JOC The Journal of Organic Chemistry

Note

I2-DMSO-H2O: A Metal Free Combination System for the Oxidative Addition of Alkynes to Access (E)-#-Iodo-#-methylsulfonylalkenes

Peng Zhou, Yupeng Pan, Hua Tan, and Weibing Liu

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b02302 • Publication Date (Web): 30 Oct 2019

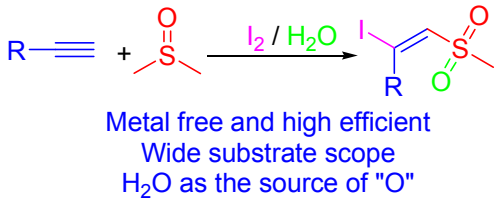
Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

I_2-DMSO-H_2O: A Metal Free Combination System for the Oxidative Addition of Alkynes to Access (*E*)-α-Iodo-β-methylsulfonylalkenes

Peng Zhou[†], Yupeng Pan*[,‡], Hua Tan[†] and Weibing Liu*[,†]

[†] College of Chemistry, Guangdong University of Petrochemical Technology, 2 Guandu Road, Maoming 525000, P. R. China; Email address: lwb409@gdupt.edu.cn; [‡] Shenzhen Grubbs Institute, Southern University of Science and Technology (SUSTech), Shenzhen, 518055, P. R. China; Email address:panyp@mail.sustc.edu.cn.



Abstract: A simple and green reaction was discovered for iodization-methylsulfoxidation of alkynes to access (*E*)-α-iodo-β-methylsulfonylalkenes. This is the first report for synthesis of iodovinyl methylsulfones by employing alkynes to react with molecular iodine (I_2), dimethyl sulfoxide (DMSO) and H_2O. Additionally, this protocol represents a new avenue for utilizing DMSO as the source of the $–SO_2Me$ group and H_2O as the "O" source for the construction of $–SO_2Me$ group from DMSO, which is a valuable finding.

Direct adjacent difunctionalization of alkynes is considered to be one of the most powerful methods to install two functional groups efficiently, in one step, onto a C-C triple bond. The reaction has evolved as one of the most straightforward approaches to synthesize structurally diverse and complex chemicals from simple starting materials.[1] To date, this methodology has been widely used to synthesize halovinyl sulfides from alkynes.[2] Halovinyl sulfides are a valuable and important class of compounds in organic synthesis, and have attracted particular interest[3] for their potentially applications

as starting materials or synthetic intermediates for synthesis of naturally occurring molecules, organic materials, bioactive compounds, pharmaceuticals and industrial chemicals. Thus far, many successful methods have been developed to access halovinyl sulfides, such as β-haloalkenylsulfones and chloroalkenylthioethers, from alkynes.[4] However, the reports for synthesis of iodovinylsulfones directly from the reaction of alkynes with molecular iodine (I_2) and dimethyl sulfoxide (DMSO) are very vare so far. Iodovinylsulfones, as versatile alkenylic intermediates with both a sulfonyl- and an iodine-bearing functionality, can be efficiently utilized for selective synthesis of alkenylsulfones, iodides and many other polysubstituted alkenes by the further transformations of the iodo and sulfonyl moieties. In recent decades, the utilization of DMSO has flourished, as DMSO is not only an effective high-boiling polar solvent[5] and a gentle oxidant,[6] but also frequently employed as a source of –C1,[7] –O,[8] –SMe,[9] –SOMe[10] and –CH_2SOMe[11] for organic transformations, being directly inserted into the target molecules.

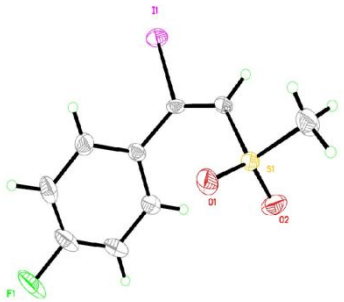
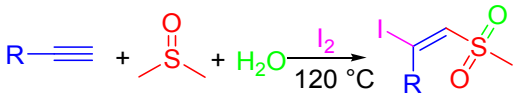


Figure 1. X-ray structure of 1-fluoro-4-((E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (**2k**).

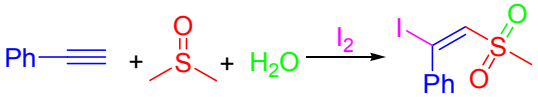
In this context, and in line with our current research interests,[12] herein we report an unprecedented reaction, which could access methylsulfones by employing DMSO as the –SO_2Me source (Scheme 1). The structure of the product **2** has been confirmed by ^{1}H NMR, ^{13}C NMR {1H} , and HR-MS, and its configuration was further verified by NMR-NOE[13] and X-ray (Figure 1). However, in a sharp contrast, the reports for utilization of DMSO as a source of –SO_2Me are extremely rare so far.[14]

Scheme 1. Synthesis of iodovinylmethylsulfones.



At the outset of our studies, phenylacetylene **1a** was employed as a model substrate to react with I_2 in DMSO and H_2O to identify the optimal reaction conditions, the results are rendered in Table 1. We are pleased to find that this reaction proceeded expeditiously at 120 °C. After screening the reaction time, we found that 25 minutes was enough for completing the reaction and resulted the expected product 1-(*E*)-1-iodo-2-(methylsulfinyl)vinyl)benzene **2a** in 80% yield (Table 1, entries 1-4). No significant improvement in yield was obtained when elevating the reaction temperature to 140 °C (Table 1, entry 5). However, a steep decline in yield was observed when the reaction temperature was lowered to 100 °C (Table 1, entry 6). The reaction could not proceed at all when it was conducted at 70 °C or at room temperature (Table 1, entries 7-8). Subsequently, the effect of I_2 loading was investigated: we found no enhancement in the yield of **2a** when increasing the I_2 loading to 1.5 equiv. or decreasing it to 0.6 equiv. (Table 1, entries 9-10).

Table 1. Optimization studies [a]



1a **2a**

Entry	Iodine(1.0 equiv.)	Temperature	Time (m)	Yield%[b]
1	I_2	120 °C	10	32
2	I_2	120 °C	20	73
3	I_2	120 °C	25	80
4	I_2	120 °C	30	80
5	I_2	140 °C	25	80
6	I_2	100°C	25	57
7	I_2	70 °C	25	--
8	I_2	R.T.	25	--
9[c]	I_2	120 °C	25	80
10[d]	I_2	120 °C	25	80

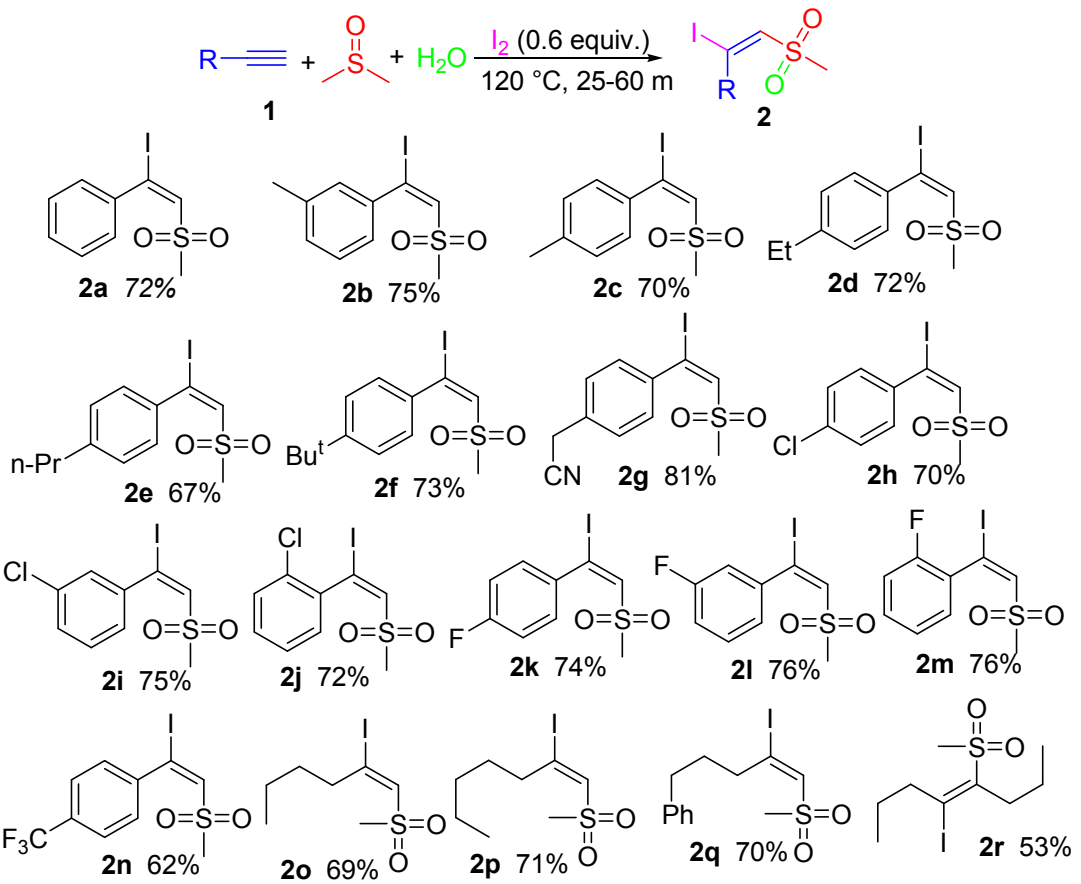
[a] Reaction conditions: **1a** (0.25 mmol), I_2 (1.0 equiv.), DMSO (1.0 mL), H_2O (0.5 mL); [b] GC yield; [c] I_2:

0.6 equiv.; [d] I_2: 1.5 equiv..

Based on the results of the above optimization study (Table 1), we decided to carry out all of the following reactions with 0.6 equiv of I_2 in DMSO at 120 °C for 25 minutes unless otherwise specified (Scheme 2). We first tested a series of different terminal alkynes to evaluate the efficiency and the substrate scope of this iodization-methylsulfoxidation to access the desired iodovinyl methylsulfones. To our satisfaction, despite the varying electronic natures of the different functional groups and substitution patterns on the phenyl ring, all of the tested terminal arynes were tolerated for this conversion and all afforded the desired products in moderate yields (Scheme 2, 62%-81%). As shown in Scheme 2, we noticed that the influence of the different functional groups and substitution patterns on this transformation was unpredictable. For instance, the electro-donating groups (3-Me, 4-Me, 4-Et, 4-nPr, 4-CH_2CN and 4-^{t}Bu) on the phenyl ring gave the required products in 67%-81% yield, whereas those bearing electro-withdrawing groups (2-Cl, 3-Cl, 4-Cl, 2-F, 3-F, 4-F and 4-CF_3) afforded the expected product with 62%-76% yields. Additionally, the outcome of the yield for this conversion appeared to be almost unaffected by the location of the same substituent at different positions of the phenyl ring. For example, when phenylacetylene was substituted by –Cl or –F at the ortho, meta or para position, the corresponding positional isomers were afforded with almost identical yields. For this reaction, it is puzzling that both the strong electro-withdrawing group $–CF_3$ and the strong electro-donating group $–OCH_3$ on the phenyl ring of phenylacetylene were unfavorable. In the former case, the substrate 1-ethynyl-4-(trifluoromethyl)benzene led to the expected product 1-(trifluoromethyl)-4-(*E*)-1-iodo-2-(methylsulfinyl)vinyl)benzene with only 62% yield. In the latter case, the substrates 4-methoxyphenylacetylene and 3,4-dimethoxyphenylacetylene failed to give their desired product.

Scheme 2. Scope of the substrates (all the reactions were carried out on **1** 0.5 mmol scale, I_2 0.6

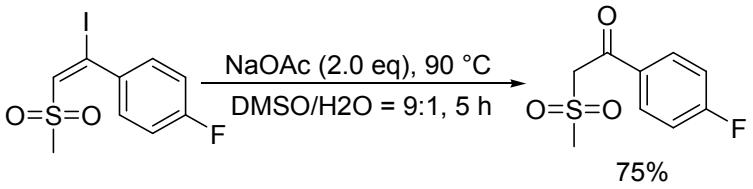
equivalent, DMSO 1.0 mL, H_2O 0.5 mL. Isolated yield is given in the Scheme.).



Next, several terminal alkyl alkynes were evaluated under the optimal conditions. We found that although all the tested substrates were compatible for this protocol, the reactivity of these compounds was slightly poorer than for the tested terminal arynes. In general, all these terminal alkyl alkynes led to their corresponding product with acceptable yield when the reaction time was prolonged to 60 m. To further expand the substrate scope, internal alkynes, such as oct-4-yne, hept-3-yne and 1-(prop-1-ynyl)benzene, were employed to conduct this conversion. These internal alkynes proved to be reluctant substrates for this transformation: the symmetrical internal alkyne oct-4-yne resulted in the expected product (*E*)-4-iodo-5-(methylsulfinyl)oct-4-ene with only 53% yield (Scheme 2, **2r**) and the unsymmetric substrates furnished a complex reaction system. Finally, it is worth noting that the liquid iodovinyl methylsulfones (**2o-2r**) are volatile compounds when pure.

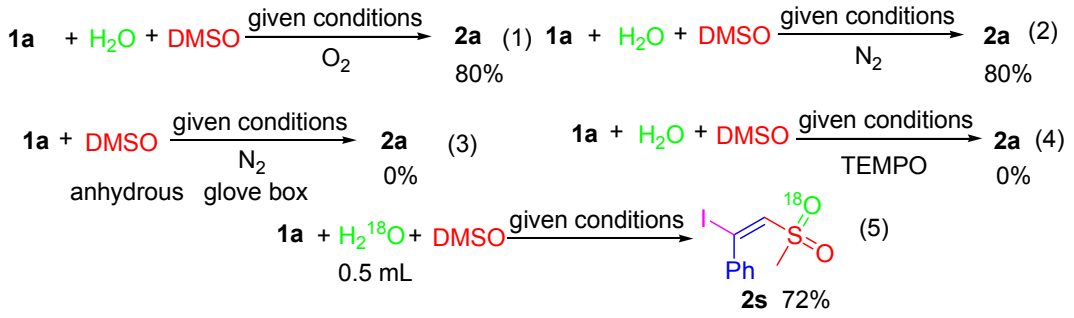
For the application of the products, a synthetic transformation of **2k** was conducted, as showed in Scheme 3. A simple workup afforded in the derived product 1-(4-fluorophenyl)-2-(methylsulfonyl)ethanone with 75% yield.

Scheme 3. Transformation of 1-fluoro-4-((E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (**2k**) to 1-(4-fluorophenyl)-2-(methylsulfonyl)ethanone.

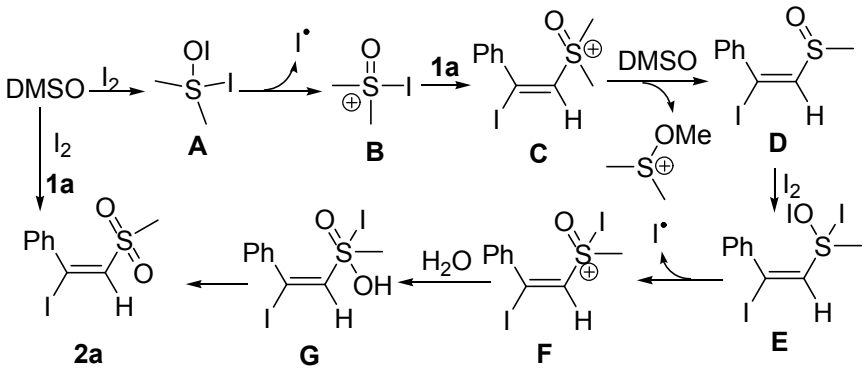


To shed some light on the mechanism of this iodization-methylsulfoxidation, several control experiments were conducted (Scheme 4). Firstly, no obvious influence on the product formation was noticed when the reaction was performed under oxygen or nitrogen atmosphere (Scheme 4, eq 1 and eq 2), which rules out the possibility of the involvement of atmospheric oxygen for the formation of $–SO_2Me$ group. However, this transformation does not occur at all when the reaction was conducted under nitrogen atmospheres in glove box with anhydrous DMSO, thereby confirming that one oxygen atom of the $–SO_2Me$ group in the product is derived from the H_2O in DMSO (Scheme 4, eq 3). As expected, radical inhibition with excess 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) entirely quenched this conversion (Scheme 4, eq 4), suggesting a radical mechanism was likely to be involved for this transformation. To gain further insight into the mechanism, when the reaction of **1a** was conducted in the presence of 0.5 mL of $H_2{}^{18}O$, the ^{18}O-labeled product **2s** was obtained in 72% yield (Scheme 4, eq 5), which completely confirmed the fact that one oxygen atom of the $–SO_2Me$ group in the product is derived from H_2O.

Scheme 4. Control experiments.



Scheme 5. Proposed mechanism.



The mechanism for this conversion is unclear. However, according to the above control experiments and the existing related literature, a possible mechanism is illustrated in Scheme 5, exemplified by the formation of **2a**. Initially, I_2 reacted with DMSO at high temperature to afford an iodinated sulphide **A**, by a similar process was reported by Braga's group.[15] At high temperature, **A** quickly decomposed and converted to a sulfinyl iodide cation **B**. The subsequent addition of **A** to the carbon-carbon triple bond of phenylacetylene (**1a**) resulted in the adduct iodovinylsulfoxidecation **C** via the mechanism proposed by Wang's group.[16] The subsequently abstraction of a methyl group from C by the weakly nucleo-philic DMSO to afford iodovinylsulfoxide species **D**.[11] In the next step, iodovinylsulfoxide species **D** underwent a similar process as from DMSO to **B** (Scheme 5) in the presence of I_2 to furnish another iodovinylsulfoxidecation **F**, which would be quickly converted to another intermediate **G** by the nucleophilic attack of H_2O. Finally, the elimilation of HI from G produces the desired product **2a**.

In conclusion, we have disclosed a simple synthetic route to achieve (*E*)-α-iodo-β-methylsulfonylalkenes, which is the first example for synthesis of iodovinyl methylsulfones via an iodization-methylsulfoxidation of alkynes with I_2 and DMSO. In this reaction, DMSO is an efficient reagent for methylsulfoxidation of alkynes at high temperature. Additionally, this protocol is a simple yet powerful method for the construction of iodovinyl methylsulfones with a broad substrate scope and excellent regio-selectivity. The presented organic transformation represents a new avenue for utilizing DMSO as a source of the methylsulfonyl group. Further studies on the mechanism and applications are in progress in our laboratory, and we expect many novel methodologies employing DMSO as –SOMe and $–SO_2Me$ sources to arise in the near future.

EXPERIMENTAL SECTION

General Information. All the reactions were carried out at 120 °C (oil bath) for 25-60 m in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR {1H} spectra were recorded on a 400MHz spectrometer in solutions of $CDCl_3$ using tetramethyl silane as the internal standard; δ values are given in ppm, and coupling constants (*J*) in Hz. HR-MS were obtained on a Q-TOF micro spectrometer.

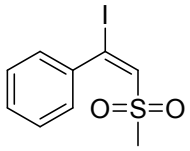
Typical procedure: 1-(*E*)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2a).

A mixture of phenylacetylene (**1a**) (52 mg, 0.5 mmol), I_2 (76 mg, 0.3 mmol), DMSO (1.0 mL) and H_2O (0.5 mL) was added successively in a round-bottom flask, and the resulting solution was stirred for 25 m at 120°C (oil bath). The mixture was purified by column chromatography on silica gel to afford product **2a** with PE/EA = 10/1 as the eluent.

Typical procedure: a larger scale experiment to synthesize 2k

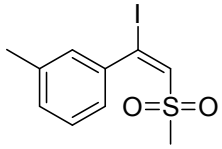
A mixture of 1-ethynyl-4-fluorobenzene (**1k**) (1.20 g, 10 mmol), I_2 (1.52 g, 6 mmol), DMSO (8.0 mL) and H_2O (0.5 mL) was added successively in a round-bottom flask, and the resulting solution was stirred for 45 m at 120°C (oil bath). The mixture was purified by column chromatography on silica gel with PE/EA = 10/1 as the eluent to afford the desired product **2k** with 69% yield (2.24 g).

1-(E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2a)



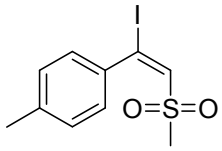
Yield: 72% (110 mg); a colorless solid; m.p. 99–101 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.46 (m, 2H), 7.41 (m, 3H), 7.31 (s, 1H), 2.67 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.3, 139.4, 130.4, 128.3, 127.8, 114.9, 43.0; HRMS (ESI): calcd for $C_9H_9INaO_2S$: [M+Na$^+$] 330.9260, found 330.9265.

1-(E)-1-iodo-2-(methylsulfonyl)vinyl)-3-methylbenzene (Scheme 2, 2b)



Yield: 75% (120 mg); a colorless solid; m.p. 105–107 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.29 (s, 1H), 7.28 (br, 3H),7.19 (m, 1H), 2.67 (s, 3H), 2.39 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.1, 139.3, 138.2, 131.2, 128.3, 128.2, 124.9, 115.2, 43.5, 21.3; HRMS (ESI): calcd for $C_{10}H_{11}INaO_2S$: [M+Na$^+$] 344.9416, found 344.9422.

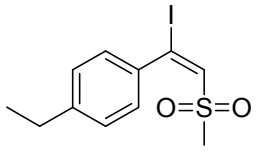
1-(E)-1-iodo-2-(methylsulfonyl)vinyl)-4-methylbenzene (Scheme 2, 2c)[17]



Yield: 70% (112 mg); a colorless solid; m.p. 108–110 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.38 (d, J = 8.4 Hz, 2H), 7.28 (s, 1H), 7.20 (d, J = 8.4 Hz, 2H), 2.67 (s, 3H), 2.37 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100

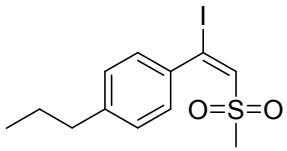
Hz) δ 140.9, 139.8, 136.5, 129.0, 128.0, 115.5, 43.0, 21.4; HRMS (ESI): calcd for $C_{10}H_{11}INaO_2S$: [M+Na$^+$] 344.9416, found 344.9418.

1-ethyl-4-(E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2d)



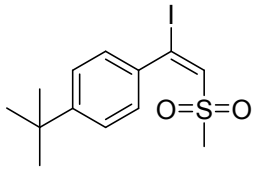
Yield: 72% (120 mg); a colorless solid; m.p. 114–116 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.41 (d, J = 8.4 Hz, 2H), 7.28 (s, 1H), 7.22 (d, J = 8.4 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.66 (s, 3H), 1.25 (t, J = 7.6 Hz, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 147.1, 139.9, 136.7, 128.1, 127.8, 115.5, 42.9, 28.7, 15.0; HRMS (ESI): calcd for $C_{11}H_{13}INaO_2S$: [M+Na$^+$] 358.9573, found 358.9565.

1-(E)-1-iodo-2-(methylsulfonyl)vinyl)-4-propylbenzene (Scheme 2, 2e)



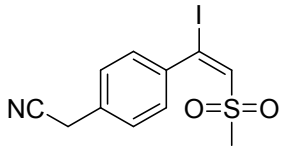
Yield: 67% (117 mg); a colorless solid; m.p. 123–124 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.40 (d, J = 8.4 Hz, 2H),7.28 (s, 1H), 7.20 (d, J = 8.4 Hz, 2H),2.64 (s, 3H), 2.60(q, J = 7.6 Hz, 2H), 1.64 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 145.7, 139.9, 136.7, 128.4, 128.0, 115.4, 42.9, 37.8, 24.1, 13.8; HRMS (ESI): calcd for $C_{12}H_{15}INaO_2S$: [M+Na$^+$] 372.9729, found 372.9740.

1-tert-butyl-4-(E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2f)



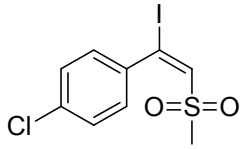
Yield: 73% (132 mg); a colorless solid; m.p. 102–104 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.42 (m, 4H), 7.29 (s, 1H), 2.64 (s, 3H), 1.33 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 154.0, 139.9, 136.3, 127.9, 125.3, 115.4, 42.9, 34.9, 31.1; HRMS (ESI): calcd for $C_{13}H_{18}IO_2S$: [M+H$^+$] 365.0066, found 365.0074.

2-(4-(E)-1-iodo-2-(methylsulfonyl)vinyl)phenyl)acetonitrile (Scheme 2, 2g)



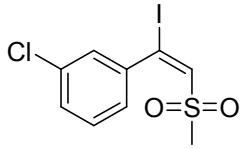
Yield: 81% (1140 mg); a pale yellow solid; m.p. 108–110 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.48 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.33 (s, 1H), 3.79 (s, 2H), 2.76 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.2, 139.4, 132.1, 128.6, 127.8, 43.2, 29.6, 23.5; HRMS (ESI): calcd for $C_{11}H_{10}INNaO_2S$: [M+Na$^+$] 369.9369, found 369.9371.

1-chloro-4-((Z)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2h)



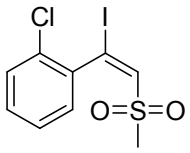
Yield: 70% (119 mg); a colorless solid; m.p. 116–117 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.38 (m, 4H), 7.31 (s, 1H), 2.75 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.3, 137.7, 136.5, 129.3, 128.6, 113.4, 43.1; HRMS (ESI): calcd for $C_9H_9ClIO_2S$: [M+H$^+$] 342.9051, found 342.9067.

1-chloro-3-((Z)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2i)



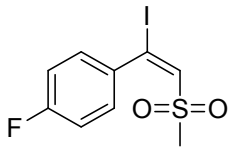
Yield: 75% (127 mg); a colorless solid; m.p. 100–102 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.41 (s, 1H), 7.35 (br, 3H), 7.32 (s, 1H), 2.76 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.9, 140.6, 134.2, 130.4, 129.5, 127.7, 125.9, 112.6, 43.2; HRMS (ESI): calcd for $C_9H_9ClIO_2S$: [M+H$^+$] 342.9051, found 342.9071.

1-chloro-2-(E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2j)



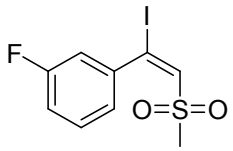
Yield: 72% (119mg); a colorless solid; m.p. 91–93 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.42 (m, 1H), 7.36 (s, 1H), 7.32 (m, 3H), 2.80 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 141.2, 137.7, 130.9, 130.3, 129.9, 128.8, 126.8, 110.9, 42.7; HRMS (ESI): calcd for $C_9H_9ClIO_2S$: [M+H$^+$] 342.9051, found 342.9066.

1-fluoro-4-((Z)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2k)



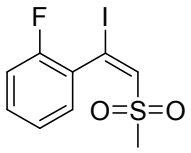
Yield: 74% (120 mg); a colorless solid; m.p. 112–114 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.47 (m, 2H), 7.31 (s, 1H), 7.08 (m, 2H), 2.73 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ161.6 (d, $^{1}J_{C\text{-}F}$ = 251.0 Hz),140.2, 135.4 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 130.2 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 115.5 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 113.7, 43.1; HRMS (ESI): calcd for $C_9H_9FIO_2S$: [M+H$^+$] 326.9346, found 326.9349.

1-fluoro-3-((Z)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2l)



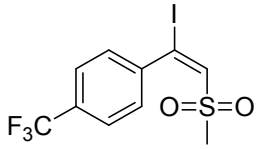
Yield: 76% (123 mg); a colorless solid; m.p. 103–105 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.38 (m, 1H), 7.32 (s, 1H), 7.23 (m, 1H), 7.14 (m, 1H), 7.08 (m, 1H), 2.75 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 163.0 (d, $^{1}J_{C\text{-}F}$ = 245.0 Hz), 145.1 (d, $^{4}J_{C\text{-}F}$ = 6.7 Hz), 140.6, 130.0 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 123.5 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 117.4 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 112.6 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 43.2; HRMS (ESI): calcd for $C_9H_9FIO_2S$: [M+H$^+$] 326.9346, found 326.9370.

1-fluoro-2-(E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2m)



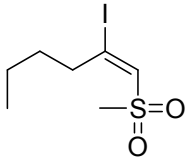
Yield: 76% (124 mg); a colorless solid; m.p. 97–99 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.40 (s, 1H), 7.35 (m, 2H),7.20 (m, 1H), 7.09 (m, 1H) 2.84 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 158.5 (d, $^{1}J_{C\text{-}F}$ = 248.0 Hz), 141.4, 132.0 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 129.5 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 127.3 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz), 124.1 (d, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 115.8 (d, $^{2}J_{C\text{-}F}$ = 20.8 Hz), 106.7, 42.7; HRMS (ESI): calcd for $C_9H_9FIO_2S$: [M+H$^+$] 326.9346, found 326.9362.

1-(trifluoromethyl)-4-((Z)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 2, 2n)



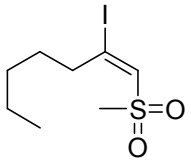
Yield: 62% (117 mg); a colorless solid; m.p. 113–114 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.66 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H),7.37 (s, 1H), 2.79 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 142.8, 140.7, 131.1, 128.1, 126.9 (q, $^{1}J_{C\text{-}F}$ = 269.5 Hz), 125.3, 112.6, 43.3; HRMS (ESI): calcd for $C_{10}H_9F_3IO_2S$: [M+H$^+$] 376.9314, found 376.9321.

(E)-2-iodo-1-(methylsulfonyl)hex-1-ene (Scheme 2, 2o)



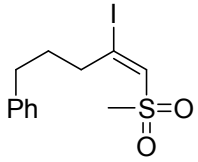
Yield: 69% (99 mg); a colorless oil; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 6.54 (s, 1H), 2.45 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H), 1.48 (m, 2H), 1.36 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 133.2, 96.9, 39.5, 30.8, 21.4, 17.4, 13.9; HRMS (ESI): calcd for $C_7H_{14}IO_2S$: [M+H$^+$] 288.9753, found 288.9750.

(E)-2-iodo-1-(methylsulfonyl)hept-1-ene (Scheme 2, 2p)



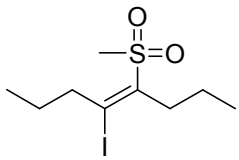
Yield: 71% (106mg); a colorless oil;[1]H NMR ($CDCl_3$, 400 Hz) δ 6.54 (s, 1H), 2.43 (t, *J* = 7.6 Hz, 2H), 2.31 (s, 3H), 1.50 (m, 2H), 1.33 (m, 4H), 0.91 (t, *J* = 7.6 Hz, 3H); [13]C NMR {1H} ($CDCl_3$, 100 Hz) δ 133.2, 97.0, 39.7, 30.4, 28.3, 22.4, 17.4, 13.9; HRMS (ESI): calcd for $C_8H_{16}IO_2S$: [M+H$^+$] 302.9910, found 302.9914.

1-(E)-4-iodo-5-(methylsulfonyl)pent-4-enyl)benzene (Scheme 2, 2q)



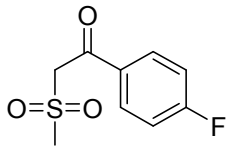
Yield: 70% (123 mg); a pale yellow oil; [1]H NMR ($CDCl_3$, 400 Hz) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (m, 3H), 7.06 (s, 1H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.91 (s, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.96 (m, 2H); [13]C NMR {1H} ($CDCl_3$, 100 Hz) δ 141.0, 138.0, 128.45, 128.41, 126.5, 126.1, 43.6, 39.6, 34.5, 31.7; HRMS (ESI): calcd for $C_{12}H_{16}IO_2S$: [M+H$^+$] 350.9910, found 350.9928.

(E)-4-iodo-5-(methylsulfonyl)oct-4-ene (Scheme 2, 2r)



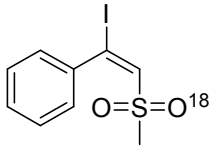
Yield: 53% (84 mg); a colorless oil; [1]H NMR ($CDCl_3$, 400 Hz) δ 2.85 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 1.57 (m, 4H), 0.97 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); [13]C NMR {1H} ($CDCl_3$, 100 Hz) δ 137.2, 106.7, 44.7, 42.5, 22.5, 21.2, 16.6, 13.5, 12.8; HRMS (ESI): calcd for $C_9H_{18}IO_2S$: [M+H$^+$] 317.0066, found 317.0061.

1-(4-fluorophenyl)-2-(methylsulfonyl)ethanone (Scheme 3) [18]



A colorless solid; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.06 (m, 2H), 7.22 (m, 2H), 4.57 (s, 2H), 3.15 (s, 3H).

1-(E)-1-iodo-2-(methylsulfonyl)vinyl)benzene (Scheme 4, eq 5, 2s)



Yield: 72% (110 mg); a colorless solid; m.p. 99–101 °C; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.46 (m, 2H), 7.40 (m, 3H), 7.31 (s, 1H), 2.66 (s, 3H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.2, 139.4, 130.4, 128.3, 127.8, 114.9, 43.0; HRMS (ESI): calcd for $C_9H_9IO^{18}OS$: [M+H$^+$] 310.9483, found 310.9494.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR {1H} of all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: lwb409@gdupt.edu.cn; panyp@mail.sustc.edu.cn

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21502066), the Foundation of Department of Science and Technology of Guangdong Provincial (No. 2016A020221038) and Guangdong Natural Science Foundation (No. 2017A030307006)

References

1. (a) Miao, T.; Xia, D.; Li, Y.; Li, P. H.; Wang, L. Direct Difunctionalization of Activated Alkynes via Domino Oxidative Benzylation/1,4-aryl Migration/Decarboxylation Reactions under Metal-free Conditions. *Chem. Commun.* **2016**, *52*, 3175 – 3178; (b) Gao, M. C.; Xu, B. Copper

Nitrate Mediated Regio- and Stereoselective Difunctionalization of Alkynes: A Direct Approach to α-Chloro-β-nitroolefins. *Org. Lett.* **2016**, 18, 47466–4749; (c) Li, Y. W.; Xiang, Y. C.; Li, Z. N.; Wu, J. Direct Vicinal Difunctionalization of Alkynes through Trifluoromethylation and Aminosulfonylation via Insertion of Sulfur dioxide under Catalyst-free Conditions. *Org. Chem. Front.* **2016**, *3*, 1493 – 1497.

2. (a) Mao, S.; Gao, Y. R.; Zhu, X. Q.; Guo, D. D.; Wang, Y. Q. Copper-Catalyzed Radical Reaction of N-Tosylhydrazones: Stereoselective Synthesis of (*E*)-vinyl sulfones. *Org. Lett.* **2015**, *7*, 1692−1695; (b) Sun, Y. D.; Abdukader, A.; Lu, D.; Zhang, H. Y.; Liu, C. J. Synthesis of (*E*)-β-Iodo vinylsulfones via Iodine-promoted Iodosulfonylation of Alkynes with Sodium Sulfinates in an Aqueous Medium at Room Temperature. *Green Chem.* **2017**, *19*, 1255−1258; (c) Hou, Y. L.; Zhu, L. Y.; Hu, H.; Chen, S. W.; Li, Z. F.; Liu, Y. J.; Gong, P. Iodine Promoted Iodosulfonylation of Alkynes with Sulfonyl Hydrazides in an Aqueous Medium: Highly Stereoselective Synthesis of (*E*)-β-Iodo vinylsulfones. *New J. Chem.* **2018**, *42*, 8752−8755; (d) Ma, Y.; Wang, K.; Zhang, D.; Sun, P. Solvent Controlled Transformation between Sulfonyl Hydrazides and Alkynes: Divergent Synthesis of Benzo[b]thiophene-1,1-dioxides and (*E*)-β-Iodo Vinylsulfones. *Adv. Synth. Catal.* **2019**, *361*, 597−602.

3. (a) Iwasaki, M.; Fujii, T.; Nakajima, K.; Nishihara, Y. Iron-Induced Regio- and Stereoselective Addition of Sulfenyl Chlorides to Alkynes by a Radical Pathway. *Angew. Chem. Int. Ed.* **2014**, *53*, 13880−13884; (b) Wan, J. P.; Hu, D.; Bai, F.; Wei, L.; Liu, Y. Hierarchical Fe_3O_4-Titanate Microspheres with Superior Removal Capability for Water Treatment: In situ Growth and Structure Tailoring via Hydrothermal Assisted Etching. *RSC Adv.* **2016**, *6*, 73132−73135.

4. (a) Iwasaki, M.; Fujii, T.; Yamamoto, A.; Nakajima, K.; Nishihara, Y. Palladium-Catalyzed

Region- and Stereoselective Chlorothiolation of Terminal Alkynes with Sulfenyl Chlorides. *Chem. Asian J.* **2014,** *9*, 58−62; (b) Zeng, K.; Chen, L.; Chen, Y.; Liu, Y. P.; Zhou, Y. B.; Au, C. T.; Yin, S. F. Iron(III) Chloride-mediated Region- and Stereoselective Chlorosulfonylation of Alkynes and Alkenes with Sodium Sulfinates. *Adv. Synth. Catal.* **2017**, *359*, 841−847.

5. (a) Johansson, S.; Kuhlmann, C.; Weber, J.; Paululat, T.; Engelhard,C.; Günne, J. S. Decomposition of P_4O_{10} in DMSO. *Chem. Commun.* **2018**, *54*, 7605−7608; (b) Riemer, D.; Mandaviya, B.; Schilling, W.; Götz, A. C.; Kühl, T.; Finger, M.; Das, S. Dominant Effect of Support Wettability on the Reaction Pathway for Catalytic Wet Air Oxidation over Pt and Ru Nanoparticle Catalysts. *ACS Catal.* **2018**, *8*, 3030−3034.

6. Xiong, M. T.; Gao, Z.; Liang, X.; Cai,P. F.; Zhu, H. P.; Pan, Y. J. Iodine-Catalyzed Synthesis of N,N′-Diaryl-o-phenylenediamines from Cyclohexanones and Anilines using DMSO and O_2 as Oxidants. *Chem. Commun.* **2018**, *54*, 9679−9682.

7. (a) Zhu, X. M.; Li, W. G.; Luo, X. A.; Deng, G. B.; Liang, Y.; Liu, J. B. A Catalyst-free and Additive-free method for the synthesis of benzothiazolethiones from o-iodoanilines, DMSO and potassium sulfide. *Green Chem.* **2018**, *20*, 1970−1974; (b) Jadhav, S. D.; Singh, A. oxidative annulations Involving DMSO and Formamide: $K_2S_2O_8$ Mediated Syntheses of Quinolines and Pyrimidines. *Org. Lett.* **2017**, *19*, 5673−5676.

8. Dong, J.; Xu, J. X. NBS /DMSO-mediated Synthesis of (2,3-dihydrobenzo [b][1,4] oxathiin-3-yl) methanols from Aryloxymethylthiiranes. *New J. Chem.* **2018**, *42*, 9037−9044.

9. (a) Hu, L.; Wang, D. D.; Chen, X.; Yu, L.; Yu, Y. Q.; Tan.,Z.; Zhu, G. G. Copper-Catalyzed Decarboxylative Methylthiolation of Aromatic Carboxylate Salts with DMSO. *Org. Biomol. Chem.* **2017**, *15*, 5674−5679; (b) Zou, J. F.; Huang, W. S.; Li, L.; Xu, Z.; Zheng, Z. J.; Yang, K.

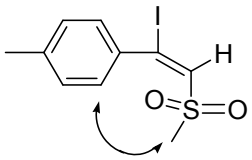
F.; Xu, L. W. DMSO as Oxidant and Sulfenylating Agent for Metal-free Oxidation and Methylthiolation of Alcohol-containing Indoles. *RSC Adv.* **2015**, *5*, 30389−30393.

10. (a) Pramanik, M. M. D.; Rastogi, N. Visible Light Catalyzed Methylsulfoxidation of (Het)aryl diazonium Salts using DMSO. *Chem. Commun.* **2016**, *52*, 8557−8560; (b) Dai, P.; Luo, K.; Yu, X.; Yang, W. C.; Wu, L.; Zhang, W. H. *Tert*-butyl Nitrite mediated Expeditious Methylsulfoxidation of Tetrazole-amines with DMSO: Metal-free Synthesis of Antifungal Active Methylsulfinyl-1H-tetrazole derivatives. *Adv. Synth. Catal.* **2018**, *360*, 468−473.

11. Huang, M. H.; Zhu, C. F.; He, C. L.; Zhu, Y. L.; Hao, W. J.; Wang, D. C.; Tu, S. J.; Jiang, B. A Free-radical-promoted Stereospecific Denitro Silylation of β-nitroalkenes with Silanes. *Org. Chem. Front.* **2018**, *5*, 1643−1650.

12. Tong, H. Q; Chen, C.; Liu, W. B.; Pan, Y. P.; Duan, L. H. Chlorothiomethylation of Alkynes with HCl and Dimethyl Sulfoxide: An Efficient Approach to (*E*)-α-Chloro-β-(methylthio) alkenes. *Asian J. Org. Chem.* **2019**, *8*, 479−481.

13. The configuration of **2c**:



14. (a) Yi, H.; Zhang, G.; Wang, H.; Huang, Z.; Wang, J.; Singh, A. K.; Lei, A. Recent Advances in Radical C–H Activation/Radical Cross-coupling. *Chem. Rev.* **2017,** *117*, 9016−9085; (b) Dai, J.-L.; Shao, N. Q.; Zhang, J.; Jia, R. P.; Wang, D. H. Cu(II)-Catalyzed ortho-Selective Aminomethylation of Phenols. *J. Am. Chem. Soc.* **2017,** *139*, 12390−12393.

15. Saba, S.; Rafique, J.; Braga, A. L. DMSO/Iodine-catalyzed Oxidative C–Se/C–S Bond formation:

A Regioselective Synthesis of Unsymmetrical Chalcogenides with Nitrogen- or Oxygen-containing Arenes. *Catal. Sci. Technol.* **2016**, *6*, 3087−3098.

16. Wei, W.; Wen, J. W.; Yang, D. S.; Jing, H. J.; You, J. M.; Wang, H. Direct Difunctionalization of Alkynes with Sulfinic Acids and Molecular Iodine: A Simple and Convenient Approach to (*E*)-β-Iodovinyl sulfones. *RSC Adv.* **2015**, *5*, 4416−4419.

17. Taniguchi, N. Cobalt-Catalyzed Stereoselective Iodosulfonylation and Diiodination of Alkynes via Oxidation of Potassium Iodide in Air. *Tetrahedron* **2018**, *74*, 1454−1460.

18. Shao, A. L.; Gao, M.; Chen, S. T.; Wang, T.; Lei, A. W. CO/O_2 Assisted Oxidative Carbon–carbon and Carbon–heteroatom Bond Cleavage for the Synthesis of Oxosulfonates from DMSO and Olefins. *Chem. Sci.* **2017**, *8*, 2175−2178.