Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Mechanochemical-Assisted Decarboxylative Sulfonylation of α,β-Unsaturated Carboxylic Acids with Sodium Sulfinate Salts

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1. General Information

Reagents information: Commercially available reagents and analytical grade solvents were purchased from Sigma-Aldrich, Toyko Chemical Company (TCI), Alfa-Aesar, MolyChem, SRL chemicals, AVRA, BLD pharm, GLR innovations, LOBA Chemie and AVARICE and were used as received without further purification. Potassium iodide was purchased from SRL chemicals (Assay 99.8%, Cas No. 7681-11-0, Product Code: 27874).

NMR Spectra: ^{1}H, and ^{13}C, NMR spectra were recorded on a JEOL (500 MHz ^{1}H, 125 MHz ^{13}C) or a Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C) spectrometers using $CDCl_3$ as solvent with tetramethylsilane (TMS) as internal standard. In the evaluation of 1H NMR spectra, chemical shift has been assigned in units of parts per million (ppm), wherein, “s” stands for singlet, “br.s” for broad singlet “d” for doublet, “t” for triplet, “q” for quartet, “dd” for doublet of doublets”, “tt” for triplet of triplets, “dt” for doublet of triplets”, “td” for triplet of doublets” and “m” for multiplet. The units of coupling constant (J) has been assigned in Hz.

Gas Chromatography Mass Spectrometry (GC-MS): Gas chromatography (GC) analysis was carried out on an Agilent GC Mass Spectrometer and PerkinElmer Clarus SQ 8T Mass Spectrometer.

Melting points (mp): Measurements were recorded on a OptiMelt, automated melting point apparatus (Stanford Research Systems, Inc.).

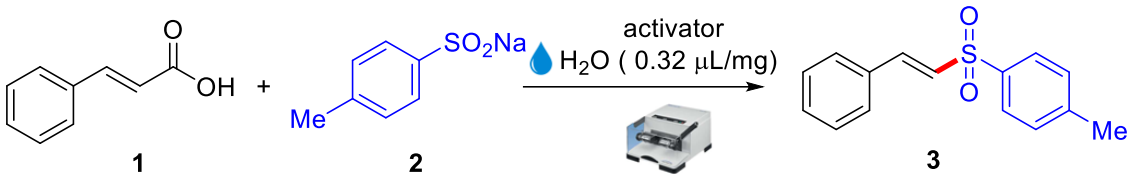
Chromatography: Reactions were monitored on Merck TLC silica gel 60 F254 plates and visualized using ultraviolet light of wavelength 254 nm. Column chromatography was performed on silica gel (100-200 mesh), eluted with hexane/ethyl acetate as a mobile phase.

Equipment information: Mixer mill equipment used for this experiment was: (a) Retsch MM400 mixer mill; (b) 10mL Retsch stainless steel jars; (c) 0.5 g, 5 mm stainless steel balls.

Heat Gun: Heat reaction on mixer mill was performed using BLACK+DECKER, heat gun, KX1800, type B103, 1800W.

2. Detailed Optimization

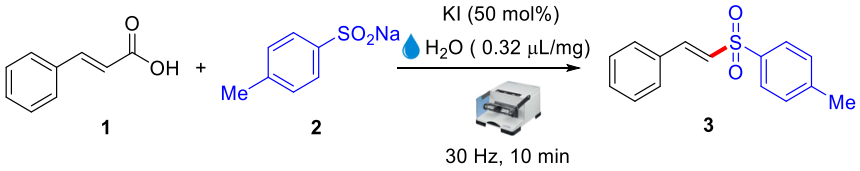
2.1 Concentration of activator



Entry	activator	Concentration	Isolated Yield%
1	KI	1 equiv.	88
2	KI	50 mol%	92
3	KI	40 mol%	73
4	KI	30 mol%	66

Reaction performed using 10 mL Retsch stainless steel milling jar, **1** (0.5 mmol), **2** (0.75 mmol), H_2O (η = 0.32 µL/mg), time: 10 min, frequency 30 Hz. Stainless steel grinding balls (5 X 5 mm grinding ball, weight 0.5 gm each).

2.2 Concentration of substrate



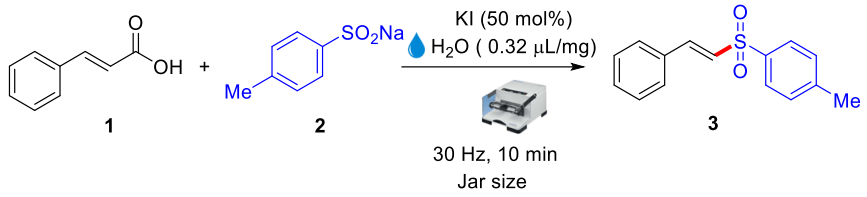
Entry	Cinnamic acid **1**	Sodium sulfinate **2**	Isolated Yield%
1	1 equiv.	1 equiv.	88
2	1 equiv.	1.5 equiv.	92
3	1 equiv.	2 equiv.	92

Reaction performed using 10 mL Retsch stainless steel milling jar, **1**, H_2O (η = 0.32 µL/mg), time: 10 min, frequency 30 Hz. Stainless steel grinding balls (5 x 5 mm grinding balls, weight 0.5 gm each).

2.3 Screening of jar size and grinding balls

a **b** **c** **d**

(a) 5 mm stainless steel grinding ball, weight 0.5 gm each.
(b) 10 mm stainless steel grinding ball, weight, 4.5 gm each.
(c) 5 mm zirconium grinding ball, weight 0.4 gm each.
(d) 10 mm zirconium grinding ball, weight 3.2 gm each.



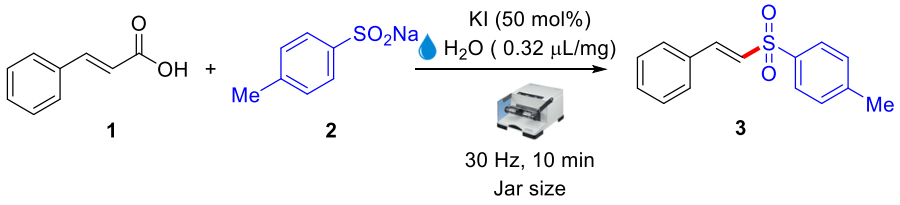
Entry	Retsch Jar-size	Grinding balls	No. of grinding balls added	Total weight of grinding balls	Isolated Yield%
1	5 mL SS jar	a	5	2.5 gm	82%
2	5 mL SS jar	b	2	9 gm	79%
3	**10 mL SS jar**	**a**	**5**	**2.5 gm**	**92%**
4	10 mL SS jar	b	2	9 gm	85%
5	10 mL zirconium Jar	c	5	2 gm	54%
6	10 mL zirconium Jar	d	2	6.4 gm	56%

*SS refers to stainless steel, Reaction performed using **1** (0.5 mmol), **2** (0.75 mmol), KI (50 mol%), H_2O (η = 0.32 µL/mg), time: 10 min, frequency 30 Hz.

Entry: 1 Entry: 2 Entry: 3 Entry: 4 Entry: 5 Entry: 6

Figure 1. Representative image of different jar size and grinding balls after 10 min at 30 Hz.

2.4 Screening of time and frequency

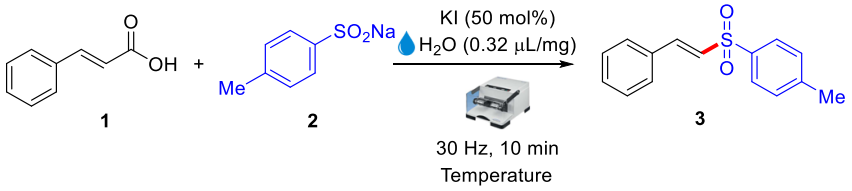


Entry	Retsch Jar-size	Time (min)	Frequency (Hz)	Yield
1	10 mL SS jar	10	20	67%
2	10 mL SS jar	10	25	80%
3	**10 mL SS jar**	**10**	**30**	**92%**
4	10 mL SS jar	20	30	92%
5	10 mL SS jar	30	30	92%

Reaction performed using 10 mL Retsch stainless steel milling jar, **1** (0.5 mmol), **2** (0.75 mmol), KI (50 mol%), H_2O (η = 0.32 µL/mg). Stainless steel grinding balls (5 x 5 mm grinding ball, weight 0.5 gm each).

2.5 Screening of internal temperature

Two sets of the same reaction were performed under standard conditions on the ball mill. For this study, safety lid of mixer mill was removed, and a heat gun was fixed above the Retsch milling jar using a clamp. The Retsch stainless steel jar was subjected to a constant heat supply for 10 min and 30 Hz and the internal temperature of jar was analyzed (103.0 °C) and 90% yield of the desired product **3** was obtained (Entry 1). In another reaction, the reaction jar was subjected to ambient temperature for 10 min and 30 Hz. After the completion of the reaction, internal temperature of jar was analyzed (25.4 °C) and 92% yield of product **3** obtained.



Entry	Medium	Reaction Time	Internal jar temp. °C	Isolated yield
1	With heating	10 min	103.0	90%
2	Room temperature	10 min	25.4	92%

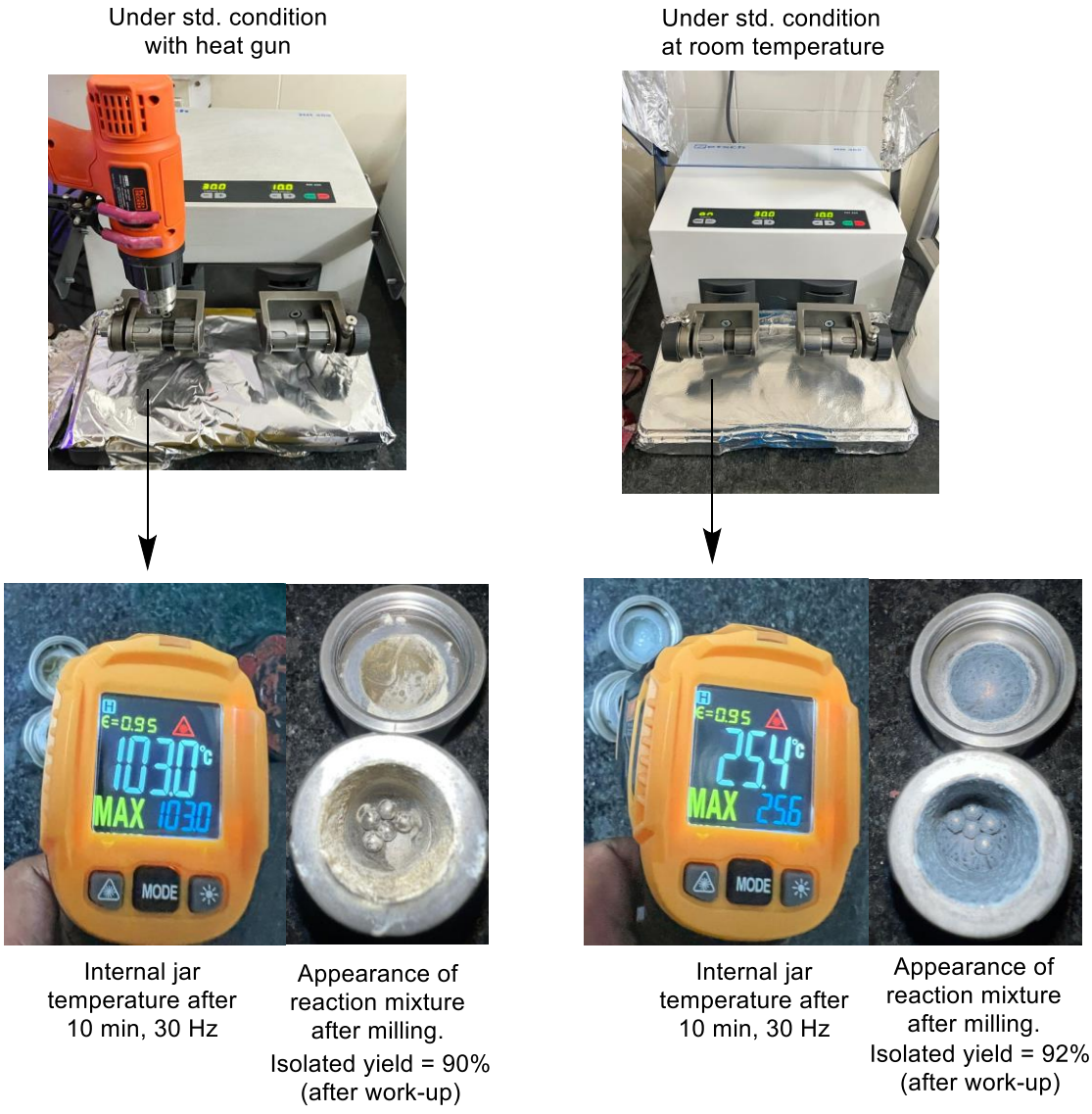
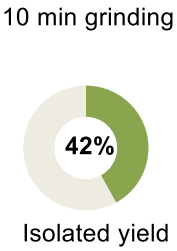


Figure 2. Representative image of temperature screening

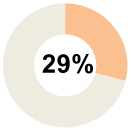
2.6 Hand grinding-based reaction



To a mortar, was charge with cinnamic acid **1** (0.5 mmol), sodium sulfinate **2** (0.75 mmol), potassium iodide (50 mol%), H_2O (η = 0.32 µL/mg). Using a pestle, the reaction was grinded continuously for 10 min. To the reaction mixture, EtOAc was added to mobilize the residue, and the mixture was decanted to a clean beaker. This step is repeated with more ethyl acetate until all residues is removed from the mortar. The mixture is then transferred to a 125 mL separating funnel and the organic layer was extracted with a saturated solution of $Na_2S_2O_3$ (15 mL x3). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was subjected to purification by column chromatography on silica gel eluting with hexane/ethyl acetate. The resulting vinyl sulfone product was obtained in 42% yield.

2.7 Solution-based reaction

In H_2O, 80 ^oC,
24 h

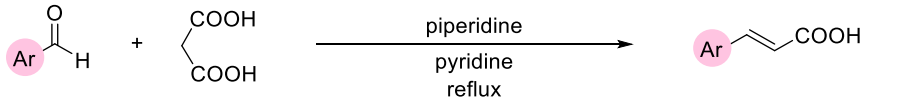


Isolated yield

To a oven dried 100 mL round bottom flask, equipped with a magnetic stirrer, with α,β-unsaturated carboxylic acid **1** (0.5 mmol), sodium sulfinate **2** (0.75 mmol), potassium iodide (50 mol%), in 5mL H_2O. The round-bottom flask was sealed with a rubber septa and the resulting mixture was stirred at 80 ° for 24 h. After completion, the reaction mixture was cooled, and quenched with ethyl acetate. The reaction mixture was slowly poured into a 125 mL separating funnel and the organic layer was extracted with a saturated solution of $Na_2S_2O_3$ (15 mL x3). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue were purified by column chromatography on silica gel eluting with hexane/ethyl acetate, and the corresponding vinyl sulfone product **3** was obtained in 29% yield.

3. General Procedure for Synthesis of Products

3.1 General procedure for the synthesis of α,β-unsaturated carboxylic acid.[1]



aldehyde malonic acid **1** α,β-unsaturated carboxylic acid

To a oven dried 100 mL round bottom flask, equipped with a magnetic stirrer, was charged with a mixture of substituted aryl aldehyde (4.00 mmol), malonic acid (8.80 mmol) and piperidine (70 µL) in pyridine (1.80 mL). The round-bottom flask was stirred under gentle reflux for 3-5 h. The reaction mixture was cooled and slowly poured into a 100 mL beaker containing ice-cold aqueous HCl (2N, 35 mL), resulting into the formation of precipitates. The precipitated crystals were filtered, washed with cold water and dried under vacuum to afford the corresponding α,β-unsaturated carboxylic acid products **1**.

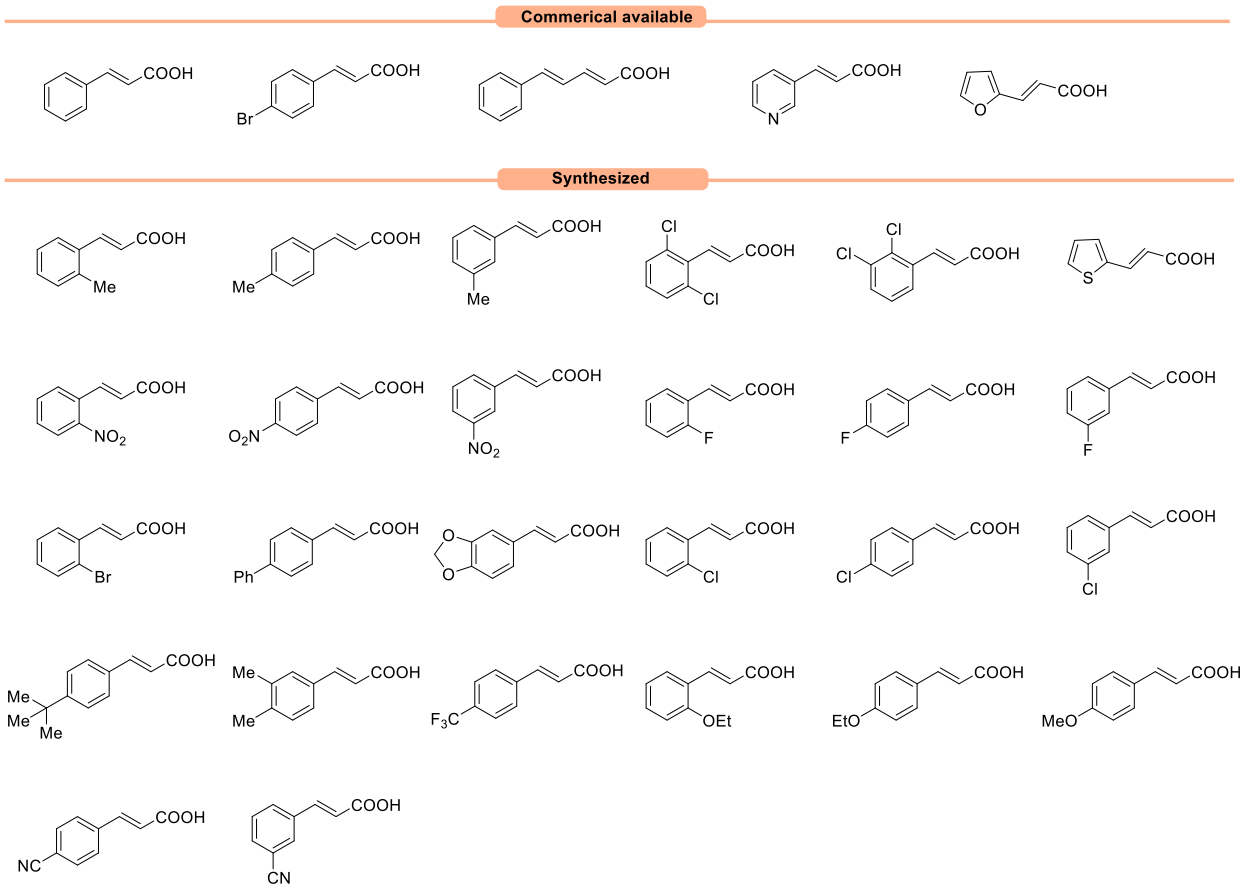
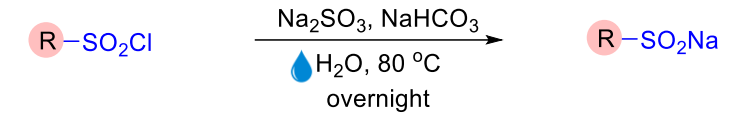


Figure 3. Various α,β-unsaturated carboxylic acid used in this experiment

3.2 General procedure for the synthesis of sodium sulfinates.[2]



To a oven dried 100 mL round-bottom flask, equipped with a magnetic stirrer, was charged with sulfonyl chloride (5 mmol), Na_2SO_3 (2.0 equiv.) followed by $NaHCO_3$ (2.0 equiv.) in water (5 mL). The round-bottom flask was sealed with a rubber septa and the resulting mixture was stirred at 80 ° for 10 h. Later, the reaction was cooled to room temperature and the water was removed in a vacuum. The residue was extracted in ethanol and recrystallization from ethanol furnished sodium sulfinates as a white or light yellow solid.

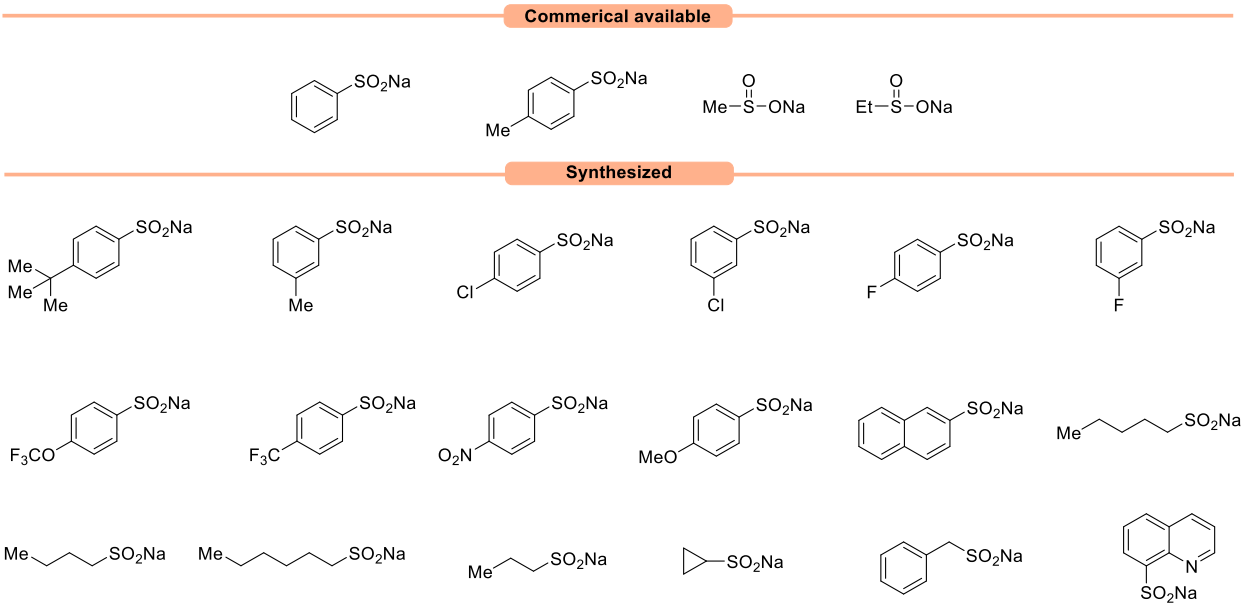
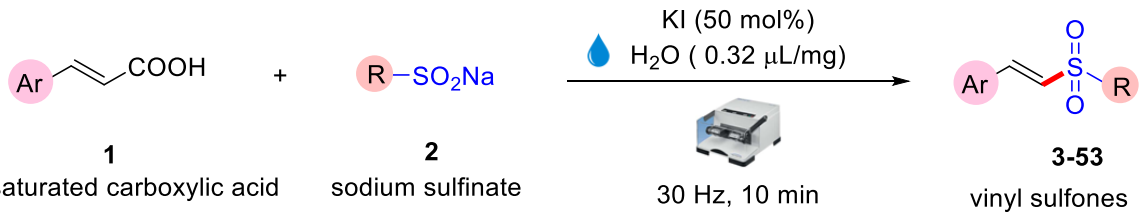


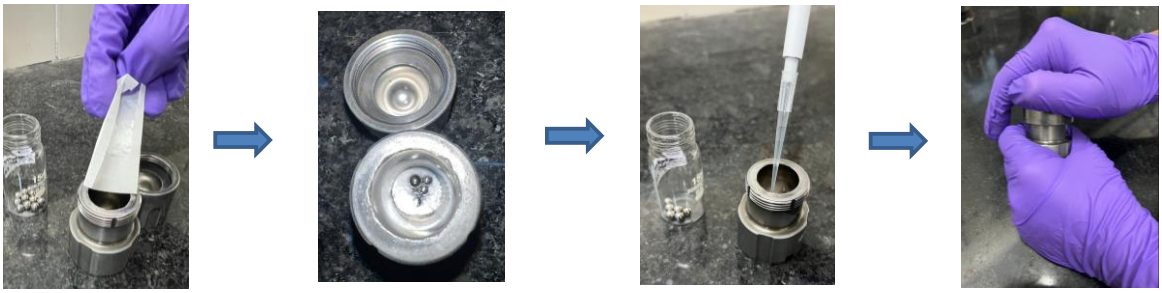
Figure 4. Various sodium sulfinates used in this experiment

3.3 General procedure for the synthesis of vinyl sulfones.



To a cleaned 10 mL Retsch stainless steel milling jar, was charge with α,β-unsaturated carboxylic acid **1** (0.5 mmol), sodium sulfinate **2** (0.75 mmol), potassium iodide (50 mol%), H_2O (η = 0.32 μL/mg), and 2.5 gm (5 x 5 mm) stainless steel grinding balls. The jar was closed and mounted to the ball mill and milled at 30 Hz for 10 min (Unless otherwise stated). After the completion of the reaction, the jar was removed from the mixer mill and opened. To the reaction mixture, ethyl acetate was added to mobilize the residue, and the mixture was decanted to a clean beaker. This step is repeated with more ethyl acetate until all residue is removed from jar. The mixture is then transferred to a 125 mL separating funnel and the organic layer was extracted with a saturated solution of $Na_2S_2O_3$ (15 mL x3). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue were purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding vinyl sulfone product **3-53**.

3.4 Procedure of mechanochemical reaction setup



1. Add weight amount of reactants to the jar.

2. Add the grinding balls to the jar.

3. Add H_2O to the jar.

4. Close the jar

5. Attach the jar to the ball mill and close the ball mill lid.

6. Set the frequency to 30 Hz and time to 10 mins (Unless otherwise stated),and then start the machine.

7. After completion, remove the jar and open.
Note: Color of reaction mixture may differ depending on the substrates.

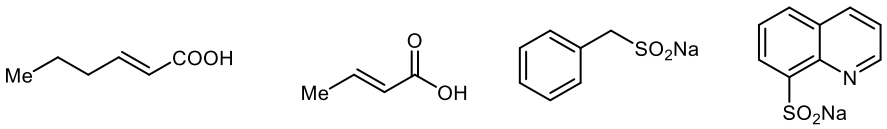
8. Add ethyl acetate to the jar to dissolve the residue.

9. Decant the reaction mixture to a clean beaker and repeat the step with more organic solvent till complete removal of residue from jar.

10. Transfer the reaction mixture to the separating funnel. Add sat. $Na_2S_2O_3$ and complete the work-up.

Figure 5. Procedure for mechanochemical reaction

3.5. Unsuitable substrates



Scheme 1. Unsuitable substrates

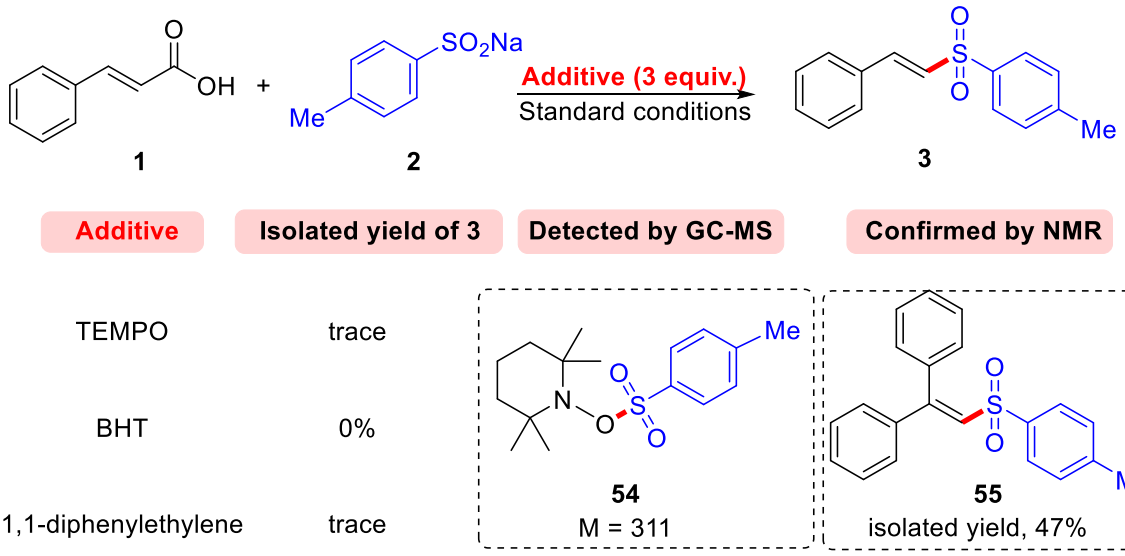
4. Procedure for the gram scale synthesis of vinyl sulfones.

To a 10 ml stainless steel jar, was charge with sodium 4-methylbenzenesulfinate **2** (0.801 g, 4.5 mmol), cinnamic acid **1** (0.444 g, 3 mmol), potassium iodide (50 mol%, 0.248 g), H_2O (η = 0.32 µL/mg), and 2.5 gm (5 x 5 mm) stainless steel grinding balls. The jar was closed and mounted to the mill. The mixer mill was set for 45 min (three sets of 15 min with 2 min interval) for efficient mixing and was set at the frequency of 30 Hz. After the completion of the reaction, the jar was removed from the mixer mill and opened. Then, to the white paste were added ethyl acetate to mobilized the residue, and using a spatula, the mixture was decanted to a clean beaker. This step was repeated with more organic solvent till complete removal of residue from jar. The reaction mixture was then transferred to a 250 mL separating funnel and the organic layer was extracted with a solution of $Na_2S_2O_3$ (20 mL x3). The organic layer was dried over Na_2SO_4, filtered and the resulting solvent was removed under reduced pressure. The residue was then purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding vinyl sulfone product **3** in 72% yield (0.557 g).

Figure 6. Gram-scale reaction

5. Mechanistic Studies

5.1 Radical trapping experiments



Scheme 2. Radical trapping experiments

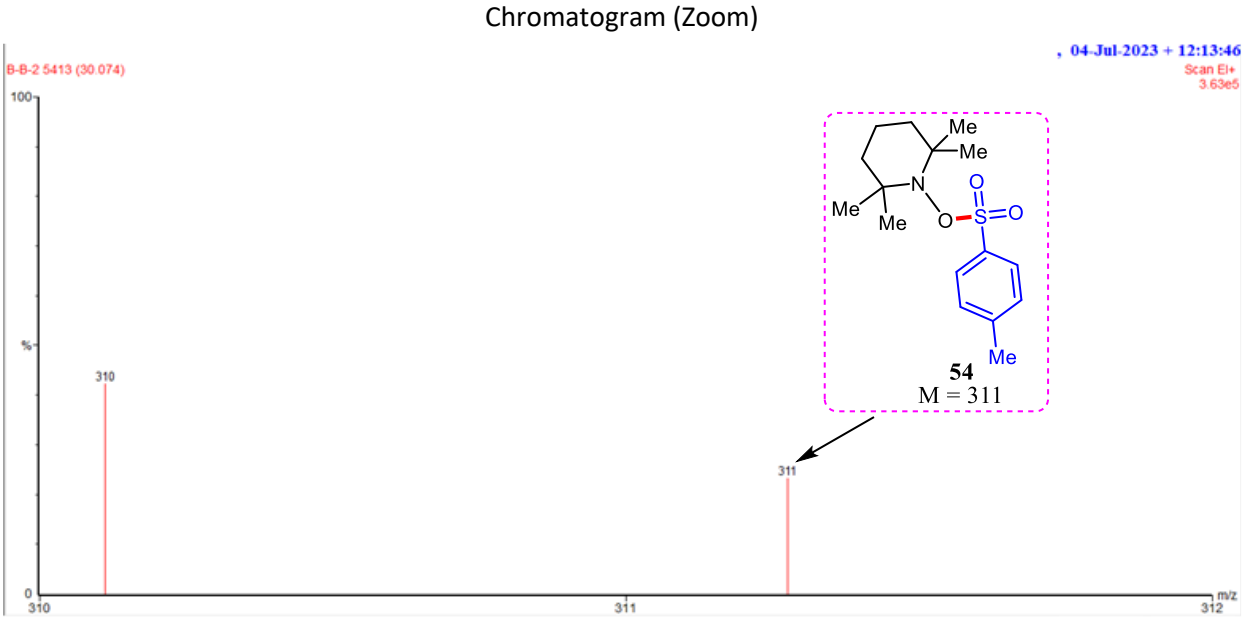


Figure 7. The detection of tosyl-TEMPO by GC-MS

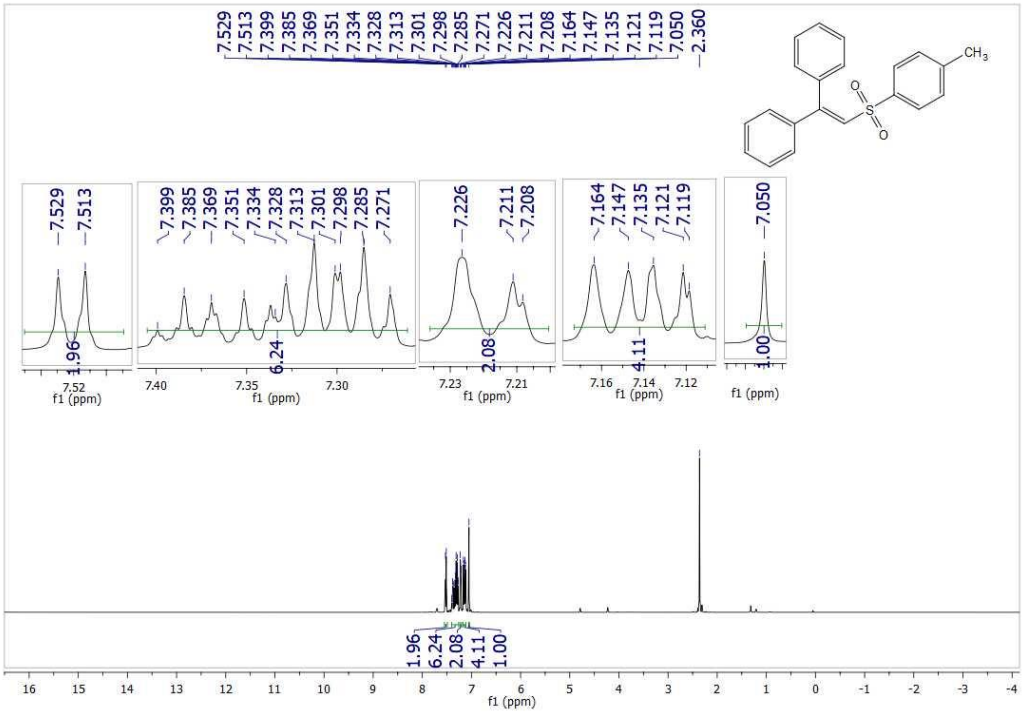


Figure 8. The ^{1}H-NMR spectrum of 1,1-diphenylethylene adduct **55**.

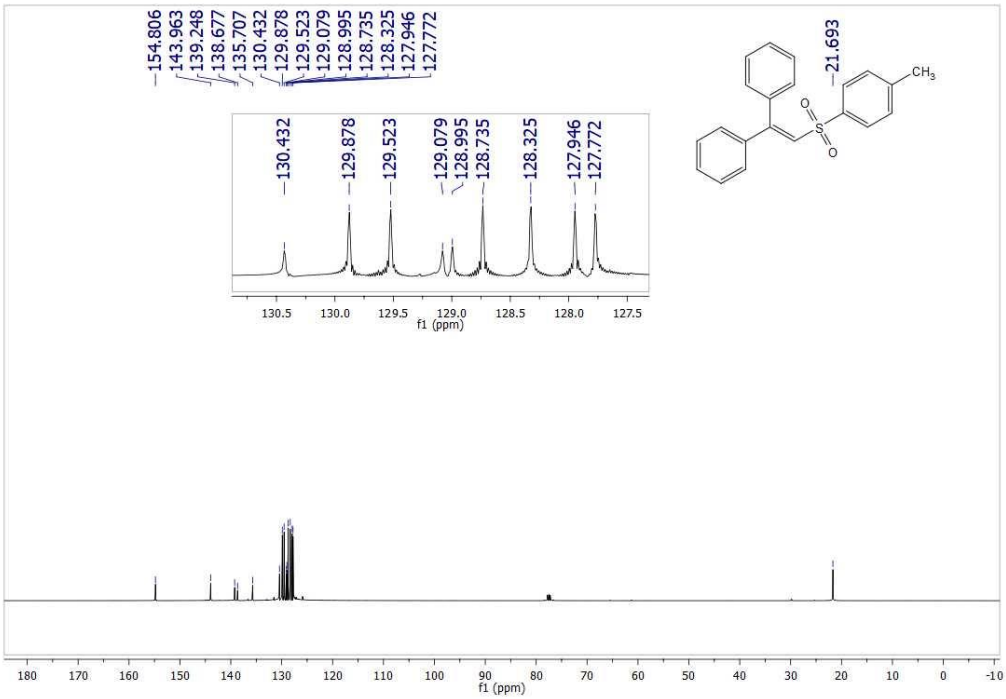
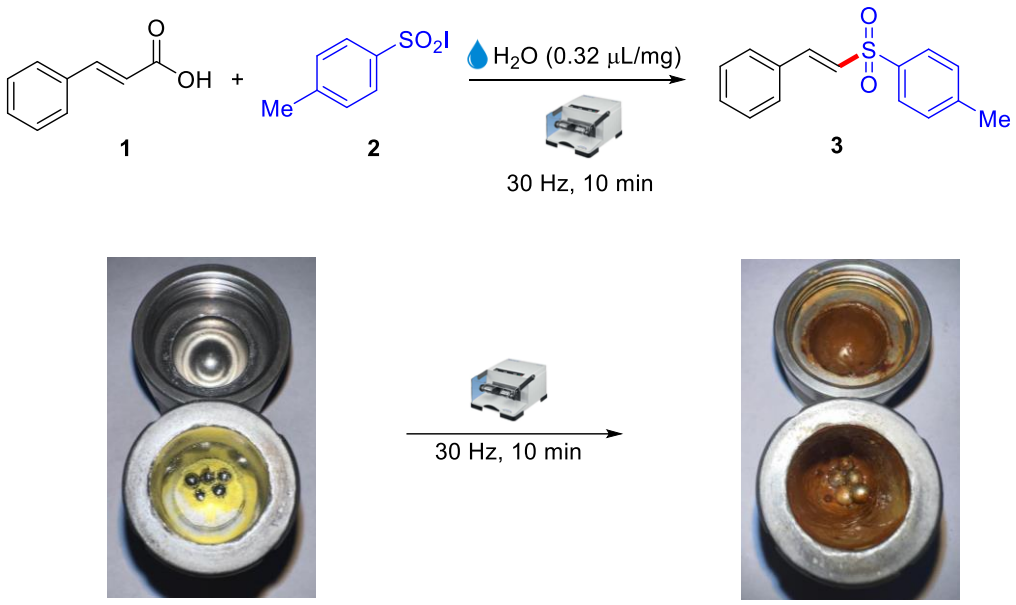


Figure 9. The ^{13}C-NMR spectrum of 1,1-diphenylethylene adduct **55**.

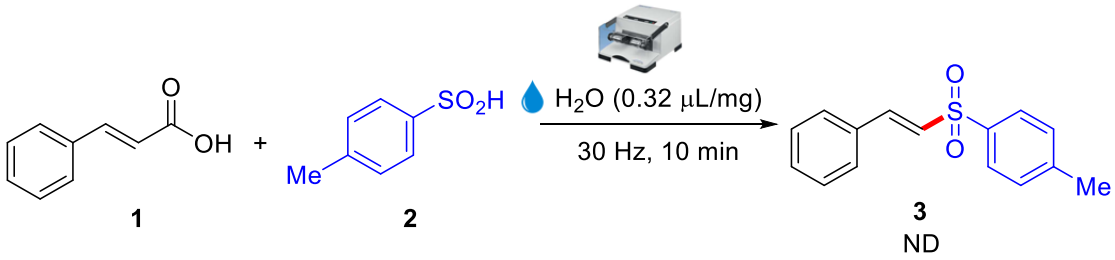
5.2 Evidence of sulfonyl iodide intermediate



Scheme 3. Evidence of sulfonyl iodide iontermediate

4-Methylbenzenesulfonyl iodide was synthesized according to known literature and was used as such without further purification.[3] To a cleaned and dried 10 mL Retsch stainless steel milling jar, was charge with 4-methylbenzenesulfonyl iodide **2** (0.75 mmol), cinnamic acid **1** (0.5 mmol), H_2O (η = 0.32 μL/mg), and 2.5 gm (5 x 5 mm) stainless steel grinding balls. The jar was closed and mounted to the mixer mill. The mixer mill was set for 10 min and frequency 30 Hz. After the completion of the reaction, the jar was removed from the mixer mill and opened. To the reaction mixture, ethyl acetate was added to mobilize the residue and the mixture was decanted to a 125 mL separating funnel. This step was repeated with more organic solvent till complete removal of residue from jar. Next, the organic layer was extracted with a saturated solution of $Na_2S_2O_3$ (15 mL x3). Th organic layer was dried over Na_2SO_4, filtered and the resulting solvent was removed under reduced pressure. The residue was then purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding vinyl sulfone product **3** in 87% yield. Based on this study, the involvement of arylsulfonyl iodide intermediate was confirmed in the reaction medium.

5.3 Evidence of sulfinic acid intermediate

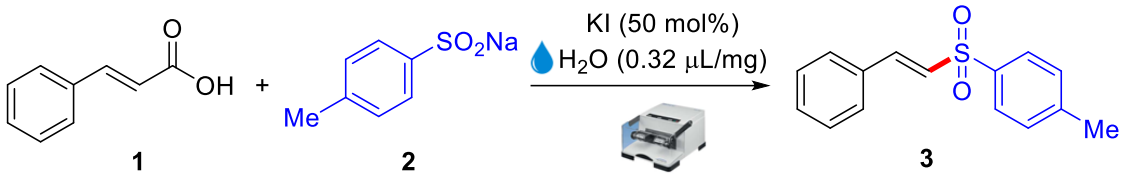


Scheme 4. Evidence of sulfinic acid intermediate

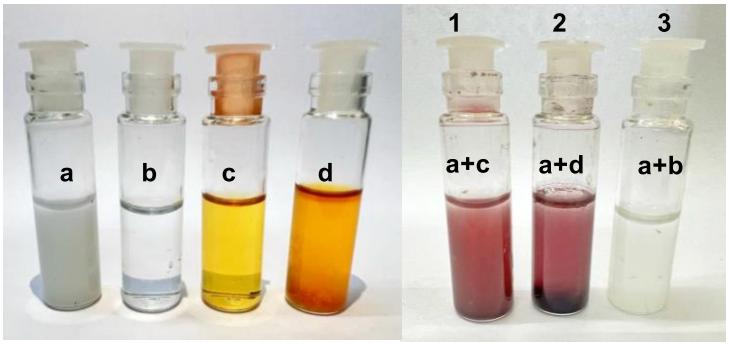
4-Methylbenzenesulfinic acid **2** was synthesized according to known literature and was used as such without further purification.[4] To a cleaned and dried 10 mL Retsch stainless steel milling jar, was charge with 4-methylbenzenesulfinic acid **2** (0.75 mmol), cinnamic acid **1** (0.5 mmol), KI (50 mol%), H_2O (η = 0.32 μL/mg), and 2.5 gm (5 x 5 mm) stainless steel grinding balls. The jar was closed and mounted to the mixer mill. The mixer mill was set for 10 min and frequency 30 Hz. After the completion of the reaction, the jar was removed from the mixer mill and opened. No desired product was detected by TLC.

5.4 Evidence of *in-situ* formation of molecular iodine (I_2)

A starch-iodine test has been carried out for confirming the involvement of molecular iodine (I_2) in the reaction mixture. As illustrated below, one set of reaction was performed under standard conditions. Glass-vial **a**, containing starch solution was prepared by a mixture of water and starch (Molychem, Cas No: 9005-25-8; product code: 19025). Glass-vial **b**, comprised of KI dissolved in H_2O. Glass-vial **c**, comprised of I_2 dissolved in a mixture of H_2O and ethanol. Lastly, glass-vial **d**, comprised of a mixture of reaction mixture with ethyl acetate and 2-3 drops ethanol. As shown in below, the glass-vial **1** containing a mixture of **a**+**c** resulted in a dark purple color mixture, which was used as a reference standard. At the same time, the glass-vial **2** containing a mixture of starch **a** and reaction mixture **d**, resulted in a dark purple color mixture similar to glass-vial **1**, thus indicating the involvement of an *in-situ* molecular iodine (I_2) in the reaction mixture. On the other hand, glass-vial **3** contains a mixture of starch **a** and KI solution **b**. No color change was observed. These tests confirmed the formation of molecular iodine (I_2) in the reaction medium.

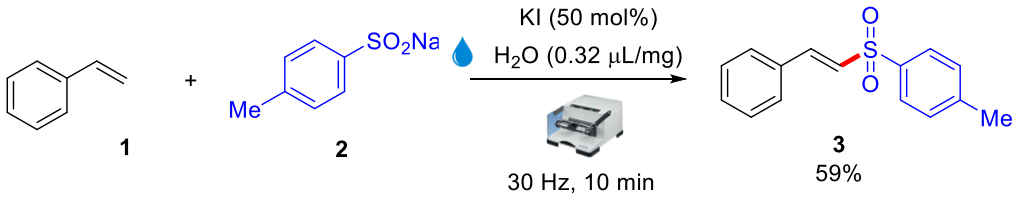


a = starch solution
b = KI solution
c = I_2 solution
d = reaction mixture solution
a+c = reference standard



Scheme 5. Evidence of *in-situ* formation of iodine (I_2) in reaction mixture

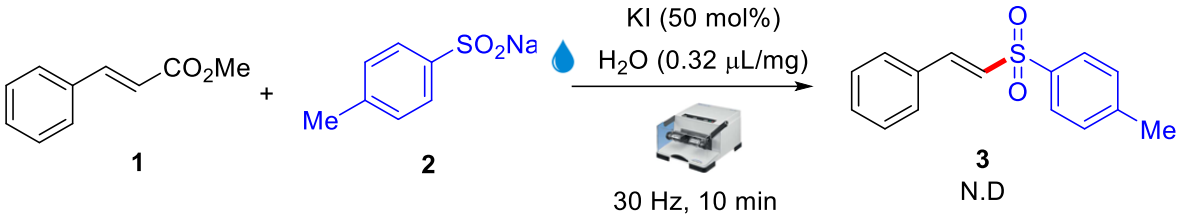
5.5 Reaction with styrene



Scheme 6. Reaction with styrene

To a cleaned 10 mL Retsch stainless steel milling jar, was charge with 4-methylbenzenesulfinate **2** (0.75 mmol), styrene **1** (0.5 mmol), KI (50 mol%), H_2O (η = 0.32 µL/mg), and 2.5 gm (5 x 5 mm) stainless steel grinding balls. The jar was closed and mounted to the mixer mill. The mixer mill was set for 10 min at 30 Hz. After the completion of the reaction, the jar was removed from the mixer mill and opened. To the reaction mixture, ethyl acetate was added to mobilize the residue, and the mixture was decanted to a 125 mL separating funnel. This step was repeated with more organic solvent till the complete removal of residue from jar. Next, the organic layer was extracted with a saturated solution of $Na_2S_2O_3$ (15 mL x3). The organic layer was dried over Na_2SO_4, filtered and the resulting solvent was removed under reduced pressure. The residue was then purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding vinyl sulfone product **3** in 59% yield.

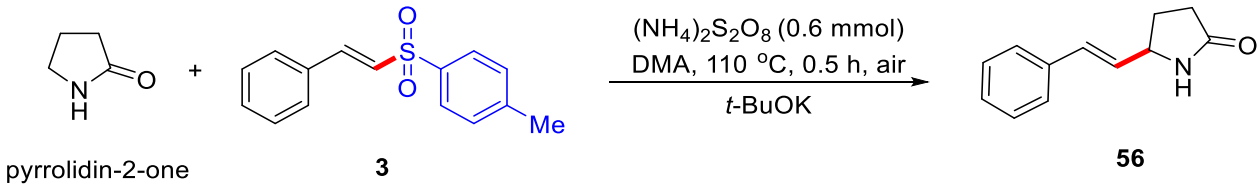
5.6 Reaction with ethyl cinnamate



Scheme 7. Reaction with ethyl cinnamate

To a cleaned 10 mL Retsch stainless steel milling jar, was charge with 4-methylbenzenesulfinate **2** (0.75 mmol), ethyl cinnamate **1** (0.5 mmol), KI (50 mol%), H_2O (η = 0.32 μL/mg), and 2.5 gm (5 x 5 mm) stainless steel grinding balls. The jar was closed and mounted to the mixer mill. The mixer mill was set for 10 min and frequency 30 Hz. After the completion of the reaction, the jar was removed from the mixer mill and opened. No desired product was detected by TLC.

5.7 Diversification of vinyl sulfones

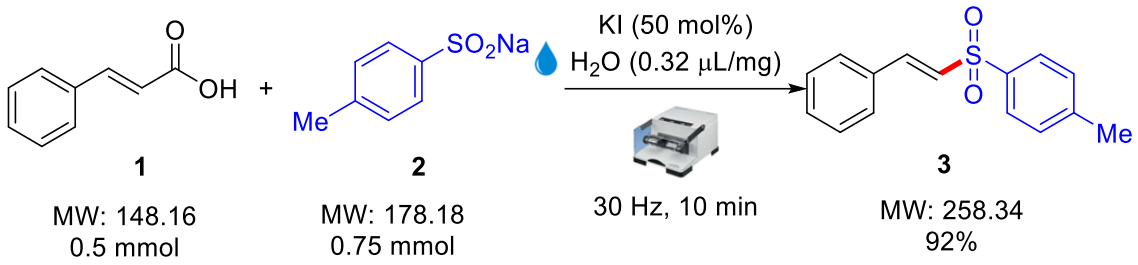


Scheme 8. Synthesis of (*E*)-5-styrylpyrrolidin-2-one

To a oven dried 10 mL vial equipped with a magnetic bar was added pyrrolidin-2-one (2 mmol), (*E*)-1-methyl-4-(styrylsulfonyl)benzene **3** (0.2 mmol), $(NH_4)_2S_2O_8$ (0.6 mmol), and *t*-BuOK (0.6 mmol) and followed by the addition of 2 mL of DMA. The mixture was stirred at 110 °C (oil bath) for 0.5 h. After the reaction was completed (as monitored by TLC), the mixture was quenched with water and extracted with EtOAc (3 × 15 mL). The organic layer was washed with saturated brine (3 × 5 mL), dried over anhydrous Na_2SO_4, filtered and the resulting solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding desired (*E*)-5-styrylpyrrolidin-2-one product **56** in 74% yield.[5]

6. Calculations of Green Chemistry Metrics

(a) Procedure for the synthesis of compound 3



Scheme 9. Synthesis of compound **3**

To a 10 mL stainless steel jar, was charge with cinnamic acid **1** (0.5 mmol, 0.074 g) sodium 4-methylbenzenesulfinate **2** (0.75 mmol, 0.133 g), potassium iodide (50 mol%, 0.0414 g), and H_2O (η = 0.32 μL/mg), with stainless steel ball. The jar was closed and fitted to the mill. The mixer mill was set for 10 min at 30 Hz. After the completion of the reaction, and purification, 0.118 g of desired product **3** was obtained in 92% yield.

(b) Investigations of green chemistry metrics

The green chemistry metrics including Atom Economy (AE), Atom Efficiency (AEf), Effective Mass Yield (EMY), Reaction Mass Efficiency (RME), Optimum Efficiency (OE), Process Mass Intensity (PMI), Mass Intensity (MI), Mass Productivity (MP), E-factor, Solvent Intensity (SI), Water Intensity (WI), Turnover Number (TON), and Turnover Frequency (TOF) were calculated according to literature.[6]

$$EMY\ (\%) = \frac{Mass\ of\ product}{Mass\ of\ non-benign\ reagents} \times 100 = \frac{0.118\ g}{0.0414\ g} \times 100 = 285.02\%$$

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100 = \frac{258.34}{148.16\ +\ 178.12} \times 100 = 79.17\%$$

$$AEt\ (\%) = AE\ \times yield\% = 79.17\ \times 92\% =\ 72.84\%$$

$$RME\ (\%) = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100\ \frac{0.118\ g}{0.074\ g + 0.133\ g + 0.0414\ g} \times 100 =\ 47.50\%$$

$$OE\ (\%) = \frac{RME}{AE} \times 100 = \frac{47.50\%}{79.17\%} \times 100 =\ 59.99\%$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (including\ solvents)}{Mass\ of\ product} = \frac{0.074\ g + 0.133\ g\ + 0.0414\ g}{0.118\ g} = 2.10$$

$$MI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (excluding\ water)}{Mass\ of\ product} = \frac{0.074\ g + 0.133\ g + 0.0414\ g}{0.118\ g} = 2.10$$

$$MP\ (\%) = \frac{1}{MI} \times 100 = \frac{1}{2.10} \times 100 = 47.61\%$$

$$E - factor = \frac{Total\ mass\ of\ wastes}{mass\ of\ product} = \frac{0.074\ g + 0.133\ g + 0.0414\ g - 0.118\ g}{0.118\ g} = 1.105$$

$$TON = \frac{Amount\ of\ desired\ product\ (mmol\ scale)}{Amount\ of\ catalyst\ used\ (mmol\ scale)} = \frac{0.456}{0.25} = 1.82$$

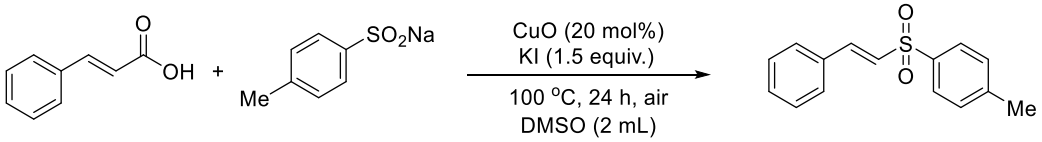
$$TOF = \frac{TON}{Time\ (hour)} = \frac{1.82}{0.167} = 10.94/h$$

$$SI = \frac{Total\ mass\ of\ solvents\ excluding\ water\ in\ the\ whole\ process}{Mass\ of\ product} = \frac{0}{0.118\ g} = 0$$

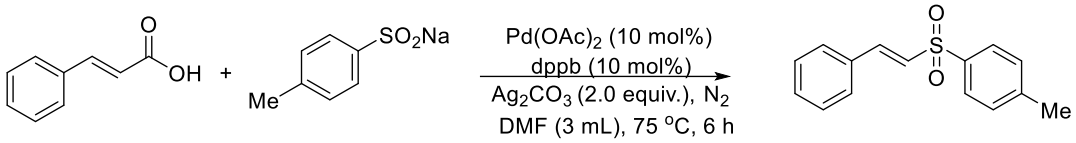
$$WI = \frac{Total\ mass\ of\ water\ in\ the\ whole\ process}{Mass\ of\ product} = \frac{0.182\ g}{0.118\ g} = 1.54$$

c) The green chemistry metrics calculation of other same type of reactions

To illustrate the advantages of this protocol in green chemistry, the green chemistry metrics of the same type of decarboxylative sulfonylation reactions were also calculated and compared to ours.[6] Comparative examples were selected from literature and detailed calculations were summarized Table 1.[7] The comparison of each green chemistry parameters are also shown in Figure 10-20.

Entry	Previous literature	Ref
1	 MW: 148.16 0.5 mmol MW: 178.18 1.5 mmol MW: 258.34 56%	7a

2



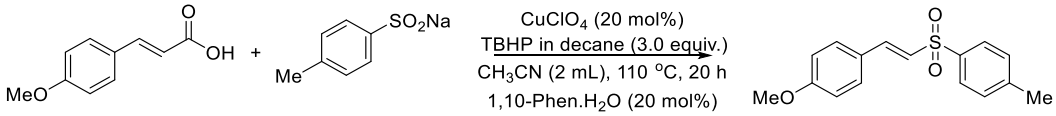
7b

MW: 148.16
0.5 mmol

MW: 178.18
1.0 mmol

MW: 258.34
60%

3



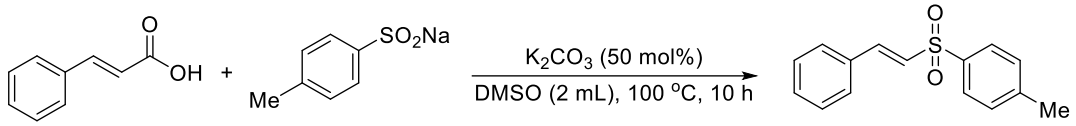
7c

MW: 178.19
0.25 mmol

MW: 178.18
1.0 mmol

MW: 288.36
83%

4



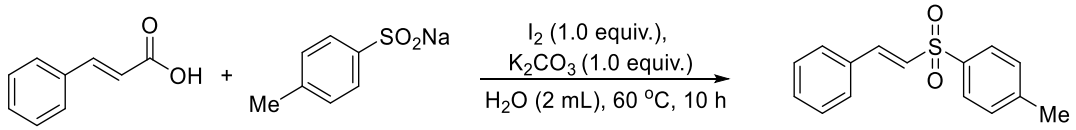
7d

MW: 148.16
0.5 mmol

MW: 178.18
0.75 mmol

MW: 258.34
87%

5



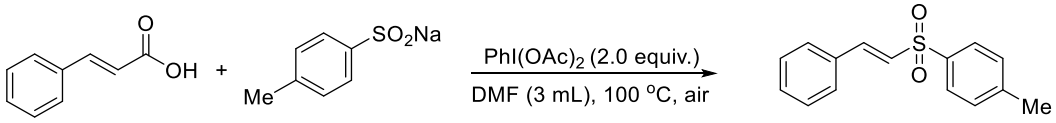
7e

MW: 148.16
0.5 mmol

MW: 178.18
0.6 mmol

MW: 258.34
81%

6



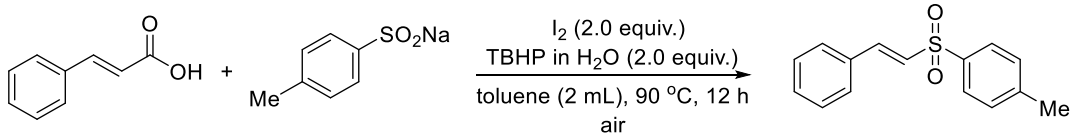
7f

MW: 148.16
0.25 mmol

MW: 178.18
4 equiv.

MW: 258.34
79%

7



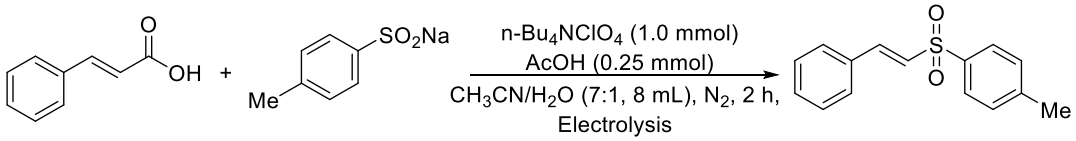
7g

MW: 148.16
0.3 mmol

MW: 178.18
1.2 mmol

MW: 258.34
90%

8



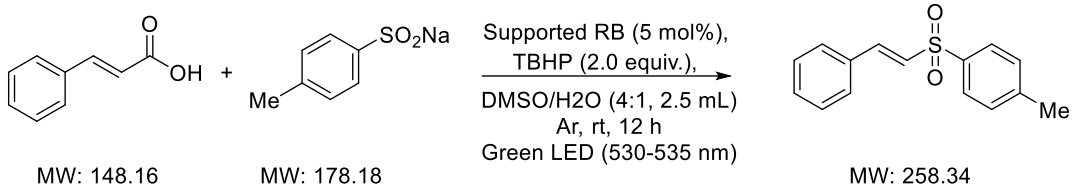
7h

MW: 148.16
0.5 mmol

MW: 178.18
1.2 mmol

MW: 258.34
81%

9



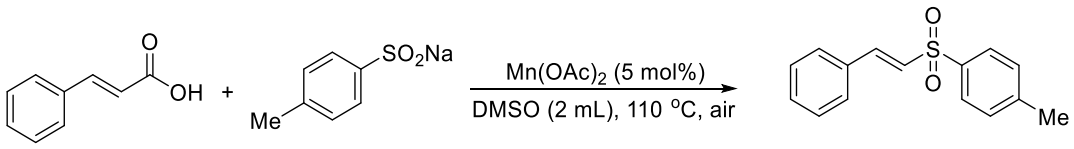
MW: 148.16
0.25 mmol

MW: 178.18
0.5 mmol

MW: 258.34
74%

7i

10



MW: 148.16
0.5 mmol

MW: 178.18
1.5 mmol

MW: 258.34
63%

7j

Table 1: Calculated green metrics													
Sr No			This	1	2	3	4	5	6	7	8	9	10
Reference			This work	7a	7b	7c	7d	7e	7f	7g	7h	7i	7j
Atmosphere			air	air	N_2	air	air	air	air	air	N_2	air	air
Cinnamic acid	M	mmol	0.5	0.5	0.5	0.25	0.5	0.5	0.25	0.3	0.5	0.25	0.5
	MW	g/mmol	148.16	148.16	148.16	178.19	148.16	148.16	148.16	148.16	148.16	148.16	148.16
	Weight	mg	74	74	74	44.5	74	74	37.04	44.448	74	37.04	74
Sodium sulfinate	M	mmol	0.75	1.5	1	0.5	0.75	0.6	1	1.2	1.2	0.5	1.5
	MW	g/mmol	178.18	178.18	178.18	178.18	178.18	178.18	178.18	178.18	178.18	178.18	178.18
	Weight	mg	133	267.27	178.18	90	133	106.908	178.18	213.816	213.82	90	267.27
Additive 1	M	mmol		1.5	1	0.75	0.25	0.5	0.5	0.6	1		
	MW	g/mmol		166	264	90.12	138.21	253.808	322.1	253.81	314.91		
	Weight	mg		249	264	67.59	34.55	126.909	161.1	152.28	314.91		
Additive 2	M	mmol						0.5		0.6	0.25		
	MW	g/mmol						138.205		90.12	60.052		
	Weight	mg						69.102		154.072	15.013		
Catalyst/ activator	M	mmol	0.25	0.1	0.05	0.05						0.0125	0.025
	MW	g/mmol	166	79.545	224.5	370.54						1017.6	245.09
	Weight	mg	41.4	7.954	11.2	18.5						12.72	6.13
Ligand	M	mmol			0.05	0.05							
	MW	g/mmol			427.47	198.22							
	Weight	mg			22	9.9							
Solvent (not water)	Solvent			DMSO	DMF	MeCN	DMSO		DMF	Toluene	MeCN	DMSO	DMSO
	Density	mg/mL		1100	944	786	110		944	867	786	110	110
	Volume	mL		2	3	2	2		3	2	7	2	2
	Weight	mg		2200	2832	1572	2200		2832	1734	5502	2200	2200
Water	Weight	mg	182	0	0	0	0	2000	0	0	1000	500	0
Co-solvent	Weight	mg		0	0	0	0	0	0	0	0	0	0
Product	M	mmol	0.456	0.279	0.299	0.207	0.434	0.404	0.197	0.269	0.402	0.184	0.314
	MW	g/mmol	258.34	258.34	258.34	288.36	258.34	258.34	258.34	258.34	258.34	258.34	258.34

	AW	mg	118	72.2	77.418	59.8	112.26	104.514	51.022	69.75	103.9	47.74	81.28
	Yield		92%	56%	60%	83%	87%	81%	79%	90%	81%	74%	63%
Effective Mass Yield		EMY	285.02%	2.94%	2.49%	3.59%	5.10%	82.36%	1.70%	3.59%	1.88%	2.17%	3.69%
Atom Economy		AE	79.17%	52.47%	43.76%	64.58%	55.61%	35.96%	39.84%	38.54%	66.85%	79.16%	79.16%
Atom Efficiency		AEF	72.84%	29.38%	26.26%	53.60%	48.38%	29.12%	31.47%	34.68%	54.15%	58.57%	49.87%
Reaction Mass Efficiency		RME	47.50%	12.07%	14.09%	25.94%	46.47%	27.73%	13.56%	15.01%	34.31%	34.15%	23.39%
Optimum Efficiency		OE	59.99%	26.72%	32.20%	40.17%	83.56%	77.11%	34.03%	38.94%	51.30%	43.14%	29.55%
Process Mass Intensty		PMI	2.1	38.75	43.67	30.14	21.74	22.74	62.88	31.52	68.52	59.48	31.34
Mass Intensity		MI	2.1	38.75	43.67	30.14	21.74	3.61	62.88	31.52	68.52	49.01	31.34
Mass Productivity		MP	47.61%	2.58%	2.29%	3.32%	4.59%	27.70%	1.59%	3.17%	1.45%	2.04%	3.19%
E-factor			1.105	37.76	42.68	29.14	20.75	21.74	61.88	30.52	67.52	58.48	30.34
Solvent Intensity		SI	0	30.47	36.58	26.28	19.59	0	55.50	24.86	52.95	46.08	27.07
Turnover Number		TON	1.82	2.79	5.98	4.41	0	0	0	0	0	14.72	12.56
Reaction Time		h	0.17	24	12	20	10	10	0.17	12	2	12	12
Turnover Frequency		/h	10.94	0.12	0.49	0.207	0	0	0	0	0	1.23	1.05
Water Intensity		WI	1.54	0	0	0	0	19.41	0	0	9.62	10.47	0

*M = amount of substance; MW = molecular weight; AW = actual weight.

Comparison of green chemistry metrics

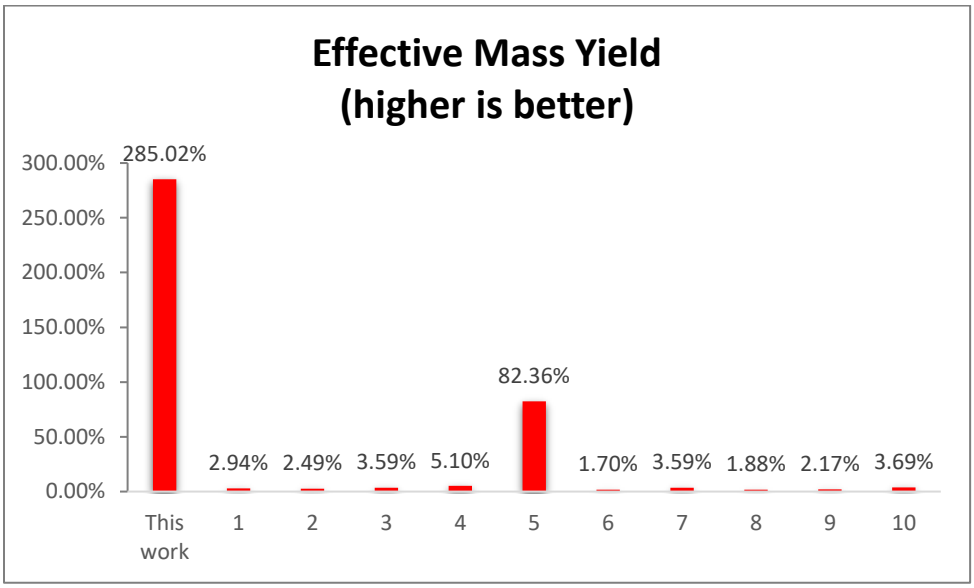


Figure 10. The Comparison of Effective Mass Yield

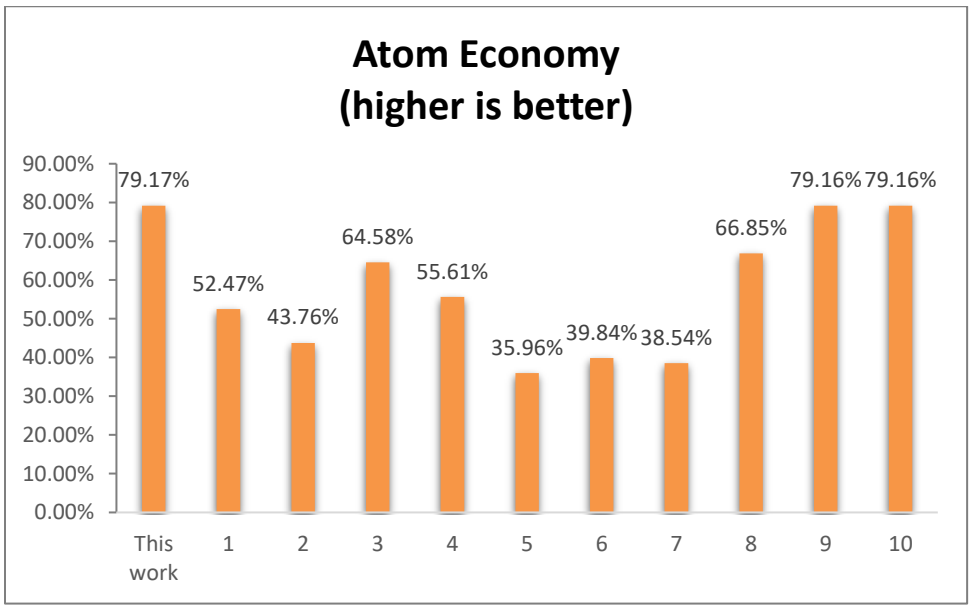


Figure 11. The Comparison of Atom Economy

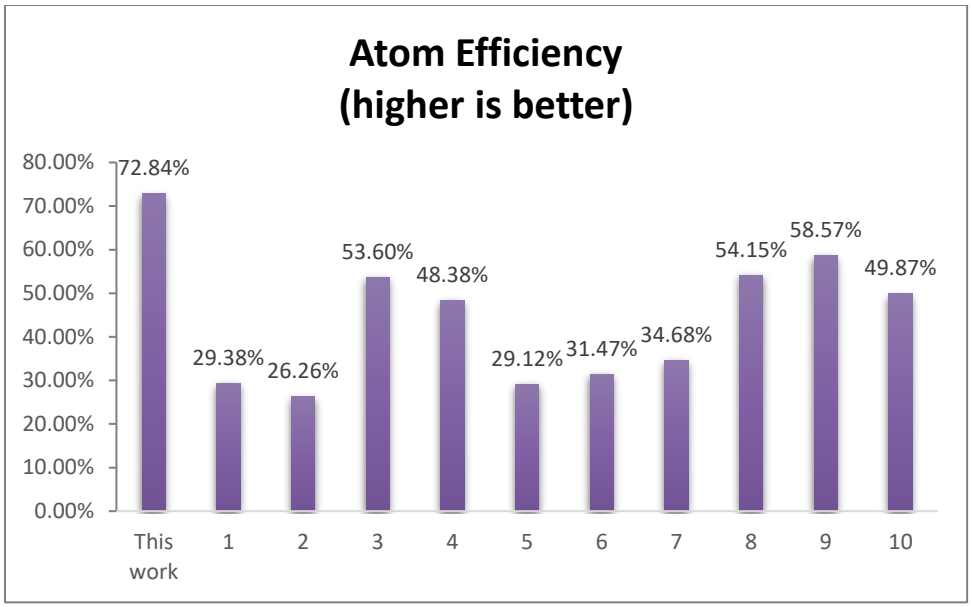


Figure 12. The Comparison of Atom Efficiency

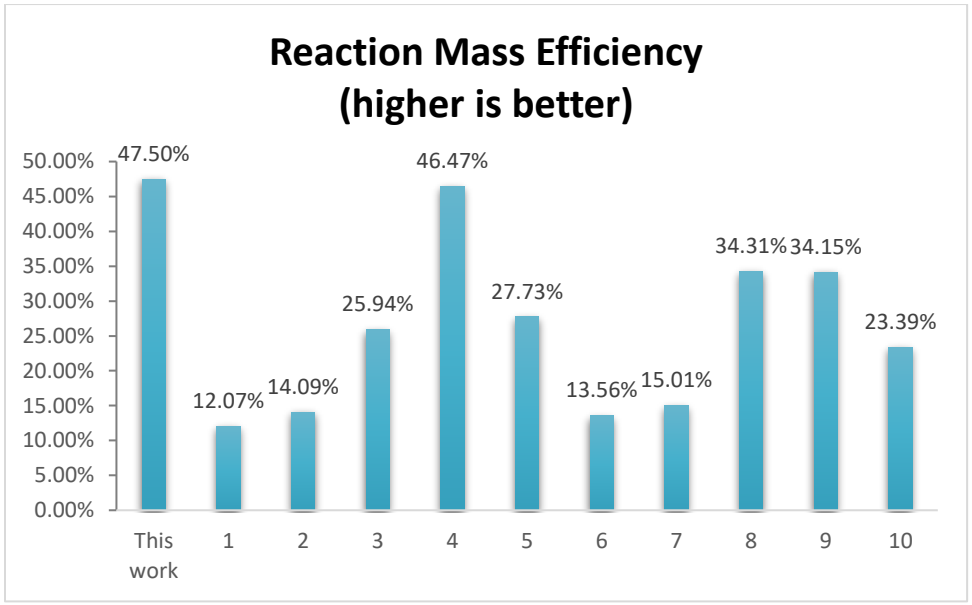


Figure 13. The Comparison of Reaction Mass Efficiency

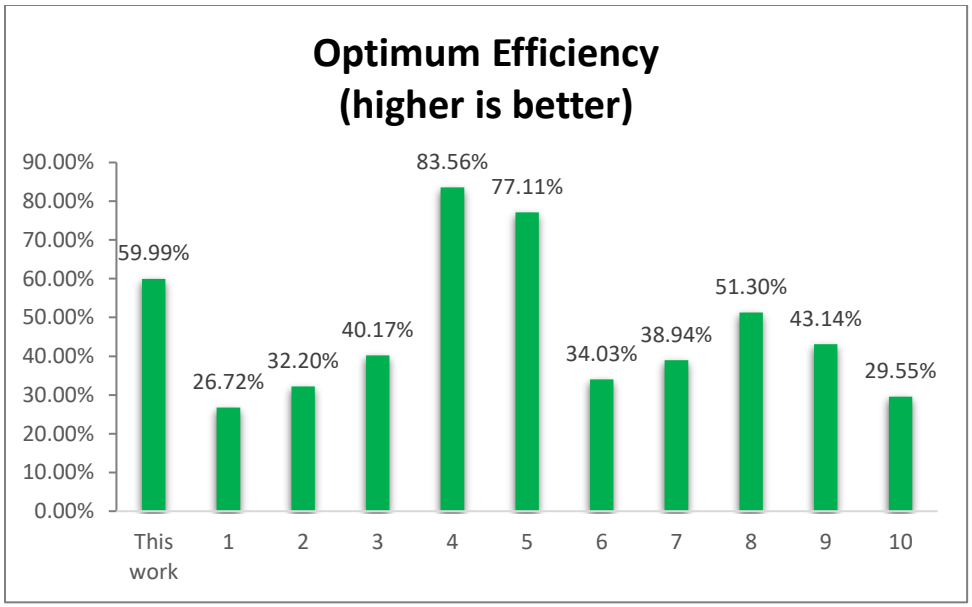


Figure 14. The Comparison of Optimum Efficiency

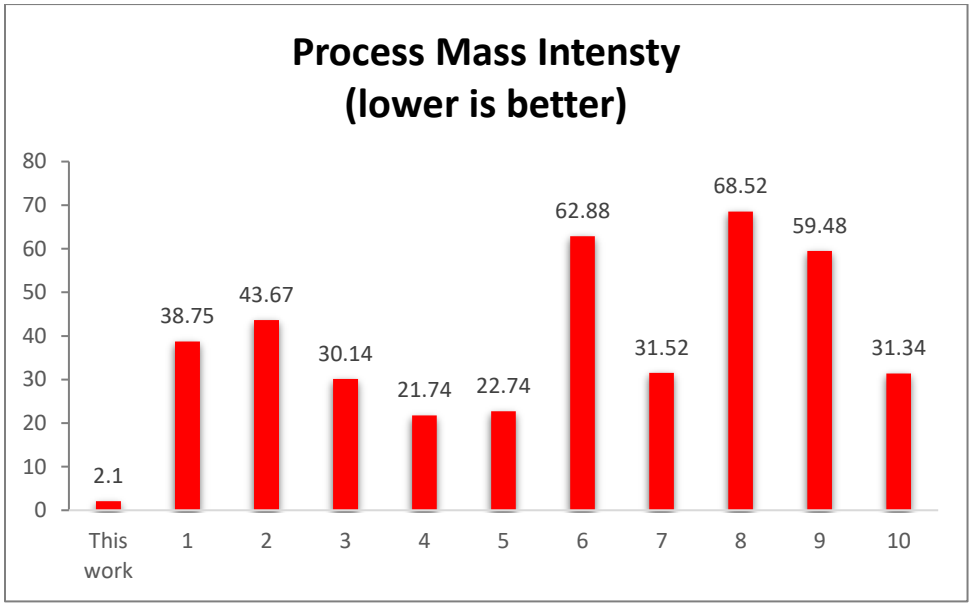


Figure 15. The Comparison of Process Mass Intensity

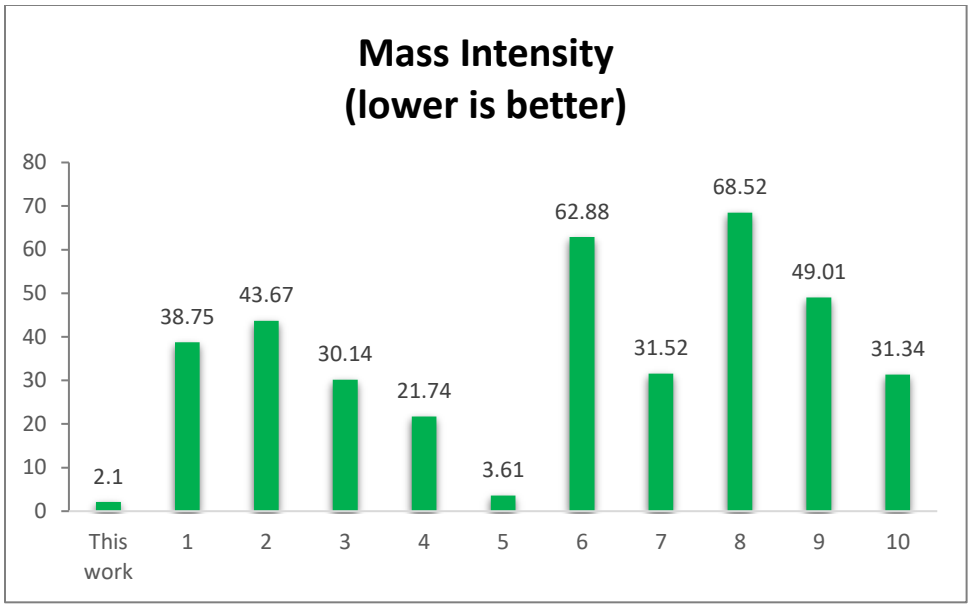


Figure 16. The Comparison of Mass Intensity

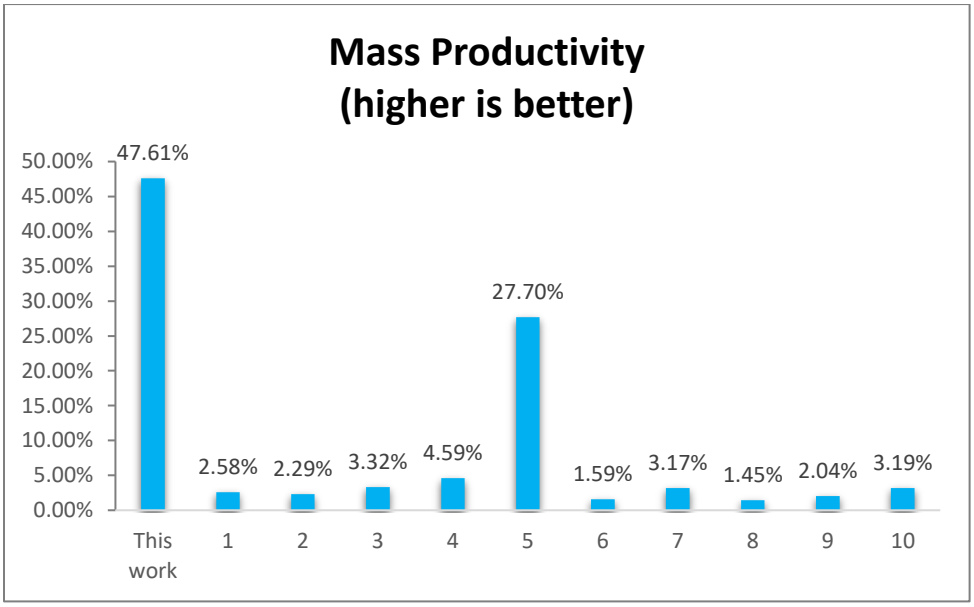


Figure 17. The Comparison of Mass Productivity

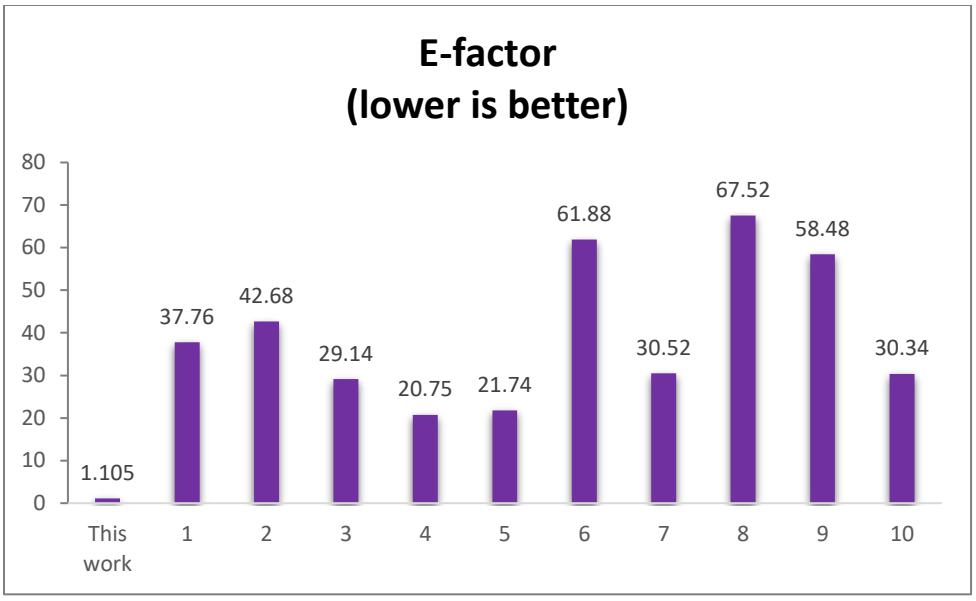


Figure 18. The Comparison of E-Factor

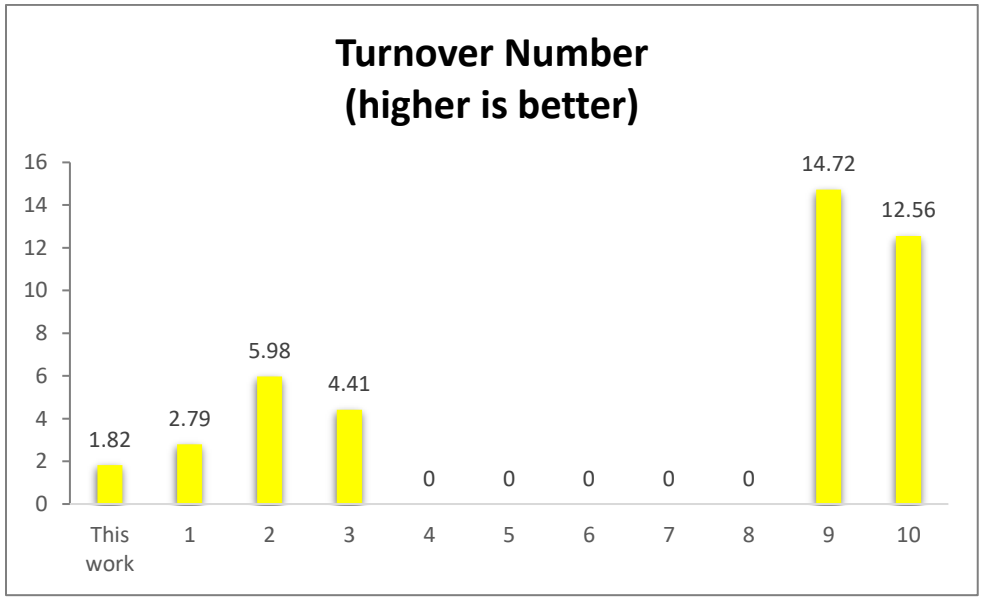


Figure 19. The Comparison of Turnover Number

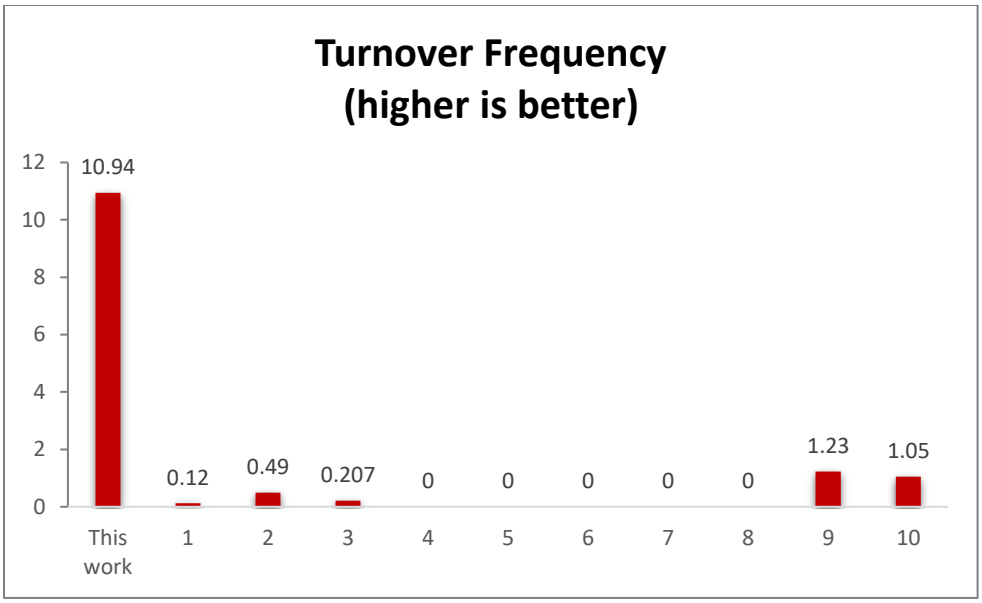


Figure 20. The Comparison of Turnover Frequency

Green chemistry metrics summary

Table 2. Summary of Green Chemistry Metrics										
Methods	EMY	AE	RME	OE	PMI	MI	MP	E-factor	TON	TOF
This work	285.02%	79.17%	47.50%	59.99%	2.1	2.1	47.61%	1.105	1.82	10.94
1	2.94%	52.47%	12.07%	26.72%	38.75	38.75	2.58%	37.756	2.79	0.12
2	2.49%	43.76%	14.09%	32.20%	43.67	43.67	2.29%	42.676	5.98	0.49
3	3.59%	64.58%	25.94%	40.17%	30.14	30.14	3.32%	29.14	4.41	0.207
4	5.10%	55.61%	46.47%	83.56%	21.74	21.74	4.59%	20.75	0	0
5	82.36%	35.96%	27.73%	77.11%	22.74	3.61	27.70%	21.74	0	0
6	1.70%	39.84%	13.56%	34.03%	62.88	62.88	1.59%	61.88	0	0
7	3.59%	38.54%	15.01%	38.94%	31.52	31.52	3.17%	30.52	0	0
8	1.88%	66.85%	34.31%	51.30%	68.52	58.9	1.69%	67.52	0	0
9	2.17%	79.16%	34.15%	43.14%	59.48	49.01	2.04%	58.48	14.72	1.23
10	3.69%	79.16%	23.39%	29.55%	31.34	31.34	3.19%	30.34	12.56	1.05

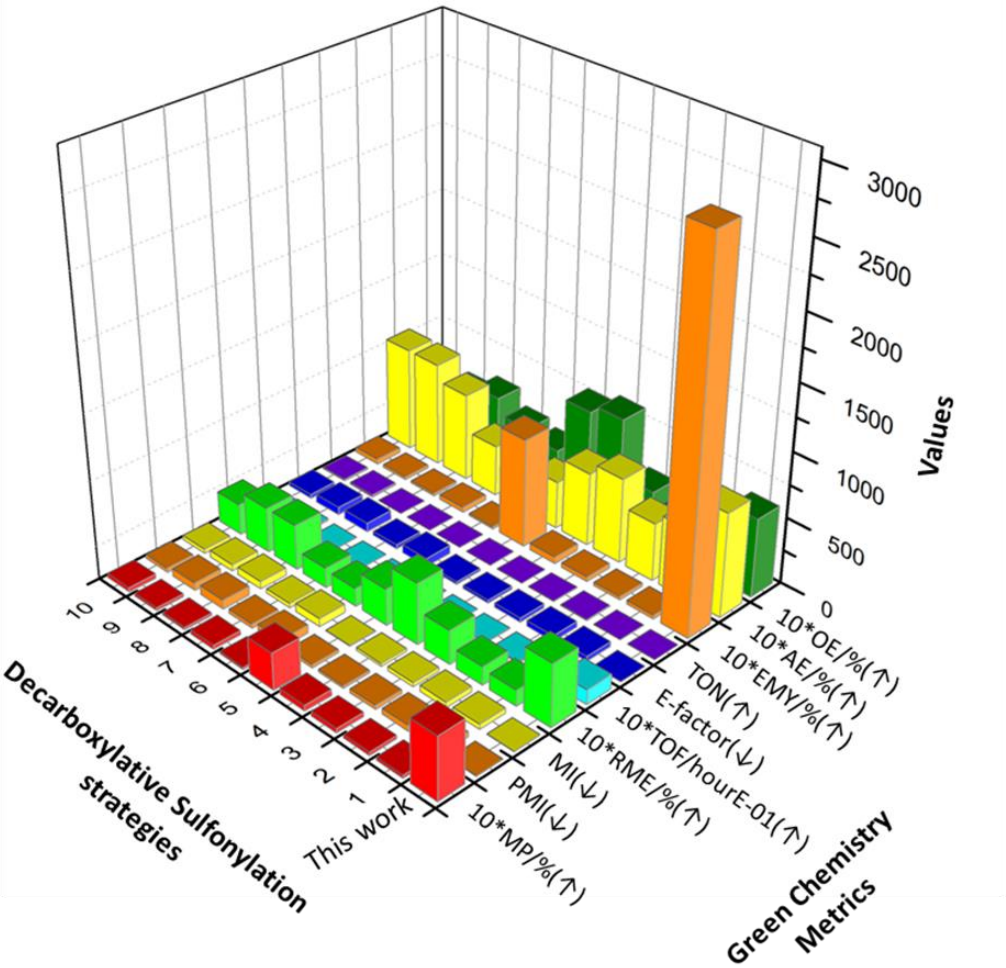


Figure 21. Summary of green chemistry metrics compared to ours

Table 3. Calculation of EcoScale[8]

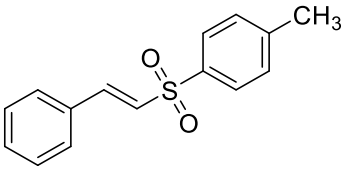
Score on **EcoScale**: > 75, Excellent; >50, Acceptable; <50, Inadequate					
Parameters					**Penalty points**
Techniques					Mixer-mill (this work) 
Solvent					H_2O (LAG)
Reaction yield % **Penalty points** = (100 – yield%)/2					92% 4
Chemical Components	mmol	MW	Price/ mmol	Price of component to obtain 10 mmol end product	
Cinnamic acid	0.5 mmol	148.158	< $1	< $1	0
Sodium 4-methylbenzene sullfinate	0.75 mmol	178.19	< $1	< $1	0
Potassium Iodide	50 mol%	166.002	< $1	< $1	0
3. Safety					
Cinnamic acid					0
Sodium 4-methylbenzene sulfinate					0
Potassium Iodide (N)					5
4. Technical Setup					
Unconventional activation technique					2
5. Temperature/Time					
Room temperature, < 1 h					0
6. Workup and purification					
Classical chromatography					10
Penalty points total					21
EcoScale = 100 – sum of individual penalties					79
Ranking of reaction					**Excellent**

*N = dangerous

7. NMR data

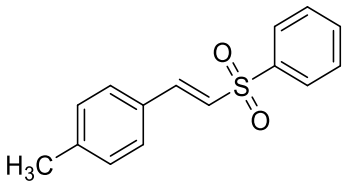
7.1 Characterization data of products

(*E*)-1-methyl-4-(styrylsulfonyl)benzene (3):



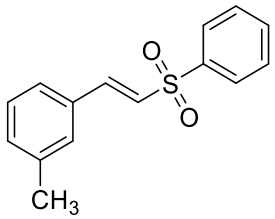
The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.
Yield: 92% (118.8 mg).
R_f: 0.58 (Mobile phase: 15% EtOAc in Hexane).
mp: 110 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 15.5 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.41-7.32 (m, 5H), 6.85 (d, J =15.5 Hz,1H), 2.43 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.5, 142.0, 137.9, 132.6, 131.2, 130.0, 129.1, 128.6, 127.8, 127.8, 21.7.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[7a]

(*E*)-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (4):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and obtained as a white solid.
Yield: 89% (114.8 mg).
R_f: 0.39 (Mobile phase: 15% EtOAc in Hexane).
mp: 134.5°C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.61 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.54 (t, *J* = 8.0, Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 15.5 Hz, 1H), 2.67 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.7, 142.0, 141.0, 133.4, 129.9, 129.7, 129.4, 128.7, 127.7, 126.1, 21.6.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-methyl-3-(2-(phenylsulfonyl)vinyl)benzene (5):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and obtained as a white solid.

Yield: 85% (109.6 mg).

R_f: 0.45 (Mobile phase: 15% EtOAc in Hexane).

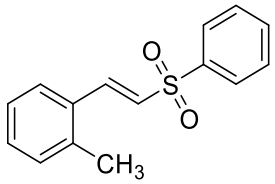
mp: 78.5 ^oC.

^1H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.97 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.23 (d, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.8, 140.9, 138.9, 133.5, 132.4, 132.2, 129.5, 129.2, 129.1, 127.7, 127.2, 126.0, 21.3.

^1H and **^{13}C NMR** of the product are in agreement with the literature. [7i]

(*E*)-1-methyl-2-(2-(phenylsulfonyl)vinyl)benzene (6):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 77% (99.3 mg).

R_f: 0.454 (Mobile phase: 15% EtOAc in Hexane).

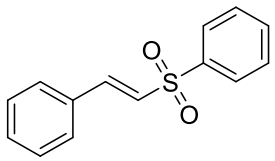
mp: 91.8 ^oC.

^1H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.99-7.93 (m, 3H), 7.62 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.23-7.15 (m, 2H), 6.79 (d, *J* = 15.5 Hz, 1H), 2.45(s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.8, 140.2, 138.3, 133.5, 131.3, 131.2, 131.1, 129.5,128.3, 127.7, 127.0, 126.6, 19.9.

^1H and **^{13}C NMR** of the product are in agreement with the literature. [7i]

(*E*)-(2-(phenylsulfonyl)vinyl)benzene (7):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 86% (105.0 mg).

R_f: 0.36 (Mobile phase: 10% EtOAc in Hexane).

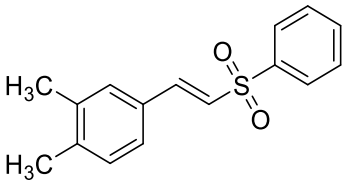
mp: 78.8°C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.95 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 15.5 Hz, 1H), 7.61 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.43-7.35 (m, 3H), 6.87 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.4, 140.9, 133.5, 132.3, 131.2, 129.4, 129.1, 128.6, 127.6, 127.6.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1,2-dimethyl-4-(2-(phenylsulfonyl)vinyl)benzene (8):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;

Yield: 89% (121.1 mg).

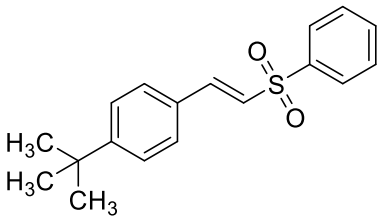
R_f: 0.53 (Mobile phase: 15% EtOAc in Hexane).

mp: 112.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.95 (d,*J* = 8.3 Hz,2H), 7.64 (d, *J* = 15.5 Hz, 1H), 7.59 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.25-7.19 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 15.0 Hz, 1H), 2.26 (s, 3H), 2.24(s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.9, 141.1, 140.7, 137.5, 133.4, 130.4, 130.1, 129.8, 129.4, 127.6, 126.4, 125.9, 20.0, 19.8.

(*E*)-1-(tert-butyl)-4-(2(phenylsulfonyl)vinyl)benzene (9):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;

Yield: 60% (61.3 mg).

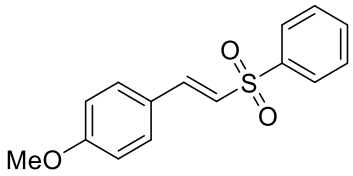
R_f: 0.52 (Mobile phase: 15% EtOAc in Hexane).

mp: 118.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.38 (m, 4H), 6.83 (d, *J* = 15.5 Hz, 1H), 1.31 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 155.1, 142.6, 141.0, 133.4, 129.7, 129.4, 128.6, 127.7, 126.4, 126.2, 35.1, 31.2.

(*E*)-1-methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (10):



The titled compound was synthesized according to the general procedure in 30 min at 30 Hz and was obtained as a white solid.

Yield: 58% (79.6 mg).

R_f: 0.34 (Mobile phase: 15% EtOAc in Hexane).

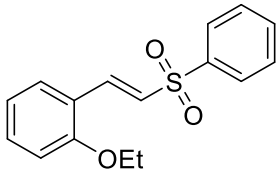
mp: 105.8 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.0 Hz, 2H), 7.65-7.47 (m, 4H), 7.41 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.72 (d, *J* = 15.5, 1H), 3.80 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.1, 142.3, 141.2, 133.2, 130.4, 129.3, 127.5, 125.0, 124.5, 114.6, 55.5.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-ethoxy-2-(2-(phenylsulfonyl)vinyl)benzene (11):



The titled compound was synthesized according to the general procedure in 30 min at 30 Hz and was obtained as a white solid.

Yield: 39% (56.2 mg).

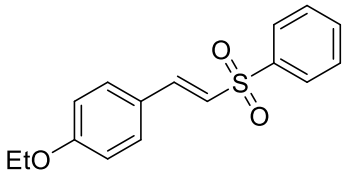
R_f = 0.44 (Mobile phase: 15% EtOAc in Hexane).

mp: 92.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 15.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.33 (t,*J* = 7.8 Hz, 1H), 7.09 (d, J = 15.5 Hz, 1H), 6.95-6.85 (m, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 158.2, 141.3, 138.7, 133.1, 132.5, 130.8, 129.3, 127.8, 127.5, 121.2, 120.7, 112.2, 64.1, 14.7.

(*E*)-1-ethoxy-4-(2-(phenylsulfonyl)vinyl)benzene (12):



The titled compound was synthesized according to the general procedure in 30 min at 30 Hz and was obtained as a white solid.

Yield: 42% (60.6 mg).

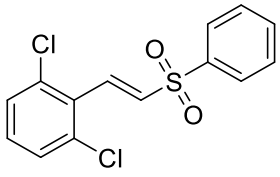
R_f= 0.36 (Mobile phase: 15% EtOAc in Hexane).

mp = 109.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 15.5 Hz, 1H), 7.58 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz,2H), 6.70 (d, J = 15.5 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.6, 142.5, 141.2, 133.3, 130.5, 129.4, 127.5, 124.8, 124.3, 115.0, 63.8, 14.8.

(*E*)-1,3-dichloro-2-(2-(phenylsulfonyl)vinyl)benzene (13):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 87% (136.1 mg).

R_f = 0.60 (Mobile phase: 15% EtOAc in Hexane).

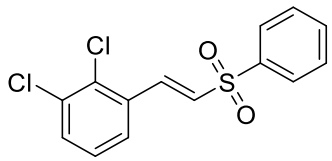
mp: 91.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.96 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.64 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.1, 135.9, 135.6, 135.4, 133.8, 130.9, 129.8, 129.5, 129.1, 127.9.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[9]

(*E*)-1,2-dichloro-3-(2-(phenylsulfonyl)vinyl)benzene (14):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 72% (112.7 mg).

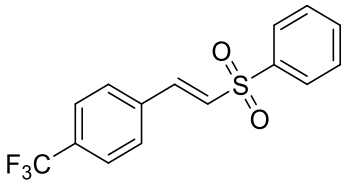
R_f: 0.38 (Mobile phase: 15% EtOAc in Hexane).

mp: 124.8 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (d, *J* = 15.5 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.57 (t,*J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 15.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.1, 138.3, 134.4, 133.8, 133.4, 133.1, 132.5, 131.4, 129.6, 128.0, 127.7, 126.5.

(*E*)-1-(2-(phenylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (15):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

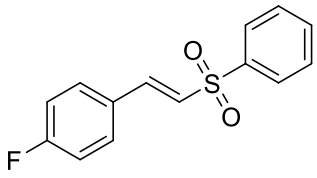
Yield: 84% (131.1 mg).

R_f: 0.476 (Mobile phase: 15% EtOAc in Hexane).

mp: 134.8 °C.

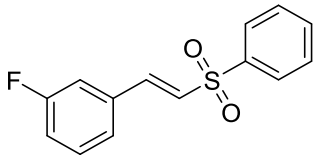
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.96 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 15.5 Hz,1H), 7.66 – 7.51 (m, 7H), 6.99 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.6, 140.2, 135.8, 133.8, 132.6 (d, *J* = 32.5 Hz), 130.1, 129.6. 128.9, 127.9, 126.1 (q, *J* = 3.9 Hz), 124.8, 122.6.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7i]

(*E*)-1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (16):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.
Yield: 77% (100.8 mg).
R_f = 0.48 (Mobile phase: 15% EtOAc in Hexane).
mp: 110.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 7.8 Hz, 2H), 7.68 – 7.59 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.08 (t,*J* = 8.5 Hz, 2H), 6.80 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 164.5 (d, *J* = 251.5 Hz), 141.3, 140.7, 133.6, 130.7 (d, *J* = 8.8 Hz), 129.5, 128.7 (d, *J* = 3.5 Hz), 127.7, 127.1 (d, *J* = 2.8 Hz), 116.43 (d, *J* = 21.9 Hz).
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

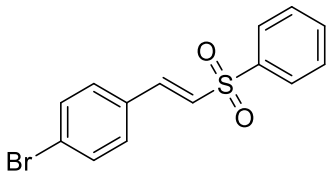
(*E*)-1-fluoro-3-(2-(phenylsulfonyl)vinyl)benzene (17):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;
Yield: 80% isolated yield (104.8 mg).
R_f = 0.33(Mobile phase: 15% EtOAc in Hexane).
mp: 75.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.3 Hz, 2H), 7.66-7.59 (m, 2H), 7.55 (t,*J* = 8.0 Hz, 2H), 7.38-7.32 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 9.5 Hz, 1H) 7.09 (td, *J* = 8.5,2.5Hz, 1H) 6.89 (d, *J* = 15.5 Hz, 1H).

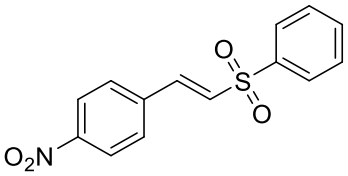
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.0 (d, *J* = 246.3 Hz), 141.0 (d, *J* = 3.0 Hz), 140.4, 134.6 (d, *J* = 7.8 Hz), 133.7, 130.8 (d, *J* = 8.3 Hz), 129.5, 128.9, 127.8, 124.8 (d, *J* = 3.0 Hz), 118.2 (d, *J* = 21.3 Hz), 114.9 (d, *J* = 22.1 Hz).
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7h]

(*E*)-1-bromo-4-(2-(phenylsulfonyl)vinyl)benzene (18):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;
Yield: 72% (116.4 mg).
R_f: 0.38 (Mobile phase: 15% EtOAc in Hexane).
mp: 153.0 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.49 (m, 6H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.1, 140.5, 133.6, 132.5, 131.4, 130.0, 129.5, 128.1, 127.8, 125.8.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

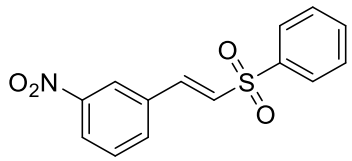
(*E*)-1-nitro-4-(2-(phenylsulfonyl)vinyl)benzene (19):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a yellow solid;
Yield: 78% (112.7 mg).
R_f = 0.096 (Mobile phase: 15% EtOAc in Hexane).
mp: 128.5 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.25 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 15.5 Hz, 1H), 7.69 – 7.63 (m, 3H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.02 (d. *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 149.0, 139.8, 139.2, 138.4, 133.9, 131.7, 129.6, 129.3, 127.9, 124.3.

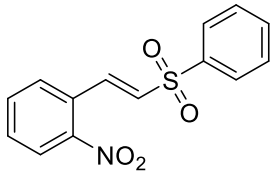
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-nitro-3-(2-(phenylsulfonyl)vinyl)benzene (20):



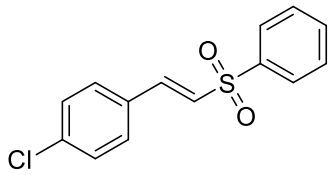
The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a yellow solid.
Yield: 62% (89.2 mg).
R_f = 0.177 (Mobile phase: 15% EtOAc in Hexane).
mp: 143.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.33 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 15.5 Hz, 1H), 7.65(t, *J* = 7.5 Hz, 1H) 7.62-7.55(m, 3H), 7.04 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 148.7, 140.0, 139.5, 134.4, 134.2, 134.0, 130.8, 130.4, 129.6, 128.0, 125.5, 122.9.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-nitro-2-(2-(phenylsulfonyl)vinyl)benzene (21):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a yellow solid.
Yield: 66% (95.0 mg).
R_f = 0.096 (Mobile phase: 15% EtOAc in Hexane).
mp: 107.6 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.17 (d, *J* = 15.5 Hz, 1H), 8.12 (dd, *J*= 8.3 Hz, 1.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.69-7.62 (m, 2H), 7.61-7.53 (m, 4H), 6.78 (d, *J* = 15.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 148.0, 140.0, 139.3, 134.1, 133.6, 132.7, 132.0, 131.2, 129.7, 129.6, 129.1, 128.1, 125.3, 124.6.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (22):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 88% (122.6 mg).

R_f = 0.48 (Mobile phase: 15% EtOAc in Hexane).

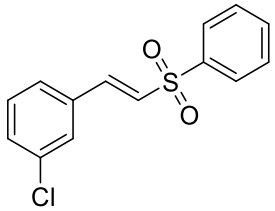
mp: 129.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.0 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.40 (d,*J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.1, 140.5, 137.3, 133.7, 130.9, 129.9, 129.5, 129.5, 128.0, 127.8.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-chloro-3-(2-(phenylsulfonyl)vinyl)benzene (23):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a colourless solid.

Yield: 63% (87.5 mg).

R_f: 0.42 (Mobile phase: 15% EtOAc in Hexane).

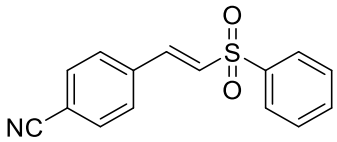
mp: 99.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 8.3 Hz, 2H), 7.65-7.51 (m, 4H), 7.44 (br.s, 1H), 7.38-7.28 (m, 3H), 6.88 (d, *J* = 15.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.8, 140.4, 135.2, 134.2, 133.7, 131.1, 130.5, 129.5, 129.0, 128.3, 127.8, 126.9.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7i]

(*E*)-4-(2-(phenylsulfonyl)vinyl)benzonitrile (24):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 90% (121.1 mg).

R_f: 0.23 (Mobile phase: 15% EtOAc in Hexane).

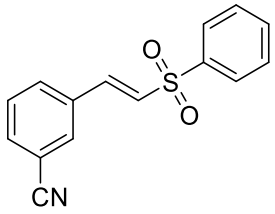
mp: 115.8, °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.95 (d, *J* = 7.8 Hz, 2H), 7.71 – 7.63 (m, 4H), 7.61 – 7.55 (m, 4H), 6.97 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.0, 139.9, 136.7, 134.0, 132.9, 131.1, 129.6, 129.0, 128.0, 118.1, 114.4.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7i]

(*E*)-3-(2-(phenylsulfonyl)vinyl)benzonitrile (25):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 82% (110.3 mg).

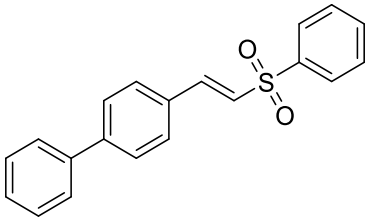
R_f: 0.256 (Mobile phase: 15% EtOAc in Hexane).

mp: 120.8 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 7.8 Hz, 2H), 7.76 (br.s, 1H), 7.71 (d. *J* = 8.0 Hz, 1H), 7.68-7.60 (m, 3H), 7.58 – 7.49 (m, 3H), 6.98 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.0, 139.7, 134.1, 133.9, 133.8, 132.7, 131.9, 130.3, 130.2, 129.6, 127.9, 117.9, 113.6.

(*E*)-4-(2-(phenylsulfonyl)vinyl)-1,1'-biphenyl (26):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 74% (118.6 mg).

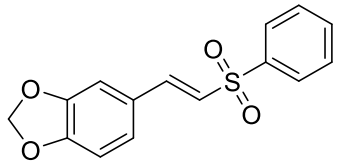
R_f: 0.71 (Mobile phase: 15% EtOAc in Hexane).

mp: 164.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.98 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 15.5 Hz, 1H), 7.65-7.54 (m, 9H), 7.46 (t, *J* = 7.0 Hz, 2H), 7.38 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.0, 142.1, 140.8, 139.8, 133.4, 131.3, 129.4, 129.1, 129.0, 128.1, 127.7, 127.7, 127.1, 127.1.

(*E*)-5-(2-(phenylsulfonyl)vinyl)benzo[d][1,3]dioxole (27):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 88% (126.9 mg).

R_f: 0.21 (Mobile phase: 15% EtOAc in Hexane).

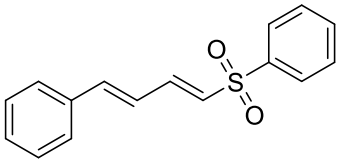
mp: 102.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 7.8 Hz, 2H), 7.62-7.50 (m, 4H), 6.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.67 (d, J = 15.5 Hz, 1H), 5.99 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.4, 148.5, 142.3, 141.0, 133.3, 129.3, 127.5, 126.7, 125.4, 124.9, 108.7, 106.8, 101.8.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7f]

(((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)sulfonyl)benzene (28):



The titled compound was synthesized according to the general procedure in 30 min at 30 Hz and was obtained as a white solid.

Yield: 77% (104.1 mg).

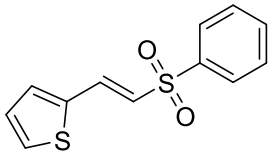
R_f: 0.34 (Mobile phase: 15% EtOAc in Hexane).

mp: 94.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 7.8 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.54 (t, J =8.0 Hz 2H), 7.48-7.40 (m, 3H), 7.39-7.28 (m, 3H), 6.98 (d, J = 15.5 Hz, 1H), 6.78 (dd. *J* = 15.3,11 Hz, 1H), 6.46 (d, J = 14.5 Hz, 1H).

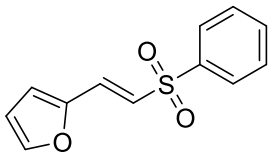
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.0, 142.4, 141.0, 135.4, 133.3, 129.7, 129.3, 128.9, 127.6, 127.5, 123.7.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7f]

(*E*)-2-(2-(phenylsulfonyl)vinyl)thiophene (29):



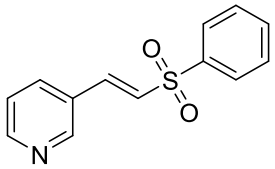
The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a yellow oil.
Yield: 69% (86.4 mg).
R_f: 0.41 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 – 7.91 (m, 2H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.60 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.30 (d,*J* = 3.5 Hz, 1H), 7.05 (dd, J = 5, 3.5 Hz, 1H), 6.64 (d, J = 15.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.9, 137.0, 135.3, 133.5, 132.7, 130.2, 129.5, 128.5, 127.7, 125.4.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-2-(2-(phenylsulfonyl)vinyl)furan (30):



The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil.
Yield: 30% (35.6 mg).
R_f: 0.31 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 – 7.91 (m, 1H), 7.91 (t, *J* = 2.5 Hz, 1H), 7.53 (tt, *J*8.5, 1.5Hz, 2H), 7.47-7.46 (m, 1H), 7.43 (d, *J* = 15.0 Hz, 1H), 6.73 (d,*J* = 15.5 Hz, 1H), 6.70 (d, J = 3.5 Hz, 1H), 6.47 (dd, J = 3.3, 1.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 148.8, 145.8, 140.9, 133.4, 129.4, 129.0, 127.6, 124.7, 117.1, 112.7.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-3-(2-(phenylsulfonyl)vinyl)pyridine (31):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a yellow solid.

Yield: 79% (96.9 mg).

R_f: 0.14 (Mobile phase: 30% EtOAc in Hexane).

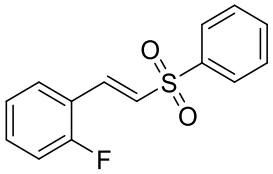
mp: 95.3 ^oC.

^1H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.69 (s, 1H), 8.59 (br.s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.69-7.59 (m, 2H), 7.54 (t, J =7.0 Hz,2H), 7.31 (t, J =7.0 Hz,1H), 6.96 (d, J =15.5 Hz,1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 151.8, 150.0, 140.1, 138.8, 134.8, 133.7, 129.6, 129.5, 128.3, 127.8, 123.9.

^1H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-fluoro-2-(2-(phenylsulfonyl)vinyl)benzene (32):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 63% (82.5 mg).

R_f = 0.46 (Mobile phase: 15% EtOAc in Hexane).

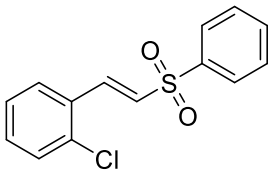
mp: 89.2 ^oC.

^1H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 16.0 Hz, 1H), 7.61 (tt, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t,*J* = 8.0 Hz, 2H), 7.44 (td, *J*= 7.5, 1.5 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 9.8 Hz, 1H), 7.02 (d, *J* = 15.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 161.6 (d, *J* = 253.8 Hz), 140.5, 135.6 (d,*J* = 2.6 Hz), 133.6, 132.9 (d, *J* = 9.0 Hz), 130.4 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 8.5 Hz), 129.5, 127.8, 124.8 (d, *J* = 3.8 Hz), 120.6 (d, *J* = 11.4 Hz), 116.5 (d, *J* = 21.6 Hz).

^1H and **^{13}C NMR** of the product are in agreement with the literature.[9]

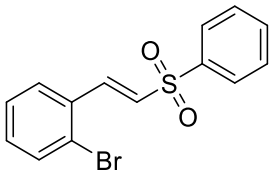
(*E*)-1-chloro-2-(2-(phenylsulfonyl)vinyl)benzene (33):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;
Yield: 69% (95.9 mg).
R_f: 0.40 (Mobile phase: 15% EtOAc in Hexane).
mp: 108.7 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.09 (d, *J* = 15.5 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.57 (t,*J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 15.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 140.3, 138.4, 135.4, 133.7, 132.1, 130.7, 130.5, 130.1, 129.5, 128.4, 127.9, 127.4.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7i]

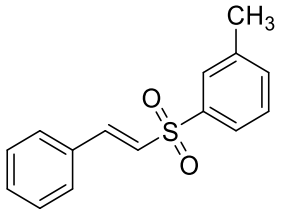
(*E*)-1-bromo-2-(2-(phenylsulfonyl)vinyl)benzene (34):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.
Yield: 78% (126.0 mg).
R_f = 0.41 (Mobile phase: 15% EtOAc in Hexane).
mp: 104.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.08 (d, *J* = 15.5 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.68-7.62 (m, 2H), 7.59 (t, *J* = 8.0 Hz,2H), 7.51 (dd, *J* = 8.8, 1.5 Hz, 2H), 7.33 (td, *J* = 7.3, 1.0 Hz, 1H), 7.27 (td, *J* =7.8, 2.0 Hz, 1H), 6.87 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 141.1, 140.3, 133.7, 133.6, 132.5, 132.2, 130.3, 129.5, 128.4, 128.0, 127.9, 125.7.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7f]

(*E*)-1-methyl-3-(styrylsulfonyl)benzene (35):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;

Yield: 84% (108.5 mg).

R_f: 0.59 (Mobile phase: 15% EtOAc in Hexane).

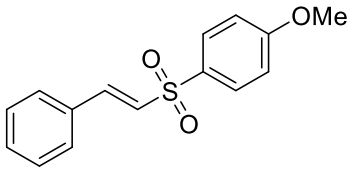
mp: 117.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79-7.75 (m, 2H), 7.70 (d, *J* = 15.5 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.48-7.41 (m, 5H), 6.88 (d, J =15.5 Hz,1H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.3, 140.6, 139.7, 134.3, 132.5, 131.3, 129.3, 129.2, 128.7, 128.0, 127.5, 124.9, 21.4.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[7i]

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene (36):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;

Yield: 72% (98.9 mg).

R_f: 0.66 (Mobile phase: 15% EtOAc in Hexane).

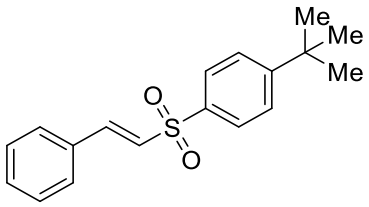
mp: 111.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 15.0 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.41-7.35 (m, 3H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J*=15.5 Hz,1H), 3.86 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 163.7, 141.5, 132.6, 132.3, 131.1, 130.0, 129.1, 128.6, 128.0, 114.7, 55.8.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7f]

(*E*)-1-(tert-butyl)-4-(styrylsulfonyl)benzene (37):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;

Yield: 78% (117.2 mg).

R_f: 0.54 (Mobile phase: 15% EtOAc in Hexane).

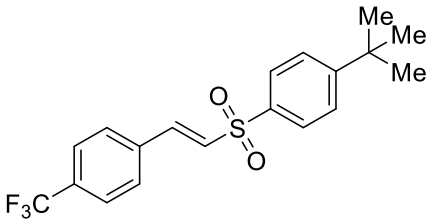
mp: 118.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.86 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.50-7.46 (m, 2H), 7.39 (t, *J* = 6.0 Hz, 2H), 6.86 (d, *J*=15.5 Hz,1H), 1.33 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.4, 142.0, 137.7, 132.6, 131.2, 129.1, 128.6, 127.7, 127.6, 126.5, 35.3, 31.1.

^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[7i]

(*E*)-1-(tert-butyl)-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene (38):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 66% (121.5 mg).

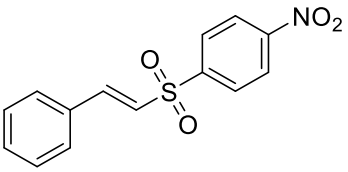
R_f: 0.54 (Mobile phase: 15% EtOAc in Hexane).

mp: 103.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 (dt, *J* = 8.5, 2.5 Hz, 2H), 7.68 (d, *J* = 15.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.61-7.56 (m, 4H), 6.95 (d, *J* = 15.5 Hz, 1H), 1.34 (s, 9H).

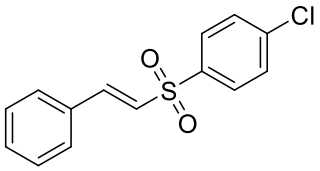
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 157.9, 140.0, 137.1, 136.0, 132.6 (d, *J* = 32.9 Hz), 130.5, 130.0, 128.8, 127.8, 126.6, 126.1 (t, *J* = 3.9 Hz), 35.4, 31.1.

(*E*)-1-nitro-4-(styrylsulfonyl)benzene (39):



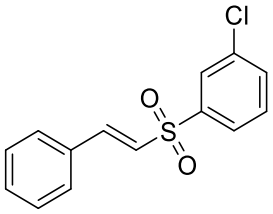
The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;
Yield: 78% (112.8 mg).
R_f: 0.38 (Mobile phase: 15% EtOAc in Hexane).
mp: 153.7 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.38 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 15.5 Hz, 1H), 7.53-7.49 (m, 2H), 7.48-7.39 (m, 3H), 6.86 (d, J =15.0 Hz,1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 150.6, 146.6, 145.0, 131.9, 131.9, 129.2, 129.1, 128.9, 125.7, 124.6.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[7i]

(*E*)-1-chloro-4-(styrylsulfonyl)benzene (40):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.
Yield: 86% (119.8 mg).
R_f: 0.52 (Mobile phase: 15% EtOAc in Hexane).
mp: 129.8 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.52-7.46 (m, 4H), 7.44-7.36 (m, 3H), 6.85 (d, *J* = 15.0 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.2, 140.2, 139.3, 132.2, 131.5, 129.8, 129.3, 129.2, 128.8, 126.9.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7a]

(*E*)-1-chloro-3-(styrylsulfonyl)benzene (41):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

Yield: 80% (111.4 mg).

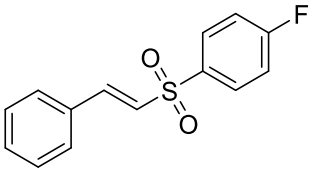
R_f: 0.55 (Mobile phase: 15% EtOAc in Hexane).

mp: 72.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (t, *J* = 2.0 Hz, 1H), 7.85-7.81 (m, 1H), 7.70 (d, *J*=15.5 Hz,1H), 7.59-7.55 (m, 1H), 7.51-7.46 (m, 3H), 7.45-7.37 (m, 3H), 6.85 (d, *J*=15.0 Hz,1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.6, 142.6, 135.6, 133.6, 132.2, 131.6, 130.8, 129.3, 128.8, 127.8, 126.6, 125.9.

(*E*)-1-fluoro-4-(styrylsulfonyl)benzene (42):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;

Yield: 79% (103.6 mg).

R_f: 0.59 (Mobile phase: 15% EtOAc in Hexane).

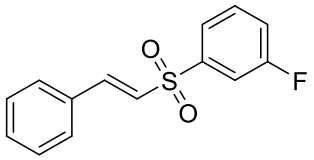
mp: 92.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00-7.91 (m, 2H), 7.67 (d, *J* = 15.5 Hz, 1H), 7.47 (d,*J* = 11.0 Hz,2H), 7.43-7.25 (m, 3H), 7.24-7.15 (m,2H), 6.87 (d, *J*=15.0 Hz,1H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 165.7 (d, *J*=254.4 Hz), 142.8, 136.9 d *J* = 3.3 Hz) , 132.3, 131.4, 130.6 (d, *J*=9.6 Hz), 129.2, 128.7, 127.2, 116.7 (d, *J*=22.5 Hz).

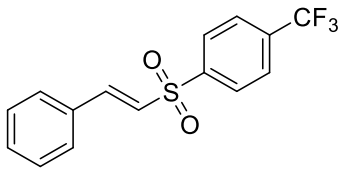
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7e]

(*E*)-1-fluoro-3-(styrylsulfonyl)benzene (43):



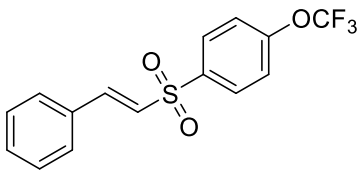
The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;
Yield: 67% (87.9 mg).
R_f: 0.52 (Mobile phase: 15% EtOAc in Hexane).
mp: 102.6 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 15.5 Hz, 1H), 7.64 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.56-7.46 (m, 3H), 7.44-7.36 (m, 3H), 7.30 (td, *J* = 8.5, 2.5 Hz, 1H), 6.87 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 162.6 (d, *J* = 250.6Hz), 143.6, 142.9 (d, *J* = 6.6 Hz), 132.2, 131.6, 131.4 (d, *J* = 7.6 Hz), 129.2, 128.8, 126.6, 123.6 (d, *J* = 3.5 Hz), 120.8, 120.7, 115.0 (d, *J* = 24.3 Hz).

(*E*)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (44):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.
Yield: 62% (96.8 mg).
R_f: 0.54 (Mobile phase: 15% EtOAc in Hexane).
mp: 128.3 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.09 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 15.5 Hz, 1H), 7.52-7.48 (m, 2H), 7.46-7.39 (m, 3H), 6.85 (d, *J*=15.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.3 (d, *J* = 31.5 Hz), 135.2 (d, *J* = 32.9 Hz), 132.1, 131.7, 129.3, 128.8, 128.3, 126.6 (d, *J*=3.9 Hz), 126.3, 124.3, 122.1.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7d]

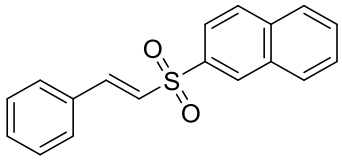
(*E*)-1-(styrylsulfonyl)-4-(trifluoromethoxy)benzene (45):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid.

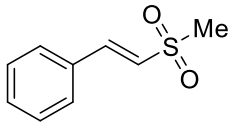
Yield: 59% (96.9 mg).
R_f: 0.69 (Mobile phase: 15% EtOAc in Hexane).
mp: 93.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.00 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.46-7.35 (m, 5H), 6.85 (d, *J* = 15.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 152.8, 143.4, 139.1, 132.2, 131.6, 130.0, 129.3, 128.8, 126.8, 121.3 (d, *J*=1.4 Hz), 119.2.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[9]

(*E*)-2-(styrylsulfonyl)naphthalene (46):



The titled compound was synthesized according to the general procedure in 30 min at 30 Hz and was obtained as a white solid;
Yield: 42% (61.8 mg).
R_f = 0.45 (Mobile phase: 15% EtOAc in Hexane).
mp: 129.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.55 (br.s, 1H), 7.99 (t, *J* = 7.3 Hz, 2H), 7.93-7.87 (m, 2H), 7.75 (d, *J* = 15.0 Hz, 1H), 7.68-7.60 (m, 2H), 7.50-7.47 (m, 2H), 7.42-7.36 (m, 3H), 6.92 (d, *J*=15.5 Hz,1H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 142.7, 137.6, 135.3, 132.5, 132.4, 131.3, 129.8, 129.5, 129.3, 129.3, 129.2, 128.7, 128.1, 127.8, 127.4, 122.7.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[7i]

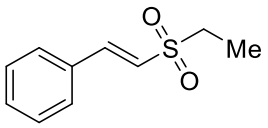
(*E*)-(2-(methylsulfonyl)vinyl)benzene (47):



The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a white solid.

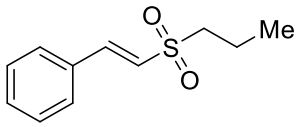
Yield: 80% (72.9 mg).
R_f = 0.34 (Mobile phase: 15% EtOAc in Hexane).
mp: 83.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58(d, *J* = 15.0 Hz,1H), 7.48 (dd, *J* = 7.8, 1.5Hz, 2H), 7.43-7.35 (m, 3H), 6.94 (d, *J*=15.5 Hz,1H), 3.00 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.9, 132.2, 131.5, 129.3, 128.7, 126.3, 43.3.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [7f]

(*E*)-(2-(ethylsulfonyl)vinyl)benzene (48):

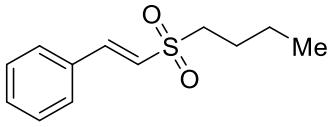


The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil;
Yield: 71% (69.6 mg).
R_f = 0.62 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 (d, *J* = 15.5 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.45-7.41 (m, 3H), 6.80 (d, *J* = 15.5 Hz, 1H), 3.08 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 145.4, 132.3, 131.5, 129.3, 128.7, 124.0, 49.5, 7.4.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10]

(*E*)-(2-(propylsulfonyl)vinyl)benzene (49):

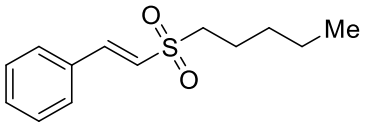


The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil;
Yield: 59% (62.0 mg).
R_f = 0.6 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.59 (d, *J* = 15.5 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.45-7.39 (m, 3H), 6.82 (d, *J* = 15.5 Hz, 1H), 3.07-3.01 (m, 2H), 1.90-1.82 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.8, 132.3, 131.3, 129.2, 128.6, 124.8, 57.0, 16.4, 13.0.
(*E*)-(2-(butylsulfonyl)vinyl)benzene (50):



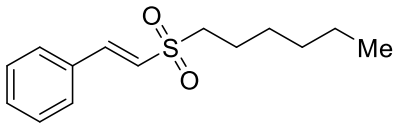
The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil;
Yield: 65% (72.9 mg).
$\mathbf{R_f}$ = 0.67 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58 (d, *J* = 15.5 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.44-7.38 (m, 3H), 6.83 (d, *J* = 15.5 Hz, 1H), 3.08-3.03 (m, 2H), 1.82-1.75 (m, 2H), 1.48-1.42 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.8, 132.3, 131.5, 129.2, 128.7, 124.8, 55.0, 24.6, 21.7, 13.7.

(*E*)-(2-(pentylsulfonyl)vinyl)benzene (51):



The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil;
Yield: 30% (35.8 mg).
$\mathbf{R_f}$ = 0.59 (Mobile phase: 10% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.56 (d, *J* = 15.5, 1H), 7.49 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.42-7.35 (m, 3H), 6.86 (d, *J* = 15.5 Hz, 1H), 3.10-2.97 (m, 2H), 1.86-1.70 (m, 2H), 1.41-1.25 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.7, 132.4, 131.4, 129.2, 128.7, 124.9, 55.1, 30.5, 22.3, 22.2, 13.8.

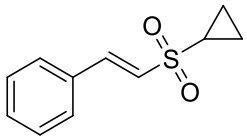
(*E*)-(2-(hexylsulfonyl)vinyl)benzene (52):



The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil;
Yield: 42% (53.0 mg).
$\mathbf{R_f}$ = 0.77 (Mobile phase: 15% EtOAc in Hexane).

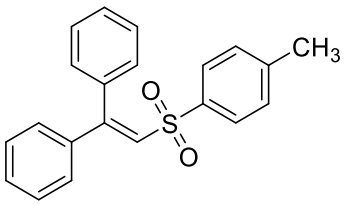
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58 (d, *J* = 15.5, 1H), 7.51(dd, *J* = 7.5, 1.0 Hz, 2H), 7.45-7.37 (m, 3H), 6.87 (d, *J* = 15.5 Hz, 1H), 3.08-3.02 (m, 2H), 1.85-1.76 (m, 2H), 1.46-1.37 (m, 2H), 1.32-1.25 (m, 2H), 0.87 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 144.7, 132.4, 131.4, 129.2, 128.7, 125.0, 55.2, 31.3, 28.1, 22.6, 22.4, 14.1.

(*E*)-(2-(cyclopropylsulfonyl)vinyl)benzene (53):



The titled compound was synthesized according to the general procedure in 40 min at 30 Hz and was obtained as a yellow oil;
Yield: 70% (72.9 mg).
R_f = 0.55 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57 (d, *J* = 15.5 Hz, 1H), 7.53 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.45-7.38 (m, 3H), 6.89 (d, *J* = 15.5 Hz, 1H), 2.48-2.41 (m, 1H), 1.09-1.05 (m, 2H), 0.90-0.75 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 143.3, 132.5, 131.2, 129.1, 128.5, 125.7, 31.4, 16.4, 13.0.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature. [10]

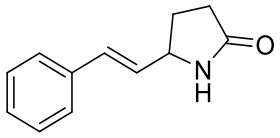
(2-tosylethene-1,1-diyl)dibenzene (55):



The titled compound was synthesized according to the general procedure in 10 min at 30 Hz and was obtained as a white solid;
Yield: 47% (78.6 mg).
R_f = 0.45 (Mobile phase: 15% EtOAc in Hexane).
mp: 103.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.52 (d, *J* = 8.0 Hz,2H), 7.41-7.25 (m, 6H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.17-7.11 (m, 4H), 7.05 (s, 1H), 2.36 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 154.8, 144.0, 139.3, 138.7, 135.7, 130.4, 129.9, 129.5, 129.1, 129.0, 128.7, 128.3, 128.0, 127.8, 21.7.

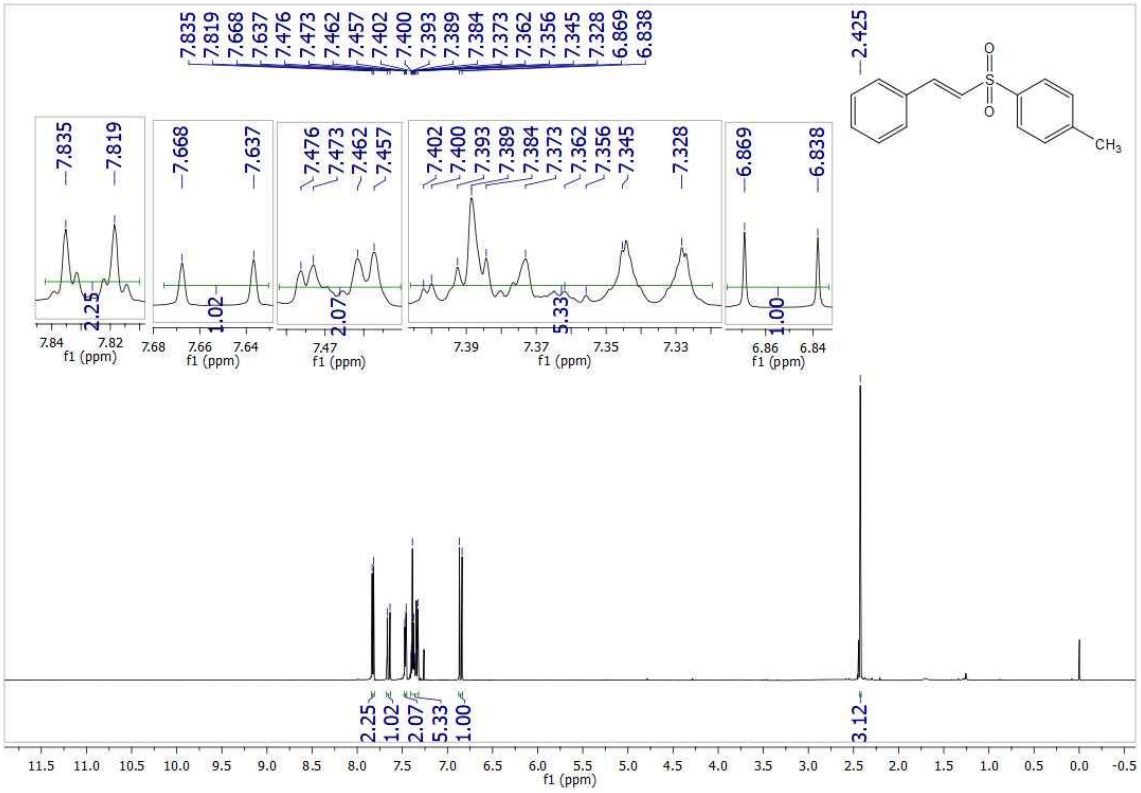
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[11]

(E)-5-styrylpyrrolidin-2-one (56):

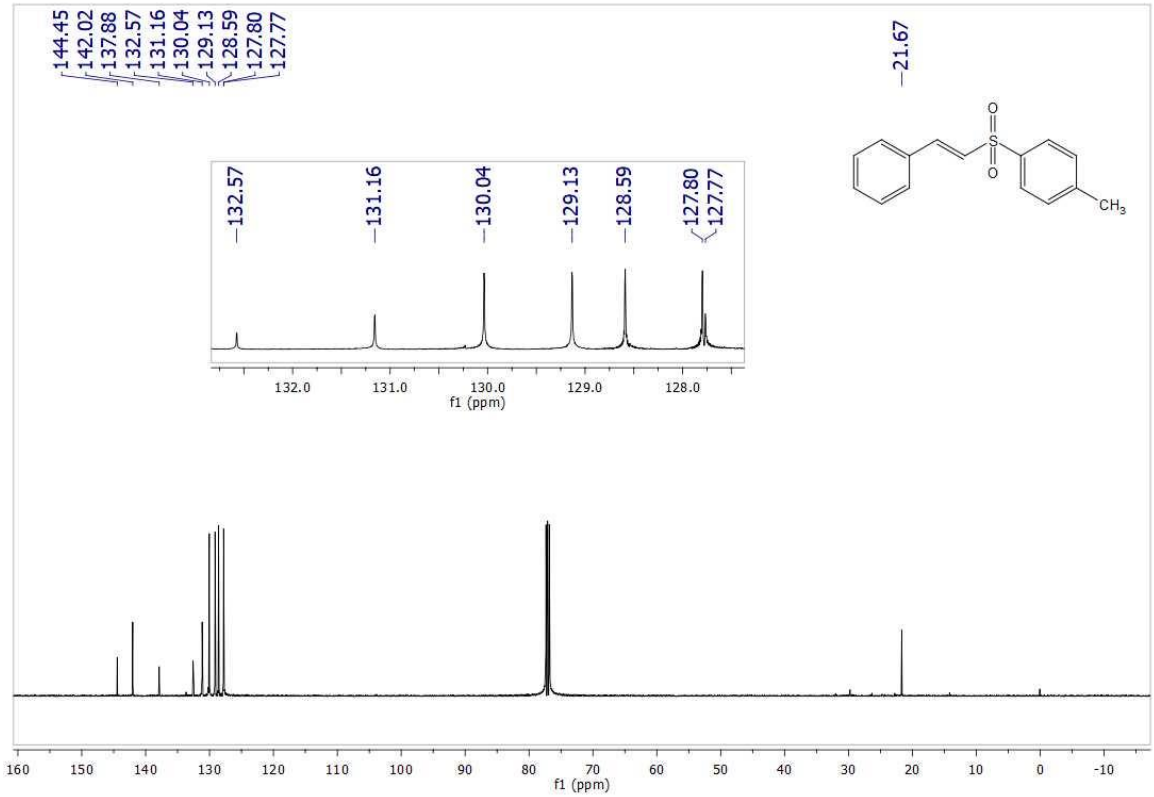


was obtained as a white solid,
Yield: 74% (27.7 mg).
R_f = 0.36 (Mobile phase: EtOAc).
mp: 73.2 °C.
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.41-7.32 (m, 4H), 7.30-7.25 (m, 1H), 6.56 (d, *J* = 16.0 Hz, 2H), 6.15 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.36 (q, *J* = 6.5 Hz, 1H), 2.44-2.36 (m, 3H), 1.98-1.92 (m, 1 H).
^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 178.5, 136.1, 131.1, 129.9, 128.7, 128.0, 126.5, 56.6, 30.0, 28.5.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[5]

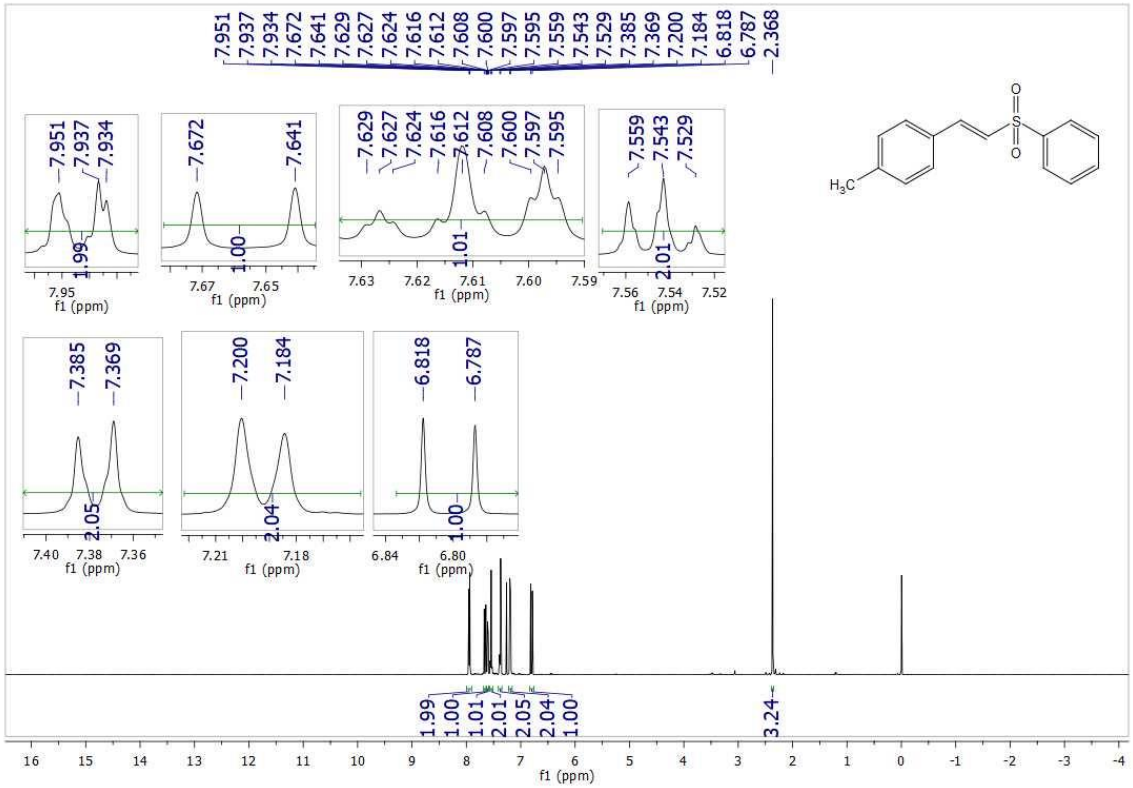
7.2 NMR copies of products



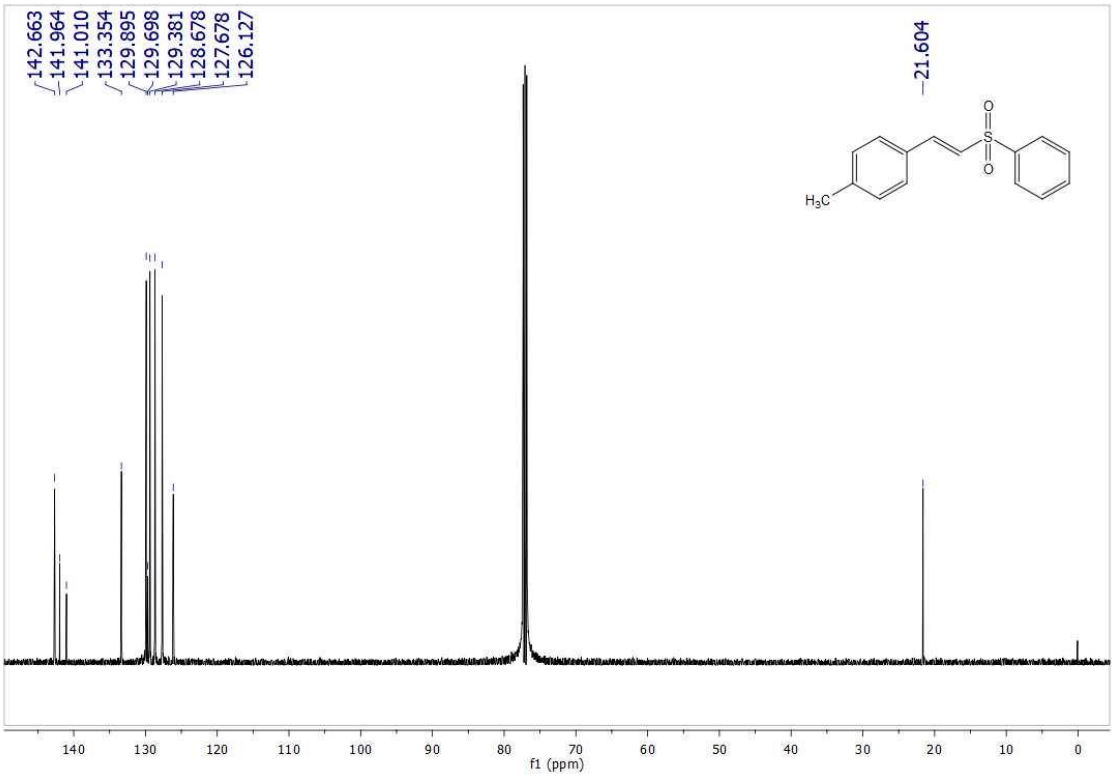
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3**.



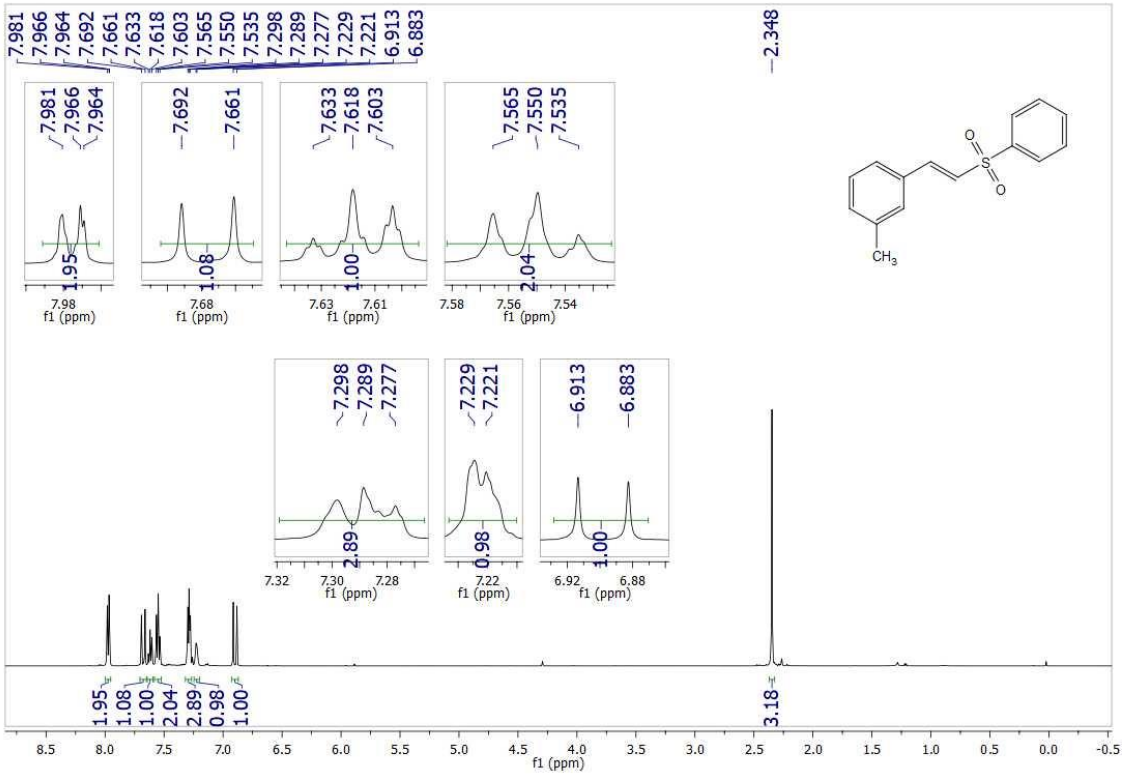
^{13}C NMR (125 MHz, $CDCl_3$) of compound **3**.



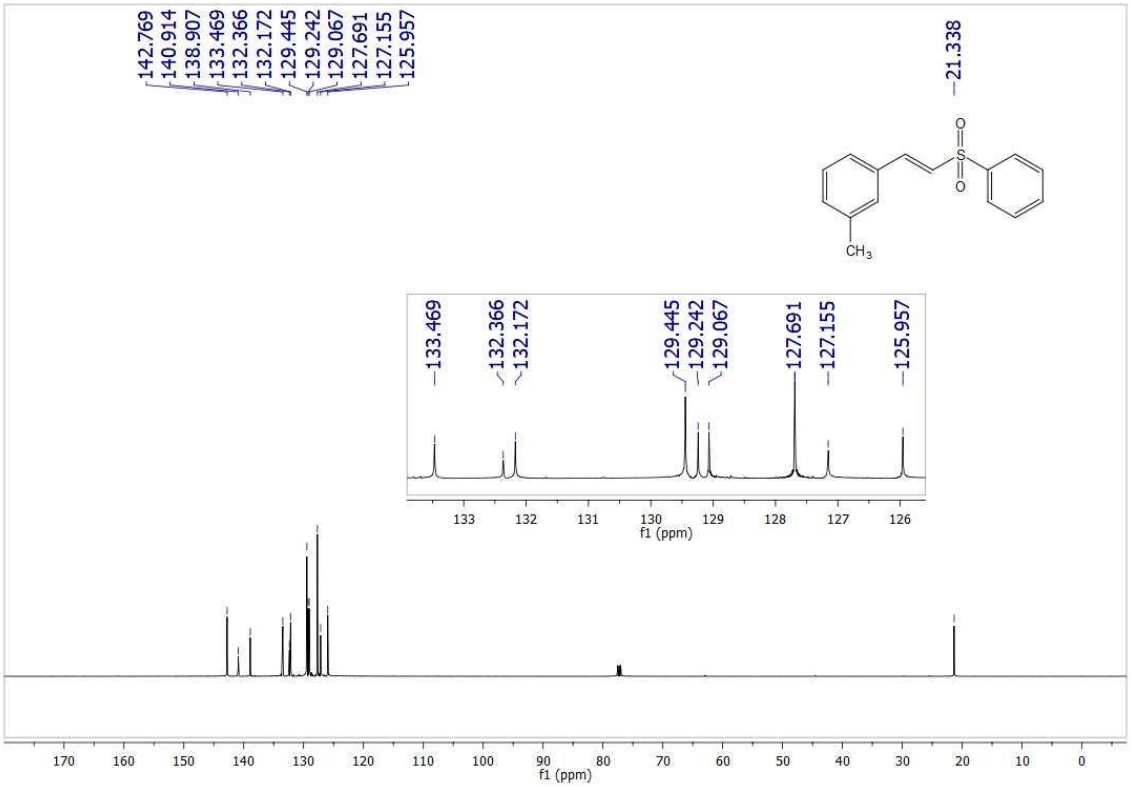
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4**.



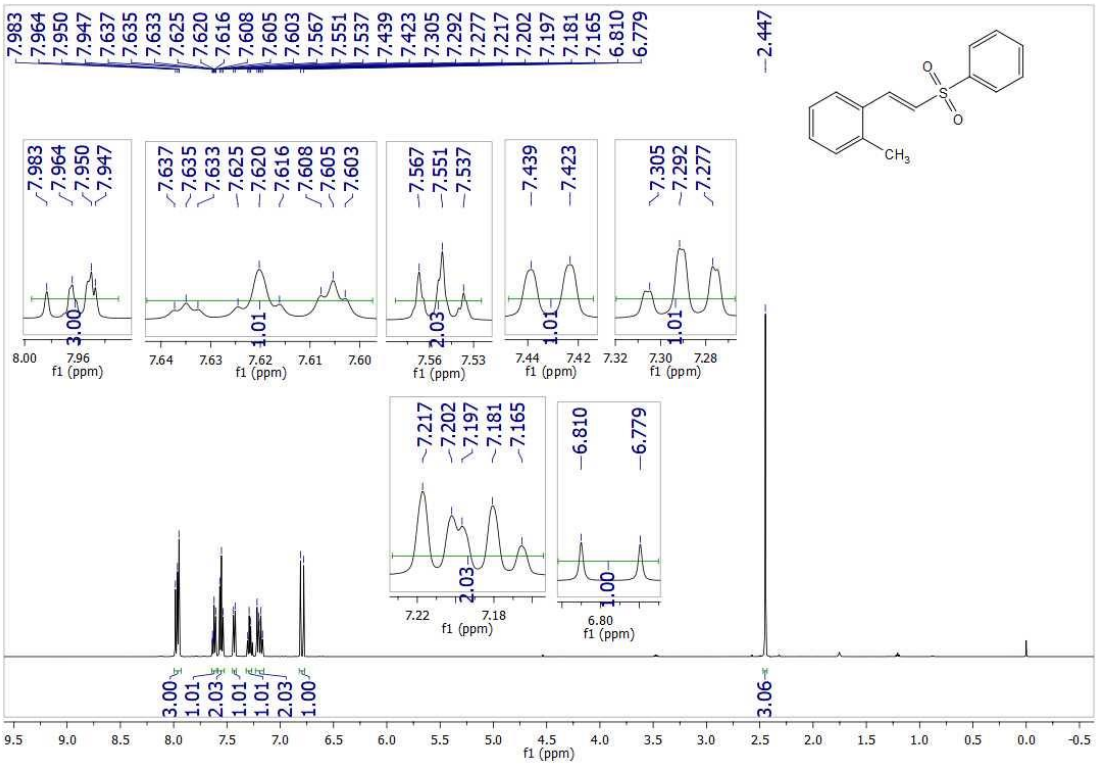
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4**.



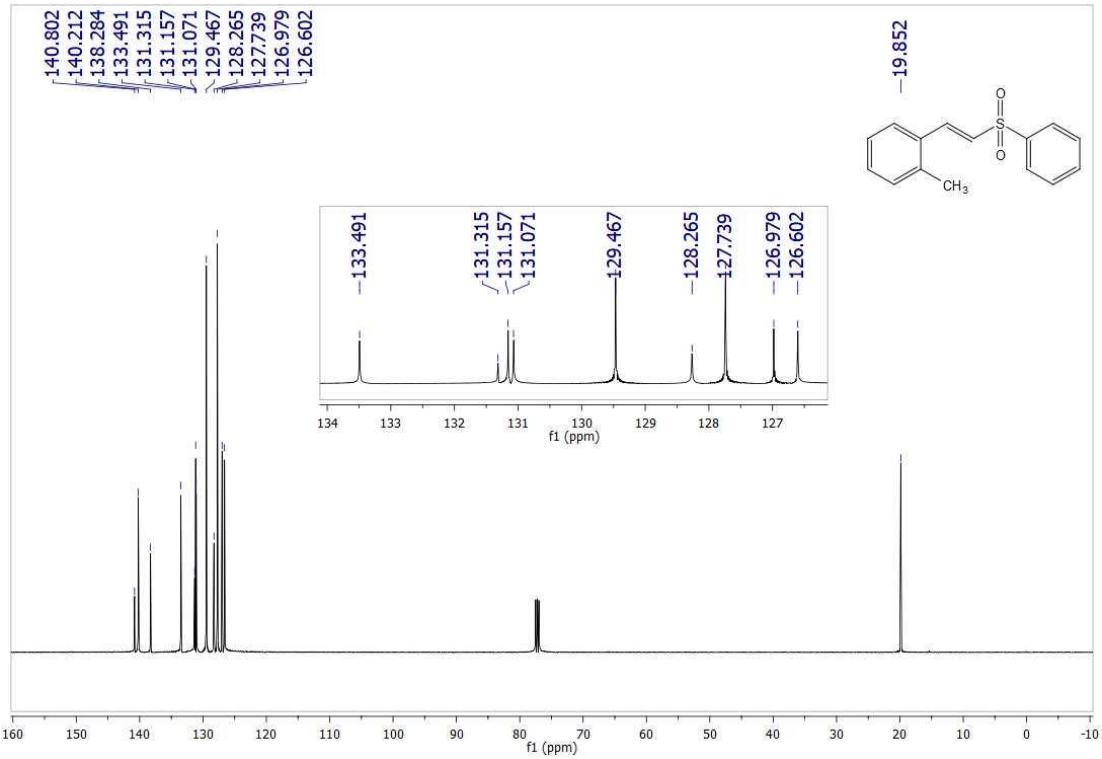
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**.



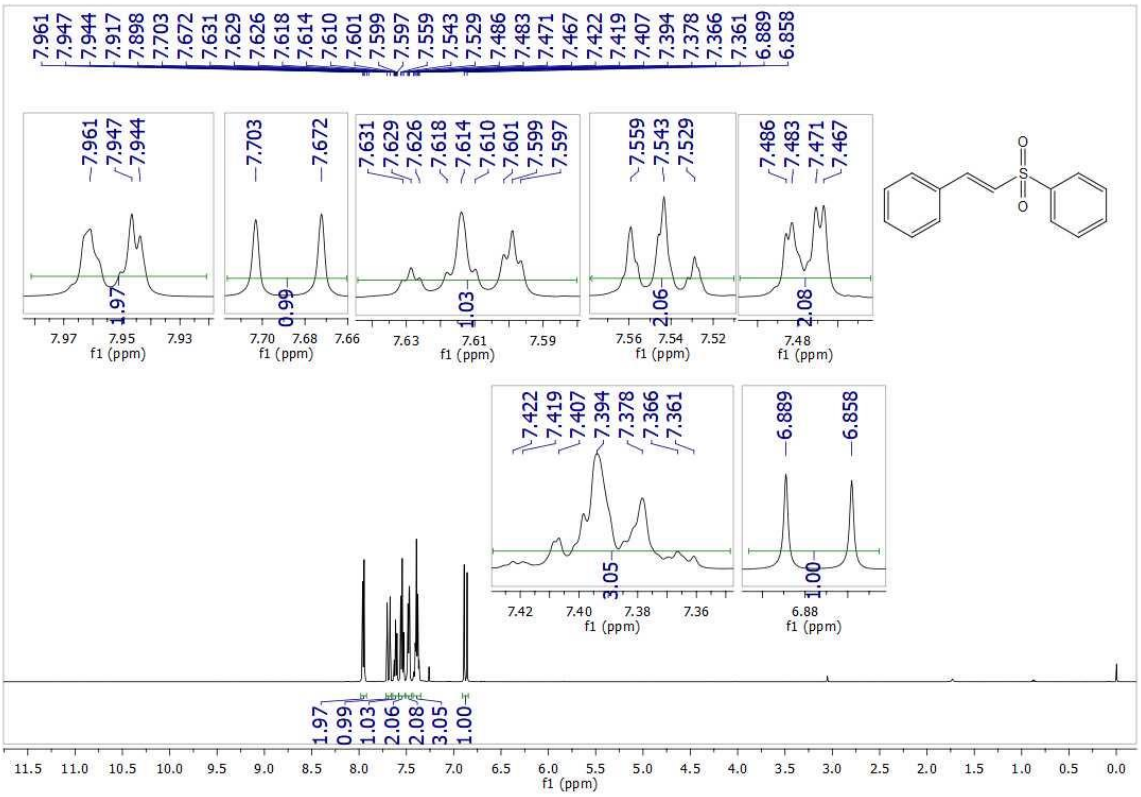
^{13}C NMR (125 MHz, $CDCl_3$) of compound **5**.



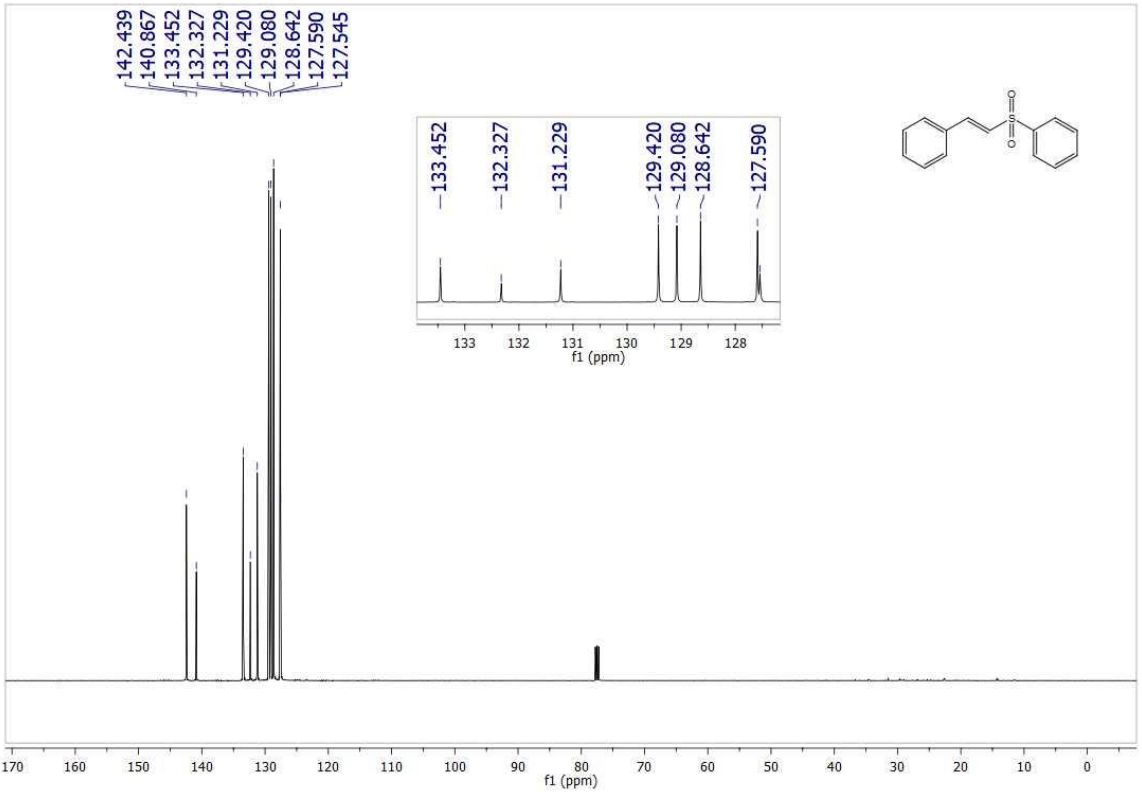
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



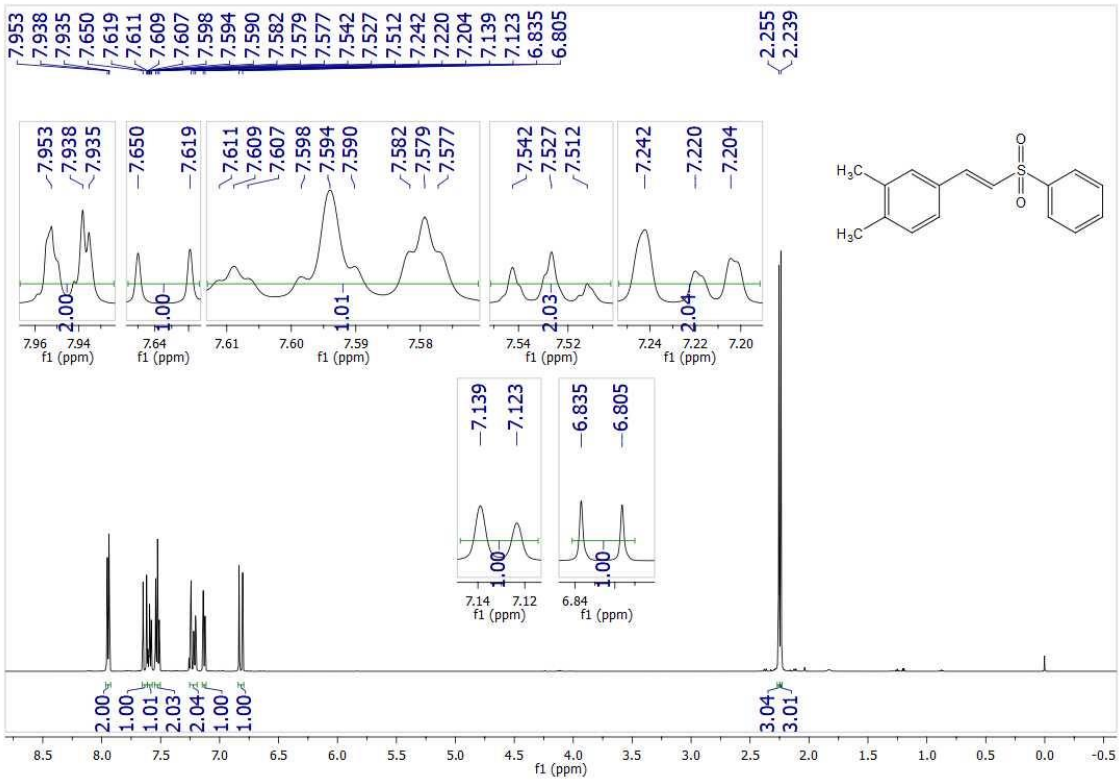
^{13}C NMR (125 MHz, $CDCl_3$) of compound **6**.



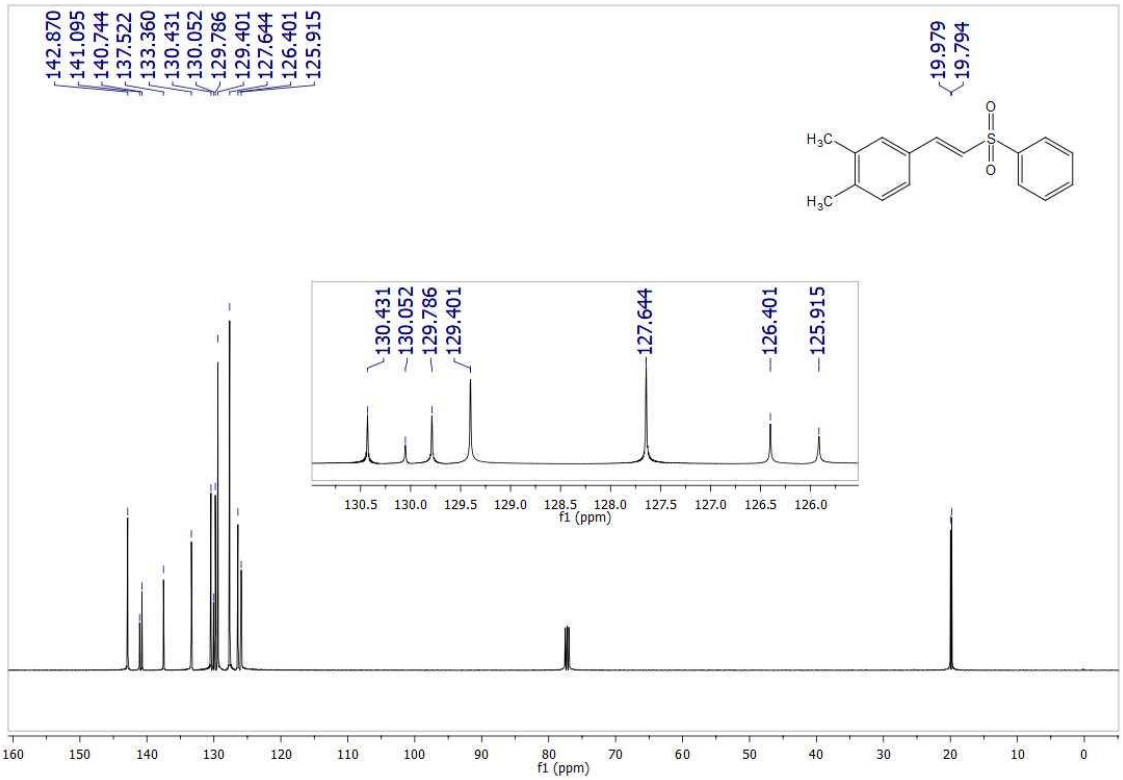
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.



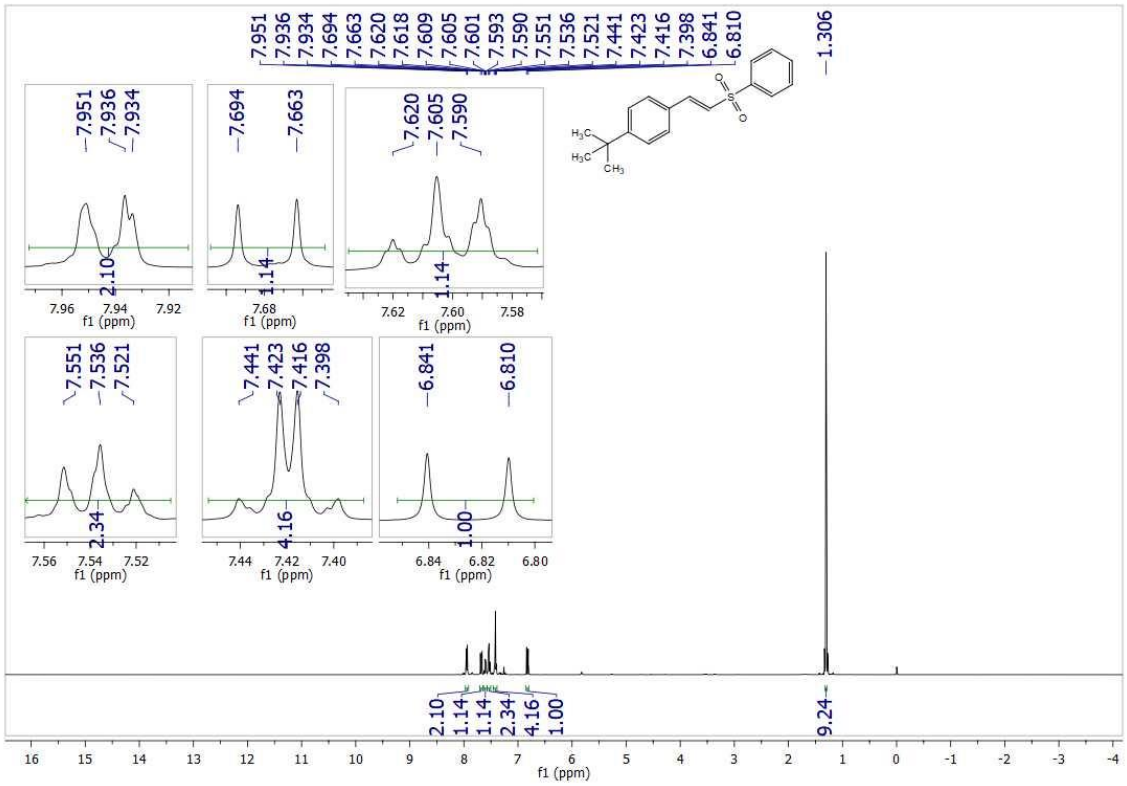
^{13}C NMR (125 MHz, $CDCl_3$) of compound **7**.



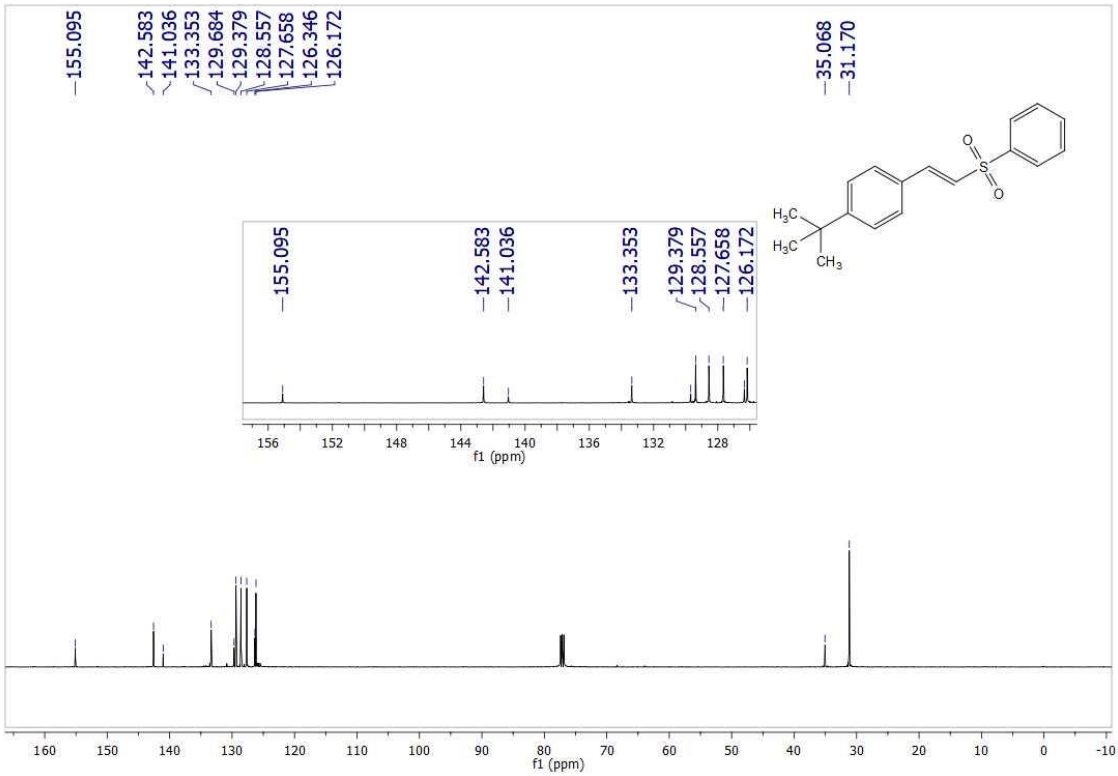
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



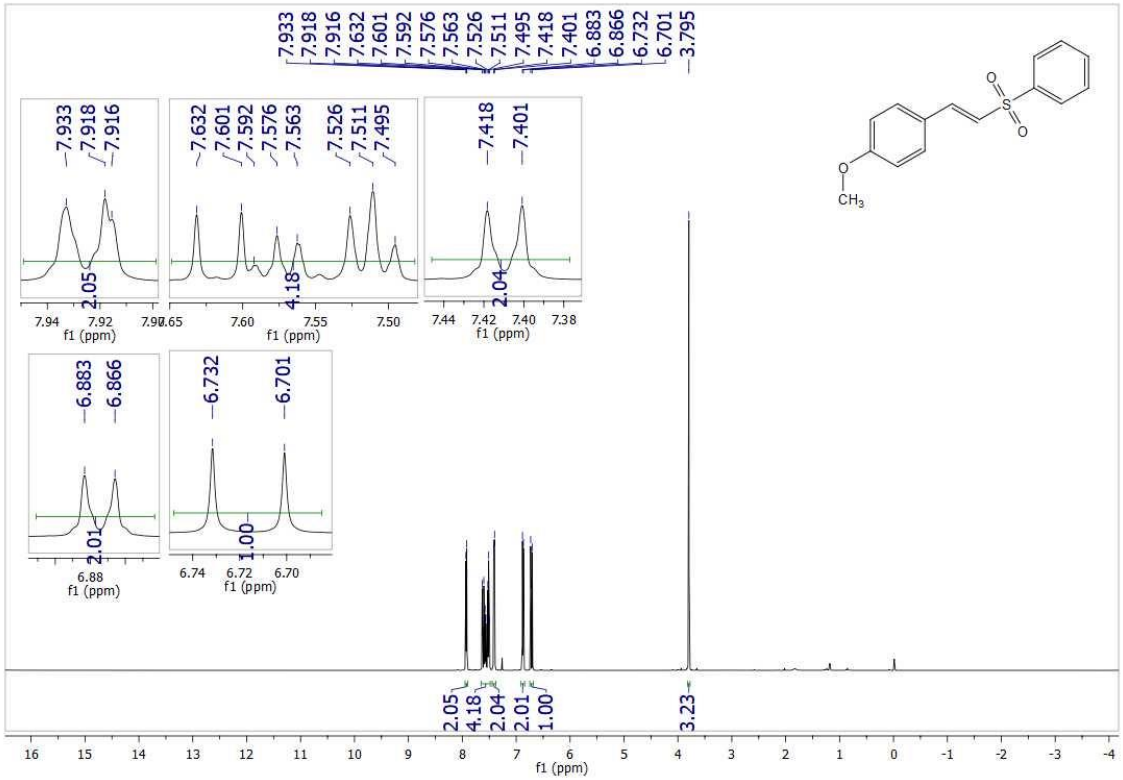
^{13}C NMR (125 MHz, $CDCl_3$) of compound **8**.



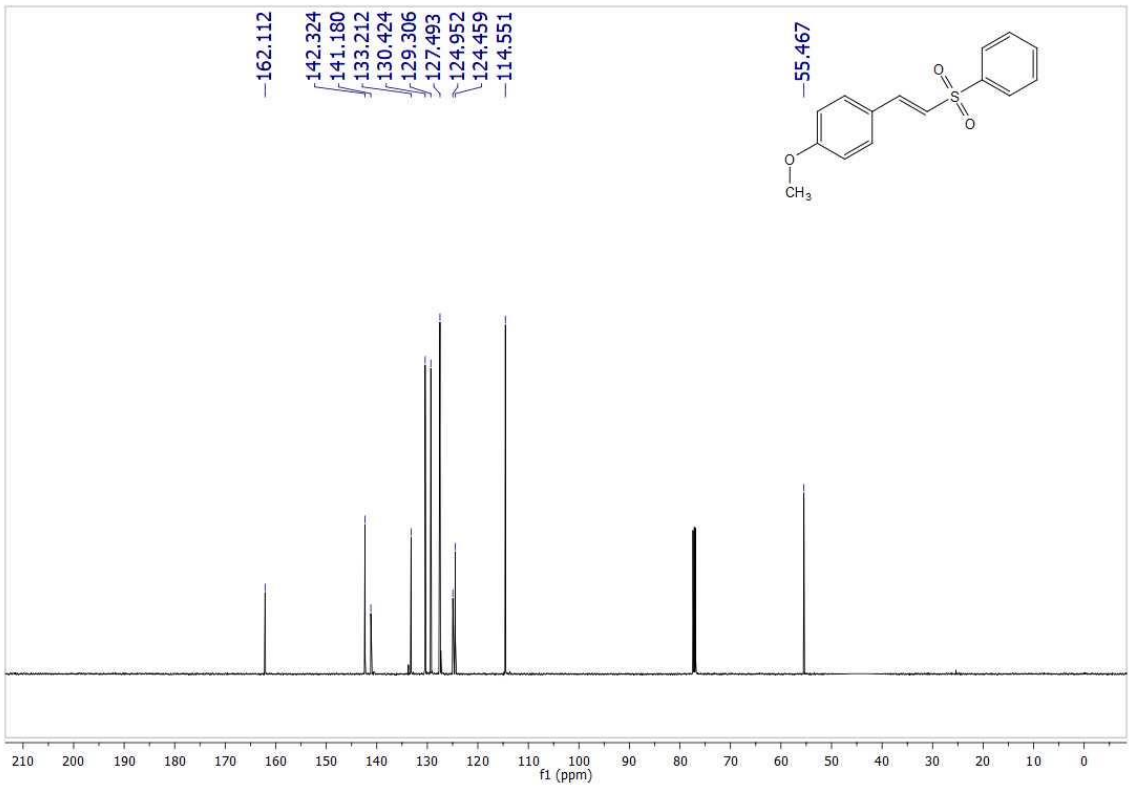
^{1}H NMR (500 MHz, $CDCl_3$) of compound **9**.



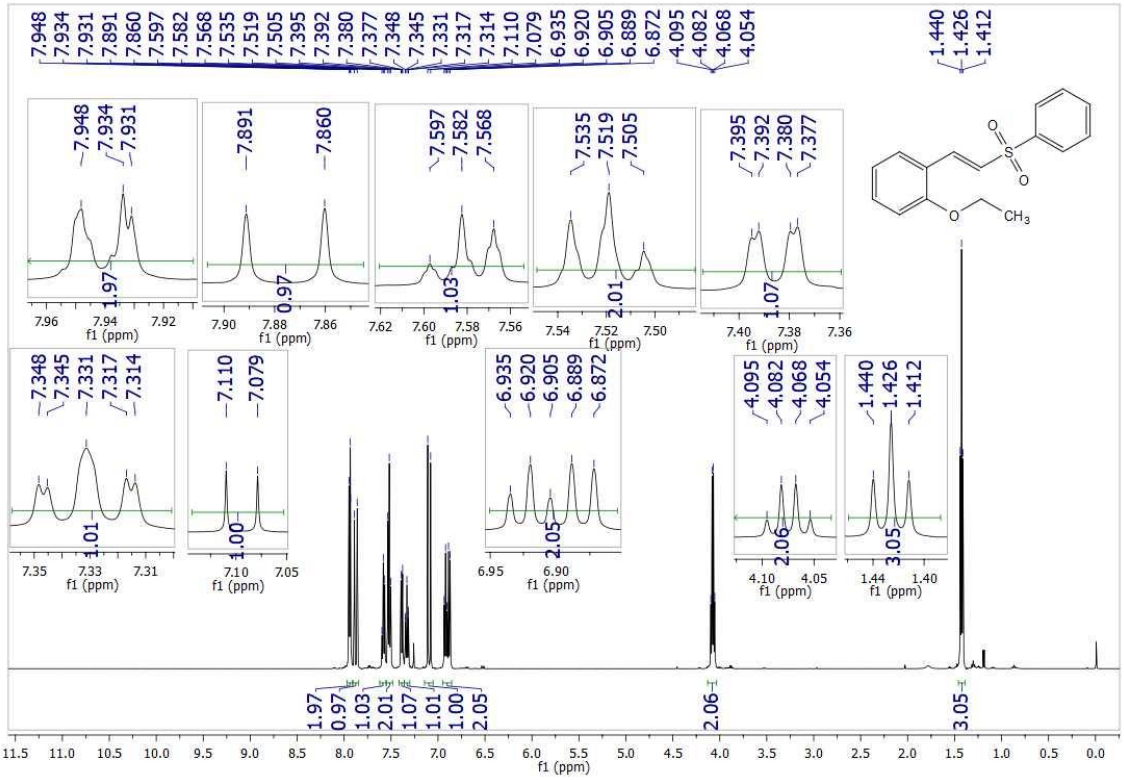
^{13}C NMR (125 MHz, $CDCl_3$) of compound **9**.



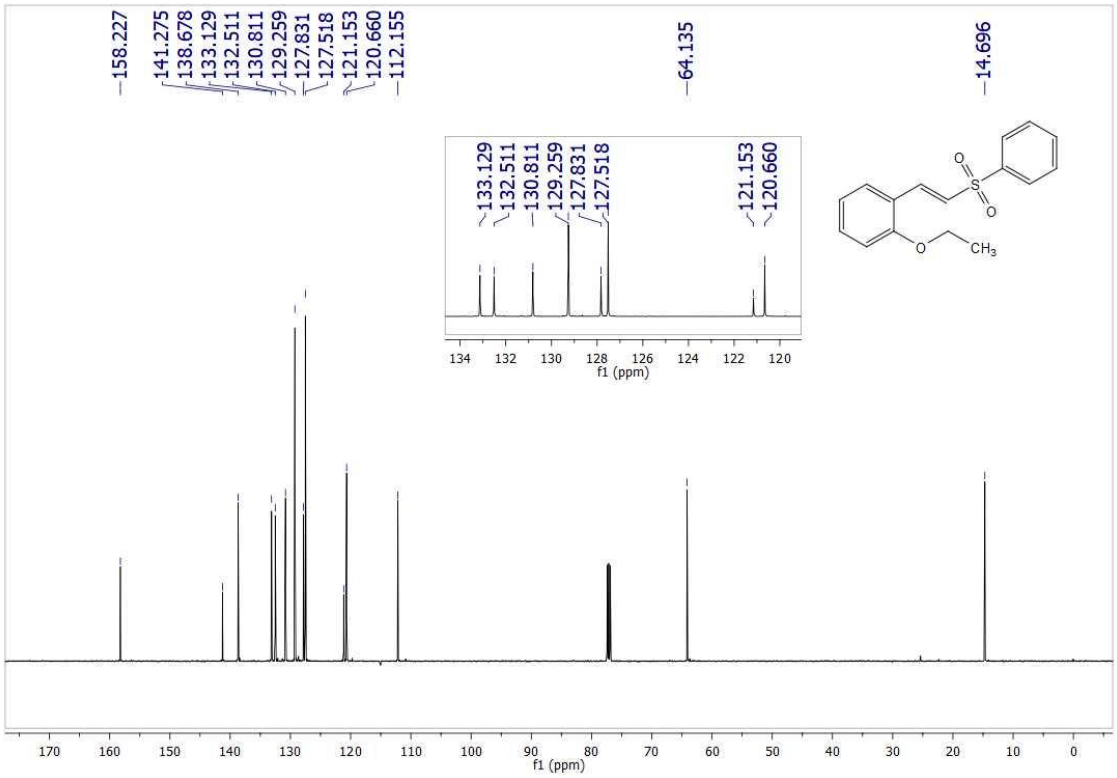
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**.



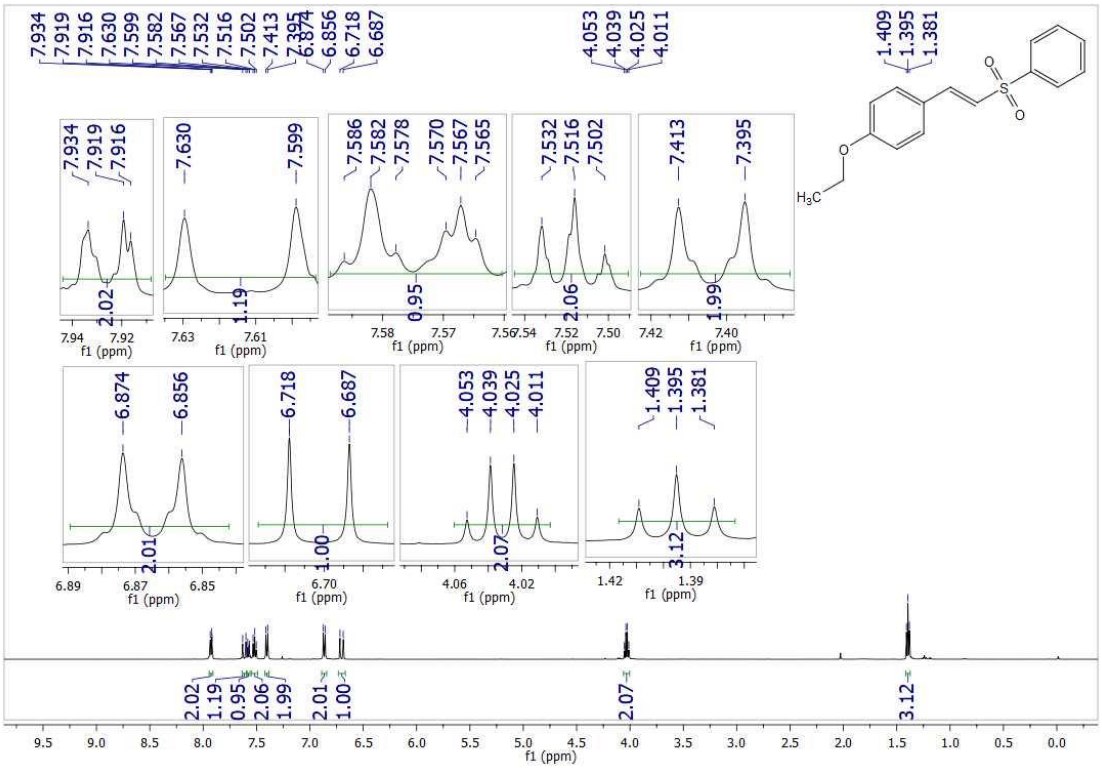
^{13}C NMR (125 MHz, $CDCl_3$) of compound **10**.



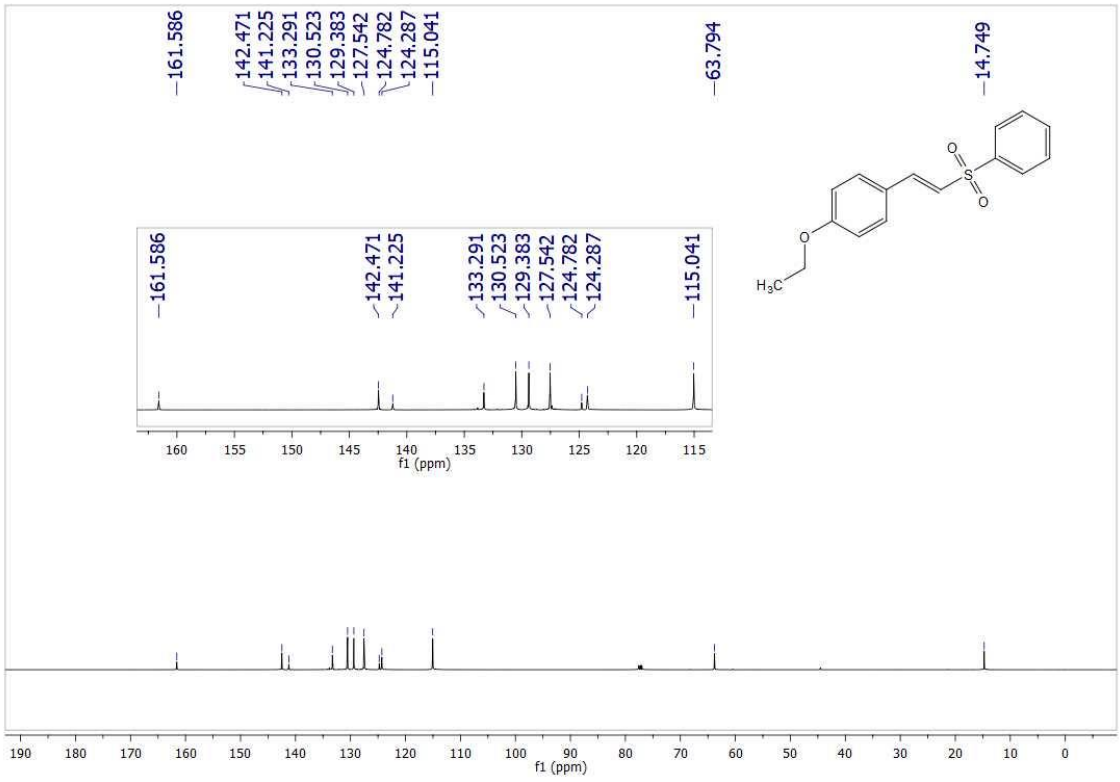
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.



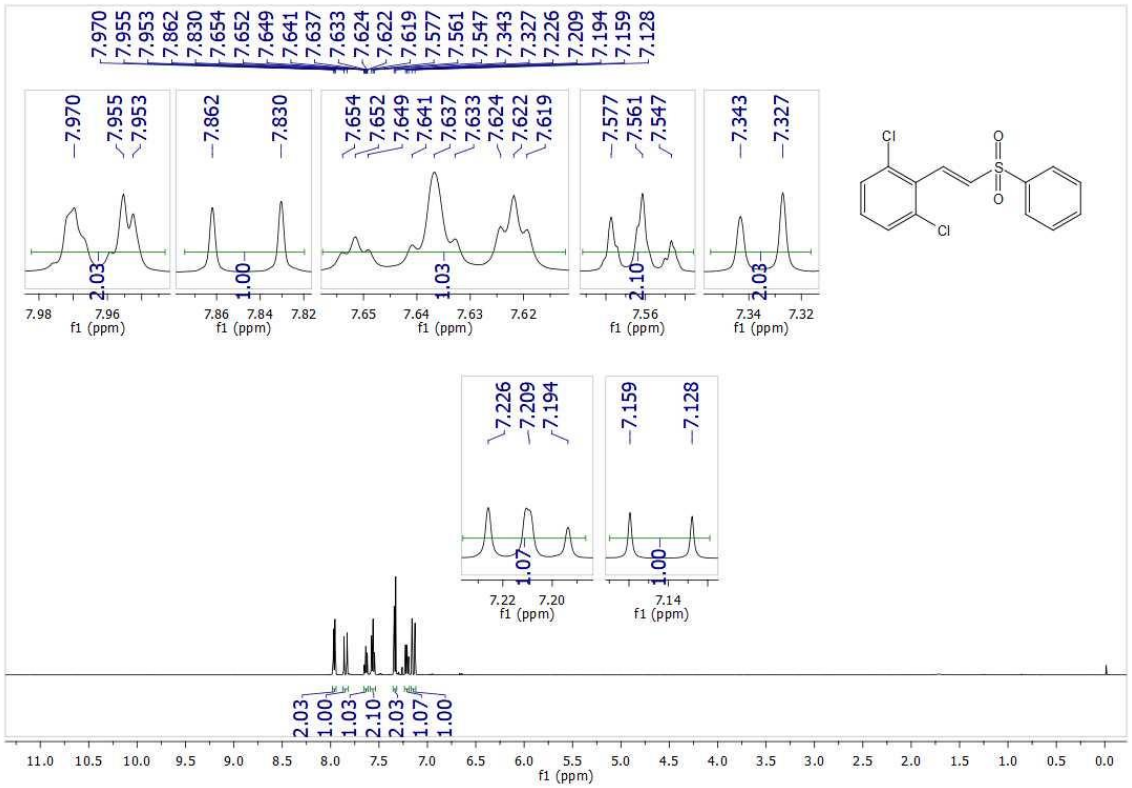
^{13}C NMR (125 MHz, $CDCl_3$) of compound **11**.



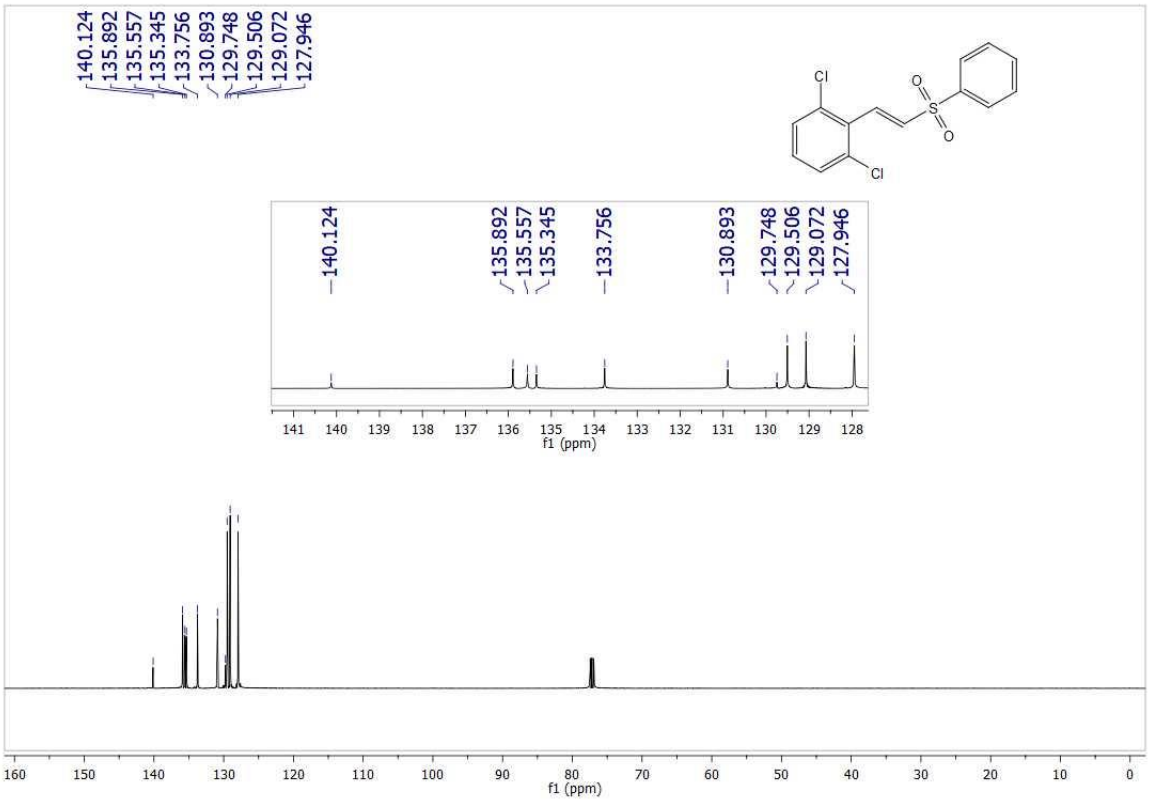
^{1}H NMR (500 MHz, $CDCl_3$) of compound **12**.



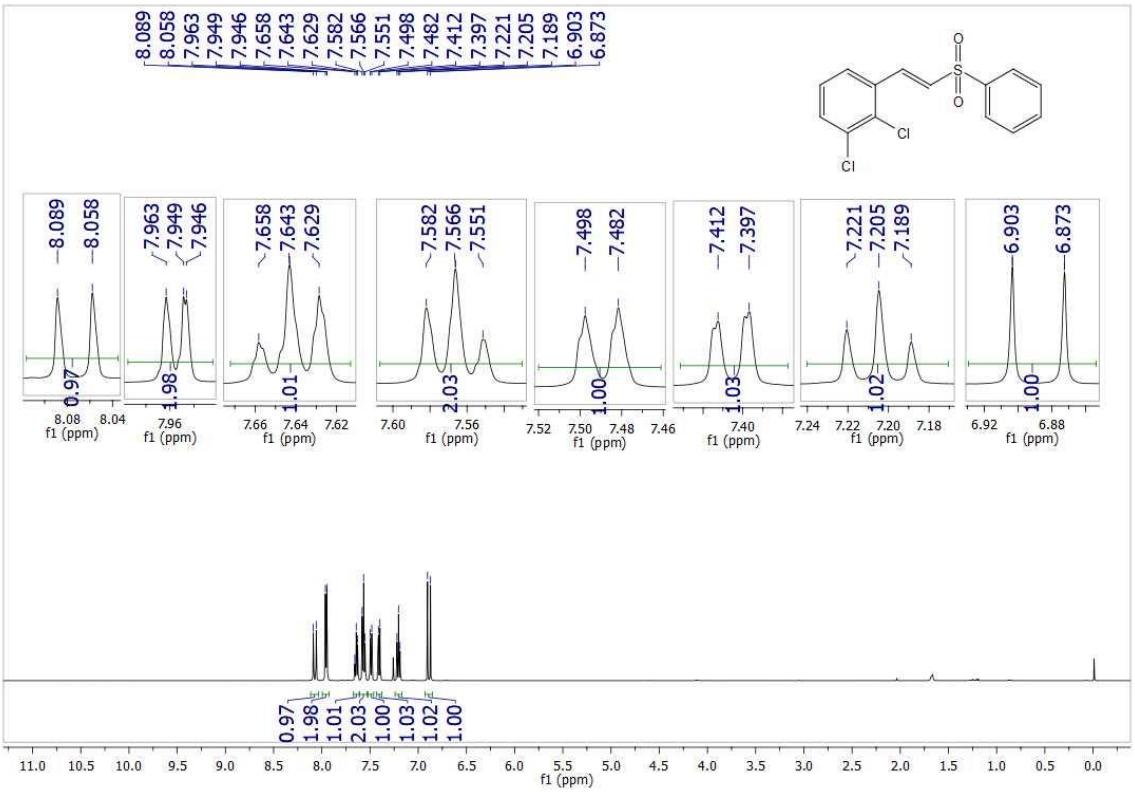
^{13}C NMR (125 MHz, $CDCl_3$) of compound **12**.



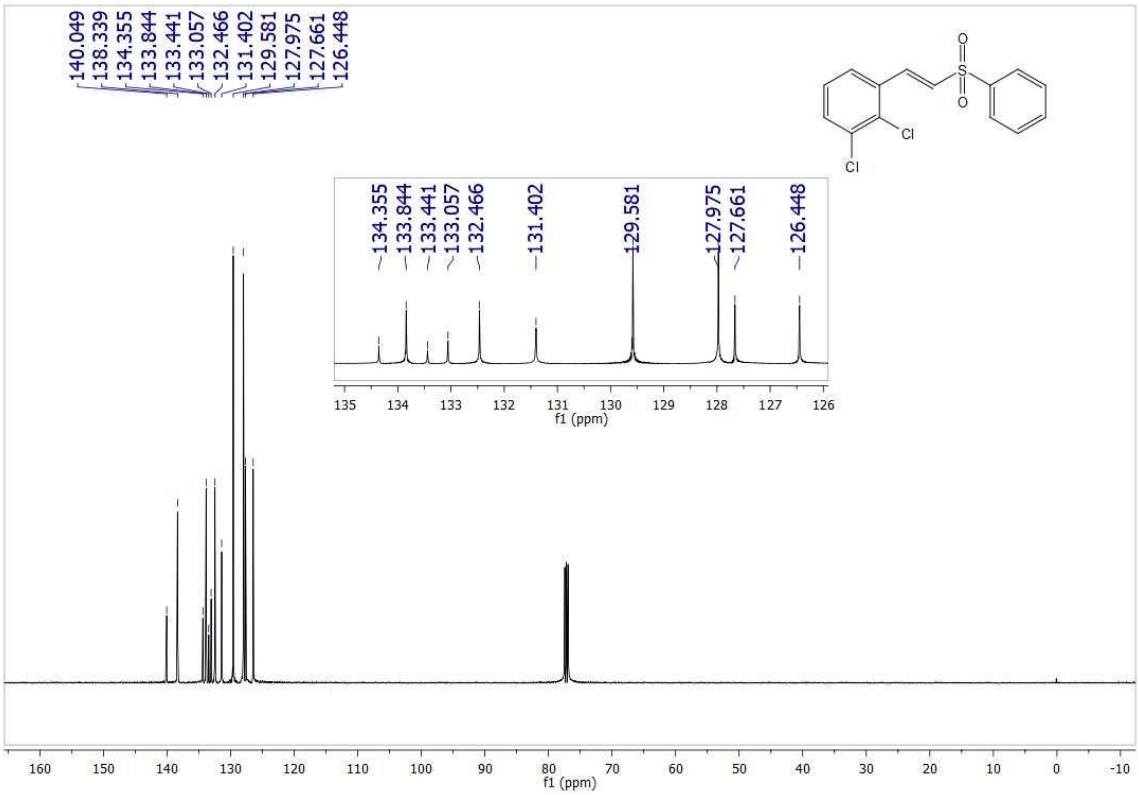
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13**.



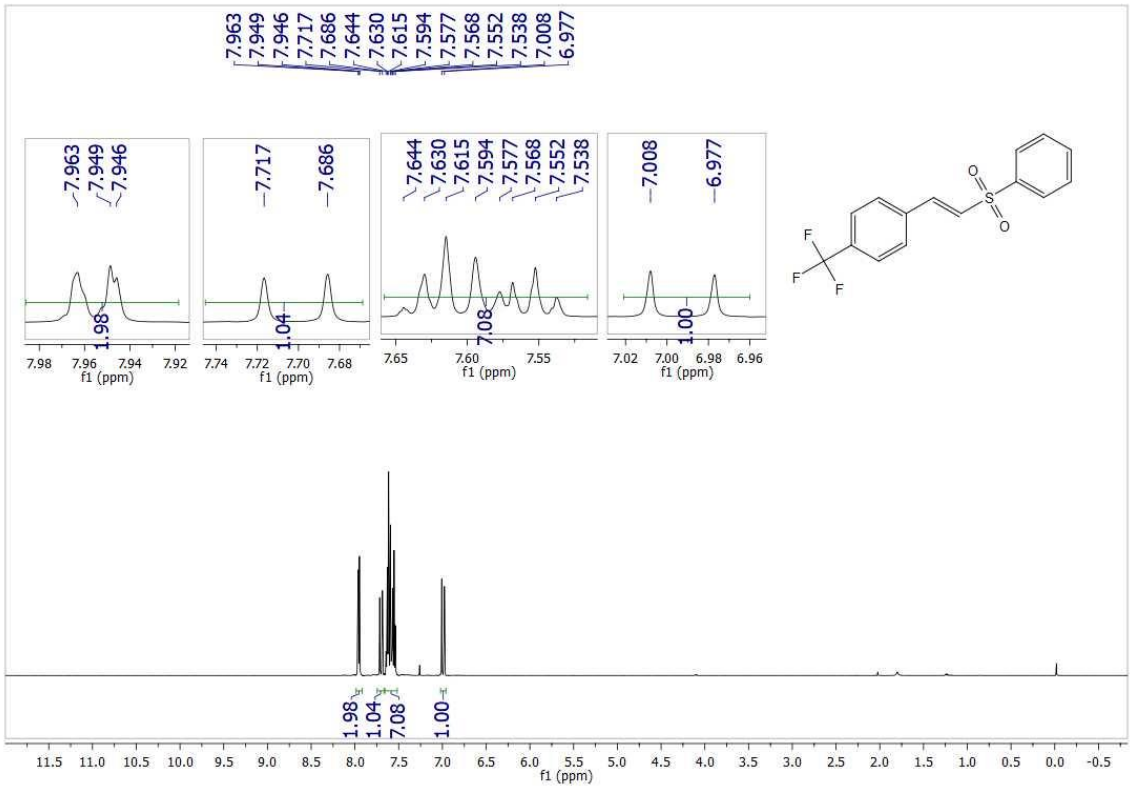
^{13}C NMR (125 MHz, $CDCl_3$) of compound **13**.



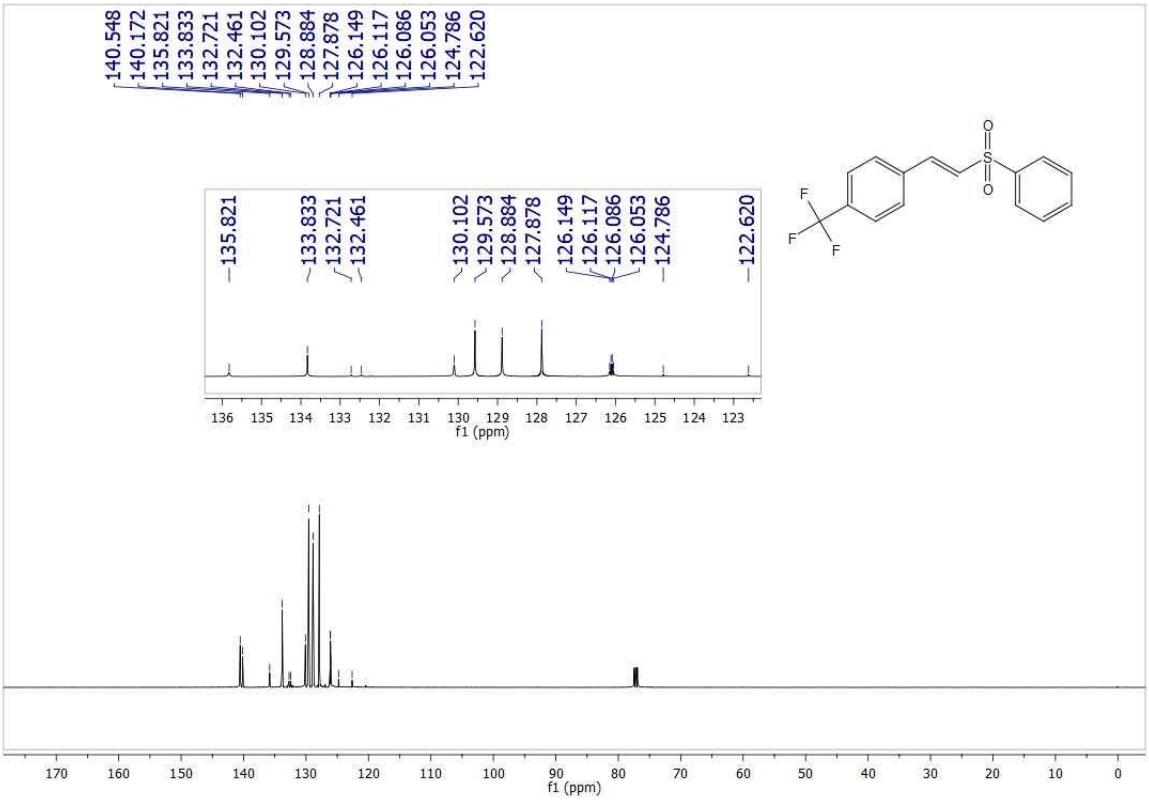
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14**.



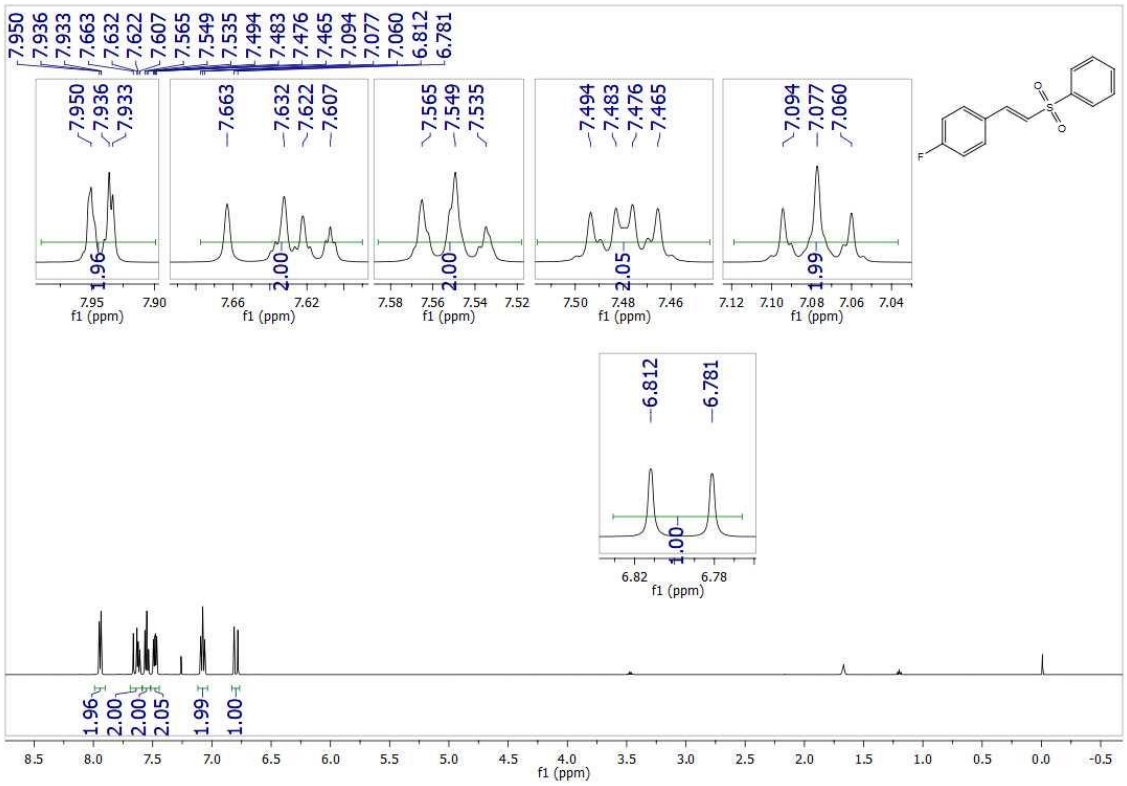
^{13}C NMR (125 MHz, $CDCl_3$) of compound **14**.



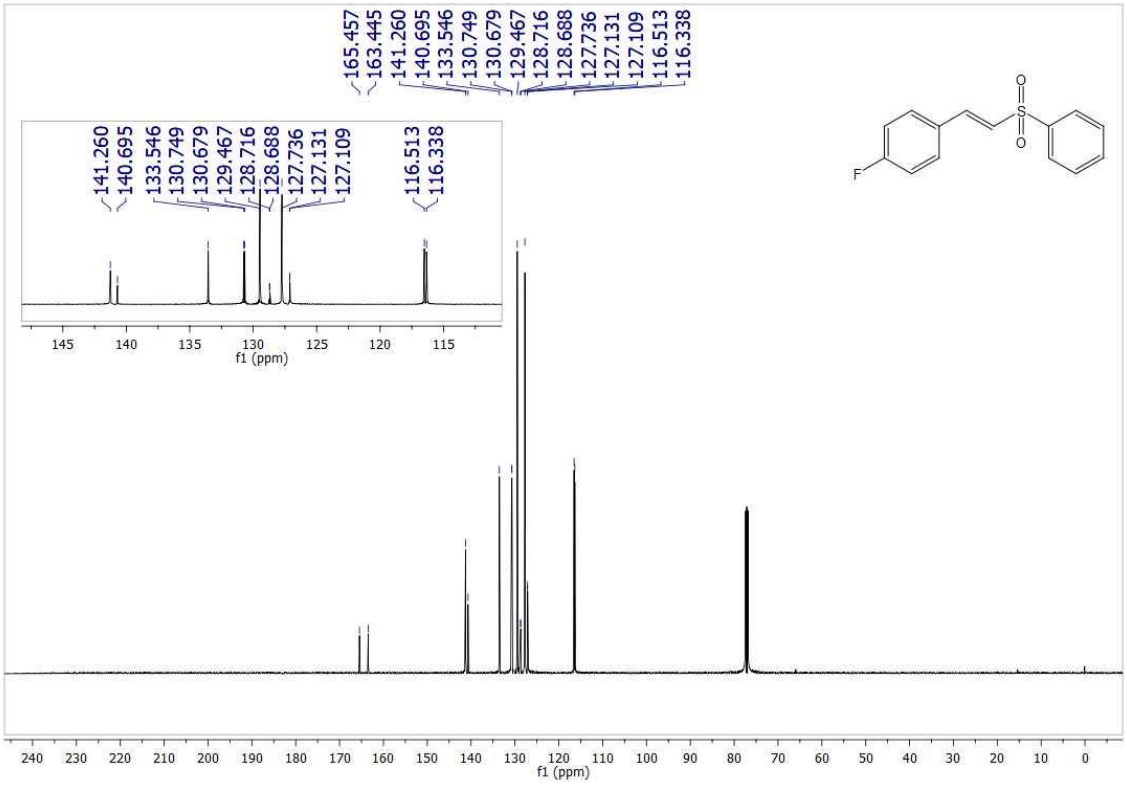
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15**.



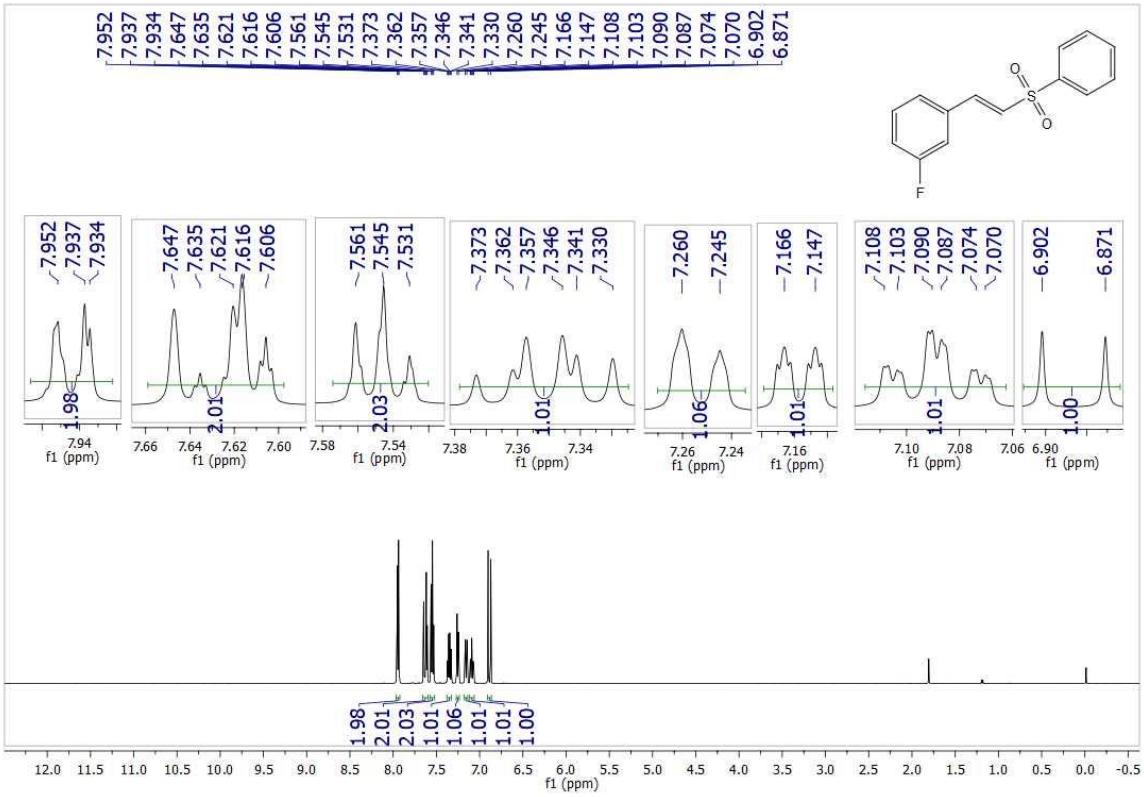
^{13}C NMR (125 MHz, $CDCl_3$) of compound **15.**



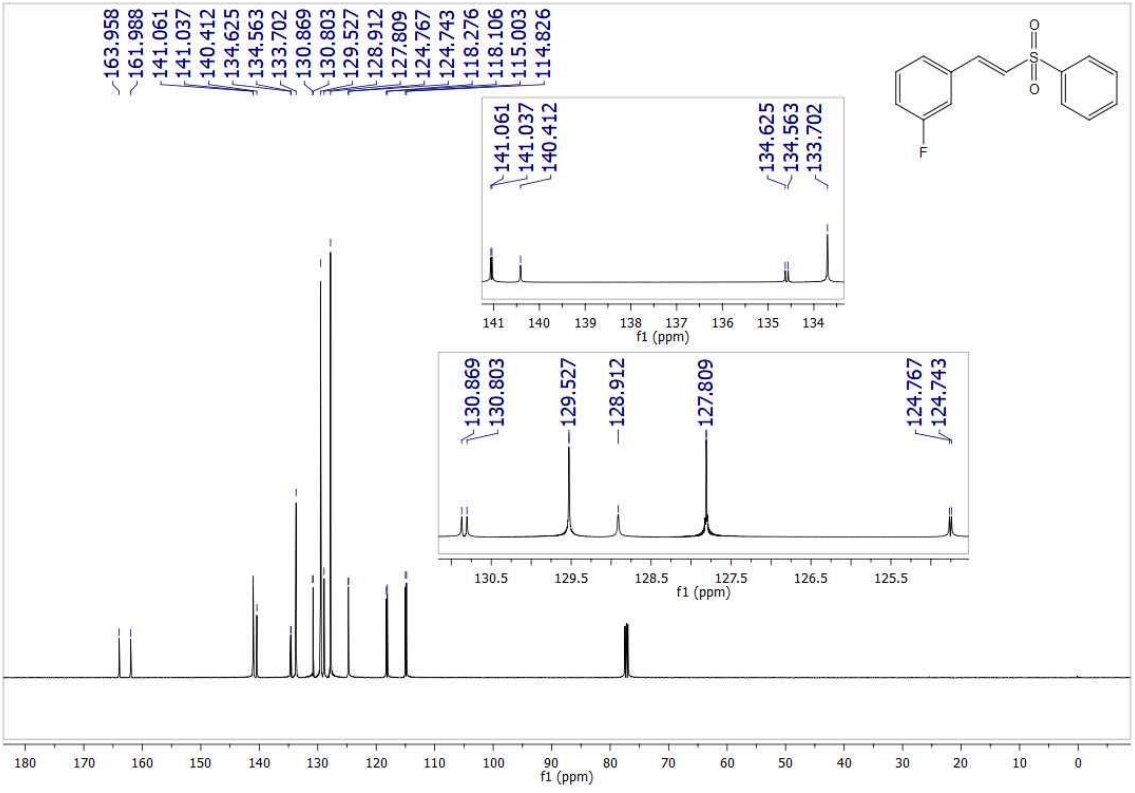
^{1}H NMR (500 MHz, $CDCl_3$) of compound **16**.



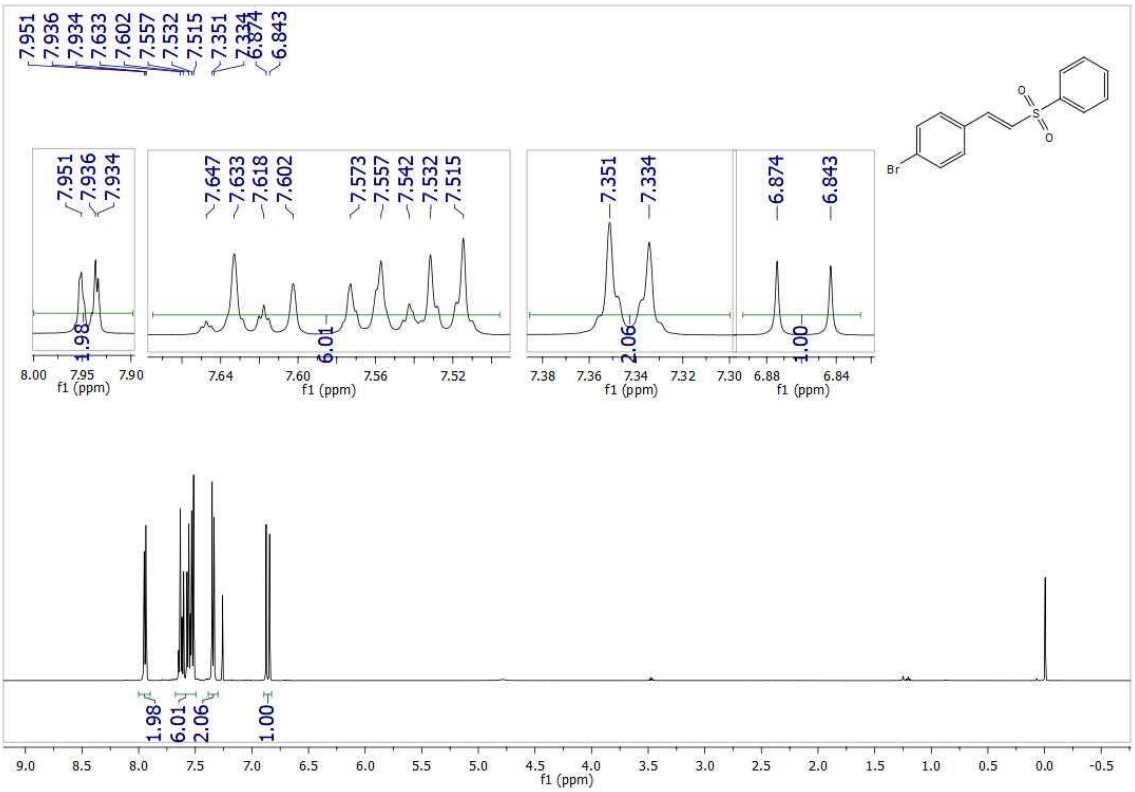
^{13}C NMR (125 MHz, $CDCl_3$) of compound **16**.



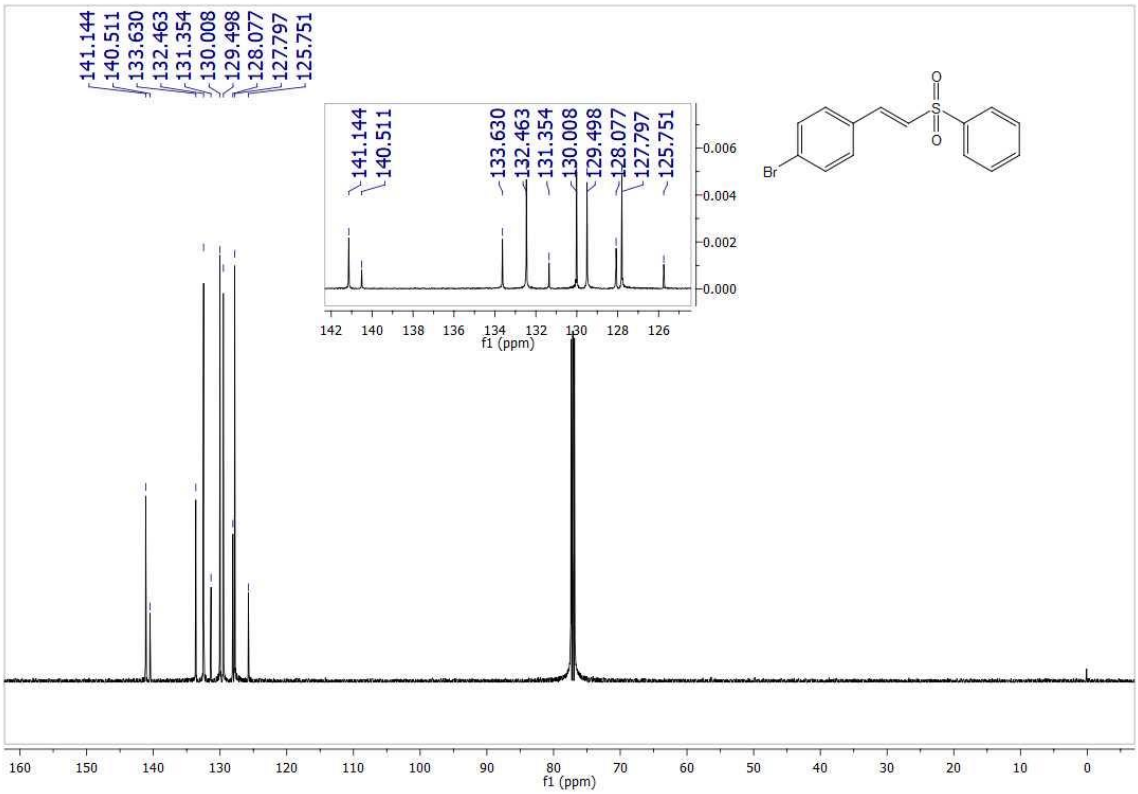
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17**.



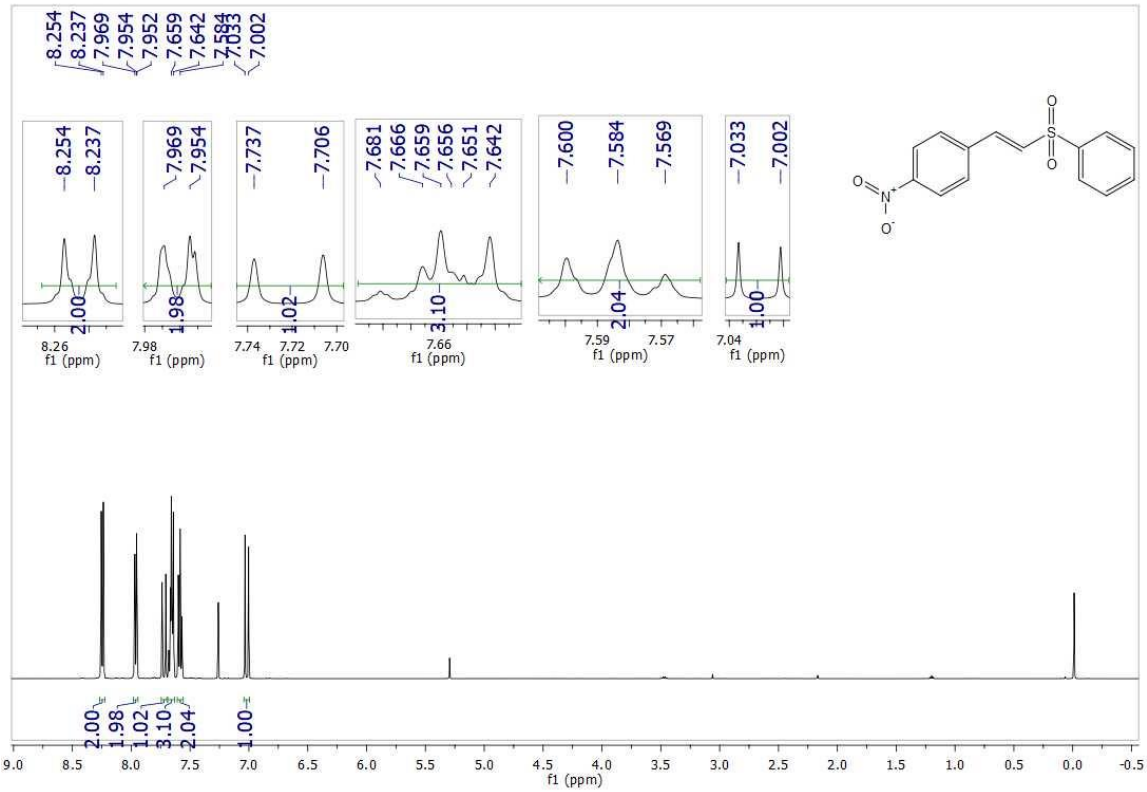
^{13}C NMR (125 MHz, $CDCl_3$) of compound **17**.



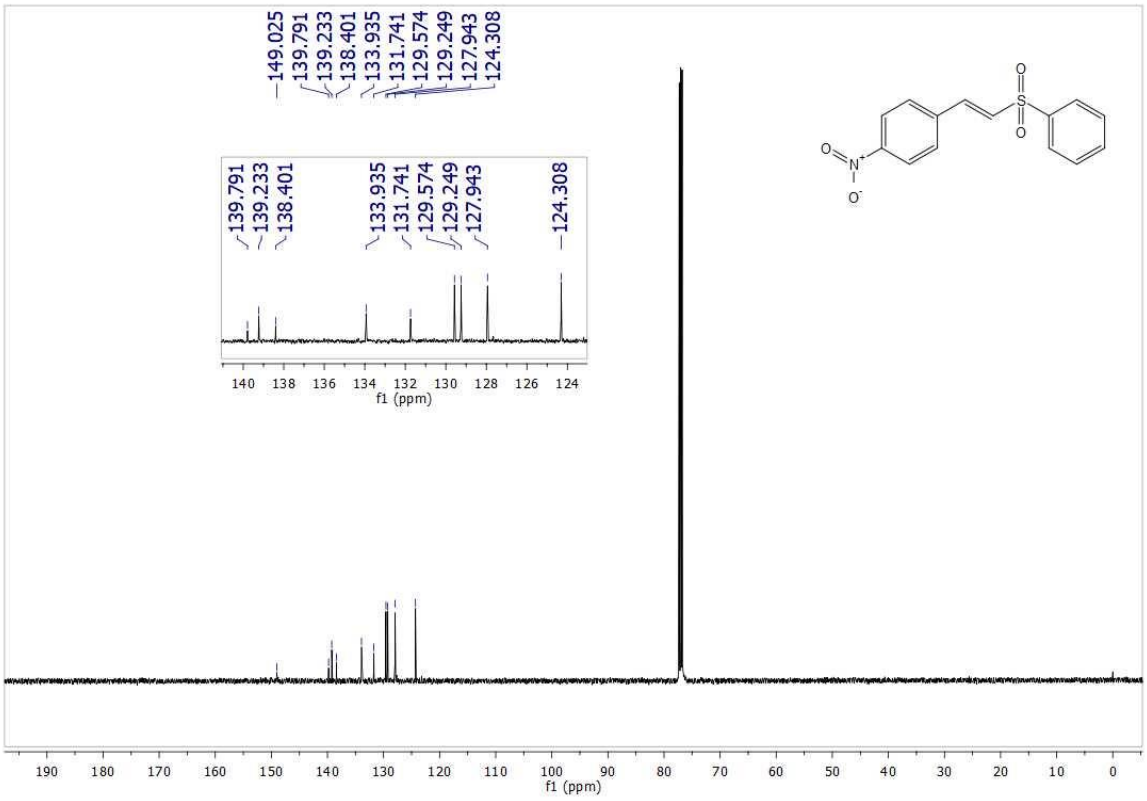
^{1}H NMR (500 MHz, $CDCl_3$) of compound **18**.



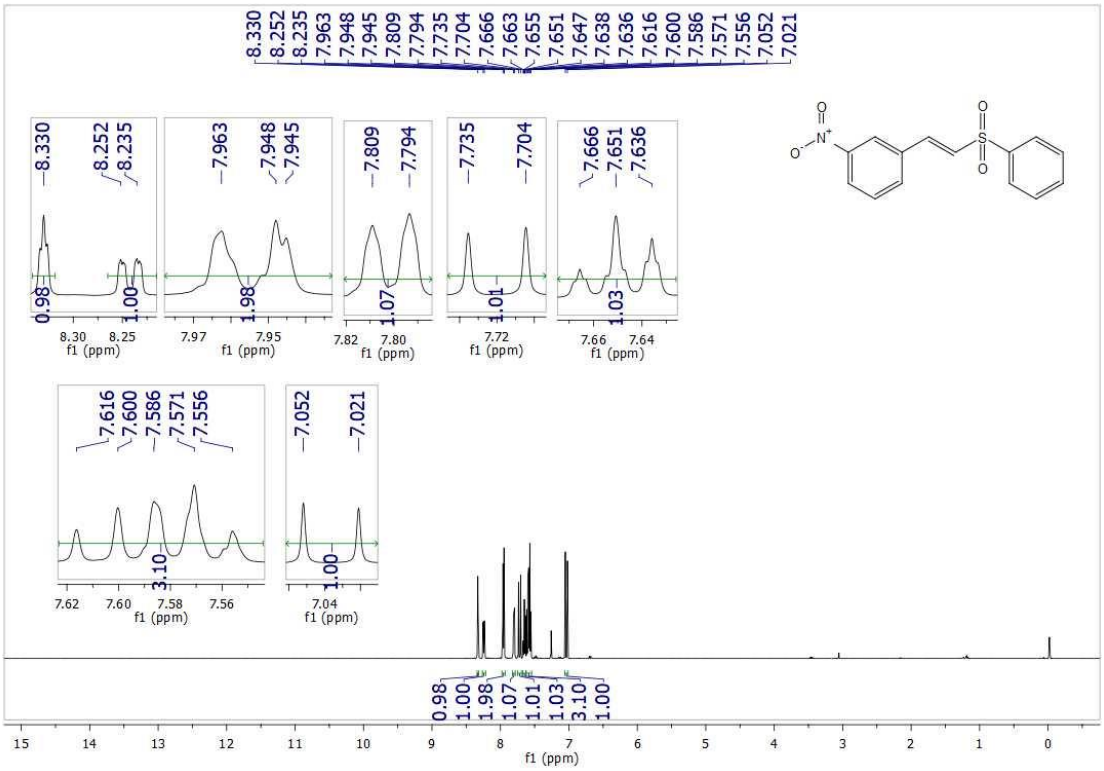
^{13}C NMR (125 MHz, $CDCl_3$) of compound **18**.



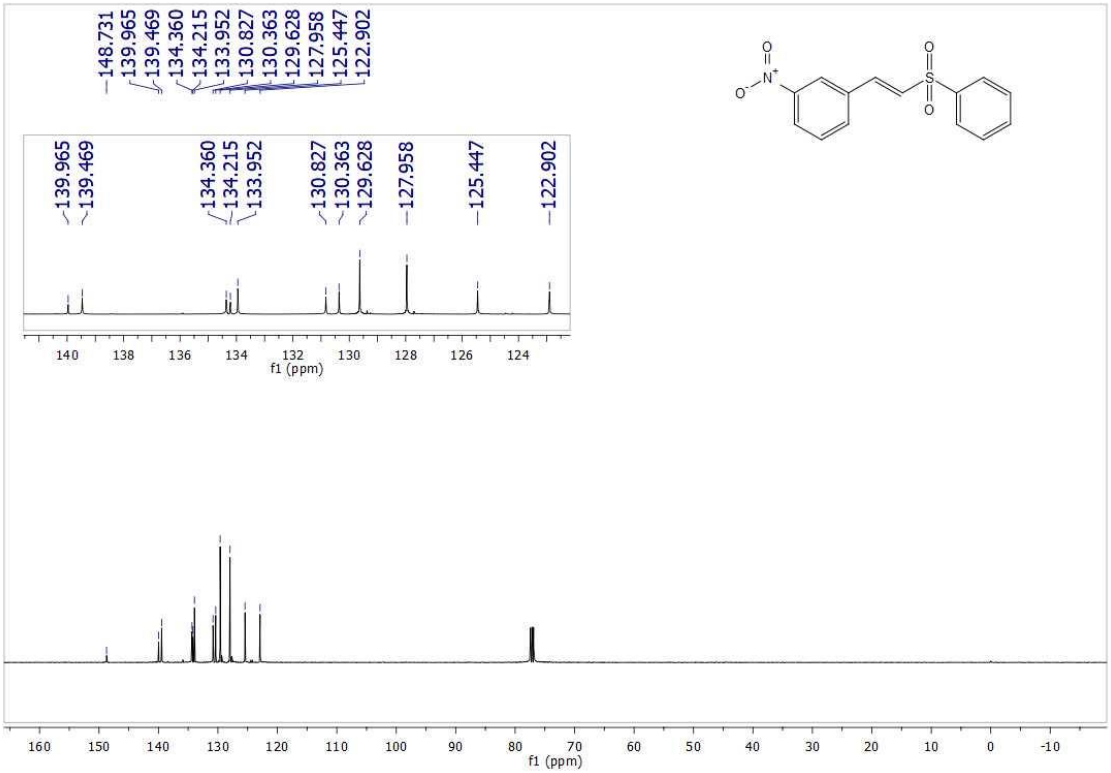
^{1}H NMR (500 MHz, $CDCl_3$) of compound **19**.



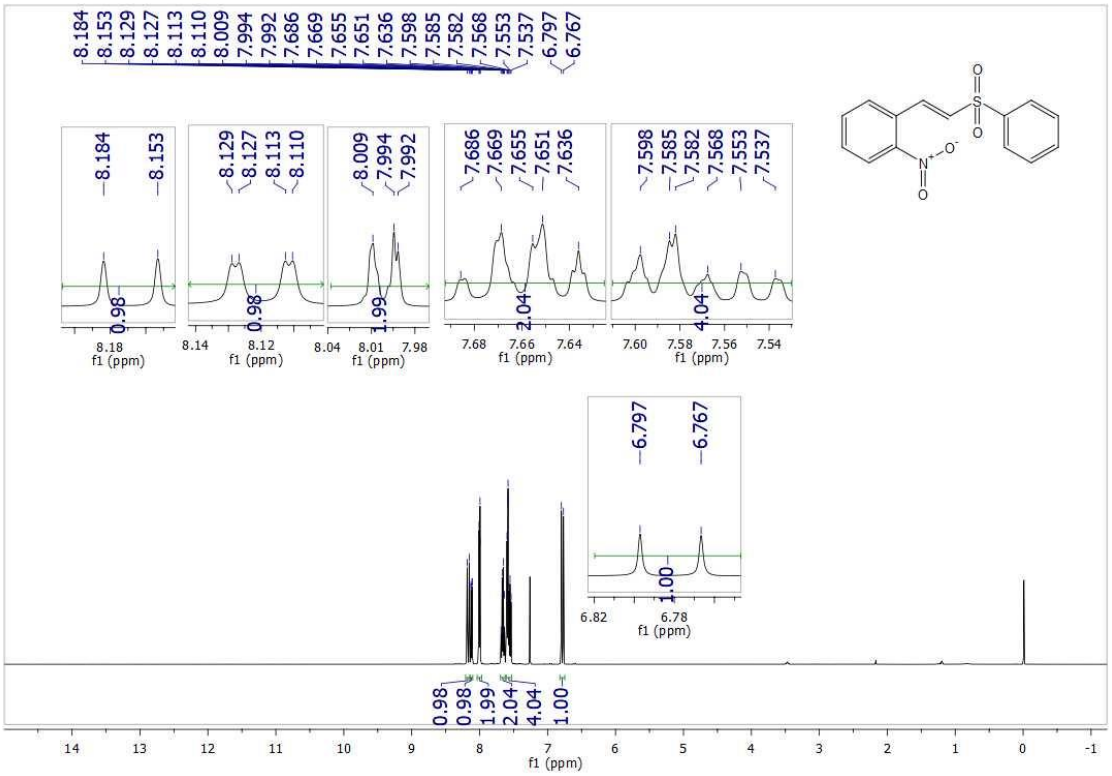
^{13}C NMR (125 MHz, $CDCl_3$) of compound **19**.



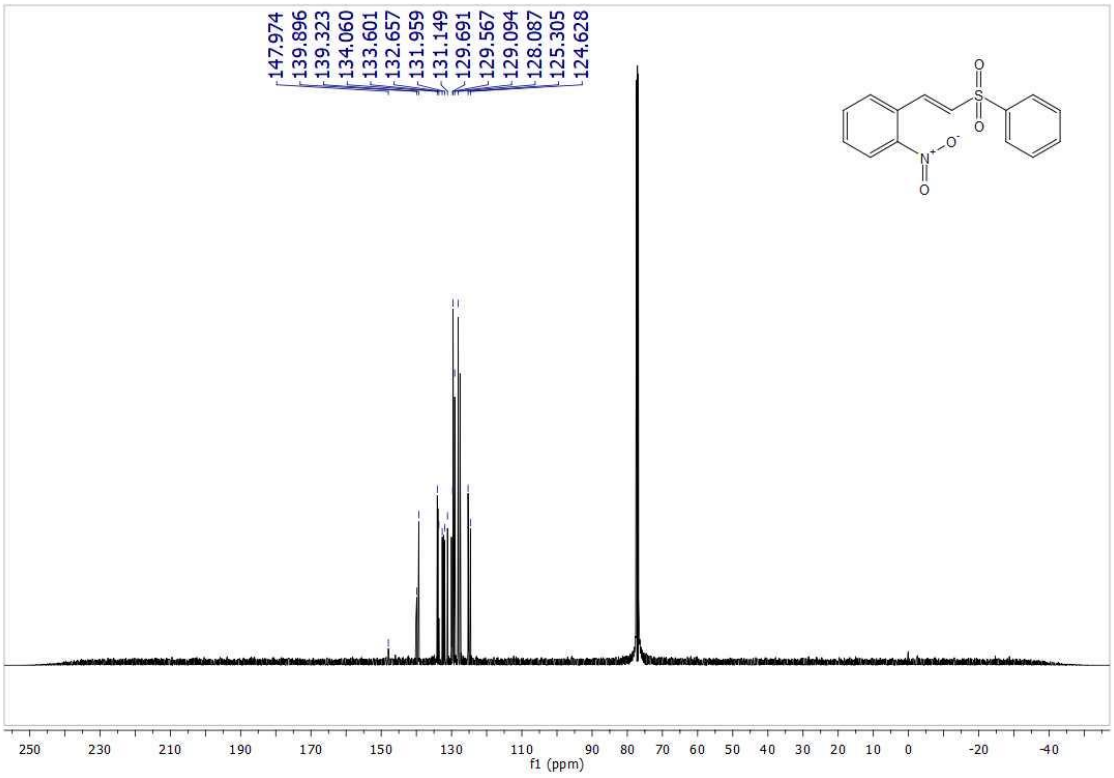
^{1}H NMR (500 MHz, $CDCl_3$) of compound **20**.



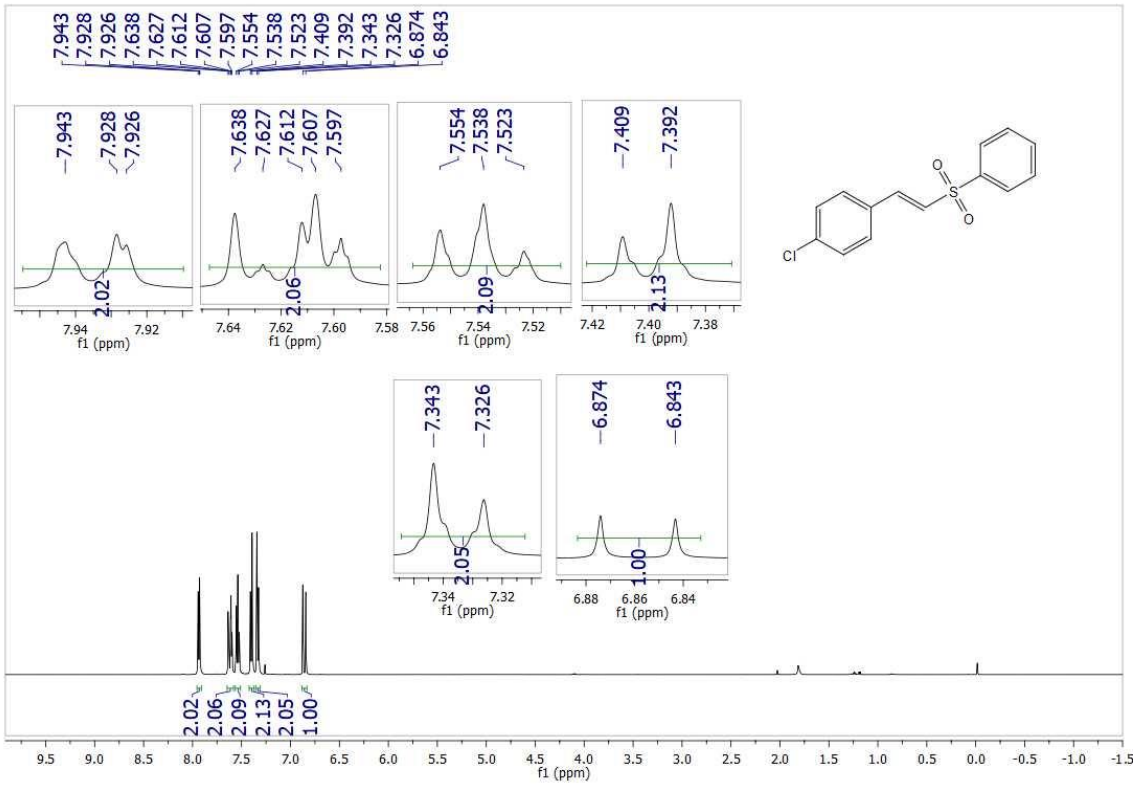
^{13}C NMR (125 MHz, $CDCl_3$) of compound **20**.



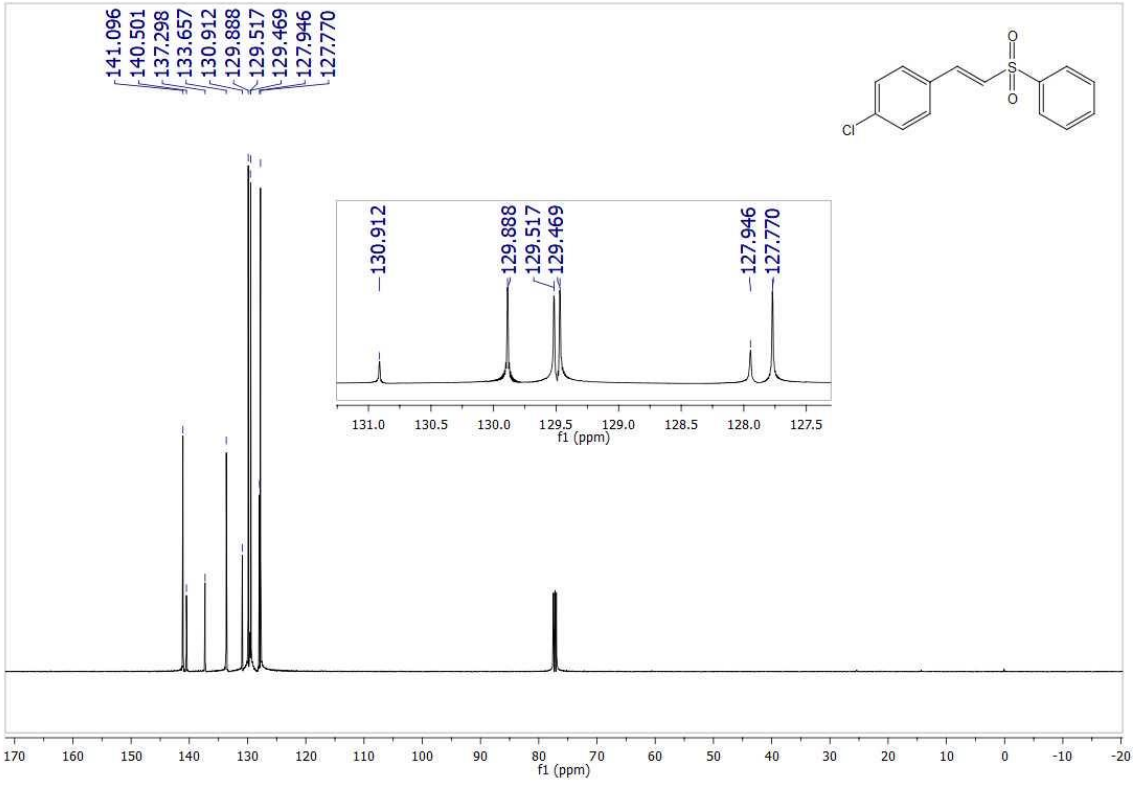
^{1}H NMR (500 MHz, $CDCl_3$) of compound **21**.



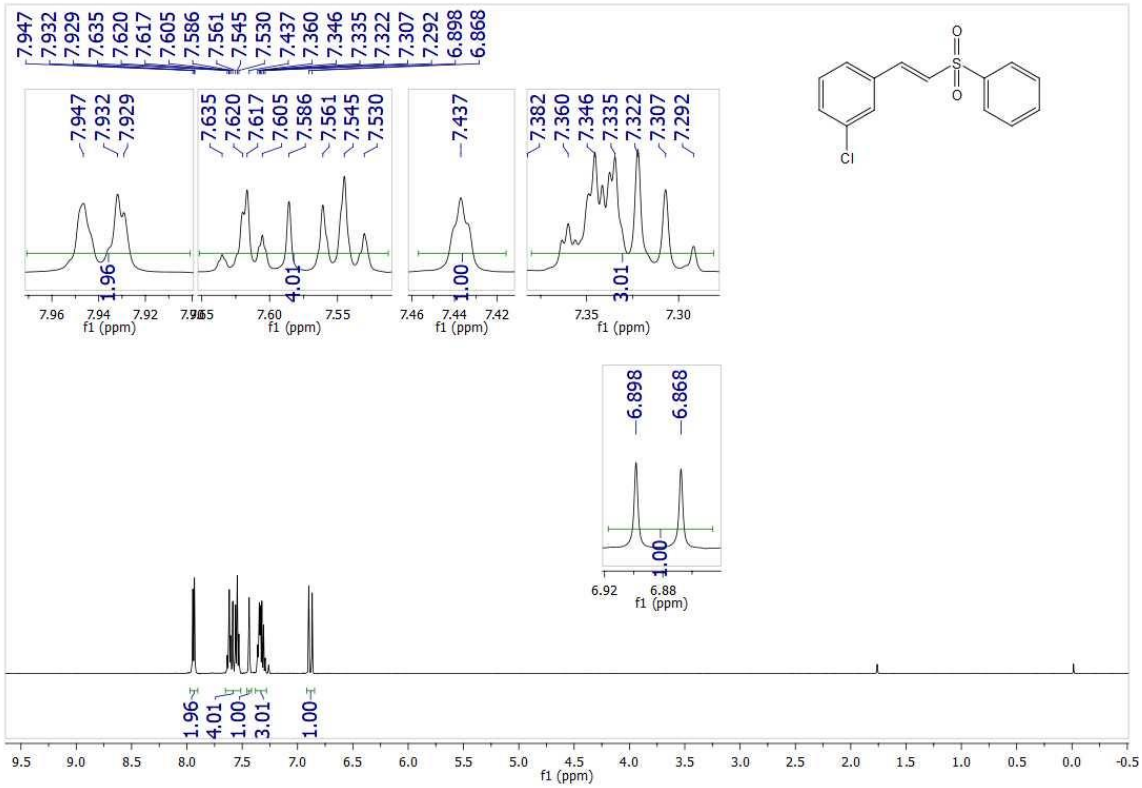
^{13}C NMR (125 MHz, $CDCl_3$) of compound **21**.



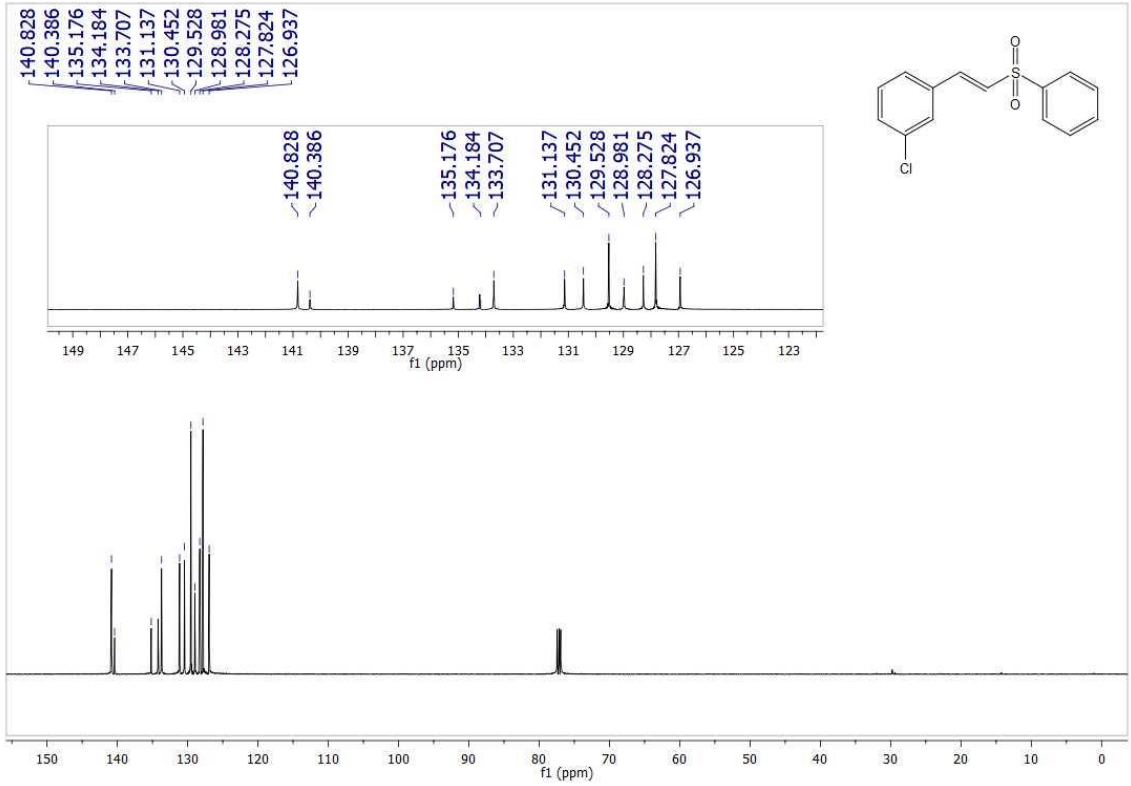
^{1}H NMR (500 MHz, $CDCl_3$) of compound **22**.



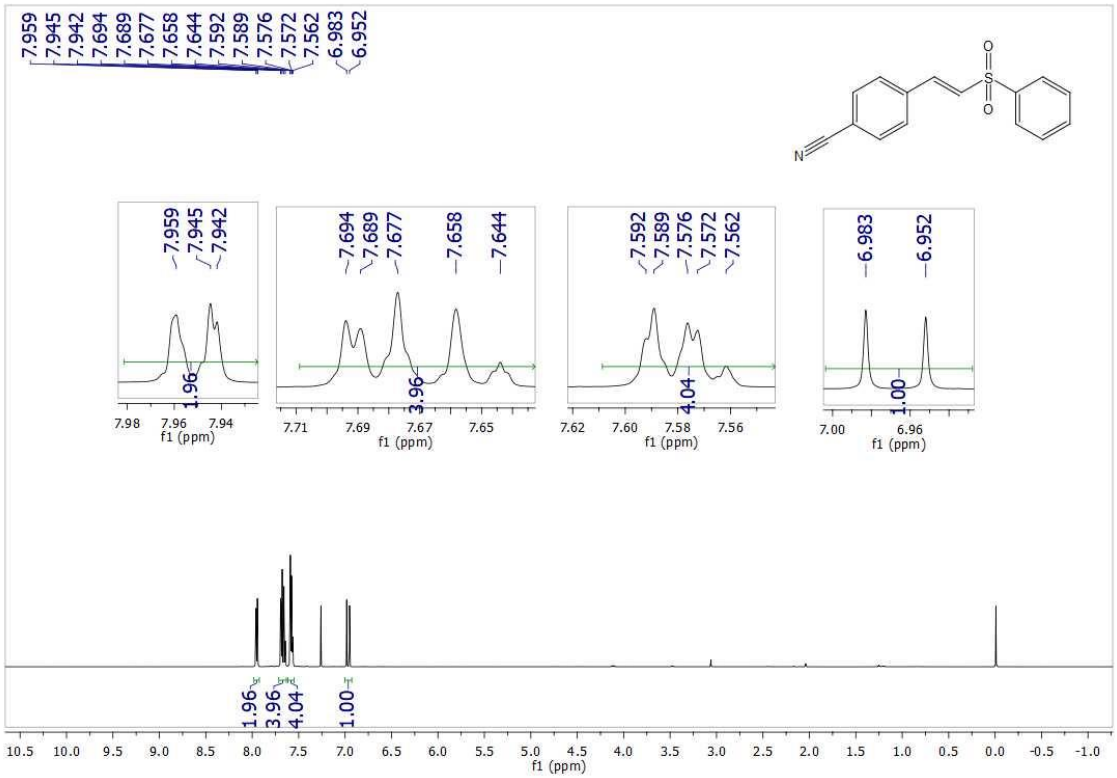
^{13}C NMR (125 MHz, $CDCl_3$) of compound **22**.



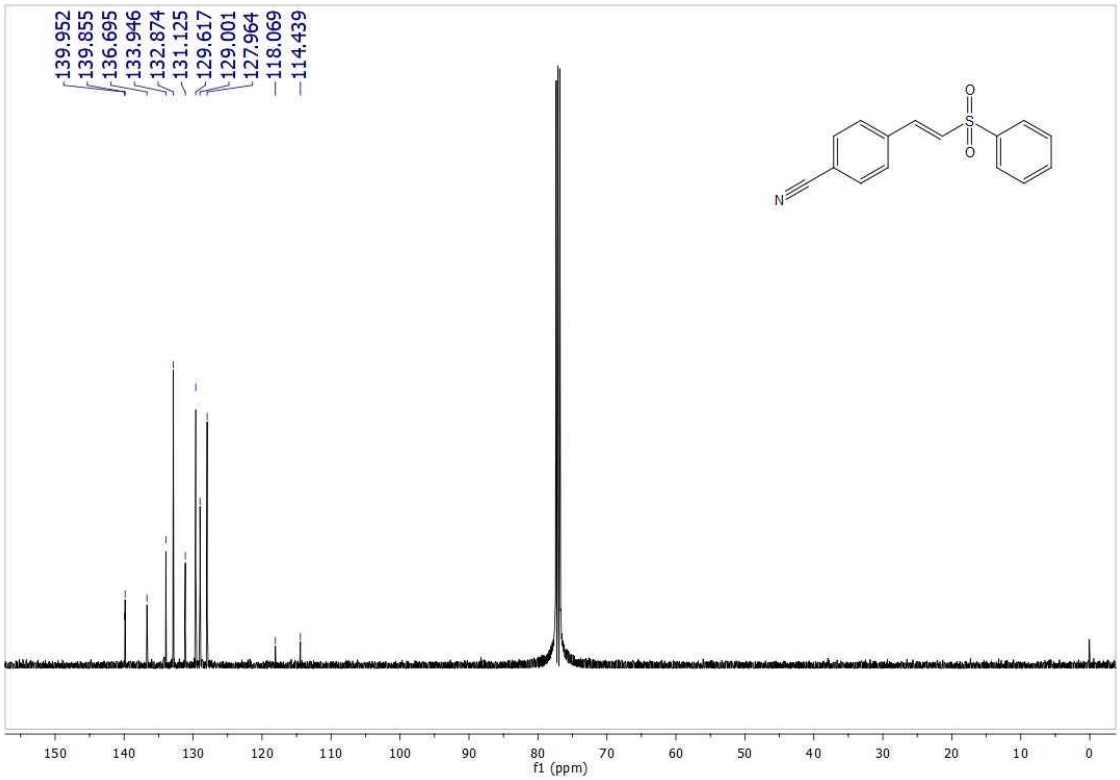
^{1}H NMR (500 MHz, $CDCl_3$) of compound **23**.



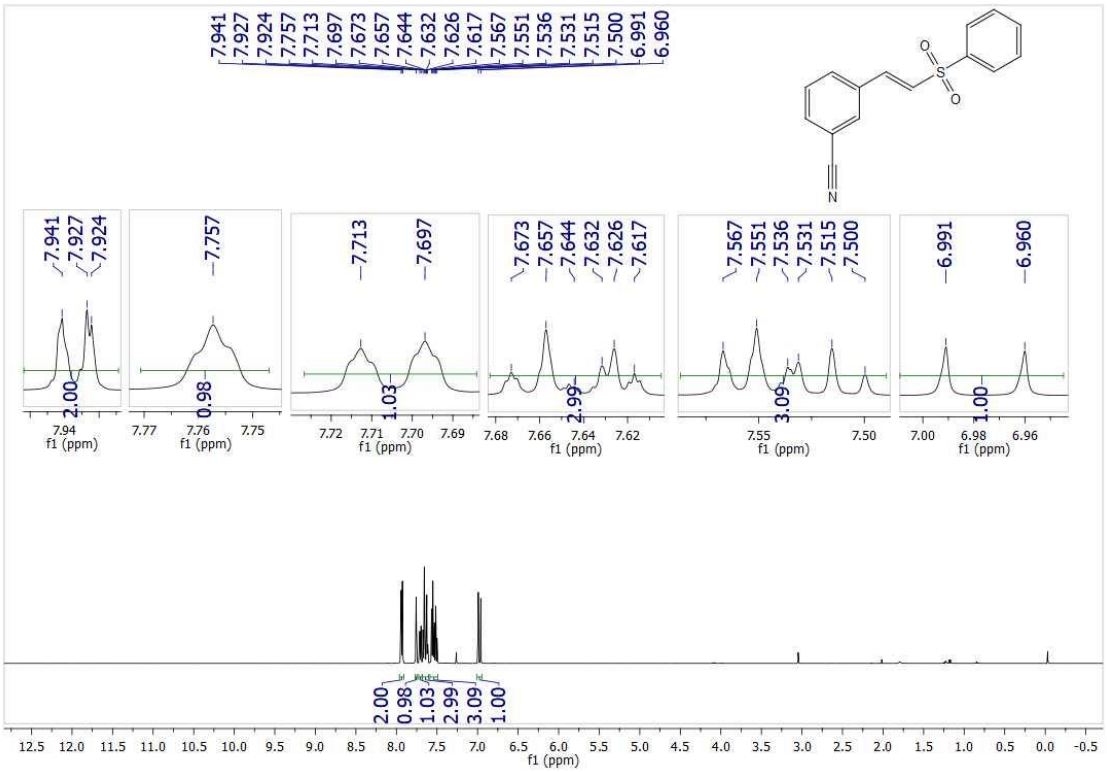
^{13}C NMR (125 MHz, $CDCl_3$) of compound **23**.



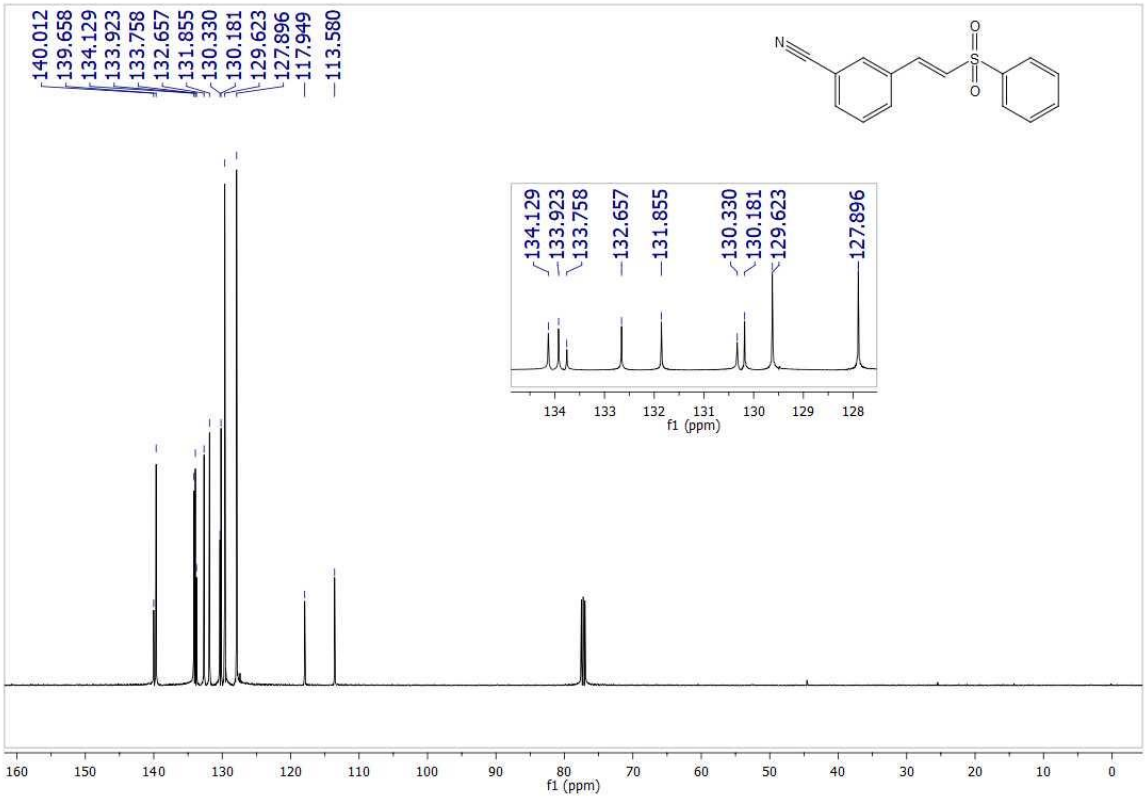
^{1}H NMR (500 MHz, $CDCl_3$) of compound **24**.



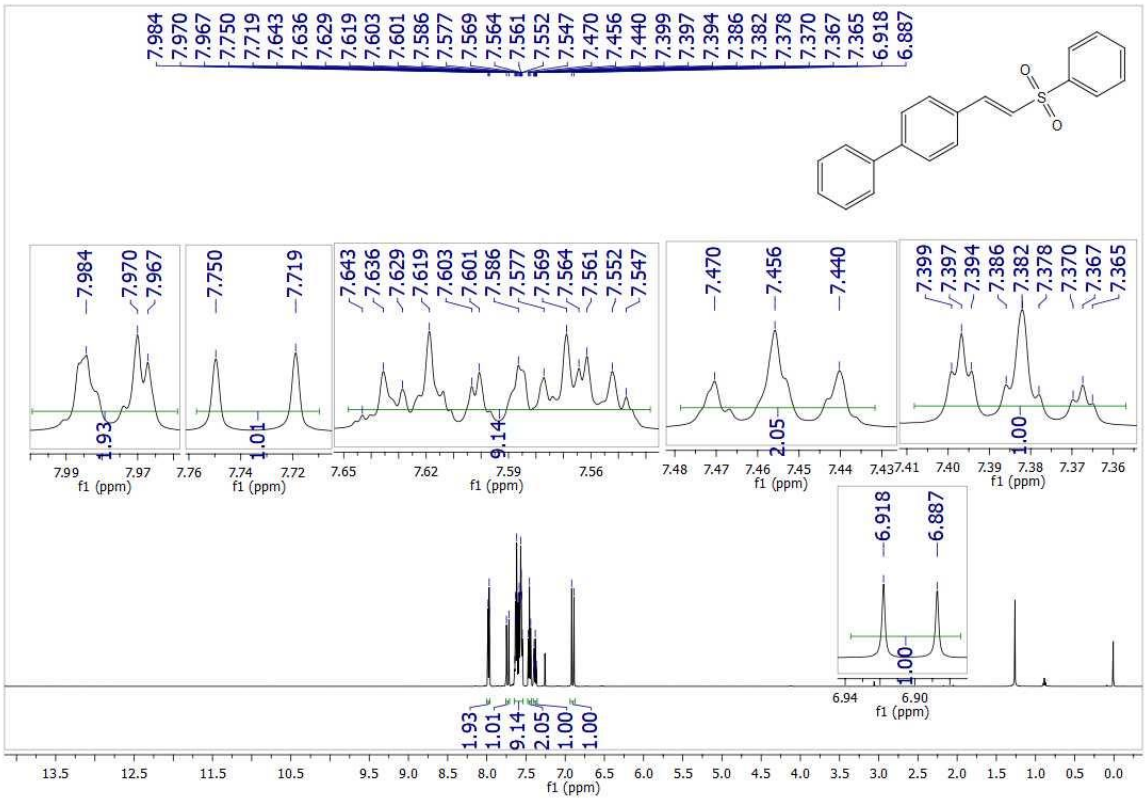
^{13}C NMR (125 MHz, $CDCl_3$) of compound **24**.



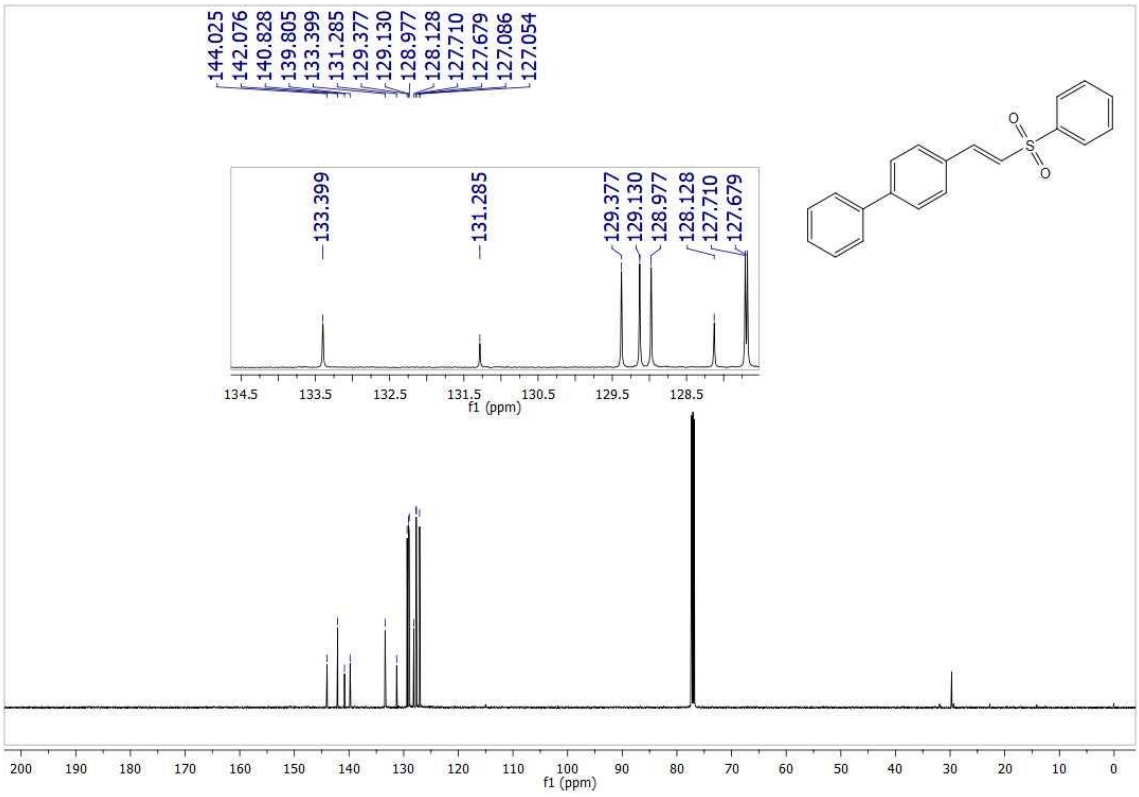
^{1}H NMR (500 MHz, $CDCl_3$) of compound **25**.



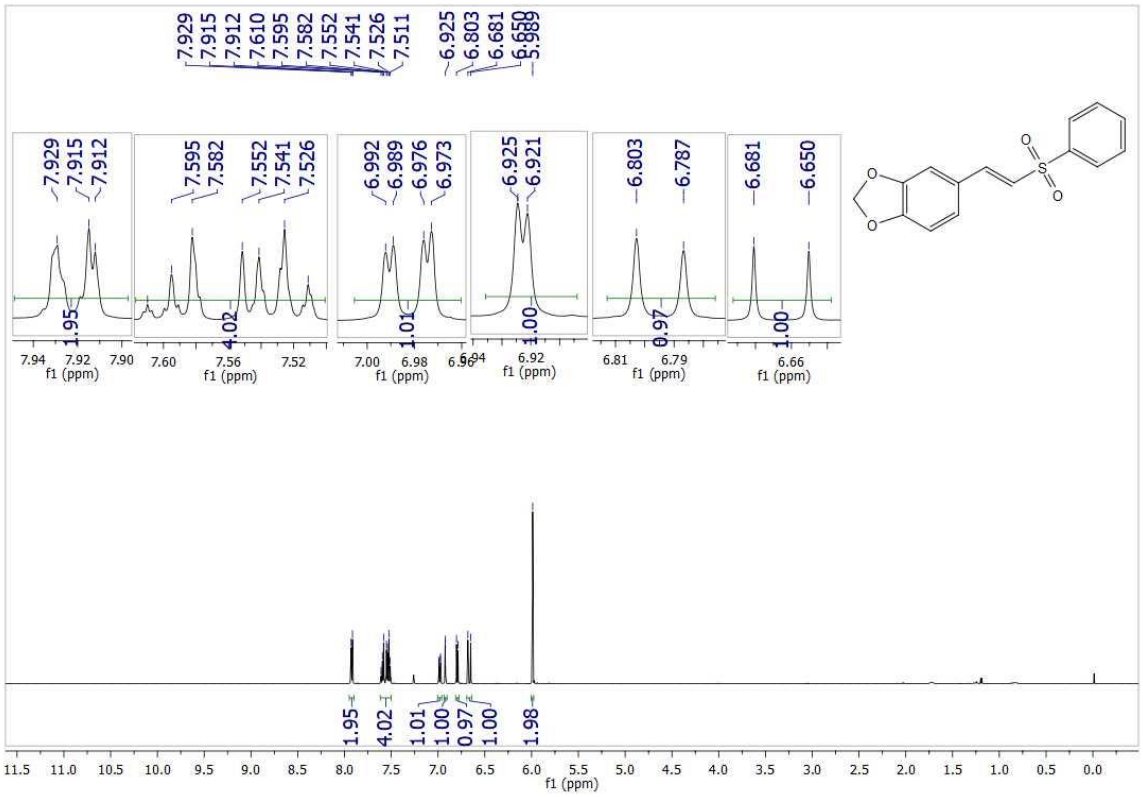
^{13}C NMR (125 MHz, $CDCl_3$) of compound **25**.



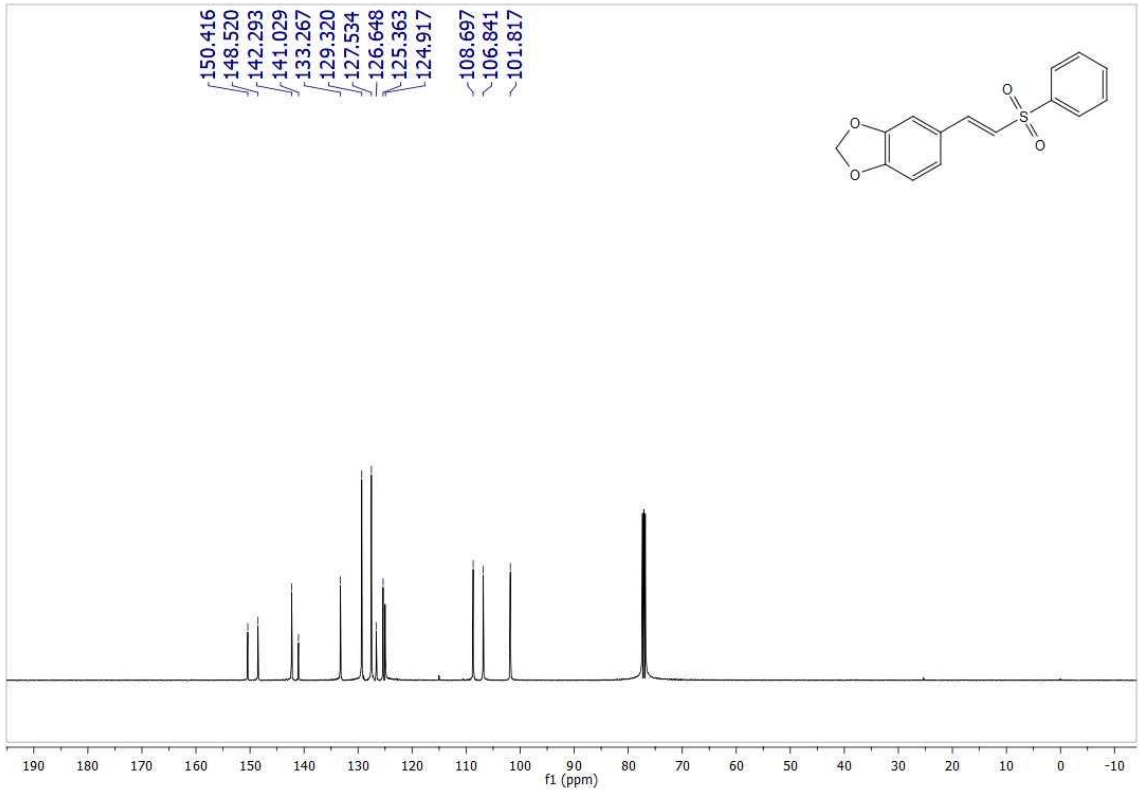
^{1}H NMR (500 MHz, $CDCl_3$) of compound **26**.



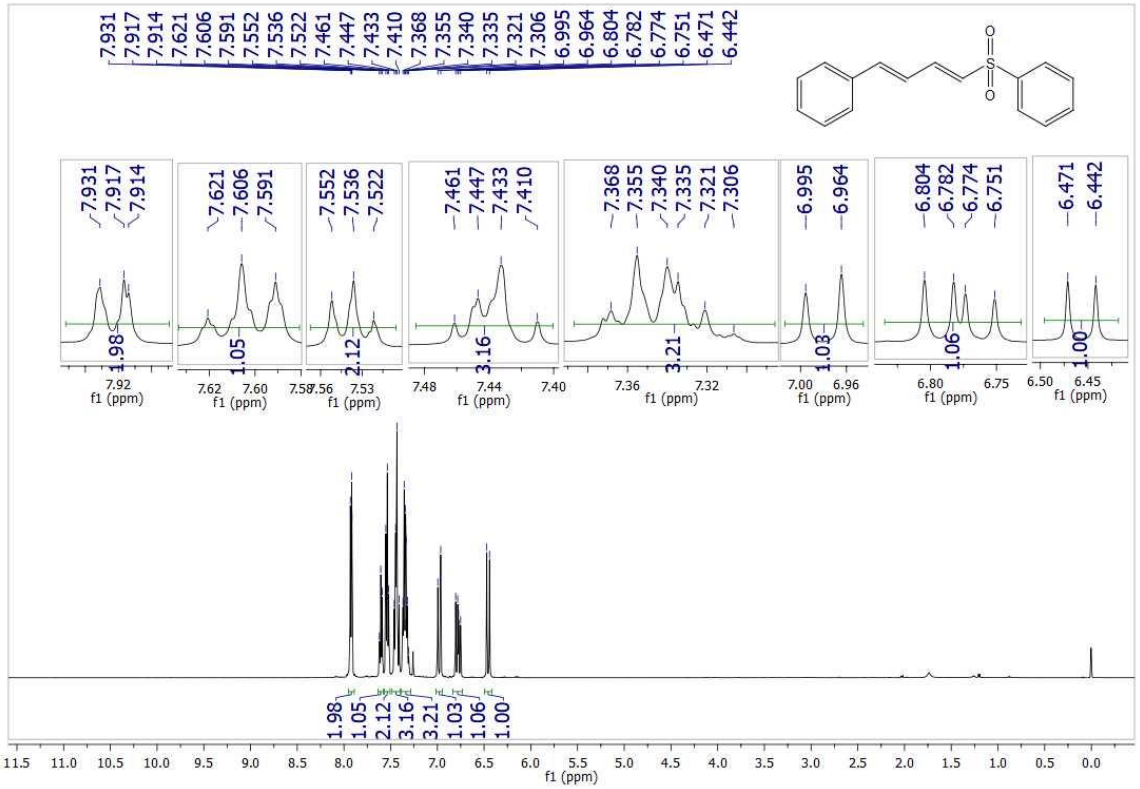
^{13}C NMR (125 MHz, $CDCl_3$) of compound **26**.



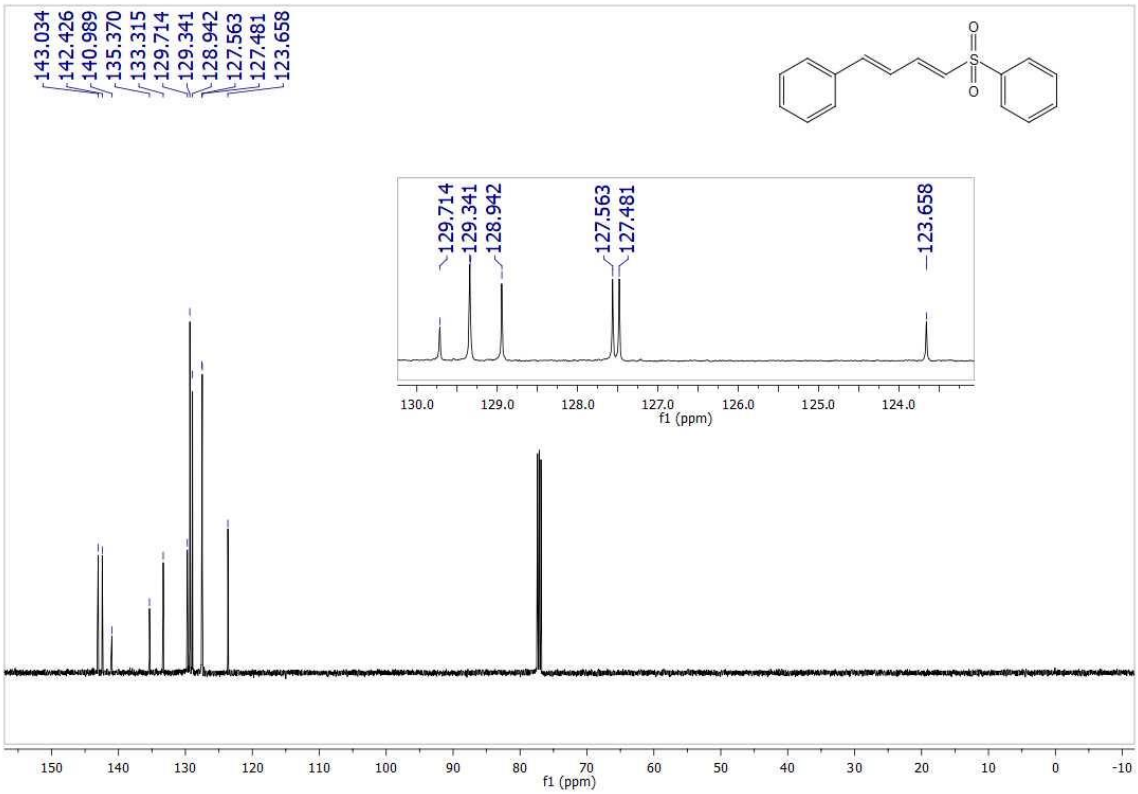
^{1}H NMR (500 MHz, $CDCl_3$) of compound **27**.



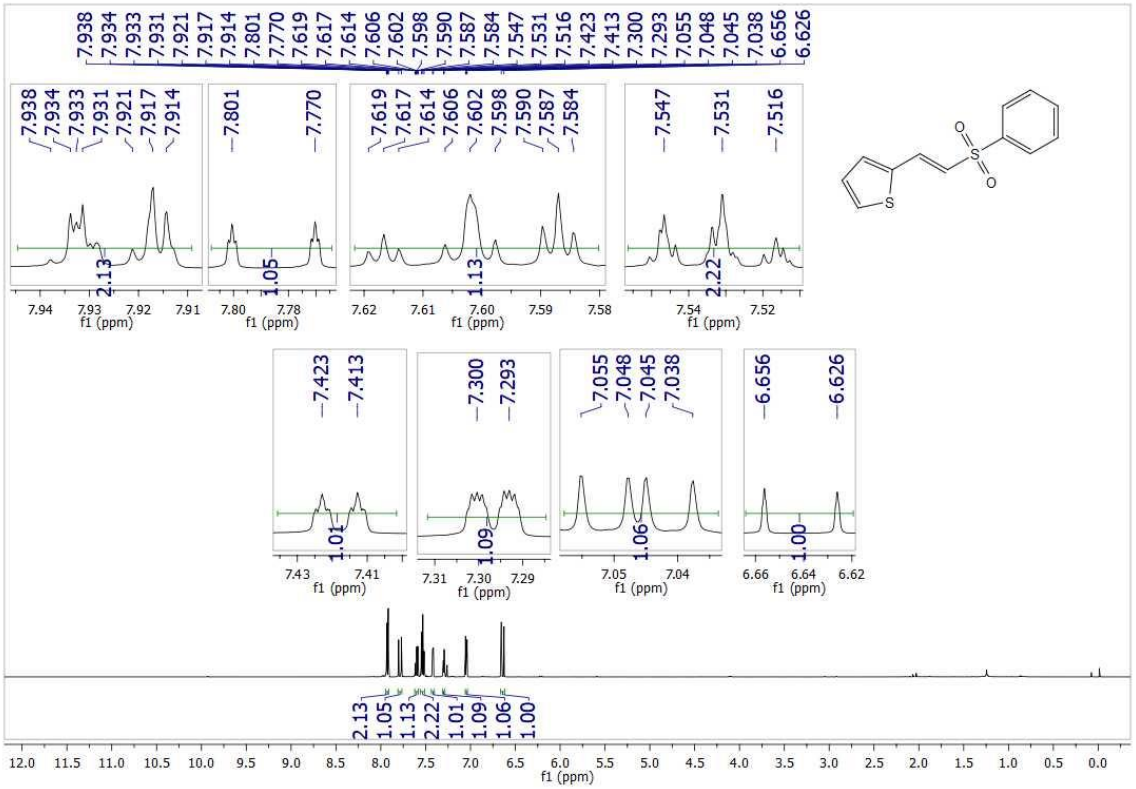
^{13}C NMR (125 MHz, $CDCl_3$) of compound **27**.



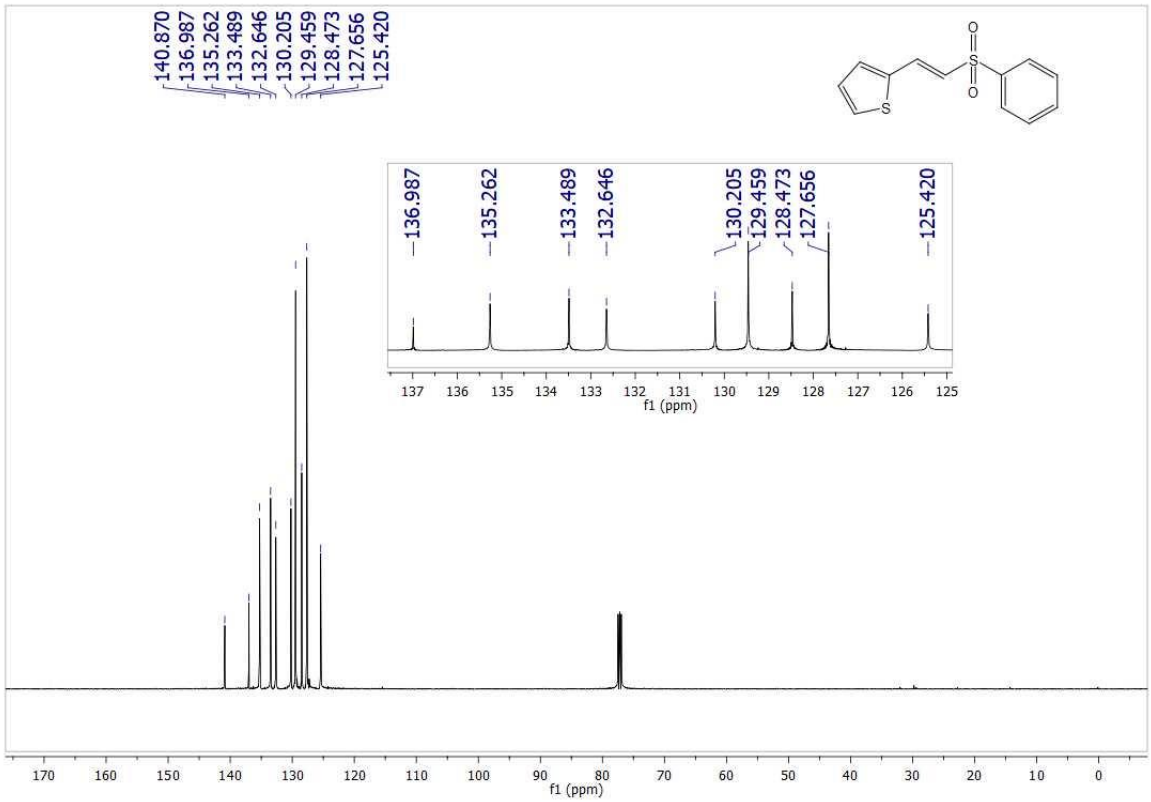
^{1}H NMR (500 MHz, $CDCl_3$) of compound **28**.



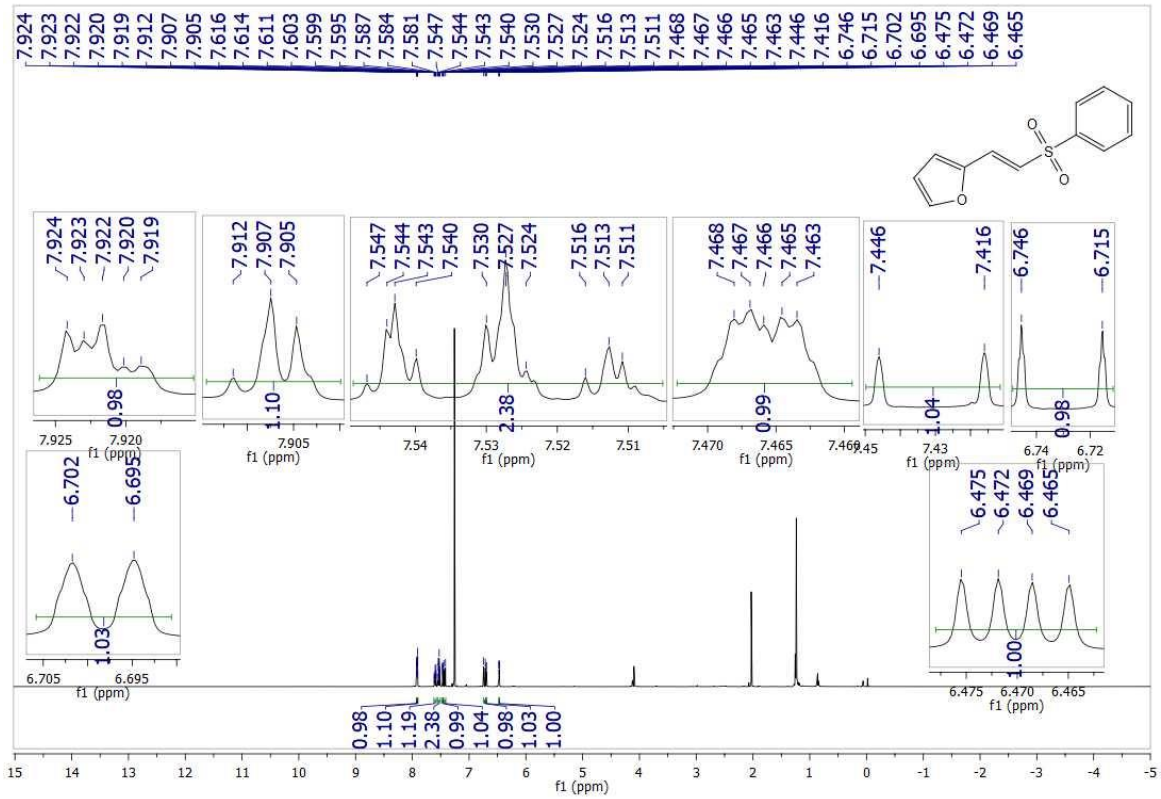
^{13}C NMR (125 MHz, $CDCl_3$) of compound **28**.



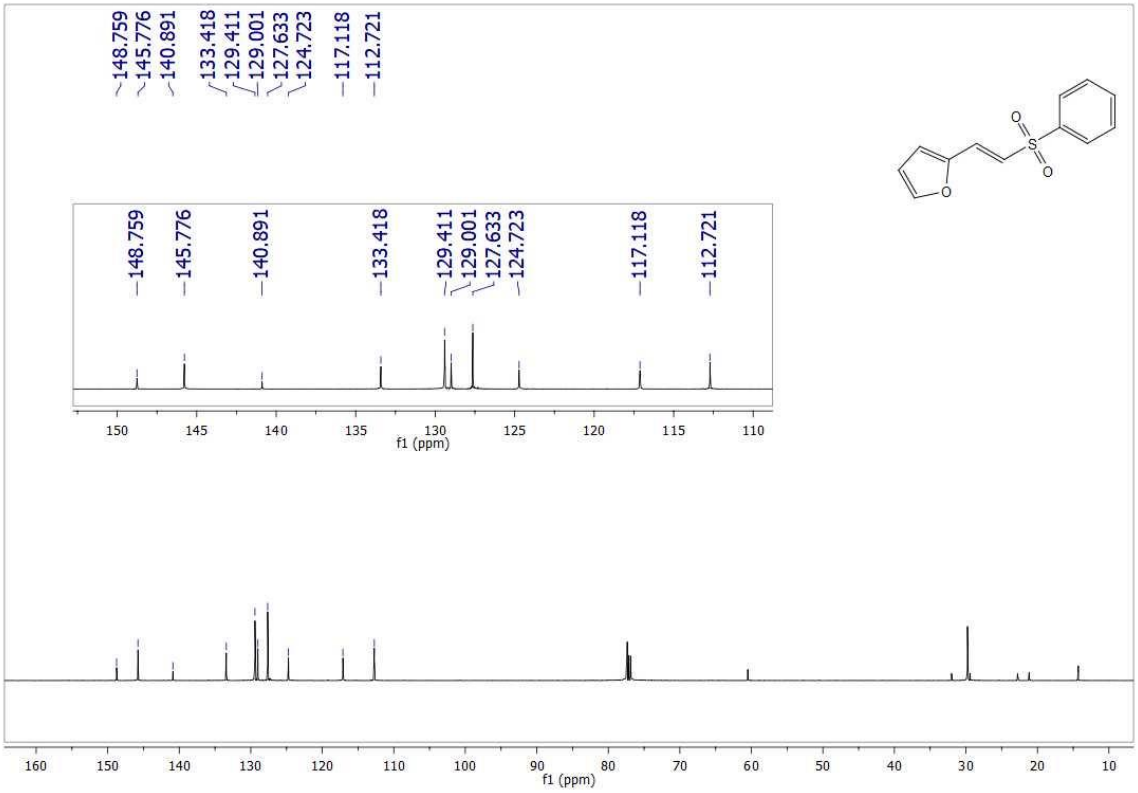
^{1}H NMR (500 MHz, $CDCl_3$) of compound **29**.



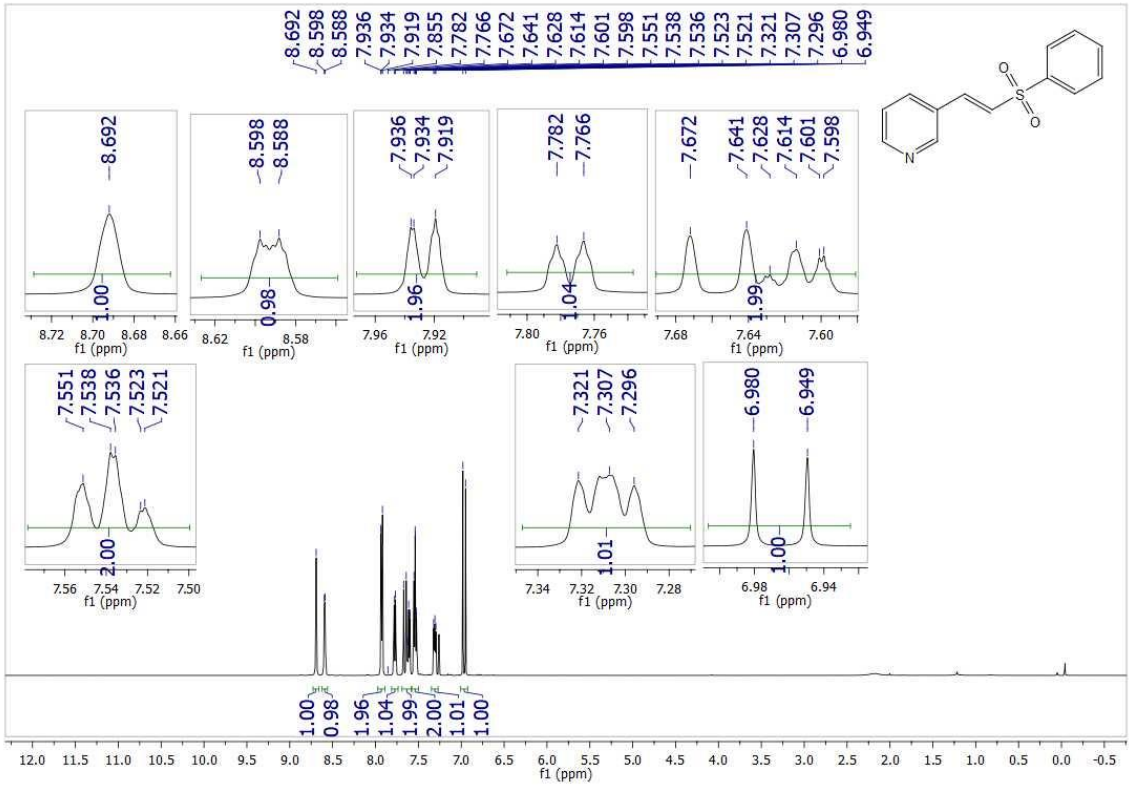
^{13}C NMR (125 MHz, $CDCl_3$) of compound **29**.



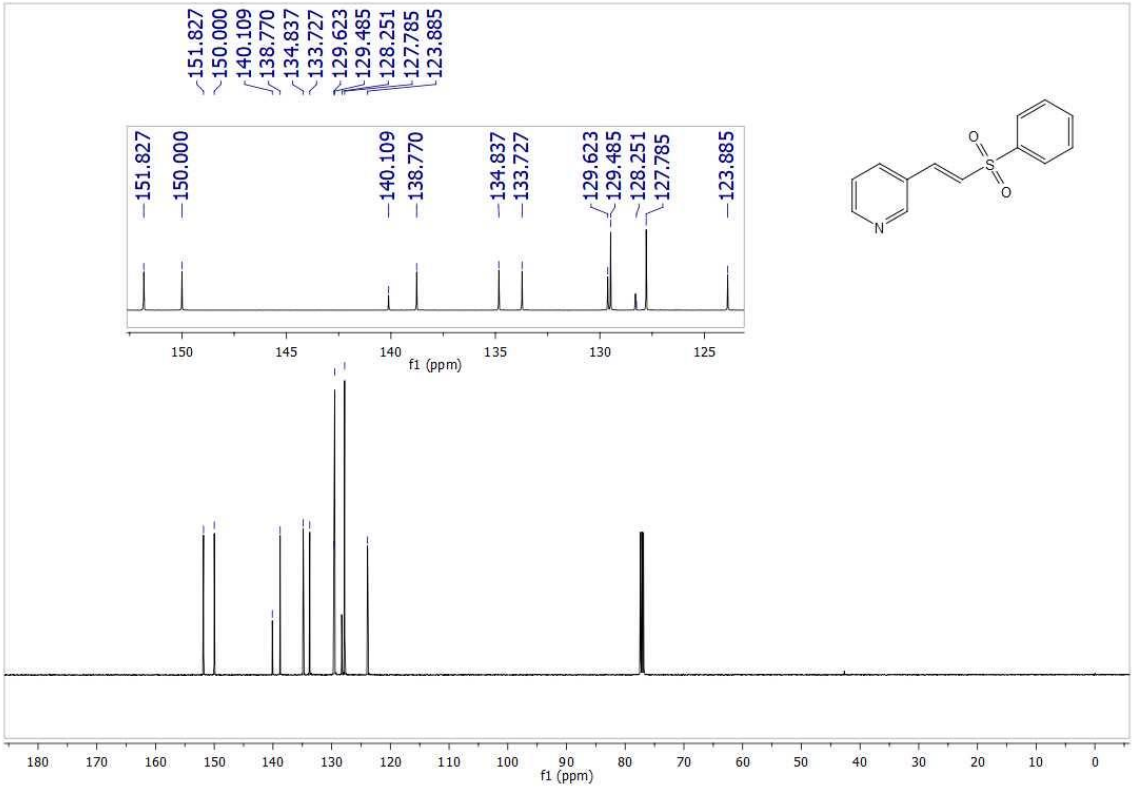
^{1}H NMR (500 MHz, $CDCl_3$) of compound **30**.



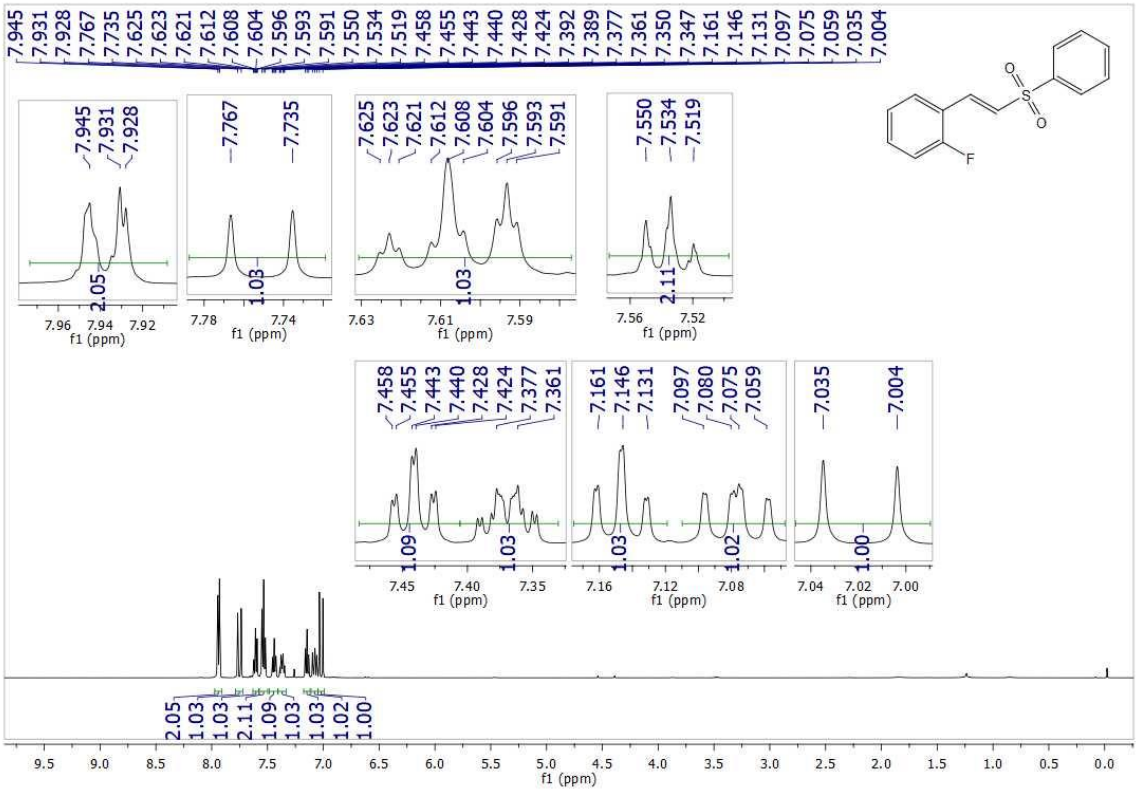
^{13}C NMR (125 MHz, $CDCl_3$) of compound **30**.



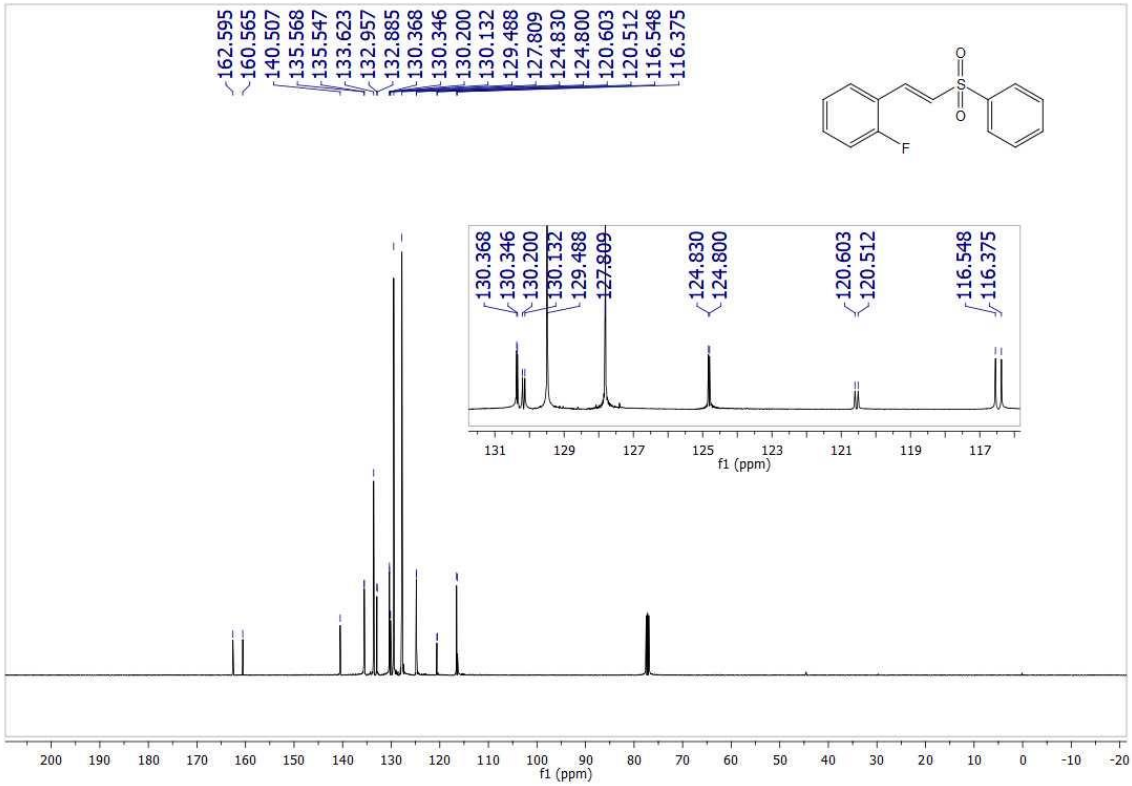
^{1}H NMR (500 MHz, $CDCl_3$) of compound **31**.



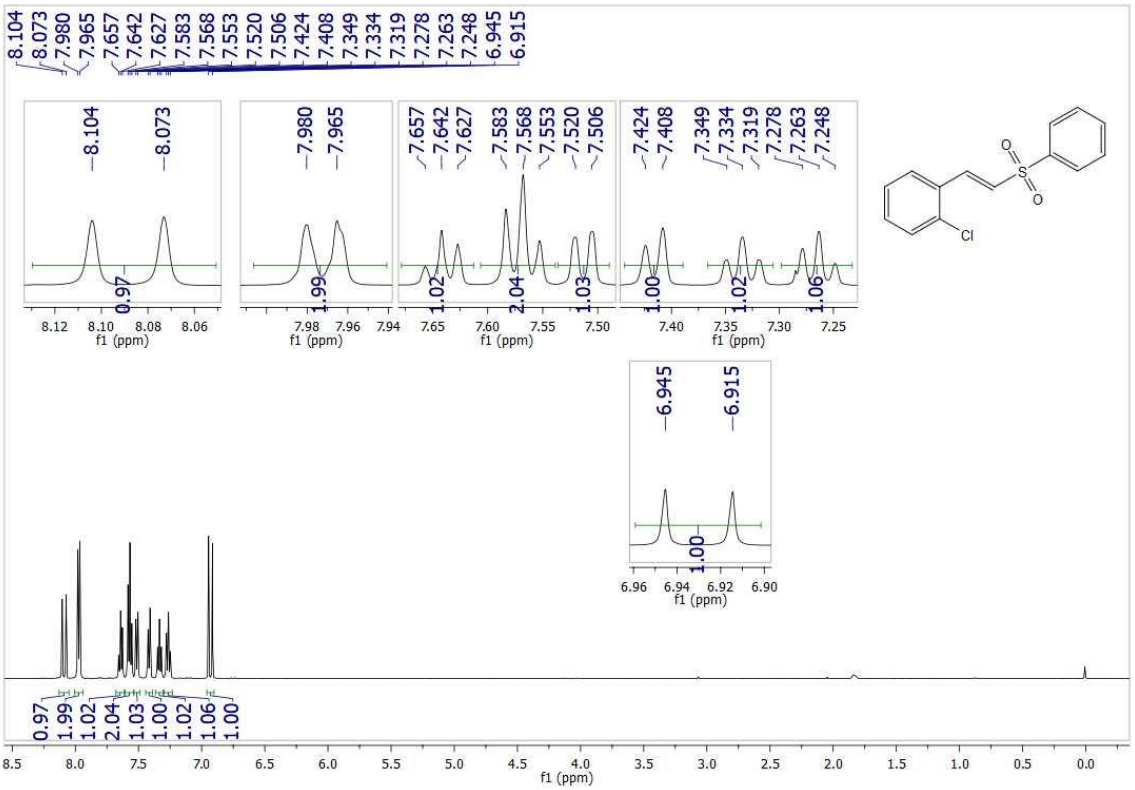
^{13}C NMR (125 MHz, $CDCl_3$) of compound **31**.



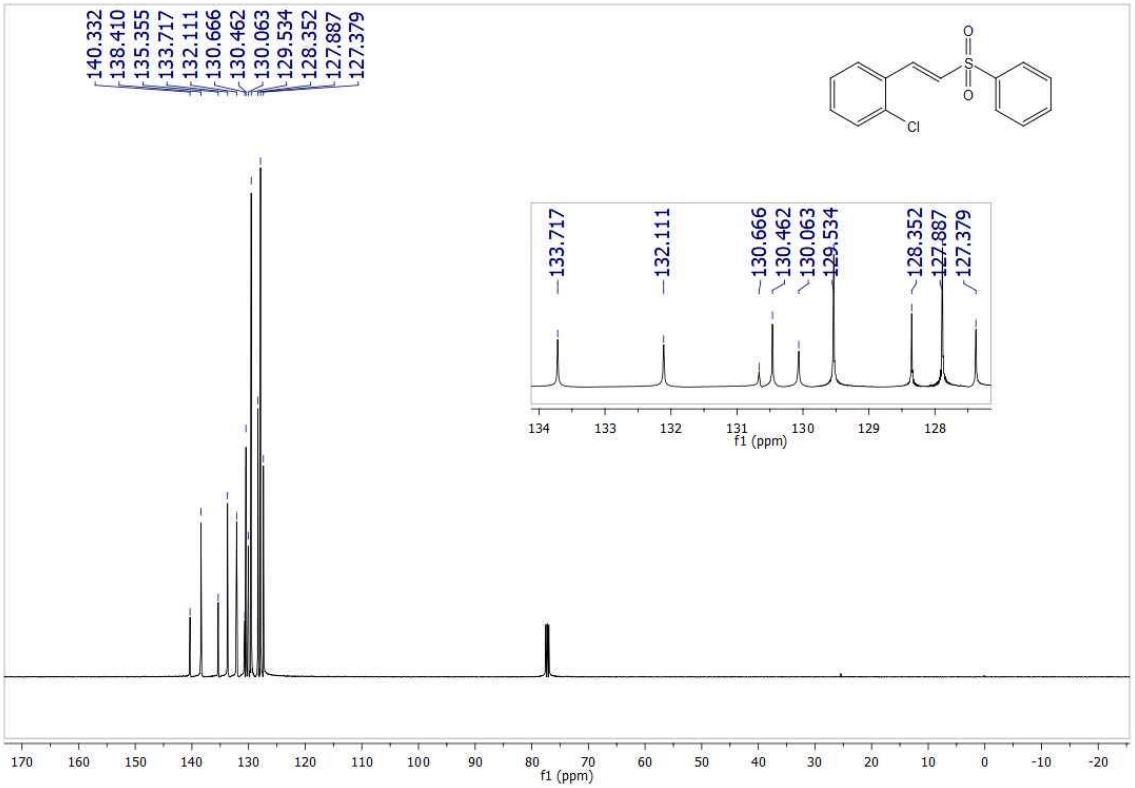
^{1}H NMR (500 MHz, $CDCl_3$) of compound **32**.



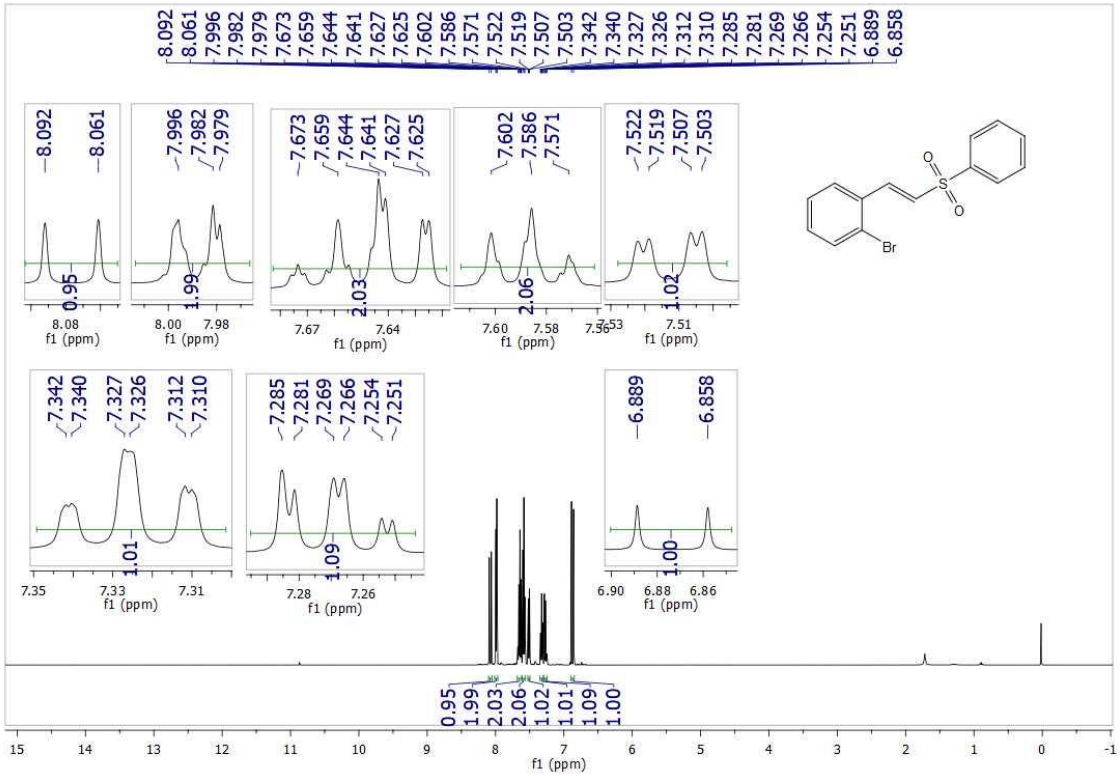
^{13}C NMR (125 MHz, $CDCl_3$) of compound **32**.



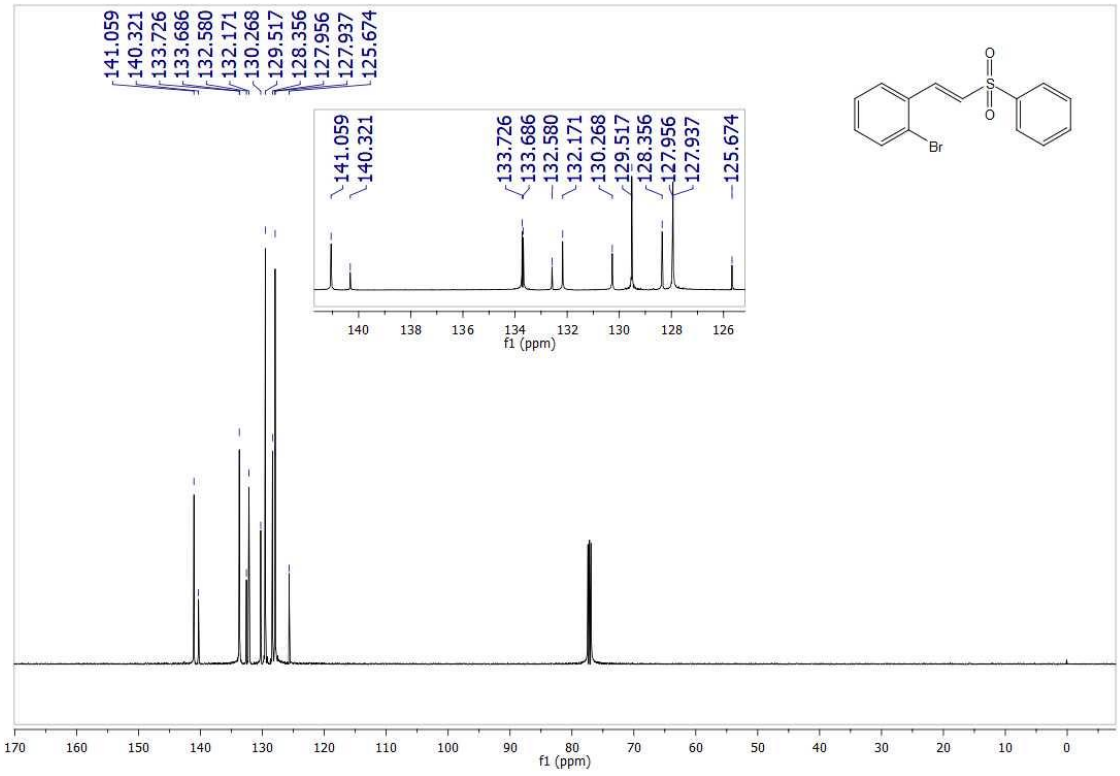
^{1}H NMR (500 MHz, $CDCl_3$) of compound **33**.



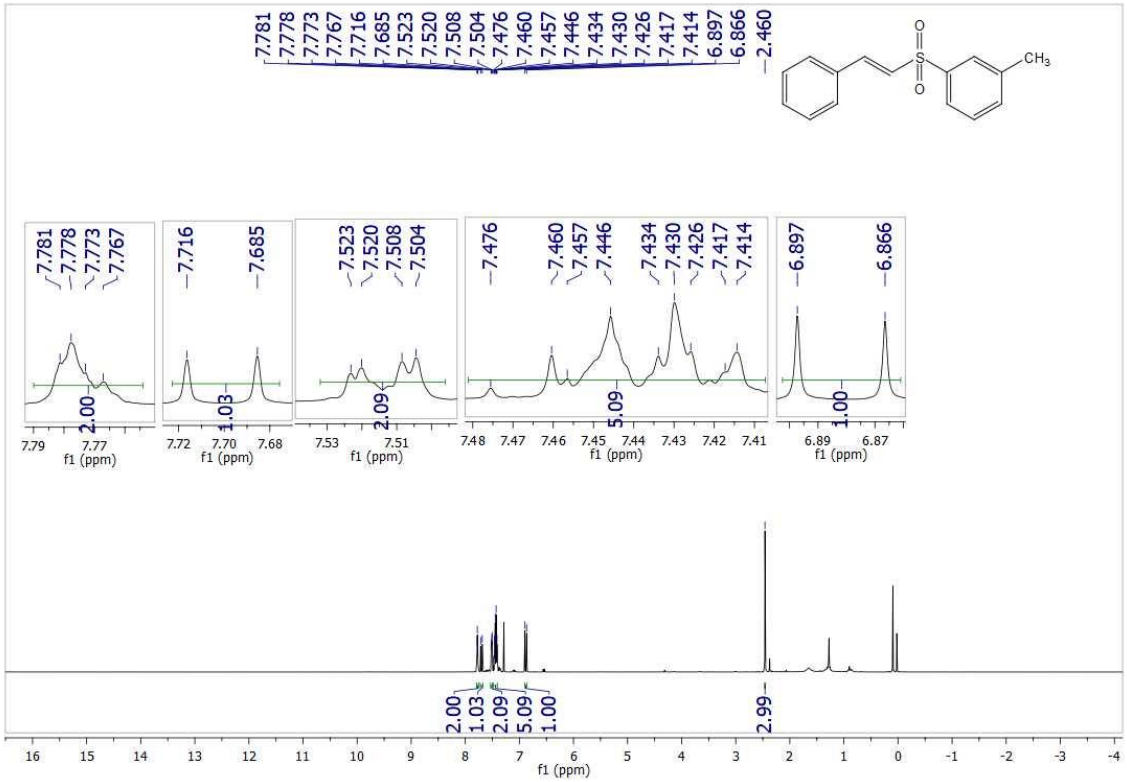
^{13}C NMR (125 MHz, $CDCl_3$) of compound **33**.



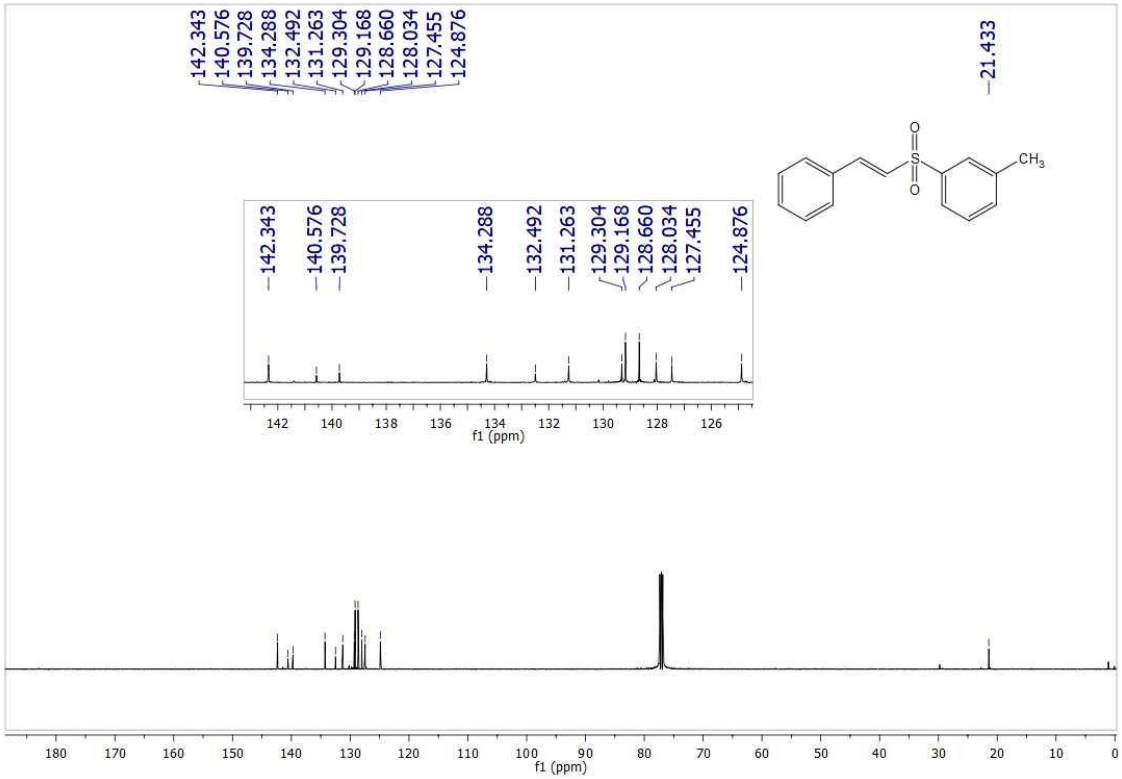
^{1}H NMR (500 MHz, $CDCl_3$) of compound **34**.



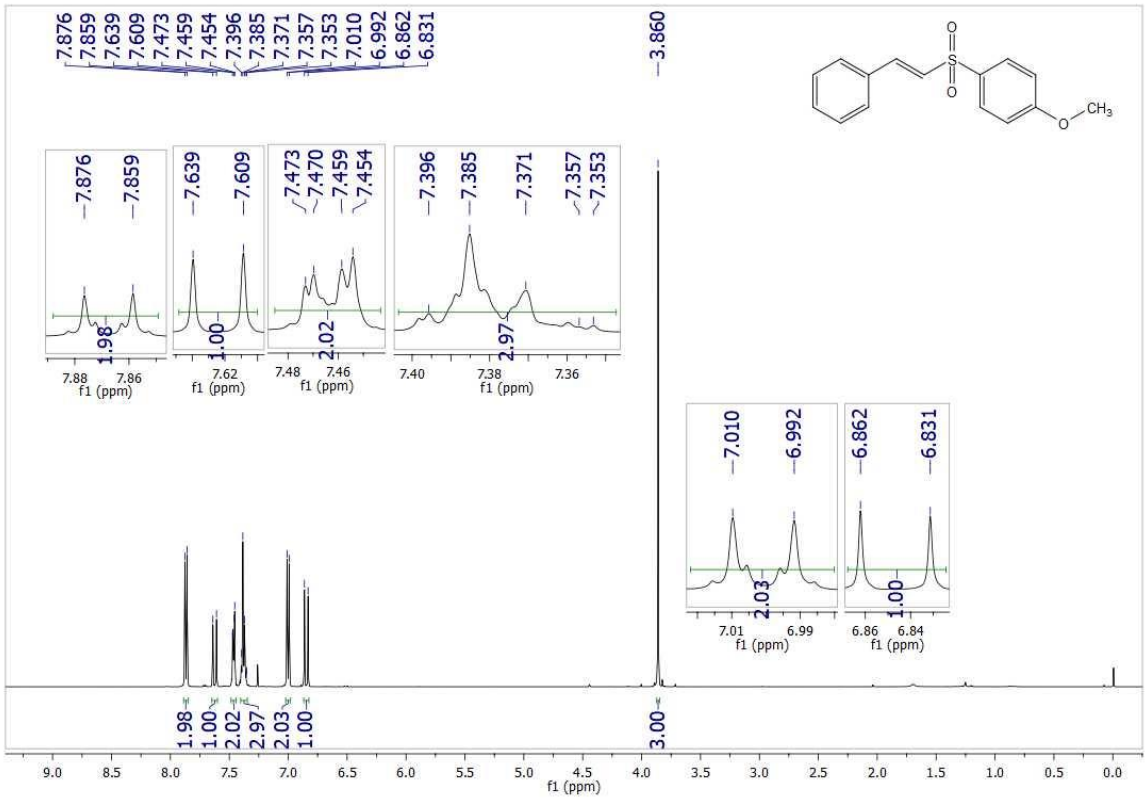
^{13}C NMR (125 MHz, $CDCl_3$) of compound **34**.



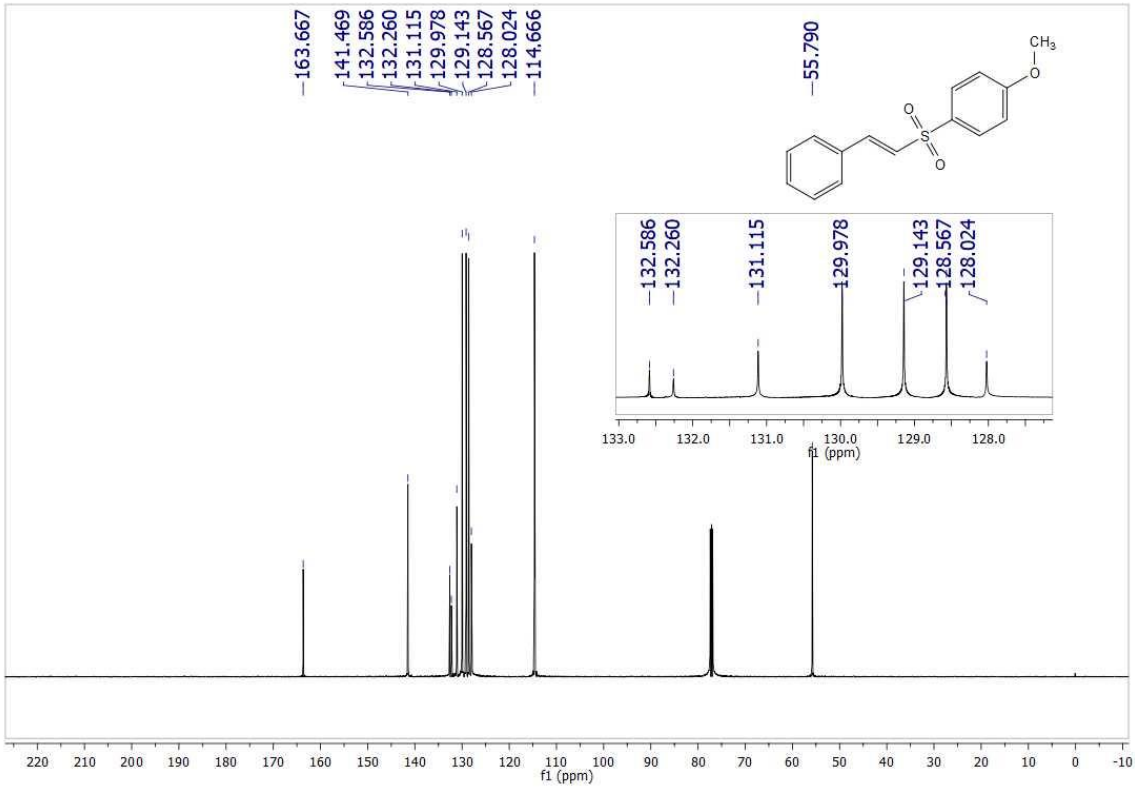
^{1}H NMR (500 MHz, $CDCl_3$) of compound **35**.



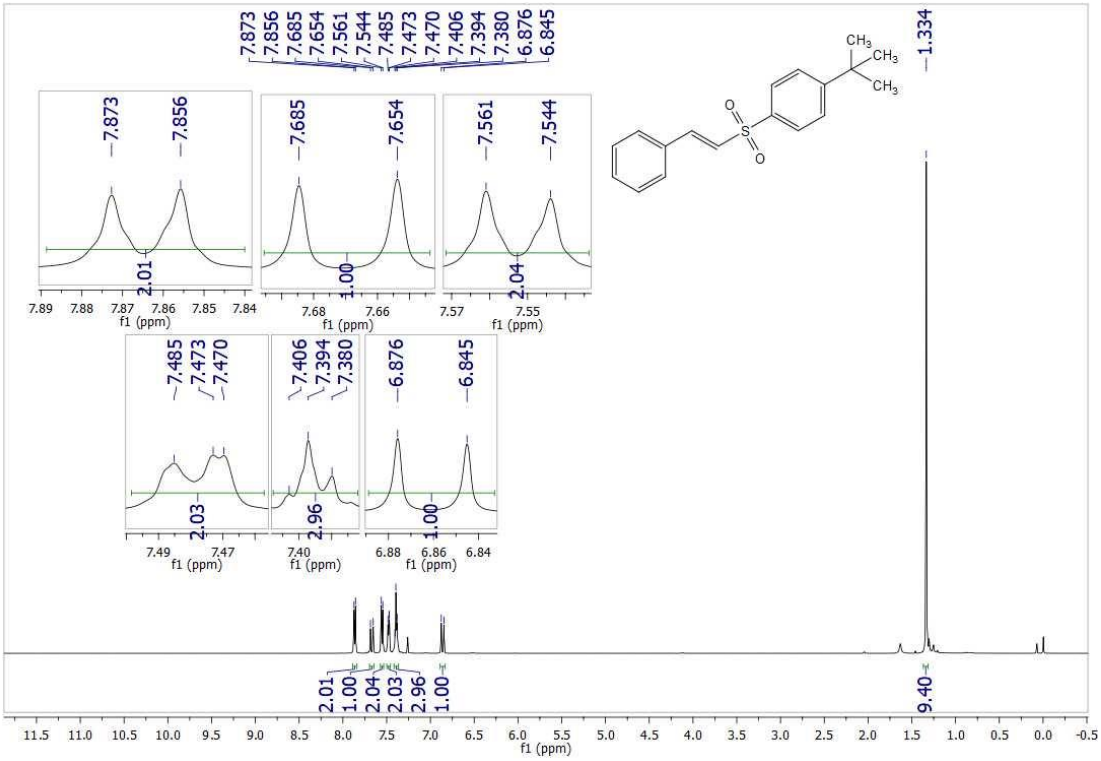
^{13}C NMR (125 MHz, $CDCl_3$) of compound **35**.



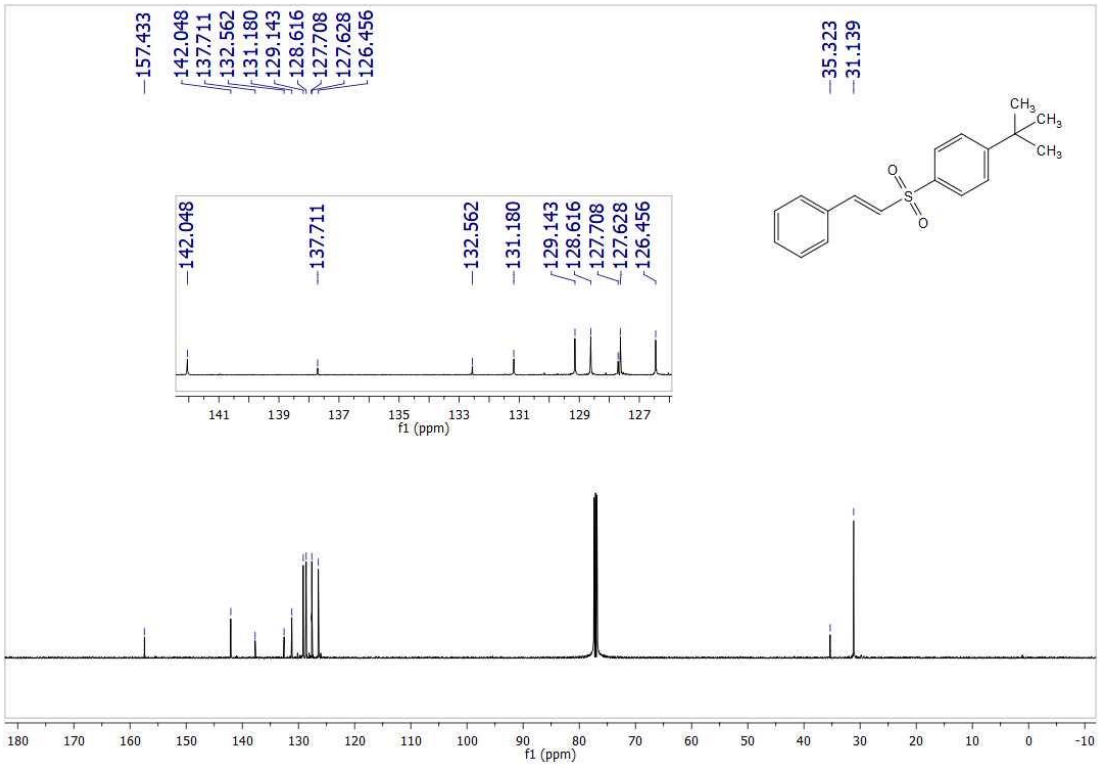
^{1}H NMR (500 MHz, $CDCl_3$) of compound **36**.



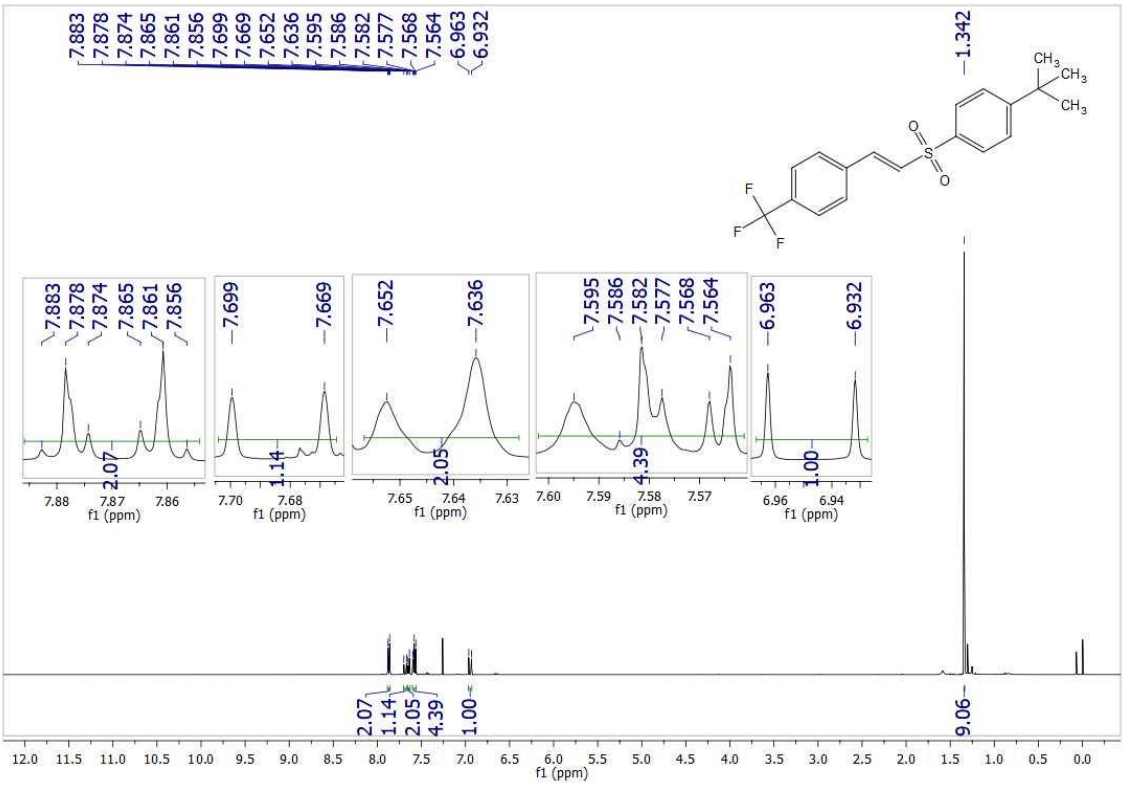
^{13}C NMR (125 MHz, $CDCl_3$) of compound **36**.



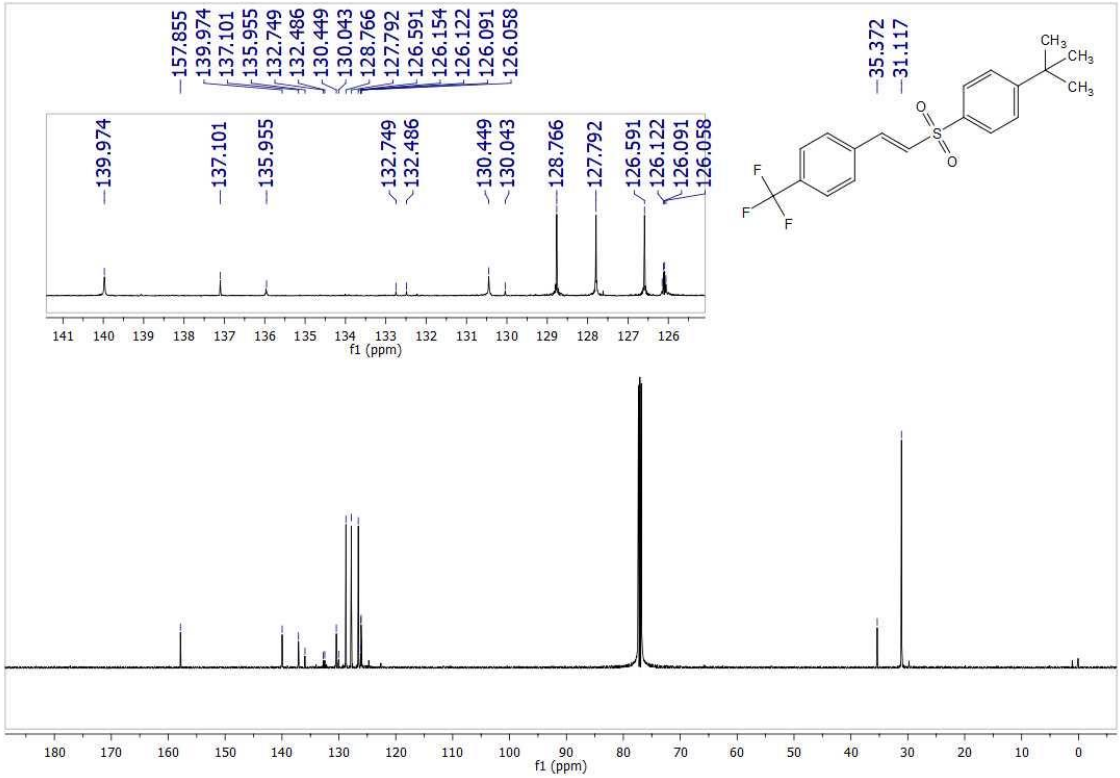
^{1}H NMR (500 MHz, $CDCl_3$) of compound **37**.



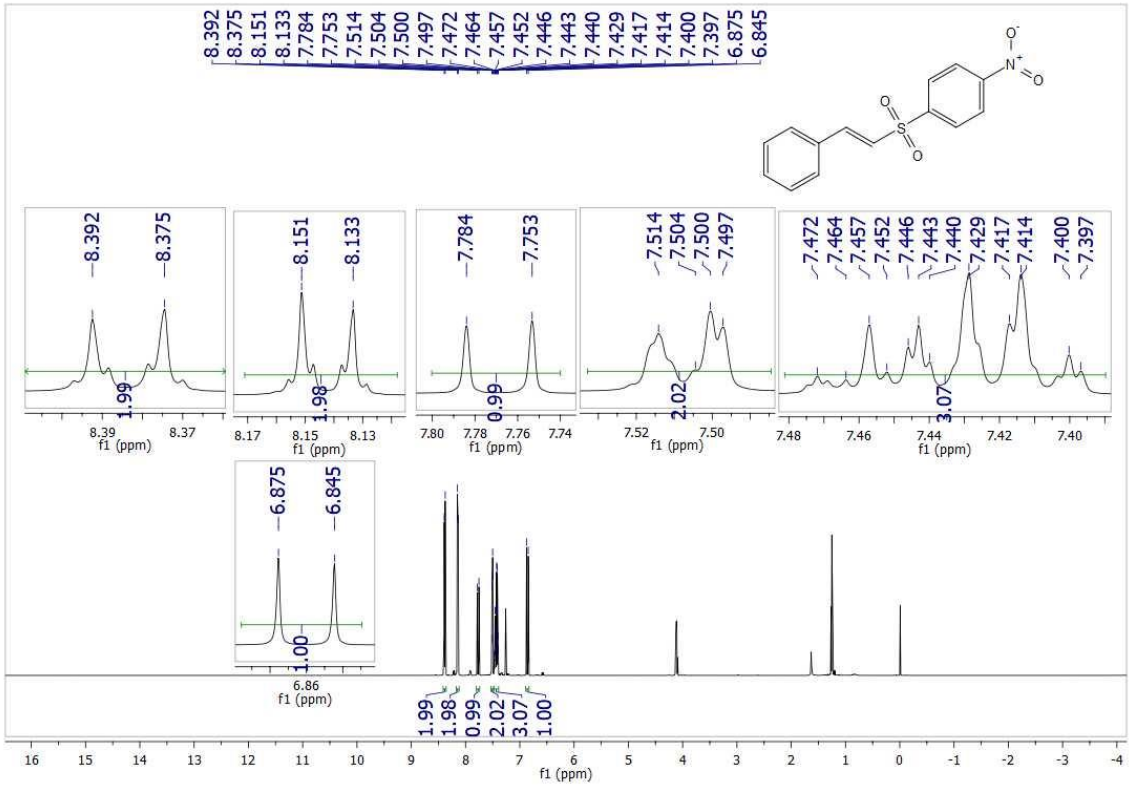
^{13}C NMR (125 MHz, $CDCl_3$) of compound **37**.



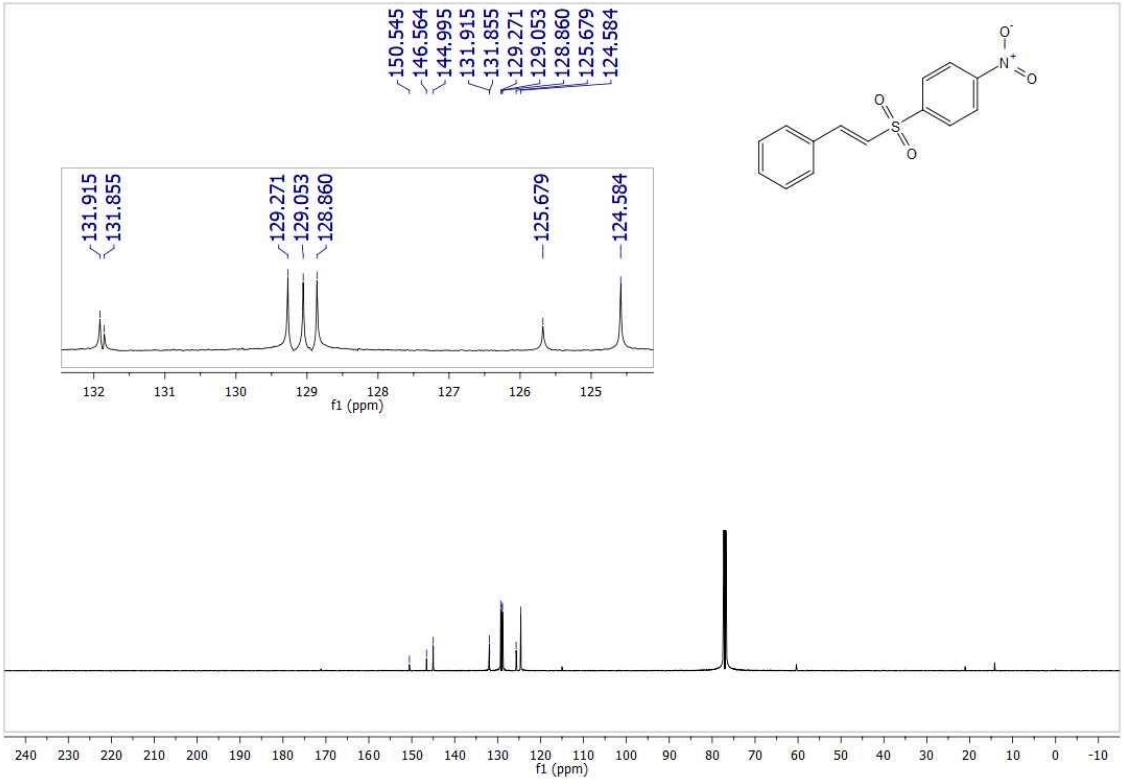
^{1}H NMR (500 MHz, $CDCl_3$) of compound **38**.



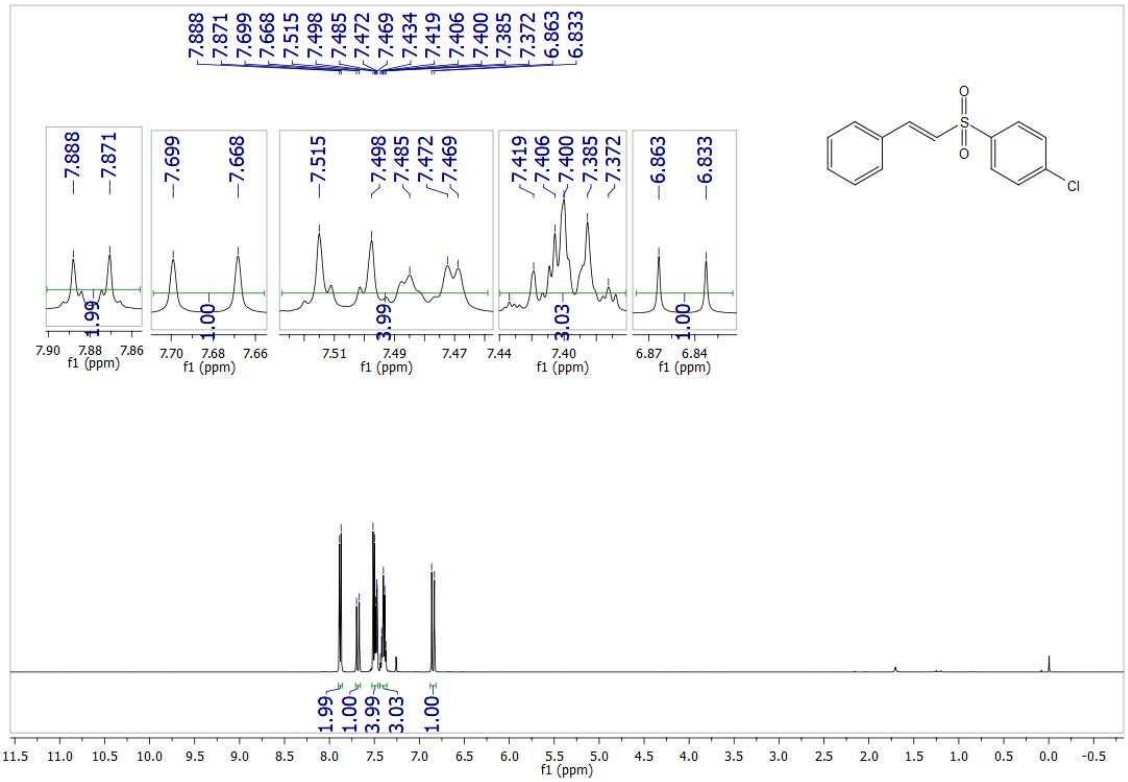
^{13}C NMR (125 MHz, $CDCl_3$) of compound **38**.



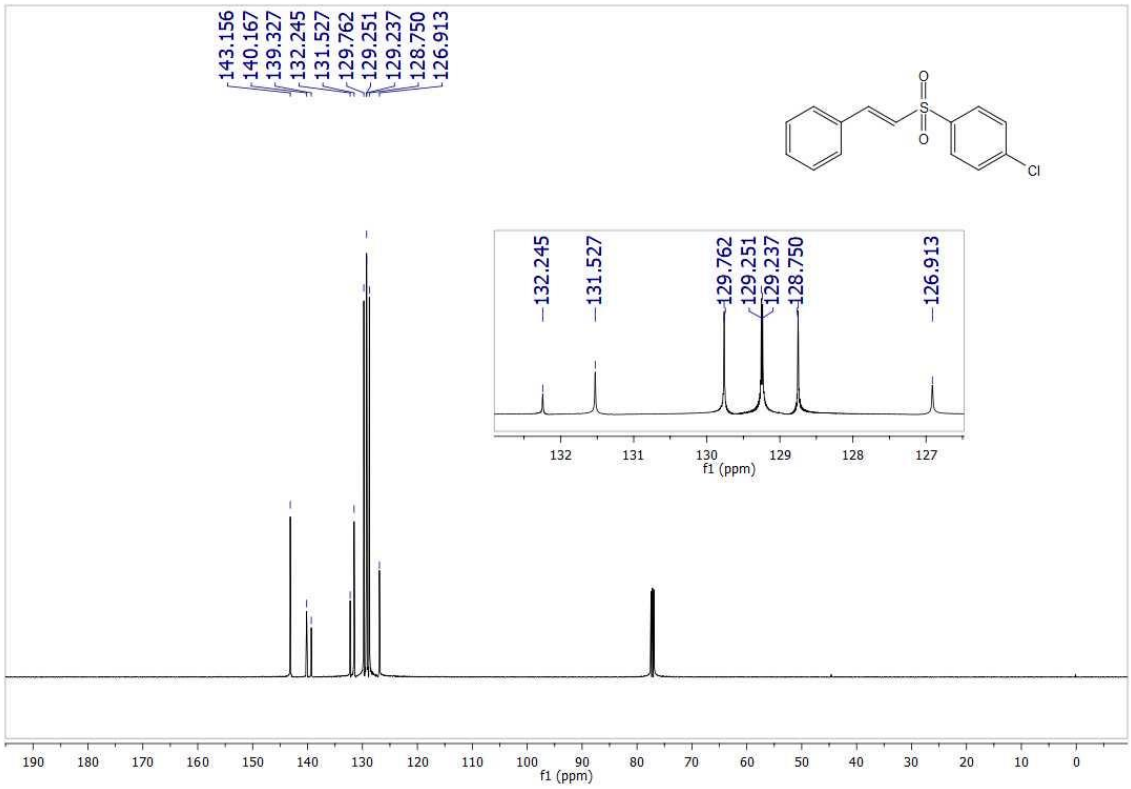
^{1}H NMR (500 MHz, $CDCl_3$) of compound **39.**



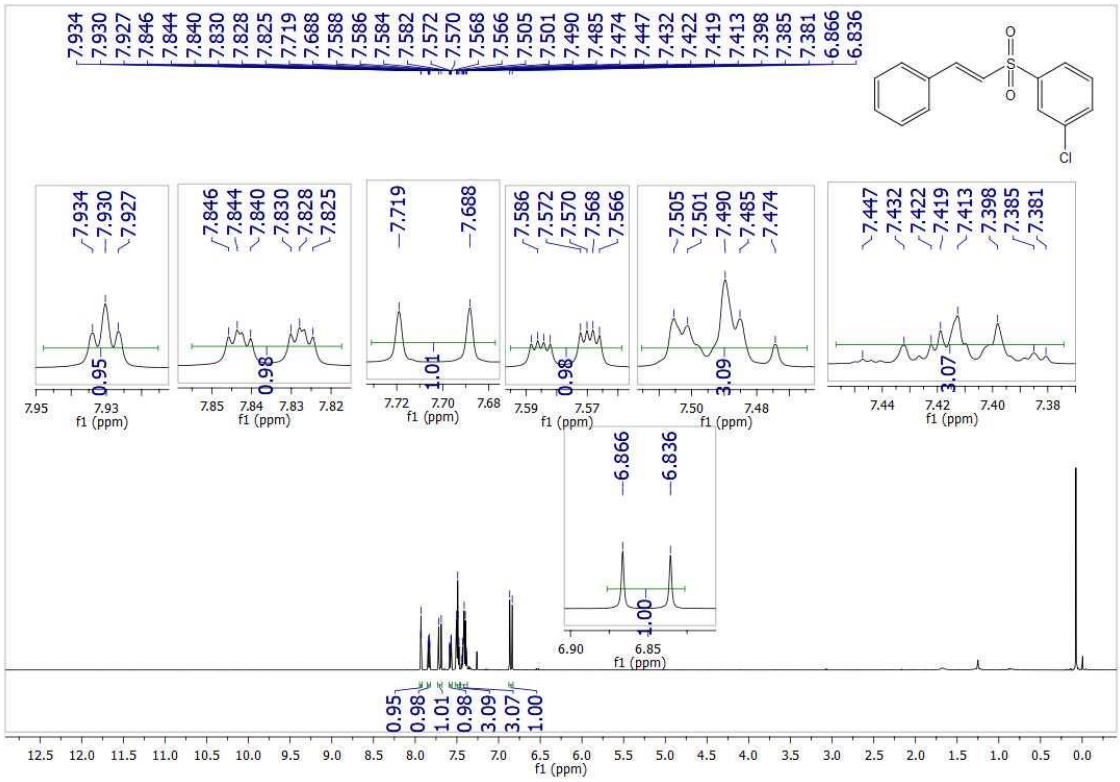
^{13}C NMR (125 MHz, $CDCl_3$) of compound **39.**



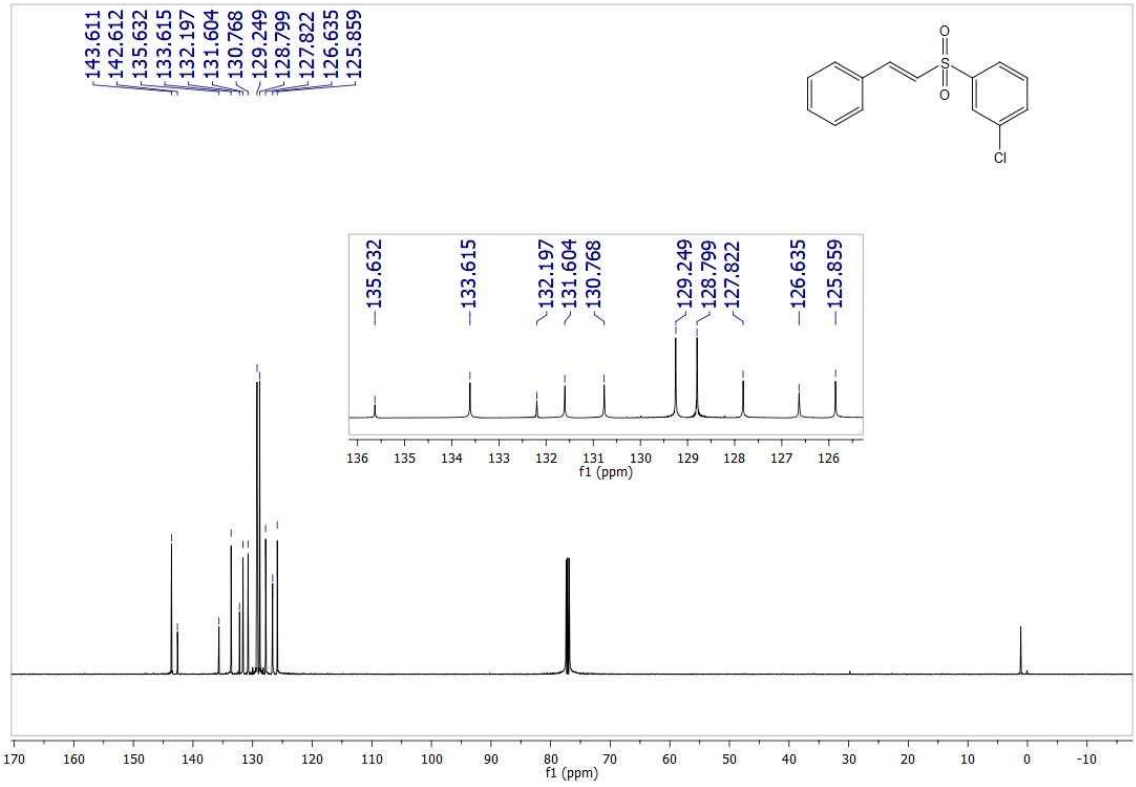
^{1}H NMR (500 MHz, $CDCl_3$) of compound **40**.



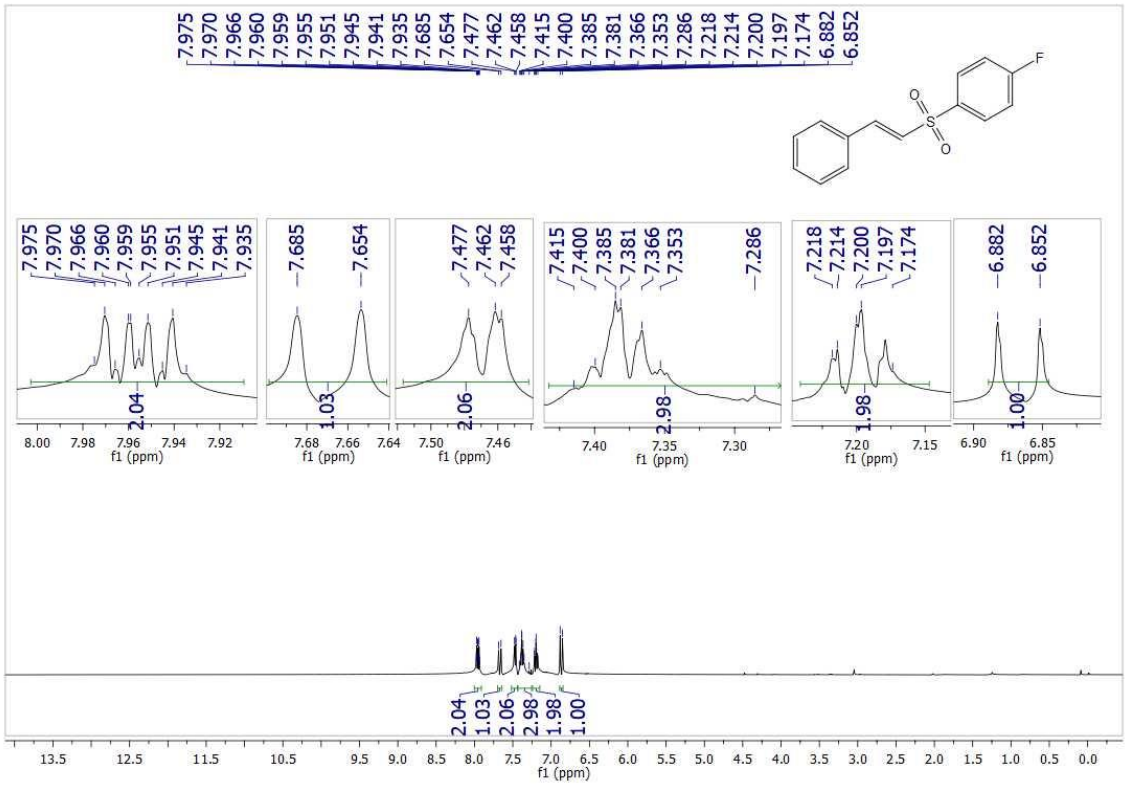
^{13}C NMR (125 MHz, $CDCl_3$) of compound **40**.



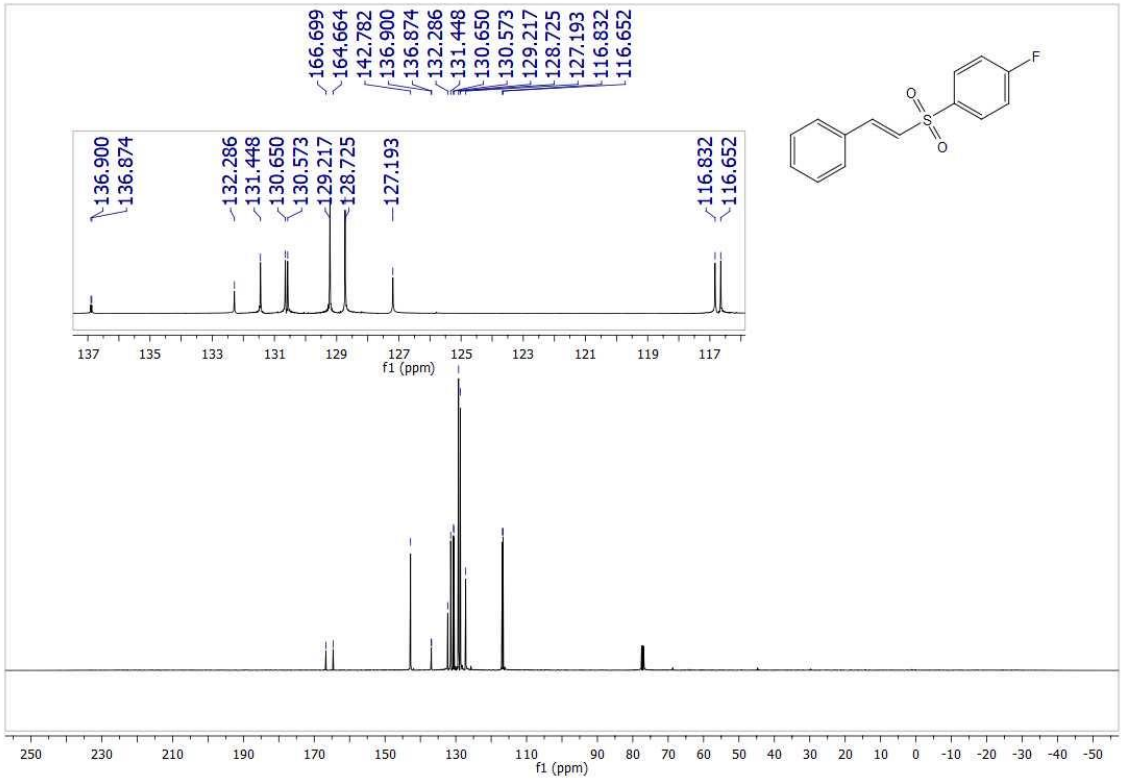
^{1}H NMR (500 MHz, $CDCl_3$) of compound **41**.



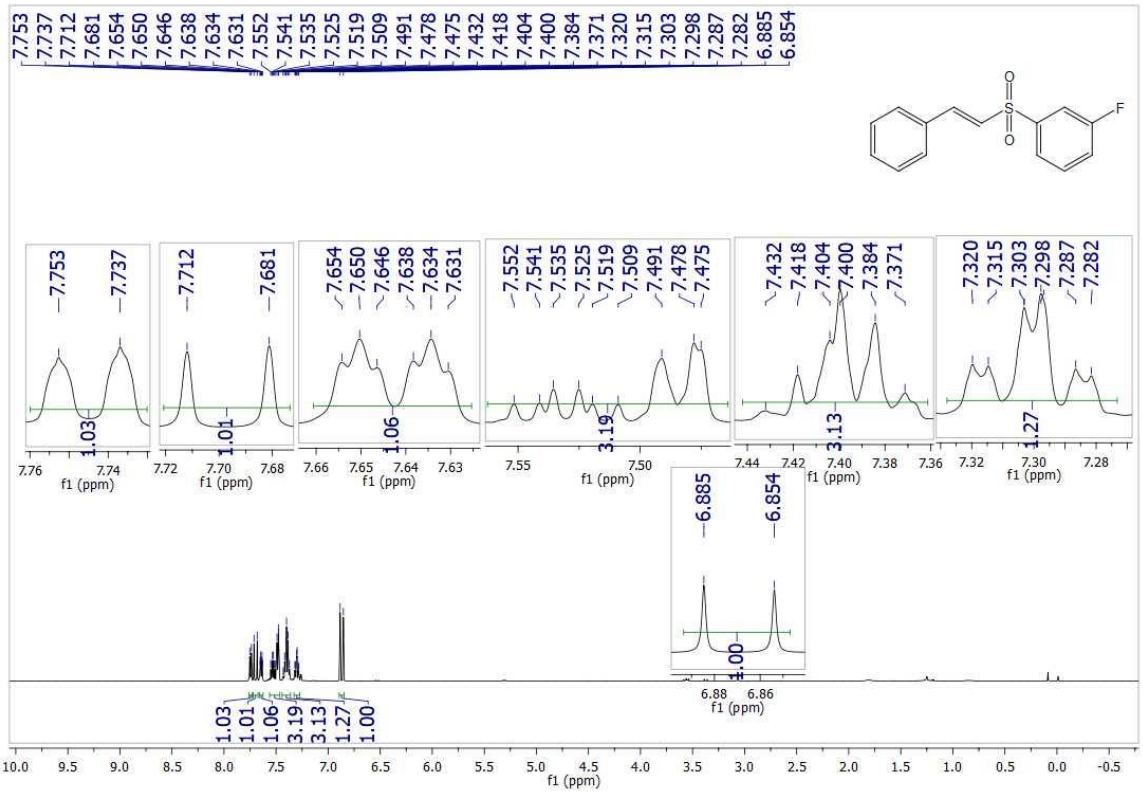
^{13}C NMR (125 MHz, $CDCl_3$) of compound **41**.



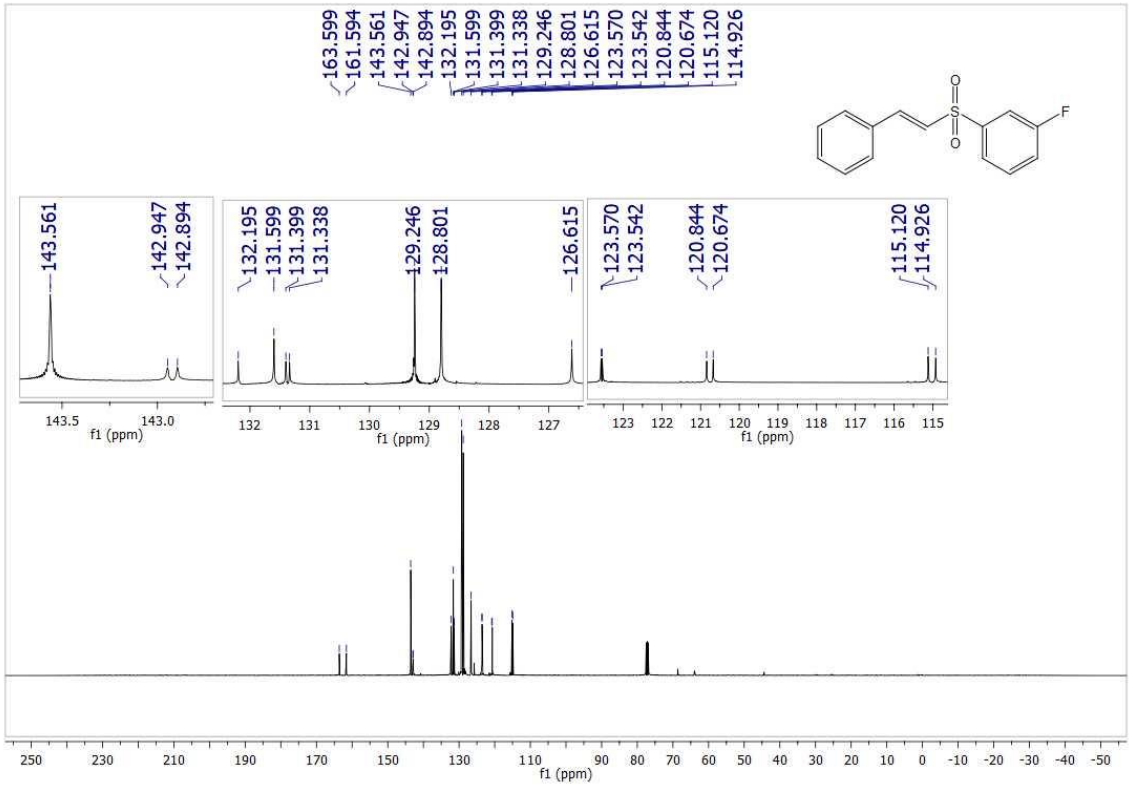
^{1}H NMR (500 MHz, $CDCl_3$) of compound **42**.



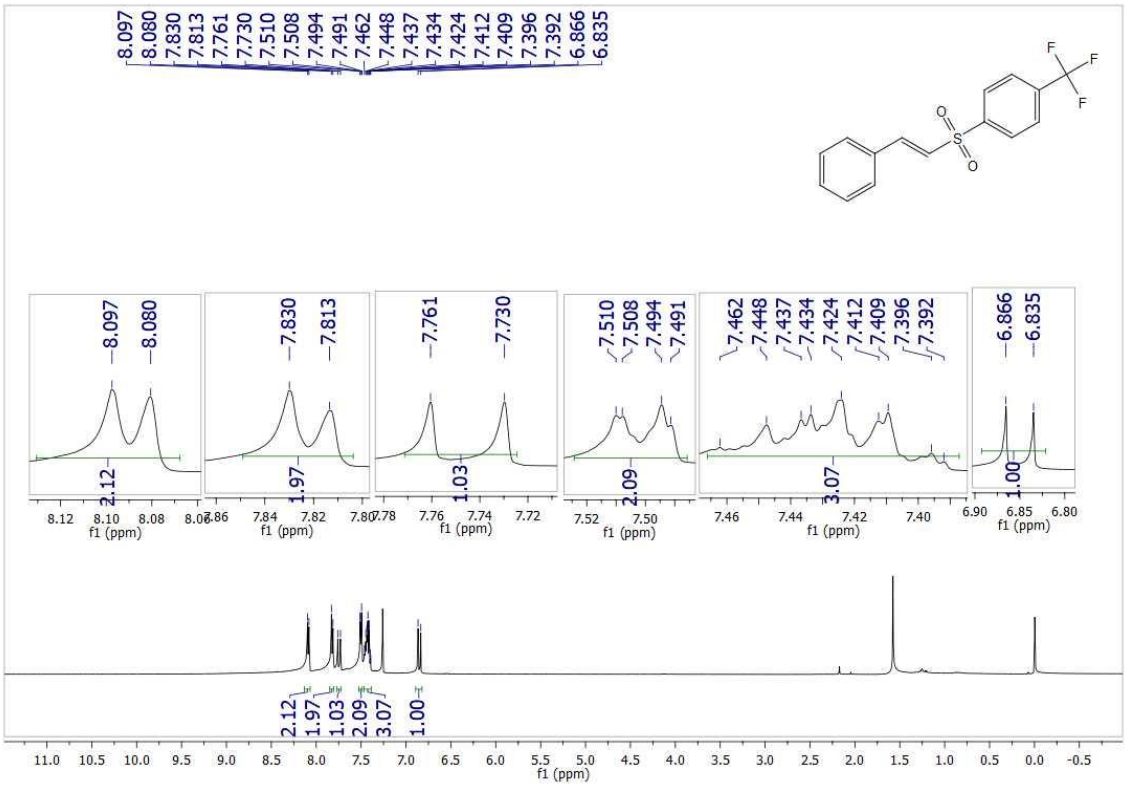
^{13}C NMR (125 MHz, $CDCl_3$) of compound **42**.



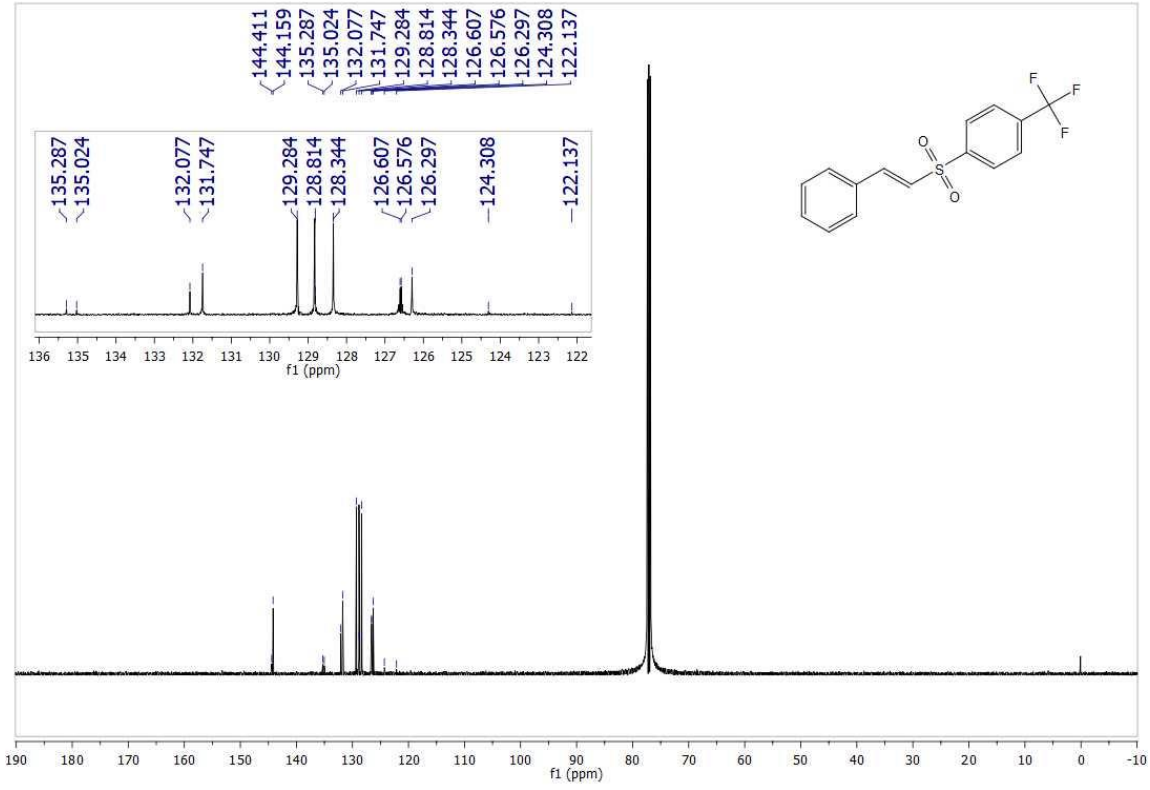
^{1}H NMR (500 MHz, $CDCl_3$) of compound **43**.



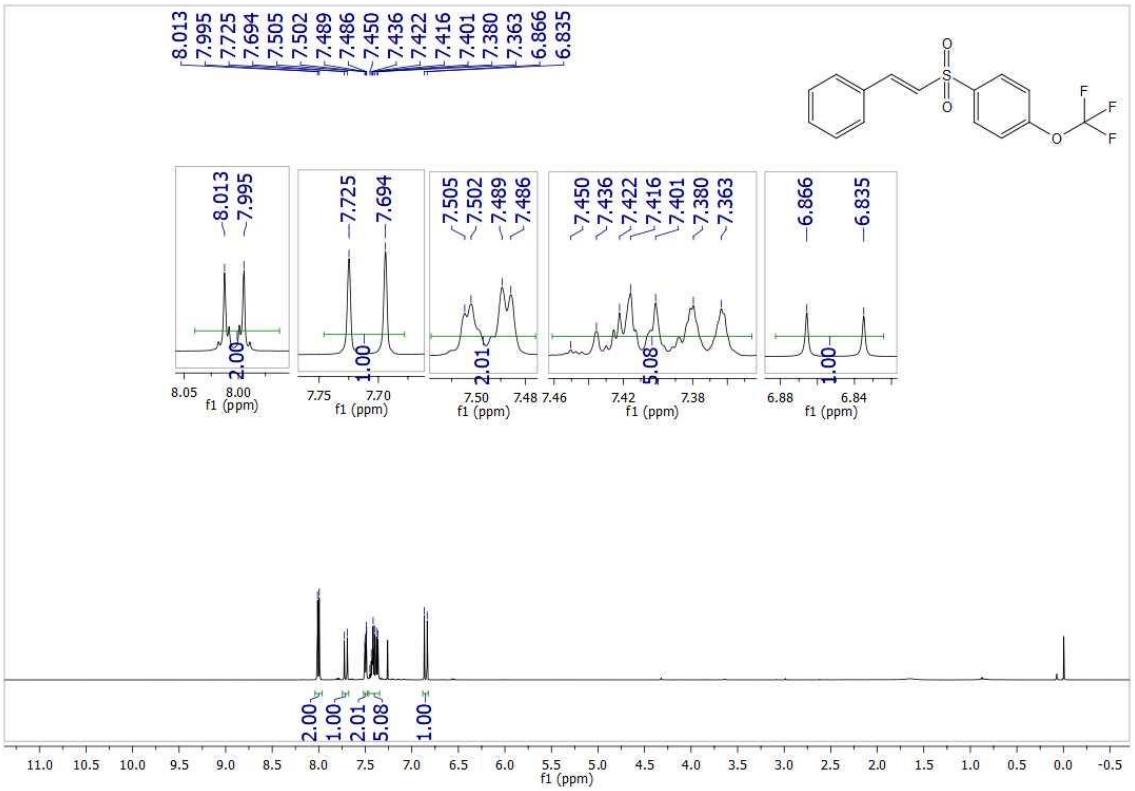
^{13}C NMR (125 MHz, $CDCl_3$) of compound **43**.



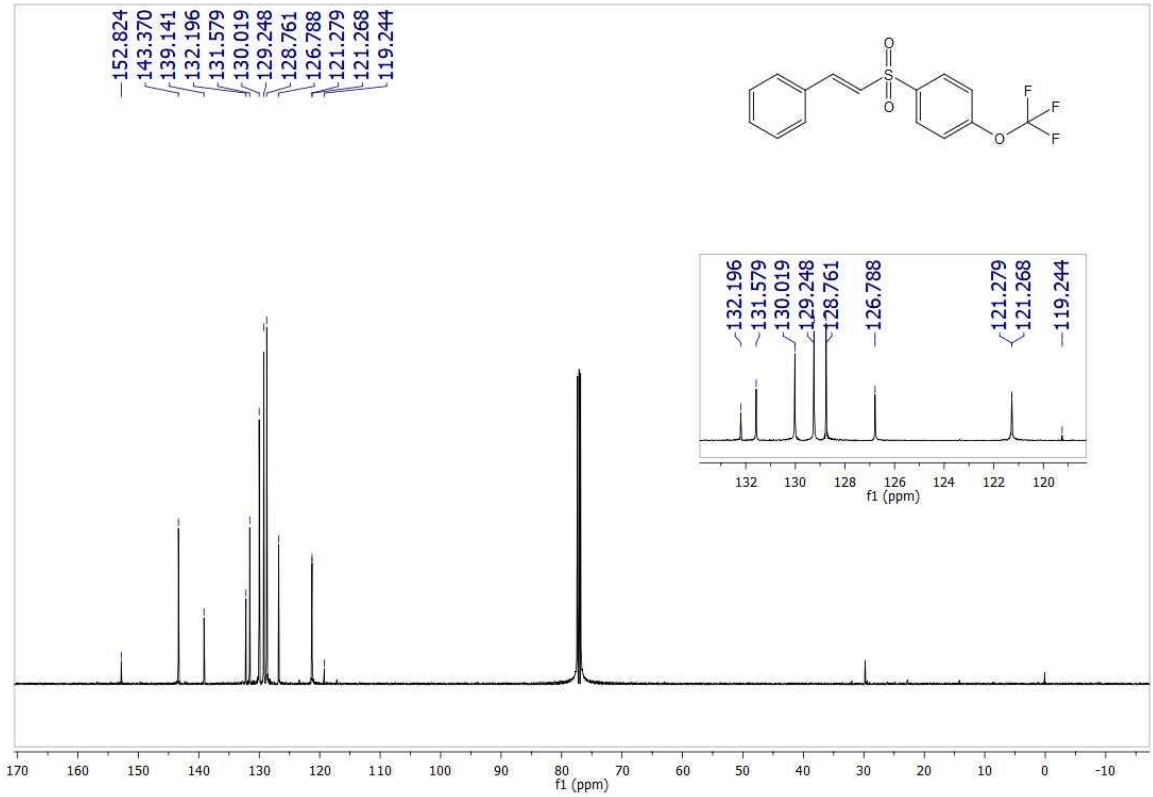
^{1}H NMR (500 MHz, $CDCl_3$) of compound **44**.



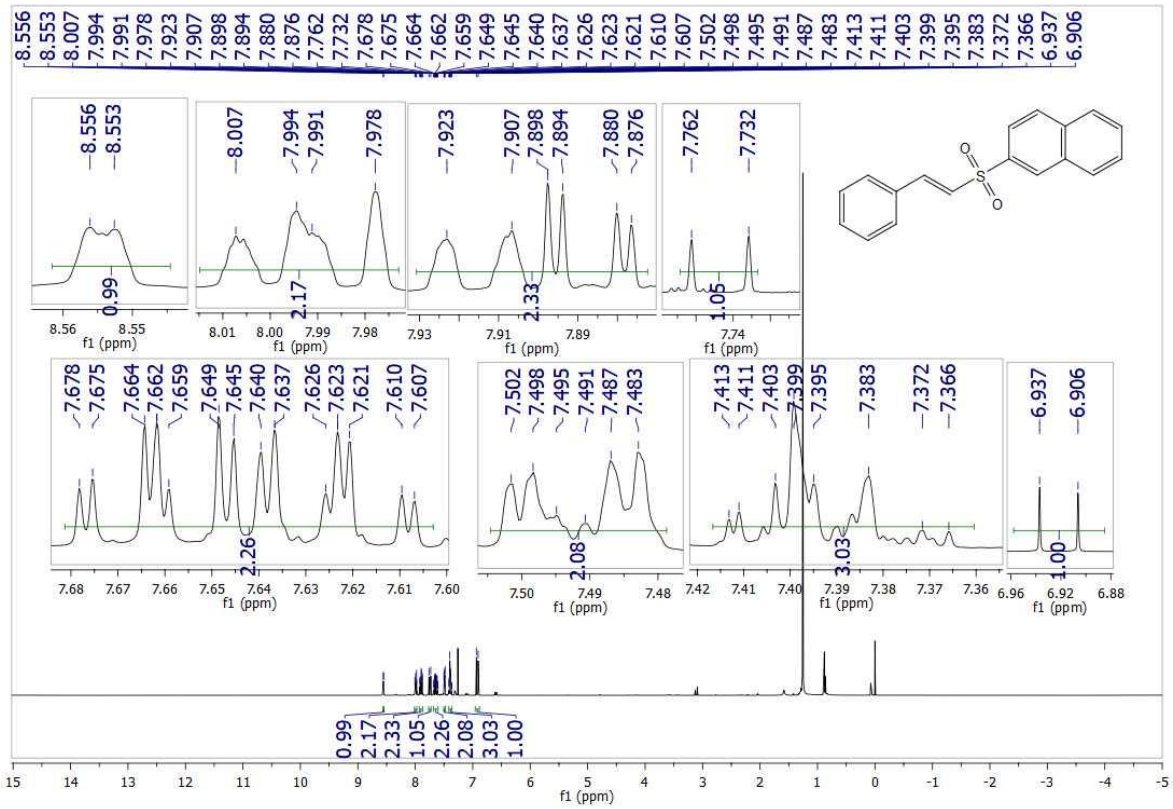
^{13}C NMR (125 MHz, $CDCl_3$) of compound **44**.



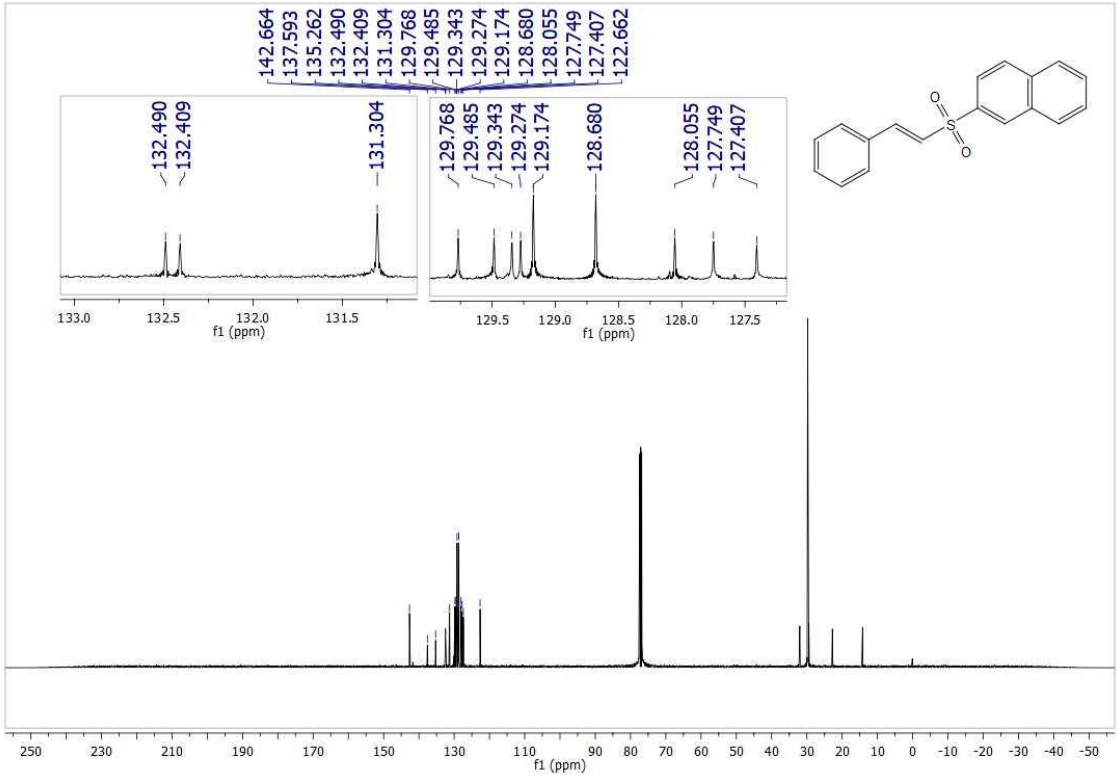
^{1}H NMR (500 MHz, $CDCl_3$) of compound **45**.



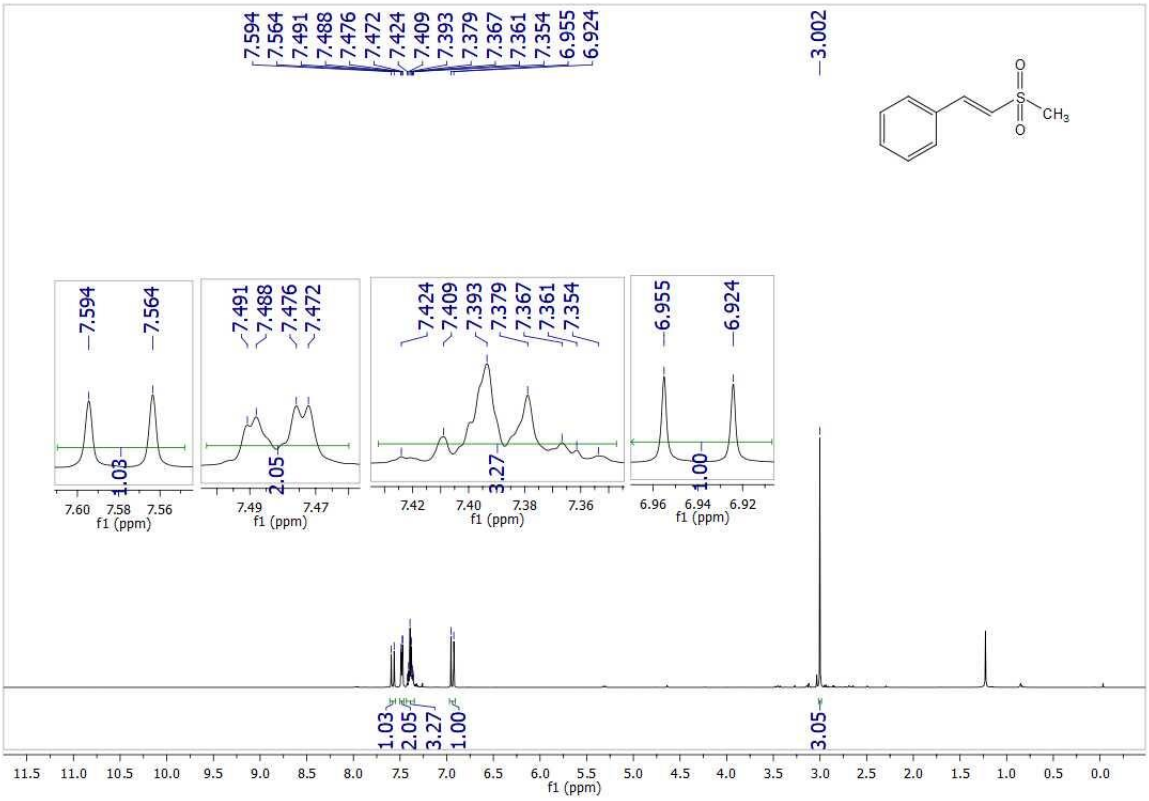
^{13}C NMR (125 MHz, $CDCl_3$) of compound **45**.



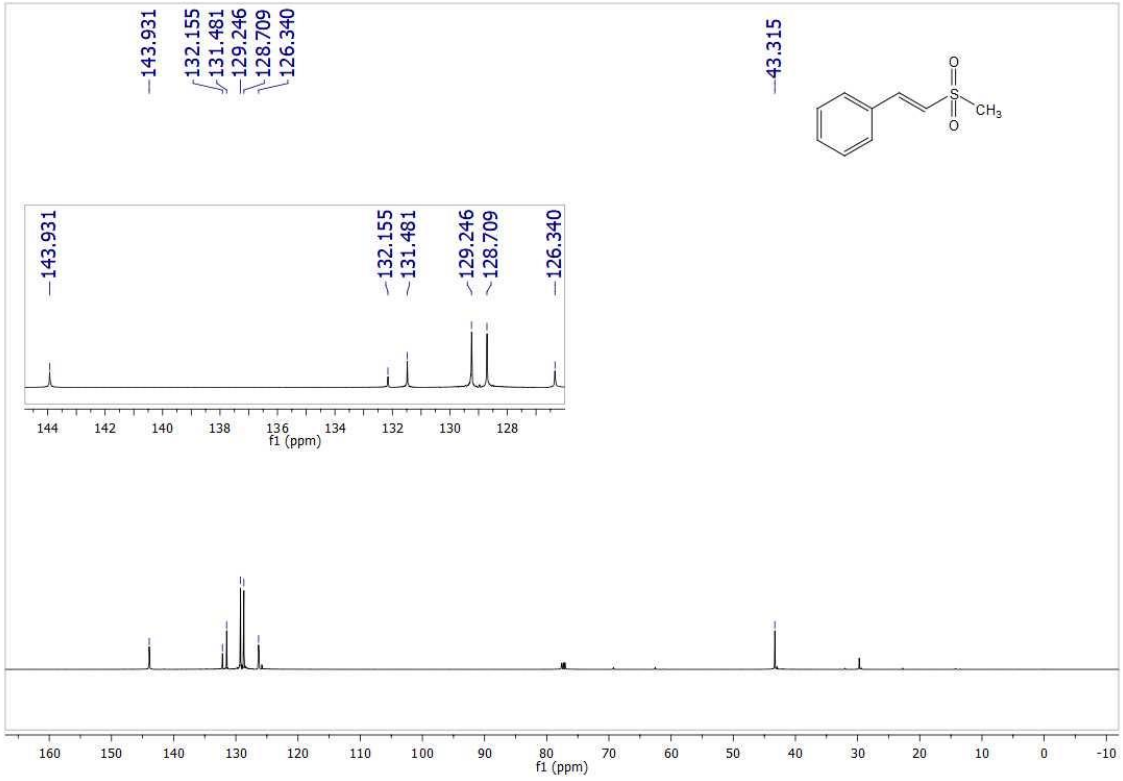
^{1}H NMR (500 MHz, $CDCl_3$) of compound **46**.



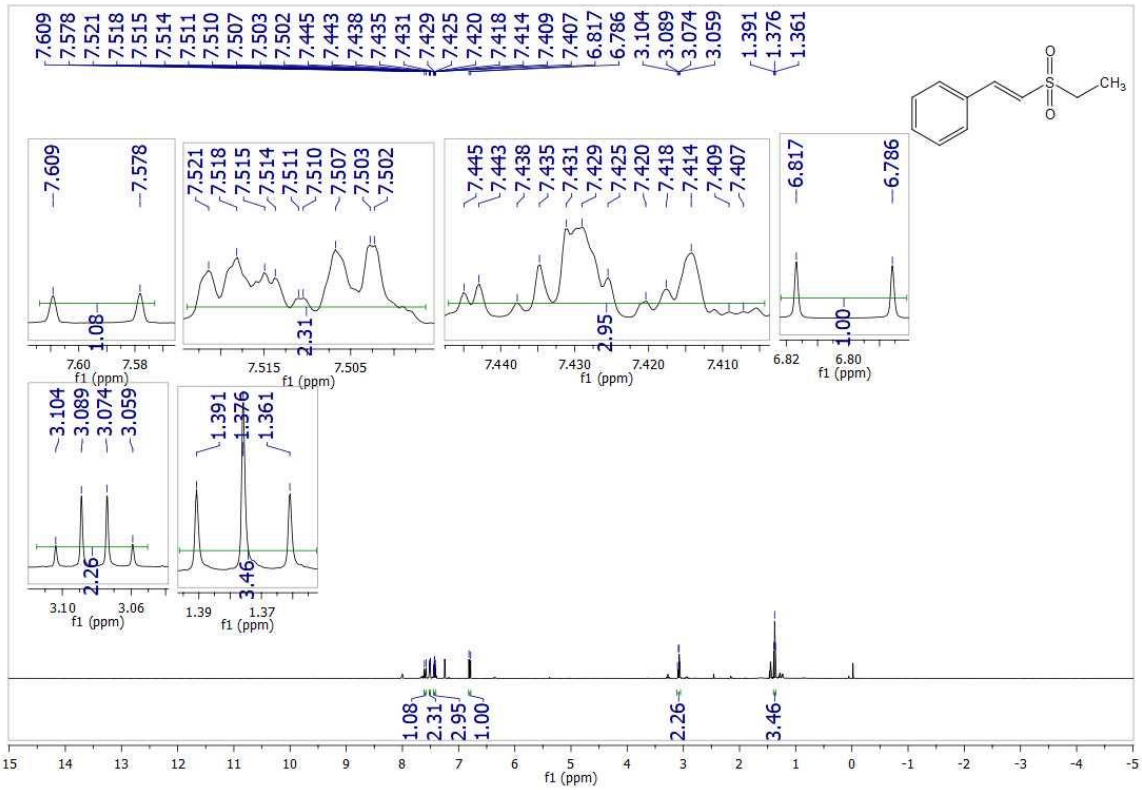
^{13}C NMR (125 MHz, $CDCl_3$) of compound **46**.



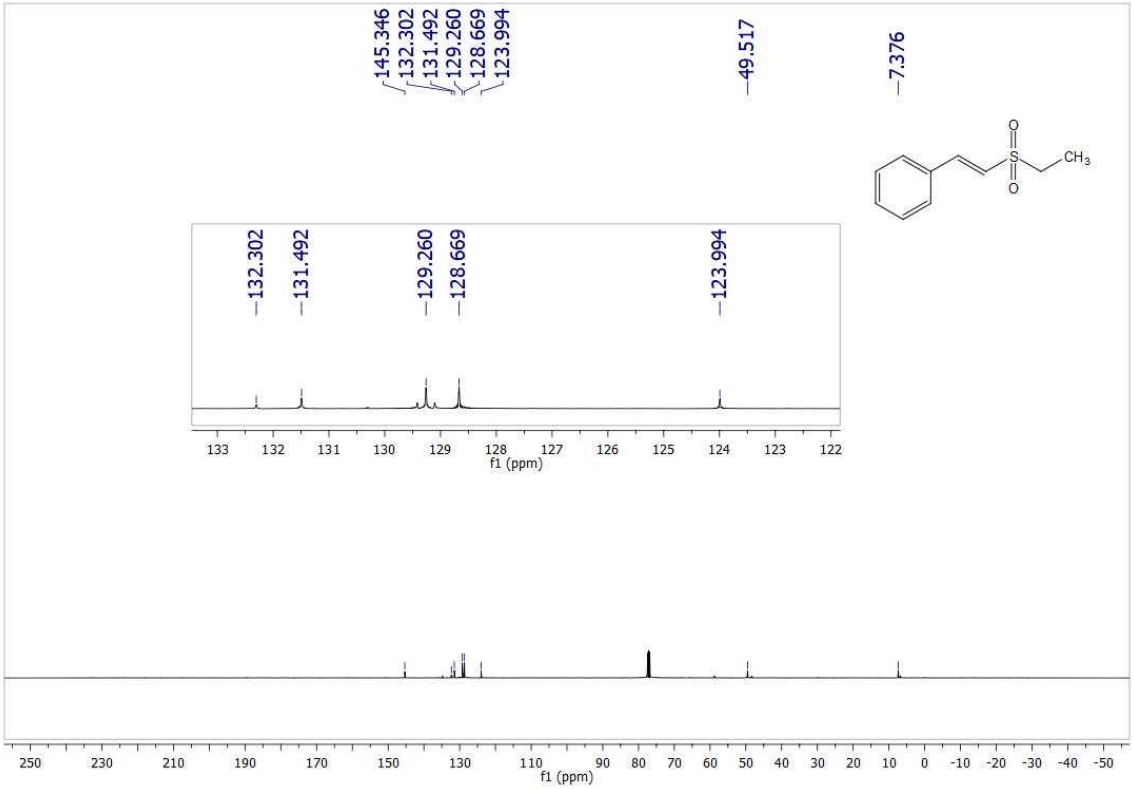
^{1}H NMR (500 MHz, $CDCl_3$) of compound **47**.



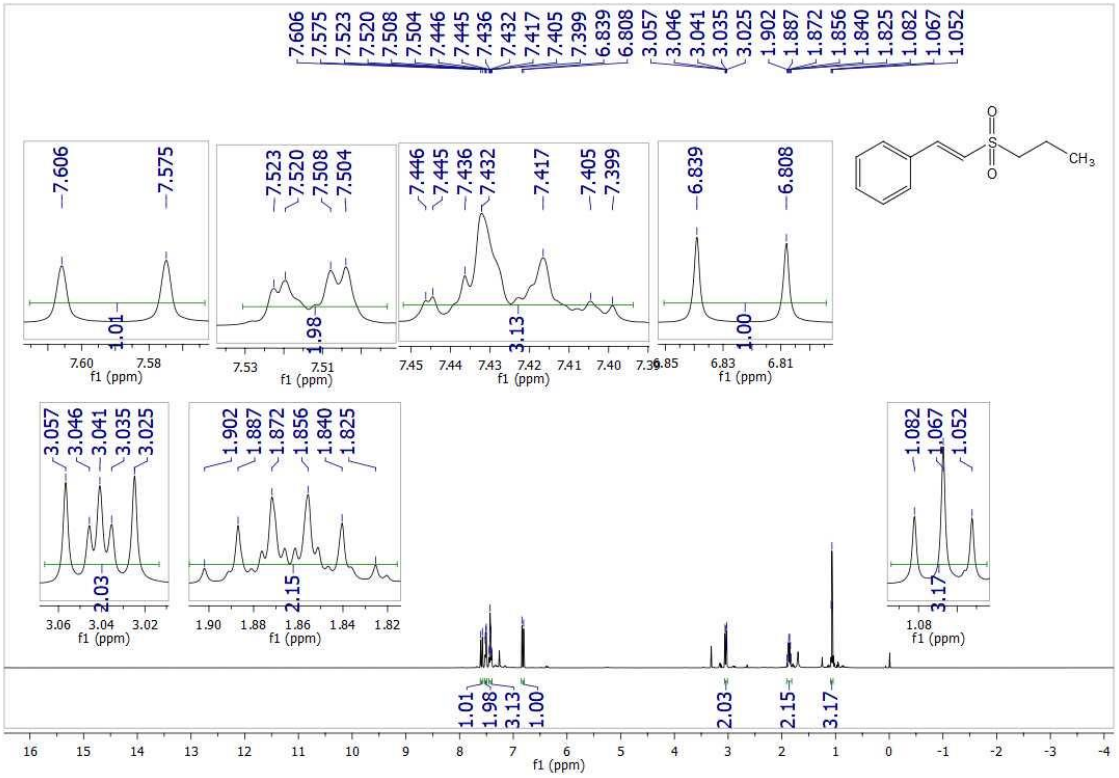
^{13}C NMR (125 MHz, $CDCl_3$) of compound **47**.



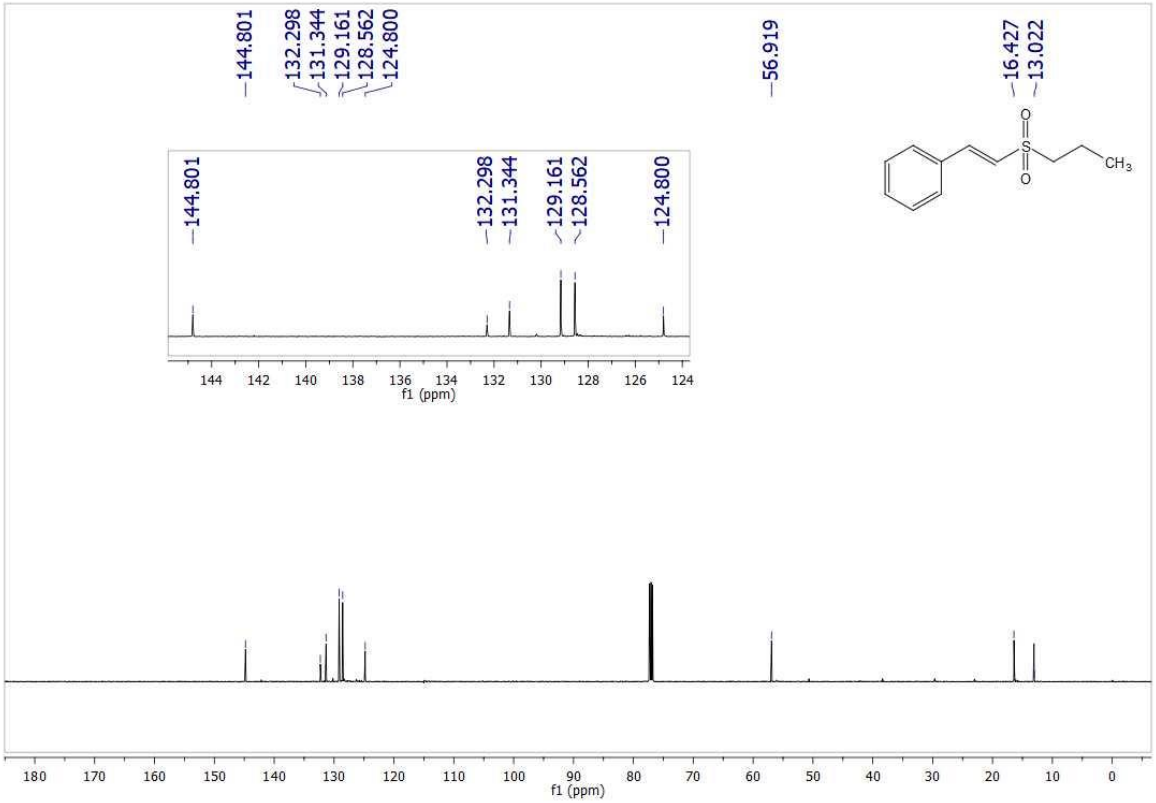
^{1}H NMR (500 MHz, $CDCl_3$) of compound **48**.



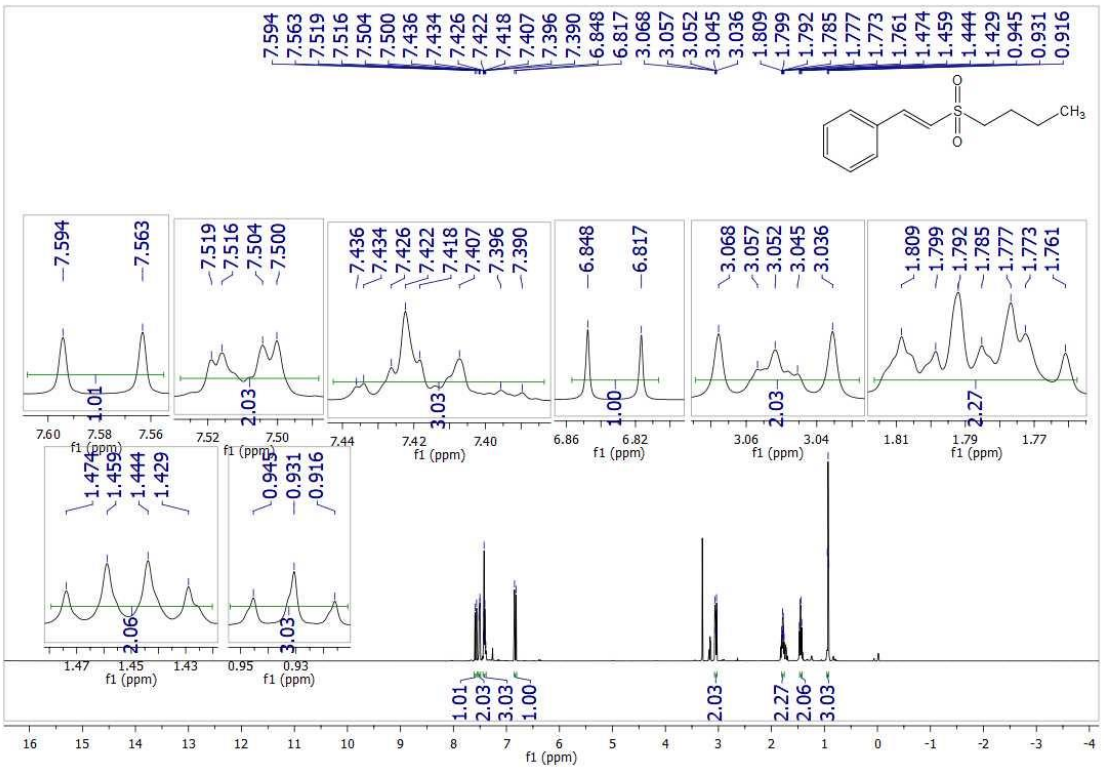
^{13}C NMR (125 MHz, $CDCl_3$) of compound **48**.



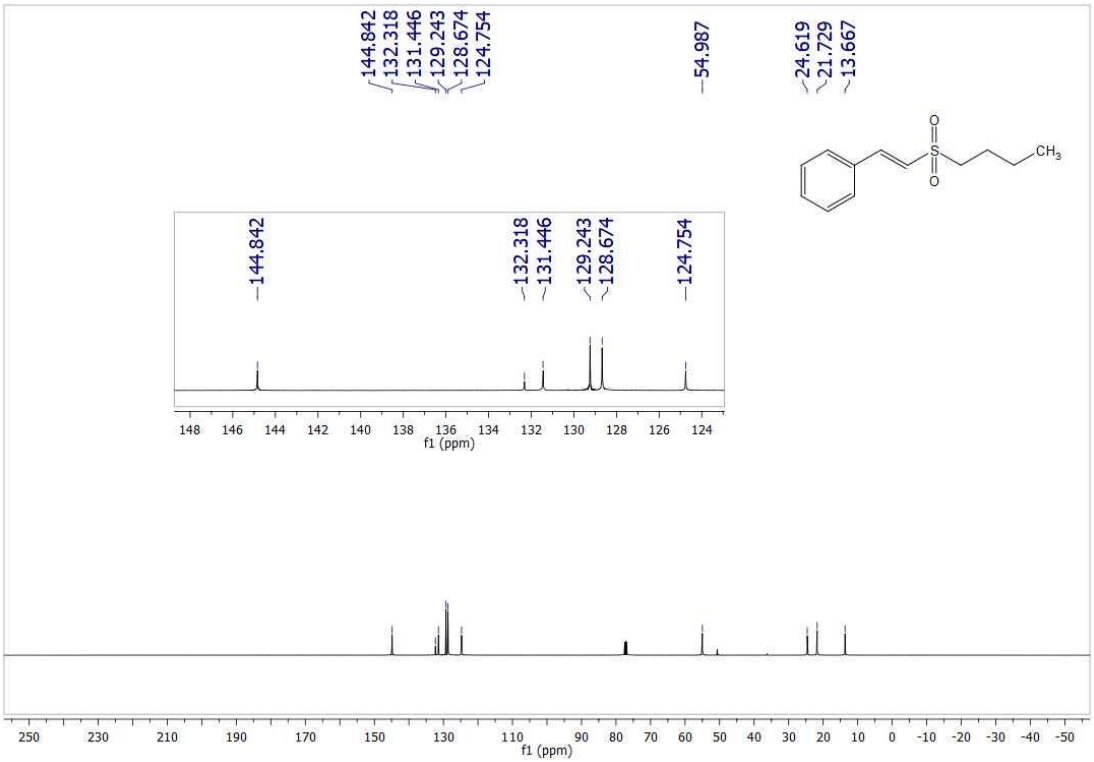
^{1}H NMR (500 MHz, $CDCl_3$) of compound **49**.



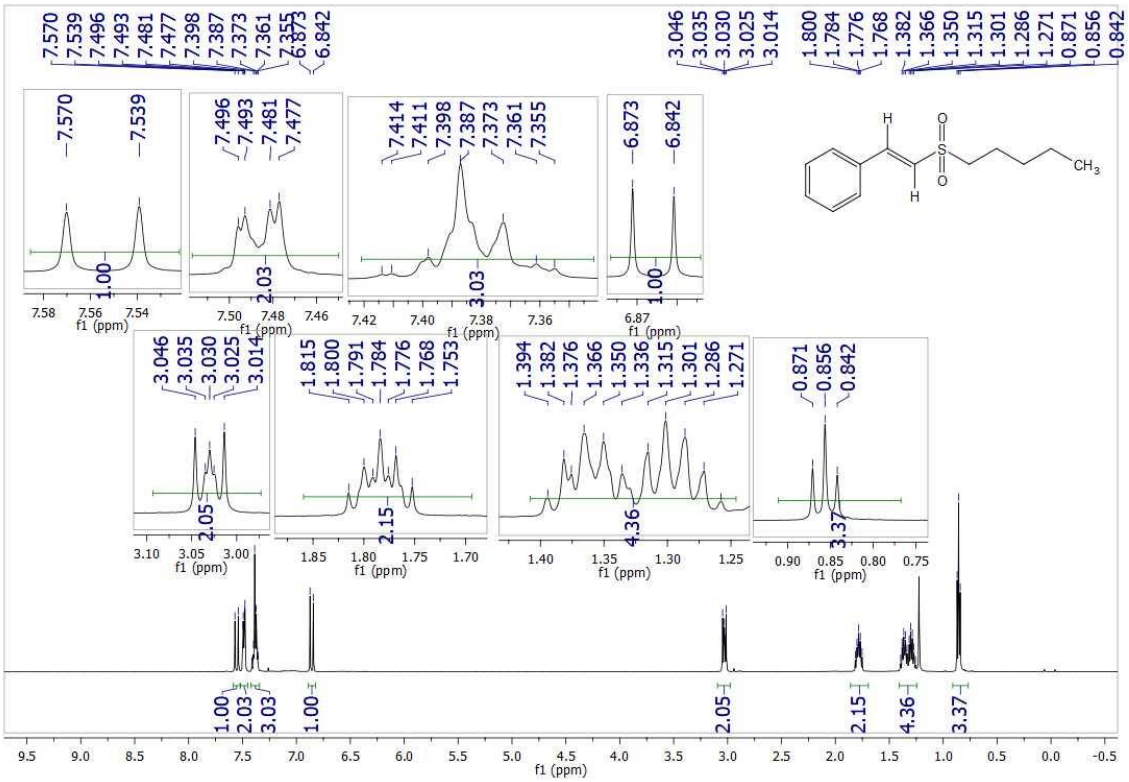
^{13}C NMR (125 MHz, $CDCl_3$) of compound **49**.



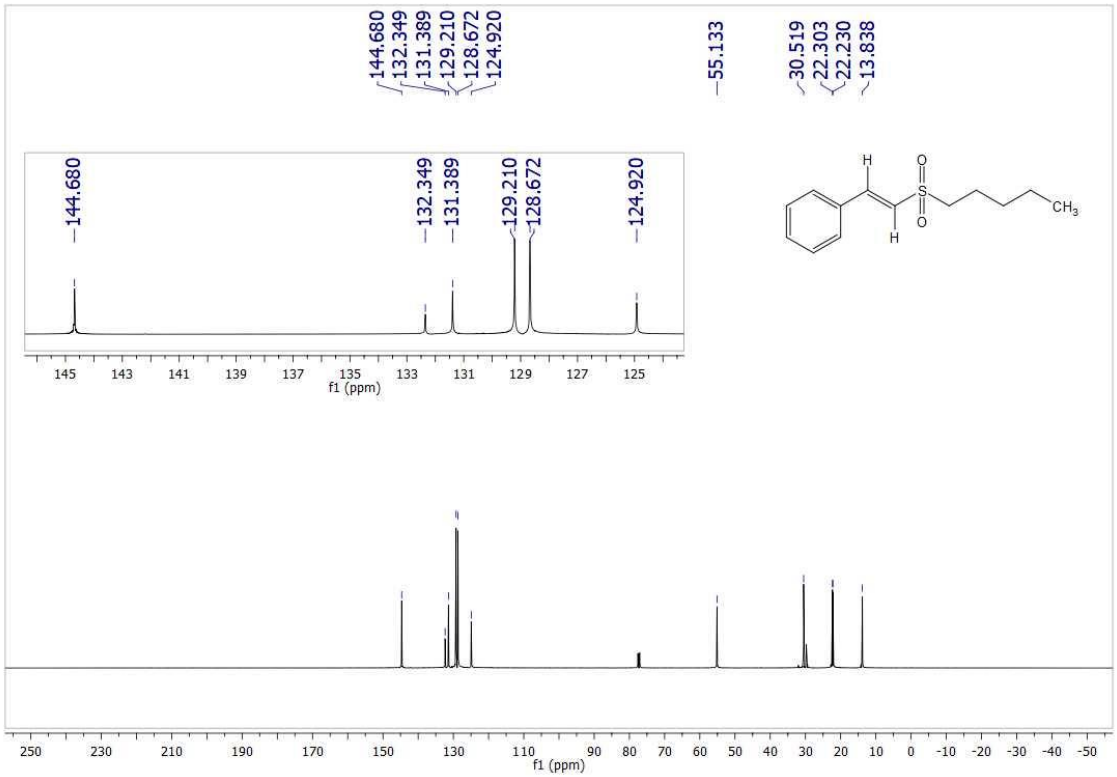
^{1}H NMR (500 MHz, $CDCl_3$) of compound **50**.



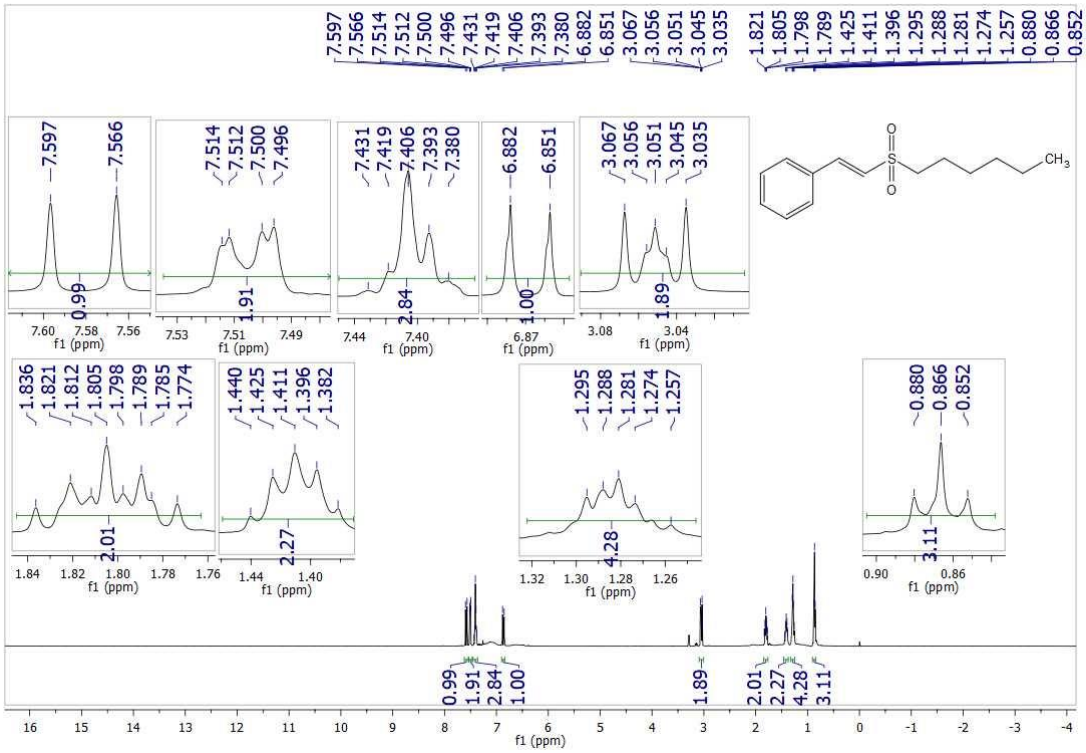
^{13}C NMR (125 MHz, $CDCl_3$) of compound **50**.



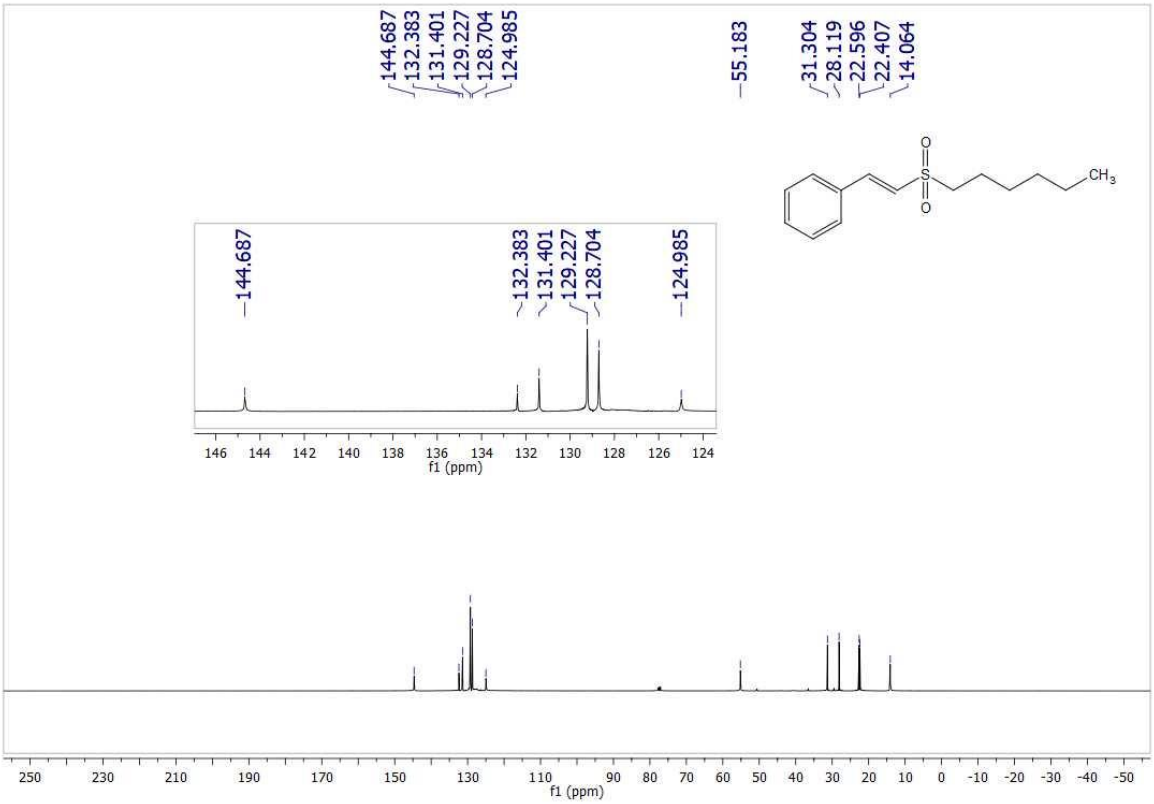
^{1}H NMR (500 MHz, $CDCl_3$) of compound **51**.



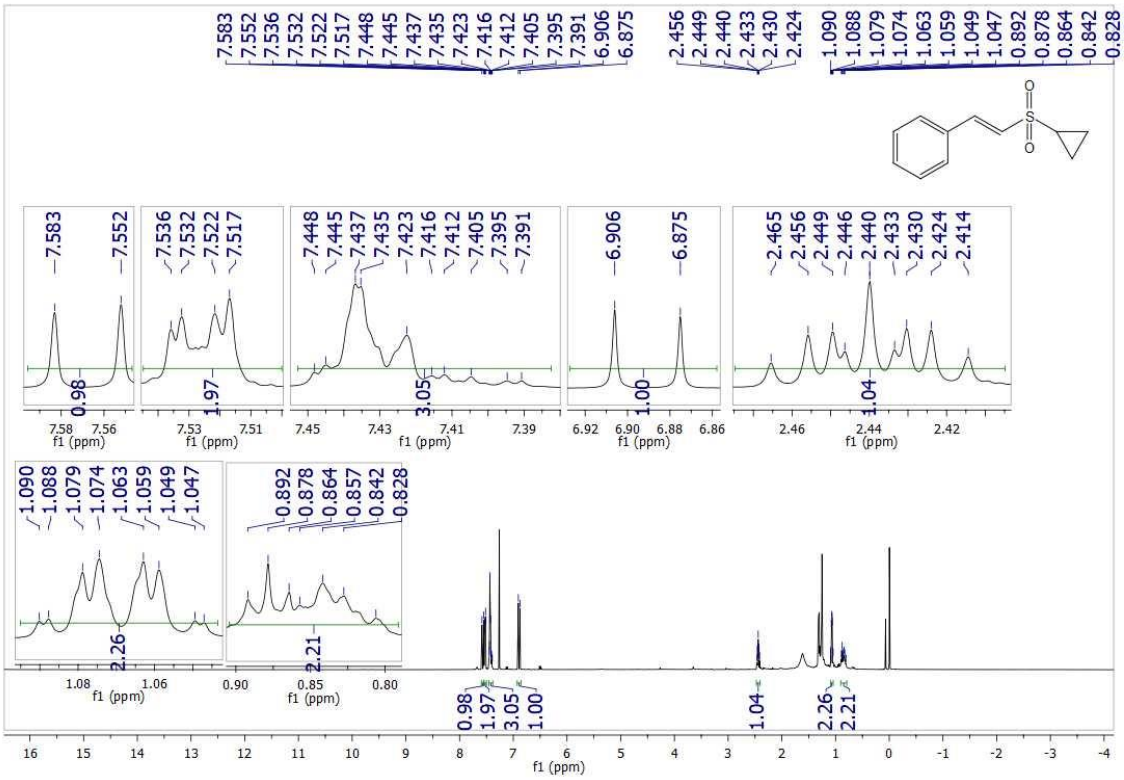
^{13}C NMR (125 MHz, $CDCl_3$) of compound **51**.



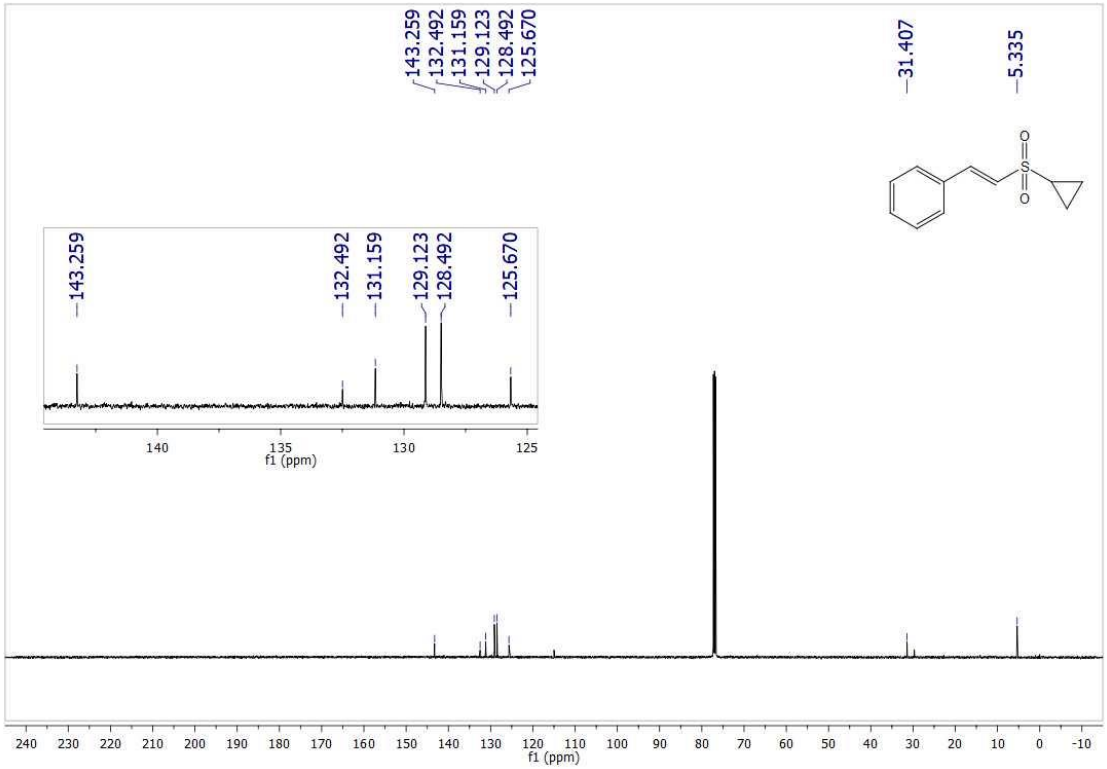
^{1}H NMR (500 MHz, $CDCl_3$) of compound **52**.



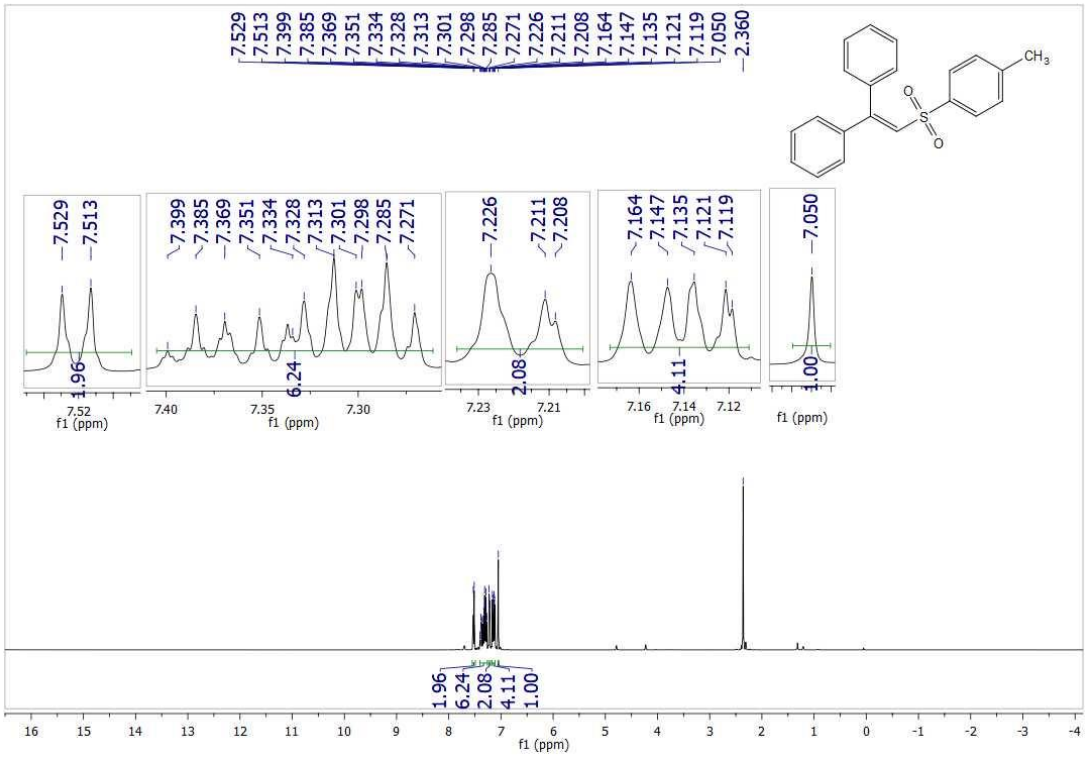
^{13}C NMR (125 MHz, $CDCl_3$) of compound **52**.



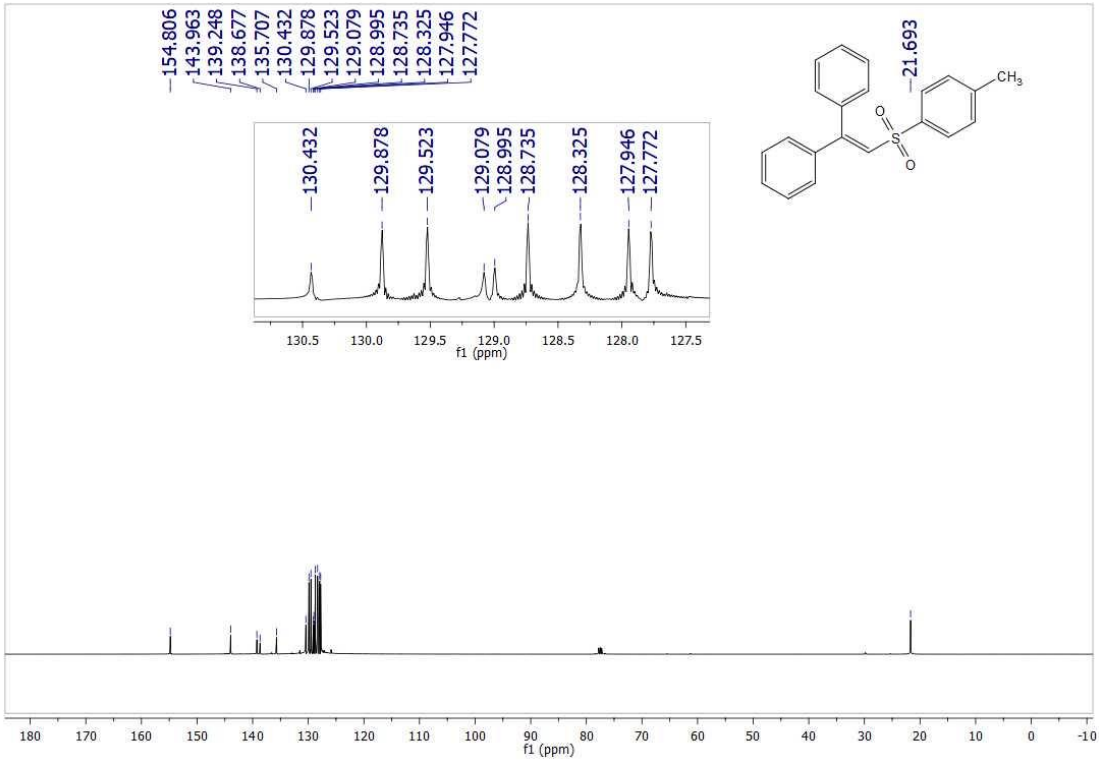
^{1}H NMR (500 MHz, $CDCl_3$) of compound **53**.



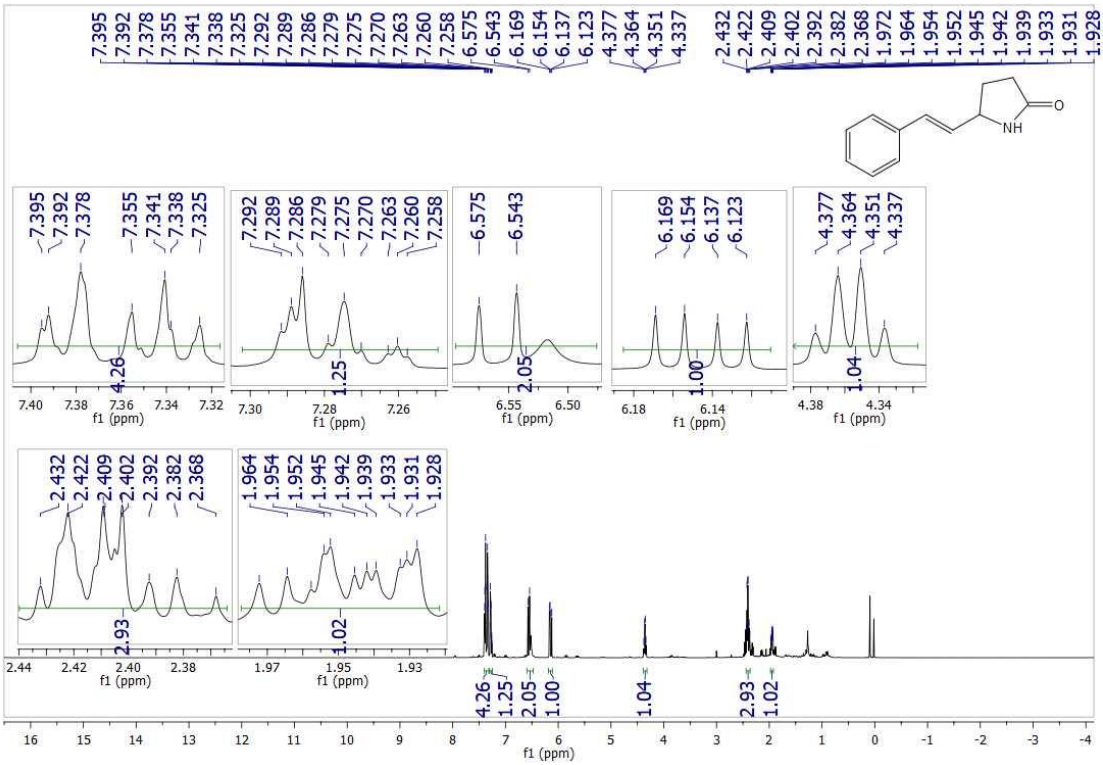
^{13}C NMR (125 MHz, $CDCl_3$) of compound **53**.



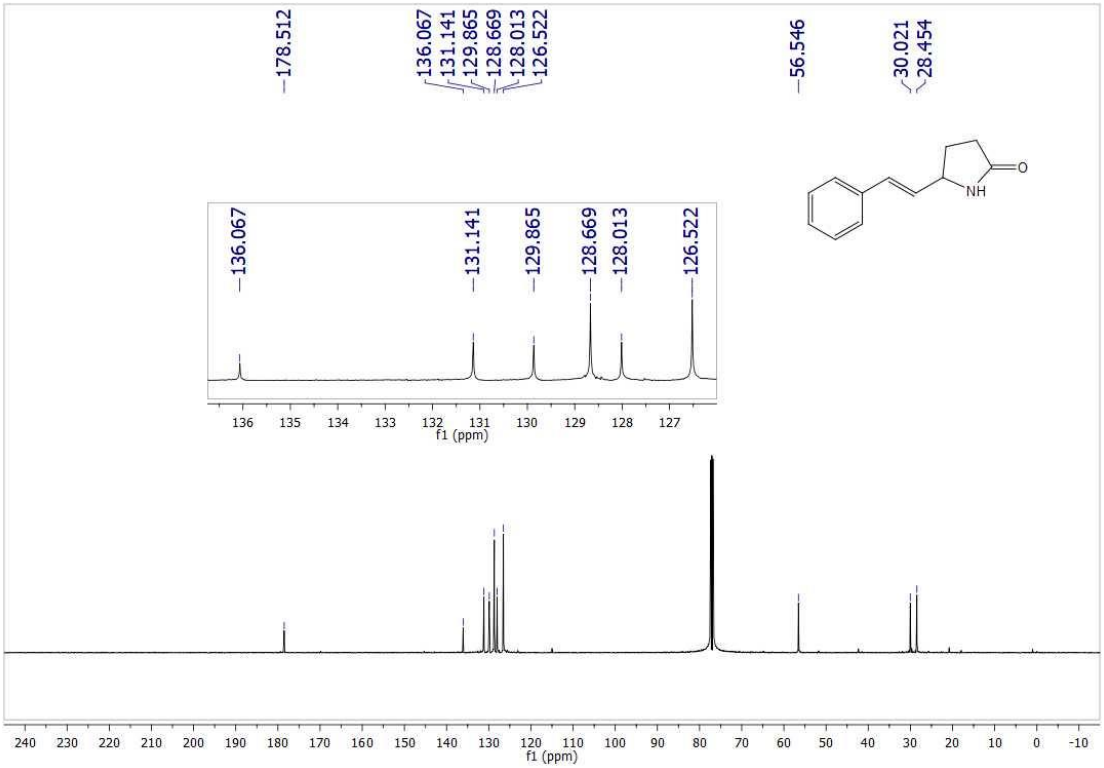
^{1}H NMR (500 MHz, $CDCl_3$) of compound **55**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **55**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **56**.



^{13}C NMR (125 MHz, $CDCl_3$) of compound **56**.

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