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Synthesis of Sulfonylated Lactones *via* Ag-Catalyzed Cascade Sulfonylation/Cyclization of 1,6-Enynes with Sodium Sulfinates

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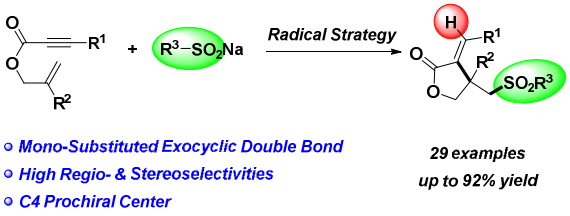


Abstract: A novel strategy for the synthesis of sulfonylated lactones *via* Ag-catalyzed radical addition/cyclization reaction of 1,6-enynes and sodium sulfinates has been developed. The reaction presents high stereoselectivity under mild conditions with C4 prochiral center construction in one step. The ESR experiments and relevant mechanistic studies indicated that a radical pathway should be involved in this transformation.

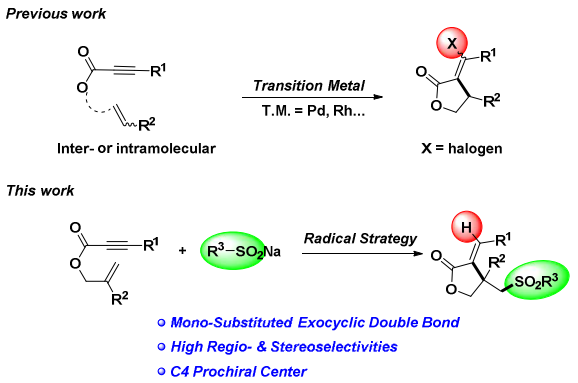
There has been a growing interest in the rational design of drug-framework molecules through the introduction of different kinds of special functional groups.[1] Owing to the distinctive structure and electronic features, the sulfonyl group is one of the most

important members of this family, which has been extensively exploited in medicinal chemistry and agrochemical industry.[2] In view of these applications, several elegant methods for incorporating the sulfonyl group into organic molecules by transition metal-catalyzed[3] as well as free radical-mediated[4] pathways have been established. Nevertheless, the scope of sulfonyl substrates was usually limited and the reaction conditions were relatively harsh. Therefore, the development of versatile and efficient methods for constructing different useful skeletons bearing sulfonyl group is highly desirable.

In addition, α-methylene-γ-butyrolactones are ubiquitous subunits in a wide variety of sequiterpenes, which are known to possess significant biological activities.[5] The exocyclic double bond is considered not only to be responsible for the interesting biological properties of γ-lactones, but also serve as a functional group for further manipulations in organic synthesis.[6] The development of methods facilitating the synthesis of γ-lactones has attracted attention from many research groups due to their intriguing biological activities and their potential as synthetic intermediates[7,8] For example, Zhang's group has reported the Rh-catalyzed oxidative cyclization of the enyne substrates to construct the γ-lactone products.[7d] Recently, a Pd-catalyzed intermolecular carboesterification of alkenes with alkynes for the synthesis of α-methylene-γ-butyrolactones has been developed by our group.[9a] However, most of these methods required prefunctionalized precursors or noble transition-metals, which generated the halo-substituted double bond products. Besides, to the best of our knowledge, the introduction of sulfone groups into the unique lactone skeleton is still

less explored. As part of our continuing program on γ-lactone synthesis[9] and sulfonylation reactions,[10] herein, we disclose a convenient and concise method for the construction of diverse sulfonylated lactones by using sulfinate sodium as the key starting materials and $AgNO_3$ as catalyst in a one-pot manner.[11] This method provides an efficient entry to the mono-substituted alkene lactone products with C4 prochiral center, which should find the potential applications in natural product synthesis and medicinal chemistry (Scheme 1).

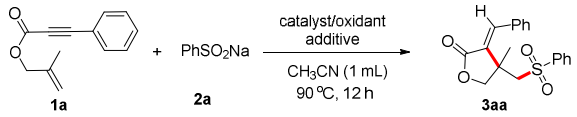
Scheme 1. Methods for Sulfonylated γ-Lactones



Initially, we chose 2-methylallyl 3-phenylpropiolate (**1a**) and sodium benzensulfinate (**2a**) as the model substrates for the condition optimization (Table 1). As expected, when **1a** was treated with **2a** in the presence of 10 mol % of $AgNO_3$ and $K_2S_2O_8$ as oxidant at 90 ^oC for 12 h, the desired sulfonylated lactone **3aa** was detected in 40% GC yield (Table 1, entry 1). And the molecular structure of **3aa** was unambiguously determined by X-ray crystallographic analysis (see the Supporting Information for details).[12] Subsequent survey on a series of representative oxidants revealed that $K_2S_2O_8$ gave the best result, however, TBHP, CuO, DDQ or $PhI(OAc)_2$ was not suitable for this reaction (Table 1, entries 2-5). These results suggested that

both Ag(0) and Ag(I) were efficient for this cyclization reaction, although the yields were not enhanced obviously (Table 1, entries 6-8). According to the literature,[13] we supposed that the nitrates or diluted nitric acid might have an acceleration effect on this reaction, and different nitrates as well as diluted nitric acid were screened for this transformation. When 2.0 equivalents of $Zn(NO_3)_2 \cdot 6H_2O$ was used as an additive, the desired product **3aa** was obtained in 58% yield (Table 1, entry 13). Pleasingly, when 0.25 mL HNO_3 (0.4 M) was added into the reaction, the yield of **3aa** was improved to 74% (Table 1, entry 15). Control experiments indicated that the product yield declined obviously in the absence of Ag catalyst (Table 1, entry 16). Additionally, when lowering the reaction temperature, the yield of **3aa** declined dramatically. Thus, the optimized reaction conditions were affirmed as follows: 10 mol % $AgNO_3$ as the catalyst, 2.0 equiv of $K_2S_2O_8$ and HNO_3 (0.4 M, 0.25 mL) as the additive in CH_3CN at 90 °C for 12 h.

Table 1. Optimization of Reaction Conditions[a]



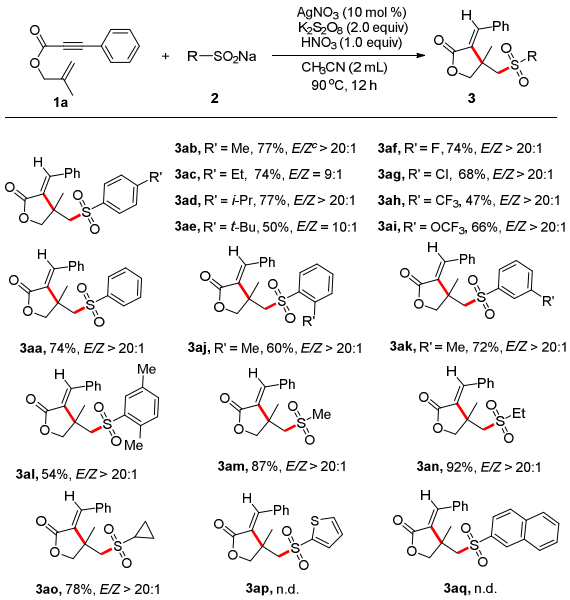
Entry[a]	Catalyst	Oxidant	Additive	Yield (%)[b]
1	$AgNO_3$	$K_2S_2O_8$	-	40
2	$AgNO_3$	TBHP	-	N.R.
3	$AgNO_3$	CuO		N.D.
4	$AgNO_3$	DDQ	-	N.R.
5	$AgNO_3$	$PhI(OAc)_2$	-	N.R.
6	Ag_2O	$K_2S_2O_8$	-	25
7	$AgCO_3$	$K_2S_2O_8$	-	34
8	Ag	$K_2S_2O_8$	-	22
9	$AgNO_3$	$K_2S_2O_8$	$Fe(NO_3)_3$	trace
10	$AgNO_3$	$K_2S_2O_8$	$Ca(NO_3)_2$	trace

11	$AgNO_3$	$K_2S_2O_8$	$Mg(NO_3)_2 \cdot 6H_2O$	9
12	$AgNO_3$	$K_2S_2O_8$	$Cu(NO_3)_2 \cdot 3H_2O$	14
13	$AgNO_3$	$K_2S_2O_8$	$Zn(NO_3)_2 \cdot 6H_2O$	58
14	$AgNO_3$	$K_2S_2O_8$	HNO_3 (4.0 equiv)	34
15	**$AgNO_3$**	**$K_2S_2O_8$**	**HNO_3 (1.0 equiv)**	**74**
16	-	$K_2S_2O_8$	HNO_3 (1.0 equiv)	23

[a] Reaction conditions: All reactions were performed with **1a** (0.1 mmol), **2a** (2.0 equiv), catalyst (10 mol %), additive (2.0 equiv), 1.0 mL solvent at 90 °C for 12 h unless otherwise noted. N.R. = no reaction. N.D. = not detected. [b] Determined by GC-MS.

With the optimized conditions in hand, the substrate scope of sodium sulfinates was examined. As shown in Table 2, the reactions of sodium benzensulfinates bearing both electron-donating (e.g., Me, *t*-Bu) and electron-withdrawing groups (e.g., F, CF_3) at *para*-position on the aryl ring worked well under the optimal conditions and afforded the corresponding γ-lactones **3aa**-**3ai** in moderate yields. In most cases, excellent *Z/E* ratios were obtained, which were determined by ^{1}H-NMR analysis. *Meta*- and *ortho*-substituents on the phenyl ring were well tolerated under this condition (**3aj**, **3ak**). The transformation of disubstituted substrate also proceeded well to give the desired product **3al**. To our delight, the alkyl sodium sulfinates, such as methyl, ethyl and cyclopropyl were compatible with this protocol and transferred to the corresponding products **3am**-**3ao** in good to excellent yields. However, the reactions of heterocyclic substituted sodium sulfinates failed to provide the desired products under the current catalytic conditions (**3ap** and **3aq**).

Table 2. The Reactions of **1a** with Different Sodium Sulfinates **2**[a, b]

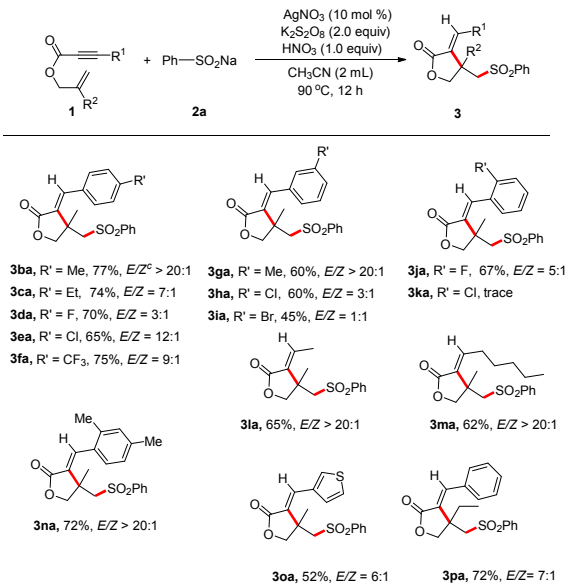


[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $AgNO_3$ (10 mol %), $K_2S_2O_8$ (2 equiv) and HNO_3 (0.4 M, 0.25 mL) in 2 mL CH_3CN at 90 °C for 12 h unless otherwise noted. n.d. = not detected. [b] Determined by GC-MS. [c]The ratio of *E/Z* was determined by ^{1}H-NMR analysis.

After successfully investigating the range of sodium sulfinates, we next evaluated the scope of 1,6-enynes. As depicted in Table 3, for the *para*-position of phenyl ring, the reactions with electron-withdrawing groups (e.g., F, CF_3) provided similar yields to those with electron-donating groups (e.g., Me, Et). Interestingly, the reaction of 2-methylallyl 3-(4-(trifluoromethyl)phenyl) propiolate gave **3fa** in 75% yield. Moreover, the 1,6-enynes with *meta*-substituent at ring position were found to be suitable for this reaction and transfer to the corresponding products **3ga-3ia** in moderate yields. It was worth noting that 2-F substitution on the phenyl ring provided the better yield (67%) than that with 2-Cl substitution. The dependence of the yield upon substitution partners was likely relied on the corresponding steric hindrance.

When R^1 was alkyl substitution, the reaction proceeded smoothly to provide the target products **3la** and **3ma** in 65% and 62% yields, respectively. In addition, the heterocyclic group, such as thienyl, attached to the triple bond was also compatible with the reaction conditions, affording the desired lactone product **3oa** in moderate yield. Substrate with germinal substituents could be converted to the corresponding product **3na** in 72% yield. When substituted allylic enyne substrate was applied to the standard conditions, 72% yield of product **3pa** was isolated, whereas no reaction occurred in the case of unsubstituted olefin (R^2 = H), indicating that the substituents in the internal position of the alkene affected the yield dramatically.

Table 3. The Reactions of Different 1,6-Enynes **1** with **2a**[a, b]



[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $AgNO_3$ (10 mol %), $K_2S_2O_8$ (2 equiv) and HNO_3 (0.4 M, 0.25 mL) in 2 mL CH_3CN at 90 °C for 12 h unless otherwise was noted. [b] Determined by GC-MS. [c]The ratio of *E/Z* was determined by ^{1}H-NMR analysis.

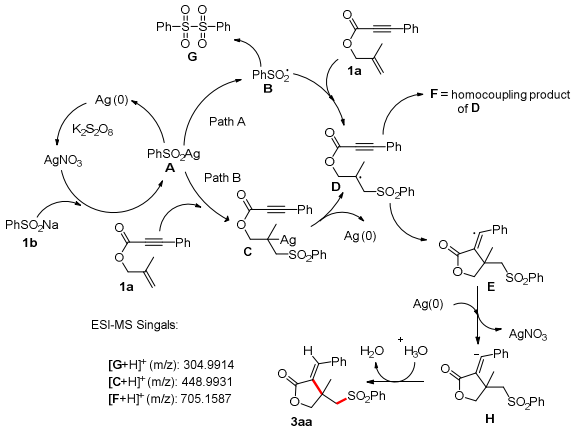
Furthermore, the reaction is scalable and practical since a synthetically useful yield (52%) of the sulfonylated lactone product was obtained when the reaction was performed on 5 mmol scales (Scheme 2).

Scheme 2. Gram-Scale of the Reaction

To gain more insight into the mechanism of this reaction, several control experiments were performed (see the Supporting Information for details). First, when the radical scavenger TEMPO (2 equiv) or BHT (2 equiv) was added under the standard conditions, the yield of product **3aa** declined obviously, indicating the transformation should proceed *via* a free-radical pathway. The electron spin resonance (ESR) experiments were further conducted to support the sulfonyl radical intermediate.[14] An isotopic labeling study with D_2O was then performed and the kinetic isotope effect radio of **3am**/**3am-*d*** was 0.42, which suggested that the source of hydrogen might come from HNO_3 or H_2O. Moreover, the observation of pH experiment was consistent with our assumption. The value increased from 0.40 to 0.61, suggesting that the diluted nitric acid could stimulate the last step of hydrolysis and enhance the product yield. It should be noted that when using the complex $PhSO_2Ag$ (**A**) as the catalyst, the reaction proceeded smoothly and afforded the lactone product in 51% yield, which proved that **A** should be the key intermediate in this process.

Base on the above results and previous reports, a possible mechanism for this transformation was proposed in Scheme 3. First, complex **A** is formed from sodium sulfinate and $AgNO_3$, which is supposed to be the key step in this transformation. When **A** is generated, it may undergo the Path A involving a sliver-promoted generation of the sulfonyl radical **B** (Scheme 4, Path A), which subsequently adds to **1a** to give the alkyl radical **D**. Another possibility for the formation of the alkyl radical **D** is the addition of **A** to **1a** and provides the silver(I) species **C**, followed by the oxidation to form the alkyl radical **D** (Scheme 4, Path B). The resulting alkyl radical **D** then undergoes an intramolecular radical addition and cyclization reaction to afford the intermediate **E**. Finally, there may be a SET process to **E** from Ag(0) to Ag(I) and then give a vinyl anion **H**, which was subsequently protonated by HNO_3 or H_2O to give the desired product **3aa**. The model reaction was also monitored by mass spectrometry experiment (See the Supporting Information for details). It is worth noting that the ESI-MS shows peaks at m/z 304.9914 and m/z 705.1578, which are corresponding to $[G+H]^+$ and $[F+H]^+$, respectively. These signals suggested that the sulfonyl radical was formed during the reaction, which strongly supporting our hypothesis that a radical pathway should be involved in this chemical process.

Scheme 3. Tentative Mechanism



In conclusion, we have established a highly efficient protocol for the synthesis of various sulfonylated lactones *via* Ag-catalyzed radical cascade sulfonylation/cyclization of 1,6-enynes with sodium sulfinates, which would be useful in organic synthesis and medicinal chemistry. With the green sodium sulfinate and $AgNO_3$ catalyst, this reaction shows high efficiency and selectivity, as well as broad substrate scope. The exocyclic mono-substituted double bond and C4 prochiral center also make the present protocol very attractive, which will find its potential applications in the synthesis of more complex and significant pharmaceuticals.[15]

Experimental Section

General Information. Melting points were measured with a melting point instrument and were uncorrected. ^1H and ^{13}C NMR spectra were recorded using a 400/600 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ is solvent. IR spectra were recorded on an FT-IR spectrometer using KBr discs. Melting points were taken on an electrothermal melting point apparatus and without correction. GC–MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer. TLC was

performed by using commercially prepared 100–400 mesh silica gel plates and visualization was effected at 254 nm.

General procedure for the preparation of 1,6-enyne derivatives (1). To a mixture of propiolic acid (10.0 equiv) and allyl alcohol (1.2 equiv) in CH_2Cl_2 (5 mL) was added a solution of DMAP (10 mol %) and DCC (1.5 equiv) in CH_2Cl_2 (5 mL) at 0 ℃. The reaction mixture was stirred for 10 h at 25 ℃ and filtered through a short plug of silica gel, which was rinsed with hexanes/EtOAc = 2/1. The filtrate was concentrated in vacuum and the residue was purified by column chromatography on silica gel (hexanes/EtOAc = 10/1) to give **1**.

General procedure for the preparation of sodium sulfinate derivatives (2). To a mixture of sodium bicarbonate (2.0 equiv) and sodium sulfite (2.0 equiv) in H_2O, was added sulfonyl chloride (5 mmol) at room temperature. The reaction mixture was stirred for 10 h at 80 ^oC and then cooled down to room temperature. Excess H_2SO_4 was added to make the solution reach pH = 1 and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was removed under vacuum and then about 10 mL H_2O was added to dissolve the solid. The solvent was basified with aqueous NaOH to reach pH = 8 and was removed under vacuum to afford the sodium sulfinates **2**.

General procedure for the preparation of sulfonylated γ-lactones (3). To a dried Schlenk tube was charged with 1,6-enynes 1 (0. 5 mmol, 1.0 equiv), sodium sulfinates 2 (1.0 mmol, 2.0 equiv.), $AgNO_3$ (0.05 mmol, 0.1 equiv.), $K_2S_2O_8$ (1.0 mmol, 2.0 equiv.), HNO_3 (0.4 M, 0.25 mL) and CH_3CN (2 mL), which was equipped with a magnetic stirring bar. The mixture was stirred for 12 h at 80 ~ 90 ^oC. After the

reaction was completed, saturated $NaHCO_3$ solvent (2 mL) was added to stop the reaction, and then ethyl acetate (3 × 5 mL) was added into the tube. The combined organic layers were washed with brine to neutral, dried over $MgSO_4$, and concentrated in vacuum. Purification of the residue on a preparative TLC afforded the desired products **3**.

(*E*)-3-Benzylidene-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3aa): Yellow solid (131 mg, 77% yield), m.p. = 129.1 - 130.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75 (d, J = 7.8 Hz, 2H), 7.71 (s, 1H), 7.63 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.41 - 7.36 (m, 3H), 7.31 - 7.28 (m, 2H), 4.72 (d, J = 9.6 Hz, 1H), 4.29 (d, J = 9.6 Hz, 1H), 3.54 (d, J = 14.5 Hz, 1H), 3.17 (d, J = 14.5 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 140.5, 139.7, 134.0, 133.2, 132.5, 129.5, 129.4, 129.1, 128.7, 127.4, 76.3, 60.8, 41.9, 24. 6; IR (KBr) ν_{max} 3628, 3111, 2925, 1753, 1641, 1524, 1310, 1146 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}O_4SNa$ 365.0818; Found 365.0823.

(*E*)-3-Benzylidene-4-methyl-4-(tosylmethyl)dihydrofuran-2(3*H*)-one (3ab): Yellow solid (137 mg, 77% yield), m.p. = 134.2 - 135.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (s, 1H), 7.62 (d, J = 7.7 Hz, 2H), 7.41 - 7.36 (m, 3H), 7.34 - 7.25 (m, 4H), 4.71 (d, J = 9.6 Hz, 1H), 4.28 (d, J = 9.6 Hz, 1H), 3.53 (d, J = 14.5 Hz, 1H), 3.15 (d, J = 14.5 Hz, 1H), 2.42 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.7, 145.1, 139.6, 137.6, 133.2, 132.5, 129.9, 129.5, 129.2, 128.7, 127.4, 76.3, 60.9, 41.9, 24.5, 21.6; IR (KBr) ν_{max} 3685, 3114, 2982, 1753, 1639, 1526, 1309, 1143 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_4SNa$ 379.0975; Found

379.0973.

3-Benzylidene-4-(((4-ethylphenyl)sulfonyl)methyl)-4-methyldihydrofuran-2(3*H*)-one (3ac): Yellow solid (136 mg, 74% yield), m.p. = 120.4 - 121.9 ^{o}C; ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.42 - 7.36 (m, 3H), 7.34- 7.28 (m,4H), 4.73 (d, J = 9.6 Hz, 1H), 4.29 (d, J = 9.6 Hz, 1H), 3.55 (d, J = 14.5 Hz, 1H), 3.17 (d, J = 14.5 Hz, 1H), 2.72 (q, J = 7.4 Hz, 2H), 1.68 (s, 3H), 1.25 (t, J = 7.3 Hz, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 151.3, 139.7, 137.9, 133.3, 132.6, 129.6, 129.3, 129.0, 128.9, 128.8, 127.6, 76.4, 61.0, 42.0, 289, 24.5, 15.1; IR (KBr) ν_{max} 3690, 3117, 2981, 2756, 1755, 1641, 1525, 1478, 1144 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_4SNa$ 393.1131; Found 393.1134.

(*E*)-3-Benzylidene-4-(((4-isopropylphenyl)sulfonyl)methyl)-4-methyldihydrofuran-2(3*H*)-one (3ad): Yellow solid (147 mg, 77% yield), m.p. = 112.1 - 113.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (s, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.42 - 7.36 (m, 3H), 7.36 (d, J = 8.1 Hz, 2H), 7.32 - 7.28 (m, 2H), 4.73 (d, J = 9.6 Hz, 1H), 4.28 (d, J = 9.6 Hz, 1H), 3.54 (d, J = 14.5 Hz, 1H), 3.17 (d, J = 14.5 Hz, 1H), 2.97 (dt, J = 13.5, 6.8 Hz, 1H), 1.68 (s, 3H), 1.25 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.7, 155.8, 139.6, 137.9, 133.2, 132.5, 129.5, 129.2, 128.7, 127.6, 127.5, 76.3, 60.9, 41.9, 34.2, 24.4, 23.5; IR (KBr) ν_{max} 3692, 3117, 2978, 2753, 1756, 1640, 1525, 1478, 1311, 1145 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{24}O_4SNa$ 407.1288; Found 407.1286.

3-Benzylidene-4-(((4-(*tert*-butyl)phenyl)sulfonyl)methyl)-4-methyldihydrofuran-2

(3*H*)-one (3ae): Yellow solid (99 mg, 50% yield), m.p. = 123.5 - 124.1 ^{o}C; ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.68 - 7.65 (m, 2H), 7.63 (s, 1H), 7.49-7.47 (m, 2H), 7.37 - 7.33 (m, 3H), 7.29 - 7.28 (m, 2H), 4.72 (d, J = 9.6 Hz, 1H), 4.23 (d, J = 9.6 Hz, 1H), 3.52 (d, J = 14.6 Hz, 1H), 3.20 (d, J = 14.6 Hz, 1H), 1.62 (s, 3H), 1.27 (s, 9H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 157.9, 139.5, 137.3, 133.0, 132.3, 129.3, 129.1, 128.5, 127.1, 126.2, 76.1, 60.7, 41.6, 35.0, 30.7, 24.4; IR (KBr) ν_{max} 3686, 3115, 2971, 2757, 1756, 1639, 1549, 1478, 1312, 1147 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{26}O_4SNa$ 421.1444; Found 421.1447.

(*E*)-3-Benzylidene-4-(((4-fluorophenyl)sulfonyl)methyl)-4-methyldihydrofuran-2(3*H*)-one (3af): Yellow solid (133 mg; 74% yield), m.p. = 134.5 - 135.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.78 - 7.73 (m, 2H), 7.72 (s, 1H), 7.43 - 7.36 (m, 3H), 7.32 - 7.27 (m, 2H), 7.18 (t, J = 8.3 Hz, 2H), 4.73 (d, J = 9.6 Hz, 1H), 4.29 (d, J = 9.6 Hz, 1H), 3.50 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.4 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 165.9 (d, J = 257.4 Hz), 139.8, 136.6 (d, J = 2.0 Hz), 133.3, 132.4, 130.4 (d, J = 9.7 Hz), 129.6, 129.2, 128.8, 116.8 (d, J = 22.7 Hz), 76.2, 61.1, 42.0, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -102.45 (s); IR (KBr) ν_{max} 3692, 3114, 2984, 2766, 1754, 1639, 1525, 1480, 1320, 1144 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}FO_4SNa$ 383.0724; Found 383.0728.

(*E*)-3-Benzylidene-4-(((4-chlorophenyl)sulfonyl)methyl)-4-methyldihydrofuran-2(3*H*)-one (3ag): Yellow solid (139 mg, 74% yield), m.p. = 132.5 - 133.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.72 (s, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.3 Hz,

2H), 7.42 - 7.38 (m, 3H), 7.32 - 7.28 (m, 2H), 4.73 (d, J = 9.6 Hz, 1H), 4.30 (d, J = 9.6 Hz, 1H), 3.51 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.5 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.9, 140.9, 140.0, 138.9, 133.2, 132.3, 129.7, 129.6, 129.2, 128.9, 128.8, 76.2, 60.9, 41.9, 24.8; IR (KBr) ν_{max} 3691, 3110, 2983, 2766, 1755, 1634, 1526, 1478, 1321, 1145 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}ClO_4SNa$ 399.0428; Found 399.0430.

(*E*)-3-Benzylidene-4-methyl-4-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ah): Yellow solid (96 mg, 47% yield), m.p.= 140.2 - 141.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.83 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 7.68 (s, 1H), 7.40 - 7.34 (m, 3H), 7.29 - 7.24 (s, 2H), 4.70 (d, J = 9.6 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 3.49 (d, J = 14.4 Hz, 1H), 3.17 (d, J = 14.4 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 143.0, 140.0, 135.8 (q, J = 33.3 Hz), 133.2, 132.2, 129.7, 129.2, 128.8, 128.1, 126.6 (q, J = 3.5 Hz), 122.9 (q, J = 271.5 Hz), 76.2, 60.8, 41.9, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -63.40 (s); IR (KBr) ν_{max} 3689, 3112, 2978, 2753, 1755, 1638, 1478, 1311, 1145 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}F_3O_4SNa$ 433.0692; Found 433.0695.

(*E*)-3-Benzylidene-4-methyl-4-(((4-(trifluoromethoxy)phenyl)sulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ai): Yellow oil (140 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8 Hz, 2H), 7.71 (s, 1H), 7.42 - 7.36 (m, 3H), 7.33 (s, 1H), 7.32 - 7.28 (m, 3H), 4.74 (d, J = 9.6 Hz, 1H), 4.28 (d, J = 9.6 Hz, 1H), 3.51 (d, J = 14.5 Hz, 1H), 3.23 (d, J = 14.5 Hz, 1H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170. 6, 153.1, 139.9, 138.6, 133.2, 132.2, 131.0, 130.0, 129.8, 129.6, 129.2, 128.7, 121.1,

76.2, 60.9, 41.9, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.69 (s); IR (KBr) ν_{max} 3690, 3111, 2983, 2767, 1755, 1640, 1525, 1256, 1150 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}F_3O_5SNa$ 449.0641; Found 449.0644.

(*E*)-3-Benzylidene-4-methyl-4-((o-tolylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3aj): Yellow oil (106 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92 (d, J = 7.9 Hz, 1H), 7.73 (s, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.41 - 7.39 (m, 3H), 7.38 - 7.29 (m, 3H), 7.27 (d, J = 3.5 Hz, 1H), 4.69 (d, J = 9.7 Hz, 1H), 4.38 (d, J = 9.7 Hz, 1H), 3.64 (d, J = 14.4 Hz, 1H), 3.07 (d, J = 14.4 Hz, 1H), 2.43 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 139.6, 138.7, 137.5, 134.1, 133.4, 133.0, 132.8, 129.5, 129.3, 129.1, 128.8, 126.9, 76.8, 60.0, 42.1, 24.8, 20.1; IR (KBr) ν_{max} 3694, 3111, 2982, 2768, 1756, 1663, 1526, 1478, 1310, 1245, 1142 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_4SNa$ 379.0975; Found 379.0978.

(*E*)-3-Benzylidene-4-methyl-4-((*m*-tolylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ak): Yellow oil (128 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 (s, 1H), 7.51 - 7.47 (m, 2H), 7.38 - 7.33 (m, 5H), 7.26 - 7.24 (m, 2H), 4.68 (d, J = 9.6 Hz, 1H), 4.23 (d, J = 9.6 Hz, 1H), 3.48 (d, J = 14.5 Hz, 1H), 3.11 (d, J = 14.5 Hz, 1H), 2.35 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.7, 140.4 139.8, 139.7, 134.7, 133.3, 132.5, 129.5, 129.3, 129.2, 128.7, 127.6, 124.5, 76.3, 60.8, 41.9, 24.6, 21.2; IR (KBr) ν_{max} 3691, 3112, 2984, 2769, 1753, 1635, 1525, 1478, 1308, 1241, 1140 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_4SNa$ 379.0975; Found 379.0976.

(*E*)-3-Benzylidene-4-(((2,5-dimethylphenyl)sulfonyl)methyl)-4-methyldihydrofur

an-2(3*H*)-one (3al): Yellow solid (100 mg, 54% yield), m.p. = 107.02 - 108.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.35 - 7.32 (m, 3H), 7.24 - 7.22 (m, 2H), 7.20 (s, 1H), 7.06 (d, J = 7.6 Hz, 1H), 4.62 (d, J = 9.5 Hz, 1H), 4.30 (d, J = 9.5 Hz, 1H), 3.55 (d, J = 14.4 Hz, 1H), 2.98 (d, J = 14.4 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 139.5, 138.3, 136.9, 134.7, 134.2, 133.4, 133.0, 132.7, 130.9, 129.5, 129.0, 128.8, 76.7, 59.8, 42.0, 24.8, 20.7, 19.5; IR (KBr) ν_{max} 3694, 3112, 2983, 2758, 1754, 1637, 1527, 1481, 1307, 1248, 1139 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_4SNa$ 393.1131; Found 393.1131.

(*E*)-3-Benzylidene-4-methyl-4-((methylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3am): White solid (121 mg, 87% yield), m.p. = 120.4 - 121.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.77 (s, 1H), 7.45 - 7.43 (m, 3H), 7.37 - 7.35 (m, 2H), 4.68 (d, J = 9.6 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 3.43 (d, J = 14.2 Hz, 1H), 3.14 (d, J = 14.2 Hz, 1H), 2.82 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 139.7, 133.3, 132.7, 129.6, 129.0, 128.8, 76.0, 59.2, 43.7, 41.6, 24.6; IR (KBr) ν_{max} 3692, 3113, 2984, 2767, 1752, 1631, 1525, 1479, 1307, 1242, 1138 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_4SNa$ 303.0662; Found 303.0661.

(*E*)-3-Benzylidene-4-((ethylsulfonyl)methyl)-4-methyldihydrofuran-2(3*H*)-one (3an): White solid (135 mg, 92% yield), m.p. = 114.8 - 115. 9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75 (s, 1H), 7.43 - 7.41 (m, 3H), 7.35 - 7.34 (m, 2H), 4.64 (d, J = 9.6 Hz, 1H), 4.29 (d, J = 9.7 Hz, 1H), 3.33 (d, J = 14.1 Hz, 1H), 2.99 (d, J = 14.1 Hz, 1H), 2.85 (q, J = 7.4 Hz, 2H), 1.71 (s, 3H), 1.22 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ ppm 170.6, 139.5, 133.7, 133.0, 129.5, 128.9, 128.8, 76.2, 56.1 50.1, 41.5, 24.8, 6.6; IR (KBr) ν_{max} 3695, 3113, 2985, 2760, 1755, 1527, 1480, 1310, 1242, 1137 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_4SNa$ 317.0818; Found 317.0820.

(*E*)-3-Benzylidene-4-((cyclopropylsulfonyl)methyl)-4-methyldihydrofuran-2(3*H*)-one (3ao): Yellow solid (119 mg, 78% yield), m.p. = 109.2 - 110.3 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.77 (s, 1H), 7.43 - 7.42 (m, 3H), 7.38 - 7.36 (m, 2H), 4.66 (d, J = 9.6 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 3.45 (d, J = 14.2 Hz, 1H), 3.15 (d, J = 14.3 Hz, 1H), 1.72 (s, 3H), 1.24 - 1.23 (m, 1H), 1.12 - 1.11 (m, 2H), 0.97 - 0.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.7, 139.6 133.4, 132.9, 129.6, 129.1, 128.8, 76.3, 58.4, 41.5, 31.9, 24.7, 5.2, 5.1; IR (KBr) ν_{max} 3694, 3112, 2983, 2766, 1754, 1639, 1526, 1478, 1321, 1246, 1136 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{18}O_4SNa$ 329.0818; Found 329.0816.

(*E*)-4-Methyl-3-(4-methylbenzylidene)-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ba): Yellow solid (137 mg, 77% yield), m.p. = 140.2 - 140.3 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.65 (s, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.24 - 7.16 (m, 4H), 4.72 (d, J = 9.6 Hz, 1H), 4.26 (d, J = 9.6 Hz, 1H), 3.63 (d, J = 14.6 Hz, 1H), 3.20 (d, J = 14.6 Hz, 1H), 2.38 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 140.5, 140.1, 139.9, 134.0, 131.3, 130.2, 129.5, 129.4, 129.4, 127.4, 76.3, 60.7, 41.8, 24.2, 21.3; IR (KBr) ν_{max} 3689, 3112, 2983, 2772, 1751, 1637, 1524, 1478, 1310, 1242, 1145 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_4SNa$ 379.0975; Found 379.0978.

3-(4-Ethylbenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ca): Yellow solid (137mg, 74% yield), m.p. = 131.7 - 132.8 ^{o}C, ***E* isomer** + ***Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, J = 8.0 Hz, 2H), 7.60 (s, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.4 Hz, 2H), 7.22 - 7.09 (m, 4H), 4.65 (d, J = 9.6 Hz, 1H), 4.21 (d, J = 9.6 Hz, 1H), 3.55 (d, J = 14.6 Hz, 1H), 3.12 (d, J = 14.6 Hz, 1H), 2.60 (dt, J = 15.2, 7.6 Hz, 2H), 1.64 (s, J = 8.0 Hz, 3H), 1.18 (t, J = 7.3 Hz, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.9, 146.4, 140.5, 139.9, 133.9, 131.4, 130.4, 129.6, 129.4, 128.2, 127.4, 76.4, 60.6, 41.8, 28.7, 24.3, 15.2; IR(KBr) ν_{max} 3691, 3112, 2980, 2769, 1752, 1636, 1525, 1478, 1311, 1144 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_4SNa$ 393.1131; Found 393.1133.

3-(4-Fluorobenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3da): Yellow solid (75.6 mg, 70% yield), m.p. = 133.2 - 134.6 ^{o}C; ***E* isomer** + ***Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.89 (m, 0.75H), 7.85 - 7.73 (m, 2H), 7.65 (t, J = 7.3 Hz, 1.6H), 7.55 (dd, J = 13.6, 6.2 Hz, 2H), 7.31 (dd, J = 7.9, 5.6 Hz, 1.4H), 7.12 - 7.10 (m, 2H), 6.76 (s, 0.25H), 4.74 (d, J = 9.6 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 3.50 (d, J = 14.5 Hz, 1H), 3.19 (d, J = 14.5 Hz, 1H), 3.56 - 3.13 (m, 2H), 1.69 (s, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 163.2 (d, J = 251.7 Hz), 140.4, 138.5, 134.1, 133.4 (d, J = 8.7 Hz), 132.3, 131.4 (d, J = 8.4 Hz), 129.5, 127.4, 116.0 (d, J = 22.0 Hz), 76.3, 60.8, 41.8, 24.3; IR (KBr) ν_{max} 3685, 3114, 2982, 1753, 1639, 1526, 1309, 1143 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}FO_4SNa$ 383.0724; Found 383.0726.

3-(4-Chlorobenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)

)-one (3ea): Yellow solid (122 mg, 65% yield), m.p. = 124.6 - 125.4 ^{o}C; ***E* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 7.5 Hz, 1H), 7.59 (s, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 4.73 (d, J = 9.6 Hz, 1H), 4.22 (d, J = 9.6 Hz, 1H), 3.44 (d, J = 24.1 Hz, 1H), 3.22 (d, J = 14.6 Hz, 1H), 1.60 (s, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 140.2, 138.2, 135.5, 134.0, 132.8, 131.5, 130.4, 129.4, 128.9, 127.3, 76.0, 60.7, 41.7, 24.4; IR (KBr) ν_{max} 3692, 3100, 2983, 2770, 1752, 1637, 1523, 1485, 1308, 1245, 1148 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}ClO_4SNa$ 399.0428; Found 399.0432.

4-Methyl-4-((phenylsulfonyl)methyl)-3-(4-(trifluoromethyl)benzylidene)dihydrof uran-2(3*H*)-one (3fa): Yellow solid (153 mg, 75% yield), m.p. = 141.5 - 142.9 ^{o}C; ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.96 - 7.77 (m, 2H), 7.79 - 7.69 (m, 2H), 7.62 (t, J = 9.1 Hz, 3H), 7.56 - 7.48 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 4.76 (d, J = 9.6 Hz, 1H), 4.23 (d, J = 9.6 Hz, 1H), 3.32 (d, J = 14.5 Hz, 1H), 3.20 (d, J = 14.5 Hz, 1H), 1.57 (s, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.1, 140.2, 137.7, 137.1, 134.4, 134.1, 130.0 (q, J = 224.0 Hz), 129. 5, 129.1, 127.5, 127.2, 125.5 (q, J = 3.5 Hz), 75.8, 61.1, 41.8, 24.9; ***E* isomer** ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.86 (s); IR (KBr) ν_{max} 3692, 3110, 2983, 2771, 1754, 1641, 1526, 1477, 1322, 1141 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}F_3O_4SNa$ 433.0692; Found 433.0695.

(*E*)-4-Methyl-3-(3-methylbenzylidene)-4-((phenylsulfonyl)methyl)dihydrofuran-2 (3*H*)-one (3ga): Yellow solid (106 mg, 60% yield), m.p.= 137.7 - 138.8 ^{o}C; ^{1}H NMR

(400 MHz, $CDCl_3$) δ ppm 7.76 (d, J = 7.6 Hz, 2H), 7.69 (s, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 7.32 - 7.25 (m, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.11 (s, 2H), 4.71 (d, J = 9.6 Hz, 1H), 4.30 (d, J = 9.6 Hz, 1H), 3.60 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.5 Hz, 1H), 2.35 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.8, 140.7, 140.0, 138.6, 134.0, 133.2, 132.3, 130.4, 130.0, 129.5, 128.6, 127.4, 126.2, 76.4, 61.0, 41.9, 24.6, 21.4; IR (KBr) ν_{max} 3690, 3110, 2982, 2770, 1754, 1641, 1525, 1478, 1311, 1146 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_4SNa$ 379.0975; Found 379.0974.

(*E*)-3-(3-Chlorobenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ha): Yellow oil (112 mg, 60% yield), ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.82 - 7.64 (m, 2H), 7.58 - 7.49 (m, 2H), 7.46 - 7.43 (m, 2H), 7.28 - 7.13 (m, 3H), 7.09 (d, J = 5.9 Hz, 0.75H), 6.69 (s, 0.25H), 4.47 - 4.67 (m, 1H), 4.19 - 4.08 (m, 1H), 3.41 - 3.11 (m, 2H), 1.58 (s, 1.25H), 1.48 (s, 1.75H). ***E* isomer + *Z* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.1, 167.5, 140.4, 140.2, 138.5, 137.8, 134.9, 134.5, 134.2, 134.0, 133.9, 133.6, 133.6, 132.5, 130.4, 129.9, 129.6, 129.5, 129.4, 129.3, 129.2, 128.8, 128.7, 127.4, 127.2, 126.8, 75.8, 74.3, 63.0, 60.9, 43.6, 41.6, 24.8, 24.6. IR (KBr) ν_{max} 3689, 3107, 2981, 2772, 1755, 1641, 1562, 1477, 1309, 1145 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}ClO_4SNa$ 399.0428; Found 399.0432.

3-(3-Bromobenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ia): Yellow oil (94 mg, 45% yield); ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92 - 7.85 (m, 1.5H), 7.78 (d, J = 7.7 Hz, 1H), 7.66 (dd, J = 23.8, 8.6

Hz, 2H), 7.53 (dd, *J* = 16.6, 8.5 Hz, 2.5H), 7.47 - 7.39 (m, 1H), 7.30 - 7.17 (m, 1.5H), 6.77 (s, .0.5H), 4.84 - 4.76 (m, 1H), 3.50 - 3.19 (m, 2H), 1.67 (s, 0.5H), 1.57 (s, 0.5H); ***E* isomer + *Z* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.0, 167.5, 140.4, 140.2, 138.4, 137.7, 135.2, 134.5, 134.0, 133.9, 133.7, 133.3, 132.6, 132.5, 132.2, 131.6, 130.1, 129.6, 129.4, 129.2, 127.5, 127.3, 127.2, 122.5, 121.8 75.8, 74.3, 63.1, 60.9, 43.7, 41.7, 24.8, 24.6; IR (KBr) ν_{max} 3689, 3108, 2981, 2769, 1750, 1636, 1555, 1476, 1306, 1141 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}BrO_4SNa$ 442.9923; Found 442.9925.

3-(2-Fluorobenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ja): Yellow oil (120mg, 67%yield); ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.82 - 7.64 (m, 2H), 7.65 - 7.61 (m, 2H), 7.58 - 7.48 (m, 2H), 7.39 (dd, *J* = 13.4, 7.1 Hz, 1H), 7.21 (dt, *J* = 25.7, 7.4 Hz, 2H), 7.09 (t, *J* = 8.9 Hz, 1H), 4.79 (d, *J* = 9.5 Hz, 1H), 4.22 (d, *J* = 9.7 Hz, 1H), 3.43 (d, *J* = 15.8 Hz, 1H), 3.26 (d, *J* = 14.4 Hz, 1H), 1.53 (s, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.9, 159.5 (d, *J* = 247.6 Hz), 140.3, 135.0, 133.9, 132.2 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 8.2 Hz), 129.9 (d, *J* = 2.2 Hz), 129.3, 127.2, 124.1 (d, *J* = 3.6 Hz), 121.0 (d, *J* = 15.0 Hz), 115.9 (d, *J* = 21.5 Hz), 75.5, 60.5, 42.0, 23.5; ***Z* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 167.4, 160.2 (d, *J* = 253.1 Hz), 140.4, 133.4, 131.7, 131.3, 131.6(d, *J* = 6.7 Hz), 129.4 (d, *J* =11.9 Hz), 127.5, 127.4, 123.4 (d, *J* = 3.6 Hz), 120.5 (d, *J* = 12.0 Hz), 114.9 (d, *J* = 21.9 Hz), 74.3, 63.1, 43.5, 24.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.68, -113.48; IR (KBr) ν_{max} 3688, 3105, 2981, 2769, 1757, 1653, 1568, 1482, 1310, 1146 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}FO_4SNa$ 383.0724; Found 383.0728.

(*E*)-3-Ethylidene-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3la): Yellow solid (91 mg, 65% yield), m.p. = 136.8 - 138.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.89 (d, J = 7.4 Hz, 2H), 7.69 - 7.63 (m, 1H), 7.57 (t, J = 7.6 Hz, 2H), 6.20 (q, J = 7.3 Hz, 1H), 4.72 (d, J = 9.7 Hz, 1H), 4.13 (d, J = 9.8 Hz, 1H), 3.32 - 3.15 (m, 2H), 2.12 (d, J = 7.3 Hz, 3H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.9, 140.7, 139.8, 134.0, 132.6, 129.5, 127.6, 74.6, 63.5, 42.5, 24.7, 13.8; IR (KBr) ν_{max} 3692, 3111, 2982, 2769, 1753, 1662, 1528, 1479, 1310, 1147 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_4SNa$ 303.0662; Found 303.0660.

(*E*)-3-Hexylidene-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3ma): Yellow solid (104 mg, 62% yield), m.p. = 84.1 - 85.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.7 Hz, 2H), 7.67 - 7.61 (m, 1H), 7.58 - 7.54 (m, 2H), 6.09 (t, J = 7.6 Hz, 1H), 4.70 (d, J = 9.7 Hz, 1H), 4.12 (d, J = 9.7 Hz, 1H), 3.34 - 3.14 (m, 2H), 2.78 - 2.47 (m, 2H), 1.55 (s, 3H), 1.42 - 1.32 (m, 2H), 1.26 - 1.25 (m, 2H), 0.84 (t, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.7, 145.2, 140.6, 134.0, 131.7, 129.5, 127.5, 74.5, 63.5, 42.3, 31.2, 28.5, 27.2, 24.8, 22.3, 13.8; IR (KBr) ν_{max} 3682, 3110, 2971, 2761, 1751, 1662, 1527, 1477, 1307, 1141 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{24}O_4SNa$ 359.1288; Found 359.1289.

(*E*)-3-(2,4-Dimethylbenzylidene)-4-methyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3na): Yellow solid (120 mg, 72% yield), m.p. = 136.4 - 137.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.73 (s, 1H), 7.69 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.02 (s, 1H), 6.97 (s, 2H), 4.68 (d, J = 9.6 Hz, 1H), 4.25 (d, J = 9.6 Hz, 1H), 3.37 (d, J = 14.5 Hz, 1H), 3.14 (d, J = 14.5 Hz, 1H), 2.32 (s,

3H), 2.18 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.4, 140.5, 139.4, 139.3, 136.5, 133.9, 132.8, 131.2, 129.7, 129.3, 127.9, 127.2, 126.2, 75.8, 61.1, 41.9, 24.9, 21.1, 19.9; IR (KBr) ν_{max} 3687, 3111, 2983, 2771, 1755, 1658, 1527, 1479, 1311, 1147 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_4SNa$ 393.1131; Found 393.1131.

4-Methyl-4-((phenylsulfonyl)methyl)-3-(thiophen-3-ylmethylene)dihydrofuran-2(3*H*)-one (3oa): Yellow oil (90 mg, 52% yield); ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.91 - 7.82 (m, 2H), 7.66 - 7.60 (m, 2H), 7.56 - 7.51 (m, 2H), 7.42 (s, 1H), 7.21 (d, J = 5.0 Hz, 1H), 4.78 (d, J = 9.7 Hz, 1H), 4.29 (d, J = 9.7 Hz, 1H), 3.75 (d, J = 14.6 Hz, 1H), 3.26 (d, J = 14.6 Hz, 1H), 1.81 (s, 2.25H), 1.69 (s, 0.25H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 140.4, 134.1, 133.2, 130.2, 129.6, 129.5, 128.7, 127.6, 127.5, 127.3, 76.9, 60.2, 41.3, 23.3; ***Z* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.3, 140.6, 134.7, 134.1, 134.0, 132.8, 132.4, 130.6, 128.5, 127.6, 125.3, 74.5, 63.6, 43.9, 24.5; IR (KBr) ν_{max} 3692, 3109, 2982, 2769, 1747, 1634, 1528, 1307, 1244, 1141 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}O_4S_2Na$ 371.0382; Found 371.0385.

3-Benzylidene-4-ethyl-4-((phenylsulfonyl)methyl)dihydrofuran-2(3*H*)-one (3pa): Yellow oil (128 mg, 72% yield); ***E* isomer + *Z* isomer** ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.83- 7.72 (m, 1H), 7.62 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.42 - 7.37 (m, 2H), 7.30 - 7.18 (m, 4H), 4.69 (d, J = 9.9 Hz, 1H), 4.29 (d, J = 10.0 Hz, 1H), 3.41 (d, J = 14.6 Hz, 1H), 3.19 (d, J = 14.5 Hz, 1H), 2.09 - 1.84 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ***E* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.0, 140.8, 140.4, 133.8,

133.3, 130.8, 129.4, 129.3, 128.8, 128.6, 127.2, 73.8, 61.4, 45.5, 31.6, 8.3; ***Z* isomer** ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 167.9, 140.9, 140.5, 133.9, 133.3, 132.6, 129.9, 129.4, 129.1, 127.9, 127.5, 73.2, 62.2, 47.0, 30.8, 7.8; IR (KBr) ν_{max} 3685, 3059, 2976, 2768, 1751, 1639, 1525, 1480, 1308, 1239, 1145 cm^{-1}; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}O_4S$ 357.1155; Found 357.1153.

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Supporting Information

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

Crystallographic data for **3aa** (CIF)

Spectral data for all new compounds and crystal data for **3aa** (PDF)

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