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Synthesis of Functionalized β-Keto Arylthioethers by the Aryne Induced [2,3] Stevens Rearrangement of Allylthioethers

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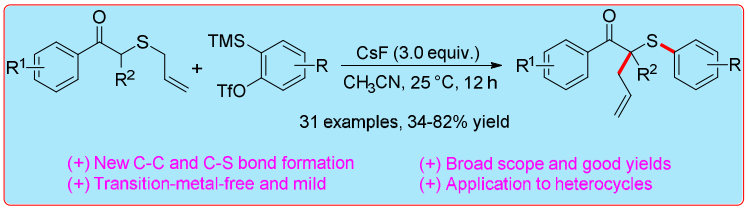


ABSTRACT: A mild and transition-metal-free synthesis of β-keto arylthioethers has been developed by the aryne triggered [2,3] Stevens rearrangement of allylthioethers. The key sulfur ylide intermediate for the rearrangement was formed by the *S*-arylation of allylthioethers with arynes generated from 2-(trimethylsilyl)aryl triflates using CsF. Later, the reaction products are converted into valuable heterocycles in two steps.

Organosulfur compounds are endowed with diverse applications in pharmaceutical chemistry and crop protection, and have attracted considerable attention from both industry and academia.[1] Among the organosulfur compounds, the β-keto thioethers are important as they are valuable core structure in various biologically active molecules. For instance, the indane 1,3-dione derived aryl thioethers (**A**) has been known as serine protease inhibitor (Figure 1).[2]

Moreover, the cyclohexanone containing thioether (**B**) is a precursor for the synthesis of Gabosines, epoforminand epiepoformin,[3] and the benzothiazine derivative (**C**) shows anti-inflammatory activity.[4] In addition, the 2-amino aryl thioethers (**D**) shows antitumor activity.[5] In view of the relevance of these molecules, synthesis of facile and straightforward synthetic routes to β-keto aryl allylthioethers are highly desirable. β-Ketothioethers are traditionally synthesized either by the reaction of diazocarbonyl compounds with thiols via the S-H insertion[6] or by the *S*-alkylation of α-haloketones.[7,8] Herein, we report the synthesis of functionalized β-keto arylthioethers by the [2,3] Stevens rearrangement of allylthioethers triggered by arynes.[9]

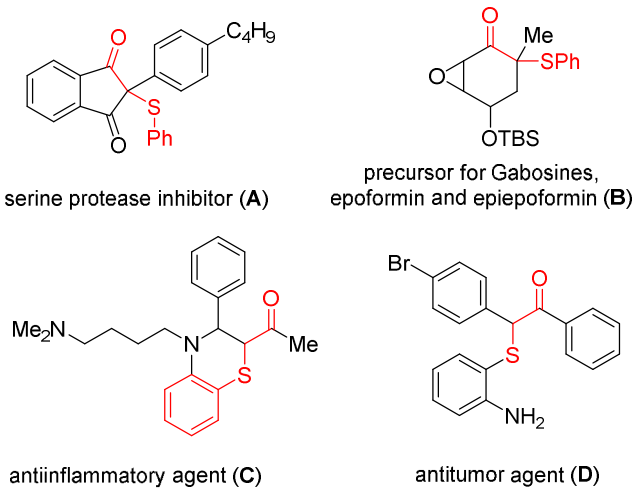
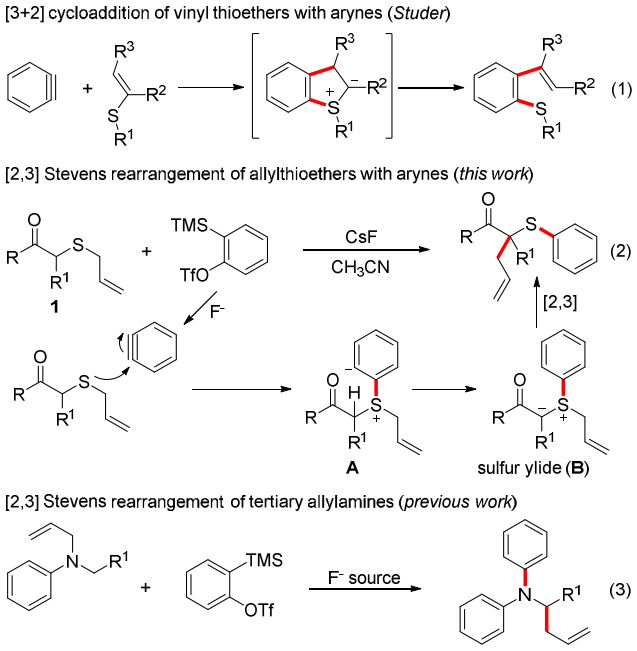


Figure 1. Biologically active molecules having β-keto thioethers moiety

Recently, the Studer group demonstrated the reaction of arynes with vinyl thioethers (having no α-C-H protons) leading to the highly selective formation of trisubstituted olefins (Scheme 1, eq 1).[10a] The reaction proceeds via the generation of cyclic sulfur ylides by the [3+2] cycloaddition of vinyl thioethers with arynes, which undergoes proton transfer and β-elimination to afford the functionalized olefin.[11] In this context we envisioned that the reaction of arynes with allylthioethers such as **1** having an α-C-H proton could generate the acyclic sulfur ylide

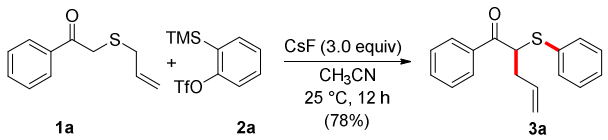
intermediate **B** via the aryl anion intermediate **A**. The [2,3] Stevens rearrangement[12] of ylide **B** could lead to the formation of functionalized β-keto arylthioethers (eq 2). The acidity of α-C-H proton in **1** will be crucial for the sulfur ylide generation and the subsequent rearrangement. It is noteworthy that the related aryne induced [2,3] Stevens rearrangement of tertiary allylic amines for the synthesis of functionalized homoallylic amines was demonstrated independently by Gu, Tian and co-workers,[13] Sweeney and co-workers,[14] and by us (eq 3).[15,16] Moreover, Greaney and co-workers uncovered the aza-Claisen rearrangement of tertiary allyl amines triggered by arynes for the synthesis of 2-allyl anilines.[17,18]



Scheme 1. Reaction of Arynes with Vinyl Thioethers and [2,3] Stevens Rearrangement Involving Arynes

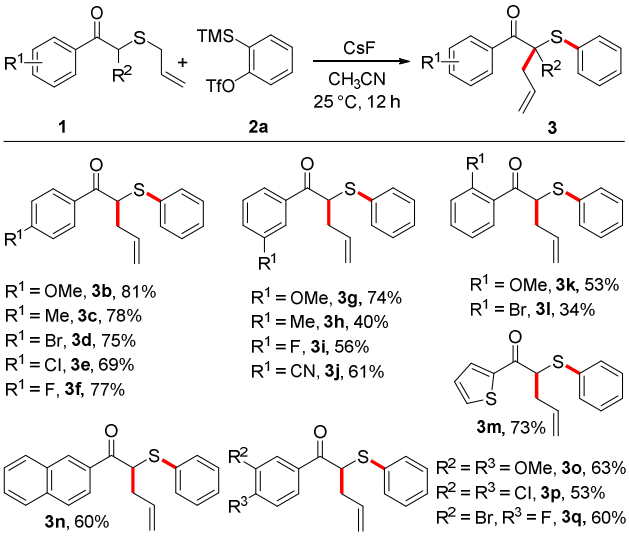
The present study was initiated by treating the allylthioether **1a** with aryne generated from 2-(trimethylsilyl)aryl triflate **2a**[19] using CsF as the fluoride source in CH_3CN solvent. Interestingly, under these conditions, the β-keto arylthioethers **3a** was formed in 78% yield in 12 h (Scheme 2). During the search for the suitable allylthioether substrate, it was found that the

reaction of allyl benzylthioether with arynes resulted in the formation of low yield of the rearranged product. This indicates that the carbonyl moiety in **1a** was essential for the reactivity as it increases the acidity of α C-H protons, which enables the smooth generation of the sulfur ylide. The reactions performed using KF in the presence of an 18-crown-6 as additive and tetrabutyl ammonium fluoride (TBAF) resulted in inferior results.[20] It may be noted that closely related [1,2] Stevens rearrangement of thioethers for the synthesis of functionalized β-keto thioethers has been demonstrated very recently by Guo, He and co-workers.[21]



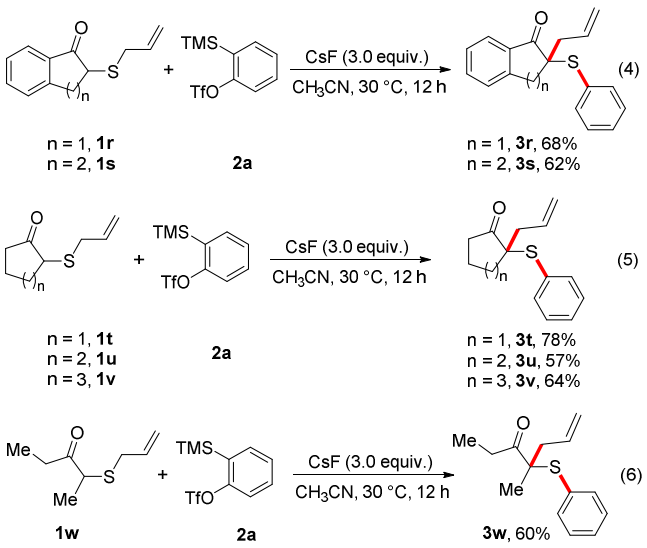
Scheme 2. Aryne Triggered [2,3] Stevens Rearrangement of Allylthioether

With the reaction conditions for the [2,3] Stevens rearrangement in hand, we then explored the substrate scope of this reaction. First, we evaluated the scope of the reaction using various allylthioethers having a benzoyl moiety at the β-position of allylthioether (Scheme 3). A series of electron-releasing and -withdrawing groups at the 4-position of benzene ring of the benzoyl moiety are well tolerated and in all cases, the β-keto arylthioethers are formed in good yields (**3b-3f**). Moreover, substrates having substitution at the 3-position as well as 2-position of the aryl ring of benzoyl moiety underwent smooth rearrangement reaction to form the expected aryl homoallyl thioethers in moderate to good yields (**3g-3l**). Interestingly, the thioether having the β-heteroaryl keto group also furnished the desired product **3m** in 73% yield. In addition, disubstitution at the aryl moiety also did not affect the outcome of this aryne triggered rearrangement reaction (**3n-3q**).[22]



Scheme 3. Scope of Allylthioethers in the Aryne Induced [2,3] Stevens Rearrangement.General conditions: **1** (0.50 mmol), **2a** (0.75 mmol), CsF (3.0 equiv), CH_3CN (3.0 mL), 25 °C and 12 h. Yields of the isolated products are given.

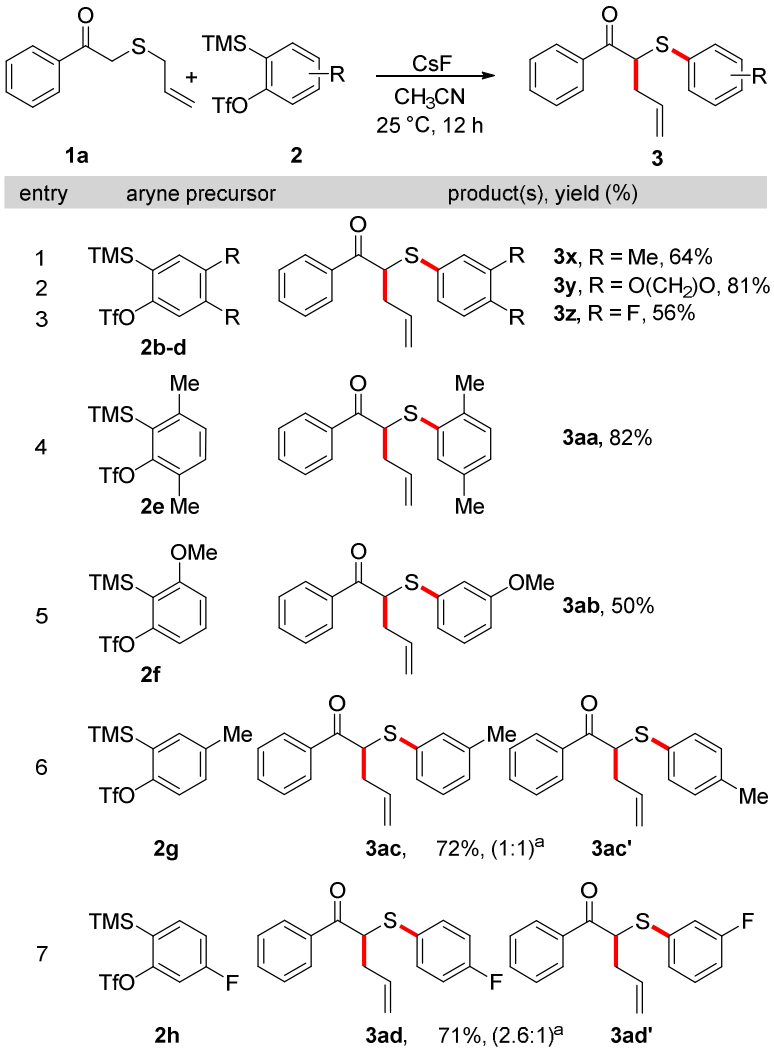
Next, we examined the scope of the reaction using cyclic ketone-derived allylthioethers with a view to synthesize quaternary β-keto allylthioethers (Scheme 4). Gratifyingly, the allyl thioethers synthesized from indanone (**1r**) and tetralone (**1s**) underwent smooth aryne-induced Stevens rearrangement leading to the formation of highly functionalized aryl allylthioethers **3r** and **3s** in good yields (eq 4). Interestingly, this rearrangement is not limited to allylthioethers having aryl ketones at the β-position, but instead other cyclic ketones-derived allylthioethers (**1t-1v**) and an acyclic ketone-derived thioethers (**1w**) were also useful for the sulfur ylide generation followed by [2,3] Stevens rearrangement sequence and in all cases, the thioethers with a quaternary centre (**3t-3w**) were formed in moderate to good yields (eq 5,6).



Scheme 4. Synthesis of Quaternary β-Keto Aryl Allylthioethers. General conditions: **1** (0.50 mmol), **2a** (0.75 mmol), CsF (3.0 equiv), CH_3CN (3.0 mL), 25 °C and 12 h. Yields of the isolated products are given.

The scope of this [2,3] rearrangement was also examined with various arynes (Table 1). Differently substituted and electronically dissimilar symmetrical arynes generated from the corresponding triflate precursors (**2b-2e**) reacted with the β-benzoyl allyl thioether **1a** under the present reaction conditions to afford the expected aryl thioethers (**3x-3aa**) in good yields. It is noteworthy that the unsymmetrical 3-methoxy benzyne generated from the precursor **2f** afforded a single regioisomer **3ab** in 50% yield. Additionally, the reaction of **1a** with unsymmetrical 4-methyl benzyne generated from the triflate **2g** resulted in the formation of two regioisomers **3ac** and **3ac'** in 72% yield and 1:1 ratio. Furthermore, the reaction using 4-fluoro benzyne resulted in the formation of two regioisomeric aryl allylthioethers **3ad** and **3ad'** in 71% yield and 2.6:1 ratio thus demonstrating the versatility of this rearrangement reaction.

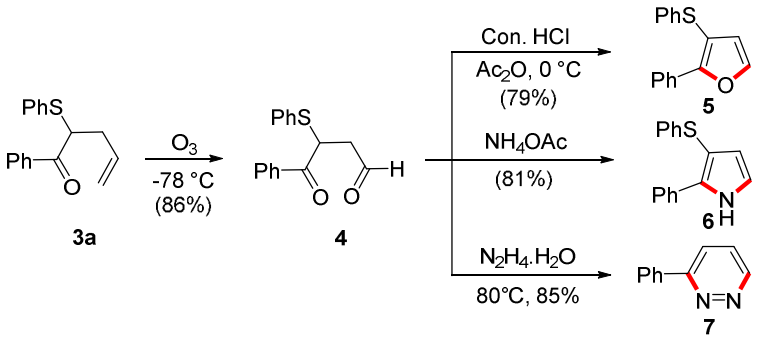
Table 1. Variation of the Aryne Moiety



General conditions: **1a** (0.50 mmol), **2** (0.75 mmol), CsF (3.0 equiv), CH_3CN (3.0 mL), 25 °C and 12 h. Yields of the isolated products are given. [a]The regioisomer ratio was determined either by GC or ^{1}H NMR analysis of crude reaction mixture.

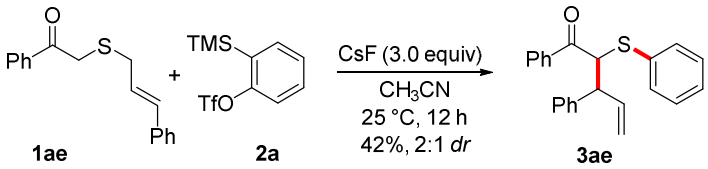
The synthetic utility of the β-keto arylthioethers has been demonstrated by the conversion of these compounds to valuable heterocycles in two steps. The ozonolysis of **3a** resulted in the formation of the 1,4-dicarbonyl compound **4** containing the thioethers moiety in 86% yield (Scheme 5). Treatment of the dicarbonyl compound **4** in the presence of Conc. HCl at 0 °C afforded the disubstituted furan **5** in 79% yield. Moreover, the reaction of **4** with NH_4OAc

resulted in the formation of the disubstituted pyrrole **6** in 81% yield. In addition, treatment of **4** with hydrazine hydrate at 80 °C furnished the 3-phenyl pyridazine **7** in 85% yield.



Scheme 5. Synthesis of Heterocycles from Allylthioethers

We also tested the feasibility of this reaction using allylthioether having a substituent at the allylic position. Treatment of β-keto cinnamyl thioether **1ae** with aryne generated from **2a** under the present reaction conditions furnished the arylthioethers **3ae** in 42% yield and 2:1 *dr* (Scheme 6). Additional experiments to improve the yield and *dr* of this transformation returned inferior results.



Scheme 6. Aryne Induced [2,3] Stevens Rearrangement of Cinnamyl Thioether

In conclusion, we have developed a transition-metal-free procedure for the synthesis of β-keto arylthioethers by the aryne triggered [2,3] Stevens rearrangement of allylthioethers. The reaction proceeds via the generation of the sulfur ylide intermediate from arynes and allylthioethers and results in the formation of a new carbon-carbon and carbon-sulfur bonds. A series of allylthioethers and differently substituted arynes are tolerated under the present reaction

conditions. Moreover, the reaction products are converted into arylheteroaryl thioethers in a two-step procedure.

Experimental Section

General Information: Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 25 °C corresponds to the room temperature of the lab when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. 18-Crown-6 was recrystallized from dry CH_3CN and KF was dried by heating at 110 °C for 12 h and left to cool under argon and stored in argon filled glove-box. The 2(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[19] ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). HRMS measurements were carried out using ESI method and ion-trap mass analyzer.

General Procedure for the preparation of Allylthioethers

Following the modified literature procedure,[23] treatment of phenacyl bromide (1.0 g, 1.0 equiv) with the corresponding allyl mercaptan (1.5 equiv) in presence of potassium carbonate (2.0 equiv) and acetonitrile as a solvent at 60 °C for 12 h afforded the corresponding 2-(allylthio)-1-phenylethan-1-one substrate. The data are matching with the corresponding literature procedure.[24]

General Procedure for the Aryne [2,3]-Stevens Rearrangement

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the CsF (228 mg, 1.5 mmol) in a glove box. The mixture was dissolved in CH_3CN (3.0 mL) under argon atmosphere. 2-(Allylthio)-1-phenylethan-1-one **1** (0.50 mmol) was added outside the glove box under argon atmosphere. To the stirring solution, aryne precursor **2** (0.75mmol) was added. Then the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography by using Pet. ether /EtOAc system on silica gel to afford the corresponding 1-phenyl-2-(phenylthio)pent-4-en-1-ones **3** in moderate to good yields.

1-Phenyl-2-(phenylthio)pent-4-en-1-one (3a):[25] (yellow oil, 0.104 g, 78% yield). R_f (Pet. ether /EtOAc = 95/05): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.59 (t,*J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.40-7.28 (m, 5H), 5.97-5.89 (m, 1H), 5.19-5.12 (m, 2H), 4.55 (t, *J* = 7.3 Hz, 1H), 2.85-2.79 (m, 1H), 2.67-2.62 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.2, 136.1, 134.8, 133.1, 131.6, 131.1, 129.2, 129.0, 128.8, 128.6, 128.6, 127.1, 117.8, 50.8, 35.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{17}OS$: 269.09946, found: 269.09955. **FTIR (cm^{-1})** 3018, 1678, 1597, 1580, 1474, 1439, 1344, 1276, 1025, 924.

1-(4-Methoxyphenyl)-2-(phenylthio)pent-4-en-1-one (3b): (colorless oil, 0.121 g, 81% yield). R_f (Pet. ether /EtOAc = 90/10): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 3H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.93 – 5.84 (m, 1H), 5.11 (dd, J_1 = 18.7 Hz, J_2 = 13.9 Hz, 2H), 4.50 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 2.82 – 2.75 (m, 1H), 2.64 – 2.57 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.1, 163.6, 135.0, 134.6, 132.0, 131.0, 129.0, 128.6, 117.7, 113.8, 55.5, 50.7, 35.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}O_2S$: 299.1100, found: 299.1095. **FTIR (cm^{-1})** 3019, 2937, 2835, 2401, 1742, 1642, 1514, 1464, 1373, 1216, 1030, 959, 772.

2-(Phenylthio)-1-(*p*-tolyl)pent-4-en-1-one (3c):[25] (viscous yellow oil, 0.110 g, 78% yield). R_f (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.1 Hz,2H), 7.40 - 7.38 (m, 2H), 7.34 - 7.26 (m, 5H), 5.97 - 5.86 (m, 1H), 5.17 - 5.09 (m, 2H), 4.53 (t, *J* = 7.2 Hz, 1H), 2.84 - 2.76 (m, 1H), 2.66 - 2.59 (m, 1H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.9, 144.0, 134.9, 134.7, 133.5, 131.7, 129.3, 129.0, 128.7, 128.7, 117.7, 77.1, 50.8, 35.2, 21.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}OS$: 283.1151, found: 283.1155. **FTIR (cm^{-1})** 3018, 1673, 1607, 1573, 1438, 1340, 1216, 1025, 924.

1-(4-Bromophenyl)-2-(phenylthio)pent-4-en-1-one (3d): (pale yellow oil 0.130 g, 75 % yield). R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.34-7.27 (m, 5H), 5.94-5.84 (m, 1H), 5.16-5.09 (m, 2H), 4.43 (t, *J* = 7.5 Hz, 1H), 2.80-2.73 (m, 1H), 2.63-2.56 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.1, 135.0, 134.9, 134.7, 131.9, 131,2, 130.2, 129.1, 129.1, 128.3, 118.0, 50.9, 34.9. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{16}OBrS$: 347.0100, found: 347.0092. **FTIR (cm^{-1})** 3019, 1679, 1585, 1475, 1438, 1396, 1273, 1217, 1071, 1010,926, 772, 691, 669.

1-(4-Chlorophenyl)-2-(phenylthio)pent-4-en-1-one (3e): (pale yellow oil, 0.104 g, 69% yield). R_f (Pet. ether /EtOAc = 95/05): 0.41; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.37-7.29 (m, 5H), 5.96-5.86 (m, 1H), 5.18-5.11 (m, 2H), 4.46 (t, *J* = 7.3 Hz, 1H), 2.82-2.75 (m, 1H), 2.66-2.59 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.0, 139.6, 135.0, 134.7, 134.4, 131.2, 130.1, 129.1, 129.1, 129.0, 118.0, 50.9, 35.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{16}OClS$: 303.0605, found: 303.0600. **FTIR (cm^{-1})** 3019, 1678, 1589, 1477, 1438, 1400, 1274, 1218, 1093, 1045, 927, 848, 772, 669.

1-(4-Fluorophenyl)-2-(phenylthio)pent-4-en-1-one (3f): (viscous yellow oil, 0.110 g, 77% yield). R_f (Pet. ether /EtOAc = 95/05): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 - 7.95 (m, 2H),

7.37 - 7.28 (m, 5H), 7.12 (t, *J* = 8.2 Hz, 2H), 5.95-5.85 (m, 1H), 5.17 - 5.10 (m, 2H), 4.47 (t, *J* = 7.1 Hz, 1H), 2.82 - 2.75 (m, 1H), 2.65 - 2.58 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 193.7, 165.8 (d, *J* = 254.1 Hz), 134.9, 134.8, 131.3 (d, *J* = 9.6 Hz), 129.1, 129.0, 117.9, 115.7 (d, *J* = 21.7 Hz), 50.9, 35.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{16}OFS$: 287.09004, found: 287.08997. **FTIR (cm^{-1})** 3077, 3018, 1678, 1598, 1474, 1300, 1157, 924, 851.

1-(3-Methoxyphenyl)-2-(phenylthio)pent-4-en-1-one (3g): (colorless oil, 0.110 g, 74% yield). R_f (Pet. ether /EtOAc = 90/10): 0.43; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 – 7.33 (m, 2H), 7.30 – 7.16 (m, 6H), 7.02 (d, *J* = 7.8 Hz, 1H), 5.83 – 5.77 (m, 1H), 5.07 – 4.99 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 1H), 3.74 (s, 3H), 2.72 – 2.64 (m, 1H), 2.55 – 2.48 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.1, 159.9, 137.5, 134.8, 131.7, 129.6, 129.1, 128.8, 121.1, 119.7, 117.9, 113.0, 55.5, 51.0, 35.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}O_2S$: 299.1100, found: 299.1096. **FTIR (cm^{-1})** 3019, 2937, 2401, 1742, 1514, 1443, 1373, 1241, 1216, 1030, 926, 815, 772.

2-(Phenylthio)-1-(m-tolyl)pent-4-en-1-one (3h): (yellow oil, 0.055 g, 40 % yield). R_f (Pet. ether /EtOAc = 95/05): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75-7.71 (m, 2H), 7.39-7.28 (m, 7H), 5.96-5.86 (m, 1H), 5.17-5.12 (m, 2H), 4.52 (t, *J* = 7.3 Hz, 1H), 2.82-2.75 (m, 1H), 2.65-2.58 (m, 1H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.5, 138.4, 136.2, 134.9, 133.9, 131.8, 129.2, 129.0, 128.8, 128.5, 125.8, 117.8, 50.9, 35.1, 21.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}OS$: 283.1151, found: 283.1146. **FTIR (cm^{-1})** 3018, 1676, 1640, 1602, 1584, 1475, 1438, 1339, 1279, 1256, 1216, 924, 769, 691, 668.

1-(3-Fluorophenyl)-2-(phenylthio)pent-4-en-1-one (3i): (pale yellow oil, 0.080 g, 56% yield). R_f (Pet. ether /EtOAc = 95/05): 0.33; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.1 Hz, 1H), 7.64 - 7.61 (m, 1H), 7.46-7.40 (m, 1H), 7.37 - 7.25 (m, 6H), 5.46 - 5.40 (m, 1H), 5.17 - 5.10 (m, 2H), 4.44 (t, *J* = 7.6 Hz, 1H), 2.81 - 2.74 (m, 1H), 2.65 - 2.58 (m, 1H). **^{13}C NMR (100 MHz,**

$CDCl_3$) δ 193.8, 162.9 (d, *J* = 248.6 Hz), 138.3, 135.1, 134.6, 131.1, 130.3 (d, *J* = 8.1 Hz), 129.1, 124.3, 124.3, 120.1 (d, *J* = 21.8 Hz), 118.0, 115.5 (d, *J* = 22.7 Hz), 51.1, 34.9. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{16}OFS$: 287.0900, found: 287.0893. **FTIR (cm^{-1})** 3077, 3018, 1681, 1588, 1483, 1339, 1273, 1216, 1148, 994.

3-(2-(Phenylthio)pent-4-enoyl)benzonitrile (3j): (pale yellow oil, 0.090 g, 61 % yield). R_f (Pet. ether /EtOAc = 95/05): 0.12; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14-8.12 (m, 2H), 7.82 (d, *J*= 7.75 Hz, 1H), 7.57 (t, *J*=8.2 Hz, 1H), 7.38-7.27 (m, 5H), 5.94-5.78 (m, 1H), 5.17-5.11 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 1H), 2.80-2.72 (m, 1H), 2.65-2.58 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.9, 137.0, 135.9, 135.2, 134.4, 132.6, 132.3, 130.7, 129.6, 129.4, 129.2, 118.3, 117.9, 113.1, 51.1, 34.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{16}ONS$: 294.0947, found: 294.0940. **FTIR (cm^{-1})** 3019, 2977, 2349, 1686, 1600, 1525, 1477, 1425, 1215, 1045, 928, 877, 849, 755, 669.

1-(2-Methoxyphenyl)-2-(phenylthio)pent-4-en-1-one (3k): (colorless oil, 0.079 g, 53% yield). R_f (Pet. ether /EtOAc = 90/10): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.08 (m, 5H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.92 - 5.81 (m, 1H), 5.03 (dd, J_1 = 17.7 Hz, J_2 = 14.1 Hz, 2H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 2.72 – 2.65 (m, 1H), 2.47 – 2.39 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.4, 158.0, 135.4, 134.1, 133.5, 132.5, 131.4, 128.7, 128.2, 127.4, 120.9, 117.2, 111.5, 55.5, 55.2, 34.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}O_2S$: 299.1100, found: 299.1096. **FTIR (cm^{-1})** 3015, 2981, 1642, 1600, 1503, 1455, 1423, 1347, 1229, 1131, 992, 872, 752.

1-(2-Bromophenyl)-2-(phenylthio)pent-4-en-1-one (3l): (yellow oil, 0.050 g, 34% yield). R_f (Pet. ether /EtOAc = 95/05): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.23-7.19 (m, 3H), 7.17-7.10 (m, 4H), 5.94-5.82 (m, 1H), 5.11-5.03 (m, 2H), 4.37 (t, *J* = 7 Hz, 1H), 2.74-2.67 (m, 1H), 2.51-2.44 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ

198.4, 140.6, 134.5, 134.0, 133.5, 132.1, 131.7, 130.2, 129.0, 128.5, 127.3, 119.4, 118.2, 55.1, 34.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{16}OBrS$: 347.0100, found: 347.0096. **FTIR (cm^{-1})** 3019, 2977, 1693, 1640, 1587, 1525, 1476, 1430, 1216, 1045, 1027, 927, 773, 690, 669.

2-(Phenylthio)-1-(thiophen-2-yl)pent-4-en-1-one (3m): (yellow oil, 0.100 g, 73% yield). R_f (Pet. ether /EtOAc = 95/05): 0.31; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.62 (m, 2H), 7.43-7.41 (m, 2H), 7.31-7.29 (m, 3H), 7.10-7.07 (m, 1H), 5.94-5.84 (m, 1H), 5.18-5.09 (m, 2H), 4.35-4.31 (m, 1H), 2.80-2.75 (m, 1H), 2.64-2.57 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.0, 143.2, 134.6, 134.1, 132.3, 129.1, 128.8, 128.1, 118.0, 53.0, 35.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{15}OS_2$: 275.0559, found: 275.0564. **FTIR (cm^{-1})** 3018, 1657, 1583, 1516, 1475, 1438, 1345, 1218, 1066, 926.

1-(Naphthalen-2-yl)-2-(phenylthio)pent-4-en-1-one (3n): (yellow oil, 0.095 g, 60% yield). R_f (Pet. ether /EtOAc = 95/05): 0.28; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (d, J = 8.1 Hz, 2H), 7.40 - 7.38 (m, 2H), 7.34 - 7.26 (m, 5H), 5.97 - 5.86 (m, 1H), 5.17 - 5.09 (m, 2H), 4.53 (t, J = 7.2 Hz, 1H), 2.84 - 2.76 (m, 1H), 2.66 - 2.59 (m, 1H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.9, 135.8, 134.7, 134.4, 134.0, 132.7, 132.4, 130.8, 128.9, 128.5, 128.4, 127.9, 127.0, 126.6, 125.9, 124.2, 118.2, 55.0, 35.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{19}OS$: 319.1151, found: 319.1145. **FTIR (cm^{-1})** 3019, 1677, 1583, 1509, 1476, 1328, 1215, 1087, 1025.

1-(3,4-Dimethoxyphenyl)-2-(phenylthio)pent-4-en-1-one (3o): (pale yellow oil, 0.103 g, 63% yield). R_f (Pet. ether /EtOAc = 70/30): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, J = 8.7 Hz, 1H), 7.49 (s, 1H), 7.39 - 7.37 (m, 2H), 7.30 - 7.28 (m, 3H), 6.86 (d, J = 8.2 Hz, 1H), 5.94 - 5.84 (m, 1H), 5.15 - 5.07 (m, 2H), 4.50 (t, J = 7.6 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 2.82 - 2.75 (m, 1H), 2.64 - 2.58 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.1, 153.4, 149.0, 134.9, 134.4, 132.3, 129.1, 129.0, 128.6, 123.1, 117.7, 110.9, 110.0, 56.1, 55.9, 50.6, 35.5. **HRMS (ESI)**

calculated $[M+H]^+$ for $C_{19}H_{21}O_3S$: 329.1206, found: 329.1209. **FTIR (cm^{-1})** 3020, 1668, 1595, 1464, 1418, 1216, 1134, 1023.

1-(3,4-Dichlorophenyl)-2-(phenylthio)pent-4-en-1-one (3p): (pale yellow oil, 0.090 g, 53% yield). R_f (Pet. ether /EtOAc = 95/05): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.36 - 7.28 (m, 5H), 5.93-5.84 (m, 1H), 5.18 - 5.04 (m, 2H), 4.37 (t, J = 7.1 Hz, 1H), 2.79 - 2.72 (m, 1H), 2.64 - 2.57 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.8, 137.6, 135.8, 135.2, 134.5, 133.3, 130.7, 130.7, 129.3, 129.2, 127.7, 118.2, 51.1, 34.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{15}OCl_2S$: 337.0215, found: 337.0209. **FTIR (cm^{-1})** 3016, 1681, 1583, 1469, 1385, 1276, 1212, 1136, 1064, 1029.

1-(3-Bromo-4-fluorophenyl)-2-(phenylthio)pent-4-en-1-one (3q): (pale yellow oil, 0.110 g, 60% yield). R_f (Pet. ether /EtOAc = 95/05): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 - 8.09 (m, 1H), 7.89 - 7.85 (m, 1H), 7.38 - 7.28 (m, 5H), 7.20 - 7.15 (m, 1H), 5.94 - 5.84 (m, 1H), 5.17 - 5.11 (m, 2H), 4.38 (t, J = 7.3 Hz, 1H), 2.80 - 2.72 (m, 1H), 2.64 - 2.57 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.5, 162.0 (d, J = 256.2), 135.1, 134.6 (d, J = 4.2 Hz), 131.1, 129.9 (d, J = 8.5 Hz), 129.3, 129.2, 118.2, 116.7 (d, J = 22.9 Hz), 109.9, 109.7, 51.0, 34.9. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{15}OBrFS$: 365.0006, found: 365.0000. **FTIR (cm^{-1})** 3019, 1681, 1590, 1492, 1438, 1396, 1251, 1046.

2-Allyl-2-(phenylthio)-2,3-dihydro-1*H*-inden-1-one (3r): (colorless oil, 0.96 g, 68% yield). R_f (Pet. ether /EtOAc = 95/05): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.28 (t, J = 7.4 Hz, 2H), 5.84 – 5.74 (m, 1H), 5.16 (dd, J_1 = 19.9 Hz, J_2 = 13.7 Hz, 2H), 3.42 (d, J = 17.9 Hz, 1H), 3.14 (d, J = 17.9 Hz, 1H), 2.67 (d, J = 7.0 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.2, 150.5, 137.2, 135.5, 135.0, 133.1, 130.2, 129.6, 128.6, 127.8, 126.2, 124.7, 119.4, 58.6, 39.4, 38.5. **HRMS**

(ESI) calculated $[M+H]^+$ for $C_{18}H_{17}OS$: 281.0995, found: 281.1002. **FTIR (cm^{-1})** 3020, 2984, 1744, 1631, 1522, 1421, 1392, 1373, 1187, 1117, 927.

2-Allyl-2-(phenylthio)-3,4-dihydronaphthalen-1(2*H*)-one (3s): (yellow oil, 0.098 g, 62% yield). R_f (Pet. ether /EtOAc = 95/05): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42-7.26 (m, 7H), 5.96-5.85 (m, 1H), 5.17-5.13 (m, 2H), 3.52-3.43 (m, 1H), 2.94-2.89 (m, 1H), 2.70-2.65 (m, 1H), 2.58-2.53 (m, 1H), 2.48-2.40 (m, 1H), 2.30-2.25 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 192.0, 142.5, 137.5, 133.8, 133.1, 131.6, 129.6, 129.2, 128.8, 128.6, 128.4, 126.8, 118.8, 57.5, 40.2, 32.3, 25.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{19}H_{19}OS$: 295.1151, found: 295.1154. **FTIR (cm^{-1})** 3019, 1674, 1638, 1601, 1474, 1430, 1355, 1308, 1218, 1126, 1044, 922, 772, 691, 669.

2-Allyl-2-(phenylthio)cyclopentan-1-one (3t): (pale yellow oil, 0.090 g, 78% yield). R_f (Pet. ether /EtOAc = 95/05): 0.18; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 - 7.28 (m, 5H), 5.86 -5.76 (m, 1H), 5.16 - 5.10 (m, 2H), 2.73 - 2.63 (m, 1H), 2.48 - 2.43 (m, 1H), 2.32 - 2.27 (m, 1H), 2.22 - 2.07 (m, 3H), 2.03 - 1.90 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 211.6, 137.3, 133.4, 129.9, 129.7, 128.8, 118.9, 59.6, 37.9, 36.0, 33.9, 18.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{17}OS$: 233.0995, found: 233.0996. **FTIR (cm^{-1})** 3018, 1727, 1639, 1523, 1473, 1319, 1215, 1165, 1068, 1002.

2-Allyl-2-(phenylthio)cyclohexan-1-one (3u): (yellow solid, 0.070 g, 57% yield). R_f (Pet. ether /EtOAc = 95/05): 0.75; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 - 7.28 (m, 5H), 5.92 -5.82 (m, 1H), 5.14 - 5.04 (m, 2H), 3.44 - 3.35 (m, 1H), 2.37 - 2.32 (m, 3H), 2.16 - 2.07 (m, 3H), 1.98 - 1.91 (m, 1H), 1.27 - 1.64 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.2, 136.3, 134.0, 130.4, 129.5, 129.0, 118.5, 60.3, 39.8, 37.8, 36.8, 27.0, 21.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{19}OS$: 247.1151, found: 247.1153. **FTIR (cm^{-1})** 3018, 1698, 1474, 1316, 1291, 1149, 1122, 1025, 998.

2-Allyl-2-(phenylthio)cycloheptan-1-one (3v):[26] (pale yellow oil, 0.083 g, 64% yield). R_f (Pet. ether /EtOAc = 95/05): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 - 7.29 (m, 5H), 6.08 -5.98 (m, 1H), 5.17 - 5.06 (m, 2H), 3.26 - 3.21 (m, 1H), 2.49 - 2.39 (m, 2H), 2.27 - 2.18 (m, 2H), 1.97 - 1.83 (m, 3H), 1.61 - 1.55 (m, 1H), 1.44 - 1.40 (m, 2H), 1.23 - 1.18 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.9, 136.7, 134.4, 130.6, 129.5, 128.9, 118.3, 62.4, 39.6, 36.3, 32.3, 30.4, 26.5, 24.5. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{21}OS$: 261.1308, found: 261.1310. **FTIR (cm^{-1})** 3017, 1692, 1439, 1217, 1156, 1065, 1022, 921.

4-Methyl-4-(phenylthio)hept-6-en-3-one (3w): (Colorless oil, 0.070 g, 60% yield). R_f (Pet. ether /EtOAc = 95/05): 0.42; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.31-7.29 (m, *5*H), 5.82-5.73 (m, 1H), 5.15-5.11 (m, 2H), 2.83 (q, *J* = 7.2 Hz, 2H), 2.63-2.59 (m, 1H), 2.47-2.43 (m, 1H), 1.39 (s, 3H), 1.14 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 208.09, 136.30, 133.32, 130.84, 129.40, 128.97, 119.01, 59.23, 41.30, 29.85, 21.30, 8.60. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{19}OS$: 235.1151, found: 235.1150. **FTIR (cm^{-1})** 3018, 1700, 1473, 1457, 1414, 1376, 1216, 1083, 976, 754, 667.

2-((3,4-Dimethylphenyl)thio)-1-phenylpent-4-en-1-one (3x): (yellow oil, 0.094 g, 64% yield). R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.58-7.54 (m, 2H), 7.47-7.43 (m, 2H), 7.10-7.03 (m, 3H), 5.94-5.84 (m, 1H), 5.15-5.06 (m, 2H), 4.44 (t, *J* = 7.3 Hz, 1H), 2.78-2.71 (m, 1H), 2.61-2.54 (m, 1H), 2.23 (s, 3H), 2.19 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.2, 138.0, 137.4, 136.5, 136.3, 135.1, 133.0, 132.8, 130.3, 128.7, 128.6, 127.7, 117.7, 50.9, 35.0, 19.7, 19.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{19}H_{21}OS$: 297.1308, found: 297.1318. **FTIR (cm^{-1})** 3081, 2924, 1678, 1640, 1597, 1580, 1485, 1448, 1383, 1344, 1217, 924, 814, 771, 687, 668.

2-(Benzo[*d*][1,3]dioxol-5-ylthio)-1-phenylpent-4-en-1-one (3y): (colorless oil, 0.127 g, 81% yield). R_f (Pet. ether /EtOAc = 70/30): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 6.84 - 6.79 (m, 2H), 6.70 (d, J = 8.0 Hz, 1H), 5.96 (s, 2H), 5.93-5.82 (m, 1H), 5.11 (dd, J_1 = 19.3 Hz, J_1 = 13.8 Hz, 2H), 4.39 (t, J = 7.3 Hz, 1H), 2.76 - 2.69 (m, 1H), 2.59 - 2.52(m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.9, 149.0, 147.8, 136.2, 134.9, 133.1, 130.6, 128.7, 128.6, 122.5, 117.8, 115.9, 108.7, 101.6, 51.0, 34.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{17}O_3S$: 313.0893, found: 313.0888. **FTIR (cm^{-1})** 3011, 2935, 1745, 1600, 1505, 1422, 1350, 1185, 1026, 991, 770.

2-((3,4-Difluorophenyl)thio)-1-phenylpent-4-en-1-one (3z): (pale yellow oil, 0.084 g, 56% yield). R_f (Pet. ether /EtOAc = 95/05): 0.39; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, J = 7.6 Hz, 2H), 7.60-7.56 (m, 1H), 7.48-7.45 (m, 2H), 7.16 (t, J = 8.7 Hz, 1H), 7.10-7.02 (m, 2H), 5.91-5.81 (m, 1H), 5.16-5.09 (m, 2H), 4.48 (t, J = 7.5 Hz 1H), 2.77-2.70 (m, 1H), 2.59-2.52 (m, 1H). **^{13}C NMR(100 MHz, $CDCl_3$)** δ 194.8, 152.0 (J_1= 14.2 Hz, J_2 = 136.0 Hz), 150.1 (J_1 = 14.0 Hz, J_2 = 136.6 Hz), 135.9, 134.4, 133.5, 132.1 (t, J = 4.81 Hz), 128.8, 128.6, 127.2 (t, J = 4.6 Hz), 124.4 (dd, J_1 = 3.7 Hz, J_2 = 14.5 Hz), 118.2, 117.8 (dd, J_1 = 7.9 Hz, J_2 = 11.0 Hz), 50.7, 34.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{15}OF_2S$: 305.0806, found: 305.0805. **FTIR (cm^{-1})** 3019, 1678, 1597, 1525, 1483, 1423, 1217, 1045, 928, 669.

2-((2,5-Dimethylphenyl)thio)-1-phenylpent-4-en-1-one (3aa): (viscous yellow oil, 0.121 g, 82% yield). R_f (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.0 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.18 (s, 1H), 7.08 - 7.0 (m, 2H), 5.97-5.87 (m, 1H), 5.18-5.09 (m, 2H), 4.56 – 4.53 (m, 1H), 2.93 – 2.86 (m, 1H), 2.72 - 2.65 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 196.1, 138.5, 136.4, 136.0, 135.5, 134.9, 133.1, 131.5, 130.4, 129.5, 128.5, 128.5, 117.8, 50.9, 35.6, 20.7, 20.5. **HRMS (ESI)**

calculated $[M+H]^+$ for $C_{19}H_{21}OS$: 297.1308, found: 297.1302. **FTIR (cm^{-1})** 3060, 2855, 1679, 1649, 1379, 1276, 997, 812.

2-((3-Methoxyphenyl)thio)-1-phenylpent-4-en-1-one (3ab): (yellow oil, 0.075 g, 50% yield). R_f (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.58 (t,*J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.98 (d,*J* = 7.7 Hz,1H), 6.89 - 6.86 (m, 2H), 5.96 - 5.86 (m, 1H), 5.18 - 5.09 (m, 2H), 4.55 (t,*J* = 7.1 Hz,1H), 3.75 (s, 3H), 2.86 - 2.79 (m, 1H), 2.67 - 2.66 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**δ 195.4, 159.6, 136.1, 134.8, 133.2, 133.0, 129.8, 128.6, 126.5, 119.4, 117.9, 114.8, 55.3, 51.0, 35.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}O_2S$: 299.1100, found: 299.1109. **FTIR (cm^{-1})** 3018, 1678, 1590, 1479, 1446, 1343, 1309, 1281, 1215, 1183, 996, 924, 777.

1-Phenyl-2-(*m*-tolylthio)pent-4-en-1-one (3ac) and 1-Phenyl-2-(*p*-tolylthio)pent-4-en-1-one (3ac'): (viscous yellow oil, 0.101 g, 72% yield). The regioisomeric ratio was determined by GC analysis of the cude reaction mixture is (1:1). R_f (Pet. ether /EtOAc = 95/05): 0.23; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (t, *J* = 8.8 Hz, 2H), 7.58 - 7.44 (m, 3H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.19 - 7.10 (m, 3H), 5.96 - 5.85 (m, 1H), 5.17 -5.09 (m, 2H), 4.52 (t, *J* = 7.2 Hz, 1H), 2.84 - 2.71 (m, 1H), 2.65 - 2.55 (m, 1H), 2.31 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.4, 138.8, 136.3, 135.5, 135.0, 133.1, 131.7, 129.0, 128.9, 117.8, 51.0, 35.2, 21.3. Representative peak for other isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.46 (t, *J* = 7.1 Hz), 2.35 (s). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.1, 139.3, 136.2, 135.4, 135.0, 133.1, 131.4, 129.7, 128.7, 117.7, 50.8, 34.9, 21.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{19}OS$: 283.1151, found: 283.1154. **FTIR (cm^{-1})** 3018, 1678, 1580, 1475, 1344, 1275, 1181, 1000, 923.

2-((4-Fluorophenyl)thio)-1-phenylpent-4-en-1-one (3ad) and 2-((3-Fluorophenyl)thio)-1-phenylpent-4-en-1-one (3ad'): (pale yellow oil, 0.102 g, 71% yield). The regioisomeric ratio

determined by ^{1}H NMR analysis of the crude reaction mixture (2.6:1). R_f (Pet. ether /EtOAc = 95/05): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$) of major isomer** δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.35 - 7.25 (m, 1H), 7.15 – 7.10 (m, 1H), 7.02 6.97 (m, 2H), 5.93 - 5.84 (m, 1H), 5.17 - 5.10 (m, 2H), 4.46 (t, *J* = 7.2 Hz, 1H), 2.85 - 2.53 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$) of major isomer** δ 194.9, 163.6 (d, *J* = 246.9 Hz), 137.8 (d, *J* = 8.8 Hz), 134.7, 134.5, 133.4, 133.2, 128.6, 117.9, 116.2 (d, *J* = 21.8 Hz), 50.7, 34.8. Representative peak for minor isomer: **^{1}H NMR (400 MHz, $CDCl_3$) of minor isomer** δ 4.57 (t, *J* = 7.4 Hz). **^{13}C NMR (100 MHz, $CDCl_3$) of minor isomer** δ 195.2, 136.1, 136.0, 130.3 (d, *J* = 8.4 Hz), 130.0 (d, *J* = 3.1 Hz,), 128.7, 121.0 (d, *J* = 23.1 Hz), 118.1, 115.8 (d, *J* = 20.7 Hz), 50.9, 35.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{16}OFS$: 287.0900, found: 287.0901. **FTIR (cm^{-1})** 3023, 1678, 1590, 1489, 1447, 1432, 1343, 1222, 921.

1,4-Diphenyl-2-(phenylthio)pent-4-en-1-one (3ae):[25] (yellow solid, 0.073 g, 42% yield). The regioisomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture (2:1). R_f (Pet. ether /EtOAc = 95/05): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.37-7.25 (m, 10H), 7.12-7.04 (m, 3H), 6.47-6.38 (m, 1H), 5.02-4.84 (m, 3H), 4.08-4.03 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.5, 141.7, 139.1, 136.7, 135.0, 132.8, 132.0, 129.0, 128.8, 128.6, 128.5, 128.2, 126.8, 117.7, 56.2, 50.1. Representative peak for minor isomer: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.6 Hz), 7.57 (t, *J* = 7.5 Hz), 7.51-7.40 (m), 7.21-7.16 (m), 6.04-5.96 (m), 5.34-5.18 (m), 4.14-4.11 (m). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.4, 140.5, 138.6, 136.9, 133.1, 132.3, 129.1, 128.9, 128.7, 128.5, 128.0, 127.1, 117.0, 56.4, 50.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{21}OS$: 345.1308, found: 345.1320. **FTIR (cm^{-1})** 3027, 1678, 1597, 1580, 1474, 1449, 1268, 1215, 1183, 1025, 921, 753.

Procedure for the Product Functionalization

Ozonolysis Reaction: A solution of 1-phenyl-2-(phenylthio)pent-4-en-1-ones **3a** (1.5 mmol) in 30 mL of CH_2Cl_2 was stirred at −78 °C as ozone was passed through the solution. After 5-10 min, the colorless reaction mixture changed to blue in color. Once blue color observed oxygen was passed to remove excess of ozone until reaction mixture was become colorless. Then to the reaction mixture dimethyl sulfide (15 ml) was added and continued the stirring at -78 °C for another 20 min. Then the reaction mixture was allowed to warm up to room temperature, and then continued stirring for another 12 h. The solvent was removed under reduced pressure. Purification of the crude material on a silica gel column chromatography ethyl acetate and pet ether afforded desired product **4** as yellow oil (350mg, 86%).

4-Oxo-4-phenyl-3-(phenylthio)butanal (4):[27] (viscous yellow oil, 350mg, 86%). $\boldsymbol{R_f}$ (Pet. ether /EtOAc = 90/10): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.77 (s, 1H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.61-7.29 (m, 8H), 4.98-4.95 (m, 1H), 3.57-3.30 (m, 1H), 3.03-2.97 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.3, 194.3, 135.5, 135.3, 133.3, 130.4, 129.4, 129.2, 128.8, 128.6, 45.4, 44.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{15}O_2S$: 271.0787, found: 271.0785. **FTIR (cm^{-1})** 3019, 2852, 1720, 1680, 1597, 1474, 1439, 1399, 1352, 1216, 1069, 972, 771.

Procedure for the Synthesis of Disubstituted Furan: To a stirred suspension of 1,4-dicarbonyl compound **4** (0.25 mmol, 68.0 mg) in 4.0 mL of Ac_2O at 0 °C, 1.0 mL con. HCl was added in dropwise under Argon protection. After the vigorous reaction, the reaction mixture was allowed to warm up to room temperature, and kept stirring for 3 h. The solvent was removed under reduced pressure. Purification of the crude material on a silica gel column chromatography ethyl acetate and pet ether afforded desired furan derivative **5** as yellow oil (50mg, 79%).

2-Phenyl-3-(phenylthio)furan (5):[28] (viscous yellow oil, 50mg, 79%). $\boldsymbol{R_f}$ (Pet. ether /EtOAc = 95/05): 0.63; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.56 (s, 1H), 7.44 (t, *J* =

7.5 Hz, 2H), 7.37-7.35 (m, 1H), 7.30-7.28 (m, 4H), 7.21-7.19 (m, 1H), 6.51 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 141.9, 137.0, 130.1, 129.1, 128.6, 128.3, 127.2, 126.1, 125.8, 117.7, 109.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{13}OS$: 253.0682, found: 253.0692. **FTIR (cm^{-1})** 3064, 3015, 2926, 2854, 1670, 1582, 1513, 1478, 1216, 1146, 1082, 1025, 885, 770.

Procedure for the Synthesis of Disubstituted Pyrrole: The mixture of 4-oxo-4-phenyl-3-(phenylthio)butanal **4** (0.25 mmol, 68.0 mg), ammonium acetate (1.25 mmol, 96.0 mg) and MeOH/H_2O (12:3 mL) was stirred for 3h at room temperature. Then the reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Purification of the crude material on a silica gel column chromatography ethyl acetate and pet ether afforded desired pyrrole derivative **6** as yellow oil (51mg, 81%).

2-Phenyl-3-(phenylthio)-1*H*-pyrrole (6):[27] (dark brown oil, 51mg, 81%). R_f (Pet. ether /EtOAc = 90/10): 0.28; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (bs, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33-7.10 (m, 6H), 6.94-6.93 (m, 1H), 6.45 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.4, 135.6, 131.8, 128.8, 128.7, 127.5, 127.0, 125.7, 124.6, 118.7, 117.2, 105.9. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{14}NS$: 252.0841, found: 252.0840. **FTIR (cm^{-1})** 3461, 3019, 2927, 2854, 1659, 1603, 1582, 1496, 1441, 1216, 1081, 1025, 770.

Procedure for the Synthesis of Disubstituted Pyridazine: The dicarbonyl compound **4**(0.25 mmol, 68.0 mg)was dissolved in ethanol (15mL) and hydrazine hydrate (1.25mmol, 63.0 mg) was added. Thereaction mixture was refluxed at 80°C for 6h. The solvent was removed under reduced pressure. Purification of the crude material on a silica gel column chromatography ethyl acetate and pet ether afforded desired pyridazinederivative **7**as white solid (33mg, 85%).

3-Phenylpyridazine (7): [29] (white solid, 33mg, 85%). R_f (Pet. ether /EtOAc = 50/50): 0.38; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.18-9.17 (m, 1H), 8.11 (d, *J* = 6.4 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.57-7.53 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.6, 150.1, 136.4, 130.2, 129.1, 127.2, 126.9, 124.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{10}H_9N_2$: 157.0760, found: 157.0762. **FTIR (cm^{-1})** 3011, 1727, 1658, 1580, 1547, 1452, 1432, 1374, 1297, 1217, 1099, 1028, 821.

Supporting Information

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

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