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# Multicomponent Reactions of β-Ketosulfones and Formaldehyde in a Bio-Based Binary Mixture Solvent System Composed of Meglumine and Gluconic Acid Aqueous Solution

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**Abstract:** A mixture of two bio-based chemicals, meglumine and gluconic acid aqueous solution (GAAS, 50 wt%), was demonstrated to be a task-specific bio-based solvent for performing the hydroxymethylation of β-ketosulfones with formaldehyde. The formed hydroxymethylation product could further react with a nucleophile, which allowed us to develop some one-pot, stepwise, three-component reactions of β-ketosulfones and formaldehyde in this binary mixture. Particularly, a one-pot, two-step, sequential four-component reaction of α-bromo ketone, sodium benzenesulfinate, thiophenol and formaldehyde was also developed. These results not only demonstrate that it is possible to develop a new bio-based system by mixing two or more bio-based chemicals together, but also confer us a convenient means for controlling the selectivity of some multicomponent reactions of formaldehyde. Because GAAS and meglumine are both highly hydrophilic, the mixed solvent system could thus be recovered after extraction of organic products. In a three-component reaction of β-ketosulfone, paraformaldehyde and α-methylstyrene, the GAAS/meglumine system could be reused at least four times without significant loss of activity.

**Keywords:** gluconic acid aqueous solution; β-ketosulfones; meglumine; one-pot stepwise multicomponent reactions

## Introduction

The realization of simple and green synthetic procedures constitutes an important goal in organic synthesis. To combat the harmful effect of volatile organic solvents frequently used in large quantities for organic transformations, many green solvent systems have been recently introduced as alternative reaction media.[1] Among all the green solvents developed so far, water and ionic liquids have gained most of the interests of chemists.[2] Because many remarkable results have been achieved in recent years, work on the replacement of conventional organic solvents with a green solvent system has become one of the most important topics of green chemistry.[3] In addition, increasing concerns about the sustainability of chemical transformations also open a new area of solvent innovation that emphasizes the concept of using bio-based materials as alternatives to conventional organic solvents.[4] Because of the apparent difference of these solvents with all the used systems, remarkable results that cannot be attained in conventional solvents could, sometimes, be obtained by using a bio-based material as solvent. However, the number of bio-based solvents is still limited at this stage, which has apparently restricted the utilization of this new generation of green solvent in organic transformations.[5] In order to further improve the development of these solvent systems, the diversity and functionality of the bio-based solvents certainly need to be extended.

Out of these considerations, most of the efforts in this area are focusing on searching for a new bio-based material that can act as a solvent. As a basic requirement of a solvent, the candidate for bio-based

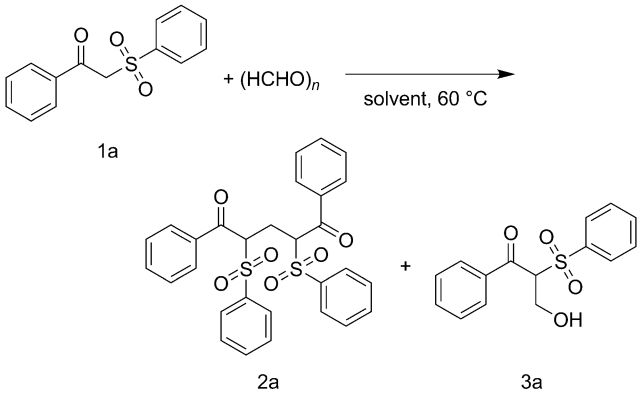
solvent should be characterized by the following factors: (i) a suitable liquid range; (ii) good chemical stability towards various substrates, and (iii) largely available in the market. However, bio-based chemicals that have been commercialized are far from abundant at this moment. All these things put together tend to, without doubt, further narrow the possibility of finding a new bio-based solvent. Therefore, we have to turn to another route for the exploration of new bio-based systems.

Recently, some bio-based materials, such as carbohydrates and glycerol, were used in establishing low melting mixtures that can be used in some organic transformations.[6] Inspired by this strategy, we envisaged that mixing two or more bio-based materials together might allow us to build up a new solvent system that possesses a synergistic promoting effect on a specific class of reactions. Quite recently, we have reported a concept that uses gluconic acid aqueous solution (GAAS, 50 wt%) as a promoting medium for organic transformations.[7] Herein we disclose the successful outcome of our recent endeavors in which a mixture of meglumine and GAAS (50 wt%) was used as a new bio-based solvent for promoting some multicomponent reactions of β-ketosulfones and formaldehyde. A specific ability of this binary bio-based solvent for controlling the selectivity of hydroxymethylation of β-ketosulfones was proved to be the key for making the three-component reactions possible. Many multicomponent reactions of β-ketosulfones and formaldehyde were successfully developed by taking advantage of this new bio-based solvent system.

## Results and Discussion

Initially, 2-(phenylsulfonyl)acetophenone (**1a**), an active C–H acid that has been widely used as a nucleophile in many organic transformations,[8] was used to react with paraformaldehyde in various solvents. We are interested in this reaction because of our expectation of forming an α-methylene-β-ketosulfone that might be an attractive intermediate for constructing new multicomponent reactions. Previous methods to access α-methylene-β-ketosulfones involve (i) oxidation of Baylis–Hillman adduct generated from phenyl vinyl sulfone and aldehyde[9] and (ii) decomposition of the aminomethylation product of a β-ketosulfone (a Mannich base).[10] Until now, there is no report on preparing α-methylene-β-ketosulfones through the Knoevenagel reaction of a β-ketosulfone and formaldehyde. As shown in Table 1, in water, glycerol, PEG400 and some common organic solvents, such as acetonitrile, 1,2-dichloroethane and nitromethane, an "ABB"-type reaction of formaldehyde and β-ketosulfone **1a** that generates **2a** was found to be predominant (entries 1 to 6). GAAS was also examined, and not surprisingly, **2a** was also formed extensively (entry 7). However, the reaction selectivity was altered significantly when GAAS was used in conjunction with the sugar-based organic base, meglumine, that is a readily available chemical reagent (entry 8). In this case, a white solid was formed during the reaction [Figure 1, (**a**)]. By means of filtration, a hydroxymethylation product of the β-ketosulfone, **3a**, was obtained in high yield. Interestingly, the hydroxymethylation can only be conducted in the GAAS/meglumine system since combining meglumine with other solvents, such as water, glycerol and PEG 400, failed to afford **3a** (entries 9 to 11). These results manifested that a synergistic effect between GAAS and meglumine might play a key role in controlling the selectivity of hydroxymethylation of **1a** with formaldehyde. In

**Table 1.** Reaction of **1a** and $(HCHO)_n$ in different solvents.[a]




| Entry | Solvent | Time [h] | Yield [%] | |
|---|---|---|---|---|
| | | | **2a** | **3a** |
| 1 | water | 12 | 98 | 0 |
| 2 | glycerol | 12 | 10 | 0 |
| 3 | PEG 400 | 12 | 96 | 0 |
| 4 | $CH_3CN$ | 12 | 40 | 0 |
| 5 | $ClCH_2CH_2Cl$ | 12 | 15 | 0 |
| 6 | $CH_3NO_2$ | 12 | 5 | 0 |
| 7 | GAAS | 12 | 5 | 0 |
| 8[b] | GAAS/meglumine | 24 | 5 | **85** |
| 9[b] | water/meglumine | 24 | 98 | 0 |
| 10[b] | glycerol/meglumine | 24 | 90 | 0 |
| 11[b] | PEG 400/meglumine | 24 | 95 | 0 |
| 12[c] | GAAS/ethanolamine | 12 | 40 | 15 |
| 13[d] | GAAS/diethanolamine | 12 | 10 | 72 |
| 14[e] | GAAS/triethanolamine | 12 | <5 | <5 |
| 15[f] | GAAS/meglumine | 12 | <5 | 70 |

[a] Solvent: 2.0 mL, **1a:** 0.25 mmol, paraformaldehyde: 0.25 mmol.
[b] **1a**/meglumine: 1.0/1.5.
[c] **1a**/ethanolamine: 1.0/1.5.
[d] **1a**/diethanolamine: 1/1.5;
[e] **1a**/triethanolamine: 1.0/1.5;
[f] **1a**/meglumine: 1.0/1.0.

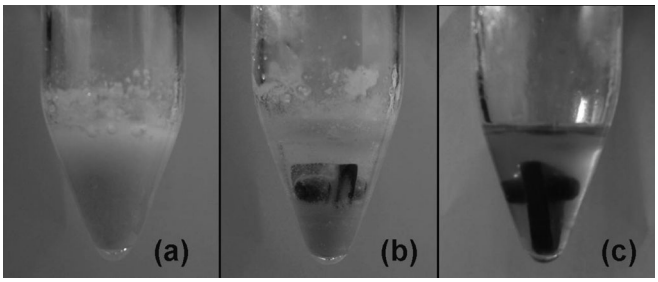


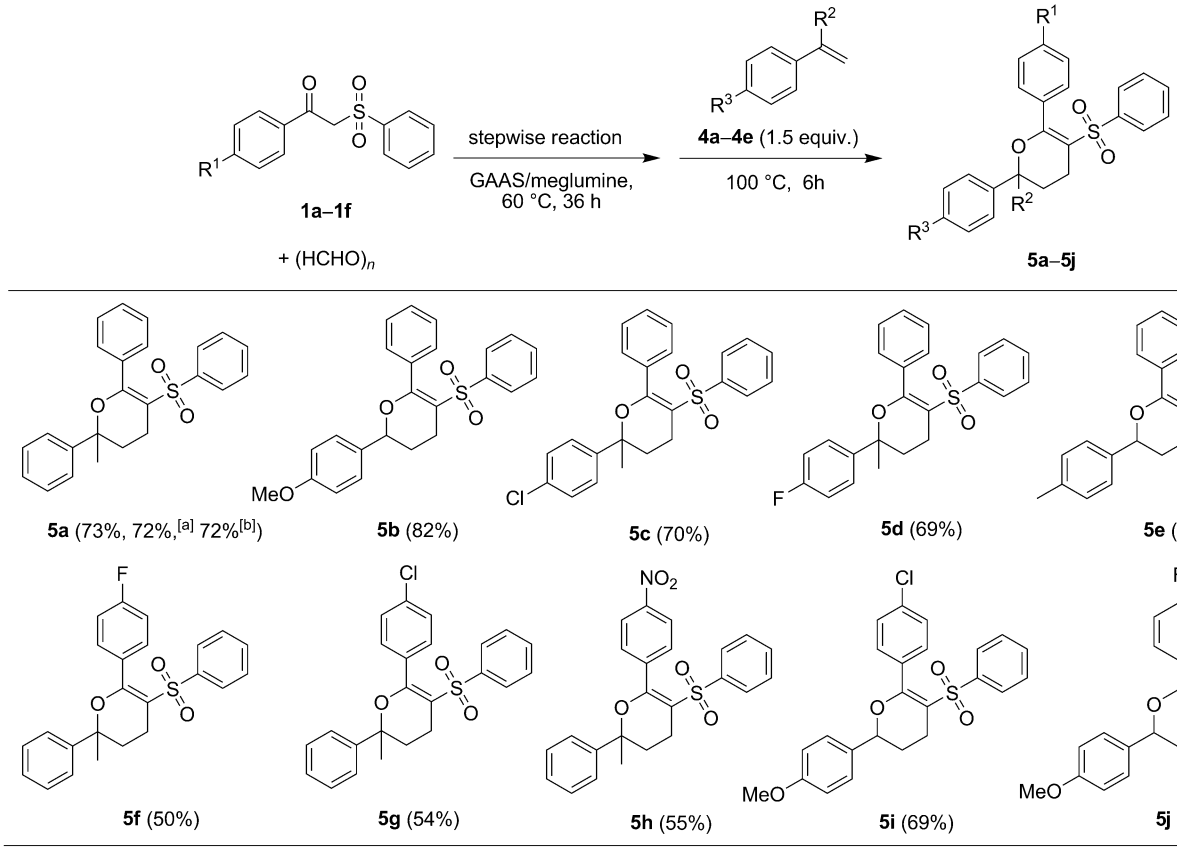

**Figure 1.** Progress of the model reaction in GAAS/meglumine (**a**: running of hydroxymethylation reaction of **1a**; **b**: the end of the hydroxymethylation reaction; **c**: the end of the one-pot stepwise reaction).

order to confirm this point, meglumine was then replaced by three organic amines including triethanolamine, diethanolamine and ethanolamine (entries 12 to 14). In these cases, although **3a** could always be observed, the highest yield was obtained with GAAS/diethanolamine system. This result implies that, for the hydroxymethylation of **1a** in GAAS, using a secondary amine as co-solvent is the key for rendering the reaction possible. Although a good performance has been observed by using the GAAS/diethanolamine system, we prefer to use the previous one, the GAAS/meglumine system. The reasons are twofold: (i) meglumine is a bio-based chemical reagent that endows the reaction system with a salient feature in meeting the sustainability requirement of current organic synthesis and (ii) meglumine is a highly hydrophilic species that allows the bio-based solvent system to be recyclable. The second point will be verified in the later experiments. It should be noted that although hydroxymethylation reactions of active C–H acids with formaldehyde have been extensively investigated,[11] a β-ketosulfone has not been examined in this type of reaction as substrate. Further investigations revealed that amount of meglumine plays also a crucial role in enhancing the yield of the model reaction, and an optimal dosage is 1.5 equivalents of meglumine with respect to **1a** (entry 15). However, despite the observed beneficial effect exerted by the GAAS/meglumine system on the model reaction, the exact nature of this influence cannot be ascribed to a single effect such as stabilization of the reaction intermediate or the solubility of **3a** in the solvent, but rather to a superposition of several factors. This point deserves further investigation.

It is well known that the hydroxymethylation products of 1,3-dicarbonyl compounds could be converted to 2-methylene-1,3-dicarbonyl compounds through a dehydration reaction under mild conditions, which can then be trapped by a suitable nucleophile.[12] On the basis of this mechanism, we have developed many multicomponent reactions of 1,3-dicarbonyl compounds and formaldehyde recently.[13] Inspired by these results, we speculated that the hydroxymethylation product, **3a**, may be also reactive toward the dehydration reaction that could generate an α-methylene-β-ketosulfone. A literature survey revealed, however, that the α-methylene-β-ketosulfone is a labile species.[14] In order to simplify the reaction operation, and to avoid the possible decomposition of the methylene intermediate, we therefore designed a one-pot, stepwise, three-component reaction in which a following connected reaction sequence is involved: (i) the hydroxymethylation of **1a** with formaldehyde in GAAS/meglumine at 60 °C and (ii) several hours of reaction after adding a nucleophile into the system. To ensure a complete consumption of **1a** and paraformaldehyde, reaction time of the first step was increased, on purpose, to 36 h. In order to facilitate the decomposition of **3a** and the following trapping of the methylene intermediate with the nucleophile, the second step was performed at an increased temperature, 100 °C.

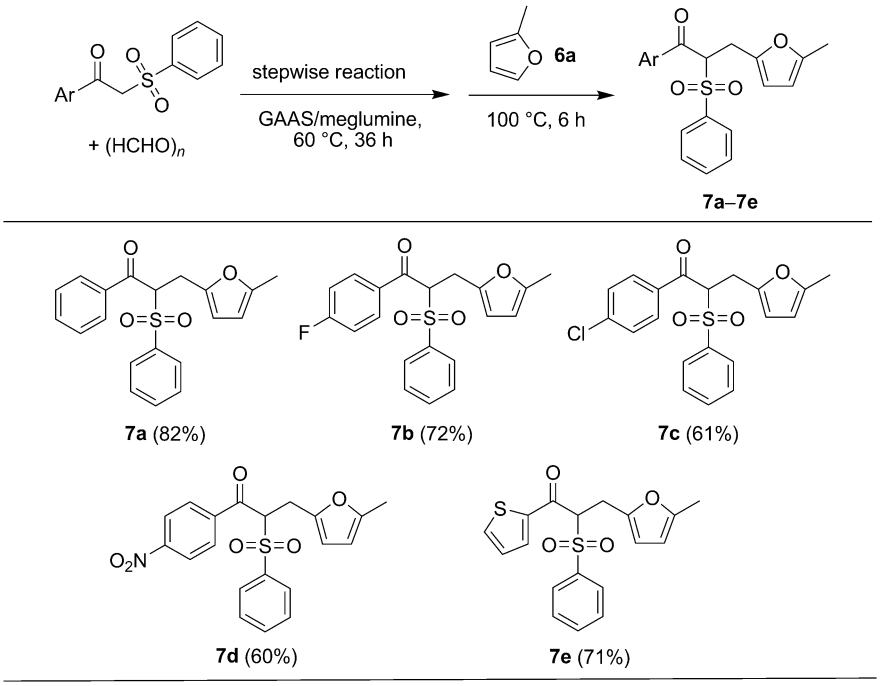
With this procedure, two nucleophiles were successfully applied in developing multicomponent reactions. The first is a styrene derivative that is able to trap the generated α-methylene-β-ketosulfone through an oxo-Diels–Alder reaction pathway. As shown in Scheme 1, when α-methylstyrene was used as substrate, the expected product, **5a**, could be obtained in 73% yield. This result manifests that **3a** is indeed unstable at 100 °C in the GAAS/meglumine system, and the generated α-methylene-β-ketosulfone thereby could be trapped easily in the presence of an appropriate nucleophile. Interestingly, although **3a** is insoluble in the GAAS/meglumine system [Figure 1, (**b**)], after adding α-methylstyrene into the system, the white solid gradually disappeared. And at the end of the reaction, a clear solution was obtained [Figure 1, (**c**)]. An investigation of the substrate scope revealed that many styrenes and β-ketosulfones could be used in this reaction, and the corresponding products were obtained in moderate to good yields. A subtle influence of the substituent functionality in the phenyl ring of styrene on the reaction yield was observed. And better yields could be obtained by using styrenes that possess an electron-donating group as substrates. It should be noted that **5a**-type dihydropyrans are known to be valuable for organic synthesis.[15] Furthermore, a reaction on a 10-mmol scale proceeded also very well, indicating the usefulness of our method for practical synthesis. The second nucleophile we have investigated in the GAAS/meglumine system is 2-methylfuran. The obtained products contain not only a β-ketosulfone fragment but also a furan ring (Scheme 2). Judging from the structure of the product, the last step of the reaction mechanism could be speculated to be a Michael addition of the formed methylene intermediate to 2-methylfuran. It should be noted that all these one-pot sequential re-



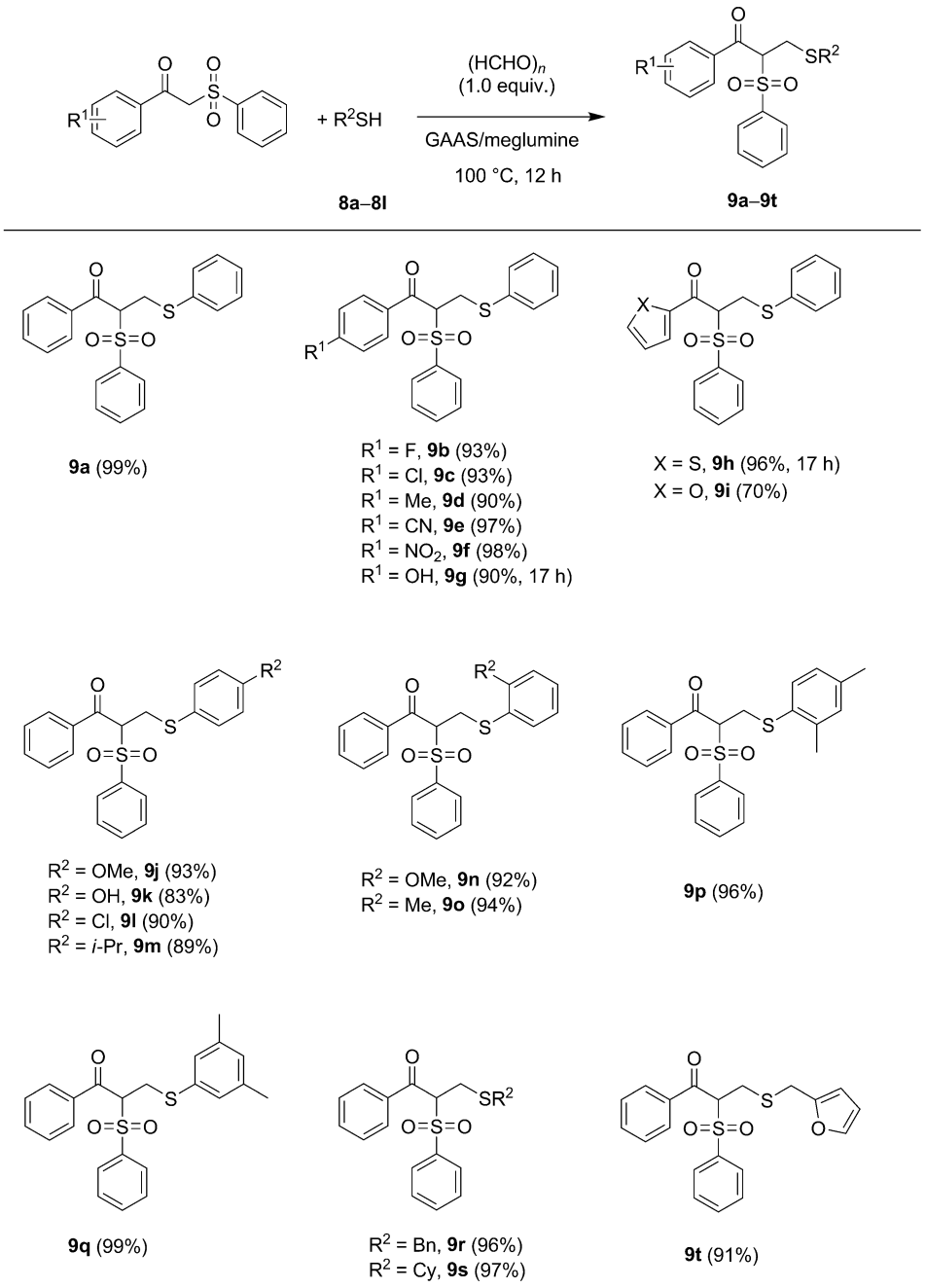

[a] GAAS/meglumine was used in the fifth run.
[b] The reaction was conducted in 10 mmol scale.

**Scheme 1.** One-pot, stepwise, three-component reaction of β-ketosulfone, paraformaldehyde and styrene in the GAAS/meglumine system.




**Scheme 2.** One-pot, stepwise, three-component reaction of β-ketosulfone, paraformaldehyde and 2-methylfuran in the GAAS/meglumine system.




**Scheme 3.** One-pot, three-component reaction of β-ketosulfone, paraformaldehyde and thiophenol or thiol in the GAAS/meglumine system [ratio of β-ketosulfone/$(HCHO)_n$/thiol or thiophenol = 1.0/1.0/1.2].

actions have not been reported previously. These results indicated that the GAAS/meglumine system can indeed be used as an effective medium for developing multicomponent reactions of β-ketosulfones and formaldehdye. In addition, because both GAAS and meglumine are highly hydrophilic, they are thus immiscible with non-polar organic solvents. Therefore, the GAAS/meglumine system can be easily recovered after extraction of organic products. In the synthesis of **5a**, the GAAS/meglumine system could be reused at least four times without any significant loss of activity.

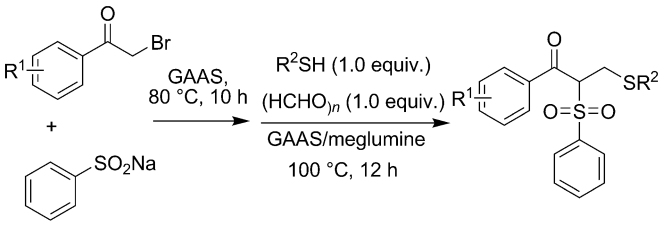
In the course of investigating the above-mentioned reactions, we have also examined the possibility of assembling all the starting materials together in a single-step reaction. However, this strategy was found to be unsuccessful for use with α-methylstyrene and 2-methylfuran as the nucleophile. Surprisingly, our idea came to reality when thiols and thiophenols were used. As shown in Scheme 3, a one-pot, three-compo-

nent reaction of **1a**, paraformaldehyde and thiophenol proceeded very well in the GAAS/meglumine system, providing a thioether in high yield. It should be noted that the high yield was obtained in the reaction that was conducted under a ratio of **1a**/$(HCHO)_n$/thiophenol = 1.0/1.0/1.2, even though all the starting materials were added at once. The present approach for the synthesis of **9a**-type thioethers turned out to be quite general, a variety of β-ketosulfones and a wide range of thiol(phenol)s underwent the coupling with formaldehyde to furnish the corresponding thioethers in good to excellent yields. It should be noted that the present three-component reaction of β-ketosulfone, formaldehyde and thiol has not been reported previously. In the reported Mannich-type three-component reactions of active C–H acids, formaldehyde and thiophenol (or amine), it was always necessary to add an excess amount of thiophenol (or amine) in order to achieve high yields.[13c] In contrast, in this work, with the above-mentioned GAAS/meglumine as reaction medium, high yields were obtained by using nearly equivalent amounts of substrate, strengthening again the green property of our method. Although a method to access **9a**-type products has been reported by Yamauchi,[16]in view of the fact that an *N*-(methylthiomethyl) piperidine-HCl salt was used in Yamauchi's report as methylthiomethylation reagent of 1,3-dicarbonyl compounds, our present method thus exhibited the great advantage of an improvement of the synthetic efficiency.

All the aforementioned methodologies, however, involve pre-formed β-ketosulfones, for which the use of organic solvents and cumbersome product isolation are, in general, mandatory. It is well known that β-ketosulfone could be easily prepared from an $S_N2$ reaction between sodium benzenesulfinate and α-bromoketone.[17] In view of the fact that, for the synthesis of β-ketosulfone, a protic solvent seems to be preferable, we thus explored the possibility of using more fundamental substrates as alternatives to β-ketosulfones which, being compatible with the standard reaction conditions, could expand the versatility of the GAAS/meglumine system. We undertook this study with the implementation of the reaction of sodium benzenesulfinate and α-bromoacetophenone. As expected, β-ketosulfone **1a** was formed quantitatively after 10 h of reaction at 80 °C in the GAAS. From this result, it can be inferred that combining the $S_N2$ reaction of sodium benzenesulfinate and α-bromoacetophenone together with the following condensation of formaldehyde and thiophenol might be feasible. As shown in Table 2, the one-pot, two-step sequential reaction of α-bromo ketone, sodium benzenesulfinate, thiophenol and formaldehyde proceeded very well in the binary GAAS/meglumine system. Furthermore, the present four-component reaction turned out to be quite general, various α-bromo ketones and a wide range of thiols or thiophenols underwent the convergent condensation with formaldehyde and sodium benzenesulfinate to furnish the corresponding products in good to excellent yields.

**Table 2.** One-pot, stepwise, four-component reaction of α-bromo ketone, sodium benzenesulfinate, paraformaldehyde and thiol or thiophenol in the GAAS/meglumine system.[a]

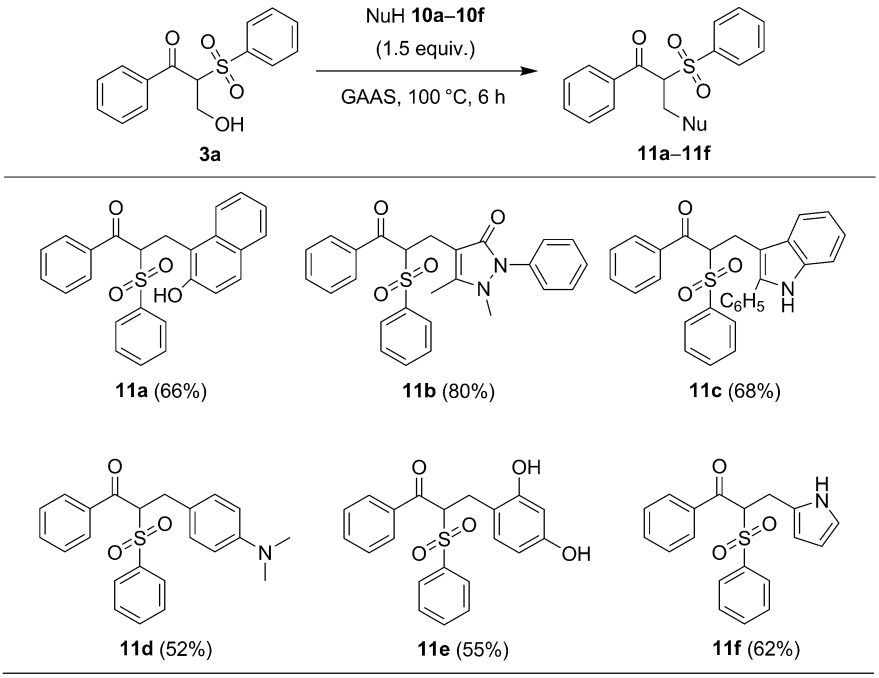



| Entry | $R^1$ | $R^2$ | Product | Yield [%] |
|---|---|---|---|---|
| 1 | 4-H | $C_6H_5$ | **9a** | 98 |
| 2 | 4-F | $C_6H_5$ | **9b** | 92 |
| 3 | 4-Cl | $C_6H_5$ | **9c** | 75 |
| 4 | 4-Me | $C_6H_5$ | **9d** | 70 |
| 5 | 4-CN | $C_6H_5$ | **9e** | 90 |
| 6 | 4-$NO_2$ | $C_6H_5$ | **9f** | 92 |
| 7 | 4-H | 4-$ClC_6H_4$ | **9l** | 92 |
| 8 | 4-H | 4-*i*-$PrC_6H_4$ | **9m** | 90 |
| 9 | 4-H | Bn | **9r** | 96 |
| 10 | 4-H | Cy | **9s** | 94 |

[a] GAAS: 2.0 mL, α-bromo ketone: 0.25 mmol, α-bromo ketone/sodium benzenesulfinate/$(HCHO)_n$/meglumine/thiol or thiophenol ratio: 1.0/1.0/1.0/1.5/1.2.

However, to our disappointment, an attempt to use other nucleophiles in the GAAS/meglumine system was in vain. Because of the fact that, with GAAS/meglumine system, we are able to synthesize **3a** in high yield from **1a** and paraformaldehyde, which cannot be attained in other ways, we were therefore intrigued by the possibility of using the hydroxymethylation product of the β-ketosulfone as substrate for organic synthesis. As shown in Scheme 4, by using GAAS as medium, **3a** could react readily with many carbon-based nucleophiles, such as 2-naphthol, *N*,*N*-dimethylaniline, pyrrole, 2-phenylindole, antipyrine and resorcin, providing the corresponding Friedel–Crafts alkylation products in good yields. GAAS might play the role of a mild acid catalyst, which not only promotes the decomposition of **3a** providing the α-methylene-β-ketosulfone intermediate, but also accelerates the Michael reaction of the intermediate and the nucleophile. These results imply that Michael reactions of the α-methylene-β-ketosulfone intermediate and nucleophiles are not always compatible with the standard conditions of forming an α-methylene-β-ketosulfone because Michael products cannot be obtained by the above-mentioned one-pot sequential methods in GAAS/meglumine system.




**Scheme 4.** Reactions of **3a** with different nucleophiles in GAAS.

## Conclusions

The combination of GAAS and meglumine was proved to be, for the first time, an effective bio-based solvent for developing multicomponent reactions of β-ketosulfones and paraformaldehyde. Nucleophiles, such as thiols, thiophenols, styrenes and 2-methylfuran, can all be successfully used in the convergent reactions with β-ketosulfone and formaldehyde. While the desired products were obtained in good yields in the GAAS/meglumine system, the synthesis cannot be performed well in the other solvent systems, indicating the great utility of the present GAAS/meglumine system. The intervention of a solvent effect on the multicomponent reaction could be speculated in (i) promoting the hydroxymethylation of β-ketosulfone and (ii) stabilizing the formed **3a**-type products. By taking advantage of the GAAS/meglumine system for the efficient synthesis of **3a**, we have a chance to directly use **3a** as a substrate for organic synthesis. In GAAS, **3a** could react readily with many carbon-based nucleophiles, such as 2-naphthol, *N*,*N*-dimethylaniline, pyrrole, 2-phenylindole, antipyrine and resorcin, providing the corresponding Friedel–Crafts alkylation products in good yields. In spite of these promising results, the reasons for the obtained high selectivity for the hydroxymethylation of β-ketosulfone by using GAAS/meglumine as medium are still unknown at this stage. This will be the next topic of our study.

## Experimental Section

All the chemicals were used as they were received. Some β-ketosulfones were prepared from β-bromo ketones and sodium benzenesulfinate according to a literature method with slight modification.[18] All reactions were conducted in a 10-mL V-type flask equipped with triangle magnetic stirring.

### Typical Procedure

In a typical reaction, GAAS (2.0 mL) was mixed with meglumine (73.2 mg, 0.38 mmol), paraformaldehyde (7.5 mg, 0.25 mmol) and 2-(phenylsulfonyl)acetophenone (**1a**, 65.1 mg, 0.25 mmol) for 36 h at 60 °C. Then β-methylstyrene (44.3 mg, 0.38 mmol) was added into the mixture. The mixture was stirred for 6 h at 100 °C. After reaction, the mixture was extracted with a mixture of ethyl acetate and *n*-heptane (v/v = 2/1, 6.0 mL × 3) at room temperature. The obtained organic phases were then combined together and dried with $Na_2SO_4$. After concentration under reduced pressure, the organic solution was then subjected to preparative TLC, and the product **5a** was obtained; yield: 73%. The recovered aqueous phase can be reused in the next run after a simple treatment at room temperature under vacuum (20 mmHg for 30 min).

The reaction on a 10-mmol scale was performed using an analogous procedure, but **5a** was isolated by silica column chromatography by using a mixture of ethyl acetate and petrol ether (60–90 °C, v/v = 1/10) as eluting solvent. The other reactions were performed with an analogous procedure, and the details are available in the Supporting Information. All the products were characterized with $^1H$ and $^{13}C$ NMR spectroscopy on a Bruker AV-400 instrument.

## Characterization Data of Newly Synthesized Products

**2-Methyl-2,6-diphenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5a):** white solid; mp 136–138 °C; $^1$H NMR ($CDCl_3$): δ = 1.58 (s, 3H), 2.05–2.13 (m,1H), 2.15–2.25 (m,1H), 2.36–2.45 (m,1H), 2.56–2.65 (m, 1H), 7.22 (td, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 2H), 7.26–7.32 (m, 4H), 7.32–7.36 (m, 5H), 7.36–7.42 (m, 4H); $^{13}$C NMR ($CDCl_3$): δ = 21.1, 29.1, 32.6, 80.8, 114.2, 124.3, 126.9, 127.4, 127.7, 128.3, 128.6, 129.7, 129.8, 132.1, 134.3, 142.1, 143.9, 161.5; IR: ν = 3033, 3001, 2933, 1631, 1494, 1449, 1380, 1350, 1308, 1271, 1203, 1152, 1111, 1084, 1069, 1030, 999, 967, 856, 765, 697, 634 cm$^{-1}$; HR-MS (ESI): *m/z* = 413.1176, calcd. for $C_{24}H_{22}NaO_3S$ $[M+Na]^+$: 413.1187.

**2-(4-Methoxyphenyl)-6-phenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5b):** green liquid; $^1$H NMR ($CDCl_3$): δ = 2.02–2.13 (m,1H), 2.21–2.30 (m, 1H), 2.57–2.68 (m, 1H), 2.69–2.78 (m, 1H), 3.77 (s, 3H), 4.97 (dd, $J_a$ = 2.0 Hz, $J_b$ = 6.0 Hz, 1H), 6.85 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 2H), 7.22 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.2 Hz, 2H), 7.28 (t, $J$ = 7.2 Hz, 2H), 7.31–7.39 (m, 5H), 7.47 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 1H), 7.54 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 23.2, 29.3, 55.4, 78.9, 114.0, 114.4, 127.4, 127.4, 127.6, 128.6, 129.7, 129.8, 131.7, 132.5, 134.2, 142.1, 159.6, 162.9; IR: ν = 3065, 2935, 2838, 1681, 1605, 1512, 1448, 1309, 1249, 1178, 1150, 1084, 1032, 1000, 970, 939, 838, 805, 750, 688, 596, 537 cm$^{-1}$; HR-MS (ESI): *m/z* = 429.1138, calcd. for $C_{24}H_{22}NaO_4S$ $[M+Na]^+$: 429.1136.

**2-(4-Chlorophenyl)-2-methyl-6-phenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5c):** white solid; mp: 120–122 °C; $^1$H NMR ($CDCl_3$): δ = 1.55 (s, 3H), 2.02–2.11 (m, 1H), 2.14–2.24 (m, 1H), 2.31–2.38 (m, 1H), 2.57–2.66 (m, 1H), 7.21–7.24 (m, 2H), 7.25–7.27 (m, 2H), 7.27–7.29 (m, 2H), 7.29–7.32 (m, 2H), 7.33–7.37 (m, 3H), 7.37–7.40 (m, 1H), 7.40–7.46 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ = 21.1, 28.9, 32.5, 80.4, 114.5, 126.0, 127.0, 127.8, 128.5, 128.8, 129.7, 130.0, 132.3, 133.3, 134.1, 142.0, 142.6, 161.3; IR: ν = 3062, 2929, 2862, 1674, 1629, 1593, 1489, 1447, 1395, 1345, 1308, 1272, 1146, 1074, 1008, 966, 922, 855, 831, 768, 747, 723, 688, 632, 571 cm$^{-1}$; HR-MS (ESI): *m/z* = 447.0789, calcd. for $C_{24}H_{21}ClNaO_3S$ $[M+Na]^+$: 447.0798.

**2-(4-Fluorophenyl)-2-methyl-6-phenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5d):** white solid; mp 140–142 °C; $^1$H NMR ($CDCl_3$): δ = 1.55 (s, 3H), 2.03–2.11 (m, 1H), 2.16–2.27 (m, 1H), 2.31–2.40 (m, 1H), 2.56–2.67 (m, 1H), 7.00 (tt, $J_a$ = 2.4 Hz, $J_b$ = 8.8 Hz, 2H), 7.23 (dd, $J_a$ = 1.6 Hz, $J_b$ = 6.4 Hz, 1H), 7.25–7.28 (m, 2H), 7.28–7.31 (m, 2H), 7.31–7.39 (m, 5H), 7.39–7.45 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ = 21.1, 29.0, 32.6, 80.4, 114.4, 115.4, 115.6, 126.2, 126.3, 127.0, 127.8, 128.5, 129.7, 129.9, 132.3, 134.2, 142.0, 161.4; IR: ν = 3062, 2970, 2921, 2844, 1626, 1594, 1502, 1447, 1404, 1382, 1347, 1306, 1273, 1220, 1156, 1140, 1102, 1072, 1011, 998, 966, 920, 904, 861, 840, 812, 766, 751, 724, 701, 687, 632, 572, 519 cm$^{-1}$; HR-MS (ESI): *m/z* = 431.1090, calcd. for $C_{24}H_{21}FNaO_3S$ $[M+Na]^+$: 431.1093.

**6-Phenyl-5-(phenylsulfonyl)-2-(*p*-tolyl)-3,4-dihydro-2*H*-pyran (5e):** white solid; mp 125–127 °C; $^1$H NMR ($CDCl_3$): δ = 2.00–2.12 (m, 1H), 2.22–2.30 (m, 1H), 2.31 (s, 3H), 2.57–2.67 (m, 1H), 2.68–2.76 (m, 1H), 5.00 (dd, $J_a$ = 2.0 Hz, $J_b$ = 10.0 Hz, 1H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.26–7.31 (m, 2H), 7.31–7.39 (m, 5H), 7.46 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.54 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 21.2, 23.1, 29.4, 79.0, 114.4, 125.9, 127.4, 127.6, 128.6, 129.3, 129.8, 132.5, 134.2, 136.6, 138.2, 142.1, 162.8; IR: ν = 3055, 2932, 2854, 1625, 1593, 1442, 1335, 1230, 1262, 1207, 1178, 1143, 1108, 1081, 1060, 1025, 999, 966, 923, 890, 846, 810, 764, 724, 670, 620, 589, 567 cm$^{-1}$; HR-MS (ESI): *m/z* = 413.1183, calcd. for $C_{24}H_{22}NaO_3S$ $[M+Na]^+$: 413.1187.

**6-(4-Fluorophenyl)-2-methyl-2-phenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5f):** pale yellow solid; mp 111–113 °C; $^1$H NMR ($CDCl_3$): δ = 1.58 (s, 3H), 2.02–2.11 (m, 1H), 2.13–2.23 (m, 1H), 2.36–2.44 (m, 1H), 2.54–2.64 (m, 1H), 7.02 (tt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H), 7.23 (dd, $J_a$ = 1.6 Hz, $J_b$ = 6.8 Hz, 1H), 7.26 (d, $J$ = 1.6 Hz, 1H), 7.27–7.31 (m, 5H), 7.33 (dd, $J_a$ = 1.2 Hz, $J_b$ = 6.8 Hz, 2H), 7.37–7.43 (m, 3H); $^{13}$C NMR ($CDCl_3$): δ = 21.3, 29.1, 32.6, 81.0, 114.6, 114.7, 114.9, 124.3, 126.9, 127.6, 128.5, 128.7, 131.9, 132.0, 132.4, 142.0, 143.8, 160.5; IR: ν = 3064, 2932, 2857, 1626, 1505, 1447, 1346, 1303, 1230, 1145, 1110, 1085, 1070, 1028, 964, 911, 861, 935, 800, 762, 724, 694, 633, 577 cm$^{-1}$; HR-MS (ESI): *m/z* = 431.1086, calcd. for $C_{24}H_{21}FNaO_3S$ $[M+Na]^+$: 431.1093.

**6-(4-Chlorophenyl)-2-methyl-2-phenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5g):** pale yellow solid; mp 107–109 °C; $^1$H NMR ($CDCl_3$): δ = 1.57 (s, 3H), 2.02–2.10 (m, 1H), 2.12–2.22 (m, 1H), 2.34–2.43 (m,1H), 2.53–2.62 (m, 1H), 7.25 (dd, $J_a$ = 1.6 Hz, $J_b$ = 6.8 Hz, 2H), 7.27–7.30 (m, 3H), 7.30–7.32 (m, 3H), 7.32–7.36 (m, 5H), 7.41 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$): δ = 21.2, 29.0, 32.5, 81.1, 114.7, 124.3, 127.0, 127.6, 128.0, 128.5, 128.7, 131.2, 132.1, 132.8, 136.1, 141.9, 143.8, 160.3; IR: ν = 3063, 2932, 1626, 1591, 1488, 1447, 1397, 1377, 1345, 1306, 1147, 1109, 1087, 1070, 1016, 965, 911, 861, 823, 762, 723, 695, 632, 570 cm$^{-1}$; HR-MS (ESI): *m/z* = 447.0794, calcd. for $C_{24}H_{21}ClNaO_3S$ $[M+Na]^+$: 447.0798.

**2-Methyl-6-(4-nitrophenyl)-2-phenyl-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5h):** pale yellow liquid; $^1$H NMR ($CDCl_3$): δ = 1.59 (s, 3H), 2.05–2.14 (m, 1H), 2.14–2.24 (m, 1H), 2.37–2.45 (m, 1H), 2.51–2.60 (m, 1H), 7.27–7.31 (m, 3H), 7.31–7.34 (m, 3H), 7.36 (dt, $J_a$ = 2.0 Hz, $J_b$ = 7.6 Hz, 1H), 7.40 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.47 (tt, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 1H), 7.61 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 21.1, 28.9, 32.3, 81.6, 115.3, 123.0, 124.2, 127.0, 127.8, 128.8, 130.8, 132.9, 140.9, 141.4, 143.5, 148.5, 158.9; IR: ν = 3066, 2980, 2857, 1632, 1593, 1523, 1447, 1377, 1347, 1309, 1202, 1150, 1109, 1070, 1028, 1000, 967, 911, 865, 759, 724, 695, 634, 569 cm$^{-1}$; HR-MS (ESI): *m/z* = 458.1031, calcd. for $C_{24}H_{21}NNaO_5S$ $[M+Na]^+$: 458.1038.

**6-(4-Chlorophenyl)-2-(4-methoxyphenyl)-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5i):** yellow liquid; $^1$H NMR ($CDCl_3$): δ = 2.00–2.11 (m, 1H), 2.20–2.29 (m, 1H), 2.52–2.64 (m, 1H), 2.67–2.77 (m, 1H), 3.77 (s, 3H), 4.95 (dd, $J_a$ = 2.0 Hz, $J_b$ = 10.0 Hz, 1H), 6.85 (dt, $J_a$ = 2.4 Hz, $J_b$ = 8.8 Hz, 2H), 7.20 (dt, $J_a$ = 2.4 Hz, $J_b$ = 8.8 Hz, 2H), 7.28 (q, $J$ = 2.8 Hz, 3H), 7.39 (td, $J_a$ = 2.0 Hz, $J_b$ = 8.0 Hz, 2H), 7.43–7.54 (m, 2H), 7.58 (dd, $J_a$ = 1.6 Hz, $J_b$ = 8.8 Hz, 2H), 7.61–7.70 (m, 1H); $^{13}$C NMR ($CDCl_3$): δ = 23.2, 29.2, 55.4, 79.1, 114.1, 114.8, 127.4, 127.4, 127.9, 128.8, 129.3, 131.2, 131.4, 132.7, 135.9, 141.9, 159.7, 161.5; IR: ν = 3065, 2935, 2838, 1681, 1589, 1513, 1486, 1447, 1401, 1310, 1249, 1206, 1178, 1151, 1087, 1032, 969, 938, 911, 832, 801, 757, 730, 689,569, 541 cm$^{-1}$; HR-MS (ESI): *m/z* = 463.0736, calcd. for $C_{24}H_{21}ClNaO_4S$ $[M+Na]^+$: 463.0747.

**6-(4-Fluorophenyl)-2-(4-methoxyphenyl)-5-(phenylsulfonyl)-3,4-dihydro-2*H*-pyran (5j):** white solid; mp 89–91 °C; $^1$H NMR ($CDCl_3$): δ = 2.03–2.12 (m, 1H), 2.21–2.30 (m, 1H), 2.54–2.65 (m, 1H), 2.68–2.77 (m, 1H), 3.77 (s, 3H), 4.95 (dd, $J_a$ = 2.0 Hz, $J_b$ = 10.0 Hz, 1H), 6.86 (dt, $J_a$ = 2.4 Hz, $J_b$ = 8.8 Hz, 2H), 6.97 (tt, $J_a$ = 2.4 Hz, $J_b$ = 8.8 Hz, 2H), 7.11 (dt, $J_a$ = 2.4 Hz, $J_b$ = 8.4 Hz, 2H), 7.31–7.35 (m, 2H), 7.38 (t, $J$ = 7.6 Hz, 2H), 7.49 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.56 (dd, $J_a$ = 1.6 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 23.3, 29.2, 55.4, 79.0, 114.1, 114.6, 114.7, 114.8, 127.3, 127.4, 128.7, 131.5, 131.8, 131.9, 132.6, 142.0, 159.7, 161.7; IR: ν = 3070, 2940, 2841, 1725, 1672, 1638, 1599, 1509, 1447, 1416, 1338, 1310, 1267, 1252, 1174, 1152, 1079, 1029, 1002, 970, 888, 837, 820, 801, 769, 752, 724, 685, 634, 566 cm$^{-1}$; HR-MS (ESI): $m/z$ = 447.1031, calcd. for $C_{24}H_{21}FNaO_4S$ $[M+Na]^+$: 447.1042.

**3-(5-Methylfuran-2-yl)-1-phenyl-2-(phenylsulfonyl)propan-1-one (7a):** brown liquid; $^1$H NMR ($CDCl_3$): δ = 2.03 (s, 3H), 3.37 (dd, $J_a$ = 10.8 Hz, $J_b$ = 14.8 Hz, 1H), 3.44 (dd, $J_a$ = 4.0 Hz, $J_b$ = 14.8 Hz, 1H), 5.46 (dd, $J_a$ = 4.0 Hz, $J_b$ = 10.8 Hz, 1H), 5.67 (dd, $J_a$ = 0.8 Hz, $J_b$ = 2.8 Hz, 1H), 5.79 (d, $J$ = 2.8 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 2H), 7.48–7.57 (m, 3H), 7.63 (tt, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 1H), 7.70 (dd, $J_a$ = 1.6 Hz, $J_b$ = 8.8 Hz, 2H), 7.84 (dd, $J_a$ = 1.6 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 13.4, 27.2, 68.3, 106.3, 108.4, 128.7, 128.9, 129.1, 129.8, 133.9, 134.4, 136.5, 137.0, 147.2, 151.6, 191.9; IR: ν = 3064, 2923, 1682, 1587, 1448, 1315, 1253, 1215, 1185, 1151, 1083, 1022, 999, 945, 856, 774, 756, 721, 687, 536 cm$^{-1}$; HR-MS (ESI): $m/z$ = 377.0804, calcd. for $C_{20}H_{18}NaO_4S$ $[M+Na]^+$: 377.0823.

**1-(4-Fluorophenyl)-3-(5-methylfuran-2-yl)-2-(phenylsulfonyl)propan-1-one (7b):** brown solid, mp 82–84 °C; $^1$H NMR ($CDCl_3$): δ = 2.04 (s, 3H), 3.35 (dd, $J_a$ = 10.8 Hz, $J_b$ = 14.4 Hz, 1H), 3.42 (dd, $J_a$ = 3.6 Hz, $J_b$ = 14.4 Hz, 1H), 5.40 (dd, $J_a$ = 3.6 Hz, $J_b$ = 10.8 Hz, 1H), 5.68 (dd, $J_a$ = 0.8 Hz, $J_b$ = 2.8 Hz, 1H), 5.79 (d, $J$ = 2.8 Hz, 1H), 7.04–7.14 (m, 2H), 7.53 (td, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 2H), 7.66 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.77–7.83 (m, 2H), 7.87–7.93 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ = 13.4, 27.3, 68.4, 106.3, 108.4, 115.8, 116.1, 129.1, 129.8, 131.7, 131.8, 134.5, 136.4, 147.1, 151.6, 190.4; IR: ν = 3118, 3073, 2975, 2926, 1723, 1675, 1595, 1509, 1446, 1413, 1370, 1325, 1239, 1190, 1150, 1085, 1025, 1003, 954,866, 822, 786, 739 cm$^{-1}$; HR-MS (ESI): $m/z$ = 395.0725, calcd. for $C_{20}H_{17}FNaO_4S$ $[M+Na]^+$: 395.0729.

**1-(4-Chlorophenyl)-3-(5-methylfuran-2-yl)-2-(phenylsulfonyl)propan-1-one (7c):** brown liquid; $^1$H NMR ($CDCl_3$): δ = 2.04 (s, 3H), 3.35 (dd, $J_a$ = 10.8 Hz, $J_b$ = 14.4 Hz, 1H), 3.42 (dd, $J_a$ = 3.6 Hz, $J_b$ = 14.4 Hz, 1H), 5.38 (dd, $J_a$ = 3.6 Hz, $J_b$ = 10.8 Hz, 1H), 5.68 (dd, $J_a$ = 1.2 Hz, $J_b$ = 3.2 Hz, 1H), 5.78 (d, $J$ = 3.2 Hz, 1H), 7.39 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H), 7.53 (td, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 2H), 7.66 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.79 (dd, $J_a$ = 1.2 Hz, $J_b$ = 3.6 Hz, 2H), 7.80–7.83 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ = 13.4, 27.3, 68.4, 106.4, 108.5, 129.1, 129.2, 129.8, 130.3, 134.6, 135.4, 136.3, 140.6, 147.1, 151.7, 190.8; IR: ν = 3098, 3067, 2957, 2924, 1725, 1684, 1587, 1486, 1448, 1402, 1323, 1253, 1216, 1181, 1152, 1136, 1085, 1016, 999, 943, 816, 788 cm$^{-1}$; HR-MS (ESI): $m/z$ = 411.0428, calcd. for $C_{20}H_{17}ClNaO_4S$ $[M+Na]^+$: 411.0434.

**3-(5-Methylfuran-2-yl)-1-(4-nitrophenyl)-2-(phenylsulfonyl)propan-1-one (7d):** pale yellow solid; mp 136–138 °C; $^1$H NMR ($CDCl_3$): δ = 2.03 (s, 3H), 3.36 (dd, $J_a$ = 10.8 Hz, $J_b$ = 14.4 Hz, 1H), 3.43 (dd, $J_a$ = 3.6 Hz, $J_b$ = 14.4 Hz, 1H), 5.43 (dd, $J_a$ = 3.6 Hz, $J_b$ = 10.8 Hz, 1H), 5.69 (dd, $J_a$ = 1.2 Hz, $J_b$ = 3.2 Hz, 1H), 5.81 (d, $J$ = 3.2 Hz, 1H), 7.54–7.60 (m, 2H), 7.70 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.78–7.84 (m, 2H), 8.02 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H), 8.27 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 13.4, 27.4, 69.1, 106.5, 108.7, 123.9, 129.3, 129.8, 129.9, 134.8, 136.1, 141.5, 146.7, 150.6, 151.8, 191.2; IR: ν = 3126, 3106, 3060, 2915, 1682, 1604, 1570, 1525, 1446, 1406, 1351, 1314, 1242, 1181, 1147, 1111, 1079, 1026, 942, 853, 791, 763, 721, 686, 640 cm$^{-1}$; HR-MS (ESI): $m/z$ = 422.0662, calcd. for $C_{20}H_{17}NNaO_6S$ $[M+Na]^+$: 422.0674.

**3-(5-Methylfuran-2-yl)-2-(phenylsulfonyl)-1-(thiophen-2-yl)propan-1-one (7e):** yellow solid; mp 116–118 °C; $^1$H NMR ($CDCl_3$): δ = 2.07 (s, 3H), 3.35 (dd, $J_a$ = 10.8 Hz, $J_b$ = 14.8 Hz, 1H), 3.43 (dd, $J_a$ = 3.6 Hz, $J_b$ = 14.8 Hz, 1H), 5.18 (dd, $J_a$ = 3.6 Hz, $J_b$ = 10.8 Hz, 1H), 5.69 (dd, $J_a$ = 0.8 Hz, $J_b$ = 2.8 Hz, 1H), 5.72 (d, $J$ = 2.8 Hz, 1H), 7.08 (dd, $J_a$ = 4.0 Hz, $J_b$ = 4.8 Hz, 1H), 7.52 (td, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 2H), 7.65 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.66–7.70 (m, 2H), 7.83 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 13.4, 26.9, 70.3, 106.3, 108.5, 128.5, 129.1, 129.8, 134.2, 134.5, 136.1, 136.4, 144.1, 147.1, 151.6, 183.7; IR: ν = 3109, 3070, 2965, 2850, 1724, 1659, 1571, 1517, 1480, 1447, 1413, 1354, 1315, 1255, 1218, 1187, 1145, 1080, 1058, 1024, 1000, 953, 892, 851, 785, 750, 722 cm$^{-1}$; HR-MS (ESI): $m/z$ = 383.0379, calcd. for $C_{18}H_{16}NaO_4S_2$ $[M+Na]^+$: 383.0388.

**1-Phenyl-2-(phenylsulfonyl)-3-(phenylthio)propan-1-one (9a):** yellow solid; mp 79–81 °C; $^1$H NMR ($CDCl_3$): δ = 3.45 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.67 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.6 Hz, 1H), 5.21 (dd, $J_a$ = 2.4 Hz, $J_b$ = 11.6 Hz, 1H), 7.15–7.25 (m, 5H), 7.39 (t, $J$ = 8 Hz, 2H), 7.49 (t, $J$ = 8 Hz, 2H), 7.56 (t, $J$ = 7.6 Hz, 1H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.71–7.77 (m, 4H); $^{13}$C NMR ($CDCl_3$): δ = 31.5, 68.6, 127.6, 128.7, 129.0, 129.2, 129.4, 129.6, 130.8, 133.2, 134.2, 134.6, 136.1, 137.1, 191.2; IR: ν = 3080, 2927, 1685, 1583, 1480, 1444, 1417, 1330, 1308, 1212, 1137, 1078, 1055, 1022, 999, 972, 916, 838, 781, 764, 735, 689, 655, 562, 535 cm$^{-1}$; HR-MS (ESI): $m/z$ = 405.0583, calcd. for $C_{21}H_{18}NaO_3S_2$ $[M+Na]^+$: 405. 0595.

**1-(4-Fluorophenyl)-2-(phenylsulfonyl)-3-(phenylthio)propan-1-one (9b):** white solid; mp 99–101 °C; $^1$H NMR ($CDCl_3$): δ = 4.20 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.6 Hz, 1H), 3.65 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 5.15 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 7.08 (td, $J_a$ = 2.0 Hz, $J_b$ = 8.4 Hz, 2H), 7.16–7.21 (m, 2H), 7.22–7.27 (m, 3H), 7.52 (t, $J$ = 7.6 Hz, 2H), 7.66 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.73 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.8 Hz, 2H), 7.81 (qd, $J_a$ = 2.0 Hz, $J_b$ = 5.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 31.5, 68.7, 115.9, 116.1, 127.7, 129.2, 129.5, 129.7, 130.9, 131.9, 132.0, 133.1, 134.7, 136.0, 189.6; IR: ν = 3074, 2990, 2944, 1672, 1593, 1481, 1447, 1413, 1324, 1308, 1271, 129, 1193, 1160, 1132, 1081, 1052, 1021, 997, 971, 914, 860, 829, 809, 748, 726, 691, 650, 602, 557, 532 cm$^{-1}$; HR-MS (ESI): $m/z$ = 423.0485, calcd. for $C_{21}H_{17}FNaO_3S_2$ $[M+Na]^+$: 423.0501.

**1-(4-Chlorophenyl)-2-(phenylsulfonyl)-3-(phenylthio)propan-1-one (9c):** pale pink solid; mp 93–95 °C; $^1$H NMR ($CDCl_3$): δ = 3.41 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.64 (dd, $J_a$ = 2.4 Hz, $J_b$ = 13.2 Hz, 1H), 5.14 (dd, $J_a$ = 2.4 Hz, $J_b$ = 11.6 Hz, 1H), 7.16–7.20 (m, 2H), 7.22–7.26 (m, 3H), 7.38 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H), 7.51 (td, $J_a$ = 2.0 Hz, $J_b$ = 7.6 Hz, 2H), 7.66 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.71 (dd, $J_a$ = 1.6 Hz, $J_b$ = 6.8 Hz, 2H), 7.73 (dd, $J_a$ = 0.8 Hz, $J_b$ =

8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 31.5, 68.7, 127.7, 129.1, 129.1, 129.2, 129.5, 129.7, 130.4, 130.9, 133.0, 134.7, 135.4, 136.0, 140.9, 190.1; IR: ν = 3010, 3060, 2953, 1676, 1582, 1480, 1443, 1404, 1327, 1307, 1266, 1230, 1146, 1085, 1013, 954, 910, 855, 803, 756, 734, 685, 638, 554, 527 $cm^{-1}$; HR-MS (ESI): *m/z* = 439.0187, calcd. for $C_{21}H_{17}ClNaO_3S_2$ $[M+Na]^+$: 439.0205.

**2-(Phenylsulfonyl)-3-(phenylthio)-1-(p-tolyl)propan-1-one (9d)**: pale yellow liquid; $^1$H NMR ($CDCl_3$): δ = 2.39 (s, 3H), 3.43 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.65 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 5.18 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 7.18–7.22 (m, 4H), 7.23–7.28 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.73 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 21.9, 31.6, 68.5, 127.6, 129.1, 129.3, 129.4, 129.5, 129.7, 130.9, 133.3, 134.6, 134.7, 136.2, 145.5, 190.5; IR: ν = 3062, 2928, 1724, 1678, 1605, 1479, 1445, 1412, 1380, 1328, 1272, 1234, 1186, 1152, 1083, 1025, 998, 962, 917, 855, 802, 744, 690, 648, 556, 532 $cm^{-1}$; HR-MS (ESI): *m/z* = 419.0745, calcd. for $C_{22}H_{20}NaO_3S_2$ $[M+Na]^+$: 419.0752.

**4-[2-(Phenylsulfonyl)-3-(phenylthio)propanoyl]benzonitrile (9e):** pale pink solid; mp 118–120 °C; $^1$H NMR ($CDCl_3$): δ = 3.40 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.6 Hz, 1H), 3.64 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.6 Hz, 1H), 5.16 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 7.13–7.19 (m, 2H), 7.23–7.27 (m, 3H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.68–7.75 (m, 5H), 7.85 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 31.5, 69.2, 117.2, 117.7, 127.9, 129.3, 129.4, 129.6, 129.7, 130.8, 132.5, 132.7, 135.0, 135.7, 139.9, 190.5; IR: ν = 3010, 3069, 2963, 2227, 1727, 1682, 1580, 1480, 1443, 1405, 1336, 1304, 1268, 1230, 1146, 1079, 1021, 999, 957, 913, 866, 845, 806, 780. 739, 687, 646, 560, 534 $cm^{-1}$; HR-MS (ESI): *m/z* = 430.0547, calcd. for $C_{22}H_{17}NNaO_3S_2$ $[M+Na]^+$: 430.0548.

**1-(4-Nitrophenyl)-2-(phenylsulfonyl)-3-(phenylthio)propan-1-one (9f):** pale yellow solid; mp124–126 °C; $^1$H NMR ($CDCl_3$): δ = 3.41 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.6 Hz, 1H), 3.65 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.6 Hz, 1H), 5.20 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 7.14–7.20 (m, 2H), 7.22–7.26 (m, 3H), 7.56 (tt, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 2H), 7.71 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.74 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.8 Hz, 2H), 7.92 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 31.5, 69.4, 123.9, 127.9, 129.4, 129.6, 129.7, 130.0, 130.8, 132.7, 135.0, 135.7, 141.3, 150.7, 190.4; IR: ν = 3064, 2968, 2928, 1688, 1604, 1527, 1447, 1346, 1326, 1315, 1299, 1269, 1227, 1184, 1149, 1083, 961, 857 $cm^{-1}$; HR-MS (ESI): *m/z* = 450.0439, calcd. for $C_{21}H_{17}NNaO_5S_2$ $[M+Na]^+$: 450.0446.

**1-(4-Hydroxyphenyl)-2-(phenylsulfonyl)-3-(phenylthio)-propan-1-one (9g)**: yellow solid, mp: 130–132 °C; $^1$H NMR ($CDCl_3$): 3.43 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.62 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 4.55–5.10 (m, 1H), 5.15 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 7.16–7.28 (m, 5H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.63–7.66 (m, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.6 Hz,2H); $^{13}$C NMR ($CDCl_3$): 31.6, 68.3, 115.8, 127.7, 129.3, 129.5, 129.7, 129.9, 131.0, 132.0, 133.2, 134.8, 136.0, 162.0, 189.2; IR ($cm^{-1}$): 3403, 3064, 2935, 1666, 1592, 1514, 1478, 1443, 1415, 1327, 1307, 1274, 1234, 1173, 1148, 1081, 1000, 964, 915, 855, 822, 741, 689, 555, 533; HRMS *m/z* (ESI) calcd for $C_{21}H_{18}NaO_4S_2$ $[M + Na]^+$ 421.0544 found 421.0539.

**2-(Phenylsulfonyl)-3-(phenylthio)-1-(thiophen-2-yl)propan-1-one (9h):** yellow liquid; $^1$H NMR ($CDCl_3$): δ = 3.42 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.6 Hz, 1H), 3.65 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.6 Hz, 1H), 4.93 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 7.06 (dd, $J_a$ = 3.6 Hz, $J_b$ = 4.8 Hz, 1H), 7.22–7.28 (m, 5H), 7.47–7.54 (m, 3H), 7.65 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.70 (dd, $J_a$ = 1.2 Hz, $J_b$ = 4.8 Hz, 1H), 7.76 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 31.1, 70.8, 127.6, 128.6, 129.2, 129.4, 129.7, 130.9, 133.2, 134.5, 134.7, 136.1, 136.4, 144.4, 182.9; IR: ν = 3098, 2932, 1722, 1659, 1582, 1515, 1478, 1444, 1412, 1358, 1325, 1273, 1243, 1189, 1151, 1080, 1025, 849, 825, 738, 689, 570, 532 $cm^{-1}$; HR-MS (ESI): *m/z* = 411.0153, calcd. for $C_{19}H_{16}NaO_3S_3$ $[M+Na]^+$: 411.0159.

**1-(Furan-2-yl)-2-(phenylsulfonyl)-3-(phenylthio)propan-1-one (9i):** pale yellow solid; mp 98–100 °C; $^1$H NMR ($CDCl_3$): δ = 3.43 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.67 (dd, $J_a$ = 2.4 Hz, $J_b$ = 13.2 Hz, 1H), 5.00 (dd, $J_a$ = 2.4 Hz, $J_b$ = 11.6 Hz, 1H), 6.52 (dd, $J_a$ = 1.6 Hz, $J_b$ = 3.6 Hz, 1H), 7.14 (d, $J_a$ = 3.6 Hz, 1H), 7.21–7.29 (m, 5H), 7.51 (t, *J* = 8.0 Hz, 3H), 7.65 (t, $J_a$ = 7.2 Hz, 1H), 7.77 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 30.6, 69.5, 113.2, 120.1, 127.6, 129.2, 129.4, 129.6, 130.9, 133.2, 134.6, 136.3, 148.1, 152.8, 178.5; IR: ν = 3159, 3145, 3130, 3063, 2978, 2920, 1724, 1670, 1564, 1462, 1418, 1395, 1324, 1308, 1284, 1256, 1228, 1198, 1171, 1133, 1080, 1068, 1035, 1019, 994, 971, 940, 887, 875, 852, 830, 765, 754, 718, 690, 665, 611, 588, 551, 532 $cm^{-1}$; HR-MS (ESI): *m/z* = 395.0384, calcd. for $C_{19}H_{16}NaO_4S_2$ $[M+Na]^+$: 395.0388.

**3-[(4-Methoxyphenyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9j):** pale brown liquid; $^1$H NMR ($CDCl_3$): δ = 3.36 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.51 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 3.78 (s, 3H), 5.16 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 6.72–6.77 (m, 2H), 7.10–7.15 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.56–7.65 (m, 2H), 7.71 (dd, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 2H), 7.81 (dd, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 33.4, 55.4, 68.8, 115.0, 123.1, 128.7, 129.1, 129.7, 134.2, 134.6, 134.6, 136.2, 137.1, 159.9, 191.2; IR: ν = 3064, 2941, 2838, 1682, 1591, 1494, 1448, 1413, 1326, 1287, 1248, 1181, 1151, 1082, 1028, 963, 917, 830, 742, 686, 556, 532 $cm^{-1}$; HR-MS (ESI): *m/z* = 435.0685, calcd. for $C_{22}H_{20}NaO_4S_2$ $[M+Na]^+$: 435.0701.

**3-[(4-Hydroxyphenyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9k):** yellow liquid; $^1$H NMR ($CDCl_3$): δ = 3.37 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.51 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 5.19 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.2 Hz, 1H), 6.65–6.70 (m, 2H), 7.02–7.07 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.71 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.79 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 31.5, 68.2, 115.8, 127.7, 129.3, 129.4, 129.5, 129.6, 130.9, 131.9, 133.1, 134.8, 135.9, 162.3, 189.2; IR: ν = 3398, 3184, 3063, 2933, 1668, 1600, 1582, 1514, 1479, 1446, 1440, 1416, 1326, 1308, 1274, 1235, 1172, 1148, 1082, 1025, 999, 916, 823, 742, 688 $cm^{-1}$; HR-MS (ESI): *m/z* = 421.0551, calcd. for $C_{21}H_{18}NaO_4S_2$ $[M+Na]^+$: 421.0544.

**3-[(4-Chlorophenyl)thio]-1-phenyl-2-(phenylsulfonyl)propan-1-one (9l):** pale yellow solid; mp 96–98 °C; $^1$H NMR ($CDCl_3$): δ = 3.46 (dd, $J_a$ = 11.2 Hz, $J_b$ = 13.2 Hz, 1H), 3.62 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.6 Hz, 1H), 5.18 (dd, $J_a$ = 2.4 Hz, $J_b$ = 7.2 Hz, 1H), 7.11 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H), 7.19 (dt, $J_a$ = 2.0 Hz, $J_b$ = 8.8 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.70–7.79 (m, 4H); $^{13}$C NMR ($CDCl_3$): δ = 31.8, 68.7, 128.8, 129.0, 129.2, 129.6, 129.7, 131.7, 132.3, 133.8, 134.3, 134.7, 136.1, 137.0, 191.0; IR: ν = 3057, 2922, 1676, 1585,

1477, 1446, 1416, 1390, 1326, 1270, 1233, 1180, 1125, 1080, 1004, 958, 912, 842, 813, 773, 741, 685, 622, 553, 530 $cm^{-1}$; HR-MS (ESI): $m/z$ = 439.0196, calcd. for $C_{21}H_{17}ClNaO_3S_2$ $[M+Na]^+$: 439.0205.

**3-[(4-Isopropylphenyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9m)**: brown liquid; $^1H$ NMR ($CDCl_3$): δ = 1.22 (s, 3H), 1.24 (s, 3H), 2.87 (sept, $J$ = 6.8 Hz, 1H), 3.40 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.61 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 5.22 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 7.09 (dd, $J_a$ = 2.0 Hz, $J_b$ = 6.4 Hz, 2H), 7.13 (dd, $J_a$ = 2.0 Hz, $J_b$ = 6.4 Hz, 2H), 7.40 (t, $J$ = 8.0 Hz, 2H), 7.49 (t, $J$ = 8.0 Hz, 2H), 7.57 (t, $J$ = 7.6 Hz, 1H), 7.63 (t, $J$ = 7.6 Hz, 1H), 7.72 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.8 Hz, 2H), 7.78 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.8 Hz, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 23.9, 24.0, 32.2, 33.8, 68.8, 127.6, 128.7, 129.1, 129.1, 129.6, 129.7, 131.7, 134.2, 134.6, 136.1, 137.1, 148.9, 191.2; IR: ν = 3064, 2961, 2870, 1683, 1593, 1490, 1448, 1415, 1326, 1311, 1270, 1229, 1187, 1151, 1134, 1083, 1000, 962, 917, 827, 740, 686, 552, 532 $cm^{-1}$; HR-MS (ESI): $m/z$ = 447.1060, calcd. for $C_{24}H_{24}NaO_3S_2$ $[M+Na]^+$: 447.1065.

**3-[(2-Methoxyphenyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9n):** white solid; mp 83–85 °C; $^1H$ NMR ($CDCl_3$): δ = 3.38 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.69 (dd, $J_a$ = 2.4 Hz, $J_b$ = 13.2 Hz, 1H), 3.73 (s, 3H), 5.18 (dd, $J_a$ = 2.4 Hz, $J_b$ = 11.2 Hz, 1H), 6.77 (td, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 6.81 (dd, $J_a$ = 0.8 Hz, $J_b$ = 8.0 Hz, 1H), 7.07 (dd, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.24–7.27 (m, 1H), 7.39 (t, $J$ = 8.0 Hz, 2H), 7.49 (t, $J$ = 8.0 Hz, 2H), 7.56 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 1H), 7.63 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 1H), 7.72 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.78 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 30.2, 55.7, 69.0, 111.1, 120.1, 121.1, 128.6, 129.1, 129.6, 129.9, 133.7, 134.0, 134.5, 136.3, 137.1, 158.9, 191.1; IR: ν = 3062, 2936, 2837, 1675, 1579, 1475, 1450, 1431, 1340, 1309, 1276, 1244, 1180, 1127, 1076, 1019, 958, 913, 843, 766, 744, 736, 687, 631, 552, 521 $cm^{-1}$; HR-MS (ESI): $m/z$ = 435.0694, calcd. for $C_{22}H_{20}NaO_4S_2$ $[M+Na]^+$: 435.0701.

**1-Phenyl-2-(phenylsulfonyl)-3-(*o*-tolylthio)propan-1-one (9o):** pale pink solid; mp 97–99 °C; $^1H$ NMR ($CDCl_3$): δ = 2.10 (s, 3H), 3.44 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.63 (dd, $J_a$ = 2.4 Hz, $J_b$ = 13.2 Hz, 1H), 5.19 (dd, $J_a$ = 2.4 Hz, $J_b$ = 11.6 Hz, 1H), 7.07–7.18 (m, 4H), 7.38 (t, $J$ = 8 Hz, 2H), 7.50 (t, $J$ = 8 Hz, 2H), 7.56 (t, $J$ = 7.2 Hz, 1H), 7.64 (t, $J$ = 7.6 Hz, 1H), 7.70–7.75 (m, 4H); $^{13}C$ NMR ($CDCl_3$): δ = 20.3, 30.5, 68.5, 126.9, 127.6, 128.7, 129.0, 129.2, 129.7, 130.3, 130.8, 132.2, 134.2, 134.6, 136.2, 137.0, 139.6, 191.1; IR: ν = 3058, 2975, 1682, 1588, 1448, 1337, 1317, 1295, 1265, 1228, 1143, 1079, 952, 926, 759, 737, 683, 665, 642, 557, 534 $cm^{-1}$; HR-MS (ESI): $m/z$ = 419.0748, calcd. for $C_{22}H_{20}NaNaO_3S_2$ $[M+Na]^+$: 419.0752.

**3-[(2,4-Dimethylphenyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9p):** yellow liquid; $^1H$ NMR ($CDCl_3$): δ = 2.09 (s, 3H), 2.26 (s, 3H), 3.39 (dd, $J_a$ = 11.2 Hz, $J_b$ = 13.2 Hz, 1H), 3.55 (dd, $J_a$ = 2.4 Hz, $J_b$ = 13.2 Hz, 1H), 5.16 (dd, $J_a$ = 2.4 Hz, $J_b$ = 11.2 Hz, 1H), 6.85 (d, $J$ = 7.6 Hz, 1H), 6.92 (s, 1H), 7.04 (d, $J$ = 7.6 Hz, 1H), 7.39 (t, $J$ = 8.0 Hz, 2H), 7.49 (t, $J$ = 8.0 Hz, 2H), 7.56 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.63 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.72 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.75 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 20.2, 21.0, 31.1, 68.6, 127.5, 128.2, 128.6, 129.0, 129.1, 129.6, 131.7, 131.8, 134.1, 134.6, 136.2, 136.9, 138.0, 140.1, 191.1; IR: ν = 3061, 2920, 2862, 1723, 1683, 1595, 1479, 1448, 1418, 1326, 1270, 1230, 1186, 1151, 1134, 1083, 1055, 1000, 963, 916, 846, 814, 741, 686, 556, 532 $cm^{-1}$; HR-MS (ESI): $m/z$ = 433.0897, calcd. for $C_{23}H_{22}NaO_3S_2$ $[M+Na]^+$: 433.0908.

**3-[(3,5-Dimethylphenyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9q):** yellow solid; mp 100–102 °C; $^1H$ NMR ($CDCl_3$): δ = 2.19 (s, 6H), 3.39 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.60 (dd, $J_a$ = 2.8 Hz, $J_b$ = 13.2 Hz, 1H), 5.18 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 1H), 6.78 (s, 2H), 6.86 (s, 1H), 7.41 (t, $J$ = 8.0 Hz, 2H), 7.50 (t, $J$ = 8.0 Hz, 2H), 7.57 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.64 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.74 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.78 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 21.2, 31.9, 68.6, 128.7, 129.1, 129.1, 129.3, 129.6, 129.7, 132.2, 134.1, 134.6, 136.3, 137.2, 139.1, 191.3; IR: ν = 3098, 2928, 1674, 1582, 1446, 1419, 1381, 1305, 1259, 1225, 1194, 1130, 1077, 1044, 997, 968, 912, 842, 766, 744, 683, 651, 556, 531 $cm^{-1}$; HR-MS (ESI): $m/z$ = 433.0901, calcd. for $C_{23}H_{22}NaO_3S_2$ $[M+Na]^+$: 433.0908.

**3-(Benzylthio)-1-phenyl-2-(phenylsulfonyl)propan-1-one (9r):** brown liquid; $^1H$ NMR ($CDCl_3$): δ = 3.11 (dd, $J_a$ = 3.2 Hz, $J_b$ = 13.6 Hz, 1H), 3.22 (dd, $J_a$ = 11.2 Hz, $J_b$ = 13.6 Hz, 1H), 3.63 (s, 2H), 5.00 (dd, $J_a$ = 3.2 Hz, $J_b$ = 11.6 Hz, 1H), 7.16–7.22 (m, 2H), 7.26–7.31 (m, 2H), 7.39 (t, $J$ = 8.0 Hz, 2H), 7.46 (t, $J$ = 8.0 Hz, 2H), 7.56 (t, $J$ = 7.6 Hz, 1H), 7.60 (t, $J$ = 7.6 Hz, 1H), 7.67 (td, $J_a$ = 0.8 Hz, $J_b$ = 8.0 Hz, 4H); $^{13}C$ NMR ($CDCl_3$): δ = 29.3, 37.8, 69.3, 127.5, 128.7, 128.9, 129.0, 129.1, 129.1, 129.6, 134.1, 134.5, 136.3, 137.0, 138.1, 191.4; IR: ν = 3062, 2928, 1721, 1681, 1593, 1493, 1449, 1412, 1324, 1274, 1230, 1186, 1150, 1083, 1000, 962, 929, 844, 758, 740, 702, 686, 554, 532 $cm^{-1}$; HR-MS (ESI): $m/z$ = 419.0748, calcd. for $C_{22}H_{20}NaO_3S_2$ $[M+Na]^+$: 419.0752.

**3-(Cyclohexylthio)-1-phenyl-2-(phenylsulfonyl)propan-1-one (9s):** pale yellow solid; mp 88–89 °C; $^1H$ NMR ($CDCl_3$): δ = 1.13–1.29 (m, 5H), 1.56 (dd, $J_a$ = 2.4 Hz, $J_b$ = 8.0 Hz, 1H), 1.63–1.75 (m, 2H), 1.78–1.90 (m, 2H), 2.51–2.62 (m, 1H), 3.17 (dd, $J_a$ = 11.2 Hz, $J_b$ = 12.8 Hz, 1H), 2.24 (dd, $J_a$ = 3.2 Hz, $J_b$ = 12.8 Hz, 1H), 3.27 (dd, $J_a$ = 3.2 Hz, $J_b$ = 11.2 Hz, 1H), 7.46 (t, $J$ = 8.0 Hz, 2H), 7.51 (t, $J$ = 8.0 Hz, 2H), 7.59 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.64 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.76 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.94 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 25.7, 26.0, 26.0, 27.3, 33.3, 33.6, 44.8, 70.2, 128.9, 129.1, 129.2, 129.7, 134.2, 134.6, 136.3, 137.3, 191.7; IR: ν = 3066, 2924, 2853, 1673, 1586, 1448, 1417, 1343, 1311, 1269, 1236, 1190, 1130, 1083, 1023, 999, 961, 912, 844, 775, 748, 685, 632, 552, 523 $cm^{-1}$; HR-MS (ESI): $m/z$ = 411.1055, calcd. for $C_{21}H_{24}NaO_3S_2$ $[M+Na]^+$: 411.1065.

**3-[(Furan-2-ylmethyl)thio]-1-phenyl-2-(phenylsulfonyl)-propan-1-one (9t):** black liquid; $^1H$ NMR ($CDCl_3$): δ = 3.15 (dd, $J_a$ = 3.6 Hz, $J_b$ = 13.6 Hz, 1H), 3.25 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.6 Hz, 1H),3.65 (dd, $J_a$ = 14.8 Hz, $J_b$ = 18.0 Hz, 2H), 5.10 (dd, $J_a$ = 3.2 Hz, $J_b$ = 11.2 Hz, 1H), 6.16 (d, $J$ = 3.2 Hz, 1H), 6.33 (dd, $J_a$ = 2.0 Hz, $J_b$ = 3.2 Hz, 1H), 7.33 (d, $J$ = 1.2 Hz, 1H), 7.43 (t, $J$ = 8.0 Hz, 2H), 7.49 (t, $J$ = 8.0 Hz, 2H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.63 (t, $J$ = 7.2 Hz, 1H), 7.72 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.84 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$): δ = 29.2, 29.4, 69.4, 108.4, 110.8, 128.7, 129.1, 129.2, 129.7, 134.2, 134.5, 136.3, 137.1, 142.6, 150.7, 191.5; IR: ν = 3065, 2930, 1681, 1593, 1052, 1448, 1412, 1325, 1311, 1275, 1232, 1185, 1150, 1083, 1012, 963, 938, 845,

741, 687, 555, 531 $cm^{-1}$; HR-MS (ESI): $m/z$ = 409.0530, calcd. for $C_{20}H_{18}NaO_4S_2$ $[M+Na]^+$: 409.0544.

**3-(2-Hydroxynaphthalen-1-yl)-1-phenyl-2-(phenylsulfonyl)propan-1-one (11a):** pale yellow solid; mp 194–196 °C; $^1$H NMR (DMSO-$d_6$): δ = 3.57 (dd, $J_a$ = 2.4 Hz, $J_b$ = 13.2 Hz, 1H), 3.84 (dd, $J_a$ = 10.8 Hz, $J_b$ = 13.2 Hz, 1H), 5.81 (dd, $J_a$ = 2.4 Hz, $J_b$ = 10.4 Hz, 1H), 7.01 (d, $J$ = 8.8 Hz, 1H), 7.23 (t, $J$ = 7.6 Hz, 1H), 7.30 (t, $J$ = 7.6 Hz, 2H), 7.40 (t, $J$ = 7.6 Hz, 1H), 7.49 (t, $J$ = 7.2 Hz, 1H), 7.56 (t, $J$ = 7.6 Hz, 3H), 7.64–7.74 (m , 4H), 7.79 (t, $J$ = 7.2 Hz, 1H), 7.99 (d, $J$ = 7.6 Hz, 2H), 9.97 (s, 1H); $^{13}$C NMR (DMSO-$d_6$): δ = 24.0, 67.1, 112.8, 117.4, 122.0, 122.4, 126.5, 128.0, 128.4, 128.6, 128.8, 129.2, 129.4, 132.5, 133.8, 134.5, 136.9, 137.4, 153.2, 192.2; IR: ν = 3378, 3066, 2931, 1661, 1584, 1513, 1444, 1404, 1355, 1330, 1304, 1268, 1213, 1186, 1131, 1079, 1043, 1004, 984, 950, 810, 741 $cm^{-1}$; HR-MS (ESI): $m/z$ = 439.0976, calcd. for $C_{25}H_{20}NaO_4S$ $[M+Na]^+$: 439.0980.

**1,5-Dimethyl-4-[3-oxo-3-phenyl-2-(phenylsulfonyl)propyl]-2-phenyl-1*H*-pyrazol-3(2*H*)-one (11b):** yellow liquid; $^1$H NMR ($CDCl_3$): δ = 2.17 (s, 3H), 2.88 (s, 3H), 3.11–3.21 (m, 2H), 6.09 (dd, $J_a$ = 6.4 Hz, $J_b$ = 8.0 Hz, 1H), 7.16 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.25 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.3 (t, $J$ = 7.6 Hz, 2H), 7.38 (td, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 2H), 7.43 (td, $J_a$ = 1.6 Hz, $J_b$ = 7.6 Hz, 2H), 7.48 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.54 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 1H), 7.83 (dd, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 2H), 7.84 (dd, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 10.9, 22.2, 35.6, 65.7, 103.5, 124.1, 126.8, 128.7, 128.9, 128.9, 129.1, 129.2, 133.8, 134.0, 134.7, 137.2, 138.3, 153.8, 165.4, 193.0; IR: ν = 3064, 2929, 1723, 1674, 1660, 1594, 1493, 1449, 1413, 1368, 1312, 1289, 1253, 1148, 1084, 1026, 1000, 968, 932, 865, 824, 754, 725, 690, 551, 536 $cm^{-1}$; HR-MS (ESI) $m/z$ = 483.1335, calcd. for $C_{26}H_{24}N_2NaO_4S$ $[M+Na]^+$: 483.1354.

**1-Phenyl-3-(2-phenyl-1*H*-indol-3-yl)-2-(phenylsulfonyl)-propan-1-one (11c):** pale green solid; mp 158–160 °C; $^1$H NMR ($CDCl_3$): δ = 3.74–3.83 (m, 2H), 5.40 (dd, $J_a$ = 6.4 Hz, $J_b$ = 8.0 Hz, 1H), 7.05–7.16 (m, 4H), 7.20 (dd, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.33 (s, 2H), 7.34 (d, $J$ = 2.8 Hz, 3H), 7.36–7.41 (m, 3H), 7.45 (t, $J$ = 8.0 Hz, 2H), 7.52 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 1H), 7.59 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.2 Hz, 1H), 7.76 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 8.09 (s, 1H); $^{13}$C NMR ($CDCl_3$): δ = 23.6, 69.0, 106.6, 110.9, 118.9, 120.2, 122.6, 127.9, 128.2, 128.4, 128.4, 128.5, 129.0, 129.1, 129.6, 132.4, 133.5, 134.2, 135.4, 135.7, 137.1, 137.1, 192.6; IR: ν = 3377, 3057, 3024, 2941, 1680, 1589, 1488, 1446, 1368, 1323, 1295, 1244, 1230, 1181, 1143, 1079, 1023, 999, 972, 937, 905, 842, 815, 775, 759, 744, 730, 686, 589, 538, 531 $cm^{-1}$; HR-MS (ESI): $m/z$ = 488.1288, calcd. for $C_{29}H_{23}NNaO_3S$ $[M+Na]^+$: 488.1296.

**3-(4-(Dimethylamino)phenyl)-1-phenyl-2-(phenylsulfonyl)propan-1-one (11d):** yellow liquid; $^1$H NMR ($CDCl_3$): δ = 2.82 (s, 6H), 3.27 (dd, $J_a$ = 11.6 Hz, $J_b$ = 13.2 Hz, 1H), 3.38 (dd, $J_a$ = 3.2 Hz, $J_b$ = 13.2 Hz, 1H), 5.29 (dd, $J_a$ = 3.2 Hz, $J_b$ = 11.2 Hz, 1H), 6.51 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 2H), 6.93 (dd, $J_a$ = 2.8 Hz, $J_b$ = 11.6 Hz, 2H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.45–7.55 (m, 3H), 7.64 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.72 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H), 7.81 (dd, $J_a$ = 1.2 Hz, $J_b$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 33.2, 40.6, 71.8, 112.9, 123.4, 128.7, 128.9, 129.0, 129.7, 129.9, 133.8, 134.4, 136.7, 137.5, 149.7, 192.7; IR: ν = 3065, 2927, 2805, 1817, 1724, 1681, 1613, 1524, 1480, 1447, 1312, 1240, 1189, 1149, 1082, 1000, 974, 944, 865, 813, 753, 727, 688, 568, 532 $cm^{-1}$; HR-MS (ESI): $m/z$ = 416.1283, calcd. for $C_{23}H_{23}NNaO_3S$ $[M+Na]^+$: 416.1296.

**3-(2,4-Dihydroxyphenyl)-1-phenyl-2-(phenylsulfonyl)propan-1-one (11e):** pale brown liquid; $^1$H NMR (DMSO-$d_6$): δ = 3.00 (dd, $J_a$ = 10.8 Hz, $J_b$ = 13.2 Hz, 1H), 3.10 (dd, $J_a$ = 3.6 Hz, $J_b$ = 13.2 Hz, 1H), 5.73 (dd, $J_a$ = 3.6 Hz, $J_b$ = 10.8 Hz, 1H), 5.88 (dd, $J_a$ = 2.4 Hz, $J_b$ = 8.0 Hz, 1H), 6.08 (d, $J$ = 2.0 Hz, 1H), 6.52 (d, $J$ = 8.4 Hz, 1H), 7.38 (t, $J$ = 8.0 Hz, 2H), 7.51–7.60 (m, 3H), 7.66–7.73 (m, 3H), 7.79 (d, $J$ = 7.6 Hz, 2H), 8.90 (s, 1H), 9.42 (s, 1H); $^{13}$C NMR (DMSO-$d_6$): δ = 29.0, 67.7, 102.8, 106.6, 112.4, 128.8, 129.2, 129.5, 129.8, 131.4, 134.4, 134.9, 137.4, 137.6, 156.4, 157.8, 192.6; IR: ν = 3178, 3067, 2961, 1680, 1609, 1521, 1452, 1385, 1306, 1241, 1149, 1104, 1082, 1045, 1024, 1000, 746, 688 $cm^{-1}$; HR-MS (ESI): $m/z$ = 405.0765, calcd. for $C_{21}H_{18}NaO_5S$ $[M+Na]^+$: 405.0773.

**1-Phenyl-2-(phenylsulfonyl)-3-(1*H*-pyrrol-2-yl)propan-1-one (11f):** black solid; mp 116–118 °C; $^1$H NMR ($CDCl_3$): δ = 3.42 (dd, $J_a$ = 10.4 Hz, $J_b$ = 14.8 Hz, 1H), 3.50 (dd, $J_a$ = 4.0 Hz, $J_b$ = 14.8 Hz, 1H), 5.34 (dd, $J_a$ = 4.0 Hz, $J_b$ = 10.0 Hz, 1H), 5.84–5.89 (m, 1H), 5.97 (dd, $J_a$ = 2.8 Hz, $J_b$ = 6.0 Hz, 1H), 6.53–6.57 (m, 1H), 7.38 (t, $J$ = 7.6 Hz, 2H), 7.51 (q, $J$ = 7.6 Hz, 3H), 7.63 (tt, $J_a$ = 1.2 Hz, $J_b$ = 7.6 Hz, 1H), 7.77 (dd, $J_a$ = 1.2 Hz, $J_b$ = 6.4 Hz, 2H), 7.79 (dd, $J_a$ = 1.2 Hz, $J_b$ = 6.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ = 26.2, 70.7, 107.5, 108.5, 117.9, 125.6, 128.8, 129.1, 129.2, 129.8, 134.2, 134.5, 136.4, 136.8, 193.0; IR: ν = 3375, 3066, 2911, 1722, 1657, 1584, 1477, 1446, 1424, 1344, 1310, 1282, 1247, 1184, 1149, 1121, 1082, 1024, 998, 974, 951, 932, 882, 850, 792, 775, 750, 722, 686, 639, 592, 544 $cm^{-1}$; HR-MS (ESI): $m/z$ = 362.0819, calcd. for $C_{19}H_{17}NNaO_3S$ $[M+Na]^+$: 362.0827.

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