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Copper(I)-Catalyzed Cascade Sulfonimidate to Sulfonamide Rearrangement: Synthesis of Imidazo[1,2-*a*][1,4]diazepin-7(6*H*)-one

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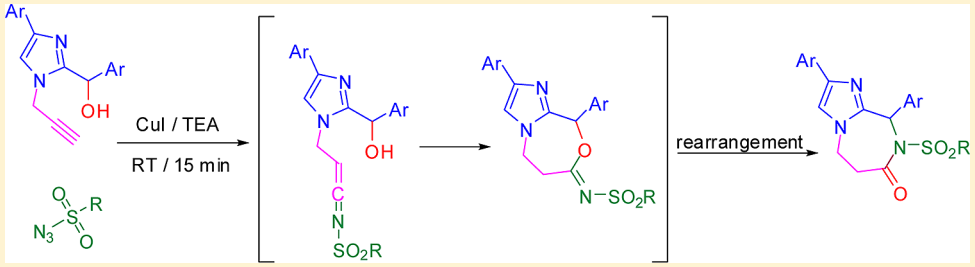
Supporting Information



ABSTRACT: A novel strategy of copper(I)-catalyzed cascade intramolecular nucleophilic attack on *N*-sulfonylketenimine followed by rearrangement of sulfonimidates to sulfonamides resulting in a library of substituted 8,9-dihydro-5*H*-imidazo[1,2-*a*]-[1,4]diazepin-7(6*H*)-ones has been developed.

Ketenimines[1] find extensive usage as building blocks to synthesize differently ring-sized nitrogen heterocycles by the addition of nucleophiles[2] and carbon-centered radicals[3] to their central carbon atom. Their structural arrangement facilitates their involvement in pericyclic events such as cycloaddition reactions, electrocyclic ring closures, and sigmatropic rearrangements.[4] Ketenimines have attracted much attention in recent years because of their easy preparation and reasonable reactivity resulting in a range of products.

Recently, the copper-catalyzed azide−alkyne cycloaddition (CuAAC) has been shown to deliver ketenimines, which can be used to construct various compounds with economic and ecological values.[5−8] The ketenimines generated by the above protocol can be subjected to nucleophilic attack by amines, alcohols, or water leading to amidines, imidates, and amides, respectively. It has been shown that substrates containing both a triple bond and nucleophile, when added with sulfonyl azide, yield cyclic compounds.[9] The electron-rich aromatic ring can also play the role of the nucleophile in this class of reactions.[10] Obviously, several ketenimine-based multiple cascade reactions are constantly being explored.[11]

Sigmatropic rearrangements have been a mainstay of synthetic organic chemistry to produce structurally complex targets with excellent regio- and stereocontrol.[12] The imidate−amide interconversion (Scheme 1) played an important role in the evolution of modern concepts of molecular structure and tautomerization.[13] Baeyer[14] in 1882, as part of his classic investigations of indigo, was the first to correctly formulate the concept of tautomerization to describe the imidic acid-amide isomerization of isatin. This type of conversion has been frequently applied as a key step in total syntheses.[15]

Scheme 1. Allylic Imidate to Amide Rearrangement

In our continued interest in synthesizing heterocyclic compounds from open chain compounds,[16] it has been planned to exploit the reactivity of ketenimine functionality to generate new heterocyclic systems. In this attempt, a seven-membered ring fused to another five-membered ring, an imidazodiazepinone nucleus, has been generated. An interesting cascade process, an internal nucleophilic addition followed by a rearrangement similar to imidate amide conversion, has been observed during this reaction.

Alkynes **1** were obtained by the sodium borohydride reduction of the respective ketones.[16e] The structure of **1a** was confirmed by single crystal X-ray analysis[17] (see the Supporting Information for details). Ketenimines are known to react with alcohols yielding imidates. Accordingly, we examined the two-component reaction of tolylsulfonyl azide (**2a**) with alkyne (**1a**) in the presence of copper iodide and triethylamine in dichloromethane at room temperature (Scheme 2). Instead of the anticipated *N*-(2,9-diphenyl-5,6-dihydroimidazo[2,1-*c*]-[1,4]oxazepin-7(9*H*)-ylidene)-4-methylbenzene sulfonamide **3a** (Scheme 2), 2,9-diphenyl-8-tosyl-8,9-dihydro-5*H*-imidazo-[1,2-*a*][1,4]diazepin-7(6*H*)-one (**4a**) was obtained in high

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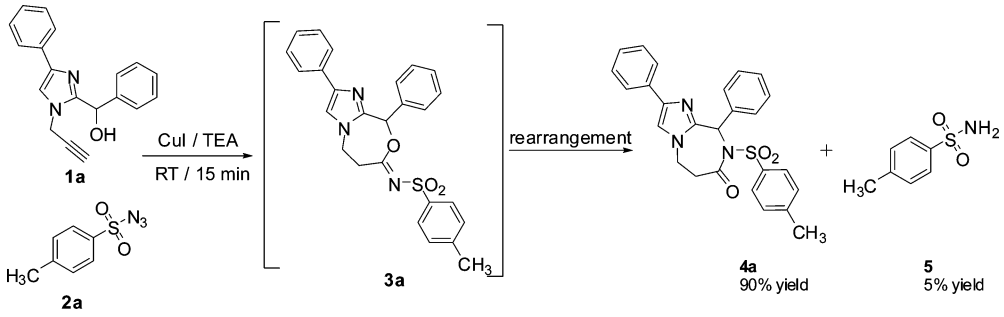
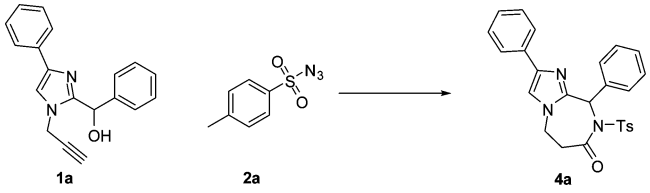
Scheme 2. Copper(I)-Catalyzed Intramolecular Rearrangement of Sulfonimidate to Sulfonamide



yield, involving the rearrangement. Trace amount of sulfonyl amide **5** has also been formed. The structure of **4** has been unambiguously assigned by spectral and analytical data, and that of **4b** has been confirmed by single crystal X-ray analysis[18] also (see the Supporting Information for details).

The reaction conditions were then optimized for the formation of **4a**, and as shown in Table 1, the desired product could

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	base	solvent	yield[b]	reaction time (h)
1	CuI (20 mol %)	TEA	DCM	90	0.5
2	CuI (10 mol %)	TEA	DCM	90	0.5
3	CuI (5 mol %)	TEA	DCM	87	1.0
4	CuI (1 mol %)	TEA	DCM	82	2.0
5	CuI (0.1 mol %)	TEA	DCM	62	5.0
6	CuI (10 mol %)	K_2CO_3	DCM	trace	5.0
7	CuI (10 mol %)	pyridine	DCM	42	4.0
8	CuI (10 mol %)	2,6-lutidine	DCM	85	1.0
9	CuBr (10 mol %)	TEA	THF	78	1.0
10	CuCl (10 mol %)	TEA	$CHCl_3$	69	1.5
11	CuI (10 mol %)	TEA	CH_3CN	48	4.0
12	CuI (10 mol %)	TEA	toluene	42	6.0
13	CuI (10 mol %)	TEA	benzene	44	6.0

[a]Reaction conditions: *p*-Toluenesulfonyl azide **2a** (1.2 mmol), **1a** (1.0 mmol), TEA (2.0 mmol), copper (I) salt, solvent (10 mL), rt, N_2 atm. [b]Isolated yield.

be obtained in 44−90% yield using CH_3CN, THF, $CHCl_3$, toluene, and CH_2Cl_2 as solvents. Dichloromethane has been found to be the solvent of choice. Other bases like pyridine and potassium carbonate resulted in lower yield of **4a**. It has been found that the presence of copper catalyst in less than 10 mol % yields the product quantitatively but requires more time for the reaction to get completed (Table 1, entries 3, 4 and 5). Addition of the catalyst in higher mole ratio has also not resulted in any improvement (Table 1, entry 1).

The interesting observation related to **4** is that the benzylic hydrogen appears relatively in the downfield region, around 7 ppm in the ^1H NMR spectra, while the corresponding carbon appears around 50 ppm in the ^{13}C NMR spectra. The scope of the reaction was extended with various sulfonyl azides **2** and differently substituted imidazole derivatives **1** under the optimized reaction condition (Table 2). It could be seen that all the aryl and alkylsulfonyl azides reacted well to give the respective **4** in excellent yields.

The reaction is believed to proceed initially through a nucleophilic attack on the ketenimine central carbon resulting in the intramolecular ring closure leading to the intermediate **3** (Scheme 3). The intermediate **3** should have undergone an intramolecular [1,3]-sigmatropic shift providing *N*-sulfonamides **4**, though a pericyclic [1,3]-sigmatropic rearrangement is thermally unfavorable. To the best of our knowledge, this is the first report of this type of rearrangement. The reported imidate amide rearrangement involves a [3,3]-sigmatropic rearrangement, and it has been found to occur in the presence of palladium reagent.[19] The rearrangement reported in this work occurs in situ, probably driven by the thermodynamic factors.

Encouraged by these results, to expand the scope of this novel cyclization, the higher homologues of propargyl alcohols **6** were treated with tosyl azide **2a**. However, the anticipated cyclic *N*-sulfonyl lactam **7** has not been formed. Only the sulfonyl amide **5** was obtained quantitatively in each case (Scheme 4).

A copper-catalyzed cascade reaction involving intramolecular nucleophilic addition to *N*-sulfonylketenimine furnishing cyclic sulfonimidate, which subsequently undergoes rearrangement to sulfonamide, has been described. A library of novel 8,9-dihydro-5*H*-imidazo[1,2-*a*][1,4]diazepin-7(6*H*)-one derivatives has been successfully synthesized.

■ EXPERIMENTAL SECTION

General Information and Materials. All the reagents were obtained commercially or synthesized according to literature procedures. Nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ using TMS as internal standard. Chemical shifts are reported in parts per million (δ), coupling constants (J values) are reported in Hertz (Hz). The hydroxyl hydrogen was not seen in many cases. ^{13}C NMR spectra were routinely run with broadband decoupling. Infrared spectra were recorded on a FT-IR instrument. Band positions are reported in reciprocal centimeters (cm^{-1}). Melting points were determined on a melting point apparatus equipped with a thermometer and were uncorrected. Column chromatography was carried out in silica gel (60−120 mesh) using petroleum ether−ethyl acetate as eluent.

General Procedure for the Preparation of (1). 4-Aryl-2-aryloyl-(1-(prop-2-ynyl)-imidazole derivatives were prepared by literature procedure.[16e,20] 4-Aryl-2-aryloyl-(1-(prop-2-ynyl)-imidazole (1.7 mmol) was dissolved in methanol (10.0 mL), and sodium borohydride (0.13 g, 3.4 mmol) was added slowly. After completion of the reaction, the

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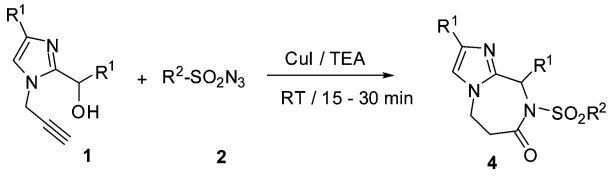
reaction mixture was poured into ice-cold water and filtered to yield **1** (80−95%).

Phenyl(4-phenyl-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (***1a***). Isolated yield 0.440 g (90%); colorless solid: mp 142−144 °C; IR

Table 2. Synthesis of Substituted Imidazo[1,2-*a*][1,4]diazepin-7(6*H*)-one[b]



1 **2** **4**

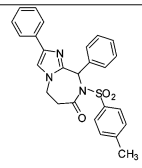
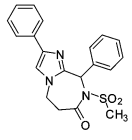
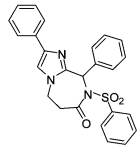
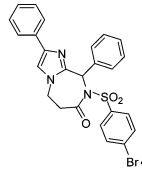
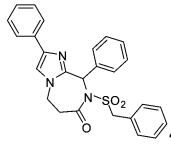
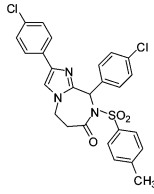
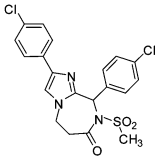
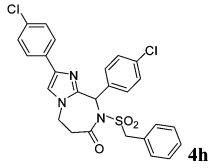
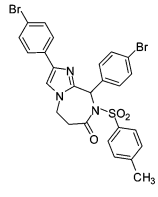
entry	R^1 **1**	R^2 **2**	**4**	time (min)	yield (%)[a]
1	Phenyl **1a**	4-Methylphenyl **2a**	 **4a**	15	90
2	Phenyl **1a**	Methyl **2b**	 **4b**	20	88
3	Phenyl **1a**	Phenyl **2c**	 **4c**	20	90
4	Phenyl **1a**	4-Bromophenyl **2d**	 **4d**	25	86
5	Phenyl **1a**	1-Phenylmethyl **2e**	 **4e**	20	89
6	4-Chlorophenyl **1b**	4-Methylphenyl **2a**	 **4f**	30	82
7	4-Chlorophenyl **1b**	Methyl **2b**	 **4g**	25	88
8	4-Chlorophenyl **1b**	1-Phenylmethyl **2e**	 **4h**	20	86
9	4-Bromophenyl **1c**	4-Methylphenyl **2a**	 **4i**	30	82

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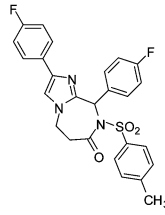
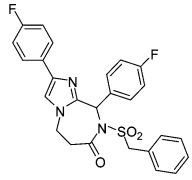
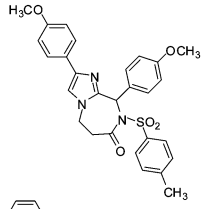
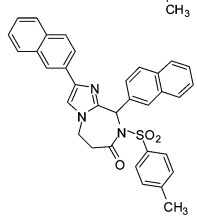
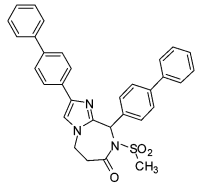
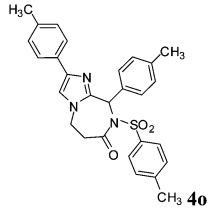
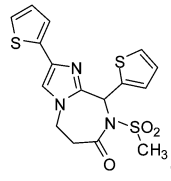
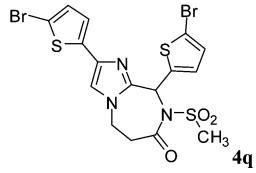
Table 2. continued

entry	R^1 **1**	R^2 **2**	**4**	time (min)	yield (%)[a]
10	4-Fluoro-phenyl **1d**	4-Methylphenyl **2a**	 **4j**	25	87
11	4-Fluoro-phenyl **1d**	1-Phenylmethyl **2e**	 **4k**	20	86
12	4-Methoxy-phenyl **1e**	4-Methylphenyl **2a**	 **4l**	30	90
13	2-Naphthyl **1f**	4-Methylphenyl **2a**	 **4m**	25	80
14	4-Phenylphenyl **1g**	Methyl **2b**	 **4n**	25	80
15	4-Methyl-phenyl **1h**	4-Methylphenyl **2a**	 **4o**	30	82
16	2-Thienyl **1i**	Methyl **2b**	 **4p**	30	72
17	5-Bromo-2-thienyl **1j**	Methyl **2b**	 **4q**	30	76

[a]Isolated yield. [b]All reactions were carried out on 1.0 mmol scale with **1**/sulfonyl azide/TEA = 1:1.2:2.0, 10 mol % of CuI with 10.0 mL of dichloromethane.

(KBr) 3279, 1285, 908, 684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (t, J = 2.4 Hz, 1H), 4.29 (dd, J = 12.0 Hz, 2.4 Hz, 1H), 4.37 (dd, J = 12.0 Hz, 2.4 Hz, 1H), 6.04 (s, 1H), 7.26−7.32 (m, 4H), 7.34 (s, 1H), 7.37−7.42 (m, 4H), 7.75 (dd, J = 7.8 Hz, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5, 68.8, 73.9, 76.5, 116.1, 124.8, 125.9, 126.9, 127.5, 128.5, 128.6, 133.4, 139.3, 139.9, 148.8; MS (M + 1) 289.25.

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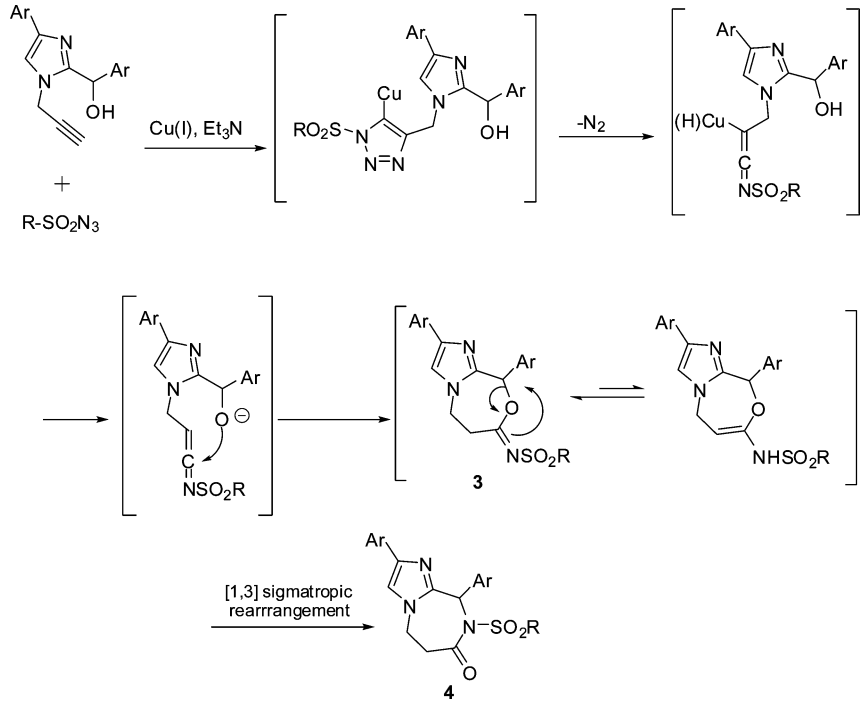
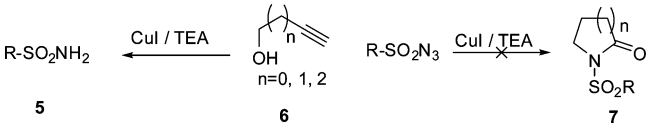
Scheme 3. Proposed Mechanism



Scheme 4. Attempted Synthesis of *N*-Sulfonyl Lactam



Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 78.98; H, 5.42; N, 9.59.

*(4-Chlorophenyl)(4-(4-chlorophenyl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1b**).* Isolated yield 0.558 g (92%); colorless solid: mp 144−146 °C; IR (KBr) 3289, 1275, 910, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.30 (t, J = 2.4 Hz, 1H), 4.28 (dd, J = 17.7, Hz, 2.4 Hz, 1H), 4.43 (dd, J = 17.7, Hz 2.4 Hz, 1H), 6.01 (s, 1H), 7.22 (s, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.29−7.35 (m, 4H), 7.62 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 68.0, 74.3, 76.4, 116.4, 125.9, 127.1, 128.5, 128.6, 131.5, 132.5, 133.4, 138.1, 138.3, 148.4; MS (M + 1) 357.17. Anal. Calcd. for $C_{19}H_{14}Cl_2N_2O$: C, 63.88; H, 3.95; N, 7.84. Found: C, 63.72; H, 3.87; N, 7.69.

*(4-Bromophenyl)(4-(4-bromophenyl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1c**).* Isolated yield 0.720 g (95%); colorless solid: mp 160−162 °C; IR (KBr) 3292, 1291, 911, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (t, J = 2.4 Hz, 1H), 4.31 (dd, J = 17.7 Hz, 2.4 Hz, 1H), 4.45 (dd, J = 17.7 Hz, 2.4 Hz, 1H), 5.98 (s, 1H), 7.22−7.27 (m, 4H), 7.45 (s, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 68.2, 74.5, 76.7, 116.6, 120.7, 121.7, 126.3, 127.5, 131.4, 131.8, 132.7, 138.5, 138.7, 148.5. Anal. Calcd. for $C_{19}H_{14}Br_2N_2O$: C, 51.15; H, 3.16; N, 6.28 Found: C, 50.98; H, 3.08; N, 6.19.

*(4-Fluorophenyl)(4-(4-fluorophenyl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1d**).* Isolated yield 0.490 g (89%); colorless solid: mp 164−166 °C; IR (KBr) 3294, 1293, 919, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.27 (t, J = 2.4 Hz, 1H), 4.28 (dd, J = 17.7 Hz, 2.4 Hz, 1H), 4.38 (dd, J = 17.7 Hz, 2.4 Hz, 1H), 6.02 (s, 1H), 6.98 (t, J = 8.7 Hz, 2H), 7.07 (t, J = 8.7 Hz, 2H), 7.17 (s, 1H), 7.30−7.35 (m, 2H), 7.63−7.68 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.4, 68.3, 74.0, 76.4, 114.7, 115.5, 115.6, 126.0, 127.5, 129.8, 136.1, 138.5, 148.5, 160.0, 163.2. Anal. Calcd. for $C_{19}H_{14}F_2N_2O$: C, 70.36; H, 4.35; N, 8.64. Found: C, 70.22; H, 4.26; N, 8.52.

*(4-Methoxyphenyl)(4-(4-methoxyphenyl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1e**).* Isolated yield 0.485 g (82%); colorless solid: mp 92−94 °C; IR (KBr) 3399, 1292, 916, 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (t, J = 2.7 Hz, 1H), 3.78 (s, 3H), 3.83 (s, 3H), 4.31 (d, J = 2.4 Hz, 2H), 5.97 (s, 1H), 6.85 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 7.15 (s, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5, 55.1, 55.2, 68.8, 73.9, 76.8, 113.9, 114.0, 115.0, 126.0, 126.4, 127.6, 132.2, 139.4, 148.5, 158.7, 159.2. Anal. Calcd. for $C_{21}H_{20}N_2O_3$: C, 72.40; H, 5.79; N, 8.04. Found: C, 72.23; H, 5.69; N, 7.96.

*Naphthalen-2-yl(4-(naphthalen-2-yl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1f**).* Isolated yield 0.561 g (85%); colorless solid: mp 88−90 °C; IR (KBr) 3388, 1289, 913, 687 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.26 (t, J = 2.4 Hz, 1H), 4.30 (dd, J = 18.0 Hz, 2.4 Hz, 1H), 4.45 (dd, J = 18.0 Hz, 2.4 Hz, 1H), 6.26 (s, 1H), 7.43−7.49 (m, 7H), 7.82−7.86 (m, 6H), 7.93 (s, 1H), 8.32 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 69.4, 74.2, 76.9, 116.7, 122.7, 123.5, 124.2,* 124.6, 125.2, 125.8, 125.9, 127.4, 127.5,* 127.8, 127.9, 128.1, 131.1, 132.4, 132.7, 133.1, 133.6, 137.6, 139.6, 148.7. Anal. Calcd. for $C_{27}H_{20}N_2O$: C, 83.48; H, 5.19; N, 7.21. Found: C, 83.34; H, 5.08; N, 7.12. [* Two carbon signals have merged together].

*Biphenyl-4-yl(4-(biphenyl-4-yl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1g**).* Isolated yield 0.629 g (84%); colorless solid: mp 182−184 °C; IR (KBr) 3379, 1272, 927, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (t, J = 2.4 Hz, 1H), 4.37 (dd, J = 17.7, 2.4 Hz, 1H), 4.48 (dd, J = 17.7, 2.4 Hz, 1H), 6.21 (s, 1H), 7.29 (s, 1H), 7.33−7.43 (m, 6H), 7.47 (d, J = 8.1 Hz, 2H), 7.56−7.65 (m, 8H), 7.81 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.9, 69.1, 74.3, 77.1, 116.4, 125.3, 126.7,* 126.9,* 127.0,* 127.2, 127.3, 128.7, 132.6, 139.0, 139.5, 139.6, 140.7, 140.8, 140.9, 148.8. Anal. Calcd. for $C_{31}H_{24}N_2O$: C, 84.52; H, 5.49; N, 6.36. Found: C, 84.36; H, 5.32; N, 6.20. [* Two carbon signals have merged together].

*(1-(Prop-2-ynyl)-4-p-tolyl-1H-imidazol-2-yl)(p-tolyl)methanol (**1h**).* Isolated yield 0.462 g (86%); colorless solid: mp 112−114 °C; IR (KBr) 3311, 1284, 916, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.20 (t, J = 2.4 Hz, 1H), 2.30 (s, 3H), 2.35 (s, 3H), 4.24 (d, J = 2.4 Hz, 2H), 6.04 (s, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.18 (s, 1H), 7.23 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 7.8, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 21.0, 35.5, 68.7, 73.8, 76.5, 115.5, 124.6, 125.9, 128.9, 129.1, 130.6, 136.3, 136.9, 137.1, 139.3, 148.6. Anal.

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Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.37; N, 8.85. Found: C, 79.63; H, 6.28; N, 8.72.

*(1-(Prop-2-ynyl)-4-(thiophen-2-yl)-1H-imidazol-2-yl)(thiophen-2-yl)methanol (**1i**).* Isolated yield 0.408 g (80%); viscous liquid: IR (KBr) 3398, 1273, 922, 697 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (t, J = 2.7 Hz, 1H), 4.49 (d, J = 2.7 Hz, 2H), 6.22 (s, 1H), 6.80 (d, J = 3.6 Hz, 1H), 6.91 (t, J = 4.2 Hz, 1H), 7.01 (t, J = 3.6 Hz, 1H), 7.14−7.18 (m, 2H), 7.25−7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 66.1, 74.3, 74.6, 116.0, 121.9, 123.4, 124.6, 125.5, 127.0, 127.5, 134.7, 136.7, 144.0, 147.7. Anal. Calcd. for $C_{15}H_{12}N_2OS_2$: C, 59.97; H, 4.03; N, 9.33; S, 21.35. Found: C, 59.82; H, 3.95; N, 9.22; S, 21.19.

*(5-Bromothiophen-2-yl)(4-(5-bromothiophen-2-yl)-1-(prop-2-ynyl)-1H-imidazol-2-yl)methanol (**1j**).* Isolated yield 0.638 g (82%); viscous liquid: IR (KBr) 3392, 1262, 928, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (t, J = 2.4 Hz, 1H), 4.50 (dd, J = 17.7 Hz, 2.4 Hz, 1H), 4.62 (dd, J = 17.7 Hz, 2.4 Hz, 1H), 6.00 (s, 1H), 6.44 (d, J = 3.3 Hz, 1H), 6.82 (d, J = 3.6 Hz, 1H), 6.88−6.92 (m, 2H), 7.11 (d, J = 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.2, 65.8, 74.8, 76.5, 110.3, 112.8, 116.3, 122.7, 125.0, 129.7, 130.3, 134.1, 138.0, 145.3, 147.3. Anal. Calcd. for $C_{15}H_{10}Br_2N_2OS_2$: C, 39.32; H, 2.20; N, 6.11; S, 14.00. Found: C, 39.07; H, 2.08; N, 6.01; S, 13.81.

General Procedure for Synthesis of Substituted Imidazo-[1,2-*a*][1,4]diazepin-7(6*H*)-one (4). To a mixture of cuprous iodide (0.02 g, 0.1 mmol), imidazole derivative **1** (1.0 mmol), and sulfonyl azide **2** (1.2 mmol) in dried dichloromethane (10.0 mL), triethylamine (0.20 g, 2.0 mmol) in dichloromethane (2.0 mL) was added under N_2 atmosphere. The mixture was then stirred at room temperature for 10−30 min. Completion of the reaction was confirmed by TLC, and then the solvent was evaporated under a vacuum. The residue was subjected to silica gel column chromatography with petroleum ether/ethyl acetate (80:20) to yield **4** (72−90%).

*2,9-Diphenyl-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a][1,4]-diazepin-7(6H)-one (**4a**).* Isolated yield 0.411 g (90%); colorless solid: mp 178−180 °C; IR (KBr) 1666, 1408, 1192 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.52 (dt, J = 14.4 Hz, 3.6 Hz, 1H), 3.00 (td, J = 14.4 Hz, 5.4 Hz, 1H), 3.98−4.13 (m, 2H), 7.15−7.18 (m, 3H), 7.26−7.35 (m, 5H), 7.40 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 35.8, 43.2, 58.1, 116.8, 125.1, 125.7, 127.3, 128.1, 128.7, 128.9, 129.3, 129.4, 133.5, 135.7, 138.8, 141.3, 142.9, 145.1, 170.5; MS (M + 1) 458.33. Anal. Calcd. for $C_{26}H_{23}N_3O_3S$: C, 68.25; H, 5.07; N, 9.18; S, 7.01. Found: C, 68.09; H, 5.01; N, 9.09; S, 6.94.

*8-(Methylsulfonyl)-2,9-diphenyl-8,9-dihydro-5H-imidazo[1,2-a]-[1,4]diazepin-7(6H)-one (**4b**).* Isolated yield 0.335 g (88%); colorless solid: mp 196−198 °C; IR (KBr) 1656, 1388, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.69 (bd, J = 14.4 Hz, 1H), 3.07 (td, J = 14.4 Hz, 5.1 Hz, 1H), 3.47 (s, 3H), 4.21−4.29 (m, 2H), 7.16 (d, J = 7.2 Hz, 2H), 7.24−7.31 (m, 4H), 7.35−7.43 (m, 4H), 7.79 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 42.6, 43.4, 57.3, 116.9, 125.1, 125.6, 127.3, 128.2, 128.7, 129.4, 133.3, 138.5, 141.4, 142.7, 172.1. Anal. Calcd. for $C_{20}H_{19}N_3O_3S$: C, 62.97; H, 5.02; N, 11.02; S, 8.41. Found: C, 62.88; H, 4.95; N, 10.98; S, 8.33.

*2,9-Diphenyl-8-(phenylsulfonyl)-8,9-dihydro-5H-imidazo[1,2-a]-[1,4]diazepin-7(6H)-one (**4c**).* Isolated yield 0.399 g (90%); colorless solid: mp 124−126 °C; IR (KBr) 1645, 1418, 1199 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.51 (dt, J = 14.1 Hz, 3.0 Hz, 1H), 2.97 (td, J = 14.1 Hz, 5.1 Hz, 1H), 4.00 (td, J = 14.1 Hz, 3.0 Hz, 1H), 4.05−4.13 (m, 1H), 7.13 (d, J = 7.2 Hz, 2H), 7.18 (s, 1H), 7.26−7.36 (m, 4H), 7.38−7.49 (m, 4H), 7.52−7.61 (m, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.99 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 43.1, 57.9, 116.9, 125.0, 125.5, 126.3, 127.2, 128.1, 128.7, 128.8, 129.0, 129.3, 134.0, 138.4, 138.5, 141.1, 142.7, 170.6. Anal. Calcd. for $C_{25}H_{21}N_3O_3S$: C, 67.70; H, 4.77; N, 9.47; S, 7.23. Found: C, 67.63; H, 4.58; N, 9.35; S, 7.11.

*8-(4-Bromophenylsulfonyl)-2,9-diphenyl-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4d**).* Isolated yield 0.449 g (86%); colorless solid: mp 152−154 °C; IR (KBr) 1670, 1400, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (dt, J = 14.4 Hz, 3.6 Hz, 1H), 3.01 (td, J = 14.4 Hz, 5.4 Hz, 1H), 4.01−4.16 (m, 2H), 7.16 (dd, J = 7.5 Hz, 1.2 Hz, 2H), 7.19 (s, 1H), 7.25−7.38 (m, 5H), 7.42 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.82 (dd, J = 7.5 Hz, 1.2 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 43.1, 58.1, 116.9, 125.1, 125.5, 127.3, 128.2, 128.7,* 129.3, 130.4, 132.1, 133.4, 137.5, 138.4, 141.3, 142.6, 170.5; MS (M + 1) 524.25. Anal. Calcd. for $C_{25}H_{20}BrN_3O_3S$: C, 57.48; H, 3.86; N, 8.04; S, 6.14. Found: C, 57.33; H, 3.74; N, 7.95; S, 6.06. [* Two carbon signals have merged together].

*8-(Benzylsulfonyl)-2,9-diphenyl-8,9-dihydro-5H-imidazo[1,2-a]-[1,4]diazepin-7(6H)-one (**4e**).* Isolated yield 0.407 g (89%); colorless solid: mp 195−197 °C; IR (KBr) 1673, 1365, 1156 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (dt, J = 13.8 Hz, 3.0 Hz, 1H), 2.92 (td, J = 13.8 Hz, 4.5 Hz, 1H), 3.86 (td, J = 13.8 Hz, 3.0 Hz, 1H), 4.04 (dt, J = 13.8 Hz, 4.5 Hz, 1H), 4.71 (d, J = 14.1 Hz, 1H), 5.04 (d, J = 14.1 Hz, 1H), 6.74 (s, 1H), 6.92−6.98 (m, 2H), 7.00−7.07 (m, 4H), 7.22 (s, 1H), 7.24−7.32 (m, 5H), 7.41 (t, J = 7.8 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 43.2, 57.7, 59.9, 116.4, 125.0, 125.6, 126.9, 127.1, 128.0, 128.5, 128.6, 129.1, 129.2, 129.7, 133.4, 138.5, 141.0, 141.1, 171.8; MS (M + 1) 458.42. Anal. Calcd. for $C_{26}H_{23}N_3O_3S$: C, 68.25; H, 5.07; N, 9.18; S, 7.01. Found: C, 68.12; H, 4.98; N, 9.06; S, 6.92.

*2,9-Bis(4-chlorophenyl)-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a]-[1,4]diazepin-7(6H)-one (**4f**).* Isolated yield 0.431 g (82%); colorless solid: mp 138−140 °C; IR (KBr) 1663, 1369, 1182 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.55 (bd, J = 14.7 Hz, 1H), 2.94 (td, J = 14.7 Hz, 4.8 Hz, 1H), 4.00−4.14 (m, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.17 (s, 1H), 7.26 (s, 1H), 7.29 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 35.6, 43.1, 57.3, 117.1, 126.3, 127.0, 128.8, 128.9, 129.5, 131.8,* 132.9, 134.3, 135.1, 137.1, 140.1, 142.5, 145.4, 170.1. Anal. Calcd. for $C_{26}H_{21}Cl_2N_3O_3S$: C, 59.32; H, 4.02; N, 7.98; S, 6.09. Found: C, 59.21; H, 3.96; N, 7.85; S, 5.99. [* Two carbon signals have merged together].

*2,9-Bis(4-chlorophenyl)-8-(methylsulfonyl)-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4g**).* Isolated yield 0.396 g (88%); colorless solid: mp 202−204 °C; IR (KBr) 1655, 1402, 1176 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.70 (dt, J = 14.4 Hz, 3.0 Hz, 1H), 3.11 (td, J = 14.4 Hz, 5.4 Hz, 1H), 3.48 (s, 3H), 4.18−4.345 (m, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.24 (s, 1H), 7.26 (s, 1H), 7.32 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 42.7, 43.3, 57.4, 117.1, 126.3, 127.0, 128.9, 129.6, 131.8, 132.9, 135.1, 140.2, 142.6, 145.4, 170.1. Anal. Calcd. for $C_{20}H_{17}Cl_2N_3O_3S$: C, 53.34; H, 3.80; N, 9.33; S, 7.12. Found: C, 53.22; H, 3.72; N, 9.22; S, 7.01

*8-(Benzylsulfonyl)-2,9-bis(4-chlorophenyl)-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4h**).* Isolated yield 0.452 g (86%); colorless solid: mp 175−177 °C; IR (KBr) 1653, 1387, 1199 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.59 (dt, J = 13.8 Hz, 3.0 Hz, 1H), 2.85 (td, J = 13.8 Hz, 4.5 Hz, 1H), 3.90 (td, J = 13.8 Hz, 3.0 Hz, 1H), 4.04 (dt, J = 13.8 Hz, 4.5 Hz, 1H), 4.71 (d, J = 14.1 Hz, 1H), 5.04 (d, J = 14.1 Hz, 1H), 6.66 (s, 1H), 6.94 (d, J = 7.2 Hz, 2H), 6.98 (s, 1H), 7.04 (t, J = 7.2 Hz, 2H), 7.21- 7.27 (m, 3H), 7.43- 7.46 (m, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 43.3, 57.1, 61.9, 116.5, 126.2, 127.0, 128.5, 128.8, 129.1, 129.4, 129.7, 129.9, 131.8, 132.8, 134.2, 137.0, 140.1, 140.8, 171.5. Anal. Calcd. for $C_{26}H_{21}Cl_2N_3O_3S$: C, 59.32; H, 4.02; N, 7.98; S, 6.09. Found: C, 59.23; H, 3.95; N, 7.84; S, 5.99.

*2,9-Bis(4-bromophenyl)-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a]-[1,4]diazepin-7(6H)-one (**4i**).* Isolated yield 0.504 g (82%); colorless solid: mp 190−192 °C; IR (KBr) 1665, 1402, 1189 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.56 (dt, J = 14.7 Hz, 3.3 Hz, 1H), 2.91 (td, J = 14.7 Hz, 5.4 Hz, 1H), 3.99−4.13 (m, 2H), 7.00 (d, J = 7.8 Hz, 2H), 7.19 (s, 1H), 7.34 (s, 1H), 7.46 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 35.8, 43.2, 58.0, 104.4, 108.6, 115.9, 121.1, 122.4, 127.3, 128.3, 130.6, 131.4, 131.5, 133.4, 135.6, 137.3, 140.4, 143.7, 170.5. Anal. Calcd. for $C_{26}H_{21}Br_2N_3O_3S$: C, 50.75; H, 3.44; N, 6.83; S, 5.21. Found: C, 50.66; H, 3.33; N, 6.78; S, 5.12.

*2,9-Bis(4-fluorophenyl)-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a]-[1,4]diazepin-7(6H)-one (**4j**).* Isolated yield 0.429 g (87%); colorless

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solid: mp 196−198 °C; IR (KBr) 1671, 1397, 1199 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.55 (dt, J = 14.7 Hz, 3.0 Hz, 1H), 2.92 (td, J = 14.7 Hz, 5.1 Hz, 1H), 3.98−4.16 (m, 2H), 7.03 (d, J = 8.1 Hz, 2H), 7.07 (s, 1H), 7.09−7.12 (m, 2H), 7.15 (s, 1H), 7.25 (t, J = 7.5 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.74−7.78 (m, 2H), 7.84 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 35.6, 43.1, 57.2, 115.5, 116.3, 116.7, 126.7, 127.4, 129.4, 129.5, 134.3, 135.1, 140.2, 142.5, 143.3, 145.4, 160.6, 163.9, 170.4. Anal. Calcd. for $C_{26}H_{21}F_2N_3O_3S$: C, 63.28; H, 4.29; N, 8.51; S, 6.50. Found: C, 63.16; H, 4.20; N, 8.46; S, 6.42.

*8-(Benzylsulfonyl)-2,9-bis(4-fluorophenyl)-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4k**).* Isolated yield 0.424 g (86%); colorless solid: mp 156−158 °C; IR (KBr) 1666, 1408, 1192 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.60 (dt, J = 13.8 Hz, 2.7 Hz, 1H), 2.91 (td, J = 13.8 Hz, 4.8 Hz, 1H), 3.90 (td, J = 13.8 Hz, 2.7 Hz, 1H), 4.07 (dt, J = 13.8 Hz, 4.8 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H), 5.04 (d, J = 14.4 Hz, 1H), 6.67 (s, 1H), 6.92 (s, 1H), 6.98 (d, J = 7.2 Hz, 2H), 7.03−7.13 (m, 4H), 7.23 (d, J = 8.1 Hz, 2H), 7.36−7.40 (m, 3H), 7.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.9, 43.2, 57.1, 59.9, 115.5, 116.0, 126.5, 127.5, 128.8, 129.1, 129.7, 130.7, 134.3, 140.3, 140.9, 143.3, 145.4, 160.6, 163.9, 171.7. Anal. Calcd. for $C_{26}H_{21}F_2N_3O_3S$: C, 63.28; H, 4.29; N, 8.51; S, 6.50. Found: C, 63.17; H, 4.18; N, 8.44; S, 6.41.

*2,9-Bis(4-methoxyphenyl)-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4l**).* Isolated yield 0.465 g (90%); colorless solid: mp 192−194 °C; IR (KBr) IR (KBr) 1666, 1408, 1192 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.44 (bd, J = 14.7 Hz, 1H), 2.99 (m, 1H), 3.75 (s, 3H), 3.81 (s, 3H), 3.98−4.11 (m, 2H), 6.83 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 7.5 Hz, 2H), 7.01 (d, J = 7.5 Hz, 2H), 7.08 (s, 1H), 7.23 (d, J = 7.8 Hz, 2H), 7.36 (s, 1H), 7.71 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 35.7, 43.0, 55.3,* 57.5, 114.2, 114.6, 115.9, 126.3, 126.9, 128.8, 129.4, 129.5, 130.7, 135.6, 140.9, 142.9, 145.1, 159.1, 159.4, 170.7. Anal. Calcd. for $C_{28}H_{27}N_3O_5S$: C, 64.97; H, 5.26; N, 8.12; S, 6.19. Found: C, 64.82; H, 5.19; N, 8.03; S, 6.11. [* Two carbon signals have merged together].

*2,9-Di(naphthalen-2-yl)-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4m**).* Isolated yield 0.446 g (80%); colorless solid: mp 182−184 °C; IR (KBr) 1669, 1405, 1193 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.24 (m, 1H), 2.96−2.98 (m, 1H), 3.61−3.64 (m, 2H), 7.22−7.25 (m, 3H), 7.29 (s, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.44−7.46 (m, 5H), 7.66 (s, 1H), 7.79−7.82 (m, 3H), 7.87−7.92 (m, 4H), 8.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 35.8, 43.2, 58.2, 117.6, 123.1, 123.4, 123.6, 124.7, 125.6, 126.3, 126.7, 126.8, 127.4, 127.7, 128.1, 128.3, 128.9, 129.5, 130.2, 130.8, 132.7, 132.8, 133.2, 133.8, 135.5, 136.0, 141.1, 143.2, 145.2, 146.2, 170.5. Anal. Calcd. for $C_{34}H_{27}N_3O_3S$: C, 73.23; H, 4.88; N, 7.54; S, 5.75. Found: C, 73.13; H, 4.76; N, 7.46; S, 5.66.

*2,9-Di(biphenyl-4-yl)-8-(methylsulfonyl)-8,9-dihydro-5H-imidazo-[1,2-a][1,4]diazepin-7(6H)-one (**4n**).* Isolated yield 0.427 g (80%); colorless solid: mp 196−198 °C; IR (KBr) 1662, 1402, 1199 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.69 (bd, J = 14.4 Hz, 1H), 3.07 (td, J = 14.4 Hz, 5.1 Hz, 1H), 3.49 (s, 3H), 4.23−4.35 (m, 2H), 7.26 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.36 (dd, J = 7.5 Hz, 2.1 Hz, 2H), 7.41−7.47 (m, 6H), 7.54 (s, 1H), 7.57 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.8, 43.4, 46.3, 57.2, 117.1, 125.5, 126.1, 126.9, 127.0, 127.2, 127.3, 127.4, 127.7, 128.0, 128.7, 128.8, 128.9, 132.3, 137.4, 139.9, 140.1, 140.8, 141.3, 172.1. Anal. Calcd. for $C_{32}H_{27}N_3O_3S$: C, 72.02; H, 5.10; N, 7.87; S, 6.01. Found: C, 71.80; H, 4.99; N, 7.72; S, 5.89.

*2,9-Di-p-tolyl-8-tosyl-8,9-dihydro-5H-imidazo[1,2-a][1,4]-diazepin-7(6H)-one (**4o**).* Isolated yield 0.398 g (82%); viscous liquid: IR (KBr) 1659, 1396, 1198 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.38−2.44 (bs, 6H), 2.49 (bd, J = 14.7 Hz, 1H), 3.00 (td, J = 14.7 Hz, 5.1 Hz, 1H), 4.00−4.12 (m, 2H), 7.00 (d, J = 8.4 Hz, 2H), 7.12−7.26 (m, 7H), 7.42 (s, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 21.2, 21.6, 35.7, 43.1, 57.8, 116.4, 124.9, 126.4, 128.8, 129.3, 129.6, 129.9, 130.6, 135.5, 135.6, 136.9, 137.8, 141.1, 142.9, 145.1, 170.6. Anal. Calcd. for $C_{28}H_{27}N_3O_3S$: C, 69.25; H, 5.60; N, 8.65; S, 6.60. Found: C, 69.12; H, 5.48; N, 8.42; S, 6.49.

*8-(Methylsulfonyl)-2,9-di(thiophen-2-yl)-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4p**).* Isolated yield 0.283 g (72%); viscous liquid: IR (KBr) 1671, 1396, 1198 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.71 (dt, J = 14.4 Hz, 3.3 Hz, 1H), 3.09 (td, J = 14.4 Hz, 5.1 Hz, 1H), 3.49 (s, 3H), 4.23−4.36 (m, 2H), 7.09 (d, J = 3.6 Hz, 1H), 7.10−7.18 (m, 2H), 7.29 (d, J = 5.7 Hz, 1H), 7.37−7.50 (m, 2H), 7.55 (d, J = 3.6 Hz, 1H), 7.80 (d, J = 5.7 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.7, 42.7, 43.4, 57.3, 100.5, 113.1, 117.3, 124.7, 125.9, 127.3, 127.6, 136.7, 137.5, 138.7, 138.8, 172.1. Anal. Calcd. for $C_{16}H_{15}N_3O_3S_3$: C, 48.84; H, 3.84; N, 10.68; S, 24.45. Found: C, 48.72; H, 3.75; N, 10.52; S, 24.22.

*2,9-Bis(5-bromothiophen-2-yl)-8-(methylsulfonyl)-8,9-dihydro-5H-imidazo[1,2-a][1,4]diazepin-7(6H)-one (**4q**).* Isolated yield 0.419 g (76%); viscous liquidIR (KBr) 1665, 1385, 1192 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.72 (dt, J = 14.4 Hz, 3.3 Hz, 1H), 3.09 (td, J = 14.4 Hz, 5.4 Hz, 1H), 3.49 (s, 3H), 4.24−4.36 (m, 2H), 7.02 (d, J = 3.9 Hz, 1H), 7.10 (d, J = 3.6 Hz, 1H), 7.16 (d, J = 3.9 Hz, 1H), 7.19 (s, 1H), 7.30 (d, J = 3.6 Hz, 1H), 7.60 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.4, 42.5, 43.7, 57.7, 11.6, 120.2, 123.1, 125.6, 130.5, 130.8, 136.2, 136.4, 138.1, 140.3, 141.6, 172.2. Anal. Calcd. for $C_{16}H_{13}Br_2N_3O_3S_3$: C, 34.86; H, 2.38; N, 7.62; S, 17.45. Found: C, 34.71; H, 2.22; N, 7.54; S, 17.31.

*4-Methylbenzenesulfonamide (**5**).* Isolated yield 0.138 g (81%); colorless solid: mp 136−138 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 3H), 5.82 (s, 2H), 7.32 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 125.9, 129.2, 139.7, 142.6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR and mass spectra for synthesized compounds and X-ray crystallographic data of **1a** and **4b**. This material is available free of cost via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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