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AN EFFICIENT SYNTHESIS OF NOVEL DISPIRO DERIVATIVES VIA THREE-COMPONENT 1,3-DIPOLAR CYCLOADDITION REACTIONS UNDER ULTRASOUND IRRADIATION

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Abstract – A series of new dispiro compounds were synthesized via the three-component 1,3-dipolar cycloaddition reaction of acenaphthenequinone, thiazolidine-4-carboxylic acid and (*Z*)-5-benzylidene-2-thioxothiazolidin-4-one or (*Z*)-5-benzylidenethiazolidine-2,4-dione in ethanol under ultrasound irradiation. This protocol has the advantages of mild reaction conditions, high yields and short reaction time.

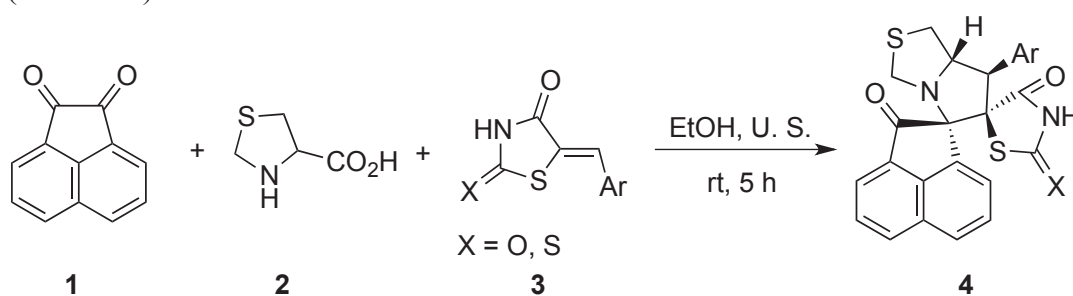
The development of combinatorial libraries for the discovery of biologically active compounds is a great challenge for the chemists and medicine scientists.¹ Traditionally the synthesis of these compounds were carried out under heating condition, however, by this method several annoying byproducts were formed. Therefore, finding a way for the resulting products easily to be formed and rapidly to be purified is a matter of prime importance. Ultrasonic irradiation,^{2,3} as a powerful tool in modern chemistry for the organic reactions, has attracted much attention of chemists. The ultrasonic irradiation with its advantages of convenient operation, mild reaction conditions, short reaction time and high efficiency has become particularly popular in recent years, and numerous examples under this condition for constructing the heterocycles with interesting properties have been reported in the literature.⁴

1,3-Dipolar cycloaddition reactions are efficient methods for the construction of heterocyclic units.⁵ One of the most important classes for 1,3-dipolar cycloaddition involves azomethine ylide. The azomethine ylides were easily formed and readily trapped by dipolarophiles. Such reaction can take place either inter- or intramolecularly,⁶ and the corresponding pyrrolidine derivatives were achieved. Particularly, 1,3-dipolar cycloaddition of azomethine ylide for synthesizing compounds with the spiro moiety are usually accompanied by highly regio- and stereo-selectivity.

Molecules with the thiazolidine nucleus have shown a wide spectrum of bioactivities and drug activity.⁶⁻⁹

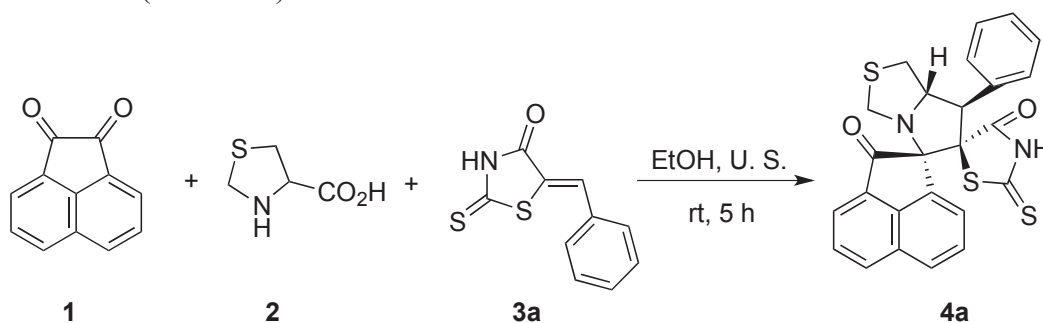
In medicine thiazolidine derivatives were well recognized for their anti-inflammatory and anti-hypertensive activities;¹⁰ in pesticides compounds with thiazolidine ring were treated as the novel pesticides for their low toxicity to human beings and excellent biological activity, such as thifluzamide, ethaboxam, benthiazole and clothianidin.

To the current literature, the research of the 1,3-dipolar cycloaddition of azomethine ylides carried out under ultrasound condition were seldom reported,¹¹⁻¹⁵ especially synthesizing of spiro compounds.^{16,17} As the interest in the synthesis of spiro compounds via the 1,3-dipolar cycloadditions of azomethine ylides,¹⁸ herein it is reported that the facile synthesis of novel dispiro compounds having thiazolone moiety via a one-pot, three-component 1,3-dipolar cycloaddition reaction of azomethine ylides under ultrasonic irradiation (Scheme 1).



Scheme 1

Choosing an appropriate solvent is of crucial importance for the successful organic synthesis. To search for the suitable solvent, the reaction of acenaphthenequinone **1**, thiazolidine-4-carboxylic acid **2** and (*Z*)-5-benzylidene-2-thioxothiazolidin-4-one **3a** was examined in different solvents for the synthesis of **4a** at different conditions (Scheme 2). The results are summarized in Table 1.



Scheme 2

Table 1. Optimization for the synthesis of **4a** under ultrasound irradiation

Entry	Solvent	Time (h)	Isolated Yield (%)
1	MeOH	6	83
2	EtOH	5	93
3	MeCN	10	47
4	dioxane	10	56
5	THF	7	63
6	CHCl ₃	9	65
7	H ₂ O	21	none

It can be seen from the Table 1, ethanol is the solvent of choice for the reaction, and the desired product is obtained in excellent yields (Table 1, Entry 2). While when water was chosen as the reaction medium the desired product is not observed. Specially, there are long reaction time (12 h) and low yield (85%) when synthesizing **4a** in ethanol without ultrasound irradiation. After optimization of the conditions, to delineate this approach, particularly in regard to library construction, this methodology was evaluated by using different dipolarophiles. Eleven dipolarophiles **3** were chosen for the library validation. Corresponding dispiro compounds **4** were synthesized by the one-pot, three-component reaction of acenaphthenequinone **1**, thiazolidine-4-carboxylic acid **2**, and dipolarophiles **3** in good yields in ethanol promoted by ultrasound. The results are summarized in Table 2. As shown in Table 2, it was found that this method works with a wide variety of substrates. A series of substituted (*Z*)-5-benzylidene-2-thioxothiazolidin-4-one or (*Z*)-5-benzylidenethiazolidine-2,4-dione were used in this reaction.

Table 2. The synthesis of dispiro compounds **4** under ultrasound irradiation

Entry	X	Ar	Isolated Yield (%)
4a	S	C ₆ H ₅	93
4b	S	4-FC ₆ H ₄	84
4c	S	4-BrC ₆ H ₄	91
4d	S	4-NO ₂ C ₆ H ₄	95
4e	S	4-MeC ₆ H ₄	90
4f	S	4-ClC ₆ H ₄	93
4g	O	C ₆ H ₅	80
4h	O	4-FC ₆ H ₄	88
4i	O	4-ClC ₆ H ₄	88
4j	O	4-BrC ₆ H ₄	86
4k	O	3-MeC ₆ H ₄	93

The structures of final products **4** were established by IR, ¹H, ¹³C NMR and HRMS spectroscopy. The structure of compound **4c** was confirmed by X-ray analysis. The crystal structure of **4c** is represented in Figure 1.

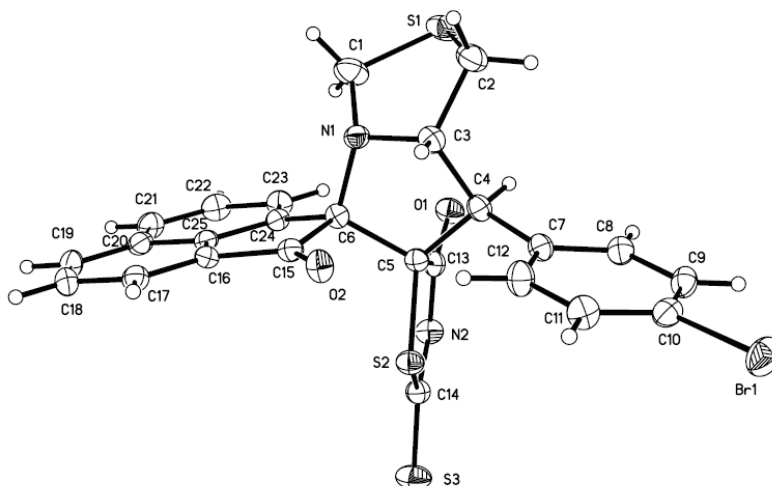
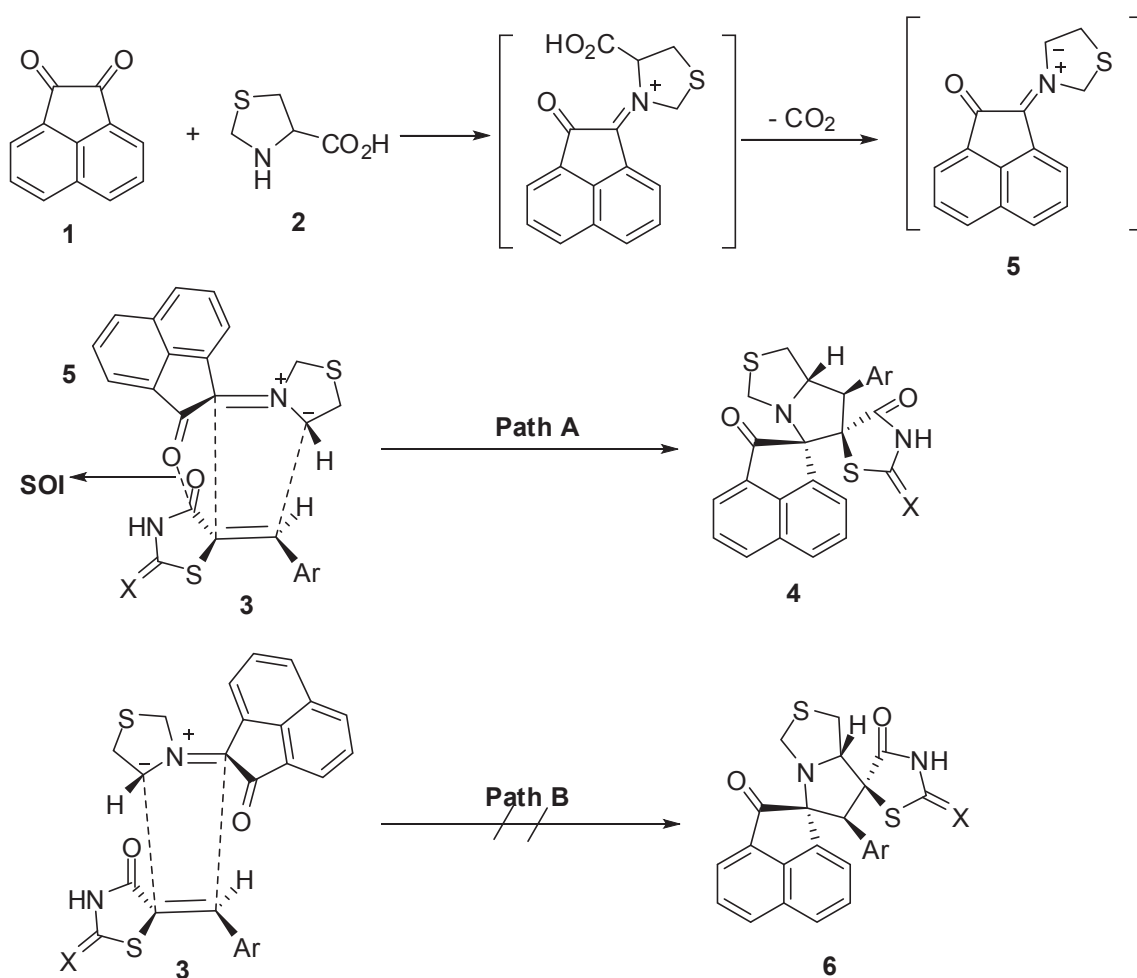


Figure 1. The X-ray structure of **4c**

Although the detailed mechanism of the above reaction has not been clarified yet, the formation of **4** can be explained by the possible mechanism presented in Scheme 3. The reaction proceeds through the generation of azomethine ylide (dipole **5**) via the condensation of acenaphthenequinone **1** with thiazolidine-4-carboxylic acid **2** and decarboxylation.^{19,20} The dipolarophiles **3** regioselectively react with azomethine ylides (dipole **5**) in ethanol to give the desired products dispiro compounds **4** (Scheme 3, Path A). The regioselectivity in the product formation can be explained by considering the secondary orbital interaction (SOI)²¹ of the orbital of the carbonyl group of dipolarophile **3** with those of the ylide **5** as shown in Scheme 3. Accordingly, the observed regioisomer **4** via path **A** is more favorable because of the secondary orbital interaction which is not possible in path **B**.



Scheme 3. Proposed reaction mechanism for the formation of compound **4**

In conclusion, it has been successfully developed that 1,3-dipolar cycloaddition of azomethine ylides under ultrasonic condition, and a series of novel dispiro cycloadducts were obtained. This method has the advantages of ultrasonic irradiation of convenient operation, mild reaction conditions, short reaction time and high efficiency.

EXPERIMENTAL

Commercial solvents and reagents were used as received. Melting points were determined in open capillaries and are uncorrected. Infrared spectra were recorded on a Varian F-1000 spectrometer as KBr pellets with absorption in cm^{-1} . ^1H NMR and ^{13}C NMR spectra were recorded on Varian Inova-400 MHz or Inova-300 MHz spectrometer as $\text{DMSO-}d_6$ solution. J values are in hertz (Hz). Chemical shifts are expressed in δ downfield from internal tetramethylsilane (TMS). HRMS data were obtained using TOF-MS or Bruker micrOTOF-Q instrument. X-Ray crystallographic analysis was performed with a Rigaku Saturn CCD X-ray diffractometer. Ultrasonication was performed in a KQ-250E medical ultrasound cleaner with a frequency of 40 KHz and an output power of 250 W. The preparation of (*Z*)-5-benzylidene-2-thioxothiazolidin-4-one or (*Z*)-5-benzylidenethiazolidine-2,4-dione were according to the literature procedure.^{22,23}

General procedure for the synthesis of dispiro compounds 4. A dry 50 mL flask was charged with acenaphthenequinone (**1**) (0.5 mmol), thiazolidine-4-carboxylic acid **2** (0.5 mmol), (*Z*)-5-benzylidene-2-thioxothiazolidin-4-one or (*Z*)-5-benzylidenethiazolidine-2,4-dione **3** (0.5 mmol) and EtOH (5 mL). The mixture was sonicated in the water bath of an ultrasonic cleaner in air at 25-30 °C for 5 h (monitored by TLC). After completion of the reaction, the solvent was removed under vacuum. The resulting crude products were purified by column chromatography using a mixture of petroleum ether-EtOAc (3:1) as eluent. The corresponding products **4** were obtained.

Compound 4a: mp 139-141 °C; IR (KBr): 3334, 3057, 2926, 2855, 1715, 1631, 1497, 1410, 1288, 1193, 1073, 784 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 2.89-2.91 (m, 1H), 3.13 (t, $J = 5.6$ Hz, 1H), 3.55 (d, $J = 6.4$ Hz, 1H), 4.04 (d, $J = 6.4$ Hz, 1H), 4.33 (d, $J = 9.2$ Hz, 1H), 4.89 (d, $J = 6.4$ Hz, 1H), 7.36 (s, 1H), 7.44 (s, 4H), 7.84-7.93 (m, 3H), 8.04 (d, $J = 6.8$ Hz, 1H), 8.16 (d, $J = 7.6$ Hz, 1H), 8.37 (d, $J = 7.2$ Hz, 1H), 13.23 (s, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 32.9, 48.9, 58.1, 70.4, 79.8, 80.3, 122.7, 125.1, 127.1, 128.4, 129.0, 129.1, 129.8, 130.4, 131.8, 133.1, 135.7, 142.4, 178.2, 199.3, 201.9. HRMS Calculated for $\text{C}_{25}\text{H}_{19}\text{N}_2\text{O}_2\text{S}_3$: $[\text{M}+\text{H}]$ 475.0603, found: 475.0605.

Compound 4b: mp 144-145 °C; IR (KBr) 3424, 2926, 2854, 1715, 1604, 1511, 1428, 1291, 1224, 1075, 1016, 833, 782 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 2.89-2.93 (m, 1H), 3.13 (t, $J = 7.6$ Hz, 1H), 3.54 (d, $J = 6.8$ Hz, 1H), 4.03 (d, $J = 6.4$ Hz, 1H), 4.34 (d, $J = 8.8$ Hz, 1H), 4.83 (d, $J = 6.4$ Hz, 1H), 7.27 (t, $J = 8.0$ Hz, 2H), 7.50 (s, 2H), 7.81-7.92 (m, 3H), 8.03 (t, $J = 6.4$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 7.6$ Hz, 1H), 13.32 (s, 1H); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 32.9, 49.0, 57.4, 70.6, 79.7, 80.2, 115.8, 116.0, 122.7, 125.1, 127.1, 129.0, 129.7, 130.4, 131.7, 131.8, 131.9, 132.0, 133.2, 142.4, 160.8, 163.2, 178.3, 199.3, 201.9. HRMS Calculated for $\text{C}_{25}\text{H}_{18}\text{FN}_2\text{O}_2\text{S}_3$: $[\text{M}+\text{H}]$ 493.0509, found: 493.0504.

Compound 4c: mp 147-149 °C; IR (KBr) 3446, 3251, 3056, 2926, 1714, 1619, 1428, 1289, 1198, 1073, 1012, 830, 781 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 2.89-2.93 (m, 1H), 3.13 (t, $J = 6.0$ Hz, 1H), 3.54 (d, $J = 6.8$ Hz, 1H), 4.05 (d, $J = 7.2$ Hz, 1H), 4.32 (d, $J = 9.2$ Hz, 1H), 4.81-4.85 (m, 1H), 7.42 (d, $J = 7.6$

Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.81-7.86 (m, 1H), 7.90 (t, $J = 7.2$ Hz, 2H), 8.04 (d, $J = 6.8$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 13.30 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 32.8, 48.9, 57.4, 70.5, 79.7, 80.1, 121.8, 122.8, 125.1, 127.2, 129.1, 129.7, 130.4, 131.7, 132.1, 133.2, 135.2, 142.4, 178.2, 199.1, 201.9. HRMS Calculated for $\text{C}_{25}\text{H}_{17}\text{BrN}_2\text{O}_2\text{S}_3$: 551.9636, found: 551.9641.

Compound 4d: mp 155-156 °C; IR (KBr) 3419, 3060, 2925, 2853, 1713, 1602, 1519, 1427, 1346, 1215, 1075, 852, 784 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.91-2.96 (m, 1H), 3.11-3.16 (m, 1H), 3.53 (d, $J = 6.6$ Hz, 1H), 4.06 (d, $J = 6.6$ Hz, 1H), 4.49 (d, $J = 9.0$ Hz, 1H), 4.88-4.91 (m, 1H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.83-7.91 (m, 3H), 8.04 (d, $J = 6.9$ Hz, 1H), 8.16 (d, $J = 7.8$ Hz, 1H), 8.29 (d, $J = 8.4$ Hz, 1H), 8.37 (d, $J = 8.1$ Hz, 1H), 13.38 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 33.2, 49.4, 58.0, 71.2, 80.0, 80.3, 123.4, 124.6, 125.6, 127.8, 129.6, 130.2, 131.0, 131.9, 132.0, 133.8, 143.1, 144.2, 147.9, 178.8, 199.4, 202.4. HRMS Calculated for $\text{C}_{25}\text{H}_{18}\text{N}_3\text{O}_4\text{S}_3$: [M+H] 520.0454, found: 520.0411.

Compound 4e: mp 140-142 °C; IR (KBr) 3195, 3026, 2920, 2863, 1713, 1597, 1514, 1495, 1449, 1426, 1292, 1192, 1076, 1020, 957, 929, 834, 782 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.31 (s, 3H), 2.87-2.2.91 (m, 1H), 3.12 (t, $J = 6.0$ Hz, 1H), 3.55 (d, $J = 6.8$ Hz, 1H), 4.06 (d, $J = 7.2$ Hz, 1H), 4.29 (d, $J = 9.6$ Hz, 1H), 4.86 (d, $J = 6.4$ Hz, 1H), 7.24 (t, $J = 8.0$ Hz, 2H), 7.31 (s, 2H), 7.83-7.90 (m, 3H), 8.03 (d, $J = 7.2$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 13.13 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 21.4, 33.4, 49.5, 58.5, 71.0, 80.3, 81.1, 123.2, 125.6, 127.5, 129.5, 130.2, 130.4, 131.0, 132.6, 133.3, 133.5, 138.1, 142.9, 179.5, 200.5, 202.4. HRMS Calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_3$: [M+H] 511.0579, found: 511.0571.

Compound 4f: mp 146-148 °C; IR (KBr) 3216, 3056, 2924, 2856, 1715, 1589, 1494, 1429, 1289, 1198, 1080, 831, 781 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.89-2.93 (m, 1H), 3.13 (t, $J = 7.6$ Hz, 1H), 3.53 (d, $J = 7.2$ Hz, 1H), 4.05 (d, $J = 7.2$ Hz, 1H), 4.34 (d, $J = 9.6$ Hz, 1H), 4.81-4.86 (m, 1H), 7.49 (s, 4H), 7.81-7.86 (m, 1H), 7.90 (t, $J = 7.2$ Hz, 2H), 8.03 (d, $J = 6.8$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.37 (d, $J = 7.6$ Hz, 1H), 13.27 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 32.8, 48.9, 57.4, 70.5, 79.7, 79.9, 122.8, 125.1, 127.2, 129.0, 129.7, 130.4, 131.7, 133.1, 133.2, 134.8, 142.4, 178.2, 199.1, 201.9. HRMS Calculated for $\text{C}_{25}\text{H}_{17}\text{ClN}_2\text{O}_2\text{S}_3$: 508.0141, found: 508.0146.

Compound 4g: mp 138-140 °C; IR (KBr) 3218, 3059, 2930, 1704, 1600, 1496, 1433, 1316, 1265, 1156, 1075, 1015, 955, 830, 782, 700 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.86-2.90 (m, 1H), 3.12 (t, $J = 6.0$ Hz, 1H), 3.52 (d, $J = 6.8$ Hz, 1H), 4.02 (d, $J = 6.8$ Hz, 1H), 4.35 (d, $J = 9.6$ Hz, 1H), 4.89-4.92 (m, 1H), 7.31-7.38 (m, 1H), 7.43 (s, 4H), 7.82 (d, $J = 7.2$ Hz, 1H), 7.88 (d, $J = 6.4$ Hz, 2H), 8.02 (d, $J = 6.8$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 12.24 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 32.7, 48.4, 56.5, 70.4, 77.8, 79.4, 121.6, 122.6, 124.8, 127.1, 129.0, 129.1, 130.0, 130.4, 131.9, 132.1, 133.1, 135.7, 142.5, 168.8, 176.2, 202.4. HRMS Calculated for $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_3\text{S}_2$: 459.0832, found: 459.0825.

Compound 4h: mp 150-151 °C; IR (KBr) 3200, 3019, 2950, 1725, 1610, 1502, 1430, 1400, 1329, 1280, 1100, 1050, 1010, 960, 820, 772, 745 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.87-2.91 (m, 1H), 3.10-3.14 (m, 1H), 3.51 (d, $J = 6.8$ Hz, 1H), 3.99 (d, $J = 6.8$ Hz, 1H), 4.35 (d, $J = 9.6$ Hz, 1H), 4.82-4.87 (m, 1H), 7.28 (t, $J = 8.0$ Hz, 2H), 7.50 (t, $J = 7.2$ Hz, 2H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.85 (d, $J = 7.2$ Hz, 1H), 7.88 (t, $J = 5.6$ Hz, 1H), 8.03 (d, $J = 7.2$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 8.0$ Hz, 1H), 12.19 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 33.2, 49.0, 56.8, 71.2, 78.6, 80.0, 116.2, 116.5, 123.1, 125.3, 127.6, 129.6, 130.6, 131.0, 132.5, 132.6, 133.0, 133.6, 143.0, 160.9, 164.1, 169.3, 176.7, 202.9. HRMS Calculated for $\text{C}_{25}\text{H}_{17}\text{FN}_2\text{O}_3\text{S}_2$: 477.0737, found: 477.0749.

Compound 4i: mp 136-137 °C; IR (KBr) 3415, 2924, 1703, 1622, 1493, 1382, 1310, 1164, 1090, 1013, 831, 782 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.88-2.92 (m, 1H), 3.10-3.14 (m, 1H), 3.52 (d, $J = 6.8$ Hz, 1H), 4.00 (d, $J = 6.8$ Hz, 1H), 4.35 (d, $J = 9.2$ Hz, 1H), 4.83-4.88 (m, 1H), 7.46-7.52 (m, 4H), 7.80-7.91 (m, 3H), 8.03 (d, $J = 6.8$ Hz, 1H), 8.16 (d, $J = 7.6$ Hz, 1H), 8.38 (d, $J = 8.0$ Hz, 1H), 12.23 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 33.2, 49.0, 56.9, 71.1, 78.4, 80.0, 123.1, 125.4, 126.0, 127.6, 129.6, 130.6, 131.0, 132.4, 132.5, 133.5, 133.6, 135.9, 143.0, 169.3, 176.8, 202.9. HRMS Calculated for $\text{C}_{25}\text{H}_{18}\text{ClN}_2\text{O}_3\text{S}_2$: [M+H] 493.0442, found: 493.0433.

Compound 4j: mp 148-150 °C; IR (KBr) 3442, 3061, 2926, 1704, 1491, 1431, 1383, 1314, 1163, 1074, 1013, 831, 783 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.87-2.91 (m, 1H), 3.09-3.14 (m, 1H), 3.50 (d, $J = 6.8$ Hz, 1H), 4.01 (d, $J = 6.8$ Hz, 1H), 4.33 (d, $J = 9.6$ Hz, 1H), 4.82-4.87 (m, 1H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.80-7.90 (m, 3H), 8.02 (d, $J = 7.2$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.38 (d, $J = 8.4$ Hz, 1H), 12.27 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 33.3, 49.0, 57.7, 70.9, 78.8, 80.0, 123.0, 125.3, 127.5, 128.8, 129.6, 130.4, 130.6, 131.0, 132.6, 133.5, 142.9, 169.5, 176.8, 202.8. HRMS Calculated for $\text{C}_{25}\text{H}_{18}\text{BrN}_2\text{O}_3\text{S}_2$: [M+H] 536.9937, found: 536.9939.

Compound 4k: mp 152-154 °C; IR(KBr) 3215, 3065, 2940, 2877, 1699, 1599, 1512, 1496, 1433, 1321, 1303, 1266, 1197, 1159, 1079, 1052, 954, 924, 833, 785 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6) δ 2.31 (s, 3H), 2.87 (t, $J = 7.2$ Hz, 1H), 3.11 (t, $J = 7.2$ Hz, 1H), 3.53 (d, $J = 6.8$ Hz, 1H), 4.01 (d, $J = 6.8$ Hz, 1H), 4.30 (d, $J = 9.2$ Hz, 1H), 4.88 (d, $J = 6.4$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 2H), 7.31 (d, $J = 6.8$ Hz, 2H), 7.82 (d, $J = 7.2$ Hz, 1H), 7.88 (d, $J = 6.0$ Hz, 2H), 8.03 (d, $J = 6.8$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.37 (d, $J = 8.4$ Hz, 1H), 12.12 (s, 1H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 21.4, 33.3, 49.1, 57.5, 70.9, 78.9, 80.0, 123.0, 125.4, 127.5, 129.5, 130.1, 130.3, 130.7, 131.0, 132.7, 133.5, 133.7, 138.1, 142.9, 169.6, 176.9, 202.8. HRMS Calculated for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3\text{S}_2$: [M+H] 473.0988, found: 473.0970.

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