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PII: S0040-4020(15)01088-1

DOI: 10.1016/j.tet.2015.07.043

Reference: TET 26988

To appear in: *Tetrahedron*

Received Date: 9 June 2015

Revised Date: 10 July 2015

Accepted Date: 14 July 2015

Please cite this article as: Fan W, Su J, Shi D, Feng B, An Effeicient One-pot, Three-Component Synthesis of Vinyl Sulfones via Iodide-catalyzed Radical Alkenylation, *Tetrahedron* (2015), doi: 10.1016/j.tet.2015.07.043.

Graphical Abstract

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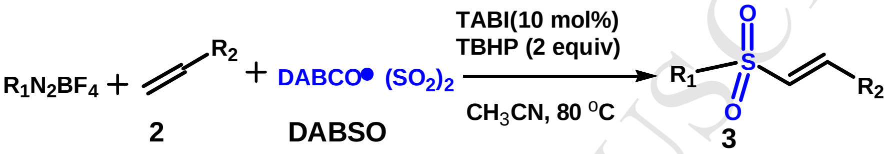

An efficient one-pot, three-component synthesis of vinyl sulfones via iodide-catalyzed radical alkenylation using aryl diazonium salts, terminal alkenes and DABSO is reported. This protocol offers good yields and tolerates a broad range of functional groups. Based on the extensive control experiments, we propose a plausible radical mechanism.

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ABSTRACT

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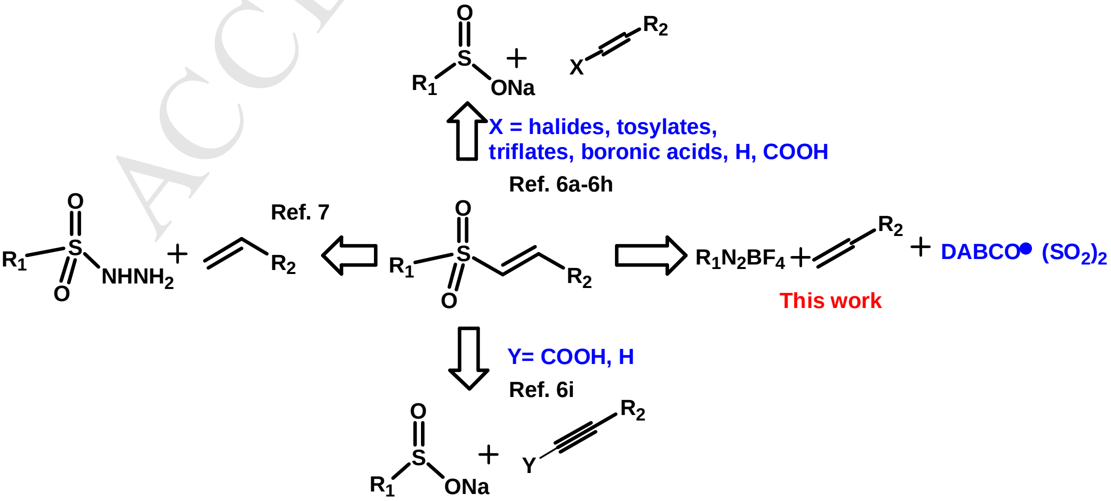
Keywords: Iodide-catalyzed, sulfones, alkenylation, radical mechanism

1. Introduction

Vinyl sulfones are an important organic structural motifs found in natural products and biologically active molecules.[1] They also exhibit interesting chemical properties and are useful intermediates in organic synthesis.[2] Thus, intense efforts have focused on the development of these synthetic methods, including the oxidation of the corresponding sulfides,[3] condensation of aromatic aldehydes with sulfonylacetic acids,[4] and β-elimination of selenosulfones or halosulfones.[5] Recently, an efficient two-component coupling method is developed, which used sulfinate salts and different vinyl sources, including vinyl halides,[6a–c] vinyl tosylates,[6d] vinyl triflates,[6e] alkenylboronic acids,[6f] alkenes,[6g] cinnamic acids[6h] or alkynes[6i] in the presence of a metal catalyst. Similarly, Lei's group reported a radical oxidative alkenylation to afford vinyl sulfones using sulfonyl hydrazides with simple alkenes.[7] Besides, Li's group has also developed a selective method for the preparation of (E)-vinyl sulfones via C–S cleavage.[8]



Scheme 1. Coupling methods for the synthesis of vinyl sulfones

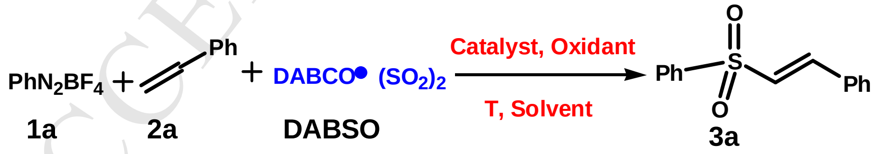
Although diverse successful synthesis of vinyl sulfones have been afforded, the scope of arylsulfinate salts reported[6] was limited due to their's not commercially available or pre-synthesized. So the development of one-pot and many-component practical synthetic methods for vinyl sulfones with more simple starting marterials is still needed. Recently, Willis developed a new convenient reagent DABSO (DABCO·SO_2, the combination of DABCO and sulfur dioxide), which can serve as a surrogate of SO_2 for the in situ formation of sulfinate salts in the synthesis of sulfonamides and sulfamides.[9] Since then, many synthesis of sulfones were reported using DABSO.[10] Inspired by these simplified synthesis, we attempted to employ the same reagent of DABSO to achieve vinyl sulfones. Herein, we report an efficient one-pot, three-component synthesis of vinyl sulfones *via* iodide-catalyzed radical alkenylation using aryl diazonium salts, terminal alkenes and DABSO. The control experiments suggested a radical mechanism.

2. Results and discussion

We initially chose phenyl diazonium salts (**1a**), phenylethylene (**2a**) and DABSO as the substrates to test the reaction (Table 1). The well-established I^-/TBHP radical system[7, 11] was chosen, in the presence of DABSO. We found that the combination of KI and TBHP with CH_3CN as solvent gave good yield of **3a** (65%) at 80 ^{o}C (Table 1, entry 1). On the contrary, the reactions did not work under the same conditions using KBr or KCl as catalyst (Table 1, entries 2–3). When nBu$_4$NI was used as catalyst instead of KI, the yield of **3a** increased to 82% (Table 1, entry 4). Other catalysts containing an iodide anion, such as CuI, NaI and I_2, gave no good results (SI-table 1). Then, other oxidants such as H_2O_2, DTBP, BPO, DDQ and $K_2S_2O_8$ were also examined (Table entries 5–9). But no improvement was afforded. The use of other solvents (Table 1, entries 10–13) or increasing the amount of loading catalyst or oxidant, led no significant improvement on the yield (SI-table 1), nevertheless, temperature influenced the reaction remarkably (Table 1, entry 14). **3a** was not afforded in the absence of nBu$_4$NI or TBHP (Table 1, entries 15–16).

Table 1

Optimization of the reaction conditions



Entry[a]	Catalyst (10 mol%)	Oxidant (2 equiv)	Sovlent /T (^{o}C)	Yield (%)[b]
1	KI	TBHP	CH_3CN/80	65
2	KBr	TBHP	CH_3CN/80	0
3	KCl	TBHP	CH_3CN/80	0
4	nBu$_4$NI	TBHP	CH_3CN/80	82
5	nBu$_4$NI	H_2O_2	CH_3CN/80	25
6	nBu$_4$NI	DTBP	CH_3CN/80	67
7	nBu$_4$NI	BPO	CH_3CN/80	49
8	nBu$_4$NI	DDQ	CH_3CN/80	0
9	nBu$_4$NI	$K_2S_2O_8$	CH_3CN/80	<5

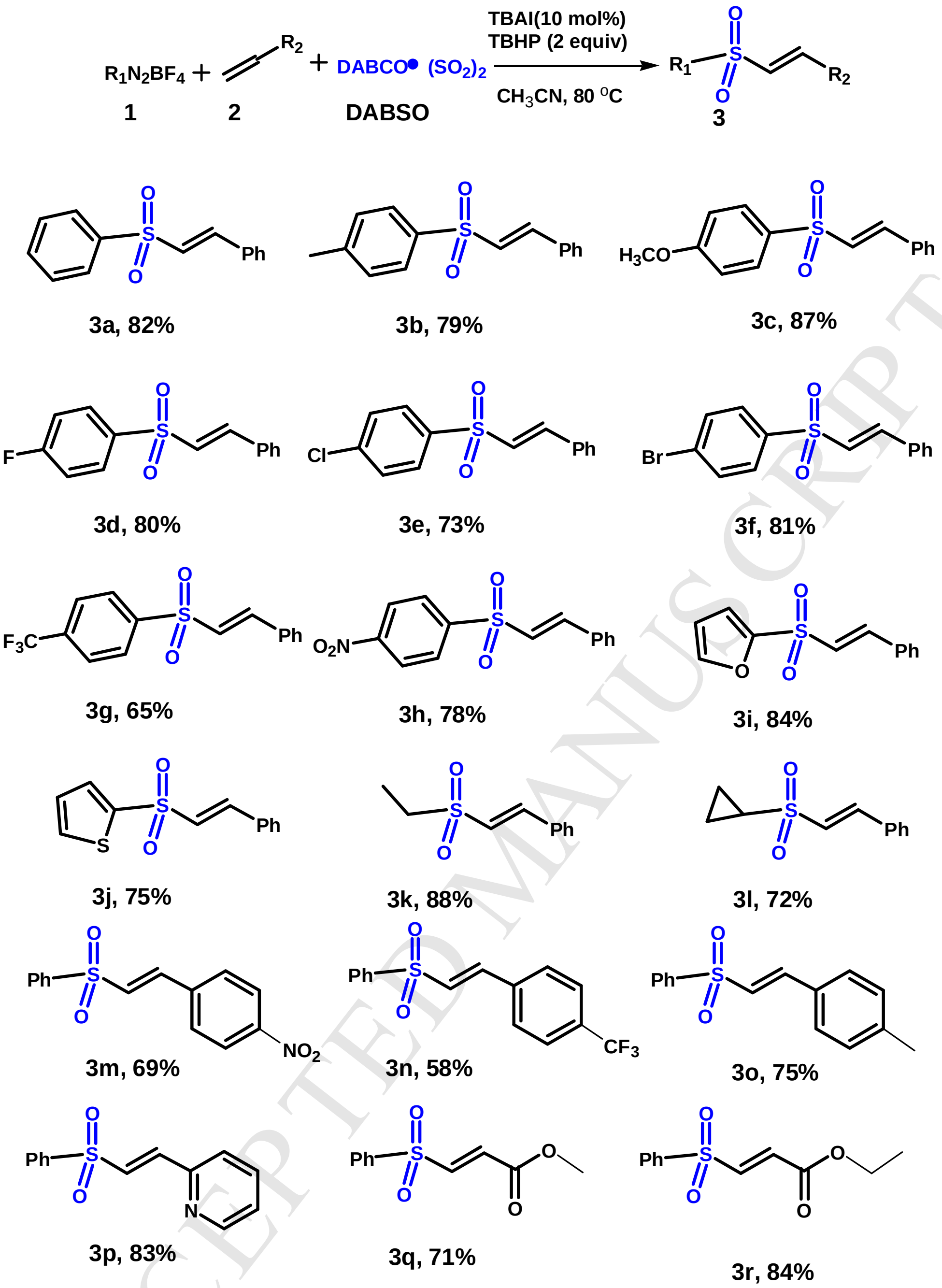
10	*n*Bu$_4$NI	TBHP	CH_3OH/65	0
11	*n*Bu$_4$NI	TBHP	DCE/90	41
12	*n*Bu$_4$NI	TBHP	Toluene/110	<5
13	*n*Bu$_4$NI	TBHP	DMSO/120	0
14	*n*Bu$_4$NI	TBHP	CH_3CN/60	49
15	no	TBHP	CH_3CN/80	0
16	*n*Bu$_4$NI	no	CH_3CN/80	0

(a) Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.25 mmol), Catalyst (10 mol%), Oxidant (2 equiv), in 5 mL Solvent at proper temperature under Ar atmosphere for 12 h; (b) isolated yield.

Encouraged by the preliminary results, we tried to explore the functional group tolerance for the synthesis of vinyl sulfones. First of all, various substituted diazonium salts were tried. The reaction showed a good tolerance to many functional groups, including electron-donating and electron-withdrawing groups (Table 2, **3a**–**3h**, e.g., OMe, Cl, Br, F, CF_3, NO_2). In addition, hetero-substitutes **3i** and **3j** also showed good activity. Besides, alkyl diazonium salts (**3k** and **3l**) were also employed well in this process, affording the corresponding products in excellent yields. Next, various alkenes were employed to synthesize alkenyl sulfones (**3m**–**3r**). Substrates with electron-withdrawing groups on arenes rings (**3m**, **3n**) afforded morderate yields. However, hetero-alkene (**3p**), methyl acrylate (**3q**) and ethyl acrylate (**3r**) showed good activity.

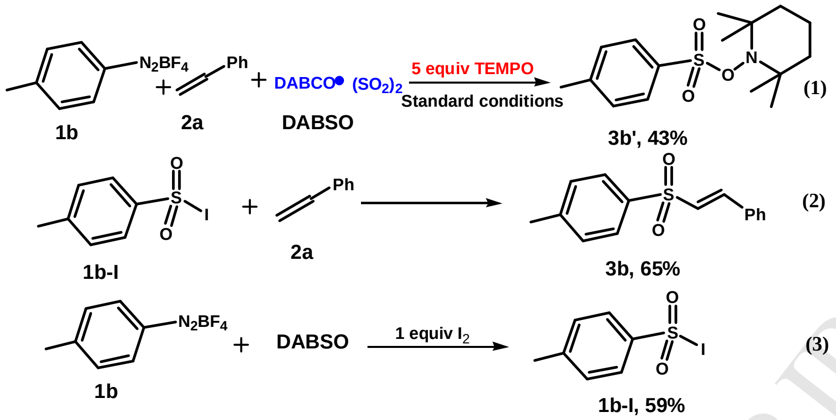
Table 2

Screening the substrates



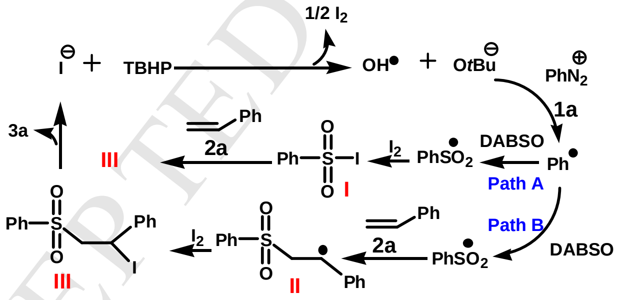
Conditions: **1** (0.2 mmol), **2** (0.3 mmol), DABSO (0.25 mmol), TBAI (10 mol%), TBHP (2 equiv), in 5 mL CH_3CN at 80 °C under Ar atmosphere for 12 h.

In order to study the mechanism for the synthesis of vinyl sulfones, control experiments were employed as shown in Scheme 2. Firstly, the reaction ceased when TEMPO (5 equiv) was employed under standard conditions and the TEMPO-radical adduct of **3b'** was isolated in 43% yield, which implied that the reaction may be proceeding through a radical intermediate. When radical inhibitor BHT (2,6-di-tert-butyl-4-methylphenol) was introduced to the reaction mixture, the formation of the desired product **3b** was completely suppressed. Secondly, we found that **3b** was obtained in moderate yields (65%) when phenylethylene (**2a**) was allowed to react with a freshly prepared p-toluenesulfonyl iodide (**1b-I**, yellowish solid).[12] Finally, **1b** reacted with DABSO in the presence of 1 equiv I_2, affording p-toluenesulfonyl iodide (**1b-I**) in 59% yield.



Scheme 2. Control experiments

On the basis of the above results, a plausible mechanism for this radical alkenylation is proposed, as shown in Scheme 3. First, TBHP decomposes to generate the tert-butoxyl and hydroxyl radicals with the assistance of the iodide anion.[13] Secondly, the decomposition of the diazonium salts in the presence of *t*BuO$^-$ forms the phenyl radical.[14] Subsequently the addition of DABSO affords sulfonyl radical. After that, two paths may be involved. From path A, the addition of sulfonyl radical to I_2 formed intermediate **I**. Sulfonyl halides (**I**) easily generate corresponding sulfonyl radicals and cause atom transfer radical additions to multiple bonds to form **III**.[15] From path B, the addition of sulfonyl radical to **2a** forms intermediate **II**.[7] The radical **II** reacts with in situ generated iodine to generate β-iodosulfone.[7] Finally, elimination of HI similar to the β-hydride elimination forms **3a** to finish the catalytic cycle.[7]



Scheme 3. Proposed formation mechanism

3. Conclusions

In summary, we present an efficient one-pot, three-component synthesis of vinyl sulfones *via* iodide-catalyzed radical alkenylation using aryl diazonium salts, terminal alkenes and DABSO. This synthesis is suitable for abroad range of substrates. The control experiments suggested a possible radical mechanism. Further studies concerning the detailed mechanism and the broader scope of substrates are currently underway in our laboratory.

4. Experiment

4.1. General

Procedure for synthesis of 3a–3r: A mixture of **1** (0.2 mmol), **2** (0.3 mmol), **DABSO**

(0.25 mmol), TBAI (10 mol%) and TBHP (2 equiv) in CH_3CN (5 mL) was stirred at 80 ^oC under Ar atmosphere for 12 h. After the reaction system was cooled to room temperature, saturated NH_4Cl solution (30 mL) and EtOAc (20 mL) were added. The combined organic phases were dried over Na_2SO_4 and then concentrated to give crude products. Further separation by column chromatography on silica gel (eluant with EtOAc and *n*-hexane) gave the corresponding products (**3a–3g**,[6i] **3j–3n**,[6h] **3p–3r**,[6h] **3b'**[16]).

4.2 Characterization Data

3h: **(E)-1-Nitro-4-(styrylsulfonyl)benzene (78%)** Yellow solid; mp 138–139 ^oC; ^1H NMR (500 MHz, $CDCl_3$): 8.14 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 14.8 Hz, 1H), 7.59 (d, *J* = 6.4 Hz, 2H), 7.45 (q, *J* =6.4 Hz, 3H), 6.89 (d, *J* =14.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 148.1, 139.7, 134.6, 132.92, 131.5, 130.2, 129.1, 128.4, 126.5; HRMS (EI^+) m/z calcd. for $C_{14}H_{11}NO_4S$ $[M]^+$: 289.0409, found 289.0412.

3i: (E)-2-(Styrylsulfonyl)oxole (84%) Pale yellow solid; mp 53–55 ^oC; ^1H NMR (500 MHz, $CDCl_3$): 7.75 (d, *J* = 3.0 Hz, 1H), 7.68–7.63 (m, 2H), 7.52 (d, *J* =15.2 Hz, 1H), 7.48 (d, *J* = 4.8 Hz, 1H), 7.44–7.39 (m, 3H), 7.14 (dd, *J* =4.8, 3.2 Hz, 1H), 6.92 (d, *J* =15.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 142.5, 141.9, 135.1, 134.8, 132.2, 131.0, 129.5, 128.7, 127.9, 127.5; HRMS (EI^+) m/z calcd. for $C_{12}H_{10}O_3S$ $[M]^+$: 234.0351, found 234.0349.

3o: (E)-1-[2-(Phenylsulfonyl)vinyl]-4-(methyl)benzene (75%) mp 121-123 ºC; ^1H NMR (500 MHz, $CDCl_3$): 8.02 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 15.0 Hz, 1H), 7.58 (m, 5H), 6.95 (d, J = 15.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 145.7, 139.5, 138.9, 137.4, 133.1, 130.8, 129.7, 129.2, 127.5, 124.3, 21.8; HRMS (EI^+) m/z calcd. for $C_{15}H_{14}O_2S$ $[M]^+$: 258.0715, found 258.0718.

Acknowledgments

This work was supported financially by grants from the National Natural Science Foundation of China (grants 21302066) and Young Program, SCF of Jiangsu Province (BK20130129).

Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/

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Supporting Information

An Effeicient One-pot, Three-Component Synthesis of Vinyl Sulfones via Iodide-catalyzed Radical Alkenylation

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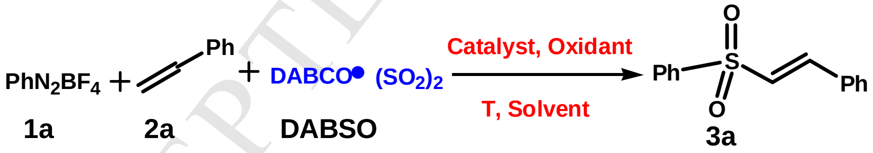
I. General remarks

All starting materials and reagents were purchased from commercial sources and used as received unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 plates. Flash column chromatography was undertaken on silica gel (200–300 mesh). ^{1}H NMR was recorded on Bruker DRX 500 and chemical shifts were referenced to the appropriate solvent peak or 7.24 ppm for residual *d*–chloroform. ^{13}C NMR was recorded on 125 MHz and fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of *d*–chloroform. High resolution mass spectra were measured on Agilent-G6540 UHD Accurate-MassQ-TOF.

II. Experimental section

1. Optimization of the transformation from 1a to 3a

SI-Table 1. Optimization the catalysts and oxidants for the transformation

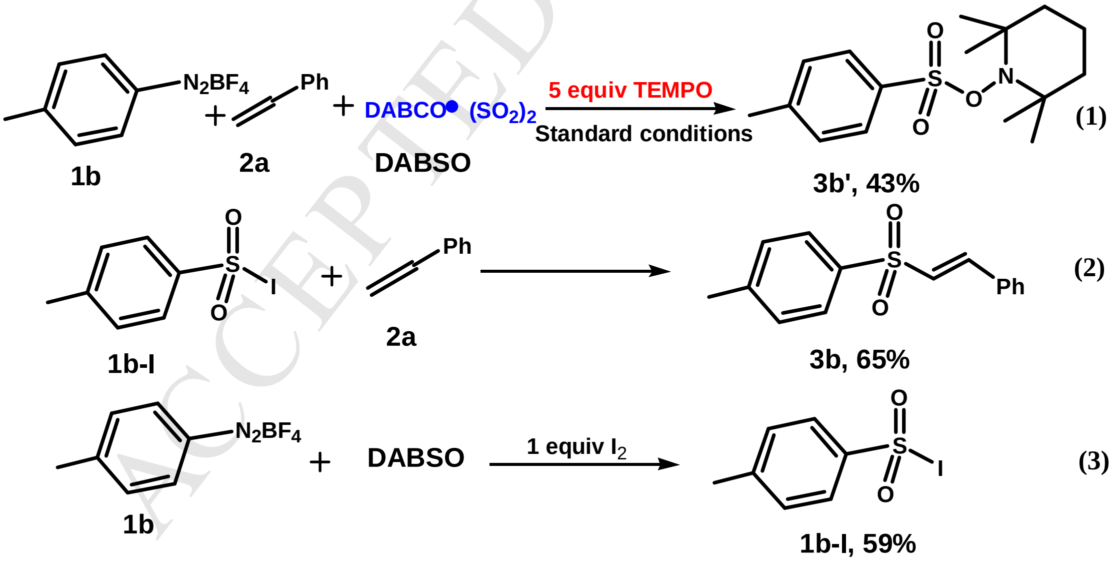


Entry[a]	Catalyst (10 mol%)	Oxidant (2 equiv)	Sovlent /T (^{o}C)	Yield (%)[h]
1	KI	TBHP	CH_3CN/80	65
2	KBr	TBHP	CH_3CN/80	0
3	KCl	TBHP	CH_3CN/80	0
4	NaI	TBHP	CH_3CN/80	41
5	CuI	TBHP	CH_3CN/80	<5
6	I_2	TBHP	CH_3CN/80	50
7	*n*Bu_4NI	TBHP	CH_3CN/80	82
8	*n*Bu_4NI	H_2O_2	CH_3CN/80	25
9	*n*Bu_4NI	DTBP	CH_3CN/80	67
10	*n*Bu_4NI	BPO	CH_3CN/80	49
11	*n*Bu_4NI	DDQ	CH_3CN/80	0
12	*n*Bu_4NI	$K_2S_2O_8$	CH_3CN/80	<5
13	*n*Bu_4NI	O_2 (1 atm)	CH_3CN/80	<5

14	*n*Bu$_4$NI	BQ	CH$_3$CN/80	0
15	*n*Bu$_4$NI	PhI(OAc)$_2$	CH$_3$CN/80	0
16	*n*Bu$_4$NI	TBHP	CH$_3$OH/65	0
17	*n*Bu$_4$NI	TBHP	DCE/90	41
18	*n*Bu$_4$NI	TBHP	Toluene/110	<5
19	*n*Bu$_4$NI	TBHP	DMSO/120	0
20	*n*Bu$_4$NI	TBHP	CH$_2$Cl$_2$/35	0
21	*n*Bu$_4$NI	TBHP	CH$_3$CN/60	49
22	*n*Bu$_4$NI	TBHP	CH$_3$CN/40	<5
23	no	TBHP	CH$_3$CN/80	0
24	*n*Bu$_4$NI	no	CH$_3$CN/80	0
25^b	*n*Bu$_4$NI (20)	TBHP	CH$_3$CN/80	85
26^c	*n*Bu$_4$NI (5)	TBHP	CH$_3$CN/80	47
27^d	*n*Bu$_4$NI	TBHP (2.5)	CH$_3$CN/80	80
28^e	*n*Bu$_4$NI	TBHP (1.5)	CH$_3$CN/80	58
29^f	*n*Bu$_4$NI	TBHP	CH$_3$CN/80	78
29^g	*n*Bu$_4$NI	TBHP	CH$_3$CN/80	65

(a) **1a** (0.2 mmol), **2a** (0.3 mmol), DABSO (0.25 mmol), Catalyst (10 mol%), Oxidant (2 equiv), in 5 mL Solvent at proper temperature under Ar atmosphere for 12 h; (b) Catalyst (20 mol%); (c) Catalyst (5 mol%); (d) Oxidant (2.5 equiv); (e) Oxidant (1.5 equiv); (f) DABSO (0.3 mmol); (g) DABSO (0.2 mmol); (h) isolated yield.

2. Supporting experiments for the proposed mechanism



A. Firstly, the reaction ceased when TEMPO (5 equiv) was employed under standard conditions and the TEMPO-radical adduct of **3b'** was isolated in 43% yield, which implied that the reaction may be proceeding through a radical intermediate. When radical inhibitor BHT (2,6-di-tert-butyl-4-methylphenol) was introduced to the reaction mixture, the formation of the desired product **3b** was completely suppressed.

B. Secondly, we found that **3b** was obtained in moderate yields (65%) when phenylethylene (**2a**) was allowed to react with a freshly prepared p-toluenesulfonyl iodide (yellowish solid).

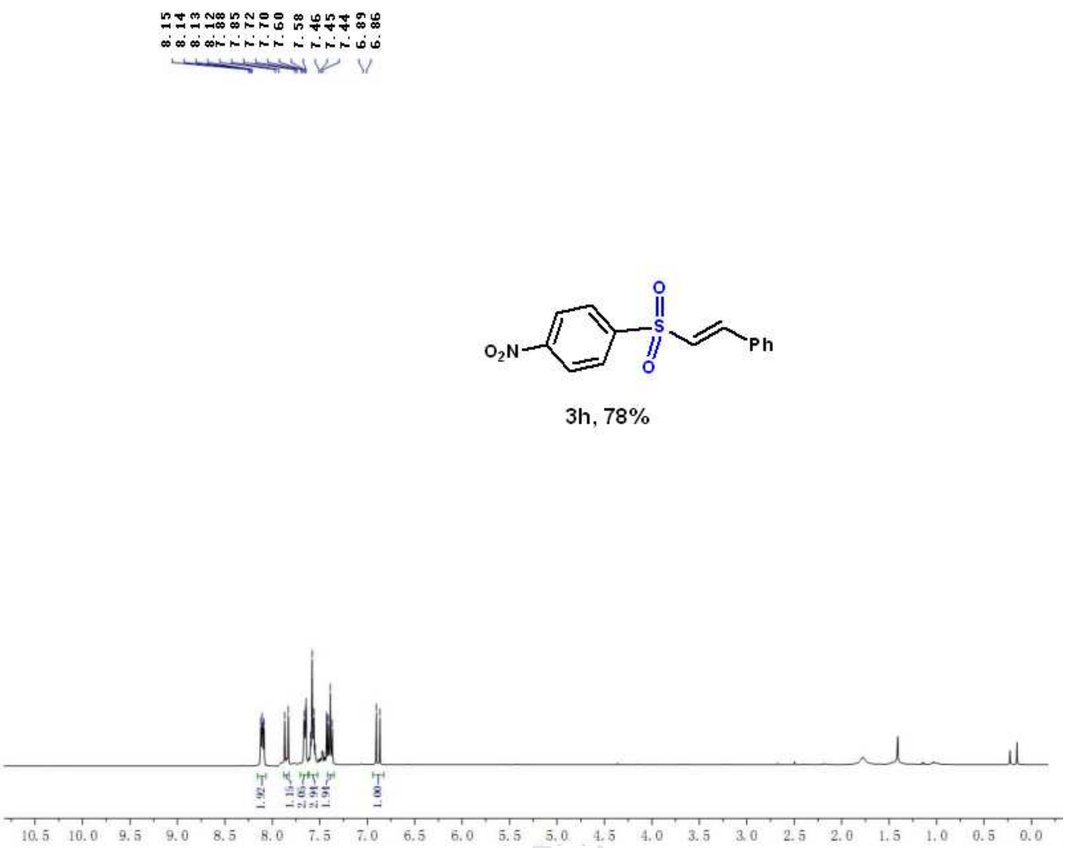
C. Finally, **1b** reacted with DABSO in the presence of 1 equiv I_2, affording p-toluenesulfonyl iodide in 59% yield.

3. Characterization data and the spectrum of new compounds

3h: **(E)-1-Nitro-4-(styrylsulfonyl)benzene (78%)** Yellow solid; mp 138–139 ^oC; ^1H NMR (500 MHz, $CDCl_3$): 8.14 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 14.8 Hz, 1H), 7.59 (d, *J* = 6.4 Hz, 2H), 7.45 (q, *J* =6.4 Hz, 3H), 6.89 (d, *J* =14.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 148.1, 139.7, 134.6, 132.92, 131.5, 130.2, 129.1, 128.4, 126.5; HRMS (EI^+) m/z calcd. for $C_{14}H_{11}NO_4S$ $[M]^+$: 289.0409, found 289.0412.

3i: (E)-2-(Styrylsulfonyl)oxole (84%) Pale yellow solid; mp 53–55 ^oC; ^1H NMR (500 MHz, $CDCl_3$): 7.75 (d, *J* = 3.0 Hz, 1H), 7.68–7.63 (m, 2H), 7.52 (d, *J* =15.2 Hz, 1H), 7.48 (d, *J* = 4.8 Hz, 1H), 7.44–7.39 (m, 3H), 7.14 (dd, *J* =4.8, 3.2 Hz, 1H), 6.92 (d, *J* =15.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 142.5, 141.9, 135.1, 134.8, 132.2, 131.0, 129.5, 128.7, 127.9, 127.5; HRMS (EI^+) m/z calcd. for $C_{12}H_{10}O_3S$ $[M]^+$: 234.0351, found 234.0349.

3o: (E)-1-[2-(Phenylsulfonyl)vinyl]-4-(methyl)benzene (75%) mp 121-123 ºC; ^1H NMR (500 MHz, $CDCl_3$): 8.02 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 15.0 Hz, 1H), 7.58 (m, 5H), 6.95 (d, J = 15.0 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 145.7, 139.5, 138.9, 137.4, 133.1, 130.8, 129.7, 129.2, 127.5, 124.3, 21.8; HRMS (EI^+) m/z calcd. for $C_{15}H_{14}O_2S$ $[M]^+$: 258.0715, found 258.0718.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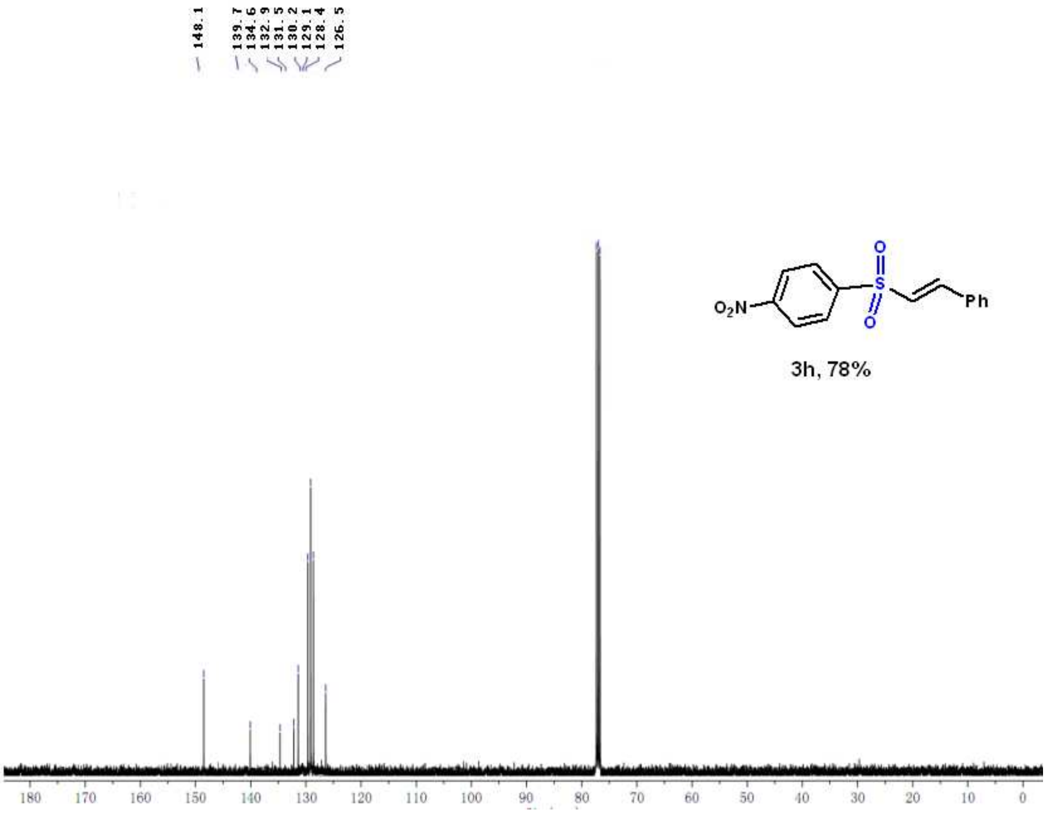
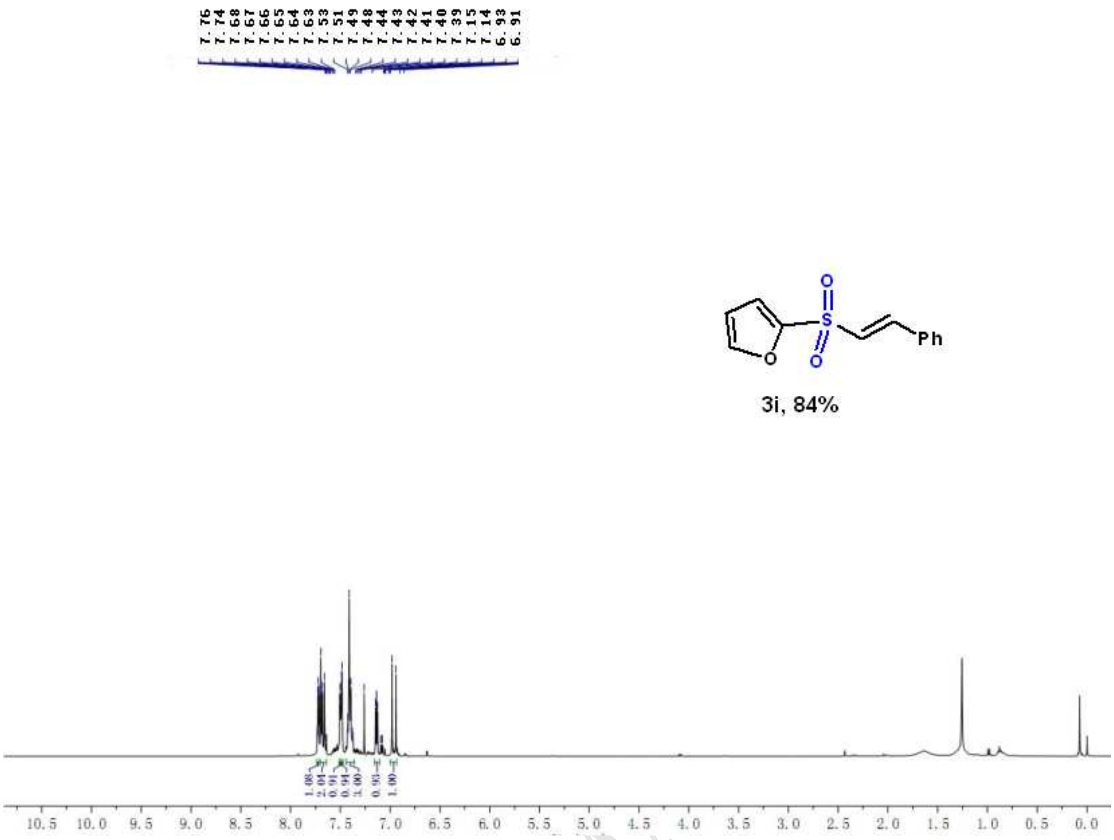
8.14
8.13
8.12
7.88
7.85
7.72
7.70
7.60
7.58
7.46
7.45
7.44
6.89
6.86
O₂N
S
O
O
Ph
1.92
1.15
2.05
2.94
1.91
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3h, 78%


148.1
139.7
134.6
132.9
131.5
130.2
129.1
128.4
126.5
O₂N
S
O
O
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3h, 78%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7.74
7.68
7.67
7.66
7.65
7.64
7.63
7.53
7.51
7.49
7.48
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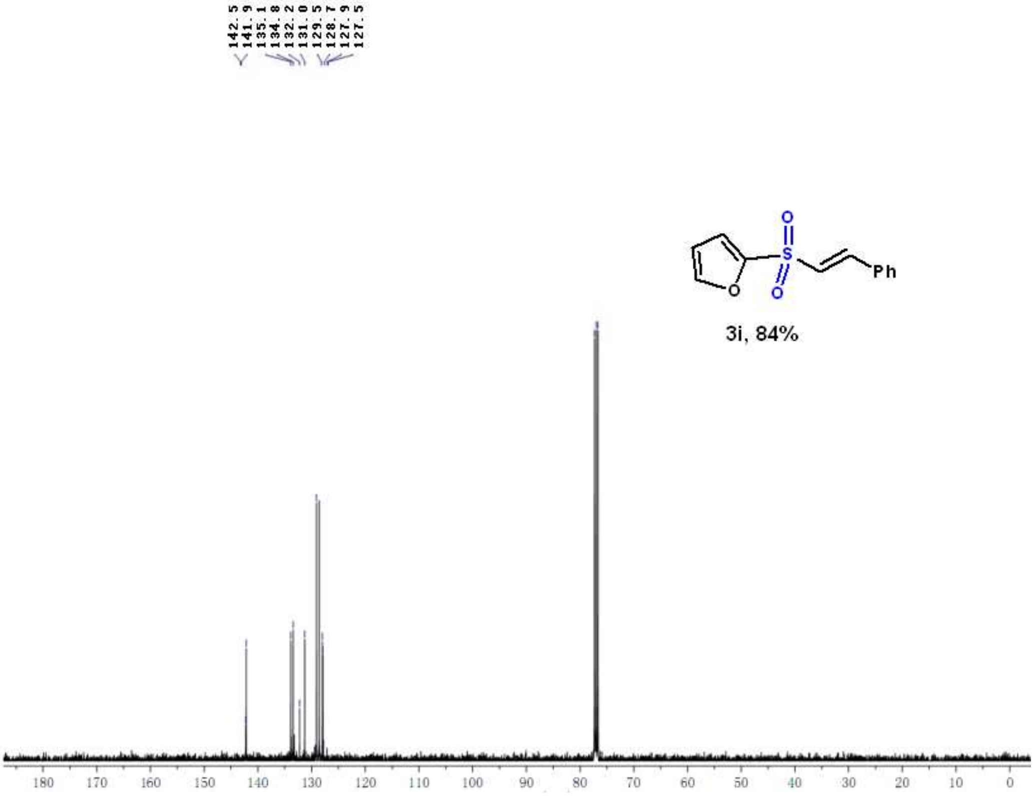
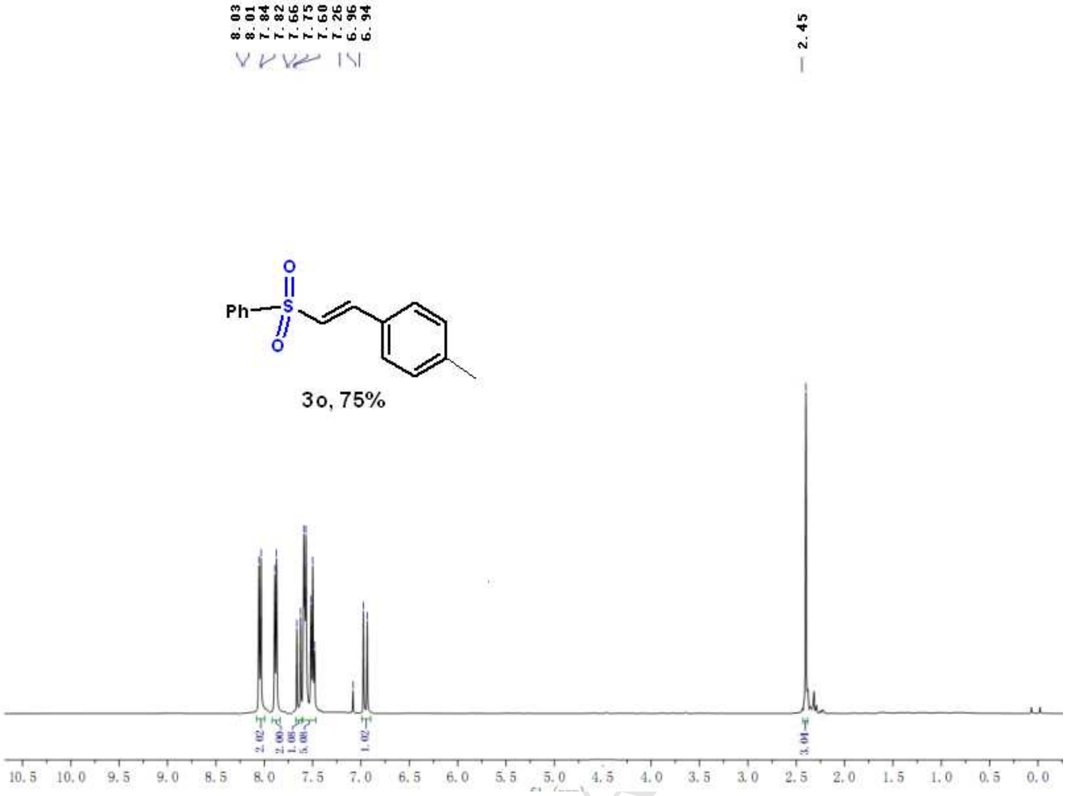
7.43
7.42
7.41
7.40
7.39
7.15
7.14
6.93
6.91
Ph
3i, 84%
1.08
2.04
0.91
0.94
1.00
0.95
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


142.5
141.9
135.1
134.8
132.2
131.0
129.5
128.7
127.9
127.5
Ph
3i, 84%
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.03
8.01
7.84
7.82
7.66
7.75
7.60
7.26
6.96
6.94
2.45
Ph
S
O
O
3o, 75%
2.02
2.00
1.05
5.08
1.02
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
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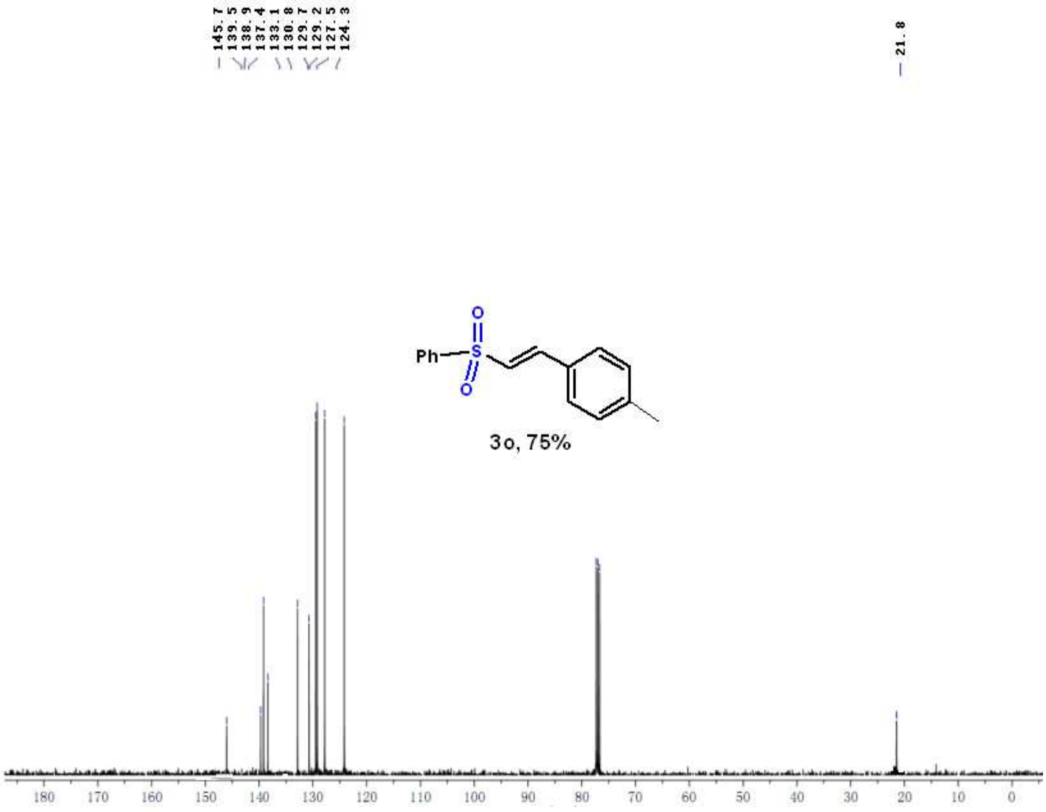
0.0


145.7
139.5
138.9
137.4
133.1
130.8
129.7
129.2
127.5
124.3
21.8
Ph
S
O
O
3o, 75%
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0