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Synthesis of difluorinated β-ketosulfones and novel *gem*-difluoromethylsulfone-containing heterocycles as fluorinated building blocks

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ABSTRACT

A series of new heterocyclic β-ketosulfides was prepared by the reaction of the corresponding heterocyclic thiols with α-bromoacetophenone and its derivatives. Oxidation of the products using *m*-CPBA gave the corresponding heterocyclic β-ketosulfones, which, on treatment with Selectfluor™ under anhydrous condition underwent electrophilic fluorination resulting in new heterocycles with difluoromethylene moiety adjacent to the sulfur atom and the carbonyl group. Base-induced cleavage of the five types of the resulting products, with different heterocyclic moieties as model compounds, afforded the difluoromethyl sulfones attached to the corresponding heterocycles. They can be considered as interesting fluorinated building blocks for further elaborations.

1. Introduction

Recently, organofluorine compounds have received much attention due to their potential use in pharmaceutical, biological, and material science [1]. The selective transfer of a fluorine atom into an organic molecule has become a considerable challenge for chemists interested in biological and medicinal applications [2]. The introduction of the difluoromethylene (CF_2) moiety into organic molecules, especially those heterocyclic compounds has been proved to be attractive due to the potential biological properties of such molecules [3–5]. This group has been recognized as an isopolar–isosteric replacement for oxygen. The formation of the C–F bond adjacent to the carbonyl or imine functionality increases the electrophilicity of these functional groups [6], improving their bioactivity [7]. Important efforts have been made toward the synthesis of compounds containing a difluoromethylene group adjacent to a carbonyl group [8–10]. Among organofluorine compounds, *gem*-difluorinated compounds with CF_2 adjacent to the sulfur atom have also attracted significant attention especially in the field of medicinal chemistry [11–14].

The preparation of *gem*-difluoromethylene substituted molecules falls broadly into two classes. The first involves direct *gem*-difluorination, and the second draws from the construction of molecules derived from CF_2-synthons [15]. Direct methods for the preparation of *gem*-difluorinated compounds by reacting appropriate substrates with fluorinating agents such as DAST [16], SF_4 [17], TBAF [18], BrF_3 [19], Selectfluor [20] or NFSI [21] have been reported. Several nucleophilic *gem*-difluoromethylation building blocks employing difluoromethylphenylsulfone ($PhSO_2CF_2H$) [22], bromodifluoromethylphenylsulfone ($PhSO_2CF_2Br$) [23], (trifluoromethyl)trimethylsilane (CF_3SiMe_3) [24], [(difluoromethyl)(phenylsulfonyl)]trimethylsilane ($PhSO_2CF_2SiMe_3$) [25], [(difluoromethyl)(phenylsulfanyl)]trimethylsilane ($PhSCF_2SiMe_3$) [26], [difluoro(phenylseleno)methyl]trimethylsilane ($PhSeCF_2SiMe_3$) [27], arylthiobromodifluoromethane ($ArSCF_2Br$) [28], diethyl bromodifluoromethylphosphonate [$P(O)(OEt)CF_2Br$] [29], dietyl difluoro(trimethylsilyl)methylphosphonate [$P(O)(OEt)CF_2Br$] [30] and diethyl difluoromethylphosphonate $P(O)(OEt)_2CF_2H$ [31] have been extensively studied.

In this article, we wish to report the synthesis of certain new *gem*-difluoromethylene-containing heterocycles, which also result in the preparation of difluoromethylsulfones attached to heterocycles as new fluorinated building blocks. Possibility of at room temperature synthesis of heterocyclic synthons, with the potential pharmaceutical effect of interest is the main advantage of the present method over the one proposed by Zafrani et al. [29].

2. Results and discussion

In an effort to prepare new fluorinated heterocyclic β-ketosulfones as well as new fluorinated building blocks, a series

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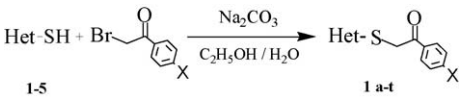
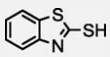
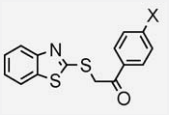
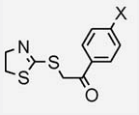
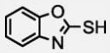
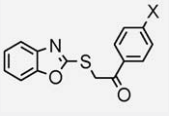
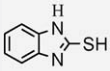
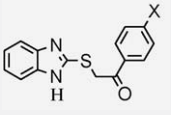
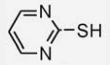
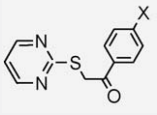
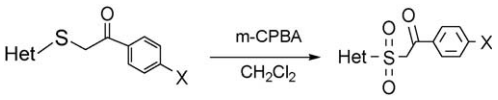
Table 1
Synthesis of heterocyclic β-ketosulfides.

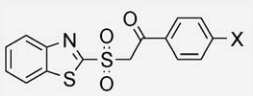
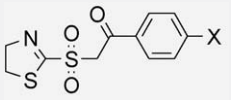
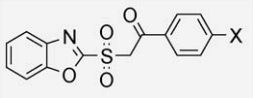
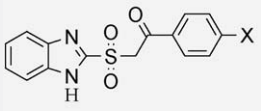
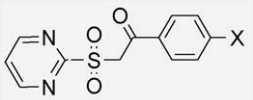


Substrate	Product		Yield (%)[a]
 **1**		(**1a**) X = H	93
		(**1b**) X = Br	96
		(**1c**) X = Cl	95
		(**1d**) X = Me	88
 **2**		(**1e**) X = H	89
		(**1f**) X = Br	95
		(**1g**) X = Cl	92
		(**1h**) X = Me	85
 **3**		(**1i**) X = H	95
		(**1j**) X = Br	95
		(**1k**) X = Cl	90
		(**1l**) X = Me	88
 **4**		(**1m**) X = H	95
		(**1n**) X = Br	96
		(**1o**) X = Cl	96
		(**1p**) X = Me	89
 **5**		(**1q**) X = H	85
		(**1r**) X = Br	87
		(**1s**) X = Cl	84
		(**1t**) X = Me	86

[a] Isolated yields.

Table 2
Sulfonation of heterocyclic β-ketosulfides.



Substrate	Product		Yield (%)[a]
1a		(**2a**) X = H	73
1b		(**2b**) X = Br	80
1c		(**2c**) X = Cl	58
1d		(**2d**) X = Me	55
1e		(**2e**) X = H	70
1f		(**2f**) X = Br	75
1g		(**2g**) X = Cl	68
1h		(**2h**) X = Me	65
1i		(**2i**) X = H	70
1j		(**2j**) X = Br	73
1k		(**2k**) X = Cl	66
1l		(**2l**) X = Me	62
1m		(**2m**) X = H	79
1n		(**2n**) X = Br	82
1o		(**2o**) X = Cl	68
1p		(**2p**) X = Me	56
1q		(**2q**) X = H	73
1r		(**2r**) X = Br	77
1s		(**2s**) X = Cl	67
1t		(**2t**) X = Me	57

[a] Isolated yields.

of heterocyclic β-ketosulfides **1a**–**t** was prepared by the reaction of heterocyclic thiols, 2-mercaptobenzothiazol (**1**), 2-mercaptothiazoline (**2**), 2-mercaptobenzoxazole (**3**), 2-mercaptobenzimidazole (**4**) and 2-mercaptopyrimidine (**5**), with α-bromoacetophenone and its derivatives in the presence of sodium carbonate (Table 1). The selected heterocyclic moieties have attracted special attention in chemistry [3–5].

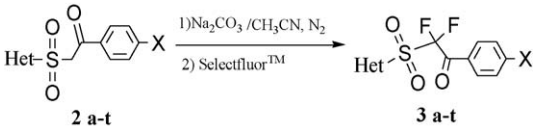
As shown in Table 1, the product yields were 85–96% (entries **1a**–**t**). Attempted fluorination of β-ketosulfides **1a**–**t** using Selectfluor (F-TEDA-BF_4) resulted in *gem*-difluorinated compounds in poor yields and the corresponding disulfides as by-products. In order to enhance activation of the methylene group adjacent to the sulfur atom and stabilize the products [32], the heterocyclic β-ketosulfides **1a**–**t** were oxidized using *m*-CPBA to the corresponding β-ketosulfones (Table 2).

The product yields of the β-ketosulfones (**2a**–**t**) were 55–80%, as shown in Table 2. In the presence of *m*-CPBA as the oxidizing agent, no competing oxidation of the heterocyclic benzothiazol and thiazoline rings was observed.

It is noteworthy that the resulting β-ketosulfones can be very useful. β-Ketosulfones are a very important group of precursors for Michael and Knoevenagel reactions and are used in the preparation of various organic compounds [33,34]. The versatile utility of heterocyclic sulfones for the preparation of carbon–carbon double bond from carbonyl compounds is well documented [35]. We used the resulted β-ketosulfones as substrates for electrophilic fluorination. Targeting nonhazardous procedure, Selectfluor™ was selected as a user-friendly fluorinating agent [36].

Fluorination of the resulted compounds **2a**–**t** (Table 3) was carried out using Selectfluor™ in the presence of sodium carbonate in dry acetonitrile, under inert atmosphere. In all cases, diflouoro derivatives were the main products when 2.5 equiv. of Selectfluor™ was used. The product yields were 38–61% (**3a**–**t**) as shown in Table 3. These new *gem*-difluorinated compounds are of

Table 3
Fluorination of heterocyclic β-ketosulfones.



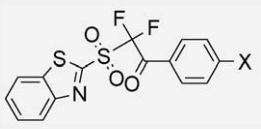
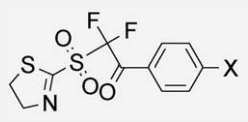
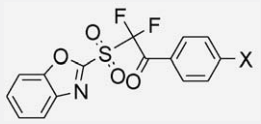
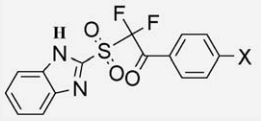
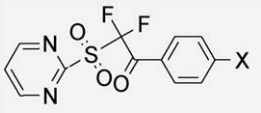
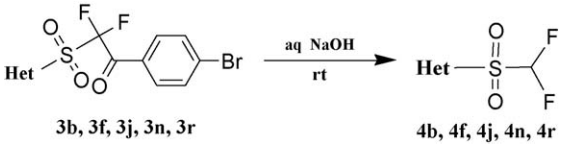
Substrate	Product		Yield (%)[a]
2a		(**3a**) X = H	48
2b		(**3b**) X = Br	56
2c		(**3c**) X = Cl	50
2d		(**3d**) X = Me	42
2e		(**3e**) X = H	50
2f		(**3f**) X = Br	52
2g		(**3g**) X = Cl	48
2h		(**3h**) X = Me	45

Table 3 (*Continued*)

Substrate	Product		Yield (%)[a]
2i		(**3i**) X = H	47
2j		(**3j**) X = Br	46
2k		(**3k**) X = Cl	45
2l		(**3l**) X = Me	38
2m		(**3m**) X = H	54
2n		(**3n**) X = Br	63
2o		(**3o**) X = Cl	53
2p		(**3p**) X = Me	46
2q		(**3q**) X = H	59
2r		(**3r**) X = Br	61
2s		(**3s**) X = Cl	57
2t		(**3t**) X = Me	41

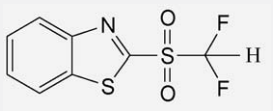
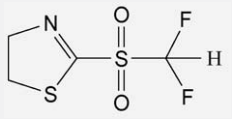
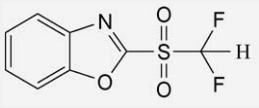
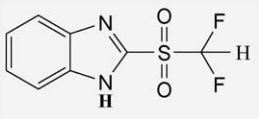
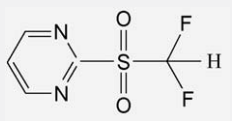
[a] Isolated yields.

Table 4
Synthesis of difluoromethyl sulfones.



3b, 3f, 3j, 3n, 3r **4b, 4f, 4j, 4n, 4r**

.

Substrate	Product	Yield (%)[a]
3b		(**4b**) 98
3f		(**4f**) 97
3j		(**4j**) 97
3n		(**4n**) 94
3r		(**4r**) 96

[a] Isolated yields.

interest due to the potential biological properties of such molecules.

The fluorination of these compounds encouraged us to examine the preparation of the corresponding fluorinated synthons. Therefore, **3b**, **3f**, **3j**, **3n** and **3r** with different heterocyclic moieties were selected as model compounds and were treated these compounds with aqueous alkali. Under this condition, these compounds underwent base-induced cleavage to afford difluoromethyl sulfones attached to the corresponding heterocycles (**4b**, **4f**, **4j**, **4n** and **4r**) in high yields (Table 4). Such fluorinated synthons can be very useful for introducing fluorinated building blocks directly into a variety of organic molecules. Our literature survey showed that only one of the resulted difluoromethylsulfone-containing heterocycle has been prepared. Calata et al. [15c] synthesized difluoromethylsulfone (**4b**) from decarboxylation reaction of realated ethyldifluoromethyl-benzothiaazolylsulfone in five steps (from mercaptoaryl as a starting material). The most advantage of our research work over the work above mentioned is working at room temperature, no expensive catalytic material, no by-product and fast reaction times.

3. Conclusions

We have prepared heterocyclic β-ketosulfides in high yields. The corresponding β-keto heterocyclic sulfones were obtained after oxidation of the resulted β-ketosulfides using *m*-CPBA. Electrophilic fluorination of these β-ketosulfones by the use of Selectfluor™ resulted in the corresponding heterocycles with difluoromethylene moiety adjacent to the sulfur atom and the carbonyl group as possible bioactive molecules. We have successfully prepared difluoromethyl sulfones via base-induced cleavage of the corresponding *gem*-difluorinated sulfones. The present synthetic methodology provides a convenient way for the preparation of new heterocyclic β-ketosulfides and β-ketosulfones as well as difluorinated β-keto heterocyclic sulfones as potential bioactive compounds. The ease and efficiency of the conversion at room temperature of β-keto heterocyclic sulfones to the corresponding fluorinated building blocks is another advantage of this method. The resulted heterocyclic difluoromethyl sulfones are expected to be useful fluorinated building blocks and the study of them as fluoroalkylating agents is underway in our laboratory.

4. Experimental

Melting points were determined using a Linkam HF591 heating stage, used in conjunction with a TC92 controller, and are uncorrected. The ^{1}H NMR spectra were recorded on either Bruker DPX-300 (300 MHz), Bruker 400 MHz or Bruker Avance-500 (500 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded at 125 MHz. The ^{19}F NMR spectra were recorded on a Bruker Avance-500 (470 MHz) spectrometer, in which the chemical shifts (δ) were measured with fluorotrichloromethane ($\delta = 0$) as an internal standard. The IR spectra were recorded on either a Jasco A-302 or a Perkin Elmer 683 infrared spectrometer. Elemental analyses were performed on a Perkin Elmer Elemental Analyzer 2400 CHN.

4.1. Typical procedure for the synthesis of β-ketosulfide (1a)

Sodium carbonate (4.5 mmol) was added to a solution of 2-mercaptobenzothiazol **1** (3 mmol) in a mixture of ethanol (15 mL) and water (15 mL). The reaction mixture was stirred at room temperature for 30 min and then α-bromoacetophenone (3 mmol) was added, and the reaction mixture was stirred at room temperature for another 1 h. The reaction was monitored by TLC and after 1 h showed the complete disappearance of the starting materials. The resulting mixture was poured into 100 mL of 1 M HCl containing 50 g of crushed ice. The crude product was filtered and the filtrate was washed

with a mixture of ethanol (10 mL) and water (10 mL). The crude product was purified by recrystallization from petroleum ether to give product **1a** as a pale yellow solid.

*4.1.1. 2-(Benzo[d]thiazol-2-ylthio)-1-phenylethanone (**1a**)*

Pale yellow solid; m.p.: 114–115 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15-7.75 (m, 4H), 7.55–7.32 (m, 5H), 5.10 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.2 (C=O), 162.1, 151.8, 135.3, 134.2, 131.1, 126.7, 126.5, 124.7, 124.1, 119.8, 119.6, 37.5. IR (KBr, cm^{-1}): 3055, 2820, 1676(C=O), 1580, 1420, 1371, 1318, 1283, 1182, 996, 750, 672. Anal. Calcd for $C_{15}H_{11}NOS_2$: C, 63.13; H, 3.89; N, 4.91. Found: C, 63.07; H, 3.86; N, 4.93.

*4.1.2. 2-(Benzo[d]thiazol-2-ylthio)-1-(4-bromophenyl)ethanone (**1b**)*

White solid; m.p.: 153–154 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15–7.45 (m, 8H), 5.23 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.9 (C=O), 162.2, 151.5, 134.7, 133.3, 129.7, 129.2, 126.1, 123.9, 123.2, 121.7, 121.4, 37.4. IR (KBr, cm^{-1}): 3027, 2943, 1683 (C=O), 1569, 1432, 1375, 1319, 1273, 1076, 986, 764. Anal. Calcd for $C_{15}H_{10}BrNOS_2$: C, 49.46; H, 2.77; N, 3.85. Found: C, 49.34; H, 2.81; N, 3.84.

*4.1.3. 2-(Benzo[d]thiazol-2-ylthio)-1-(4-chlorophenyl)ethanone (**1c**)*

Pale yellow solid; m.p.: 139–140 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15–7.42 (m, 8H), 5.23 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.7 (C=O), 162.2, 151.5, 137.6, 133.3, 129.3, 129.1, 125.2, 123.9, 123.2, 121.6, 121.4, 37.4. IR (KBr, cm^{-1}): 3070, 2908, 1685 (C=O), 1582, 1432, 1292, 1205, 1097, 986, 805, 750. Anal. Calcd for $C_{15}H_{10}ClNOS_2$: C, 56.33; H, 3.15; N, 4.38. Found: C, 56.28; H, 3.15; N, 4.46.

*4.1.4. 2-(Benzo[d]thiazol-2-ylthio)-1-p-tolylethanone (**1d**)*

Pale yellow solid; m.p.: 121–122 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15–7.23 (m, 8H), 5.22 (s, 2H), 2.65 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.4 (C=O), 162.2, 151.4, 141.5, 133.2, 132.9, 128.0, 127.7, 123.9, 123.1, 121.6, 121.5, 37.4, 23.7. IR (KBr, cm^{-1}): 3086, 2924, 1680 (C=O), 1579, 1418, 1296, 1194, 1090, 991, 817, 747. Anal. Calcd for $C_{16}H_{13}NOS_2$: C, 64.18; H, 4.38; N, 4.68. Found: C, 64.19; H, 4.35; N, 5.78.

*4.1.5. 2-(4,5-Dihydrothiazol-2-ylthio)-1-phenylethanone (**1e**)*

Pale yellow solid; m.p.: 58–60 °C; ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.20–7.55 (m, 5H), 4.82 (s, 2H), 4.05 (t, 2H, J = 7.5 Hz), 3.42 (t, 2H, J = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.1 (C=O), 161.2, 135.5, 132.4, 127.9, 127.3, 54.9, 36.2, 31.3. IR (KBr, cm^{-1}): 3117, 2912, 1678 (C=O), 1544, 1263, 1159, 971, 776. Anal. Calcd for $C_{11}H_{11}NOS_2$: C, 55.67; H, 4.67; N, 5.90. Found: C, 55.56; H, 4.64; N, 27.03.

*4.1.6. 2-(4,5-Dihydrothiazol-2-ylthio)-1-(4-bromophenyl)ethanone (**1f**)*

Pale yellow solid; m.p.: 110–111 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15–7.26 (m, 4H), 4.82 (s, 2H), 4.05 (t, 2H, J = 7.5 Hz) 3.42 (t, 2H, J = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.7 (C=O), 161.2, 134.9, 130.7, 130.1, 126.8, 54.9, 36.1, 31.2. IR (KBr, cm^{-1}): 3081, 2902, 1690 (C=O), 1558, 1276, 1166, 963, 788. Anal. Calcd for $C_{11}H_{10}BrNOS_2$: C, 41.78; H, 3.19; N, 4.43. Found: C, 41.78; H, 3.23; N, 4.38.

*4.1.7. 2-(4,5-Dihydrothiazol-2-ylthio)-1-(4-chlorophenyl)ethanone (**1g**)*

White solid; m.p.: 87–88 °C; ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.19–7.78 (m, 4H), 4.82 (s, 2H), 4.05 (t, 2H, J = 7.5 Hz), 3.42 (t, 2H, J = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.6 (C=O), 161.8, 137.7, 133.9, 129.6, 128.2, 54.9, 35.9, 31.3. IR (KBr, cm^{-1}): 3072, 2850, 1694 (C=O), 1560, 1386, 1351, 1272, 1195, 1082, 960, 811. Anal. Calcd for $C_{11}H_{10}ClNOS_2$: C, 48.61; H, 3.71; N, 5.15. Found: C, 48.52; H, 3.68; N, 5.22.

*4.1.8. 2-(4,5-Dihydrothiazol-2-ylthio)-1-p-tolylethanone (**1h**)*

White solid; m.p.: 75–76 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.12 (d, 2H, J = 7.8 Hz), 7.27 (d, 2H, J = 7.8 HZ), 4.80 (s, 2H), 3.96 (t, 2H, J = 7.5 Hz), 3.38 (t, 2H, J = 7.5 Hz), 2.63 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.1 (C=O), 161.8, 161.9, 142.1, 128.2, 127.8, 54.9, 36.9, 31.2, 23.8. IR (KBr, cm^{-1}): 3112, 2891, 1688 (C=O), 1556, 1374, 1362, 1259, 1187, 1070, 963, 818. Anal. Calcd for $C_{12}H_{13}NOS_2$: C, 57.34; H, 5.21; N, 5.57. Found: C, 57.32; H, 5.21; N, 5.52.

*4.1.9. 2-(Benzo[d]oxazol-2-ylthio)-1-phenylethanone (**1i**)*

Colorless solid; m.p.: 124–125 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.86–7.21 (m, 9H), 4.58 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.1 (C=O), 164.3, 148.9, 140.8, 136.1, 132.6, 128.0, 127.8, 124.1, 122.9, 118.3, 109.6, 37.3. IR (KBr, cm^{-1}): 3027, 2581, 1671 (C=O), 1593, 1492, 1447, 1382, 1326, 1291, 1230, 1182, 1025, 993, 738. Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20. Found: C, 66.96; H, 4.06; N, 5.17.

*4.1.10. 2-(Benzo[d]oxazol-2-ylthio)-1-(4-bromophenyl)ethanone (**1j**)*

White solid; m.p.: 138–139 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.75–7.21 (m, 9H), 4.58 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.7 (C=O), 164.1, 148.9, 140.7, 135.1, 127.2, 125.8, 125.2, 124.2, 122.8, 118.3, 109.5, 36.8. IR (KBr, cm^{-1}): 3035, 2976, 1684 (C=O), 1582, 1490, 1458, 1195, 1117, 982, 807, 730. Anal. Calcd for $C_{15}H_{10}BrNO_2S$: C, 51.74; H, 2.89; N, 4.02. Found: C, 51.71; H, 2.87; N, 4.15.

*4.1.11. 2-(Benzo[d]oxazol-2-ylthio)-1-(4-chlorophenyl)ethanone (**1k**)*

Pale yellow solid; m.p.: 129–130 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.80–7.20 (m, 9H), 4.58 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.3 (C=O), 164.2, 148.9, 140.8, 134.2, 131.2, 130.4, 127.0, 124.2, 122.7, 118.2, 109.6, 36.6. IR (KBr, cm^{-1}): 3073, 2618, 1687 (C=O), 1595, 1486, 1455, 1182, 993, 818, 714. Anal. Calcd for $C_{15}H_{10}ClNO_2S$: C, 59.31; H, 3.32; N, 4.61. Found: C, 59.22; H, 3.27; N, 4.61.

*4.1.12. 2-(Benzo[d]oxazol-2-ylthio)-1-p-tolylethanone (**1l**)*

White solid; m.p.: 127–128 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.74–7.11 (m, 8H), 5.22 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.4 (C=O), 164.2, 148.8, 142.1, 140.8, 133.2, 128.6, 128.2, 124.1, 122.8, 118.4, 109.6, 36.9, 23.8. IR (KBr, cm^{-1}): 3094, 2711, 1681 (C=O), 1578, 1497, 1436, 1172, 981, 802, 727. Anal. Calcd for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94. Found: C, 67.75; H, 4.63; N, 4.89.

*4.1.13. 2-(1H-benzo[d]imidazol-2-ylthio)-1-phenylethanone (**1m**)*

White solid; m.p.: 168–170 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.1 (s, 1H), 7.79–7.18 (m, 9H), 3.92 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.2 (C=O), 146.9, 137.8, 137.5, 134.8, 131.3, 126.5, 126.3, 122.7, 122.5, 11.3.3, 113.1, 36.5. IR (KBr, cm^{-1}): 3048, 1670 (C=O), 1455, 1412, 1273, 970, 744. Anal. Calcd for $C_{15}H_{12}N_2OS$: C, 67.14; H, 4.51; N, 10.44. Found: C, 66.27; H, 4.13; N, 4.78.

*4.1.14. 2-(1H-benzo[d]imidazol-2-ylthio)-1-(4-bromophenyl)ethanone (**1n**)*

White solid; m.p.: 212–214 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.4 (s, 1H), 7.68–7.18 (m, 8H), 3.89 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 192.4 (C=O), 145.1, 136.8, 136.7, 133.7, 129.5, 129.0, 125.4, 121.0, 120.8, 113.1, 112.9, 36.4. IR (KBr, cm^{-1}): 3046, 1687

(C=O), 1448, 1403, 1285, 966, 750. Anal. Calcd for $C_{15}H_{11}BrN_2OS$: C, 51.89; H, 3.19; N, 8.07. Found: C, 51.22; H, 3.27; N, 8.21.

4.1.15. 2-(1H-benzo[d]imidazol-2-ylthio)-1-(4-chlorophenyl)ethanone (1o)

White solid; m.p.: 189–191 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.3 (s, 1H), 7.72–7.17 (m, 8H), 4.93 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 192.3 (C=O), 145.1, 136.9, 136.7, 136.5, 132.9, 128.2, 126.8, 121.1, 120.9, 113.3, 113.1, 36.5. IR (KBr, cm^{-1}): 3057, 1689 (C=O), 1447, 1407, 1289, 960, 754. Anal. Calcd for $C_{15}H_{11}ClN_2OS$: C, 59.50; H, 3.66; N, 9.25. Found: C, 60.03; H, 3.54; N, 9.37.

4.1.16. 2-(1H-benzo[d]imidazol-2-ylthio)-1-p-tolylethanone (1p)

White solid; m.p.: 184–186 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.0 (s, 1H), 7.66–7.08 (m, 8H), 4.94 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.5 (C=O), 145.1, 140.8, 136.9, 136.7, 131.8, 127.0, 126.7, 121.2, 121.0, 113.3, 113.1, 36.6, 21.8. IR (KBr, cm^{-1}): 3041, 1683 (C=O), 1441, 1408, 1371, 1269, 965, 740. Anal. Calcd for $C_{16}H_{14}N_2OS$: C, 68.06; H, 5.00; N, 9.92. Found: C, 67.91; H, 5.14; N, 9.76.

4.1.17. 1-Phenyl-2-(pyrimidin-2-ylthio)ethanone (1q)

White solid; m.p.: 98–99 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.79–7.19 (m, 8H), 3.91 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 195.2 (C=O), 169.9, 154.9, 134.8, 131.2, 126.8, 126.6, 114.3, 36.8. IR (KBr, cm^{-1}): 3029, 2583, 1674 (C=O), 1439, 1410, 1269, 973, 740. Anal. Calcd for $C_{12}H_{10}N_2OS$: C, 62.59; H, 4.38; N, 12.16. Found: C, 62.51; H, 4.53; N, 12.28.

4.1.18. 1-(4-Bromophenyl)-2-(pyrimidin-2-ylthio)ethanone (1r)

White solid; m.p.: 108–110 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.00–7.09 (m, 7H), 3.87 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.8 (C=O), 169.9, 154.9, 133.8, 129.6, 129.1, 125.5, 114.3, 36.8. IR (KBr, cm^{-1}): 3038, 2971, 1692 (C=O), 1449, 1401, 1271, 959, 738. Anal. Calcd for $C_{12}H_9BrN_2OS$: C, 46.62; H, 2.93; N, 9.06. Found: C, 46.03; H, 2.81; N, 9.27.

4.1.19. 1-(4-Chlorophenyl)-2-(pyrimidin-2-ylthio)ethanone (1s)

White solid; m.p.: 101–102 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.03–7.06 (m, 7H), 3.92 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.4 (C=O), 169.9, 154.8, 136.6, 132.9, 128.2, 126.8, 114.2, 36.7. IR (KBr, cm^{-1}): 3078, 2621, 1691 (C=O), 1451, 1411, 1292, 965, 743. Anal. Calcd for $C_{12}H_9ClN_2OS$: C, 54.44; H, 3.43; N, 10.58. Found: C, 54.32; H, 3.51; N, 10.76.

4.1.20. 2-(Pyrimidin-2-ylthio)-1-p-tolylethanone (1t)

White solid; m.p.: 97–98 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.73–7.08 (m, 7H), 3.95 (s, 2H), 2.54 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 195.5 (C=O), 169.9, 155.0, 140.8, 131.8, 127.0, 126.7, 114.3, 36.8, 22.3. IR (KBr, cm^{-1}): 3099, 2718, 1685 (C=O), 1432, 1412, 1361, 1270, 961, 731. Anal. Calcd for $C_{13}H_{12}N_2OS$: C, 63.91; H, 4.95; N, 11.47. Found: C, 63.75; H, 4.63; N, 11.26.

4.2. Typical procedure for the synthesis of β-ketosulfone (2a)

To a stirred solution of β-ketosulfide **1a** (1 mmol) in CH_2Cl_2 (20 mL) at 0 °C, *m*-CPBA (3 mmol) was added. After 10 min, the cold bath was removed and the reaction was stirred for 1 h. The progress of the reaction was monitored by TLC. After completion of the reaction, saturated aqueous sodium sulfite solution (50 mL) was added and the reaction mixture was stirred at room temperature for another 1 h. The CH_2Cl_2 layer was washed with water, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Purification of the crude mixture by flash silica gel chromatography (AcOEt/petroleum ether = 3:7) afforded the sulfone **2a** as a white solid.

4.2.1. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-phenylethanone (2a)

White solid; m.p.: 150–151 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.17–7.76 (m, 4H), 7.56–7.33 (m, 5H), 5.53 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 188.1 (C=O), 153.9, 151.8, 135.4, 134.3, 131.1, 126.8, 126.5, 124.7, 124.0, 119.9, 119.6, 59.7. IR (KBr, cm^{-1}): 3034, 2818, 1678 (C=O), 1593, 1412, 1330, 1141, 1137, 964, 787, 748. Anal. Calcd for $C_{15}H_{11}NO_3S_2$: C, 56.76; H, 3.49; N, 4.41. Found: C, 56.72; H, 3.49; N, 4.46.

4.2.2. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-(4-bromophenyl)ethanone (2b)

White solid; m.p.: 196–198 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.16–7.47 (m, 8H), 5.67 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 188.1 (C=O), 154.1, 151.5, 134.8, 133.2, 129.7, 129.1, 126.2, 123.9, 123.1, 121.7, 121.2, 59.8. IR (KBr, cm^{-1}): 3010, 2800, 1684 (C=O), 1570, 1401, 1328, 1150, 1122, 970, 803, 752. Anal. Calcd for $C_{15}H_{10}BrNO_3S_2$: C, 45.46; H, 2.54; N, 3.53. Found: C, 45.49; H, 2.50; N, 3.43.

4.2.3. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-(4-chlorophenyl)ethanone (2c)

White solid; m.p.: 181–182 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15–7.45 (m, 8H), 5.63 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 187.9 (C=O), 154.1, 151.5, 137.5, 133.2, 129.4, 129.1, 125.2, 123.8, 123.2, 121.5, 121.3, 61.3. IR (KBr, cm^{-1}): 3062, 2814, 1686 (C=O), 1582, 1418, 1333, 1147, 1135, 961, 812, 744. Anal. Calcd for $C_{15}H_{10}ClNO_3S_2$: C, 51.21; H, 2.86; N, 3.98. Found: C, 51.17; H, 2.78; N, 4.03.

4.2.4. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-p-tolylethanone (2d)

White solid; m.p.: 166–167 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.15–7.27 (m, 8H), 5.70 (s, 2H), 2.65 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 189.2 (C=O), 154.1, 151.3, 141.5, 133.3, 132.9, 128.1, 127.7, 123.8, 123.1, 121.6, 121.5, 42.5, 23.8. IR (KBr, cm^{-1}): 3074, 2950, 1681 (C=O), 1569, 1392, 1318, 1153, 1139, 968, 817, 754. Anal. Calcd for $C_{16}H_{13}NO_3S_2$: C, 57.99; H, 3.95; N, 4.23. Found: C, 57.93; H, 4.03; N, 4.23.

4.2.5. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-1-phenylethanone (2e)

White solid; m.p.: 89–91 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.22–7.58 (m, 5H), 5.36 (s, 2H), 4.08 (t, 2H, *J* = 7.5 Hz), 3.44 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 189.0 (C=O), 162.1, 135.4, 132.5, 127.9, 127.2, 60.9, 54.9, 31.4. IR (KBr, cm^{-1}): 3056, 2927, 1682 (C=O), 1541, 1328, 1262, 1142, 976, 768. Anal. Calcd for $C_{11}H_{11}NO_3S_2$: C, 49.05; H, 4.12; N, 5.20. Found: C, 49.17; H, 4.23; N, 5.07.

4.2.6. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-1-(4-bromophenyl)ethanone (2f)

White solid; m.p.: 141–142 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.16–7.64 (m, 4H), 5.38 (s, 2H), 4.08 (t, 2H, *J* = 7.5 Hz), 3.45 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 199.2 (C=O), 162.2, 134.8, 130.7, 129.9, 126.8, 54.8, 41.3, 31.3. IR (KBr, cm^{-1}): 3078, 2917, 1698 (C=O), 1563, 1314, 1165, 1149, 1100, 958, 744. Anal. Calcd for $C_{11}H_{10}BrNO_3S_2$: C, 37.94; H, 2.89; N, 4.02. Found: C, 37.79; H, 2.78; N, 4.14.

4.2.7. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-1-(4-chlorophenyl)ethanone (2g)

Pale yellow solid; m.p.: 134–135 °C; ^{1}H NMR (500 MHz; $CDCl_3$): δ 8.20–7.79 (m, 4H), 5.32 (s, 2H), 4.05 (t, 2H, *J* = 7.5 Hz), 3.41 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 198.6 (C=O), 162.7, 137.7, 133.8, 129.5, 128.2, 60.8, 54.9, 31.3. IR (KBr, cm^{-1}): 3066, 2864, 1701 (C=O), 1536, 1379, 1348, 1286, 1189, 1073, 802. Anal. Calcd for $C_{11}H_{10}ClNO_3S_2$: C, 43.49; H, 3.32; N, 4.61. Found: C, 43.63; H, 3.32; N, 4.67.

*4.2.8. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-1-p-tolylethanone (**2h**)*

White solid; m.p.: 117–118 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.14 (d, 2H, *J* = 7.8 Hz), 7.27 (d, 2H, *J* = 7.8 Hz), 5.34 (s, 2H), 3.92 (t, 2H, *J* = 7.5 Hz), 3.33 (t, 2H, *J* = 7.5 Hz), 2.65 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 199.1 (C=O), 162.8, 162.0, 142.1, 128.3, 127.8, 56.1, 54.9, 36.8, 23.7. IR (KBr, cm^{-1}): 3106, 2912, 1696 (C=O), 1546, 1367, 1351, 1181, 1027, 954, 816. Anal. Calcd for $C_{12}H_{13}NO_3S_2$: C, 50.86; H, 4.62; N, 4.94. Found: C, 51.03; H, 4.71; N, 4.96.

*4.2.9. 2-(Benzo[d]oxazol-2-ylsulfonyl)-1-phenylethanone (**2i**)*

White solid; m.p.: 132–133 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.02–7.26 (m, 9H), 5.16 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 199.4 (C=O), 150.7, 148.8, 140.8, 136.2, 132.5, 128.1, 127.8, 124.1, 122.9, 118.3, 109.7, 61.9. IR (KBr, cm^{-1}): 3118, 2612, 1676 (C=O), 1589, 1483, 1539, 1380, 1342, 1329, 1293, 1199, 1012, 992. Anal. Calcd for $C_{15}H_{11}NO_4S$: C, 59.79; H, 3.68; N, 4.65. Found: C, 59.84; H, 3.75; N, 4.62.

*4.2.10. 2-(Benzo[d]oxazol-2-ylsulfonyl)-1-(4-bromophenyl)ethanone (**2j**)*

Pale yellow solid; m.p.: 145–146 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.76–7.23 (m, 9H), 5.18 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 198.8 (C=O), 150.9, 148.9, 140.7, 135.0, 127.3, 125.8, 125.3, 124.3, 122.7, 118.3, 109.6, 60.7. IR (KBr, cm^{-1}): 3084, 2993, 1688 (C=O), 1586, 1477, 1462, 1317, 1197, 1132, 992, 823, 712. Anal. Calcd for $C_{15}H_{10}BrNO_4S$: C, 47.38; H, 2.65; N, 3.68. Found: C, 47.54; H, 2.65; N, 3.57.

*4.2.11. 2-(Benzo[d]oxazol-2-ylsulfonyl)-1-(4-chlorophenyl)ethanone (**2k**)*

White solid; m.p.: 143–144 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.80–7.22 (m, 9H), 5.07, (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 198.4 (C=O), 150.6, 148.9, 140.8, 134.3, 131.4, 130.4, 127.1, 124.2, 122.8, 118.2, 109.8, 60.7. IR (KBr, cm^{-1}): 3043, 2611, 1694 (C=O), 1599, 1403, 1450, 1316, 1191, 980, 820, 724. Anal. Calcd for $C_{15}H_{10}ClNO_4S$: C, 53.66; H, 3.00; N, 4.17. Found: C, 53.48; H, 3.12; N, 4.21.

*4.2.12. 2-(Benzo[d]oxazol-2-ylsulfonyl)-1-p-tolylethanone (**2l**)*

White solid; m.p.: 136–137 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.76–7.11 (m, 8H), 5.75 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 199.6 (C=O), 150.5, 148.7, 141.2, 140.8, 133.0, 128.6, 128.1, 124.2, 122.8, 118.3, 109.7, 60.3, 23.8. IR (KBr, cm^{-1}): 3078, 2720, 1687 (C=O), 1566, 1484, 1430, 1327, 1154, 977, 815, 748. Anal. Calcd for $C_{16}H_{13}NO_4S$: C, 60.94; H, 4.16; N, 4.44. Found: C, 60.85; H, 4.17; N, 4.22.

*4.2.13. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-1-phenylethanone (**2m**)*

White solid; m.p.: 148–150 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.4 (N–H, 1H), 7.85–7.37 (m, 9H), 5.41 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 197.4 (C=O), 139.5, 137.9, 137.6, 134.8, 131.2, 126.8, 126.5, 121.1, 120.9, 113.0, 112.8, 61.3. IR (KBr, cm^{-1}): 3038, 1682 (C=O), 1441, 1408, 1311, 1270, 972, 741. Anal. Calcd for $C_{15}H_{12}N_2O_3S$: C, 59.99; H, 4.03; N, 9.33. Found: C, 60.14; H, 4.17; N, 9.15.

*4.2.14. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-1-(4-bromophenyl)ethanone (**2n**)*

White solid; m.p.: 160–162 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.8 (N–H, 1H), 7.71–7.36 (m, 8H), 5.55 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 197.8 (C=O), 139.5, 137.0, 136.8 133.8, 129.5, 129.0, 125.6, 122.0, 121.2, 113.8, 113.4, 61.1. IR (KBr, cm^{-1}): 3045, 1695 (C=O), 1438, 1411, 1305, 1267, 969, 739. Anal. Calcd for $C_{15}H_{11}BrN_2O_3S$: C, 47.51; H, 2.92; N, 7.39. Found: C, 47.46; H, 3.04; N, 7.45.

*4.2.15. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-1-(4-chlorophenyl)ethanone (**2o**)*

White solid; m.p.: 157–159 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.7 (N–H, 1H), 7.76–7.36 (m, 8H), 5.51 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 197.5 (C=O), 139.7, 136.8, 136.6, 136.4, 132.9, 128.2, 126.7, 121.4, 121.1, 113.6, 113.2, 61.2. IR (KBr, cm^{-1}): 3059, 1698 (C=O), 1440, 1422, 1314, 1269, 963, 734. Anal. Calcd for $C_{15}H_{11}N_2O_3S$: C, 53.82; H, 3.31; N, 8.37. Found: C, 53.79; H, 3.22; N, 8.51.

*4.2.16. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-1-p-tolylethanone (**2p**)*

White solid; m.p.: 149–151 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.3 (N–H, 1H), 7.70–7.27 (m, 8H), 5.57 (s, 2H), 2.66 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 197.6 (C=O), 140.8, 139.1, 136.9, 136.6, 131.8, 127.0, 126.7, 121.3, 121.0, 113.2, 113.0, 61.3, 22.2. IR (KBr, cm^{-1}): 3046, 1691 (C=O), 1446, 1417, 1372, 1322, 1275, 978, 747. Anal. Calcd for $C_{16}H_{14}N_2O_3S$: C, 61.13; H, 4.49; N, 8.91. Found: C, 61.85; H, 4.27; N, 8.73.

*4.2.17. 1-Phenyl-2-(pyrimidin-2-ylsulfonyl)ethanone (**2q**)*

White solid; m.p.: 103–104 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 9.01–7.47 (m, 8H), 5.41 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 201.6 (C=O), 165.0, 156.2, 134.8, 131.1, 126.7, 126.5, 123.9, 61.6. IR (KBr, cm^{-1}): 3120, 2611, 1680 (C=O), 1443, 1412, 1314, 1263, 969, 736. Anal. Calcd for $C_{12}H_{10}N_2O_3S$: C, 54.95; H, 3.84; N, 10.68. Found: C, 55.12; H, 3.68; N, 10.47.

*4.2.18. 1-(4-Bromophenyl)-2-(pyrimidin-2-ylsulfonyl)ethanone (**2r**)*

White solid; m.p.: 115–117 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 9.01–7.67 (m, 7H), 5.54 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 200.8 (C=O), 165.2, 156.1, 133.8, 129.6, 129.0, 125.5, 123.8, 61.6. IR (KBr, cm^{-1}): 3087, 2986, 1692 (C=O), 1433, 1407, 1301, 1259, 961, 731. Anal. Calcd for $C_{12}H_9BrN_2O_3S$: C, 42.24; H, 2.66; N, 8.21. Found: C, 42.21; H, 2.58; N, 8.34.

*4.2.19. 1-(4-Chlorophenyl)-2-(pyrimidin-2-ylsulfonyl)ethanone (**2s**)*

White solid; m.p.: 113–115 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 9.03–7.48 (m, 7H), 5.22 (s, 2H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 200.6 (C=O), 165.0, 156.2, 136.7, 132.9, 128.2, 126.8, 123.7, 61.5. IR (KBr, cm^{-1}): 3048, 2617, 1699 (C=O), 1442, 1425, 1312, 1270, 961, 737. Anal. Calcd for $C_{12}H_9ClN_2O_3S$: C, 48.57; H, 3.06; N, 9.44. Found: C, 48.45; H, 3.09; N, 9.58.

*4.2.20. 2-(Pyrimidin-2-ylsulfonyl)-1-p-tolylethanone (**2t**)*

White solid; m.p.: 106–108 °C; ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.98–7.27 (m, 7H), 5.56 (s, 2H), 2.65 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 201.8 (C=O), 164.9, 156.2, 140.8, 131.7, 127.0, 126.7, 123.9, 61.6, 22.1. IR (KBr, cm^{-1}): 3081, 2717, 1691 (C=O), 1449, 1421, 1362, 1320, 1267, 973, 751. Anal. Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14. Found: C, 56.37; H, 4.17; N, 10.31.

*4.3. Typical procedure for fluorination of β-ketosulfone (**2b**)*

Under N_2 atmosphere, Na_2CO_3 (2.2 mmol) was added to a 50-mL Schlenk flask containing **2b** (1 mmol), and dry acetonitrile (20 mL) at room temperature. The reaction mixture was stirred for 2 h. Selectfluor™ (2.5 mmol) was added and the mixture was stirred at ambient temperature overnight. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was quenched by the addition of water and was extracted with methylene chloride (3× 20 mL). The organic phase was separated, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was further purified by silica gel column chromatography using AcOEt/petroleum ether (3:7) as eluent to give product **3b** as a white solid.

*4.3.1. 2-(Benzo[d]thiazol-2-ylsulfonyl)-2,2-difluoro-1-phenylethanone (**3a**)*

White solid; m.p.: 161–162 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.82–6.96 (m, 9H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 184.2 (C=O), 153.7, 151.8, 135.5, 134.1, 131.0, 126.7, 126.2, 124.5, 123.2, 119.3, 118.9, 112.2 (t, *J* = 301.1 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.82 (s, 2F). IR (KBr, cm^{-1}): 3078, 1695 (C=O), 1568, 1412, 1372, 1315, 1271, 1246, 982, 743. Anal. Calcd for $C_{15}H_9F_2NO_3S_2$: C, 50.98; H, 2.57; N, 3.96. Found: C, 51.93; H, 2.46; N, 4.12.

*4.3.2. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-(4-bromophenyl)-2,2-difluoroethanone (**3b**)*

White solid; m.p.: 189–191 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.82–7.78 (m, 4H), 7.65–7.43 (m, 4H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 184.2 (C=O), 153.8, 151.5, 134.9, 133.0, 129.5, 128.8, 126.2, 123.0, 122.9, 120.9, 119.8, 112.7 (t, *J* = 301.8 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.73 (s, 2F). IR (KBr, cm^{-1}): 3068, 1698 (C=O), 1573, 1440, 1366, 1321, 1279, 1215, 1061, 983. Anal. Calcd for $C_{15}H_8BrF_2NO_3S_2$: C, 41.68; H, 1.87; N, 3.24. Found: C, 41.59; H, 1.76; N, 3.32.

*4.3.3. 2-(Benzo[d]thiazol-2-ylsulfonyl)-1-(4-chlorophenyl)-2,2-difluoroethanone (**3c**)*

White solid; m.p.: 171–172 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.82–7.78 (m, 4H), 7.70–7.27 (m, 4H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 183.9 (C=O), 154.2, 151.4, 137.2, 133.0, 129.1, 128.7, 125.2, 123.6, 123.1, 121.3, 120.9, 114.2 (t, *J* = 301.7 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.69 (s, 2F). IR (KBr, cm^{-1}): 3076, 1700 (C=O), 1593, 1423, 1289, 1218, 1214, 1092, 991, 812. Anal. Calcd for $C_{15}H_8ClF_2NO_3S_2$: C, 46.46; H, 2.08; N, 3.61; Found: C, 46.52; H, 2.15; N, 3.53.

*4.3.4. 2-(Benzo[d]thiazol-2-ylsulfonyl)-2,2-difluoro-1-p-tolylethanone (**3d**)*

White solid; m.p.: 168–169 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.82–7.78 (m, 4H), 7.64–7.06 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 183.7 (C=O), 154.1, 151.3, 141.2, 133.5, 132.7, 128.2, 127.7, 123.9, 122.8, 122.2, 121.5, 111.6 (t, *J* = 301.3 Hz, CF_2), 23.7. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.97 (s, 2F). IR (KBr, cm^{-1}): 3121, 1699 (C=O), 1587, 1420, 1286, 1222, 1201, 1077, 986, 807. Anal. Calcd for $C_{16}H_{11}F_2NO_3S_2$: C, 52.31; H, 3.02; N, 3.81. Found: C, 52.32; H, 2.94; N, 3.75.

*4.3.5. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-2,2-difluoro-1-phenylethanone (**3e**)*

White solid; m.p.: 93–94 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.76–7.48 (m, 4H), 4.15 (t, 2H, *J* = 7.5 Hz), 3.43 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 185.2 (C=O), 162.2, 135.4, 132.2, 127.5, 127.1, 114.0 (t, *J* = 301.2 Hz, CF_2), 53.9, 31.3. ^{19}F NMR (470 MHz; $CDCl_3$): δ −100.02 (s, 2F). IR (KBr, cm^{-1}): 3113, 2901, 1687 (C=O), 1551, 1273, 1186, 1160, 964, 770. Anal. Calcd for $C_{11}H_9F_2NO_3S_2$: C, 43.27; H, 2.97; N, 4.59. Found: C, 43.31; H, 2.97; N, 4.47.

*4.3.6. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-1-(4-bromophenyl)-2,2-difluoroethanone (**3f**)*

White solid; m.p.: 159–160 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.65–7.43 (m, 4H), 4.15 (t, 2H, *J* = 7.5 Hz), 3.43 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 195.4 (C=O), 162.2, 134.4, 130.8, 129.5, 126.8, 94.3 (t, *J* = 301.8 Hz, CF_2) 53.7, 31.3. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.98 (s, 2F). IR (KBr, cm^{-1}): 3102, 2921, 1712 (C=O), 1563, 1271, 1193, 1158, 983, 727. Anal. Calcd for $C_{11}H_8BrF_2NO_3S_2$: C, 34.39; H, 2.10; N, 3.65. Found: C, 34.28; H, 2.08; N, 3.69.

*4.3.7. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-1-(4-chlorophenyl)-2,2-difluoroethanone (**3g**)*

White solid; m.p.: 147–148 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.60–7.28 (m, 4H), 4.15 (t, 2H, *J* = 7.5 Hz), 3.43 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.7 (C=O), 162.5, 137.6, 133.8, 128.9, 128.1, 114.3 (t, *J* = 301.7 Hz, CF_2), 53.9, 31.2. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.93 (s, 2F). IR (KBr, cm^{-1}): 3058, 2853, 1716 (C=O), 1555, 1393, 1347, 1269, 1202, 1183, 1081, 971, 823. Anal. Calcd for $C_{11}H_8ClF_2NO_3S_2$: C, 38.88; H, 2.37; N, 4.12. Found: C, 38.79; H, 2.38; N, 4.08.

*4.3.8. 2-(4,5-Dihydrothiazol-2-ylsulfonyl)-2,2-difluoro-1-p-tolylethanone (**3h**)*

White solid; m.p.: 112–113 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.64–7.14 (m, 4H), 4.15 (t, 2H, *J* = 7.5 Hz), 3.75 (s, 3H), 3.43 (t, 2H, *J* = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 196.7 (C=O), 162.8, 162.1, 141.8, 128.3, 127.7, 109.5 (t, *J* = 301.3 Hz, CF_2), 54.1, 36.7, 23.7. ^{19}F NMR (470 MHz; $CDCl_3$): δ −100.12 (s, 2F). IR (KBr, cm^{-1}): 3084, 2894, 1708 (C=O), 1568, 1368, 1359, 1260, 1226, 1172, 1083, 947, 802. Anal. Calcd for $C_{12}H_{11}F_2NO_3S_2$: C, 45.13; H, 3.47; N,4.39. Found: C, 45.12; H, 3.41; N, 4.35.

*4.3.9. 2-(Benzo[d]oxazol-2-ylsulfonyl)-2,2-difluoro-1-phenylethanone (**3i**)*

White solid; m.p.: 156–157 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.89–7.22 (m, 9H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 195.5 (C=O), 150.8, 148.6, 141.1, 136.2, 132.1, 128.2, 127.7, 125.2 (t, *J* = 301.2 Hz, CF_2), 124.1, 122.0, 118.1, 109.6. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.41 (s, 2F). IR (KBr, cm^{-1}): 3143, 2617, 1689 (C=O), 1598, 1497, 1544, 1383, 1321, 1280, 1215, 1176, 1017, 987, 714. Anal. Calcd for $C_{15}H_9F_2NO_4S$: C, 53.41; H, 2.69; N, 4.15. Found: C, 53.34; H, 2.74; N, 4.09.

*4.3.10. 2-(Benzo[d]oxazol-2-ylsulfonyl)-1-(4-bromophenyl)-2,2-difluoroethanone (**3j**)*

White solid; m.p.: 183–184 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.65–7.43 (m, 4H), 7.35–7.10 (m, 4H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.9 (C=O), 150.9, 148.8, 140.2, 135.2, 127.0, 125.3, 124.9, 123.7, 122.7, 118.3, 113.8 (t, *J* = 301.8 Hz, CF_2), 109.5. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.35 (s, 2F). IR (KBr, cm^{-1}): 3102, 1704 (C=O), 1581, 1488, 1463, 1204, 1187, 996, 823, 746. Anal. Calcd for $C_{15}H_8BrF_2NO_4S$: C, 43.29; H, 1.94; N, 3.37. Found: C, 43.31; H, 2.01; N, 3.26.

*4.3.11. 2-(Benzo[d]oxazol-2-ylsulfonyl)-1-(4-chlorophenyl)-2,2-difluoroethanone (**3k**)*

White solid; m.p.: 152–153 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.70–7.12 (m, 8H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.4 (C=O), 150.5, 148.9, 140.6, 134.3, 131.3, 130.4, 127.0, 124.4, 124.0 (t, *J* = 301.7 Hz, CF_2) 121.9, 118.2, 109.5. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.28 (s, 2F). IR (KBr, cm^{-1}): 3089, 2627, 1706 (C=O), 1581, 1473, 1458, 1214, 1159, 979, 812, 713. Anal. Calcd for $C_{15}H_8ClF_2NO_4S$: C, 48.46; H, 2.17; N, 3.77. Found: C, 48.46; H, 2.12; N, 3.68.

*4.3.12. 2-(Benzo[d]oxazol-2-ylsulfonyl)-2,2-difluoro-1-p-tolylethanone (**3l**)*

White solid; m.p.: 157–158 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.64–7.14 (m, 4H), 7.35–7.10 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 193.5 (C=O), 150.4, 148.7, 140.8, 140.7, 133.2, 129.4 (t, *J* = 301.3 Hz, CF_2), 128.5, 124.2, 122.8, 118.1, 109.7, 23.7. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.48 (s, 2F). IR (KBr, cm^{-1}): 3098, 2703, 1711 (C=O), 1571, 1493, 1437, 1217, 1163, 982, 827, 718. Anal. Calcd for $C_{16}H_{11}F_2NO_4S$: C, 54.70; H, 3.16; N, 3.99. Found: C, 54.57; H, 3.05; N, 3.87.

*4.3.13. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-2,2-difluoro-1-phenylethanone (**3m**)*

White solid; m.p.: 128–130 °C; ^{1}H NMR (300 MHz; DMSO): δ 12.9 (N–H, 1H), 7.82–7.37 (m, 9H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 192.5 (C=O), 139.5, 137.0, 136.8, 134.8, 131.2, 126.8, 126.5, 121.2

(t, J = 301.3 Hz, CF_2), 121.0, 120.8, 113.6, 113.0. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.45 (s, 2F). IR (KBr, cm^{-1}): 3051, 1675 (C=O), 1463, 1427, 1320, 1281, 972, 746. Anal. Calcd for $C_{15}H_{10}F_2N_2O_3S$: C, 53.57; H, 3.00; N, 8.33. Found: C, 53.22; H, 3.17; N, 8.14.

*4.3.14. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-1-(4-bromophenyl)-2,2-difluoroethanone (**3n**)*

White solid; m.p.: 155–157 °C; ^1H NMR (300 MHz; DMSO): δ 13.2 (N–H, 1H), 7.76–7.36 (m, 8H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 189.8 (C=O), 139.8, 136.8, 136.6, 133.6, 129.4, 129.0, 125.5, 121.2, 120.9, 113.3, 113.0, 109.7 (t, J = 302.4 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.41 (s, 2F). IR (KBr, cm^{-1}): 3064, 1689 (C=O), 1458, 1420, 1315, 1277, 964, 735. Anal. Calcd for $C_{15}H_9BrF_2N_2O_3S$: C, 43.39; H, 2.18; N, 6.75. Found: C, 43.35; H, 2.12; N, 6.68.

*4.3.15. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-1-(4-chlorophenyl)-2,2-difluoroethanone (**3o**)*

White solid; m.p.: 126–128 °C; ^1H NMR (300 MHz; DMSO): δ 13.2 (N–H, 1H), 7.71–7.35 (m, 8H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 191.5 (C=O), 139.2, 137.0, 136.8, 136.6, 132.9, 128.2, 126.8, 121.5, 121.2, 120.1 (t, J = 303.1 Hz, CF_2), 113.3, 113.0. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.32 (s, 2F). IR (KBr, cm^{-1}): 3077, 1691 (C=O), 1455, 1441, 1323, 1270, 958, 728. Anal. Calcd for $C_{15}H_9ClF_2N_2O_3S$: C, 48.59; H, 2.45; N, 7.56. Found: C, 48.33; H, 2.54; N, 7.50.

*4.3.16. 2-(1H-benzo[d]imidazol-2-ylsulfonyl)-2,2-difluoro-1-p-tolylethanone (**3p**)*

White solid; m.p.: 131–132 °C; ^1H NMR (300 MHz; DMSO): δ 12.7 (N–H, 1H), 7.70–7.36 (m, 8H), 2.37 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 190.4 (C=O), 140.8, 139.5, 136.9, 136.7, 131.8, 127.0, 126.7, 125.5 (t, J = 302.1 Hz, CF_2), 113.3, 113.1, 121.4, 121.0, 22.3. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.54 (s, 2F). IR (KBr, cm^{-1}): 3065, 1686 (C=O), 1465, 1429, 1375, 1332, 1270, 979, 740. Anal. Calcd for $C_{16}H_{12}F_2N_2O_3S$: C, 54.85; H, 3.45; N, 8.00. Found: C, 54.78; H, 3.51; N, 8.12.

*4.3.17. 2,2-Difluoro-1-phenyl-2-(pyrimidin-2-ylsulfonyl)ethanone (**3q**)*

White solid; m.p.: 126–128 °C; ^1H NMR (300 MHz; $CDCl_3$): δ 9.02–7.56 (m, 8H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 196.7 (C=O), 165.0, 156.2, 134.8, 131.3, 126.7, 126.3, 123.9, 122.3 (t, J = 301.4 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.43 (s, 2F). IR (KBr, cm^{-1}): 3145, 1693 (C=O) 1465, 1432, 1327, 1277, 969, 751. Anal. Calcd for $C_{12}H_8F_2N_2O_3S$: C, 48.32; H, 2.70; N, 9.39. Found: C, 48.49; H, 2.63; N, 9.43.

*4.3.18. 1-(4-Bromophenyl)-2,2-difluoro-2-(pyrimidin-2-ylsulfonyl)ethanone (**3r**)*

White solid; m.p.: 153–154 °C; ^1H NMR (300 MHz; $CDCl_3$): δ 9.01–7.69 (m, 7H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 196.1 (C=O), 165.8, 156.0, 133.8, 129.4, 129.1, 125.5, 123.7, 110.4 (t, J = 301.7 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.38 (s, 2F). IR (KBr, cm^{-1}): 3107, 1708 (C=O), 1460, 1423, 1317, 1281, 960, 736. Anal. Calcd for $C_{12}H_7BrF_2N_2O_3S$: C, 38.21; H, 1.87; N, 7.43. Found: C, 38.02; H, 1.80; N, 7.27.

*4.3.19. 1-(4-Chlorophenyl)-2,2-difluoro-2-(pyrimidin-2-ylsulfonyl)ethanone (**3s**)*

White solid; m.p.: 122–124 °C; ^1H NMR (300 MHz; $CDCl_3$): δ 9.07–7.74 (m, 7H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 196.5 (C=O), 165.0, 156.2, 136.7, 132.9, 128.2, 126.8, 123.9, 122.3 (t, J = 301.5 Hz, CF_2). ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.30 (s, 2F). IR (KBr, cm^{-1}): 3095, 1710 (C=O), 1459, 1440, 1320, 1271, 953, 723. Anal. Calcd for $C_{12}H_7ClF_2N_2O_3S$: C, 43.32; H, 2.12; N, 8.42. Found: C, 43.28; H, 2.14; N, 8.53.

*4.3.20. 2,2-Difluoro-2-(pyrimidin-2-ylsulfonyl)-1-p-tolylethanone (**3t**)*

White solid; m.p.: 127–128 °C; ^1H NMR (300 MHz; $CDCl_3$): δ 8.96–7.38 (m, 7H), 2.67 (s, 3H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 194.8 (C=O), 165.2, 156.3, 140.8, 131.8, 127.6 (t, J = 301.1 Hz, CF_2), 127.0, 126.7, 123.8, 22.5. ^{19}F NMR (470 MHz; $CDCl_3$): δ −99.51 (s, 2F). IR (KBr, cm^{-1}): 3103, 1715 (C=O), 1466, 1420, 1361, 1327, 1272, 961, 735. Anal. Calcd for $C_{13}H_{10}F_2N_2O_3S$: C, 50.00; H, 3.23; N, 8.97. Found: C, 50.21; H, 3.17; N, 8.86.

*4.4. Typical procedure for the synthesis of difluoromethyl sulfone (**4b**)*

To a solution of 10% aqueous NaOH (5 mL) was added the difluoromethyl sulfone **3b** (1 mmol) at room temperature and the mixture was stirred for 30 min. After completion of the reaction as monitored by TLC, the reaction mixture was extracted with diethyl ether after the addition of water. The organic extract was dried over anhydrous $MgSO_4$ and evaporated to give the crude product, which was purified by chromatography on silica gel (hexane/ethyl acetate = 8:2) to afford the heterocyclic difluoromethyl sulfone **4b** as a white solid.

*4.4.1. 2-(Difluoromethylsulfonyl)benzo[d]thiazol (**4b**)*

White solid; m.p.: 149 °C; ^1H NMR (400 MHz; $CDCl_3$): δ 8.4–7.7 (m, 4H), 6.61 (t, 1H $^2J_{H-F}$ = 53.2 Hz, $-CF_2H$). ^{13}C NMR (126 MHz; $CDCl_3$): δ 158.7, 152.9, 137.9, 129.1, 128.3, 126.3, 122.4, 114.4 (t, J = 286 Hz, $-CF_2H$). ^{19}F NMR (470 MHz; $CDCl_3$): δ −121.8 (d, 2F $^2J_{H-F}$ = 52.9 Hz). IR (KBr, cm^{-1}): 3050, 2611, 1678, 1568, 1410, 1290, 1255, 1043, 885, 738, 708. Anal. Calcd for $C_8H_5F_2NO_2S_2$: C, 38.55; H, 2.02; N, 5.62. Found: C, 38.46; H, 2.14; N, 5.48.

*4.4.2. 2-(Difluoromethylsulfonyl)-4,5-dihydrothiazol (**4f**)*

White solid; m.p.: 131 °C; ^1H NMR (400 MHz; $CDCl_3$): δ 6.60 (t, 1H $^2J_{H-F}$ = 53.2 Hz, $-CF_2H$), 4.41 (t, 2H, J = 7.5 Hz), 3.42 (t, 2H, J = 7.5 Hz). ^{13}C NMR (126 MHz; $CDCl_3$): δ 165.8, 113.3 (t, J = 284 Hz, $-CF_2H$), 54.1, 31.7. ^{19}F NMR (470 MHz; $CDCl_3$): δ −122.6 (d, 2F $^2J_{H-F}$ = 51.2 Hz). IR (KBr, cm^{-1}): 2856, 1687, 1562, 1412, 1383, 1274, 1056, 879, 740, 702. Anal. Calcd for $C_4H_5F_2NO_2S_2$: C, 23.88; H, 2.50; N, 6.96. Found: C, 23.74; H, 2.57; N, 6.87.

*4.4.3. 2-(Difluoromethylsulfonyl)benzo[d]oxazole (**4j**)*

White solid; m.p.: 155 °C; ^1H NMR (400 MHz; $CDCl_3$): δ 8.7–7.6 (m, 4H), 6.63 (t, 1H $^2J_{H-F}$ = 53.2 Hz, $-CF_2H$). ^{13}C NMR (126 MHz; $CDCl_3$): δ 158.8, 153.0, 137.8, 129.1, 128.2, 126.2, 122.4, 114.5 (t, J = 286 Hz, $-CF_2H$). ^{19}F NMR (470 MHz; $CDCl_3$): δ −149.2 (d, 2F $^2J_{H-F}$ = 24.2 Hz). IR (KBr, cm^{-1}): 3045, 2625, 1680, 1567, 1409, 1296, 1255, 1062, 880, 746, 707. Anal. Calcd for $C_8H_5F_2NO_3S$: C, 41.20; H, 2.16; N, 6.01. Found: C, 41.12; H, 2.23; N, 6.18.

*4.4.4. 2-(Difluoromethylsulfonyl)-1H-benzo[d]imidazole (**4n**)*

White solid; m.p.: 218 °C; ^1H NMR (300 MHz; DMSO): 13.2 (N–H, 1H), 8.7–8.26 (m, 4H), 6.68 (t, 1H $^2J_{H-F}$ = 51.2 Hz, $-CF_2$). ^{13}C NMR (126 MHz; $CDCl_3$): δ 145.5, 142.9, 142.2, 127.3, 127.1, 119.5, 119.3, 114.23 (t, J = 281 Hz, $-CF_2H$). ^{19}F NMR (470 MHz; $CDCl_3$): δ −134.3 (d, 2F $^2J_{H-F}$ = 23.8 Hz). IR (KBr, cm^{-1}): 3058, 1456, 1423, 1319, 1274, 970, 743. Anal. Calcd for $C_8H_6F_2N_2O_2S$: C, 41.38; H, 2.60; N, 12.06. Found: C, 41.29; H, 2.71; N, 12.01.

*4.4.5. 2-(Difluoromethylsulfonyl)pyrimidine (**4r**)*

White solid; m.p.: 142 °C; ^1H NMR (300 MHz; $CDCl_3$): 9.98–8.72 (m, 3H), 6.71 (t, 1H $^2J_{H-F}$ = 52.4 Hz, $-CF_2H$). ^{13}C NMR (126 MHz; $CDCl_3$): δ 171.5, 162.1, 129.8, 114.03 (t, J = 278 Hz, $-CF_2H$). ^{19}F NMR (470 MHz; $CDCl_3$): δ −131.4 (d, 2F $^2J_{H-F}$ = 24.1 Hz). IR (KBr, cm^{-1}): 3138, 1460, 1428, 1329, 1267, 963, 750. Anal. Calcd for $C_5H_4F_2N_2O_2S$: C, 30.93; H, 2.08; N, 14.43. Found: C, 30.74; H, 2.21; N, 14.36.

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