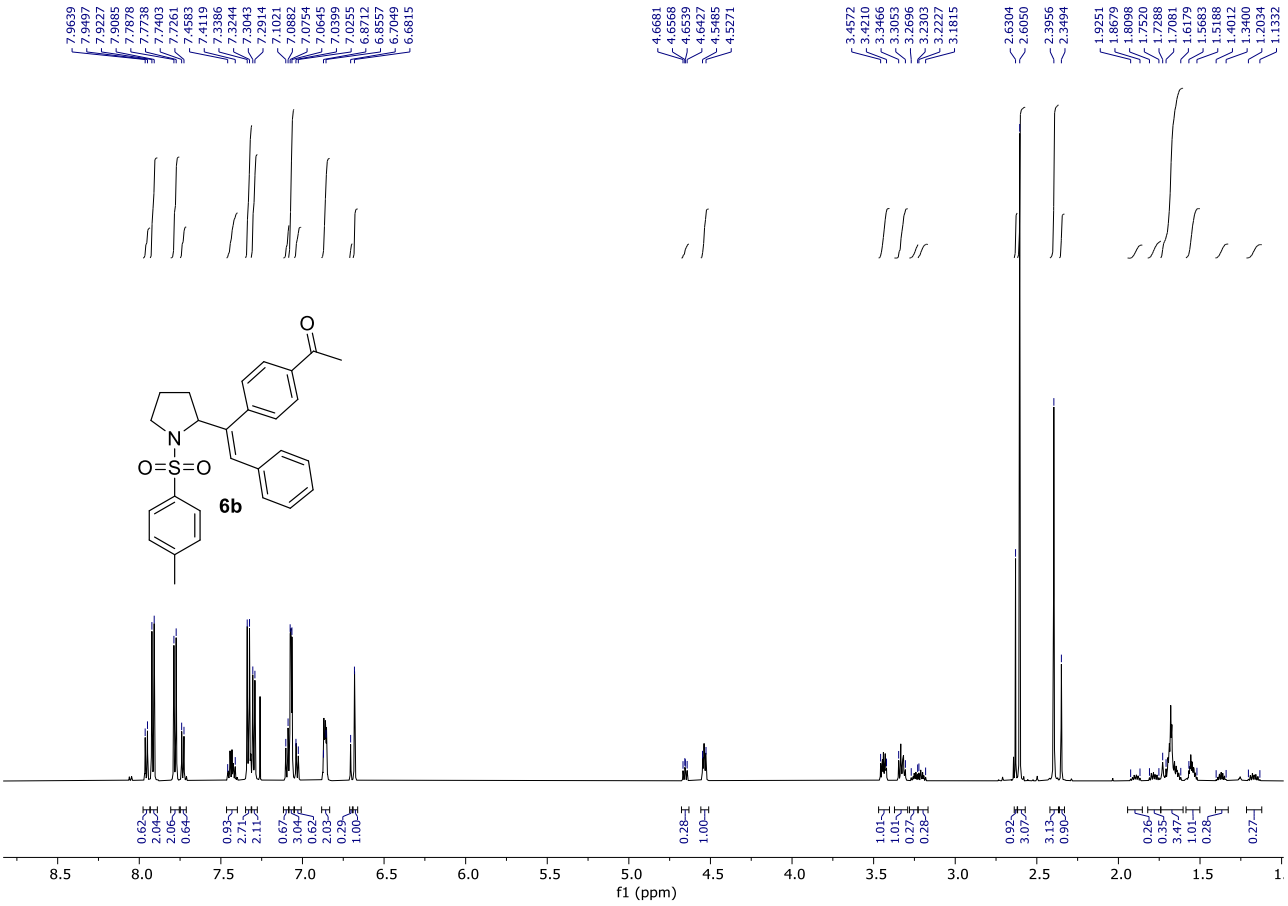
Comparison between DEPT-135 and ^{13}C-NMR of compound 6a (150 MHz, $CDCl_3$)



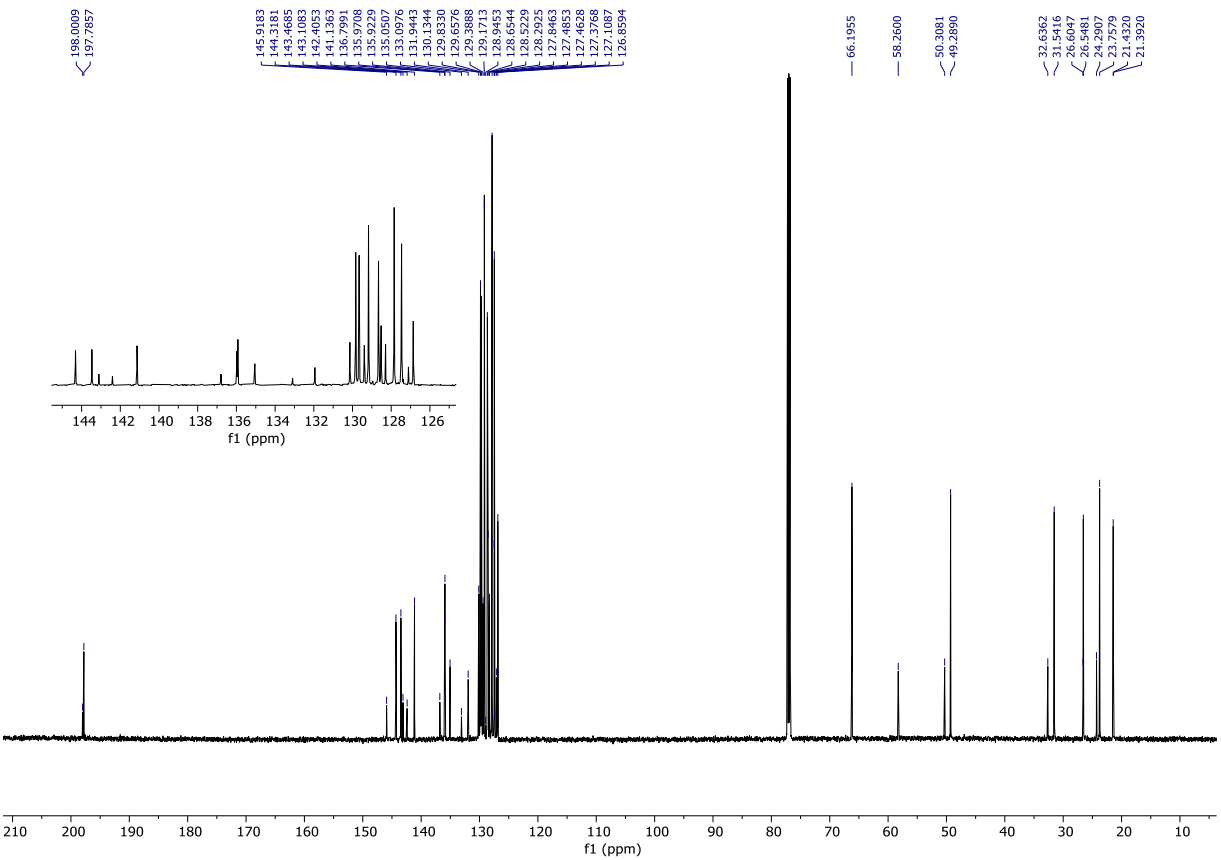
COSY-NMR of compound 6a (600 MHz, $CDCl_3$)



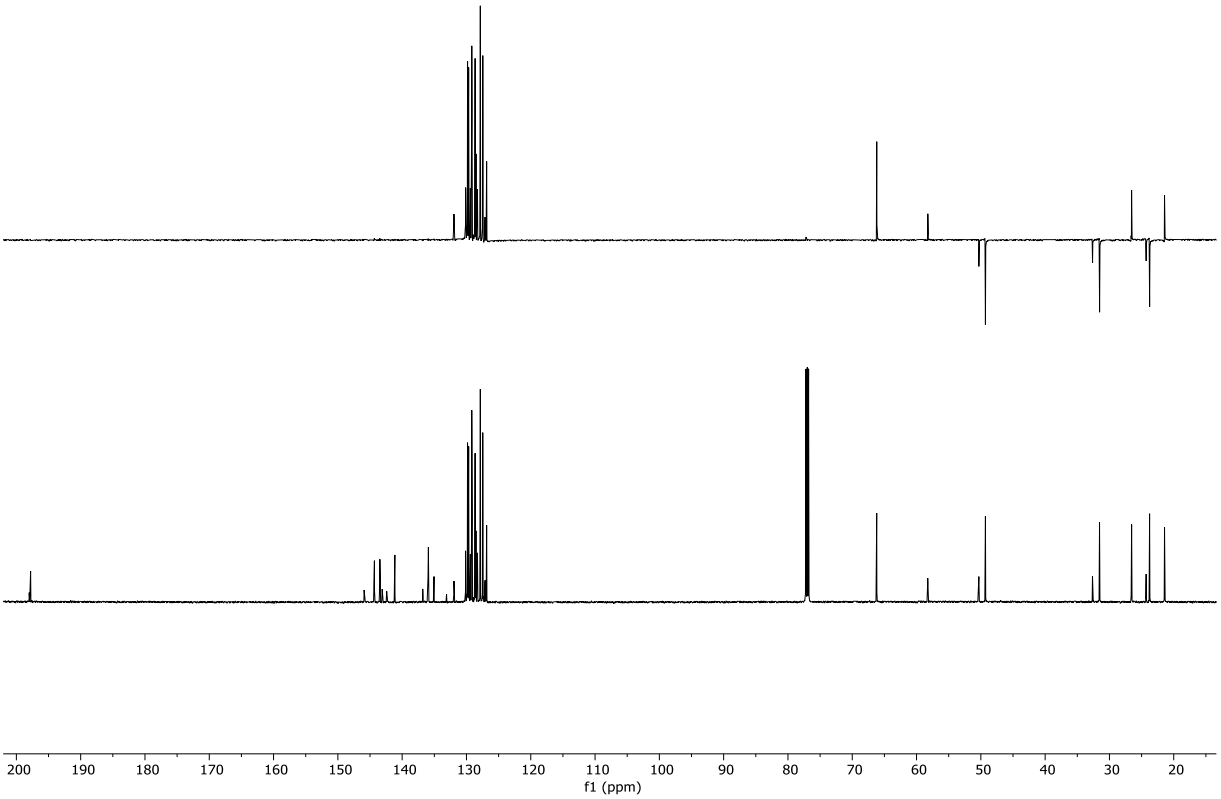
^{1}H-NMR of compound 6b (600 MHz, $CDCl_3$)



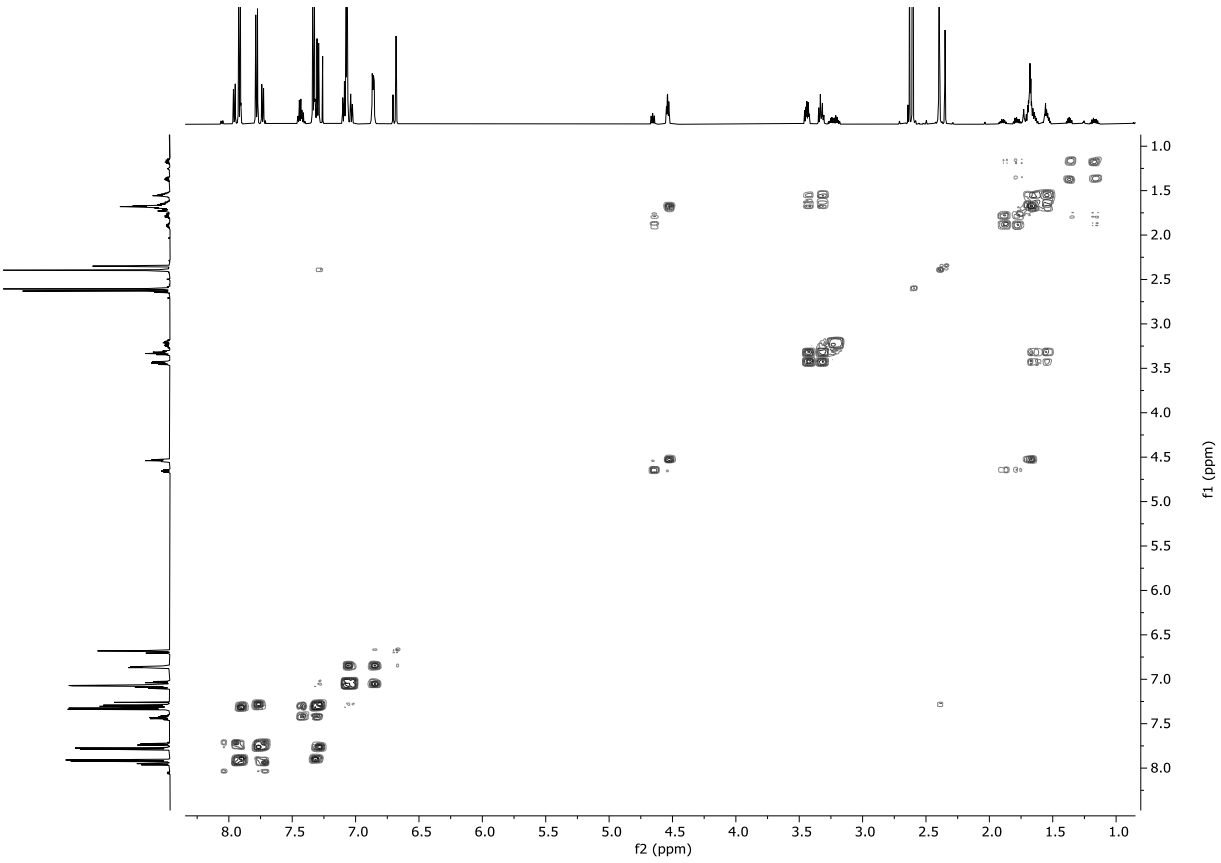
^{13}C-NMR of compound 6b (150 MHz,$CDCl_3$)



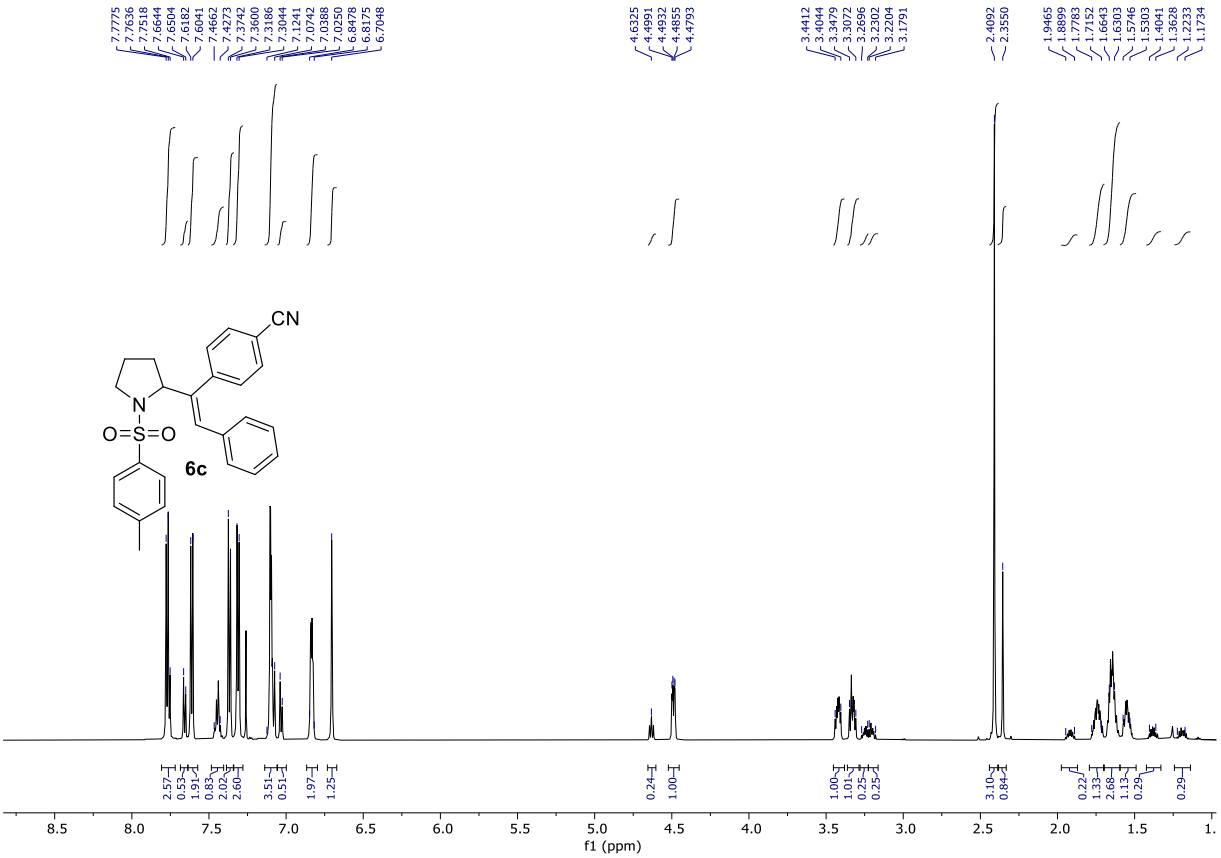
Comparison between DEPT-135 and ^{13}C-NMR of compound 6b (150 MHz, $CDCl_3$)



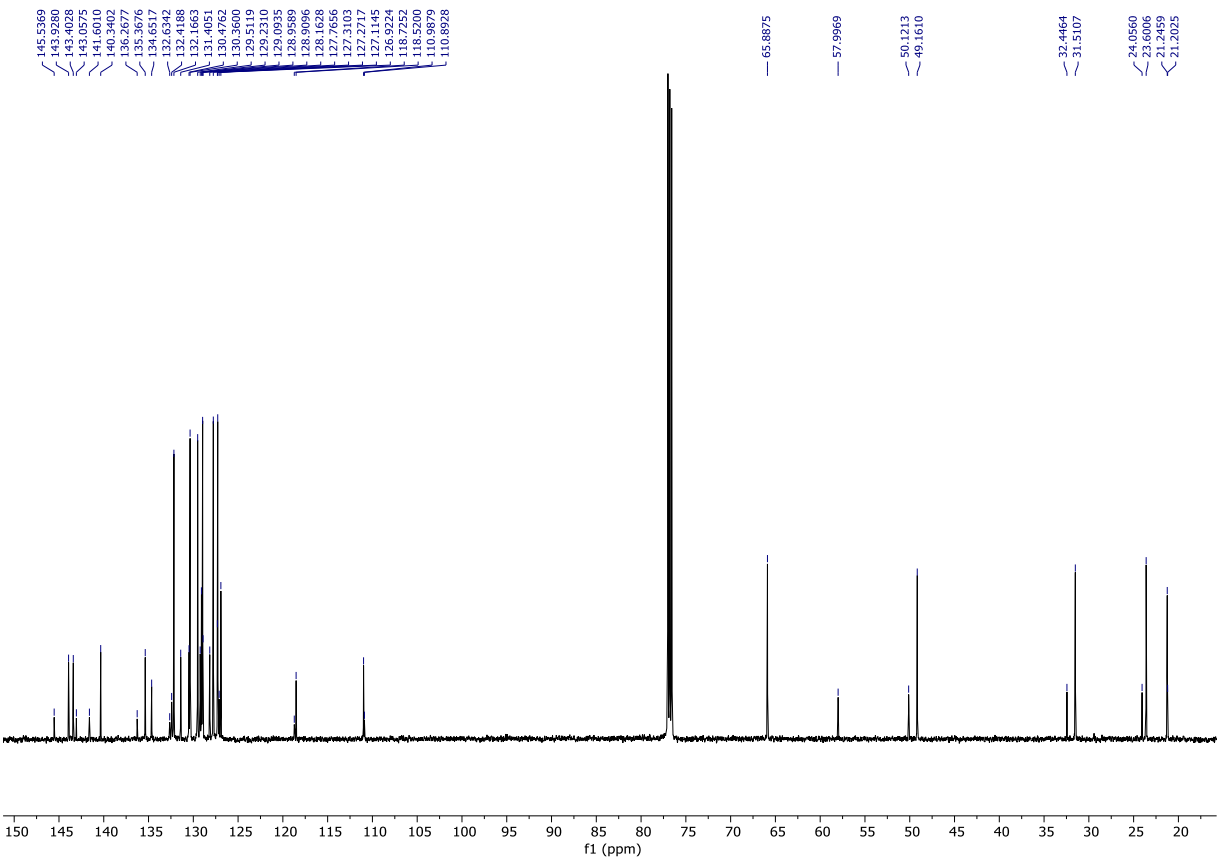
COSY-NMR of compound 6b (600 MHz, $CDCl_3$)



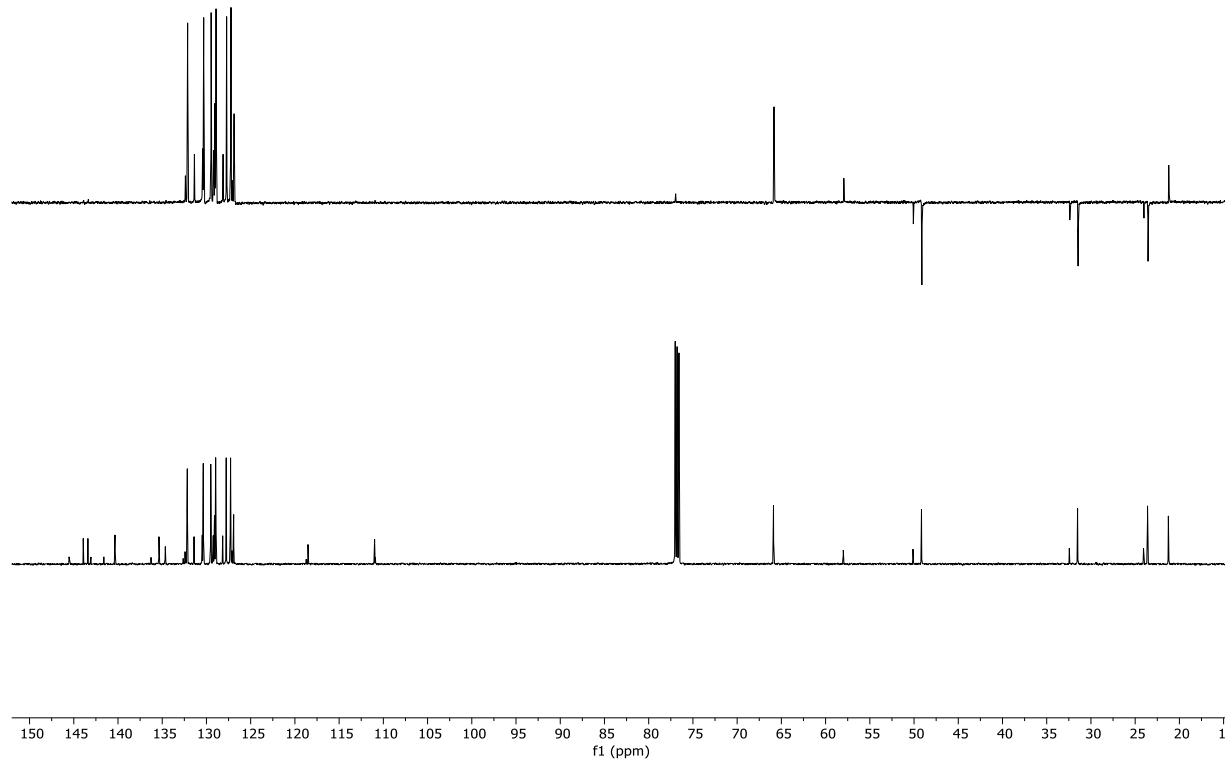
^{1}H-NMR of compound 6c (600 MHz, $CDCl_3$)



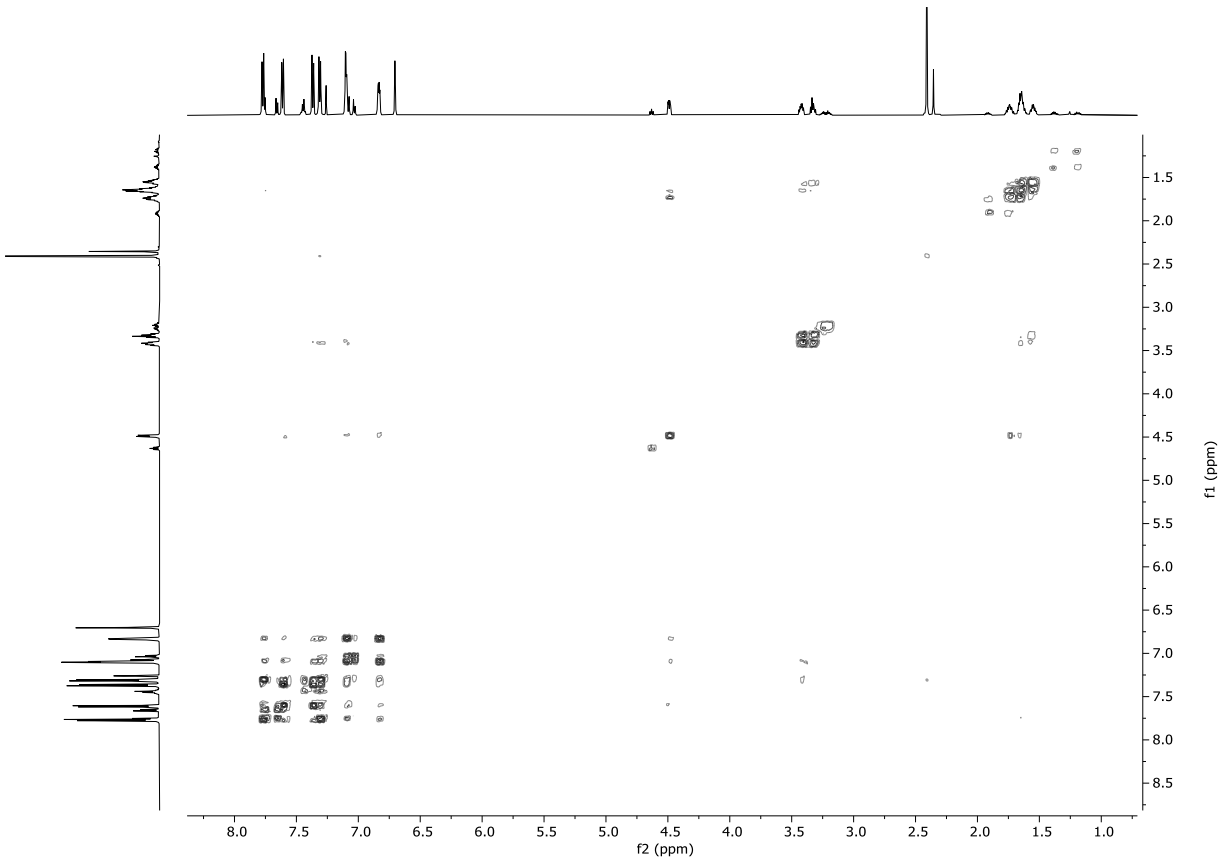
^{13}C-NMR of compound 6c (150 MHz ,$CDCl_3$)



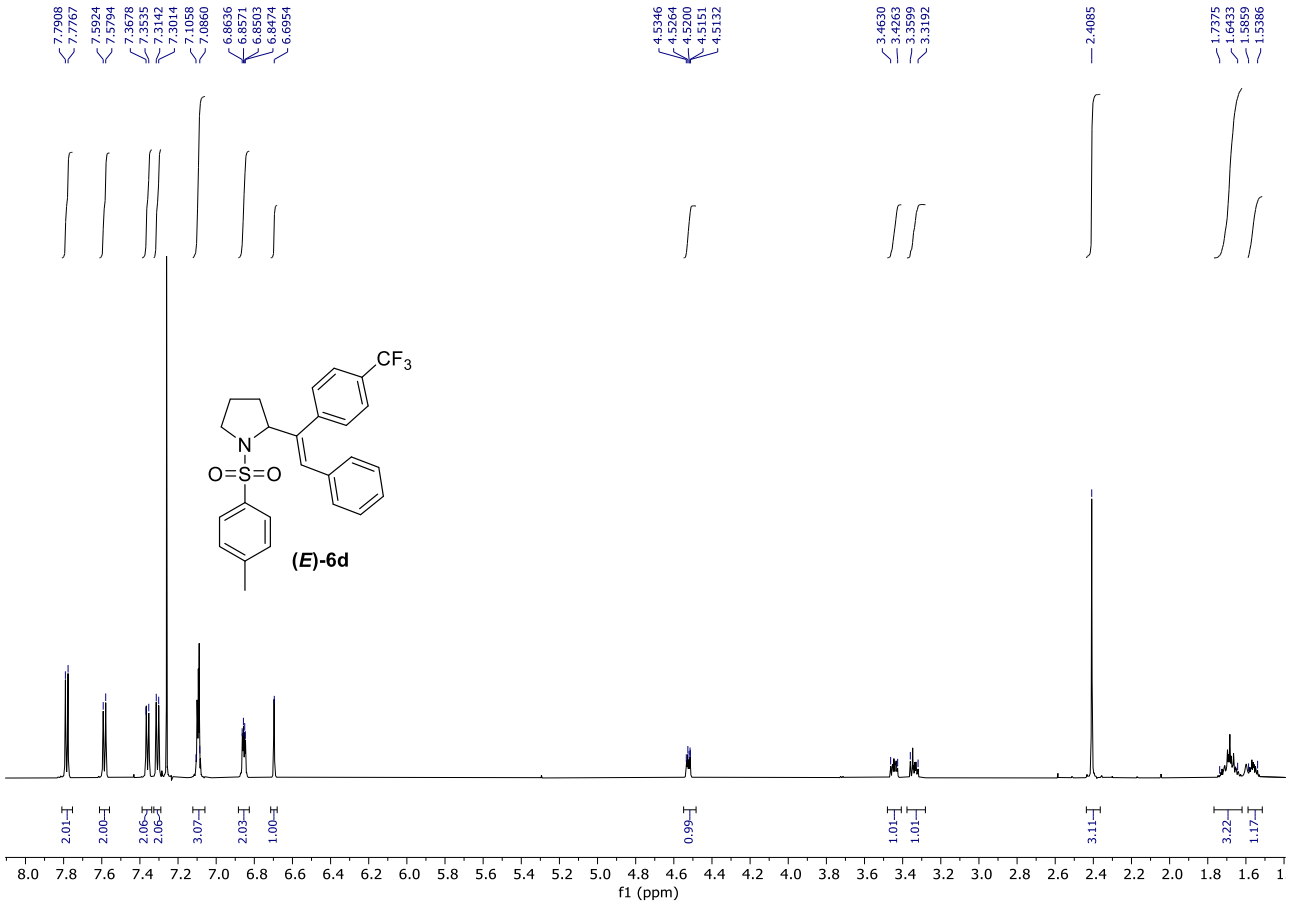
Comparison between DEPT-135 and ^{13}C-NMR of compound 6c (150 MHz, $CDCl_3$)



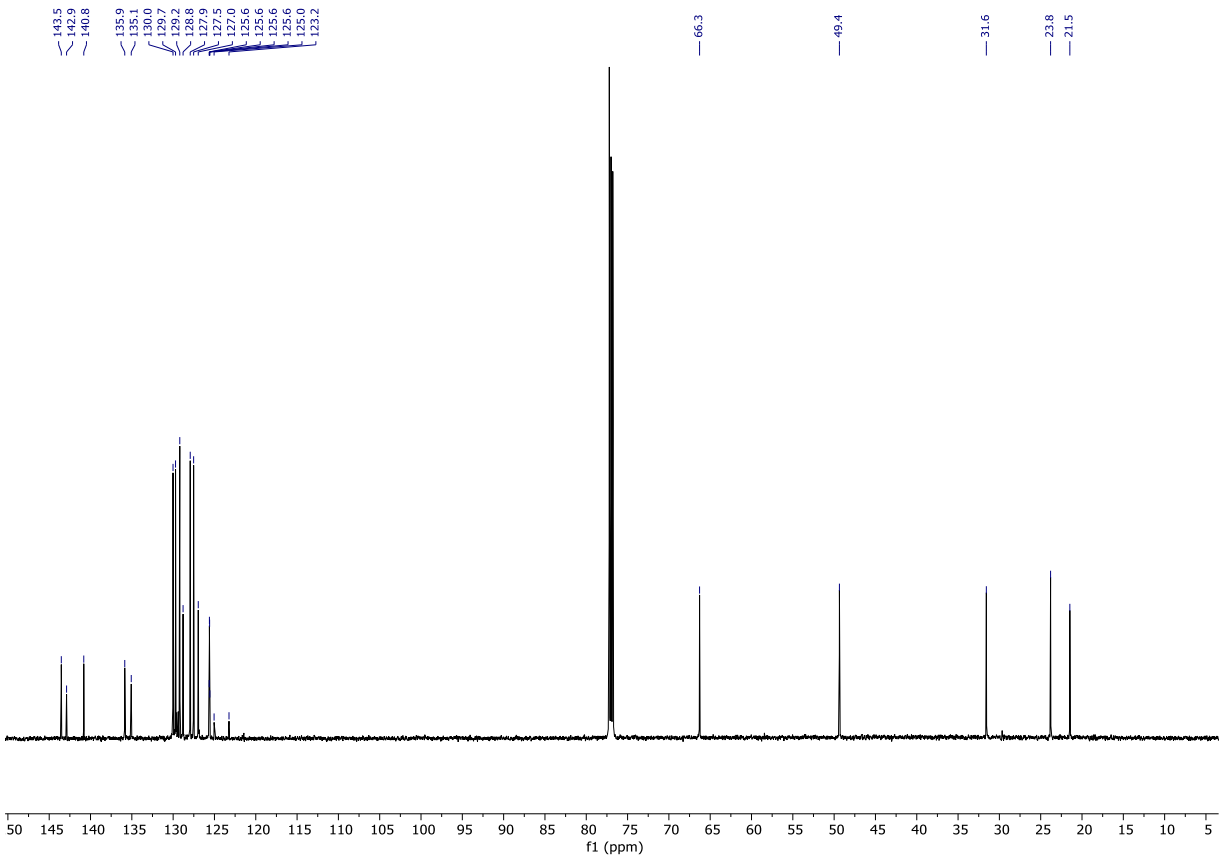
COSY-NMR of compound 6c (600 MHz, $CDCl_3$)



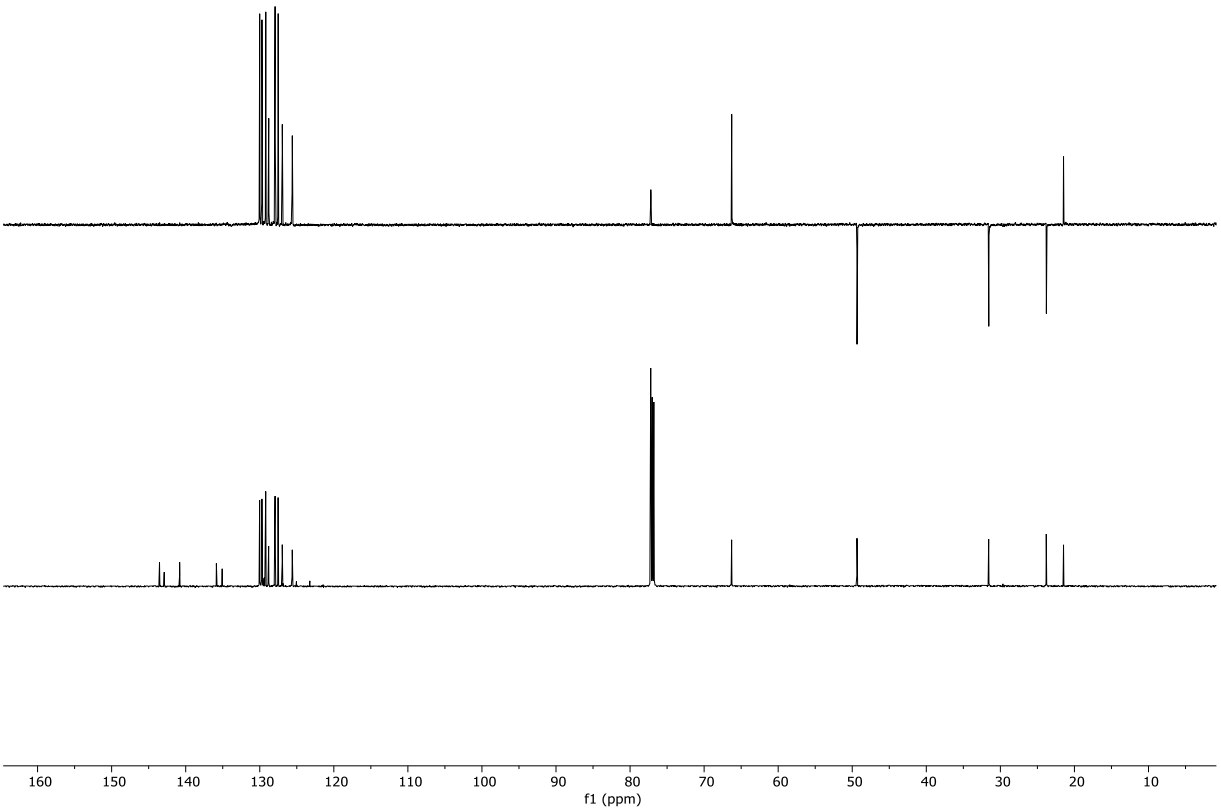
^{1}H-NMR of compound (*E*)-6d major isomer (600 MHz, $CDCl_3$)



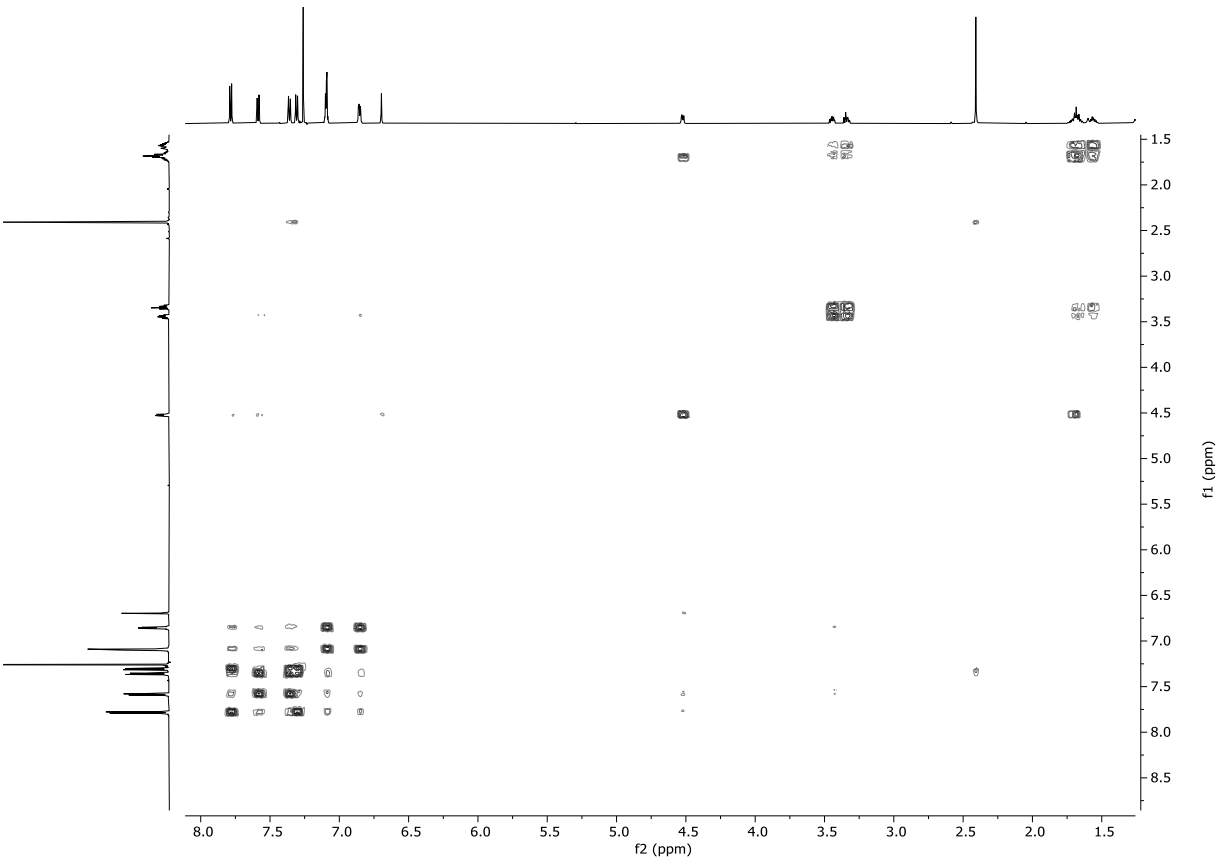
^{13}C-NMR of compound (*E*)-6d major isomer (150 MHz, $CDCl_3$)



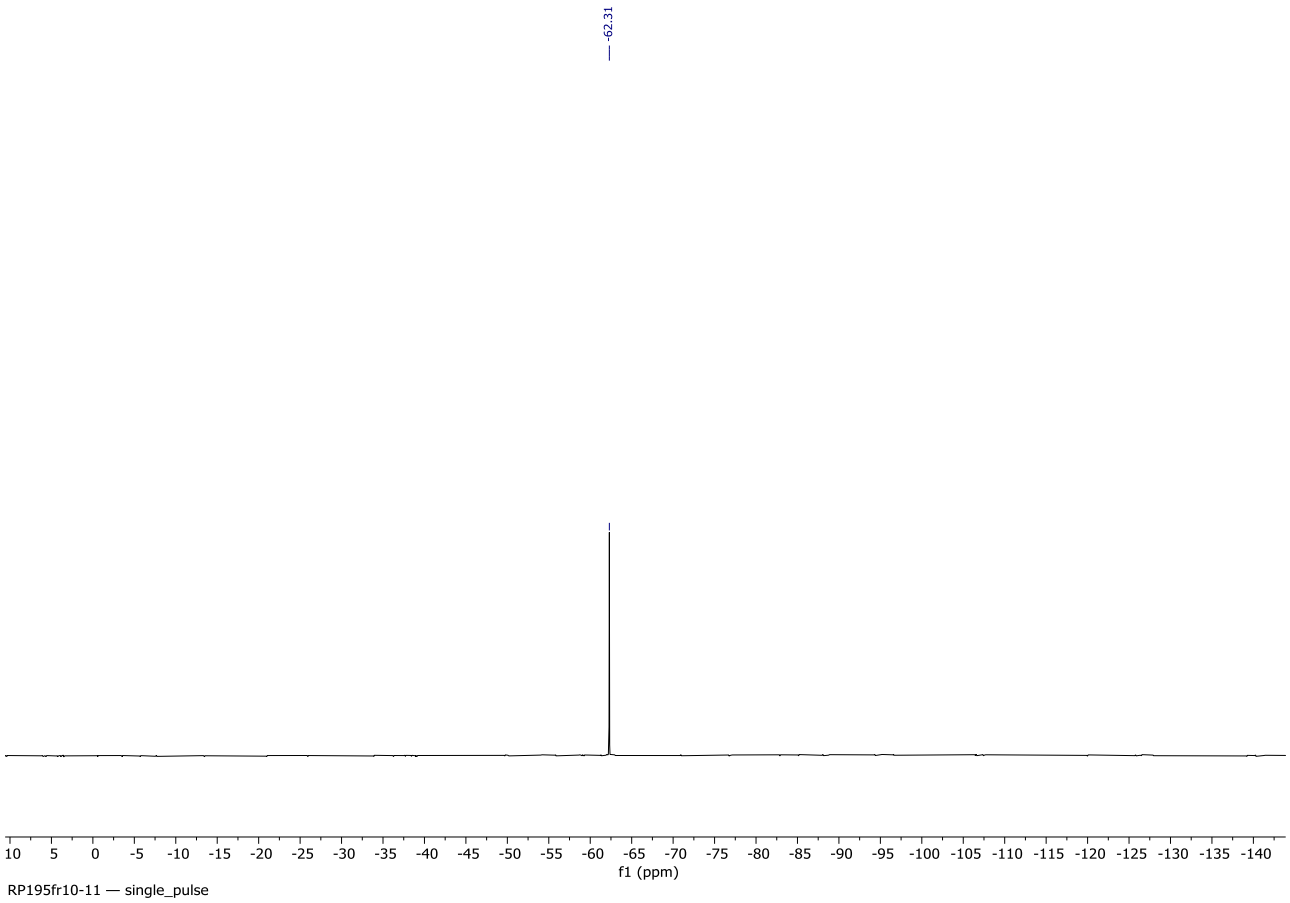
Comparison between DEPT-135 and ^{13}C-NMR of compound (*E*)-6d major isomer (150 MHz, $CDCl_3$)



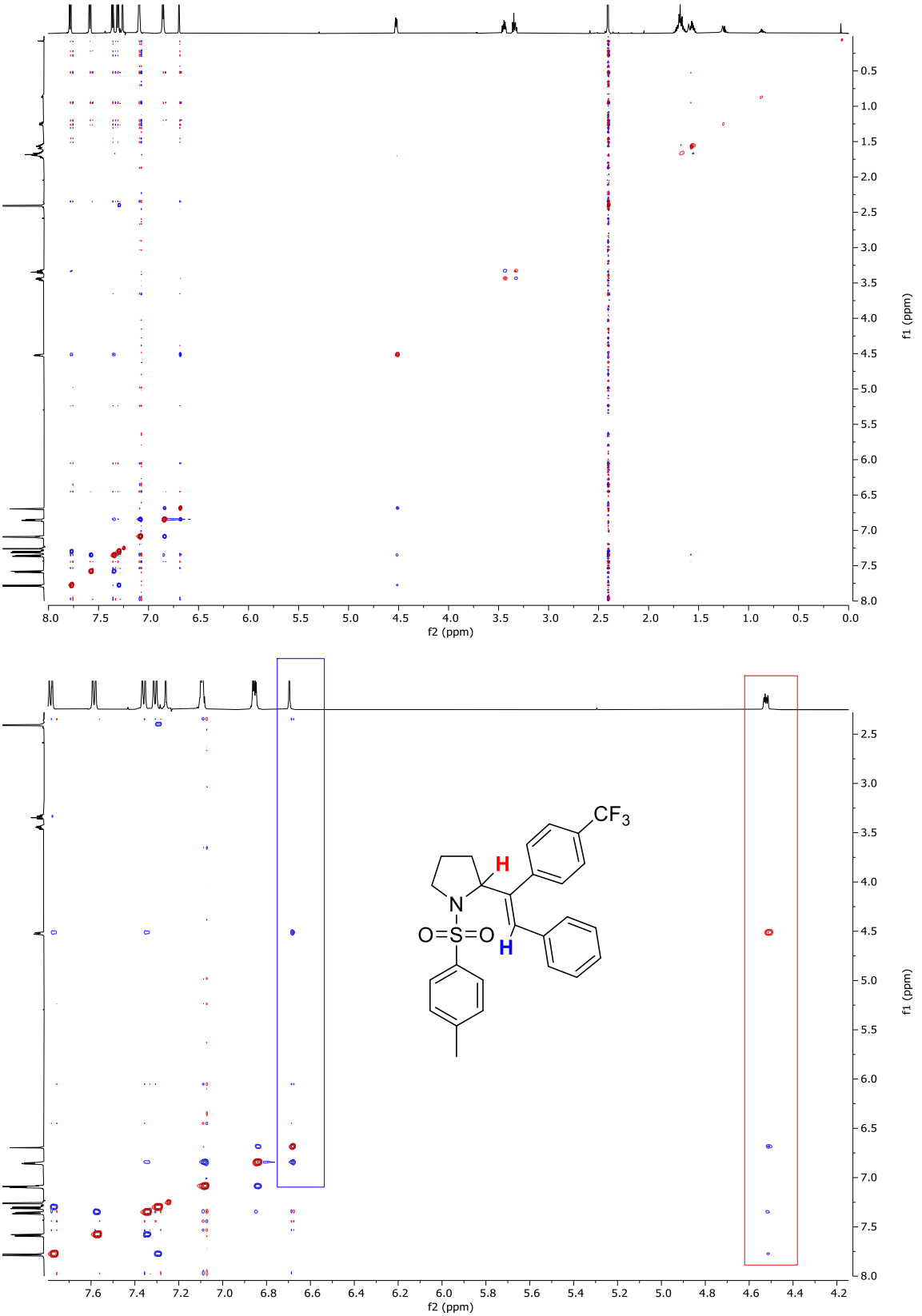
COSY-NMR of compound (*E*)-6d major isomer (600 MHz, $CDCl_3$)



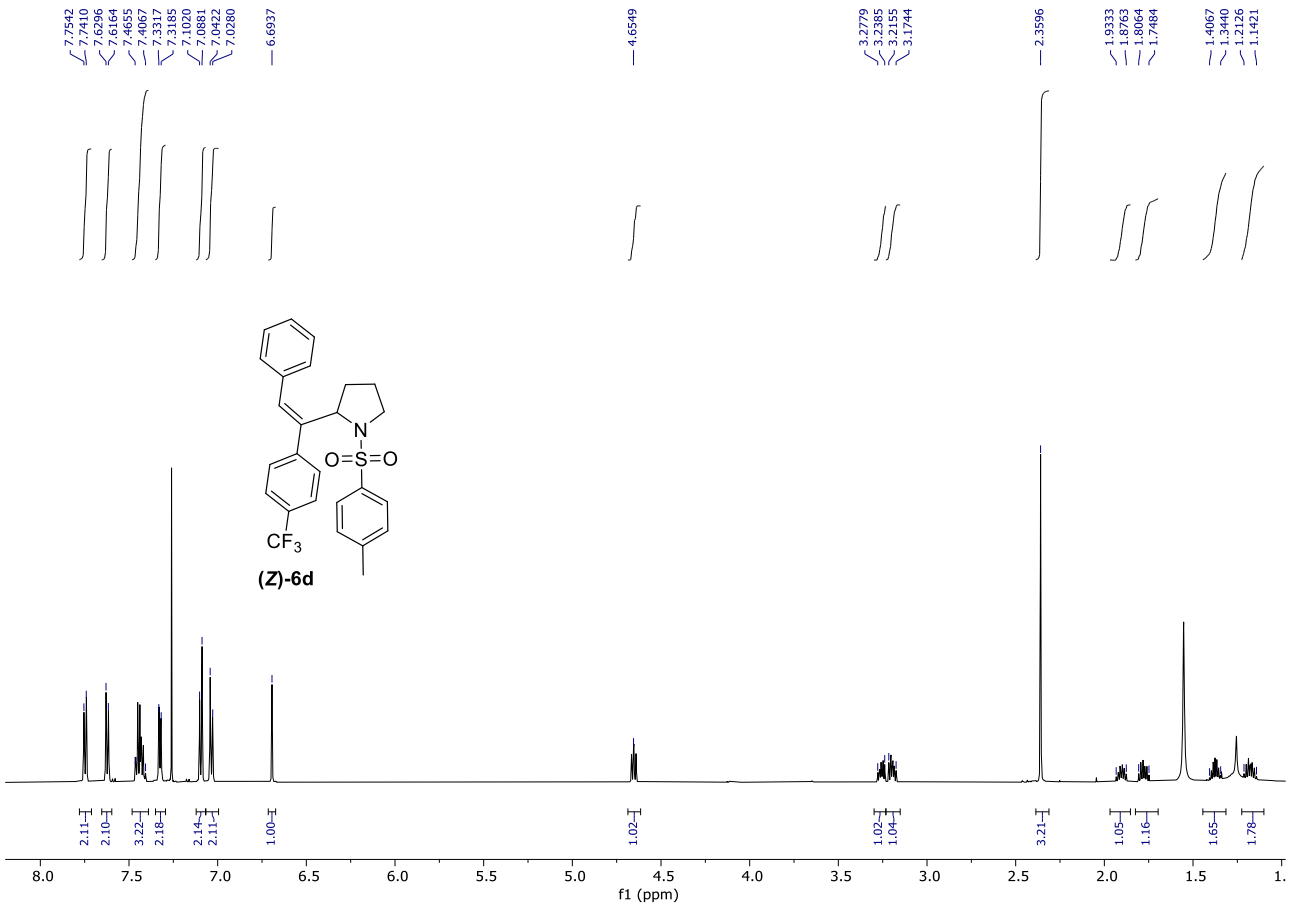
^{19}F-NMR of compound (*E*)-6d major isomer (600 MHz, $CDCl_3$)



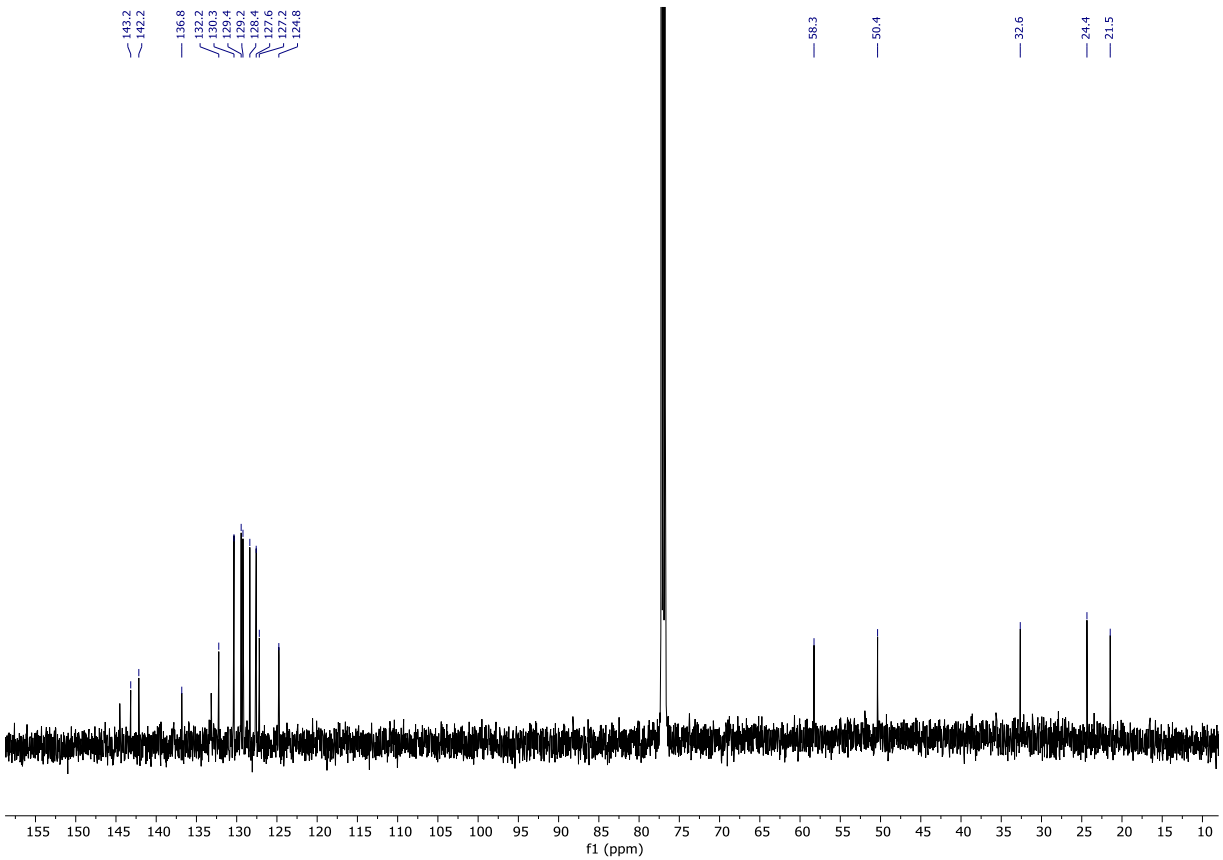
NOESY-NMR of compound (*E*)-6d major isomer (600 MHz, $CDCl_3$)



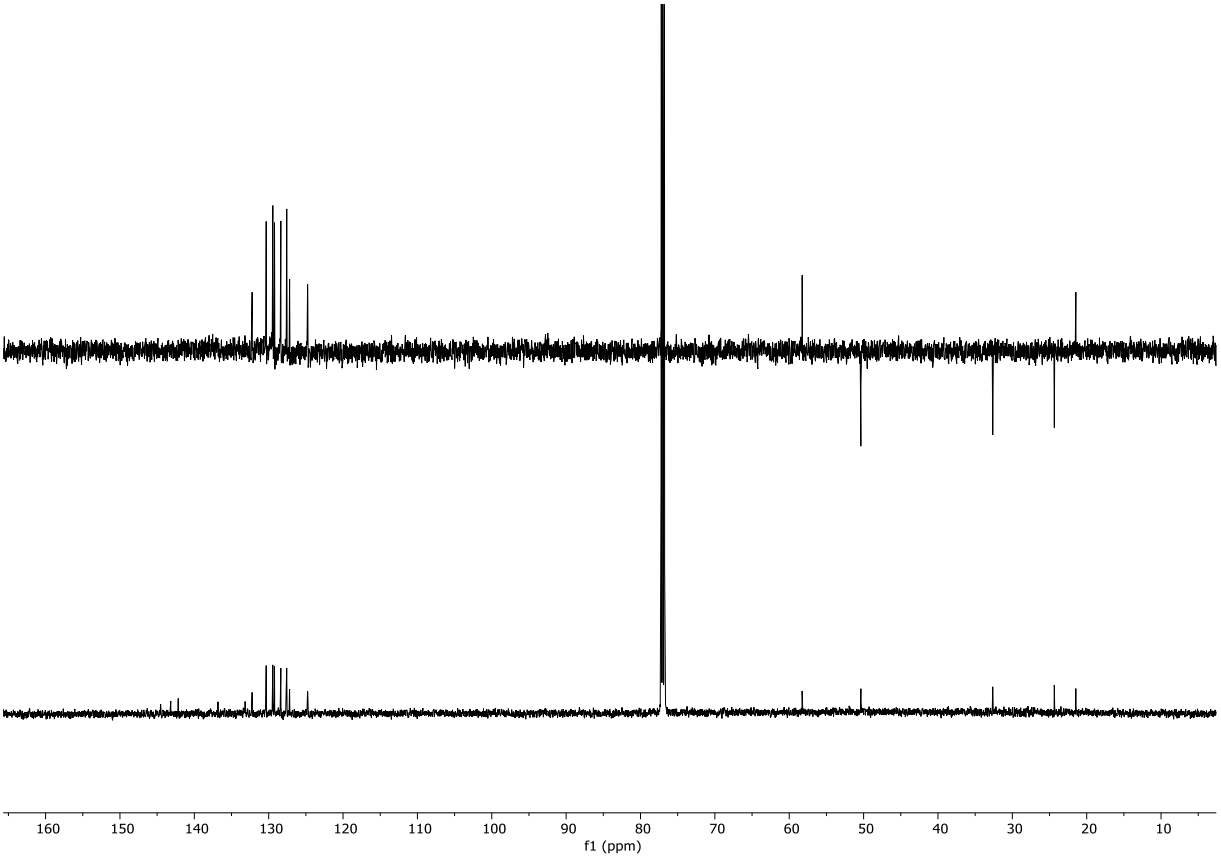
^{1}H-NMR of compound (*Z*)-6d minor isomer (600 MHz, $CDCl_3$)



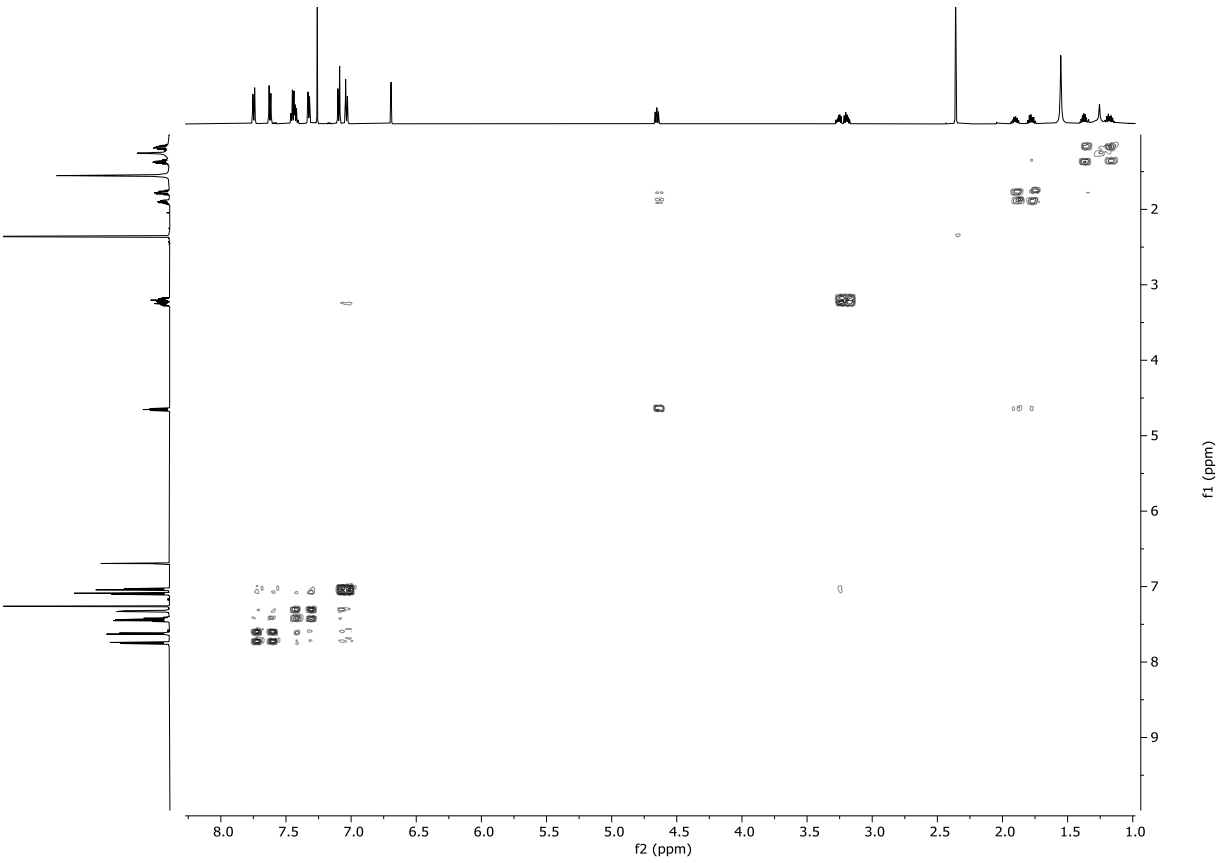
^{13}C-NMR of compound (*Z*)-6d minor isomer (150 MHz, $CDCl_3$)



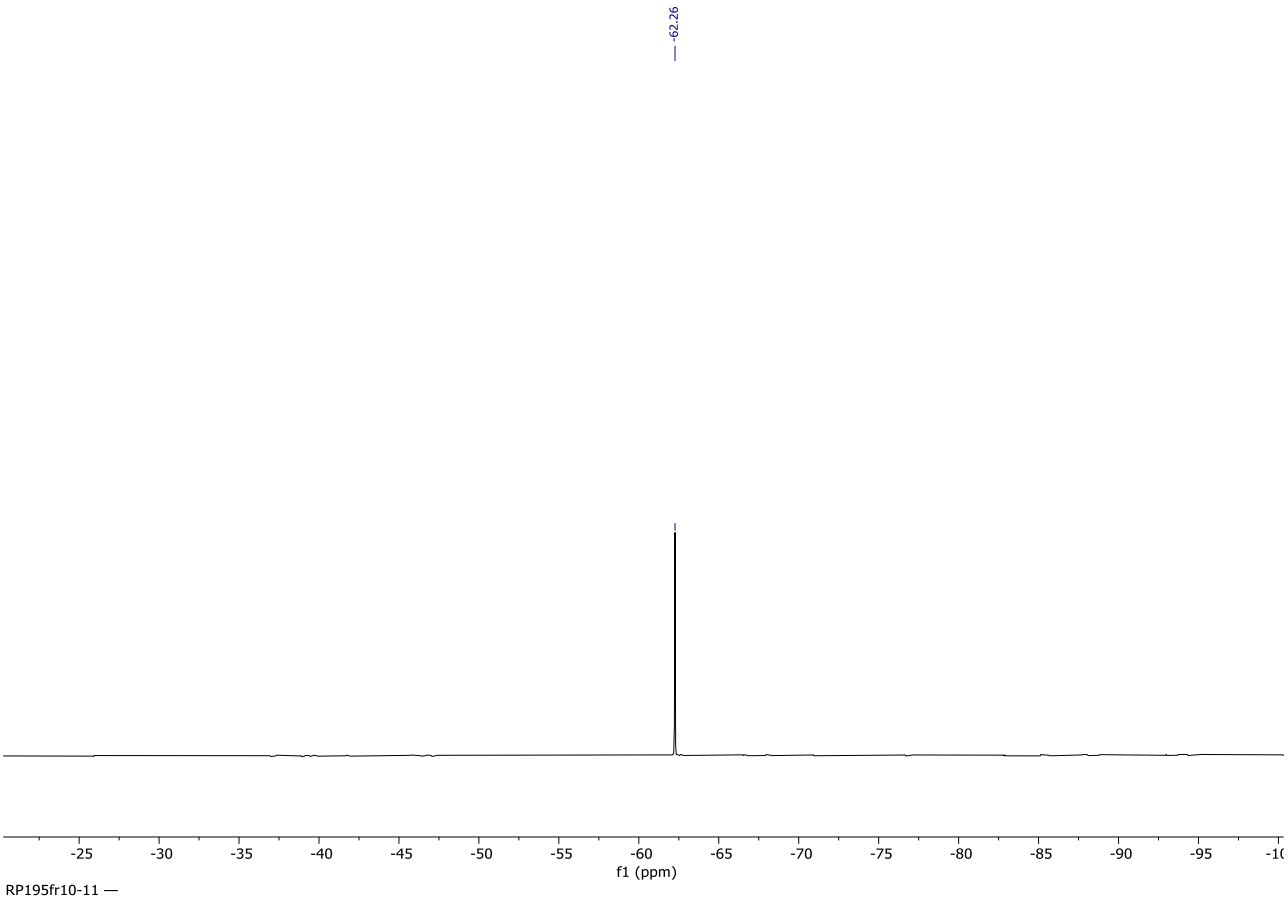
Comparison between DEPT-135 and ^{13}C-NMR of compound (*Z*)-6d minor isomer (150 MHz, $CDCl_3$)



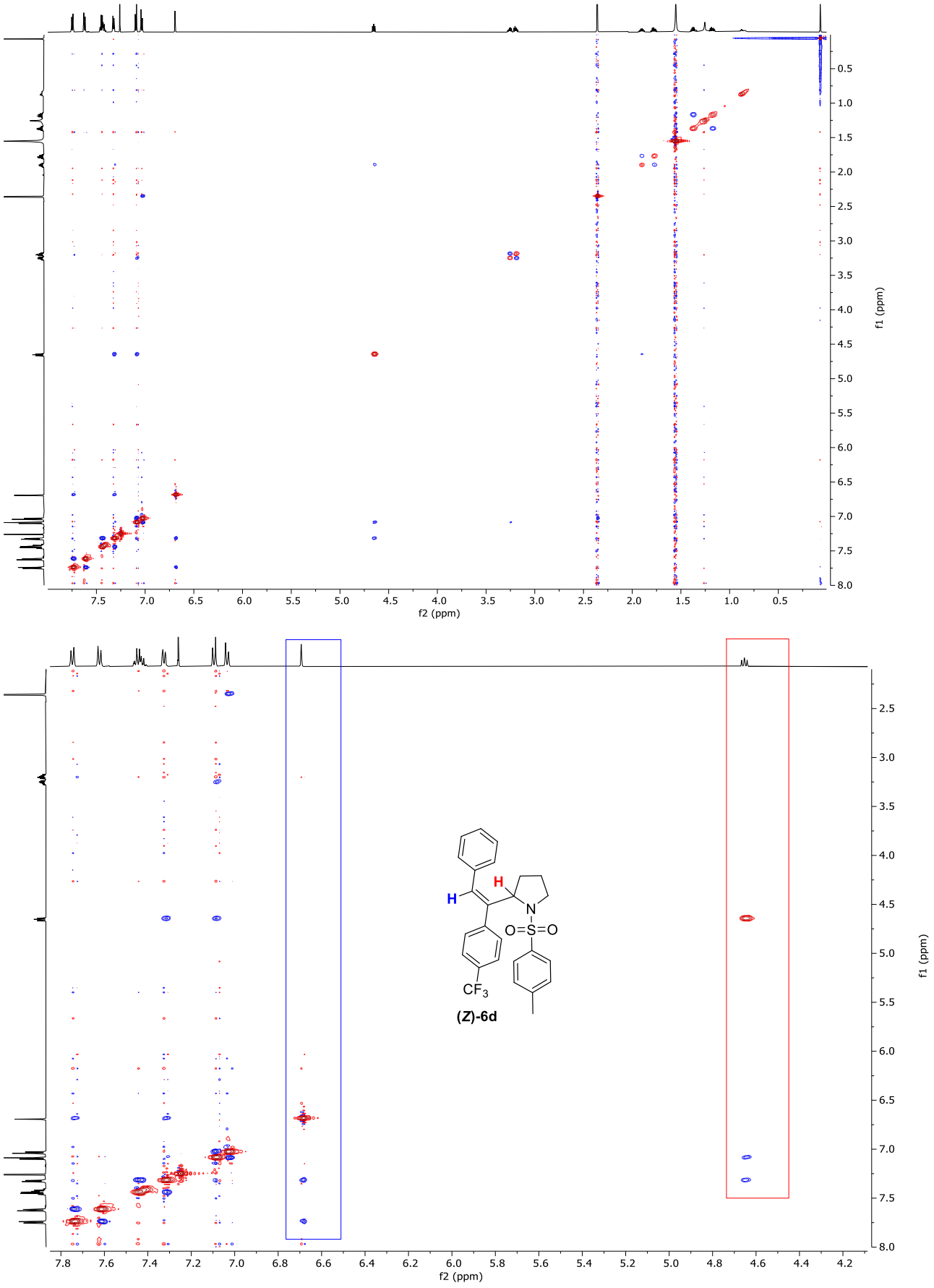
COSY-NMR of compound (*Z*)-6d minor isomer (600 MHz, $CDCl_3$)



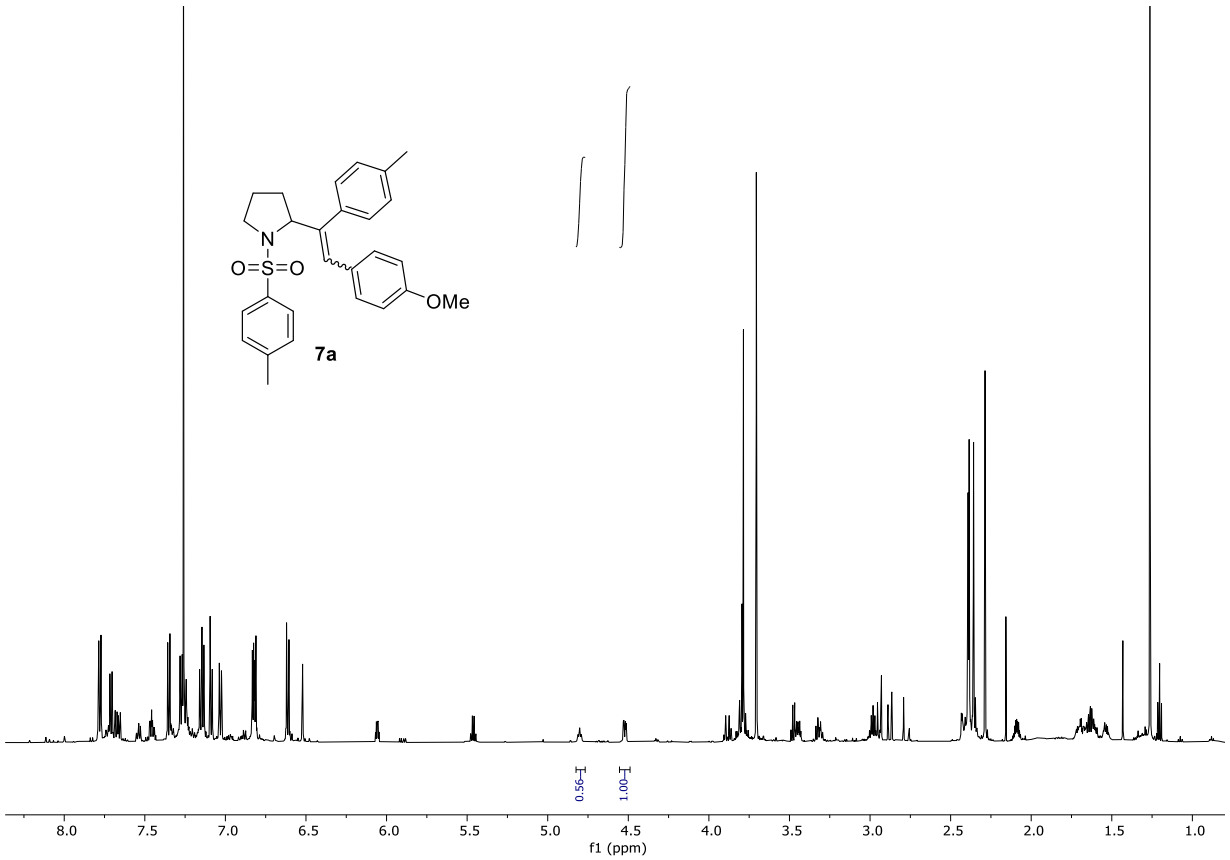
^{19}F-NMR of compound (*Z*)-6d minor isomer (600 MHz, $CDCl_3$)



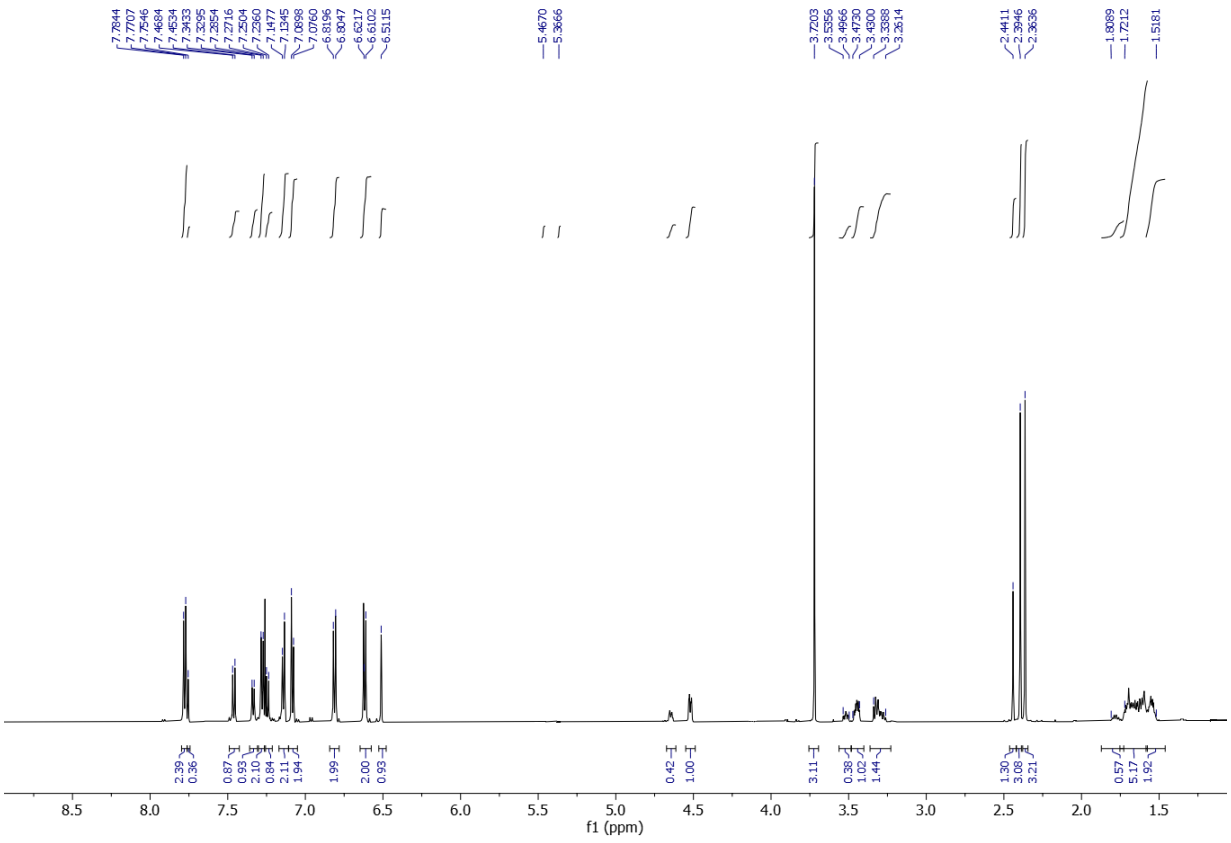
NOESY-NMR of compound (*Z*)-6d minor isomer (600 MHz, $CDCl_3$)



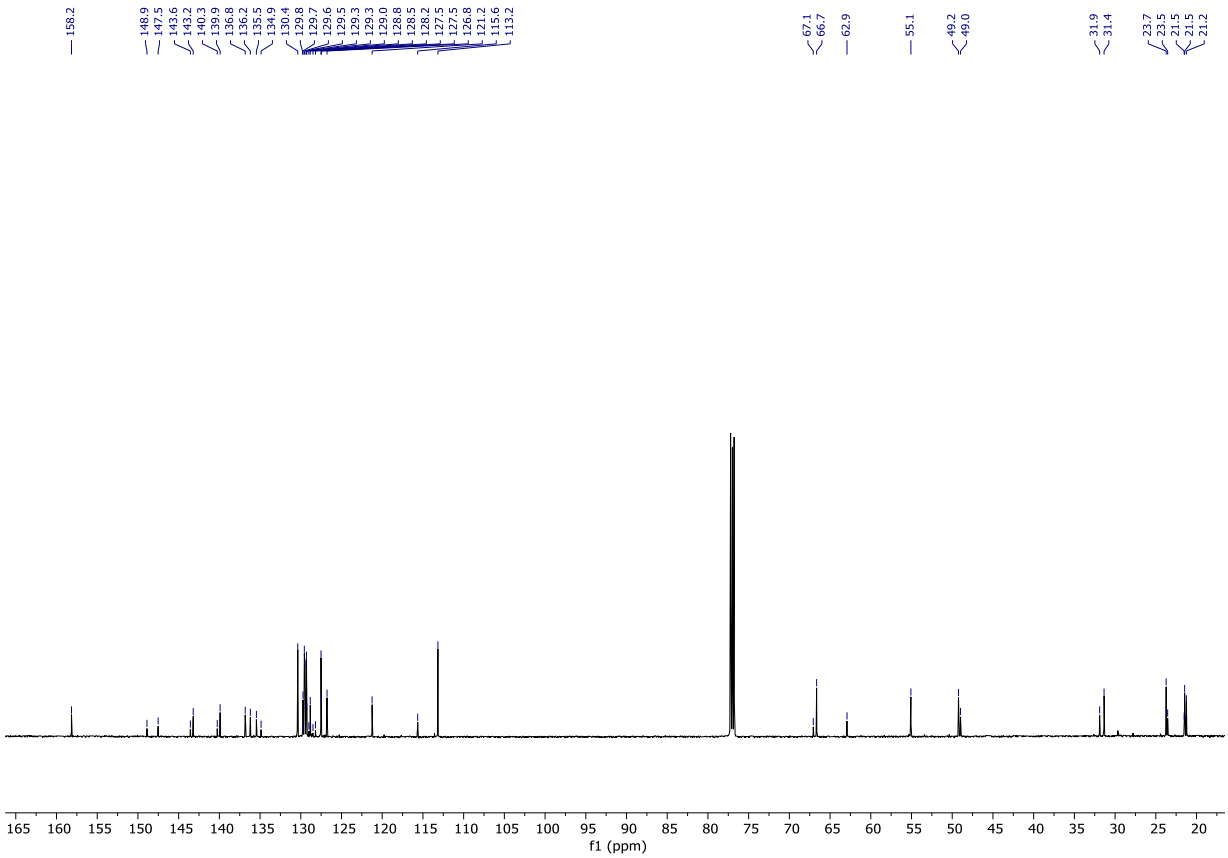
^{1}H-NMR of compound 7a crude reaction mixture (600 MHz, $CDCl_3$)



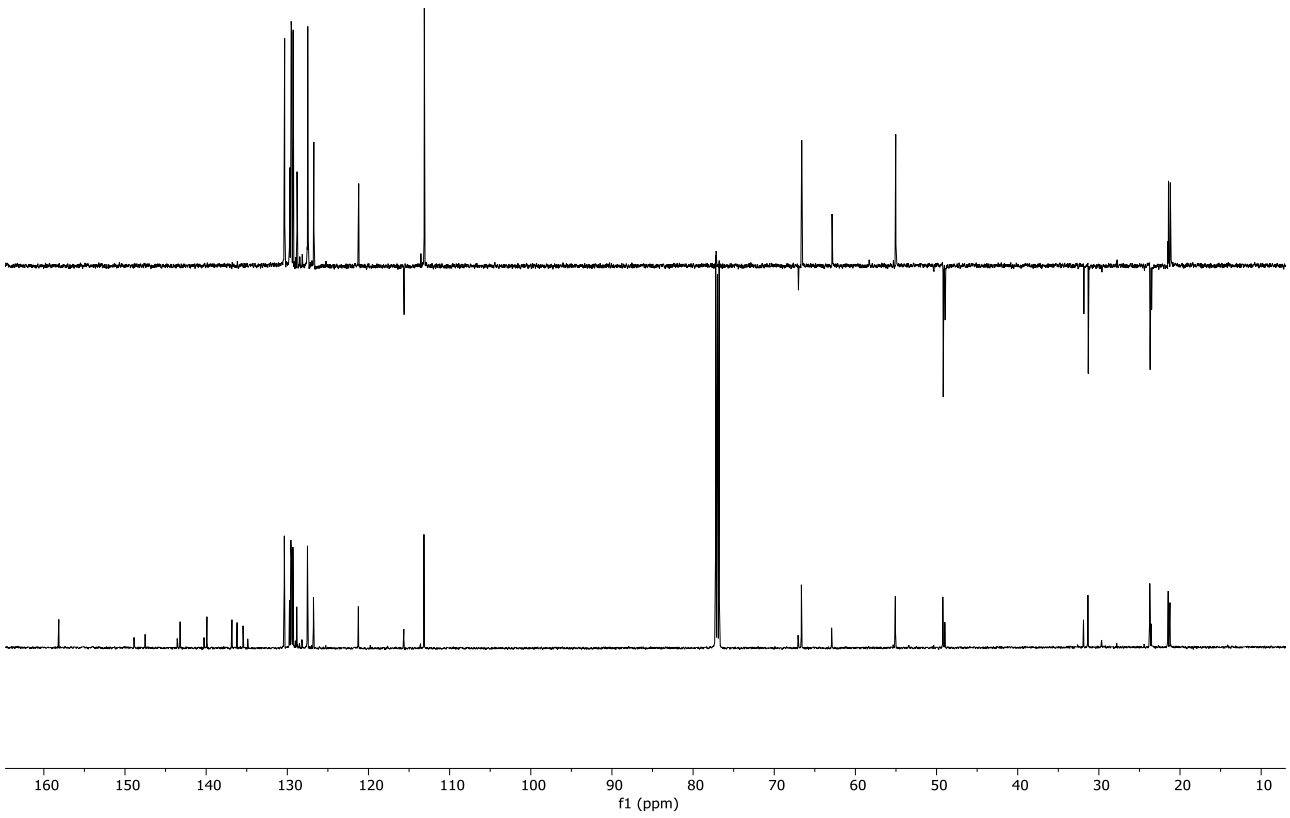
^{1}H-NMR of compound 7a (600 MHz, $CDCl_3$)



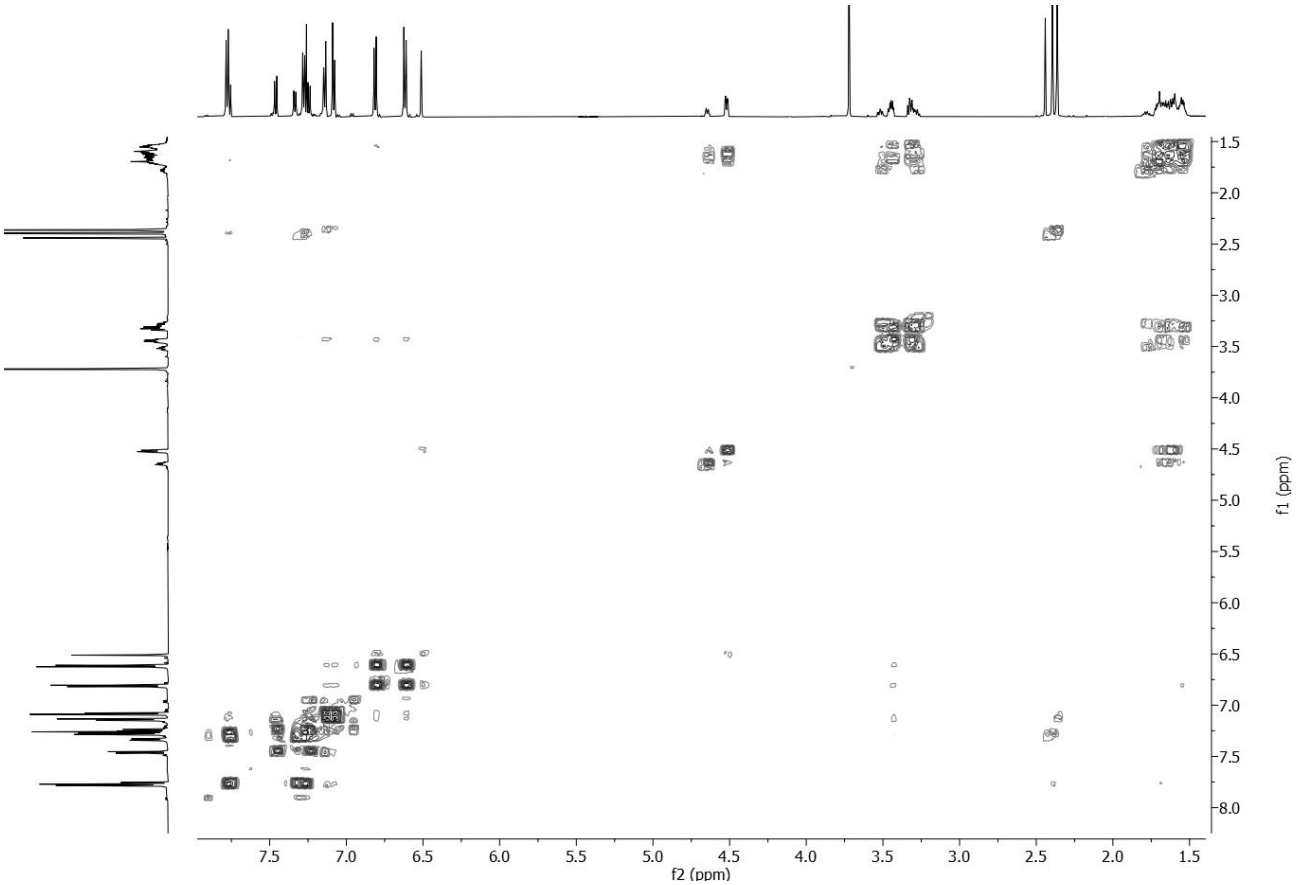
^{13}C-NMR of compound 7a mixture of isomers (150 MHz, $CDCl_3$)



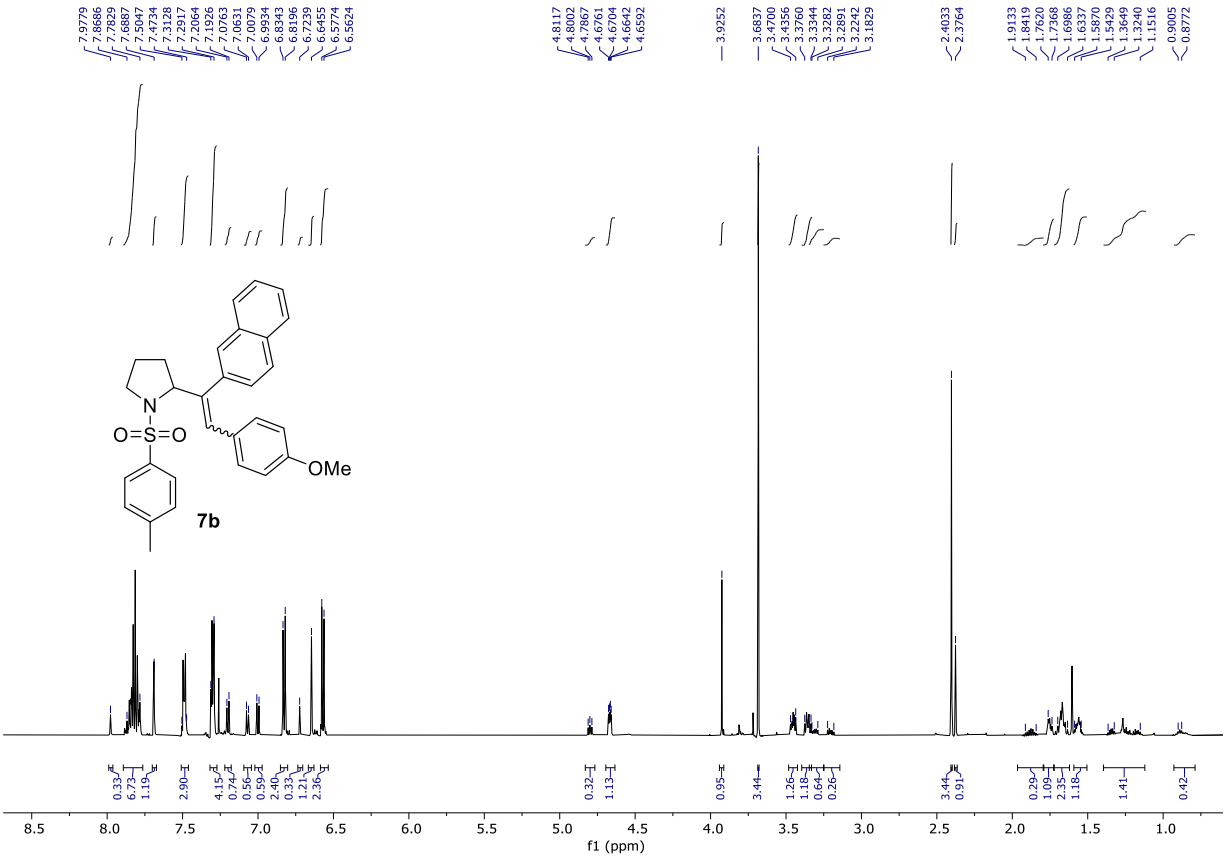
Comparison between DEPT-135 and ^{13}C-NMR of compound 7a (150 MHz, $CDCl_3$)



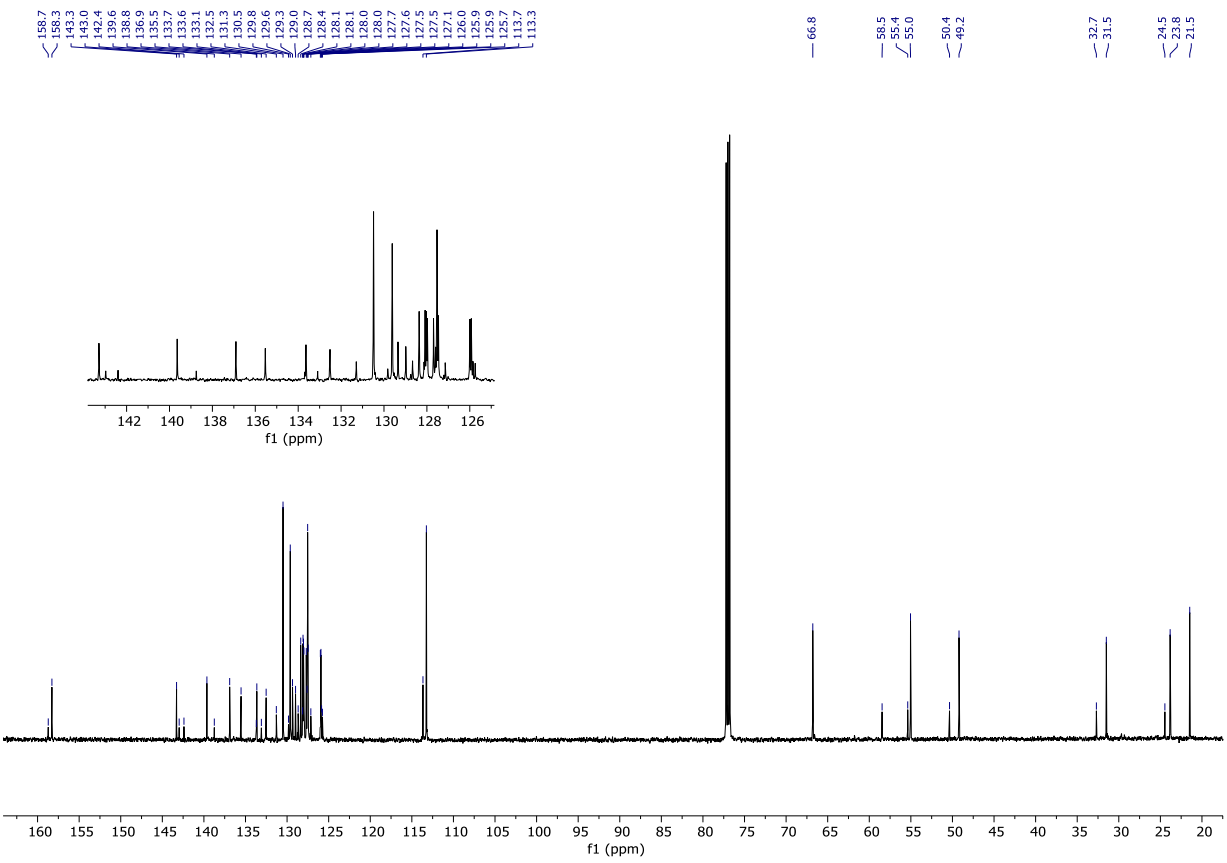
COSY-NMR of compound 7a mixture of isomers (600 MHz, $CDCl_3$)



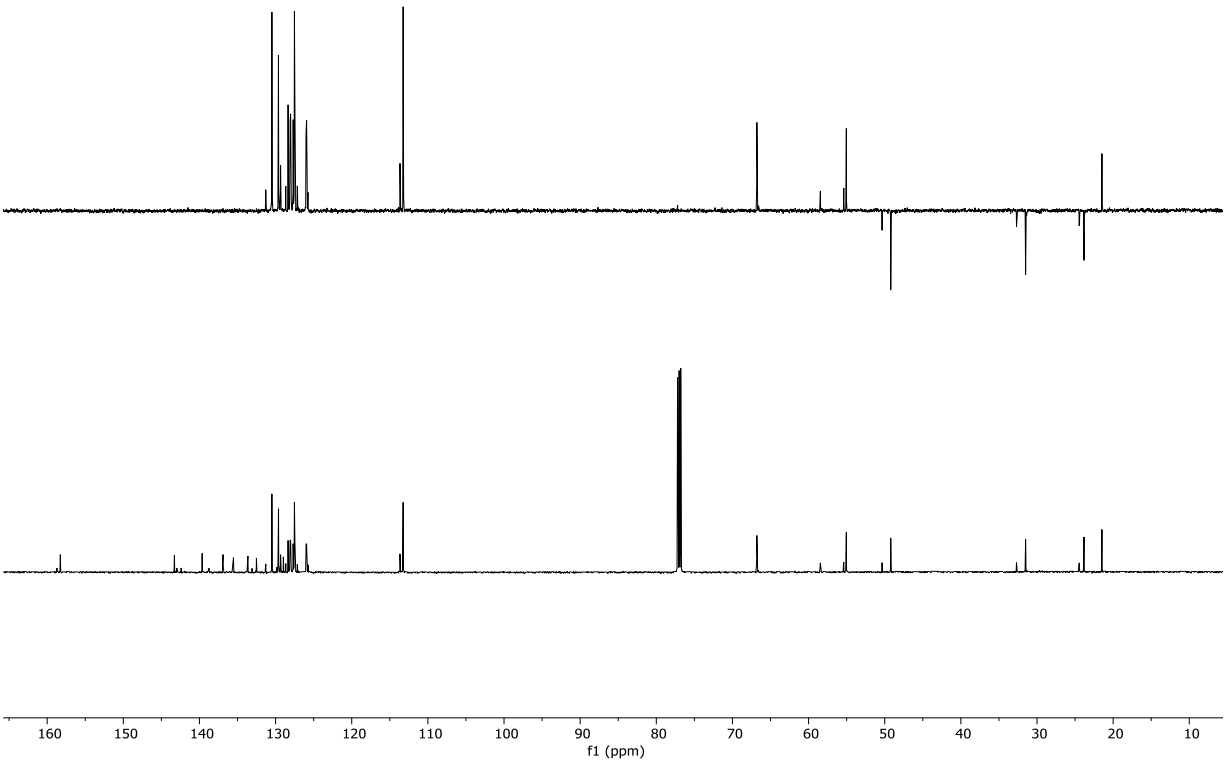
^{1}H-NMR of compound 7b crude reaction mixture (600 MHz, $CDCl_3$)



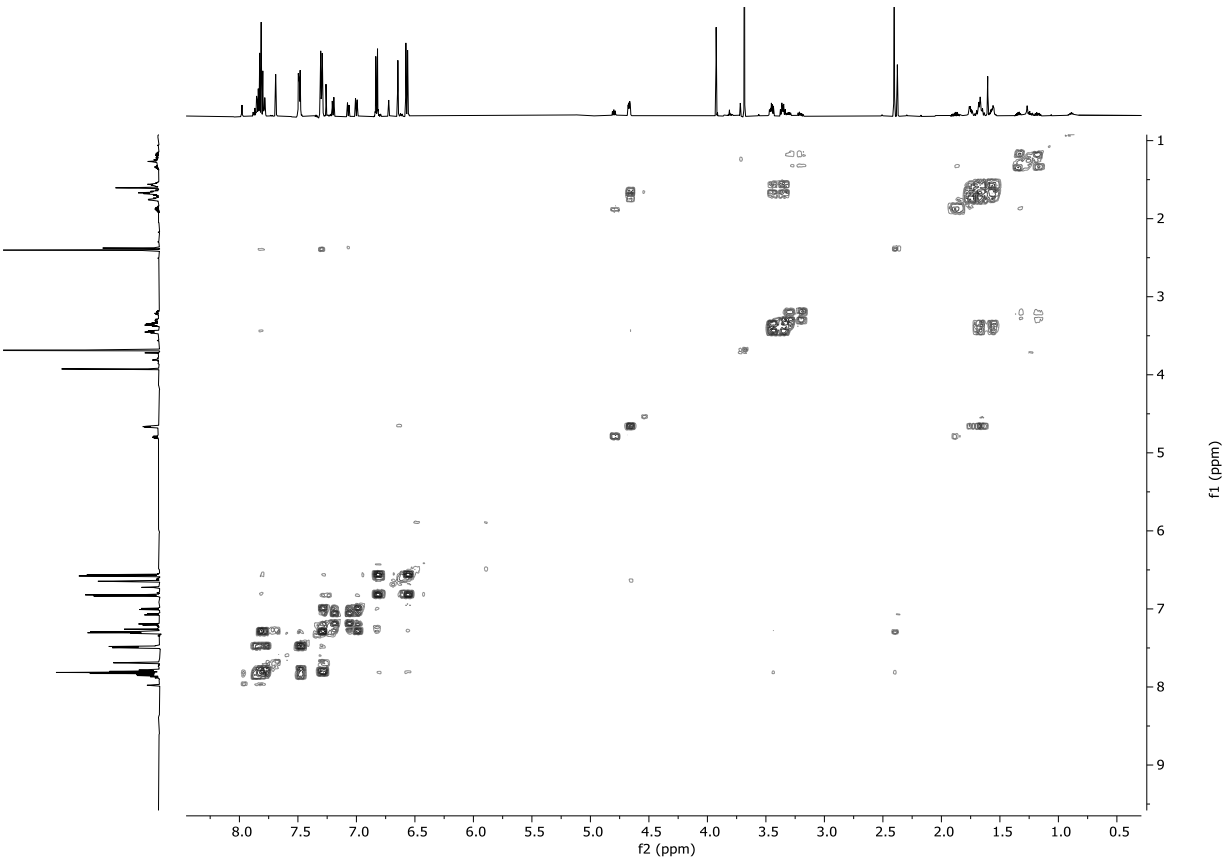
^{13}C-NMR of compound 7b mixture of isomers (150 MHz, $CDCl_3$)



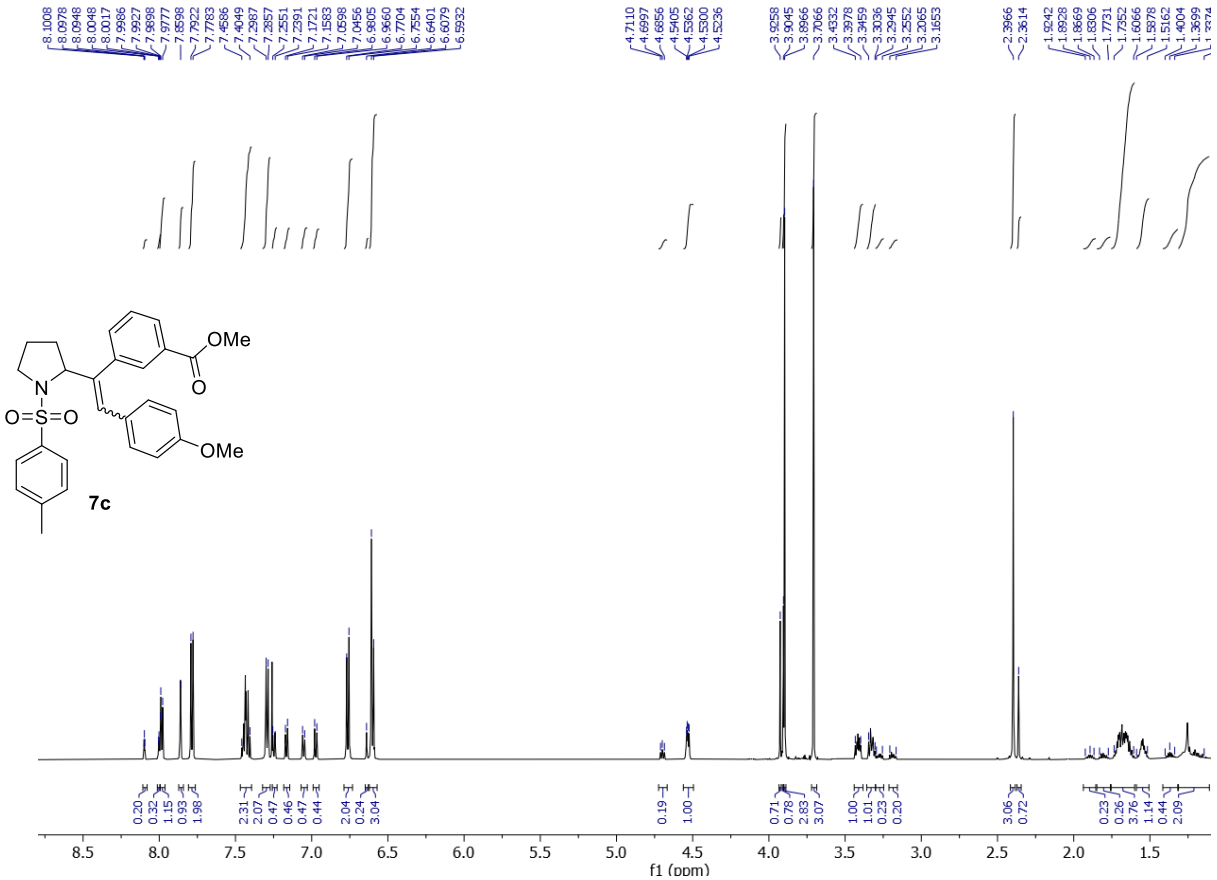
Comparison between DEPT-135 and ^{13}C-NMR of compound 7b (150 MHz, $CDCl_3$)



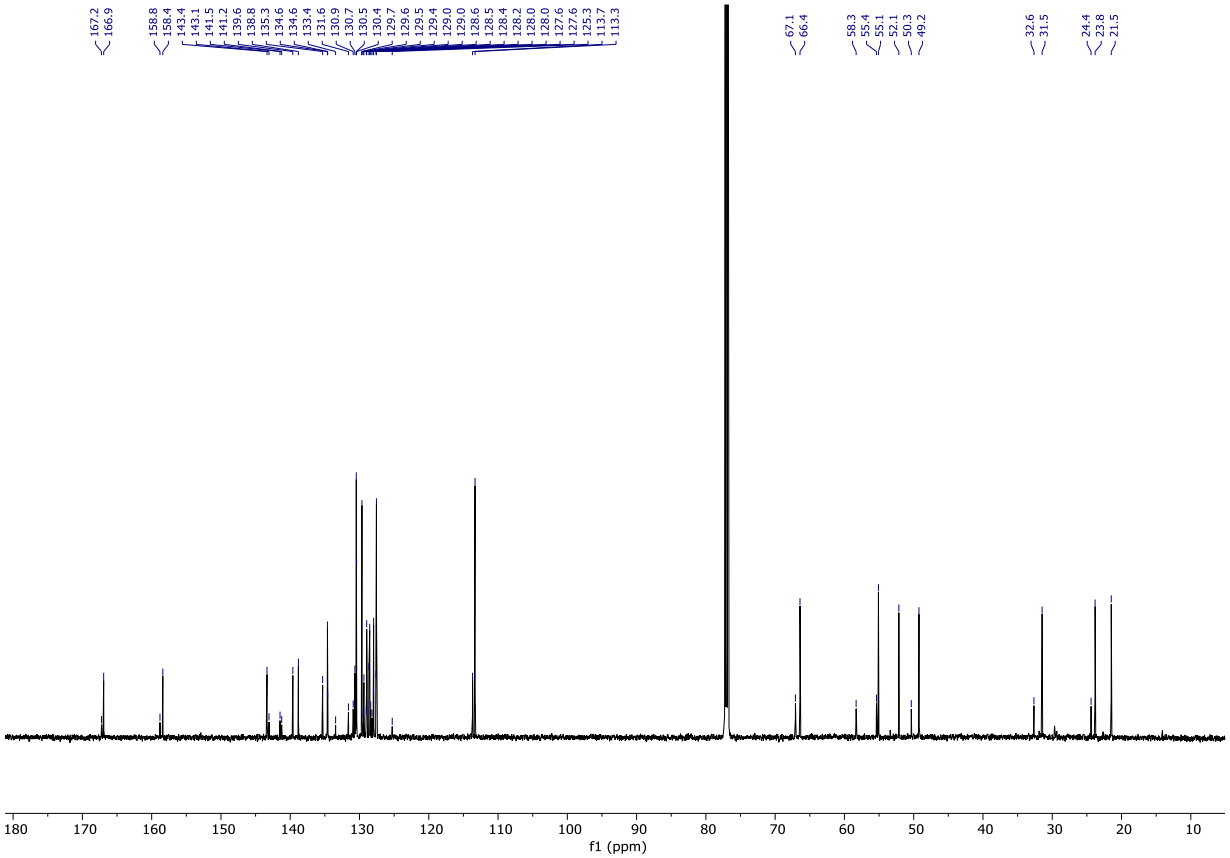
COSY-NMR of compound 7b (600 MHz, $CDCl_3$)



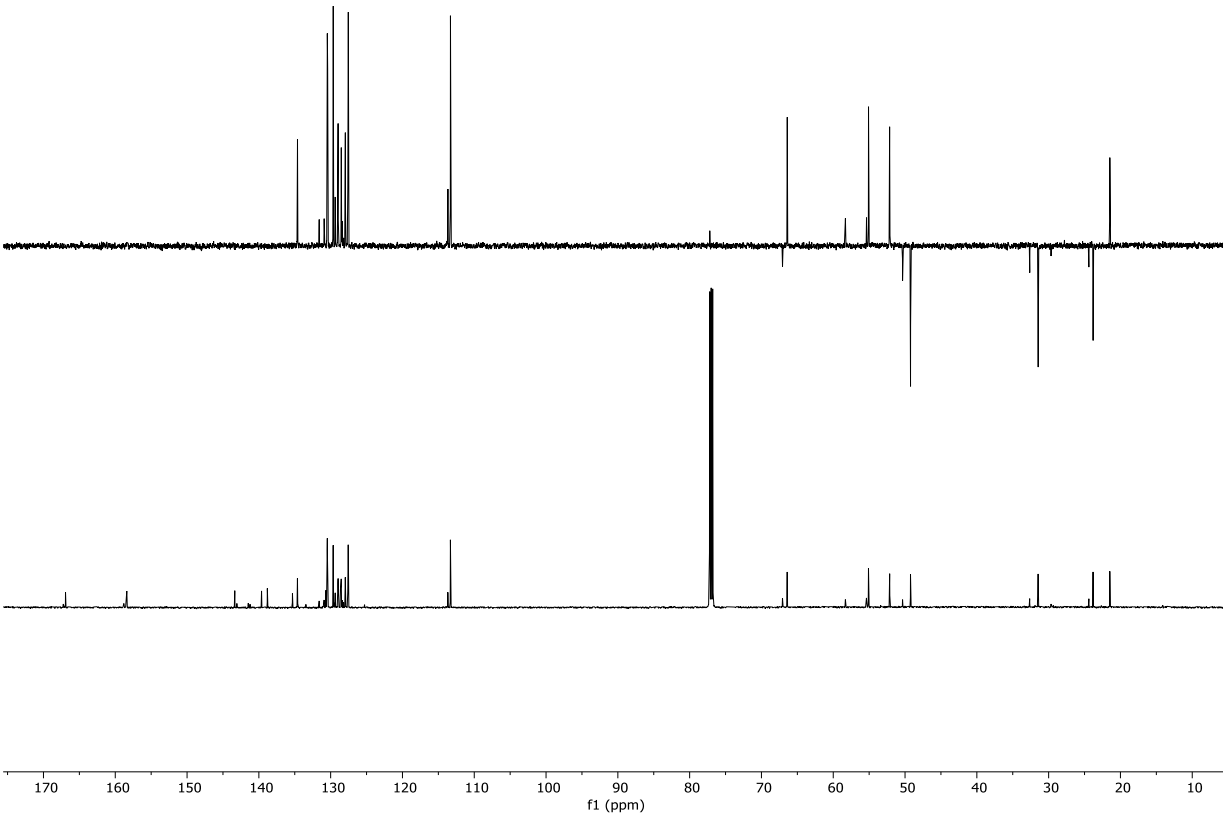
^{1}H-NMR of compound 7c mixture of isomers (600 MHz, $CDCl_3$)



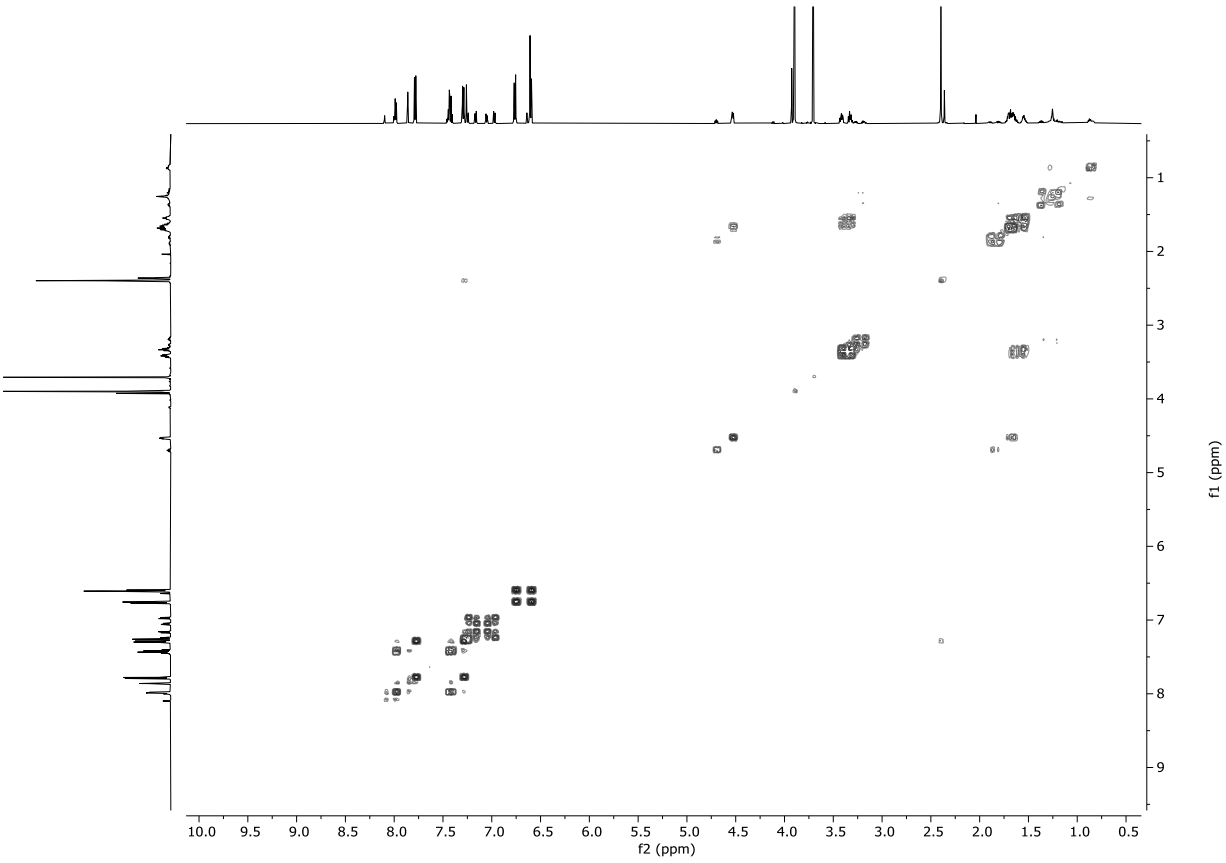
^{13}C-NMR of compound 7c mixture of isomers (150 MHz, $CDCl_3$)



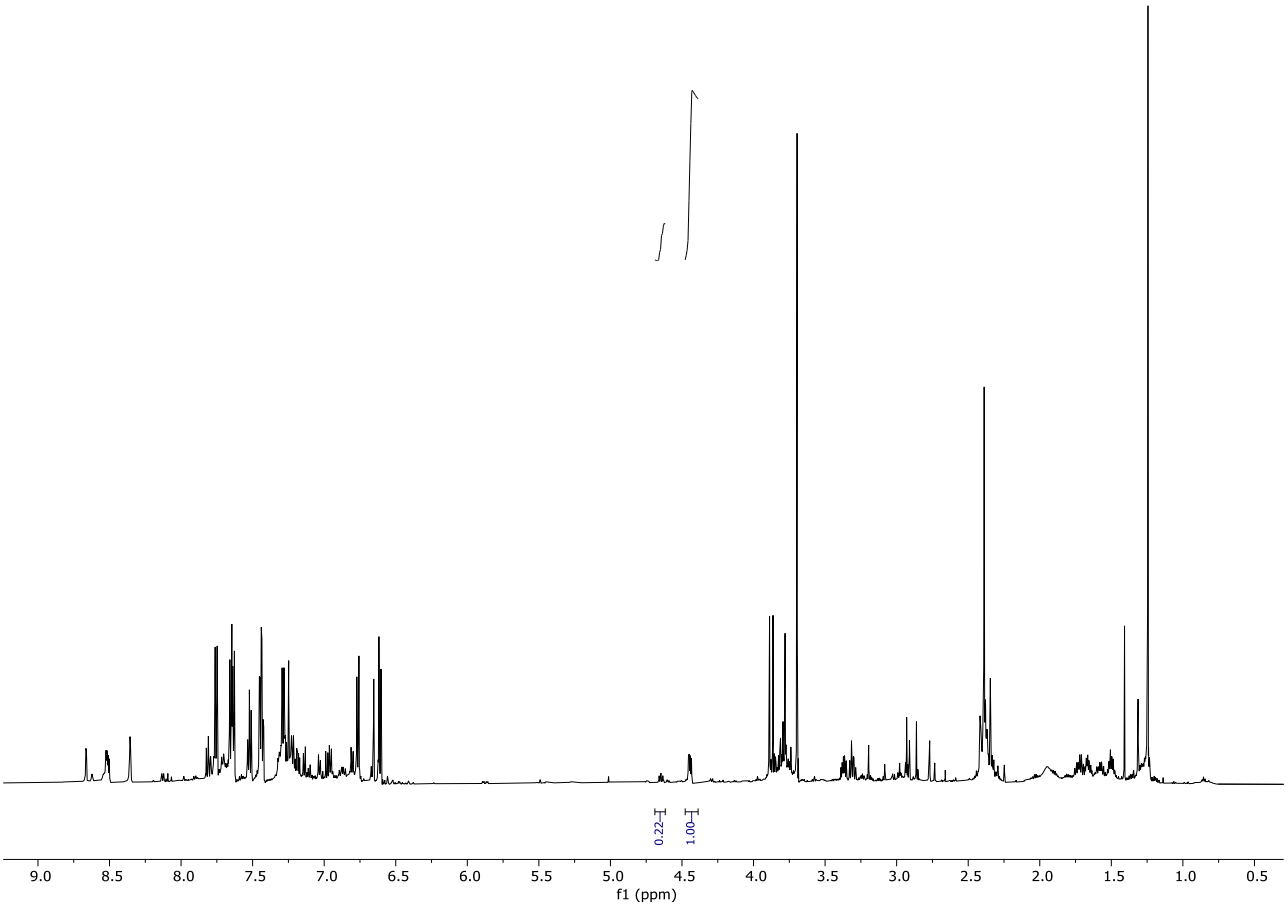
Comparison between DEPT-135 and ^{13}C-NMR of compound 7c (150 MHz, $CDCl_3$)



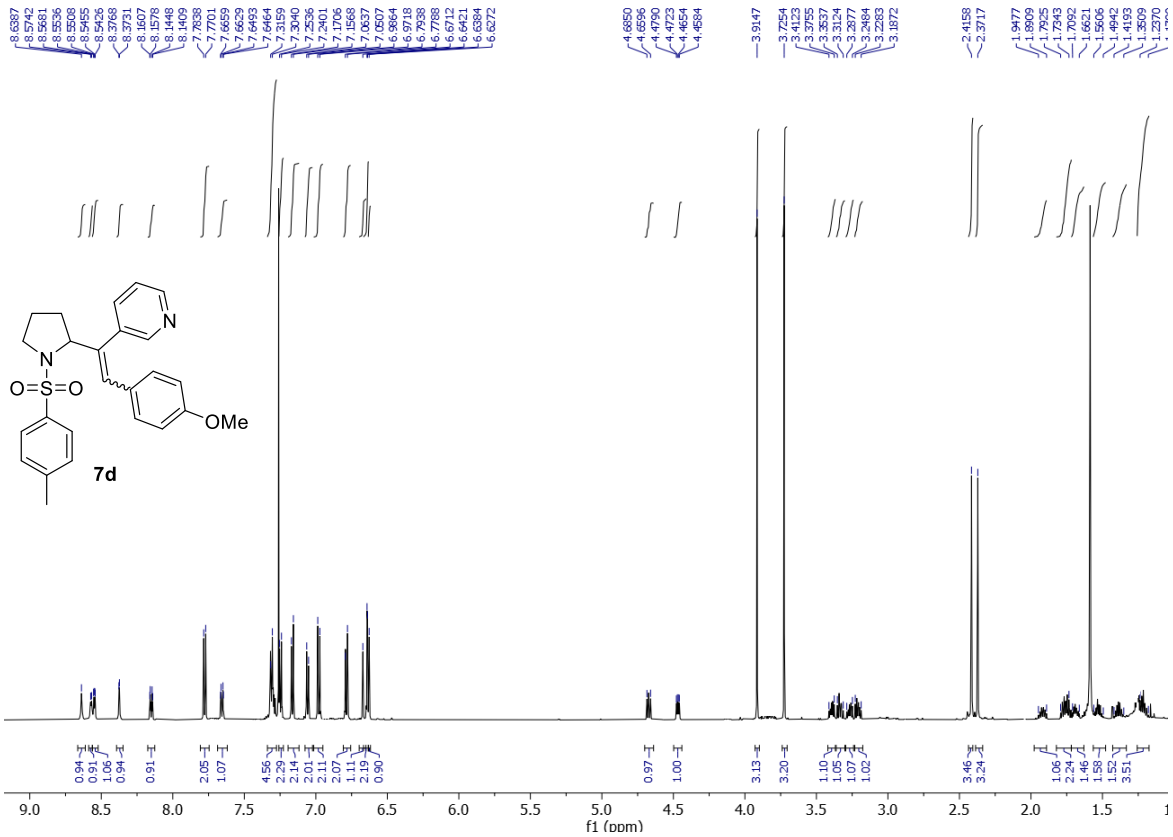
COSY-NMR of compound 7c mixture of isomers (600 MHz, $CDCl_3$)



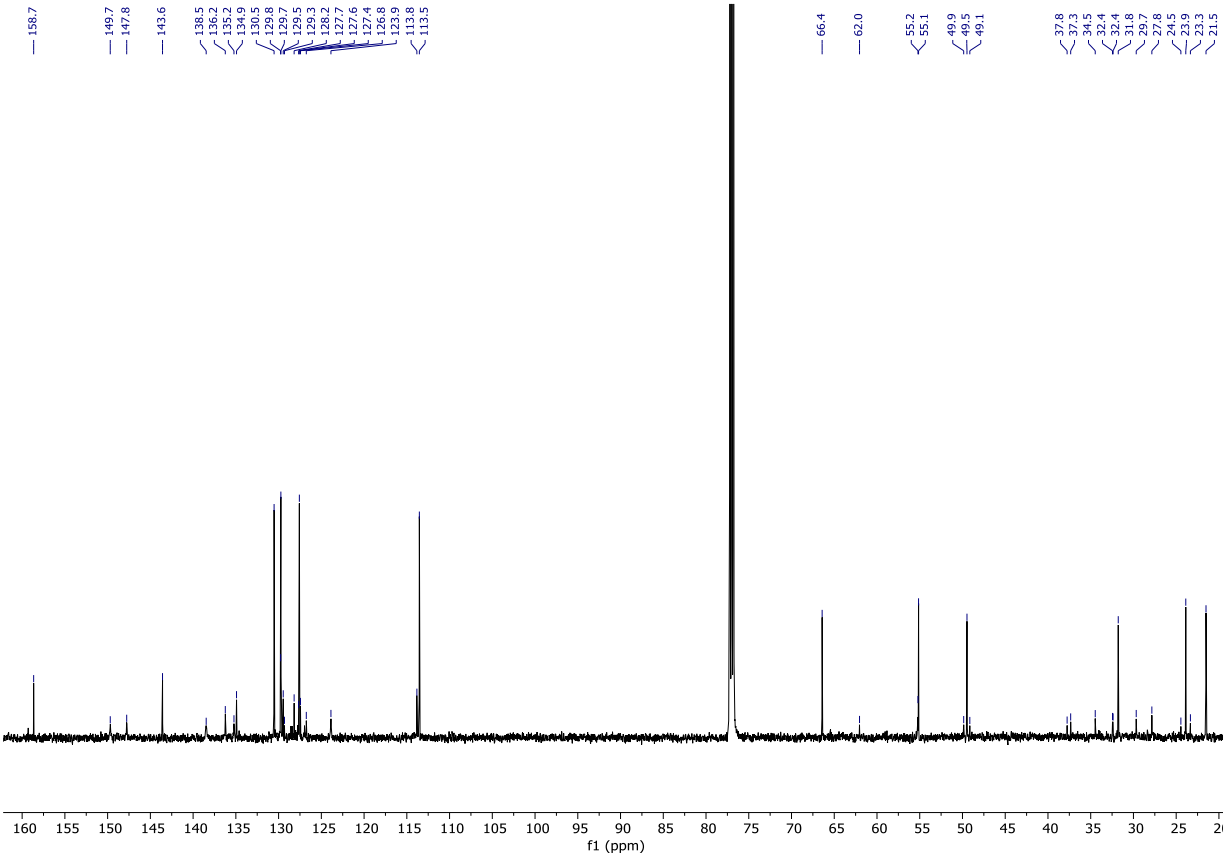
^{1}H-NMR of compound 7d crude (600 MHz, $CDCl_3$)



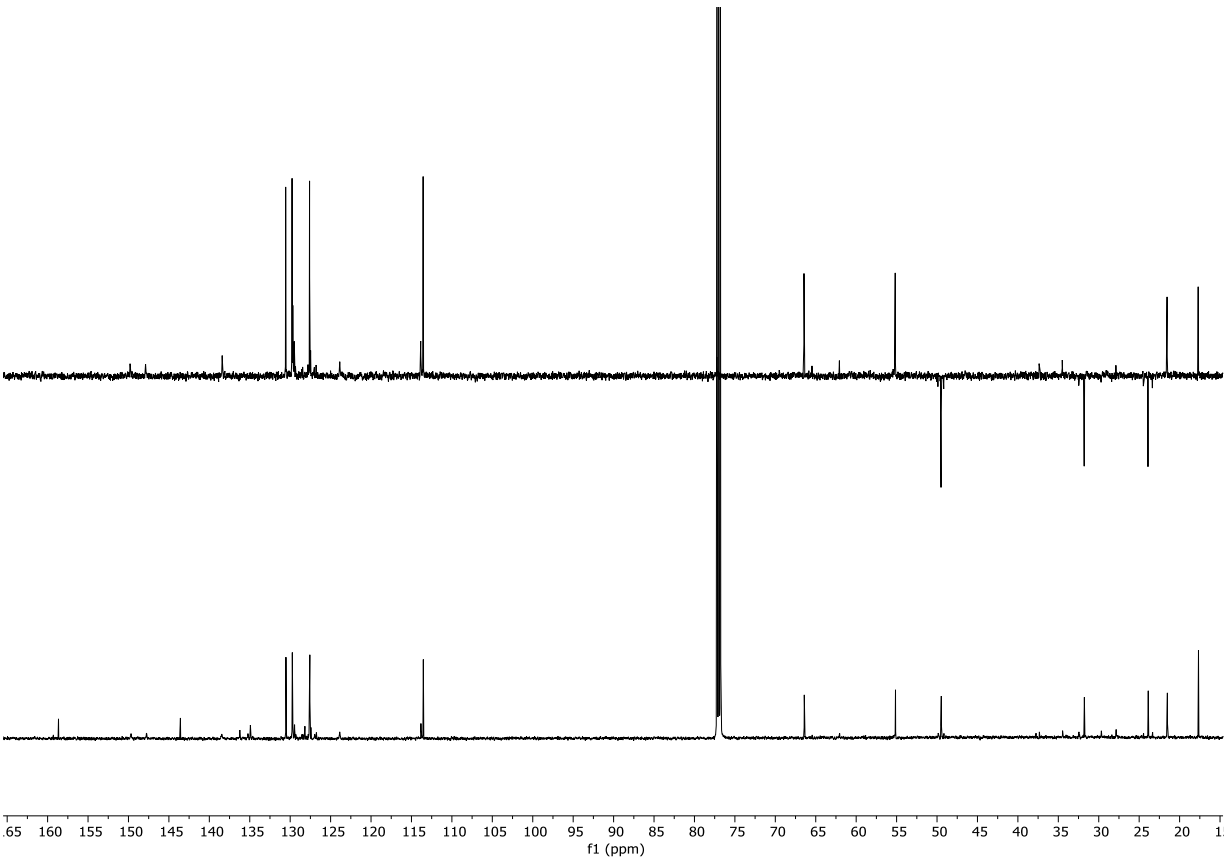
^{1}H-NMR of compound 7d mixture of isomers (600 MHz, $CDCl_3$)



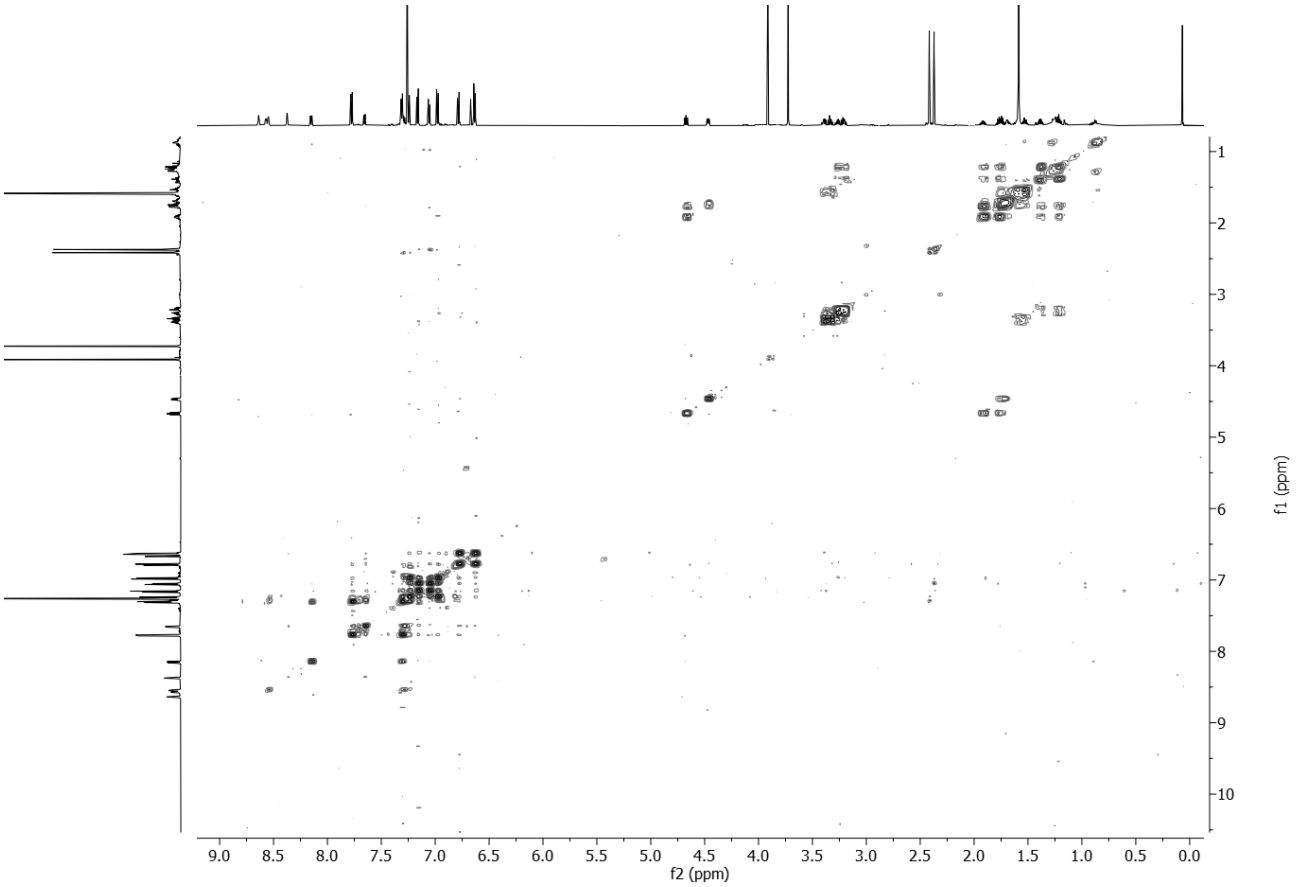
^{13}C-NMR of compound 7d mixture of isomers (150 MHz, $CDCl_3$)



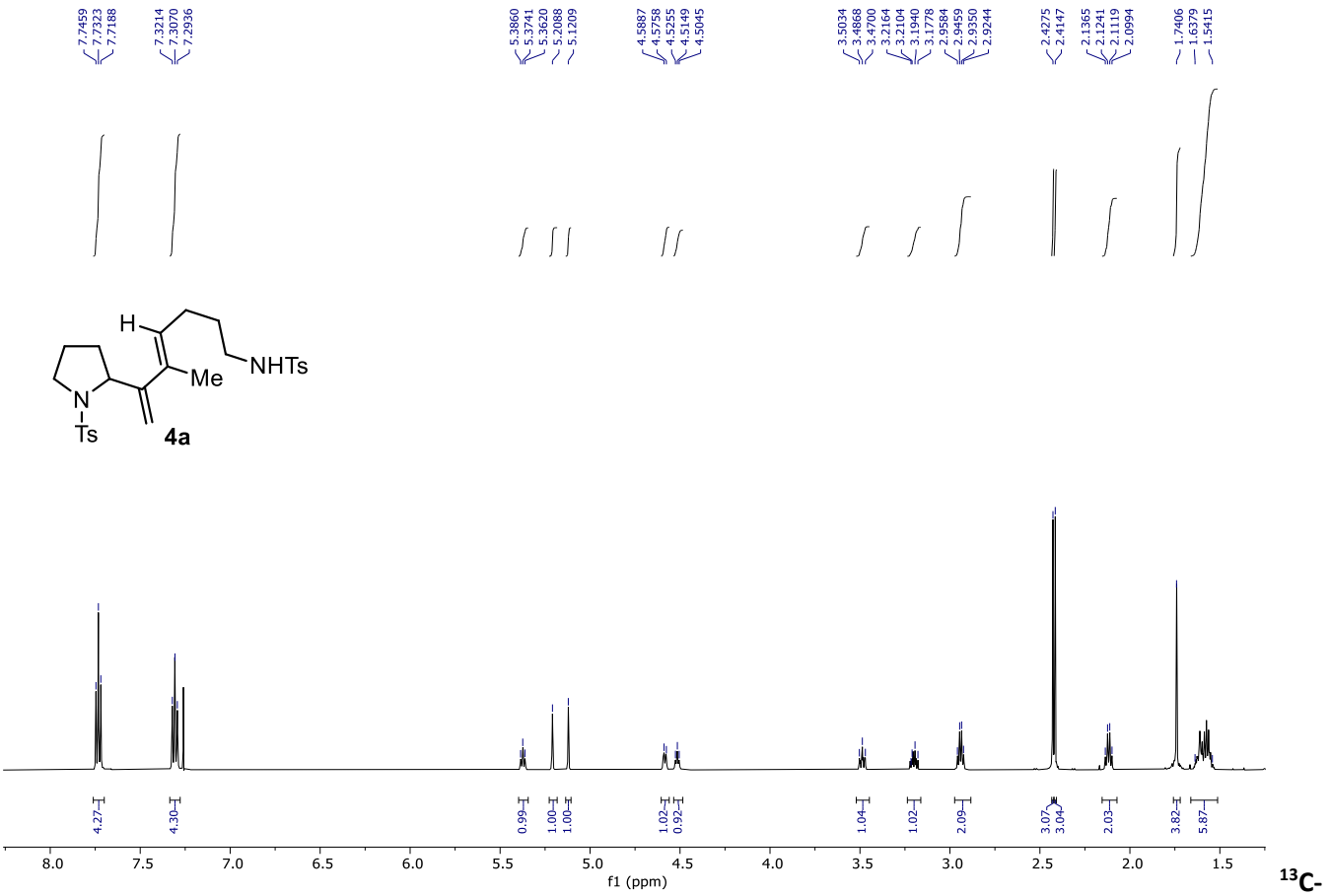
Comparison between DEPT-135 and ^{13}C-NMR of compound 7d (150 MHz, $CDCl_3$)



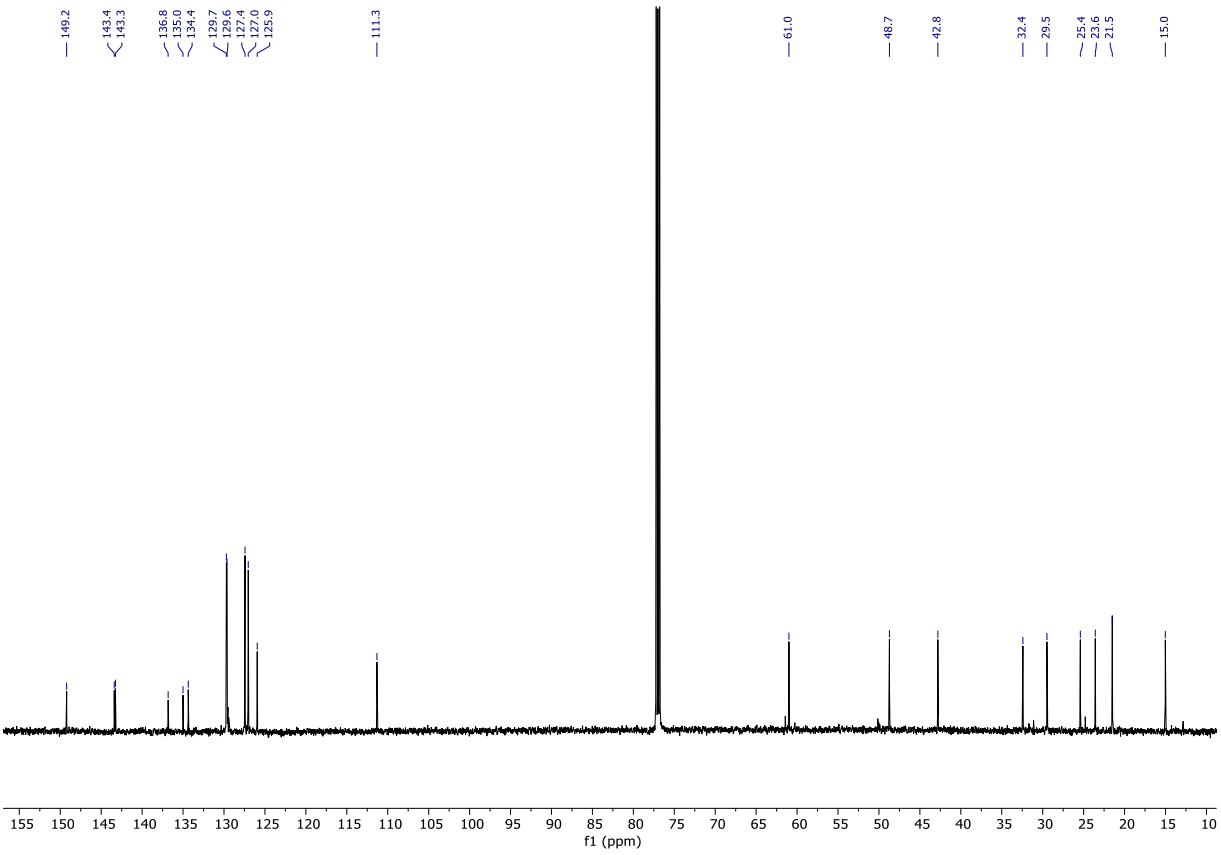
COSY-NMR of compound 7d mixture of isomers (600 MHz, $CDCl_3$)



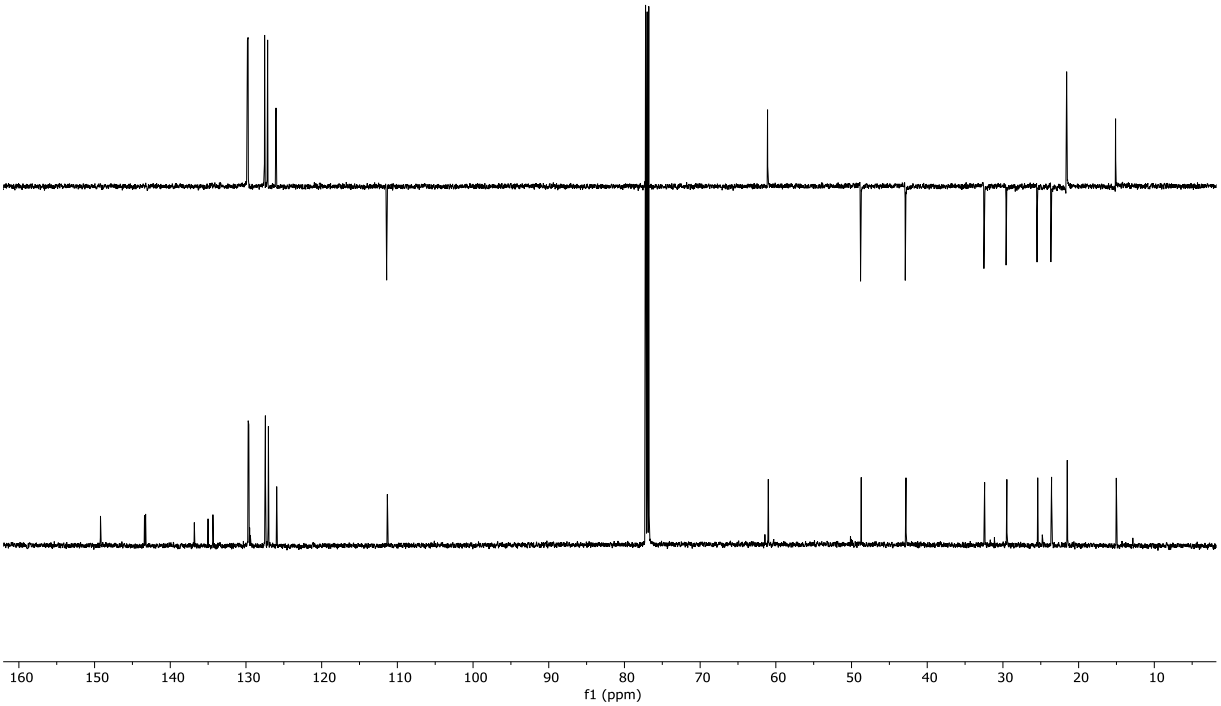
^{1}H-NMR of compound 4a (600 MHz, $CDCl_3$)



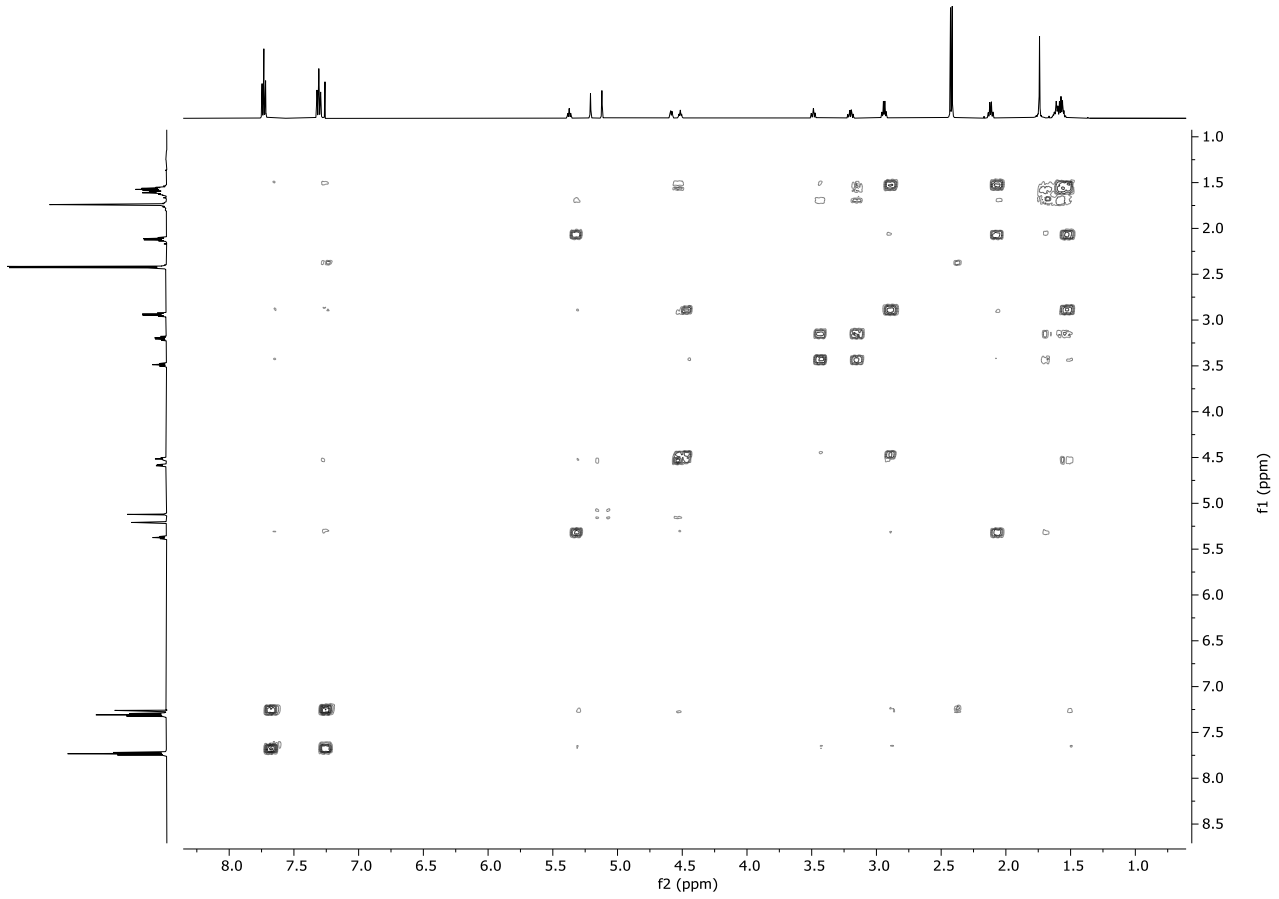
^{13}C-NMR of compound 4a (150 MHz, $CDCl_3$)



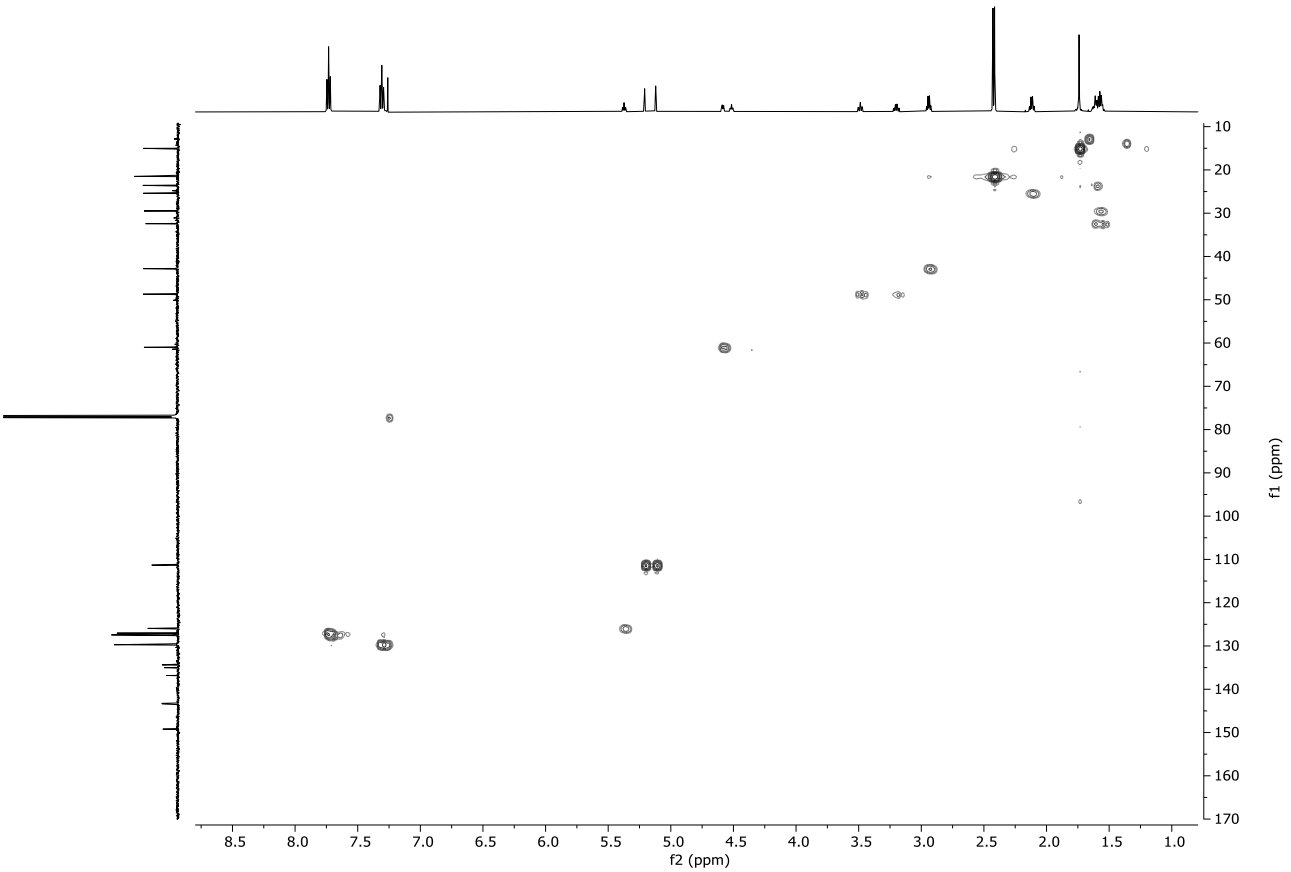
Comparison between DEPT-135 and ^{13}C-NMR of compound 4a (150 MHz, $CDCl_3$)



COSY-NMR of compound 4a (600 MHz, $CDCl_3$)

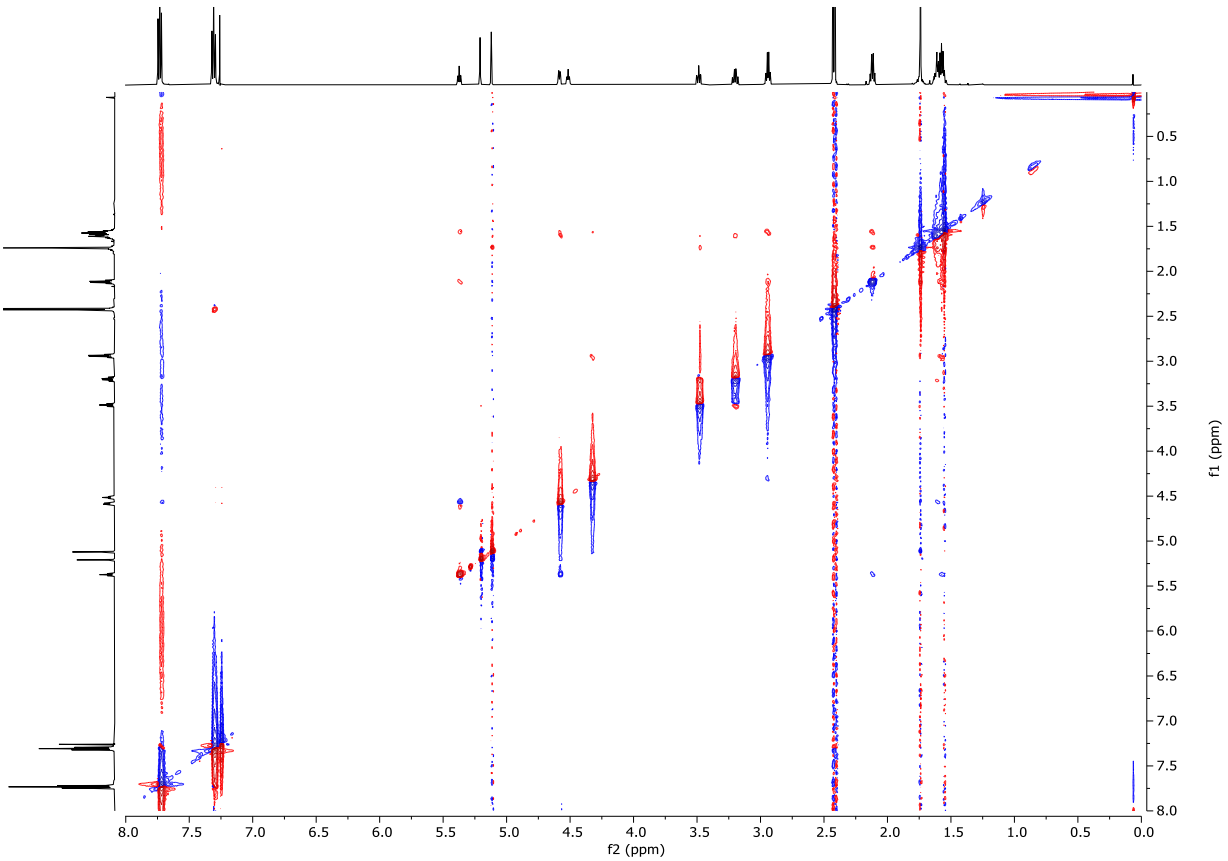


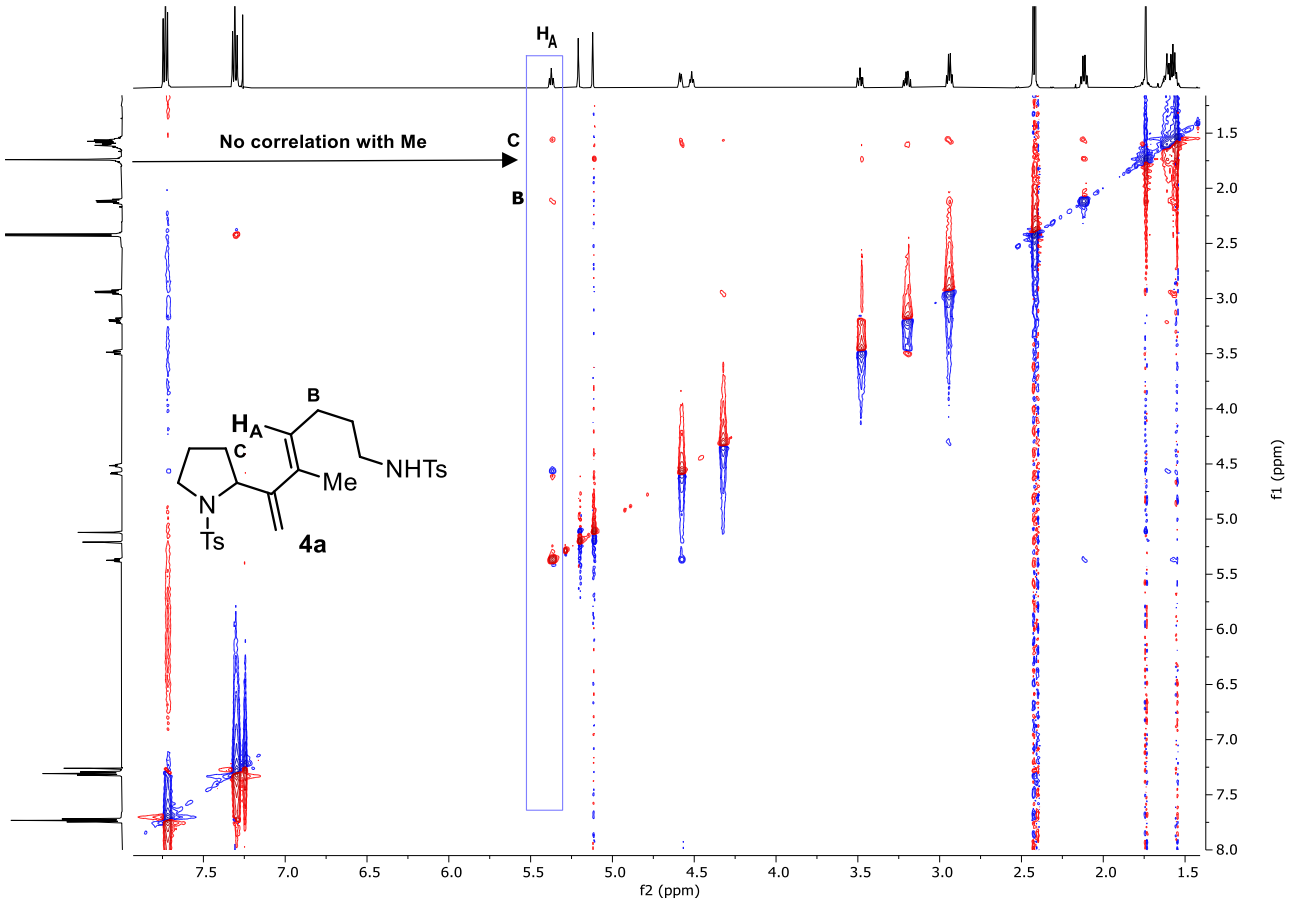
HMQC-NMR of compound 4a (150 MHz, $CDCl_3$)



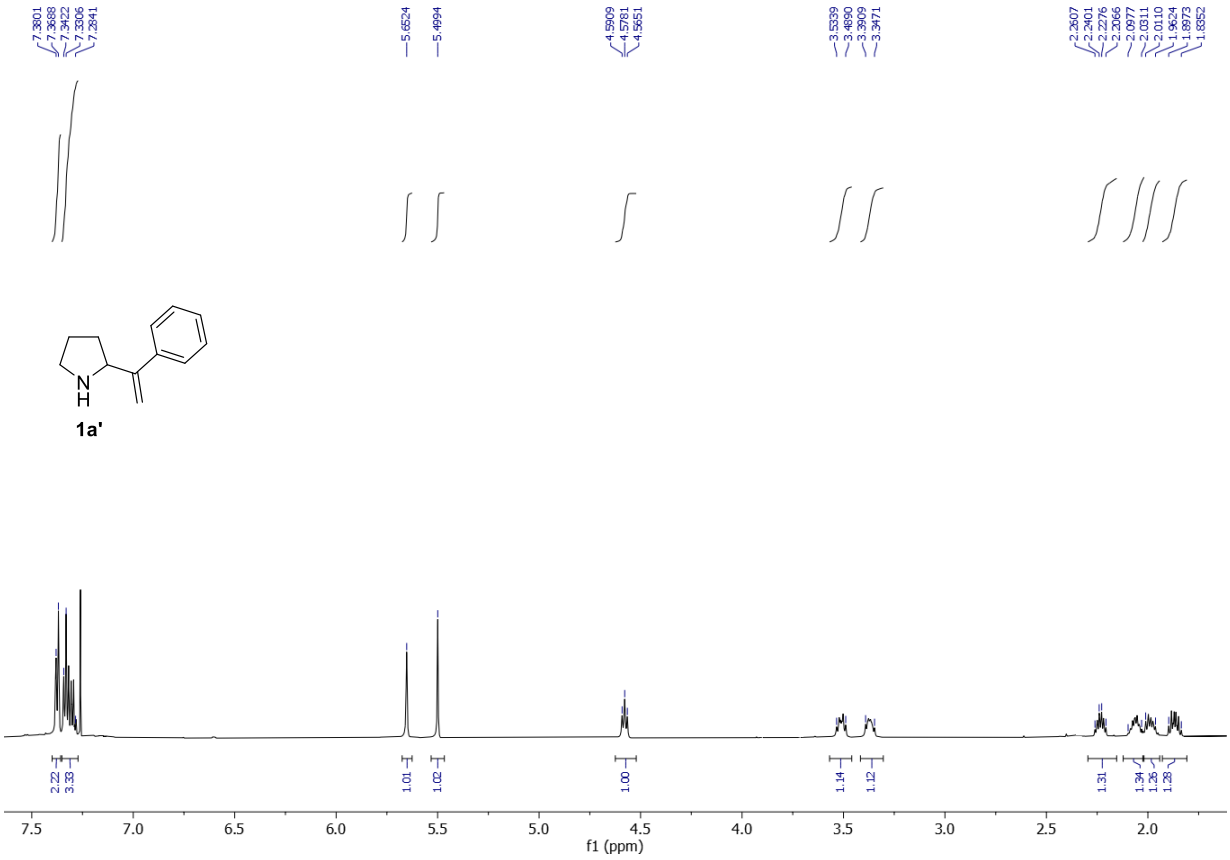
RP059b-FR15 — gradient enhanced HMQC with X-decoupling

NOESY-NMR of compound 4a (600 MHz, $CDCl_3$)

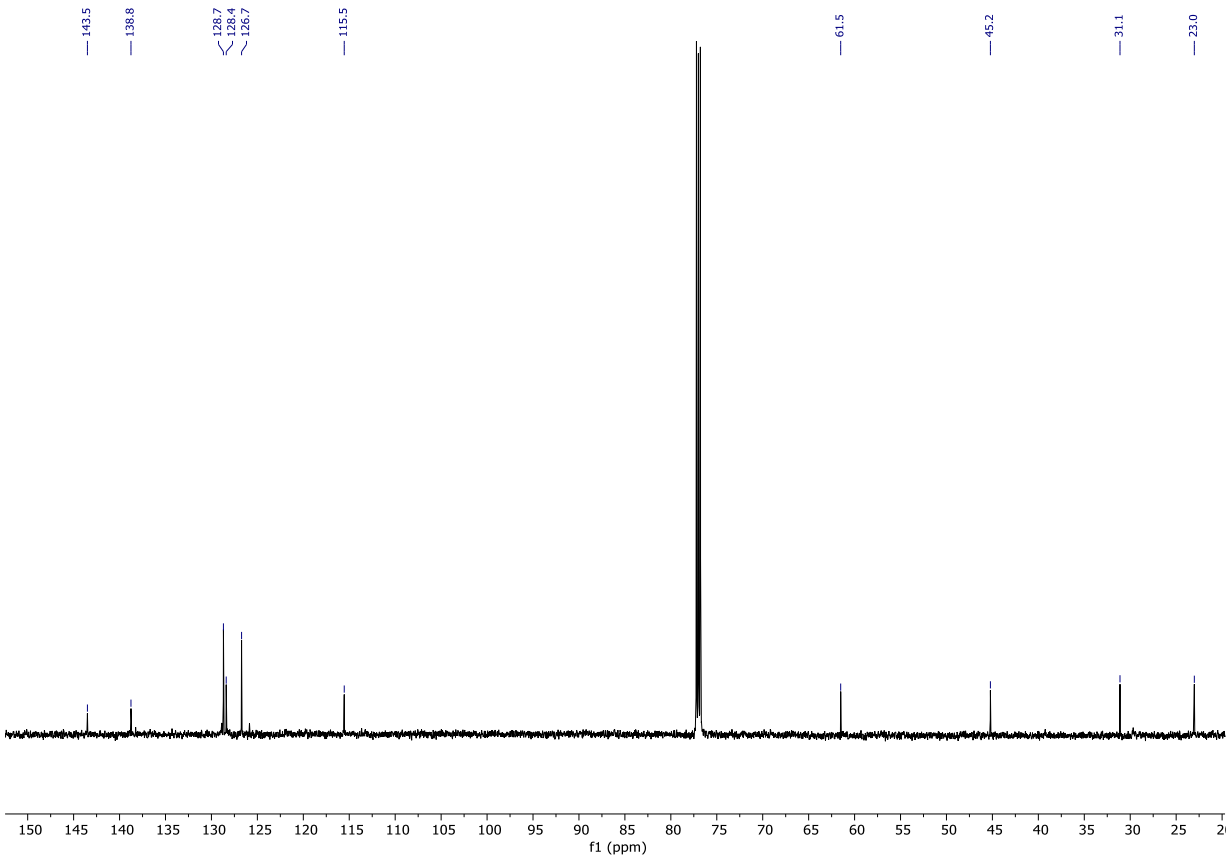



H_A
No correlation with Me
C
B
B
H_A
C
N
Ts
Me
NHTs
4a
f2 (ppm)
f1 (ppm)

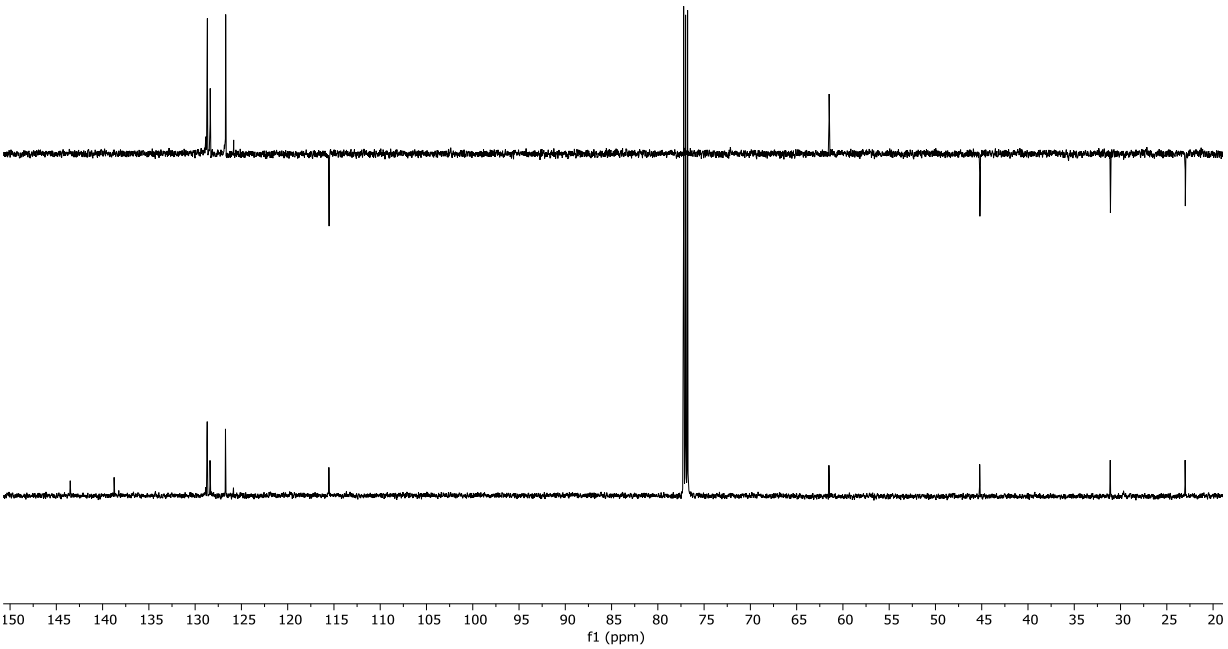
^{1}H-NMR of compound 1a' (600 MHz, $CDCl_3$)



^{13}C-NMR of compound 1a' (150 MHz, $CDCl_3$)



Comparison between DEPT-135 and ^{13}C-NMR of compound 1a' (150 MHz, $CDCl_3$)



COSY-NMR of compound 1a' (600 MHz, $CDCl_3$)