

Supporting Information

Copper-catalyzed Difunctionalization of Allenes with Sulfonyl Iodides Leading to (*E*)- α -Iodomethyl Vinylsulfones

Ning Lu^a, Zhiguo Zhang,^{*a} Guisheng Zhang,^{*a} Nana Ma, Conghui Wu^a, Qingfeng Liu^a, Tongxin Liu^a

^a Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Key Laboratory of Organic Functional Molecule and Drug Innovation, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, 453007, China. Fax: (+86)-373-332-5250; E-mail: zgs6668@yahoo.com or zhangzg@htu.edu.cn

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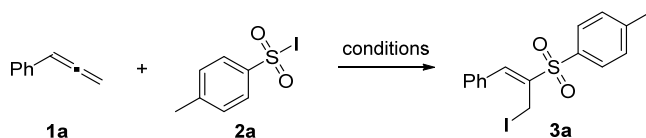
I. General Remarks:

All reactions were carried out at 25 °C, unless otherwise indicated. All other reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Petroleum ether (PE) used here refers to the 60-90 °C boiling point fraction of petroleum. Ethyl acetate is abbreviated as EA. ¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance/600 (¹H: 600 MHz, ¹³C: 150 MHz at 25 °C) or Bruker Avance/400 (¹H: 400 MHz, ¹³C: 100 MHz at 25 °C) and tetramethylsilane as the internal standard. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, and m = multiplet), and coupling constants in Hertz (Hz). All high-resolution mass spectra (HRMS) were measured on a mass spectrometer by using electrospray ionization orthogonal acceleration time-of-flight (ESI-oe-TOF), and the purity of all samples used for HRMS (>95%) was confirmed by ¹H NMR and ¹³C NMR spectroscopic analysis. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All reactions were monitored by thin-layer chromatography (TLC) with GF254 silica gel-coated plates, and in general, it was designated as the end of the reaction when the starting material **2** was consumed. Flash chromatography was carried out on SiO₂ (silica gel 60–100 mesh).

II. Screening reaction conditions.

Propa-1,2-dienylbenzene (**1a**) and *p*-toluenesulfonyl iodide (**2a**) was selected as a model substrate to explore the optimal conditions for this reaction. The key experiments are summarized in Table S1. In the beginning, 48% of product (*E*)-1-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (**3a**) were isolated when we treated the mixture of **1a** and **2a** with 0.2 equiv of CuI and 0.5 equiv of 1,10-phen in dichloromethane (DCM) solvent at 25 °C for 0.5 h (Table S1, entry 1). Next, 0.4 equiv of CuI was employed to the reaction, to our delight, the desired product **3a** was obtained in 70% yield, without the isolation of other isomers (Table S1, entry 2). However, increasing the amount of CuI to 0.6 equiv could not further enhance the yield of **3a** (Table S1, entry 3). The conversion proceeds not well if the reaction was performed in the absence of CuI (Table S1, entry 4).^[1] Furthermore, decreasing the amount of 1,10-phen resulted in a lower yield of **3a** (Table S1, entries 5-8). Other monovalent copper salt including CuCl and CuBr gave a lower yield of **3a** (54 and 53%, respectively) than that of CuBr (Table S1, entries 9 and 10). On the other hand, lower product yields were also observed on repeating the reaction with 2,2'-bipyridine (BIPY) or pyridine additive (Table S1, entries 11 and 12). The reaction was also screened to several solvents, including MeOH, MeCN, DMSO, DMF, Et₂O, 1,4-dioxane and toluene. However, all of them were found to be much less efficient than DCM (Table S1, entries 13-19). It is noteworthy that this reaction was found to be amenable to gram-scale synthesis, as exemplified by the reaction of **1a** (0.87 g, 7.5 mmol) with **2a** (1.41 g, 5.0 mmol), which afforded **3a** in 53% yield (1.05 g, 2.6 mmol).

Table S1. Survey of the Reaction Conditions.^a

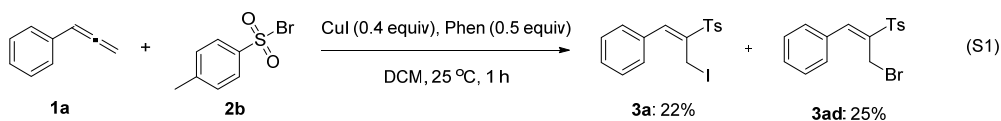


Entry	CuI (equiv)	Additive (equiv)	Solvent	Time/h	Yield of 3a /%
1	CuI (0.2)	1,10-phen (0.5)	DCM	0.5	48
2	CuI (0.4)	1,10-phen (0.5)	DCM	20 min	70

3	CuI (0.6)	1,10-phen (0.5)	DCM	15 min	66
4	CuI (0)	1,10-phen (0.5)	DCM	1	31
5	CuI (0.4)	1,10-phen (0)	DCM	1	39
6	CuI (0)	1,10-phen (0)	DCM	1	trace
7	CuI (0.4)	1,10-phen (0.2)	DCM	1	58
8	CuI (0.4)	1,10-phen (0.4)	DCM	0.5	57
9	CuCl (0.4)	1,10-phen (0.5)	DCM	1	54
10	CuBr (0.4)	1,10-phen (0.5)	DCM	1	53
11	CuI (0.4)	BIPY (0.5)	DCM	1	51
12	CuI (0.4)	Pyridine (0.5)	DCM	1	26
13	CuI (0.4)	1,10-phen (0.5)	MeOH	0.5	46
14	CuI (0.4)	1,10-phen (0.5)	MeCN	1	46
15	CuI (0.4)	1,10-phen (0.5)	DMSO	1	11
16	CuI (0.4)	1,10-phen (0.5)	DMF	1	35
17	CuI (0.4)	1,10-phen (0.5)	Et ₂ O	1	33
18	CuI (0.4)	1,10-phen (0.5)	1,4-dioxane	1	66
19	CuI (0.4)	1,10-phen (0.5)	toluene	1	42 ^b

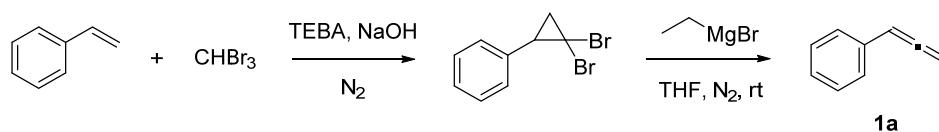
^a Unless otherwise indicated, all reactions were carried with **1a** (0.45 mmol), **2a** (0.3 mmol), CuI, and 1,10-phen in solvent in 1 mL at 25 °C. ^b Reaction was performed at 80 °C.

In order to clarify the X⁻ donors, we carried out several control experiments. We found the reaction of **1a** and **2b** afforded a mixture of **3a** and **3ad** in 22% and 25% yield, respectively. These observations indicated that the X⁻ in the product **3** might come from CuX and sulfonyl halides (eq S1).



III. Typical Experimental Procedure

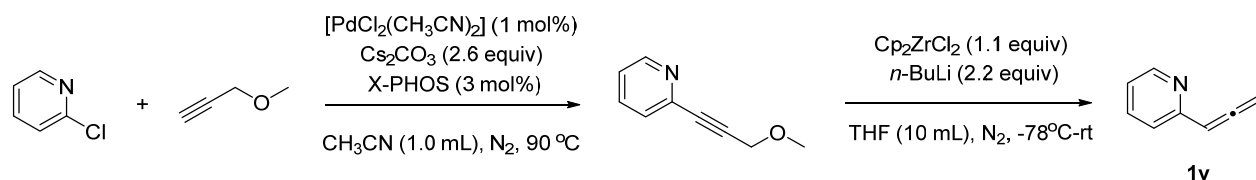
For **1** (**1a** as an example):^[2]



Step 1. Styrene (5.2 g, 50 mmol), CHBr_3 (19 g, 75 mmol) and triethylbenzylammonium chloride (125 mg, 0.5 mmol) were added to a 100 mL round-bottom flask under nitrogen atmosphere. A solution of sodium hydroxide (8 g in 8 mL of H_2O) was added dropwise to the mixture (The reaction mixture was kept below $50\text{ }^\circ\text{C}$). After all the sodium hydroxide had been added, the reaction mixture was stirred for an additional 2 hours at $60\text{ }^\circ\text{C}$. The resulting mixture was diluted by 50 mL of water and extracted with dichloromethane ($50\text{ mL} \times 3$). The combined organic layer was washed with brine, and dried with anhydrous Na_2SO_4 . After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: PE) to give (2,2-dibromocyclopropyl)benzene as a yellow oil (10.7 g, 78%).

Step 2. EtMgBr (2.0 M in THF, 1.5 equiv, 8 mL) was added dropwise to a solution of (2,2-dibromocyclopropyl)benzene (2.8 g, 10 mmol) in dry THF (20 mL) under nitrogen atmosphere at room temperature. The resulting mixture was allowed to stir at room temperature for an additional 30 minutes. Then the reaction was quenched by saturated NH_4Cl solution (25 mL), and extracted with petroleum ether ($25\text{ mL} \times 3$). The combined organic layers was washed with brine ($25\text{ mL} \times 3$), and dried with anhydrous Na_2SO_4 . After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: PE) to give propa-1,2-dien-1-ylbenzene **1a** as a yellow oil (1.1 g, 93%).

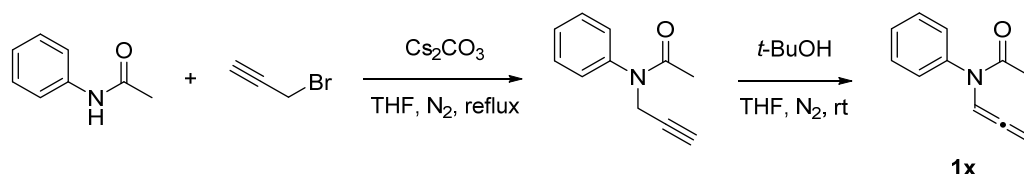
For **2-(propa-1,2-dien-1-yl)pyridine**:^[3]



Step 1. An oven dried schlenk tube was evacuated and backfilled with nitrogen (the cycle was performed twice) and then charged under a positive pressure of nitrogen with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (12 mg, 0.5 μmol), X-PHOS (66 mg, 0.14 mol), Cs_2CO_3 (3.91 g, 12 mmol), followed by anhydrous acetonitrile (10 mL) and the aryl chloride (4.62 mmol). The slightly yellow suspension was stirred for 25 min. Then the alkyne (6 mmol) was injected, the schlenk tube was sealed with a teflon valve, and the reaction mixture was stirred at the desired temperature for the indicated period of time. The resulting suspension was allowed to reach room temperature, diluted with water (3 mL), and extracted with diethyl ether (4×4 mL). The combined organic layers were dried over MgSO_4 . After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: EA/PE = 1/10) to give 2-(3-methoxyprop-1-yn-1-yl)pyridine as a brown oil (0.6 g, 82%).

Step 2. To a solution of Cp_2ZrCl_2 (0.94 g, 3.2 mmol) in THF (10 mL) was added dropwise of *n*-BuLi (6.4 mmol, 4.4 mL, 1.6 M solution in hexane) under nitrogen atmosphere at -78°C . After stirring for 1 h at the same temperature, γ -(2-pyridyl)propargyl methyl ether (2 mmol) was added and the reaction mixture was warmed up to room temperature and stirred for 3 h. The reaction was quenched with saturated NaHCO_3 solution and extracted with EA. The extract was washed with water, brine, and dried over anhydrous Na_2SO_4 . After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: EA/PE = 1/10) to give 2-(propa-1,2-dien-1-yl)pyridine as a yellow oil (0.08 g, 39%).

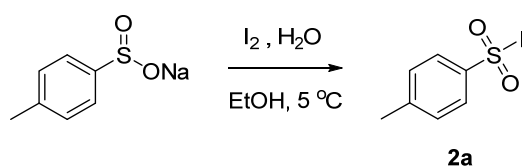
For *N*-phenyl-*N*-(propa-1,2-dien-1-yl)acetamide:^[4]



Step 1. To a schlenk tube (100 mL) were added *N*-phenylacetamide (1.4 g, 10 mmol), propargyl bromide (0.9 mL, 12 mmol), Cs₂CO₃ (4.9 g, 15 mmol) and anhydrous THF (10 mL) under nitrogen atmosphere and reflux overnight (the whole process was closely monitored by TLC). After the completion of the reaction, the reaction was quenched by water (20 mL), the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na₂SO₄. After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: EA/PE = 1/10) to give *N*-phenyl-*N*-(prop-2-yn-1-yl)acetamide as a yellow solid (1.0 g, 58%).

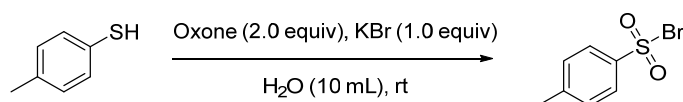
Step 2. To a schlenk tube (50 mL) were added *N*-phenyl-*N*-(prop-2-yn-1-yl)acetamide (5 mmol), *t*-BuOK (0.17 g, 1.5 mmol) and anhydrous THF (3 mL) at room temperature (the whole process was closely monitored by TLC). After the completion of the reaction, the reaction was quenched by water (20 mL), the mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na₂SO₄. After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: EA/PE = 1/10) to give *N*-phenyl-*N*-(propa-1,2-dien-1-yl)acetamide as a yellow solid (0.6 g, 74%).

For **2** (**2a** as an example):^[5]



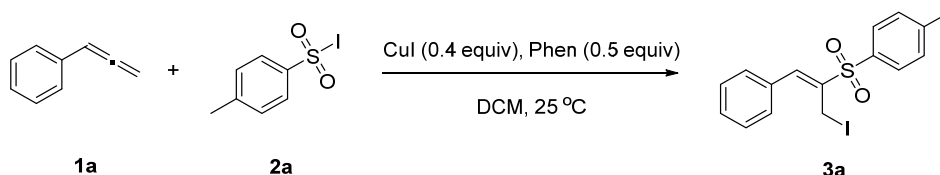
To a round-bottom flask (100 mL) was added sodium *p*-tolylsulfinate (2.5g, 14 mmol), dissolved in 50 mL of distilled water at room temperature. A saturated solution of iodine (2.1 g, 11.2 mmol) in alcohol (10 mL) was prepared and added gradually to the sodium *p*-tolylsulfinate solution until a slight excess of iodine was present. During this period, the yellow precipitate was formed gradually. The precipitate was filtered, washed with cold water, and dried carefully at room temperature to give *p*-toluenesulfonyl iodide **2a** as a yellow solid (3.6 g, 91%).

For **4-methylbenzenesulfonyl bromide**:^[6]



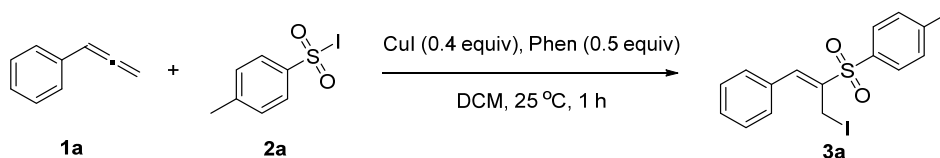
To a round-bottom flask (50 mL) was added 4-methylbenzenethiol (3.4 mmol), oxone (8.6 mmol), KBr (3.4 mmol), and water (10 mL) at room temperature (the whole process was closely monitored by TLC). After the completion of the reaction, the reaction mixture was extracted with ethyl acetate (4 × 5 mL). The combined organic layers were dried over Na₂SO₄. After filtration and concentration, the crude product was purified by a short flash silica gel column chromatography (eluent: PE) to give 4-methylbenzenesulfonyl bromide as a yellow solid (0.4 g, 50%)

For **3** (**3a** as an example):



To a round-bottom flask (25 mL) were added propa-1,2-dienylbenzene **1a** (52 mg, 0.45 mmol), *p*-toluenesulfonyl iodide **2a** (85 mg, 0.3 mmol), CuI (23 mg, 0.12 mmol), Phen (27 mg, 0.15 mmol), the mixture was well stirred for 20 min in DCM (1.0 mL) at 25 °C (the whole process was closely monitored by TLC). After the completion of the reaction, the residue was purified by a short flash silica gel column chromatography (eluent: EA/PE = 1/50) to give (*E*)-1-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene **3a** as light yellow solid (84 mg, 70%) and the recovery of **1a** was 23%.

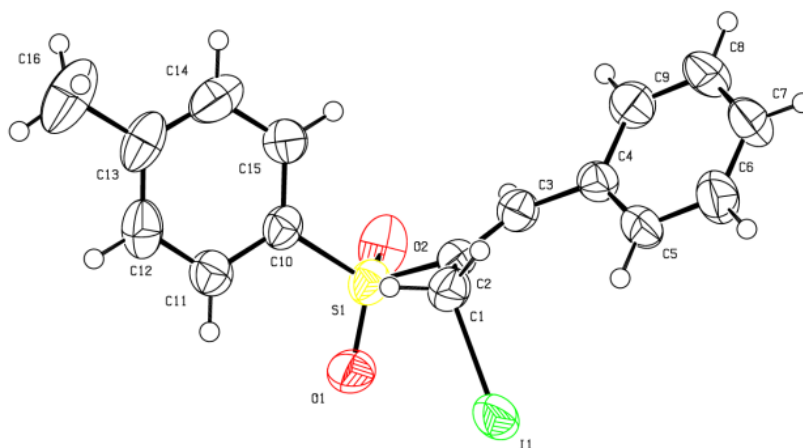
For synthetic method example, at 5 mmol scale:



To a round-bottom flask (50 mL) were added propa-1,2-dienylbenzene **1a** (0.87 g, 7.5 mmol), *p*-toluenesulfonyl iodide **2a** (1.41 g, 5.0 mmol), CuI (0.38 g, 2.0 mmol), Phen (0.45 g, 2.5 mmol), the mixture was well stirred for 1 h in DCM (5.0 mL) at 25 °C (the whole process was closely monitored

by TLC). After the completion of the reaction, the residue was purified by a short flash silica gel column chromatography (eluent: EA/PE = 1/50) to give (*E*)-1-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene **3a** as light yellow solid (1.05 g, 53%).

IV. X-ray single crystal diffraction data of **3a**.



Note: Ortep drawing of **3a** with thermal ellipsoids set at 50% probability.

Table S2. Crystal data and structure refinement for **3a**.

Identification code	3a	
Empirical formula	$\text{C}_{16}\text{H}_{15}\text{IO}_2\text{S}$	
Formula weight	398.24	
Temperature	293(2) K	
Wavelength	1.54184	
Crystal system, space group	Monoclinic, $P2_1/c$	
Unit cell dimensions	$a = 7.5922(4) \text{ \AA}$	$\alpha = 90.00 \text{ deg.}$
	$b = 37.3596(14) \text{ \AA}$	$\beta = 98.554(6) \text{ deg.}$
	$c = 5.5648(3) \text{ \AA}$	$\gamma = 90.00 \text{ deg.}$
Volume	$1560.85(13) \text{ \AA}^3$	
Z, Calculated density	4, 1.695 Mg/m^3	
Absorption coefficient	17.356 mm^{-1}	
$F(000)$	784.0	
Theta range for data collection	9.47 to 134.128 deg.	

Limiting indices	$-9 \leq h \leq 9, -41 \leq k \leq 44, -6 \leq l \leq 5$
Reflections collected / unique	5981 / 2778 [R(int) = 0.0314]
Completeness to theta = 67.031	99.9 %
Absorption correction	Empirical
Refinement method	SHELXL
Data / restraints / parameters	2778/0/182
Goodness-of-fit on F ²	1.040
Final R indices [I > 2sigma(I)]	R1 = 0.0443, wR2 = 0.1076
R indices (all data)	R1 = 0.0610, wR2 = 0.1189
Largest diff. peak and hole	0.95 and -0.63 e.Å ⁻³

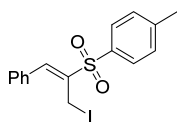
Table S3. Bond lengths [Å] and angles [deg] for **3a**.

C(1)-C(2)	1.472(7)	C(10)-C(11)	1.392(8)
C(1)-I(1)	2.171(5)	C(10)-C(15)	1.367(8)
C(2)-C(3)	1.338(7)	C(10)-S(1)	1.773(5)
C(2)-S(1)	1.772(5)	C(11)-C(12)	1.385(9)
C(3)-C(4)	1.471(7)	C(12)-C(13)	1.385(10)
C(4)-C(5)	1.380(8)	C(13)-C(14)	1.383(10)
C(4)-O(9)	1.393(7)	C(13)-C(16)	1.507(9)
C(5)-C(6)	1.381(8)	C(14)-C(15)	1.380(9)
C(6)-C(7)	1.358(9)	O(1)-S(1)	1.434(4)
C(7)-C(8)	1.383(9)	O(2)-S(1)	1.437(5)
C(8)-C(9)	1.376(8)		
C(2)-C(1)-I(1)	114.9(2)	C(15)-C(10)-S(1)	120.4(5)

C(1)-C(2)-S(3)	114.9(17)	C(12)-C(11)-C(10)	118.5(6)
C(3)-C(2)-C(1)	128.7(17)	C(11)-C(12)-C(13)	122.0(6)
C(3)-C(2)-S(1)	116.3(17)	C(12)-C(13)-C(16)	120.5(7)
C(2)-C(3)-C(4)	128.7(19)	C(14)-C(13)-C(12)	117.8(6)
C(5)-C(4)-C(3)	123.6(18)	C(14)-C(13)-C(16)	121.7(7)
C(5)-C(4)-C(9)	117.6(2)	C(15)-C(14)-C(13)	121.4(7)
C(9)-C(4)-C(3)	118.7(17)	C(10)-C(15)-C(14)	120.0(6)
C(4)-C(5)-C(6)	120.8(2)	C(3)-S(1)-C(10)	104.5(2)
C(7)-C(6)-C(5)	121.1(18)	O(1)-S(1)-C(2)	108.8(2)
C(6)-C(7)-C(8)	119.3(2)	O(1)-S(1)-C(10)	107.8(3)
C(9)-C(8)-C(7)	119.9(3)	O(1)-S(1)-O(2)	118.2(3)
C(8)-C(9)-C(4)	121.3(2)	O(2)-S(1)-C(2)	109.5(3)
C(11)-C(10)-S(1)	119.0(18)	O(2)-S(1)-C(10)	107.4(3)
C(15)-C(10)-C(11)	120.5(19)		
C(1)-C(2)-C(3)-C(4)	5.8(9)	C(11)-C(10)-C(15)-C(14)	-0.2(9)
C(1)-C(2)-S(1)-C(10)	62.9(4)	C(11)-C(10)-S(1)-C(2)	-122.8(4)
C(1)-C(2)-S(1)-O(1)	-51.8(5)	C(11)-C(10)-S(1)-O(1)	-7.2(5)
C(1)-C(2)-S(1)-O(2)	177.7(4)	C(11)-C(10)-S(1)-O(1)	121.0(5)
C(2)-C(3)-C(4)-C(5)	31.2(10)	C(11)-C(12)-C(13)-C(14)	0.3(9)
C(2)-C(3)-C(4)-C(9)	-150.4(6)	C(11)-C(12)-C(13)-C(16)	-177.2(6)
C(3)-C(2)-S(1)-C(10)	-112.6(4)	C(12)-C(13)-C(14)-C(15)	0.4(10)
C(3)-C(2)-S(1)-O(1)	132.7(4)	C(13)-C(14)-C(15)-C(10)	-0.4(10)

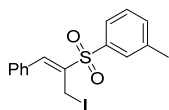
C(3)-C(2)-S(1)-O(2)	2.1(5)	C(15)-C(10)-C(11)-C(12)	0.8(8)
C(3)-C(4)-C(5)-C(6)	178.2(6)	C(15)-C(10)-S(1)-C(2)	59.9(5)
C(3)-C(4)-C(9)-C(8)	179.8(6)	C(15)-C(10)-S(1)-O(1)	175.5(5)
C(4)-C(5)-C(6)-C(7)	0.7(12)	C(15)-C(10)-S(1)-O(2)	-56.3(5)
C(5)-C(4)-C(9)-C(8)	-1.7(9)	C(16)-C(13)-C(14)-C(15)	177.9(6)
C(5)-C(6)-C(7)-C(8)	0.7(12)	I(1)-C(1)-C(2)-C(3)	-96.3(6)
C(6)-C(7)-C(8)-C(9)	-2.7(11)	I(1)-C(1)-C(2)-S(1)	88.8(4)
C(7)-C(8)-C(9)-C(4)	3.2(10)	S(1)-C(2)-C(3)-C(4)	-179.4(5)
C(9)-C(4)-C(5)-C(6)	-0.2(10)	S(1)-C(10)-C(11)-C(12)	-176.5(4)
C(10)-C(11)-C(12)-C(13)	-0.8(9)	S(1)-C(10)-C(15)-C(14)	177.1(5)

V. Analytical Data



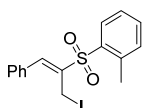
(*E*)-1-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (3a)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (84 mg, 70%). mp: 119-120 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.98 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.55-7.41 (m, 3H), 7.37 (d, *J* = 7.8 Hz, 2H), 4.30 (s, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 140.3, 138.8, 137.0, 133.2, 130.4, 130.1, 129.3, 128.8, 21.8, -5.8. HRMS (ESI), *m/z* calcd. for C₁₆H₁₅IO₂SNa ([M+Na]⁺) 420.9730, found: 420.9725.



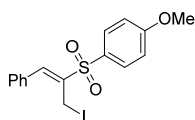
(*E*)-1-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)-3-methylbenzene (3b)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow oil (92 mg, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.78 (t, *J* = 3.5 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.54-7.36 (m, 5H), 4.30 (s, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 139.7, 138.6, 134.7, 133.1, 130.5, 129.34, 129.28, 129.1, 21.5, -5.8. HRMS (ESI), *m/z* calcd. for C₁₆H₁₅IO₂SNa ([M+Na]⁺) 420.9730, found: 420.9733.



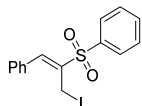
(*E*)-1-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)-2-methylbenzene (3c)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (79 mg, 66%). mp: 121-123 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.2 Hz, 1H), 8.00 (s, 1H), 7.70-7.62 (m, 2H), 7.60-7.41 (m, 5H), 7.32 (d, *J* = 7.2 Hz, 1H), 4.23 (s, 2H), 2.57 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 139.2, 137.0, 136.8, 134.3, 133.0, 132.9, 131.1, 130.5, 130.4, 129.4, 126.9, 20.0, -5.8. HRMS (ESI), *m/z* calcd. for C₁₆H₁₅IO₂SNa ([M+Na]⁺) 420.9730, found: 420.9722.



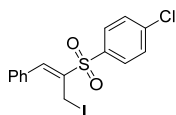
(*E*)-1-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methoxybenzene (3d)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (107 mg, 86%). mp: 130-132 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (s, 1H), 7.93-7.84 (m, 2H), 7.62 (d, J = 6.8 Hz, 2H), 7.56-7.41 (m, 3H), 7.03 (d, J = 8.8 Hz, 2H), 4.30 (s, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 139.0, 139.1, 133.3, 131.4, 131.1, 130.4, 130.3, 129.3, 114.7, 55.9, -5.7. HRMS (ESI), m/z calcd. for $\text{C}_{16}\text{H}_{15}\text{IO}_3\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 436.9679, found: 436.9677.



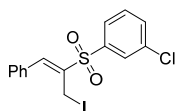
(E)-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzene (3e)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (83 mg, 72%). mp: 76-78 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.01 (s, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.67-7.63 (m, 3H), 7.58 (t, J = 7.8 Hz, 2H), 7.51-7.45 (m, 3H), 4.30 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 140.7, 140.0, 138.5, 134.0, 133.1, 130.52, 130.45, 129.44, 129.37, 128.8, -5.9. HRMS (ESI), m/z calcd. for $\text{C}_{15}\text{H}_{13}\text{IO}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 406.9573, found: 406.9563.



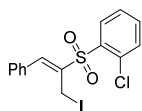
(E)-1-Chloro-4-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzene (3f)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (78 mg, 62%). mp: 117-118 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.00 (s, 1H), 7.92 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.52-7.48 (m, 3H), 4.32 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 141.1, 140.8, 138.7, 138.3, 133.0, 130.7, 130.5, 130.3, 129.8, 129.5, -5.9. HRMS (ESI), m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{ClIO}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 440.9183, found: 440.9180.



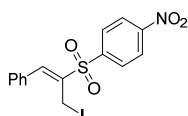
(E)-1-Chloro-3-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzene (3g)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (90 mg, 72%). mp: 131-132 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.66-7.61 (m, 3H), 7.54-7.48 (m, 4H), 4.32 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.0, 141.4, 138.0, 135.7, 134.1, 132.9, 130.8, 130.7, 130.6, 129.5, 128.9, 127.0, -6.0. HRMS (ESI), m/z calcd. for $\text{C}_{15}\text{H}_{12}\text{ClIO}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 440.9183, found: 440.9180.



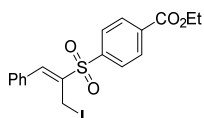
(*E*)-1-Chloro-2-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzene (3h)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (107 mg, 85%). mp: 128-129 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.33-8.30 (m, 1H), 8.12 (s, 1H), 7.67-7.65 (m, 2H), 7.63-7.58 (m, 1H), 7.56-7.48 (m, 5H), 4.28 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 136.7, 135.5, 135.2, 133.9, 133.0, 132.7, 132.3, 130.6, 130.4, 129.4, 127.6, -5.8. HRMS (ESI), *m/z* calcd. for C₁₅H₁₂ClIO₂SNa ([M+Na]⁺) 440.9183, found: 440.9187.



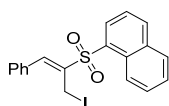
(*E*)-1-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-nitrobenzene (3i)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (103 mg, 80%). mp: 169-171 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H), 8.07 (s, 1H), 7.66-7.64 (m, 2H), 7.52 (dd, *J* = 2.0, 2.0 Hz, 3H), 4.36 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 151.0, 146.3, 142.5, 137.4, 132.6, 131.1, 130.6, 130.2, 129.6, -5.9. HRMS (ESI), *m/z* calcd. for C₁₅H₁₂INO₄SNa ([M+Na]⁺) 451.9424, found: 451.9425.



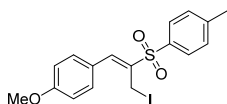
Ethyl (*E*)-4-((3-iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzoate (3j)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (94 mg, 69%). mp: 151-152 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.4 Hz, 2H), 8.07 (s, 1H), 8.04 (d, *J* = 4.0 Hz, 2H), 7.65 (d, *J* = 2.0, 1H), 7.63 (s, 1H), 7.52-7.48 (m, 3H), 4.42 (q, *J* = 7.2 Hz, 2H), 4.33 (s, 1H), 1.42 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 144.1, 141.5, 138.1, 135.4, 132.9, 130.8, 130.5, 129.5, 128.8, 62.0, 14.4, -6.0. HRMS (ESI), *m/z* calcd. for C₁₈H₁₇IO₄SNa ([M+Na]⁺) 478.9784, found: 478.9789.



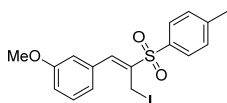
(*E*)-1-((3-Iodo-1-phenylprop-1-en-2-yl)sulfonyl)naphthalene (3k)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow oil (82 mg, 63%). ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 8.08 (s, 1H), 8.05-8.00 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.7-7.62 (m, 4H), 7.52-7.46 (m, 3H), 4.34 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 138.3, 136.0, 134.5, 133.6, 133.0, 132.2, 130.4, 129.4, 128.7, 127.1, 124.7, 124.0, -6.4. HRMS (ESI), *m/z* calcd. for C₁₉H₁₅IO₂SNa ([M+Na]⁺) 456.9730, found: 456.9728.



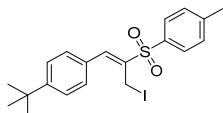
(*E*)-1-((3-Iodo-1-(4-methoxyphenyl)prop-1-en-2-yl)sulfonyl)-4-methylbenzene (3l)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (113 mg, 88%). mp: 127-129 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.33 (s, 2H), 3.87 (s, 3H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 144.7, 140.0, 137.2, 135.4, 133.0, 130.0, 128.6, 125.6, 114.85, 55.6, 21.8, -4.4. HRMS (ESI), *m/z* calcd. for C₁₇H₁₇IO₃SNa ([M+Na]⁺) 450.9835, found: 450.9835.



(*E*)-1-(3-Iodo-2-tosylprop-1-en-1-yl)-3-methoxybenzene (3m)

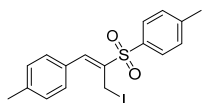
The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (99 mg, 77%). mp: 180-182 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.39-7.36 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.02-7.0 (m, 1H), 4.30 (s, 2H), 3.86 (s, 3H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 145.1, 140.3, 139.0, 137.0, 134.4, 130.4, 130.1, 128.9, 123.0, 116.8, 114.6, 55.7, 21.9, -5.7. HRMS (ESI), *m/z* calcd. for C₁₇H₁₇IO₃SNa ([M+Na]⁺) 450.9835, found: 450.9821.



(*E*)-1-(Tert-butyl)-4-(3-iodo-2-tosylprop-1-en-1-yl)benzene (3n)

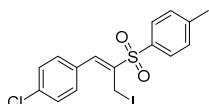
The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow oil (117 mg, 86%). ¹H NMR (400 MHz, CDCl₃) δ 8.0 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.32 (s, 2H), 2.45 (s, 3H), 1.34 (s, 9H). ¹³C

NMR (100 MHz, CDCl₃) δ 154.3, 144.9, 140.3, 137.5, 137.2, 130.7, 130.3, 130.0, 128.7, 126.4, 35.2, 31.2, 21.8, -5.0. HRMS (ESI), m/z calcd. for C₂₀H₂₄IO₂S ([M+H]⁺) 455.0536, found: 455.0528.



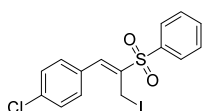
(E)-1-((3-Iodo-1-(p-tolyl)prop-1-en-2-yl)sulfonyl)-4-methylbenzene (3o)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (94 mg, 76%). mp: 182-183 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.31 (s, 2H), 2.45 (s, 3H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 144.9, 141.2, 140.4, 137.5, 137.2, 130.7, 130.4, 130.1, 130.0, 128.8, 21.8, 21.7, -5.2. HRMS (ESI), m/z calcd. for C₁₇H₁₇IO₂SNa ([M+Na]⁺) 434.9886, found: 434.9885.



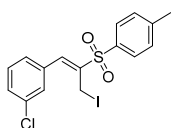
(E)-1-Chloro-4-(3-iodo-2-tosylprop-1-en-1-yl)benzene (3p)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (98 mg, 76%). mp: 198-200 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 4.25 (s, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 139.4, 138.7, 136.7, 136.6, 131.7, 131.6, 130.2, 129.7, 128.9, 21.9, -6.2. HRMS (ESI), m/z calcd. for C₁₆H₁₄ClIO₂SNa ([M+Na]⁺) 454.9340, found: 454.9347.



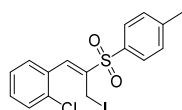
(E)-1-Chloro-4-(3-iodo-2-(phenylsulfonyl)prop-1-en-1-yl)benzene (3q)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (93 mg, 74%). mp: 120-121 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98-7.94 (m, 3H), 7.68-7.64 (m, 1H), 7.60-7.56 (m, 4H), 7.46 (d, J = 8.8 Hz, 2H), 4.26 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 139.16, 139.13, 136.7, 134.1, 131.7, 131.5, 129.7, 129.5, 128.8, -6.4. HRMS (ESI), m/z calcd. for C₁₅H₁₂ClIO₂SNa ([M+Na]⁺) 440.9183, found: 440.9181.

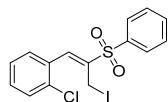


(E)-1-Chloro-3-(3-iodo-2-tosylprop-1-en-1-yl)benzene (3r)

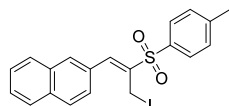
The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (80 mg, 62%). mp: 124-125 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.60 (s, 1H), 7.52-7.48 (m, 1H), 7.43 (d, *J* = 5.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.3, 140.5, 138.5, 136.6, 135.3, 134.9, 130.6, 130.3, 130.2, 130.0, 128.9, 128.1, 21.9, -6.8. HRMS (ESI), *m/z* calcd. for C₁₆H₁₄ClIO₂SNa ([M+Na]⁺) 454.9340, found: 454.9337.

**(E)-1-Chloro-2-(3-iodo-2-tosylprop-1-en-1-yl)benzene (3s)**

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (101 mg, 78%). mp: 76-78 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 4.6 Hz, 1H), 7.48-7.46 (m, 1H), 7.41-7.37 (m, 4H), 4.12 (s, 2H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 141.5, 138.1, 136.7, 134.9, 132.0, 131.1, 130.3, 130.2, 128.9, 128.7, 127.3, 21.9, -7.8. HRMS (ESI), *m/z* calcd. for C₁₆H₁₄ClIO₂SNa ([M+Na]⁺) 454.9340, found: 454.9331.

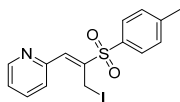
**(E)-1-Chloro-2-(3-iodo-2-(phenylsulfonyl)prop-1-en-1-yl)benzene (3t)**

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (90 mg, 72%). mp: 78-80 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.70-7.65 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.48-7.46 (m, 1H), 7.40-7.38 (m, 2H), 4.12 (s, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 141.1, 139.6, 138.4, 134.9, 134.1, 131.8, 131.2, 130.3, 129.5, 128.8, 128.7, 127.3, -7.9. HRMS (ESI), *m/z* calcd. for C₁₅H₁₂ClIO₂SNa ([M+Na]⁺) 440.9183, found: 440.9186.

**(E)-2-(3-Iodo-2-tosylprop-1-en-1-yl)naphthalene (3u)**

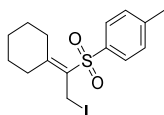
The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (74 mg, 55%). mp: 159-160 °C; ¹H NMR (600 MHz, CDCl₃) δ 8.18 (s, 1H), 8.14 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.60-7.54 (m,

2H), 7.38 (d, $J = 8.4$ Hz, 2H), 4.40 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 145.0, 140.4, 138.8, 137.1, 133.8, 133.3, 131.3, 130.7, 130.1, 129.1, 129.0, 128.9, 128.1, 128.0, 127.2, 126.6, 21.9, -5.4. HRMS (ESI), m/z calcd. for $\text{C}_{20}\text{H}_{17}\text{IO}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 470.9886, found: 470.9895.



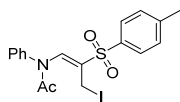
(*E*)-2-(3-iodo-2-tosylprop-1-en-1-yl)pyridine (3v)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (92 mg, 82%). mp: 104-105 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.76 (d, $J = 5.6$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.78 (s, 1H), 7.76 (m, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 1H), 5.00 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.9, 150.5, 145.1, 143.6, 136.9, 136.6, 135.5, 130.1, 129.0, 128.6, 124.0, 21.9, -5.0. HRMS (ESI), m/z calcd. for $\text{C}_{15}\text{H}_{14}\text{INO}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 421.9682, found: 421.9681.



1-((1-cyclohexylidene-2-iodoethyl)sulfonyl)-4-methylbenzene (3w)

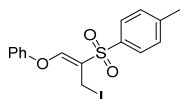
The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (40 mg, 38%). mp: 104-105 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 4.46 (s, 2H), 2.54 (t, $J = 8.0$ Hz, 2H), 2.44 (s, 3H), 2.27 (t, $J = 8.0$ Hz, 2H), 1.73-1.77 (m, 2H), 1.54-1.48 (m, 2H), 1.31-1.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 144.1, 139.8, 132.9, 129.7, 127.5, 34.5, 33.0, 27.4, 27.2, 25.8, 21.8. HRMS (ESI), m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{IO}_2\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 413.0043, found: 413.0043.



(*E*)-*N*-(3-Iodo-2-tosylprop-1-en-1-yl)-*N*-phenylacetamide (3x)

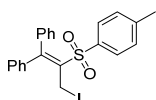
The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (115 mg, 84%). mp: 147-149 °C; ^1H NMR (600 MHz, CDCl_3) δ 8.66 (s, 1H), 7.78 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 7.2$ Hz, 3H), 7.41 (d, $J = 7.2$ Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 2H), 3.36 (s, 2H), 2.43 (s, 4H), 2.00 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 144.5, 138.4, 137.6, 136.3, 130.3, 130.2, 129.9, 129.2,

128.6, 121.4, 23.1, 21.8, -7.6. HRMS (ESI), m/z calcd. for $C_{18}H_{18}INO_3SNa$ ($[M+Na]^+$) 477.9944, found: 477.9958.



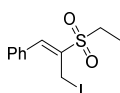
(E)-1-((3-Iodo-1-phenoxyprop-1-en-2-yl)sulfonyl)-4-methylbenzene (3y)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (71 mg, 57%). mp: 118-120 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.82 (d, J = 8.44 Hz, 2H), 7.44-7.36 (m, 4H), 7.24 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 4.15 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 154.4, 144.8, 137.4, 130.3, 130.1, 129.8, 128.4, 125.8, 122.2, 117.7, 115.4, 21.8, -10.2. HRMS (ESI), m/z calcd. for $C_{16}H_{15}IO_3SNa$ ($[M+Na]^+$) 436.9679, found: 436.9697.



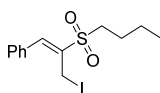
(3-Iodo-2-tosylprop-1-ene-1,1-diyl)dibenzene (3z)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (121 mg, 85%). mp: 190-191 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 7.31-7.28 (m, 2H), 7.19 (t, J = 7.4 Hz, 1H), 7.09 (t, J = 7.6 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 7.2 Hz, 2H), 4.45 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 143.7, 141.0, 140.5, 138.5, 137.6, 129.1, 128.9, 128.8, 128.3, 128.0, 127.7, 126.7, 100.1, 21.7, -0.7. HRMS (ESI), m/z calcd. for $C_{22}H_{19}IO_2SNa$ ($[M+Na]^+$) 497.0043, found: 497.0046.



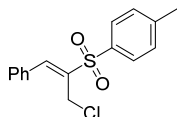
(E)-(2-(ethylsulfonyl)-3-iodoprop-1-en-1-yl)benzene (3aa)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (80 mg, 84%). mp: 97-98 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.65 (s, 1H), 7.63 (s, 1H), 7.54-7.48 (m, 3H), 4.47 (s, 2H), 3.36 (q, J = 7.6 Hz, 2H), 1.39 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 136.3, 132.9, 130.6, 130.3, 129.4, 50.5, 7.2, -3.7. HRMS (ESI), m/z calcd. for $C_{11}H_{13}IO_2SNa$ ($[M+Na]^+$) 358.9572, found: 358.9573.



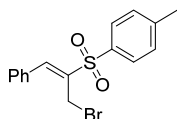
(E)-(2-(butylsulfonyl)-3-iodoprop-1-en-1-yl)benzene (3ab)

The product was isolated by flash chromatography (eluent: PE/EA = 50/1) as a light yellow solid (100 mg, 96%). mp: 47-48 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 1H), 7.65 (s, 1H), 7.64 (s, 1H) 7.55-7.48 (m, 3H), 4.48 (s, 2H), 3.35-3.31 (m, 2H), 1.84-1.76 (m, 2H), 1.55-1.46 (m, 2H), 1.00-0.94 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.7, 136.9, 133.0, 130.6, 130.4, 129.4, 55.9, 24.5, 21.7, 13.8, -3.6. HRMS (ESI), m/z calcd. for C₁₃H₁₇IO₂SNa ([M+Na]⁺) 386.9886, found: 386.9886.



(E)-1-((3-chloro-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (3ac)

The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a light yellow solid (45 mg, 49%). mp: 105-106 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.65-7.57 (m, 2H), 7.46 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 2.45 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 144.9, 143.1, 137.9, 137.2, 132.6, 130.9, 130.2, 130.0, 129.3, 128.7, 37.5, 21.8. HRMS (ESI), m/z calcd. for C₁₆H₁₅ClO₂SNa ([M+Na]⁺) 329.0373, found: 329.0367.



(E)-1-((3-bromo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (3ad)

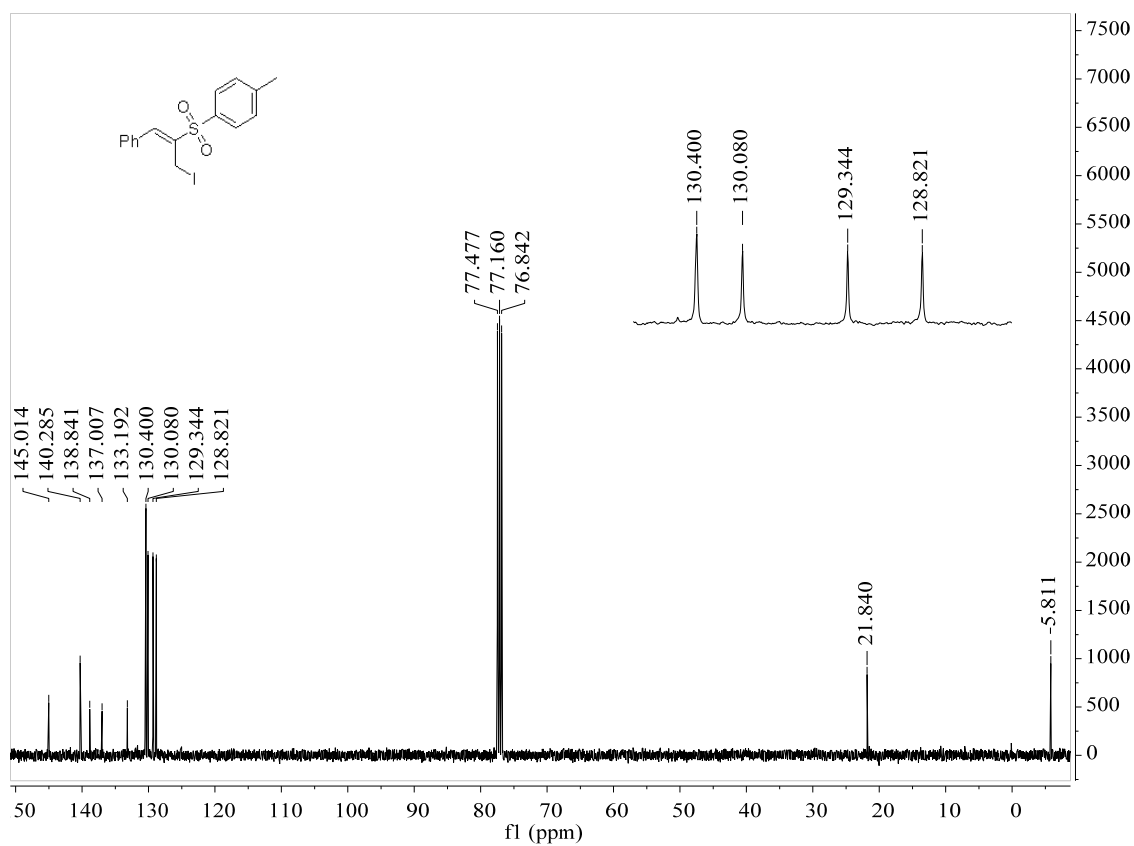
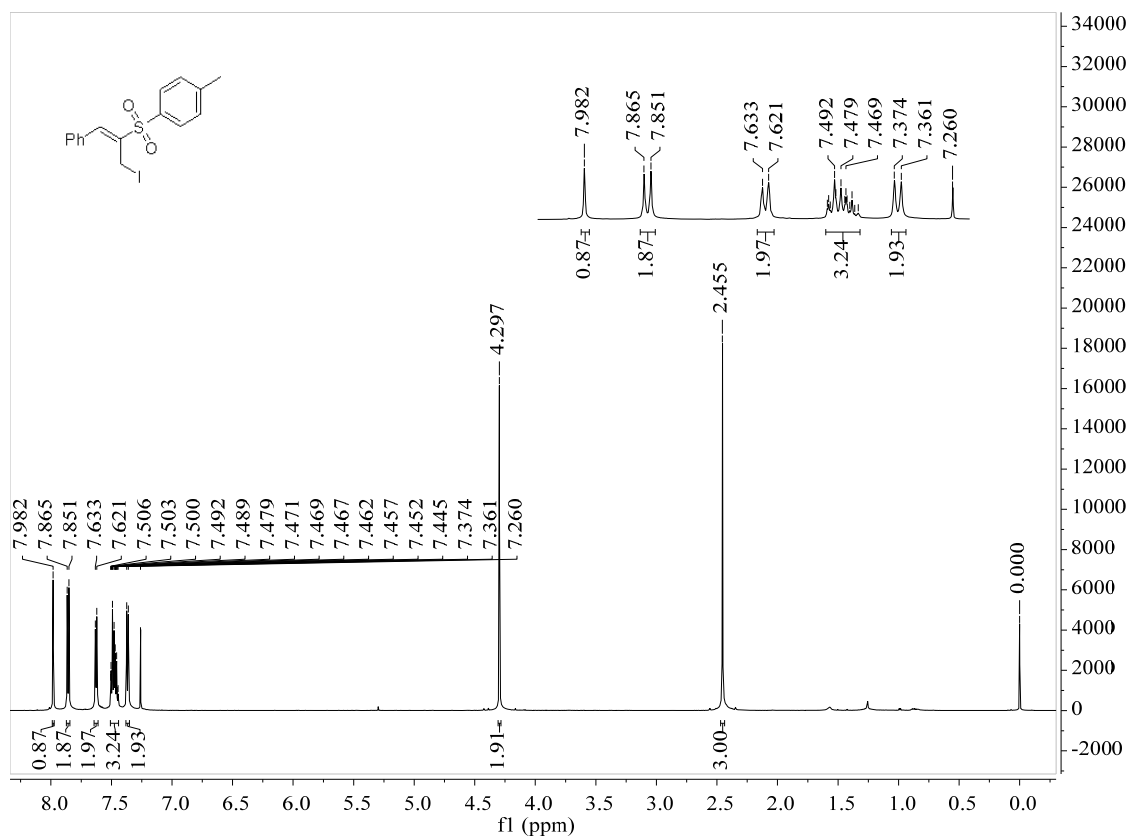
The product was isolated by flash chromatography (eluent: PE/EA = 20/1) as a light yellow solid (68 mg, 65%). mp: 102-104 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.39 (s, 2H), 2.45 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 144.9, 142.4, 138.1, 137.2, 132.8, 130.8, 130.3, 130.0, 129.3, 128.8, 23.7, 21.8. HRMS (ESI), m/z calcd. for C₁₆H₁₆BrO₂S ([M+H]⁺) 351.0049, found: 351.0050

VI. References

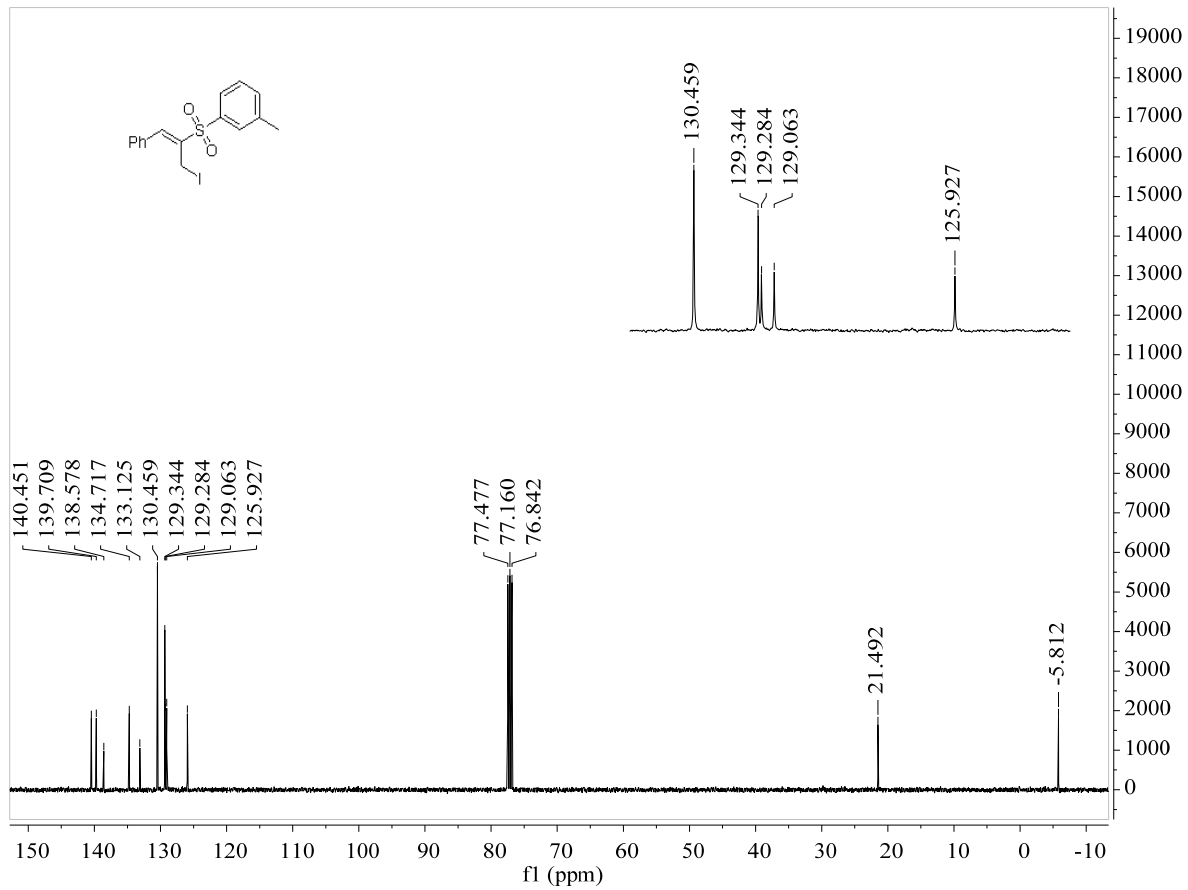
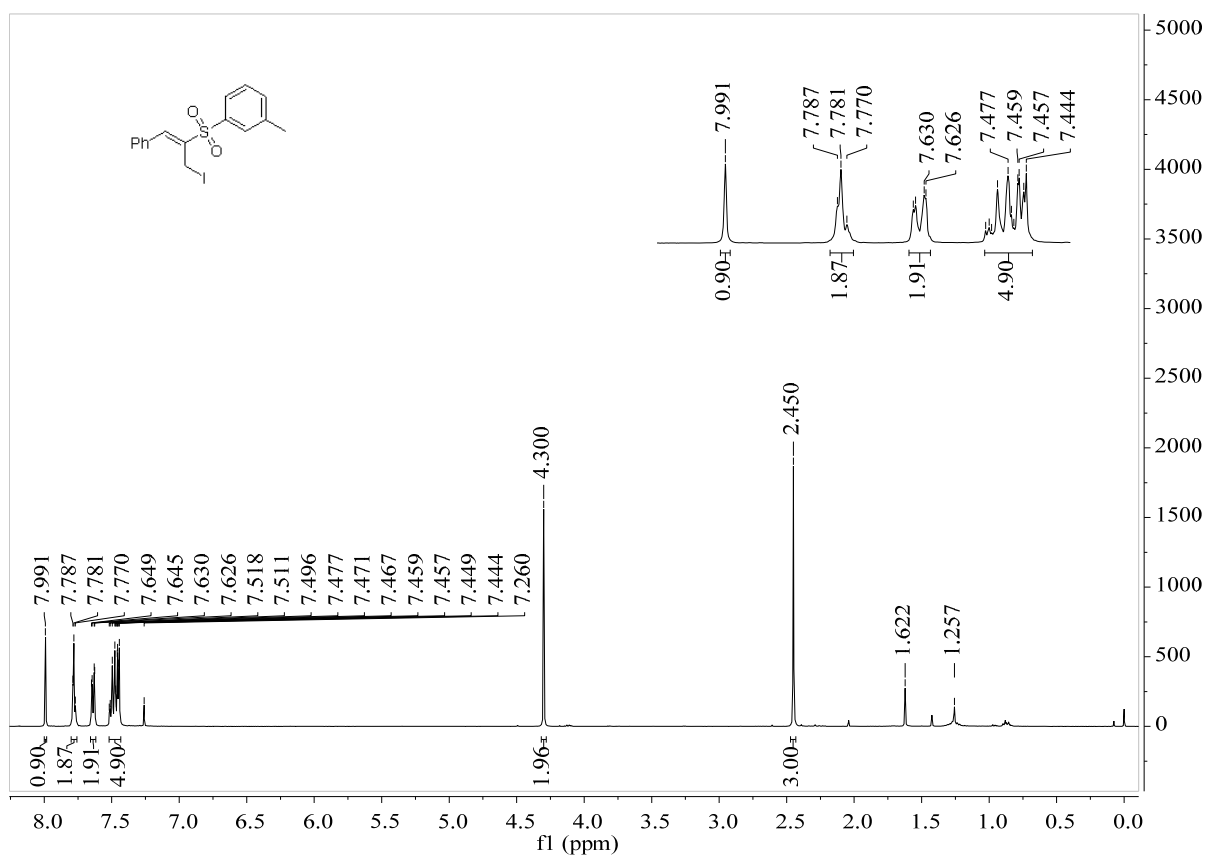
- [1] Huang, Z.; Lu, Q.; Liu, Y. *Org. Lett.*, **2016**, *18*, 3940.
- [2] J. H. Hu, Y. J. Xie, H. M. Huang. *Angew. Chem. Int. Ed.*, **2014**, *53*, 7272.
- [3] a) D. Gelman, S. L. Buchwald. *Angew. Chem. Int. Ed.*, **2003**, *42*, 5993. b) X. X. Fan, Y. H. Liu. *Organometallics.*, **2013**, *32*, 1636.
- [4] Y. Li, J. Y. Chen, R. H. Qiu. *Tetrahedron Lett.*, **2015**, *56*, 5504.
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- [6] S. Madabhushi, R. Jillella. *Green Chem.*, **2014**, *16*, 3125.

VII. ^1H NMR and ^{13}C NMR Spectra Copies

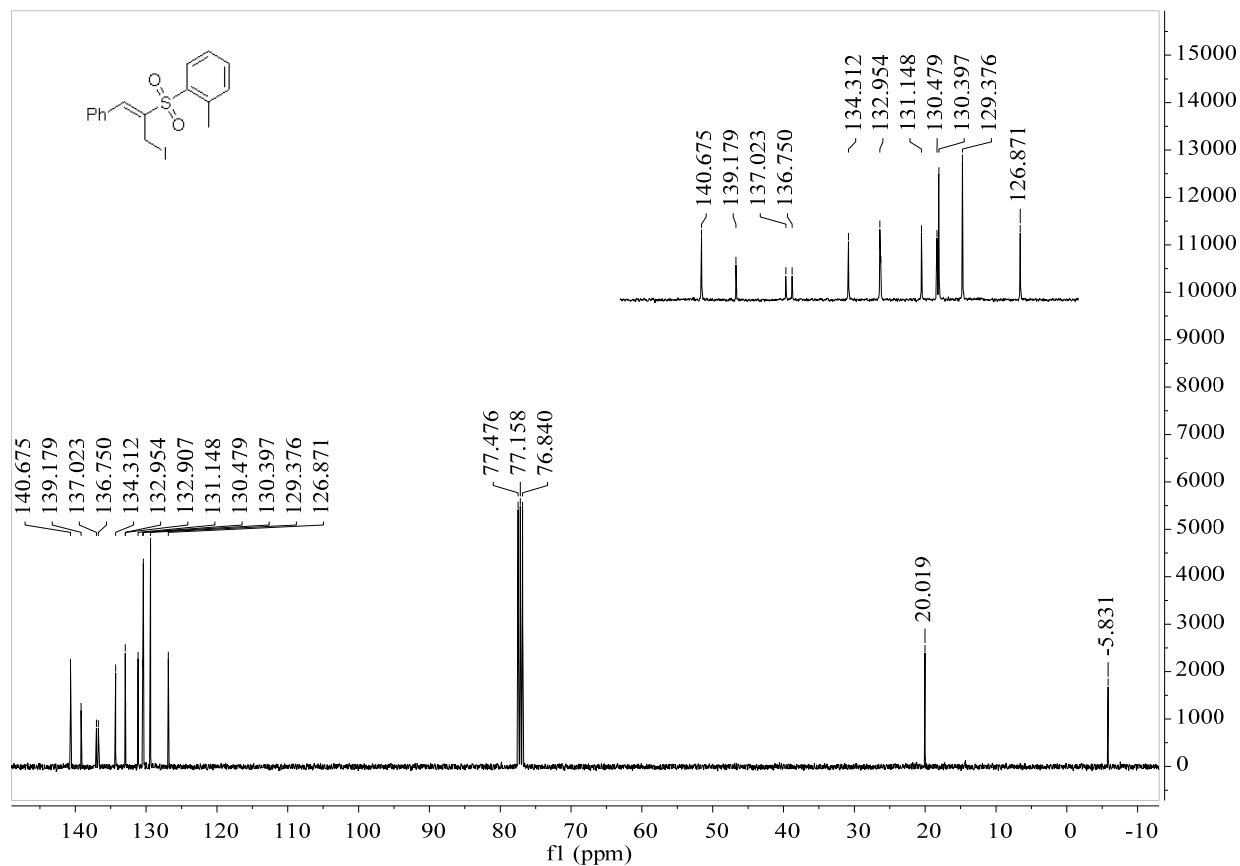
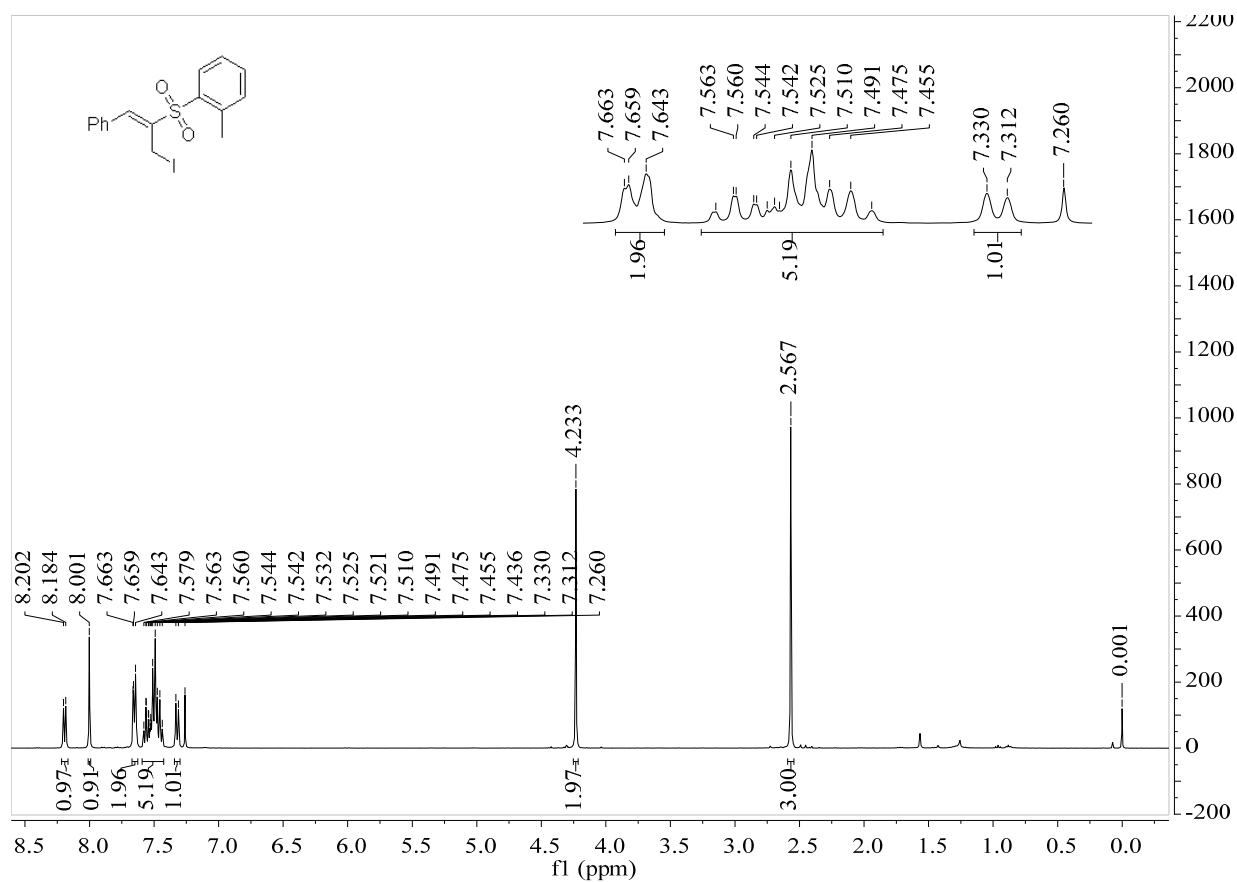
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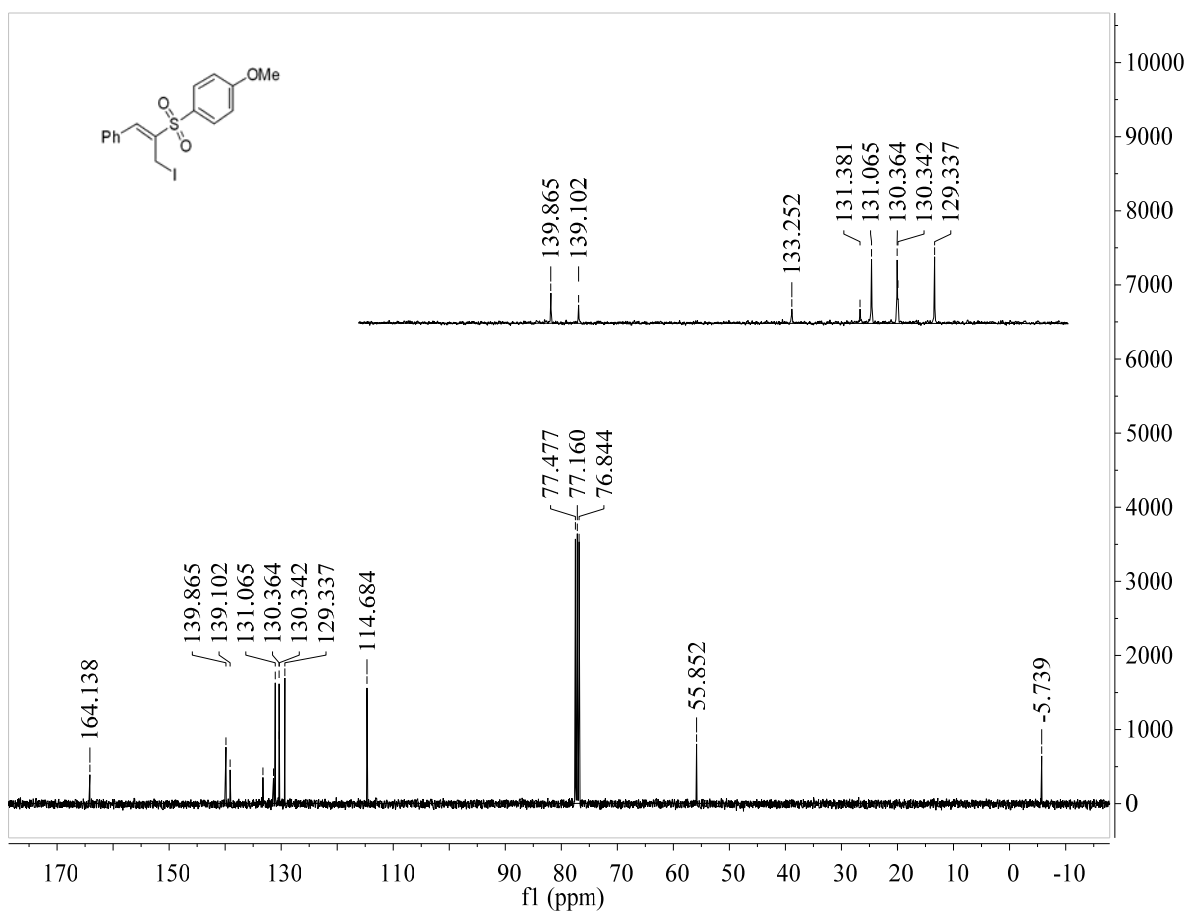
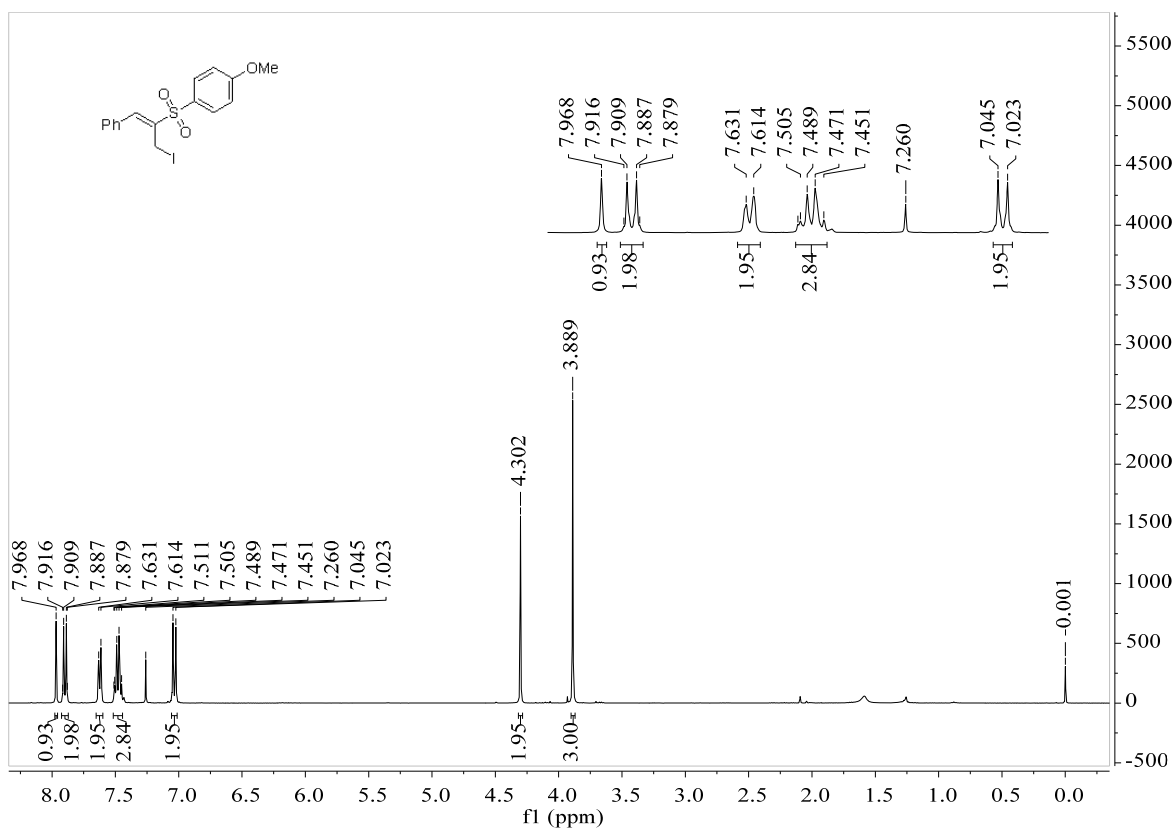
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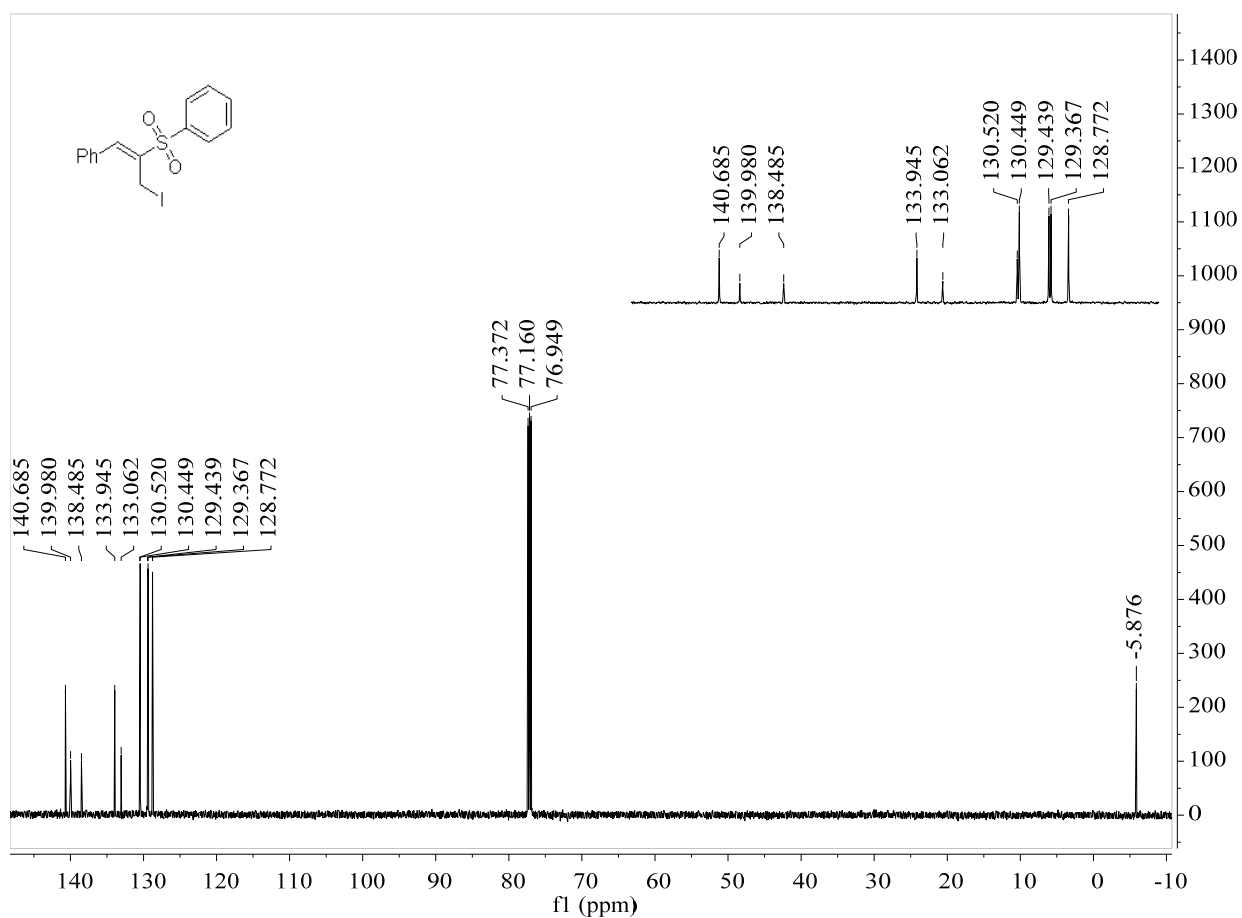
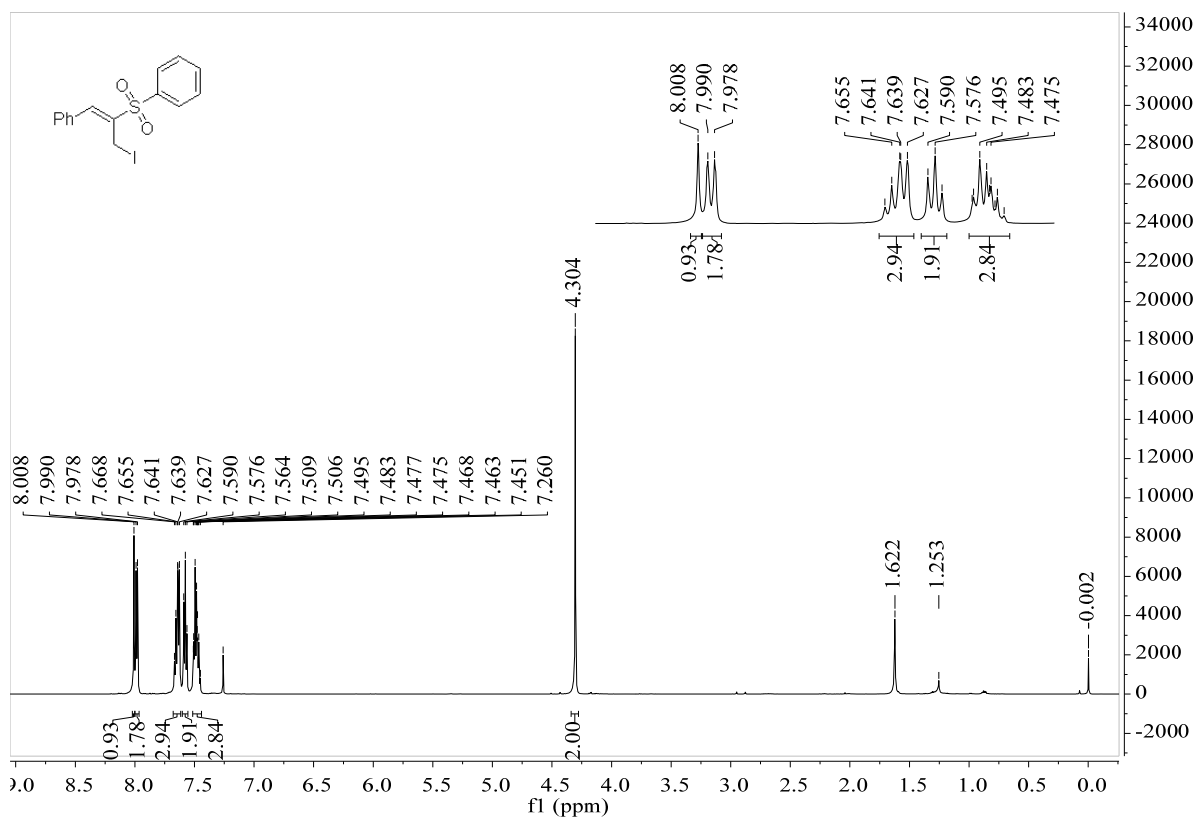
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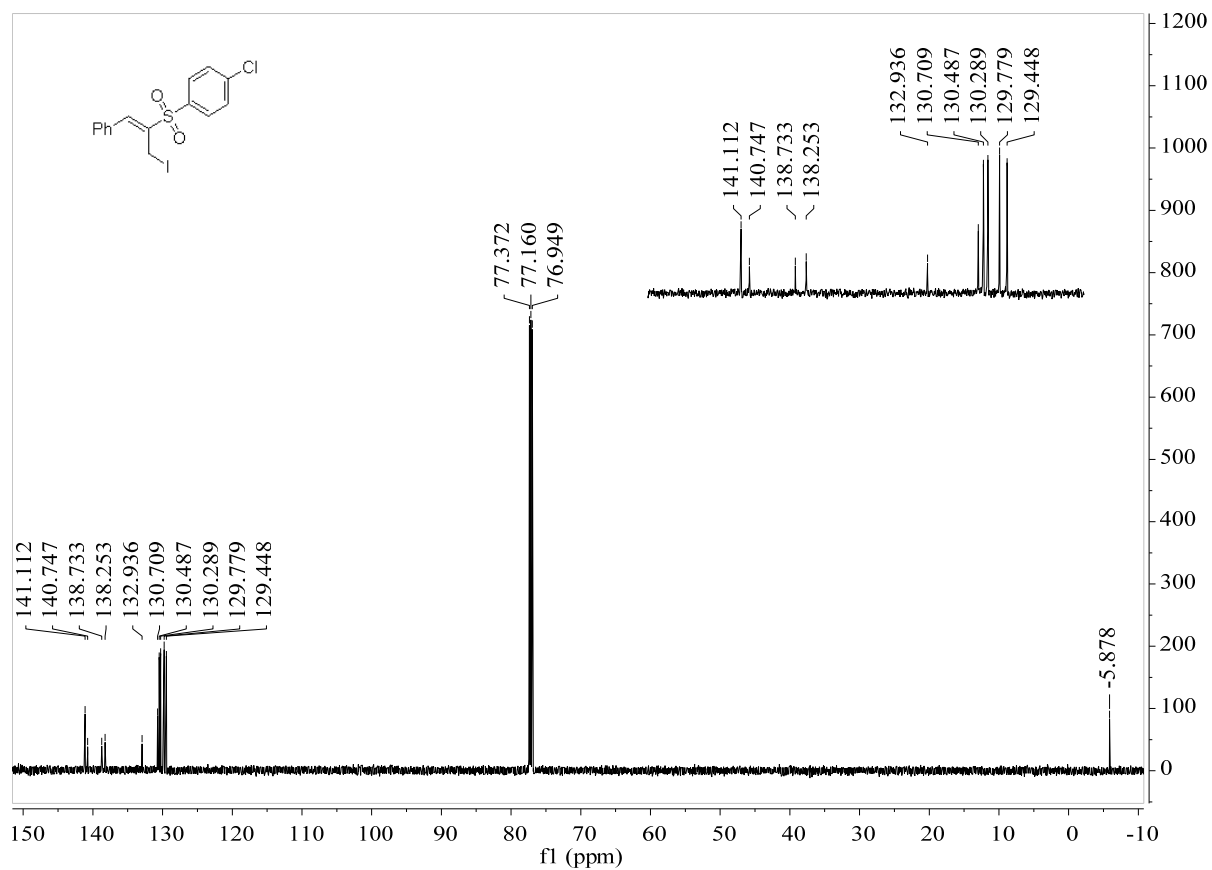
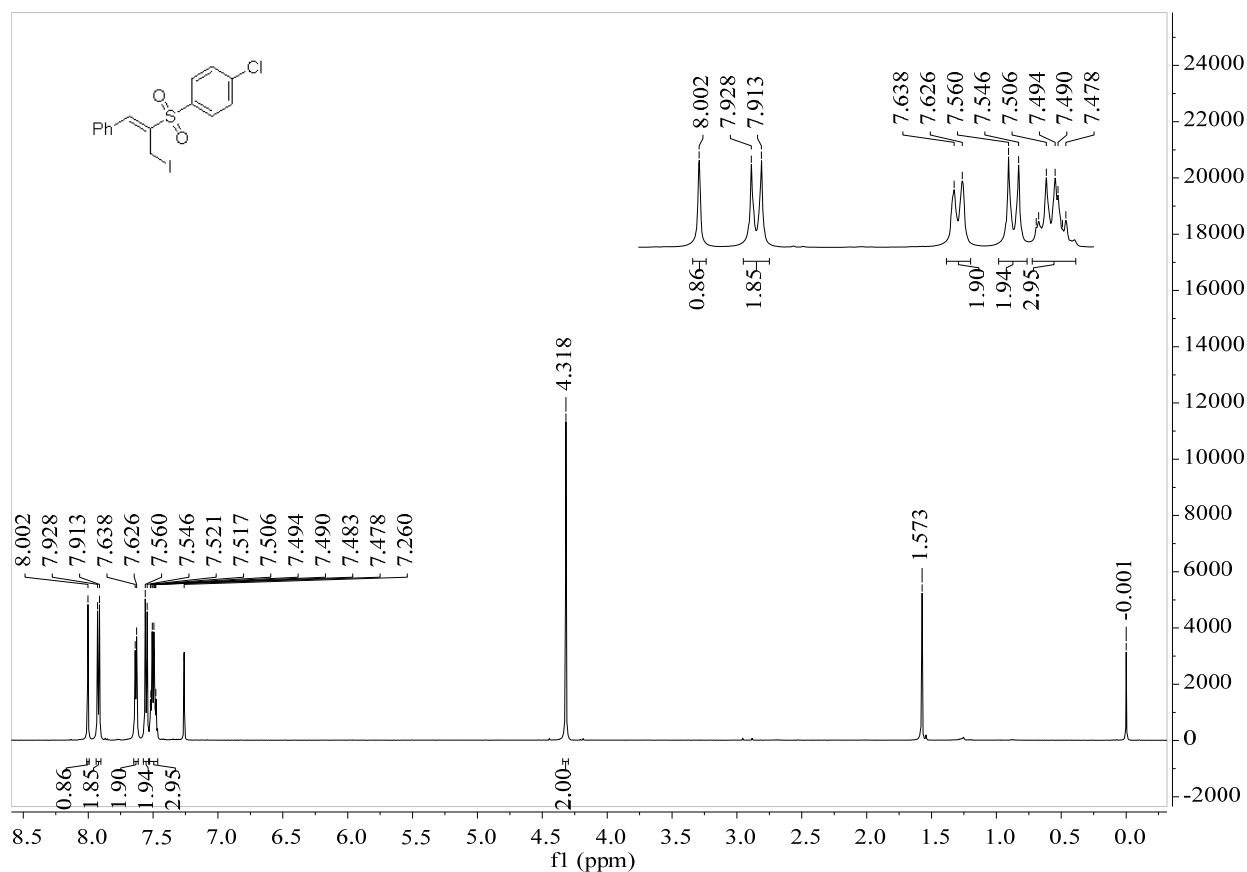
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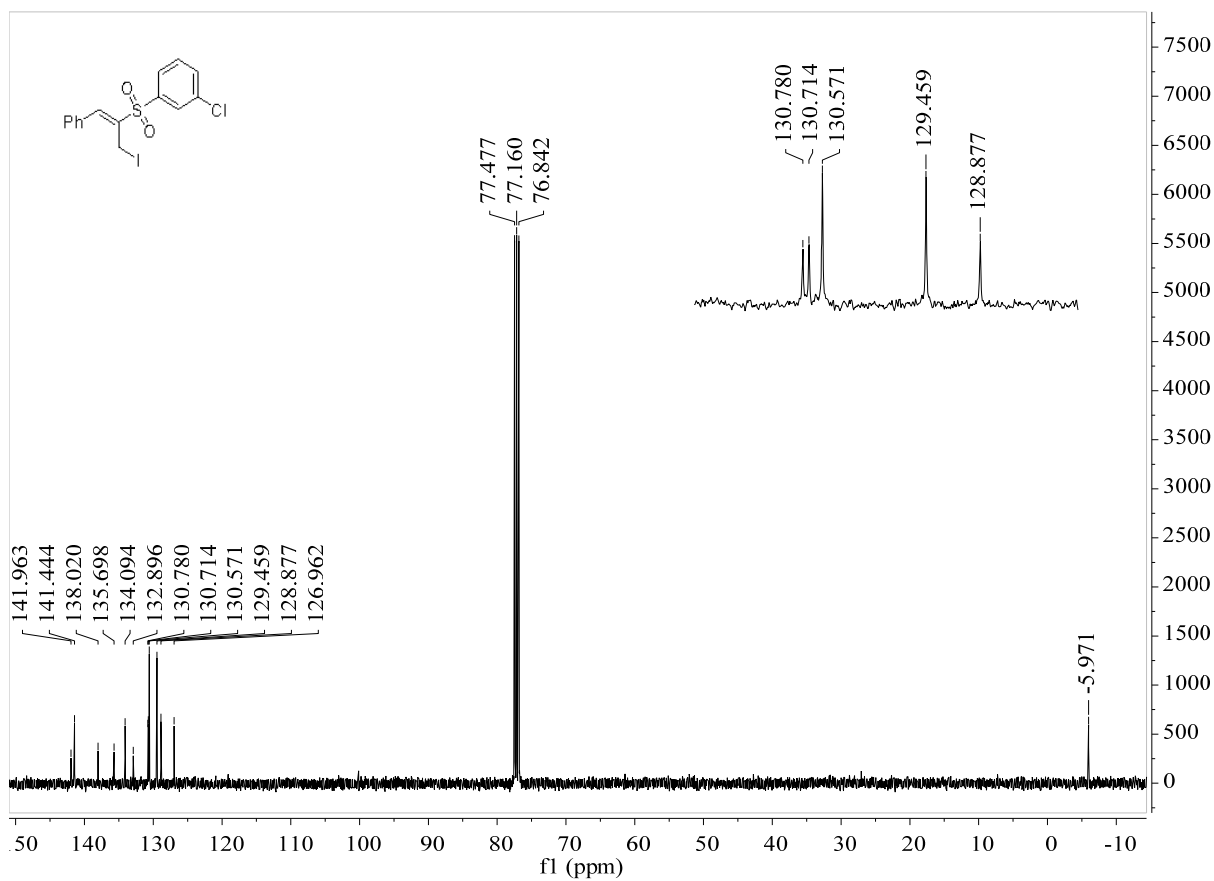
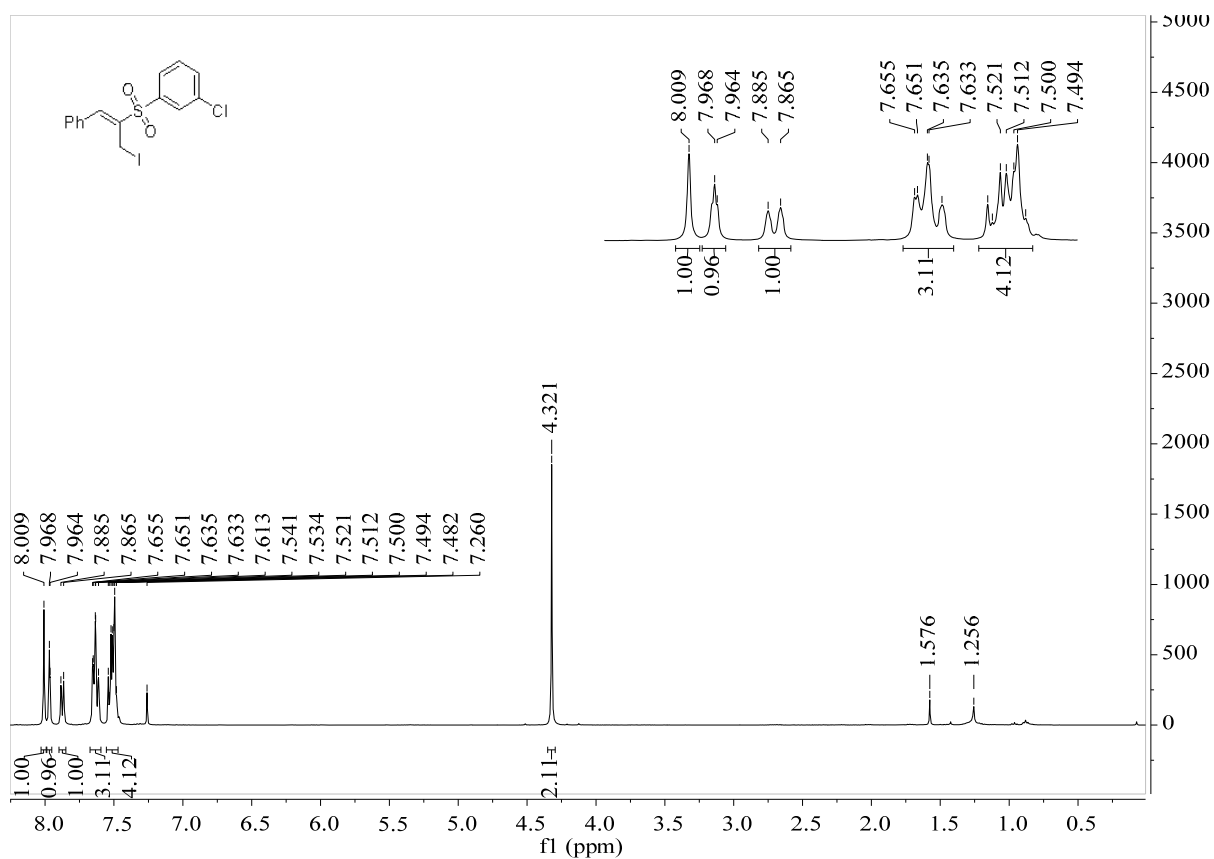
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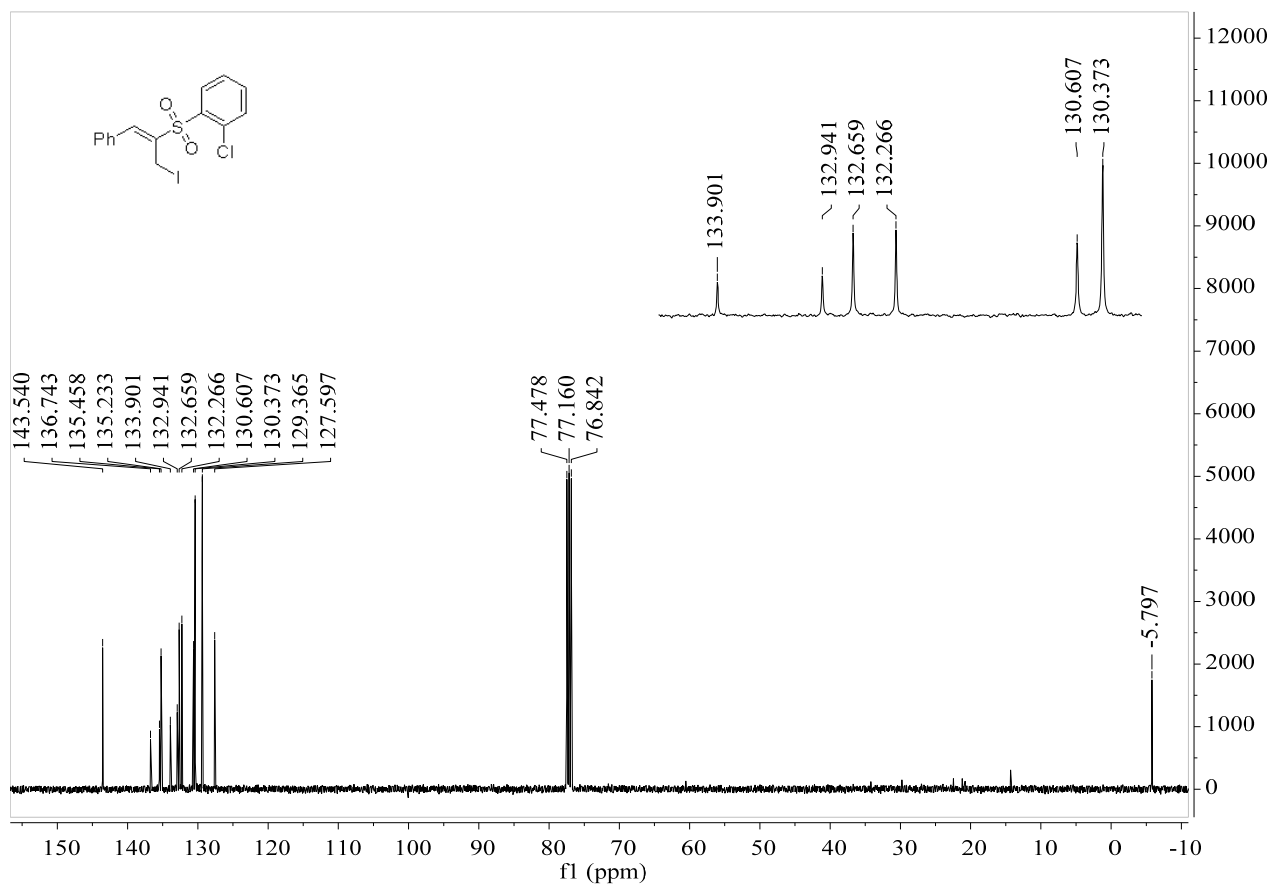
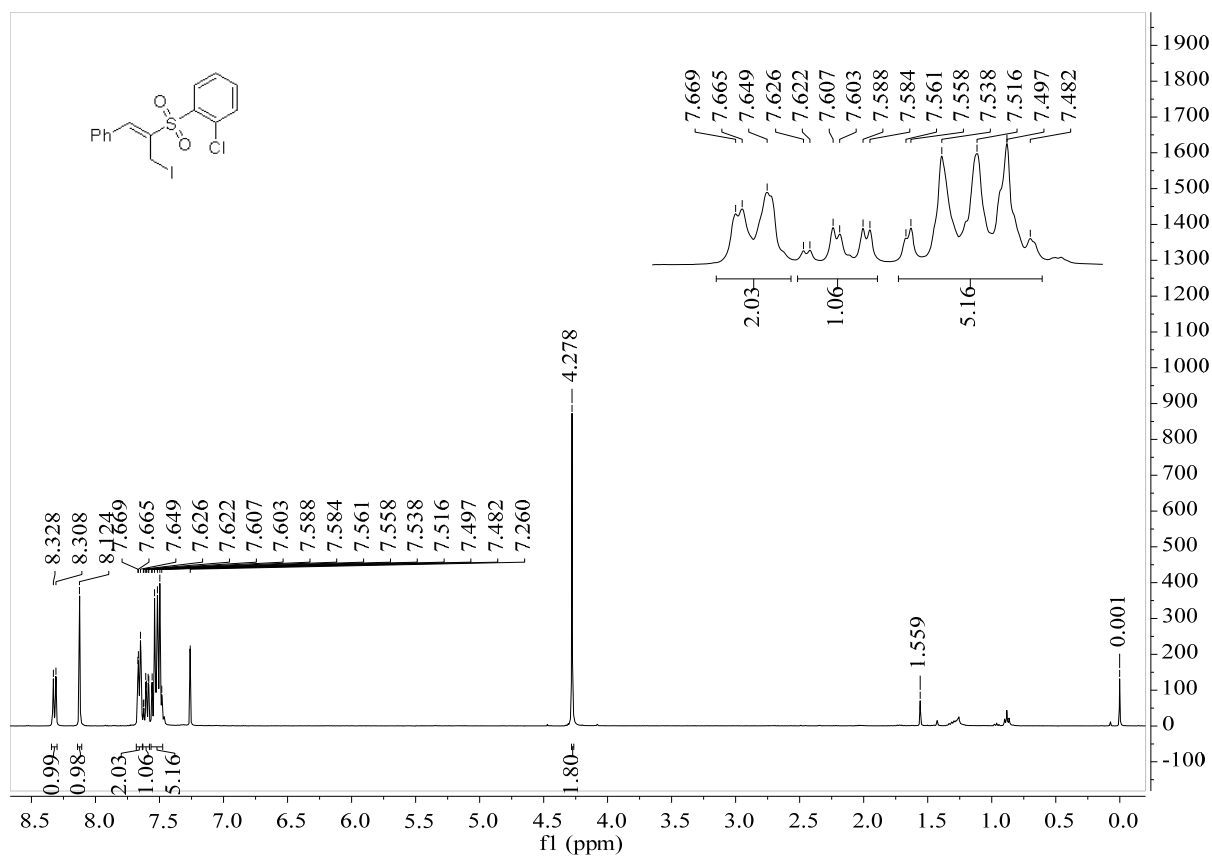
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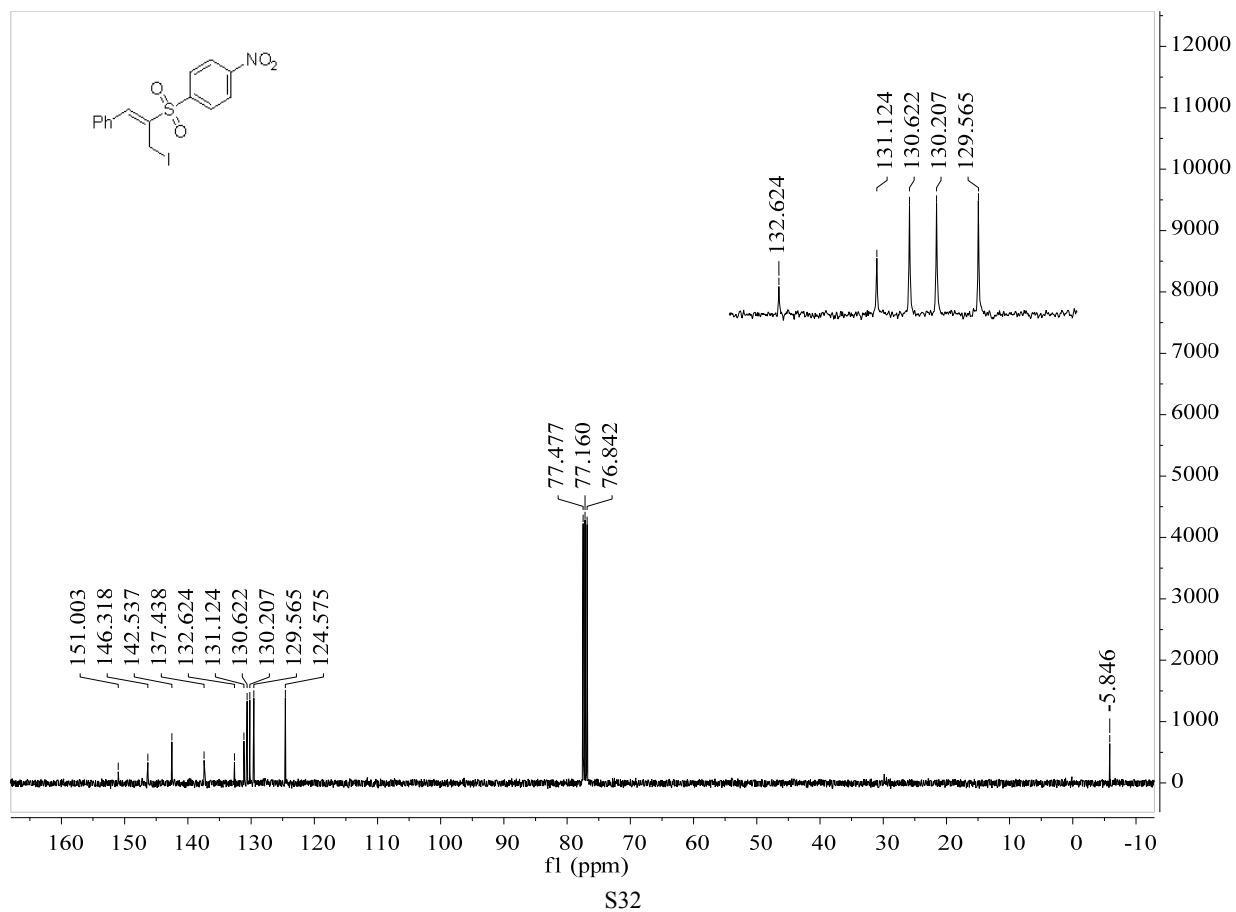
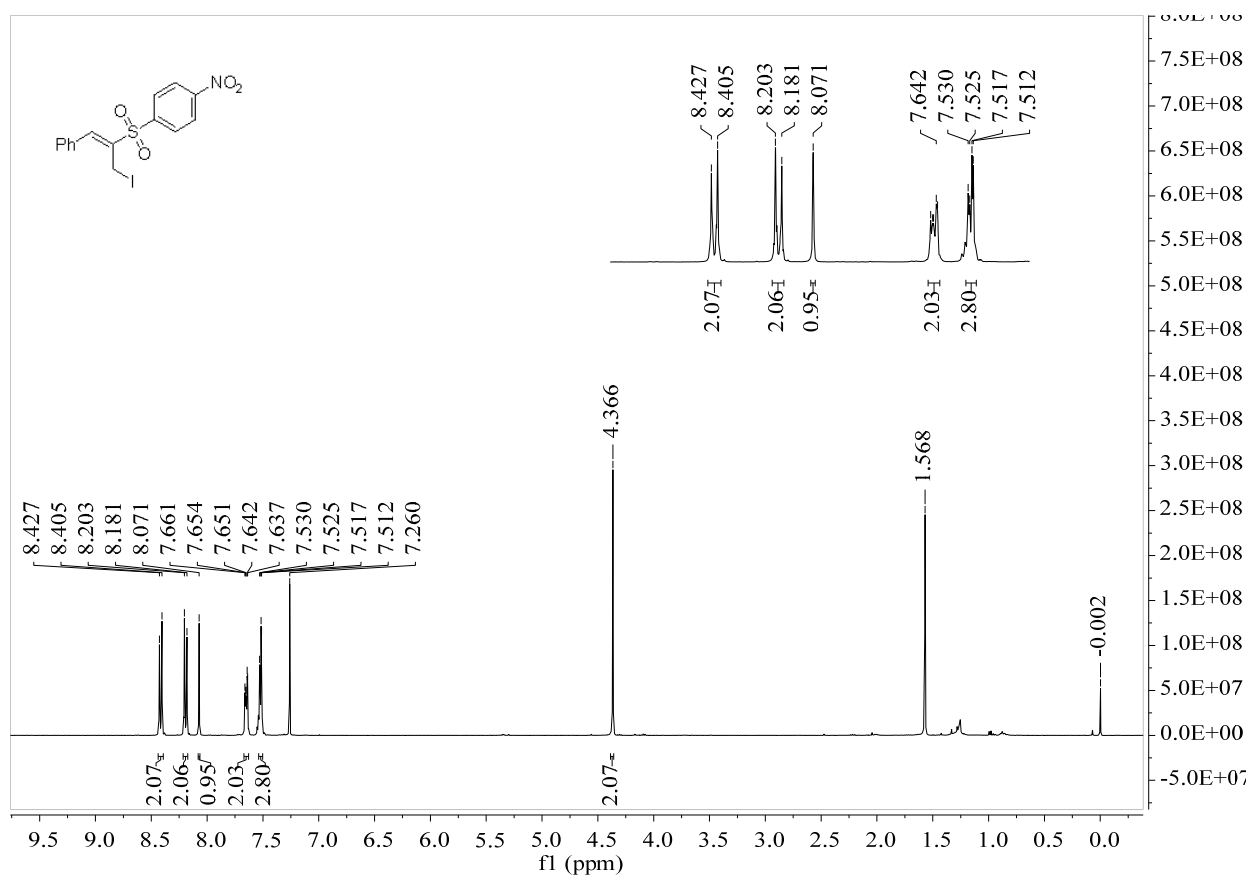
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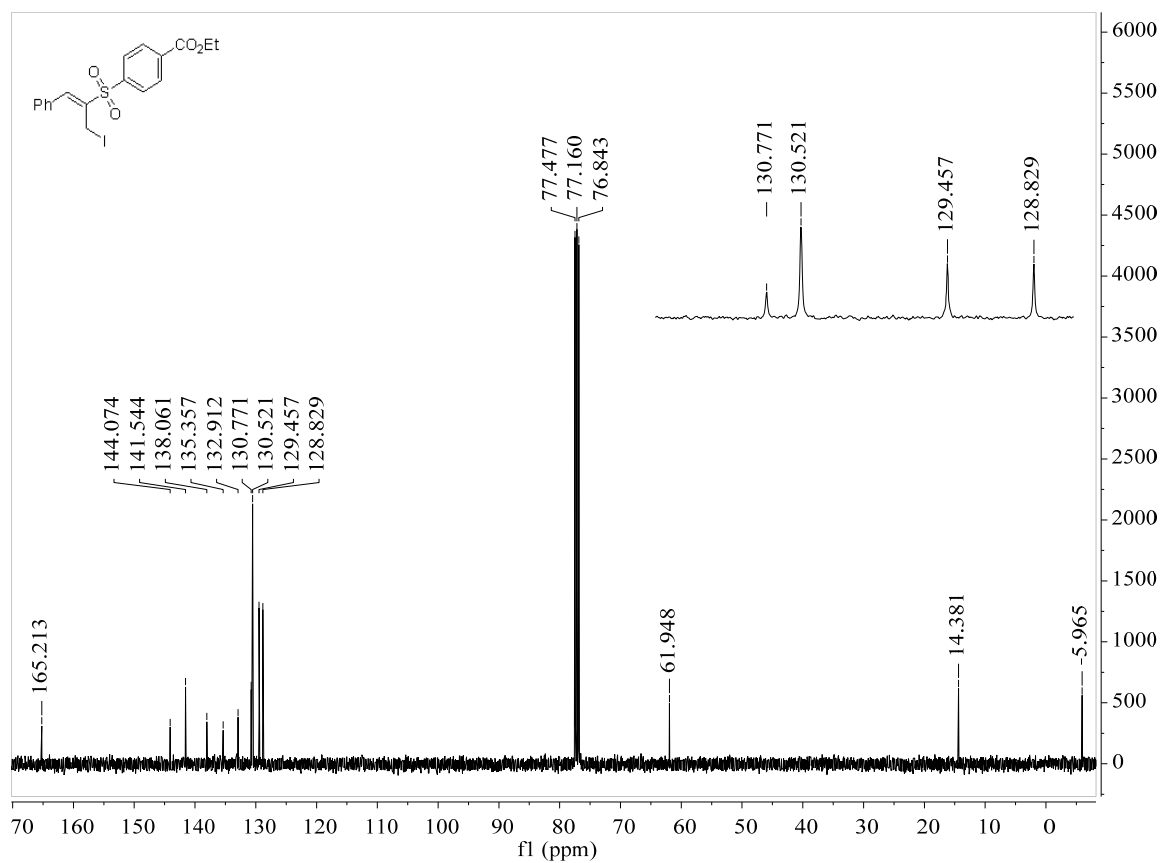
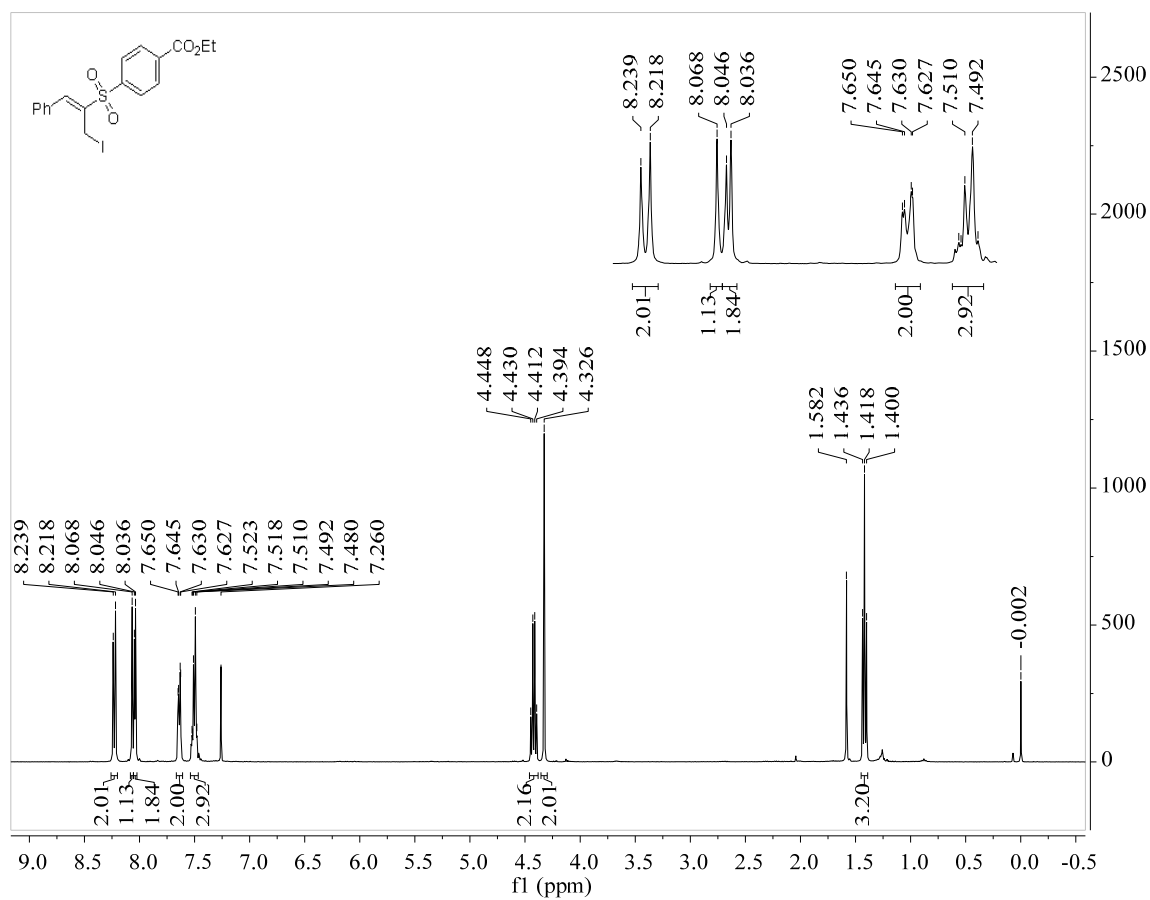
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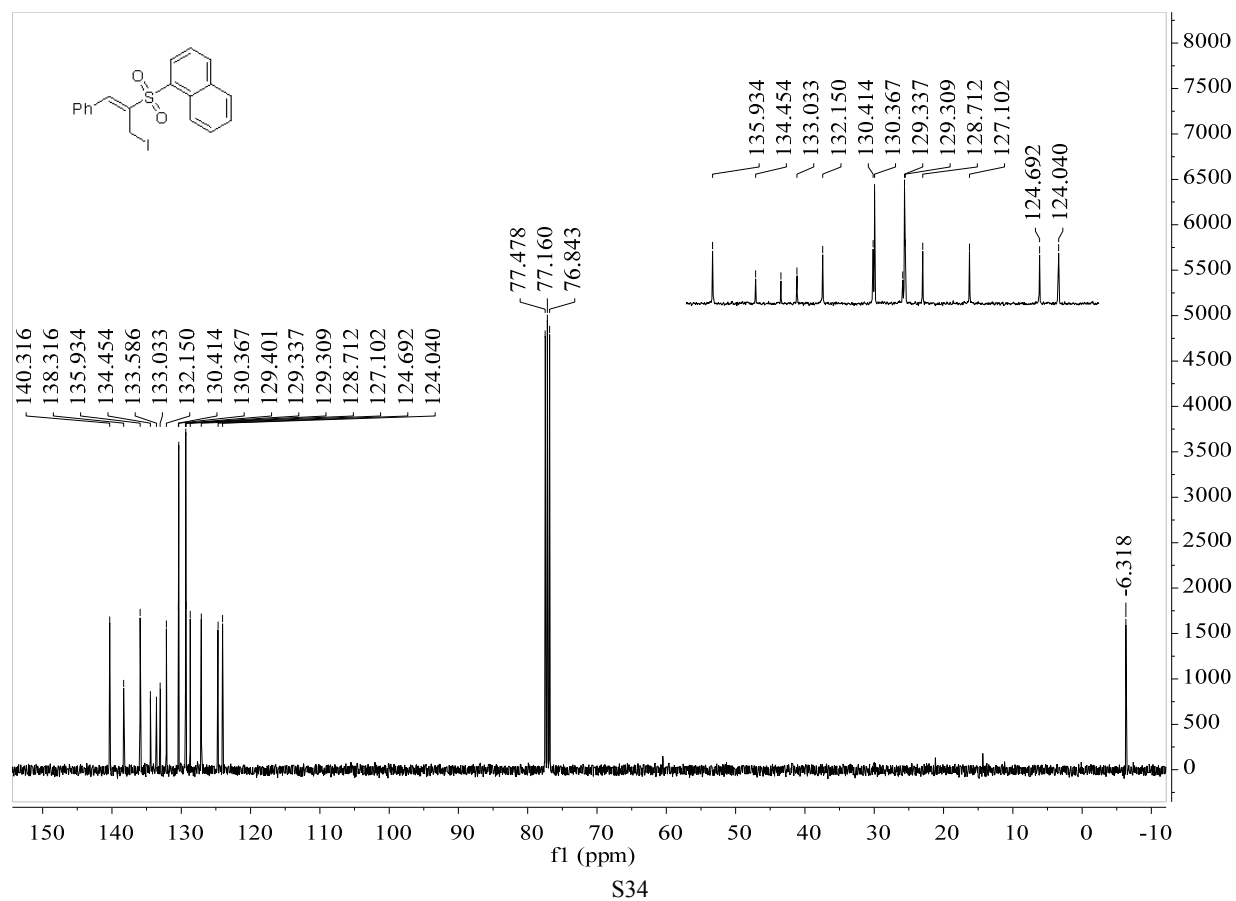
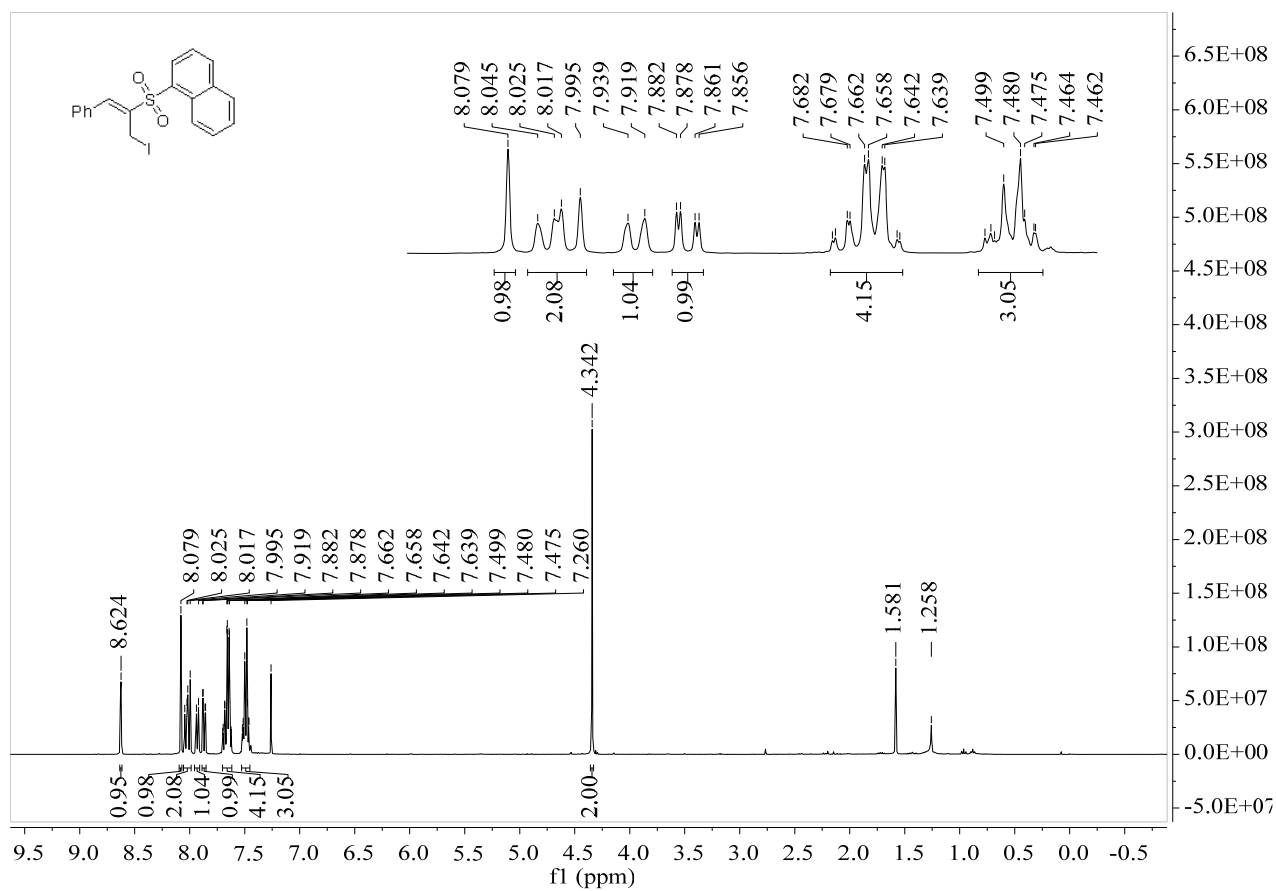
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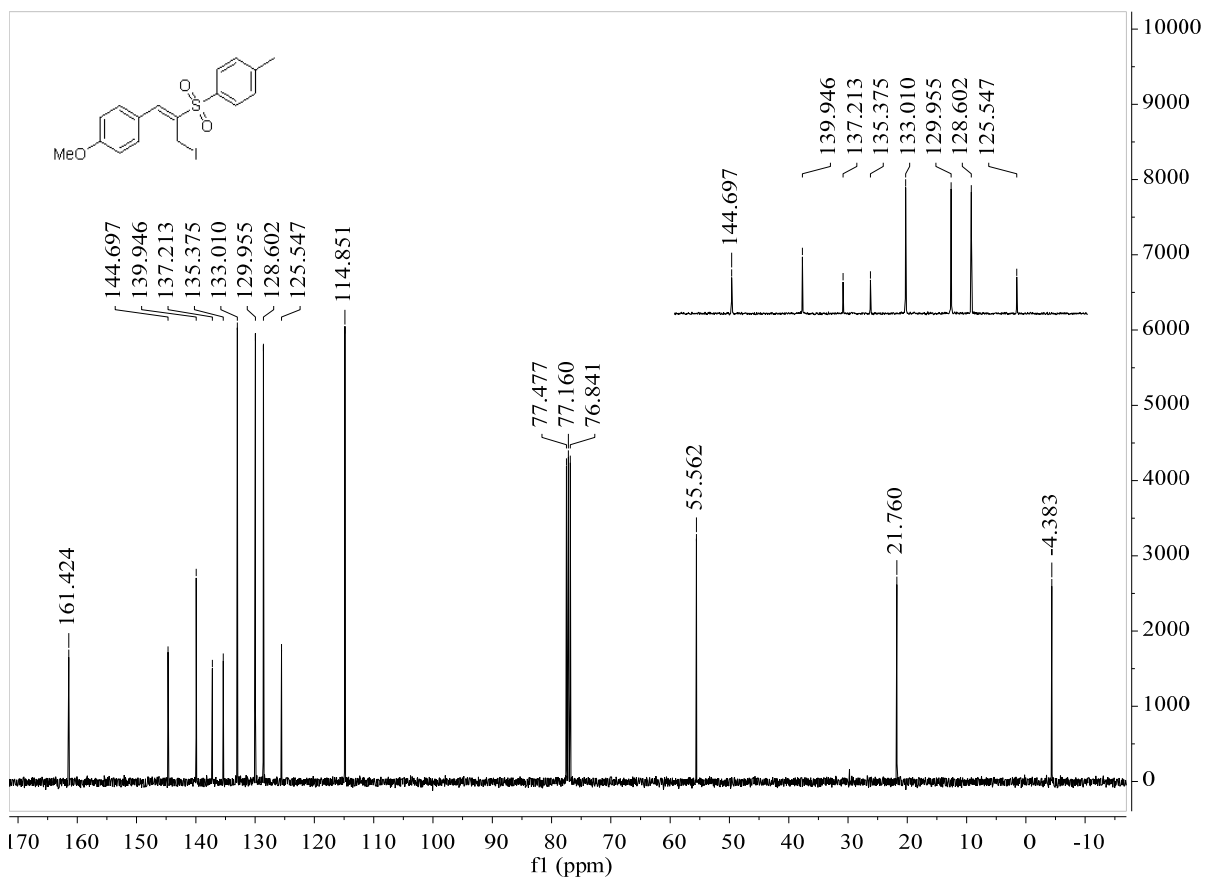
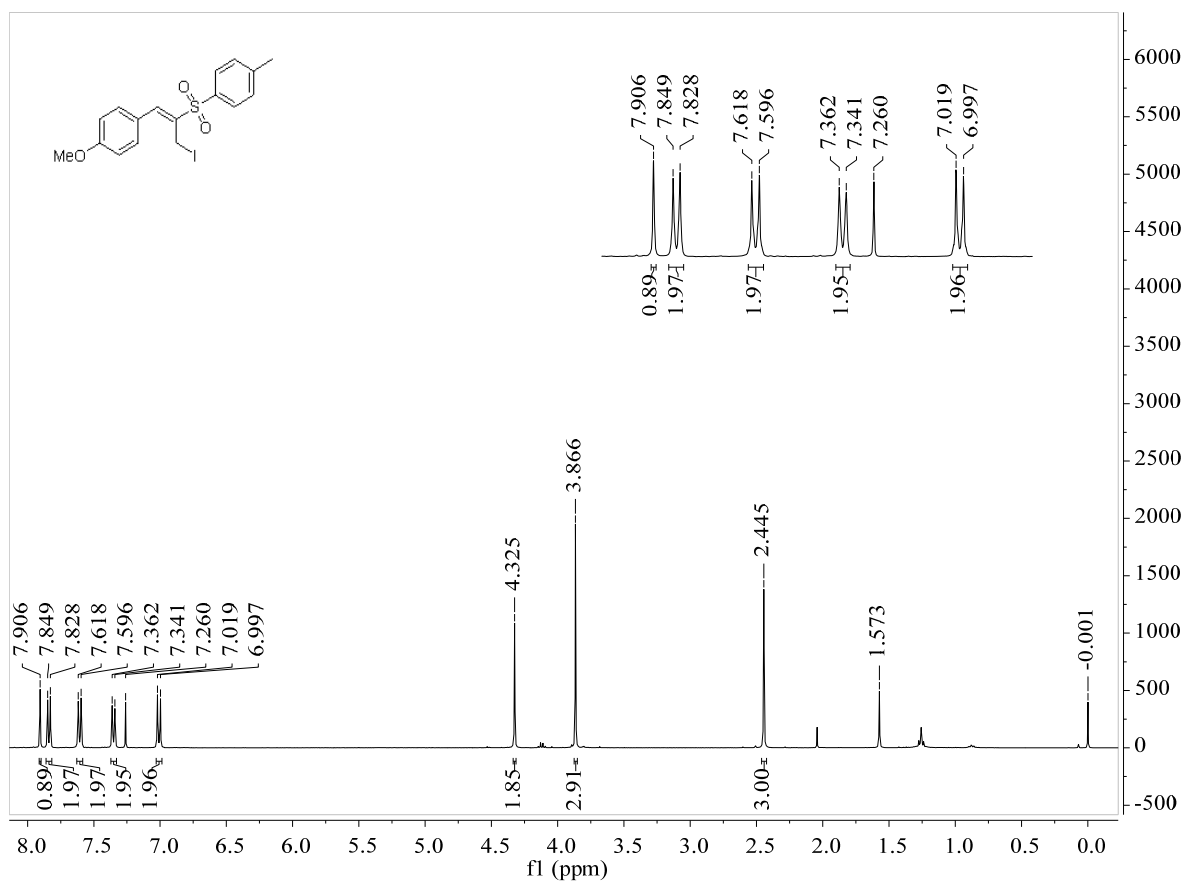
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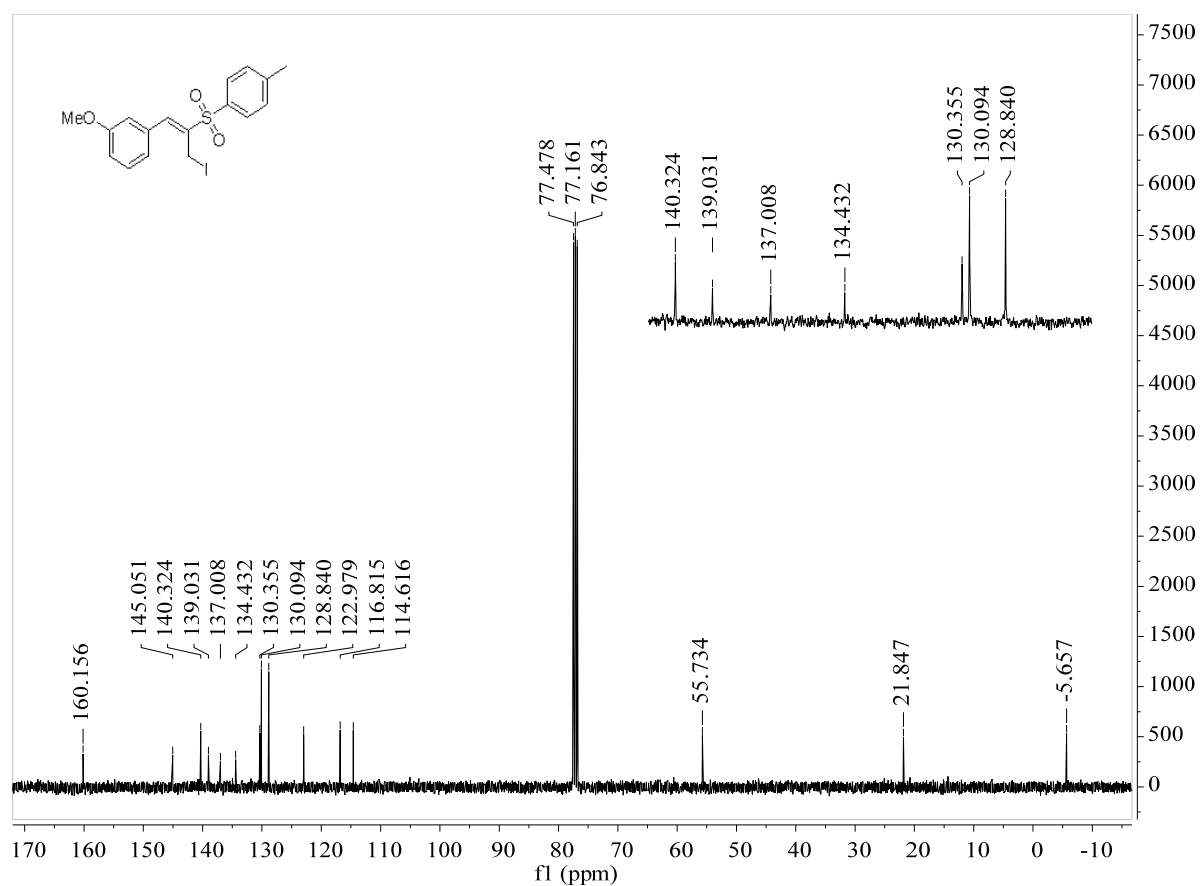
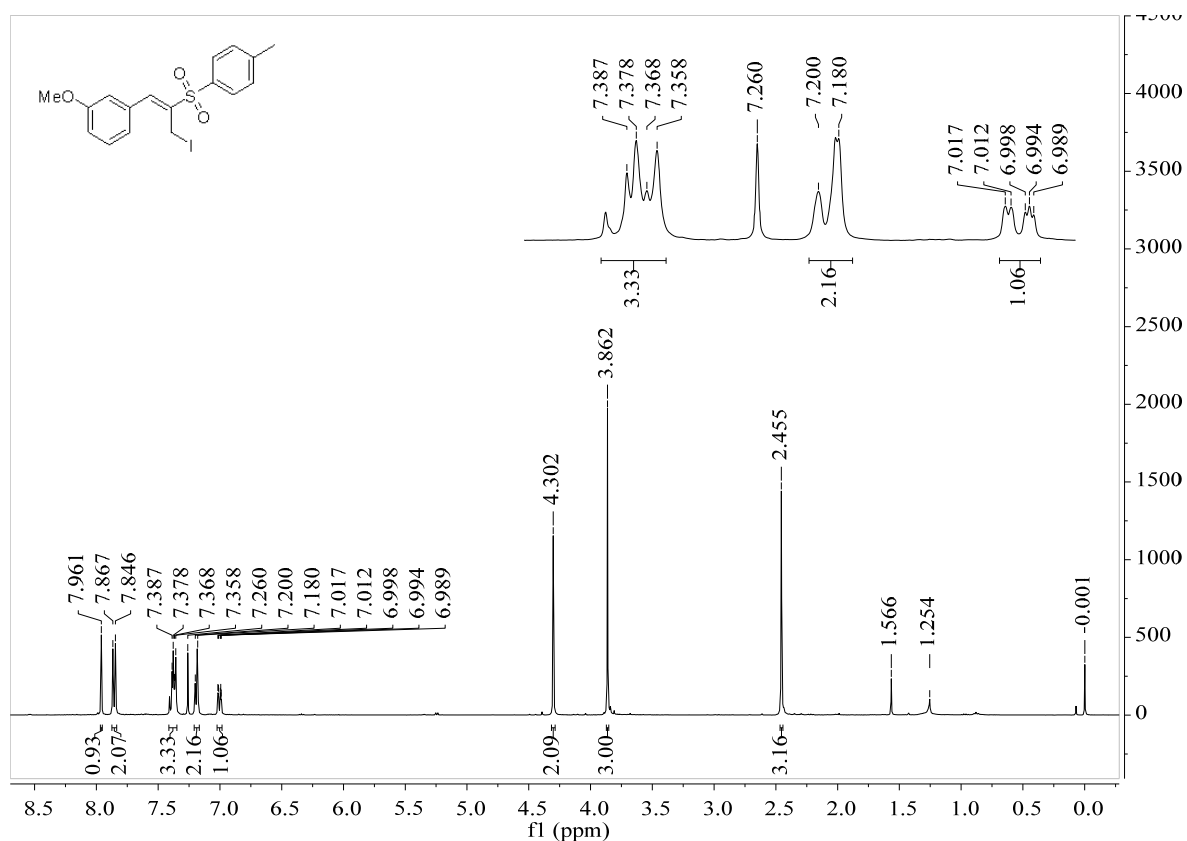
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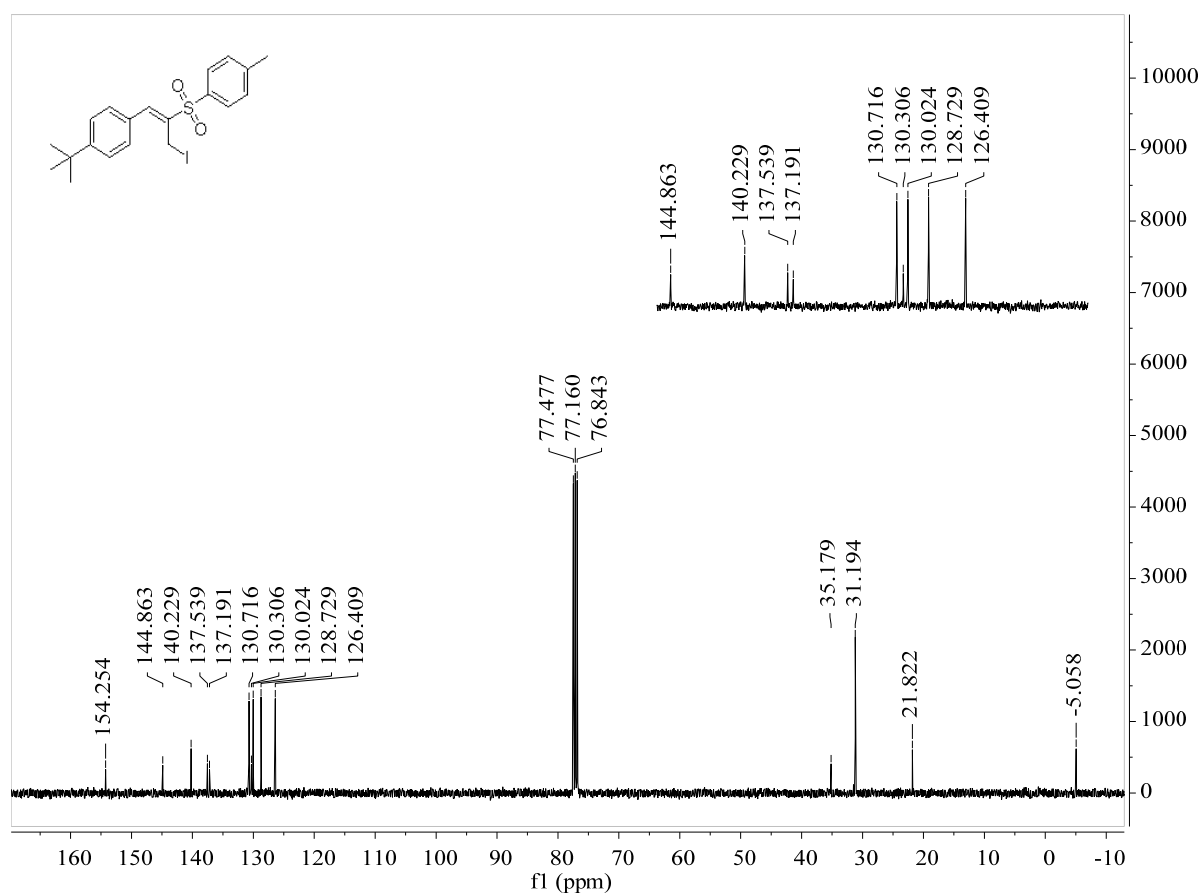
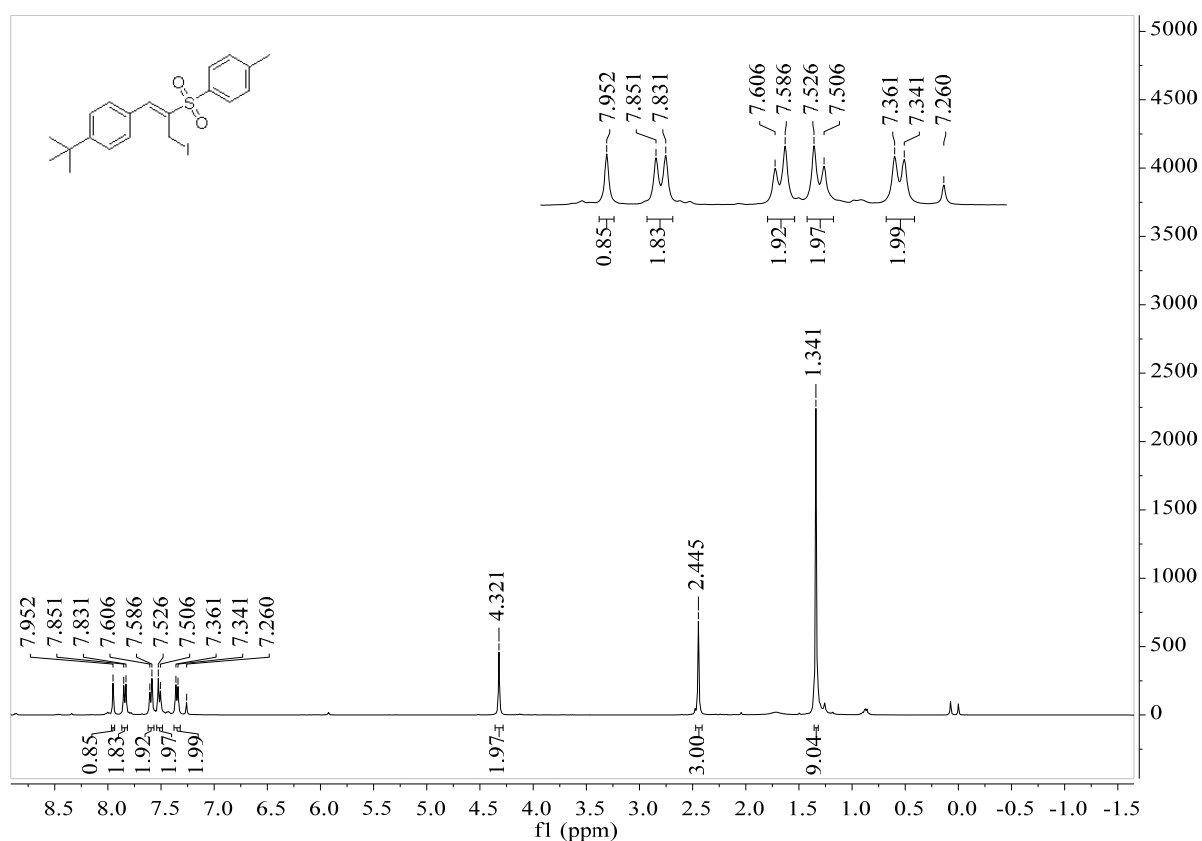
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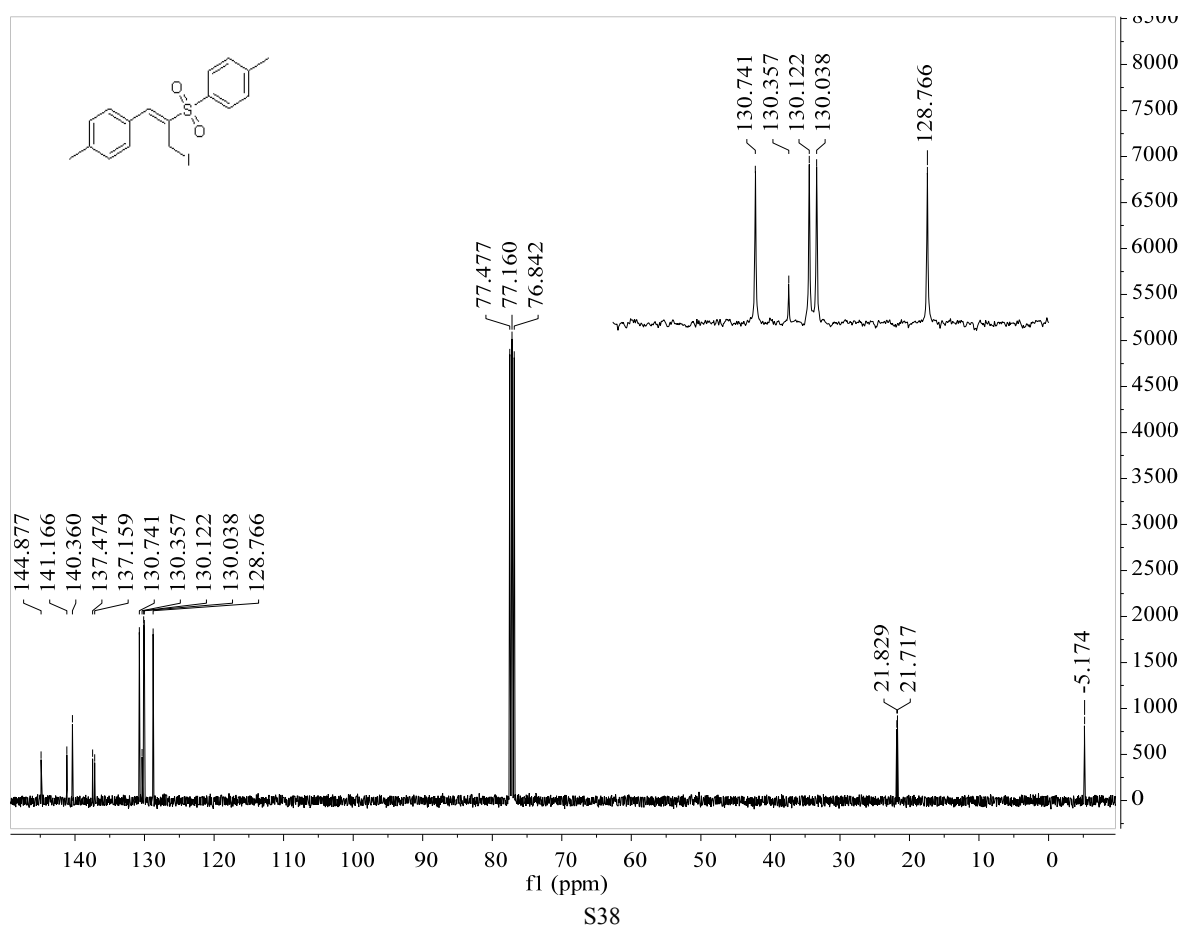
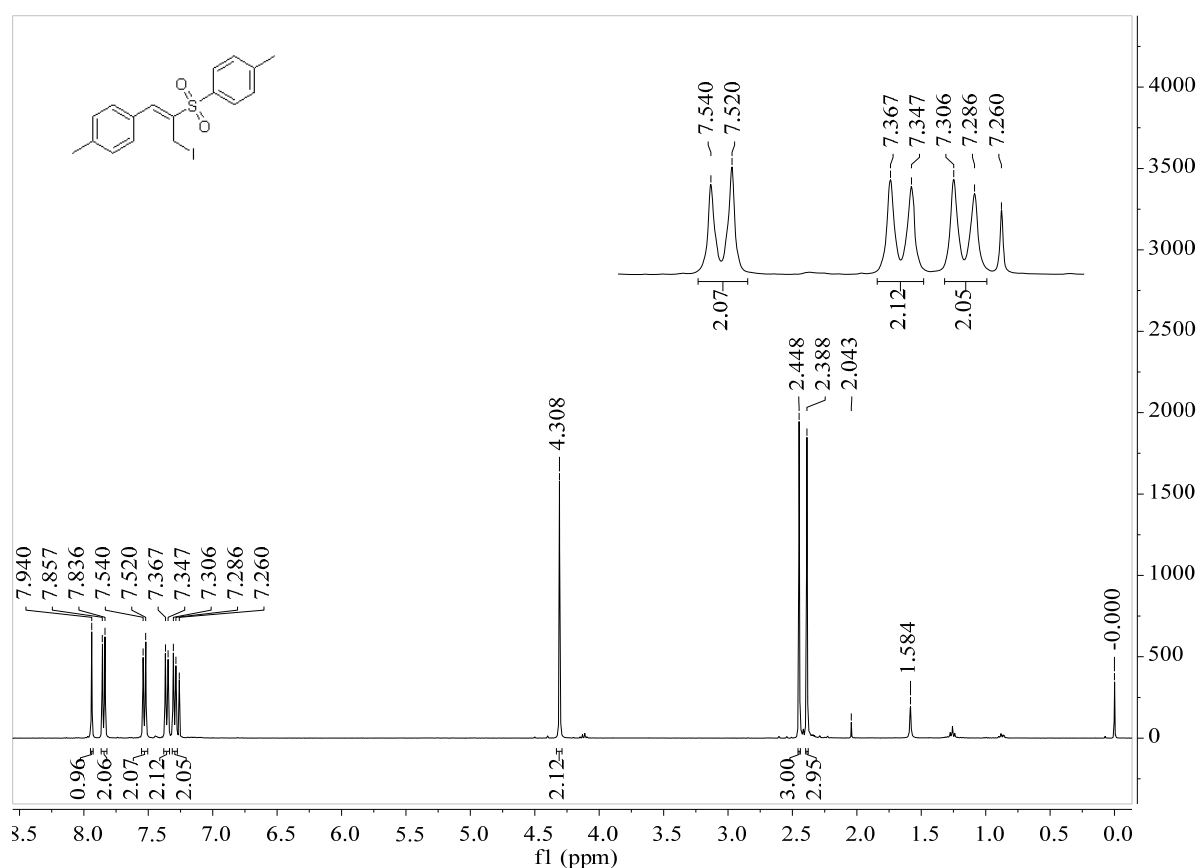
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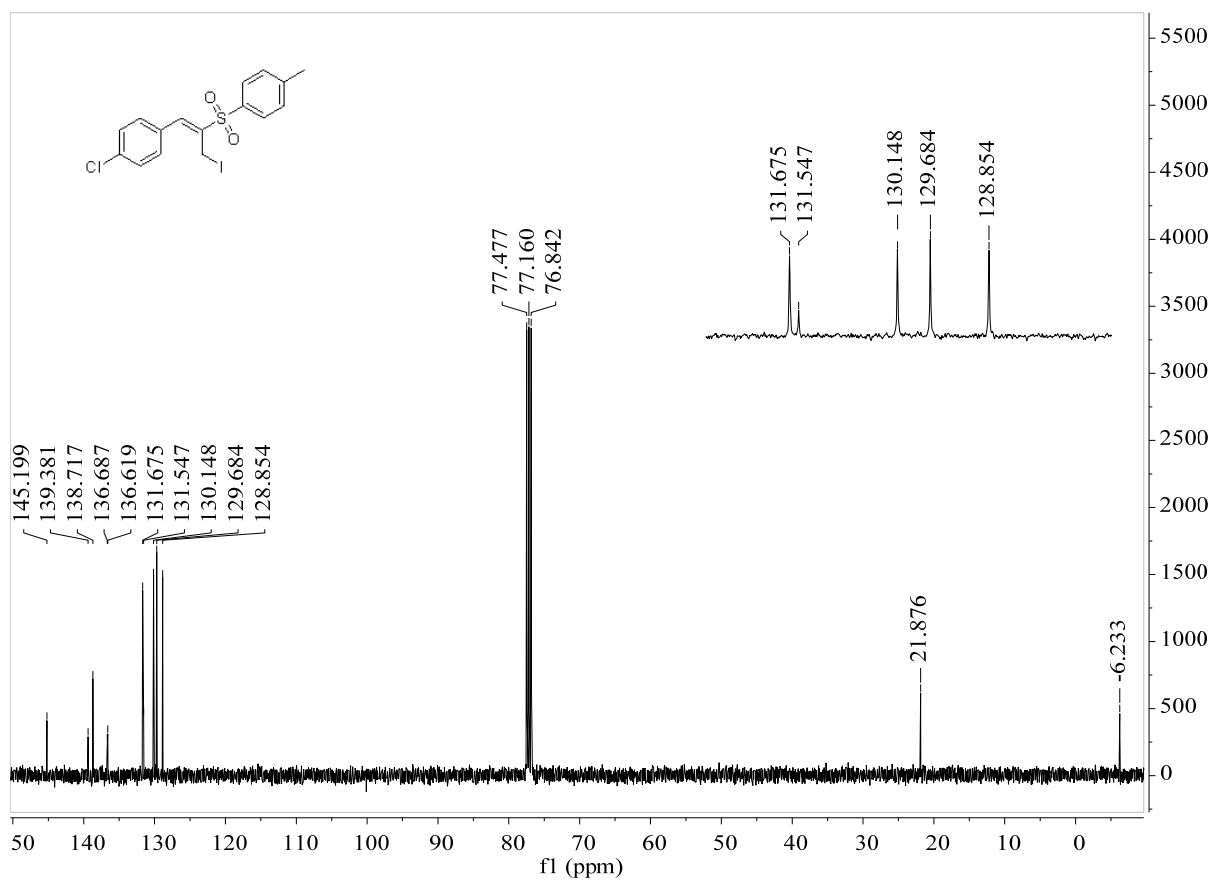
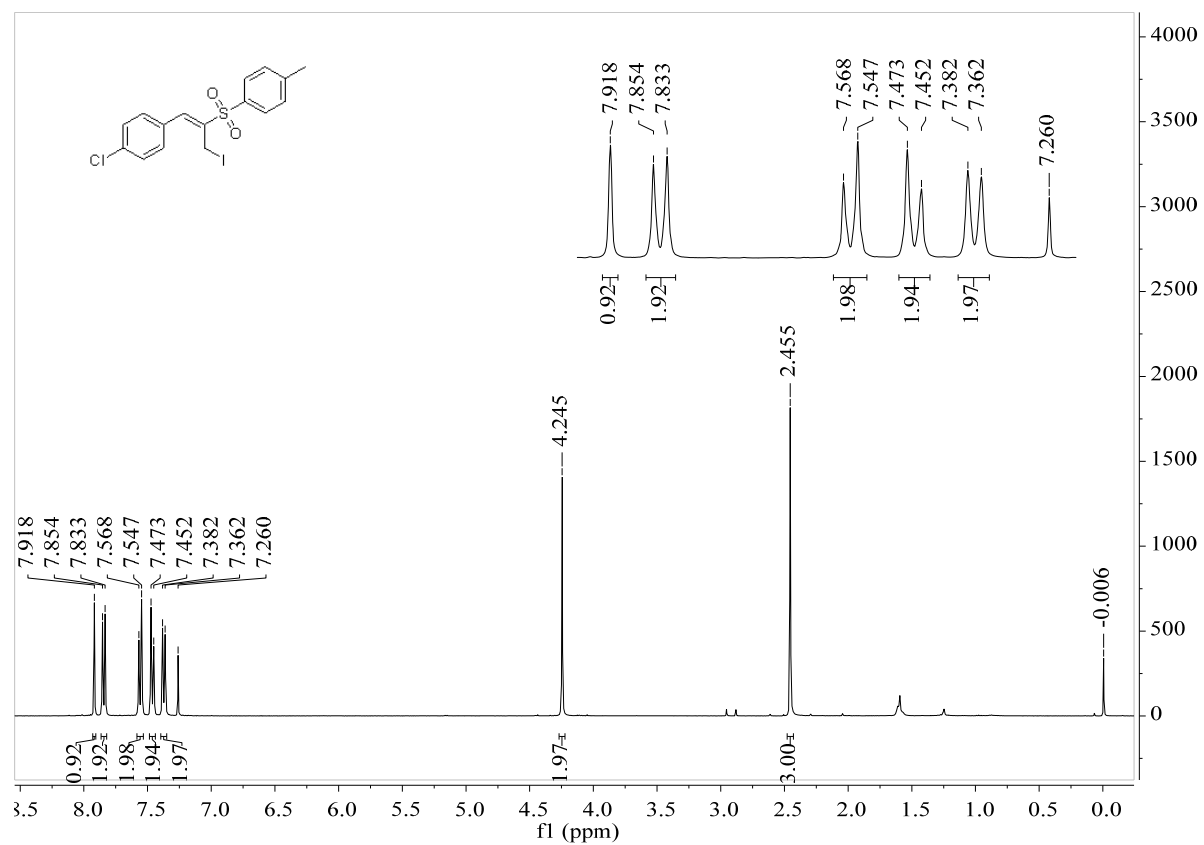
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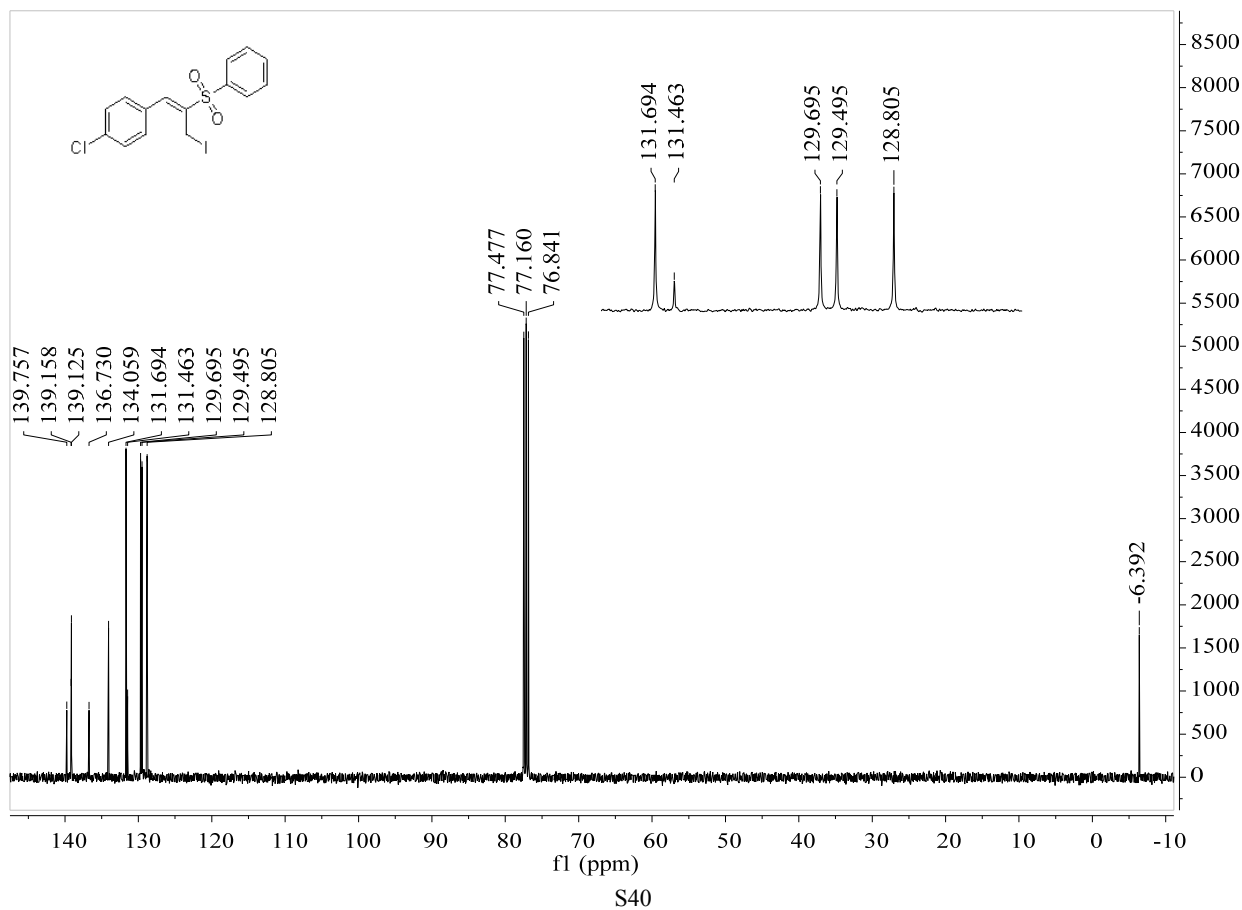
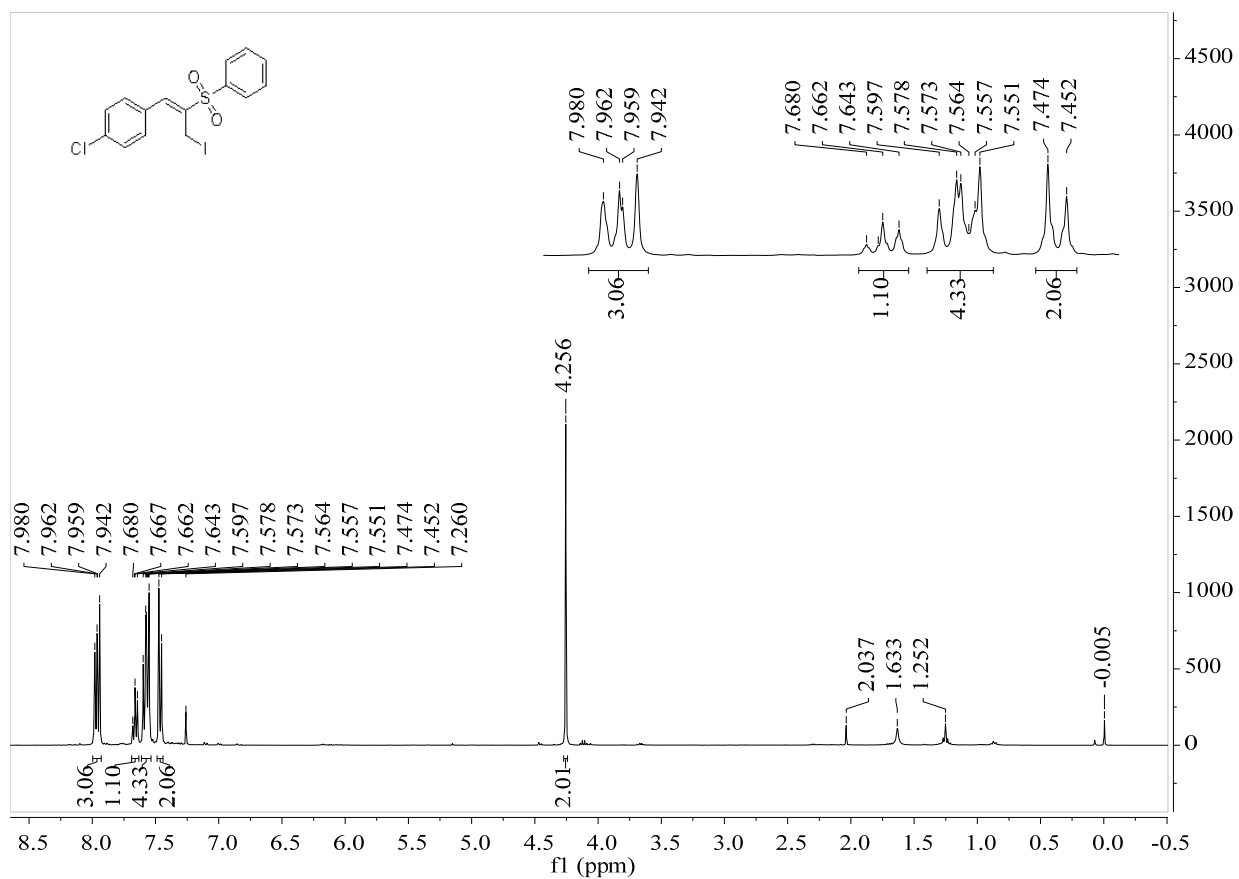
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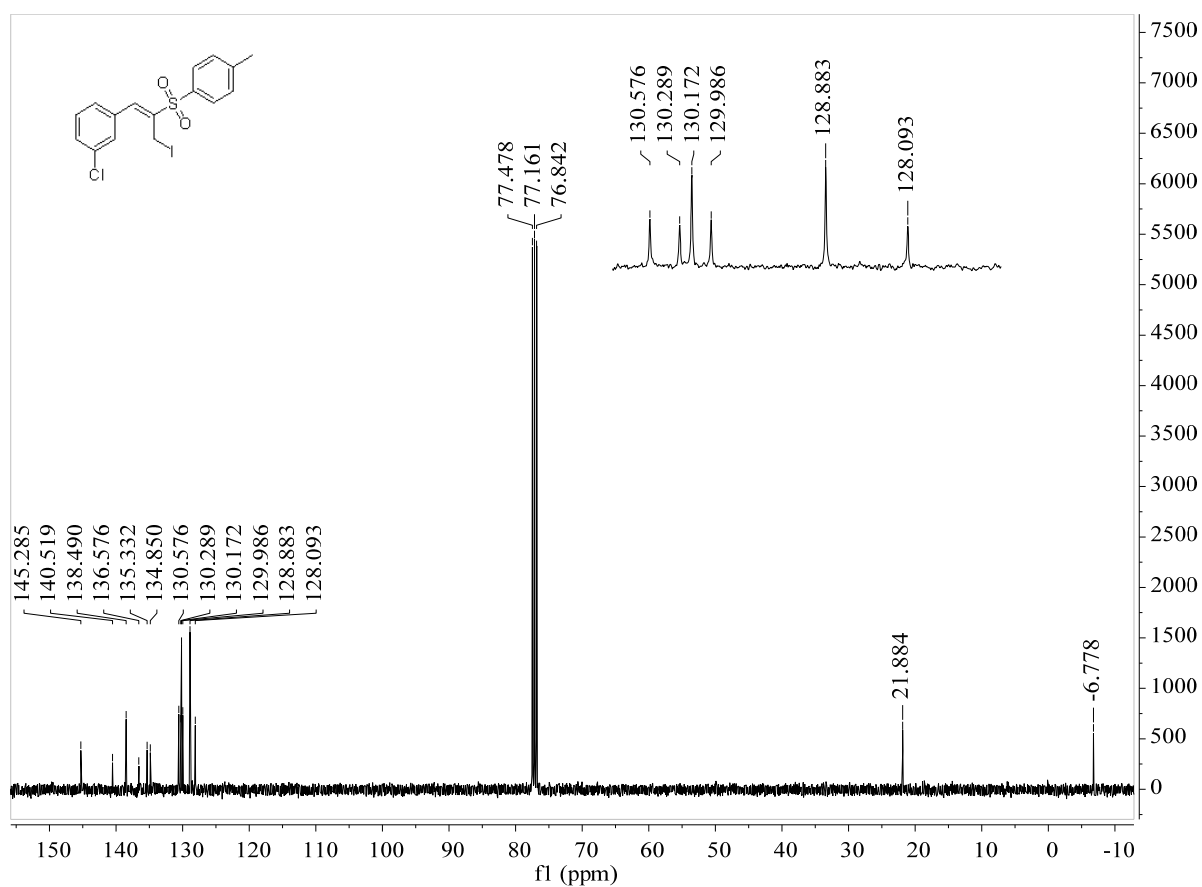
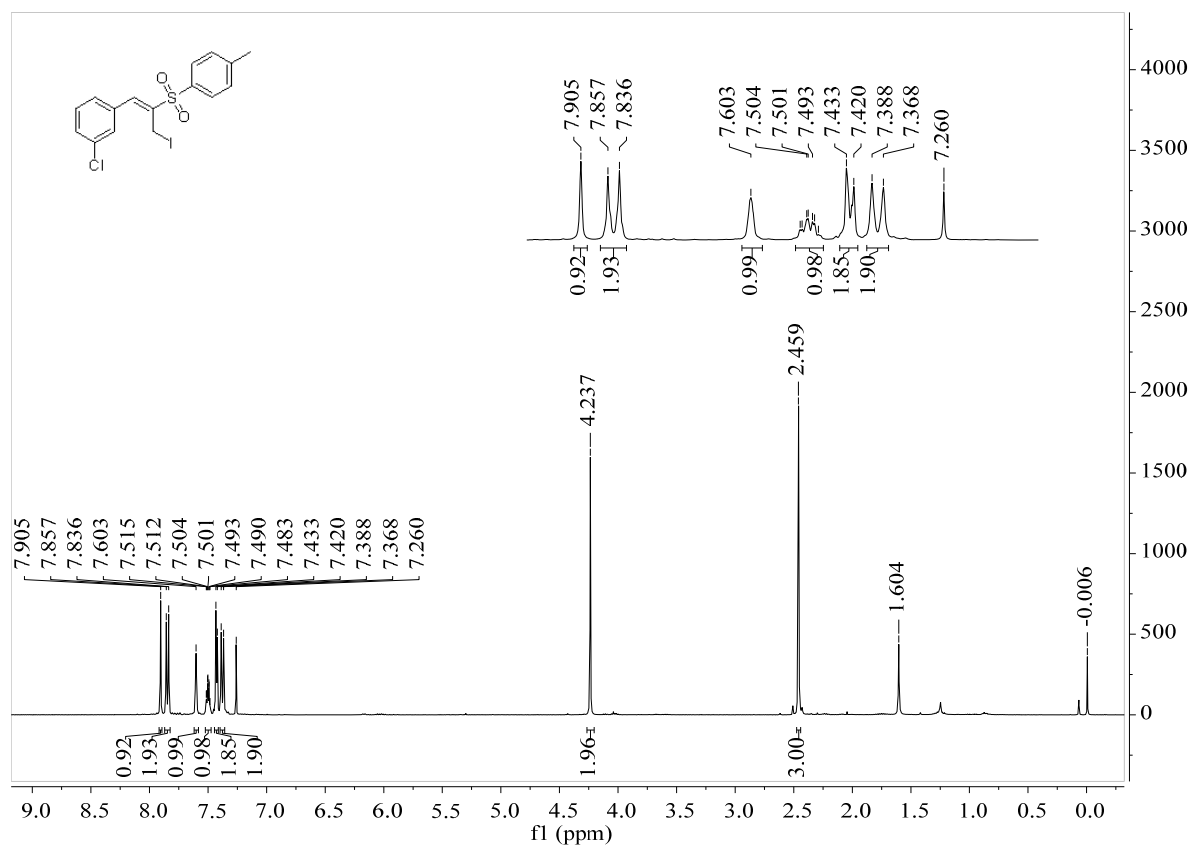
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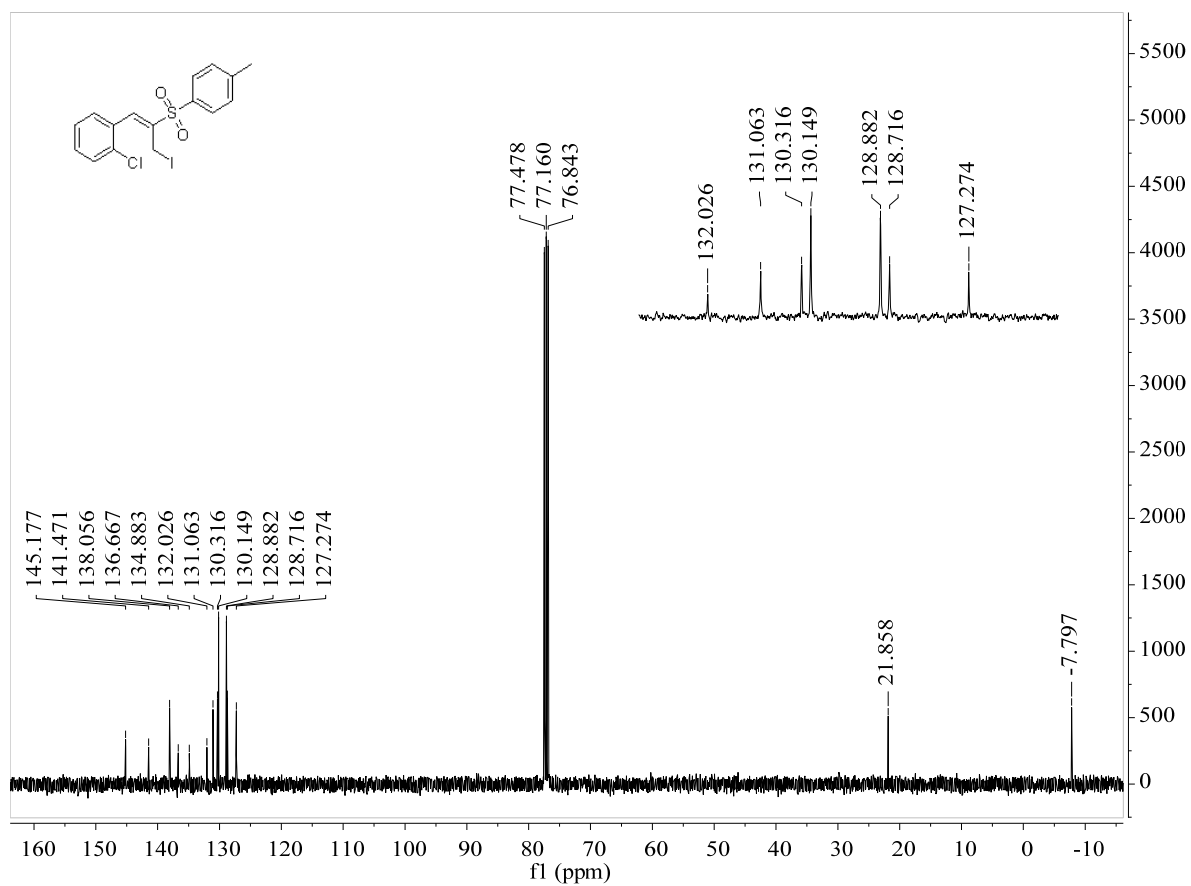
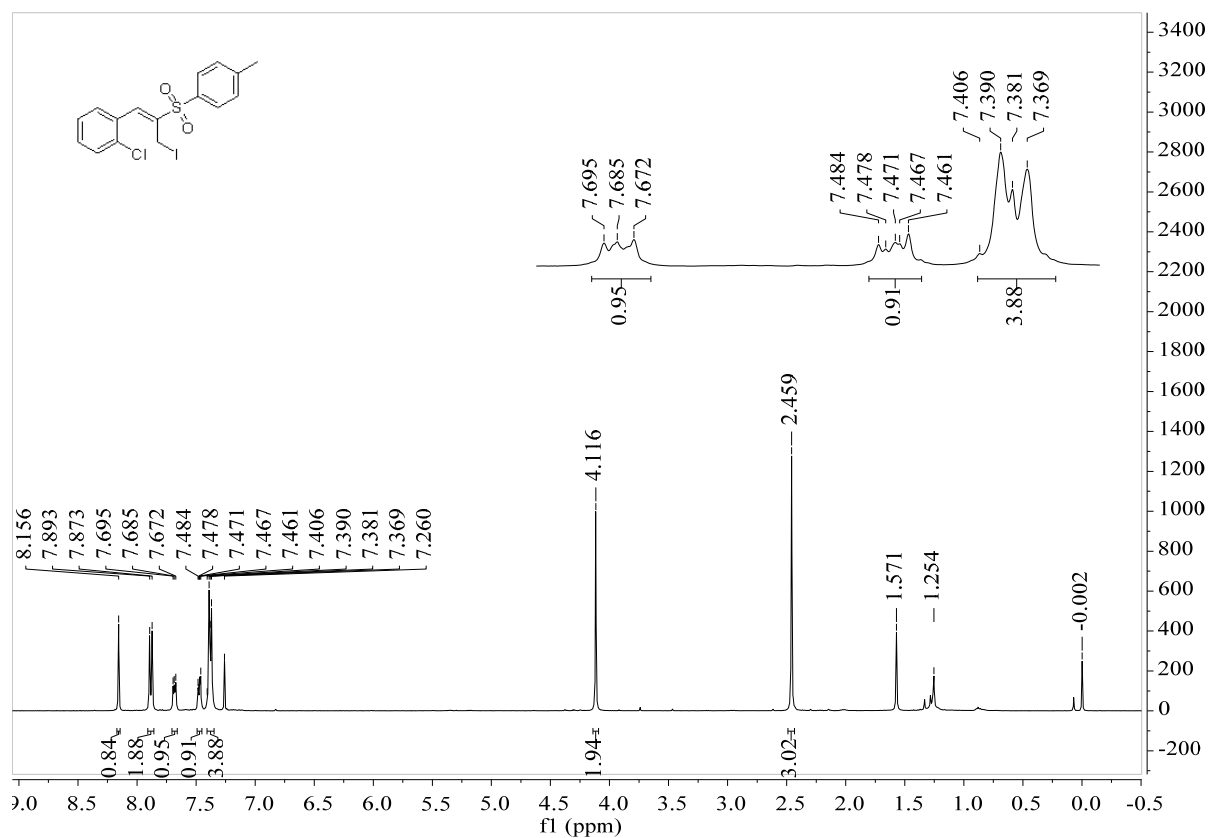
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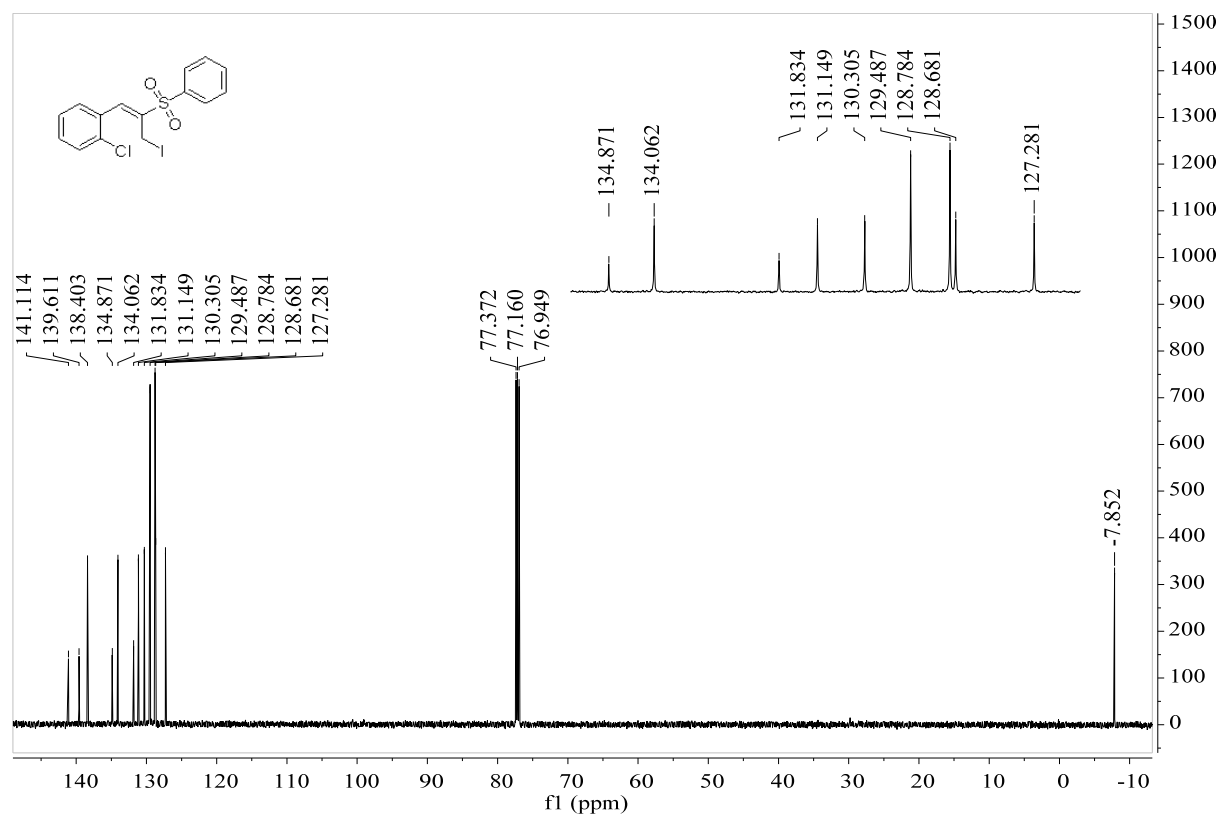
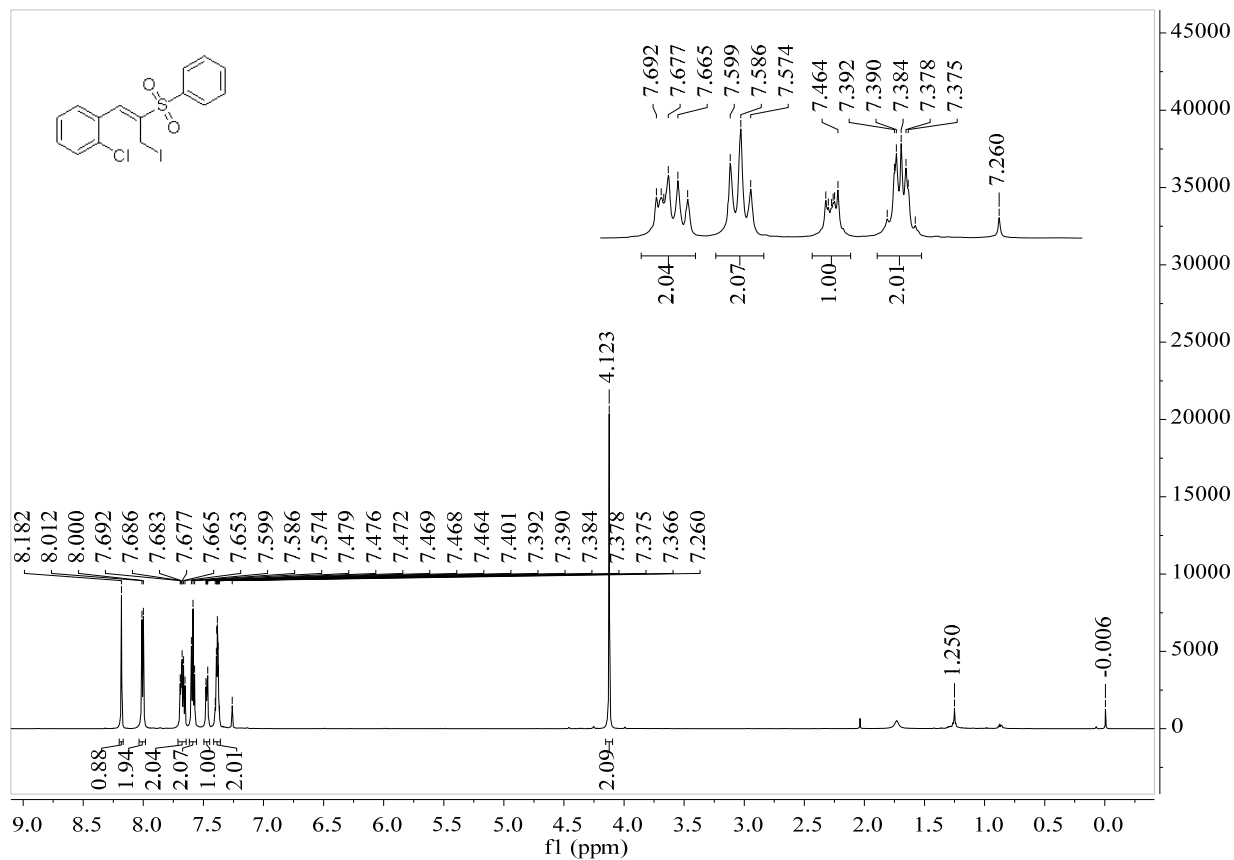
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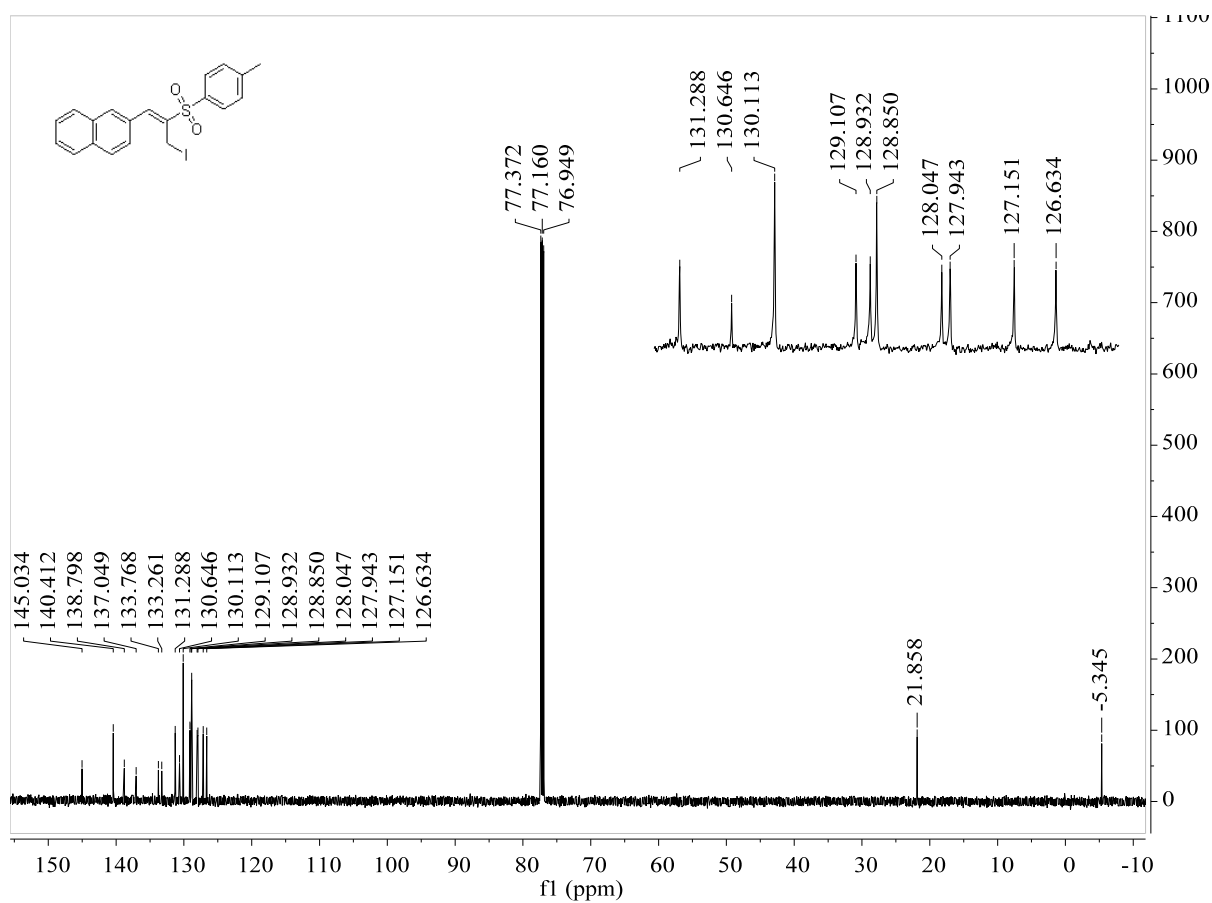
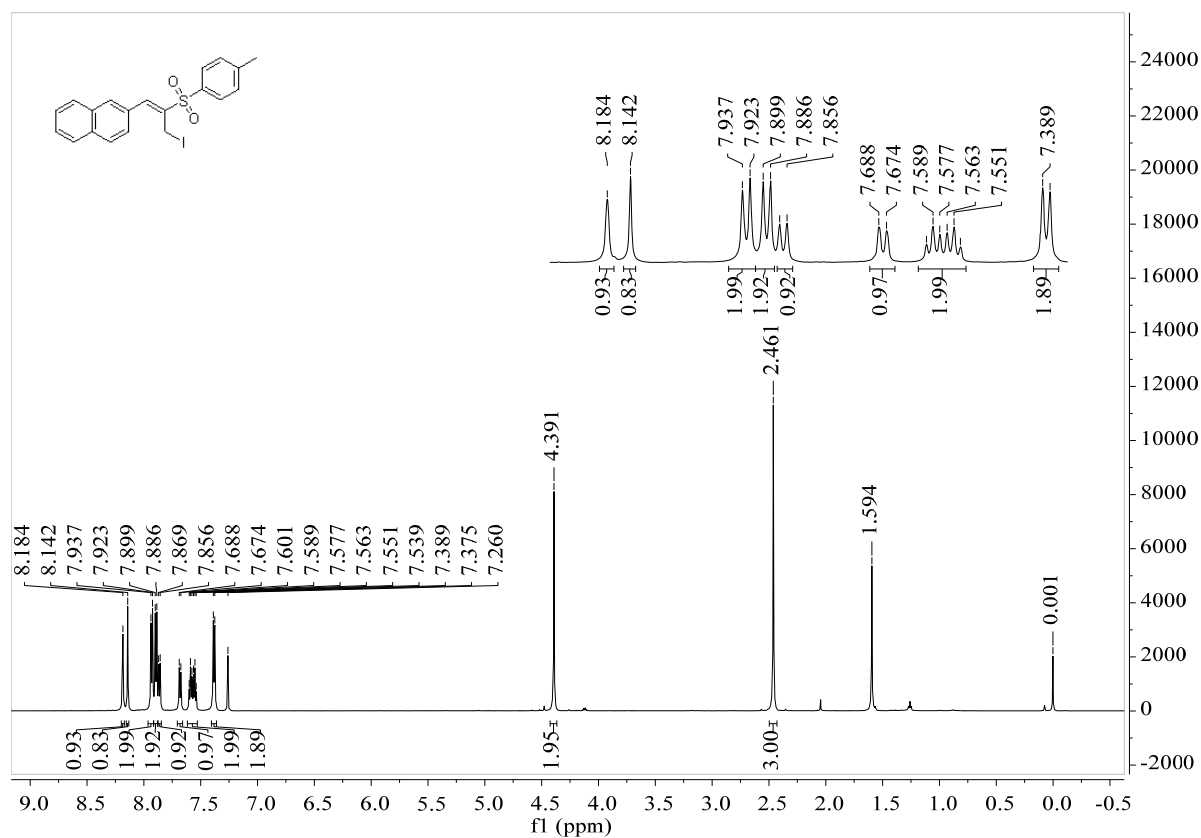
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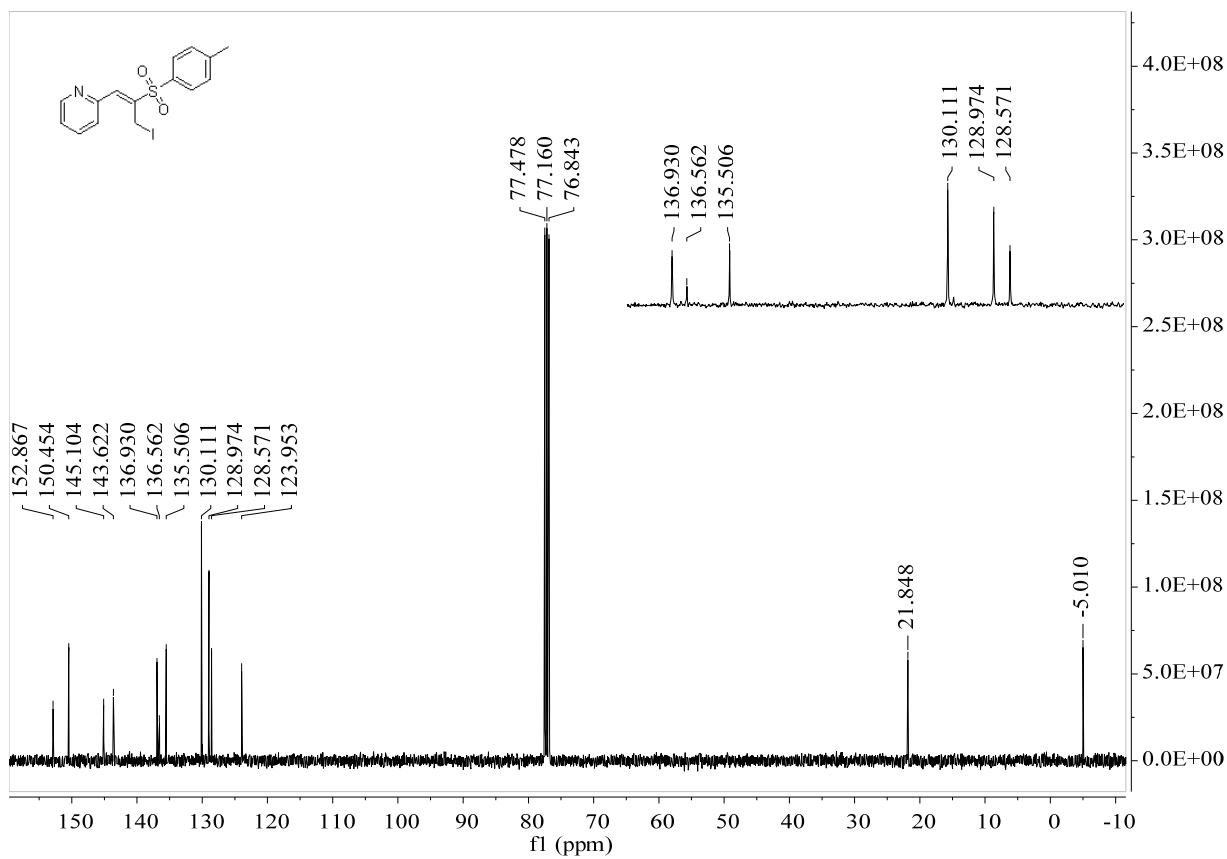
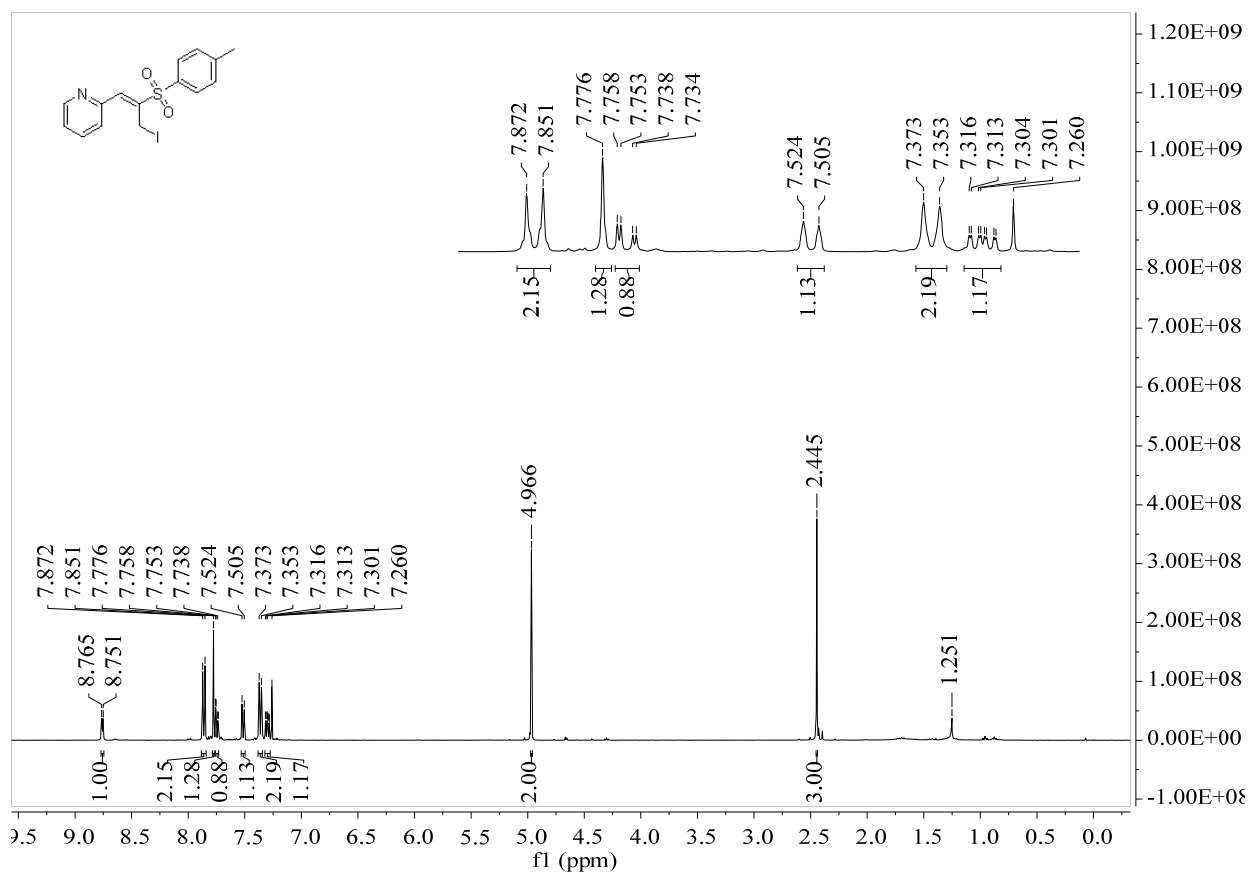
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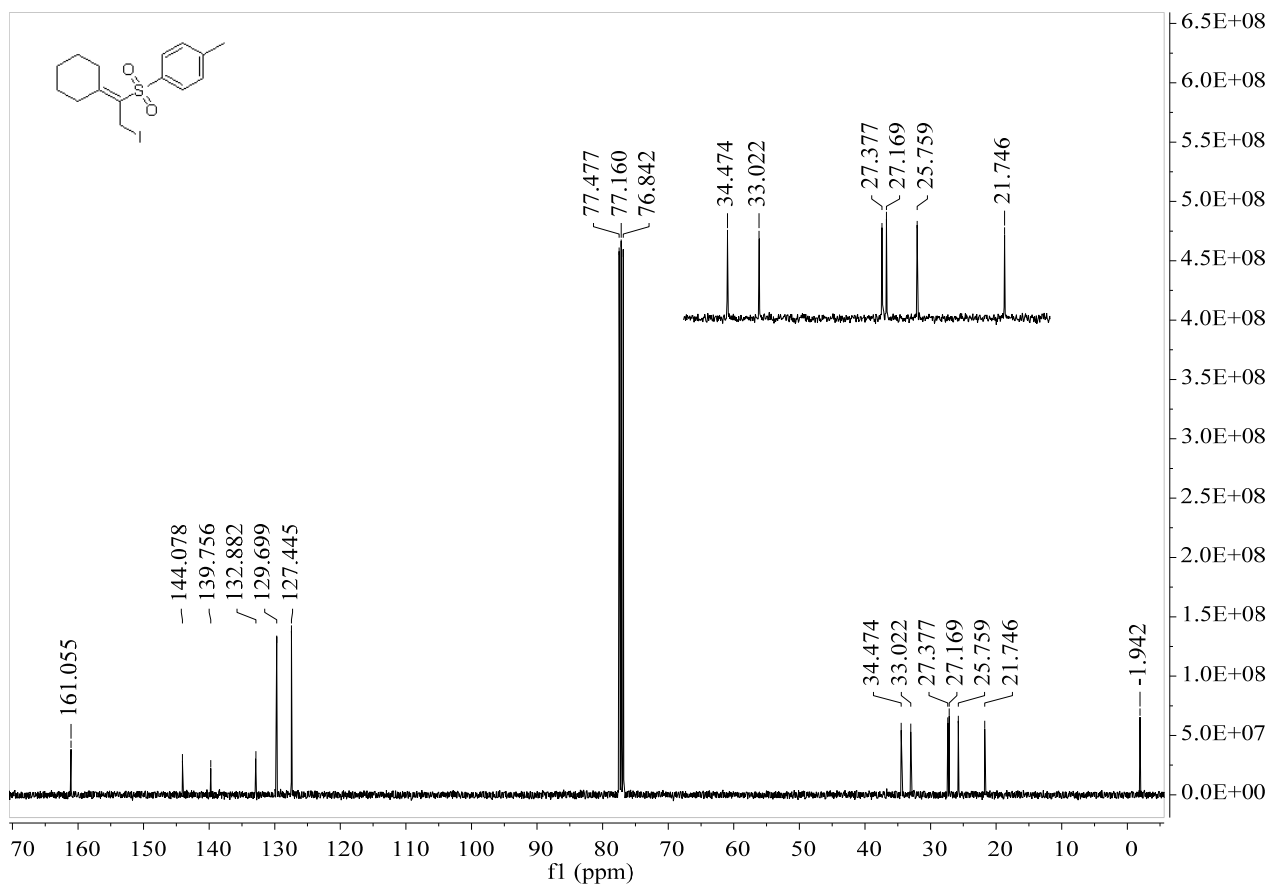
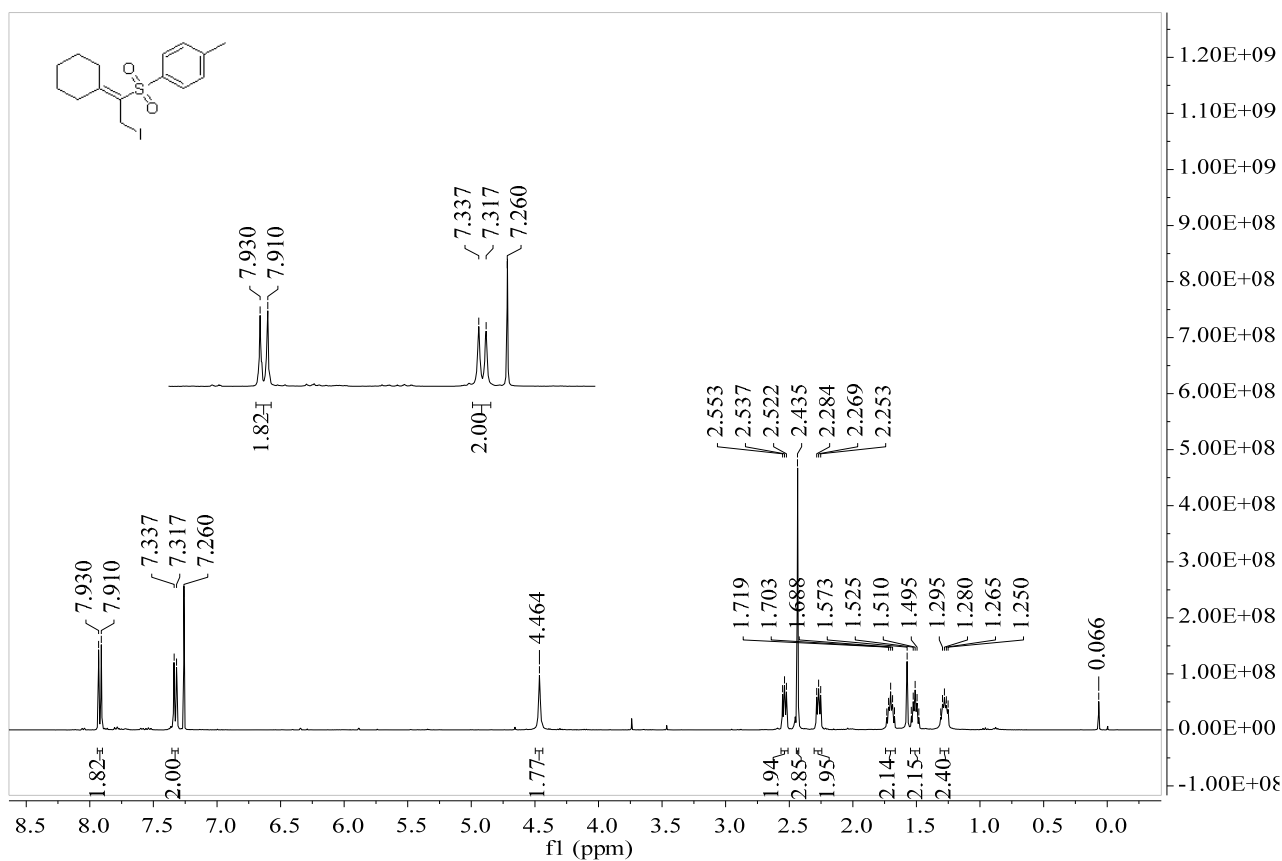
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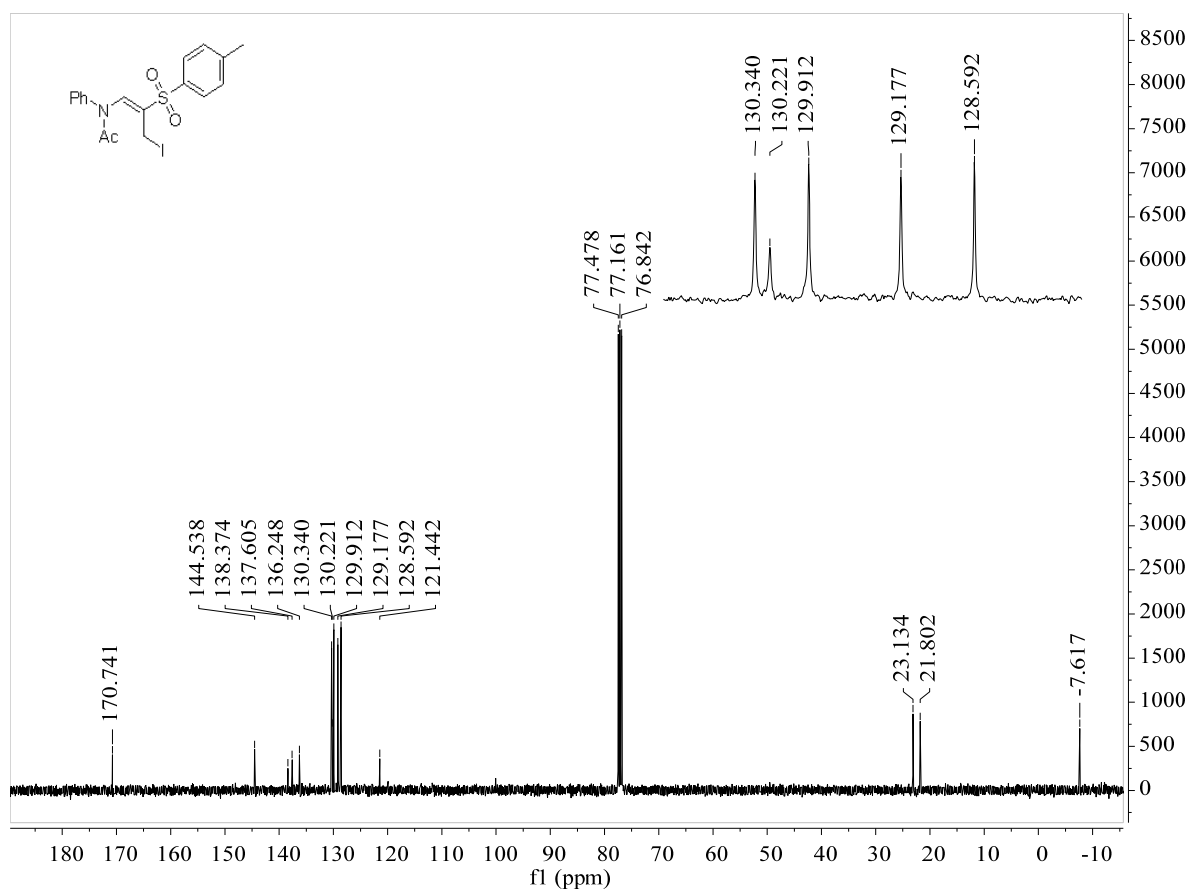
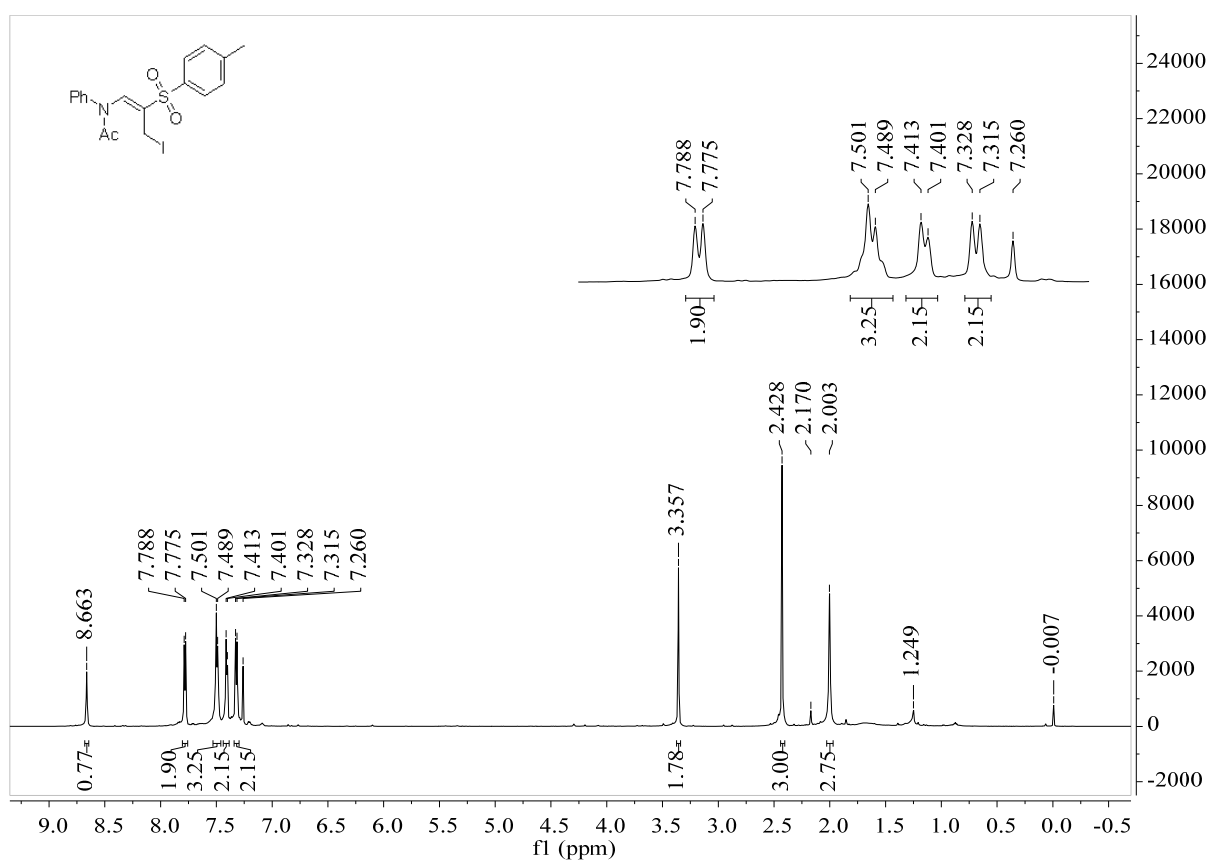
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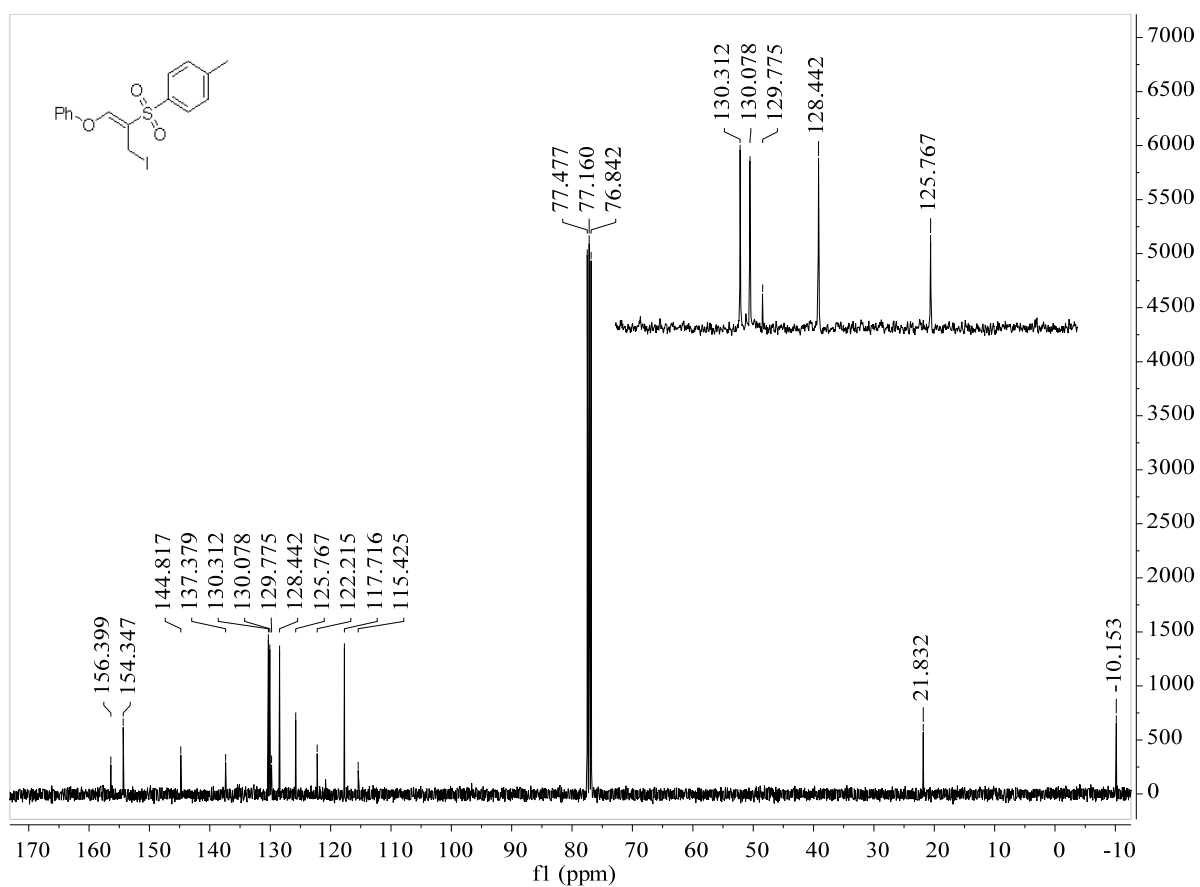
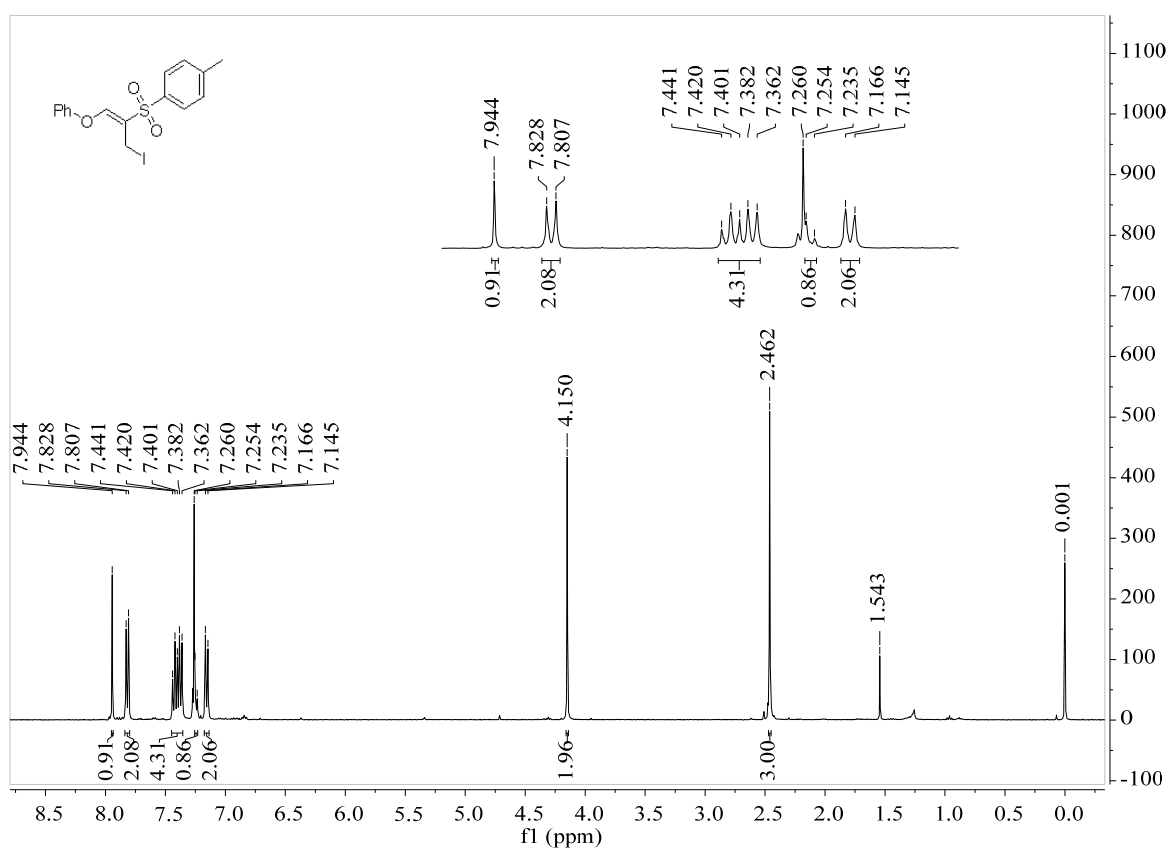
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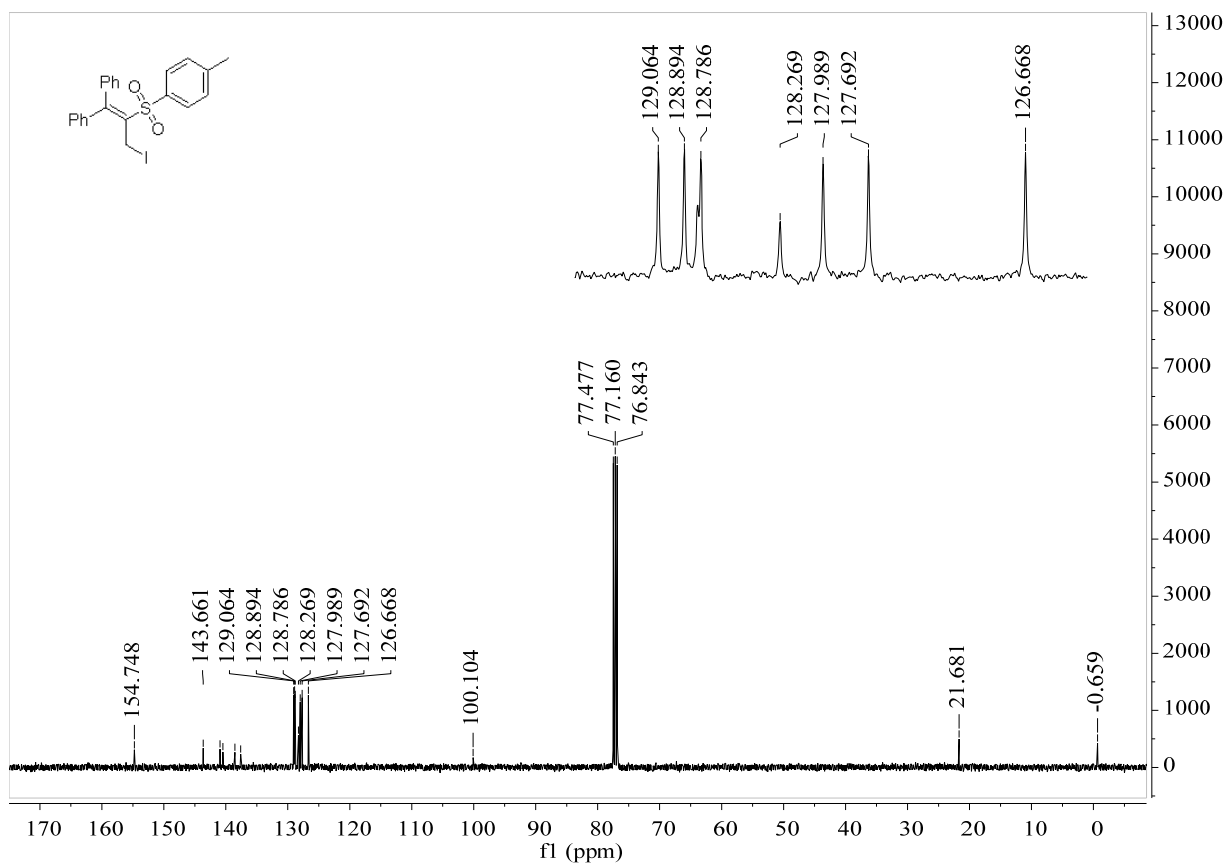
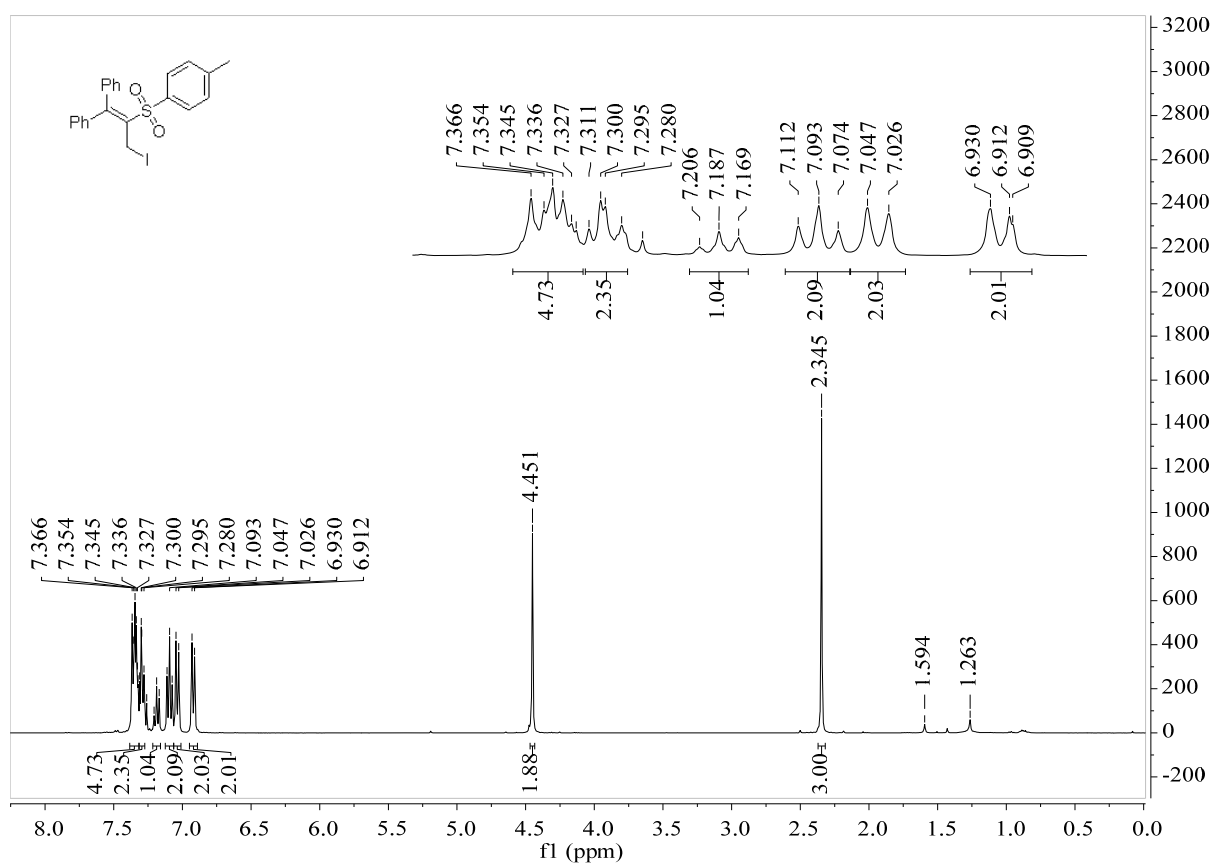
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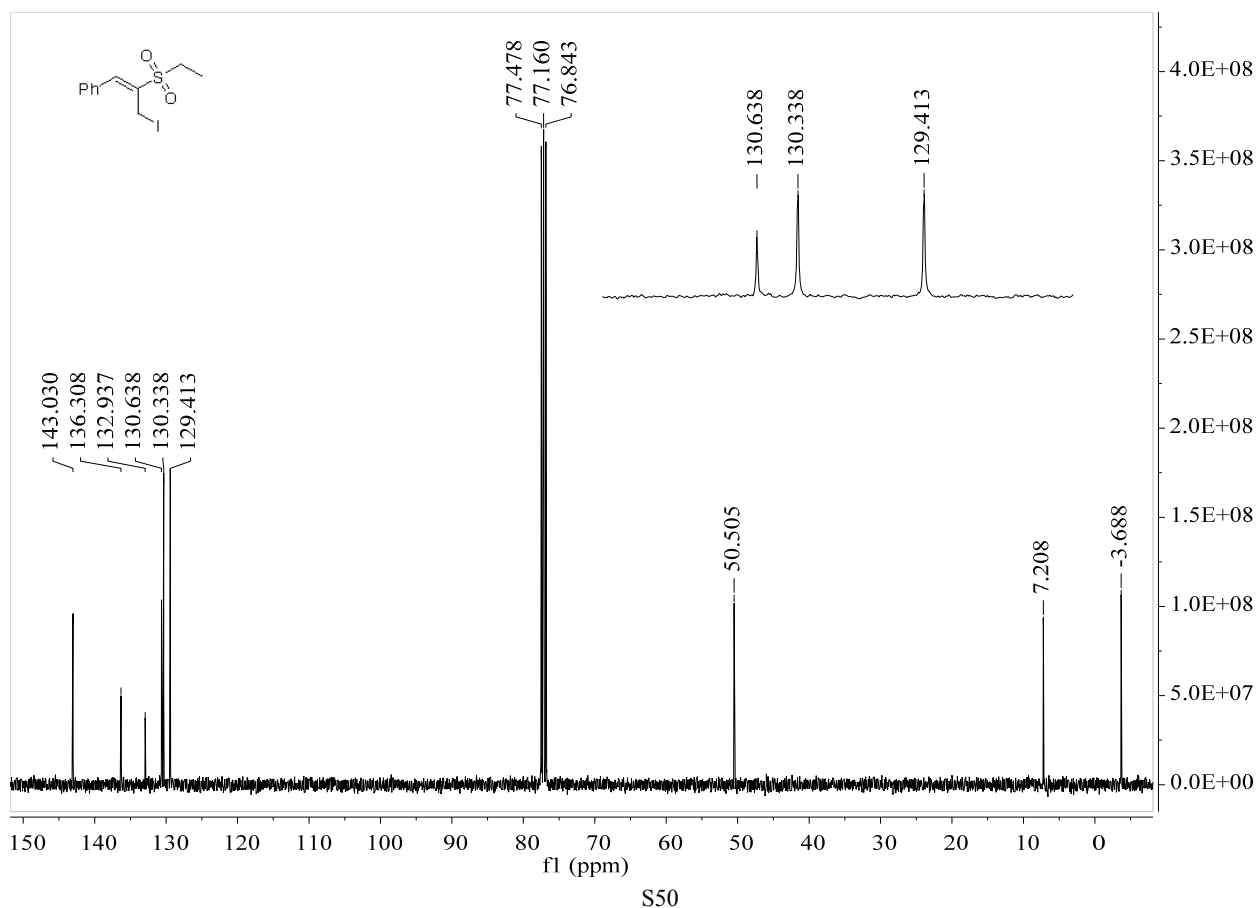
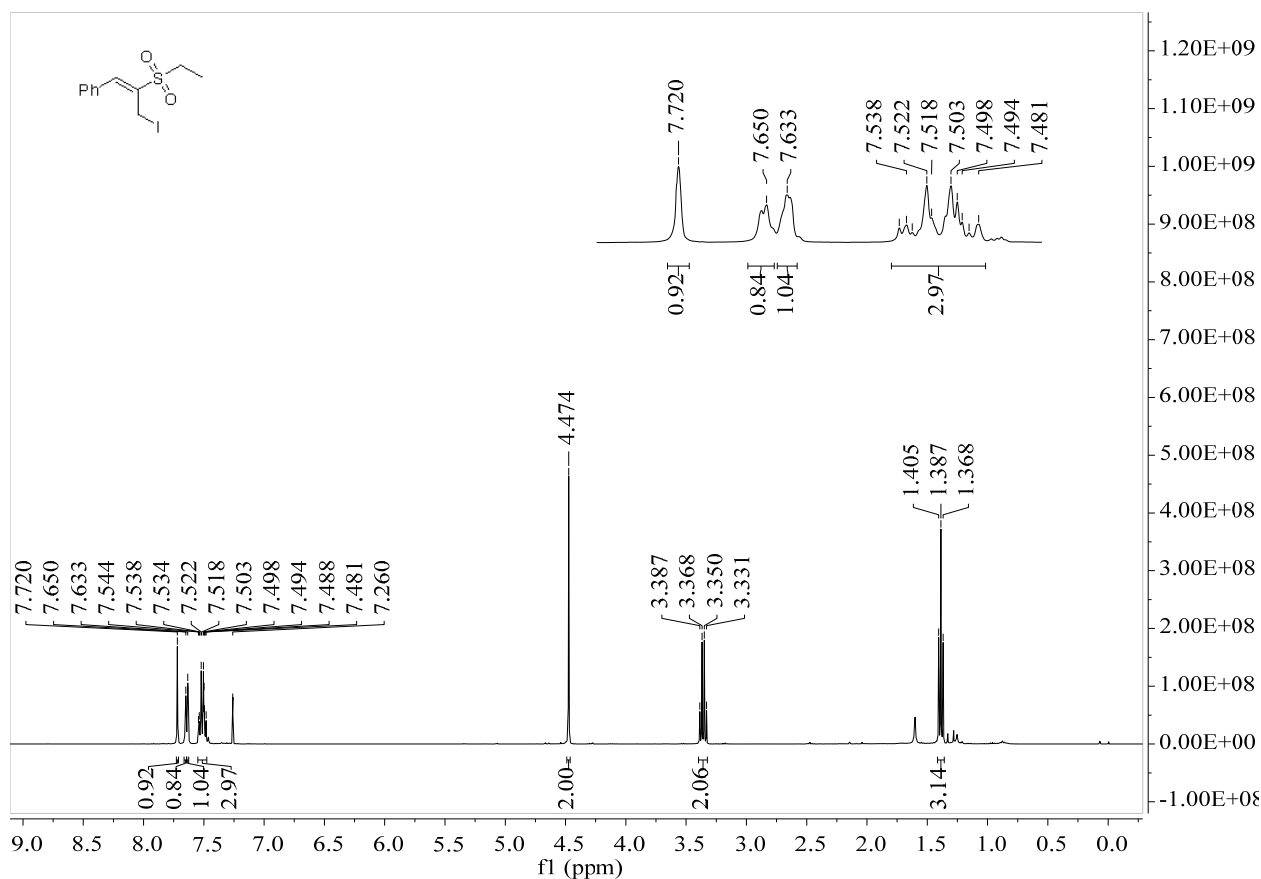
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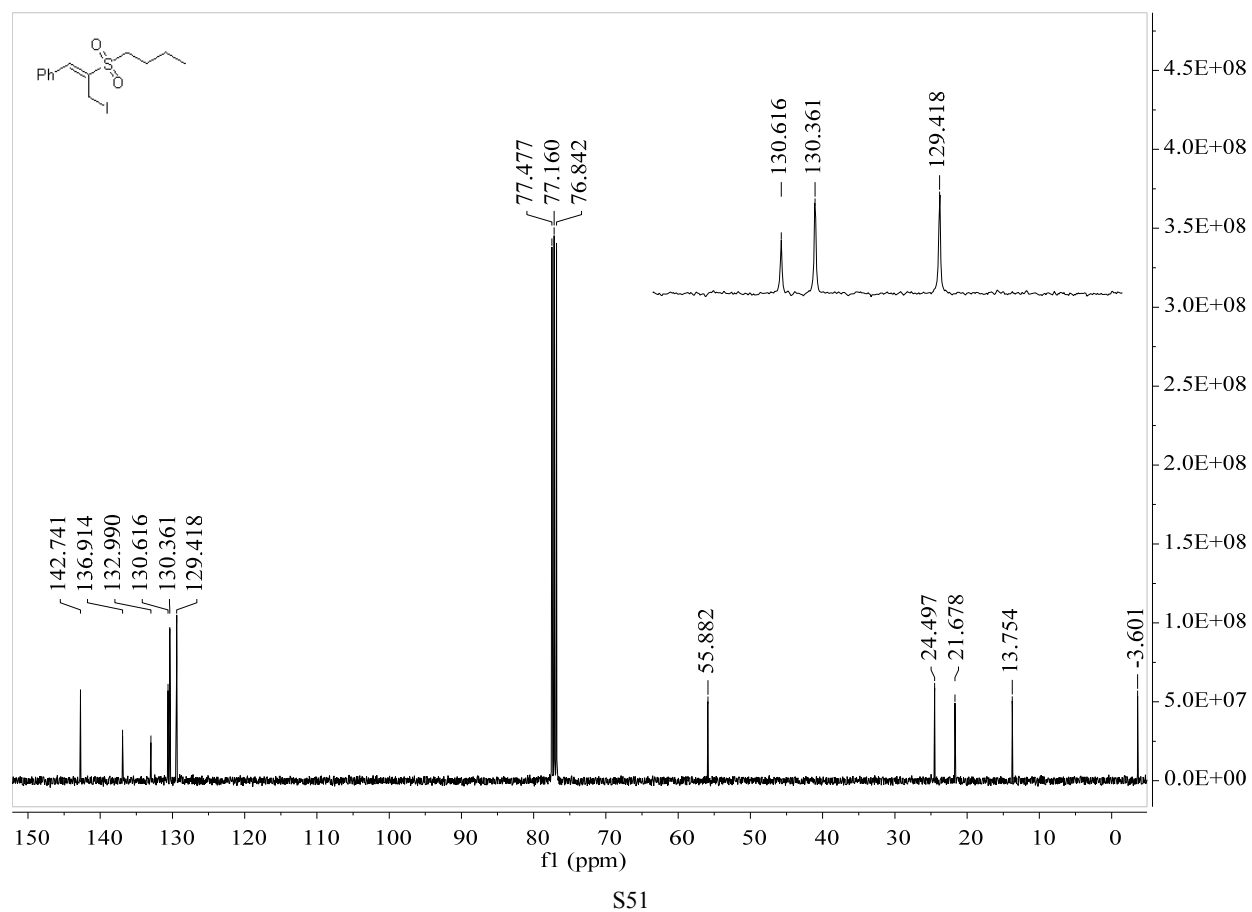
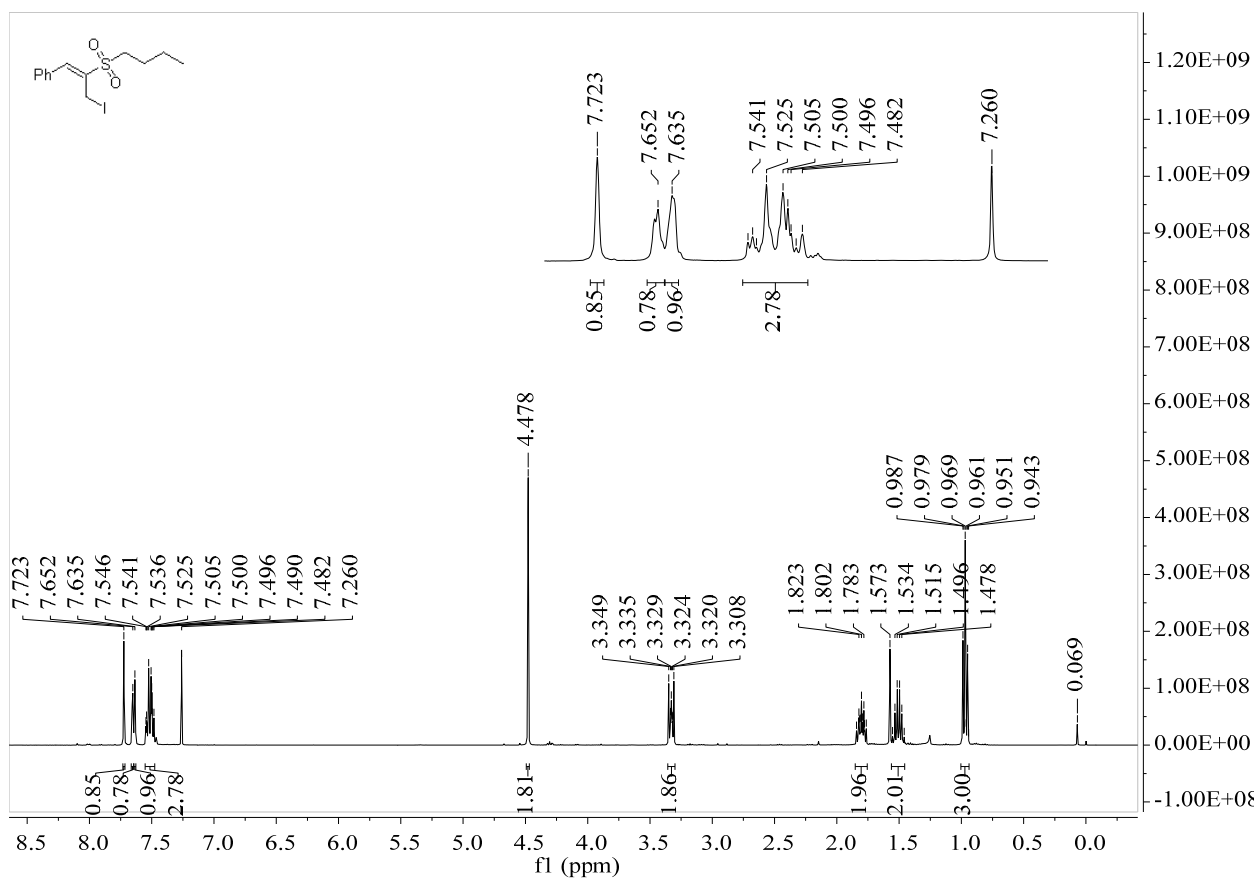
Compound 3z



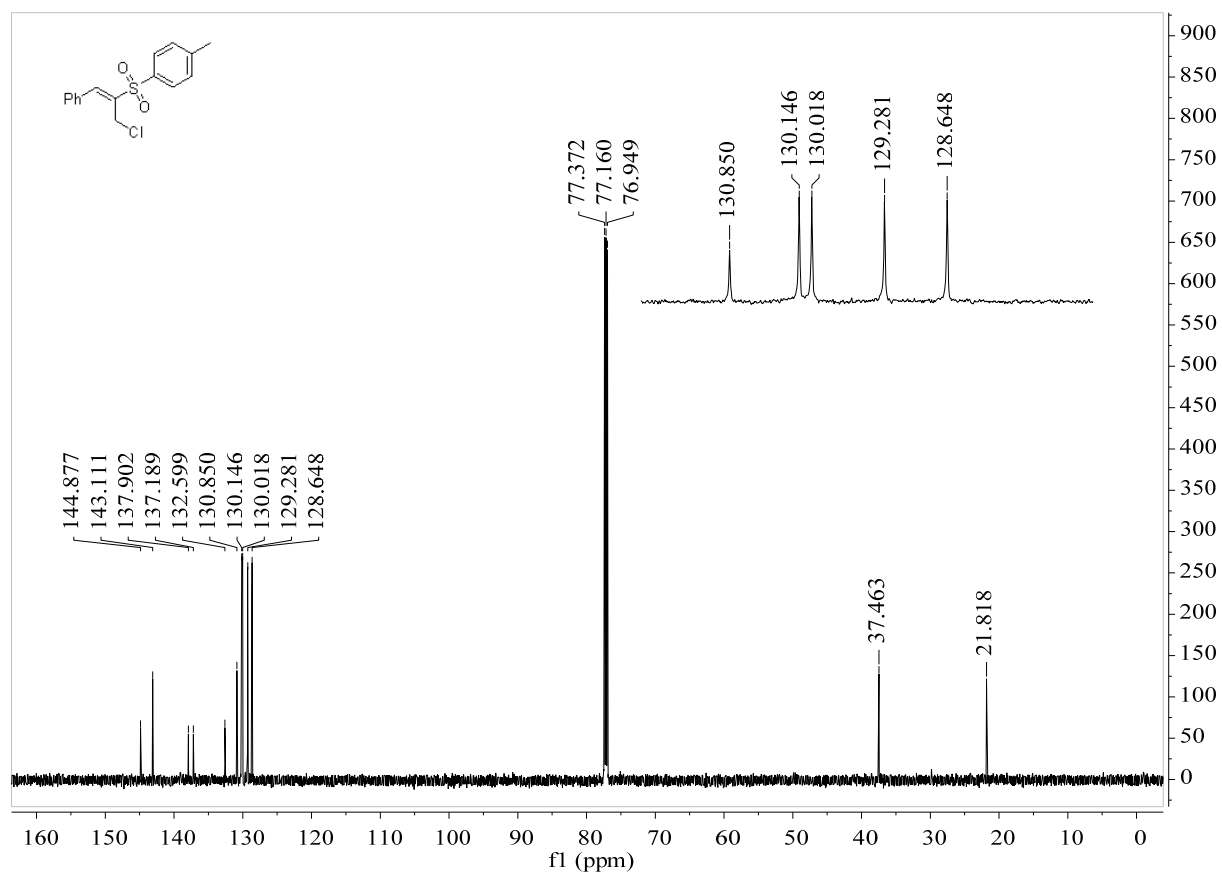
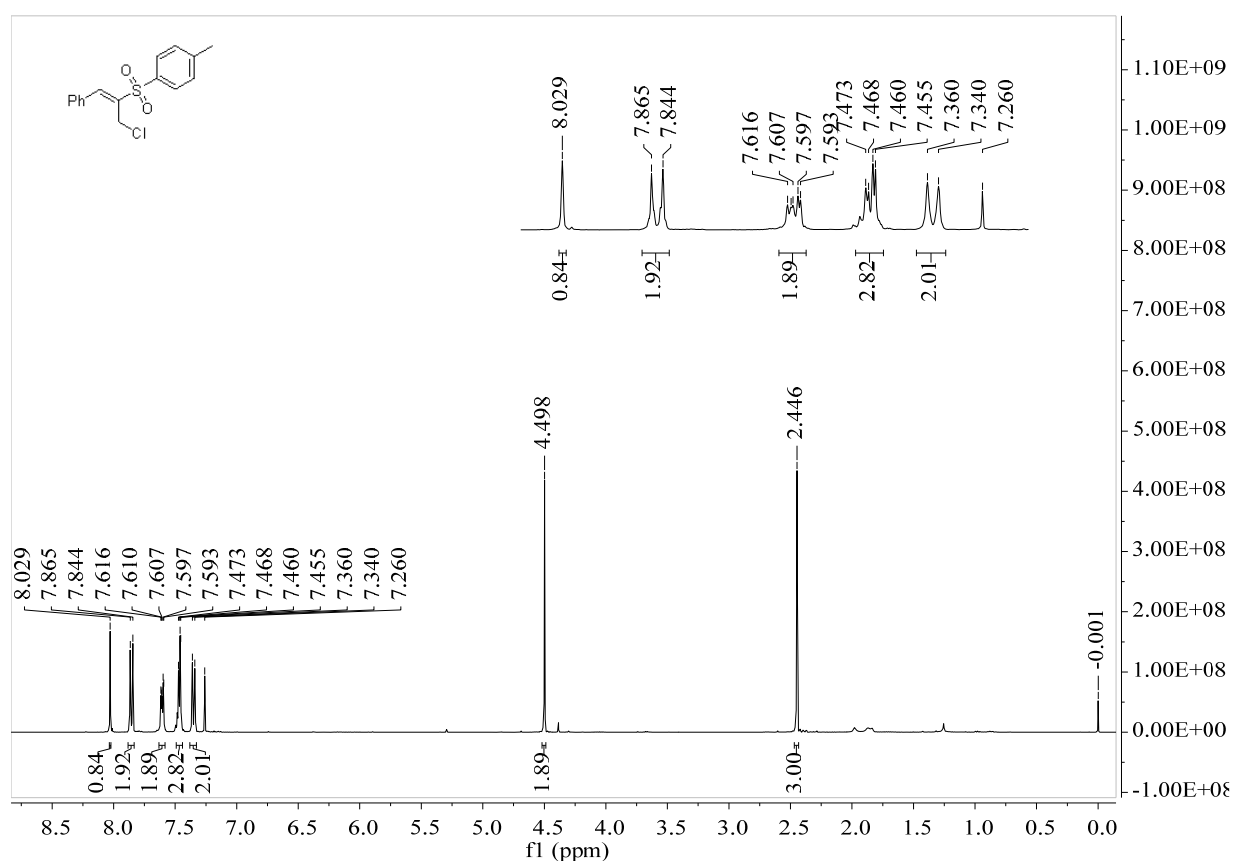
Compound 3aa



Compound 3ab



Compound 3ac



Compound 3ad

