Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information

Three-Component Three-Bond Forming Cascade *via* Palladium Photoredox Catalysis

Contents

General information

General remarks

All reactions were performed in oven-dried glassware under argon, unless otherwise stated. Reaction temperatures are referred to the ones of the heating/cooling media (heating block, cryogenic bath), unless otherwise stated. Reactions were stirred using PTFE-coated magnetic stirring bars at ~ 1000 rpm, unless otherwise stated.

Low boiling solvents (<110°C) were removed by rotary evaporation under reduced pressure, heating the solution with a water bath at 40°C. High boiling solvents (>110°C) were removed *in vacuo* (< 1 mbar) at room temperature or under mild heating (< 50°C), unless otherwise stated.

Yields refer to chromatographically and spectroscopically (^{1}H, ^{13}C, ^{19}F) homogeneous material, unless otherwise stated. The identity literature-known compounds was assessed by comparison of ^{1}H NMR spectra and therefore reported. New compounds were characterized by means of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR (when applicable), HRMS, retention factor on thin layer chromatography.

Analytical techniques

Thin layer chromatography (TLC) was performed using Merck silica gel 60 F254 aluminum plates and visualization was accomplished with UV light (254 nm) and/or staining with basic $KMnO_4$ solution (4 g of $KMnO_4$, 10 g K_2CO_3, 1 g NaOH in 200 ml of distilled water).

GC samples were filtered over a short plug of silica (length: 2-3 cm, diameter: 4 mm) eluting with EtOAc before analysis, if not stated otherwise. GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system (Agilent 5975C VL MSD or an Agilent 5975 MSD) or Agilent Intuvo 9000 (Agilent 5977B MSD), and a HP-5MS column (0.25 mm ·30 m, film: 0.25 µm).

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at room temperature on a Bruker Avance 300 (^{1}H: 300.13 MHz; ^{13}C: 75.48 MHz), Avance 400 (^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz), Avance Neo 400 (^{1}H: 400.23 MHz; ^{13}C: 100.65 MHz), Varian 500 MHz INOVA (^{1}H: 499.83 MHz; ^{13}C: 125.70 MHz) or Varian Unity plus 600 (^{1}H: 599.31 MHz; ^{13}C: 150.71 MHz) in deuterated solvents (> 99.5 Deuteration) purchased from Eurisotop ($CDCl_3$) or Sigma-Aldrich (DMSO-d_6; D_2O, CD_3OD, THF-d_8, C_6D_6). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in parts per million (ppm) relative to tetramethylsilane (TMS) using the residual solvent signals as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δ_H= 7.26 ppm, δ_C= 77.16 ppm, DMSO-d_6: δ_H= 2.05 ppm, δ_C= 29.84 or 206.26 ppm, CD_3OD: δ_H= 3.31 ppm, δ_C= 49.00 ppm, D_2O: δ_H= 4.79 ppm, δ_C= absolute referencing, acetone-d_6: δ_H= 2.05 ppm, δ_C= 206.26, THF-d_8: δ_H= 3.58 or 1.73 ppm; C_6D_6: δ_H= 7.16 ppm, δ_C= 128.06 ppm). ^{19}F

and ^{31}P NMR spectra were calibrated using absolute referencing system, as suggested by IUPAC.[1] NMR-signals multiplicities that can be analyzed as first order multiplets are reported using the following abbreviations (or combination thereof): s = singlet, d = doublet, t =triplet, q = quartet, p= quintet, hept = heptet; m =multiplet, br =broad signal. All spectra were processed using MestReNova 12 using standard phase and baseline correction automations. When the isomer ratio was found to be >95:5, only one isomer was quoted. Otherwise, clearly recognizable and diagnostic signals of the minor isomer have been reported.

ESI accurate mass spectra (HRMS) were recorded on a MicroTof (Bruker Daltronics, Bremen) with loop injection. Mass calibration was performed using sodium formate cluster ions immediatley followed by the sample in a "quasi-internal" calibration or alternatively on an LTQ Orbitap LTQ XL (Thermo-Fisher Scientific, Bremen) with nano spray.

Photocatalytic setup

Photochemical reactions were performed in a Hepatochem EvoluChem™ PhotoRedOx Box Duo device and irradiated with two EvoluChem™ P303-30-1 LEDs (30 W, λ_{max}= 450 nm). The reaction temperature was measured to be between 25 °C and 30 °C using this setup.

[1] R. K. Harris, E. B. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Pure Appl. Chem*., 2008, **80**, 59–84.

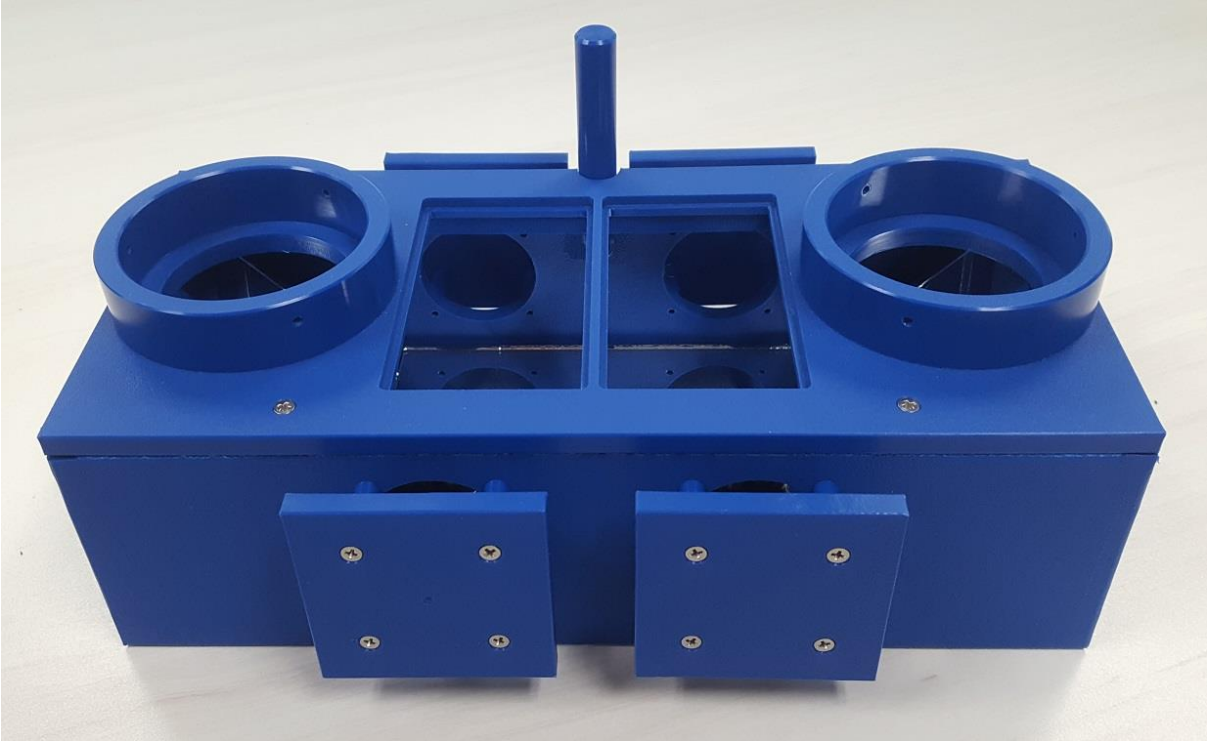


Figure S1. Hepatochem EvoluChem™ PhotoRedOx Box Duo (without light sources and vial holders). Courtesy of Hepatochem.

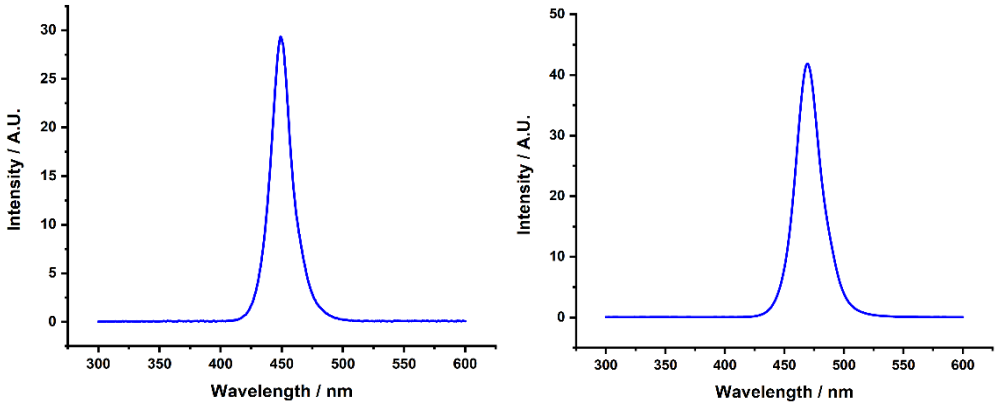


Figure S2. Measured emission spectra of the EvoluChem™ P303-30-1 LEDs light source (left) and Kessil H150 blue (right)

Large scale photocatalytic reactions in batch were performed using two Kessil H150 blue (34 W, 455 nm) as light sources. The lights were placed at 3 cm away from the vessel, while a cooling fan avoided excessive temperature increase (see **Figure S3**). A standard stirring plate (approx. 1000 rpm) ensured proper stirring of the reaction. The monitored reaction temperature was found to reach 35-35.5 °C over the course of the reaction.

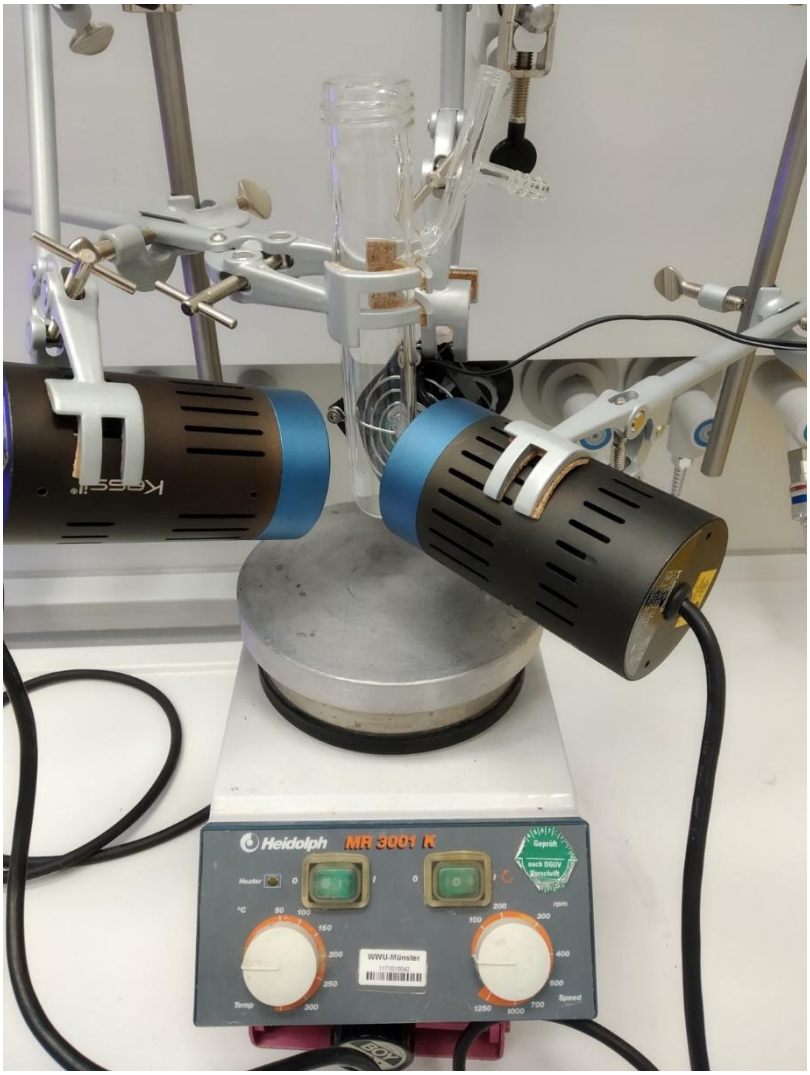


Figure S3. Custom-made setup for large scale reactions.

Flow chemistry setup

Reactions were performed in a Hepatochem PhotoRedOx™ Flow Reactor (HCK1006-01-022, volume: 2 ml) in the Hepatochem EvoluChem™ PhotoRedOx Box Duo equipped with EvoluChem™ P303-30-1 LEDs (30 W, λ_{max}= 450 nm) lights. The reaction solution was dispensed using a WPI SP101i syringe pump loaded with HENKE-JECT® plastic syringes. The syringe was connected to the tubing via a ChromTech F-300 FingerTight III 10-32 PEEK fitting.

Purification techniques

Flash column chromatography was performed according to the report of Still and co-workers[2] using ACROS Organics silica for chromatography 0.035-0.070 mm, 60 Å as stationary phase under a slight positive pressure, using the reported solvent mixture as mobile phase.

Solvents

Unless otherwise stated, dry (H_2O content < 50 ppm) reaction solvents were used to perform reactions. The following solvents (ACROS ExtraDry solvents with ACROSeal® cap) were purchased from ACROS Organics, stored under 3 or 4 Å activated molecular sieves and collected under positive argon pressure: dimethylsulfoxide (DMSO), ethyl acetate (EtOAc), 1,4-dioxane. The following solvents were purchased from ACROS Organics, Sigma-Aldrich and Fischer Scientific (HPLC grade) and purified using a custom SPS with activated alumina columns (built by the "Feinmechanische Werkstatt des Organisch-Chemischen Instituts") and collected under positive argon pressure according to Grubbs procedure[3]: acetonitrile (MeCN), tetrahydrofuran (THF), diethyl ether (Et_2O), *N*,*N*-dimethylformamide (*N*,*N*-DMF), hexane, toluene, 1,2-dichloroethane (1,2-DCE) and dichloromethane (DCM).

Solvents for flash column chromatography (*n*-pentane, CH_2Cl_2, EtOAc) and work-up procedures were of technical grade and purified by atmospheric distillation. MeOH was purchased from Sigma-Aldrich (reagent grade) and used without further purification. Brine refers to a saturated NaCl solution in deionized water.

Purchased chemicals

The following chemicals were purchased from commercial sources and used without further purification, unless otherwise stated.

Table S1. List of commercially available chemicals.

CAS #	Chemical	Grade	Producer
166-99-0	1,3-butadiene 2 M in THF	---	TCI
824-79-3	Sodium *p*-toluenesulfinate	95%	Lancaster
14221-01-3	$Pd(PPh_3)_4$	98%	Carbolution
166330-10-5	DPEPhos	98%	Sigma- Aldrich
98327-87-8	*rac*-BINAP	97%	Fluorochem

[2] W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem*., 1978, **43**, 2923–2925

[3] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics,* 1996, **15**, 1518–1520

161265-03-8	Xantphos	98%	Fluorochem
603-35-0	PPh_3	99%	Fluorochem
584-08-7	K_2CO_3	99%	Applichem
534-17-8	Cs_2CO_3	99%	Fluorochem
127-08-2	KOAc	99%	Sigma-Aldrich
144-55-8	$NaHCO_3$	99.5%	ACROS Organics
1310-73-2	NaOH	98%	ACROS Organics
7087-68-5	DIPEA (dry)	>99.5%	ACROS Organics
1310-58-3	KOH	>85%	ACROS Organics
121-44-8	Et_3N (dry)	99.7%	ACROS Organics
109-02-4	*N*-Me-morpholine	98%	Karl Roth
7632-00-0	$NaNO_2$	98.5%	ACROS Organics
7647-01-0	HCl 37%	Reag. Gr.	VWR chemicals
74-95-3	CH_2Br_2	99%	Sigma-Aldrich
7681-11-0	KI	Reag. Gr.	Prolabo
115-18-4	2-Methyl-3-Buten-2-ol	98%	Alfa Aesar
10035-10-6	HBr 48%	97%	Flurochem
7790-94-5	Chlorosulfonic acid	97%	ACROS Organics
7757-83-7	Na_2SO_3	98.5%	ACROS Organics
874-63-5	3,5-Dimethylanisole	99%	Alfa Aesar
623-12-1	4-Chloroanisole	99%	Alfa Aesar
594-44-5	Ethanesulfonyl chloride	98%	Combiblocks
124-63-0	Methanesulfonyl chloride	99.5%	ACROS Organics
123-30-8	4-Aminophenol	>98%	TCI
26628-22-8	NaN_3	98%	TCI
122-51-0	Triethyl orthoformate	98%	ACROS Organics
110-13-4	Hexane-2,5-dione	>97%	Merck
6192-52-5	*p*-Toluenesulphonic acid·H_2O	>98%	Carl Roth
1895-39-2	Sodium chlorodifluoroacetate	>99%	TCI
7726-95-6	Bromine	>99%	ACROS Organics
452-72-2	4-Fluoro-*o*-cresol	98%	Chempur
90-43-7	2-Phenylphenol	99%	Alfa Aesar
124-40-3	Dimethylamine 40% H_2O	--	ACROS Organics
92-69-3	4-Phenylphenol	97%	Aldrich
123-31-9	Hydroquinone	99%	Alfa Aesar
95-65-8	3,4-Dimethylphenol	99%	ACROS Organics
501-94-0	2-(4-Hydroxyphenyl)ethanol	98%	Combiblocks
106-22-9	(±)-Citronellol	95%	Alfa Aesar
513-81-5	2,3-Dimethylbutadiene	98%	Alfa Aesar
110-91-8	Morpholine	99%	Alfa Aesar
123-75-1	Pyrrolidine	99%	ACROS Organics
110-89-4	Piperidine	99%	Alfa Aesar
111-49-9	Hexamethyleneimine	>98%	Alfa Aesar

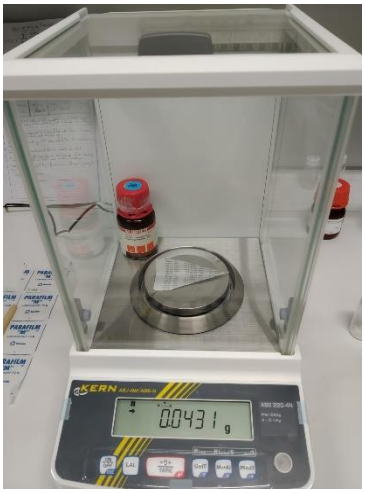
109-89-7	Diethylamine	99%	ABCR
100-60-7	*N*-Methylcyclohexylamin	98%	VWR
109-05-7	2-Methylpiperidine	>98%	Alfa Aesar
91-21-4	1,2,3,4-Tetrahydroisoquinoline	97%	Alfa Aesar
92-54-6	1-Phenylpiperazine	98%	Alfa Aesar
120-72-9	1*H*-Indole	97%	Fluorochem
1006-94-6	5-Methoxyindole	97%	Chempur
86-74-8	9*H*-Carbazole	>95%	Aldrich
90-05-1	Guaiacol	98%	Aldrich
150-19-6	3-Methoxyphenol	97%	Alfa Aesar
150-76-5	Mequinol	>98%	Alfa Aesar
619-60-3	4-(Dimethylamino)phenol	95%	Fluorochem
103-90-2	Paracetamol	98%	ACROS Organics
57-63-6	Ethynylestradiol	>98%	Aldrich
53-16-7	Estrone	>98%	Fluorochem
874-23-7	2-Acetylcyclohexanone	98%	Alfa Aesar
105-53-3	Diethyl malonate	>99%	TCI
1655-07-8	Ethyl-2-oxocyclohexancarboxylate	95%	ACROS Organics
815-57-6	3-Methylacetylacetone	95%	Alfa Aesar
22560-16-3	Lithium triethylborohydride 1.7 M	--	ACROS Organics
19978-61-1	$Pd(dppe)Cl_2$	99%	Strem
79-03-8	Propionyl chloride	98%	ACROS Organics
7550-45-0	$TiCl_4$	>99%	Alfa Aesar
2564-83-2	TEMPO	98%	Carbolution
1191-15-7	DIBAL-H 1M in hexanes	--	Sigma-Aldrich
16940-66-2	$NaBH_4$	99%	ACROS Organics
10217-52-4	$NH_2NH_2{\cdot}H_2O$ (51%)	80%	ACROS Organics
2622-14-2	PCy_3	98%	ABCR
1663-45-2	dppe	99%	Aldrich

Step-by-step graphical procedures

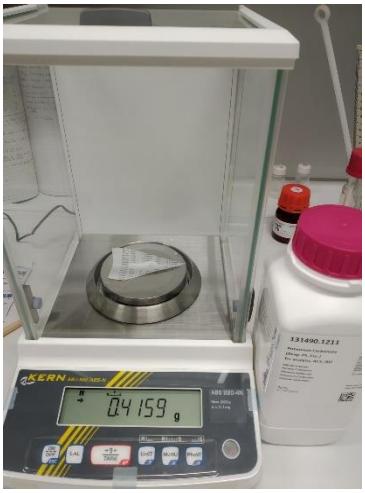
Step-by-step graphical procedure for large scale reaction

Note: The order of weighting of solid reagents is random. For liquid reagents, we suggest adding the butadiene solution at the end to avoid loss of gaseous reagent.

1) Nucleophile sodium *p*-toluenesulfinate **3a** weighted under air.



2) Ligand DPEPhos is weighted under air.



3) Base K_2CO_3 is weighted under air.

4) $Pd(PPh_3)_4$ is weighted under air.

5) The reaction vessel is connected to the Schlenk line and evacuated-back filled with argon four times.

6) The solvent 1,4-dioxane is added under argon counterflow.

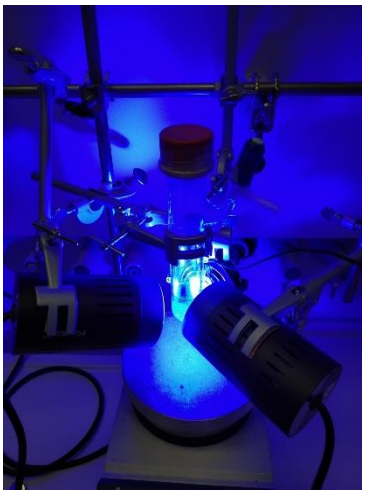
7) Appearance of the reaction (yellow suspension)

8) The bromide**1a** is weighted using a tared plastic syringe.

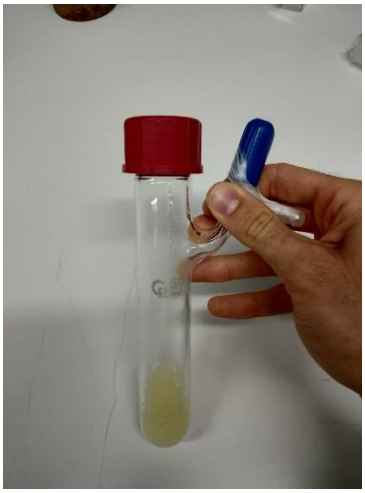
9) The bromide **1a** is transferred to the vessel under argon counterflow.

10) The solution of butadiene in THF is transferred to the vessel under argon counterflow, then the vessel is tightly sealed.

11) The reaction is placed in the photoreactor, stirring set to approximately 1000 rpm.



12) The reaction is irradiated at 450 nm using the above described setup. A cooling fan is placed to prevent the reaction temperature to raise above 35°C (measured).



13) The reaction appearance after irradiation.

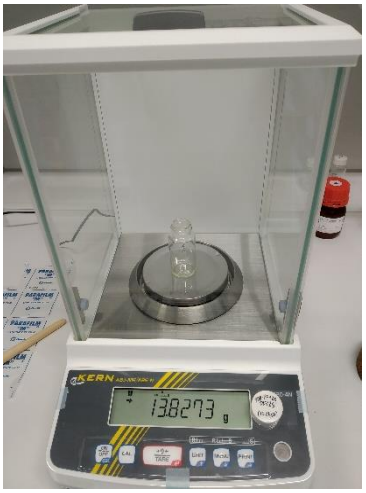
14) Thin layer chromatography (*n*-pentane/EtOAc = 5/1) of the crude reaction mixture, stained with basic $KMnO_4$ solution.

R_f ~ 1.0 PPh_3, apolar bprod.
R_f = 0.45, product **4a**

15) The reaction was filtered through a short pad of silica, washing thoroughly with ethyl acetate.

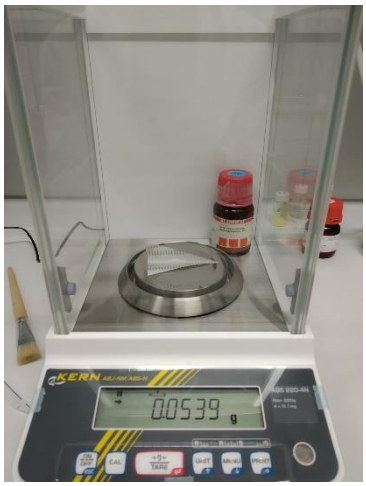
16) The solvent was removed *in vacuo* by rotary evaporation (40 °C) and loaded on silica.

17) The reaction was purified by flash column chromatography on silica, using *n*-pentane/EtOAc = 6/1 to 5/1 as eluant.



18) The product **4a** was obtained as a colorless viscous oil/gum (tare: 13.2457 g) after evaporation of the fractions and drying under high vacuum overnight.

Step-by-step graphical procedure for reaction in flow



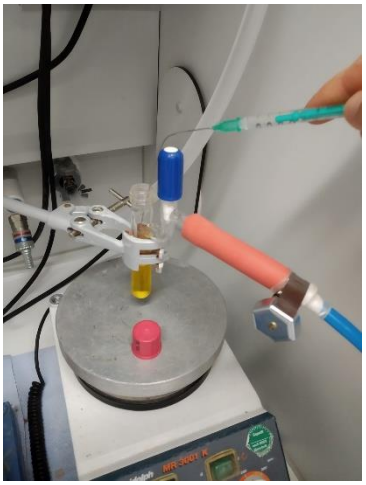
1) Ligand DPEPhos is weighted under air.

2) Palladium source $Pd(PPh_3)_4$ is weighted under air.

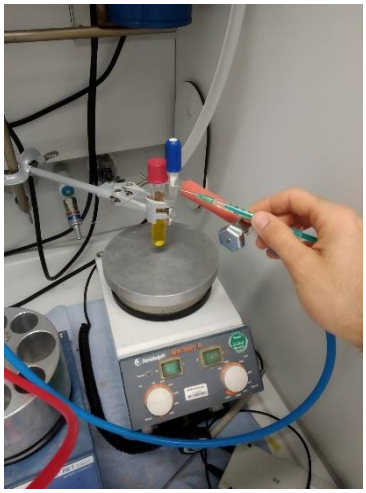
3) The solid reagents are added to the Schlenk tube, then the vessel is evacuated and back-filled with argon four times.

4) Dry 1,4-dioxane is added, then the suspension was stirred until dissolution (most likely thanks to the ligation of DPEPhos with Pd).

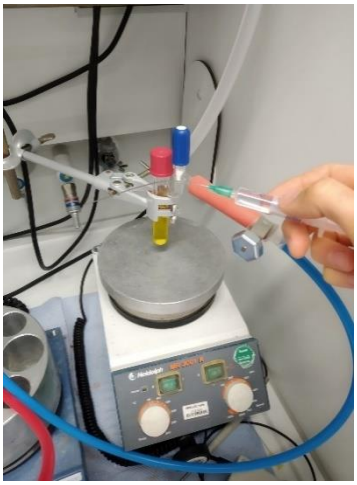
5) The bromide **1b** is weighted under air using a Hamilton Glasstight syringe, then transferred to the reaction solution under argon counterflow.



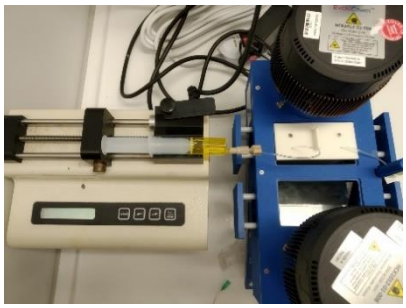
6) The base Et_3N is added under argon counterflow.



7) The nucleophile morpholine is added under argon counterflow.

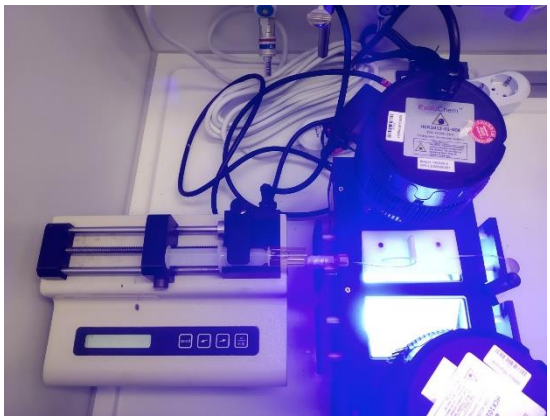


8) Solution of butadiene in THF is added under argon counterflow and the vessel immediately sealed to avoid loss of the volatile reagent).



9) The solution is transferred to a plastic syringe and connected to the flow set-up.

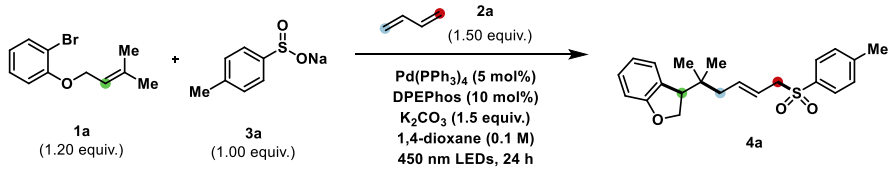
10) Set-up with opened lid before usage, with syringe pump (left) connected to the flow reactor (right).



11) Reaction irradiation 450 nm using the flow set-up.

Sensitivity Assessment

According to the adapted procedure from Glorius and co-workers,[4] the sensitivity of the reaction towards different experimental conditions was assessed.



Preparation of stock solution (for 10 aliquots)

In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol, 5 mol%) and DPEPhos (53.9 mg, 0.10 mmol, 10 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (7.0 ml) was added, followed by bromide **1a** (289.4 mg, 1.20 mmol, 1.20 equiv.), then the solution was stirred until complete dissolution of the reactants.

Preparation of the reactions (0.1 mmol scale)

In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, sodium *p*-toluenesulfinate **3a** (17.8 mg, 0.10 mmol, 1.00 equiv.) and K_2CO_3 (20.7 mg, 0.15 mmol, 1.50 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon four times. The amount of additional 1,4-dioxane (see **Table S2**) was added, followed by 700 µl of stock solution. If required, further additives or procedures were added/performed at this stage. 1,3-butadiene 2 M in THF (75 µl, 0.15 mmol, 1.50 equiv.) was added, then the vessel was sealed and irradiated with the standard setup at 450/455 nm for 24 hours, except when different conditions were needed (see table and images below). After irradiation, the reaction was filtered through a short pad of silica, rinsing with EtOAc, then the volatiles were removed *in vacuo*. The reaction mixture was analyzed by ^{1}H NMR, using dibromomethane as internal standard (relaxation delay d_1 = 30 s.).

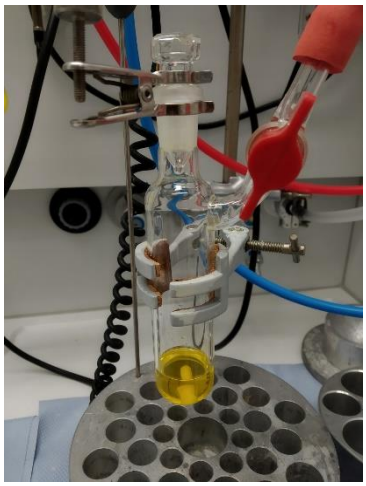
[4] L. Pitzer, F. Schäfers, F. Glorius, *Angew. Chem. Int. Ed.*, 2019, **58**, 8572-8576.

Table S2. Reactions performed in the condition-based sensitivity screening.

Entry		Add. 1,4-dioxane	Additive	Add. procedure
1	Standard	225 µl	--	--
2	Low concentration (-10%)	325 µl	--	--
3	High concentration (+10%)	125 µl	--	--
4	High intensity (~16x)	225 µl	--	0.5 cm from light source
5	Low intensity (~1/16x)	225 µl	--	8.8 cm from light source
6	High temperature	225 µl	--	Aluminum wrapped
7	Low temperature	225 µl	--	Jacketed Schlenk with water cooling
8	Low temperature ref.	225 µl	--	Jacketed Schlenk, no flow
9	High H_2O (10000 ppm)	225 µl	10 µl H_2O	--
10	Low O_2	225 µl	--	Freeze-pump-thaw (3x)
11	High O_2	225 µl	10 ml air injected	--
12	Large Scale	Isolated reaction		

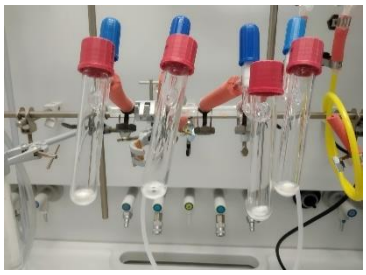
Step-by-step graphical procedure for sensitivity assessment set-up

1) Sodium *p*-toluenesulfinate **3a** and K_2CO_3 were weighted under air.

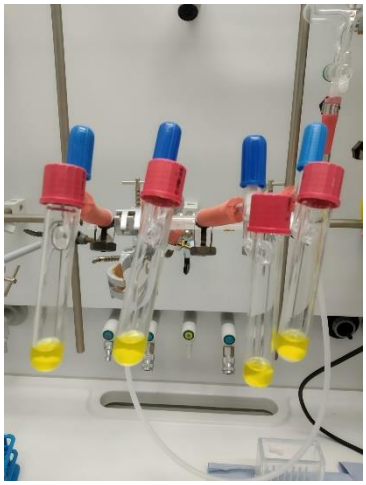


2) The stock solution of $Pd(PPh_3)_4$, DPEPhos and bromide.

3) The vessels were evacuated and back-filled with argon four times.



4) The additional amount of solvent was added under argon counterflow.

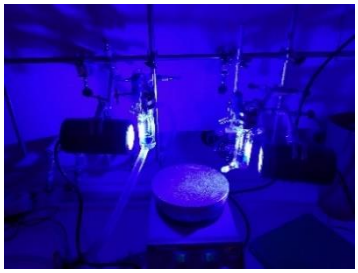


5) The stock solution is added under argon counterflow.

6) Additional procedures (*e.g.* freeze-pump-thaw) were performed at this stage.

7) Butadiene solution in THF was added and the vessel sealed.

8) The reaction was irradiated at 450/455 nm. Shown the custom set-up for reaction at high/low intensity and high temperature (aluminum wrapped).



9) Water-jacketed Schlenk tubes for low temperature reaction. The left one connected to the water cooling, right one filled with water but not flowing.

Results and comment

■ <30%; ■ 30-39%; ■ 40-49%; ■ 50-59%; ■ <60-69%; ■ 70-79%; ■ >80%.

Table 3. Results of the condition-based sensitivity screening.

Entry		Yield %	Deviation
1	Reference	84	--
2	Low concentration (-10%)	84	0
3	High concentration (+10%)	84	0
4	High intensity (~16x)	74	-10
5	Low intensity (~1/16x)	76	-8
6	High temperature	48	-40
7[a]	Low temperature	52	-32
8	Low temperature reference	84	--
9	High H_2O (10000 ppm)	80	-8
10	Low O_2	82	-2
11	High O_2	2	-98
12[b]	Big scale (10 times)	79	-2
13	Large scale reference (isolated, 0.2 mmol)	81	--

[a] The *E/Z* ratio drops to approximately 2:1 with the temperature reduction. Yield referred to the isomer *E*.

[b] The conditions were modified (see detail the the dedicated section) to reduce the loading (2 mol%).

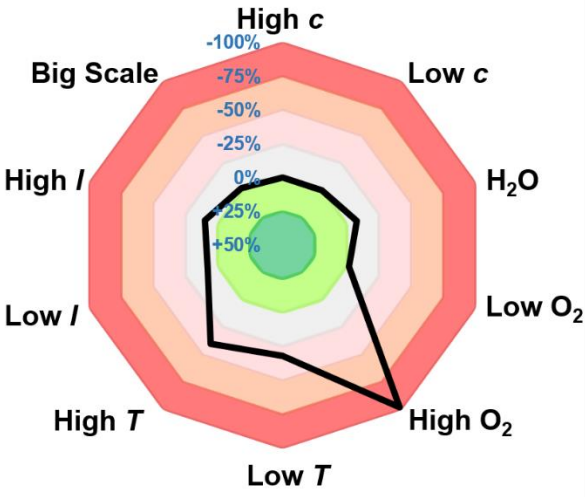


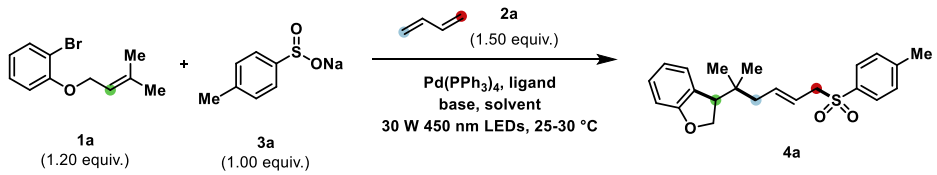
Figure S4 Radar diagram of the condition-based sensitivity screening.

As shown in **Figure S4**, slight modifications of concentration, running the reaction on large scale, presence of water, increased or decreased light intensity and further degassing by freeze-pump-thaw had a negligible effect on the reaction yield. Differently, oxygen completely inhibited the reaction and high temperature caused a 40% decrease in the yield. This can be either attributed to the decomposition of the catalytically active species or due to the volatility of butadiene, which increased upon temperature increase. Low temperature reaction caused a drop in the yield towards the *E* isomer and an increase of the presence of the *Z* isomer, while the overall yield was not severely affected.

Optimization

Sulfinate nucleophiles

In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, sodium *p*-



toluenesulfinate **3a** (17.8 mg, 0.10 mmol, 1.00 equiv.), the appropriate base (*if solid*, 0.15 mmol, 1.50 equiv.), the appropriate ligand (see **Table S4** for amount) and $Pd(PPh_3)_4$ (see **Table S4** for amount) were charged under air, then the vessel was evacuated and back-filled with argon four times. The appropriate solvent, followed by bromide **1a** (28.9 mg, 0.12 mmol, 1.20 equiv.), base (*if liquid*, 0.15 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (75 µl, 0.15 mmol, 1.50 equiv.) and further liquid additives were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 24 hours, unless otherwise stated. The reaction was filtered through a short pad of silica, rinsing with EtOAc, then the volatiles were removed *in vacuo*. The reaction mixture was analyzed by ^1H NMR, using dibromomethane as internal standard (relaxation delay $d_1 = 30$ s.). In **Table S4**, selected optimization results are reported. The following colour code was used to graphically represent yield intervals:

■ <30%; ■ 30-39%; ■ 40-49%; ■ 50-59%; ■ <60-69%; ■ 70-79%; ■ >80%.

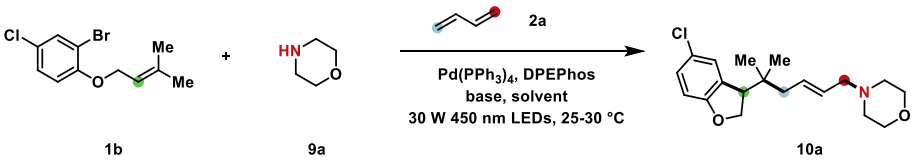
Table S4. Optimization with regards of the sulfinate nucleophiles.

Entry	Pd source	Ligand	Base	Solvent	yield%
1	**$Pd(PPh_3)_4$ (5 mol%)**	**DPEPhos (10 mol%)**	**K_2CO_3 (1.5 equiv.)**	**1,4-dioxane (0.1 M)**	**88**
2	$Pd(PPh_3)_4$ (5 mol%)	BINAP (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	76
3	$Pd(PPh_3)_4$ (5 mol%)	Xantphos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	38
4	$Pd(PPh_3)_4$ (5 mol%)	PPh_3 (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	36
5[a]	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	DMA (0.1 M)	40
6	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	THF (0.1 M)	78
7	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	*N,N*-DMF (0.1 M)	34
8	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	MeCN (0.1 M)	68
9	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	Et_2O (0.1 M)	74
10	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	DMSO (0.1 M)	44
11	$Pd(PPh_3)_4$ (10 mol%)	DPEPhos (12 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	88
12[a]	$Pd(PPh_3)_4$ (2 mol%)	DPEPhos (4 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	77
13	$Pd(PPh_3)_4$ (1 mol%)	DPEPhos (2 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	62
14	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (6 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	84

15	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.2 M)	87
16	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	KOAc (1.5 equiv.)	1,4-dioxane (0.1 M)	88
17	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	Et_3N (1.5 equiv.)	1,4-dioxane (0.1 M)	86
18	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	$NaHCO_3$ (1.5 equiv.)	1,4-dioxane (0.1 M)	80
19	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	KOH (1.5 equiv.)	1,4-dioxane (0.1 M)	60
20	---	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	<5
2[b]	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	<5
22[c]	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	<5
23	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	---	1,4-dioxane (0.1 M)	66
24[d]	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	82
25	$Pd(PPh_3)_4$ (5 mol%)	--	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	45

Notes: Yields were determined by ^1H NMR (relaxation delay = 30 s.) using dibromomethane as internal standard; [a] 48 h of irradiation; [b] Stirred in absence of light; [c] Stirred in absence of light at 100 °C; [d] 10 equiv. of degassed H_2O added.

Amines as nucleophiles



1b 9a 10a

In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the appropriate base (if solid, see **Table S5** for amount), DPEPhos (5.4 mg, 0.01 mmol, 10 mol%) and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. The appropriate solvent, followed by bromide **1b** (see **Table S5** for amount) base (if liquid, see **Table S5** for amount), morpholine **9a** (see **Table S5** for amount) and 1,3-butadiene 2 M in THF (see **Table S5** for amount) were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 24 hours, unless otherwise stated. The reaction was filtered through a short pad of silica, rinsing with CH_2Cl_2, then the volatiles were removed *in vacuo*. The reaction mixture was analyzed by ^1H NMR, using dibromomethane as internal standard (relaxation delay d_1 = 30 s.).

■ <30%; ■ 30-39%; ■ 40-49%; ■ 50-59%; ■ <60-69%; ■ 70-79%; ■ >80%.

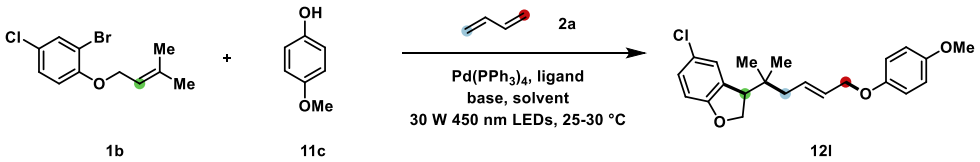
Table 5. Optimization with regards of the amine nucleophiles.

Entry	Pd source	Ligand	Base	Solvent	yield%
Reagents ratios: bromide (1.2 equiv.), butadiene (1.5 equiv.), nucleophile (1.0 equiv.), base (1.5 equiv.)					
1	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (1.5 equiv.)	1,4-dioxane (0.1 M)	64
2	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	KOAc (1.5 equiv.)	1,4-dioxane (0.1 M)	66
3	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	Et_3N (1.5 equiv.)	1,4-dioxane (0.1 M)	72
Reagents ratios: bromide (1.0 equiv.), butadiene (3.0 equiv.), nucleophile (1.5 equiv.), base (3.0 equiv.)					

5	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (3.0 equiv.)	1,4-dioxane (0.1 M)	68
6	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	KOAc (3.0 equiv.)	1,4-dioxane (0.1 M)	74
7	**$Pd(PPh_3)_4$ (5 mol%)**	**DPEPhos (10 mol%)**	**Et_3N (3.0 equiv.)**	**1,4-dioxane (0.1 M)**	**82**
8	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	iPr_2NEt (3.0 equiv.)	1,4-dioxane (0.1 M)	76
9	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	*N*-Me-morpholine (3.0 equiv.)	1,4-dioxane (0.1 M)	78

Notes: Yields were determined by ^1H NMR (relaxation delay = 30 s.) using dibromomethane as internal standard.

Phenols as nucleophiles



In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, *p*-methoxyphenol **11c** (see **Table S6** for amounts), the appropriate base (if solid, 0.30 mmol, 3.00 equiv.), the appropriate ligand (10 mol%) and $Pd(PPh_3)_4$ (5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. The appropriate solvent, followed by bromide **1b** (see **Table S6** for amounts), base (if liquid, 0.30 mmol, 3.00 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 3.00 equiv.) and further liquid additives were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 24 hours, unless otherwise stated. The reaction was filtered through a short pad of silica, rinsing with EtOAc, then the volatiles were removed *in vacuo*. The reaction mixture was analyzed by ^1H NMR, using dibromomethane as internal standard (relaxation delay d_1 = 30 s.).

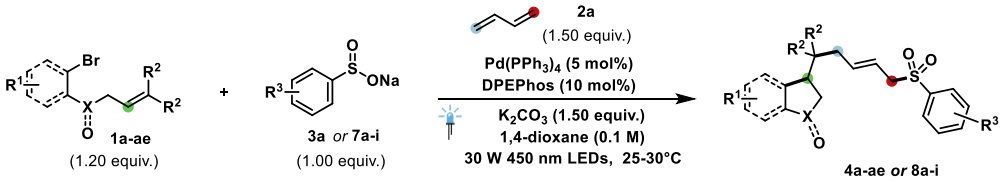
■ <30%; ■ 30-39%; ■ 40-49%; ■ 50-59%; ■ 60-69%; ■ 70-79%; ■ >80%.

Table S6. Optimization with regards of the phenol nucleophiles.

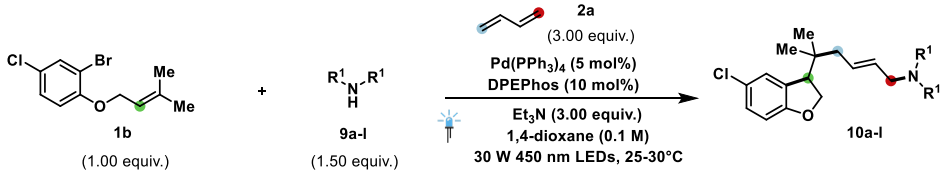
Entry	Pd source	Ligand	Base	Solvent	yield%
Reagents ratios: bromide (1.0 equiv.), butadiene (3.0 equiv.), nucleophile (1.5 equiv.), base (3.0 equiv.)					
1	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (3.0 equiv.)	1,4-dioxane (0.1 M)	52
2	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	KOAc (3.0 equiv.)	1,4-dioxane (0.1 M)	46
3	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	KOH (3.0 equiv.)	1,4-dioxane (0.1 M)	<5
4	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	Et_3N (3.0 equiv.)	1,4-dioxane (0.1 M)	<5
Reagents ratios: bromide (1.5 equiv.), butadiene (3.0 equiv.), nucleophile (1.0 equiv.), base (3.0 equiv.)					
5	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (3.0 equiv.)	1,4-dioxane (0.1 M)	62
6	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	Na_2CO_3 (3.0 equiv.)	1,4-dioxane (0.1 M)	8
7	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	Cs_2CO_3 (3.0 equiv.)	1,4-dioxane (0.1 M)	messy
8	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	$NaHCO_3$ (3.0 equiv.)	1,4-dioxane (0.1 M)	<5
9	$Pd(PPh_3)_4$ (5 mol%)	DPEPhos (10 mol%)	K_2CO_3 (3.0 equiv.)	1,4-dioxane (0.2 M)	66
10[a]	**$Pd(PPh_3)_4$ (5 mol%)**	***rac*-BINAP (10 mol%)**	**K_2CO_3 (3.0 equiv.)**	1,4-dioxane (0.2 M)	**82**

Notes: Yields were determined by ^{1}H NMR (relaxation delay = 30 s.) using dibromomethane as internal standard; [a] 40 h of irradiation.

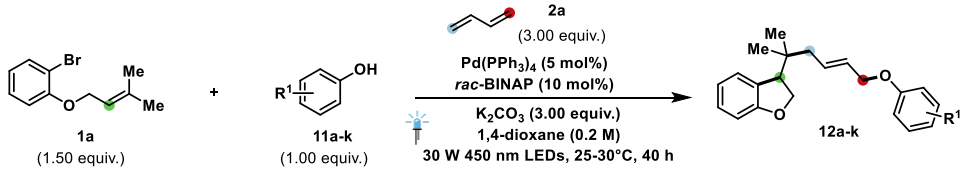
General procedures



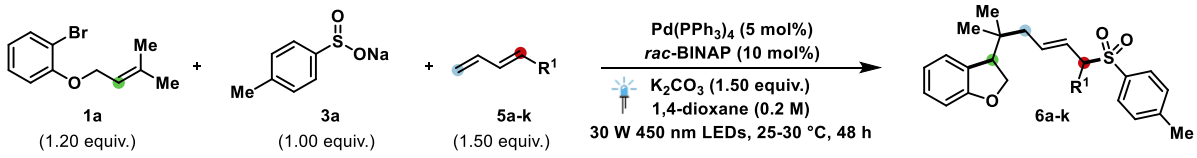
General procedure 1 (GP1) for the catalytic reaction of sulfinates. In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the corresponding sulfinate (1.00 equiv.), the appropriate bromide (*if solid or gum*, 1.20 equiv.), K_2CO_3 (1.50 equiv.), DPEPhos (10 mol%) and $Pd(PPh_3)_4$ (5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.1 M), followed by the appropriate bromide (*if liquid*, 1.20 equiv.) and 1,3-butadiene 2 M in THF (1.50 equiv.) were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for the indicated amount of time. Upon completion of the irradiation, the volatiles were removed *in vacuo*. The reaction mixture was loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc, CH_2Cl_2/EtOAc or CH_2Cl_2/MeOH mixtures), affording the corresponding sulfone product.



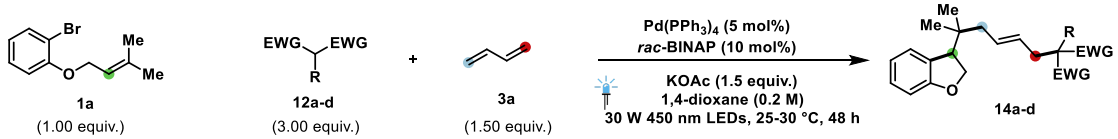
General procedure 2 (GP2) for the catalytic reaction of amines. In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the appropriate amine (*if solid*, 1.50 equiv.), DPEPhos (10 mol%) and $Pd(PPh_3)_4$ (5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.1 M), bromide **1b** (1.00 equiv.), followed by dry Et_3N (3.00 equiv.), the appropriate amine (*if liquid*, 1.50 equiv.) and 1,3-butadiene 2 M in THF (3.00 equiv.) were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 24 hours, unless otherwise stated. Upon completion of the irradiation, the volatiles were removed *in vacuo*. The reaction mixture was loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N mixtures), affording the corresponding amine product.



General procedure 3 (GP3) for the catalytic reaction of phenols. In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the appropriate phenol (*if solid*, 1.00 equiv.), K_2CO_3 (3.00 equiv.), *rac*-BINAP (10 mol%) and $Pd(PPh_3)_4$ (5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.2 M), bromide **1a** (1.50 equiv.), the appropriate phenol (*if liquid,* 1.00 equiv.) and 1,3-butadiene 2 M in THF (3.00 equiv.) were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 40 hours, unless otherwise stated. Upon completion of the irradiation, the volatiles were removed *in vacuo*. The reaction mixture was loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc mixtures), affording the corresponding ether product.

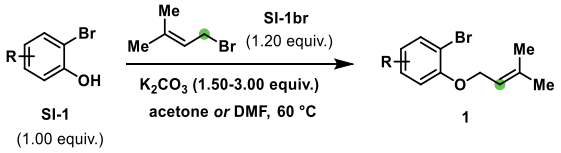


General procedure 4 (GP4) for the catalytic reaction of substituted dienes with sulfinates. In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, sodium *p*-toluenesulfinate (1.00 equiv.), K_2CO_3 (1.50 equiv.), *rac*-BINAP (10 mol%) and $Pd(PPh_3)_4$ (5 mol%) and the corresponding substituted 1,3-diene (*if solid*, 1.50 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.2 M), followed by the bromide **1a** (1.20 equiv.) and the corresponding substituted 1,3-diene (*if liquid,* 1.50 equiv.) were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 48 hours, unless otherwise stated. Upon completion of the irradiation, the volatiles were removed *in vacuo*. The reaction mixture was loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc mixtures), affording the corresponding sulfone product.



General procedure 5 (GP5) for the catalytic reaction of 1,3-dicarbonyl compounds. In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the 1,3-dicarbonyl compound (*if solid*, 3.00 equiv.), *rac*-BINAP (10 mol%), $Pd(PPh_3)_4$ (5 mol%) and KOAc (1.50 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.2 M), followed by the bromide **1a** (1.00 equiv.), the corresponding

1,3-dicarbonyl compound (*if liquid,* 3.00 equiv.) and 1,3-butadiene 2 M in THF (1.50 equiv.) were added, then the vessel was sealed and irradiated with the standard setup at 450 nm for 48 hours, unless otherwise stated. Upon completion of the irradiation, the volatiles were removed *in vacuo*. The reaction mixture was loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc mixtures), affording the corresponding alkylated 1,3-dicarbonylic compound.



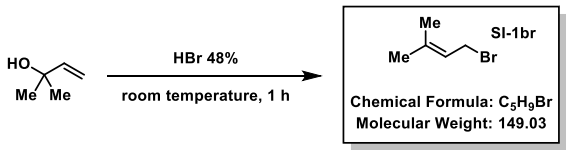
General procedure 6 (GP6) for the alkylation of phenols. In a round-bottom flask, the corresponding phenol **SI-1** (1.00 equiv.), dimethylallyl bromide **SI-1br** (1.20 equiv.) and K_2CO_3 (1.50-3.00 equiv.) in acetone or DMF (0.5 M) were charged, then reaction was heated under stirring at 60°C until consumption of the starting material. The reaction was cooled to room temperature, filtered over a short pad of Celite® to remove the insoluble salts and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica (*n*-pentane/CH_2Cl_2 or *n*-pentane/EtOAc mixtures) or by recrystallization using the specified solvent system.

Note: The reaction was found to be rather insensitive to water, therefore no dry solvents are needed. Furthermore, the reaction is largely insensitive towards the amount of added base.

Synthesis of starting materials

Starting materials **1a-e, 1g-m, 1r-s, 1u-x, 1z-ad, 1af-ai, 5a-i, 7a, 7b, 7d, 7e, 7g, 7d-e, 7g, 11e, 11j, 17** were synthesized according to the referenced literature procedures.[5,6]

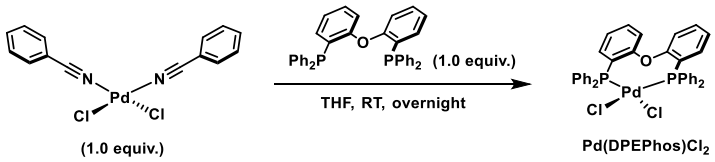
General usage reagents



1-bromo-3-methylbut-2-ene (SI-1br). The product was obtained using a slightly modified procedure from patent US2009156706, issued by Synthor Fine Chemicals Ltd.

In a round-bottom flask equipped with a PTFE-coated stirring bar, HBr 48% (20 ml) was charged, then 2-methylbut-3-en-2-ol (10.0 ml, 95.7 mmol, 1.00 equiv.) was slowly added (*the solution becomes turbid*) and the reaction was stirred for 60 minutes at room temperature, then transferred to a separatory funnel (*two layers are observed*). The aqueous layer was discarded, then the faint yellow organic layer was washed once with water, dried over $MgSO_4$. The crude bromide was judged pure enough to be used for the next step without further purification.

Amount: 9.70 g, 65.1 mmol, 68%. **Physical aspect**: faint yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.52 (th, *J* = 8.5, 1.5 Hz, 1H), 4.01 (d, *J* = 8.4 Hz, 2H), 1.78 (d, *J* = 1.4 Hz, 3H), 1.73 (d, *J* = 1.4 Hz, 3H). **GC-MS** (EI, 50_40_4min): 4.36 min, m/z = 147.9 ([M]$^+$, 100); 149.9 ([M+2]$^+$, 100). The experimental data are in agreement with the literature reports.[7] **Notes and troubleshooting**: The product contained slight amounts of the tertiary bromide isomer, which did not interfere with the next step. The product was stored in the darkness at -26 °C to avoid any undesired decomposition.



Dichlorobis(diphenylphosphinophenyl)ether palladium (II). The complex was synthesized according to a procedure reported by van Leeuwen and co-workers.[8] In an oven-dried Schlenk

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[5] M. Koy, P. Bellotti, F. Katzenburg, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed*., 2020, **59**, 2375-2379.

[6] H.-M. Huang, P. Bellotti, P. M. Pflüger, J. L. Schwarz, B. Heidrich, F. Glorius, *J. Am. Chem. Soc.,* 2020, **142**, 10173-10183.

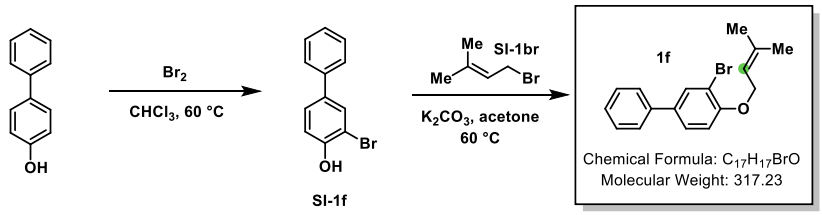
[7] N. Kishali, M. F. Polat Ramazan, A. Yunus Kara, *Helv. Chem. Acta,* 2008, **91**, 67-72.

[8] M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem*., 1998, 155-157.

tube equipped with a PTFE-coated stirring bar, $Pd(PhCN)_2Cl_2$ (70.0 mg, 0.182 mmol, 1.00 equiv.) and DPEPhos (98.0 mg, 0.182 mmol, 1.00 equiv.) were charged, then the vessel was evacuated and back-filled with argon three times. Dry THF (8 ml) was added, then the stirred suspension gradually changed color from orange to yellow. After reacting at room temperature overnight, the solvent was removed *in vacuo*, then the residue was suspended in Et_2O (10 ml), collected by filtration over a porous frit and washed three times with Et_2O (7-10 ml each time). The obtained yellow powder (98 mg, 0.136 mmol, 75%) was further dried under high vacuum.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.55 (m, 6H), 7.42 – 7.27 (m, 16H), 6.99 – 6.93 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 8.6 Hz, 2H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.6. The experimental data are in agreement with the literature report.[9,10]

Bromides



3-bromo-4-((3-methylbut-2-en-1-yl)oxy)-1,1'-biphenyl (**1f**). The title compound was synthesized according to the following two-step procedure.

Step 1. **SI-1f** was obtained using a slightly modified procedure from Kwang and co-workers.[11] In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, 4-phenylphenol (1.70 g, 10.0 mmol, 1.00 equiv.) and $CHCl_3$ (15 ml) were charged under air, and then heated at 60 °C. A solution of Br_2 (513 µl, 10.0 mmol, 1.00 equiv.) in $CHCl_3$ (3 ml) was added dropwise, then the reaction was stirred at 60°C for 2 hours. The reaction was warmed to room temperature, diluted with CH_2Cl_2 (30 ml) and washed with saturated $Na_2S_2O_3$ solution (20 ml). The organic layer was dried over $MgSO_4$, then the solvent volume was reduced to approximately 5 ml *in vacuo*. *n*-pentane (20 ml) was added to initiate the precipitation of a white crystalline solid, which was collected by filtration and washed once with *n*-pentane/CH_2Cl_2 (20/1, 15 ml), followed by pure *n*-pentane (15 ml). The white solid (**SI-1f**) was dried *in vacuo* and judged pure to be used for the next step without further purification. **Note**: the mother liquor contains product that could be obtained using the abovementioned procedure after reduction of the volume. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J*

[9] M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem*., 1998, 155-157.

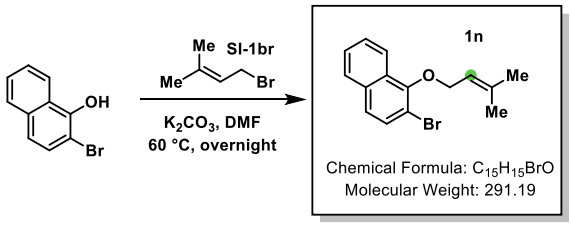
[10] P. Zhang, C. Wolf, *Chem. Commun*., 2013, **49**, 7010-7012.

[11] C. D. Gutsche, H. N. Kwang, *J. Org. Chem*., 1982, **47**, 2708-2712.

= 2.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.39 (m, 3H), 7.33 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 5.52 (s, 1H). The experimental data are in accordance with the literature reports.[12]

Step 2. The reaction was performed according to **GP6** using the intermediate phenol **SI-1f** (954 mg, 3.83 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (532 µl, 4.60 mmol, 1.20 equiv.) and K_2CO_3 (795 mg, 5.75 mmol, 1.50 equiv.) in acetone (8 ml). Compound **1f** was obtained by purification by flash column chromatography on silica (*n*-pentane/CH_2Cl_2 = 9/1).

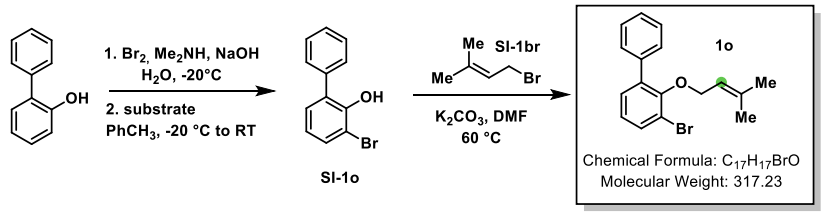
Amount: 1.17 g, 3.69 mmol, 96%. **Physical aspect**: white crystalline solid. $\mathbf{R_f}$ (*n*-pentane/CH_2Cl_2 = 20/1): 0.50. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.3 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.48 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.33 (tt, *J* = 7.4, 1.3 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 5.54 (thept, *J* = 6.6, 1.4 Hz, 1H), 4.65 (d, *J* = 6.4 Hz, 2H), 1.82 (q, *J* = 1.3 Hz, 3H), 1.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 139.6, 138.4, 135.2, 132.0, 129.0, 127.3, 127.0, 126.9, 119.5, 113.9, 112.9, 66.4, 26.0, 18.5. **HRMS (Orbitrap)** *m/z* calc. for [$C_{17}H_{17}O^{79}BrNa$] ([M+Na$^+$]) 339.0355, found 339.0356. **Note**: Two aromatic ^{13}C signal missing due to overlap.



2-bromo-1-((3-methylbut-2-en-1-yl)oxy)naphthalene (**1n**). The reaction was performed according to **GP6** using 2-bromo-1-naphtol (669 mg, 3.00 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (492 mg, 3.30 mmol, 1.10 equiv.) and K_2CO_3 (829 mg, 6.00 mmol, 2.00 equiv.) in DMF (6 ml). Compound **1n** was obtained by purification by flash column chromatography on silica (*n*-pentane 100%).

Amount: 658 mg, 2.26 mmol, 75%. **Physical aspect**: white solid. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 20/1): 0.50. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 1H), 5.57 (t, *J* = 6.6 Hz, 1H), 4.75 (d, *J* = 6.6 Hz, 2H), 1.80 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.4, 138.5, 133.3, 130.1, 128.8, 128.1, 127.7, 126.4, 124.5, 119.8, 116.0, 110.0, 67.3, 26.0, 18.5. **HRMS (MicroToF)** *m/z* calc. for [$C_{15}H_{15}O^{79}BrNa$] ([M+Na$^+$]) 313.0198, found 313.0201.

[12] B. Schmidt, F. Hölter, *Org. Biomol. Chem*., 2011, **9**, 4914-4920



3-bromo-2-((3-methylbut-2-en-1-yl)oxy)-1,1'-biphenyl (**1o**). The title compound was synthesized according to the following two-step procedure.

Step 1. The product was obtained using a slightly modified procedure from Budzelaar and co-workers.[13] In an oven-dried round-bottom flask equipped with a PTFE-coated stirring bar, Me_2NH 40% in water (1.67 ml, 13.2 mmol, 1.12 equiv.) was charged, then cooled to -20°C. NaOH (1.03 g, 25.8 mmol, 2.19 equiv.) and was added under vigorous stirring, followed by the dropwise addition of Br_2 (660 µl, 12.9 mmol, 1.09 equiv.), then the reaction was stirred at the same temperature for 30 minutes. The water layer was extracted once with toluene (15 ml), then transferred dropwise to a solution of 2-phenylphenol (2.00 g, 11.8 mmol, 1.00 equiv.) in toluene (60 ml), pre-cooled at -20°C. Upon completion of the addition, the reaction was warmed at room temperature and stirred for 1 hour, then HCl 5% (10 ml) and water (60 ml) were added, then the layers were separated. The organic layer was dried over $MgSO_4$, then the solvent was removed *in vacuo*. The residue was dissolved in hexane (40 ml) and stored in the freezer at -20°C overnight, causing the crystallization of the product. The mother liquors were decanted off, then the solid was washed three times with a small amount of *n*-pentane, then dried *in vacuo*. The product **SI-1o** (white solid) was pure enough to be used for the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.49 – 7.41 (m, 3H), 7.37 (tt, *J* = 6.9, 1.4 Hz, 1H), 7.30 – 7.20 (m, 1H), 6.88 (tdd, *J* = 7.8, 5.9, 1.2 Hz, 1H), 5.68 (s, 1H). The experimental data are in agreement with the literature reports.[14]

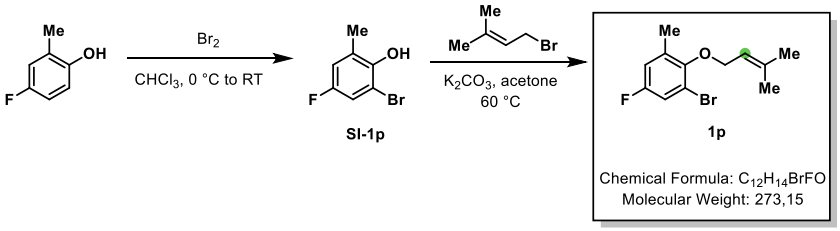
Step 2. The reaction was performed according to **GP6** using the intermediate phenol **SI-1o** (1.06 g, 4.26 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (591 µl, 5.11 mmol, 1.20 equiv.) and K_2CO_3 (1.24 g, 8.95 mmol, 2.10 equiv.) in DMF (8.5 ml). Compound **1o** was obtained by purification by flash column chromatography on silica (*n*-pentane/CH_2Cl_2 = 9/1).

Amount: 639 mg, 2.00 mmol, 47%. **Physical aspect**: white solid. $\mathbf{R_f}$ (*n*-pentane/CH_2Cl_2 = 9/1): 0.32. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 3H), 7.45 – 7.38 (m, 2H), 7.35 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 5.25 (ddt, *J* = 8.9, 6.0, 1.4 Hz, 1H), 4.05 (d, *J* = 7.5 Hz, 2H), 1.65 (s, 3H), 1.38 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.4, 139.2,

[13] E. N. T. Cuthbert, V. Busico, D. E. Herbert, P. H. M. Budzelaar, *Eur. J. Inorg. Chem*., 2019, 3396-3410.

[14] S. Suárez-Pantiga, D. Palomas, E. Rubio, J. M. González, *Angew. Chem. Int. Ed*., 2009, **48**, 7857-7861.

138.3, 137.6, 132.5, 130.3, 129.4, 128.4, 127.6, 125.4, 119.7, 119.0, 69.7, 25.9, 17.7. **HRMS (MicroToF)** *m/z* calc. for [$C_{17}H_{17}O^{79}BrNa$] ([M+Na$^+$]) 339.0355, found 339.0352.



1-bromo-5-fluoro-3-methyl-2-((3-methylbut-2-en-1-yl)oxy)benzene (1p). The title compound was synthesized according to the following two-step procedure.

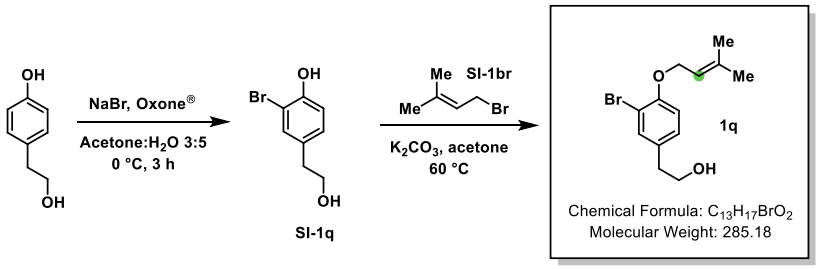
Step 1. **SI-1p** was obtained using a slightly modified procedure from patent CN110872212, issued by Dalian Qikai Pharmaceutical Technology Co., Ltd.

In a round-bottom flask equipped with a PTFE-coated stirring bar, 4-fluoro-2-methylphenol (1.26 g, 10.0 mmol, 1.00 equiv.) was dissolved in $CHCl_3$ (20 ml), then cooled to 0°C. A solution of Br_2 (0.53 ml, 10.5 mmol, 1.05 equiv.) in $CHCl_3$ (4 ml) was added dropwise, then the reaction was warmed at room temperature and stirred for 2 hours. The reaction was quenched with a saturated solution of sodium thiosulfate (15 ml), then the layers were separated and the aqueous layer was extracted twice with CH_2Cl_2 (30 ml each time), then the combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The light yellow solid (**SI-1p**) was judged pure enough to be used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (ddd, *J* = 7.6, 3.0, 0.7 Hz, 1H), 6.83 (dd, *J* = 8.7, 3.0 Hz, 1H), 5.36 (s, 1H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1 (d, *J* = 241.8 Hz), 147.2 (d, *J* = 2.7 Hz), 127.0 (d, *J* = 7.9 Hz), 117.4 (d, *J* = 22.5 Hz), 116.0 (d, *J* = 25.9 Hz), 109.3 (d, *J* = 10.9 Hz), 17.1 (d, *J* = 1.4 Hz). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ -122.79. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -122.79 (dd, *J* = 8.7, 7.6 Hz).

Step 2. The reaction was performed according to **GP6** using the intermediate phenol **SI-1p** (1.03 g, 5.00 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (894 µl, 6.00 mmol, 1.20 equiv.) and K_2CO_3 (1.04 g, 7.50 mmol, 1.50 equiv.) in acetone (10 ml). The title compound was obtained by purification by flash column chromatography on silica (*n*-pentane/EtOAc = 100/1).

Amount: 845 mg, 3.09 mmol, 62%. **Physical aspect**: colorless oil. **R$_f$** (*n*-pentane/EtOAc = 100/1): 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 7.7, 3.1 Hz, 1H), 6.84 (ddt, *J* = 8.6, 3.0, 0.8 Hz, 1H), 5.59 (tsept, *J* = 7.3, 1.2 Hz, 1H), 4.40 (d, *J* = 7.3 Hz, 2H), 2.32 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 157.1, 151.0 (d, *J* = 3.2 Hz), 139.1, 134.8 (d, *J* = 8.5 Hz), 119.9, 117.7 (d, *J* = 11.0 Hz), 116.8 (d, *J* = 22.1 Hz), 69.7 (d, *J* = 1.5 Hz), 26.0, 18.2, 17.2 (d, *J* = 1.5 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -117.92 (dd, *J* = 8.7, 7.8 Hz). **^{19}F{^{1}H} NMR** (377 MHz, $CDCl_3$) δ -117.93. **HRMS (Orbitrap)** *m/z* calc. for [$C_{12}H_{14}O^{79}BrFNa$] ([M+Na$^+$]) 285.0104, found 285.0106.



2-(3-bromo-4-((3-methylbut-2-en-1-yl)oxy)phenyl)ethan-1-ol (1q). The title compound was synthesized according to the following two-step procedure.

Step 1. **SI-1q** was obtained using a slightly modified procedure from Maruoka and co-workers.[15] In a round-bottom flask equipped with a PTFE-coated stirring bar and a dropping funnel, 4-hydroxyethylphenol (569 mg, 4.12 mmol, 1.00 equiv.), NaBr (424 mg, 4.12 mmol, 1.00 equiv.) and acetone (12 ml) were charged, then the solution was cooled to 0°C. A solution of Oxone® (1.88 g, 12.4 mmol, 3.00 equiv.) in distilled water (20 ml) was added dropwise over 60 minutes through the dropping funnel, then the reaction was quenched with saturated $Na_2S_2O_3$ (30 ml), extracted three times with EtOAc = (30 ml each time), then the combined organic layers were washed once with brine (30 ml), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude was purified by flash column chromatography on silica (CH_2Cl_2/MeOH = 20/1), affording the intermediate bromophenol **SI-1q** (764 mg, 3.52 mmol, 85%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 5.71 – 5.40 (m, 1H), 3.82 (t, *J* = 6.5 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 2H). The experimental data are in agreement with the literature reports.[16]

Step 2. The reaction was performed according to **GP6** using the intermediate phenol **SI-1q** (764 mg, 3.52 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (940 µl, 4.23 mmol, 1.20 equiv.) and K_2CO_3 (730 mg, 5.28 mmol, 1.50 equiv.) in acetone (10 ml). Compound **1q** was obtained by purification by flash column chromatography on silica (*n*-pentane/EtOAc = 2/1).

Amount: 730 mg, 2.56 mmol, 73%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 2/1): 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.49 (ddt, *J* = 8.0, 5.2, 1.4 Hz, 1H), 4.57 (dt, *J* = 6.7, 1.2 Hz, 2H), 3.81 (t, *J* = 6.5 Hz, 3H), 2.77 (t, *J* = 6.5 Hz, 2H), 1.78 (q, *J* = 1.2 Hz, 3H), 1.74 (d, *J* = 1.3 Hz, 3H), 1.55 – 1.45 (br, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.1, 138.2, 133.81, 132.3, 129.0, 119.6, 114.0, 112.6, 66.4, 63.7, 38.0, 25.9, 18.4. **HRMS (Orbitrap)** *m/z* calc. for [$C_{13}H_{17}O_2{}^{79}BrFNa$] ([M+Na$^+$]) 307.0310, found 307.0312.

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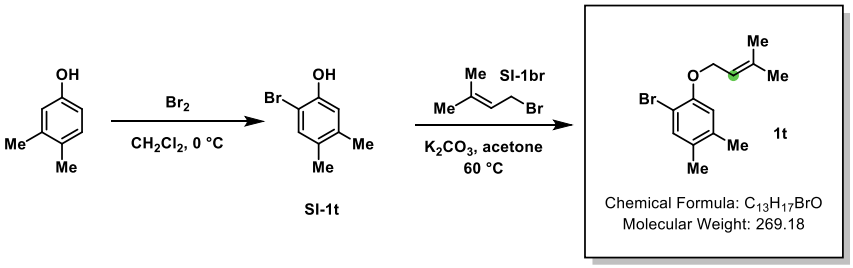
[15] T. Hashimoto, Y. Shimazaki, Y. Omatsu, K. Maruoka, *Angew. Chem. Int. Ed*., 2018, **57**, 7200-7204.

[16] P. Bovicelli, F. Bottaro, C. Sappino, M. Tomei, V. Nardi, I. Proietti Silvestri, B. Macchi, C. Frezza, G. Righi *Synth. Commun*., 2016, **46**, 242-248



1-bromo-4,5-dimethyl-2-((3-methylbut-2-en-1-yl)oxy)benzene (1t). The title compound was synthesized according to the following two-step procedure.

Step 1. **SI-1t** was obtained using a slightly modified procedure from Beau and co-workers.[17] In a round-bottom flask equipped with a PTFE-coated stirring bar, 3,4-dimethylphenol (1.83 g, 15.0 mmol, 1.00 equiv.) and CH_2Cl_2 (75 ml) were charged, then the solution was cooled to 0°C. Bromine (0.77 ml, 15.0 mmol, 1.00 equiv.) in CH_2Cl_2 (5 ml) was added dropwise over 10 minutes (*the reaction occurs immediately*), then the solvent was removed *in vacuo* and the residue was re-crystallized from boiling *n*-pentane, affording the intermediate bromophenol **SI-1t** (1.43 g, 7.11 mmol, 47%) as a white crystalline solid.

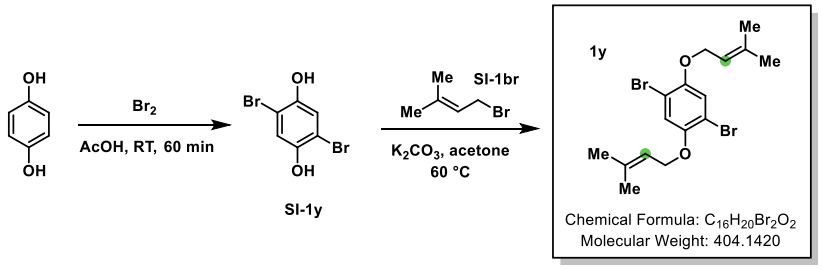
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 6.82 (s, 1H), 5.23 (s, 1H), 2.18 (s, 3H), 2.17 (s, 3H). The experimental data are in agreement with the literature reports.[18]

Step 2. The reaction was performed according to **GP6** using the intermediate phenol **SI-1t** (719 mg, 3.58 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (500 µl, 4.29 mmol, 1.20 equiv.) and K_2CO_3 (742 mg, 5.37 mmol, 1.50 equiv.) in acetone (10 ml). Compound **1t** was obtained by purification by flash column chromatography on silica (*n*-pentane/EtOAc = 50/1).

Amount: 969 mg, 3.58 mmol, >99%. **Physical aspect**: colourless oil. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 50/1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.71 (s, 1H), 5.51 (thept, *J* = 6.6, 1.3 Hz, 1H), 4.55 (d, *J* = 6.5 Hz, 2H), 2.21 (s, 3H), 2.17 (s, 3H), 1.79 (d, *J* = 1.3 Hz, 3H), 1.74 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.3, 138.0, 136.8, 134.0, 130.4, 119.9, 115.9, 109.0, 66.6, 26.0, 20.0, 18.8, 18.5. **HRMS (Orbitrap)** *m/z* calc. for [$C_{13}H_{17}O^{79}BrNa$] ([M+Na$^+$]) 291.0355, found 291.0356.

[17] V. X. Chen, F.-D. Boyer, C. Rameau, P. Retailleau, J.-P. Vors, J.-M. Beau, *Chem. Eur. J.*, 2010, **16**, 13941-13945.

[18] H. Jiang, Y. Zhang, W. Xiong, J. Cen, L. Wang, R. Cheng, C. Qi, and W. Wu, *Org. Lett.*, 2019, **21**, 345-349.



1,4-dibromo-2,5-bis((3-methylbut-2-en-1-yl)oxy)benzene (1y). The title compound was synthesized according to the following two-step procedure.

Step 1. **SI-1y** was obtained using a slightly modified procedure from Valiyaveettil and co-workers.[19] In a round-bottom flask equipped with a PTFE-coated stirring bar, hydroquinone (2.20 g, 20.0 mmol, 1.00 equiv.) was dissolved in glacial acetic acid (20 ml), then bromine (2.05 ml, 40.0 mmol, 2.00 equiv.) in glacial acetic acid (4 ml) was added dropwise. The reaction was stirred at room temperature for 90 minutes (*after 60 minutes a precipitate could be observed*), then the volume of the reaction was reduced to 5 ml *in vacuo*. The solids were filtered, then washed with ice-cold *n*-pentane (20 ml), *n*-pentane/EtOAc (10/1, 10 ml) and *n*-pentane (10 ml). The solid was re-crystallized from boiling toluene/AcOH (2/1), then the collected solid was washed three times with toluene (10 ml each time) and dried *in vacuo*, affording the intermediate bis-bromide **SI-1y** (1.52 g, 5.68 mmol, 28%) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.23 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.02 (td, *J* = 7.7, 1.5 Hz, 1H). The experimental data are in agreement with the literature reports.[20]

Step 2. The reaction was performed according to **GP6** using the intermediate phenol **SI-1y** (804 mg, 3.00 mmol, 1.00 equiv.), dimethylallyl bromide **SI-1br** (830 µl, 7.20 mmol, 2.40 equiv.) and K_2CO_3 (1.24 g, 9.00 mmol, 3.00 equiv.) in acetone (4 ml). After filtration and evaporation of the volatiles *in vacuo*, the crude product was purified by recrystallization from boiling ethanol.

Amount: 591 mg, 1.46 mmol, 49%. **Physical aspect**: white crystalline solid. $\mathbf{R_f}$ (*n*-pentane/CH_2Cl_2 = 20/1): 0.50. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.11 (s, 2H), 5.48 (ddt, *J* = 8.1, 5.3, 1.4 Hz, 2H), 4.51 (d, *J* = 6.7 Hz, 4H), 1.79 (q, *J* = 1.2 Hz, 6H), 1.77 – 1.71 (m, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 150.1, 138.8, 119.3, 119.2, 111.5, 67.4, 26.0, 18.5. **HRMS (Orbitrap)** *m/z* calc. for [$C_{16}H_{20}O_2{}^{79}Br_2Na$] ([M+Na$^+$]) 424.9722, found 424.9724; calc. for [$C_{16}H_{20}O_2{}^{81}Br_2Na$] ([M+Na$^+$]) 426.9703, found 426.9702.

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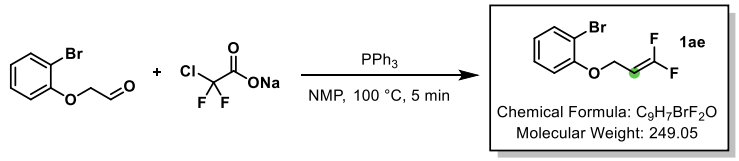
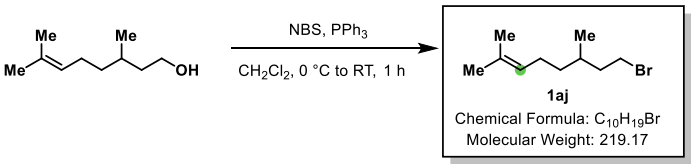
[19] M. Vetrichelvan, S. Valiyaveettil, *Chem. Eur. J.*, 2005, **11**, 5889-5898.

[20] S.-P. Huang, T.-H. Jen, Y.-C. Chen, A.-E. Hsiao, S.-H. Yin, H.-Y. Chen, S.-A. Chen, *J. Am. Chem. Soc.*, 2008, **130**, 4699-4707.



1-bromo-2-((3,3-difluoroallyl)oxy)benzene (1ae). The product was obtained applying the procedure reported by Loh and co-workers.[21] In an oven-dried round-bottom flask equipped with a PTFE-coated stirring bar, 2-(2-bromophenoxy)acetaldehyde (885 mg, 4.12 mmol, 1.00 equiv.), PPh_3 (2-16 g, 8.24 mmol, 2.00 equiv.) and NMP (21 ml) were charged, then the mixture was heated at 100°C. Sodium chlorodifluoroacetate (1.26 g, 8.24 mmol, 2.00 equiv.) was slowly added portionwise (*Warning: vigorous gas evolution was observed*) and the reaction was stirred at 100°C for 5 minutes, then was cooled to room temperature and quenched with water (20 ml). The water layer was extracted twice with EtOAc (30 ml each time), then the combined organic extracts were washed once with H_2O_2 2 M (30 ml) and four times with brine (30 ml each time), then were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica (*n*-pentane/CH_2Cl_2 = 1/0 → 10/1).

Amount: 401 mg, 1.61 mmol, 39%. **Physical aspect**: colorless liquid. $\mathbf{R_f}$ (*n*-pentane 100%): 0.28 **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.27 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 2H), 6.90 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.87 (td, *J* = 7.6, 1.4 Hz, 1H), 4.72 – 4.61 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.9 (dd, *J* = 292.2, 290.8 Hz), 154.7, 133.8, 128.6, 122.8, 114.1, 112.8, 75.8 (dd, *J* = 24.8, 17.9 Hz), 61.6 (d, *J* = 8.8 Hz). **^{19}F NMR** (564 MHz, $CDCl_3$) δ -83.31 (dq, *J* = 32.1, 1.7 Hz), -84.69 (dddd, *J* = 32.0, 22.6, 2.7, 0.9 Hz). **Note:** The compound does not ionize under the available conditions to provide molecular ion.



8-bromo-2,6-dimethyloct-2-ene (1aj). In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, (±)-citronellol (1.81 ml, 10.0 mmol, 1.00 equiv.) and PPh_3 (3.15 g, 12.0 mmol, 1.20 equiv.) were dissolved in dry CH_2Cl_2 (20 ml) under argon, then NBS (2.14 g, 12.0 mmol, 1.20 equiv.) was added portionwise *(the reaction started to gently reflux spontaneously*), then the reaction was stirred at room temperature for 60 minutes, then the solvent volume was reduced

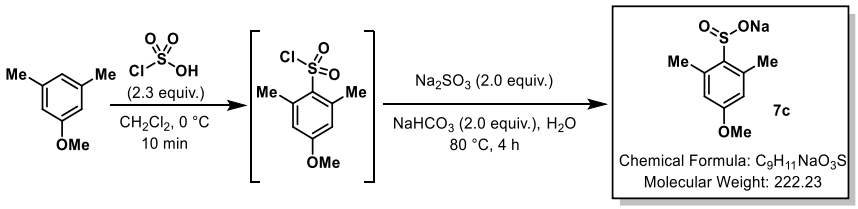
[21] H.-J. Tang, L.-Z. Lin, C. Feng, T.-P. Loh, *Angew. Chem. Int. Ed*., 2017, **56**, 9874-9876.

to 4 ml *in vacuo*. The solution was diluted with *n*-pentane (30 ml), causing the precipitation of triphenylphosphine oxide and succinimide. The solution was filtered through a short pad of Celite®, rinsing thoroughly with *n*-pentane. The volatiles were removed *in vacuo*, then the residue was purified by flash column chromatography on silica (*n*-pentane 100%).

Amount: 955 mg, 4.36 mmol, 44%. **Physical aspect**: colorless oil. $\mathbf{R_f}$ (*n*-pentane 100%): 0.50. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.09 (thept, *J* = 7.1, 1.4 Hz, 1H), 3.50 – 3.36 (m, 2H), 2.07 – 1.94 (m, 2H), 1.94 – 1.83 (m, 1H), 1.74 – 1.62 (m, 5H), 1.61 (s, 3H), 1.34 (dddd, *J* = 13.2, 9.4, 6.4, 5.1 Hz, 1H), 1.18 (dddd, *J* = 13.4, 9.4, 7.5, 6.1 Hz, 1H), 0.90 (d, *J* = 6.4 Hz, 3H). The experimental data are in agreement with the literature reports. [22] **Note**. Drying under high vacuum for prolonged time was avoided due to the volatility of the product.

[22] J. C. Siu, J. B Parry, S. Lin, *J. Am. Chem. Soc.,* 2019, **141**, 2825-2831.

Sulfinates



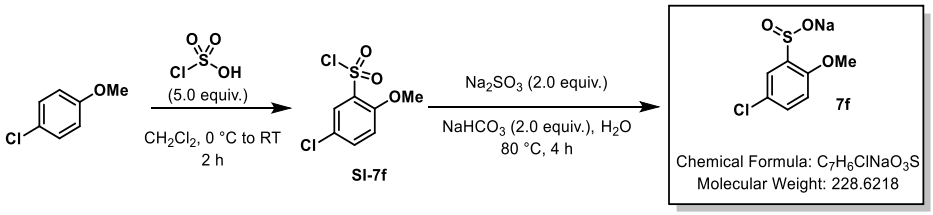
Sodium 4-methoxy-2,6-dimethylbenzenesulfinate (7c). The title compound was synthesized according to the following two-step procedure.

Step 1. The intermediate sulfonyl chloride was synthesized according to a slightly modified procedure from patent US2010173889, issued by Gruenenthal GmbH.

In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, 3,5-dimethylanisole (2.12 ml, 15.0 mmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (15 ml), then the solution was cooled to 0 °C. Chlorosulfonic acid (2.29 ml, 34.5 mmol, 2.30 equiv.) was added dropwise (*Warning: if addition is too fast, the mixture can start boiling. Do NOT use plastic syringes, as they are corroded by the reagent within seconds*), then the reaction was stirred at the same temperature for 10 minutes. The reaction was carefully quenched with ice/water (approx. 40 ml), then the layers were separated and the water layer was extracted twice with DCM (40 ml each time). The combined organic layers were dried over $MgSO_4$, then the solvent was removed *in vacuo* to afford the crude sulfonyl chloride as a colorless thick oil.

Step 2. To the same flask, Na_2SO_3 (3.78 g, 30.0 mmol, 2.00 equiv.), $NaHCO_3$ (2.52 g, 30.0 mmol, 2.00 equiv.) and water (15 ml) were consecutively added, then the neck was equipped with a reflux condenser and the mixture was heated at 80 °C for 4 hours, then the volatiles were removed *in vacuo*, then the residue was taken-up with toluene and water was azeotropically removed (repeated twice), and any residual water was removed under 60 °C heating under vacuum. The residue was extracted once with absolute ethanol (40 ml), then the solids were removed by filtration and the filtrate was dried *in vacuo* to afford the analytically pure product **7c.**

Amount: 2.11 g, 9.49 mmol, 63% over two steps. **Physical aspect**: white solid. **^{1}H NMR** (599 MHz, CD_3OD) δ 6.49 – 6.47 (m, 2H), 3.74 (s, 3H), 2.64 – 2.63 (m, 6H). **^{13}C NMR** (151 MHz, CD_3OD) δ 160.8, 143.7, 139.0, 115.4, 55.5, 19.4. **HRMS (Orbitrap)** *m/z* calc. for $[C_9H_{11}O_3S]$ ($[M^-]$) 199.0434, found 199.0424. **Notes and troubleshooting**: The proton signals quoted as multiplets show unresolved ^4J couplings (aromatic and benzylic protons).



Sodium 5-chloro-2-methoxybenzenesulfinate (7f). The title compound was prepared according to the following two-step procedure.

Step 1. **SI-7f** was prepared according to a slightly modified procedure from Hornby and co-workers.[23] In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, chlorosulfonic acid (3.33 ml, 50.0 mmol, 5.00 equiv.) was charged and cooled to 0°C, then 4-chloroanisole (1.23 ml, 10.0 mmol, 1.00 equiv.) was carefully added dropwise over 5 minutes, then the reaction was gently warmed at room temperature and stirred for 2 hours. The reaction was poured in ice (40 ml), then extracted with CH_2Cl_2 for three times (30 ml each time), then the combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1), affording **SI-7f** as a white crystalline solid (1.86 g, 7.73 mmol, 77%).

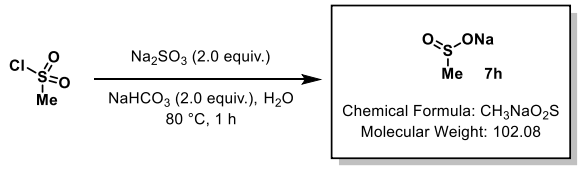
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.6 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 4.06 (s, 3H). The experimental data are in agreement with the literature reports.[24]

Step 2. In a round bottom flask equipped with a reflux condenser, the intermediate sulfonyl chloride **SI-7f** (1.86 g, 7.73 mmol, 1.00 equiv.), Na_2SO_3 (1.95 g, 15.5 mmol, 2.00 equiv.), $NaHCO_3$ (1.30 g, 15.5 mmol, 2.00 equiv.) and water (10 ml) were consecutively added, then the neck was equipped with a reflux condenser and the mixture was heated at 80 °C for 4 hours, then the volatiles were removed *in vacuo*, then the residue was taken-up with toluene and water was azeotropically removed (repeated twice), and any residual water was removed under 60 °C heating under vacuum. The residue was extracted once with absolute ethanol (40 ml), then the solids were removed by filtration and the filtrate was dried *in vacuo* to afford the analytically pure product **7f**.

Amount: 445 mg, 1.82 mmol, 24%. **Physical aspect**: white solid. **^{1}H NMR** (400 MHz, CD_3OD) δ 7.68 (d, *J* = 2.7 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, CD_3OD) δ 157.5, 146.3, 131.4, 126.8, 124.5, 114.0, 56.4. **HRMS (Orbitrap)** *m/z* calc. for $[C_7H_6O_3S^{35}Cl]$ ($[M^-]$) 204.9732, found 204.9730.

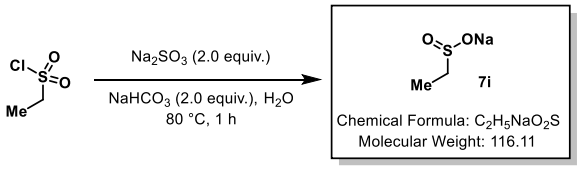
[2323] R. J. W. Cremlyn, R. Hornby, *J. Chem. Soc. C*, 1969, 1341-1345.

[24] J. Ajenjo, B. Klepetářová, M. Greenhall, D. Bím, M. Culka, L. Rulíšek, P. Beier, *Chem. Eur. J.,* 2019, **25**, 11375-11382.



Sodium methanesulfinate (7h). In a round-bottom flask equipped with a PTFE-coated stirring bar, Na_2SO_3 (1.26 g, 10.0 mmol, 2.00 equiv.), $NaHCO_3$ (840 mg, 10.0 mmol, 2.00 equiv.) and water (5 ml) were consecutively added and the mixture was heated at 80 °C, then methansulfonyl chloride (537 mg, 5.00 mmol, 1.00 equiv.) was added dropwise, then the reaction was stirred at the same temperature for 60 minutes. The volatiles were removed *in vacuo*, then the residue was taken-up with toluene and water was azeotropically removed (repeated twice), and any residual water was removed under 60 °C heating under vacuum. The residue was extracted once with absolute ethanol (15 ml), then the solids were removed by filtration and the filtrate was concentrated down to 5 ml, cooled to room temperature and the solids collected by filtration, dried *in vacuo* to afford **7h**

Amount: 476 mg, 4.67 mmol, 93%. **Physical aspect**: white solid. **^{1}H NMR** (400 MHz, CD_3OD) δ 2.16 (s, 1H). The experimental data are in agreement with the literature reports.[25]



Sodium ethanesulfinate (7i). In a round-bottom flask equipped with a PTFE-coated stirring bar, Na_2SO_3 (1.26 g, 10.0 mmol, 2.00 equiv.), $NaHCO_3$ (840 mg, 10.0 mmol, 2.00 equiv.) and water (5 ml) were consecutively added and the mixture was heated at 80 °C, then ethansulfonyl chloride (643 mg, 5.00 mmol, 1.00 equiv.) was added dropwise, then the reaction was stirred at the same temperature for 60 minutes. The volatiles were removed *in vacuo*, then the residue was taken-up with toluene and water was azeotropically removed (repeated twice), and any residual water was removed under 60 °C heating under vacuum. The residue was extracted once with absolute ethanol (15 ml), then the solids were removed by filtration and the filtrate was concentrated down to 5 ml, cooled to room temperature and the solids collected by filtration, dried *in vacuo* to afford **7i**. **Amount:** 287 mg, 2.47 mmol, 49%. **Physical aspect**: white solid. **^{1}H NMR** (400 MHz, CD_3OD) δ 2.21 (q, J = 7.6 Hz, 2H), 1.09 (t, J = 7.6 Hz, 3H). The experimental data are in agreement with the literature reports.[26]

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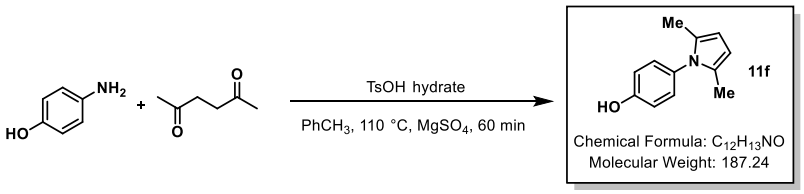
[25] J. Lacour, D. Monchaud, J. Mareda, F. Favarger, G. Bernardinelli, *Helv. Chem. Acta,* 2003, **86**, 65-81.

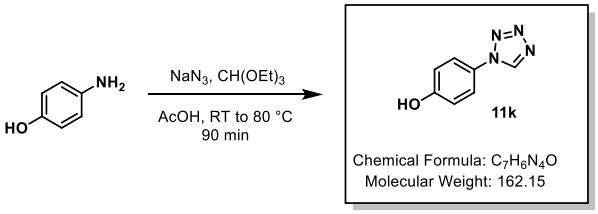
[26] A. U. Meyer, K. Straková, T. Slanina, B. König, *Chem. Eur. J.,* 2016, **22**, 8694-8699.

Phenols



4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenol (11f). The title product was synthesized according to a slightly modified procedure from Liu and co-workers.[27] In a Schlenk tube equipped with a PTFE-coated stirring bar, 4-aminophenol (340 mg, 3.12 mmol, 1.04 equiv.), 2,5-haxadione (351 µl, 3.00 mmol, 1.00 equiv.), *p*-toluenesulfonic acid monohydrate (3.0 mg), toluene (3 ml) and a tip of spatula of $MgSO_4$ were charged, then the reaction was stirred at 110°C for one hour. After cooling to room temperature, the reaction was filtered through a short pad of silica (2 cm length), rinsing with CH_2Cl_2. The volatiles were removed *in vacuo*, then the residue (*yellow thick oil*) was purified by flash column chromatography on silica (pentane/EtOAc = 6:1).

Amount: 560 mg, 2.99 mmol, >99%. **Physical aspect**: faint yellow crystalline solid. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.71 (br s, 1H), 7.05 – 6.97 (m, 1H), 6.88 – 6.81 (m, 2H), 5.73 (s, 2H), 1.92 (s, 6H). The experimental data are in agreement with the literature reports.[28]



4-(1*H*-tetrazol-1-yl)phenol (11k). The title product was synthesized according to a modified procedure from patent WO2011153435, issued by Metabolex Inc.

In a Schlenk tube equipped with a PTFE-coated stirring bar, 4-aminophenol (1.09 g, 10.0 mmol, 1.00 equiv.), NaN_3 (813 mg, 12.5 mmol, 1.25 equiv.), glacial acetic acid (9.15 ml) and triethyl orthoformate (5.32 ml, 32.0 mmol, 3.20 equiv.) were charged, then the suspension was stirred at room temperature for 10 minutes, then heated at 80°C for 90 minutes. The reaction was cooled down to room temperature, diluted with water (20 ml) and the tan precipitate was collected by filtration. The light tan solid was washed twice with water (10 ml each time), once with *n*-pentane/EtOAc = 10/1 (15 ml), once with methanol (10 ml) and once more with *n*-pentane/EtOAc = 10/1 (15 ml), then dried *in vacuo* to afford analytically pure product **11k**.

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[27] T.-J. Gong, B. Xiao, Z.-J. Liu, J. Wan, J. Xu, D.-F. Luo, Y. Fu, L. Liu, *Org. Lett.,* 2011, **13**, 3235-3237.

[28] H. T. Nguyen, D.-K. Nguyen Chau, P. H. Tran, *New J. Chem*., 2017, **41**, 12481-12489

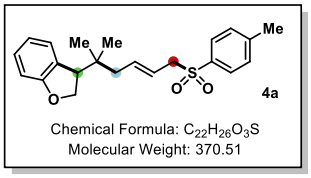
Amount: 999 mg, 6.16 mmol, 62%. **Physical aspect**: off-white fibrous solid. **^{1}H NMR** (400 MHz, CD_3OD) δ 9.59 (s, 1H), 7.68 – 7.59 (m, 2H), 7.02 – 6.93 (m, 2H). The experimental data are in agreement with the literature reports.[29]

[29] X. Chen, J. Ma, J. Song, I. Nashashibi, (Metabolex, Inc.), WO2011/153435, **2011**

Product characterization

Bromides as coupling partners

(*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4a).



The title compound was obtained from bromide **1a** (86.7 mg, 0-36 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (225 µl) and sodium *p*-toluenesulfinate **3a** (53.4 mg, 0.30 mmol, 1.00 equiv.) in dry 1,4-dioxane (2.80 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 7/1).

Amount: 89.7 mg, 0.241 mmol, 81%. **Physical aspect**: pale yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 7/1): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.10 (m, 2H), 6.82 (td, *J* = 7.5, 1.0 Hz, 1H), 6.76 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.59 (dt, *J* = 15.3, 7.4 Hz, 1H), 5.41 (dt, *J* = 15.3, 7.4 Hz, 1H), 4.43 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.35 (t, *J* = 9.2 Hz, 1H), 3.77 (dd, *J* = 7.4, 1.2 Hz, 2H), 3.00 (dd, *J* = 9.1, 4.1 Hz, 1H), 2.39 (s, 3H), 2.05 – 1.95 (m, 2H), 0.81 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9, 144.7, 137.7, 135.7, 129.8, 128.5, 128.4, 127.9, 126.4, 120.0, 119.2, 109.6, 73.0, 60.2, 50.9, 42.8, 37.0, 24.3, 24.0, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{26}O_3SNa$] ([M+Na^+]) 393.1495, found 393.1492.

Scale-up reaction at 2% palladium catalyst loading.

In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, $Pd(PPh_3)_4$ (46.2 mg, 0.040 mmol, 2 mol%) and DPEPhos (43.1 mg, 0.080 mmol, 4.0 mol%), sodium *p*-toluenesulfinate **3a** (376.4 mg ,2.00 mmol, 1.00 equiv.) and K_2CO_3 (415 mg, 3.00 mmol, 1.50 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (7.0 ml, 0.2 M) was added, followed by bromide **1a** (579 mg, 2.40 mmol, 1.20 equiv.) and 1,3-butadiene 2 M inTHF (3.00 ml, 6.00 mmol, 3.00 equiv.), then the vessel was sealed and irradiated for 48 hours at 455 nm using the Kessil light set-up. The reaction was filtered over a short pad of silica, rinsing with EtOAc. The volatiles were removed *in vacuo*, then the residue was loaded on silica and purified by flash column chromatography (*n*-pentane/EtOAc = 6/1 → 5/1), affording **4a** as a colourless gum (581.6 mg, 1.57 mmol, 79%).

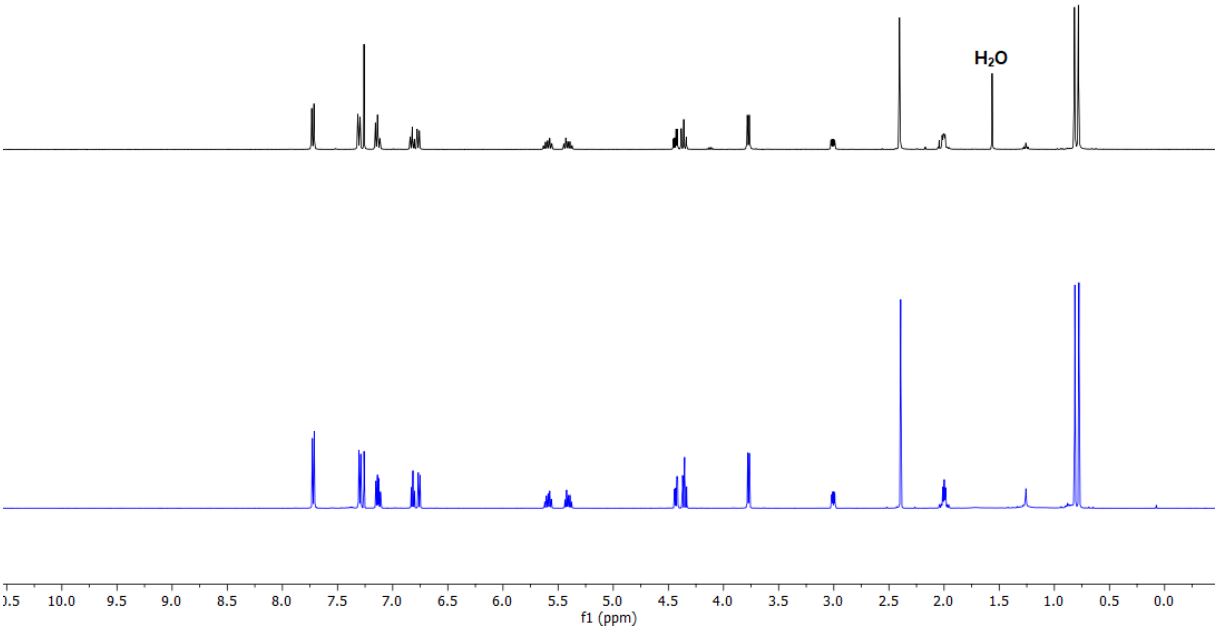
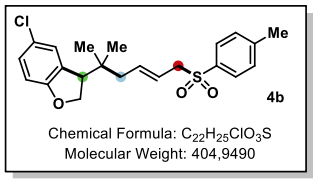


Figure S5 Comparison of the sample **4a** isolated on 2.0 mmol scale with 2% Pd loading (**black**, 400 MHz) with the one obtained on 0.2 mmol scale (**blue**, 500 MHz).

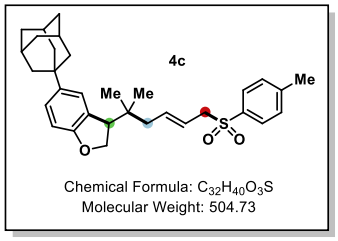
(*E*)-5-chloro-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4b).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1).

Amount: 60.8 mg, 0.150 mmol, 75%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.33 – 7.29 (m, 2H), 7.10 – 7.06 (m, 2H), 6.69 – 6.65 (m, 1H), 5.59 (dtt, *J* = 15.3, 7.5, 1.2 Hz, 1H), 5.41 (dtt, *J* = 15.2, 7.3, 1.3 Hz, 1H), 4.44 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.38 (t, *J* = 9.2 Hz, 1H), 3.78 (d, *J* = 7.4 Hz, 2H), 2.99 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.40 (s, 3H), 2.01 (dd, *J* = 13.9, 7.9 Hz, 1H), 1.96 (dd, *J* = 13.9, 7.2 Hz, 1H), 0.82 (s, 3H), 0.77 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 144.8, 137.3, 135.7, 129.94, 129.88, 128.4, 126.3, 124.6, 119.5, 110.5, 73.7, 60.2, 50.9, 42.8, 37.0, 24.3, 23.9, 21.7. **HRMS (Orbitrap)** *m/z* calc. for $[C_{22}H_{25}O_3S^{35}ClNa]$ ($[M+Na^+]$) 427.1105, found 427.1102. **Notes:** One aromatic signal is missing in the ^{13}C NMR spectrum, most likely due to overlap with another peak.

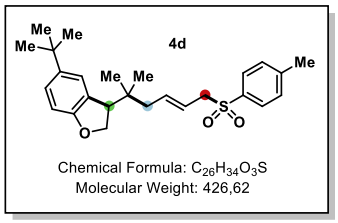
5-(adamantan-1-yl)-3-((*E*)-2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4c).



The title compound was obtained from bromide **1c** (90.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 7/1 → 6/1).

Amount: 98.9 mg, 0.196 mmol, 98%. **Physical aspect**: yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.50. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.33 – 7.28 (m, 2H), 7.16 (d, *J* = 2.1 Hz, 1H), 7.12 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.59 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.41 (dt, *J* = 15.2, 7.3 Hz, 1H), 4.43 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.35 (t, *J* = 9.1 Hz, 1H), 3.78 (dd, *J* = 7.2, 1.1 Hz, 2H), 2.98 (dd, *J* = 8.9, 3.9 Hz, 1H), 2.39 (s, 3H), 2.12 – 2.07 (m, 3H), 2.07 – 1.93 (m, 2H), 1.88 (d, *J* = 2.9 Hz, 6H), 1.84 – 1.70 (m, 6H), 0.83 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.7, 144.7, 143.3, 137.8, 135.7, 129.8, 128.4, 127.5, 124.8, 122.9, 119.1, 108.7, 73.3, 60.3, 51.3, 43.7, 42.8, 37.0, 36.9, 35.8, 29.1, 24.5, 24.1, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{32}H_{40}O_3SNa$] ([M+Na$^+$]) 527.2590, found 527.2588.

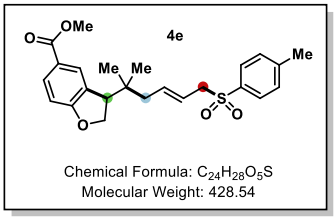
(*E*)-5-(tert-butyl)-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4d).



The title compound was obtained from bromide **1d** (71.3 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 56.7 mg, 0.130 mmol, 65%. **Physical aspect**: yellow oil. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.26. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.20 – 7.12 (m, 2H), 6.68 (d, *J* = 8.3 Hz, 1H), 5.60 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.40 (dt, *J* = 15.1, 7.3 Hz, 1H), 4.43 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.35 (t, *J* = 9.1 Hz, 1H), 3.78 (d, *J* = 7.2 Hz, 2H), 2.97 (dd, *J* = 8.8, 3.9 Hz, 1H), 2.39 (s, 3H), 2.08 – 1.91 (m, 2H), 1.30 (s, 9H), 0.82 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.6, 144.7, 142.8, 137.8, 135.7, 129.8, 128.4, 127.5, 125.2, 123.4, 119.1, 108.6, 73.3, 60.3, 51.2, 42.8, 37.0, 34.3, 31.9, 24.4, 24.0, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{26}H_{34}O_3SNa$] ([M+Na$^+$]) 449.21209, found 449.21172.

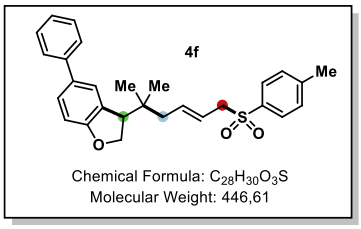
methyl (*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran-5-carboxylate (4e).



The title compound was obtained from bromide **1e** (71.8 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 4/1 → 7/2).

Amount: 48.9 mg, 0.114 mmol, 57%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 4/1): 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.60 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.42 (dt, *J* = 15.4, 7.4 Hz, 1H), 4.51 (dd, *J* = 9.6, 4.3 Hz, 1H), 4.44 (t, *J* = 9.3 Hz, 1H), 3.87 (s, 3H), 3.77 (d, *J* = 7.3 Hz, 2H), 3.02 (dd, *J* = 9.1, 4.3 Hz, 1H), 2.38 (s, 3H), 2.02 (dd, *J* = 14.1, 7.9 Hz, 1H), 1.96 (dd, *J* = 13.9, 7.3 Hz, 1H), 0.82 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.1, 165.0, 144.8, 137.4, 135.7, 131.5, 129.9, 128.4, 128.1, 122.3, 119.5, 109.3, 74.1, 60.2, 52.0, 50.3, 42.8, 37.0, 24.2, 23.8, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{28}O_5SNa$] ([M+Na$^+$]) 451.1550, found 451.1542. **Note**: One ^{13}C signal expected in the aromatic region is missing, most likely due to overlap.

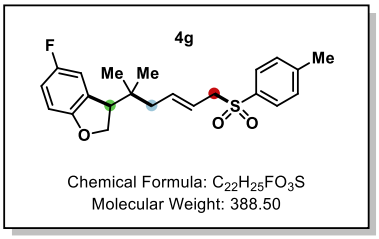
(*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)-5-phenyl-2,3-dihydrobenzofuran (4f).



The title compound was obtained from bromide **1f** (76.3 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1).

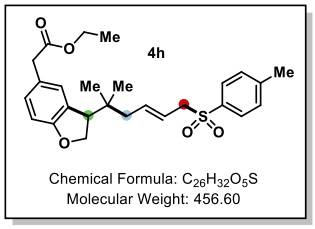
Amount: 68.0 mg, 0.152 mmol, 76%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.55 – 7.51 (m, 2H), 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.32 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.31 – 7.27 (m, 2H), 6.87 – 6.82 (m, 1H), 5.63 (dddd, *J* = 15.1, 7.6, 6.4, 1.2 Hz, 1H), 5.43 (ddt, *J* = 15.3, 7.4, 1.3 Hz, 1H), 4.50 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.43 (t, *J* = 9.2 Hz, 1H), 3.79 (d, *J* = 7.4 Hz, 2H), 3.08 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.37 (s, 3H), 2.11 – 1.99 (m, 2H), 0.88 (s, 3H), 0.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 144.8, 141.5, 137.6, 135.7, 133.6, 129.8, 128.8, 128.7, 128.4, 127.7, 126.9, 126.7, 125.2, 119.3, 109.7, 73.5, 60.2, 51.0, 42.9, 37.0, 24.4, 24.0, 21.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{28}H_{30}O_3SNa$] ([M+Na$^+$]) 469.1808, found 469.1808.

(*E*)-5-fluoro-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4g). The title compound was obtained from bromide **1g** (62.2 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1).



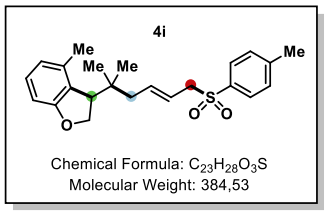
Amount: 54.3 mg, 0.140 mmol, 70%. **Physical aspect**: yellow oil. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.16. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.36 – 7.27 (m, 2H), 6.90 – 6.75 (m, 2H), 6.71 – 6.61 (m, 1H), 5.59 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.40 (dt, *J* = 15.2, 7.3 Hz, 1H), 4.48 – 4.32 (m, 2H), 3.78 (d, *J* = 7.2 Hz, 2H), 2.99 (dd, *J* = 8.8, 4.4 Hz, 1H), 2.40 (s, 3H), 2.08 – 1.87 (m, 2H), 0.82 (s, 3H), 0.77 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 157.0 (d, *J* = 236.2 Hz), 156.9 (d, *J* = 1.4 Hz),144.8, 137.4, 135.7, 129.9, 129.3 (d, *J* = 8.1 Hz), 128.4, 119.4, 114.6 (d, *J* = 24.0 Hz), 113.4 (d, *J* = 24.9 Hz), 109.6 (d, *J* = 8.6 Hz), 73.7, 60.2, 51.1 (d, *J* = 1.7 Hz), 42.8, 37.0, 24.3, 23.9, 21.7.**^{19}F{^{1}H} NMR** (282 MHz, $CDCl_3$) δ -124.82. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{25}O_3FSNa$] ([M+Na$^+$]) 411.1401, found 411.1401.

ethyl (*E*)-2-(3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran-5-yl)acetate (4h). The title compound was obtained from bromide **1h** (78.5 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 7/2).



Amount: 74.3 mg, 0.163 mmol, 82%. **Physical aspect**: pale yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 4/1): 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 1.9 Hz, 1H), 7.02 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.58 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.40 (dt, *J* = 15.2, 7.3 Hz, 1H), 4.43 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.35 (t, *J* = 9.2 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 7.2 Hz, 2H), 3.53 (s, 2H), 2.98 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.39 (s, 3H), 2.05 – 1.91 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.81 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.1, 160.0, 144.7, 137.6, 135.7, 129.8, 129.4, 128.4, 128.3, 127.3, 125.6, 119.2, 109.4, 73.3, 60.8, 60.2, 51.0, 42.8, 41.0, 36.9, 24.3, 23.9, 21.6, 14.3. **HRMS (Orbitrap)** *m/z* calc. for [$C_{26}H_{32}O_5SNa$] ([M+Na$^+$]) 479.1863, found 479.1856.

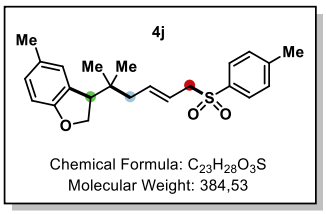
(*E*)-4-methyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4i).



The title compound was obtained from bromide **1i** (61.2 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 37.5 mg, 0.098 mmol, 49%. **Physical aspect**: pale yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.32 – 7.28 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.95 (ddt, *J* = 7.5, 1.4, 0.7 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 5.59 (dtt, *J* = 15.1, 7.6, 1.2 Hz, 1H), 5.41 (dtt, *J* = 15.3, 7.3, 1.1 Hz, 1H), 4.44 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.35 (t, *J* = 9.2 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 3.02 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.40 (s, 3H), 2.19 (s, 3H), 2.06 – 1.94 (m, 2H), 0.81 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.3, 144.7, 137.8, 135.7, 129.8, 129.7, 128.4, 127.1, 123.8, 119.8, 119.7, 119.1, 72.8, 60.3, 51.3, 42.9, 36.9, 24.3, 24.1, 21.7, 15.3. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{28}O_3SNa$] ([M+Na$^+$]) 407.1651, found 407.1650.

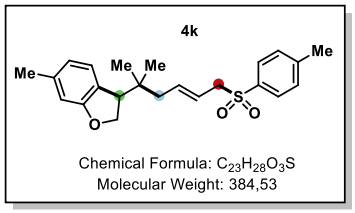
(*E*)-5-methyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4j).



The title compound was obtained from bromide **1j** (61.2 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 53.3 mg, 0.139 mmol, 70%. **Physical aspect**: pale yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.33 – 7.28 (m, 2H), 6.97 – 6.90 (m, 2H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.60 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.41 (dt, *J* = 15.1, 7.3 Hz, 1H), 4.41 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.33 (t, *J* = 9.2 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 2.96 (dd, *J* = 8.9, 4.0 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H), 2.07 – 1.92 (m, 2H), 0.81 (s, 3H), 0.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8, 144.7, 137.8, 135.7, 129.8, 129.1, 128.9, 128.4, 127.9, 127.0, 119.2, 109.1, 73.2, 60.3, 51.1, 42.8, 36.9, 24.3, 24.0, 21.7, 21.1. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{28}O_3SNa$] ([M+Na$^+$]) 407.16514, found 407.16499.

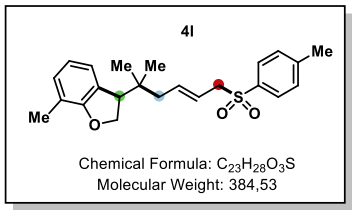
(*E*)-6-methyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4k).



The title compound was obtained from bromide **1k** (61.2 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 51.8 mg, 0.135 mmol, 68%. **Physical aspect**: pale yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.59 (s, 1H), 5.59 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.40 (dt, *J* = 15.1, 7.3 Hz, 1H), 4.41 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.34 (t, *J* = 9.2 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.96 (dd, *J* = 8.9, 4.1 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 2.05 – 1.91 (m, 2H), 0.80 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 144.7, 138.7, 137.8, 135.7, 129.8, 128.4, 125.9, 124.9, 120.7, 119.2, 110.3, 73.3, 60.3, 50.7, 42.8, 36.9, 24.2, 24.0, 21.7, 21.5. **HRMS (Orbitrap)** *m/z* calc. for $[C_{23}H_{28}O_3SNa]$ ($[M+Na^+]$) 407.16514, found 407.16496.

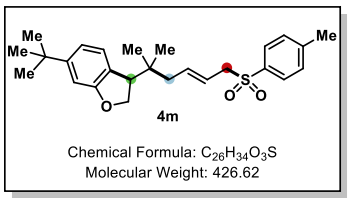
(*E*)-7-methyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4l).



The title compound was obtained from bromide **1l** (61.2 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 54.5 mg, 0.142 mmol, 71%. **Physical aspect**: pale yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 5.63 – 5.54 (m, 1H), 5.37 (dt, *J* = 15.0, 7.4 Hz, 1H), 4.51 (dd, *J* = 9.3, 0.8 Hz, 1H), 4.23 (dd, *J* = 9.2, 7.5 Hz, 1H), 3.76 (d, *J* = 7.3 Hz, 2H), 2.93 (d, *J* = 7.3 Hz, 1H), 2.42 (s, 3H), 2.27 (s, 3H), 2.07 (dd, *J* = 13.7, 8.0 Hz, 1H), 1.95 (dd, *J* = 13.6, 7.1 Hz, 1H), 0.80 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 144.7, 137.9, 135.9, 135.9, 129.9, 128.5, 128.4, 127.4, 122.7, 119.1, 106.9, 73.9, 60.3, 50.5, 43.0, 39.1, 25.1, 24.1, 21.7, 21.3. **HRMS (Orbitrap)** *m/z* calc. for $[C_{23}H_{28}O_3SNa]$ ($[M+Na^+]$) 407.16514, found 407.16495.

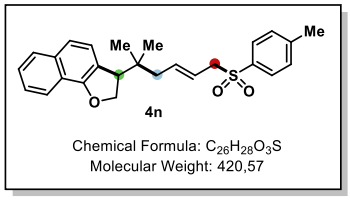
(*E*)-6-(*tert*-butyl)-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4m).



The title compound was obtained from bromide **1m** (71.3 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1).

Amount: 76.0 mg, 0.178 mmol, 89%. **Physical aspect**: light yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.84 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.81 (d, *J* = 1.7 Hz, 1H), 5.58 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.42 (dtt, *J* = 15.2, 7.4, 1.3 Hz, 1H), 4.42 (dd, *J* = 9.3, 4.3 Hz, 1H), 4.35 (t, *J* = 9.2 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.98 (dd, *J* = 9.0, 4.3 Hz, 1H), 2.40 (s, 3H), 2.05 – 1.96 (m, 2H), 1.29 (s, 9H), 0.81 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 152.4, 144.7, 137.8, 135.7, 129.8, 128.4, 125.6, 124.8, 119.1, 117.0, 106.8, 73.2, 60.3, 50.9, 42.9, 37.0, 34.8, 31.6, 24.3, 24.1, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{26}H_{34}O_3SNa$] ([M+Na$^+$]) 449.2121, found 449.2118.

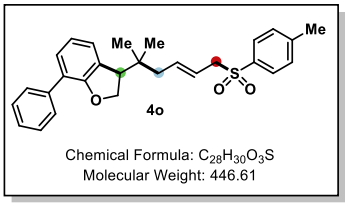
(*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan (4n).



The title compound was obtained from bromide **1n** (69.9 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 25.8 mg, 0.061 mmol, 31%. **Physical aspect**: light yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.21. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.65 (m, 4H), 7.45 – 7.37 (m, 1H), 7.32 – 7.24 (m, 3H), 7.11 (d, *J* = 8.7 Hz, 1H), 5.65 – 5.55 (m, 1H), 5.37 (dt, *J* = 15.1, 7.3 Hz, 1H), 4.69 (d, *J* = 10.4 Hz, 1H), 4.43 (dd, *J* = 9.3, 8.0 Hz, 1H), 3.76 (d, *J* = 7.3 Hz, 2H), 3.36 (d, *J* = 7.5 Hz, 1H), 2.34 (s, 3H), 2.15 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.00 (dd, *J* = 13.7, 6.9 Hz, 1H), 0.85 (s, 3H), 0.79 (s, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.1, 144.8, 137.9, 135.8, 132.0, 130.1, 129.9, 129.7, 128.9, 128.4, 126.2, 124.7, 122.6, 120.1, 119.1, 112.2, 74.9, 60.3, 50.7, 43.3, 39.2, 25.9, 24.5, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{26}H_{28}O_3SNa$] ([M+Na$^+$]) 443.1651, found 443.1649.

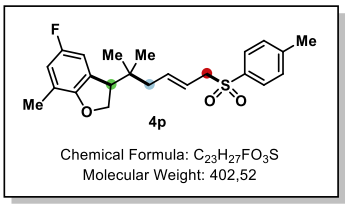
(*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)-7-phenyl-2,3-dihydrobenzofuran (4o).



The title compound was obtained from bromide **1o** (76.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 7/1 → 6/1).

Amount: 63.0 mg, 0.141 mmol, 71%. **Physical aspect**: yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.55. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 2H), 7.67 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.33 – 7.29 (m, 4H), 7.14 (dt, *J* = 7.5, 1.1 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 5.62 (dtd, *J* = 15.2, 7.7, 6.4, 1.2 Hz, 1H), 5.43 (dtt, *J* = 15.2, 7.4, 1.4 Hz, 1H), 4.52 (dd, *J* = 9.4, 3.9 Hz, 1H), 4.41 (t, *J* = 9.2 Hz, 1H), 3.79 (d, *J* = 7.4 Hz, 2H), 3.06 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.41 (s, 3H), 2.09 – 2.01 (m, 2H), 0.86 (s, 3H), 0.83 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.0, 144.7, 137.7, 137.4, 135.7, 129.8, 128.8, 128.5, 128.44, 128.42, 127.2, 125.5, 123.7, 120.5, 119.2, 73.1, 60.3, 51.0, 42.8, 37.0, 24.3, 24.0, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{38}H_{30}O_3SNa$] ([M+Na$^+$]) 469.1808, found 469.1803. **Note:** One aromatic ^{13}C signal missing due to overlap.

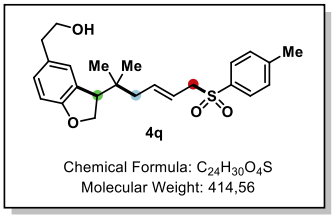
(*E*)-5-fluoro-7-methyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4p).



The title compound was obtained from bromide **1p** (65.6 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1).

Amount: 58.8 mg, 0.146 mmol, 73%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.30. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.32 – 7.29 (m, 2H), 6.66 (dt, *J* = 9.0, 0.8 Hz, 2H), 5.58 (dtt, *J* = 15.0, 7.9, 1.1 Hz, 1H), 5.40 (dtt, *J* = 15.1, 7.3, 1.3 Hz, 1H), 4.43 (dd, *J* = 9.4, 4.4 Hz, 1H), 4.36 (t, *J* = 9.3 Hz, 1H), 3.77 (d, *J* = 7.4 Hz, 2H), 2.99 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.40 (s, 3H), 2.15 (s, 3H), 2.00 (dd, *J* = 13.9, 7.8 Hz, 1H), 1.96 (dd, *J* = 14.0, 7.2 Hz, 1H), 0.81 (s, 3H), 0.77 (s, 3H). **^{13}C{^{1}H, ^{19}F} NMR** (151 MHz, $CDCl_3$) δ 156.8, 155.2, 144.8, 137.5, 135.7, 129.9, 128.4, 128.1, 120.3, 119.4, 115.8, 110.5, 73.2, 60.2, 51.5, 42.9, 36.9, 24.3, 24.0, 21.7, 15.4. **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 156.8 (d, *J* = 235.8 Hz), 155.2 (d, *J* = 1.3 Hz), 144.8, 137.5, 135.7, 129.9, 128.4, 128.1 (d, *J* = 8.6 Hz), 120.3 (d, *J* = 8.3 Hz), 119.4, 115.8 (d, *J* = 23.7 Hz), 110.5 (d, *J* = 24.7 Hz), 73.2, 60.2, 51.5 (d, *J* = 1.9 Hz), 42.9, 36.9, 24.3, 24.0, 21.7, 15.4 (d, *J* = 1.3 Hz). **^{19}F{^{1}H} NMR** (564 MHz, $CDCl_3$) δ -125.31. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -125.31 (t, *J* = 9.0 Hz). **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{27}O_3SFNa$] ([M+Na$^+$]) 425.1557, found 425.1548.

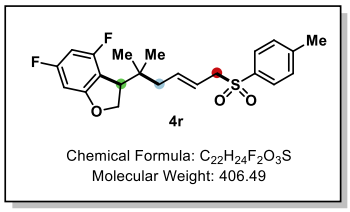
(*E*)-2-(3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran-5-yl)ethan-1-ol (4q).



The title compound was obtained from bromide **1q** (68.4 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/2).

Amount: 76.9 mg, 0.186 mmol, 93%. **Physical aspect**: yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 1/1): 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.32 – 7.27 (m, 2H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.97 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.59 (dtt, *J* = 15.3, 7.5, 1.1 Hz, 1H), 5.41 (dtt, *J* = 15.3, 7.4, 1.0 Hz, 1H), 4.42 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.34 (t, *J* = 9.2 Hz, 1H), 3.83 – 3.73 (m, 4H), 2.98 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H), 2.07 – 1.92 (m, 2H), 1.78 – 1.63 (br, 1H), 0.81 (s, 3H), 0.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 144.7, 137.7, 135.7, 129.9, 129.8, 129.0, 128.4, 128.3, 127.1, 119.1, 109.4, 73.2, 64.1, 60.2, 51.0, 42.9, 38.8, 36.9, 24.3, 24.0, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{30}O_4SNa$] ([M+Na$^+$]) 437.1757, found 437.1749.

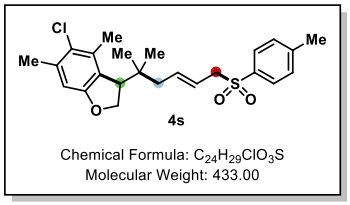
(*E*)-4,6-difluoro-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4r).



The title compound was obtained from bromide **1r** (66.5 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1 → 4/1).

Amount: 49.1 mg, 0.121 mmol, 61%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.25. **^{1}H{^{19}F} NMR** (599 MHz, $CDCl_3$) δ 7.73 – 7.71 (m, 2H), 7.33 – 7.29 (m, 2H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.67 (dd, *J* = 2.5, 0.9 Hz, 1H), 5.60 (dt, *J* = 15.2, 7.8, 7.3 Hz, 1H), 5.41 (dtt, *J* = 15.2, 7.4, 1.2 Hz, 1H), 4.54 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.46 (t, *J* = 9.3 Hz, 1H), 3.78 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.06 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.40 (s, 3H), 2.02 (dd, *J* = 14.0, 7.9 Hz, 1H), 1.96 (dd, *J* = 14.0, 7.2 Hz, 1H), 0.83 (s, 3H), 0.79 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 156.1 (dd, *J* = 239.7, 8.9 Hz), 146.7 (dd, *J* = 248.2, 12.9 Hz), 144.85, 143.8 (dd, *J* = 10.4, 2.6 Hz), 137.1, 135.8, 131.9 (dd, *J* = 9.3, 3.8 Hz), 129.9, 128.4, 119.7, 108.8 (dd, *J* = 24.5, 3.8 Hz), 103.8 (dd, *J* = 27.7, 20.9 Hz), 74.7, 60.1, 51.7, 42.9, 37.0, 24.3, 23.9, 21.7. **^{13}C{^{1}H, ^{19}F} NMR** (151 MHz, $CDCl_3$) δ 156.1, 146.7, 144.9, 143.8, 137.1, 135.8, 131.9, 129.9, 128.38, 119.7, 108.8, 103.8, 74.7, 60.1, 51.7, 42.9, 37.0, 24.3, 23.9, 21.7. **^{19}F NMR** (564 MHz, $CDCl_3$) δ -121.32 (t, *J* = 8.5 Hz), -135.45 (d, *J* = 10.3 Hz). **^{19}F{^{1}H} NMR** (564 MHz, $CDCl_3$) δ -121.32, -135.46. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{24}O_3SF_2Na$] ([M+Na$^+$]) 429.1306, found 429.1298.

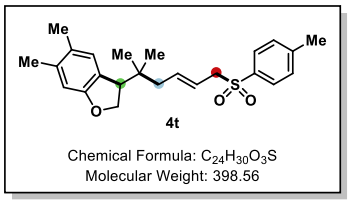
(*E*)-5-chloro-4,6-dimethyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4s).



The title compound was obtained from bromide **1s** (72.9 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1 → 4/1).

Amount: 33.3 mg, 0.077 mmol, 39%. **Physical aspect**: pale yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 5/1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.55 (s, 1H), 5.57 (dt, *J* = 15.4, 7.5 Hz, 1H), 5.38 (dtt, *J* = 15.3, 7.5, 1.3 Hz, 1H), 4.50 (dd, *J* = 9.3, 1.1 Hz, 1H), 4.24 (dd, *J* = 9.3, 7.4 Hz, 1H), 3.76 (d, *J* = 7.3 Hz, 2H), 2.93 (d, *J* = 7.3 Hz, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 2.25 (s, 3H), 2.05 (dd, *J* = 13.8, 8.0 Hz, 1H), 1.92 (dd, *J* = 13.6, 6.9 Hz, 1H), 0.77 (s, 3H), 0.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.9, 144.8, 137.7, 136.4, 135.8, 133.7, 129.9, 128.4, 126.64, 126.58, 119.2, 109.4, 74.3, 60.3, 51.1, 42.9, 39.1, 25.0, 23.9, 21.7, 21.4, 20.5. **HRMS (Orbitrap)** *m/z* calc. for $[C_{24}H_{29}O_3S^{35}ClNa]$ ($[M+Na^+]$) 455.1418, found 455.1416.

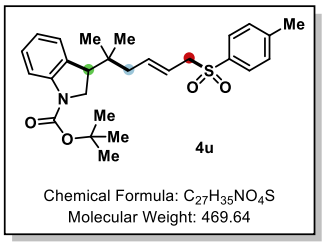
(*E*)-5,6-dimethyl-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (4t).



The title compound was obtained from bromide **1t** (64.6 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 61.0 mg, 0.156 mmol, 78%. **Physical aspect**: faint yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 7/1): 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.33 – 7.28 (m, 2H), 6.91 (s, 1H), 6.57 (s, 1H), 5.60 (dtt, *J* = 15.3, 7.5, 1.1 Hz, 1H), 5.41 (dtt, *J* = 15.2, 7.3, 1.2 Hz, 1H), 4.39 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.31 (t, *J* = 9.1 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 2.95 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.40 (s, 3H), 2.20 (s, 3H), 2.19 (s, 3H), 2.05 – 1.93 (m, 2H), 0.80 (s, 3H), 0.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 144.7, 137.9, 136.7, 135.7, 129.8, 128.4, 127.6, 127.3, 125.0, 119.1, 110.6, 73.1, 60.3, 51.1, 42.8, 36.9, 24.2, 24.0, 21.7, 20.2, 19.5. **HRMS (Orbitrap)** *m/z* calc. for $[C_{24}H_{30}O_3SNa]$ ($[M+Na^+]$) 421.1808, found 421.1801.

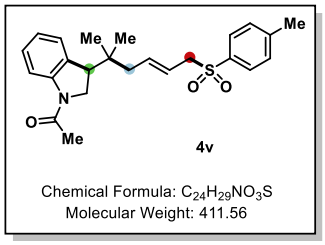
***tert*-butyl (*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)indoline-1-carboxylate (4u).**



The title compound was obtained from bromide **1u** (81.7 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 4/1).

Amount: 85.1 mg, 0.181 mmol, 91%. **Physical aspect**: faint yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 3/1): 0.50. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.73 – 7.69 (m, 2H), 7.38 – 7.34 (m, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 5.63 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.32 (dt, *J* = 15.2, 7.3 Hz, 1H), 4.12 – 4.00 (m, 2H), 3.82 – 3.72 (m, 1H), 3.71 – 3.62 (m, 1H), 2.67 (dd, *J* = 9.6, 4.0 Hz, 1H), 2.30 (s, 3H), 1.97 – 1.87 (m, 2H), 1.51 (s, 9H), 0.69 (s, 3H), 0.60 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 151.4, 144.0, 143.8 – 143.0 (br, visible in HMBC), 136.9, 135.6, 129. 6, 127.7, 127.6, 126.3 – 126.1 (br), 121.6, 119.5, 114.3 – 113.8 (br), 81.2 – 79.7 (br, visible in HMBC), 58.4, 49.6, 47.1 – 46.2 (br), 42.3, 36.7, 28.0, 23.8, 23.0, 20.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{27}H_{35}NO_4SNa$] ([M+Na$^+$]) 492.2184, found 492.2176. **Note.** Due to the presence of amide rotamers, some ^{1}H NMR signals appear broadened. In ^{13}C NMR, two aromatic signals are missing due to broadening, but visible using heterocorrelated spectroscopy.

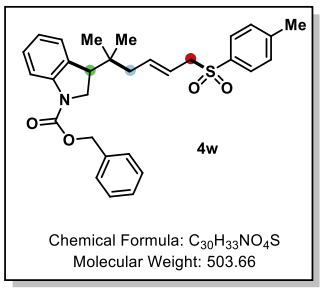
(*E*)-1-(3-(2-methyl-6-tosylhex-4-en-2-yl)indolin-1-yl)ethan-1-one (4v).



The title compound was obtained from bromide **1v** (67.7 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 2/3).

Amount: 50.5 mg, 0.123 mmol, 61%. **Physical aspect**: faint yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 2/3): 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.18 – 7.09 (m, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 5.61 (dt, *J* = 15.2, 7.5 Hz, 1H), 5.42 (dt, *J* = 15.2, 7.4 Hz, 1H), 3.88 (d, *J* = 4.0 Hz, 2H), 3.77 (d, *J* = 7.3 Hz, 2H), 3.03 – 2.76 (m, 1H), 2.39 (s, 3H), 2.23 (s, 3H), 2.01 (d, *J* = 7.6 Hz, 2H), 0.91 – 0.68 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.4, 144.8, 143.8, 137.5, 135.8, 131.9, 129.9, 128.3, 128.2, 126.2, 123.1, 119.3, 116.9, 60.2, 51.5, 48.8, 42.9, 37.6, 24.4, 24.0, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{29}NO_3SNa$] ([M+Na$^+$]) 434.1766, found 434.1756. **Note.** Due to the presence of amide rotamers, some ^{1}H NMR signals appear distorted and/or splitted. In ^{13}C NMR some signals are splitted and one aliphatic signal is missing due to broadening.

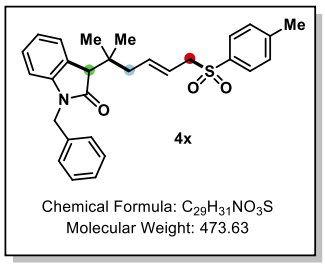
benzyl (*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)indoline-1-carboxylate (4w).



The title compound was obtained from bromide **1w** (89.8 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 4/1).

Amount: 57.1 mg, 0.113 mmol, 57%. **Physical aspect**: faint yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 3/1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.25 (m, 8H), 7.26 – 7.09 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 5.58 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.40 (dt, *J* = 14.9, 7.2 Hz, 1H), 5.34 – 5.19 (m, 2H), 4.07 – 3.90 (m, 1H), 3.83 (dd, *J* = 11.7, 9.7 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.89 (dd, *J* = 9.8, 3.6 Hz, 1H), 2.38 (s, 3H), 2.08 – 1.94 (m, 2H), 0.81 (s, 3H), 0.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.8 – 152.1 (br), 144.7, 143.9 – 143.1 (br), 137.6, 136.8 – 136.3 (br), 135.7, 131.9 – 131.5 (br), 129.8, 128.7, 128.4, 128.3, 128.2, 126.9 – 126.0 (br), 122.2, 119.3, 115.3 – 114.6 (br), 67.2, 60.2, 50.8 – 49.6 (br), 48.7 – 47.6 (br), 42.8, 37.6, 24.4, 23.9, 21.7. **HRMS (Orbitrap)** *m/z* calc. for $[C_{30}H_{33}NO_4SNa]$ ($[M+Na^+]$) 526.2028, found 526.2024. **Note.** A little amount of residual EtOAc = cannot be removed from the product, even after several days under high vacuum (10^{-2} mbar). Due to the presence of amide rotamers, some ^{1}H NMR signals appear distorted and/or splitted. In ^{13}C NMR some signals are splitted and one aromatic signal is missing due to broadening.

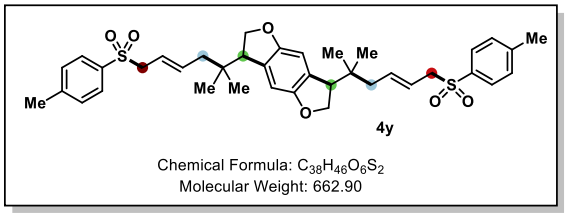
(*E*)-1-benzyl-3-(2-methyl-6-tosylhex-4-en-2-yl)indolin-2-one (4x).



The title compound was obtained from bromide **1x** (82.6 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 4/1 → 3/1).

Amount: 73.8 mg, 0.156 mmol, 78%. **Physical aspect**: faint yellow oil. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 4/1): 0.32. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.31 – 7.19 (m, 8H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.96 (td, *J* = 7.6, 1.1 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 5.70 (dt, *J* = 15.3, 7.2 Hz, 1H), 5.52 (dt, *J* = 15.2, 7.3 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 4.71 (d, *J* = 15.7 Hz, 1H), 3.79 (d, *J* = 7.2 Hz, 2H), 3.04 (s, 1H), 2.56 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.30 (s, 3H), 2.16 (dd, *J* = 13.7, 7.0 Hz, 1H), 1.05 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.4, 144.7, 144.2, 137.7, 136.2, 135.5, 129.7, 128.8, 128.5, 128.0, 127.6, 127.4, 127.2, 126.1, 121.8, 119.9, 108.8, 60.4, 52.7, 43.6, 42.6, 38.2, 25.7, 24.2, 21.6. **HRMS (Orbitrap)** *m/z* calc. for $[C_{29}H_{31}NO_3SNa]$ ($[M+Na^+]$) 496.1917, found 496.1912.

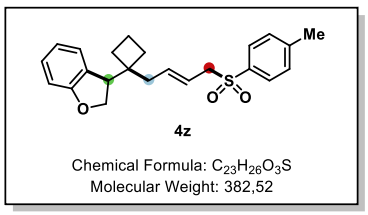
3,7-bis((*E*)-2-methyl-6-tosylhex-4-en-2-yl)-2,3,6,7-tetrahydrobenzo[1,2-*b*:4,5-*b*']difuran (4y).



The title compound was obtained from bromide **1y** (80.8 mg, 0.20 mmol, 1.00 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and sodium *p*-toluenesulfinate **3a** (106.9 mg, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 455 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 2/1), affording an inseparable mixture of diastereoisomers.

Amount: 99.1 mg, 0.159 mmol, 80%, 50:50 dr. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 2/1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 4H), 7.29 (dd, *J* = 8.4, 2.6 Hz, 4H), 6.54 (d, *J* = 3.1 Hz, 2H), 5.57 (dt, *J* = 15.3, 7.5 Hz, 2H), 5.38 (dt, *J* = 15.3, 7.3 Hz, 2H), 4.43 – 4.28 (m, 4H), 3.76 (d, *J* = 7.3 Hz, 4H), 2.95 – 2.87 (m, 2H), 2.38 (d, *J* = 5.6 Hz, 6H), 2.04 – 1.91 (m, 4H), 0.79 (s, 3H, *single diastereoisomer*), 0.78 (s, 3H, *single diastereoisomer*), 0.76 (s, 3H, *single diastereoisomer*), 0.75 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6, 154.5, 144.7, 137.7, 137.6, 135.60, 135.58, 129.8, 128.4, 127.5, 127.4, 119.19, 119.16, 107.3, 107.2, 73.42, 73.41, 60.2, 51.3, 51.2, 42.84, 42.82, 36.91, 36.90, 24.27, 24.25, 23.99, 23.97, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{38}H_{46}O_6S_2Na$] ([M+Na$^+$]) 685.2628, found 685.2630. **Note**. Some ^{13}C signals belonging to different diastereoisomers overlap, therefore all the signals are quoted together.

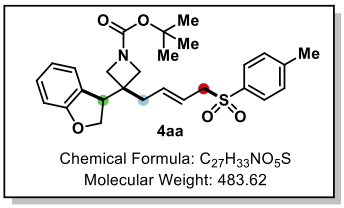
(*E*)-3-(1-(4-tosylbut-2-en-1-yl)cyclobutyl)-2,3-dihydrobenzofuran (4z).



The title compound was obtained from bromide **1z** (60.8 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1).

Amount: 36.9 mg, 0.096 mmol, 48%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.40. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.31 – 7.28 (m, 2H), 7.15 – 7.09 (m, 2H), 6.81 (td, *J* = 7.4, 1.0 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.53 (dtt, *J* = 15.2, 7.4, 1.2 Hz, 1H), 5.40 (dtt, *J* = 15.2, 7.3, 7.2, 1.3 Hz, 1H), 4.42 (t, *J* = 9.3 Hz, 1H), 4.23 (dd, *J* = 9.2, 4.6 Hz, 1H), 3.73 (d, *J* = 7.3 Hz, 2H), 3.37 (dd, *J* = 9.4, 4.6 Hz, 1H), 2.38 (s, 3H), 2.06 (d, *J* = 7.3 Hz, 2H), 1.99 – 1.84 (m, 2H), 1.79 – 1.61 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9, 144.7, 137.7, 135.7, 129.8, 128.6, 128.5, 128.2, 125.3, 120.3, 118.9, 109.7, 73.5, 60.4, 49.7, 44.3, 39.6, 29.0, 28.9, 21.7, 14.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{26}O_3SNa$] ([M+Na$^+$]) 405.1495, found 405.1496.

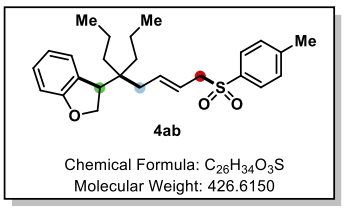
***tert*-butyl (*E*)-3-(2,3-dihydrobenzofuran-3-yl)-3-(4-tosylbut-2-en-1-yl)azetidine-1-carboxylate (4aa).**



The title compound was obtained from bromide **1aa** (85.0 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 2/1).

Amount: 32.7 mg, 0.068 mmol, 34%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 2/1): 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.16 (td, *J* = 7.8, 1.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.83 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.60 – 5.42 (m, 2H), 4.48 (t, *J* = 9.4 Hz, 1H), 3.78 – 3.66 (m, 4H), 3.60 (d, *J* = 8.7 Hz, 1H), 3.55 (d, *J* = 8.8 Hz, 1H), 3.47 (dd, *J* = 9.2, 4.6 Hz, 1H), 2.47 – 2.41 (m, 1H), 2.40 (s, 3H), 2.32 – 2.19 (m, 2H), 1.41 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 156.1, 144.8, 135.5, 135.4, 129.8, 129.2, 128.3, 126.4, 125.0, 120.7, 120.6, 110.1, 79.8, 73.0, 60.0, 47.2, 39.5, 38.0, 29.7, 28.4, 21.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{27}H_{33}O_5SNNa$] ([M+Na$^+$]) 506.1972, found 506.1969. **Note**: One aliphatic ^{13}C signal cannot be detected due to broadening caused by the presence of amide rotamers (somehow distorted baseline is visible at approx. 65 ppm).

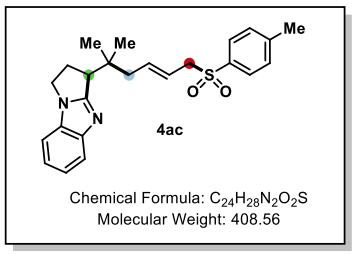
(*E*)-3-(4-propyl-8-tosyloct-6-en-4-yl)-2,3-dihydrobenzofuran (4ab).



The title compound was obtained from bromide **1ab** (71.3 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1).

Amount: 38.2 mg, 0.090 mmol, 45%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.30. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.35 – 7.26 (m, 2H), 7.16 – 7.05 (m, 2H), 6.79 (td, *J* = 7.4, 1.1 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.49 – 5.24 (m, 2H), 4.45 (dd, *J* = 9.5, 4.4 Hz, 1H), 4.33 (t, *J* = 9.5 Hz, 1H), 3.67 (d, *J* = 6.6 Hz, 2H), 3.25 (dd, *J* = 9.6, 4.3 Hz, 1H), 2.42 (s, 3H), 2.09 – 1.89 (m, 2H), 1.36 – 1.07 (m, 8H), 0.93 – 0.78 (m, 6H). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 161.0, 144.7, 138.1, 135.8, 129.8, 128.4, 128.3, 126.3, 120.0, 118.4, 109.6, 72.6, 60.2, 48.4, 42.0, 39.3, 38.3, 37.9, 21.7, 17.1, 17.0, 15.12, 15.10. **HRMS (Orbitrap)** *m/z* calc. for [$C_{26}H_{34}O_3SNa$] ([M+Na$^+$]) 449.2126, found 449.2118. **Note**. One aromatic signal missing due to overlap.

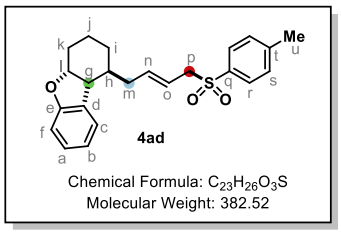
(*E*)-3-(2-methyl-6-tosylhex-4-en-2-yl)-2,3-dihydro-1H-benzo[*d*]pyrrolo[1,2-*a*]imidazole (4ac).



The title compound was obtained from bromide **1ac** (67.0 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 455 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/2 → 10/7).

Amount: 73.2 mg, 0.179 mmol, 90%. **Physical aspect**: colorless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 3/2): 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 1H), 7.69 – 7.64 (m, 2H), 7.32 – 7.27 (m, 1H), 7.25 – 7.16 (m, 4H), 5.67 (dt, *J* = 15.2, 7.7 Hz, 1H), 5.45 (dt, *J* = 15.2, 7.3 Hz, 1H), 4.07 (ddd, *J* = 10.1, 8.8, 4.4 Hz, 1H), 3.93 (ddd, *J* = 10.1, 8.5, 6.6 Hz, 1H), 3.80 – 3.64 (m, 2H), 3.00 (dd, *J* = 8.9, 7.0 Hz, 1H), 2.62 (dtd, *J* = 13.2, 8.7, 4.5 Hz, 1H), 2.54 – 2.42 (m, 1H), 2.35 (s, 3H), 2.34 – 2.22 (m, 2H), 0.98 (s, 3H), 0.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.8, 148.6, 144.6, 137.7, 135.7, 132.0, 129.8, 128.3, 121.84 121.7, 119.8, 119.1, 109.5, 60.2, 45.3, 43.3, 41.7, 36.9, 28.6, 24.4, 24.2, 21.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{28}O_2N_2SNa$] ([M+Na$^+$]) 431.1764, found 431.1757.

1-((*E*)-4-tosylbut-2-en-1-yl)-1,2,3,4,4a,9b-hexahydrodibenzo[*b,d*]furan (4ad).

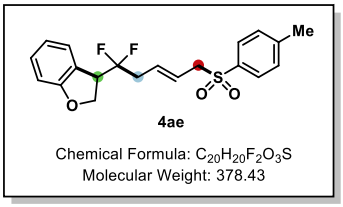


The title compound was obtained from bromide **1ad** (60.8 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1 → 4/1).

Amount: 39.5 mg, 0.103 mmol, 52%, >95:5 dr. **Physical aspect**: pale yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 5/1): 0.35. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H, H_r), 7.30 – 7.27 (m, 2H, H_s), 7.17 – 7.15 (m, 1H), 7.14 (td, *J* = 7.6, 1.4 Hz, 1H), 6.86 – 6.82 (m, 2H), 5.48 – 5.38 (m, 2H, $H_{n,o}$), 4.55 – 4.51 (m, 1H, H_l), 3.79 – 3.70 (m, 2H, H_p), 2.47 – 2.43 (m, 1H, H_g), 2.42 (s, 3H, H_u), 2.38 – 2.32 (m, 1H, $H_{m'}$), 2.27 – 2.21 (m, 1H, $H_{k'}$), 1.98 – 1.91 (m, 1H, $H_{m''}$), 1.70 – 1.58 (m, 2H, $H_{k'',j'}$), 1.50 – 1.42 (m, 2H, $H_{i',j''}$), 1.13 (dddt, *J* = 12.3, 10.1, 8.9, 3.5 Hz, 1H, H_h), 0.82 (dtd, *J* = 13.7, 12.4, 2.8 Hz, 1H, $H_{i''}$). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.6, 144.7, 139.1, 135.5, 133.9, 129.8, 128.5, 128.2, 124.7, 120.3, 118.6, 110.3, 83.3, 60.3, 45.6, 39.7, 36.4, 28.5, 27.8, 21.7, 20.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{26}O_3SNa$] ([M+Na$^+$]) 405.1495, found 405.1495. **Note**: The relative stereochemistry of the ring-junction was assigned as *cis* from previous reports featuring a crystal structure and by observation of strong NOE between the protons. The relative stereochemistry between C_g and C_h

was assigned as *trans*, due to the absence of NOE enhancement and from analogous literature precedent.[30]

(*E*)-3-(1,1-difluoro-5-tosylpent-3-en-1-yl)-2,3-dihydrobenzofuran (4ae).

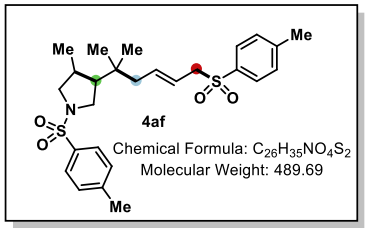


The title compound was obtained from bromide **1ae** (59.8 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1).

Amount: 49.2 mg, 0.130 mmol, 65%. **Physical aspect**: yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.35. **^{1}H{^{19}F} NMR** (500 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.89 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 5.56 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.49 (dt, *J* = 15.5, 6.7 Hz, 1H), 4.56 – 4.49 (m, 2H), 3.77 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.74 (d, *J* = 7.0 Hz, 2H), 2.56 (ddd, *J* = 15.0, 6.6, 1.0 Hz, 1H), 2.45 (dd, *J* = 15.3, 6.9 Hz, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.9, 144.9, 135.4, 130.7 (t, *J* = 5.0 Hz), 130.1, 129.9, 128.5, 126.0, 123.2 (t, *J* = 245.3 Hz), 123.0 (dd, *J* = 5.9, 2.1 Hz), 122.6, 121.0, 110.2, 71.1 (dd, *J* = 7.2, 3.8 Hz), 60.0, 48.8 (t, *J* = 26.6 Hz), 36.9 (t, *J* = 25.5 Hz), 21.7. **^{13}C{^{1}H, ^{19}F} NMR** (126 MHz, $CDCl_3$) δ 160.9, 144.9, 135.4, 130.7, 130.1, 129.9, 128.5, 126.0, 123.2, 123.0, 122.6, 121.0, 110.2, 71.1, 60.0, 48.8, 36.9, 21.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -100.18 (ddt, *J* = 248.5, 22.2, 12.7 Hz), -101.22 (ddt, *J* = 248.5, 21.1, 11.9 Hz). **^{19}F{^{1}H} NMR** (470 MHz, $CDCl_3$) δ -100.18 (d, *J* = 248.5 Hz), -101.22 (d, *J* = 248.4 Hz). **HRMS (Orbitrap)** *m/z* calc. for [$C_{20}H_{20}O_3SF_2Na$] ([M+Na$^+$]) 401.0993, found 401.0992.

[30] M. Koy, P. Bellotti, F. Katzenburg, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.*, 2020, **59**, 2375-2379.

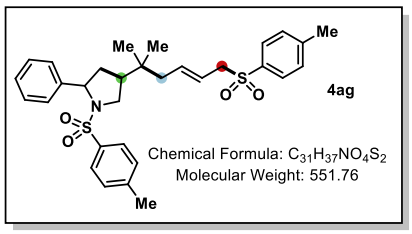
(*E*)-3-methyl-4-(2-methyl-6-tosylhex-4-en-2-yl)-1-tosylpyrrolidine (4af).



The title compound was obtained from bromide **1af** (86.5 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 455 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/1 → 20/7), affording a partially separable mixture of diastereoisomers.

Amount: 84.2 mg, 0.172 mmol, 86%, 71:29 dr. **Physical aspect**: colorless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 3/1): 0.33. **^{1}H NMR** (599 MHz, $CDCl_3$, *major diastereoisomer*) δ 7.71 – 7.68 (m, 4H, *), 7.34 – 7.29 (m, 4H, *), 5.54 – 5.47 (m, 1H, *), 5.36 – 5.28 (m, 1H, *), 3.70 (d, *J* = 7.3 Hz, 2H), 3.26 (dd, *J* = 9.4, 7.8 Hz, 1H), 3.23 – 3.19 (m, 1H, *), 3.11 – 3.07 (m, 1H, *), 3.05 (d, *J* = 9.7 Hz, 1H), 2.42 (s, 3H, *), 2.41 (s, 3H, *), 2.17 (dtd, *J* = 12.5, 7.0, 5.3 Hz, 1H), 1.93 – 1.84 (m, 2H), 1.70 – 1.64 (m, 1H), 0.78 (s, 3H), 0.74 (s, 3H), 0.72 (d, *J* = 7.1 Hz, 3H). **^{1}H NMR** (599 MHz, $CDCl_3$, *minor diastereoisomer*) δ 7.71 – 7.69 (m, 2H, *), 7.67 – 7.65 (m, 2H), 7.34 – 7.29 (m, 4H, *), 5.54 – 5.47 (m, 1H, *), 5.36 – 5.28 (m, 1H, *), 3.73 (d, *J* = 7.4 Hz, 2H), 3.24 – 3.20 (m, 1H, *), 3.12 – 3.08 (m, 1H, *), 2.90 (dd, *J* = 10.0, 7.1 Hz, 1H), 2.65 (dd, *J* = 9.4, 6.5 Hz, 1H), 2.42 (s, 6H, *), 2.01 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.83 (d, *J* = 7.5 Hz, 2H), 1.46 (dt, *J* = 8.7, 6.8 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.68 (s, 3H), 0.64 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, *major diastereoisomer*) δ 144.8, 143.4, 137.35, 134.3, 129.9, 129.71, 128.35, 127.4, 119.2, 60.1, 56.8, 50.5, 45.9, 45.6, 34.7, 34.6, 26.1, 24.8, 21.7, 21.61, 16.0. **^{13}C NMR** (151 MHz, $CDCl_3$, *minor diastereoisomer*) δ 144.7, 143.6, 137.41, 135.8, 129.66, 128.37, 128.0, 119.1, 60.2, 55.9, 54.2, 49.5, 43.9, 35.8, 33.8, 24.6, 24.0, 21.63, 20.8. **HRMS (Orbitrap)** *m/z* calc. for $[C_{36}H_{35}O_4S_2NNa]$ ($[M+Na^+]$) 512.1900, found 512.1894. **Note**: Overlapping signals between the two diastereoisomers are denoted with "*". The tentative number of protons belonging to each species is reported in brackets. The major isomer is tentatively assigned as ***cis***, due to the ^3J coupling constant between ring protons and the NOE spectrum. *Major isomer*: One aromatic signal missing in ^{13}C spectrum due to overlap. *Minor isomer*: Two aromatic signals and one aliphatic missing in ^{13}C spectrum due to overlap with the major isomer.

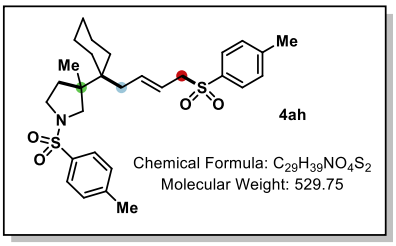
(*E*)-4-(2-methyl-6-tosylhex-4-en-2-yl)-2-phenyl-1-tosylpyrrolidine (4ag).



The title compound was obtained from bromide **1ag** (101.4 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/1), affording an inseparable mixture of diastereoisomers.

Amount: 90.1 mg, 0.163 mmol, 82%, 68:32 dr. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 3/1): 0.38. **^{1}H NMR** (599 MHz, $CDCl_3$, *major diastereoisomer*) δ 7.74 – 7.70 (m, 2H, *), 7.69 – 7.66 (m, 2H, *), 7.57 – 7.54 (m, 2H, *), 7.35 – 7.32 (m, 2H, *), 7.32 – 7.20 (m, 5H, *), 5.50 (dtt, *J* = 15.2, 7.7, 1.1 Hz, 1H), 5.34 (dtt, *J* = 15.2, 7.3, 1.2 Hz, 1H), 4.58 – 4.53 (m, 1H), 3.72 (d, *J* = 7.3 Hz, 2H), 3.70 – 3.64 (m, 1H, *), 3.30 – 3.25 (m, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 2.21 – 2.12 (m, 1H), 1.88 – 1.81 (m, 2H), 1.63 – 1.57 (m, 2H), 0.73 (s, 3H), 0.70 (s, 3H). **^{1}H NMR** (599 MHz, $CDCl_3$, *minor diastereoisomer*) δ 7.74 – 7.70 (m, 2H, *), 7.69 – 7.66 (m, 2H, *), 7.57 – 7.54 (m, 2H, *), 7.35 – 7.32 (m, 2H, *), 7.32 – 7.20 (m, 5H, *), 5.49 – 5.42 (m, 1H, *), 5.28 (dddd, *J* = 15.1, 7.5, 6.7, 1.2 Hz, 1H), 4.90 (dd, *J* = 7.6, 2.1 Hz, 1H), 3.70 – 3.64 (m, 2H, *), 3.53 (dd, *J* = 9.5, 7.7 Hz, 1H), 3.04 (dd, *J* = 10.8, 9.5 Hz, 1H), 2.42 (s, 3H, *), 2.42 (s, 3H, *), 2.07 (ddt, *J* = 12.0, 10.8, 7.3 Hz, 1H), 1.81 – 1.74 (m, 2H), 1.69 – 1.62 (m, 2H, *), 0.62 (s, 3H), 0.59 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, *major diastereoisomer*) δ 144.8, 143.3, 142.7, 137.2, 135.8, 135.5, 129.84, 129.6, 128.43, 128.35, 127.51, 126.5, 126.1, 119.2, 64.5, 60.11, 50.6, 47.3, 44.41, 38.8, 34.12, 24.0, 24.0, 21.68, 21.58. **^{13}C NMR** (151 MHz, $CDCl_3$, *minor diastereoisomer*) δ 144.7, 143.5, 143.0, 137.1, 135.7, 134.96, 129.80, 129.7, 128.38, 128.34, 127.53, 127.3, 127.1, 63.0, 60.05, 49.5, 45.6, 44.40, 35.5, 34.13, 23.9, 21.66, 21.59. **HRMS (Orbitrap)** *m/z* calc. for [$C_{31}H_{37}O_4S_2NNa$] ([M+Na$^+$]) 574.2056, found 574.2055. **Note**: Overlapping signals between the two diastereoisomers are denoted with "*". The tentative number of protons belonging to each species is reported in brackets. NOE 1D spectrum did **not** allow to unequivocally assign the relative ring stereochemistry. *Minor isomer*: One aromatic signal and one aliphatic missing in ^{13}C spectrum due to overlap with the major isomer.

(*E*)-3-methyl-1-tosyl-3-(1-(4-tosylbut-2-en-1-yl)cyclohexyl)pyrrolidine (4ah).

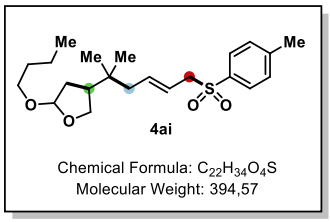


The title compound was obtained from bromide **1ah** (96.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/1).

Amount: 36.3 mg, 0.069 mmol, 35%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 3/1): 0.37. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 2H), 7.70 – 7.67 (m, 2H), 7.35 – 7.29 (m, 4H), 5.55 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.36 (dtt, *J* = 15.2, 7.4, 1.4 Hz, 1H), 3.72 (d, *J* = 7.3 Hz, 2H), 3.24 (td, *J* = 9.2, 2.0 Hz, 1H), 3.16 (d, *J* = 9.8 Hz, 1H), 3.07 (td, *J* = 9.8, 6.8 Hz, 1H), 2.75 (d, *J* = 9.8 Hz, 1H), 2.43 (s, 3H), 2.43 (s, 3H), 2.27 (dd, *J* = 15.5, 7.2 Hz, 1H), 2.12 (dd, *J* = 15.4, 7.6 Hz, 1H), 1.76 (dt, *J* = 12.6, 9.7 Hz, 1H), 1.65 – 1.58 (m, 1H), 1.52 – 1.44 (m, 2H), 1.44 – 1.35 (m, 2H), 1.29 (tt, *J* = 13.2, 3.4 Hz, 2H), 1.25 – 1.23 (m, 1H), 1.20 (ddd, *J* = 12.4, 7.0, 2.0 Hz, 1H), 1.06 (td, *J* = 12.1, 10.9, 3.9 Hz, 1H), 1.03 – 0.94 (m, 1H), 0.69 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.8, 143.4, 138.9, 136.1, 133.9,

129.9, 129.7, 128.4, 127.6, 117.8, 60.3, 55.8, 49.2, 46.9, 40.0, 35.1, 33.1, 30.7 – 30.5 (br), 29.8, 29.2 – 29.0 (br), 25.7, 21.77, 21.75, 21.65, 20.9. **Note**. Due to the presence of the cyclohexyl ring, two ^{13}C NMR signals appear broadened. **HRMS (Orbitrap)** *m/z* calc. for [$C_{29}H_{39}O_4S_2NNa$] ([M+Na$^+$]) 552.2213, found 552.2210.

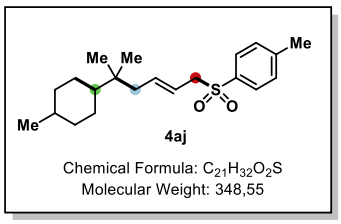
2-butoxy-4-((*E*)-2-methyl-6-tosylhex-4-en-2-yl)tetrahydrofuran (4ai).



The title compound was obtained from bromide **1ai** (63.6 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1), affording an inseparable mixture of diastereoisomers.

Amount: 55.7 mg, 0.141 mmol, 71%, 67:33 dr. **Physical aspect**: pale yellow viscous oil. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.50. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, $2H_M + 2H_m$), 7.34 – 7.30 (m, $2H_M + 2H_m$), 5.59 – 5.52 (m, $1H_M + 1H_m$), 5.39 – 5.32 (m, $1H_M + 1H_m$), 5.04 (dd, *J* = 5.3, 2.9 Hz, $1H_M$), 5.03 (d, *J* = 5.2 Hz, $1H_m$), 3.82 (t, *J* = 8.6 Hz, $1H_m$), 3.77 – 3.73 (m, $2H_M + 2H_m$), 3.68 (t, *J* = 7.8 Hz, $1H_M$), 3.65 – 3.60 (m, $1H_M + 1H_m$), 3.60 – 3.57 (m, $1H_m$), 3.51 (dd, *J* = 10.2, 8.4 Hz, $1H_M$), 3.36 – 3.30 (m, $1H_M + 1H_m$), 2.42 (s, $3H_M + 3H_m$), 2.24 (dq, *J* = 9.9, 7.9 Hz, $1H_m$), 1.99 – 1.91 (m), 1.91 – 1.83 (m), 1.75 (dd, *J* = 12.7, 8.0 Hz, $1H_m$), 1.62 (ddd, *J* = 12.6, 10.1, 5.1 Hz, $1H_m$), 1.55 – 1.48 (m), 1.38 – 1.30 (m), 0.89 (tt, *J* = 7.4, 1.0 Hz, $3H_M + 3H_m$), 0.75 (s, $3H_M$), 0.74 (s, $3H_M$), 0.71 – 0.69 (m, $6H_m$). **^{13}C NMR** (151 MHz, $CDCl_3$, *major isomer*) δ 144.67, 137.9, 135.7, 129.8, 128.4, 118.8, 104.4, 67.3, 66.8, 60.24, 47.6, 45.0, 34.3, 34.0, 31.94, 24.5, 24.4, 21.7, 19.47, 13.96. **^{13}C NMR** (151 MHz, $CDCl_3$, *minor isomer*) δ 144.65, 137.8, 128.5, 118.9, 104.3, 67.7, 67.0, 60.23, 45.9, 44.6, 34.7, 33.9, 31.89, 24.03, 23.96, 19.45, 13.97. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{34}O_4SNa$] ([M+Na$^+$]) 417.2070, found 417.2062. **Note**. In related compounds, epimerization of the acetal carbon in solution ($CDCl_3$) has been observed, causing fast loss of diasteroisomeric excess. Due to extensive signal overlap, signals belonging to different diastereoisomers were quoted together. Overlapping signals between the two diastereoisomers are denoted with "*". The tentative number of protons belonging to each species is reported in brackets, whenever possible. Two aromatic and one aliphatic ^{13}C NMR signals of the minor isomer are missing due to overlap (visible by 2D NMR).

(*E*)-1-methyl-4-((5-methyl-5-(4-methylcyclohexyl)hex-2-en-1-yl)sulfonyl)benzene (4aj).

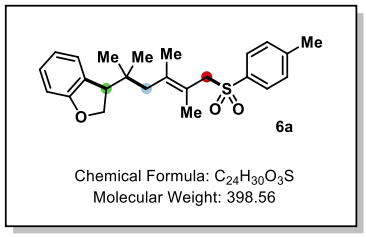


The title compound was obtained from bromide **1aj** (52.6 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 11/1), affording an inseparable mixture of a major isomer and other unknown isomers.

Amount: 36.5 mg, 0.105 mmol, 53%, 86:24 major isomer:other isomers. **Physical aspect**: colourless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 10/1): 0.45. **^{1}H NMR** (599 MHz, $CDCl_3$, *major isomer*) δ 7.75 – 7.71 (m, 2H), 7.34 – 7.31 (m, 2H), 5.55 (dddt, *J* = 15.2, 8.7, 7.6, 1.2 Hz, 1H), 5.34 (dtt, *J* = 15.1, 7.4, 1.3 Hz, 1H), 3.76 (d, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.91 (d, *J* = 7.5 Hz, 2H), 1.72 – 1.67 (m, 2H), 1.64 – 1.59 (m, 2H), 1.26 – 1.19 (m, 1H), 0.99 – 0.86 (m, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.83 – 0.78 (m, 2H), 0.69 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$, *major isomer*) δ 144.6, 138.9, 135.9, 129.8, 128.5, 118.0, 60.4, 45.8, 43.6, 35.9, 35.7, 33.0, 27.0, 24.7, 22.8, 21.7. **HRMS (Orbitrap)** *m/z* calc. for [$C_{21}H_{32}O_2SNa$] ([M+Na$^+$]) 371.2015, found 371.2013. **Note.** Minor isomer signals cannot be assigned due to extensive overlap in ^{1}H and ^{13}C NMR.

Substituted dienes as coupling partners

(*E*)-3-(2,4,5-trimethyl-6-tosylhex-4-en-2-yl)-2,3-dihydrobenzofuran (6a).

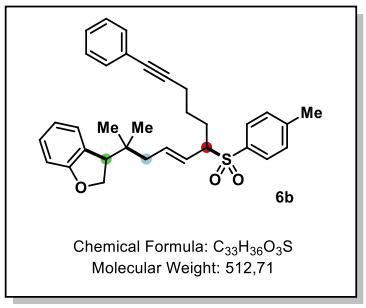


The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5a** (33.9 µl, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 8/1 → 7/1).

The configuration of the double bond was determined to be *E* due to absence of NOE signal between the appended methyls and based on literature precedence.

Amount: 29.5 mg, 0.074 mmol, 37%. **Physical aspect**: white waxy solid. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 7/1): 0.50. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.34 – 7.30 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.14 (td, *J* = 7.8, 1.4 Hz, 1H), 6.84 (td, *J* = 7.4, 1.1 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.56 (dd, *J* = 9.4, 3.7 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.89 (s, 2H), 3.14 (dd, *J* = 9.0, 3.7 Hz, 1H), 2.43 (s, 3H), 2.19 (d, *J* = 13.3 Hz, 1H), 1.97 (d, *J* = 13.3 Hz, 1H), 1.71 (q, *J* = 1.5 Hz, 3H), 1.49 (q, *J* = 1.6 Hz, 3H), 0.91 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 144.7, 137.2, 137.1, 129.9, 128.6, 128.5, 128.0, 126.7, 120.6, 120.0, 109.7, 73.5, 62.5, 53.5, 43.3, 39.5, 25.4, 24.4, 22.3, 21.7, 20.8. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{30}O_3SNa$] ([M+Na$^+$]) 421.1808, found 421.1801.

3-((*E*)-2-methyl-11-phenyl-6-tosylundec-4-en-10-yn-2-yl)-2,3-dihydrobenzofuran (6b).

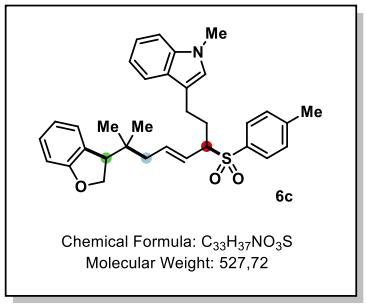


The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5b** (58.9 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 7/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 47.0 mg, 0.092 mmol, 46%, 50:50 dr. **Physical aspect**: faint yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 8/1): 0.33. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.37 – 7.23 (m, 7H), 7.18 – 7.10 (m, 2H), 6.87 – 6.80 (m, 1H), 6.77 (dd, *J* = 8.5, 1.1 Hz, 1H), 5.58 (dtd, *J* = 15.2, 7.5, 4.8 Hz, 1H), 5.27 (dd, *J* = 15.2, 9.4 Hz, 1H), 4.44 (ddd, *J* = 9.4, 4.2, 2.5 Hz, 1H), 4.35 (td, *J* = 9.1, 1.5 Hz, 1H), 3.68 – 3.55 (m, 1H), 2.99 (ddd, *J* = 11.2, 8.8, 4.1 Hz, 1H), 2.47 – 2.40 (m, 2H), 2.39 (s, 3H, *single diastereoisomer*), 2.35 (s, 3H, *single diastereoisomer*), 2.31 – 2.15 (m, 1H), 2.07 – 1.92 (m, 2H), 1.89 – 1.48 (m, 3H), 0.81 (s, 6H, *single diastereoisomer*), 0.79 (s, 3H, *single diastereoisomer*), 0.77 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 160.9, 144.62, 144.57, 137.0, 134.9, 134.8, 131.6, 129.69, 129.66, 129.1, 129.0, 128.54, 128.52, 128.3, 127.9, 127.8, 126.42, 126.37, 124.8, 124.7, 123.7, 120.00, 119.97, 109.6, 88.9, 81.6, 73.1, 68.84, 68.80, 51.0, 42.89, 42.87, 37.0, 26.8,

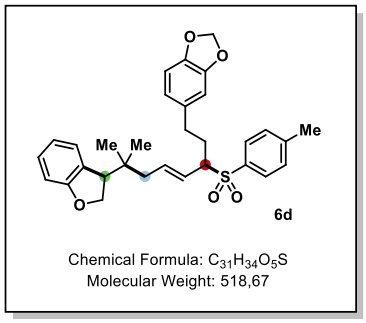
25.81, 25.78, 24.4, 24.3, 24.2, 23.9, 21.70, 21.65, 19.1. **HRMS (Orbitrap)** *m/z* calc. for [$C_{33}H_{36}O_3SNa$] ([M+Na$^+$]) 535.2277, found 535.2276.

3-((*E*)-7-(2,3-dihydrobenzofuran-3-yl)-7-methyl-3-tosyloct-4-en-1-yl)-1-methyl-1*H*-indole (6c).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5c** (63.4 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1) and obtained as an inseparable mixture of diastereoisomers. **Amount:** 46.6 mg, 0.088 mmol, 44%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 7/1): 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.64 (m, 2H), 7.43 (dq, *J* = 8.0, 1.1 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.21 – 7.13 (m, 2H), 7.06 (ddt, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.86 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.82 – 6.77 (m, 2H), 5.57 (dtd, *J* = 15.1, 7.5, 3.4 Hz, 1H), 5.39 – 5.30 (m, 1H), 4.47 (ddd, *J* = 9.7, 5.7, 4.1 Hz, 1H), 4.39 (t, *J* = 9.2 Hz, 1H), 3.74 (s, 3H), 3.63 (dddd, *J* = 10.8, 8.9, 5.6, 3.1 Hz, 1H), 3.03 (ddd, *J* = 16.9, 9.0, 4.1 Hz, 1H), 2.94 – 2.85 (m, 1H), 2.74 – 2.64 (m, 1H), 2.57 – 2.47 (m, 1H), 2.41 (s, 3H, *single diastereoisomer*), 2.38 (s, 3H, *single diastereoisomer*), 2.13 – 1.96 (m, 3H), 0.85 (s, 3H, *single diastereoisomer*), 0.84 (s, 3H, *single diastereoisomer*), 0.82 (s, 3H, *single diastereoisomer*), 0.81 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.89, 160.88, 144.51, 144.46, 137.1, 137.03, 137.00, 134.93, 134.87, 129.64, 129.61, 129.1, 128.9, 128.6, 128.5, 127.90, 127.89, 127.74, 127.73, 126.43, 126.38, 126.32, 125.0, 124.9, 121.7, 120.01, 119.98, 118.83, 118.82, 113.0, 109.6, 109.3, 73.10, 73.09, 68.7, 68.6, 51.04, 50.97, 43.0, 42.9, 37.04, 37.03, 32.7, 28.0, 24.4, 24.3, 24.2, 24.0, 22.11, 22.05, 21.69, 21.65. **HRMS (Orbitrap)** *m/z* calc. for [$C_{33}H_{37}NO_3SNa$] ([M+Na$^+$]) 550.2386, found 550.2384.

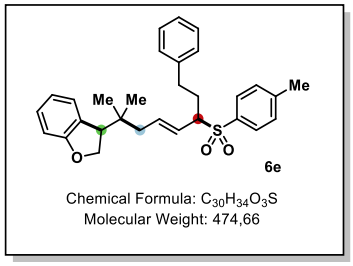
5-((*E*)-7-(2,3-dihydrobenzofuran-3-yl)-7-methyl-3-tosyloct-4-en-1-yl)benzo[*d*][1,3]dioxole (6d).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5d** (60.7 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6.5/1 → 5.5/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 73.0 mg, 0.141 mmol, 71%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 8/1): 0.20. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.1, 5.1 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.19 – 7.12 (m, 2H), 6.84 (tdd, *J* = 7.6, 2.1, 1.1 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.58 (t, *J* = 1.8 Hz, 1H), 6.54 (dt, *J* = 7.9, 1.8, 1.7 Hz, 1H), 5.92 (s, 2H), 5.54 (dtd, *J* = 15.2, 7.5, 3.5 Hz, 1H), 5.32 – 5.23 (m, 1H), 4.46 (dt, *J* = 9.4, 4.7 Hz, 1H), 4.38 (t, *J* = 9.2 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.02 (ddd, *J* = 16.8, 9.0, 4.1 Hz, 1H), 2.67 (ddd, *J* = 12.9, 8.7, 5.1 Hz, 1H), 2.50 – 2.29 (m, 5H), 2.12 – 1.96 (m, 2H), 1.94 – 1.81 (m, 1H), 0.83 (s, 6H, *single diastereoisomer),* 0.81 (s, 3H, *single diastereoisomer*), 0.80 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 160.9, 147.8, 146.1, 144.62, 144.57, 137.17, 137.15, 134.8, 134.7, 133.9, 129.7, 129.6, 129.1, 129.0, 128.6, 128.5, 127.8, 126.40, 126.35, 124.9, 124.8, 121.3, 120.01, 119.98, 109.6, 108.8, 108.3, 101.0, 73.1, 68.34, 68.28, 51.1, 51.0, 42.9, 42.8, 37.0, 32.4, 32.3, 29.2, 24.4, 24.3, 24.2, 24.0, 21.69, 21.65. **HRMS (Orbitrap)** *m/z* calc. for [$C_{31}H_{34}O_5SNa$] ([M+Na$^+$]) 541.2019, found 541.2019.

3-((*E*)-2-methyl-8-phenyl-6-tosyloct-4-en-2-yl)-2,3-dihydrobenzofuran (6e).

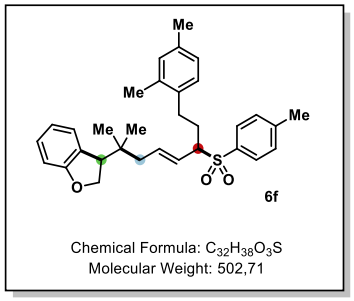


The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5e** (47.5 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 8/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 66.4 mg, 0.140 mmol, 70%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 8/1): 0.30**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.31 – 7.25 (m, 4H), 7.23 – 7.08 (m, 5H), 6.85 (tt, *J* = 7.5, 1.4 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.55 (dtd, *J* = 15.2, 7.5, 3.5 Hz, 1H), 5.35 – 5.25 (m, 1H), 4.47 (ddd, *J* = 9.5, 5.4, 4.1 Hz, 1H), 4.39 (t, *J* = 9.2 Hz, 1H), 3.52 (dddd, *J* = 14.5, 8.9, 5.5, 3.1 Hz, 1H), 3.03 (ddd, *J* = 17.2, 9.0, 4.1 Hz, 1H), 2.77 (dddd, *J* = 16.2, 11.9, 4.6, 2.2 Hz, 1H), 2.57 – 2.43 (m, 2H), 2.41 (s, 3H, *single diastereoisomer*), 2.38 (s, 3H, *single diastereoisomer*),

2.13 – 1.86 (m, 3H), 0.84 (br s, 6H, *single diastereoisomer*), 0.82 (s, 3H, *single diastereoisomer*), 0.81 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.88, 160.87, 144.60, 144.55, 140.2, 137.2, 137.1, 134.84, 134.77, 129.7, 129.6, 129.1, 129.0, 128.64, 128.56, 128.5, 128.46, 128.45, 127.9, 126.41, 126.36, 124.9, 124.8, 120.01, 119.97, 109.6, 73.08, 73.07, 68.51, 68.46, 51.10, 51.05, 42.9, 42.8, 37.02, 37.01, 32.64, 32.60, 28.87, 28.86, 24.4, 24.3, 24.2, 24.0, 21.7, 21.6. **HRMS (Orbitrap)** *m/z* calc. for $[C_{30}H_{34}O_3SNa]$ ($[M+Na^+]$) 497.2121, found 497.2118.

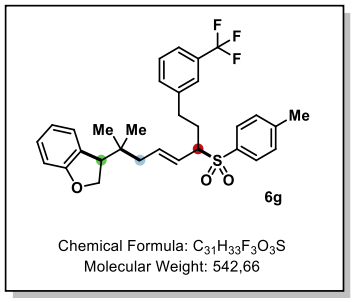
3-((*E*)-8-(2,4-dimethylphenyl)-2-methyl-6-tosyloct-4-en-2-yl)-2,3-dihydrobenzofuran (6f).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5f** (55.9 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 13/1 →11/1 → 9/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 66.7 mg, 0.133 mmol, 67%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 13/1): 0.35**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.31 – 7.27 (m, 2H), 7.20 – 7.13 (m, 2H), 6.98 – 6.91 (m, 3H), 6.85 (tdd, *J* = 7.5, 2.2, 1.1 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.61 (dtd, *J* = 15.2, 7.5, 5.0 Hz, 1H), 5.33 (dddt, *J* = 15.2, 9.3, 2.1, 1.4 Hz, 1H), 4.48 (dt, *J* = 9.1, 4.5 Hz, 1H), 4.39 (td, *J* = 9.2, 1.1 Hz, 1H), 3.57 (dddd, *J* = 10.6, 9.2, 6.1, 3.1 Hz, 1H), 3.04 (ddd, *J* = 15.6, 9.0, 4.1 Hz, 1H), 2.74 – 2.63 (m, 1H), 2.53 – 2.44 (m, 1H), 2.42 (s, 3H, *single diastereoisomer*), 2.39 (s, 3H, *single diastereoisomer*), 2.34 (ddd, *J* = 13.7, 6.9, 3.4 Hz, 1H), 2.29 (s, 3H), 2.20 (s, 3H, *single diastereoisomer*), 2.20 (s, 3H, *single diastereoisomer*), 2.11 – 2.00 (m, 2H), 1.93 – 1.79 (m, 1H), 0.88 – 0.85 (m, 6H, *single diastereoisomer*), 0.83 (s, 3H, *single diastereoisomer*), 0.82 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 144.6, 144.5, 137.14, 137.12, 136.0, 135.81, 135.80, 135.5, 134.9, 134.8, 131.3, 129.7, 129.6, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 127.9, 126.8, 126.41, 126.36, 125.0, 124.9, 120.01, 119.98, 109.6, 73.08, 73.07, 68.93, 68.87, 51.1, 51.0, 43.0, 42.9, 37.03, 29.95, 29.9, 27.9, 24.4, 24.3, 24.2, 24.0, 21.69, 21.65, 21.0, 19.3. **HRMS (Orbitrap)** *m/z* calc. for $[C_{32}H_{38}O_3SNa]$ ($[M+Na^+]$) 525.2434, found 525.2432.

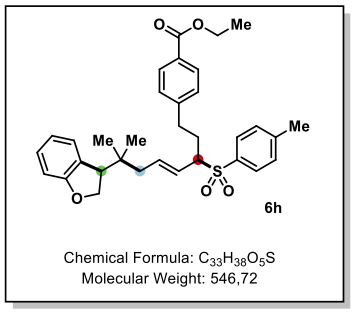
3-((*E*)-2-methyl-6-tosyl-8-(3-(trifluoromethyl)phenyl)oct-4-en-2-yl)-2,3-dihydrobenzofuran (6g).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5g** (67.9 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 7/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 69.3 mg, 0.128 mmol, 64%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 8/1): 0.33. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.66 (tt, *J* = 8.6, 1.9 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.26 (m, 2H), 7.18 – 7.13 (m, 2H), 6.84 (tdd, *J* = 7.4, 2.8, 1.0 Hz, 1H), 6.80 – 6.77 (m, 1H), 5.57 – 5.49 (m, 1H), 5.33 – 5.26 (m, 1H), 4.45 (td, *J* = 9.1, 4.1 Hz, 1H), 4.38 (td, *J* = 9.2, 1.3 Hz, 1H), 3.48 (dtd, *J* = 10.7, 9.3, 3.4 Hz, 1H), 3.03 (dd, *J* = 9.1, 4.0 Hz, 1H, *single diastereoisomer*), 2.98 (dd, *J* = 9.0, 4.1 Hz, 1H, *single diastereoisomer*), 2.82 (ddd, *J* = 14.2, 9.5, 4.9 Hz, 1H), 2.60 (dt, *J* = 14.0, 8.4 Hz, 1H), 2.47 – 2.42 (m, 1H), 2.41 (s, 3H, *single diastereoisomer*), 2.37 (s, 3H, *single diastereoisomer*), 2.07 (ddd, *J* = 13.9, 7.4, 1.4 Hz, 1H, *single diastereoisomer*), 2.05 – 1.93 (m, 3H), 0.83 (s, 3H, *single diastereoisomer*), 0.83 (s, 3H, *single diastereoisomer*), 0.81 (s, 3H, *single diastereoisomer*), 0.80 (s, 3H, *single diastereoisomer*). **^{13}C{^{1}H, ^{19}F} NMR** (151 MHz, $CDCl_3$) δ 160.90, 160.89, 144.81, 144.75, 141.21, 141.20, 137.50, 137.47, 134.72, 134.65, 131.86, 131.85, 130.9, 129.8, 129.7, 129.19, 129.17, 129.0, 128.9, 128.60, 128.57, 127.8, 126.4, 126.3, 125.2, 124.7, 124.6, 124.2, 123.39, 123.38, 120.04, 120.00, 109.7, 73.07, 73.05, 68.5, 68.4, 51.14, 51.09, 42.9, 42.8, 37.00, 36.98, 32.52, 32.49, 28.77, 28.76, 24.4, 24.3, 24.2, 24.0, 21.7, 21.6. **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 160.90, 160.89, 144.81, 144.75, 141.21, 141.20, 137.50, 137.47, 134.72, 134.65, 131.86, 131.85, 130.9 (q, *J* = 32.0 Hz), 129.8, 129.7, 129.19, 129.17, 129.0, 128.9, 128.60, 128.57, 127.8, 126.4, 126.3, 125.2 (q, *J* = 3.7 Hz), 124.7, 124.6, 124.2 (q, *J* = 272.0 Hz), 123.5 – 123.3 (m), 123.38, 120.04, 120.00, 109.7, 73.07, 73.05, 68.5, 68.4, 51.14, 51.09, 42.9, 42.8, 37.00, 36.98, 32.52, 32.49, 28.77, 28.76, 24.4, 24.3, 24.2, 24.0, 21.7, 21.6. **^{19}F{^{1}H} NMR** (564 MHz, $CDCl_3$) δ -62.59. **HRMS (Orbitrap)** *m/z* calc. for [$C_{31}H_{33}O_3SF_3Na$] ([M+Na$^+$]) 565.1995, found 565.1993.

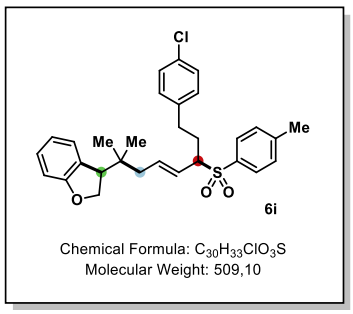
ethyl 4-((*E*)-7-(2,3-dihydrobenzofuran-3-yl)-7-methyl-3-tosyloct-4-en-1-yl)benzoate (6h).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5h** (69.1 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 62.6 mg, 0.115 mmol, 58%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 8/1): 0.17. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.68 – 7.61 (m, 2H), 7.31 – 7.23 (m, 2H), 7.21 – 7.10 (m, 4H), 6.83 (tt, *J* = 7.5, 1.3 Hz, 1H), 6.80 – 6.74 (m, 1H), 5.51 (dtd, *J* = 15.1, 7.5, 2.0 Hz, 1H), 5.34 – 5.22 (m, 1H), 4.45 (dt, *J* = 9.4, 4.0 Hz, 1H), 4.41 – 4.32 (m, 3H), 3.47 (ddt, *J* = 10.7, 9.2, 3.5 Hz, 1H), 2.99 (ddd, *J* = 13.3, 8.9, 4.2 Hz, 1H), 2.81 (ddd, *J* = 14.1, 9.2, 5.0 Hz, 1H), 2.58 (dt, *J* = 13.8, 8.3 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.40 (s, 3H, *single diastereoisomer*), 2.36 (s, 3H, *single diastereoisomer*), 2.11 – 1.87 (m, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.84 – 0.81 (m, 6H, *single diastereoisomer*), 0.80 (s, 3H, *single diastereoisomer*), 0.78 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (76 MHz, $CDCl_3$) δ 166.6, 160.9, 145.5, 144.72, 144.67, 137.36, 137.35, 134.7, 134.6, 129.9, 129.71, 129.68, 129.0, 128.9, 128.8, 128.57, 128.55, 128.45, 127.8, 126.4, 126.3, 124.7, 124.6, 120.02, 119.98, 109.7, 73.1, 68.40, 68.35, 61.0, 51.11, 51.06, 42.8, 42.7, 37.00, 36.98, 32.64, 32.61, 28.5, 24.4, 24.3, 24.2, 24.0, 21.7, 21.6, 14.4. **HRMS (Orbitrap)** *m/z* calc. for [$C_{33}H_{38}O_5SNa$] ([M+Na$^+$]) 569.2332, found 569.2333.

3-((*E*)-8-(4-chlorophenyl)-2-methyl-6-tosyloct-4-en-2-yl)-2,3-dihydrobenzofuran (6i).

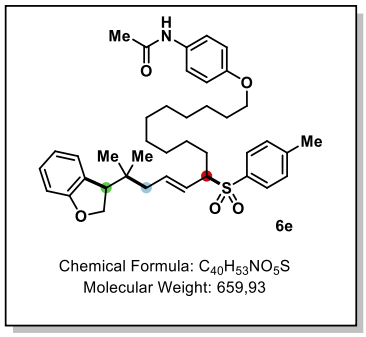


The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5i** (57.8 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 8/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 64.3 mg, 0.126 mmol, 63%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 8/1): 0.35. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.30 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 7.15 (dddd, *J* = 9.1, 7.7, 2.7, 1.2 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.84 (tdd, *J* = 7.5, 3.5, 1.1 Hz, 1H), 6.80 – 6.77 (m, 1H), 5.54 – 5.46 (m, 1H), 5.31 – 5.24 (m, 1H), 4.46 (dd, *J* = 7.3, 4.2 Hz, 1H, *single diastereoisomer*), 4.44 (tt, *J* = 7.2, 7.2, 4.1, 4.1 Hz, 1H, *single diastereoisomer*), 4.37 (td, *J* = 9.2, 1.3 Hz, 1H), 3.51 – 3.44 (m, 1H), 3.02 (dd, *J* = 9.1, 4.0 Hz, 1H, *single diastereoisomer*), 2.98 (dd, *J* = 9.0, 4.1 Hz, 1H, *single diastereoisomer*), 2.76 – 2.69 (m, 1H), 2.50 (dt, *J* = 14.0, 8.4 Hz,

1H), 2.44 – 2.38 (m, 1H + 3H of *single diastereoisomer*), 2.37 (s, 3H, *single diastereoisomer*), 2.06 (ddd, *J* = 14.0, 7.3, 1.1 Hz, 1H, *single diastereoisomer*), 2.03 – 1.96 (m, 1H + *1H of single diastereoisomer*), 1.96 – 1.87 (m, 1H), 0.82 (s, 3H, *single diastereoisomer*), 0.82 (s, 3H, *single diastereoisomer*), 0.80 (s, 3H, *single diastereoisomer*), 0.79 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.90, 160.88, 144.71, 144.66, 138.7, 137.3, 137.2, 134.8, 134.7, 132.20, 132.19, 129.82, 129.81, 129.72, 129.69, 129.1, 1129.0, 128.78, 128.77, 128.60, 128.58, 127.82, 127.81, 126.4, 126.3, 124.8, 124.7, 120.04, 120.00, 109.7, 73.07, 73.06, 68.40, 68.35, 51.2, 51.1, 42.9, 42.8, 37.02, 37.00, 32.02, 31.98, 28.79, 28.77, 24.4, 24.3, 24.2, 24.0, 21.70, 21.65. **HRMS (Orbitrap)** *m/z* calc. for [$C_{30}H_{33}O_3S^{35}ClNa$] ([M+Na$^+$]) 531.1731, found 531.1732.

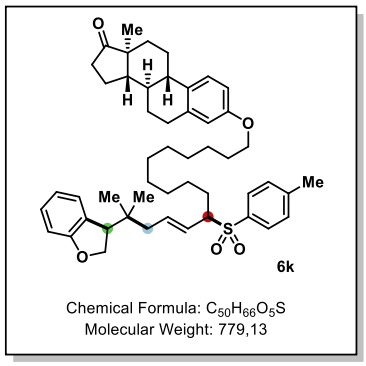
***N*-(4-(((*E*)-15-(2,3-dihydrobenzofuran-3-yl)-15-methyl-11-tosylhexadec-12-en-1-yl)oxy)phenyl)acetamide (6j**).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5e** (103.1 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/1 → 1/1) and obtained as an inseparable mixture of diastereoisomers.

Amount: 79.0 mg, 0.120 mmol, 60%, 50:50 dr. **Physical aspect**: colourless gum. **R_f** (*n*-pentane/EtOAc = 3/2): 0.17. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 3H), 7.41 – 7.35 (m, 2H), 7.27 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.13 (ddt, *J* = 7.7, 5.8, 1.7 Hz, 2H), 6.85 – 6.79 (m, 3H), 6.78 – 6.73 (m, 1H), 5.50 (dtd, *J* = 15.1, 7.5, 5.2 Hz, 1H), 5.26 – 5.14 (m, 1H), 4.42 (dt, *J* = 8.9, 4.3 Hz, 1H), 4.34 (td, *J* = 9.2, 2.4 Hz, 1H), 3.90 (t, *J* = 6.5 Hz, 2H), 3.56 – 3.41 (m, 1H), 2.97 (ddd, *J* = 17.4, 9.0, 4.1 Hz, 1H), 2.40 (s, 3H*, single diastereoisomer*), 2.36 (s, 3H*, single diastereoisomer*), 2.10 (s, 3H), 2.06 – 1.87 (m, 3H), 1.78 – 1.69 (m, 2H), 1.66 – 1.54 (m, 1H), 1.48 – 1.14 (m, 15H), 0.79 (s, 6H*, single diastereoisomer*), 0.76 (s, 3H*, single diastereoisomer*), 0.75 (s, 3H*, single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 160.8, 155.9, 144.6, 144.5, 136.5, 134.9, 134.8, 131.1, 129.64, 129.60, 129.0, 128.9, 128.49, 128.47, 127.8, 126.4, 126.3, 125.1, 125.0, 121.9, 120.0, 119.9, 114.8, 109.6, 73.03, 73.02, 69.4, 69.3, 68.3, 51.0, 50.9, 42.80, 42.78, 36.9, 29.5, 29.44, 29.35, 29.3, 29.1, 27.2, 26.71, 26.69, 26.0, 24.3, 24.2, 24.1, 23.9, 21.7, 21.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{40}H_{53}NO_5SNa$] ([M+Na$^+$]) 682.3537, found 682.3540.

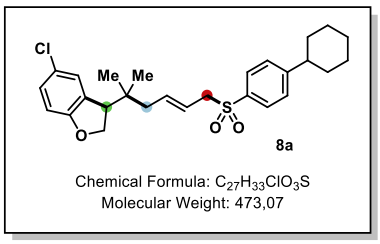
(8*R*,9*S*,13*S*,14*S*)-3-(((*E*)-15-(2,3-dihydrobenzofuran-3-yl)-15-methyl-11-tosylhexadec-12-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (6k).



The title compound was obtained from bromide **1a** (57.9 mg, 0.24 mmol, 1.20 equiv.), diene **5k** (138.8 mg, 0.30 mmol, 1.50 equiv.) and sodium *p*-toluenesulfinate (35.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.00 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP4**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1) and obtained as an inseparable mixture of diastereoisomers. **Amount:** 123.6 mg, 0.159 mmol, 80%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 5/1): 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.29 (dd, *J* = 8.2, 3.2 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.83 (tdd, *J* = 7.5, 2.7, 1.0 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.64 (d, *J* = 2.7 Hz, 1H), 5.51 (dtd, *J* = 15.1, 7.4, 5.4 Hz, 1H), 5.23 (dddd, *J* = 13.7, 8.2, 2.7, 1.3 Hz, 1H), 4.44 (dt, *J* = 8.8, 4.2 Hz, 1H), 4.35 (td, *J* = 9.2, 2.5 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 3.55 – 3.44 (m, 1H), 2.98 (ddd, *J* = 17.6, 9.0, 4.1 Hz, 1H), 2.93 – 2.84 (m, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 (s, 3H, *single diastereoisomer*), 2.37 (s, 3H, *single diastereoisomer*), 2.29 – 2.20 (m, 1H), 1.82 – 1.70 (m, 3H), 0.91 (s, 3H), 0.83 – 0.79 (m, 6H, *single diastereoisomer*), 0.78 (s, 3H, *single diastereoisomer*), 0.76 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 221.0, 160.8, 157.2, 144.5, 144.4, 137.7, 136.4, 135.0, 134.9, 131.9, 129.59, 129.56, 129.0, 128.9, 128.47, 128.45, 127.8, 126.32, 126.30, 125.2, 125.1, 119.93, 119.89, 114.6, 112.2, 109.6, 73.02, 73.00, 69.33, 69.29, 67.9, 50.93, 50.90, 50.4, 48.1, 44.0, 42.81, 42.78, 38.4, 36.9, 35.9, 31.6, 29.7, 29.54, 29.46, 29.38, 29.35, 29.1, 27.15, 27.14, 26.71, 26.68, 26.62, 26.1, 26.0, 24.3, 24.2, 24.1, 23.8, 21.7 – 21.6 (m), 21.61, 13.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{50}H_{66}O_5SNa$] ([M+Na$^+$]) 801.4523, found 801.4528. **Note.** Aliphatic signals belonging to the long chain and part of the steroid structure are not reported due to overlap and dispersion of signals due to presence of diastereoisomers.

Sulfinates as nucleophiles

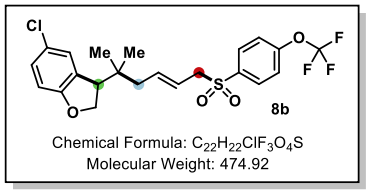
(*E*)-5-chloro-3-(6-((4-cyclohexylphenyl)sulfonyl)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (8a).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7a** (49.3 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 69.0 mg, 0.146 mmol, 73%. **Physical aspect**: yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.32 **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.36 – 7.32 (m, 2H), 7.10 – 7.06 (m, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.57 (dt, *J* = 15.2, 7.2 Hz, 1H), 5.43 (dtt, *J* = 15.3, 7.4, 1.0 Hz, 1H), 4.44 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.37 (t, *J* = 9.2 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 3.00 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.55 (dp, *J* = 11.7, 4.1, 3.4 Hz, 1H), 2.01 (dt, *J* = 14.1, 8.0 Hz, 1H), 1.95 (dt, *J* = 13.9, 7.0 Hz, 1H), 1.90 – 1.79 (m, 4H), 1.79 – 1.72 (m, 1H), 1.44 – 1.32 (m, 4H), 1.31 – 1.20 (m, 2H), 0.80 (s, 3H), 0.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 154.6, 137.2, 135.9, 129.9, 128.5, 128.4, 127.7, 126.3, 124.6, 119.6, 110.5, 73.6, 60.2, 51.0, 44.7, 42.8, 37.0, 34.2 (d, *J* = 2.2 Hz), 26.7, 26.0, 24.3, 23.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{27}H_{33}O_3S^{35}ClNa$] ([M+Na$^+$]) 495.1731, found 495.1728. **Notes and troubleshooting:** Splitting of one aliphatic ^{13}C signal is observed.

(*E*)-5-chloro-3-(2-methyl-6-((4-(trifluoromethoxy)phenyl)sulfonyl)hex-4-en-2-yl)-2,3-dihydrobenzofuran (8b).

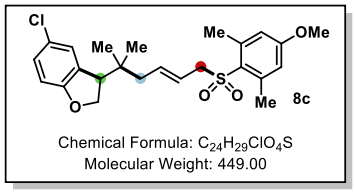


The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7b** (49.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1).

Amount: 65.0 mg, 0.137 mmol, 69%. **Physical aspect**: faint yellow gummy semi-solid. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.33. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.39 – 7.34 (m, 2H), 7.12 – 7.10 (m, 1H), 7.09 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.62 (dtt, *J* = 15.0, 7.5, 1.1 Hz, 1H), 5.43 (dtt, *J* = 15.1, 7.4, 1.3 Hz, 1H), 4.47 (dd, *J* = 9.5, 4.1 Hz, 1H), 4.41 (t, *J* = 9.3 Hz, 1H), 3.80 (dd, *J* = 7.3, 1.1 Hz, 2H), 3.07 (dd, *J* = 9.0, 4.1 Hz, 1H), 2.03 (ddd, *J* = 14.0, 7.7, 1.2 Hz, 1H), 1.97 (ddd, *J* = 14.0, 7.3, 1.3 Hz, 1H), 0.82 (s, 3H), 0.79 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 153.1 (d, *J* = 1.9 Hz), 138.1, 137.0, 130.8, 129.8, 128.5, 126.3, 124.7, 121.1 (q, $^3J_{C\text{-}F}$ = 1.2 Hz), 120.3 (q, $^1J_{C\text{-}F}$ = 260.0 Hz) 118.9, 110.6, 73.7, 60.2, 51.4, 42.6, 37.0, 24.2, 24.0. **^{13}C{^{1}H, ^{19}F} NMR** (151 MHz, $CDCl_3$) δ 159.6, 153.1, 138.1, 136.9, 130.8, 129.8, 128.5, 126.3, 124.7, 121.0, 120.3, 118.9, 110.6,

73.7, 60.2, 51.4, 42.6, 37.0, 24.2, 24.0. **$^{19}F\{^{1}H\}$ NMR** (564 MHz, $CDCl_3$) δ -57.70. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{22}O_4S^{35}ClF_3Na$] ([M+$Na^+$]) 497.0772, found 497.0768.

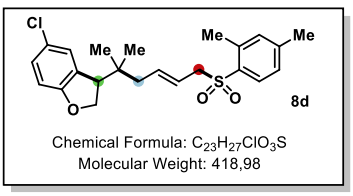
(*E*)-5-chloro-3-(6-((4-methoxy-2,6-dimethylphenyl)sulfonyl)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (8c).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7c** (44.4 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/1).

Amount: 68.6 mg, 0.153 mmol, 77%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.23. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 – 7.05 (m, 2H), 6.68 – 6.64 (m, 1H), 6.60 (s, 2H), 5.59 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.47 (dtt, *J* = 15.2, 7.3, 1.0 Hz, 1H), 4.43 (dd, *J* = 9.5, 4.2 Hz, 1H), 4.36 (t, *J* = 9.3 Hz, 1H), 3.79 (d, *J* = 7.3 Hz, 2H), 3.76 (s, 3H), 2.96 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.64 (s, 6H), 2.04 – 1.93 (m, 2H), 0.81 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.0, 159.6, 142.8, 137.0, 130.0, 128.4, 127.5, 126.3, 124.6, 119.6, 116.4, 110.5, 73.6, 60.4, 55.4, 50.9, 42.9, 36.9, 24.3, 23.8, 23.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{29}O_4S^{35}ClNa$] ([M+$Na^+$]) 471.1367, found 471.1365.

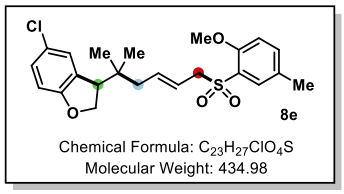
(*E*)-5-chloro-3-(6-((2,4-dimethylphenyl)sulfonyl)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (8d).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7d** (38.4 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1 → 5/1).

Amount: 56.3 mg, 0.134 mmol, 67%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 4/1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.14 – 7.03 (m, 4H), 6.67 (d, *J* = 8.3 Hz, 1H), 5.59 (dt, *J* = 15.3, 7.3 Hz, 1H), 5.39 (dtt, *J* = 15.2, 7.3, 1.2 Hz, 1H), 4.42 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.34 (t, *J* = 9.2 Hz, 1H), 3.83 (d, *J* = 7.3 Hz, 2H), 2.91 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.64 (s, 3H), 2.31 (s, 3H), 2.02 – 1.89 (m, 2H), 0.79 (s, 3H), 0.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 144.7, 137.8, 137.1, 133.8, 133.4, 130.8, 130.0, 128.4, 127.3, 126.3, 124.6, 119.6, 110.5, 73.6, 59.4, 50.8, 42.9, 36.9, 24.3, 23.8, 21.4, 20.5. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{27}O_3S^{35}ClNa$] ([M+$Na^+$]) 441.1262, found 441.1258.

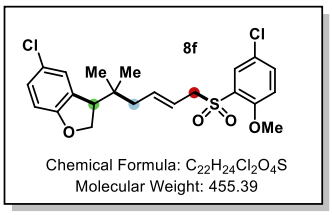
(*E*)-5-chloro-3-(6-((2-methoxy-5-methylphenyl)sulfonyl)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (8e).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7e** (41.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 4/1 → 3/1).

Amount: 39.7 mg, 0.091 mmol, 46%. **Physical aspect**: faint yellow gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 3/1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.1 Hz, 1H), 7.28 (dt, *J* = 8.5, 2.3, 0.7 Hz, 1H), 7.06 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 5.62 (dtd, *J* = 15.3, 7.1, 1.1 Hz, 1H), 5.40 (dtt, *J* = 15.3, 7.4, 1.1 Hz, 1H), 4.36 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.25 (t, *J* = 9.3 Hz, 1H), 4.12 (dd, *J* = 13.8, 7.8 Hz, 1H), 4.04 (dd, *J* = 13.7, 7.1 Hz, 1H), 3.97 (s, 3H), 2.68 (dd, *J* = 9.2, 4.2 Hz, 1H), 2.16 (s, 3H), 2.00 – 1.85 (m, 2H), 0.72 (s, 3H), 0.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6, 155.1, 136.9, 136.1, 131.0, 130.9, 130.0, 128.3, 126.3, 126.0, 124.6, 120.2, 112.3, 110.4, 73.6, 58.2, 56.6, 50.4, 43.0, 36.9, 24.1, 23.6, 20.2. **HRMS (Orbitrap)** *m/z* calc. for $[C_{23}H_{27}O_4S^{35}ClNa]$ ($[M+Na^+]$) 457.1211, found 457.1209.

(*E*)-5-chloro-3-(6-((5-chloro-2-methoxyphenyl)sulfonyl)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (8f).



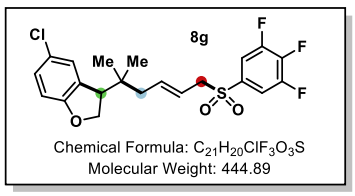
The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7f** (45.7 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/2).

Fast dechlorination of the aryl sulfone moiety occurs during the work-up and purification procedure, therefore the product is contaminated with approximately 10% of byproduct. NMR characterization at 600 MHz spectrometer was performed after 24 hours after the isolation, therefore product/byproduct ratio decreased compared to the record at 400 MHz, which was performed immediately after purification.

Amount: 67.7 mg, 0.149 mmol, 75%. **Physical aspect**: colourless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 2/1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.7 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 5.63 (dt, *J* = 15.1, 7.5 Hz, 1H), 5.39 (dtt, *J* = 15.1, 7.5, 1.3 Hz, 1H), 4.41 (dd, *J* = 9.5, 4.1 Hz, 1H), 4.33 (t, *J* = 9.2 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.99 (s, 3H), 2.84 (dd, *J* = 9.1, 4.1 Hz, 1H), 1.97 (dd, *J* = 13.8, 8.0 Hz, 1H), 1.91 (dd, *J* = 13.8, 7.2 Hz, 1H), 0.73 (s, 3H), 0.69 (s, 3H). **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.7 Hz, 1H), 7.47 (dd, *J* =

8.8, 2.7 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.63 (dt, *J* = 15.3, 7.6 Hz, 1H), 5.39 (dtt, *J* = 15.3, 7.4, 1.4 Hz, 1H), 4.41 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.33 (t, *J* = 9.3 Hz, 1H), 4.11 – 4.01 (m, 2H), 3.99 (s, 3H), 2.85 (dd, *J* = 9.2, 4.0 Hz, 1H), 1.97 (dd, *J* = 13.9, 8.0 Hz, 1H), 1.91 (dd, *J* = 14.0, 7.3 Hz, 1H), 0.73 (s, 3H), 0.70 (s, 3H). **^{1}H NMR** (400 MHz, $CDCl_3$) (diagnostic peaks for dechlorinated product) δ 7.52 (ddd, *J* = 8.4, 6.6, 1.7 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 4.00 (s, 3H), 2.79 (dd, *J* = 9.1, 4.2 Hz, 1H), 0.70 (s, 3H), 0.65 (s, 3H). **^{1}H NMR** (599 MHz, $CDCl_3$) (diagnostic peaks for dechlorinated product) δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.52 (ddd, *J* = 9.0, 7.5, 1.7 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.29 (t, *J* = 9.3 Hz, 1H), 4.00 (s, 3H), 2.81 (dd, *J* = 9.2, 4.1 Hz, 1H), 0.71 (s, 3H), 0.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.59, 155.7, 137.5, 135.3, 130.7, 129.8, 128.4, 127.1, 126.5, 126.24, 124.6, 119.5, 113.75, 110.5, 73.6, 58.10, 56.9, 50.9, 42.6, 36.92, 24.0, 23.74. **^{13}C NMR** (101 MHz, $CDCl_3$, non-overlapped signals) (dechlorinated product) δ 159.56, 157.2, 136.9, 135.7, 130.9, 130.0, 128.3, 126.4, 124.5, 121.01, 119.9, 112.2, 110.42, 58.14, 56.5, 50.7, 42.8, 36.87, 24.1, 23.66. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.60, 155.8, 137.5, 135.3, 130.7, 129.8, 128.4, 127.9, 126.5, 126.25, 124.6, 119.5, 113.8, 110.5, 73.62, 58.1, 56.94, 50.9, 42.7, 36.92, 24.0, 23.8. **^{13}C NMR** (151 MHz, $CDCl_3$, non-overlapped signals) (dechlorinated product) δ 159.58, 157.2, 136.9, 135.7, 130.9, 130.0, 128.3, 126.27, 124.5, 121.0, 120.0, 112.3, 110.4, 73.60, 58.2, 56.5, 50.7, 42.8, 36.87, 24.1, 23.7. **HRMS (Orbitrap)** *m/z* calc. for $[C_{22}H_{24}O_4S^{35}Cl_2Na]$ ($[M+Na^+]$) 477.0665, found 477.0664. **HRMS (Orbitrap)** (dechlorinated byproduct) *m/z* calc. for $[C_{22}H_{25}O_4S^{35}ClNa]$ ($[M+Na^+]$) 443.1060, found 443.1054.

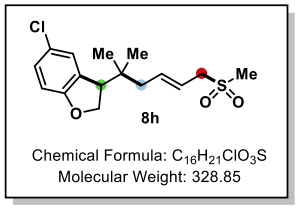
(*E*)-5-chloro-3-(2-methyl-6-((3,4,5-trifluorophenyl)sulfonyl)hex-4-en-2-yl)-2,3-dihydrobenzofuran (8g).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7g** (43.6 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 15/2 → 6/1).

Amount: 60.9 mg, 0.137 mmol, 69%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 6/1): 0.45. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.14 – 7.11 (m, 1H), 7.09 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 5.69 (dt, *J* = 15.3, 7.5 Hz, 1H), 5.42 (dtt, *J* = 15.2, 7.4, 1.4 Hz, 1H), 4.50 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.43 (t, *J* = 9.3 Hz, 1H), 3.79 (d, *J* = 7.3 Hz, 2H), 3.11 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.06 (ddd, *J* = 14.0, 7.7, 1.2 Hz, 1H), 2.03 – 1.94 (m, 1H), 0.87 (s, 3H), 0.84 (s, 3H). **^{13}C {^{1}H, ^{19}F} NMR** (151 MHz, $CDCl_3$) δ 159.62, 151.29, 144.13 – 143.01 (m), 138.78, 134.76, 129.72, 128.55, 126.34, 124.73, 118.27, 113.81, 110.60, 73.66, 60.14, 51.54, 42.47, 37.02, 24.26, 24.03. **^{19}F{^{1}H} NMR** (564 MHz, $CDCl_3$) δ -128.90 (d, *J* = 19.8 Hz), -149.74 (t, *J* = 19.8 Hz). **HRMS (Orbitrap)** *m/z* calc. for $[C_{21}H_{20}O_3S^{35}ClF_3Na]$ ($[M+Na^+]$) 467.0666, found 467.0666.

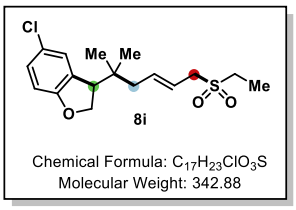
(*E*)-5-chloro-3-(2-methyl-6-(methylsulfonyl)hex-4-en-2-yl)-2,3-dihydrobenzofuran (8h).



The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7h** (20.4 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 2/1).

Amount: 27.3 mg, 0.083 mmol, 42%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 2/1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 1H), 7.10 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.87 (dtt, *J* = 15.3, 7.5, 1.1 Hz, 1H), 5.60 (dtt, *J* = 15.2, 7.4, 1.0 Hz, 1H), 4.54 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.46 (t, *J* = 9.3 Hz, 1H), 3.69 (d, *J* = 7.4 Hz, 2H), 3.19 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.85 (s, 3H), 2.14 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.06 (dd, *J* = 13.5, 7.1 Hz, 1H), 0.95 (s, 3H), 0.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 137.7, 129.9, 128.6, 126.4, 124.7, 119.7, 110.6, 73.7, 58.7, 51.7, 42.6, 39.5, 37.2, 24.5, 24.2. **HRMS (Orbitrap)** *m/z* calc. for $[C_{16}H_{21}O_3S^{35}ClNa]$ ($[M+Na^+]$) 351.0792, found 351.0793.

(*E*)-5-chloro-3-(6-(ethylsulfonyl)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (8i).

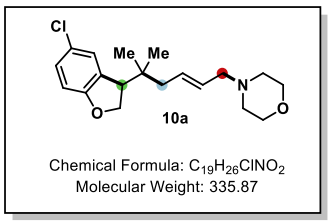


The title compound was obtained from bromide **1b** (66.1 mg, 0.24 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and sodium sulfinate **7i** (23.2 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (1.85 ml) upon irradiation for 24 hours using 455 nm LEDs, according to **GP1**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/2 → 2/1).

Amount: 24.6 mg, 0.072 mmol, 36%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 2/1): 0.44. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 1H), 7.09 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.85 (dt, *J* = 15.2, 7.5 Hz, 1H), 5.57 (dtt, *J* = 15.3, 7.4, 1.1 Hz, 1H), 4.54 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.46 (t, *J* = 9.2 Hz, 1H), 3.65 (d, *J* = 7.4 Hz, 2H), 3.18 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.96 (q, *J* = 7.5 Hz, 2H), 2.15 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.05 (dd, *J* = 13.6, 7.1 Hz, 1H), 1.38 (t, *J* = 7.5 Hz, 3H), 0.94 (s, 3H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 137.4, 129.9, 128.5, 126.4, 124.7, 119.4, 110.6, 73.7, 56.0, 51.6, 46.0, 42.6, 37.2, 24.4, 24.2, 6.6. **HRMS (Orbitrap)** *m/z* calc. for $[C_{17}H_{23}O_3S^{35}ClNa]$ ($[M+Na^+]$) 365.0949, found 365.0945.

Amines as nucleophiles

(*E*)-4-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)morpholine (10a).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and morpholine **9a** (26.0 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.5).

Amount: 51.9 mg, 0.155 mmol, 78%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.5): 0.37. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.3 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.61 (dt, *J* = 15.3, 7.1 Hz, 1H), 5.50 (dt, *J* = 15.2, 6.5 Hz, 1H), 4.52 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.43 (t, *J* = 9.3 Hz, 1H), 3.70 (t, *J* = 4.7 Hz, 4H), 3.18 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.96 (d, *J* = 6.6 Hz, 2H), 2.48 – 2.37 (m, 4H), 2.10 – 1.93 (m, 2H), 0.90 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 130.3, 130.2, 129.8, 128.3, 126.4, 124.6, 110.4, 73.8, 67.1, 61.4, 53.7, 51.2, 42.8, 36.90 24.4, 24.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{19}H_{27}O_2{}^{35}ClN$] ([M+H$^+$]) 336.1725, found 336.1725.

Scale-up reaction at 1% palladium catalyst loading.

In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, $Pd(PPh_3)_4$ (23.1 mg, 0.020 mmol, 1 mol%) and DPEPhos (21.5 mg, 0.040 mmol, 2.0 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (7.0 ml, 0.2 M) was added, followed by bromide **1b** (551 mg, 2.00 mmol, 1.00 equiv.), dry Et_3N (836 µl, 6.00 mmol, 3.00 equiv.), morpholine **9a** (347 µl, 4.00 mmol, 2.00 equiv.) and 1,3-butadiene 2 M inTHF (3.00 ml, 6.00 mmol, 3.00 equiv.), then the vessel was sealed and irradiated for 48 hours at 455 nm using the Kessil light set-up. The reaction was filtered over a short pad of silica, rinsing with CH_2Cl_2. The volatiles were removed *in vacuo*, then the residue was loaded on silica and purified by flash column chromatography (pentane/EtOAc/Et_3N = 7/1/0.5), affording **10a** as a faint yellow gum (433.0 mg, 1.29 mmol, 65%).

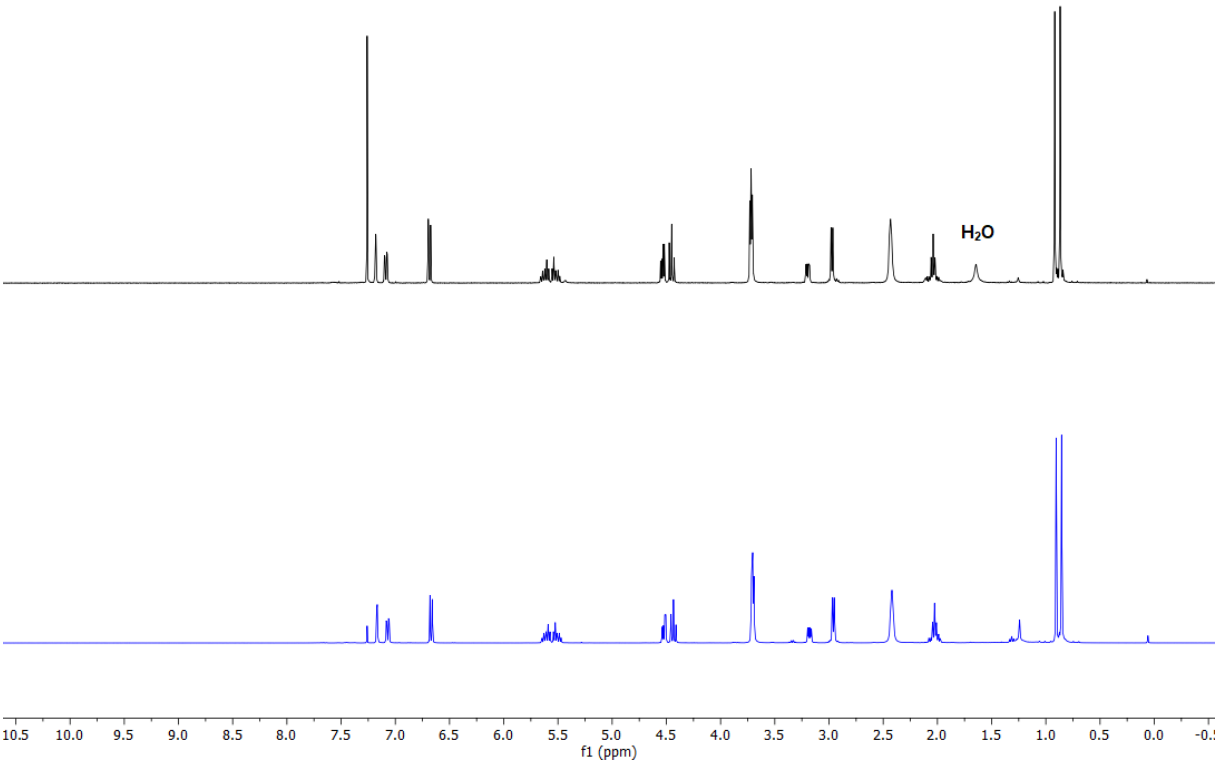
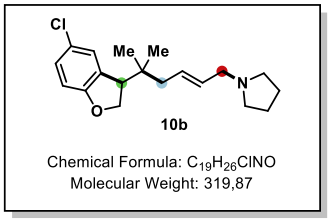


Figure S6 Comparison of the sample **10a** isolated on 2.0 mmol scale with 1% Pd loading (**black**, 400 MHz) with the one obtained on 0.2 mmol scale (**blue**, 400 MHz).

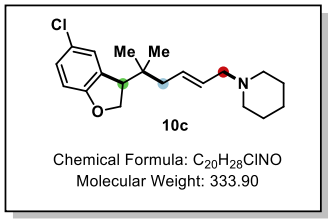
(*E*)-1-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)pyrrolidine (10b).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and pyrrolidine **9b** (24.6 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.5).

Amount: 45.4 mg, 0.142 mmol, 71%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.5): 0.37. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.07 (ddd, *J* = 8.5, 2.3, 0.6 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.64 – 5.56 (m, 2H), 4.52 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.44 (t, *J* = 9.3 Hz, 1H), 3.20 (dd, *J* = 9.2, 4.2 Hz, 1H), 3.12 – 3.02 (m, 2H), 2.53 – 2.44 (m, 4H), 2.06 – 1.98 (m, 2H), 1.80 – 1.74 (m, 4H), 0.91 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.7, 131.5, 130.3, 128.6, 128.3, 126.4, 124.6, 110.4, 73.8, 58.4, 54.1, 51.0, 42.9, 37.0, 24.4, 23.9, 23.6. **HRMS (Orbitrap)** *m/z* calc. for [$C_{19}H_{27}O^{35}ClN$] ([M+H$^+$]) 320.1776, found 320.1776.

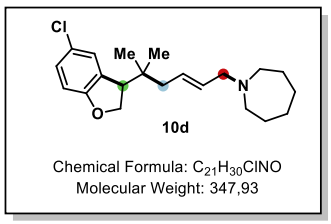
(*E*)-1-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)piperidine (10c).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and piperidine **9c** (29.6 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.2).

Amount: 52.0 mg, 0.156 mmol, 78%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.2): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.3 Hz, 1H), 7.07 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.62 – 5.49 (m, 2H), 4.52 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.43 (t, *J* = 9.3 Hz, 1H), 3.19 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.98 – 2.87 (m, 2H), 2.44 – 2.26 (br, 4H), 2.08 – 1.96 (m, 2H), 1.57 (p, *J* = 5.6 Hz, 4H), 1.50 – 1.34 (m, 2H), 0.91 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 130.8, 130.3, 129.4, 128.3, 126.4, 124.6, 110.4, 73.8, 61.8, 54.5, 51.1, 42.9, 36.9, 26.1, 24.5, 24.4, 23.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{20}H_{29}O^{35}ClN$] ([M+H$^+$]) 334.1932, found 334.1931.

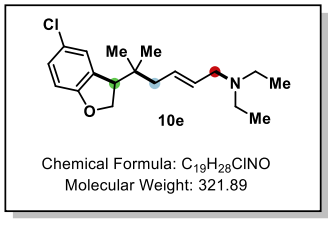
(*E*)-1-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)azepane (10d).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and azepane **9d** (33.9 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.2).

Amount: 50.9 mg, 0.146 mmol, 73%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.2): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 1H), 7.07 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.62 – 5.49 (m, 2H), 4.53 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.12 – 3.04 (m, 2H), 2.64 – 2.54 (m, 4H), 2.09 – 1.95 (m, 2H), 1.69 – 1.53 (m, 8H), 0.91 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 131.7, 130.3, 128.9, 128.3, 126.4, 124.6, 110.4, 73.8, 60.9, 55.6, 51.1, 43.0, 37.0, 28.2, 27.0, 24.4, 23.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{21}H_{31}ON^{35}Cl$] ([M+H$^+$]) 348.2089, found 348.2087.

(*E*)-5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-*N,N*-diethyl-5-methylhex-2-en-1-amine (10e).

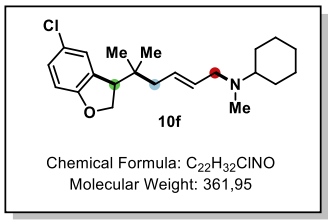


The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and diethylamine **9e** (31.0 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm

LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.2).

Amount: 46.6 mg, 0.145 mmol, 73%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc:Et_3N 9/1/0.2): 0.37. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.3 Hz, 1H), 7.07 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.64 – 5.47 (m, 2H), 4.53 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.44 (t, *J* = 9.3 Hz, 1H), 3.19 (dd, *J* = 9.1, 4.2 Hz, 1H), 3.07 (dd, *J* = 5.6, 1.5 Hz, 2H), 2.51 (q, *J* = 7.1 Hz, 4H), 2.09 – 1.95 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 6H), 0.91 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 131.0, 130.3, 129.0, 128.3, 126.4, 124.6, 110.4, 73.8, 55.3, 51.1, 46.6, 43.0, 36.9, 24.4, 23.9, 11.8. **HRMS (Orbitrap)** *m/z* calc. for [$C_{19}H_{28}ON^{35}Cl$] ([M+H$^+$]) 322.1932, found 322.1931.

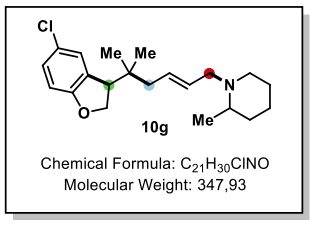
(*E*)-N-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-*N*-methylcyclohexanamine (10f).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and N-Me-cyclohexylamine **9f** (39.2 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.2).

Amount: 51.6 mg, 0.143 mmol, 72%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.2): 0.50. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 1H), 7.07 (ddd, *J* = 8.5, 2.3, 0.6 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.64 – 5.44 (m, 2H), 4.53 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 9.0, 4.3 Hz, 1H), 3.10 – 3.04 (m, 2H), 2.46 – 2.31 (m, 1H), 2.21 (s, 3H), 2.11 – 1.94 (m, 2H), 1.85 – 1.70 (m, 4H), 1.66 – 1.54 (m, 1H), 1.28 – 1.11 (m, 5H), 0.92 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.7, 132.0, 130.3, 128.7, 128.3, 126.4, 124.6, 110.4, 73.8, 61.8, 56.30, 51.1, 42.9, 37.5, 37.0, 28.8, 28.7, 26.5, 26.1, 24.4, 23.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{33}ON^{35}Cl$] ([M+H$^+$]) 362.2245, found 362.2242. **Note.** One ^{13}C aliphatic signal missing due to overlap (overlap of one diastereotopic pair of the cyclohexyl ring).

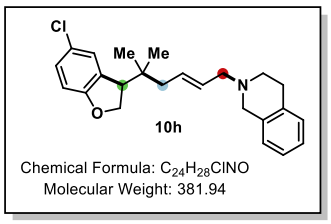
1-((*E*)-5-(-5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-2-methylpiperidine (10g).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and (±)-2-methylpiperidine **9g** (35.3 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.2) and obtained as an inseparable mixture of diastereoisomers.

Amount: 49.7 mg, 0.143 mmol, 72%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.2): 0.50. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.19 – 7.15 (m, 1H), 7.07 (ddd, *J* = 8.5, 2.3, 0.6 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.65 – 5.48 (m, 2H), 4.53 (dd, *J* = 9.4, 4.3 Hz, 1H), 4.44 (td, *J* = 9.2, 1.1 Hz, 1H), 3.39 – 3.28 (m, 1H), 3.19 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.03 – 2.91 (m, 1H), 2.83 (dtd, *J* = 11.6, 3.9, 1.4 Hz, 1H), 2.23 (dhept, *J* = 9.2, 3.2 Hz, 1H), 2.10 (dddd, *J* = 12.1, 10.7, 3.2, 1.7 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.71 – 1.45 (m, 3H), 1.37 – 1.18 (m, 2H), 1.08 (s, 3H, *single diastereoisomer*), 1.06 (s, 3H, *single diastereoisomer*), 0.91 (d, *J* = 1.3 Hz, 3H), 0.85 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.7, 130.3, 130.0, 129.41, 129.38, 128.3, 126.4, 124.6, 110.4, 73.8, 56.50, 56.46, 55.93, 55.90, 52.5, 51.13, 51.10, 43.0, 42.9, 36.9, 34.9, 26.3, 24.4, 24.3, 24.3, 24.0, 19.4. **HRMS (Orbitrap)** *m/z* calc. for [$C_{21}H_{31}ON^{35}Cl$] ([M+H$^+$]) 348.2089, found 348.2087. **Note.** multiplicities reported in the ^{1}H NMR characterization are the one that have been experimentally observed, but they often arise (at least partially) from the signal overlap between the two diastereoisomers rather than an actual scalar coupling. Signals belonging to a single diastereoisomer were reported with number of protons corrected for the abundancy in the mixture.

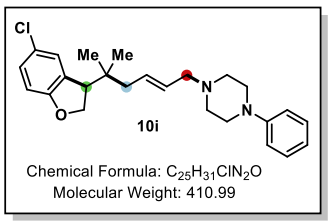
(*E*)-2-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-1,2,3,4-tetrahydroisoquinoline (10h).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and tetrahydroisoquinoline **9h** (37.6 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.1).

Amount: 61.3 mg, 0.160 mmol, 80%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc/Et_3N = 9/1/0.1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 1H), 7.16 – 7.07 (m, 4H), 7.04 – 6.99 (m, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 5.76 – 5.57 (m, 2H), 4.56 (dd, *J* = 9.4, 4.2 Hz, 1H), 4.47 (t, *J* = 9.2 Hz, 1H), 3.63 (s, 2H), 3.23 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.16 (d, *J* = 5.5 Hz, 2H), 2.92 (t, *J* = 5.9 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.15 – 2.02 (m, 2H), 0.96 (s, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 134.8, 134.4, 130.5, 130.3, 129.9, 128.8, 128.3, 126.7, 126.4, 126.2, 125.7, 124.6, 110.5, 73.8, 60.6, 56.1, 51.2, 50.6, 42.9, 37.0, 29.2, 24.4, 24.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{29}ON^{35}Cl$] ([M+H$^+$]) 382.1932, found 382.1933.

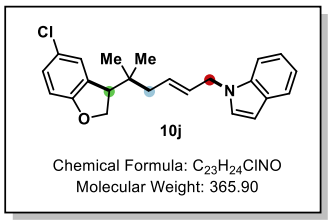
(*E*)-1-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-4-phenylpiperazine (10i).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and *N*-phenylpiperazine **9i** (45.9 µl, 0.30 mmol, 1.50 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (CH_2Cl_2/EtOAc = 2/1).

Amount: 64.1 mg, 0.156 mmol, 78%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (CH_2Cl_2/EtOAc = 2/1): 0.40. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.20 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.10 (ddd, *J* = 8.5, 2.3, 0.6 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.86 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 5.73 – 5.52 (m, 2H), 4.55 (dd, *J* = 9.5, 4.3 Hz, 1H), 4.46 (t, *J* = 9.2 Hz, 1H), 3.26 – 3.17 (m, 5H), 3.05 (d, *J* = 5.6 Hz, 2H), 2.66 – 2.57 (m, 4H), 2.15 – 1.99 (m, 2H), 0.94 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.6, 151.4, 130.23, 130.21, 130.1, 129.2, 128.3, 126.4, 124.6, 119.8, 116.1, 110.5, 73.8, 61.0, 53.2, 51.2, 49.2, 42.8, 36.9, 24.4, 24.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{25}H_{32}ON^{35}Cl$] ([M+H$^+$]) 411.2198, found 411.2200.

(*E*)-1-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-1*H*-indole (10j).

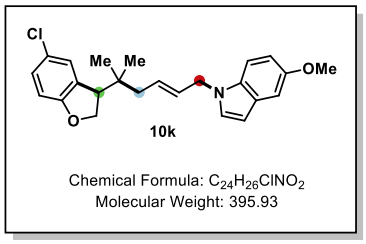


The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and 1*H*-indole **9j** (35.1 mg, 0.30 mmol, 1.50 equiv.) and KOH (33.5 mg, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 60/1 → 40/1).

Amount: 50.0 mg, 0.137 mmol, 69%, 93:7 *E/Z.* **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 40/1): 0.50. **^{1}H NMR** (500 MHz, $CDCl_3$, *major isomer*) δ 7.66 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.22 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.18 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.14 – 7.09 (m, 3H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.53 (dd, *J* = 3.1, 0.9 Hz, 1H), 5.67 (dt, *J* = 15.3, 5.6 Hz, 1H), 5.58 (dtt, *J* = 15.2, 7.4, 1.2 Hz, 1H), 4.71 (dd, *J* = 5.6, 1.2 Hz, 2H), 4.51 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.42 (t, *J* = 9.3 Hz, 1H), 3.15 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.06 (dd, *J* = 14.0, 7.7 Hz, 1H), 1.99 (dd, *J* = 13.9, 7.1 Hz, 1H), 0.90 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, *major isomer*) δ 159.7, 136.1, 130.1, 129.62, 128.9, 128.8, 128.4, 127.7, 126.4, 124.6, 121.6, 121.1, 119.5, 110.5, 109.7, 101.50, 73.76, 51.4, 48.3, 42.3, 36.9, 24.4, 24.0. **^{1}H NMR** (500 MHz, $CDCl_3$, *minor isomer – diagnostic signals*) δ 6.74 (d, *J* = 8.5 Hz, 1H), 5.80 – 5.71 (m, 2H), 4.75 (dd, *J* = 5.8, 1.3 Hz, 2H), 4.60 (dd, *J* = 9.5, 3.8 Hz, 1H), 3.27 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.28 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.16 (dd, *J* = 14.4, 6.4 Hz, 1H), 1.01 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, *minor isomer – non-overlapping signals*) δ 130.0,

129.0, 128.6, 127.8, 127.4, 126.5, 110.6, 109.5, 101.54, 73.84, 51.6, 43.4, 37.2, 24.1. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{25}ON^{35}Cl$] ([M+H$^+$]) 366.1619, found 366.1621. **Note.** *E/Z* ratio determined using long-relaxation time sequence (30 seconds).

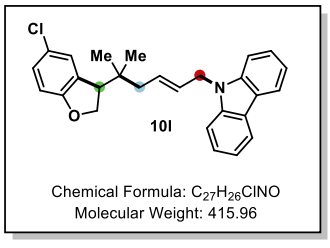
(*E*)-1-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-5-methoxy-1*H*-indole (10k).



The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and 5-MeO-1*H*-indole **9k** (44.2 mg, 0.30 mmol, 1.50 equiv.) and KOH (33.5 mg, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 25/1 → 20/1).

Amount: 45.7 mg, 0.115 mmol, 58%, *E/Z* 94:6. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 25/1): 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$, major isomer) δ 7.22 (d, *J* = 8.8 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.10 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.06 (d, *J* = 3.1 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.44 (d, *J* = 3.0 Hz, 1H), 5.70 – 5.51 (m, 2H), 4.66 (d, *J* = 5.3 Hz, 2H), 4.51 (dd, *J* = 9.5, 4.1 Hz, 1H), 4.41 (t, *J* = 9.3 Hz, 1H), 3.86 (s, 3H), 3.14 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.05 (dd, *J* = 13.8, 7.3 Hz, 1H), 1.98 (dd, *J* = 13.8, 6.8 Hz, 1H), 0.89 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, major isomer) δ 159.6, 154.1, 131.5, 130.1, 129.6, 129.2, 128.9, 128.4, 128.2, 126.4, 124.6, 111.9, 110.5, 110.4, 102.7, 101.0, 73.8, 56.0, 51.4, 48.5, 42.2, 36.9, 24.3, 24.0. **^{1}H NMR** (400 MHz, $CDCl_3$, minor isomer, diagnostic peaks) δ 6.73 (d, *J* = 8.5 Hz, 1H), 5.79 – 5.69 (m, 2H), 4.70 (d, *J* = 4.9 Hz, 2H), 4.59 (dd, *J* = 9.5, 3.9 Hz, 1H), 3.25 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.26 (dd, *J* = 14.4, 6.4 Hz, 1H), 2.13 (dd, *J* = 14.5, 5.6 Hz, 1H), 1.00 (s, 3H), 0.97 (s, 3H). **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{26}O_2N^{35}ClF_3Na$] ([M+Na$^+$]) 418.1544, found 418.1542. **Notes and troubleshooting**: Detection of the ^{13}C signals is hampered by the small amount of substance present in the sample, as well as extensive overlap with the major isomer. *E/Z* ratio determined using long-relaxation time sequence (30 seconds).

(*E*)-9-(5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-9*H*-carbazole (10l).



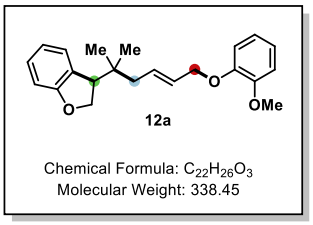
The title compound was obtained from bromide **1b** (55.1 mg, 0.20 mmol, 1.20 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and carbazole **9l** (50.2 mg, 0.30 mmol, 1.50 equiv.) and KOH (33.5 mg, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (1.70 ml) upon irradiation for 24 hours using 450 nm LEDs, according to **GP2**. The

crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 80/1 → 70/1 → 60/1 → 50/1).

Amount: 47.2 mg, 0.113 mmol, 57%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 80/1): 0.30. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.13 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.48 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.39 (dt, *J* = 8.3, 1.0 Hz, 2H), 7.26 (td, *J* = 7.2, 1.2 Hz, 2H), 7.14 – 7.12 (m, 1H), 7.09 (ddd, *J* = 8.4, 2.3, 0.6 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.64 (dt, *J* = 15.2, 5.0 Hz, 1H), 5.51 (dtt, *J* = 15.4, 7.5, 1.2 Hz, 1H), 4.90 (dd, *J* = 4.9, 1.3 Hz, 2H), 4.45 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.35 (t, *J* = 9.2 Hz, 1H), 3.07 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.05 – 1.86 (m, 2H), 0.82 (s, 3H), 0.76 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.6, 140.4, 130.1, 129.0, 128.3, 127.7, 126.4, 125.8, 124.6, 123.1, 120.5, 119.1, 110.42, 108.9, 73.7, 51.3, 44.7, 42.2, 36.9, 24.2, 23.8. **HRMS (Orbitrap)** *m/z* calc. for [$C_{27}H_{26}ON^{35}ClNa$] ([M+Na^+]) 438.1595, found 438.1597.

Phenols as nucleophiles

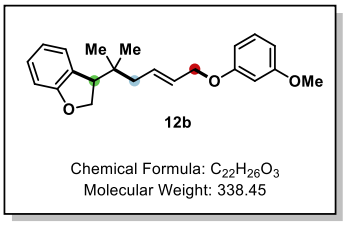
(*E*)-3-(6-(2-methoxyphenoxy)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (12a).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and guaiacol **11a** (24.8 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 20/1 → 15/1).

Amount: 50.5 mg, 0.149 mmol, 75%. **Physical aspect**: colourless gum. **R*f*** (*n*-pentane/EtOAc = 15/1): 0.40. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 7.5 Hz, 1H), 7.14 (td, *J* = 7.7, 1.4 Hz, 1H), 6.96 – 6.86 (m, 4H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.84 (dt, *J* = 15.4, 6.9 Hz, 1H), 5.75 (dt, *J* = 15.3, 5.6 Hz, 1H), 4.61 (dd, *J* = 5.5, 1.1 Hz, 2H), 4.51 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.41 (t, *J* = 9.2 Hz, 1H), 3.87 (s, 3H), 3.17 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.14 – 2.03 (m, 2H), 0.90 (s, 3H), 0.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 149.7, 147.9, 131.2, 128.4, 128.1, 126.4, 121.3, 120.7, 119.8, 114.0, 111.8, 109.5, 73.1, 69.6, 55.9, 50.9, 42.7, 36.9, 24.2, 23.9. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{26}O_3Na$] ([M+Na$^+$]) 361.1774, found 361.1770.

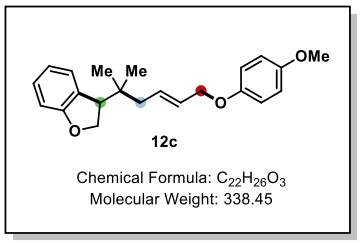
(*E*)-3-(6-(3-methoxyphenoxy)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (12b).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and 3-methoxyphenol **11b** (24.8 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 40/1 → 30/1).

Amount: 46.7 mg, 0.138 mmol, 69%. **Physical aspect**: colourless gum. **R*f*** (*n*-pentane/EtOAc = 40/1): 0.33. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.85 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.56 – 6.47 (m, 3H), 5.87 (dtt, *J* = 14.6, 7.4, 1.2 Hz, 1H), 5.73 (dtt, *J* = 15.3, 5.7, 1.0 Hz, 1H), 4.54 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.50 (dd, *J* = 5.8, 1.1 Hz, 2H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.78 (s, 3H), 3.22 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.18 – 2.05 (m, 2H), 0.94 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 160.9, 160.0, 131.2, 129.9, 128.5, 128.2, 128.1, 126.5, 119.9, 109.6, 107.2, 106.5, 101.5, 73.2, 68.6, 55.4, 51.1, 42.8, 37.0, 24.3, 24.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{26}O_3Na$] ([M+Na$^+$]) 361.1774, found 361.1773.

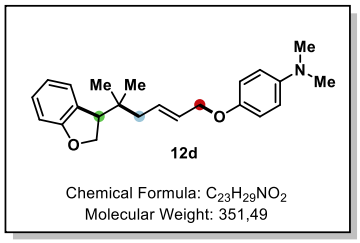
(*E*)-3-(6-(4-methoxyphenoxy)-2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (12c).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and mequinol **11c** (24.8 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 455 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 15/1).

Amount: 59.3 mg, 0.175 mmol, 88%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 15/1): 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.4 Hz, 1H), 7.15 (td, *J* = 7.6, 1.4 Hz, 1H), 6.89 – 6.81 (m, 5H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.84 (dtt, *J* = 15.4, 7.3, 1.2 Hz, 1H), 5.72 (dtt, *J* = 15.4, 5.7, 1.0 Hz, 1H), 4.53 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.47 (dd, *J* = 5.7, 1.1 Hz, 2H), 4.43 (t, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.20 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.16 – 2.04 (m, 2H), 0.93 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 154.0, 152.8, 131.0, 128.6, 128.5, 128.1, 126.5, 119.9, 116.1, 114.7, 109.6, 73.2, 69.4, 55.8, 51.0, 42.8, 37.0, 24.3, 24.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{26}O_3Na$] ([M+Na$^+$]) 361.1774, found 361.1774.

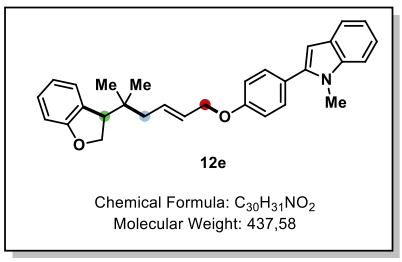
(*E*)-4-((5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)-N,N-dimethylaniline (12d).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and *N,N*-dimethyl-4-hydroxyaniline **11d** (27.4 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 15/1 → 13/1 → 11/1).

Amount: 44.5 mg, 0.127 mmol, 64%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 15/1): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.4 Hz, 1H), 7.15 (td, *J* = 7.7, 1.4 Hz, 1H), 6.89 – 6.81 (m, 3H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.77 – 6.70 (m, 2H), 5.83 (dtt, *J* = 15.4, 7.2, 1.2 Hz, 1H), 5.72 (dtt, *J* = 15.4, 5.8, 1.0 Hz, 1H), 4.52 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.46 (dd, *J* = 5.6, 1.1 Hz, 2H), 4.42 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.86 (s, 6H), 2.16 – 2.04 (m, 2H), 0.93 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 150.9, 146.0, 130.8, 128.9, 128.4, 128.2, 126.5, 119.9, 116.1, 114.8, 109.6, 73.2, 69.5, 51.0, 42.9, 41.9, 37.0, 24.3, 24.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{29}NO_3$] ([M+H$^+$]) 352.2271, found 352.2271.

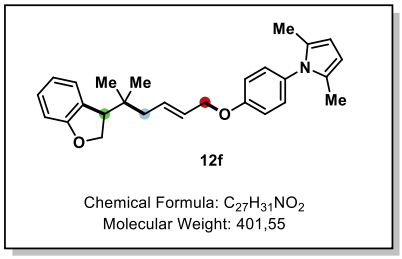
(*E*)-2-(4-((5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)phenyl)-1-methyl-1*H*-indole (12e).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and phenol **11e** (44.7 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 40/1 → 30/1 → 120/4.5).

Amount: 45.2 mg, 0.103 mmol, 52%. **Physical aspect**: white solid. $\mathbf{R_f}$ (*n*-pentane:CH_2Cl_2 3/1) 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.15 (tdd, *J* = 7.1, 4.0, 1.2 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.85 (td, *J* = 7.4, 1.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 0.8 Hz, 1H), 5.89 (dtt, *J* = 15.4, 7.3, 1.2 Hz, 1H), 5.76 (dtt, *J* = 15.3, 5.8, 0.9 Hz, 1H), 4.57 (d, *J* = 5.7 Hz, 2H), 4.54 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.71 (s, 3H), 3.22 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.19 – 2.06 (m, 2H), 0.95 (s, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 158.6, 141.5, 138.3, 131.5, 130.7, 128.5, 128.12, 128.10, 128.08, 126.5, 125.5, 115.0, 109.6, 101.1, 73.2, 68.7, 51.2, 42.7, 37.0, 31.2, 24.4, 24.1. **HRMS (Orbitrap)** *m/z* calc. for $[C_{30}H_{31}ON_2Na]$ ($[M+Na^+]$) 460.2247, found 460.2247.

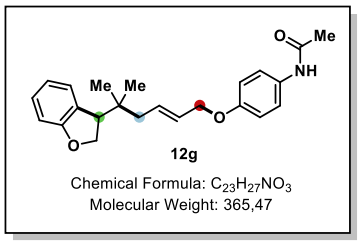
(*E*)-1-(4-((5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)phenyl)-2,5-dimethyl-1*H*-pyrrole (12f).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and phenol **11f** (37.4 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/CH_2Cl_2 = 3/1 → 2/1 → 1/1).

Amount: 75.3 mg, 0.186 mmol, 93%. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/CH_2Cl_2 = 3/1) 0.30. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.3 Hz, 1H), 7.17 – 7.07 (m, 4H), 6.98 – 6.92 (m, 2H), 6.83 (td, *J* = 7.4, 1.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.93 – 5.81 (m, 3H), 5.73 (dtt, *J* = 15.3, 5.6, 1.1 Hz, 1H), 4.57 – 4.49 (m, 3H), 4.42 (t, *J* = 9.2 Hz, 1H), 3.21 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.18 – 2.05 (m, 2H), 1.99 (s, 6H), 0.92 (s, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 157.9, 131.9, 131.5, 129.3, 129.1, 128.5, 128.1, 128.0, 126.5, 120.0, 115.2, 109.6, 105.4, 73.2, 68.8, 51.2, 42.6, 37.0, 24.4, 24.1, 13.1. **HRMS (Orbitrap)** *m/z* calc. for $[C_{27}H_{31}O_2NNa]$ ($[M+Na^+]$) 424.2247, found 424.2246.

(*E*)-*N*-(4-((5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)phenyl)acetamide (12g).



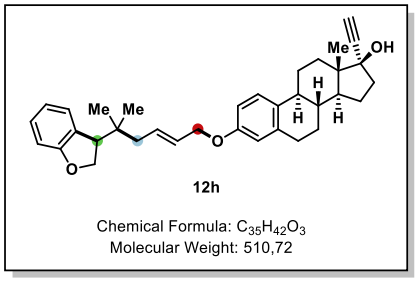
12g

Chemical Formula: $C_{23}H_{27}NO_3$
Molecular Weight: 365,47

The title compound was obtained from bromide **1g** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and paracetamol **11g** (30.2 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 3/2 → 1/1).

Amount: 65.5 mg, 0.179 mmol, 90%. **Physical aspect**: faint yellow gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 1/1): 0.45. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (br, 1H), 7.40 – 7.35 (m, 2H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.13 (td, *J* = 7.8, 1.4 Hz, 1H), 6.87 – 6.80 (m, 3H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.83 (dtt, *J* = 15.2, 7.5, 1.3 Hz, 1H), 5.69 (dtt, *J* = 15.3, 5.8, 1.0 Hz, 1H), 4.51 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.47 (d, *J* = 5.9 Hz, 2H), 4.41 (t, *J* = 9.2 Hz, 1H), 3.18 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.16 – 2.03 (m, 5H), 0.91 (s, 3H), 0.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.5, 160.9, 155.5, 131.3, 131.2, 128.4, 128.2, 128.1, 126.5, 121.9, 119.9, 115.3, 109.5, 73.2, 68.9, 51.1, 42.7, 36.9, 24.3, 24.3, 24.0. **HRMS (Orbitrap)** *m/z* calc. for $[C_{23}H_{27}NO_3Na]$ ($[M+Na^+]$) 388.1883, found 388.1881.

(8*R*,9*S*,13*S*,14*S*,17*R*)-3-(((*E*)-5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)-17-ethynyl-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (12h).



12h

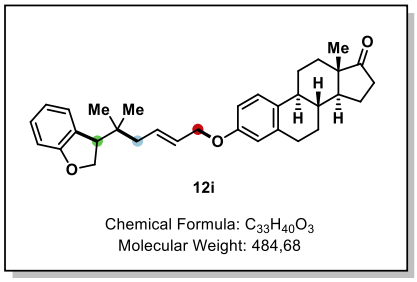
Chemical Formula: $C_{35}H_{42}O_3$
Molecular Weight: 510,72

The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and ethynylestradiol **11h** (59.3 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 10/1 → 7/1).

Amount: 102.7 mg, 0.200 mmol, >99%, 50:50 dr. **Physical aspect**: white foam. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 10/1): 0.25. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.25 (br d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.74 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 5.85 (dtd, *J* = 15.1, 7.3, 1.3 Hz, 1H), 5.77 – 5.69 (m, 1H), 4.53 (ddd, *J* = 9.3, 4.0, 2.6 Hz, 1H), 4.51 (br d, *J* = 5.7 Hz, 2H), 4.42 (td, *J* = 9.2, 6.9 Hz, 1H), 3.20 (td, *J* = 9.2, 3.9 Hz, 1H), 2.90 – 2.79 (m, 2H), 2.62 (s, 1H), 2.40 – 2.32 (m, 2H), 2.22 (tt, *J* = 11.5, 4.8 Hz, 1H), 2.16 – 2.07 (m, 3H), 2.04 (ddd, *J* = 13.6, 12.1, 4.1 Hz, 1H), 1.93 (td, *J* = 13.0, 4.3 Hz, 1H), 1.90 – 1.85 (m, 1H), 1.84 – 1.78 (m, 1H), 1.77 – 1.67 (m, 2H), 1.50 (td, *J* = 12.9, 4.0 Hz, 1H), 1.47 – 1.40 (m, 1H), 1.40 – 1.32 (m, 1H), 0.95 (s, 3H), 0.90 (s, 3H, *single diastereoisomer*), 0.90 (s, 3H, *single diastereoisomer*), 0.89 (s, 3H, *single diastereoisomer*), 0.89 (s, 3H, *single diastereoisomer*). **^{13}C NMR**

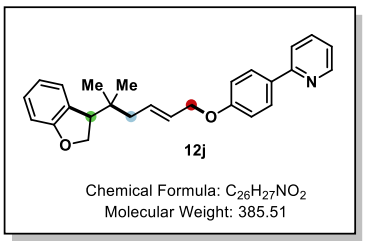
(151 MHz, $CDCl_3$) δ 160.9, 156.54, 156.51, 138.0, 132.78, 132.77, 130.9, 130.8, 128.6, 128.4, 128.13, 128.12, 126.44, 126.39, 119.9, 115.1, 115.0, 112.62, 112.58, 109.6, 87.7, 79.9, 74.1, 73.2, 68.6, 51.00, 50.96, 49.6, 47.2, 43.61, 43.60, 42.83, 42.81, 39.50, 39.48, 39.1, 36.97, 36.96, 32.8, 29.9, 27.343, 27.337, 26.5, 24.4, 24.3, 24.01, 23.99, 22.9, 12.8. **HRMS (Orbitrap)** *m/z* calc. for [$C_{35}H_{42}O_3Na$] ([M+Na$^+$]) 533.3026, found 533.3028.

(8*R*,9*S*,13*S*,14*S*)-3-(((*E*)-5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (12i). The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and estrone **11i** (54.1 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 10/1 → 9/1).



Amount: 94.6 mg, 0.195 mmol, 98%, 50:50 dr. **Physical aspect**: white foam. **R$_f$** (*n*-pentane/EtOAc = 10/1): 0.50. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.24 (br d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.84 (td, *J* = 7.5, 1.0 Hz, 1H), 6.78 (br d, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.68 – 6.65 (m, 1H), 5.85 (dtq, *J* = 15.4, 7.0, 1.3 Hz, 1H), 5.75 – 5.68 (m, 1H), 4.52 (ddd, *J* = 9.3, 4.0, 2.6 Hz, 1H), 4.50 – 4.48 (m, 2H), 4.41 (td, *J* = 9.2, 6.1 Hz, 1H), 3.19 (td, *J* = 9.4, 4.0 Hz, 1H), 2.94 – 2.82 (m, 2H), 2.51 (dd, *J* = 19.1, 8.8 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.28 – 2.19 (m, 1H), 2.18 – 2.03 (m, 4H), 2.00 (dddd, *J* = 9.8, 6.9, 3.6, 1.8 Hz, 1H), 1.97 – 1.92 (m, 1H), 1.67 – 1.60 (m, 1H), 1.60 – 1.53 (m, 1H), 1.53 – 1.46 (m, 3H), 1.46 – 1.36 (m, 1H), 0.94 (s, 3H), 0.91 (s, 3H, *single diastereoisomer*), 0.91 (s, 3H, *single diastereoisomer*), 0.88 (s, 3H, *single diastereoisomer*), 0.88 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 220.9, 160.9, 156.68, 156.66, 137.8, 132.27, 132.25, 130.92, 130.88, 128.5, 128.43, 128.42, 128.12, 128.11, 126.43, 126.35, 119.9, 115.12, 115.08, 112.69, 112.65, 109.6, 73.2, 68.6, 51.01, 50.96, 50.5, 48.1, 44.1, 44.0, 42.82, 42.80, 38.44, 38.42, 36.97, 36.96, 36.0, 31.7, 29.7, 26.632, 26.627, 26.0, 24.36, 24.35, 24.00, 23.99, 21.7, 14.0. **HRMS (Orbitrap)** *m/z* calc. for [$C_{33}H_{40}O_3Na$] ([M+Na$^+$]) 507.2870, found 507.2868.

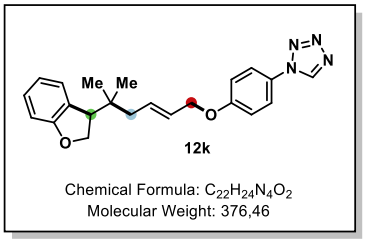
(*E*)-2-(4-((5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)phenyl)pyridine (12j).



The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and phenol **11j** (34.2 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 10/1 → 9/1).

Amount: 55.2 mg, 0.143 mmol, 72%, 86:14 *E/Z*. **Physical aspect**: colourless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 10/1): 0.37.**^{1}H NMR** (599 MHz, $CDCl_3$, major isomer) δ 8.65 (ddd, *J* = 4.8, 1.9, 1.0 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.70 (ddd, *J* = 8.0, 7.3, 1.8 Hz, 1H), 7.65 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.24 (ddt, *J* = 7.5, 1.5, 0.7 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.02 – 6.99 (m, 2H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 – 6.77 (m, 1H), 5.88 (dtt, *J* = 15.0, 7.5, 1.3 Hz, 1H), 5.75 (dtt, *J* = 15.4, 5.8, 1.2 Hz, 1H), 4.57 (br d, *J* = 5.9 Hz, 2H), 4.53 (dd, *J* = 9.3, 4.0 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.22 (dd, *J* = 9.1, 3.9 Hz, 1H), 2.11 (qdd, *J* = 13.9, 7.4, 1.2 Hz, 2H), 0.93 (s, 3H), 0.89 (s, 3H). **^{1}H NMR** (599 MHz, $CDCl_3$, minor isomer – diagnostic signals) δ 4.60 (dd, *J* = 6.5, 1.4 Hz, 2H), 4.45 (t, *J* = 9.0 Hz, 2H), 3.27 (dd, *J* = 9.0, 3.8 Hz, 1H), 2.23 (ddd, *J* = 14.3, 8.2, 1.3 Hz, 1H), 0.97 (s, 3H), 0.94 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, major isomer) δ 160.94, 159.59, 157.2, 149.6, 136.7, 132.2, 131.3, 128.5, 128.2, 128.10, 128.09, 126.48, 121.5, 119.94, 119.89, 115.1, 109.6, 73.19, 68.7, 51.1, 42.7, 37.0, 24.33, 24.07. **^{13}C NMR** (151 MHz, $CDCl_3$, minor isomer – diagnostic signals) δ 160.91, 159.63, 149.7, 132.3, 130.2, 128.6, 128.3, 127.2, 126.46, 120.0, 119.90, 115.0, 109.7, 73.24, 64.1, 51.3, 37.5, 37.2, 24.25, 24.12. **HRMS (Orbitrap)** *m/z* calc. for $[C_{26}H_{28}O_2N]$ ($[M+H^+]$) 386.2115, found 386.2116.

(*E*)-1-(4-((5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)oxy)phenyl)-1H-tetrazole (12k).



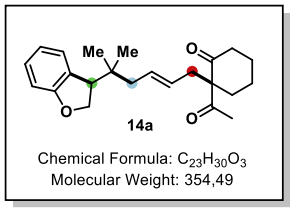
The title compound was obtained from bromide **1a** (72.3 mg, 0.30 mmol, 1.50 equiv.), 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) and phenol **11k** (32.4 mg, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.7 ml) upon irradiation for 40 hours using 450 nm LEDs, according to **GP3**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 5/2 → 2/1).

Amount: 22.8 mg, 0.061 mmol, 31%. **Physical aspect**: colourless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 5/2): 0.27. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 7.61 – 7.54 (m, 2H), 7.23 (br d, *J* = 7.5 Hz, 1H), 7.14 (td, *J* = 7.7, 1.4 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.83 (td, *J* = 7.5, 1.1 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.89 (dtt, *J* = 14.8, 7.4, 1.3 Hz, 1H), 5.72 (dtt, *J* = 15.4, 5.9, 1.0 Hz, 1H), 4.57 (br d, *J* = 5.8 Hz, 2H), 4.52 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.42 (t, *J* = 9.2 Hz, 1H), 3.20 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.18 – 2.04 (m, 2H), 0.93 (s, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 159.8, 140.7, 132.1, 128.6,

128.0, 127.3, 127.1, 126.4, 123.0, 120.0, 116.2, 109.7, 73.2, 69.1, 51.3, 42.6, 37.0, 24.4, 24.1. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{24}O_2N_4Na$] ([M+Na^+]) 399.1792, found 399.1790.

Enolates as nucleophiles

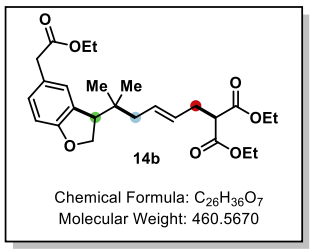
2-acetyl-2-((*E*)-5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)cyclohexan-1-one (14a).



The title compound was obtained from bromide **1a** (48.2 mg, 0.20 mmol, 1.00 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and 2-acetylcyclohexan-1-one **13a** (78.0 µl, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (0.85 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP5**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 10/1 → 9/1).

Amount: 50.7 mg, 0.143 mmol, 72%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 10/1): 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.4 Hz, 1H), 7.12 (td, *J* = 7.7, 1.4 Hz, 1H), 6.82 (tt, *J* = 7.4, 0.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.47 (dtt, *J* = 14.9, 7.9, 1.3 Hz, 1H), 5.25 (dt, *J* = 15.2, 7.4 Hz, 1H), 4.49 (dd, *J* = 9.4, 4.1 Hz, 1H), 4.41 (td, *J* = 9.2, 0.8 Hz, 1H), 3.16 (dd, *J* = 9.1, 4.1 Hz, 1H), 2.58 (dd, *J* = 14.4, 7.3 Hz, 1H), 2.50 – 2.33 (m, 3H), 2.31 – 2.20 (m, 1H), 2.08 (s, 3H, single diastereoisomer), 2.07 (s, 3H, single diastereoisomer), 2.03 – 1.88 (m, 3H), 1.78 – 1.59 (m, 3H), 1.50 – 1.42 (m, 1H), 0.87 (s, 3H), 0.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.8, 206.2, 206.1, 160.9, 130.55, 130.54, 128.4, 128.2, 127.42, 127.39, 126.48, 126.47, 119.90, 119.89, 109.5, 73.2, 67.9, 67.8, 51.2, 42.8, 41.92, 41.91, 37.9, 36.87, 36.86, 34.2, 34.1, 27.3, 26.51, 26.49, 24.28, 24.26, 24.0, 22.23, 22.21. **HRMS (Orbitrap)** *m/z* calc. for [$C_{23}H_{30}O_3Na$] ([M+Na$^+$]) 377.2087, found 377.2084.

diethyl (*E*)-2-(5-(5-(2-ethoxy-2-oxoethyl)-2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)malonate (14b).

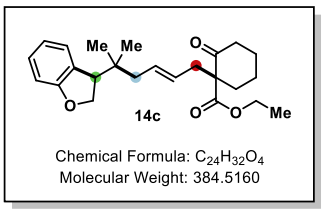


The title compound was obtained from bromide **1h** (65.4 mg, 0.20 mmol, 1.00 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and diethyl malonate **13b** (30.4 µl, 0.20 mmol, 1.00 equiv.) in dry 1,4-dioxane (0.85 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP5**, except that K_2CO_3 (41.5 mg, 0.30 mmol, 1.50 equiv.) was used instead of KOAc. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 4/1).

Amount: 53.1 mg, 0.115 mmol, 58%, **Physical aspect**: colourless gum. $\mathbf{R_f}$ (*n*-pentane/EtOAc = 4/1): 0.40. **^{1}H NMR** (400 MHz, acetone-d_6) δ 7.23 (d, *J* = 1.2 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 5.65 (dt, *J* = 15.0, 7.4 Hz, 1H), 5.48 (dt, *J* = 15.2, 6.9 Hz, 1H), 4.56 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.42 (t, *J* = 9.3 Hz, 1H), 4.20 – 4.06 (m, 6H), 3.56 (s, 2H), 3.48 (t, *J* = 7.5 Hz, 1H), 3.25 (dd, *J* = 9.1, 4.0 Hz, 1H), 2.58 (t, *J* = 7.2 Hz, 4H), 2.12 – 1.96 (m, 2H, *overlaps with solvent*), 1.29 – 1.15 (m, 9H), 0.92 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (101 MHz, acetone-d_6) δ 172.3, 169.6, 161.1, 130.5, 130.1, 130.0, 129.6, 128.4, 126.9, 109.7, 74.0, 61.8, 61.0, 52.8, 51.5, 43.6, 41.2, 37.6, 32.8, 24.6, 24.1, 14.7, 14.5. **HRMS (Orbitrap)** *m/z* calc. for [$C_{26}H_{36}O_7Na$] ([M+Na$^+$]) 483.2359, found 483.2348.

Note. While chemically inequivalent, carbon atoms beloning to the malonate moiety give rise to a single set of signals.

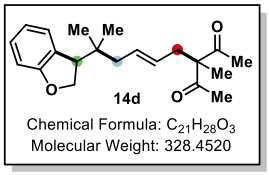
ethyl 1-((*E*)-5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-2-oxocyclohexane-1-carboxylate (14c).



The title compound was obtained from bromide **1a** (48.2 mg, 0.20 mmol, 1.00 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and ethyl 2-oxocyclohexane-1-carboxylate **13c** (95.6 µl, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (0.85 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP5**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 20/1 → 18/1).

Amount: 38.3 mg, 0.100 mmol, 50%, 50:50 dr. **Physical aspect**: colourless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 20/1): 0.40. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (ddt, *J* = 7.4, 1.5, 0.7 Hz, 1H), 7.12 (dddd, *J* = 7.9, 7.3, 1.4, 0.6 Hz, 1H), 6.82 (tdd, *J* = 7.4, 1.1, 0.5 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.48 (dtd, *J* = 14.6, 7.7, 6.8, 1.1 Hz, 1H), 5.38 (dt, *J* = 15.2, 7.0 Hz, 1H), 4.50 (dd, *J* = 9.3, 4.1 Hz, 1H), 4.42 (td, *J* = 9.2, 1.0 Hz, 1H), 4.22 – 4.12 (m, 2H), 3.19 (dd, *J* = 9.0, 4.0 Hz, 1H), 2.57 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.50 – 2.40 (m, 3H), 2.34 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.05 – 1.92 (m, 3H), 1.78 – 1.56 (m, 2H), 1.45 (ddd, *J* = 13.7, 11.9, 4.4 Hz, 1H), 1.24 (apt td, *J* = 7.1, 0.9 Hz, 3H), 0.89 (s, 3H), 0.83 (apt d, *J* = 1.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.8, 171.69, 171.67, 160.97, 130.36, 130.35, 128.4, 128.3, 128.03, 128.01, 126.5, 119.91, 109.56, 109.55, 73.3, 61.33, 61.32, 61.18, 61.15, 51.10, 51.08, 43.02, 43.01, 41.28, 41.27, 38.39, 38.38, 36.9, 35.9, 27.65, 27.64, 24.29, 24.27, 24.0, 22.6, 14.3. **HRMS (Orbitrap)** *m/z* calc. for [$C_{24}H_{32}O_4Na$] ([M+Na$^+$]) 407.2193, found 07.2197.

(*E*)-3-(5-(2,3-dihydrobenzofuran-3-yl)-5-methylhex-2-en-1-yl)-3-methylpentane-2,4-dione (14d).

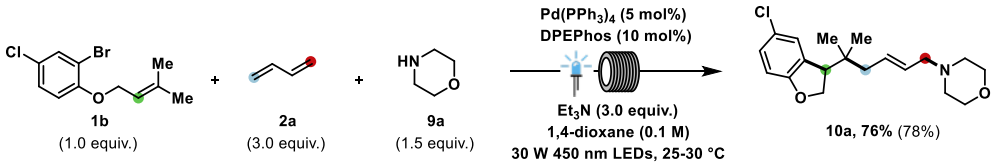


The title compound was obtained from bromide **1a** (48.2 mg, 0.20 mmol, 1.00 equiv.), 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) and pentan-2,4-dione **13d** (69.8 µl, 0.60 mmol, 3.00 equiv.) in dry 1,4-dioxane (0.85 ml) upon irradiation for 48 hours using 450 nm LEDs, according to **GP5**. The crude product was purified by flash column chromatography on silica (*n*-pentane/EtOAc = 10/1 → 9/1).

Amount: 37.6 mg, 0.114 mmol, 57%. **Physical aspect**: colourless gum. $\mathbf{R}_f$ (*n*-pentane/EtOAc = 9/1): 0.45. **^{1}H NMR** (599 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.4 Hz, 1H), 7.12 (td, *J* = 7.8, 1.4 Hz, 1H), 6.82 (td, *J* = 7.4, 1.0 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 5.53 (dddt, *J* = 15.0, 8.2, 7.1, 1.3 Hz, 1H), 5.21 (dtt, *J* = 14.8, 7.3, 1.3 Hz, 1H), 4.49 (dd, *J* = 9.3, 4.0 Hz, 1H), 4.41 (t, *J* = 9.2 Hz, 1H), 3.17 (dd, *J* = 9.1, 3.9 Hz, 1H), 2.57 (d, *J* = 7.2 Hz, 2H), 2.11 – 2.08 (m, 6H), 2.00 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.94 (dd, *J* = 14.1, 6.8 Hz, 1H), 1.30 (s, 3H), 0.88 (s, 3H), 0.84 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 206.91, 206.90,

160.9, 131.2, 128.5, 128.1, 127.1, 126.5, 119.9, 109.6, 73.2, 66.7, 51.3, 42.8, 37.9, 36.9, 26.81, 26.80, 24.3, 24.1, 18.3. **HRMS (Orbitrap)** *m/z* calc. for [$C_{21}H_{28}O_3Na$] ([M+Na^+]) 351.1931, found 351.1933.

Flow reaction



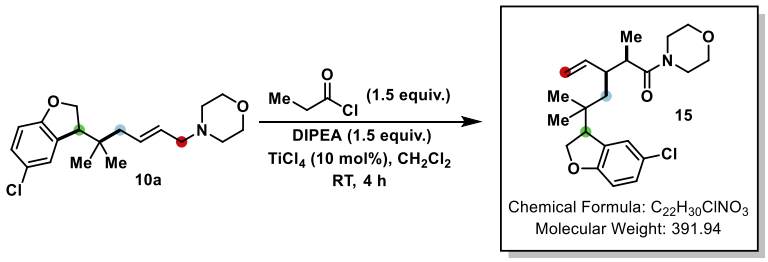
For a pictorial description of of the set-up procedure, please check the step by step graphical procedure section.

In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, DPEPhos (10.8 mg, 0.02 mmol, 10 mol%) and $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (1.70 ml), followed by bromide **1b** (55.1 mg, 0.20 mmol, 1.00 equiv.), morpholine **9a** (26.0 µl, 0.30 mmol, 1.50 equiv.), Et_3N (83.6 µl, 0.60 mmol,3.00 equiv.) and 1,3-butadiene 2 M in THF (300 µl, 0.60 mmol, 3.00 equiv.) were added under argon counterflow, then the vessel was sealed and stirred for 5 minutes. The solution was collected under argon counterflow using a plastic syringe and connected to the flow photochemical manifold. The optimal reactions parameters that were used are the following: flow rate: 66.7 µl/min, residence time: 30 minutes. The output solution was concentrated *in vacuo*, analyzed by ^1H NMR to determine the crude yield (78%, dibromomethane as standard with 30 s. relaxation time), then loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc/Et_3N = 9/1/0.5), affording the product **10a** (51.1 mg, 152 mmol, 76%) as a colourless gum.

The same procedure, except that the reaction was irradiated for 30 minutes *in batch* using the standard photochemical, delivered the product in 36% yield (determined by ^1H NMR using dibromomethane as standard, with relaxation time of 30 s.).

Notes and troubleshooting. The precipitation of insoluble ammonium salts in the flow reaction as consequence of the reaction progression can lead to clogging of the system. Therefore, when conducting the reaction on >0.2 mmol scale, we opted for split injection of approx. 0.2 mmol, followed by a "cleaning" run with CH_2Cl_2 (approx. 2 ml), which dissolves the precipitated substances.

Synthetic applications



(*syn*)-5-(5-chloro-2,3-dihydrobenzofuran-3-yl)-2,5-dimethyl-1-morpholino-3-vinylhexan-1-one (15).

In an oven-dried Schlenk tube, **10a** (73.2 mg, 0.22 mmol, 1.00 equiv.) was charged under air, then the vessel was evacuated and back-filled with argon three times, then dry CH_2Cl_2 (1.5 ml) and DIPEA (57.0 µl, 0.33 mmol, 1.50 equiv.) was added. To the well-stirred solution, $TiCl_4$ (2.4 µl, 0.022 mmol, 10 mol%) was added (*the solution turned immediately dark red*) and the solution was stirred for 5 minutes, then a solution of propionyl chloride (28.6 µl, 0.33 mmol, 1.50 equiv.) in dry CH_2Cl_2 (300 µl) was added dropwise over 5 minutes. The reaction was stirred at room temperature for 4 hours, then quenched with NaOH 1M (5 ml), partitioned between CH_2Cl_2/H_2O (1/1, 30 ml), then the water layer was extracted twice with CH_2Cl_2 (15 ml each time). The combined organic layers were washed once with brine (30 ml), then dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude was purified by flash column chromatography on silica (CH_2Cl_2/EtOAc = 9/1 → 7/1) and **15** was obtained as an inseparable mixture (50:50) of diastereoisomers. The relative stereochemistry of the γ,δ-unsaturated amide was assigned based upon literature precedence[31] and analysis of the *Zimmerman-Traxler* like transition state.

Amount: 78.3 mg, 0.200 mmol, 92%, 97:3 *syn:anti*. **Physical aspect**: colourless gum. $\mathbf{R_f}$ (CH_2Cl_2/EtOAc = 6/1): 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 2.2 Hz, 1H, *single diastereoisomer*), 7.14 (d, *J* = 2.3 Hz, 1H, *single diastereoisomer*), 7.06 (dt, *J* = 8.4, 1.8 Hz, 1H), 6.65 (apt dd, *J* = 8.5, 4.1 Hz, 1H), 5.75 (dtd, *J* = 17.7, 9.4, 6.5 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.52 – 4.33 (m, 2H), 3.69 – 3.54 (m, 6H), 3.51 – 3.42 (m, 2H), 3.22 (apt ddd, *J* = 17.3, 9.0, 4.1 Hz, 1H), 2.62 (p, *J* = 6.8 Hz, 1H), 2.43 – 2.32 (m, 1H), 1.57 (dd, *J* = 14.3, 1.9 Hz, 1H, *single diastereoisomer*), 1.47 – 1.37 (m, 1H), 1.30 – 1.21 (m, 1H), 1.08 (apt dd, *J* = 6.8, 4.7 Hz, 3H), 0.95 (s, 3H, *single diastereoisomer*), 0.93 (s, 3H, *single diastereoisomer*), 0.83 (s, 3H, *single diastereoisomer*), 0.81 (s, 3H, *single diastereoisomer*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 174.0, 159.69, 159.68, 142.7, 130.3, 130.2, 128.2, 126.6, 126.5, 124.5, 115.9, 115.8, 110.40, 110.35, 74.1, 73.9, 67.1, 66.8, 52.2, 51.4, 46.4, 43.1, 43.0, 42.1, 40.8, 40.8, 40.2, 39.6, 37.0, 36.8, 25.3, 24.9, 24.6, 24.1, 14.61, 14.56. **HRMS (Orbitrap)** *m/z* calc. for [$C_{22}H_{30}NO_3{}^{35}ClNa$] ([M+Na$^+$]) 414.1806, found 414.1801.

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[31] T. P. Yoon, V. M. Dong, D. W. C. MacMillan, *J. Am. Chem. Soc.*, 1999, **121**, 9726–9727.

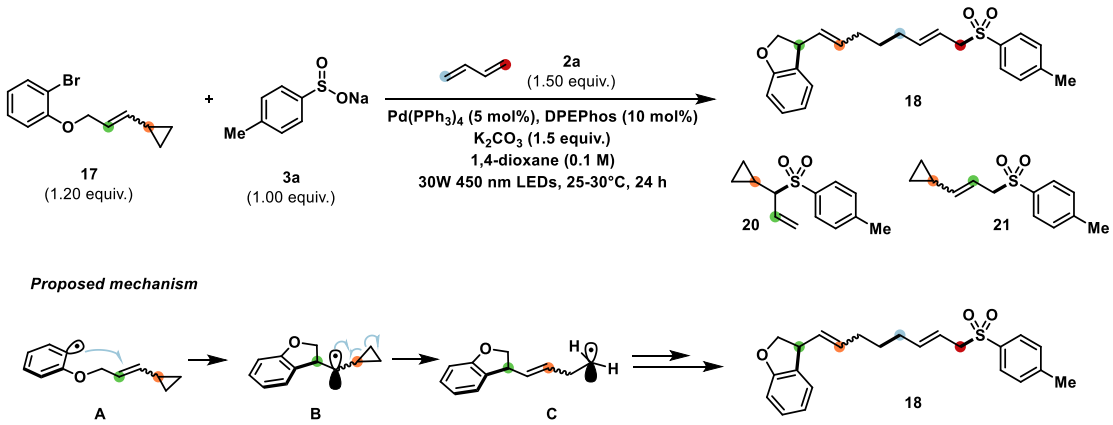
(*E*)-3-(2-methylhex-4-en-2-yl)-2,3-dihydrobenzofuran (16).

In an oven-dried Schlenk tube, **4a** (101.0 mg, 0.27 mmol, 1.00 equiv.) and Pd(dppe)Cl_2 (15.5 mg, 0.027 mmol, 10 mol%) were charged under argon, then dry THF (2.7 ml) was added. To the well-stirred solution, $LiEt_3BH$ 1.7M in THF (323 µl, 0.546 mmol, 2.00 equiv.) was added dropwise, then the reaction was stirred for 60 minutes at room temperature, then quenched by carefully adding NaOH 2 M (5 ml). The reaction was partitioned between CH_2Cl_2/H_2O (1:1, 30 ml), then the water layer was extracted twice wit CH_2Cl_2 (15 ml each time), then the combined organic extracts were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude was purified by flash column chromatography on silica (*n*-pentane/CH_2Cl_2 = 7/1 → 5/1).

Amount: 45.8 mg, 0.212 mmol, 78%. **Physical aspect**: colourless thick oil. $\mathbf{R_f}$ (*n*-pentane 100%): 0.25. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.4 Hz, 1H), 7.14 (td, *J* = 7.7, 1.4 Hz, 1H), 6.84 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.54 – 5.41 (m, 2H), 4.53 (dd, *J* = 9.3, 4.2 Hz, 1H), 4.44 (t, *J* = 9.2 Hz, 1H), 3.25 (dd, *J* = 9.1, 4.2 Hz, 1H), 2.06 – 1.95 (m, 2H), 1.77 – 1.63 (m, 3H), 0.92 (s, 3H), 0.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 128.5, 128.3, 128.2, 127.2, 126.5, 119.9, 109.5, 73.3, 50.8, 43.3, 36.9, 24.3, 23.9, 18.3. **HRMS (Orbitrap)** *m/z* calc. for [$C_{15}H_{20}OAg$] ([M+Ag^+]) 323.0560, found 323.0560.

Mechanistic studies

Radical probe experiment



In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the *p*-toluenesulfinate **3a** (35.6 mg, 0.20 mmol, 1.00 equiv.), K_2CO_3 (41.5 mg, 0.30 mmol, 1.50 equiv.), DPEPhos (10.8 mg, 0.02 mmol, 10 mol%) and $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (1.85 ml), followed by bromide **17** (60.8 mg, 0.24 mmol, 1.20 equiv.) and 1,3-butadiene 2 M in THF (150 µl, 0.30 mmol, 1.50 equiv.) were added under argon counterflow, then the vessel was sealed and irradiated with the standard setup at 455 nm for 24 hours. The reaction was concentrated *in vacuo*, then loaded on silica and purified by flash column chromatography on silica (*n*-pentane/EtOAc = 6/1), affording a set of three fractions which allowed identification of the main reaction products.

18 (Mixture of *E,E and Z,E* isomers) (8.8 mg, 0.023, 12%).

^{1}H NMR (599 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.32 (tt, *J* = 7.8, 0.8 Hz, 2H), 7.13 (ddddd, *J* = 8.1, 7.4, 2.0, 1.4, 0.8 Hz, 1H), 7.08 (dddd, *J* = 8.5, 4.4, 1.7, 0.8 Hz, 1H), 6.87 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.79 (dtd, *J* = 8.0, 1.2, 0.6 Hz, 1H), 6.06 – 5.96 (m, 1H), 5.66 (dt, *J* = 13.9, 7.0 Hz, 1H, single isomer), 5.60 (dtd, *J* = 15.2, 6.7, 0.8 Hz, 1H), 5.56 (s, 1H), 5.49 – 5.44 (m, 1H), 5.44 – 5.38 (m, 1H), 4.68 (ddd, *J* = 9.2, 8.7, 1.3 Hz, 1H), 4.17 (td, *J* = 8.5, 3.5 Hz, 1H), 4.10 – 4.04 (m, 1H), 3.77 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.72 (dq, *J* = 7.3, 0.9 Hz, 1H), 2.44 (s, 3H, single isomer), 2.42 (s, 3H, single isomer), 2.09 (q, *J* = 8.2 Hz, 1H), 2.06 – 2.00 (m, 2H), 2.00 – 1.94 (m, 1H), 1.48 (p, *J* = 7.5 Hz, 1H), 1.39 (p, *J* = 7.4 Hz, 1H). Multiplicity could be apparent due to presence of *E*/*Z* isomers.

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 141.2, 139.7, 137.3, 132.6, 132.4, 130.3, 130.2, 130.10, 130.05, 129.81, 129.75, 129.4, 128.64, 128.61, 128.51, 128.49, 124.93, 124.91, 120.7, 116.6, 115.9, 109.7, 76.80, 76.79, 60.5, 60.3, 46.10, 46.07, 32.1, 32.0, 31.9, 31.7, 28.7, 28.4, 21.78, 21.75.

20 (S_N2' reaction with phenol displacement).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.85 (ddd, *J* = 17.1, 10.3, 7.9 Hz, 1H), 5.35 (dt, *J* = 10.3, 1.0 Hz, 1H), 5.24 (dt, *J* = 17.1, 1.2 Hz, 1H), 2.97 (ddt, *J* = 9.0, 7.8, 1.0 Hz, 1H), 2.44 (s, 3H), 1.06 (dddd, *J* = 13.0, 8.9, 8.1, 4.9 Hz, 1H), 0.67 – 0.54 (m, 2H), 0.36 – 0.22 (m, 1H), 0.16 (dtd, *J* = 9.7, 5.0, 4.6, 2.3 Hz, 1H).

21 (S_N2 reaction with phenol displacement - *E* isomer).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.36 – 7.31 (m, 2H), 5.44 (dt, *J* = 15.2, 7.5 Hz, 1H), 4.99 (ddt, *J* = 15.3, 8.9, 1.1 Hz, 1H), 3.69 (dd, *J* = 7.5, 1.1 Hz, 2H), 2.45 (s, 3H), 1.38 (ddq, *J* = 13.1, 8.6, 4.7 Hz, 1H), 0.74 – 0.66 (m, 2H), 0.28 (dt, *J* = 6.6, 4.5 Hz, 2H).

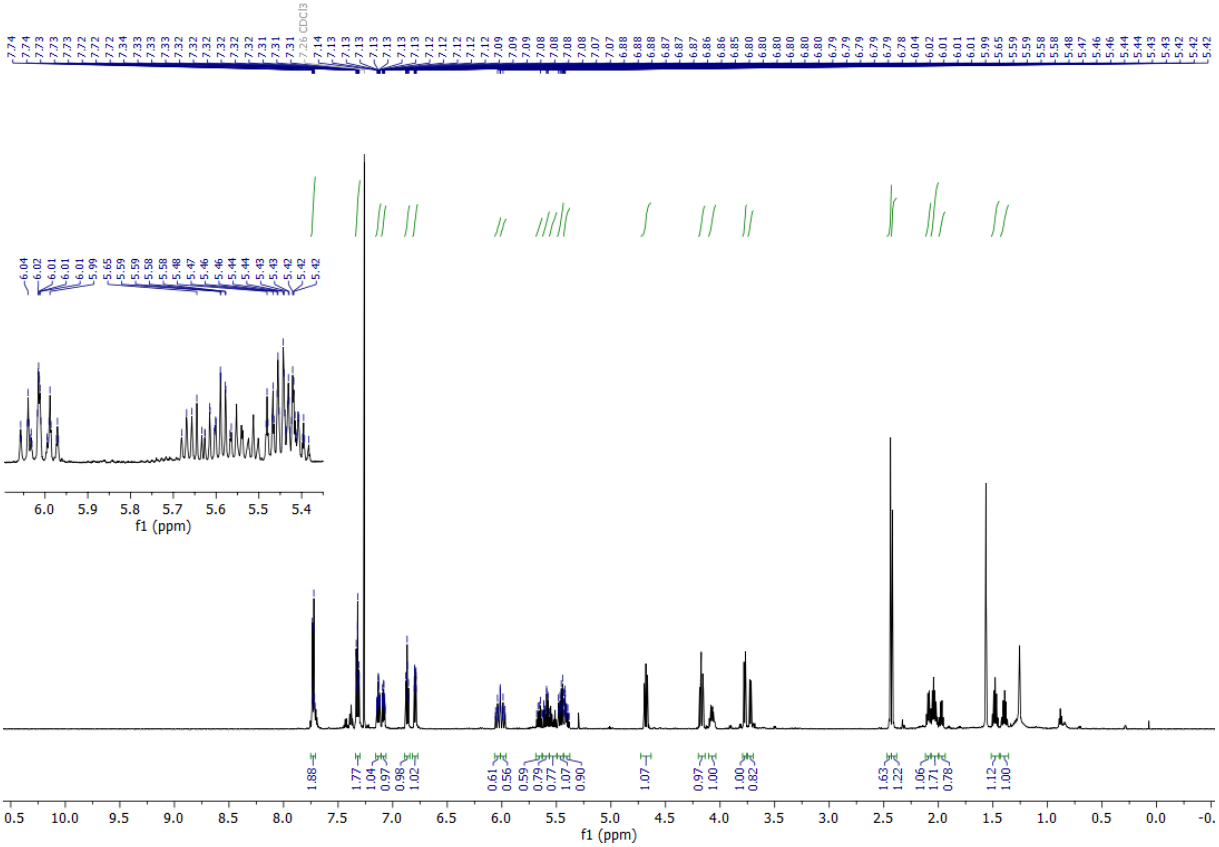


Figure S7 ^{1}H NMR (599 MHz, $CDCl_3$) of compound **18**.

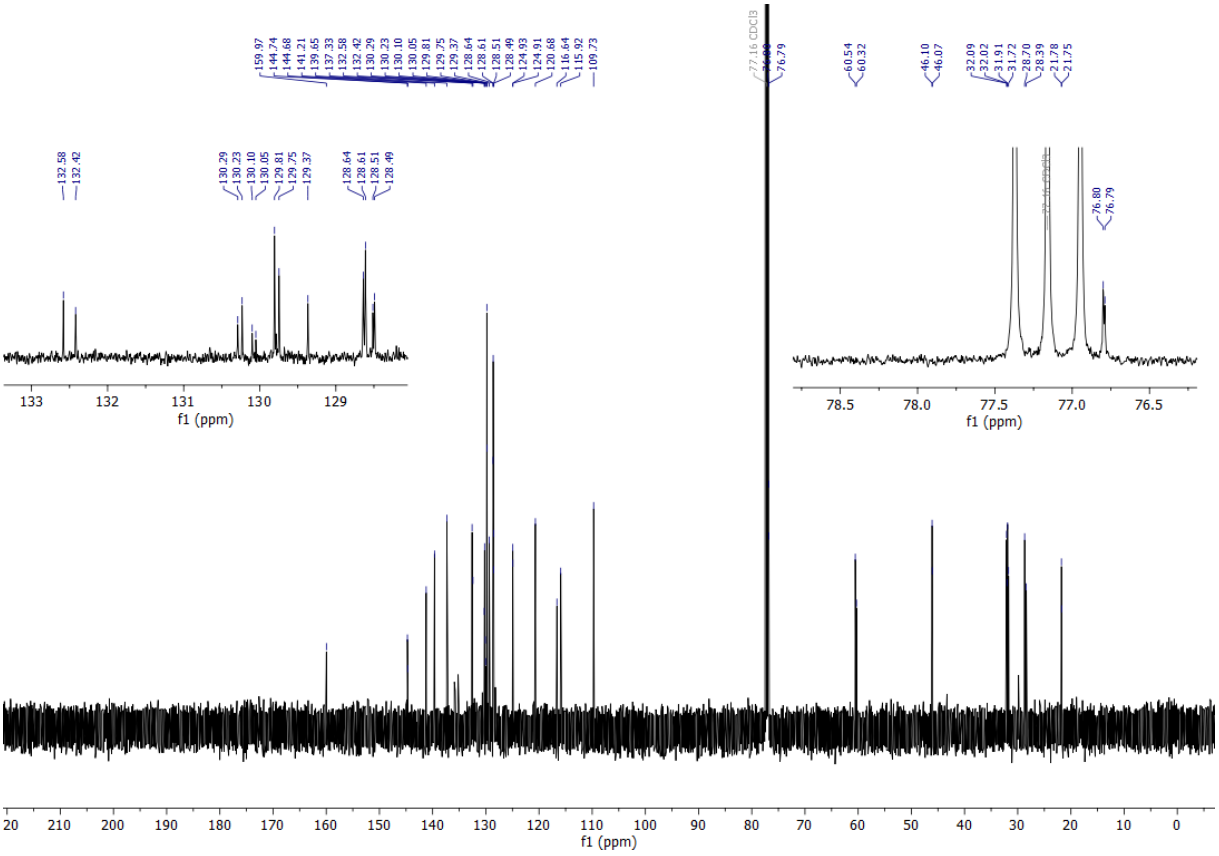


Figure S8 ^{13}C NMR (599 MHz, $CDCl_3$) of compound **18**.

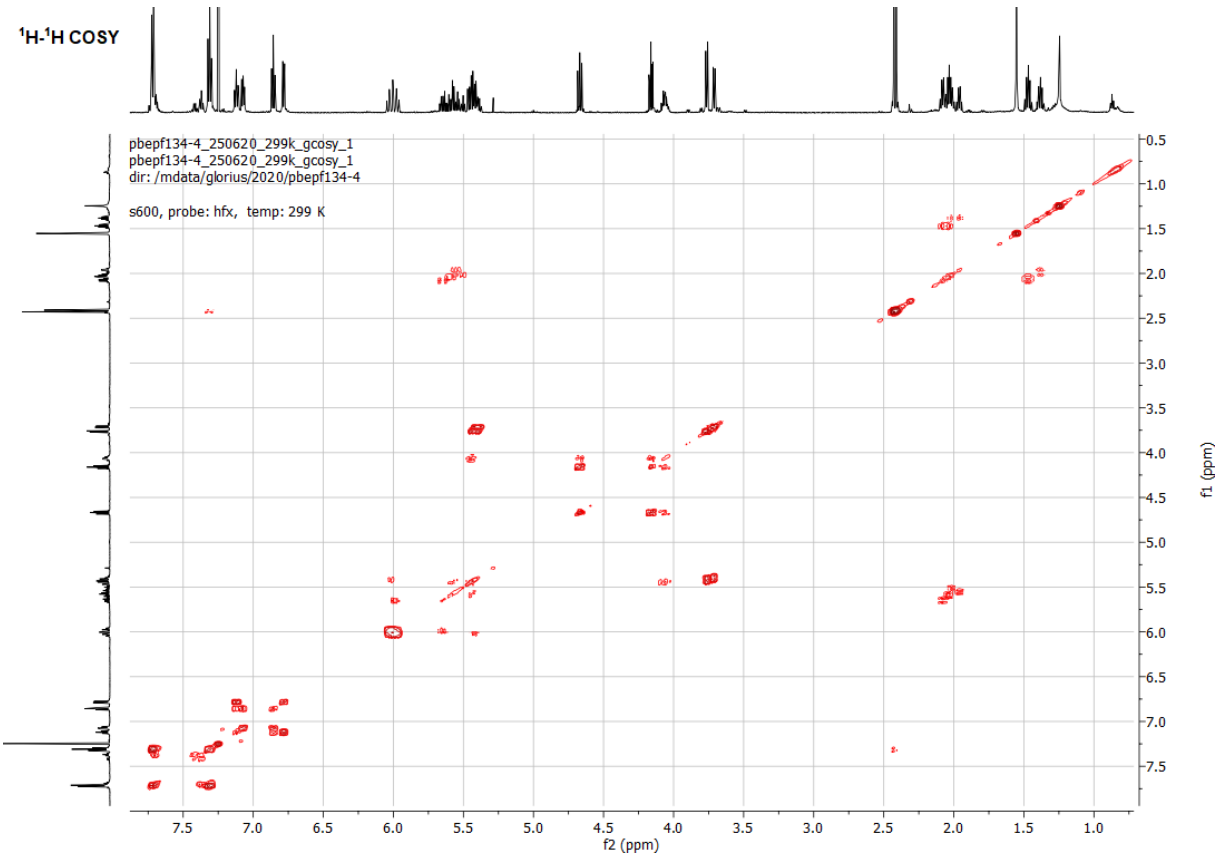


Figure S9 ^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$) of compound **18**.

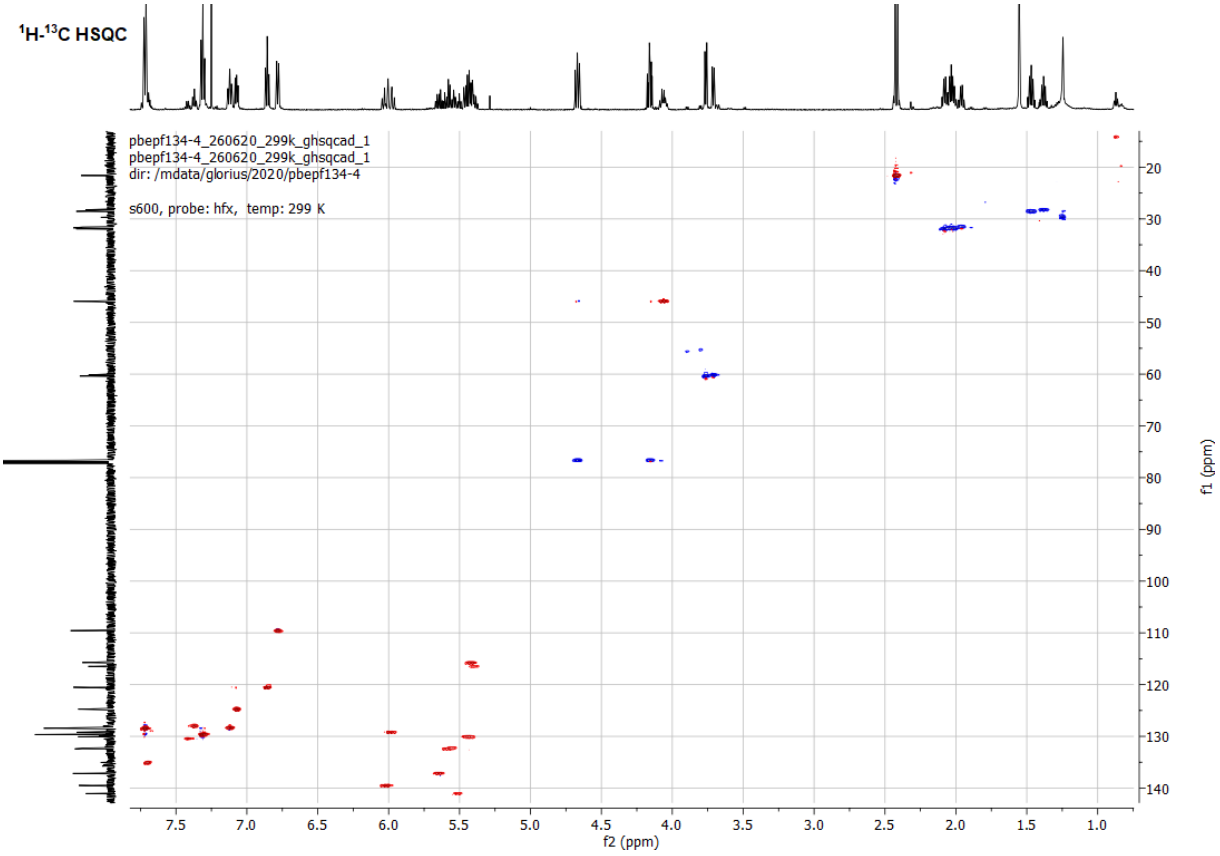


Figure S10 ^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$) of compound **18**.

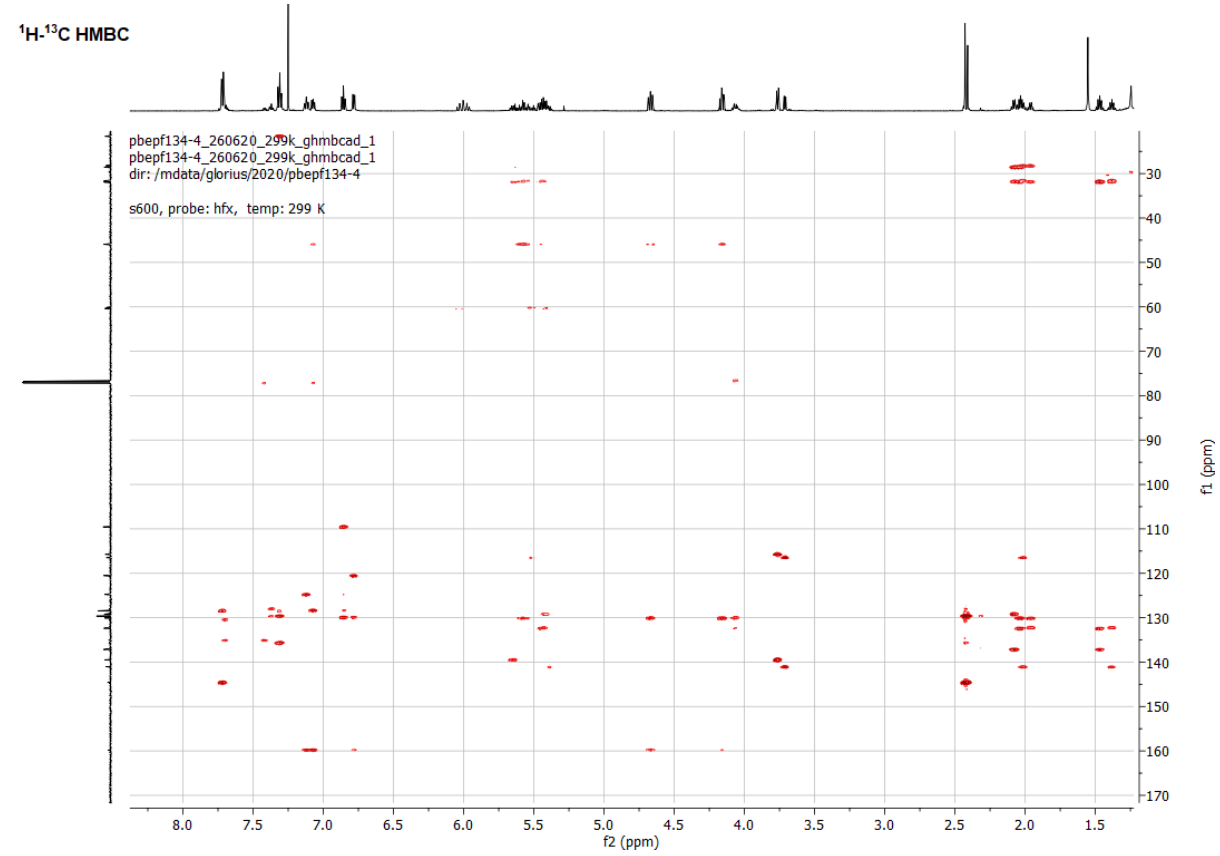


Figure S11 ^{1}H-^{13}C HHMC NMR (599 MHz, $CDCl_3$) of compound **18**.

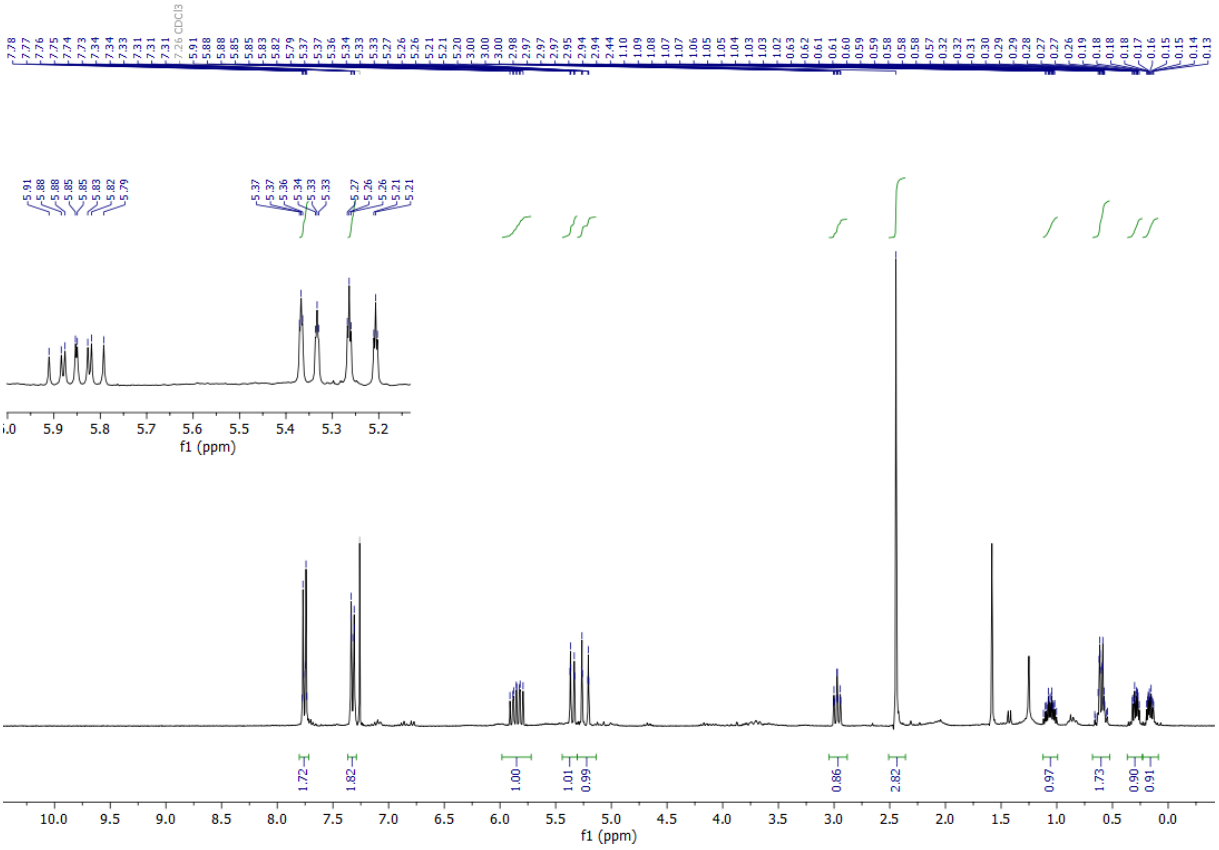


Figure S12 ^{1}H NMR (599 MHz, $CDCl_3$) of compound **20**.

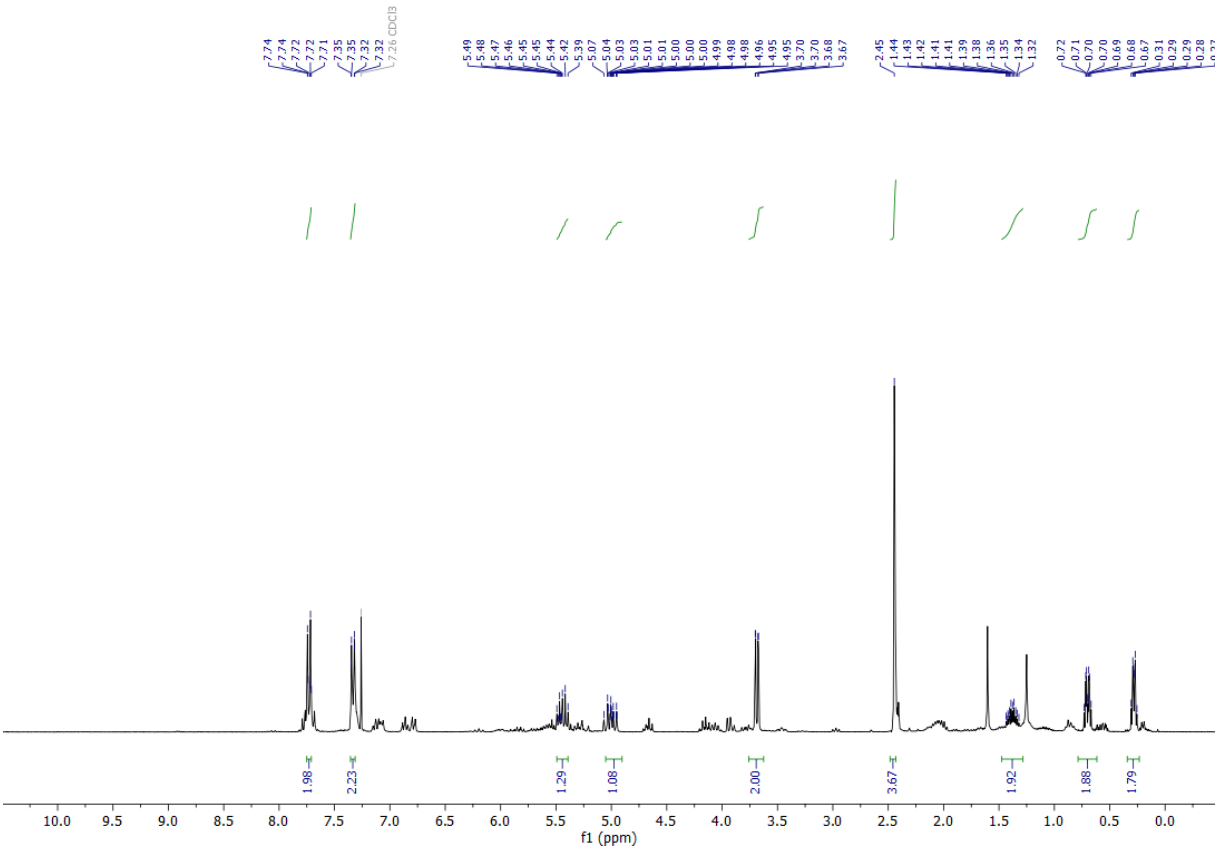
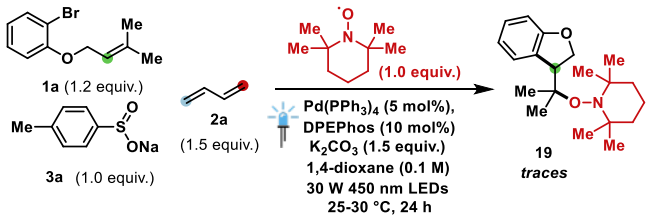


Figure S13 ^{1}H NMR (599 MHz, $CDCl_3$) of compound **21**.

Comment on the results: The ring-opening of the cyclopropyl system (**18**) could be clearly detected thanks to the absence of the typically low-shifted signals. This confirms that the ring closure proceeds *via* the formation of a carbon radical species. An approximately 1:1 mixture of *E,E* and *E,Z* isomers was obtained, as confirmed using 2D NMR.

TEMPO trapping experiment

Catalytic experiment



In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the *p*-toluenesulfinate **3a** (17.8 mg, 0.10 mmol, 1.00 equiv.), K_2CO_3 (20.7 mg, 0.15 mmol, 1.50 equiv.), DPEPhos (5.4 mg, 0.01 mmol, 10 mol%) and $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5 mol%) and TEMPO (15.6 mg, 0.10 mmol, 1.00 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.93 ml), followed by bromide **1a** (28.9 mg, 0.12 mmol, 1.20 equiv.) and 1,3-butadiene 2 M in THF (75 µl, 0.15 mmol, 1.50 equiv.) were added under argon counterflow, then the vessel was sealed and irradiated with the standard setup at 450 nm for 24 hours. The reaction was filtered over a short pad of silica, rinsing with EtOAc, then concentrated and analyzed using GC-MS and HRMS, thus allowing the detection of adduct **19**.

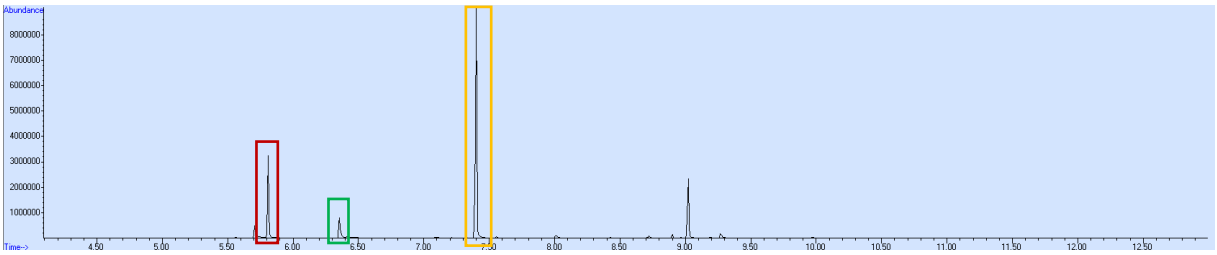
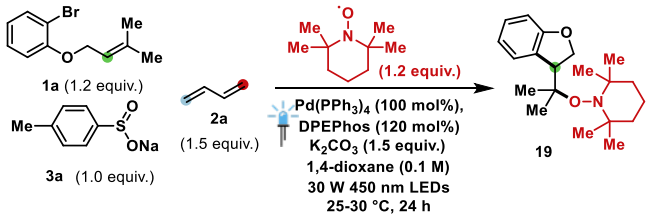


Figure S14 HRMS trace of the crude reaction product. In **red** box: TEMPO; in **green** box: adduct **19**; in **orange** box: bromide **1a**.

Stoichiometric experiment



In an oven-dried Schlenk tube equipped with an oval-shaped PTFE-coated stirring bar, the *p*-toluenesulfinate **3a** (17.8 mg, 0.10 mmol, 1.00 equiv.), K_2CO_3 (20.7 mg, 0.15 mmol, 1.50 equiv.), DPEPhos (64.8 mg, 0.12 mmol, 120 mol%) and $Pd(PPh_3)_4$ (115.6 mg, 0.10 mmol, 100 mol%) and

TEMPO (18.8 mg, 0.12 mmol, 1.20 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon four times. Dry 1,4-dioxane (0.93 ml), followed by bromide **1a** (28.9 mg, 0.12 mmol, 1.20 equiv.) and 1,3-butadiene 2 M in THF (75 µl, 0.15 mmol, 1.50 equiv.) were added under argon counterflow, then the vessel was sealed and irradiated with the standard setup at 450 nm for 24 hours. The reaction was filtered and analysed by means of GC-MS and ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography on silica (n-pentane/EtOAc/MeOH = 100/1/0 → 9/1/0 → 0/1/0 → 0/19/1), affording **19** (26.0 mg, 0.082 mmol, 68%), triphenylphospine oxide (70.2 mg, 0.252 mmol, 63%) and DPEPhos bis-oxide (69.0 mg, 0.120 mmol, 100%).

19: ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.83 (td, *J* = 7.4, 1.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 4.74 (dd, *J* = 9.4, 5.4 Hz, 1H), 4.54 (t, *J* = 9.5 Hz, 1H), 3.95 (dd, *J* = 9.6, 5.4 Hz, 1H), 1.60 – 1.48 (m, 5H), 1.39 (s, 3H), 1.32 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.17 (s, 3H), 1.16 (s, 3H), 1.16 (s, 3H), 1.13 (s, 3H), 1.12 (s, 3H). The experimental data are in agreement with the literature report.[32]

Triphenylphosphine oxide: ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 6H), 7.52 – 7.48 (m, 3H), 7.45 – 7.40 (m, 6H). The experimental data are in agreement with the literature report.[33]

DPEPhos bis-oxide: ^{1}H NMR (599 MHz, $CDCl_3$) δ 7.73 – 7.57 (m, 5H), 7.49 – 7.43 (m, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.13 (dddd, *J* = 8.2, 7.3, 1.8, 0.8 Hz, 1H), 7.06 (tdd, *J* = 7.5, 1.8, 1.1 Hz, 1H), 6.03 (ddd, *J* = 8.3, 4.9, 1.0 Hz, 1H). The experimental data are in agreement with the literature report.[34]

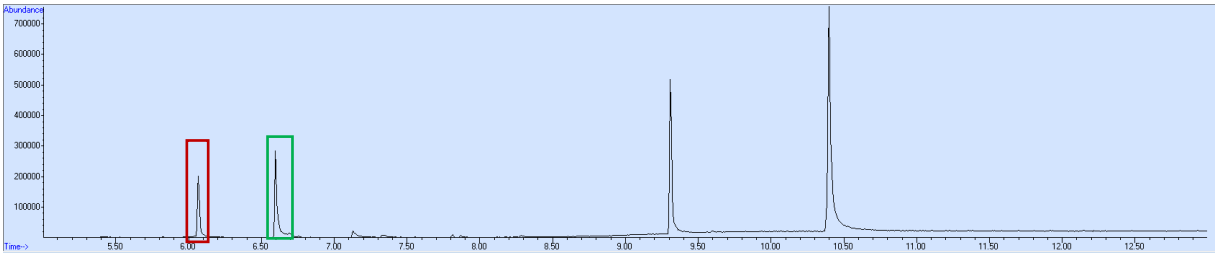


Figure S15 HRMS trace of the crude reaction product. In **red** box: TEMPO; in **green** box: adduct **19**. At higher retention times PPh_3 and triphenylphosphine oxide are detected.

[32] T. Nagashima, A. Rivkin, D. P. Curran, *Can. J. Chem.,* 2000, **78**, 791-799.

[33] R. Shen, H. Liu, *RSC Adv*., 2016, **6**, 33731-33739.

[34] M. Congiu, M. Alamiry, O. Moudam, S. Ciorba, P. R. Richardson, L. Maron, A. C. Jones, B. S. Richards, N. Robertson, *Dalton Trans*., 2013, **42**, 13537-13545.

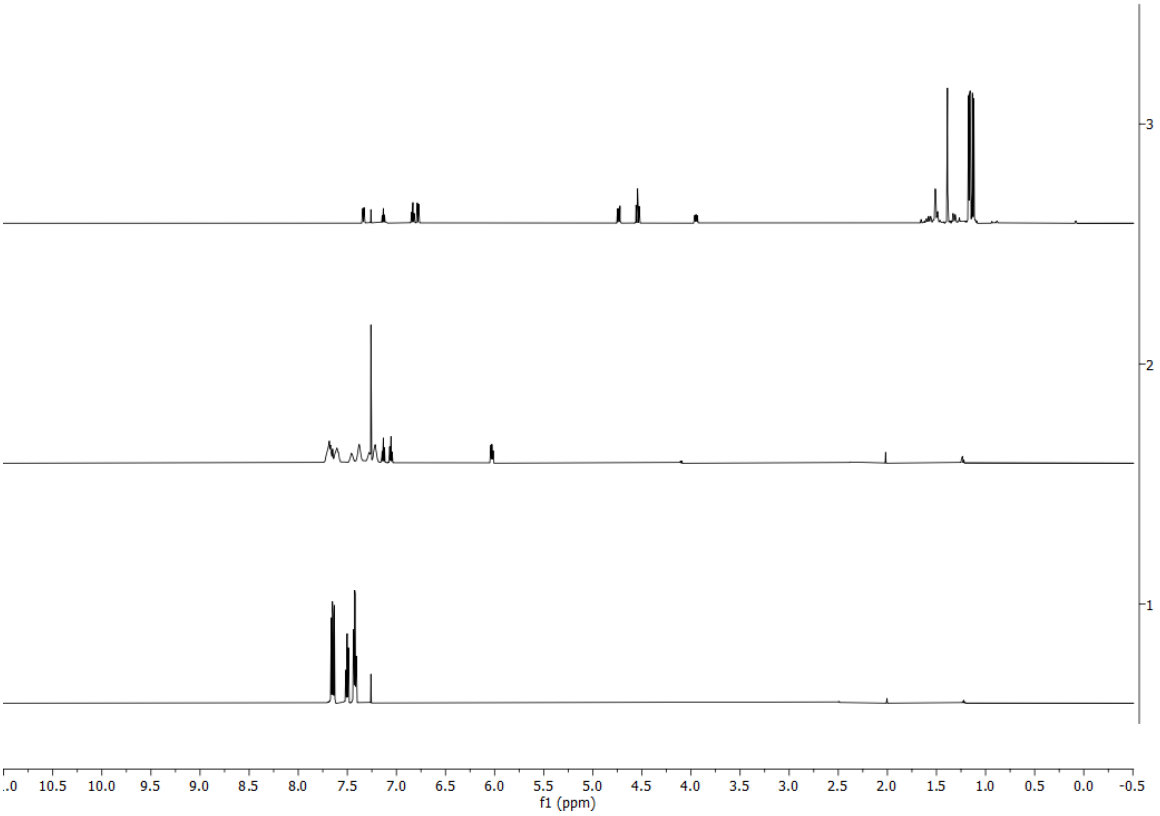


Figure S16 ^{1}H NMR spectra (599 MHz) of triphenylphosphine oxide (1), DPEPhos bis-oxide (2) and TEMPO-adduct **19** (3) isolated from the reaction.

Comment on results: The isolation of the cyclized TEMPO-adduct **19** even in the presence of the radical scavenger TEMPO testifies that the ability of generating aryl radicals and further intramolecular cyclization – which is faster than intermolecular radical-radical coupling – is not hampered by the presence of TEMPO. On the other hand, by observing the presence of residual bromide **1a** under catalytic conditions, in comparison with full consumption under stoichiometric ones, it appears that TEMPO prevents the catalyst turnover, likely by intercepting the intermediate radical and preventing further Pd(II)-Pd(0) elemental steps to occur.

UV-visible reaction analysis

UV-visible absorption spectra were recorded on a Jasco V-650 spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in Starna Fluorometer Semi-Micro quartz cuvettes (volume: 1.4 ml, path length: 10 mm) equipped with a PTFE-stopper. The spectra have been acquired from 300 to 700 nm using 0.5 nm steps. The 1,4-dioxane solutions were prepared using dry and degassed solvent under argon atmosphere, according to the reaction concentration (**1a**, 0.12 M; **2a**, 0.15 M; **3a**, 0.10 M, $Pd(PPh_3)_4$, 0.005 M; DPEPhos, 0.01 M).

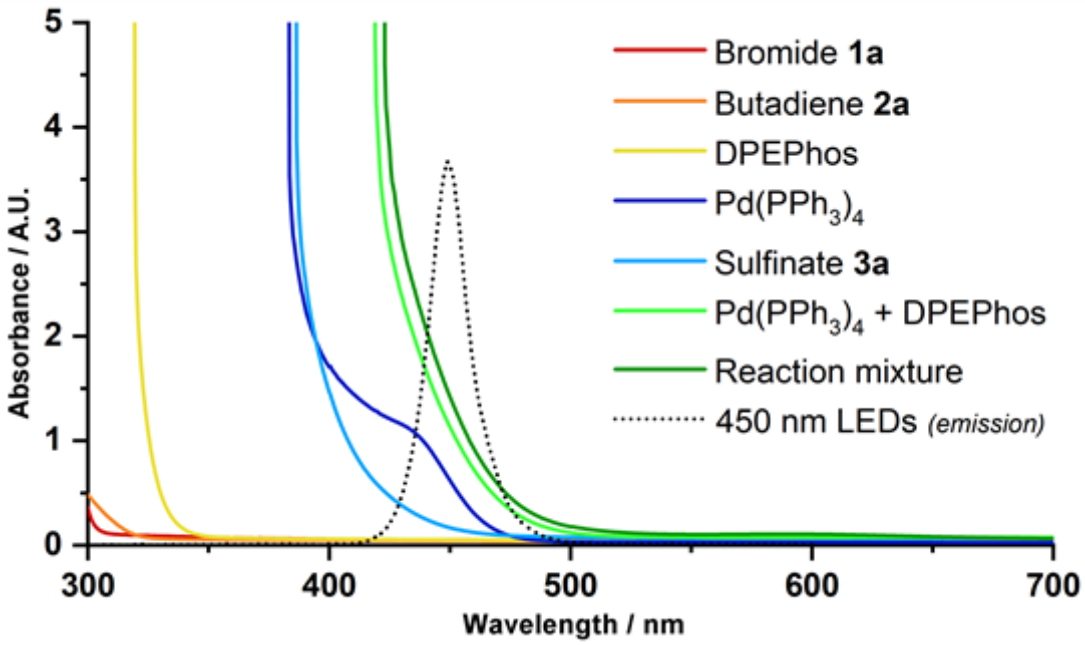


Figure S17 UV-visible spectrum of the reaction components.

Comment on the results: A shown in **Figure S17,** the only species that has considerable absorption at the irradiation wavelength (450 nm) is $Pd(PPh_3)_4$ or the $Pd(PPh_3)_4$/DPEPhos mixture. Furthermore, the absorption profile of the reaction mixture overlaps with the $Pd(PPh_3)_4$/DPEPhos mixture, thus suggesting that metal/ligand system is responsible for the catalytic activity of the process. Interestingly, a red shift of the absorption band is observed when DPEPhos is used as ligand, thus reinforcing the notion that bidentate ligands can enhance the photocatalytic ability of palladium by influencing its absorption in the visible region.

Fluorescence analysis

Fluorescence spectra were recorded on a Jasco FP-8300 spectrofluorometer. The following parameters were employed: excitation bandwidth = 5 nm, data interval = 0.2 nm, scan speed = 500 nm·min^{-1}, response time = 0.2 sec. Excitation were performed at 450 nm (maximum of the reaction light source), emission was measured in the 500-700 nm range. The samples were measured in Hellma fluorescence QS quartz cuvettes (chamber volume = 1.4 mL, H × W × D = 46 mm × 12.5 mm, 12.5 mm) fitted with a PTFE stopper. The 1,4-dioxane solutions were prepared using dry and degassed solvent under argon atmosphere, where $Pd(PPh_3)_4$ (10^{-3} M) and DPEPhos ($2{\cdot}10^{-3}$ M) were dissolved. The indicated amounts of **1b** were added under argon.

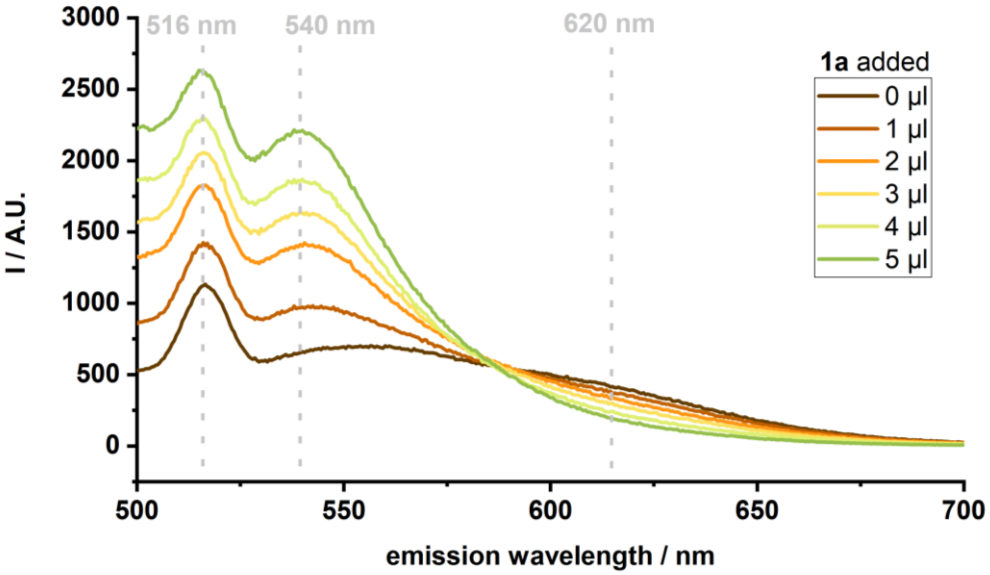
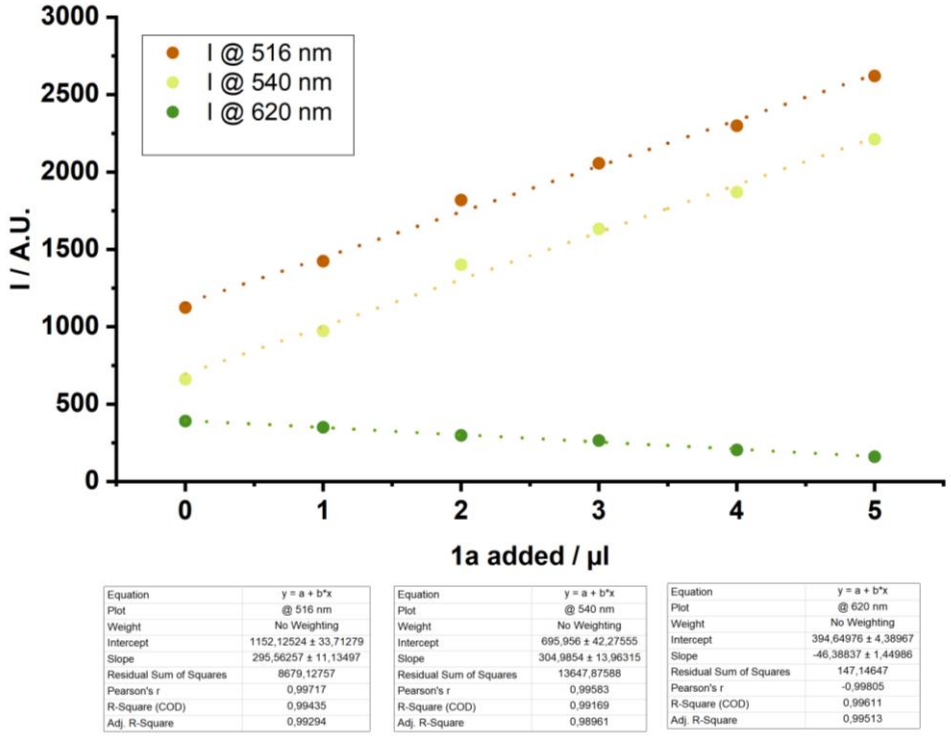


Figure S18 Fluorescence spectrum of $Pd(PPh_3)_4$/DPEPhos mixtures upon addition of increasing amounts of **1a**.



Equation	y = a + b*x
Plot	@ 516 nm
Weight	No Weighting
Intercept	1152,12524 ± 33,71279
Slope	295,56257 ± 11,13497
Residual Sum of Squares	8679,12757
Pearson's r	0,99717
R-Square (COD)	0,99435
Adj. R-Square	0,99294

Equation	y = a + b*x
Plot	@ 540 nm
Weight	No Weighting
Intercept	695,956 ± 42,27555
Slope	304,9854 ± 13,96315
Residual Sum of Squares	13647,87588
Pearson's r	0,99583
R-Square (COD)	0,99169
Adj. R-Square	0,98961

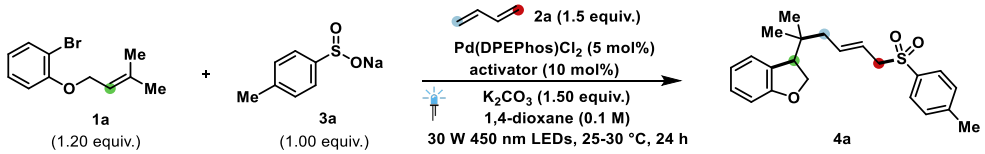
Equation	y = a + b*x
Plot	@ 620 nm
Weight	No Weighting
Intercept	394,64976 ± 4,38967
Slope	-46,38837 ± 1,44986
Residual Sum of Squares	147,14647
Pearson's r	-0,99805
R-Square (COD)	0,99611
Adj. R-Square	0,99513

Figure S19 Plot of the measured intensities at 516 (●), 540 (●) and 620 nm (●) at different additions of **1a**.

Comment on the results: Upon increasingly high amounts of **1a**, instead of a quenching of palladium fluorescence, a linear growth of the two bands with maxima at 516 nm and 540 nm, respectively, could be observed (**Figure S19**). This most likely indicates a chemical reaction which causes an increase in the concentration of the species responsible of the emission. In comparison with classical photocatalysts (*e.g.* Ir-based), palladium species can undergo facile ligand de-coordination and re-binding, thus complicating their behaviour analysis. On the other hand, the

much weaker band which we could tentatively locate around 620 nm decreases in intensity,[35] thus indicating either reaction or actual fluorescence quenching. Furthermore, we can observe the presence of an isosbestic point, which suggests that the two emitting species are stoichiometrically related. In conclusion, the observed behaviour strongly suggests that **1a** interacts (*e.g.* from Pd(0) to Pd(I) or similar) in solution with the palladium system, thus influencing its fluorescence.

In-situ generation of Pd(0)-DPEPhos complex



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, sodium *p*-toluenesulfinate (17.8 mg, 0.10 mmol, 1.00 equiv.), Pd(DPEPhos)Cl_2 (3.6 mg, 0.005 mmol, 5 mol%) and K_2CO_3 (20.8 mg, 0.15 mmol, 1.50 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon three times. Dry 1,4-dioxane (500 µl) was added, then to the vigorously stirred suspension was added the potential activator (10 mol%) and the system was allowed reacting at room temperature under argon for 5 minutes. A 1,4-dioxane solution of bromide **1a** (28,.9 mg, 0.12 mmol, 1.20 equiv.) and 1,3-butadiene 2 M in THF (75 µl, 0.15 mmol, 1.50 equiv.) was added, then the vessel was sealed and irradiated with the standard set-up (30 W, 450 nm LEDs) for 24 hours. The crude reaction was filtered through a short pad of silica, eluting with EtOAc. The volatiles were removed *in vacuo*, then the reaction was analyzed by ^{1}H NMR, using dibromomethane as internal standard (relaxation delay = 30 s).

Results:

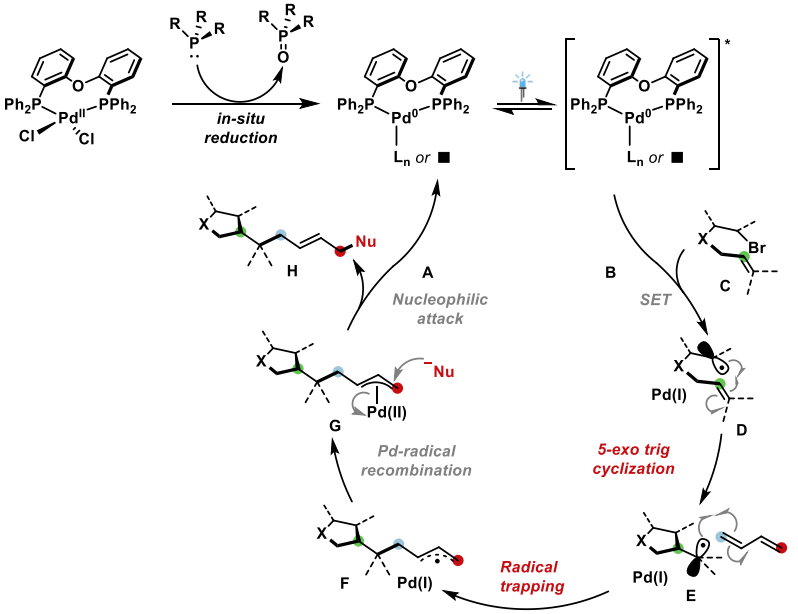
■ <30%; ■ 30-39%; ■ 40-49%; ■ 50-59%; ■ <60-69%; ■ 70-79%; ■ >80%.

Table S7. Results of the *in-situ* activation from Pd(II)

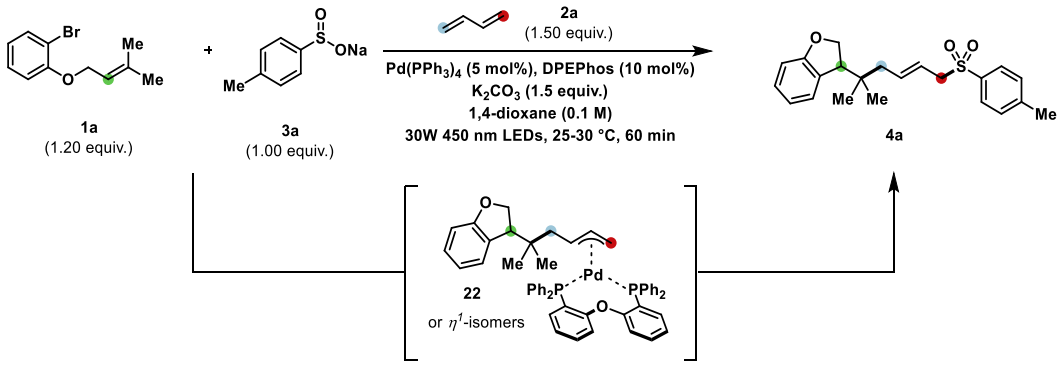
Entry	Additive	Yield %
1	---	<5
2	DIBAL-H (10 mol%)	<5
3	PPh_3 (10 mol%)	60
4	DPEPhos (10 mol%)	62
5	PCy_3 (10 mol%)	54
6	dppe (10 mol%)	<5
7	$NH_2NH_2{\cdot}H_2O$	<5
8	$NaBH_4$ (10 mol%)	<5

[35] D. Kurandina, M. Rivas, M. Radzhabov, V. Gevorgyan, *Org. Lett.*, 2018, **20**, 357-360.

Comment on the results: While numerous reducing species were attempted to promote the formation of catalytically competent Pd(0) species (see catalytic cycle proposed below), phosphines proved to be the only suitable species among the ones attempted (**Table S7**). The identity of the phosphine proved to be of little influence, except in the case of bidentate species that can compete with DPEPhos, which caused disturbance of the desired reaction. Such findings corroborate the idea that Pd-DPEPhos ligated species are catalytically active.



Mass detection of reaction intermediates



In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, sodium *p*-toluenesulfinate (17.8 mg, 0.10 mmol, 1.00 equiv.), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 5 mol%), DPEPhos (5.4 mg, 0.010 mmol, 10 mol%) and K_2CO_3 (20.8 mg, 0.15 mmol, 1.50 equiv.) were charged under air, then the vessel was evacuated and back-filled with argon three times. Dry 1,4-dioxane (925 µl) was added, followed by bromide **1a** (28.9 mg, 0.12 mmol, 1.20 equiv.) and 1,3-butadiene 2 M in THF (75 µl, 0.15 mmol, 1.50 equiv.), then the vessel was sealed and irradiated

with the standard setup at 450 nm for 1 hour. The reaction was filtered through a short pad of silica, the analysed by accurate MS using Thermo Fisher Scientific Orbitrap Velos Pro with nanospray injection.

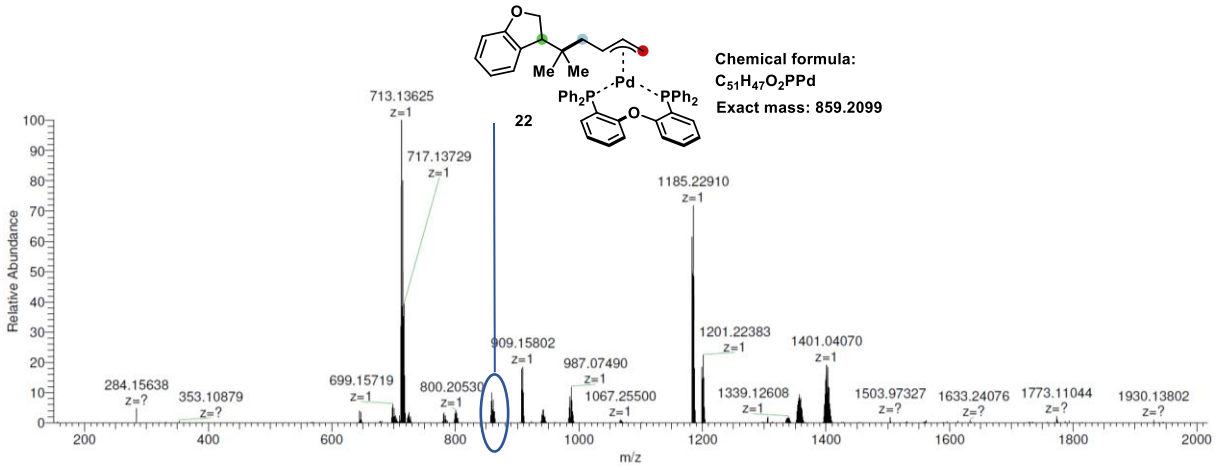


Figure S20 Accurate Mass Spectrometry analysis of the reaction mixture.

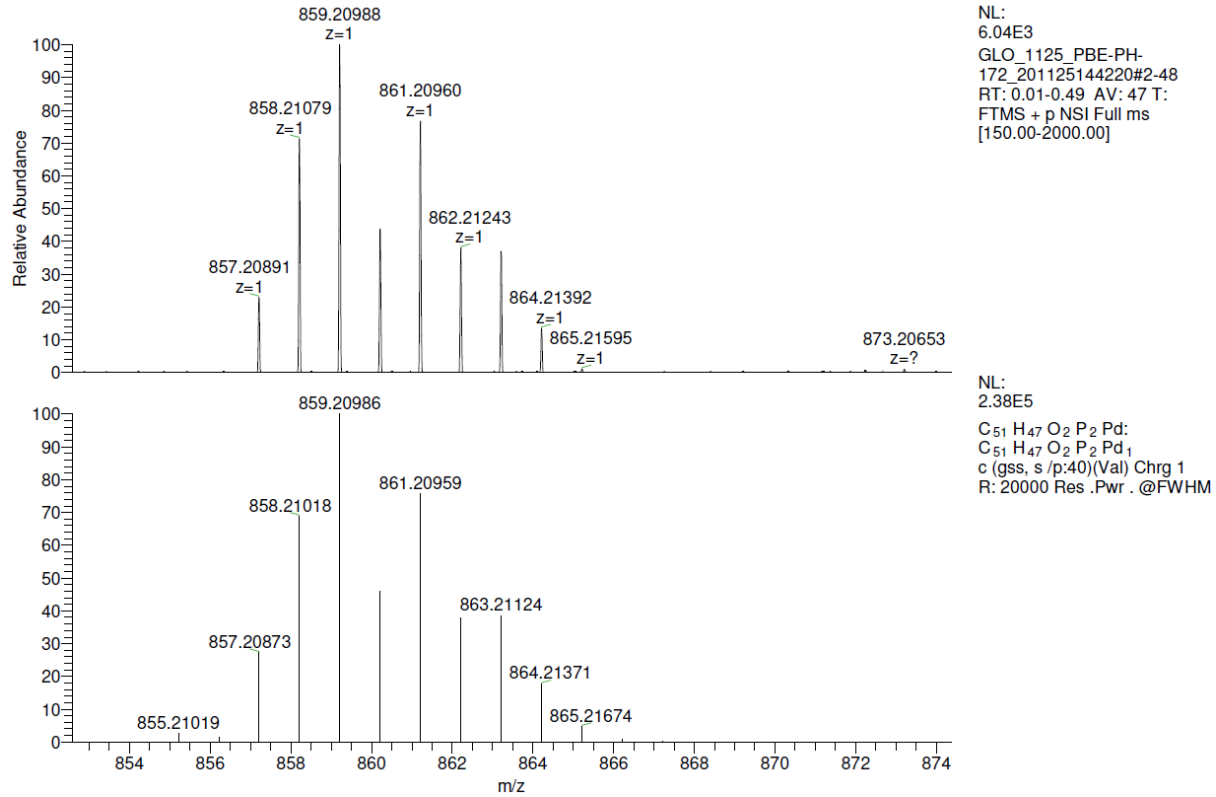


Figure S21 Molecular ion of the Pd(allyl)(DPEPhos) intermediate **22**.

Comment on the results: By means of accurate MS analysis (**Figure S20-21**), the presence of the postulated Pd(allyl)(DPEPhos) intermediate **22**, which arises from the initial cyclization and 1,3-butadiene trapping, could be detected, thus reinforcing our proposed mechanism.

^{31}P NMR analysis of the catalytic system

In order to confirm the ligand exchange between $Pd(PPh_3)_4$ and DPEPhos, which should occour in account to the known favourable displacement of monodentate ligands with bidentate ones, we performed ^{31}P NMR analysis of the catalytic system. THF-d_8 was chosen as solvent for its availability and good performances in the catalytic reaction (analogous to 1,4-dioxane).

As reported in **Figure S22**, we recorded the ^{31}P NMR spectra of PPh_3 (5, 0.01 M), DPEPhos (4, 0.01 M), $Pd(PPh_3)_4$ (3, 0.005 M), $Pd(PPh_3)_4$ + DPEPhos (2 & 1, 0.005 M for $Pd(PPh_3)_4$ and 0.01 M for DPEPhos, respectively). In the case of 2, the NMR tube was irradiated at 450 nm for 20 minutes prior measurement.

While strictly anaerobic conditions were enforced and THF-d_8 was previously degassed, in-solution oxidation of P(III) to P(V) was inevitably observed, both in the absence and presence of palladium. Despite that, valuable information concerning the system ligation can be obtained.

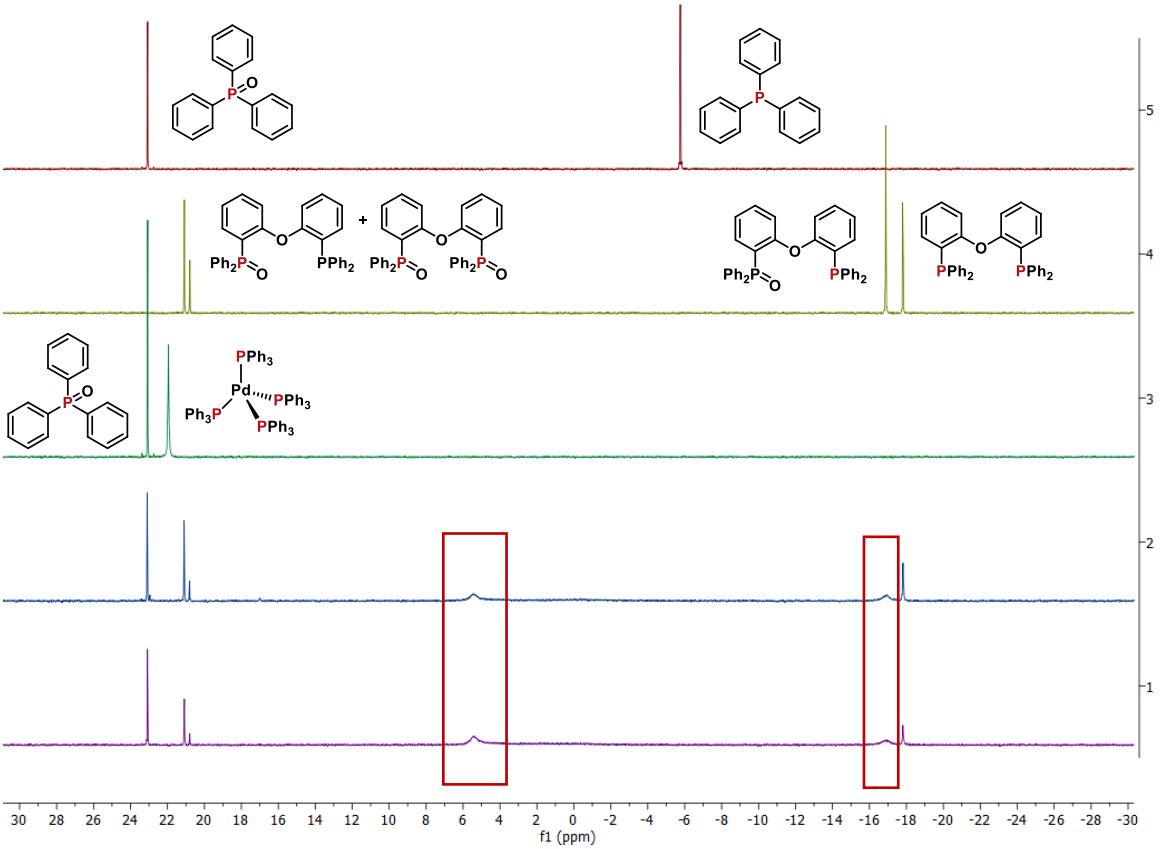


Figure S22 ^{31}P NMR analysis (THF-d_8, 400 MHz) of the catalytic system. (5) PPh_3; (4) DPEPhos; (3) $Pd(PPh_3)_4$; (2) $Pd(PPh_3)_4$ + DPEPhos under 450 nm LEDs irradiation; (1) $Pd(PPh_3)_4$ + DPEPhos.

Comment on the results: By comparison of unligated species PPh_3 (5), DPEPhos (4) and $Pd(PPh_3)_4$ (3) with the pre-catalyst/ligand mixture (1 and 2), the following considerations can be drawn:

- The signal belonging to $Pd(PPh_3)_4$ phosphine ligands disappears, while two broadened signals appear (see **red** boxes);

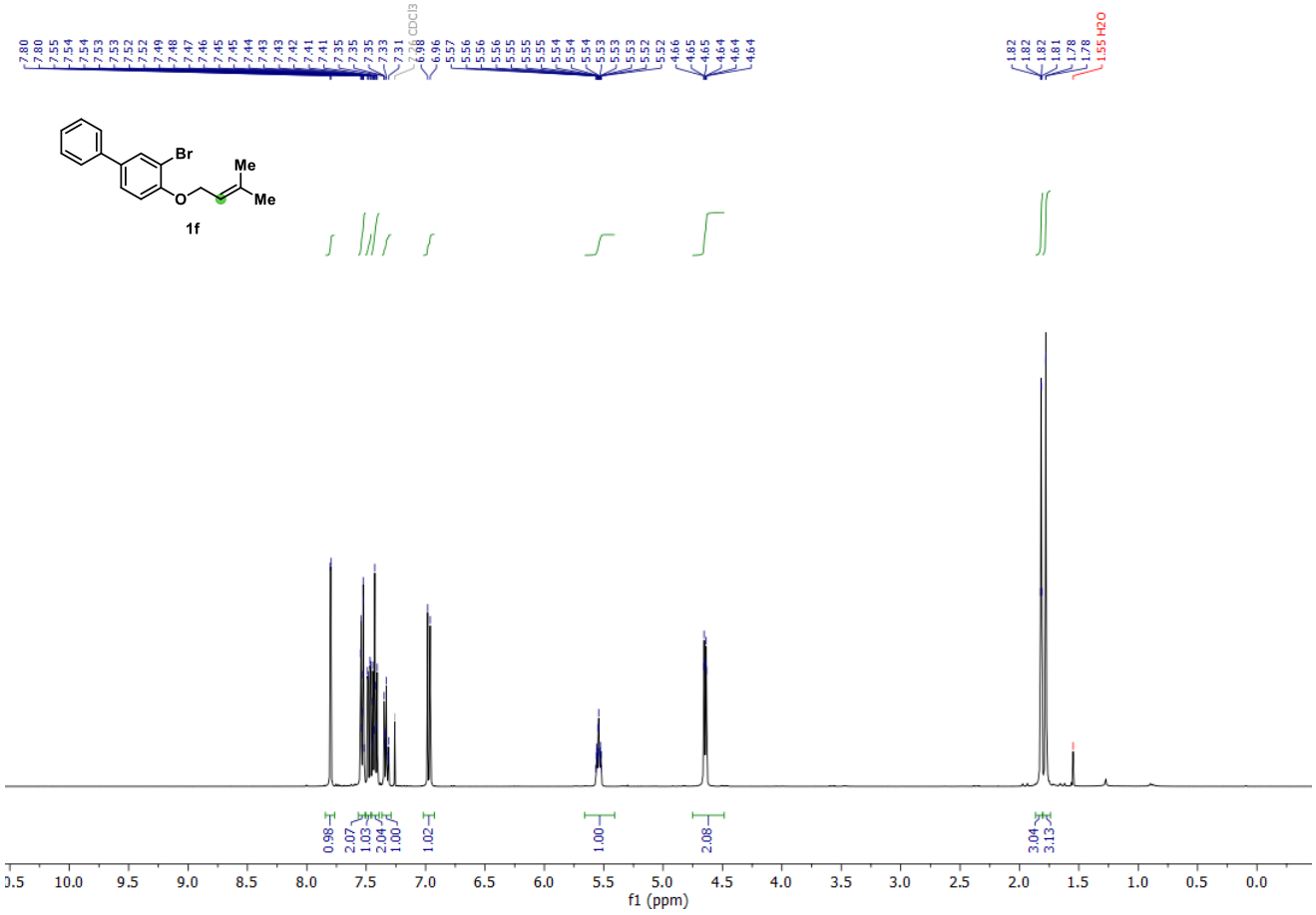
- No signal belonging to non-ligated could PPh_3 be observed, while the $O{=}PPh_3$ signal is clearly visible;
- Unbound DPEPhos could be observed, in addition to its oxidized analogues.

Overall, this information strongly suggests that $Pd(PPh_3)_4$ converts – upon DPEPhos addition – into new species bearing the bidentate ligand. Irradiation at 450 nm has negligible influence on the ^{31}P NMR analysis of the mixture.

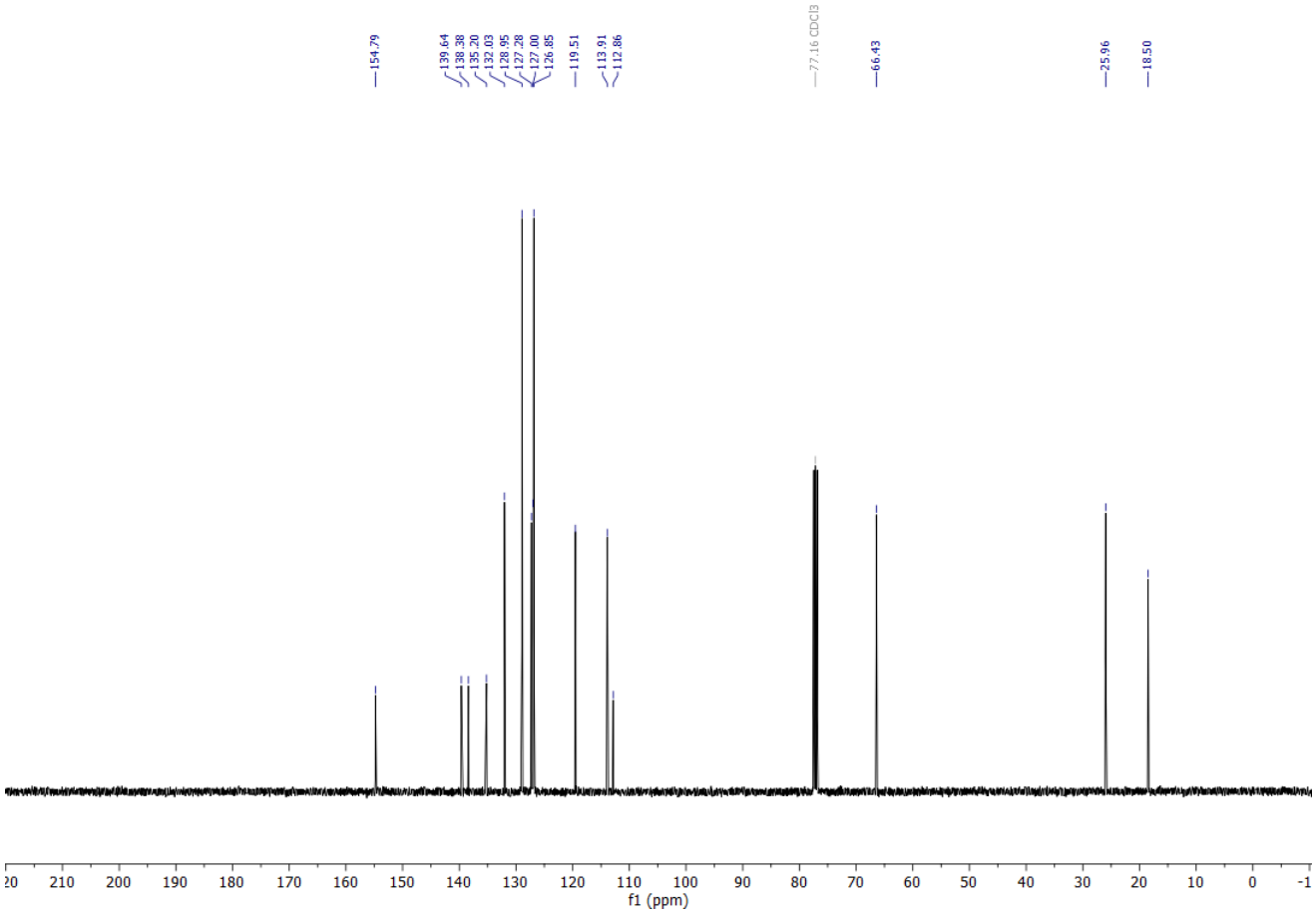
NMR spectra

NMR spectra of bromides

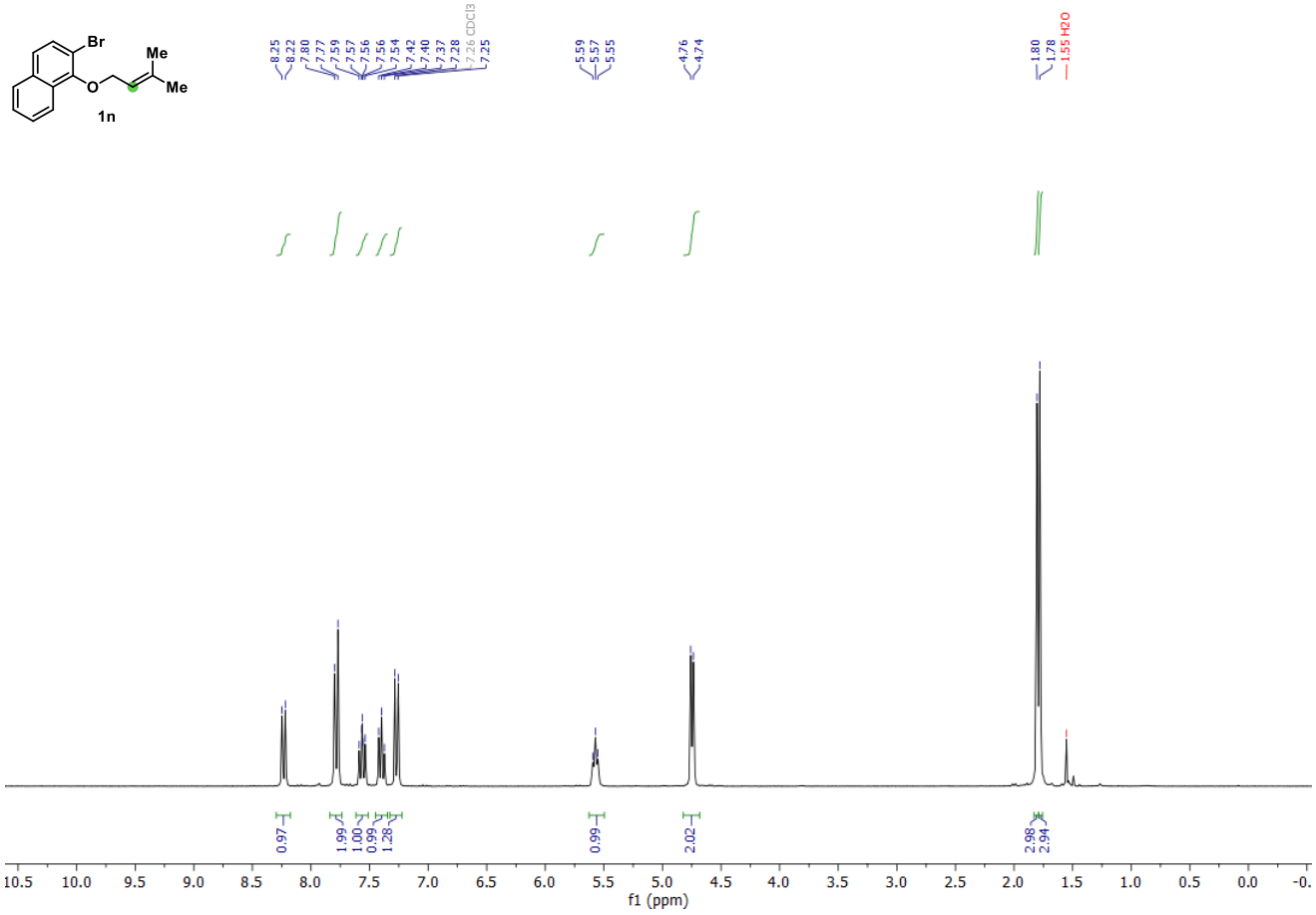
^{1}H NMR (400 MHz, $CDCl_3$)



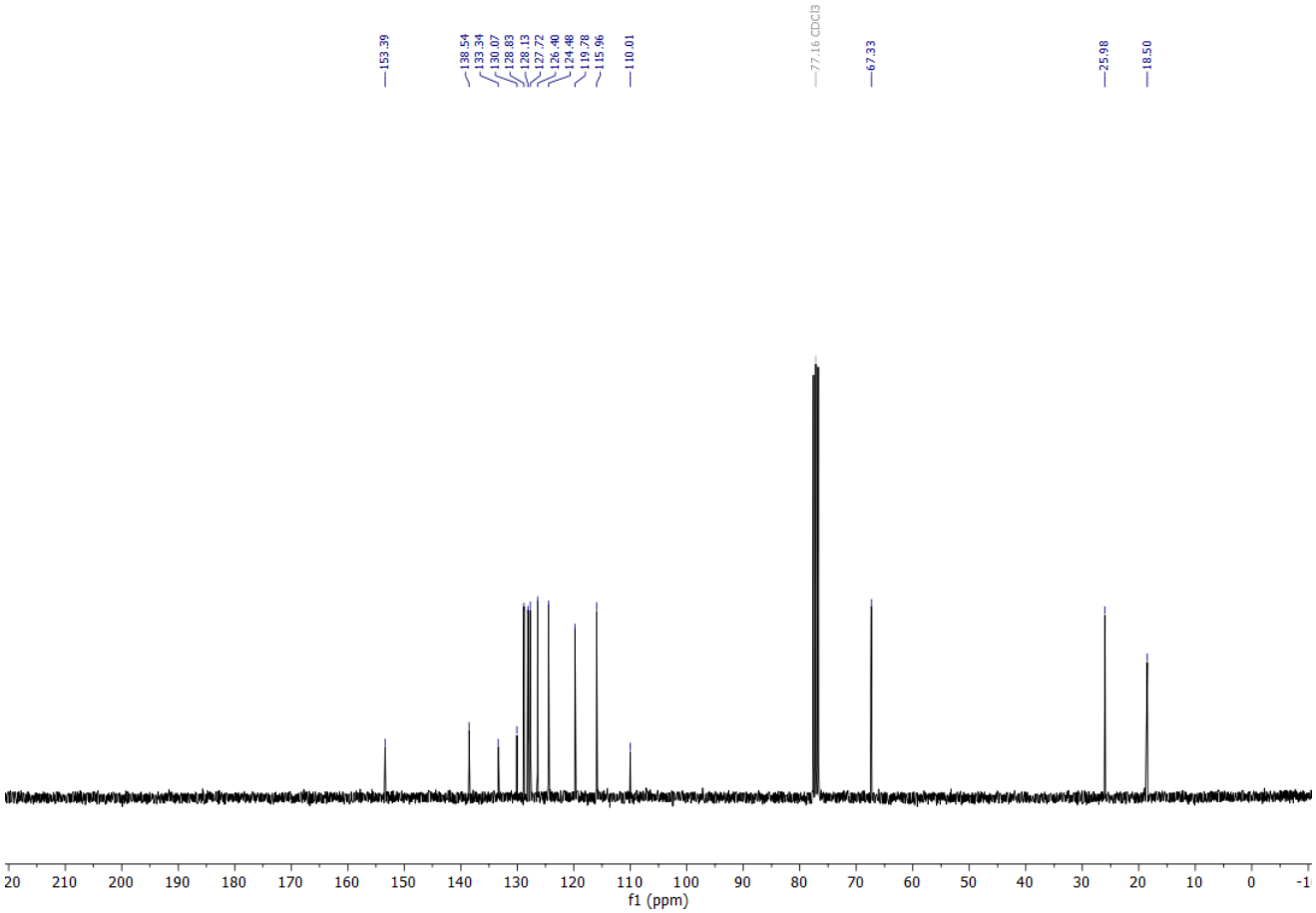
^{13}C NMR (101 MHz, $CDCl_3$)



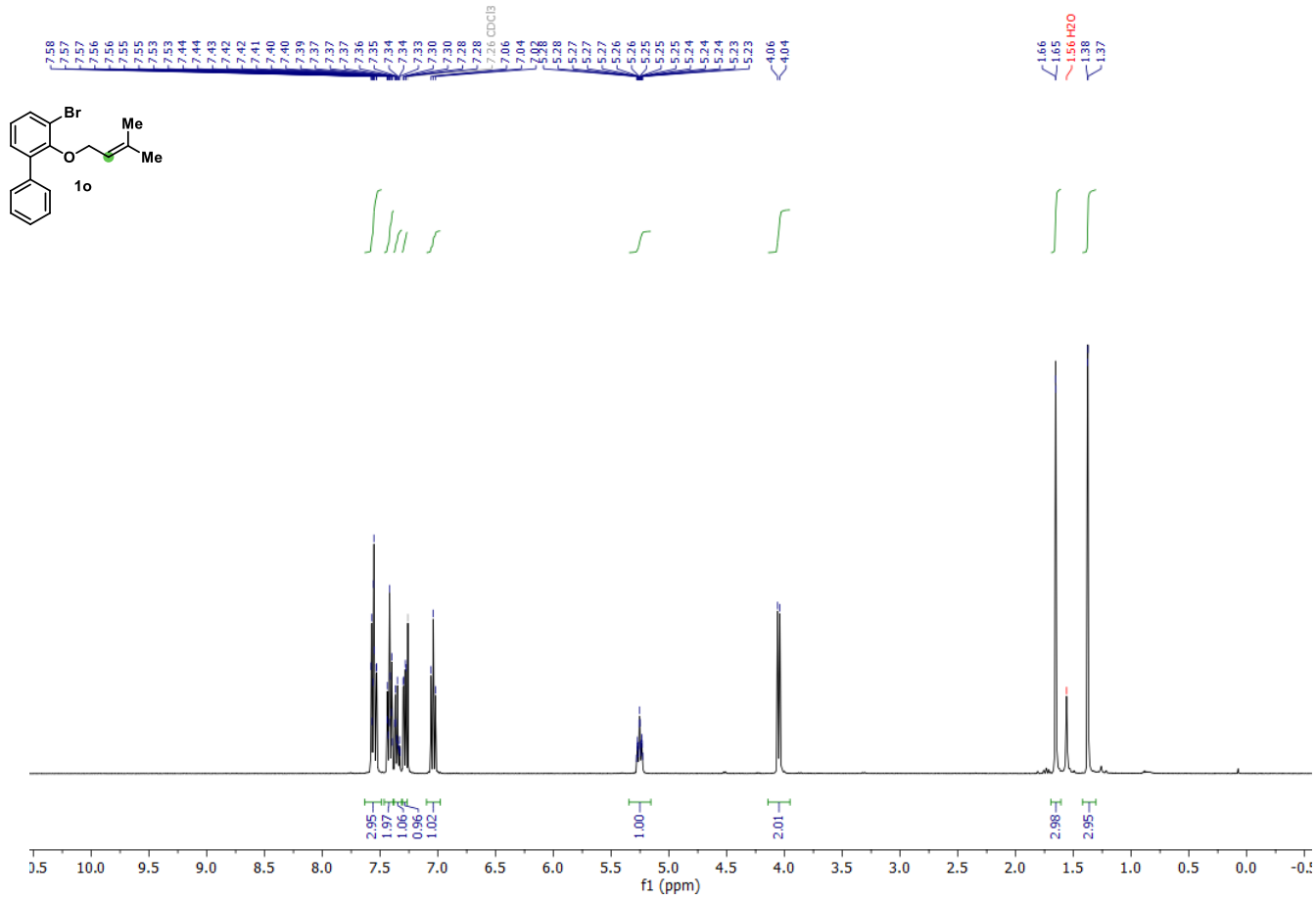
^{1}H NMR (300 MHz, $CDCl_3$)



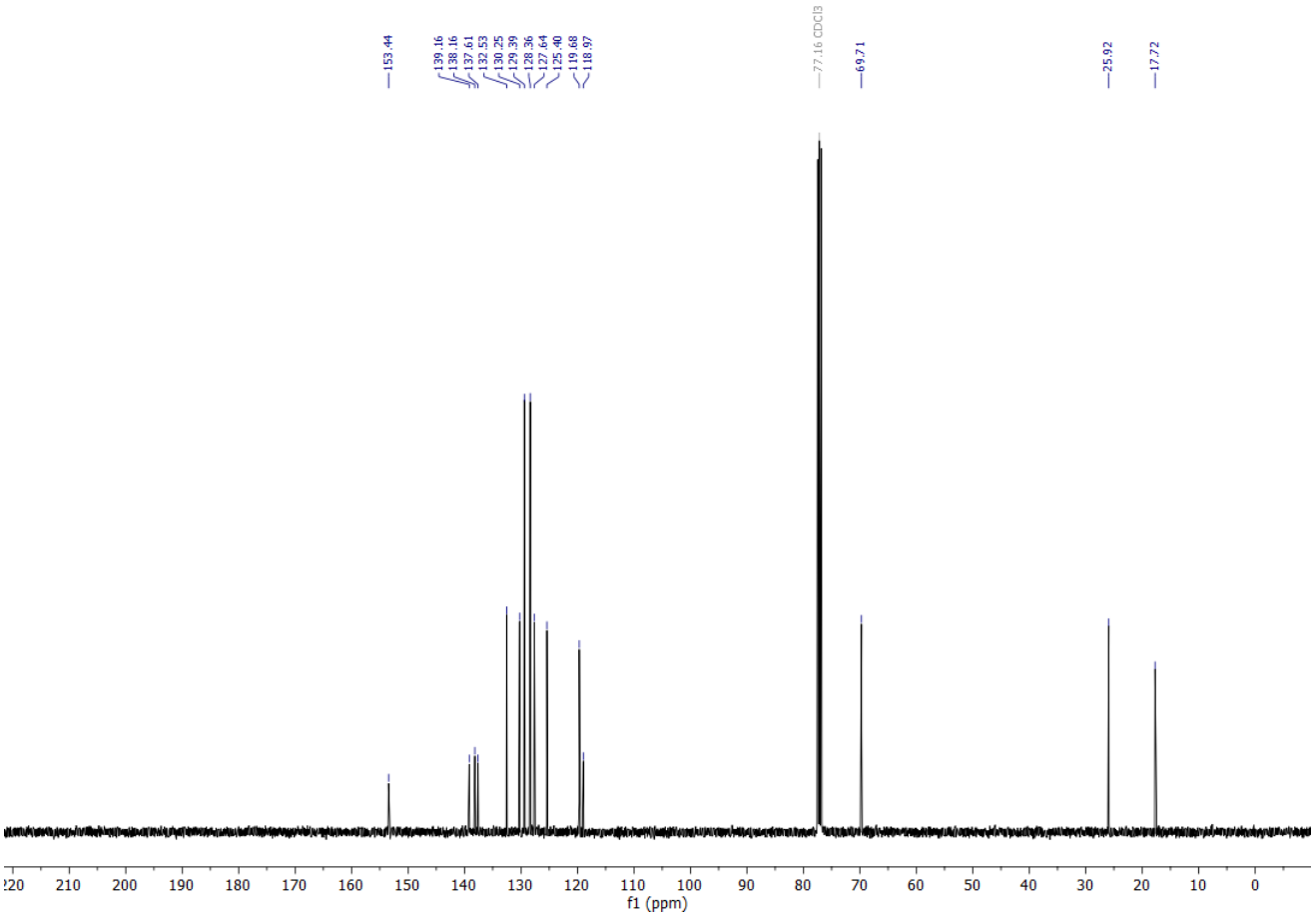
^{13}C NMR (75 MHz, $CDCl_3$)



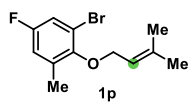
^{1}H NMR (400 MHz, $CDCl_3$)



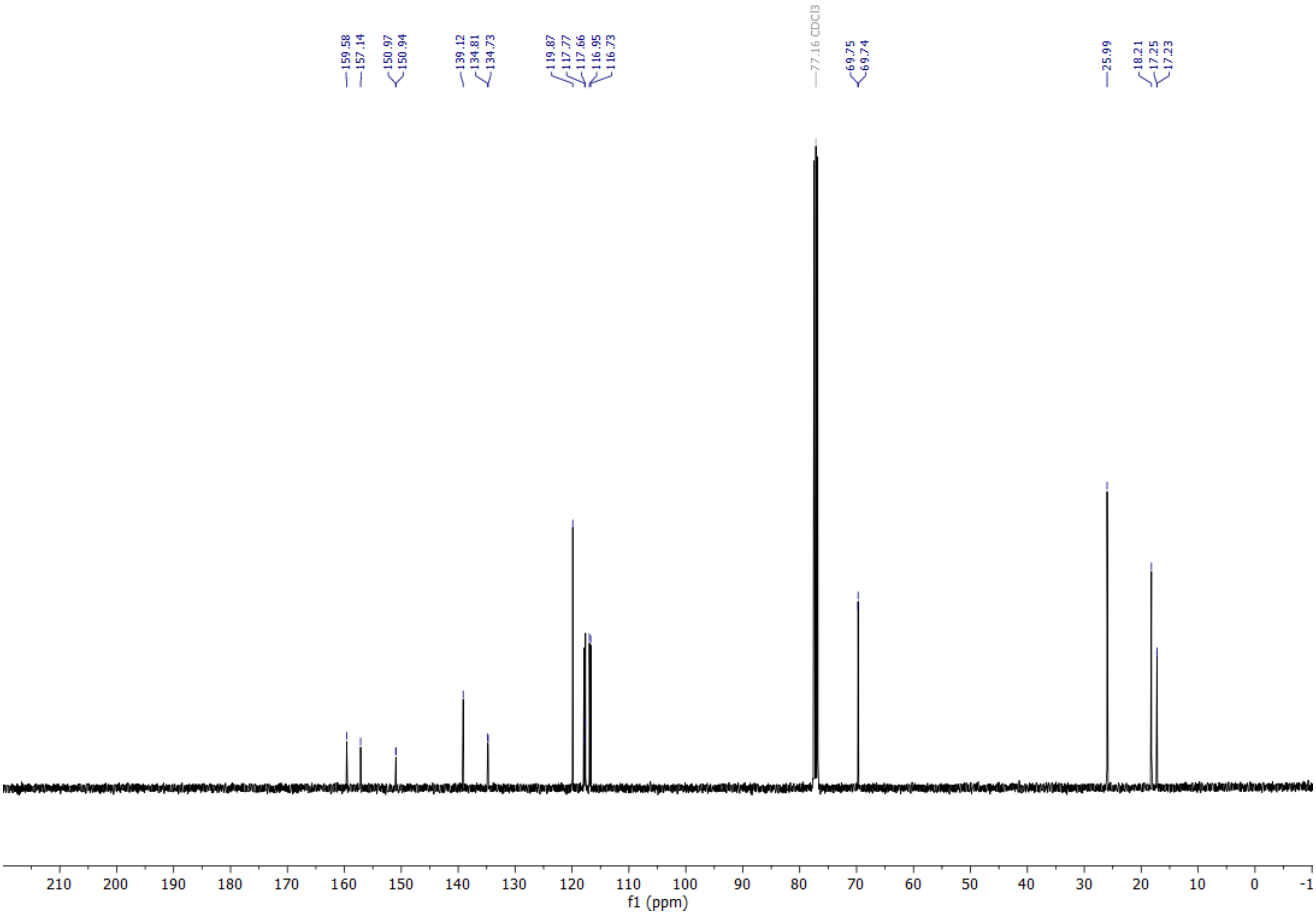
^{13}C NMR (101 MHz, $CDCl_3$)



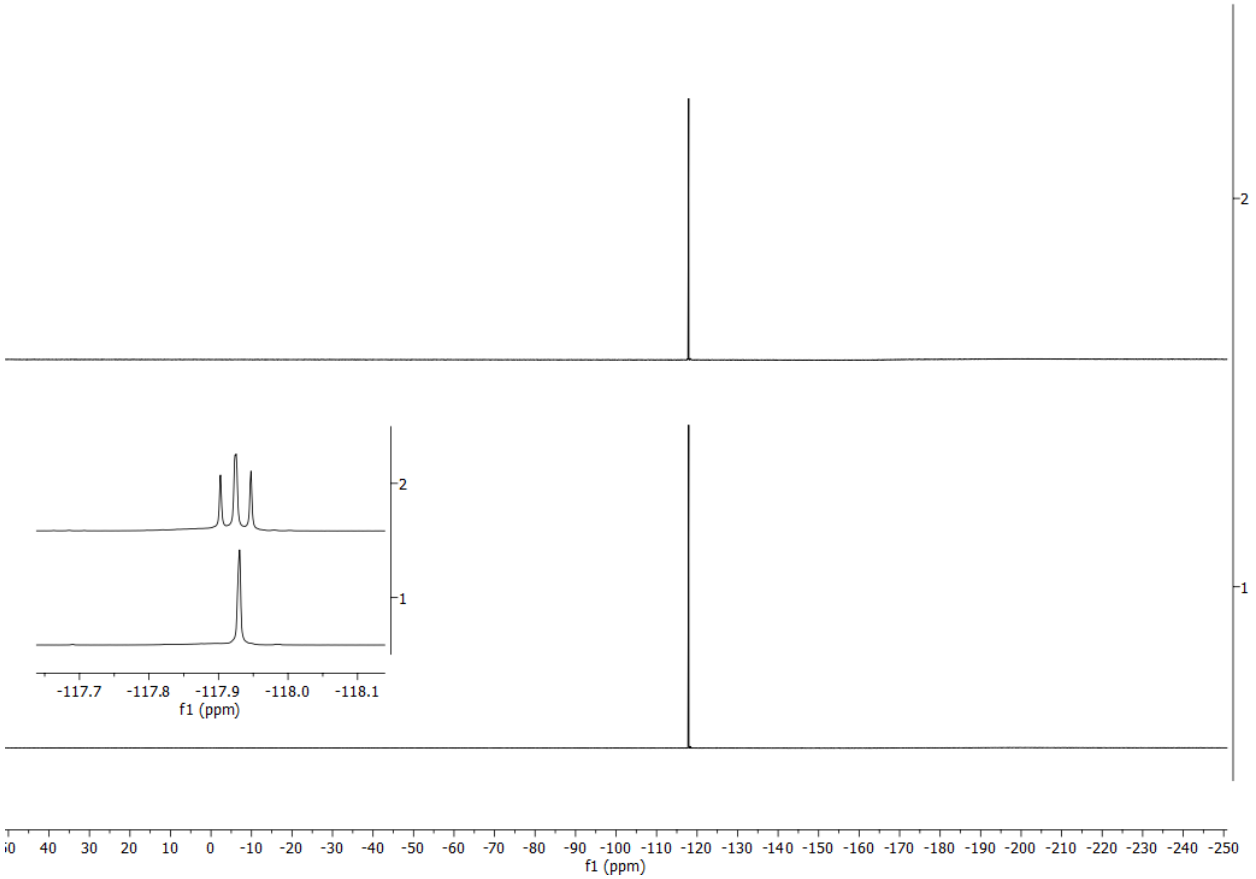
^{1}H NMR (400 MHz, $CDCl_3$)



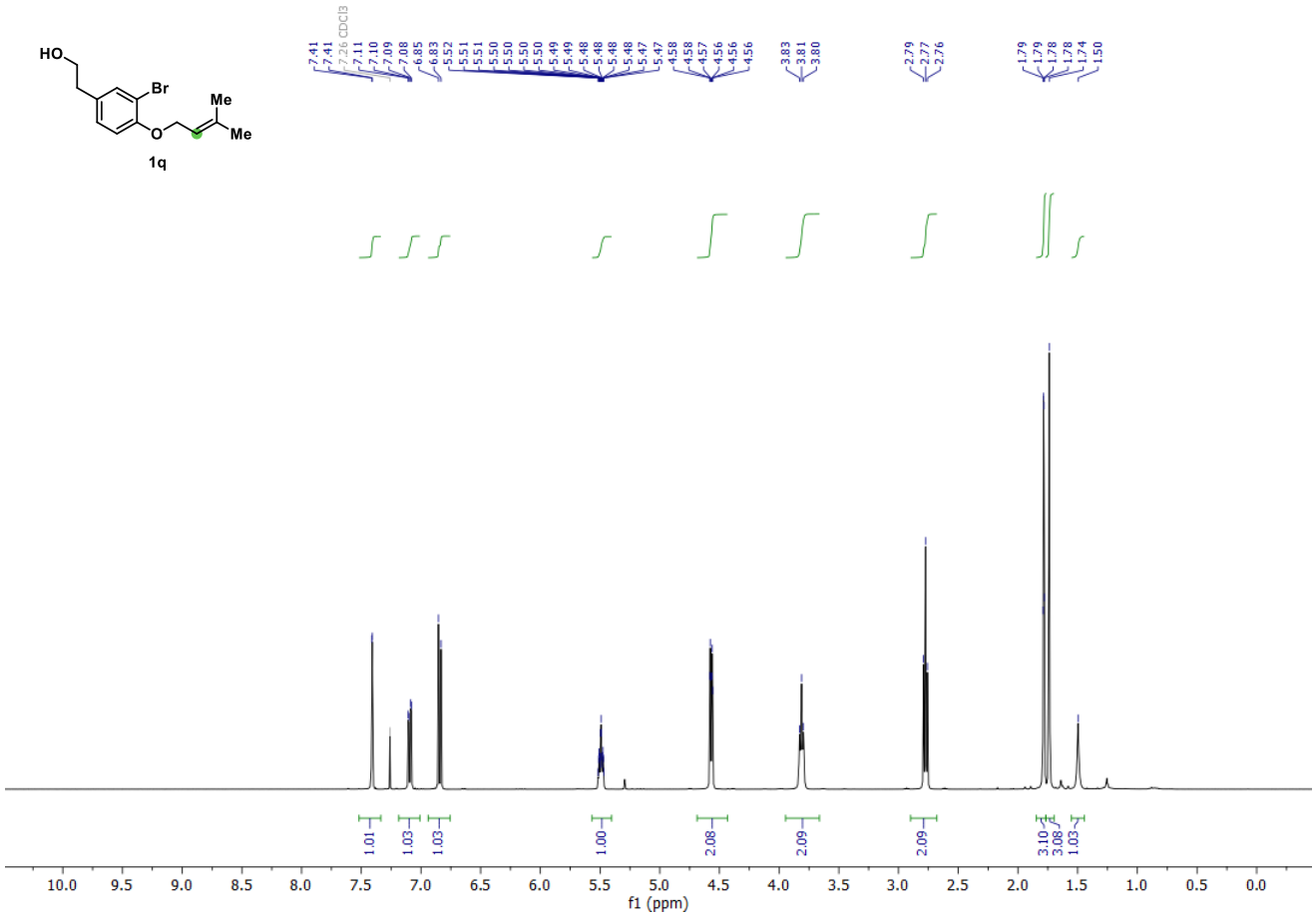
^{13}C NMR (101 MHz, $CDCl_3$)



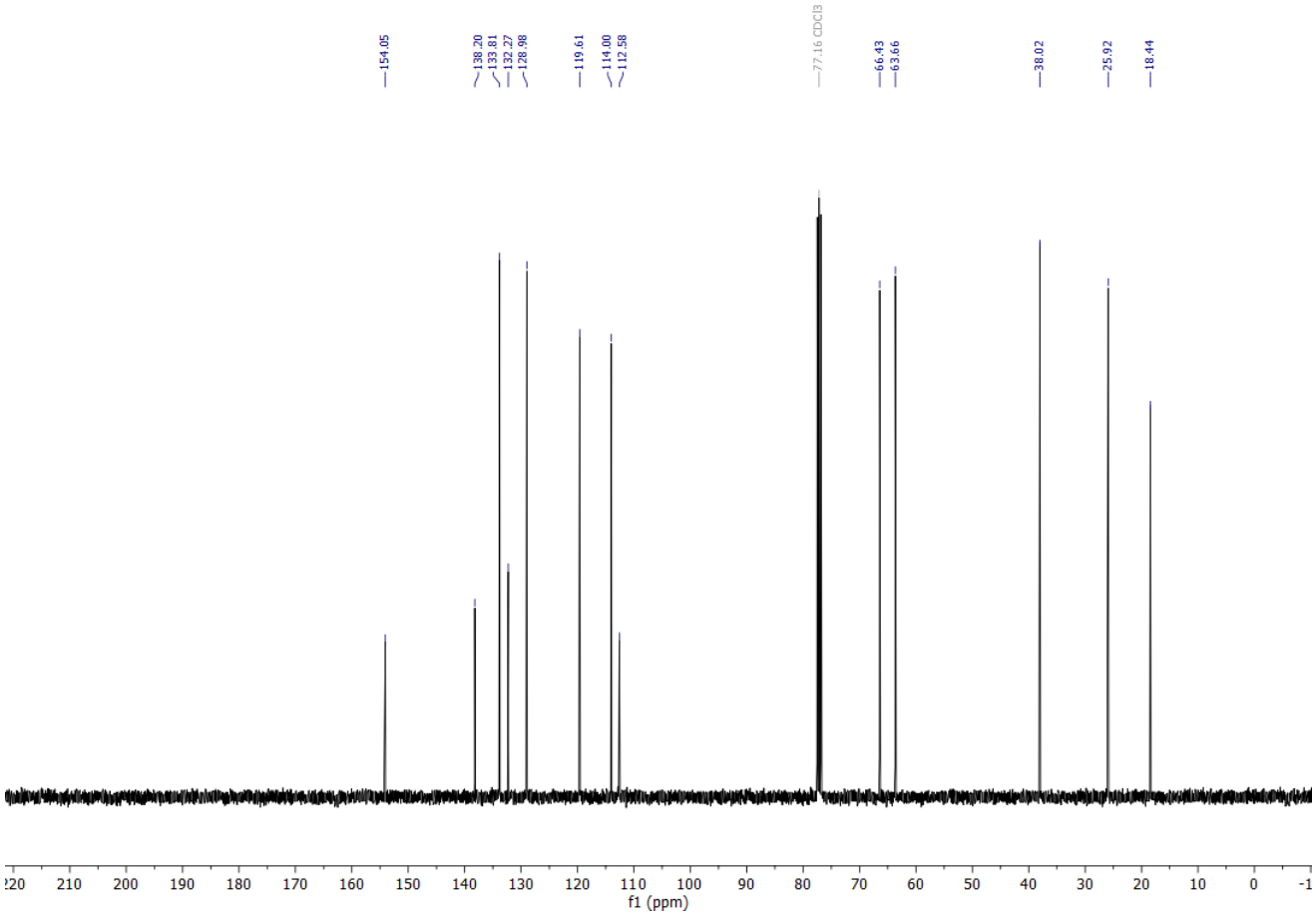
^{19}F NMR (377 MHz, $CDCl_3$)



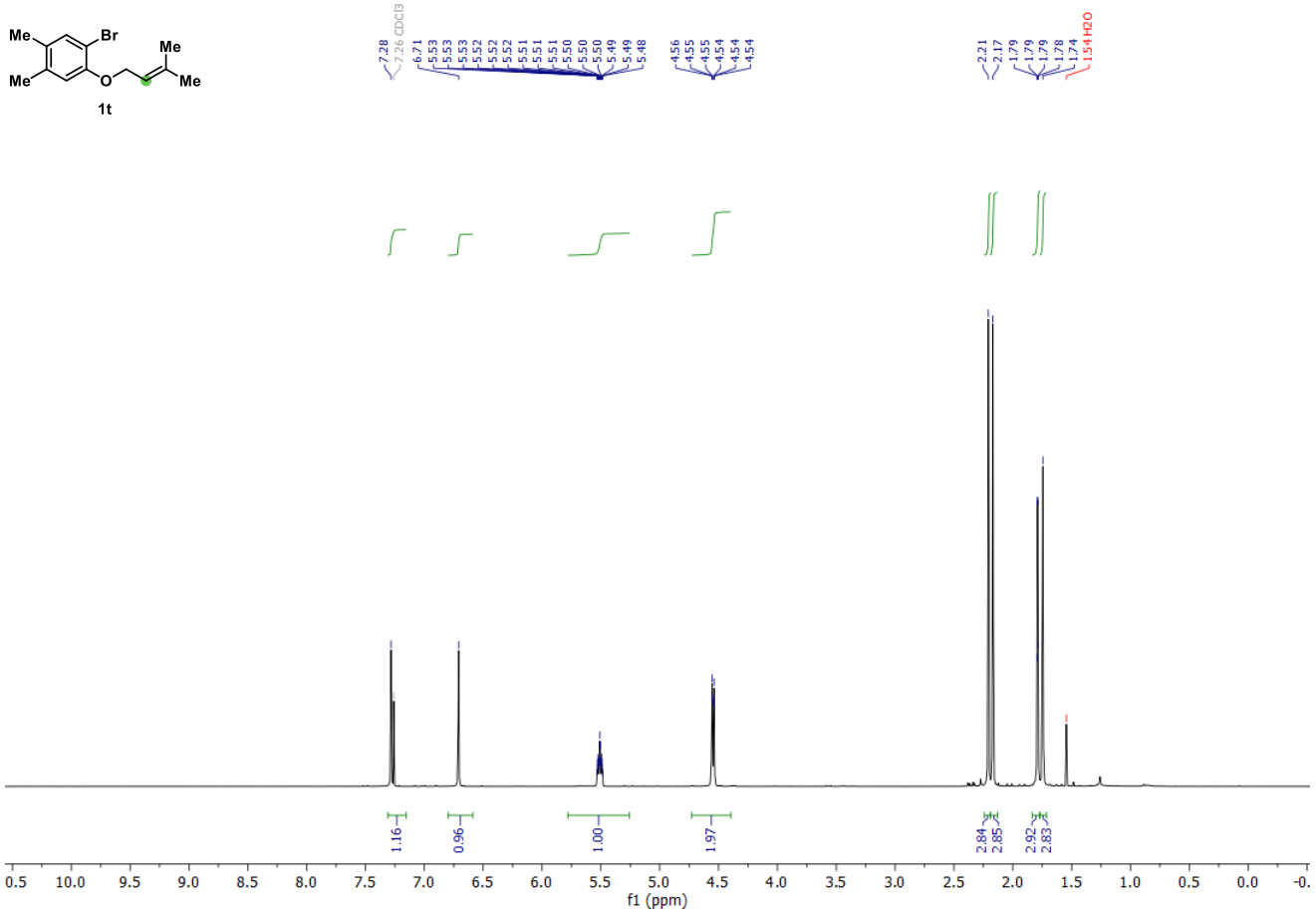
^{1}H NMR (400 MHz, $CDCl_3$)



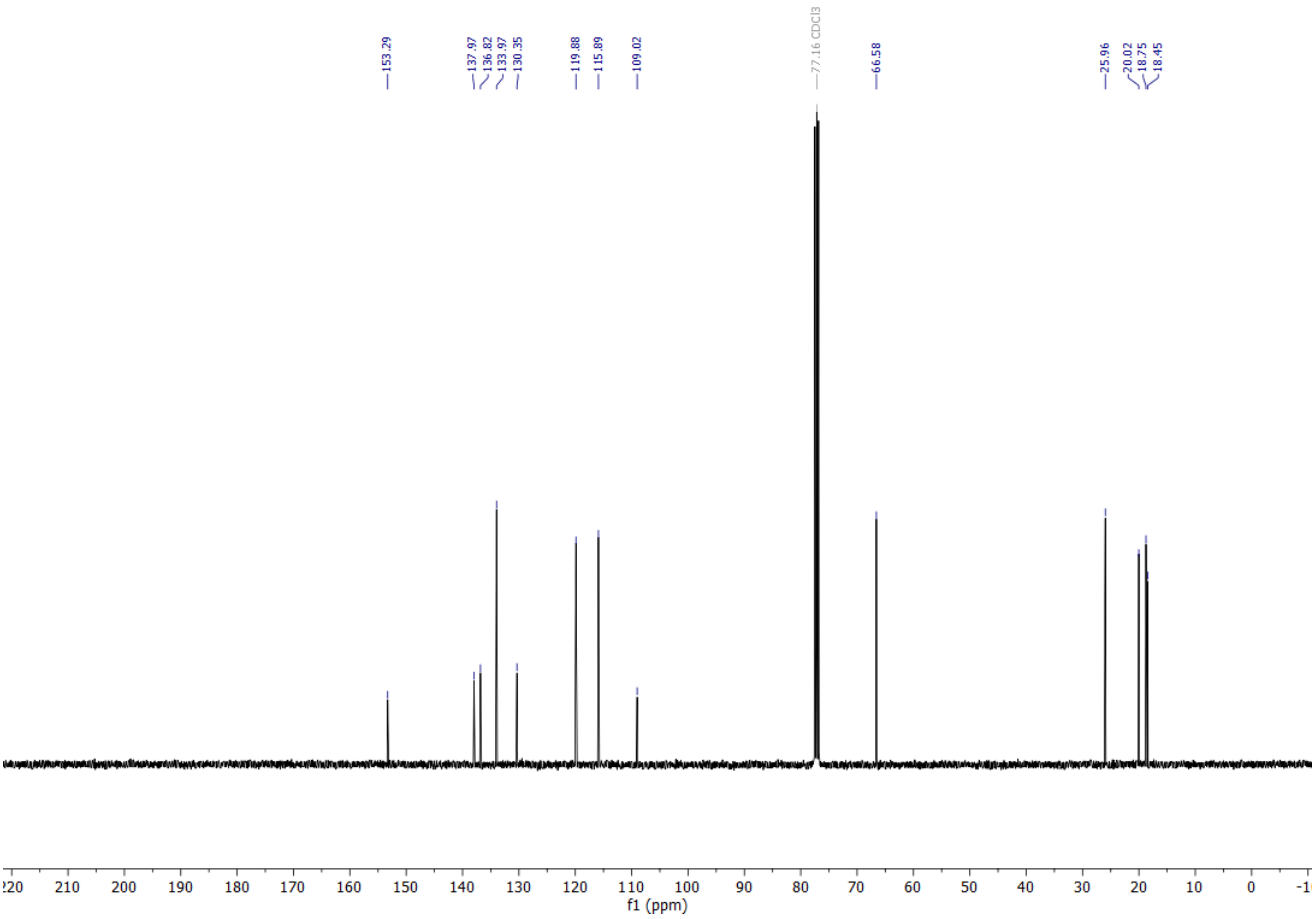
^{13}C NMR (101 MHz, $CDCl_3$)



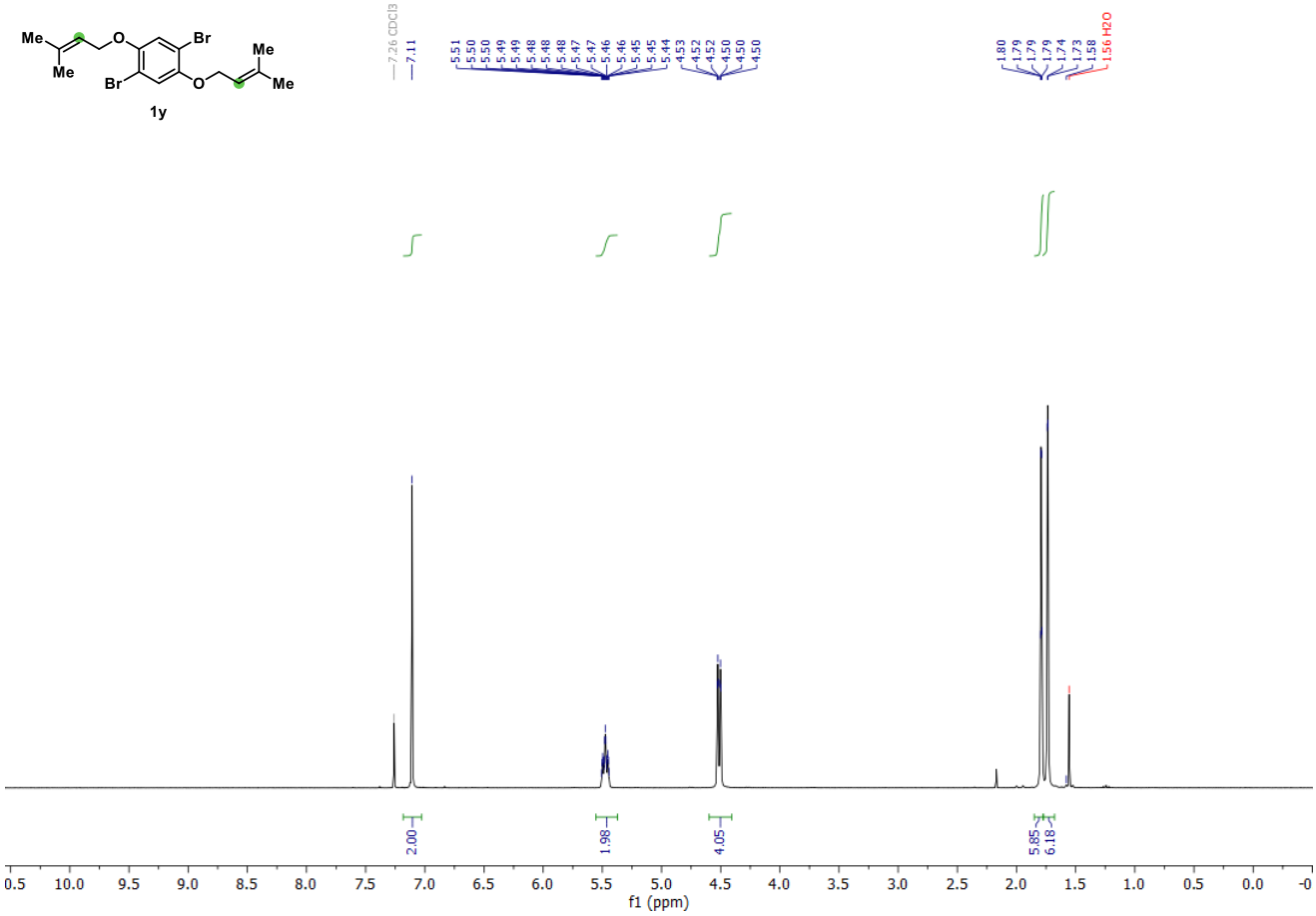
^{1}H NMR (400 MHz, $CDCl_3$)



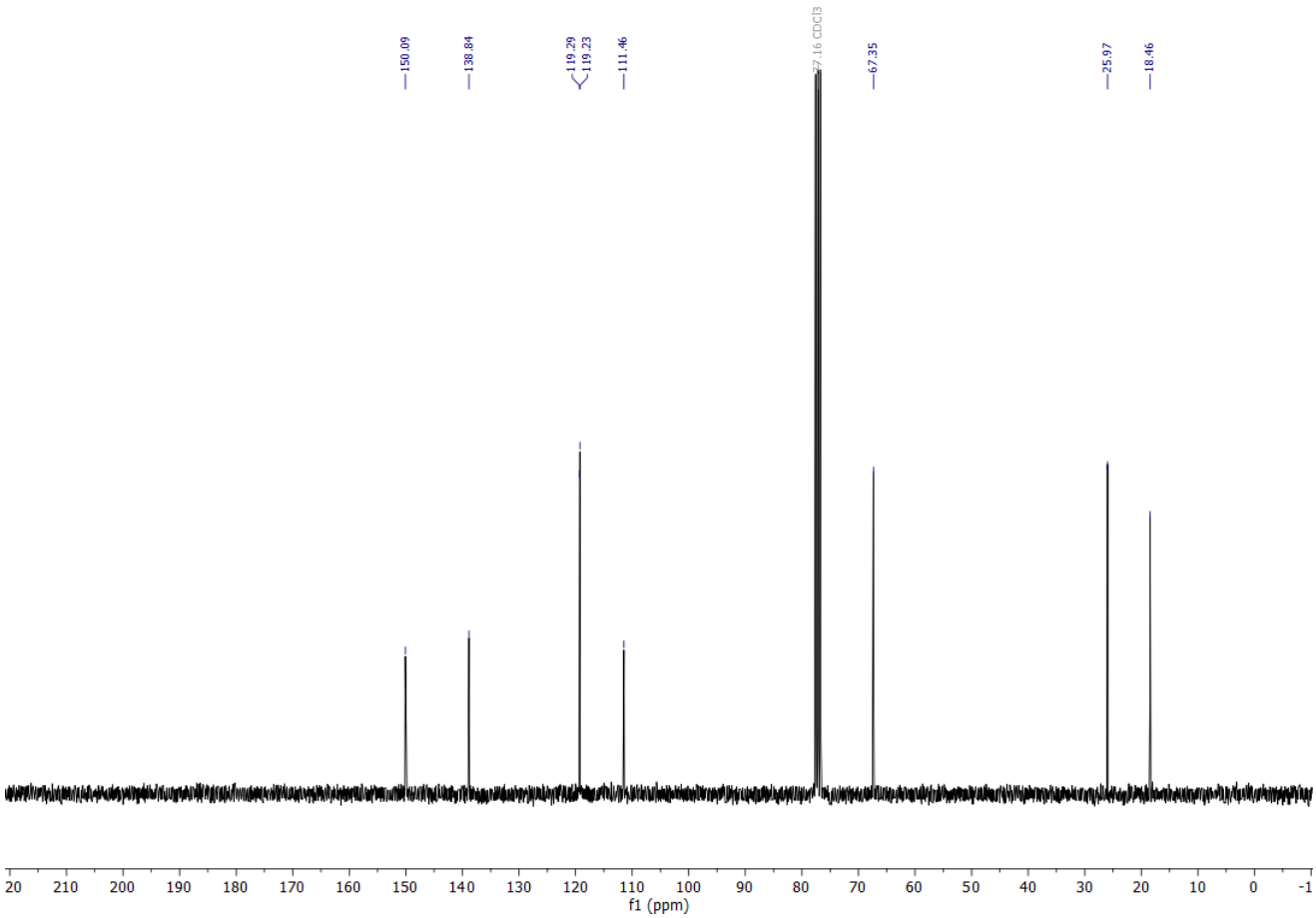
^{13}C NMR (101 MHz, $CDCl_3$)



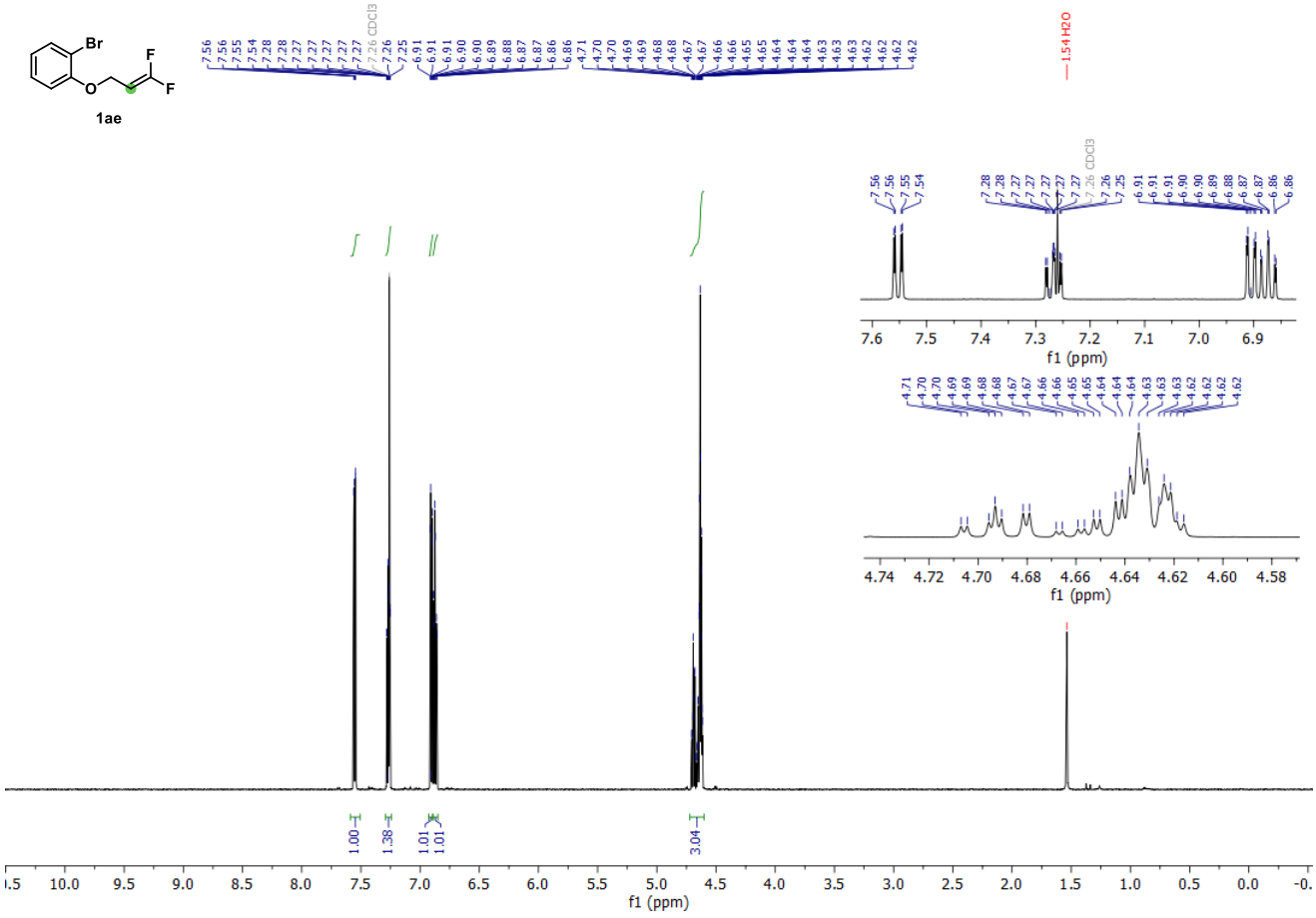
^{1}H NMR (300 MHz, $CDCl_3$)



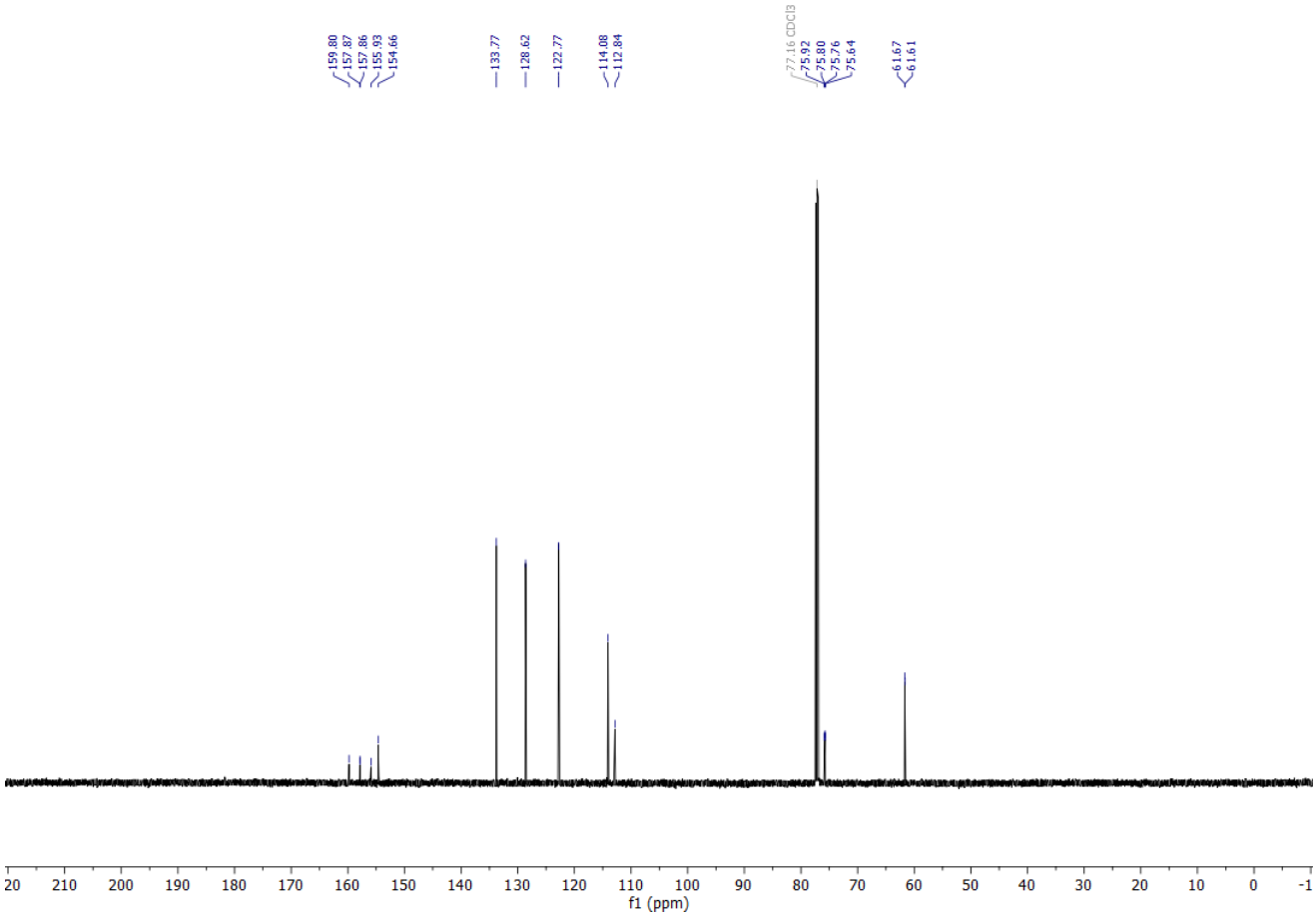
^{13}C NMR (75 MHz, $CDCl_3$)



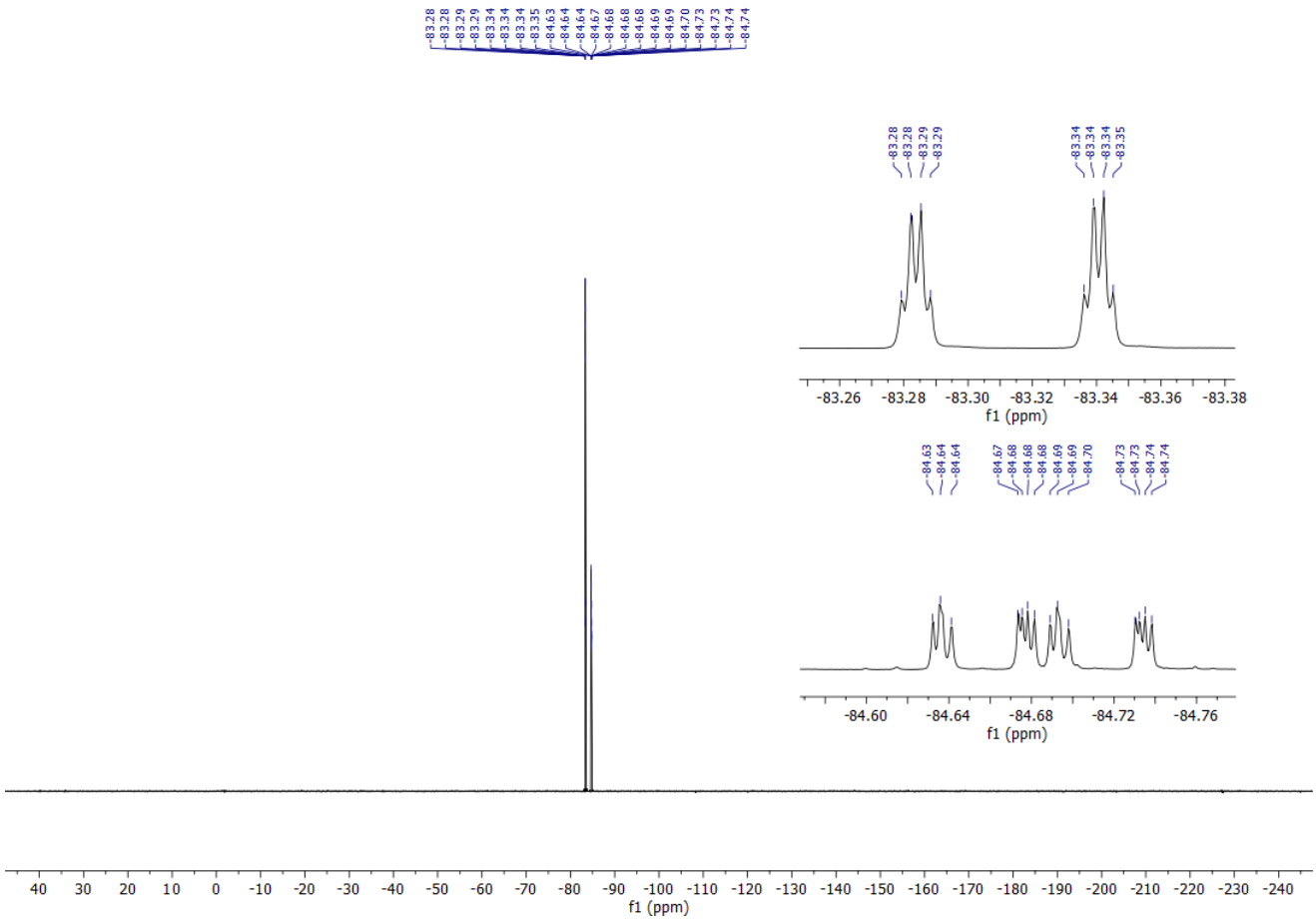
^{1}H NMR (599 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

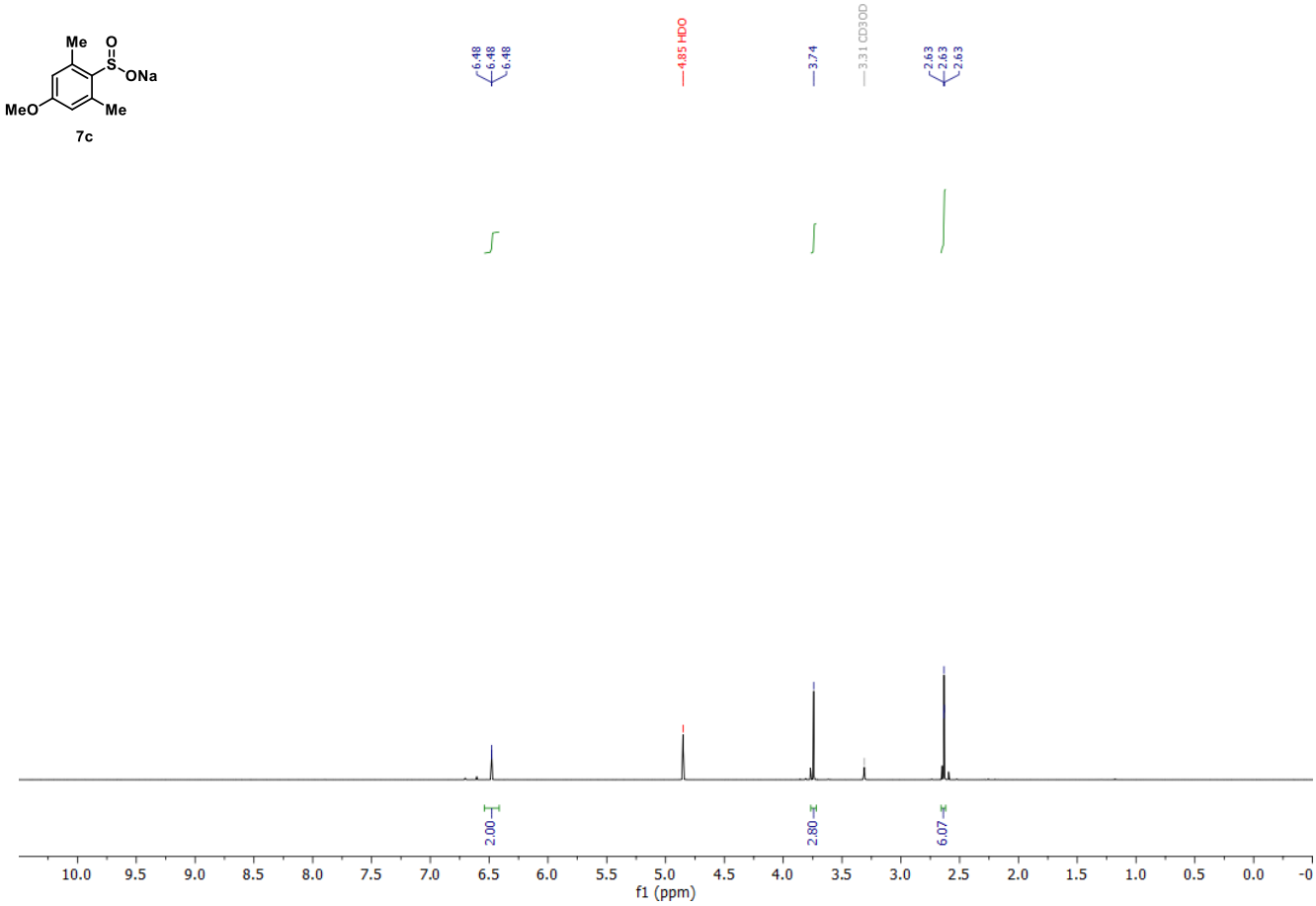


^{19}F NMR (564 MHz, $CDCl_3$)

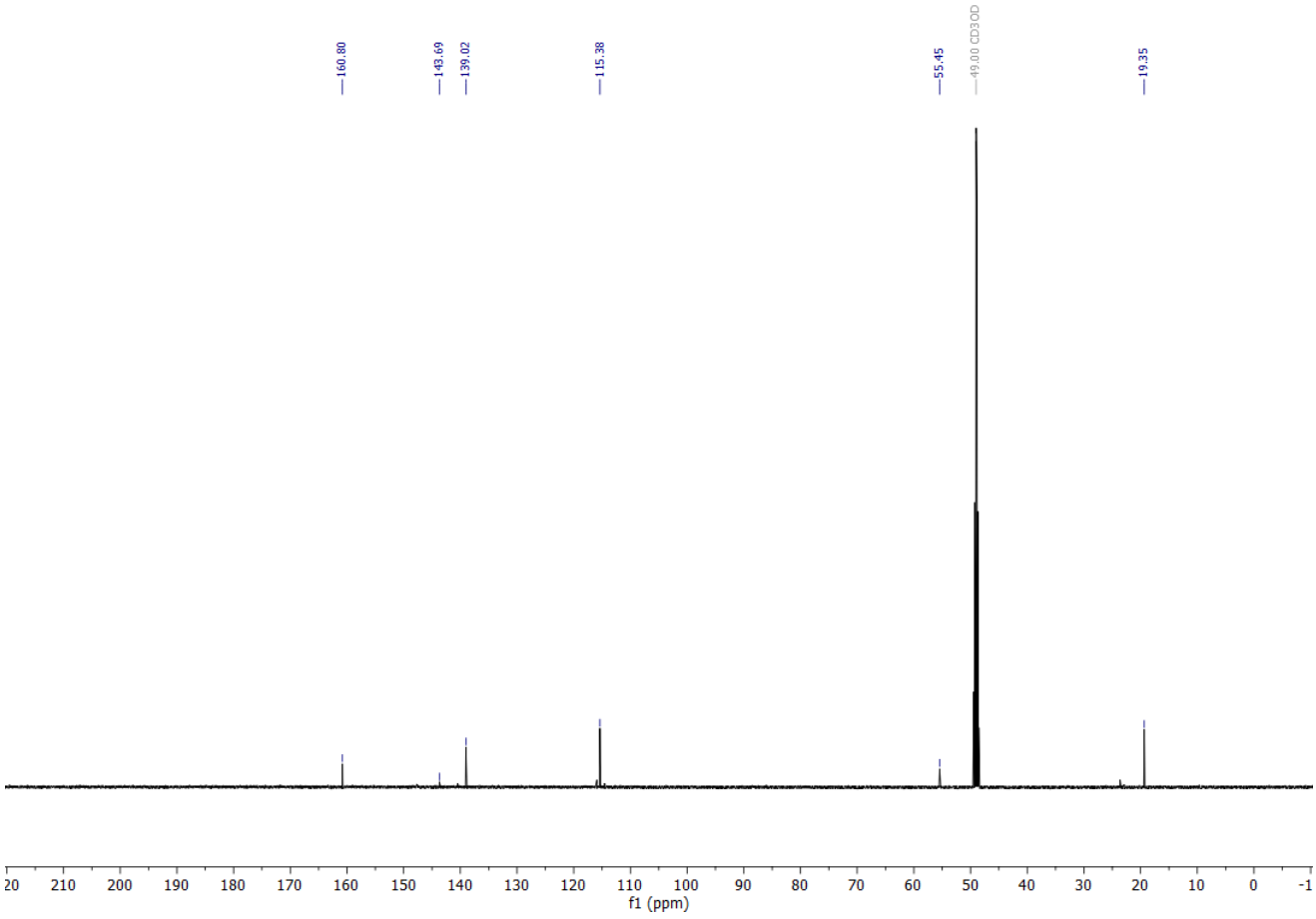


NMR spectra of sulfinates

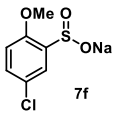
^{1}H NMR (599 MHz, CD_3OD)



^{13}C NMR (151 MHz, CD_3OD)

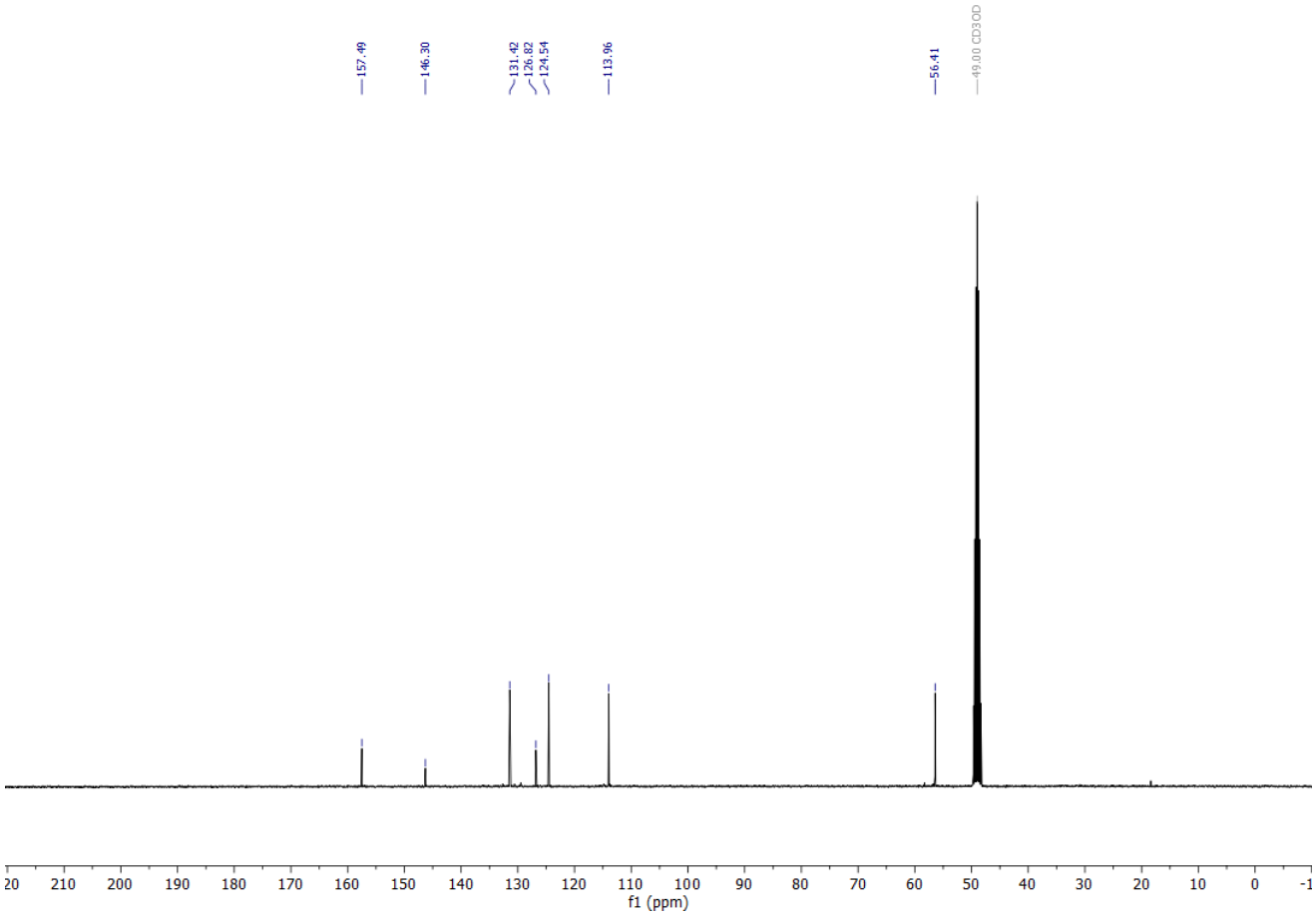


^{1}H NMR (400 MHz, CD_3OD)



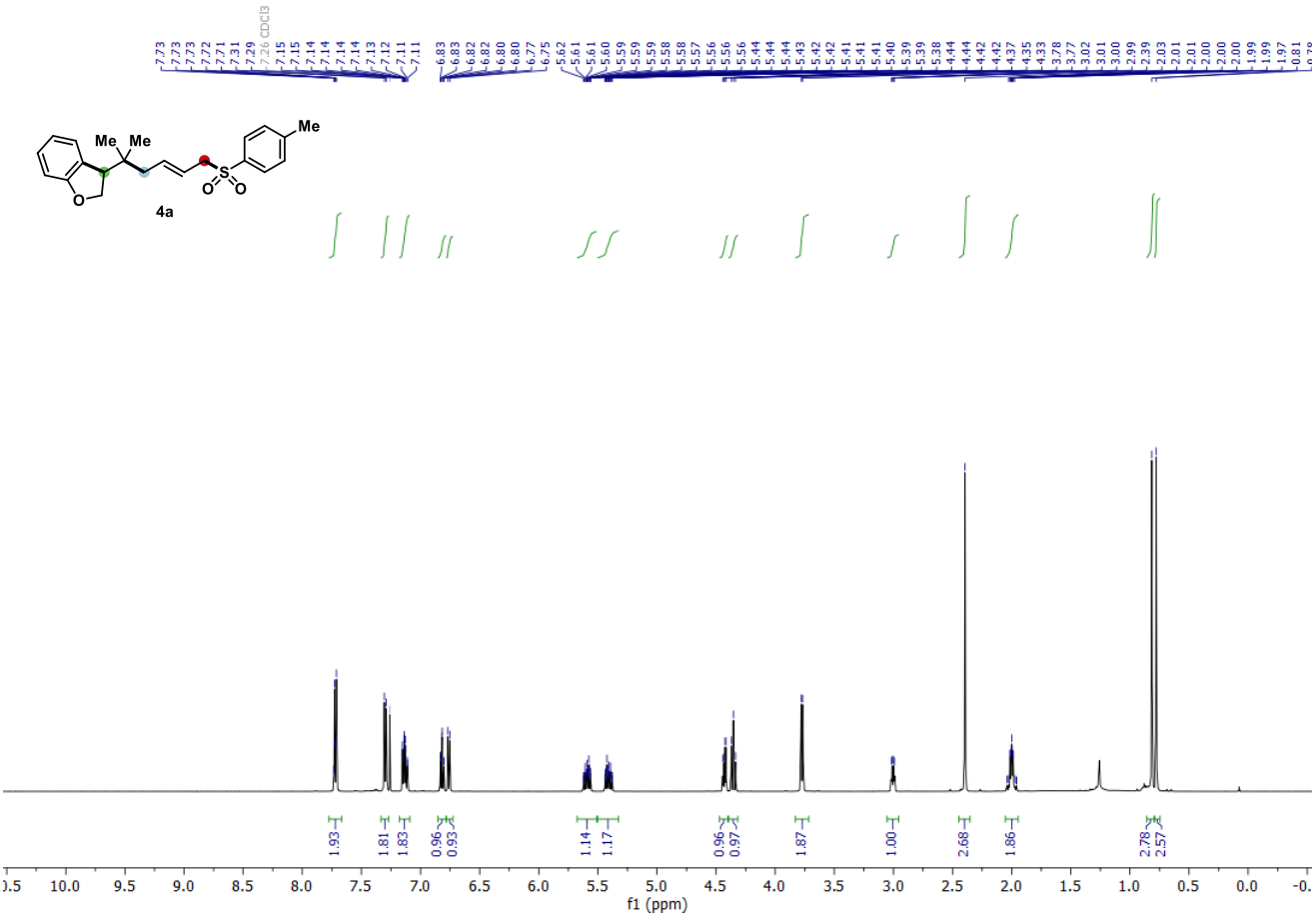
7f

^{13}C NMR (101 MHz, CD_3OD)

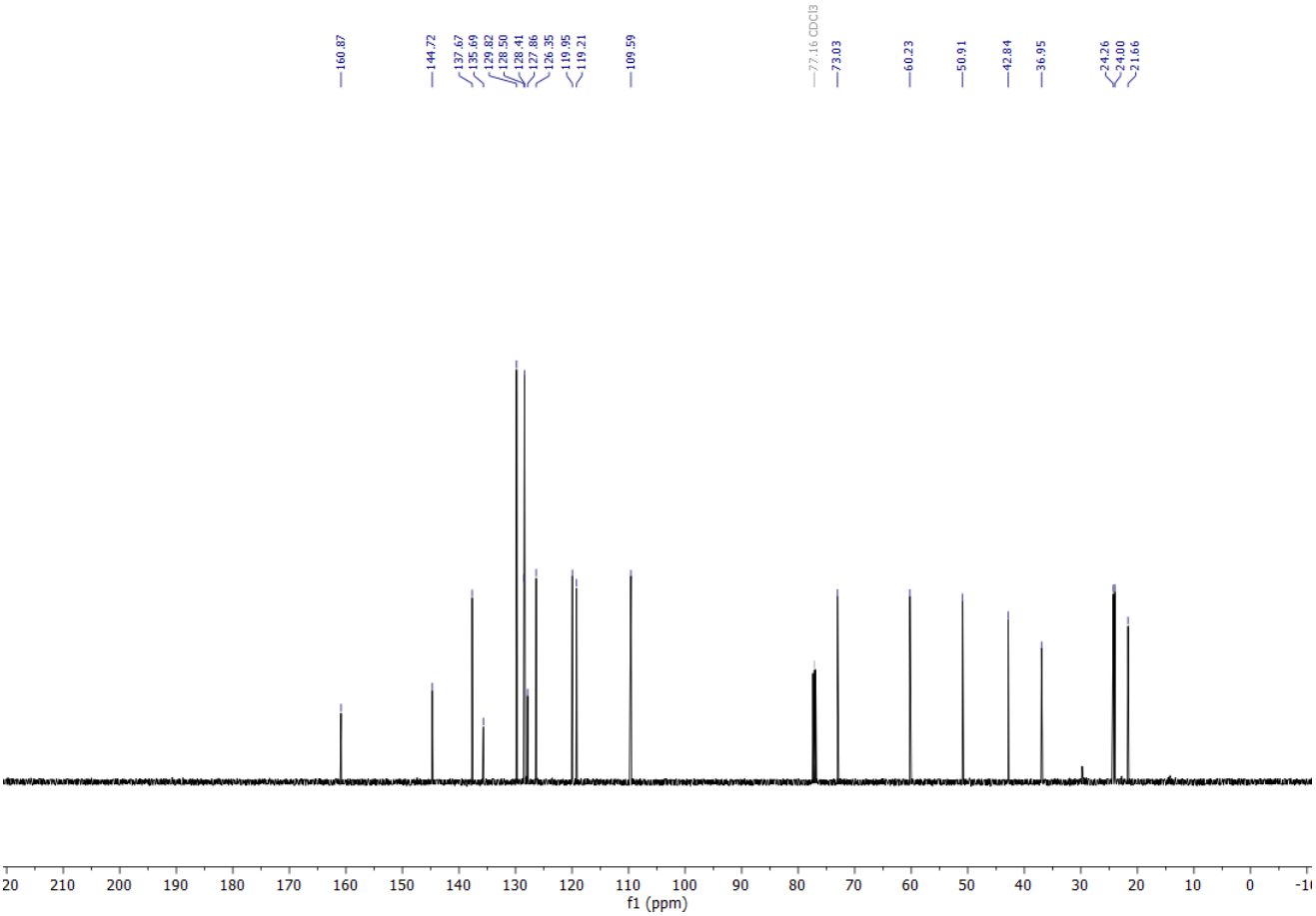


NMR spectra of products 4a-aj

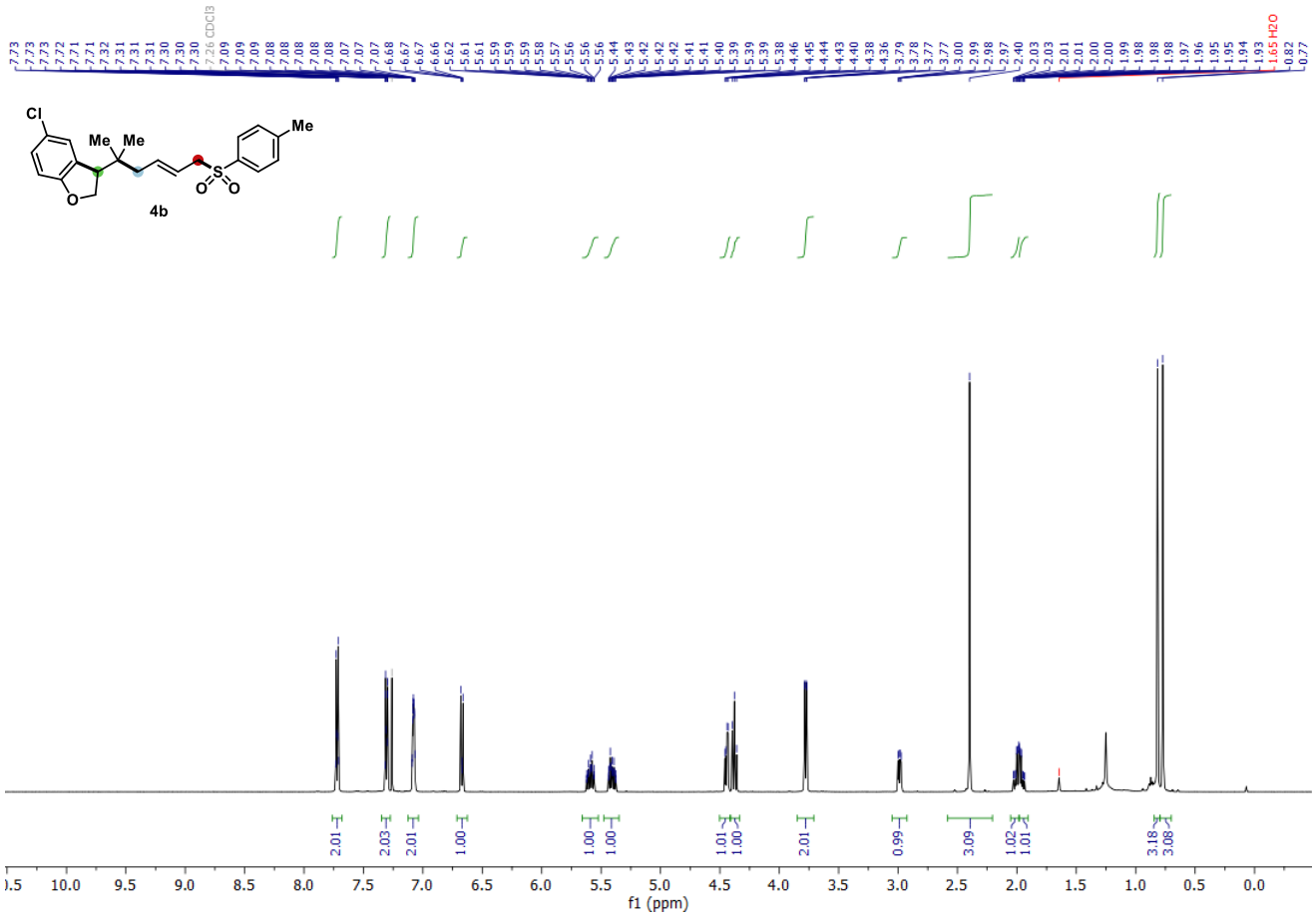
^{1}H NMR (500 MHz, $CDCl_3$)



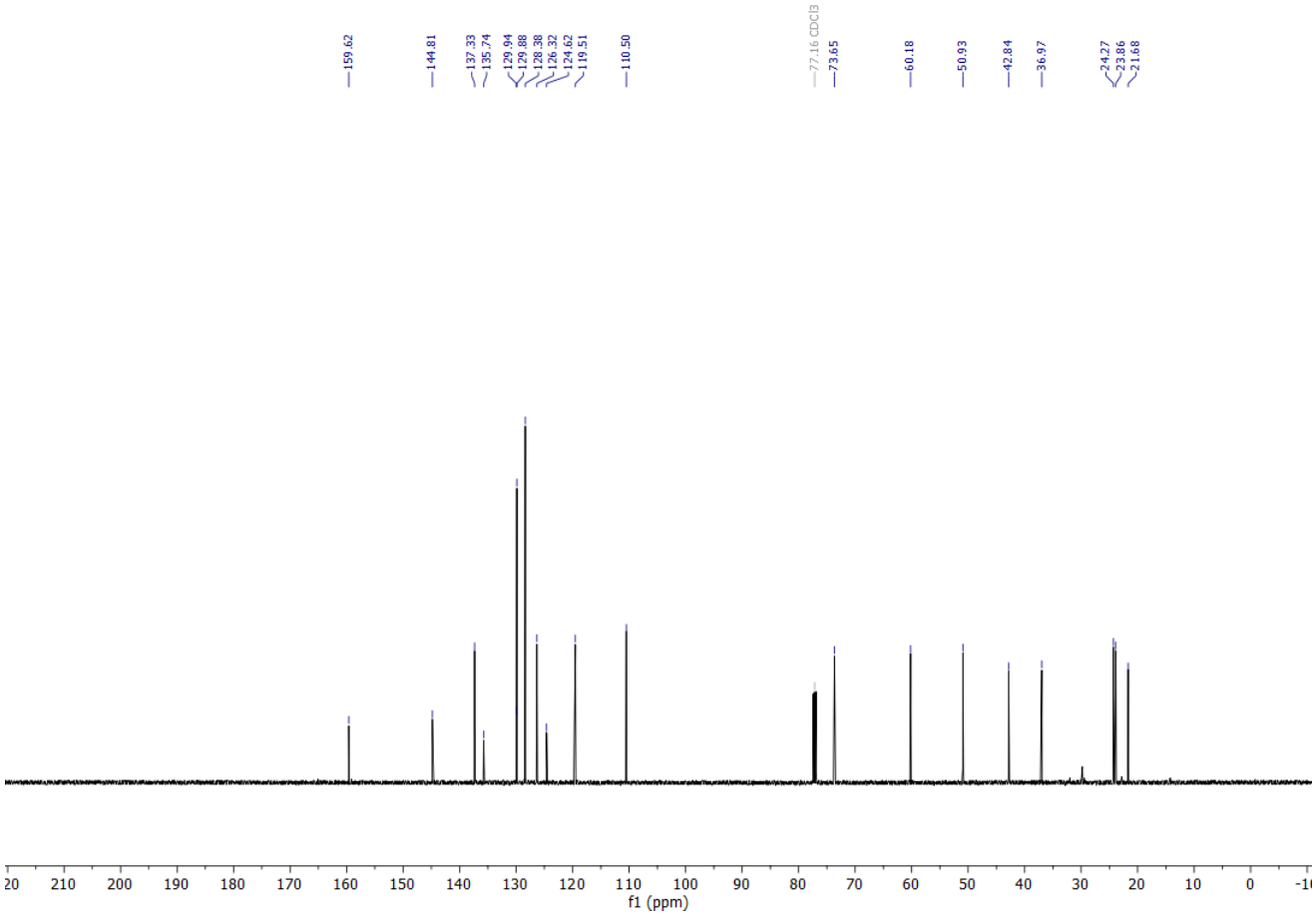
^{13}C NMR (126 MHz, $CDCl_3$)



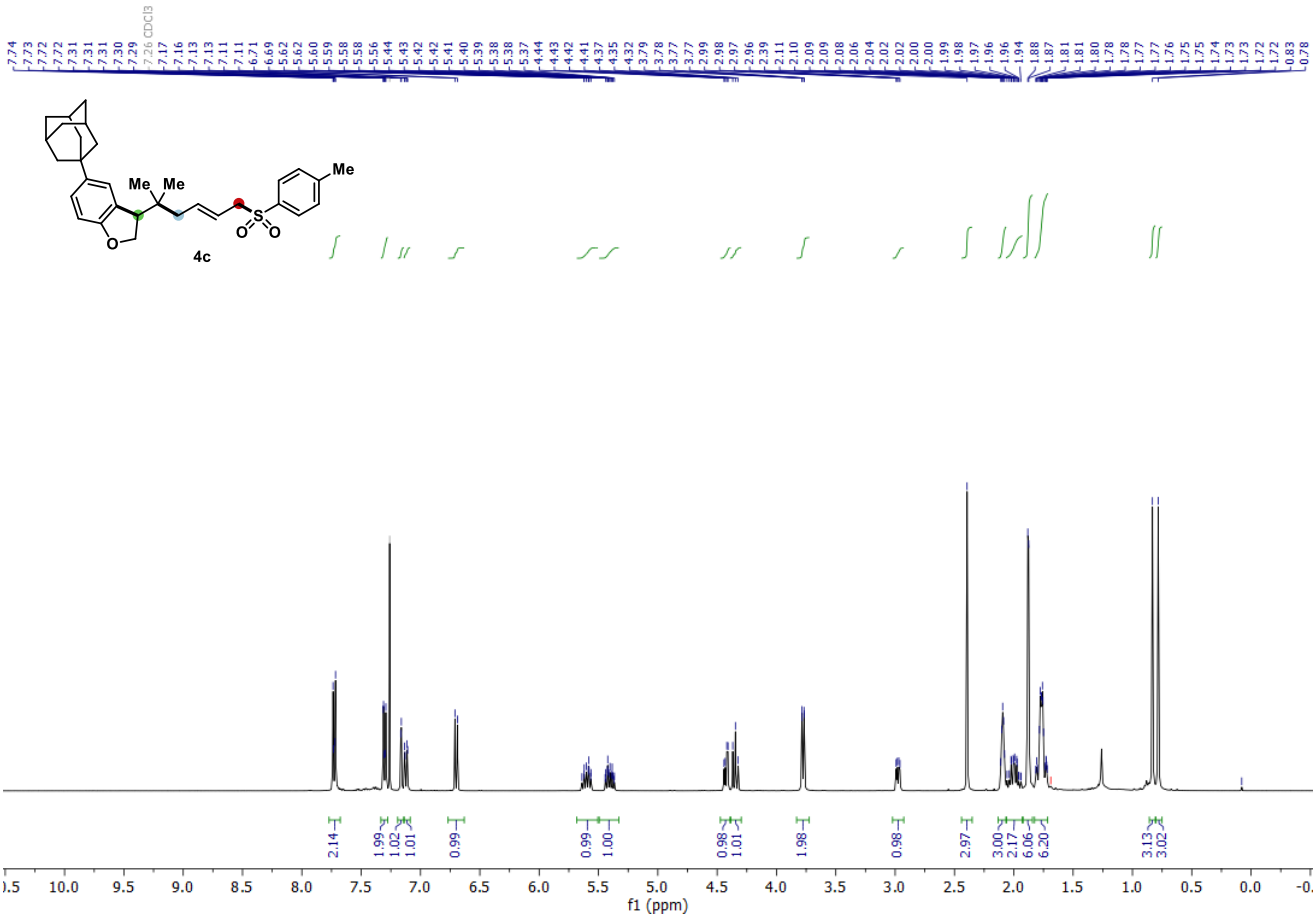
^{1}H NMR (500 MHz, $CDCl_3$)



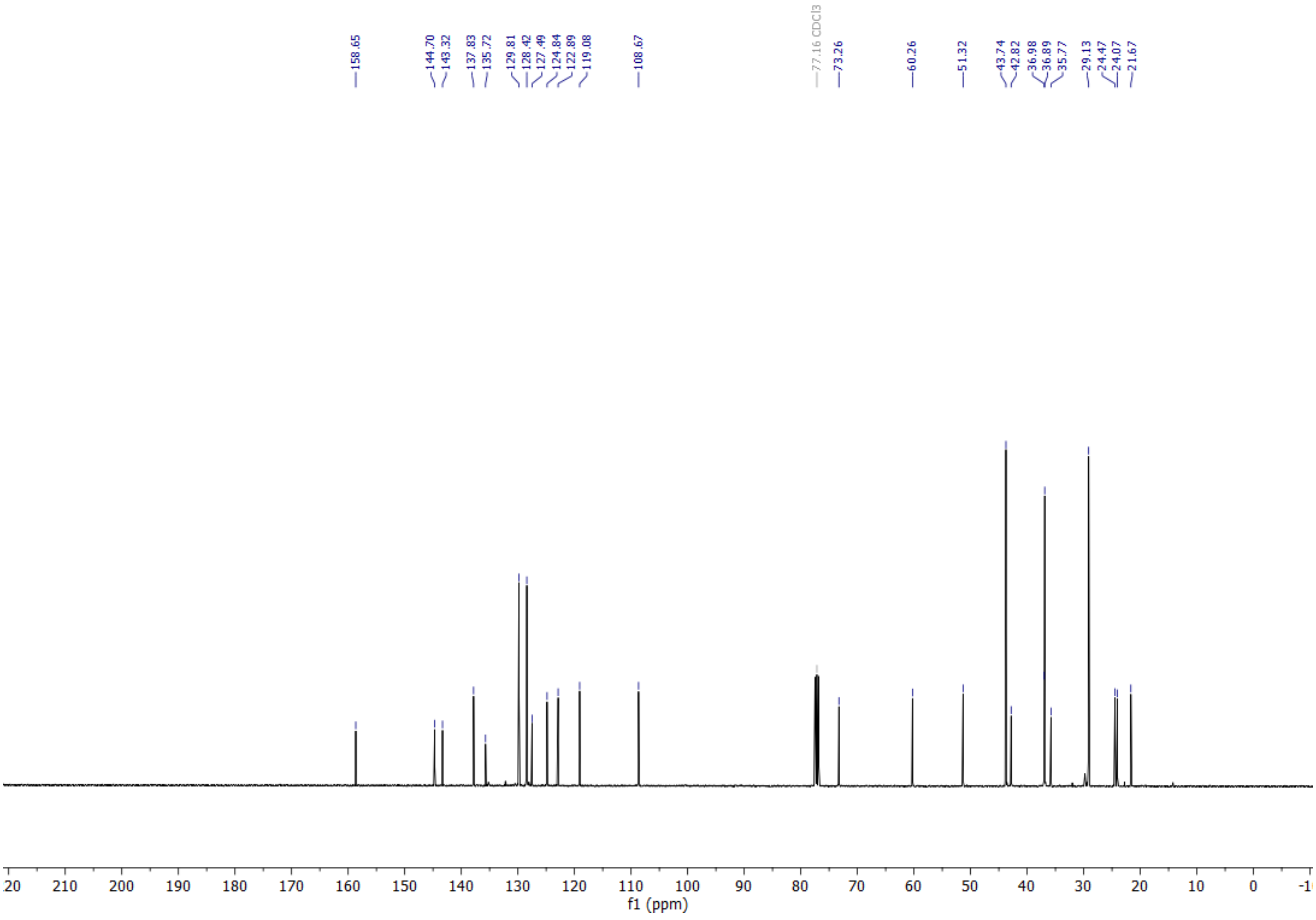
^{13}C NMR (126 MHz, $CDCl_3$)



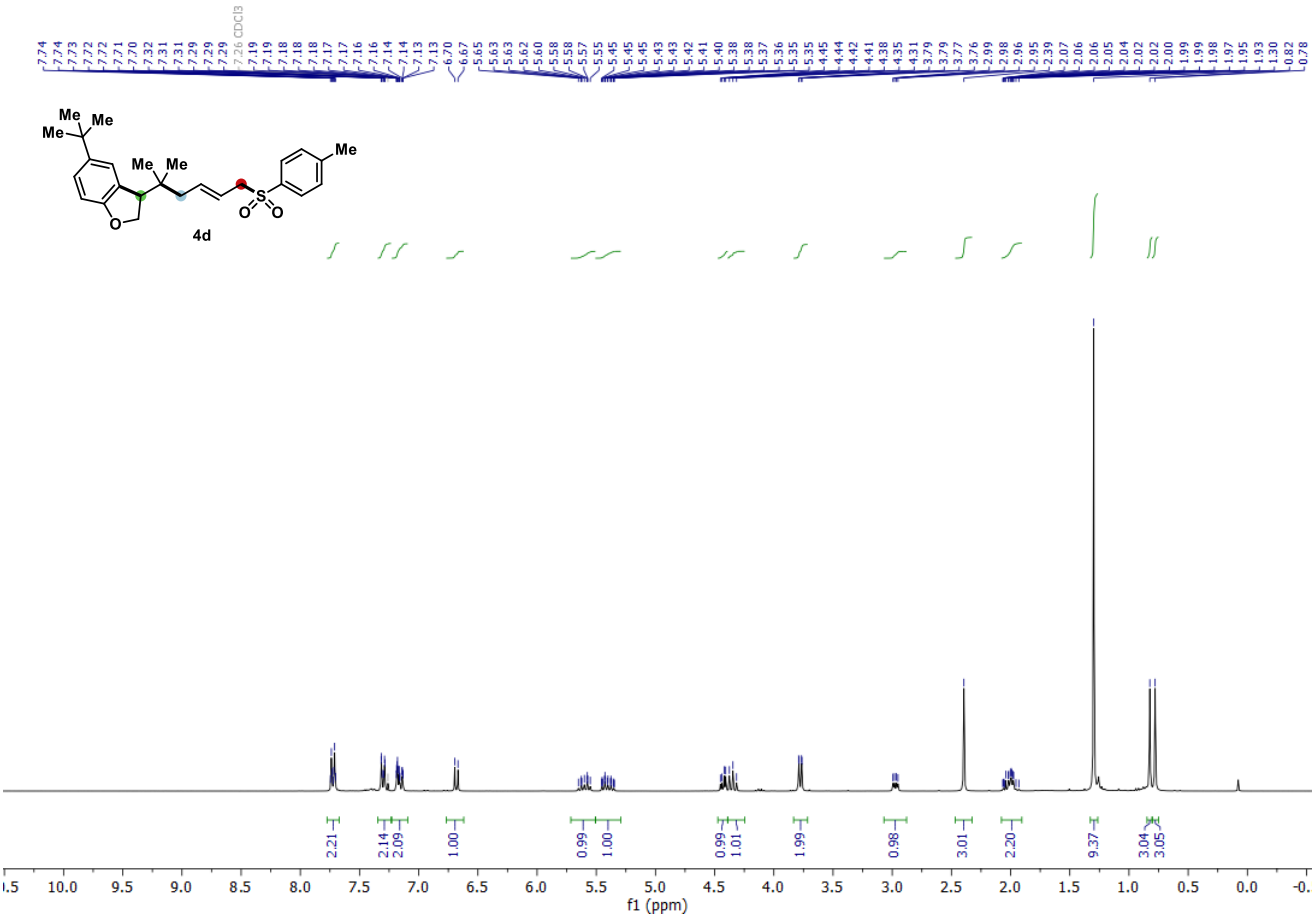
^{1}H NMR (400 MHz, $CDCl_3$)



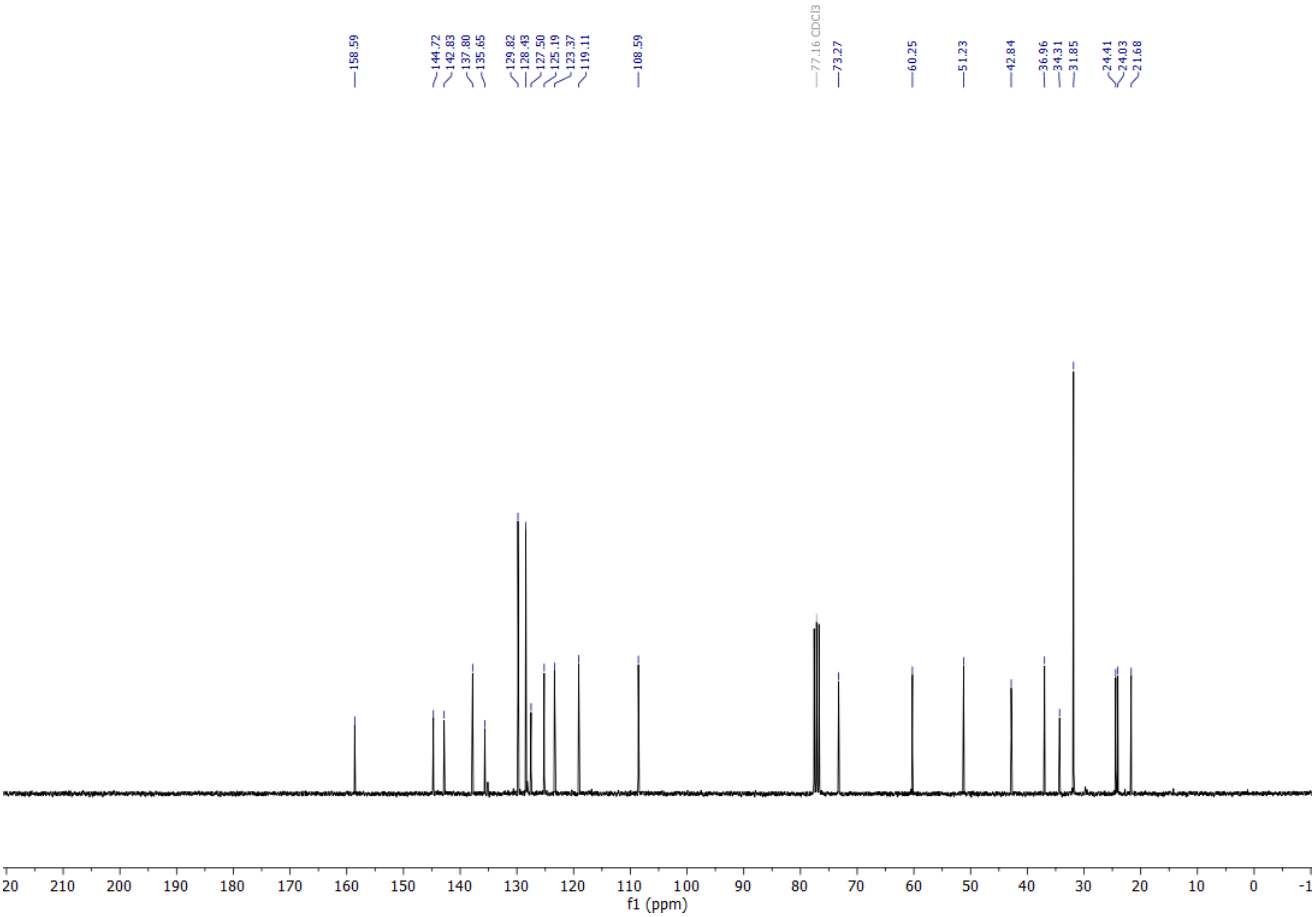
^{13}C NMR (101 MHz, $CDCl_3$)



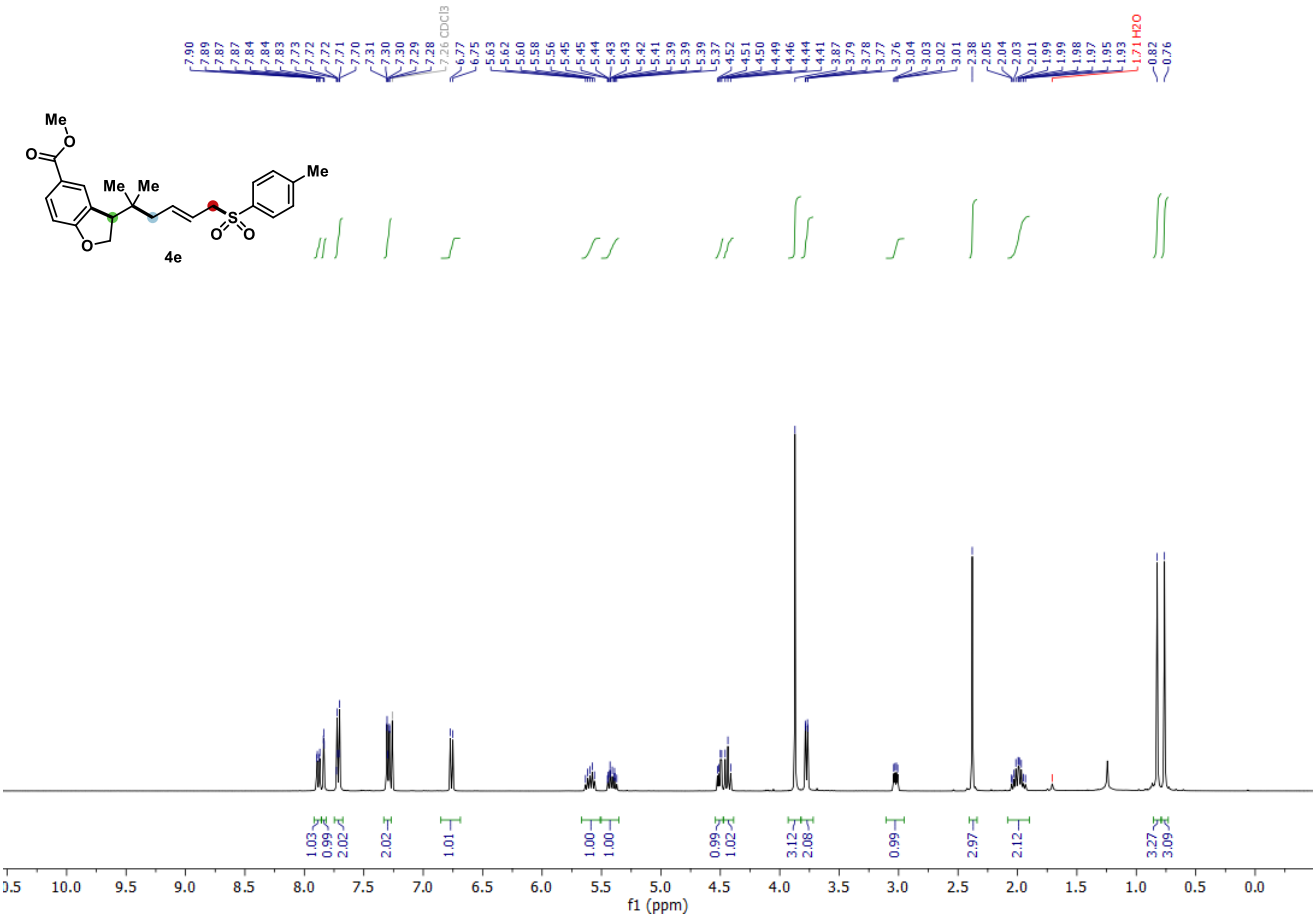
^{1}H NMR (300 MHz, $CDCl_3$)



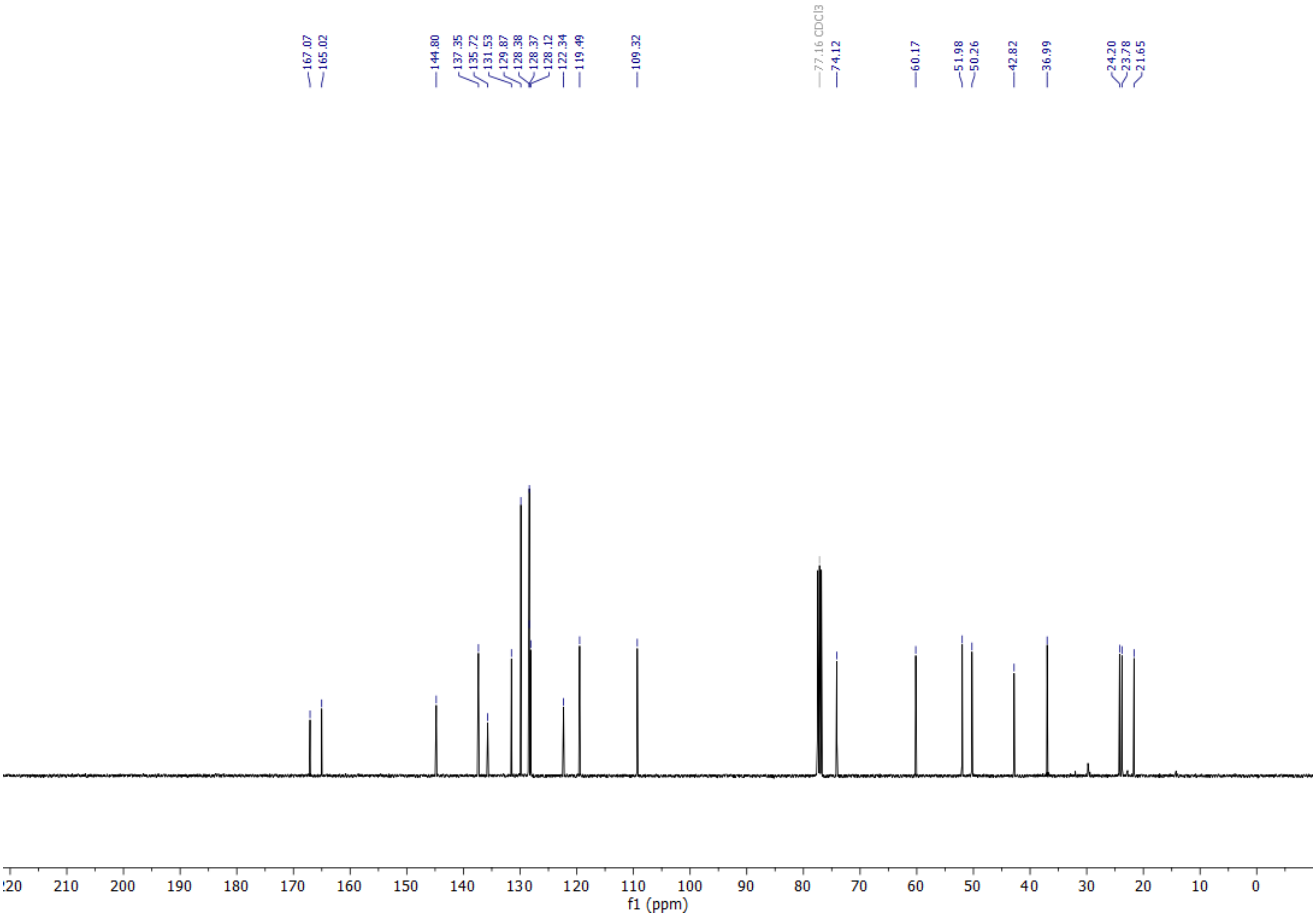
^{13}C NMR (75 MHz, $CDCl_3$)



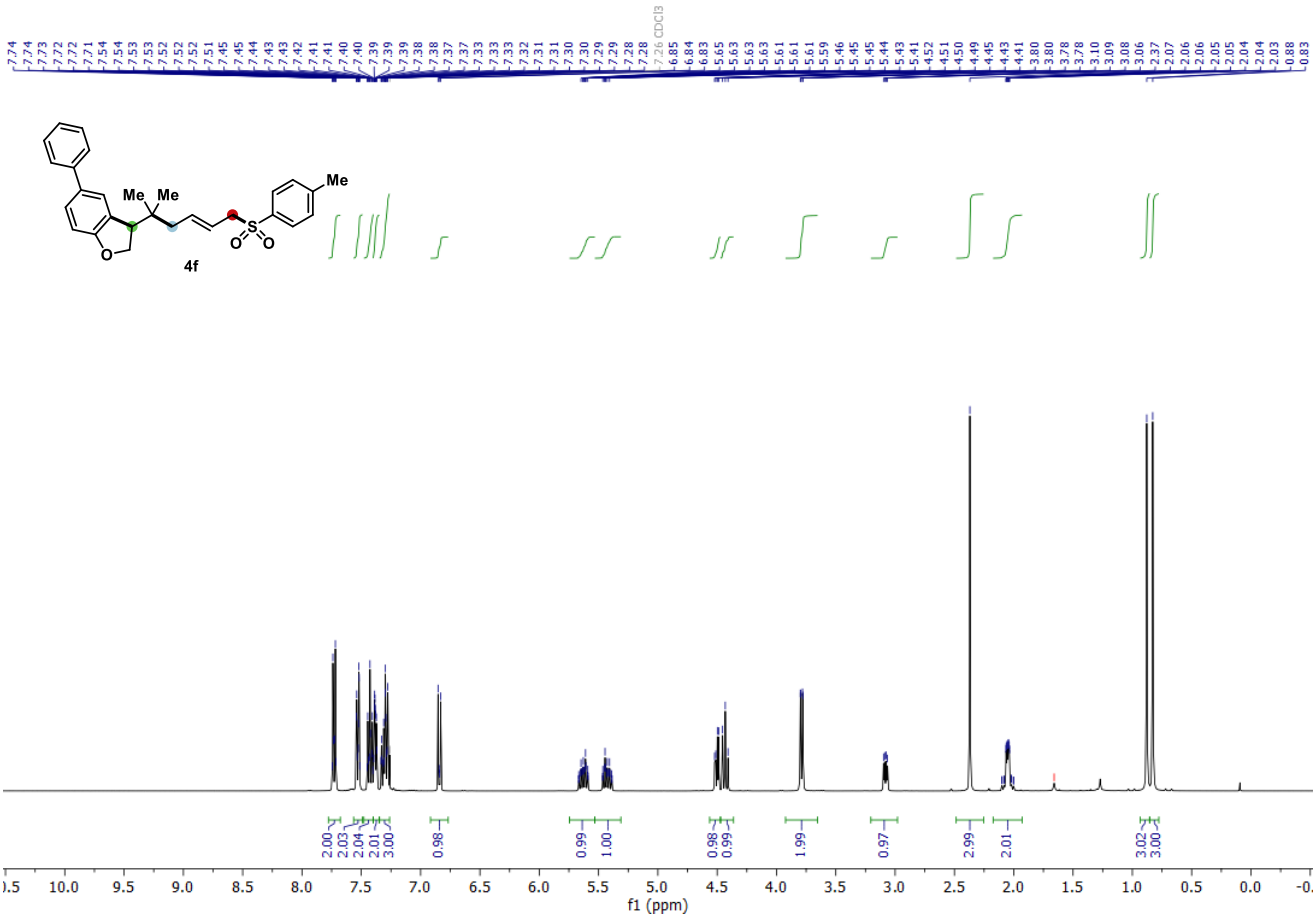
^{1}H NMR (400 MHz, $CDCl_3$)



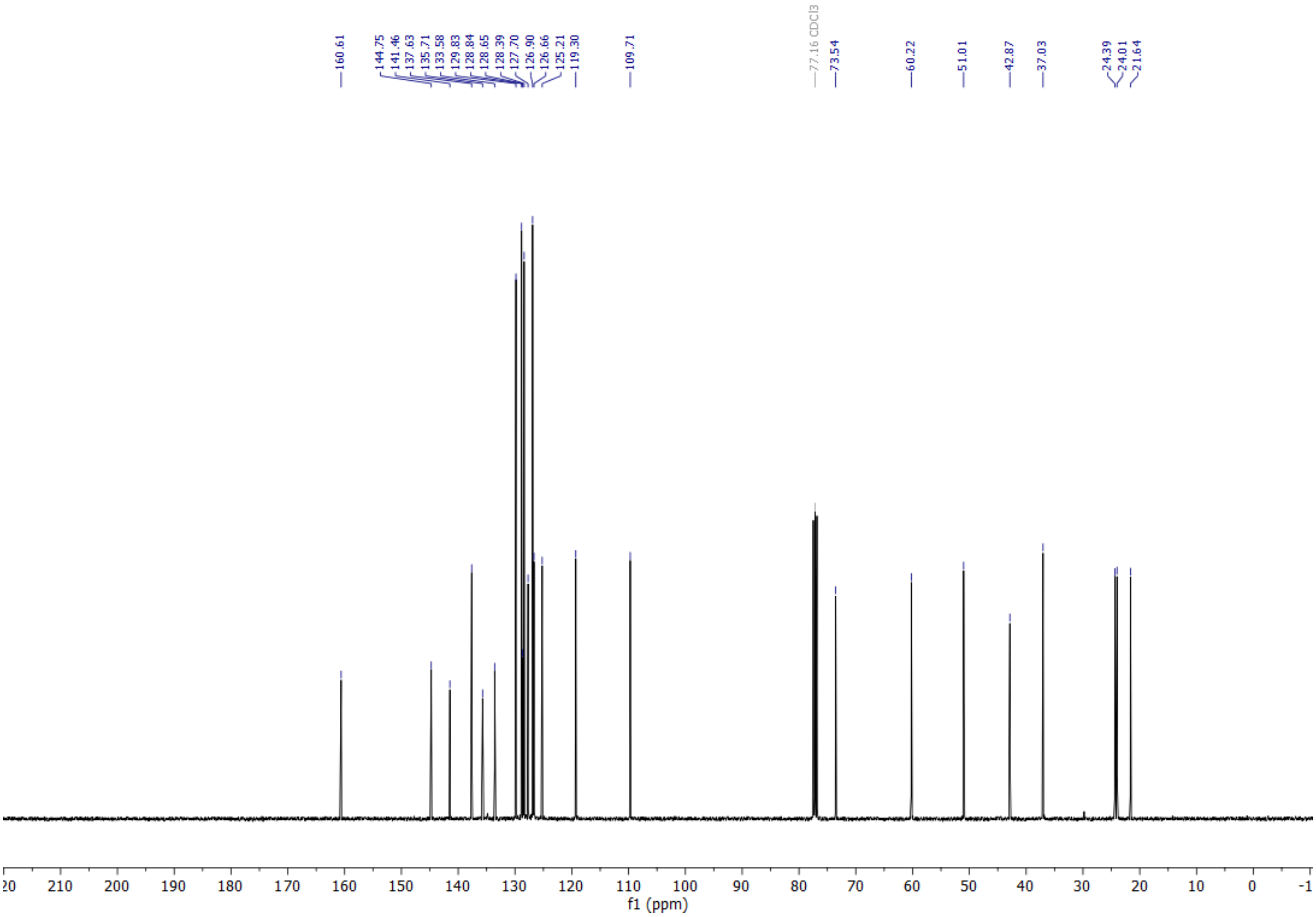
^{13}C NMR (101 MHz, $CDCl_3$)



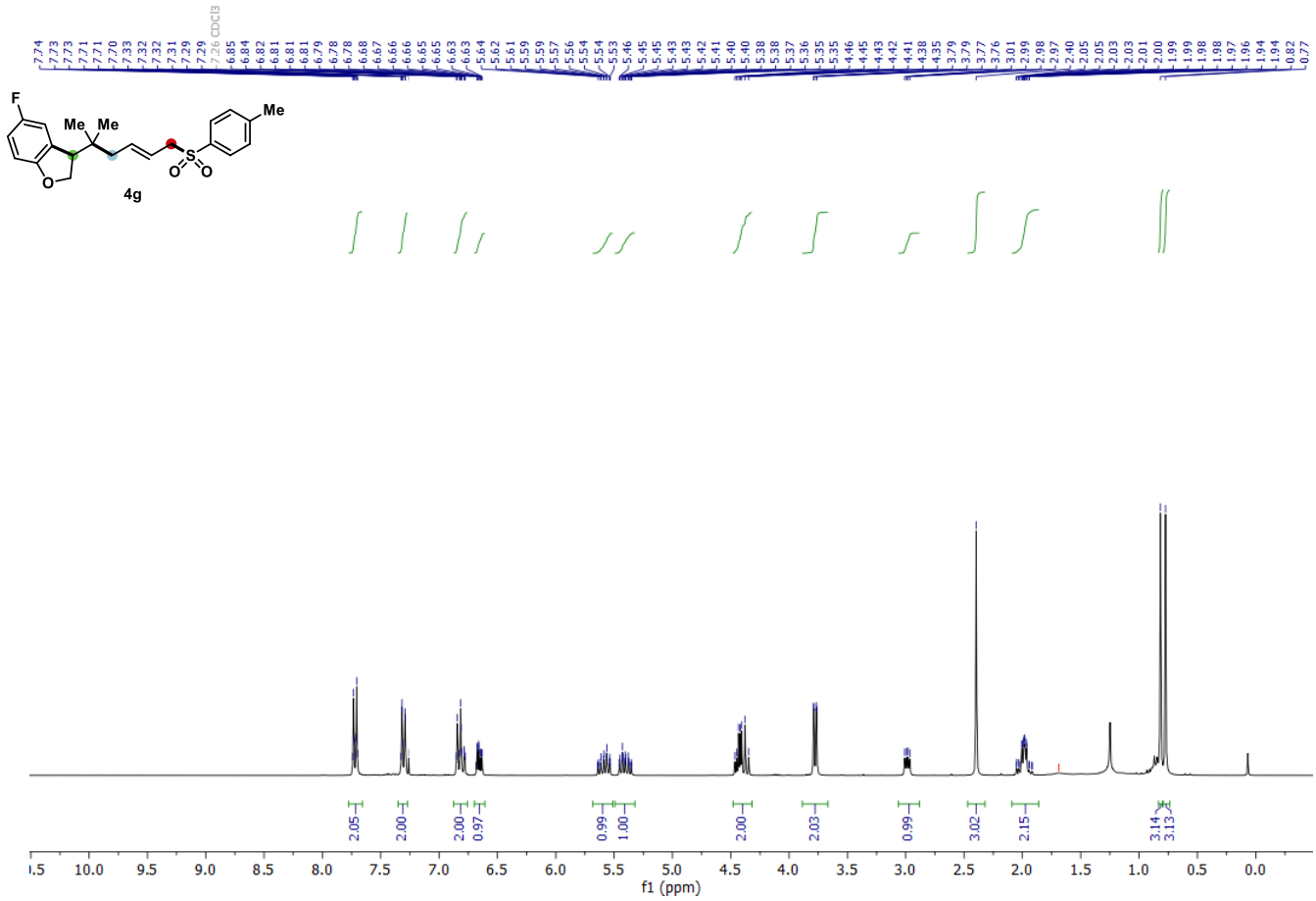
^{1}H NMR (400 MHz, $CDCl_3$)



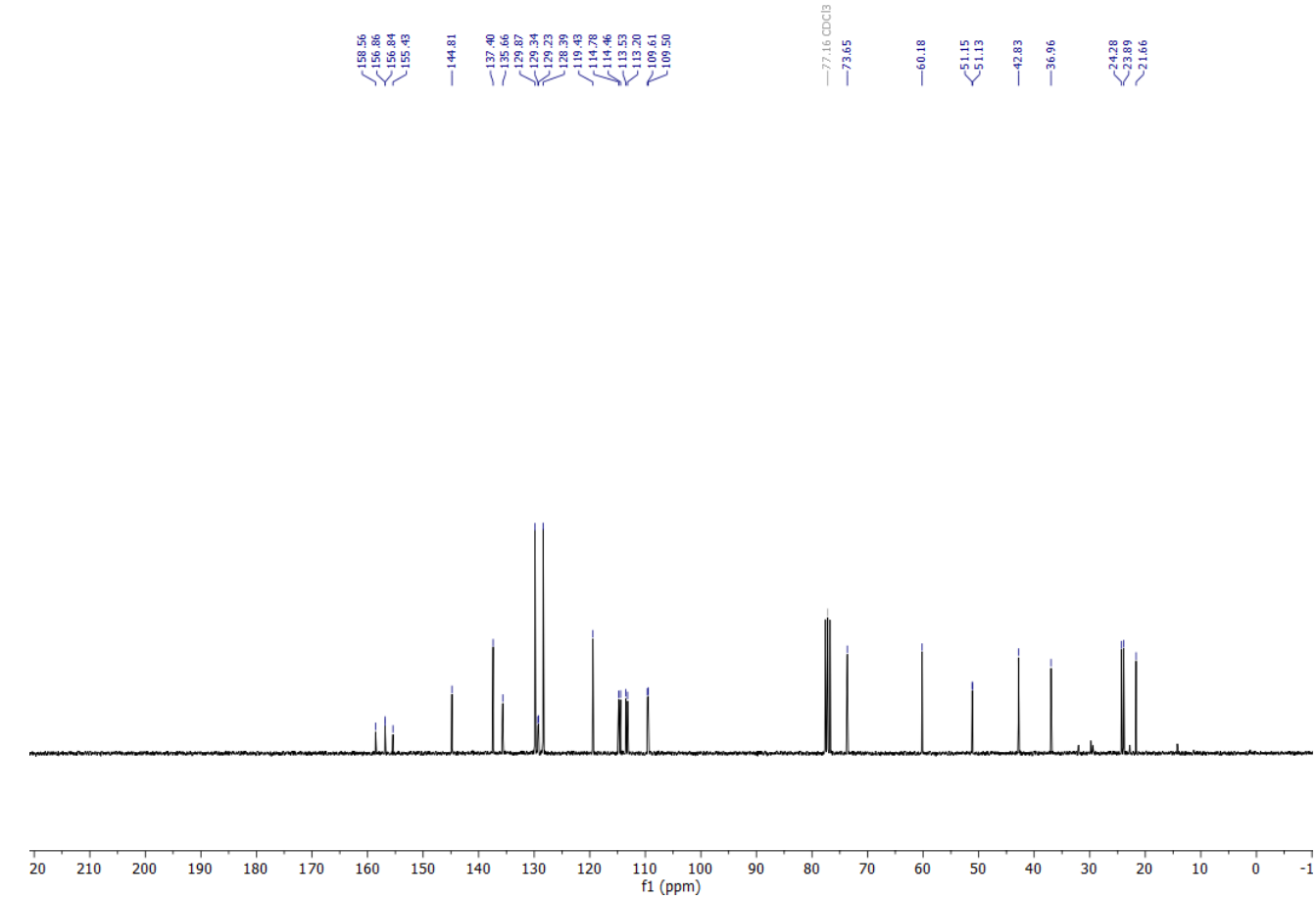
^{13}C NMR (101 MHz, $CDCl_3$)



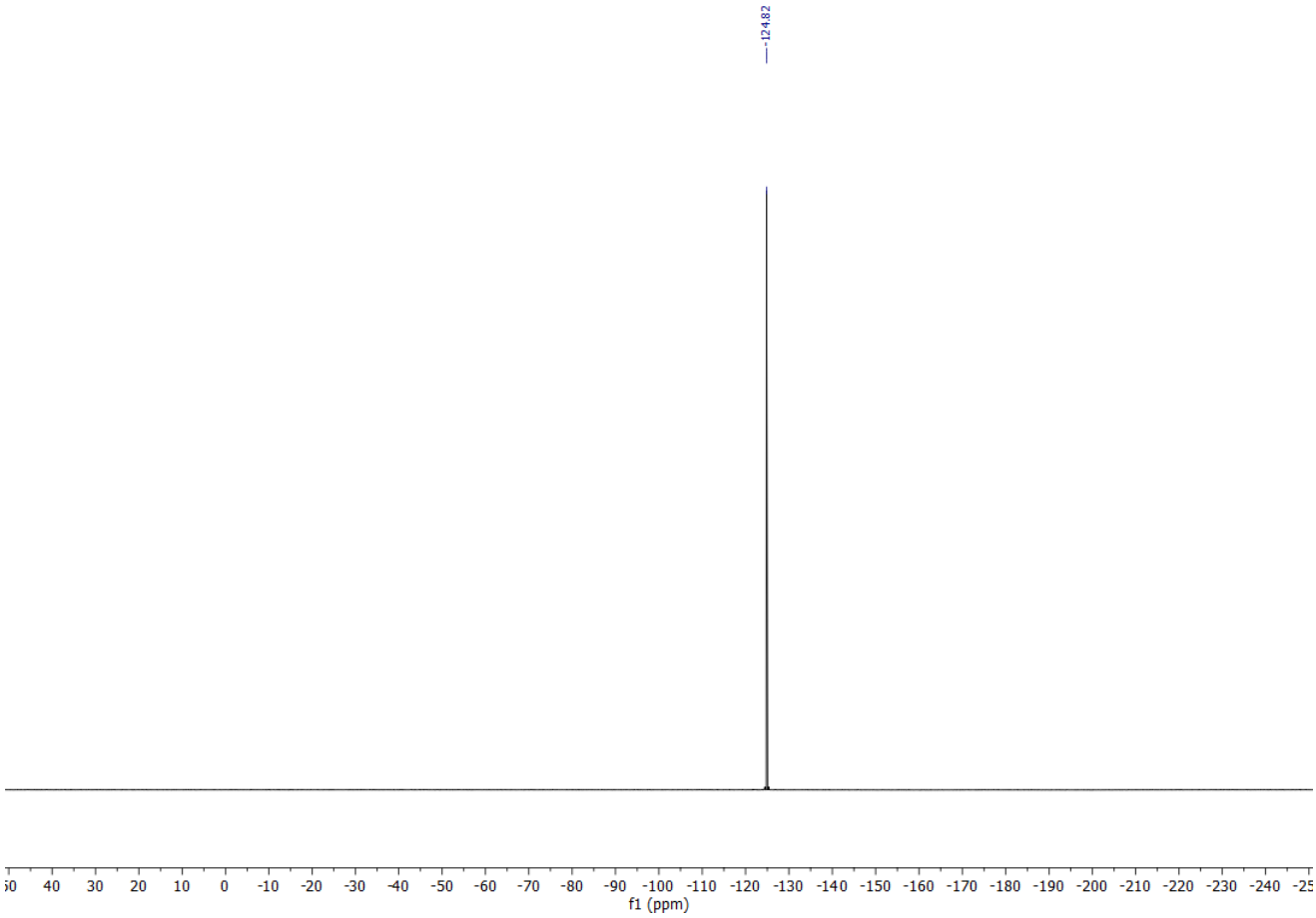
^{1}H NMR (300 MHz, $CDCl_3$)



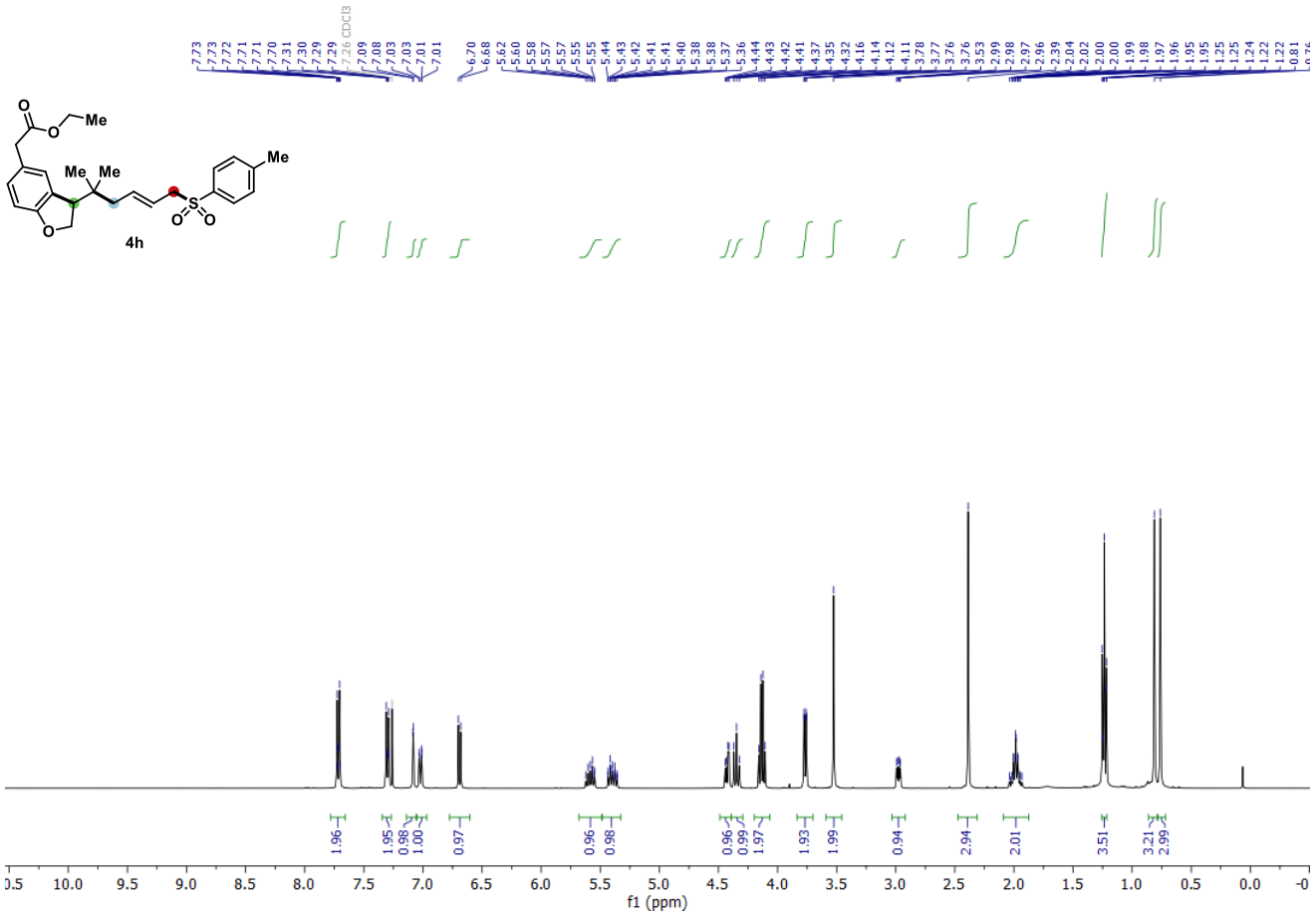
^{13}C NMR (75 MHz, $CDCl_3$)



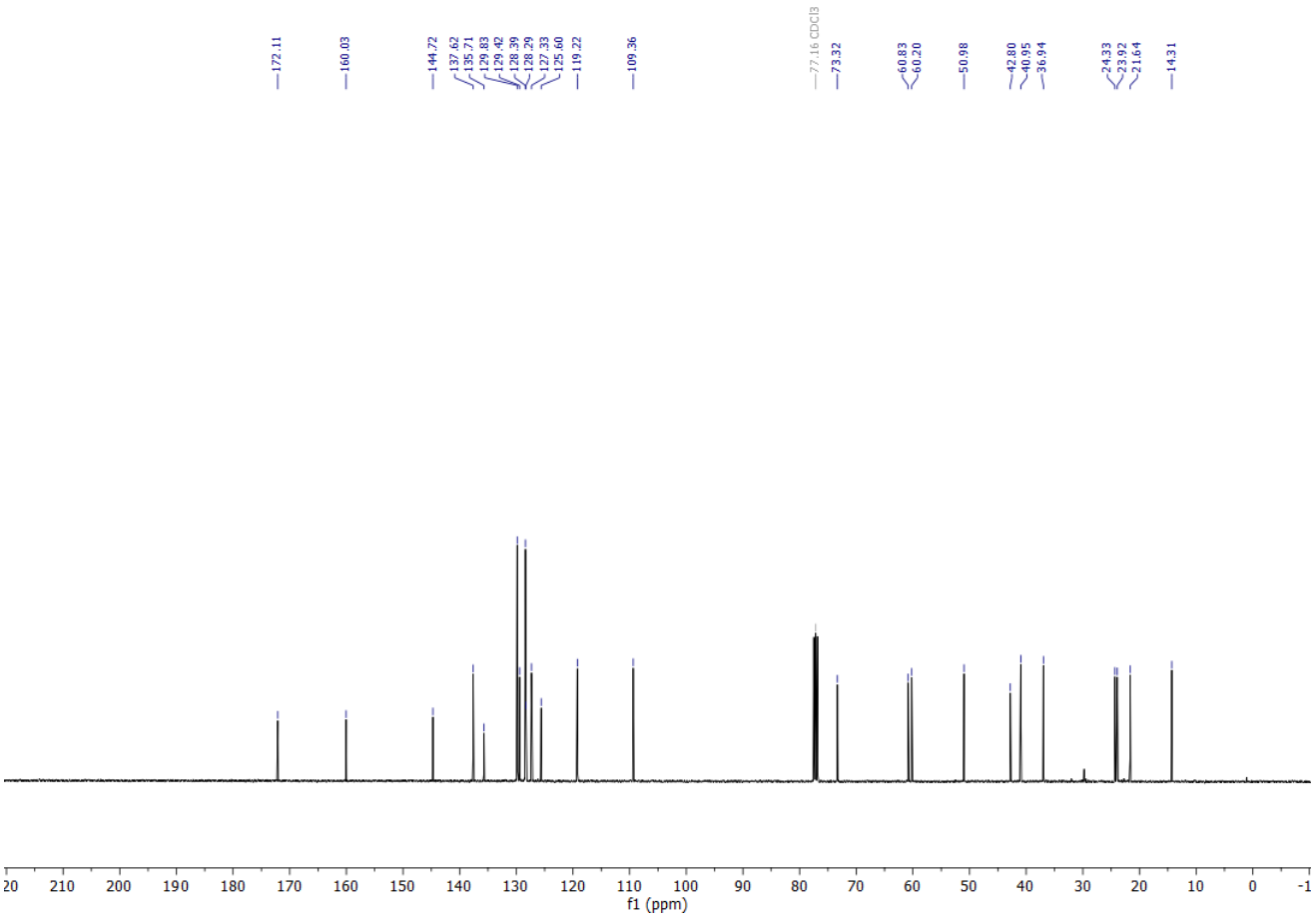
$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



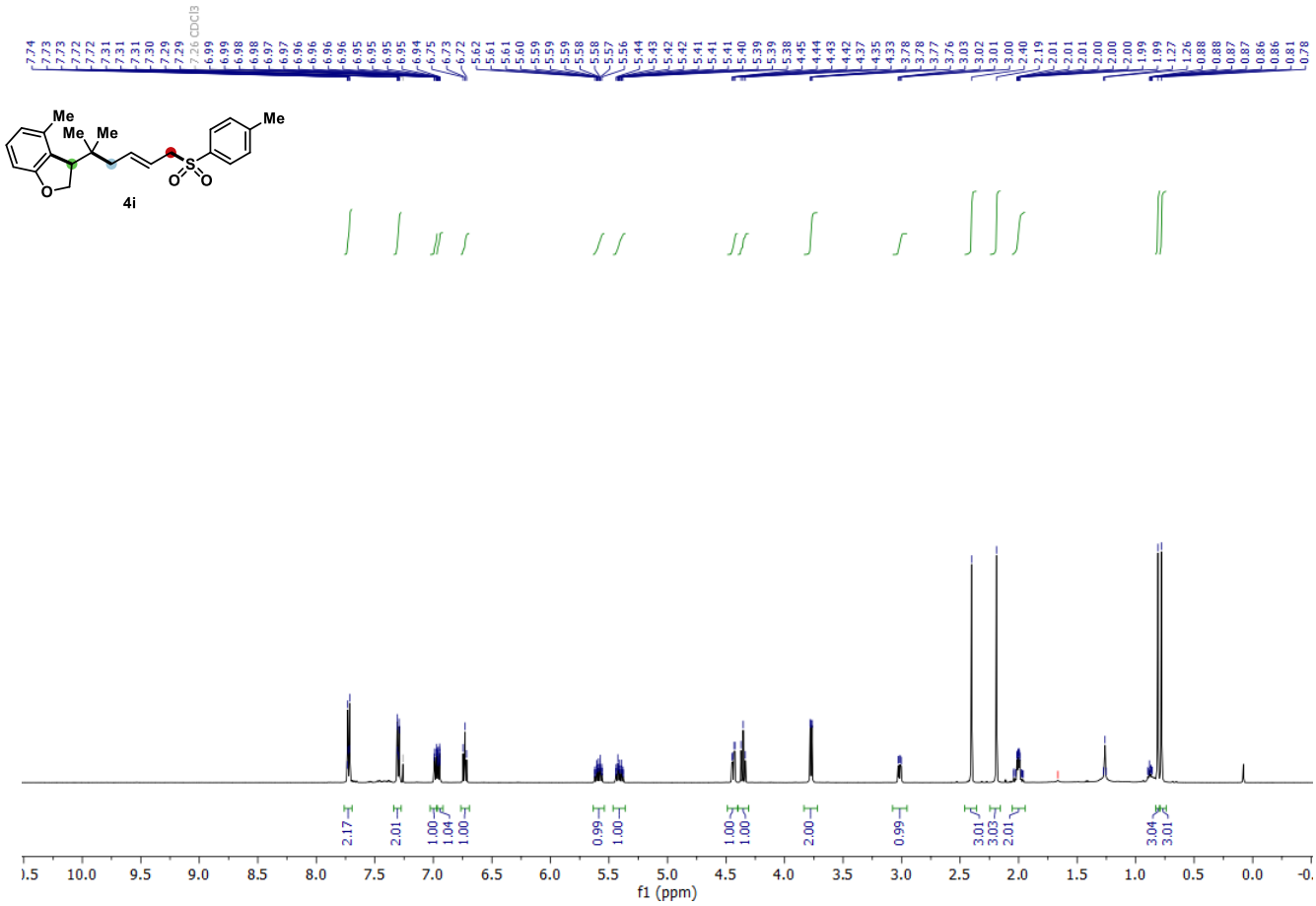
^{1}H NMR (400 MHz, $CDCl_3$)



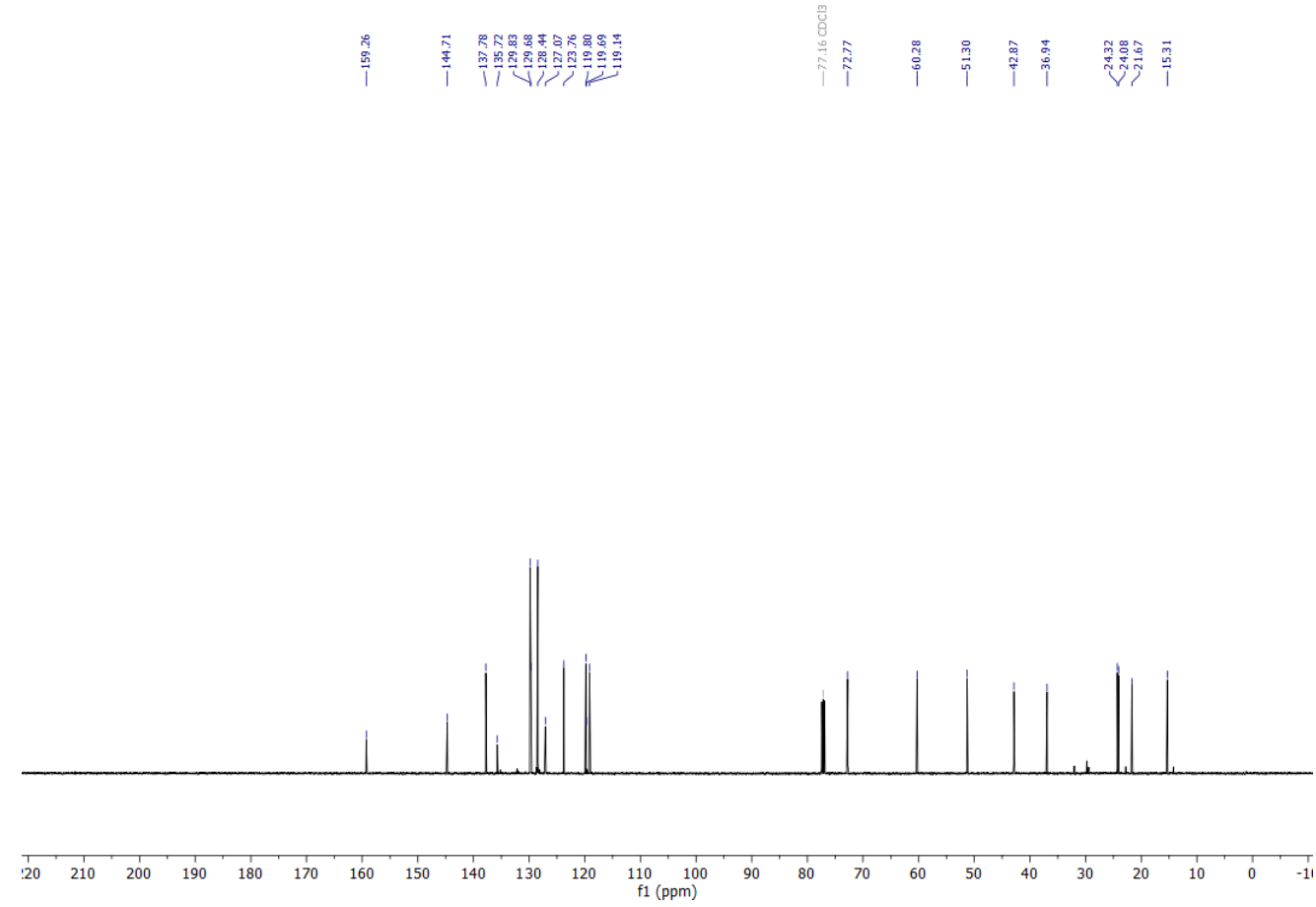
^{13}C NMR (101 MHz, $CDCl_3$)



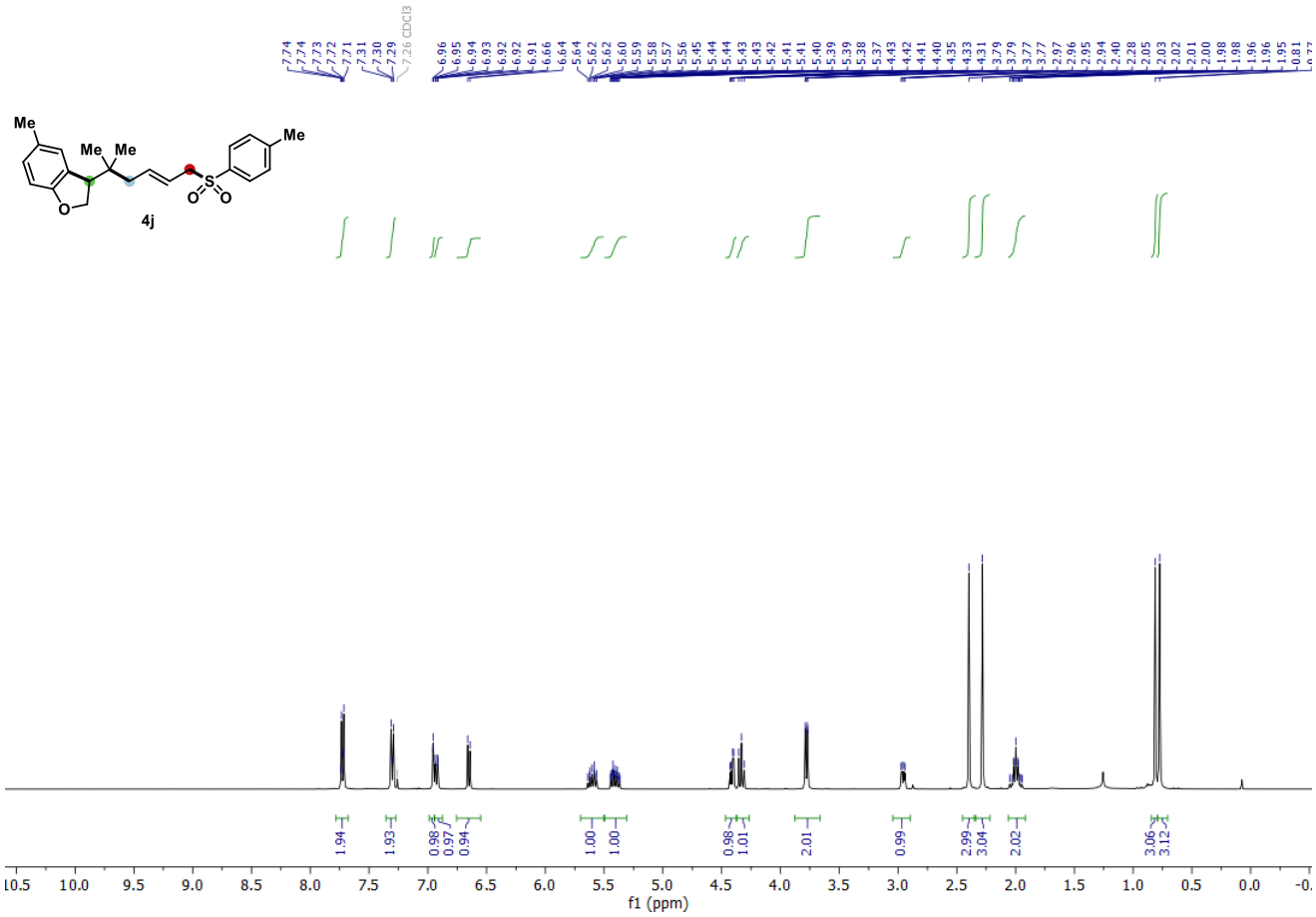
^{1}H NMR (500 MHz, $CDCl_3$)



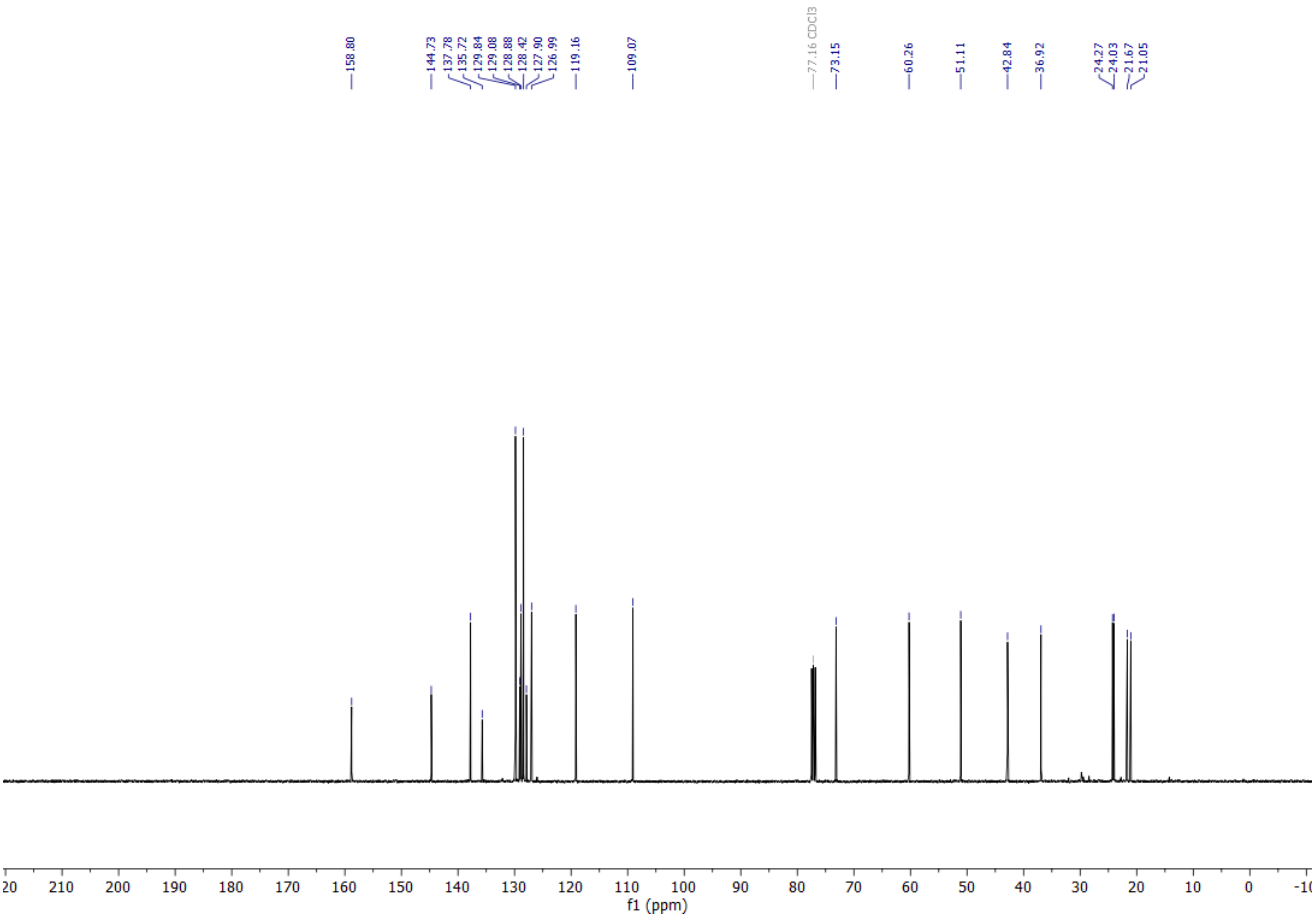
^{13}C NMR (126 MHz, $CDCl_3$)



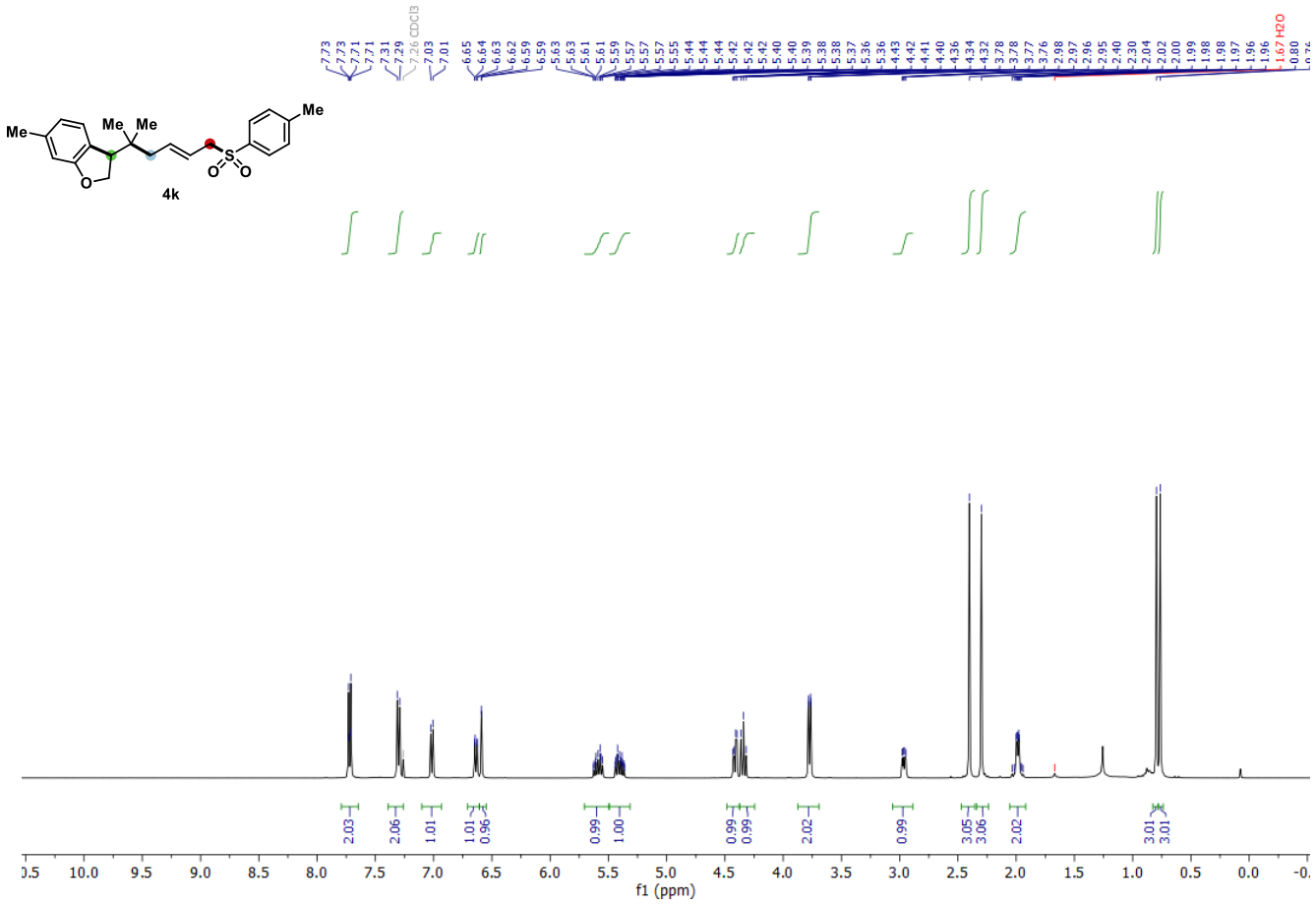
^{1}H NMR (400 MHz, $CDCl_3$)



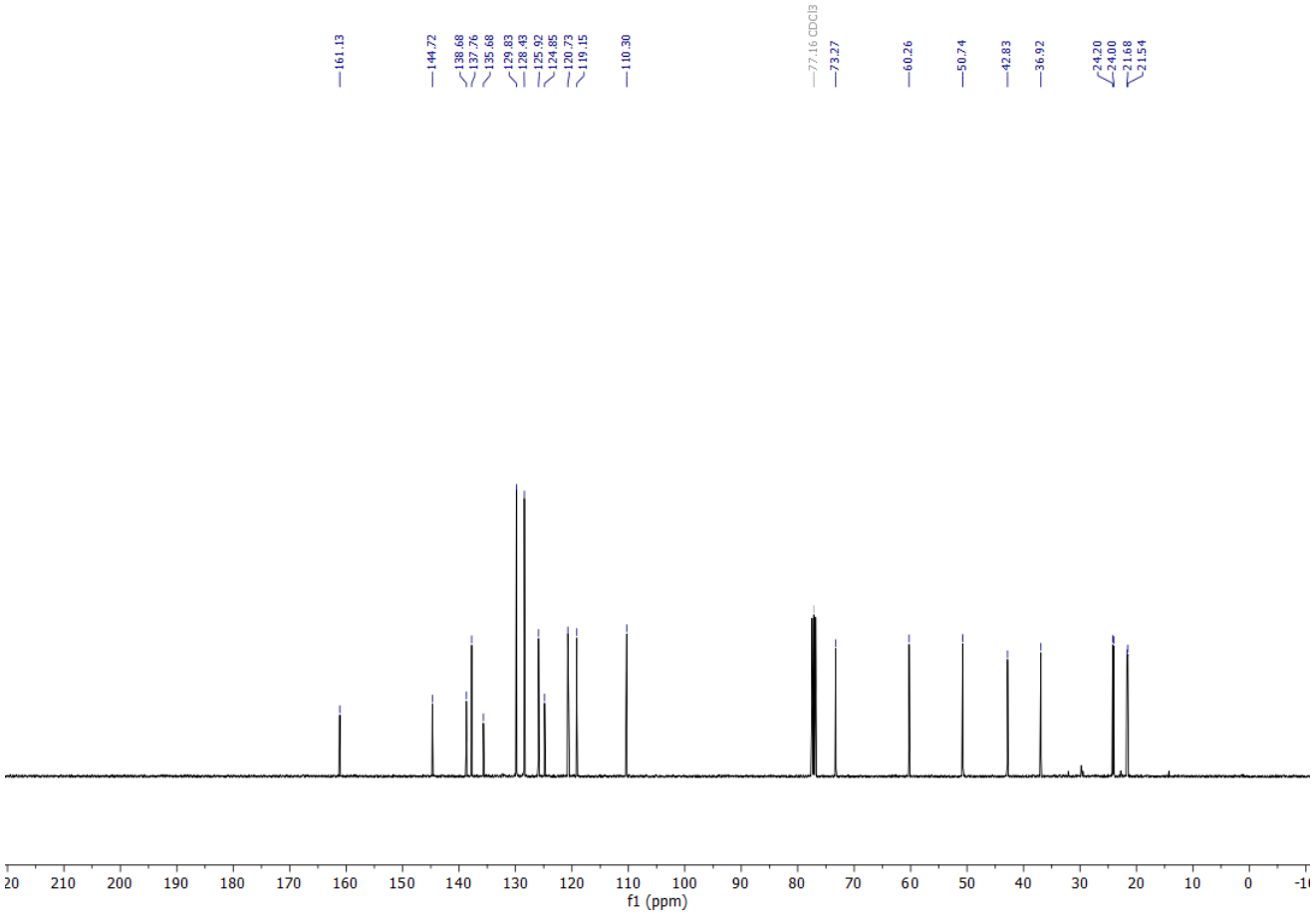
^{13}C NMR (101 MHz, $CDCl_3$)



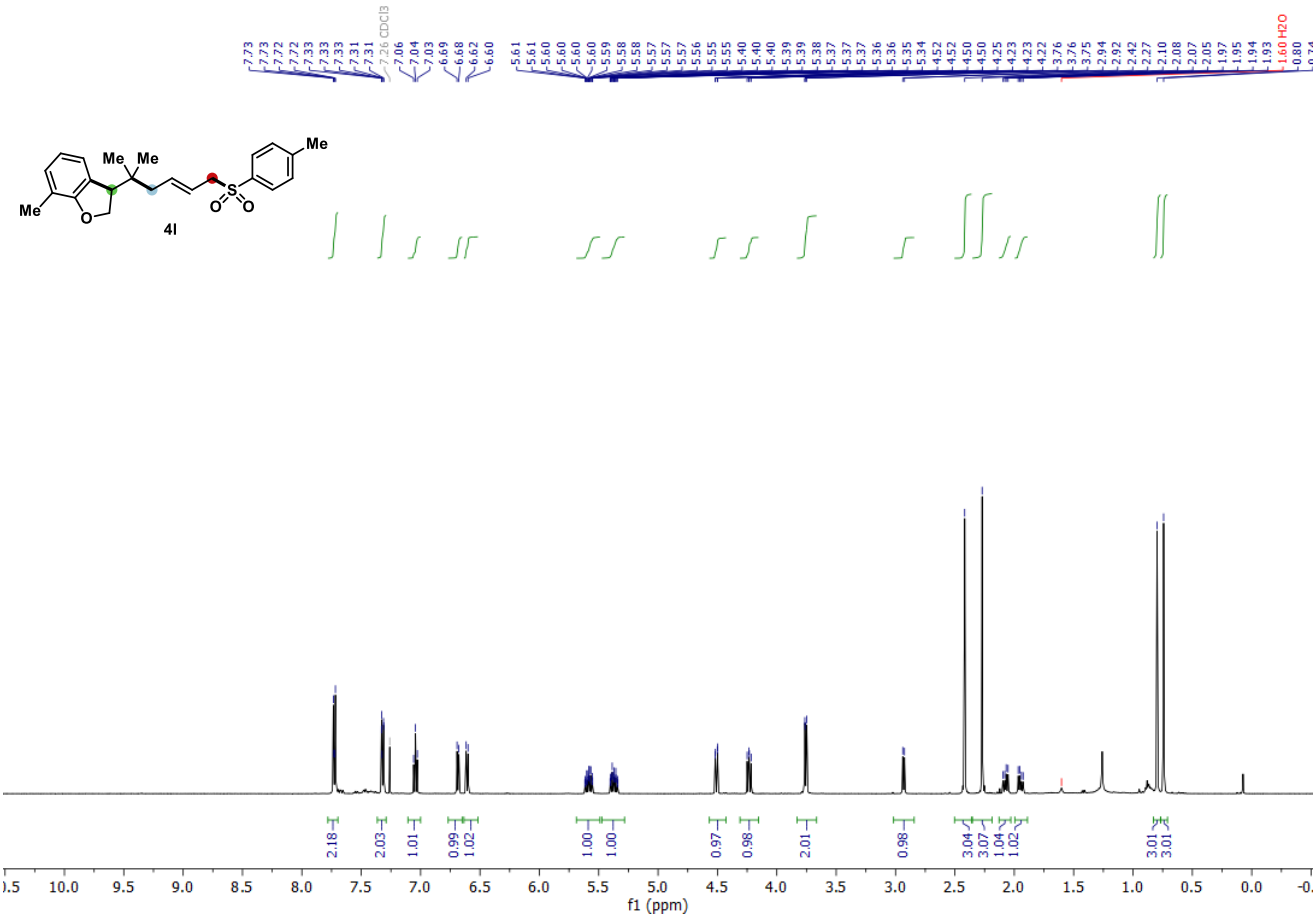
^{1}H NMR (400 MHz, $CDCl_3$)



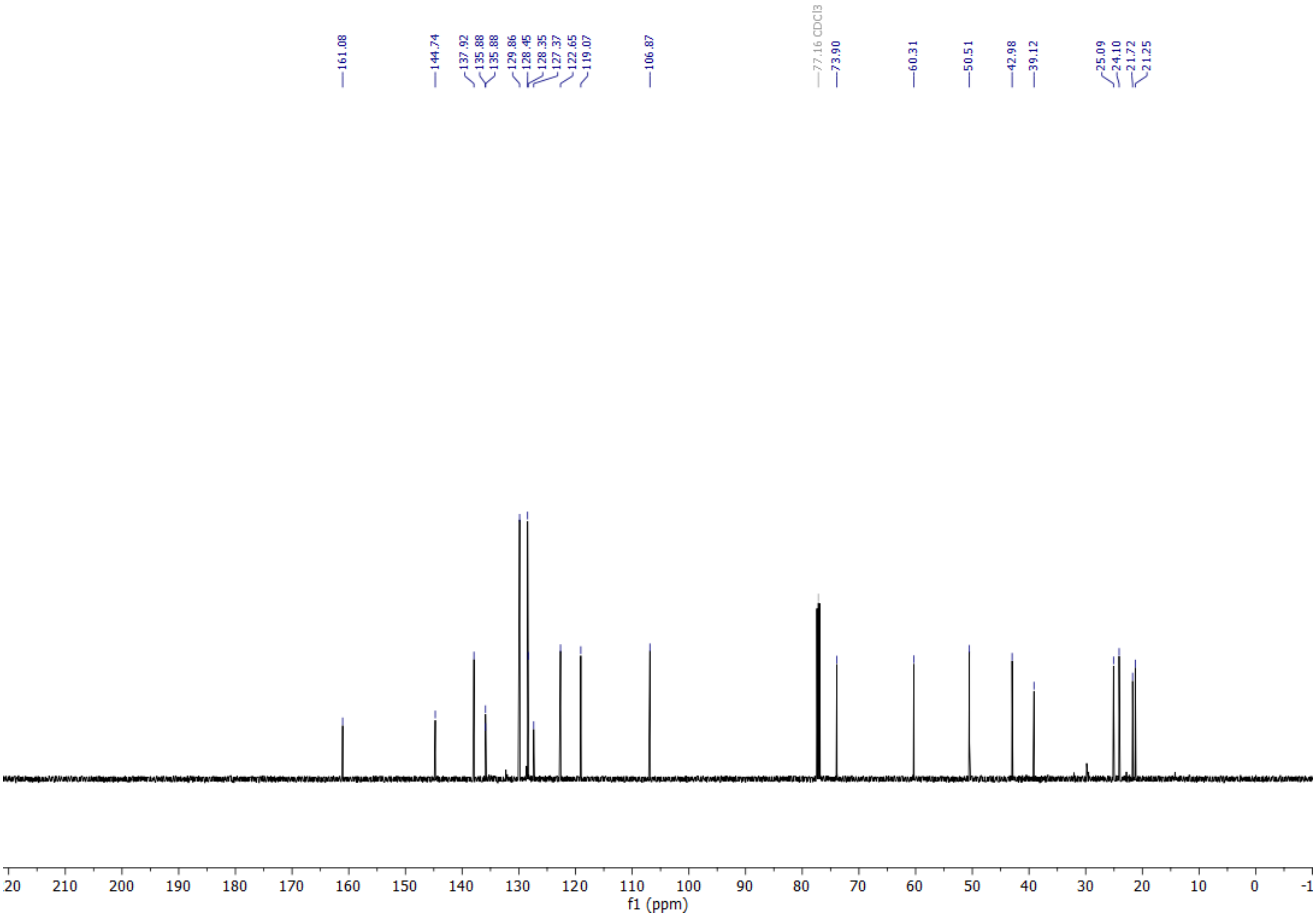
^{13}C NMR (101 MHz, $CDCl_3$)



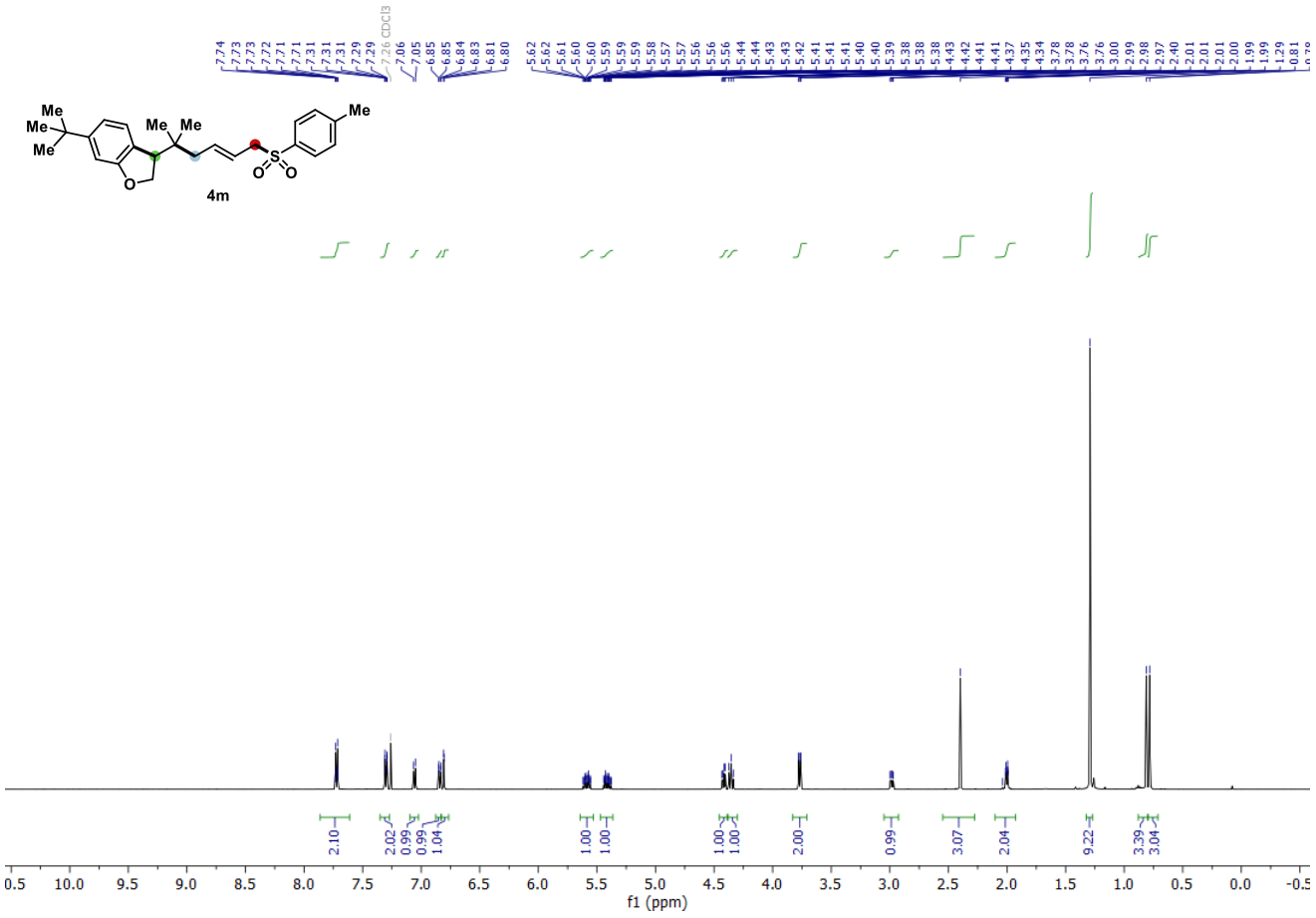
^{1}H NMR (500 MHz, $CDCl_3$)



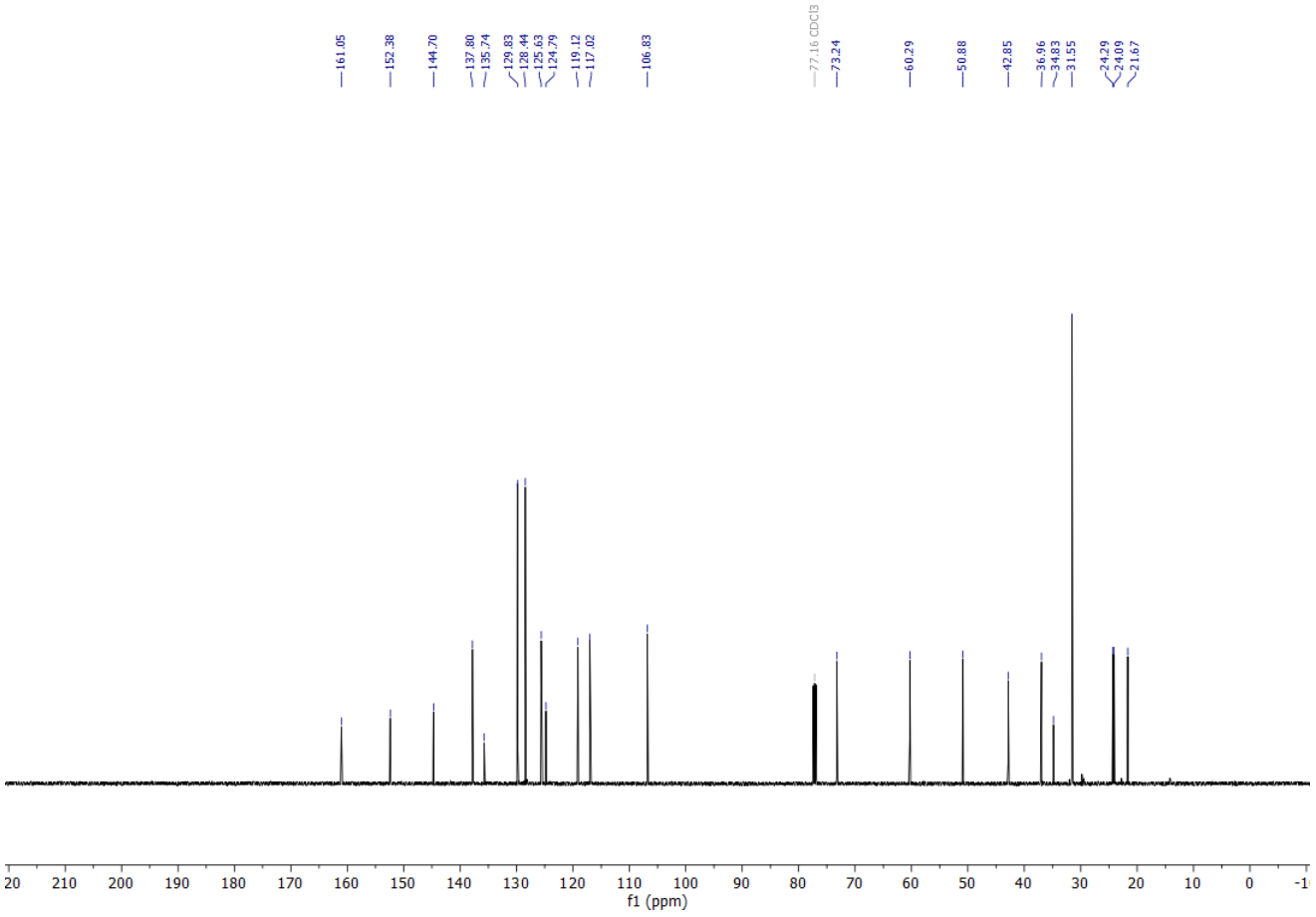
^{13}C NMR (126 MHz, $CDCl_3$)



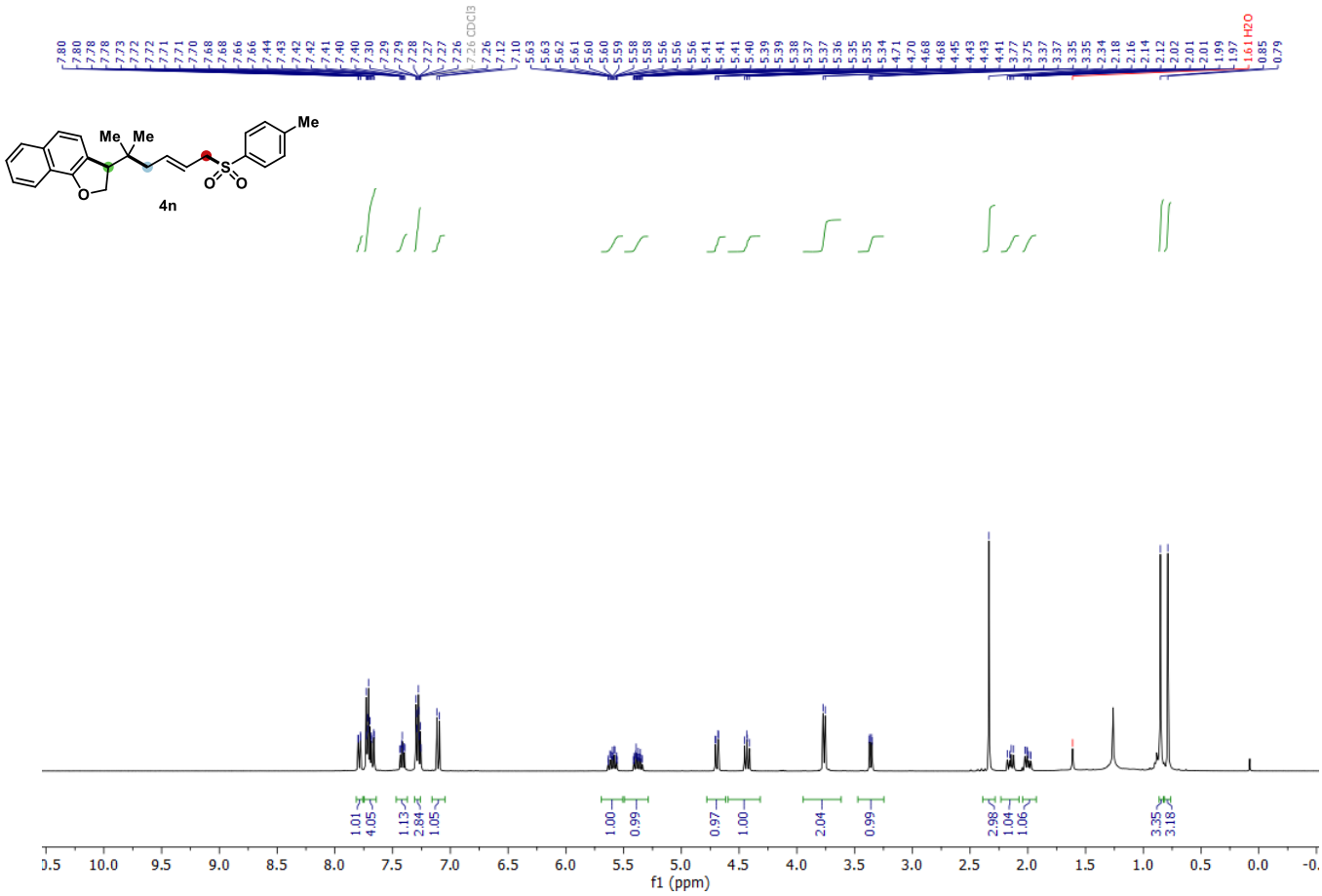
^{1}H NMR (500 MHz, $CDCl_3$)



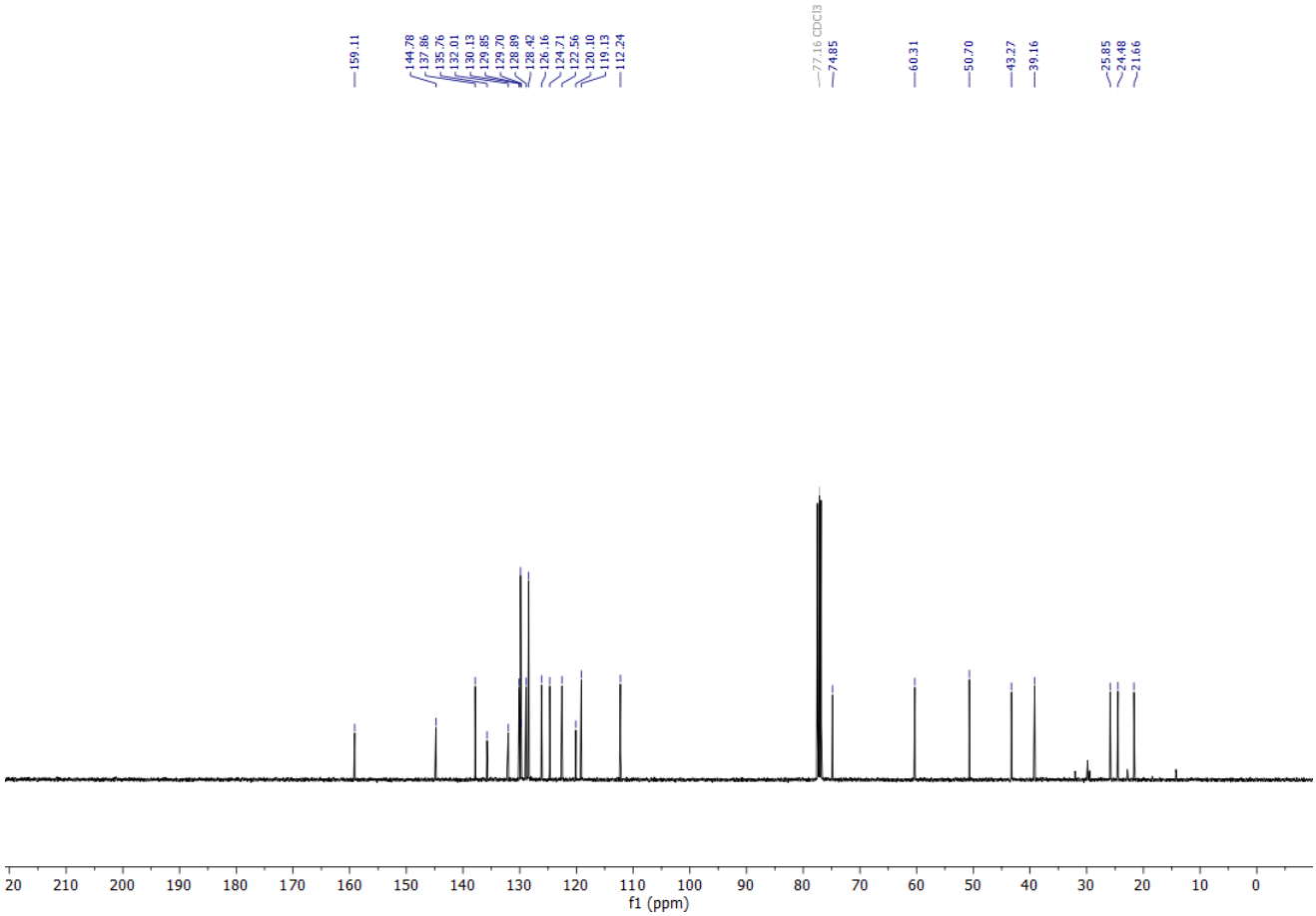
^{13}C NMR (126 MHz, $CDCl_3$)



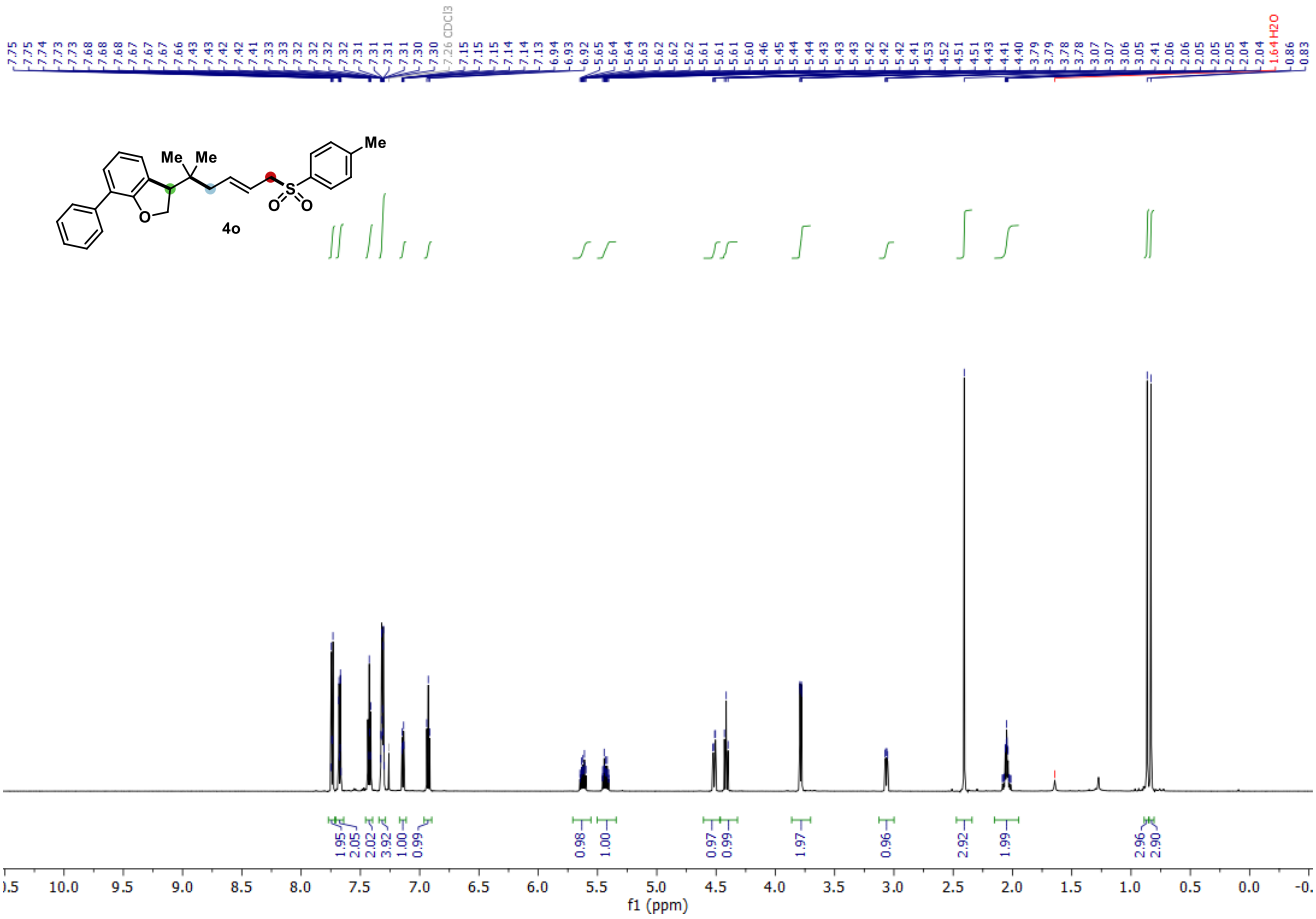
^{1}H NMR (400 MHz, $CDCl_3$)



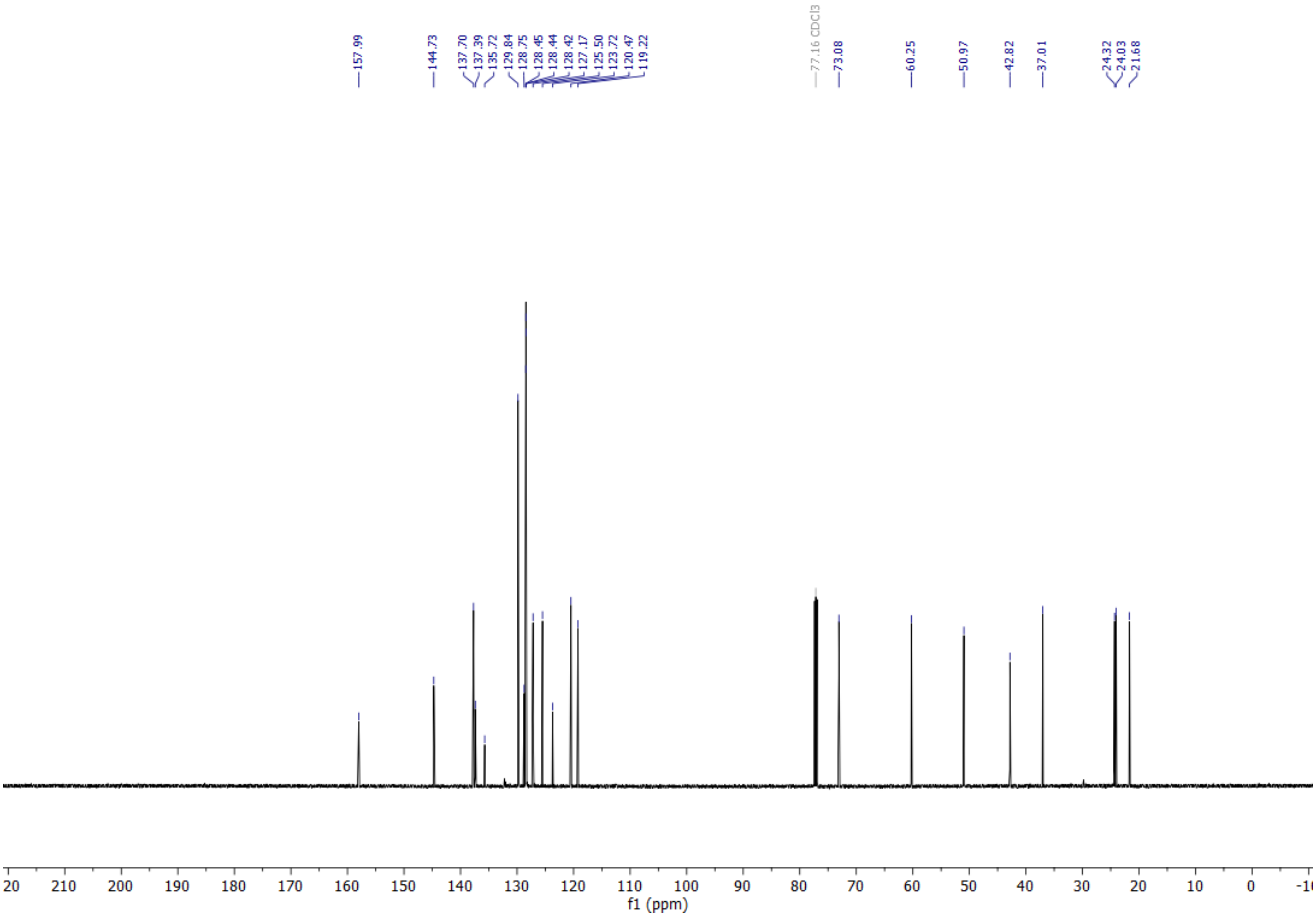
^{13}C NMR (101 MHz, $CDCl_3$)



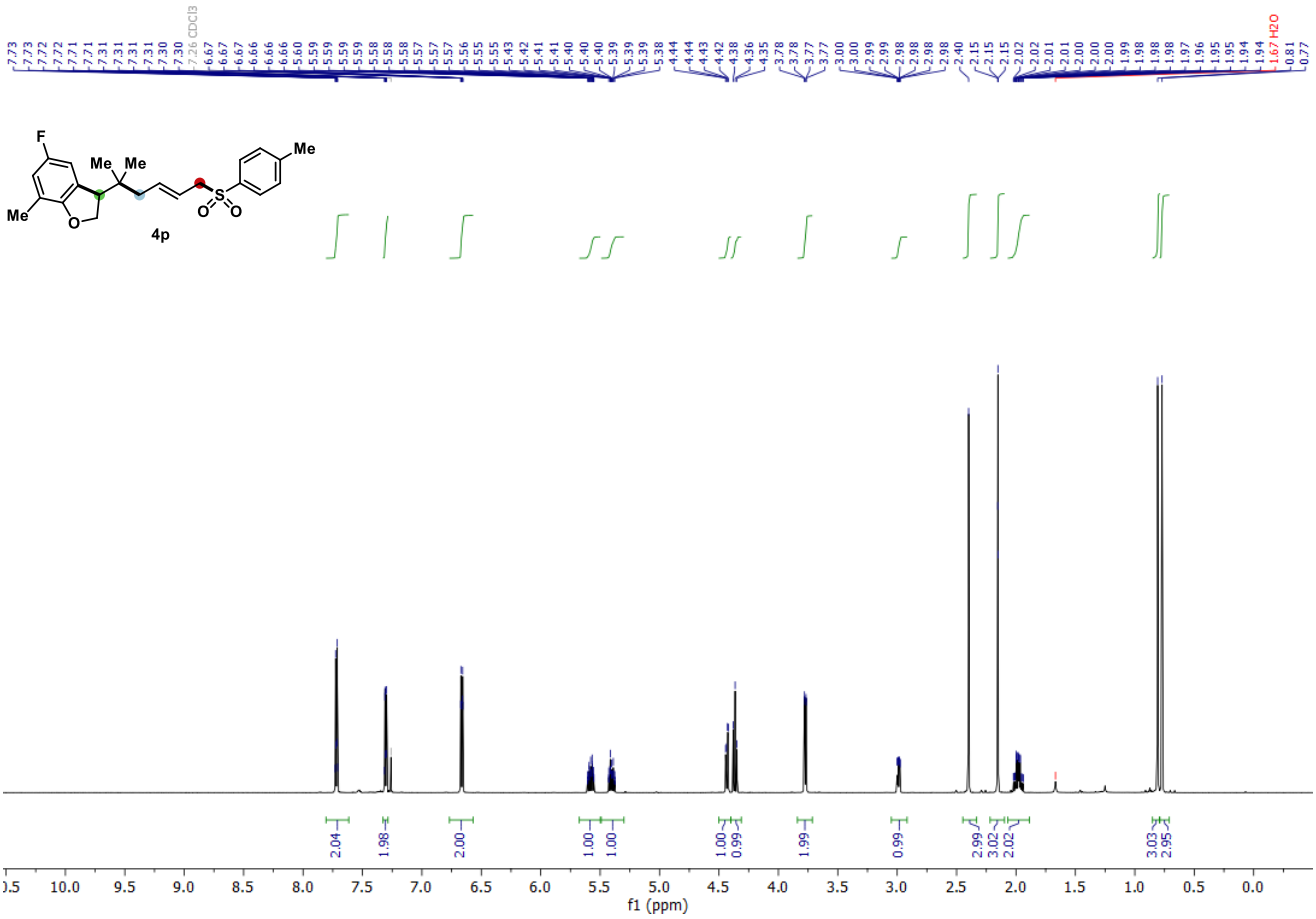
^{1}H NMR (599 MHz, $CDCl_3$)



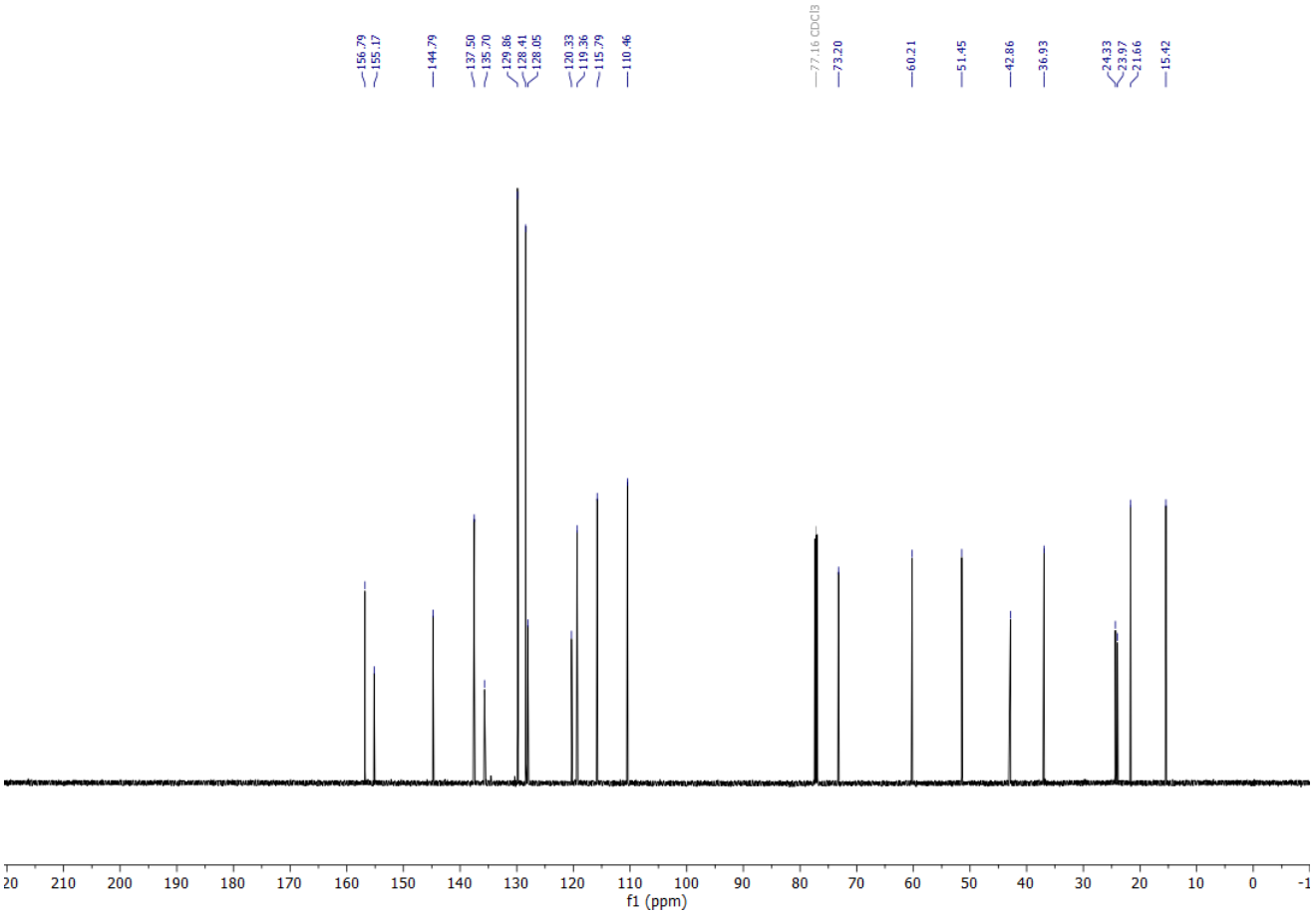
^{13}C NMR (151 MHz, $CDCl_3$)



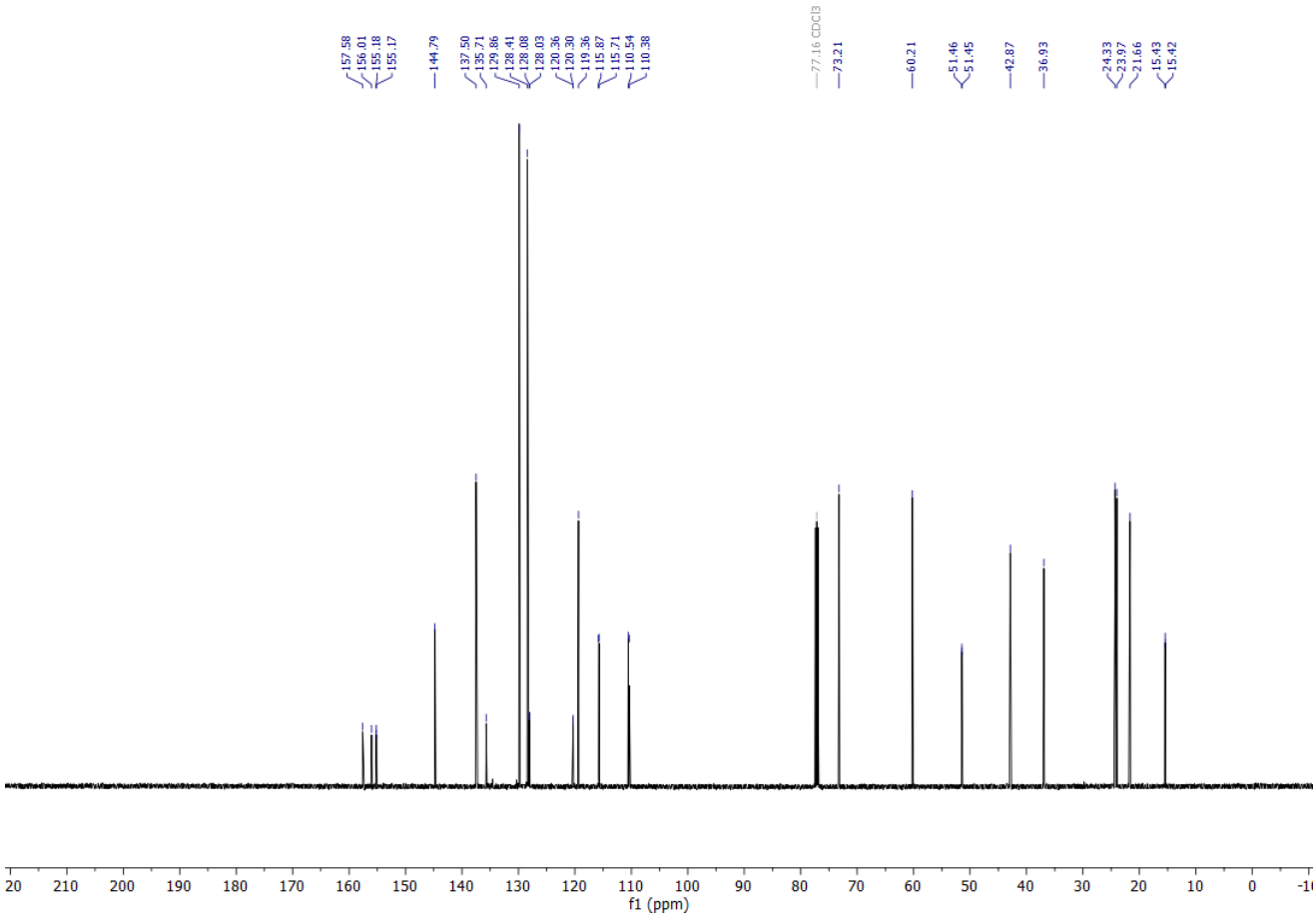
^{1}H NMR (599 MHz, $CDCl_3$)



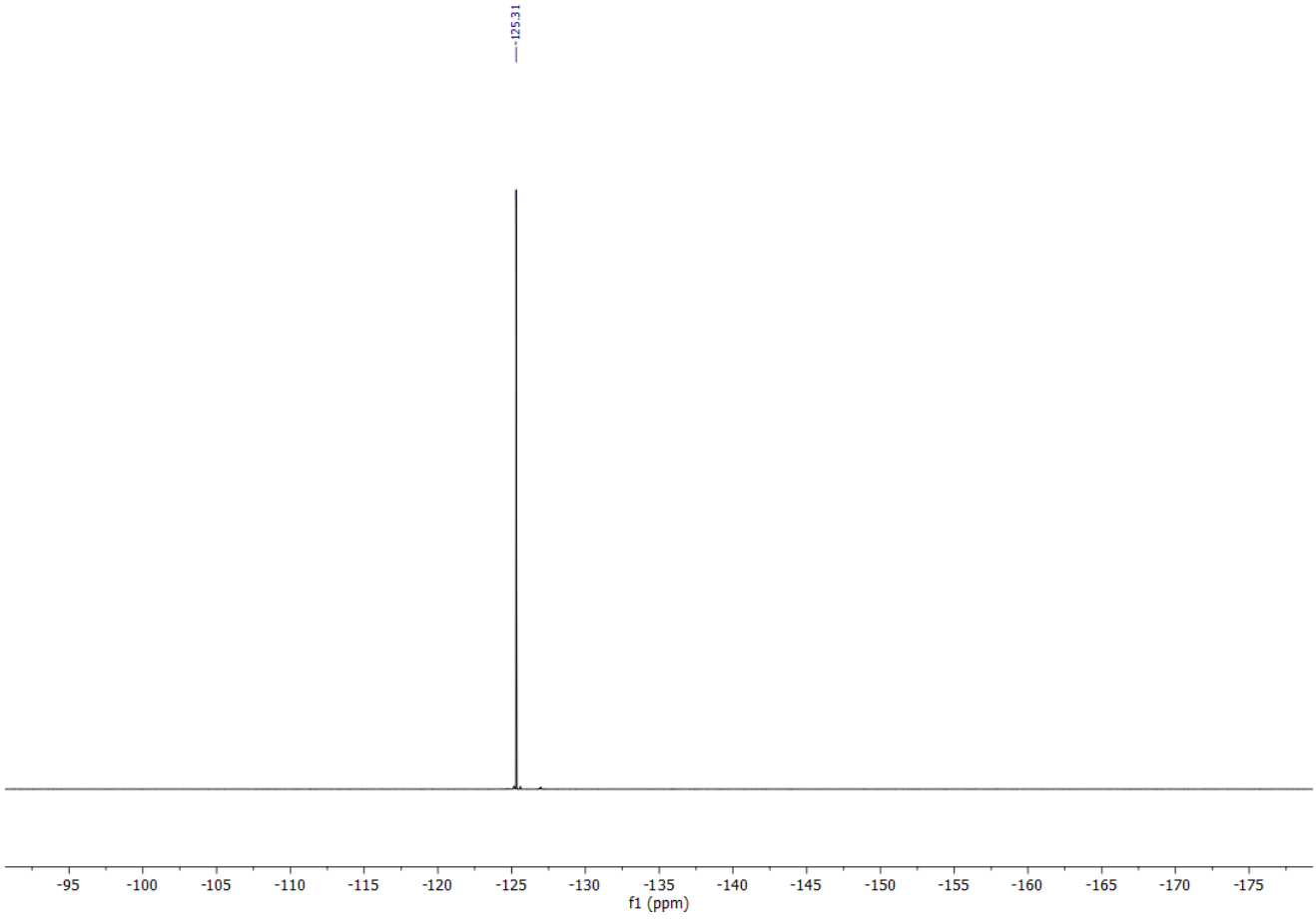
^{13}C{^{1}H, ^{19}F} NMR (151 MHz, $CDCl_3$)



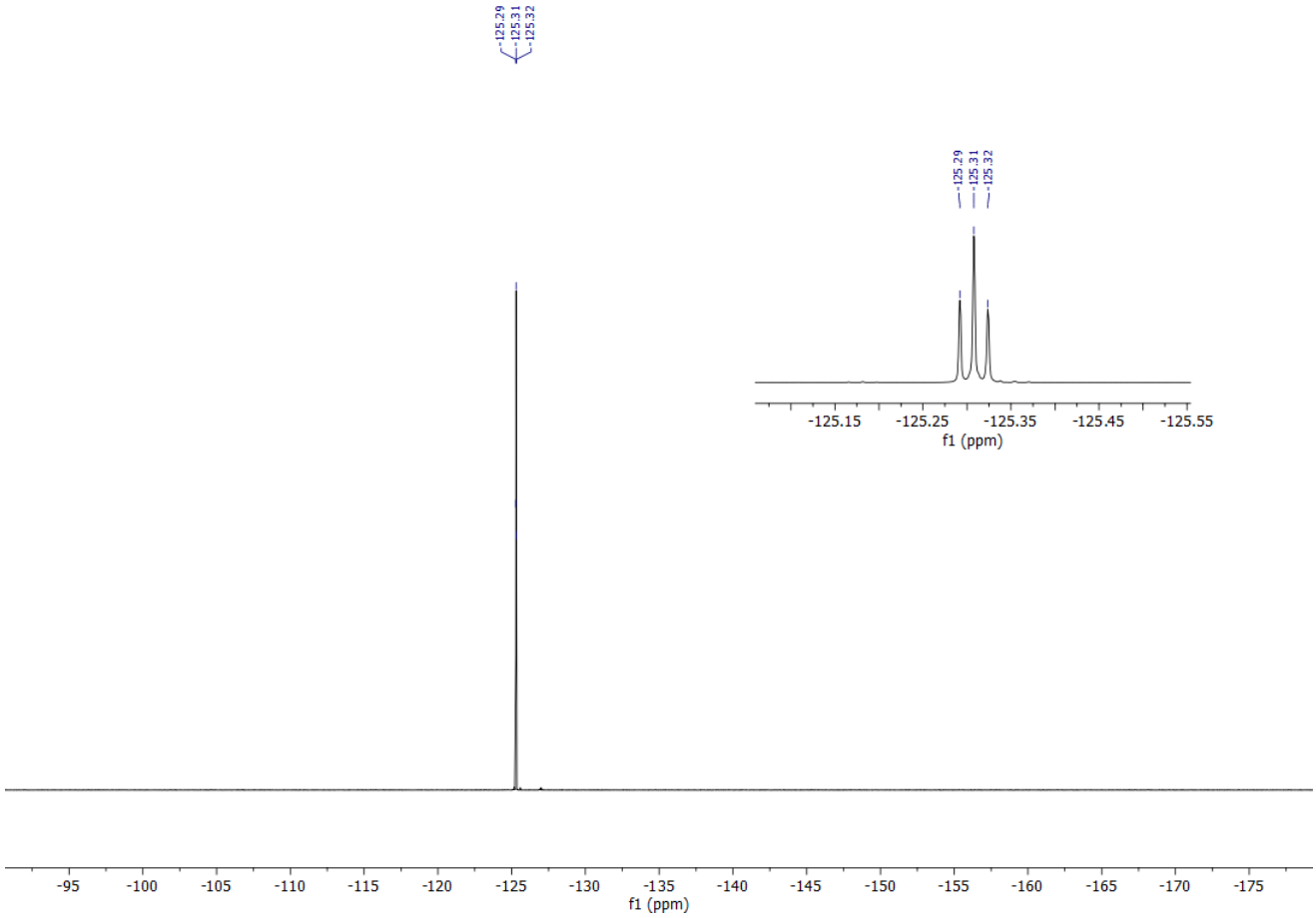
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



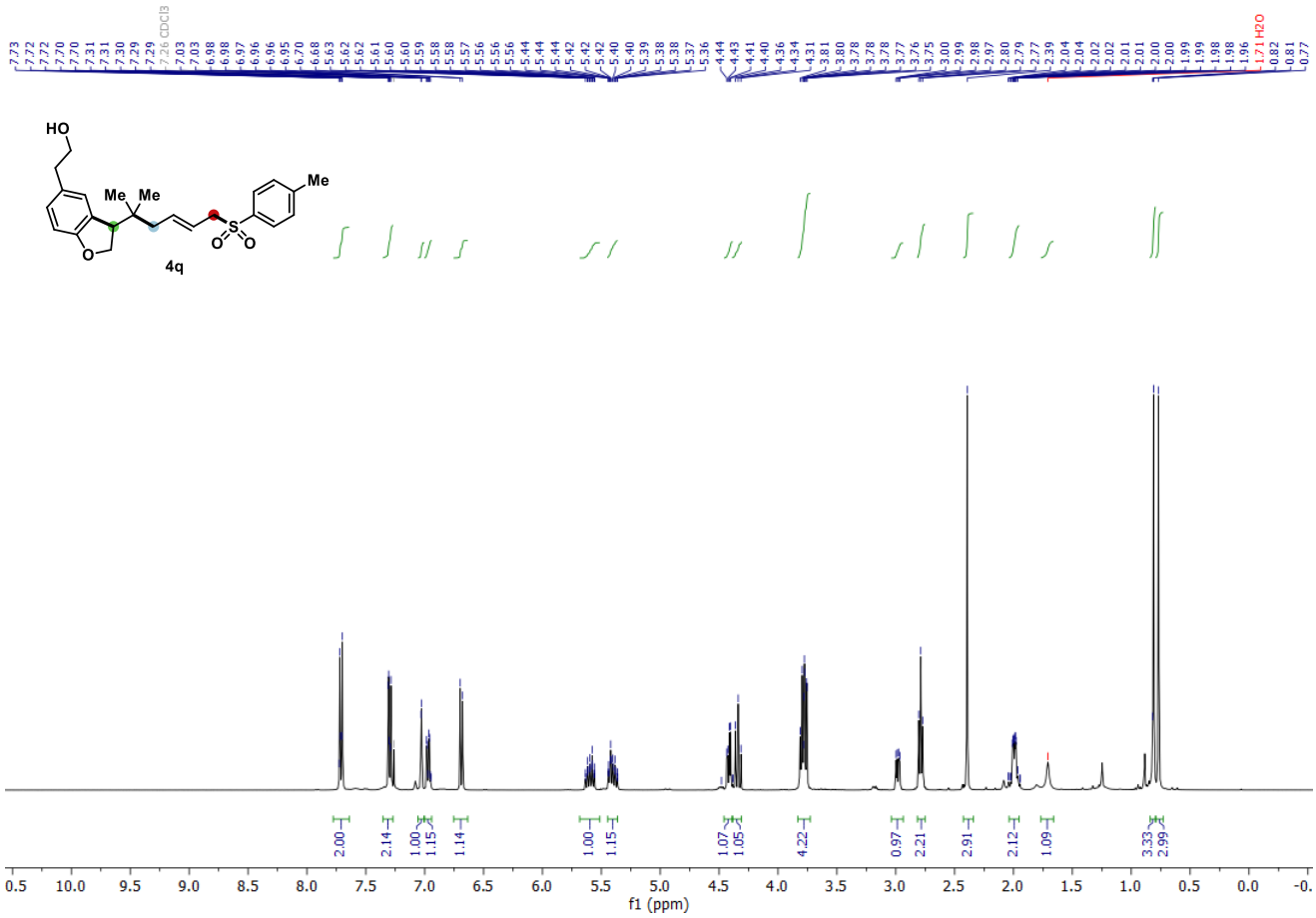
$^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$)



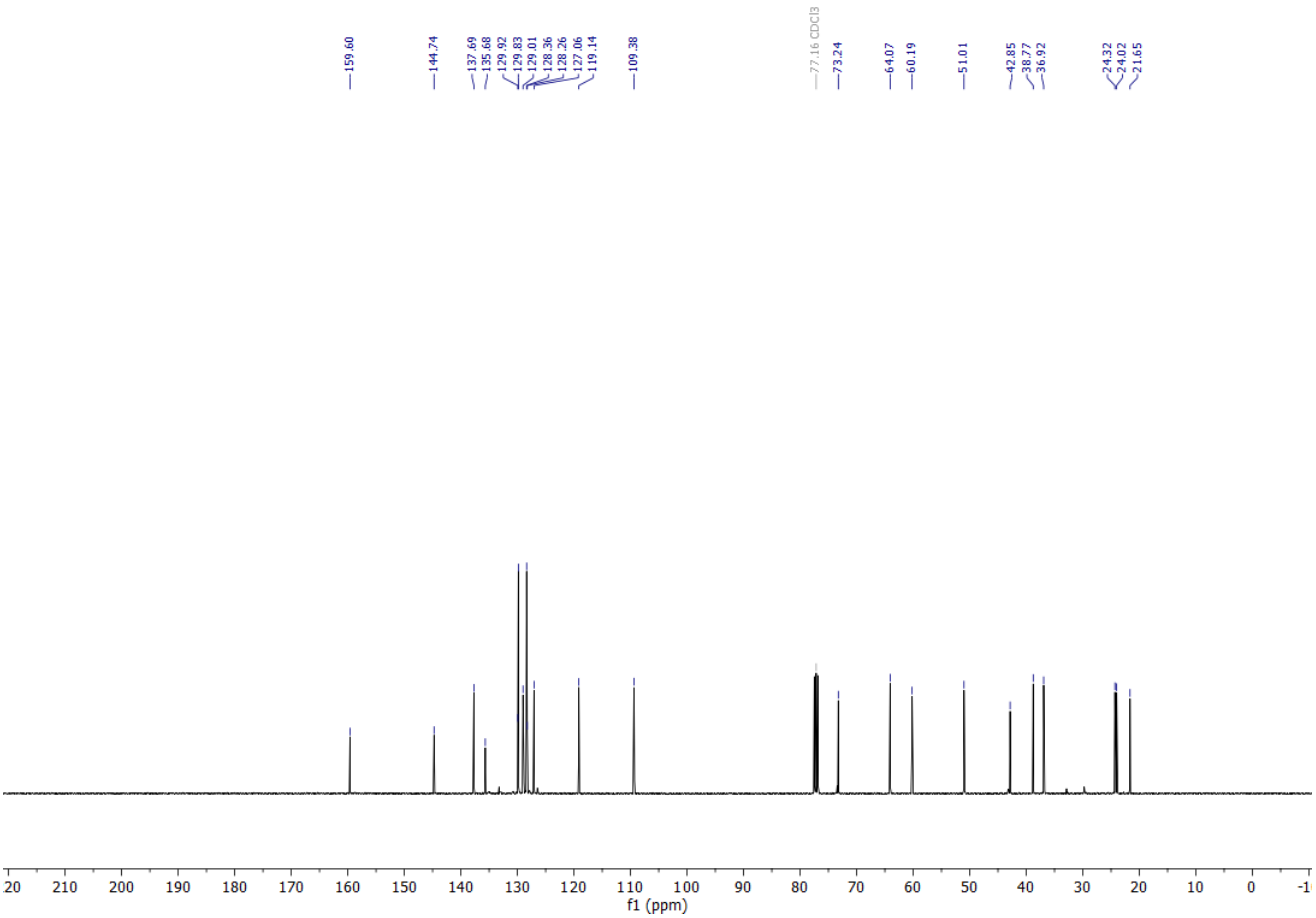
^{19}F NMR (564 MHz, $CDCl_3$)



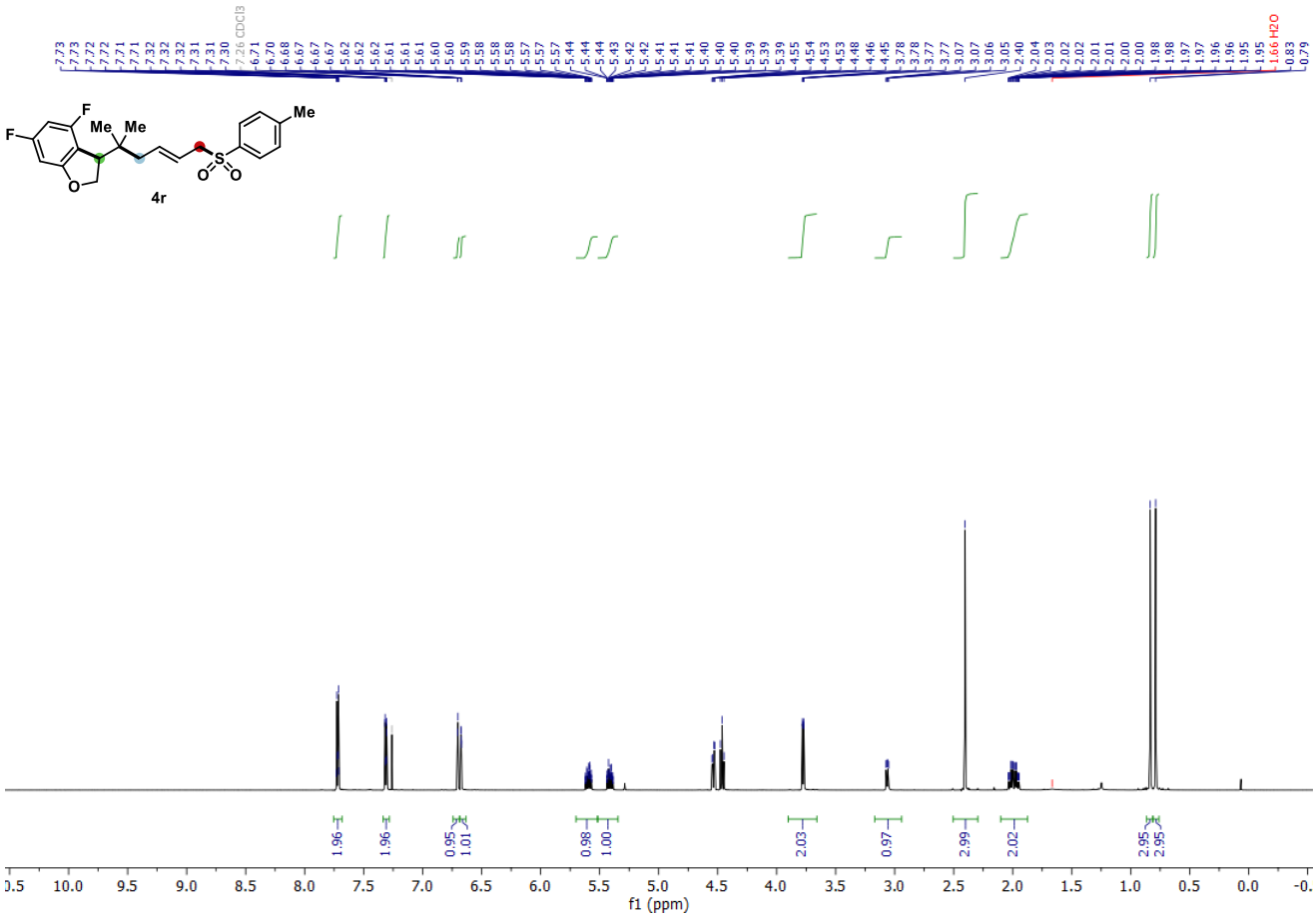
^{1}H NMR (400 MHz, $CDCl_3$)



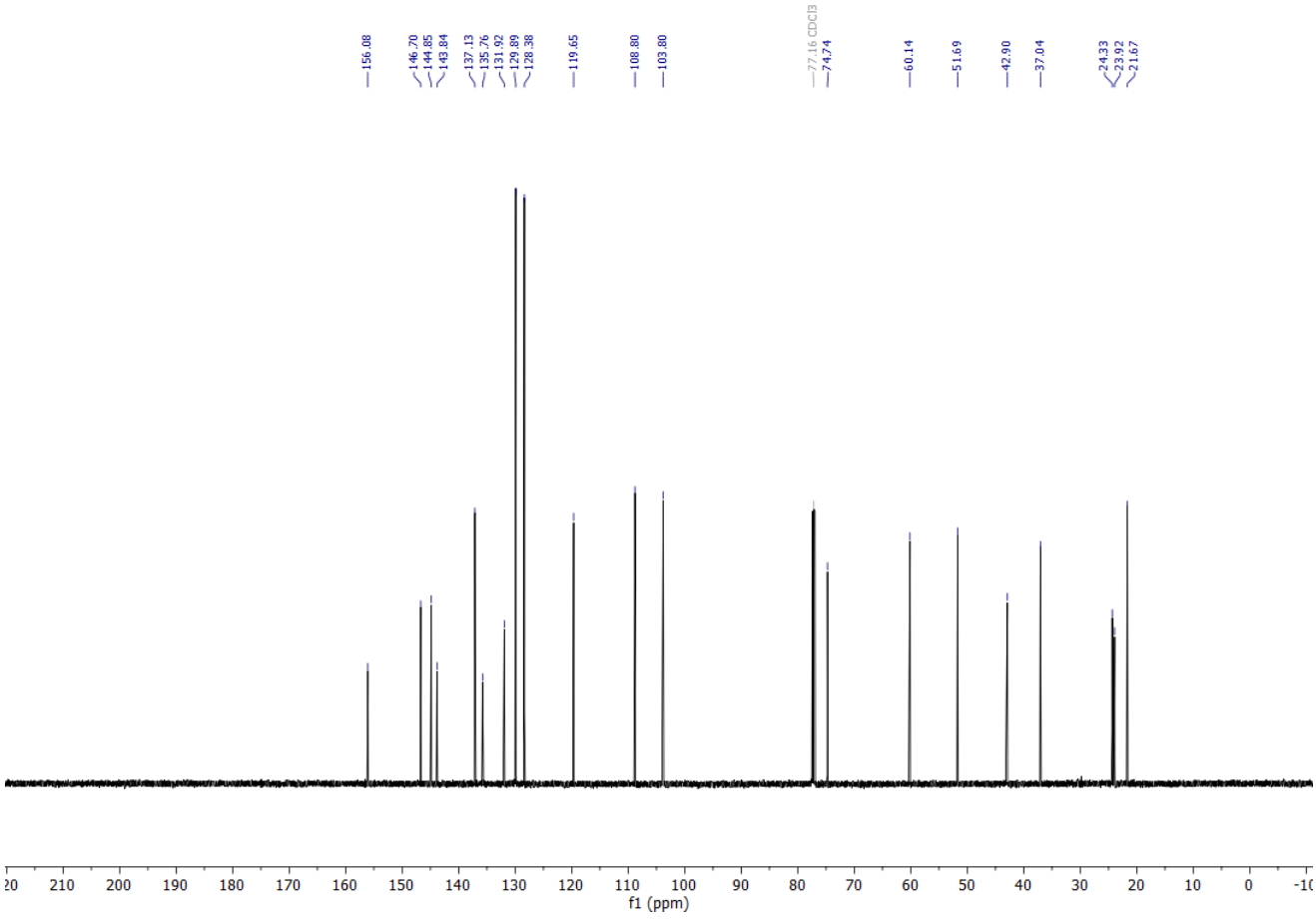
^{13}C NMR (101 MHz, $CDCl_3$)



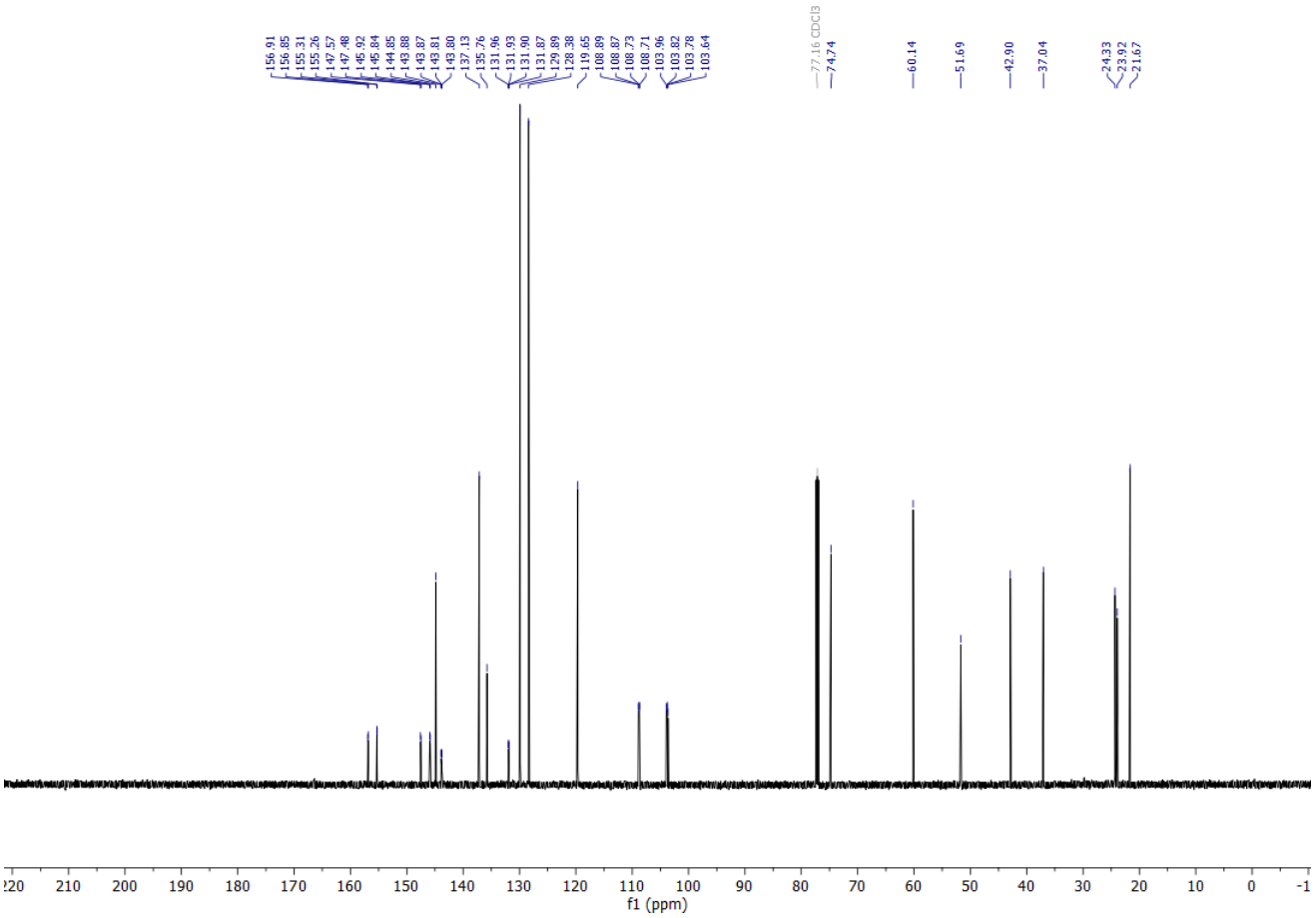
$^{1}H\{^{19}F\}$ NMR (599 MHz, $CDCl_3$)



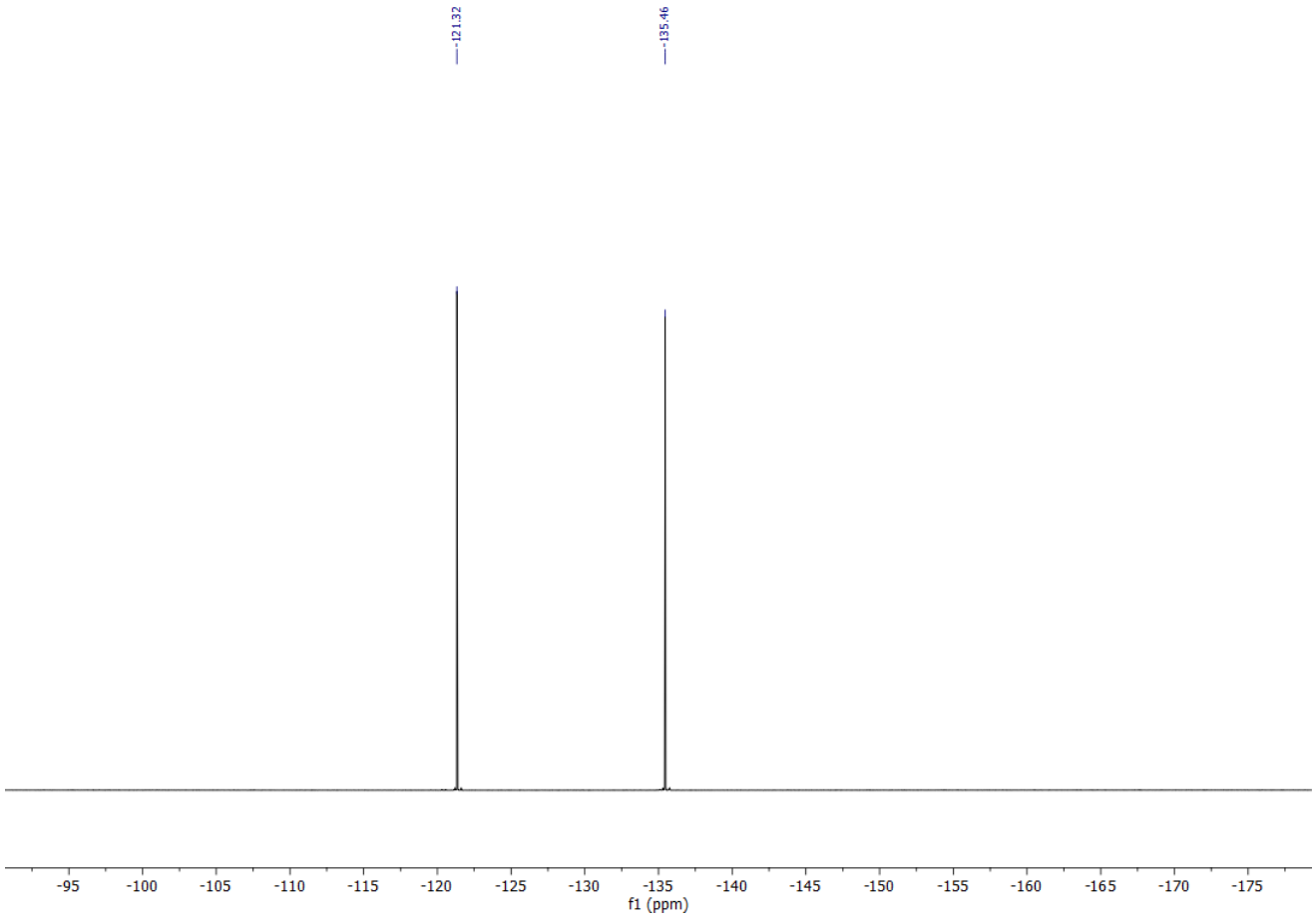
$^{13}C\{^{1}H, ^{19}F\}$ NMR (151 MHz, $CDCl_3$)



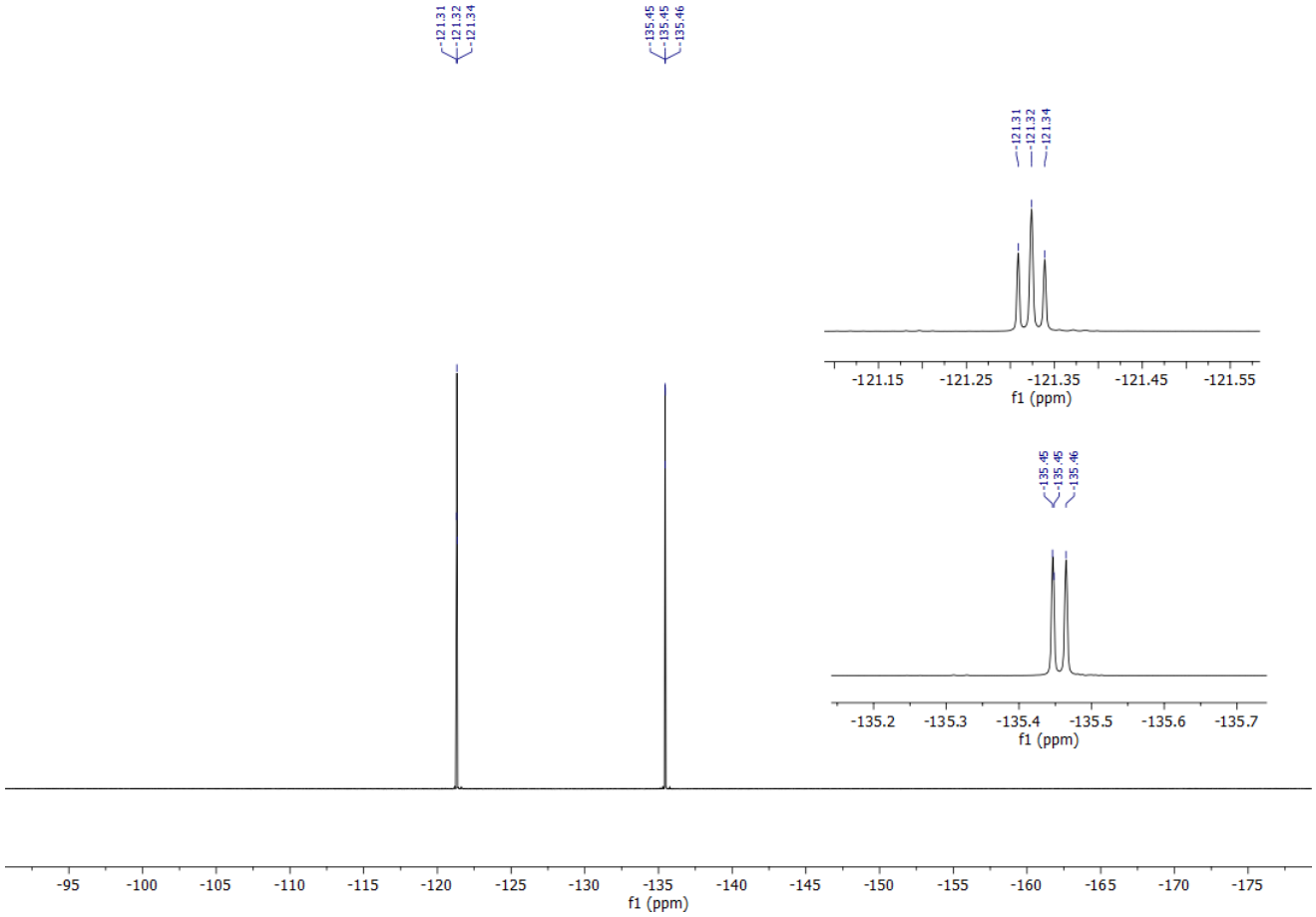
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



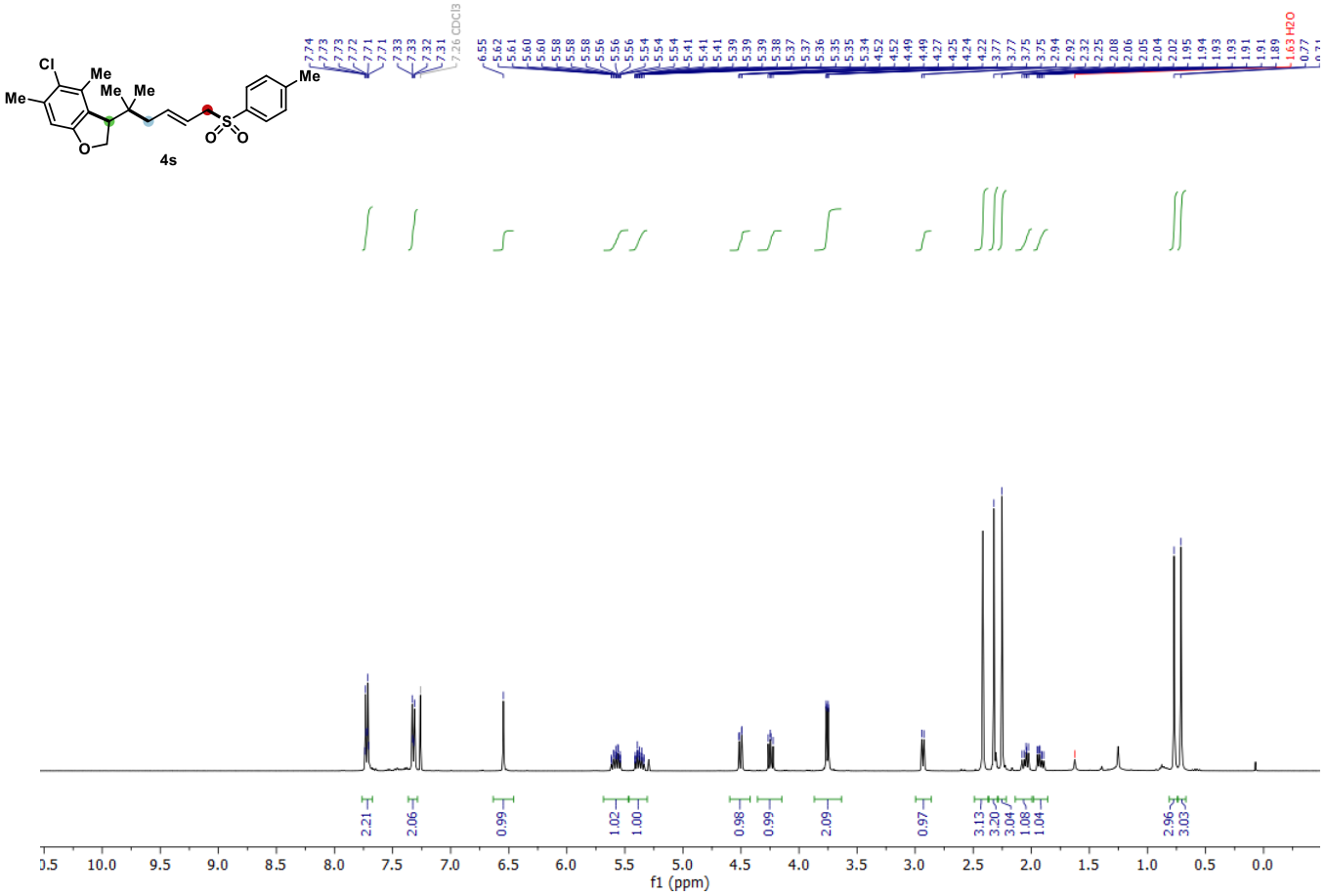
$^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$)



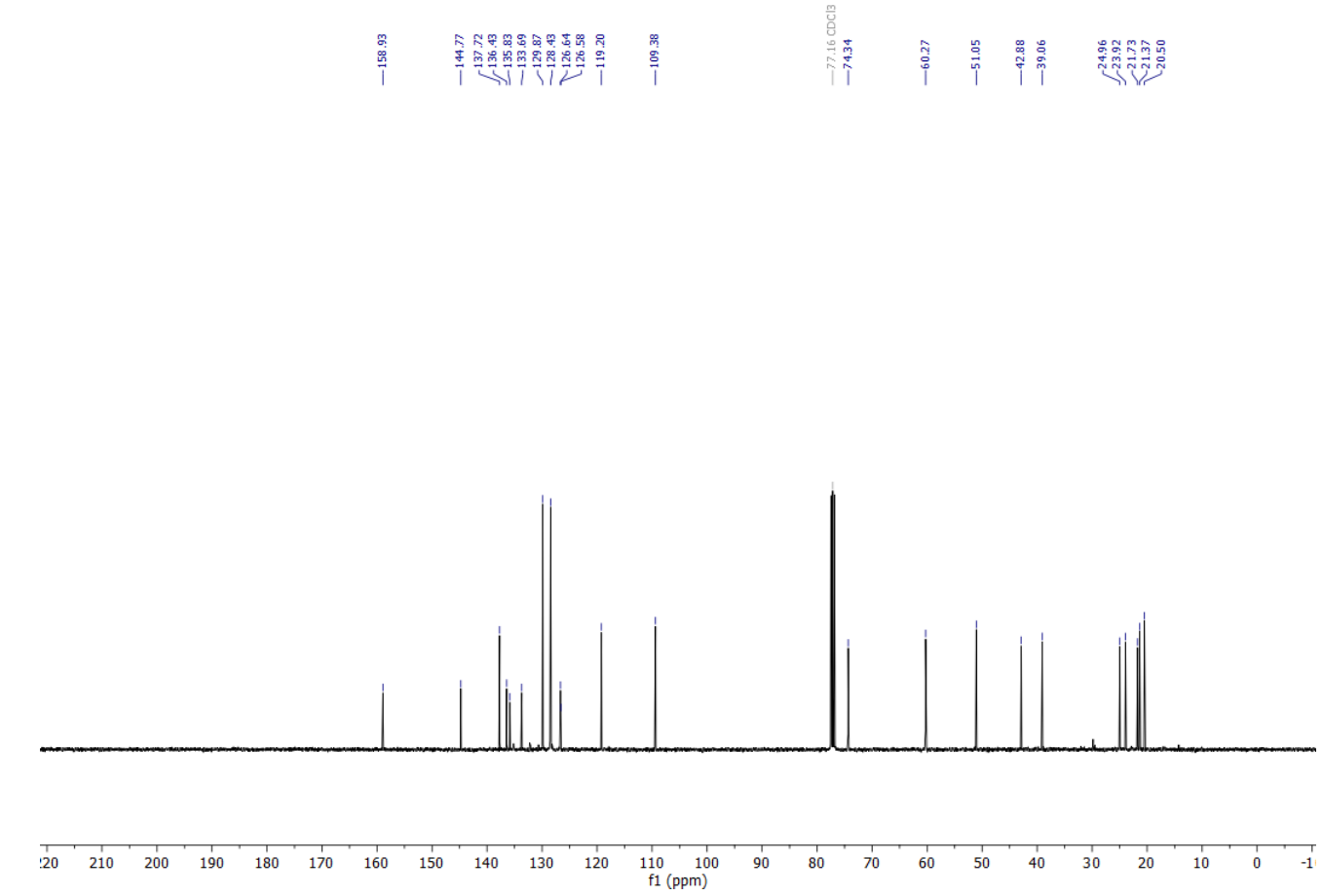
^{19}F NMR (564 MHz, $CDCl_3$)



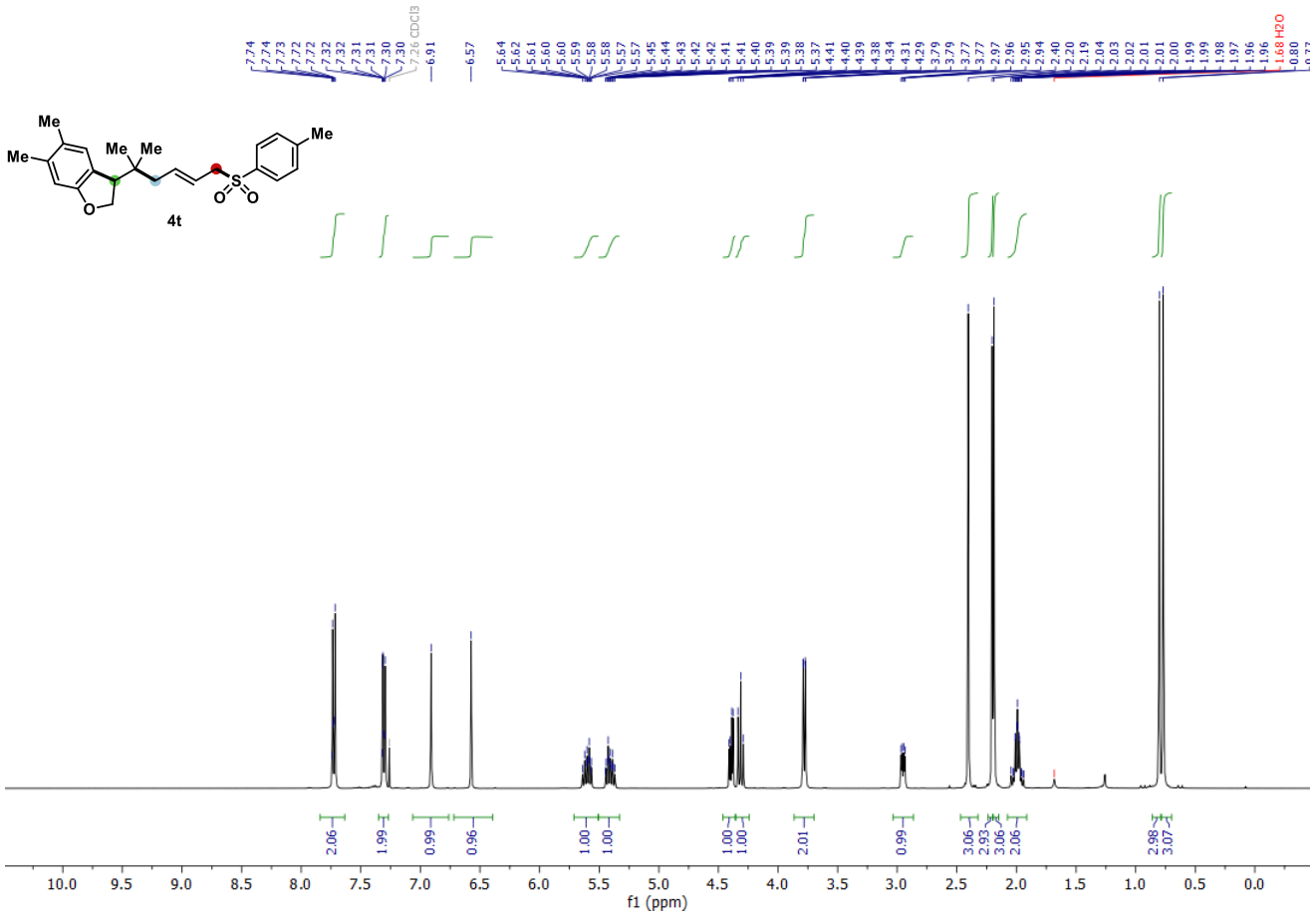
^{1}H NMR (400 MHz, $CDCl_3$)



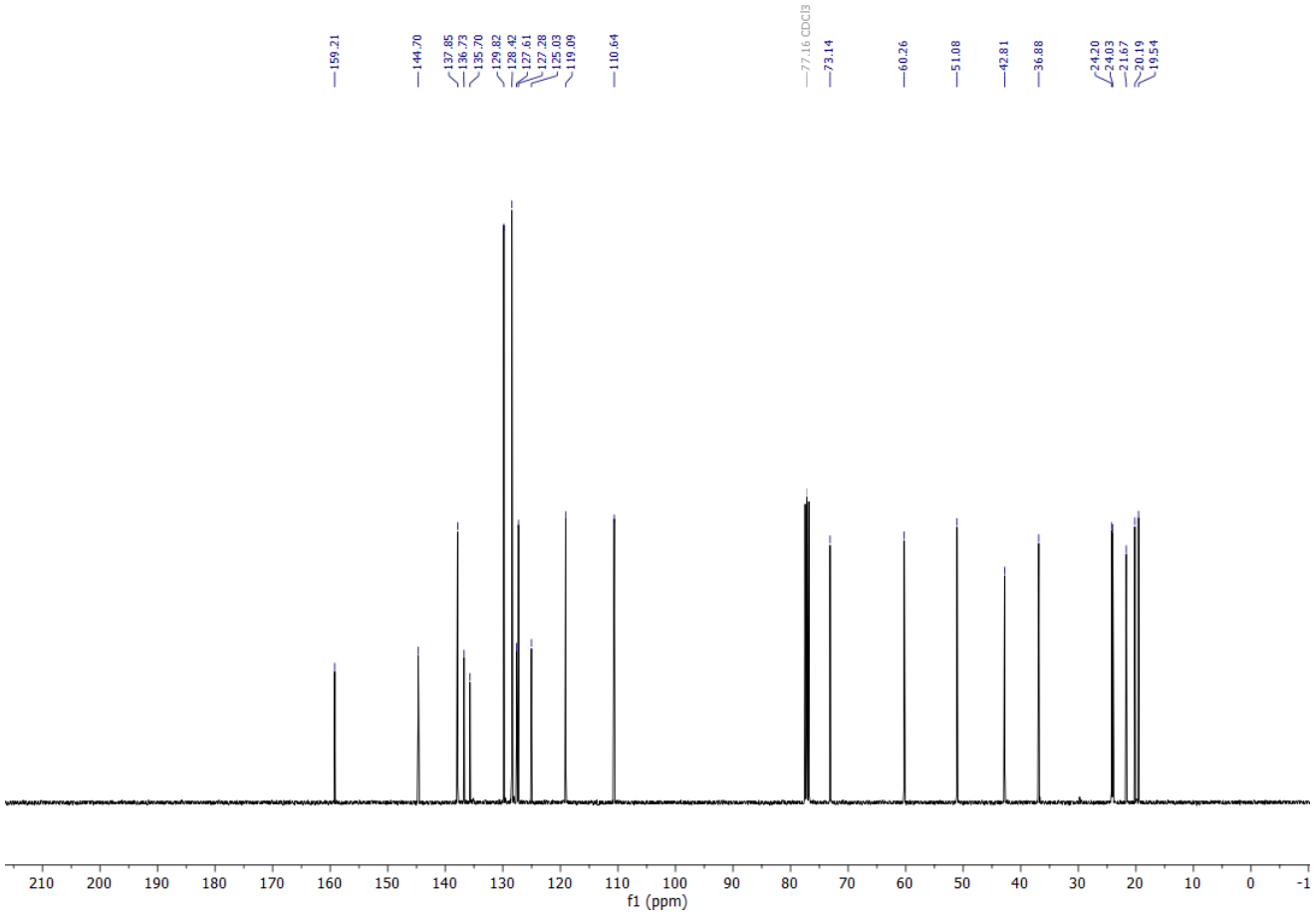
^{13}C NMR (101 MHz, $CDCl_3$)



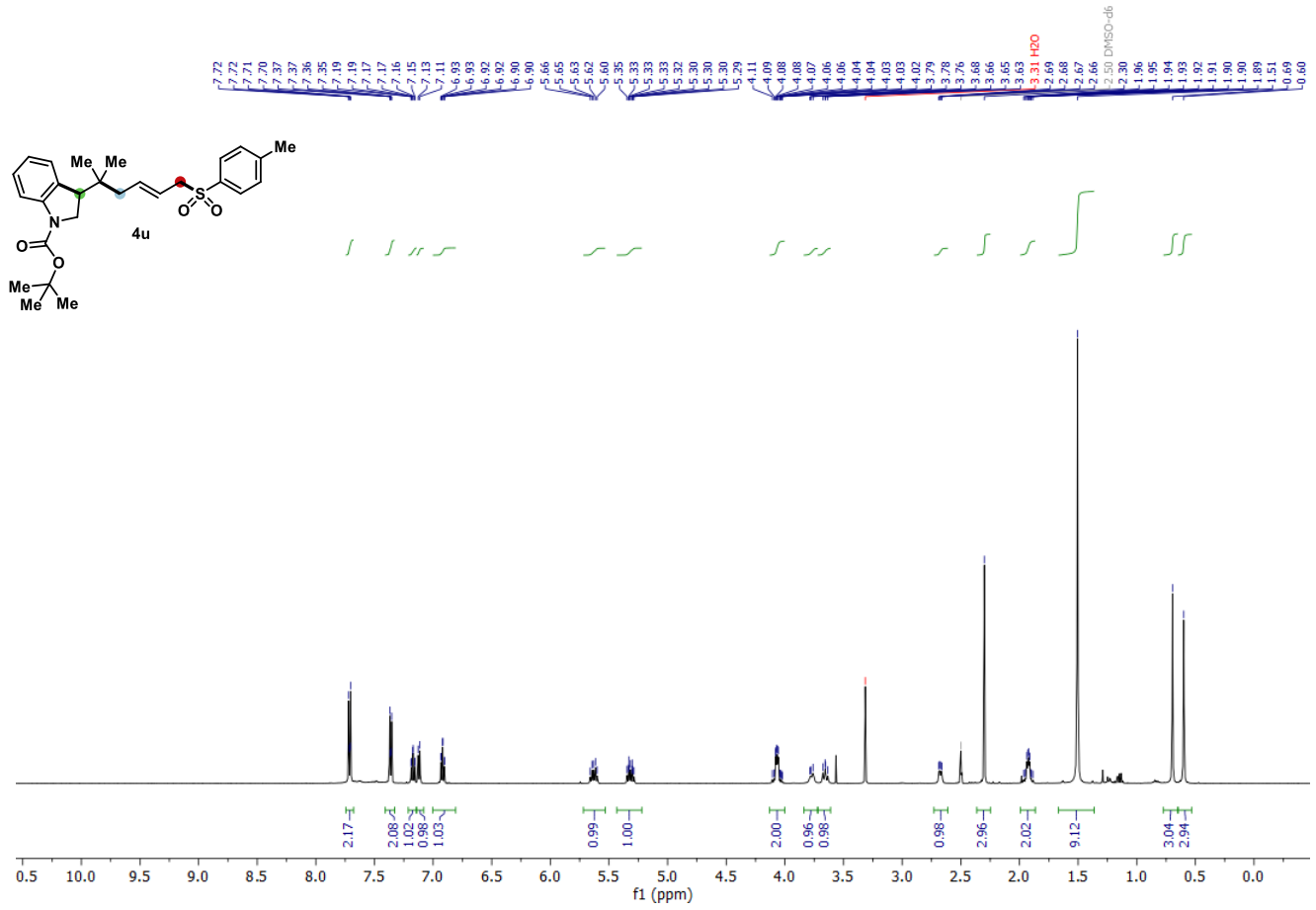
^{1}H NMR (400 MHz, $CDCl_3$)



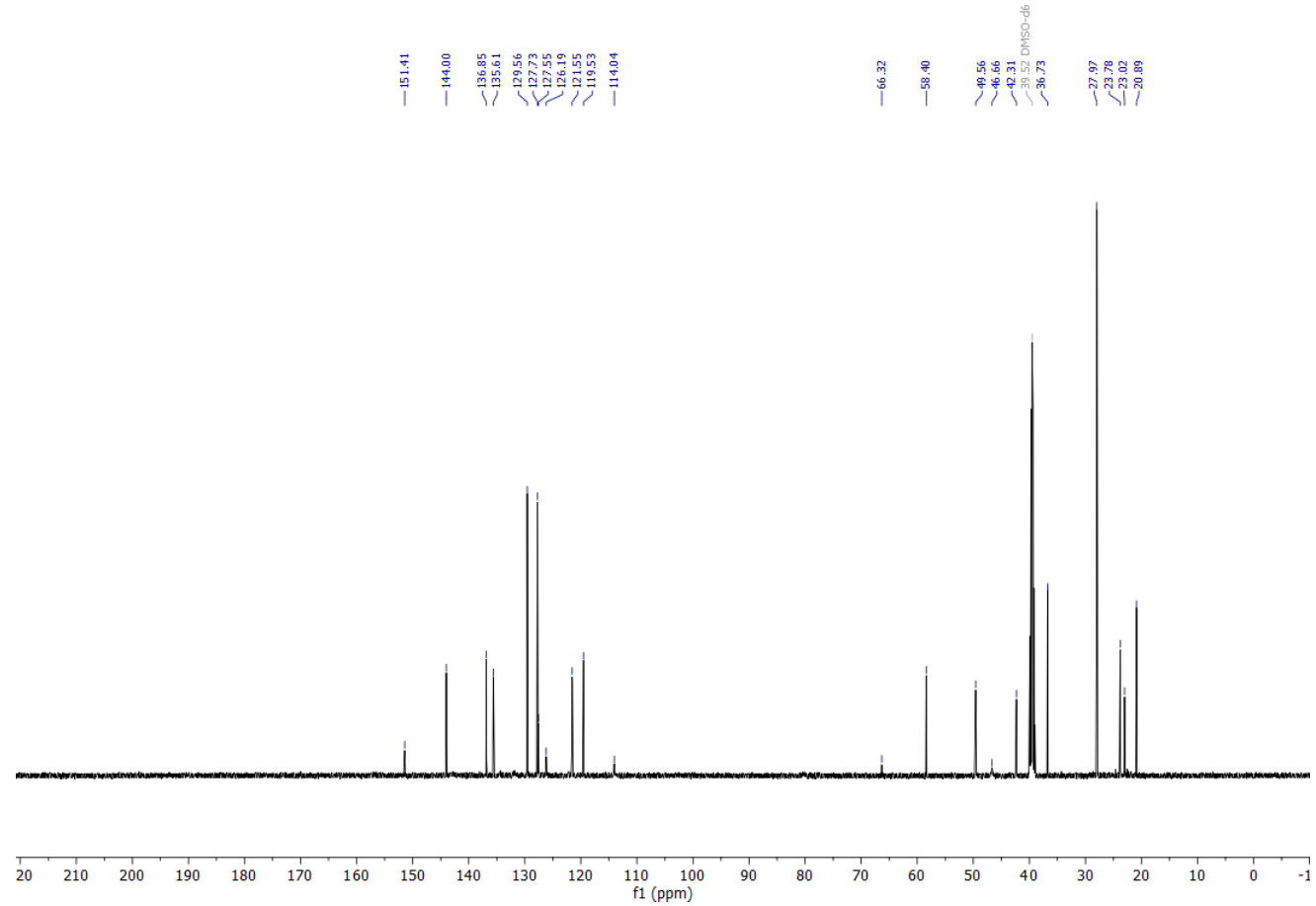
^{13}C NMR (101 MHz, $CDCl_3$)



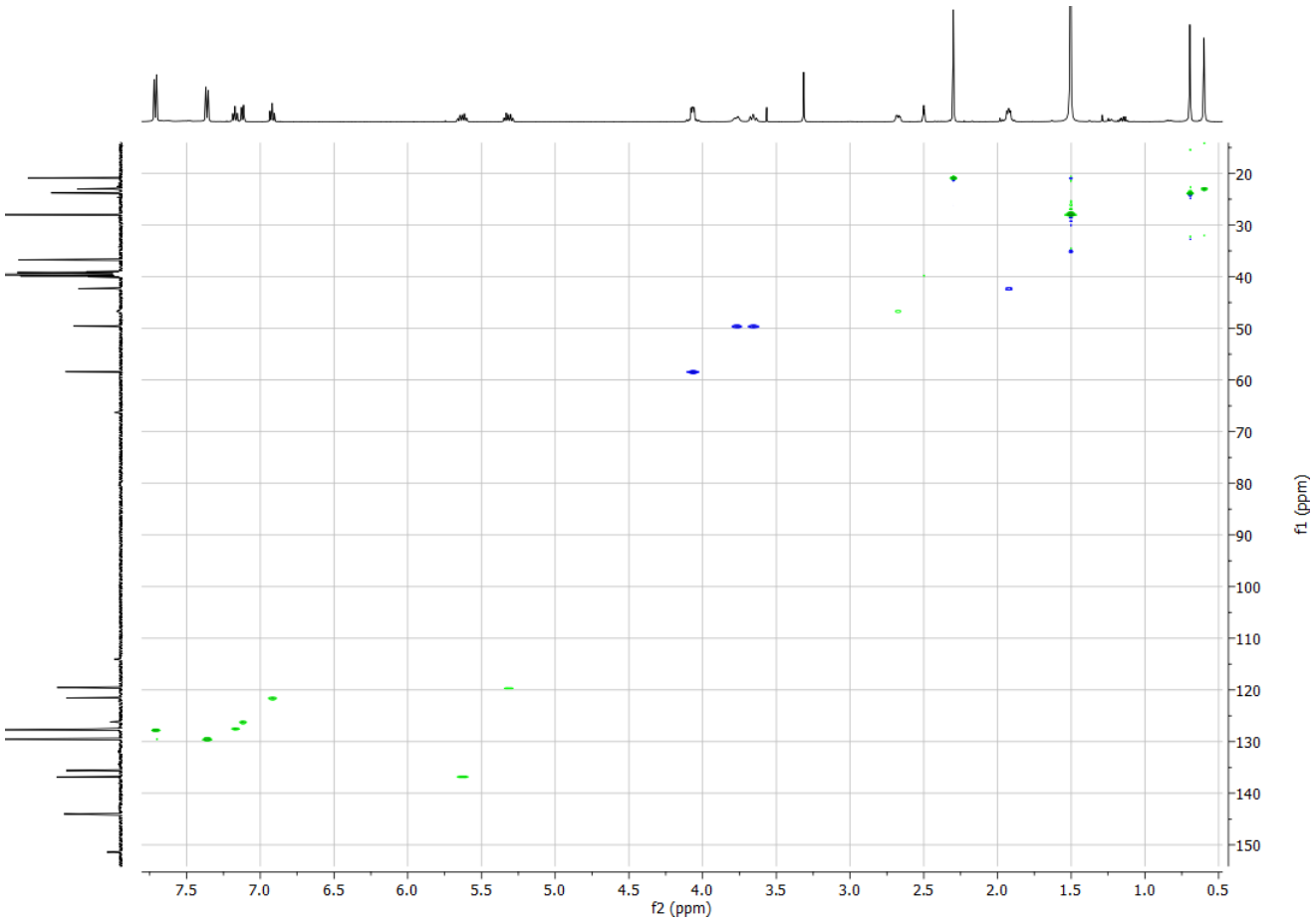
^{1}H NMR (500 MHz, DMSO-d_6)



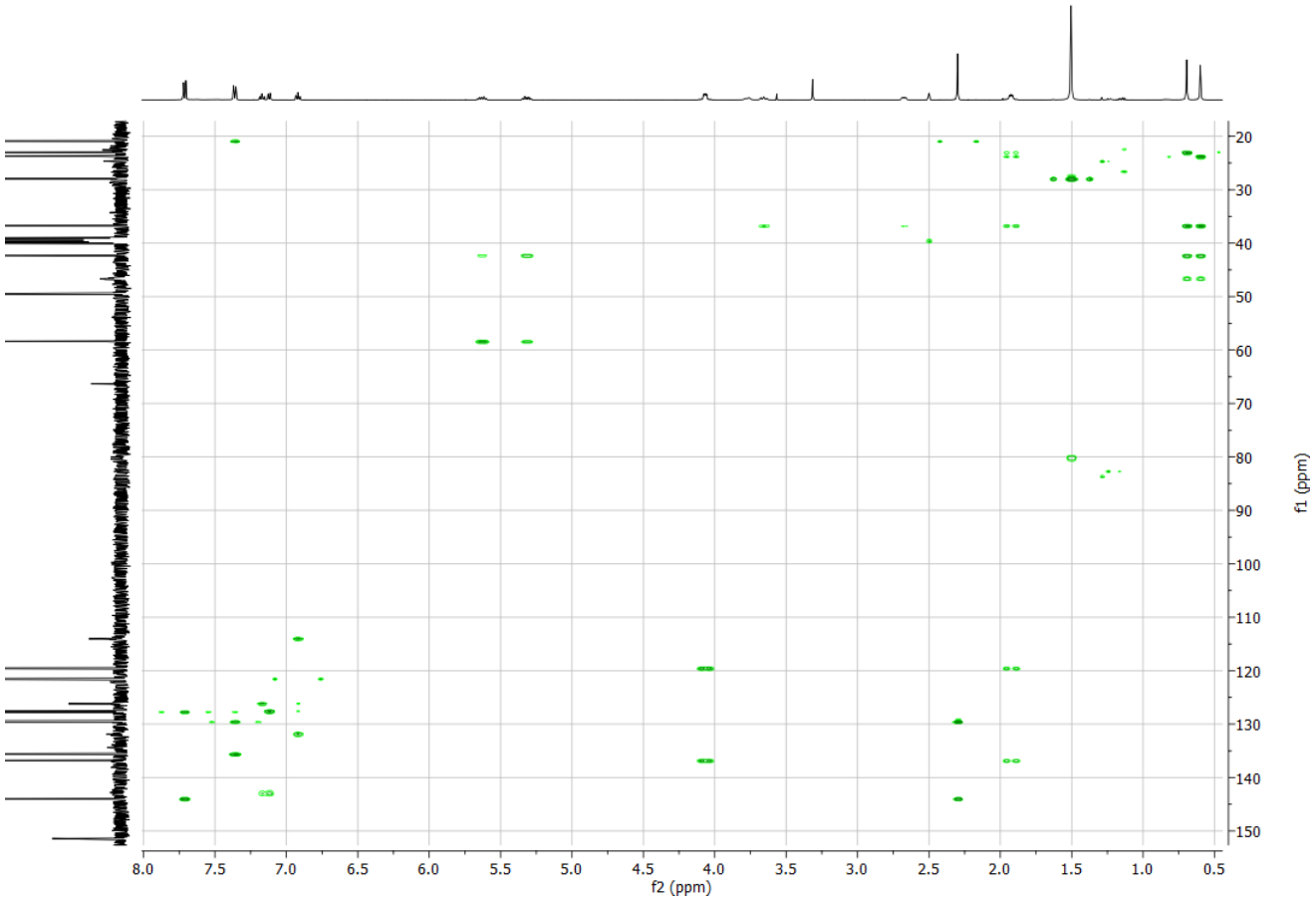
^{13}C NMR (126 MHz, DMSO-d_6)



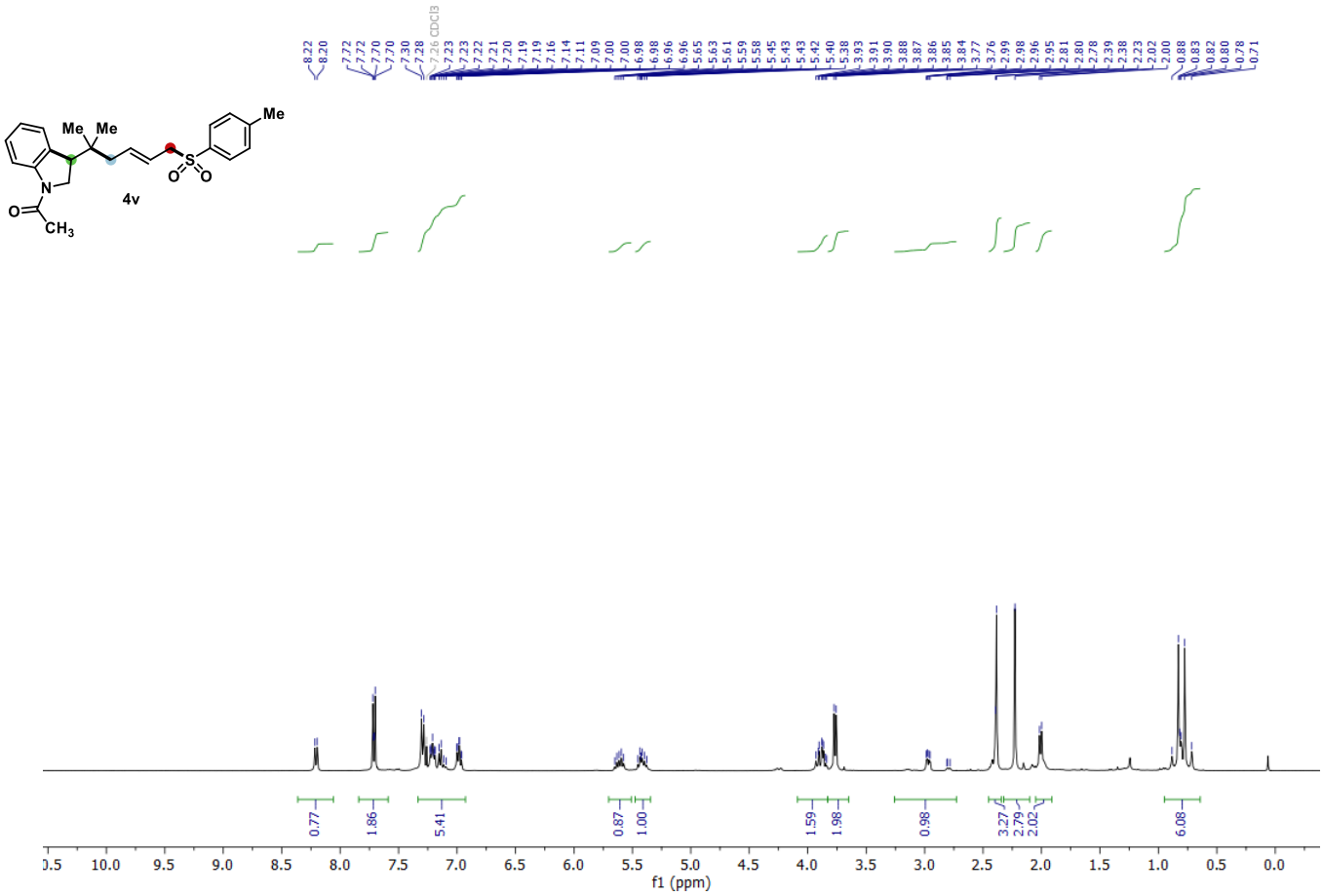
^{1}H-^{13}C HSQC NMR (500 MHz, DMSO-d_6)



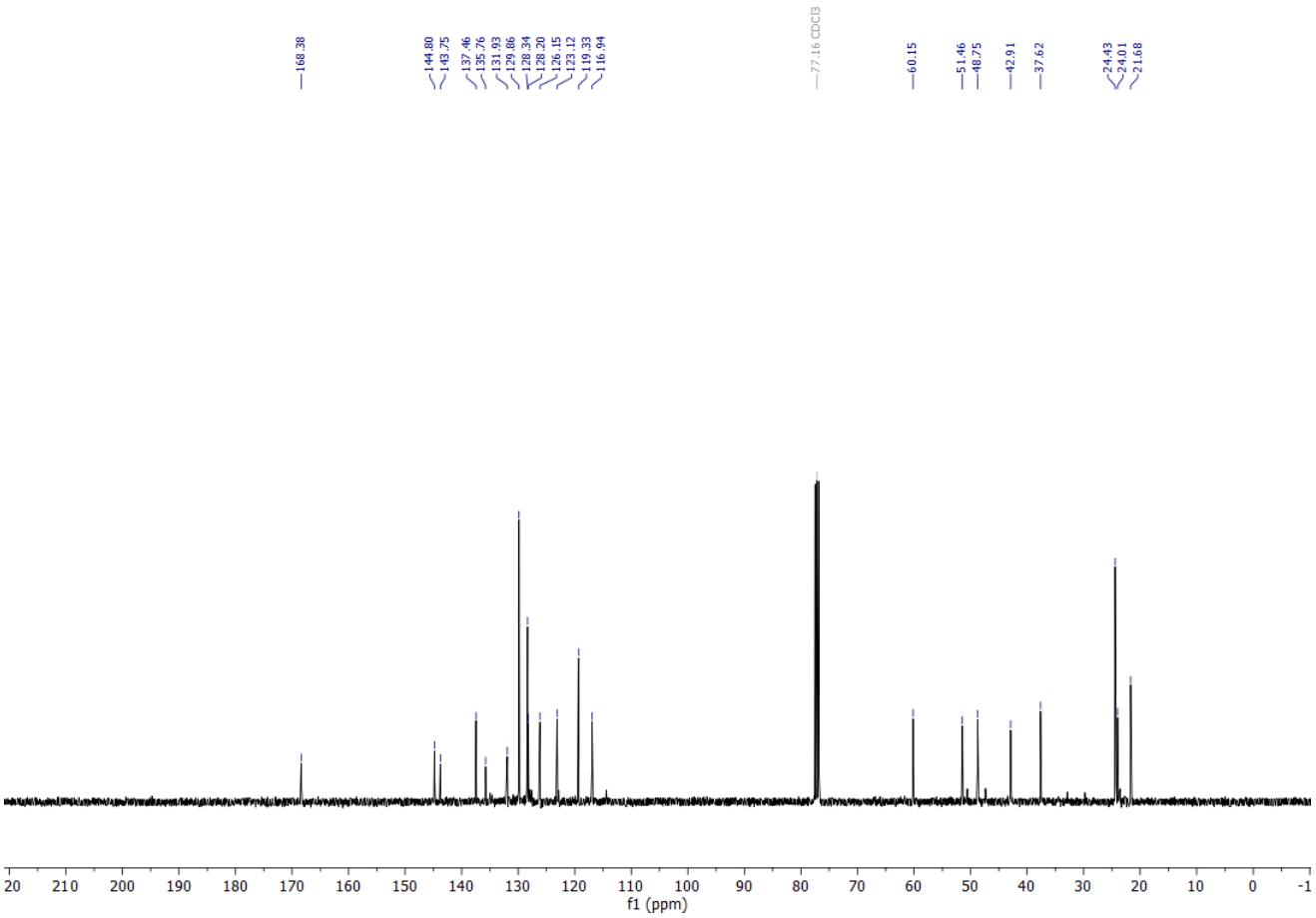
^{1}H-^{13}C HMBC NMR (500 MHz, DMSO-d_6)



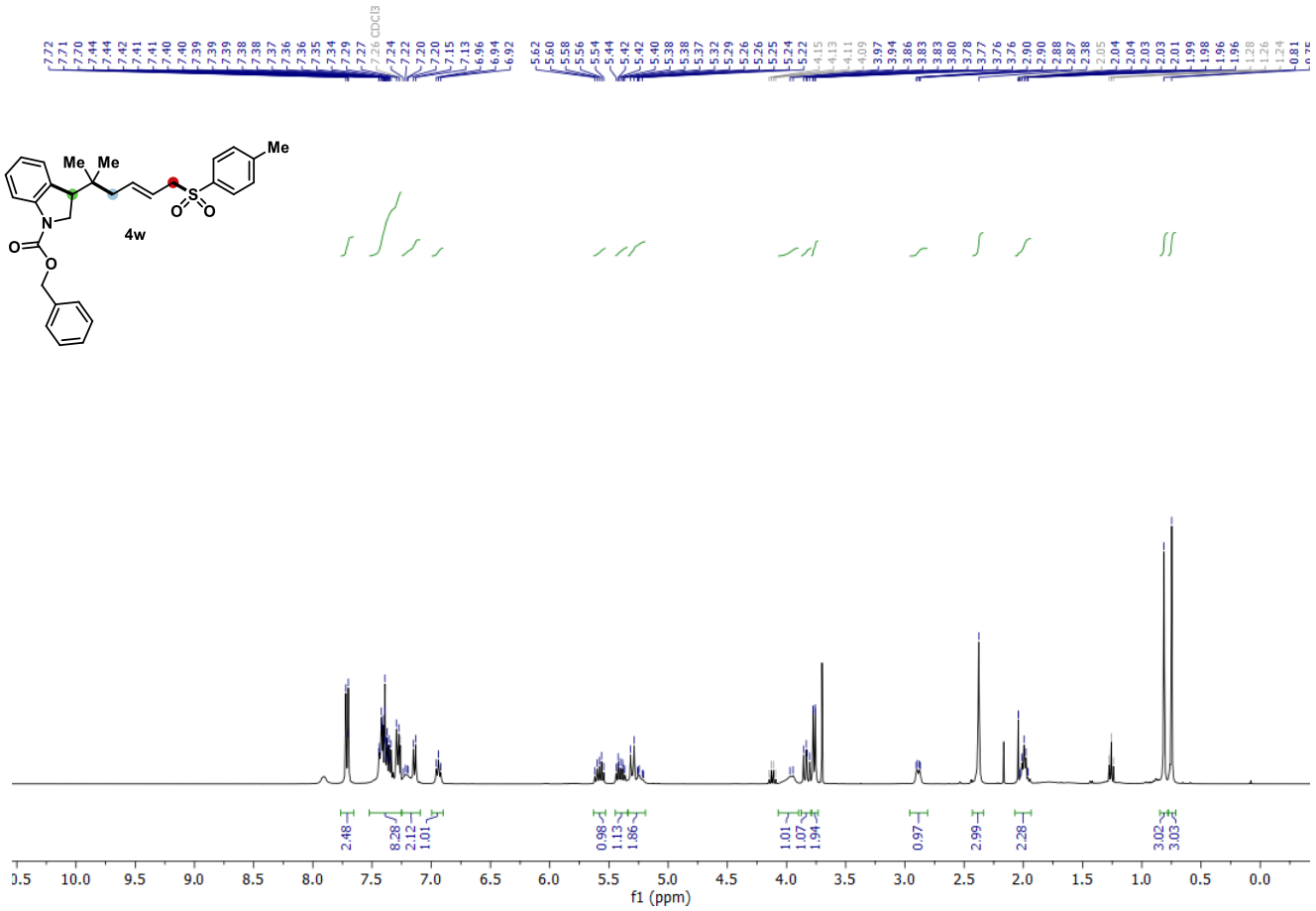
^{1}H NMR (400 MHz, $CDCl_3$)



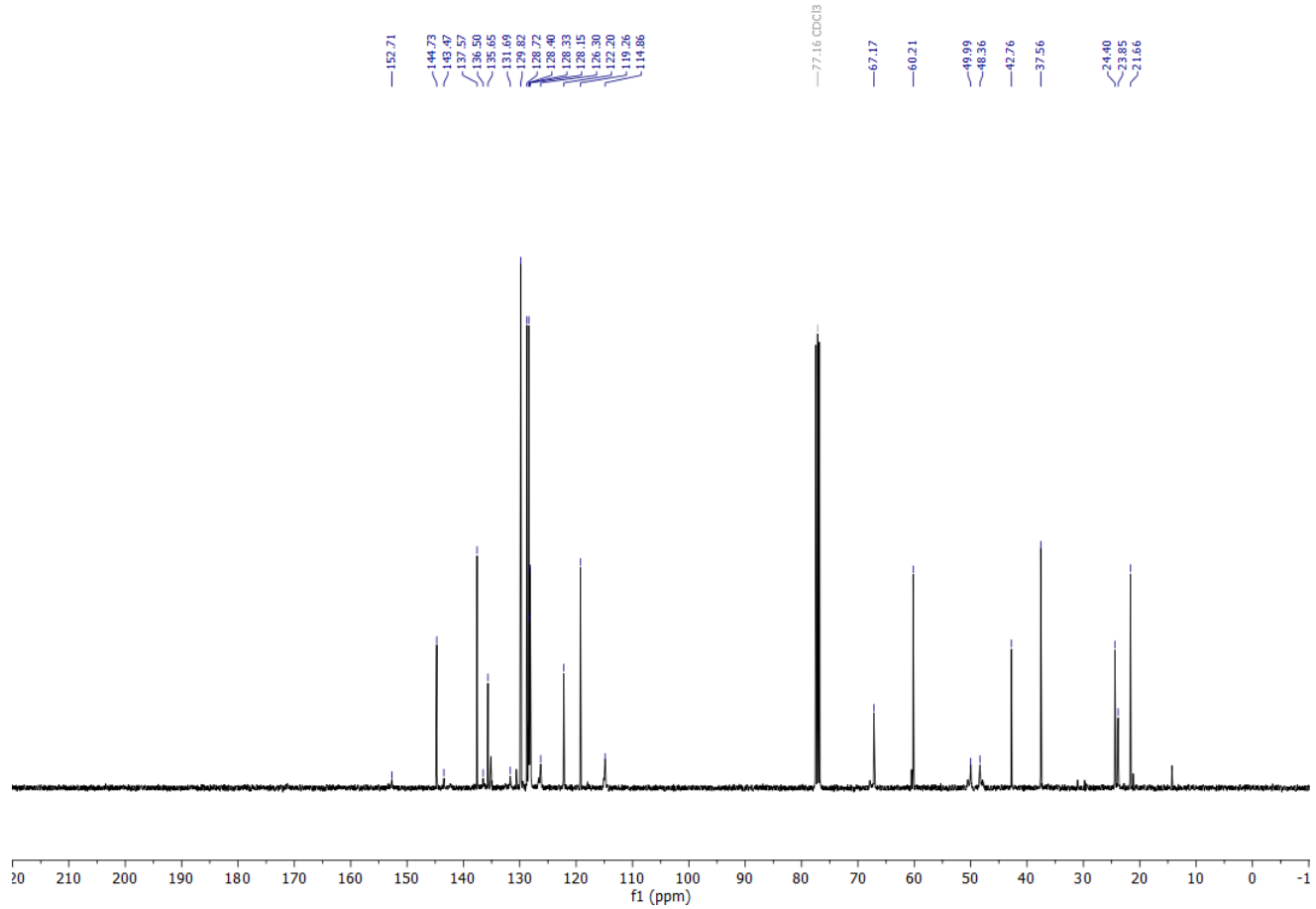
^{13}C NMR (101 MHz, $CDCl_3$)



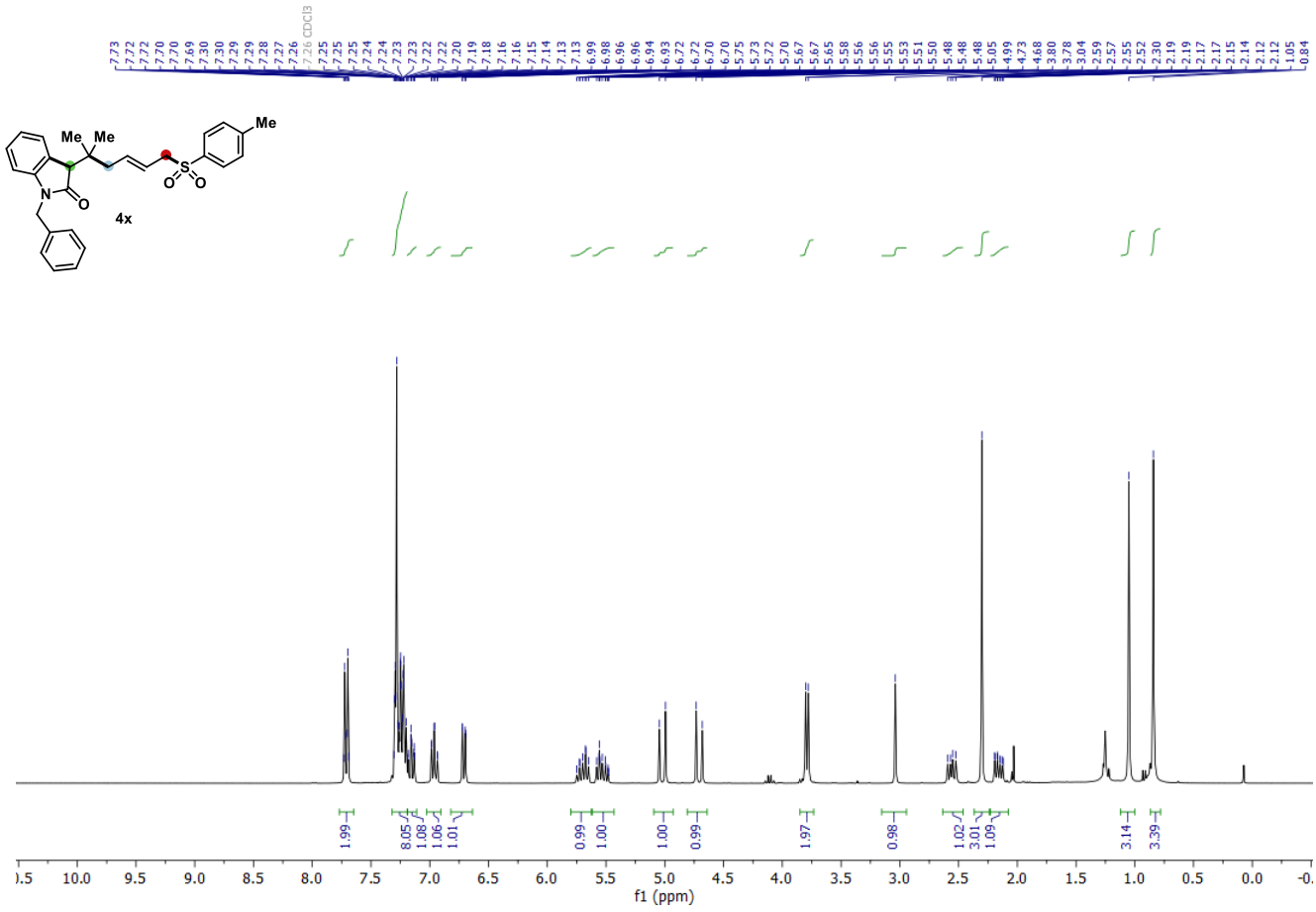
^{1}H NMR (400 MHz, $CDCl_3$)



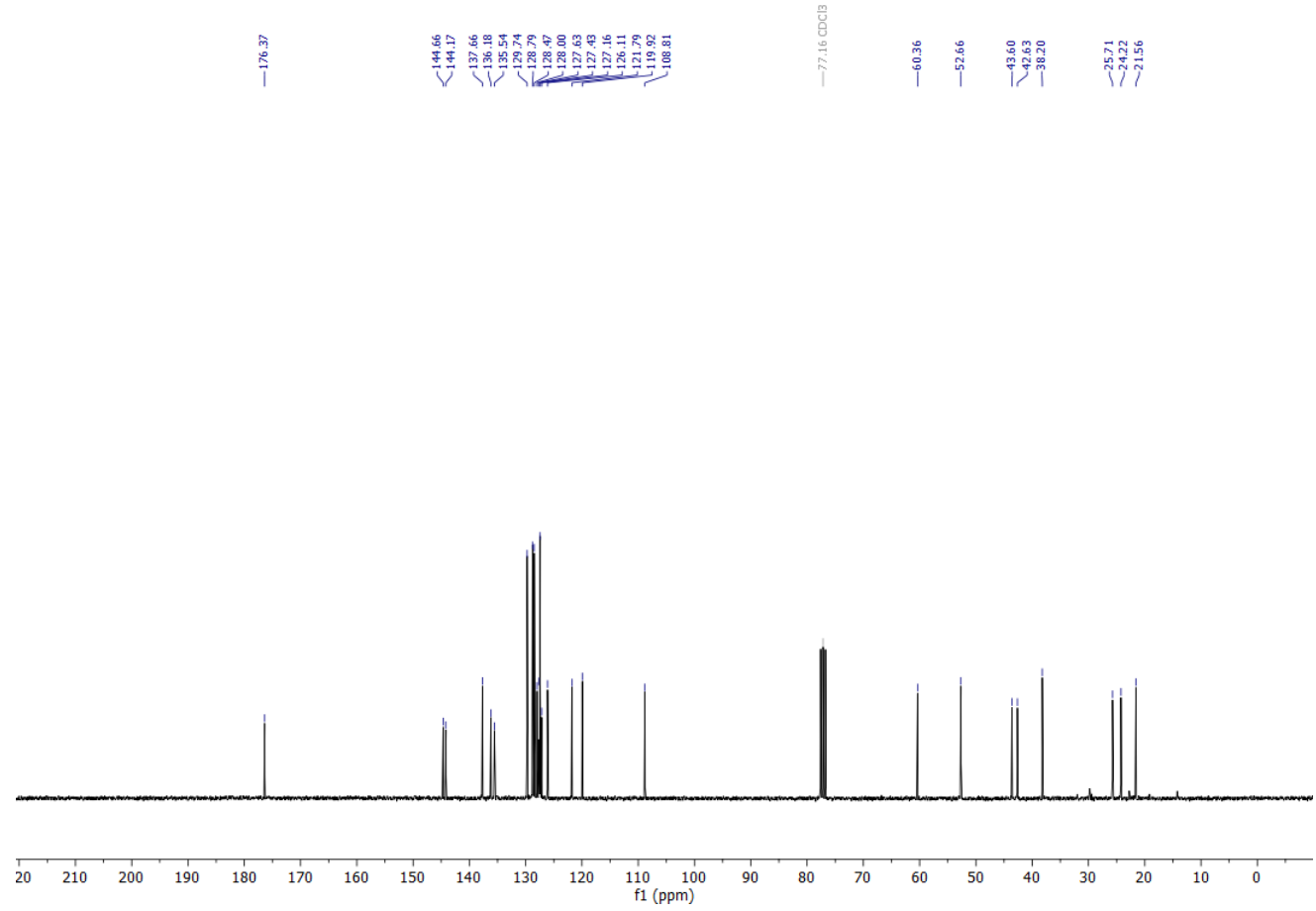
^{13}C NMR (101 MHz, $CDCl_3$)



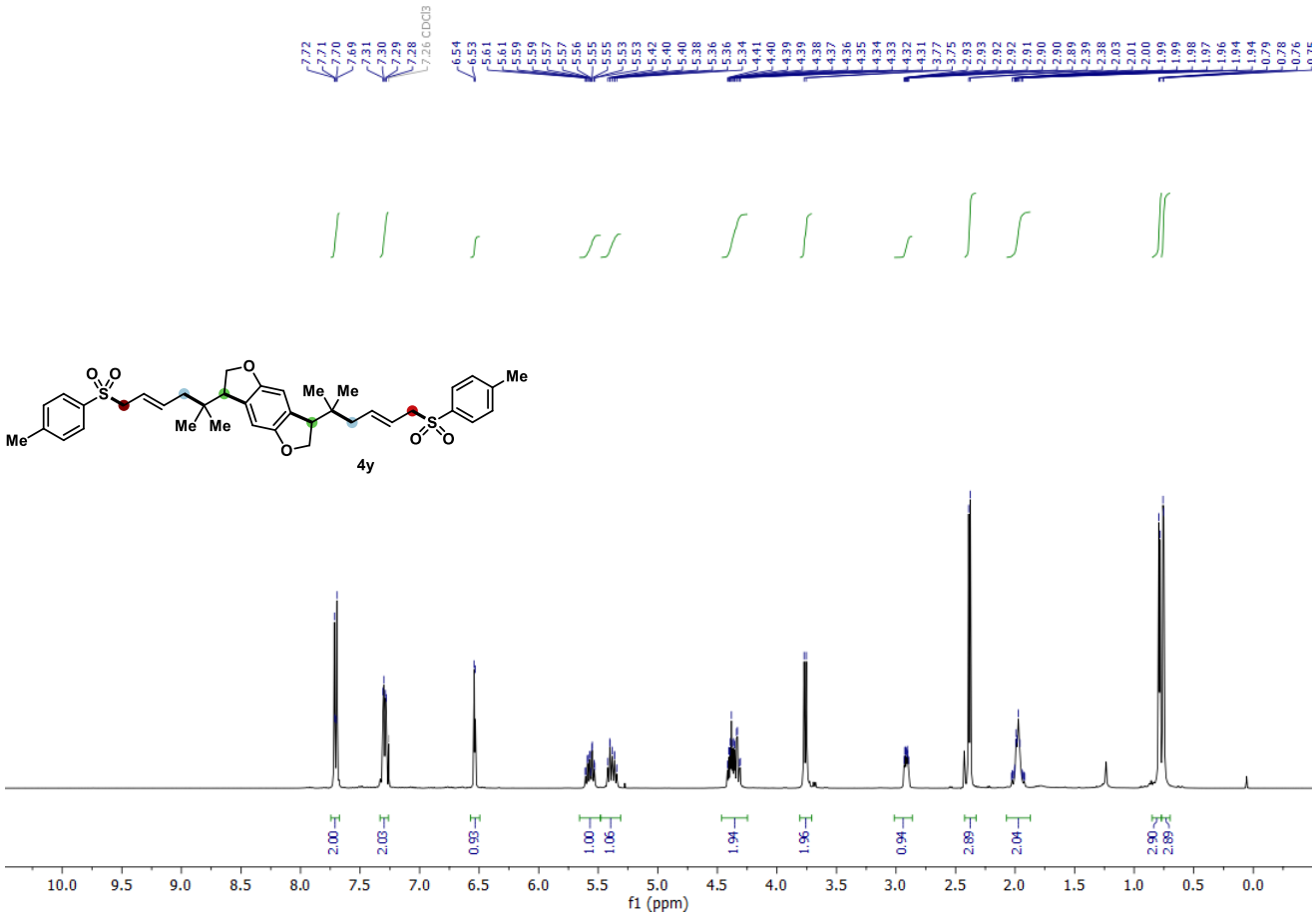
^{1}H NMR (300 MHz, $CDCl_3$)



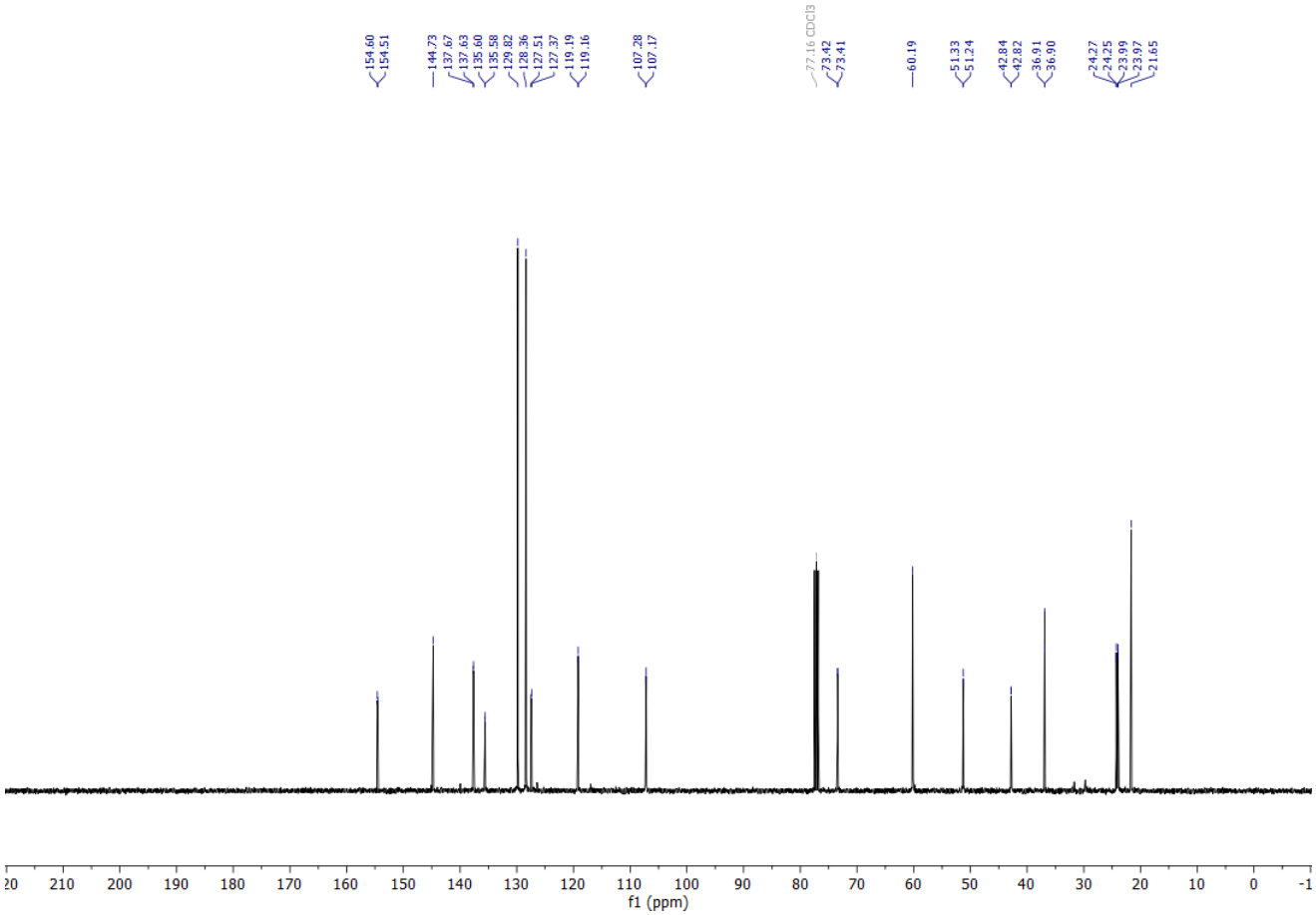
^{13}C NMR (75 MHz, $CDCl_3$)



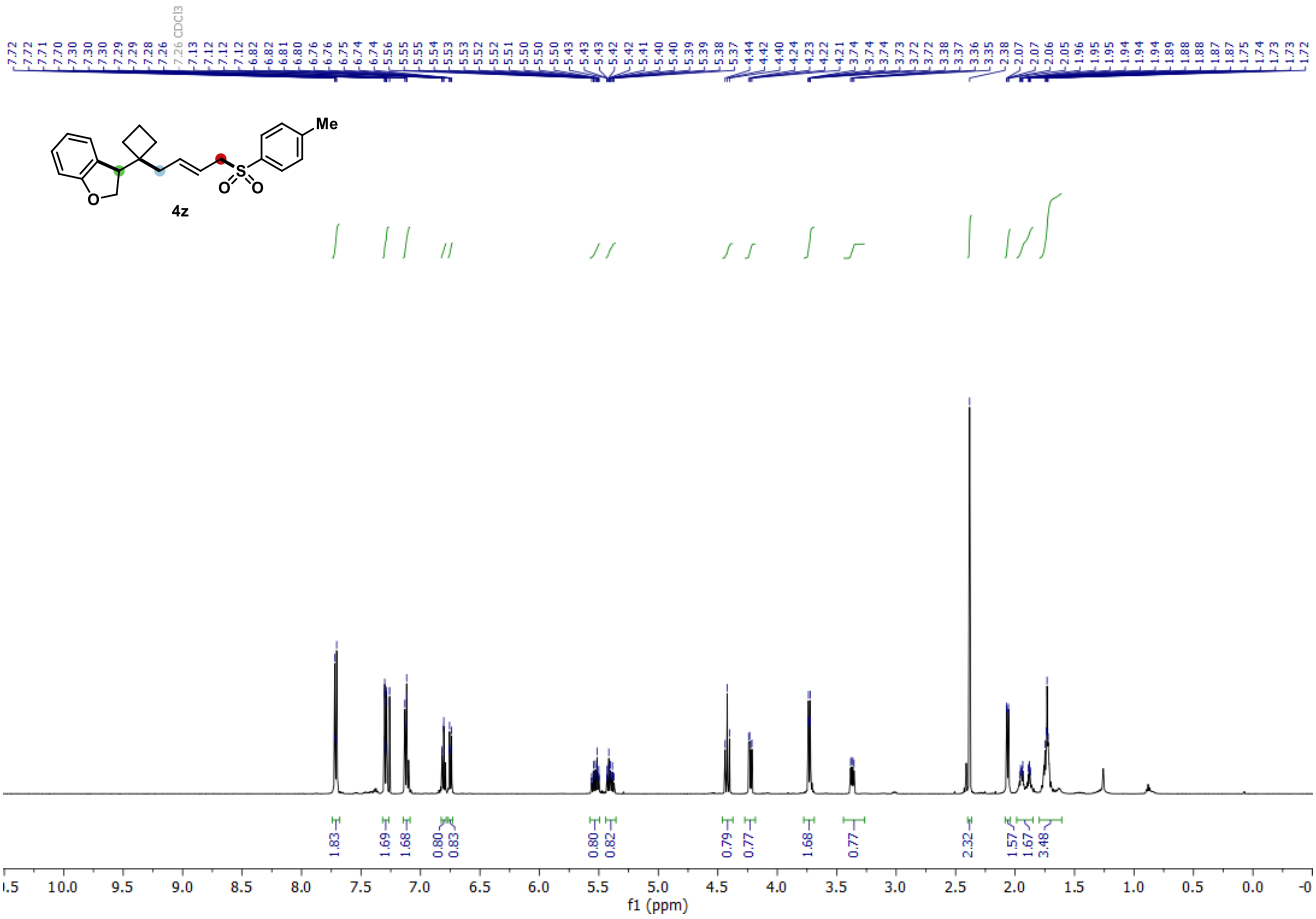
^{1}H NMR (400 MHz, $CDCl_3$)



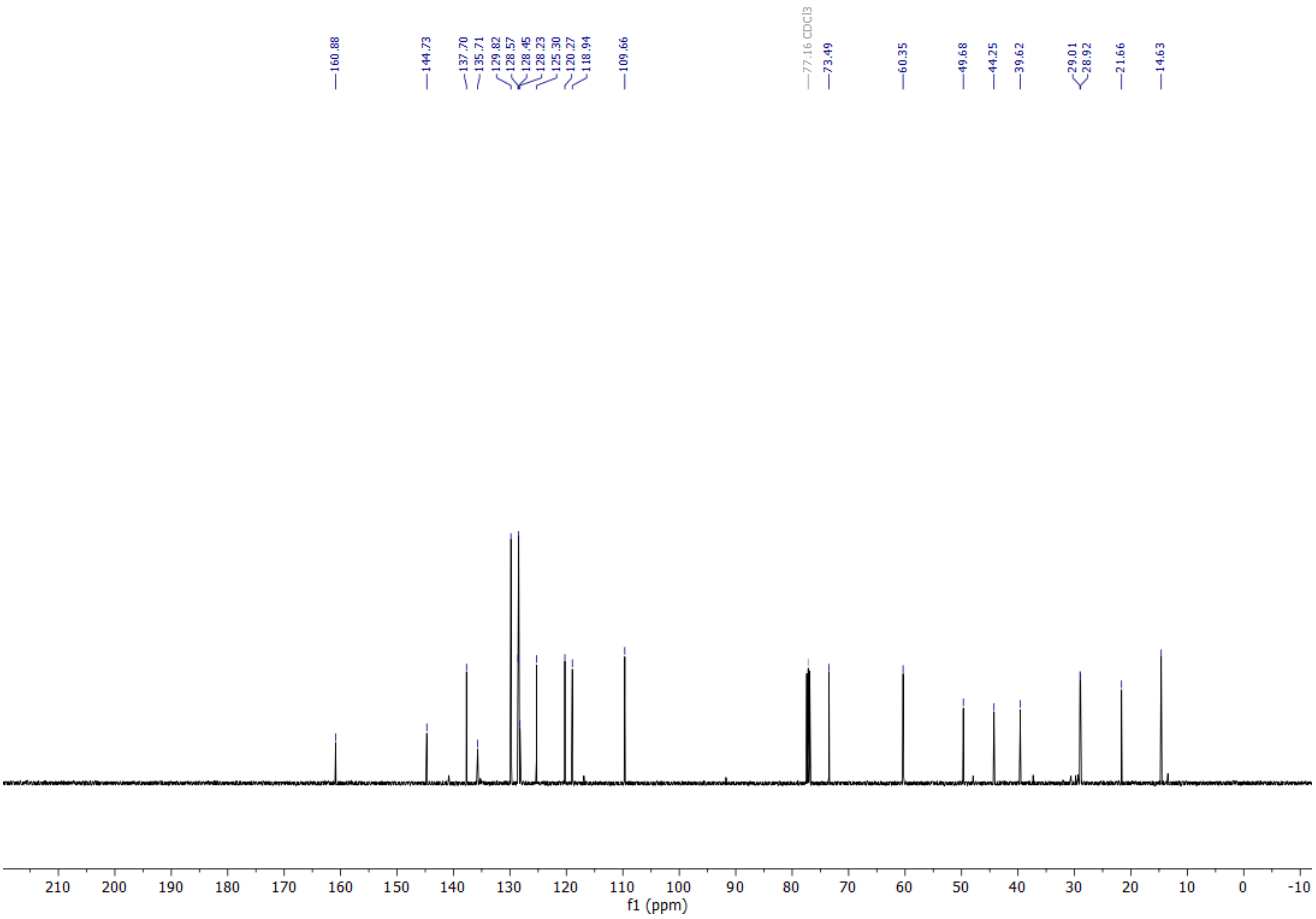
^{13}C NMR (101 MHz, $CDCl_3$)



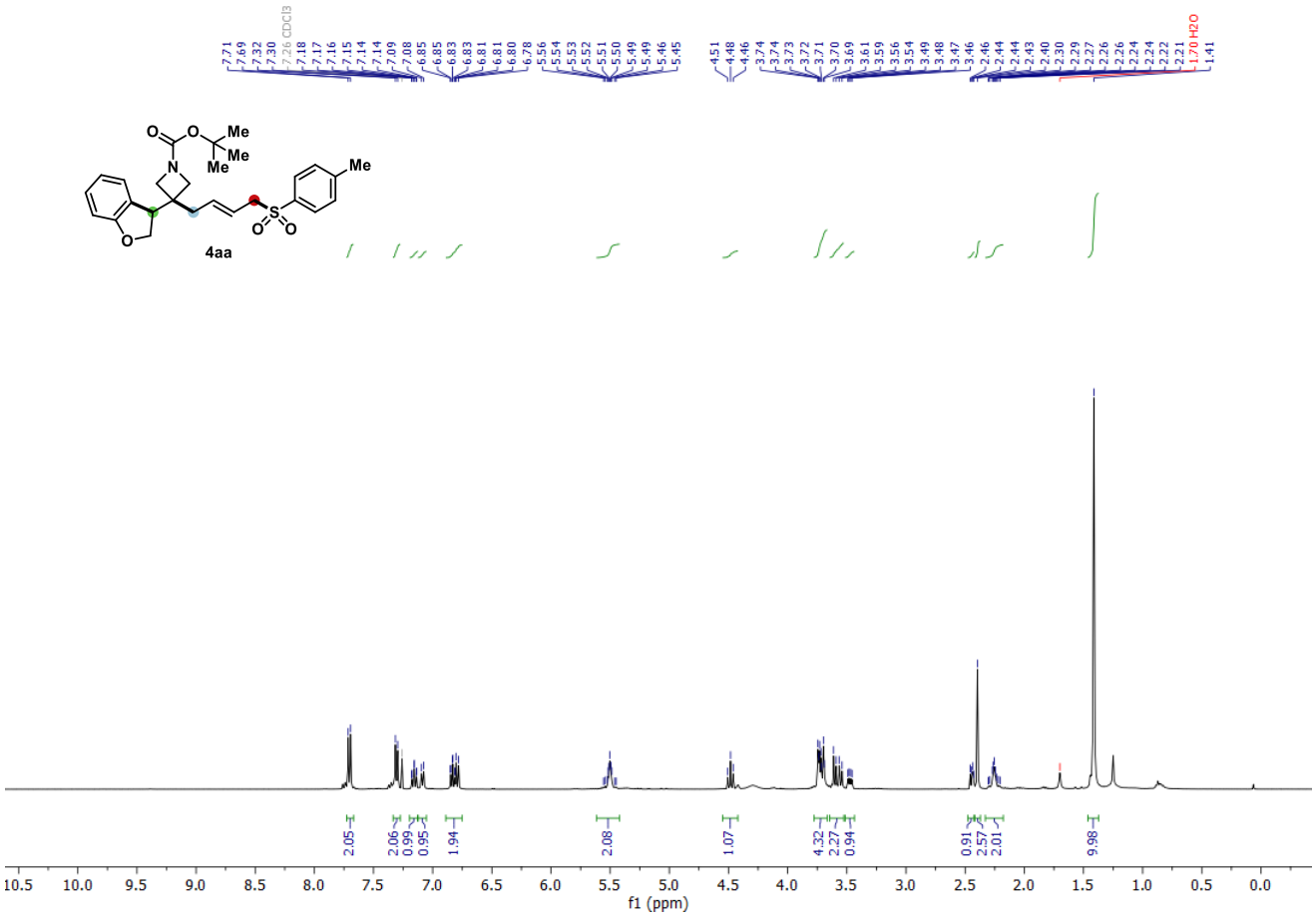
^{1}H NMR (500 MHz, $CDCl_3$)



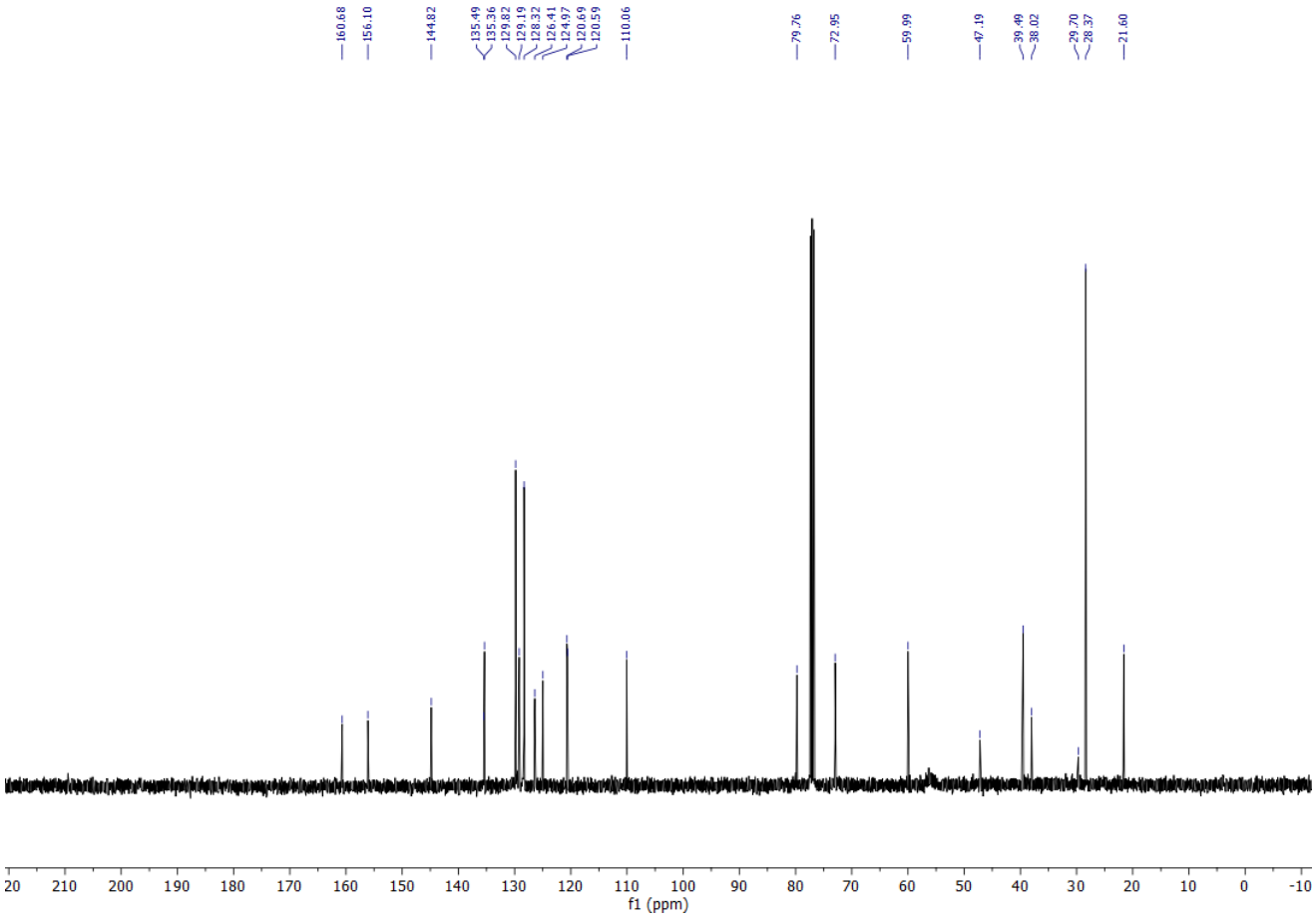
^{13}C NMR (126 MHz, $CDCl_3$)



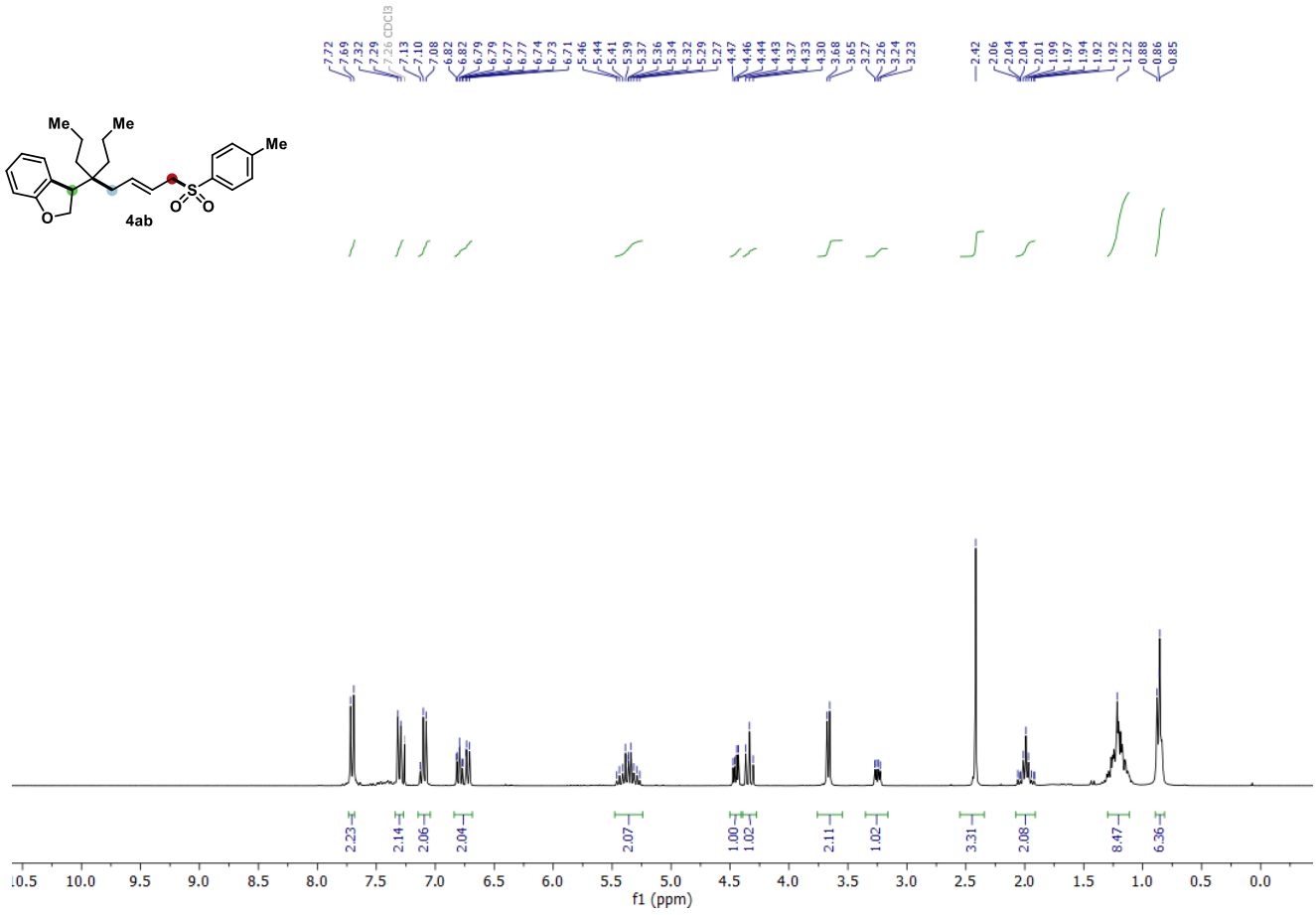
^{1}H NMR (400 MHz, $CDCl_3$)



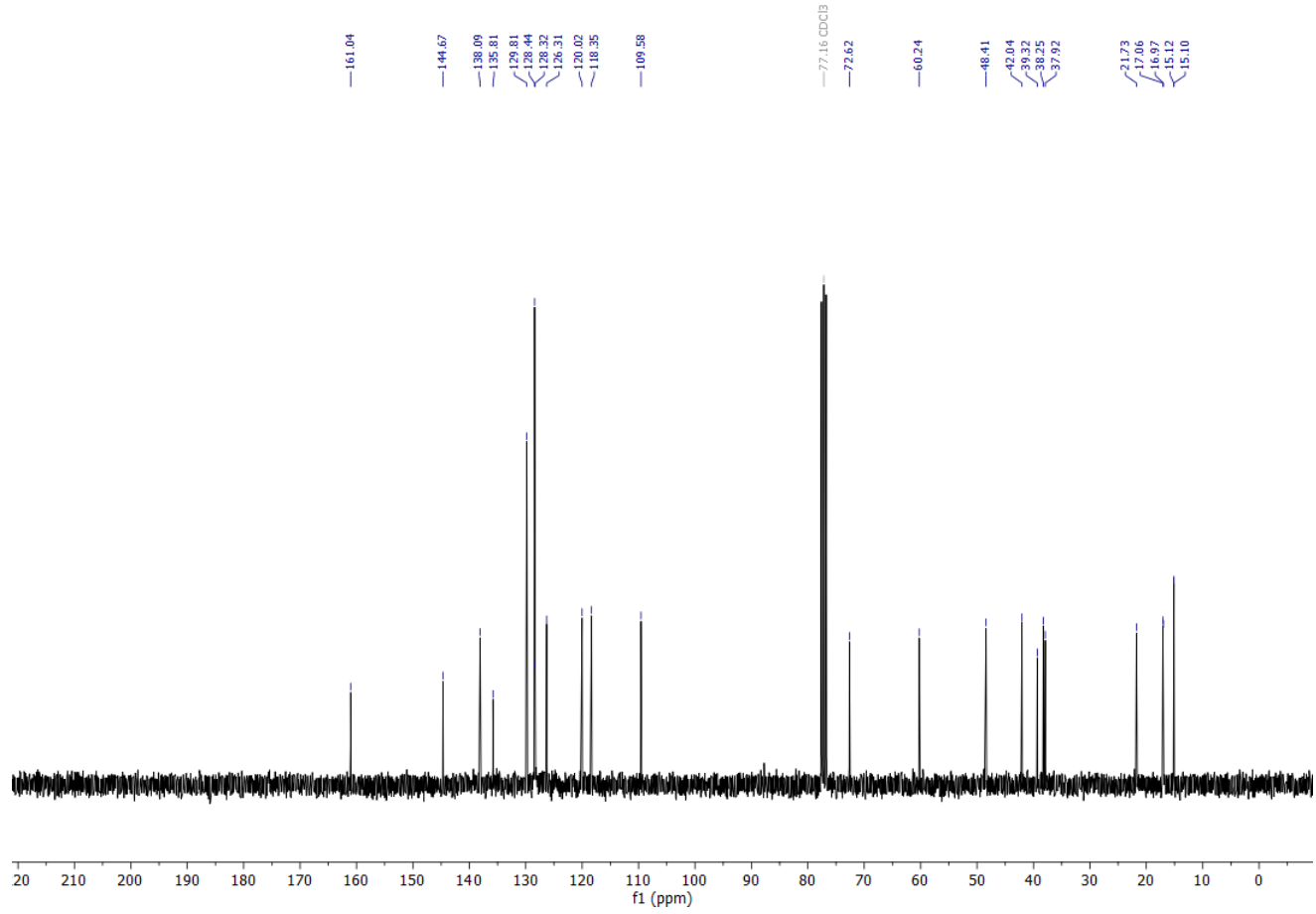
^{13}C NMR (101 MHz, $CDCl_3$)



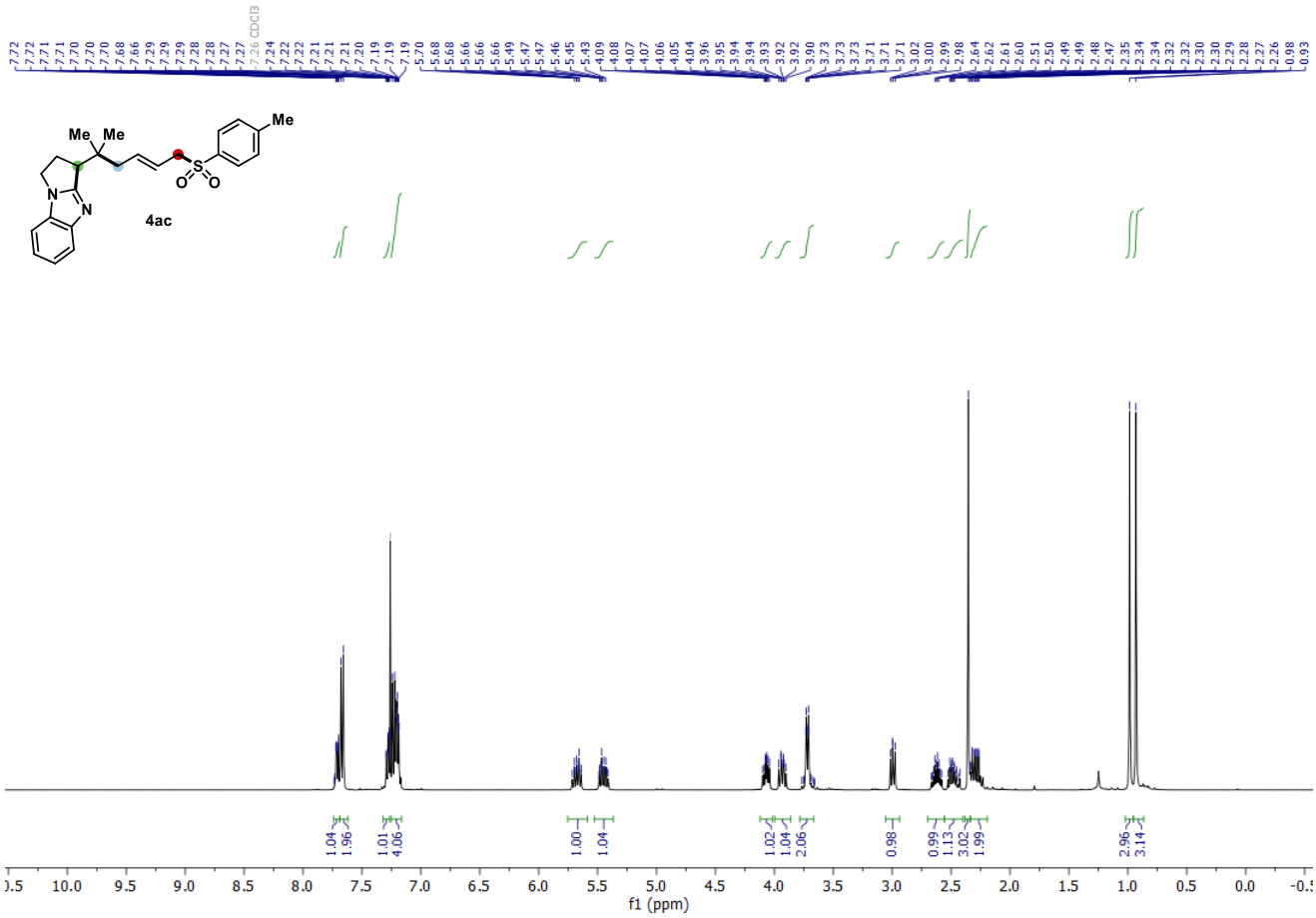
^{1}H NMR (300 MHz, $CDCl_3$)



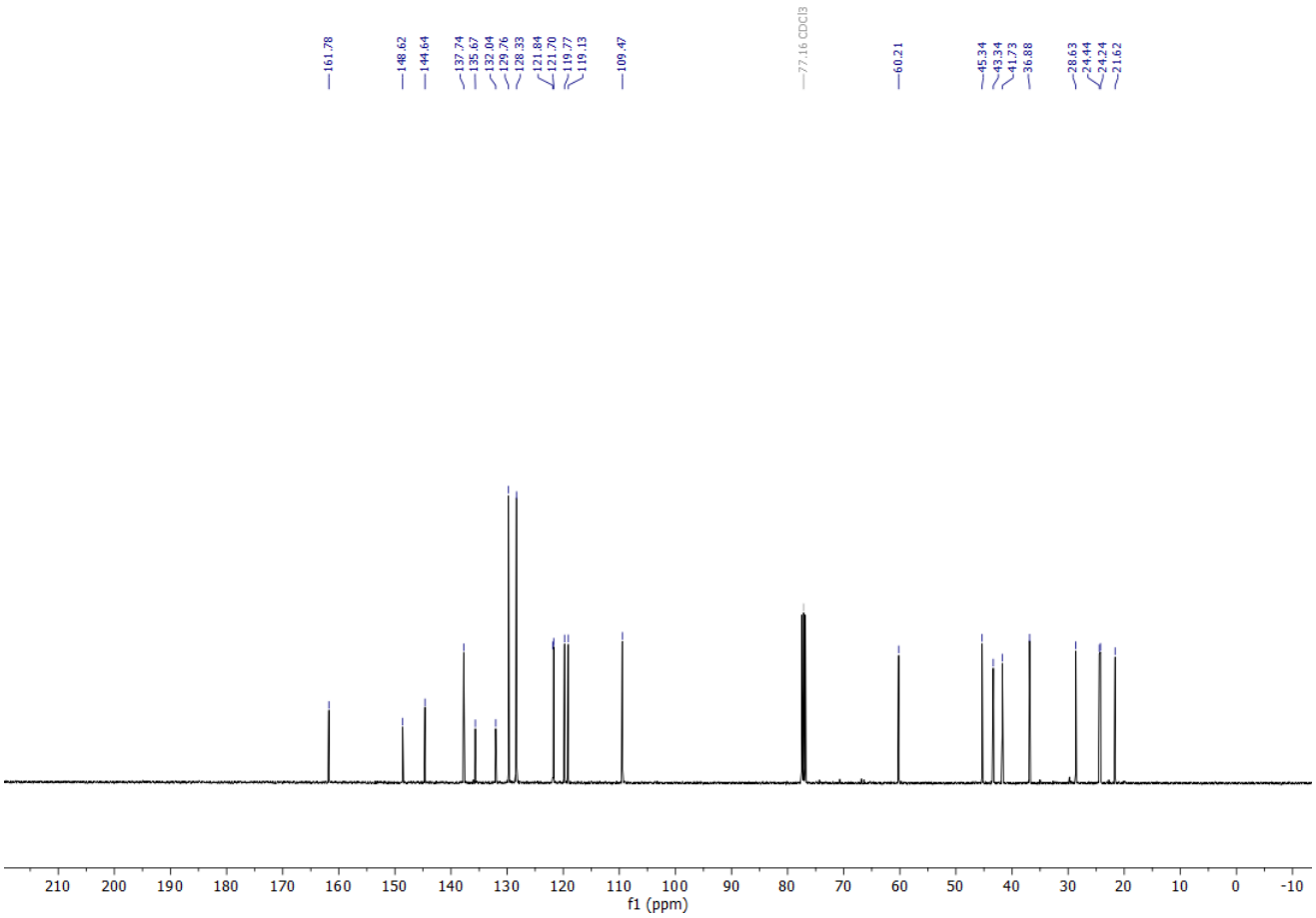
^{13}C NMR (76 MHz, $CDCl_3$)



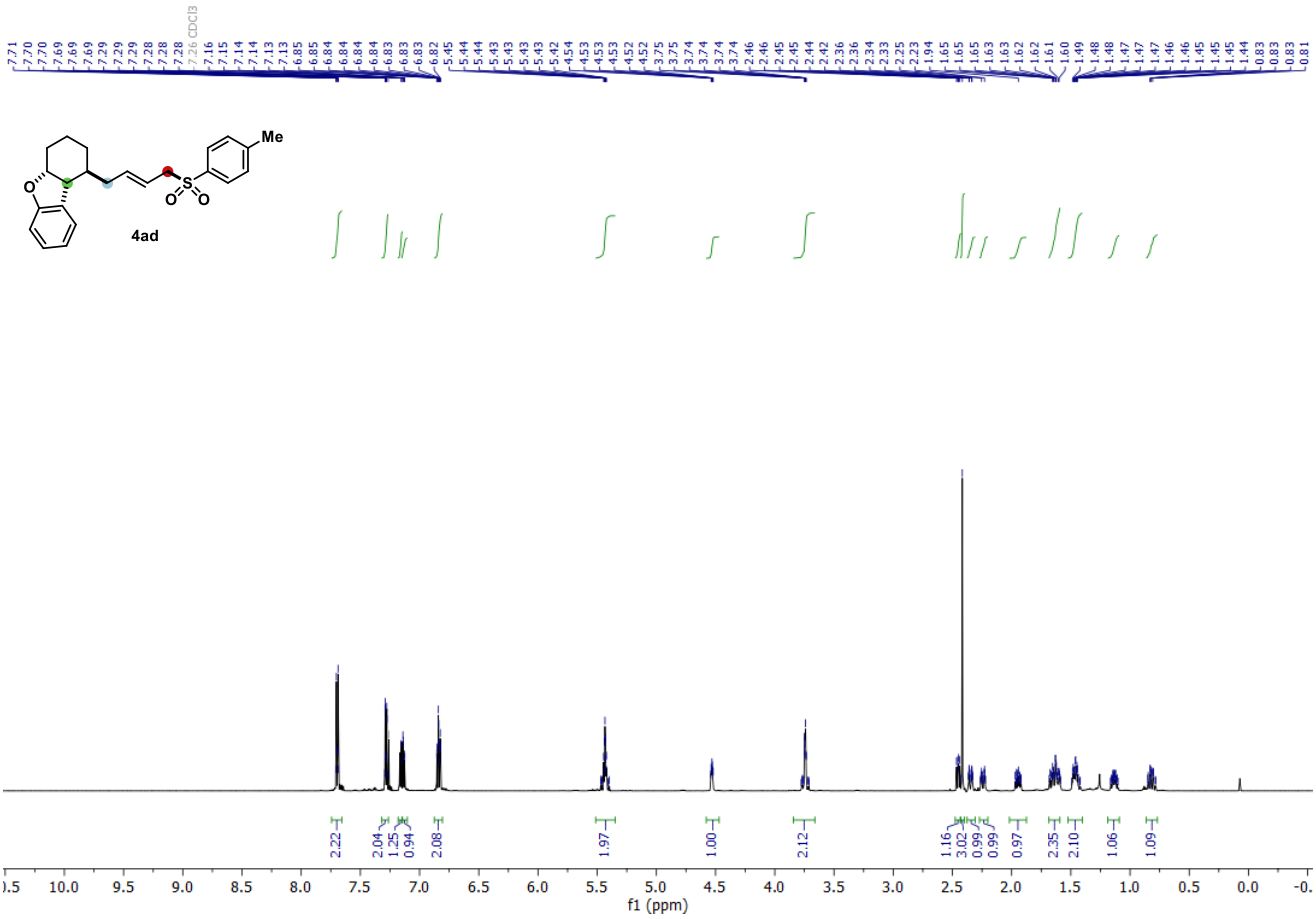
^{1}H NMR (400 MHz, $CDCl_3$)



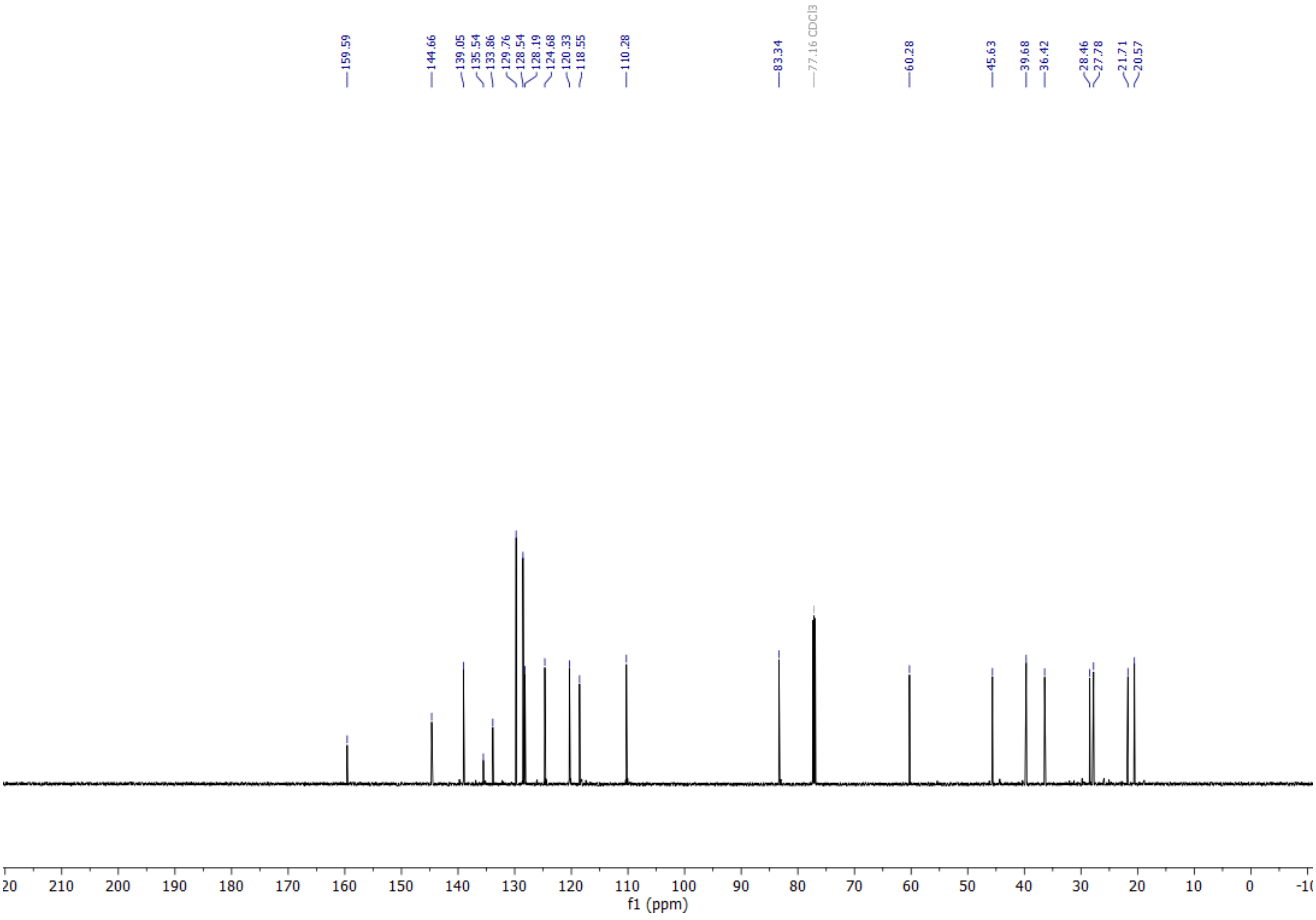
^{13}C NMR (101 MHz, $CDCl_3$)



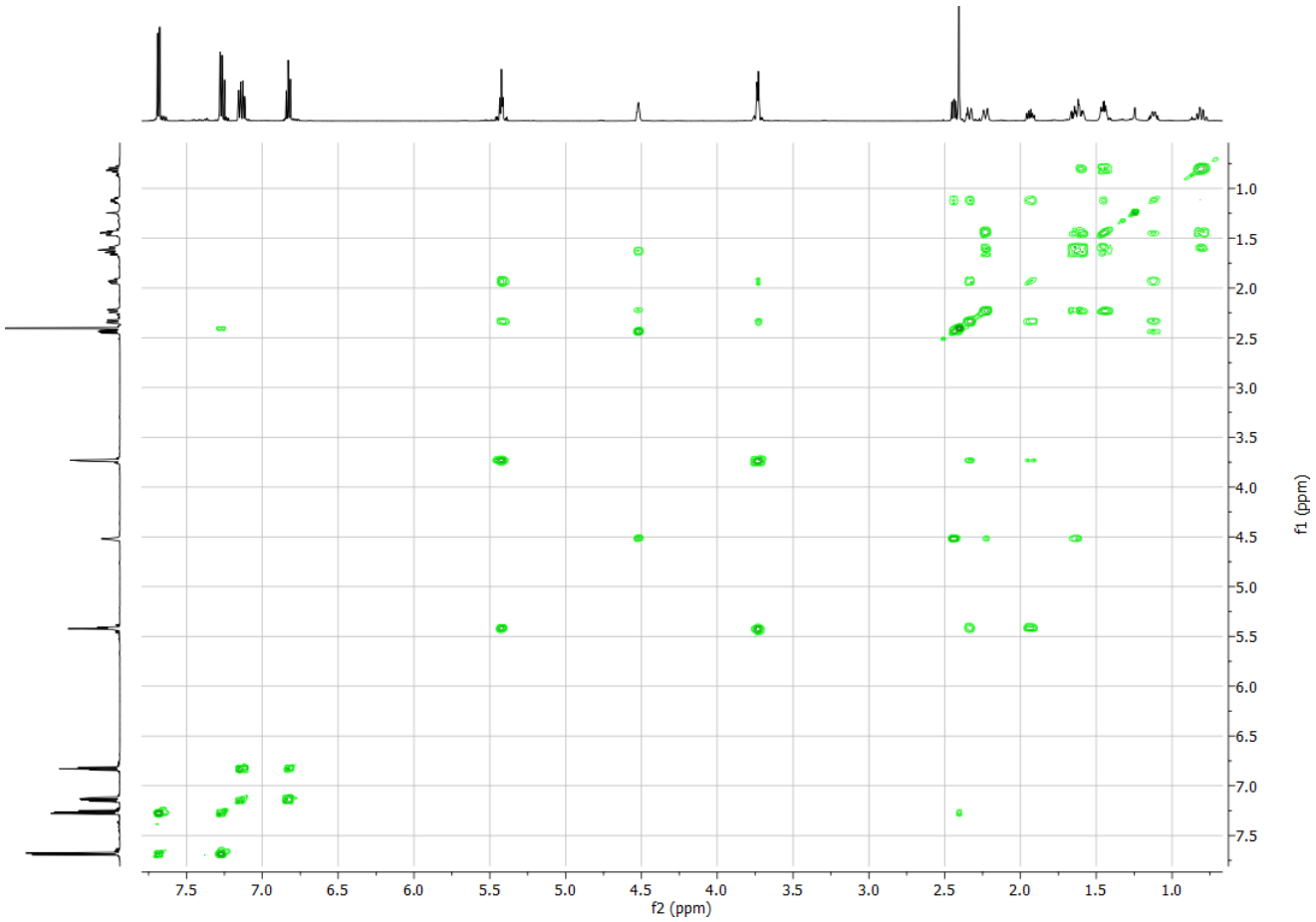
^{1}H NMR (599 MHz, $CDCl_3$)



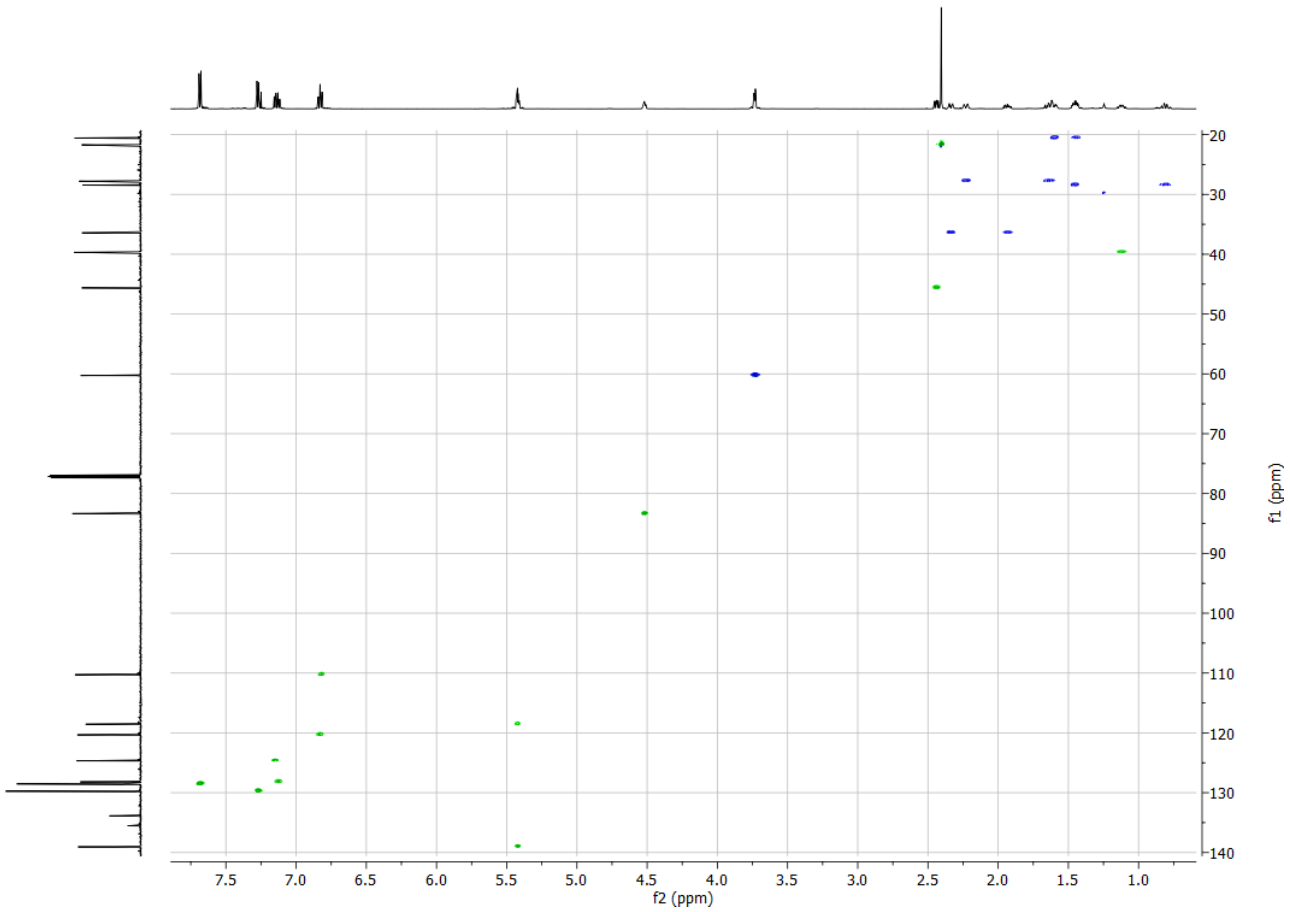
^{13}C NMR (151 MHz, $CDCl_3$)



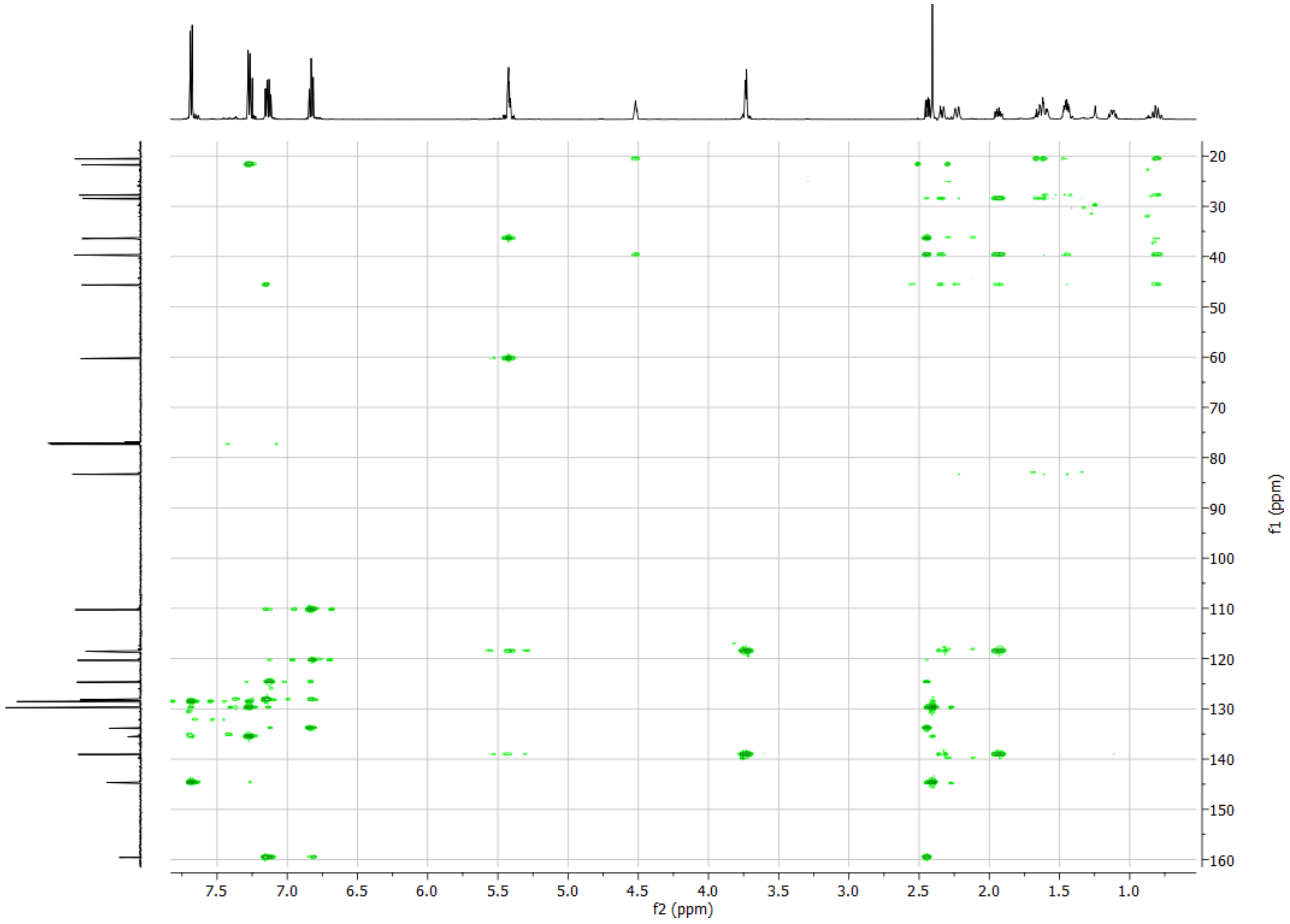
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



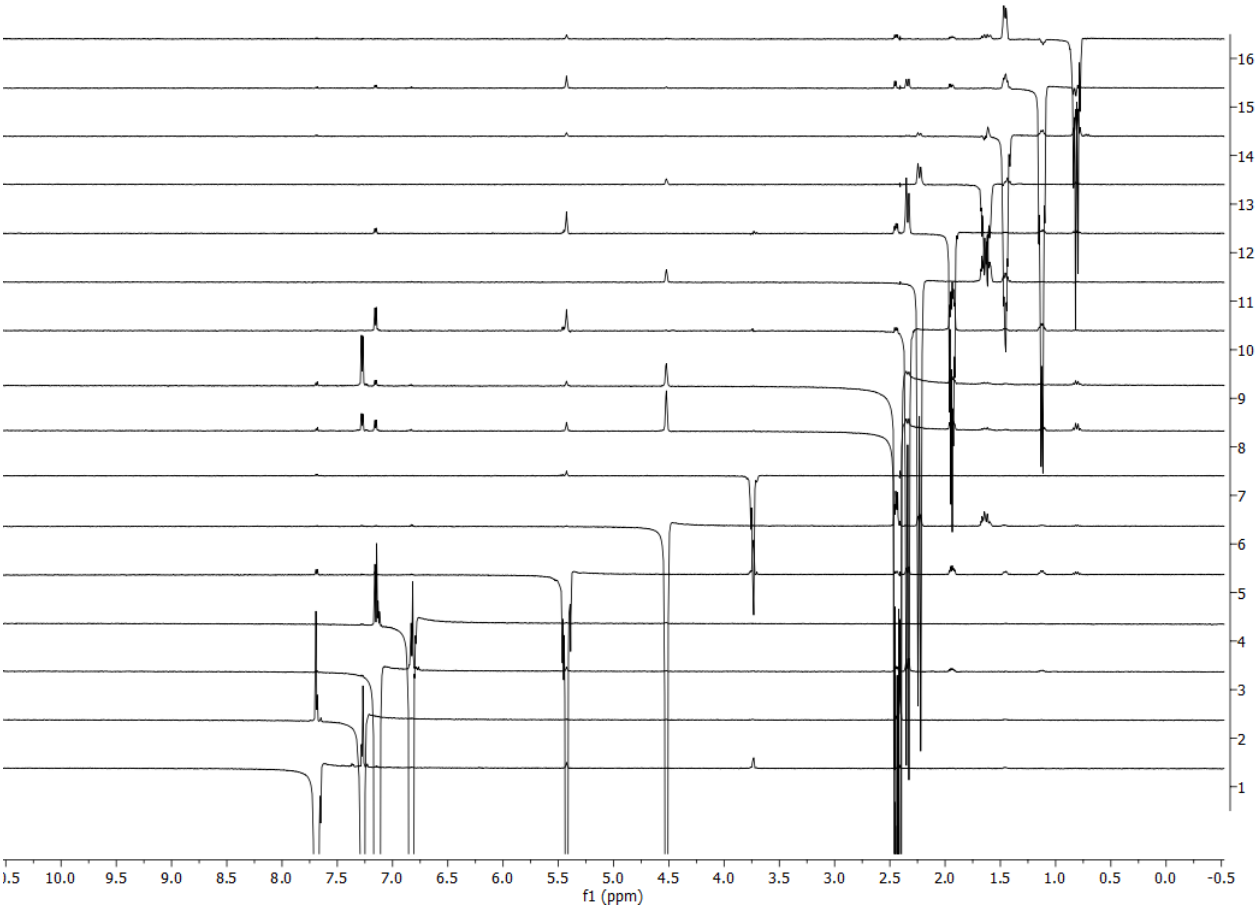
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



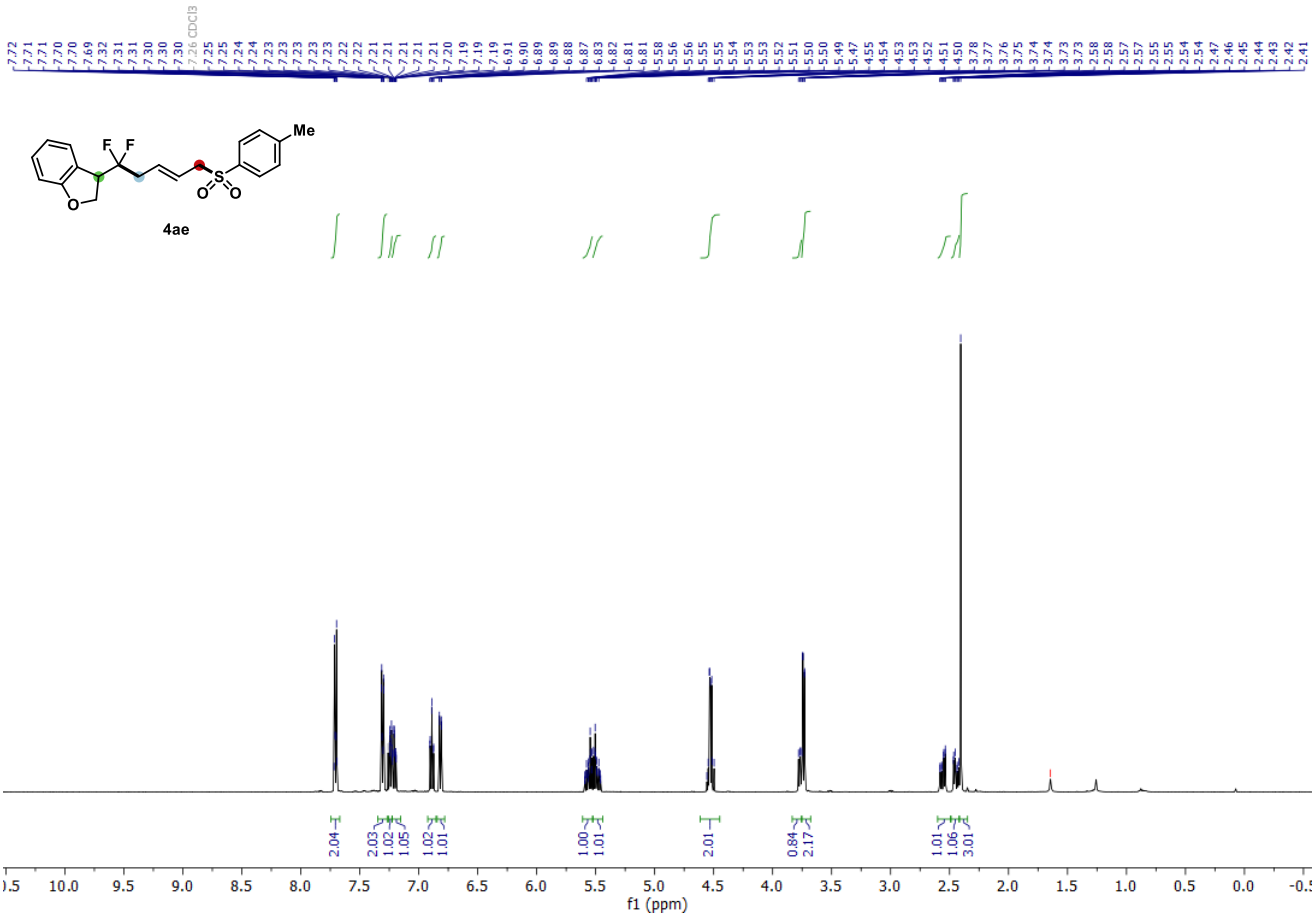
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



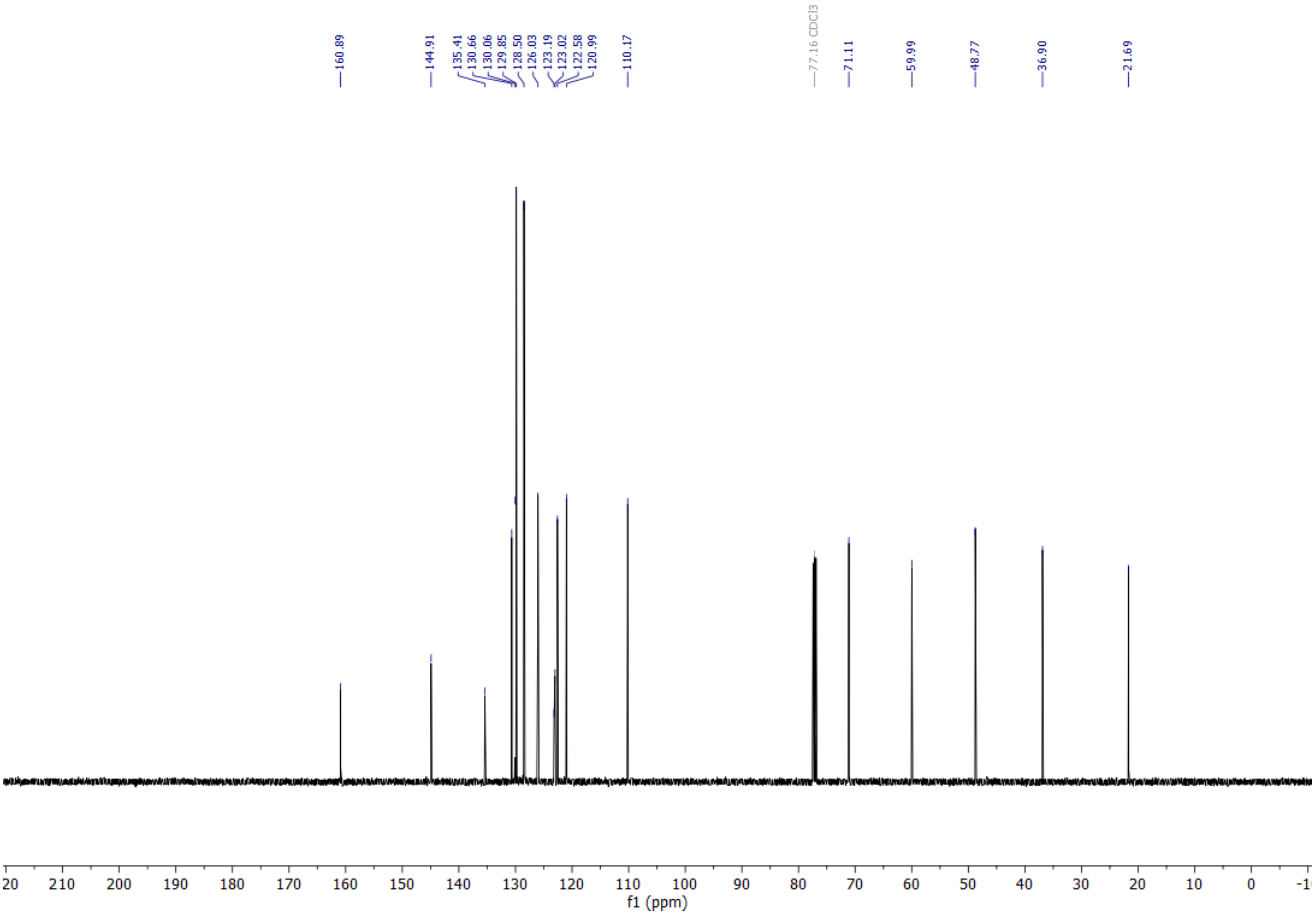
1D NOESY NMR (599 MHz, $CDCl_3$)



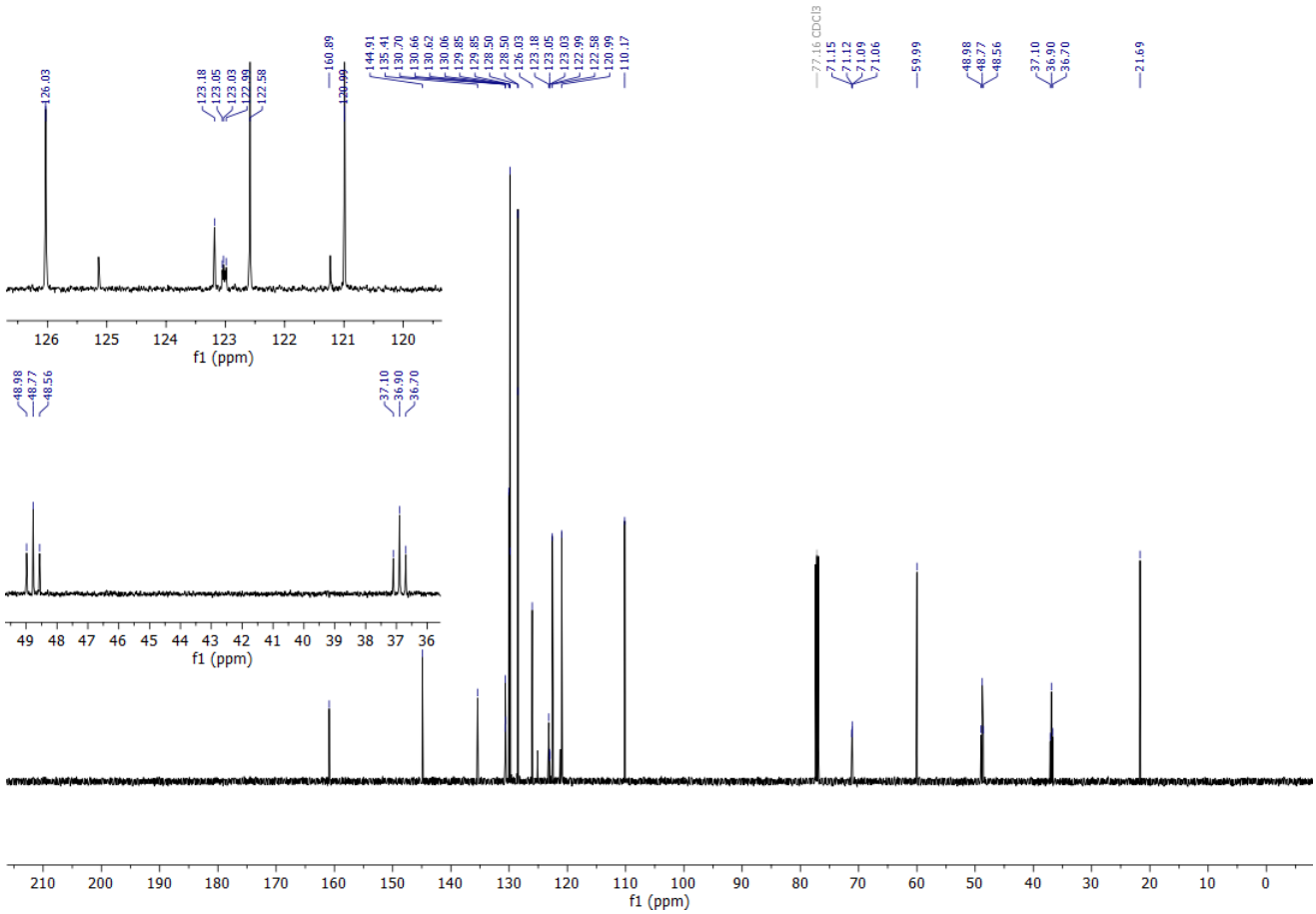
^{1}H NMR (500 MHz, $CDCl_3$)



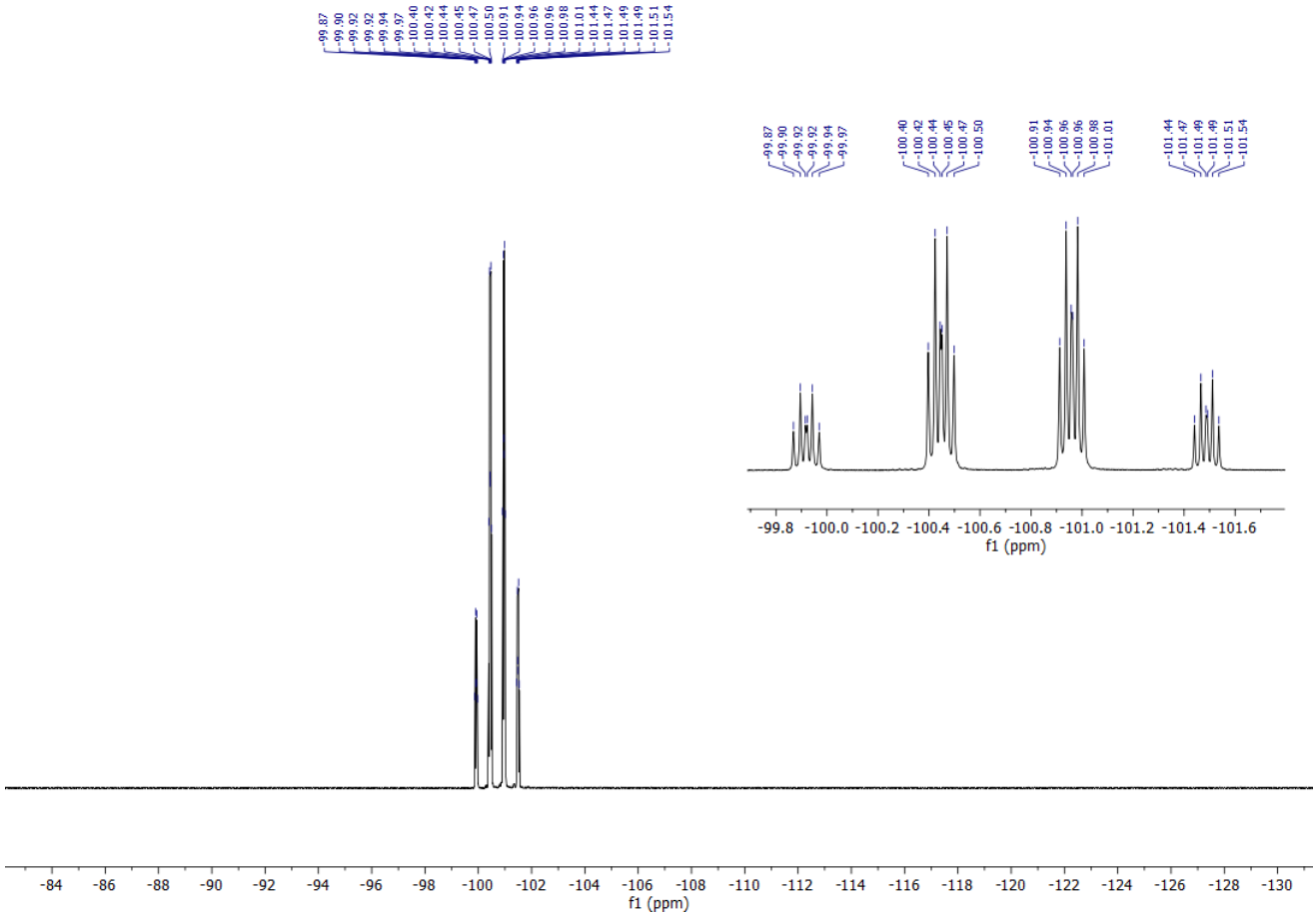
^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$)



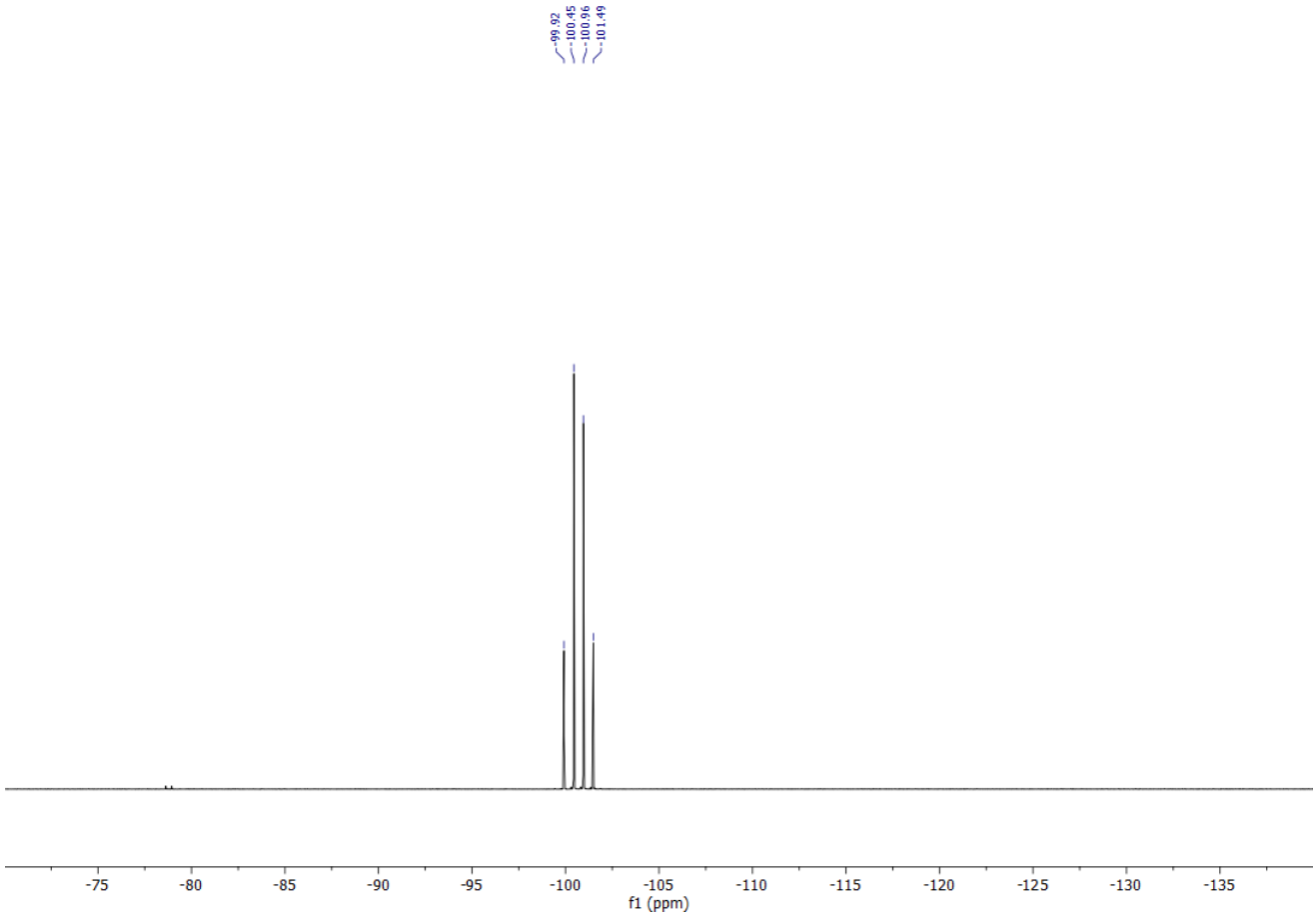
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



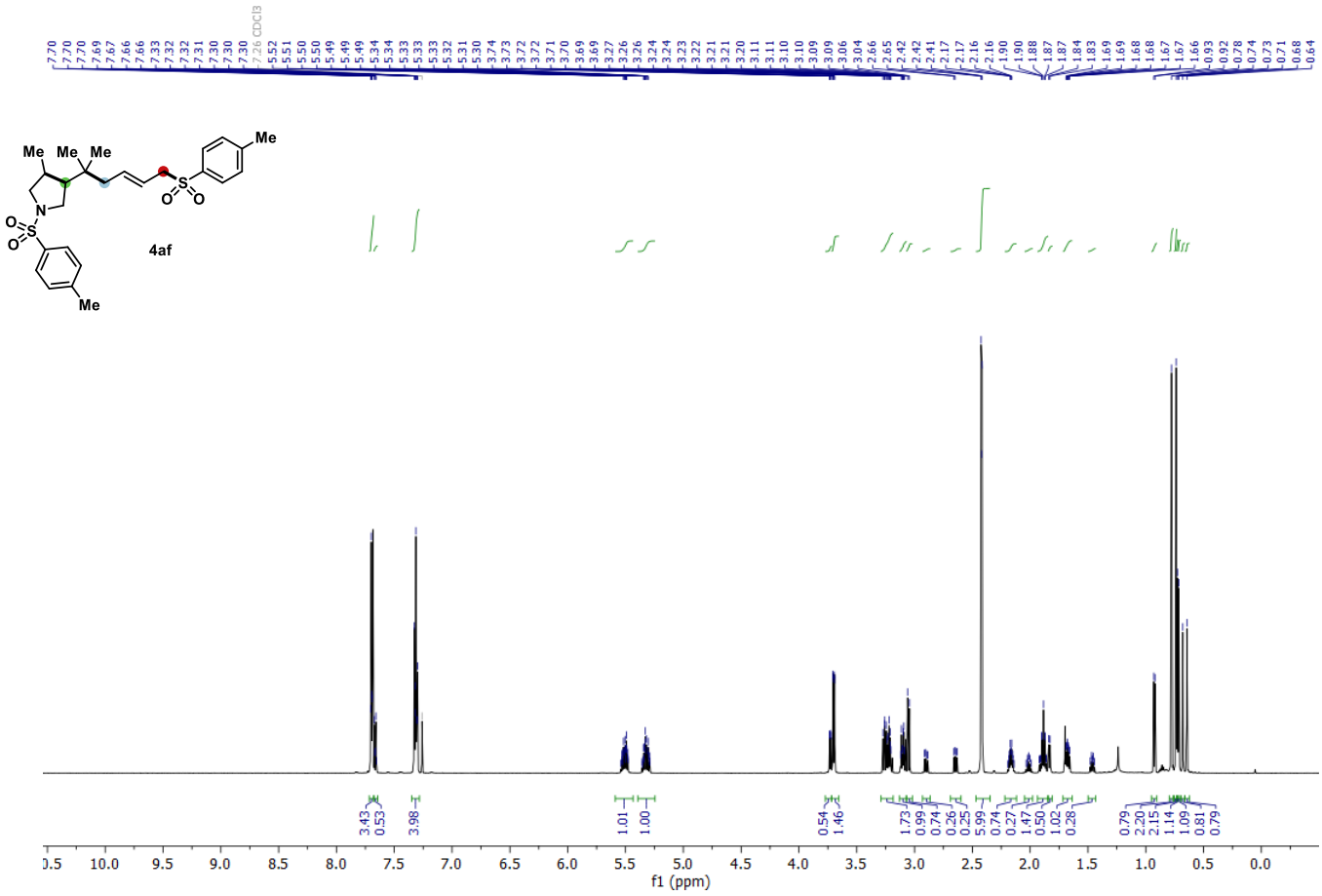
^{19}F NMR (470 MHz, $CDCl_3$)



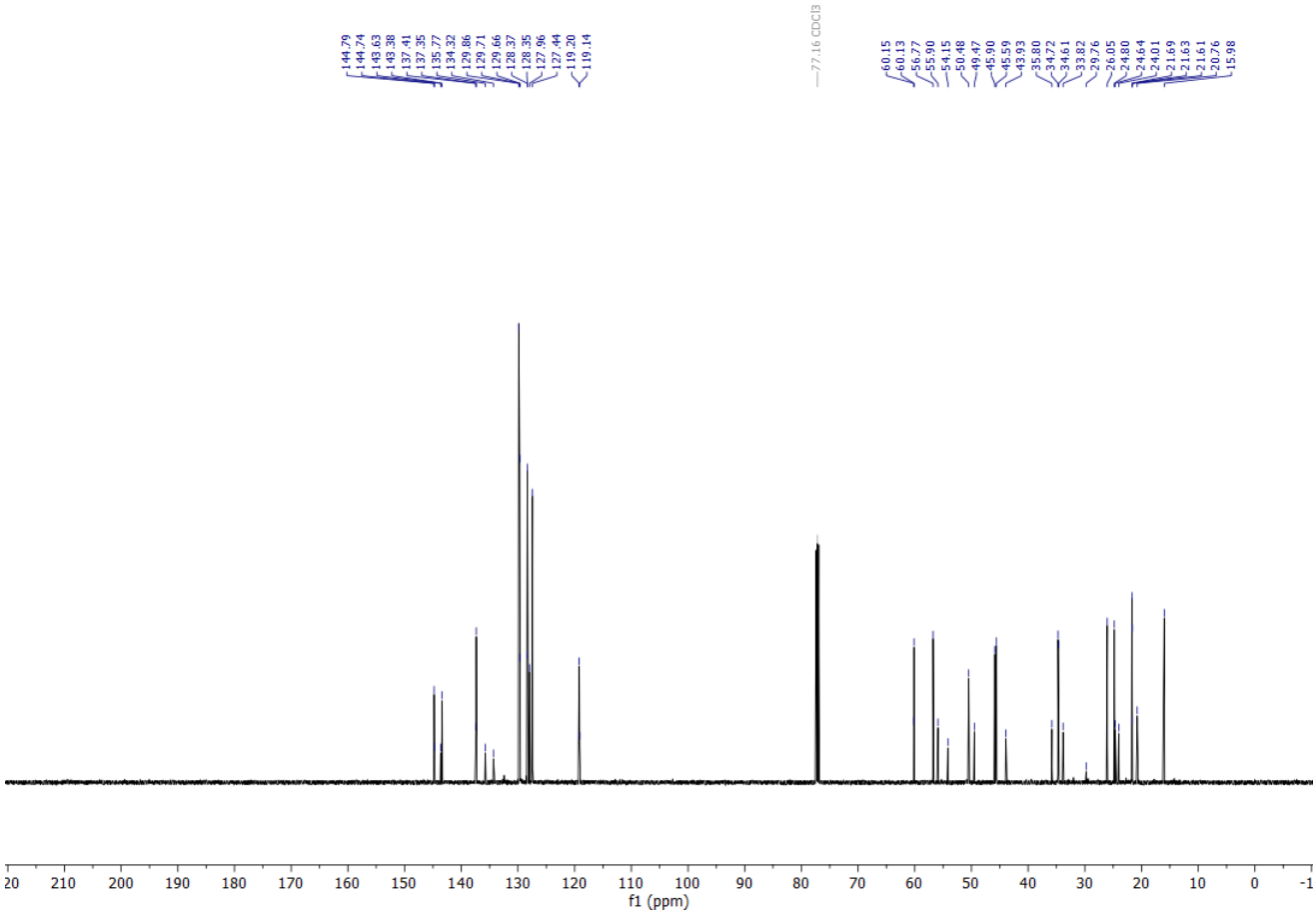
$^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$)



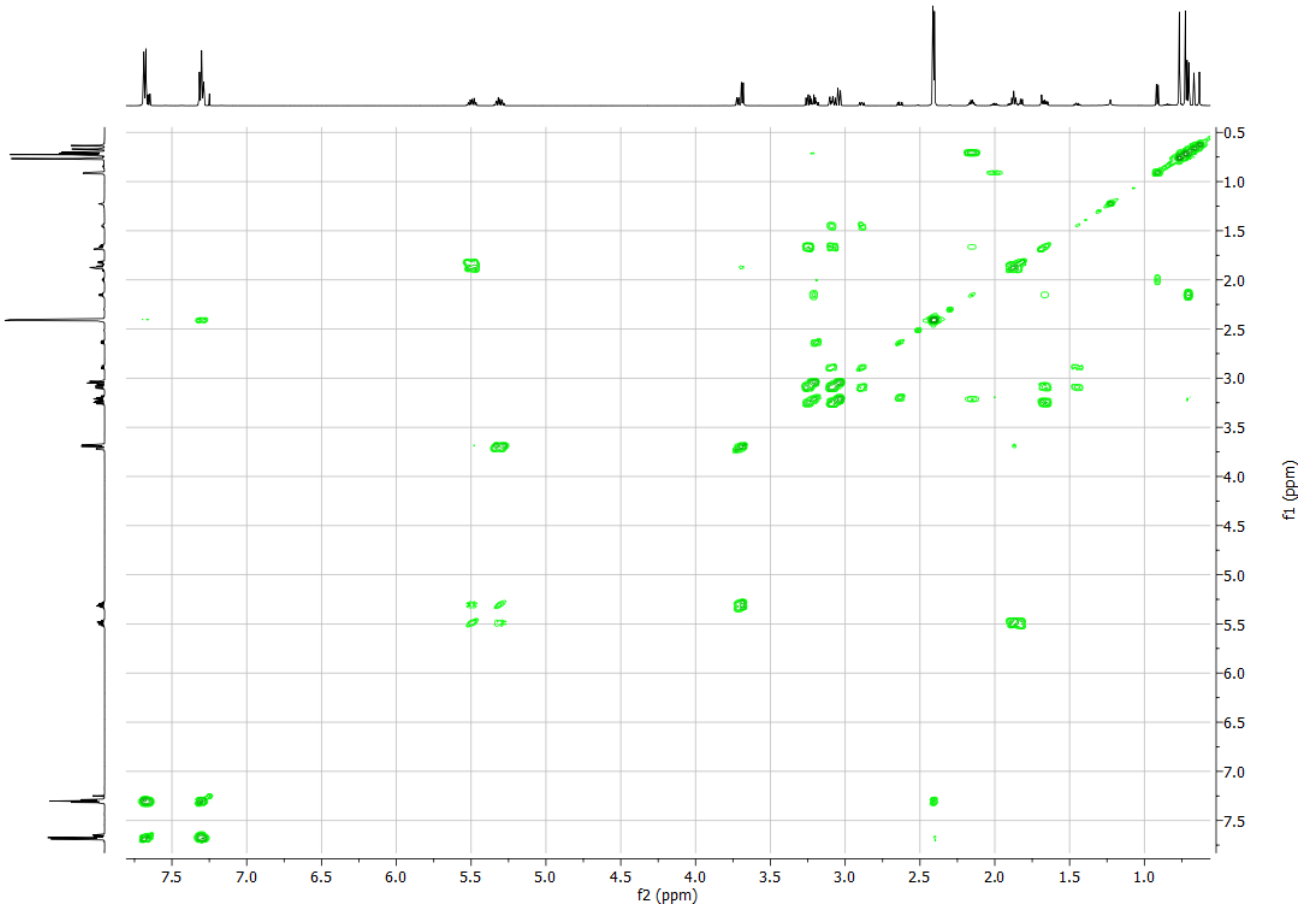
^{1}H NMR (599 MHz, $CDCl_3$)



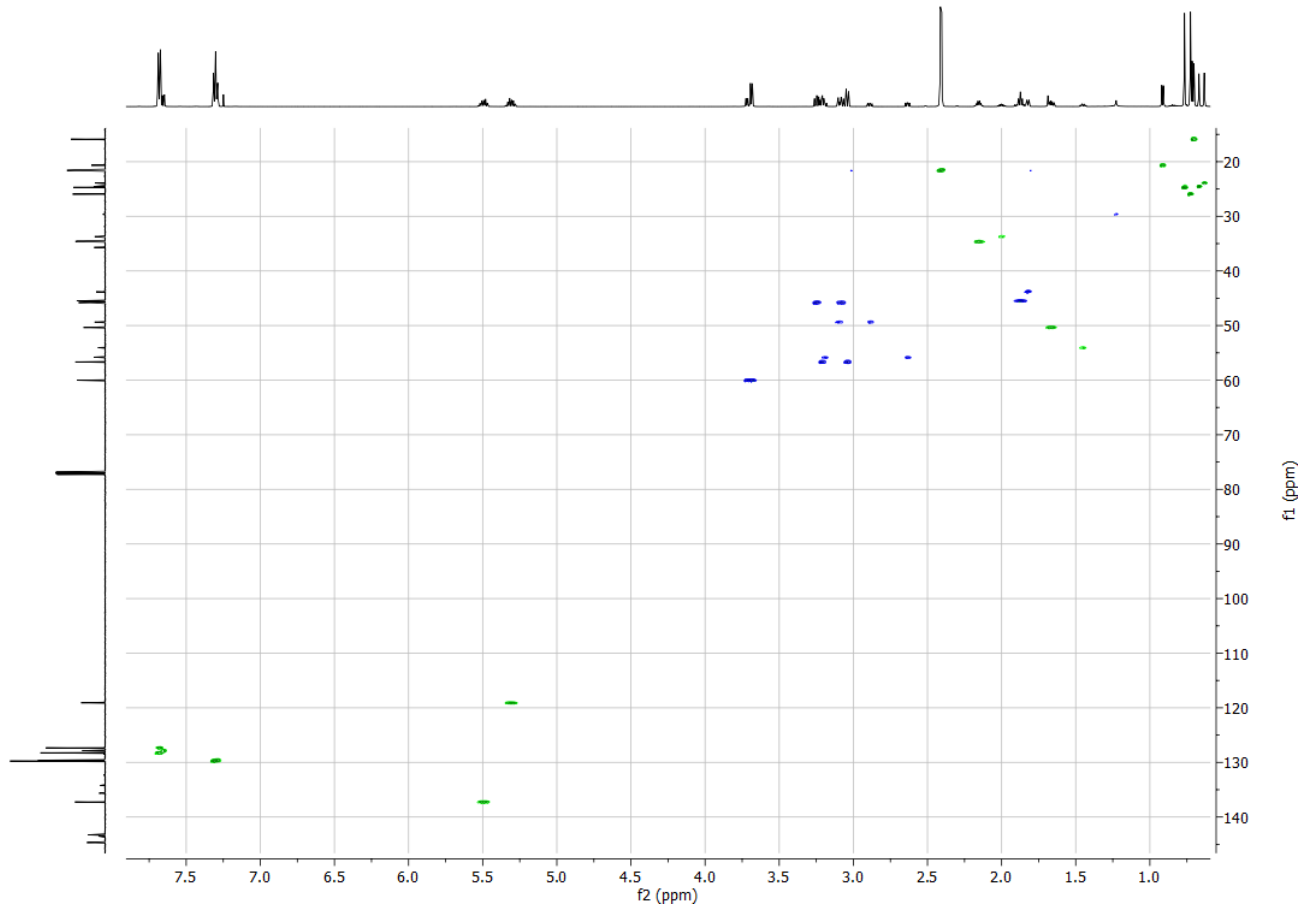
^{13}C NMR (151 MHz, $CDCl_3$)



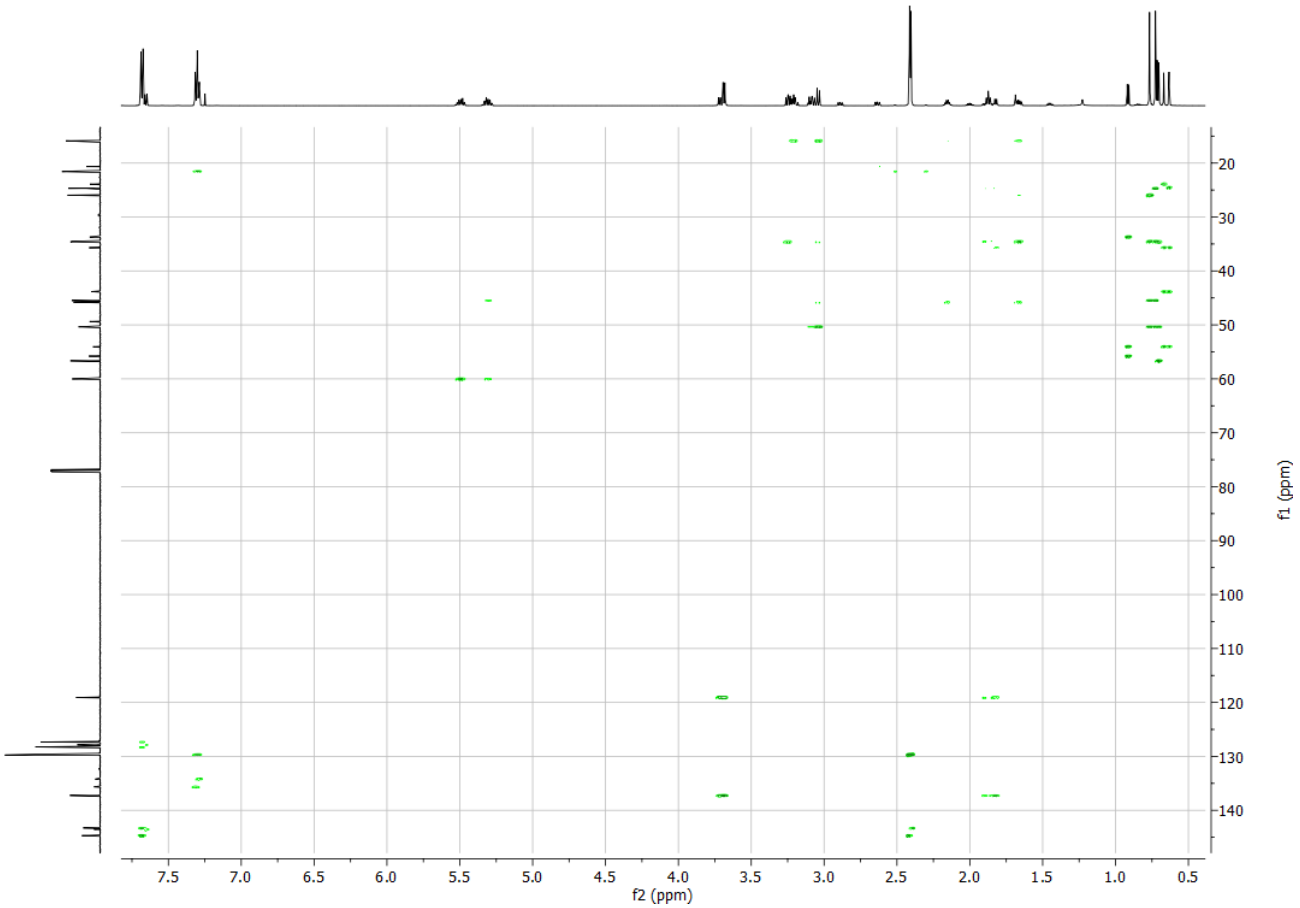
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



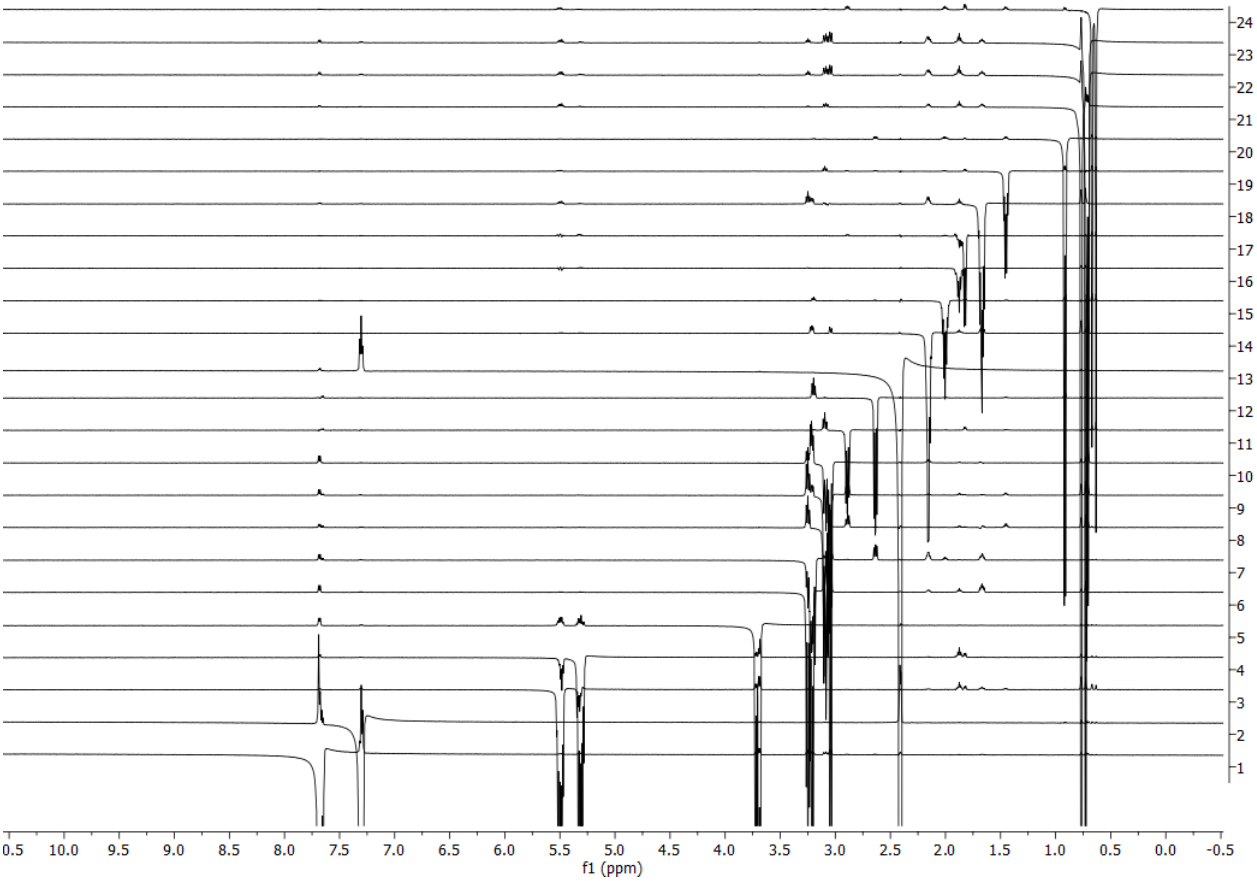
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



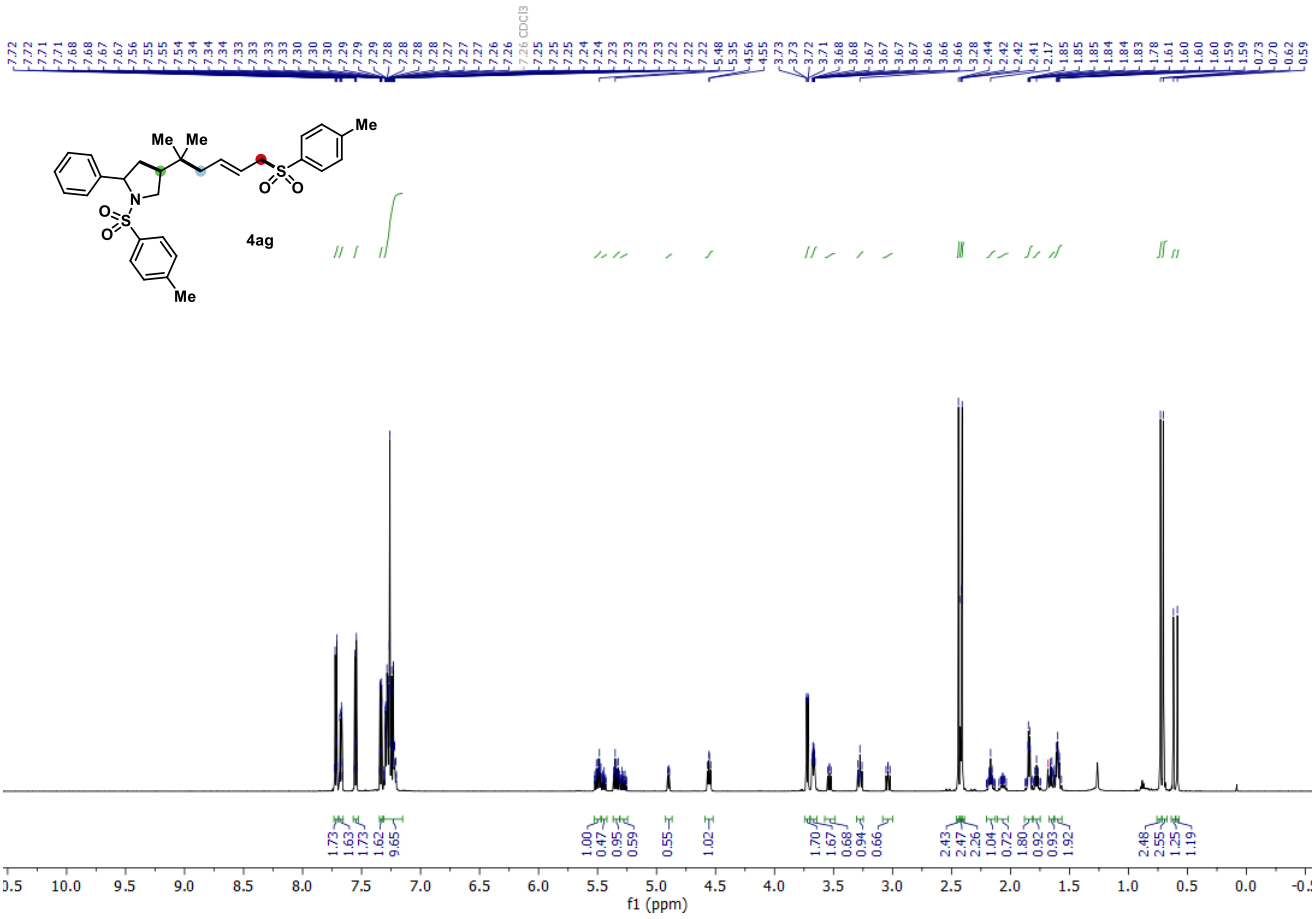
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



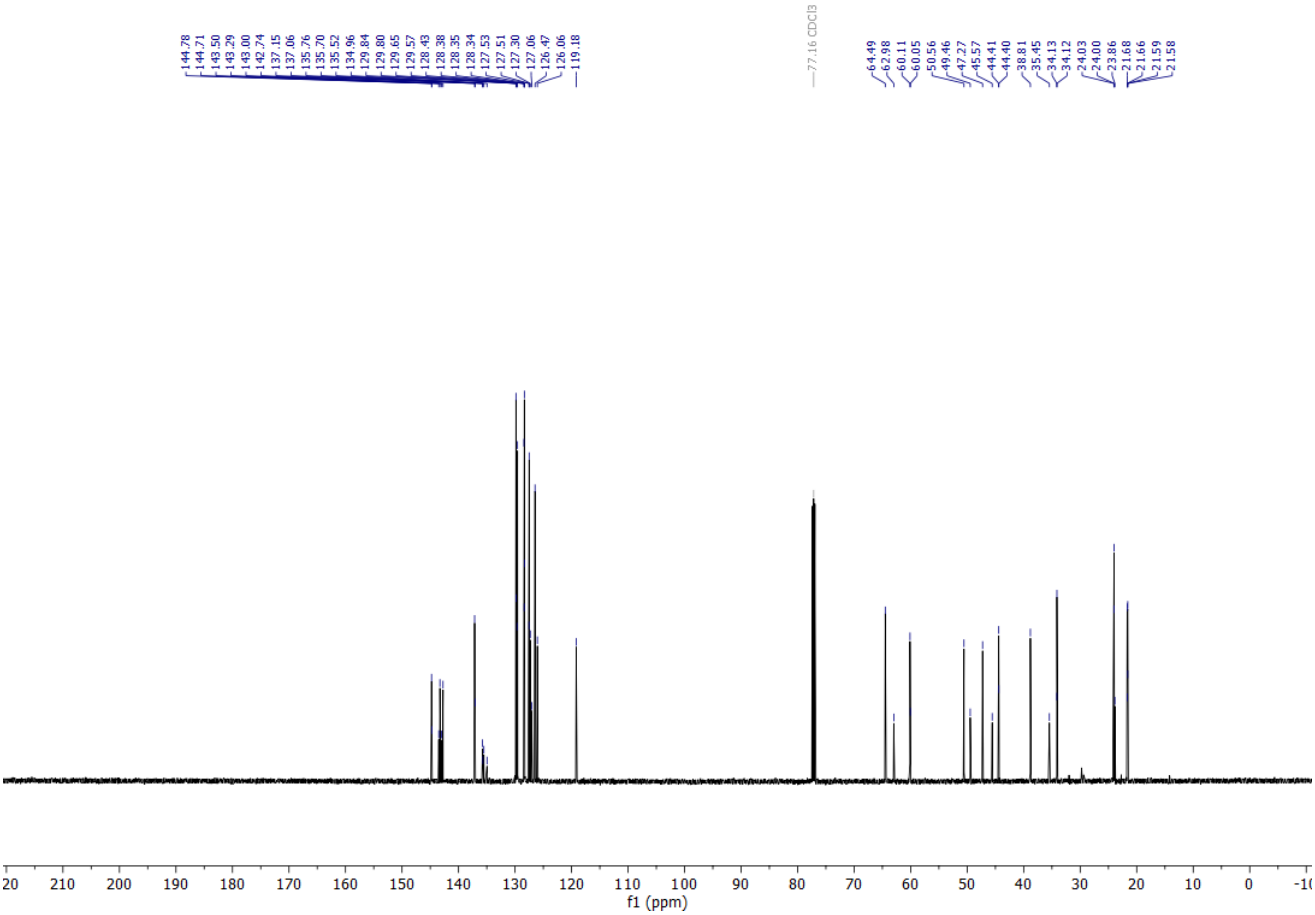
1D NOESY NMR (599 MHz, $CDCl_3$)



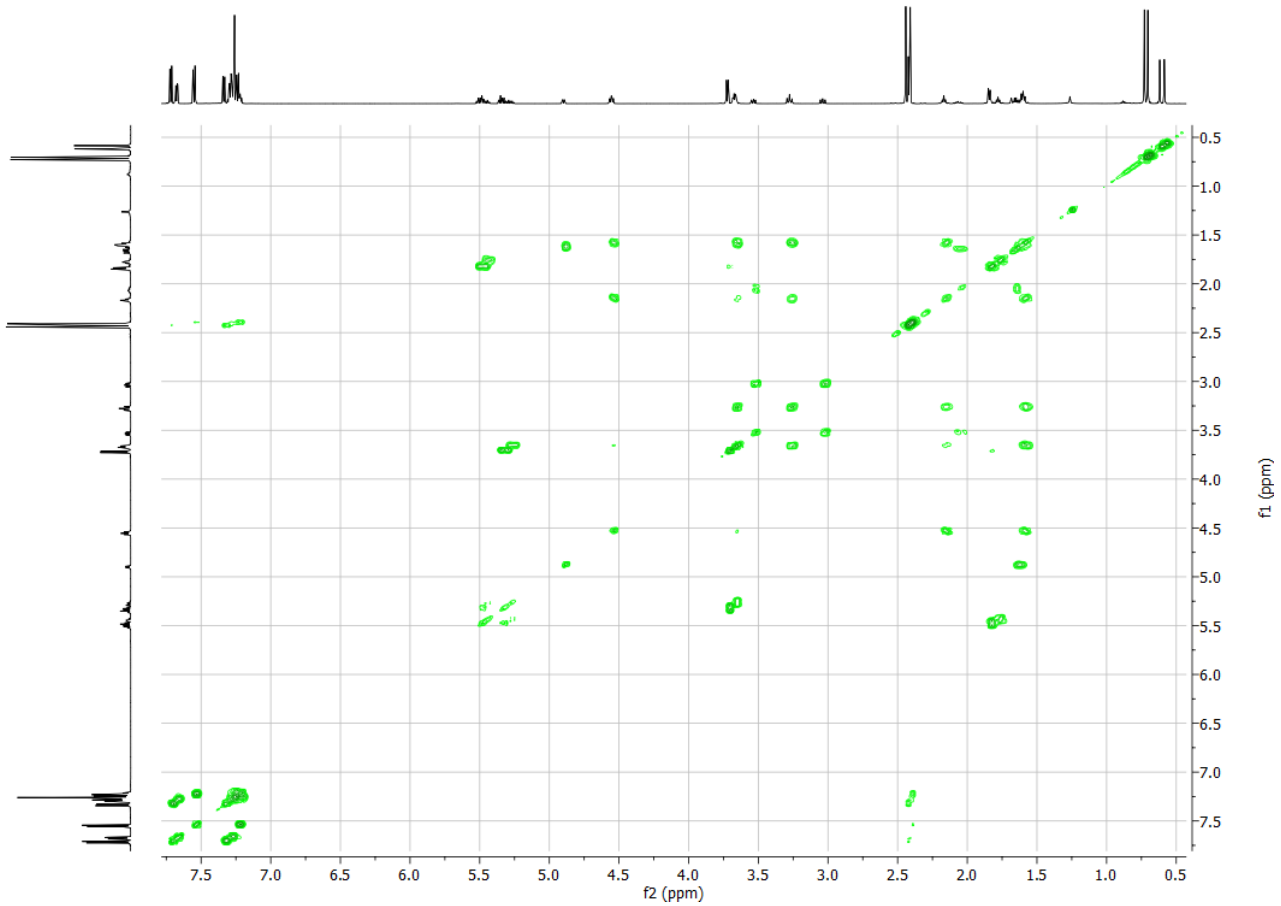
^{1}H NMR (599 MHz, $CDCl_3$)



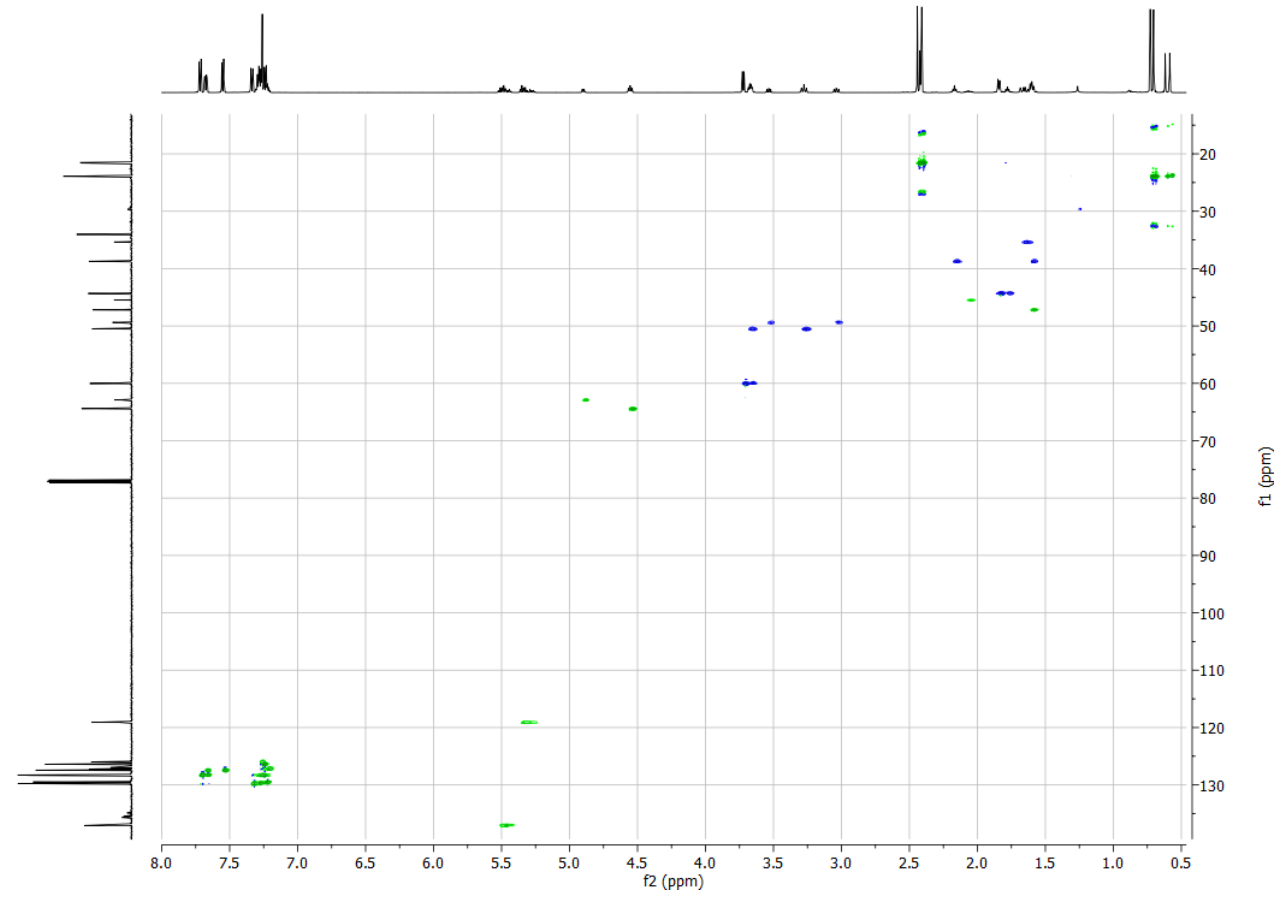
^{13}C NMR (151 MHz, $CDCl_3$)



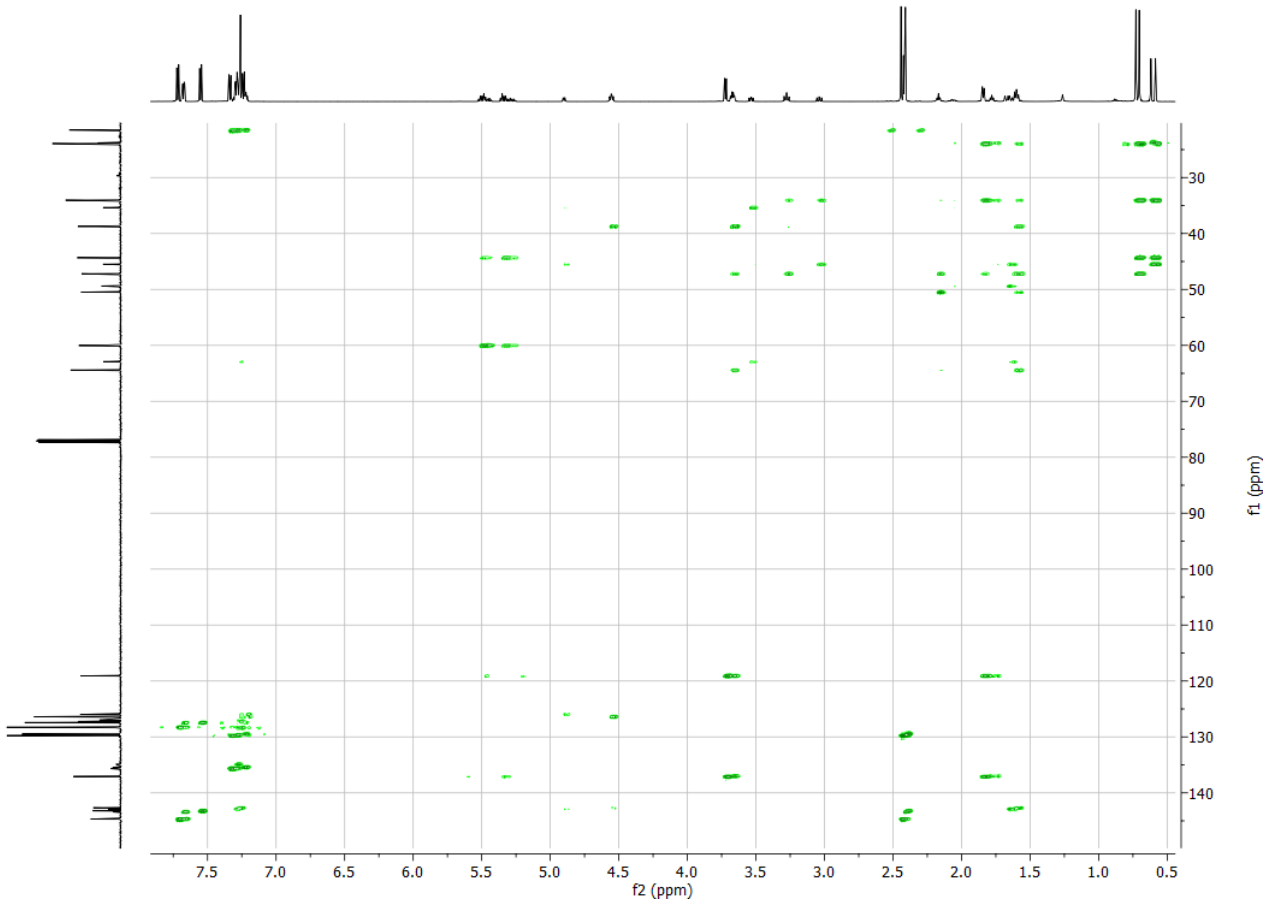
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



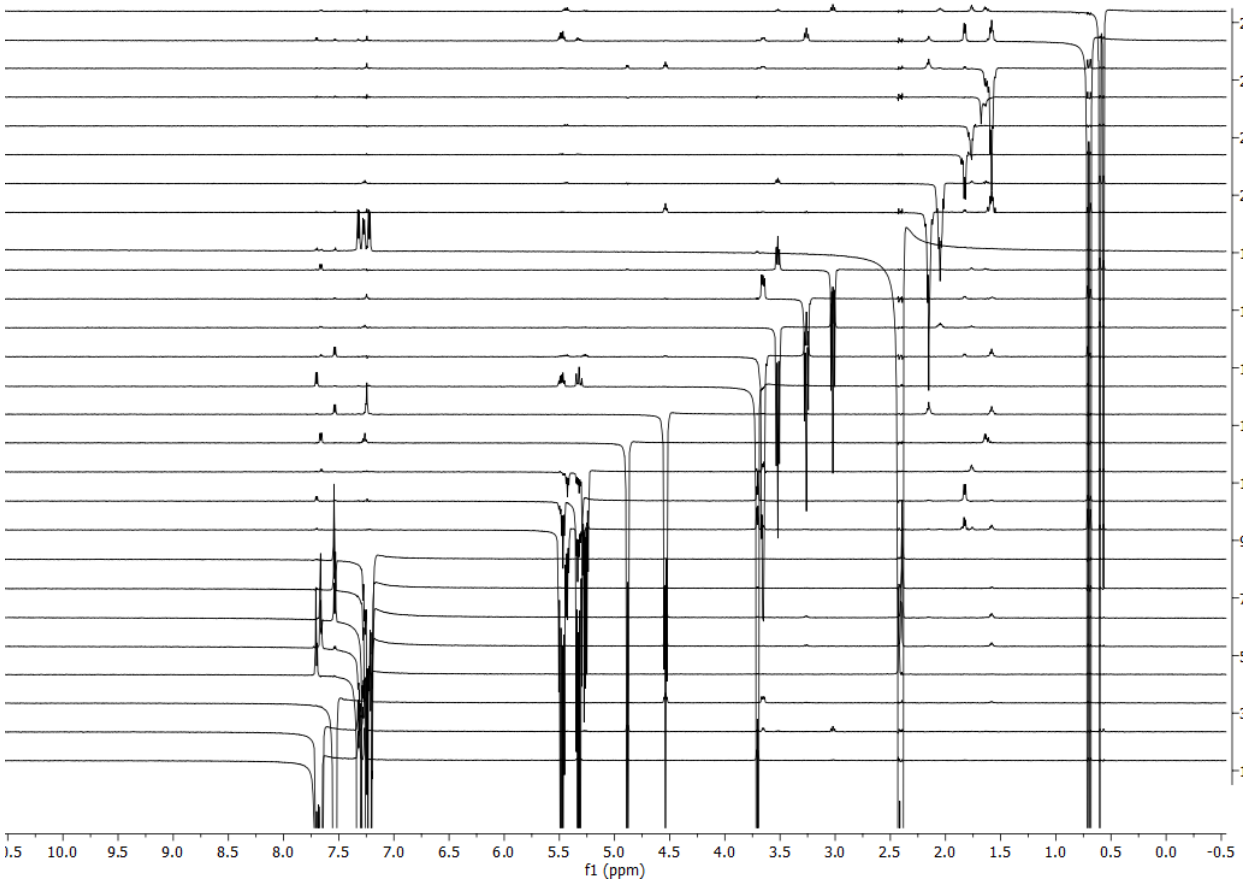
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



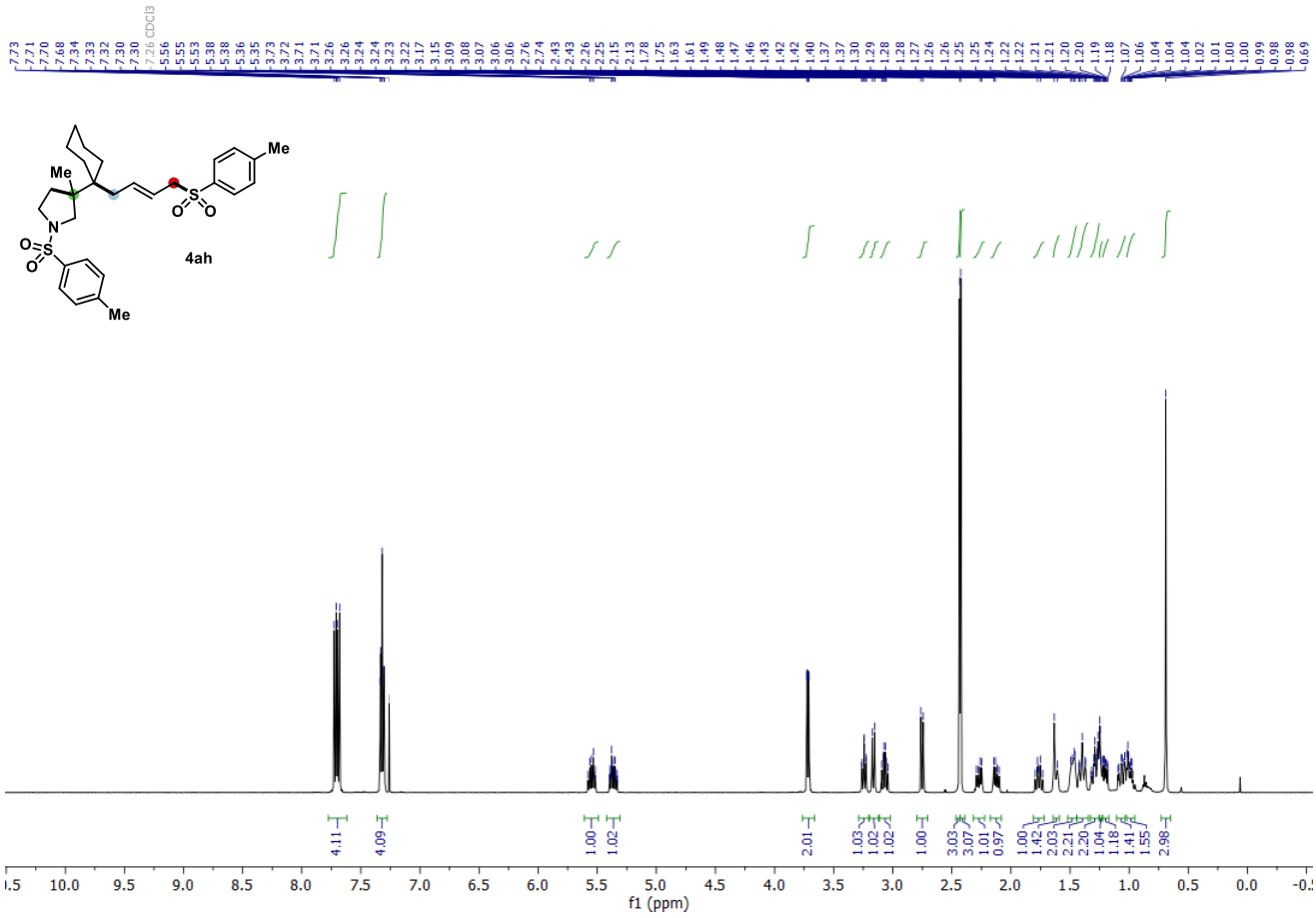
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



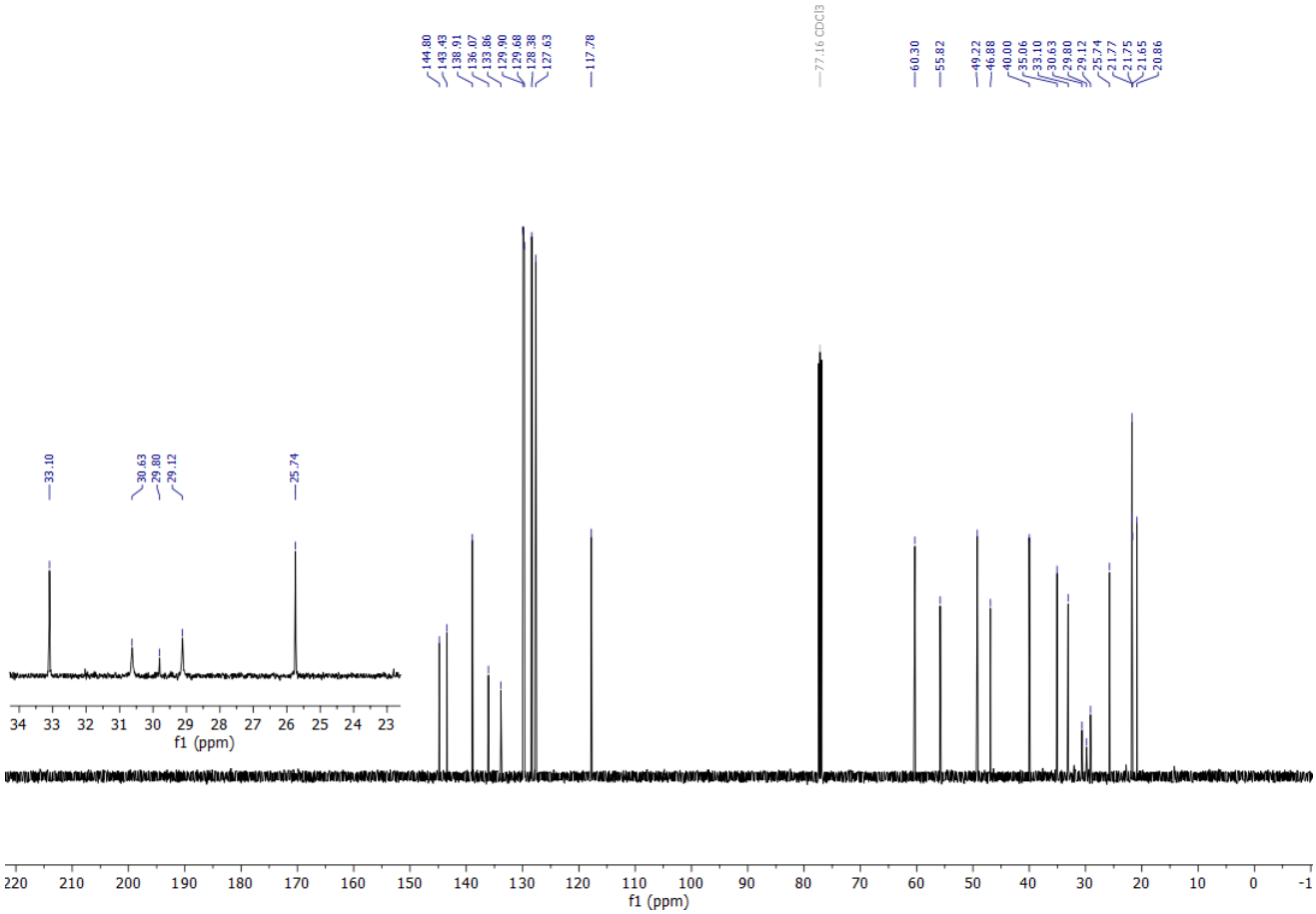
1D NOESY NMR (599 MHz, $CDCl_3$)



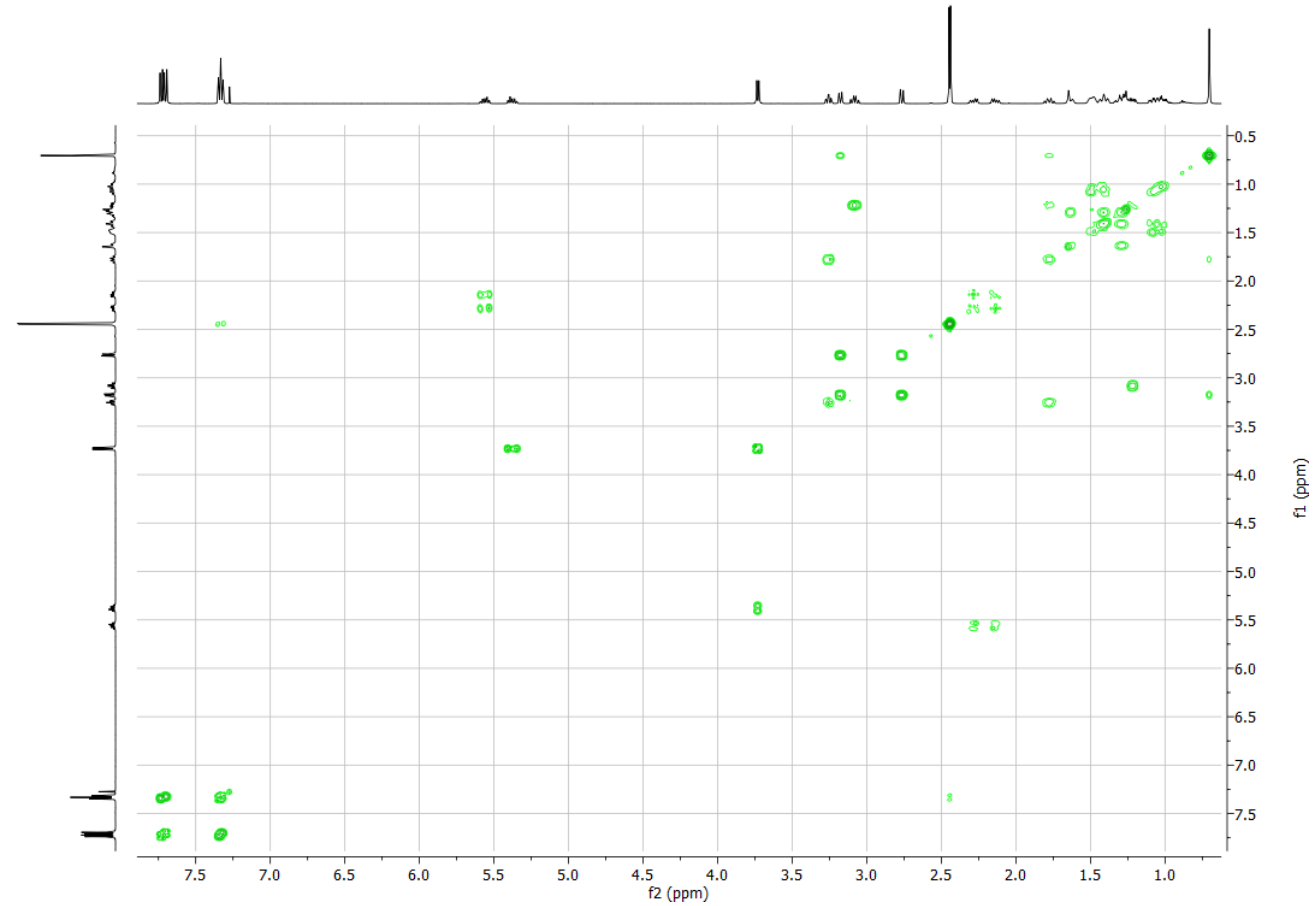
^{1}H NMR (500 MHz, $CDCl_3$)



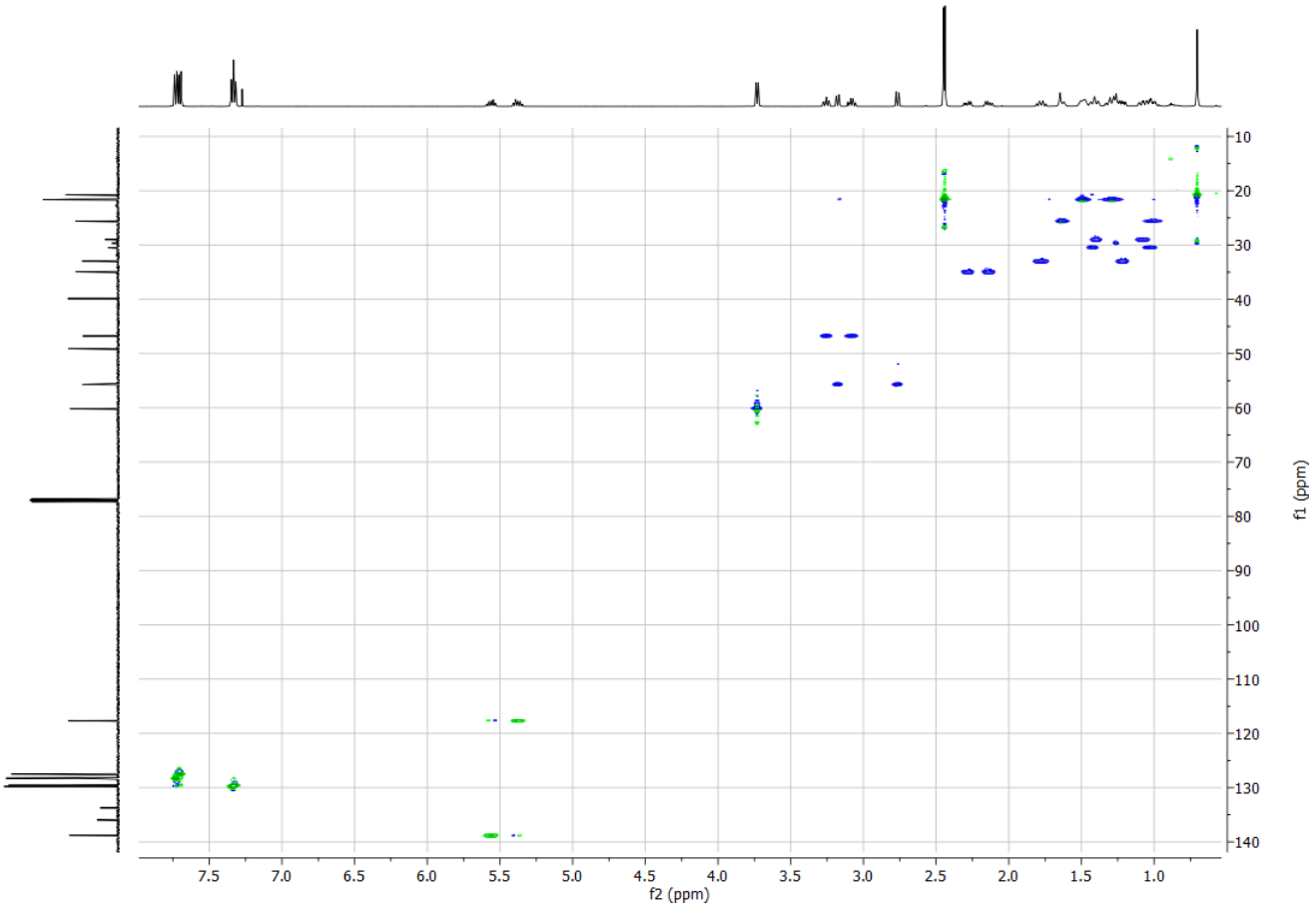
^{13}C NMR (126 MHz, $CDCl_3$)



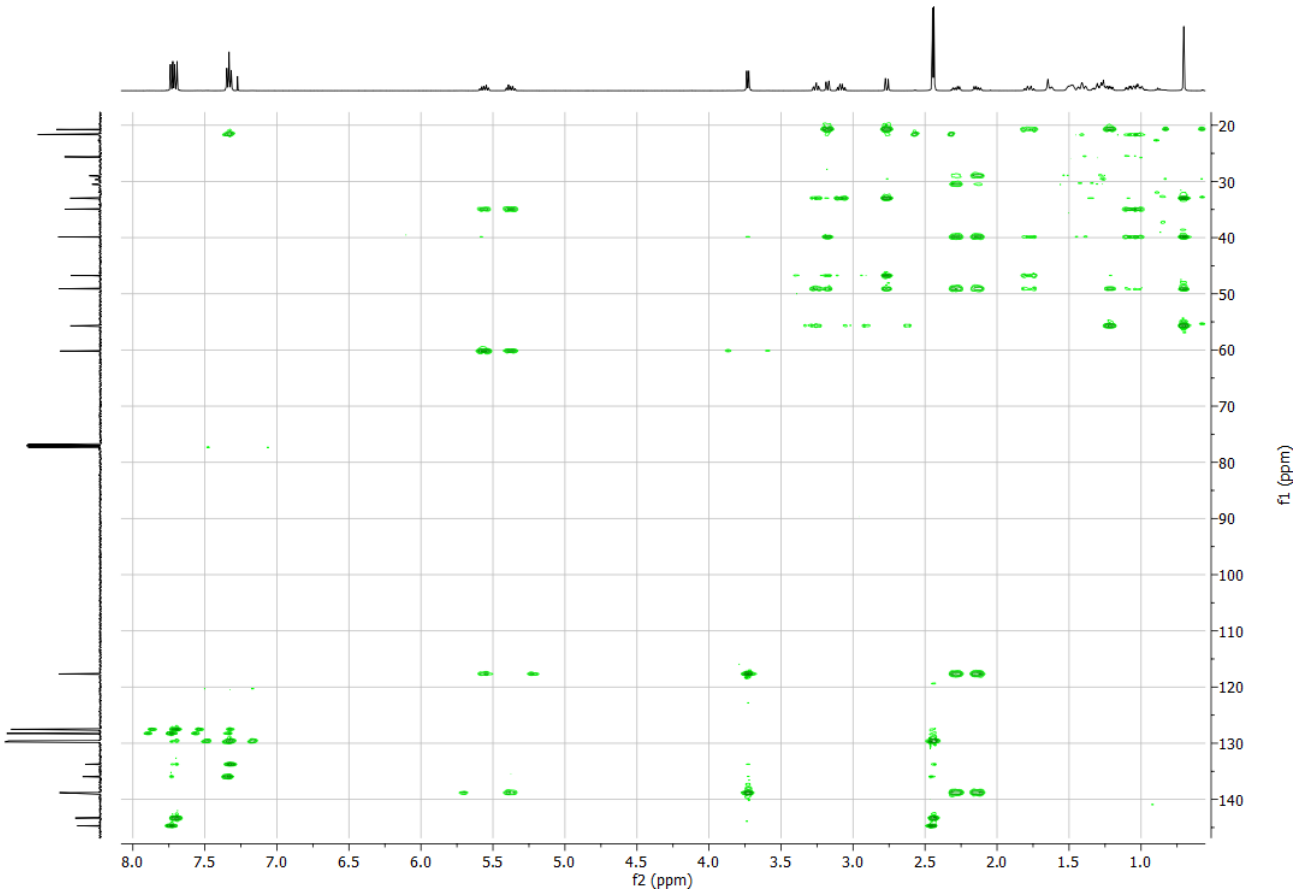
^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$)



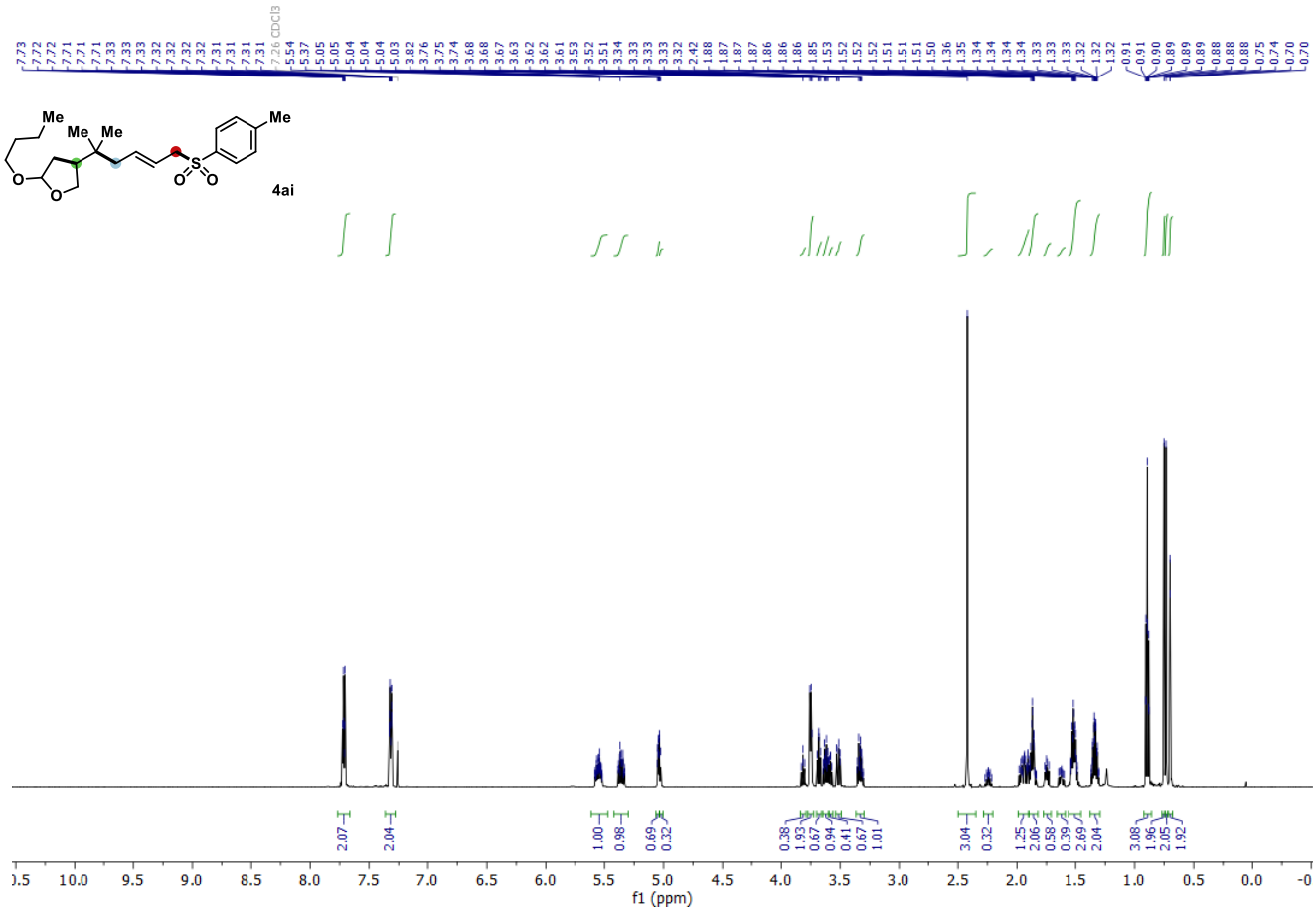
^{1}H-^{13}C HSQC NMR (500 MHz, $CDCl_3$)



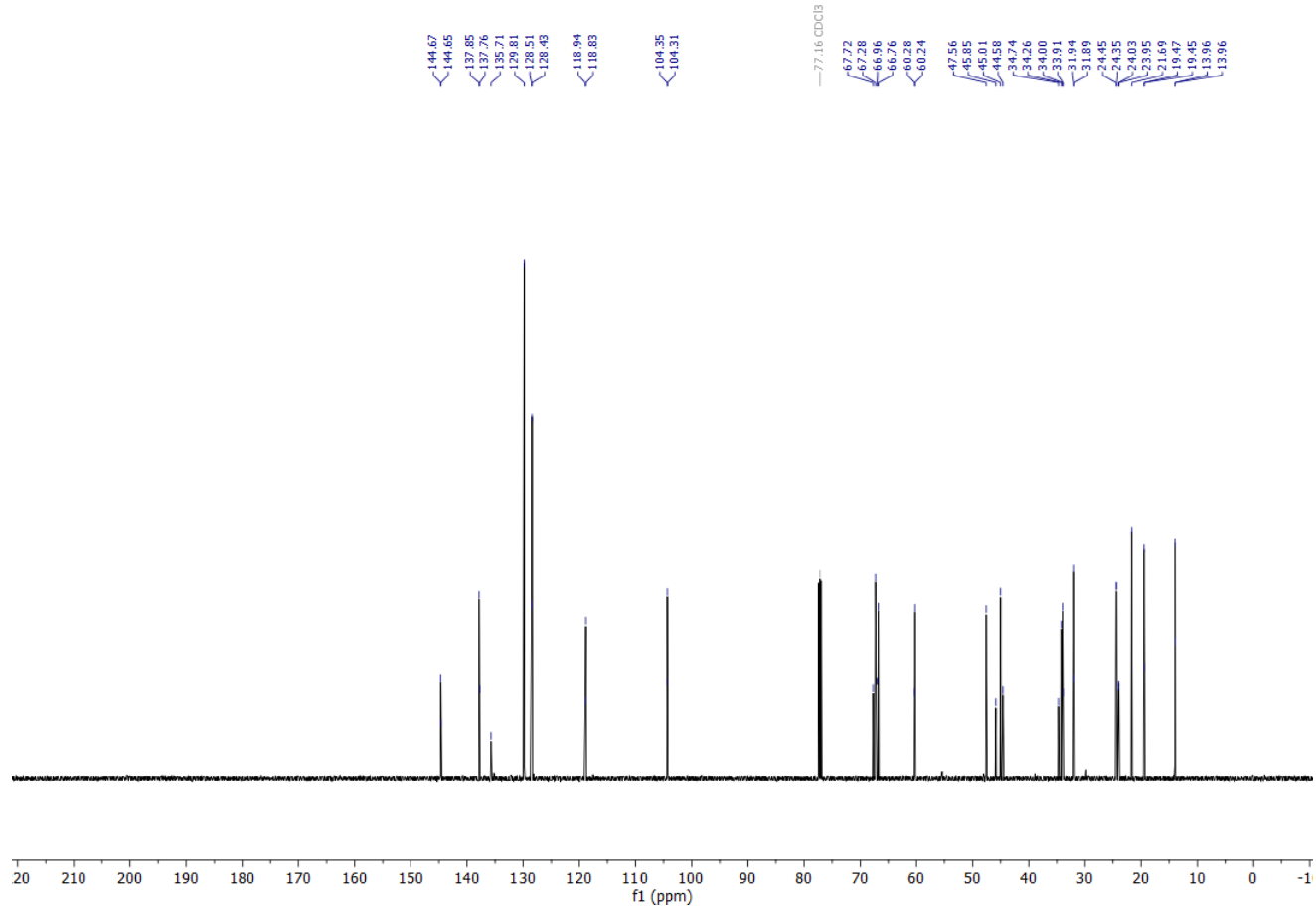
^{1}H-^{13}C HMBC NMR (500 MHz, $CDCl_3$)



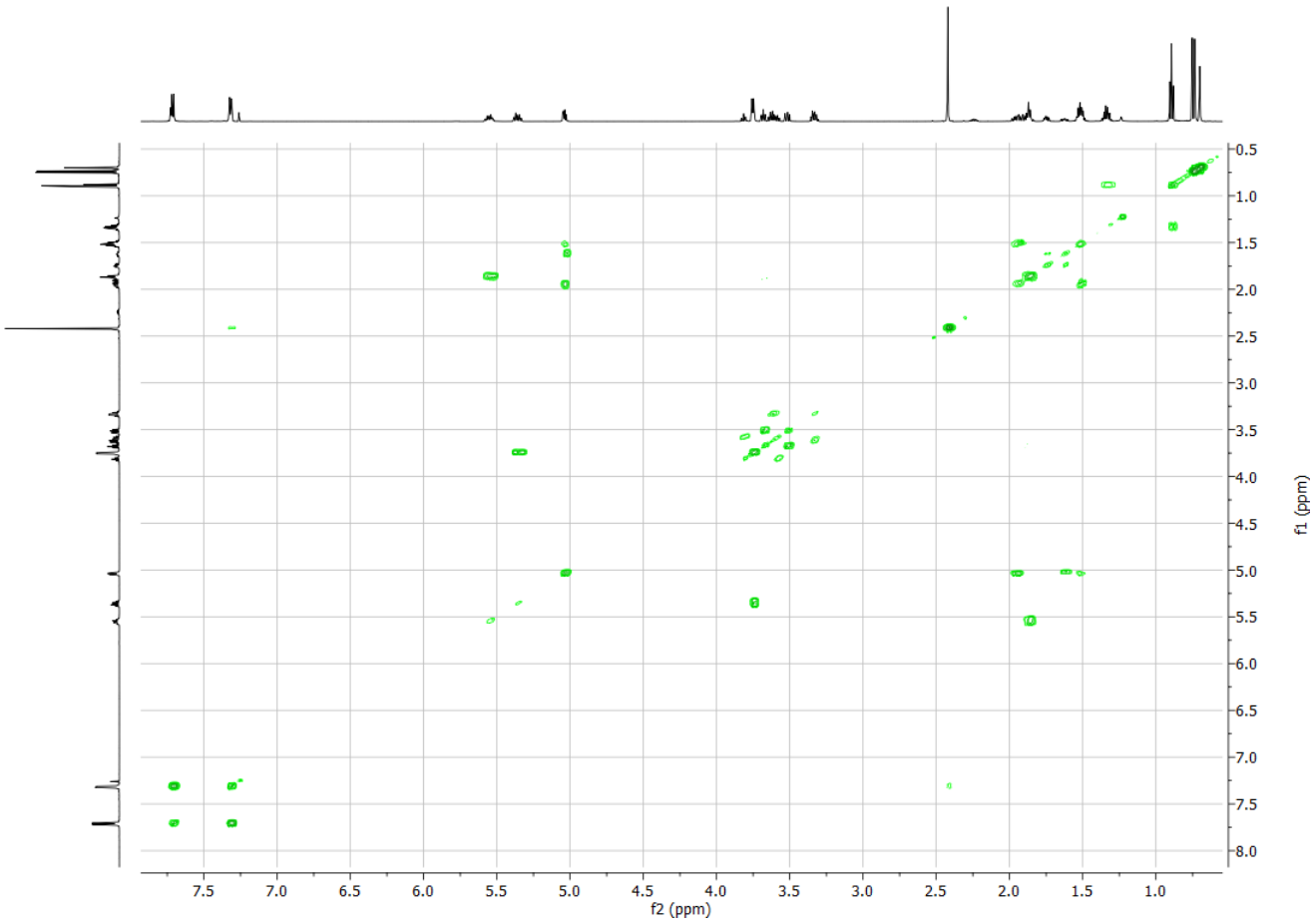
^{1}H NMR (599 MHz, $CDCl_3$)



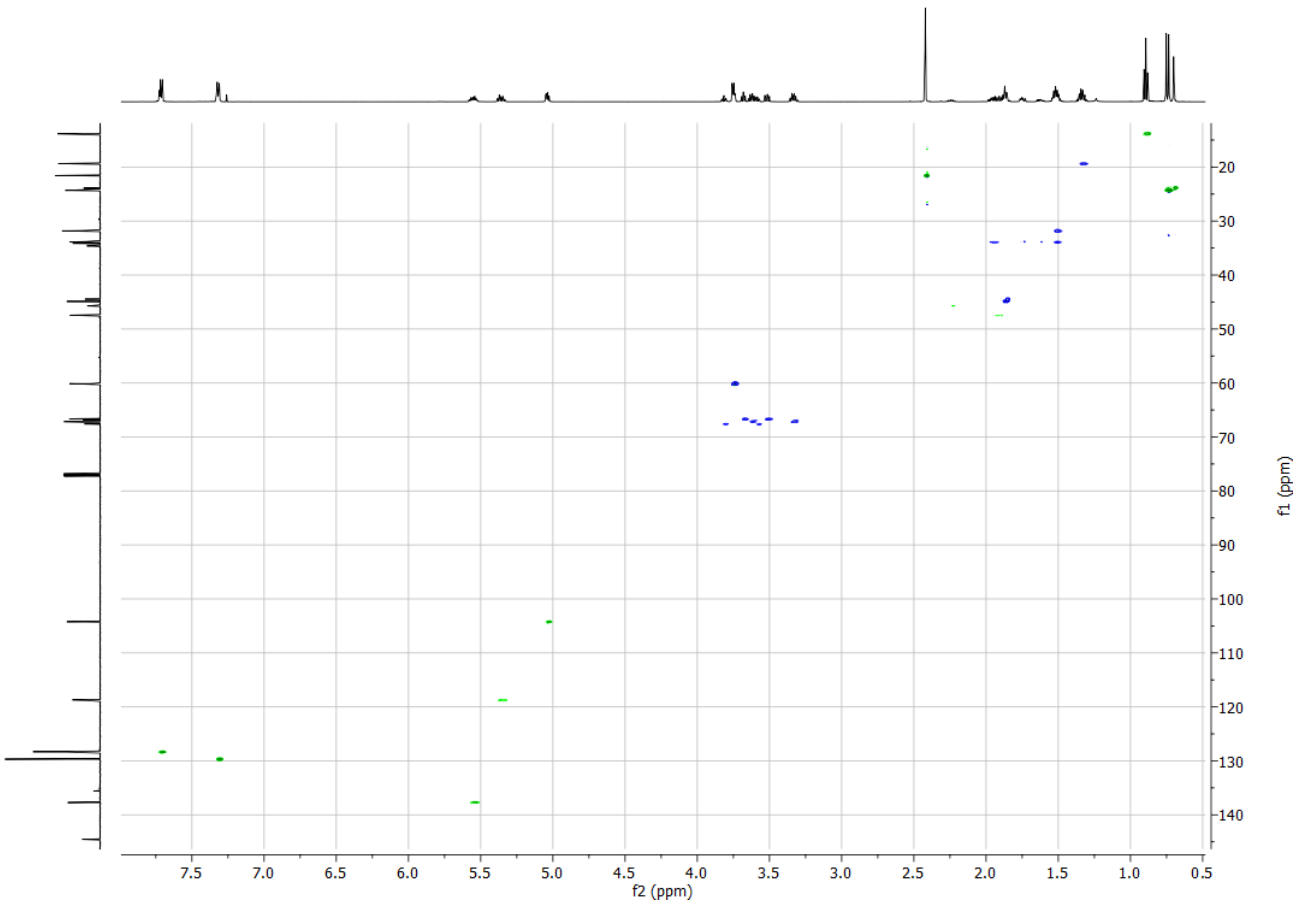
^{13}C NMR (151 MHz, $CDCl_3$)



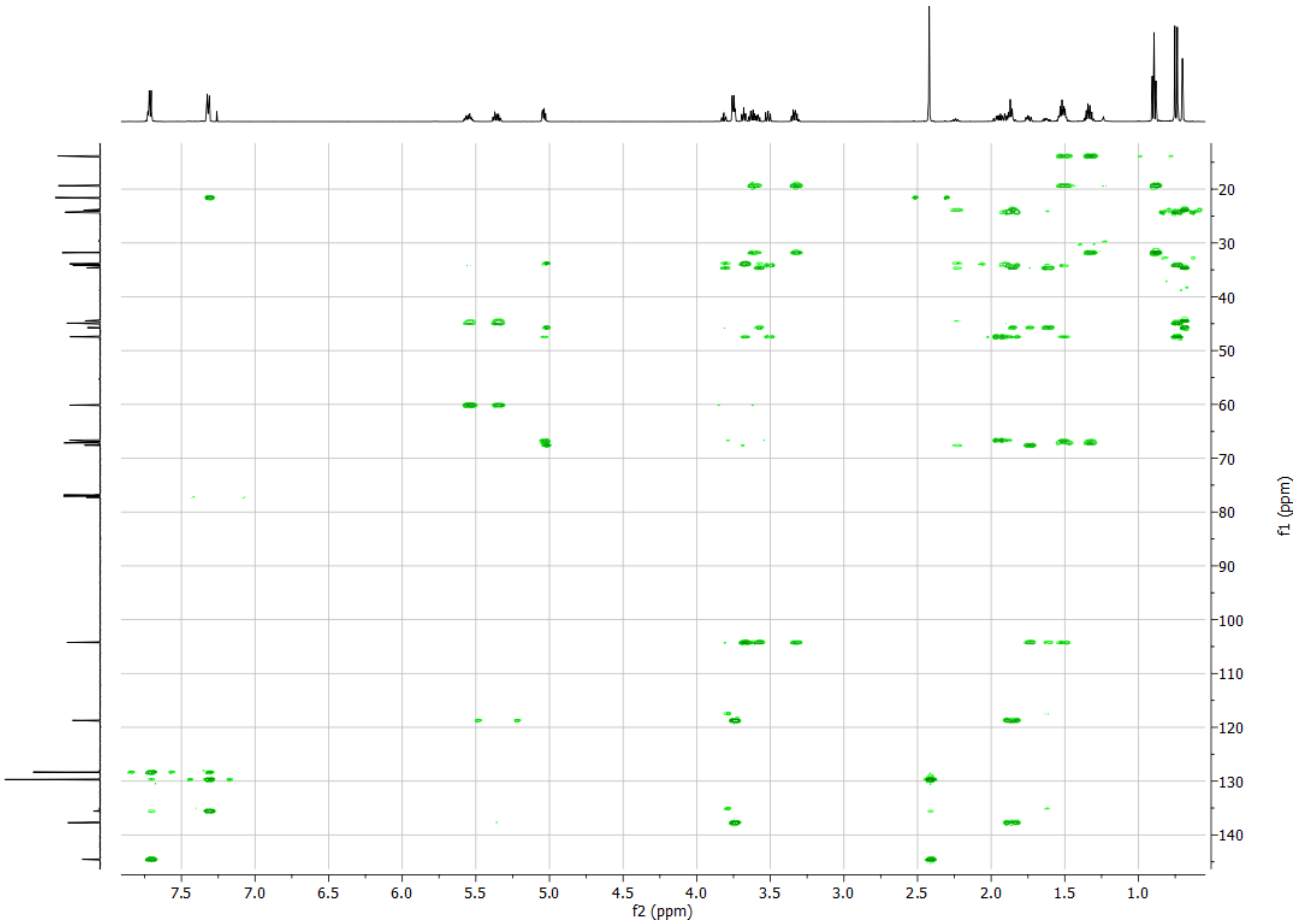
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



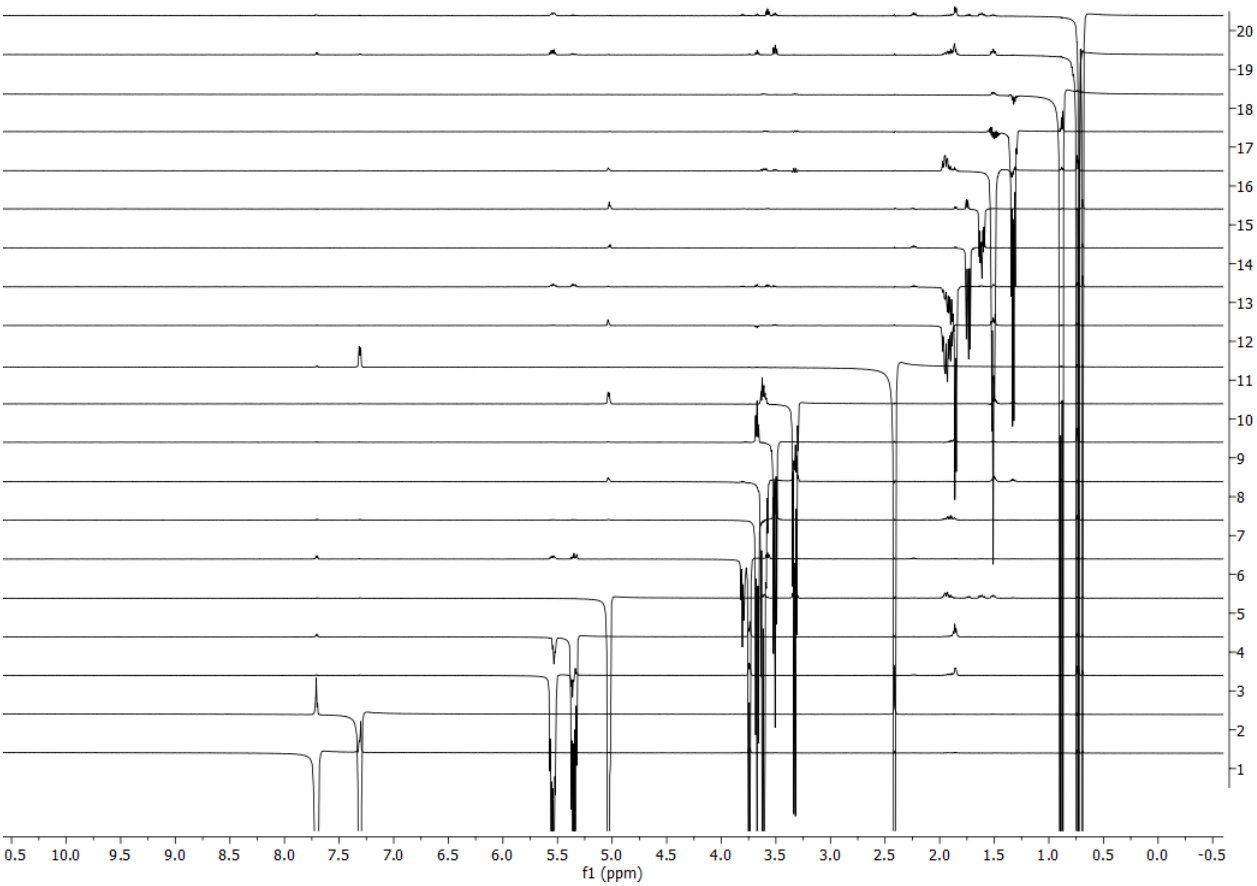
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



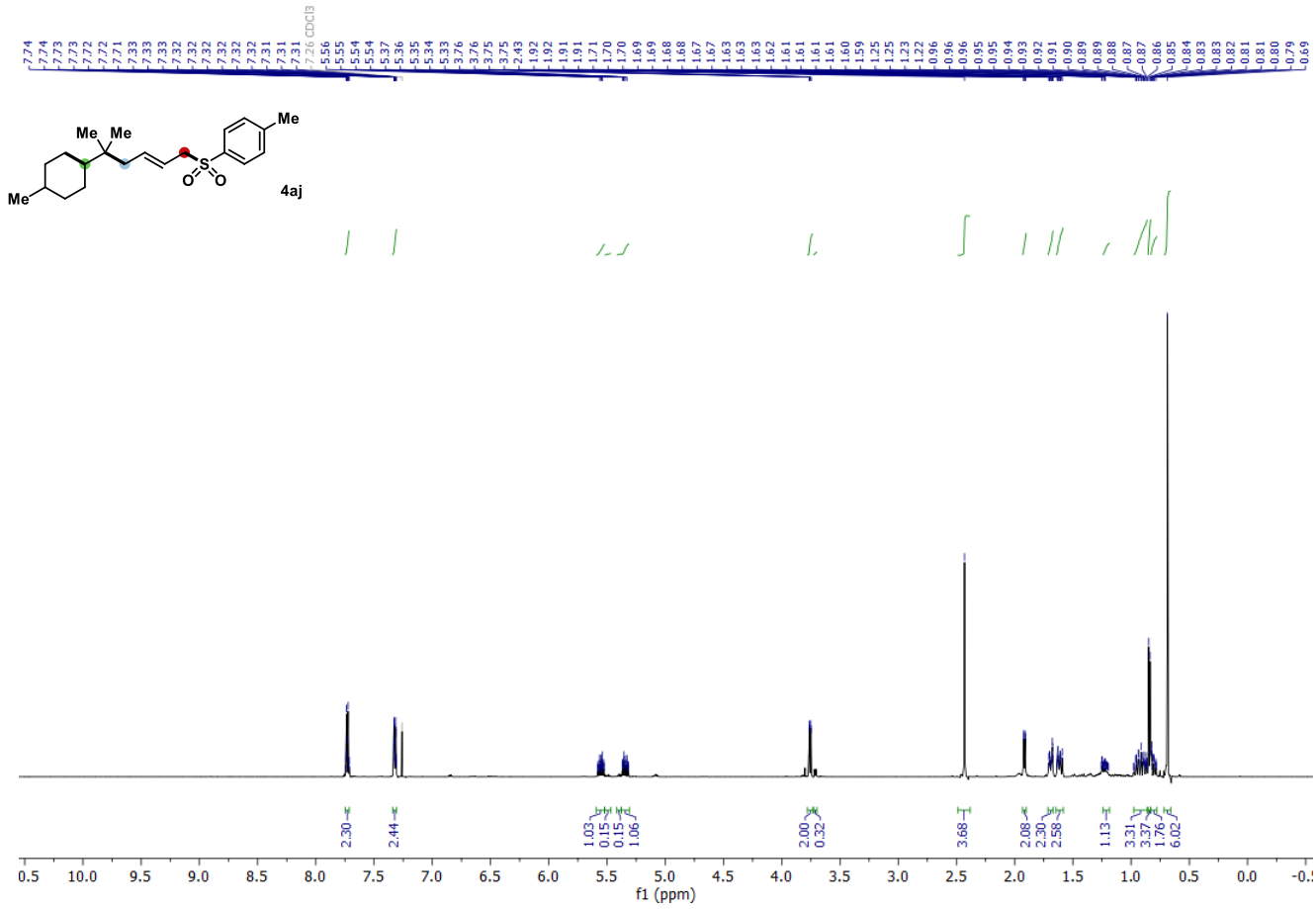
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



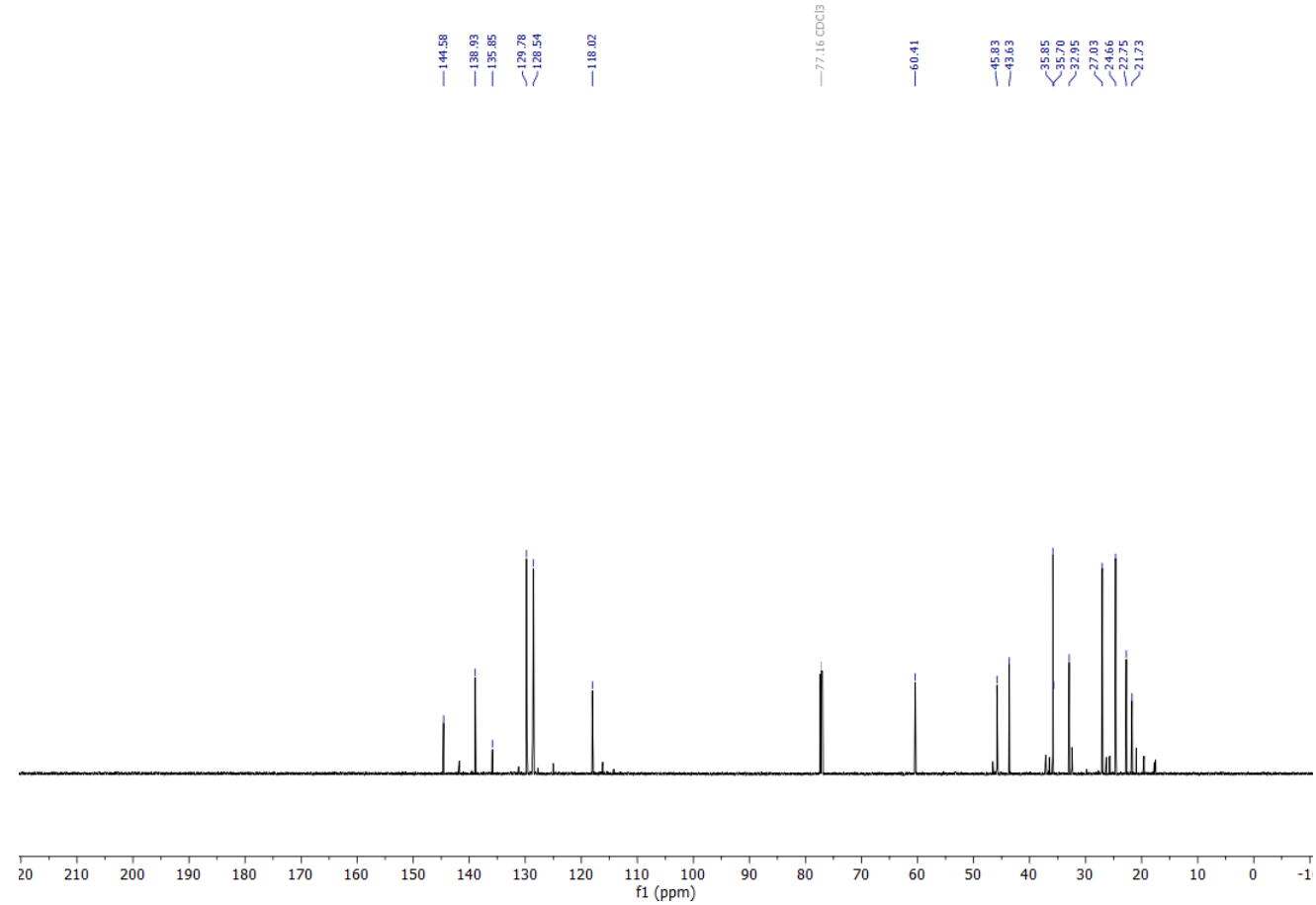
1D NOESY NMR (599 MHz, $CDCl_3$)



^{1}H NMR (599 MHz, $CDCl_3$)

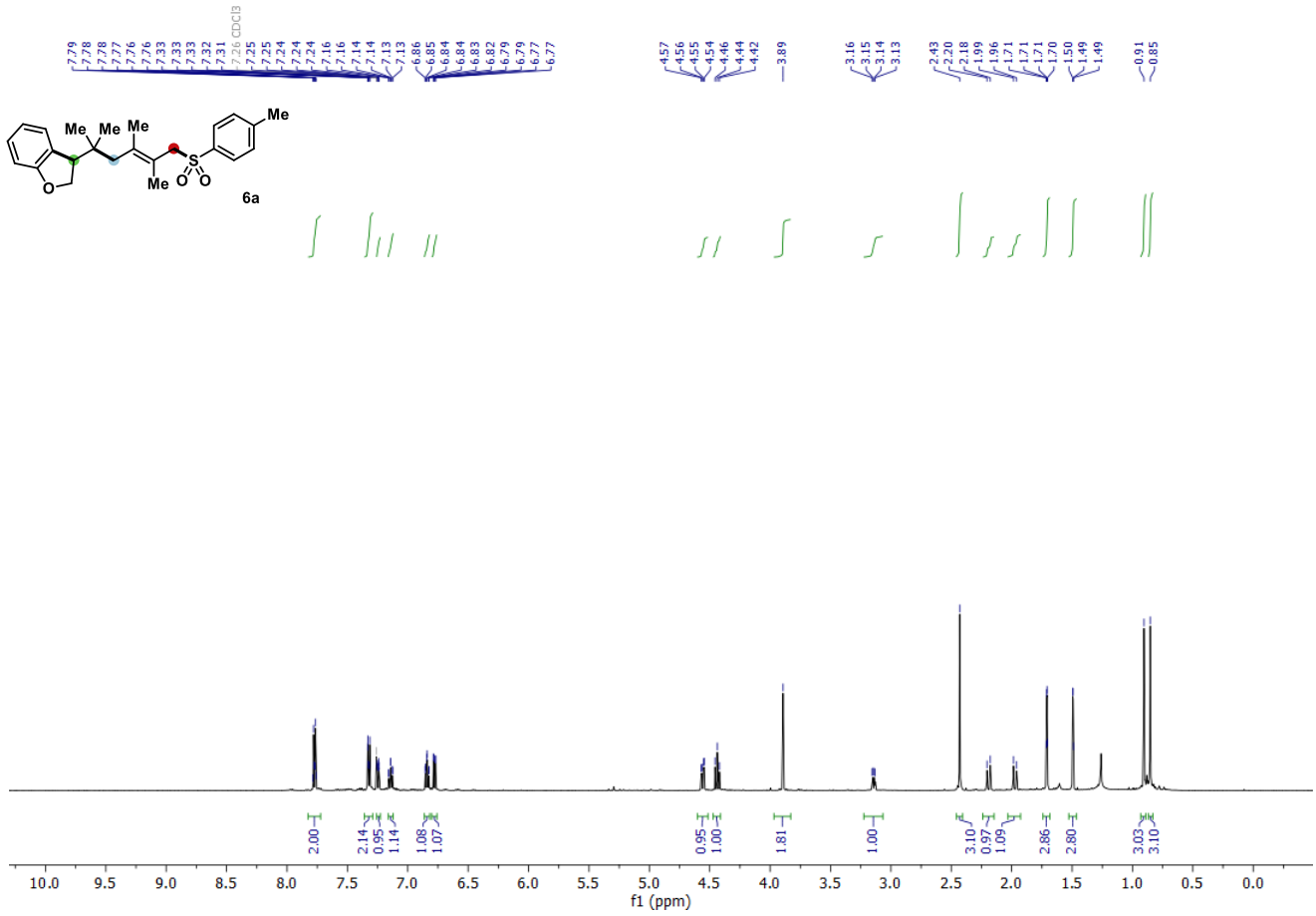


^{13}C NMR (151 MHz, $CDCl_3$)

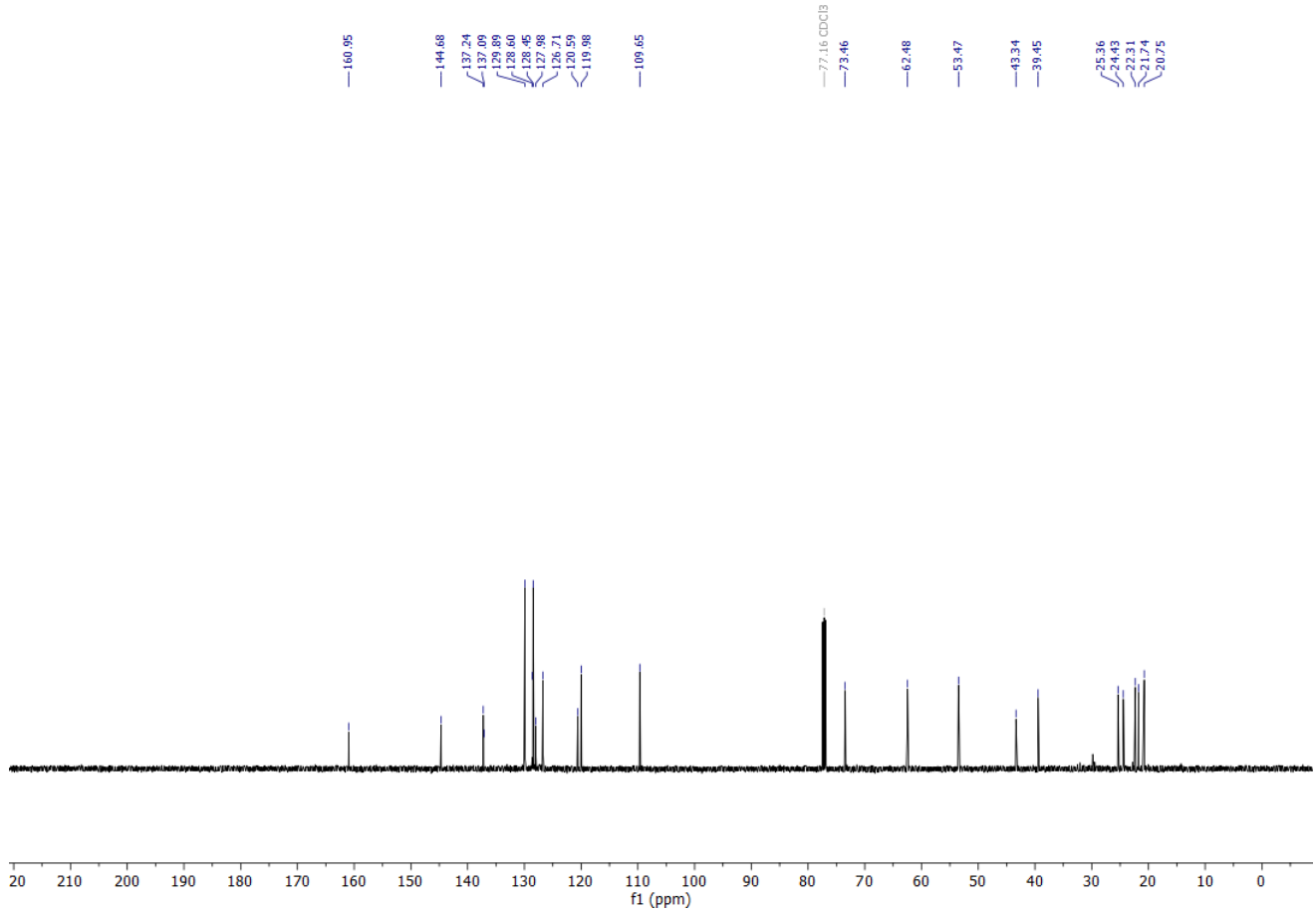


NMR spectra of products 6a-k

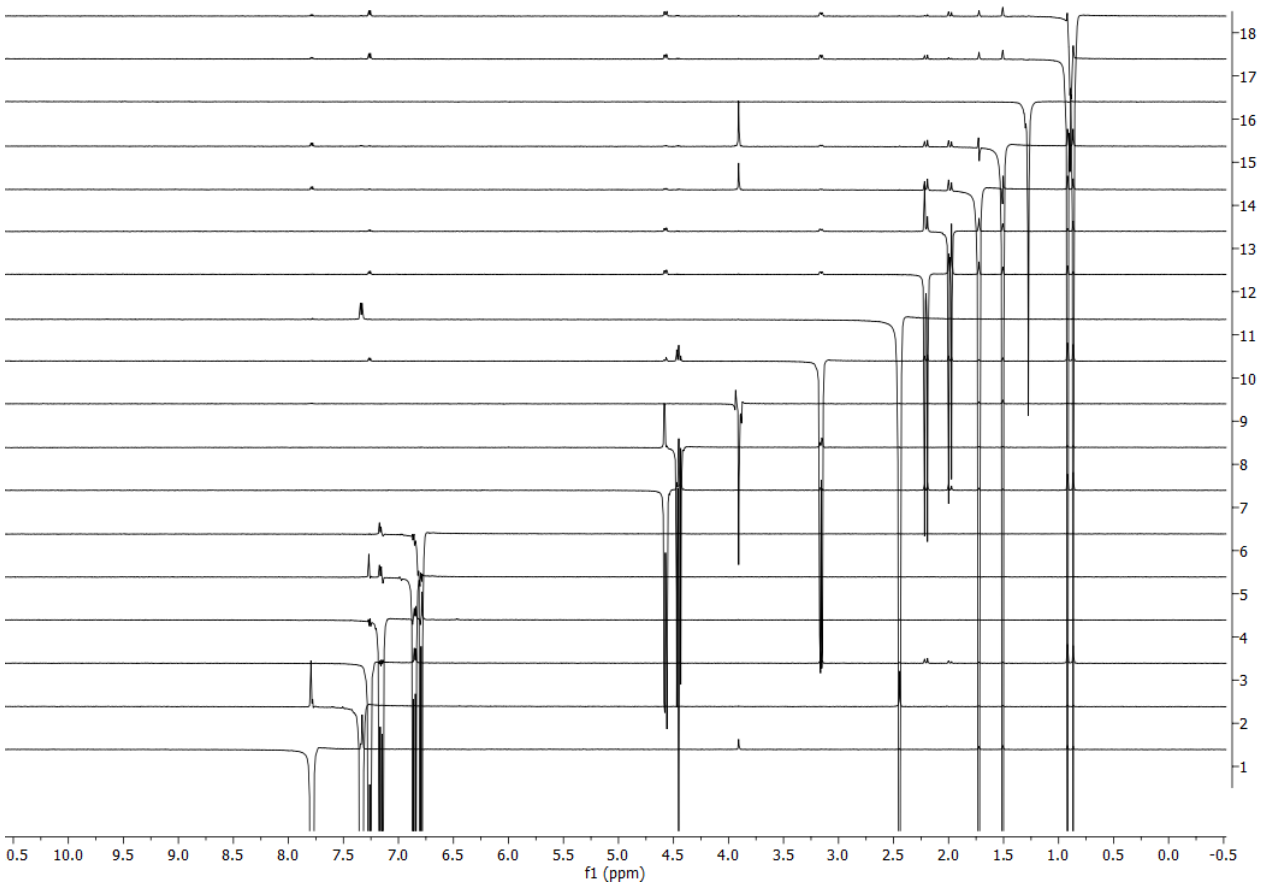
^{1}H NMR (500 MHz, $CDCl_3$)



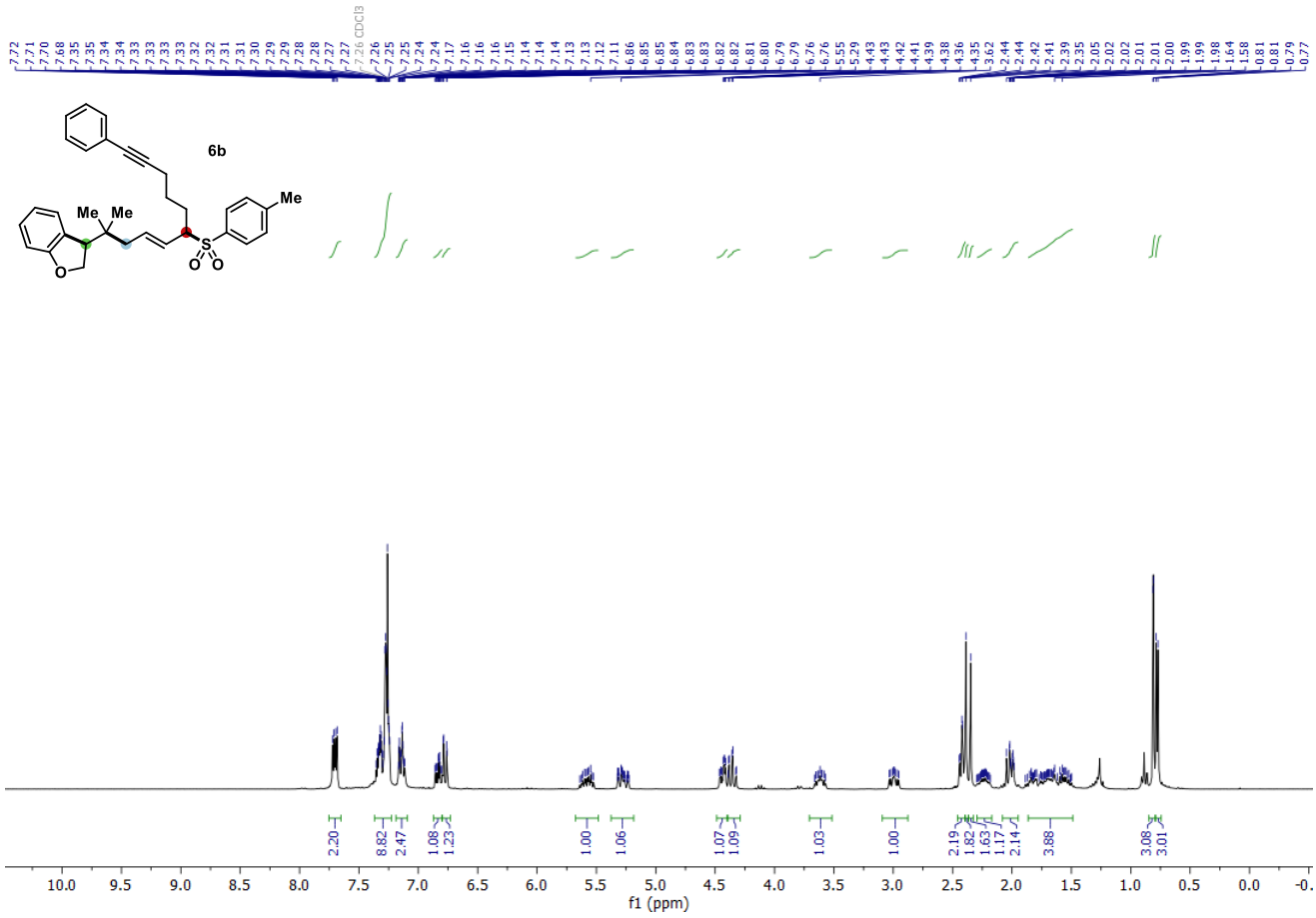
^{13}C NMR (126 MHz, $CDCl_3$)



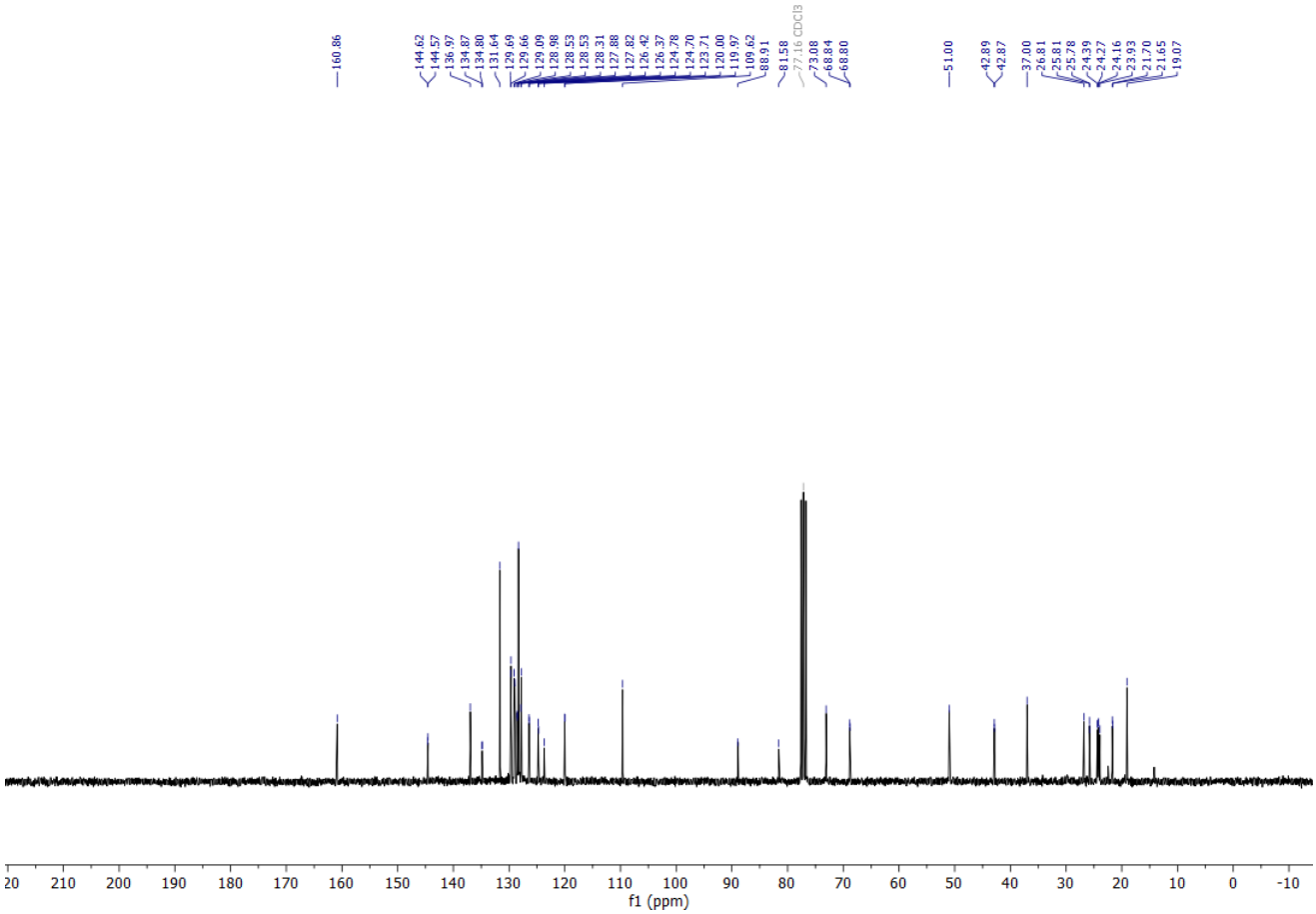
1D NOESY (500 MHz, $CDCl_3$)



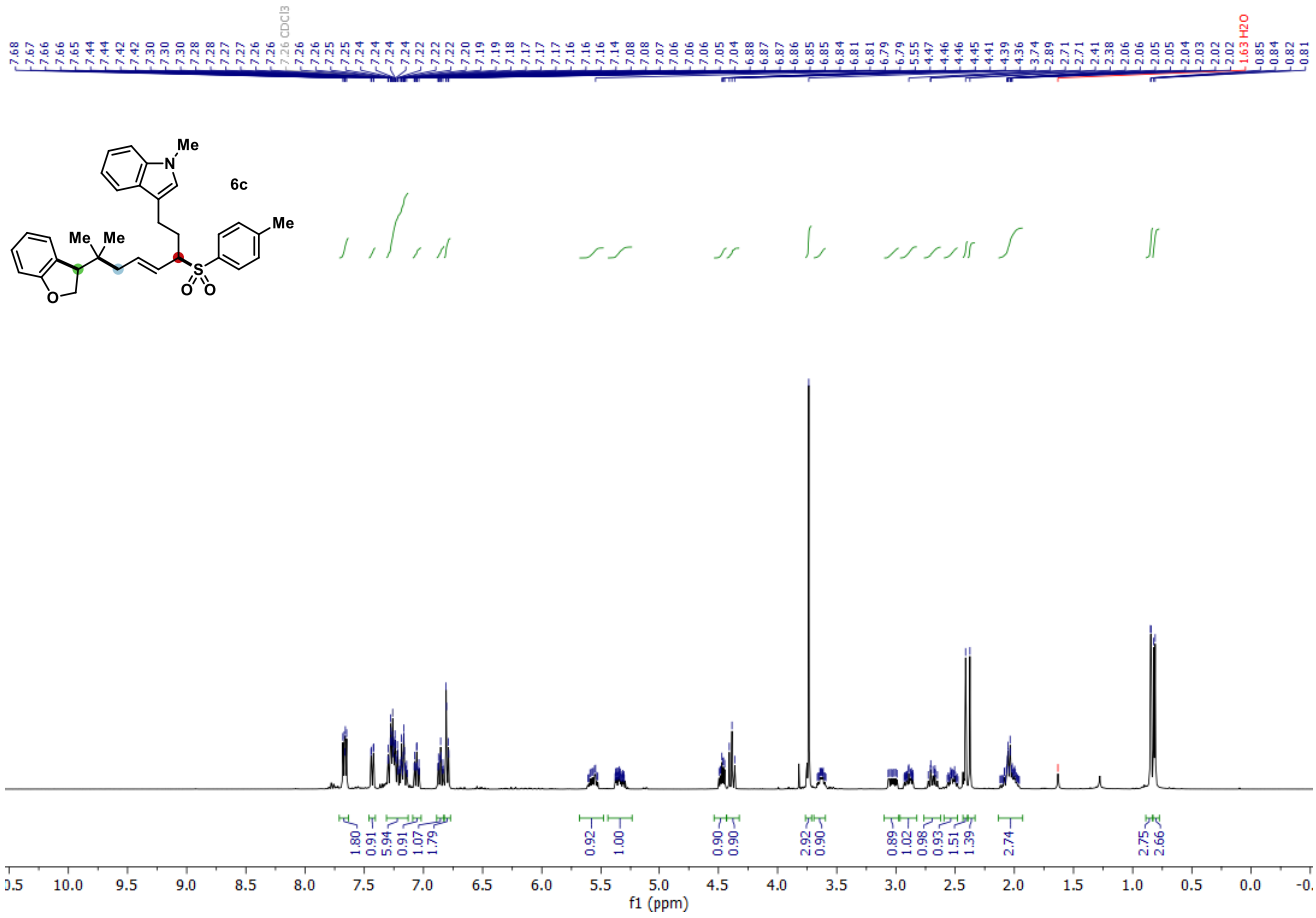
^{1}H NMR (300 MHz, $CDCl_3$)



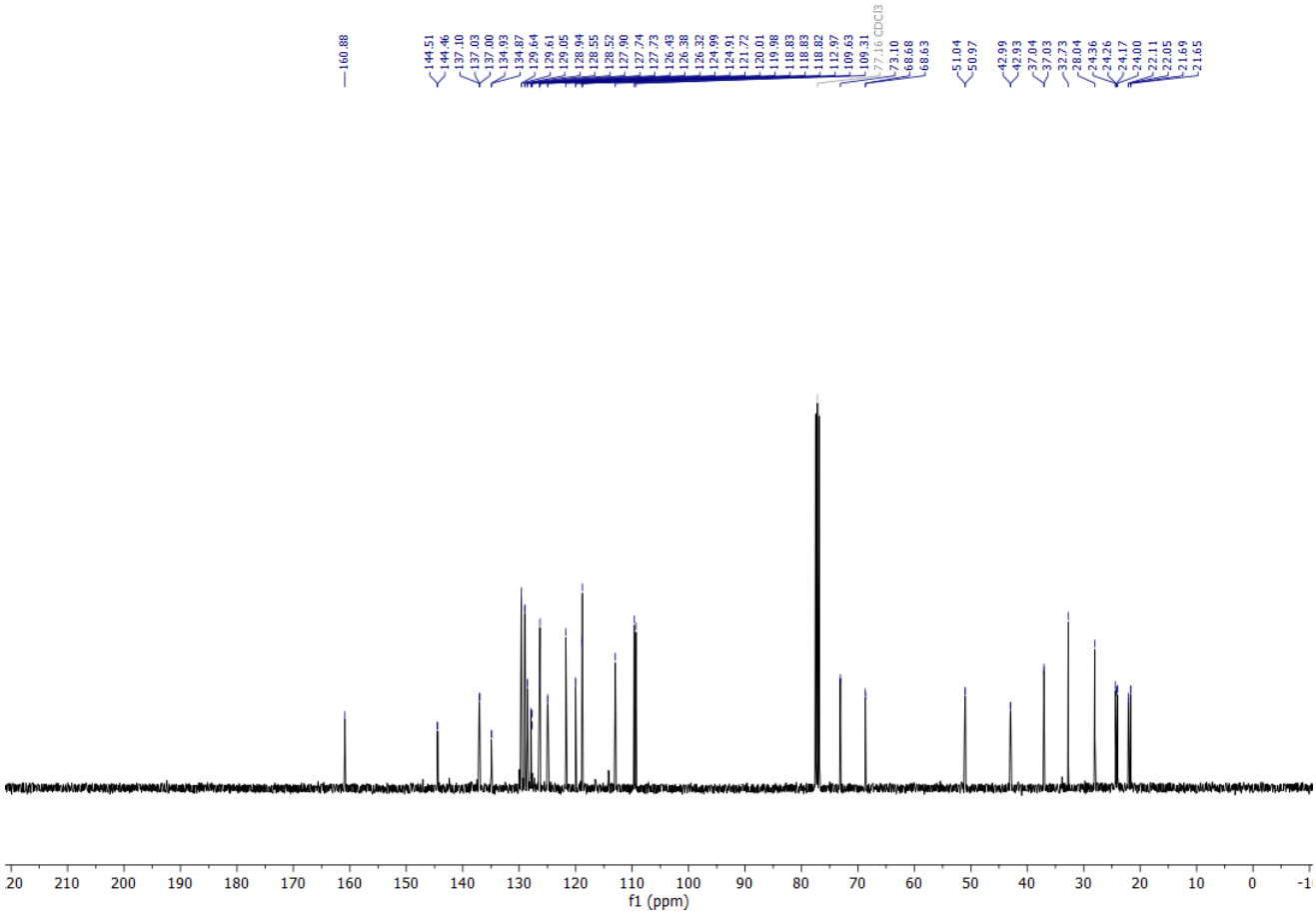
^{13}C NMR (75 MHz, $CDCl_3$)



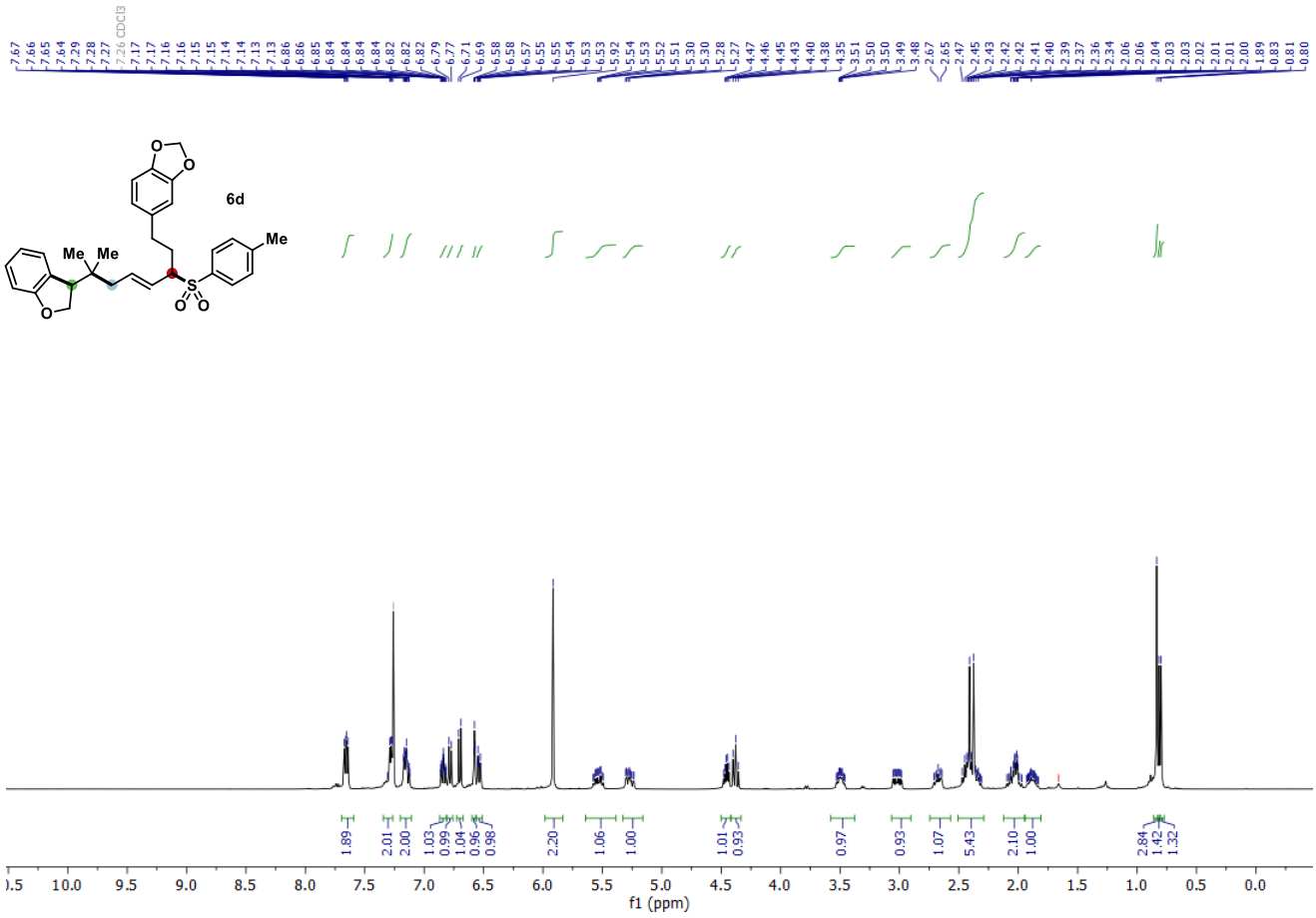
^{1}H NMR (400 MHz, $CDCl_3$)



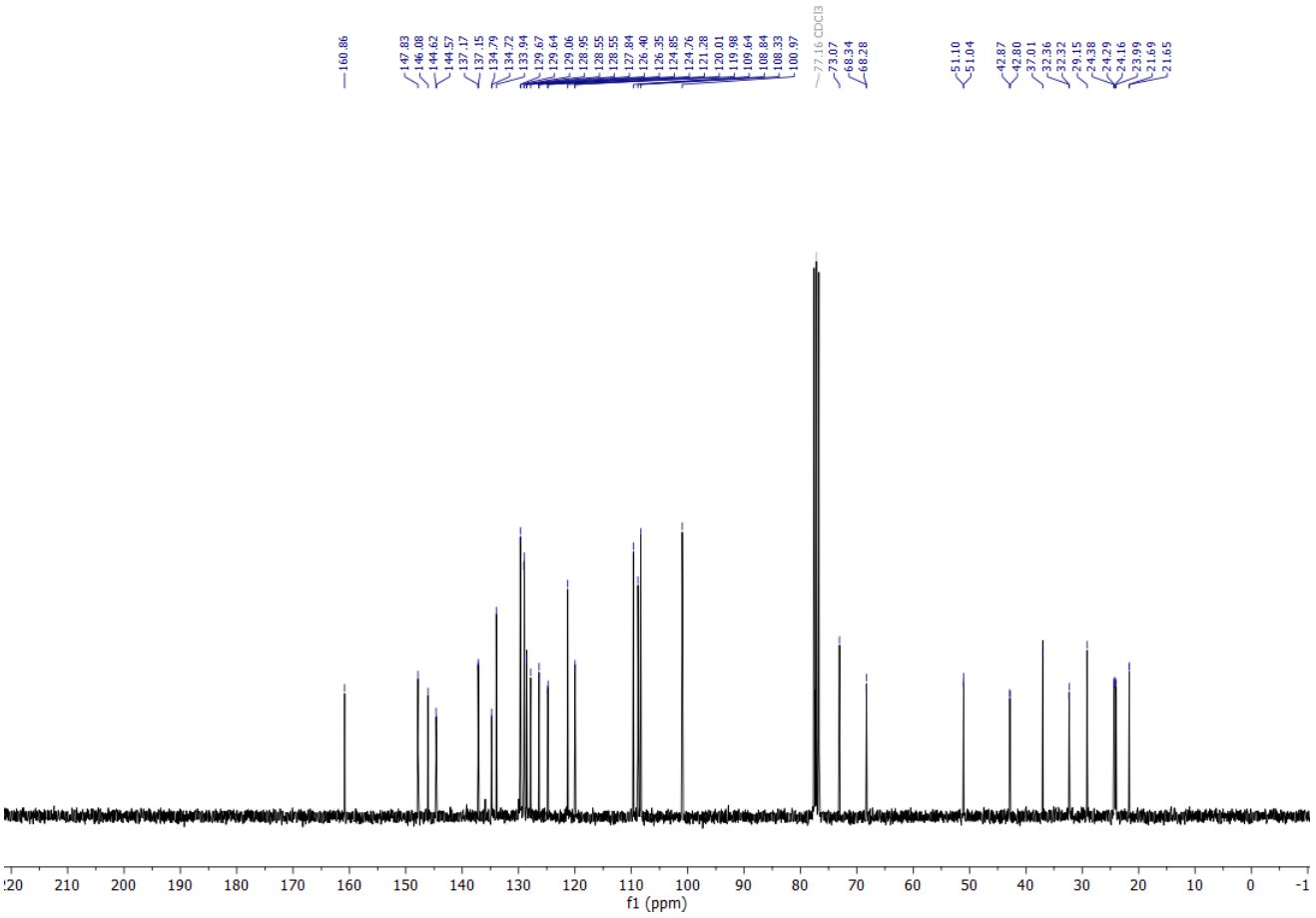
^{13}C NMR (101 MHz, $CDCl_3$)



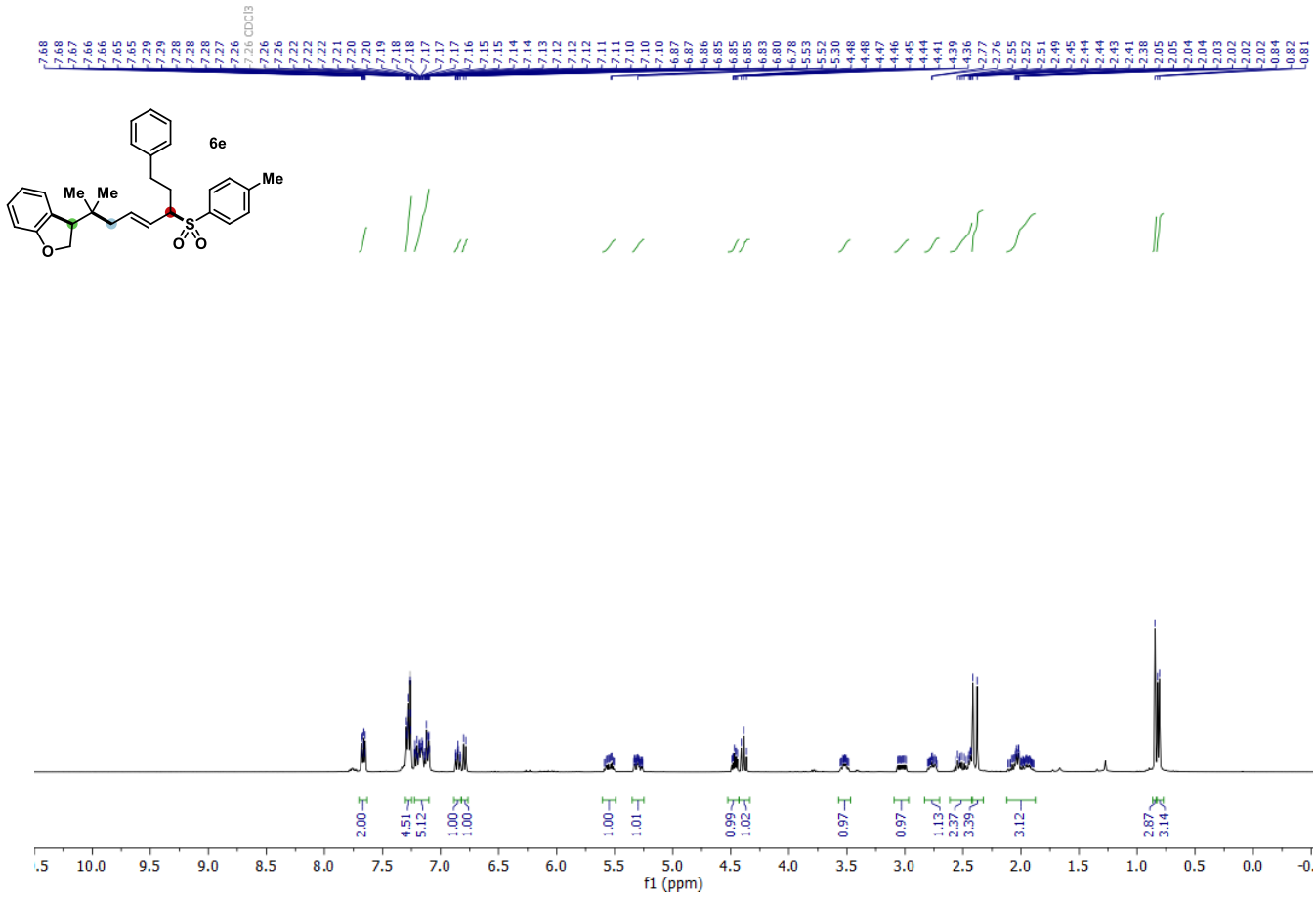
^{1}H NMR (400 MHz, $CDCl_3$)



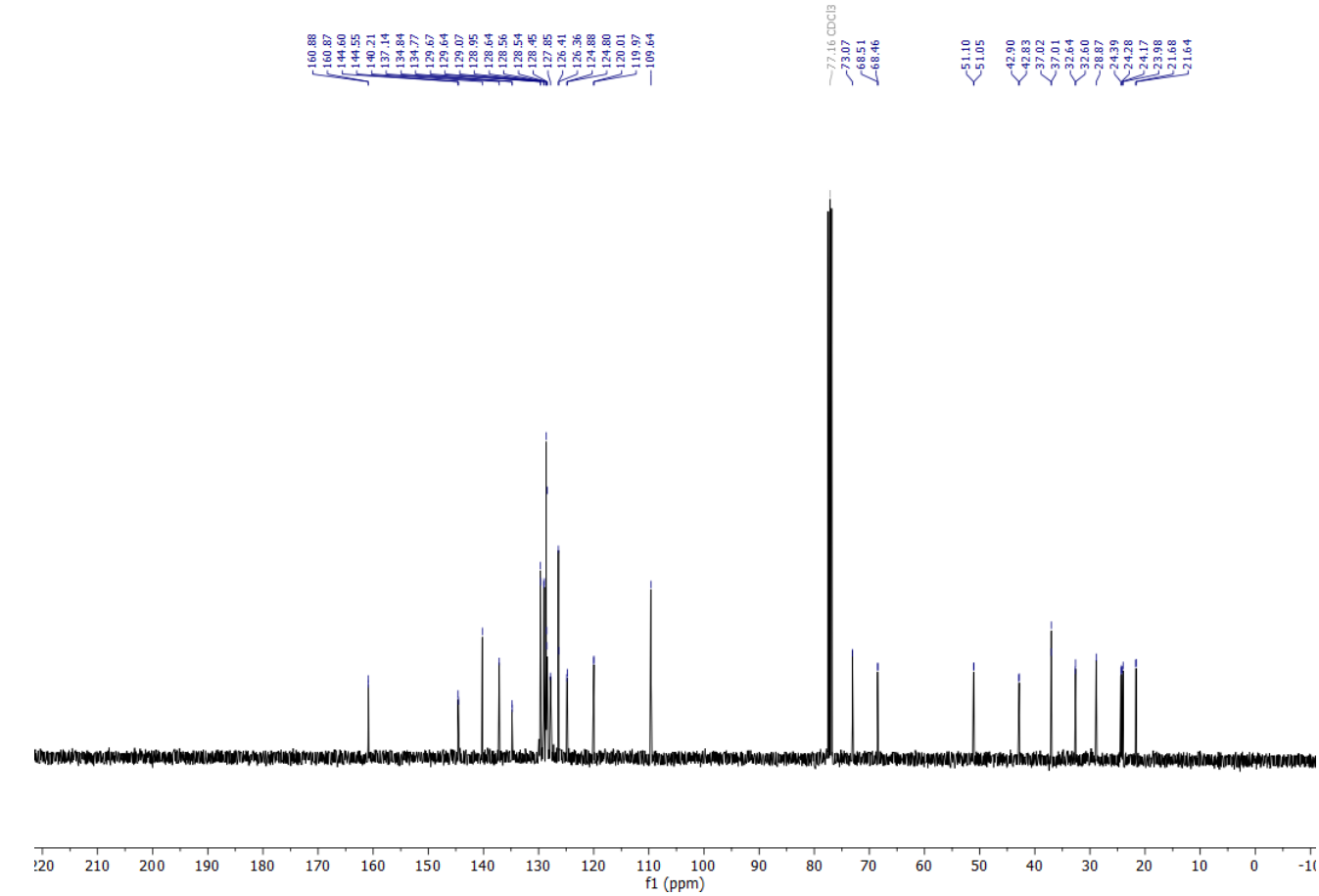
^{13}C NMR (101 MHz, $CDCl_3$)



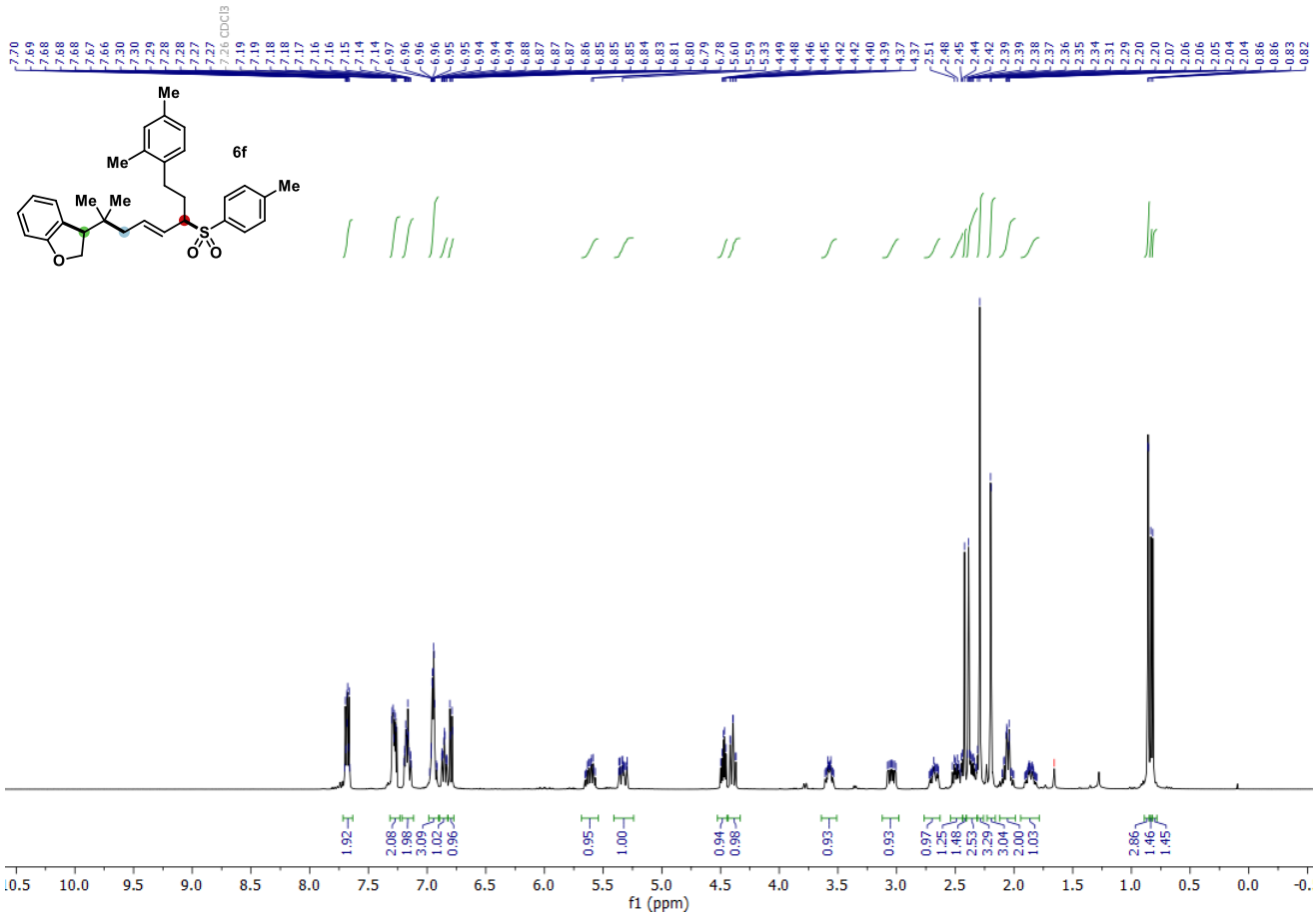
^{1}H NMR (400 MHz, $CDCl_3$)



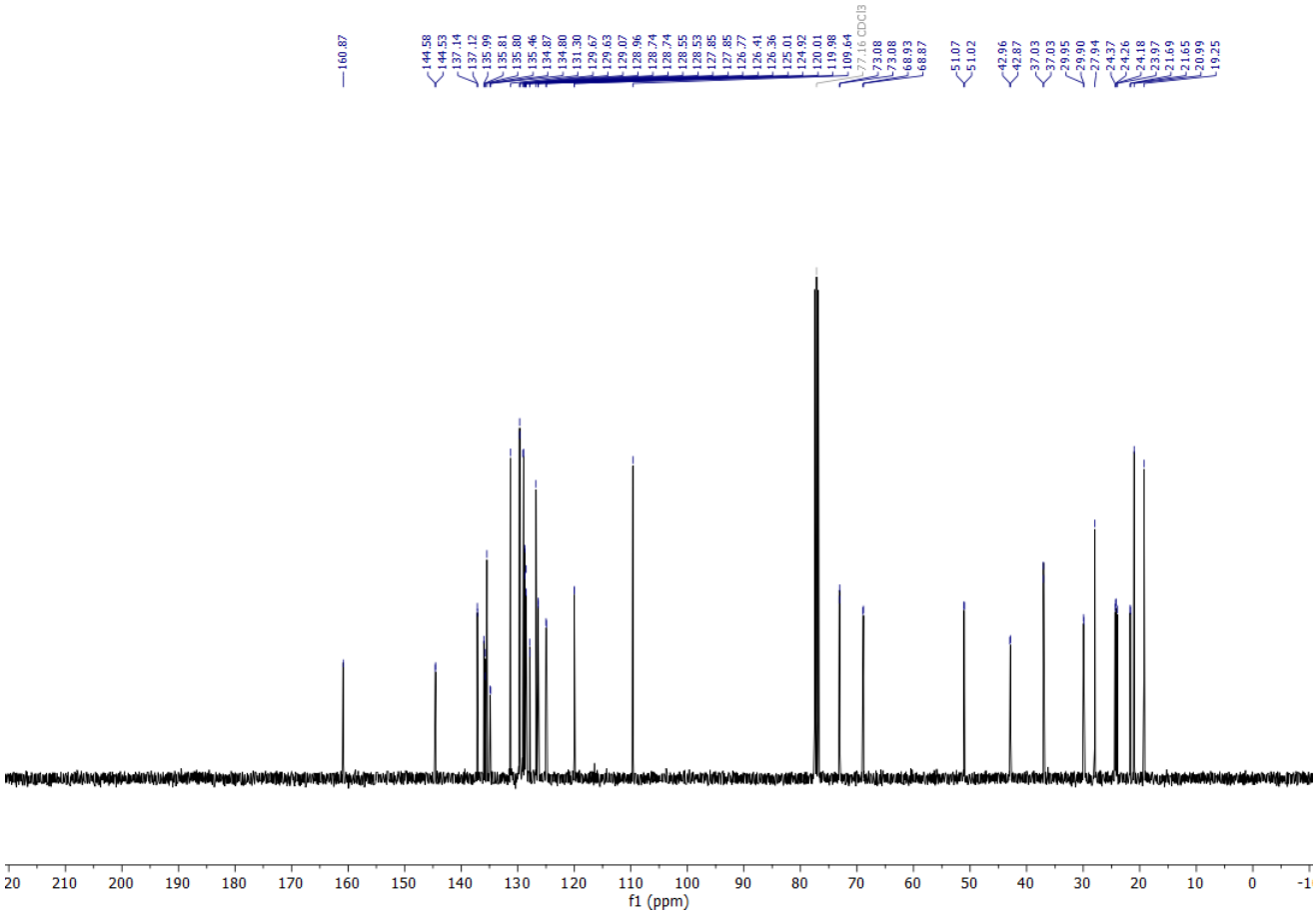
^{13}C NMR (101 MHz, $CDCl_3$)



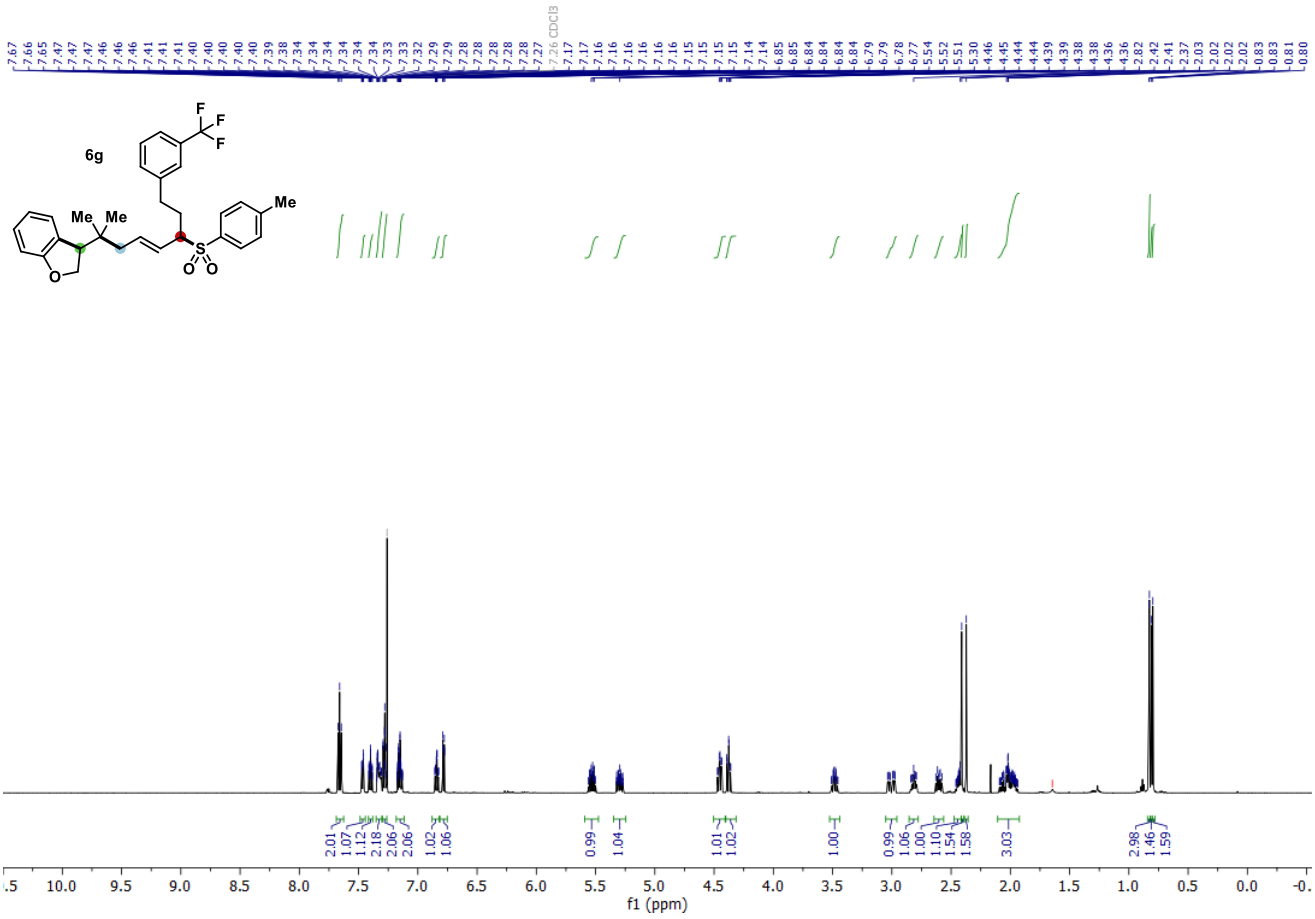
^{1}H NMR (400 MHz, $CDCl_3$)



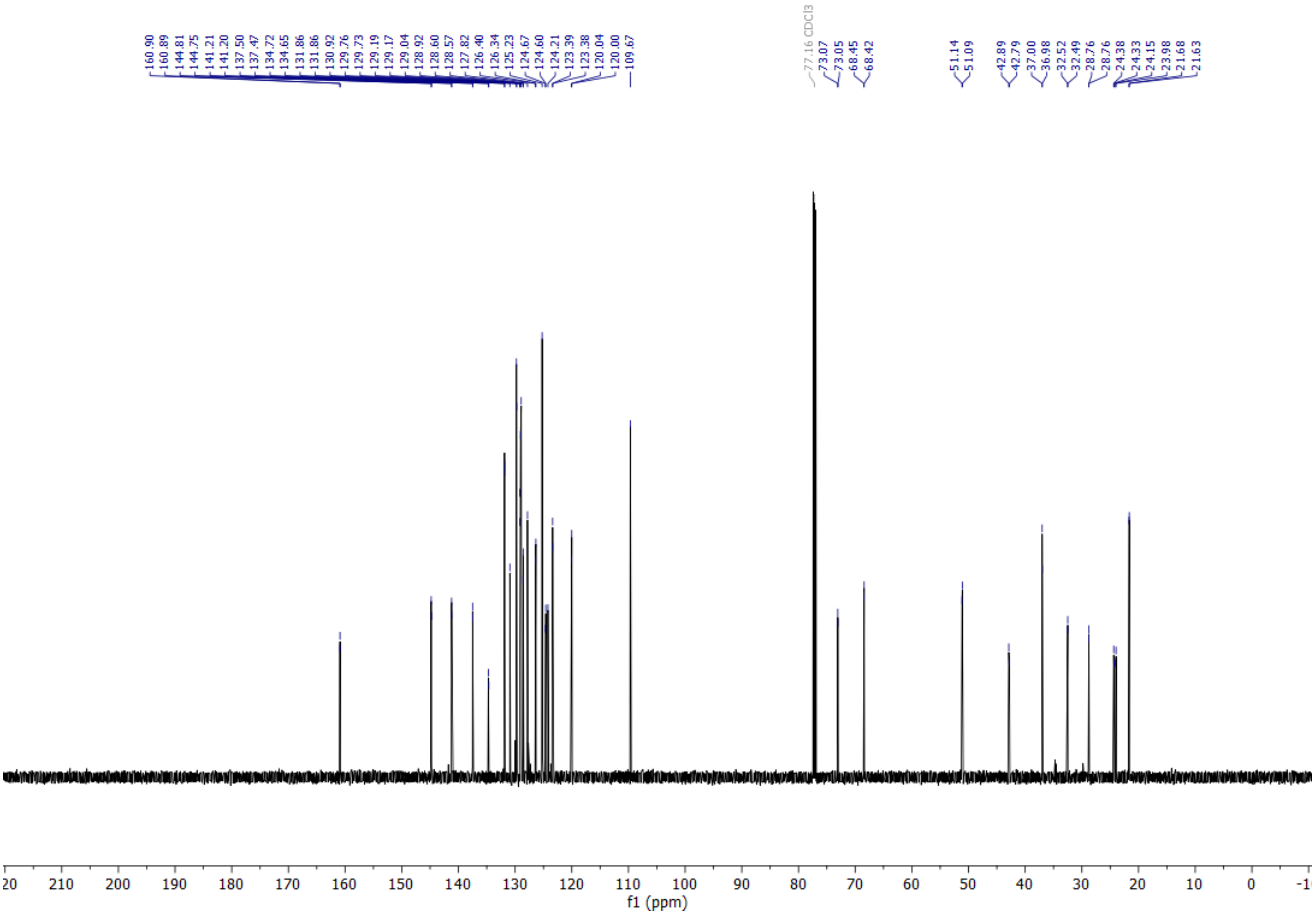
^{13}C NMR (101 MHz, $CDCl_3$)



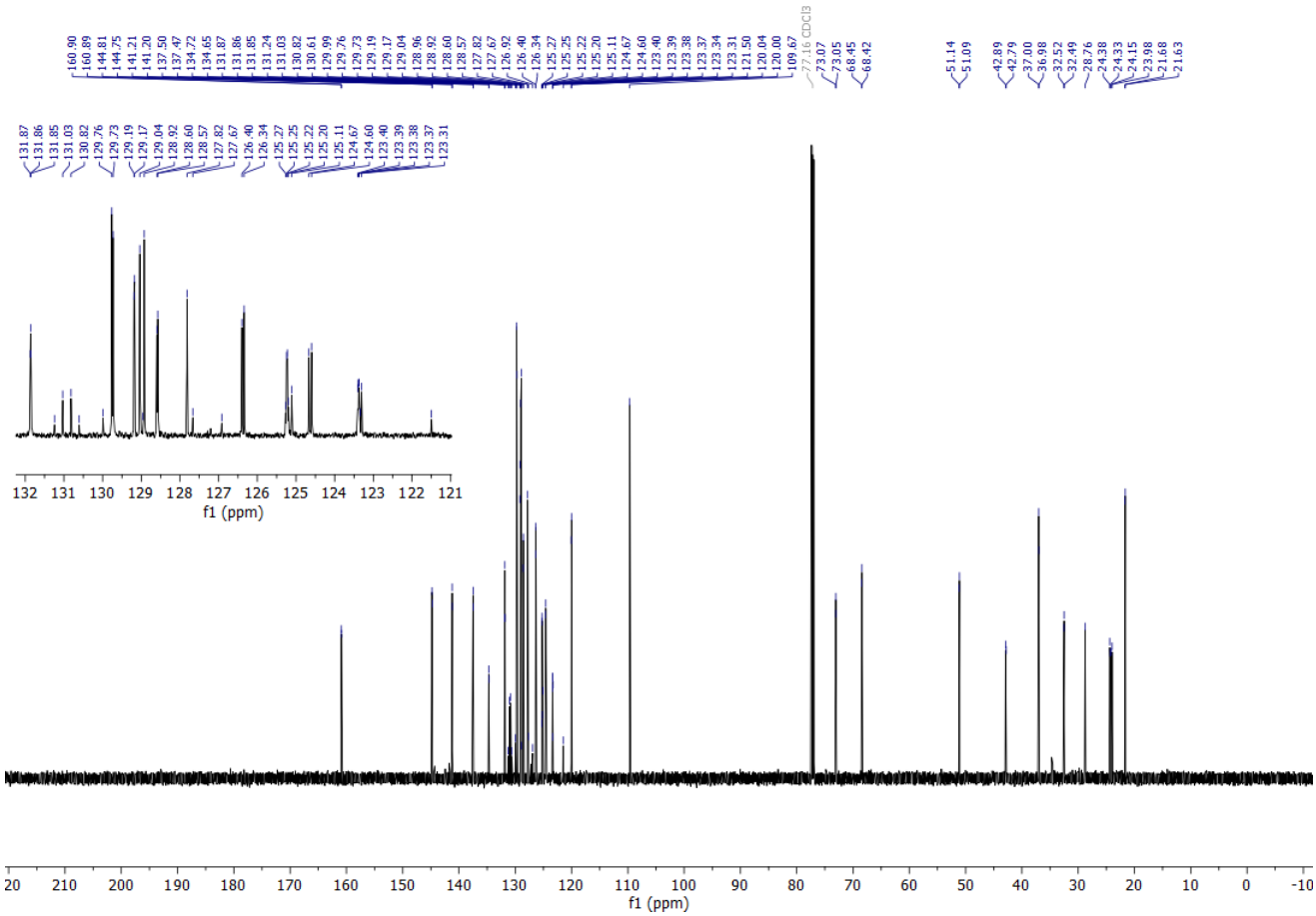
^{1}H NMR (599 MHz, $CDCl_3$)



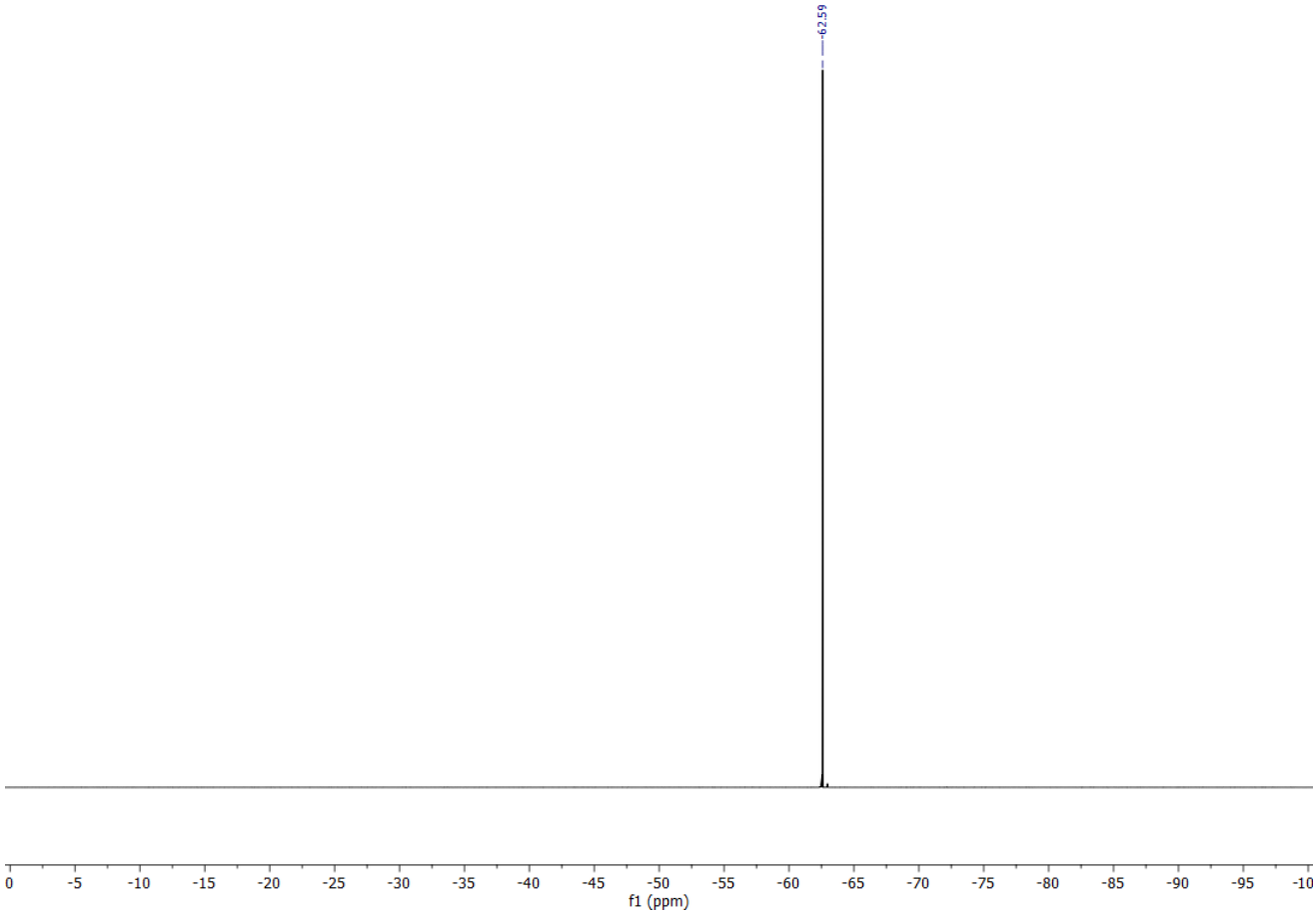
^{13}C{^{1}H, ^{19}F} NMR (151 MHz, $CDCl_3$)



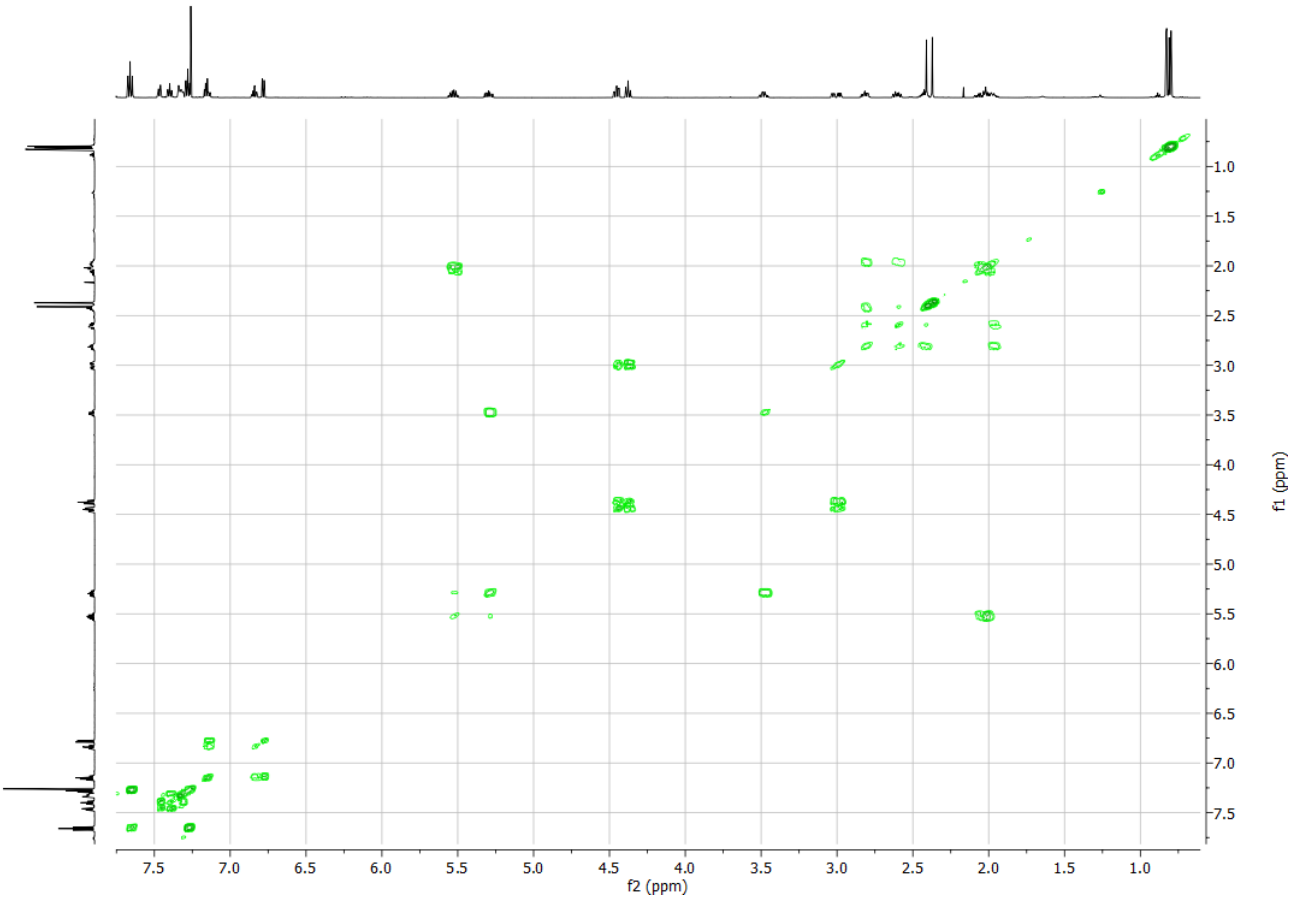
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)



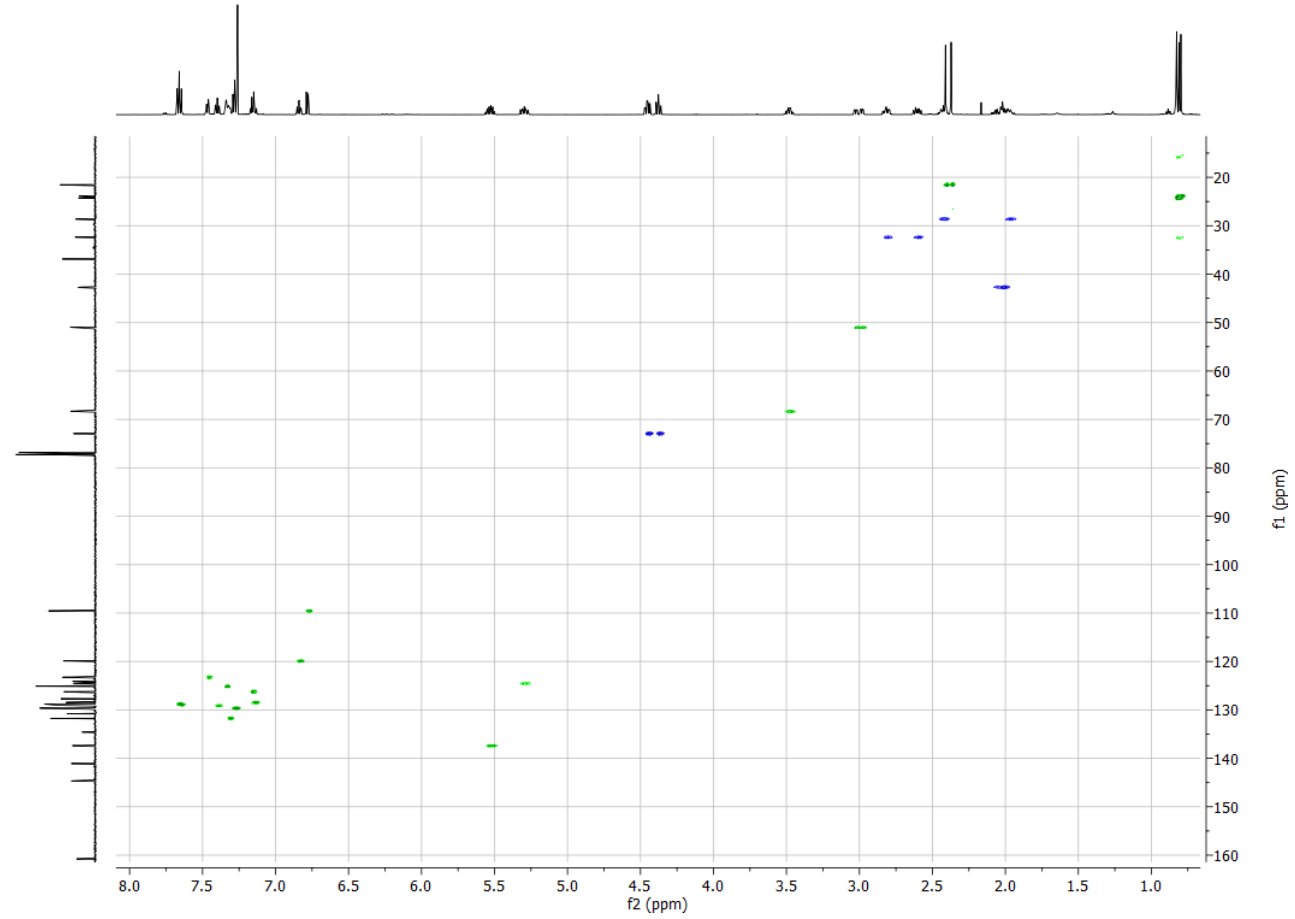
$^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$)



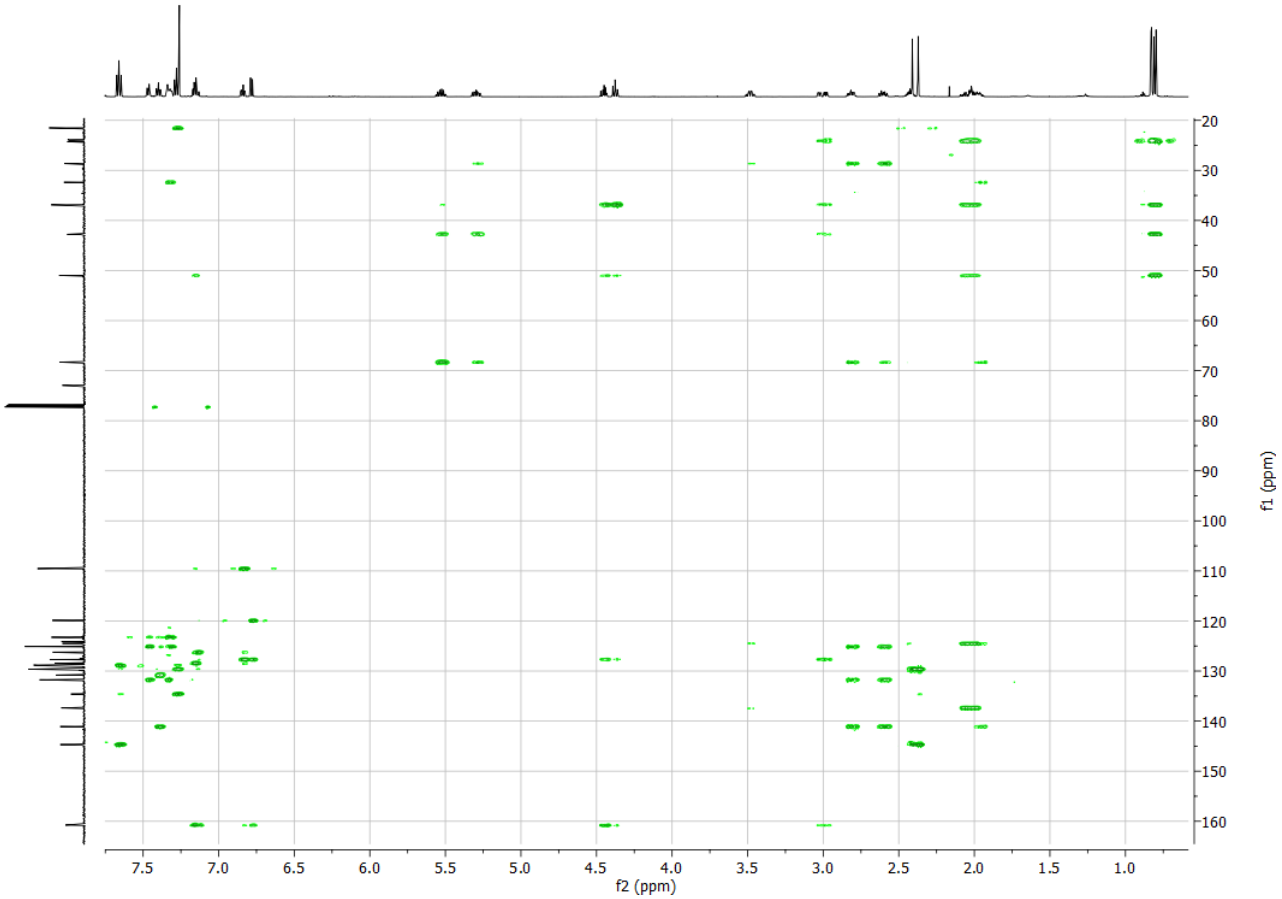
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



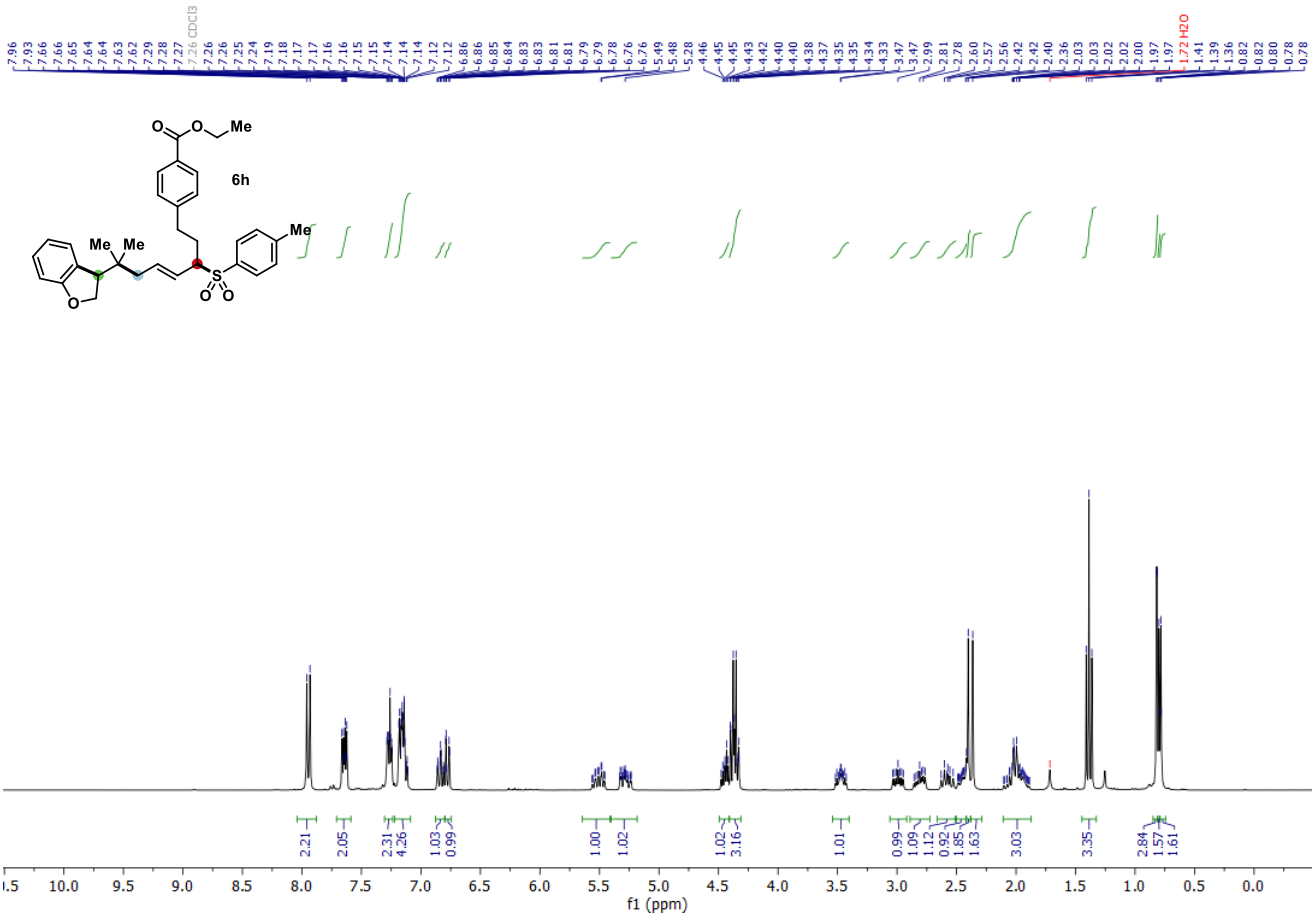
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



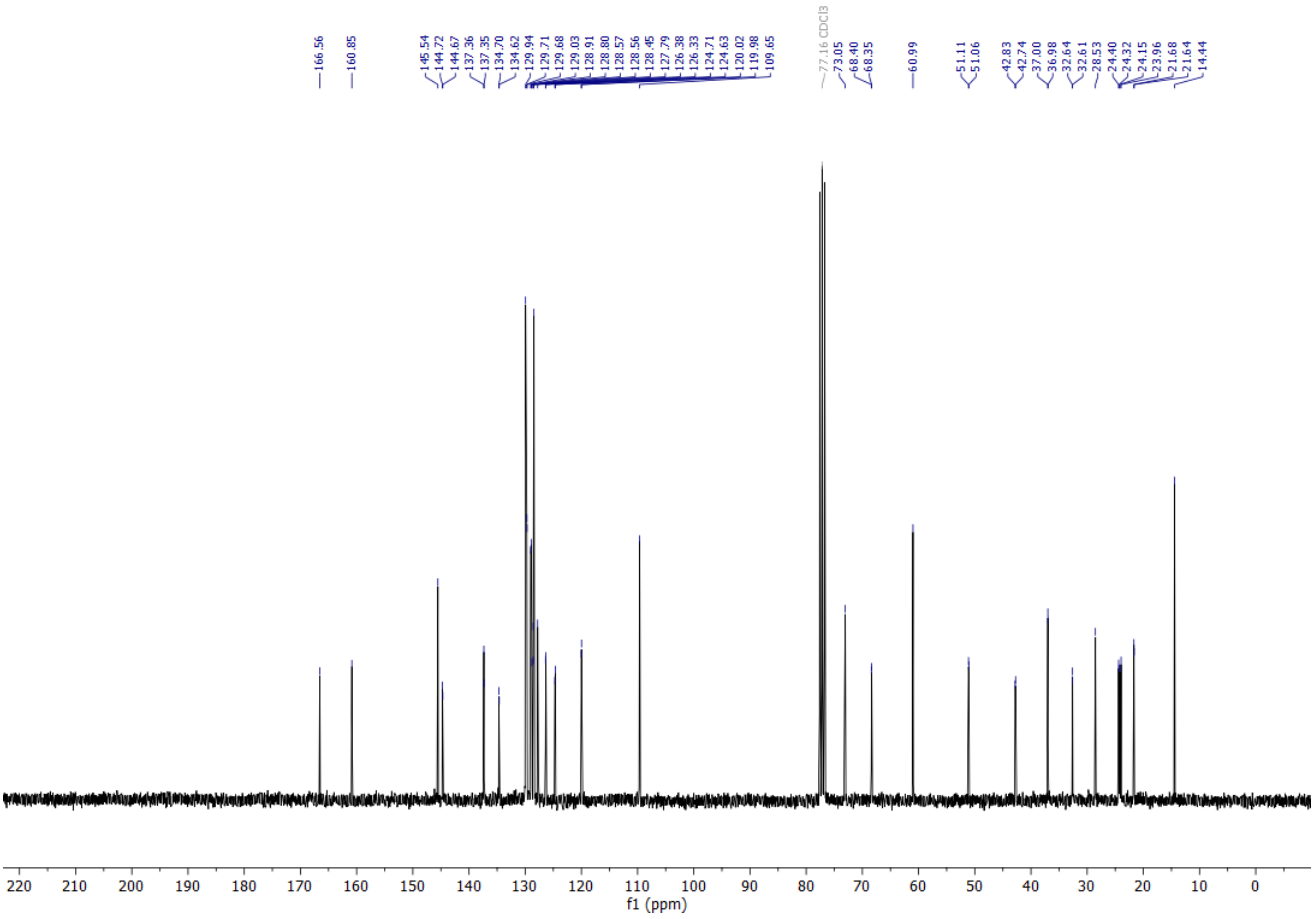
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



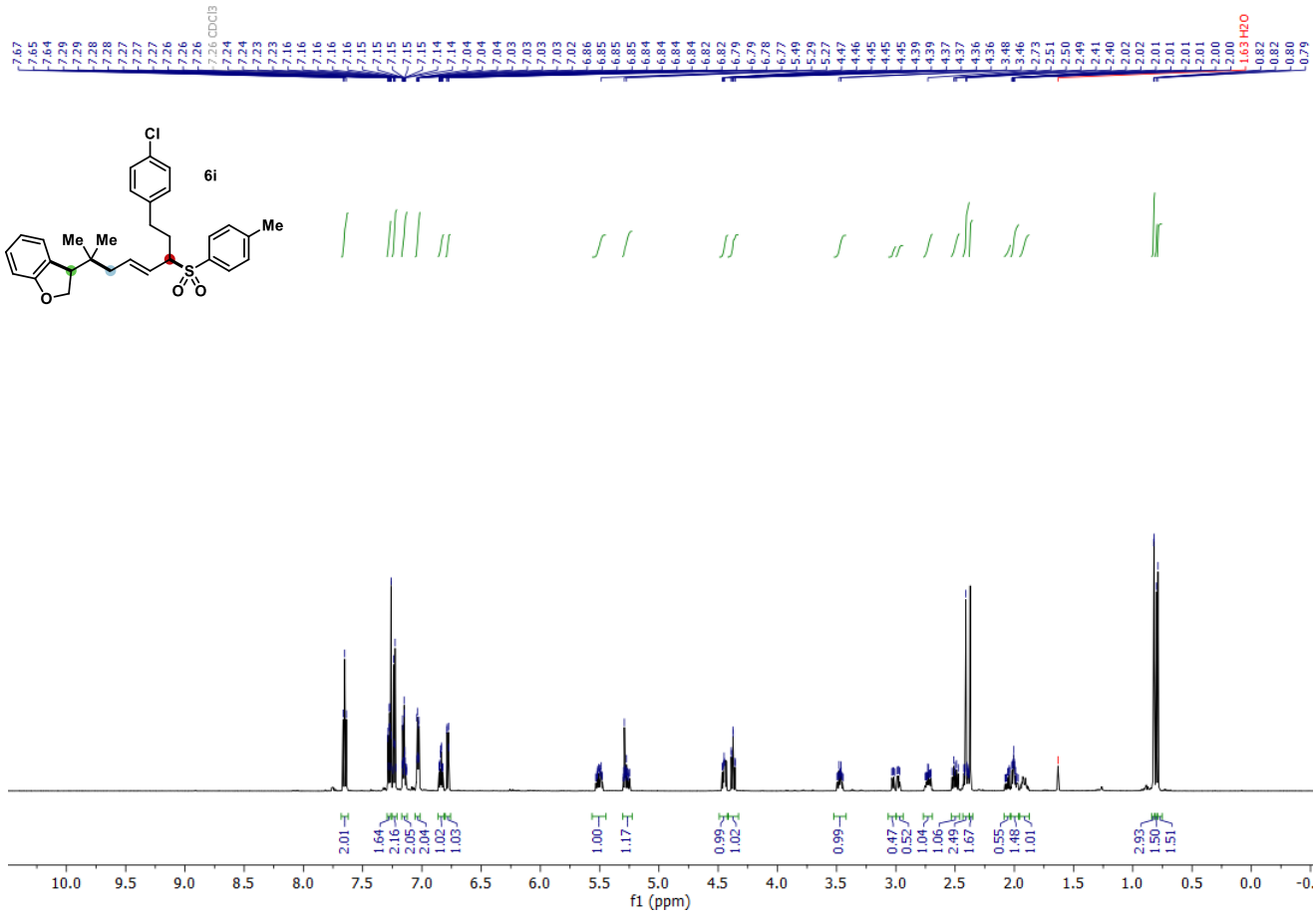
^{1}H NMR (300 MHz, $CDCl_3$)



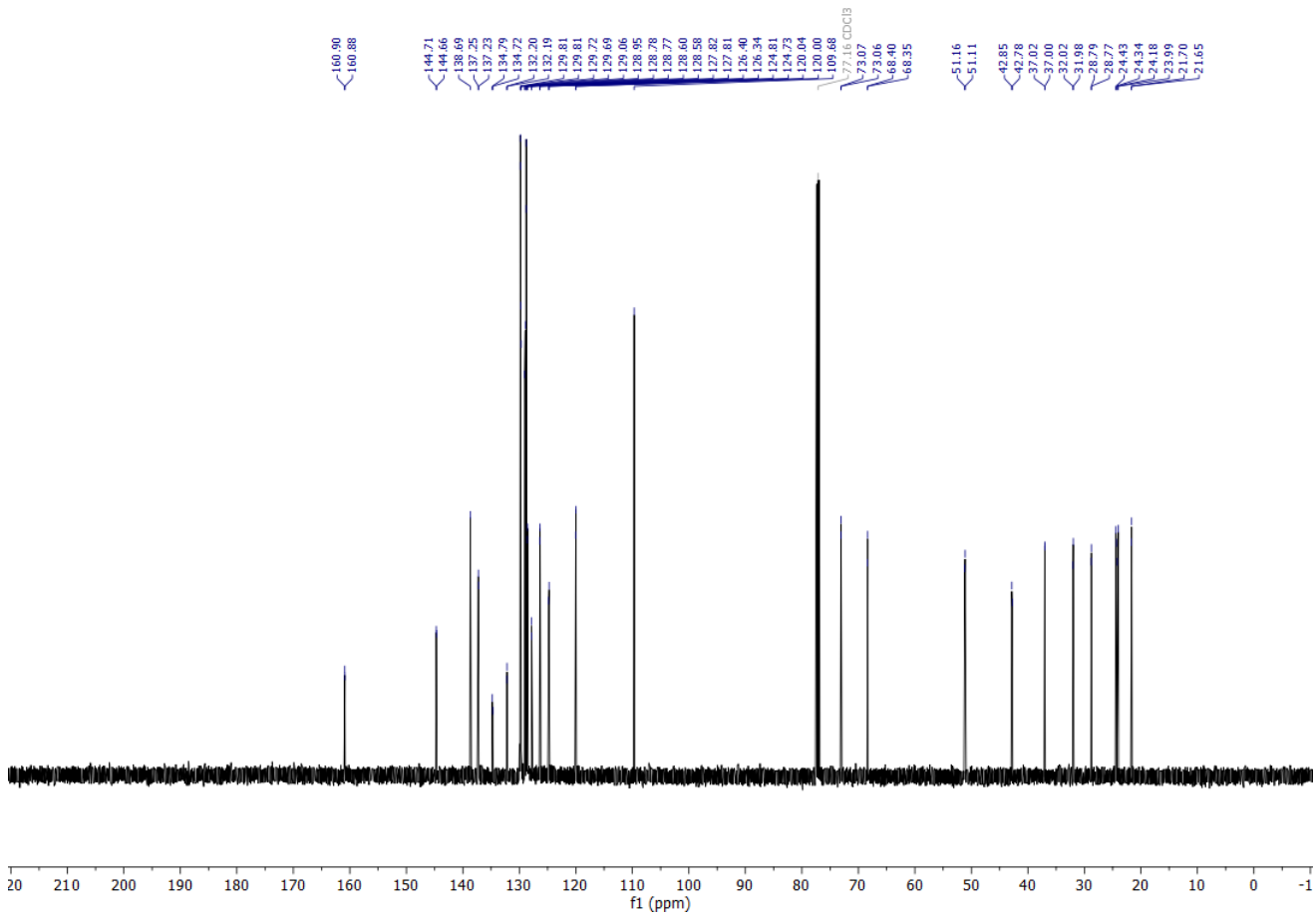
^{13}C NMR (75 MHz, $CDCl_3$)



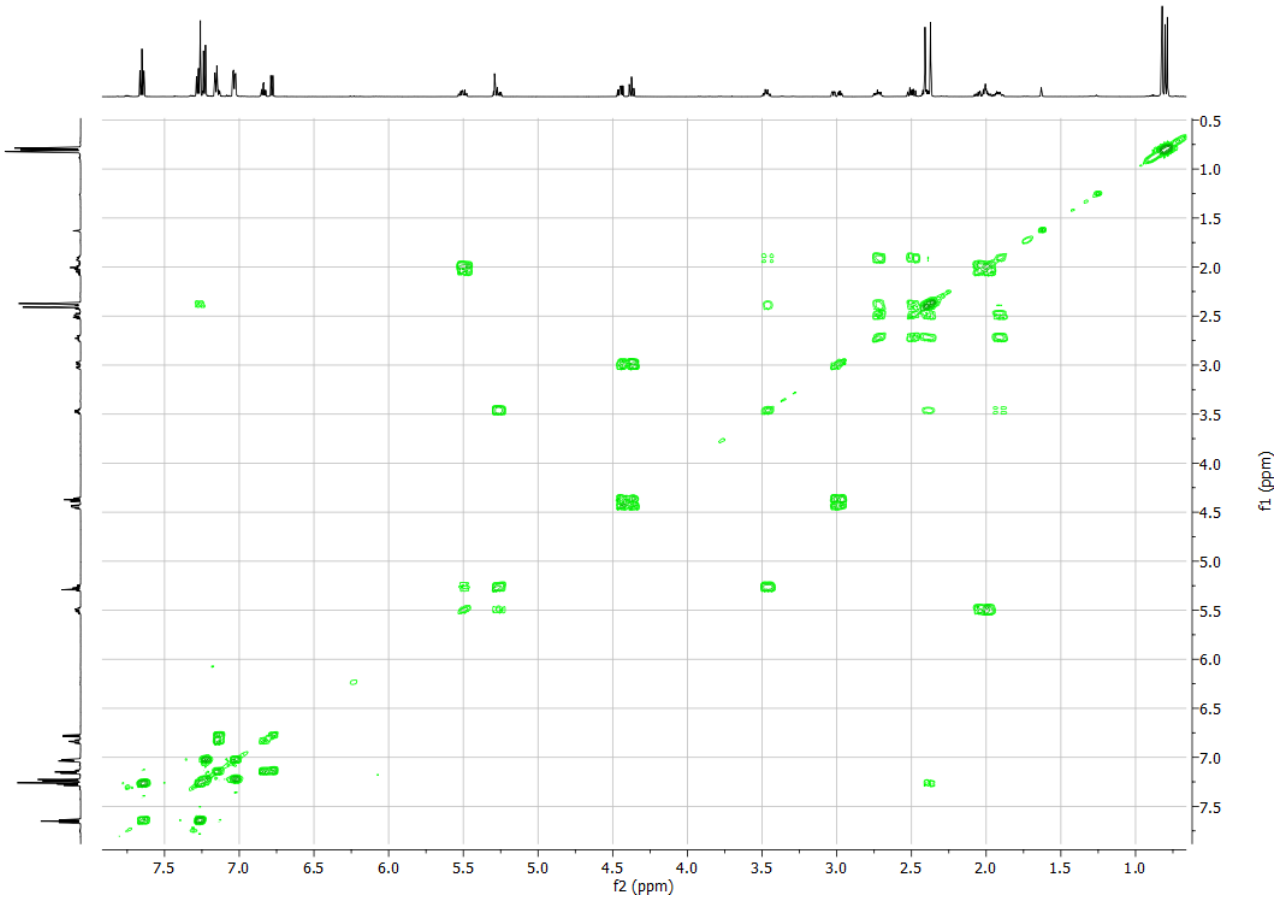
^{1}H NMR (599 MHz, $CDCl_3$)



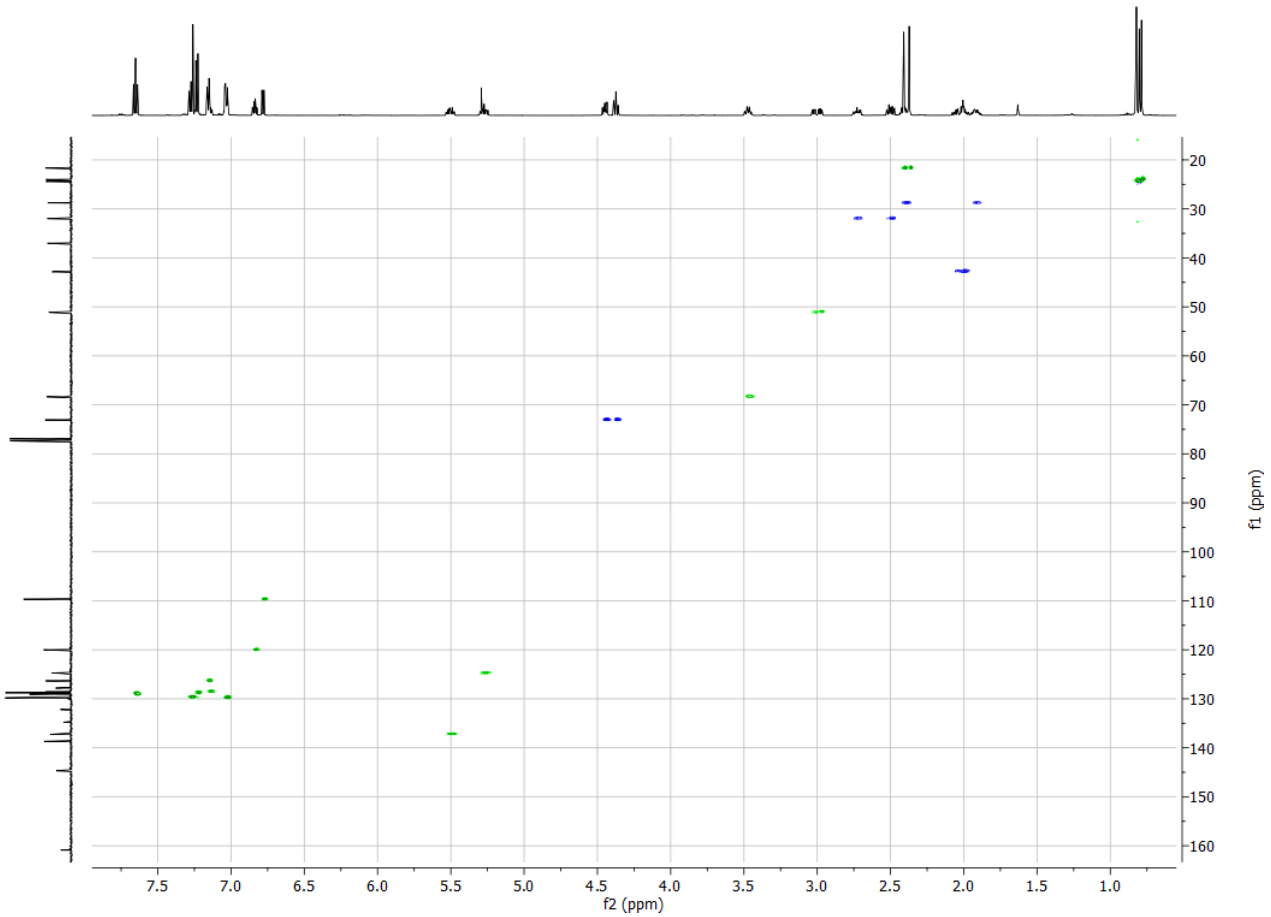
^{13}C NMR (151 MHz, $CDCl_3$)



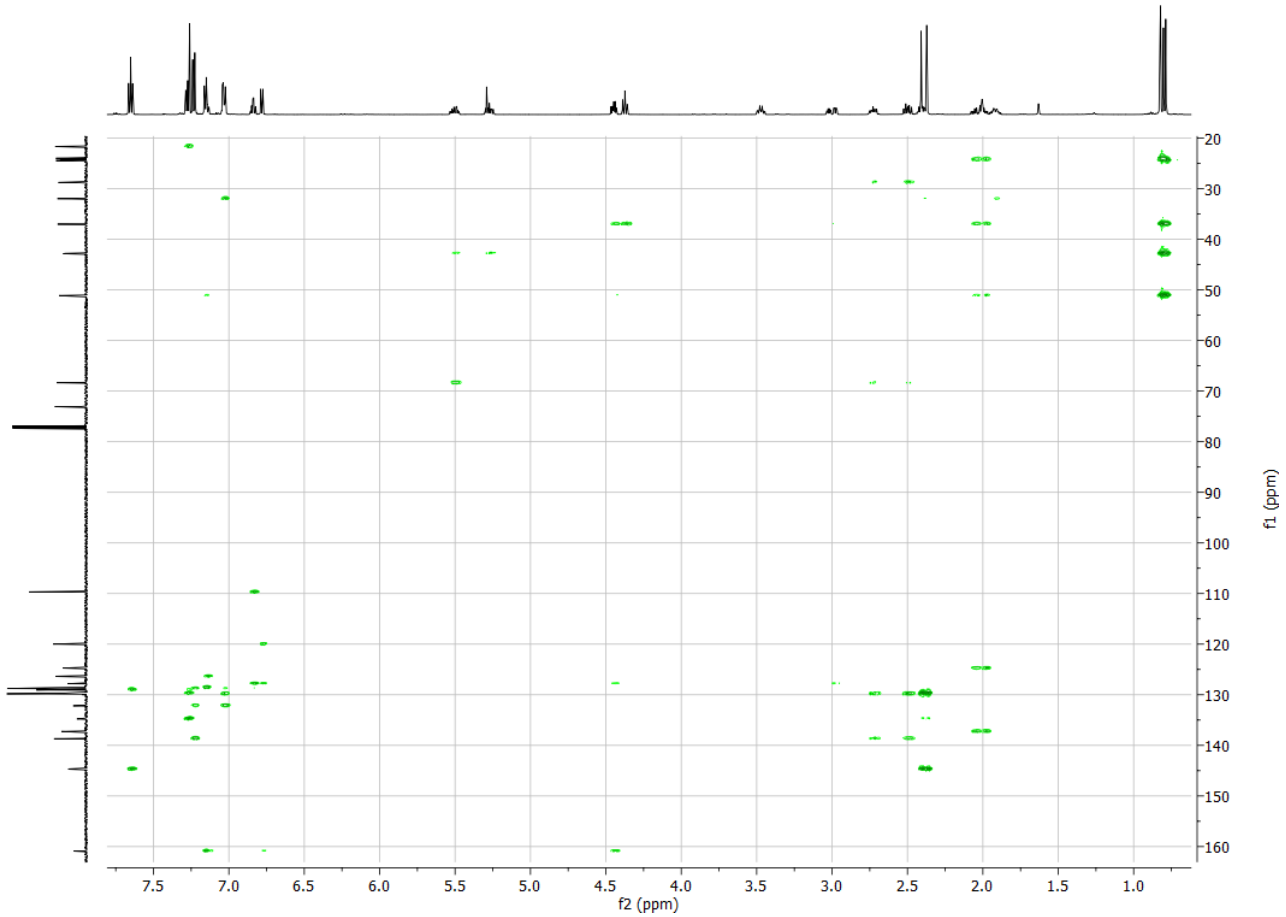
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



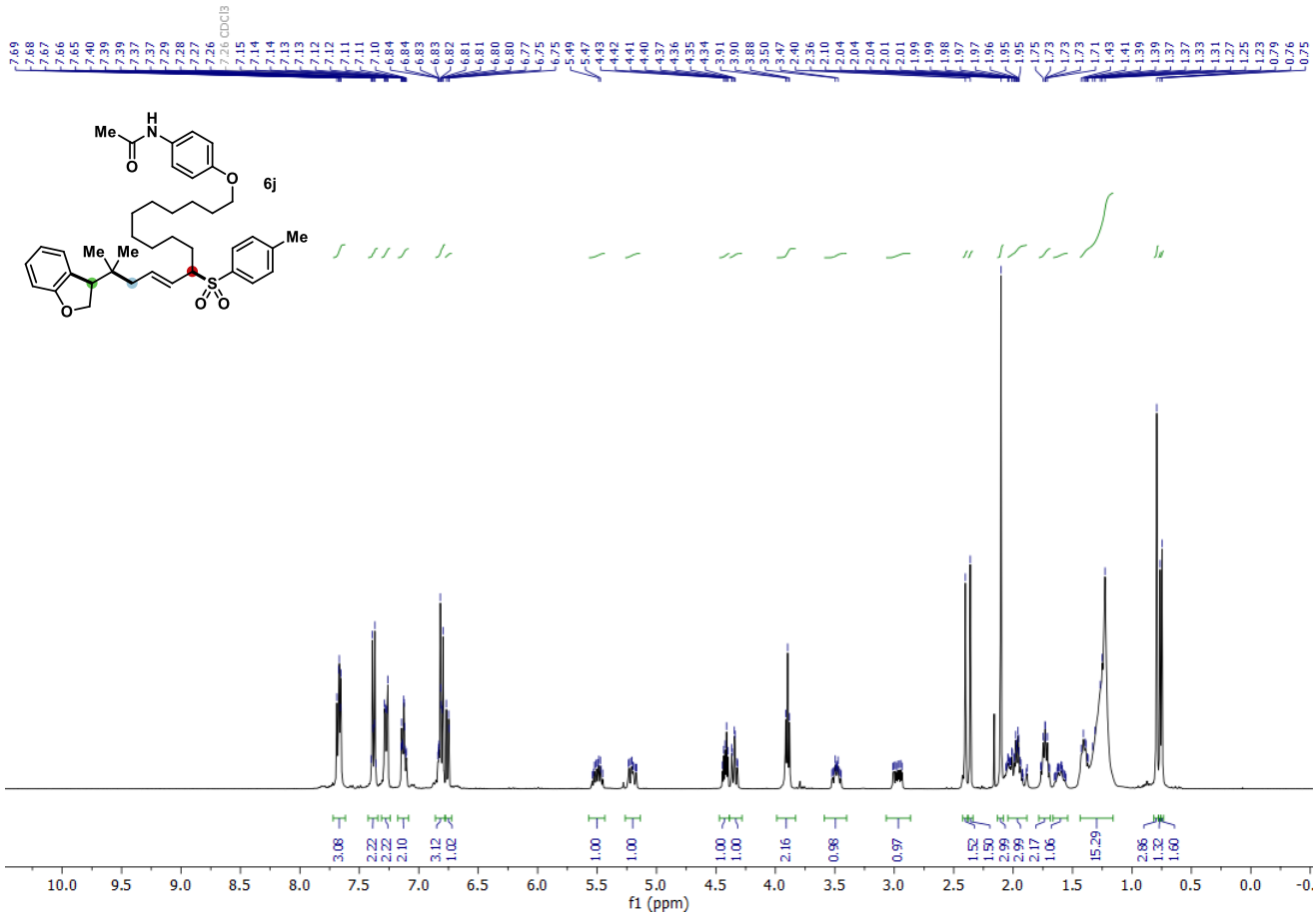
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



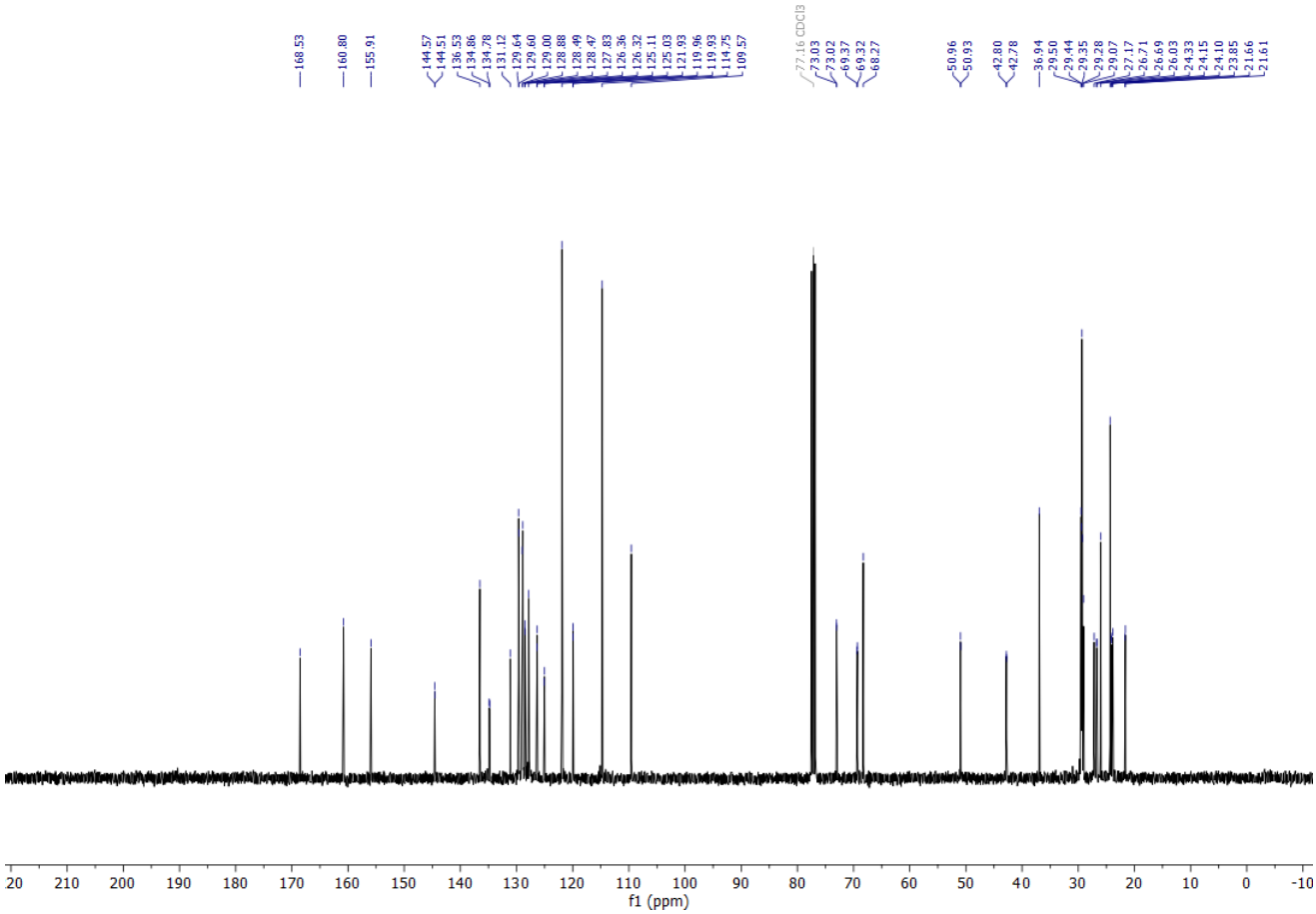
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



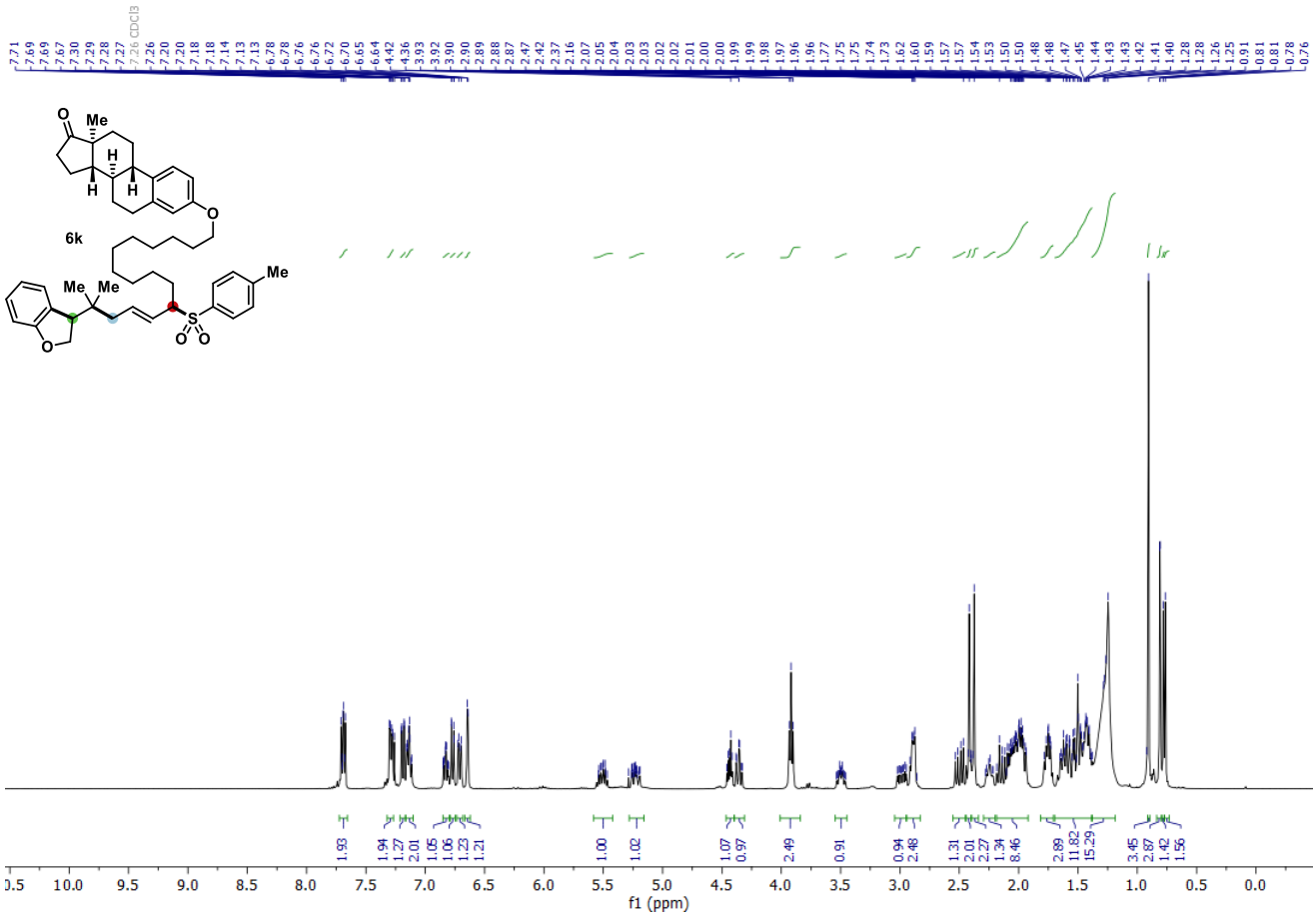
^{1}H NMR (400 MHz, $CDCl_3$)



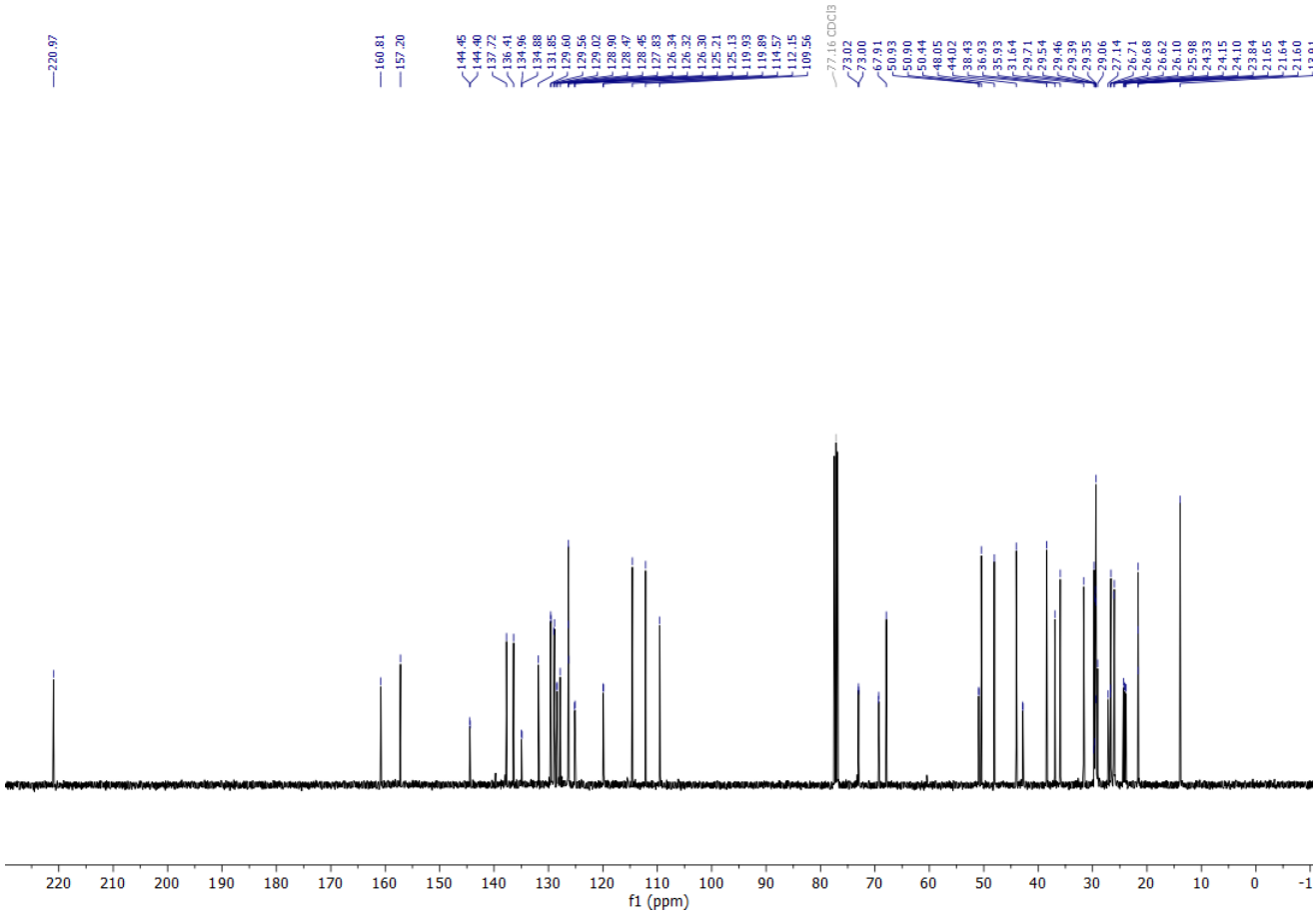
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

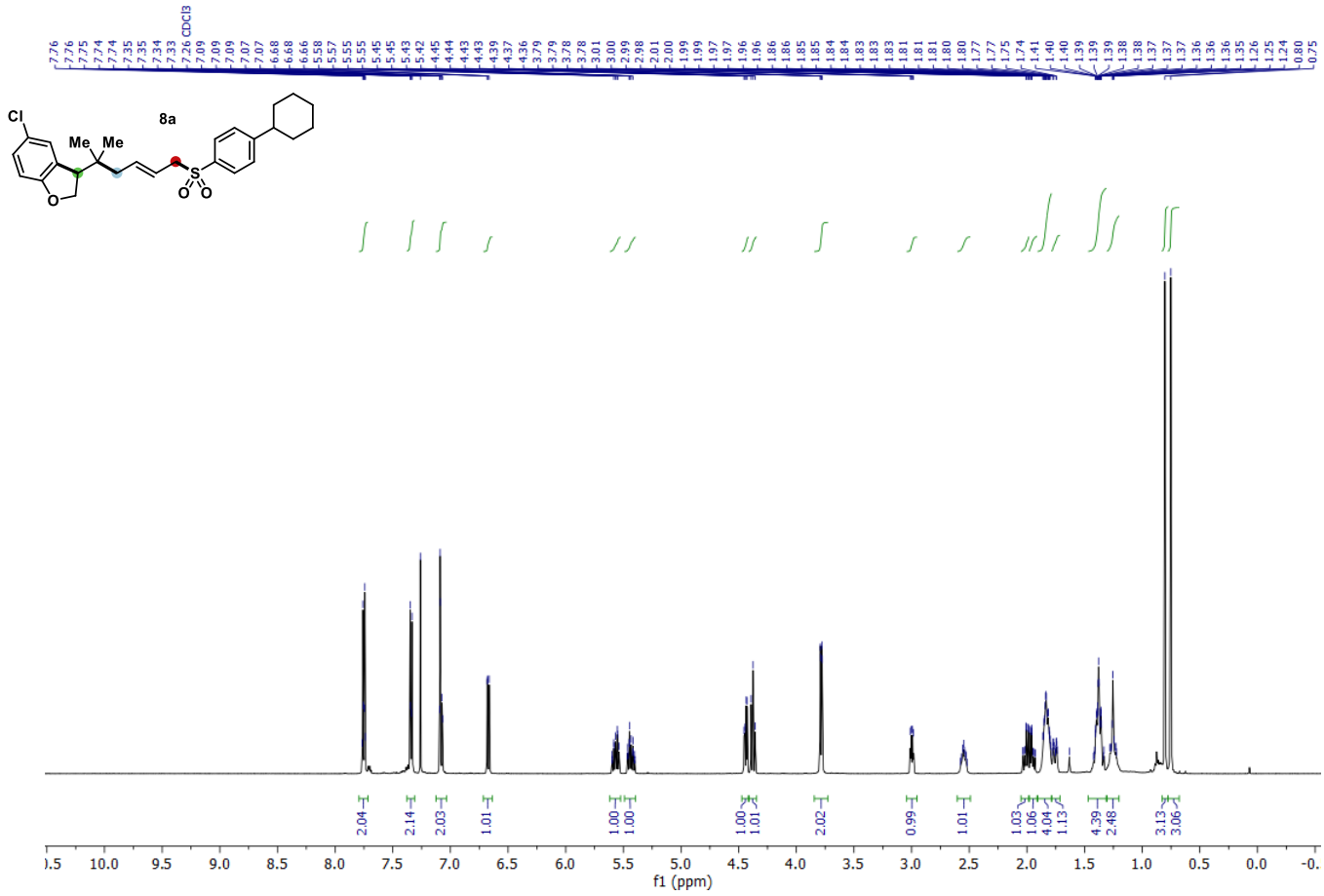


^{13}C NMR (101 MHz, $CDCl_3$)

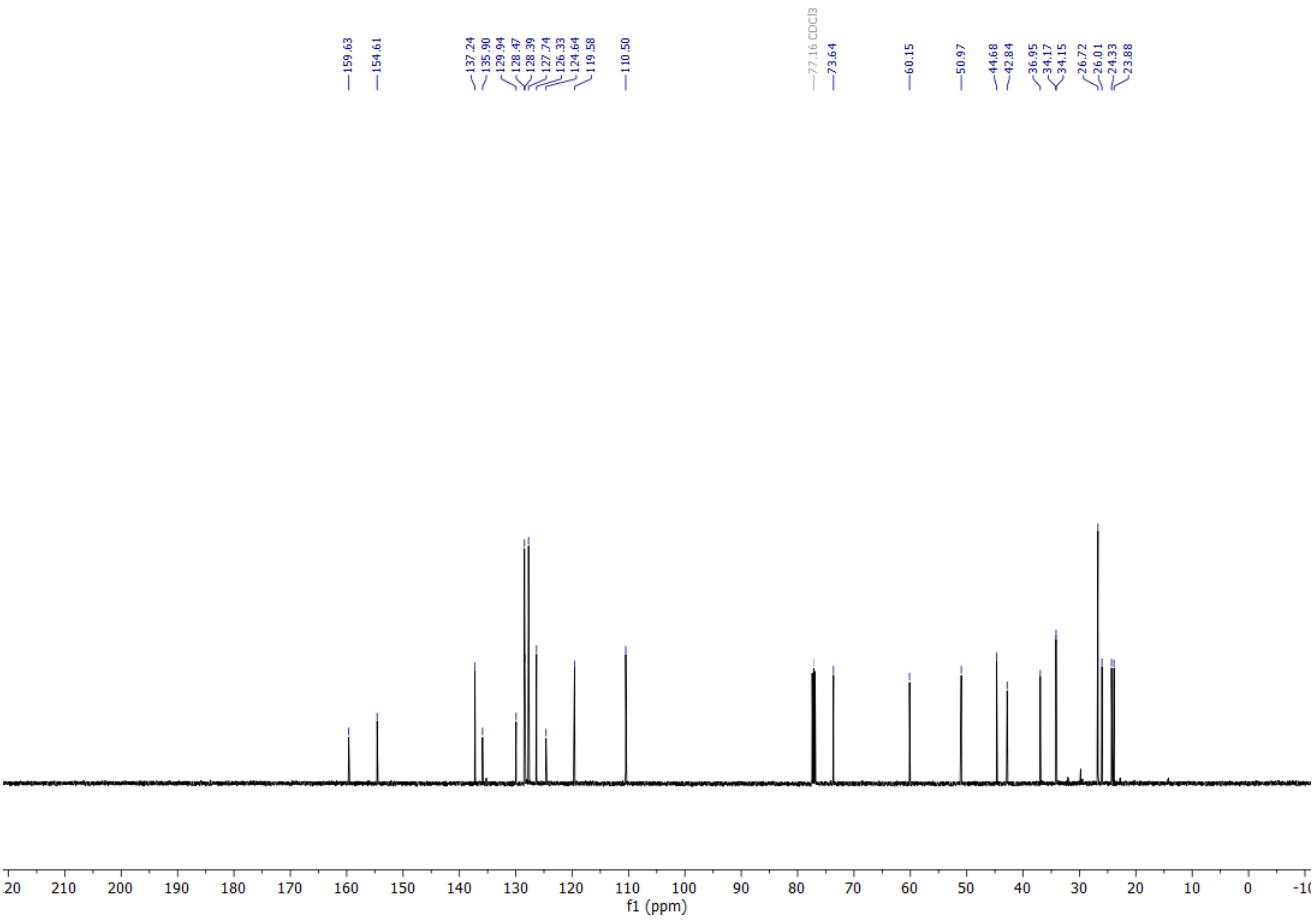


NMR spectra of products 8a-i

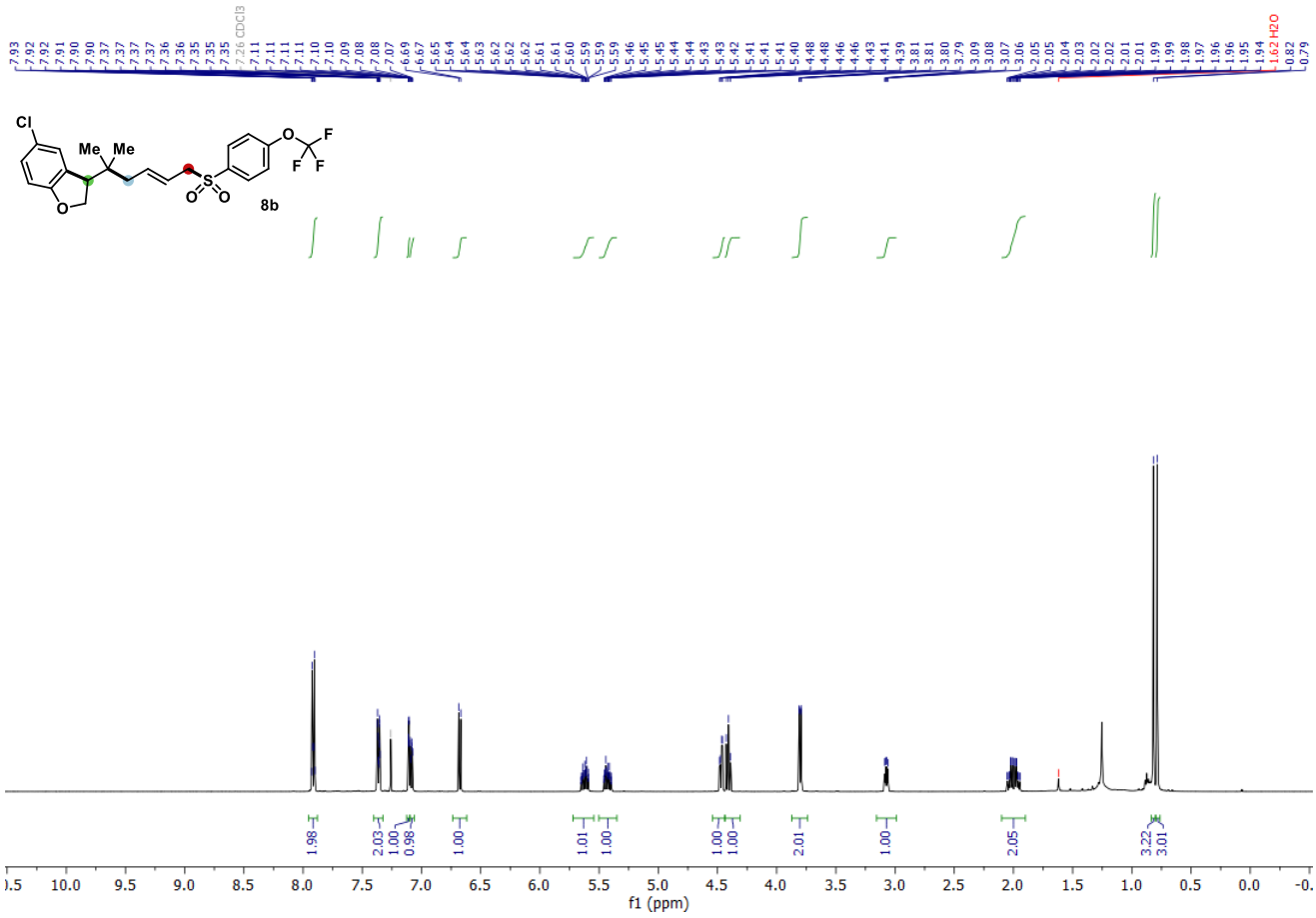
^{1}H NMR (500 MHz, $CDCl_3$)



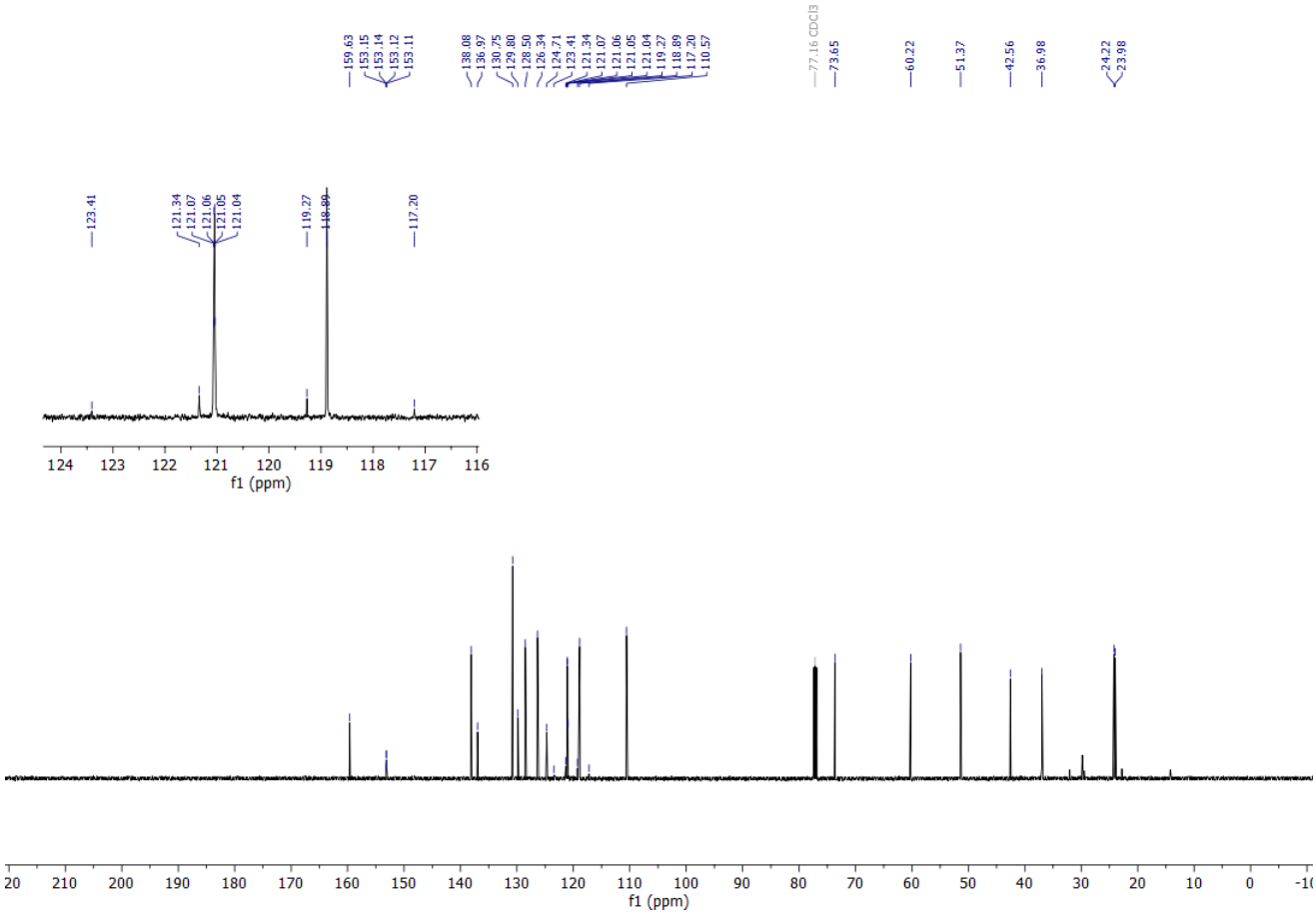
^{13}C NMR (126 MHz, $CDCl_3$)



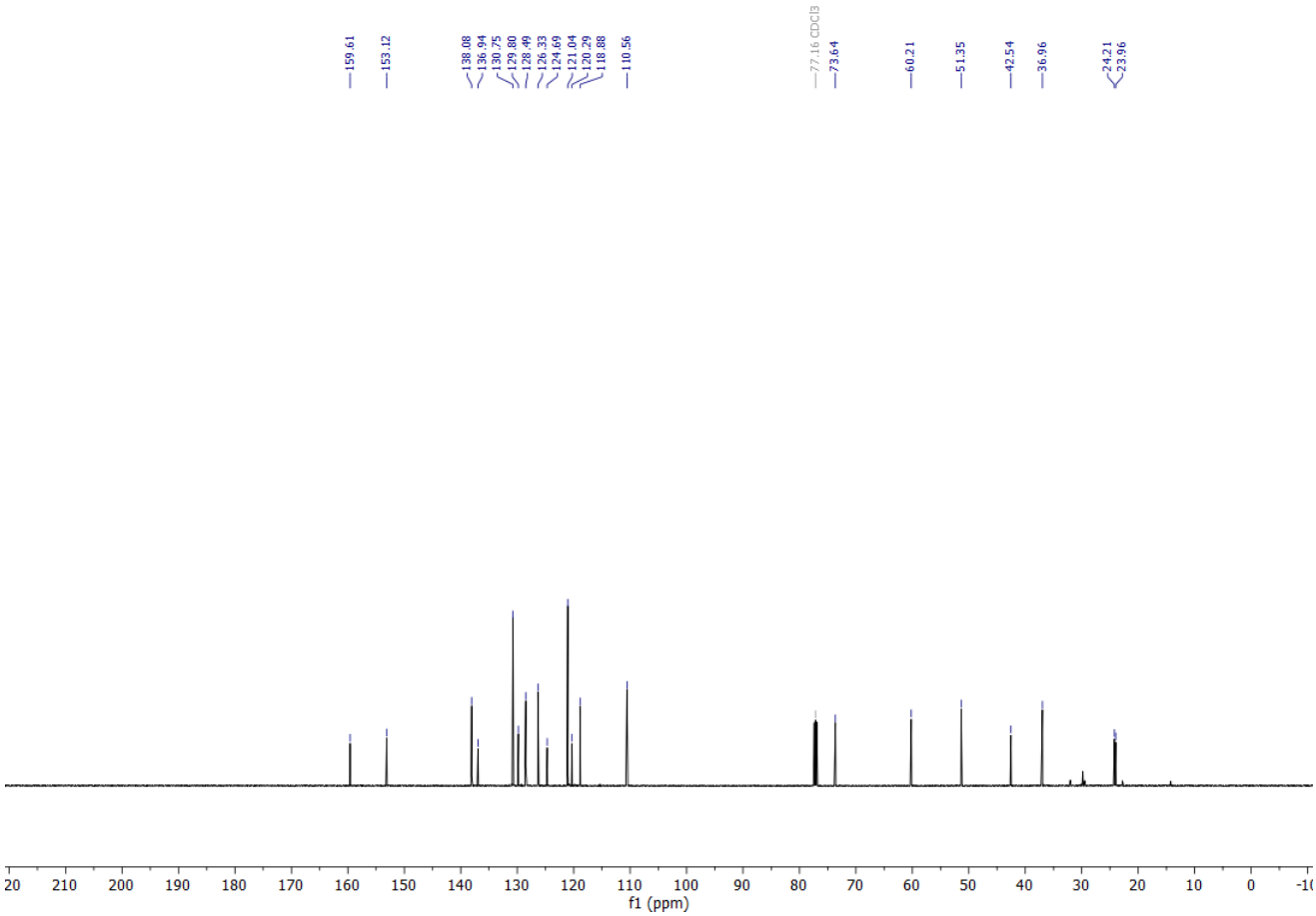
^{1}H NMR (500 MHz, $CDCl_3$)



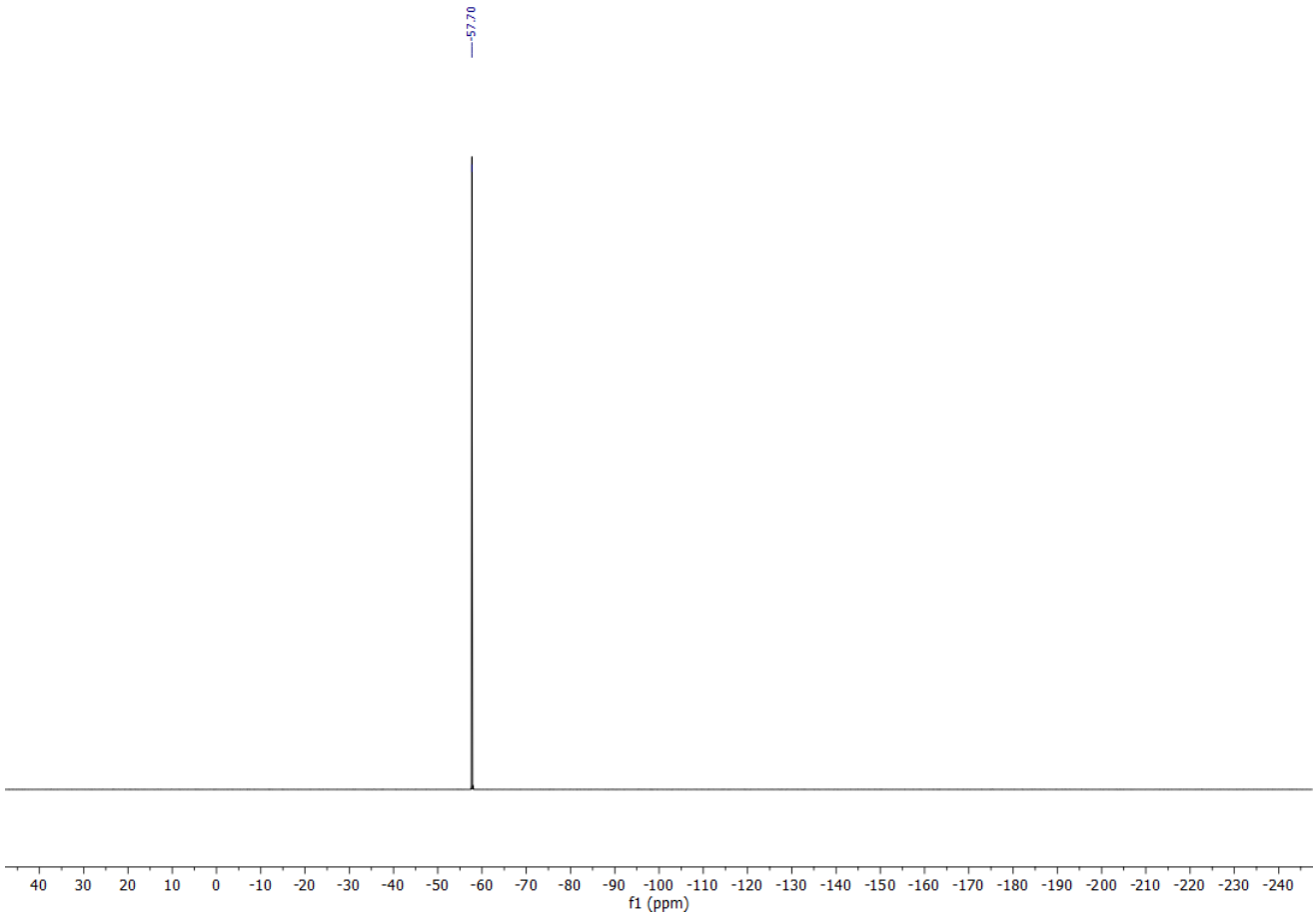
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



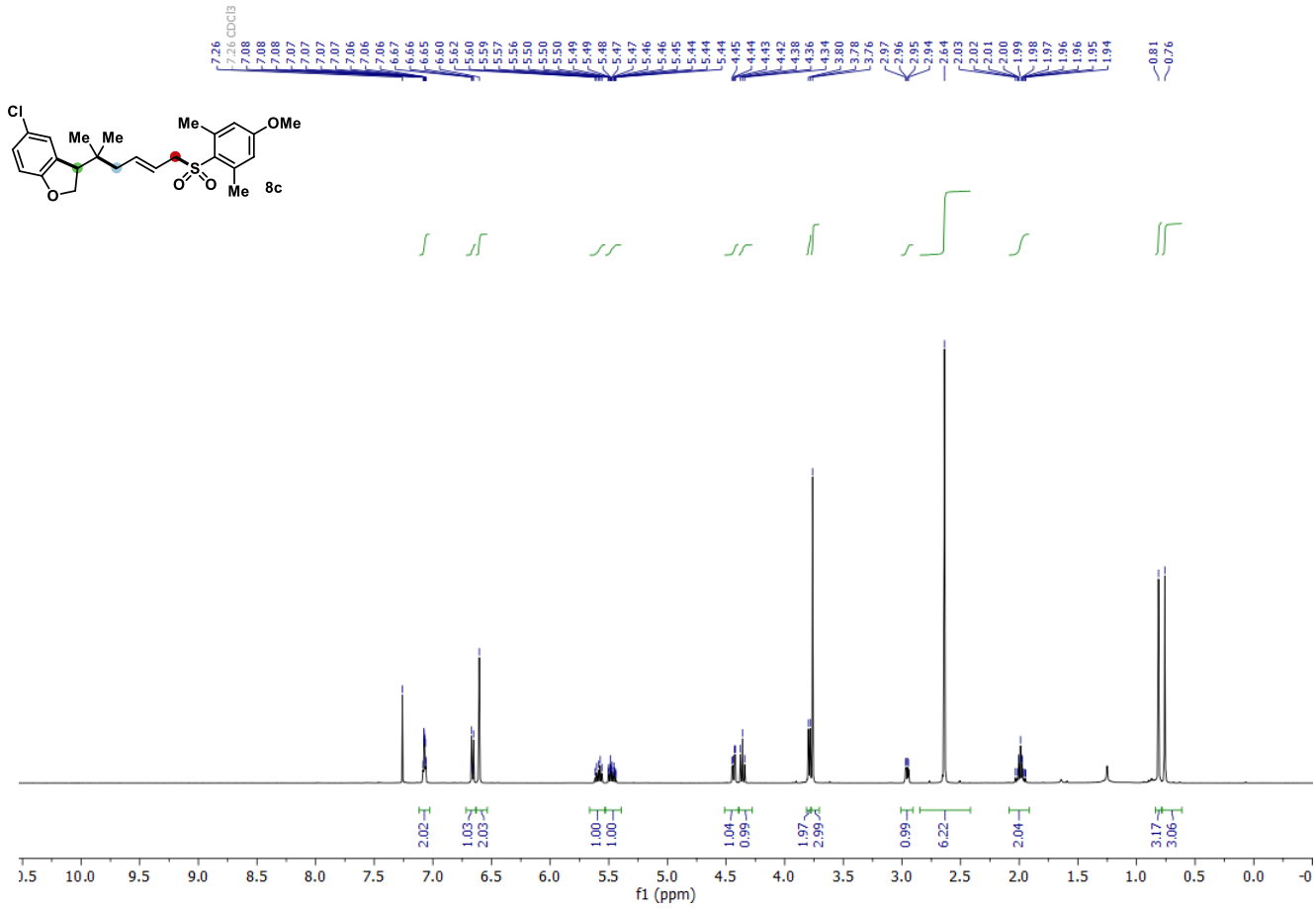
$^{13}C\{^{1}H, ^{19}F\}$ NMR (126 MHz, $CDCl_3$)



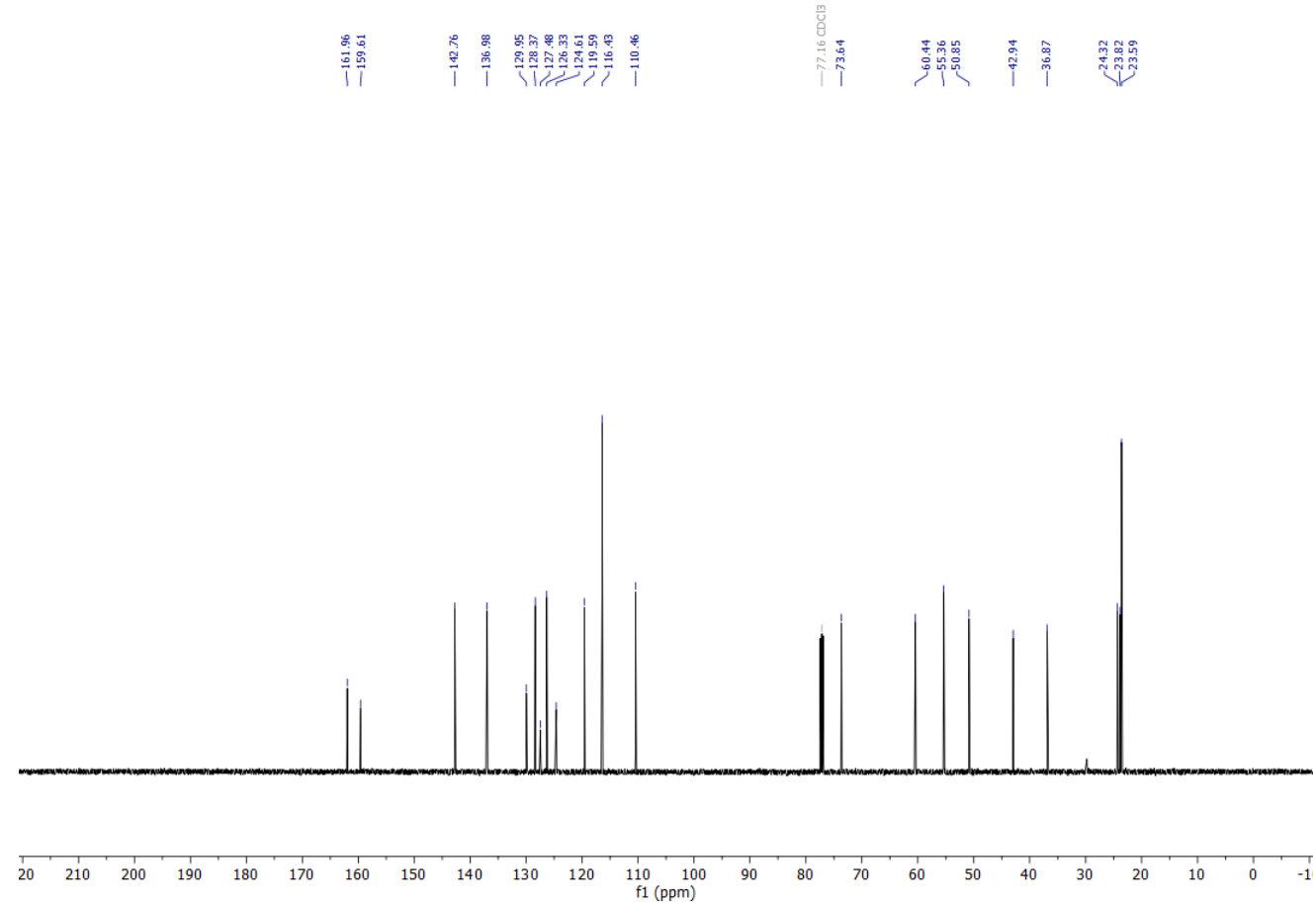
$^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$)



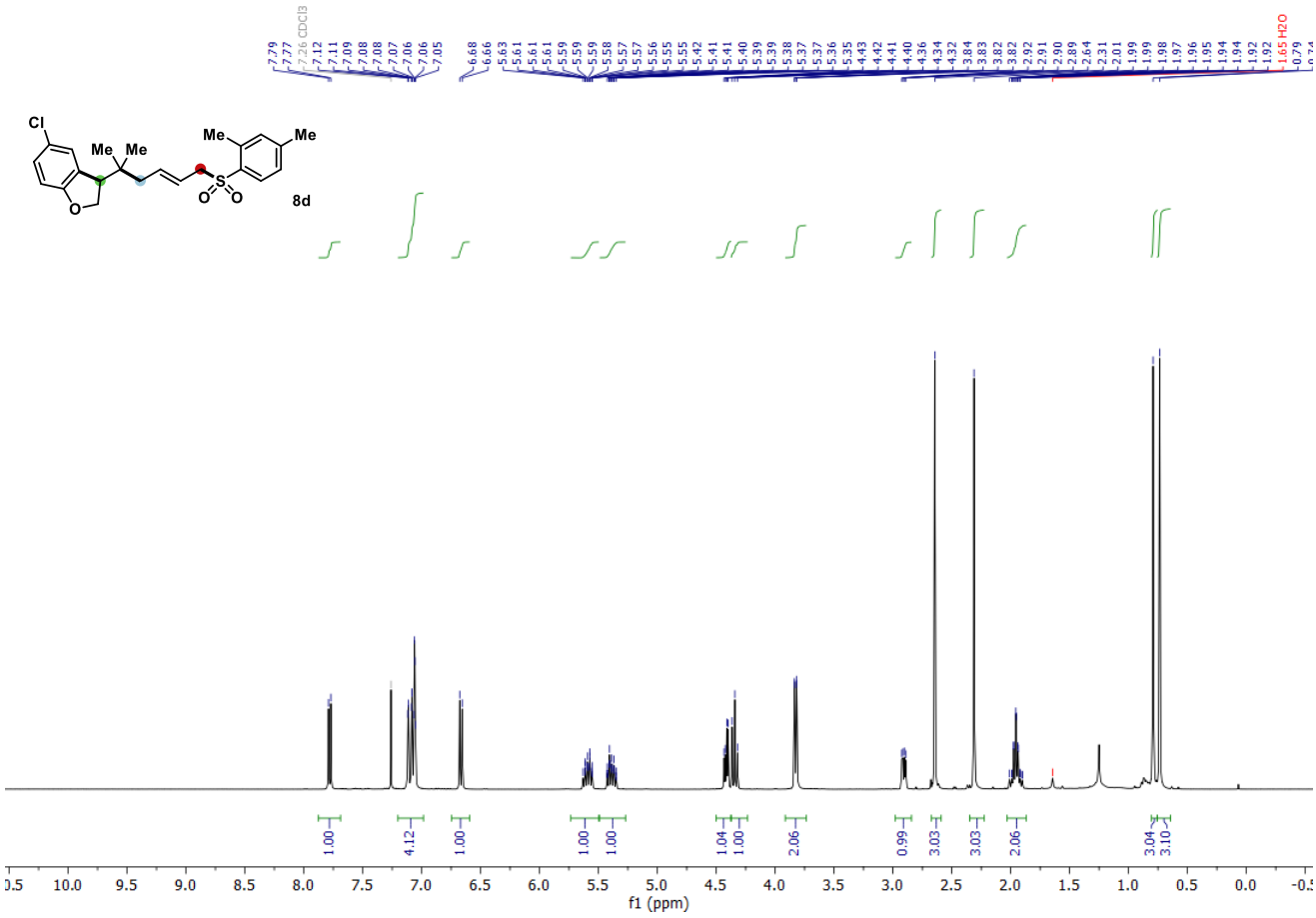
^{1}H NMR (500 MHz, $CDCl_3$)



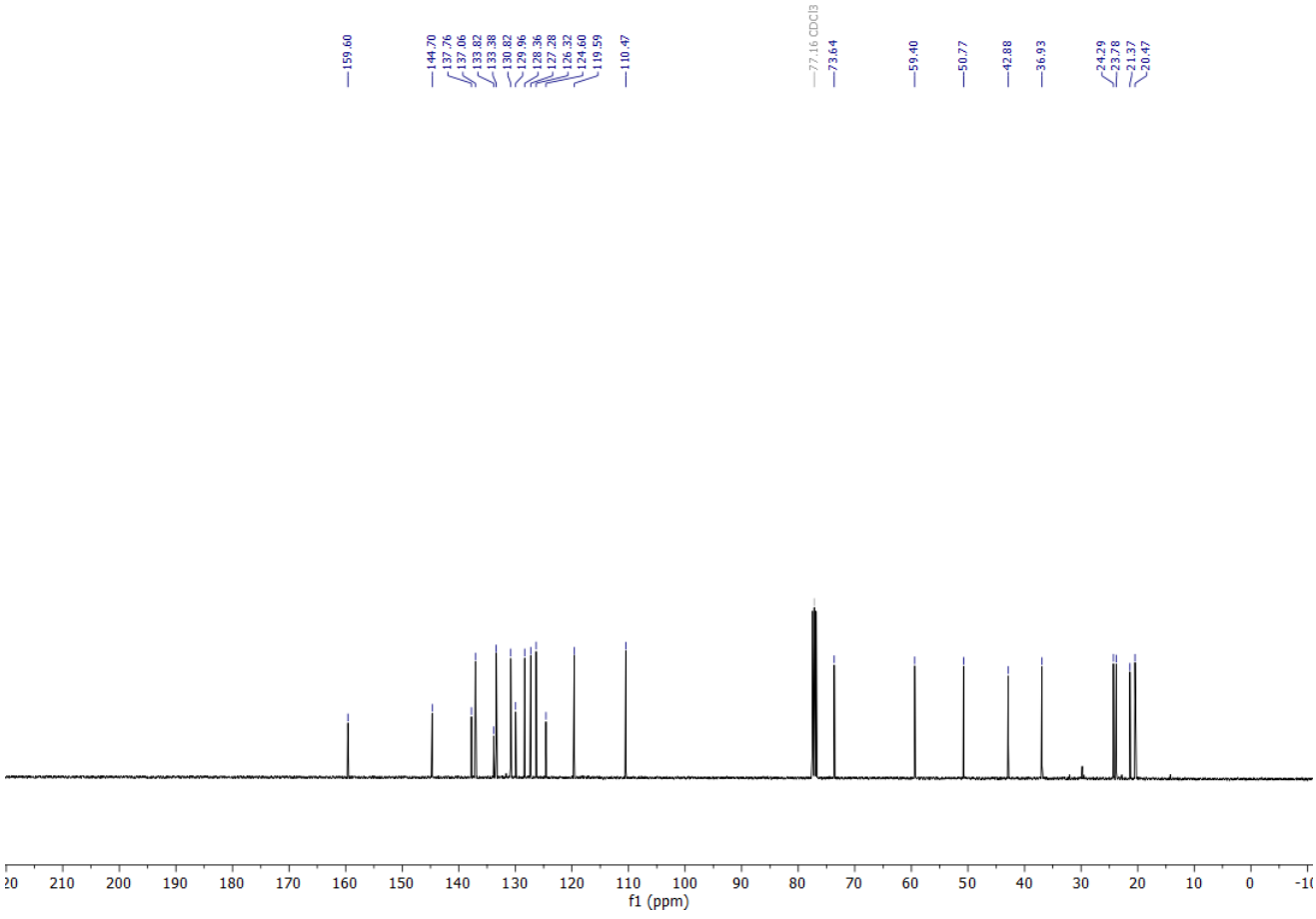
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



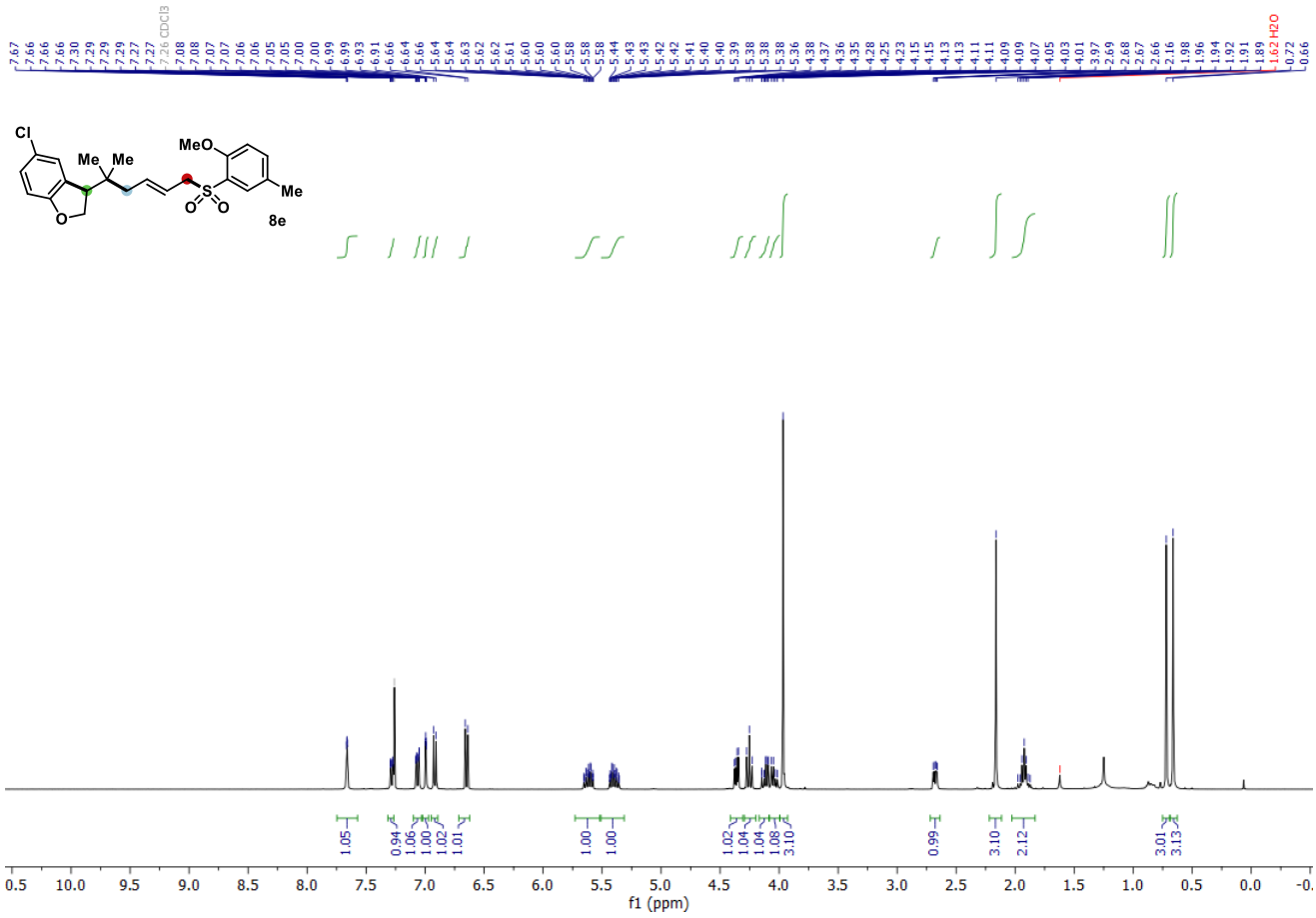
^{1}H NMR (400 MHz, $CDCl_3$)



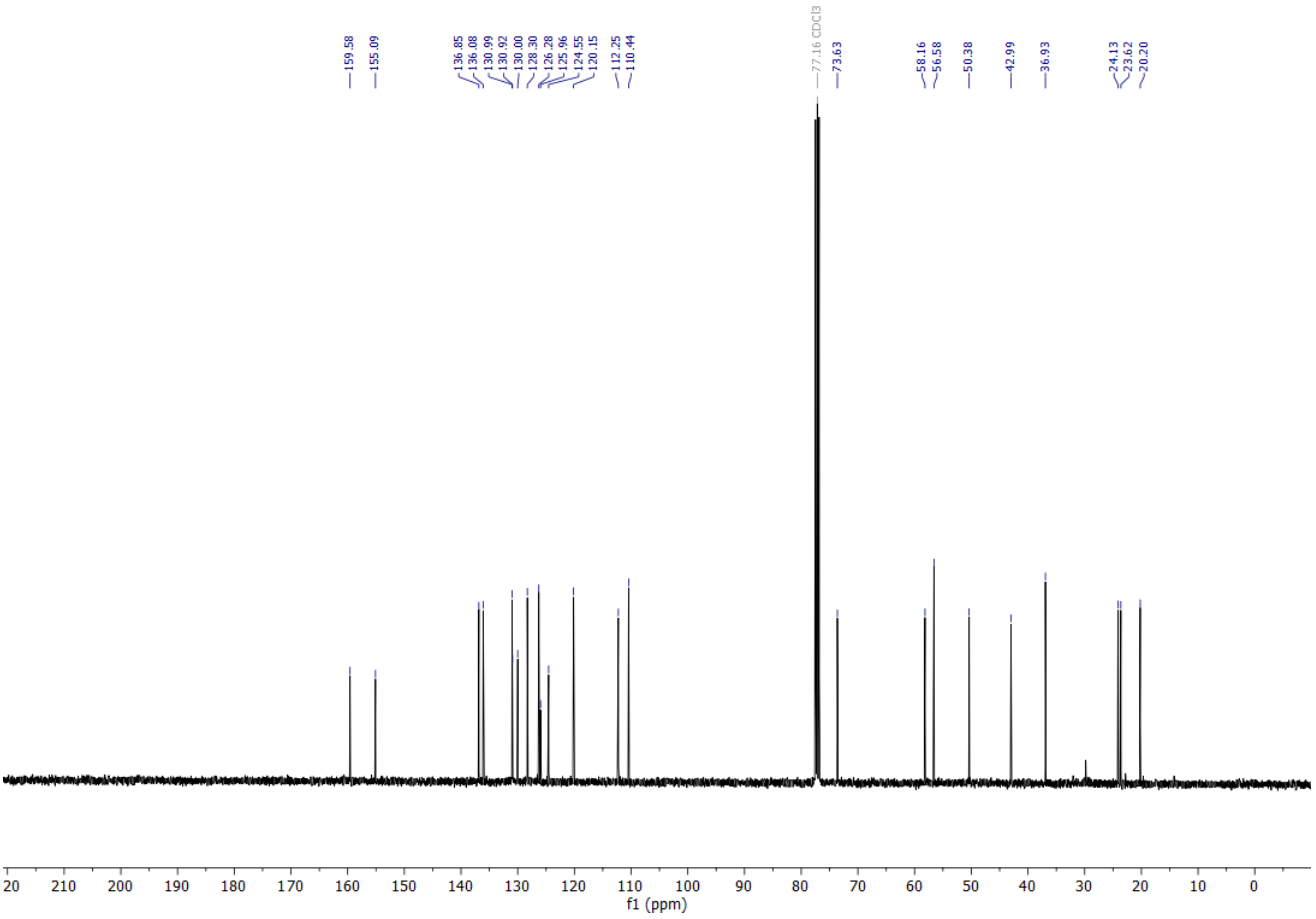
^{13}C NMR (101 MHz, $CDCl_3$)



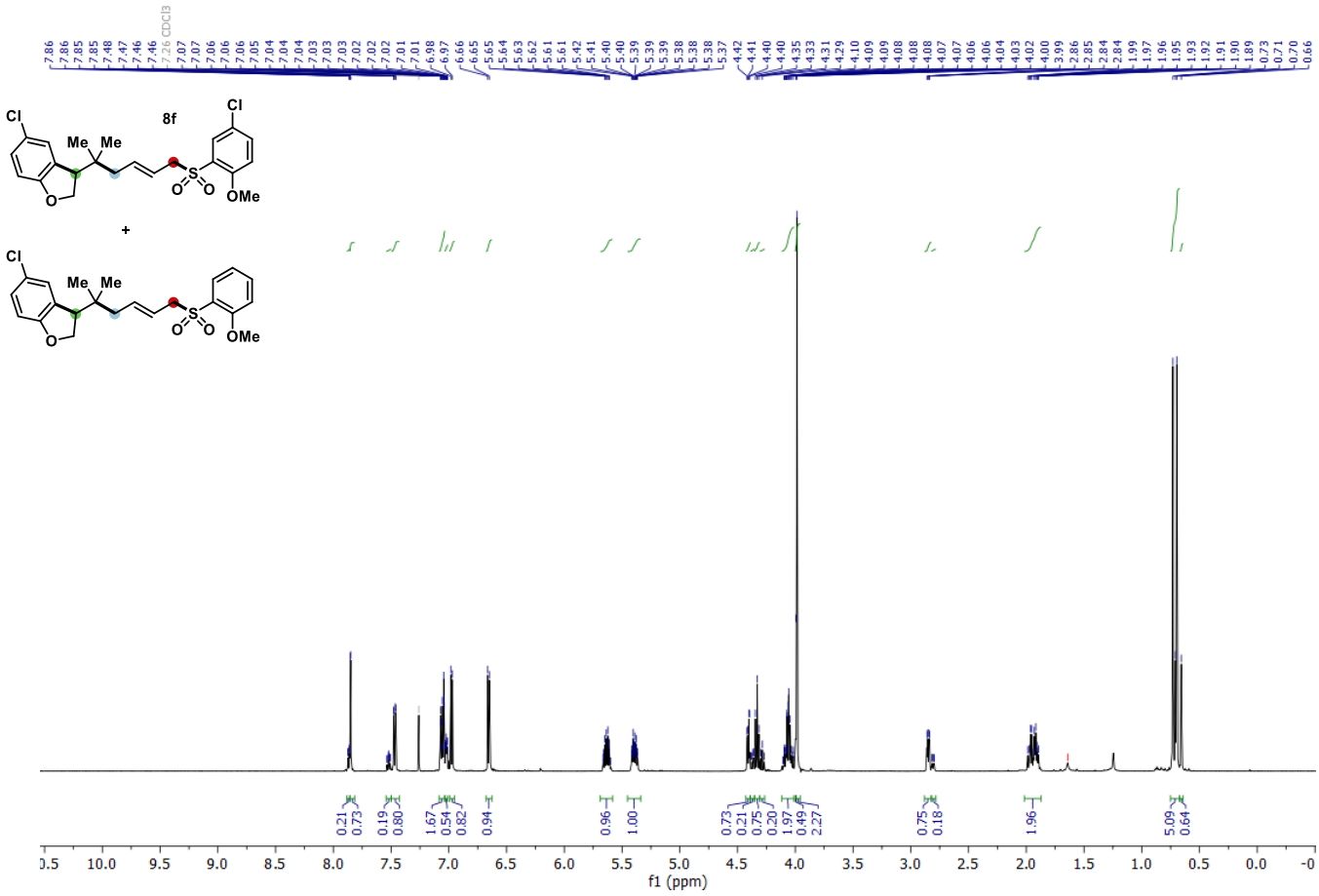
^{1}H NMR (400 MHz, $CDCl_3$)



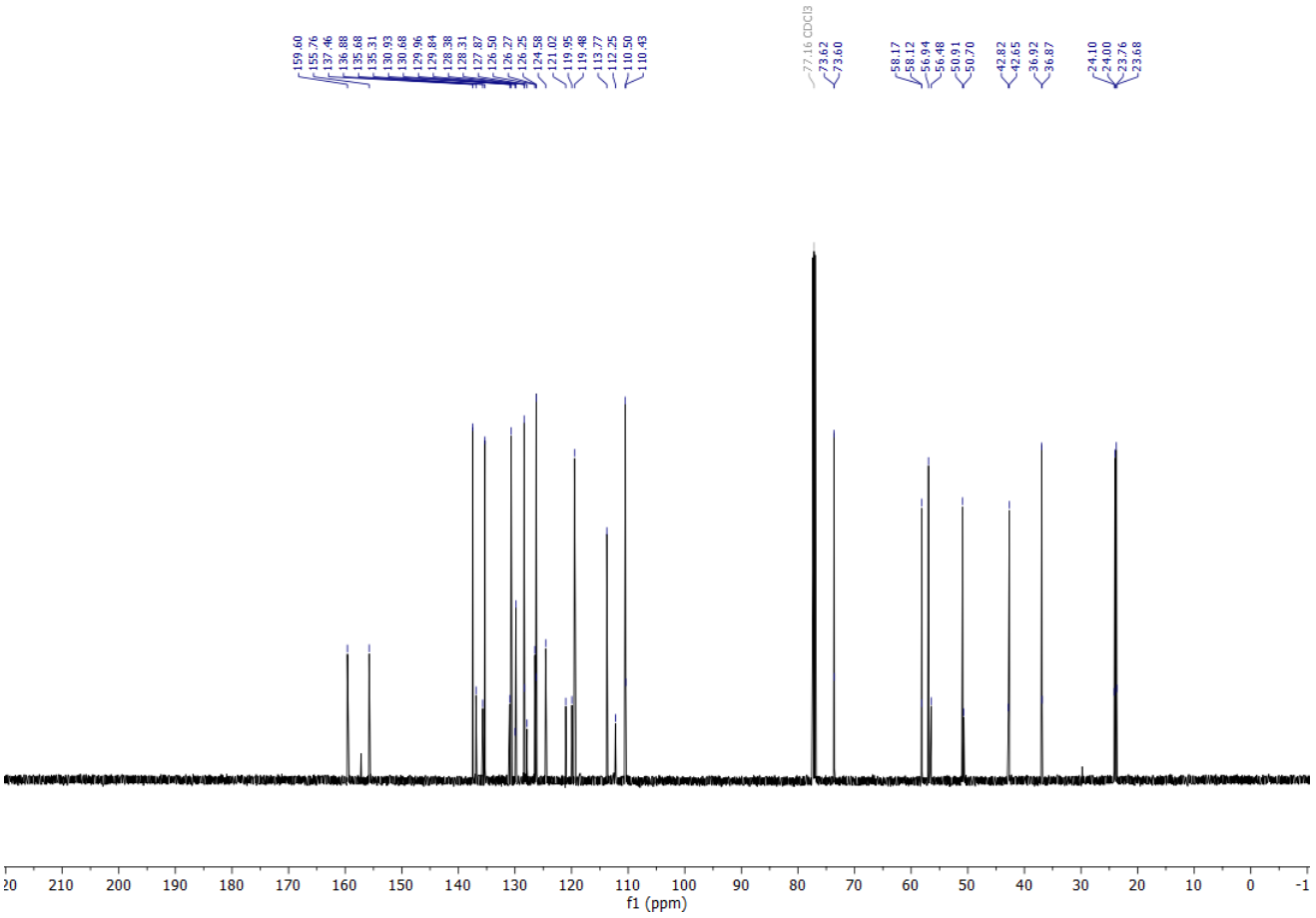
^{13}C NMR (101 MHz, $CDCl_3$)



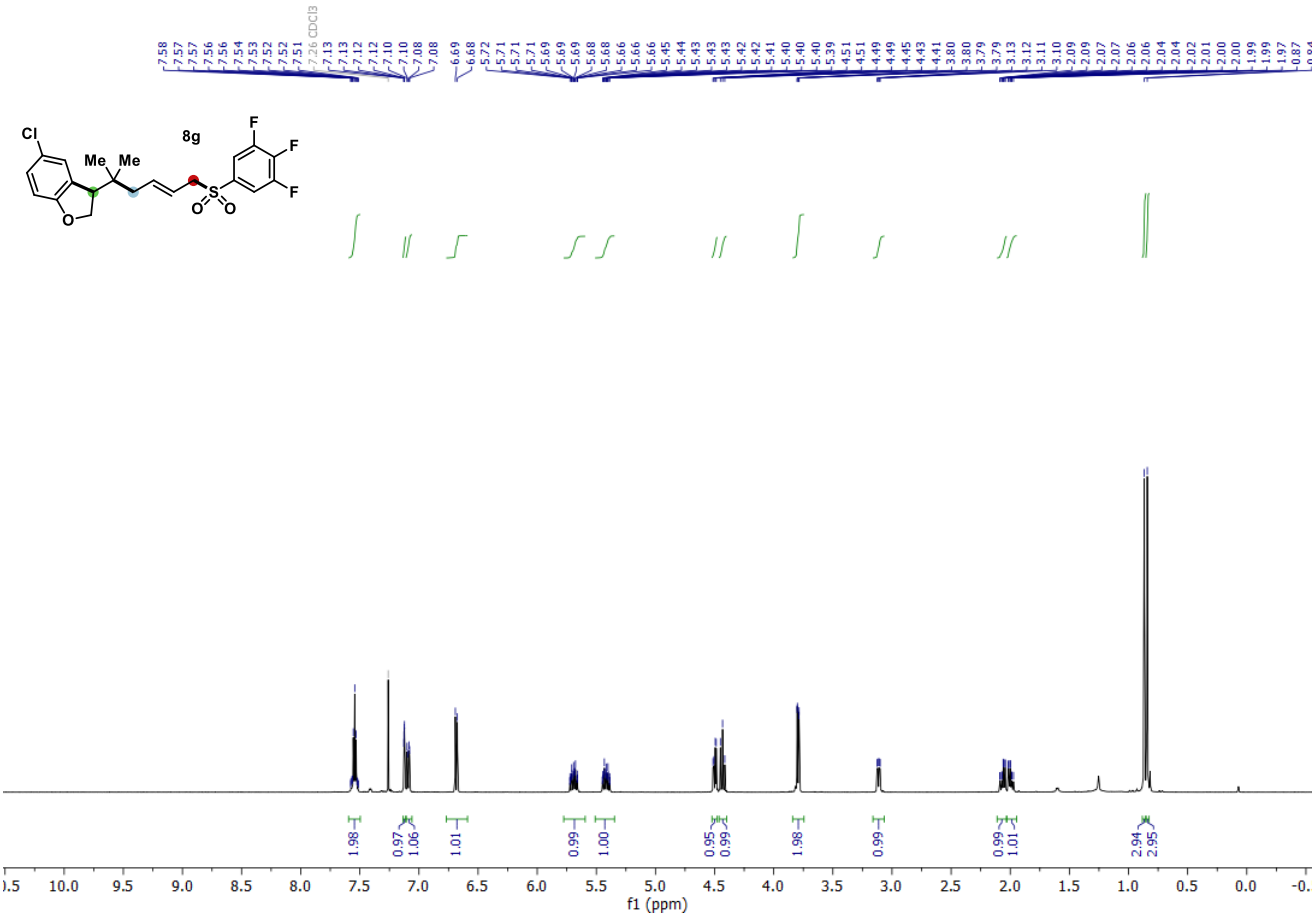
^{1}H NMR (599 MHz, $CDCl_3$)



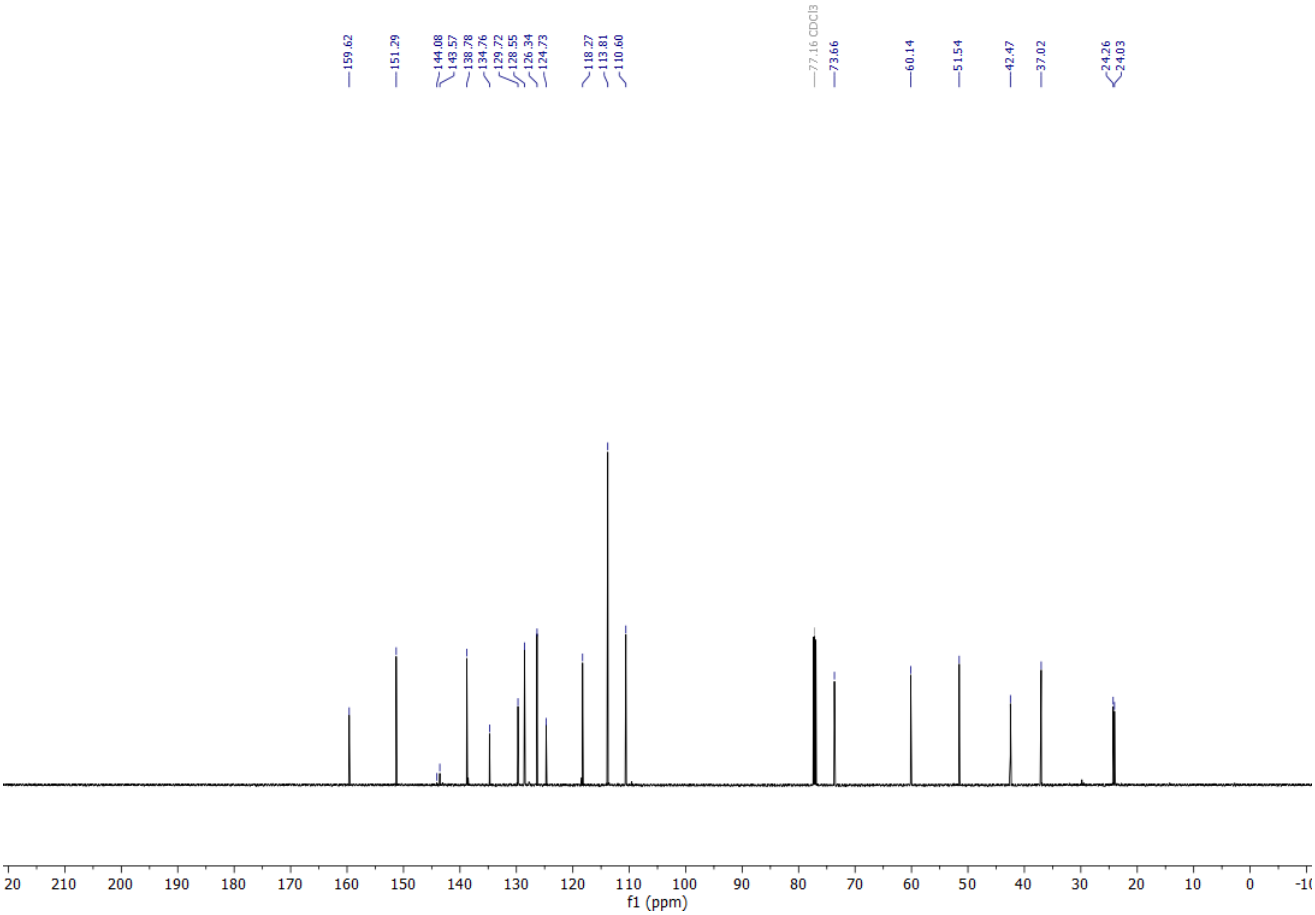
^{13}C NMR (151 MHz, $CDCl_3$)



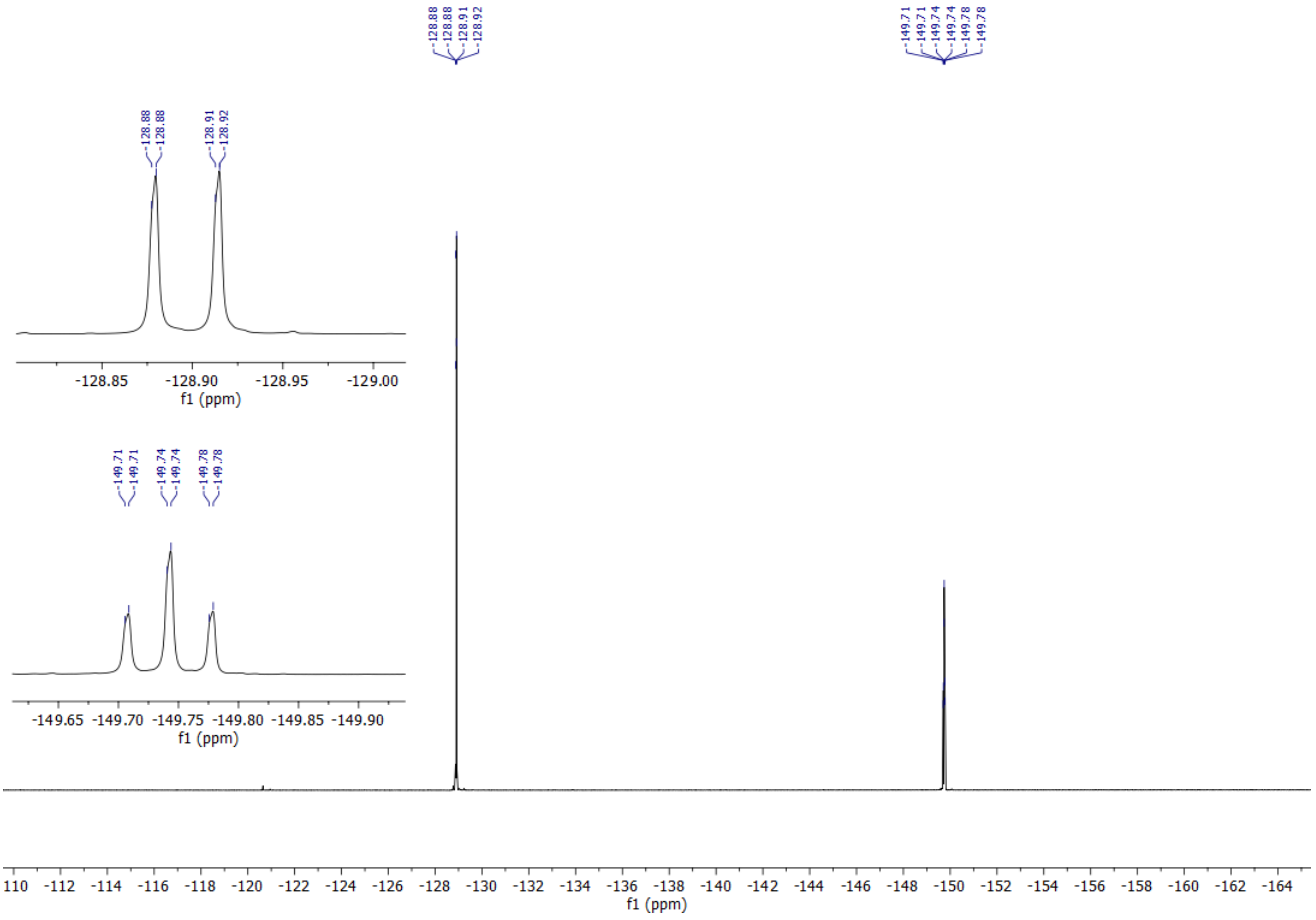
^{1}H NMR (500 MHz, $CDCl_3$)



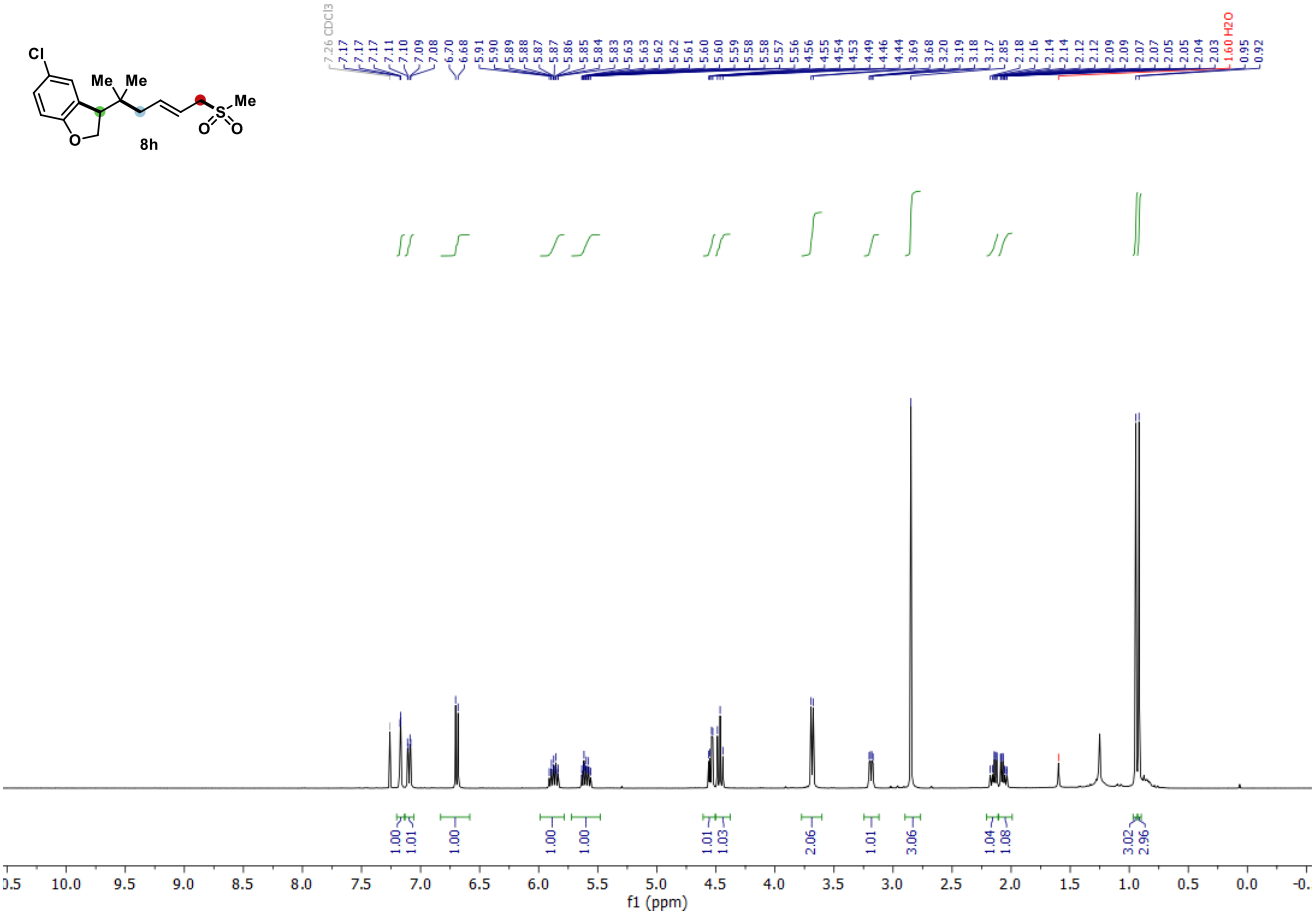
^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$)



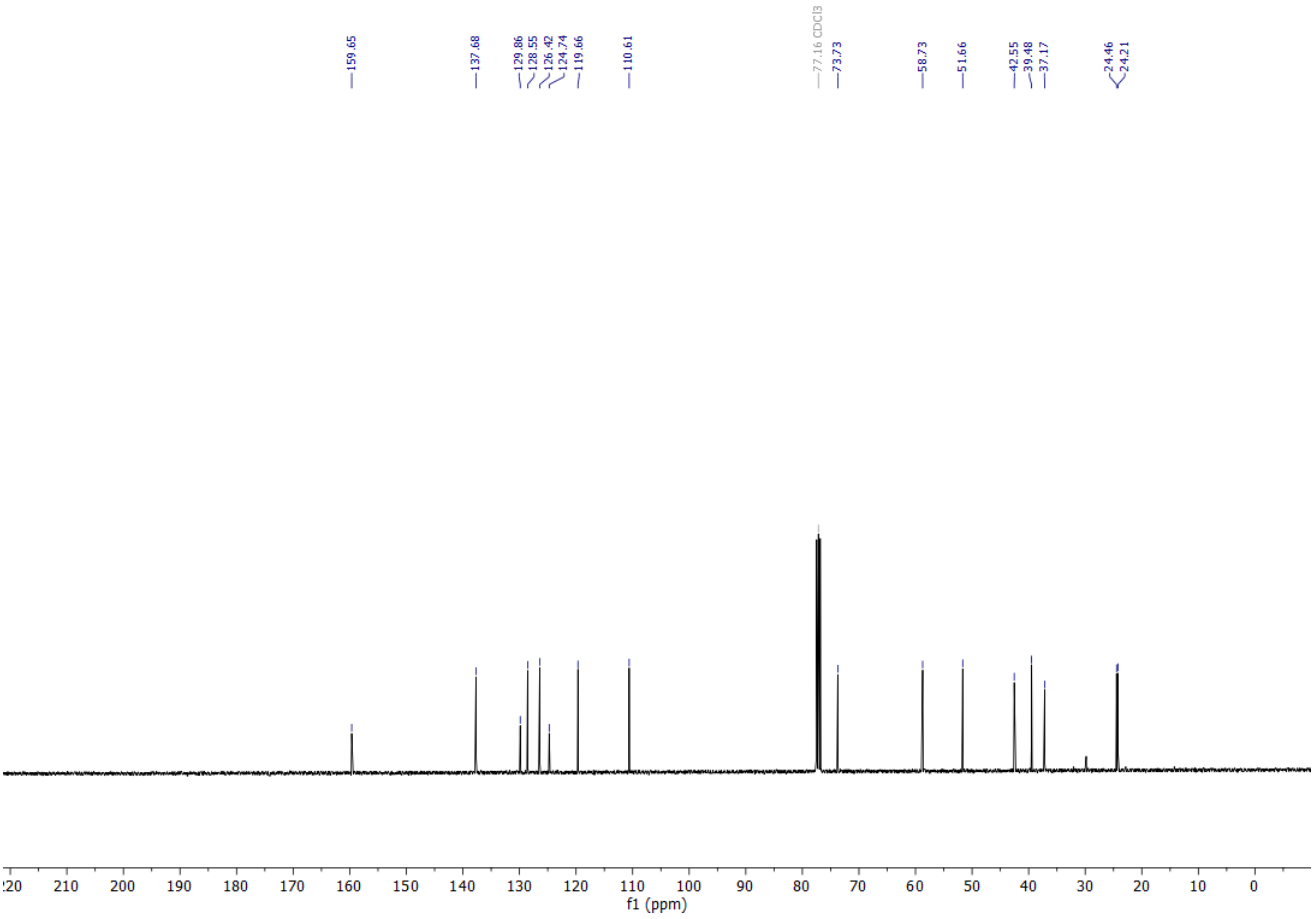
$^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$)



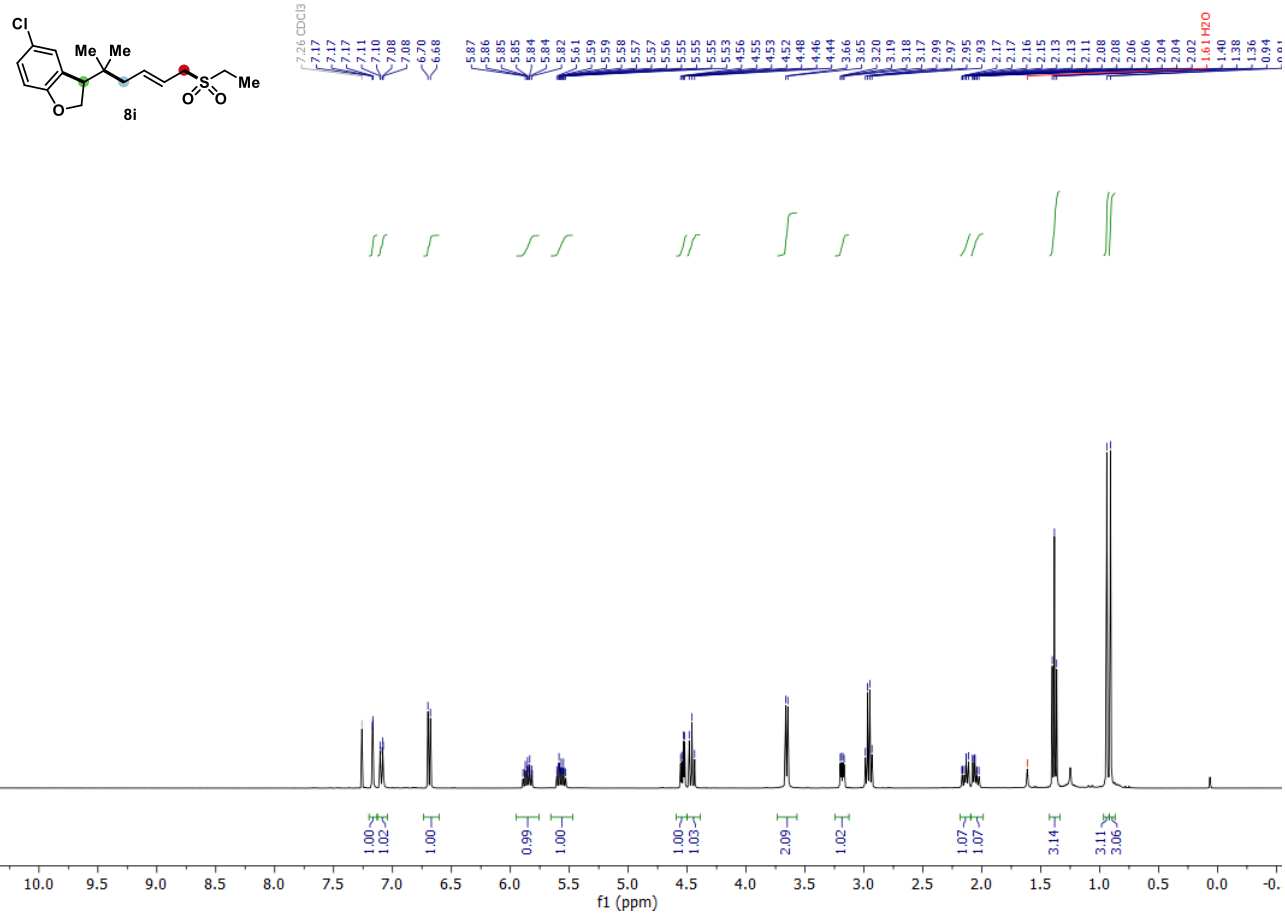
^{1}H NMR (400 MHz, $CDCl_3$)



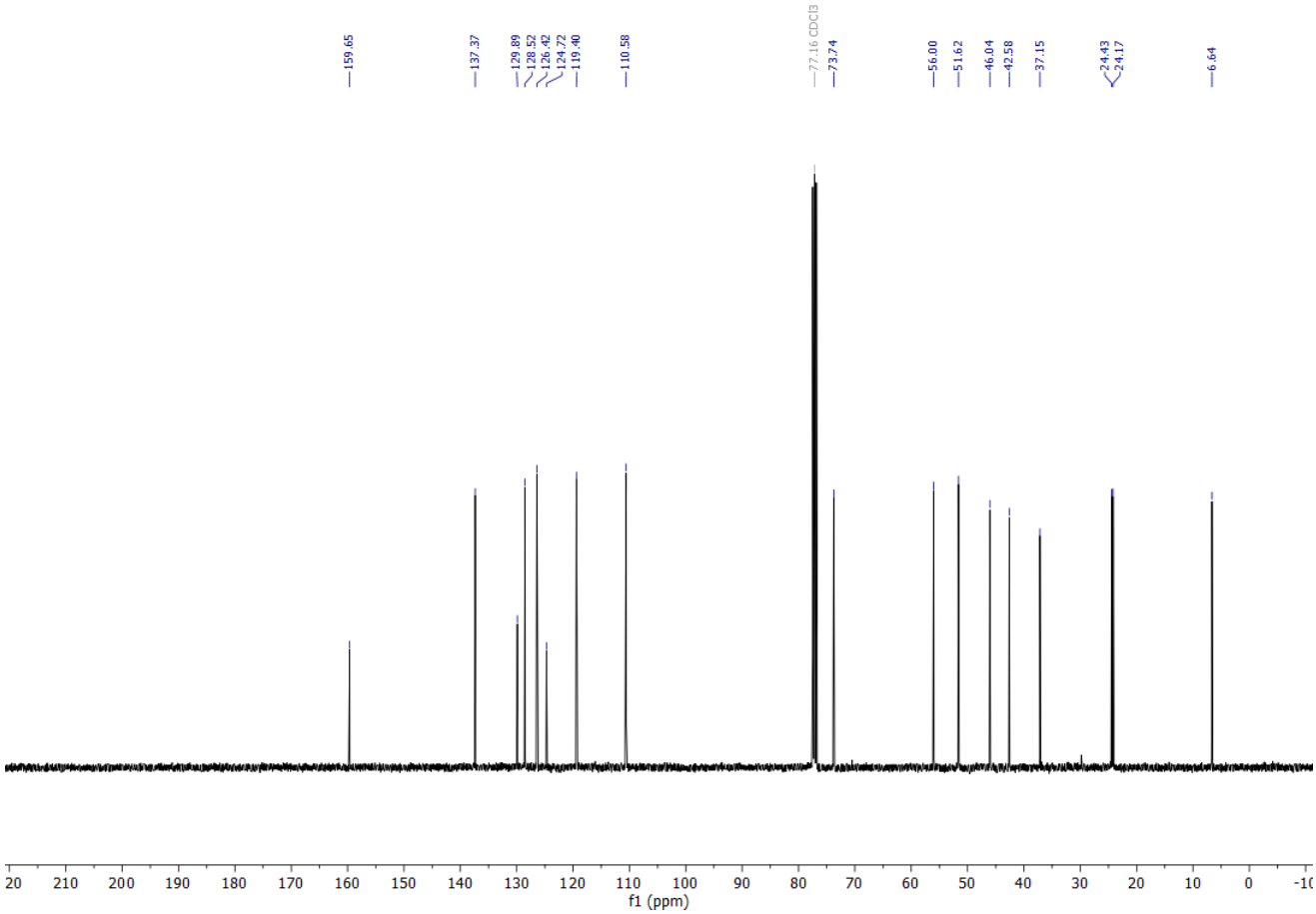
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

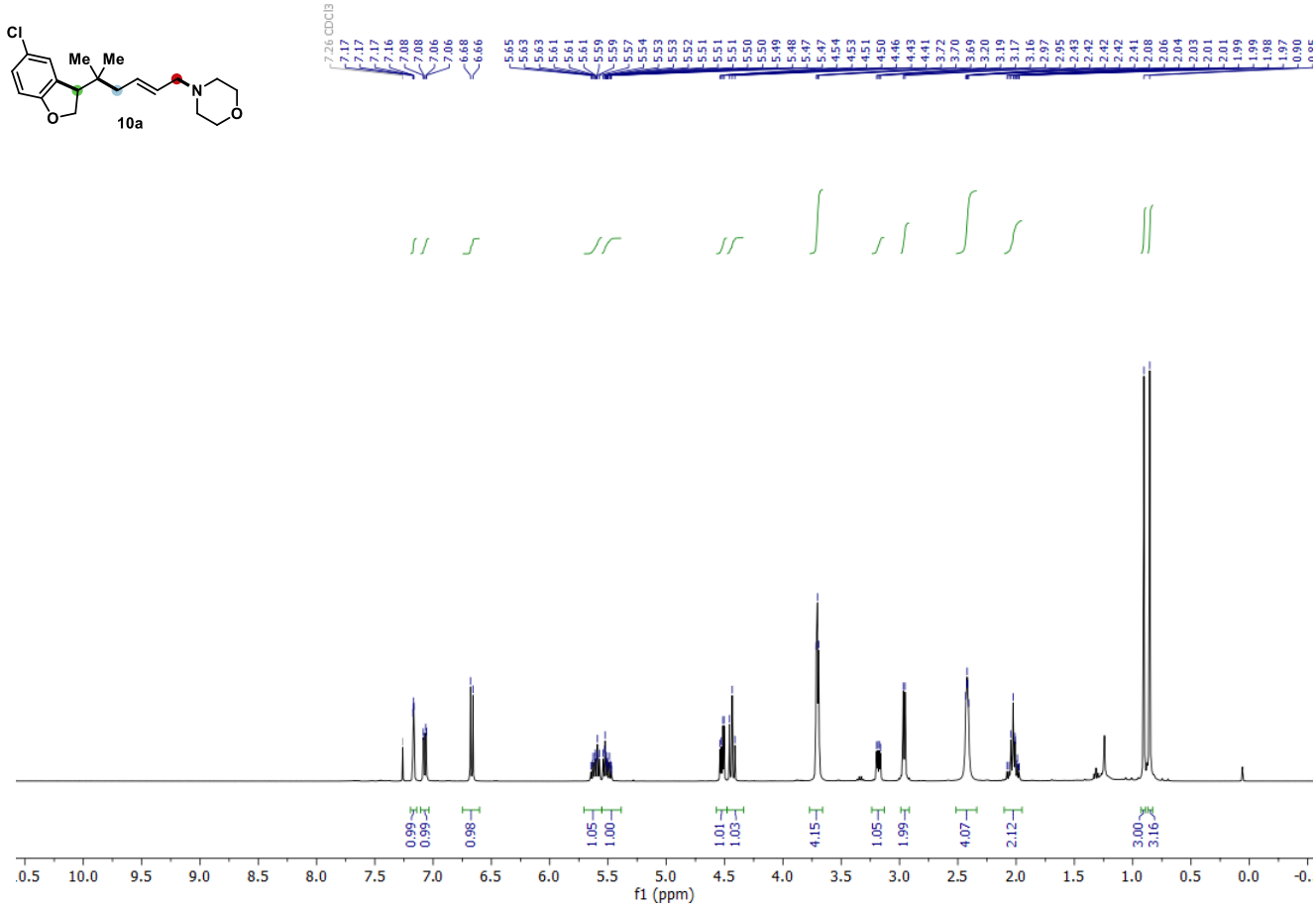


^{13}C NMR (101 MHz, $CDCl_3$)

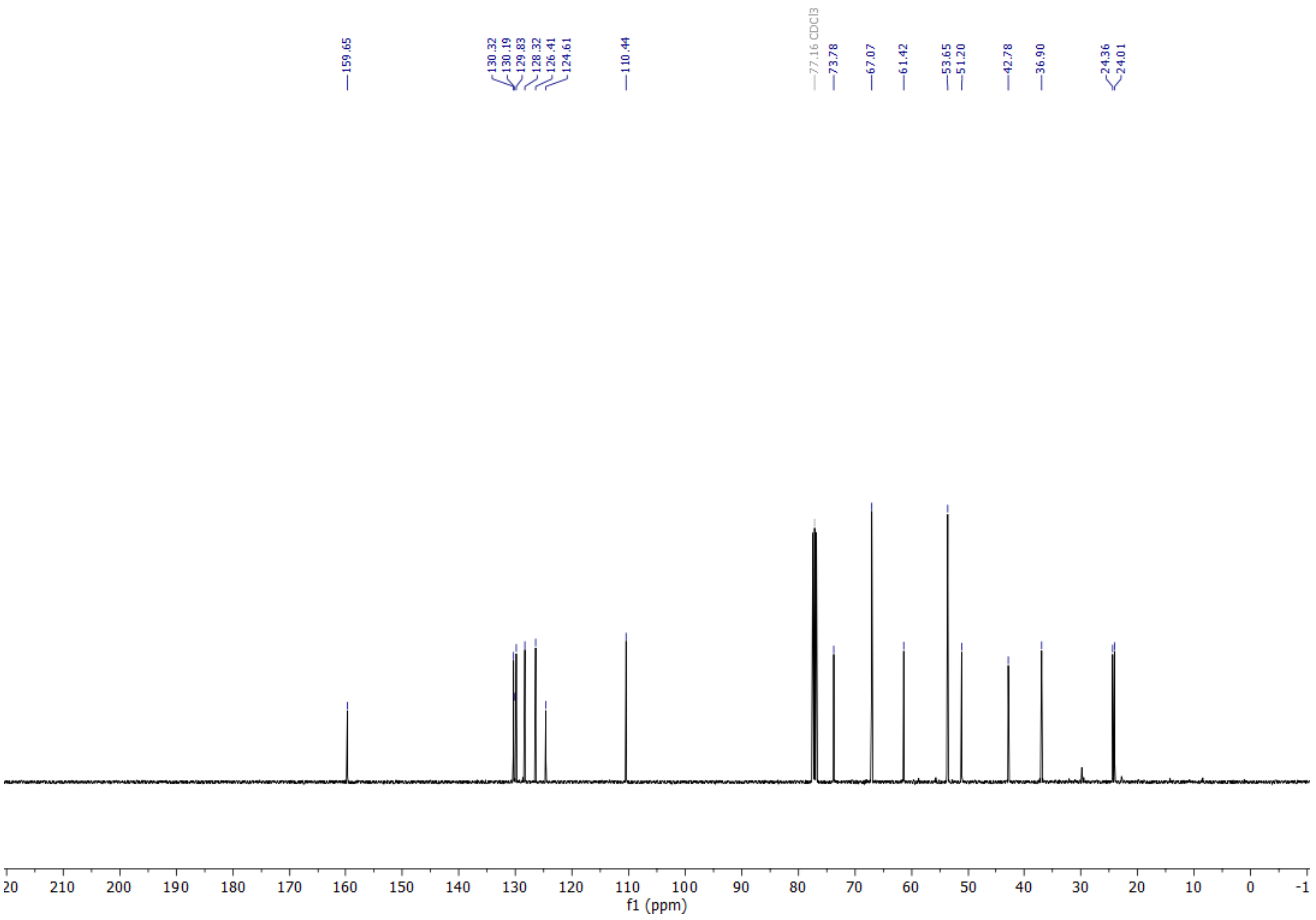


NMR spectra of products 10a-l

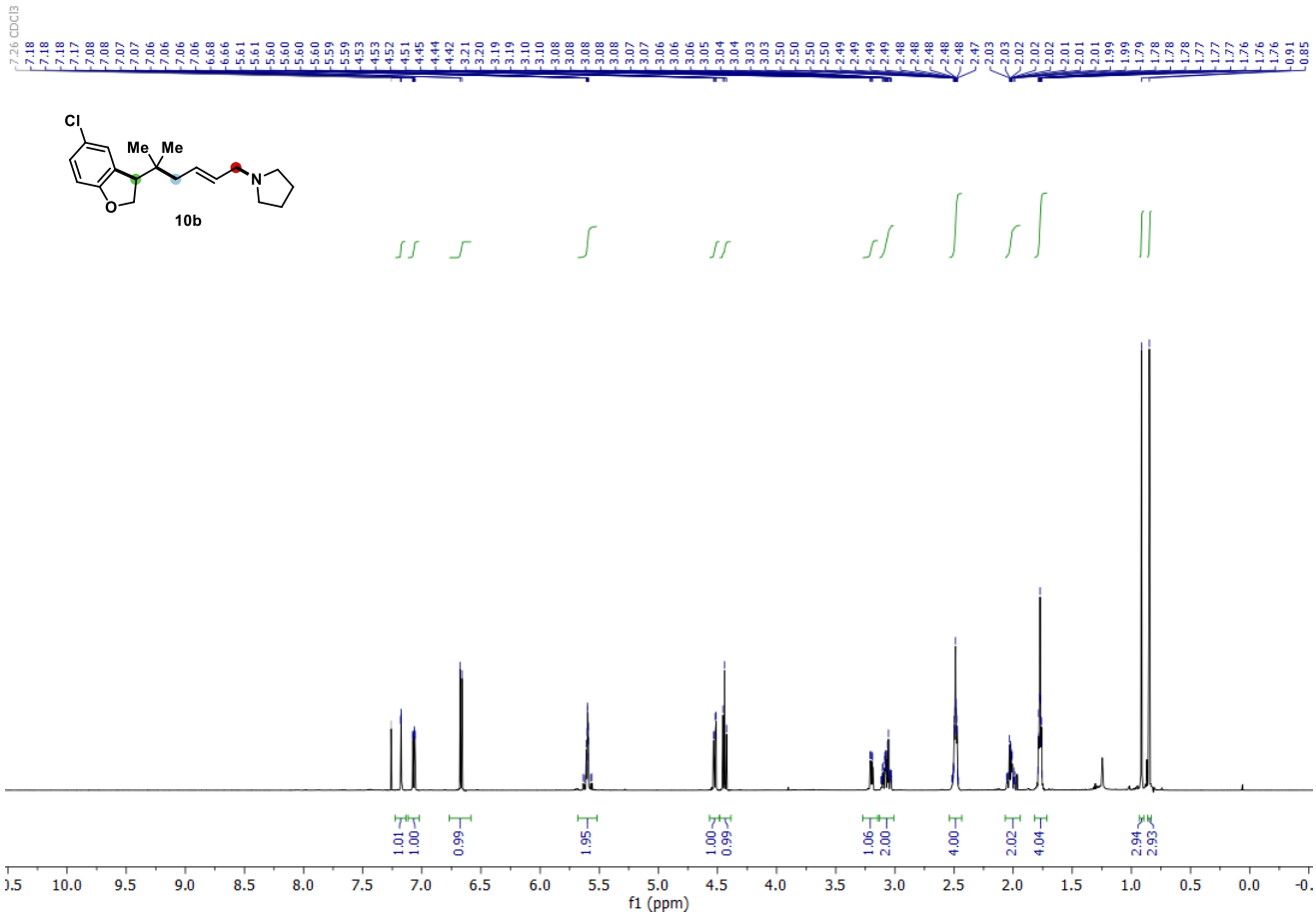
^{1}H NMR (400 MHz, $CDCl_3$)



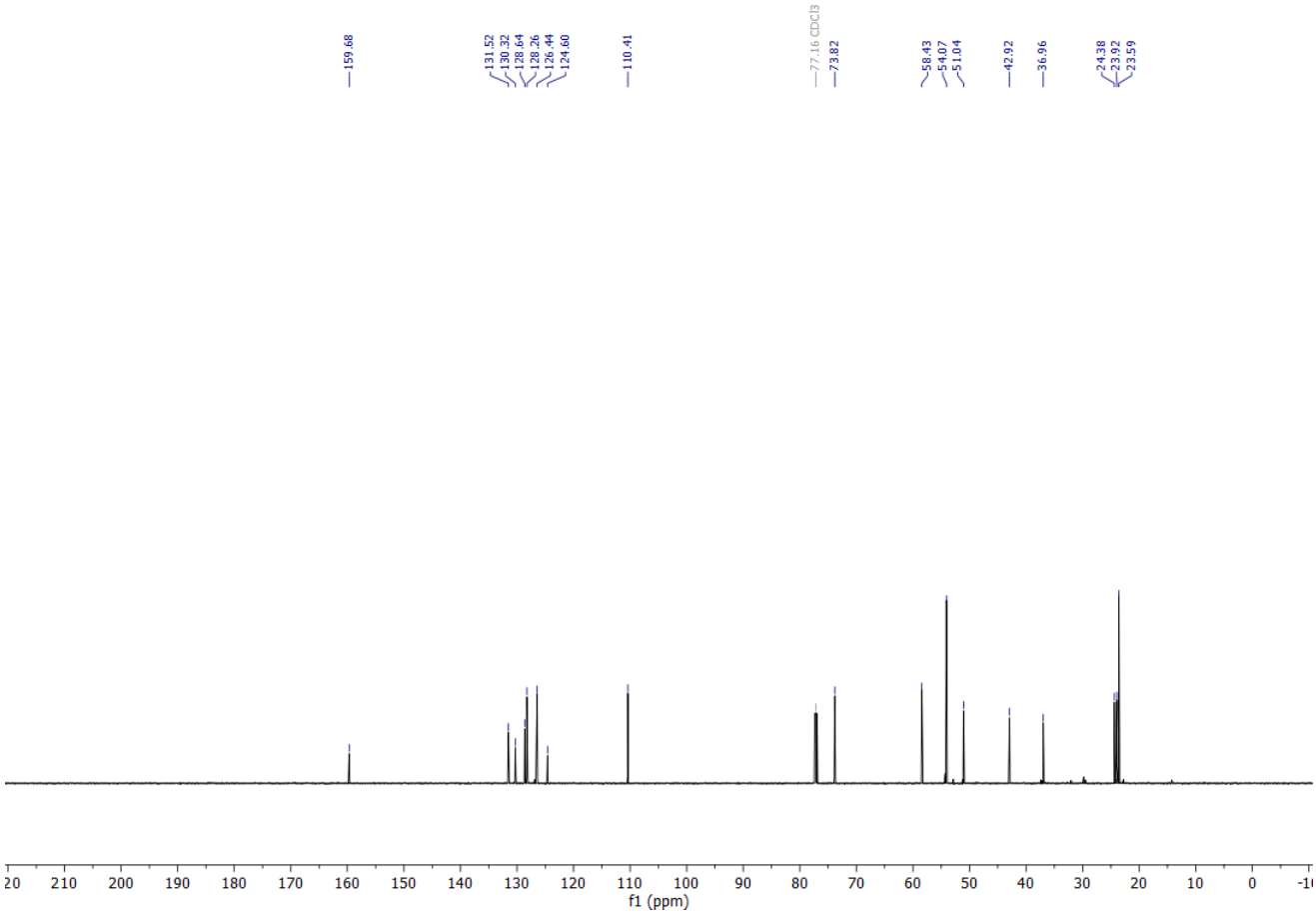
^{13}C NMR (101 MHz, $CDCl_3$)



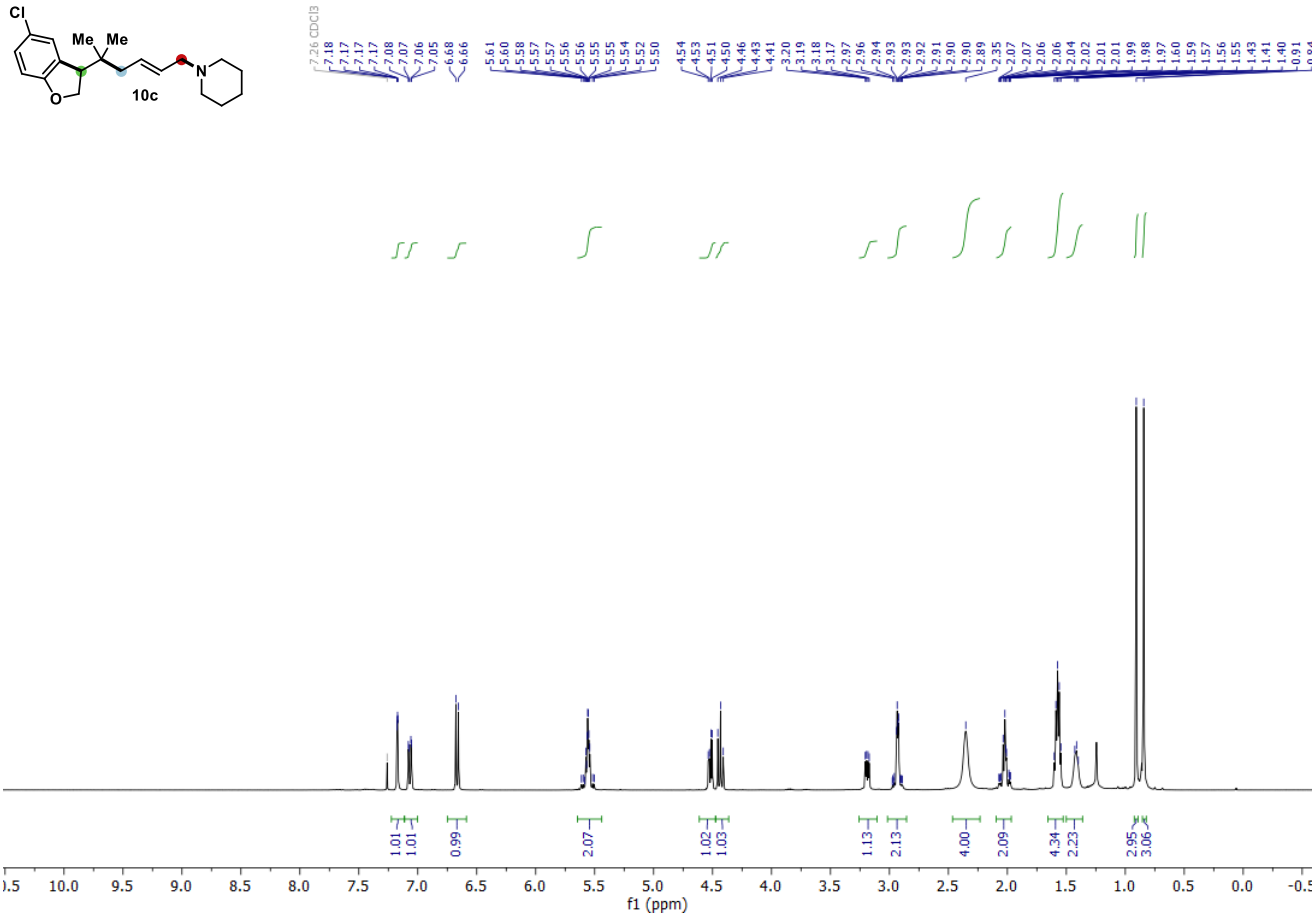
^{1}H NMR (599 MHz, $CDCl_3$)



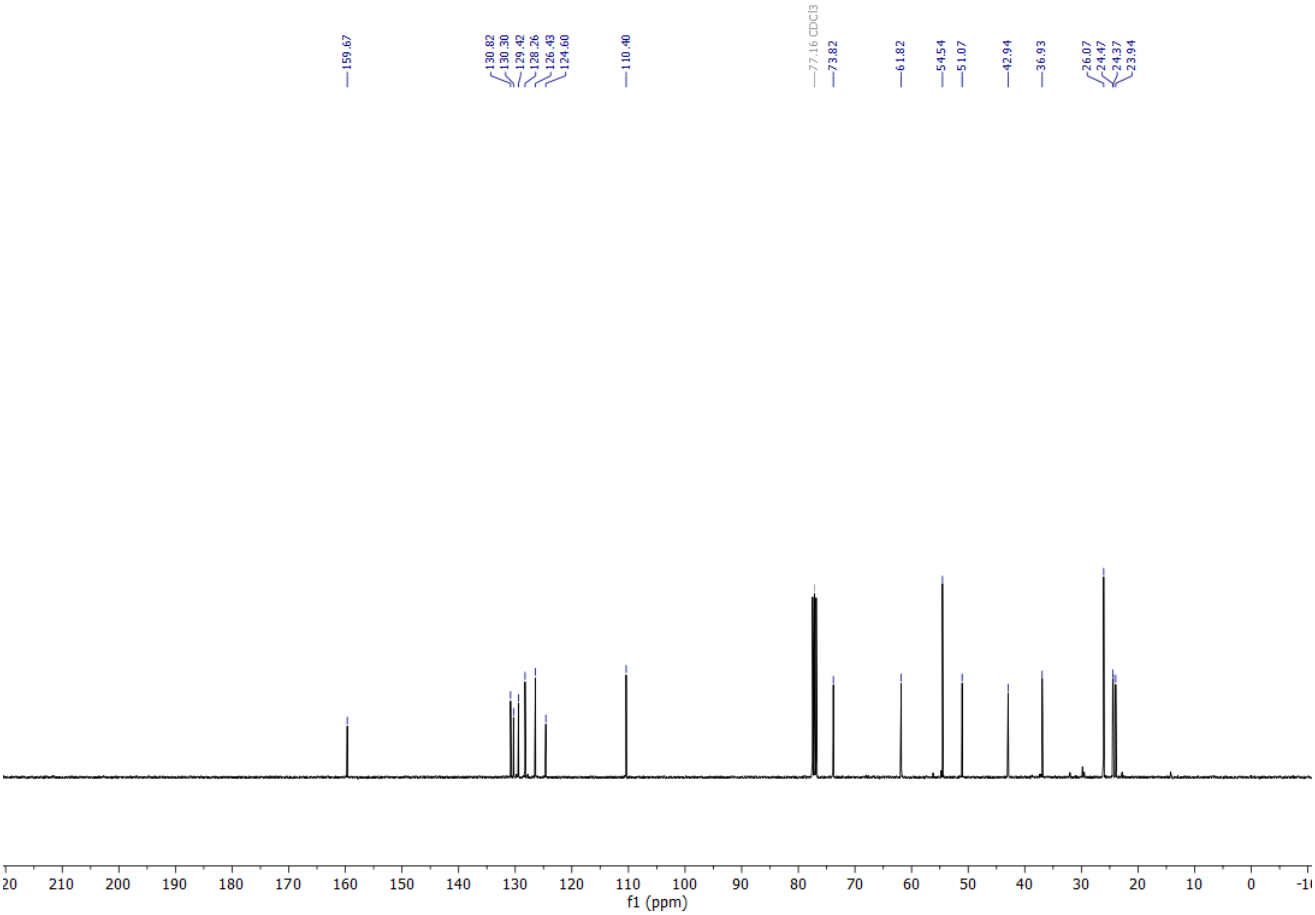
^{13}C NMR (151 MHz, $CDCl_3$)



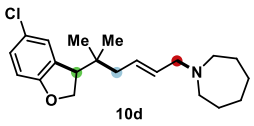
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

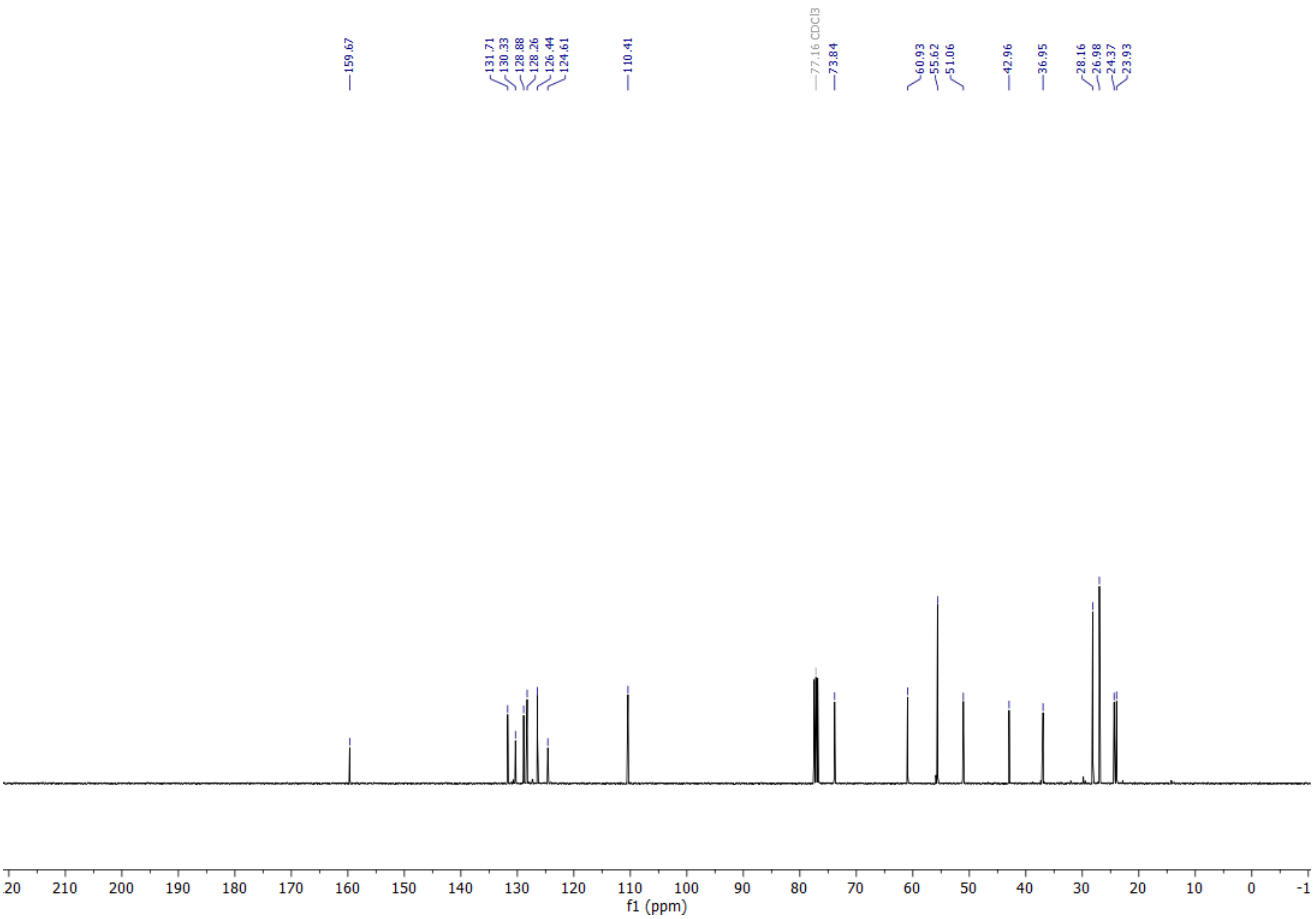


^{1}H NMR (400 MHz, $CDCl_3$)

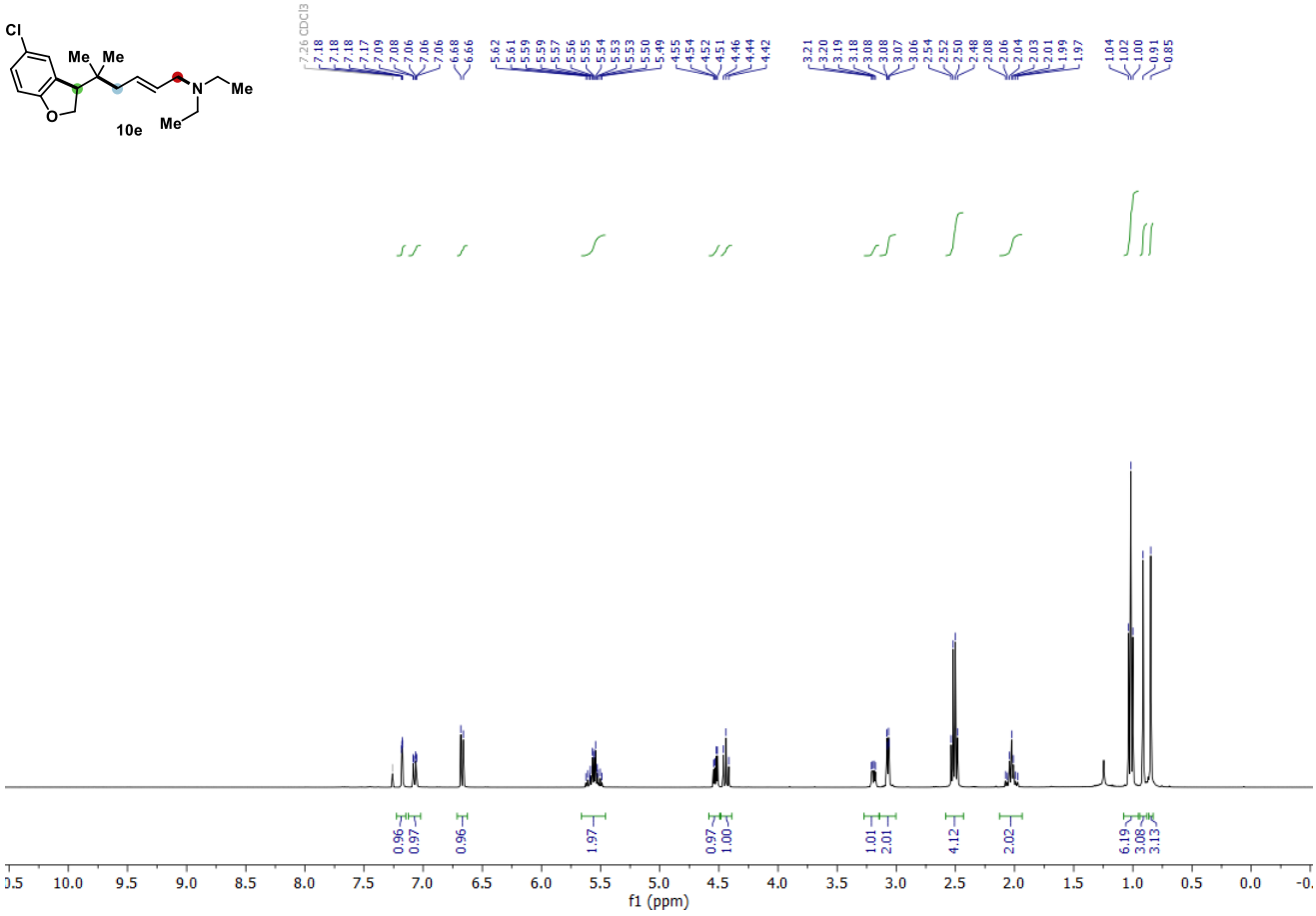


10d

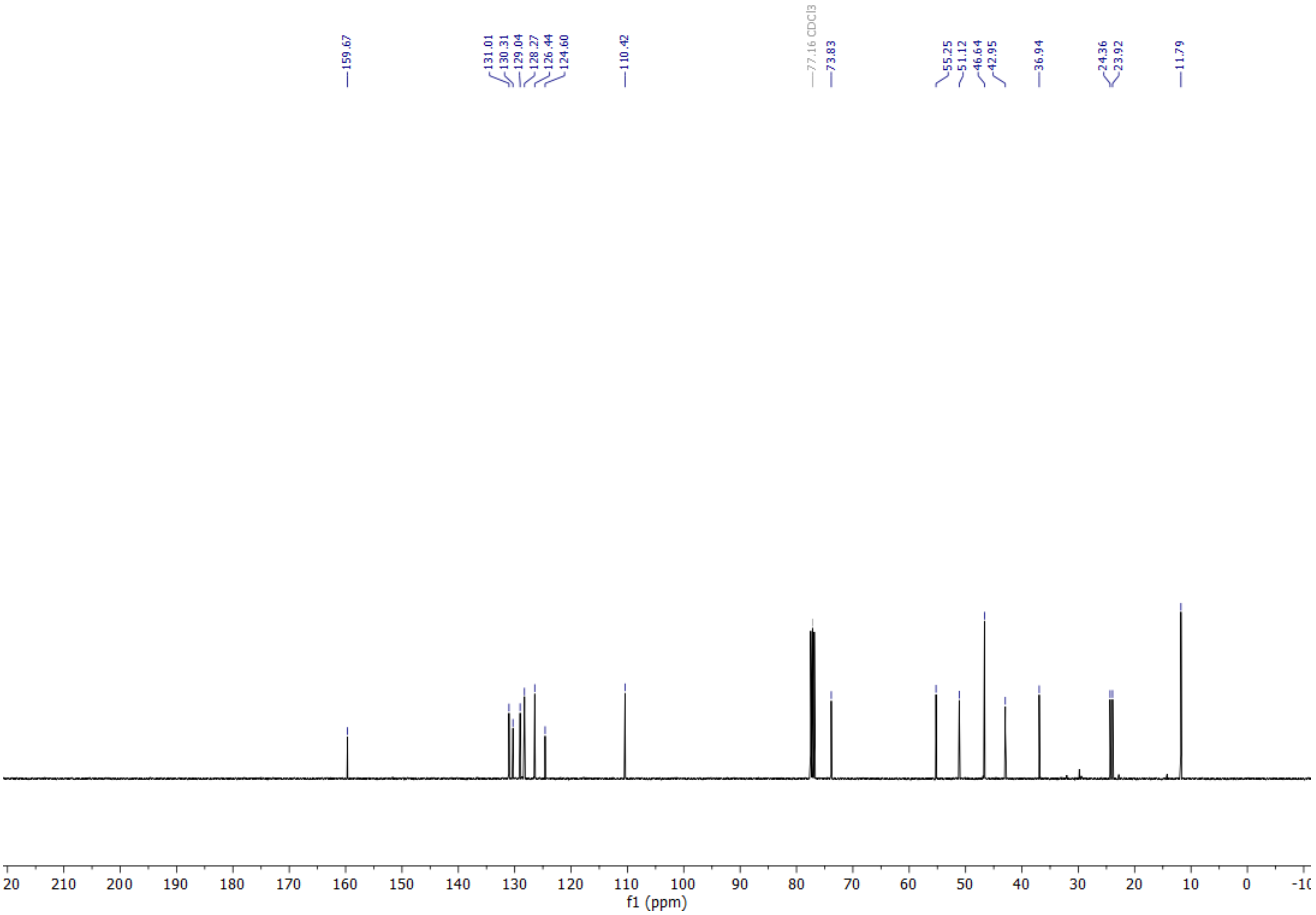
^{13}C NMR (101 MHz, $CDCl_3$)



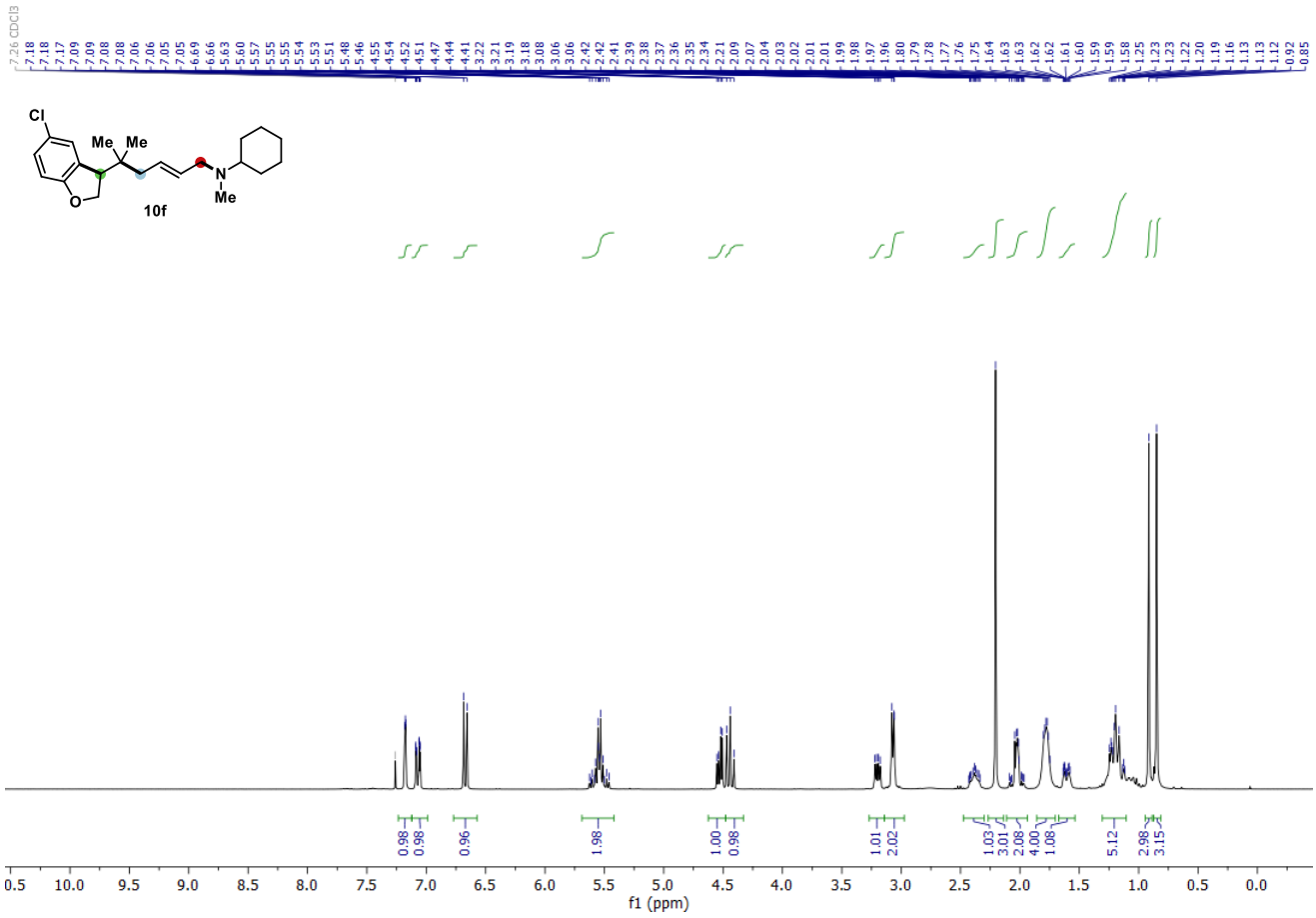
^{1}H NMR (400 MHz, $CDCl_3$)



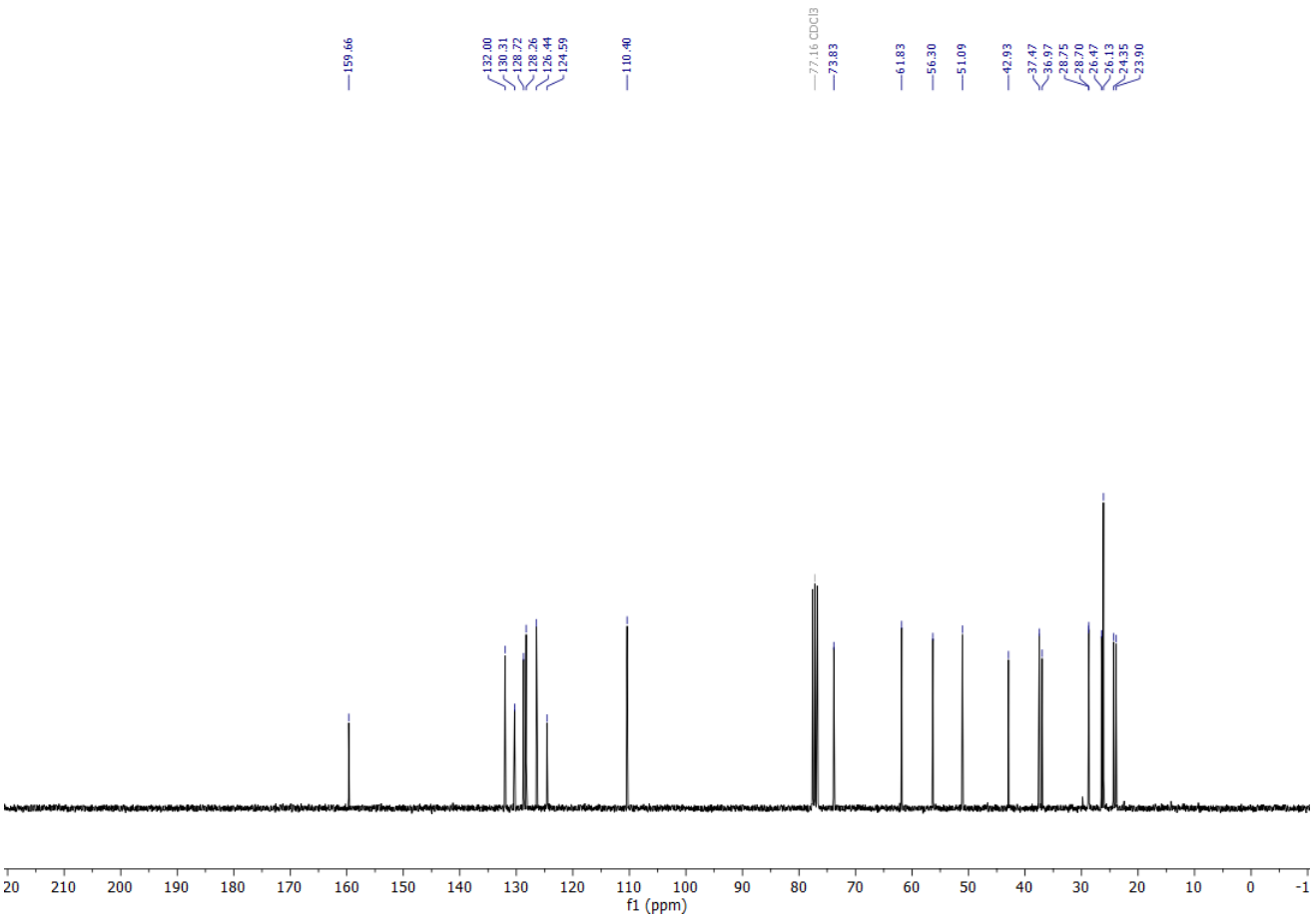
^{13}C NMR (101 MHz, $CDCl_3$)



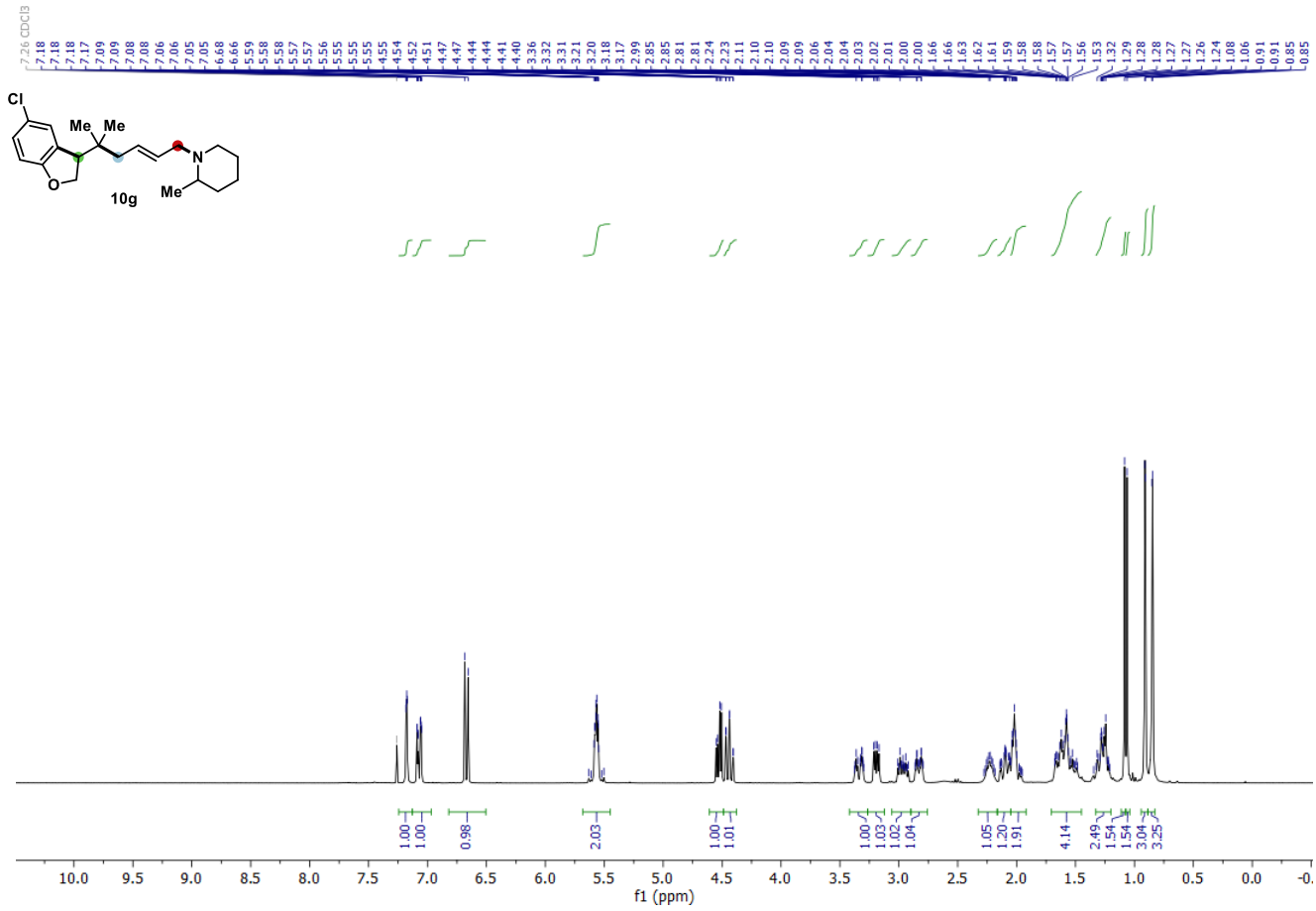
^{1}H NMR (300 MHz, $CDCl_3$)



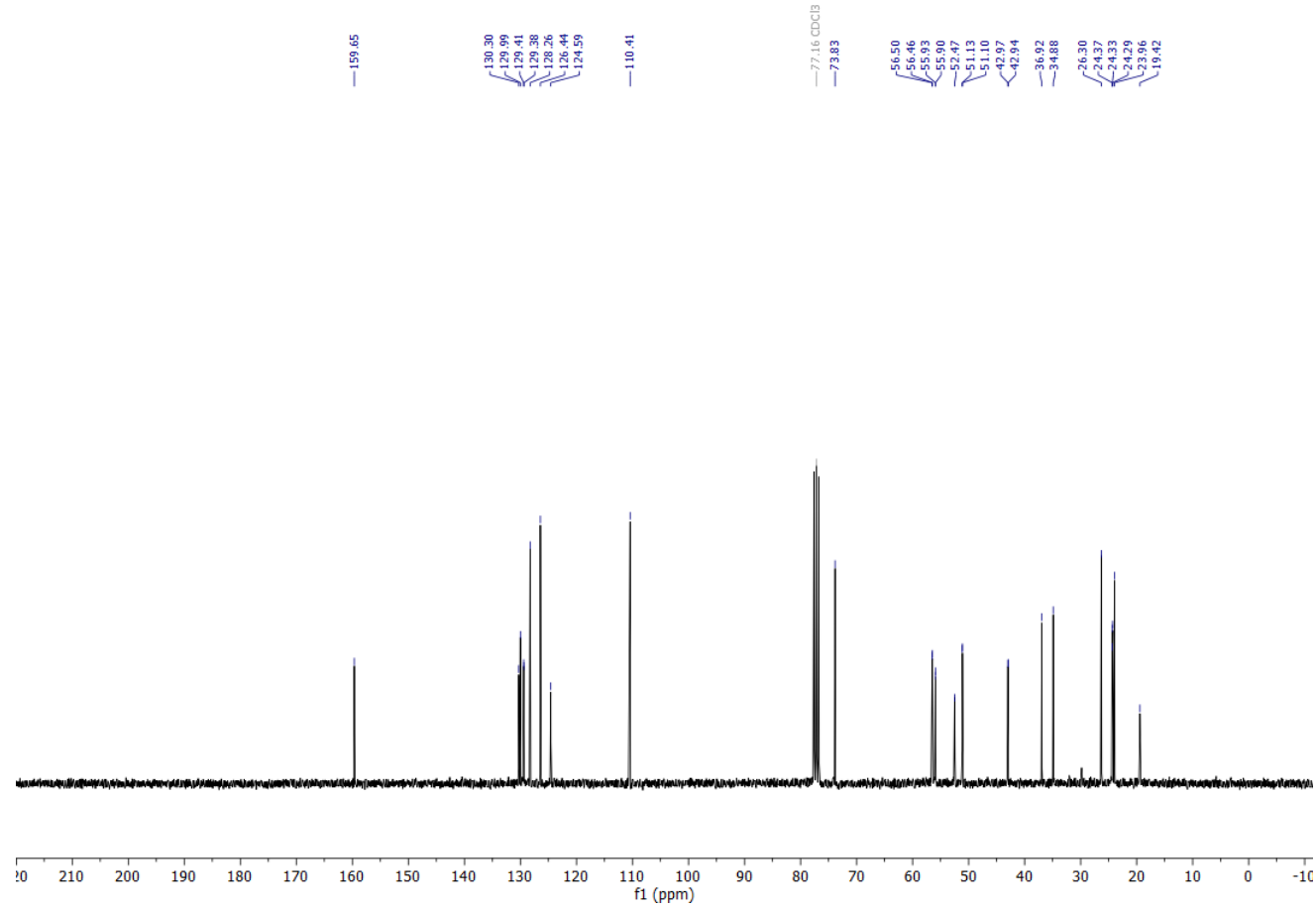
^{13}C NMR (75 MHz, $CDCl_3$)



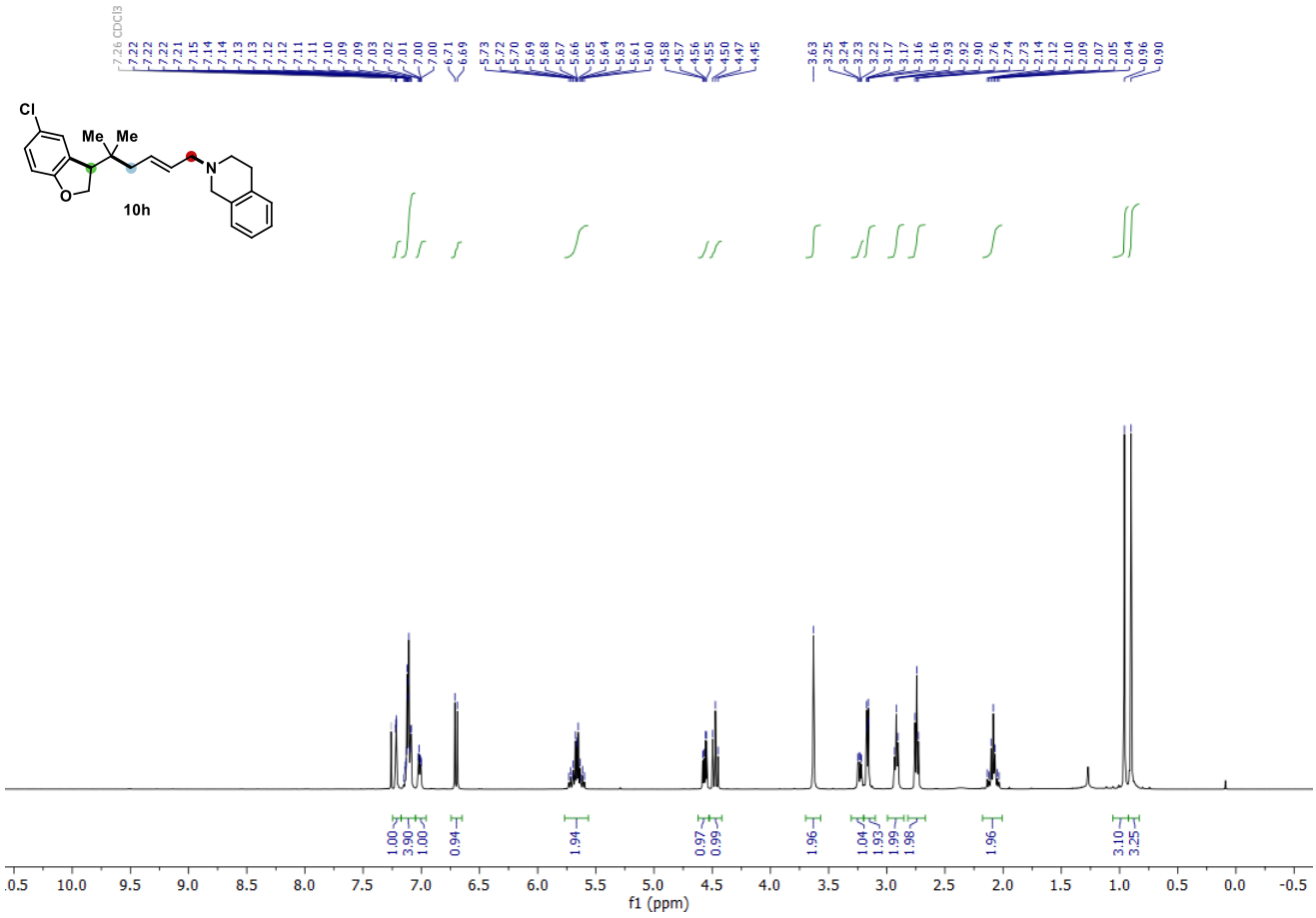
^{1}H NMR (300 MHz, $CDCl_3$)



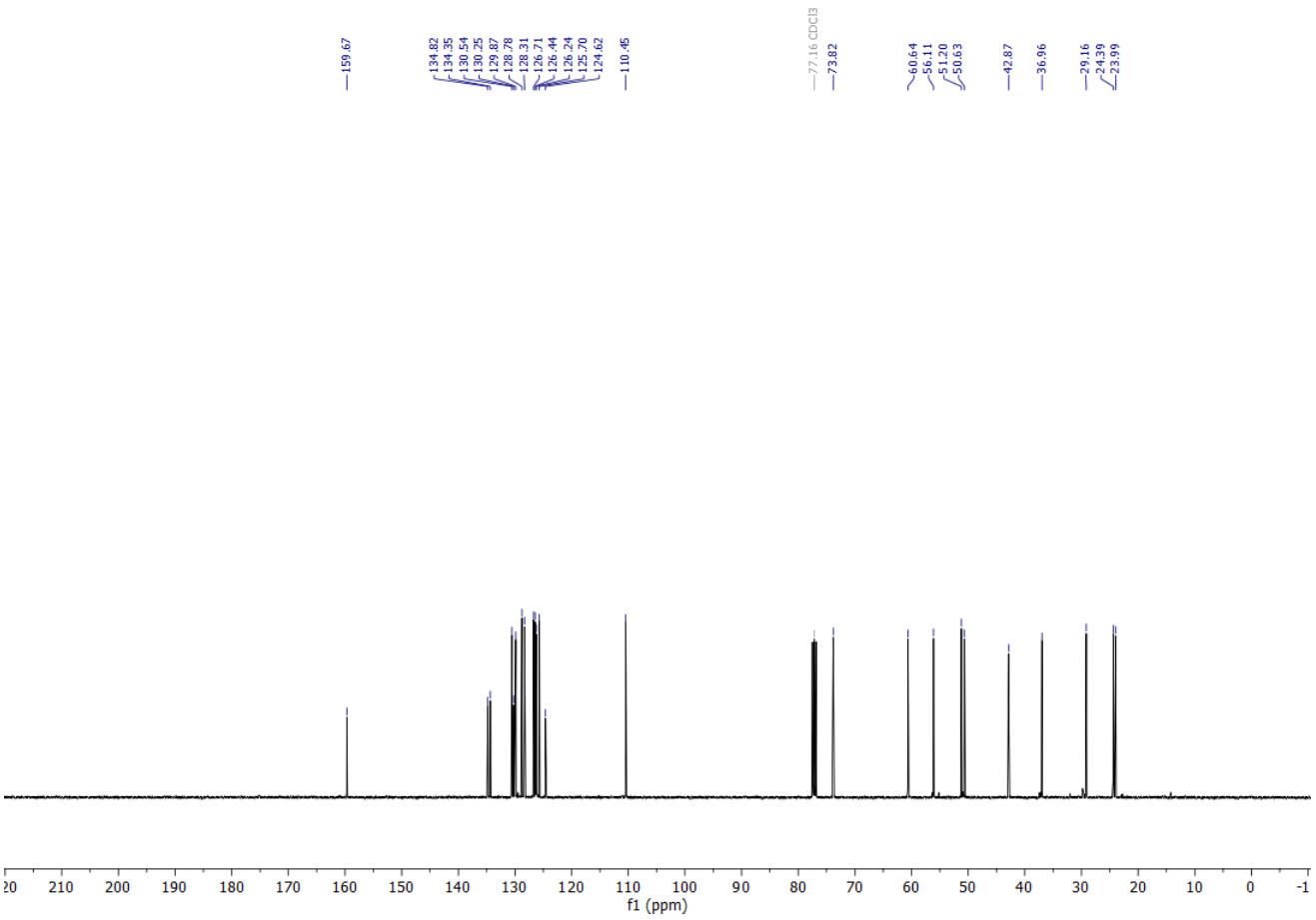
^{13}C NMR (75 MHz, $CDCl_3$)



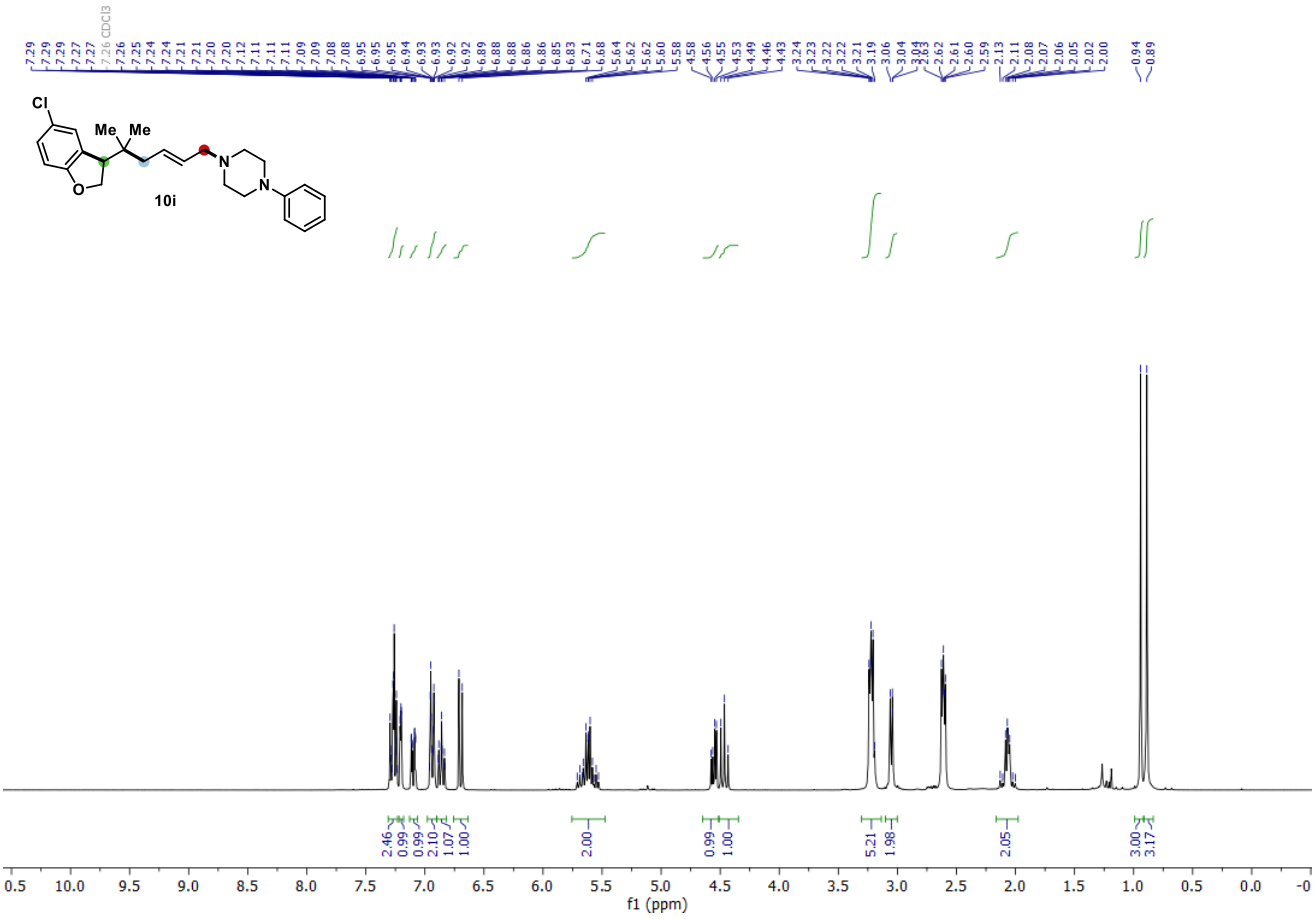
^{1}H NMR (400 MHz, $CDCl_3$)



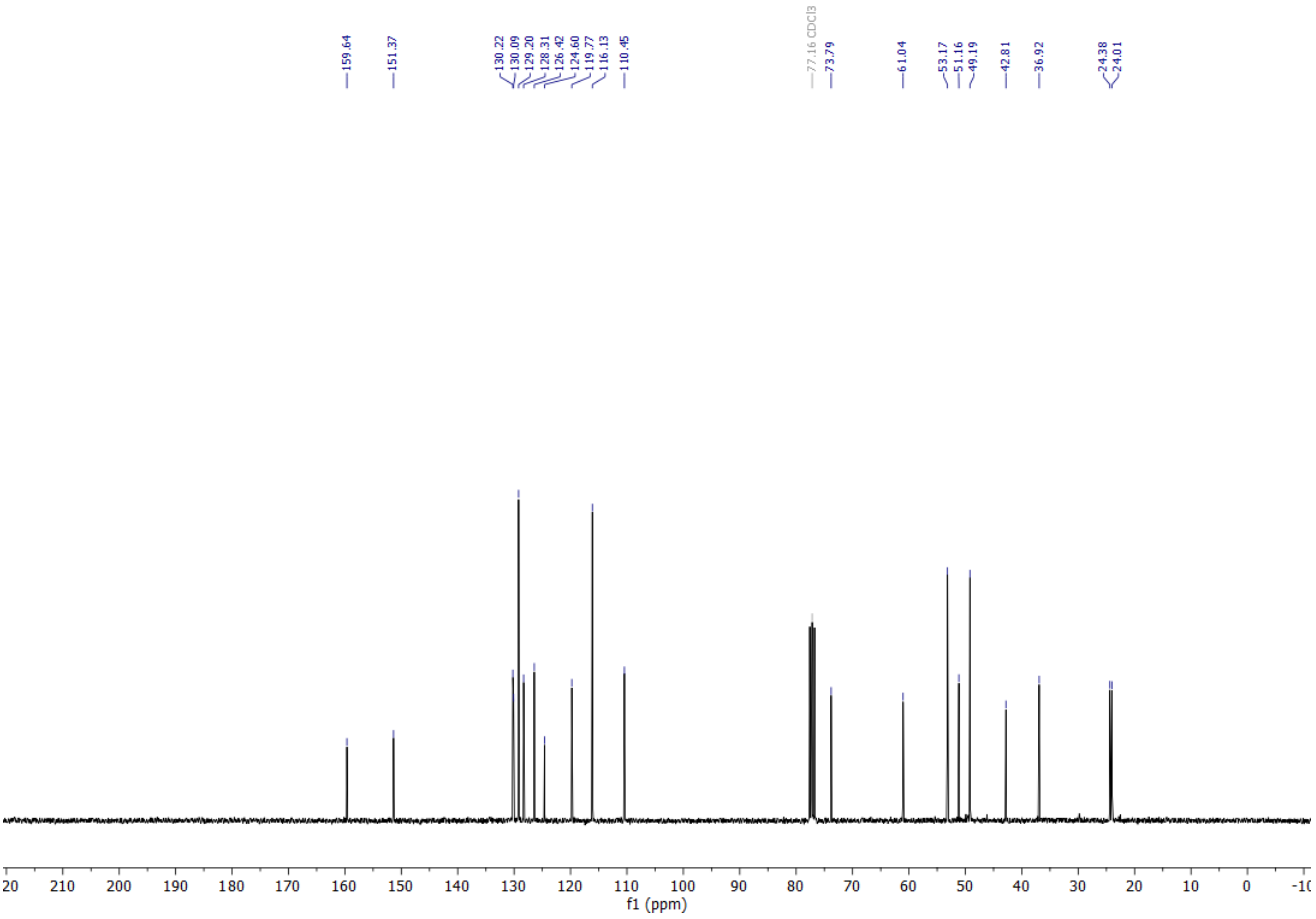
^{13}C NMR (101 MHz, $CDCl_3$)



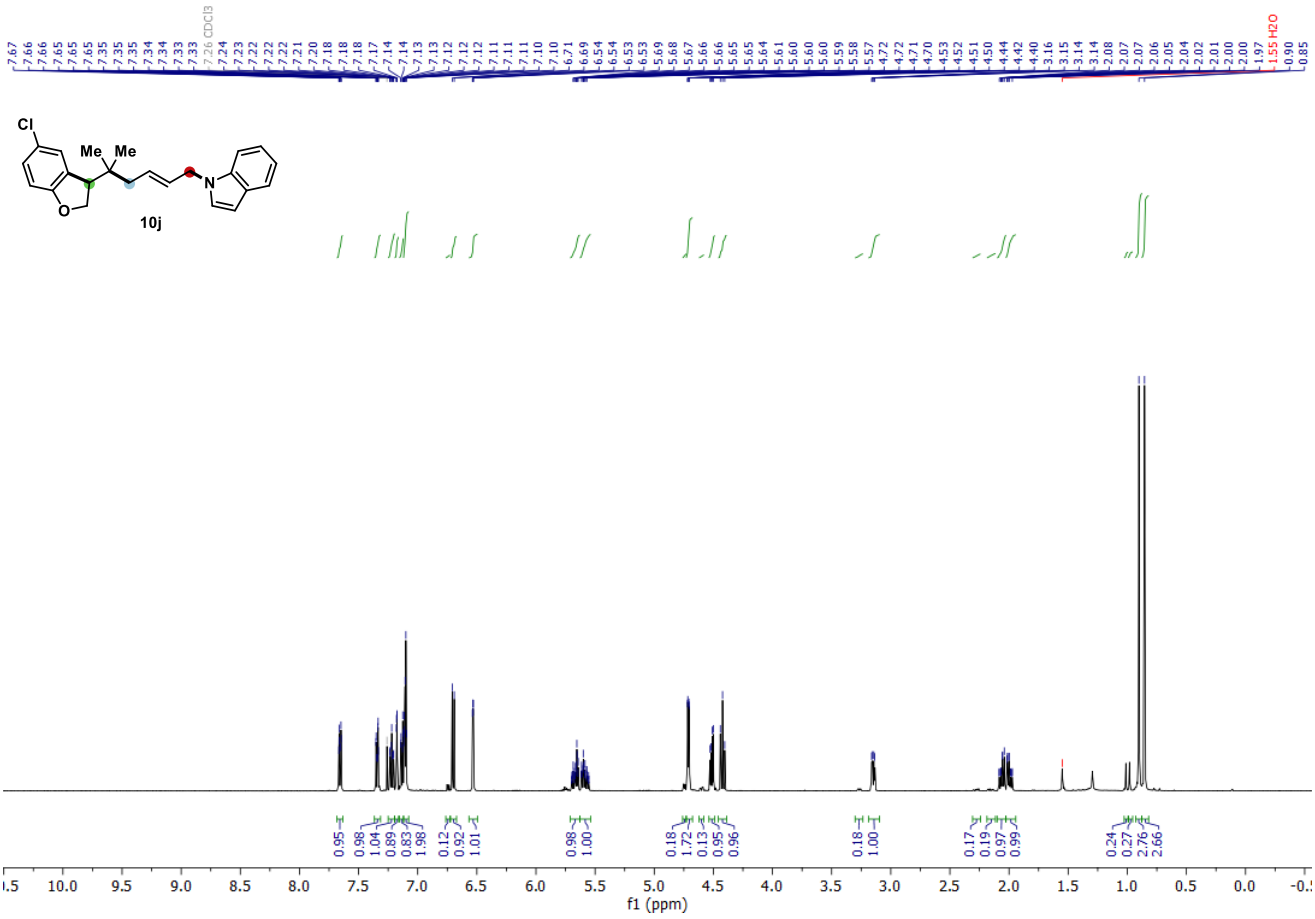
^{1}H NMR (300 MHz, $CDCl_3$)



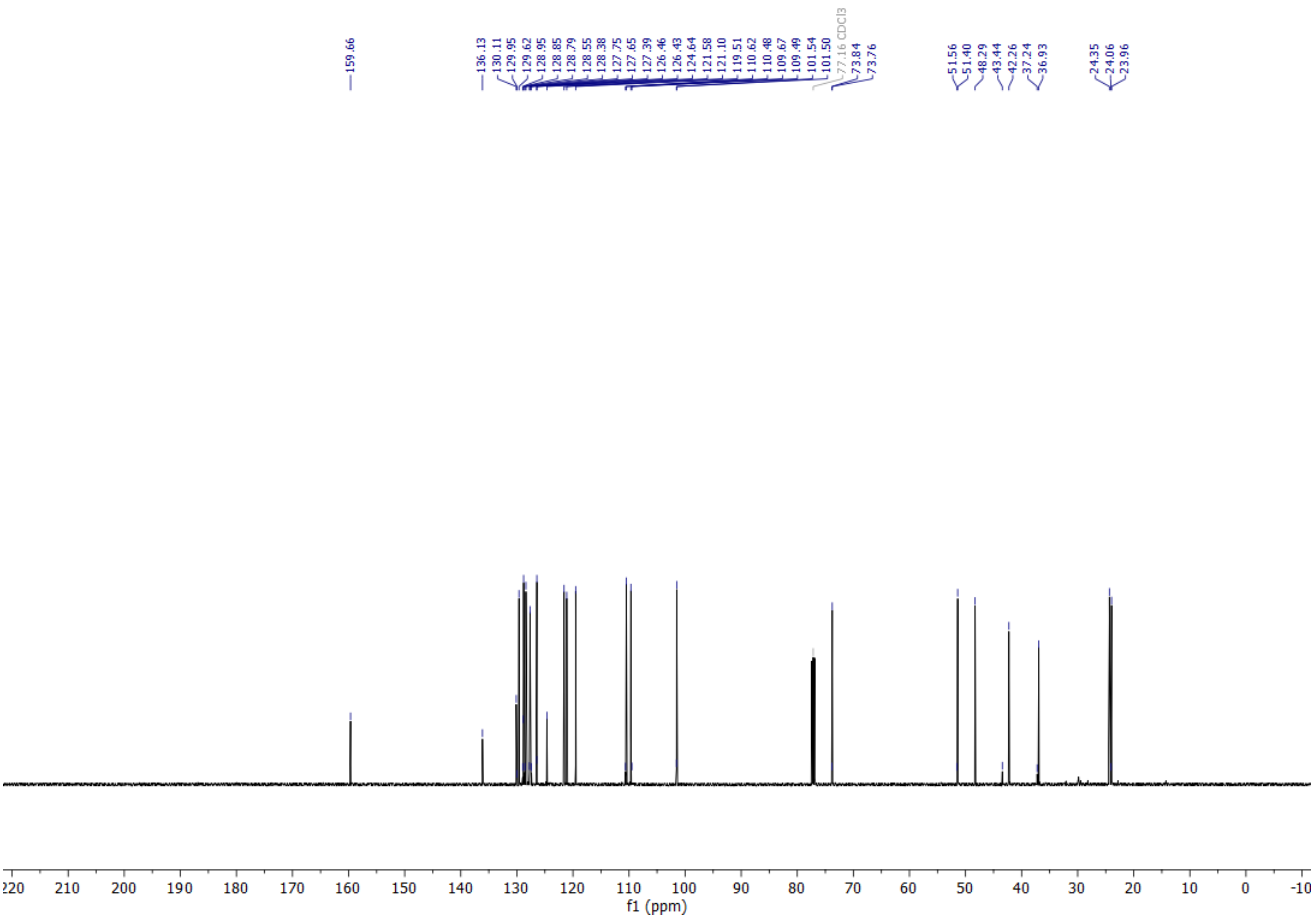
^{13}C NMR (75 MHz, $CDCl_3$)



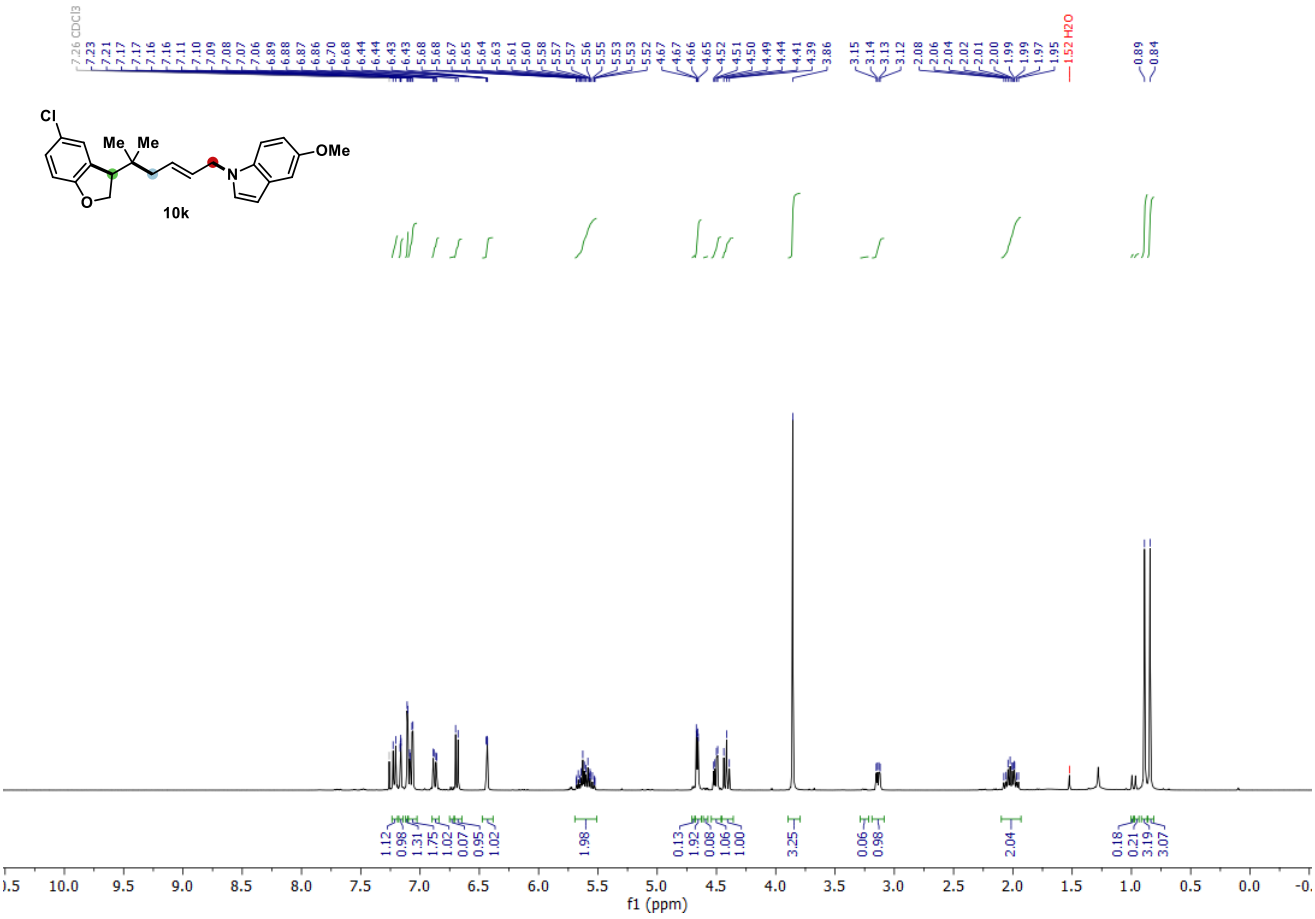
^{1}H NMR (500 MHz, $CDCl_3$)



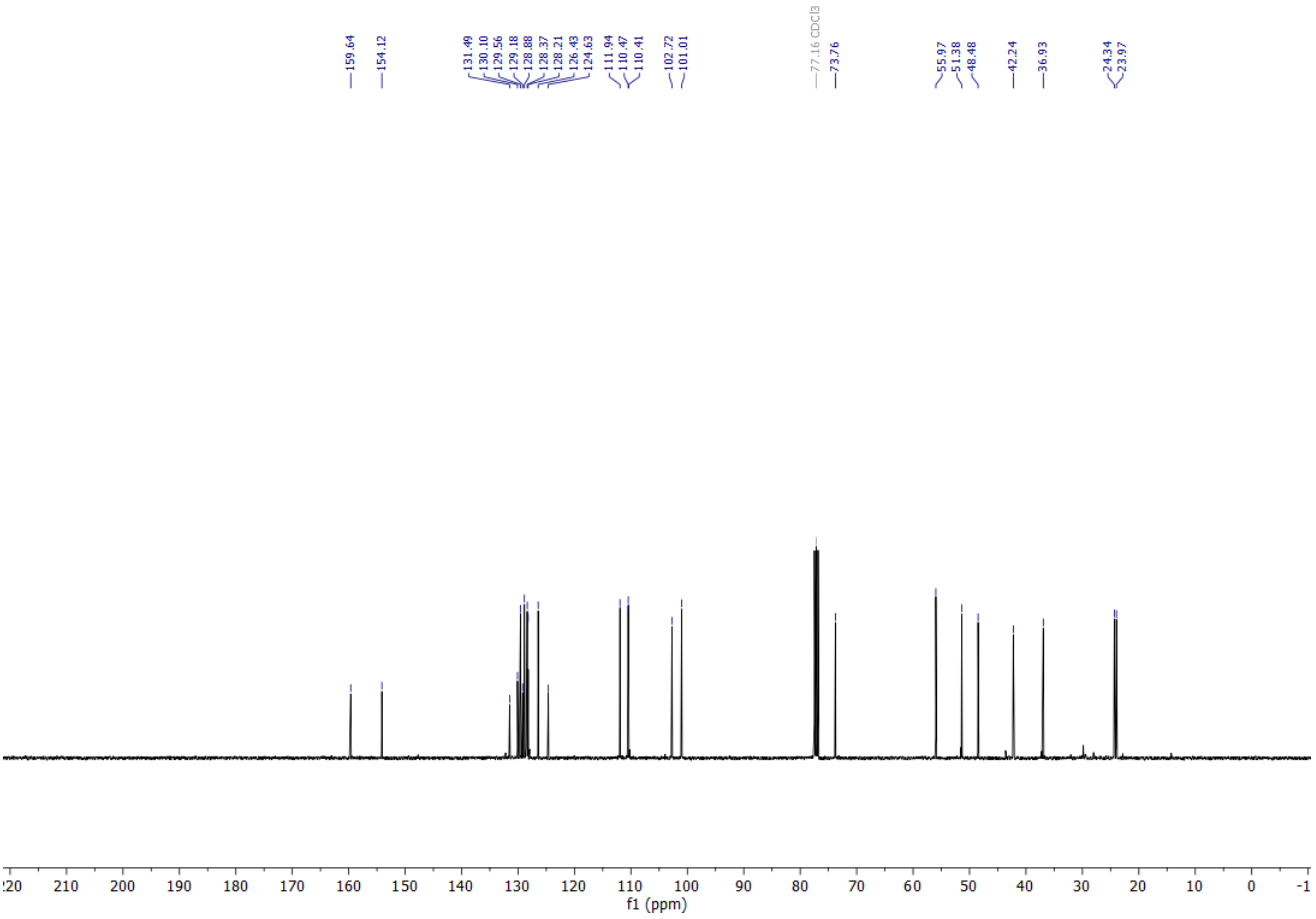
^{13}C NMR (126 MHz, $CDCl_3$)



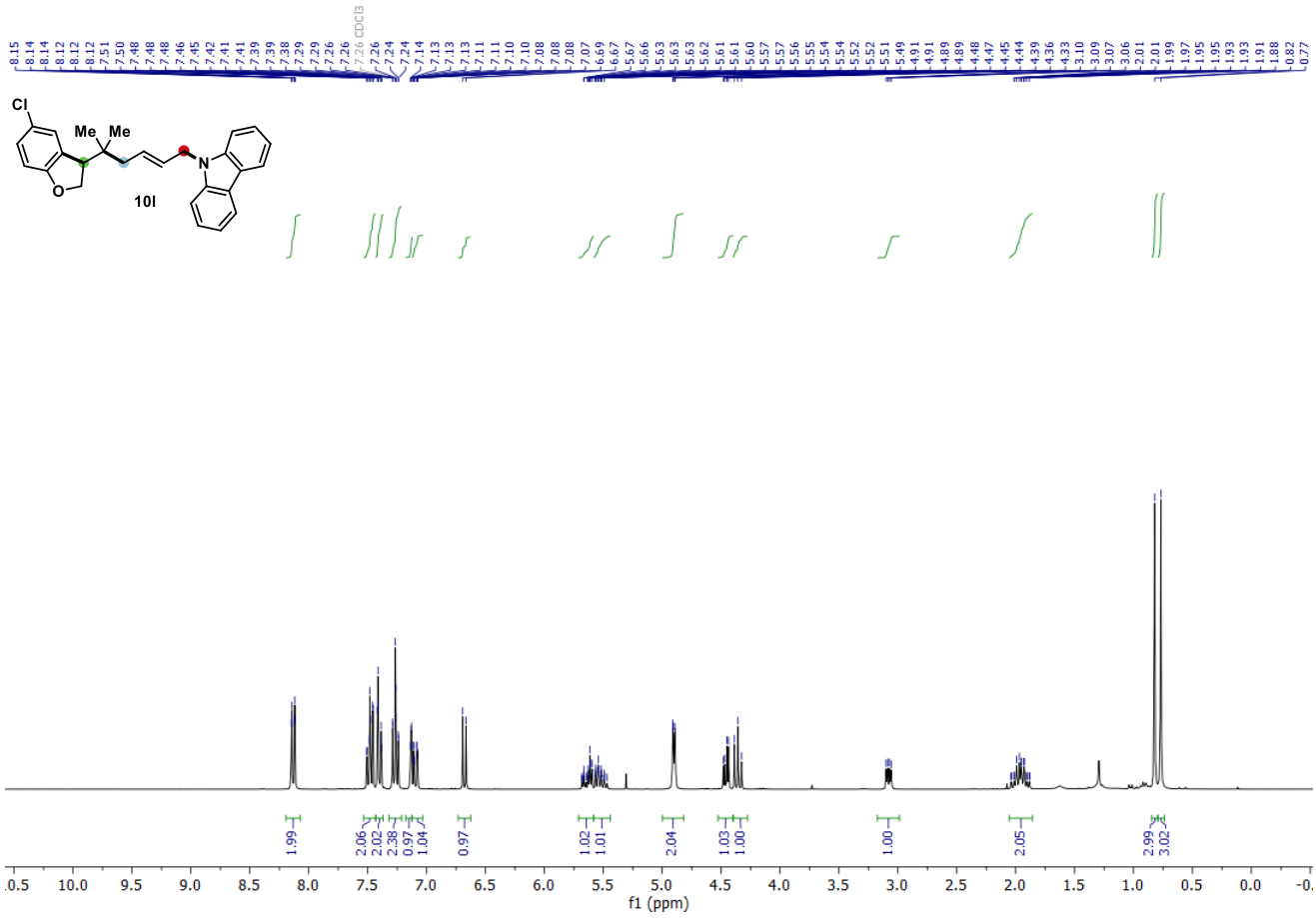
^{1}H NMR (400 MHz, $CDCl_3$)



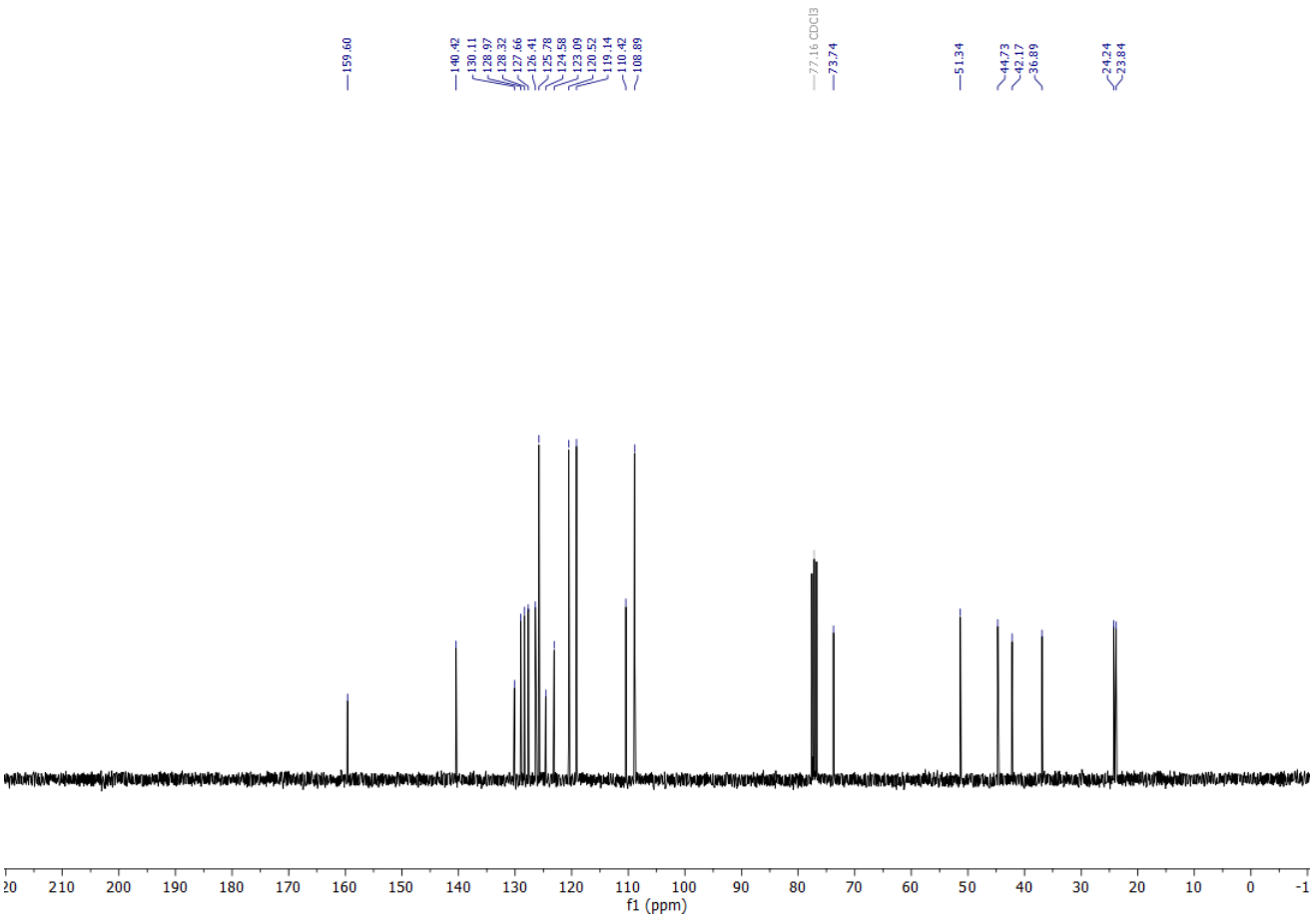
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

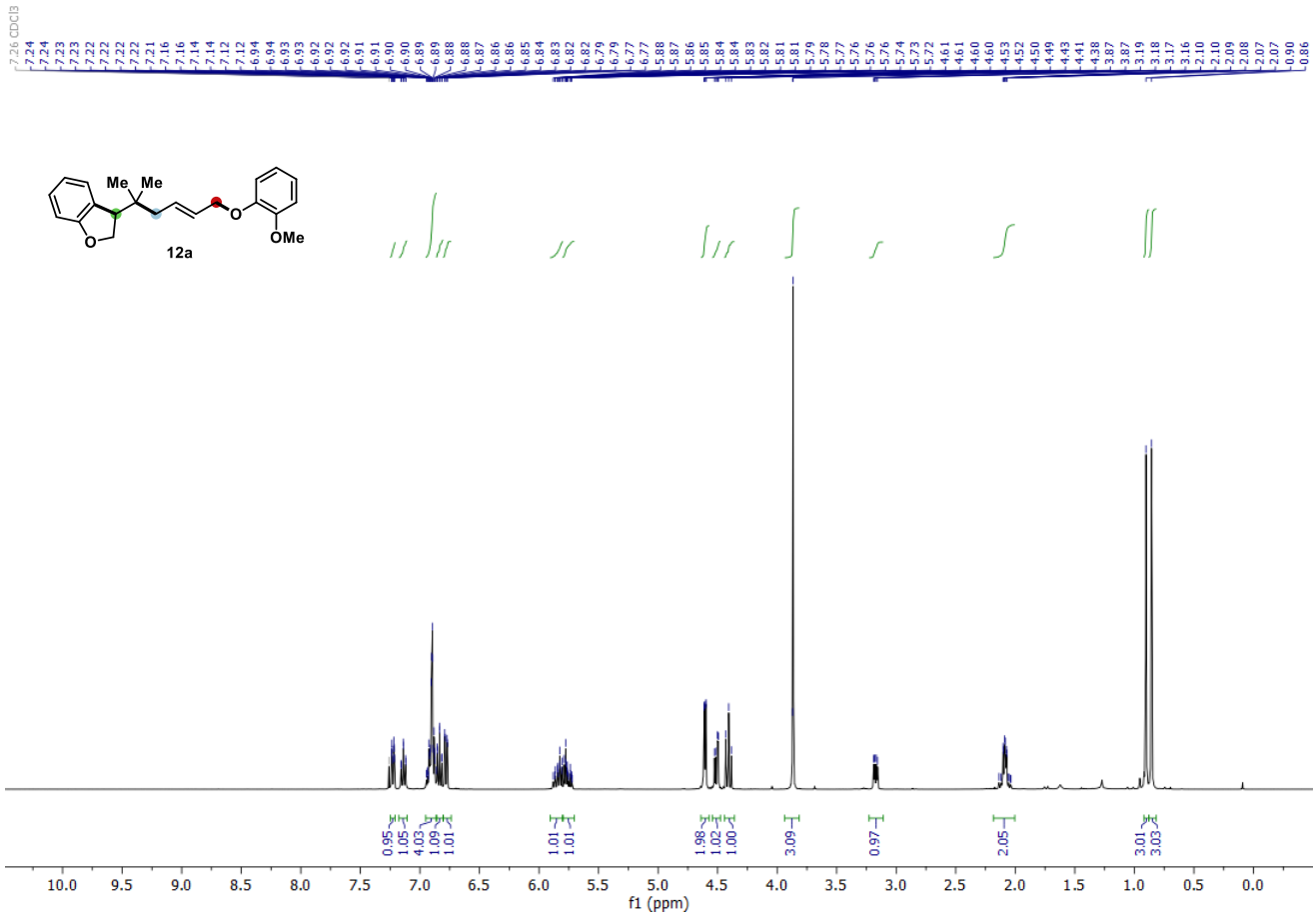


^{13}C NMR (75 MHz, $CDCl_3$)

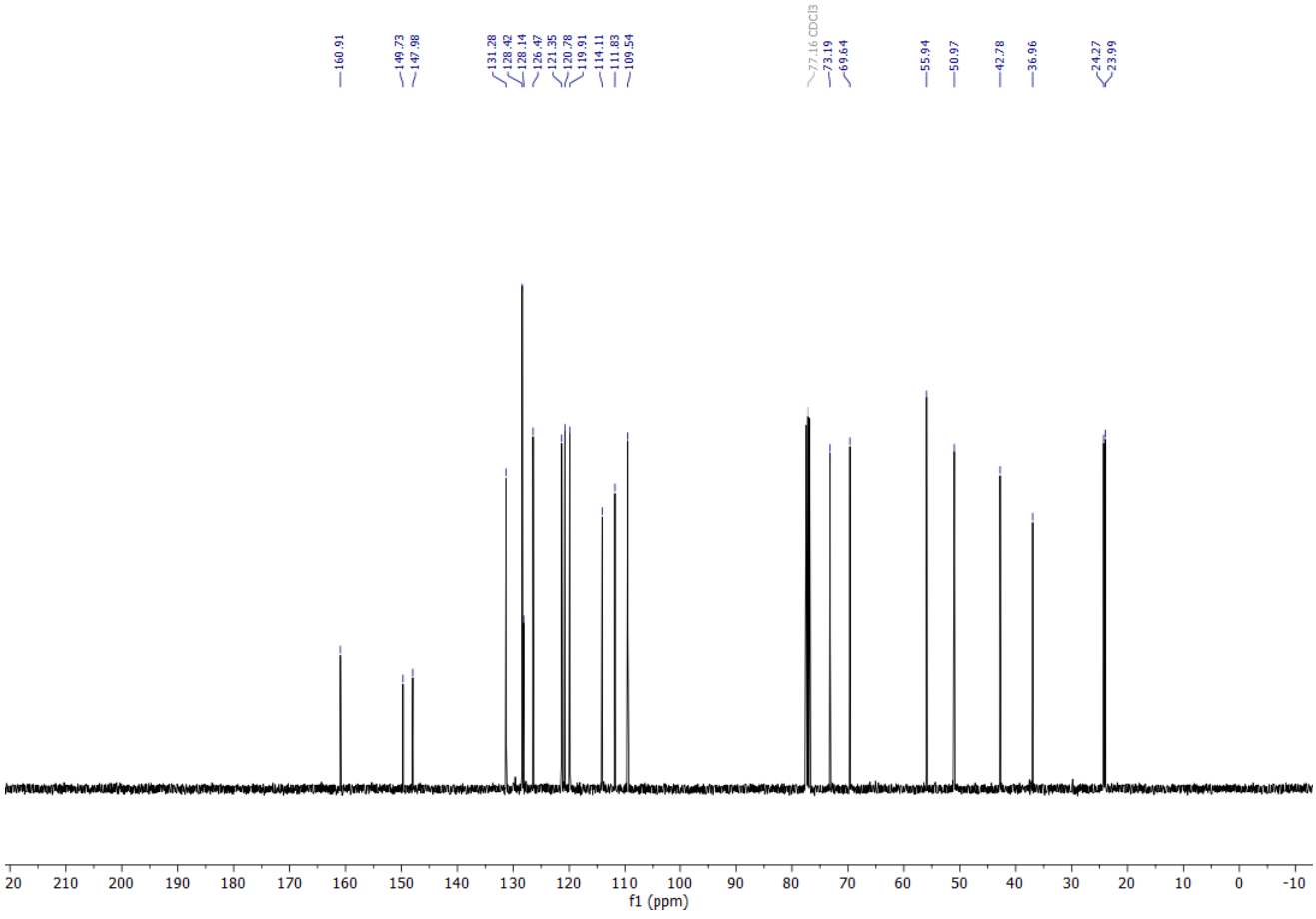


NMR spectra of products 12a-k

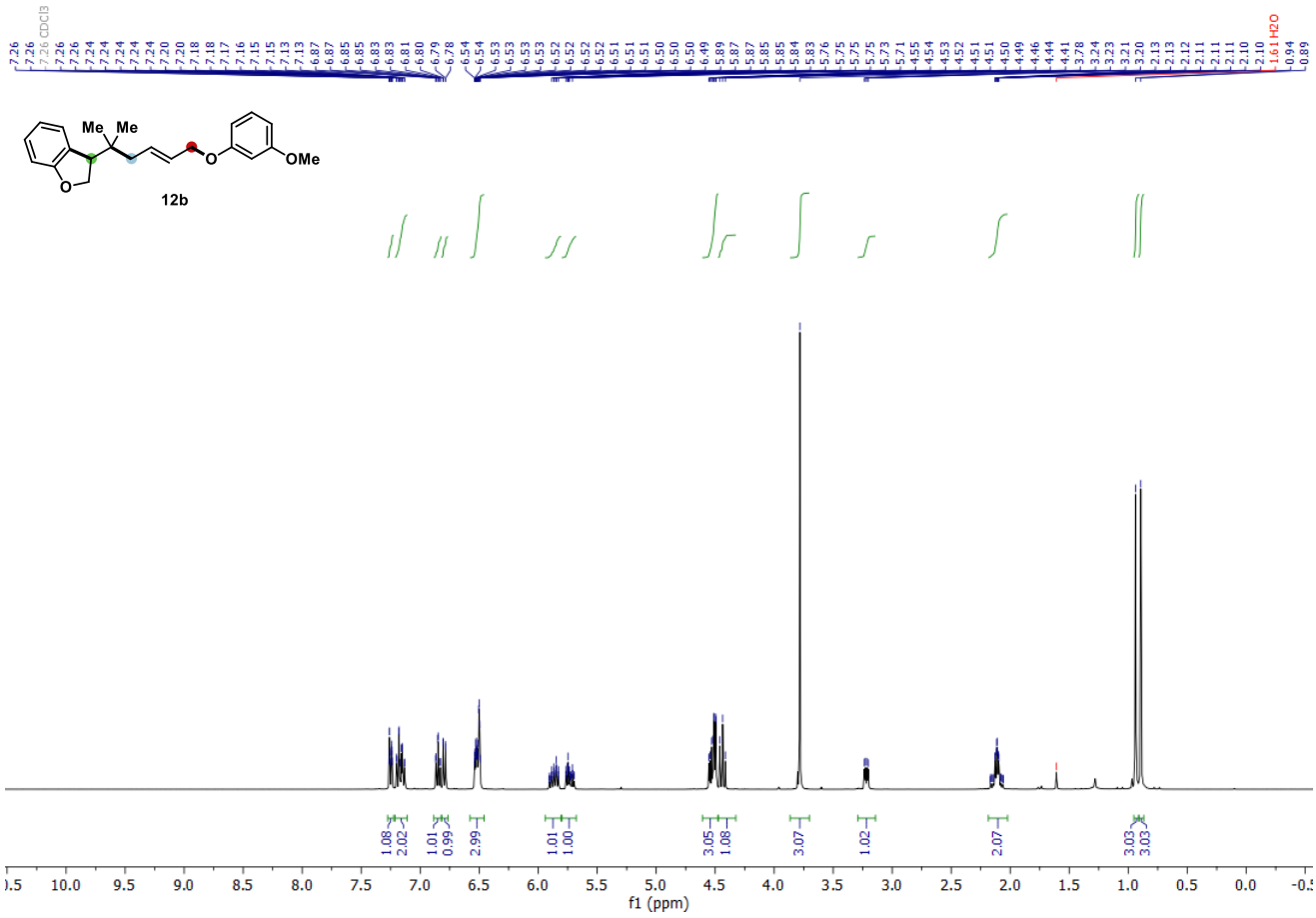
^{1}H NMR (400 MHz, $CDCl_3$)



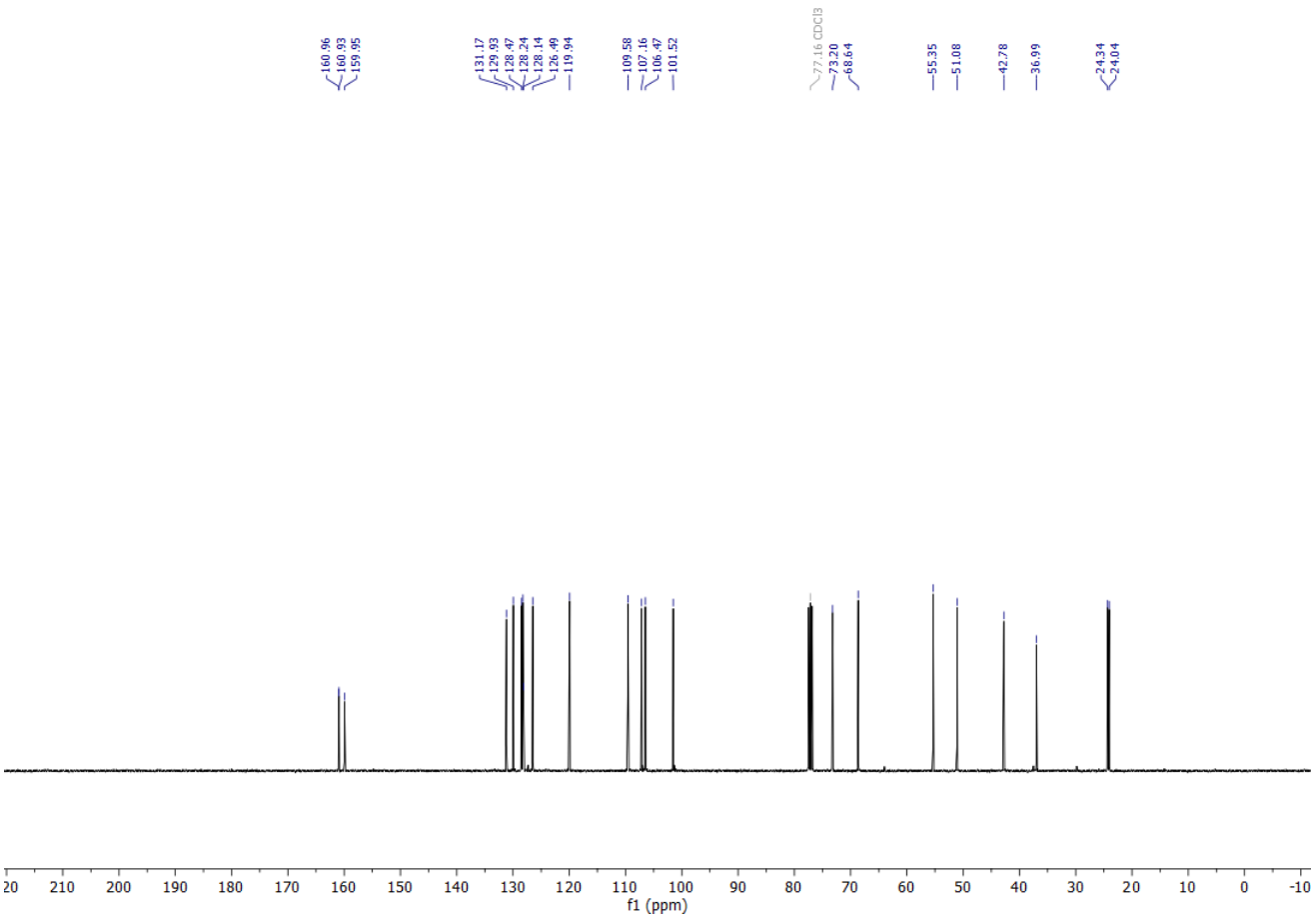
^{13}C NMR (101 MHz, $CDCl_3$)



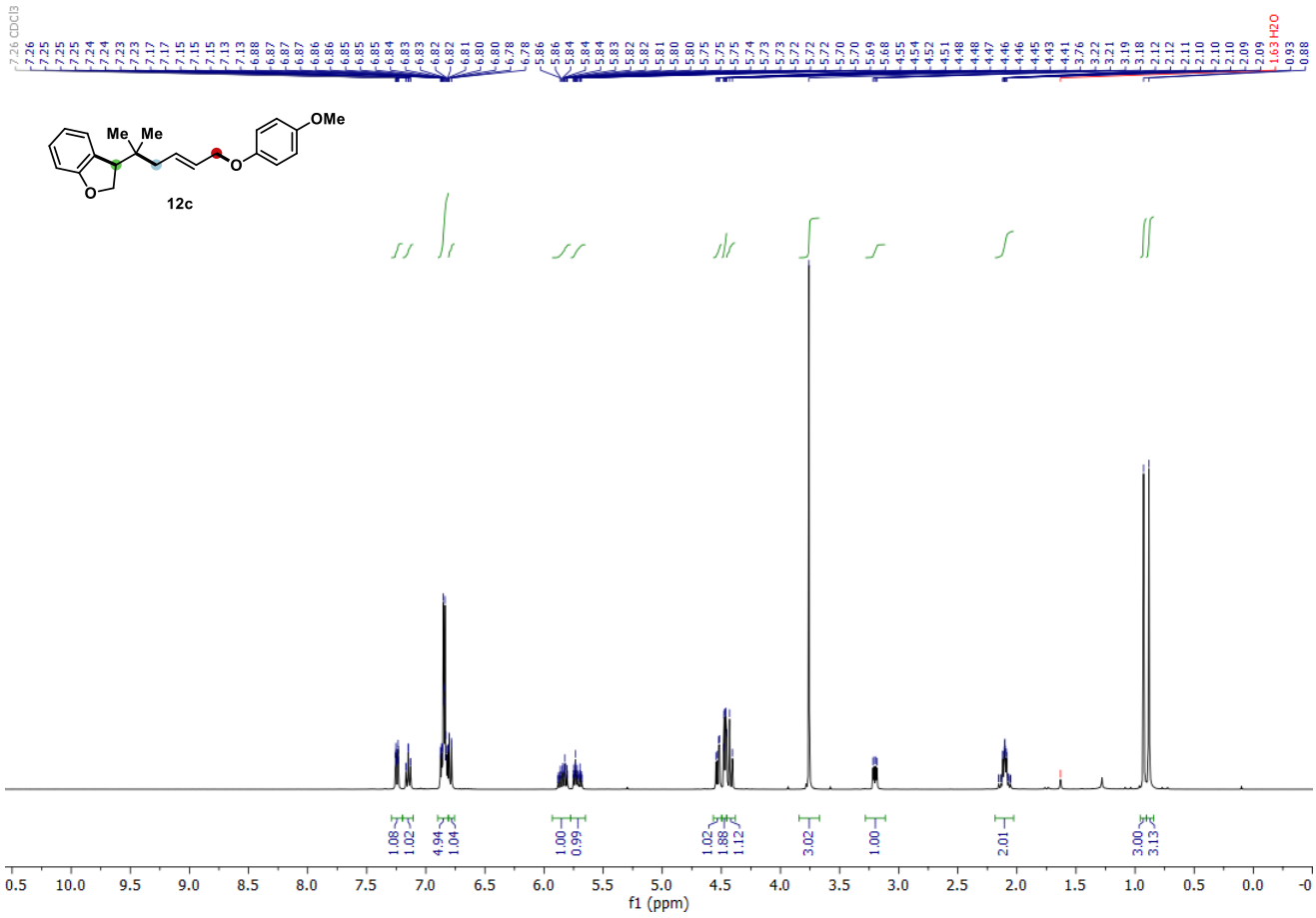
^{1}H NMR (400 MHz, $CDCl_3$)



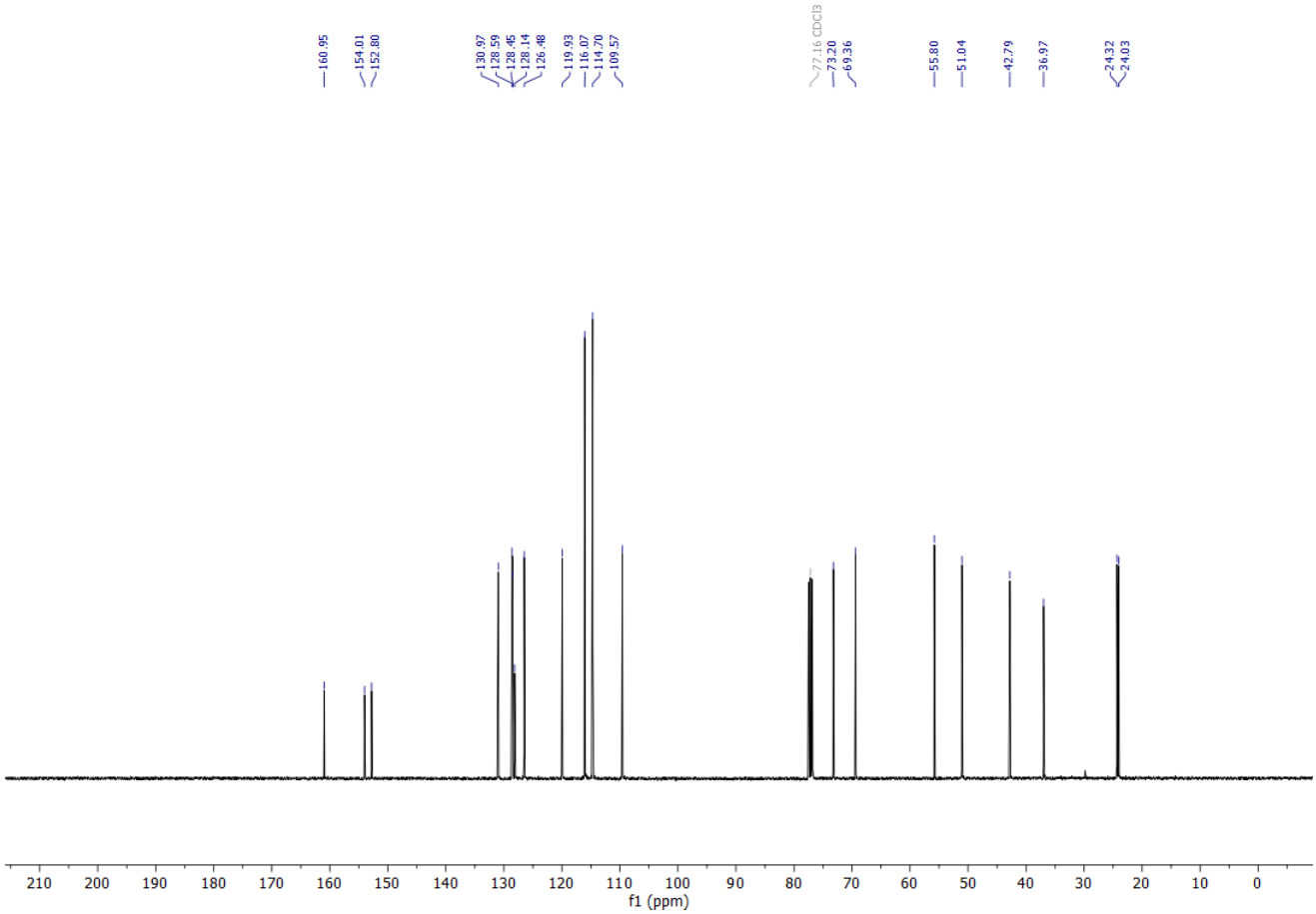
^{13}C NMR (101 MHz, $CDCl_3$)



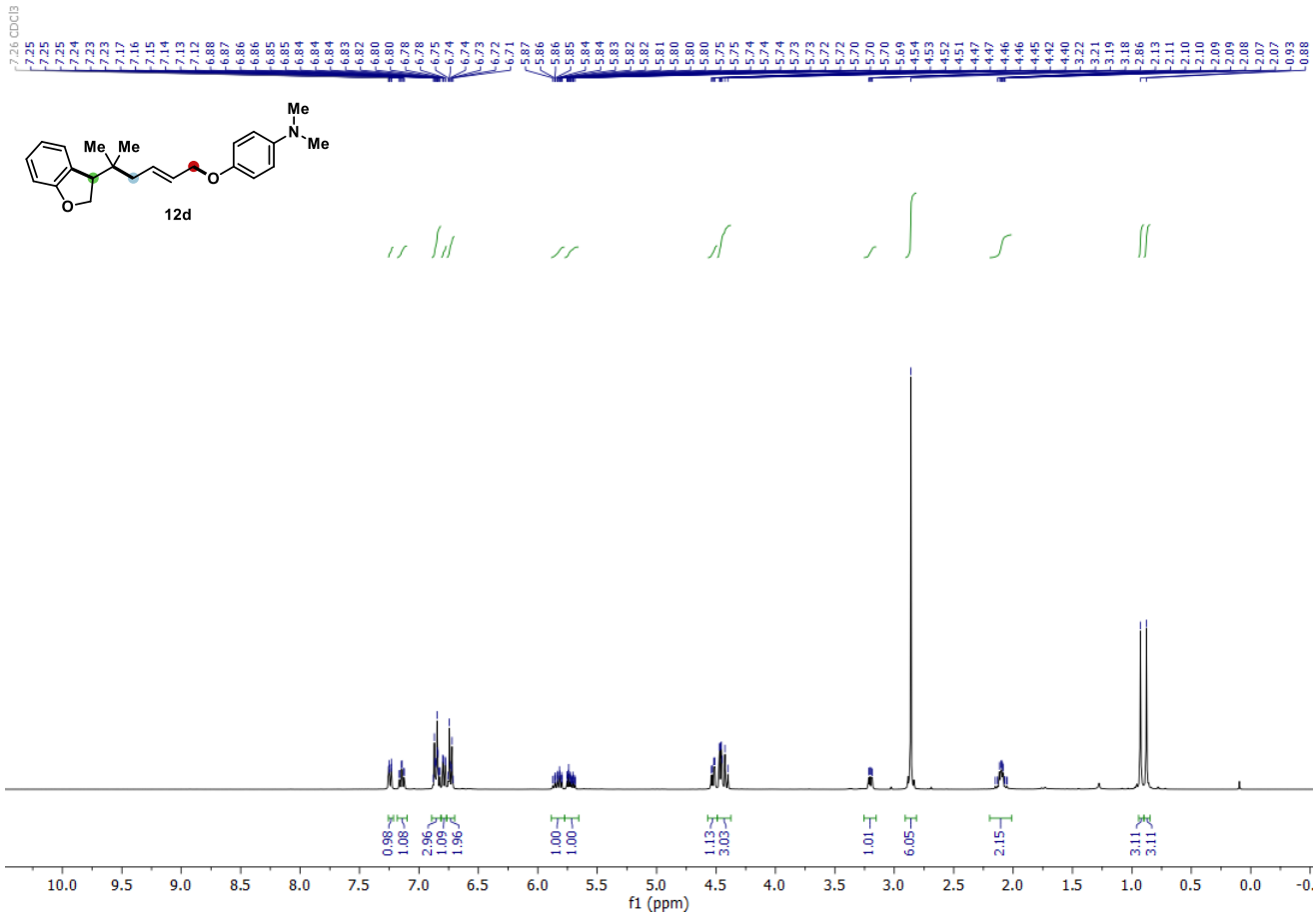
^{1}H NMR (400 MHz, $CDCl_3$)



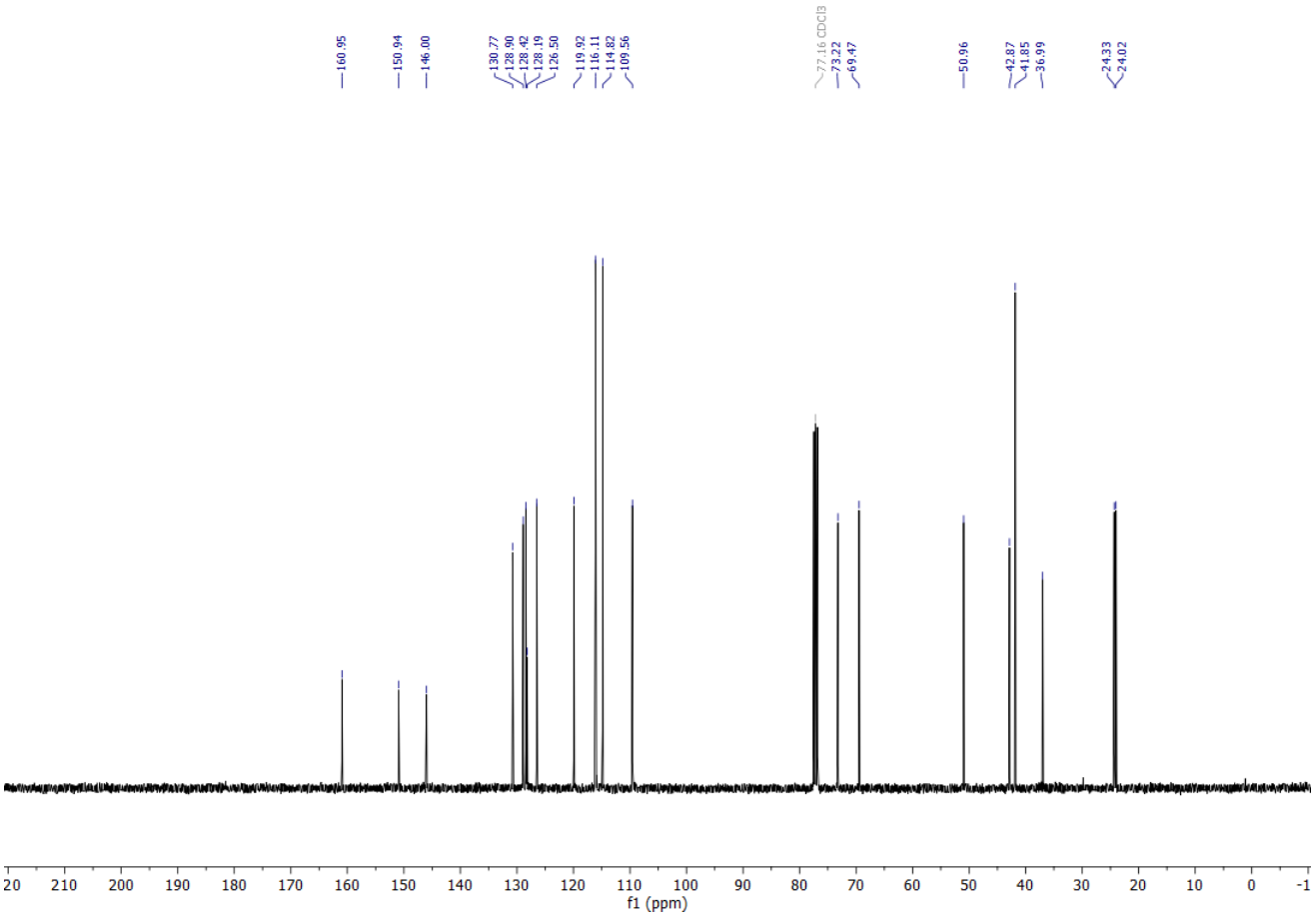
^{13}C NMR (101 MHz, $CDCl_3$)



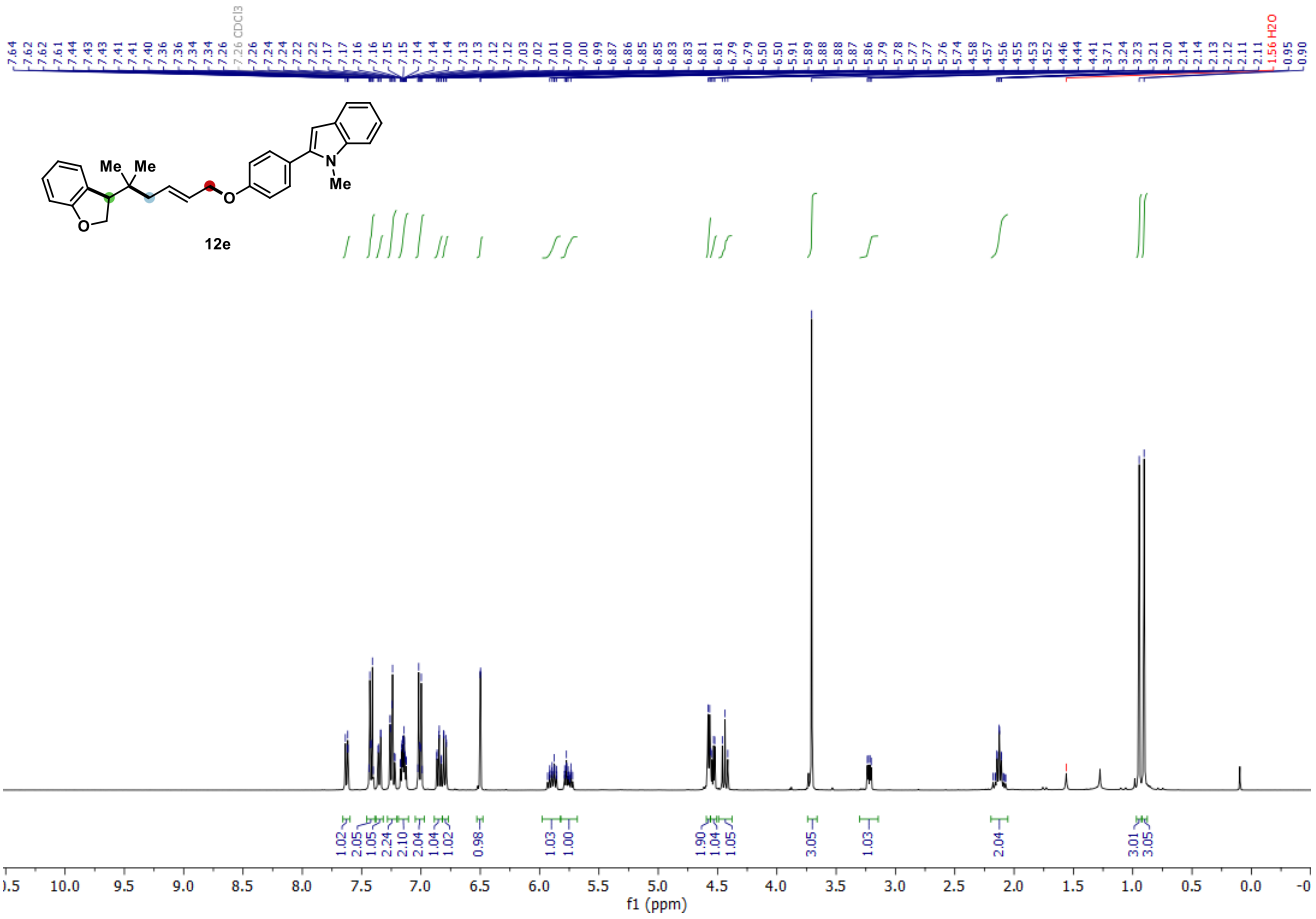
^{1}H NMR (400 MHz, $CDCl_3$)



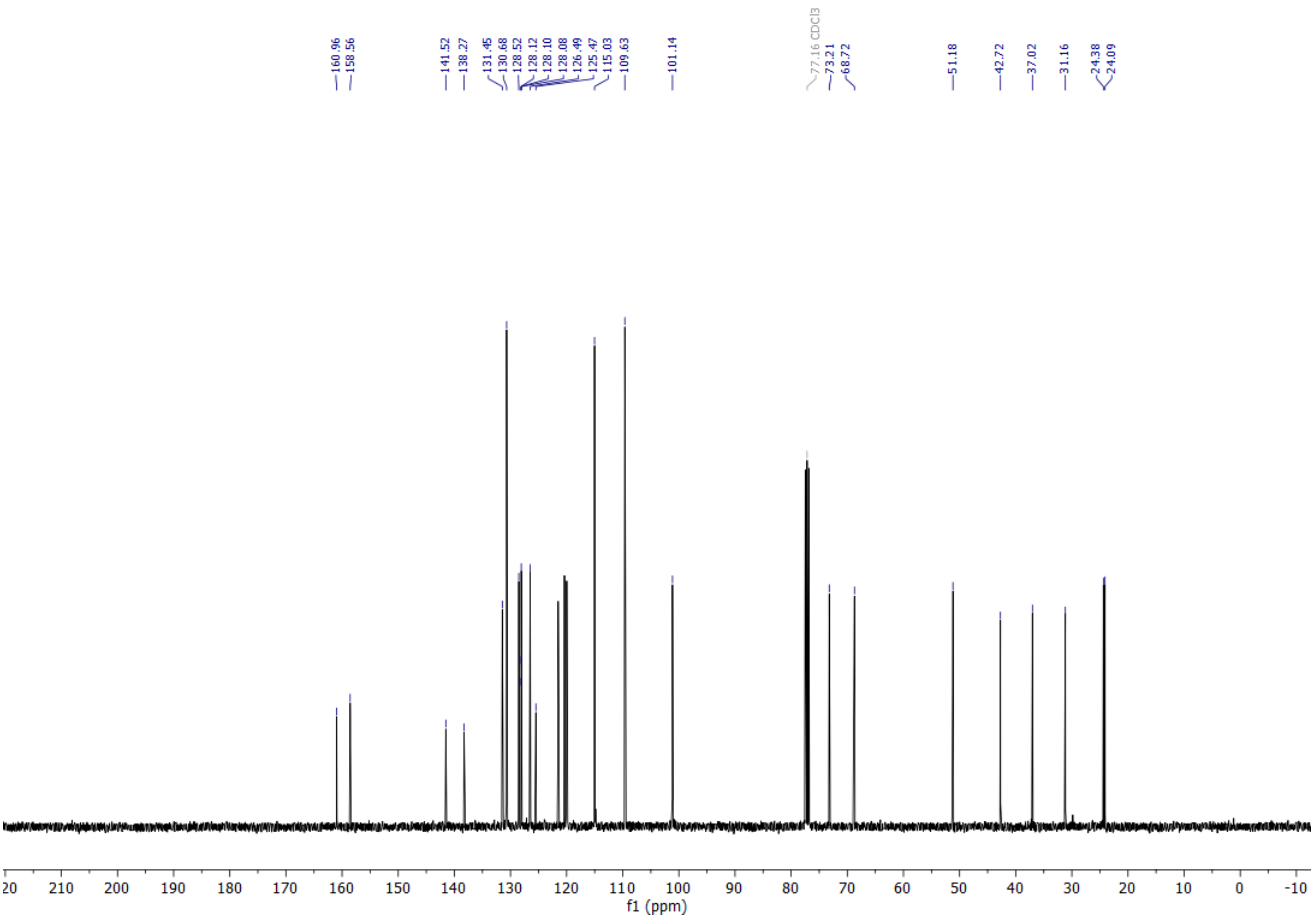
^{13}C NMR (101 MHz, $CDCl_3$)



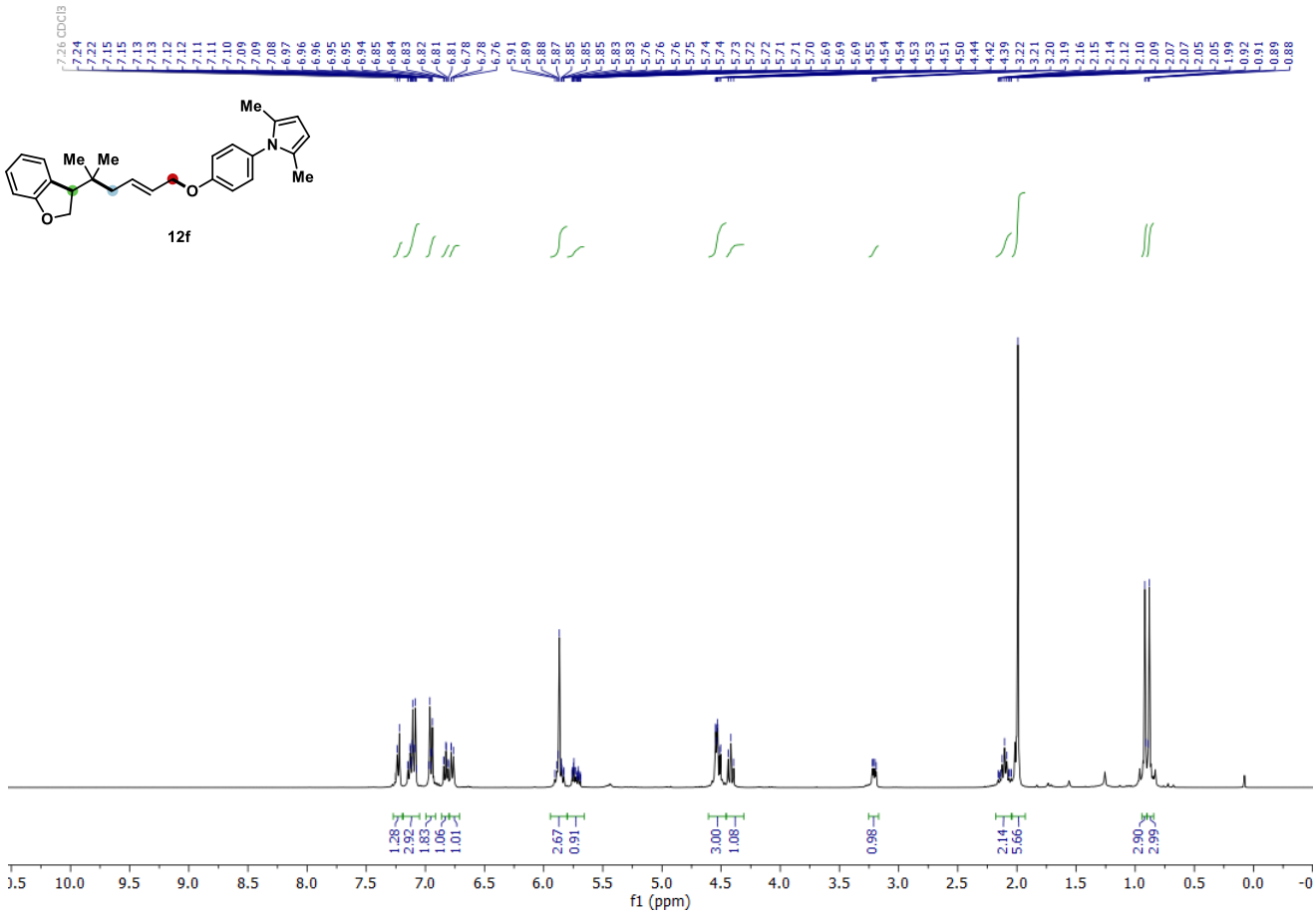
^{1}H NMR (400 MHz, $CDCl_3$)



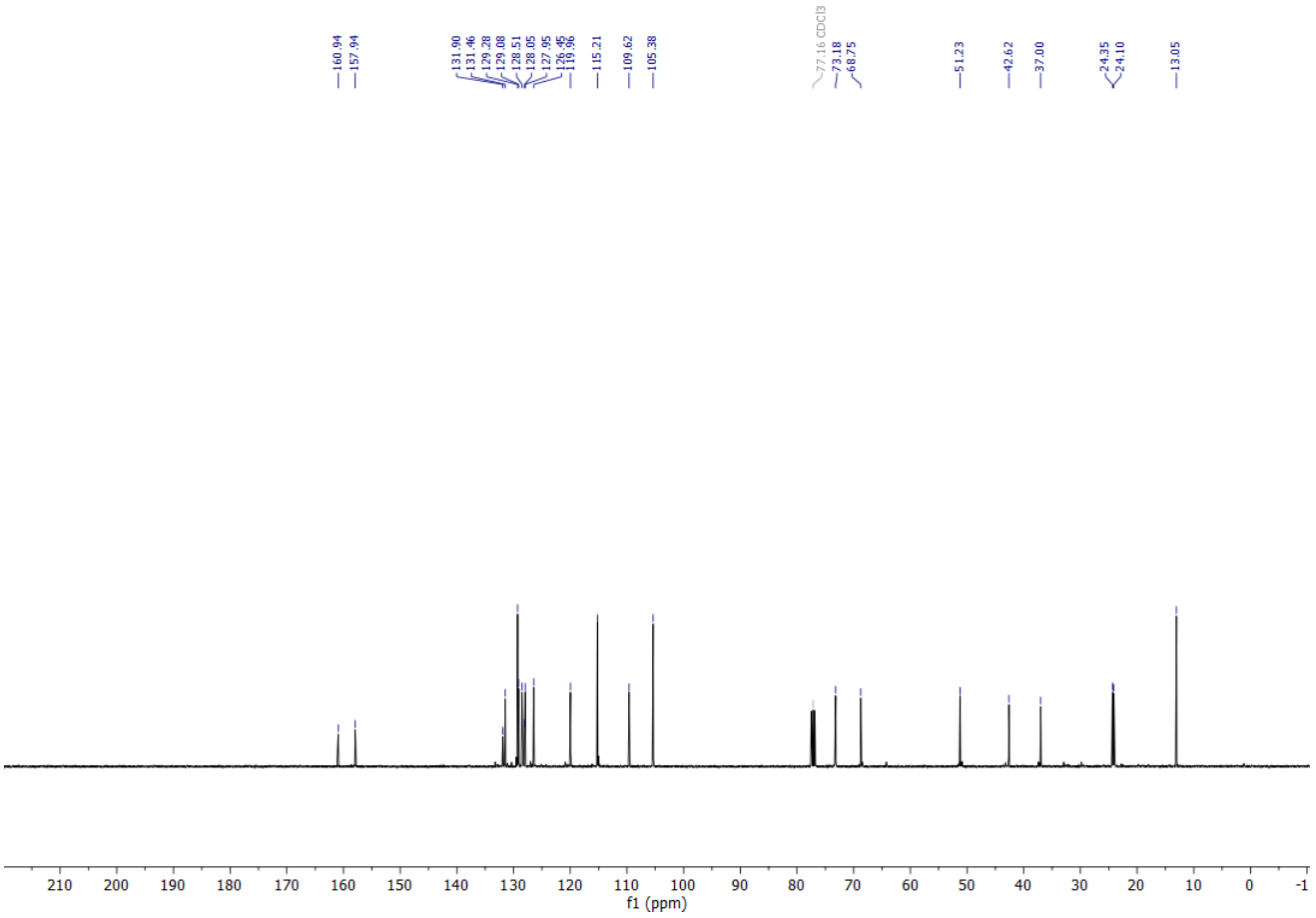
^{13}C NMR (101 MHz, $CDCl_3$)



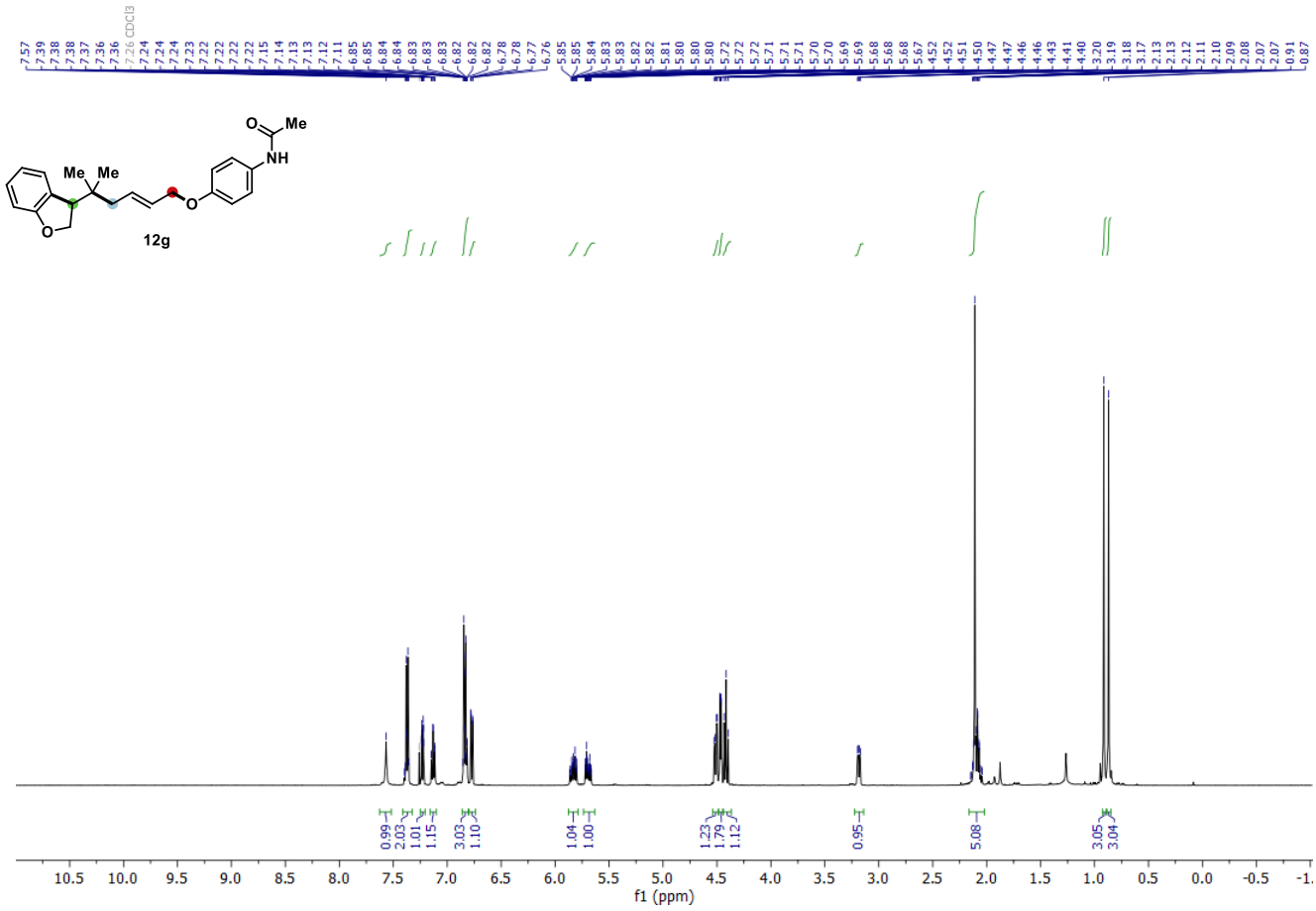
^{1}H NMR (400 MHz, $CDCl_3$)



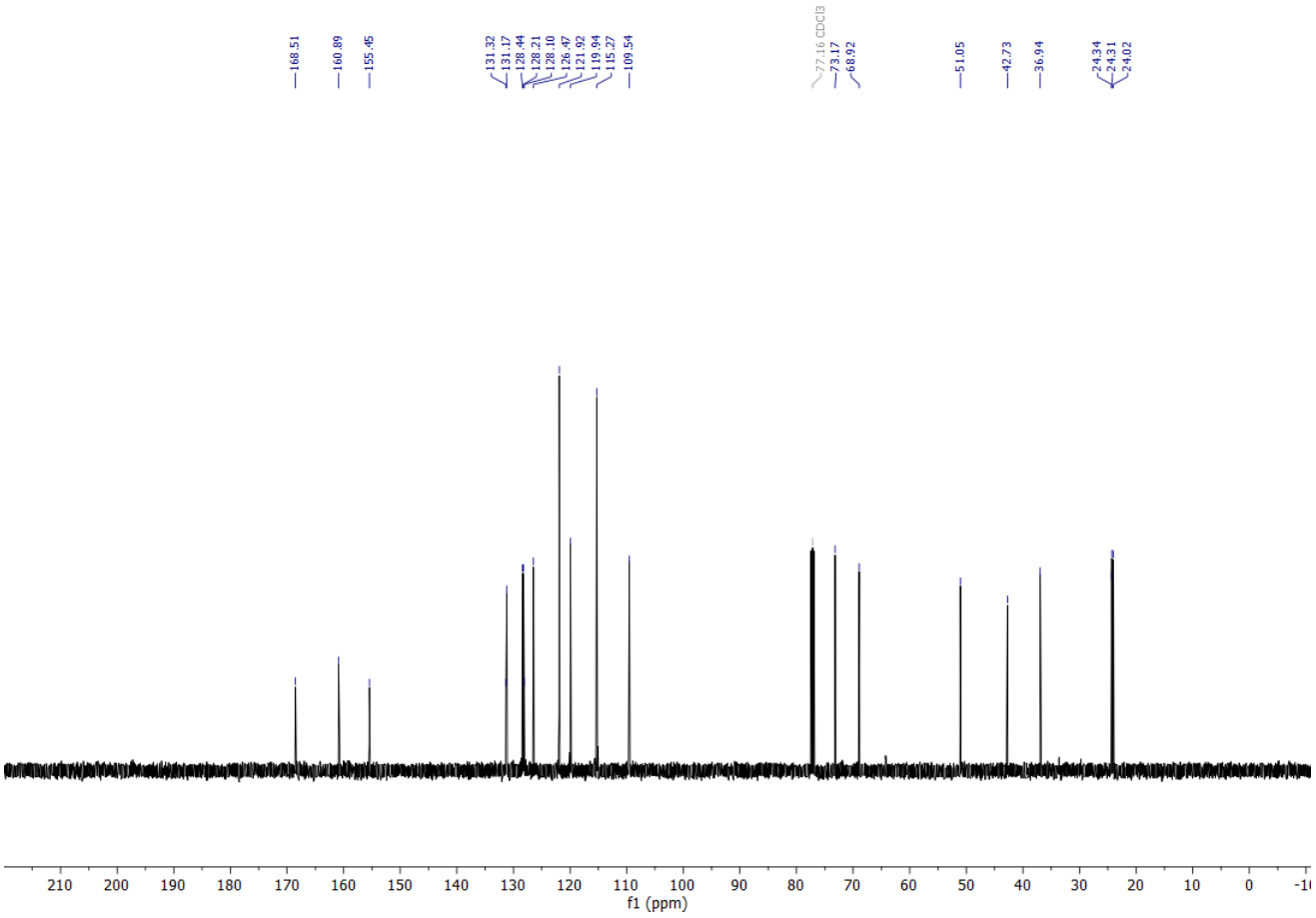
^{13}C NMR (101 MHz, $CDCl_3$)



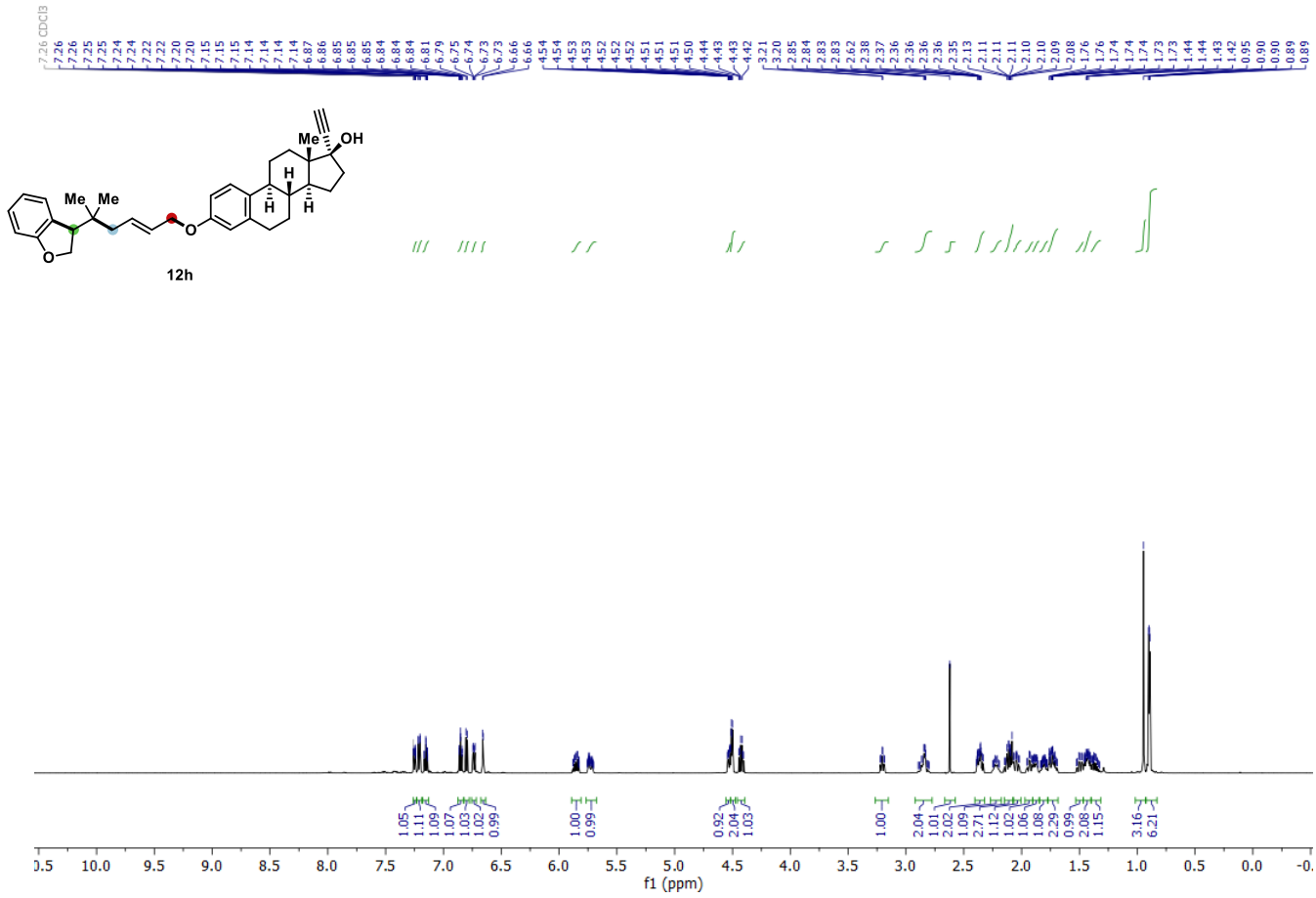
^{1}H NMR (500 MHz, $CDCl_3$)



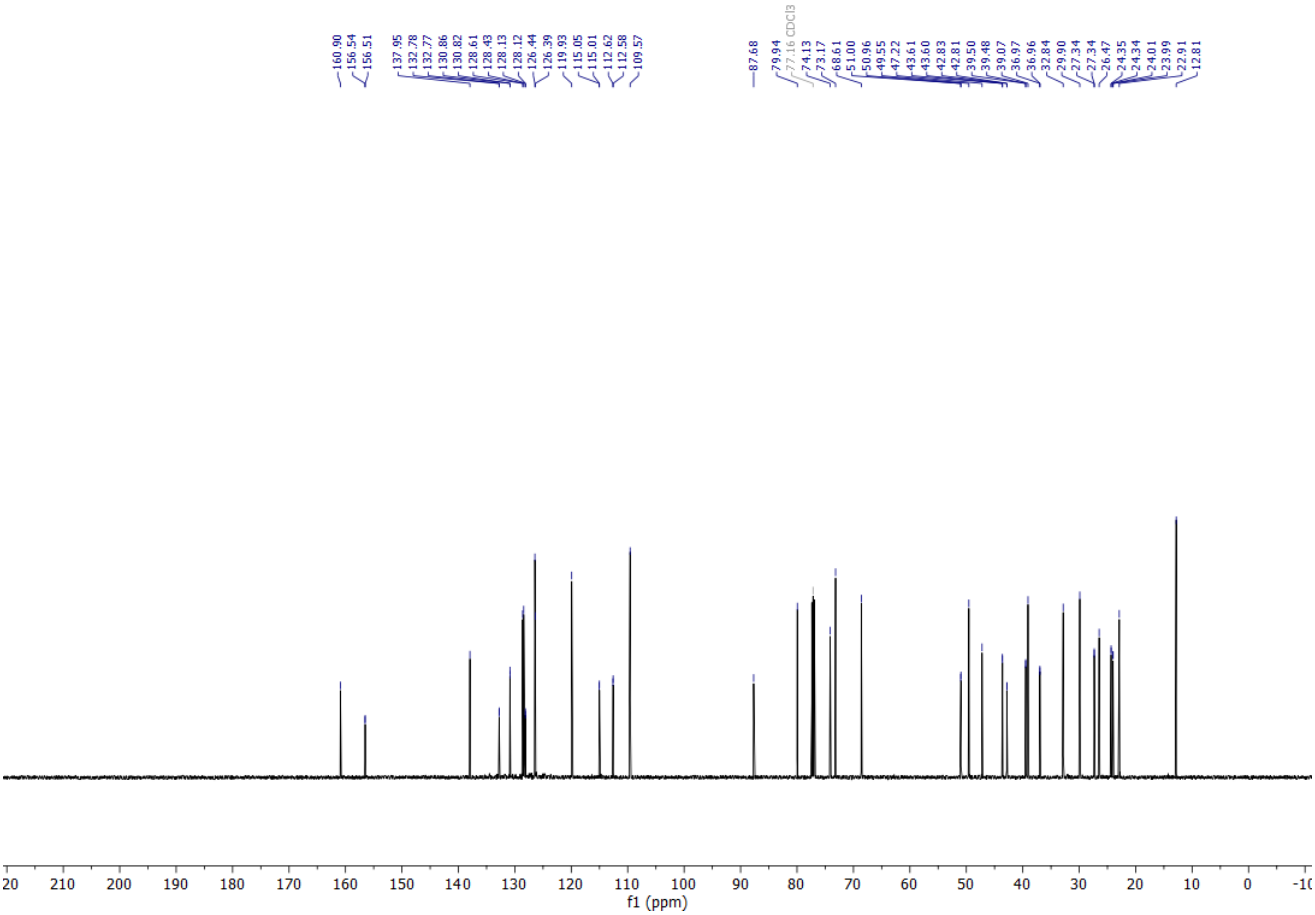
^{13}C NMR (126 MHz, $CDCl_3$)



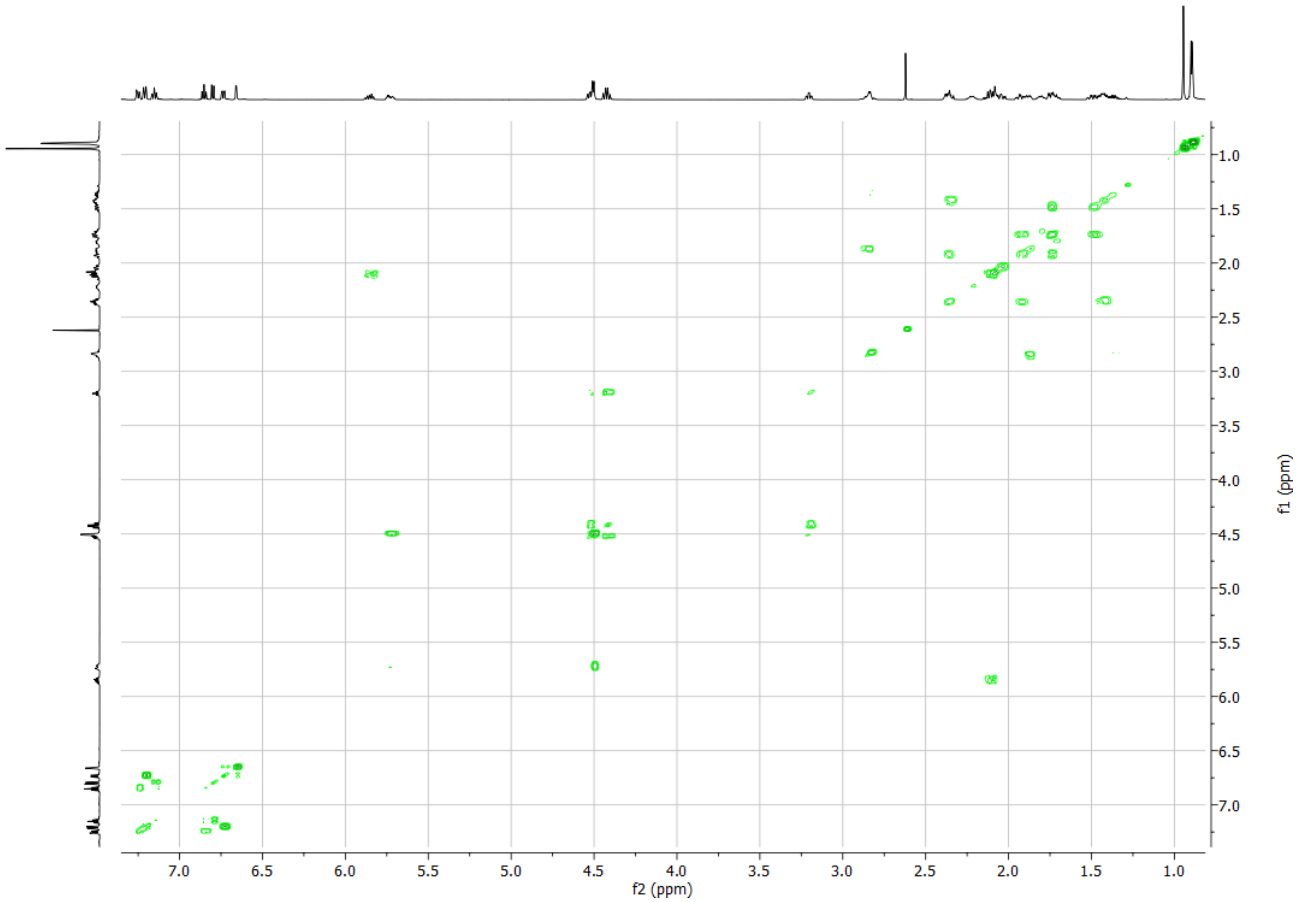
^{1}H NMR (599 MHz, $CDCl_3$)



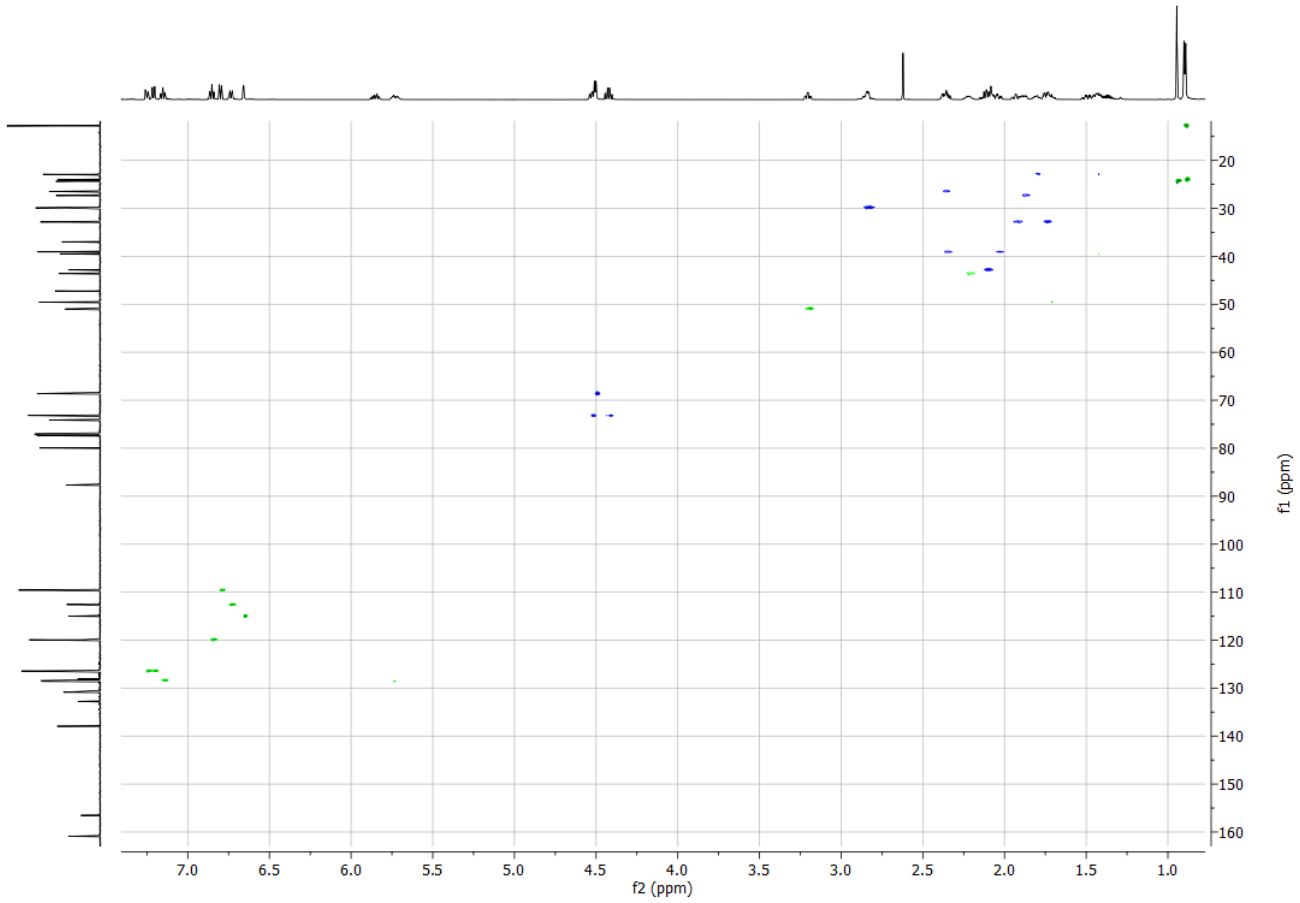
^{13}C NMR (151 MHz, $CDCl_3$)



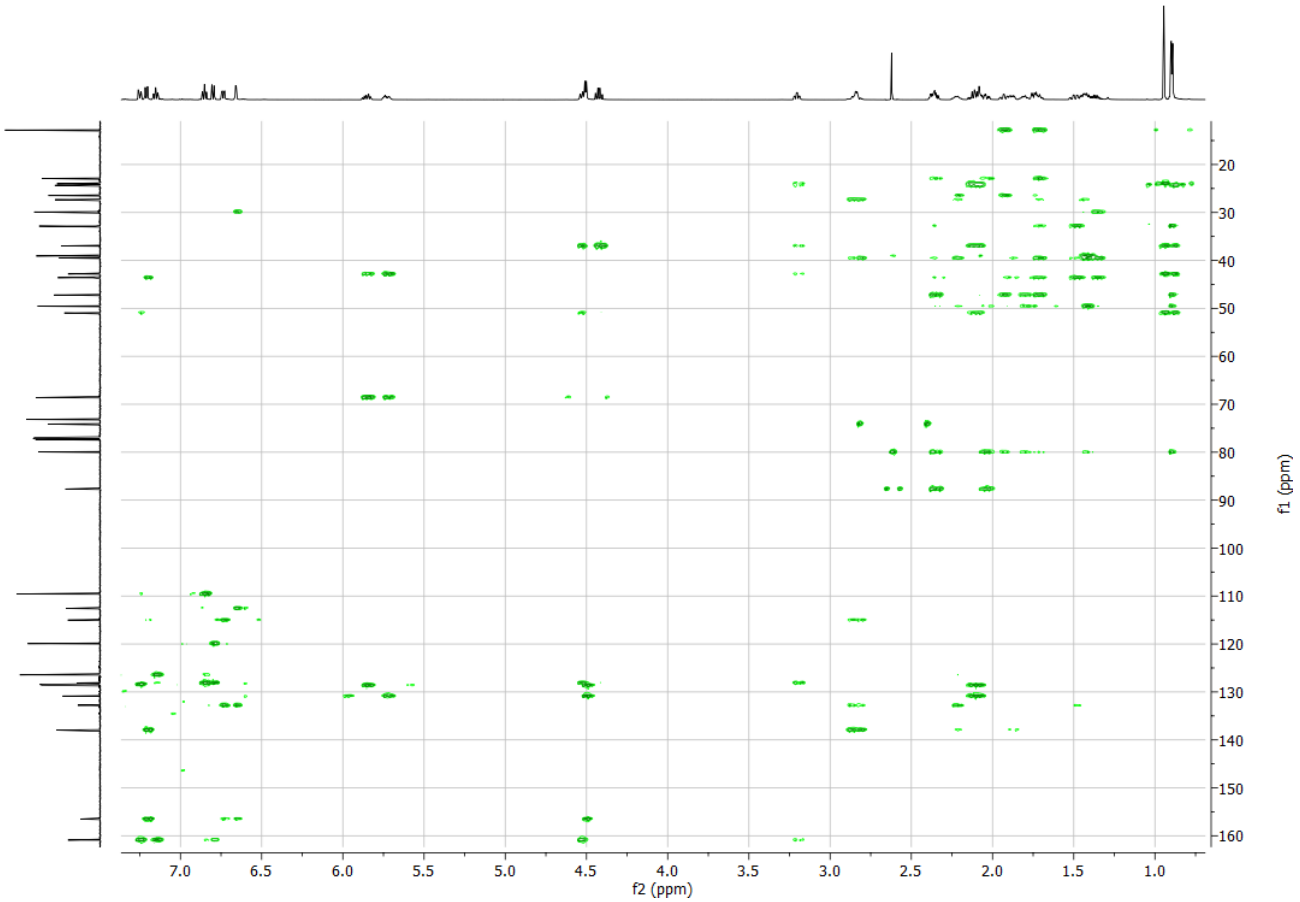
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



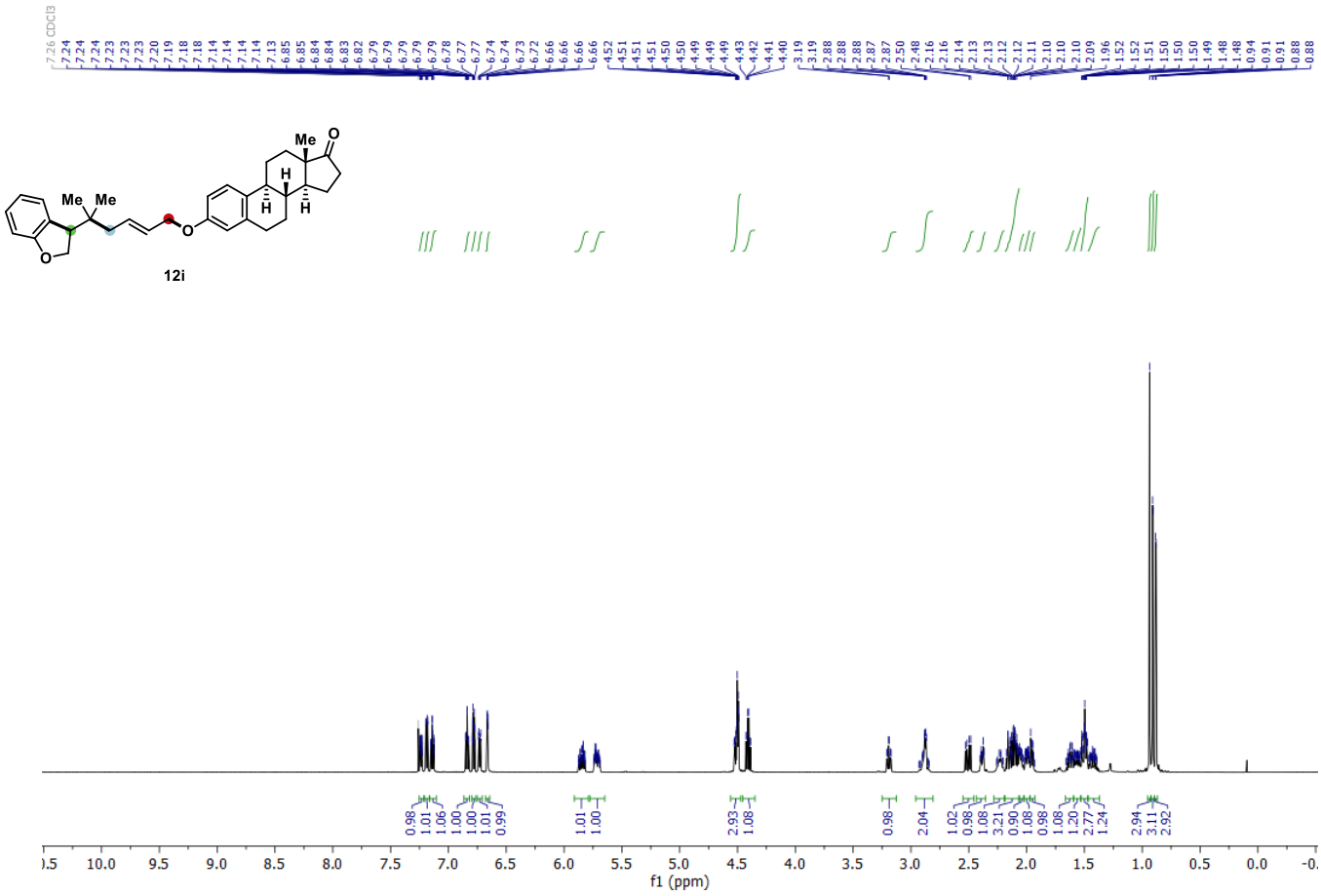
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



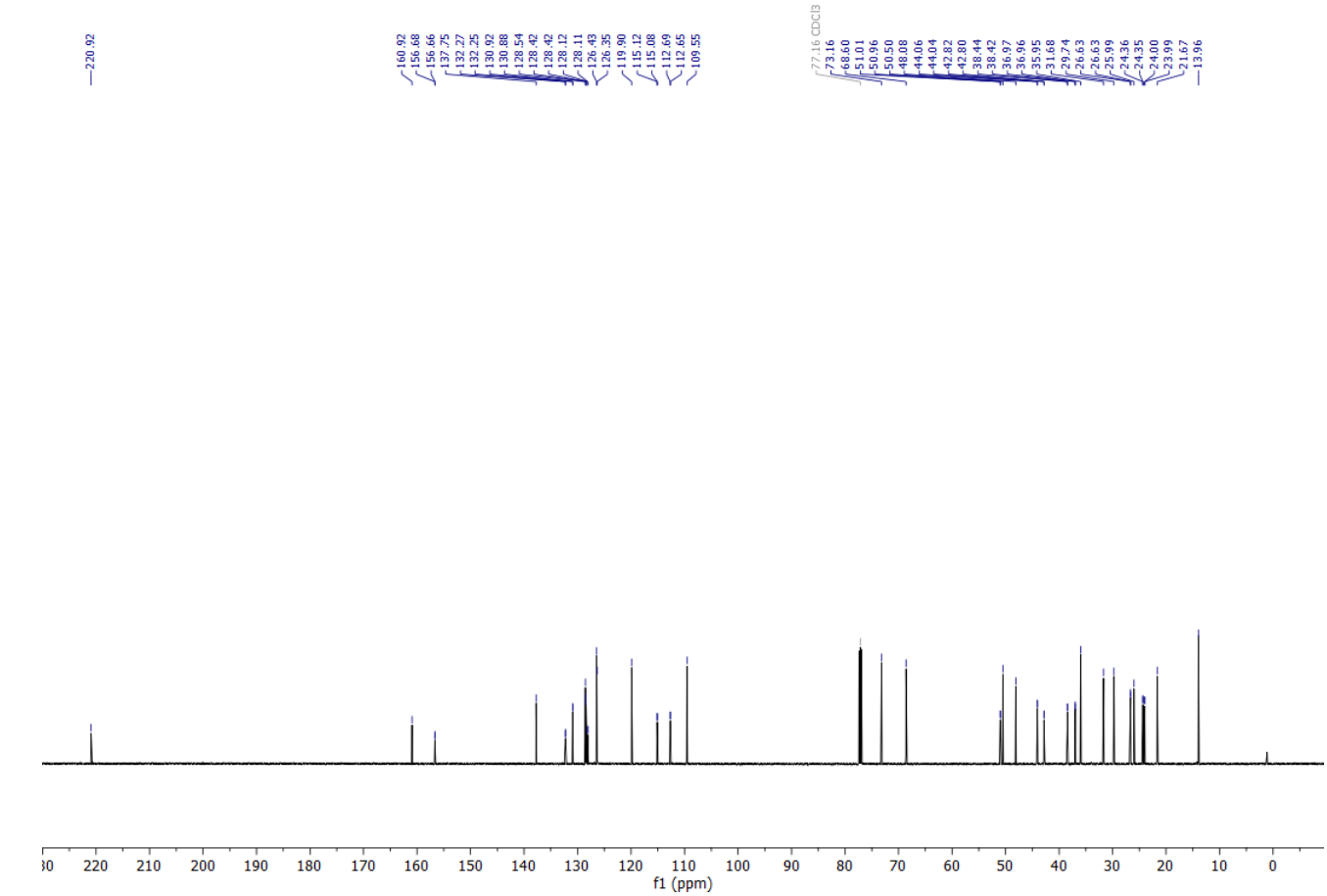
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



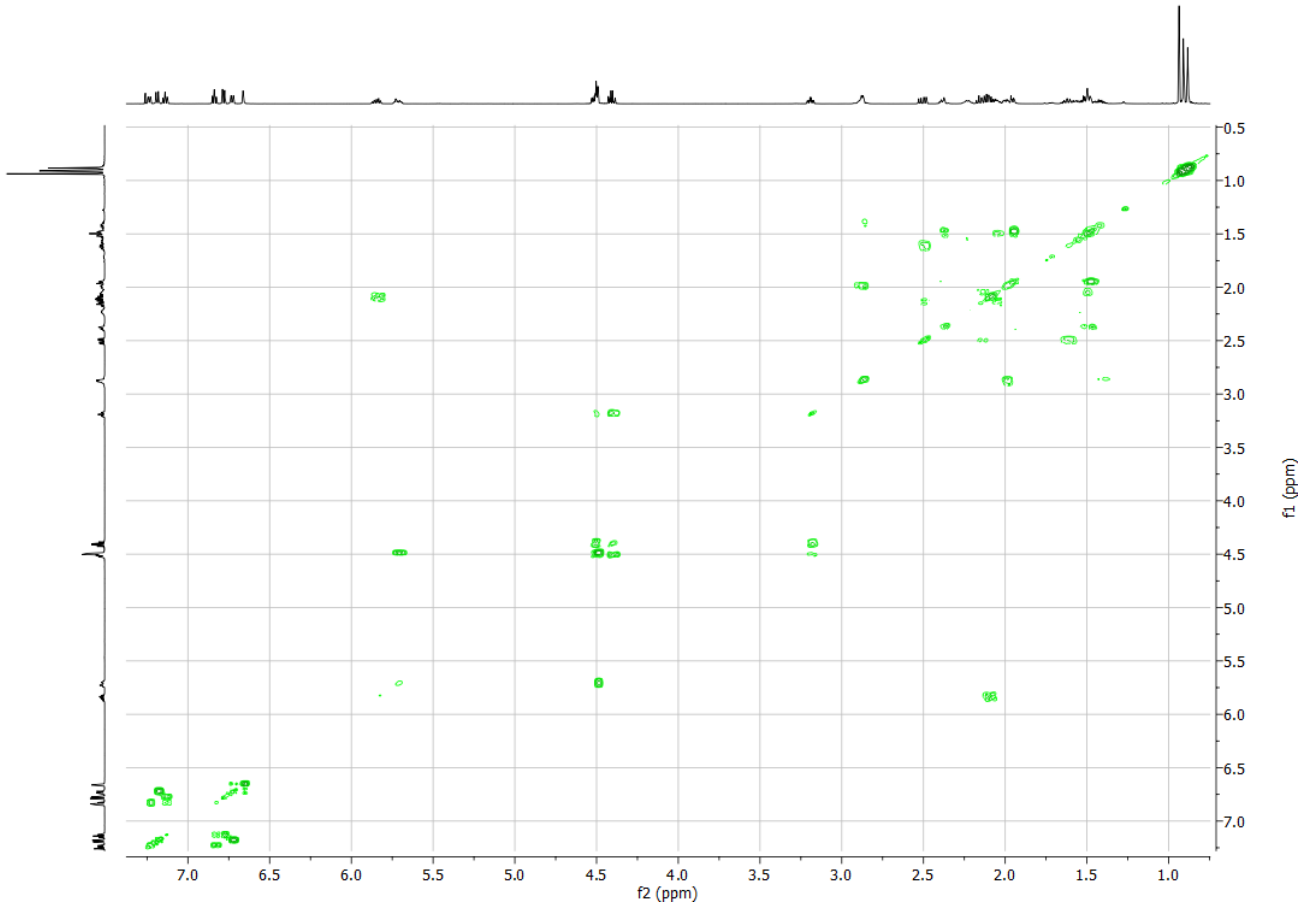
^{1}H NMR (599 MHz, $CDCl_3$)



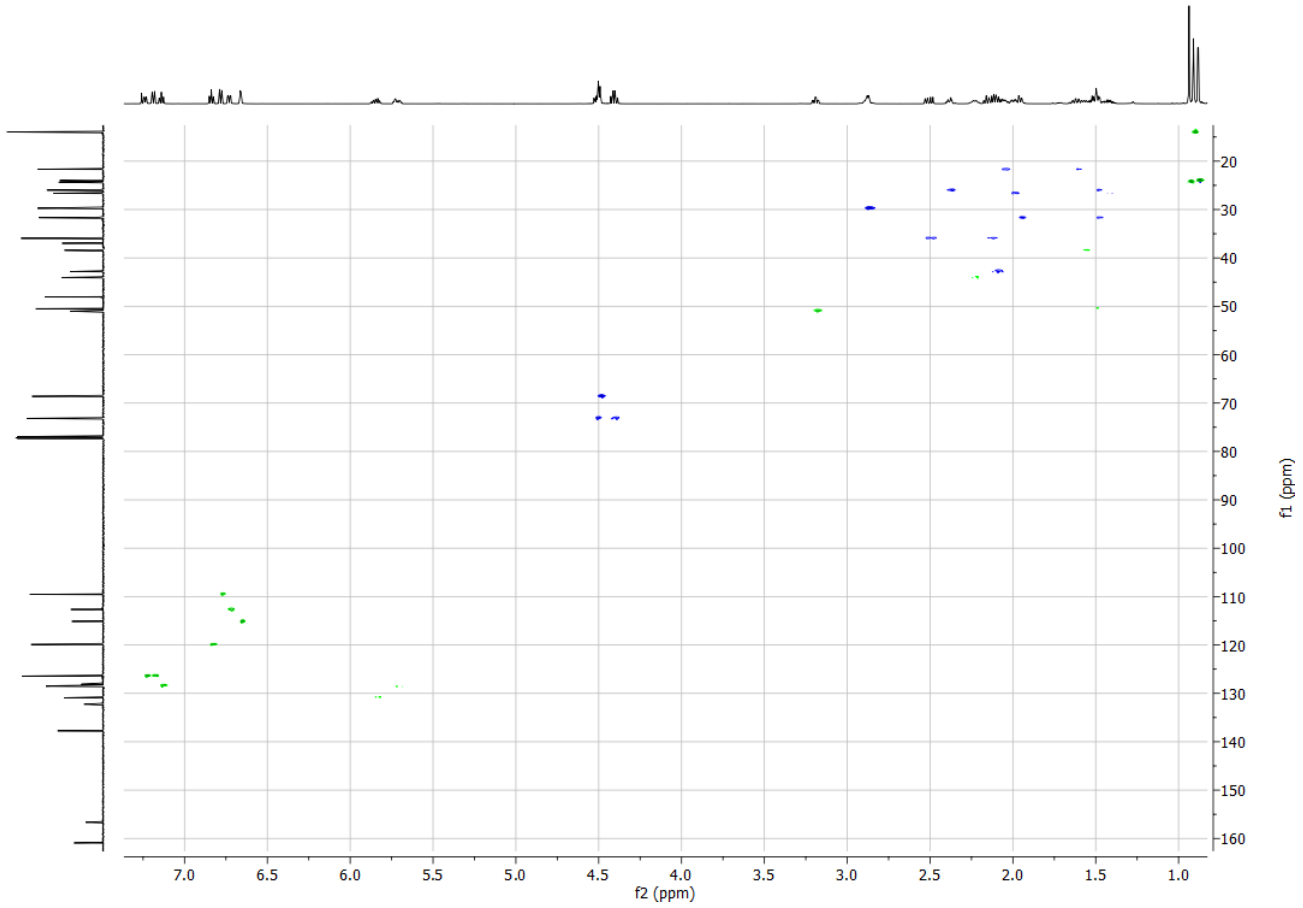
^{13}C NMR (151 MHz, $CDCl_3$)



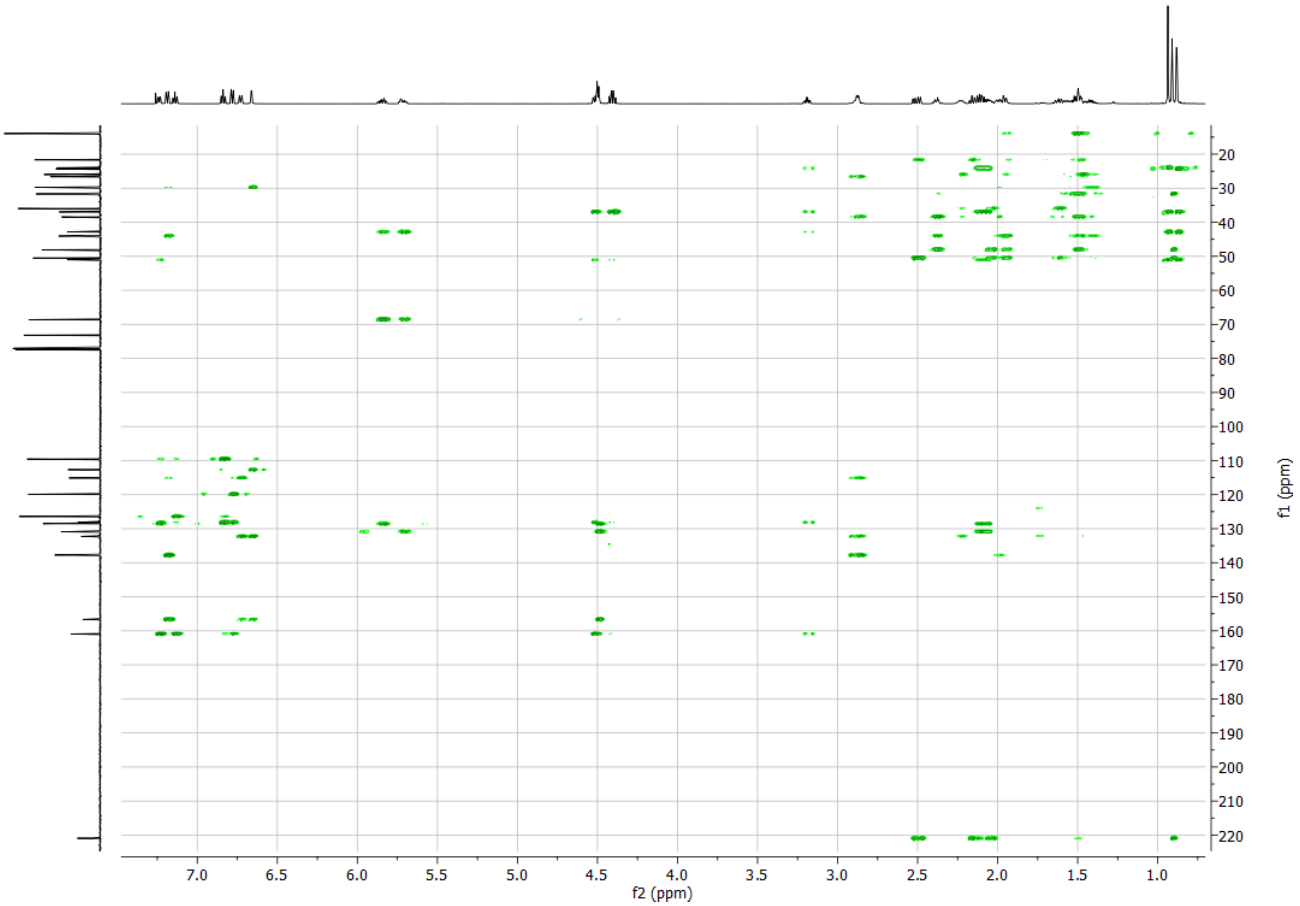
^{1}H-^{1}H COSY NMR (599 MHz, $CDCl_3$)



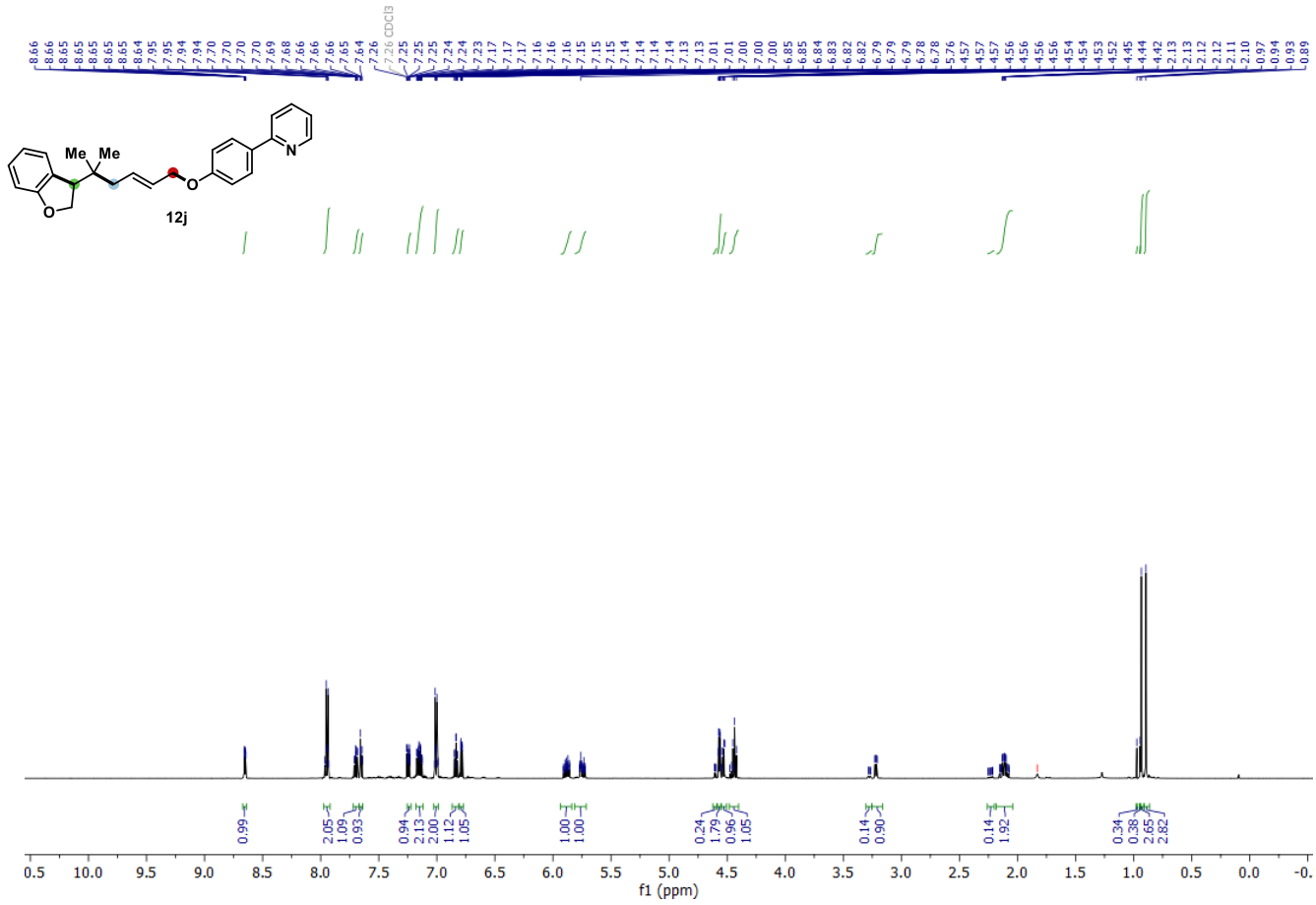
^{1}H-^{13}C HSQC NMR (599 MHz, $CDCl_3$)



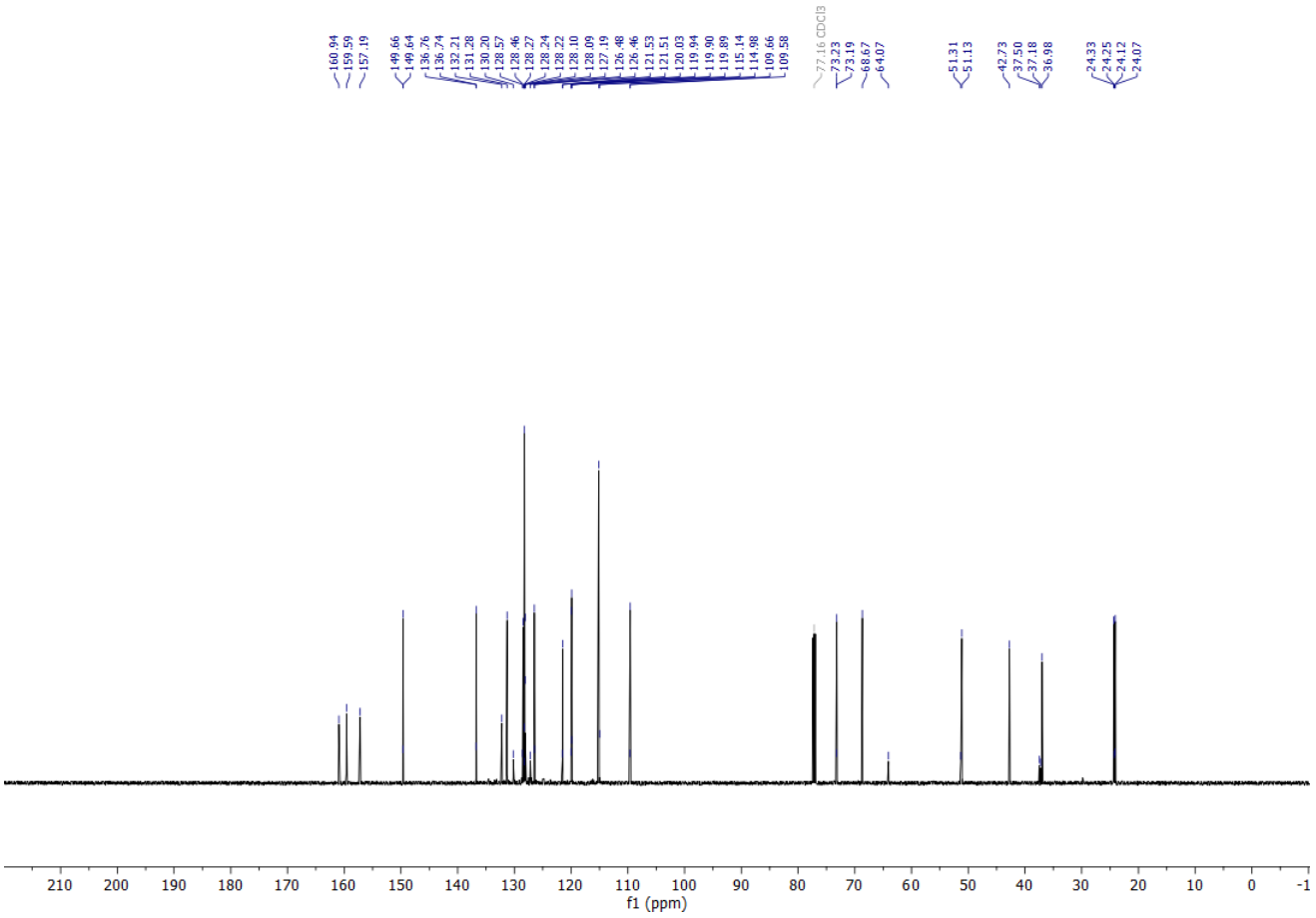
^{1}H-^{13}C HMBC NMR (599 MHz, $CDCl_3$)



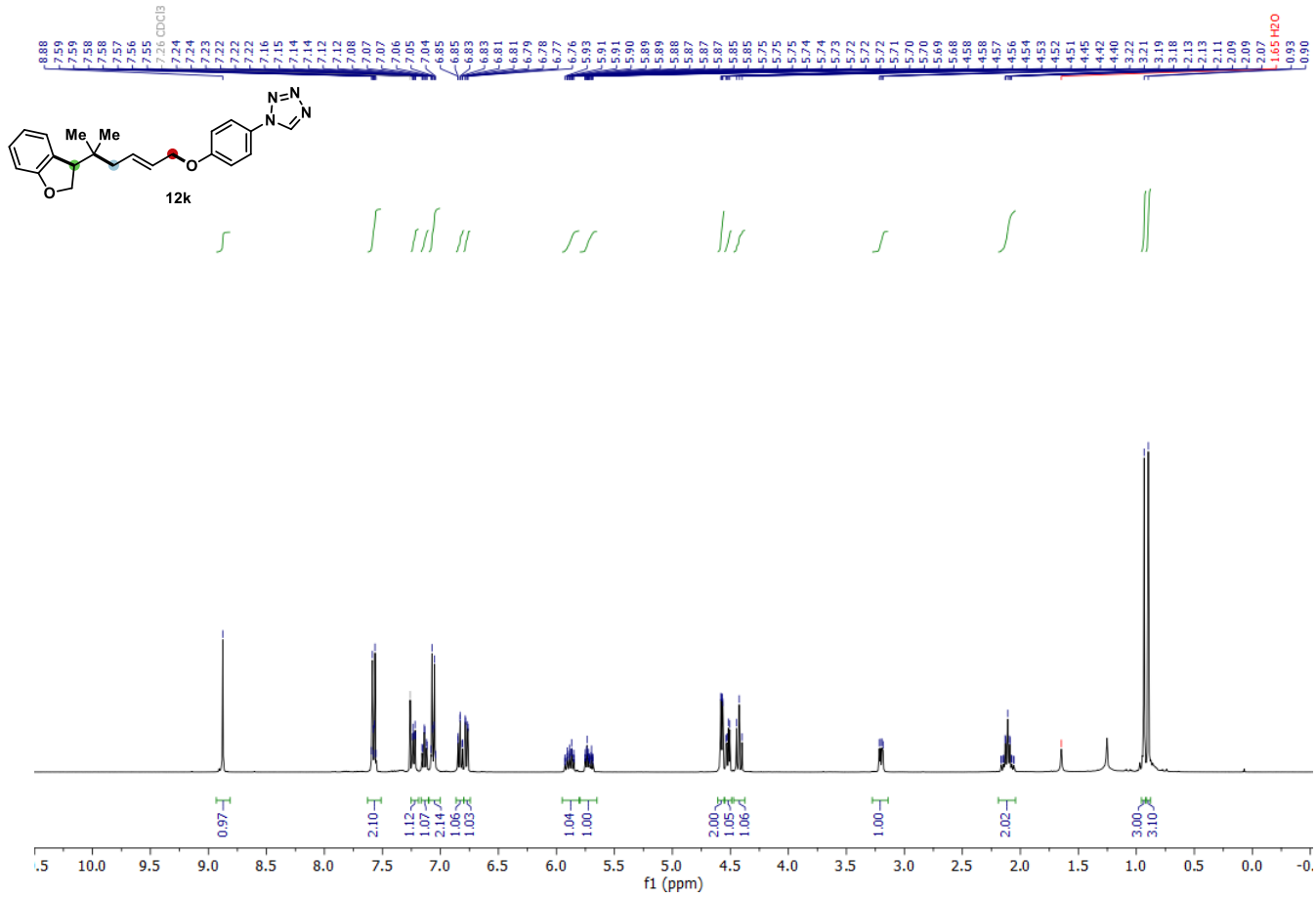
^{1}H NMR (599 MHz, $CDCl_3$)



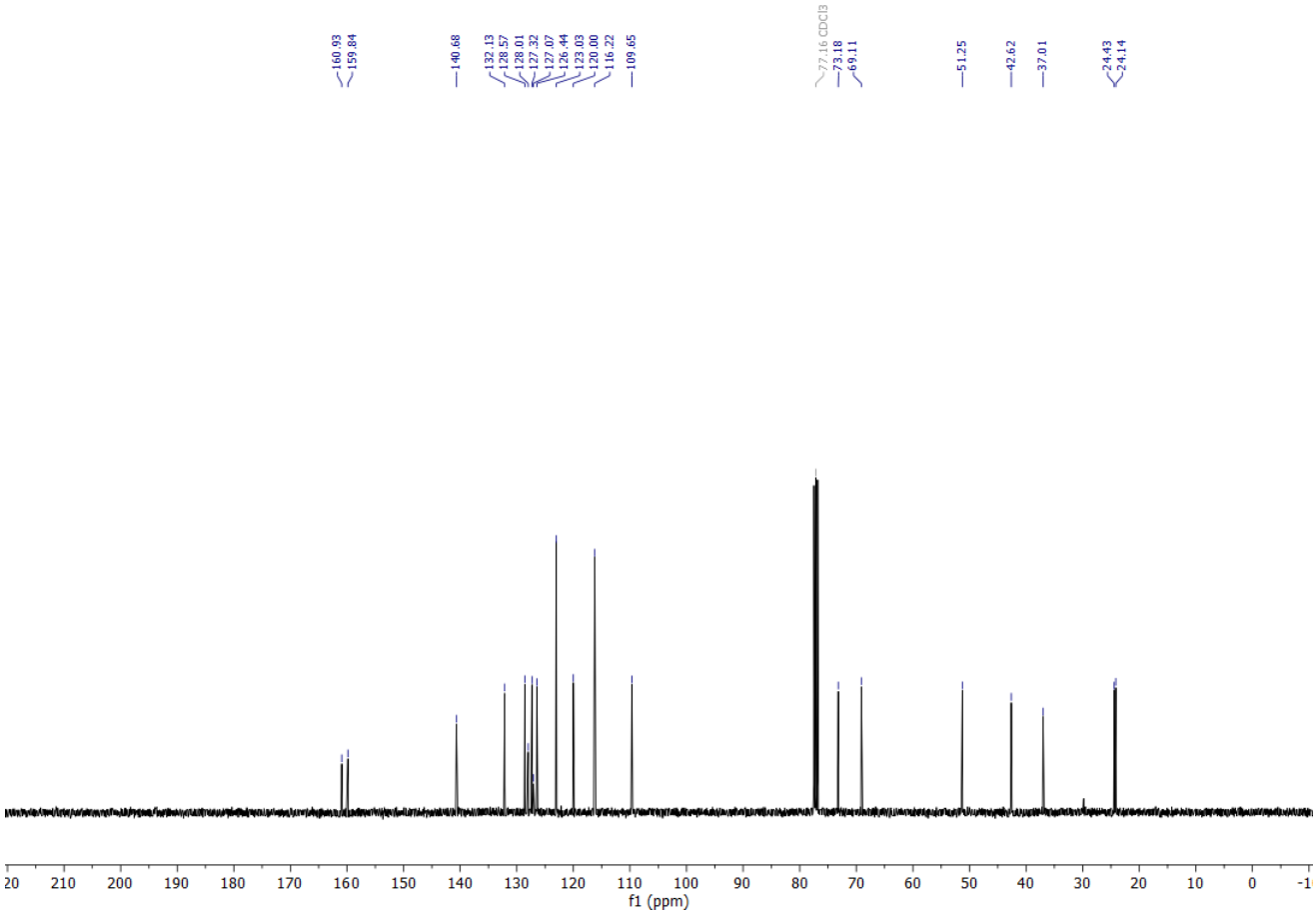
^{13}C NMR (151 MHz, $CDCl_3$)



^{1}H NMR (400MHz, $CDCl_3$)

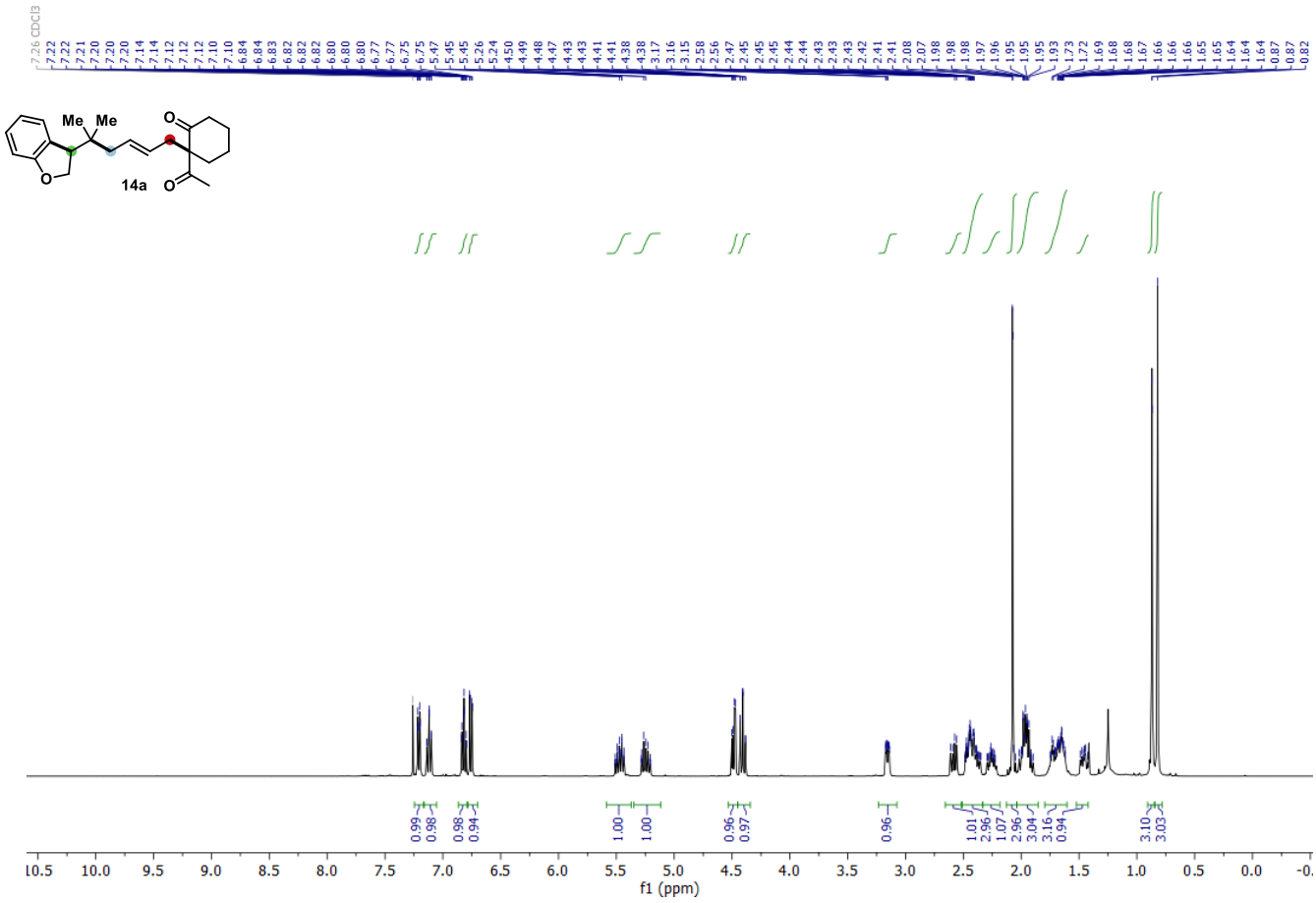


^{13}C NMR (101 MHz, $CDCl_3$)

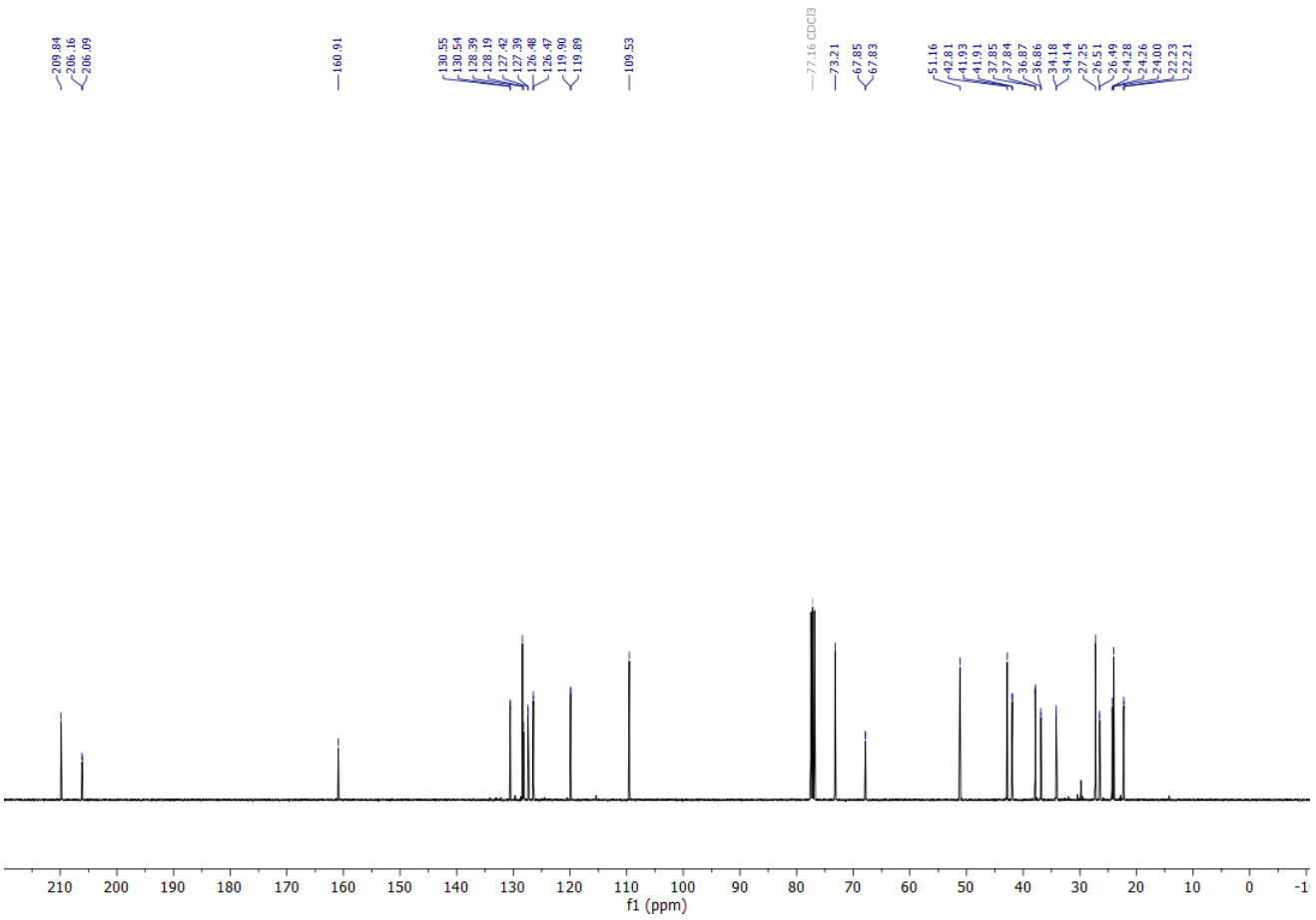


NMR spectra of products 14a-d

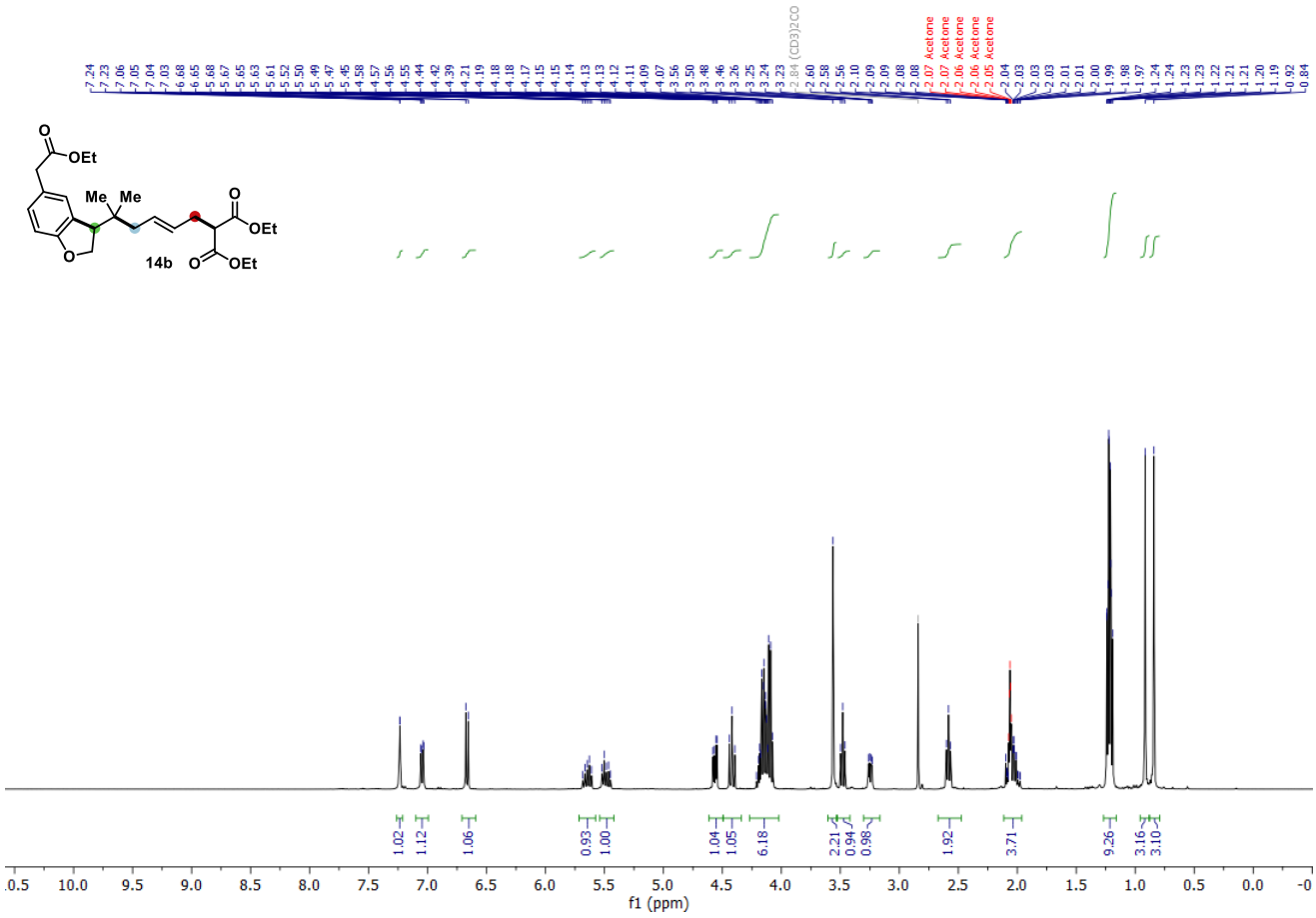
^{1}H NMR (400MHz, $CDCl_3$)



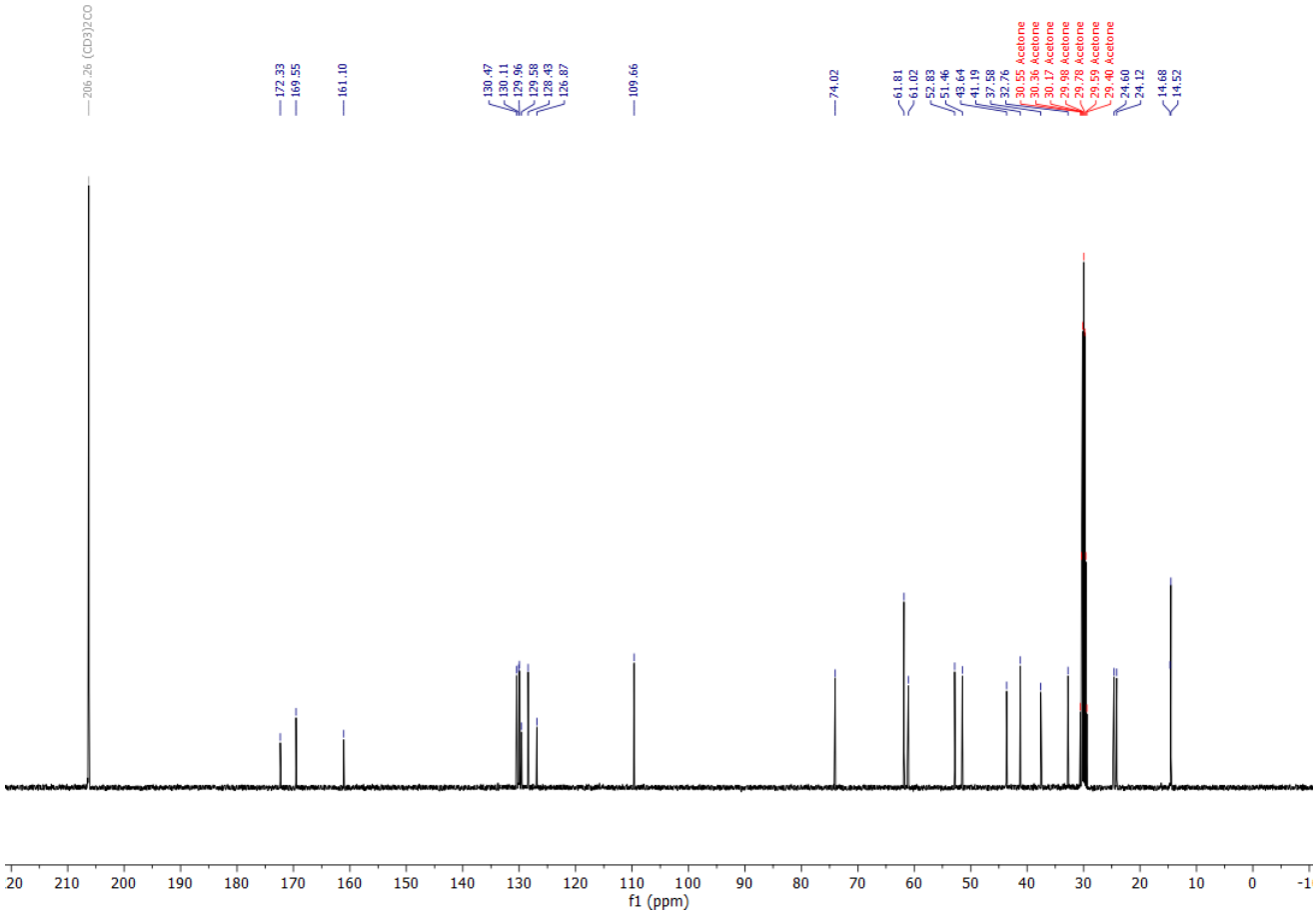
^{13}C NMR (101 MHz, $CDCl_3$)



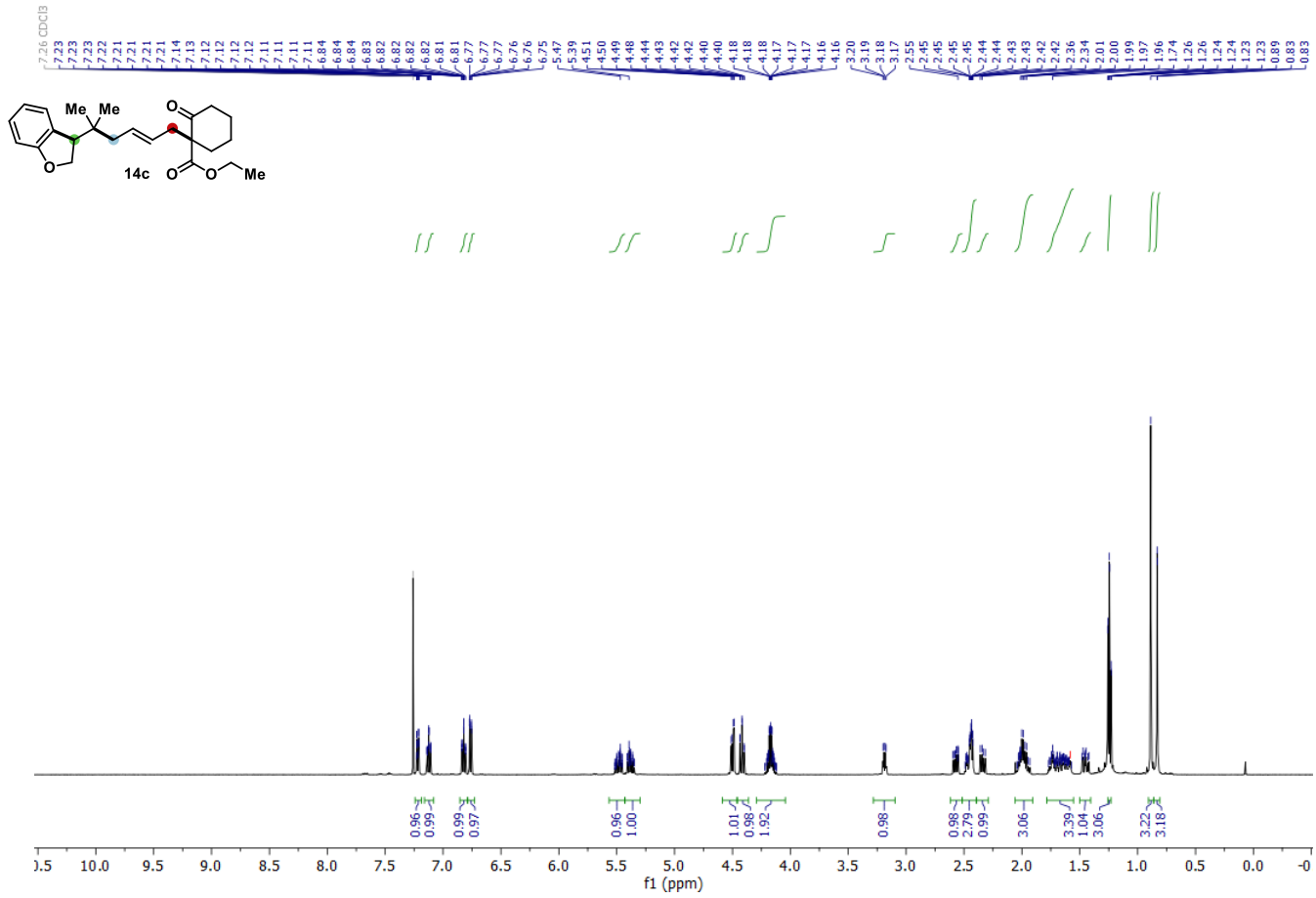
^{1}H NMR (400 MHz, acetone-d_6)



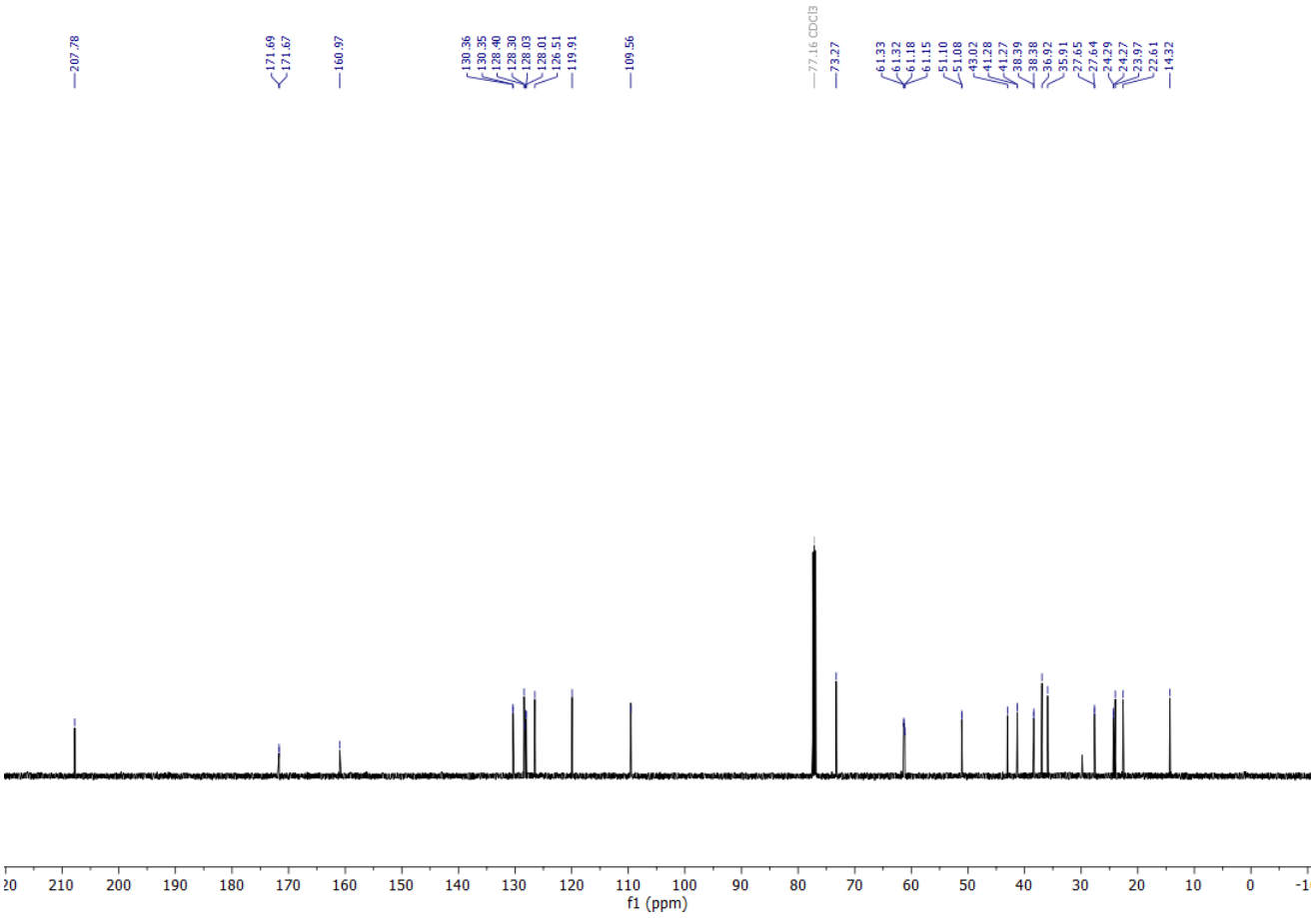
^{13}C NMR (101 MHz, acetone-d_6)



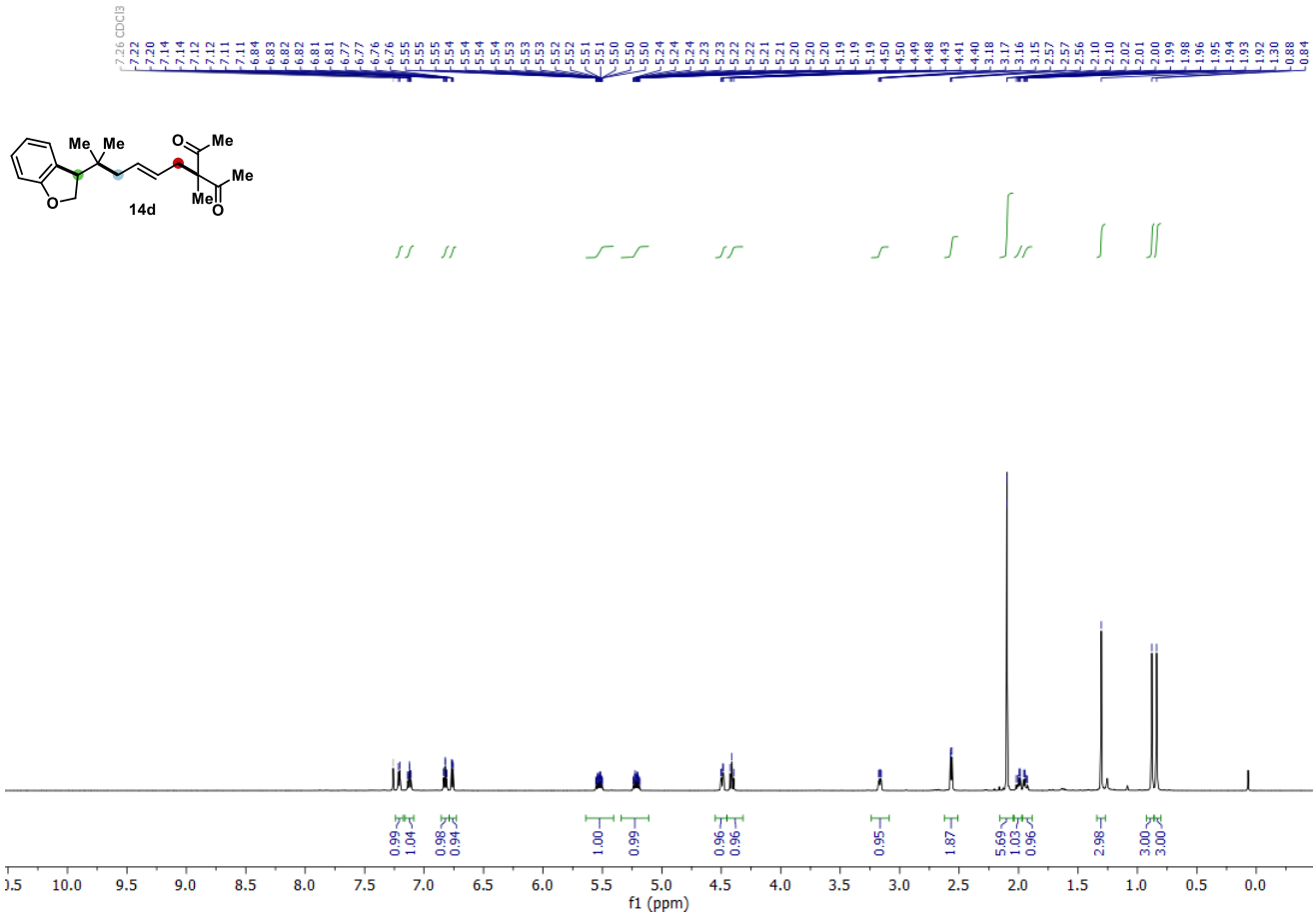
^{1}H NMR (500 MHz, $CDCl_3$)



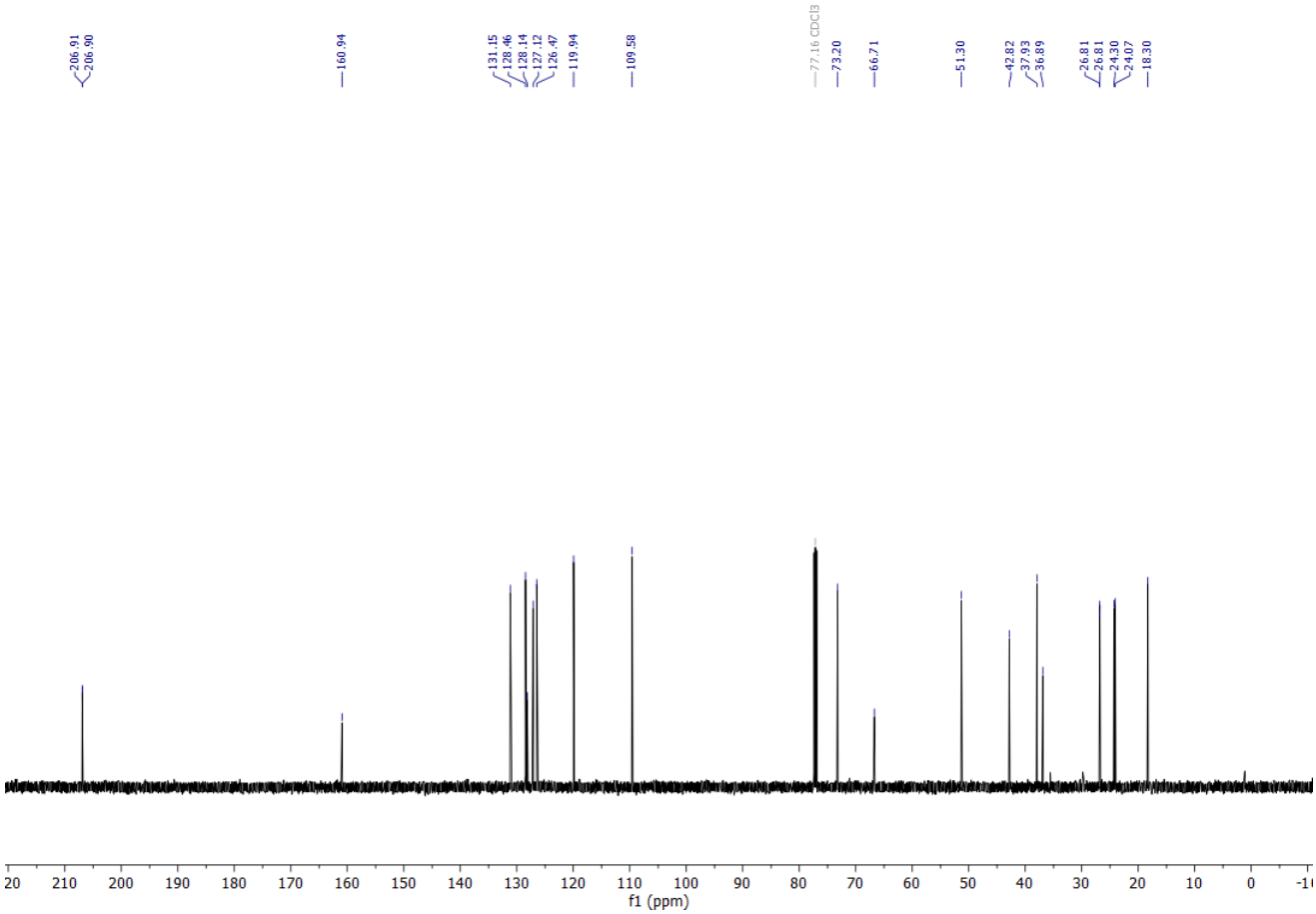
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (599 MHz, $CDCl_3$)

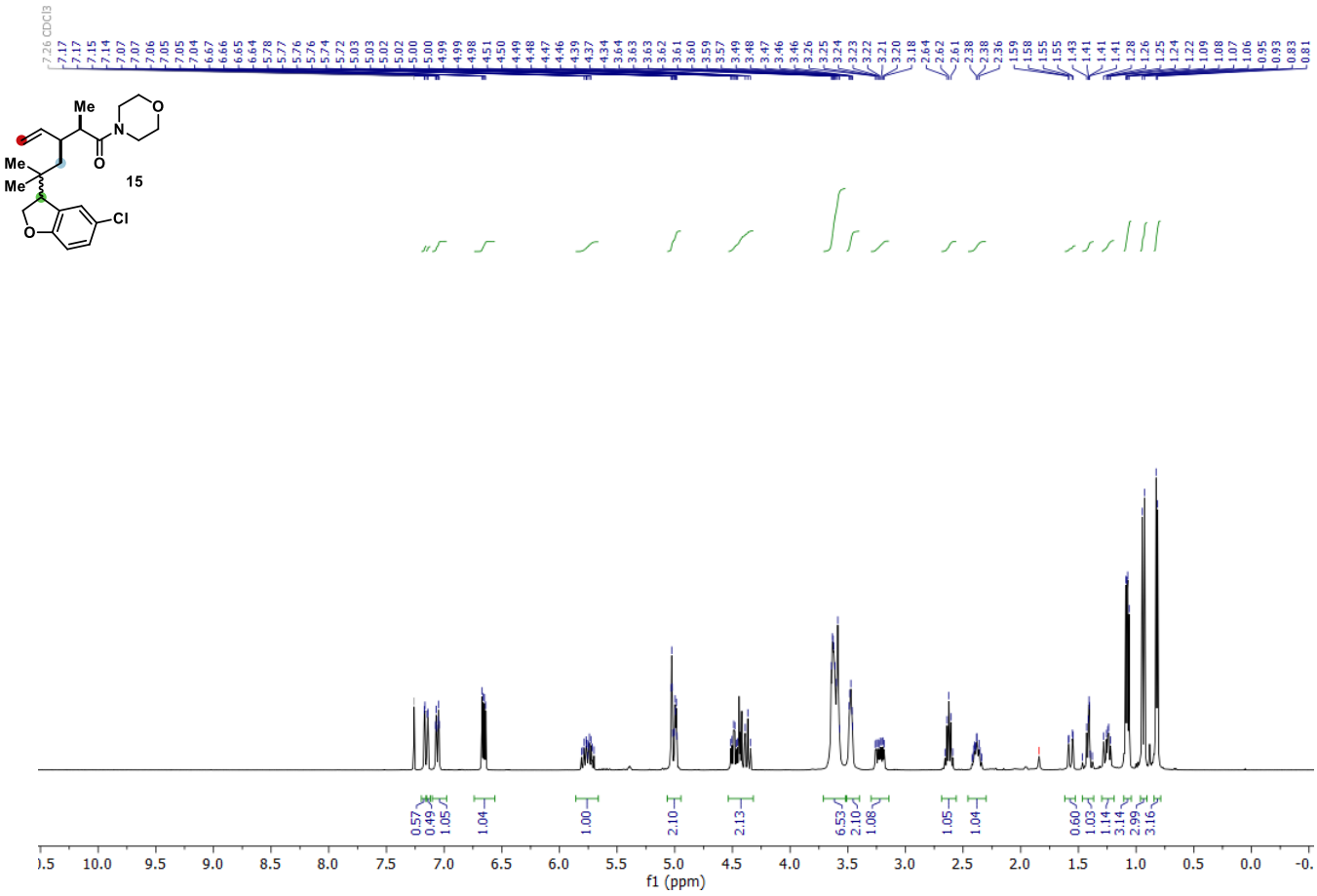


^{13}C NMR (151 MHz, $CDCl_3$)

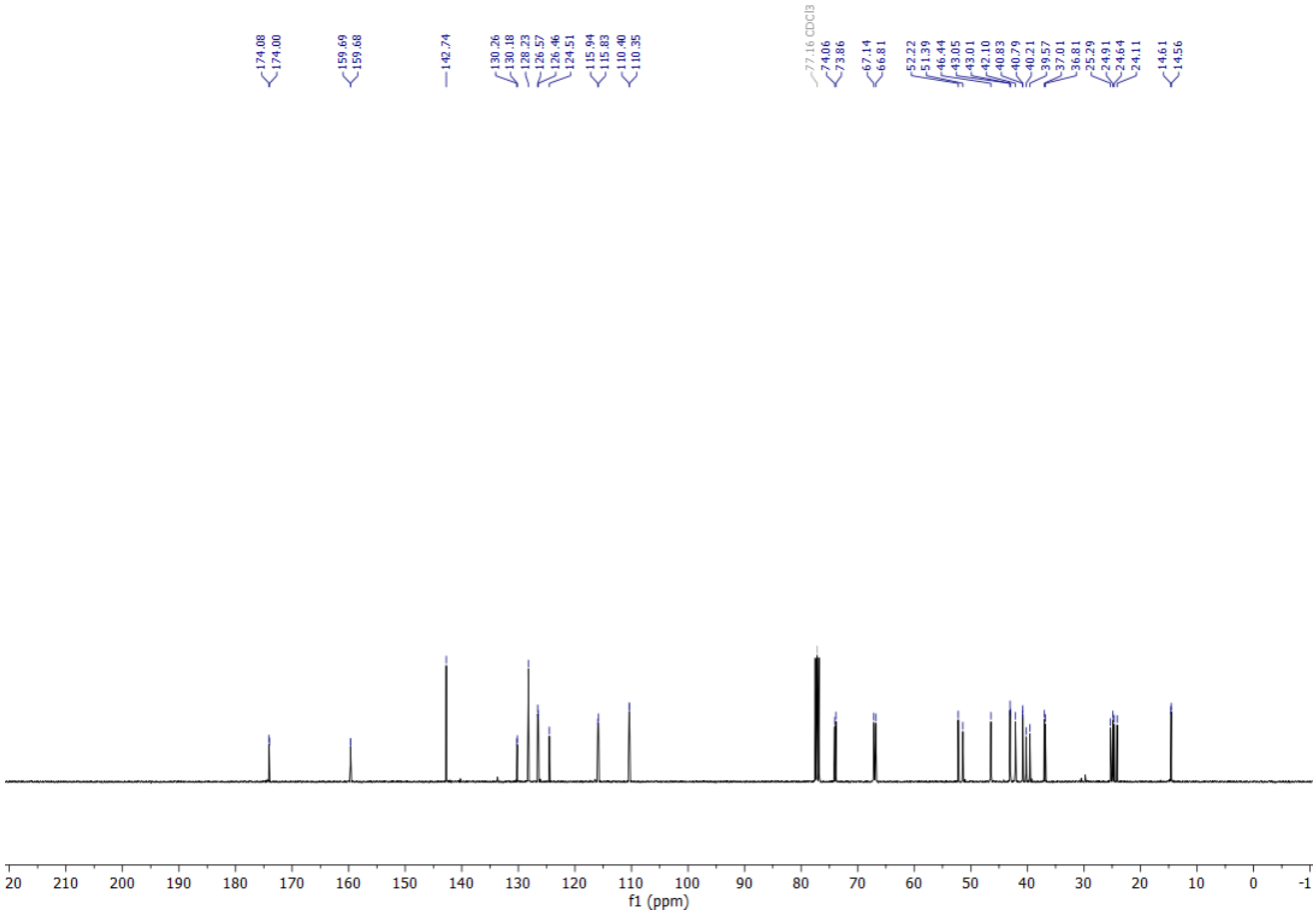


NMR spectra of products 15-16

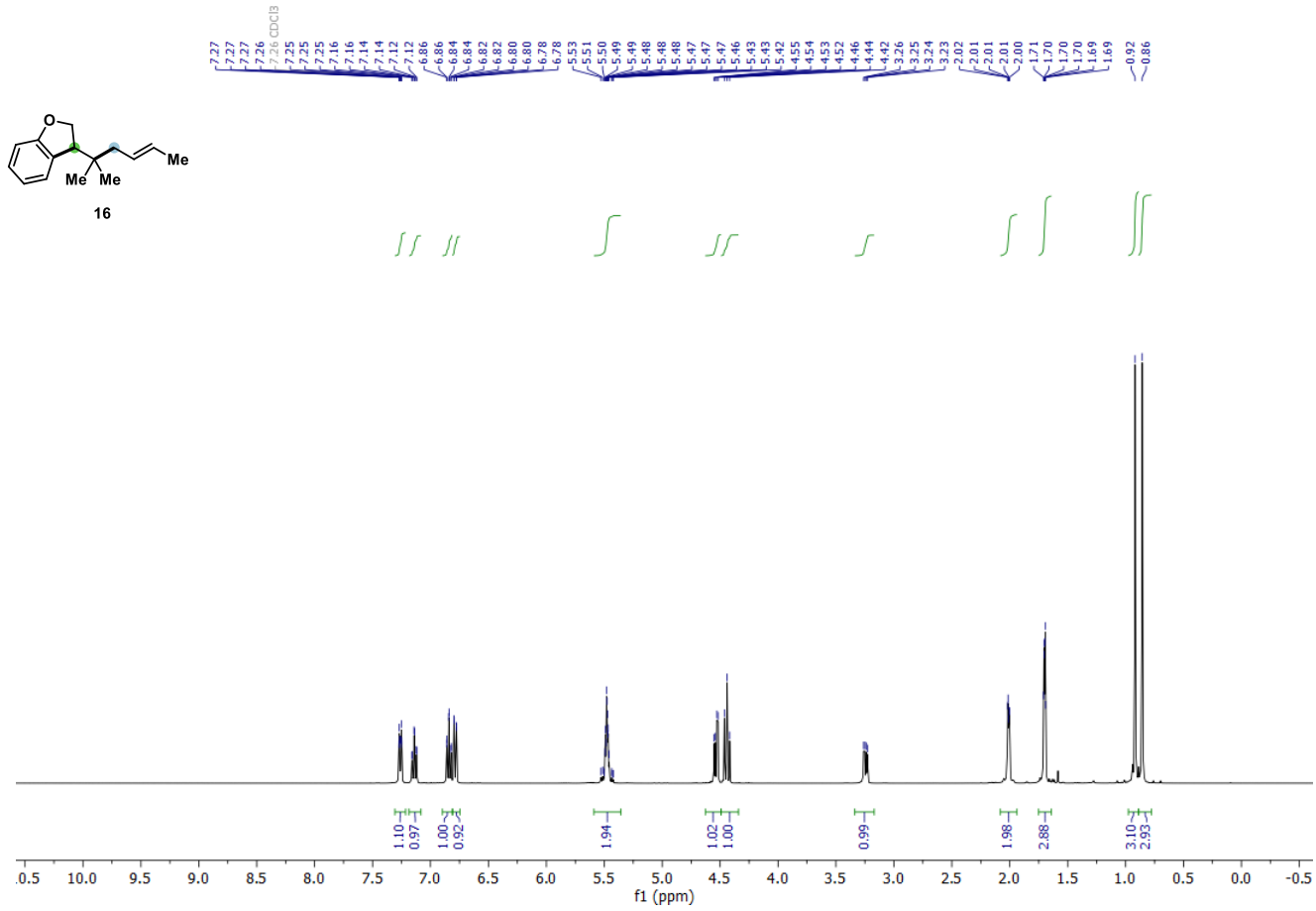
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)