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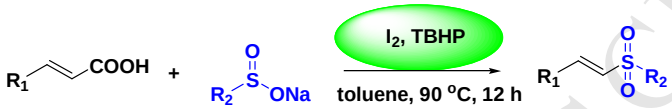

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ABSTRACT

We have developed a practical example of metal-free iodine-promoted decarboxyltive couplings between cinnamic acids and sodium benzene sulfinates, which represents an effective synthesis of vinyl sulfones *via* C–S bond formation reaction.

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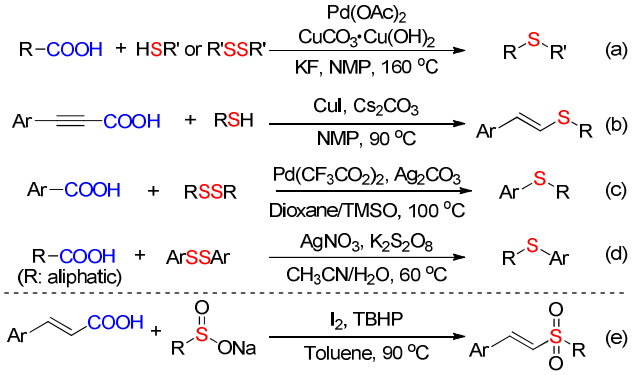
1. Introduction

It is well known that vinyl sulfones are valuable building blocks which are popular as Michael acceptors[1] and most of them usually show a wide range of medicinal activities[2]. Thus, the development of efficient synthetic methods about vinyl sulfones gains great attention. In the past several years, many methods for the synthesis of vinyl sulfones focused on palladium- or copper-catalyzed sulfonylation of alkynes[3], olefins[4], vinyl halides[5], alkenyl boronic acids[6], vinyl tosylates[7] or epoxides[8]. Although great efforts have been made, we thought it would be interesting to synthesize vinyl sulfones through some straight ways.

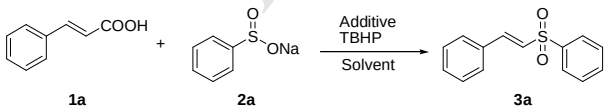


Scheme 1. Decarboxylative C–S Cross-Couplings.

Recently, metal-catalyzed decarboxylative cross-couplings of carboxylic acids have emerged as effective and reliable tools for the formation of C–C[9], C–N[10] and C–P[11]. Also, many methods have been developed for decarboxylative C–S bond formation (Scheme 1a-1d)[12-15], but the use of metal-catalysts (i.e., Pd, Ag and Cu) was not friendly to the environment. In addition, few attention has been paid on decarboxylative C–S bond formation through sulfonylation of cinnamic acid (Scheme 1e).[16] During the process of preparation of this manuscript, palladium-, silver- or copper-catalyzed decarboxylative coupling between sodium sulfinates and cinnamic acids have been reported by several groups.[16a-16d] However, the problem of the potential metal contamination will limit their massive applications in big-scale synthesis, especially in the pharmaceutical industry, where needs serious monitoring of the metal contamination in the products. Herein, as a continuation of the research on decarboxylative cross-coupling of cinnamic acids,[17] we will develop an iodine-promoted decarboxylative C–S bond formation through cinnamic acids and sodium benzene sulfinates in the absence of metal catalyst.

2. Results and discussion

Table 1. Optimization of the Reaction Conditions [a]



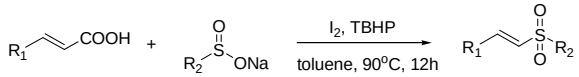
1a 2a 3a

entry	**2a** (equiv)	Additive (equiv)	Solvent	Yield (%)[b]
1	2	–	CH_3CN	4
2	2	TBAB (0.1)	CH_3CN	ND
3	2	TBAI (0.1)	CH_3CN	8
4	2	KI (0.1)	CH_3CN	ND
5	2	NaI (0.1)	CH_3CN	6
6	2	I_2 (0.1)	CH_3CN	11
7	2	$PhI(OAc)_2$ (0.1)	CH_3CN	ND
8	2	I_2 (0.1)	AcOH	ND
9	2	I_2 (0.1)	THF	Trace
10	2	I_2 (0.1)	Toluene	19
11	2	I_2 (0.1)	ethanol	13
12[c]	2	I_2 (0.1)	Toluene	11
13[d]	2	I_2 (0.1)	Toluene	9
14[e]	2	I_2 (0.1)	Toluene	18
15	4	I_2 (0.1)	Toluene	27
16	4	I_2 (0.4)	Toluene	40
17	4	I_2 (0.5)	Toluene	48
18	4	I_2 (0.6)	Toluene	53
19	4	I_2 (1.0)	Toluene	59
20	4	I_2 (1.5)	Toluene	82
21	4	I_2 (2.0)	Toluene	86
22[f]	4	I_2 (2.0)	Toluene	81
23[g]	4	I_2 (2.0)	Toluene	92
24[h]	4	I_2 (2.0)	Toluene	88
25[i]	4	I_2 (2.0)	Toluene	89

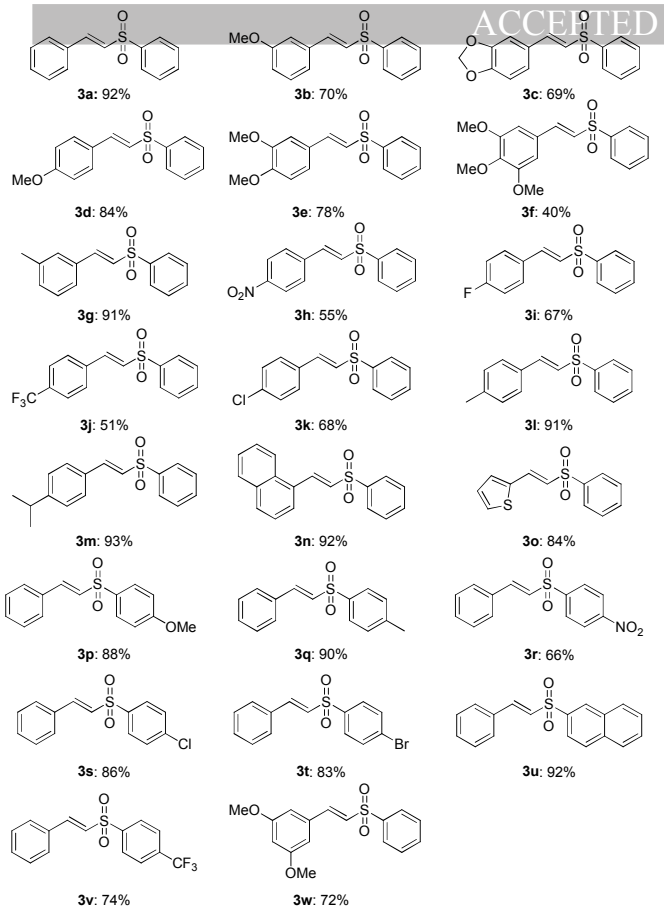
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6-1.2 mmol), additive (0.1-2 equiv), TBHP in H_2O (0.6 mmol), toluene (2 mL), 80 °C, air, 12 h. [b] Isolated yield based on **1a**. [c] DTBP. [d] DCP. [e] TBHP in decane. [f] 70 °C; [g] 90 °C; [h] 100 °C. [i] **1a** (1 g), **2a** (4 equiv), I_2 (2 equiv), TBHP in H_2O (2 equiv), toluene (45 mL), 90 °C, air, 12 h.

The screening of various reaction conditions for the synthesis of (*E*)-vinyl sulfones is listed in Table 1. First, the reaction of cinnamic acid **1a** (0.3 mmol) with sodium benzene sulfinate **2a** (0.6 mmol) was performed tert-butyl hydroperoxide (TBHP) (0.6 mmol) as an oxidant in acetonitrile (2 mL) at 80 °C for 12 h, affording the desired product 3a in 4% yield (Table 1, entry 1). Considering the poor solubility of sodium benzene sulfinate in organic solvent, we added phase transfer catalysts into the system, such as TBAB and TBAI (Table 1, entries 2-3). The use of TBAI led to enhanced yield (8%, Table 1, entry 3). Then we tried other iodine reagents including KI, NaI, I_2 and $PhI(OAc)_2$ (Table 1, entries 4−7). Among them, iodine proved to be the most effective and led to an increase in the yield to 11% (Table 1, entry 6). Then, various solvents were tested for this transformation (Table 1, entries 8−11), and toluene was found to be the best (Table 1, entry 10). Then, we explored other oxidants, including di-tert-butyl peroxide (DTBP), dicumyl peroxide (DCP), and TBHP (in decane) (Table 1, entries 12−14). The results revealed that they were less effective than TBHP in water (Table 1, entry 10). Notably, increasing the amount of sodium sulfinate from 2 to 4 equiv improved the yield of 3a to 27% (Table 1, entry 15). We believed that in this case sodium benzene sulfinate worked not only as the substrate but also as the base. Furthermore, higher loading of iodine resulted in the higher yield of 3a (Table 1, entries 16−21). The satisfactory yield was obtained when 2 equiv of iodine was employed (86% yield, Table 1, entry 21). Through further exploration of the reaction conditions (Table 1, entries 22−24), it was found that the yield could be improved to 92% when the reaction temperature was 90 °C (Table 1, entry 23). Under the optimal conditions, the reaction was performed in gram scale. It can be seen the good result could be obtained (89% yield, entry 25, Table 1).

Table 2. Substrate Scope for Iodine-Mediated Decarboxylation of Cinnamic Acids with Sodium Benzene Sulfinates[a]

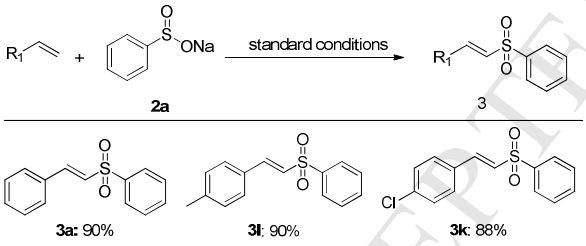


1 2 3



[a] Reaction conditions: **1** (0.3 mmol), **2** (1.2 mmol), I_2 (2 equiv), TBHP in H_2O (0.6 mmol), toluene (2 mL), 90 °C, air, 12 h; Isolated yield based on **1**.

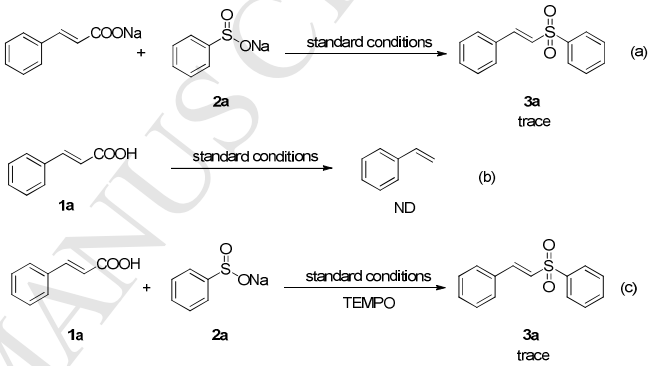
Table 3. Reaction of Alkenes with Sodium Benzene Sulfinate[a]



[a] Reaction conditions: **Alkene** (0.3 mmol), **2a** (1.2 mmol), I_2 (2 equiv), TBHP in H_2O (0.6 mmol), toluene (2 mL), 90 °C, air, 12 h; Isolated yield based on alkene.

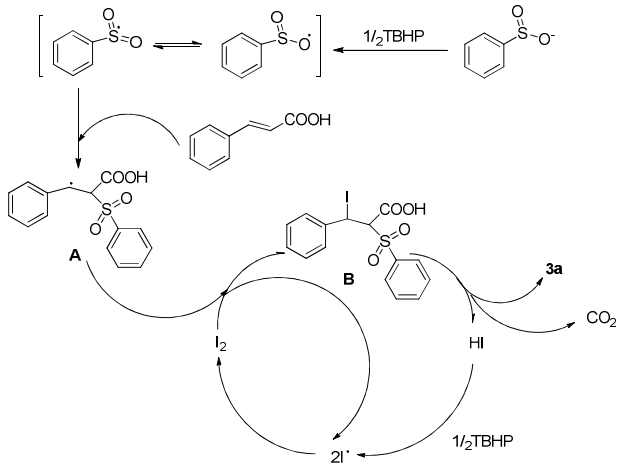
With the optimized conditions in hand, we began to evaluate the scope of this reaction with different substituted cinnamic acids and sodium benzene sulfinates. As demonstrated in Table 2, it was found that electron-rich, -neutral, and -poor cinnamic acids could successfully decarboxylative sulfonylation to give the desired products in modest to excellent yields. For instance, cinnamic acids with alkoxyl groups gave the corresponding products in 40−80% yield (**3b-3f**). Notably, more methoxyl groups on the aromatic ring from cinnamic acids will lead to lower yield of **3**. Unfortunately, in the reaction of electron-deficient cinnamic acids, such as NO_2, F, CF_3, Cl groups, the expected products was obtained only in 51−68% yield (**3h-3k**). In addition, electron-neutral cinnamic acids under the standard conditions afforded the desired vinyl sulfones in high yields (**3g, 3l, 3m**). Furthermore, naphthalenes and thiophenes can also be employed in the reaction to give the desired products (**3n, 3o**) in 84% and 92% yield, respectively. Next, we began to explore the scope of sodium benzene sulfinates partners. To our delight, no matter whether the electron-rich or -neutral sodium benzene sulfinates, the reaction proceeded smoothly (**3p, 3q, 3w**). Functional groups such as Cl and Br could be tolerated, which gave the good yields in 83% and 86% (**3s**, **3t**). Sodium benzene sulfinates with NO_2 and CF_3 group could not react very well, and only 66% and 74% yields were obtained (**3r**, **3v**). Encouragingly, 2-naphthalene sulfinic acid sodium salt successfully coupled with cinnamic acid to afford a good result (**3u**).

When cinnamic acid was replaced by styrene under the standard conditions, 90% yield of desired product could be acquired (Table 2, **3a**). Besides, styrenes with electron donating group (CH_3) and electron withdrawing group (Cl) were suitable substrates for this transformation with the yields up to 90% (Table 2, **3i** and **3k**).



Scheme 2. Control Experiments.

To clarify the reaction mechanism, control experiments were carried out under the standard conditions as shown in Scheme 2. Trace of **3a** was obtained when sodium cinnamate was subjected to the standard reaction conditions (Scheme 2a). Moreover, only cinnamic acid was placed under the standard reaction conditions in the absence of sodium benzene sulfinate, and we could not detect styrene for 12 hours by GC-MS, which supports the possibility for the lack of the participation of styrene (Scheme 2b). When the reaction between cinnamic acid and sodium benzene sulfinate in the presence of TEMPO was conducted under the standard conditions, only trace of **3a** was observed (Scheme 2c). This suggested that the reaction probably underwent a radical pathway.



Scheme 3. The Plausible Mechanism

According to the above results and pioneering works,[18] the mechanism for the reaction of cinnamic acid with sodium benzene sulfinate was proposed as shown in Scheme 3. In the presence of TBHP the sodium benzene sulfinate will be oxidized to generate the oxygen-centered radical. Then the oxygen-centered radical with cinnamic acid can generate an intermediate **A**, which then combines with molecular iodine to form the intermediate **B** and an iodide radical. **B** then goes through decarboxylation and elimination to get the desired product **3a**, HI and CO_2. Further, HI is reoxidized to iodide radical by TBHP, and molecular iodine is generated from two iodide radicals to complete the cycle.

3. Conclusions

In conclusion, we have demonstrated an efficient system for decarbonylative C−S cross-coupling reaction of readily available cinnamic acids with sodium benzene sulfinates. Low-cost iodine together with TBHP could promote such decarboxylative reactions to prepare various useful vinyl sulfones, which represents a practical method. This metal-free protocol will probably be applied in the synthesis of some pharmaceutical intermediates in some cases. The further study on decarboxylation of other acids and its application is underway in our laboratory.

4. Experiment

4.1 General information

All reactions were carried out under air. Solvents were dried and degassed by standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were measured in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (400 MHz or 300 MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR and MS data in the literature.

4.2 General Procedure for preparation of iodine-mediated decarboxylation between cinnamic acid and sodium benzene sulfinate:

A 25 mL tube was charged with cinnamic acid (0.3 mmol), sodium benzene sulfinate (1.2 mmol), iodine (2 equiv)，TBHP in H_2O (0.6 mmol) and toluene (2 mL). The resulting reaction mixture was kept stirring at 90 ^{o}C for 12 h. Upon completion of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

(*E*)-(2-(phenylsulfonyl)vinyl)benzene (3a). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 16.0 Hz, 1H), 7.37−7.45 (m, 3H), 7.48−7.51 (m, 2H), 7.54−7.58 (m, 2H), 7.61−7.65 (m, 1H), 7.71 (d, *J* = 16.0 Hz, 1H), 7.96−7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.7, 128.6, 129.1, 129.4, 131.3, 132.4, 133.4, 140.7, 142.5; LRMS: m/z calcd for $C_{14}H_{12}O_2S$ (M + H): 245.1, found: 245.1.

(*E*)-1-methoxy-3-(2-(phenylsulfonyl)vinyl)benzene (3b). White solid, mp = 112 − 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.88 (d, *J* = 15.2 Hz, 1H), 6.96−7.01 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 15.6 Hz, 1H), 7.94−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 113.4, 117.2, 121.2, 127.6, 127.7, 129.4, 130.1, 133.4, 133.7, 140.7, 142.5, 160.0; LRMS: m/z calcd for $C_{15}H_{14}O_3S$ (M + H): 275.1, found: 275.1

(*E*)-5-(2-(phenylsulfonyl)vinyl)benzo[d][1,3]dioxole (3c). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (s, 6H), 6.69 (d, *J* = 15.2 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 6.99−7.02 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.53−7.64 (m, 4H), 7.93−7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.8, 106.8, 108.7, 125.0, 125.4, 126.6, 127.5, 129.3, 133.3, 141.0, 142.3, 148.5, 150.4; LRMS: m/z calcd for $C_{15}H_{12}O_4S$ (M + H): 289.0, found: 289.0.

(*E*)-1-methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (3d). White solid, mp = 108 − 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.52−7.60 (m, 3H), 7.64 (d, *J* = 15.2 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 114.5, 124.4, 125.0, 127.5, 129.3, 130.4, 133.2, 141.1, 142.3, 162.1; LRMS: m/z calcd for $C_{15}H_{14}O_3S$ (M + H): 275.1, found: 275.0.

(*E*)-1,2-dimethoxy-4-(2-(phenylsulfonyl)vinyl)benzene (3e). White solid, mp = 153 − 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.89 (s, 3H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.51−7.64 (m, 4H), 7.93−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 56.0, 110.0, 111.1, 123.6, 124.7, 125.2, 127.5, 129.3, 133.2, 141.1, 142.6, 149.3, 151.9; LRMS: m/z calcd for $C_{16}H_{16}O_4S$ (M + H): 305.1, found: 305.1.

(*E*)-1,2,3-trimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (3f). Pale yellow solid, mp = 165 − 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 6H), 3.85 (s, 3H), 6.73 (s, 2H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.52−7.63 (m, 4H), 7.93−7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 61.0, 105.9, 126.4, 127.6, 127.8, 129.4, 133.4, 140.8, 142.6, 153.5; LRMS: m/z calcd for $C_{17}H_{18}O_5S$ (M + H): 335.1, found: 335.1.

(*E*)-1-methyl-3-(2-(phenylsulfonyl)vinyl)benzene (3g). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.88 (d, *J* = 15.6 Hz, 1H), 7.23−7.24 (m, 1H), 7.28−7.31 (m, 3H), 7.54−7.64 (m, 3H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.96−7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 125.9, 127.0, 127.6, 129.0, 129.2, 129.4, 132.1, 132.3, 133.4, 138.9, 140.8, 142.7; LRMS: m/z calcd for $C_{15}H_{14}O_2S$ (M + H): 259.1, found: 259.0.

(*E*)-1-nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3h). Pale yellow solid, mp = 173 − 175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 15.6 Hz, 1H), 7.59−7.62 (m, 2H), 7.66−7.70 (m, 3H), 7.74 (d, *J* = 15.6 Hz, 1H), 7.97−7.99 (m, 2H), 8.26 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3, 127.9, 129.3, 129.6, 131.7, 134.0, 138.4, 139.3, 139.8, 149.0; LRMS: m/z calcd for $C_{14}H_{11}NO_4S$ (M + H): 290.0, found: 290.0.

(*E*)-1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3i). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 15.6 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 7.48−7.69 (m, 6H), 7.95−7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.4 (d, *J* = 21.0 Hz), 127.0 (d, *J* = 2.0 Hz), 128.5 (d, *J* = 174.0 Hz), 128.6 (d, *J* = 3.0

Hz), 130.7 (d, *J* = 7.0 Hz), 133.5, 140.6, 141.2, 163.1, 165.6; 275.0. LRMS: m/z calcd for $C_{14}H_{11}FO_2S$ (M + H): 263.0, found: 263.0.

(*E*)-1-(2-(phenylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (3j). Pale yellow solid, mp = 133 − 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 15.6 Hz, 1H), 7.58−7.68 (m, 7H), 7.73 (d, *J* = 15.2 Hz, 1H), 7.97−7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6 (d, *J* = 270.0 Hz), 126.1 (q, *J* = 3.5 Hz), 127.8, 128.8, 129.5, 130.0, 132.6 (q, J = 32.5.0 Hz), 133.8, 135.7, 140.1, 140.5; LRMS: m/z calcd for $C_{15}H_{11}F_3O_2S$ (M + H): 313.0, found: 313.0.

(*E*)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3k). White solid, mp = 127 − 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 15.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.55−7.58 (m, 2H), 7.62−7.67 (m, 2H), 7.95−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.7, 127.9, 129.4, 129.4, 129.8, 130.9, 133.6, 137.2, 140.5, 141.0; LRMS: m/z calcd for $C_{14}H_{11}ClO_2S$ (M + H): 279.0, found: 279.0.

(*E*)-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3l). White solid, mp = 130 − 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.61−7.66 (m, 1H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 126.1, 127.6, 128.6, 129.3, 129.6, 129.8, 133.3, 140.9, 141.9, 142.6; LRMS: m/z calcd for $C_{15}H_{14}O_2S$ (M + H): 259.1, found: 259.0.

(*E*)-1-isopropyl-4-(2-(phenylsulfonyl)vinyl)benzene (3m). White solid, mp = 98 − 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 3H), 1.24 (s, 3H), 2.87−2.94 (m, 1H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.51−7.55 (m, 2H), 7.57−7.62 (m, 1H), 7.67 (d, *J* = 15.2 Hz, 1H), 7.94−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7, 34.1, 126.2, 127.2, 127.6, 128.8, 129.3, 130.0, 133.3, 141.0, 142.6, 152.8; LRMS: m/z calcd for $C_{17}H_{18}O_2S$ (M + H): 287.1, found: 287.1.

(*E*)-1-(2-(phenylsulfonyl)vinyl)naphthalene (3n). White solid, mp = 99 − 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 15.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.54−7.68 (m, 6H), 7.91 (dd, *J* = 14.8 Hz, 8.0, 2H), 8.01 (d, *J* = 7.2 Hz , 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.0, 125.3, 125.8, 126.6, 127.4, 127.8, 128.9, 129.4, 129.5, 129.6, 131.3, 131.5, 133.5, 133.7, 139.6, 140.6; LRMS: m/z calcd for $C_{18}H_{14}O_2S$ (M + H): 295.1, found: 295.0.

(*E*)-2-(2-(phenylsulfonyl)vinyl)thiophene (3o). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, *J* = 15.2 Hz, 1H), 7.07−7.09 (m, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.45 (d, *J* = 4.8 Hz, 1H), 7.54−7.58 (m, 2H), 7.61−7.65 (m, 1H), 7.81 (d, *J* = 15.2 Hz, 1H), 7.94−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.4, 127.6, 128.4, 129.4, 130.1, 132.5, 133.4, 135.2, 136.9, 140.8; LRMS: m/z calcd for $C_{12}H_{10}O_2S_2$ (M + H): 251.0, found: 251.0.

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene (3p). Pale yellow solid, mp = 108 − 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.87 (d, *J* = 15.2 Hz, 1H), 7.02 (d, *J* = 9.2 Hz, 2H), 7.36−7.42 (m, 3H), 7.47−7.49 (m, 2H), 7.64 (d, *J* = 15.6 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 114.6, 127.9, 128.5, 129.1, 129.9, 131.1, 132.2, 132.5, 141.4, 163.6; LRMS: m/z calcd for $C_{15}H_{14}O_3S$ (M + H): 275.1, found:

(*E*)-1-methyl-4-(styrylsulfonyl)benzene (3q). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 6.87 (d, *J* = 15.2 Hz, 1H), 7.36−7.44 (m, 5H), 7.49−7.51 (m, 2H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 127.6, 127.7, 128.5, 129.1, 130.0, 131.1, 132.5, 137.7, 142.0, 144.4; LRMS: m/z calcd for $C_{15}H_{15}O_2S$ (M + H): 259.1, found: 259.0.

(*E*)-1-nitro-4-(styrylsulfonyl)benzene (3r). Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 15.6 Hz, 1H), 7.41−7.50 (m, 3H), 7.52−7.54 (m, 2H), 7.79 (d, *J* = 15.2 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 2H), 8.40 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.6, 125.6, 128.9, 129.1, 129.3, 131.8, 131.9, 145.0, 146.5, 150.5; LRMS: m/z calcd for $C_{14}H_{11}NO_4S$ (M + H): 290.0, found: 290.0.

(*E*)-1-chloro-4-(styrylsulfonyl)benzene (3s). White solid, mp = 78 − 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 15.6 Hz, 1H), 7.39−7.47 (m, 3H), 7.49−7.55 (m, 4H), 7.71 (d, *J* = 15.2 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8, 128.7, 129.2, 129.7, 131.5, 132.2, 139.2, 140.1, 143.1; LRMS: m/z calcd for $C_{14}H_{11}ClO_2S$ (M + H): 279.0, found: 279.0.

(*E*)-1-bromo-4-(styrylsulfonyl)benzene (3t). White solid, mp = 98 − 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 15.2 Hz, 1H), 7.39−7.47 (m, 3H), 7.49−7.52 (m, 2H), 7.69−7.73 (m, 3H), 7.83 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8, 128.7, 129.2, 129.3, 131.5, 132.2, 132.7, 139.8, 143.2; LRMS: m/z calcd for $C_{14}H_{11}BrO_2S$ (M + H): 323.0, found: 323.0.

(*E*)-2-(styrylsulfonyl)naphthalene (3u). White solid, mp = 138 − 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 15.6 Hz, 1H), 7.38−7.46 (m, 3H), 7.50−7.53 (m, 2H), 7.63−7.71 (m, 2H), 7.77 (d, *J* = 15.2 Hz, 1H), 7.90−7.95 (m, 2H), 8.00−8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.6, 127.3, 127.7, 128.0, 128.6, 129.1, 129.2, 129.3, 129.4, 129.7, 131.3, 132.3, 132.4, 135.2, 137.5, 142.6; LRMS: m/z calcd for $C_{18}H_{14}O_2S$ (M + H): 295.1, found: 295.0.

(*E*)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (3v). White solid, mp = 125 − 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 15.4 Hz, 1H), 7.40−7.49 (m, 3H), 7.51−7.55 (m, 2H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.12 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.2 (d, *J* = 272.0 Hz), 126.2, 126.5 (q, *J* = 3.5 Hz), 128.3, 128.8, 129.2, 131.7, 132.0, 135.1 (q, *J* = 32.5 Hz), 144.1, 144.4; LRMS: m/z calcd for $C_{15}H_{11}F_3O_2S$ (M + H): 313.0, found: 313.0.

(*E*)-1,3-dimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (3w). Pale yellow solid, mp = 125 − 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 6.52 (t, *J* = 2.2 Hz, 1H), 6.63 (d, *J* = 2.4 Hz 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 7.54−7.65 (m, 4H), 7.95−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 103.4, 106.5, 127.7, 127.7, 129.4, 133.5, 134.1, 140.6, 142. 6, 161.1; LRMS: m/z calcd for $C_{16}H_{16}O_4S$ (M + H): 305.1, found: 305.1.

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SUPPORTING INFORMATION

Iodine-Promoted Decarboxylative C−S Cross-Coupling of Cinnamic Acids with Sodium Benzene Sulfinates

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General Procedures

General experimental: All reactions were carried out under air. Solvents were dried and degassed by standard methods. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were measured in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (400 MHz or 300 MHz) with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR and TOF-MS data in the literature.

Characterization of the corresponding products:

(*E*)-(2-(phenylsulfonyl)vinyl)benzene (3a)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 16.0 Hz, 1H), 7.37−7.45 (m, 3H), 7.48−7.51 (m, 2H), 7.54−7.58 (m, 2H), 7.61−7.65 (m, 1H), 7.71 (d, *J* = 16.0 Hz, 1H), 7.96−7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.7, 128.6, 129.1, 129.4, 131.3, 132.4, 133.4, 140.7, 142.5; LRMS: m/z calcd for $C_{14}H_{12}O_2S$ (M + H): 245.1, found: 245.1.

(*E*)-1-methoxy-3-(2-(phenylsulfonyl)vinyl)benzene (3b)

White solid, mp: 112 − 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.88 (d, *J* = 15.2 Hz, 1H), 6.96−7.01 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 15.6 Hz, 1H), 7.94−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 113.4, 117.2, 121.2, 127.6, 127.7, 129.4, 130.1, 133.4, 133.7, 140.7, 142.5, 160.0; LRMS: m/z calcd for $C_{15}H_{14}O_3S$ (M + H): 275.1, found: 275.1

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

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (s, 6H), 6.69 (d, *J* = 15.2 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 1.6 Hz, 1H), 6.99−7.02 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.53−7.64 (m, 4H), 7.93−7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.8, 106.8, 108.7, 125.0, 125.4, 126.6, 127.5, 129.3, 133.3, 141.0, 142.3, 148.5, 150.4; LRMS: m/z calcd for $C_{15}H_{12}O_4S$ (M + H): 289.0, found: 289.0.

(*E*)-1-methoxy-4-(2-(phenylsulfonyl)vinyl)benzene (3d)

White solid, mp: 108 − 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.52−7.60 (m, 3H), 7.64 (d, *J* = 15.2 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 114.5, 124.4, 125.0, 127.5, 129.3, 130.4, 133.2, 141.1, 142.3, 162.1; LRMS: m/z calcd for $C_{15}H_{14}O_3S$ (M + H): 275.1, found: 275.0.

(*E*)-1,2-dimethoxy-4-(2-(phenylsulfonyl)vinyl)benzene (3e)

White solid, mp: 153 − 154 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.89 (s, 3H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.51−7.64 (m, 4H), 7.93−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 56.0, 110.0, 111.1, 123.6, 124.7, 125.2, 127.5, 129.3, 133.2, 141.1, 142.6, 149.3, 151.9; LRMS: m/z calcd for $C_{16}H_{16}O_4S$ (M + H): 305.1, found: 305.1.

(*E*)-1,2,3-trimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (3f)

Pale yellow solid, mp: 165 − 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 6H), 3.85 (s, 3H), 6.73 (s, 2H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.52−7.63 (m, 4H), 7.93−7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 61.0, 105.9, 126.4, 127.6, 127.8, 129.4, 133.4, 140.8, 142.6, 153.5; LRMS: m/z calcd for $C_{17}H_{18}O_5S$ (M + H): 335.1, found: 335.1.

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

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.88 (d, *J* = 15.6 Hz, 1H), 7.23−7.24 (m, 1H), 7.28−7.31 (m, 3H), 7.54−7.64 (m, 3H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.96−7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 125.9, 127.0, 127.6, 129.0, 129.2, 129.4, 132.1, 132.3, 133.4, 138.9, 140.8, 142.7; LRMS: m/z calcd for $C_{15}H_{14}O_2S$ (M + H): 259.1, found: 259.0.

(*E*)-1-nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3h)

Pale yellow solid, mp: 173 − 175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 15.6 Hz, 1H), 7.59−7.62 (m, 2H), 7.66−7.70 (m, 3H), 7.74 (d, *J* = 15.6 Hz, 1H), 7.97−7.99 (m, 2H), 8.26 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3, 127.9, 129.3, 129.6, 131.7, 134.0, 138.4, 139.3, 139.8, 149.0; LRMS: m/z calcd for $C_{14}H_{11}NO_4S$ (M + H): 290.0, found: 290.0.

(*E*)-1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3i)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 15.6 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 7.48−7.69 (m, 6H), 7.95−7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.4 (d, *J* = 21.0 Hz), 127.0 (d, *J* = 2.0 Hz), 128.5 (d, *J* = 174.0 Hz), 128.6 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 7.0 Hz), 133.5, 140.6, 141.2, 163.1, 165.6; LRMS: m/z calcd for $C_{14}H_{11}FO_2S$ (M + H): 263.0, found: 263.0.

(*E*)-1-(2-(phenylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (3j)

Pale yellow solid, mp: 133 − 135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 15.6 Hz, 1H), 7.58−7.68 (m, 7H), 7.73 (d, *J* = 15.2 Hz, 1H), 7.97−7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.6 (d, *J* = 270.0 Hz), 126.1 (q, *J* = 3.5 Hz), 127.8, 128.8, 129.5, 130.0, 132.6 (q, *J* = 32.5.0 Hz), 133.8, 135.7, 140.1, 140.5; LRMS: m/z calcd for $C_{15}H_{11}F_3O_2S$ (M + H): 313.0, found: 313.0.

(*E*)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3k)

White solid, mp: 127 − 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 15.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.55−7.58 (m, 2H), 7.62−7.67 (m, 2H), 7.95−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.7, 127.9, 129.4, 129.4, 129.8, 130.9, 133.6, 137.2, 140.5, 141.0; LRMS: m/z calcd for $C_{14}H_{11}ClO_2S$ (M + H): 279.0, found: 279.0.

(*E*)-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3l)

White solid, mp: 130 − 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.61−7.66 (m, 1H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.97 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 126.1, 127.6, 128.6, 129.3, 129.6, 129.8, 133.3, 140.9, 141.9, 142.6; LRMS: m/z calcd for $C_{15}H_{14}O_2S$ (M + H): 259.1, found: 259.0.

(*E*)-1-isopropyl-4-(2-(phenylsulfonyl)vinyl)benzene (3m)

White solid, mp: 98 − 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 3H), 1.24 (s, 3H), 2.87−2.94 (m, 1H), 6.84 (d, *J* = 15.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.51−7.55 (m, 2H), 7.57−7.62 (m, 1H), 7.67 (d, *J* = 15.2 Hz, 1H), 7.94−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7, 34.1, 126.2, 127.2, 127.6, 128.8, 129.3, 130.0, 133.3, 141.0, 142.6, 152.8; LRMS: m/z calcd for $C_{17}H_{18}O_2S$ (M + H): 287.1, found: 287.1.

(*E*)-1-(2-(phenylsulfonyl)vinyl)naphthalene (3n)

White solid, mp: 99 − 101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 15.2 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.54−7.68 (m, 6H), 7.91 (dd, *J* = 14.8, 8.0 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.0, 125.3, 125.8, 126.6, 127.4, 127.8, 128.9, 129.4, 129.5, 129.6, 131.3, 131.5, 133.5, 133.7, 139.6, 140.6; LRMS: m/z calcd for $C_{18}H_{14}O_2S$ (M + H): 295.1, found: 295.0.

(*E*)-2-(2-(phenylsulfonyl)vinyl)thiophene (3o)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, *J* = 15.2 Hz, 1H), 7.07−7.09 (m, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.45 (d, *J* = 4.8 Hz, 1H), 7.54−7.58 (m, 2H), 7.61−7.65 (m, 1H), 7.81 (d, *J* = 15.2 Hz, 1H), 7.94−7.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.4, 127.6, 128.4, 129.4, 130.1, 132.5, 133.4, 135.2, 136.9, 140.8; LRMS: m/z calcd for $C_{12}H_{10}O_2S_2$ (M + H): 251.0, found: 251.0.

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene (3p)

Pale yellow solid, mp: 108 − 110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 6.87 (d, *J* = 15.2 Hz, 1H), 7.02 (d, *J* = 9.2 Hz, 2H), 7.36−7.42 (m, 3H), 7.47−7.49 (m, 2H), 7.64 (d, *J* = 15.6 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 114.6, 127.9, 128.5, 129.1, 129.9, 131.1, 132.2, 132.5, 141.4, 163.6; LRMS: m/z calcd for $C_{15}H_{14}O_3S$ (M + H): 275.1, found: 275.0.

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

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 6.87 (d, *J* = 15.2 Hz, 1H), 7.36−7.44 (m, 5H), 7.49−7.51 (m, 2H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 127.6, 127.7, 128.5, 129.1, 130.0, 131.1, 132.5, 137.7, 142.0, 144.4; LRMS: m/z calcd for $C_{15}H_{15}O_2S$ (M + H): 259.1, found: 259.0.

(*E*)-1-nitro-4-(styrylsulfonyl)benzene (3r)

Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 15.6 Hz, 1H), 7.41−7.50 (m, 3H), 7.52−7.54 (m, 2H), 7.79 (d, *J* = 15.2 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 2H), 8.40 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.6, 125.6, 128.9, 129.1, 129.3, 131.8, 131.9, 145.0, 146.5, 150.5; LRMS: m/z calcd for $C_{14}H_{11}NO_4S$ (M + H): 290.0, found: 290.0.

(*E*)-1-chloro-4-(styrylsulfonyl)benzene (3s)

White solid, mp: 78 − 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 15.6 Hz, 1H), 7.39−7.47 (m, 3H), 7.49−7.55 (m, 4H), 7.71 (d, *J* = 15.2 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8, 128.7, 129.2, 129.7, 131.5, 132.2, 139.2, 140.1, 143.1; LRMS: m/z calcd for $C_{14}H_{11}ClO_2S$ (M + H): 279.0, found: 279.0.

(*E*)-1-bromo-4-(styrylsulfonyl)benzene (3t)

White solid, mp: 98 − 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 15.2 Hz, 1H), 7.39−7.47 (m, 3H), 7.49−7.52 (m, 2H), 7.69−7.73 (m, 3H), 7.83 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8, 128.7, 129.2, 129.3, 131.5, 132.2, 132.7, 139.8, 143.2; LRMS: m/z calcd for $C_{14}H_{11}BrO_2S$ (M + H): 323.0, found: 323.0.

(*E*)-2-(styrylsulfonyl)naphthalene (3u)

White solid, mp: 138 − 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 15.6 Hz, 1H), 7.38−7.46 (m, 3H), 7.50−7.53 (m, 2H), 7.63−7.71 (m, 2H), 7.77 (d, *J* = 15.2 Hz, 1H), 7.90−7.95 (m, 2H), 8.00−8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.6, 127.3, 127.7, 128.0, 128.6, 129.1, 129.2, 129.3, 129.4, 129.7, 131.3, 132.3, 132.4, 135.2, 137.5, 142.6; LRMS: m/z calcd for $C_{18}H_{14}O_2S$ (M + H): 295.1, found: 295.0.

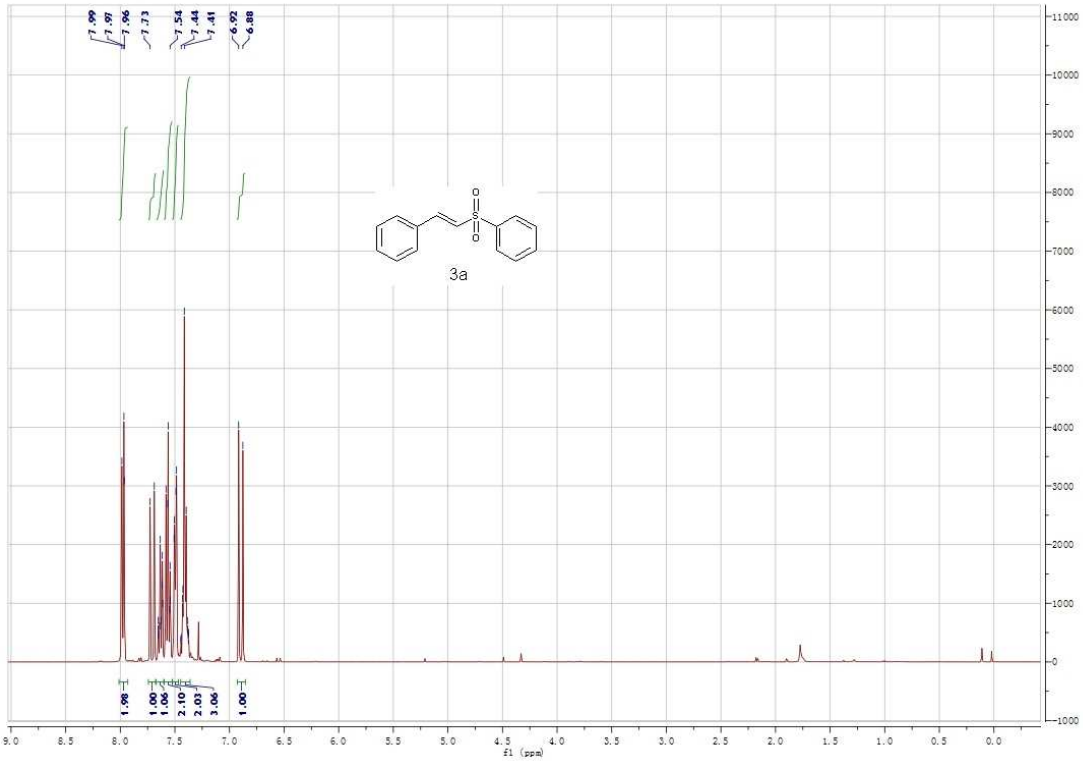
(*E*)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (3v)

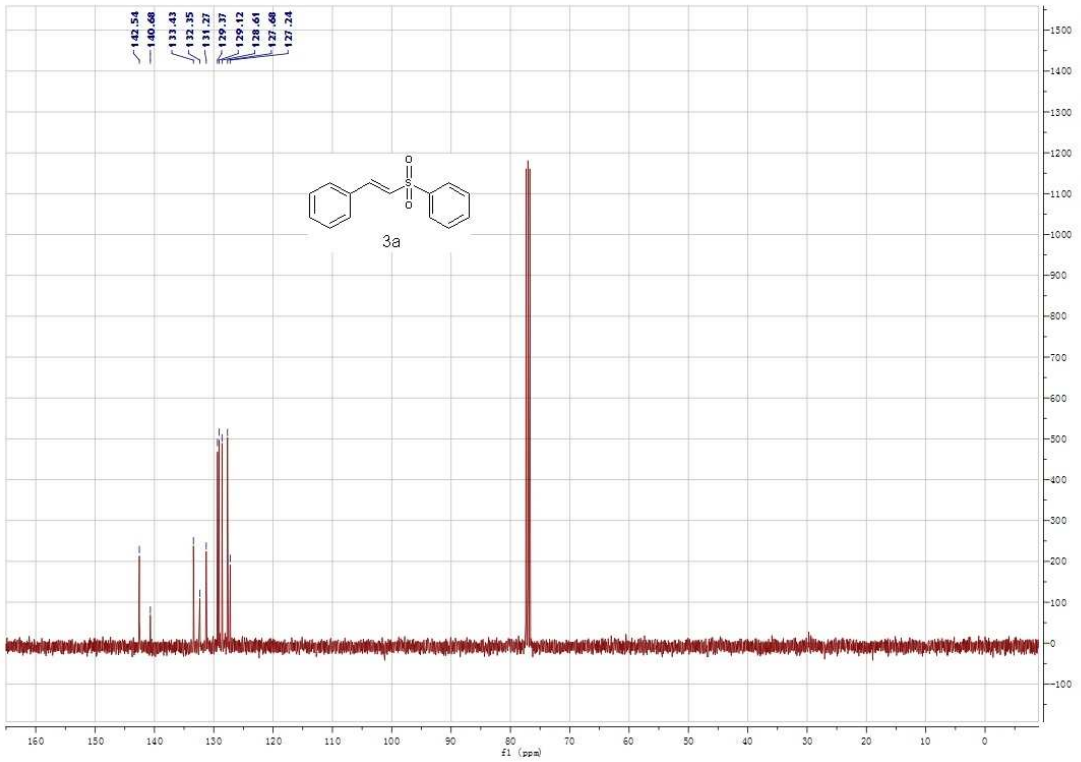
White solid, mp: 125 − 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 15.4 Hz, 1H), 7.40−7.49 (m, 3H), 7.51−7.55 (m, 2H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.2 (d, *J* = 272.0 Hz), 126.2, 126.5 (q, *J* = 3.5 Hz), 128.3, 128.8, 129.2, 131.7, 132.0, 135.1 (q, *J* = 32.5 Hz), 144.1, 144.4; LRMS: m/z calcd for $C_{15}H_{11}F_3O_2S$ (M + H): 313.0, found: 313.0.

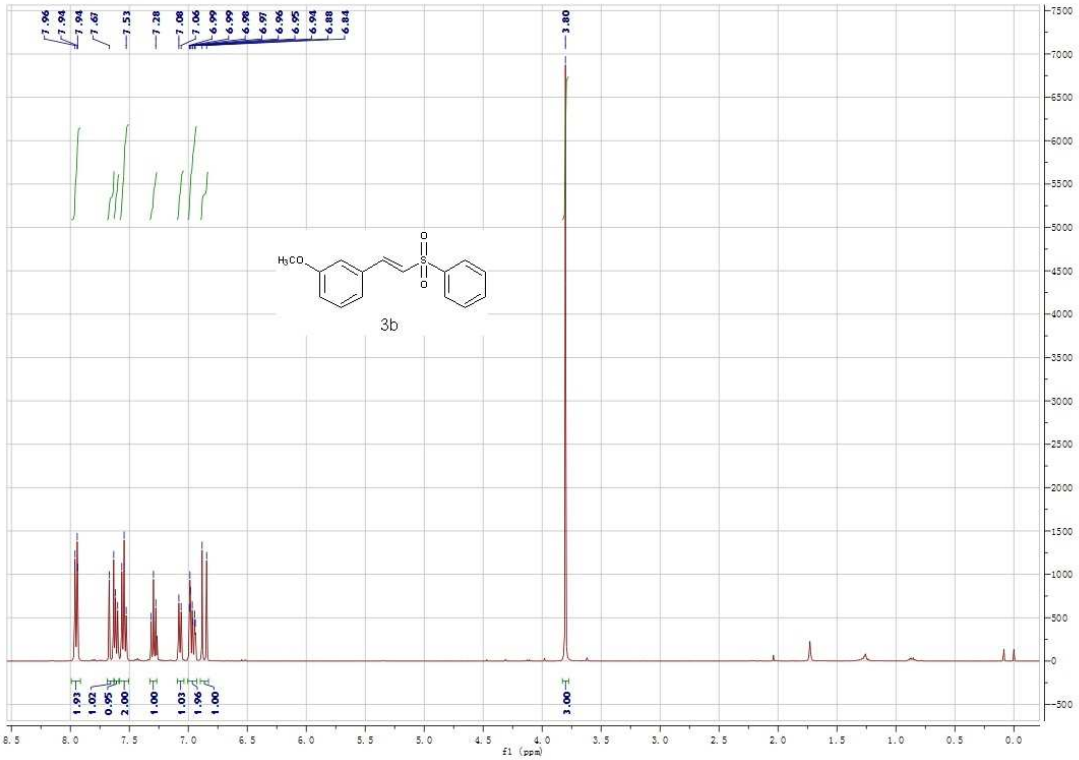
(*E*)-1,3-dimethoxy-5-(2-(phenylsulfonyl)vinyl)benzene (3w)

Pale yellow solid, mp: 125 − 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 6H), 6.52 (t, *J* = 2.2 Hz, 1H), 6.63 (d, *J* = 2.4 Hz 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 7.54−7.65 (m, 4H), 7.95−7.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 103.4, 106.5, 127.7, 127.7, 129.4, 133.5, 134.1, 140.6, 142. 6, 161.1; LRMS: m/z calcd for $C_{16}H_{16}O_4S$ (M + H): 305.1, found: 305.1.

Copy of NMR Spectra for desired products:



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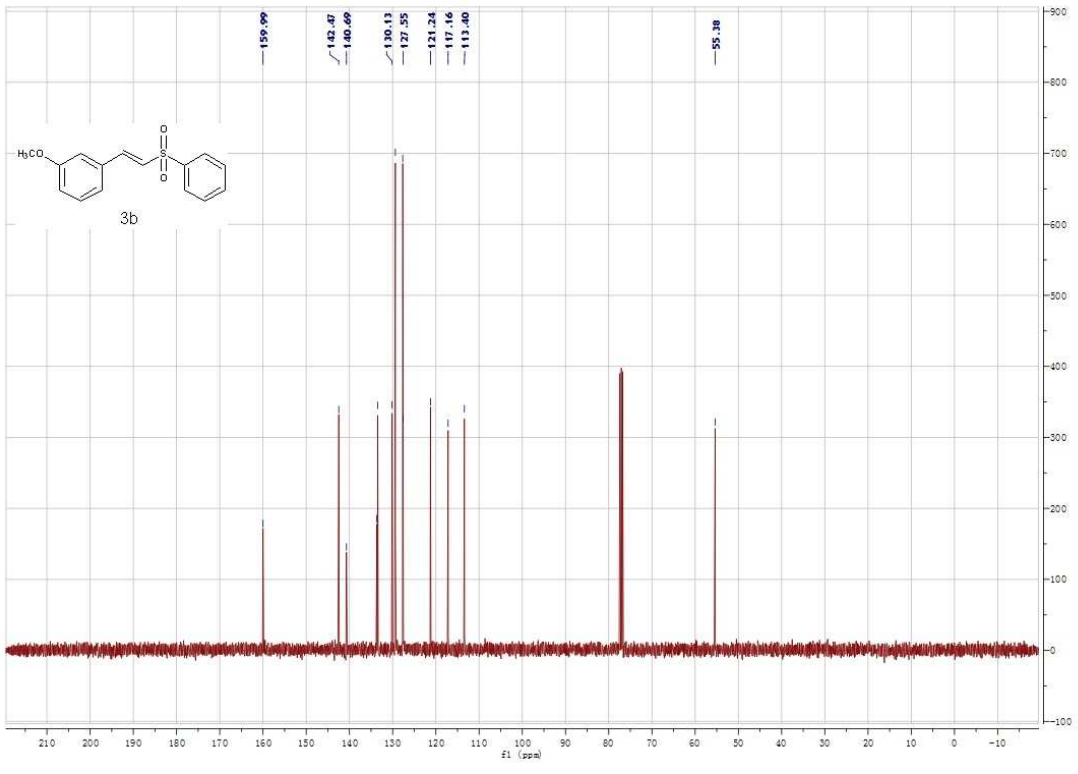
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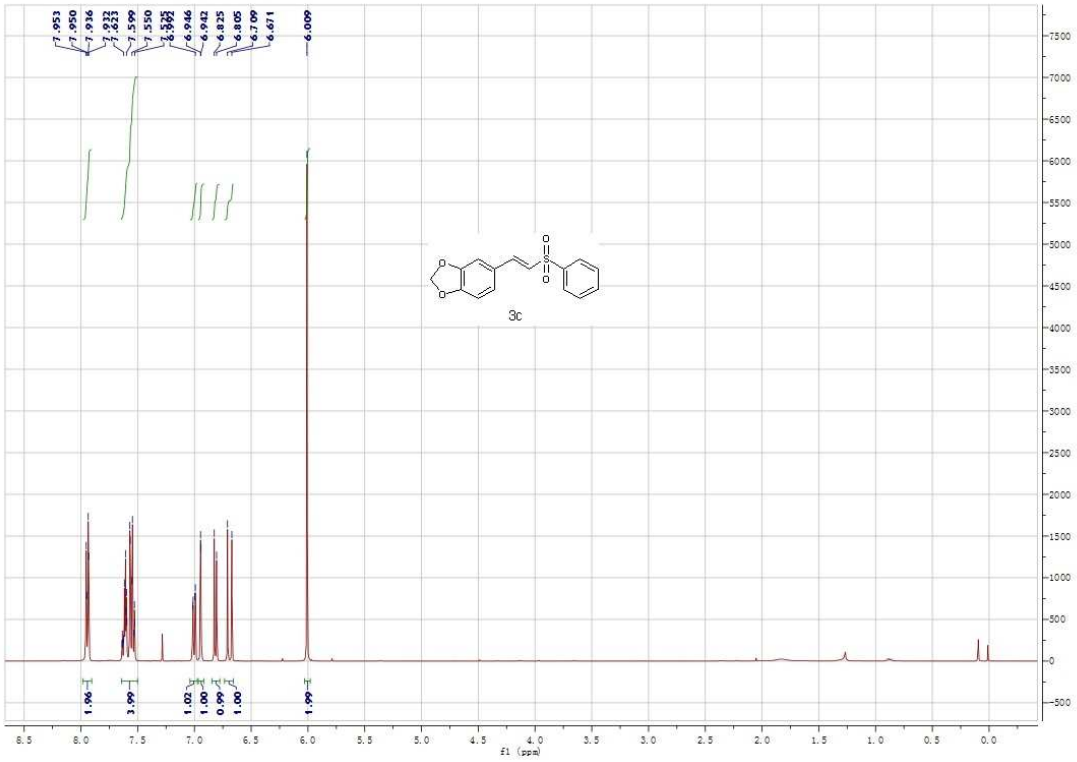
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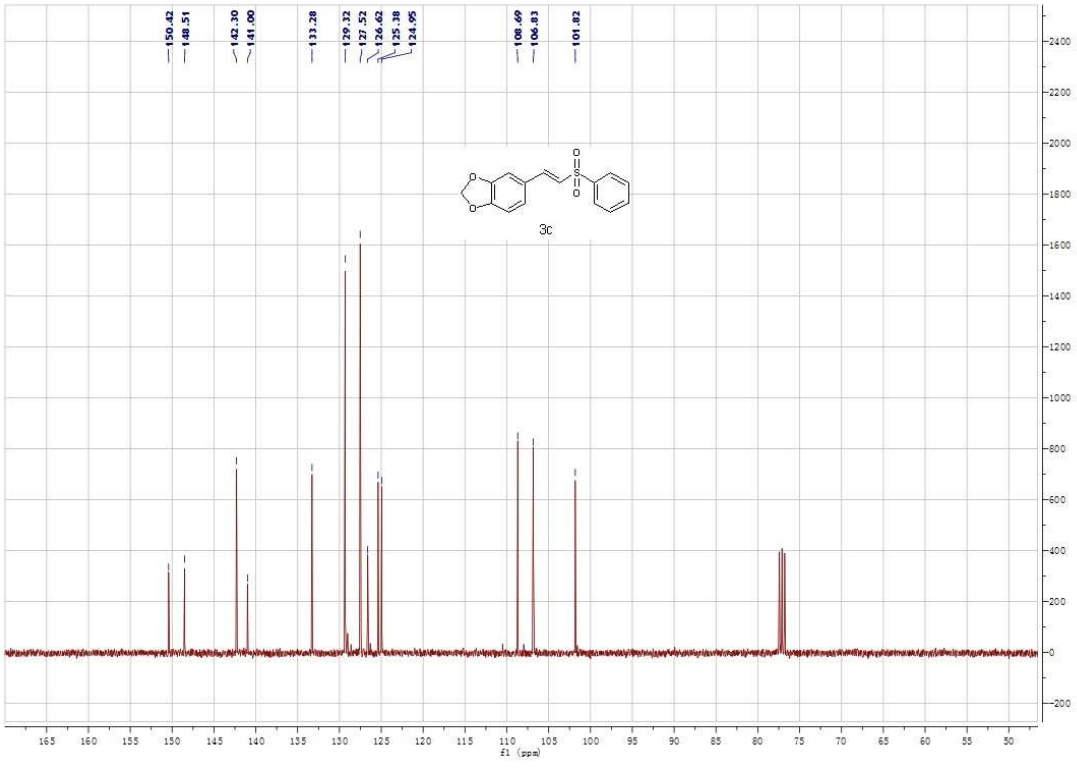
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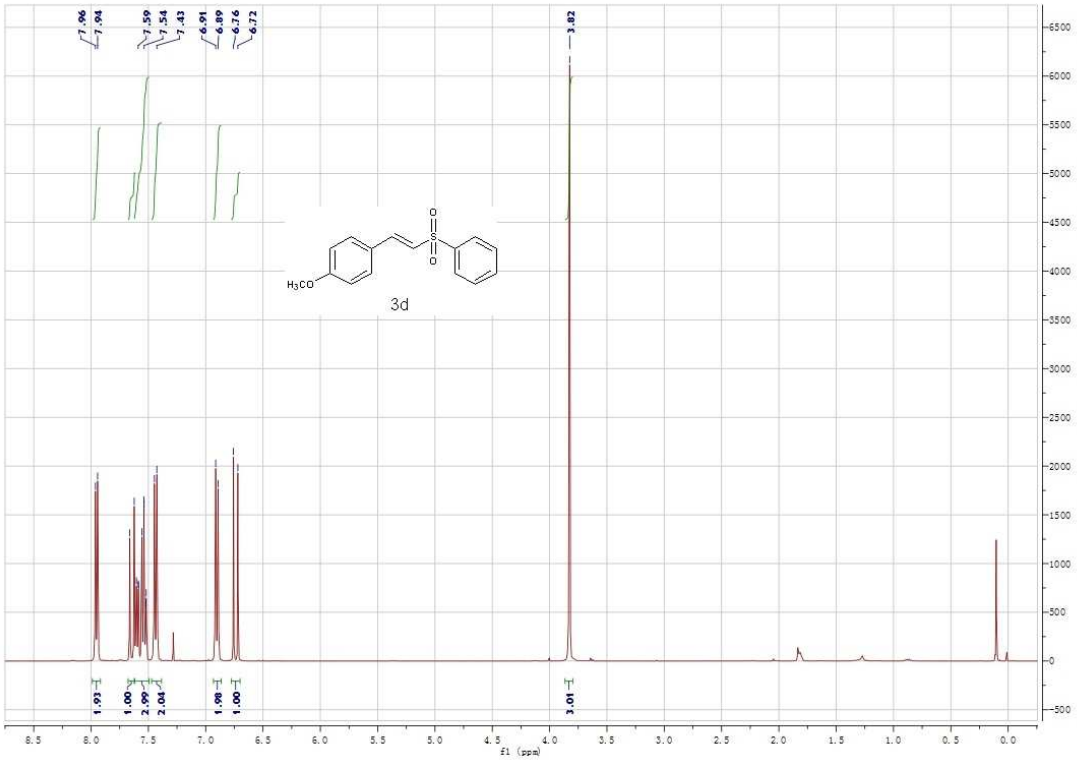
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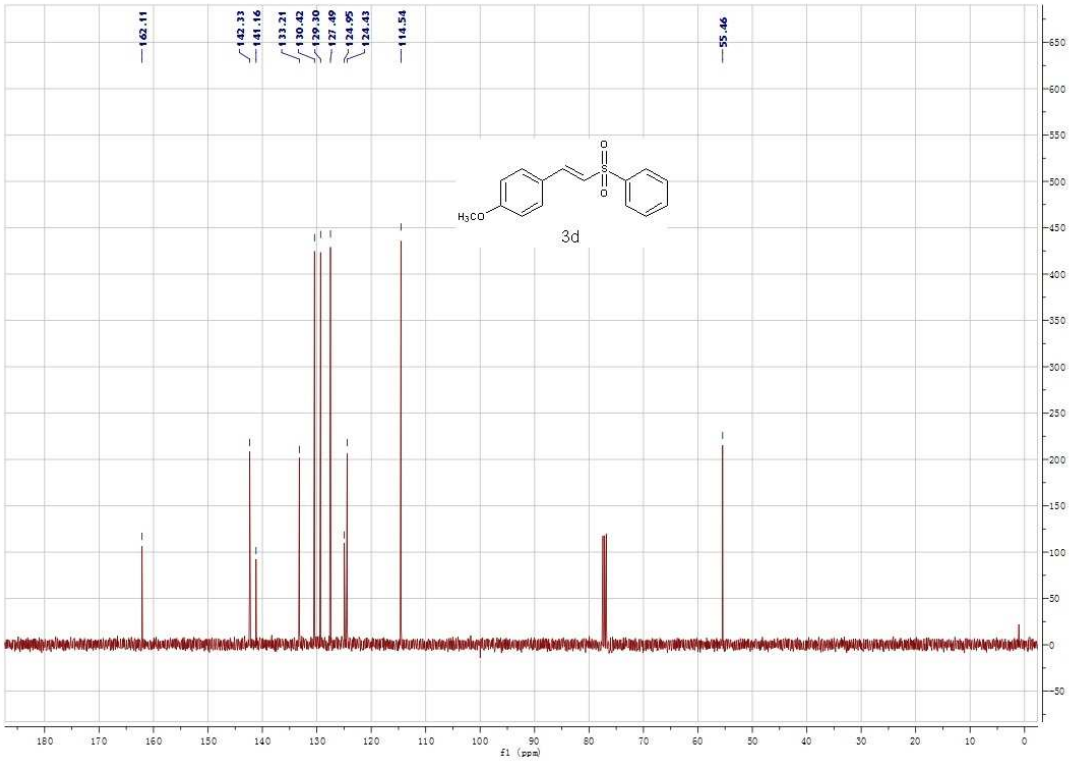
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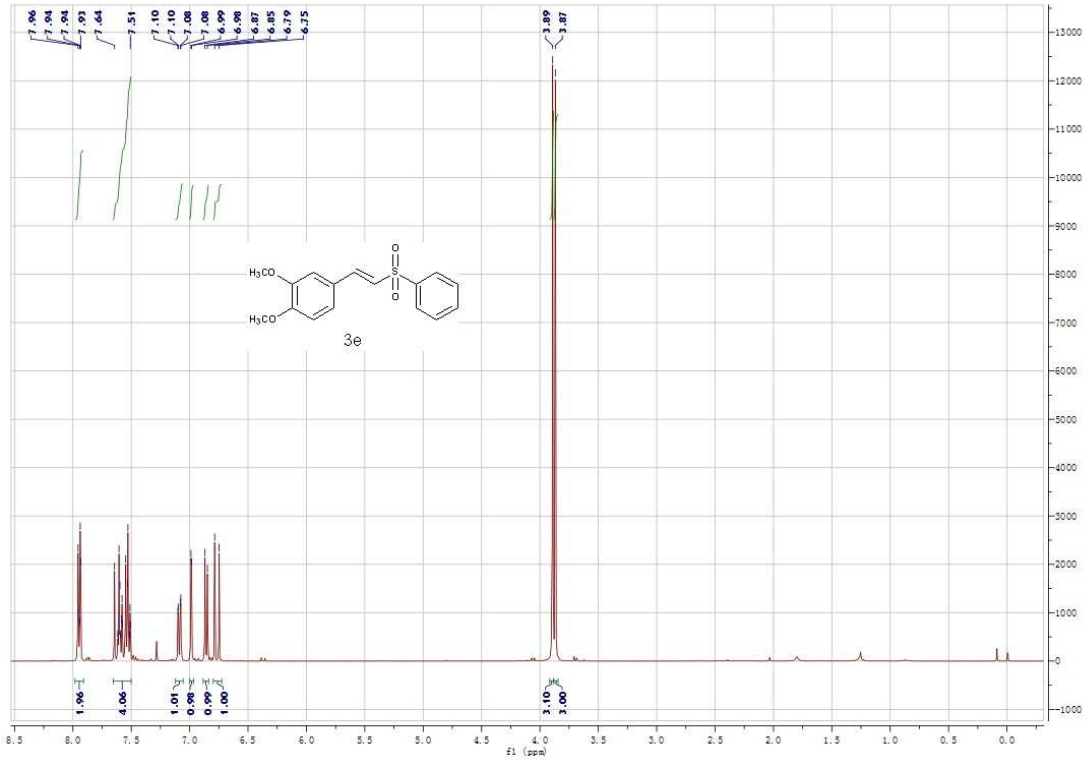
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H3CO
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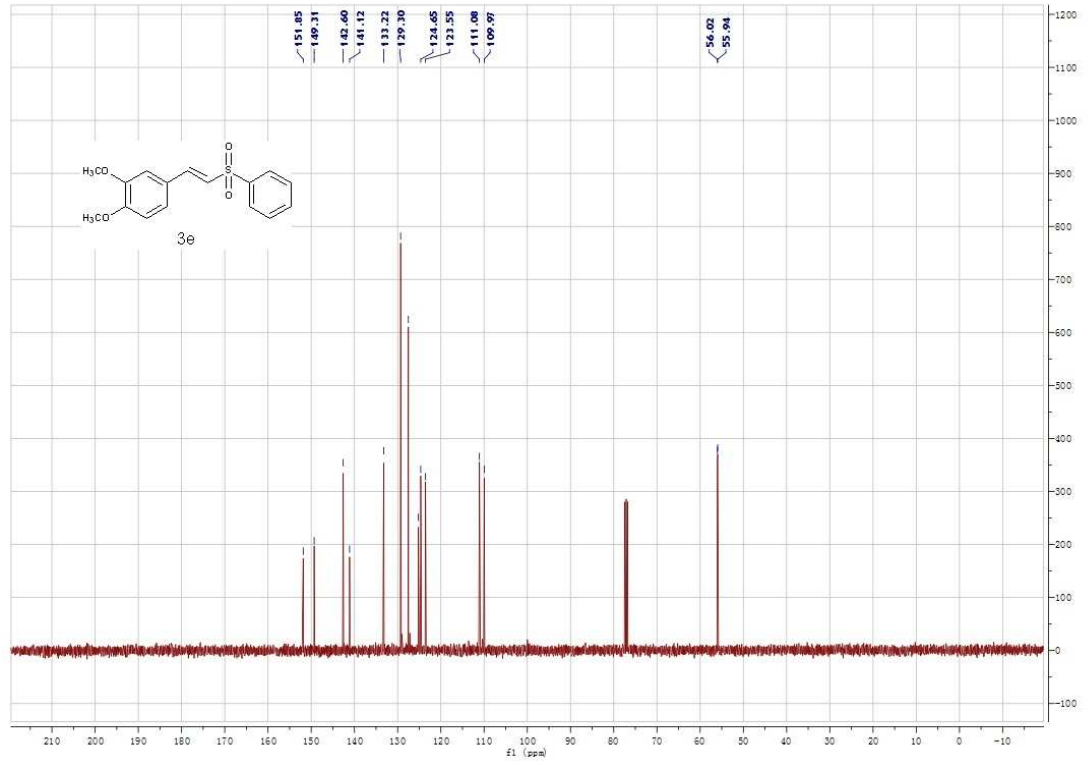
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O
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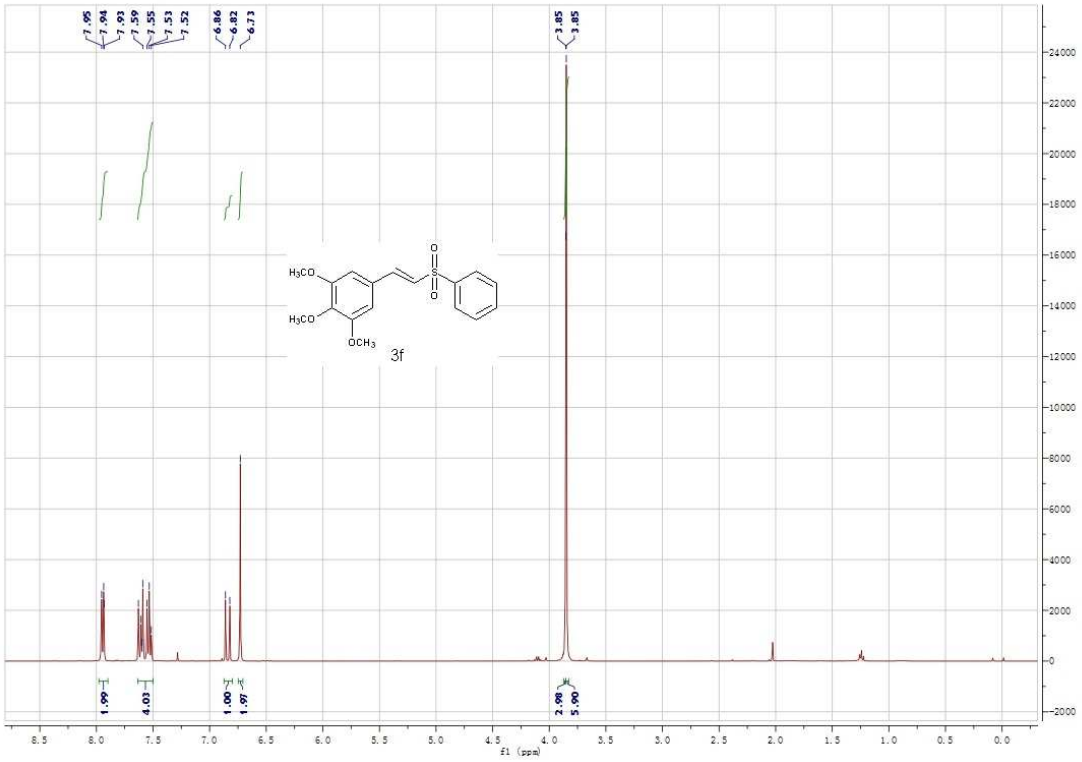
f1 (ppm)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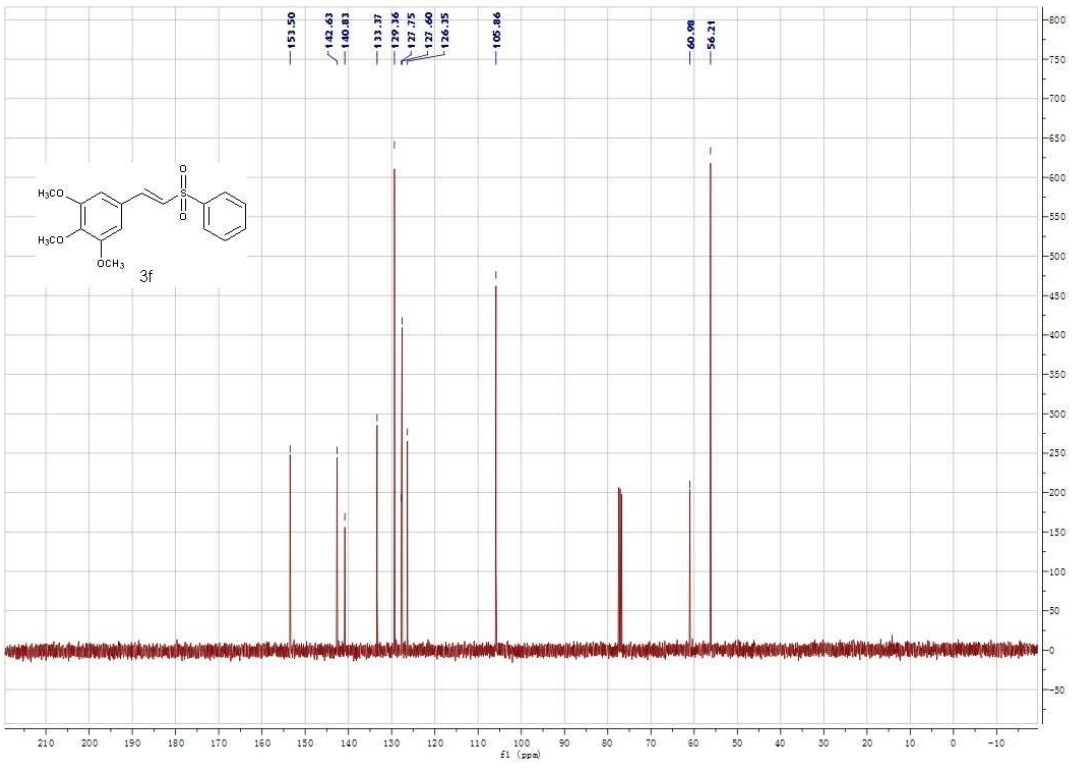
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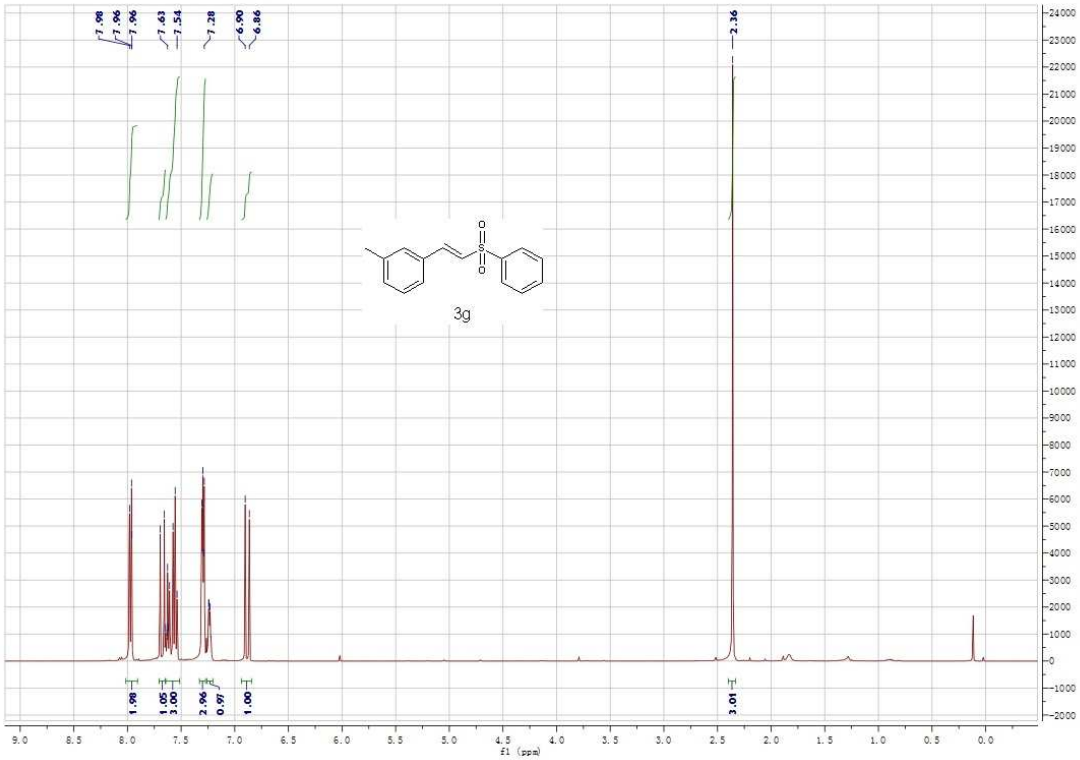
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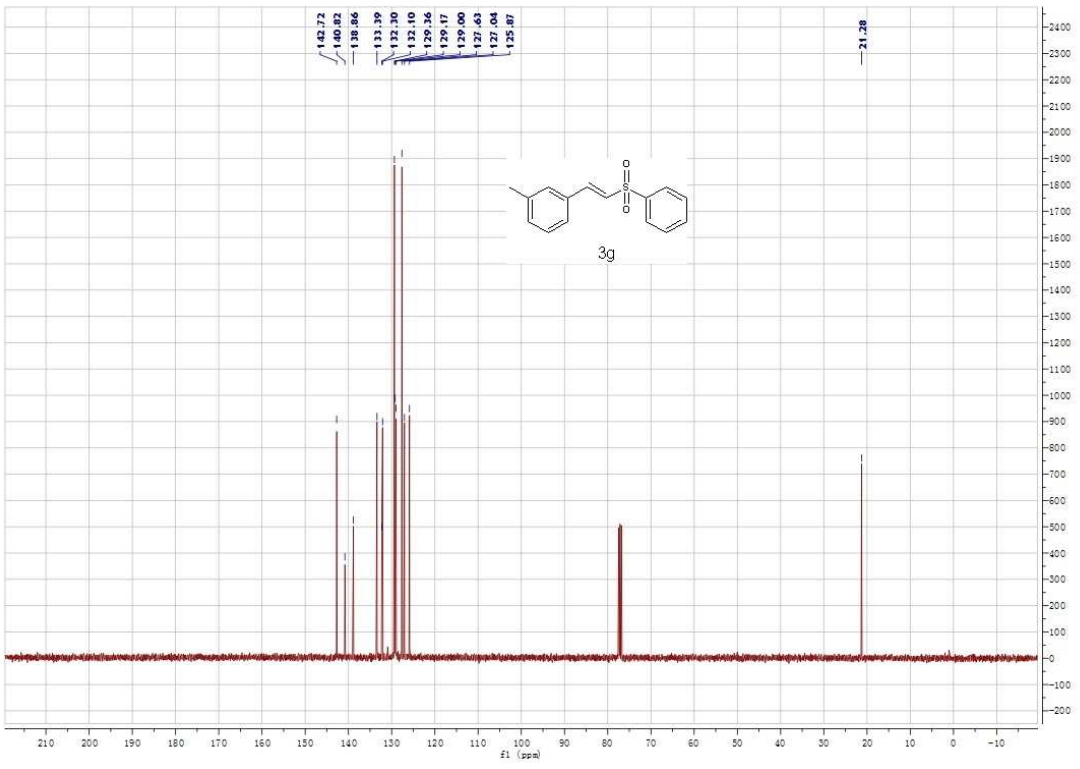
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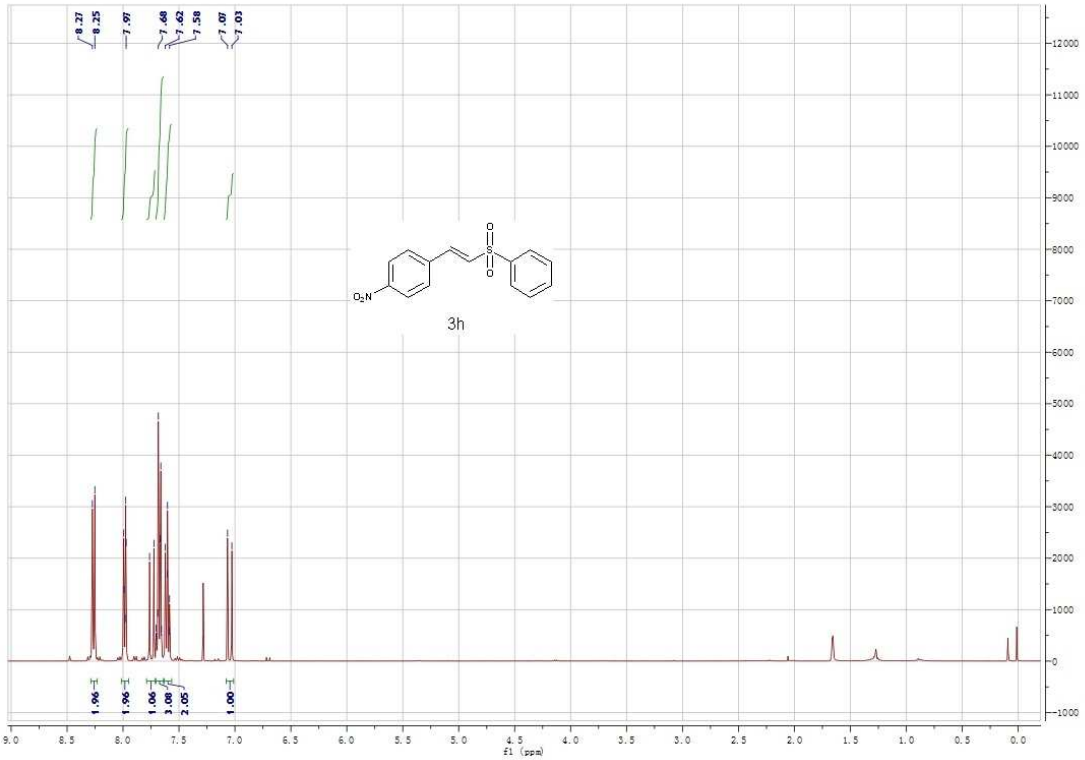
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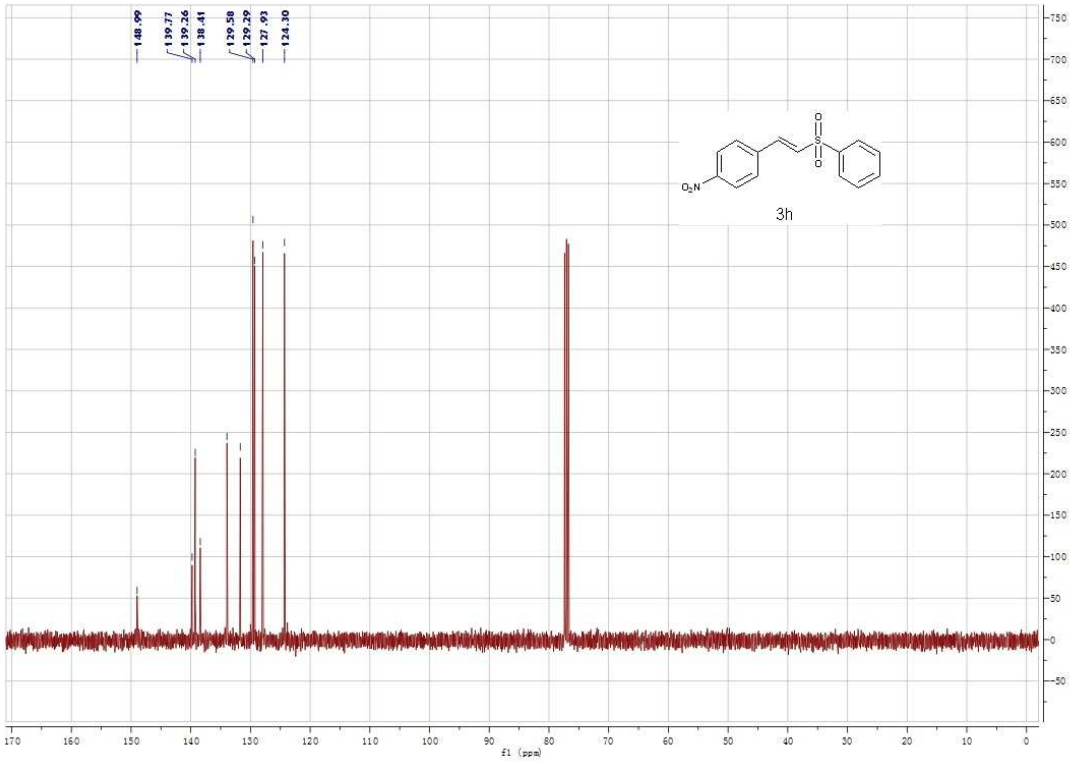
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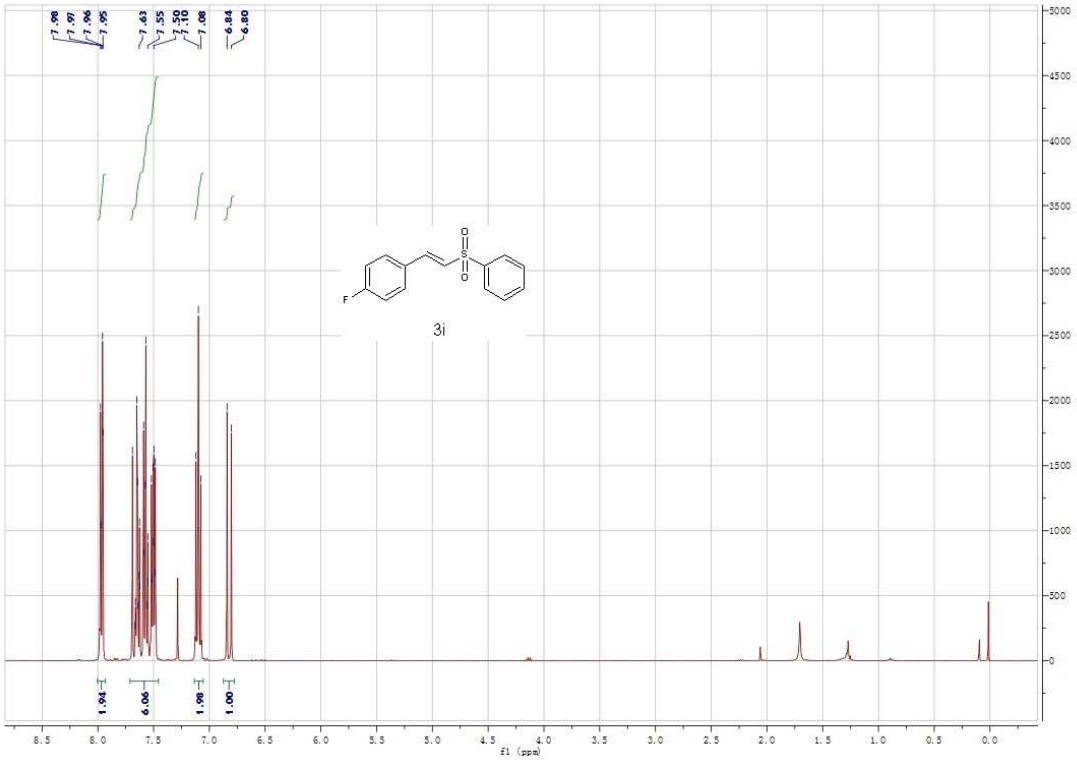
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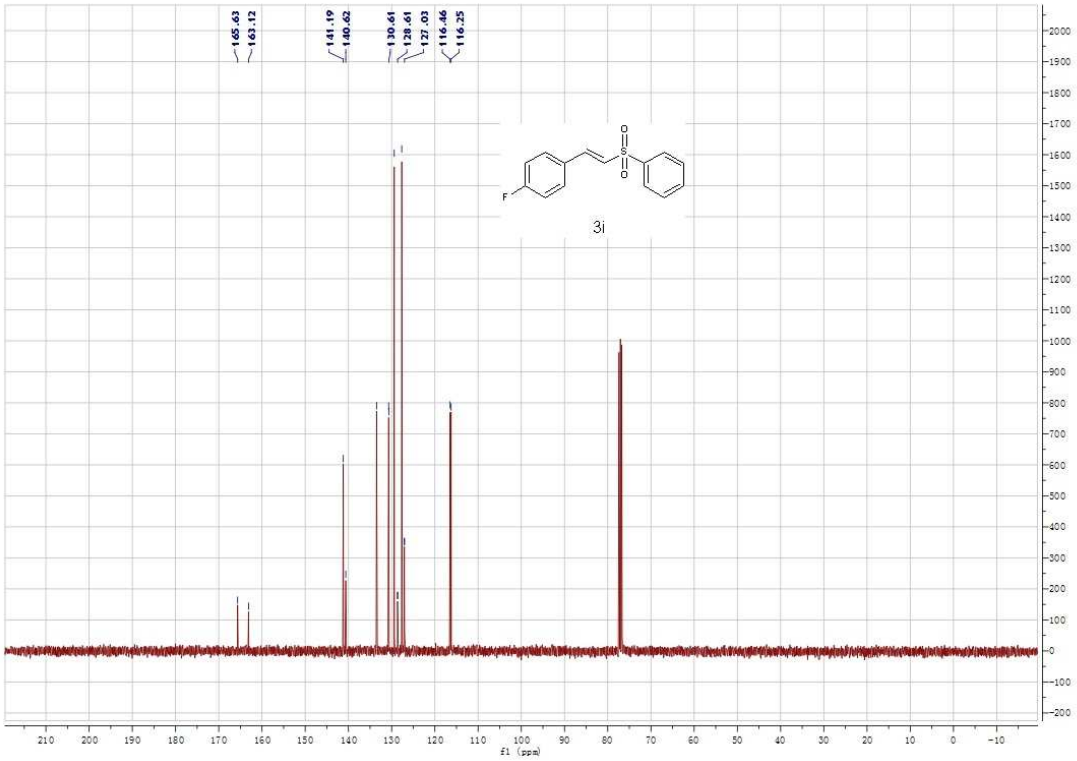
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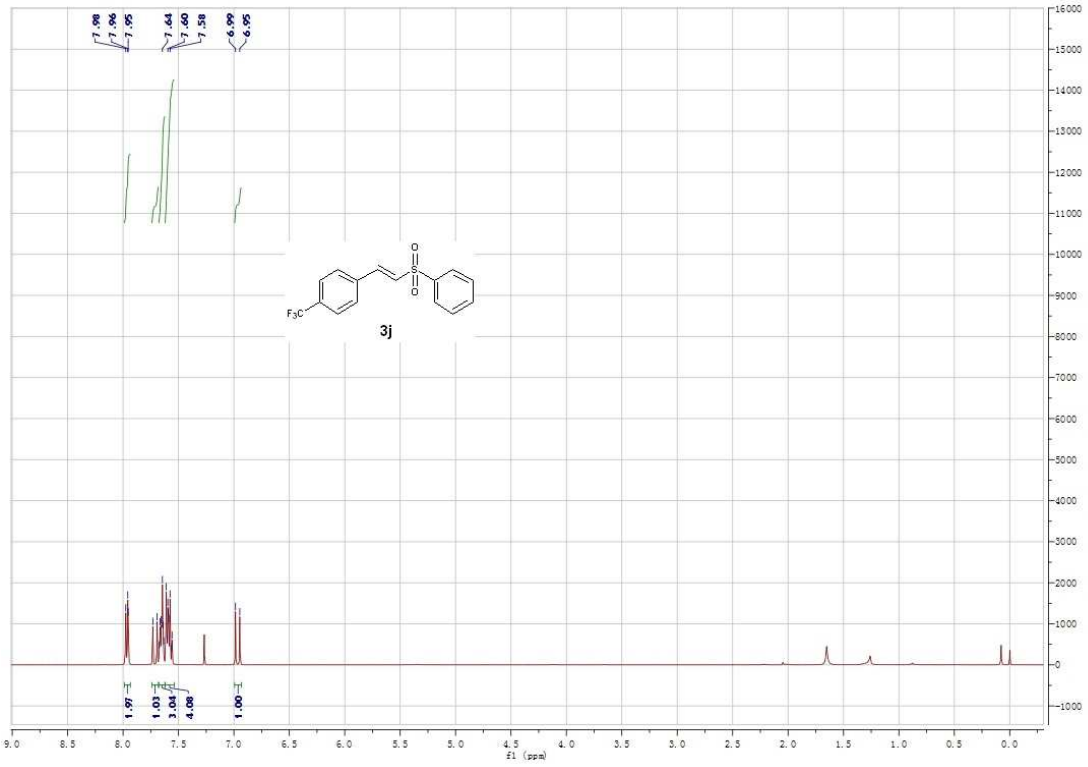
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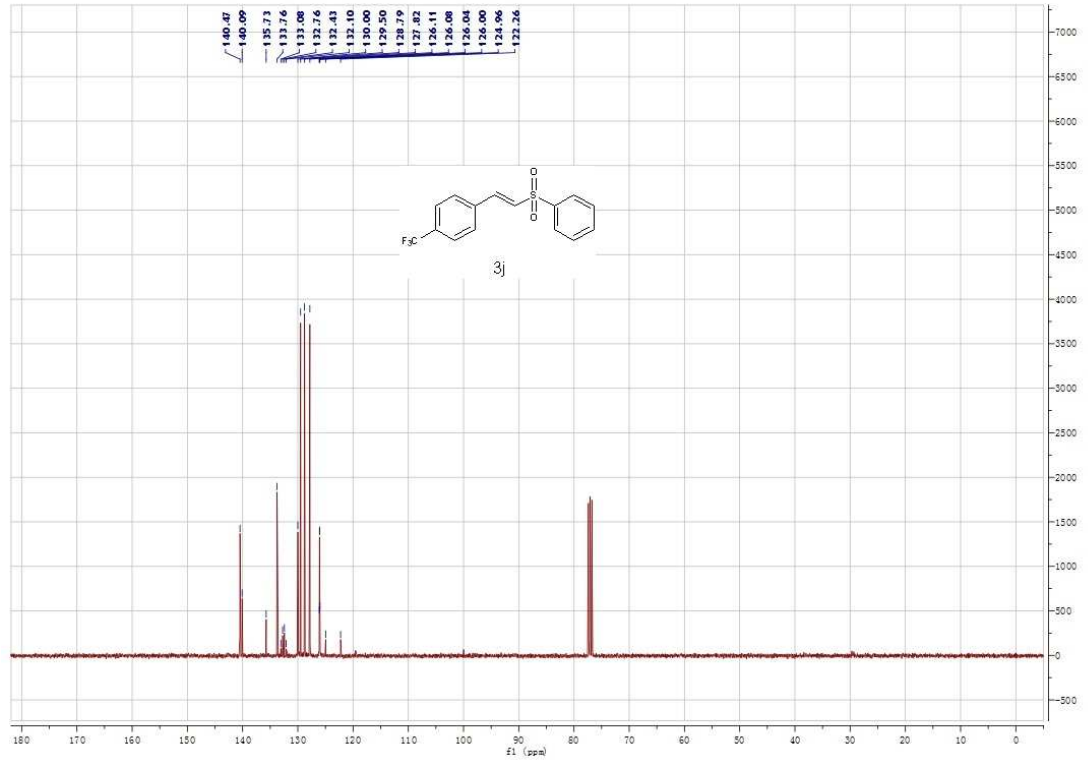
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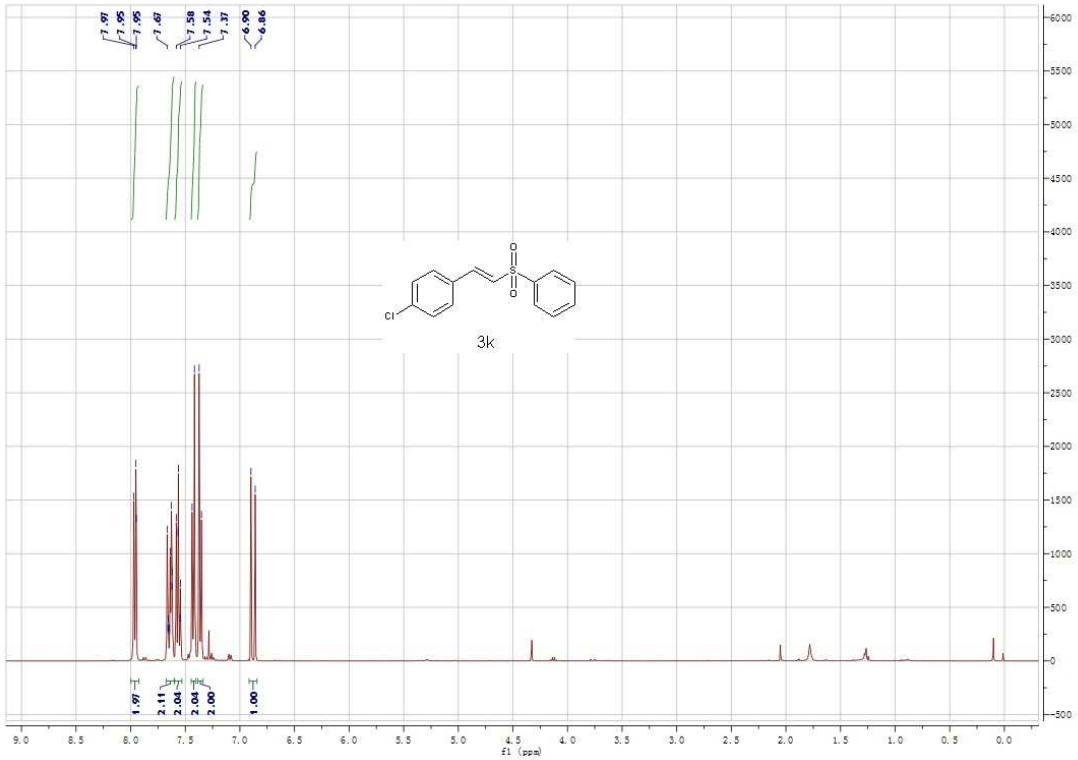
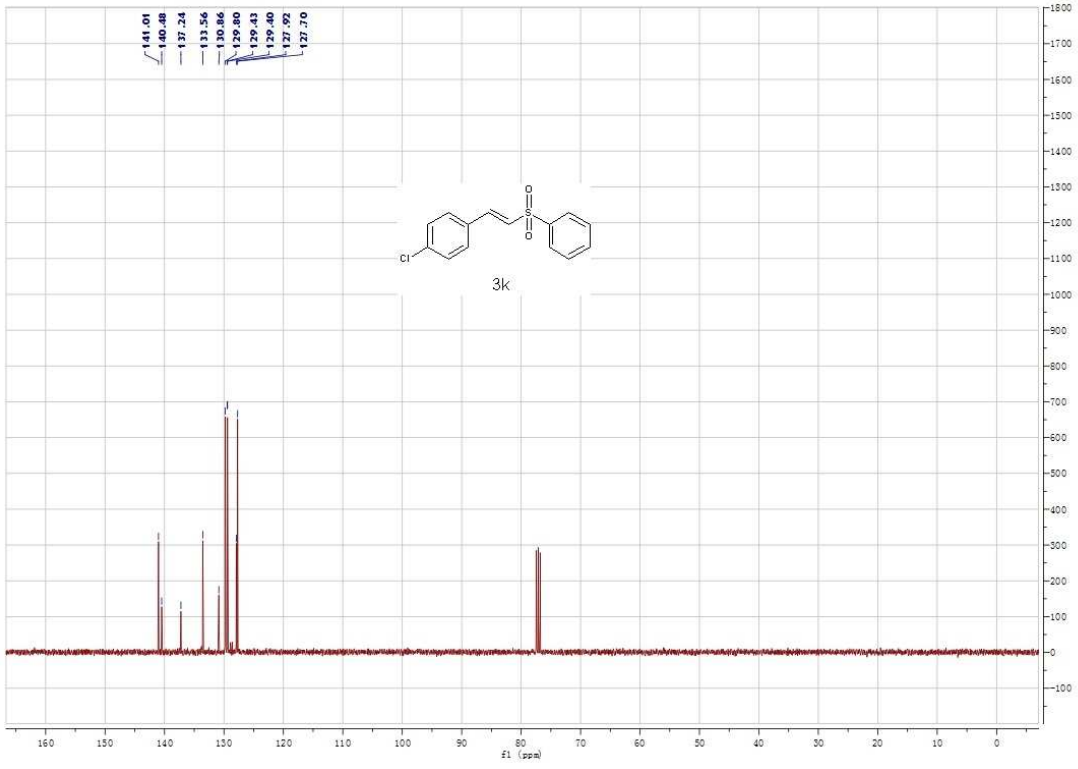
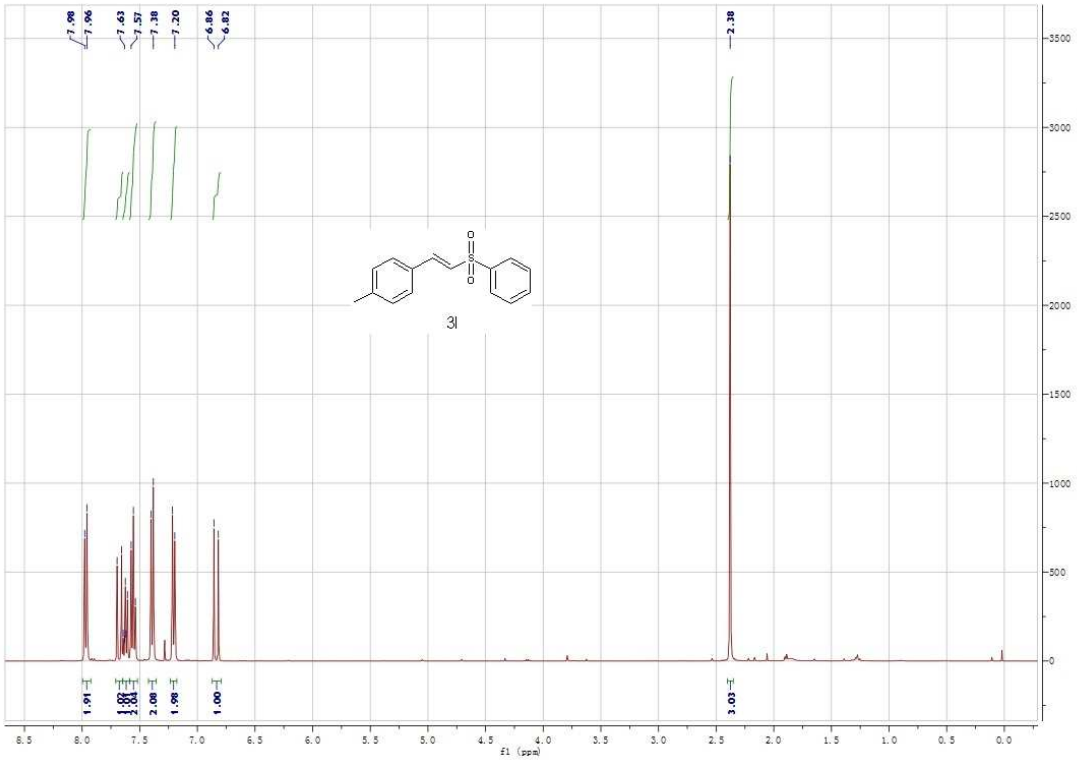
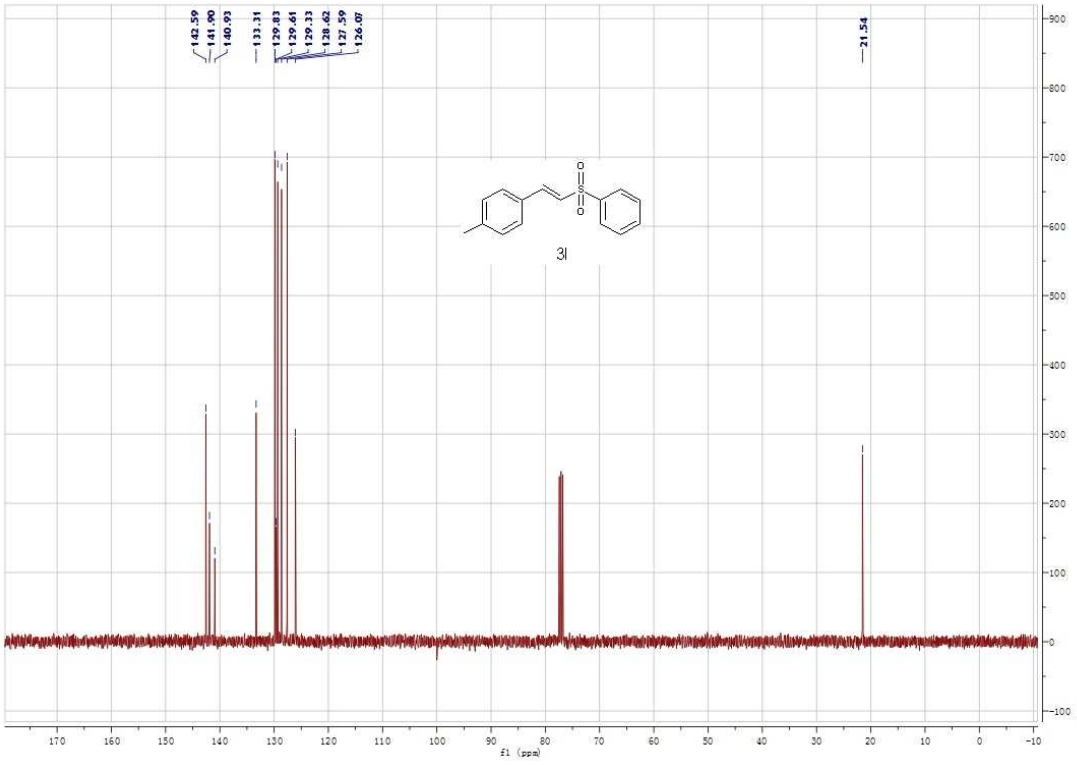
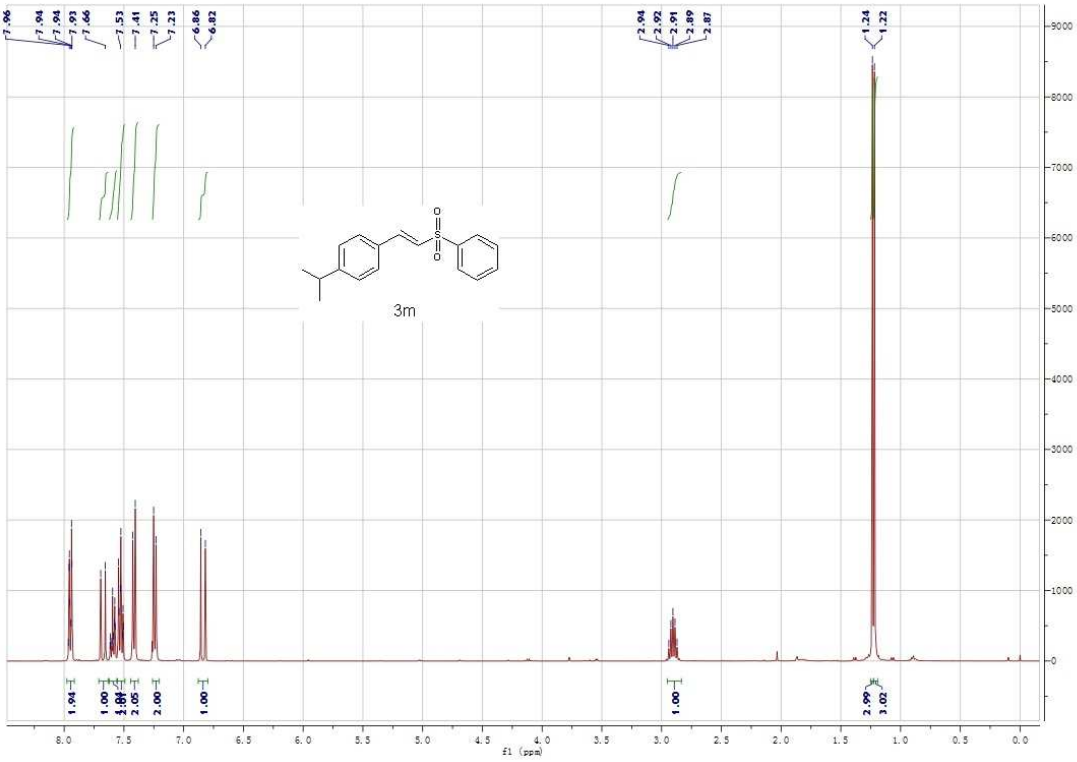
3j
f1 (ppm)

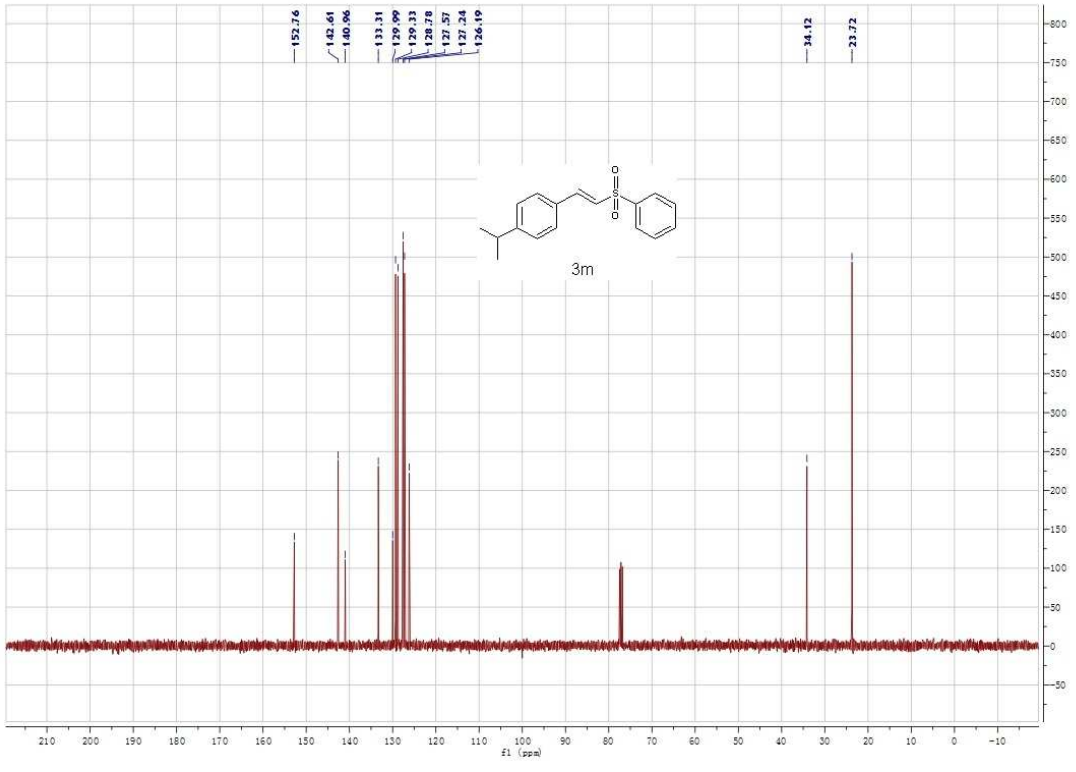

7.97
7.95
7.95
7.67
7.58
7.54
7.37
6.90
6.86
3k
1.97
2.11
2.04
2.04
2.00
1.00
f1 (ppm)

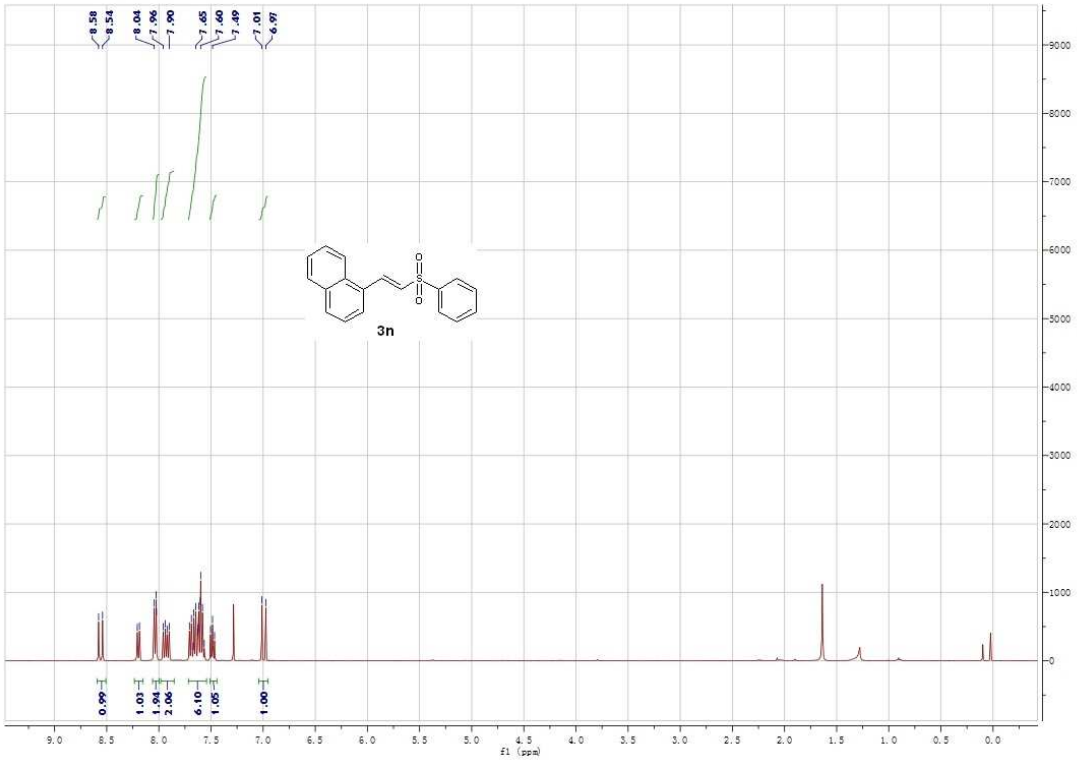

141.01
140.48
137.24
133.56
130.86
129.80
129.43
129.40
127.92
127.70
3k
f1 (ppm)

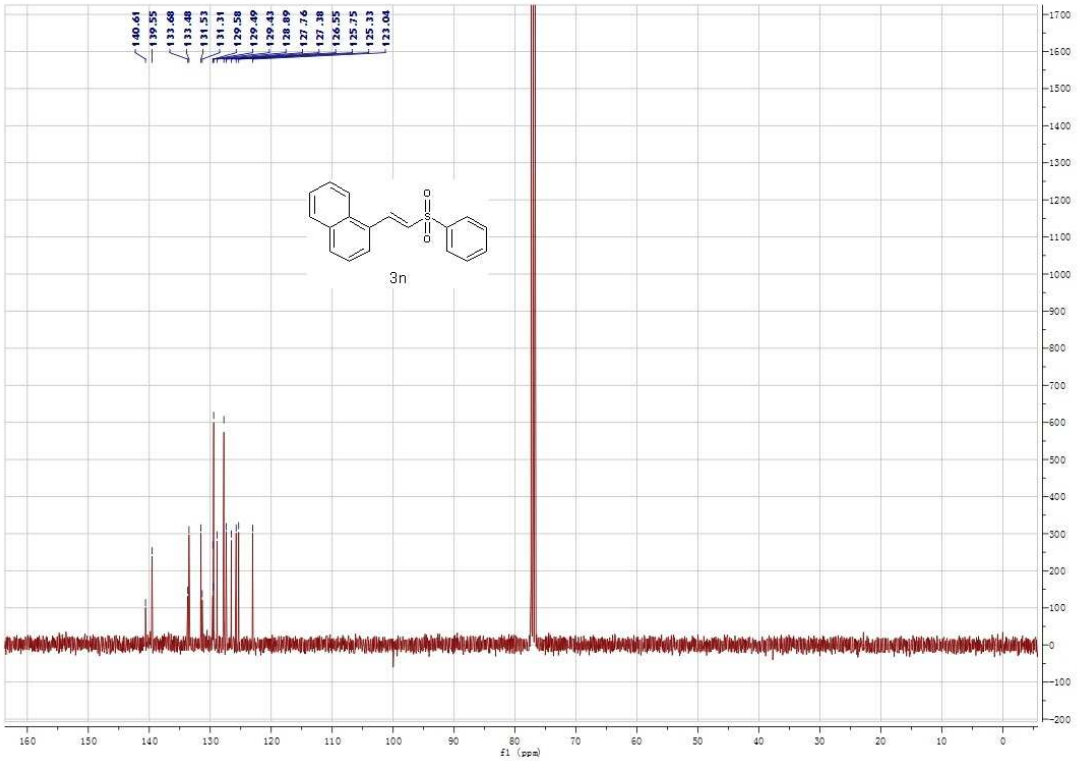

7.98
7.96
7.63
7.57
7.38
7.20
6.86
6.82
2.38
3l
1.91
2.08
1.98
1.00
3.03
f1 (ppm)

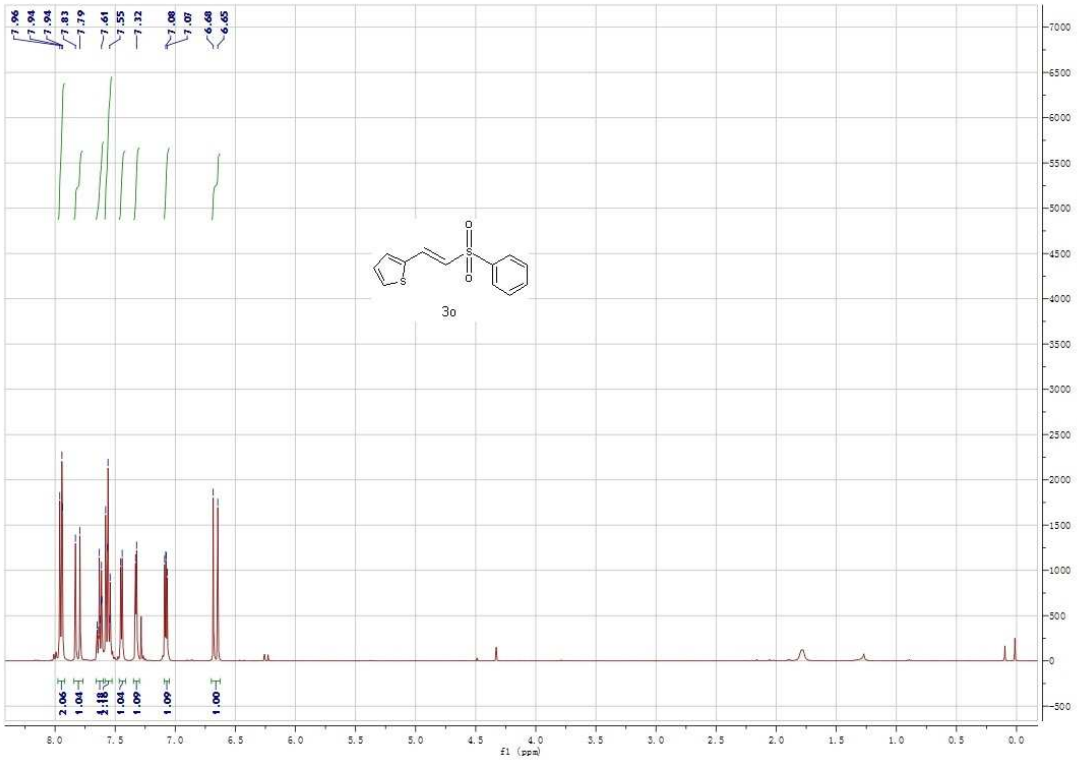

142.59
141.90
140.93
133.31
129.83
129.61
129.33
128.62
127.59
126.07
21.54
3l
f1 (ppm)

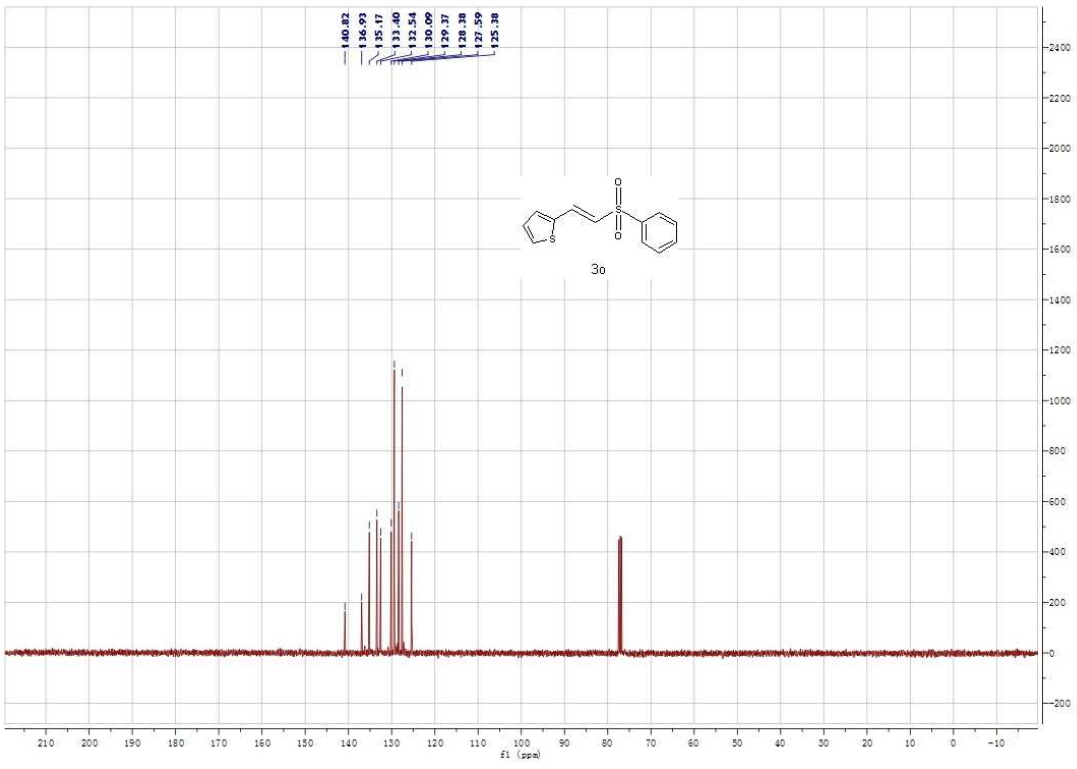

3m

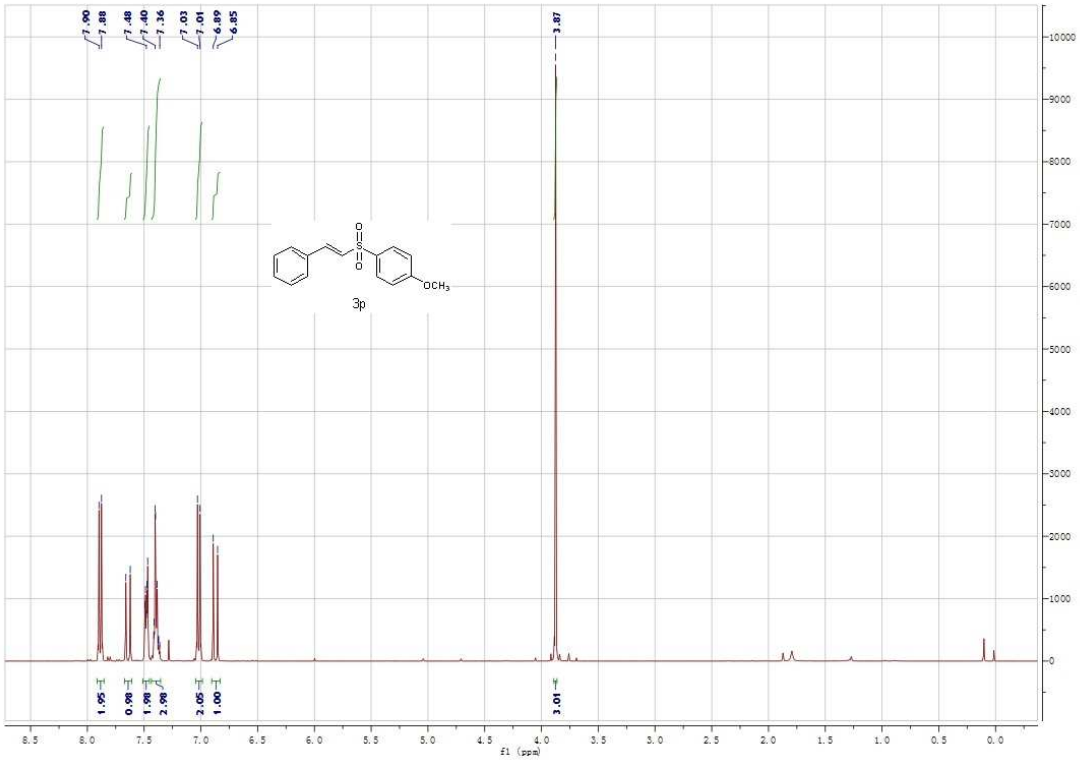

3m

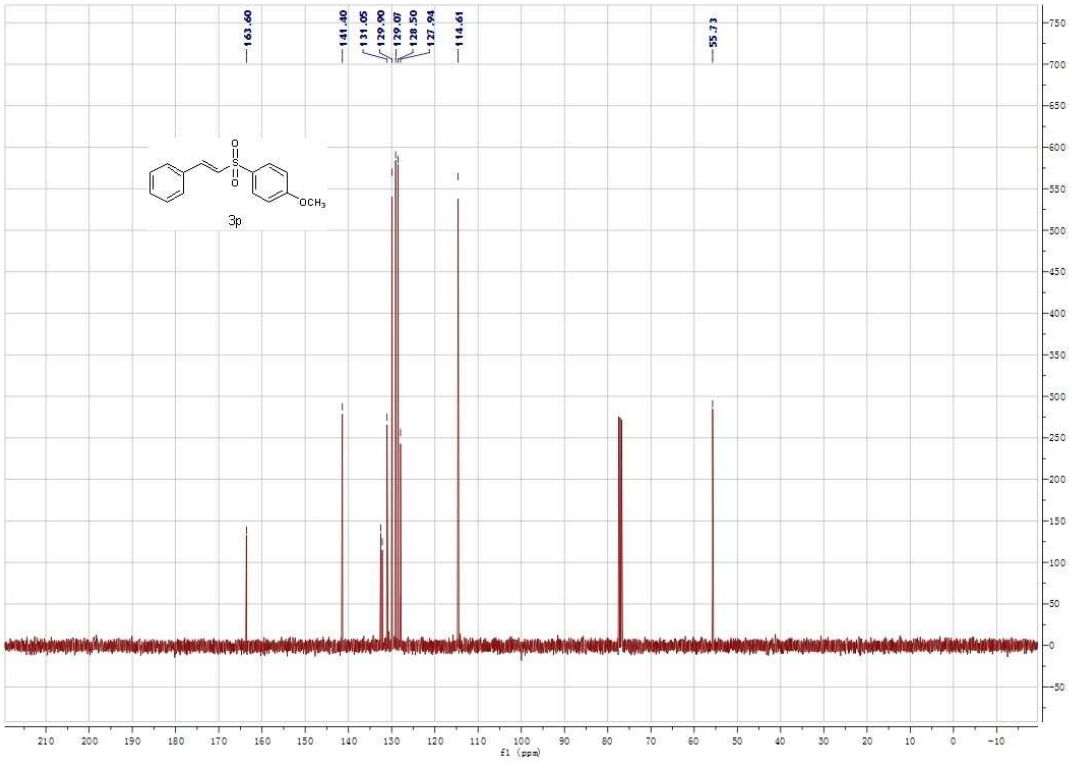

8.58
8.54
8.04
7.96
7.90
7.65
7.60
7.49
7.01
6.97
3n
0.99
1.03
1.04
2.06
6.10
1.05
1.00
f1 (ppm)

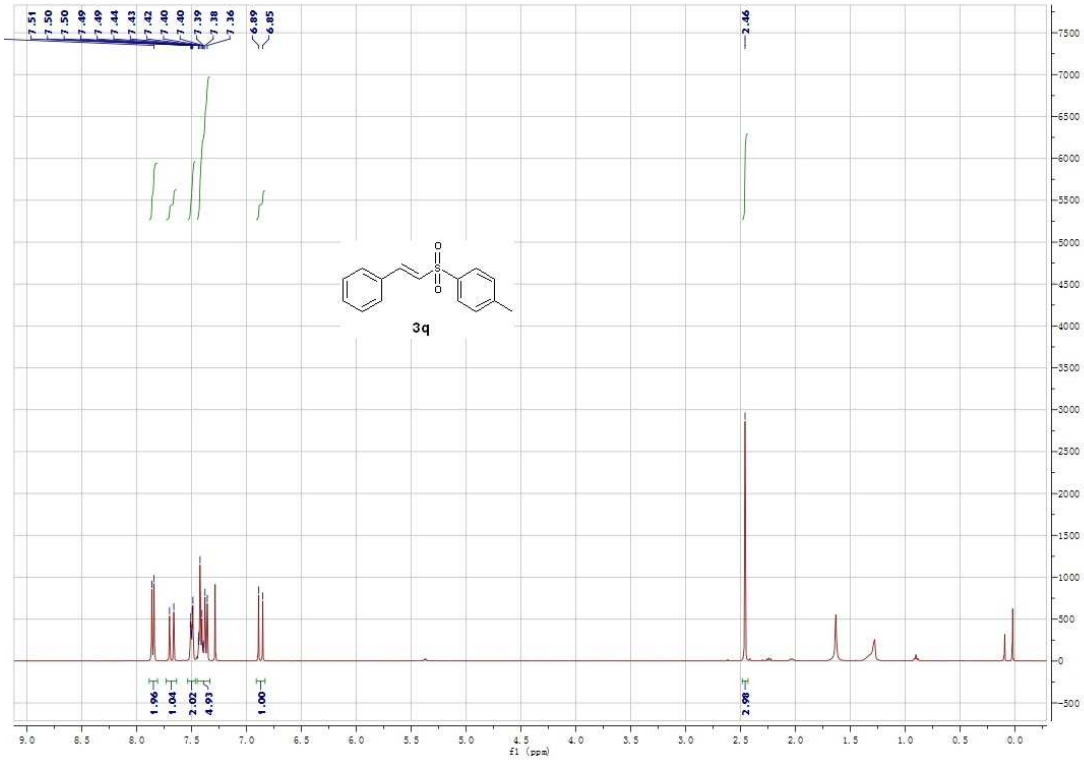

140.61
139.55
133.68
133.48
131.53
131.31
129.58
129.49
129.43
128.89
127.76
127.38
126.55
125.75
125.33
123.04
3n
f1 (ppm)

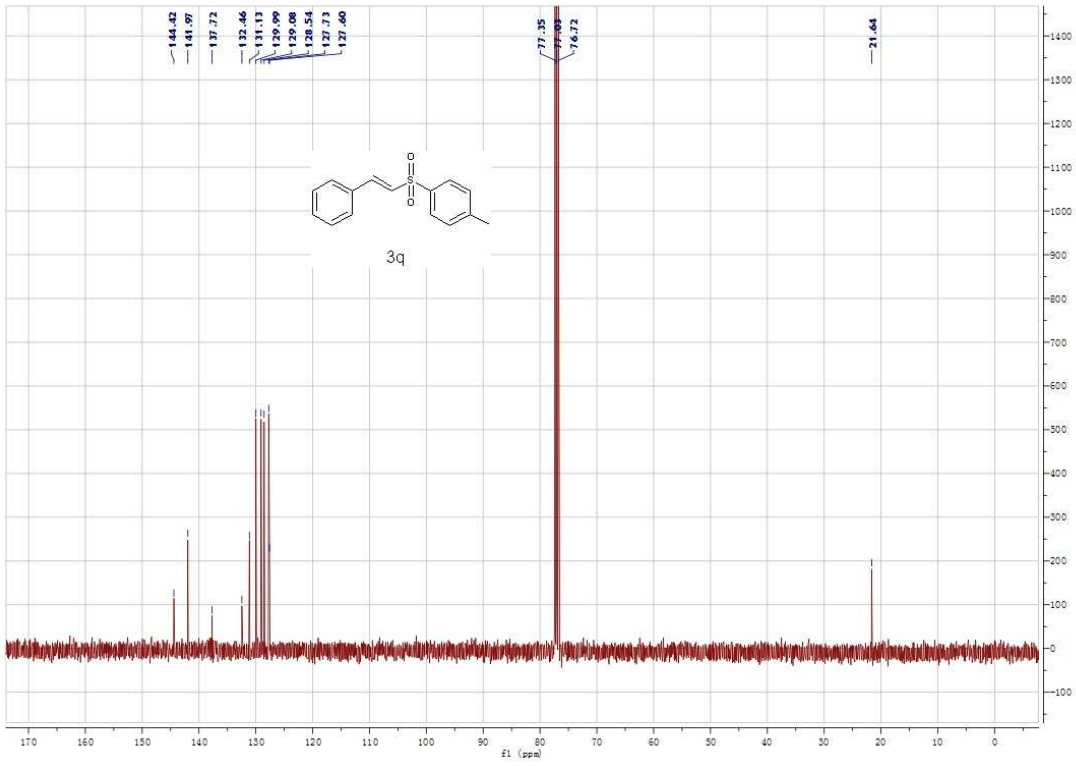

7.96
7.94
7.94
7.83
7.79
7.61
7.55
7.32
7.08
7.07
6.68
6.65
3o
2.06
1.04
2.18
1.04
1.09
1.09
1.00
f1 (ppm)

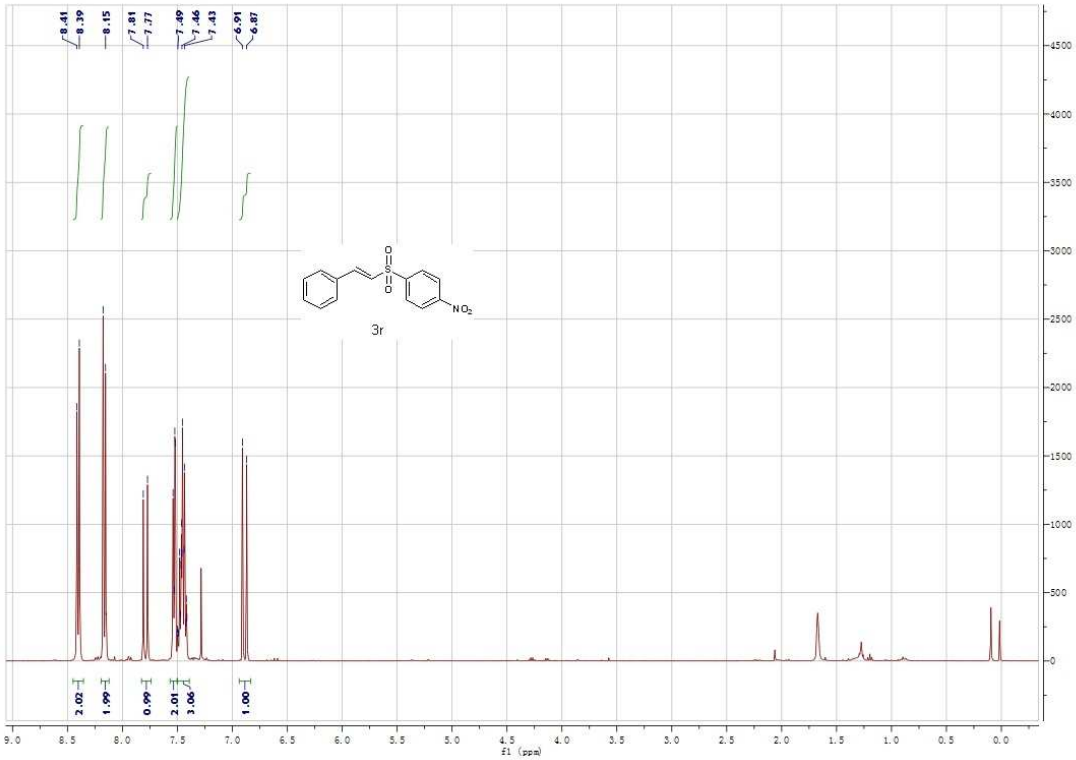

140.82
136.93
135.17
133.40
132.54
130.09
129.37
128.38
127.59
125.38
3o
f1 (ppm)

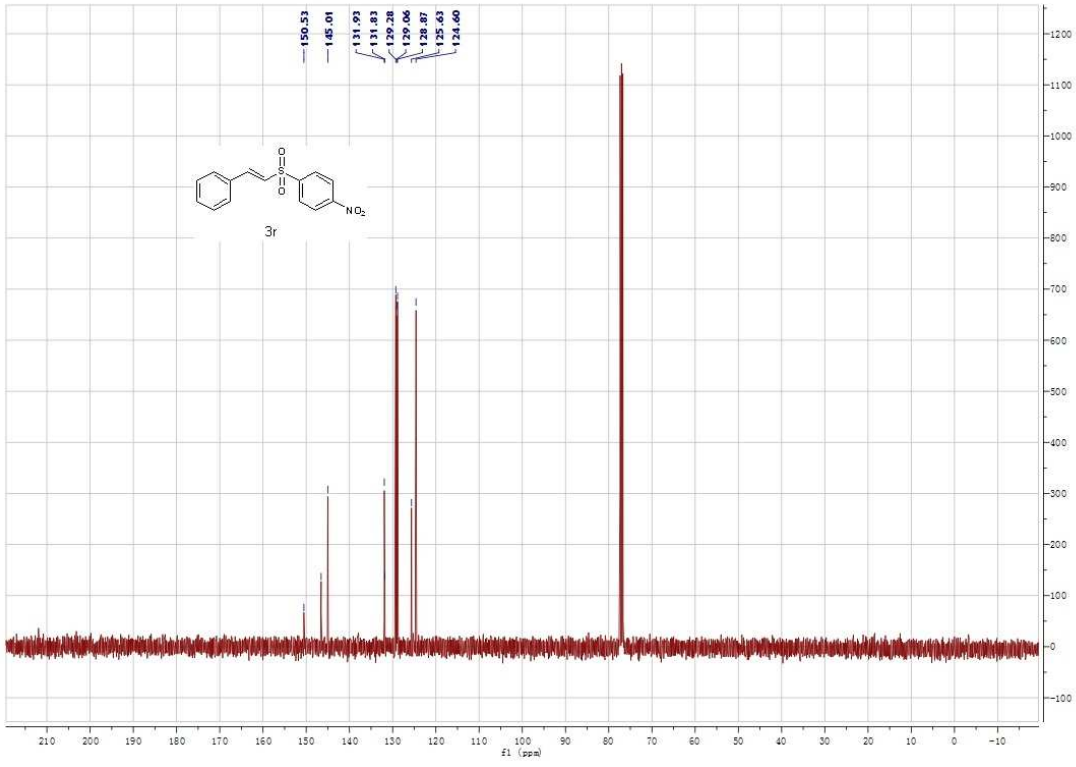

7.90
7.88
7.48
7.40
7.36
7.03
7.01
6.89
6.85
3.87
3p
1.95
0.98
1.98
2.98
2.05
1.00
3.01
f1 (ppm)

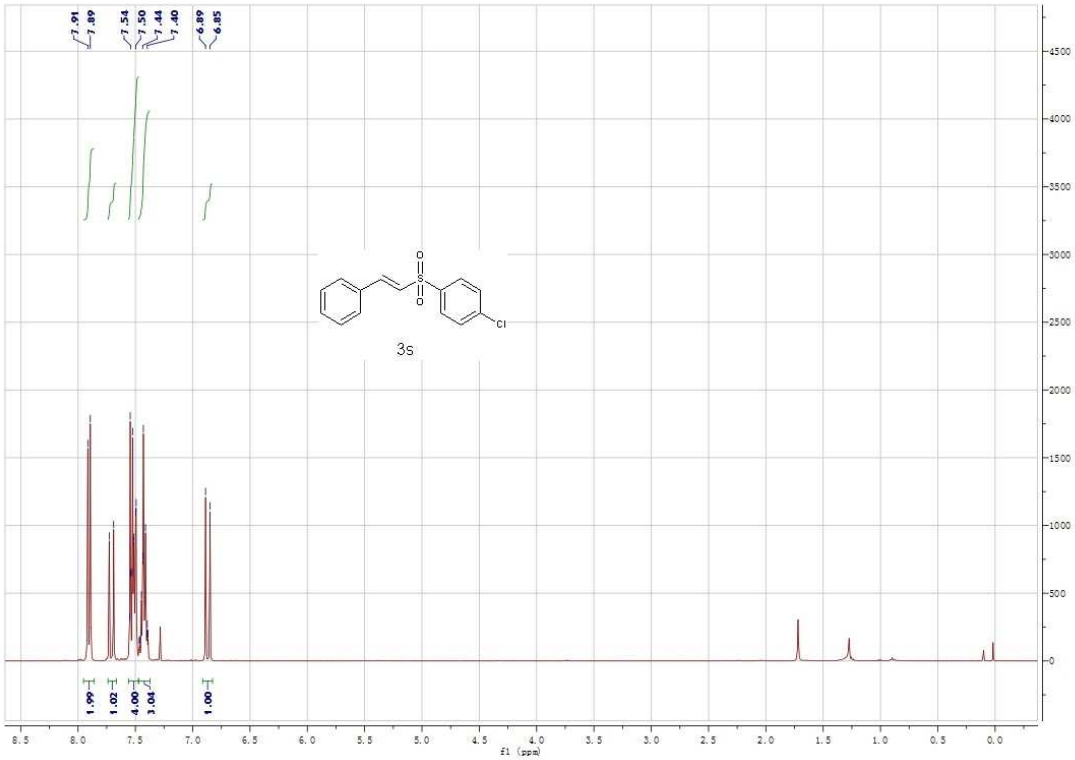

163.60
141.40
131.05
129.90
129.07
128.50
127.94
114.61
55.73
3p
f1 (ppm)

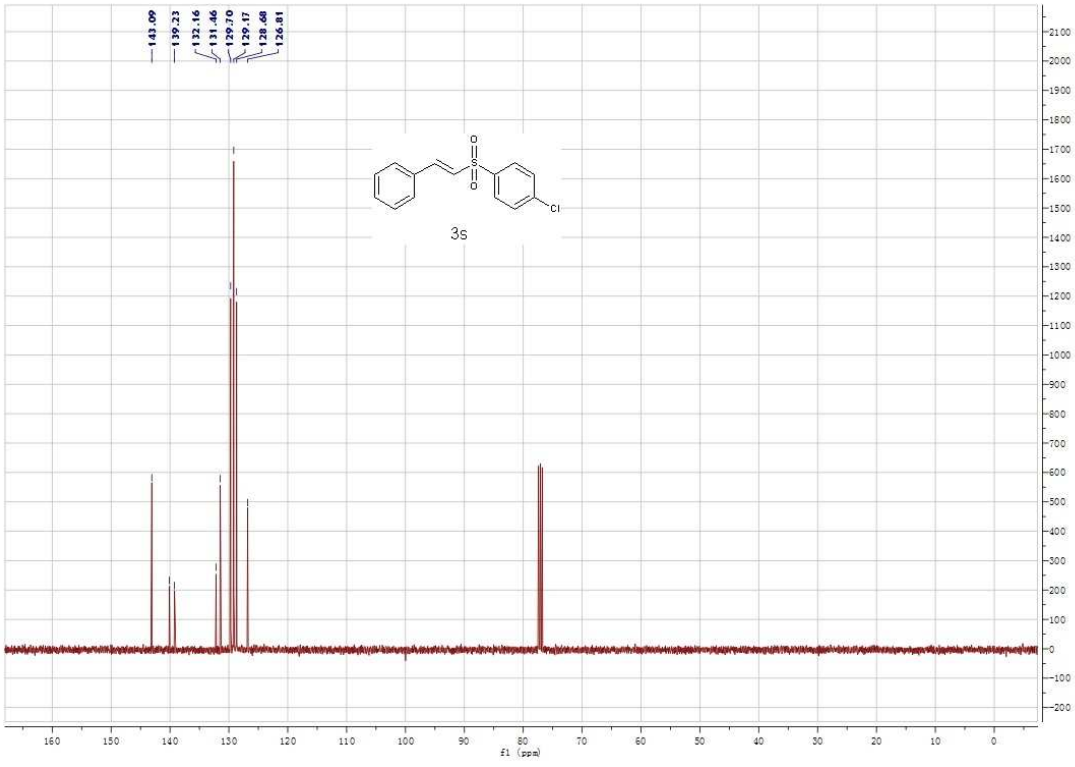

7.51
7.50
7.50
7.49
7.49
7.49
7.44
7.43
7.42
7.40
7.40
7.39
7.38
7.36
6.89
6.85
2.46
3q
1.06
1.04
2.02
4.93
1.00
2.98
f1 (ppm)

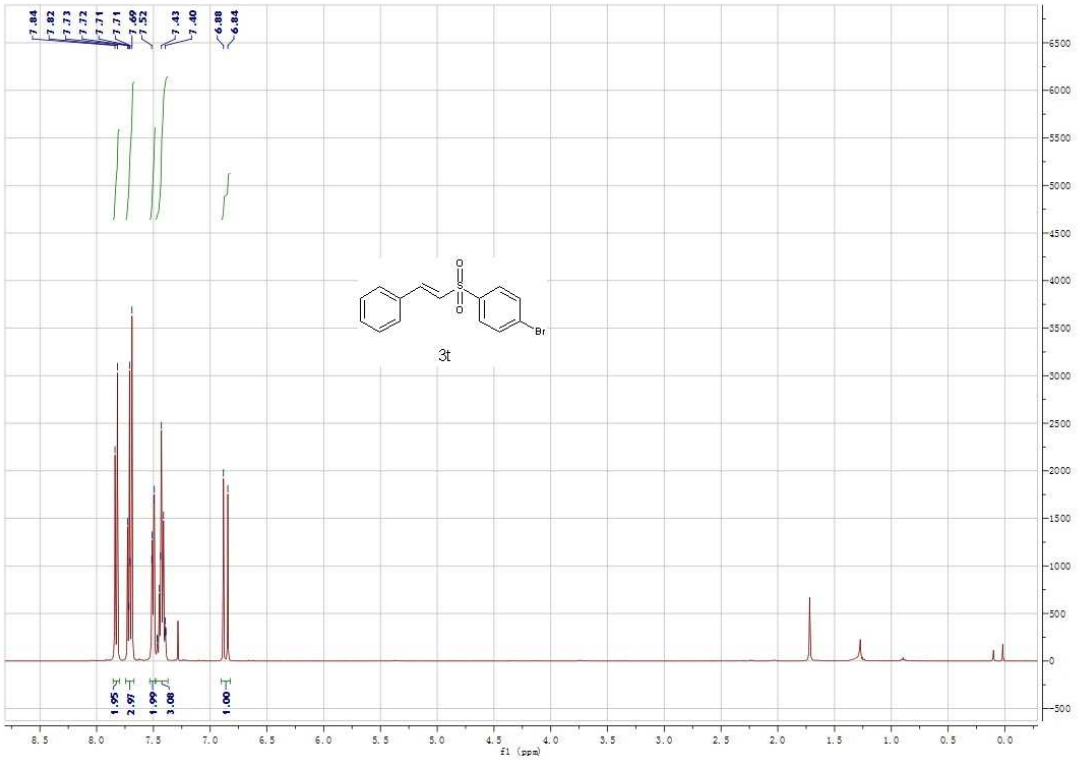

144.42
141.97
137.72
132.46
131.13
129.99
129.08
128.54
127.73
127.60
77.35
77.03
76.72
21.64
3q
f1 (ppm)

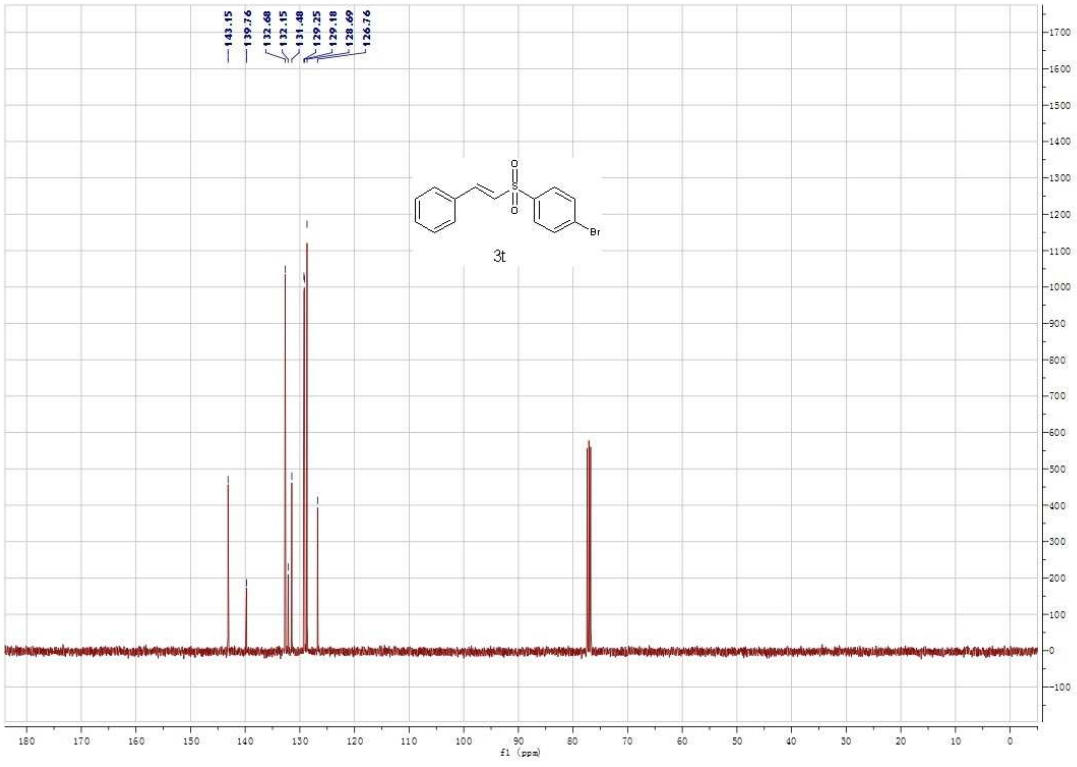

8.41
8.39
8.15
7.81
7.77
7.49
7.46
7.43
6.91
6.87
3r
2.02
1.99
0.99
2.01
3.06
1.00
f1 (ppm)

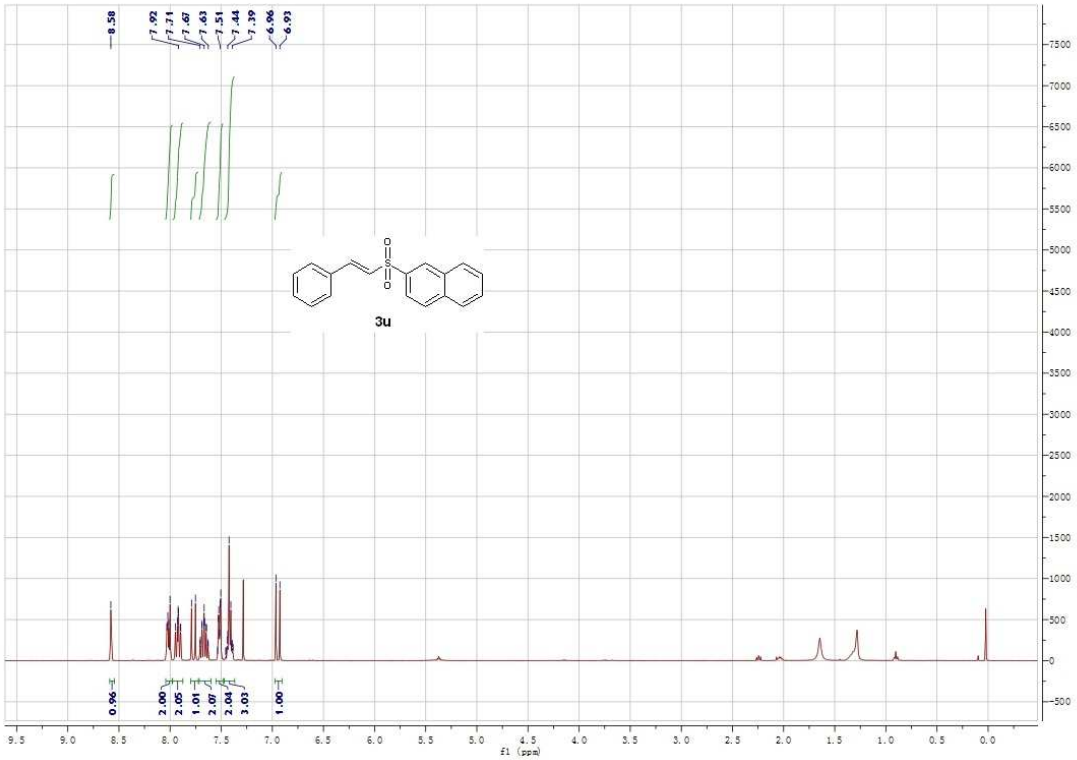

150.53
145.01
131.93
131.83
129.28
129.06
128.87
125.63
124.60
3r
f1 (ppm)

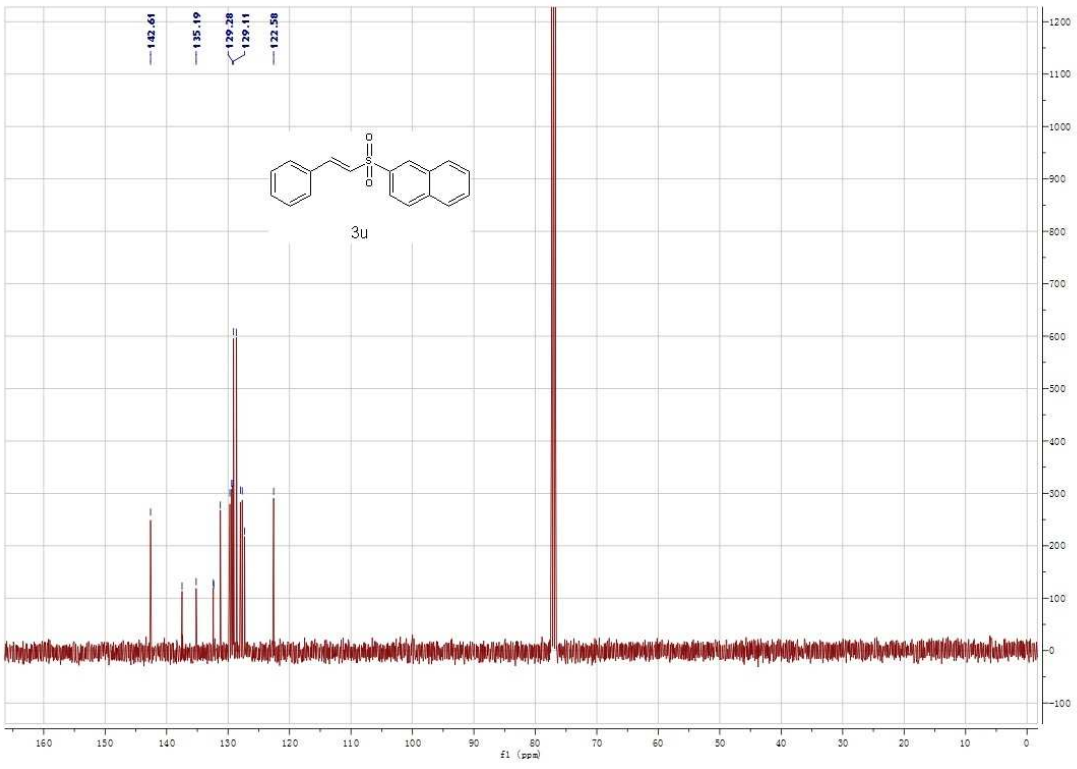

7.91
7.89
7.54
7.50
7.44
7.40
6.89
6.85
3s
1.99
1.02
4.00
3.04
1.00
f1 (ppm)

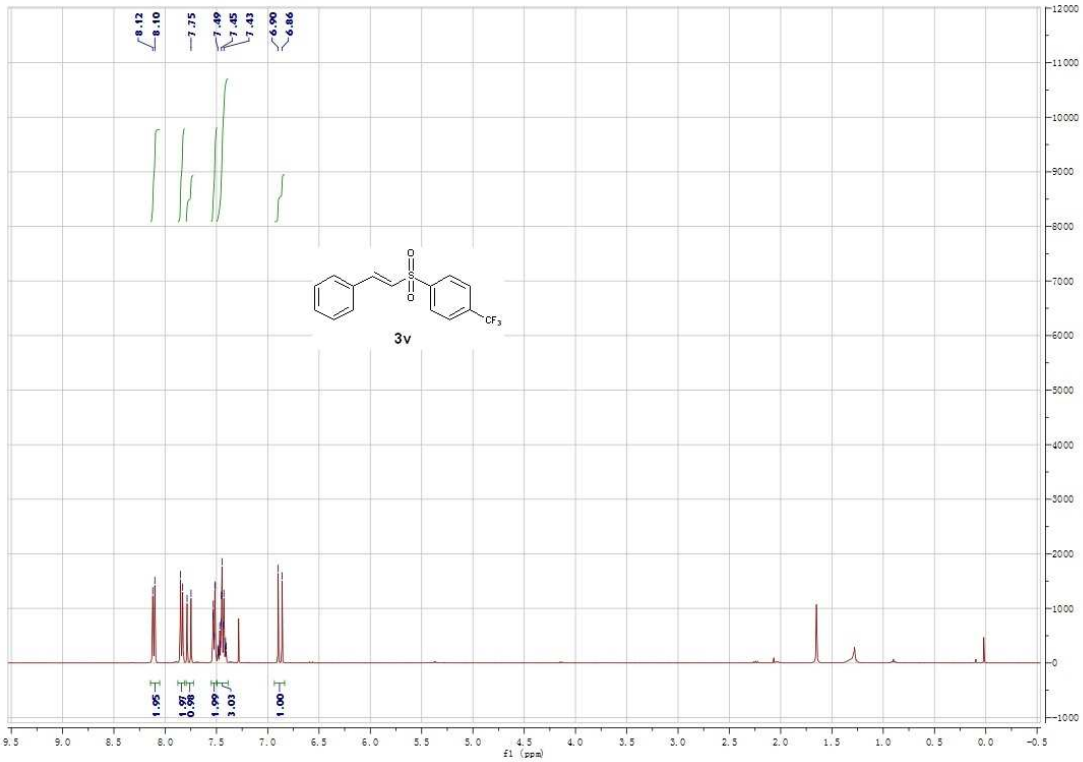

143.09
139.23
132.16
131.46
129.70
129.17
128.68
126.81
3s
f1 (ppm)

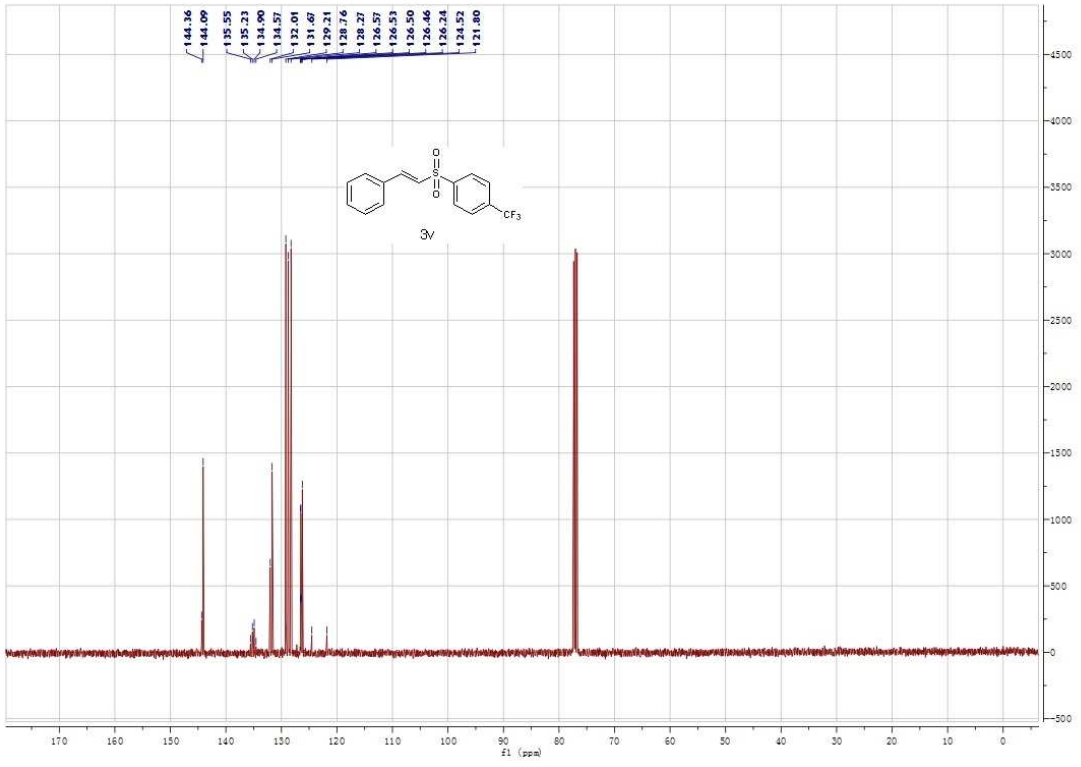

7.84
7.82
7.73
7.72
7.71
7.71
7.69
7.52
7.43
7.40
6.88
6.84
1.95
2.97
1.99
3.08
1.00
3t
f1 (ppm)

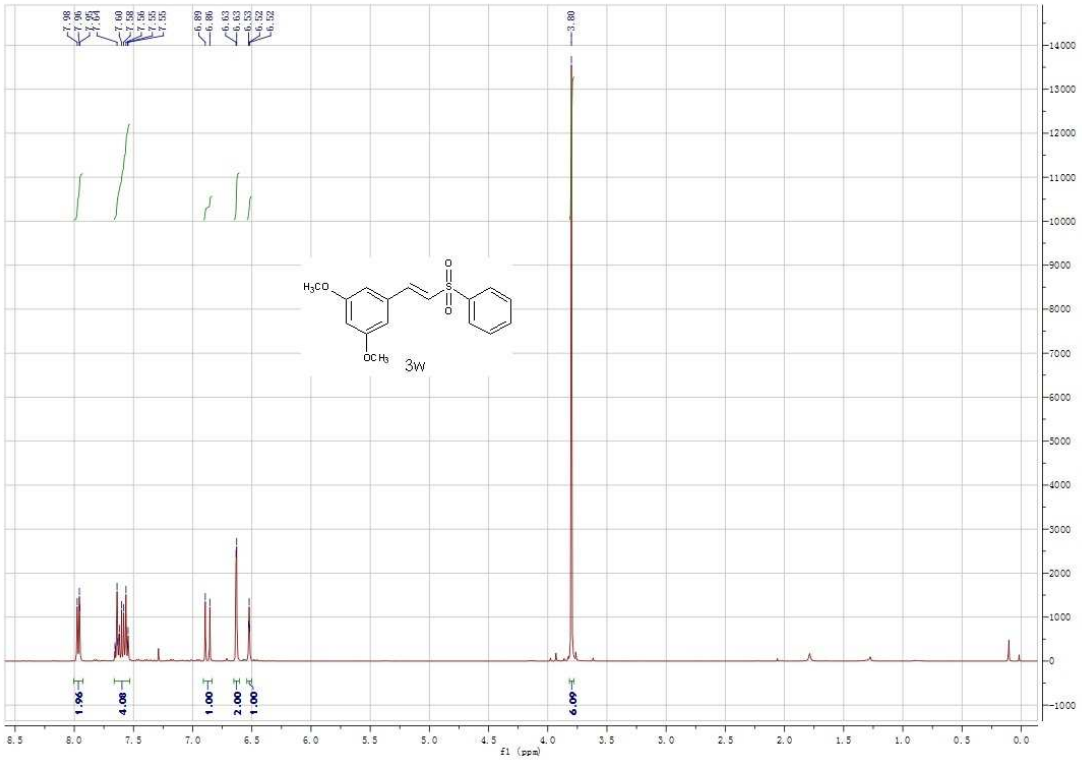

143.15
139.76
132.68
132.15
131.48
129.25
129.18
128.69
126.76
3t
f1 (ppm)

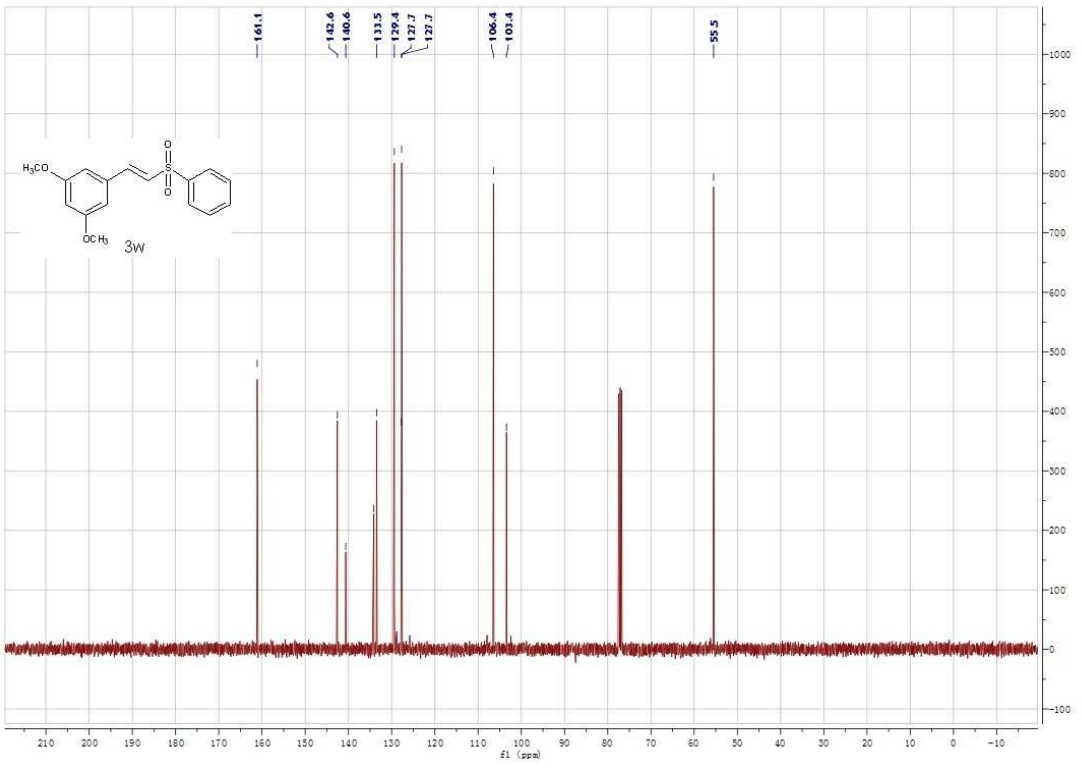

8.58
7.92
7.71
7.67
7.63
7.51
7.44
7.39
6.96
6.93
3u
0.96
2.00
2.05
1.01
2.07
2.04
3.03
1.00
f1 (ppm)


142.61
135.19
129.28
129.11
122.58
3u
f1 (ppm)


8.12
8.10
7.75
7.49
7.45
7.43
6.90
6.86
3v
1.95
1.97
0.98
1.99
3.03
1.00
f1 (ppm)


144.36
144.09
135.55
135.23
134.90
134.57
132.01
131.67
129.21
128.76
128.27
126.57
126.53
126.50
126.46
126.24
124.52
121.80
3v
f1 (ppm)


7.98
7.96
7.95
7.93
7.60
7.58
7.56
7.55
7.55
6.89
6.86
6.63
6.63
6.53
6.52
6.52
3.80
H3CO
OCH3
3W
1.96
4.08
1.00
2.00
1.00
6.09
f1 (ppm)


161.1
142.6
140.6
133.5
129.4
127.7
127.7
106.4
103.4
55.5
H3CO
OCH3
3W
f1 (ppm)