Inexpensive and Bench Stable Diarylmethylium Tetrafluoroborates as Organocatalysts in the Light Mediated Hydrosulfonylation of Unactivated Alkenes

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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. Acetic acid 99-100% was employed as received. Sodium benzenesulfinate **2a** and sodium 4-methylbenzenesulfinate **2b** were used as received from Merck. Sodium 4-chlorobenzenesulfinate **2c**, sodium 4-acetylbenzenesulfinate **2d** and sodium 2,4,6-trimethylbenzenesulfinate **2d** were prepared according to a literature procedure employing Milli-Q water as the solvent.[1] Alkene **1u** was synthesized according to the procedure reported by Kang *et al*.[2] Alkene **1v** was prepared according to a reported procedure.[3] Alkene **1w** derived from (*R*)-pulegone was prepared following the procedure reported by our group.[4] Alkene **1y** derived from (*S*)-Ibuprofen was synthesized according to the procedure reported by Carnell group.[5] Alkene **1z** derived from cholesterol was prepared following the procedure reported by Echavarren's group.[6]

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 Purple or Blue Lamp (390 or 456 nm) was used as the irradiation source. The irradiation source was located at 4 cm from the walls of the Schlenck tube.

NMR spectra were recorded employing a Jeol ECZR instrument. ^{1}H NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 or CD_3CN at 600 MHz. $^{13}C\{^1H\}$-NMR spectra were recorded in $CDCl_3$, CD_2Cl_2 or CD_3CN at 150 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 the resonance of CH_2Cl_2 (δ= 5.32) for ^{1}H NMR, to the peak of CD_2Cl_2 (δ= 54.0) for ^{13}C NMR and to the resonance of CH_3CN (δ= 1.94) for ^{1}H NMR, to the peak of CD_3CN (δ= 118.7, CN group) for ^{13}C NMR. DEPT experiments were carried out with a DEPT-135 sequence. ^{1}H NMR coupling constants (*J*) were reported in Hertz (Hz) and multiplicities are indicated as follows s (singlet), d (doublet), t (triplet), q (quartet), quint (quintuplet), ept (eptuplet), m (multiplet), dd (doublet of doublets), dq (doublet of quartet), dm (doublets of multiplet), td (triplet of doublets), tt (triplet of triplet), tm (triplet of multiplets), qd (quartet of doublet), bs (broad singlet), bd (broad doublet), bt (broad triplet), btt (broad triplet of triplet), bm (broad multiplet). Structural assignments were made with additional information from gCOSY, gNOESY experiments.

UV–vis spectra were carried out with a Varian Cary "100 Scan" spectrophotometer.

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) experiments were carried out in the following conditions:

- Electrodes: glassy carbon disc (working electrode), glassy carbon rod (counter electrode), Ag/AgCl/TEACl 0.1 M in CH_3CN (reference electrode)
- 0.1 M Bu_4NPF_6 in CH_2Cl_2 solution
- Catalyst concentration 0.3 mM
- Scan Rates: 10, 50, 100 and 200 mV s^{-1}
- Irradiation: KESSIL LAMP 1170 W m^{-2} and λ = 360 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 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. Estimate of catalyst **I** cost

Reagent	Supplier	Amount	Prize	Employed	Effective cost
1,2-Dimethylindole ≥98%	TCI Europe	5 g	40 €	450 mg (3 mmol)	3.60 €
2-Methoxy-1-naphthaldehyde ≥98%	TCI Europe	5 g	25 €	670 mg (3.6 mmol)	3.35 €
Tetrafluoroboric acid/ether complex	Merck	25 ml	61 €	(0.59 g, 3.6 mmol) 0.50 ml	1.22 €
CH3CN extra dry over MS, AcroSeal™	Thermo Scientific	100 ml	67 €	15 ml	10 €

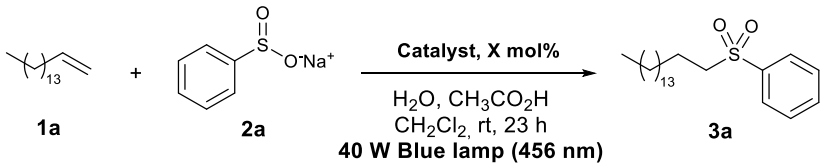
The reaction for the synthesis of catalyst **I** proceeds with a 94% yield producing 2.84 mmol (1.14 g, molecular mass 401 g/mol) starting from 3 mmol of 1,2-dimethylindole as described in the general procedure. The estimate cost for 2.84 mmol of salt **I** is 18.2 € which corresponds to a cost of **6.40 € per mmol**.

In order to compare the cost of catalyst **I** with iridium-based catalyst, we checked the prizes of the different iridium catalysts employed in the visible-light hydrosulfonylation of alkenes (see References 25-28).

Ir-catalyst	Ref.	Supplier	Amount	Prize	Cost per mmol
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	25-27	Merck	500 mg	862 €	**2155 €**
fac-$Ir(ppy)_3$	28	Merck Strem	500 mg 250 mg	604 € 288 €	**1041.4 €** **993.1 €**

3. Screening of reaction conditions

Table S1. Screening of the catalyst under 40 W blue light (456 nm)[a]



Entry	*Catalyst*	*Cat. amount [mol %]*	*Yield [%]*[b]
1	$Ir[dF(CF_3)ppy]_2(bpy)^+PF_6^-$	1	32
2	II	10	traces
3	I	10	22
4	I	15	24
5	I	20	8
6	I	5	traces
7	I	10	0[c]
8	I	10	0[d]

[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium benzenesulfinate **2a** (0.8 mmol, 1.6 eq.), catalyst (X mol%), H_2O (10 eq) and CH_3CO_2H (4.5 eq) in CH_2Cl_2 under illumination with a 40W Kessil blue LED lamp (456 nm), 23 h, room temperature. [b]Determined on the isolated product. [c]No irradiation.[d] No irradiation, 40°C.

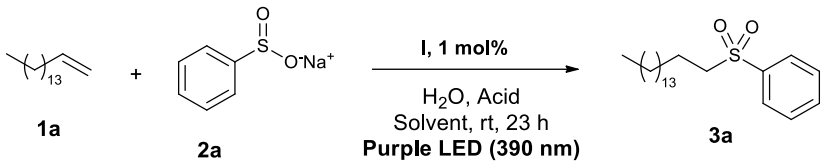


Table S2. Screening of the amount of the tetrafluoborate salt I[a]

Entry	*I amount [mol %]*	*CH_3CO_2H [eq]*	*H_2O [eq]*	*Solvent CH_2Cl_2 [ml]*	*Yield [%]*[b]
1	10	4.5	10	2.5	71
2	10	4.5	10	2.5	60[c]
3	5	4.5	10	2.5	87
4	3	4.5	10	2.5	83
5	2	4.5	10	2.5	66
6	1	4.5	10	2.5	80
7	-	4.5	10	2.5	0

[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium benzenesulfinate **2a** (0.8 mmol, 1.6 eq.), **I** (X mol%), H_2O (10 eq) and CH_3CO_2H (4.5 eq) in CH_2Cl_2 under illumination with a 40W Kessil purple LED lamp (390 nm), 23 h, room temperature. [d]Determined on the isolated product. [c]Reaction time: 48h.

Table S3: Solvent screening[a]

Entry	*I amount [mol %]*	*CH_3CO_2H [eq]*	*H_2O [eq]*	*Solvent [ml]*	*Yield [%]*[b]
1	1%	4.5	10	$CHCl_3$	50
2	1%	4.5	10	DMF	0
3	1%	4.5	10	THF	50
4	1%	4.5	10	2 Me-THF	13
5	1%	4.5	10	CH_3CN	30
6	1%	4.5	10	CH_2Cl_2[c]	64
7	1%	4.5	10	$CHCl_3$	50

[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium benzenesulfinate **2a** (0.8 mmol, 1.6 eq.), **I** (1 mol%), H_2O (10 eq) and CH_3CO_2H (4.5 eq) in 2.5 ml of the reported solvent under illumination with a 40W Kessil purple LED lamp (390 nm), 23 h, room temperature. [b] Determined on the isolated product. [c] 5 ml.

Table S4: Acid screening[a]

Entry	*I amount [mol %]*	*Acid [eq]*	*H_2O [eq]*	*Solvent CH_2Cl_2 [ml]*	*Yield [%][b]*
1	1%	HCOOH 4.5 eq	10	2.5	77
2	1%	HCl 4.5 Eq	10	2.5	40
3	1%	H_2SO_4 4.5 Eq	10	2.5	45
4	1%	CH_3COOH 4.5 eq	10	2.5	80
5	1%	CH_3COOH 1 eq	10	2.5	41[c]

[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium benzenesulfinate **2a** (0.8 mmol, 1.6 eq.), **I** (1 mol%), H_2O (10 eq) and acid (X eq) in 2.5 ml of CH_2Cl_2 as solvent under illumination with a 40W Kessil purple LED lamp (390 nm), 23 h, room temperature. [b]Determined on the isolated product. [c]Determined by NMR with CH_3NO_2 as the internal standard.

Table S5: Equivalents of water screening[a]

Entry	*I amount [mol %]*	*CH_3CO_2H [eq]*	*H_2O [eq]*	*Solvent CH_2Cl_2 [ml]*	*Yield [%][b]*
1	1%	4.5	0	2.5	0
2	1%	4.5	3	2.5	40[c]
3	1%	4.5	6	2.5	66[c]
4	1%	4.5	10	2.5	86[c]/80
5	1%	4.5	20	2.5	72[c]
6	1%	4.5	0	2.5	0

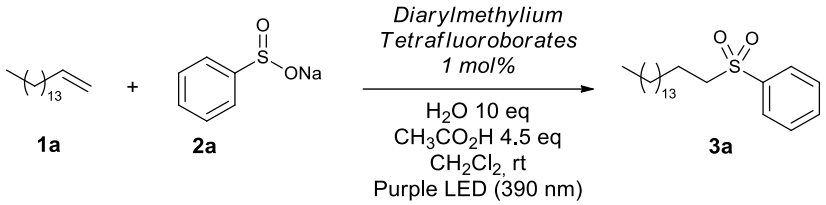
[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium benzenesulfinate **2a** (0.8 mmol, 1.6 eq.), **I** (1 mol%), H_2O (X eq) and CH_3CO_2H (4.5 eq) in 2.5 ml CH_2Cl_2 as solvent under illumination with a 40W Kessil purple LED lamp (390 nm), 23 h, room temperature. [b] Determined on the isolated product. [c] Determined by NMR with CH_3NO_2 as the internal standard

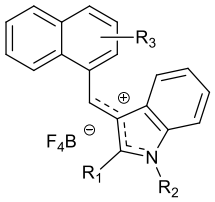
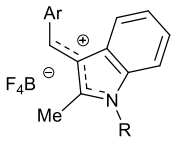
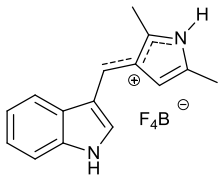
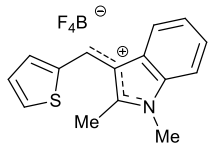
Table S6: Screening of sulfinate 2a amount[a]

Entry	*I amount [mol %]*	*Sulfinate 2a [eq]*	*CH_3CO_2H [eq]*	*H_2O [eq]*	*Solvent CH_2Cl_2 [ml]*	*Yield [%][b]*
1	1%	1.1	4.5	10	2.5	59
2	1%	1.6	4.5	10	2.5	80
3	1%	3	4.5	10	2.5	70

[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium benzenesulfinate **2a** (X eq.), **I** (1 mol%), H_2O (10 eq) and CH_3CO_2H (4.5 eq) in 2.5 ml CH_2Cl_2 as solvent under illumination with a 40W Kessil purple LED lamp (390 nm), 23 h, room temperature. [b]Determined on the isolated product.

Table S7: Screening and characterization of diarylmethylium tetrafluoborates I – XII

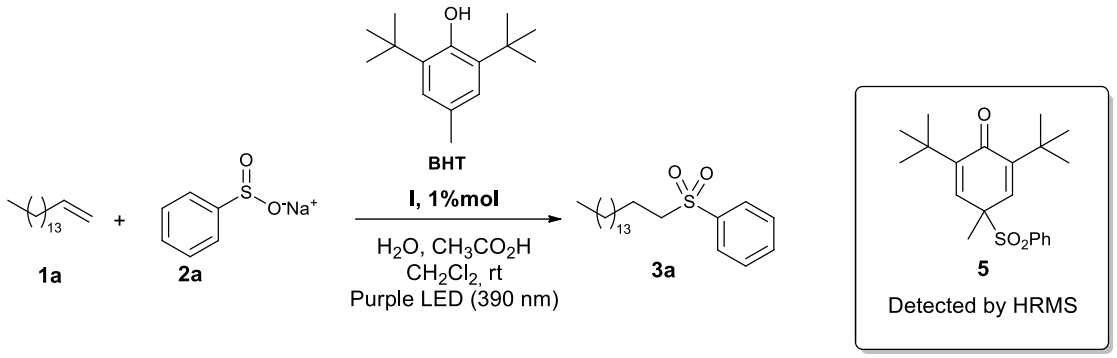


Entry	Diarylmethylium salt		3a Yield [%][b]	λ_{max} abs [nm]	E^{0c} [V]
1		**I** R_1, R_2 = Me, R_3 = 2-OMe	80	522	**-0.395** (I,c); +1.25 (I,a,w); +1.57 (I,a,w)
2		**II** R_1 = Me, R_2 = H, R_3 = 2-OMe	62	504	**-0.38** (I,c); +1.25 (I,a,w)
3		**III** R_1= Ph, R_2 = Me, R_3 = 2-OMe	70	539	**-0.285** (I,c); +1.35 (R,a,w)
4		**IV** R_1= 2-naphthyl, R_2= Me, R_3 = 2-OMe	66	543	**-0.275** (I,c); +1.45 (I,a,w)
5		**V** R_1= 2-naphthyl, R_2= H, R_3 = 2-OMe	70	533	**-0.48** (I,c); +0.30 (I,c,w); +1.05 (I,a,w); +1.20 (I,a,w)
6		**VI**[d] R_1 = Me, R_2 = Me, R_3 = 4-OMe	78	542	**-0.48** (I,c); +0.90 (I,a,w); +1.20 (I,a,w)
7		**VII** Ar= 2,4,6-triMePh, R = Me	57	416	-0.30 (I,c); +1.10 (I,a,w)
8		**VIII** Ar= 2-MeOPh, R = H	2	446	-0.49 (I,c); +0.80 (I,a,w); +0.95 (I,a,w)
9		**IX** Ar= 4-ClPh, R = H	8	409	-0.50 (I,c,d); +0.15 (I,c,w); +1.20 (I,a,w)
10		**X** Ar= 4-NO_2Ph, R = H	35	392	-0.38 (I,c); +0.10 (I,c); +0.95 (R,a,w), +0.85 (R,c,w); +1.12 (I,a,w)
11		**XI**	62	478	**-0.68** (I,c); +1.38 (I,a,w)
12		**XII**	29	444	**-0.255** (I,c); +1.14 (I,a,w); +1.31 (I,a,w)

[a]Reaction conditions: Hexadec-1-ene **1a** (0.5 mmol), sodium phenylsulfinate **2a** (0.8 mmol, 1.6 eq.), diarylmethylium salt (1 mol%) in CH_2Cl_2 (2.5 mL), CH_3COOH (2.25 mmol, 4.5 eq), H_2O (5 mmol, 10 eq), 40W Kessil purple LED lamp (390 nm), 23 h, room temperature. [b]Determined on the isolated product. [c] CV (V v. Ag/AgCl). R = reversible, I = irreversible, a = anodic, c = catodic, w = weak. [d]4-MeOnapthyl replaces the 2-MeOnaphtyl moiety.

4. Mechanistic Investigations

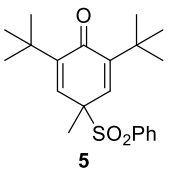
4.1 Trapping Experiment with butylhydroxytoluene (BHT)



In order to study the formation of radicals, two trapping experiments with BHT were realized. The reactions were carried out employing 2 eq of BHT in the presence of catalytic amounts of tetrafluoborate **I**.

Procedure: A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2 for 5 minutes, then the N_2 flow was removed and the flask was closed with a septum. Hexadec-1-ene **1a** (112 mg, 0.5 mmol, 1 eq) was placed in the Schlenk tube followed by diarylmethylium salt **I** (2 mg, 0.005 mmol, 1 mol%) and sodium benzenesulfinate **2a** (135 mg, 0.8 mmol, 1.6 eq), then 2.5 ml of CH_2Cl_2 were added. The intense red solution was left under stirring until its colour faded to transparent. Always under stirring, water (90 mg, 5 mmol, 10 eq) and acetic acid (135 mg, 2.2 mmol, 4.5 eq) were added followed by the radical trapper BHT (220 mg, 1 mmol, 2 eq). In a second experiment, BHT was added after 4h from the start of the reaction.
The Schlenk tube was closed with a septum and then stirred at 4 cm from a Kessil purple lamp (390 nm) at room temperature for 23 h.
The crude reaction mixtures were analysed by HRMS in order to detect possible radical intermediates.

Results in the presence of BHT as radical scavenger: Product **3a** was obtained in 10% yield (*vs* 80% in the standard condition) and BHT-sulfonyl radical adduct **5** was detected by HRMS of the crude reaction mixture. When BHT was added after 4h of reaction, product **3a** was formed in 19% yield together with the BHT-sulfonyl radical adduct.



2,6-di-*Tert*-butyl-4-methyl-4-(phenylsulfonyl)cyclohexa-2,5-dien-1-one 5: **HRMS** (ESI, *m/z*): Chemical formula $C_{21}H_{28}O_3S$, **[M+Na]⁺** theoretical *m/z* **383.1651**, found *m/z* 383.1654.

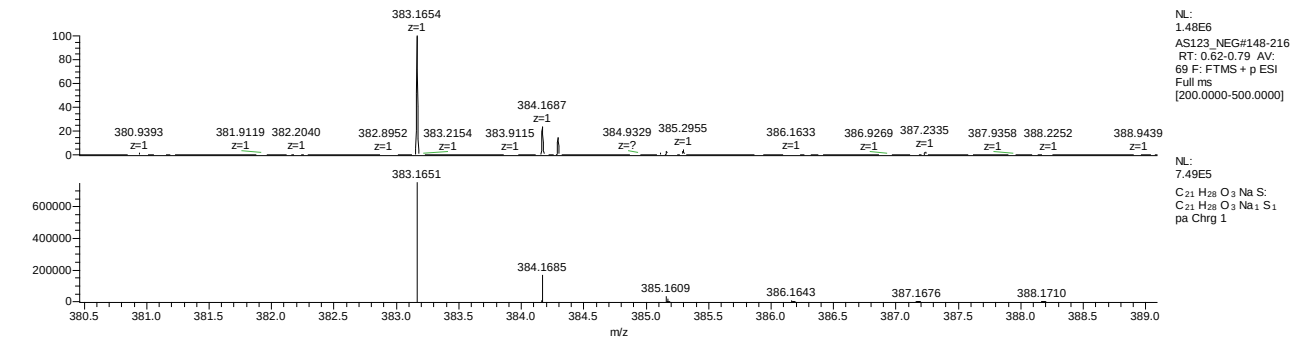
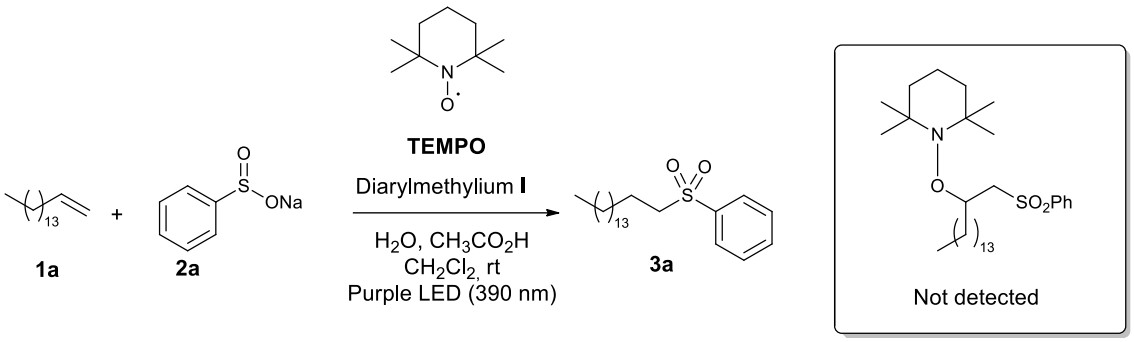


Figure S1. HRMS trace of crude mixture of the reaction with BHT as radical trapper. The trace shows the exact mass of compound **5** as $[M+Na]^+$ adduct.

4.2 Trapping Experiment with TEMPO



In order to study the formation of radicals, a trapping experiment with TEMPO was realized. The reaction was carried out employing 2 eq of TEMPO in the presence of catalytic amounts of salt **I**.

Procedure: A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under a flow of N_2 for 5 minutes, then the N_2 flow was removed and the flask was closed with a septum. Hexadec-1-ene **1a** (112 mg, 0.5 mmol, 1 Eq) was placed in the Schlenk tube followed by salt **I** (2 mg, 0.005 mmol, 1 mol%) and sodium benzenesulfinate **2a** (135 mg, 0.8 mmol, 1.6 eq), then 2.5 ml of CH_2Cl_2 were added. The intense red solution was left under stirring until its colour faded to transparent. Always under stirring, water (90 mg, 5 mmol, 10 eq), acetic acid (135 mg, 2.2 mmol, 4.5 eq) and the radical trapper TEMPO (156 mg, 1 mmol, 2 eq) were added.
The Schlenk tube was closed with a septum and then stirred at 4 cm from a Kessil purple lamp (390 nm) at room temperature for 21 h.
The crude reaction mixtures were analysed by MS in order to detect possible radical intermediate.
Results in the presence of TEMPO as radical scavenger: Starting material **1a** was not totally consumed (20% **1a** recovered) in the presence of TEMPO, and product **3a** was obtained in 16% yield (*vs* 80% in the standard condition). Any TEMPO adduct could not be detected by HRMS.

4.3 Light/Dark Experiment

In order to unveil the fundamental role of the light in promoting this hydrosulfinylation reaction at room temperature, we realised a light/dark experiment on the model reaction between Hexadec-1-ene **1a** and sodium benzenesulfinate **2a**. Thus, we set up a model reaction according to the general procedure reported in Section 4.4. The reaction mixture under stirring was submitted to light/dark cycles of variable time length according to Table S8.

Table S8. 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 60 min	60	1.5
Light OFF for 60 min	120	1.5
Light ON for 60 min	180	8
Light OFF for 60 min	240	8
Light ON for 60 min	300	17
Light OFF for 60 min	360	17
Light ON for 60 min	1400	88

For each point, 0.2 mL of crude reaction mixture were withdrawn with a syringe. The solution was transferred in a test tube, where it was diluted with 2 mL of CH_2Cl_2 and then washed with 1 mL of a saturated aqueous solution of $NaHCO_3$. 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 CH_3NO_2 (0.0224 mmol) as the internal standard.

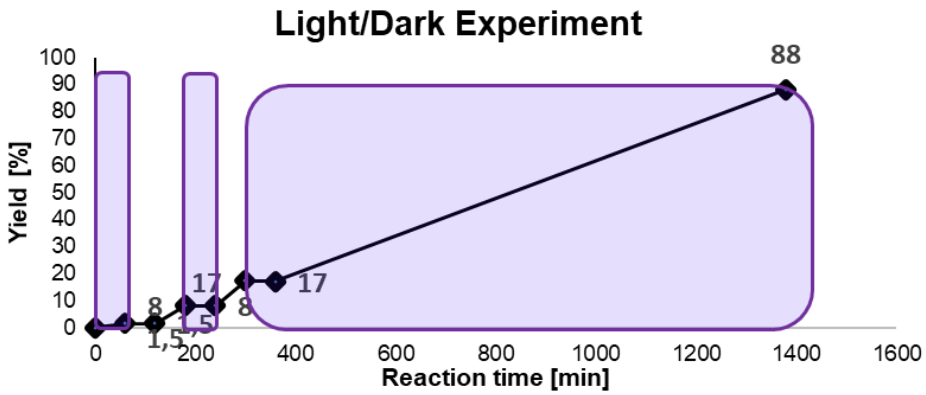
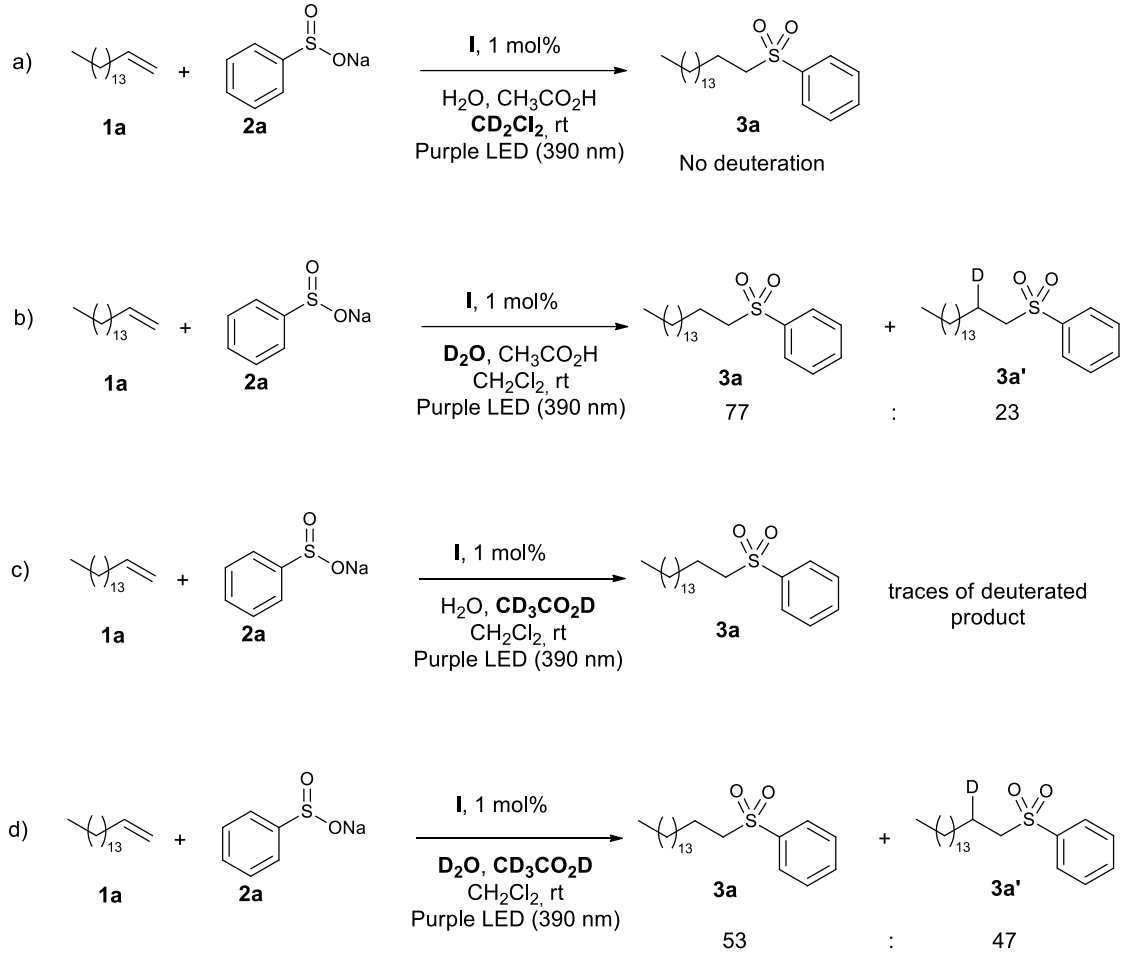


Figure S2. Light/dark experiment graph for the model reaction between hexadec-1-ene **1a** and sodium benzenesulfinate **2a**.

4.4 Deuterium Exchange Experiments

Following the general procedure of hydrosulfinylation between hexadec-1-ene **1a** and sodium benzenesulfinate **2a** deuterium exchange experiments were performed in order to unveil the reaction mechanism. The first experiment (**Scheme S1**) was carried out employing CD_2Cl_2 as the solvent instead of CH_2Cl_2, in this case only the not deuterated product **3a** was recovered. As shown in **Scheme S1b**, the second experiment was performed in the presence of D_2O. In this case a mixture of not deuterated and deuterated product in 77:23 ratio, respectively **3a** and **3a'**, was detected by NMR (see **Figure S3**). Deuterium was introduced in the β-position of sulfone as indicated in the comparison between ^{1}H- and D-NMR (**Figure S4**).



Scheme S1: Summary of the deuterium exchange experiments performed.

The third experiment was realized employing CD_3CO_2D instead of normal acetic acid (**Scheme S1c**). In this case, traces of deuterated product **3a'** were formed. The last experiment was performed in the presence of both D_2O and CD_3CO_2D (**Scheme S1d**). A mixture of **3a**/**3a'** was formed in a 53:47 ratio. The incorporation of deuterium was also confirmed by HRMS of the crude reaction mixture of experiment d (**Figure S7**).

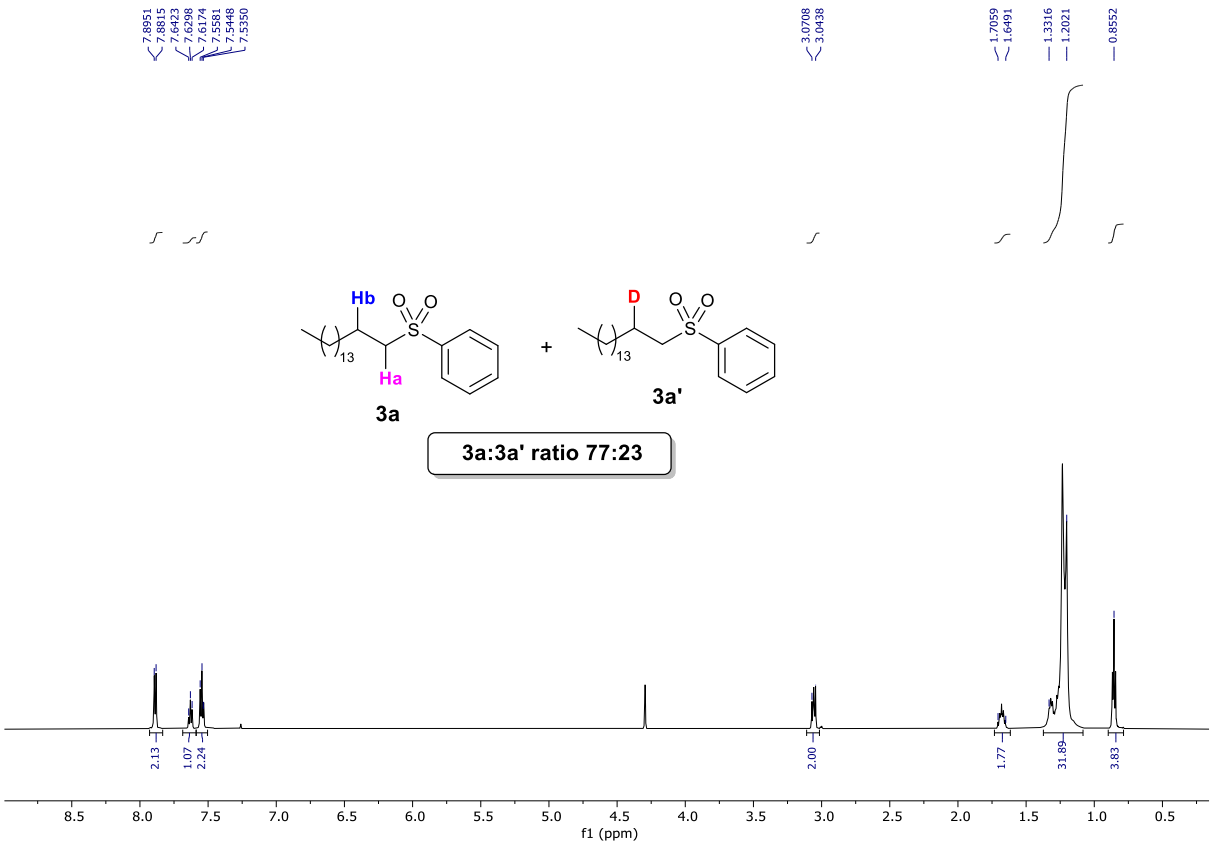


Figure S3. ^{1}H-NMR of the crude reaction mixture of deuteration experiment b in Scheme S1 in the presence of D_2O. The ^{1}H-NMR was recorded in $CDCl_3$ in the presence of CH_3NO_2 as internal standard.

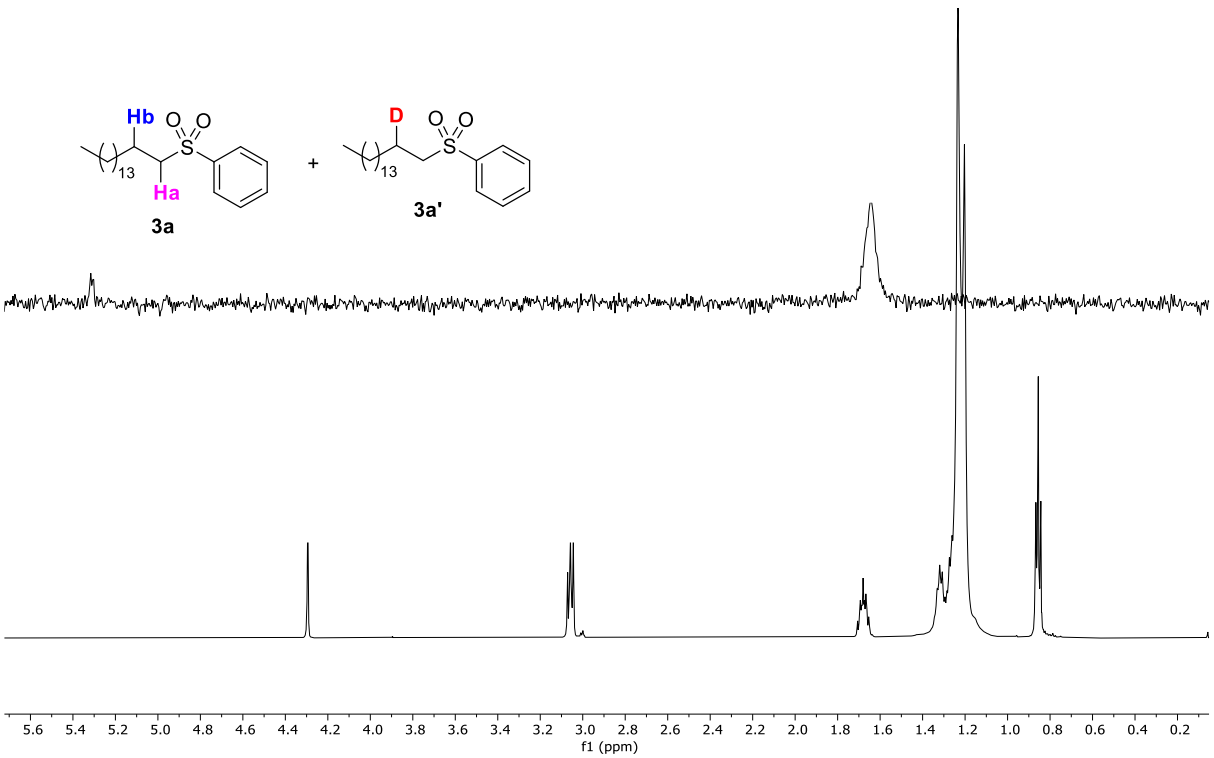


Figure S4. Comparison between the ^{1}H-NMR and the D-NMR of the crude reaction mixture of deuteration experiment b in Scheme S1. The ^{1}H-NMR was recorded in $CDCl_3$ in the presence of CH_3NO_2 as internal standard, while the D-NMR was recorded in CH_2Cl_2.

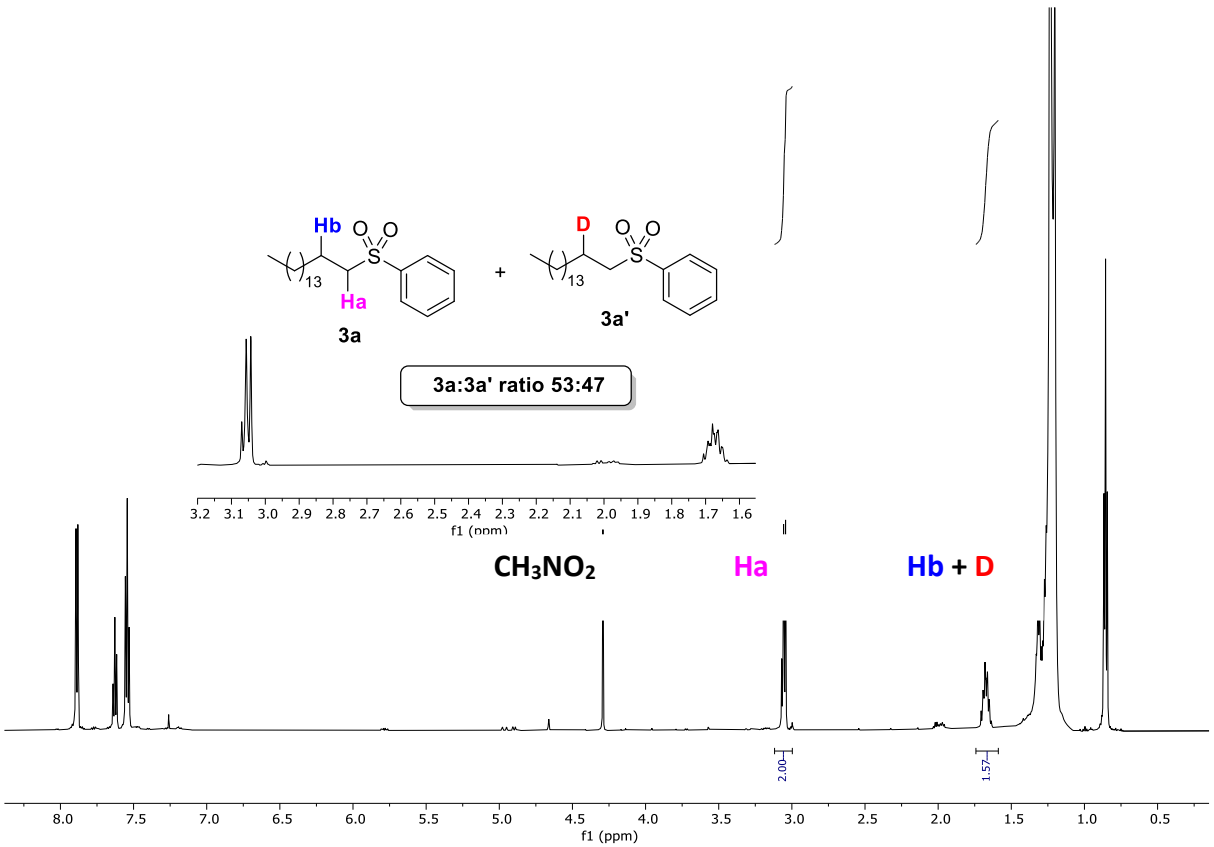


Figure S5. ^{1}H-NMR of the crude reaction mixture of deuteration experiment d in Scheme S1 in the presence of D_2O and CD_3CO_2D. The ^{1}H-NMR was recorded in $CDCl_3$ and CH_3NO_2 as internal standard.

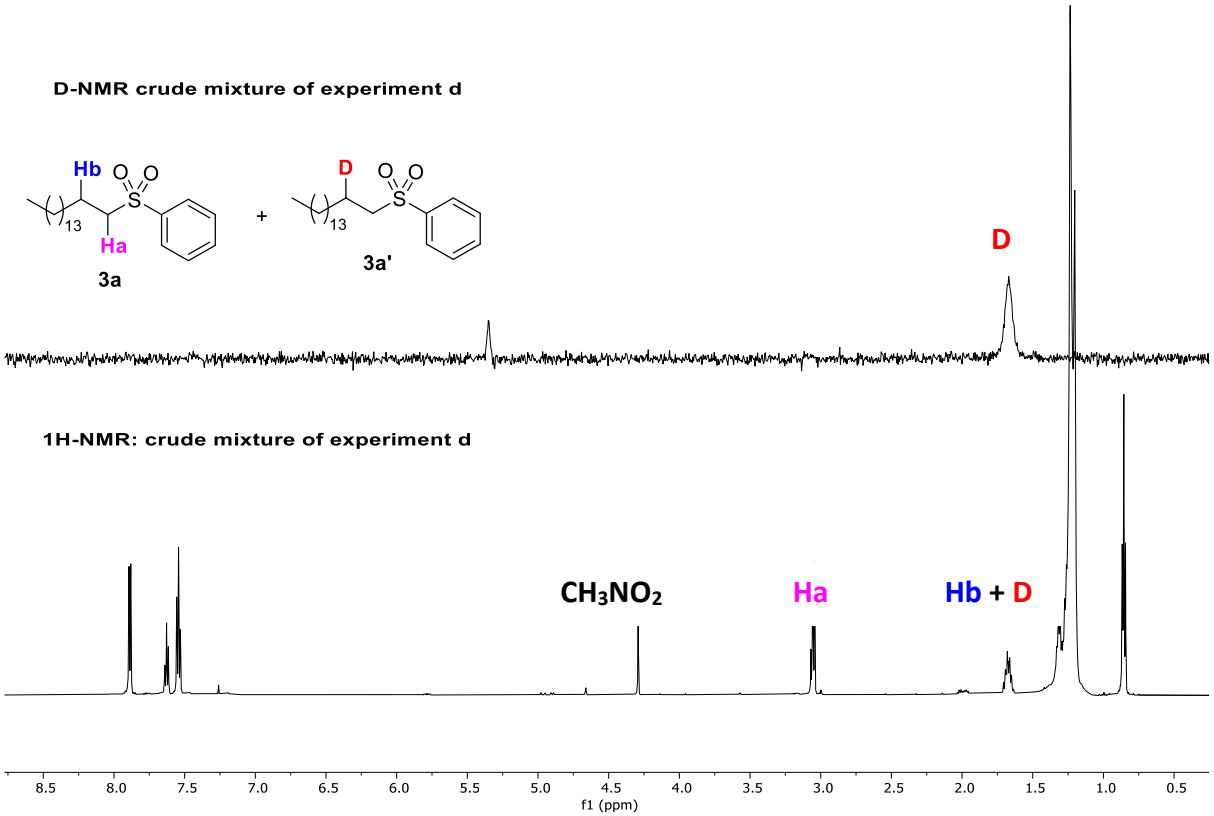


Figure S6. Comparison between the ^{1}H-NMR and the D-NMR of the crude reaction mixture of deuteration experiment d in Scheme S1 in the presence of D_2O and CD_3CO_2D. The ^{1}H-NMR was recorded in $CDCl_3$ with CH_3NO_2 as internal standard, while the D-NMR was recorded in CH_2Cl_2.

(Hexadecylsulfonyl)benzene 3a: **HRMS** (ESI, *m/z*): Chemical formula $C_{22}H_{38}O_2S$, **[M+H]$^+$** theoretical *m/z* 367.2665, found *m/z* 367.2670.
Deuterated (hexadecylsulfonyl)benzene 3a': **HRMS** (ESI, *m/z*): Chemical formula $C_{22}H_{37}DO_2S$, **[M+H]$^+$** theoretical *m/z* 368.2728, found *m/z* 3682732.

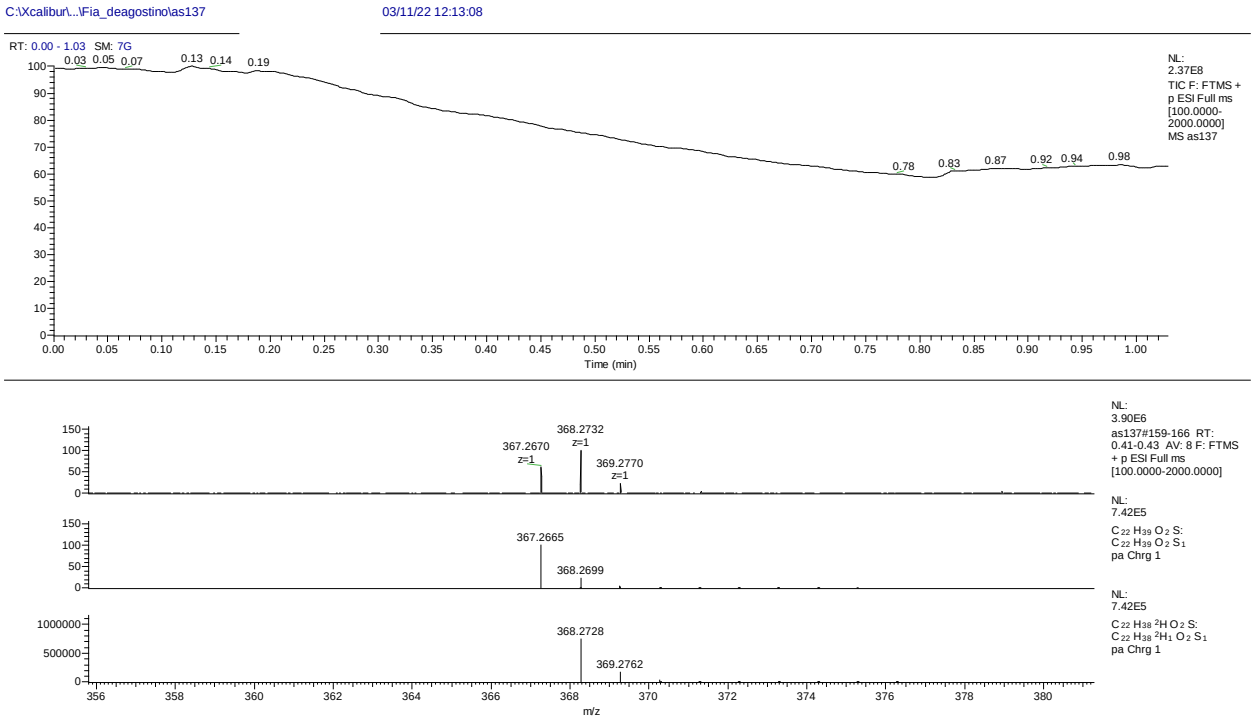


Figure S7. HRMS trace of the crude mixture of the model reaction with hexadec-1-ene **1a** and sodium benzenesulfinate **2a** in the presence of D_2O and CD_3CO_2D, deuteration experiment d in Scheme S1. The trace shows the exact mass of compounds **3a** and **3a'** as $[M+H]^+$ adducts.

4.5 UV-Vis Characterization of the diarylmethylium tetrafluoborates I – XII

Extinction measurements in the UV–vis range were carried out with a Varian Cary "100 Scan" spectrophotometer. The absorption was measured on freshly prepared solution the of diarylmethylium tetrafluoborates **I** – **XII** (20 mM) using CH_2Cl_2 as the solvent (**Figure S8-S18**). The optical path length was 1 cm. The solutions were stable during the timescales necessary for the measurements, and the results of repeated measures were reproducible. Solutions were not stirred during the measures. In the following figures the UV-Vis spectra of **I** – **XII** (before adding the sulfinate) are reported together with a picture of the cuvette before the analysis. The compounds can be divided in three different groups on dependence of the absorption spectra:

- **VIII**, **XI**, **XII**: absorption in the range 440-480 nm
- **II**, **III**, **IV**, **V**, **VI**: absorption in the range 500-550 nm
- **VII**, **IX**, **X**: absorption in the range 390-420 nm

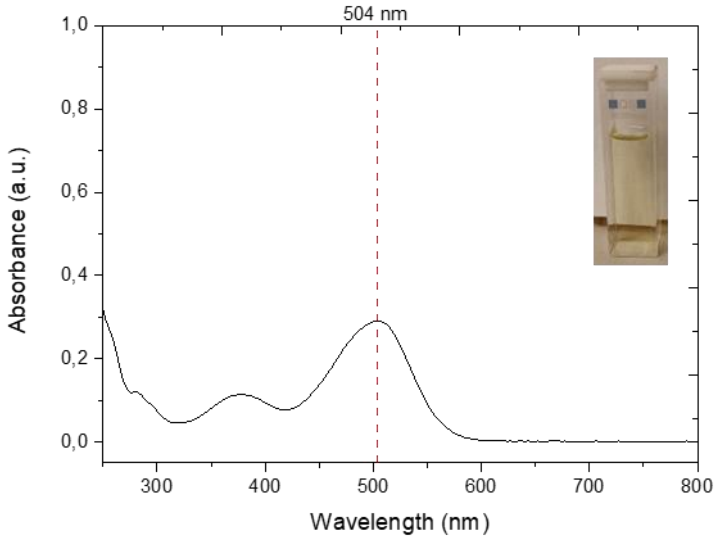


Figure S8. UV-Vis spectrum of diarylmethylium tetrafluoborate **II** (20 mM) in CH_2Cl_2

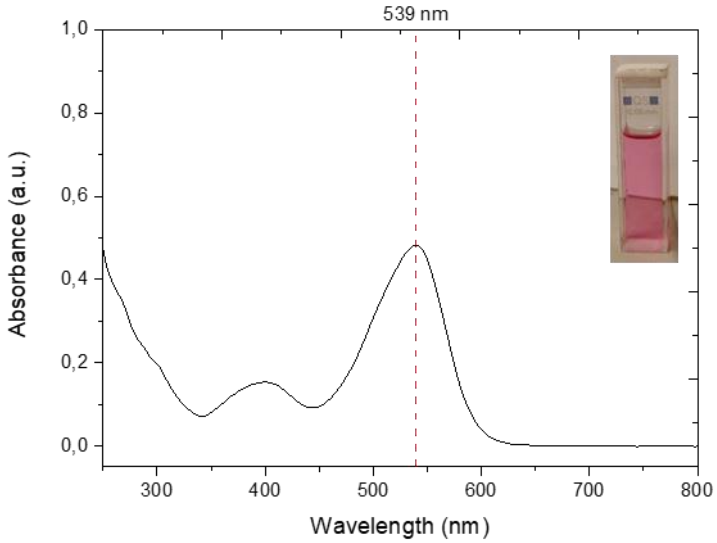


Figure S9. UV-Vis spectrum of diarylmethylium tetrafluoborate **III** (20 mM) in CH_2Cl_2

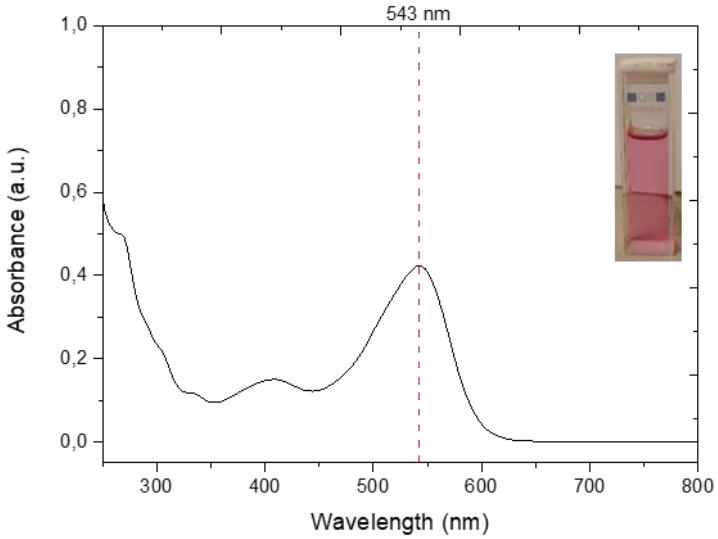


Figure S10. UV-Vis spectrum of diarylmethylium tetrafluoborate **IV** (20 mM) in CH_2Cl_2

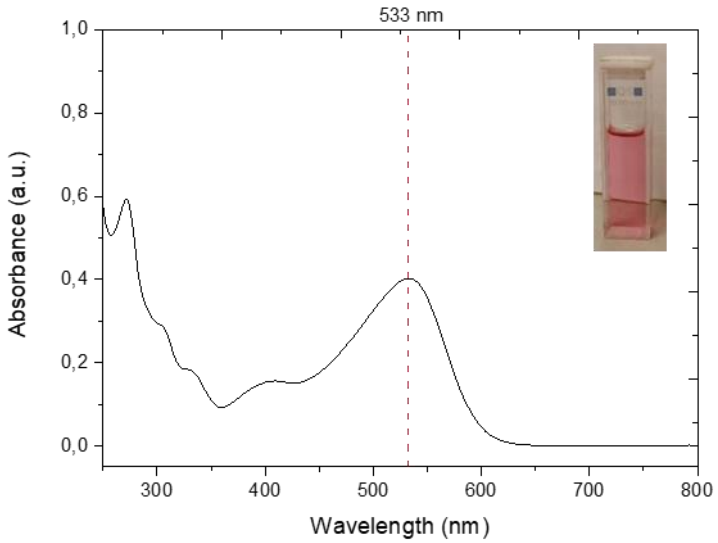


Figure S11. UV-Vis spectrum of diarylmethylium tetrafluoborate **V** in CH_2Cl_2

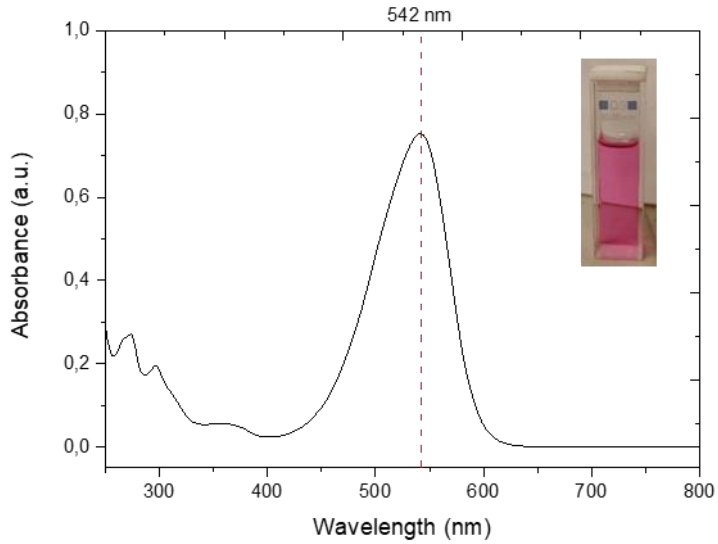


Figure S12. UV-Vis spectrum of diarylmethylium tetrafluoborate **VI** (20 mM) in CH_2Cl_2

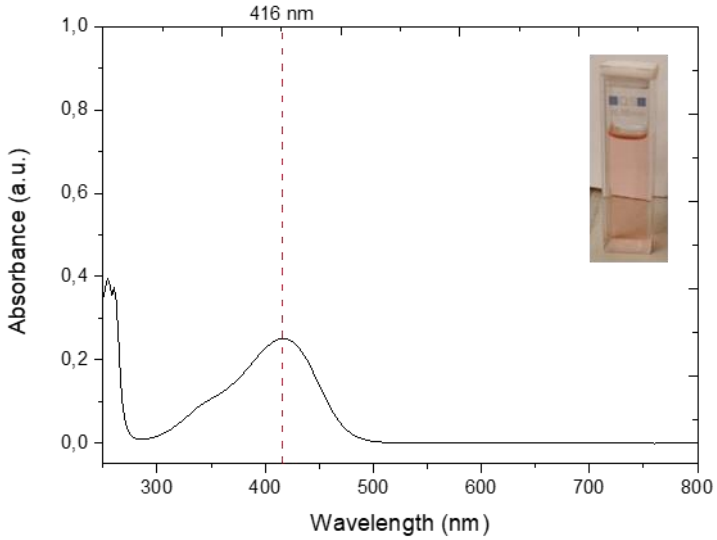


Figure S13. UV-Vis spectrum of diarylmethylium tetrafluoborate **VII** (20 mM) in CH_2Cl_2

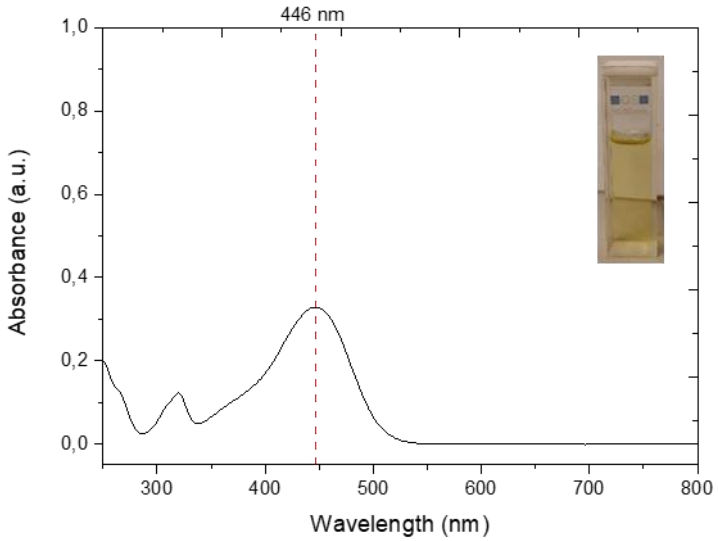


Figure S14. UV-Vis spectrum of diarylmethylium tetrafluoborate **VIII** 20 mM) in CH_2Cl_2

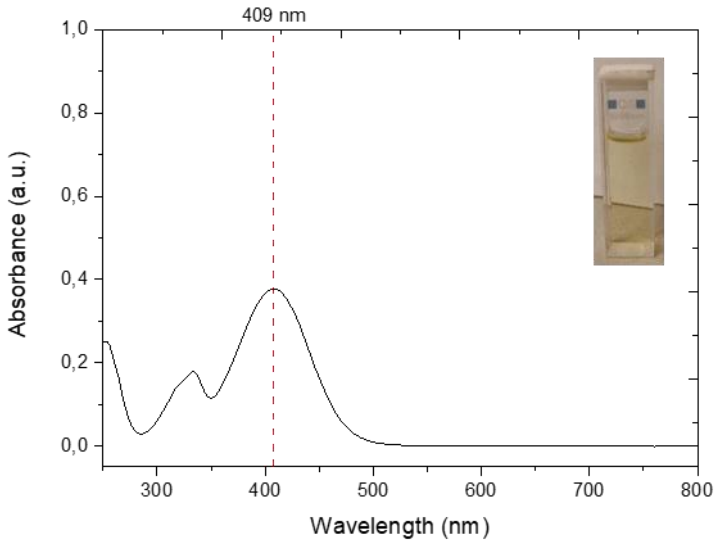


Figure S15. UV-Vis spectrum of diarylmethylium tetrafluoborate **IX** (20 mM) in CH_2Cl_2

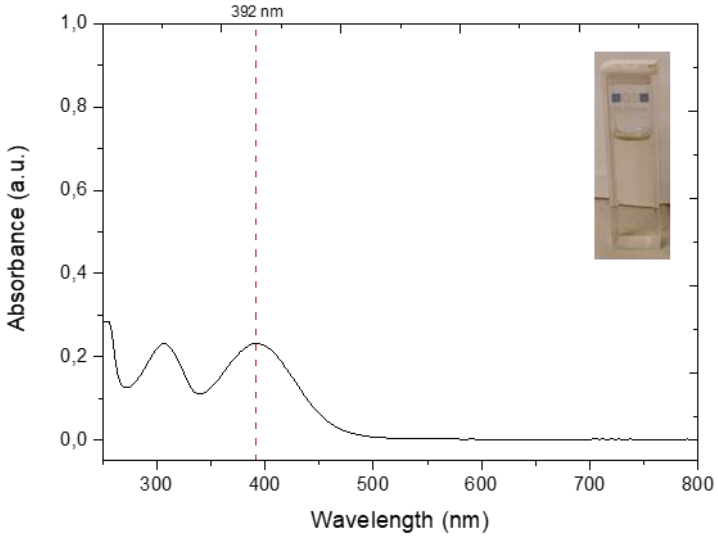


Figure S16. UV-Vis spectrum of diarylmethylium tetrafluoborate **X** (20 mM) in CH_2Cl_2

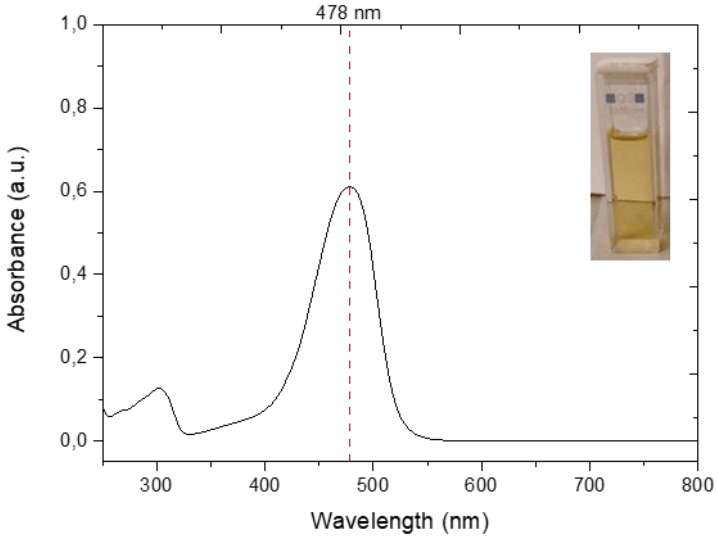


Figure S17. UV-Vis spectrum of diarylmethylium tetrafluoborate **XI** (20 mM) in CH_2Cl_2

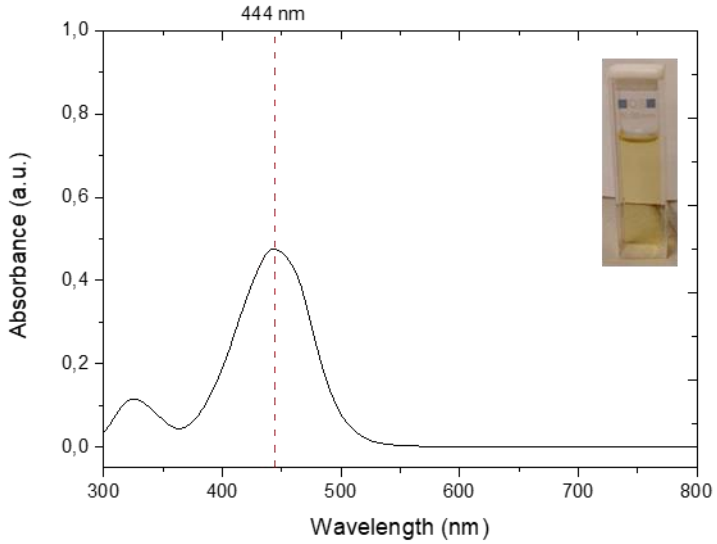


Figure S18. UV-Vis spectrum of diarylmethylium tetrafluoborate **XII** (20 mM) in CH_2Cl_2

4.6 UV-Vis Characterization of selected diarylmethylium tetrafluoborates in the presence of phenyl sulfinate 2a

Extinction measurements in the UV–vis range were carried out with a Varian Cary "100 Scan" spectrophotometer. The absorption was measured on freshly prepared solution the of diarylmethylium tetrafluoborates **IV**, **V**, **VI** and **VIII** (20 mM) in the presence of 1.6 eq of phenyl sulfinate **2a** using CH_2Cl_2 as the solvent (**Figure S19-S22**). The optical path length was 1 cm. Solutions were not stirred during the measures.

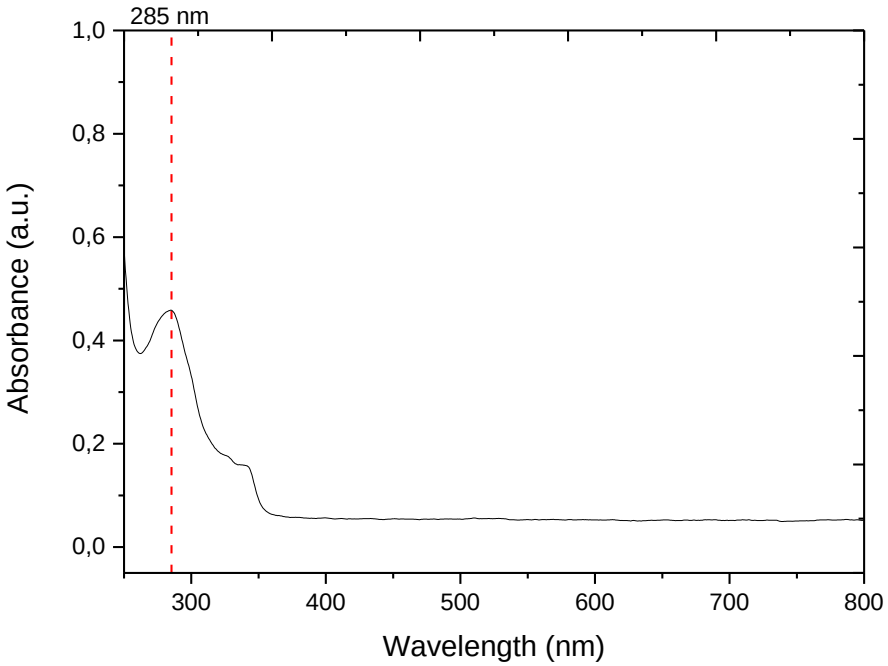


Figure S19. UV-Vis spectrum of diarylmethylium tetrafluoborate **IV** (20 mM) with 1.6 eq of **2a** in CH_2Cl_2

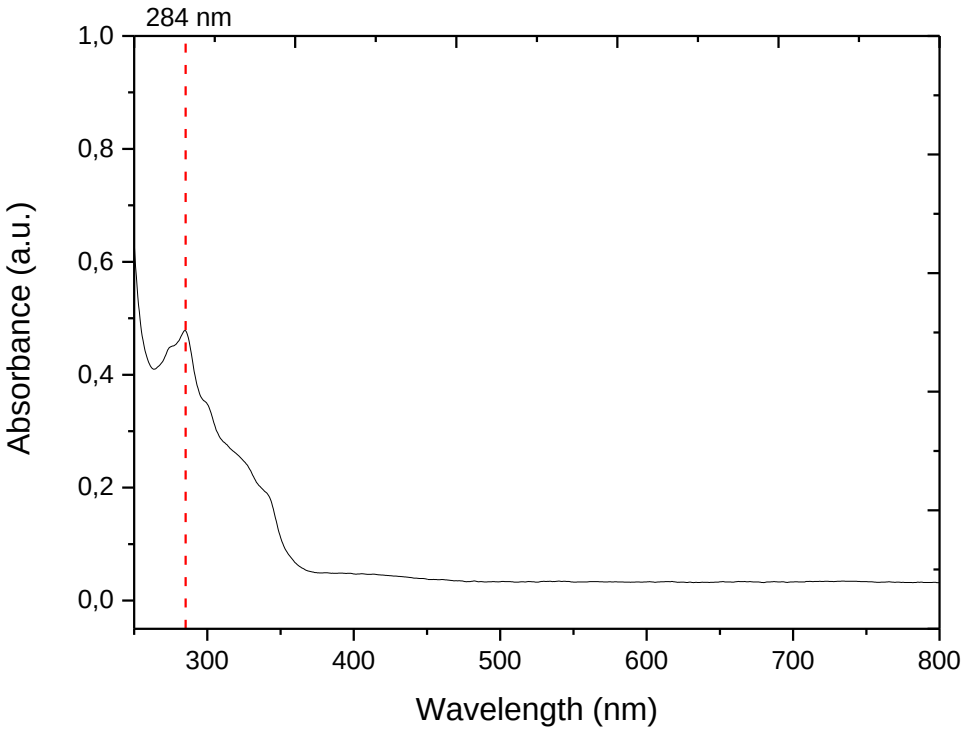


Figure S20. UV-Vis spectrum of diarylmethylium tetrafluoborate **V** (20 mM) with 1.6 eq of **2a** in CH_2Cl_2

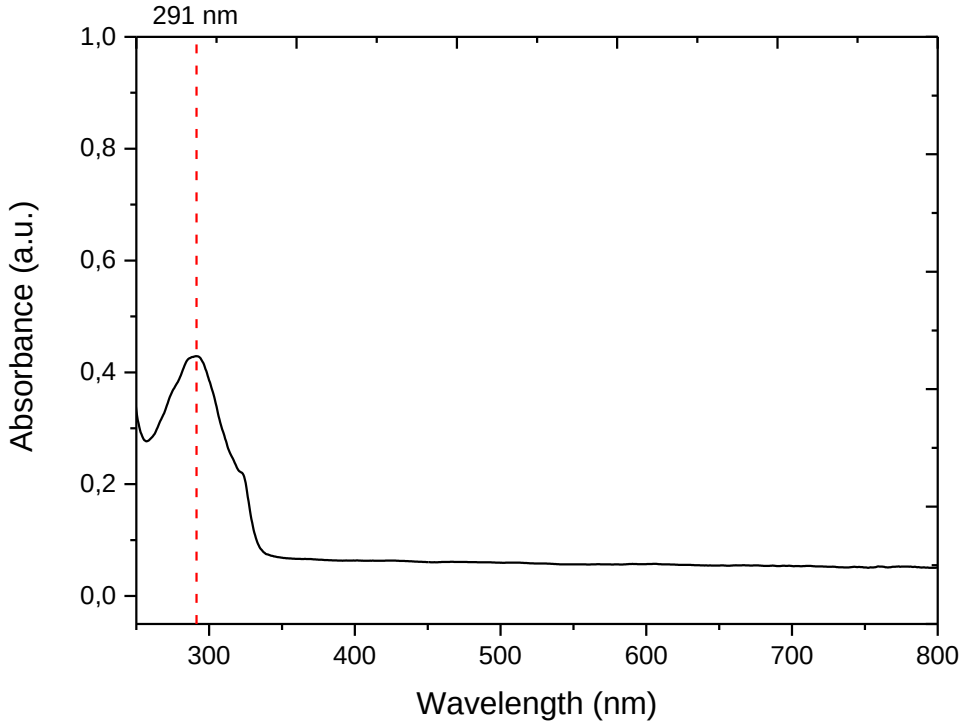


Figure S21. UV-Vis spectrum of diarylmethylium tetrafluoborate **VI** (20 mM) with 1.6 eq of **2a** in CH_2Cl_2

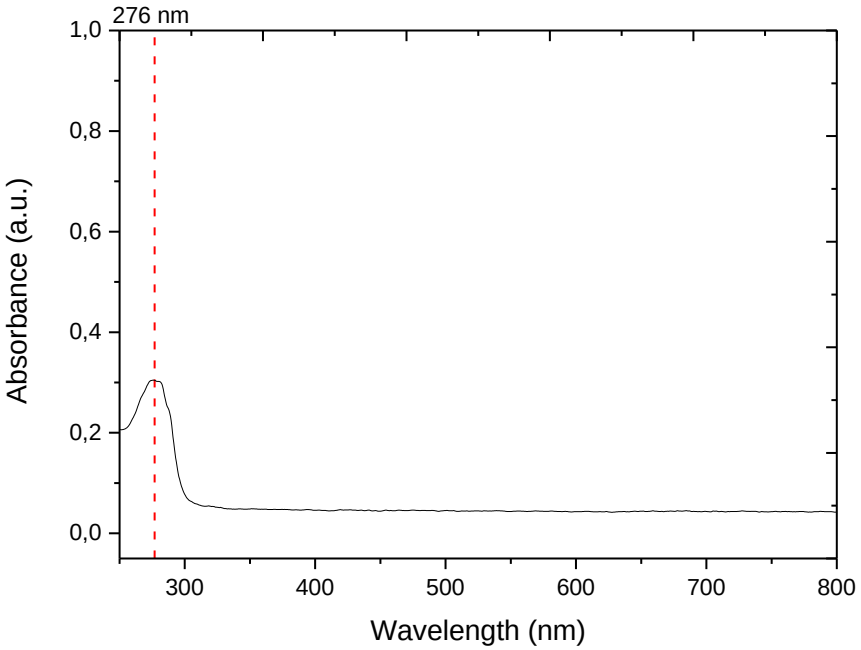


Figure S22. UV-Vis spectrum of diarylmethylium tetrafluoborate **VIII** (20 mM) with 1.6 eq of **2a** in CH_2Cl_2

4.7 Cyclic Voltammetry Experiments

CV measurements were performed at different scan rates (**Figure S23**) to investigate the different electrochemical processes, which can occur at the electrode. As reported in the case of the salt **I** (**Figure S23**), we observed a decrease in the current diminishing the scan rate. Faster scan rates can be advantageous for the higher signals which can be obtained, nevertheless slower scan rates allow a more accurate determination of the potential of the redox processes, because capacitive currents are reduced compared with Faradaic current. Moreover, at slow scan rates, the current reaches its diffusion limit at potential values closer to the current onset, as it is clearly visible for the irreversible cathodic peak of **I** (**Figure S23**), whose potential can be determined more accurately at 10 mV s^{-1}. Conversely, the potential values of the irreversible anodic peaks around 1.2/1.4 V vs. Ag/AgCl cannot be determined at 10 mV s^{-1}, where the current recorded is indistinguishable from the blank current. In this and in other similar cases (vide infra) a trade-off between accuracy and sensitivity led to the consideration of the most suitable scan rate(s) for the assessment of peak potentials.
CV measurements on the catalysts showed the presence of an irreversible reduction peak at -0.2 / -0.7 V vs Ag/AgCl, depending on its structure (**Figure S23** and **Figure S24**). This feature was the most distinctive for all the tetrafluoroborate salts tested, even though few species demonstrated the additional presence of less intense anodic peaks and compound **IX** only displayed minor redox features. The cathodic peak disappeared when sulfinate was added to the electrolyte. As displayed in the cases of **V**, **VI**, **VIII** and **IV** the anodic peak was no longer detectable, while its current was significantly reduced in the case of **I**. The disappearance of the reduction peak, or the reduction of its current, witnesses the charge transfer nature of the formed adduct.
The addition of sulfinate caused the disappearance of the colour of the catalyst in the electrolyte, and the subsequent CV showed the appearance of an irreversible anodic peak at 1.40 V for **I**, 1.17 V for **V**, 1.26 V for **VI**, and 1.37 V for **IV** (**Figure S25**). Only in the case of **VIII** we observed two irreversible peaks at 1.17 V and 1.40 V. This feature could be ascribed to the sulfinate moiety, nevertheless sulfinate in CH_2Cl_2 is sparingly soluble, and no peaks in the CV were observed (**Figure S26**). Conversely, the CV of a sulfinate methanol solution displayed a clear irreversible oxidation peak at 0.95 V. This evidence is coherent with the formation of an adduct between catalyst and sulfinate. The adduct increases the total solubility of sulfinate species, nonetheless, once the adduct is formed, its oxidation becomes less favourable, compared with sulfinate in methanol. This shift in the oxidation potential witnesses that the catalysts bind more favourably the reduced form of the sulfinate compared with its oxidized form. This evidence is coherent with the proposed formation of adduct **AD**. Assuming that the solvent has no effect on sulfinate oxidation potential, that the oxidation reactions of both sulfinate and adducts are monoelectronic, and that the adduct formation is negligible with the oxidized sulfinate, the formation constants for the adduct diarylmethylium tetrafluoborate/sulfinate can be estimated as 5.4 10^3 for **V** and **VIII**, 1.8 10^5 for **VI**, 1.3 10^7 for **IV** and 4.2 10^7 for **I**. Therefore for **I** the corresponding free energy for the formation of the adduct **AD** calculated as RT lnK is 10.4 kcal mol^{-1}, which agrees very well with the value found computationally of 9.9 kcal mol^{-1}.

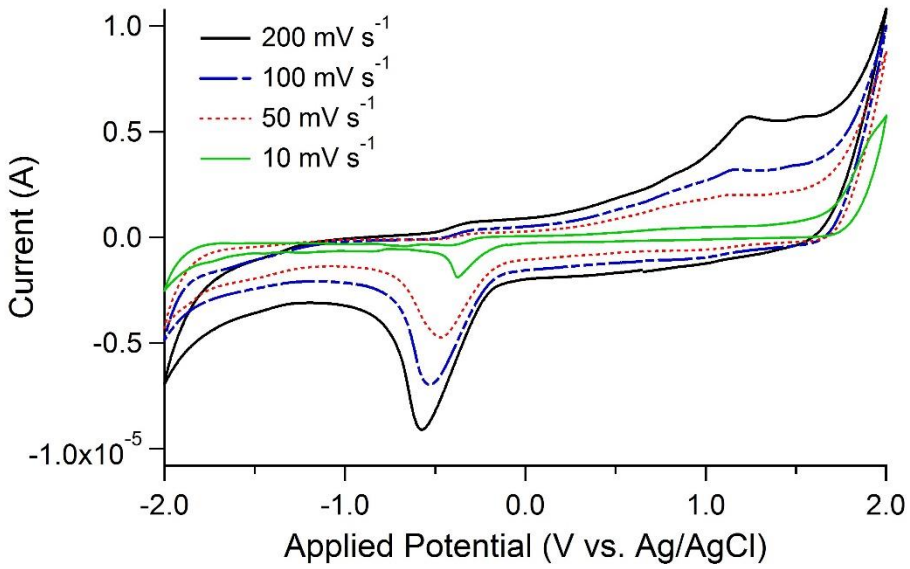


Figure S23. CV experiments at different potential scan rates for the diarylmethylium salt **I**.

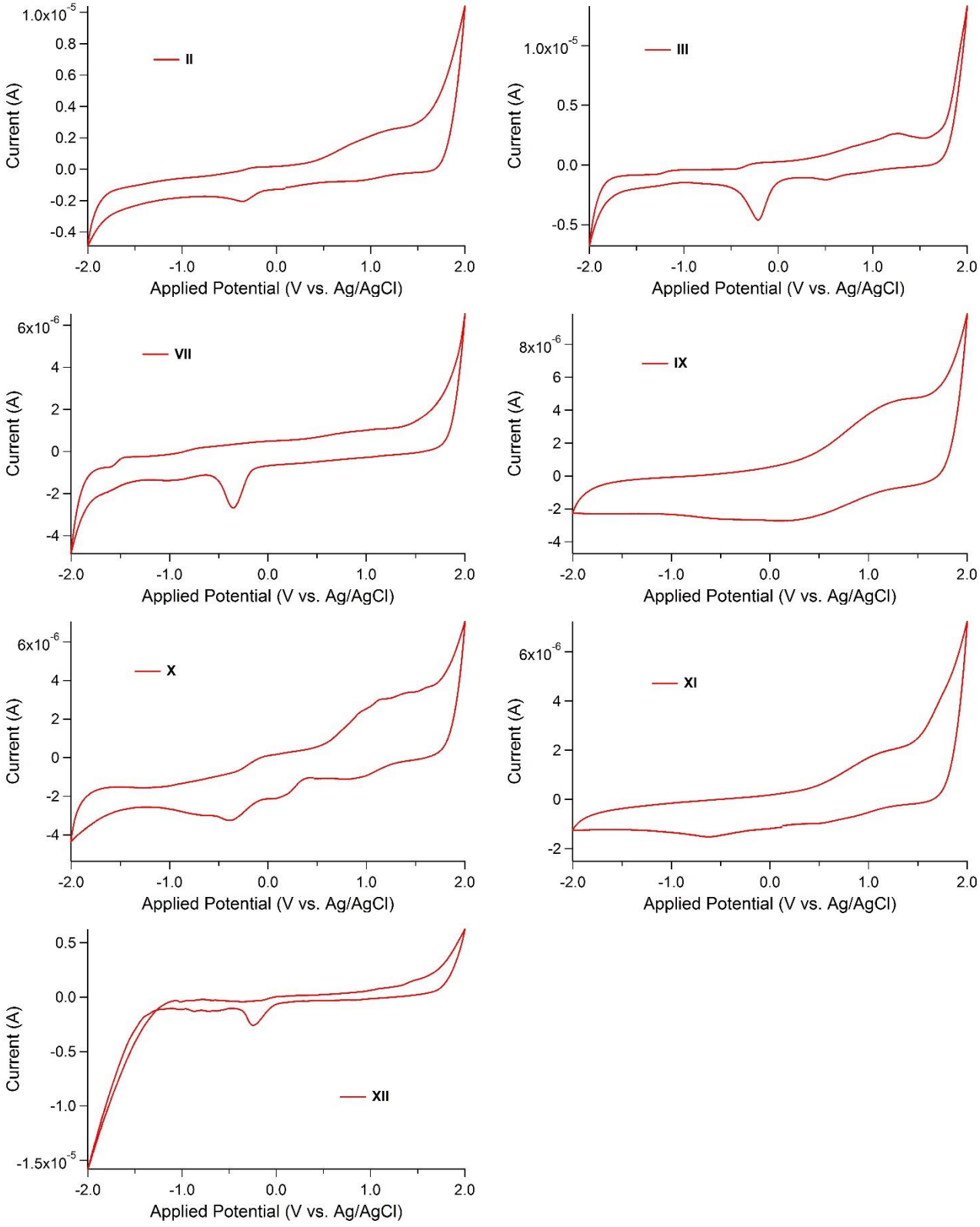


Figure S24. CV experiment of the catalysts in CH_2Cl_2 with Bu_4NPF_6 as electrolyte: **II**, **III**, **VII**, **X**, **XI** at 50 mV s^{-1}; **IX** at 200 mV s^{-1} and ; **XII** at 200 mV s^{-1}.

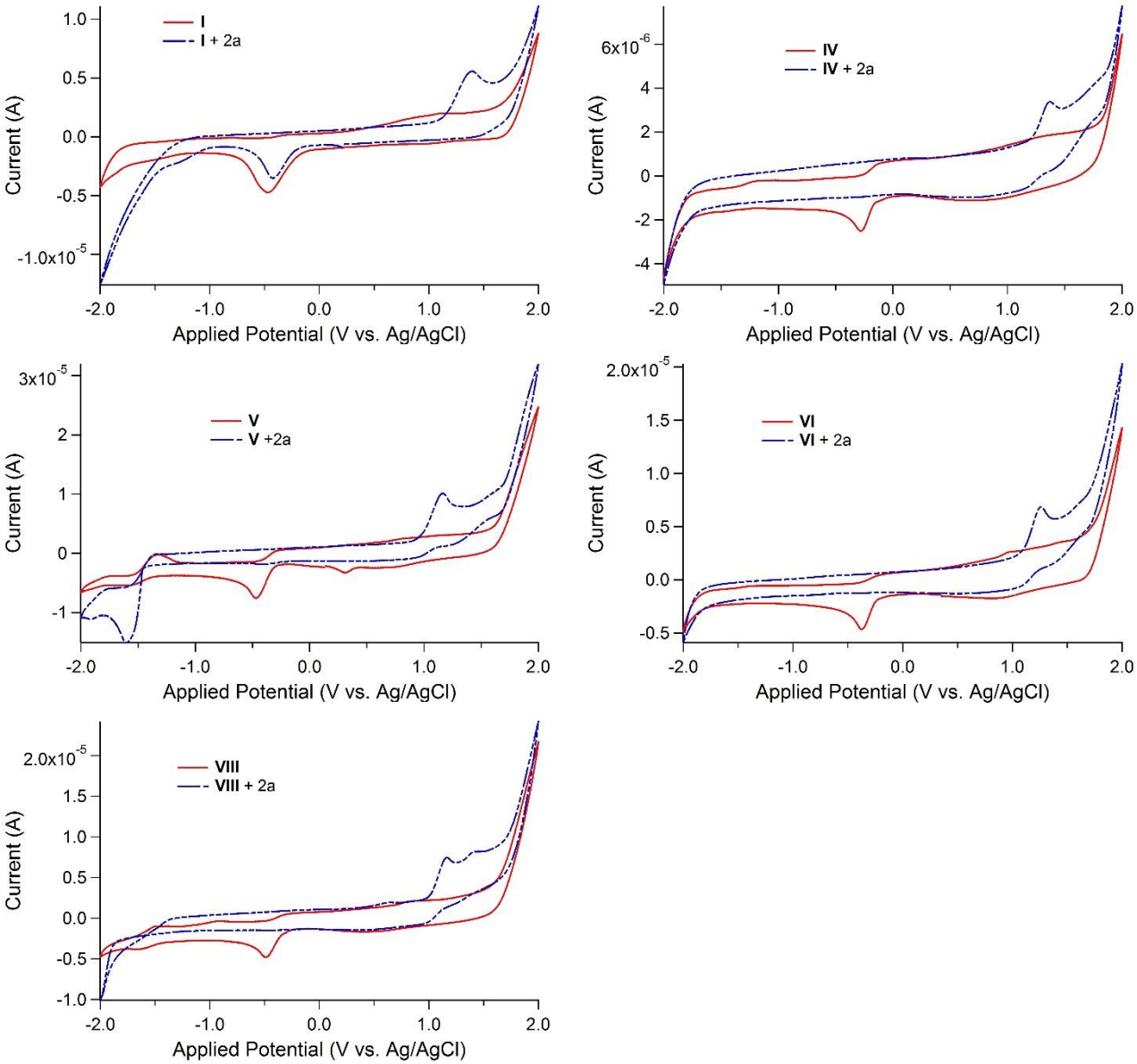


Figure S25. CV experiments at 50 mV s^{-1} of **I**, **IV**, **V**, **VI**, **VIII** in the absence and in the presence of **2a**.

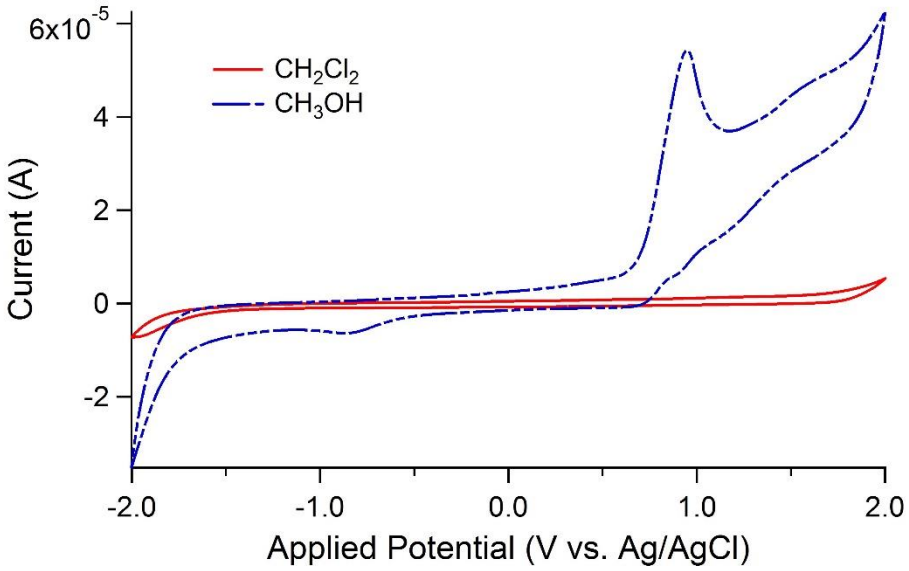


Figure S26. CV of **2a** at 50 mV s^{-1} in different solvents with Bu_4NPF_6 as electrolyte.

4.8 NMR spectra of catalyst I and of the mixture I/2a in CD_2Cl_2

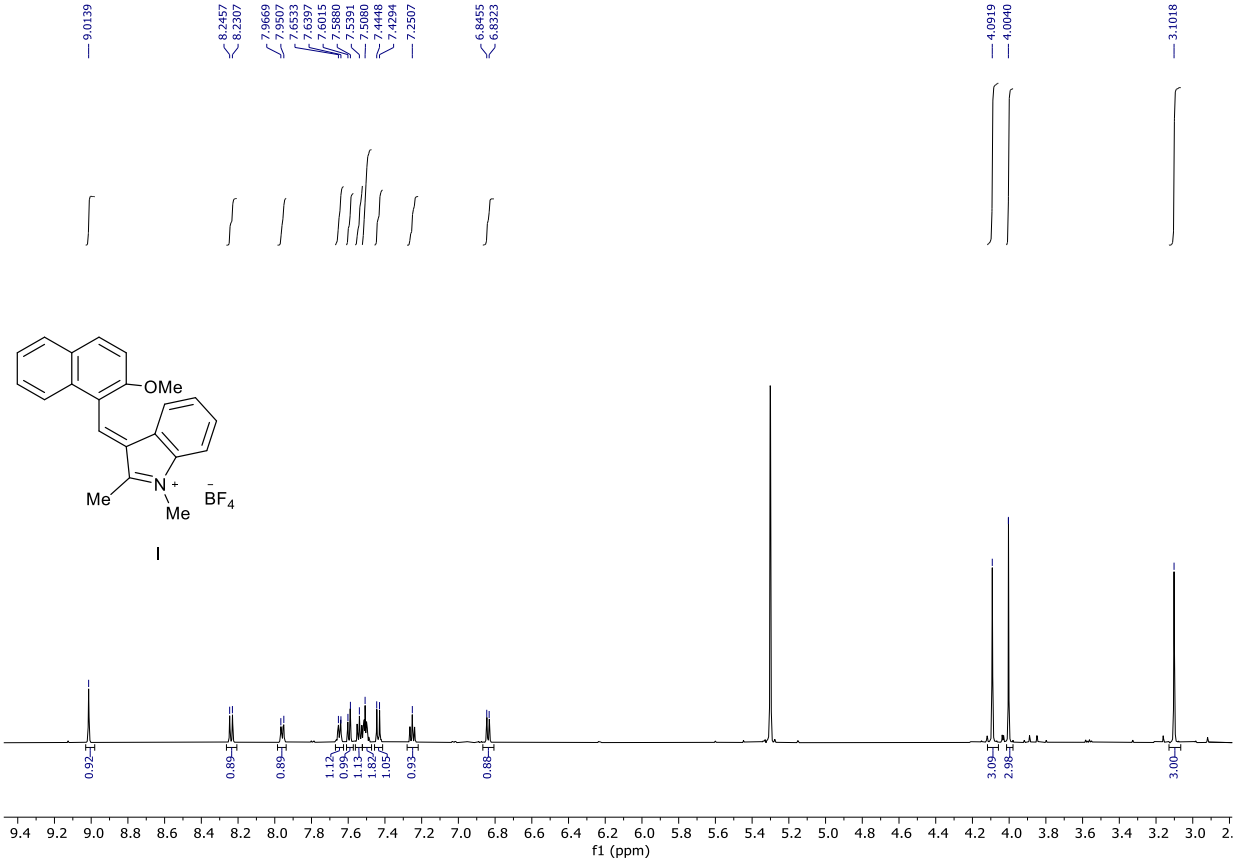


Figure S27. ^1H NMR of catalyst **I** in CD_2Cl_2.

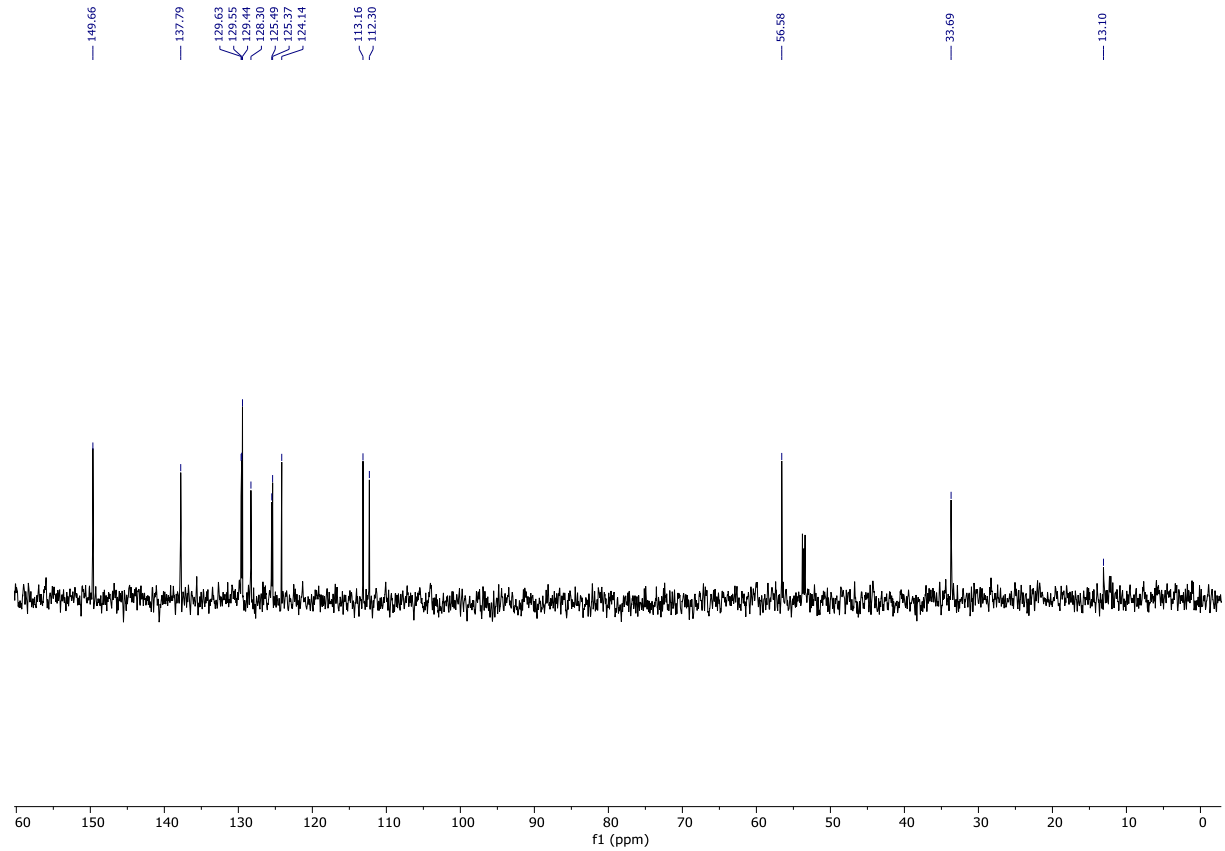


Figure S28. DEPT-135 of catalyst **I** in CD_2Cl_2.

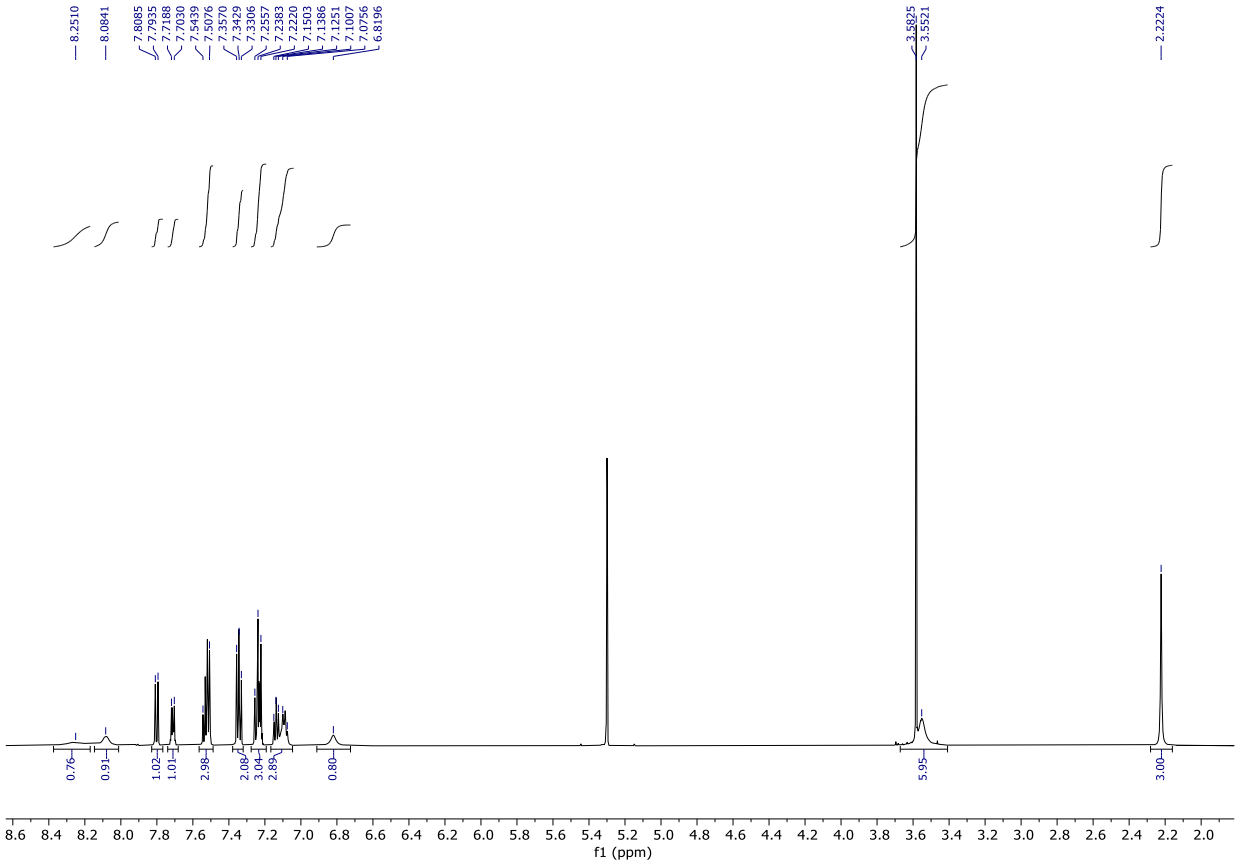


Figure S29. ^{1}H NMR of the mixture **I**/**2a** in CD_2Cl_2.

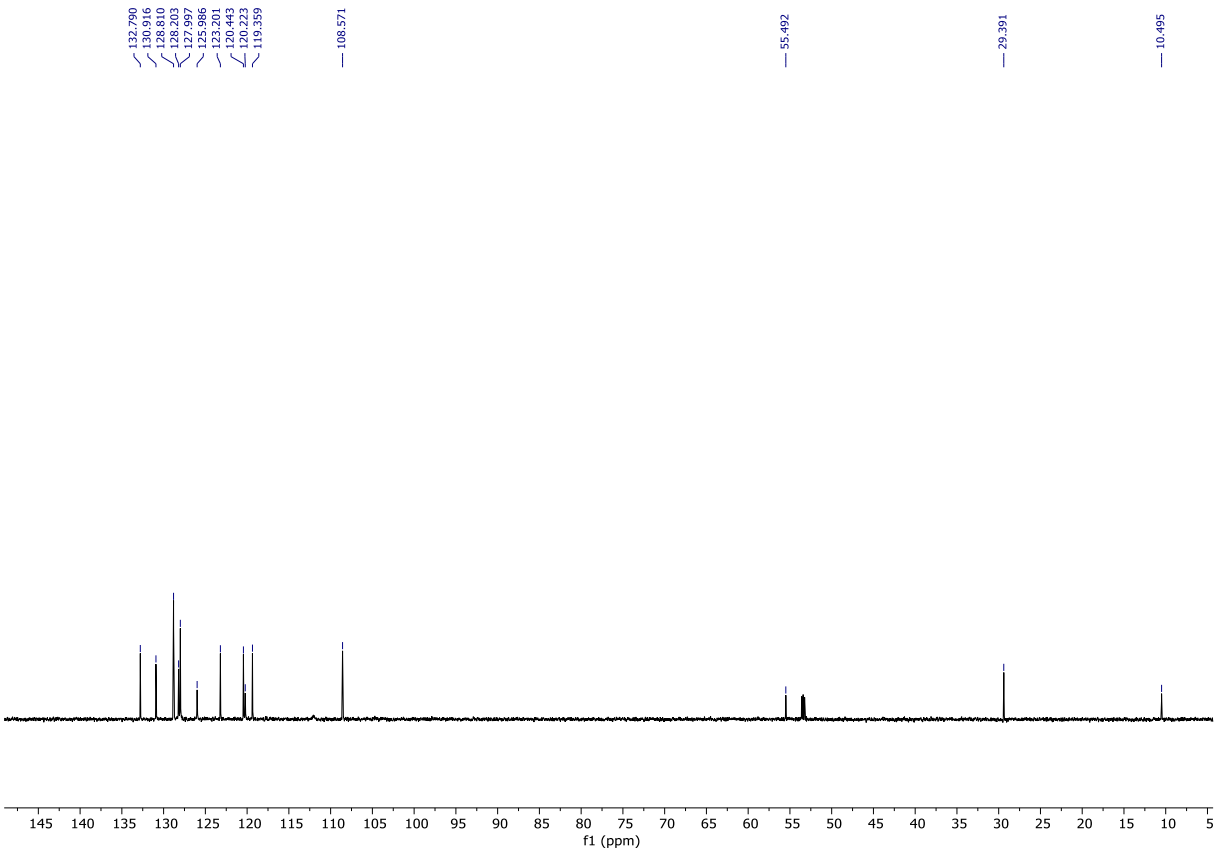
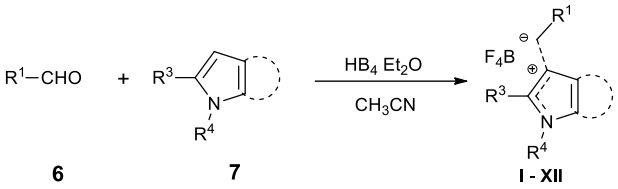


Figure S30. DEPT-135 of the mixture **I**/**2a** in CD_2Cl_2.

^{1}H-NMR of the mixture I/2a (600 MHz, CD_2Cl_2): ^{1}H-NMR: 2.22 (s, 3H), 3.55 (bs, 3H), 3.58 (s, 3H), 6.82 (sb, 1H), 7.04-7.15 (m, 3H), 7.21-7.27 (m, 3H), 7.34 (m, 2H), 7.49-7.56 (m, 3H), 7.71 (m, 1H), 7.80 (d, 1H, *J*= 9.0 Hz), 8.08 (bs, 1H), 8.25 (bs, 1H).
DEPT-135 NMR of the mixture I/2a (150 MHz, CD_2Cl_2): 10.6 (CH_3), 29.5 (CH_3), 55.6 (CH_3), 108.6 (CH), 112.1 (CH), 119.4 (CH), 120.3 (CH), 123.3 (CH), 126.1 (CH), 128.1 (CH), 128.9 (CH), 131.0 (CH), 132.9 (CH).

5. Experimental Procedures

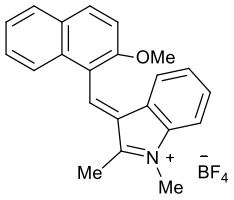
5.1 General procedure for the synthesis of diarylmethylium salts I – XII



6 **7** **I - XII**

A solution of compound **7** (3.0 mmol) in anhydrous MeCN (5 mL) was added dropwise at rt and under stirring to a mixture of aldehyde **6** (3.6 mmol) and tetrafluoroboric acid/ether complex (0.59 g, 3.6 mmol) in anhydrous MeCN (15 mL) in an open vessel. Most of the time a red or orange solid separated from the solution. The reaction was stirred at room temperature until all compound **7** was totally consumed. Then Et_2O was added to complete the separation, and the solid was separated by filtration on a Buchner funnel, washed with Et_2O, and dried under reduced pressure.

5.2 Characterization of diarylmethylium salts I-VII, XII



I

(*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-1,2-dimethyl-3*H*-indol-1-ium tetrafluoroborate I Following the described procedure, 450 mg (3 mmol) of 1,2-dimethylindole and 670 mg (3.6 mmol) of 2-methoxy-1-naphthaldehyde were reacted under the optimized conditions to afford 1.14 g €(*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-1,2-dimethyl-3*H*-indol-1-ium tetrafluoroborate **I** as a coral red solid (94% yield).

^{1}H-NMR (600 MHz, CD_3CN): δ= 2.10 (s, 3H, CH_3 + H_2O), 2.98 (s, 3H, N-CH_3), 3.94 (s, 3H, O-CH_3), 6.84 (d, 1H, *J*= 7.92 Hz; CH=*cH*-C-OMe), 7.20 (td, 1H; *J*= 7.9, 1.1 Hz; C-*CH*=CH), 7.44 (td, 1H; *J*= 7.5, 1.1 Hz; CH=*CH*-CH), 7.45-7.51 (m, 2H, C_4H and C_5H *indole ring*), 7.53-7.56 (m, 2H, C_6H *indole ring* and CH-*CH*=C), 7.74 (m, 1H, CH-*CH*=C), 7.98 (m, 1H, CH=*CH*-C), 8.27 (d, 1H; *J*= 9.12 Hz; C_7H *indole ring*), 9.05 (s, 1H, *CH*=C).

^{13}C{^{1}H}-NMR (150 MHz, CD_3CN): δ= 14.1 (CH_3), 34.9 (CH_3), 57.8 (OCH_3), 114.6 (CH), 115.0 (CH), 117.0 (Cq), 125.4 (CH), 125.8 (Cq), 126.4 (CH), 126. 4 (CH), 129.6 (CH), 130.0 (Cq), 130.3 (CH), 130.7 (CH), 131.0 (CH), 132.6 (Cq), 134.2 (Cq), 138.0 (CH), 144.2 (Cq), 150.9 (CH), 159.7 (Cq), 173.6 (Cq).

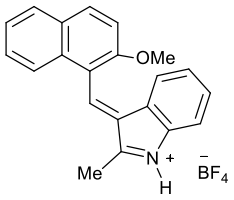
^{1}H-NMR of I (600 MHz, CD_2Cl_2): ^{1}H-NMR: 3.10 (s, 3H), 4.00 (s, 3H), 4.09 (s, 3H), 6.84 (d, 1H, *J*= 7.9 Hz), 7.25 (t, 1H, *J*= 7.3 Hz), 7.44 (d, 1H, *J*= 9.2 Hz), 7.48-7.52 (m, 2H), 7.54 (t, 1H, *J*= 7.8 Hz), 7.59 (d, 1H, *J*= 8.1 Hz), 7.64 (bd, 1H, *J*= 8.16 Hz), 7.96 (m, 1H), 8.24 (d, 1H, *J*= 9.0 Hz), 9.02 (s, 1H).

^{13}C{^{1}H}-NMR (150 MHz, CD_2Cl_2): 13.0 (CH_3), 33.6 (CH_3), 56.5 (CH_3), 112.2 (CH), 113.1 (CH), 115.9 (Cq), 124.0 (CH), 124.1 (Cq), 125.4 (CH), 125.7 (CH), 128.2 (CH), 128.5 (Cq), 129.3 (CH), 129.5 (CH), 131.0 (Cq), 131.8 (Cq), 137.7 (CH), 142.2 (Cq), 149.6 (CH), 159.1 (Cq), 170.6 (Cq).

IR (neat, *cm^{-1}*): 1611 cm^{-1}, 1560 cm^{-1}, 1262 cm^{-1}, 1150 cm^{-1}, 1100 cm^{-1}, 1061 cm^{-1}, 1047 cm^{-1}, 934 cm^{-1}, 807 cm^{-1}, 768 cm^{-1}, 757 cm^{-1}.

HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{22}H_{20}NO]^+$ 314.1536; Found 314.1539.

Mp: 235.7-236°C.



II

(*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-2-methyl-*3H*-indol-1-ium tetrafluoroborate II Following the described procedure, 393 mg (3 mmol) of 2-methyl-*1H*-indole and 614 mg (3.6 mmol) of 2-methoxy-1-naphthaldehyde were reacted under the optimized conditions to afford 929 mg of (*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-2-methyl-*3H*-indol-1-ium tetrafluoroborate **II** as a carmine red solid (80% yield).

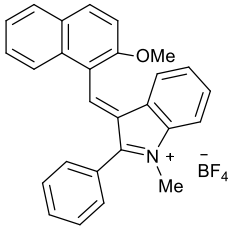
^{1}H-NMR (600 MHz, CD_3CN): δ= 3.04 (s, 3H, CH_3), 3.92 (s, 3H, OCH_3), 6.88 (d, 1H, *J*= 7.92 Hz; CH=*CH*-C-OMe), 7.25 (td, 1H; *J*= 7.6, 1.1 Hz; C-*CH*=CH), 7.49 (td, 1H; *J*= 8.0, 1.1 Hz; C_5H *indole ring*), 7.52-7.56 (m, 2 H, C_4H *indole ring* and CH-*CH*=C), 7.59 (t, 2H, *J*= 9.3 Hz; CH=*CH*-CH and C_6H *indole ring*), 7.79 (m, 1H, CH=*CH*-CH), 8.03 (m, 1H, CH-*CH*=C), 8.31 (d, 1H, *J*= 9.2 Hz; C_7H *indole ring*), 9.09 (s, 1H, *CH*=C), 12.4 (bs, 1H, N-*H*).

^{13}C{^{1}H}-NMR (150 MHz, CD_3CN): δ= 15.3 (CH_3), 57.8 (OCH_3), 114.5 (CH), 116.2 (CH), 117.1 (Cq), 125.5 (CH), 126.1 (Cq), 126.6 (CH), 126.8 (CH), 129.1 (CH),130.0 (Cq), 130.5 (CH), 130.8 (CH), 130.9 (CH), 132.7 (Cq), 134.0 (Cq), 138.7 (CH), 141.4 (Cq), 152.4 (CH), 160.3 (Cq), 174.7 (Cq).

IR (neat, *cm^{-1}*): 1697 cm^{-1}, 1560 cm^{-1}, 1512 cm^{-1}, 1371 cm^{-1}, 1338 cm^{-1}, 1284 cm^{-1}, 1258 cm^{-1}, 1196 cm^{-1},1084 cm^{-1}, 1015 cm^{-1}, 916 cm^{-1}, 875 cm^{-1}, 810 cm^{-1}, 751 cm^{-1}.

HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{21}H_{18}NO]^+$ 300.1383; Found 300.1382.

Mp: 207.5°C.



III

(*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-1-methyl-2-phenyl-*3H*-indol-1-ium tetrafluoroborate III Following the described procedure, 311 mg (1.5 mmol) of 1-methyl-2-phenylindole and 335 mg (1.8 mmol) of 2-methoxy-1-naphthaldehyde were reacted under the optimized conditions to afford 450 mg of (*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-1-methyl-2-phenyl-*3H*-indol-1-ium tetrafluoroborate **III** as a brick red solid (65% yield).

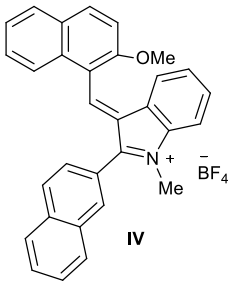
^{1}H-NMR (600 MHz, CD_3CN): δ= 3.96 (s, 3H, N-CH_3), 3.99 (s, 3H, OCH_3), 6.93 (d, 1H, *J*= 7.8 Hz; C(OMe)=*CH*-CH), 7.35 (t, 1H, *J*= 7.7 Hz; CH=*CH*-C(OMe)), 7.46-7.54 (m, 2H, *C_5H indole ring* and CH=*CH*-CH), 7.57 (d, 1H, *J*= 9.2 Hz; *C_6H indole ring*), 7.66 (td, 1H; *J*= 7.9, 1.2 Hz; CH=*CH*-C), 7.70 (bd, 1H, *J*= 8.6 Hz), 7.76-7.84 (m, 5H, *phenyl ring*), 7.87 (tt, 1H; *J*= 7.3, 1.6 Hz; CH-*CH*=CH), 8.03 (d, 1H, *J*= 8,1 Hz; CH=*CH*-C), 8.33 (d, 1H, *J*= 9.2 Hz; *C_7H indole ring*), 8.54 (s, 1H, *CH*=C).

^{13}C{^{1}H}-NMR (150 MHz, CD_3CN): δ= 36.1 (CH_3), 57.9 (OCH_3), 114.3 (CH), 115.7 (CH), 117.8 (Cq), 125.4 (CH), 125.7 (Cq), 126.2 (Cq), 126.5 (CH), 126.6 (CH), 129.7 (CH), 129.8 (Cq), 130.6 (CH), 130.7 (CH), 130.8 (CH), 131.2 (CH), 132.3 (Cq), 133.0 (CH), 134.1 (Cq), 134.5 (CH), 139.2 (CH), 144.1 (Cq), 155.3 (CH), 160.7 (Cq), 170.5 (Cq).

IR (neat, *cm^{-1}*): 1587 cm^{-1}, 1538 cm^{-1}, 1512cm^{-1}, 1472 cm^{-1}, 1458 cm^{-1}, 1384 cm^{-1}, 1350cm^{-1}, 1275 cm^{-1}, 1262 cm^{-1}, 1249 cm^{-1}, 1048 cm^{-1}, 1036 cm^{-1}, 901 cm^{-1}, 863 cm^{-1}, 821 cm^{-1}, 763 cm^{-1}, 755 cm^{-1}, 706 cm^{-1}.

HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{27}H_{22}NO]^+$ 376.1696; Found 376.1697.

Mp: 197.3-198.5°C.



IV

(*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-1-methyl-2-(naphthalen-2-yl)-*3H*-indol-1-ium tetrafluoroborate IV Following the described procedure, 168 mg (0.65 mmol) of 1-methyl-2-(naphthalen-2-yl)-*1H*-indole and 146 mg (0.78 mmol) of 2-methoxy-1-naphthaldehyde were reacted under the optimized conditions to afford 178 mg of (*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-1-methyl-2-(naphthalen-2-yl)-*3H*-indol-1-ium tetrafluoroborate **IV** as a red oxide solid (64% yield).

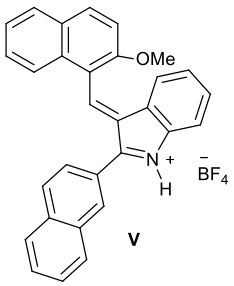
^{1}H-NMR (600 MHz, CD_3CN): δ= δ= 3.94 (s,3H, N-CH_3), 4.06 (s, 3H, OCH_3), 7.37 (t, 1H, *J*= 7.7 Hz; C-*CH*=CH), 7.47-7.54 (m, 2H, C-*CH*=C and CH=*CH*-CH), 7.57 (d, 1H, *J*= 9.2 Hz; CH=*CH*-CH), 7.68 (td, 1H, *J*= 8.6, 1.1 Hz; CH=*CH*-C), 7.72-7.75 (m, 2H, CH-*CH*=CH and C=*CH*-CH), 7.79 (ddd, 1H, *J*= 8.3, 7.1, 1.3 Hz; CH-*CH*=CH), 7.84 (d, 1H, *J*= 8.1 Hz; *C_4H indole ring*), 7.87 (dd, 1H, *J*= 8.6, 1.8 Hz; *C_5H indole ring*), 8.03 (d, 1H, *J*= 8.7 Hz; CH=*CH*-C), 8.14 (d, 1H, *J*= 7.4 Hz; C-*CH*=CH), 8.16 (d, 1H, *J*= 8.2 Hz; C-*CH*=CH), 8.28 (d, 1H, *J*= 9.0 Hz; *C_6H indole ring*), 8.33 (d, 1H, *J*= 9.12 Hz; *C_7H indole ring*), 8.38 (bs, 1H, C=*CH*-CH), 8.62 (s, 1H, *CH*=C).

^{13}C{^{1}H}-NMR (150 MHz, CD_3CN): δ= 36.3 (CH_3), 57.9 (OCH_3), 114.4 (CH), 115.6 (CH), 118.2 (Cq), 123.6 (Cq), 125.7 (CH), 125.9 (Cq), 126.6 (CH), 126.6 (CH), 127.8 (CH), 129.3 (CH), 129.5 (CH), 129.8 (CH), 129.9 (Cq), 130.5 (CH), 130.6 (CH), 130.7 (CH), 130.8 (CH), 130.8 (CH), 131.2 (CH), 132.4 (Cq), 133.8 (Cq), 134.3 (Cq), 135.6 (CH), 136.3 (Cq), 139.3 (CH), 144.3 (Cq), 155.9 (CH), 160.9 (Cq), 170.4 (Cq).

IR (neat, *cm^{-1}*): 1579 cm^{-1}, 1543 cm^{-1}, 1514 cm^{-1}, 1462 cm^{-1}, 1357 cm^{-1}, 1336 cm^{-1}, 1254 cm^{-1}, 1234 cm^{-1}, 1196 cm^{-1}, 1138 cm^{-1}, 1046 cm^{-1}, 1035 cm^{-1}, 912 cm^{-1}, 868 cm^{-1}, 836 cm^{-1}, 818 cm^{-1}, 755 cm^{-1}, 704 cm^{-1}.

HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{31}H_{24}NO]^+$ 426.1852; Found 426.1847.

Mp: 185.2-187.3°C.

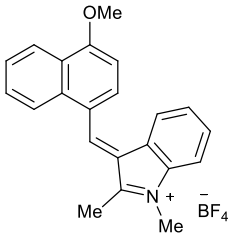


V

(*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-2-(naphthalen-2-yl)-*3H*-indol-1-ium tetrafluoroborate V Following the described procedure, 365 mg (1.5 mmol) of 2-(naphthalen-2-yl)-1H-indole and 335 mg (1.8 mmol) of 2-methoxy-1-naphthaldehyde were reacted under the optimized conditions to afford 292 mg of (*E*)-3-((2-methoxynaphthalen-1-yl)methylene)-2-(naphthalen-2-yl)-*3H*-indol-1-ium tetrafluoroborate **V** as a seal brown solid (39% yield).

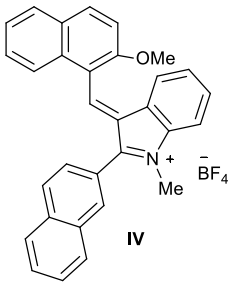
^{1}H-NMR (600 MHz, CD_3CN): δ= 3.97 (s, 3H, OCH_3), 6.94 (d, 1H, *J*= 7.92 Hz; CH=*CH*-C-OMe), 7.29 (t, 1H; *J*= 7.9 Hz; C-*CH*=CH), 7.48-7.55 (m, 2H, *C_5H indole ring* and), 7.56-7.62 (m, 2H, *C_6H indole ring*), 7.71 (t, 1H, *J*= 8.3 Hz;), 7.76 (d, 1H, *J*= 7.9 Hz;), 7.79 (t, 1H, *J*= 6.9 Hz;), 7.85 (bd, 1H, *J*= 8.4 Hz;), 8.01 (d, 1H, *J*= 8.5 Hz;), 8.05 (d, 1H, *J*= 8.5 Hz;), 8.10 (d, 1H, *J*= 8.3 Hz;), 8.16 (d, 1H, *J*= 8.1 Hz;), 8.26 (d, 1H, *J*= 8.5 Hz;), 8.37 (d, 1H, *J*= 9.2 Hz; *C_7H indole ring*), 8.52 (s, 1H, *CH*=C), 8.98 (s, 1H, CH-*CH*=CH), 12.6 (bs, 1H, N-H).

$^{13}C\{^1H\}$-NMR (150 MHz, CD_3CN): δ= 58.1 (OCH_3), 114.5 (CH), 116.5 (CH), 125.0 (Cq), 125.9 (CH), 126.3 (Cq), 126.7 (CH), 126.8 (CH), 127.3 (CH), 129.1 (CH), 129.4 (CH), 129.5 (CH), 130.0 (Cq), 131.0 (CH), 130.9 (CH), 131.1(CH), 131.2 (CH), 131.3 (CH), 131.4 (CH), 132.5 (Cq), 132.7 (Cq), 134.1 (Cq), 136.9 (Cq), 136.9 (CH), 140.3 (CH), 141.7 (Cq), 157.3 (CH), 161.8 (Cq), 169.0 (Cq).
IR (neat, *cm^{-1}*): 1620 cm^{-1}, 1590 cm^{-1}, 1562 cm^{-1}, 1544 cm^{-1}, 1508 cm^{-1}, 1455 cm^{-1}, 1436 cm^{-1}, 1371 cm^{-1}, 1255 cm^{-1}, 1193 cm^{-1}, 1151 cm^{-1}, 1098 cm^{-1}, 1071 cm^{-1}, 1050 cm^{-1}, 1021 cm^{-1}, 975 cm^{-1}, 897 cm^{-1}, 863 cm^{-1}, 832 cm^{-1}, 820 cm^{-1}, 761 cm^{-1}, 756 cm^{-1}, 703 cm^{-1}, 656 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{30}H_{22}NO]^+$ 412.1696; Found 412.1687.
Mp: 194.3-195.7°C.



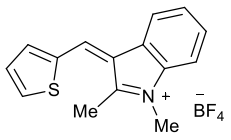
VI

(*E*)-3-((4-methoxynaphthalen-1-yl)methylene)-1,2-dimethyl-3*H*-indol-1-ium tetrafluoroborate VI Following the described procedure, 218 mg (1.5 mmol) of 1,2-dimethylindole and 335 mg (1.8 mmol) of 4-methoxy-1-naphthaldehyde were reacted under the optimized conditions to afford 367 mg of (*E*)-3-((4-methoxynaphthalen-1-yl)methylene)-1,2-dimethyl-3*H*-indol-1-ium tetrafluoroborate **VI** as a scarlet red solid (61% yield).
^1H-NMR (600 MHz, CD_3CN): δ= 2.97 (s, 3H, *CH_3*), 3.97 (s, 3H, N-*CH_3*), 4.19 (s, 3H, O*CH_3*), 7.20 (d, 1H, *J*= 8.34 Hz; C(OMe)=*CH*-CH), 7.41 (td, 1H; *J*= 7.7, 1.0 Hz; *CH indol ring*), 7.60 (td, 1H; *J*= 7.7, 1.0 Hz; *CH indol ring*), 7.68-7.74 (m, 2H, *C_4H indole ring* and CH=*CH*-CH), 7.79 (ddd, 1H; *J*= 8.3, 6.9, 1.3 Hz; CH=*CH*-CH), 7.96 (d, 1H, *J*= 7.9 Hz; *CH indol ring*), 8.23 (d, 1H, *J*= 8.4 Hz; CH-*CH*=C), 8.38 (d, 1H, *J*= 8.2 Hz; C=*CH*=CH), 8.41 (d, 1H, *J*= 8.7 Hz; C=*CH*-CH), 9.22 (s, 1H, *CH*=C).
$^{13}C\{^1H\}$-NMR (150 MHz, CD_3CN): δ= 13.9 (CH_3), 34.6 (CH_3), 57.9 (OCH_3), 106.5 (CH), 115.0 (CH), 124.0 (CH), 124.4 (Cq), 124.5 (CH), 125.7 (CH), 126.0 (Cq), 126.9 (Cq), 128.5 (CH), 129.4 (CH), 130.2 (Cq), 130.8 (CH), 130.9 (CH), 134.7 (Cq), 136.9 (CH), 144.2 (Cq), 155.7 (CH), 163.8 (Cq), 171.9 (Cq).
IR (neat, *cm^{-1}*): 1609 cm^{-1}, 1559 cm^{-1}, 151 cm^{-1}, 1467 cm^{-1}, 1361 cm^{-1}, 1259 cm^{-1}, 1240 cm^{-1}, 1198 cm^{-1}, 1152 cm^{-1}, 1099 cm^{-1}, 1046 cm^{-1}, 932 cm^{-1}, 918 cm^{-1}, 806 cm^{-1}, 768 cm^{-1}, 755 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{22}H_{20}NO]^+$314.1539; Found 314.1535.
Mp: 226.2-227.3°C.



IV

(*E*)-1,2-dimethyl-3-(2,4,6-trimethylbenzylidene)-*3H*-indol-1-ium tetrafluoroborate VII Following the described procedure, 430 mg (3 mmol) of 1,2-dimethylindole and 533 mg (3.6 mmol) of 2,4,6-trimethylbenzaldehyde were reacted under the optimized conditions to afford 929 mg of (*E*)-1,2-dimethyl-3-(2,4,6-trimethylbenzylidene)-*3H*-indol-1-ium tetrafluoroborate **VII** as a red solid (80% yield).
^1H-NMR (600 MHz, CD_3CN): δ= 2.19 (s, 9H, *CH_3*), 2.38 (s, 3H, *CH_3*), 2.97 (s, 3H, *CH_3*), 6.97 (d, 1H, *J*= 7.8 Hz; *C_4H indole ring*), 7.11 (s, 2H, *CH*-Ph), 7.34 (td, 1H; *J*= 7.7, 1.1 Hz; *C_5H indole ring*), 7.54 (td, 1H; *J*= 7.6, 1.1 Hz; *C_6H indole ring*), 7.60 (d, 1H; *J*= 8.0 Hz; *C_7H indole ring*), 8.83 (s, 1H, *CH*=C).
$^{13}C\{^1H\}$-NMR (150 MHz, CD_3CN): δ= 15.3 (CH_3), 20.6 (CH_3), 21.7 (CH_3), 116.7 (CH), 124.9 (CH), 126.3 (Cq), 130.2 (CH), 130.5 (CH), 131.2 (Cq), 131.8 (CH), 136.0 (Cq), 137.7 (Cq), 141.7 (Cq), 142.9 (Cq), 160.1 (CH), 175.9 (Cq).
IR (neat, *cm^{-1}*): 1604 cm^{-1}, 1578 cm^{-1}, 1459 cm^{-1}, 1402 cm^{-1}, 1381 cm^{-1}, 1341 cm^{-1}, 1297 cm^{-1}, 1214 cm^{-1}, 1067 cm^{-1}, 1036 cm^{-1}, 994 cm^{-1}, 957 cm^{-1},891 cm^{-1}, 762 cm^{-1}, 665 cm^{-1}, 653 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{19}H_{20}N]^+$ 276.1747; Found 276.1744.
Mp: 207.1-209.8°C.



XII

(*E*)-1,2-dimethyl-3-(thiophen-2-ylmethylene)-3*H*-indol-1-ium tetrafluoroborate XII Following the described procedure, 215 mg (1.5 mmol) of 1,2-dimethylindole and 200 mg (1.8 mmol) of thiophene-2-carbaldehyde were reacted under the optimized conditions to afford 318 mg of (*E*)-1,2-dimethyl-3-(thiophen-2-ylmethylene)-3*H*-indol-1-ium tetrafluoroborate **XII** as a persimmon orange solid (65% yield).
^1H-NMR (600 MHz, CD_3CN): δ= 2.85 (s, 3H, *CH_3*), 3.89 (s, 3H, N-*CH_3*), 7.49 (dd, 1H; *J*= 4.5, 3.9 Hz; S-CH=*CH*=CH), 7.60-7.67 (m, 2H, *C_4H* and *C_5H indole ring*), 7.70 (dd, 1H; *J*= 7.7, 2.0 Hz; *C_6H indole ring*), 8.23 (bd, 1H, *J*= 3.4 Hz; CH=*CH*=C), 8.37 (dt, 1H, *J*= 4.9, 1.1 Hz; CH=*CH*-S), 8.66 (m, 1H; *C_7H indole ring*), 8.73 (s, 1H, *CH*=C).
$^{13}C\{^1H\}$-NMR (150 MHz, CD_3CN): δ= 12.5 (CH_3), 33.4 (CH_3), 114.0 (CH), 123.4 (Cq), 123.7 (CH), 125.9 (Cq), 128.3 (CH), 129.7 (CH), 130.7 (CH), 137.3 (Cq), 142.5 (CH), 142.7 (Cq), 144.9 (CH), 146.5 (CH), 171.9 (Cq).
IR (neat, *cm^{-1}*): 1586 cm^{-1}, 1552 cm^{-1}, 1459 cm^{-1}, 1415 cm^{-1}, 1386 cm^{-1}, 1323 cm^{-1}, 1246 cm^{-1}, 1215 cm^{-1}, 1096 cm^{-1}, 1045 cm^{-1}, 1032 cm^{-1}, 864 cm^{-1}, 811 cm^{-1}, 743 cm^{-1}.
HRMS (ESI) *m/z*: $[M]^+$ Calcd for $[C_{15}H_{14}NS]^+$ 240.0841; Found 240.0951. **Mp**: 218.5-219.1°C.

5.3 Summary of alkenes 1a-z, 1aa-1ab and sulfinates 2a-e

Alkenes


1a

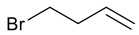

1b


1c


1d

1e


1f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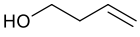
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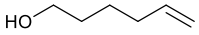
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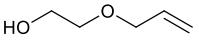
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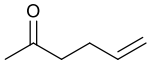
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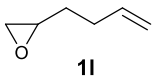
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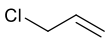
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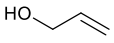
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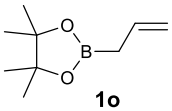
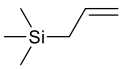

1o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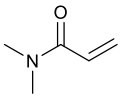
1q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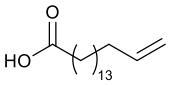
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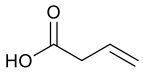
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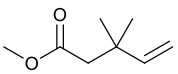
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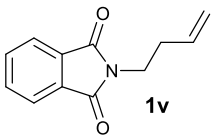
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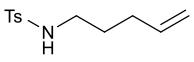
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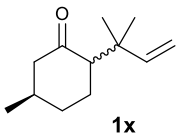
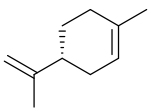
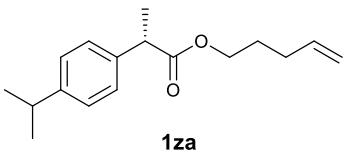

1x

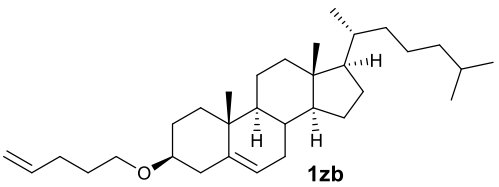
from (R)-Pulegone


1y

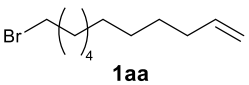
(R)-Limonene

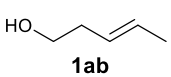

1za

from (S)-Ibuprofen

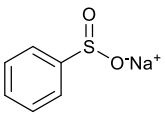

1zb

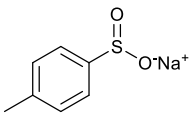
from Colesterol

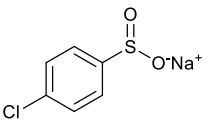

1aa

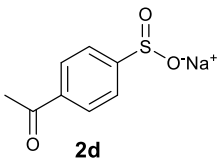

1ab

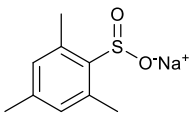
Sodium Sulfinates


2a

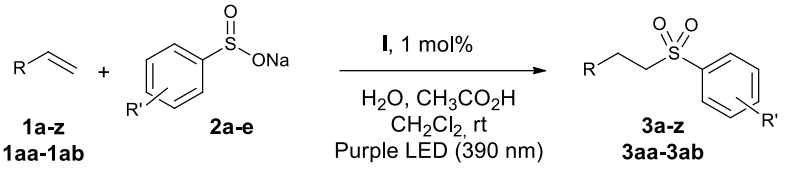

2b


2c


2d


2e

5.4 General procedure for the photocatalysed reaction of alkenes



A Schlenk tube, equipped with a magnetic stirring bar, was dried and placed under N_2 for 5 minutes, then the N_2 flow was removed and the flask closed with a septum. Alkene **1a**-**z** and **1aa**-**1ab** (0.50 mmol, 1 Eq; **Figure S27**) followed by salt **I** (2 mg, 0.005 mmol, 1 mol%) and sodium sulfinate **2a**-**e** (0.82 mmol, 1.65 Eq) were placed in the flask in this order then 2.5 ml of CH_2Cl_2 were added. The intense red solution was left under stirring until its colour faded to transparent, then water (90 mg, 5.0 mmol, 10 Eq) and acetic acid (135 mg, 2.25 mmol, 4.5 Eq) were added. The Schlenk tube was closed with a septum and then stirred at room temperature for 23 h under the irradiation of a Kessil purple lamp placed at 4 cm of distance (390 nm). Reaction work-up: the reaction mixture was diluted with 5 ml of CH_2Cl_2 and the organic phase was washed with $NaHCO_3$ (1 x 2 ml). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 ml). The collected organic phases were dried over Na_2SO_4. After solvent removal, the crude mixture was purified by flash chromatography when necessary to afford product **3**.

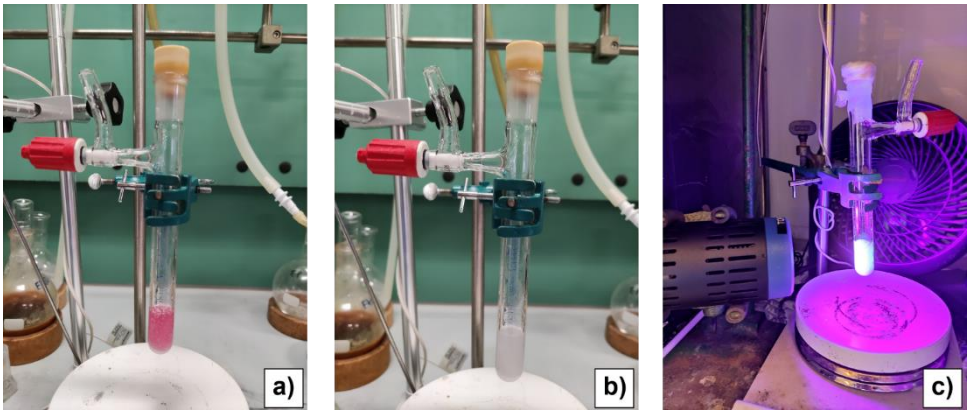
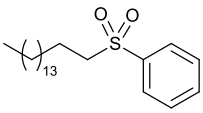


Figure S27. Pictures of reaction workflow: the initial addition of alkene and catalyst (a), followed by the addition of sulfinate; (b) and finally, the addition of all the remaining reagents, under illumination with 390 nm Kessil purple LEDs.

5.5 Characterization of sulfones 3a-z and 3aa-3ab

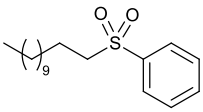


3a

(Hexadecylsulfonyl)benzene 3a Following the described procedure, 112 mg (0.50 mmol) of 1-hexadecene **1a** and 135 mg (0.82 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 147 mg of (hexadecylsulfonyl)benzene **3a** as a white solid (EP/Et_2O 8/2, yield 80%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.86 (t, 3H; *J*= 6.6 Hz; *CH_3*-CH_2), 1.15-1.34 (m, 26H; C*H_2* alkyl chain), 1.68 (m, 2H; C*H_2*-CH_2SO_2Ph), 3.06 (m, 2H; C*H_2*-SO_2Ph), 7.52-7.57 (m, 2H; Ar-*H_{meta}*), 7.63 (tt, 1H; *J*= 7.2, 1.8 Hz; Ar-*H_{para}*), 7.87-7.91 (m, 2H; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.1 (CH_3), 22.6 (CH_2), 22.7 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.62 (CH_2), 29.62 (CH_2), 29.64 (CH_2), 29.65 (CH_2), 31.9 (CH_2), 56.3 (CH_2), 128.0 (CH), 129.2 (CH), 133.6 (CH), 139.2 (Cq). The characterization data matched with the reported one.[7]

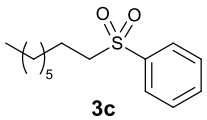


3b

(Dodecylsulfonyl)benzene 3b Following the described procedure, 84 mg (0.50 mmol) of 1-dodecene **1b** and 135 mg (0.82 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 102 mg of (hexadecylsulfonyl)benzene **3b** as an amber oil (no need for column chromatography, yield 66%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.86 (t, 3H; *J*= 6.8 Hz, *CH_3*), 1.14-1.28 (m, 16H, *CH_2chain*), 1.29-1.36 (m, 2H, *CH_2*-$(CH_2)_2$-S), 1.68 (m, 2H, *CH_2*-CH_2-S), 3.06 (m, 2H, C*H_2*-SO_2Ph), 4.30 (s, CH_3NO_2 as internal standard), 7.55 (t, 2H; *J*= 8.1 Hz; Ar-*H_{meta}*), 7.63 (t, 1H; *J*= 7.3 Hz; Ar-*H_{para}*), 7.89 (d, 2H; *J*= 7.4 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.0 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 127.9 (CH), 129.2 (CH), 133.5 (CH), 139.0 (Cq). The characterization data matched with the reported one. [8]

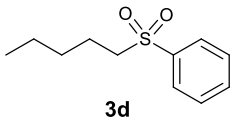


3c

(Octylsulfonyl)benzene 3c Following the described procedure, 112 mg (1.0 mmol) of 1-ottene **1c** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 205 mg of (octylsulfonyl)benzene **3c** as an amber oil (no need for column chromatography, yield 80%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.84 (t, 3H; *J*= 6.9 Hz, C*H*$_3$-CH_2), 1.17-1.27 (m, 8H, *CH*$_2$ chain), 1.29-1.35 (m, 2H, *CH*$_2$-$(CH_2)_2$-S), 1.68 (m, 2H, *CH*$_2$-CH_2-S), 3.06 (m, 2H, C*H*$_2$-SO_2Ph), 4.30 (s, CH_3NO_2 as internal standard), 7.55 (t, 2H; *J*= 8.4 Hz, Ar-*H*$_{meta}$), 7.64 (tt, 1H; *J*= 7.5, 1.3 Hz, Ar-*H*$_{para}$), 7.87-7.90 (m, 2H, Ar-*H*$_{ortho}$).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 18.8 (CH_3), 22.3 (CH_2), 22.4 (CH_2), 28.0 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 56.0 (CH_2), 127.8 (CH), 129.1 (CH), 133.4 (CH), 139.0 (Cq). The characterization data matched with the reported one. [9]

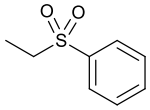


3d

(Pentylsulfonyl)benzene 3d Following the described procedure, 212 mg (1.0 mmol) of 1-pentene **1d** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 120 mg of (pentylsulfonyl)benzene **3d** as a pale yellow oil (EP/Et_2O 8/2, yield 57%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.86 (t, 3H, *J*= 7.2 Hz; C*H*$_3$-CH_2), 1.25-1.36 (m, 4H; CH_3-*(CH*$_2$*)*$_2$-CH_2), 1.71 (m, 2H; CH_2-C*H*$_2$-CH_2-SO_2Ph), 3.07 (m, 2H; C*H*$_2$-SO_2Ph), 7.57 (t, 2H, *J*= 8.0 Hz; Ar-*H*$_{meta}$), 7.66 (t, 1H; *J*= 7.4 Hz; Ar-*H*$_{para}$), 7.90 (d, 2H, *J*= 8.5 Hz; Ar-*H*$_{ortho}$).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 13.7 (CH_3), 22.1 (CH_2), 22.3 (CH_2), 30.3 (CH_2), 56.3 (CH_2), 128.1 (CH), 129.2 (CH), 133.6 (CH), 139.2 (Cq). The characterization data matched with the reported one.[10]

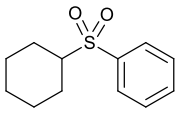


3e

(Ethylsulfonyl)benzene 3e Following the described procedure, ethylene **1e** gas in excess and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 68 mg of (ethylsulfonyl)benzene **3e** as a white solid (no need for column chromatography, yield 40%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.27 (t, 3H, *J*= 7.4 Hz; *CH*$_3$-CH_2), 3.12 (q, 2H, *J*= 7.4 Hz; *CH*$_2$-CH_3), 7.57 (bt, 2H, *J*= 8.5 Hz; Ar-*H*$_{meta}$), 7.65 (bt, 1H, *J*= 7.5, 1.2 Hz; Ar-*H*$_{para}$), 7.91 (d, 2H, *J*= 8.5 Hz; Ar-*H*$_{ortho}$).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 7.4 (CH_3), 50.5 (CH_2), 128.2 (CH), 129.2 (CH), 133.6 (CH), 138.5 (Cq). The characterization data matched with the reported one.[11]

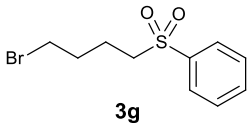


3f

(Cyclohexylsulfonyl)benzene 3f Following the described procedure, 41 mg (0.50 mmol) of cyclohexene **1f** and 135 mg (0.82 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 58 mg of (cyclohexylsulfonyl)benzene **3f** as a light yellow oil (EP/Et_2O 2/1, yield 52%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.09-1.29 (m, 3H), 1.40 (qd, 2H; *J*= 12.4, 3.5 Hz), 1.66 (m, 1H), 1.85 (dq, 2H; *J*= 13.7, 3.2 Hz), 2.06 (m, 2H), 2.89 (tt, 1H; *J*= 12.2, 3.4 Hz; *CH*$_2$-SO_2), 7.56 (t, 2H; *J*= 8.2 Hz; Ar-*H*$_{meta}$), 7.65 (tt, 1H; *J*= 7.4, 1.3 Hz; Ar-*H*$_{para}$), 7.86-7.88 (m, 2H; Ar-*H*$_{ortho}$).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 24.9 (CH_2), 24.9 (CH_2), 25.4 (CH_2), 63.3 (CH), 128.9 (CH), 133.5 (CH), 137.2 (CH), 147.2 (Cq). The characterization data matched with the reported one. [8]



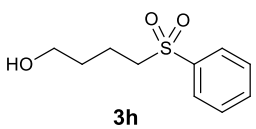
3g

((4-Bromobutyl)sulfonyl)benzene 3g Following the described procedure, 68 mg (0.50 mmol) of 4-bromo-1-butene **1g** and 135 mg (0.82 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 95 mg of ((4-bromobutyl)sulfonyl)benzene **3g** as an amber oil (no need for column chromatography, yield 69%).

Following the described procedure, 135 mg (1.0 mmol) of 4-bromo-1-butene **1g** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 220 mg of ((4-bromobutyl)sulfonyl)benzene **3g** as an amber oil (no need for column chromatography, yield 79%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.86-1.92 (m, 2H, CH_2-*CH*$_2$-CH_2), 1.93-1.99 (m, 2H, CH_2-*CH*$_2$-CH_2), 3.12 (m, 2H, CH_2-*CH*$_2$-SO_2), 3.37 (t, 2H, *J*= 6.3 Hz; Br-*CH*$_2$-CH_2), 7.58 (t, 2H, *J*= 8.2 Hz; Ar-*H*$_{meta}$), 7.67 (btt, 1H, *J*= 7.4, 1.3 Hz; Ar-*H*$_{para}$), 7.89-7.93 (m, 2H, Ar-*H*$_{ortho}$).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 21.5 (CH_2), 30.8(CH_2), 32.2 (CH_2), 62.5 (CH_2), 128.0 (CH), 129.4 (CH), 133.8 (CH), 138.9 (Cq). The characterization data matched with the reported one. [9]

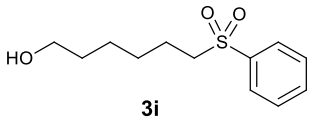


3h

4-(phenylsulfonyl)butan-1-ol 3h Following the described procedure, 72 mg (0.50 mmol) of but-3-en-1-ol **1h** and 135 mg (0.82 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 84 mg of 4-(phenylsulfonyl)butan-1-ol **3h** as a light yellow oil (EP/EtOAc 25/75, yield 78%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.58-1.63 (m, 2H, CH_2-*CH*$_2$-CH_2), 1.77-1.83 (m, 2H, CH_2-*CH*$_2$-CH_2), 1.99 (bs, 1H, OH), 3.13 (m, 2H, CH_2-*CH*$_2$-SO_2), 3.59 (t, 2H, *J*= 6.1 Hz; OH-*CH*$_2$-CH_2), 7.55 (tm, 2H, *J*= 8.2 Hz; Ar-*H*$_{meta}$), 7.68 (btt, 1H, *J*= 7.4, 1.2 Hz; Ar-*H*$_{para}$), 7.88 (dd, 2H, *J*= 8.5, 1.2 Hz; Ar-*H*$_{ortho}$).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 19.4 (CH_2), 30.8 (CH_2), 55.9 (CH_2), 61.7 (OCH_2), 127.9 (CH), 129.2 (CH), 133.7 (CH), 138.9 (Cq). The characterization data matched with the reported one. [12]

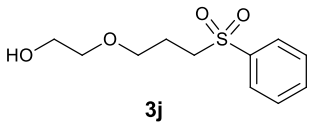


3i

6-(phenylsulfonyl)hexan-1-ol 3i Following the described procedure, 100 mg (1.0 mmol) of hex-5-en-1-ol **1i** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 205 mg of 6-(phenylsulfonyl)hexan-1-ol **3i** as a caramel oil (no need for column chromatography, yield 90%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.30-1.49 (m, 5H, CH_2-*CH_2*-*CH_2*-CH_2 and OH), 1.51 (m, 2H, HO-CH_2-*CH_2*-CH_2), 1.72 (m, 2H, CH_2-*CH_2*-CH_2-S), 3.06-3.10 (m, 2H, CH_2-*CH_2*-SO_2), 3.59 (t, 2H, *J*= 6.5 Hz; OH-*CH_2*-CH_2), 7.56 (bt 2H, *J*= 8.2 Hz; Ar-*H_{meta}*), 7.65 (btt, 1H, *J*= 8.3, 1.4 Hz; Ar-*H_{para}*), 7.89 (dd, 2H, *J*= 7.8, 1.3 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 22.2 (CH_2), 24.9 (CH_2), 27.6 (CH_2), 31.8 (CH_2), 55.8 (CH_2SO_2), 61.9 (OCH_2), 127.6 (CH), 129.0 (CH), 133.4 (CH), 138.7 (Cq). The characterization data matched with the reported one.[8]



3j

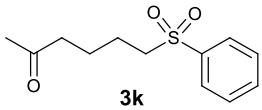
2-(3-(phenylsulfonyl)propoxy)ethan-1-ol 3j Following the described procedure, 102 mg (1.0 mmol) of 2-allyloxyethanol **1j** and 270 mg (1.6 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 181 mg of 2-(3-(phenylsulfonyl)propoxy)ethan-1-ol **3j** as a colorless oil (EtOAc/EP 7/3, yield 74%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.92 (bs, 1H; OH), 1.98-2.03 (m, 2H; C*H_2*-C*H_2*-CH_2), 3.20 (m, 2H; C*H_2*-SO_2Ph), 3.47 (t, 2H, *J*= 4.5 Hz; O-C*H_2*-CH_2-OH), 3.53 (t, 2H, *J*= 8.5 Hz; O-C*H_2*-CH_2), 3.67 (t, 2H, *J*= 4.6 Hz; C*H_2*-OH), 7.56 (t, 2H, *J*= 8.2 Hz; Ar-*H_{meta}*), 7.64 (tt, 1H; *J*= 7.5, 1.3 Hz; Ar-*H_{para}*), 7.89 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 23.0 (CH_2), 53.1 (CH_2), 61.4 (CH_2), 68.3 (CH_2), 71.9 (CH_2), 127.8 (CH), 129.2 (CH), 133.6 (CH), 138.9 (Cq).

IR (thin film, *cm^{-1}*): 3388.2 cm^{-1}, 2866.5 cm^{-1}, 1738.2 cm^{-1}, 1446.2 cm^{-1}, 1304.5 cm^{-1}, 1141.1 cm^{-1}, 1119.9 cm^{-1}, 1085.0 cm^{-1}, 887.0 cm^{-1}, 732.6 cm^{-1}, 689.9 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{11}H_{17}O_4S]^+$ 245.0842; Found 245.0840.

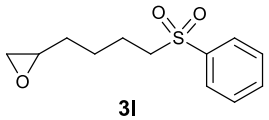


3k

(6-(phenylsulfonyl)hexan-2-one 3k Following the described procedure, 240 mg (1.0 mmol) of hex-5-en-2-one **1k** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 125 mg of 6-(phenylsulfonyl)hexan-2-one **3k** as a yellow oil (EP/Et_2O from 1/1 to 1/3, yield 52%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.61-1.67 (m, 2H; CH_2-*CH_2*-CH_2), 1.69-1.75 (m, 2H; CH_2-*CH_2*-CH_2), 2.11 (s, 3H; *CH_3*-CO), 2.44 (t, 2H, *J*= 7.1 Hz; CO-*CH_2*-CH_2), 3.09 (m, 2H; C*H_2*-SO_2Ph), 7.57 (t, 2H, *J*= 8.2 Hz; Ar-*H_{meta}*), 7.66 (t, 1H; *J*= 7.5 Hz; Ar-*H_{para}*), 7.91 (d, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 22.2 (CH_3), 29.7 (CH_2), 29.9 (CH_2), 42.7 (CH_2), 56.0 (CH_2), 128.0 (CH), 129.3 (CH), 133.7 (CH), 139.1 (Cq), 207.7 (C=O). The characterization data matched with the reported one.[13]

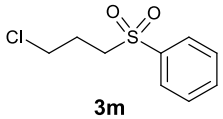


3l

2-(4-(phenylsulfonyl)butyl)oxirane 3l Following the described procedure, 240 mg (1.0 mmol) of 2-(but-3-en-1-yl)oxirane **1l** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 238 mg of 2-(4-(phenylsulfonyl)butyl)oxirane **3l** as an orange oil (no need for column chromatography, yield 99%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.39 (m, 1H; CH_2-C(*H*)H-CH), 1.50-1.60 (m, 3H; CH_2-C(*H*)H-CH and CH_2-C*H_2*-CH_2), 1.74-1.79 (m, 2H; C*H_2*-SO_2Ph), 2.41 (bm, 1H; CH-C(*H*)H-O), 2.71 (tm, 1H, *J*= 3.8 Hz; CH-C(*H*)H-O), 2.84 (m, 1H; CH_2-C*H*-O), 3.09 (m, 2H; C*H_2*-SO_2Ph), 7.56 (bt, 2H, *J*= 7.5 Hz; Ar-*H_{meta}*), 7.65 (tm, 1H; *J*= 8.4 Hz; Ar-*H_{para}*), 7.89 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 22.2 (CH_2), 24.5 (CH_2), 31.6 (CH_2), 46.6 (CH_2), 51.4 (CH), 55.8 (CH_2), 127.8 (CH), 129.1 (CH), 133.5 (CH), 138.9 (Cq). The characterization data matched with the reported one.[14]

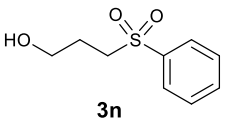


3m

((3-Chloropropyl)sulfonyl)benzene 3m Following the described procedure, 77 mg (1.0 mmol) of allyl chloride **1m** and 164 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 77 mg of ((3-chloropropyl)sulfonyl)benzene **3m** as a yellow oil (EP/EtOAc 5/1, yield 35%). (Allylsulfonyl)benzene **3m-sub** was obtained as byproduct in 18% yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 2.20-2.25 (m, 2H, CH_2-*CH_2*-CH_2), 3.27 (m, 2H, CH_2-*CH_2*-SO_2), 3.63 (t, 2H, *J*= 6.2 Hz; Cl-*CH_2*-CH_2), 7.59 (bt, 2H, *J*= 8.2 Hz; Ar-*H_{meta}*), 7.68 (t, 1H, *J*= 7.5 Hz; Ar-*H_{para}*), 7.92 (d, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 25.8 (CH_2), 42.6 (CH_2), 53.5 (CH_2), 127.9 (CH), 129.4 (CH), 133.9 (CH), 138.8 (Cq). The characterization data matched with the reported one.[15]

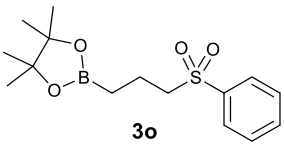


3n

Phenylsulfonylpropan-1-ol 3n Following the described procedure, 58 mg (1.0 mmol) of allyl alcohol **1n** and 164 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 126 mg of phenylsulfonylpropan-1-ol **3n** as a yellow oil (EP/EtOAc from 7/3 to 2/8, yield 63%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.82 (sb, 1H, OH), 1.98 (m, 2H, CH_2-*CH_2*-CH_2), 3.24 (m, 2H, CH_2-*CH_2*-SO_2), 3.73 (t, 2H, *J*= 6.0 Hz; HO-*CH_2*-CH_2), 7.57 (t, 2H, *J*= 8.2 Hz; Ar-*H_{meta}*), 7.66 (t, 1H, *J*= 7.5 Hz; Ar-*H_{para}*), 7.91 (d, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 25.6 (CH_2), 53.2 (CH_2), 60.3 (CH_2), 127.9 (CH), 129.3 (CH), 133.8 (CH), 138.8 (Cq). The characterization data matched with the reported one.[16]



3o

4,4,5,5-Tetramethyl-2-(3-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane 3o Following the described procedure, 168 mg (1.0 mmol) of allyl boronic acid pinacol ester **1o** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 298 mg of 4,4,5,5-tetramethyl-2-(3-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane **3o** as an amber oil (no need for column chromatography, yield 96%).

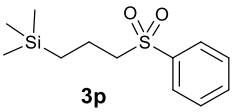
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.83 (t, 2H, *J*= 7.6 Hz; B-*CH_2*-CH_2), 1.19 (s, 12H, (*CH_3*)$_4$), 1.79 (m, 2H, CH_2-*CH_2*-CH_2), 3.15 (m, 2H, CH_2-*CH_2*-SO_2), 7.56 (bt, 2H, *J*= 8.0 Hz; Ar-*H_{meta}*), 7.64 (btt, 1H, *J*= 7.5 Hz; Ar-*H_{para}*), 7.90 (d, 2H, *J*= 8.4 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 9.54 (CH_2), 17.4 (CH_2), 24.6 (CH_3), 57.7 (CH_2), 83.1 (Cq), 127.9 (CH), 129.0 (CH), 133.3 (CH), 139.0 (Cq).

^{11}B{^{1}H}-NMR (192 MHz, $CDCl_3$): δ= 32.3.

IR (thin film, *cm^{-1}*): 2980.0 cm^{-1}, 1745.6 cm^{-1}, 1583.7 cm^{-1}, 1476.2 cm^{-1}, 1372.9 cm^{-1}, 1311.8 cm^{-1}, 1221.7 cm^{-1}, 1142.8 cm^{-1}, 1092.0 cm^{-1}, 1015.6 cm^{-1}, 840.0 cm^{-1}, 758.9 cm^{-1}, 728.3 cm^{-1}, 629.6 cm^{-1}, 563.8 cm^{-1}, 461.0 cm^{-1}.

HRMS (ESI) *m/z*: $[M - H]^+$ Calcd for $[C_{15}H_{22}BO_4S]^+$ 309.1326; Found 309.1323.



3p

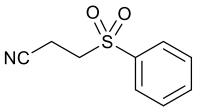
Trimethyl(3-(phenylsulfonyl)propyl)silane 3p Following the described procedure, 114 mg (1.0 mmol) of allyltrimethylsilane **1p** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 209 mg of trimethyl(3-(phenylsulfonyl)propyl)silane **3p** as a caramel oil (no need for column chromatography, yield 82%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.04 (s, 9H, Si(*CH_3*)$_3$, 0.54 (m, 2H, Si-*CH_2*-CH_2), 1.79 (m, 2H, CH_2-*CH_2*-CH_2), 3.09 (m, 2H, CH_2-*CH_2*-SO_2), 7.57 (bt, 2H, *J*= 8.0 Hz; Ar-*H_{meta}*), 7.65 (tt, 1H, *J*= 7.4, 1.2 Hz; Ar-*H_{para}*), 7.91 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 2.05 (CH_3), 15.4 (CH_2), 17.3 (CH_2), 59.2 (CH_2), 127.8 (CH), 129.1 (CH), 133.5 (CH), 139.2 (Cq).

IR (thin film, *cm^{-1}*): 2952.8 cm^{-1}, 1735.0 cm^{-1}, 1446.0 cm^{-1}, 1300.3 cm^{-1}, 1247.8 cm^{-1}, 1145.7 cm^{-1}, 1084.4 cm^{-1}, 835.6 cm^{-1}, 725.7 cm^{-1}, 688.7 cm^{-1}, 583.7 cm^{-1}, 550.6 cm^{-1}, 527.3 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{12}H_{21}O_2SSi]^+$ 257.1031; Found 257.1024.

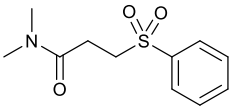


3q

3-(Phenylsulfonyl)propanenitrile 3q Following the described procedure, 53 mg (1.0 mmol) of acrylonitrile **1q** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 98 mg of 3-(phenylsulfonyl)propanenitrile **3q** a yellow/orange oil (no need for column chromatography, yield 50%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 2.83 (t, 2H, *J*= 6.9 Hz; CN-*CH_2*-CH_2), 3.39 (t, 2H, *J*= 6.9 Hz; CH_2-*CH_2*-SO_2), 7.63 (dm, 2H, *J*= 8.3 Hz; Ar-*H_{meta}*), 7.45 (tt, 1H, *J*= 7.5, 1.3 Hz; Ar-*H_{para}*), 7.94 (dm, 2H, *J*= 8.4 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 11.9 (CH_2), 50.9 (CH_2), 116.0 (CN), 128.2 (CH), 129.7 (CH), 134.6 (CH), 137.8 (Cq). The characterization data matched with the reported one.[10]

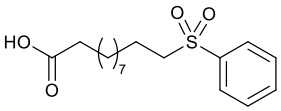


3r

***N,N*-Dimethyl-3-(phenylsulfonyl)propionanamide 3r** Following the described procedure, 100 mg (1.0 mmol) of *N,N*-dimethylacrylamide **1r** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 21 mg of *N,N*-dimethyl-3-(phenylsulfonyl)propanamide **3r** as a yellow oil (EP/EtOAc from 1/1 to 100% EtOAc, yield 10%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 2.81 (t, 2H, *J*= 7.7 Hz; CH_2-*CH_2*-CO), 2.89 (s, 3H, *CH_3*), 2.99 (s, 3H, *CH_3*), 3.45 (m, 2H, CH_2-*CH_2*-SO_2), 7.57 (tm, 2H, *J*= 8.2 Hz; Ar-*H_{meta}*), 7.66 (tt, 1H, *J*= 6.4, 1.0 Hz; Ar-*H_{para}*), 7.91 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 26.1 (CH_2), 35.6 (CH_3), 37.0 (CH_3), 52.0 (CH_2), 127.9 (CH), 129.3 (CH), 133.8 (CH), 139.1 (Cq), 168.6 (CO). The characterization data matched with the reported one.[17]

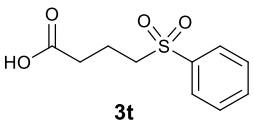


3s

11-(Phenylsulfonyl)undecanoic acid 3s Following the described procedure, 184 mg (1.0 mmol) of undec-10-enoic acid **1s** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 301 mg of 11-(phenylsulfonyl)undecanoic acid **3s** as a light yellow solid (no need for column chromatography, yield 92%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.20-1.35 (m, 12H), 1.62 (p, 2H, *J*= 7.5 Hz; CH_2-*CH_2*-CH_2), 1.70 (m, 2H, CH_2-*CH_2*-CH_2), 2.34 (t, 2H, *J*= 6.9 Hz; CO_2H-*CH_2*-CH_2), 3.08 (m, 2H, CH_2-*CH_2*-SO_2), 7.57 (tm, 2H, *J*= 8.1 Hz; Ar-*H_{meta}*), 7.65 (tt, 1H, *J*= 7.5, 1.2 Hz; Ar-*H_{para}*), 7.91 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 22.4 (CH_2), 24.4 (CH_2), 27.9 (CH_2), 28.7 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 33.9 (CH_2), 55.9 (CH_2), 127.8 (CH), 129.1 (CH), 133.45 (CH), 138.9 (Cq), 179.7 (COOH). The characterization data matched with the reported one.[18]

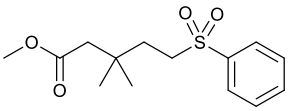


3t

4-(phenylsulfonyl)butanoic acid 3t Following the described procedure, 86 mg (1.0 mmol) of vinyl acetic acid **1t** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 153 mg of 4-(phenylsulfonyl)butanoic acid **3t** as a solid (no need for column chromatography, yield 67%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 2.04 (m, 2H; CH_2-C*H_2*-CH_2), 2.52 (t, 2H, *J*= 7.1 Hz; *CH_2*-COOH), 3.19 (m, 2H, C*H_2*-SO_2Ph), 7.58 (t, 2H, *J*= 8.1 Hz; Ar-*H_{meta}*), 7.67 (tt, 1H; *J*= 7.5, 1.3 Hz; Ar-*H_{para}*), 7.91 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 17.9(CH_2), 32.0(CH_2), 54.9 (CH_2), 127.9 (CH), 129.3 (CH), 133.8 (CH), 138.7 (Cq), 177.5 (C=O). The characterization data matched with the reported one.[19]



3u

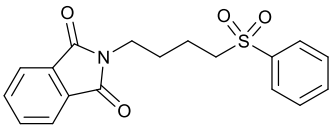
Methyl 3,3-dimethyl-5-(phenylsulfonyl)pentanoate 3u Following the described procedure, 142 mg (1.0 mmol) of methyl 3,3-dimethylpent-4-enoate **1u** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 175 mg of methyl 3,3-dimethyl-5-(phenylsulfonyl)pentanoate **3u** as a light yellow oil (EP/EE 1/1, yield 62%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.97 (s, 6H, (*CH_3*)$_2$), 1.72 (m, 2H, CH_2-*CH_2*-C), 2.14 (s, 2H, C-*CH_2*-CO), 3.11 (m, 2H, SO_2-*CH_2*-CH_2), 3.57 (s, 3H, O*CH_3*), 7.58 (tm, 2H, *J*= 7.4 Hz; Ar-*H_{meta}*), 7.67 (tt, 1H, *J*= 7.5, 1.2 Hz; Ar-*H_{para}*), 7.92 (dm, 2H, *J*= 8.5 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 27.1 (CH_3), 32.6 (Cq), 33.7 (CH_2), 45.2 (CH_2), 51.2 (OCH_3), 52.2 (CH_2), 128.0 (CH), 129.2 (CH), 133.6 (CH), 133.9 (Cq), 171.6 (CO_2CH_3).

IR (thin film, *cm^{-1}*): 2954.3 cm^{-1}, 1729.1 cm^{-1}, 1447.1 cm^{-1}, 1303.2 cm^{-1}, 1233.2 cm^{-1}, 1145.7 cm^{-1}, 1087.4 cm^{-1}, 912.3 cm^{-1}, 737.3 cm^{-1}, 688.6 cm^{-1}, 588.6 cm^{-1}, 559.4 cm^{-1}, 536.1 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{14}H_{21}O_4S]^+$ 285.1155; Found 285.1152.

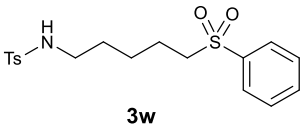


3v

2-(4-(phenylsulfonyl)butyl)isoindoline-1,3-dione 3v Following the described procedure, 201 mg (1.0 mmol) of 2-(but-3-en-1-yl)isoindoline-1,3-dione **1v** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 242 mg of 2-(4-(phenylsulfonyl)butyl)isoindoline-1,3-dione **3v** as a white solid (EtOAc/EP 1/1, yield 71%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.72 (m, 4H, C*H_2*-*$(CH_2)_2$*-CH_2), 3.12 (m, 2H; C*H_2*-SO_2Ph), 3.60 (t, 2H, *J*= 6.7 Hz; N-C*H_2*-CH_2), 7.51 (t, 2H, *J*= 8.3 Hz; Ar-*H_{meta}*), 7.59 (tt, 1H; *J*= 7.5, 1.3 Hz; Ar-*H_{para}*), 7.66 (m, 2H; phthalimide aromatics), 7.76 (m, 2H; phthalimide aromatics), 7.85 (dm, 2H, *J*= 8.3 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 19.9 (CH_2), 26.9 (CH_2), 36.7 (CH_2), 55.3 (CH_2), 123.1 (CH), 127.9 (CH), 129.1 (CH), 131.8 (Cq), 133.6 (CH), 133.9 (CH), 138.8 (Cq), 168.0 (Cq).

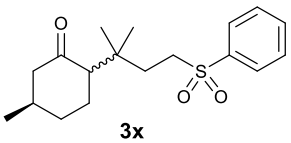


3w

4-methyl-*N*-(5-(phenylsulfonyl)pentyl)benzenesulfonamide 3w Following the described procedure, 119 mg (0.5 mmol) of 4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide **1w** and 135 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 133 mg of 4-methyl-*N*-(5-(phenylsulfonyl)pentyl)benzenesulfonamide **3w** as an amber oil (EP/EtOAC from 5/1 to 1/1, yield 70%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.33 (m, 2H; CH_2-*CH_2*-CH_2), 1.41 (m, 2H; NH-CH_2-*CH_2*-CH_2), 1.63 (m, 2H; SO_2-CH_2-*CH_2*-CH_2), 2.40 (s, 3H; CH_3), 2.85 (q, 2H, *J*= 6.4 Hz; N-C*H_2*-CH_2), 3.00 (m, 2H; C*H_2*-SO_2Ph), 4.99 (bt, 1H, *J*= 6.2 Hz; *NH*), 7.27 (d, 2H; *J*= 8.3 Hz; Ar-*H*), 7.55 (t, 2H, *J*= 7.6 Hz; Ar-*H_{meta}*), 7.64 (t, 1H; *J*= 7.4 Hz; Ar-*H_{para}*),), 7.69 (d, 2H; *J*= 8.3 Hz; Ar-*H*), 7.86 (d, 2H, *J*= 7.0 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 21.4 (CH_3), 22.0 (CH_2), 25.1 (CH_2), 28.9 (CH_2), 42.6 (CH_2), 55.8 (CH_2),, 126.9 (CH), 127.9 (CH), 129.3 (CH), 129.7 (CH), 133.7 (CH), 136.8 (Cq), 138.1 (Cq), 143.4 (Cq). The characterization data matched with the reported one.[8]



3x

(5R)-5-methyl-2-(2-methyl-4-(phenylsulfonyl)butan-2-yl)cyclohexan-1-one 3x Following the described procedure, 161 mg (0.5 mmol) of (5R)-5-methyl-2-(2-methylbut-3-en-2-yl)cyclohexan-1-one **1x** (1/1 isomers mixture) and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 2-(4(5*R*)-5-methyl-2-(2-methyl-4-(phenylsulfonyl)butan-2-yl)cyclohexan-1-one **3x** as a mixture of diasterosiomers. Major diasteroisomer: 48 mg, colorless oil (yield 30%); minor diasteroisomer: 20 mg (yield 13%); pale yellow oil (EP/Et_2O from 2/1 to 1/1). The relative configuration of diasteroisomers was assigned in analogy to what reported by Miles at al. for a similar compound obtained by Pulegone.[20]

Major diasteroisomer (*trans* isomer)

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.90 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 0.97 (d, 3H, *J*= 6.5 Hz; CH_3-CH), 1.28 (ddd, 1H, *J*= 15.6, 13.1, 3.5 Hz; CH-C(*H*)H-CH_2), 1.39 (ddd, 1H, *J*= 15.8, 12.5, 3.3 Hz; CH-C(*H*)H-CH_2), 1.67-1.75 (m, 1H; C-C(*H*)H-CH), 1.77-1.83 (m, 1H; CH_3-C*H*-CH_2), 1.84-1.90 (m, 2H; C-C(*H*)H-CH_2 and CH-C(*H*)H-CH_2), 1.94 (td, 1H, *J*= 12.7, 1.3 Hz; CH-C(*H*)H-CO), 1.98-2.06 (m, 2H; CO-C(*H*)H-CH and CO-C*H*-C), 2.20 (ddd, 1H, *J*= 12.2, 4.0, 2.2 Hz; CO-C(*H*)H-CH), 3.02 (m, 2H; CH_2-SO_2Ph), 7.57 (t, 2H, *J*= 8.2 Hz; Ar-H_{meta}), 7.66 (tt, 1H; *J*= 7.4, 1.3 Hz; Ar-H_{para}), 7.88 (dm, 2H, *J*= 8.5 Hz; Ar-H_{ortho}).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 22.2 (CH_3), 24.3 (CH_3), 24.5 (CH_3), 28.0 (CH_2), 31.7 (CH_2), 33.8 (Cq), 34.5 (CH_2), 36.2 (CH), 52.2 (CH_2), 52.3 (CH_2), 57.5 (CH), 127.9 (CH), 129.2 (CH), 133.6 (CH), 139.0 (Cq), 211.0 (C=O).

IR (thin film, *cm^{-1}*): 2921.0 cm^{-1}, 2870.3 cm^{-1}, 1704.6 cm^{-1}, 1446.1 cm^{-1}, 1365.2 cm^{-1}, 1297.5 cm^{-1}, 1146.0 cm^{-1}, 1085.7 cm^{-1}, 965.6 cm^{-1}, 806.4 cm^{-1}, 745.3 cm^{-1}, 689.1 cm^{-1}.

HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $[C_{18}H_{27}O_3S]^+$ 323.1675; Found 323.1663.

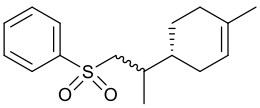
Minor diasteroisomer (*cis* isomer)

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.90 (d, 3H, *J*= 7.0 Hz; CH_3-CH), 0.92 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 1.59 (bm, 2H; CH-CH_2-CH_2), 1.66-1.76 (m, 2H, C-C(*H*)H-CH_2 and CH-C(*H*)H-CH_2), 1.77-1.89 (m, 2H, C-C(*H*)H-CH_2 and CH-C(*H*)H-CH_2), 2.00 (m, 1H, CO-C*(H)*H-CH), 2.07 (dd, 1H, *J*= 10.3, 4.4 Hz; CO-C*H*-CH_2), 2.31 (bm, 1H; CH_3-C*H*), 2.44 (dd, 1H, *J*= 14.1, 7.0 Hz; CO-C*(H)*H-CH), 2.99-3.09 (m, 2H; CH_2-SO_2Ph), 7.58 (t, 2H, *J*= 8.2 Hz; Ar-H_{meta}), 7.66 (t, 1H; *J*= 7.6 Hz; Ar-H_{para}), 7.89 (d, 2H, *J*= 7.2 Hz; Ar-H_{ortho}).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 19.0 (CH_3), 23.8 (CH_2), 24.5 (CH_3), 24.7 (CH_3), 31.3 (CH_2), 32.0 (CH), 32.1 (CH_2), 34.0 (Cq), 50.2 (CH_2), 52.3 (CH_2), 57.4 (CH), 128.0 (CH), 129.2 (CH), 133.7 (CH), 139.0 (Cq), 211.9 (C=O). The minor diasterosiomer was isolated in a mixture with the major diasterosiomer.

IR (thin film, *cm^{-1}*): 2921.6 cm^{-1}, 2870.1 cm^{-1}, 1704.5 cm^{-1}, 1446.3 cm^{-1}, 1365.1 cm^{-1}, 1297.8 cm^{-1}, 1145.9 cm^{-1}, 1084.1 cm^{-1}, 806.6 cm^{-1}, 745.0 cm^{-1}, 688.8 cm^{-1}.

HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $[C_{18}H_{27}O_3S]^+$ 323.1675; Found 323.1662.



3y

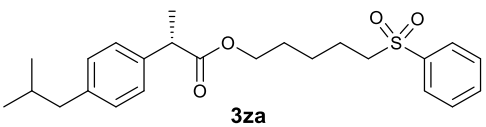
((2-((R)-4-Methylcyclohex-3-en-1-yl)propyl)sulfonyl)benzene 3y Following the described procedure, 136 mg (1.0 mmol) of (4*R*)-(-)-limonene **1y** and 270 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 153 mg of ((2-((R)-4-methylcyclohex-3-en-1-yl)propyl)sulfonyl)benzene **3y** as a pale yellow oil (EP/Et_2O 2/1, yield 55%).

^{1}H-NMR (600 MHz, $CDCl_3$, 1/1 mixture of diasteroisomers): δ= 1.06 (d, 3H, *J*= 2.2 Hz; *CH_3*-CH),1.07 (d, 3H, *J*= 2.2 Hz; *CH_3*-CH), 1.13-1.26 (m, 2H, CH_2-*CH_2*-CH), 1.41-1.54 (m, 4H, CH_2-*CH_2*-C= and CH_2-*CH*-CH_2), 1.60 (s, 6H, 2*CH_3 both diasteroisomers), 1.61-1.72 (m, 2H, CH_2-*C(H)H*-C= both diasteroisomers), 1.77-2.00 (m, 6H, CH-*CH_2*-CH and CH_2-*CH_2*-CH), 2.02-2.12 (m, 2H, CH_3-*CH*), 2.91 (2 dd, 2H; *J*= 11.9, 8.9 Hz; SO_2-*C(H)*H-CH diasteroisomer 1; *J*= 12.0, 8.9 Hz; SO_2-*C(H)*H-CH diasteroisomer 2), 3.15 (2 dd, 2H; *J*= 14.2, 3.2 Hz; SO_2-*C(H)*H-CH diasteroisomer 1; *J*= 14.2, 3.1 Hz; SO_2-*C(H)*H-CH diasteroisomer 2), 5.29 (bm, 2H, CH_2-*CH*-C= both diasteroisomers), 7.56 (t, 4H, *J*= 8.6 Hz; Ar-H_{meta} both diasteroisomers), 7.65 (bt, 2H, *J*= 8.0 Hz; Ar-H_{para} both diasteroisomers), 7.92 (d, 4H, *J*= 8.3 Hz; Ar-H_{ortho} both diasteroisomers).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$, 1/1 mixture of diasteroisomers): δ= 16.4 (CH_3), 16.8 (CH_3), 23.3 (CH), 25.1 (CH_2), 26.1 (CH_2), 27.2 (CH_2), 28.3 (CH_2), 30.3 (CH_2), 30.4 (CH_2), 32.5 (CH), 38.5 (CH), 38.6 (CH), 60.4 (CH_2), 60.6 (CH_2), 119.9 (CH), 119.9 (CH), 127.8 (CH), 129.2 (CH), 133.5 (CH), 133.9 (Cq), 134.0 (Cq), 139.9 (Cq), 140.0 (Cq).

IR (neat, *cm^{-1}*): 2966.0 cm^{-1}, 2913.4 cm^{-1}, 2884.2 cm^{-1}, 1446.2 cm^{-1}, 1303.2 cm^{-1}, 1142.8 cm^{-1}, 1084.4 cm^{-1}, 743.2 cm^{-1}, 722.7 cm^{-1}, 688.4 cm^{-1}, 594.7 cm^{-1}, 579.8 cm^{-1}, 538.9 cm^{-1}.

HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $[C_{16}H_{23}O_2S]^+$ 279.1419; Found 279.1414.



3za

5-(phenylsulfonyl)pentyl (S)-Ibuprofen 3za Following the described procedure, 137 mg (0.5 mmol) of pent-4-en-1-yl (S)-ibuprofen **1za** and 135 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 124.8 mg of 5-(phenylsulfonyl)pentyl (*S*)-2-(4-isobutylphenyl)propanoate **3za** as a pale yellow solid (EP/EtOAc 100/0 to 7/3, yield 60%).

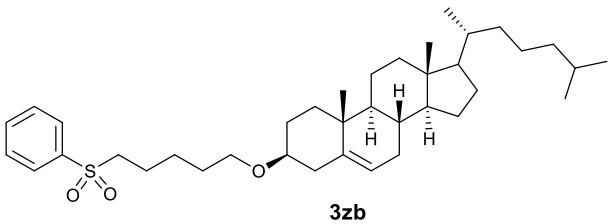
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.87 (d, 6H, *J*= 6.7 Hz; *$(CH_3)_2$*-CH), 1.28 (m, 2H; CH_2-*CH_2*-CH_2), 1.45 (d, 3H, *J*= 7.1 Hz; *CH_3*-CH), 1.50-1.56 (m, 2H; O-CH_2-*CH_2*-CH_2), 1.63-1.69 (m, 2H; SO_2-CH_2-*CH_2*-CH_2), 1.82 (ept, 1H, *J*= 6.7 Hz; $(CH_3)_2$-*CH*), 2.42 (d, 2H, *J*= 7.1 Hz; *CH_2*-CH), 2.99 (m, 2H, *CH_2*-SO_2Ph), 3.64 (q, 1H, *J*= 7.1 Hz; CH_3-*CH*), 3.96-4.04 (m, 2H; O-*CH_2*), 7.06 (d, 2H; *J*= 8.3 Hz; Ar-*H*), 7.16 (d, 2H; *J*= 8.1 Hz; Ar-*H*), 7.59 (tm, 2H; *J*= 8.2 Hz; Ar-*H_{meta}*), 7.64 (tt, 1H; *J*= 7.4, 1.1 Hz; Ar-*H_{para}*), 7.88 (m, 2H; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 18.3 (CH_3), 22.2 (CH_2), 22.3 (CH_3), 24.5 (CH_2), 27.9 (CH_2), 30.1 (CH), 44.9 (CH_2), 45.0 (CH), 55.9 (CH_2), 63.8 (CH_2), 127.0 (CH), 127.9 (CH), 129.2 (CH), 129.2 (CH), 133.6 (CH), 137.7 (Cq), 139.1 (Cq), 140.4 (Cq), 174.6 (Cq).

IR (thin film, *cm^{-1}*): 2951.6 cm^{-1}, 1726.7 cm^{-1}, 1447.0 cm^{-1}, 1203.8 cm^{-1}, 1142.9 cm^{-1}, 1085.3 cm^{-1}, 1070.2 cm^{-1}, 953.4 cm^{-1}, 796.3 cm^{-1}, 735.8 cm^{-1}, 689.7 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{24}H_{33}O_4S]^+$ 416.2021; Found 416.2028.

Mp: 50-51°C



3zb

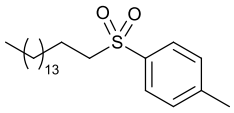
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-((5-(phenylsulfonyl)pentyl)oxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene 3zb Following the described procedure, 250 mg (0.55 mmol) of **1zb**, derived from chloresterol, and 148 mg (1.64 mmol) of sodium benzenesulfinate **2a** were reacted under the optimized conditions to afford 246 mg of (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-3-((5-(phenylsulfonyl)pentyl)oxy) 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene **3zb** as a waxy solid (EP/EtOAc 9/1, yield 75%). In order to have full convertion of the starting material the reaction time was increased to 46 hours.

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.66 (s, 3H; *CH_3*-C), 0.85 (m, 6H; *$(CH_3)_2$*-CH), 0.90 (d, 3H, *J*= 6.6 Hz; *CH_3*-CH), 0.97 (s, 3H; *CH_3*-C), 1.02-1.17 (m, 8H), 1.19-1.37 (m, 5H), 1.38-1.57 (m, 12H), 1.72 (m, 2H), 1.82 (m, 3H), 1.92-2.00 (m, 2H; C=CH-*CH_2*-CH), 2.12 (bt, 1H, *J*= 14.0 Hz), 2.29 (m, 1H), 3.08 (m, 3H; O-*CH*-CH_2 and O-*CH_2*-CH_2), 3.39 (m, 2H; *CH_2*-SO_2Ph), 5.31 (bm, 1H; C=*CH*-CH_2), 7.55 (t, 2H, *J*= 8.6 Hz; Ar-*H_{meta}*), 7.64 (t, 1H, *J*= 7.3 Hz; Ar-*H_{para}*), 7.89 (d, 2H, *J*= 8.4 Hz; Ar-*H_{ortho}*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 11.8 (CH_3), 18.7 (CH_3), 19.3 (CH_3), 21.0 (CH_2), 22.5 (CH_2), 22.5 (CH_3), 22.8 (CH_3), 23.8 (CH_2), 24.2 (CH_2), 25.1 (CH_2), 27.9 (CH), 28.2 (CH_2), 28.3 (CH_2), 29.5 (CH_2), 31.8 (CH), 31.9 (CH_2), 35.7 (CH), 36.1 (CH_2), 36.8 (Cq), 37.2 (CH_2), 39.1 (CH_2), 39.5 (CH_2), 39.7 (CH_2), 42.3 (Cq), 50.1 (CH), 56.1 (CH), 56.2 (CH_2), 56.7 (CH), 67.2 (CH_2), 78.9 (CH), 121.5 (CH), 128.0 (CH), 129.2 (CH), 133.6 (CH), 139.1 (Cq), 140.9 (Cq).

IR (thin film, *cm^{-1}*): 2932.1 cm^{-1}, 2864.8 cm^{-1}, 2847.6 cm^{-1}, 1463.8 cm^{-1}, 1376.3 cm^{-1}, 1320.0 cm^{-1}, 1146.7 cm^{-1}, 1103.3 cm^{-1}, 728.7 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{38}H_{61}O_3S]^+$ 597.4336; Found 597.4327.

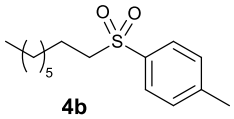


4a

4-(Hexadecylsulfonyl)-toluene 4a Following the described procedure, 224 mg (1.0 mmol) of 1-hexadecene **1a** and 292 mg (1.64 mmol) of sodium 4-methylbenzenesulfinate **2b** were reacted under the optimized conditions to afford 270 mg of 1-(hexadecylsulfonyl)-4-methylbenzene **4a** as a white solid (EP/Et_2O 8/2, yield 71%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.86 (t, 3H; *J*= 6.8 Hz; *CH_3*-CH_2), 1.20-1.33 (m, 26H; alkyl chain), 1.67 (m, 2H; CH_2-*CH_2*-CH_2), 2.43 (s, 3H, Ar-*CH_3*), 3.05 (m, 2H; CH_2-*CH_2*-SO_2), 7.33 (d, 2H; *J*= 8.1 Hz; Ar-*H*), 7.76 (d, 2H; *J*= 8.2 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.0 (CH_3), 21.5 (CH_3), 22.6 (CH_2), 22.6 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 56.3 (CH_2), 127.9 (CH), 129.8 (CH), 136.2 (Cq), 144.4 (Cq). The characterization data matched with the reported one.[21]

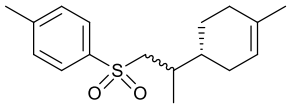


4b

1-Methyl-4-(octylsulfonyl)benzene 4b Following the described procedure, 112 mg (1.0 mmol) of 1-ottene **1c** and 292 mg (1.64 mmol) of sodium 4-methylbenzenesulfinate **2b** were reacted under the optimized conditions to afford 208 mg of 1-methyl-4-(octylsulfonyl)benzene **4b** as an amber oil (no need for column chromatography, yield 80%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.86 (t, 3H; *J*= 7.1 Hz; CH_3), 1.17-1.28 (m, 8H, CH_2 chain), 1.33 (m, 2H, CH_2-*CH_2*-CH_2), 1.69 (m, 2H, CH_2-*CH_2*-CH_2), 2.45 (s, 3H, CH_3), 3.05 (m, 2H, CH_2-*CH_2*-SO_2), 7.35 (t,2H; *J*= 8.0 Hz; Ar-*H*), 7.78 (d, 2H; *J*= 8.3 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.0 (CH_3), 21.6 (CH_3), 22.5 (CH_2), 22.7 (CH_2), 28.2 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 31.6 (CH_2), 56.4 (CH_2), 128.1 (CH), 129.8 (CH), 136.3 (Cq), 144.5 (Cq). The characterization data matched with the reported one.[22]



4c

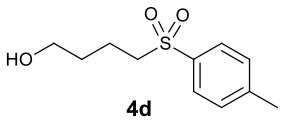
4-((2-((*R*)-4-Methylcyclohex-3-en-1-yl)propyl)sulfonyl)toluene 4c Following the described procedure, 136 mg (1 mmol) of (4*R*)-(-)-limonene **1w** and 292 mg (1.64 mmol) of sodium 4-methylbenzenesulfinate **2b** were reacted under the optimized conditions to afford 166 mg of 4-((2-((*R*)-4-Methylcyclohex-3-en-1-yl)propyl)sulfonyl)toluene **4c** as a pale yellow oil (EP/Et_2O 1/1, yield 57%, 1:1 mixture of diasteroisomers).

^{1}H-NMR (600 MHz, $CDCl_3$; 1/1 mixture of diasteroisomers): δ= 1.06 (d, 3H, *J*= 2.6 Hz; *CH_3*-CH diasteroisomer 1),1.07 (d, 3H, *J*= 2.6 Hz; *CH_3*-CH diasteroisomer 2), 1.14-1.29 (m, 3H, CH_2-*CH_2*-CH), 1.44-1.55 (m, 3H, CH_2-*CH_2*-C= and CH_2-*CH*-CH_2), 1.56 (s, 6H, 2**CH_3*-C=), 1.62-1.73 (m, 2H, CH_2-*CH*-CH_2, 1.78-1.99 (m, 8H, CH-*CH_2*-CH), 1.99-2.16 (m, 2H, CH_3-*CH*-CH), 2.45 (s, 6H, *CH_3*-Ar), 2.87 (dd, 1H; *J*= 14.2, 9.0 Hz; SO_2-*C(H)*H-CH diasteroisomer 1) 2.89 (dd, 1H; *J*= 14.2, 9.0 Hz; SO_2-*C(H)*H-CH diasteroisomr 2), 3.12 (dd, 1H; *J*= 14.2, 3.2 Hz; SO_2-*C(H)*H-CH diasteroisomer 1) 3.14 (dd, 1H; *J*= 14.2, 3.2 Hz; SO_2-*C(H)*H-CH diasteroisomer 2), 5.27-5.33 (m, 2H, CH_2-*CH*-C= both diasteroisomers), 7.35 (d, 4H, *J*= 7.1 Hz; Ar-*H* both diasteroisomers), 7.78 (d, 2H, *J*= 8.4 Hz; Ar-*H* both diasteroisomers).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$, 1/1 mixture of diasteroisomers): δ= 16.5 (CH_3), 16.8 (CH_3), 21.6 (CH_3), 23.3 (CH_3), 25.2 (CH_2), 26.2 (CH_2), 27.2 (CH_2), 28.4 (CH_2), 30.4 (CH_2), 30.5 (CH_2), 32.6 (CH_3), 38.6 (CH_3), 38.7 (CH), 60.6 (CH_2), 60.8 (CH_2), 119.9 (CH), 120.0 (CH), 127.9 (CH), 129.9 (CH), 134.0 (Cq), 134.1 (Cq), 137.2 (Cq), 144.4 (Cq).

IR (thin film, *cm^{-1}*): 2967.0 cm^{-1}, 2914.4 cm^{-1}, 2883.2 cm^{-1}, 1447.2 cm^{-1}, 1302.2 cm^{-1}, 1147.8 cm^{-1}, 1085.4 cm^{-1}, 742.2 cm^{-1}, 723.7 cm^{-1}, 689.4 cm^{-1}, 595.7 cm^{-1}, 579.8 cm^{-1}, 539.9 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{17}H_{25}O_2S]^+$ 293.1570; Found 293.1569.

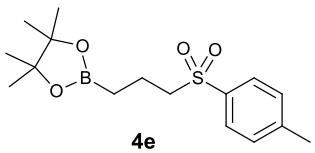


4d

4-Tosylbutan-1-ol 4d Following the described procedure, 72 mg (0.50 mmol) of but-3-en-1-ol **1h** and 146 mg (0.82 mmol) of sodium 4-methylbenzenesulfinate **2b** were reacted under the optimized conditions to afford 64 mg of 4-tosylbutan-1-ol **4d** as a yellow oil (EP/EtOAc 25/75, yield 56%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.60 (m, 2H, $HOCH_2$-*CH_2*-CH_2), 1.77 (m, 2H, CH_2-*CH_2*-CH_2), 2.42 (s, 3H, CH_3), 3.10 (m, 2H, CH_2-*CH_2*-SO_2), 3.58 (t, 2H, *J*= 6.1 Hz; OH-*CH_2*-CH_2), 7.33 (d, 2H, *J*= 8.0 Hz; Ar-*H*), 7.68 (d, 2H, *J*= 8.3 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 19.4 (CH_2), 21.5 (CH_3), 30.8 (CH_2), 56.0 (CH_2), 61.7 (OCH_2), 128.0 (CH), 129.8 (CH), 135.9 (Cq), 144.6 (Cq). The characterization data matched with the reported one.[23]

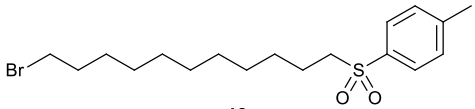


4e

4,4,5,5-Tetramethyl-2-(3-tosylpropyl)-1,3,2-dioxaborolane 4e Following the described procedure, 168 mg (1.0 mmol) of allyl boronic acid pinacol ester **1n** and 292 mg (1.64 mmol) of sodium 4-methylbenzenesulfinate **2b** were reacted under the optimized conditions to afford 256 mg of 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4e** as an amber oil (no need for column chromatography, yield 79%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.79 (t, 2H, *J*= 7.7 Hz; B-*CH_2*-CH_2), 1.17 (s, 12H, (*CH_3*)$_4$), 1.75-1.81 (m, 2H, CH_2-*CH_2*-CH_2), 2.41 (s, 3H; CH_3), 3.09 (m, 2H, CH_2-*CH_2*-SO_2), 7.31 (d, 2H, *J*= 8.3 Hz; Ar-*H*), 7.74 (d, 2H, *J*= 8.3 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 9.64 (CH_2), 17.5 (CH_2), 21.5 (CH_3), 24.7 (CH_3), 57.9 (CH_2), 83.2 (Cq), 127.9 (CH), 129.7 (CH), 136.2 (Cq), 144.3 (Cq). The characterization data matched with the reported one.[24]



4f

1-((11-Bromoundecyl)sulfonyl)-4-toluene 4f Following the described procedure, 233 mg (1.0 mmol) of 11-bromoundec-1-ene **1aa** and 292 mg (1.64 mmol) of sodium 4-methylbenzenesulfinate **2b** were reacted under the optimized conditions to afford 342 mg of 1-((11-bromoundecyl)sulfonyl)-4-methylbenzene **4f** as an orange waxy solid (no need for column chromatography, yield 88%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.08-1.23 (bm, 10H, CH_2 chain), 1.23-1.30 (m, 2H, CH_2-*CH_2*-CH_2), 1.31-1.36 (m, 2H, CH_2-*CH_2*-CH_2-CH_2Br), 1.61 (m, 2H, CH_2-*CH_2*-CH_2SO_2), 1.76 (quint, 2H *J*= 7.1 Hz; CH_2-*CH_2*-CH_2Br), 2.36 (s, 3H, *CH_3*), 2.99 (m, 2H, SO_2-*CH_2*-CH_2), 3.32 (t, 2H, *J*= 6.9 Hz; Br-*CH_2*-CH_2),

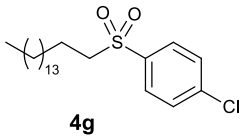
7.28 (d, 2H, *J*= 8.5 Hz; Ar-*H*), 7.70 (d, 2H, *J*= 8.6 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 21.3 (CH_3), 22.4 (CH_2), 27.8 (CH_2), 27.9 (CH_2), 28.4 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 28.9 (CH_2) 32.5 (CH_2), 33.8 (CH_2), 56.0 (CH_2), 127.7 (CH), 129.6 (CH), 136.0 (Cq), 144.2 (Cq).

IR (neat, *cm^{-1}*): 2916.3 cm^{-1}, 2849.2 cm^{-1}, 1737.9 cm^{-1}, 1597.8 cm^{-1}, 1373.2 cm^{-1}, 1314.0 cm^{-1}, 1288.6 cm^{-1}, 1230.3 cm^{-1}, 1142.8 cm^{-1}, 1084.4 cm^{-1}, 813.2 cm^{-1}, 772.3 cm^{-1}, 643.9 cm^{-1}, 635.2 cm^{-1}, 565.9 cm^{-1}, 524.9 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{18}H_{29}BrO_2S]^+$ 389.1150 and 391.1129; Found 89.1150 and 391.1133.

Mp: 65.1-66.8°C



4g

1-(Hexadecylsulfonyl)-4-chlorobenzene 4g[25] Following the described procedure, 112 mg (1.0 mmol) of 1-hexadecene **1a** and 163 mg (0.82 mmol) of sodium 4-chlorobenzenesulfinate **2c** were reacted under the optimized conditions to afford 156 mg of 1-(hexadecylsulfonyl)-4-chlorobenzene **4g** as a cream solid (no need for column chromatography, yield 78%).

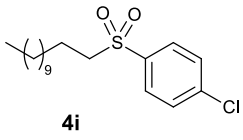
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.87 (t, 3H; *J*= 7.1 Hz; *CH*$_3$-CH$_2$), 1.18-1.38 (m, 26H; alkyl chain), 1.69 (m, 2H; CH$_2$-C*H*$_2$-CH$_2$), 3.06 (m, 2H; CH$_2$-C*H*$_2$-SO$_2$), 7.54 (d, 2H; *J*= 8.8 Hz; Ar-*H*), 7.84 (d, 2H; *J*= 8.8 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.1 (CH_3), 22.64 (CH_2), 22.67 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.62 (CH_2), 29.63 (CH_2), 29.65 (CH_2), 29.67 (CH_2), 31.9 (CH_2), 56.4 (CH_2), 127.56 (CH), 129.58 (CH), 137.7 (Cq), 140.4 (Cq).

IR (neat, *cm^{-1}*): 2915.5 cm^{-1}, 2846.3 cm^{-1}, 1740.8 cm^{-1}, 1586.2 cm^{-1}, 1474.8 cm^{-1}, 1364.5 cm^{-1}, 1300.5 cm^{-1}, 1279.9 cm^{-1}, 1227.4 cm^{-1}, 1139.9 cm^{-1}, 1090.3 cm^{-1}, 1014.7 cm^{-1}, 827.8 cm^{-1}, 792.8 cm^{-1}, 579.8 cm^{-1}, 556.9 cm^{-1}, 466.4 cm^{-1}.

HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for [$C_{22}H_{38}ClO_2S$]$^+$ 401.2281 and 403.2252; Found 401.2277 and 403.2236.

Mp: 61.3-62.9°C

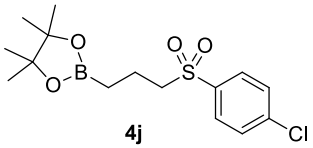


4i

1-Chloro-4-(dodecylsulfonyl)benzene 4i Following the described procedure, 84 mg (0.50 mmol) of 1-dodecene **1b** and 163 mg (0.82 mmol) of sodium 4-chlorobenzenesulfinate **2c** were reacted under the optimized conditions to afford 335 mg of 1-chloro-4-(dodecylsulfonyl)benzene **4i** as a yellow solid (no need for column chromatography, yield 97%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.87 (t, 3H; *J*= 7.0 Hz, *CH*$_3$), 1.15-1.29 (bm, 16H, *CH*$_2$ chain), 1.29-1.37 (m, 2H, *CH*$_2$-(CH$_2$)$_2$-SO$_2$), 1.68 (m, 2H, *CH*$_2$-CH$_2$-SO$_2$), 3.06 (m, 2H, CH$_2$-C*H*$_2$-SO$_2$), 7.59 (d, 2H; *J*= 8.8 Hz; Ar-*H*), 7.84 (d, 2H; *J*= 8.8 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.0 (CH_3), 22.6 (CH_2), 22.6 (CH_2), 22.6 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.50 (CH_2), 29.52 (CH_2), 31.8 (CH_2), 56.3 (CH2), 129.6 (CH), 129.6 (CH), 137.7 (Cq), 140.3 (Cq). The characterization data matched with the reported one.[8]



4j

2-(3-((4-Chlorophenyl)sulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4j Following the described procedure, 168 mg (1.0 mmol) of allyl boronic acid pinacol ester **1n** and 326 mg (1.64 mmol) of sodium 4-chlorobenzenesulfinate **2c** were reacted under the optimized conditions to afford 287 mg of 2-(3-((4-chlorophenyl)sulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4j** as an amber oil (no need for column chromatography, yield 84%).

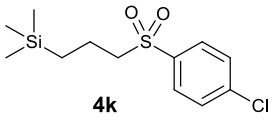
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.84 (t, 2H, *J*= 7.7 Hz; B-*CH*$_2$-CH$_2$), 1.20 (s, 12H, (*CH*$_3$)$_4$), 1.75-1.81 (m, 2H, CH$_2$-*CH*$_2$-CH$_2$), 3.14 (m, 2H, CH$_2$-*CH*$_2$-SO$_2$), 7.54 (d, 2H, *J*= 8.8 Hz; Ar-*H*), 7.84 (d, 2H, *J*= 8.8 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 9.5 (CH_2), 17.4 (CH_2), 24.5 (CH_3), 57.9 (CH_2), 83.1 (Cq), 129.3 (CH), 129.4 (CH), 137.5 (Cq), 139.9 (Cq).

^{11}B{^{1}H}-NMR (192 MHz, CDCl3): δ= 32.4

IR (thin film, *cm^{-1}*): 2983.4 cm^{-1}, 1743.7 cm^{-1}, 1580.3 cm^{-1}, 1478.2 cm^{-1}, 1373.2 cm^{-1}, 1312.1 cm^{-1}, 1221.5 cm^{-1}, 1142.5 cm^{-1}, 1090.3 cm^{-1}, 1013.8 cm^{-1}, 839.4 cm^{-1}, 757.7 cm^{-1}, 728.6 cm^{-1}, 629.5 cm^{-1}, 562.2 cm^{-1}, 460.2 cm^{-1}.

HRMS (ESI) *m/z*: [M - H]$^+$ Calcd for [$C_{15}H_{21}BClO_4S$]$^+$ 343.0937 and 345.0907; Found 343.0932 and 345.0897.



4k

(3-((4-Chlorophenyl)sulfonyl)propyl)trimethylsilane 4k Following the described procedure, 57 mg (0.5 mmol) of allyl silane **1o** and 163 mg (0.82 mmol) of sodium 4-chlorobenzenesulfinate **2c** were reacted under the optimized conditions to afford 73 mg of (3-((4-chlorophenyl)sulfonyl)propyl)trimethylsilane **4k** as a waxy amber solid (no need for column chromatography, yield 50%).

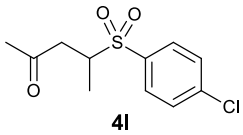
^{1}H-NMR (600 MHz, $CDCl_3$): δ= - 0.04 (s, 9H, Si(*CH*$_3$)$_3$), 0.53 (m, 2H, Si-*CH*$_2$-CH$_2$), 1.72 (ddd, 2H, *J*= 16.1, 8.1, 4.9 Hz; CH$_2$-*CH*$_2$-CH$_2$), 3.07 (m, 2H, CH$_2$-*CH*$_2$-SO$_2$), 7.53 (d, 2H, *J*= 8.8 Hz; Ar-*H*), 7.83 (d, 2H, *J*= 8.5 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= -1.9 (CH_3), 15.6 (CH_2), 17.5 (CH_2), 59.4 (CH_2), 129.5 (CH), 129.6 (CH), 137.8 (Cq), 140.3 (Cq).

IR (thin film, *cm^{-1}*): 2950.6 cm^{-1}, 1746.6 cm^{-1}, 1580.6 cm^{-1}, 1476.2 cm^{-1}, 1317.8 cm^{-1}, 1294.5 cm^{-1}, 1245.8 cm^{-1}, 1142.8 cm^{-1}, 1087.4 cm^{-1}, 1014.4 cm^{-1}, 830.6 cm^{-1}, 784.0 cm^{-1}, 751.9 cm^{-1}, 693.6 cm^{-1}, 623.6 cm^{-1}, 530.2 cm^{-1}, 474.8 cm^{-1}.

HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for [$C_{12}H_{20}ClO_2SSi$]$^+$ 291.0637 and 293.0607; Found 291.0636 and 293.0610.

Mp: 67.4-68.3°C

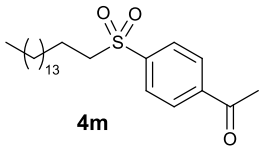


4l

4-((4-Chlorophenyl)sulfonyl)pentan-2-one 4l Following the described procedure, 43 mg (0.50 mmol) of 3-penten-2-ol **1ab** and 163 mg (0.82 mmol) of sodium 4-chlorobenzenesulfinate **2c** were reacted under the optimized conditions to afford 26 mg of 4-((4-chlorophenyl)sulfonyl)pentan-2-one **4l** as a yellow oil (EP/EE from 1/1 to 1/2, yield 20%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 1.23 (d, 3H, *J*= 6.9 Hz; *CH*$_3$-CH), 2.19 (s, 3H; *CH*$_3$-CO), 2.59 (dd, 1H, *J*= 18.0, 9.3 Hz; CO-*C(H)H*-CH), 3.19 (dd, 1H, *J*= 17.4, 3.4 Hz; CO-*C(H)H*-CH), 3.65 (m, 1H, *CH*-SO_2), 7.55 (d, 2H, *J*= 8.8 Hz; Ar-*H*), 7.81 (d, 2H, *J*= 8.8 Hz; Ar-*H*)

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.2 (CH_3), 30.4 (CH_3), 42.2 (CH_2), 55.6 (CH), 129.6 (CH), 130.3 (CH). 135.5 (Cq), 140.8 (Cq), 203.8 (CO). The characterization data matched with the reported one. [26]



4m

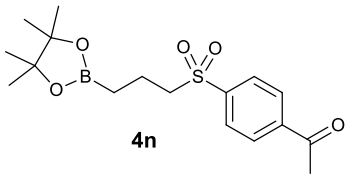
1-(4-Hexadecylsulfonylphenyl)ethanone 4m Following the described procedure, 112 mg (0.50 mmol) of 1-hexadecene **1a** and 169 mg (0.82 mmol) of sodium 4-acetylbenzenesulfinate **2d** were reacted under the optimized conditions to afford 41 mg of 1-(4-hexadecylsulfonylphenyl)ethanone **4m** as a white solid (EP/EE from 8/2 to 1/1, yield 20%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.88 (t, 3H; *J*= 7.0 Hz; *CH*$_3$-CH_2), 1.19-1.31 (m, 24H; CH_2 chain), 1.32-1.37 (m, 2H; CH_2-C*H*$_2$-CH_2), 1.70 (m, 2H, CH_2-C*H*$_2$-CH_2), 2.67 (s, 3H, CO-*CH*$_3$), 3.09 (m, 2H; CH_2-C*H*$_2$-SO_2), 8.01 (d, 2H; *J*= 8.8 Hz; Ar-*H*), 8.12 (d, 2H; *J*= 8.8 Hz; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.1 (CH_3), 22.5 (CH_2), 22.6 (CH_2), 26.9 (CH_3), 28.2 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.43 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 56.4 (CH_2), 128.5 (CH), 129.9 (CH), 140.8 (Cq), 142.9 (Cq), 196.7 (CO).

IR (thin film, *cm^{-1}*): 1735.0 cm^{-1}, 1585.2 cm^{-1}, 1474.3 cm^{-1}, 1366.5 cm^{-1}, 1301.5 cm^{-1}, 1280.9 cm^{-1}, 1227.4 cm^{-1}, 1139.4 cm^{-1}, 1092.3 cm^{-1}, 792.9 cm^{-1}, 578.8 cm^{-1}, 559.9 cm^{-1}, 467.4 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{24}H_{41}O_3S]^+$ 409.2776; Found 409.2779.



4n

1-(4-((3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)sulfonyl)phenyl)ethan-1-one 4n Following the described procedure, 84 mg (0.50 mmol) of allyl boronic acid pinacol ester **1n** and 169 mg (0.82 mmol) of sodium 4-acetylbenzenesulfinate **2d** were reacted under the optimized conditions to afford 44 mg of 1-(4-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)sulfonyl)phenyl)ethan-1-one **4n** as a pale yellow solid (no need for column chromatography, yield 25%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.83 (t, 2H, *J*= 7.7 Hz; B-*CH*$_2$-CH_2), 1.19 (s, 12H, (*CH*$_3$)$_4$), 1.78 (m, 2H, CH_2-*CH*$_2$-CH_2), 2.66 (s, 3H, CO-*CH*$_3$), 3.16 (m, 2H, CH_2-*CH*$_2$-SO_2), 7.99 (d, 2H, *J*= 8.8 Hz; Ar-*H*), 8.10 (d, 2H, *J*= 8.8 Hz; Ar-*H*).

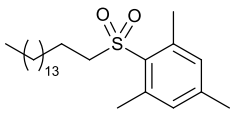
^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 9.8 (CH_2), 17.6 (CH_2), 24.7 (CH_3), 26.9 (CH_3), 57.7 (CH_2), 83.3 (Cq), 128.5 (CH), 128.9 (CH), 140.7 (Cq), 142.9 (Cq), 196.8 (C=O).

^{11}B{^{1}H}-NMR (192 MHz, CDCl3): δ= 32.3

IR (thin film, *cm^{-1}*): 2971.8 cm^{-1}, 1735.0 cm^{-1}, 1682.4 cm^{-1}, 1373.2 cm^{-1}, 1256.6 cm^{-1}, 1215.7 cm^{-1}, 1148.6 cm^{-1}, 1087.4 cm^{-1}, 967.7 cm^{-1}, 886.1 cm^{-1}, 842.3 cm^{-1}, 789.8 cm^{-1}, 727.7 cm^{-1}, 620.6 cm^{-1}, 553.5 cm^{-1}.

HRMS (ESI) *m/z*: $[M - H]^+$ Calcd for $[C_{17}H_{24}BO_5S]^+$ 351.1432; Found 351.1421.

Mp: 107.2-108.0°C



4o

2-(Hexadecylsulfonyl)-1,3,5-trimethylbenzene 4o Following the described procedure, 224 mg (1 mmol) of 1-hexadecene **1a** and 338 mg (1.64 mmol) of sodium 2,4,6-trimethylbenzenesulfinate **2e** were reacted under the optimized conditions to afford 61 mg of 2-(hexadecylsulfonyl)-1,3,5-trimethylbenzene **4o** as a yellow solid (EP/EE 8/2, yield 15%).

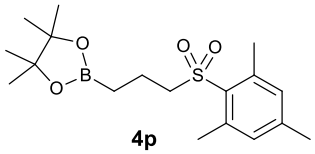
^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.88 (t, 3H; *J*= 7.1 Hz; CH_3-CH_2), 1.17-1.32 (m, 24H; CH_2 chain), 1.33-1.41 (m, 2H; CH_2-CH_2-CH_2), 1.75 (m, 2H, CH_2-CH_2-CH_2), 2.30 (s, 3H, CH_3), 2.66 (s, 6H, CH_3), 3.07 (m, 2H; CH_2-CH_2-SO_2), 6.96 (s, 2H; Ar-*H*).

^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 14.1 (CH_3), 20.9 (CH_3), 21.9 (CH_2), 22.7 (CH_2), 22.9 (CH_3), 28.4 (CH_2), 28.7 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.61 (CH_2), 29.64 (CH_2), 29.66 (CH_2), 29.67 (CH_2), 31.9 (CH_2), 56.2 (CH_2), 132.2(CH), 133.2 (Cq), 139.9 (Cq), 143.0 (Cq).

IR (thin film, cm^{-1}): 2913.4 cm^{-1}, 2849.2 cm^{-1}, 1740.8 cm^{-1}, 1370.8 cm^{-1}, 1317.8 cm^{-1}, 1227.4 cm^{-1}, 1218.6 cm^{-1}, 1137.0 cm^{-1}, 848.2 cm^{-1}, 769.4 cm^{-1}, 667.2 cm^{-1}, 582.7 cm^{-1}, 562.3 cm^{-1}, 538.9 cm^{-1}, 524.4 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $[C_{25}H_{45}O_2S]^+$ 409.3135; Found 409.3137.

Mp: 65.8-64.6°C



4p

2-(3-(Mesitylsulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4p Following the described procedure, 84 mg (0.50 mmol) of allyl boronic acid pinacol ester **1n** and 169 mg (0.82 mmol) of sodium 2,4,6-trimethylbenzenesulfinate **2e** were reacted under the optimized conditions to afford 41 mg of 2-(3-(Mesitylsulfonyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4p** as a yellow oil (EP/EE 2/1, yield 23%).

^{1}H-NMR (600 MHz, $CDCl_3$): δ= 0.86 (t, 2H, *J*= 10.1 Hz; B-CH_2-CH_2), 1.21 (s, 12H, $(CH_3)_4$), 1.86 (m, 2H, CH_2-CH_2-CH_2), 2.30 (s, 3H, CH_3), 2.66 (s, 6H, CH_3), 3.15 (m, 2H, CH_2-CH_2-SO_2), 6.95 (s, 2H, Ar-*H*).

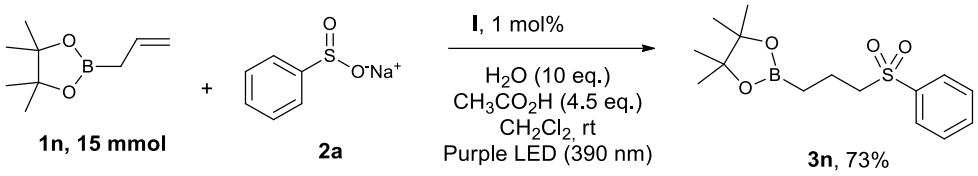
^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): δ= 16.9 (CH_2), 20.9 (CH_3), 22.9 (CH_3), 24.8 (CH_3), 57.8 (CH_2), 83.3 (Cq), 132.2 (CH), 133.2 (Cq), 140.0 (Cq), 142.9 (Cq).

^{11}B{^{1}H}-NMR (192 MHz, CDCl3): δ= 32.2

IR (thin film, cm^{-1}): 2969.2 cm^{-1}, 2925.4 cm^{-1}, 1741.0 cm^{-1}, 1372.6 cm^{-1}, 1308.3 cm^{-1}, 1232.2 cm^{-1}, 1217.6 cm^{-1}, 1141.6 cm^{-1}, 729.3 cm^{-1}, 662.0 cm^{-1}, 579.2 cm^{-1}, 545.0 cm^{-1}.

HRMS (ESI) *m/z*: $[M - H]^+$ Calcd for $[C_{18}H_{28}BO_4S]^+$ 351.1796; Found 351.1786.

5.6 Reaction scale-up



A 250 ml Schlenk flask, equipped with a magnetic stirring bar, was dried and placed under N_2 for 5 minutes, then the N_2 flow was removed and the flask closed with a septum. Allyl boronic acid pinacol ester **1n** (2.52 g, 15 mmol, 1 Eq), salt **I** (60.2 mg, 0.15 mmol, 1 mol%) and sodium benzenesulfinate **2a** (4.03 g, 24.6 mmol, 1.64 Eq) were placed in the flask in this order then 75 ml of CH_2Cl_2 were added. The intense red solution was left under stirring until its colour faded to transparent, then water (8 g, 150 mmol, 8 ml 10 Eq) and acetic acid (4.05 g, 67.5 mmol, 3.9 ml, 4.5 Eq) were added. The Schlenk tube was closed with a septum and then stirred at 4 cm from two Kessil purple lamp (390 nm) at room temperature for 27 h (**Figure S28**).

Reaction work-up: the reaction mixture was transferred in a separation funnel and the organic phase was washed with $NaHCO_3$ (1 x 75 ml). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 30 ml). The collected organic phases were dried over Na_2SO_4. After solvent removal, 4,4,5,5-tetramethyl-2-(3-(phenylsulfonyl)propyl)-1,3,2-dioxaborolane **3n** was obtained as an amber oil in 73% yield without need for column chromatography.

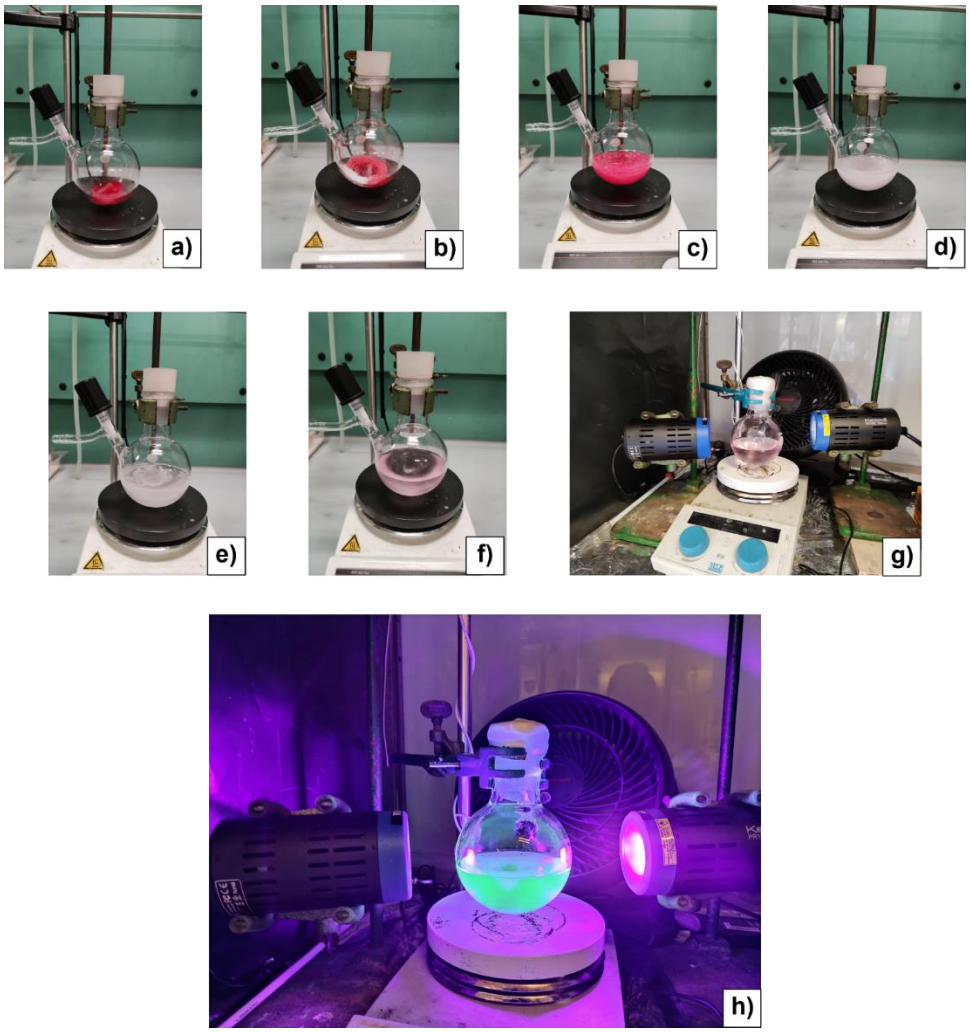


Figure S28. Pictures of large scale reaction workflow: initial addition of alkene **1n** and diarylmethylium salt **I** (a), followed by the addition of sulfinate **2a** (b), and DCM (c). After color change, (d) water was added (e) followed by acetic acid (f). The flask was positioned between two Kessil purple lamp (390 nm) (g) and finally the LEDs were turned on. The reaction was left under continuous stirring and fan ventilation.

6. References

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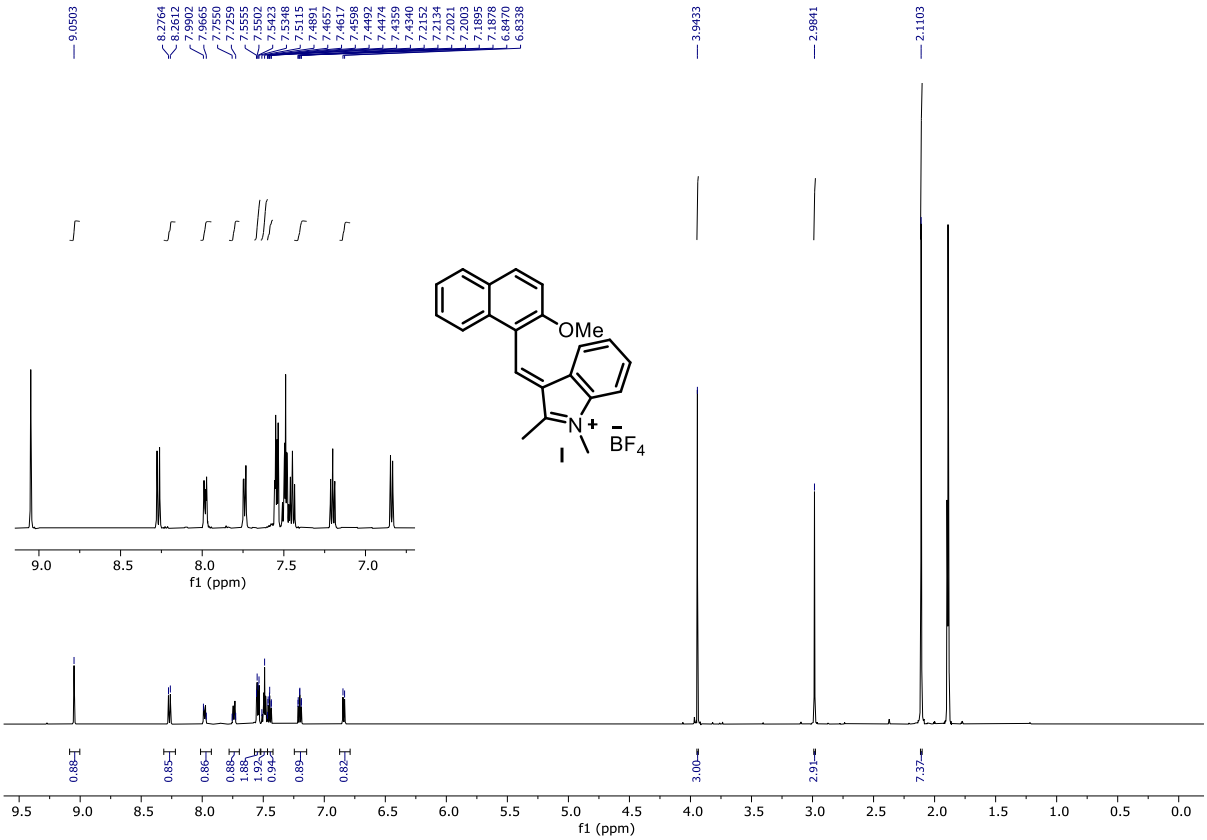
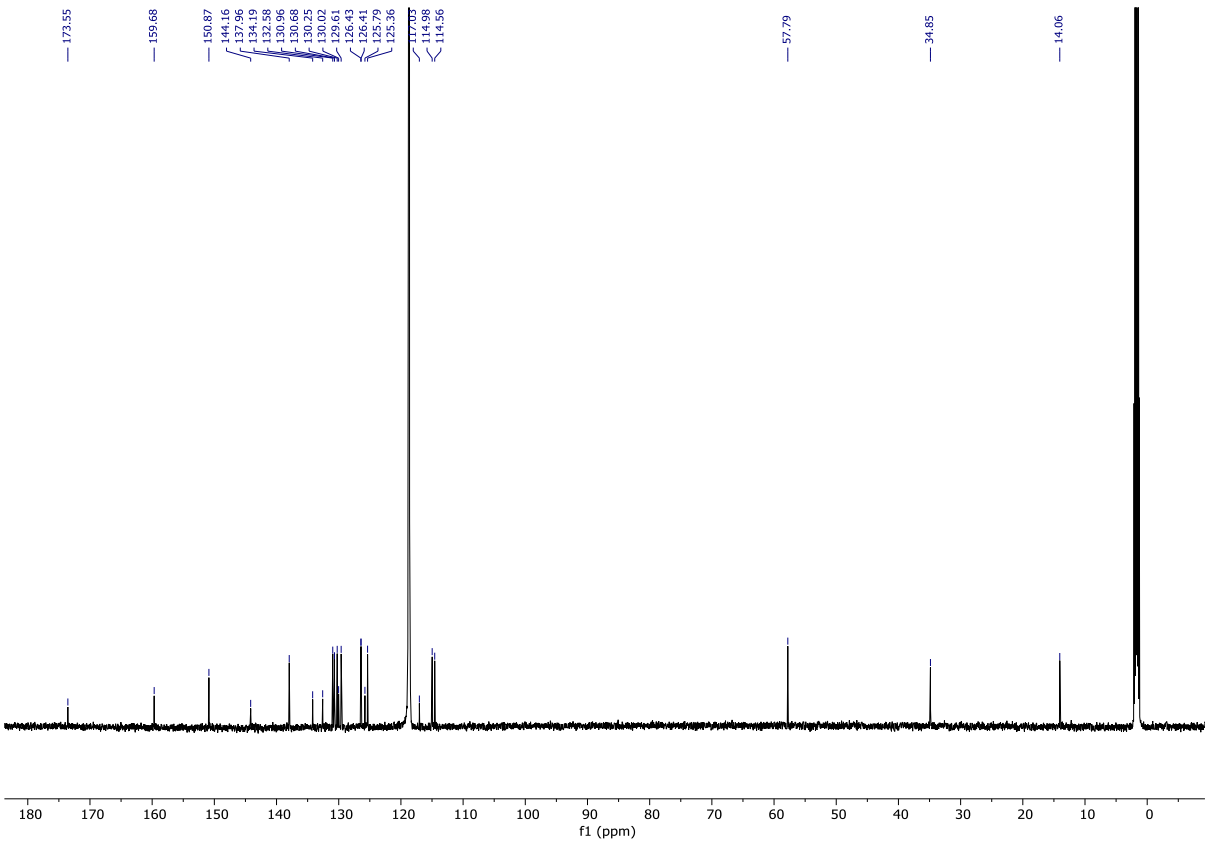
26. Commercially available from Aurora Fine Chemicals LLC (USA, Austria)

7. Copies of NMR spectra of catalysts and products

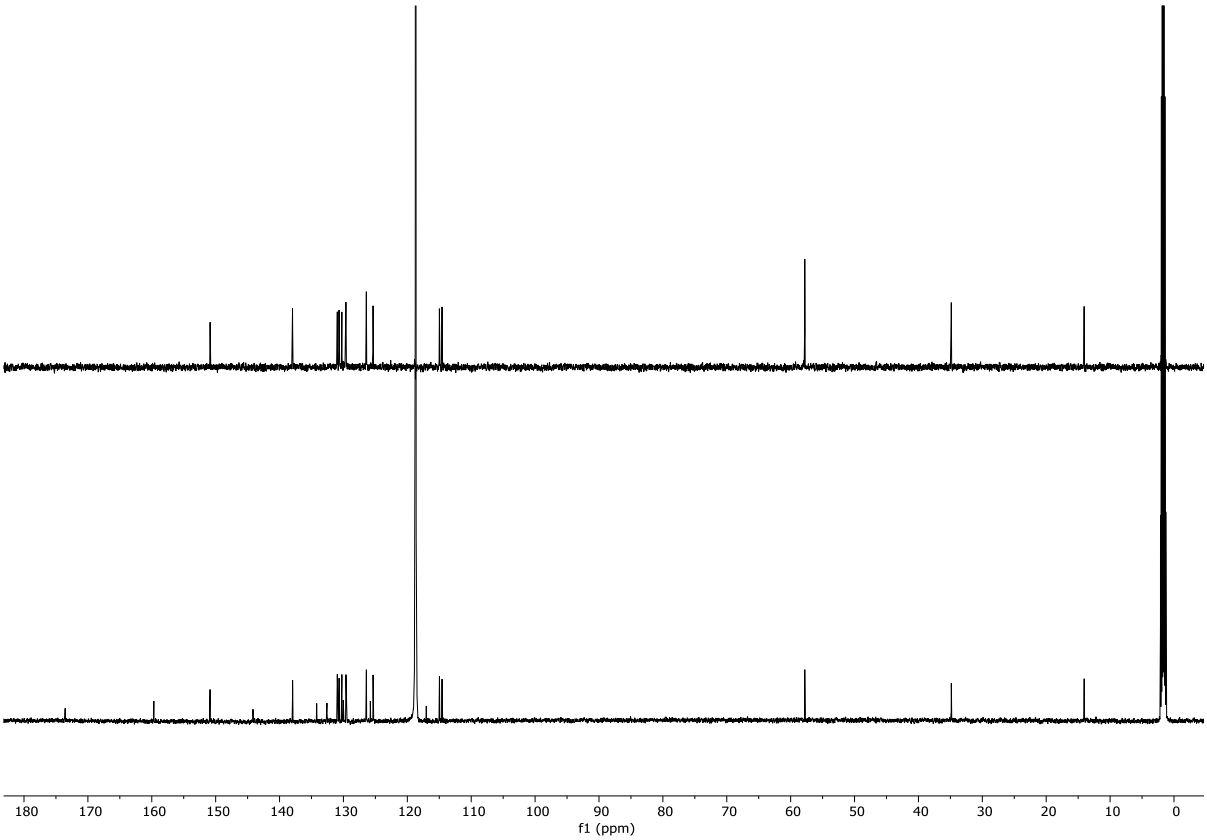
^{1}H-NMR of compound I (600 MHz, CD_3CN)



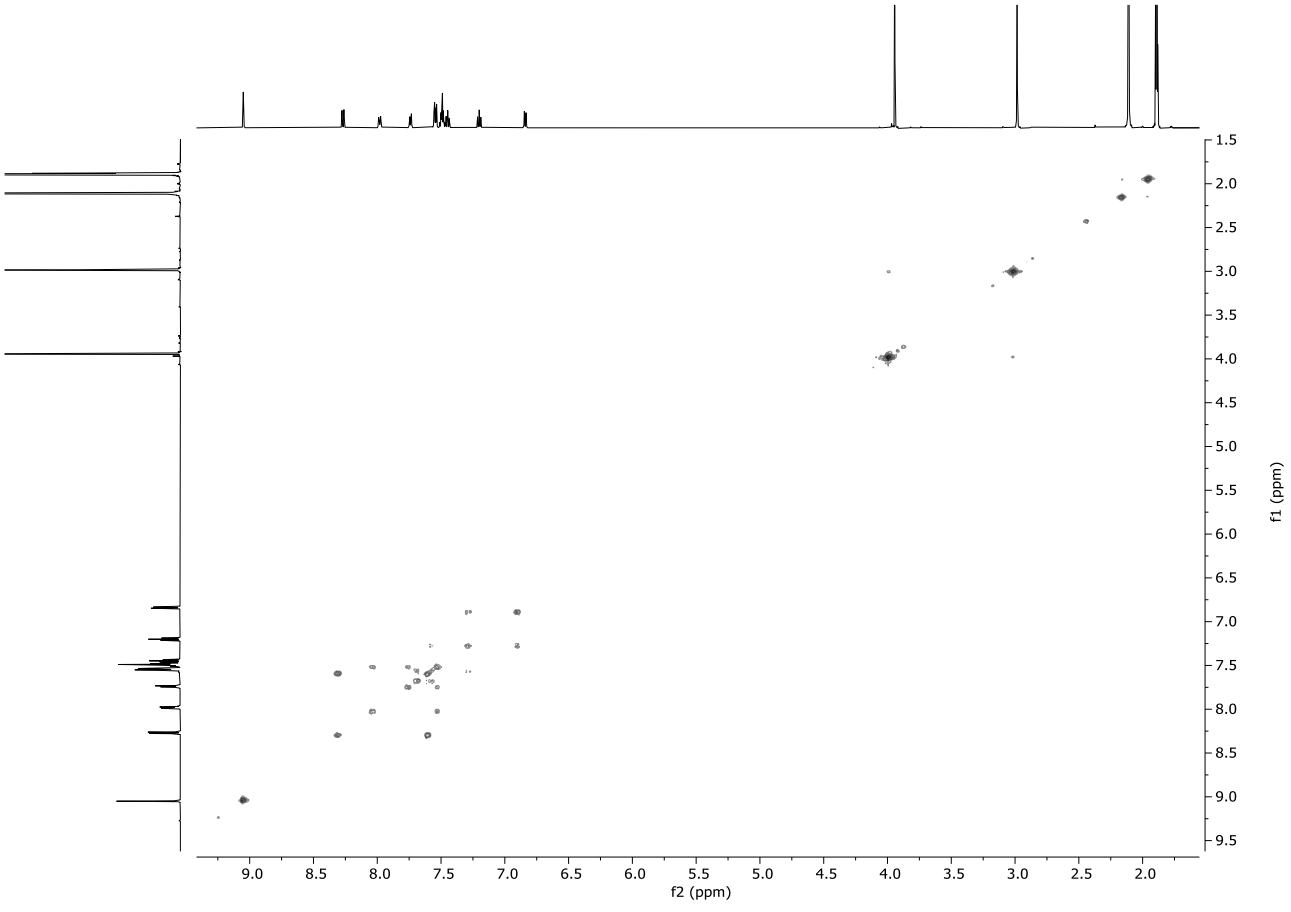
^{13}C{^{1}H}-NMR of compound I (150 MHz, CD_3CN)



Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound I (150 MHz, CD_3CN)



COSY-NMR of compound I (600 MHz, CD_3CN)



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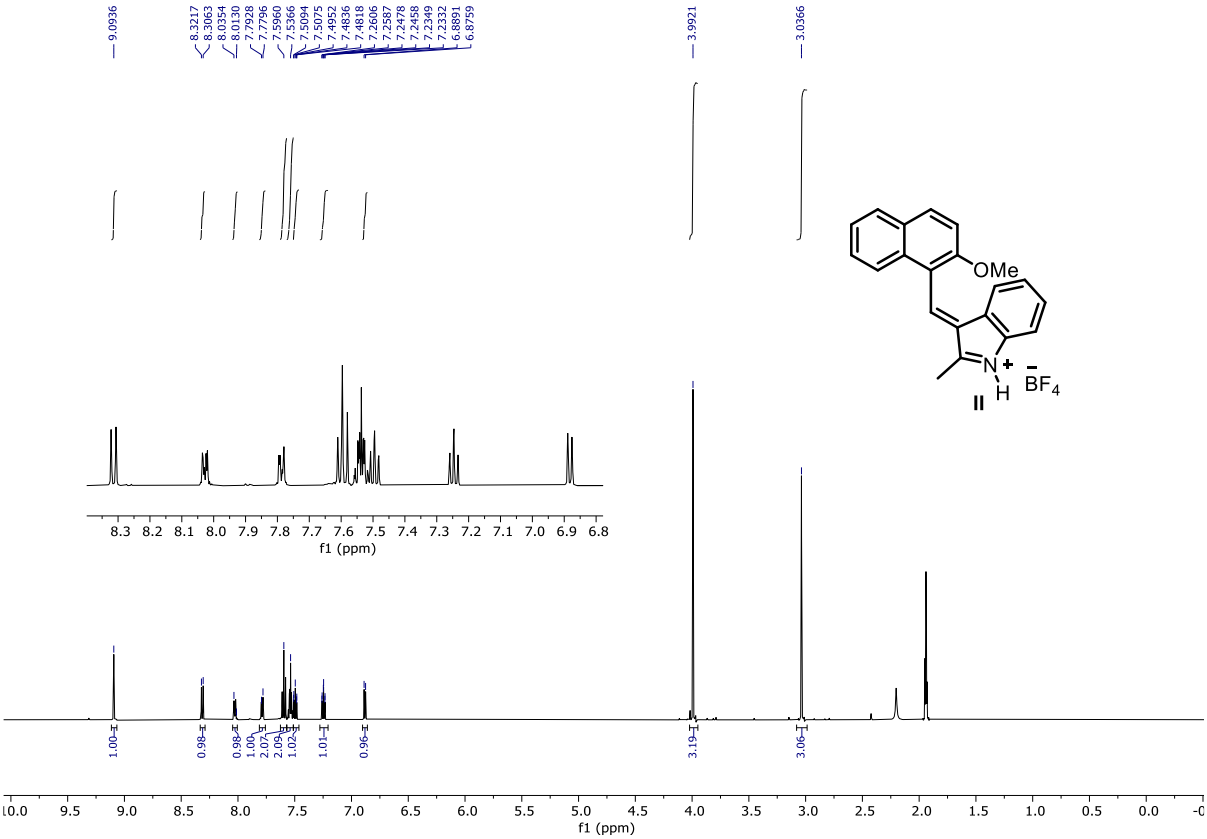

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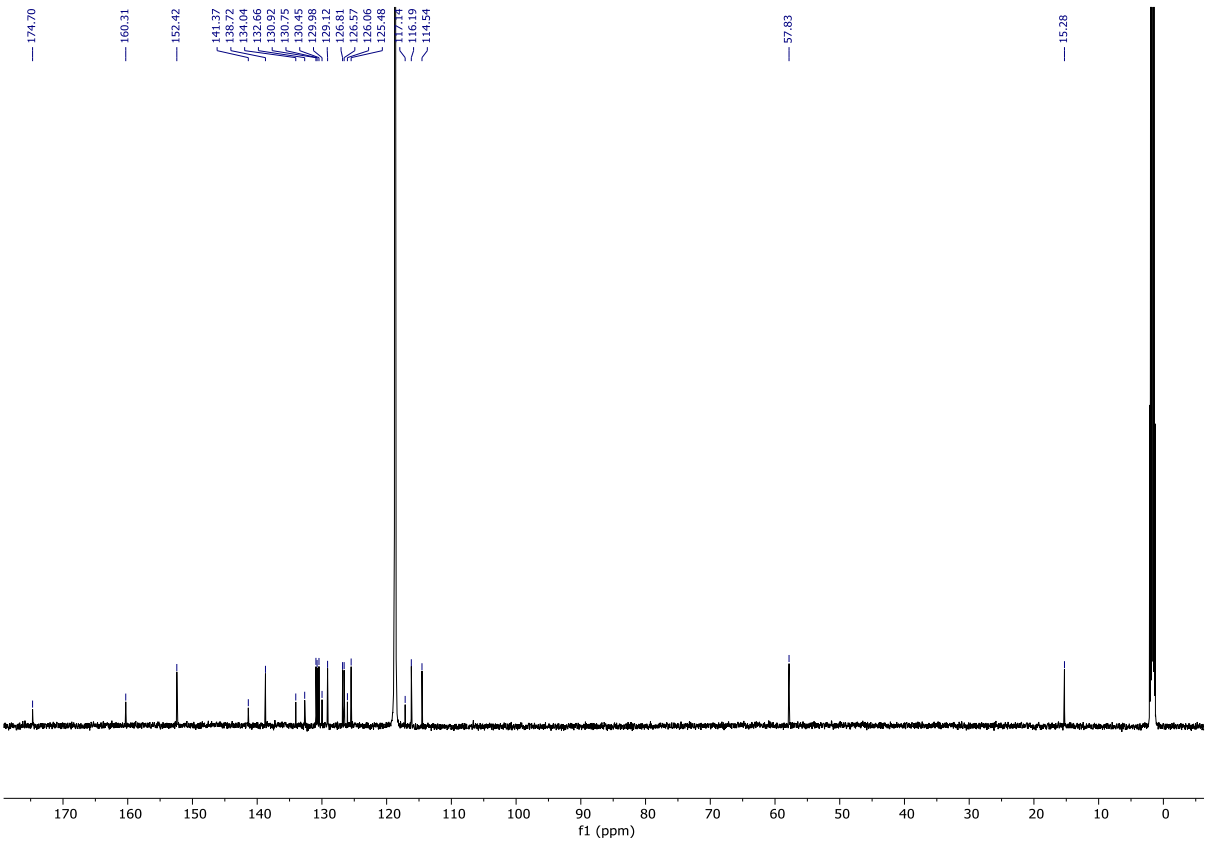

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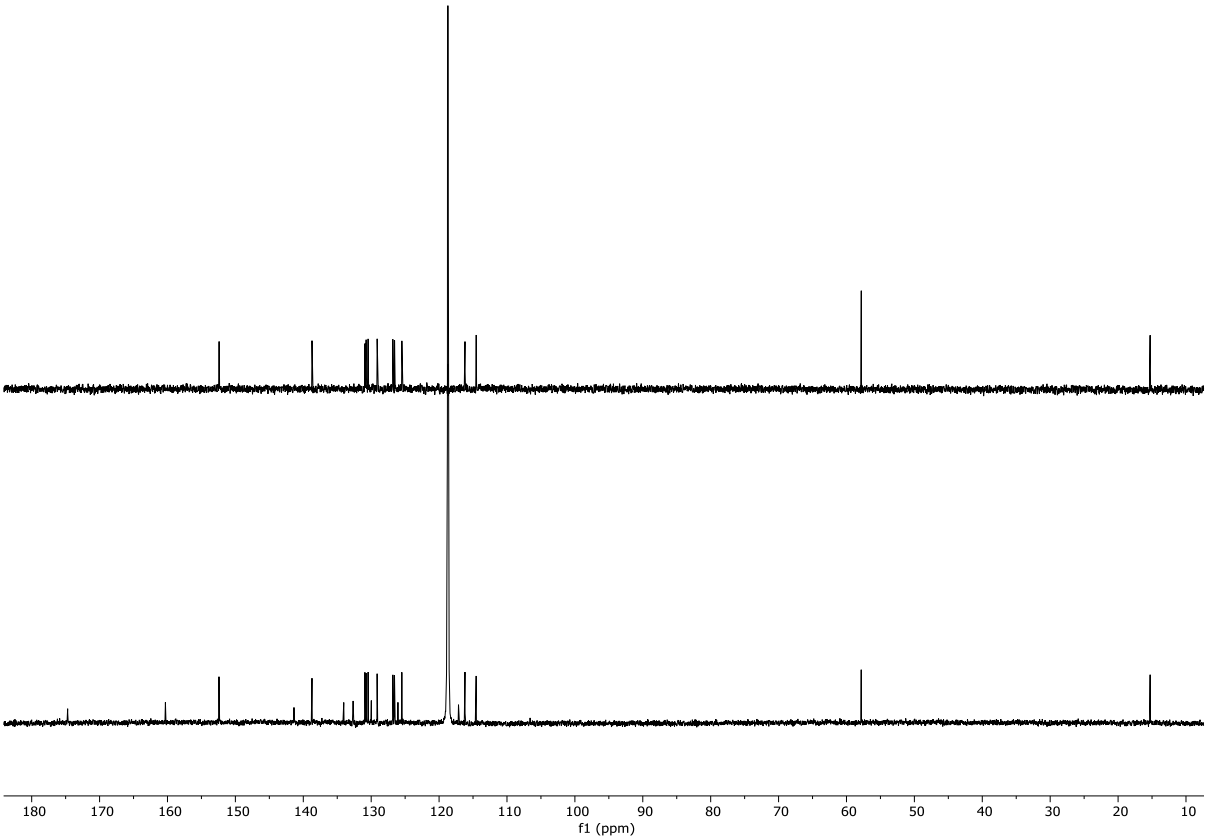
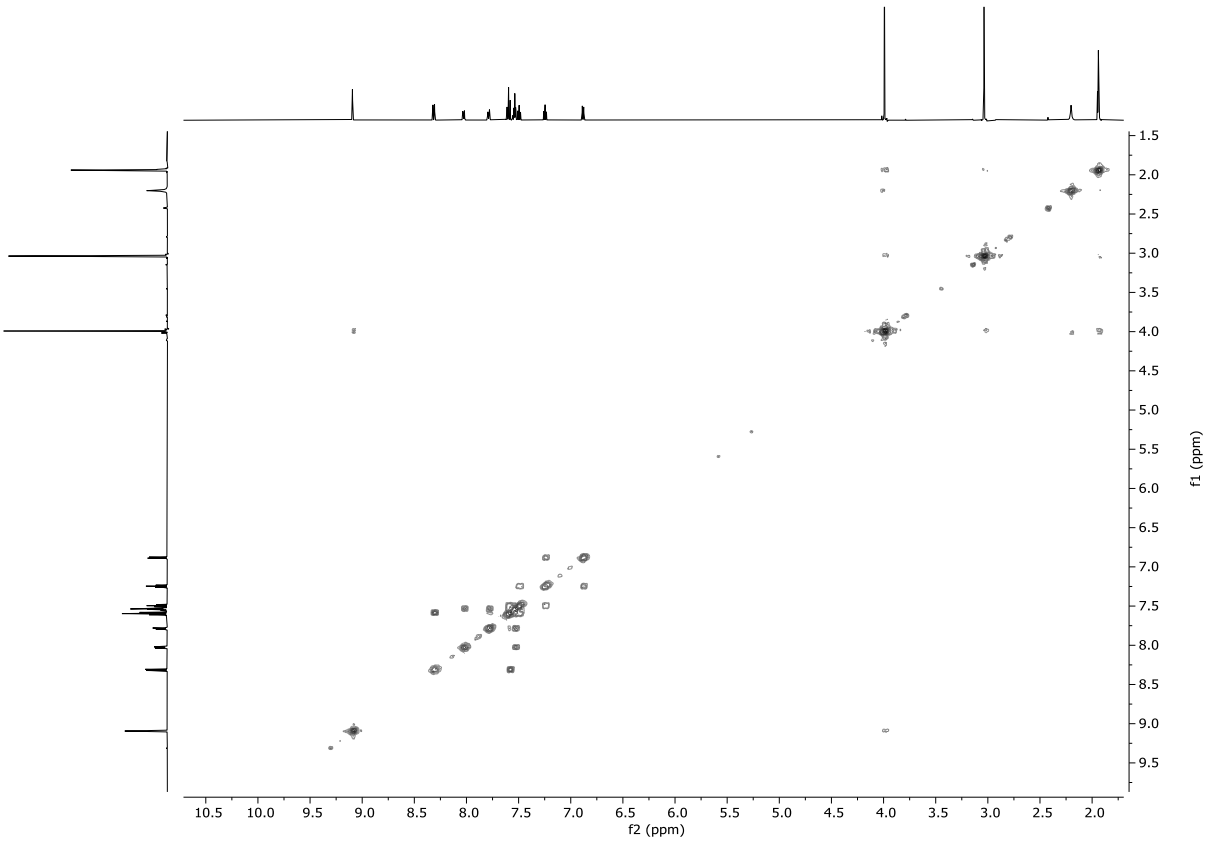


COSY-NMR of compound II (600 MHz, CD_3CN)



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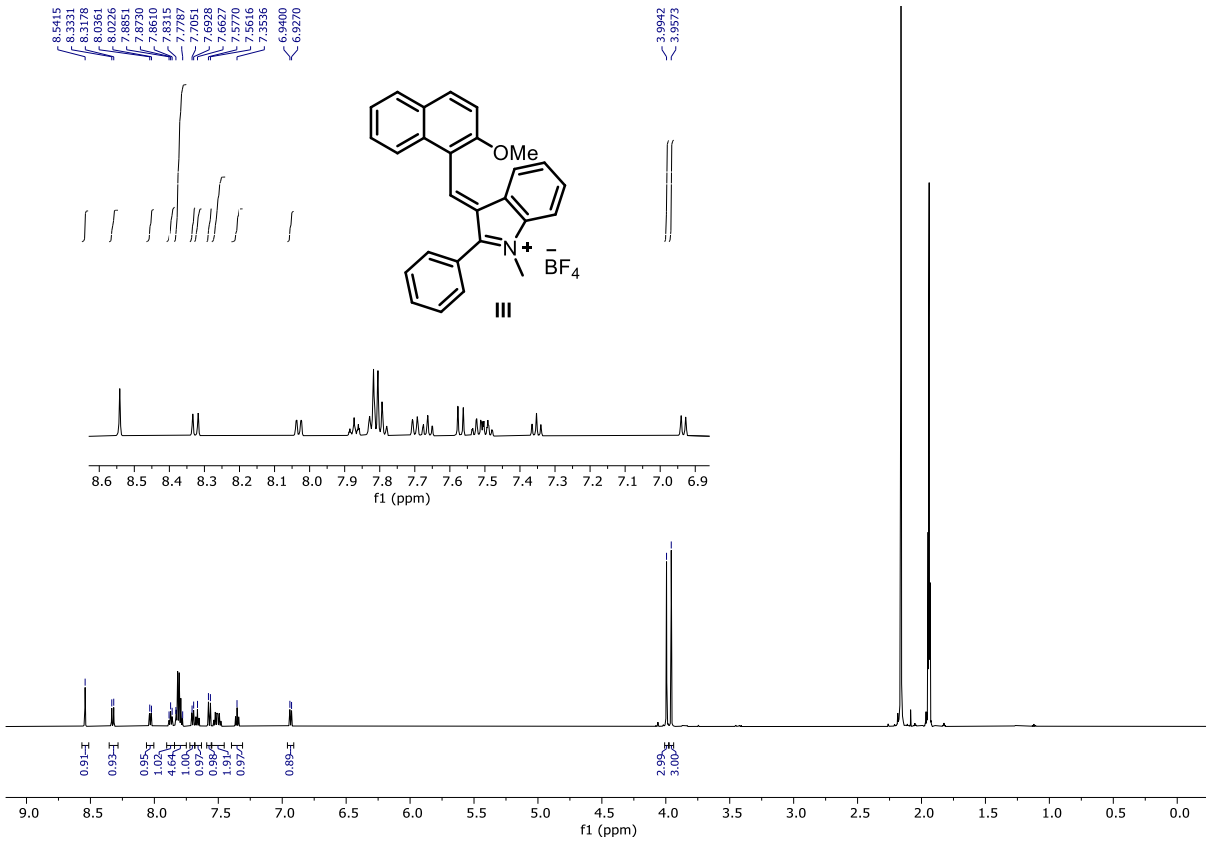

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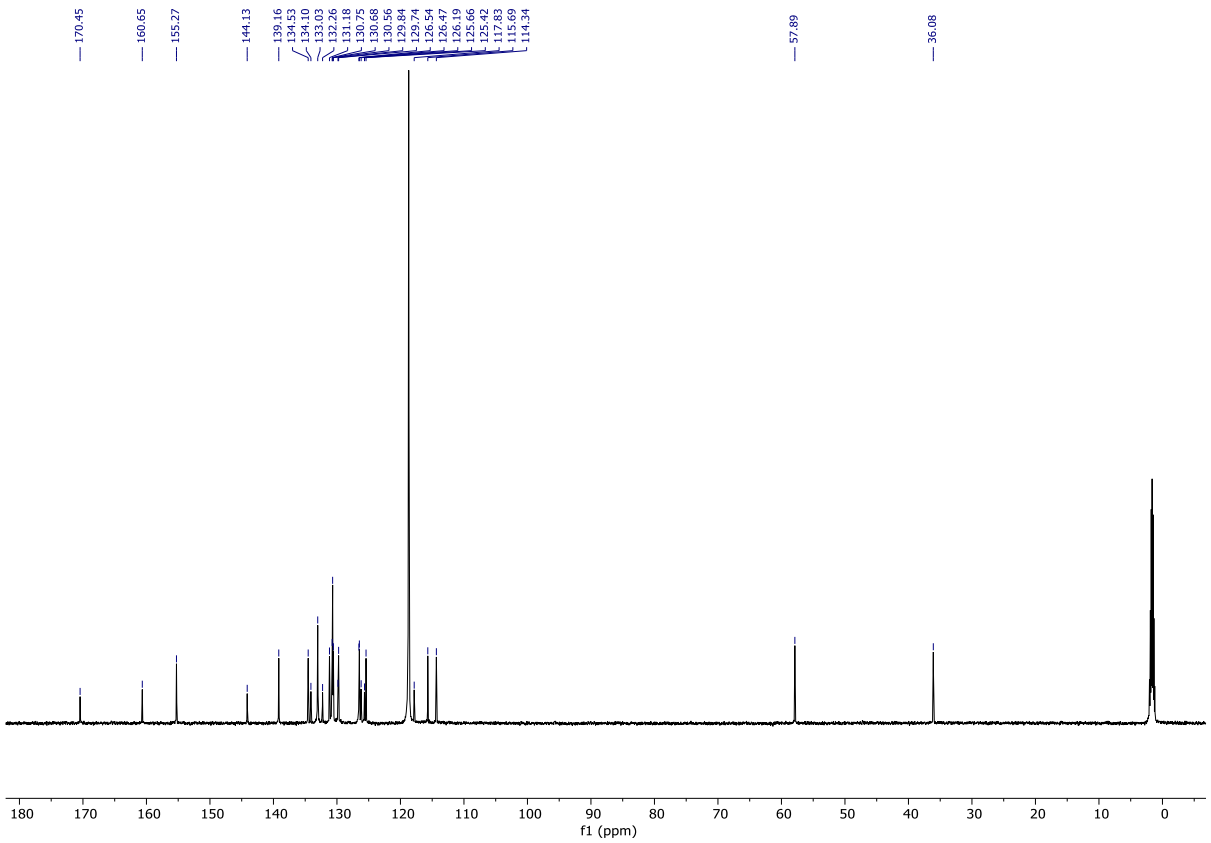

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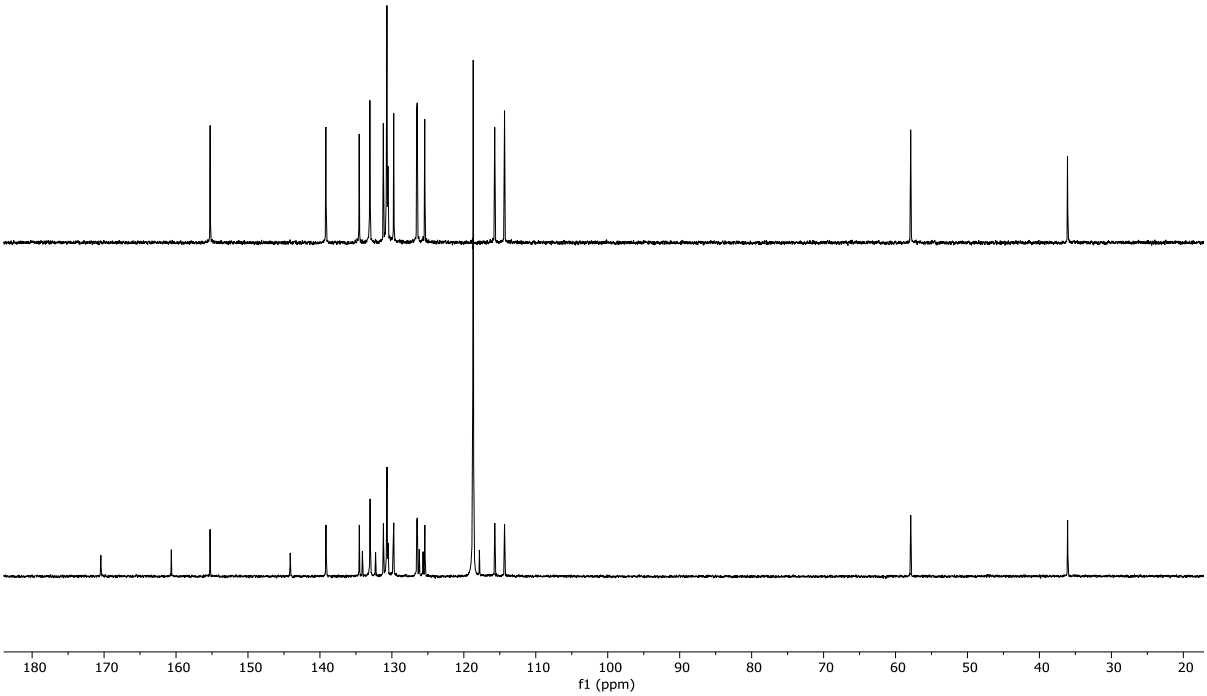
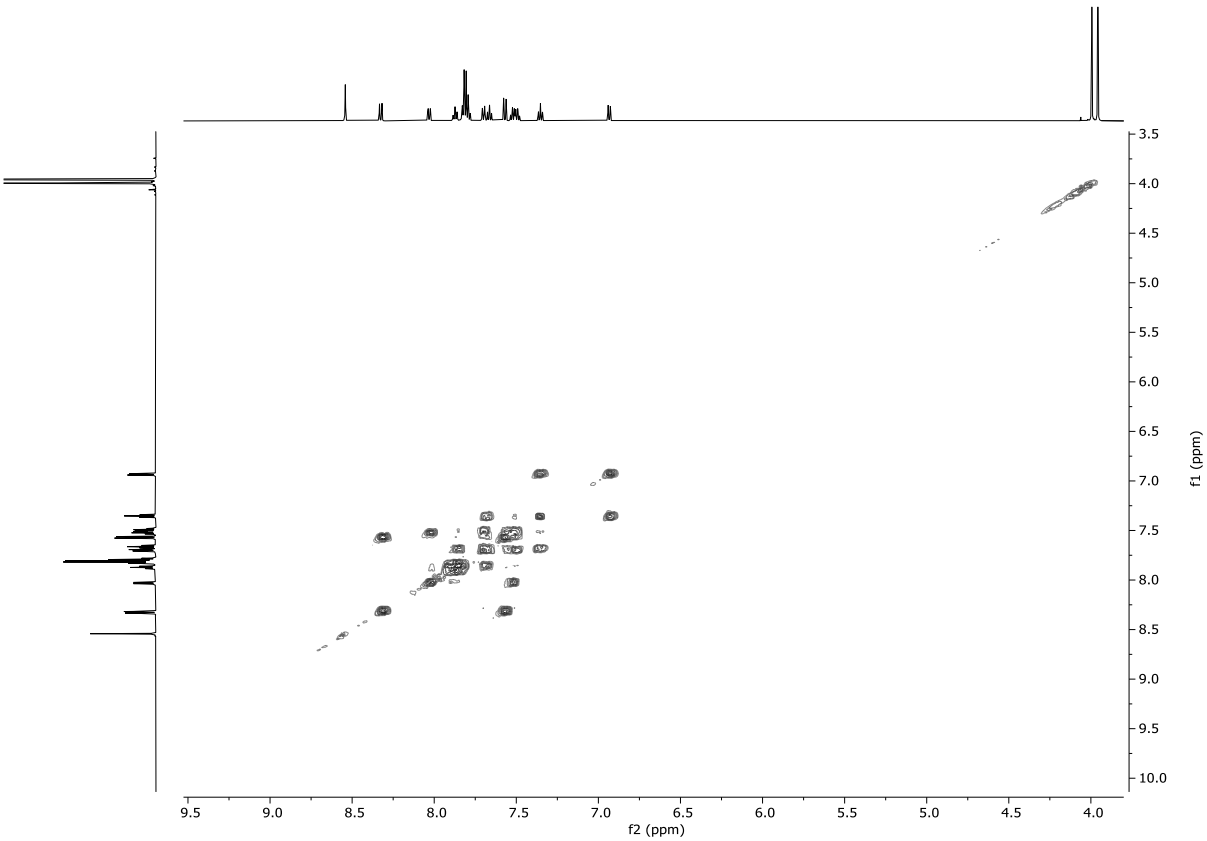
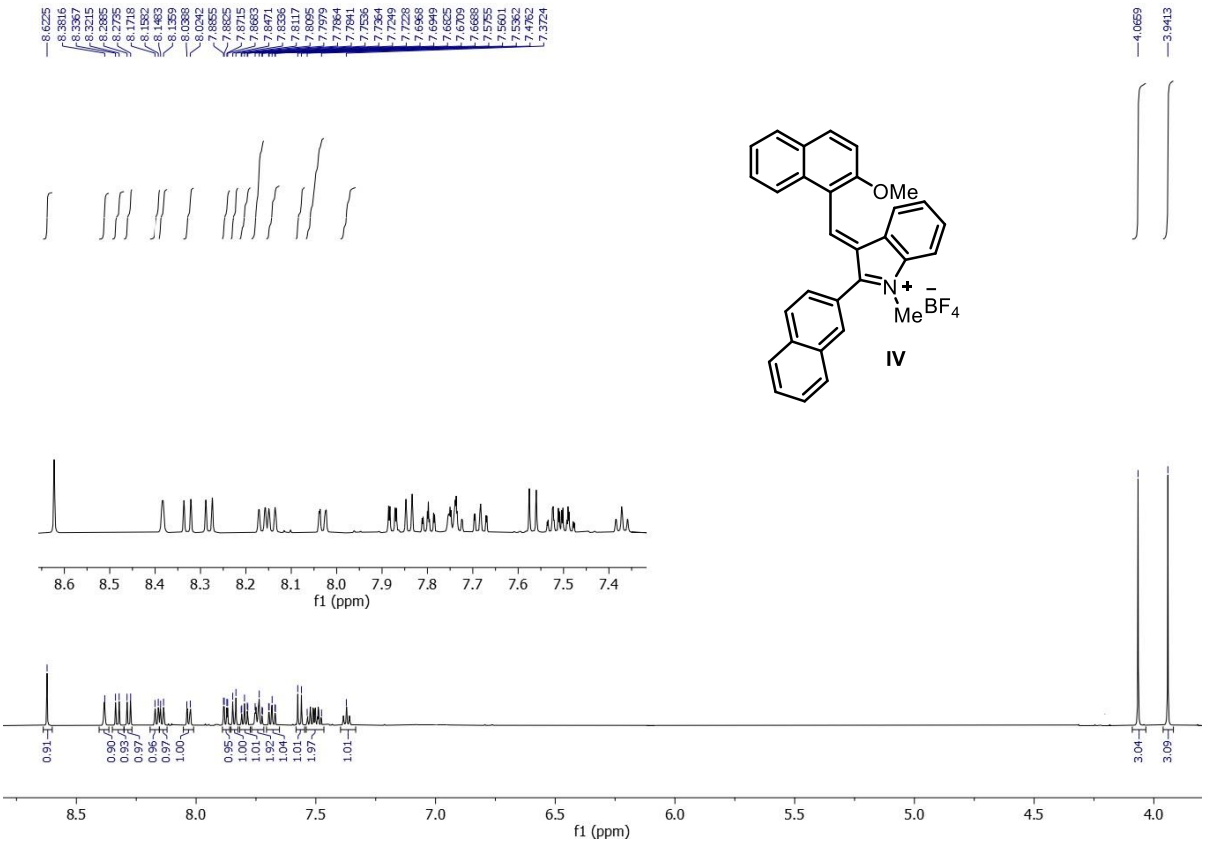


COSY-NMR of compound III (600 MHz, CD_3CN)



^{1}H-NMR of compound IV (600 MHz, CD_3CN)



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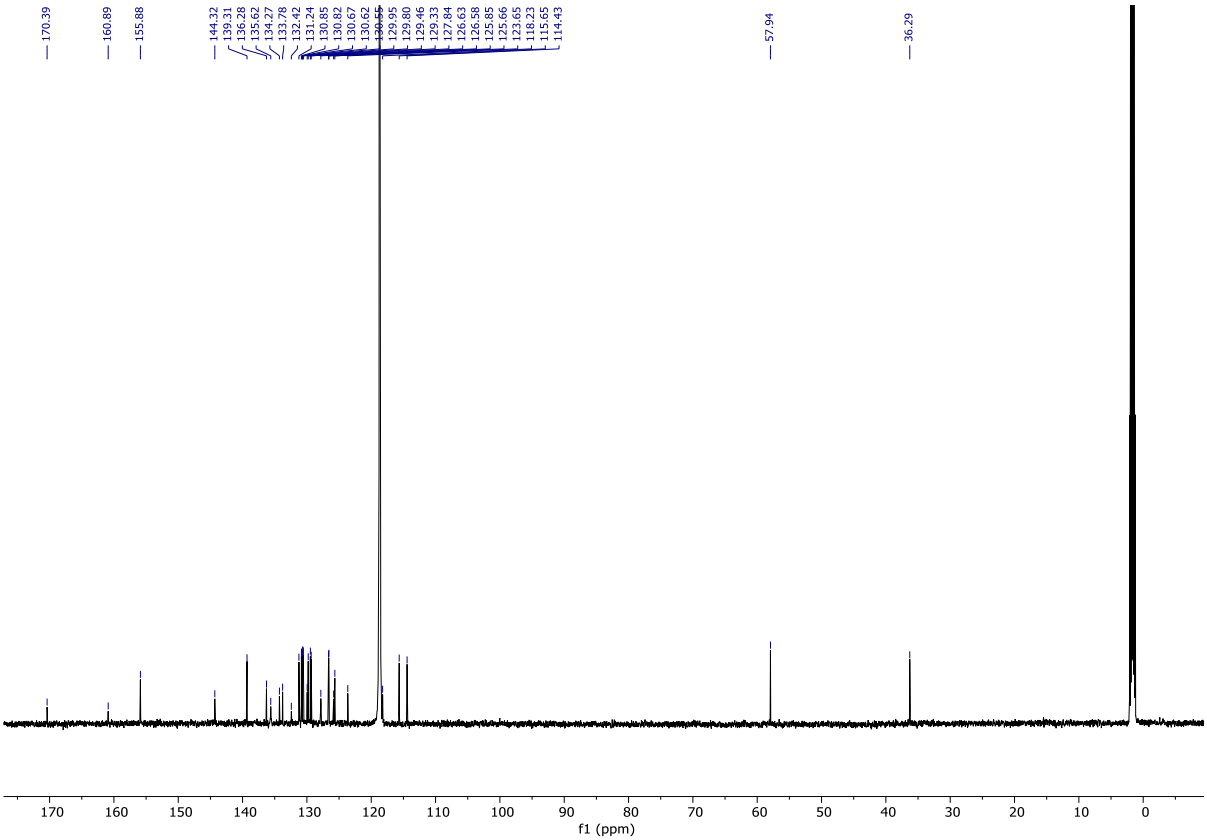

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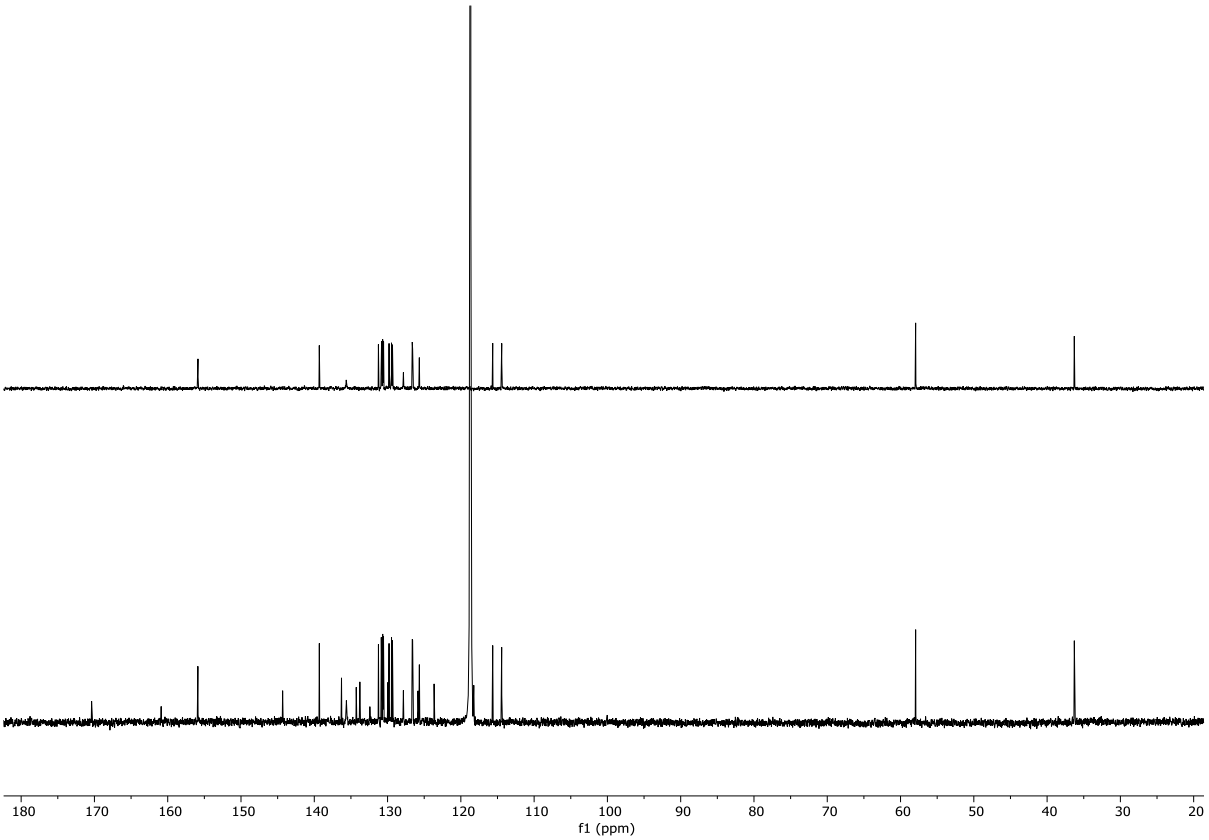

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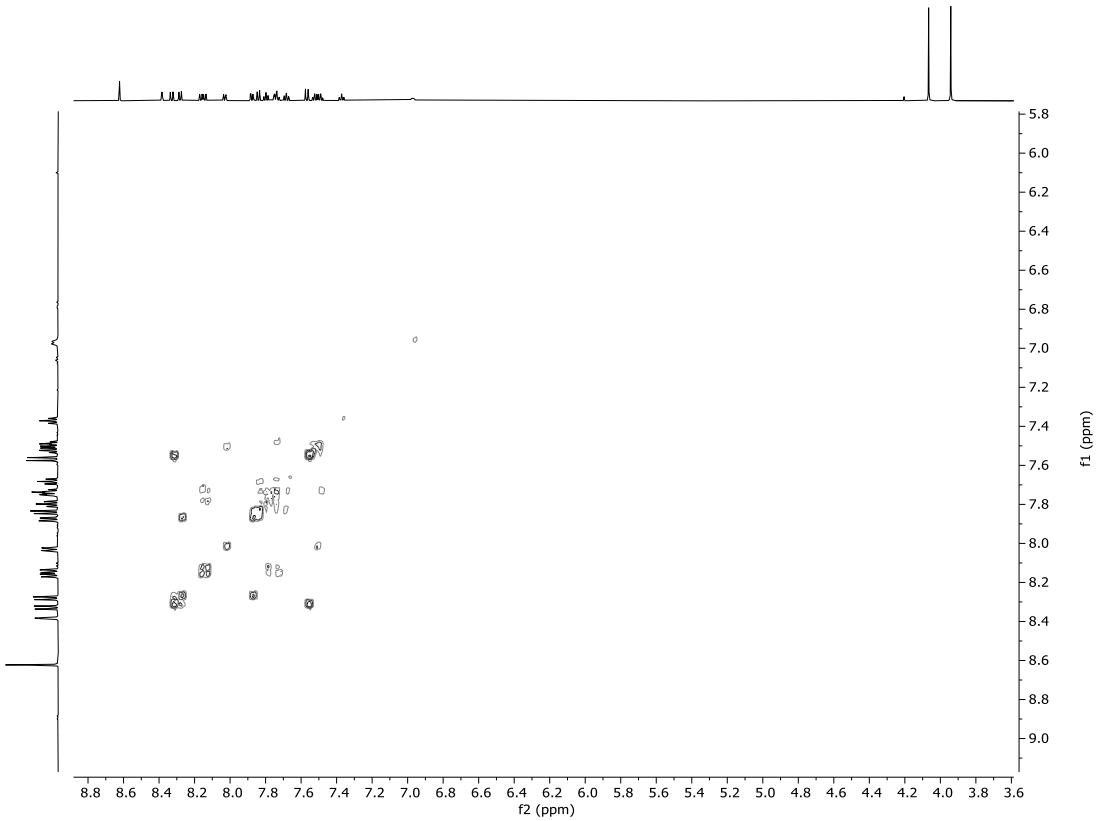
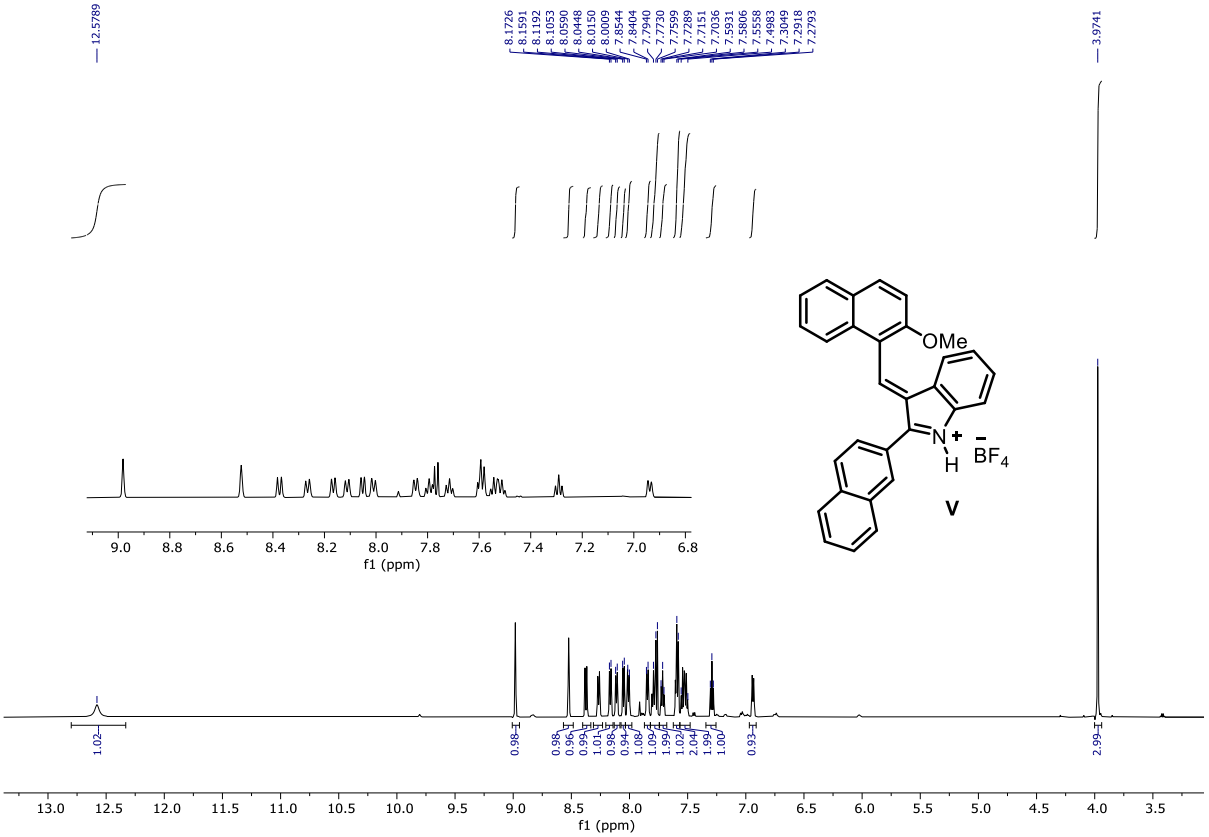


^{1}H-NMR of compound V (600 MHz, CD_3CN)



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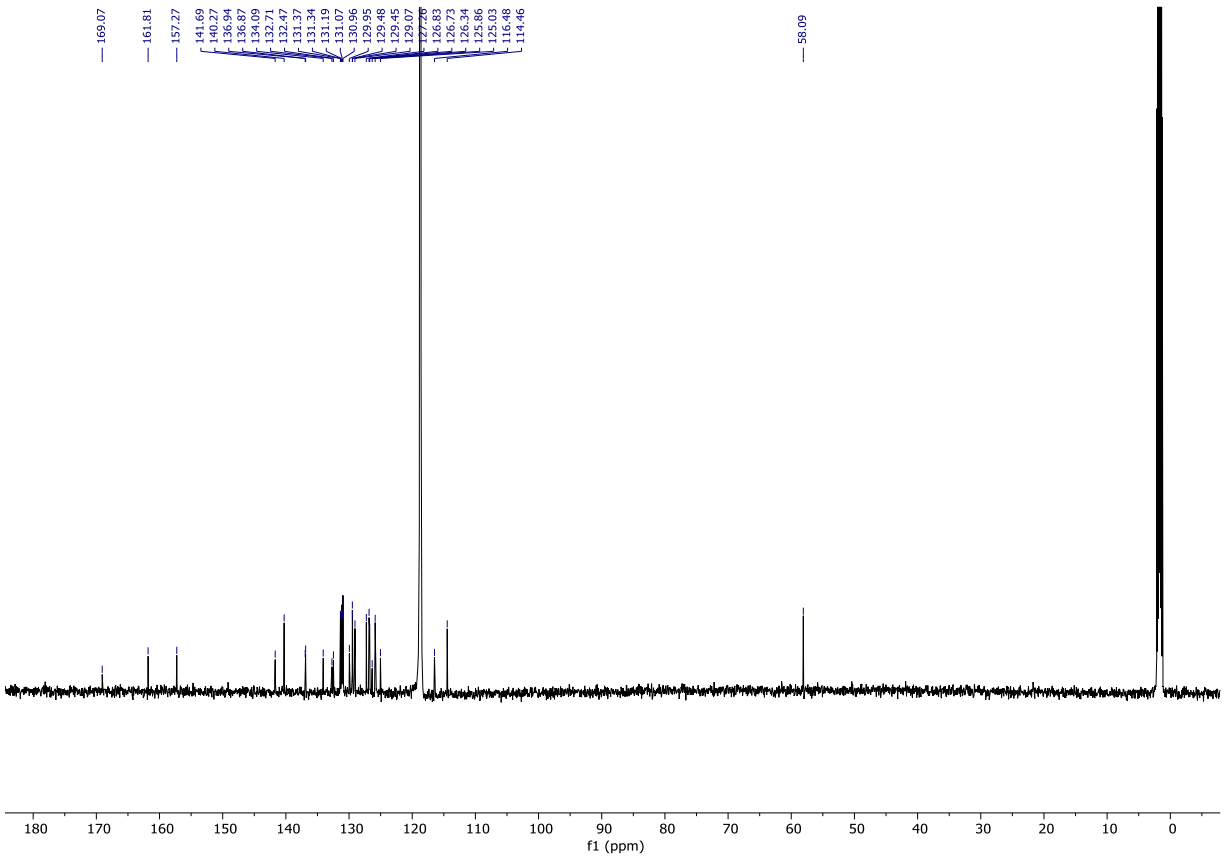

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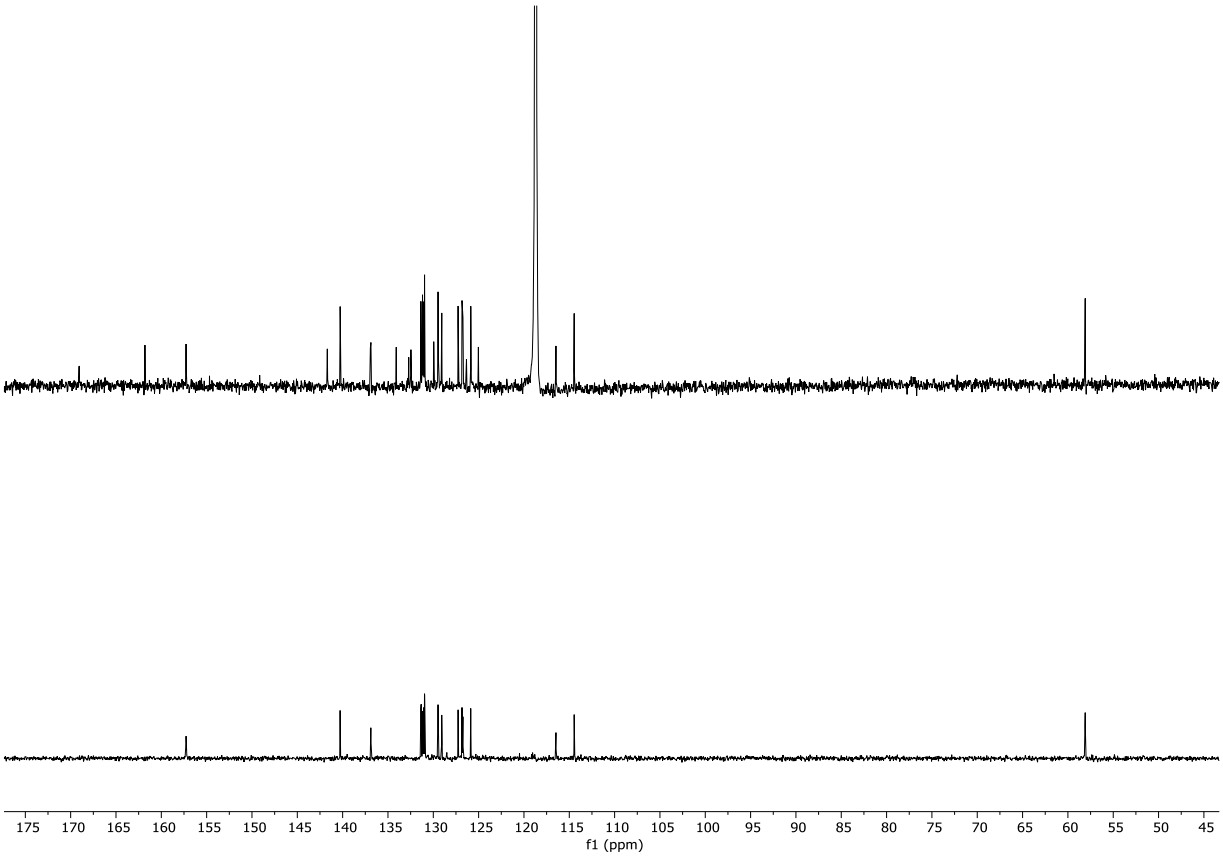

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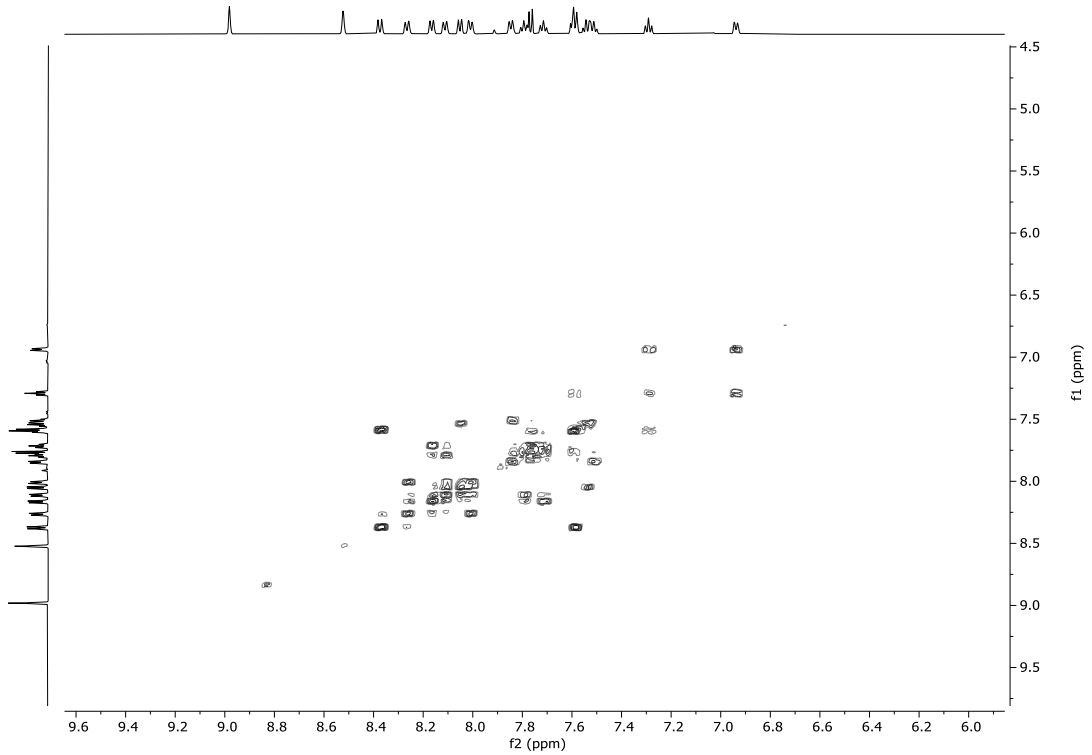
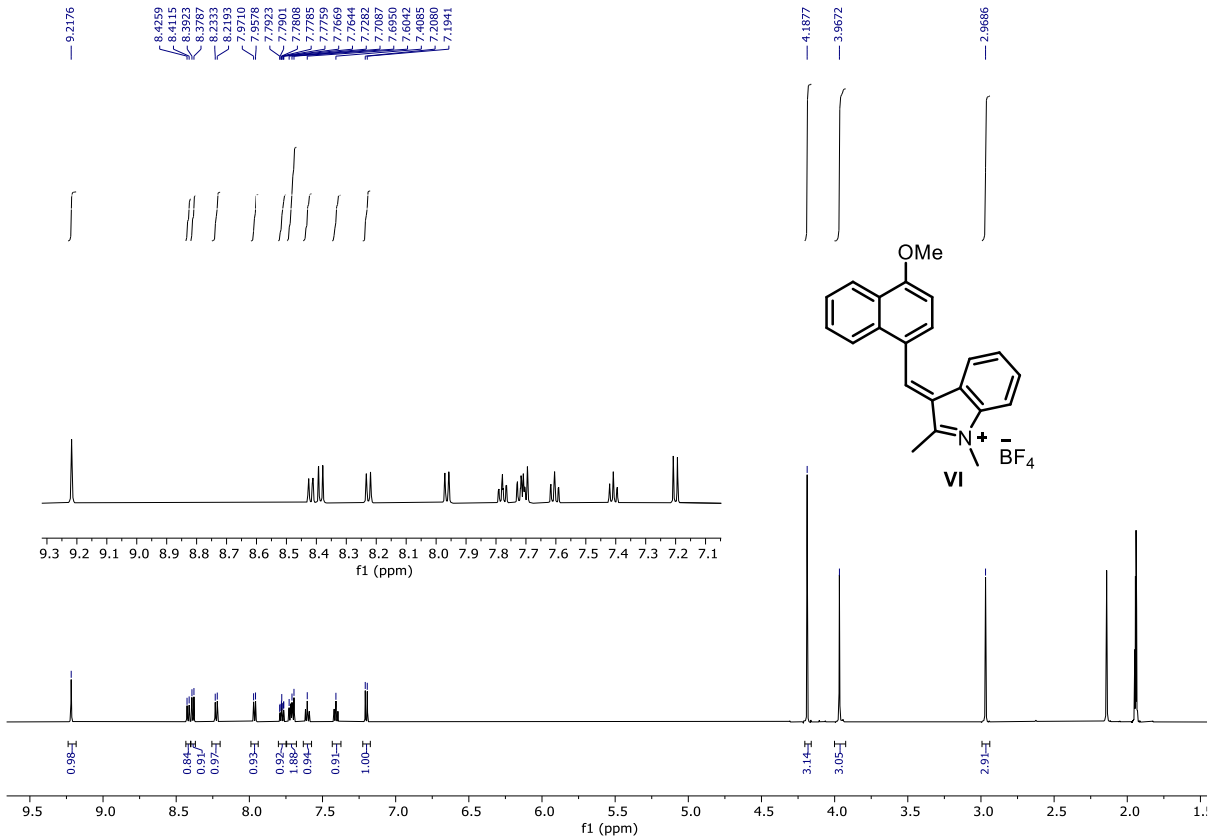


^{1}H-NMR of compound VI (600 MHz, CD_3CN)



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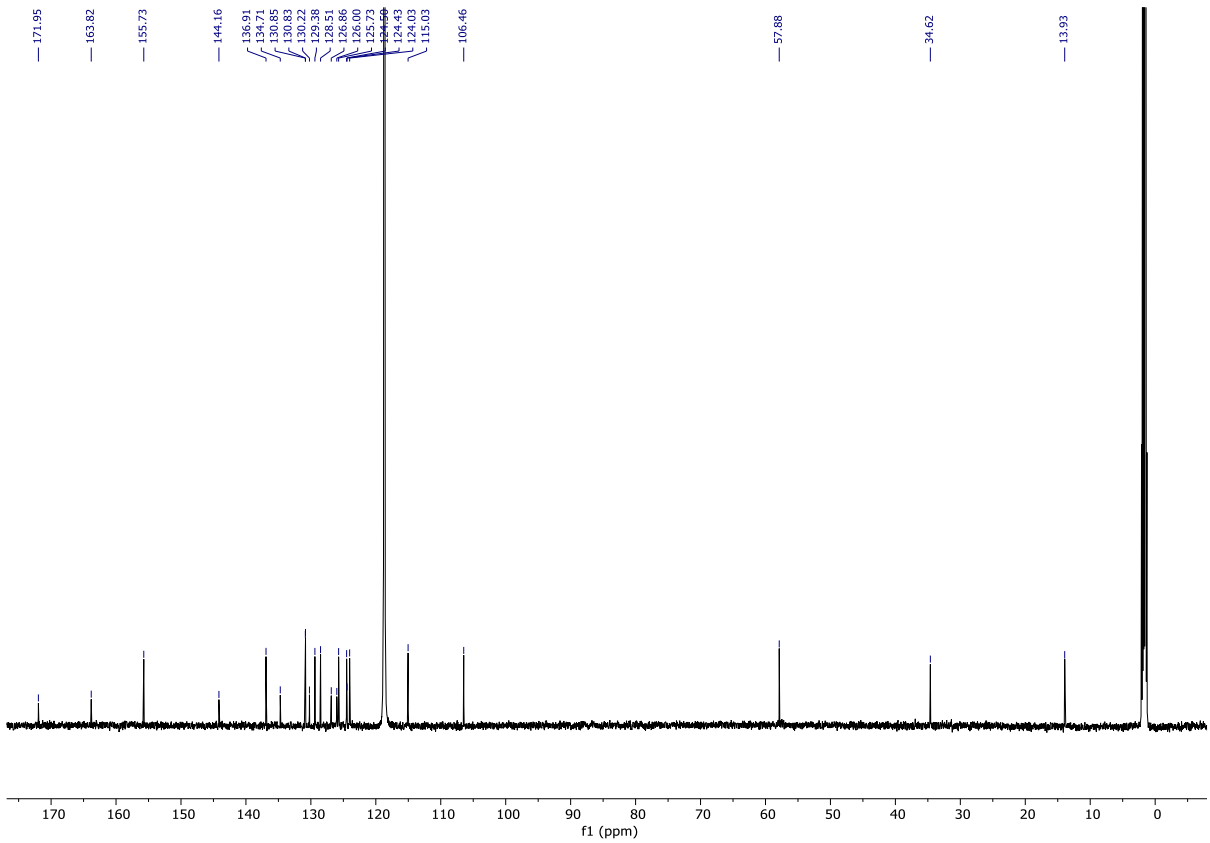

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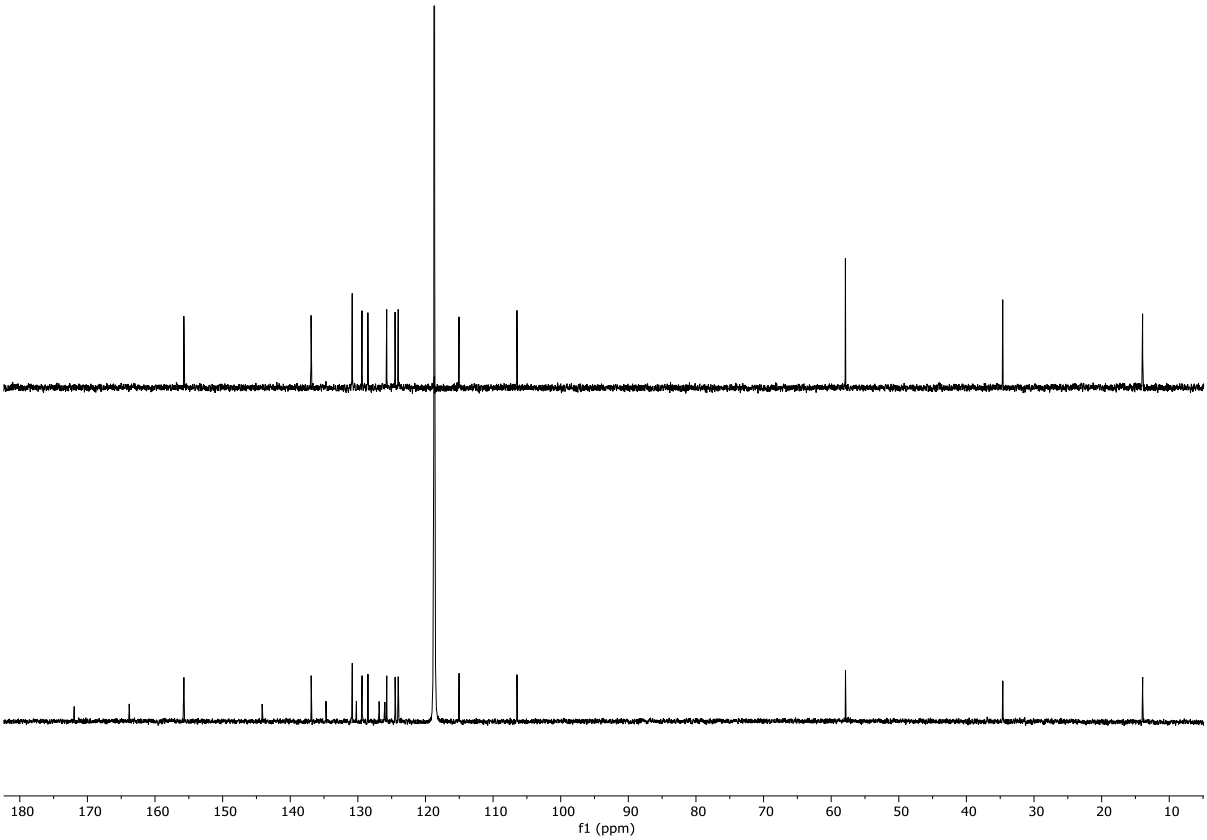

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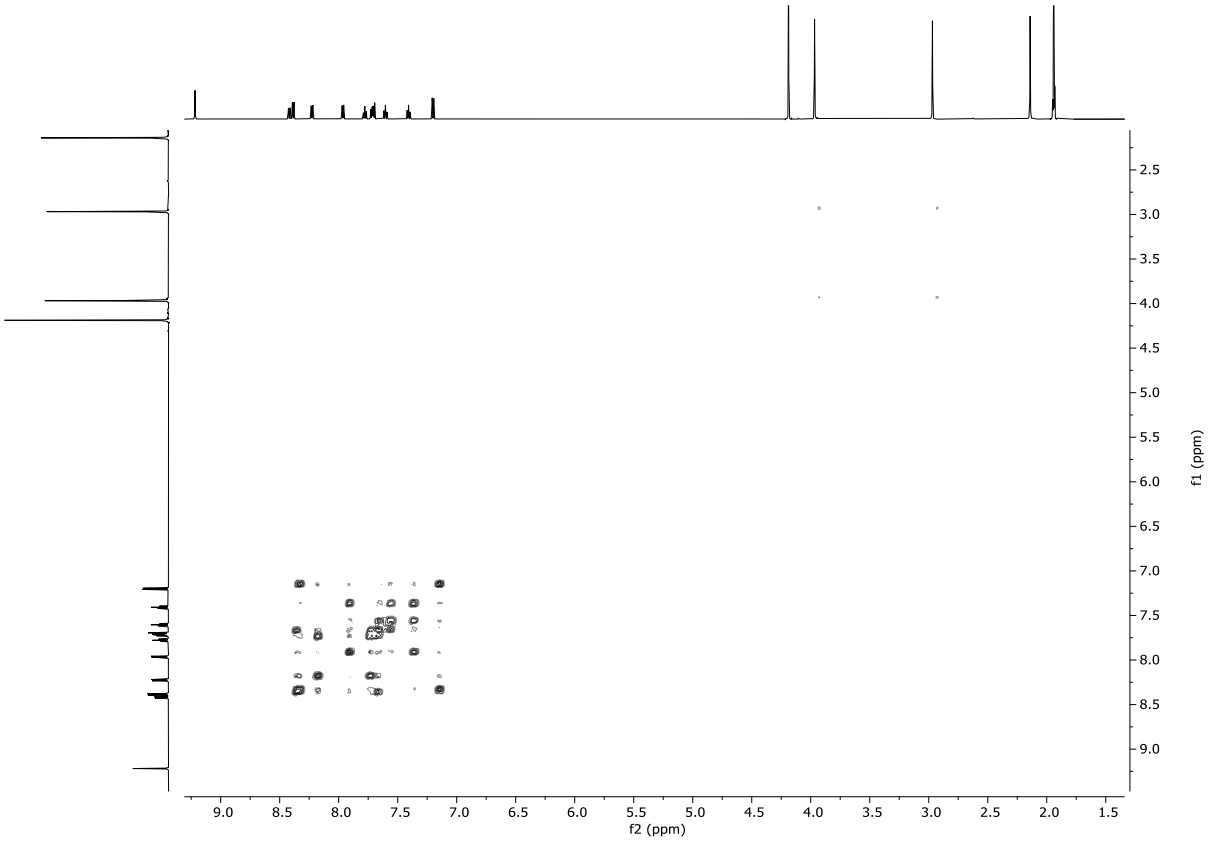

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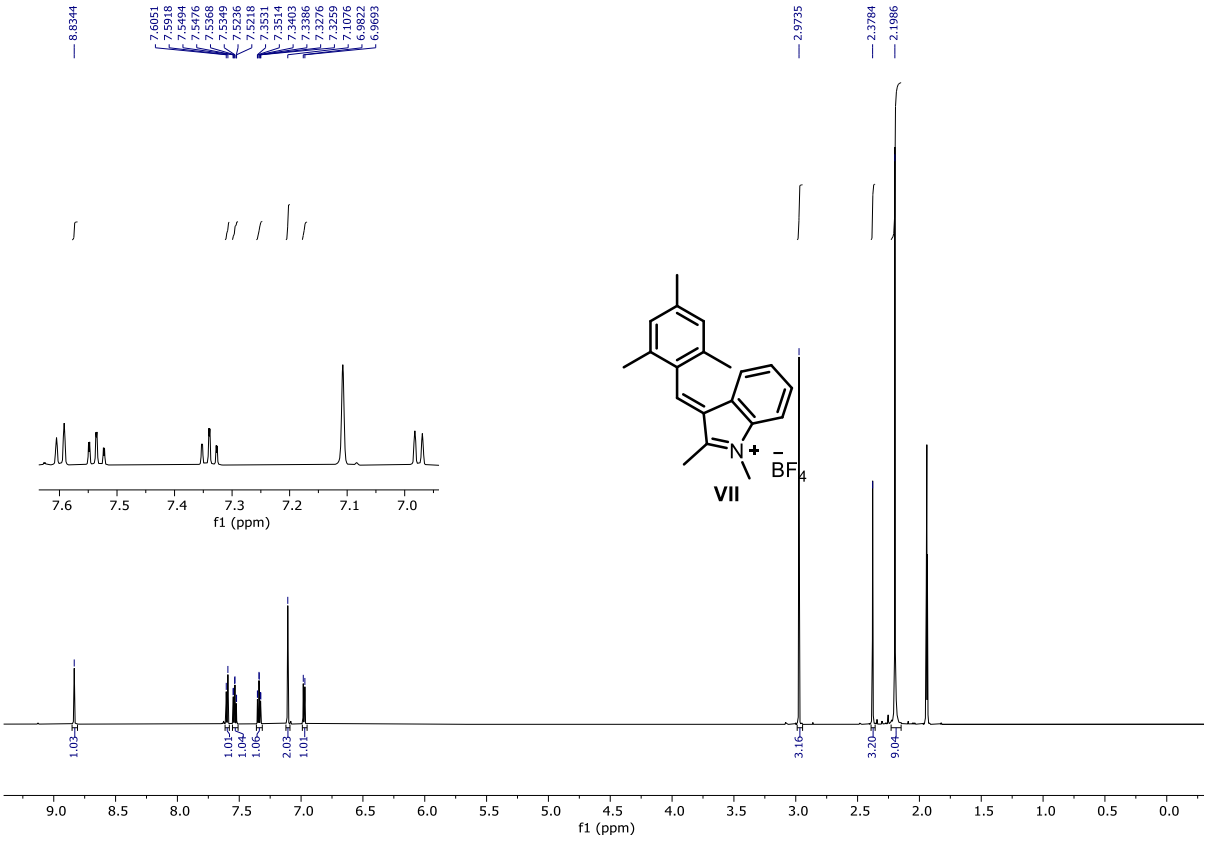

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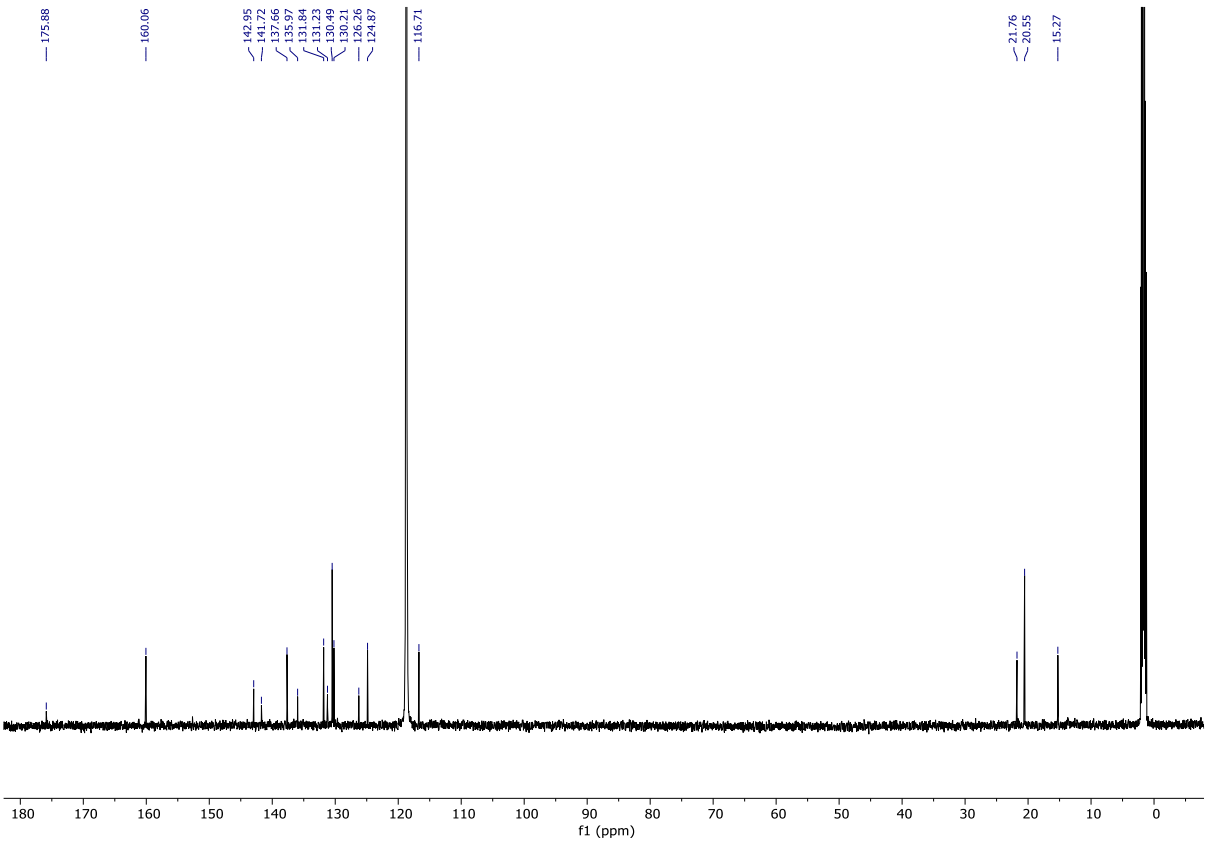
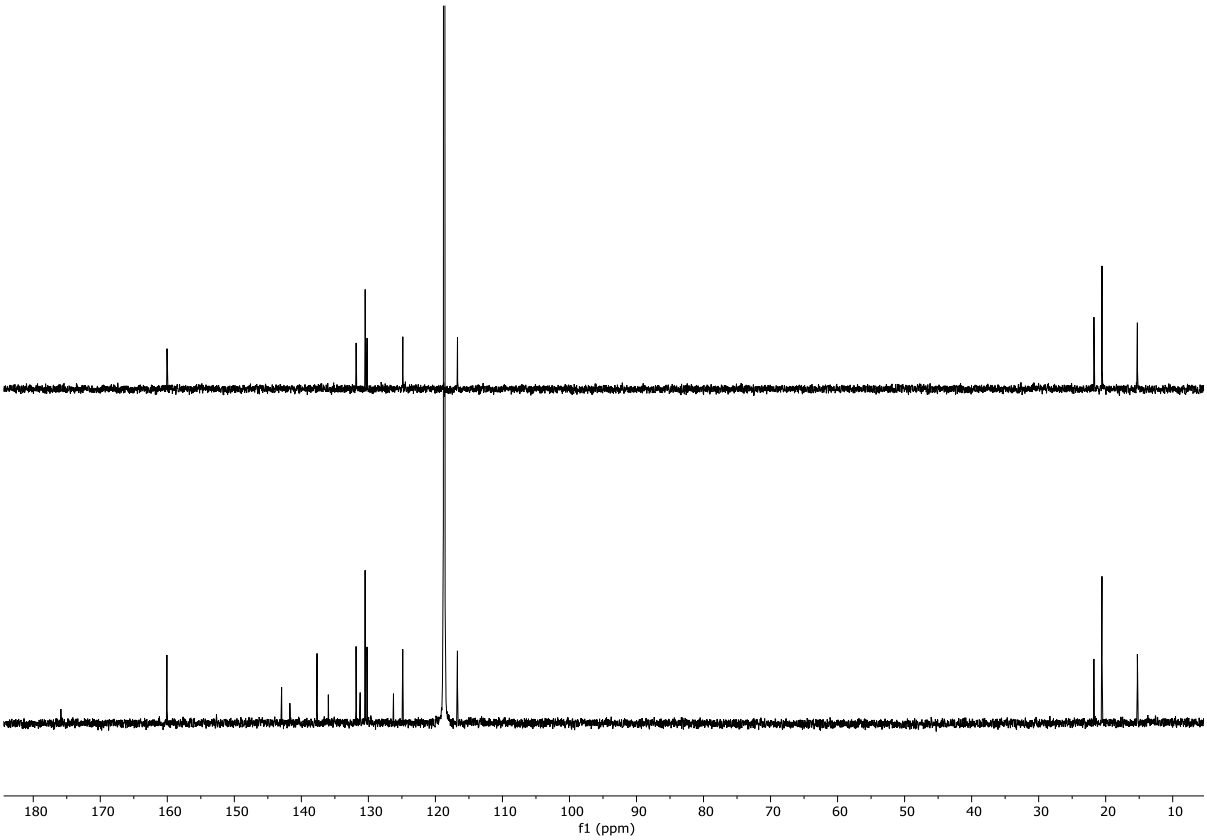
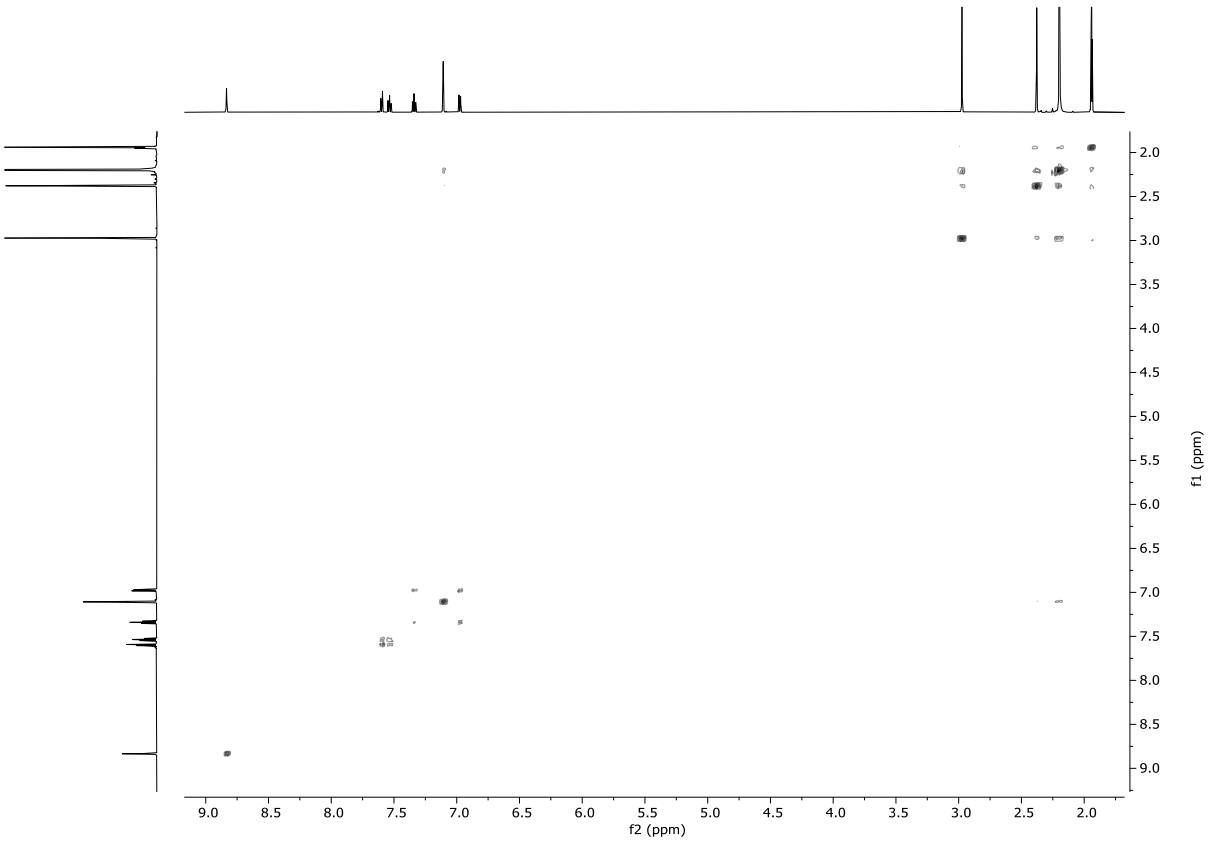


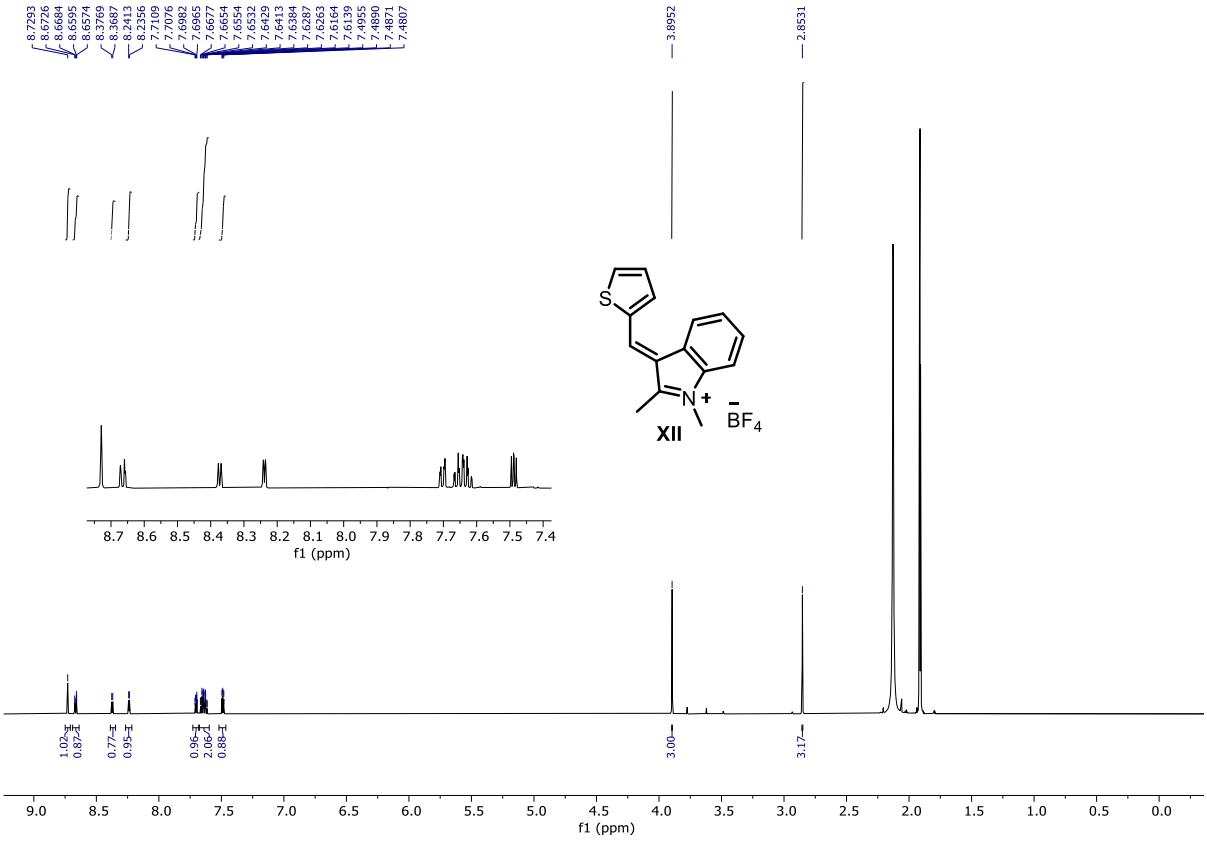
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound VII (150 MHz, CD_3CN)



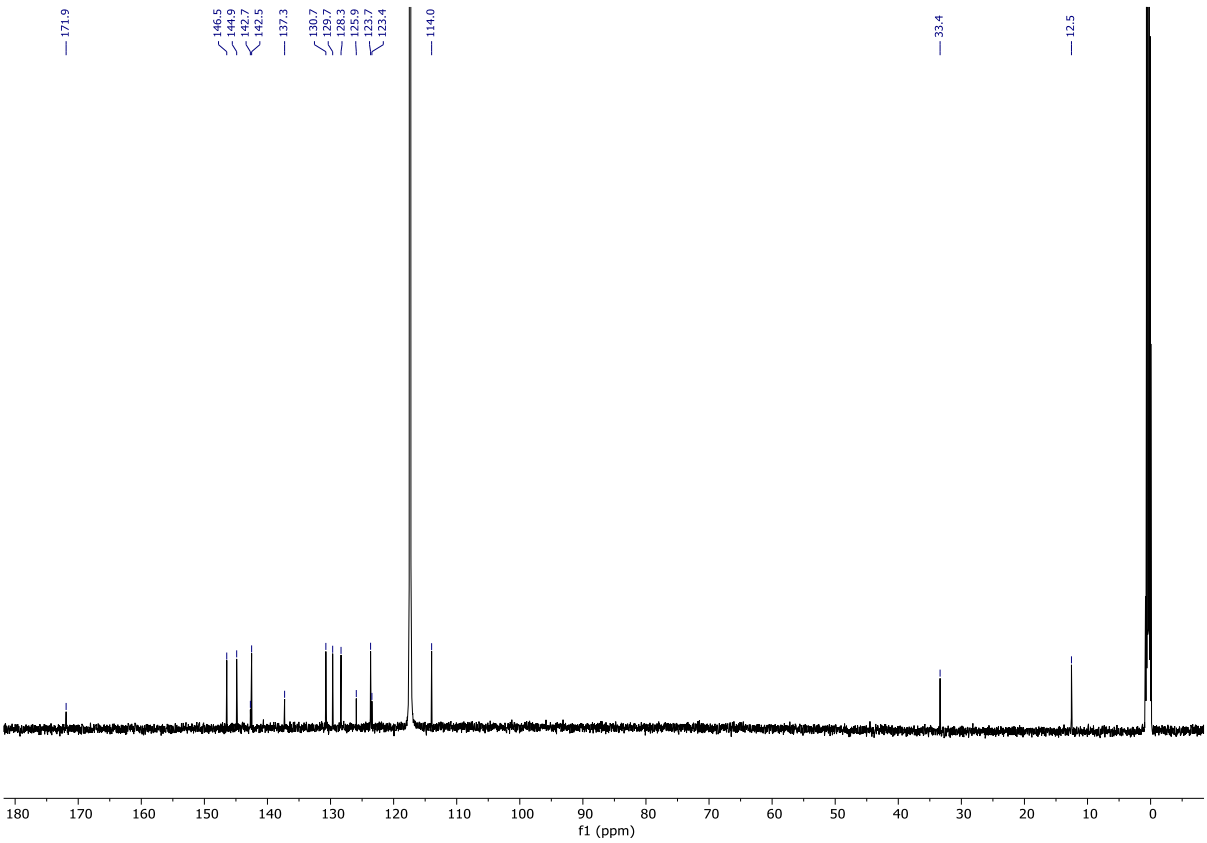
COSY-NMR of compound VII (600 MHz, CD_3CN)



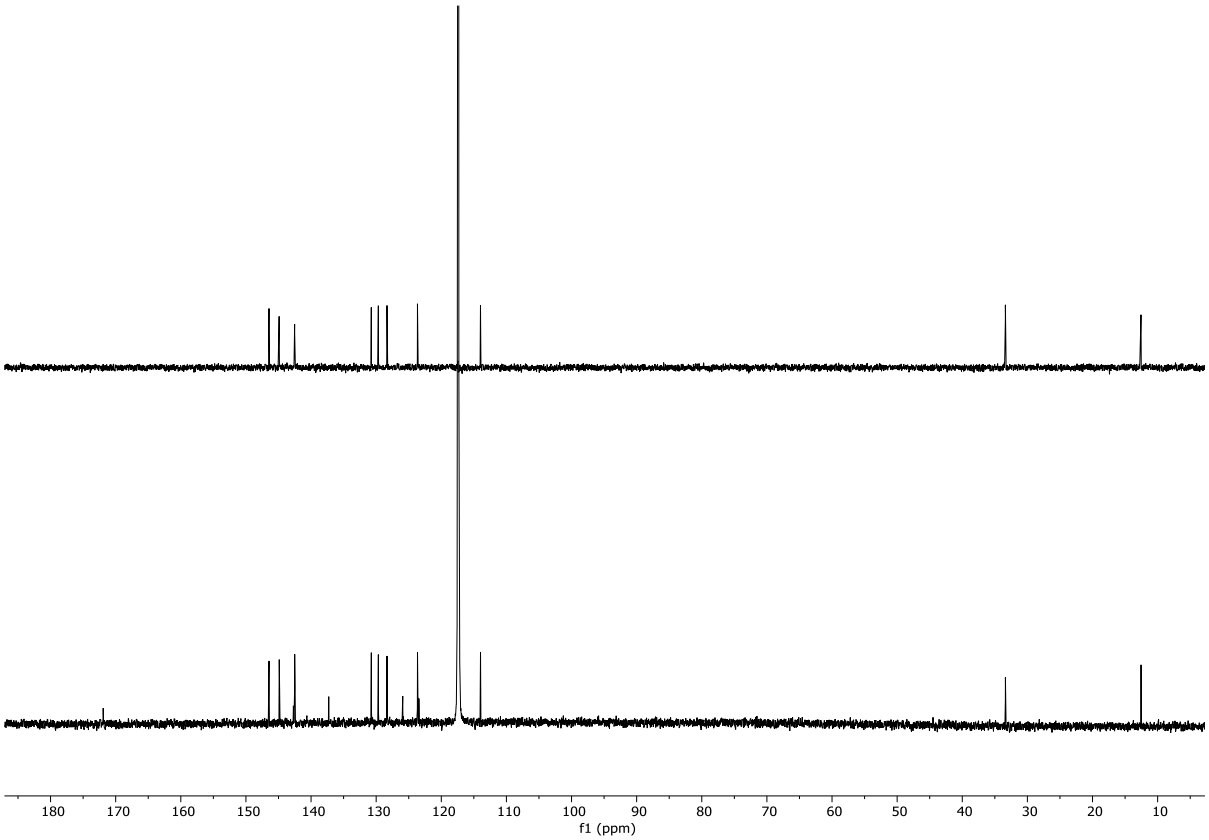
^{1}H-NMR of compound XII (600 MHz, CD_3CN)



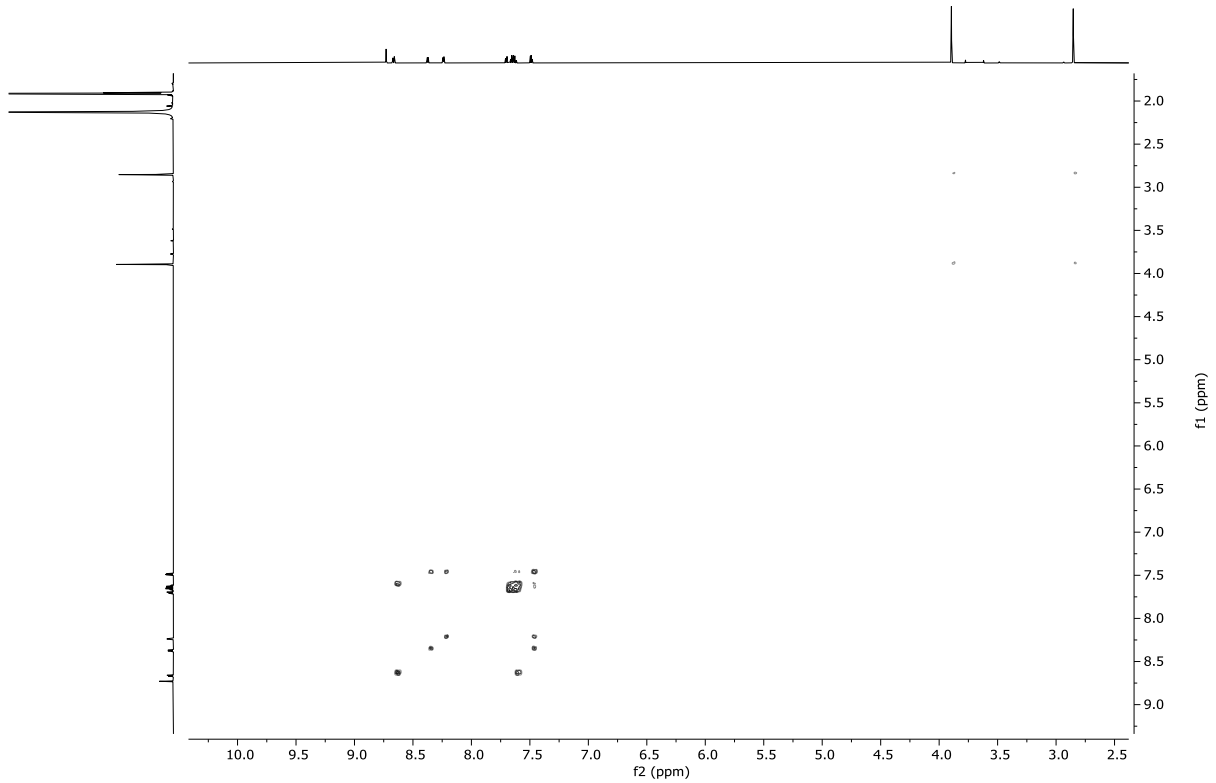
^{13}C{^{1}H}-NMR of compound XII (150 MHz, CD_3CN)



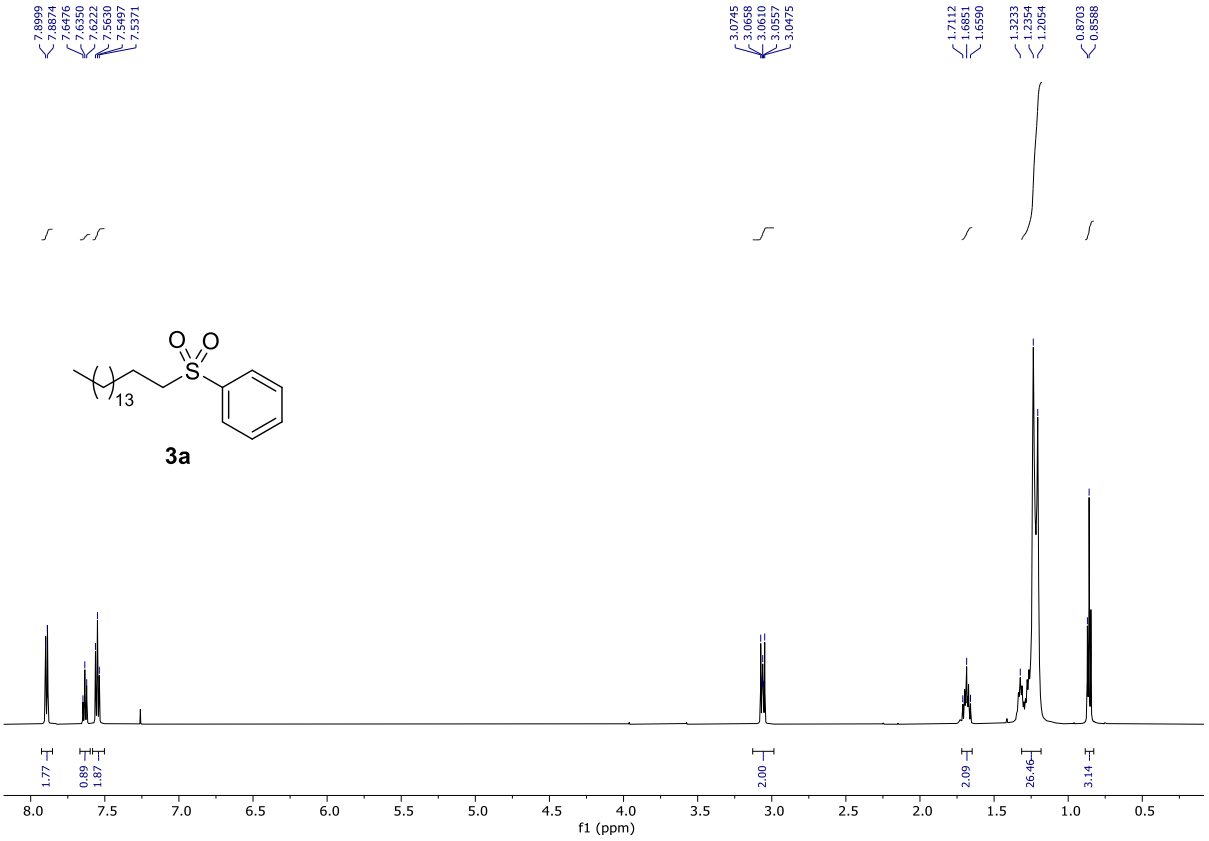
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound XII (150 MHz, CD_3CN)



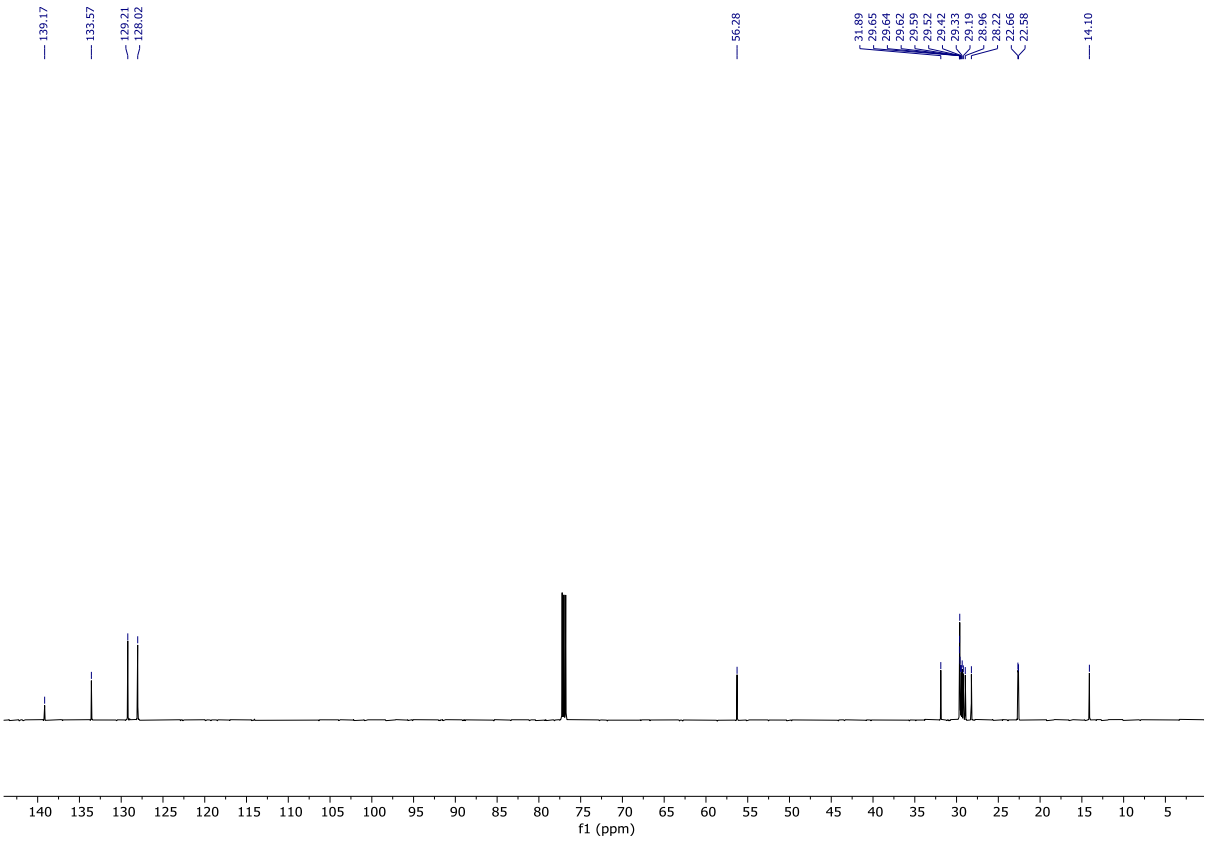
COSY-NMR of compound XII (600 MHz, CD_3CN)



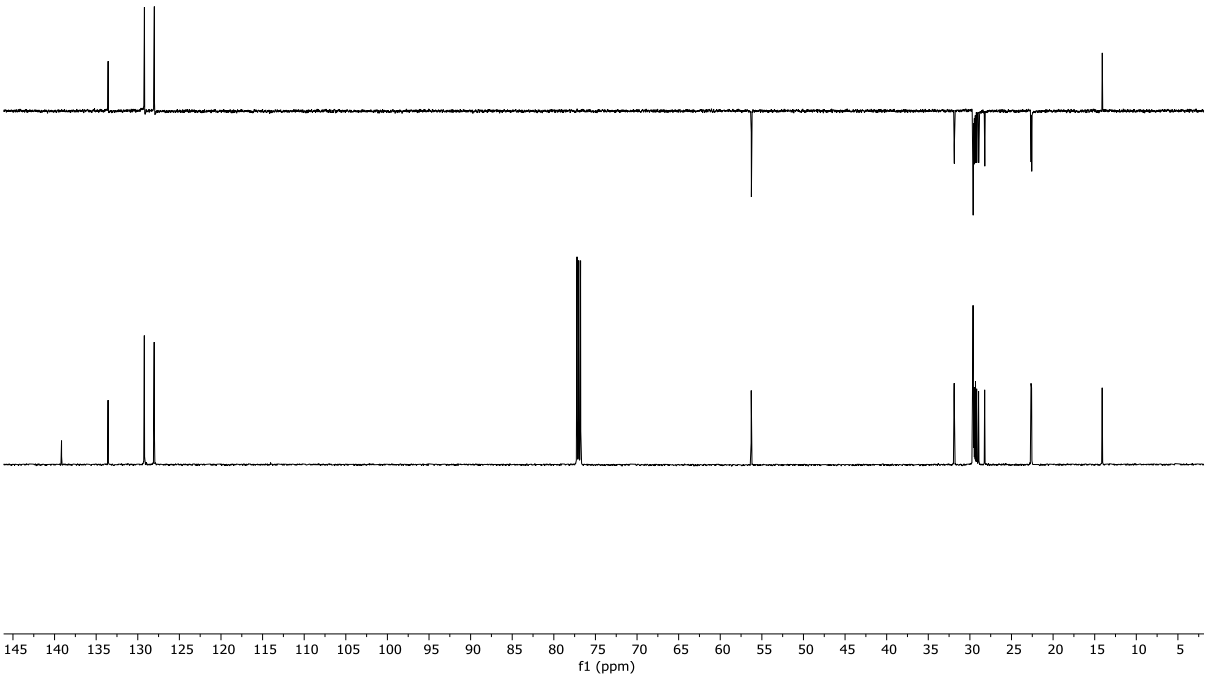
^{1}H-NMR of compound 3a (600 MHz, $CDCl_3$)



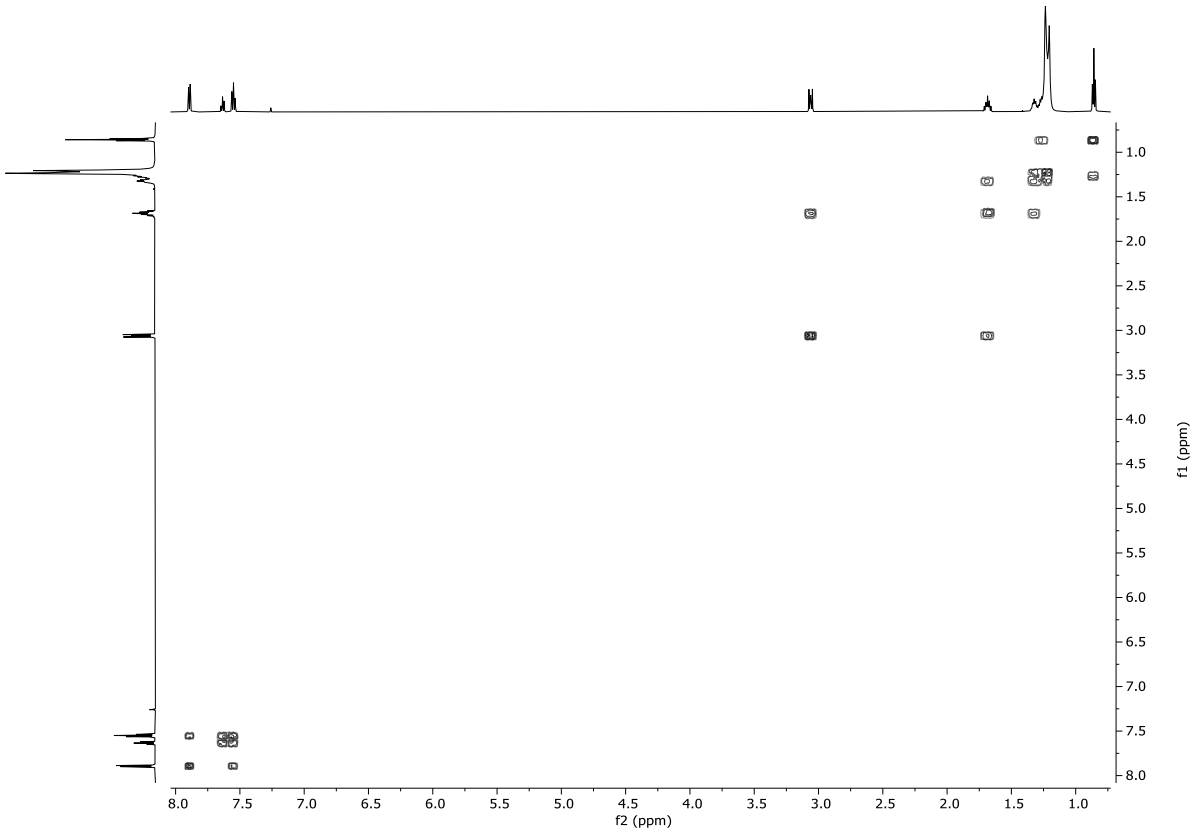
^{13}C{^{1}H}-NMR of compound 3a (150 MHz, $CDCl_3$)



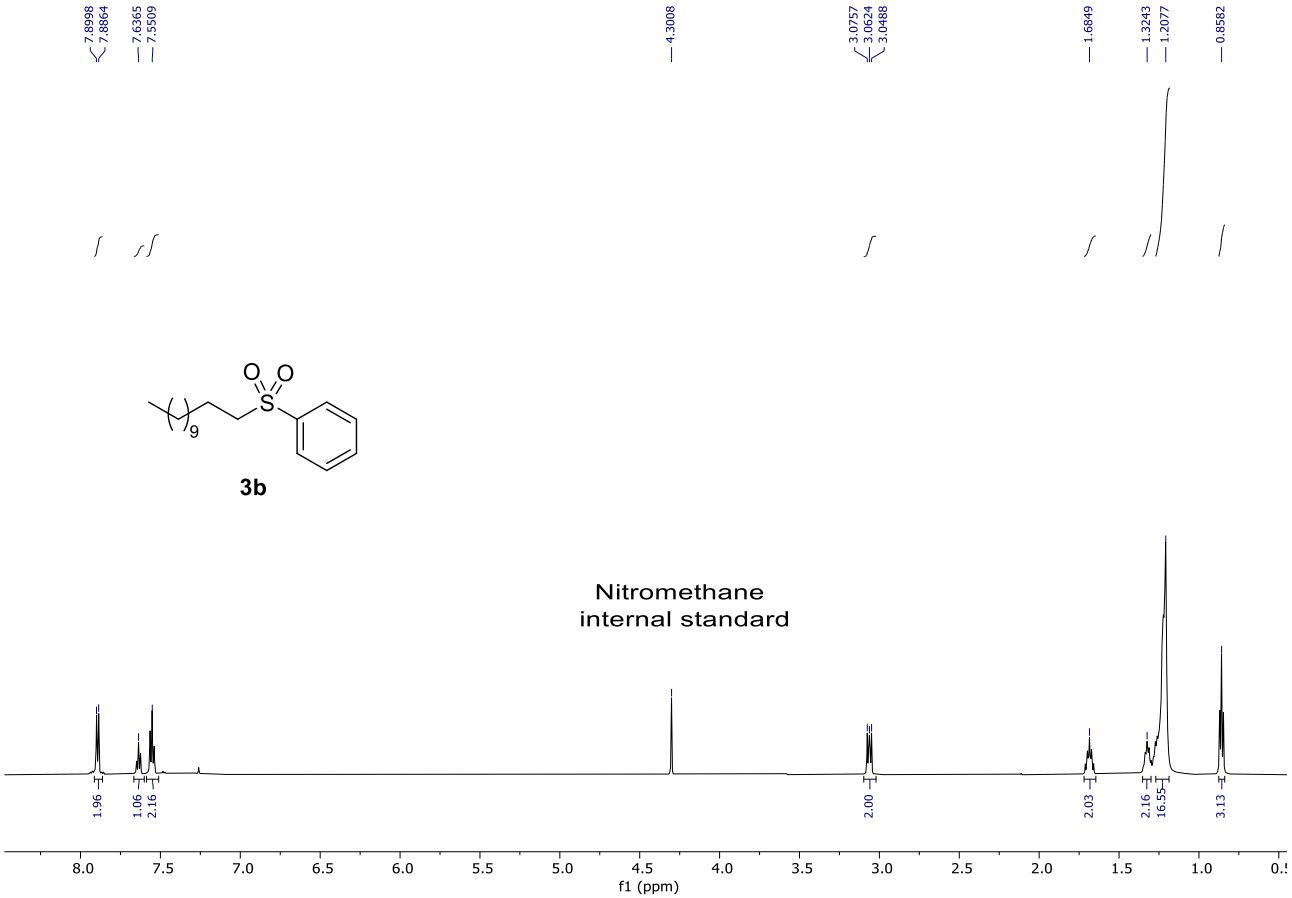
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3a (150 MHz, $CDCl_3$)



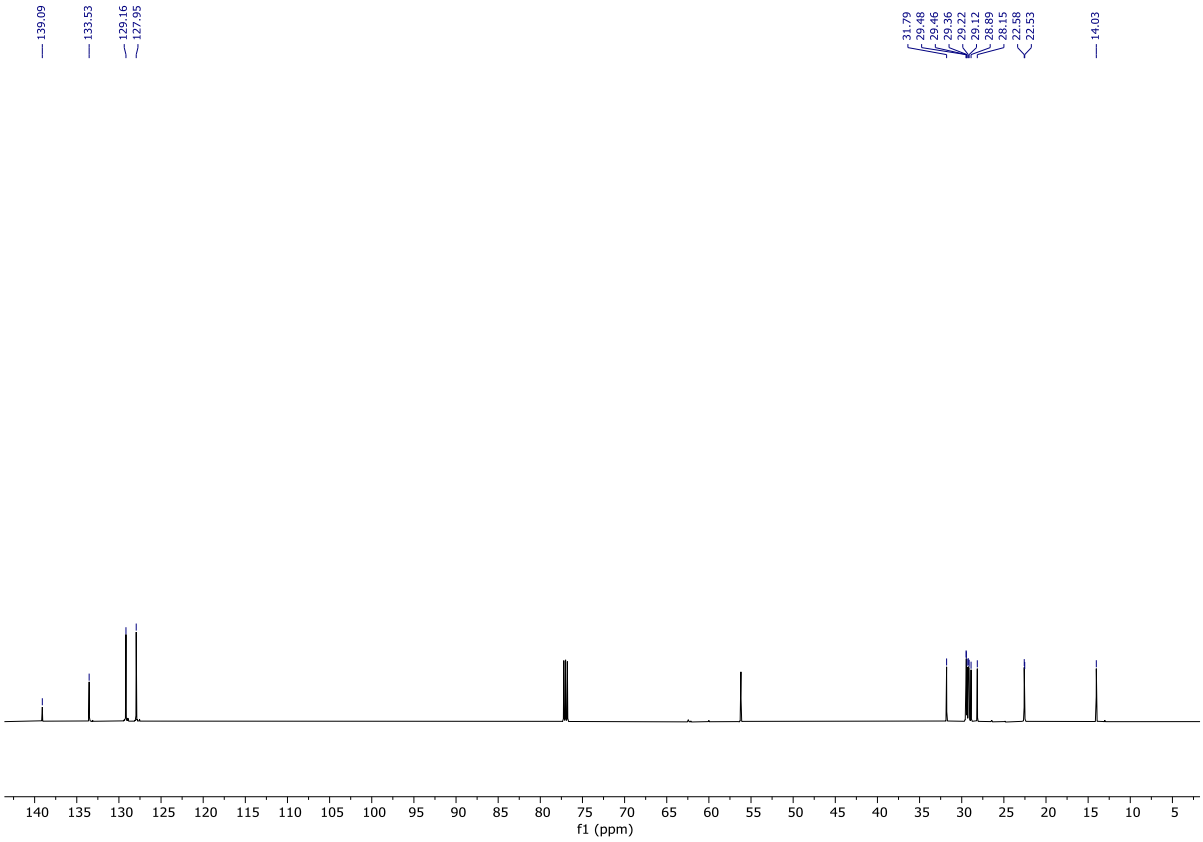
COSY-NMR of compound 3a (600 MHz, $CDCl_3$)



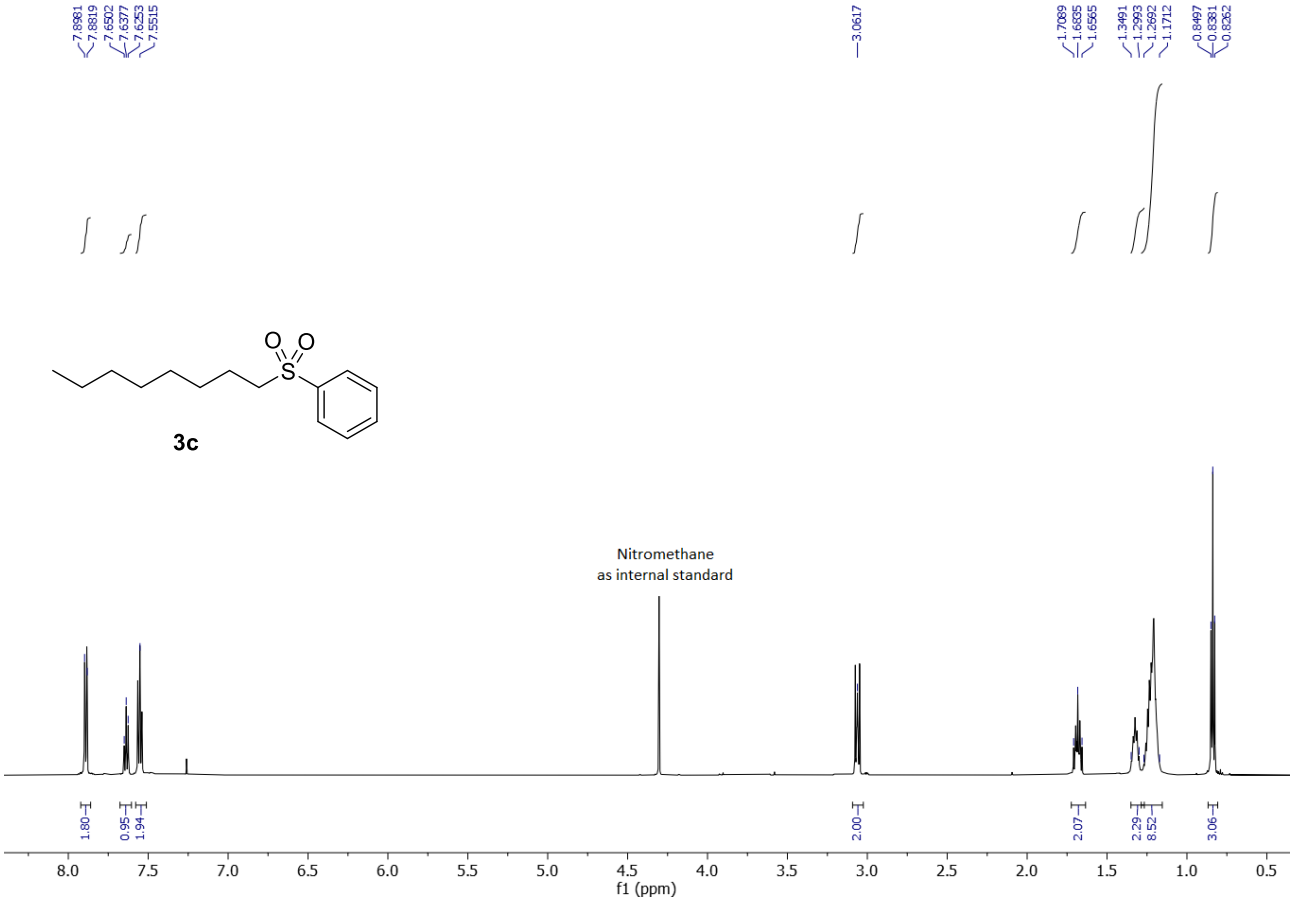
^{1}H-NMR of compound 3b (600 MHz, $CDCl_3$)



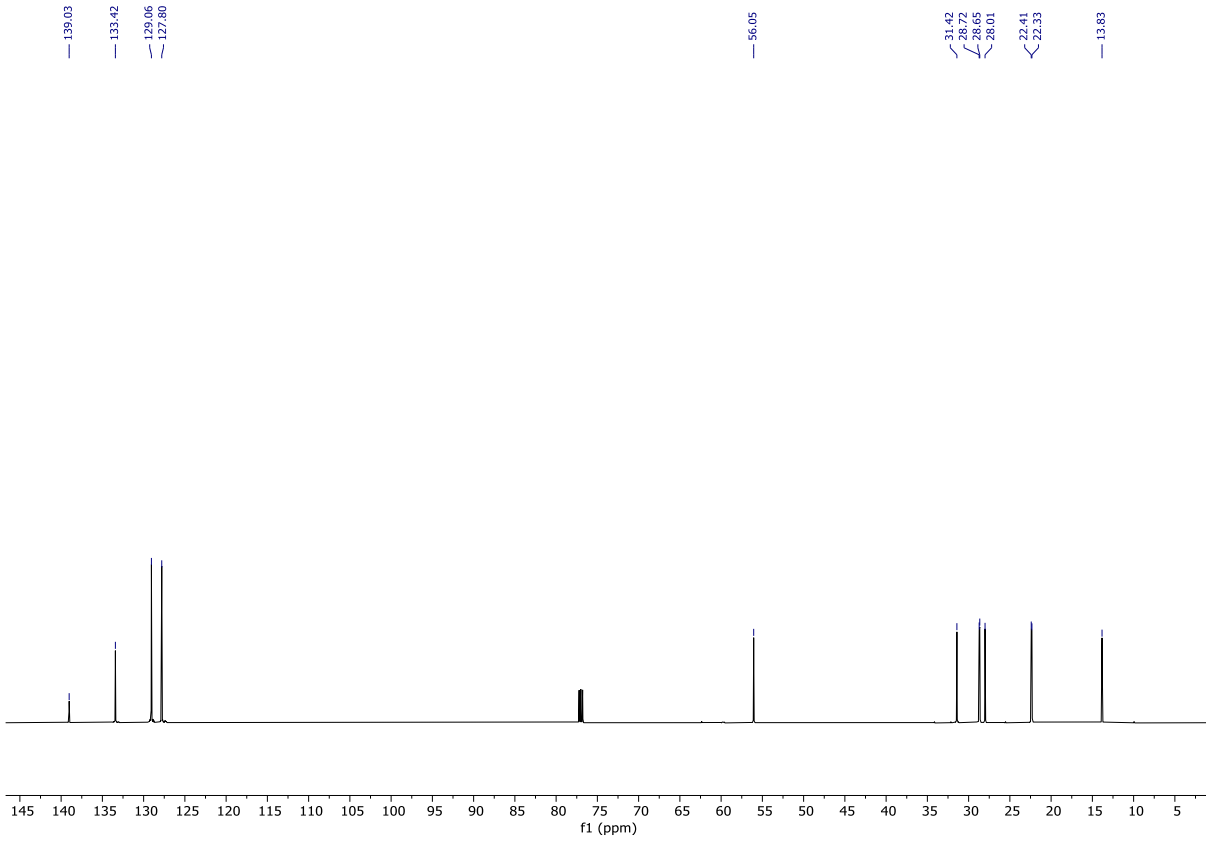
^{13}C{^{1}H}-NMR of compound 3b (150 MHz, $CDCl_3$)



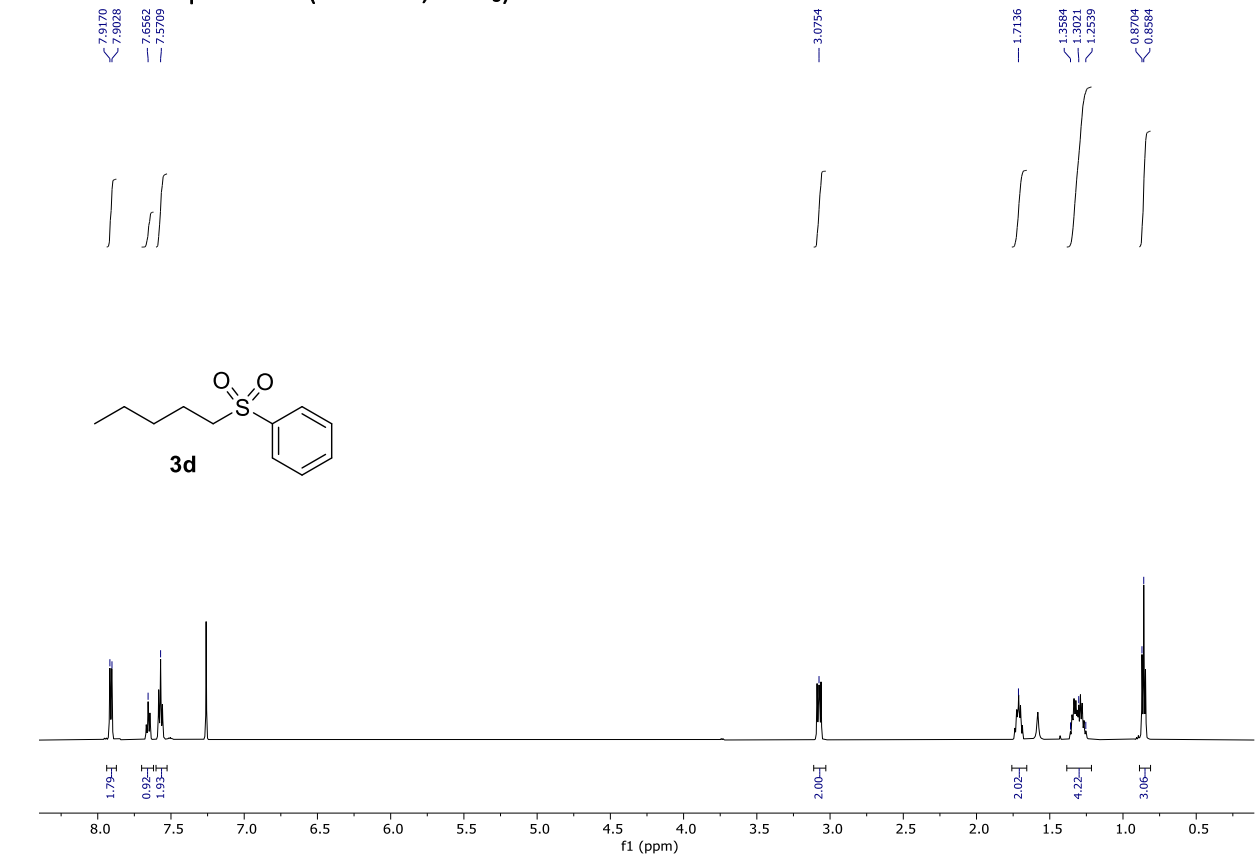
^{1}H-NMR of compound 3c (600 MHz, $CDCl_3$)



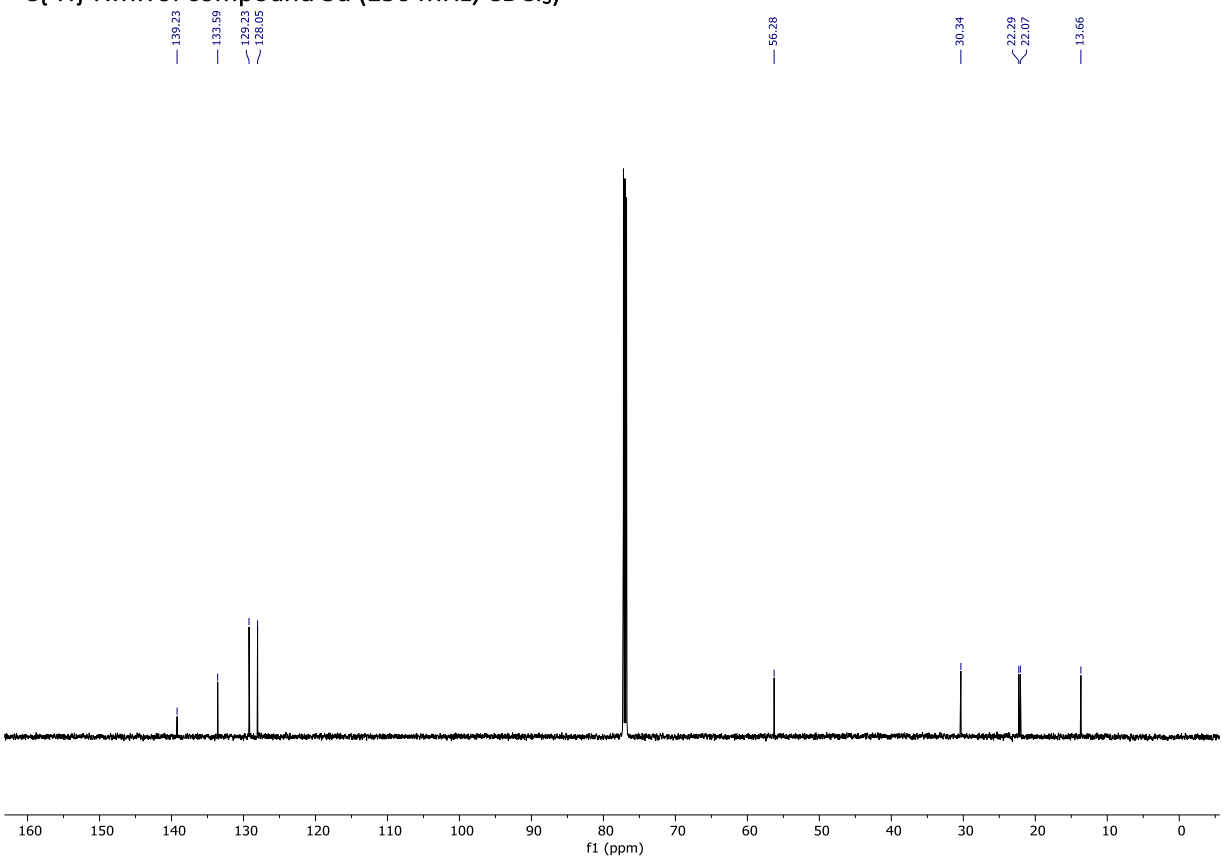
^{13}C{^{1}H}-NMR of compound 3c (150 MHz, $CDCl_3$)



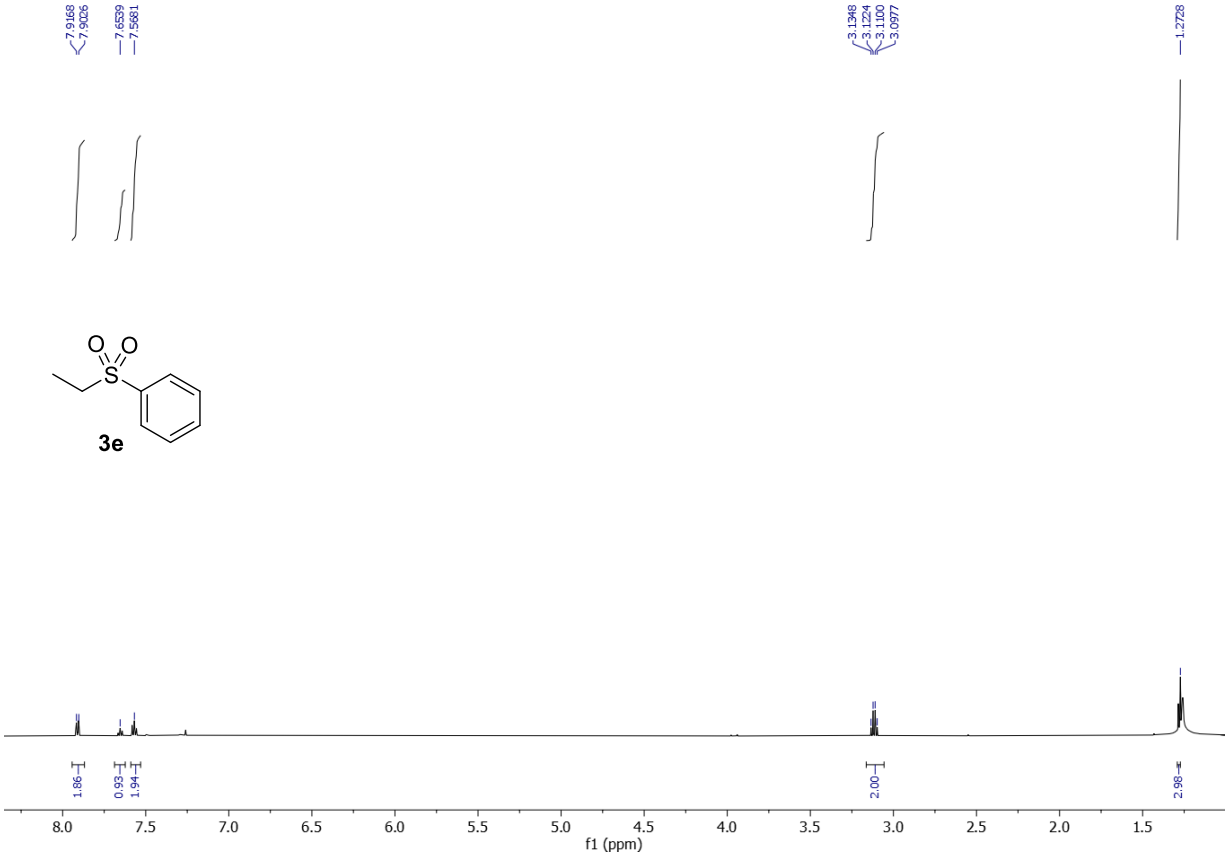
^{1}H-NMR of compound 3d (600 MHz, $CDCl_3$)



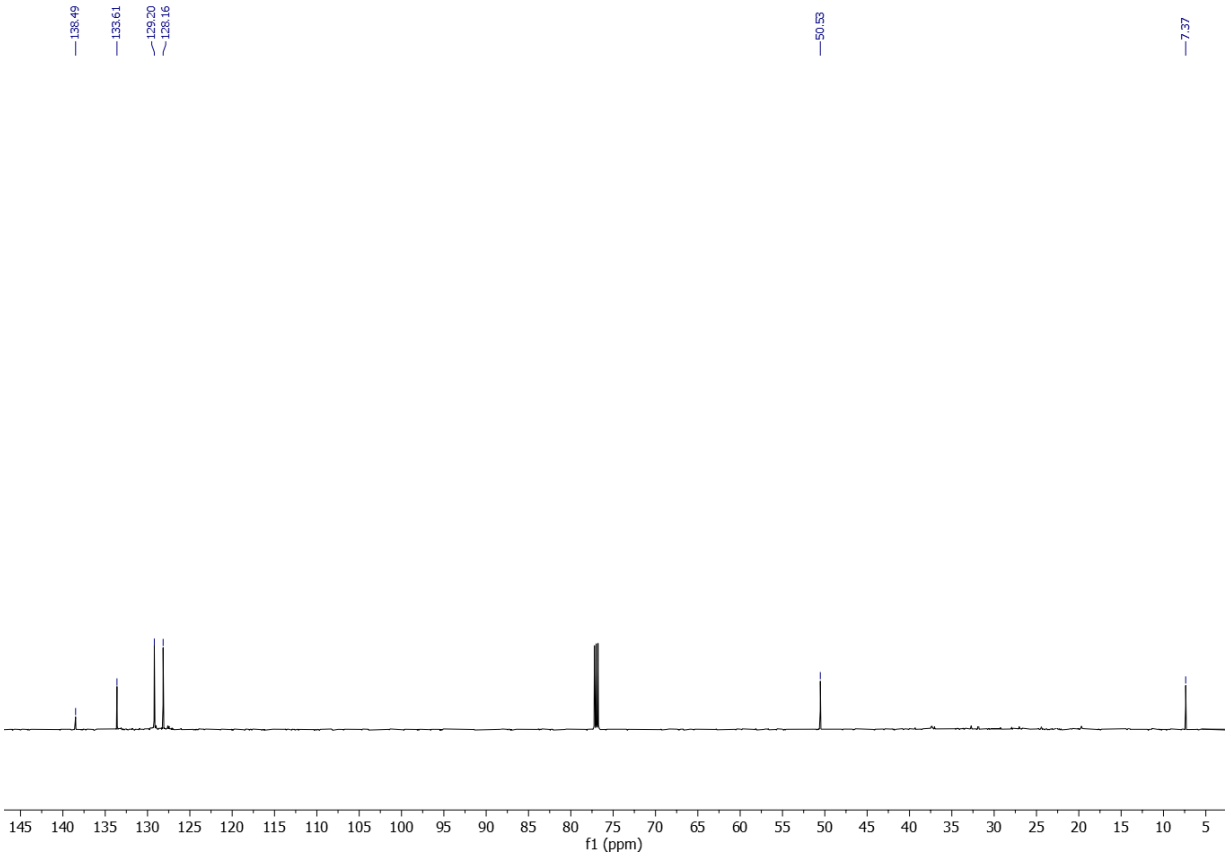
^{13}C{^{1}H}-NMR of compound 3d (150 MHz, $CDCl_3$)



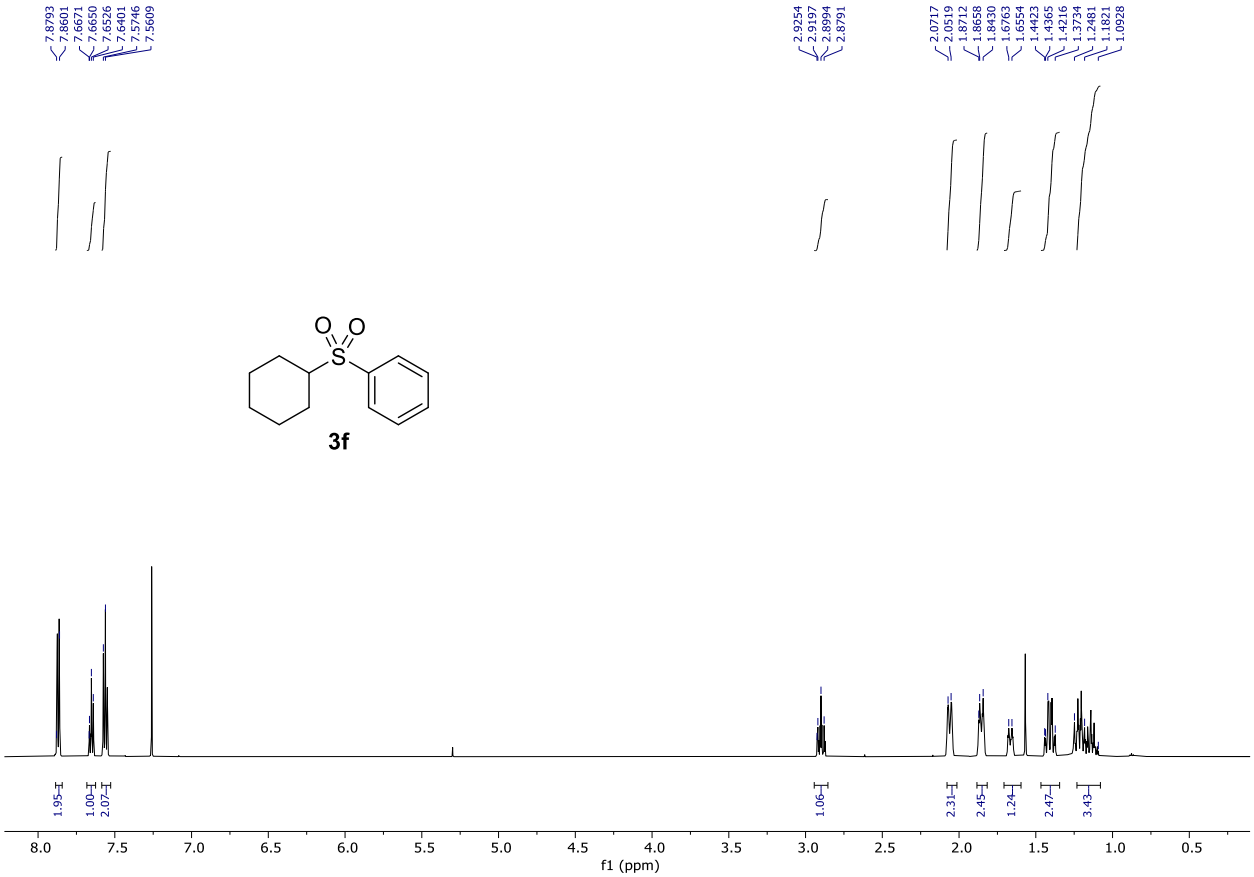
^{1}H-NMR of compound 3e (600 MHz, $CDCl_3$)



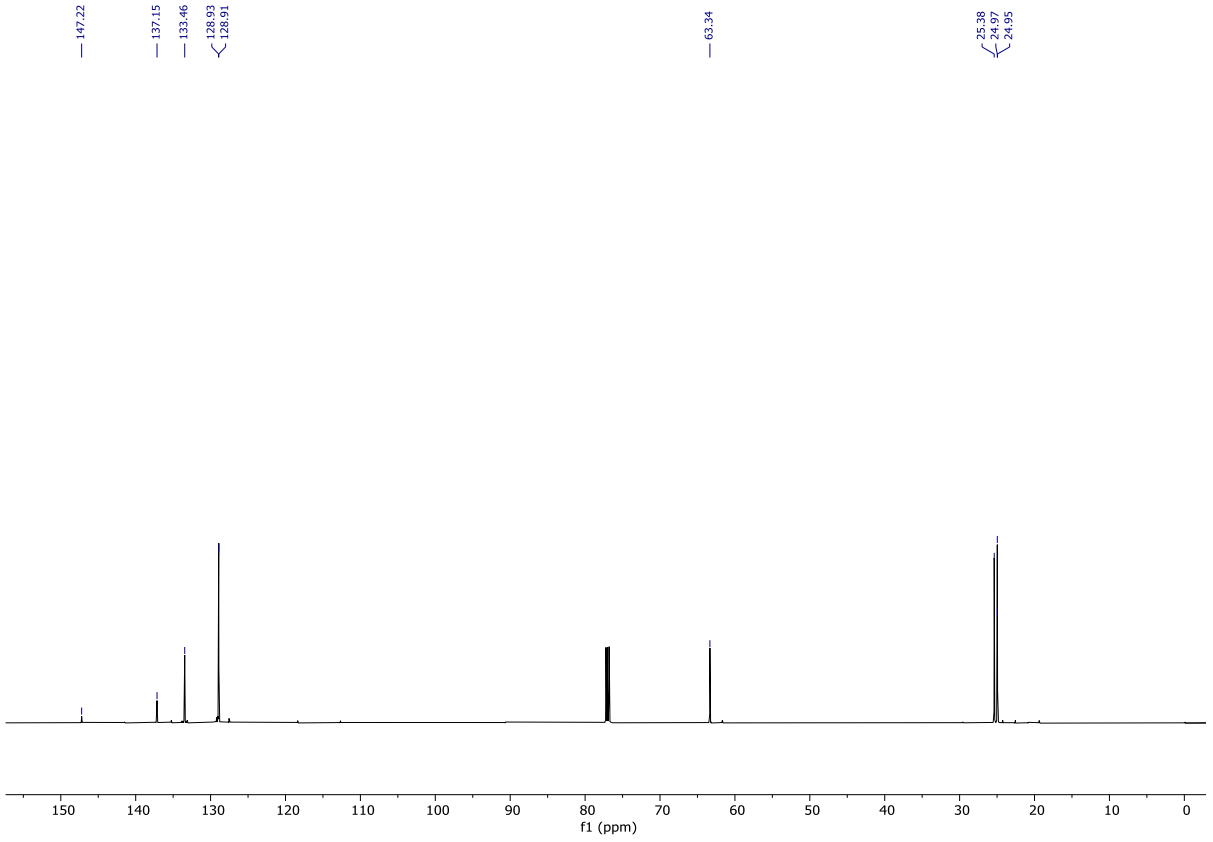
^{13}C{^{1}H}-NMR of compound 3e (150 MHz, $CDCl_3$)



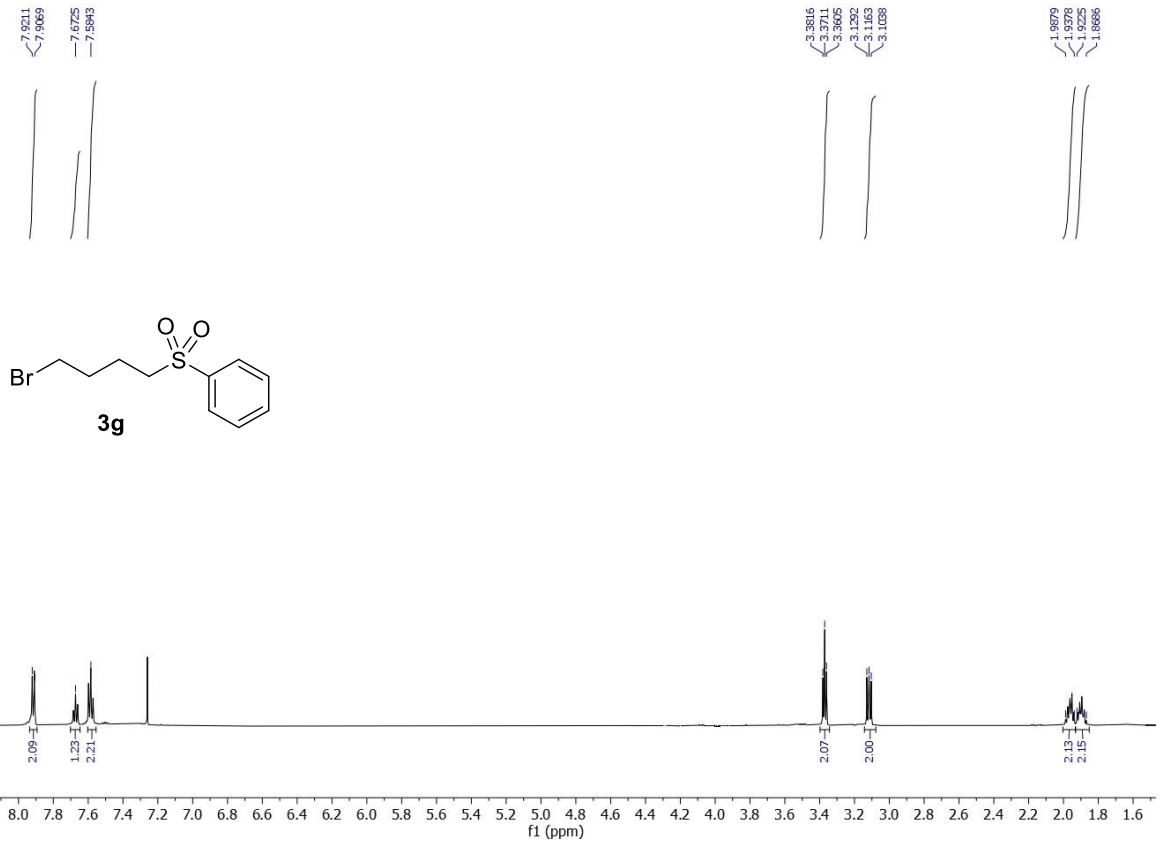
^{1}H-NMR of compound 3f (600 MHz, $CDCl_3$)



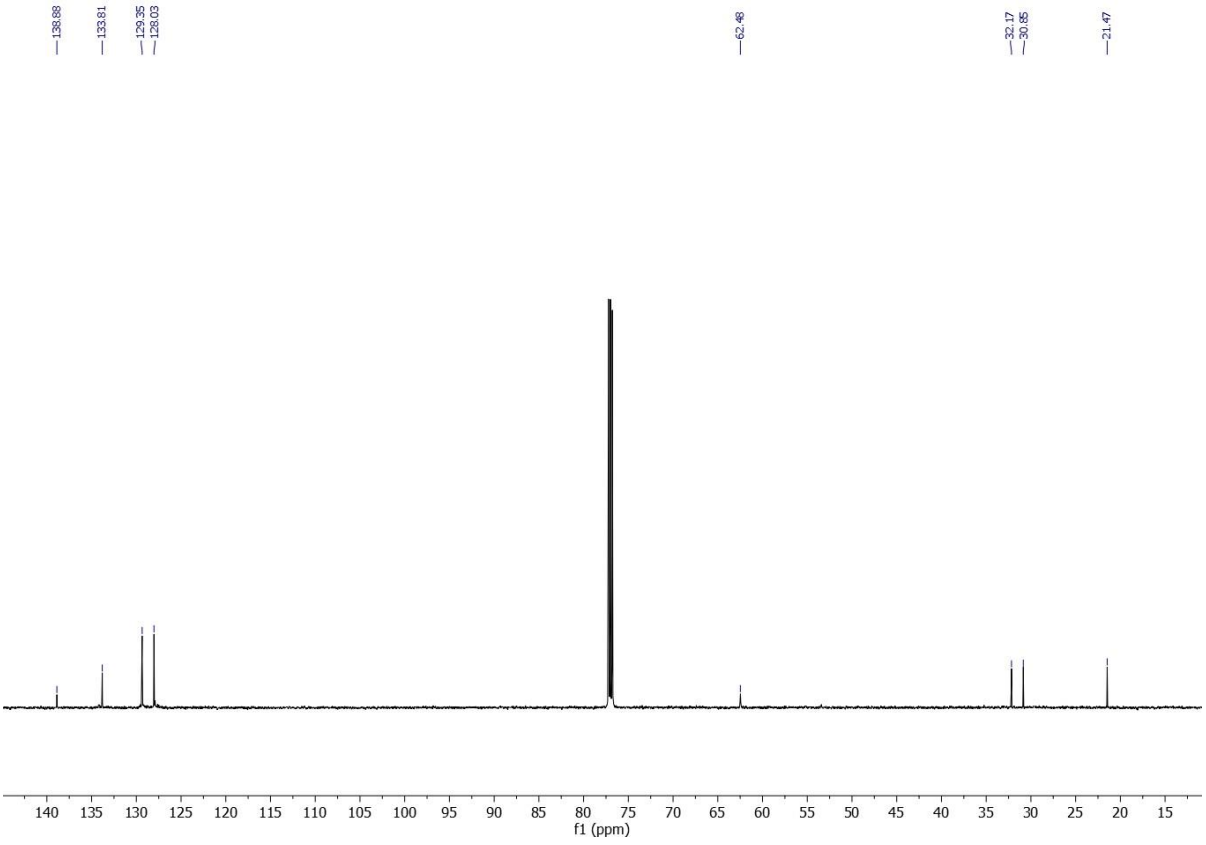
^{13}C{^{1}H}-NMR of compound 3f (150 MHz, $CDCl_3$)



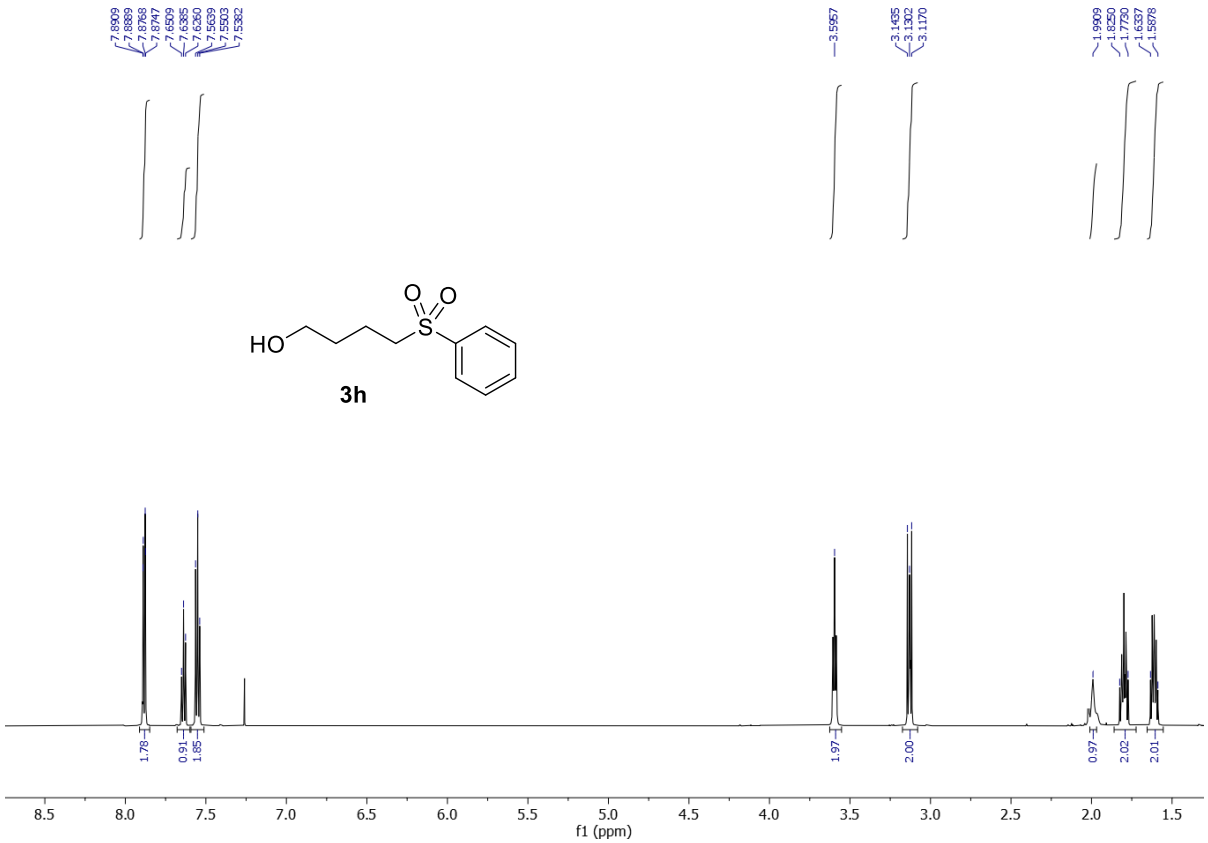
^{1}H-NMR of compound 3g (600 MHz, $CDCl_3$)



^{13}C{^{1}H}-NMR of compound 3g (150 MHz, $CDCl_3$)

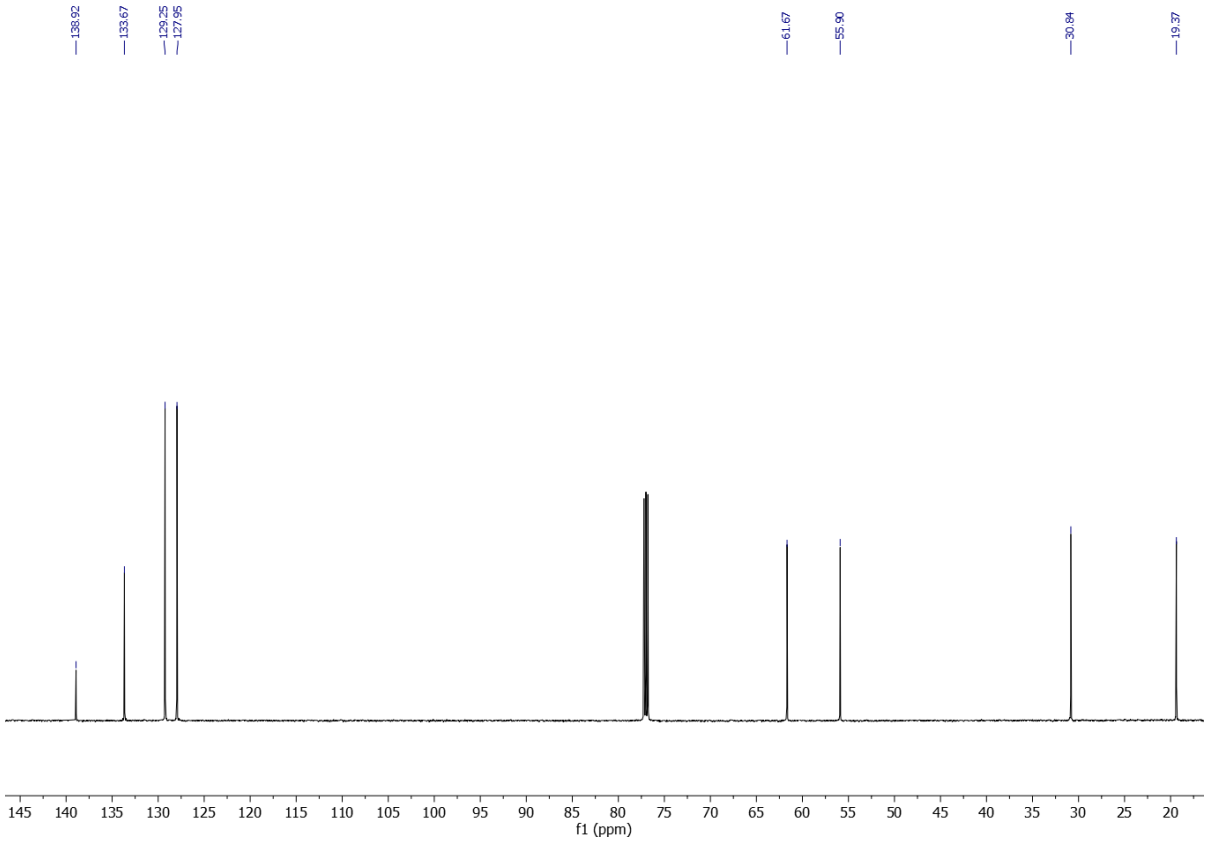


^{1}H-NMR of compound 3h (600 MHz, $CDCl_3$)

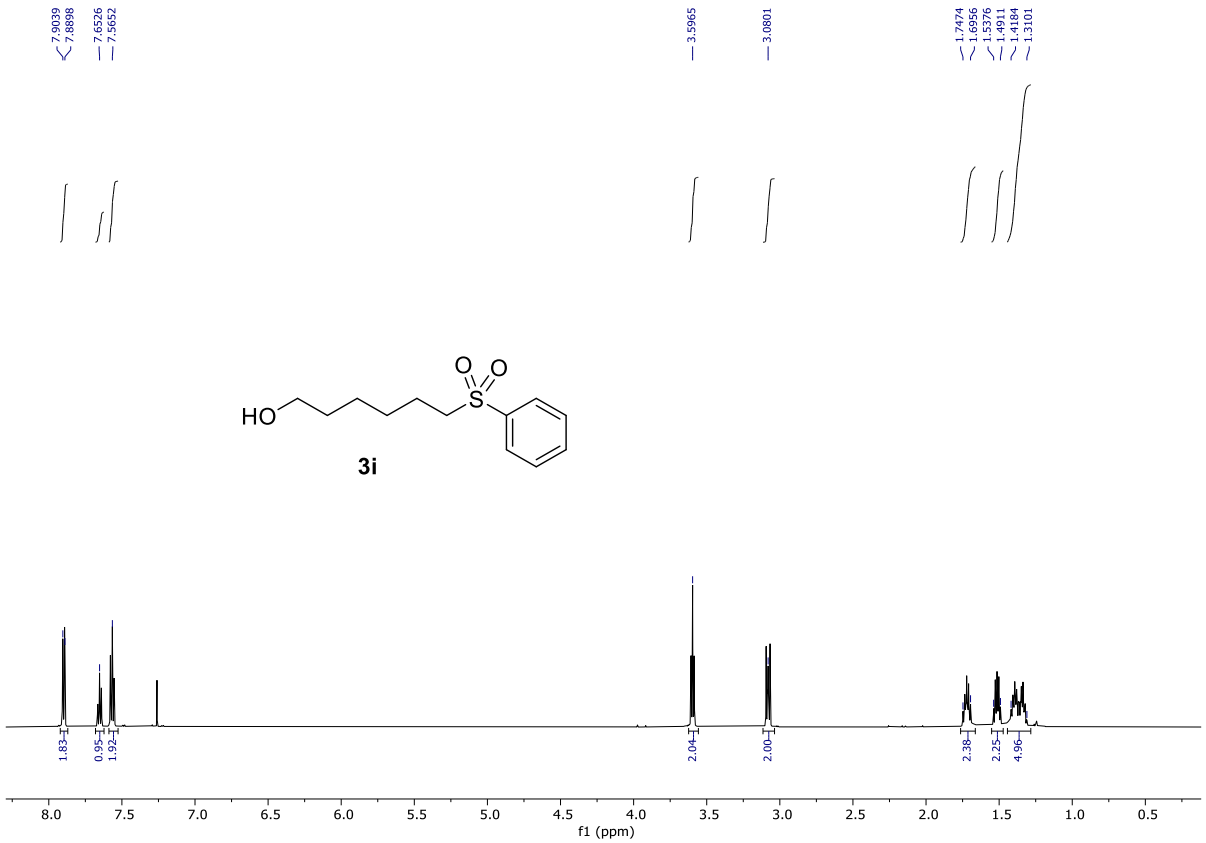


3h

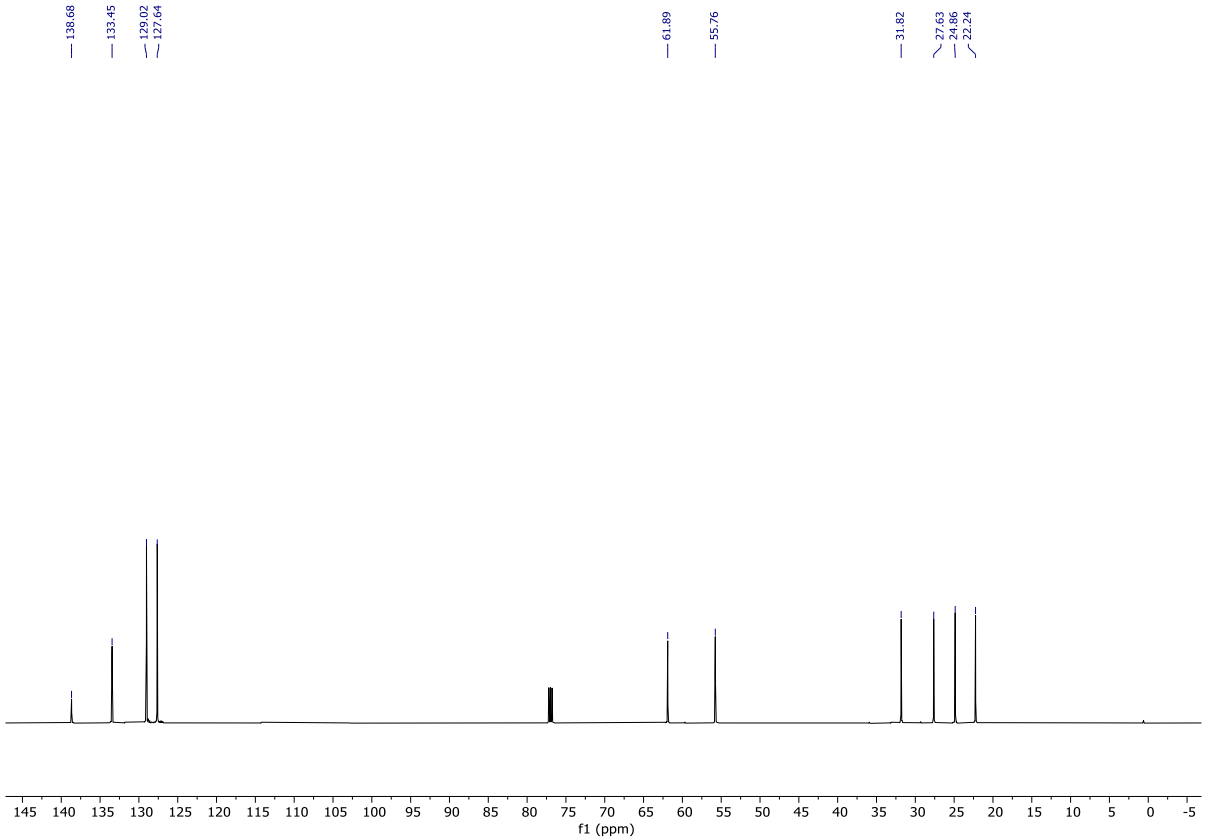
^{13}C{^{1}H}-NMR of compound 3h (150 MHz, $CDCl_3$)



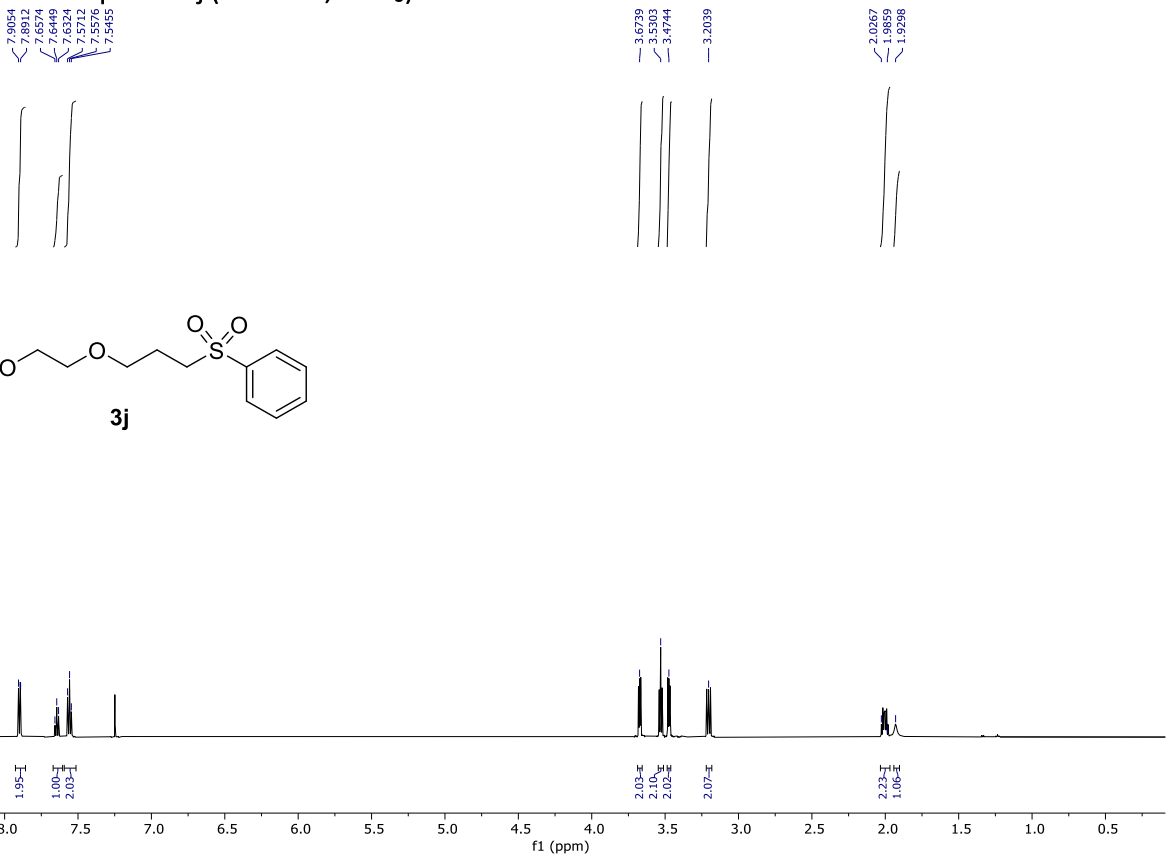
^{1}H-NMR of compound 3i (600 MHz, $CDCl_3$)



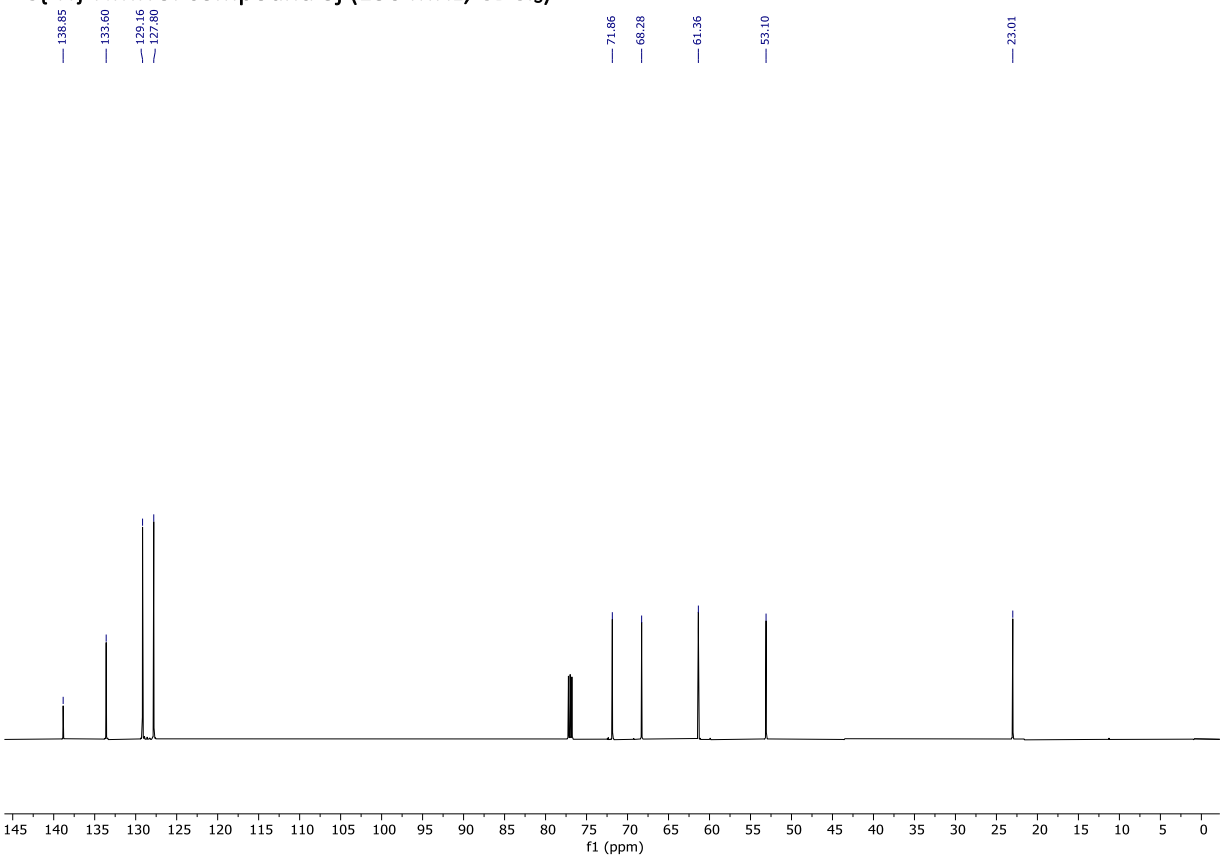
^{13}C{^{1}H}-NMR of compound 3i (150 MHz, $CDCl_3$)



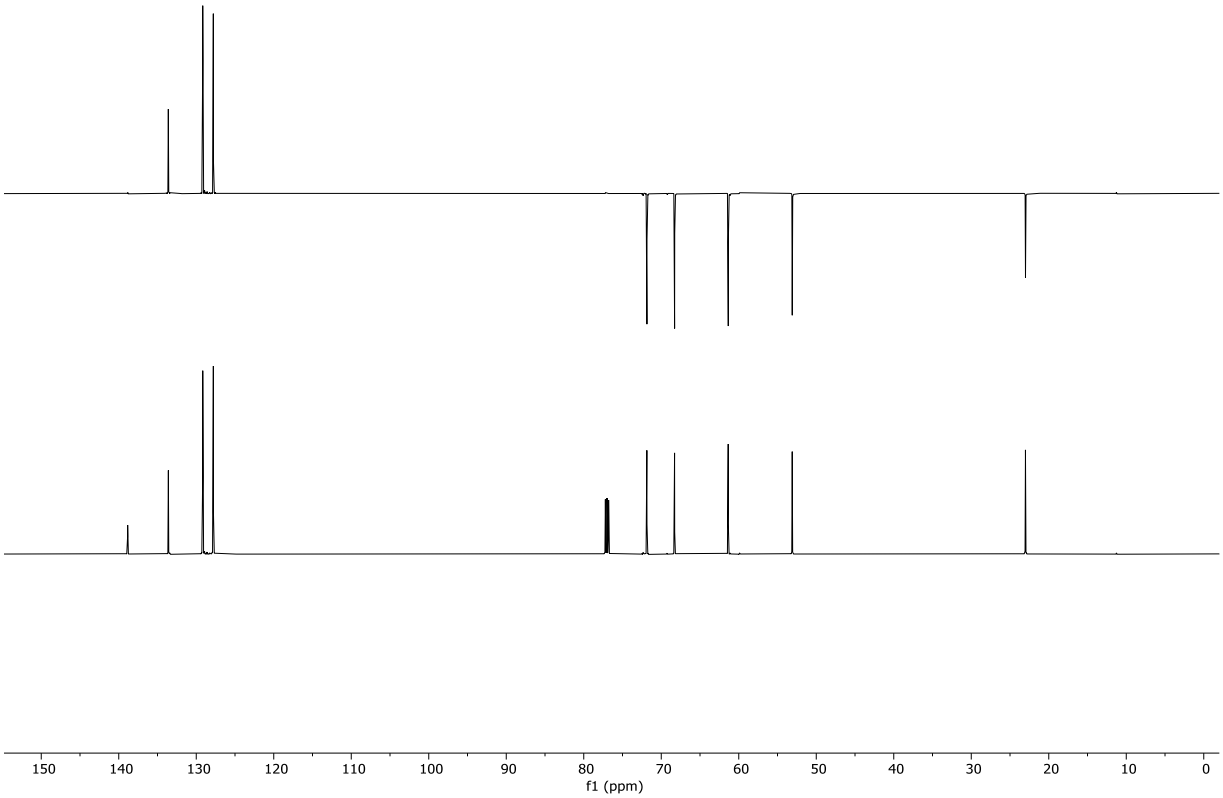
^{1}H-NMR of compound 3j (600 MHz, $CDCl_3$)



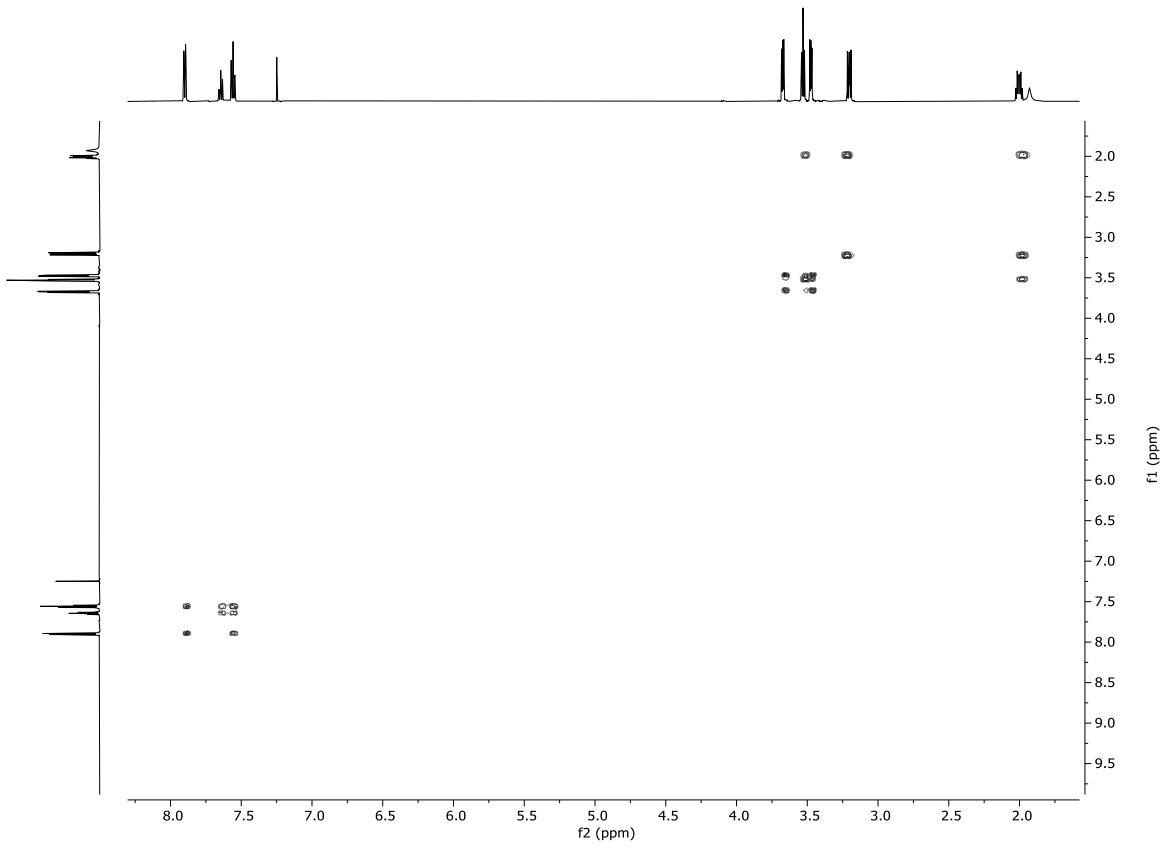
^{13}C{^{1}H}-NMR of compound 3j (150 MHz, $CDCl_3$)



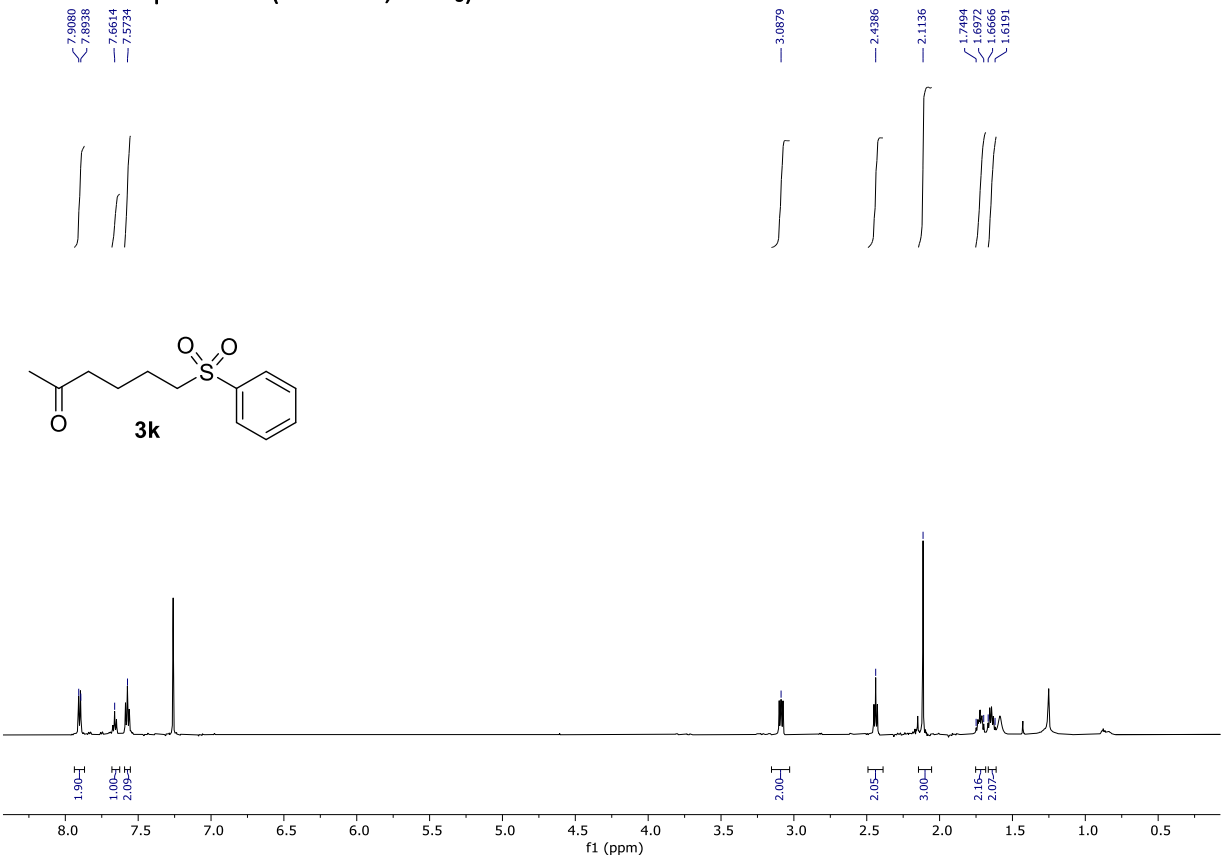
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3j (150 MHz, $CDCl_3$)



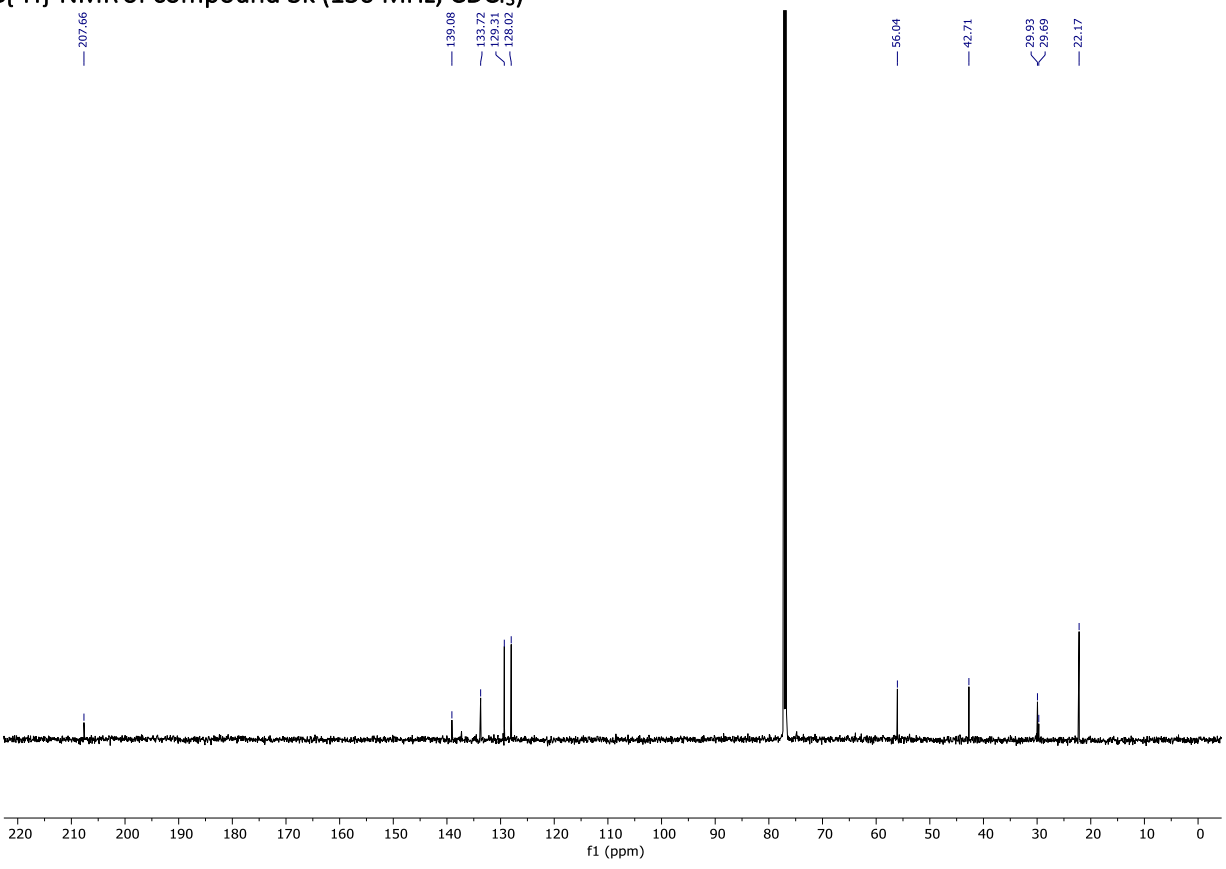
COSY-NMR of compound 3j (600 MHz, $CDCl_3$)



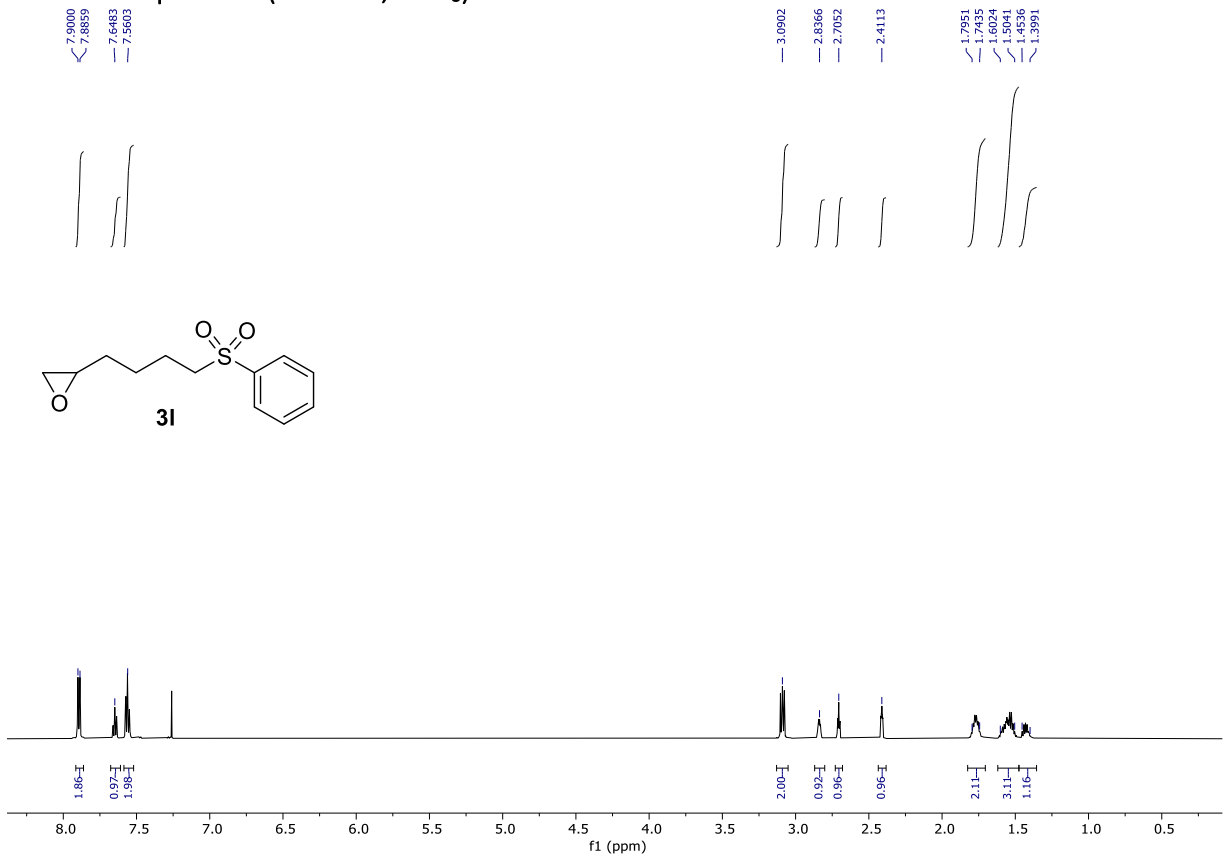
^{1}H-NMR of compound 3k (600 MHz, $CDCl_3$)



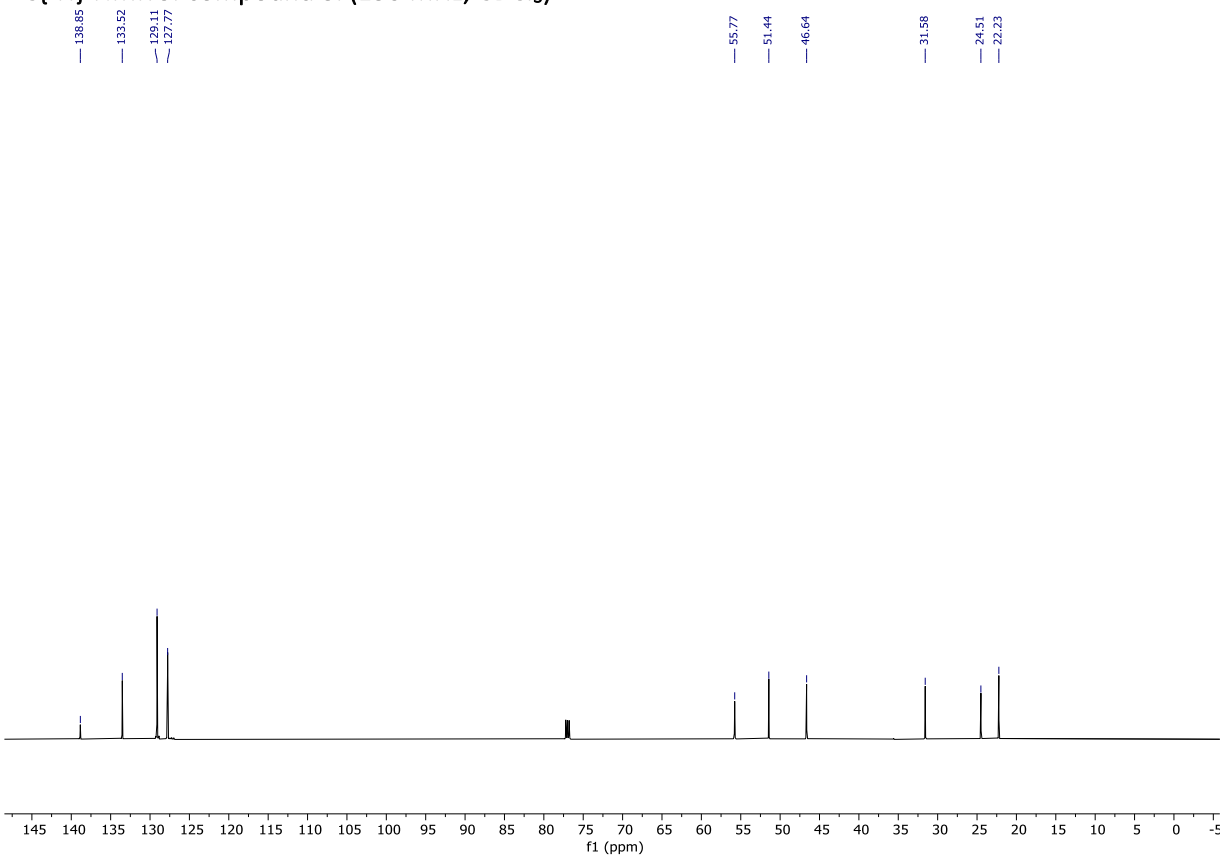
^{13}C{^{1}H}-NMR of compound 3k (150 MHz, $CDCl_3$)



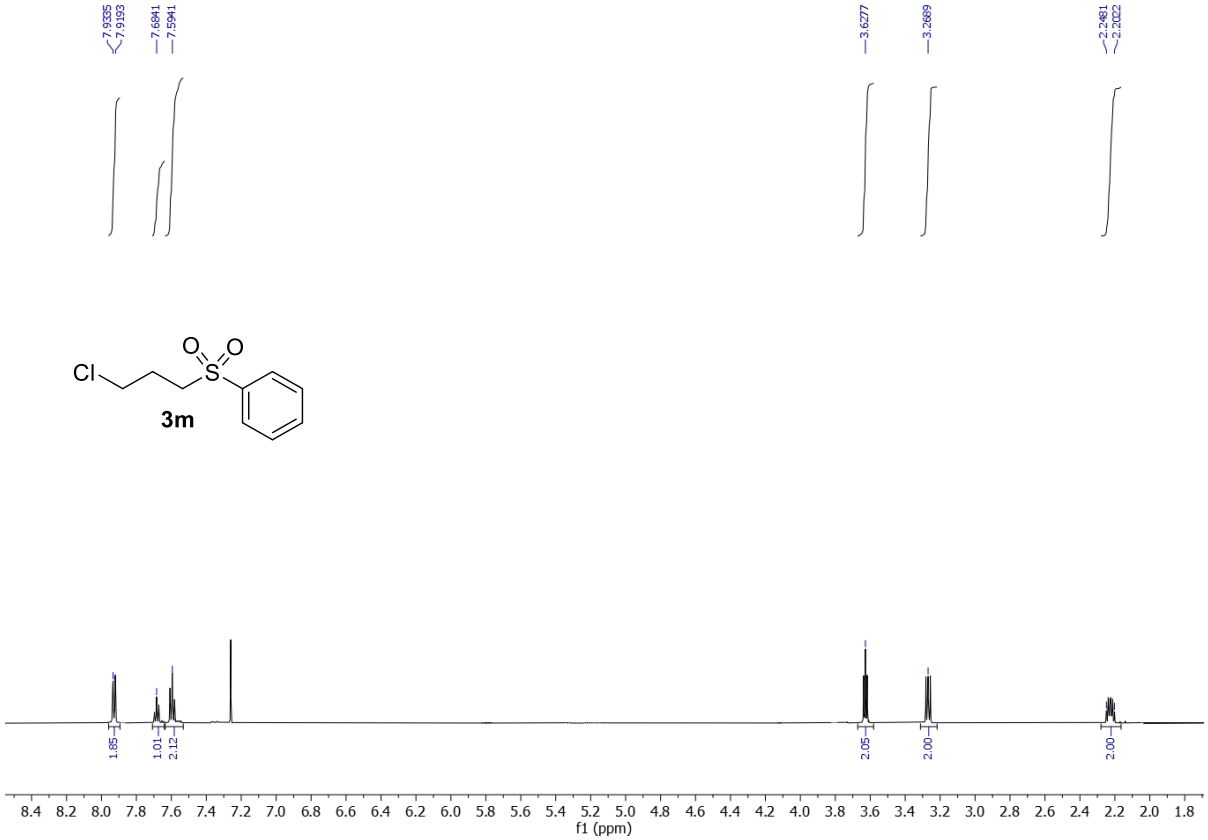
^{1}H-NMR of compound 3l (600 MHz, $CDCl_3$)



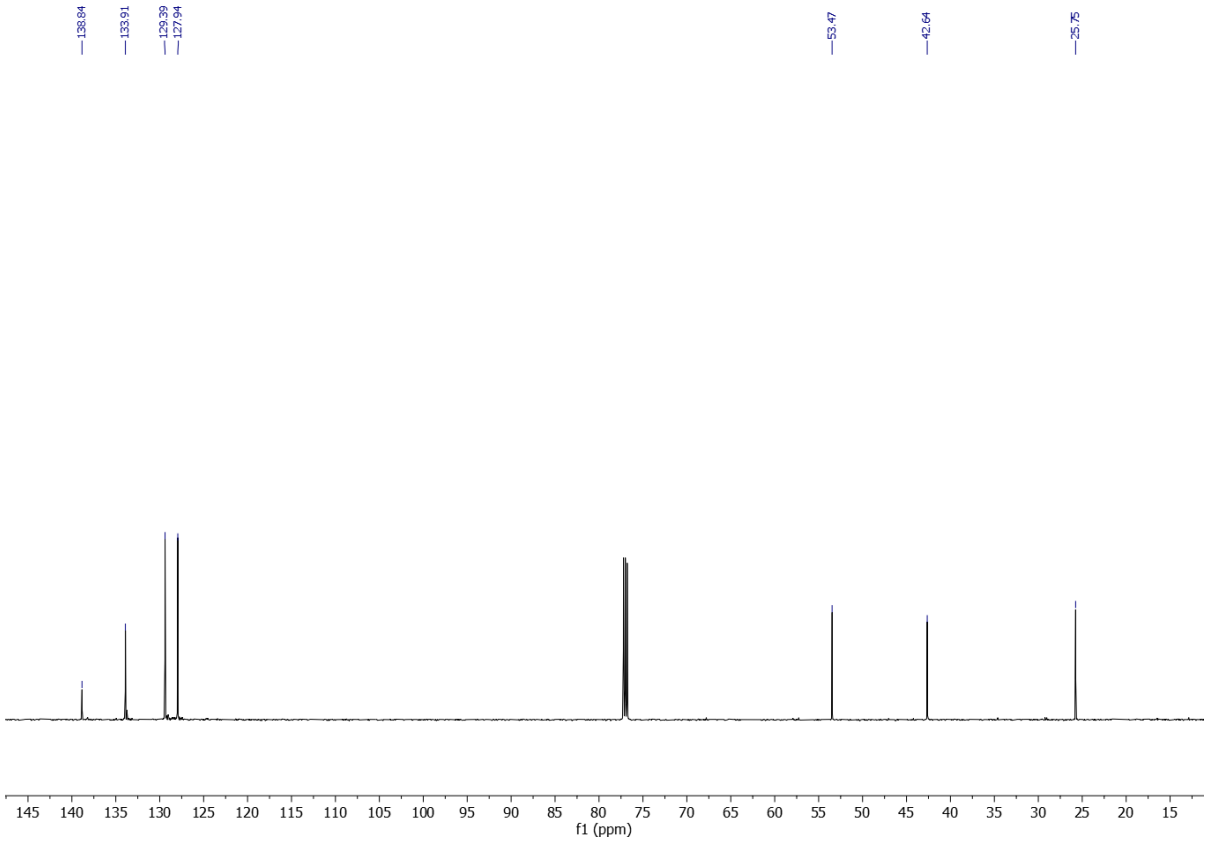
^{13}C{^{1}H}-NMR of compound 3l (150 MHz, $CDCl_3$)



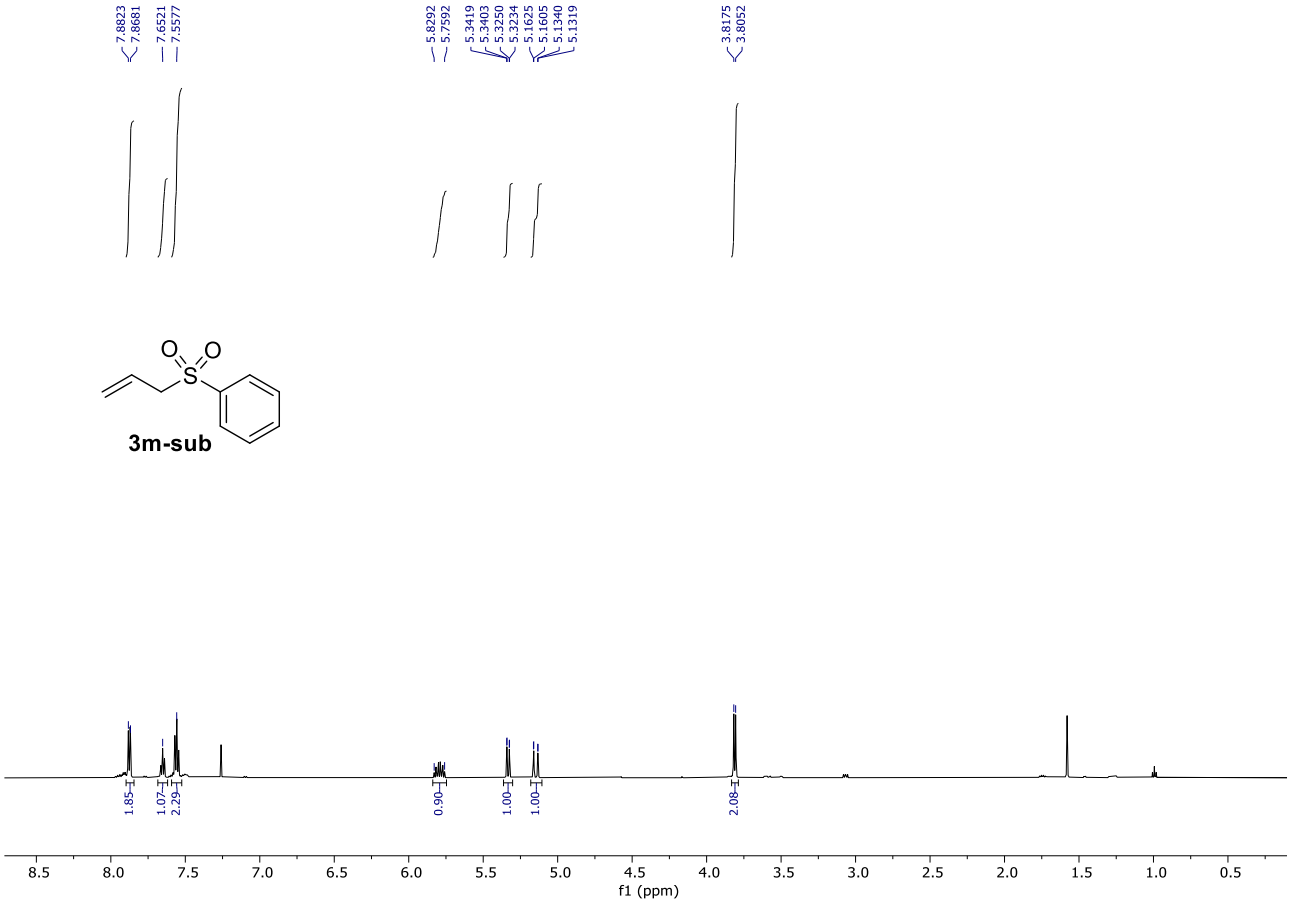
^{1}H-NMR of compound 3m (600 MHz, $CDCl_3$)



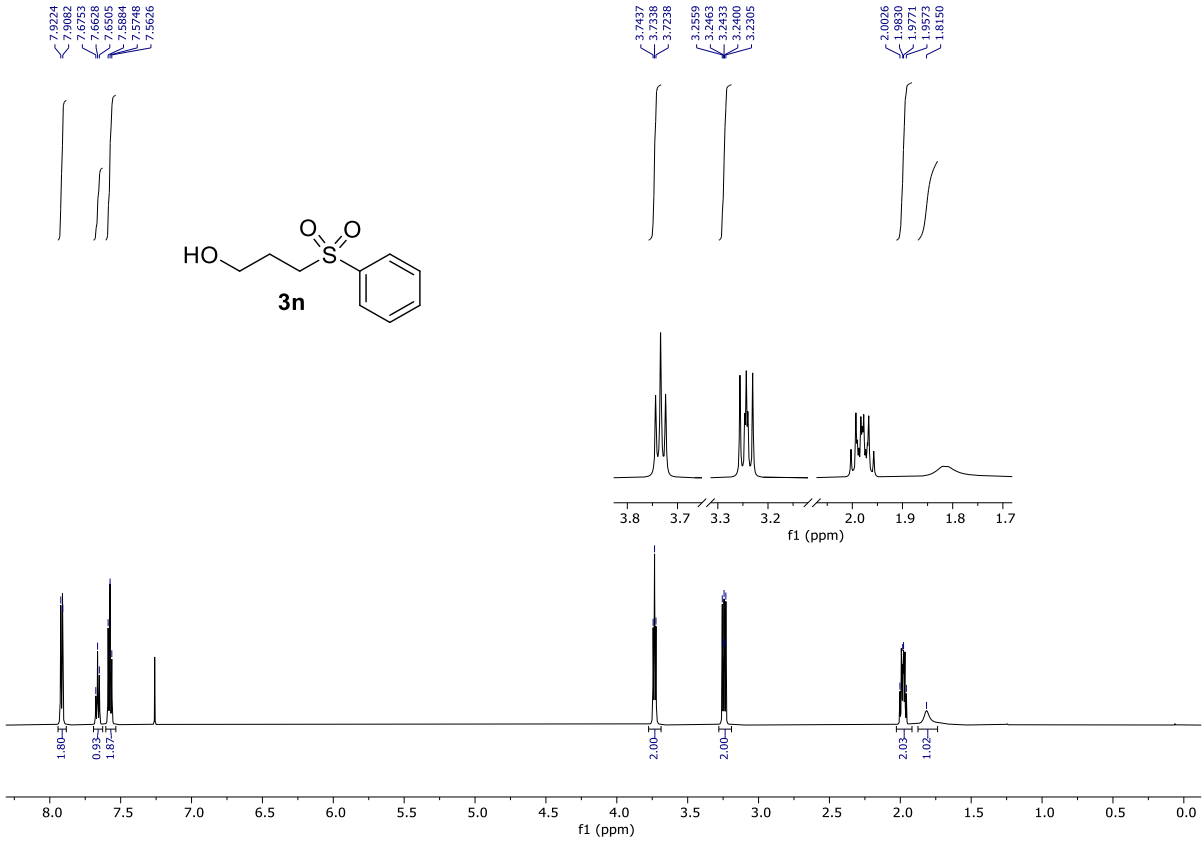
^{13}C{^{1}H}-NMR of compound 3m (150 MHz, $CDCl_3$)



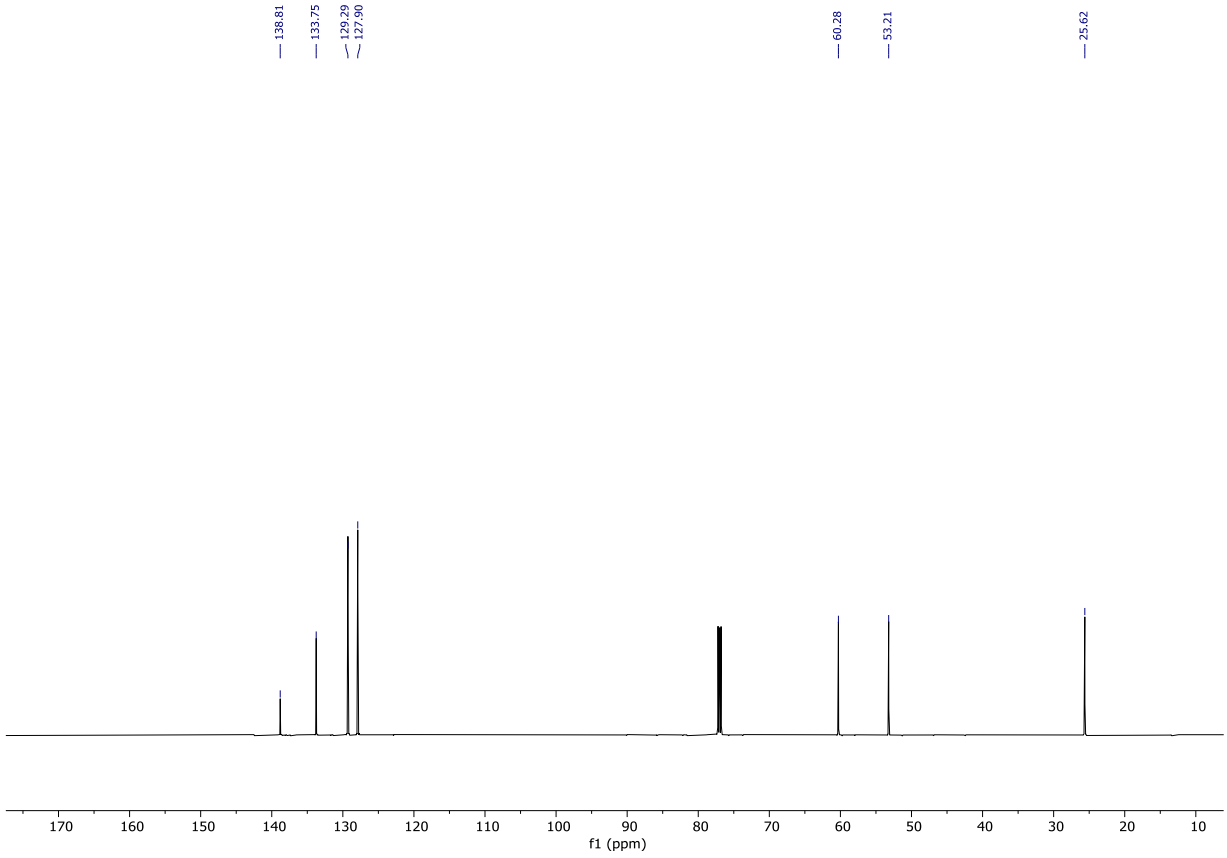
^{1}H-NMR of compound 3m-sub (600 MHz, $CDCl_3$)



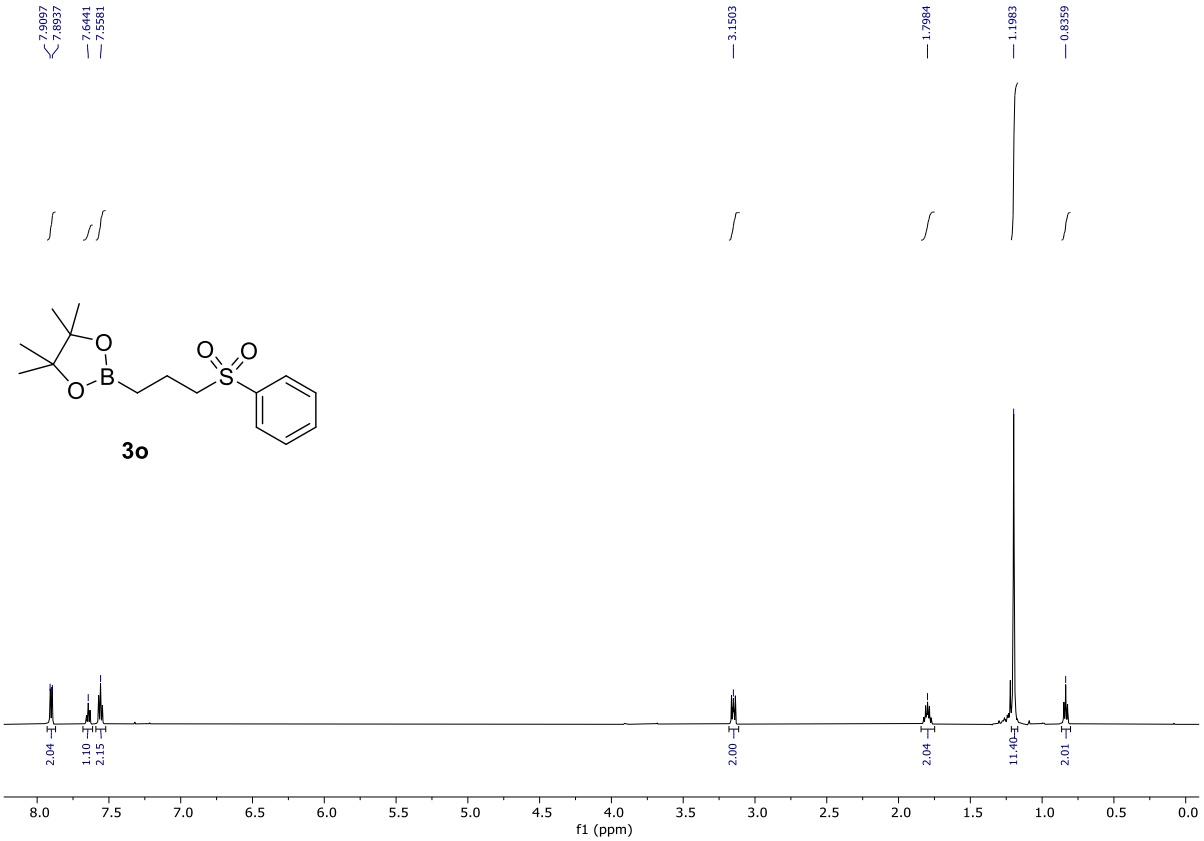
^{1}H-NMR of compound 3n (600 MHz, $CDCl_3$)



^{13}C{^{1}H}-NMR of compound 3n (150 MHz, $CDCl_3$)

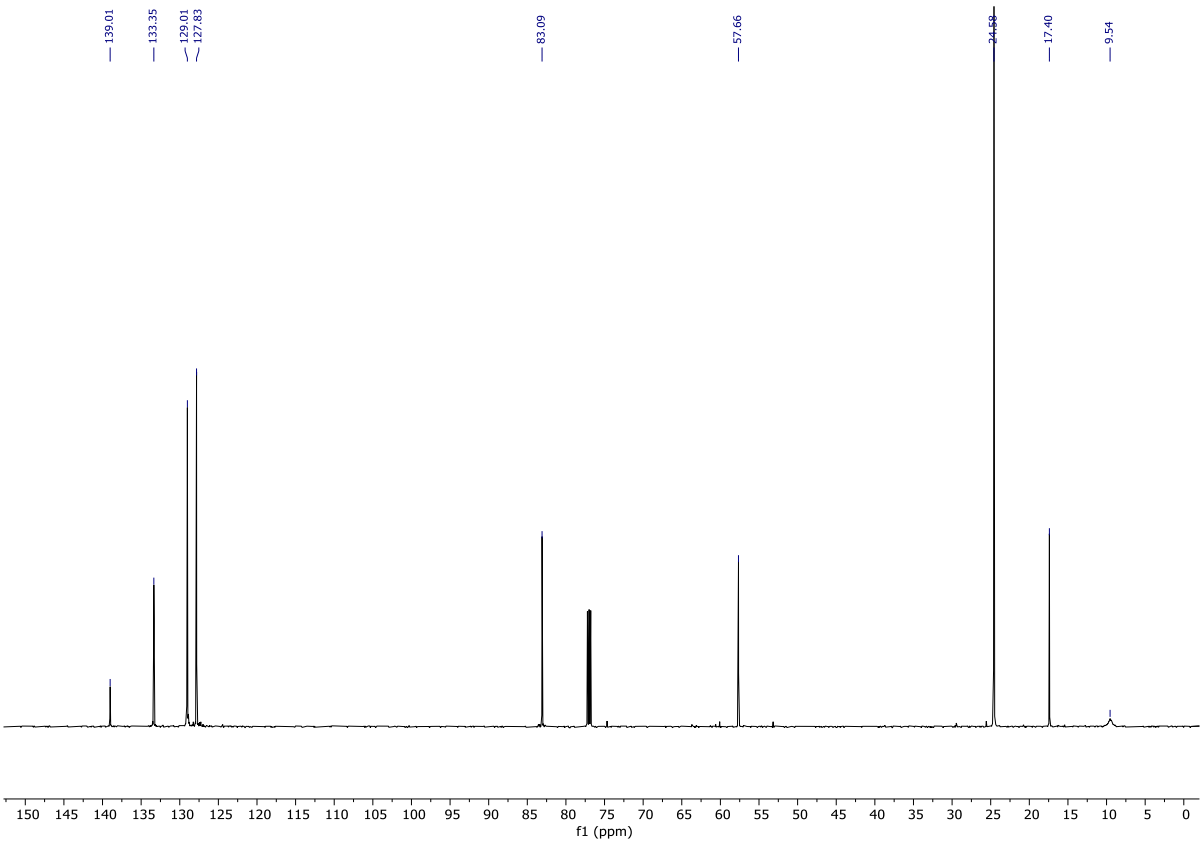


^{1}H-NMR of compound 3o (600 MHz, $CDCl_3$)

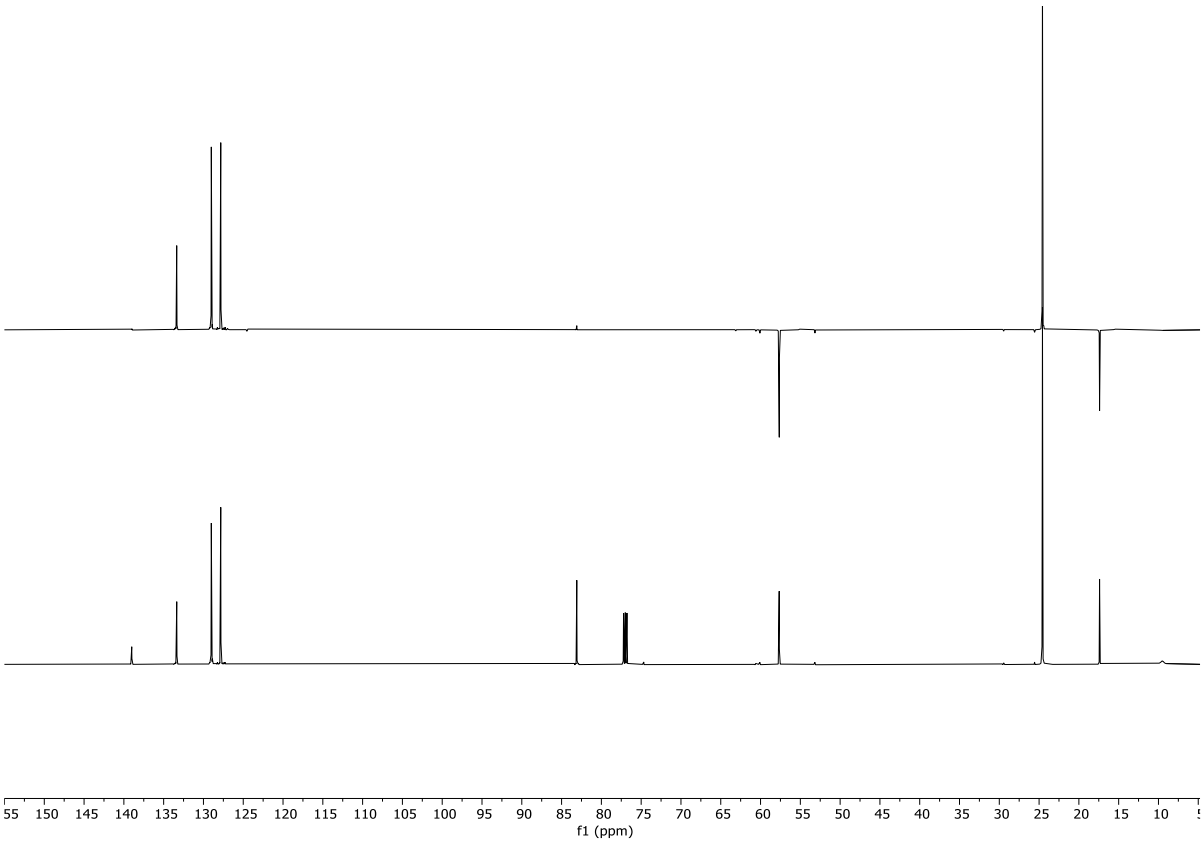


3o

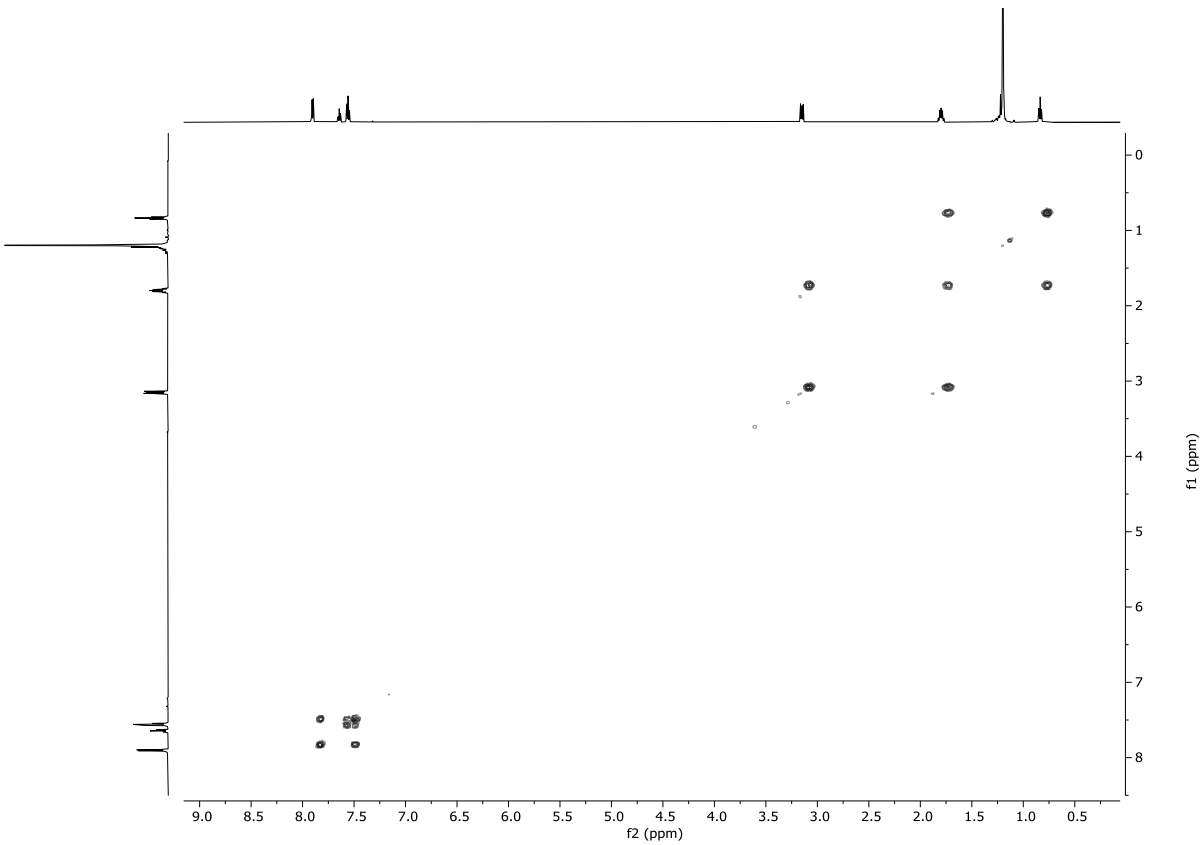
^{13}C{^{1}H}-NMR of compound 3o (150 MHz, $CDCl_3$)



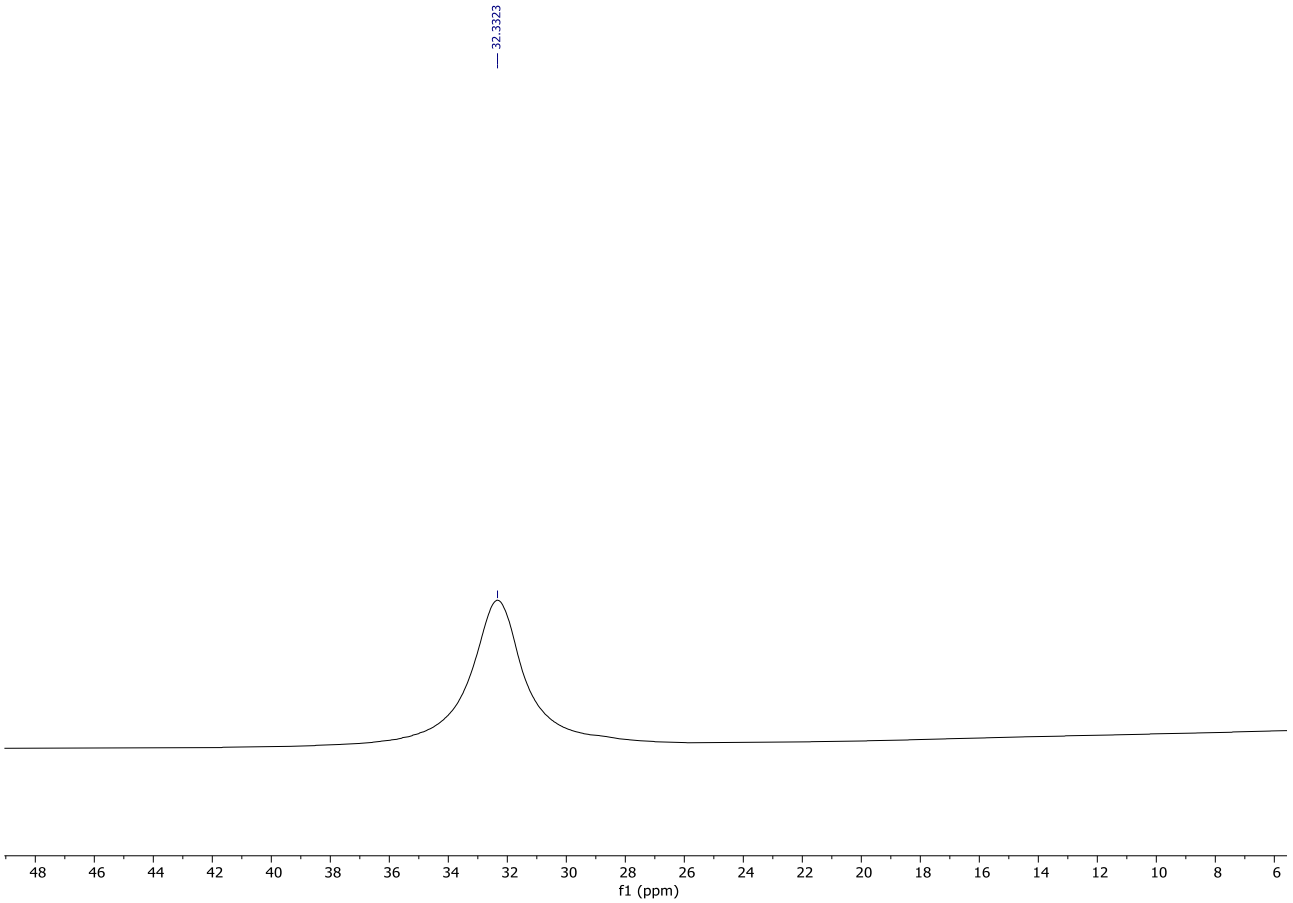
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3o (150 MHz, $CDCl_3$)



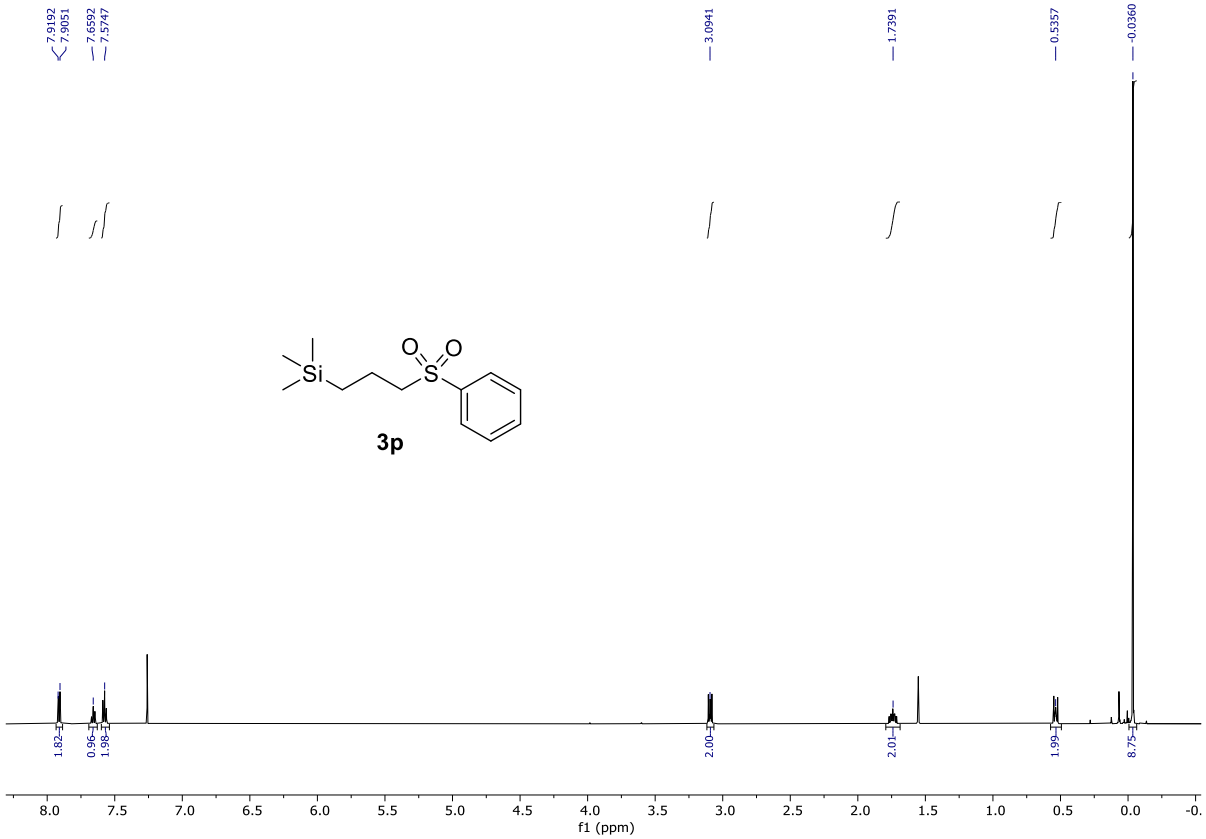
COSY-NMR of compound 3o (600 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$-NMR -NMR of compound 3o (192 MHz, $CDCl_3$)

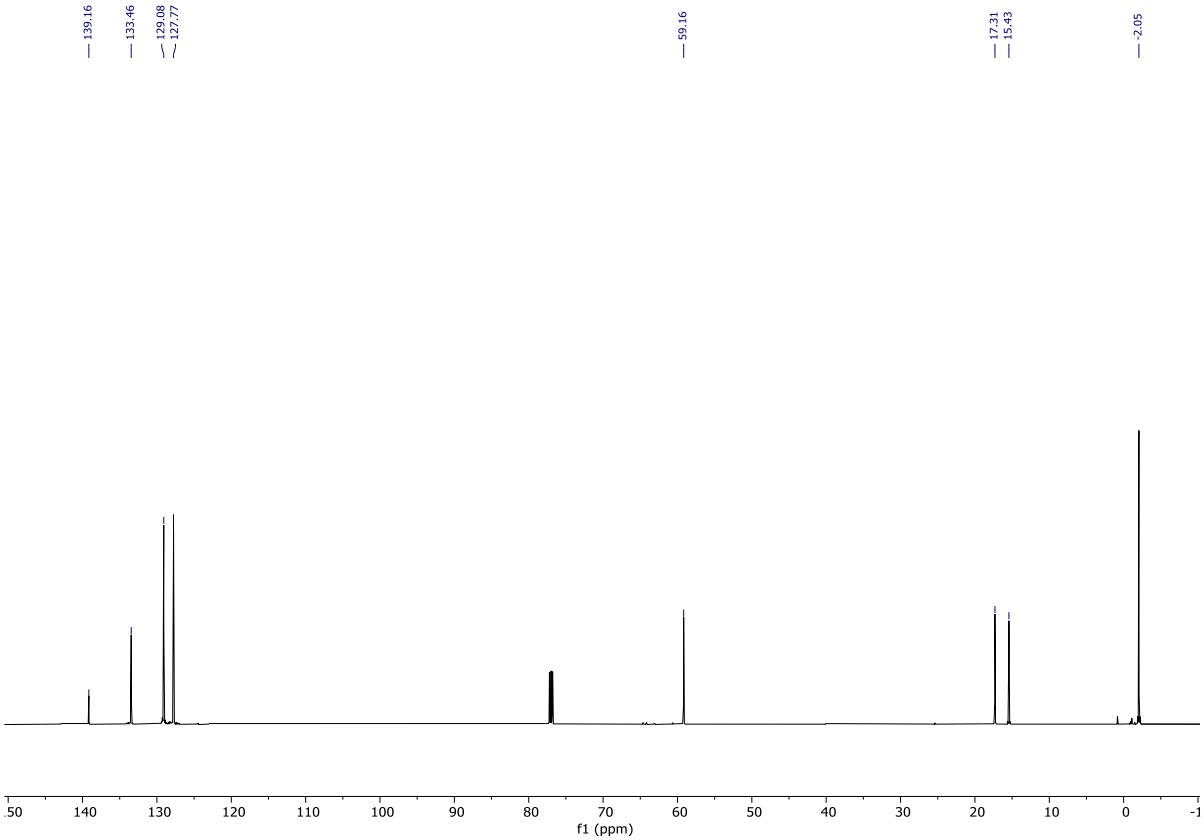


^{1}H-NMR of compound 3p (600 MHz, $CDCl_3$)

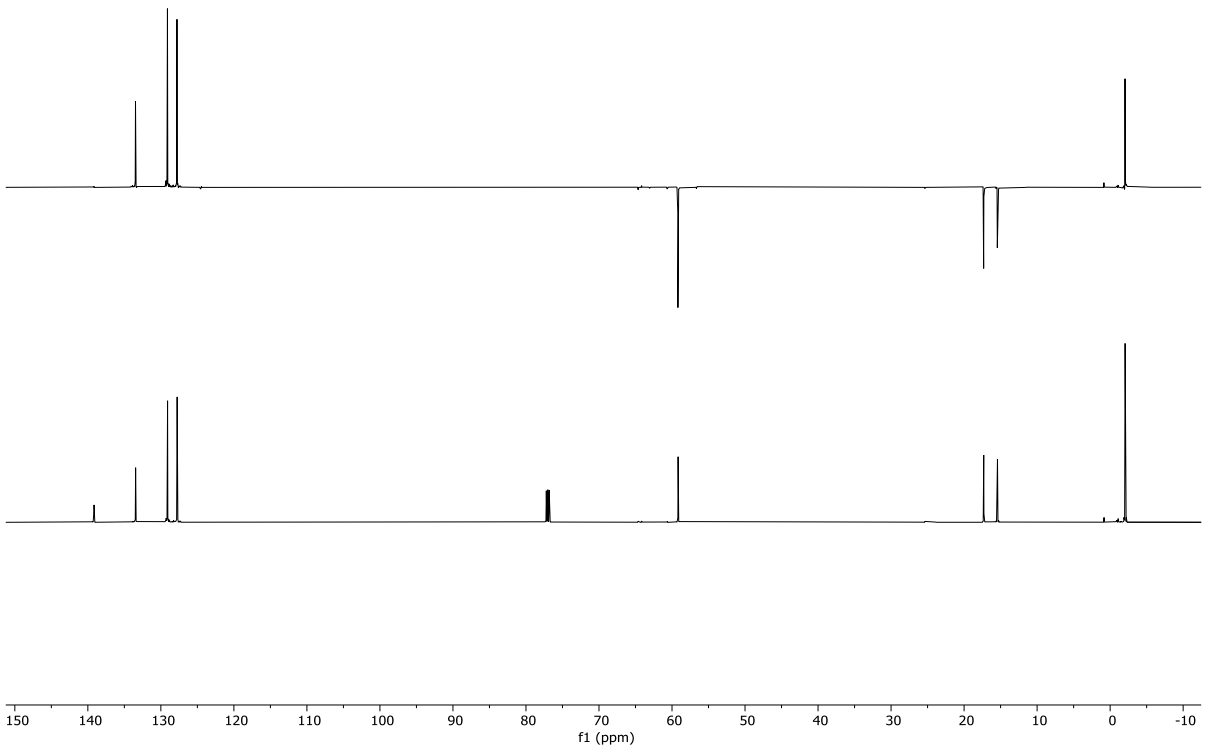


3p

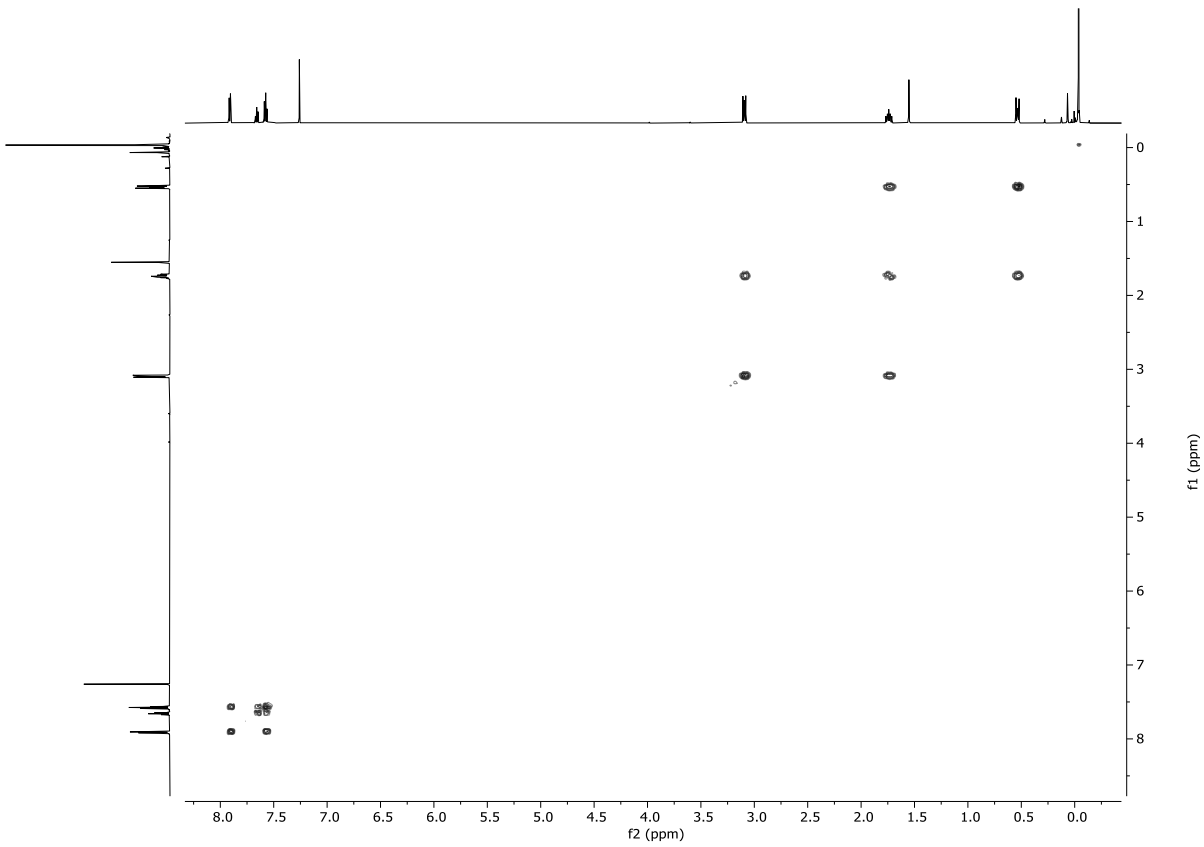
^{13}C{^{1}H}-NMR of compound 3p (150 MHz, $CDCl_3$)



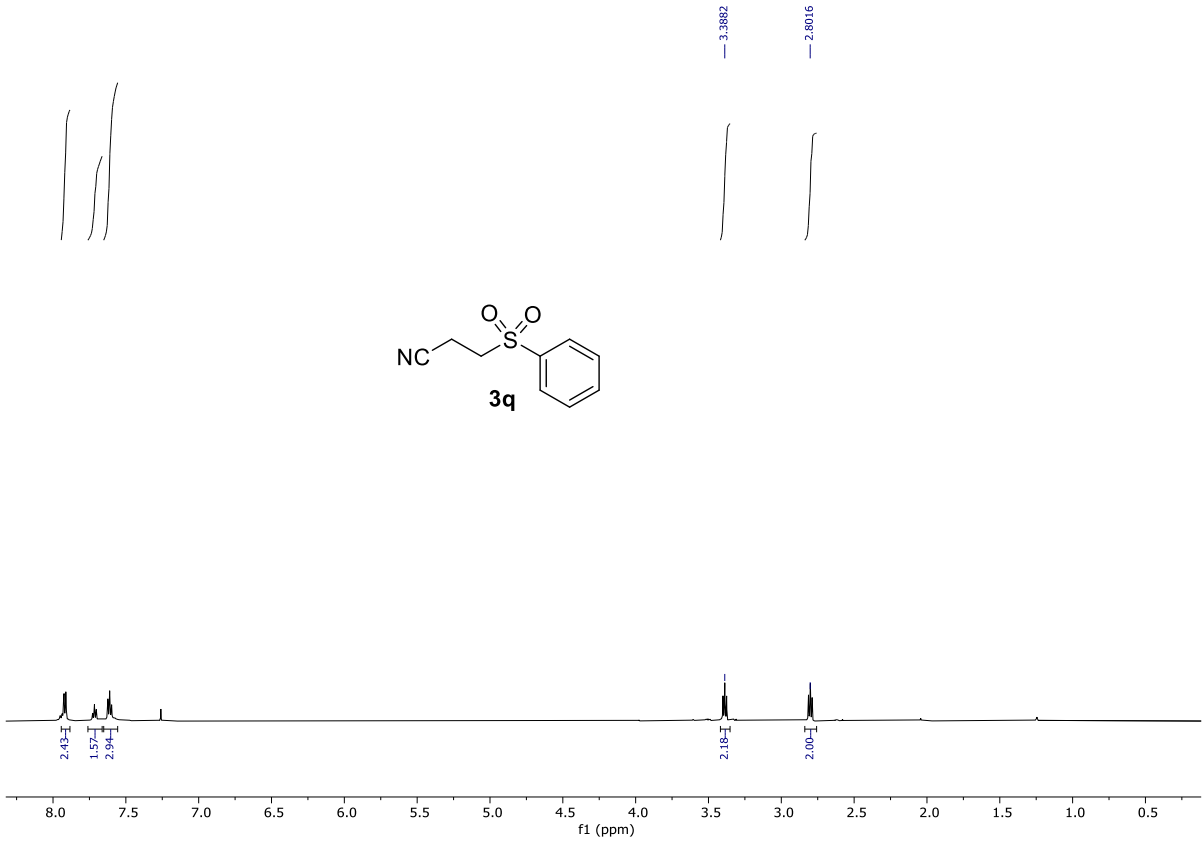
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3p (150 MHz, $CDCl_3$)



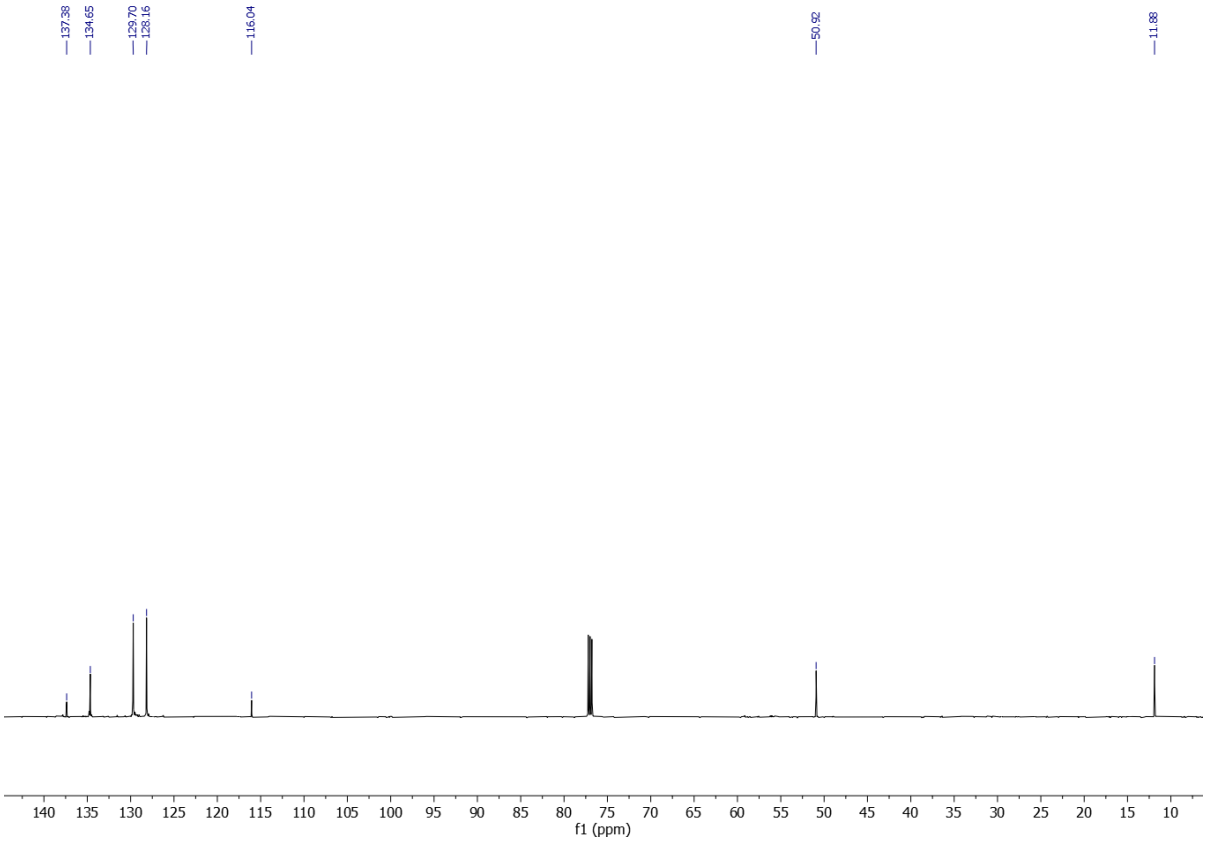
COSY-NMR of compound 3p (600 MHz, $CDCl_3$)



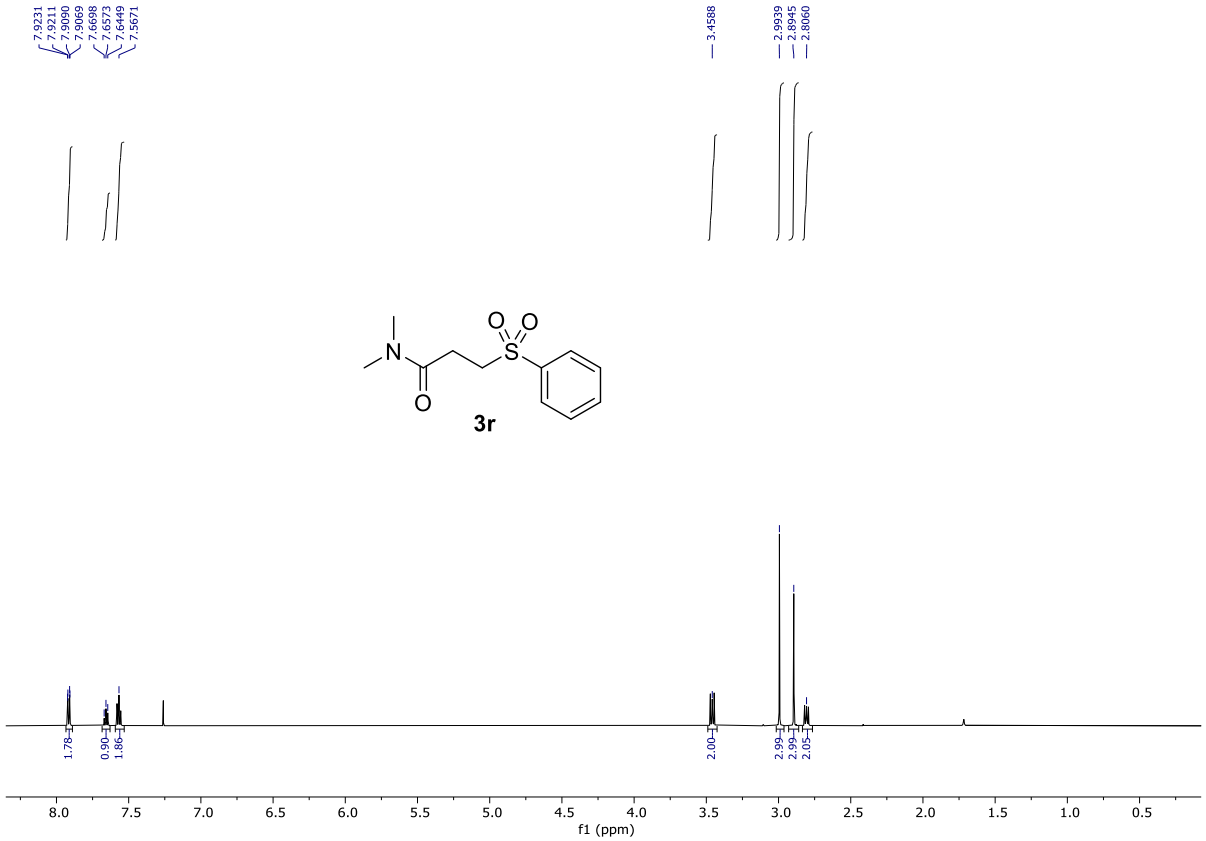
^{1}H-NMR of compound 3q (600 MHz, $CDCl_3$)



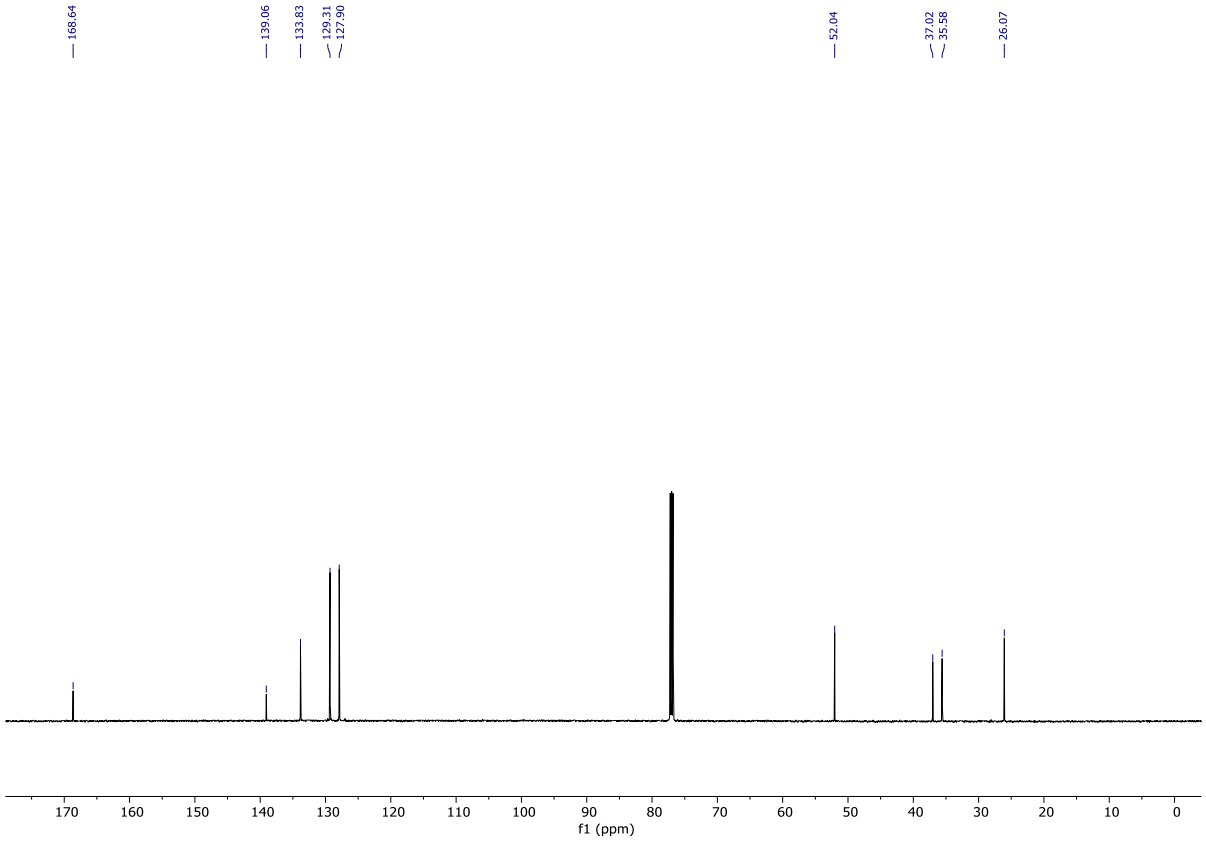
^{13}C{^{1}H}-NMR of compound 3q (150 MHz, $CDCl_3$)



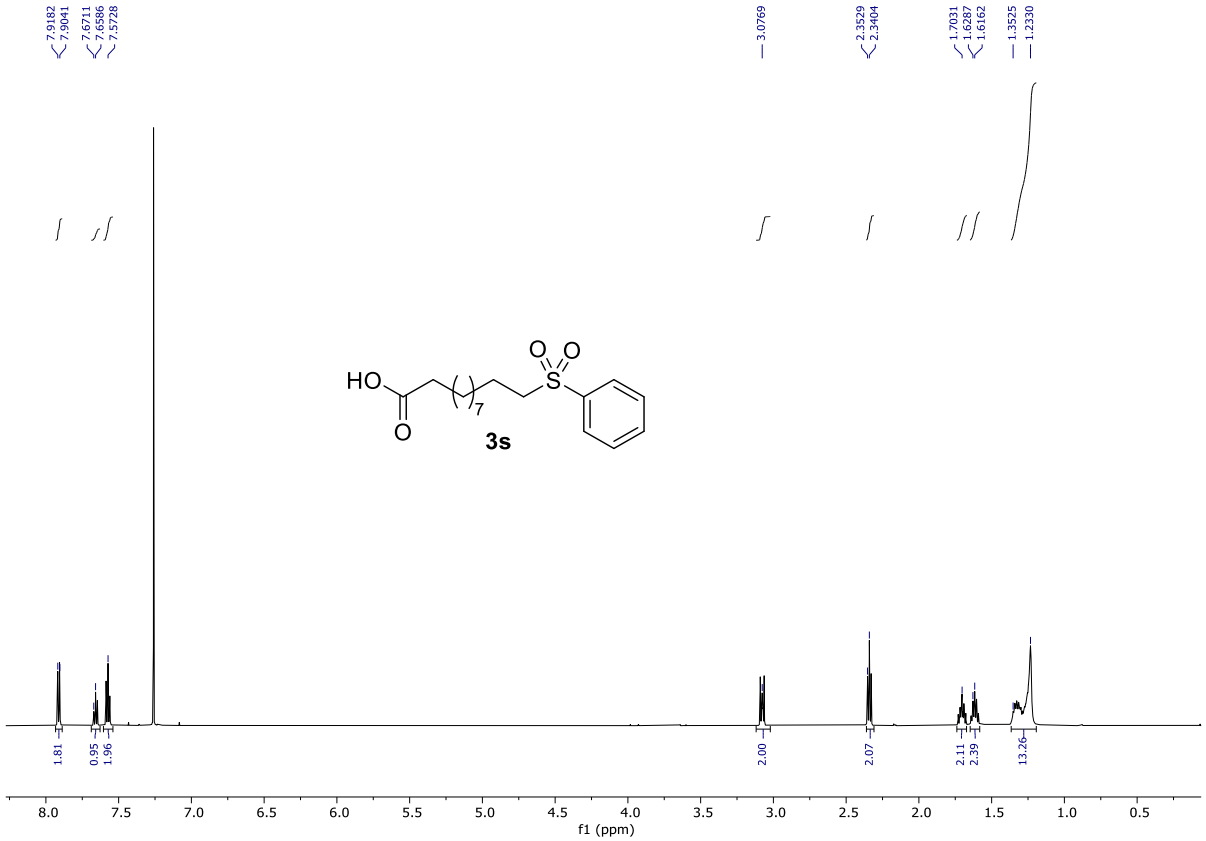
^{1}H-NMR of compound 3r (600 MHz, $CDCl_3$)



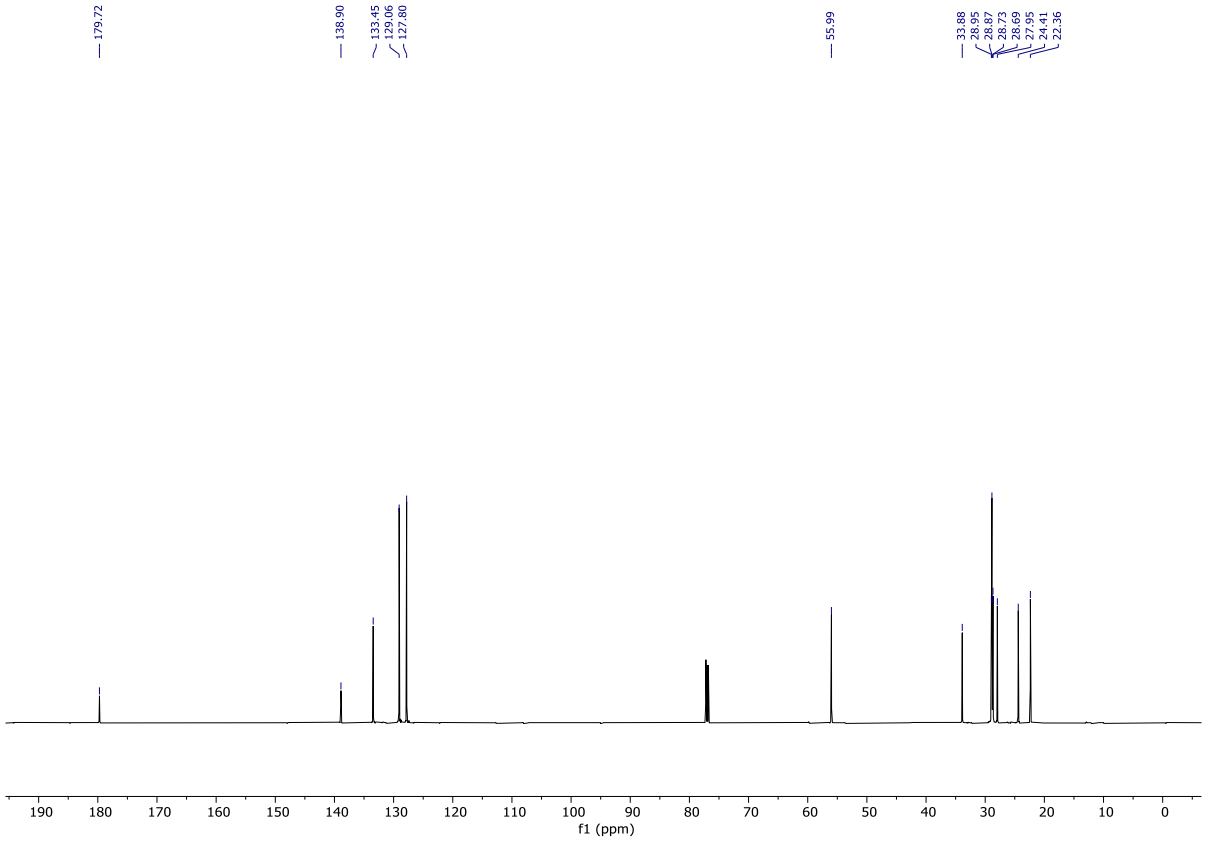
^{13}C{^{1}H}-NMR of compound 3r (150 MHz, $CDCl_3$)



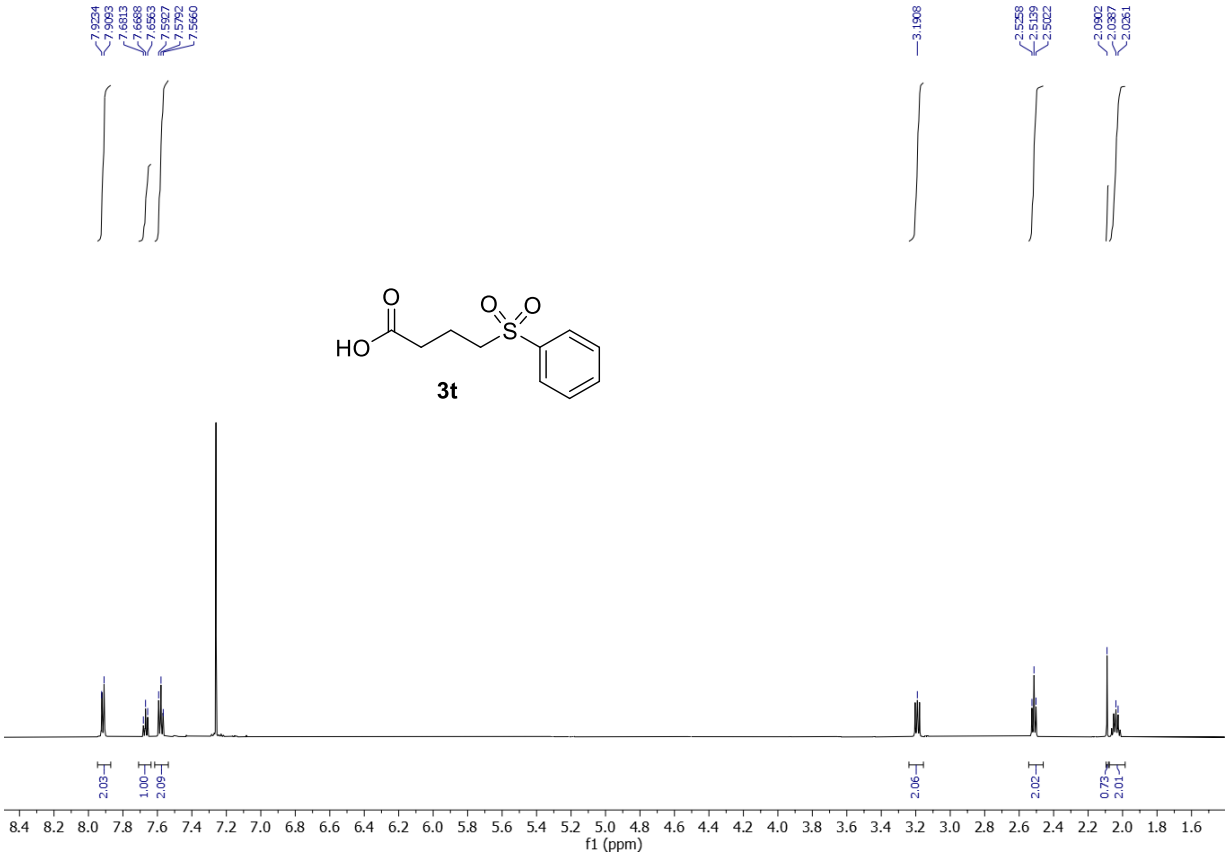
^{1}H-NMR of compound 3s (600 MHz, $CDCl_3$)



^{13}C{^{1}H}-NMR of compound 3s (150 MHz, $CDCl_3$)

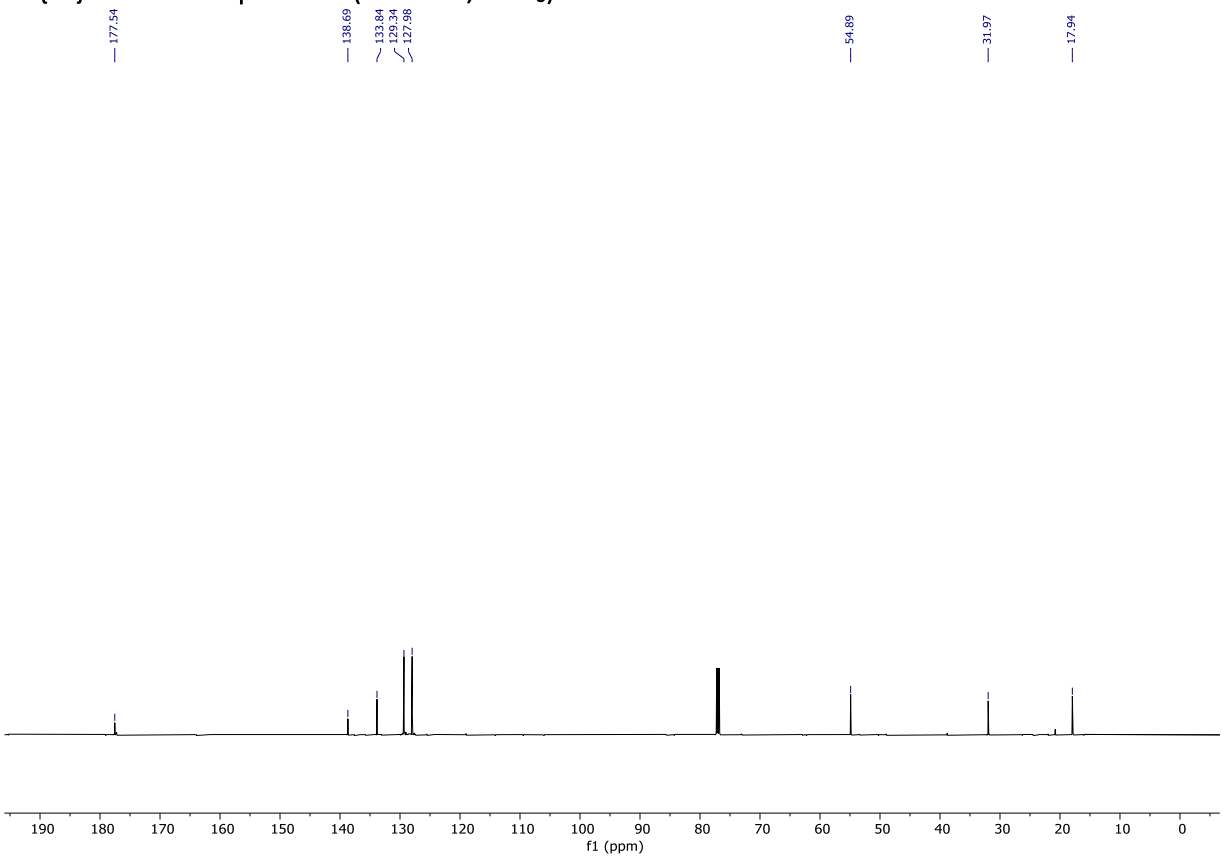


^{1}H-NMR of compound 3t (600 MHz, $CDCl_3$)

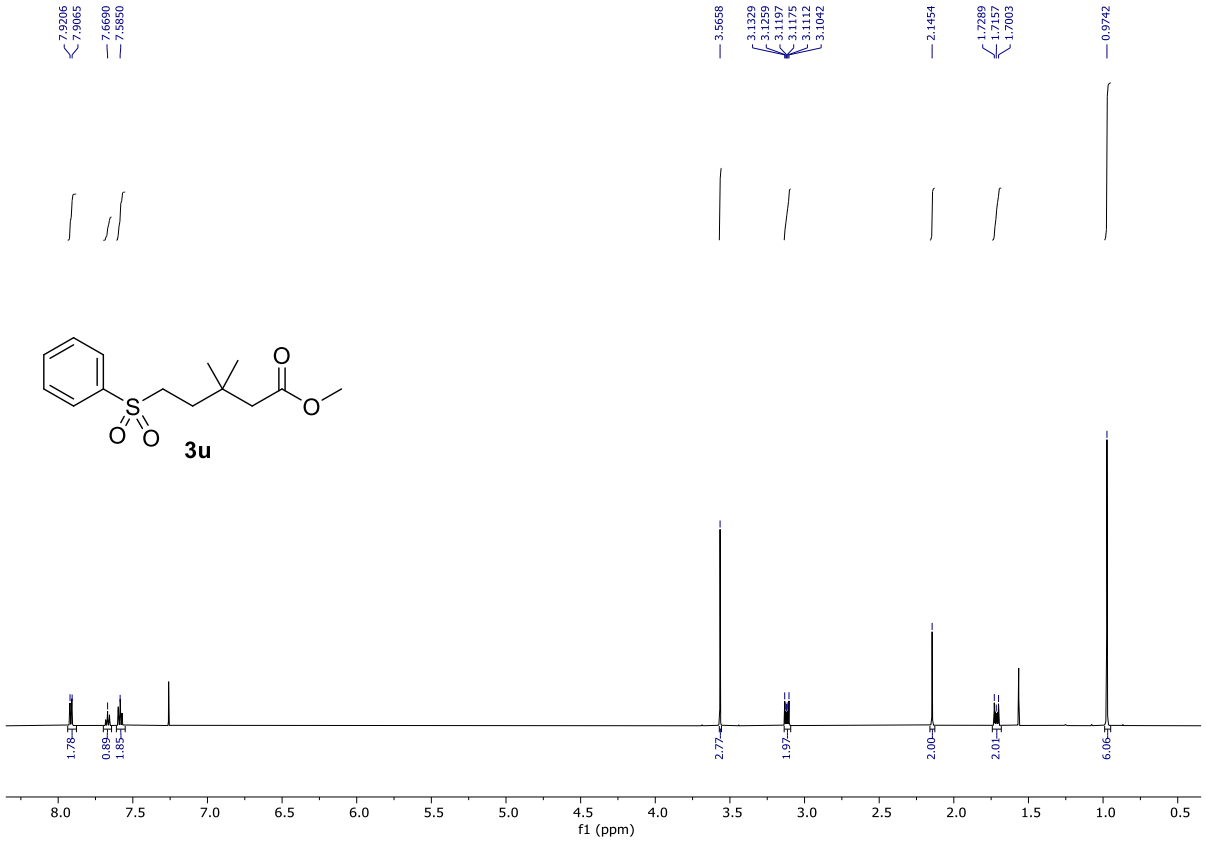


3t

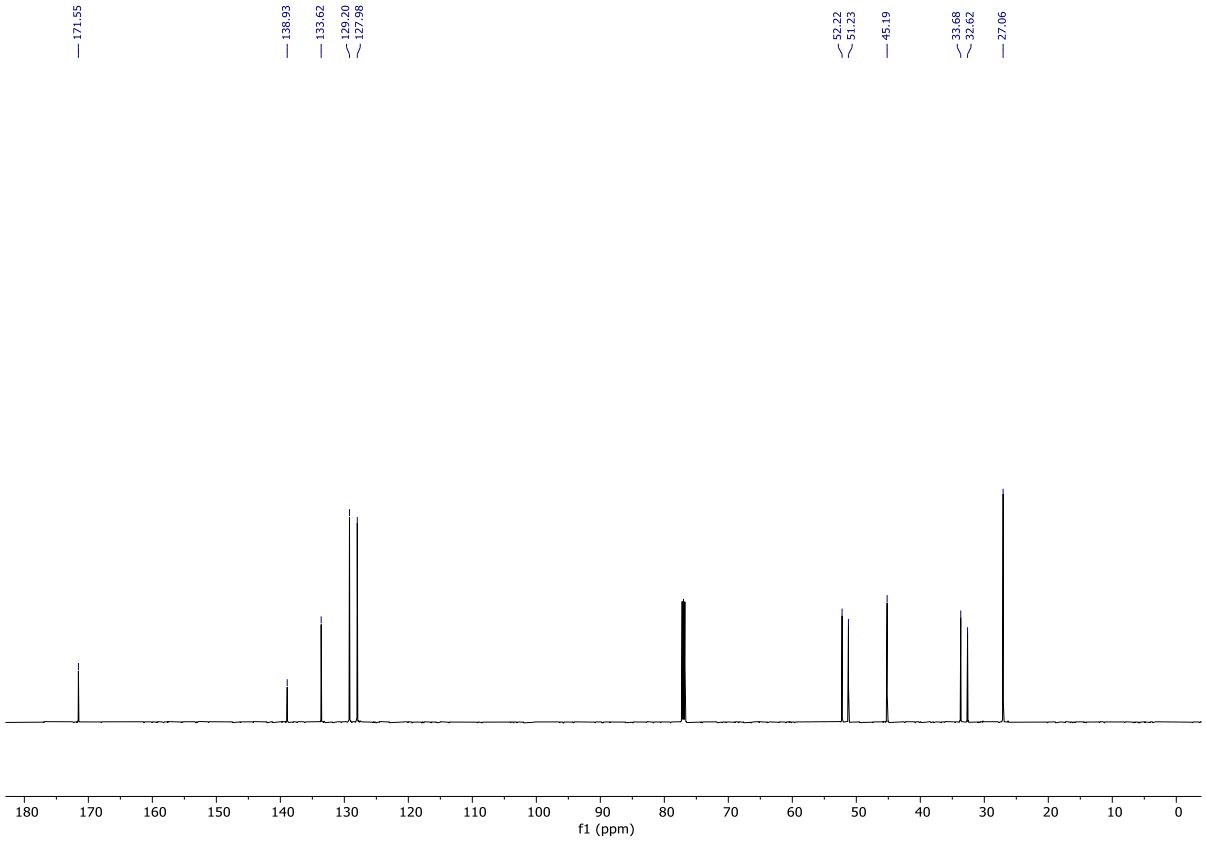
^{13}C{^{1}H}-NMR of compound 3t (150 MHz, $CDCl_3$)



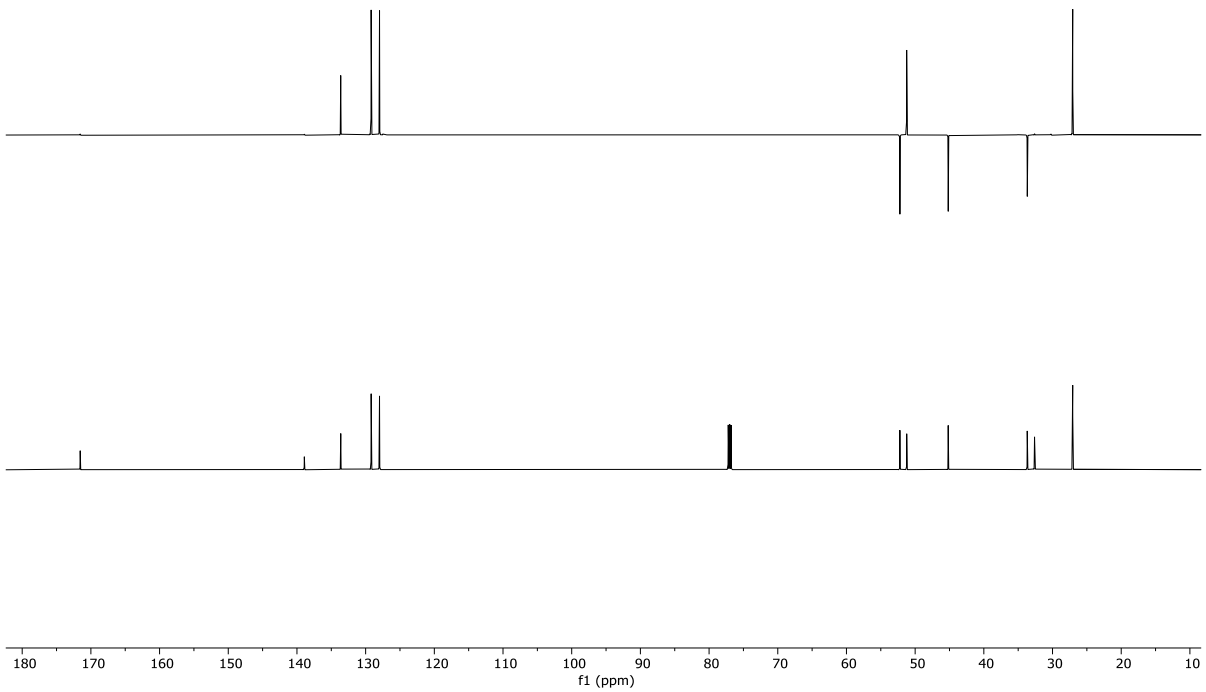
^{1}H-NMR of compound 3u (600 MHz, $CDCl_3$)



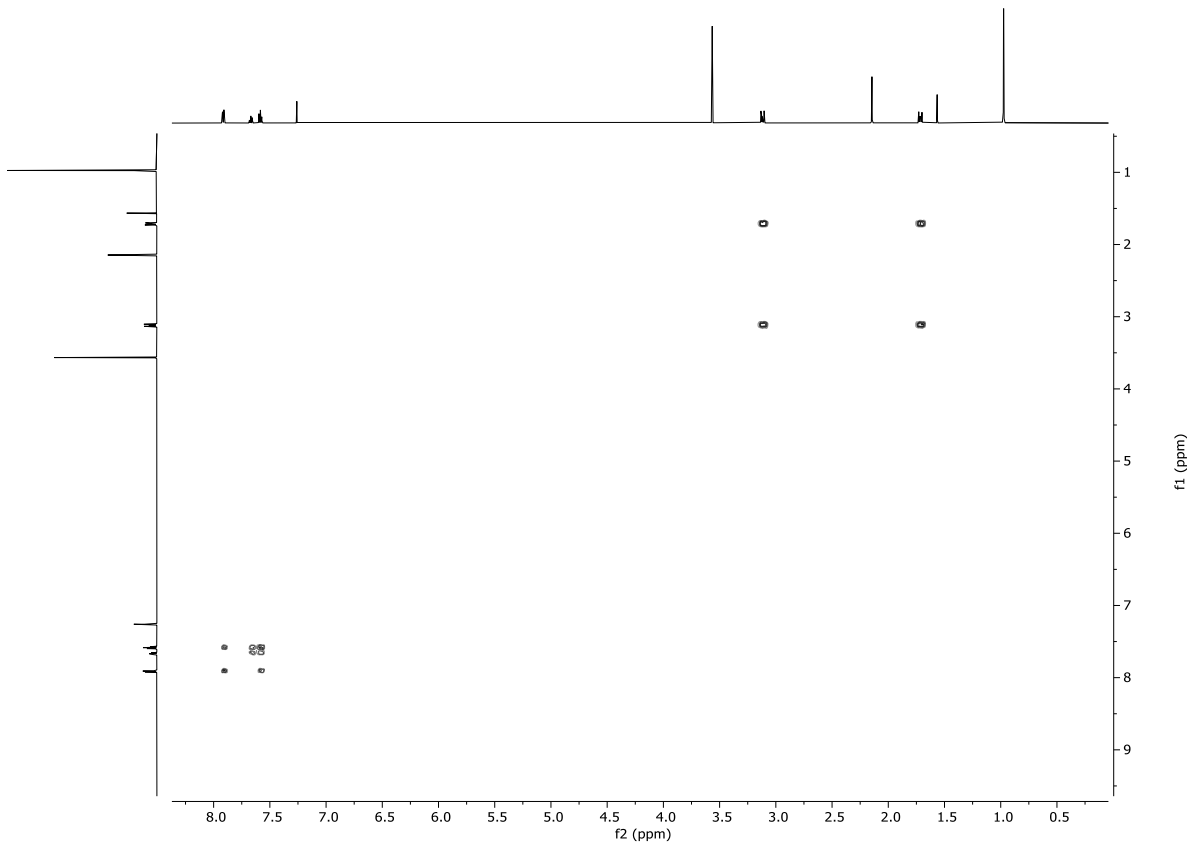
^{13}C{^{1}H}-NMR of compound 3u (150 MHz, $CDCl_3$)



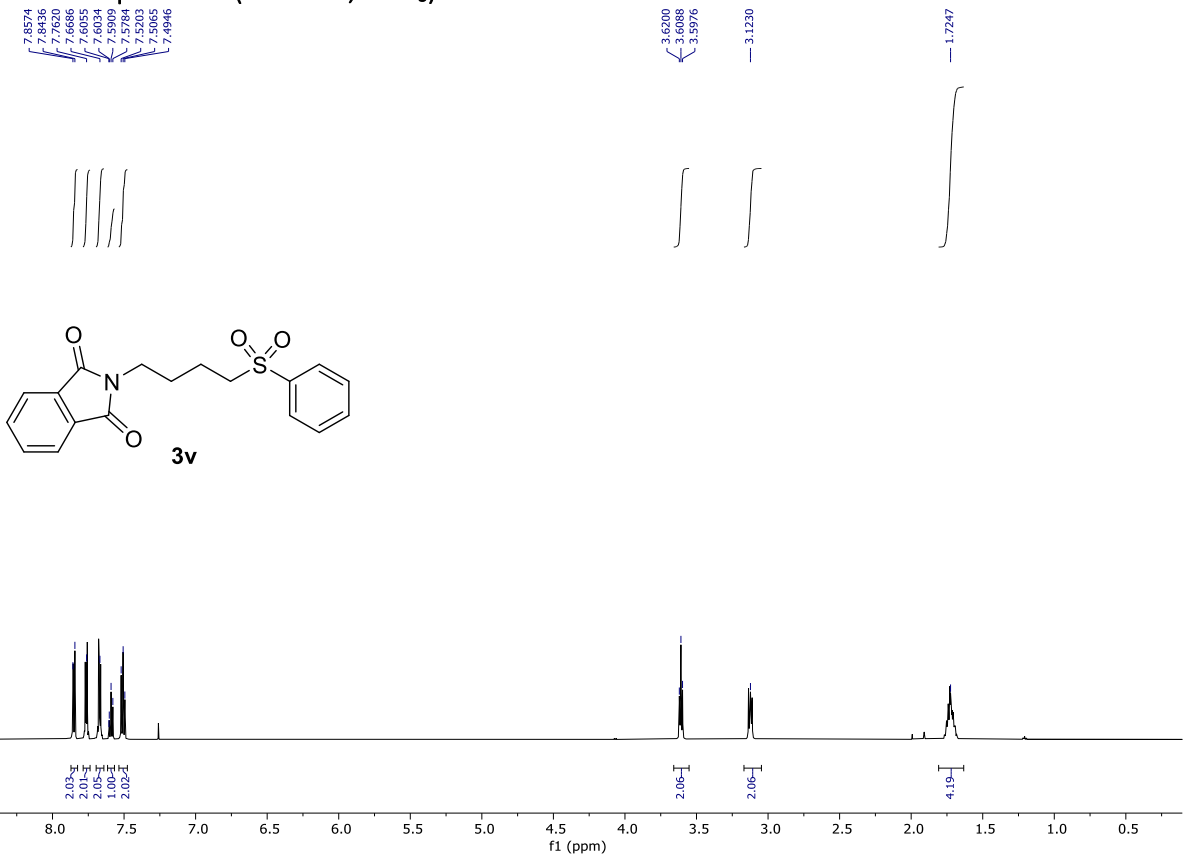
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3u (150 MHz, $CDCl_3$)



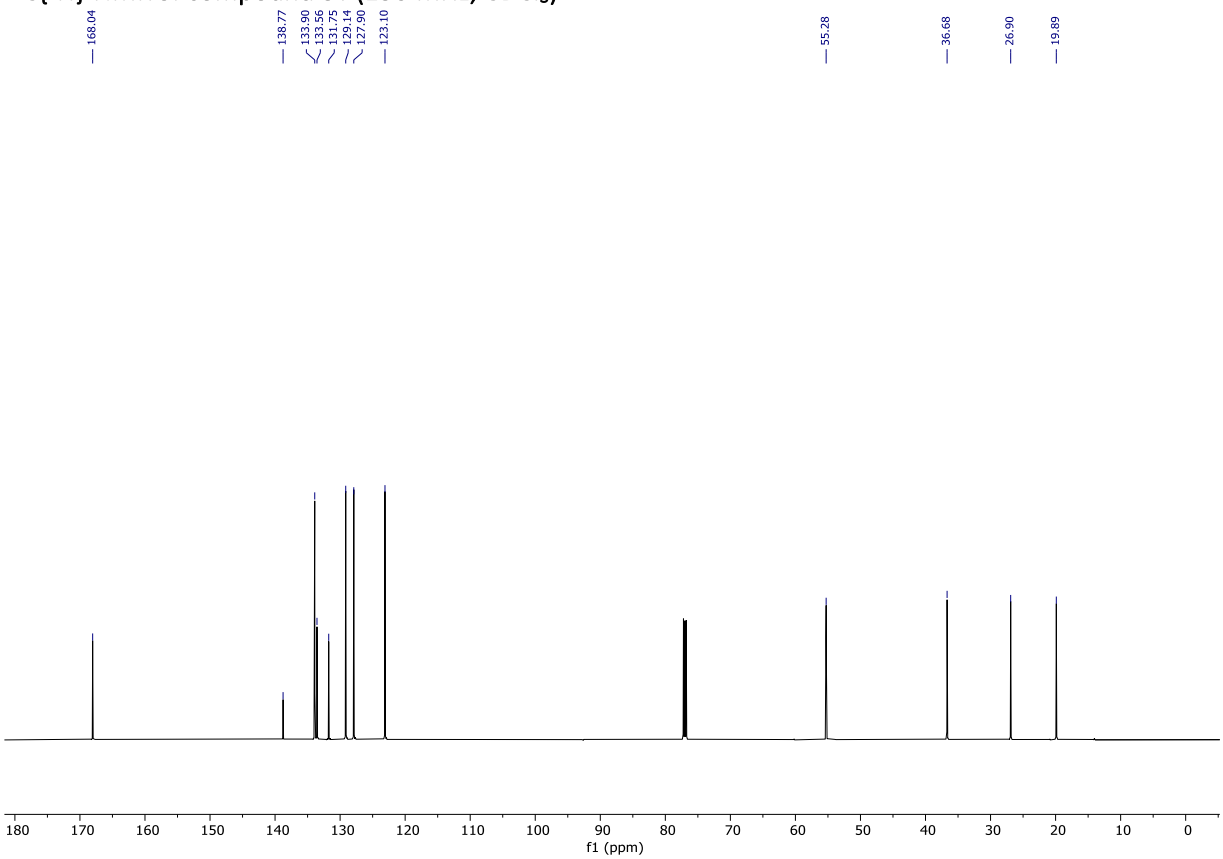
COSY-NMR of compound 3u (600 MHz, $CDCl_3$)



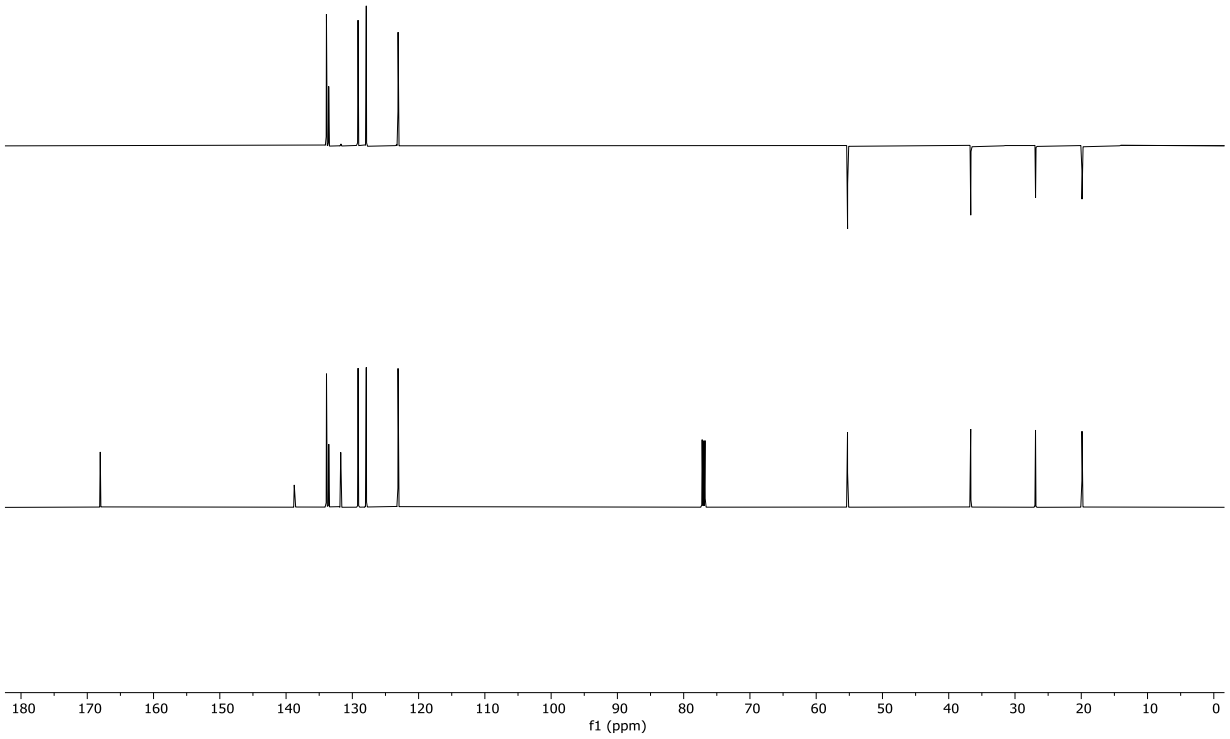
^{1}H-NMR of compound 3v (600 MHz, $CDCl_3$)



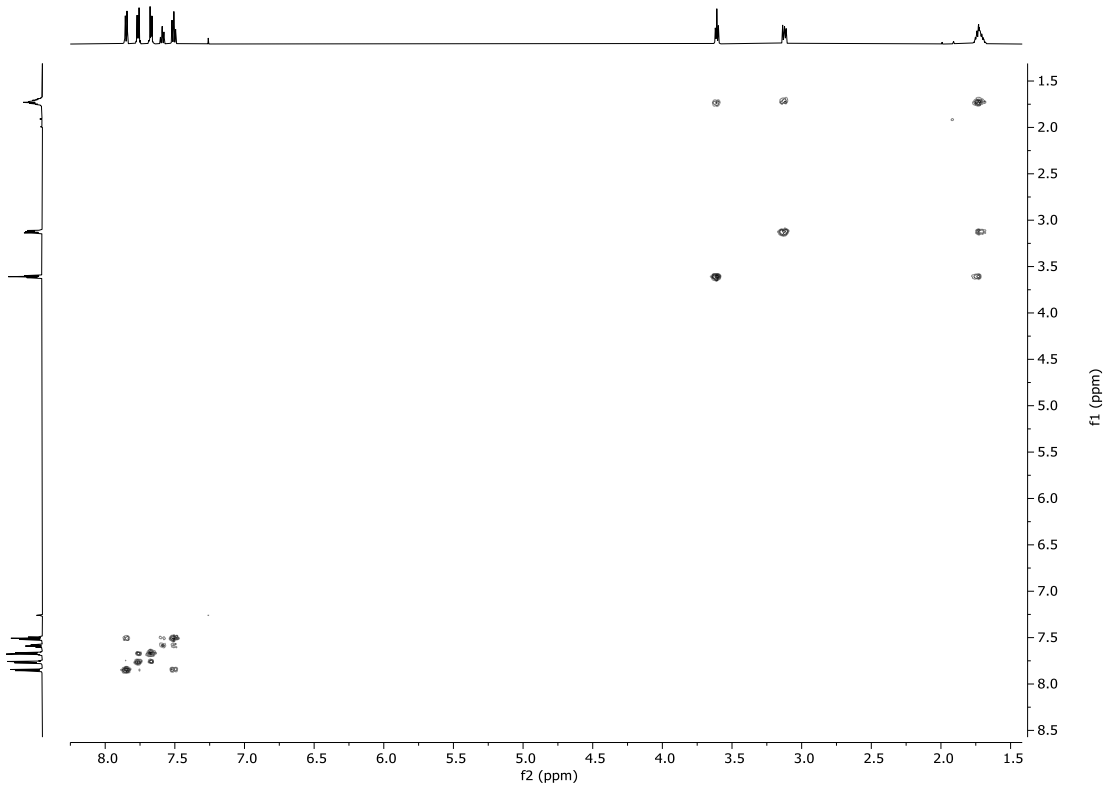
^{13}C{^{1}H}-NMR of compound 3v (150 MHz, $CDCl_3$)



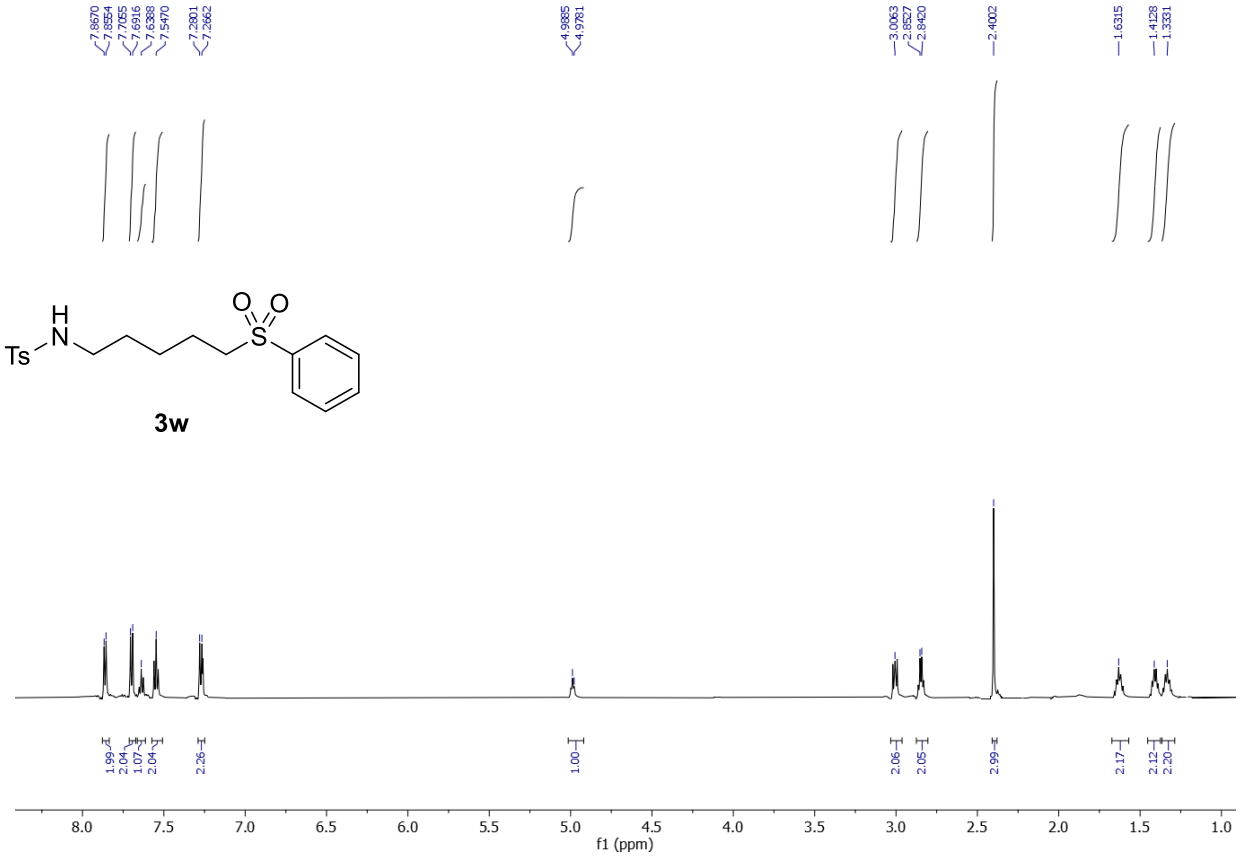
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3v (150 MHz, $CDCl_3$)



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

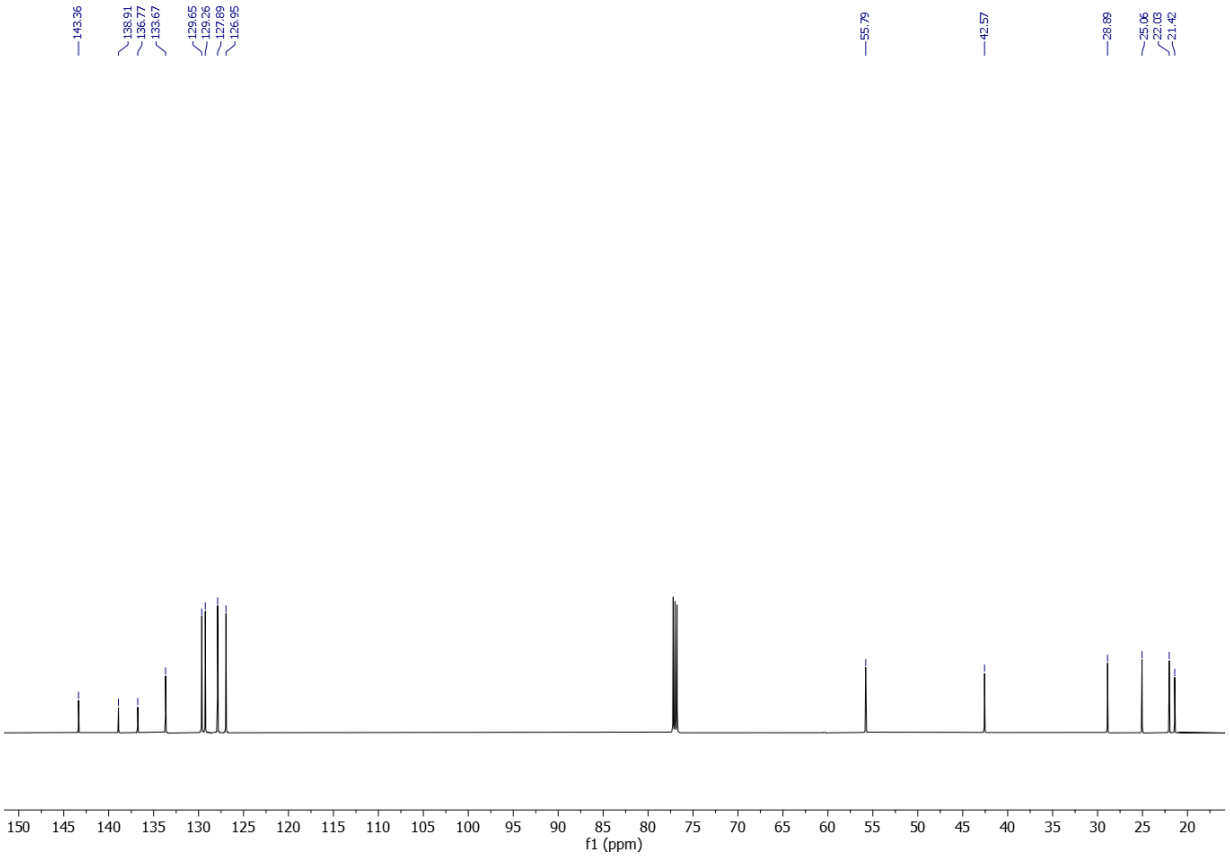


^{1}H-NMR of compound 3w (600 MHz, $CDCl_3$)

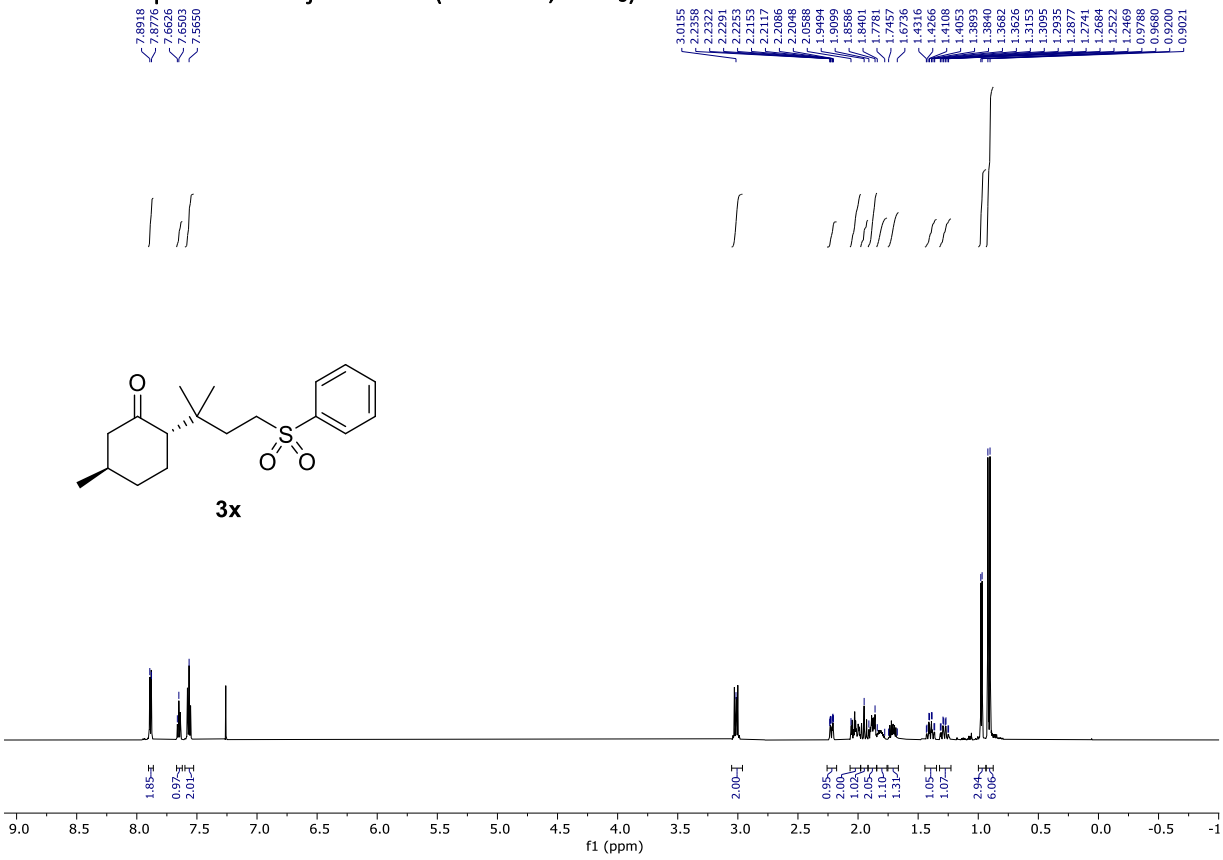


3w

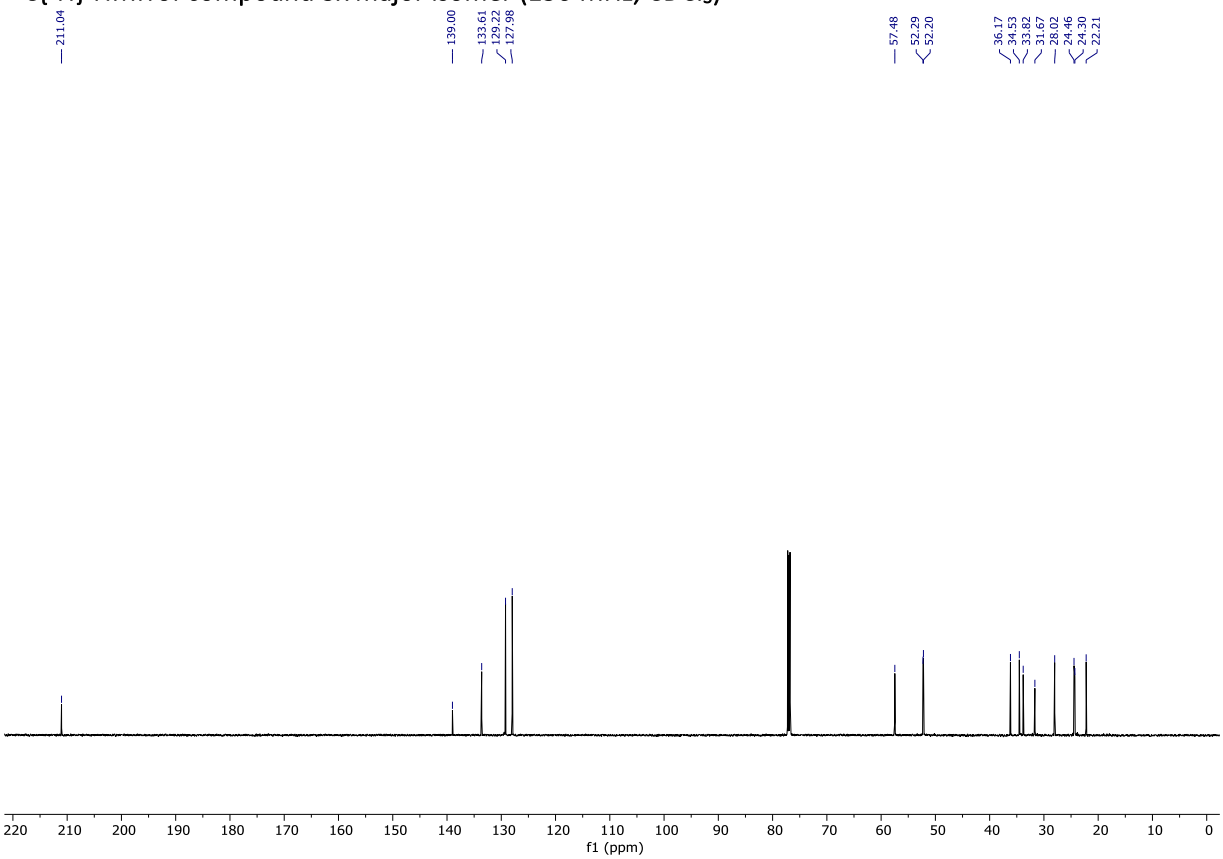
^{13}C{^{1}H}-NMR of compound 3w (150 MHz, $CDCl_3$)



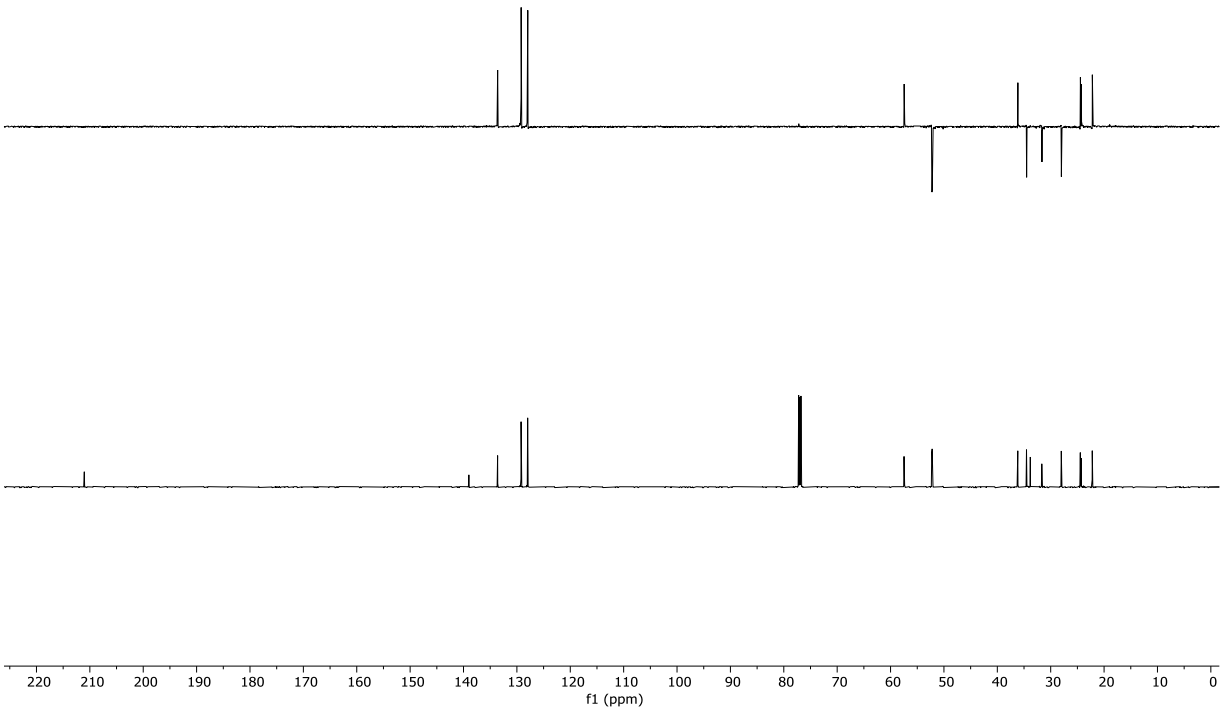
^{1}H-NMR of compound 3x major isomer (600 MHz, $CDCl_3$)



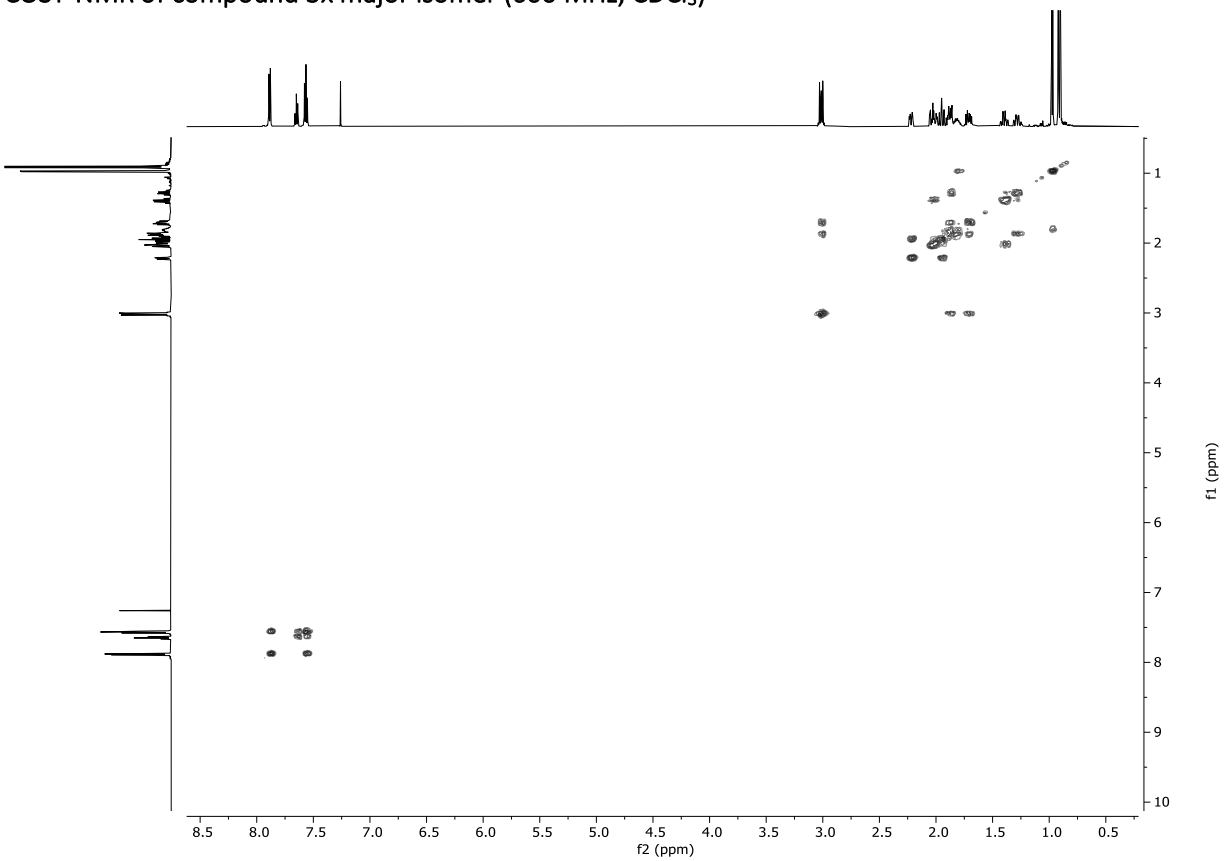
^{13}C{^{1}H}-NMR of compound 3x major isomer (150 MHz, $CDCl_3$)



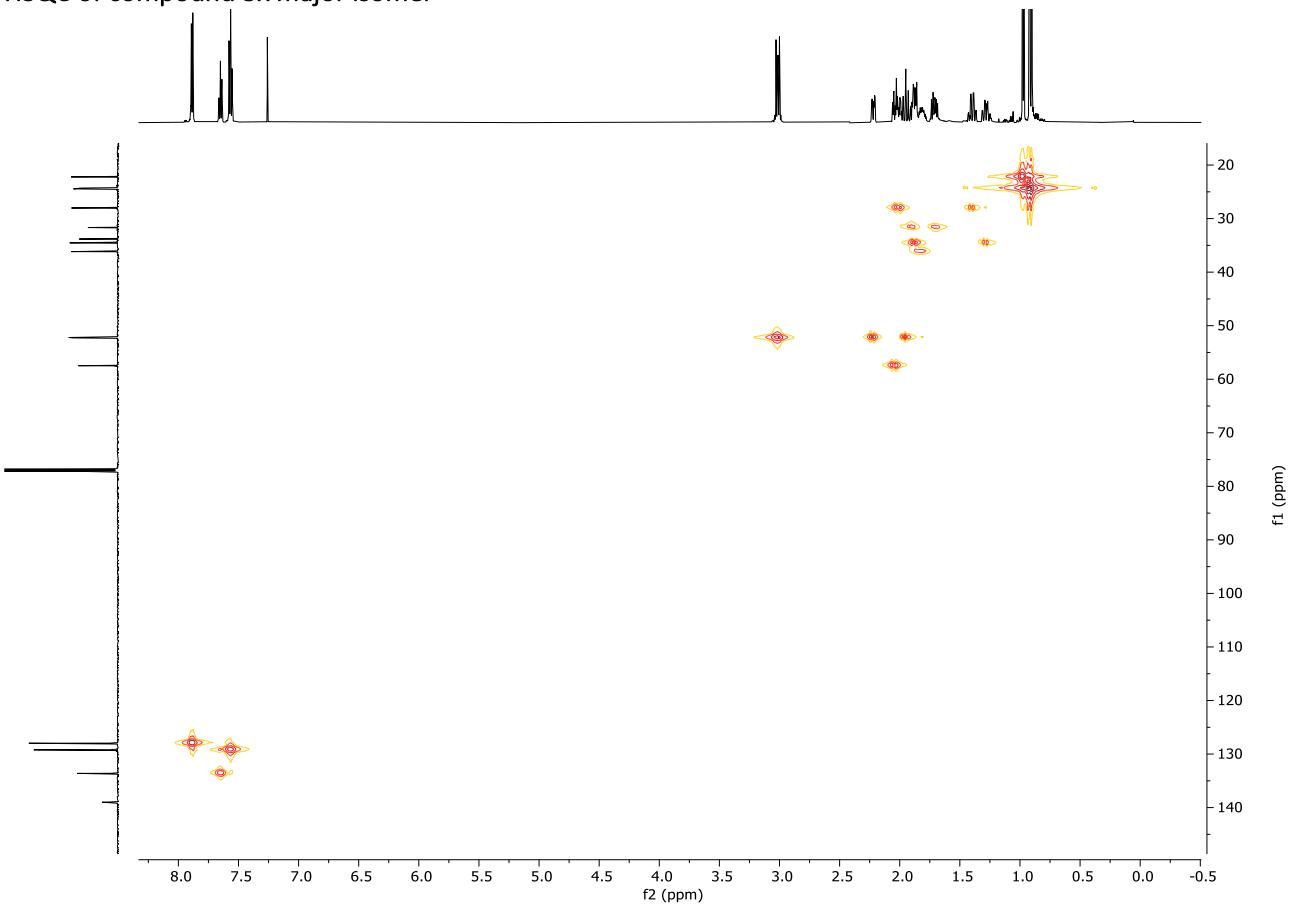
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3x major isomer (150 MHz, $CDCl_3$)



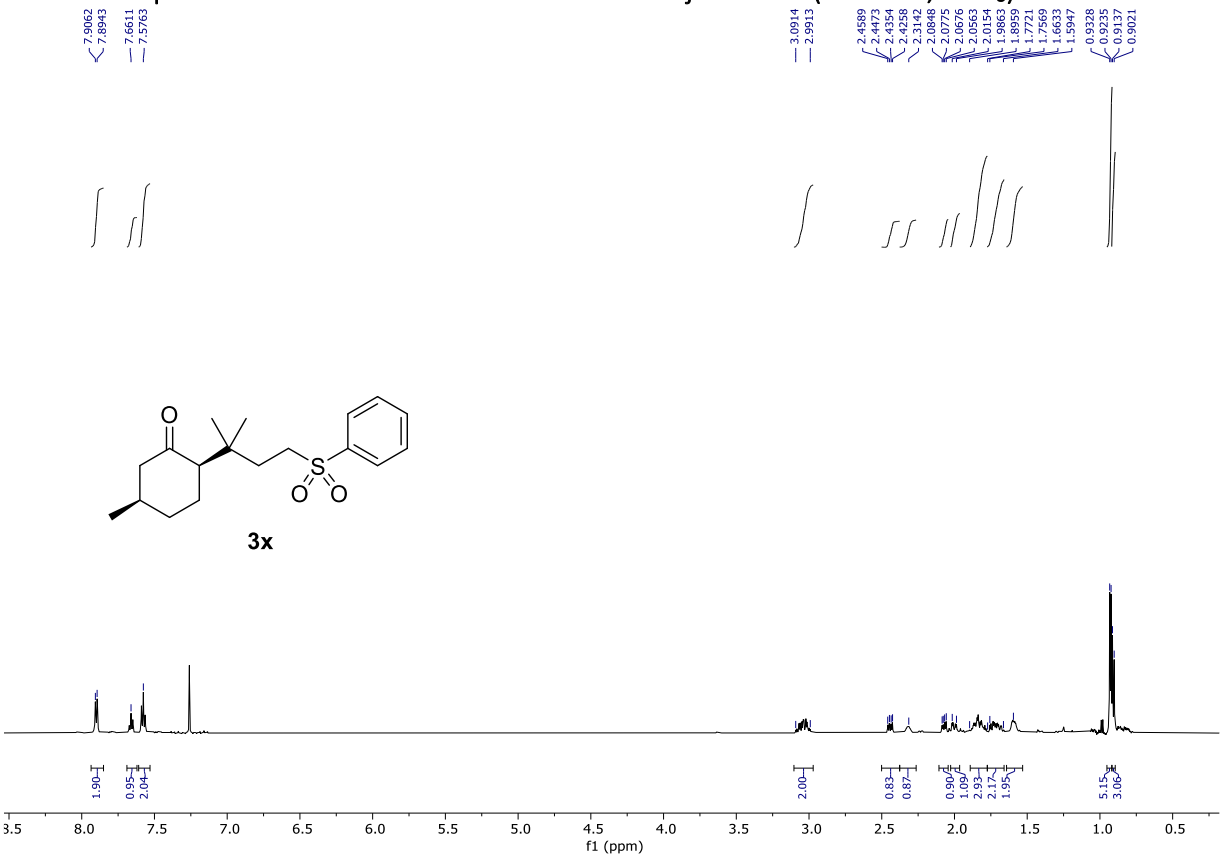
COSY-NMR of compound 3x major isomer (600 MHz, $CDCl_3$)



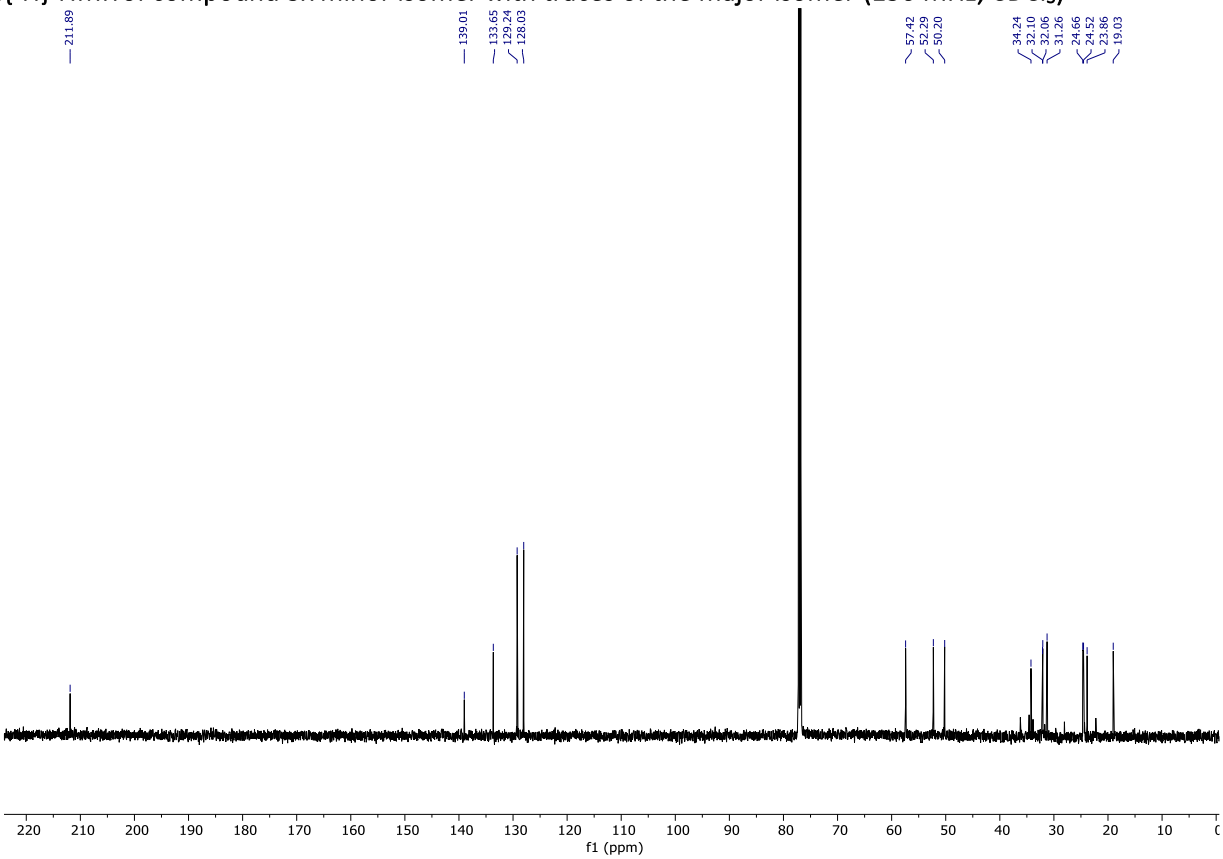
HSQC of compound 3x major isomer



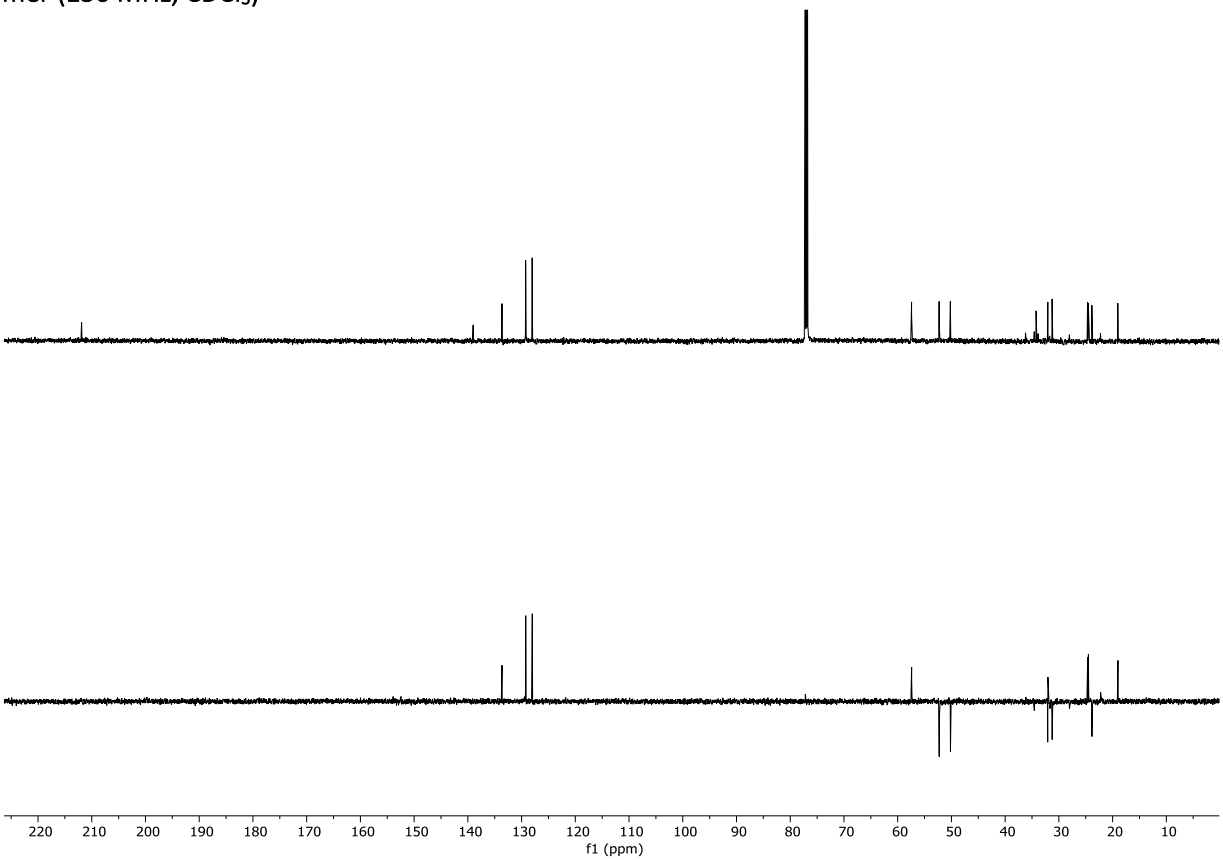
^{1}H-NMR of compound 3x minor isomer with traces of the major isomer (600 MHz, $CDCl_3$)



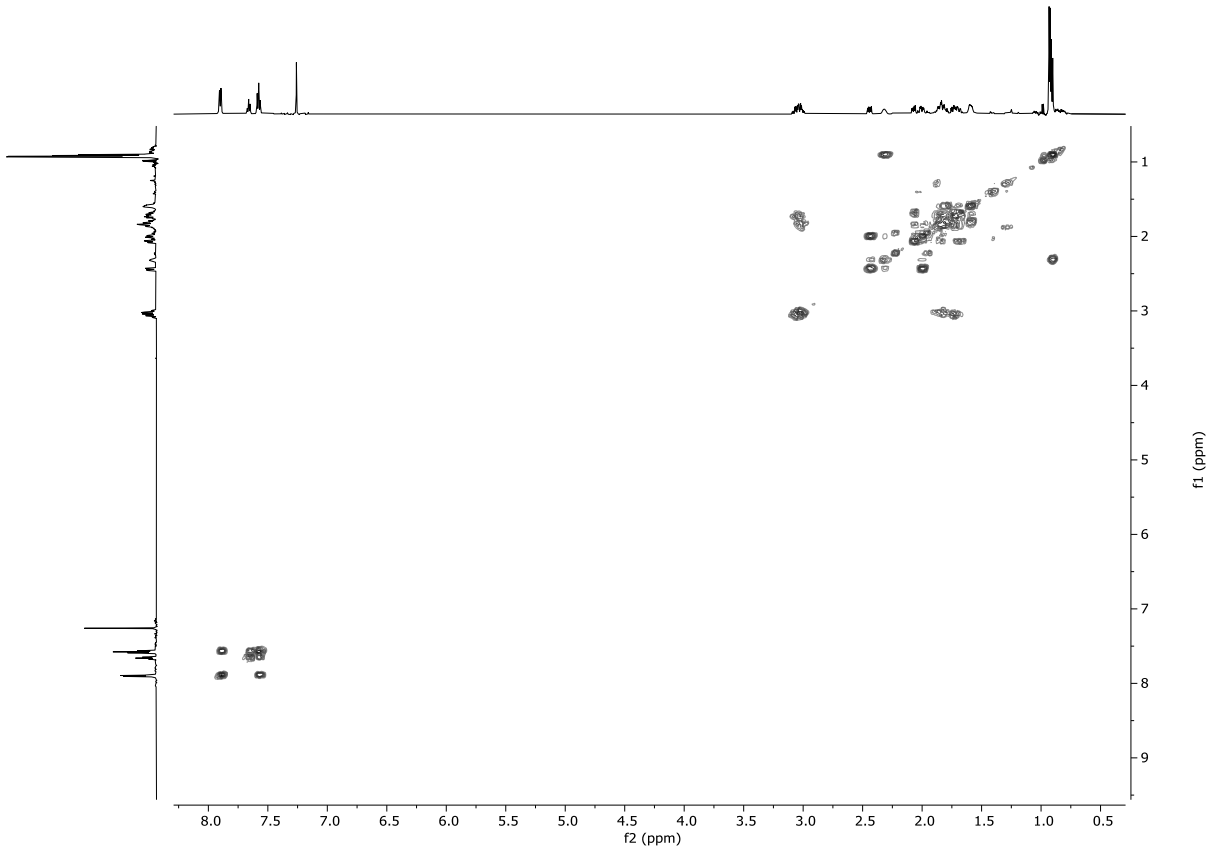
^{13}C{^{1}H}-NMR of compound 3x minor isomer with traces of the major isomer (150 MHz, $CDCl_3$)



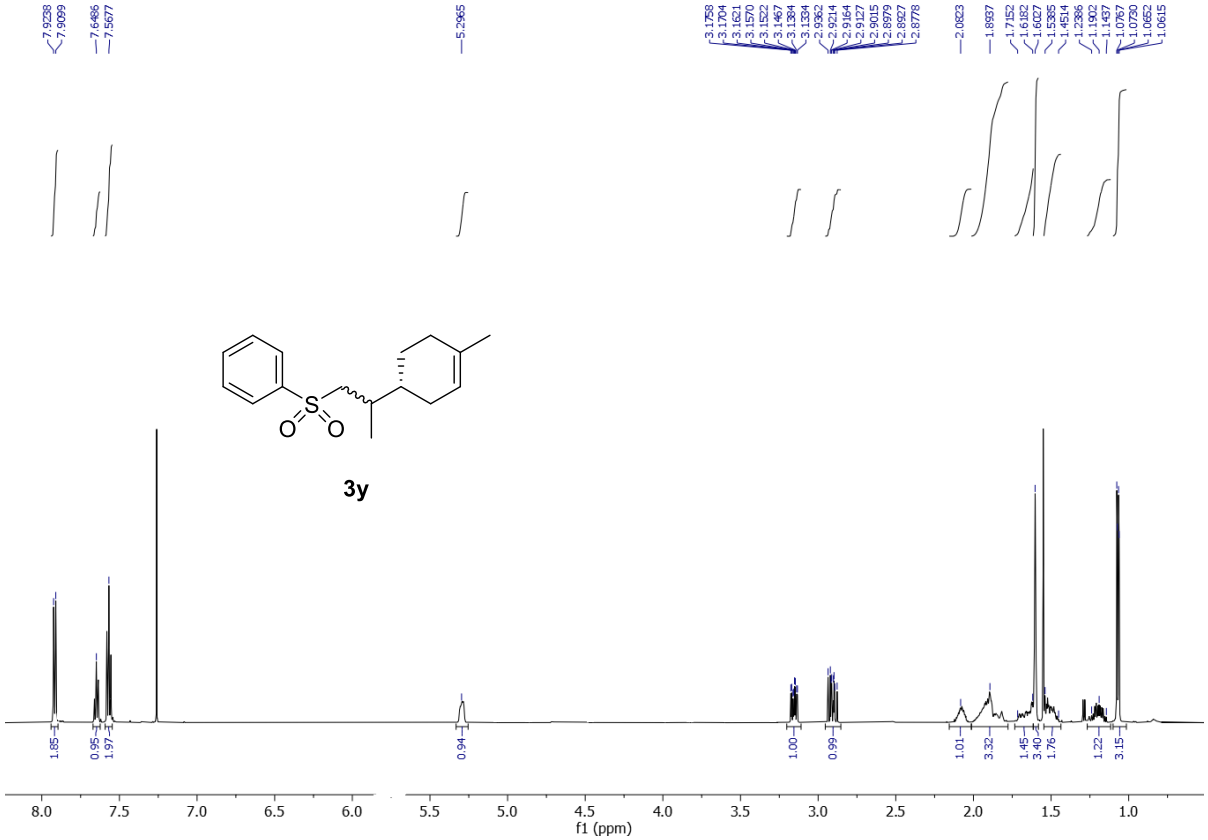
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3x minor isomer with traces of the major isomer (150 MHz, $CDCl_3$)



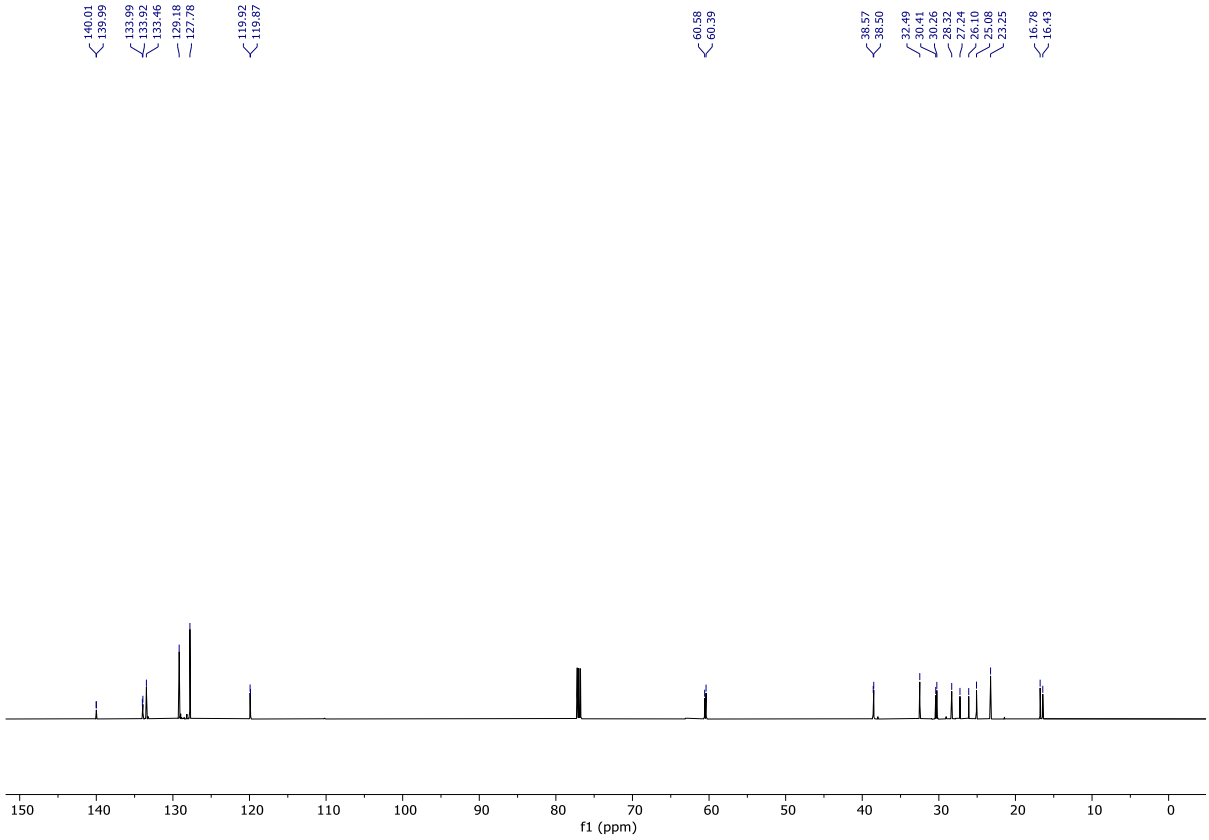
COSY-NMR of compound 3x minor isomer with traces of the major isomer (600 MHz, $CDCl_3$)



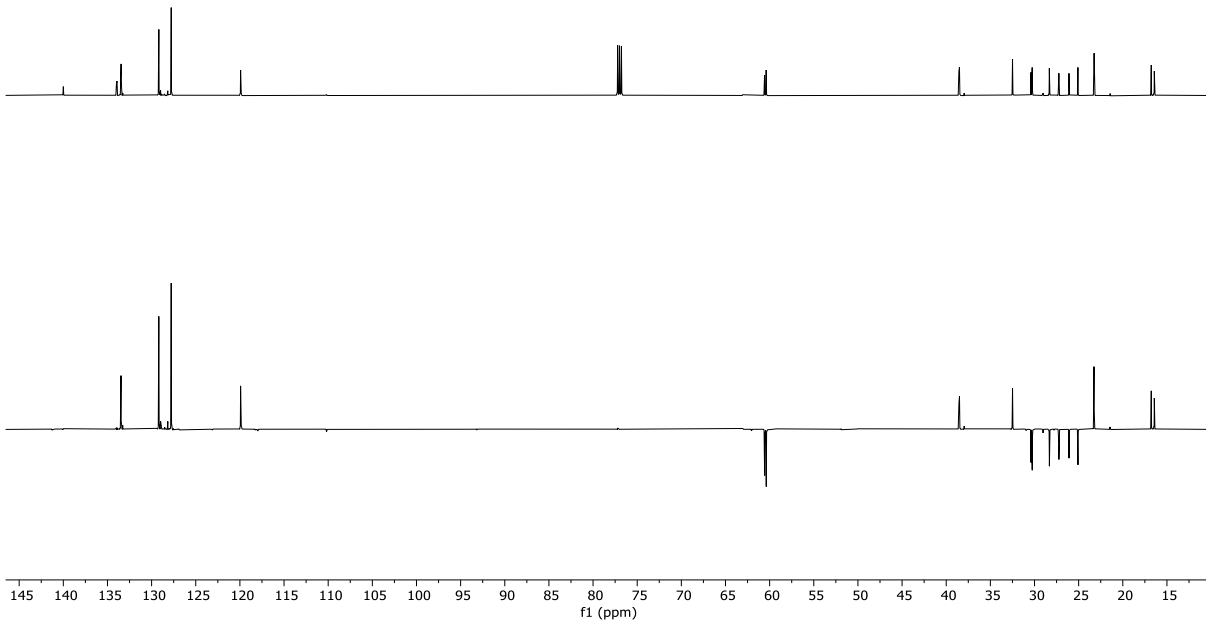
^{1}H-NMR of compound 3y (600 MHz, $CDCl_3$)



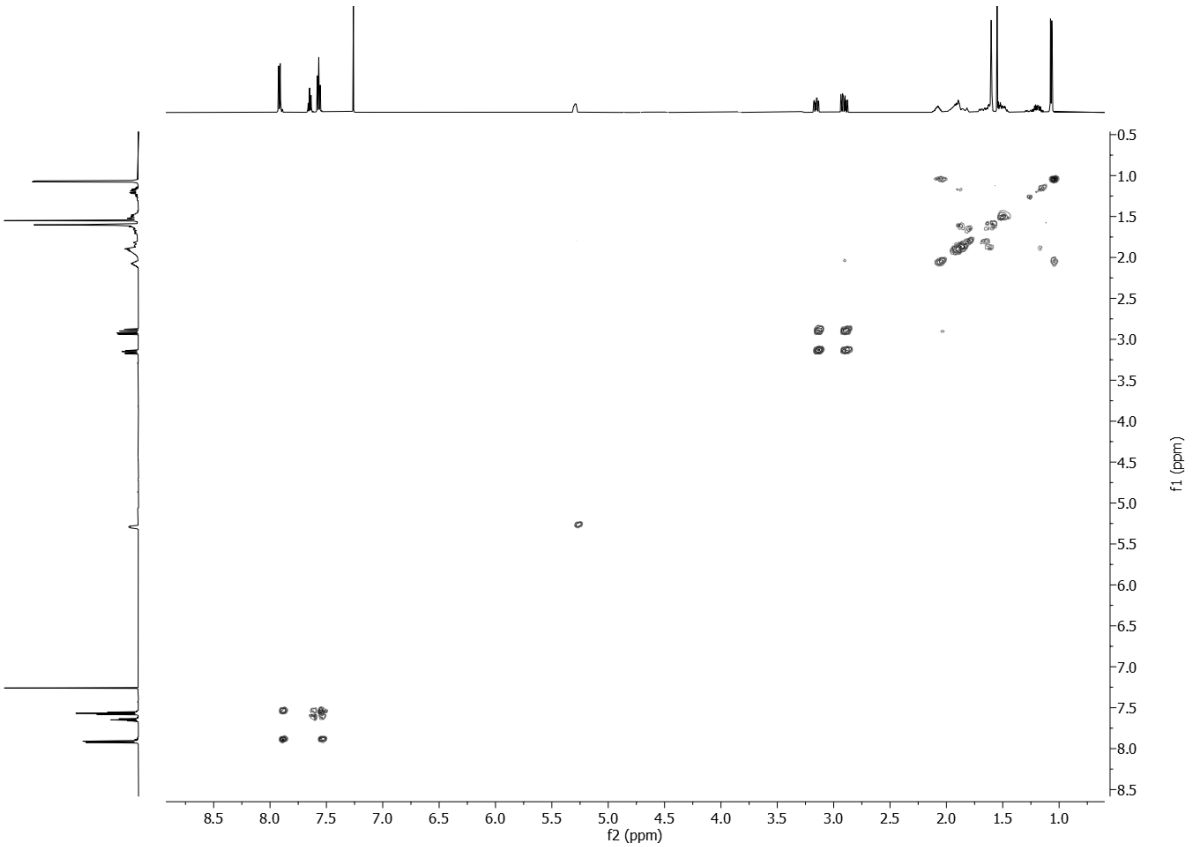
^{13}C{^{1}H}-NMR of compound 3y (150 MHz, $CDCl_3$)



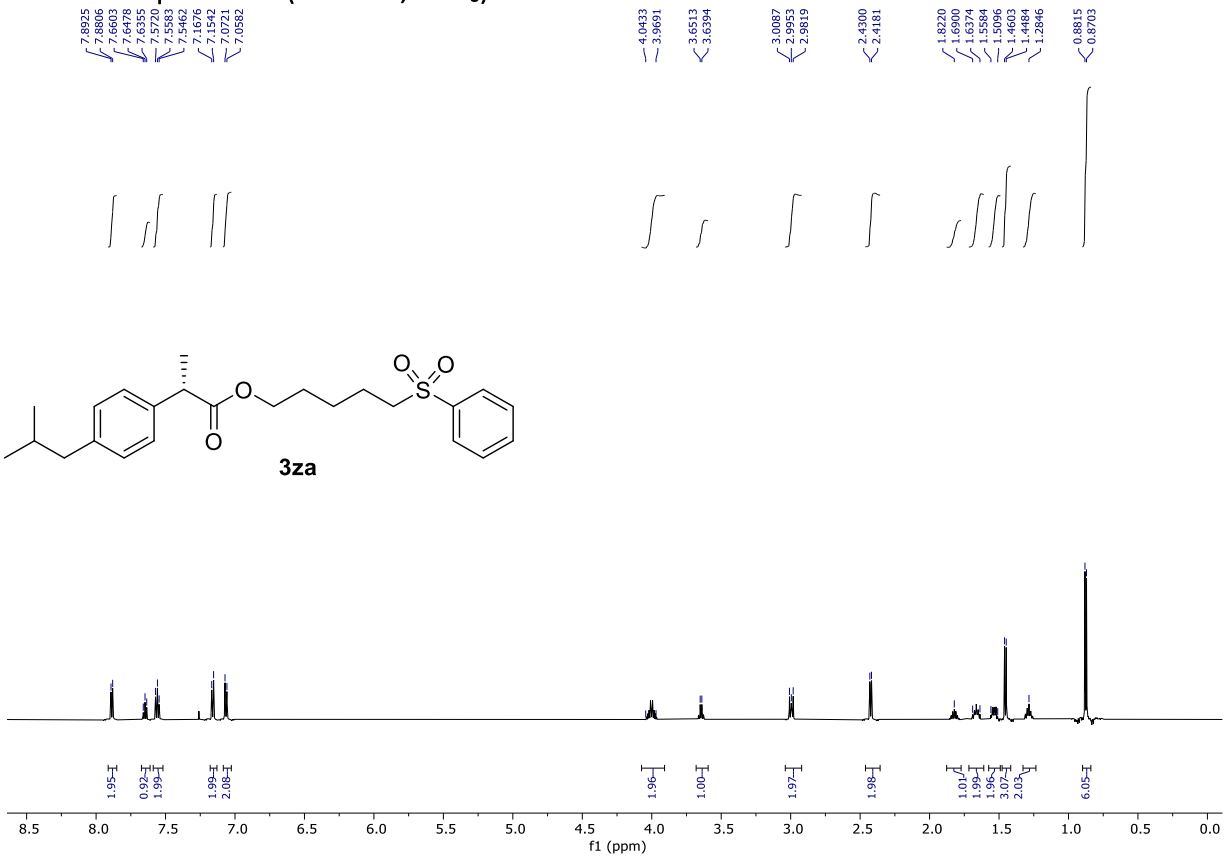
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3y (150 MHz, $CDCl_3$)



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

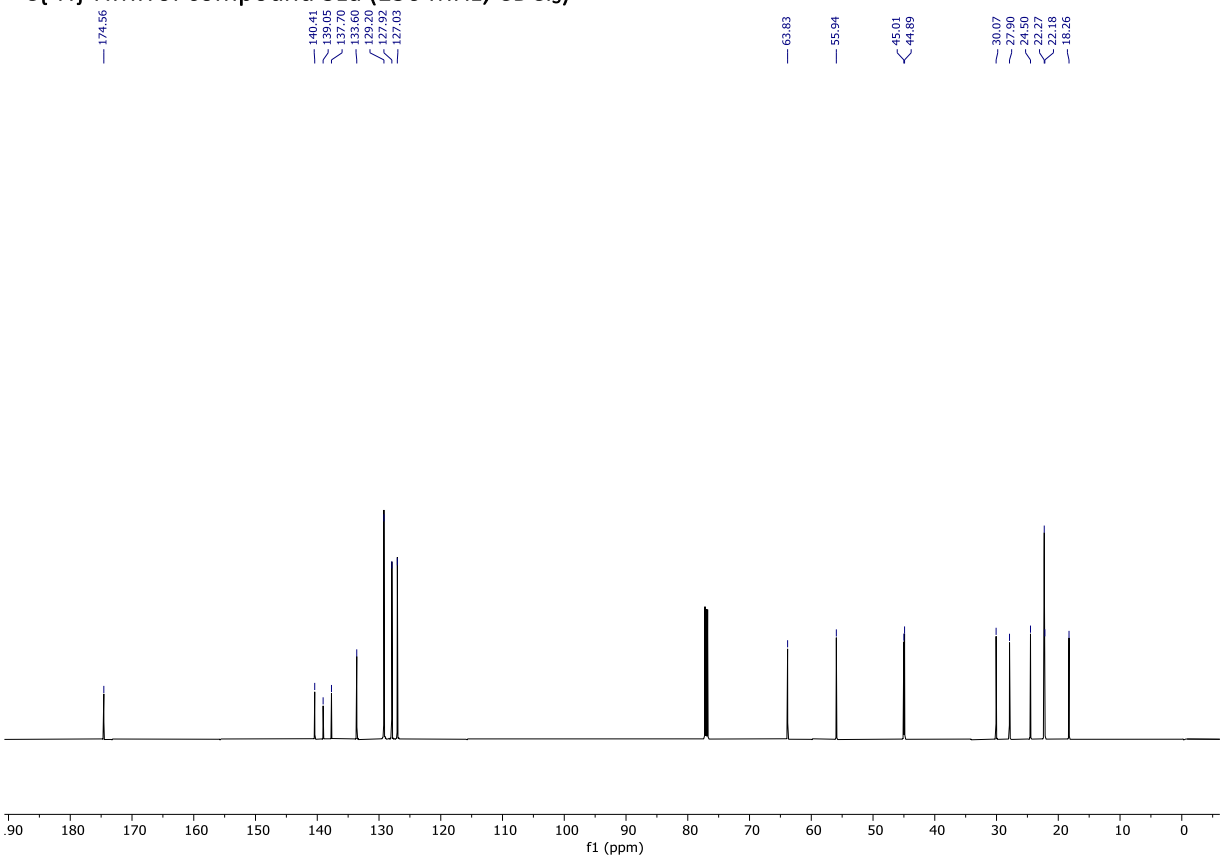


^{1}H-NMR of compound 3za (600 MHz, $CDCl_3$)

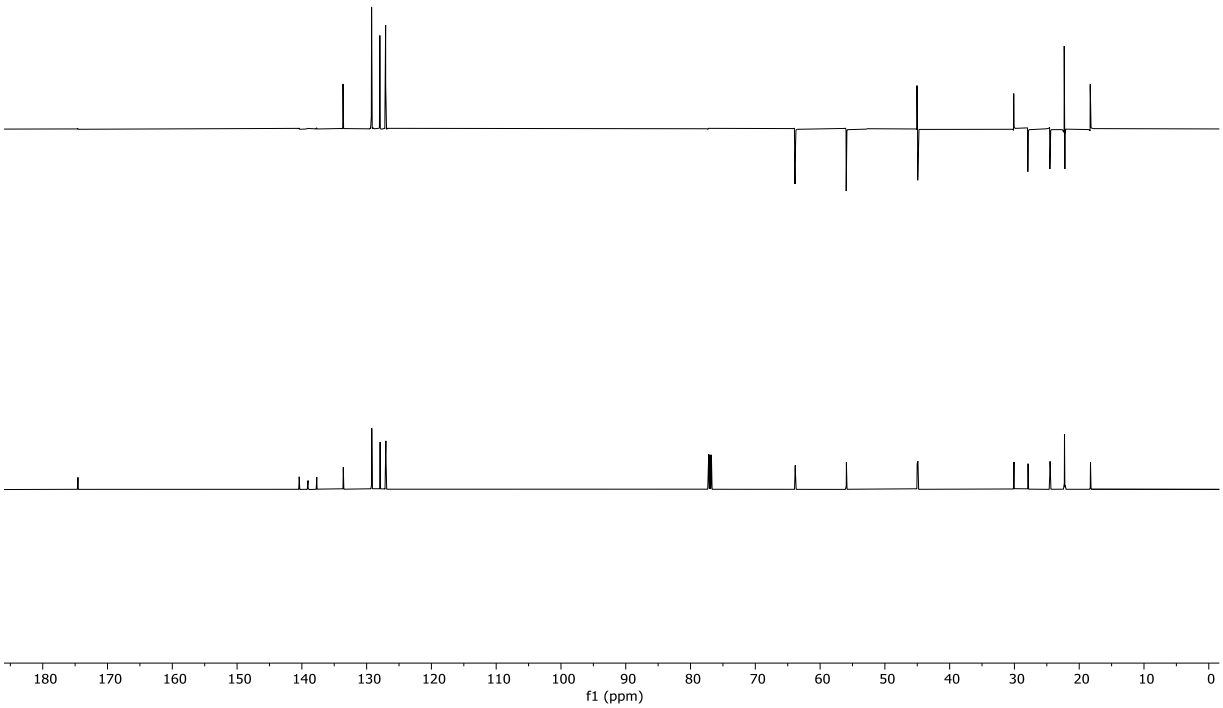


3za

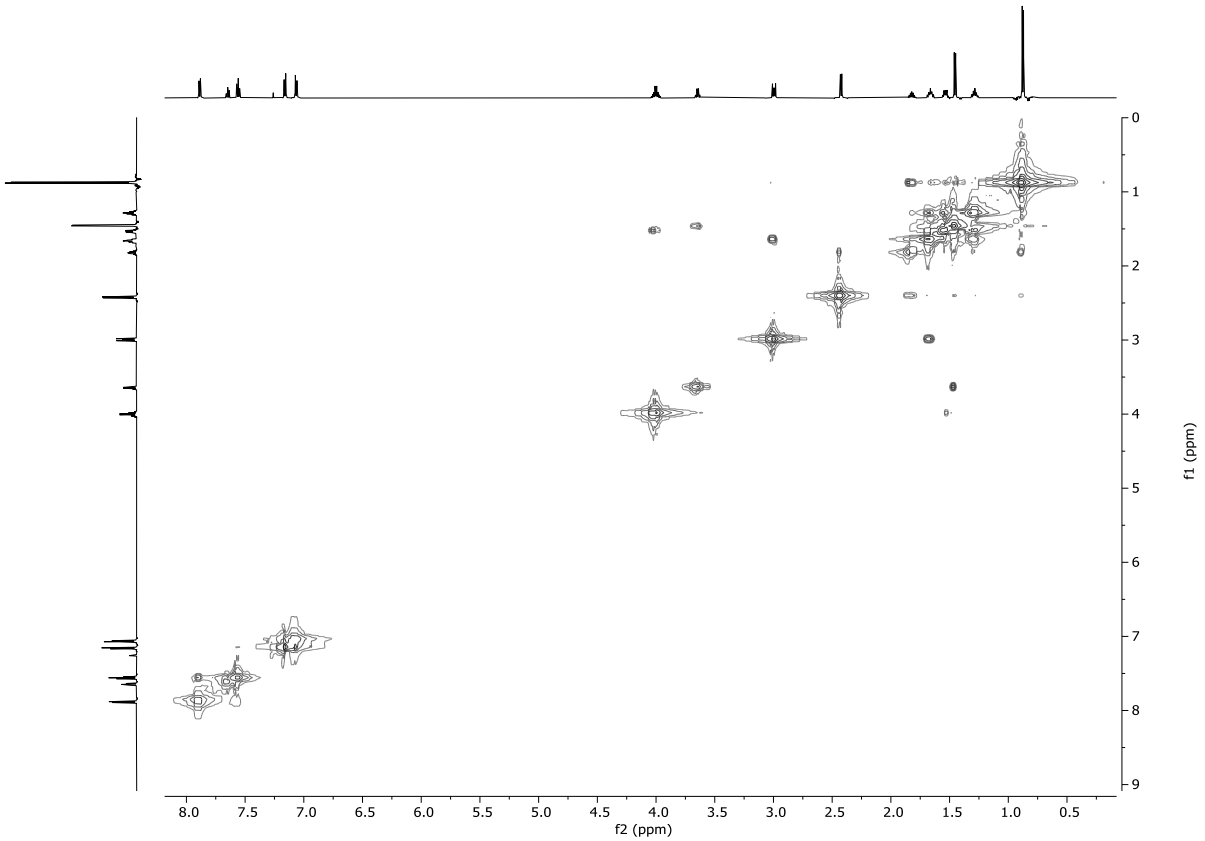
^{13}C{^{1}H}-NMR of compound 3za (150 MHz, $CDCl_3$)



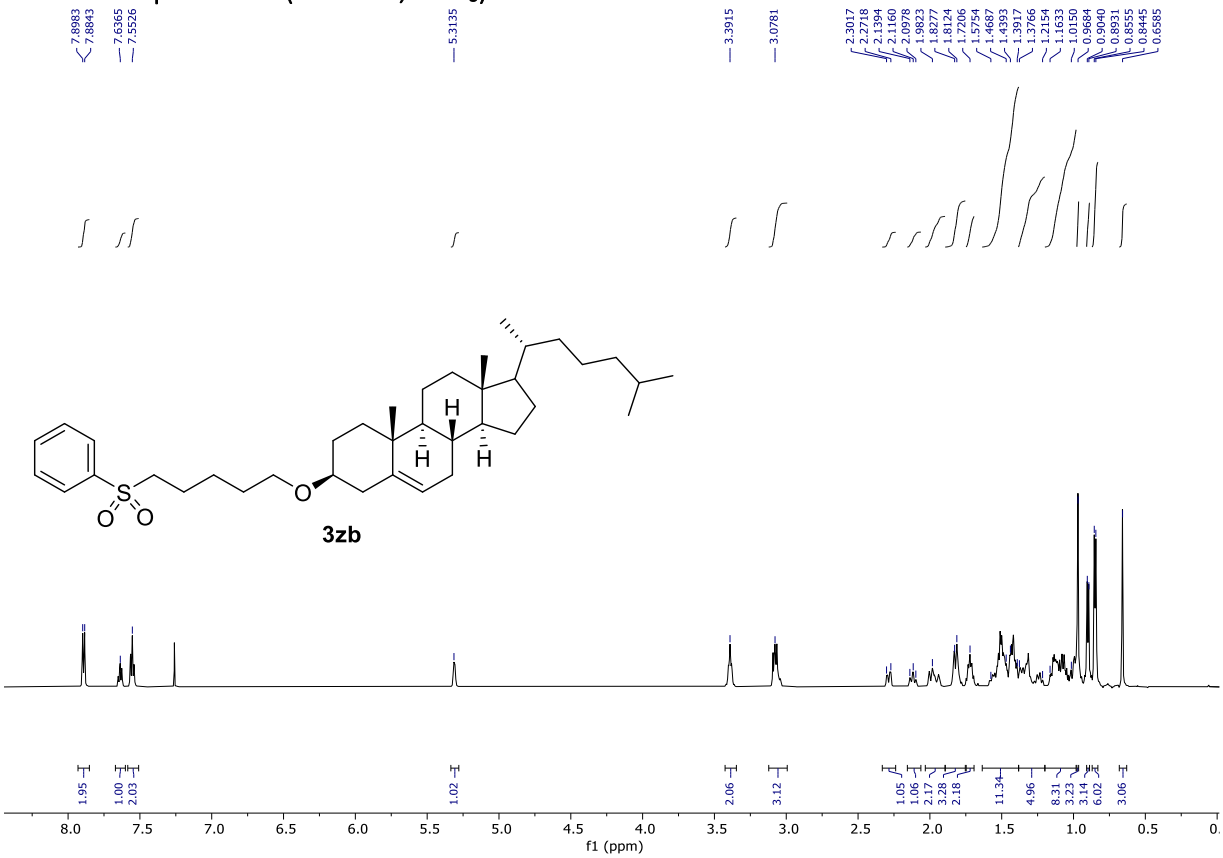
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3za (150 MHz, $CDCl_3$)



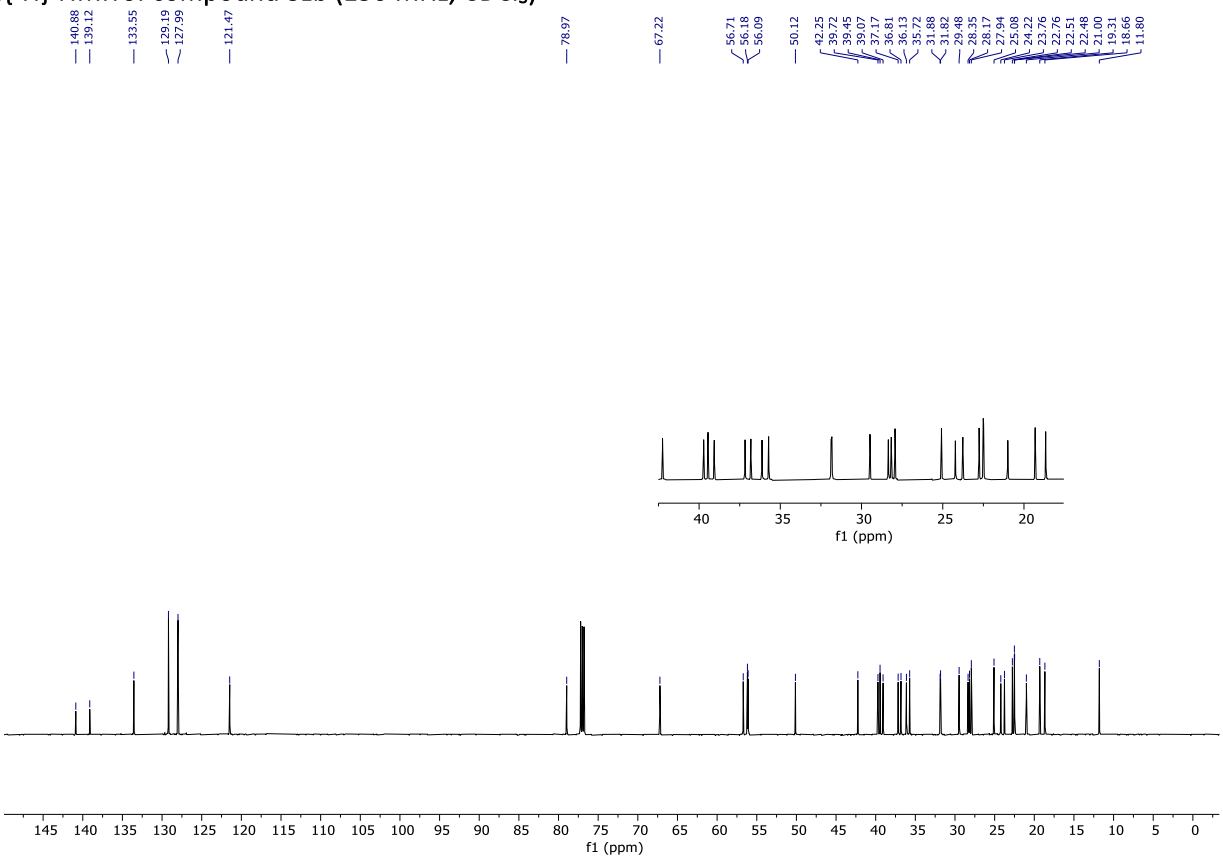
COSY-NMR of compound 3za (600 MHz, $CDCl_3$)



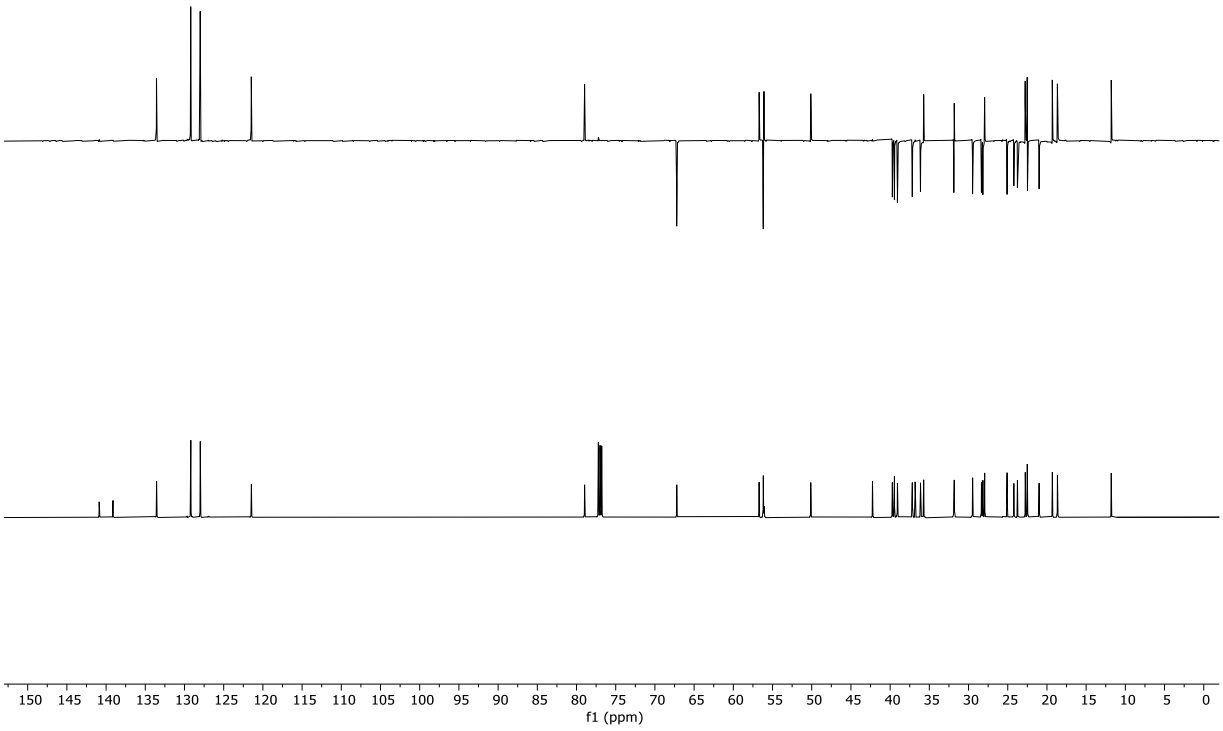
^{1}H-NMR of compound 3zb (600 MHz, $CDCl_3$)



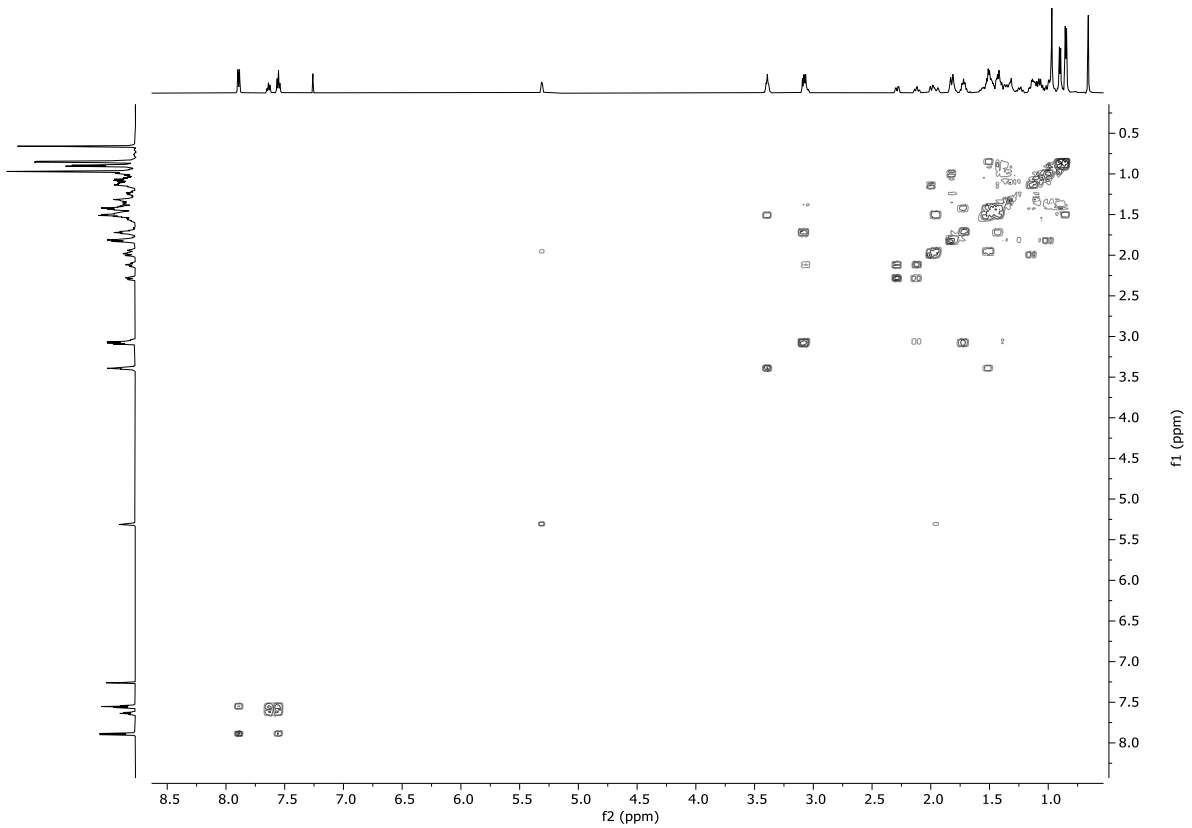
^{13}C{^{1}H}-NMR of compound 3zb (150 MHz, $CDCl_3$)



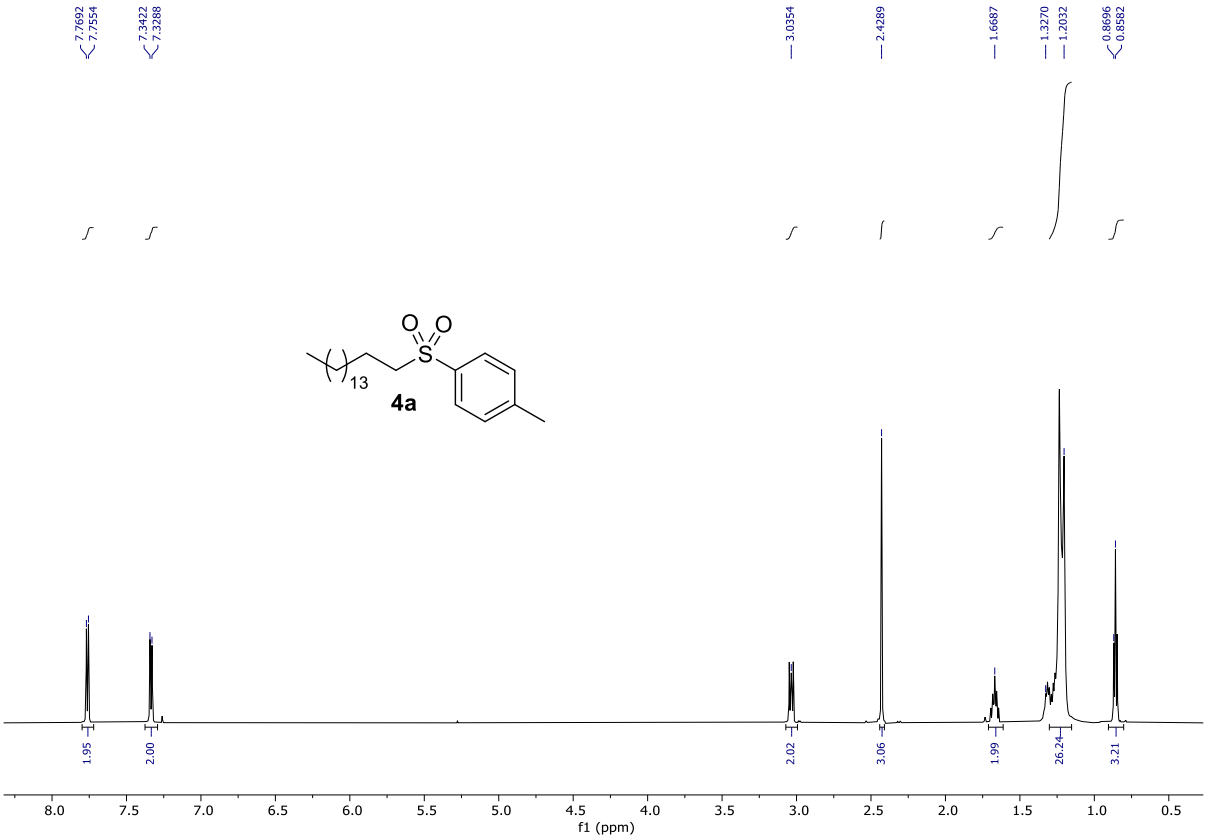
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 3zb (150 MHz, $CDCl_3$)



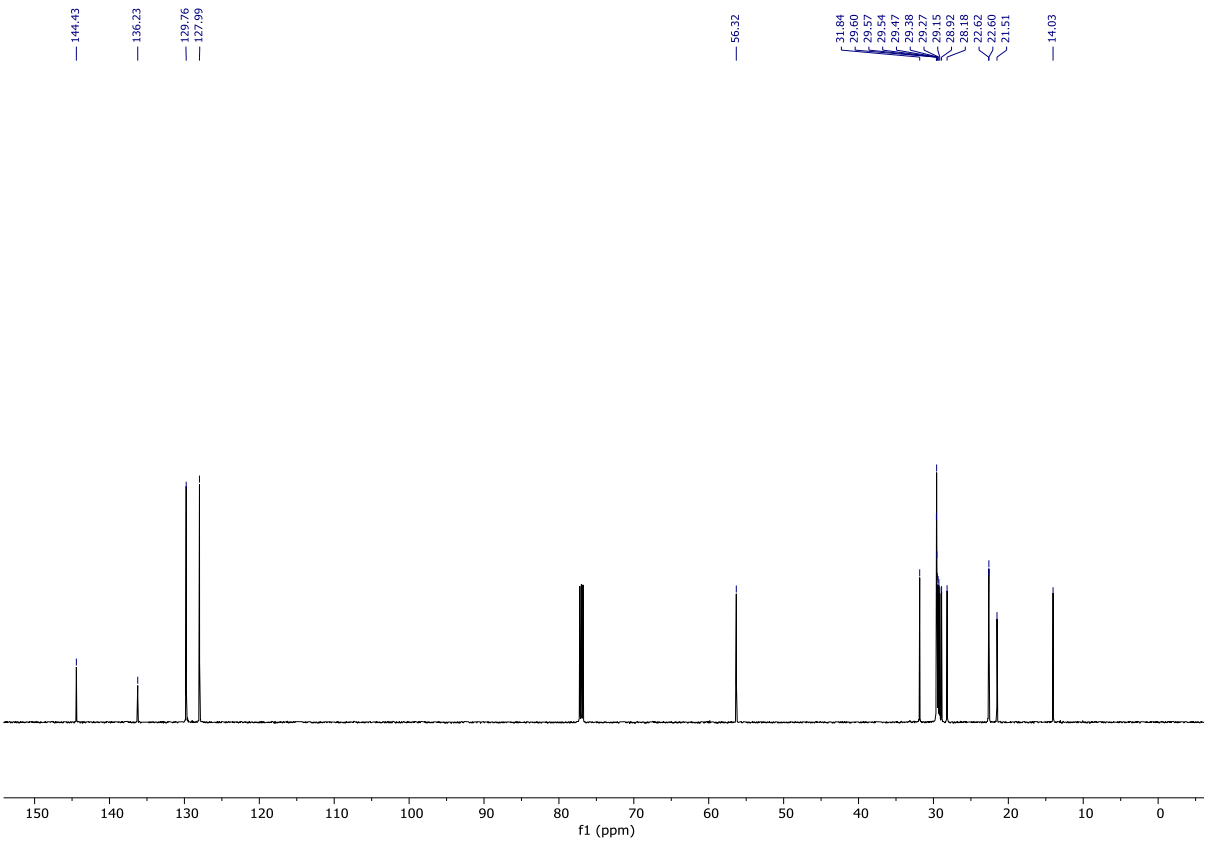
COSY-NMR of compound 3zb (600 MHz, $CDCl_3$)



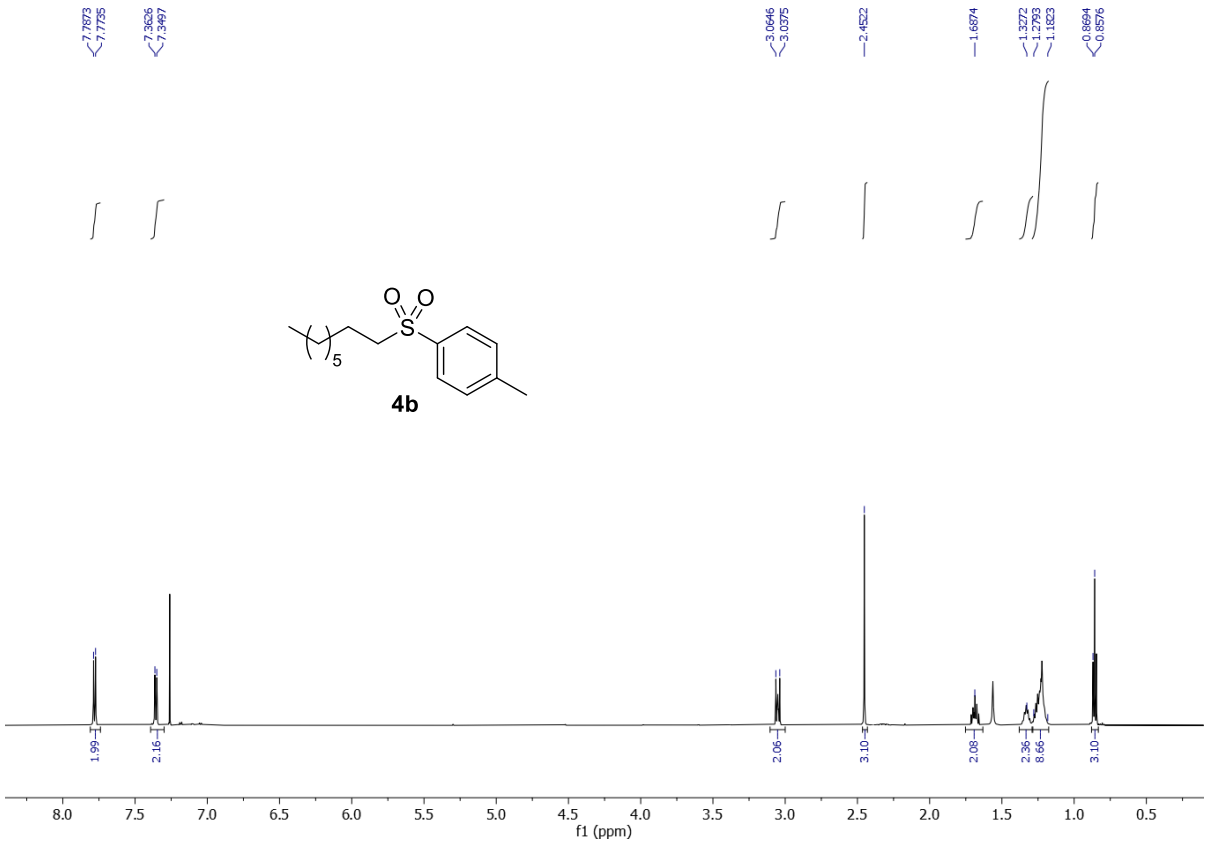
^{1}H-NMR of compound 4a (600 MHz, $CDCl_3$)



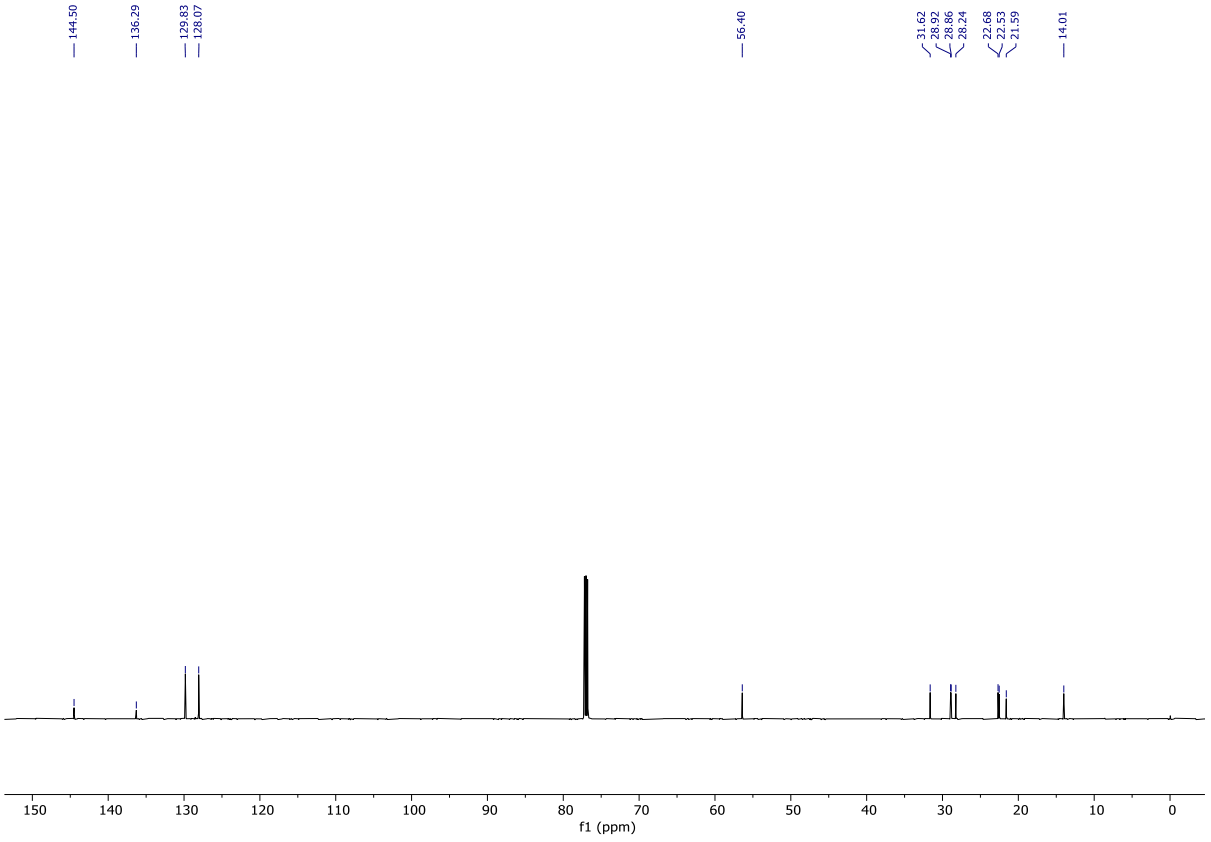
^{13}C{^{1}H}-NMR of compound 4a (150 MHz, $CDCl_3$)



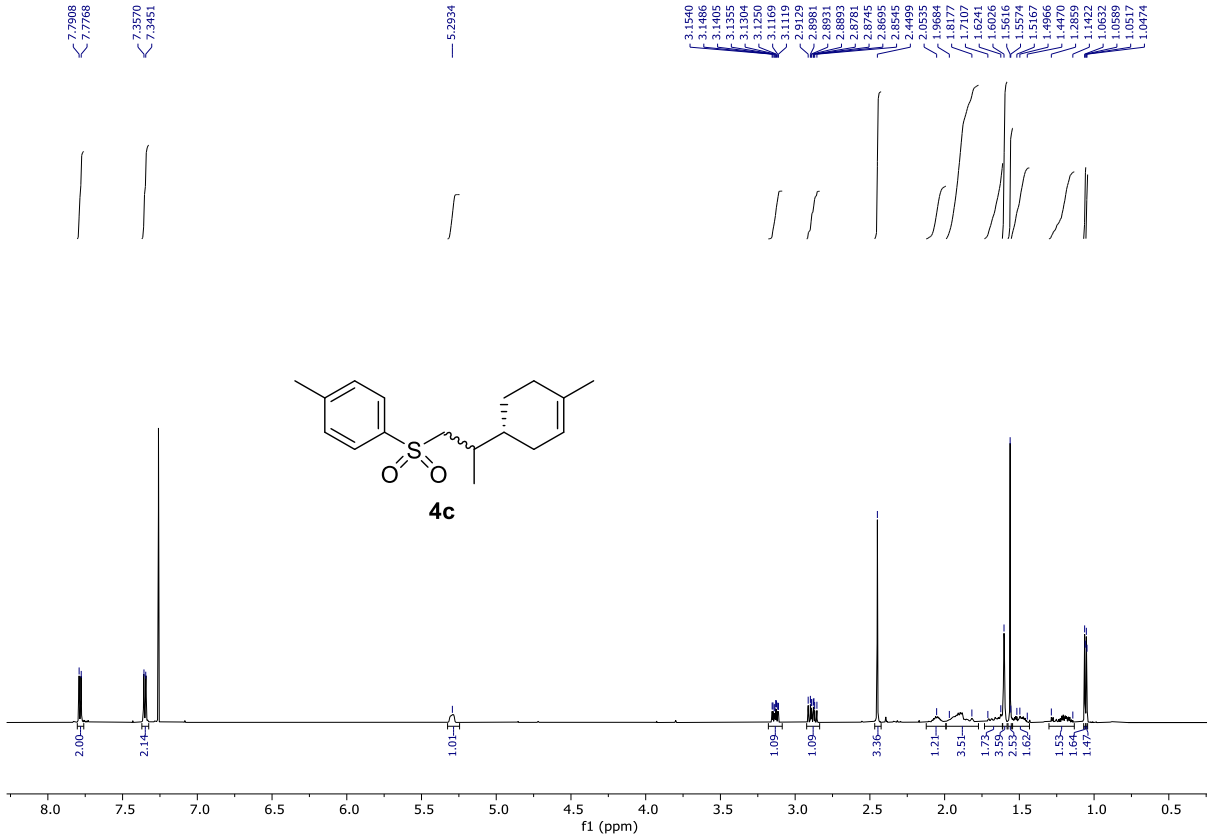
^{1}H-NMR of compound 4b (600 MHz, $CDCl_3$)



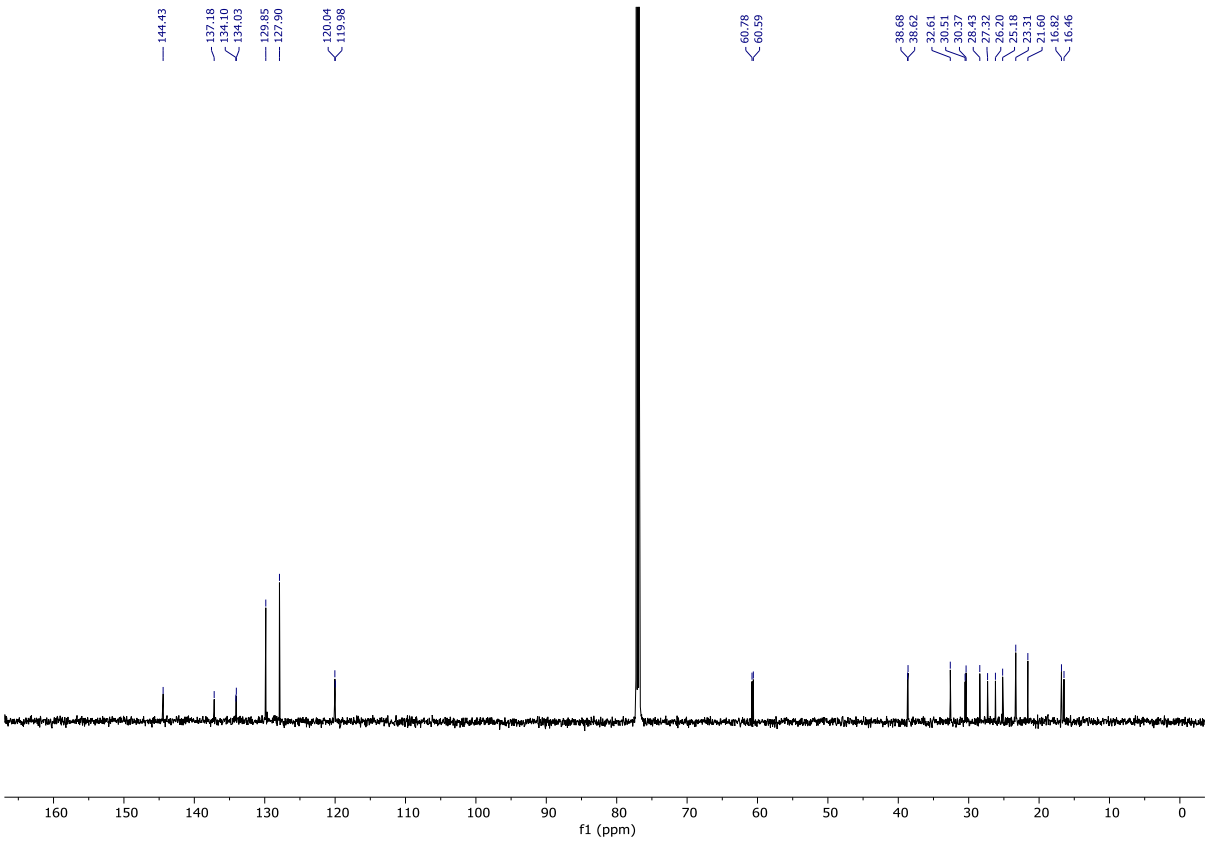
^{13}C{^{1}H}-NMR of compound 4b (150 MHz, $CDCl_3$)



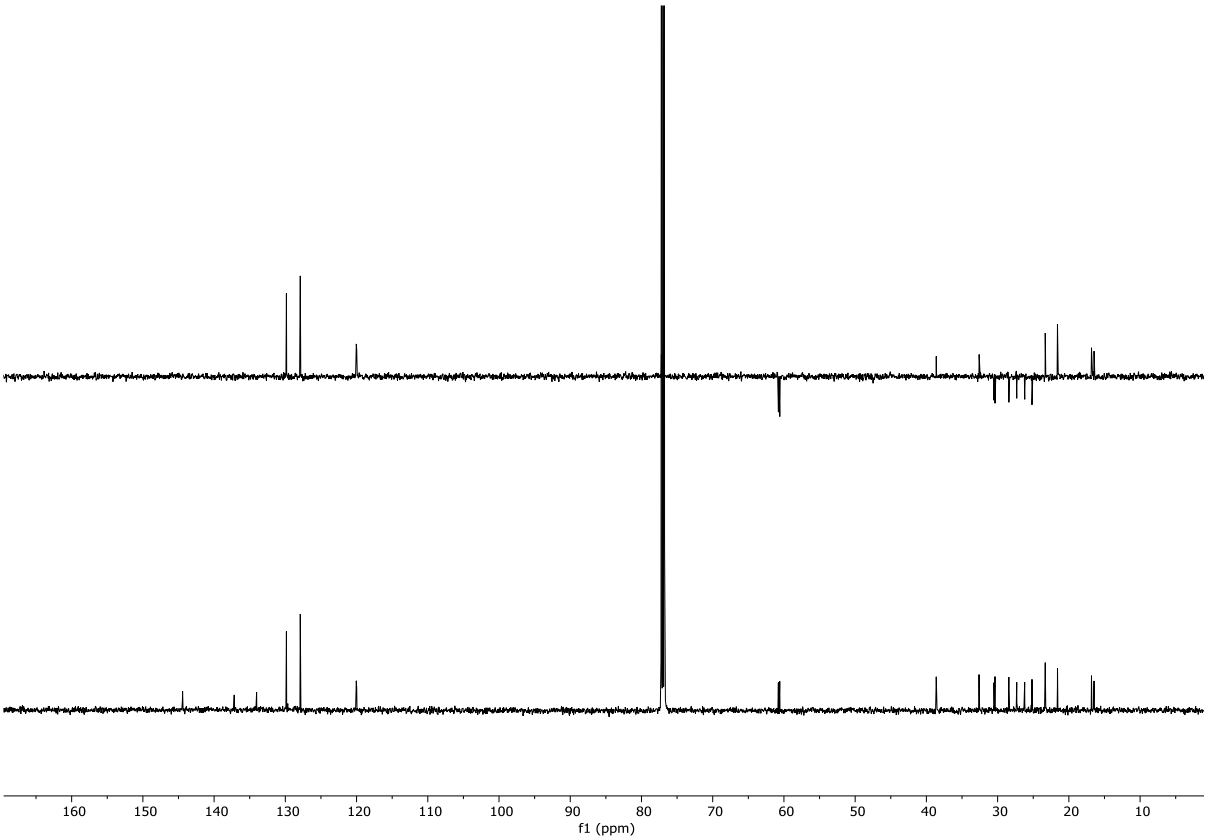
^{1}H-NMR of compound 4c (600 MHz, $CDCl_3$)



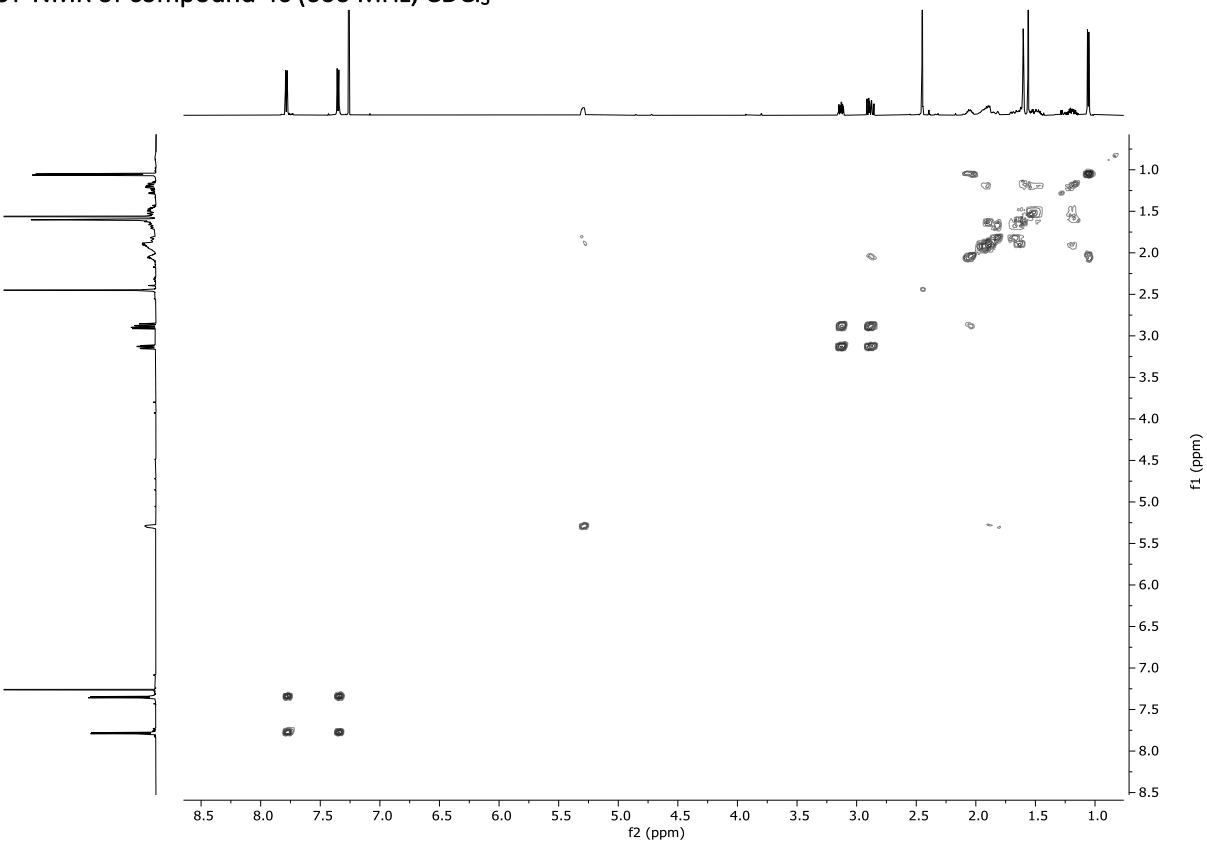
^{13}C{^{1}H}-NMR of compound 4c (150 MHz, $CDCl_3$)



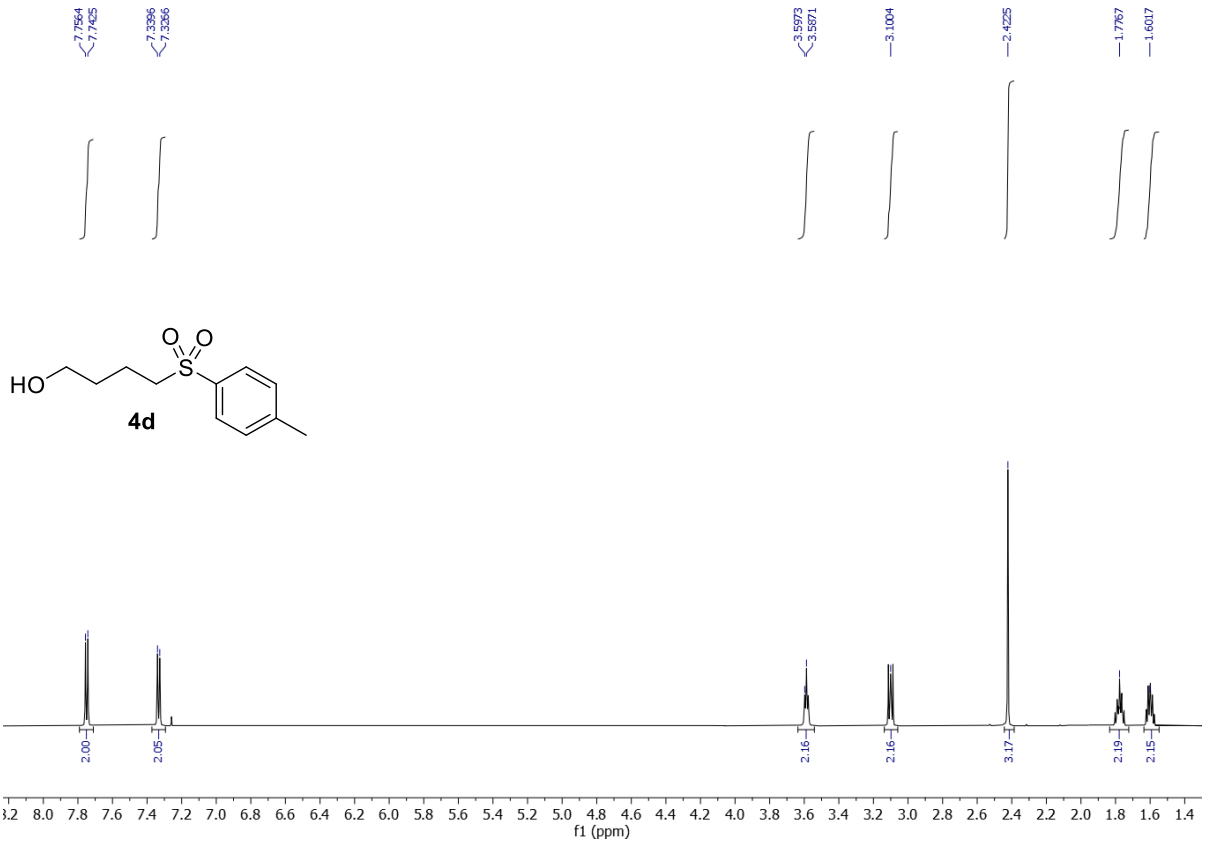
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4c (150 MHz, $CDCl_3$)



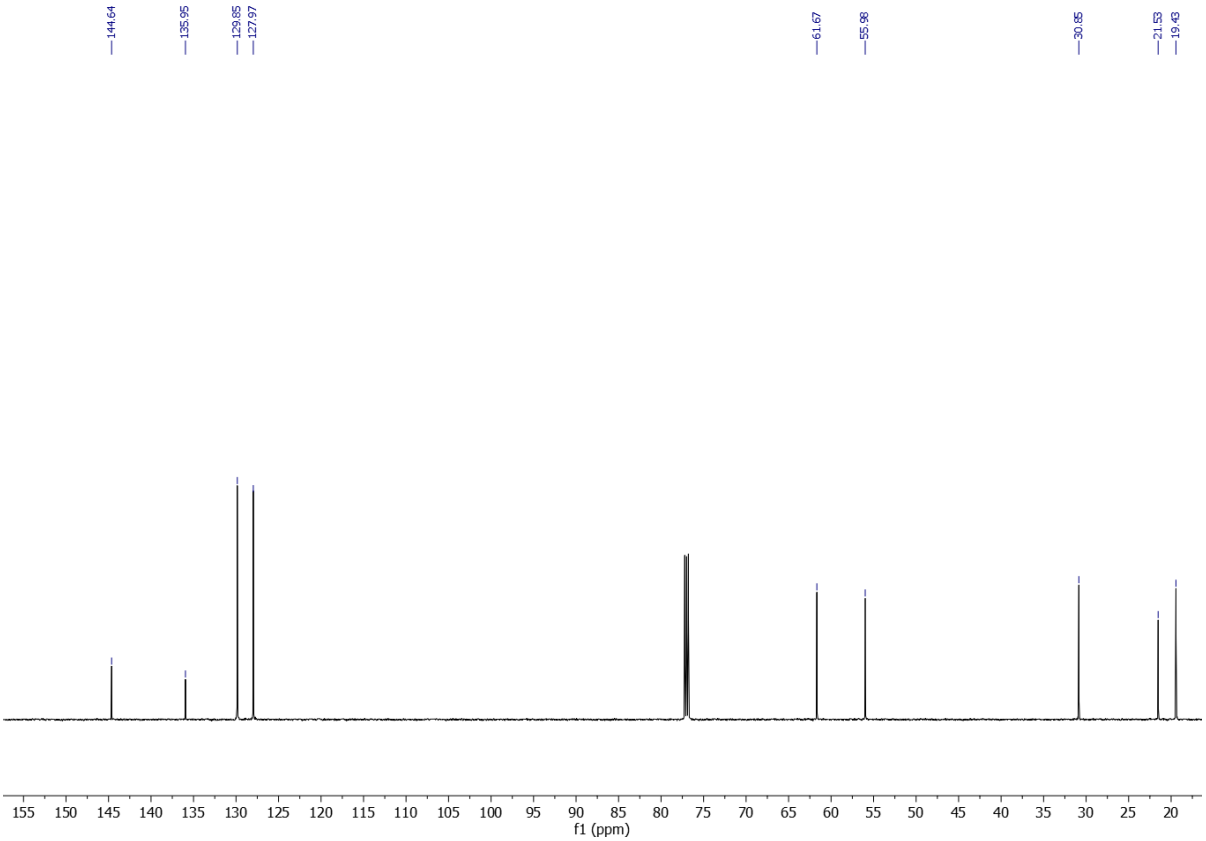
COSY-NMR of compound 4c (600 MHz, $CDCl_3$



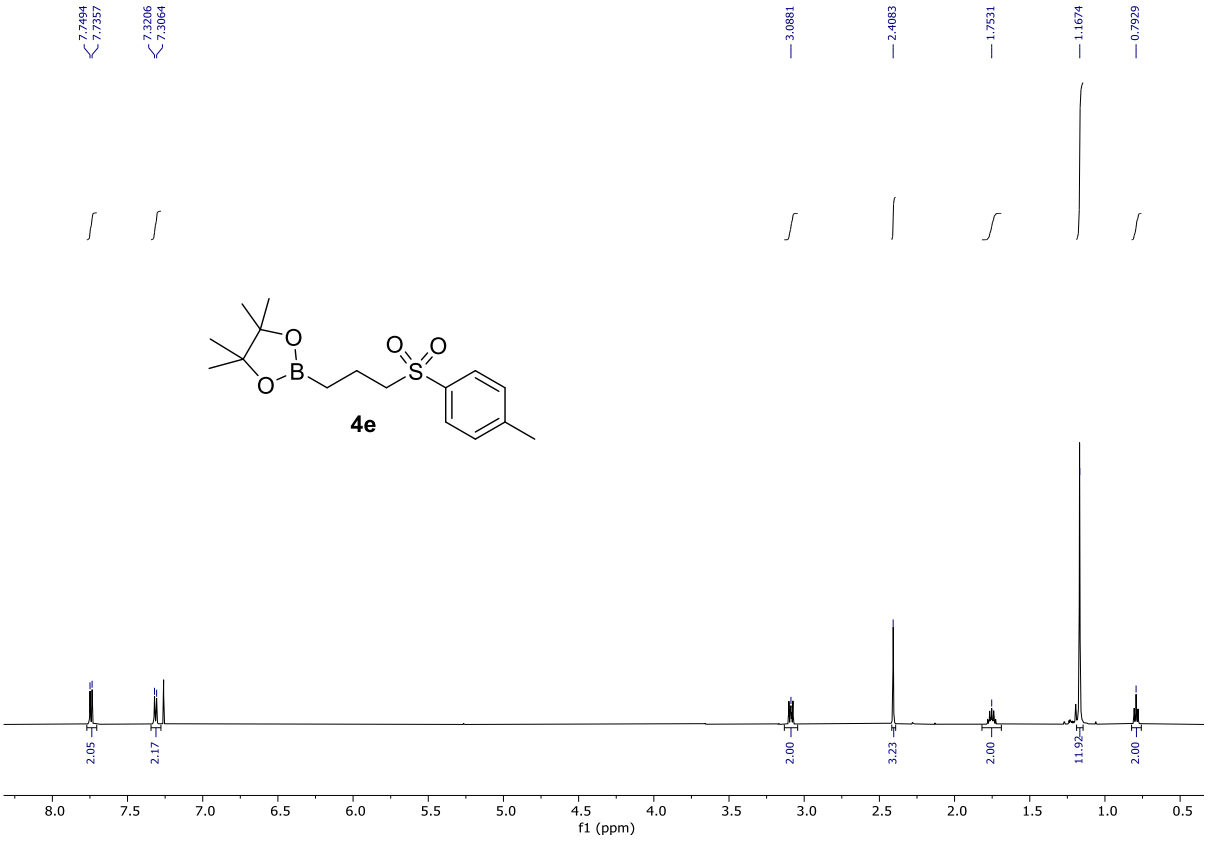
^{1}H-NMR of compound 4d (600 MHz, $CDCl_3$)



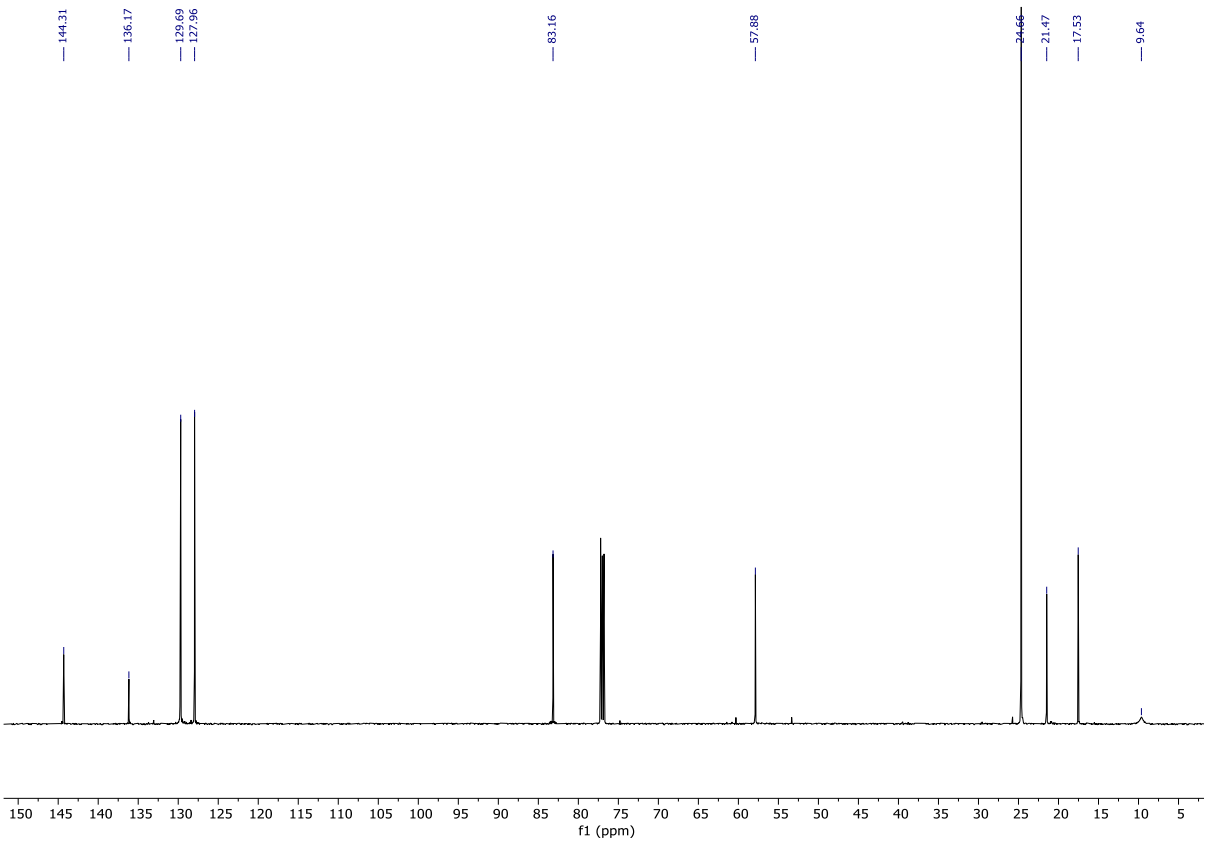
^{13}C{^{1}H}-NMR of compound 4d (150 MHz, $CDCl_3$)



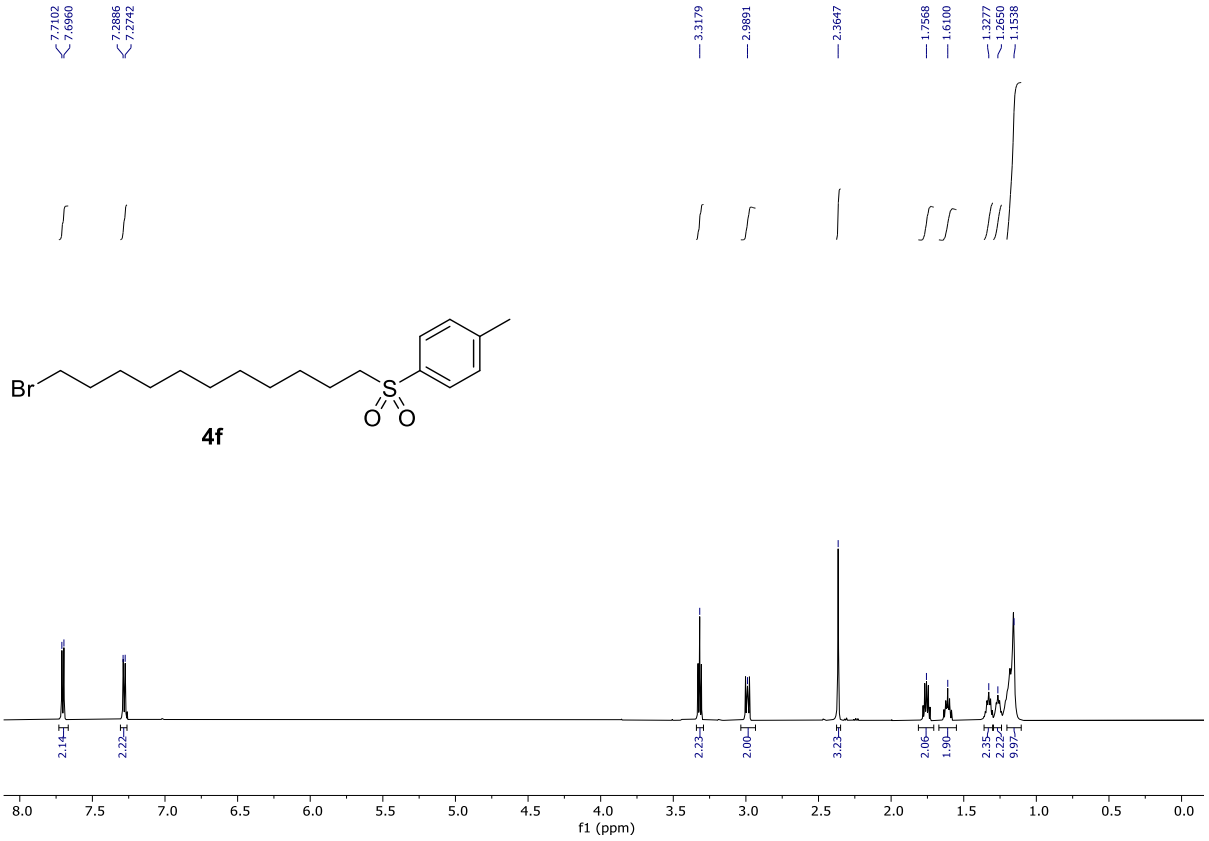
^{1}H-NMR of compound 4e (600 MHz, $CDCl_3$)



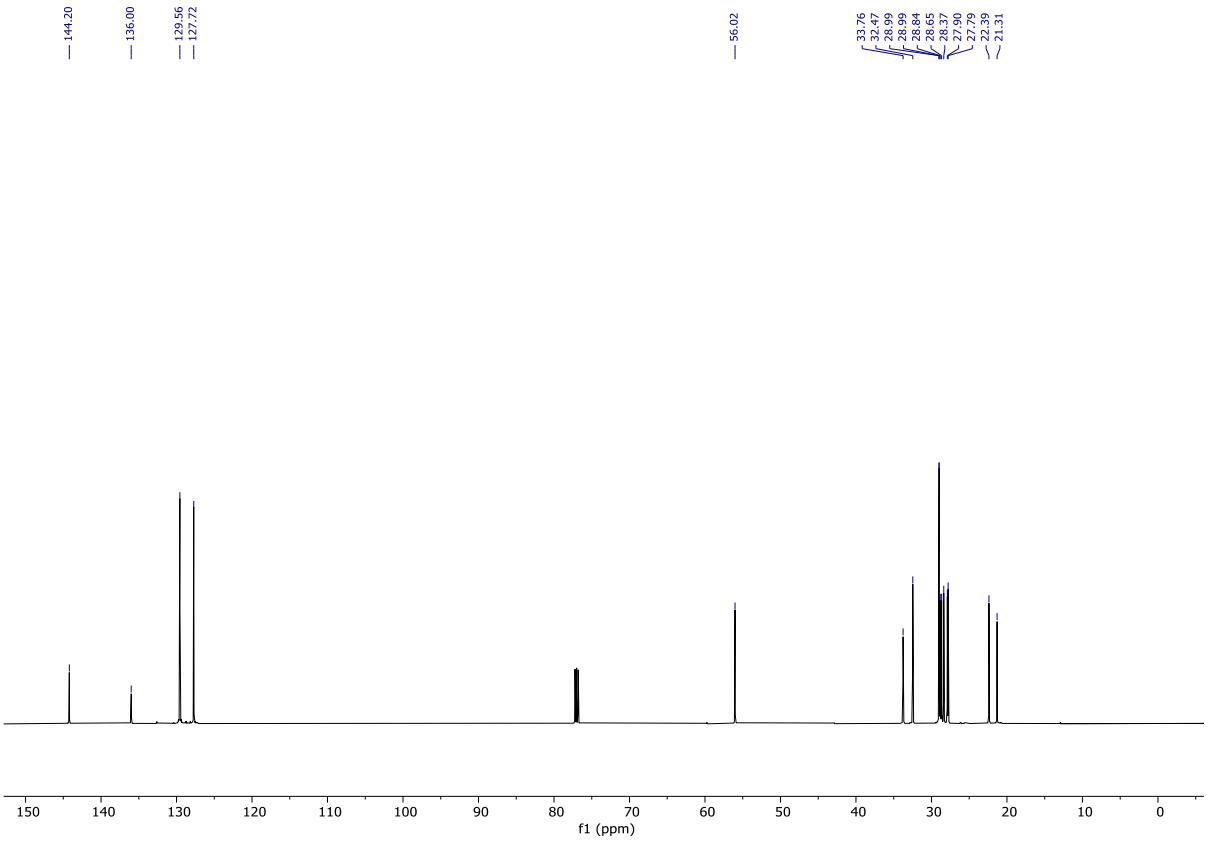
^{13}C{^{1}H}-NMR of compound 4e (150 MHz, $CDCl_3$)



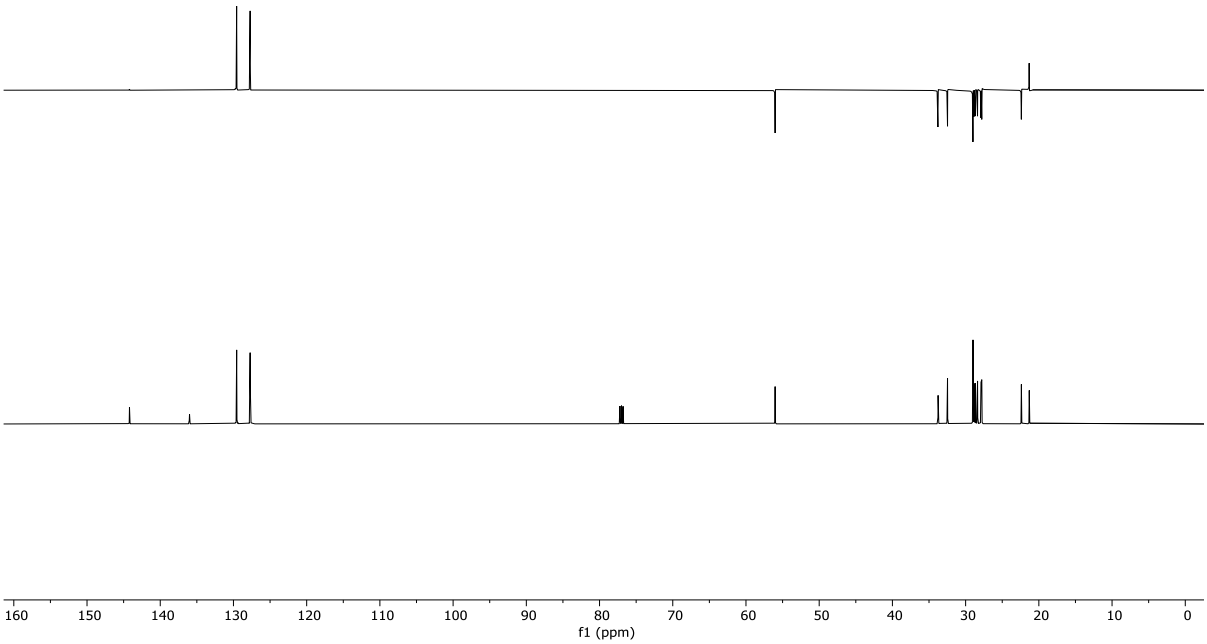
^{1}H-NMR of compound 4f (600 MHz, $CDCl_3$)



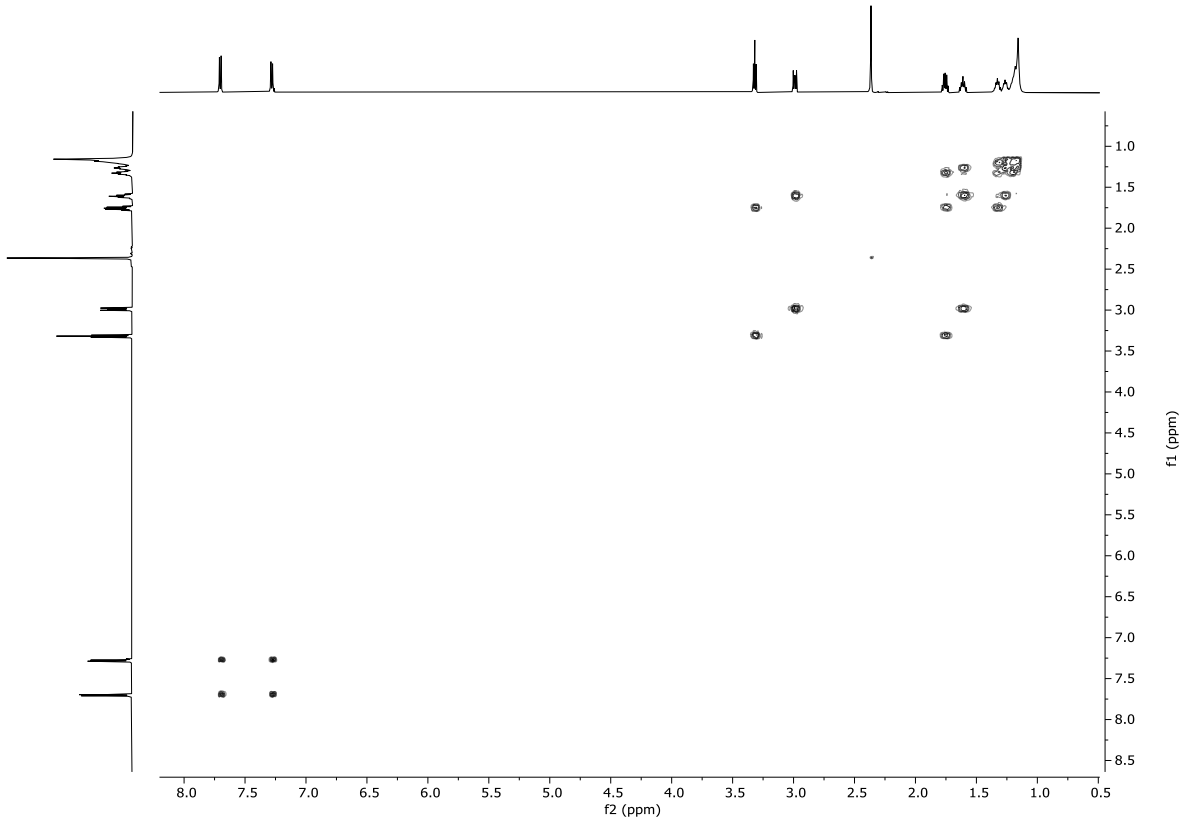
^{13}C{^{1}H}-NMR of compound 4f (150 MHz, $CDCl_3$)



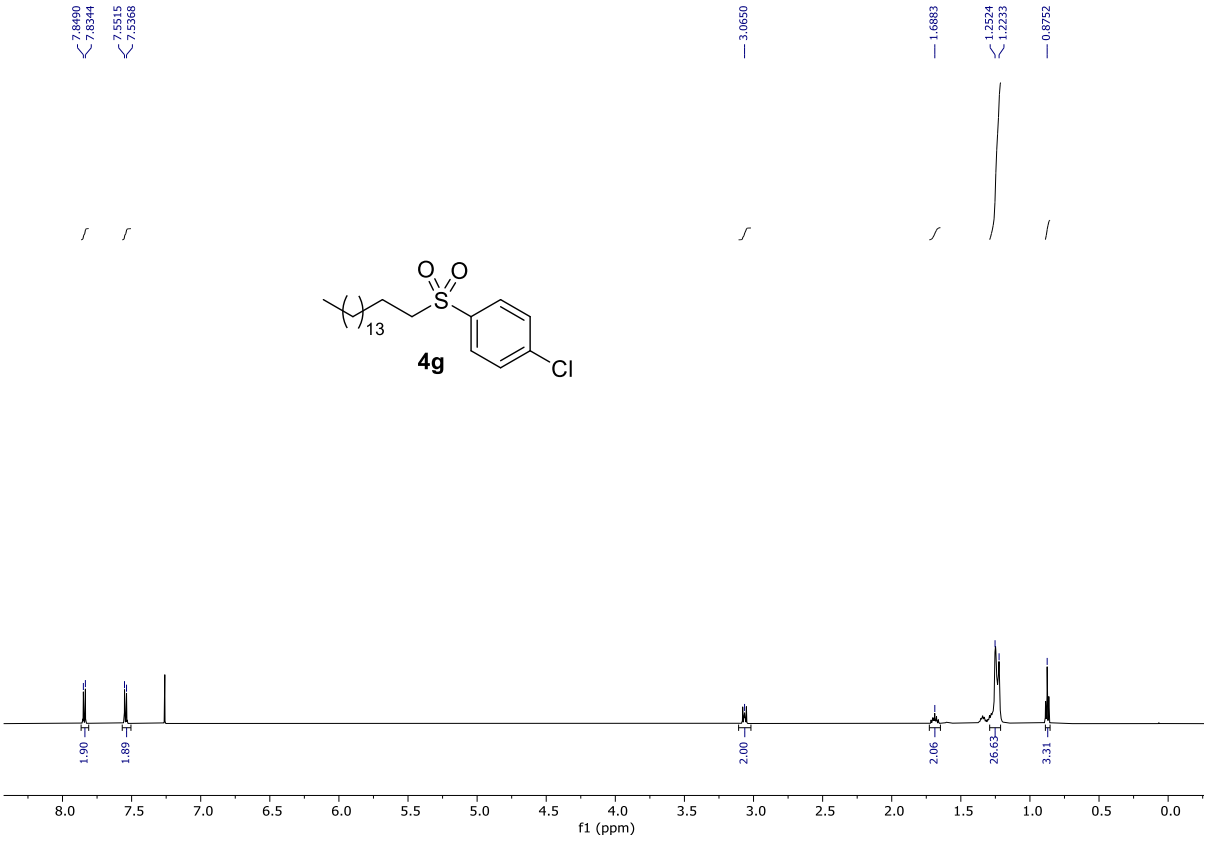
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4f (150 MHz, $CDCl_3$)



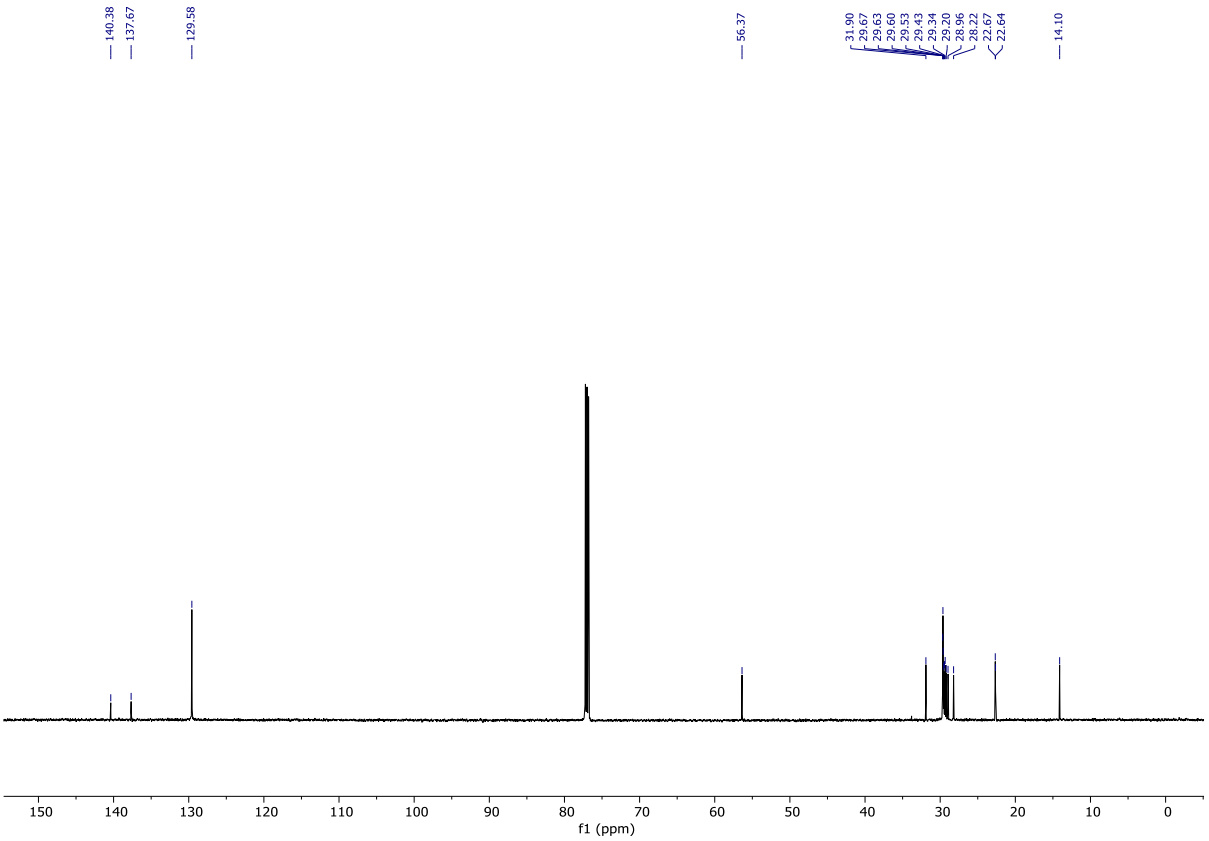
COSY-NMR of compound 4f (600 MHz, $CDCl_3$)



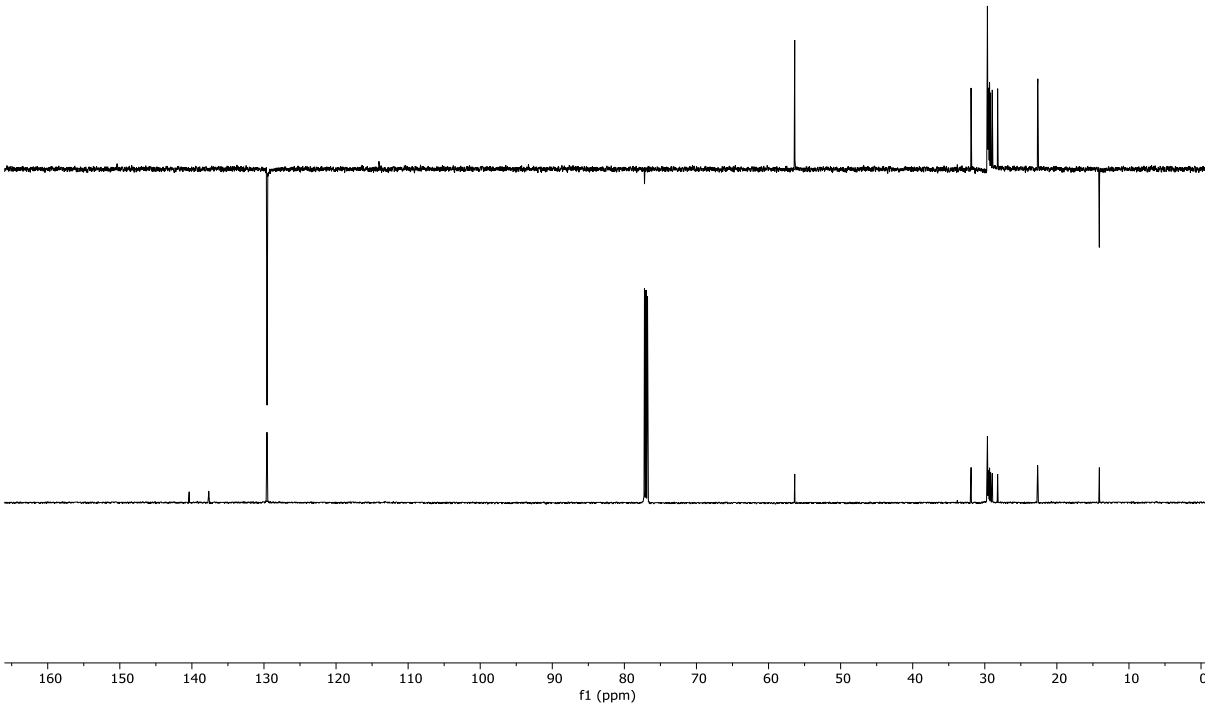
^{1}H-NMR of compound 4g (600 MHz, $CDCl_3$)



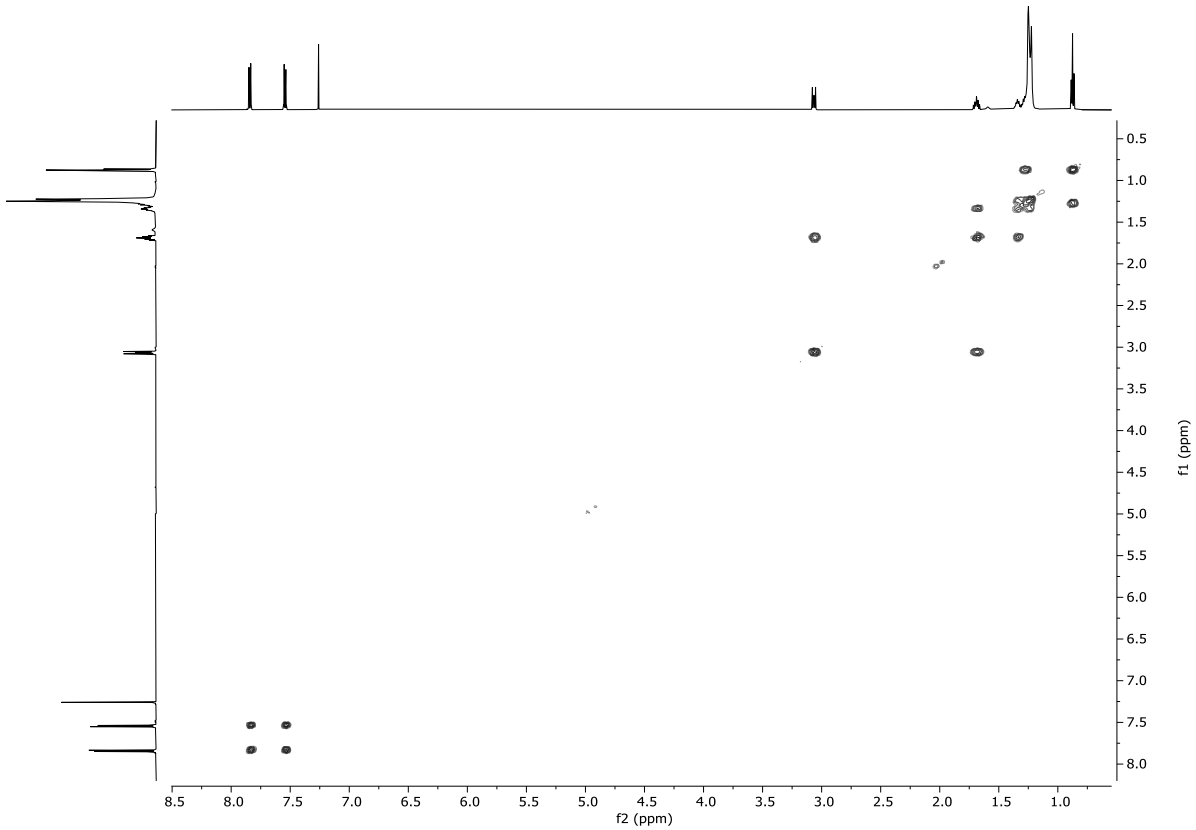
^{13}C{^{1}H}-NMR of compound 4g (150 MHz, $CDCl_3$)



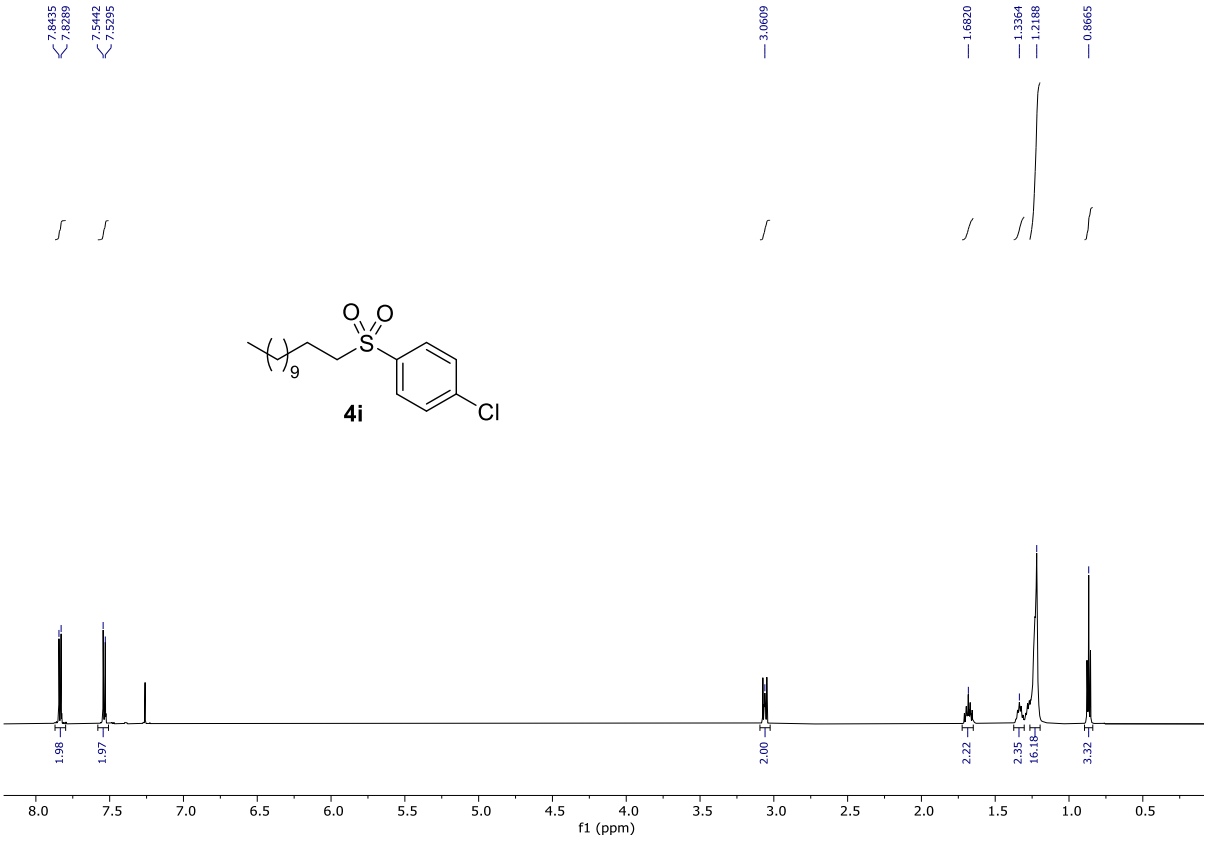
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4g (150 MHz, $CDCl_3$)



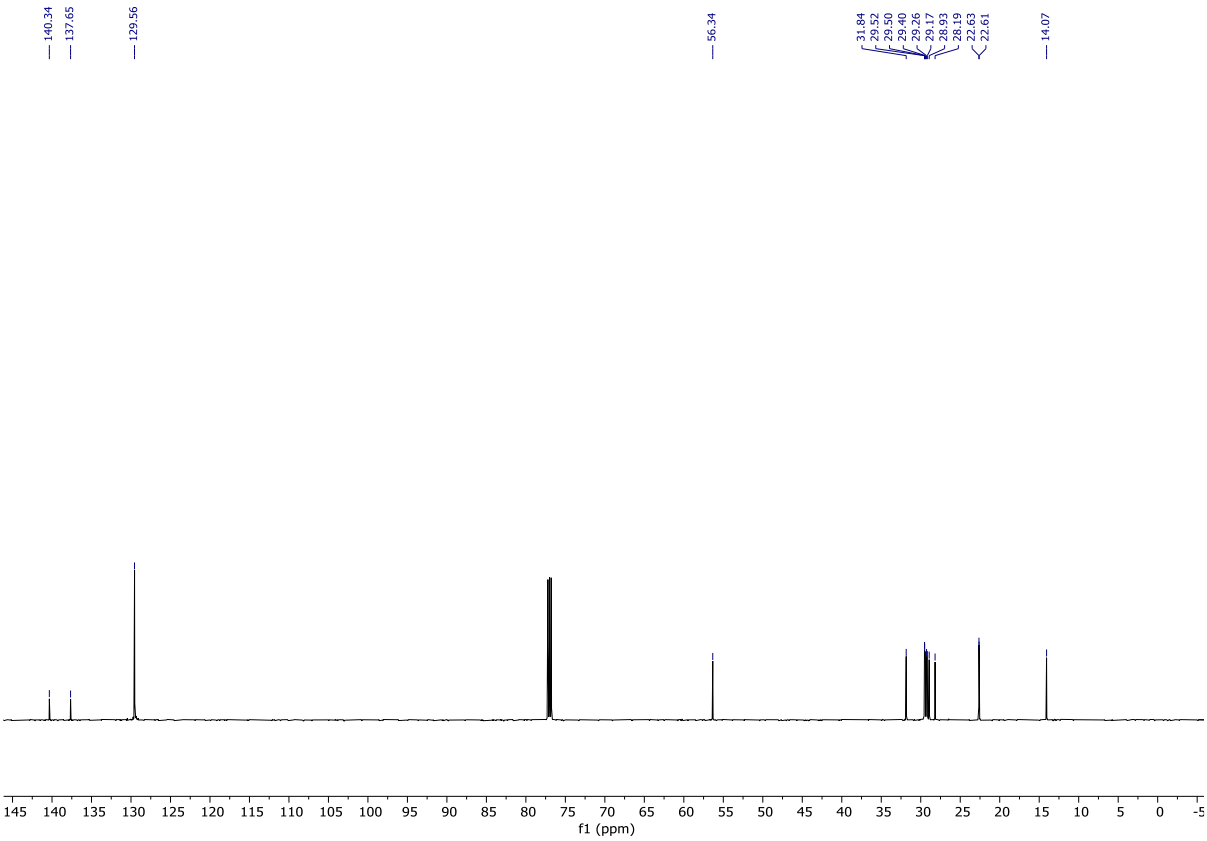
COSY-NMR of compound 4g (600 MHz, $CDCl_3$)



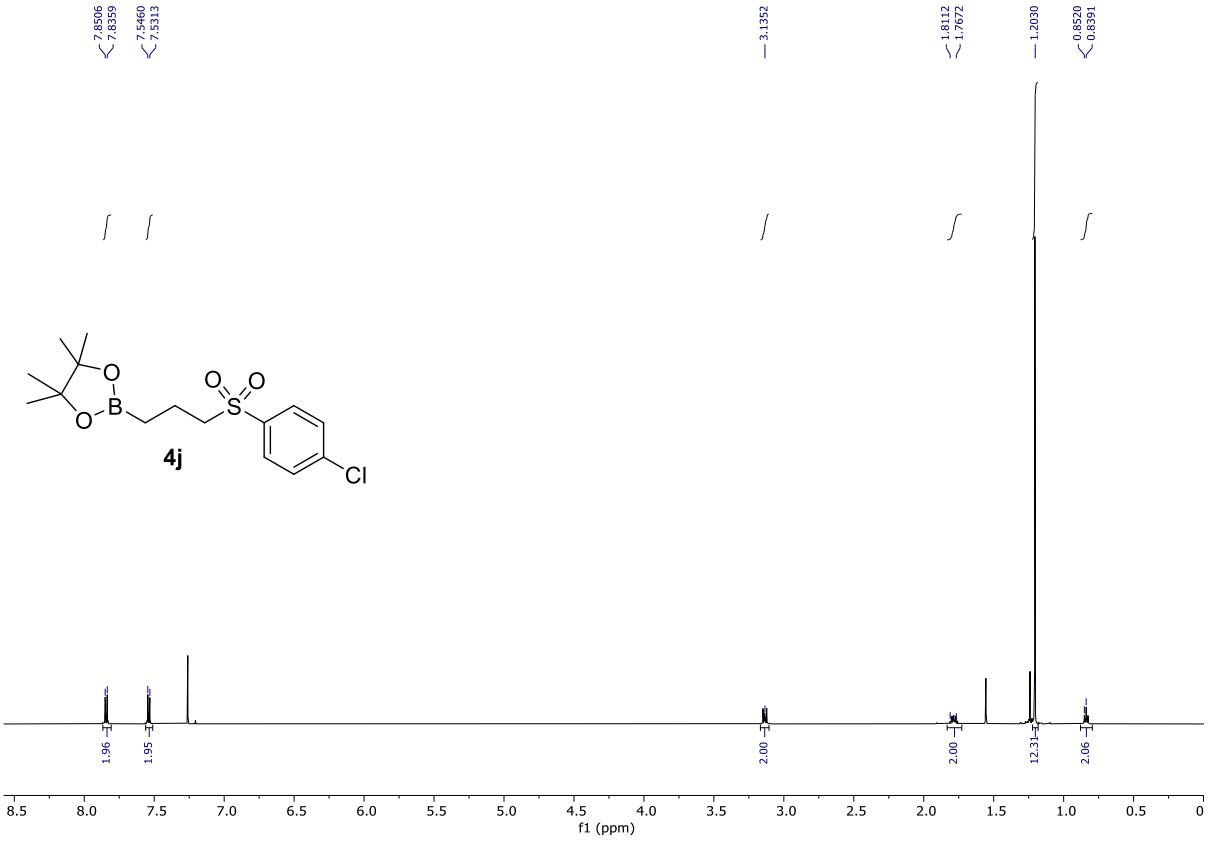
^{1}H-NMR of compound 4i (600 MHz, $CDCl_3$)



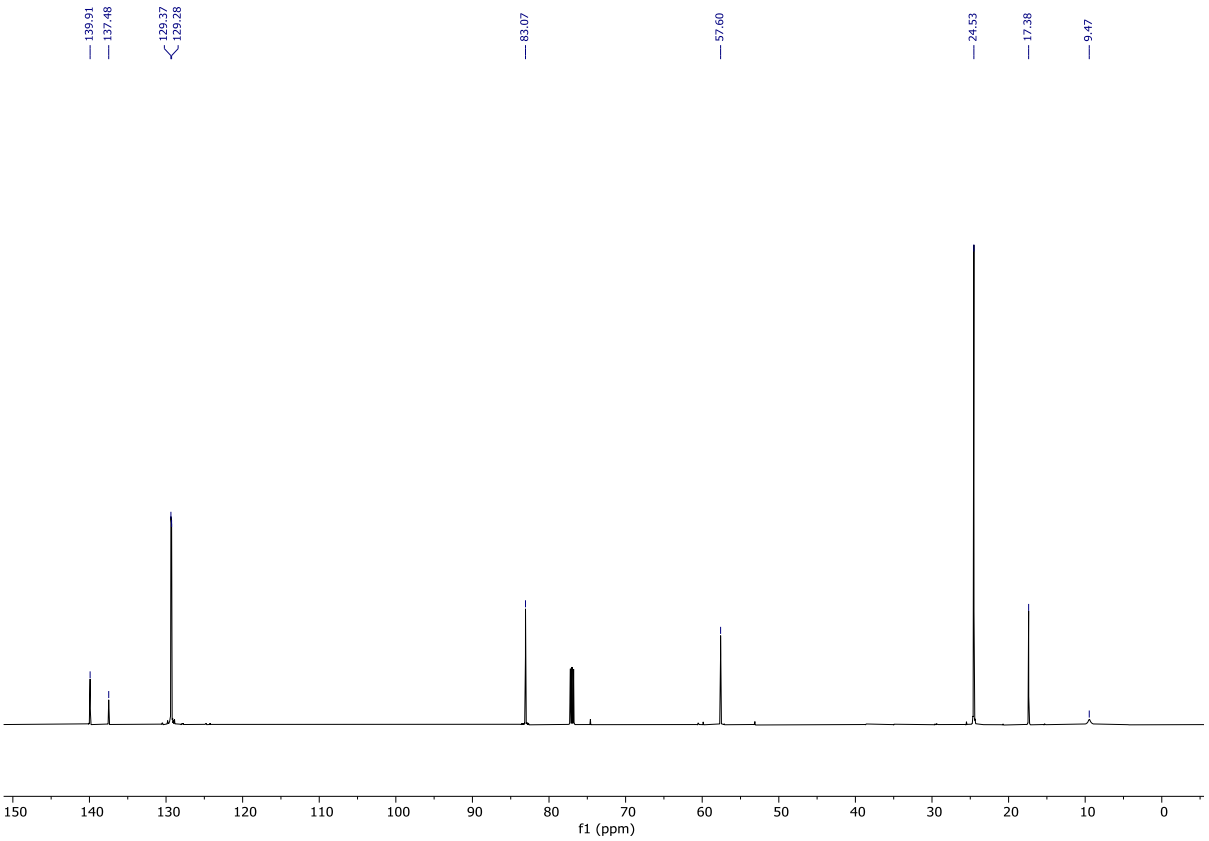
^{13}C{^{1}H}-NMR of compound 4i (150 MHz, $CDCl_3$)



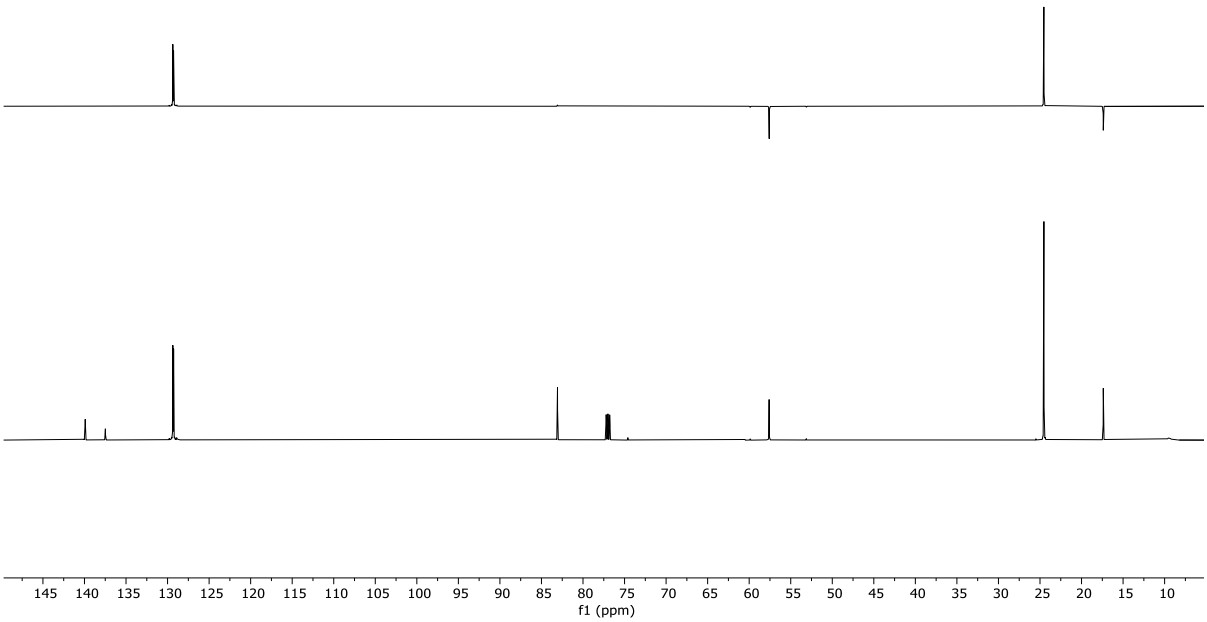
^{1}H-NMR of compound 4j (600 MHz, $CDCl_3$)



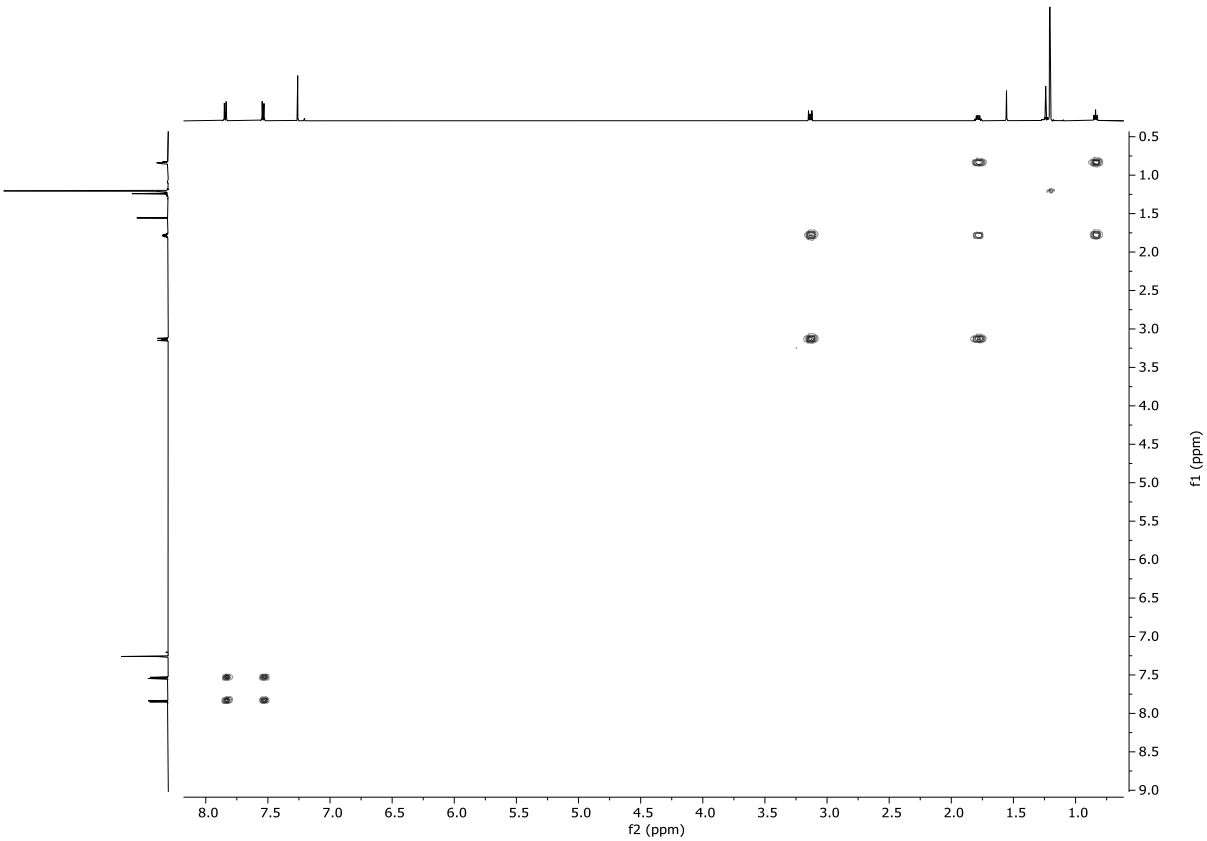
^{13}C{^{1}H}-NMR of compound 4j (150 MHz, $CDCl_3$)



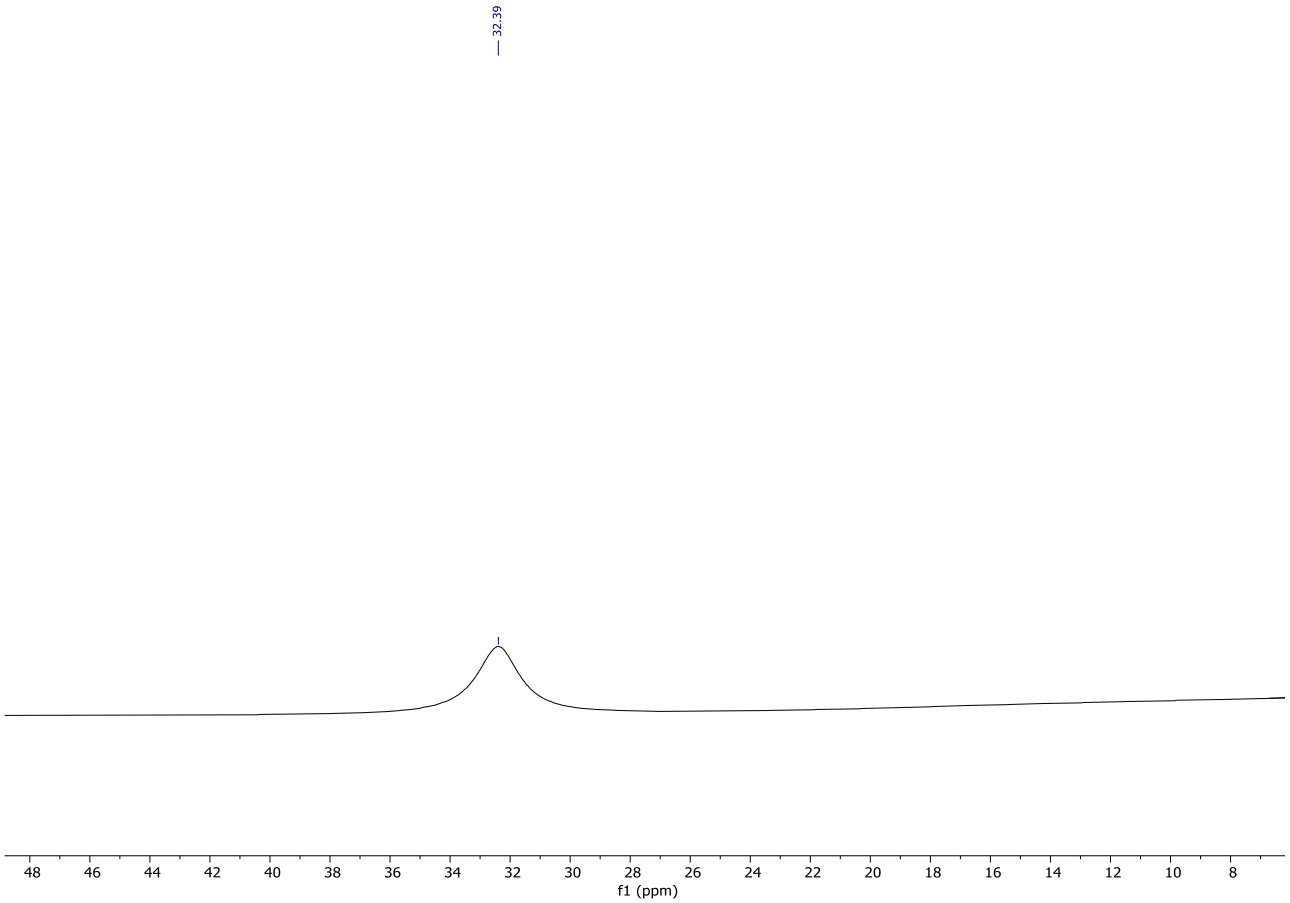
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4j (150 MHz, $CDCl_3$)



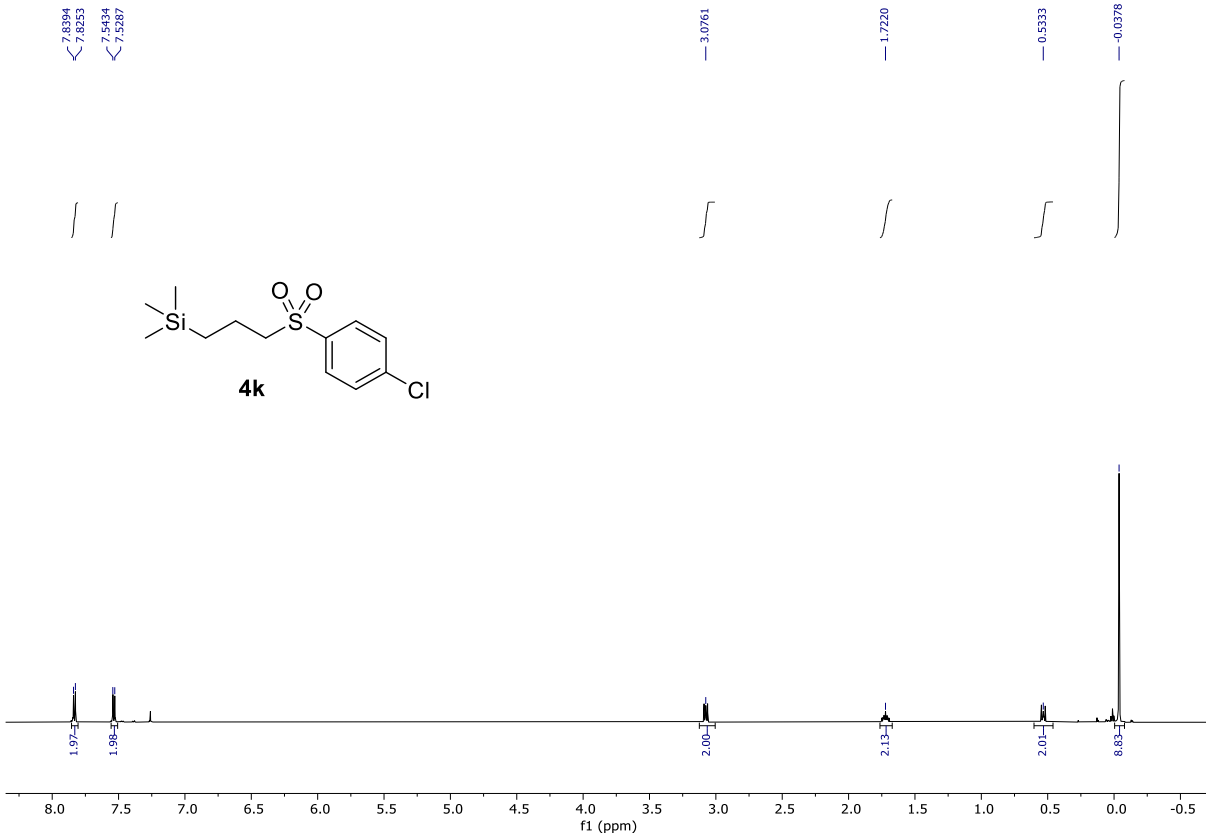
COSY-NMR of compound 4j (600 MHz, $CDCl_3$)



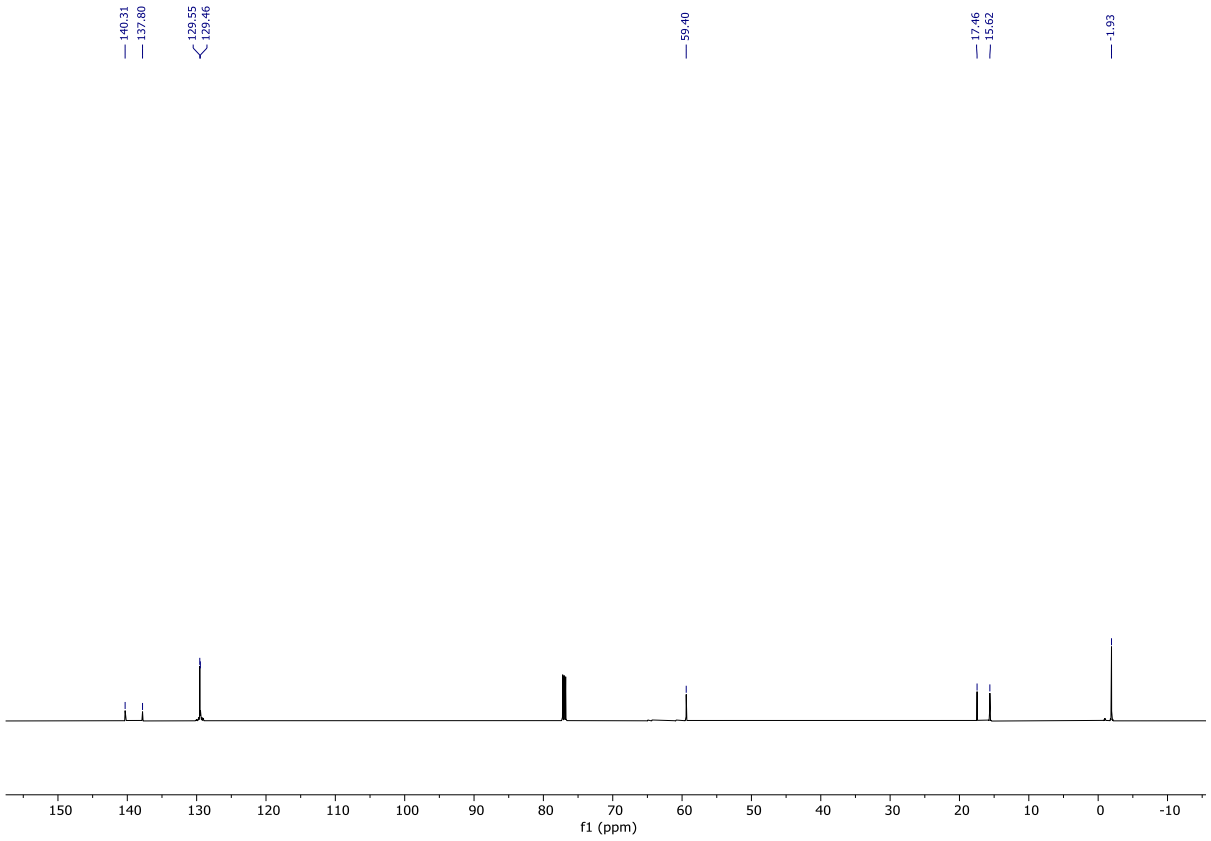
$^{11}B\{^{1}H\}$-NMR of compound 4j (192 MHz, $CDCl_3$)



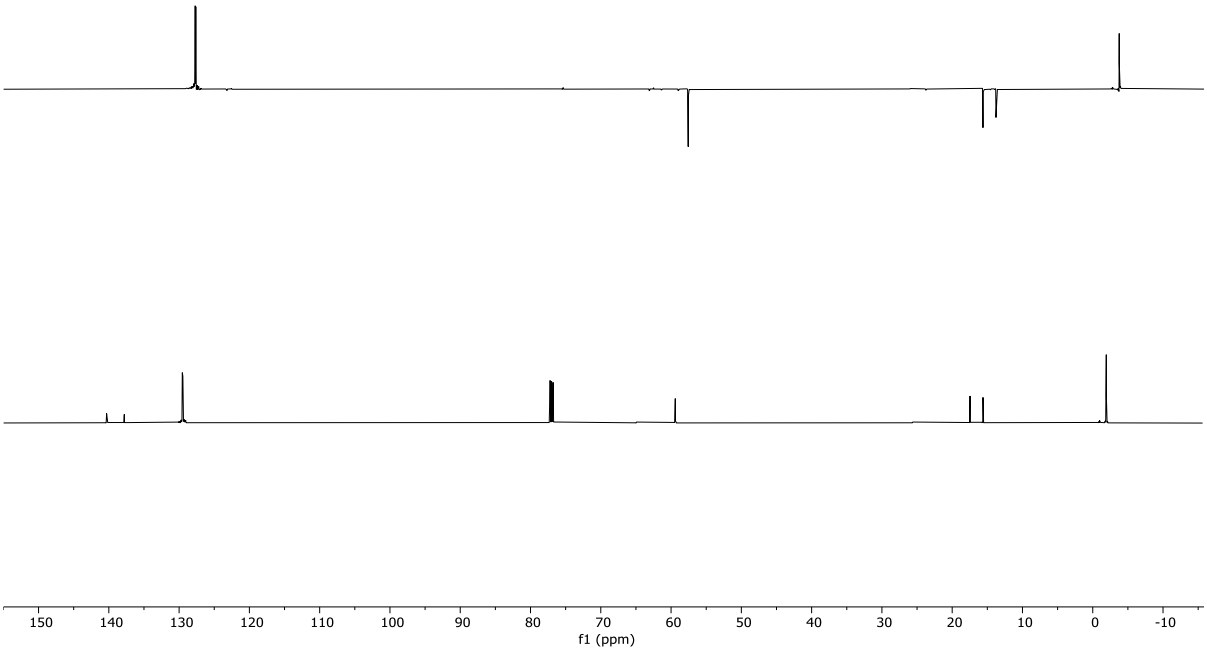
^{1}H-NMR of compound 4k (600 MHz, $CDCl_3$)



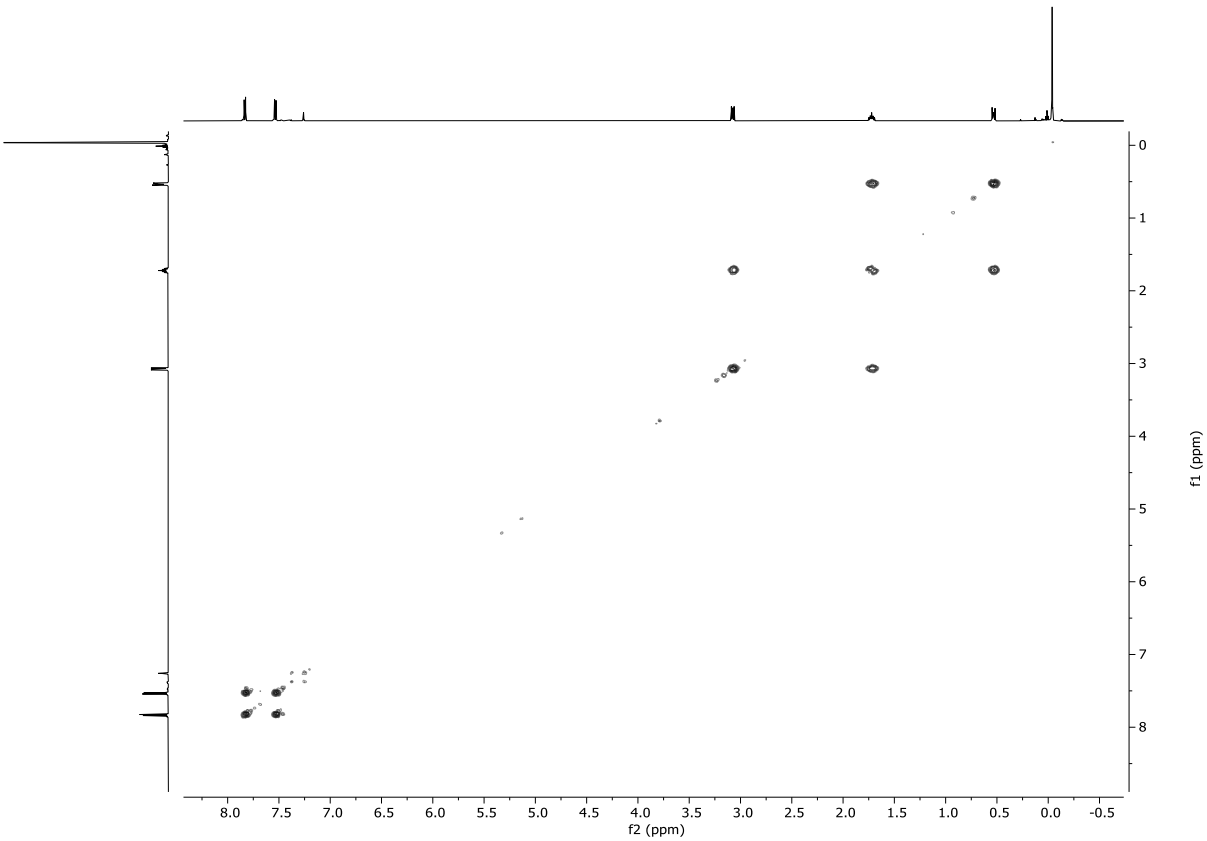
^{13}C{^{1}H}-NMR of compound 4k (150 MHz, $CDCl_3$)



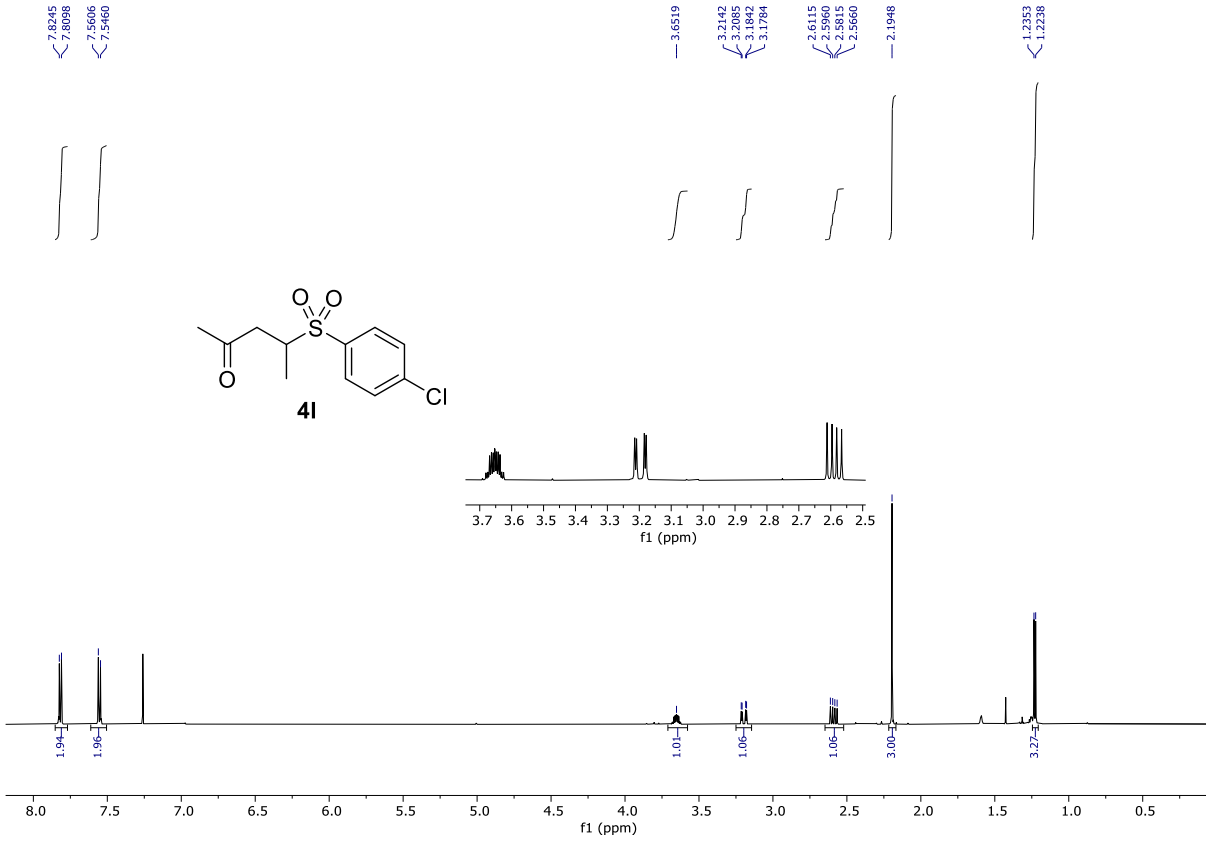
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4k (150 MHz, $CDCl_3$)



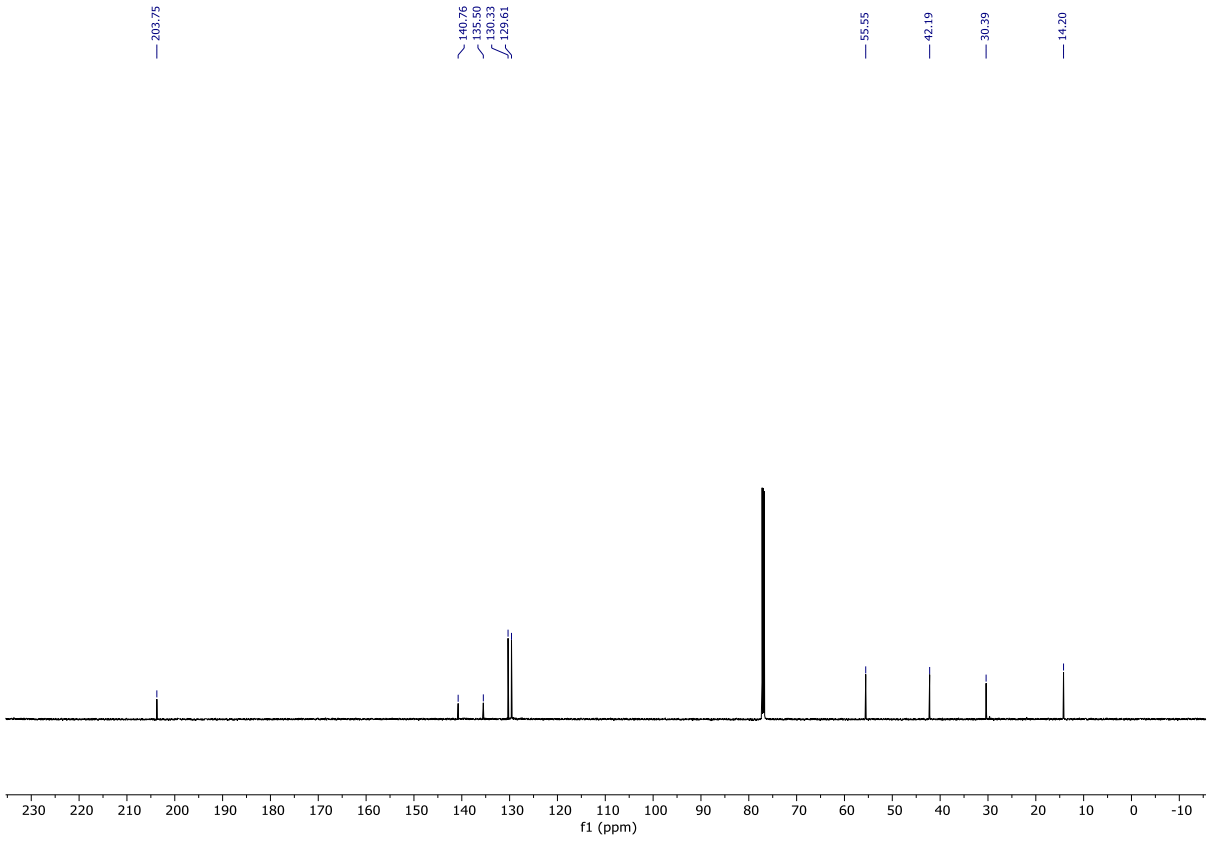
COSY-NMR of compound 4k (600 MHz, $CDCl_3$)



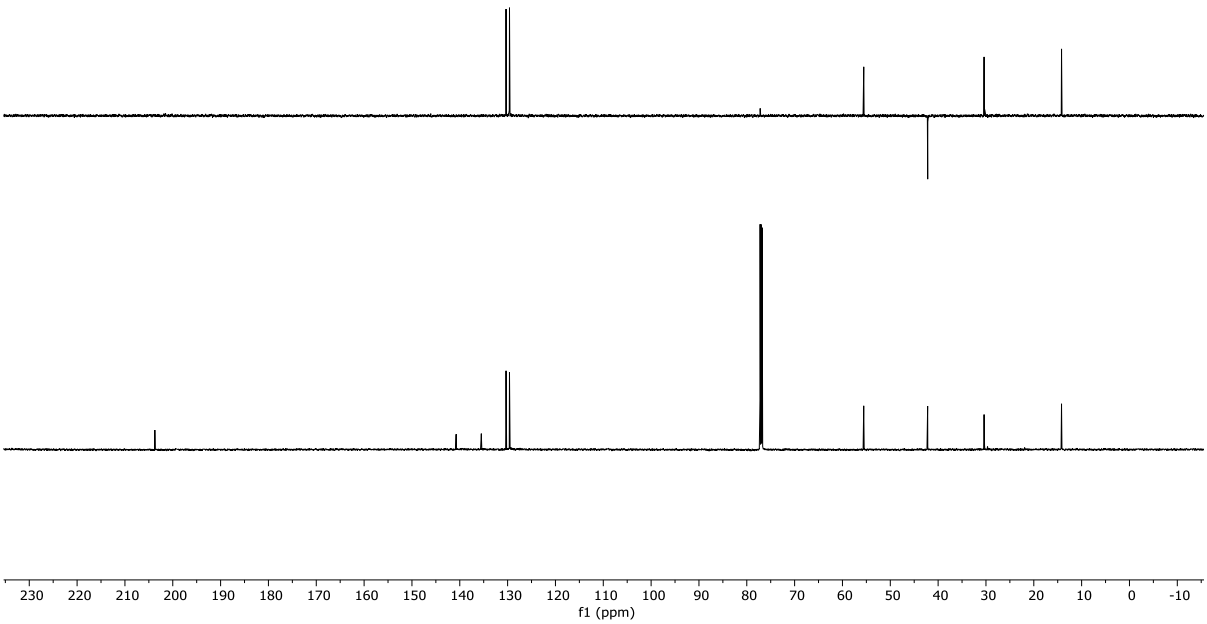
H-NMR of compound 4l (600 MHz, $CDCl_3$)



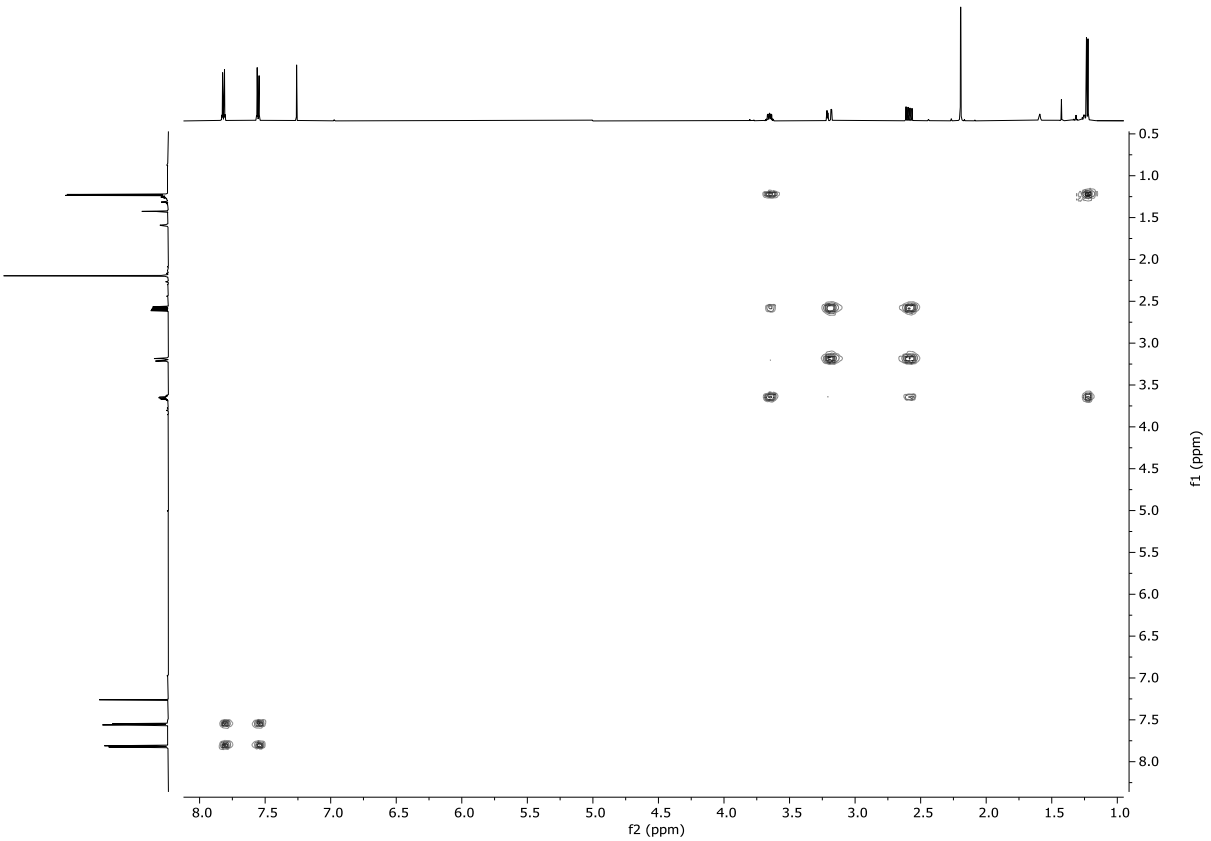
$^{13}C\{^1H\}$-NMR of compound 4l (150 MHz, $CDCl_3$)



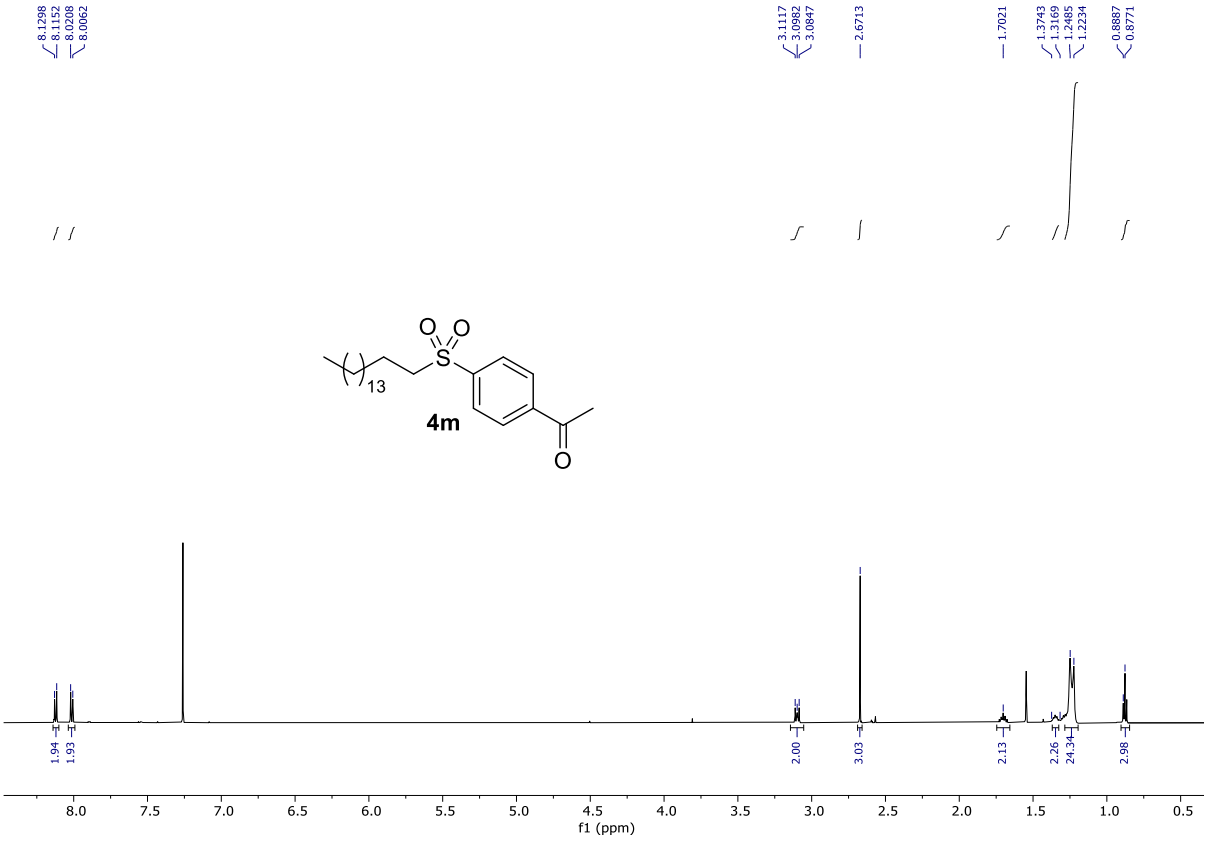
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4l (150 MHz, $CDCl_3$)



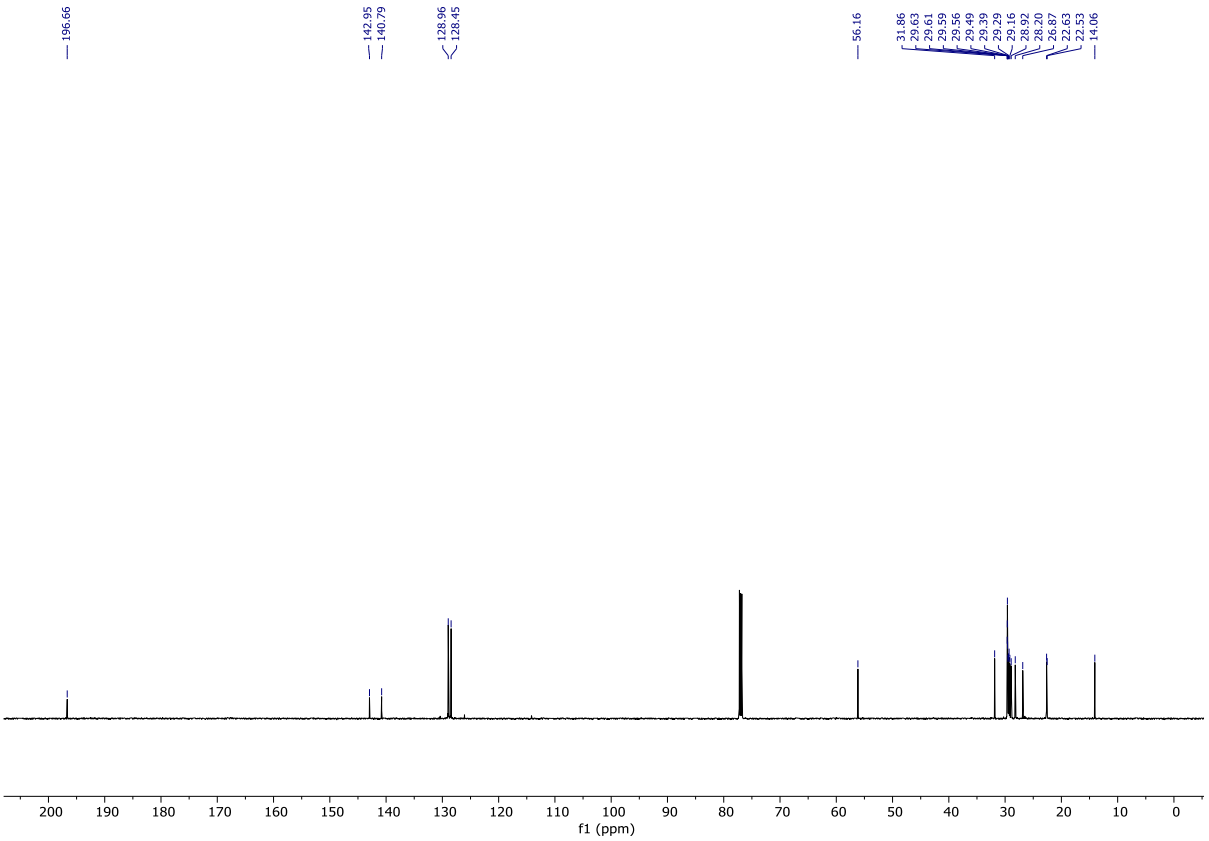
COSY-NMR of compound 4l (600 MHz, $CDCl_3$)



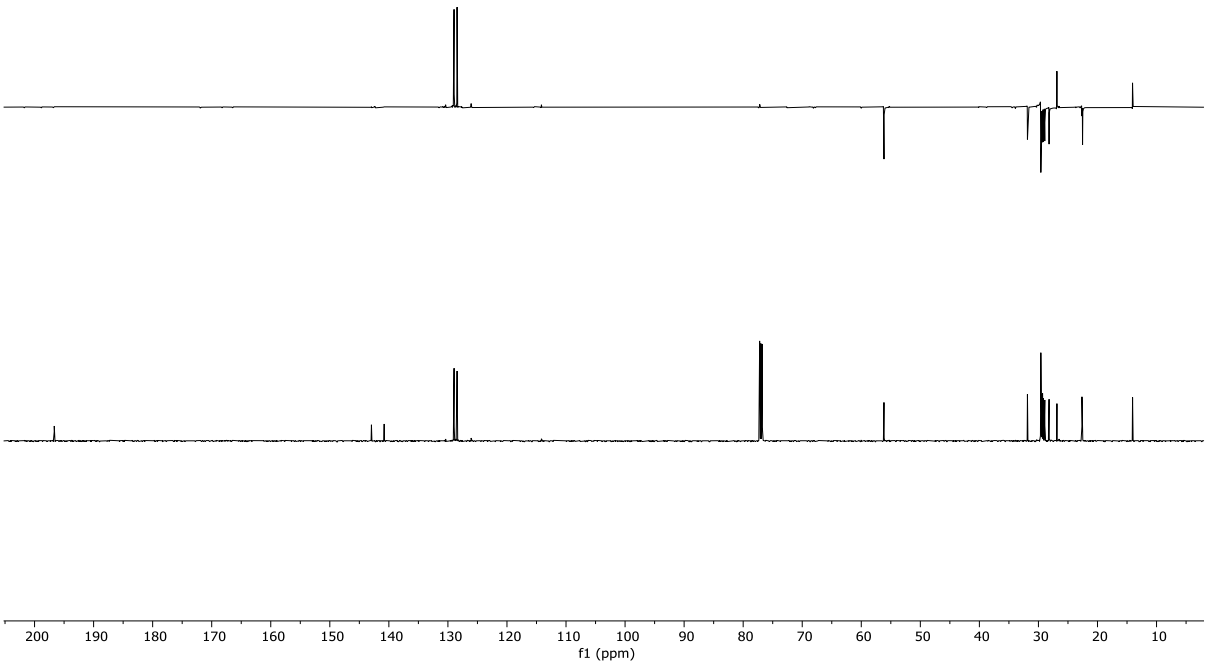
^{1}H-NMR of compound 4m (600 MHz, $CDCl_3$)



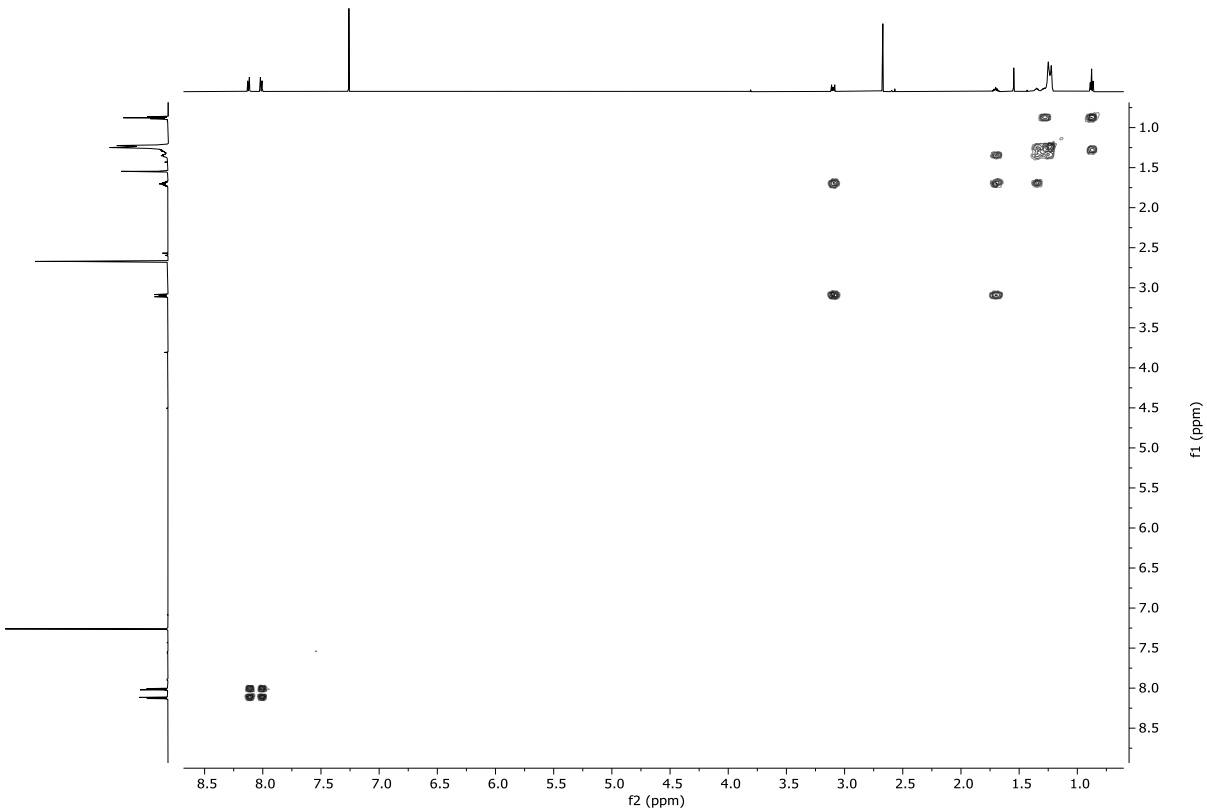
^{13}C{^{1}H}-NMR of compound 4m (150 MHz, $CDCl_3$)



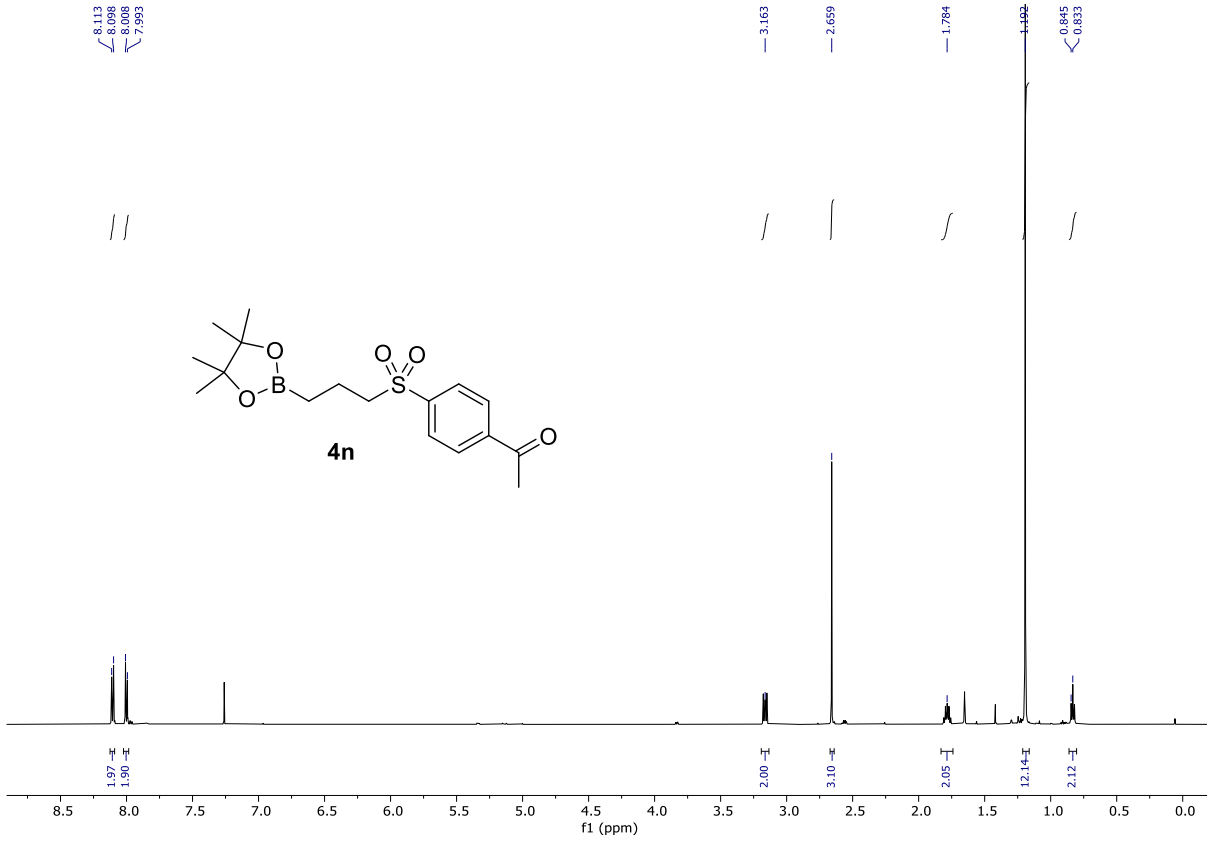
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4m (150 MHz, $CDCl_3$)



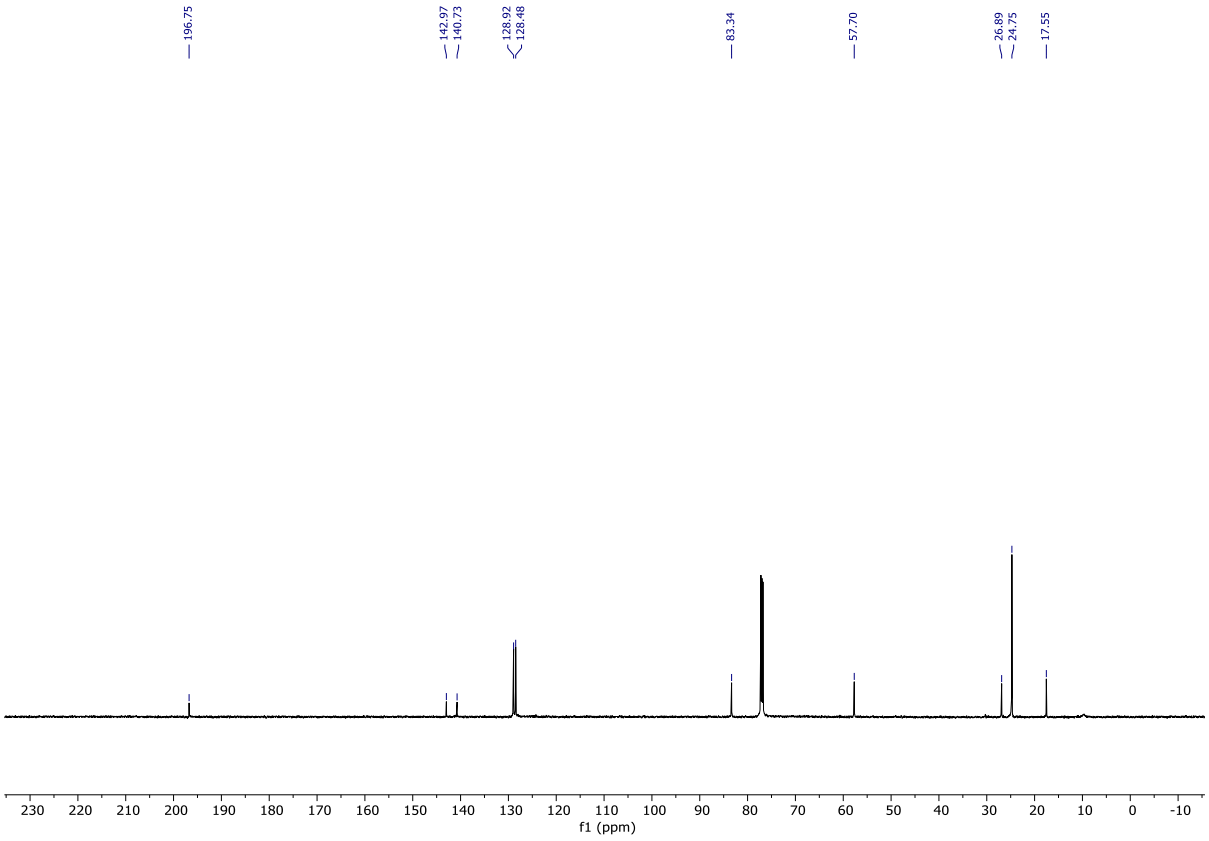
COSY-NMR of compound 4m (600 MHz, $CDCl_3$)



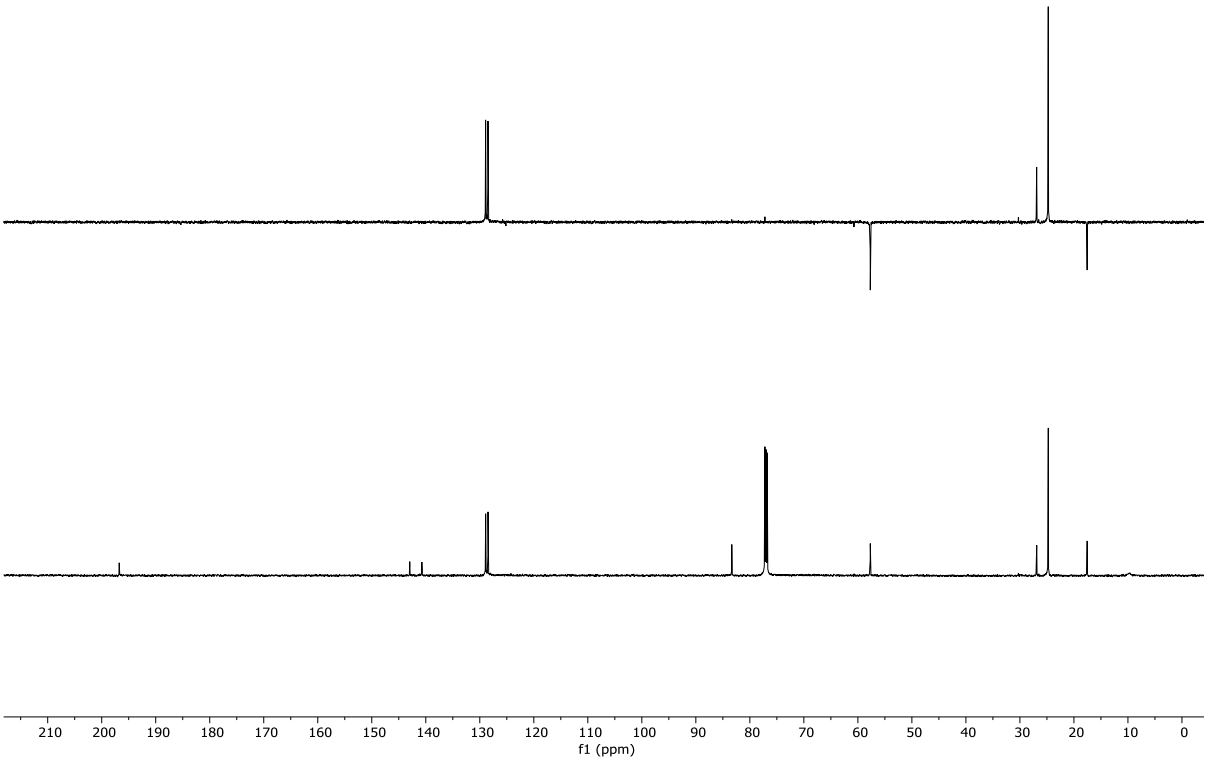
^{1}H-NMR of compound 4n (600 MHz, $CDCl_3$)



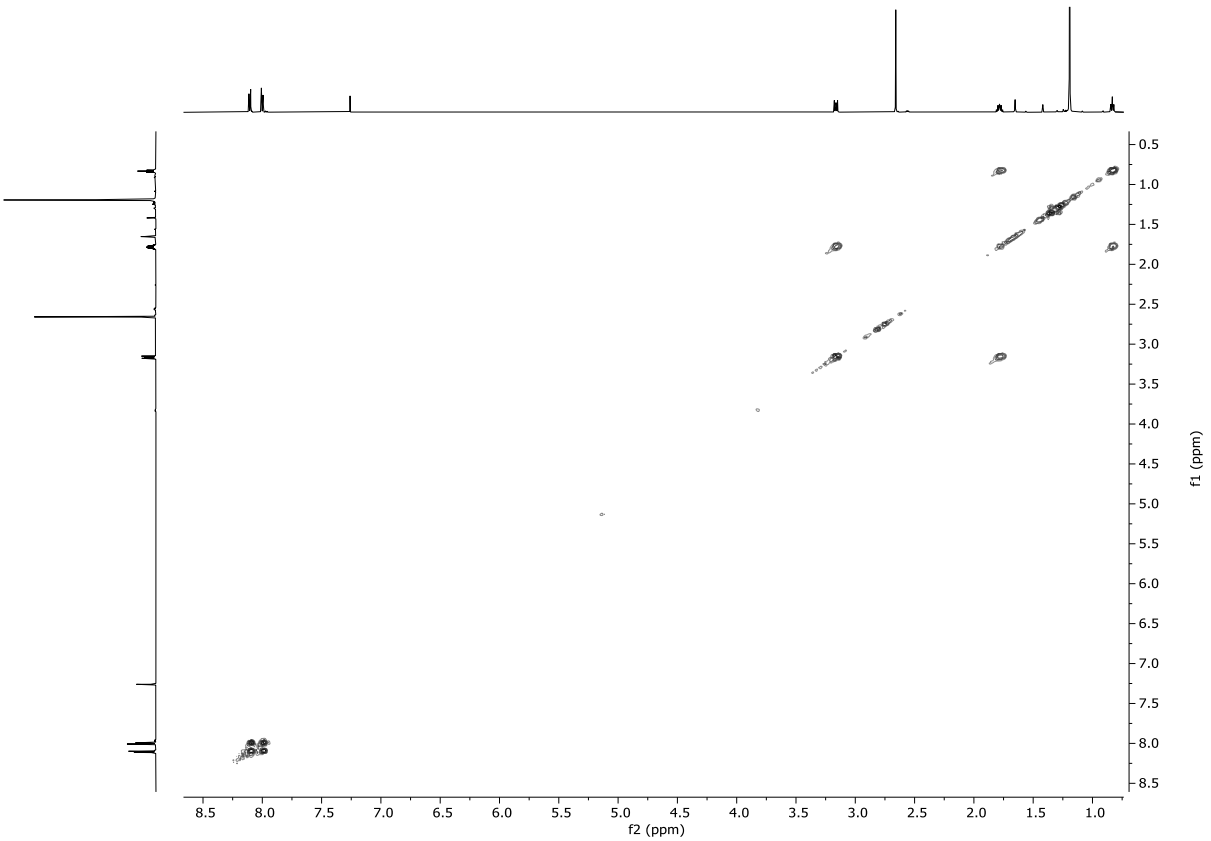
^{13}C{^{1}H}-NMR of compound 4n(150 MHz, $CDCl_3$)



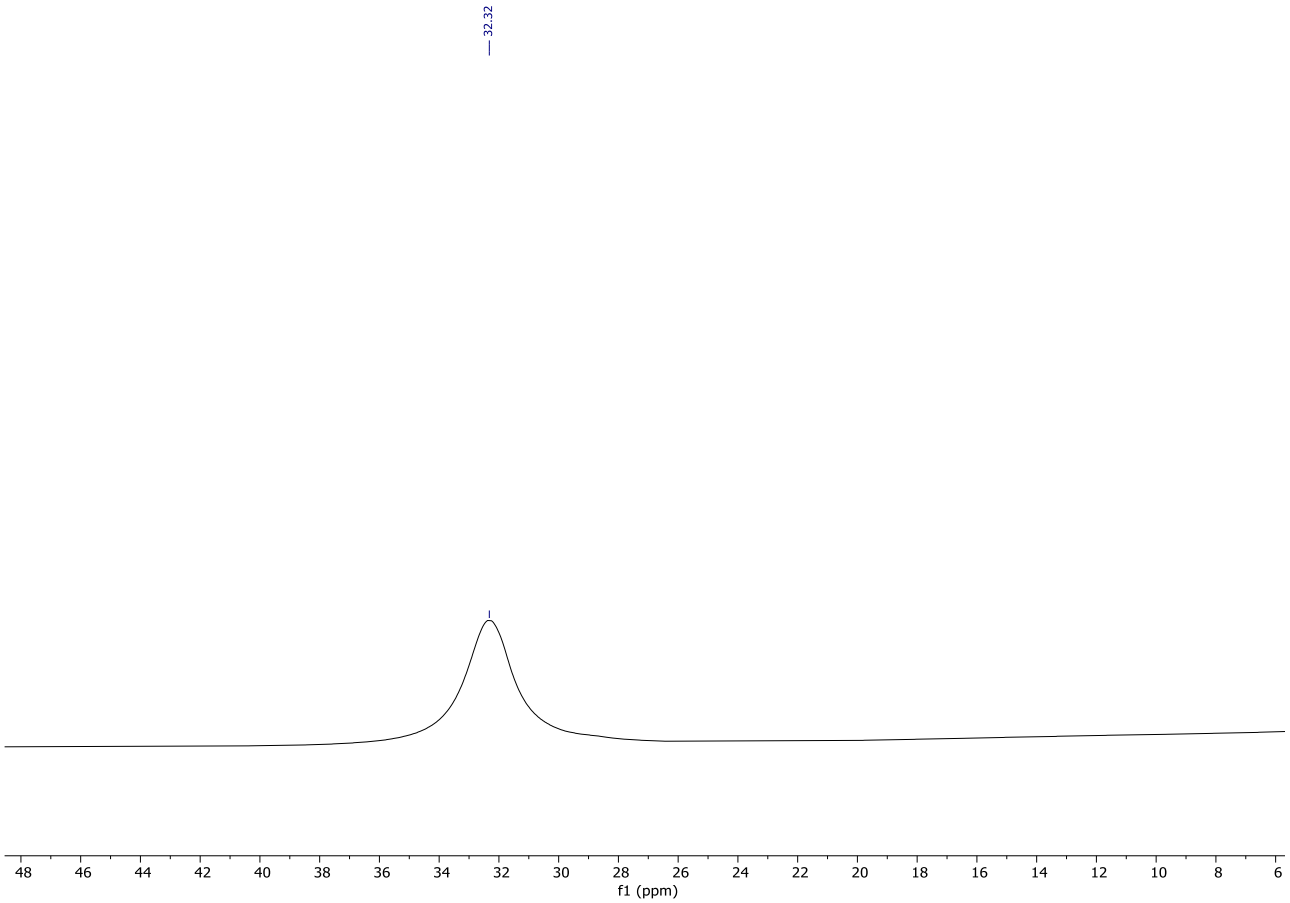
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4n (150 MHz, $CDCl_3$)



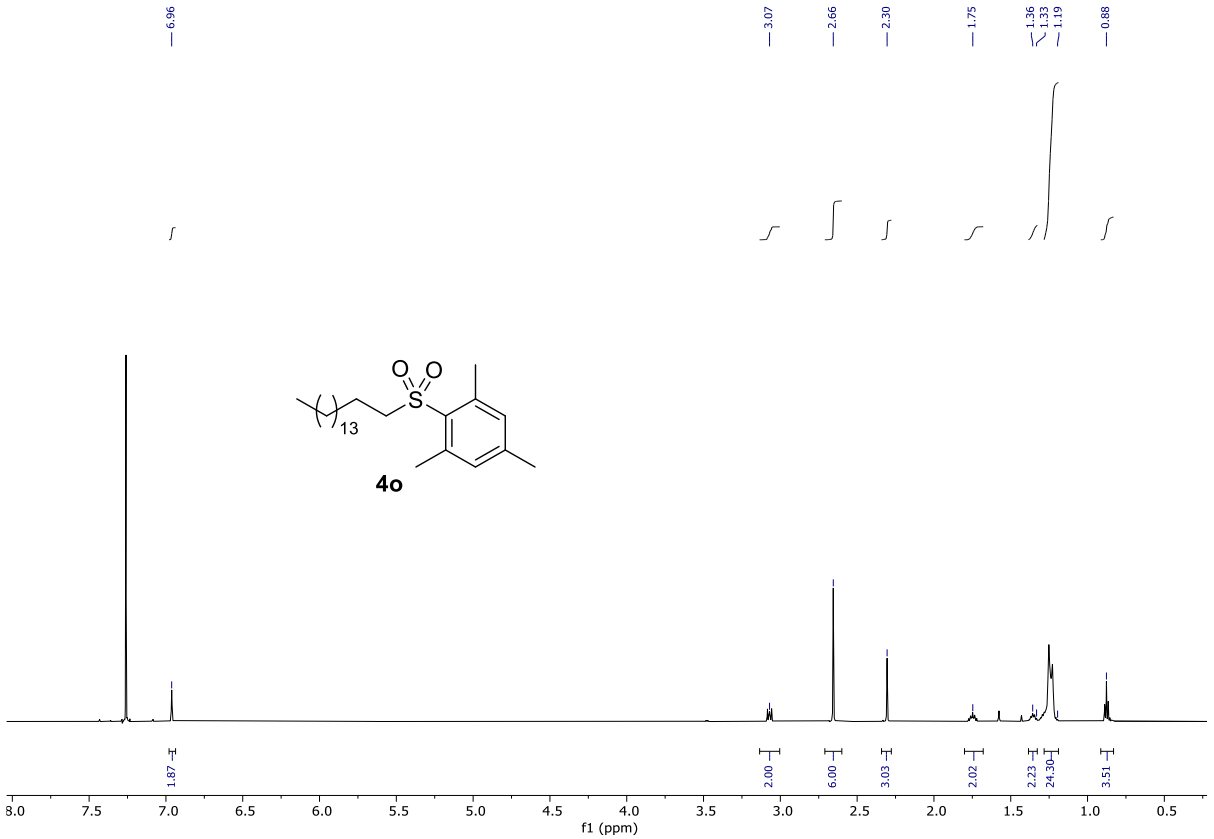
COSY-NMR of compound 4n (600 MHz, $CDCl_3$)



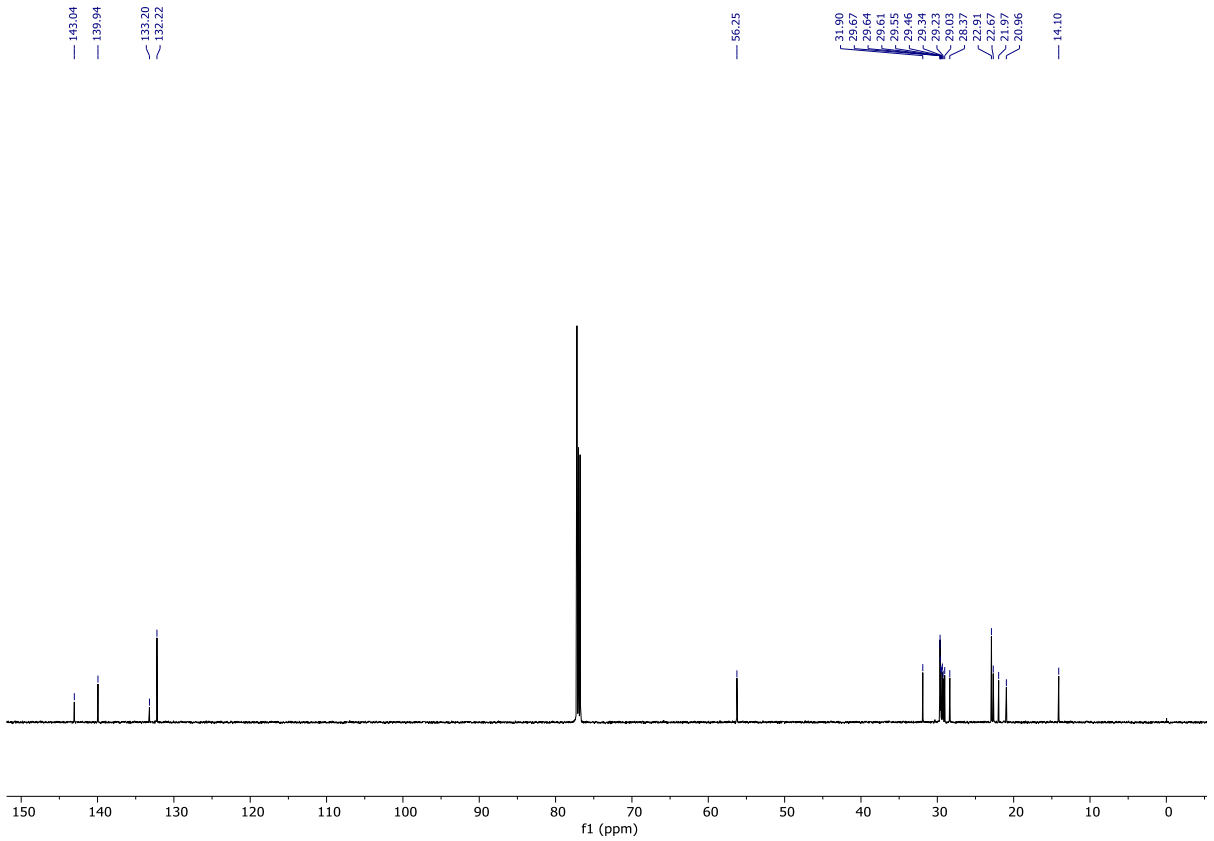
$^{11}B\{^{1}H\}$-NMR of compound 4n (192 MHz, $CDCl_3$)



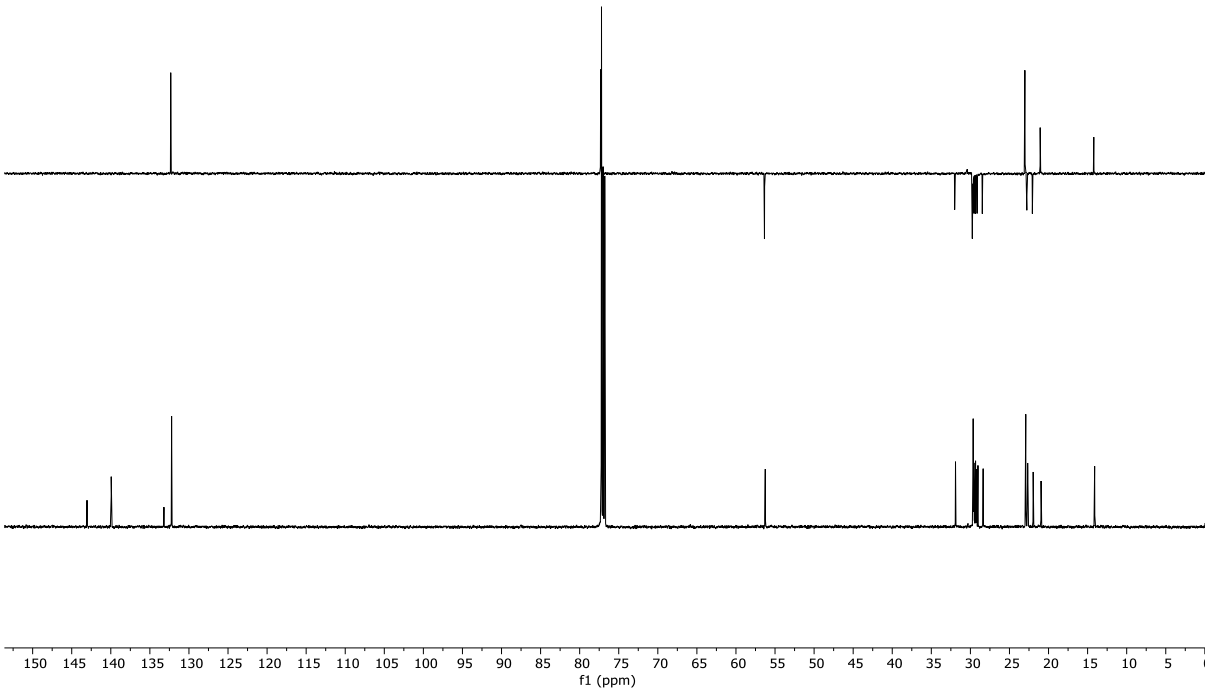
^{1}H-NMR of compound 4o (600 MHz, $CDCl_3$)



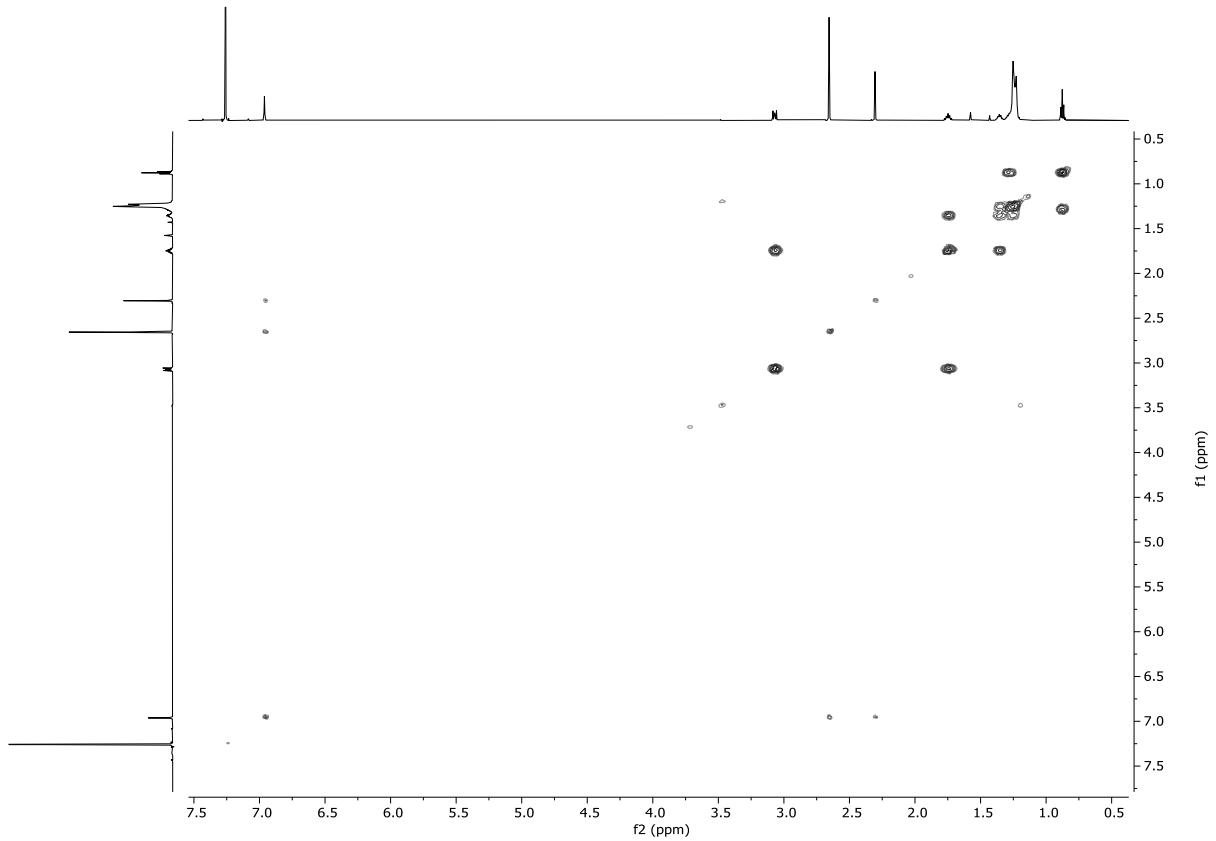
^{13}C{^{1}H}-NMR of compound 4o (150 MHz, $CDCl_3$)



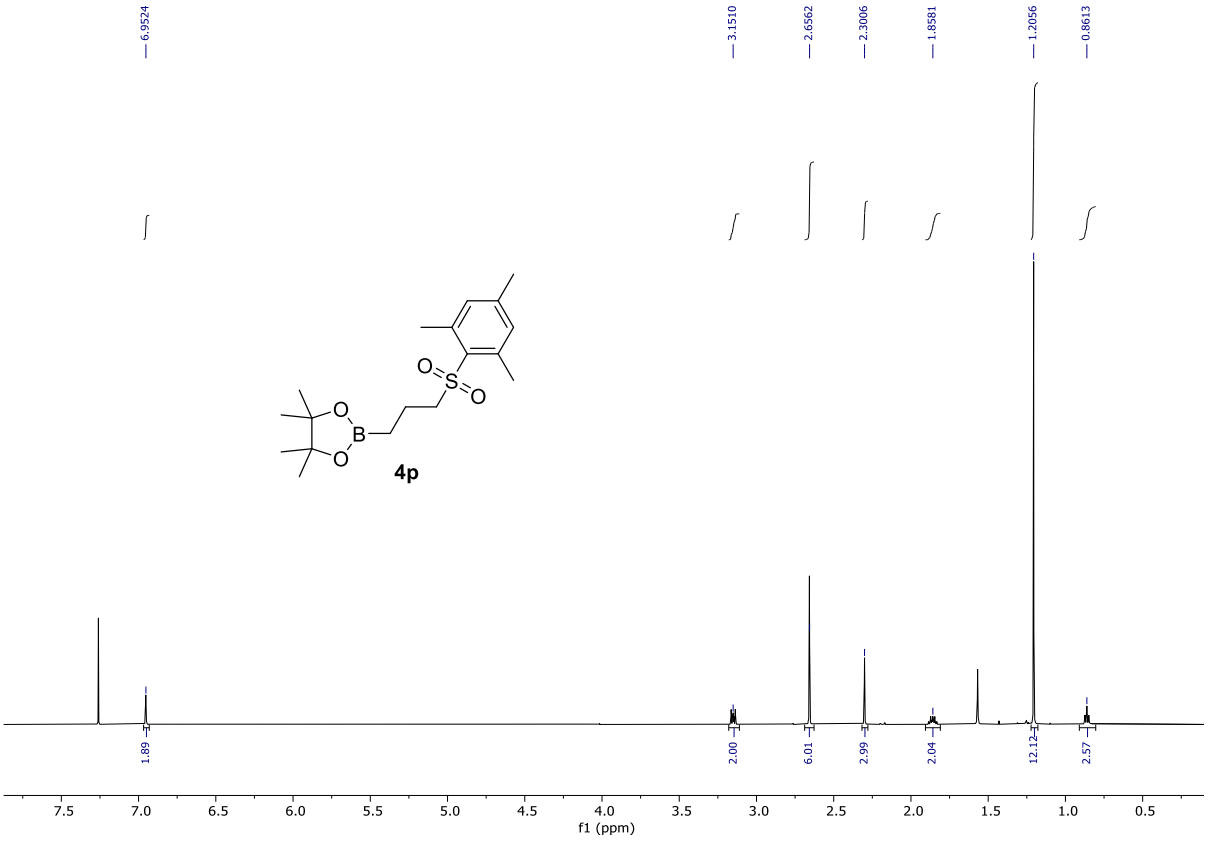
Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4o (150 MHz, $CDCl_3$)



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

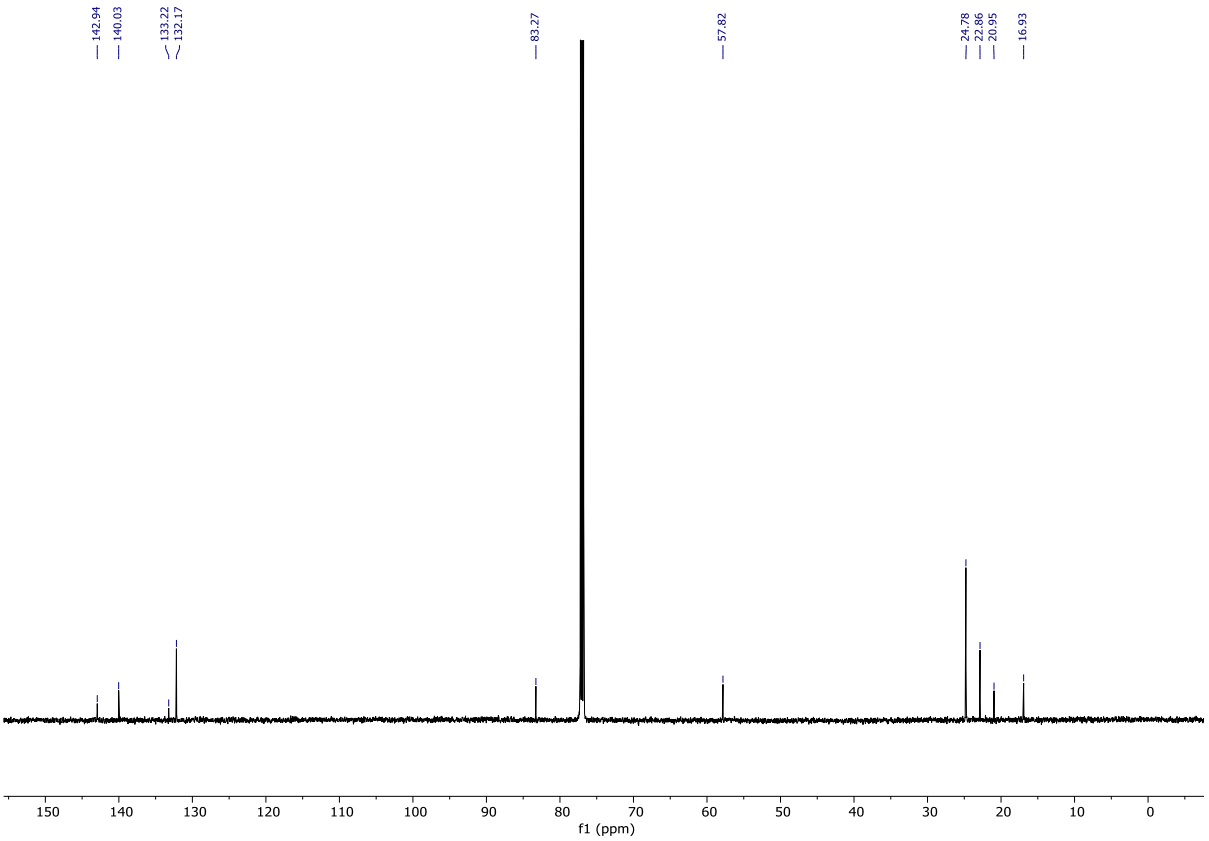


^{1}H-NMR of compound 4p (600 MHz, $CDCl_3$)

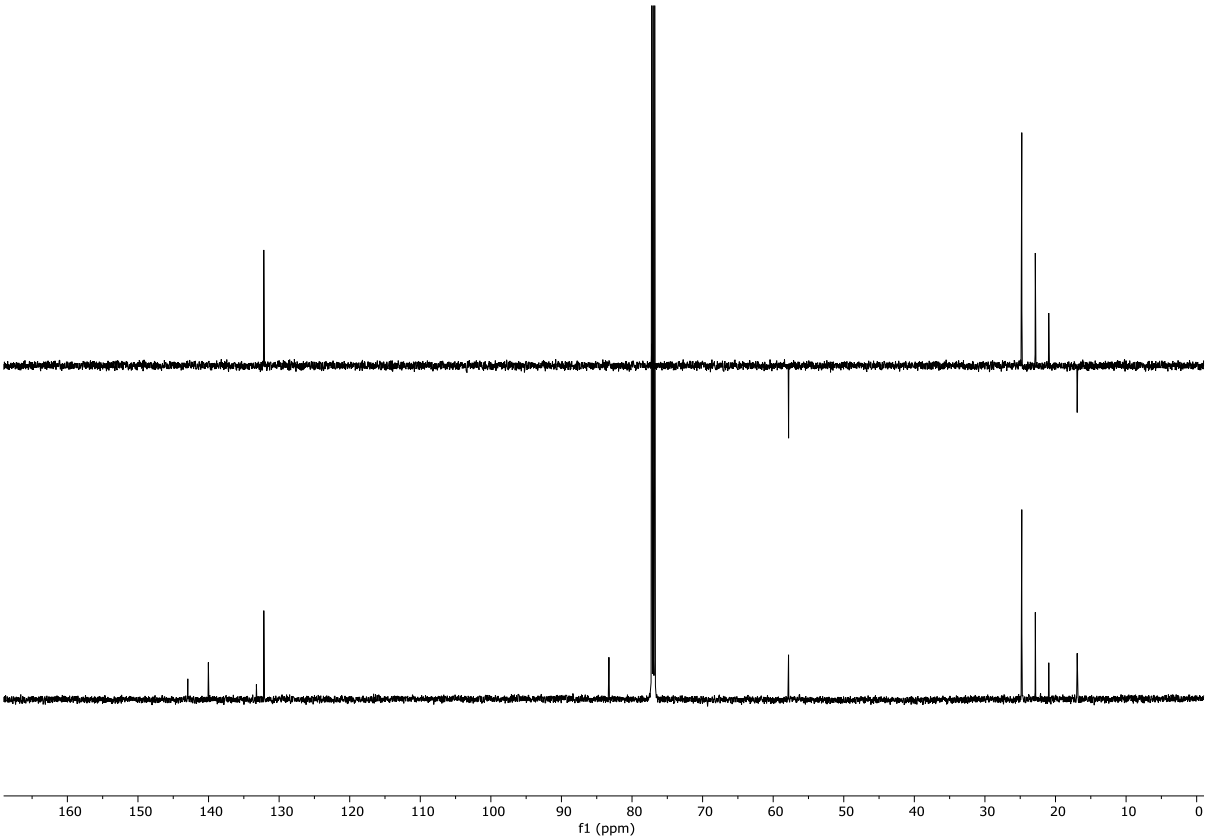


4p

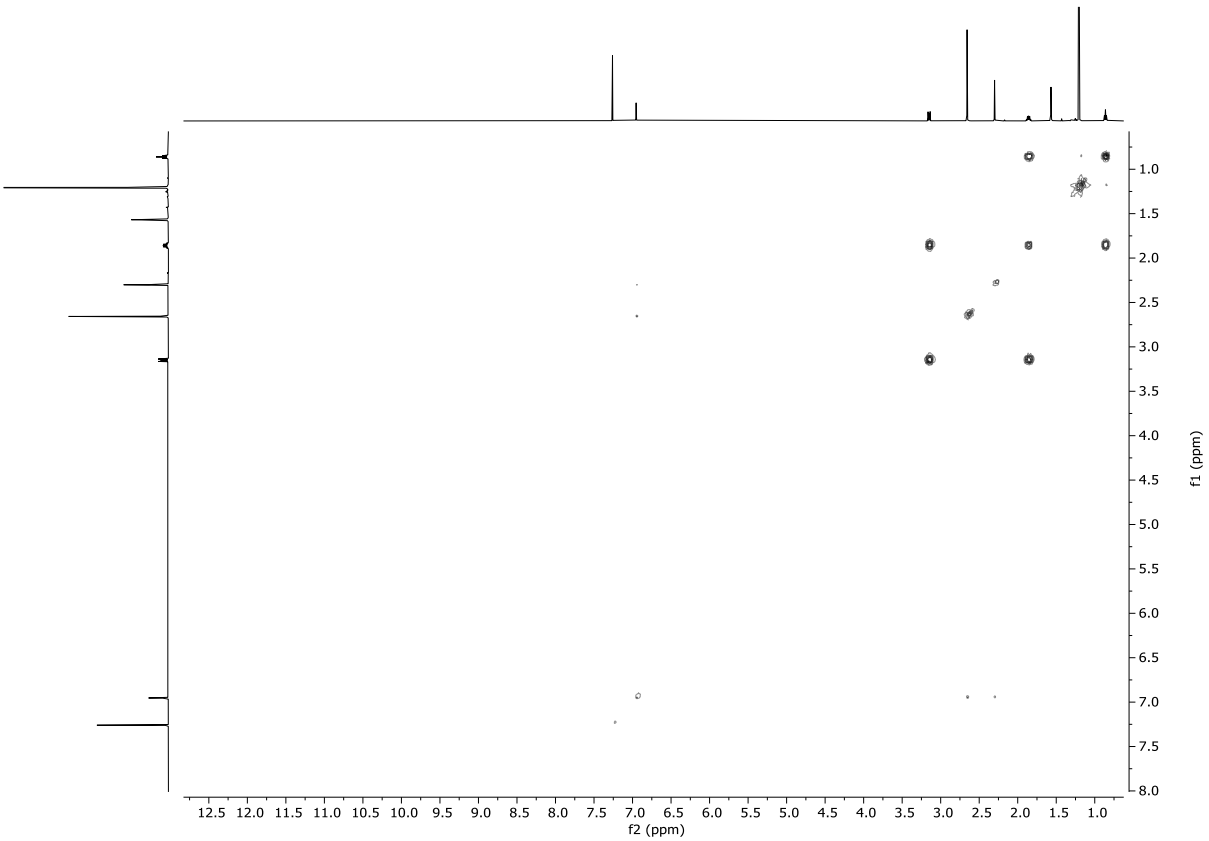
^{13}C{^{1}H}-NMR of compound 4p (150 MHz, $CDCl_3$)



Comparison between DEPT-135 and $^{13}C\{^{1}H\}$-NMR of compound 4p (150 MHz, $CDCl_3$)



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



$^{11}B\{^{1}H\}$-NMR of compound 4p (192 MHz, $CDCl_3$)