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Access to Polysubstituted (Furyl)methylthioethers *via* Base-Promoted S-H Insertion Reaction of Conjugated Enynones

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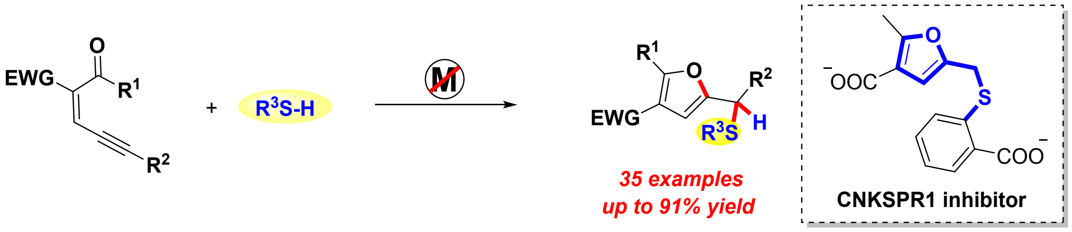


- **S-H Insertion of conjugated enynones**
- **Broad substrate scope and high atom economy**
- **Late-stage functionalization of Glutathione**
- **C(sp^3)-S and C(sp^2)-O bond formations in one pot**

Abstract:

A convenient and applicable approach to the construction of diverse functionalized (2-furyl)methylthioether derivatives *via* base-promoted S-H insertion of conjugated enynones with thiophenols or thiols has been developed. This reaction features readily available starting materials, high atom economy, broad substrate scope and versatile operation. Moreover, the synthetic utility of this method has been demonstrated by the efficient synthesis of CNKSPR1 inhibitor precursor and late-stage functionalization of

glutathione.

Introduction

Sulfur-containing compounds are well known for their wide existence in a large number of natural products, pharmaceutical compounds and bioactive molecules.[1] Furthermore, all of the top 10 best-selling drugs in 2012 were sulfur-containing compounds.[2] Among which, (2-furyl)methylthioethers are quite extraordinary due to their widespread occurrence in different kinds of *anti*-cancer drugs. For example, compound **A** inhibits the process of UDP-glucose dehydrogenase in the treatment of prostate cancer, and **B** is proved to act as an inhibitor of leukotriene biosynthesis, while **C** is illustrated to have certain effects in stunting the growth of cancer cells (Figure 1).[3] Thus, the synthesis of (furyl)methylthioether core structure has received much interest over the past few years, and most of the approaches mainly proceed through two pathways: (i) intramolecular cyclization of unsaturated thioethers[4] and (ii) sulfuration of furan rings.[5] However, limitations still exist, such as narrow substrate scope, harsh reaction conditions and prefunctionalization of the starting materials. Therefore, the exploration of new and general methods to assemble the (2-furyl)methylthioether skeleton is of significant importance.[6]

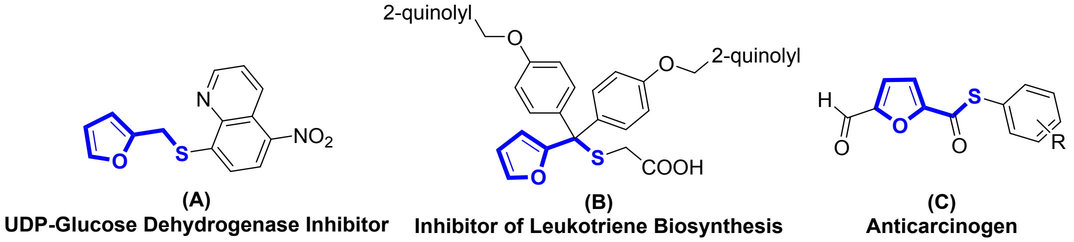
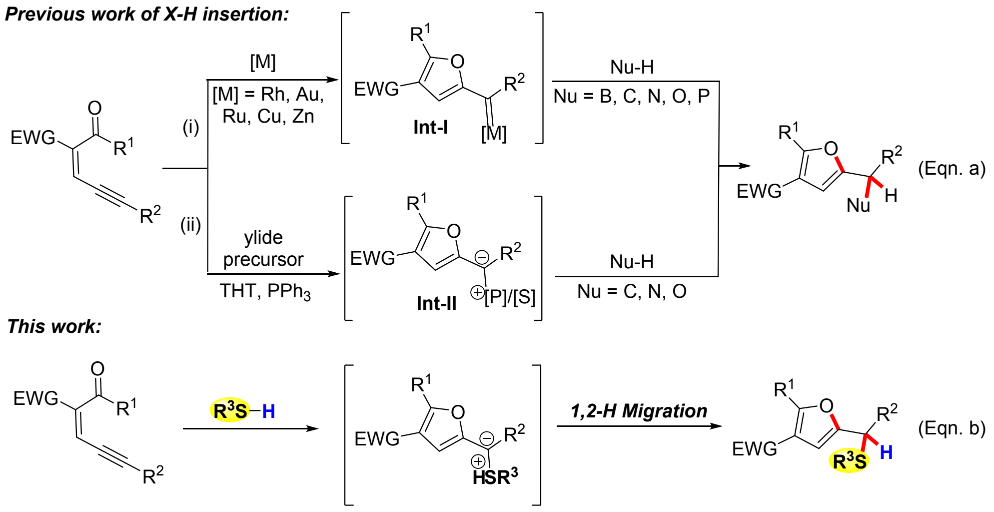


Figure 1. Biologically Active Molecules with (2-Furyl)methylthioether Skeleton

On the other hand, as readily available and versatile synthons, conjugated enynones exhibit abundant and tunable reactivities in the building of different functionalized furans.[7] In particular, the X-H (X = C,[8] O,[9] N,[9,10] B,[11] P,[12] Si,[13] *etc.*) insertion reactions of conjugated enynones, which can construct various furan rings as well as forming multiple new C-X bonds in one step, have been investigated broadly in recent years. Generally, the main reaction modes of X-H insertion reactions include (Scheme 1, Eqn. a): (i) the carbene insertion of X-H (X = C, O, N, B, P) in the transition metal catalysis; (ii) the organocatalytic approach *via* a sulfur or phosphine-mediated ylide intermediate especially for N/O-H insertion. Despite many elegant works that have been achieved in this field, the S-H insertion reaction of conjugated enynones remains unexplored, which might be ascribed to the distinct coordination nature of sulfur atom and the instability of the newly generated C-S bond in the presence of transition metals.[14] As our continuous interest in the construction of multi-substituted furans,[15] herein, we present an S-H insertion reaction of conjugated enynones with thiophenols or thiols under mild reaction conditions, in which the C(sp^3)-S and C(sp^2)-O bonds are formed in one pot with high atom and step economy (Scheme 1, Eqn. b).

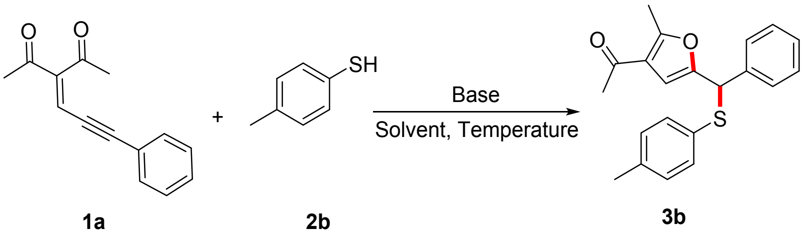
Scheme 1. General X-H Insertion Strategy of Conjugated Enynones



Result and Discussion

We commenced our investigations by monitoring the reaction of 3-(3-phenylprop-2-yn-1-ylidene)pentane-2,4-dione (**1a**) and 4-methylbenzenethiol (**2b**) to establish the optimal reaction system (Table 1). To our delight, the desired product 1-(2-methyl-5-(phenyl(phenylthio)methyl)furan-3-yl) ethan-1-one (**3b**) was obtained in 72% yield when the reaction was conducted in MeCN at 50 ^{o}C under the treatment of 2.0 equiv of K_2CO_3 (Table 1, entry 1). Encouraged by this result, other bases such as DABCO, Et_3N, and DBU were then investigated for this 5-*exo*-dig cyclization reaction, and DBU gave the best result (Table 1, entries 2-5). Control experiment suggested that the base was essential to this reaction (Table 1, entry 6). Further investigation of the base dosage revealed that 1.0 equiv of base was preferable for this transformation (Table 1, entries 7 and 8). The examination of temperature showed that 60 ^{o}C was the optimal choice, giving **3a** in 91% isolated yield (Table 1, entries 9-11). In addition, the employment of other solvents including DMSO, DMF, Et_3N and MeCN, did not show much positive effect (Table 1, entries 12-15). Thus, the optimal conditions for this reaction were defined as follows: DBU (1 equiv) as base in MeCN at 60 ^{o}C for 6 h (Table 1, entry 10).

Table 1. Optimization of the Reaction Conditions[a]

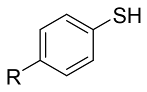
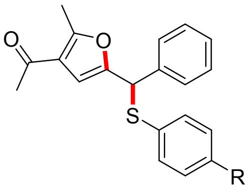
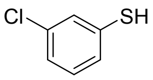
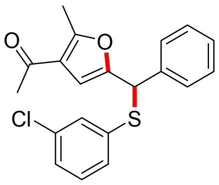
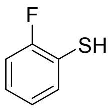
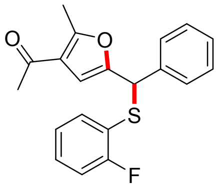
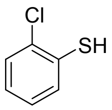
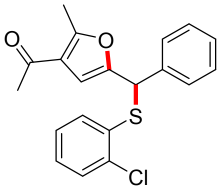
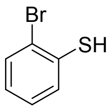
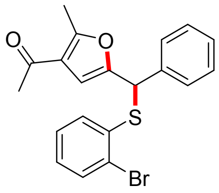


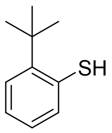
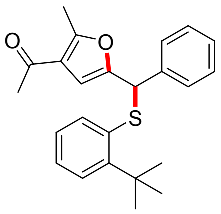
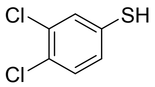
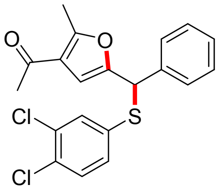
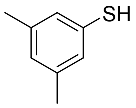
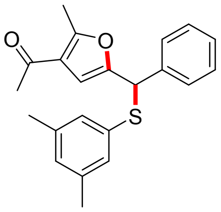
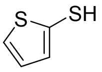
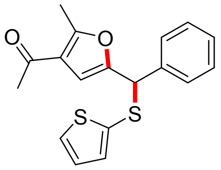
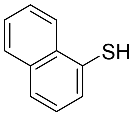
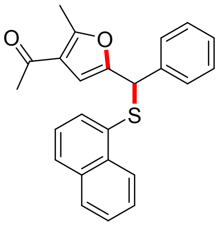
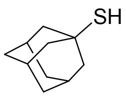
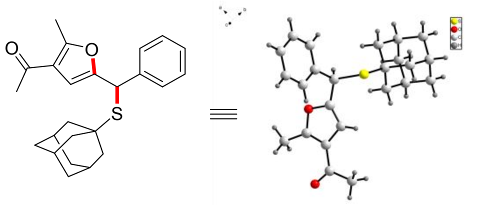
entry	Base (equiv)	temp (^{o}C)	solvent	yield (%)[b]
1	K_2CO_3 (2)	50	MeCN	72
2	KOH (2)	50	MeCN	n.d.
3	DABCO (2)	50	MeCN	33
4	Et_3N (2)	50	MeCN	20
5	DBU (2)	50	MeCN	89
6	-	50	MeCN	n.d.
7	DBU (1)	50	MeCN	90
8	DBU (0.5)	50	MeCN	66
9	DBU (1)	40	MeCN	59
10	**DBU** (1)	**60**	**MeCN**	**96 (91)**
11	DBU (1)	70	MeCN	43
12	DBU (1)	60	DMSO	10
13	DBU (1)	60	DMF	85
14	DBU (1)	60	Et_3N	75
15	DBU (1)	60	MeCN	22

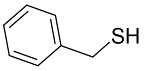
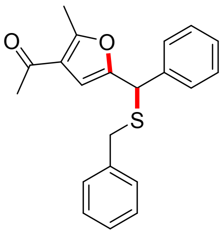
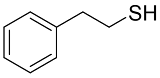
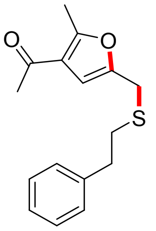
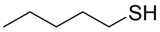
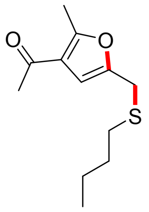
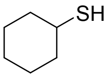
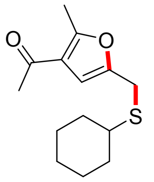
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), base, and solvent (2.0 mL) for 6 h. n.d. = not detected. [b]Determined by ^{1}H NMR using CH_3NO_2 as internal standard. Data in parentheses is isolated yield.

With the optimized reaction conditions in hand, we then investigated the generality and limitations of thiophenols or thiols for this cyclization reaction, and the results are summarized in Table 2. Gratifyingly, a wide range of substitution patterns of thiophenols were compatible in this transformation and the desired products could be obtained in moderate to excellent yields. For instance, different *para*-substituted thiophenols with either electron-donating groups (-Me, -*t*Bu, $-NH_2$, -OMe, *etc.*) or electron-withdrawing groups (-COOMe, $-CF_3$, *etc.*) were converted into the corresponding cyclization products in 44-91% yields (**3b**-**3g**). Moreover, different halo groups, including -F, -Cl, -Br, were well tolerated in this reaction, which allowed the subsequent functionalization to assemble structurally diverse molecules. The steric hindrance had little effect on this reaction due to the fact that *ortho*-*t*Bu substituted thiophenol proceeded well in this chemical process and transformed to the target product **3n** in 76% yield. Satisfactory yields were observed when disubstituted thiophenols were used in this reaction (**3o**-**3p**). It should be noted that the thiophenols containing heterocyclic or naphthyl rings were also well tolerated, and the desired products **3q** and **3r** could be formed in moderate yields. Importantly, the thiols were also applicable to this transition-metal-free system and the corresponding furan products **3s** and **3t** were obtained in 91% and 93% yields, respectively. The structure of **3s** was further unambiguously elucidated by X-ray crystallography (see the Supporting Information for details).[16] Pleasingly, the reactions of 3-(3-(trimethylsilyl)prop-2-yn-1-ylidene)pentane-2,4-dione with different thiols also proceeded smoothly to produce the corresponding (2-furyl)methylthioethers **3u**-**3w** in excellent yields (88%, 92% and 89%, respectively).

Table 2. Substrate Scope of Thiophenols or Thiols^a

Entry	2	Product	Yield [%]
1	 **2a**, R = H **2b**, R = Me **2c**, R = t-Bu **2d**, R = OMe **2e**, R = NH_2 **2f**, R = COOMe **2g**, R = CF_3 **2h**, R = Cl **2i**, R = Br	 **3a**, R = H **3b**, R = Me **3c**, R = t-Bu **3d**, R = OMe **3e**, R = NH_2 **3f**, R = COOMe **3g**, R = CF_3 **3h**, R = Cl **3i**, R = Br	**3a,** 82% **3b,** 91% **3c,** 90% **3d,** 44% **3e,** 63% **3f,** 90% **3g,** 86% **3h,** 84% **3i**, 86%
2	 **2j**	 **3j**	81
3	 **2k**	 **3k**	89
4	 **2l**	 **3l**,	79
5	 **2m**	 **3m**	82

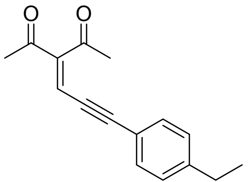
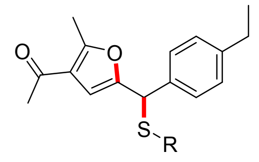
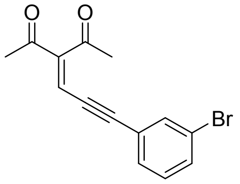
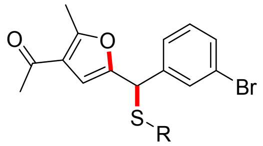
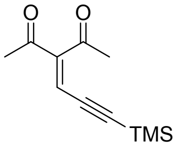
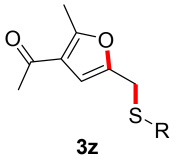
6	 **2n**	 **3n**	76
7	 **2o**	 **3o**	86
8	 **2p**	 **3p**	75
9	 **2q**	 **3q**	55
10	 **2r**	 **3r**	55
11	 **2s**	 **3s**	91

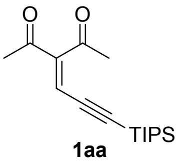
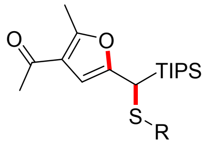
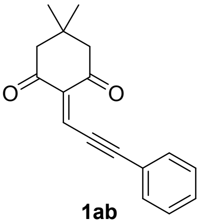
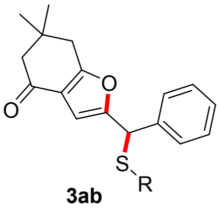
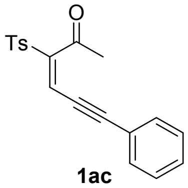
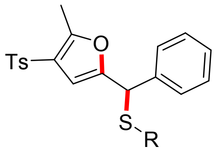
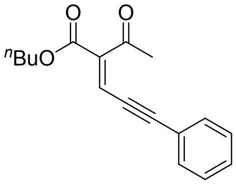
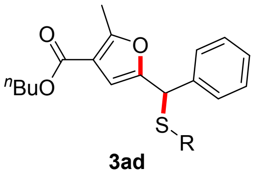
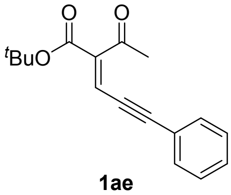
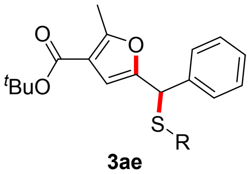
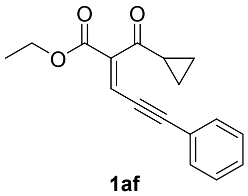
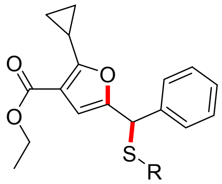
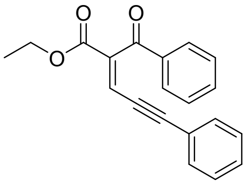
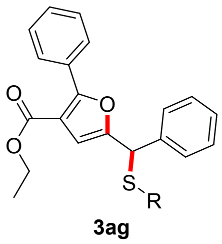
12	 **2t**	 **3t**	93
13	 **2u**	 **3u**, R^1 = TMS	88
14	 **2v**	 **3v**, R^1 = TMS	92
15	 **2w**	 **3w**, R^1 = TMS	89

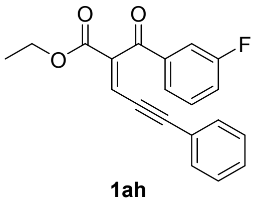
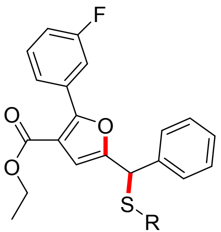
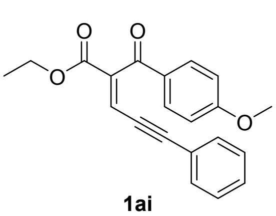
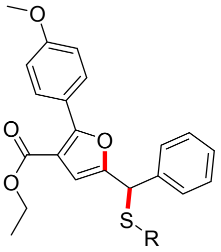
[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), DBU (0.2 mmol), MeCN (2.0 mL) at 60 ^{o}C for 6 h. Isolated yields were given. [b]Unless otherwise stated, R^1 = Ph.

Next, the scope of different conjugated enynones was evaluated (Table 3). It was found that the reaction was tolerated to a broad range of R^1 groups on the alkyne terminus, including alkyl- and bromo-substituted arenes, giving the corresponding products **3x** and **3y** in 80% and 82% yields, respectively. Interestingly, when TMS-substituted enynone substrate (R^1 = TMS, **1z**) was employed as the substrate, the desilylated furan product **3z** was isolated in 82% yield while TIPS-substituted enynone (R^1 = TIPS, **1aa**) was converted to **3aa**, in which the silicon substituent was retained. Delta ketone substituted ene-yne-ketone **1ab** also reacted with **2b** smoothly and the desired product **3ab** could be provided in 71% yield. Additionally, when one of the carbonyl groups was replaced by other electron-withdrawing substituents, such as ester and tosyl group (**1ac-1ae**), the reactions still proceeded well and afforded the expected furan derivatives **3ac-3ae** in 56-86% yields. In addition, the strained-ring substituent in R^2 position (**1af**) was also a suitable substrate for this transformation, and the desired product **3af** was obtained in 86% yield. Moreover, the substrates with R^2 replaced by phenyl or substituted phenyl groups (**1ag-1ai**) were able to transfer to the corresponding cyclization products in 63-72% yields (**3ag-3ai**).

Table 3. Substrate Scope of Conjugated Enynones^a

Entry	**1**	Product	Yield [%]
1	 **1x**	 **3x**	80
2	 **1y**	 **3y**	82
3	 **1z**	 **3z**	82

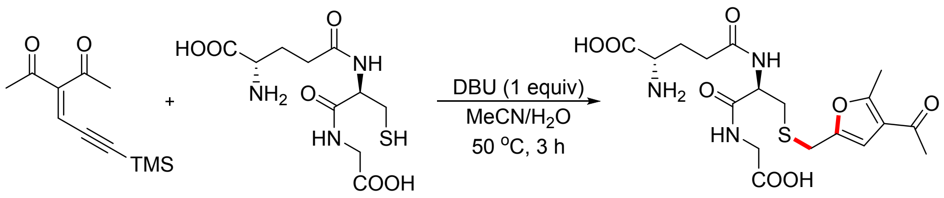
4	 **1aa**	 **3aa**	94
5	 **1ab**	 **3ab**	71
6	 **1ac**	 **3ac**	56
7	 **1ad**	 **3ad**	81
8	 **1ae**	 **3ae**	85
9	 **1af**	 **3af**	86
10	 **1ag**	 **3ag**	63

11	 **1ah**	 **3ah**	72
12	 **1ai**	 **3ai**	63

*a*Reaction conditions: **1** (0.2 mmol), **2b** (0.24 mmol), DBU (0.2 mmol), MeCN (2.0 mL) at 60 °C for 6 h. Isolated yields were given.

To further demonstrate the applicablity of this method, glutathione, a common natural product with multiple nucleophilic groups, was employed as the substrate in this reaction. Fortunately, the desired product **3aj** was isolated in 76% yield under the standard conditions with excellent chemoselectivity, which provided more possibilities for furhter applications in biochemistry, proteomics, and drug delivery,[17] such as late-stage functionalization of amino acids (Scheme 2).

Scheme 2. Late-Stage Functionalization of Glutathione

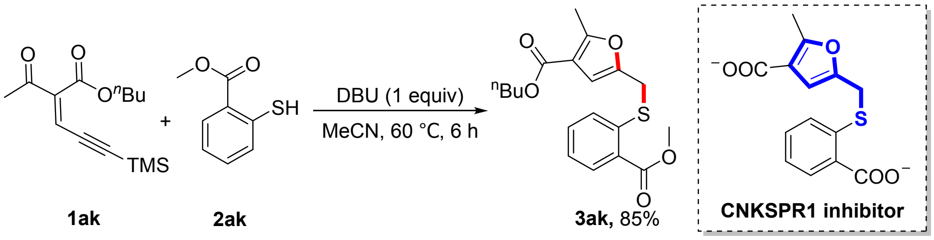


1aj **2z** **3aj**, 76%

Notably, this method could also be applied to the synthesis of a precursor of CNKSPR1 inhibitor,[18] a potential drug in blocking the growth of mut-KRAS cancer cells. The desired product **3ak** was isolated in 85% yield under the optimal conditions

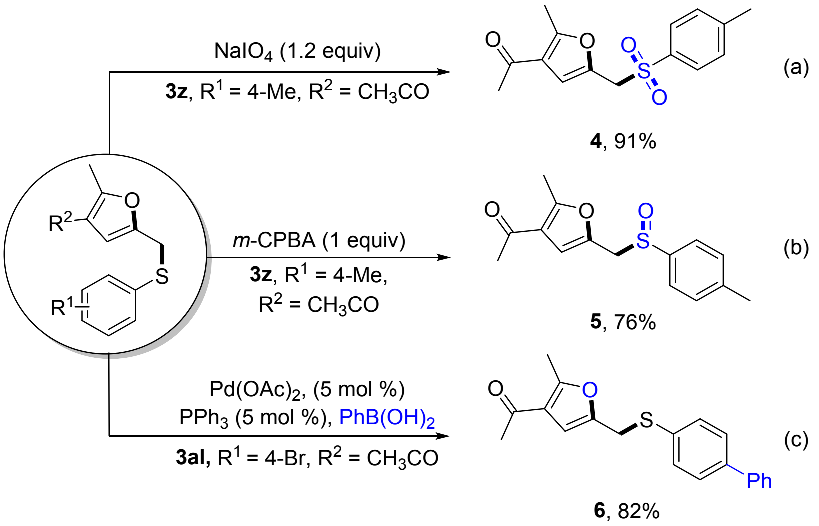
(Scheme 3), indicating the potential value in medicinal chemistry.

Scheme 3. Synthesis of CNKSPR1 Inhibitor Precursor



The utility of the newly formed (2-furyl)methylthioethers as useful building blocks for further elaborations was demonstrated (Scheme 4). For instance, in the presence of $NaIO_4$ or *m*-CPBA as oxidants, **3z** was converted to the sulfone or sulfoxide products **4** and **5** in 91% and 76% yields, respectively (Scheme 4a and 4b).[19] Additionally, the Suzuki coupling reaction of **3ai** proceeded well and the desired conjugated product **6** was afforded in 82% yield (Scheme 4c),[20] thus allowing for great structural diversity.

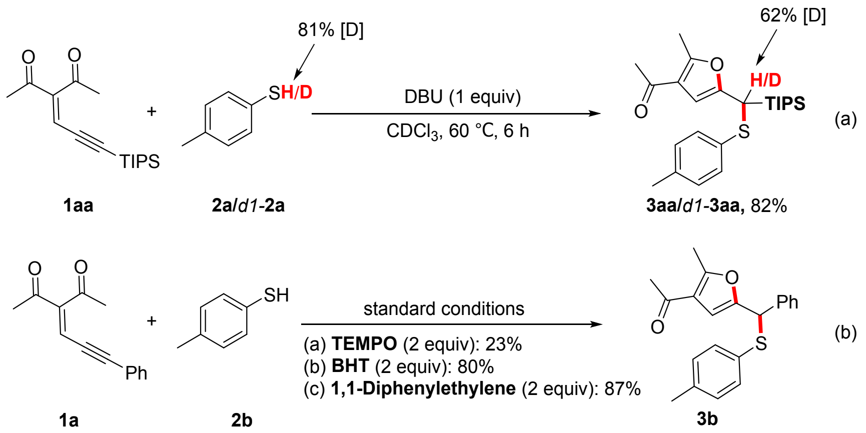
Scheme 4. Synthetic Applications



To gain more insight into the reaction mechanism, several control experiments were performed (Scheme 5). The deuterium-experiment indicated that the hydrogen atom at methylene position of **3aa**/*d1*-**3aa** was from thiophenols (Scheme 5a). Moreover, when radical inhibitor (2,2,6,6-tetramethyl-1- piperidinyloxyl), BHT

(2,6-di-*tert*-butyl-p-cresol) or 1,1-diphenylethylene was added respectively to the system under the standard reaction conditions, the corresponding product **3b** could be obtained in moderate to good yields, suggesting that a radical process should not be involved (Scheme 5b).

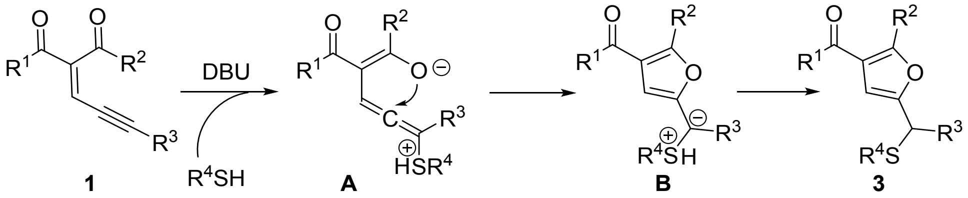
Scheme 5. Mechanistic Studies



[a]Determined by ^{1}H NMR using CH_3NO_2 as internal standard.

Based on the above experimental results and previous reports,[21] a plausible mechanism is proposed in Scheme 6. First, the reaction is initiated by the regioselective attack of thiophenol or thiols to the alkyne moiety of conjugated enynones, giving the allene intermediate **A**,[7d] which would undergo a 5-*exo*-dig cyclization to provide the intermediate **B**.[9] Finally, proton transfer of **B** affords the furan product **3**.

Scheme 6. Proposed Mechanism



Conclusion

In summary, we have developed a metal-free synthesis of (2-furyl)methylthioether derivatives *via* S-H insertion of conjugated enynones, in which constructed the C(sp^3)-S and C(sp^2)-O bonds in one pot. Moreover, this method can be highlighted by its application in the synthesis of the precursor of CNKSPR1 inhibitor and late-stage functionalization of glutathione. The high atom economy and good chemoselectivity, broad functional group tolerance as well as the mild reaction conditions make the present protocol attractive.

Experimental Section

General Information

Melting points were determined with a Buchi Melting Point B-545 instrument. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. All the reaction temperatures reported are oil bath temperatures. Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification.

Typical Procedure for the Synthesis of Conjugated Enynones[9d]

To a 25 mL round bottom flask, a mixture of 1,3-diketones (0.5 mmol, 50 mg), AcOH (0.1 mmol, 6 mg), pyrrolidine (0.05 mmol, 3.6 mg) and dry $MgSO_4$ (0.5 mmol, 60 mg) was added to a solution of alkyne aldehyde (0.6 mmol, 78 mg) in toluene (10 mL, 0.05 M). The reaction was carried out at 40 °C stirring for 4 h and monitored by TLC. After the completion of the reaction, the reaction mixture was filtered through *celite* and removal of the solvent by rotary evaporation to give the crude product. The conjugated enynones were purified by chromatography on silica gel with the appropriate mixture of petroleum ether and ethyl acetate (5: 1 for **1ac** and 20: 1 for other conjugated enynones) in 63-96% yields.

1a-1x, **1az**, **1aa**, **1ab**, **1ad**, **1af**, **1ag**, and **1ai** are known compounds and the NMR data are in good agreement with the literature.[9a,9c,12] **1y**, **1ac**, **1ad** and **1ah** are unknown compounds and the corresponding analytical data are shown as bellow:

3-(3-(3-Bromophenyl)Prop-2-yn-1-ylidene)pentane-2,4-dione (1y): Yellow oil (96%, 139 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.23 (t, J = 7.9 Hz, 1H), 6.89 (s, 1H), 2.54 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.3, 195.2, 149.8, 134.2, 132.8, 130.4, 129.7, 123.2, 122.1, 121.1, 104.1, 85.8, 30.7, 27.0 ppm; ν_{max}(KBr)/cm^{-1} = 2926, 2193, 1680, 1578, 1367, 1237, 877, 780; HRMS-ESI (m/z) calcd for $C_{14}H_{12}BrO_2$ $[M + H]^+$: 291.0021, found 291.0016.

(*E*)-6-Phenyl-3-tosylhex-3-en-5-yn-2-one (1ac): Yellow oil (71%, 115 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.61 (s, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.60 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.6, 148.8, 144.8, 136.7, 132.2, 130.7, 129.6, 128.7, 128.7, 126.2, 120.9, 110.3, 84.2, 34.2, 21.6 ppm; ν_{max}(KBr)/cm^{-1} = 3649, 3545, 2926, 2183, 1634, 1302,1140, 674; HRMS-ESI (m/z) calcd for $C_{19}H_{16}SO_3Na$ [M + Na]$^+$: 347.0718, found 347.0714.

Butyl (*E*)-2-Acetyl-5-phenylpent-2-en-4-ynoate (1ad): Yellow oil (90%, 122 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 3H), 7.02 (s, 1H), 4.34 (t, *J* = 6.7 Hz, 2H), 2.40 (s, 3H), 1.78 - 1.66 (m, 2H), 1.44 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.9, 165.5, 141.4, 132.1, 129.9, 128.5, 124.5, 121.9, 106.3, 85.4, 65.5, 30.7, 19.1, 14.0, 13.6 ppm; ν_{max}(KBr)/cm^{-1} = 3572, 3423, 2391, 2192, 1682, 1570, 1369, 778; HRMS-ESI (m/z) calcd for $C_{17}H_{18}NaO_3$ [M + Na]$^+$: 293.1154, found 293.1147.

Ethyl (*E*)-2-(3-Fluorobenzoyl)-5-phenylpent-2-en-4-ynoate (1ah): Yellow oil (93%, 150 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 1H), 7.59 - 7.35 (m, 2H), 7.28 (d, *J* = 10.2 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.4, 164.0, 163.6-161.6 (*J* = 200 Hz), 140.4, 138.1 (*J* = 60 Hz) 132.2, 130.4-130.3 (*J* = 7.0 Hz), 129.7, 128.3, 125.2-125.1 (*J* = 90 Hz), 124.1, 121.3, 120.8-120.6 (*J* = 29 Hz), 115.7-115.6 (*J* = 11 Hz), 105.1, 84.7, 61.7, 13.9 ppm; ^{19}F

NMR (376 MHz, $CDCl_3$) δ -111.6; ν_{max}(KBr)/cm^{-1} = 3068, 2958, 873, 2191, 1240, 761; HRMS-ESI (m/z) calcd for $C_{20}H_{15}FNaO_3$ [M + Na]$^+$: 345.0903, found 345.0901.

General Procedure for the Synthesis of (2-Furyl)methylthioethers (3)

To a solution of conjugated enynone (**1**, 0.20 mmol, 1.0 equiv) and DBU (0.2 mmol, 1.0 equiv) in MeCN (1 mL, 0.1 M) was added thiophenol or thiol (**2**, 0.24 mmol, 1.2 equiv). The mixture was stirred at 60 °C (oil bath) for 6 h. After the reaction was completed (monitored by TLC), the reaction was quenched with H_2O, and the crude product was extracted with ethyl acetate (6 mL × 3). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum. The resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate (10: 1 to 30: 1) as eluent to afford the desired products **3** in 44-94% yields.

1-(2-Methyl-5-(phenyl(phenylthio)methyl)furan-3-yl)ethan-1-one (3a): Yellow oil (82%, 53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.22 (m, 10H), 6.39 (s, 1H), 5.34 (s, 1H), 2.54 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.0, 167.0, 158.4, 151.4, 138.3, 134.5, 132.3, 128.8, 128.6, 128.3, 127.9, 127.6, 122.0, 108.9, 77.3, 77.00, 76.7, 51.2, 29.1, 14.4 ppm; ν_{max}(KBr)/cm^{-1} = 2924, 1672, 1564, 140, 1228, 1020, 813, 743; HRMS-ESI (m/z) calcd for $C_{21}H_{20}SO_2Na$ [M + Na]$^+$: 345.0925, found 345.0918.

1-(2-Methyl-5-(phenyl(*p*-tolylthio)methyl)furan-3-yl)ethan-1-one (3b): Yellow oil (91%, 61 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36-7.24 (m, 7H), 7.10-7.12 (d, J = 8.0 Hz, 2H), 7.08 (m, 2H), 6.58 (s, 1H), 5.73 (s, 1H), 2.31 (s, 3H), 2.27 (s, 3H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 193.9, 157.8, 151.7, 138.9, 137.6, 132.2, 130.8, 130.1, 129.0, 128.6, 128.2, 122.4, 109.1, 49.6, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 29.6, 21.0, 14.5 ppm; v_{max}(KBr)/cm^{-1} = 3347, 3065, 2924, 1672, 1570, 1227, 951, 753 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{21}H_{21}NaSO_2$ [M + Na]$^+$: 359.1082, found 359.1080.

1-(5-(((4-(*tert*-Butyl)phenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3c): Yellow oil (90%, 68 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52-7.42 (m, 7H), 7.34-7.29 (m, 2H), 6.57 (s, 1H), 5.78 (s, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 1.23 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 193.9, 157.8, 151.8, 150.6, 139.2, 131.5, 129.1, 128.6, 128.2, 126.3, 122.3, 109.1, 49.4, 34.7, 31.4, 29.6, 14.5 ppm; v_{max}(KBr)/cm^{-1} = 3059, 2924, 1672, 1569, 1428, 1231, 1021, 951 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{24}H_{27}SO_2$ [M + H]$^+$: 379.1726, found 379.1728.

1-(5-(((4-Methoxyphenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3d): Yellow oil (44%, 31 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.21 (m, 7H), 6.75-6.73 (d *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 5.18 (s, 1H), 3.73 (s, 3H), 2.54 (s, 3H), 2.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl$_3$) δ 193.9, 159.9, 158.1, 151.4, 138.5, 135.8, 128.5, 128.2, 127.7, 124.4, 121.9, 114.3, 108.7, 77.3, 77.0, 76.7, 55.1, 52.4, 29.0, 14.3, 14.1 ppm; v_{max}(KBr)/cm^{-1} = 3446, 2923, 2846, 1664, 1561, 1237, 1033 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{21}H_{20}SO_3Na$ [M + Na]$^+$: 375.1031, found 375.1029.

1-(5-(((4-Aminophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3e): Brown oil (63%, 42 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.28 (m, 5H), 7.09 (d, *J*

= 8.0 Hz, 2H), 6.52-6.50 (d, *J* = 32.0 Hz, 2H), 5.12 (s, 1H), 6.36 (s, 1H), 3.53 (s, 1H), 2.54 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) *δ* 194.2, 158.3, 151.75, 146.9, 138.8, 136.3, 128.5, 128.4, 127.7, 122.0, 121.4, 115.3, 108.7, 77.4, 77.1, 76.8, 52.8, 29.2, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2990, 1757, 1666, 1562, 1456, 1383, 1241, 1053 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{20}H_{19}SNO_2Na$ [M + Na]$^+$: 360.1034, found 360.1025.

Methyl 4-(((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)thio)benzoate (3f): Yellow oil (90%, 68 mg); ^1H NMR (400 MHz, DMSO-d_6) *δ* 7.83 (d, *J* = 8.3 Hz, 2H), 7.54 - 7.45 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 6.66 (s, 1H), 6.11 (s, 1H), 3.82 (s, 3H), 2.50 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) *δ* 193.8, 166.2, 156.0, 151.0, 142.0, 138.2, 130.0, 129.2, 128.9, 128.6, 128.5, 127.7, 122.5, 109.5, 52.6, 47.4, 29.6, 14.6 ppm. ν_{max}(KBr)/cm^{-1} = 2926, 2869, 1676, 1563, 1227, 951, 808, 631; HRMS-ESI (m/z) calcd for $C_{22}H_{21}SO_4$ [M + H]$^+$: 381.1155, found 381.1157.

1-(2-Methyl-5-(phenyl((4-(trifluoromethyl)phenyl)thio)methyl)furan-3-yl)ethan-1-one (3g): Yellow oil (86%, 67 mg); ^1H NMR (400 MHz, DMSO-d_6) *δ* 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 18.5 Hz, 4H), 7.36 (dd, *J* = 17.9, 10.2 Hz, 3H), 6.65 (s, 1H), 6.10 (s, 1H), 2.49 (s, 3H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) *δ* 194.0, 158.1, 151.0, 138.2, 138.1, 129.8, 129.2, 128.6, 128.5, 126.1, 125.9, 123.2, 122.5, 109.5, 47.6, 29.6, 14.4 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) *δ* -60.9 (s); ν_{max}(KBr)/cm^{-1} = 2938, 2850, 1719, 1672, 1280, 1113, 952, 700; HRMS-ESI (m/z) calcd for $C_{21}H_{17}F_3NaSO_2$ [M + Na]$^+$: 413.0799, found 413.0796.

1-(5-(((4-Chlorophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3h)

Yellow oil (84%, 60 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (m, 2H), 7.50-7.44 (m, 3H), 7.38-7.29 (m, 4H), 6.62 (s, 1H), 6.00 (s, 1H), 2.50 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.8, 157.9, 151.2, 138.3, 137.1, 133.8, 134.0, 130.2, 129.5, 129.2, 128.6, 128.4, 127.5, 122.4, 109.4, 48.4, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 29.6 ppm; v_{max}(KBr)/cm^{-1} = 2931, 2850, 1675, 1582, 1266, 1116, 700 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{20}H_{17}ClSO_2Na$ [M + Na] $^+$: 379.0535, found 379.0529.

1-(5-(((4-Bromophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3i):

Brown oil (86%, 69 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53-7.46 (m, 4H), 7.36 (s, 2H), 7.34-7.22 (m, 3H), 6.65 (s, 1H), 5.98 (s, 1H), 2.49 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.8, 158.0, 151.2, 138.5, 134.2, 133.3, 132.3, 129.1, 128.7, 128.3, 122.4, 121.0, 109.4, 47.6, 29.5, 14.5 ppm; v_{max}(KBr)/cm^{-1} = 3063, 2923, 1671, 1563, 1225, 949, 820, 744 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{20}H_{17}BrSO_2$ [M + Na]$^+$: 423.0030, found 423.0023.

1-(5-(((3-Chlorophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3j):

Yellow oil (81%, 58 mg); IR: ^{1}H NMR (400 MHz, DMSO-d_6) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50-7.52 (d, *J* = 7.3 Hz, 2H), 7.38-7.44 (m, 3H), 7.29 (s, 4H), 6.62 (s, 1H), 6.00 (s, 1H), 2.50 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.9, 158.1, 150.9, 138.1, 133.9, 131.5, 130.1, 129.2, 128.6, 128.5, 128.1, 124.5, 122.5, 109.5, 47.6, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 29.6, 14.5 ppm; v_{max}(KBr)/cm^{-1} = 3067, 2924, 1673, 1225, 951, 755, 700, 629 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{20}H_{17}ClSO_2Na$ [M + Na]$^+$: 379.0535, found 379.0529.

1-(5-(((2-Fluorophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3k): Yellow oil (89%, 61 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (d, J = 25.4 Hz, 3H), 7.33 (d, J = 32.8 Hz, 4H), 7.16 (d, J = 34.7 Hz, 2H), 6.61 (s, 1H), 5.82 (s, 1H), 2.48 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.8, 162.8, 160.4, 151.1, 138.2, 134.8, 130.7-130.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.0, 128.6, 125.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 122.4, 121.0 (d, $J_{C\text{-}F}$ = 15.3 Hz), 116.1 (d, $J_{C\text{-}F}$ = 17.0 Hz), 109.4, 48.6, 29.5, 14.4 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ -108.8 ppm; ν_{max}(KBr)/cm^{-1} = 2933, 2581, 1718, 1675, 1284, 1117, 830, 700; HRMS-ESI (m/z) calcd for $C_{20}H_{17}FSO_2Na$ [M + Na]$^+$: 363.0831, found 363.0833.

1-(5-(((2-Chlorophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3l): Yellow oil (79%, 56 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (m, 2H), 7.46 (m, 2H), 7.39 (m, 2H), 7.35 (m, 2H), 7.30-7.15 (m, 3H), 6.64 (s, 1H), 6.00 (s, 1H), 2.49 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.9, 158.1, 150.9, 138.1, 133.9, 131.5, 130.1, 129.2, 128.6, 128.5, 128.1, 124.5, 122.5, 109.5, 47.6, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 29.6, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2991, 1757, 1667, 1459, 1240, 1530, 780, cm^{-1}; HRMS-ESI (m/z) calcd for $C_{20}H_{17}ClSO_2Na$ [M + Na]$^+$: 379.0535, found 379.0529.

1-(5-(((2-Bromophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3m): Brown oil (82%, 66 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60-7.50 (m, 1H), 7.49-7.43 (m, 2H), 7.36-7.09 (m, 6H), 6.65 (s, 1H), 5.98 (s, 1H), 2.49 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.8, 158.1 150.9, 138.0, 136.1 133.3, 131.0, 129.2, 128.6, 128.5, 123.9, 122.5, 109.5, 47.9, 40.6, 40.4, 40.2, 40.00, 39.8, 39.6, 39.4, 29.6, 14.6 ppm; v_{max}(KBr)/cm^{-1} = 3061, 2923, 2852, 1674, 1563, 1226, 747, 630 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{20}H_{17}BrSO_2$ [M + Na]$^+$: 423.0030, found 423.0023.

1-(5-(((2-(*tert*-Butyl)phenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3n): Yellow oil (76%, 57 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (d, J = 7.3 Hz, 2H), 7.40 - 7.23 (m, 7H), 6.58 (s, 1H), 5.75 (s, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.8, 157.7, 151.9, 150.5, 139.0, 131.5, 131.22 129.1, 128.6, 128.1, 126.3, 122.3, 109.0, 49.4, 34.5, 31.4, 29.5, 14.5 ppm; v_{max}(KBr)/cm^{-1} = 3067, 2961, 2867, 1675, 1563, 1227, 950, 825, 630 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{24}H_{26}SO_2Na$ [M + Na]$^+$: 401.1551, found 401.1555.

1-(5-(((3,4-Dichlorophenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3o): Yellow oil (86%, 67 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 (s, 1H), 7.50 (d, J = 6.0 Hz, 3H), 7.40-7.26 (m, 4H), 6.63 (s, 1H), 6.03 (s, 1H, 3.36 (s, 2H), 2.48 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO) δ 193.8, 158.1, 151.0, 138.1, 135.7, 132.4, 131.9, 131.2, 131.1, 130.3, 129.2, 128.7, 128.5, 122.4, 109.6, 48.5, 29.6, 14.6 ppm; v_{max}(KBr)/cm^{-1} = 3062, 2926, 1669, 1570, 1435, 1229, 1029, 817, 712; HRMS-ESI (m/z) calcd for $C_{20}H_{16}Cl_2SO_2Na$ [M + Na]$^+$: 413.0146, found 413.013.

1-(5-(((3,5-Dimethylphenyl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3p): Yellow oil (75%, 53 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.49 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 7.29 (d, J = 7.2 Hz, 1H), 6.98 (s, 2H), 6.85 (s, 1H), 6.60 (s, 1H), 5.79 (s, 1H), 2.49 (s, 3H), 2.32 (s, 3H), 2.18 (s, 6H); ^{13}C{^{1}H} NMR (100

MHz, DMSO) δ 193.8, 157.8, 151.7, 139.0, 138.5, 134.2, 129.3, 129.0, 129.0, 128.7, 128.2, 122.4, 109.2, 48.9, 29.6, 21.1, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2926, 2836, 1659, 1468, 1137, 1023, 751; HRMS-ESI (m/z) calcd for $C_{22}H_{22}NaO_2S$ [M + Na]$^+$: 373.1238, found 373.1235.

1-(2-Methyl-5-(phenyl(thiophen-2-ylthio)methyl)furan-3-yl)ethan-1-one (3q): Yellow oil (55%, 36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 6H), 6.95-6.91 (m, 2H), 6.39 (s, 1H), 5.21 (s, 1H), 2.57 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.0, 158.6, 150.7, 137.8, 135.9, 132.0, 131.0, 128.7, 128.4, 128.1, 127.4, 122.1, 109.3, 77.6, 77.0, 76.7, 54.3, 29.1, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2924, 1712, 1468, 1227, 794, 696, 479 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{18}H_{16}NaO_2S_2$ [M + Na]$^+$: 351.0489, found 351.0483.

1-(2-Methyl-5-((naphthalen-1-ylthio)(phenyl)methyl)furan-3-yl)ethan-1-one (3r): Yellow solid (55%, 42 mg); m.p. 99.0-99.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.70 (m, 2H), 7.68-7.66 (m, 2H), 7.44-7.42 (m, 4H), 7.32-7.22 (m, 4H), 6.40 (s, 1H), 5.45 (s, 1H), 2.53 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.0, 158.4, 151.5, 138.4, 134.5, 132.4, 128.9, 128.7, 128.3, 127.9, 127.7, 122.1, 108.9, 77.4, 76.7, 51.2, 29.1, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 3036, 2922, 1671, 1571, 1412, 1229, 952, 705 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{24}H_{20}NaO_2S$ [M + Na]$^+$: 395.1082, found 395.1081.

1-(5-((Adamantan-1-yl)thio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3s): White solid (91%, 69 mg); m.p. 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 1 H), 6.43 (s, 1 H), 5.14 (s, 1 H), 2.54 (s, 3 H), 2.36 (s, 3 H), 2.01 (s, 3 H), 1.85 (s, 6 H), 1.67 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.7, 158.5, 154.4, 141.6, 129.2, 128.6, 127.9, 122.7, 108.8, 47.8, 44.2, 42.6, 36.7, 30.3, 29.7, 15.1 ppm; ν_{max}(KBr)/cm^{-1} = 3057, 2910, 2851, 1674, 1563, 1406, 1227, 739, 702, cm^{-1}; HRMS-ESI (m/z)calcd for $C_{24}H_{28}NaO_2S$ [M + Na]$^+$: 403.1707, found 403.1698.

1-(5-((Benzylthio)(phenyl)methyl)-2-methylfuran-3-yl)ethan-1-one (3t): Yellow oil (93%, 62 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 10H), 6.41 (s, 1H), 4.86 (s, 1H), 3.70- 3.59 (dd, 2H), 2.52 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.0, 158.3, 151.8, 138.5, 137.5, 129.0, 128.8, 128.6, 128.4, 127.9, 127.2, 122.1, 108.5, 77.5, 77.2, 76.8, 46.2, 36.6, 29.2, 14.6 ppm; ν_{max}(KBr)/cm^{-1} = 2935, 2836, 2046, 1866, 1670, 1578, 1477, 1029 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{21}H_{20}SO_2Na$ [M + Na]$^+$: 359.1082, found 359.1076.

1-(2-Methyl-5-((phenethylthio)methyl)furan-3-yl)ethan-1-one (3u): Yellow oil (88%, 48 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 7.27 (t, J = 7.3 Hz, 2H), 7.22-7.13 (m, 3H), 6.61 (s, 1H), 3.75 (s, 2H), 2.80 (t, J = 7.2 Hz, 2H), 2.71 (t, J = 7.3 Hz, 2H), 2.50 (s, 3H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 194.0, 157.5, 150.2, 140.9, 129.0, 128.8, 126.6, 122.4, 108.7, 35.6, 32.9, 29.6, 27.4, 14.6 ppm; ν_{max}(KBr)/cm^{-1} = 3034, 2925, 1672, 1571, 1021, 726; HRMS-ESI (m/z) calcd for $C_{16}H_{18}SO_2Na$ [M + Na]$^+$: 297.0925, found 297.0919.

1-(5-((Butylthio)methyl)-2-methylfuran-3-yl)ethan-1-one (3v): Yellow oil (92%, 21 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 6.61 (s, 1H), 3.73 (s, 2H), 2.52 (s, 3H), 2.49 (d, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.55-1.44 (m, 2H), 1.36 (dt, J = 14.6, 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 194.0, 157.3, 150.4, 122.5, 108.4, 31.2, 31.1, 29.6, 27.4, 21.8, 14.5, 14.0 ppm; ν_{max}(KBr)/cm^{-1} = 2930, 2127, 1662, 1021, 826, 764; HRMS-ESI (m/z) calcd for $C_{12}H_{18}NaO_2S$ [M + Na]$^+$: 249.0925, found 249.0922.

1-(5-((Cyclohexylthio)methyl)-2-methylfuran-3-yl)ethan-1-one (3w): Yellow oil (89%, 45 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 6.59 (s, 1H), 3.76 (s, 2H), 2.67 (s, 1H), 2.51 (s, 3H), 2.36 (s, 3H), 1.91 (s, 2H), 1.68 (s, 2H), 1.56 (s, 1H), 1.26 (s, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 194.0, 157.2, 150.8, 122.5, 108.2, 43.2, 33.4, 29.6, 26.0, 25.8, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2927, 1673, 1569, 1416, 854, 616; HRMS-ESI (m/z) calcd for $C_{14}H_{20}SO_2Na$ [M + Na]$^+$: 275.1082, found 275.1081.

1-(5-((4-Ethylphenyl)(*p*-tolylthio)methyl)-2-methylfuran-3-yl)ethan-1-one (3x): Yellow oil (80%, 58 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.57 (s, 1H), 5.69 (s, 1H), 2.56 (d, *J* = 22.7 Hz, 2H), 2.47 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H), 1.13 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 193.8, 157.6, 151.9, 143.7, 137.4, 136.1, 132.0, 131.1, 130.0, 128.5, 128.4, 122.4, 109.0, 49.4, 29.5, 28.2, 21.0, 15.8 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2966, 2926, 1676, 1563, 1404, 1227, 951, 808, 631 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{26}H_{22}NaO_2S$ [M + Na]$^+$: 421.1238, found 421.1238.

1-(5-((3-Bromophenyl)(*p*-tolylthio)methyl)-2-methylfuran-3-yl)ethan-1-one (3y): Yellow oil (82%, 68 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 7.63 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.31 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 2H), 6.62 (s, 1H), 5.80 (s, 1H), 2.49 (s, 3H), 2.33 (s, 3H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ

193.9, 158.0, 151.0, 141.6, 137.9, 132.4, 131.3, 131.2, 131.1, 130.2, 130.2, 130.1, 127.7, 122.4, 122.1, 109.4, 48.7, 29.6, 21.1, 14.5 ppm; v_{max}(KBr)/cm^{-1} = 2925, 2857, 1672, 1571, 1411, 1234, 804, 699 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{21}H_{20}BrO_2SNa$ $[M + Na]^+$: 437.0187, found 437.0182.

1-(2-Methyl-5-((*p*-tolylthio)methyl)furan-3-yl)ethan-1-one (3z): Yellow oil (82%, 43 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.74 (s, 1H), 4.38 (s, 2H), 2.71 (s, 3H), 2.53 (s, 3H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 193.7, 157.4, 149.5, 136.5, 131.8, 130.2, 130.1, 122.4, 108.9, 30.4, 29.4, 20.9, 14.4 ppm; v_{max}(KBr)/cm^{-1} = 3016, 2921, 1675, 1565, 1232, 953, 805, 632 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{15}H_{16}NaO_2S$ $[M + Na]^+$: 283.0769, found 283.0760.

1-(2-Methyl-5-((*p*-tolylthio)(triisopropylsilyl)methyl)furan-3-yl)ethan-1-one (3aa): Yellow oil (94%, 74 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 6.8 Hz, 2H), 6.38 (s, 1H), 3.97 (s, 1H), 2.48 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 1.25 (dd, *J* = 14.5, 7.1 Hz, 3H), 1.09 (dd, *J* = 20.2, 7.2 Hz, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 193.9, 156.5, 152.5, 136.4, 133.1, 130.2, 129.8, 122.7, 107.4, 30.0, 29.5, 21.0, 19.0, 14.6, 11.6; v_{max}(KBr)/cm^{-1} = 2924, 1672, 1564, 140, 1228, 1020, 813, 743; HRMS-ESI (m/z) calcd for $C_{24}H_{37}SiSO_2$ $[M + H]^+$: 417.2277, found 417.2275.

6,6-Dimethyl-2-(phenyl(*p*-tolylthio)methyl)-6,7-dihydrobenzofuran-4(5*H*)-one (3ab): Yellow oil (71%, 53 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.37 - 7.23 (m, 5H), 7.08 (s, 2H), 6.40 (s, 1H), 5.79 (s, 1H), 2.71 (s, 2H), 2.51 (s, 2H), 2.24 (s, 3H), 1.03 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 193.3, 166.8, 154.7, 138.7, 137.7, 132.4, 130.6, 130.1, 129.1, 128.6, 128.3, 120.2, 104.6, 51.7, 49.6, 35.4, 28.5, 28.1, 21.1 ppm; ν_{max}(KBr)/cm^{-1} = 2985, 1727, 1689, 1382, 1240, 1052, 693 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{24}H_{24}NaO_2S$ [M + Na]$^+$: 399.1389, found 399.1385.

2-Methyl-5-(phenyl(*p*-tolylthio)methyl)-3-tosylfuran (3ac): Yellow oil (56%, 50 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 7.75 (d, J = 7.9 Hz, 2H), 7.45 - 7.22 (m, 7H), 7.18 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.7 Hz, 2H), 6.44 (d, s, 1H), 5.69 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H), 2.21 (d, J = 8.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 156.2, 153.0, 144.6, 139.5, 138.2, 137.9, 132.8, 130.5, 130.2, 130.0 129.1, 128.6, 128.3, 127.0, 123.4, 108.2, 49.5, 21.5, 21.0, 13.0 ppm; ν_{max}(KBr)/cm^{-1} = 3040, 2926, 2853, 1671, 1571, 1405, 1231, 952, 761, 698, 629 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{26}H_{25}O_3S_2$ [M + H]$^+$: 449.1240, found 449.1241.

Butyl 2-Methyl-5-(phenyl(*p*-tolylthio)methyl)furan-3-carboxylate (3ad): Yellow oil (81%, 64 mg); ^1H NMR (400 MHz, DMSO-d_6) δ 7.34-7.05 (m, 9H), 6.40 (s, 1H), 5.76 (s, 1H), 4.12 (m, 2H), 3.34 (s, 3H), 2.24 (s, 3H), 1.58 (m, 2H), 1.36(m, 2H), 0.89 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 163.4, 158.9, 152.1, 138.8, 137.6, 132.1, 130.9, 130.1, 129.1, 128.6, 128.2, 114.0, 109.0, 64.0, 49.4, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 30.7, 21.1, 19.2, 14.0 ppm; ν_{max}(KBr)/cm^{-1} = 2951, 1712, 1649, 1427, 1234, 1073, 1009, 806 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{24}H_{26}NaO_3S$ [M + Na]$^+$: 417.1500, found 417.1500.

***tert*-Butyl 2-Methyl-5-(phenyl(*p*-tolylthio)methyl)furan-3-carboxylate (3ae):**

Yellow oil (85%, 67 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46-7.44 (m, 2H), 7.38-7.33 (m, 5H), 7.26-7.07 (m, 2H), 6.35 (s, 1H), 5.75 (s, 1H), 3.36 (s, 2H), 2.45 (s, 3H), 2.27 (s, 3H), 1.46 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.7, 158.3, 151.8, 138.9, 137.5, 131.9, 134.0, 130.1, 129.6, 129.0, 128.6, 128.2, 115.4, 109.2, 96.4, 80.7, 49.4, 40.7, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 28.3, 21.1, 14.0 ppm; v_{max}(KBr)/cm^{-1} = 2973, 1707, 1591, 1402, 1243, 1164, 1080, 804 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{24}H_{26}NaO_3S$ [M + Na]$^+$: 417.1500, found 417.1500.

Ethyl 2-Cyclopropyl-5-(phenyl(*p*-tolylthio)methyl)furan-3-carboxylate (3af): Yellow oil (86%, 67 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (s, 2H), 7.29 (d, J = 47.6 Hz, 5H), 7.09 (d, J = 7.6 Hz, 2H), 6.31 (s, 1H), 5.71 (s, 1H), 4.19 (s, 2H), 2.66 (s, 1H), 2.24 (s, 3H), 1.25 (s, 3H), 1.02 (s, 2H), 0.79 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.5, 162.6, 151.0, 138.7, 137.6, 132.3, 130.8, 130.0, 129.0, 128.5, 128.2, 113.4, 109.1, 60.3, 49.4, 21.1, 14.6, 9.4, 9.1, 8.9 ppm; v_{max}(KBr)/cm^{-1} = 2926, 1707, 1590, 1308, 1229, 1060, 804, 709 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{24}H_{24}NaO_3S$ [M + Na]$^+$: 415.1344, found 415.1341.

Ethyl 2-Phenyl-5-(phenyl(*p*-tolylthio)methyl)furan-3-carboxylate (3ag): Yellow oil (63%, 54 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (s, 2H), 7.54 (d, J = 7.3 Hz, 2H), 7.49 - 7.24 (m, 8H), 7.13 (s, 2H), 6.60 (s, 1H), 5.90 (s, 1H), 4.21 (s, 2H), 2.26 (s, 3H), 1.22 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.9, 156.3, 153.4, 138.5, 137.7, 136.5, 132.3, 130.1, 130.0, 129.7, 129.2, 128.7, 128.6, 128.4, 128.3, 114.5, 111.2, 60.8, 49.4, 21.0, 14.4 ppm; v_{max}(KBr)/cm^{-1} = 2963, 1710, 1549, 1476, 1386, 1249, 1064, 1028, 801, 688, 495 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{27}H_{24}NaO_3S$ [M +

Na]$^+$: 451.1344, found 451.1336.

Ethyl 2-(3-Fluorophenyl)-5-(phenyl(*p*-tolylthio)methyl)furan-3-carboxylate (3ah): Yellow oil (72%, 64 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70- 7.62 (m, 2H), 7.52 (dd, J = 16.0, 7.2 Hz, 3H), 7.40 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 7.4 Hz, 4H), 7.13 (d, J = 4.9 Hz, 2H), 6.61 (s, 1H), 5.92 (s, 1H), 4.22 (q, J = 6.8 Hz, 2H), 2.24 (d, J = 16.2 Hz, 3H), 1.24 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.9, 154.6, 154.1, 138.4, 137.9, 132.4, 131.4-131.3 (d, J_{C-F} = 8.7 Hz), 131.1-131.0 (d, J_{C-F} = 8.6 Hz), 130.2, 129.3, 128.8, 128.6, 128.5, 124.3, 117.0, 116.7, 115.5, 115.0, 115.1-114.8 (d, J_{C-F} = 24 Hz), 111.3, 61.1, 49.4, 21.1, 14.5 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.8 ppm; v_{max}(KBr)/cm^{-1} = 2985, 1762, 1669, 1557, 1240, 1052, 810, 692 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{27}H_{23}FNaO_3S$ [M + Na]$^+$: 469.1250, found 469.1245.

Ethyl 2-(4-Methoxyphenyl)-5-(phenyl(*p*-tolylthio)methyl)furan-3-carboxylate (3ai): Orange oil (63%, 58 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (s, 2H), 7.55 (s, 2H), 7.39 (s, 4H), 7.04 (d, J = 21.8 Hz, 5H), 6.58 (s, 1H), 5.87 (s, 1H), 4.21 (s, 2H), 3.80 (s, 3H), 2.24 (s, 3H), 1.20 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.0, 160.7, 156.7, 152.5, 138.7, 137.7, 132.3, 130.8, 130.0, 129.1, 128.6, 128.3, 114.1, 113.1, 111.1, 60.6, 55.7, 49.5, 21.0, 14.4 ppm; v_{max}(KBr)/cm^{-1} = 2975, 1709, 1496, 1247, 1050, 1023, 827, 504 cm^{-1}; HRMS-ESI (m/z)calcd for $C_{28}H_{26}NaO_4S$ [M + Na]$^+$: 481.1449, found 481.1440.

N^5-((*R*)-3-(((4-Acetyl-5-methylfuran-2-yl)methyl)thio)-1-((carboxymethyl)amino) -1-oxopropan-2-yl)-L-glutamine (3aj): Yellow oil (76%, 67 mg); $[\alpha]_D^{22}$ 13.00 (*c* 10 mg/mL, MeCN); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.62 (s, 1H), 4.03 (q, J = 7.0 Hz, 1H), 3.83 (s, 2H), 3.27 (s, 2H), 2.34 (s, 4H), 1.99 (s, 1H), 1.52 (s, 5H), 1.22 (d, J = 38.1 Hz, 5H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 194.0, 168.2, 157.3, 150.1, 122.4, 108.6, 61.1, 48.3, 29.5, 28.1, 24.5, 14.5. ν_{max}(KBr)/cm^{-1} = 2924, 1672, 1564, 140, 1228, 1020, 813, 743; HRMS-ESI (m/z) calcd for $C_{18}H_{26}N_3O_8S$ [M + H]$^{+}$: 444.1435, found 444.1434.

***n*-Butyl 5-(((2-(Methoxycarbonyl)phenyl)thio)methyl)-2-methylfuran-3-carboxylate (3ak):** Yellow oil (85%, 62 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 3.2 Hz, 2H), 7.22 (ddd, J = 7.8, 5.3, 2.5 Hz, 1H), 6.50 (s, 1H), 4.24 (s, 2H), 4.11 (t, J = 6.5 Hz, 2H), 3.80 (s, 3H), 2.46 (s, 3H), 1.65 - 1.52 (m, 2H), 1.40 - 1.27 (m, 2H), 0.87 (td, J = 7.3, 1.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.6, 163.4, 158.6, 149.3, 139.8, 133.1, 131.2, 128.0, 126.9, 125.1, 114.2, 109.3, 64.1, 52.6, 30.7, 28.4, 19.3, 14.0, 13.9 ppm; ν_{max}(KBr)/cm^{-1} = 2950, 1708, 1577, 1439, 1261, 1050, 742; HRMS-ESI (m/z)calcd for $C_{19}H_{22}NaO_5S$ [M + Na]$^{+}$: 385.1080, found 385.1083.

1-(5-(((4-Bromophenyl)thio)methyl)-2-methylfuran-3-yl)ethan-1-one (3al): Yellow oil (88%, 57 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.39 (d, J = 8.5 Hz, 2H), 7.26-7.1 (d, J = 11.0 Hz, 2H), 6.31 (s, 1H), 4.00 (s, 1H), 2.55 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 193.7, 158.1, 148.5, 134.2, 132.3, 132.0, 122.1, 121.1, 108.4, 76.7, 31.4, 29.0, 14.3 ppm; ν_{max}(KBr)/cm^{-1} = 2922, 1671, 1564, 1402, 1229, 850, 811; HRMS-ESI (m/z)calcd for $C_{14}H_{13}BrNaO_2S$ $[M + Na]^+$: 346.9712, found 346.9707.

Typical Procedure for Larger Scale Synthesis of 1-(2-methyl-5-(phenyl(p-tolylthio)methyl)furan-3-yl)ethan-1-one (3b)

To a solution of 3-(3-phenylprop-2-yn-1-ylidene)pentane-2,4-dione (**1a**, 2.0 mmol, 424 mg) and DBU (2.0 mmol, 125 mg) in MeCN (20 mL, 0.1 M) was added benzenethiol (**2b**, 310 mg, 2.5 mmol). The mixture was stirred at 60 ^{o}C (oil bath) for 6 h. After the reaction was completed (monitored by TLC), the reaction was quenched with H_2O, and the crude product was extracted with ethyl acetate (30 mL × 3). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum. The resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate (20: 1) as eluent to afford the desired product **3b** in 85% yield (571 mg).

Typical Procedure for Preparation of 1-(2-Methyl-5-(tosylmethyl)furan-3-yl)ethan-1-one (4)

To a solution of 1-(2-methyl-5-((*p*-tolylthio)methyl)furan-3-yl)ethan-1-one (**3u**, 0.20 mmol, 52.0 mg) in MeOH/H_2O (3 mL) was added $NaIO_4$ (0.24 mmol, 47.5 mg). The mixture was stirred at room temperature for 24 h. After the reaction was completed (monitored by TLC), the reaction was quenched with H_2O, and the crude product was extracted with ethyl acetate (6 mL × 3). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum. The resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate (10: 1).

1-(2-Methyl-5-(tosylmethyl)furan-3-yl)ethan-1-one (4): Yellow oil (91%, 53 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (s, 2H), 7.43 (s, 2H), 6.60 (s, 1H), 4.76 (s, 1H), 2.42 (s, 6H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 193.8, 158.7, 145.1, 141.7, 136.0, 130.2, 128.7, 122.9, 113.0, 54.8, 29.6, 21.6, 14.4 ppm; ν_{max}(KBr)/cm^{-1} = 3644, 2923, 1673, 1564, 1314, 1148, 954, 820; HRMS-ESI (m/z)calcd for $C_{15}H_{16}NaO_4S$ [M + Na]$^+$: 315.0667, found 315.0666.

Typical Procedure for the Synthesis of 1-(2-Methyl-5-((*p*-tolylsulfinyl)methyl)furan-3-yl)ethan-1-one (5)

To a solution of 1-(2-methyl-5-((*p*-tolylthio)methyl)furan-3-yl)ethan-1-one (**3u**, 0.20 mmol, 52.0 mg) in CH_2Cl_2 (1 mL) was added *m*-CPBA (0.16 mmol, 27.6 mg). The mixture was stirred at room temperature for 4 h. After the reaction was completed (monitored by TLC), the reaction was quenched with H_2O, and the crude product was extracted with ethyl acetate (6 mL × 3). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum. The resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate (10: 1).

1-(2-Methyl-5-((*p*-tolylsulfinyl)methyl)furan-3-yl)ethan-1-one (5): Yellow oil (76%, 42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.36 (s, 1H), 3.94 (t, J = 12.1 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 193.6, 159.1, 142.0, 141.7, 139.4, 129.7, 124.1, 122.3, 111.9, 55.9, 28.9, 21.3, 14.2 ppm; v_{max}(KBr)/cm^{-1} = 3686, 1673, 1570, 1467, 1223, 1653, 945, 750, 692; HRMS-ESI (m/z)calcd for $C_{15}H_{16}NaO_3S$ [M + Na]$^+$: 299.0718, found 299.0713.

General Procedure for Preparation of 1-(5-(([1,1'-Biphenyl]-4-ylthio)methyl)-2-methylfuran-3-yl)ethan-1-one (6)

To a solution of 1-(5-(((4-bromophenyl)thio)methyl)-2-methylfuran-3-yl)ethan-1-one (3ad, 0.2 mmol, 64.8 mg), PPh_3 (15 mol %, 39.3 mg) and $Pd(OAc)_2$ (5 mol %, 11.2 mg) was added $PhB(OH)_2$ (0.4 mmol, 48.8 mg) in THF/H_2O = 2/1 (3.0 mL). The mixture was stirred at room temperature for 12 h. After the reaction was completed (monitored by TLC), the reaction was quenched with H_2O, and the crude product was extracted with ethyl acetate (6 mL × 3). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuum. The resulting residue was purified by column chromatography on silica gel with light petroleum ether/ethyl acetate (20: 1).

1-(5-(([1,1'-Biphenyl]-4-ylthio)methyl)-2-methylfuran-3-yl)ethan-1-one (6): White solid (82%, 53 mg); m.p. 70.4-70.8 ^oC ; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 23.7 Hz, 4H), 7.44 - 7.31 (m, 5H), 6.33 (s, 1H), 4.04 (s, 2H), 2.55 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.6, 157.8, 148.9, 140.1, 139.9, 134.1, 131.0, 128.8, 127.5, 126.8, 122.0, 108.3, 31.4, 29.0, 14.4 ppm; v_{max}(KBr)/cm^{-1} = 2927, 1748, 1570, 1439, 1261, 1050, 742; HRMS-ESI (m/z)calcd for $C_{20}H_{18}NaO_2S$ [M + Na] $^+$: 345.0925, found 345.0925.

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra data for all compounds. X-ray crystallographic data for **3s**. This material is available free of charge via the Internet at http://pubs.acs.org.

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