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An Unexpected Domino Reaction of *β*-Keto Sulfones with Acetylene Ketones Promoted by Base: Facile Synthesis of 3(*2H*)-Furanones and Sulfonylbenzenes

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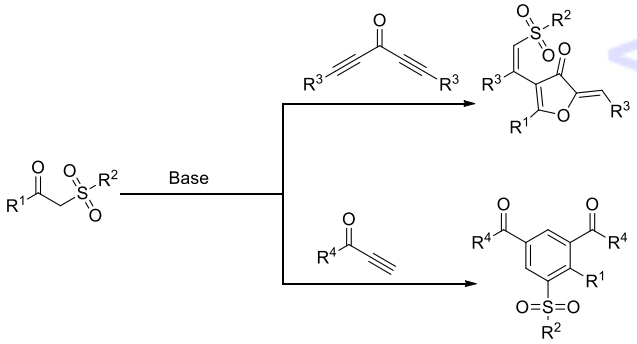
Abstract. An unexpected domino reaction of *β*-keto sulfones with acetylene ketones has been developed. The domino reaction of *β*-keto sulfones with diynones proceeded smoothly in the 30% mol K_2CO_3 without other additives, and afforded the novel 3(*2H*)-furanone derivatives. Replaced diynones with terminal alkyne ketones, the reaction regioselectivity was changed and sulfonylbenzenes were obtained *via* the benzannulation in good yields.

Keywords: domino reaction; *β*-keto sulfones; acetylene ketones; reaction regioselectivity; 3(*2H*)-furanones; sulfonylbenzenes

Introduction

Sulfones are considered as an important class of organic compounds in both synthetic and medicinal chemistry because of their various applications in synthesis[1] and versatile biological activities[2]. Among sulfone derivatives, great attention is drawn to *β*-keto sulfones[3] as their different functional groups (ketone and sulfone). *β*-Keto sulfones are important intermediates that have been used for the preparation of different classes of organic compounds such as alkenes (Julia Kocienski olefination)[4], alkynes[5], chalcones[6], 2,3-dihydrofurans[7], 1,2,3-triazoles[8], pyrroles[9] and *4H*-pyrans[10]. In the past years, great effort has been focus on the Michael reaction of *β*-keto sulfones with conjugated olefins.[11] In contrast, the additions of *β*-keto sulfones with alkynes have been scarcely explored. Yamamoto[12] reported the allylation of carbon nucleophiles with alkynes under the catalysis of palladium/acetic acid. Takai[13] found that *δ*-keto sulfones were obtained via the additions of *β*-keto sulfones with terminal alkynes promoted by rhenium catalyst.

Recently, we have studied the coupling of acetylene ketones with trimethylsilyl azide[14], glycine esters[15] and water[16]. In this context, we focus on the Michael additions of *β*-keto sulfones and acetylene ketones (Scheme 1). In this work, the base-induced domino reactions of *β*-keto sulfones with diynones afforded a series of sulfonylvinyl-containing 3(*2H*)-furanone derivatives which are an unexplored class of compounds and predicted to possess biological activities duo to the combination of active groups sulfonylvinyl[17] and 3(*2H*)-furanone core[18]. Furthermore, we achieved the transformation of reaction regioselectivity by replacing diynones with terminal alkyne ketones, and highly substituted sulfonylbenzene derivatives were obtained *via* the benzannulation reaction.



Scheme 1. The base-promoted domino reactions of *β*-keto sulfones with acetylene ketones.

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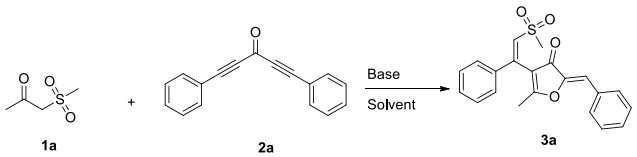
Results and Discussion

Initially, the Michael addition of 1-(methylsulfonyl)-propan-2-one **1a** with 1,5-diphenylpenta-1,4-diyn-3-one **2a** was investigated. When the reaction was treated with 30% mol Cs_2CO_3 in 1,4-Dioxane at 75 °C, an unexpected product **3a** was obtained in 65% yield (Table 1, entry 1). Then the reaction conditions were further optimized and results are summarized in Table 1. K_2CO_3 was found to be the most suitable base and the yield is up to 75% (Table 1, entries 2-5). The decrease of K_2CO_3 amount resulted in the serious loss of yield (Table 1, entry 6), and the increase of K_2CO_3 loading hadn't significant impact on the yield of **3a**, so we chose 30% mol K_2CO_3 according to the economic principle (Table 1, entries 7 and 8). Solvents were also investigated, 1,4-Dioxane proven to be the most suitable solvent, other solvents such as Toluene, DMSO, THF, DMF, EtOH and CH_3CN are incompatible with the reaction (Table 1, entries 9-14).

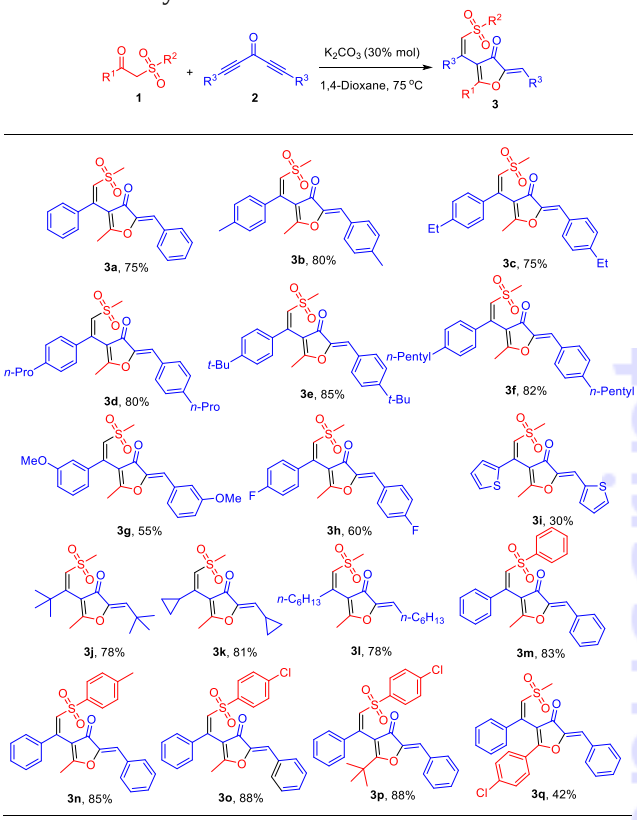
Table 1. Optimization of the domino reaction conditions. [a]



Entry	Base	Solvent	Yield (%)[b]
1	Cs_2CO_3	1,4-Dioxane	65
2	KOH	1,4-Dioxane	40
3	Et_3N	1,4-Dioxane	trace
4	*t*-BuOK	1,4-Dioxane	34
5	K_2CO_3	1,4-Dioxane	75
6[c]	K_2CO_3	1,4-Dioxane	30
7[d]	K_2CO_3	1,4-Dioxane	74
8[e]	K_2CO_3	1,4-Dioxane	76
9	K_2CO_3	Toluene	n.r.[f]
10	K_2CO_3	DMSO	n.r.
11	K_2CO_3	THF	55
12	K_2CO_3	DMF	trace
13	K_2CO_3	EtOH	n.r.
14	K_2CO_3	CH_3CN	20
15[g]	K_2CO_3	1,4-Dioxane	10
16[h]	K_2CO_3	1,4-Dioxane	20

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), base (0.06 mmol), solvent (2 mL), 75 °C, 1 h.
[b] Isolated yield.
[c] With 10% mol K_2CO_3.
[d] With 50% mol K_2CO_3.
[e] With 100% mol K_2CO_3.
[f] n.r. = No reaction.
[g] The reaction was carried out at 90 °C.
[h] The reaction was carried out at 50 °C.

Table 2. Substrate scope for the domino reaction of *β*-keto sulfones and diynones. [a, b]



[a] Reaction conditions: **1** (0.36 mmol), **2** (0.3 mmol), K_2CO_3 (0.09 mmol), 1,4-Dioxane (2 mL), 75 °C, 0.5 h.
[b] Isolated yield.

The increase or decrease of temperature is unfavorable for the reaction (Table 1, entries 15 and 16).

With the optimal reaction conditions in hand, the substrate scope was examined by using various *β*-keto sulfones and diynones, and results are summarized in Table 2. The aromatic diynones bearing an alkyl on the benzene ring reacted smoothly, and afforded the desired products in high yields (Table 2, **3b**-**3f**). The structure of **3c** was confirmed by X-ray crystal structure analysis (Fig. 1). The 3-$MeOC_6H_4$ substituent resulted in the light drop in the yield, **3g** was obtained in 55% yield. The 4-FC_6H_4 substituent gave **3h** in moderate yield 60%. The thienyl led to significant drop in the yield and **3i** was prepared in 30% yield. The alkyl diynones are tolerant and good yields were observed (Table 2, **3j**-**3l**). In the *β*-keto sulfone moiety, the substrates with a phenyl substituent in R^2 position generated the corresponding products in high yields (Table 2, **3m**-**3o**). The R^1 as other substituents was also tested, the *tert*-butyl provided **3p** in excellent yield, the 4-ClC_6H_4 resulted in the serious loss of yield and gave **3q** in 42% yield.

Interestingly, the treatment of 1-(methylsulfonyl)-propan-2-one **1a** with 1-phenylpenta-1,4-diyn-3-one

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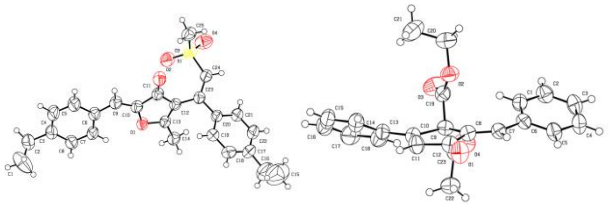
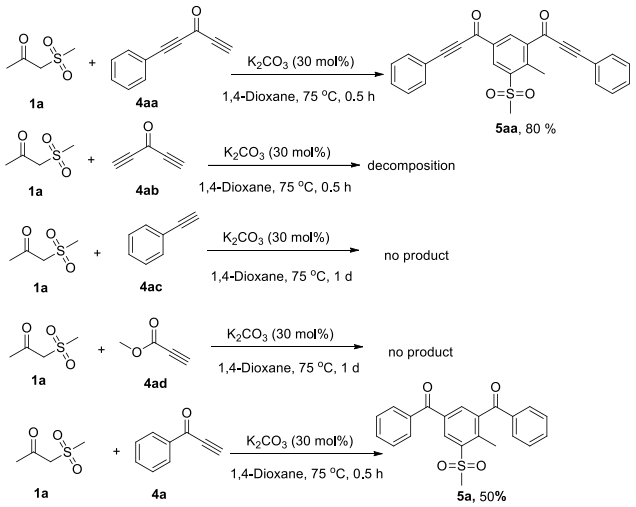


Fig 1. X-ray crystal structures of **3c** and **7ea**.

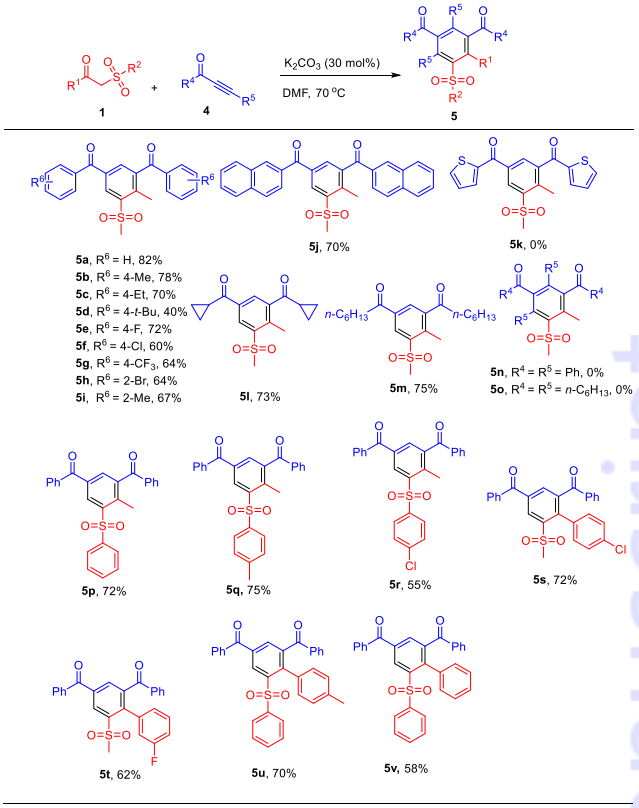
4aa in the same condition gave an unexpected product **5aa** in 80% yield (Scheme 2). Replaced **4aa** with **4ab**, **4ac** and **4ad**, no product was obtained, and **4ab** was easy to decompose under the standard condition. We speculated that only alkyne ketones were well compatible with the benzannulation. Then the 1-phenylprop-2-yn-1-one **4a** was employed, and the reaction proceeded smoothly. Therefore, the reaction of **1a** with **4a** was chosen as the model reaction to further optimize the conditions (see Supporting Information). Finally, the optimum conditions of benzannulation are 30% mol K_2CO_3 in DMF at 75 °C for 0.5 h.

The substrate scope of the benzannulation was examined and results are showed on the Table 3. Terminal alkyne ketones bearing various aromatic substituents were well tolerated. In detail, the electron-donating and electron-withdrawing groups on the benzene ring gave moderate yields (Table 3, **5a**-**5g**). The *ortho* substitutions on the benzene ring hadn't obvious effect on the reactivity and yield (Table 3, **5h** and **5i**). The naphthyl substituent generated **5j** in 70% yield. When 1-(thiophen-2-yl)prop-2-yn-1-one **4k** as substrate, no desired product **5k** was observed. Alkyl-substituted terminal alkyne ketones are suitable, **5l** and **5m** were obtained



Scheme 2. The benzannulation of **1a** with terminal alkynes.

Table 3. Substrate scope for the benzannulation. [a, b]



[a] Reaction conditions: **1** (0.25 mmol), **4** (0.6 mmol), K_2CO_3 (0.075 mmol), DMF (2 mL), 75 °C, 0.5 h.
[b] Isolated yield.

in 75% and 73%, respectively. Di-substituted alkyne ketones were also examined, but no products were obtained (**5n** and **5o**), we speculated the sterically hindered substrates were unfavorable in the benzannulation. In the *β*-keto sulfone moiety, phenyl substituents in R^1 and R^2 positions also led to the benzannulation successfully, products were obtained in moderate yields (Table 3, **5p**-**5v**).

The domino reactions of other carbonyl compounds with acetylene ketones were also studied (Scheme 3). In the reaction of *α*-nitroketones with **2a**, no product was detected (Scheme 3, eq. (1)). *β*-Keto sulfoxide is incompatible with **2a**, the reaction was complicated and no major product was obtained (Scheme 3, eq. (2)). The Michael additions of *β*-dicarbonyl compounds with diynones afforded cyclopentenones as products (Scheme 3, eq. (3)). The structure of **7ea** was confirmed by X-ray crystal structure analysis (Fig 1). In the reactions of *α*-nitroketone, *β*-keto sulfoxide and *β*-dicarbonyl compounds with **4a**, no product or no major products were observed (Scheme 3, eq. (4)-(6)). We found that, compared with other carbonyl compounds, the sulfone was helped to cleavage the carbon-carbon single bond and efficiently improved the reaction regioselectivity.

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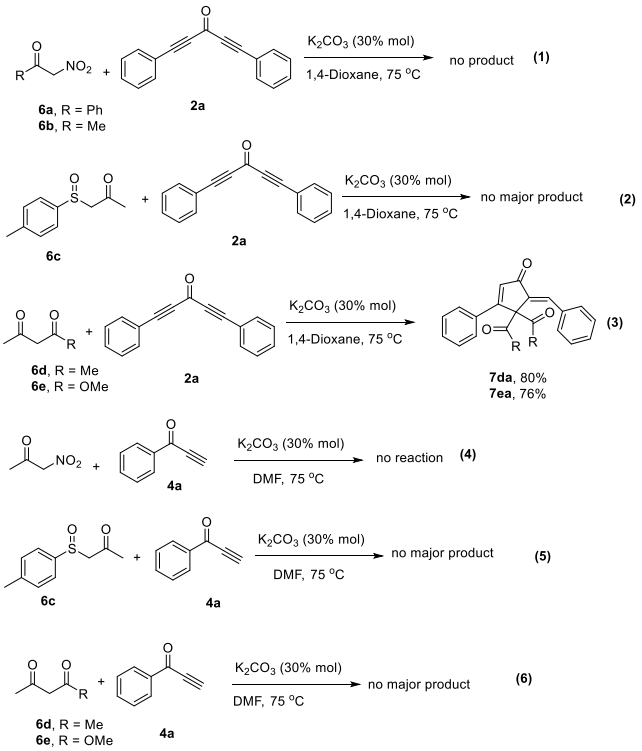
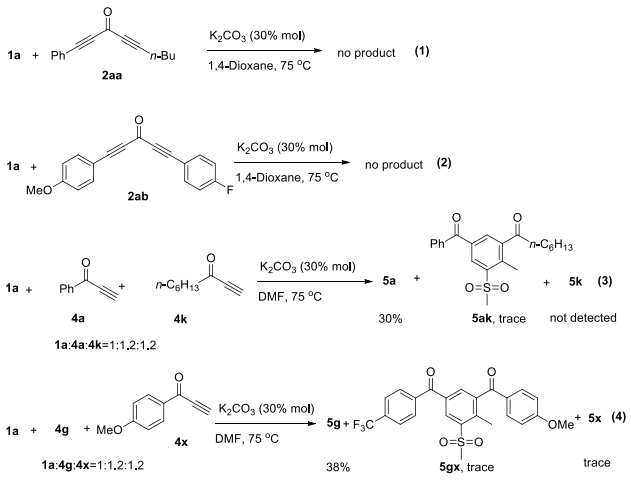


Scheme 3. The domino reactions of other carbonyl compounds with acetylene ketones.

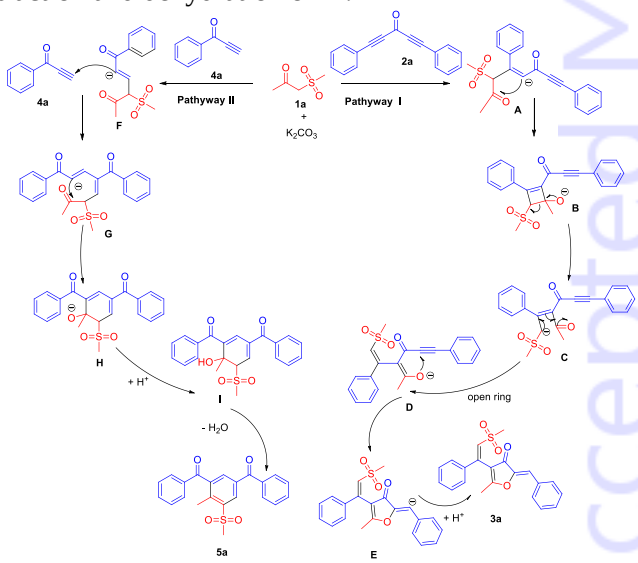
To studied the domino reaction of *β*-keto sulfones with acetylene ketones, some competitive experiments were carried out (Scheme 4). Firstly, the reaction of unsymmetrical diynones with **1a** was examined, no product was detected (Scheme 4, eqs. (1) and (2)). The stronger bases and the long reaction time were tried, but resulted in the diynones decomposition. Unsymmetrical diynones were unsuitable in this reaction. Secondly, the cross reaction of **1a**, **4a** and **4k** was investigated, **5a** was



Scheme 4. Competitive experiments

obtained in 30% yield and trace **5ak** was detected by LC/MS, no **5k** was observed (see Supporting Information). Compared with alkyl alkyne ketone, the *β*-keto sulfone tended to react with phenyl alkyne ketone. On the other way, the cross reaction of **1a**, **4g** and **4x** provided **5g** in 38% yield and trace **5gx** and **5x** (see Supporting Information). The trifluoromethyl is more favorable than the methoxyl in the benzannulation, because the electron-withdrawing substituent is more compatible with the Michael addition.

The proposed pathways for the domino reactions of *β*-keto sulfones and acetylene ketones are proposed in Scheme 5. For the **pathway I**: the base-induced Michael addition of **1a** and **2a** generated the intermediate **A**. Then the intermediate **A** occurred intramolecular cycloaddition and gave the intermediate **B**. Duo to the ring strain, the cyclobutene intermediate **B** was easy to open ring and generated the intermediate **D**.[13, 19] After the second addition, the 3(*2H*)-furanone **3a** was obtained. For the **pathway II** [20]: the base-induced Michael addition of **1a** and **4a** afforded the intermediate **F**. Then the intermediate **F** reacted with another molecule **4a** and gave the intermediate **G**. The intramolecular cyclization of **G** generated the intermediate **H**. Finally, the product **5a** was obtained *via* the H-abstraction and dehydration of **H**.



Scheme 5. Proposed pathways for domino reactions of *β*-keto sulfones with acetylene ketones.

Conclusion

In summary, we have established a domino reaction of *β*-keto sulfones with acetylene ketones promoted by 30% mol K_2CO_3 without any other additives. The domino reactions generated 3(*2H*)-furanone derivatives and sulfonylbenzenes in excellent yields. Furthermore, the 3(*2H*)-furanone compounds are

currently used for biological activity test to study the potential biological activities in our laboratory.

Experimental Section

General experimental procedure for the synthesis of 3(*2H*)-furanones 3.
A solution of **1** (0.36 mmol), **2** (0.3 mmol), K_2CO_3 (0.09 mmol) and 1,4-Dioxane (2 mL) in a 15 mL test tube was stirred at 75 °C for 30 min. Then the mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography to give **3**.

2-((*Z*)-benzylidene)-5-methyl-4-((*Z*)-2-(methylsulfonyl)-1-phenylvinyl)furan-3(*2H*)-one (3a): yellow solid (82.4 mg, 75%), mp: 182.2–183.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.43 (ddd, *J* = 7.1, 4.2, 1.6 Hz, 8H), 6.87 (s, 1H), 6.81 (s, 1H), 3.18 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 178.7, 145.3, 143.6, 137.4, 131.7, 130.8, 130.4, 129.2, 129.2, 129.0, 127.6, 115.6, 114.4, 42.8, 15.6. HRMS (m/z) (ESI): calcd for $C_{21}H_{19}O_4S$ 367.1004 $[M+H]^+$, found 367.0995.

5-methyl-2-((*Z*)-4-methylbenzylidene)-4-((*Z*)-2-(methylsulfonyl)-1-(p-tolyl)vinyl)-furan-3(*2H*)-one (3b): yellow solid (94.7 mg, 80%), mp: 153.4–155.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 9.5 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 6.78 (s, 1H), 3.17 (s, 3H), 2.39 (d, *J* = 9.0 Hz, 6H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 178.4, 145.0, 143.7, 141.4, 141.0, 134.4, 131.8, 129.8, 129.8, 129.0, 128.1, 127.5, 115.6, 114.6, 42.8, 21.4, 15.6. HRMS (m/z) (ESI): calcd for $C_{23}H_{23}O_4S$ 395.1317 $[M+H]^+$, found 395.1308.

2-((*Z*)-4-ethylbenzylidene)-4-((*Z*)-1-(4-ethylphenyl)-2-(methylsulfonyl)vinyl)-5-methylfuran-3(*2H*)-one (3c): : yellow oil (95.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 1H), 6.82 (s, 1H), 3.15 (s, 3H), 2.71–2.63 (m, 4H), 2.13 (s, 3H), 1.27–1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 178.3, 147.6, 147.2, 145.1, 143.6, 134.6, 131.9, 129.2, 128.7, 128.6, 128.2, 127.6, 115.5, 114.5, 42.8, 28.9, 28.6, 15.6, 15.3, 15.2. HRMS (m/z) (ESI): calcd for $C_{25}H_{27}O_4S$ 423.1630 $[M+H]^+$, found 423.1621.

5-methyl-4-((*Z*)-2-(methylsulfonyl)-1-(4-propylphenyl)vinyl)-2-((*Z*)-4-propylbenzylidene)furan-3(*2H*)-one (3d): yellow oil (87.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 1H), 6.80 (s, 1H), 3.16 (s, 3H), 2.62 (d, *J* = 9.5 Hz, 4H), 2.14 (s, 3H), 1.66 (dd, *J* = 12.3, 7.4 Hz, 4H), 0.94 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 178.4, 146.1, 145.8, 145.1, 143.8, 134.6, 133.3, 131.8, 129.6, 129.4, 129.3, 129.2, 128.1, 127.5, 115.5, 114.6, 42.9, 38.1, 37.8, 24.3, 24.3, 15.6, 13.8, 13.8. HRMS (m/z) (ESI): calcd for $C_{27}H_{31}O_4S$ 451.1943 $[M+H]^+$, found 451.1932.

2-((*Z*)-4-(tert-butyl)benzylidene)-4-((*Z*)-1-(4-(tert-butyl)phenyl)-2-(methylsulfonyl)vinyl)-5-methylfuran-3(*2H*)-one (3e): yellow oil (122.1 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 10.0 Hz, 4H), 6.86 (s, 1H), 6.82 (s, 1H), 3.15 (s, 3H), 2.16 (s, 3H), 1.33 (d, *J* = 11.9 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 178.4, 154.5, 154.0, 145.1, 143.6, 134.1, 131.6, 129.4, 128.9, 128.2, 127.2, 126.2, 126.0, 125.9, 115.3, 114.4, 42.8, 35.0, 34.8, 31.1, 31.1, 15.6. HRMS (m/z) (ESI): calcd for $C_{29}H_{35}O_4S$ 479.2256 $[M+H]^+$, found 479.2253.

5-methyl-4-((*Z*)-2-(methylsulfonyl)-1-(4-pentylphenyl)vinyl)-2-((*Z*)-4-pentylbenzylidene)furan-3(*2H*)-one (3f): yellow oil (89.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 6.80 (s, 1H), 3.16 (s, 3H), 2.67–2.61 (m, 4H), 2.14 (s, 3H), 1.66–1.60 (m, 4H), 1.36–1.30 (m, 8H), 0.91–0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 178.3, 150.5, 146.7, 146.3, 146.0, 145.0, 143.7, 134.5, 133.2, 131.7, 129.6, 129.2, 129.1, 129.1, 128.1, 127.4, 115.5, 114.5, 42.8, 40.1, 35.9, 35.6, 31.4, 31.4, 30.8, 30.8, 22.5, 22.4, 15.6, 13.9. HRMS (m/z) (ESI): calcd for $C_{21}H_{17}O_4S$ 507.2569$[M+H]^+$, found 507.2564.

2-((*Z*)-3-methoxybenzylidene)-4-((*Z*)-1-(3-methoxyphenyl)-2-(methylsulfonyl)vinyl)-5-methylfuran-3(*2H*)-one (3g): brown oil (70.4 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.18 (m, 5H), 6.94 – 6.84 (m, 5H), 6.73 (s, 2H), 3.76–3.74 (m, 3H), 3.72 (d, *J* = 4.3 Hz, 3H), 3.09 (s, 3H), 2.05 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 178.7, 160.0, 159.7, 145.3, 143.4, 138.7, 132.8, 130.2, 129.9, 129.2, 124.4, 110.0, 116.6, 116.2, 116.2, 115.5, 114.3, 113.0, 55.4, 55.3, 42.7, 15.6. HRMS (m/z) (ESI): calcd for $C_{23}H_{23}O_6S$ 427.1215 $[M+H]^+$, found 427.1209.

2-((*Z*)-4-fluorobenzylidene)-4-((*Z*)-1-(4-fluorophenyl)-2-(methylsulfonyl)vinyl)-5-methylfuran-3(*2H*)-one (3h): yellow solid (72.4mg, 60%), mp: 179.2–180.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.46–7.40 (m, 2H), 7.16–7.06 (m, 4H), 6.82 (s, 1H), 6.77 (s, 1H), 3.16 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 178.6, 164.3 (d, *J*=251.1), 163.7 (d, *J* = 251.9), 144.8 (d, *J* = 2.8 Hz), 142.3 , 133.8 (d, *J* = 8.6 Hz), 133.3 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 8.6 Hz), 129.0 (d, *J* = 1.3 Hz), 127.9 (d, *J* = 3.4 Hz), 116.4 (d, *J* = 7.9 Hz), 116.2 (d, *J* = 7.8 Hz)., 115.4, 113.3, 42.7, 15.6. HRMS (m/z) (ESI): calcd for $C_{21}H_{17}F_2O_4S$ 403.0816 $[M+H]^+$, found 403.0809.

(*Z*)-5-methyl-4-((*E*)-2-(methylsulfonyl)-1-(thiophen-2-yl)vinyl)-2-(thiophen-2-ylmethylene)furan-3(*2H*)-one (3i): brown solid (34.1 mg, 30%), mp: 111.5–113.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 5.1 Hz, 1H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.46 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.24 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.16–7.12 (m, 2H), 7.07 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.87 (d, *J* = 5.2 Hz, 1H), 3.12 (s, 3H), 2.31 (s,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.4, 177.9, 143.6, 140.9, 136.9, 134.8, 134.0, 132.6, 130.1, 129.5, 128.6, 128.1, 125.8, 115.2, 108.3,43.2, 15.6. HRMS (m/z) (ESI): calcd for $C_{17}H_{15}O_4S_3$ 379.0132 $[M+H]^+$, found 379.0135.

(*Z*)-4-((*Z*)-3,3-dimethyl-1-(methylsulfonyl)but-1-en-2-yl)-2-(2,2-dimethylpropylidene)-5-methylfuran-3(*2H*)-one (3j): white solid (76.4 mg, 78%), mp: 117.3–118.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 1.0 Hz, 1H), 5.91 (d, *J* = 1.6 Hz, 1H), 2.80 (d, *J* = 1.4 Hz, 3H), 2.18 (d, *J* = 1.4 Hz, 3H), 1.21 (d, *J* = 1.4 Hz, 9H), 1.08 (d, *J* = 1.4 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.1, 177.7, 156.5, 145.0, 129.7, 126.5, 112.9, 43.3, 39.6, 32.9, 29.7, 28.3, 16.0. HRMS (m/z) (ESI): calcd for $C_{17}H_{27}O_4S$ 327.1630 $[M+H]^+$, found 327.1637.

(*Z*)-4-((*Z*)-1-cyclopropyl-2-(methylsulfonyl)vinyl)-2-(cyclopropylmethylene)-5-methylfuran-3(*2H*)-one (3k): white solid (71.5 mg, 81%), mp: 153.7–154.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (d, *J* = 11.8 Hz, 1H), 6.09 (s, 1H), 2.98 (s, 3H), 2.20 (s, 3H), 1.93–1.78 (m, 2H), 1.40–1.31 (m, 2H), 1.21–1.04 (m, 3H), 0.89–0.81 (m, 2H), 0.78–0.68 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 199.2, 191.8, 172.0, 148.9, 128.6, 128.5, 86.8, 39.9, 26.9, 16.2, 14.5, 13.0, 12.1, 10.3, 10.3. HRMS (m/z) (ESI): calcd for $C_{15}H_{19}O_4S$ 295.1004 $[M+H]^+$, found 295.0997.

(*Z*)-2-heptylidene-5-methyl-4-((*Z*)-1-(methylsulfonyl) oct-1-en-2-yl)furan-3(*2H*)-one (3l): white oil (89.5 mg, 78%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (s, 1H), 6.13 (s, 1H), 2.88 (s, 3H), 2.51 (d, *J* = 7.6 Hz, 2H), 2.23 (s, 3H), 1.63 (d, *J* = 7.6 Hz, 2H), 1.46 (d, *J* = 7.6 Hz, 2H), 1.30 (ddd, *J* = 13.0, 8.1, 4.0 Hz, 14H), 0.88 (d, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 177.2, 169.5, 162.6, 152.3, 128.9, 122.7, 112.2, 42.8, 38.4, 33.4, 31.5, 31.4, 28.8, 28.6, 26.6, 26.5, 22.5, 22.4, 18.8, 14.0, 14.0. HRMS (m/z) (ESI): calcd for $C_{21}H_{34}O_4S$ 383.2251 $[M+H]^+$, found 383.2242.

(*Z*)-2-benzylidene-5-methyl-4-((*Z*)-1-phenyl-2-(phenylsulfonyl)vinyl)furan-3(*2H*)-one (3m): yellow solid (106.7 mg, 83%), mp: 158.5–160.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 7.1 Hz, 2H), 7.58 (s, 1H), 7.52–7.43 (m, 6H), 7.37 (d, *J* = 4.8 Hz, 4H), 6.98 (s, 1H), 6.73 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3, 178.2, 145.2, 142.4, 140.8, 136.6, 133.5, 131.7, 130.8, 130.7, 130.3, 129.2, 129.1, 129.0, 127.9, 127.2, 114.7, 113.6, 15.6. HRMS (m/z) (ESI): calcd for $C_{26}H_{21}O_4S$ 429.1161 $[M+H]^+$, found 429.1153.

(*Z*)-2-benzylidene-5-methyl-4-((*Z*)-1-phenyl-2 tosylvinyl) furan-3(*2H*)-one (3n)*:* yellow solid (112.8 mg, 85%), mp: 160.1–161.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 13.8, 7.5 Hz, 4H), 7.46 (d, *J* = 7.6 Hz, 3H), 7.37 (dt, *J* = 8.6, 3.7 Hz, 5H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.96 (s, 1H), 6.73 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.32, 178.03, 145.26, 144.50, 141.70, 136.67, 131.88, 131.62, 131.08, 130.67, 130.26, 129.87, 129.07, 129.02, 128.97, 127.91, 127.19, 113.39, 21.65, 15.52. HRMS (m/z) (ESI): calcd for $C_{27}H_{23}O_4S$ 443.1317 $[M+H]^+$, found 443.1312.

(*Z*)-2-benzylidene-4-((*Z*)-2-((4-chlorophenyl)sulfonyl)-1-phenylvinyl)-5-methylfuran-3(*2H*)-one (3o): yellow oil (122.2 mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.86 (m, 2H), 7.84 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 5H), 7.40–7.34 (m, 5H), 6.93 (s, 1H), 6.76 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 184.2, 178.1, 145.2, 142.8, 140.2, 139.2, 136.5, 131.8, 131.7, 130.9, 130.4, 130.1, 129.5, 129.4, 129.1, 129.0, 1273, 114.79, 113.8, 15.5. HRMS (m/z) (ESI): calcd for $C_{26}H_{20}ClO_4S$ 463.0771 $[M+H]^+$; found 463.0769.

(*Z*)-2-benzylidene-5-(tert-butyl)-4-((*Z*)-1-phenyl-2-tosylvinyl)furan-3(*2H*)-one (3p): brown solid (128.4 mg, 88%), mp: 170.2–171.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.47–7.38 (m, 8H), 7.34 (s, 2H), 6.89 (d, *J* = 0.8 Hz, 1H), 6.82 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.23, 184.29, 144.43, 143.55, 140.20, 139.23, 137.65, 132.12, 131.58, 130.72, 130.22, 129.54, 129.49, 129.09, 129.06, 129.00, 127.08, 113.51, 112.61, 36.21, 27.81. HRMS (*m/z*) (ESI): calcd for $C_{29}H_{26}ClO_4S$ 505.1240 $[M+H]^+$, found 505.1245.

(*Z*)-2-benzylidene-5-(4-chlorophenyl)-4-((*Z*)-2-(methylsulfonyl)-1-phenylvinyl)furan-3(*2H*)-one (3q): yellow oil (58.3 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.74–7.71 (m, 2H), 7.51–7.44 (m, 6H), 7.37–7.33 (m, 4H), 7.01 (s, 1H), 6.99 (s, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 171.1, 145.1, 144.1, 139.1, 136.1, 131.9, 131.1, 130.7, 129.7, 129.6, 129.3, 129.2, 127.4, 126.2, 115.4, 114.3, 42.9. HRMS (*m/z*) (ESI): calcd for $C_{26}H_{20}ClO_4S$ 463.0771 $[M+H]^+$, found 463.0779.

1,1'-(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis(3-phenylprop-2-yn-1-one) (5aa): yellow solid (85.3 mg, 80%), mp: 174.5–176.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.15 (s, 1H), 7.65 (t, *J* = 7.2 Hz, 4H), 7.50–7.46 (m, 2H), 7.39–7.33 (m, 4H), 3.22 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 174.8, 144.9, 142.0, 139.6, 136.5, 135.0, 133.6, 133.4 133.3, 131.4, 131.4, 128.8, 119.2, 95.8, 94.9, 88.2, 86.1, 43.8, 17.7. HRMS (m/z) (ESI): caled for $C_{22}H_{19}O_4S$ 427.1004 $[M+H]^+$, found 427.0991.

General Experimental Procedure for Synthesis of sulfonylbenzenes 5.

The mixture of *β*-keto sulfone **1** (0.25 mmol), alkyne ketone **4** (0.6 mmol), K_2CO_3 (0.075 mmol) and DMF (2 mL) was stirred at 70 ºC for 30 min. Then the solution was diluted with water and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to give the product **5**.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene) bis(phenylmethanone) (5a): white solid (77.6 mg, 82%), mp: 172.1–174.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.95 (s, 1H), 7.79 (t, *J* = 8.2 Hz, 4H), 7.63 (dd, *J* = 14.1, 7.2 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 4H), 3.18 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 193.8,

142.7, 140.6, 139.8, 136.1, 136.0, 135.8, 134.5, 133.3, 133.0, 131.8, 130.1, 129.9, 129.0, 128.7, 43.8, 17.4. HRMS (m/z) (ESI): caled for $C_{26}H_{19}O_4S$ 379.1004 $[M+H]^+$, found 379.0997.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis(p-tolylmethanone) (5b): yellow oil (79.3 mg, 78%). ^1H NMR (400 MHz, CDCl3) δ 8.58 (s, 1H), 7.91 (s, 1H), 7.69 (d, *J* = 6.9 Hz, 4H), 7.29 (d, *J* = 7.9 Hz, 4H), 3.17 (s, 3H), 2.70 (s, 3H), 2.43 (d, *J* = 2.7 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 195.9, 193.6, 145.8, 144.3, 142.9, 140.3, 139.9, 136.1, 133.5, 133.5, 132.8, 131.6, 130.3, 130.1, 129.7, 129.4, 43.7, 21.8, 21.7, 17.3. HRMS(m/z) (ESI): caled for $C_{24}H_{23}O_4S$ 407.1317 $[M+H]^+$, found 407.1310.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis((4-ethylphenyl)methanone) (5c): yellow oil (76 mg, 70 %). ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.7 Hz, 1H), 7.93 (d, *J* = 1.7 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 3.18 (s, 3H), 2.72 (s, 3H), 1.29 (d, *J* = 1.9 Hz, 2H), 1.27 (d, *J* = 2.0 Hz, 2H), 1.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 193.6, 151.9, 150.5, 143.0, 140.5, 139.4, 136.2, 133.8, 133.8, 132.9, 131.6, 130.5, 130.3, 128.8, 128.3, 43.8, 29.7, 29.1, 17.4, 15.1, 15.1. HRMS (m/z) (ESI): caled for $C_{26}H_{27}O_4S$ 435.1630 $[M+H]^+$, found 435.1622.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis((4-(tert-butyl)phenyl)methanone) (5d): yellow oil (78.5 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.7 Hz, 1H), 7.94 (d, *J* = 1.7 Hz, 1H), 7.74 (dd, *J* = 8.4, 1.4 Hz, 4H), 7.51 (d, *J* = 8.3 Hz, 4H), 3.19 (s, 3H), 2.73 (s, 3H), 1.35 (d, *J* = 1.7 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 193.5, 158.6, 157.3, 142.9, 140.4, 139.5, 136.1, 1335, 133.5, 133.0, 131.6, 130.2, 130.0, 126.0, 125.7, 43.8, 35.3, 35.2, 31.0, 31.0, 17.3. HRMS (m/z) (ESI): caled for $C_{30}H_{35}O_4S$ 491.2256 $[M+H]^+$, found 491.1906.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis((4-fluorophenyl)methanone) (5e): yellow solid (74.6 mg, 72%), mp: 165.0–168.1°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 7.85–7.79 (m, 4H), 7.20–7.15 (m, 4H), 3.18 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 192.2, 166.5 (d, *J* = 256.7), 165.8 (d, *J* = 254.6), 142.5, 140.7, 139.8, 135.7, 132.9 (d, *J* = 9.7 Hz), 132.7, 132.6 (d, *J* = 9.4 Hz),132.4 (d, *J* = 2.9 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7, 116.4 (d, *J* = 22.1 Hz), 116.0 (d, *J* = 22.1 Hz), 43.7, 17.4. HRMS (m/z) (ESI): caled for $C_{22}H_{17}F_2O_4S$ 415.0816 $[M+H]^+$, found 415.0809.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis((4-chlorophenyl)methanone) (5f) : yellow solid (67.1 mg, 60%), mp: 130.9–132.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.8 Hz, 1H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.77 – 7.71 (m, 4H), 7.50 (ddd, *J* = 6.8, 3.9, 1.8 Hz, 4H), 3.19 (s, 3H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 192.5, 142.4, 141.4, 140.9, 140.1, 140.1, 135.6, 134.4, 134.3, 132.8, 131.9, 131.5, 131.3, 129.5, 129.2, 43.8, 17.5. HRMS (m/z) (ESI): caled for $C_{22}H_{17}Cl_2O_4S$ 447.0225 $[M+H]^+$, found 447.0218.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis((4-(trifluoromethyl)phenyl)methanone) (5g): yellow oil (82.3 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.2 Hz, 1H), 7.97 (d, *J* = 1.2 Hz, 1H), 7.91 (dd, *J* = 15.2, 8.2 Hz, 4H), 7.79 (d, *J* = 8.2 Hz, 4H), 3.20 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 195.0, 192.5, 142.3, 141.2, 140.9, 139.0, 138.6, 135.8 (q, *J* = 32.7 Hz), 135.1, 134.8 (q, *J* = 33.7 Hz), 133.0, 132.3, 130.4, 130.1, 126.2 (q, *J* = 3.7 Hz), 125.9 (q, *J* = 3.7 Hz), 123.4 (q, *J* =271.1 Hz), 123.3 (q, *J* =271.3 Hz), 43.8, 17.6. HRMS (m/z) (ESI): caled for $C_{24}H_{17}F_6O_4S$ 515.0752 $[M+H]^+$, found 515.0743.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis((2-bromophenyl)methanone) (5h): yellow oil (53.6 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 7.67–7.61 (m, 2H), 7.56–7.52 (m, 1H), 7.47–7.41 (m, 3H), 7.41–7.38 (m, 1H), 7.35 (dd, *J* = 7.4, 1.9 Hz, 1H), 3.17 (s, 3H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 193.3, 143.5, 142.1, 141.5, 139.0, 138.8, 134.4, 134.4, 134.3, 133.5, 133.4, 133.3, 132.2, 131.4, 129.5, 127.8, 127.7, 120.9, 119.6, 43.8, 17.7. HRMS (m/z) (ESI): caled for $C_{22}H_{17}Br_2O_4S$ 536.9194 $[M+H]^+$, found 536.9114.

(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis(o-tolylmethanone) (5i): yellow oil (68.1 mg, 67%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.91 (s, 1H), 7.62 (d, *J* = 15.1 Hz, 2H), 7.54 (t, *J* = 6.5 Hz, 2H), 7.46–7.36 (m, 4H), 3.18 (s, 3H), 2.72 (s, 3H), 2.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.50, 194.13, 142.81, 140.57, 139.73, 139.08, 138.77, 136.25, 136.1, 136.0, 135.4, 134.2, 133.0, 131.8, 130.4, 128.9, 128.5, 127.7, 127.3, 43.8, 21.4, 21.4, 17.4. HRMS (m/z) (ESI): caled for $C_{24}H_{23}O_4S$ 407.1317 $[M+H]^+$, found 407.1310.

(4-methyl-5-(methylsulfonyl)-1,3- phenylene)bis (naphthalen-2-ylmethanone) (5j) : yellow solid (83.7 mg, 70%), mp: 183.3–186.1°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.26 (s, 1H), 8.17 (s, 1H), 8.07–8.00 (m, 2H), 7.98–7.86 (m, 7H), 7.67–7.52 (m, 4H), 3.22 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 193.9, 142.8, 140.8, 139.9, 136.1, 135.5, 133.4, 133.4, 133.3, 133.1, 132.3, 132.2, 132.1, 131.9, 129.8, 129.5, 129.5, 129.2, 128.9, 128.8, 127.9, 127.8, 127.3, 127.1, 125.2, 124.3, 43.8, 17.4. HRMS (m/z) (ESI): caled for $C_{30}H_{23}O_4S$ 479.1317 $[M+H]^+$, found 479.1303.

1,1'-(4-methyl-5-(methylsulfonyl)-1,3-phenylene)bis(heptan-1-one) (5l): yellow oil (74.0 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.7 Hz, 1H), 8.21 (d, *J* = 1.7 Hz, 1H), 3.15 (s, 3H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.77 (s, 3H), 1.76–1.67 (m, 4H), 1.39–1.29 (m, 12H), 0.89 (dd, *J* = 7.0, 5.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 197.94, 143.8, 141.0, 140.4, 135.1, 130.4, 130.2, 43.7, 43.2, 38.6, 31.6, 31.5, 28.8, 28.8, 23.9, 23.8, 22.5, 22.4, 17.2, 14.0, 14.0. HRMS (m/z) (ESI): caled for $C_{22}H_{35}O_4S$ 395.2256 $[M+H]^+$, found 395.2248.

(4-methyl-5-(methylsulfonyl)-1, 3-phenylene) bis(cyclopropylmethanone) (5m): white solid (55.9 mg, 73%), mp: 180.1–182.3 °C. ^1H NMR (400 MHz, $CDCl_3$) δ

8.81 (d, *J* = 1.8 Hz, 1H), 8.36 (d, *J* = 1.8 Hz, 1H), 3.17 (s, 3H), 2.83 (s, 3H), 2.71 (s, 1H), 2.35 (s, 1H), 1.39–1.34 (m, 2H), 1.33–1.28 (m, 2H), 1.17 (ddd, *J* = 13.4, 7.5, 3.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 198.3, 144.5, 140.8, 139.9 136.1, 131.0, 130.3, 43.8, 22.1, 17.4, 17.3, 13.4, 12.7. HRMS (m/z) (ESI): caled for $C_{26}H_{19}O_4S$ 307.0999 $[M+H]^+$, found 307.0988.

(4-methyl-5-(phenylsulfonyl)-1,3-phenylene) bis(phenylmethanone) (5p): yellow oil (79.3 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.92–7.88 (m, 3H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.65–7.61 (m, 3H), 7.50 (dd, *J* = 13.1, 5.6 Hz, 6H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 193.9, 142.6, 141.0, 140.2, 140.1, 136.3, 136.1, 135.6, 134.4, 133.7, 133.3, 133.0, 131.8, 130.1, 129.9, 129.3, 128.9, 128.8, 128.7, 128.6, 127.9, 127.9, 17.3. HRMS (m/z) (ESI): caled for $C_{27}H_{21}O_4S$ 441.1161 $[M+H]^+$, found 441.1155.

(4-methyl-5-tosyl-1,3-phenylene)bis(phenylmethanone) (5q): yellow oil (85.2 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 7.81–7.73 (m, 6H), 7.66–7.60 (m, 2H), 7.48 (dd, *J* = 16.5, 8.6 Hz, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.44 (d, *J* = 2.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 194.0, 144.9, 142.5, 141.3, 140.1, 137.1, 136.3, 136.1, 135.4, 134.4, 133.3, 132.8, 131.7, 130.1, 130.0, 130.0, 128.9, 128.7, 128.0, 21.6, 17.3. **HRMS** (m/z) (ESI): caled for $C_{28}H_{23}O_4S$ 455.1317 $[M+H]^+$, found 455.1311.

(5-((4-chlorophenyl)sulfonyl)-4-methyl-1,3-phenylene)bis(phenylmethanone) (5r): yellow oil (65.3 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.8 Hz, 1H), 8.42 (s, 1H), 7.95 (d, *J* = 1.8 Hz, 1H), 7.87 – 7.85 (m, 3H), 7.83 (dd, *J* = 4.4, 3.8 Hz, 2H), 7.77 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.65 (dd, *J* = 6.9, 1.4 Hz, 2H), 7.54 (s, 4H), 2.47 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 196.0, 194.0, 143.6, 141.3, 139.9, 137.1, 136.5, 136.2, 133.6, 133.5, 133.0, 132.6, 130.9, 130.1, 129.5, 128.9, 128.6, 128.3, 127.8, 127.0, 29.7. HRMS (m/z) (ESI): caled for $C_{27}H_{20}ClO_4S$ 475.0771 $[M+H]^+$, found 475.0760.

(4'-chloro-6-(methylsulfonyl)-[1,1'-biphenyl]- 2,4 diyl) bis(phenylmethanone) (5s): yellow oil (85.5 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 1.7 Hz, 1H), 7.67–7.62 (m, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.35–7.29 (m, 5H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.06–7.00 (m, 4H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 195.5, 193.6, 143.4, 141.1, 140.9, 137.6, 136.2, 135.9, 135.4, 134.0, 133.5, 132.7, 132.2, 131.9, 130.9, 130.0, 129.6, 128.8, 128.5, 127.9, 43.6. HRMS (m/z) (ESI): caled for $C_{27}H_{20}ClO_4S$ 475.0771 $[M+H]^+$, found 475.0764.

(3'-fluoro-6-(methylsulfonyl)-[1,1'-biphenyl]-2,4-diyl)bis(phenylmethanone) (5t): yellow solid (71.1 mg, 62%), mp: 198.5-199.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 1.7 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H), 7.88–7.84 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57–7.49 (m, 5H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.21 (td, *J* = 7.9, 5.9 Hz, 1H), 7.10 –7.02 (m, 2H), 6.97 (td, *J* = 8.5, 1.9 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 193.6, 161.6 (d, *J* = 248.8 Hz), 143.3, 140.9, 140.8 (d, *J* = 1.9 Hz), 137.8, 136.3, 136.0, 135.6 (d, *J* = 8.0 Hz), 133.9, 133.5, 132.8, 131.0, 130.0, 129.7, 129.3 (d, *J* = 8.3 Hz), 128.8, 128.5, 126.7 (d, *J* = 3.2 Hz), 118.4 (d, *J* = 22.9 Hz), 116.2 (d, *J* = 20.9 Hz), 43.7. HRMS (m/z) (ESI): caled for $C_{27}H_{20}FO_4S$ 459.1066 $[M+H]^+$, found 459.1059.

(6-tosyl-[1,1'-biphenyl]-2,4-diyl)bis(phenylmethanone) (5u): yellow oil (90.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 1.8 Hz, 1H), 8.06 (d, *J* = 1.8 Hz, 1H), 7.91–7.88 (m, 2H), 7.65 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.44 (dd, *J* = 5.8, 4.5 Hz, 3H), 7.26 (dd, *J* = 9.8, 5.5 Hz, 2H), 7.08 (dd, *J* = 14.0, 7.9 Hz, 3H), 6.96 (dd, *J* = 14.7, 6.5 Hz, 4H), 6.83–6.78 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 194.0, 144.1, 143.6, 143.0, 141.7, 137.0, 137.0, 136.5, 136.3, 133.6, 133.4, 133.2, 132.4, 131.0, 130.9, 130.1, 129.5, 129.2, 128.8, 128.3, 128.3, 127.9, 127.0, 21.6. HRMS (m/z) (ESI): caled for $C_{33}H_{25}O_4S$ 517.1474 $[M+H]^+$, found 517.1465.

(6-(phenylsulfonyl)-[1,1'-biphenyl]-2,4-diyl)bis(phenylmethanone) (5v): yellow oil (94.2 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 1.8 Hz, 1H), 8.16 (t, *J* = 3.7 Hz, 1H), 8.02–7.97 (m, 2H), 7.78–7.73 (m, 1H), 7.68–7.63 (m, 2H), 7.57–7.44 (m, 5H), 7.38 –7.30 (m, 3H), 7.28–7.26 (m, 2H), 7.20–7.15 (m, 1H), 7.01 (dd, *J* = 10.7, 4.9 Hz, 2H), 6.90–6.82 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ 196.1, 194.0, 143.6, 143.0, 141.3, 139.9, 137.1, 136.5, 136.2, 133.6, 133.5, 133.1, 133.0, 132.6, 131.1, 130.9, 130.1, 129.5, 128.9, 128.6, 128.3, 128.3, 127.8, 127.0. HRMS (m/z) (ESI): caled for $C_{33}H_{23}O_4S$ 503.1317 $[M+H]^+$, found 503.1307.

(*E*)-1,1'-(5-benzylidene-4-oxo-2-phenylcyclopent-2-ene-1,1-diyl)diethanone (7da): yellow oil (79.3 mg, 82%). ^{1}H NMR (400 MHz, CDCl3): δ 7.81 (s, 1H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.55 (d, *J* = 3.2 Hz, 2H), 7.48–7.43 (m, 6H), 7.20 (s, 1H), 1.99 (s, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 199.5, 195.2, 166.9, 138.0, 132.7, 132.2, 132.0, 132.0, 131.8, 131.4, 131.1, 129.4, 129.0, 128.5, 76.36, 27.19. HRMS (m/z) (ESI): calcd for $C_{22}H_{19}O_3$ 331.1334 $[M+H]^+$, found 331.1326.

(*E*)-ethyl 1-acetyl-5-benzylidene-4-oxo-2-phenyl cyclopent-2-enecarboxylate (7ea): yellow oil (81.09 mg, 75%). ^{1}H NMR (400 MHz, CDCl3): δ 7.71 (s, 1H), 7.65 (ddd, *J* = 10.0, 5.9, 2.3 Hz, 4H), 7.43–7.39 (m, 6H), 7.09 (s, 1H), 4.02 (dd, *J* = 7.1, 0.8 Hz, 2H), 1.94 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl3): δ 199.62, 194.82, 166.75, 166.47, 136.77, 132.93, 132.32, 131.96, 131.58, 131.55, 130.90, 129.01, 128.68, 128.43, 77.44, 77.12, 76.81, 71.40, 62.09, 26.32, 13.53. HRMS (m/z) (ESI): calcd for $C_{23}H_{21}O_4$ 361.1440 $[M+H]^+$, found 361.1432.

"CCDC for compound **3c**: 1525701 and for compound **7ea**: 1548541 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif."

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References

[1] a) M. Petrini, *Chem. Rev.* **2005**, *105*, 3949; b) T. G. Back, K. N. Clary, D. Gao, *Chem. Rev.* **2010**, *110*, 4498; c) J.-E. Bäckvall, R. Chinchilla, C. Nájera, M. Yus, *Chem. Rev.* **1998**, *98*, 2291; d) A. N. R. Alba, X. Companyó, R. Rios, *Chem. Soc. Rev.* **2010**, *39*, 2018.

[2] a) S. F. Barbuceanu, G. L. Almajan, I. Saramet, C. Draghici, A. I. Tarcomnicu, G. Bancescu, *Eur. J. Med. Chem.* **2009**, *44*, 4752; b) M. Artico, R. Silvestri, E. Pagnozzi, B. Bruno, E. Novellino, G. Greco, S. Massa, A. Ettorre, A. Giulia Loi, F. Scintu, P. La Colla, *J. Med. Chem.* **2000**, *43*, 1886; c) V. Padmavathi, P. Thriveni, G. S. Reddy, D. Deepti, *Eur. J. Med. Chem.* **2008**, *43*, 917; d) Z.-H. Wen, C.-H. Chao, M.-H. Wu, J.-H. Sheu, *Eur. J. Med. Chem.* **2010**, *45*, 5998; e) C. R. Lee, J. A. Balfour, *Drug.* **1994**, *48*, 907; f) L. A. Taylor, J. W. Clader, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2209.

[3] Y. M. Markitanov, V. M. Timoshenko, Y. G. Shermolovich, *J. Sulfur. Chem.* **2014**, *35*, 188.

[4] a) M. Julia, J. M. Paris, *Tetrahedron Lett.* **1973**, *14*, 4833; b) T. Mandai, T. Yanagi, K. Araki, Y. Morisaki, M. Kawada, J. Otera, *J. Am. Chem. Soc.* **1984**, *106*, 3670; c) G. Pandey, J. Vaitla, *Org. Lett.* **2015**, *17*, 4890.

[5] M. Nielsen, C. B. Jacobsen, M. W. Paixao, N. Holub, K. A. Jørgensen, *J. Am. Chem. Soc.* **2009**, *131*, 10581.

[6] A. Kumar, S. Sharma, V. D. Tripathi, S. Srivastava, *Tetrahedron.* **2010**, *66*, 9445.

[7] C. Curti, M. D. Crozet, P. Vanelle, *Tetrahedron*, **2009**, *65*, 200.

[8] M. T. Saraiva, G. P. Costa, N. Seus, R. F. Schumacher, G. Perin, M. W. Paixão, R. Luque, D. Alves, *Org. let.* **2015**, *17*, 6206.

[9] M. Y. Chang, Y. C. Cheng, Y. J. Lu, *Org. Lett.* **2014**, *16*, 6252.

[10] J. L. Marco, *J. Org. Chem.* **1997**, *62*, 6575.

[11] a) S. Kiren, A. Padwa, *J. Org. Chem*. **2009**, *74*, 7781; b) J. Alemán, V. Marcos, L. Marzo, J. L. García Ruano, *Eur. J. Org. Chem.* **2010**, 4482; c) O. Garcia Mancheno, P. Tangen, R. Rohlmann, R. Froehlich, J. Aleman, *Chem. Eur. J.* **2011**, *17*, 984; d) J. Deng, F. Wang, W. Yan, J. Zhu, H. Jiang, W. Wang, J. Li, *Chem Commun*. **2012**, *48*,148; e) Q. G. Wang, Q. Q. Zhou, J. G. Deng, Y. C. Chen, *Org. Lett.* **2013**, *15*, 4786.

[12] N.T. Patil, I. Kadota, A Shibuya, Y. S. Gyoung, Y. Yamamoto, *Adv. Synth. Catal.* **2004**, *346*, 800.

[13] Y. Kuninobu, H. Matsuzaki, M. Nishi, K. Takai, *Org. Lett.* **2011**, *13*, 2959.

[14] Y. He, Y. Y. Xie, Y. C. Wang, X. M. Bin, D. C. Hu, H. S. Wang, Y. M. Pan, *RSC. Adv.* **2016**, *6*, 58988-58993.

[15] Q. H. Teng, Y. L. Xu, Y. Liang, H. S. Wang, Y. C. Wang, Y. M. Pan, *Adv. Synth. Catal.* **2016**, *358*, 1897.

[16] Y. L. Xu, Q. H. Teng, W. Tong, H. S. Wang, Y. M. Pan, X. L. Ma, *Molecules*. **2017**, *22*, 109.

[17] a) S. Y. Woo, J. H. Kim, M. K. Moon, S. H. Han, S. K. Yeon, J. W. Choi, B. K. Jang, H. J. Song, Y. G. Kang, J. W. Kim, J. Lee, D. J. Kim, O. Hwang, K. D. Park, *J. Med. Chem*. **2014**, *57*, 1473; b) E. Dunny, W. Doherty, P. Evans, J. P. G. Malthouse, D. Nolan, A. Knox, *J. Med. Chem.* **2013**, *56*, 6638; c) D. C. Meadows, J. Gervay-Hague, *Med. Res. Rev.* **2006**, *26*, 793.

[18] a) H. T. Sakamoto, D. Flausino, E. E. Castellano, C. B. W. Stark, P. J. Gates, N. P. Lopes, *J. Nat. Prod.* **2003**, *66*, 693; b) V. L. Goncalves de Moraes, V. M. Rumjanek, J. B. Calixto, *Eur. J. Pharmacol.* **1996**, *312*, 333; c) M. Togashi, S. Ozawa, S. Abe, T. Nishimura, M. Tsuruga, K. Ando, G. Tamura, S. Kuwahara, M. Ubukata, J. Magae, *J. Med. Chem.* **2003**, *46*, 4113; d) S. S. Shin, Y. Byun, K. M. Lim, J. K. Choi, K.-W. Lee, J. H. Moh, J. K. Kim, Y. S. Jeong, J. Y. Kim, Y. H. Choi, H.-J. Koh, Y. -H. Park, Y. I. Oh, M. -S. Noh, S. Chung, *J. Med. Chem.* **2004**, *47*, 792.

[19] a) X. Cheng, Y. Zhou, F. Zhang, K. Zhu, Y.Liu, Y. Li, *Chem. Eur. J.* **2016**, *22*, 12655; b) Q. Yao, L. Kong, F. Zhang, X. Tao, Y. Li, *Adv. Synth. Catal.* **2017**, DOI: 10.1002/adsc.201700565; c) M. Murai, M. Nakamura, K. Takai, *Org. Lett.* **2014**, *16*, 5784; d) Y. Kuninobu, A. Kawata, M. Nishi, S. Yudha, J. Chen, K. Takai, *Chem. Asian J.* **2009**, *4*, 1424.

[20] Q. F. Zhou, F. Yang, Q. X. Guo, S. Xue, *Synlett*. **2007**, 2073.

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FULL PAPER

An Unexpected Domino Reaction of *β*-Keto Sulfones with Acetylene Ketones Promoted by Base: Facile Synthesis of 3(*2H*)-Furanones and Sulfonylbenzenes

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