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Synthesis of (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones by two-step, one-pot gold-catalyzed tandem heterocyclization/Petasis–Ferrier rearrangement of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes

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ABSTRACT

A two-step, one-pot synthetic method that relies on gold(I)-catalyzed tandem heterocyclization/Petasis–Ferrier rearrangement and Brønsted acid-assisted debenzoxylation of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes to prepare (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones efficiently is reported. The reactions proceed rapidly under mild and operationally straightforward conditions for a wide variety of aldehyde substrates containing electron-withdrawing, electron-donating, and sterically demanding functional groups and afforded the corresponding benzo-fused azaheterocyclic products in moderate to excellent yields.

1. Introduction

The 1*H*-benzo[*b*]azepine ring system is found in many pharmaceutically important compounds (Fig. 1).[1–6] It is therefore not surprising to find the development of new methods to access this member of the *N*-heterocyclic family of compounds has received and continues to receive an immense amount of attention.[7] While this has led to a myriad of elegant works to the benzo-fused nitrogen ring motif, there remains a need for novel approaches for their construction, with control of substitution patterns, from starting materials that are readily accessible, atom economical, and low cost.

Gold-catalyzed alkyne cycloisomerizations have emerged as one of the most efficient and convenient strategies for heterocyclic synthesis in recent years.[7a,8–11] For example, recently we reported one method to prepare benzo[*b*]oxepin-3(2*H*)-ones that relied on gold-mediated heterocyclization/Petasis–Ferrier rearrangement of 2-(prop-2-ynyloxy)benzaldehydes (Scheme 1, Eq. 1).[9] In the course of this study, the steric interactions between the substituent at the

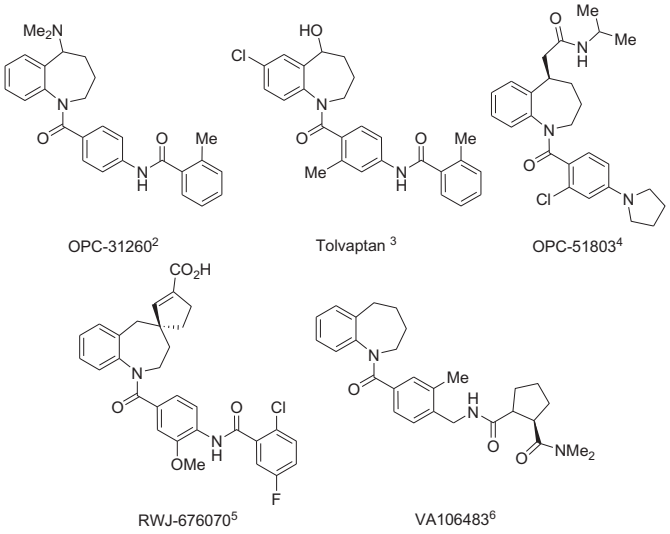

Fig. 1. Structures of pharmaceutically important compounds containing the 1*H*-benzo[*b*]azepine motif.

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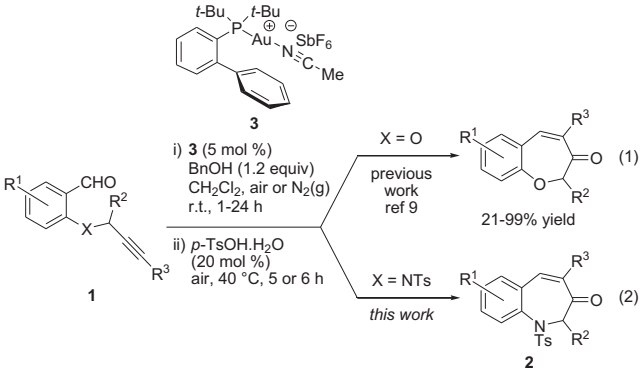
position *ortho* to the ethereal group on the salicylaldehyde ring with that of the acetylenic side chain in the substrate was found to dramatically enhance reactivity. This mode of reactivity was also found to differ to that previously reported for reactions of alkynyl tethered aldehydes catalyzed by gold complexes, which were shown to preferentially undergo carbonyl metathesis.[10] Building on our earlier findings, we reasoned that substrates in which the ethereal oxygen atom is replaced by a protected amine functional group might also occupy a similar conformation and, therefore, exhibit comparable reactivities. As part of an ongoing program exploring the utility of gold catalysis in heterocyclic synthesis,[11] we herein describe a tandem heterocyclization/Petasis–Ferrier rearrangement of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes with the aid of gold(I) catalysis (Scheme 1, Eq. 2). Achieved without the need for a substituent at the *ortho* position of the aniline moiety in the substrate to promote reactivity, this two-step, one-pot process provides a synthetic route to (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones in 34–87% yield for a wide variety of substrates under mild and operationally simplistic conditions.

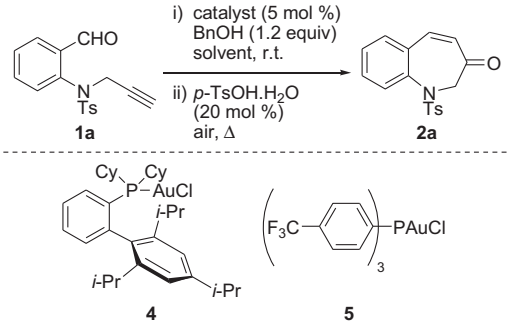


Scheme 1. Gold(I)-catalyzed synthesis of benzo[*b*]oxepin-3(2*H*)-ones and (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones.

2. Results and discussion

Following our success of using Au(I) complex **3** to effect the tandem heterocyclization/Petasis–Ferrier rearrangement of 2-(prop-2-ynyloxy)benzaldehydes,[9] we chose this metal catalyst and 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehyde **1a** as the model substrate to establish the reaction conditions (Table 1). This study revealed treating **1a** with 5 mol % of **3** and 1.2 equiv of BnOH in CH_2Cl_2 at room temperature under a nitrogen gas atmosphere for 1 h followed by *p*-TsOH·H_2O (20 mol %) at 40 °C for 5 h under atmospheric conditions gave the best result (entry 1). Under these conditions, (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-one **2a** was furnished in 81% yield. The structure of the nitrogen-containing ring product was determined by ^{1}H NMR spectroscopic measurements and X-ray crystallographic analysis (see Fig. 2).[12] On the other hand, repeating the reaction under atmospheric conditions or these latter conditions with both the Lewis and Brønsted acid catalysts co-currently present was found to result in lower yields of 57 and 55%, respectively (entries 2 and 3). Likewise, lower product yields were obtained on introducing $CaSO_4$ or 4 Å molecular sieves (MS) to remove water from the reaction conditions or conducting the first step at 80 °C in 1,2-dichloroethane (entries 4–6). A survey of other solvent systems and gold catalysts was also found to provide no improvements (entries 7–24). Changing the solvent from dichloromethane to 1,2-dichloroethane, MeCN, $MeNO_2$, toluene or 1,4-dioxane gave **2a** in low yields of 7–50% or, in the case of THF, the recovery of

Table 1
Optimization of the reaction conditions[a]



Entry	Catalyst	Solvent	Time[b] (h)	Yield[c] (%)
1	**3**	CH_2Cl_2	1/5	81
2[d]	**3**	CH_2Cl_2	1/5	57
3[d]	**3**	CH_2Cl_2	5/—	55
4[e]	**3**	CH_2Cl_2	1/5	68
5[f]	**3**	CH_2Cl_2	1/5	20
6	**3**	$(CH_2Cl)_2$	1/2[g]	43
7	**3**	$(CH_2Cl)_2$	1/2	50
8	**3**	MeCN	23/2	16
9	**3**	$MeNO_2$	24/2	19
10	**3**	PhMe	1/2	26
11	**3**	THF	23/—	—[h]
12	**3**	1,4-Dioxane	24/2	7
13	AuCl	CH_2Cl_2	1/5	13
14	AuCl/$AgSbF_6$	CH_2Cl_2	1/5	36
15	AuCl/AgOTf	CH_2Cl_2	24/—	—[h]
16	$AuCl_3$	CH_2Cl_2	1/5	34
17	$AuCl_3$/$AgSbF_6$	CH_2Cl_2	1/5	53
18	$AuCl_3$/AgOTf	CH_2Cl_2	1/5	32
19	Ph_3PAuCl	CH_2Cl_2	24/—	—[h]
20	$Ph_3PAuCl/AgSbF_6$	CH_2Cl_2	1/5	29
21	Ph_3PAuCl/AgOTf	CH_2Cl_2	1/5	30
22	$Ph_3PAuNTf_2$	CH_2Cl_2	1/5	31
23	**4**	CH_2Cl_2	24/—	—[h]
24	**5**	CH_2Cl_2	24/—	—[h]
25	TfOH	CH_2Cl_2	20/—	—[h]

[a] All reactions were performed with 0.3 mmol of **1a** and 5 mol % of catalyst at room temperature followed by 20 mol % of *p*-TsOH·H_2O at reflux.
[b] Isolated yields.
[c] The first value indicates the initial reaction time and the second value indicates the reaction time after the addition of *p*-TsOH·H_2O.
[d] Reaction conducted under atmospheric conditions.
[e] Reaction conducted with 50 mg of $CaSO_4$.
[f] Reaction conducted with 50 mg of 4 Å MS.
[g] First step carried out in $(CH_2Cl)_2$ at 80 °C for 1 h.
[h] No reaction based on ^{1}H NMR spectroscopy and TLC analysis of the crude mixture.

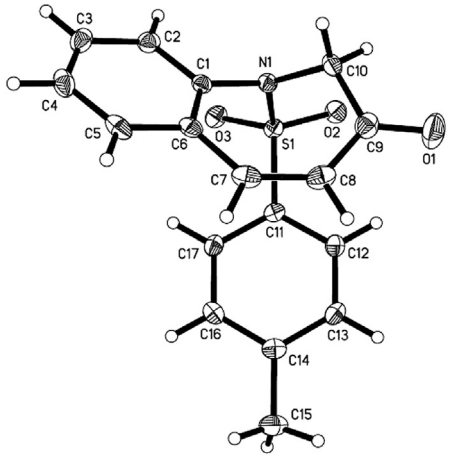


Fig. 2. ORTEP drawing of 1-tosyl-1*H*-benzo[*b*]azepin-3(2*H*)-one (**2a**) with thermal ellipsoids at 50% probability levels.[12]

the substrate (entries 7–12). A similar outcome was found when the reaction was carried out with gold(I) complexes **4**, **5**, AuCl, $AuPPh_3Cl$, $AuPPh_3NTf_2$, and $AuCl_3$ and combination of these catalysts with AgOTf or $AgSbF_6$ (entries 13–24). A final control experiment with TfOH in place of gold(I) complex **3** as the catalyst leading to the recovery of **1a** in near quantitative yield additionally provided evidence that the cationic Au(I) complex is the catalytically active species (entry 25).

To define the scope of the present procedure, we next turned our attention to the reactions of a series of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes and the results are summarized in Table 2. Overall, these experiments showed that with the Au(I)

Table 2
Tandem heterocyclization/Petasis–Ferrier rearrangement of **1b–r** catalyzed by **3**[a]

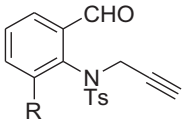
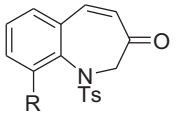
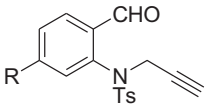
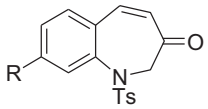
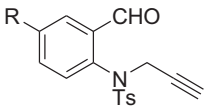
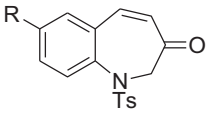
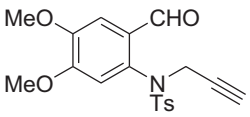
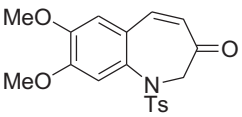
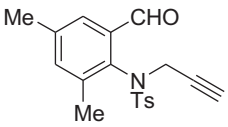
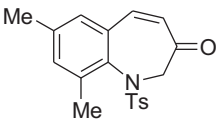
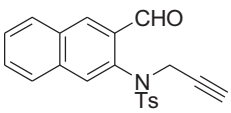
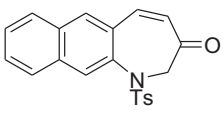
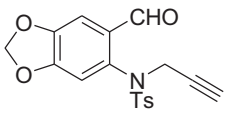
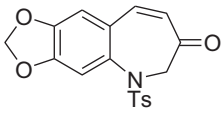
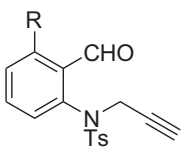
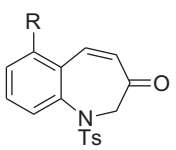
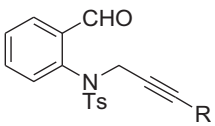
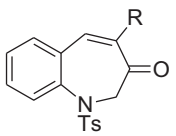
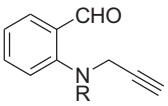
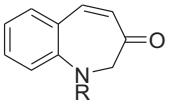
Entry	Substrate	Time (h)	Product		Yield[b] (%)
1	 **1b-c**	1	 **2b-c**	R=OMe	55
2		22		R=Cl	59
3	 **1d-e**	23	 **2d-e**	$R=CF_3$	56
4		1		R=OMe	80
5	 **1f-h**	22	 **2f-h**	R=Cl	71
6		2		R=Br	60
7		3		R=Me	58
8	 **1i**	3	 **2i**		67
9	 **1j**	1	 **2j**		87
10	 **1k**	24	 **2k**		65
11	 **1l**	3	 **2l**		63
12	 **1m-n**	1	 **2m-n**	R=Me	60
13		2		R=Cl	35[c]
14	 **1o-p**	22	 **2o-p**	R=Me	76
15		22		R=Ph	34[c]

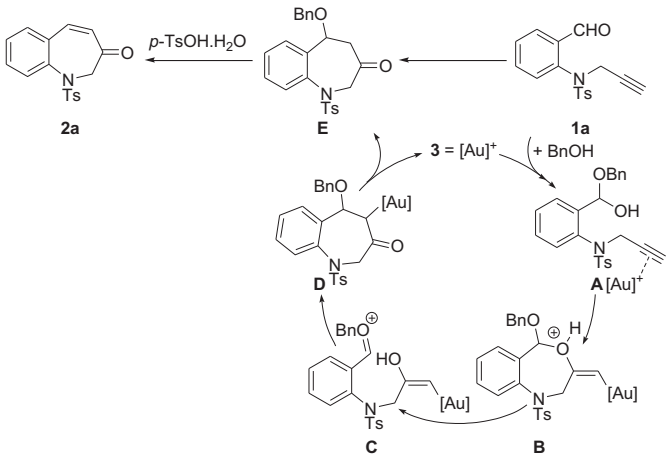
Table 2 (*continued*)

Entry	Substrate	Time (h)	Product		Yield[b] (%)
16	 **1q-r**	24	 **2q-r**	R=Ms	77
17		25		R=*p*-Ns	75

[a] Unless otherwise stated, reactions were performed in CH_2Cl_2 (3 mL) with 0.3 mmol of **1** and 5 mol % of catalyst at room temperature for the stated amount of time followed by 20 mol % of *p*-TsOH·H_2O at reflux for 5 h.
[b] Isolated yields.
[c] Side product additionally obtained that could not be identified by NMR spectroscopic analysis.

complex **3** as the catalyst, the reaction conditions were found to be broad and a variety of (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones could be isolated in 34–87% yield. Starting 2-aminobenzaldehydes with a pendant electron-donating or electron-withdrawing group at the position *ortho* to the amino moiety on the aniline ring were found to react well, giving the corresponding products **2b** and **2c** in 55 and 59% yields, respectively (entries 1 and 2). Similarly, the presence of an electron-donating or electron-withdrawing group or a benzo-fused ring at various positions on the 2-aminobenzaldehyde ring was found to have no influence on the course of the reaction (entries 3–13). In these transformations, the corresponding (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones **2d**–**m** were obtained in 56–87% yield. The only exception was that of **1n** in which the position adjacent or *ortho* to the aldehyde moiety on the aromatic ring is occupied by a Cl substituent (entry 13). In this reaction, the corresponding nitrogen-containing ring product **2n** was furnished in a lower yield of 35%. Substrates containing an acetylene moiety with a pendant Me (**1o**) or Ph (**1p**) group were also investigated under the standard conditions (entries 14 and 15). In these experiments, cycloisomerization of **1o** was found to give the corresponding benzo-fused adduct **2o** in 76% yield whereas a lower product yield of 34% was obtained for the analogous cyclization of **1p** to **2p**. This method was also applicable to Ms- and 4-Ns-protected starting materials **1q** and **1r** (entries 16 and 17). Under the standard conditions, these latter reactions gave the corresponding *N*-sulfonyl protected heterocycles **2q** and **2r** in 77 and 75% yields, respectively.

A plausible mechanism for the present Au(I)-mediated cycloisomerization reactions is illustrated in Scheme 2. In a manner similar to that proposed in our earlier work,[9] this could initially involve in situ formation of the hemiacetal **A** from reaction of BnOH with **1** in the presence of the Lewis acidic catalyst. This is followed by activation of the acetylene bond of this newly formed hemiacetal species by gold(I) complex **3**. This results in cyclization of the pendant aniline group to the alkyne moiety and formation of the putative vinyl gold intermediate **B**. Petasis–Ferrier rearrangement of this aurated azaheterocyclic intermediate involving cycloreversion to furnish the enolic gold complex **C** that subsequently undergoes cyclization would then deliver the organogold species **D**.[13] Protodeauration followed by *p*-TsOH·H_2O-mediated debenzoxylation provides **2** and regeneration of the gold(I) catalyst. We surmise the gradual decrease in product yields as the steric demand of the substituent *ortho* to the aldehyde moiety in the substrate increases on going from **1a**→**1m**→**1n** would be consistent with typical reactivities found in a hemiacetal forming step. A similar rationale could be applied to account for the gradual decrease in product yield as the steric bulk of the pendant group at the acetylenic carbon center increases on going from **1a**→**1o**→**1p**. It might be anticipated that the formation of a vinyl gold intermediate of the type **B** may not be expected to be as efficient as steric interactions between the metal catalyst and the geminal functional group increase as the steric bulk of the latter increases.



Scheme 2. Proposed mechanism.

3. Conclusion

In summary, an efficient synthetic route to (*Z*)-1,2-dihydro-1-tosylbenzo[*b*]azepin-3-ones based on rearrangement of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes has been reported. The two-step, one-pot method to this member of the *N*-heterocyclic family of compounds was achieved under mild conditions and shown to be applicable to a wide variety of 2-aminobenzaldehyde substrates containing electron-withdrawing, electron-donating, and sterically encumbered functional groups. This contrasts to our earlier works in the analogous gold(I)-mediated cycloisomerization of 2-(prop-2-ynyloxy)benzaldehydes to benzo[*b*]oxepin-3(2*H*)-ones,[9] which were found to require a substituent at the position *ortho* to the ethereal group on the substrate to enhance reactivity.

4. Experimental section

4.1. General

All reactions were performed under a nitrogen atmosphere unless otherwise stated. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Gold complexes **3**–**5** and PPh_3AuNTf_2 were purchased from commercial sources and used as received; they can also be prepared following the literature procedures.[14–16] Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica

gel plates. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (EtOAc/*n*-hexane as eluent). ^{1}H and ^{13}C NMR spectra were measured on Bruker Avance 300 and 400 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: br s (broad singlet), s (singlet), br d (broad doublet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), br m (broad multiplet) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in hertz (Hz). Infrared spectra were recorded on a Shimadzu IR Prestige-21 FTIR spectrometer. All samples were examined as a thin film between NaCl salt plates. Solid samples were examined as a thin film between NaCl salt plates using chloroform as the solvent. High-resolution mass spectra (HRMS) were obtained using a Q-TOF LC/HRMS mass spectrometer using simultaneous electrospray (ESI) or a DART TOF mass spectrometer.

4.2. General experimental procedure for the preparation of 2-(*N*-(prop-2-ynyl)-*N*-tosylamino)benzaldehydes (1a)–(1r)

Propargyl bromide (0.27 mL, 3 mmol, 1.5 equiv) was added to a solution of 2-(tosylamino)benzaldehyde (2 mmol) and K_2CO_3 (0.829g, 6 mmol, 3 equiv) in acetone (20 mL). The resulting reaction mixture was stirred at reflux under atmospheric conditions for 4 h. On cooling to room temperature, the reaction mixture was filtered through Celite and the filtrate was concentrated under reduced pressure and purified by silica gel flash column chromatography (9:1 *n*-hexane/EtOAc as eluent) to give the title compound.

4.3. General procedure for the preparation of 1-tosyl-1*H*-benzo[*b*]azepin-3(2*H*)-ones (2a)–(2r)

Benzyl alcohol (0.36 mmol) was added to a dichloromethane (3 mL) solution containing **3** (11.6 mg, 5 mol %), and **1** (0.3 mmol) at room temperature. The reaction mixture was monitored by TLC analysis until no more starting material could be observed. At this point, *p*-TsOH·H_2O (11.4 mg, 20 mol %) was added to the reaction mixture. The reaction mixture was then stirred at reflux under atmospheric conditions for 5 h. On cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the crude product was purified by silica gel flash column chromatography (9:1 *n*-hexane/EtOAc as eluent) to give the title compound.

4.4. Characterization data

*4.4.1. N-(2-Formylphenyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (**1a**).* Yield 80%; 0.281 g; white solid; mp 79–81 °C; R_f (25% EtOAc/*n*-hexane) 0.23; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.39 (s, 1H), 7.99–7.97 (m, 1H), 7.51–7.47 (m, 4H), 7.28–7.26 (m, 2H), 6.91–6.89 (m, 1H), 4.47 (br s, 2H), 2.42 (s, 3H), 2.20 (t, 1H, J=2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.2, 144.6, 141.0, 135.9, 134.4, 134.3, 129.7, 129.2, 128.5, 128.4, 128.0, 76.9, 74.9, 41.7, 21.6; IR (neat): 3306, 1695, 1597, 1356, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{16}NO_3S$ (M^++H): 314.0851, found: 314.0866.

*4.4.2. N-(2-Formyl-6-methoxyphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1b**).* Yield 65%; 0.451 g; white solid; mp 146–147 °C; R_f (50% EtOAc/*n*-hexane) 0.54; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (s, 1H), 7.58 (dd, 1H, J=0.6, 7.8 Hz), 7.47 (d, 2H, J=8.0 Hz), 7.41 (t, 1H, J=8.0 Hz), 7.24 (d, 2H, J=8.0 Hz), 7.00 (dd, 1H, J=1.0, 8.2 Hz), 4.84 (dd, 1H, J=2.4, 17.2 Hz), 4.23 (dd, 1H, J=2.4, 17.2 Hz), 3.27 (s, 3H), 2.40 (s, 3H), 2.18 (t, 1H, J=2.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 156.5, 143.7, 138.1, 136.4, 130.2, 129.3, 128.2, 127.5, 119.5, 116.5, 76.8, 74.1, 55.2, 39.9, 21.5; IR (neat): 3306, 1697, 1585, 1356, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S$ (M^++H): 344.0957, found: 344.0965.

*4.4.3. N-(2-Chloro-6-formylphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1c**).* Yield 88%; 0.166 g; yellow solid; mp 128–129 °C; R_f (25% EtOAc/*n*-hexane) 0.58; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.22 (s, 1H), 7.94 (dd, 1H, J=1.5, 6.3 Hz), 7.57–7.62 (m, 3H), 7.45 (t, 1H, J=7.8 Hz), 7.28 (d, 2H, J=8.1 Hz), 4.92 (dd, 1H, J=2.4, 18.0 Hz), 4.29 (dd, 1H, J=2.4, 18.0 Hz), 2.42 (s, 3H), 2.27 (t, 1H, J=2.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.8, 144.5, 139.1, 137.3, 136.4, 135.7, 135.3, 130.4, 129.9, 127.5, 127.0, 77.0, 75.0, 40.2, 21.6; IR (neat): 3304, 1694, 1597, 1584, 1449, 1358, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{35}ClNO_3S$ (M^++H): 348.0461, found: 348.0458.

*4.4.4. N-(2-Formyl-5-(trifluoromethyl)phenyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (**1d**).* Yield 35%; 0.0798 g; white solid; mp 140–141 °C; R_f (25% EtOAc/*n*-hexane) 0.56; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.42 (s, 1H), 8.12 (d, 1H, J=8.1 Hz), 7.73 (d, 1H, J=8.1 Hz), 7.47 (d, 2H, J=8.3 Hz), 7.30 (d, 2H, J=8.1 Hz), 7.07 (s, 1H), 4.48 (br s, 2H), 2.44 (s, 3H), 2.21 (t, 1H, J=2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.9, 145.2, 141.4, 138.6, 135.4 (1C, d, $J_{C,F}$=33.1 Hz), 133.8, 129.8, 129.2, 128.0, 125.9 (1C, q, $J_{C,F}$=3.6 Hz), 124.6, 121.0, 76.3, 75.4, 41.6, 21.6; IR (neat): 3306, 1701, 1362, 1327, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_3S$ (M^++H): 382.0725, found: 382.0724.

*4.4.5. N-(2-Formyl-5-methoxyphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1e**).* Yield 15%; 0.0364 g; pale yellow liquid; R_f (50% EtOAc/*n*-hexane) 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (s, 1H), 7.80 (d, 1H, J=8.8 Hz), 7.58 (d, 2H, J=8.4 Hz), 7.29 (d, 2H, J=8.0 Hz), 6.98 (dd, 1H, J=2.4, 8.8 Hz), 6.46 (d, 1H, J=2.4 Hz), 4.45 (br s, 2H), 3.75 (s, 3H), 2.44 (s, 3H), 2.20 (t, 1H, J=2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.0, 164.1, 144.5, 142.9, 134.8, 130.5, 129.7, 129.1, 128.2, 114.9, 114.3, 74.8, 55.7, 41.9, 21.6; IR (neat): 3306, 1684 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S$ (M^++H): 344.0957, found: 344.0967.

*4.4.6. N-(4-Chloro-2-formylphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1f**).* Yield 20%; 0.0276 g; white solid; mp 90–92 °C; R_f (25% EtOAc/*n*-hexane) 0.50; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.29 (s, 1H), 7.96 (d, 1H, J=2.4 Hz), 7.52 (d, 2H, J=8.4 Hz), 7.46 (dd, 1H, J=2.7, 8.6 Hz), 7.31 (d, 2H, J=8.1 Hz), 6.88 (d, 1H, J=8.4 Hz), 4.44 (br s, 2H), 2.43 (s, 3H), 2.20 (t, 1H, J=2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.7, 144.9, 139.3, 137.2, 135.7, 134.2, 134.1, 129.9, 129.8, 128.5, 128.0, 76.6, 75.2, 41.6, 21.6; IR (neat): 3306, 1694, 1597, 1477, 1360, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{35}ClNO_3S$ (M^++H): 348.0461, found: 348.0455.

*4.4.7. N-(4-Bromo-2-formylphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1g**).* Yield 58%; 0.485 g; pale orange solid; mp 106–107 °C; R_f (25% EtOAc/*n*-hexane) 0.37; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.29 (s, 1H), 8.07 (d, 1H, J=2.3 Hz), 7.59 (dd, 1H, J=2.3, 8.5 Hz), 7.48 (d, 2H, J=8.2 Hz), 7.28 (d, 2H, J=8.1 Hz), 6.78 (d, 1H, J=8.5 Hz), 4.44 (br s, 2H), 2.42 (s, 3H), 2.22 (t, 1H, J=2.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.7, 144.9, 139.9, 137.2, 137.1, 134.0, 131.5, 130.0, 129.9, 128.0, 123.6, 76.6, 75.2, 41.6, 21.6; IR (neat): 3304, 1692, 1597, 1478, 1358, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{79}BrNO_3S$ (M^++H): 391.9956, found: 391.9974.

*4.4.8. N-(2-Formyl-4-methylphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1h**).* Yield 87%; 0.0541 g; yellow solid; mp 102–105 °C; R_f (25% EtOAc/*n*-hexane) 0.43; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.79 (s, 1H), 7.52 (d, 2H, J=8.2 Hz), 7.27 (d, 3H, J=7.6 Hz), 6.80 (d, 1H, J=8.1 Hz), 4.44 (br s, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.4, 144.4, 139.6, 138.5, 135.5, 135.0, 134.7, 129.7, 128.9, 128.4, 128.0, 74.7, 41.8, 21.6, 21.1; IR (neat): 3306, 1688, 1599, 1493, 1354, 1163 cm^{-1};

HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ (M^++H): 328.1007, found: 328.1010.

*4.4.9. N-(2-Formyl-4,5-dimethoxyphenyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (**1i**).* Yield 66%; 0.481 g; orange solid; mp 159–161 °C; R_f (50% EtOAc/*n*-hexane) 0.42; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.14 (s, 1H), 7.59 (d, 2H, *J*=8.1 Hz), 7.44 (s, 1H), 7.30 (d, 2H, *J*=7.8 Hz), 6.38 (s, 1H), 4.48 (br s, 2H), 3.95 (s, 3H), 3.65 (s, 3H), 2.44 (s, 3H), 2.25 (t, 1H, *J*=2.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.0, 153.6, 149.5, 144.5, 135.4, 134.9, 129.6, 129.4, 128.2, 111.1, 108.9, 76.7, 74.8, 56.2, 56.0, 42.1, 21.6; IR (neat): 3304, 1682, 1597, 1512, 1358, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NO_5S$ (M^++H): 374.1062, found: 374.1053.

*4.4.10. N-(2-Formyl-4,6-dimethylphenyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (**1j**).* Yield 79%; 0.510 g; pale orange solid; mp 120–122 °C; R_f (50% EtOAc/*n*-hexane) 0.80; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 1H), 7.60–7.56 (m, 3H), 7.30–7.26 (m, 3H), 4.79 (dd, 1H, *J*=2.5, 17.9 Hz), 4.18 (dd, 1H, *J*=2.4, 17.8 Hz), 2.41 (s, 3H), 2.35 (s, 3H), 2.25 (t, 1H, *J*=2.5 Hz), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 144.3, 139.6, 139.4, 138.0, 136.6, 136.5, 136.0, 130.0, 127.2, 127.1, 77.3, 74.8, 41.3, 21.6, 21.0, 17.7; IR (neat): 3304, 1686, 1597, 1354, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NO_3S$ (M^++H): 342.1164, found: 342.1149.

*4.4.11. N-(3-Formylnaphthalen-2-yl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1k**).* Yield 21%; 0.0871 g; orange solid; mp 117–120 °C; R_f (50% EtOAc/*n*-hexane) 0.63; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.50 (s, 1H), 8.55 (s, 1H), 8.04–8.01 (m, 1H), 7.72–7.69 (m, 1H), 7.64–7.59 (m, 2H), 7.56 (d, 2H, *J*=8.3 Hz), 7.43 (s, 1H), 7.30–7.28 (m, 2H), 4.50–4.62 (br m, 2H), 2.47 (s, 3H), 2.21 (t, 1H, *J*=2.42 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 144.5, 136.4, 135.5, 134.7, 132.7, 132.2, 131.1, 129.9, 129.7, 129.2, 128.8, 128.2, 128.0, 127.9, 77.2, 74.7, 42.1, 21.7; IR (neat): 3304, 1694, 1593, 1356, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}NO_3S$ (M^++H): 364.1007, found: 364.1027.

*4.4.12. N-(6-Formylbenzo[d][1,3]dioxol-5-yl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (**1l**).* Yield 68%; 0.303 g; brown solid; mp 113–114 °C; R_f (25% EtOAc/*n*-hexane) 0.26; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.08 (s, 1H), 7.59 (d, 2H, *J*=8.2 Hz), 7.38 (d, 1H, *J*=0.5 Hz), 7.30 (d, 2H, *J*=8.1 Hz), 6.41 (d, 1H, *J*=1.3 Hz), 6.07 (s, 2H), 4.31–4.54 (m, 2H), 2.45 (s, 3H), 2.22 (t, 1H, *J*=2.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.6, 152.4, 148.6, 144.6, 137.3, 134.8, 131.4, 129.8, 128.1, 108.7, 106.8, 102.7, 76.9, 75.0, 42.1, 21.6; IR (neat): 3302, 1689, 1597, 1481, 1356, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{16}NO_5S$ (M^++H): 358.0749, found: 358.0761.

*4.4.13. N-(2-Formyl-3-methylphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1m**).* Yield 71%; 0.348 g; white solid; mp 112–113 °C; R_f (33% EtOAc/*n*-hexane) 0.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.57 (s, 1H), 7.49 (d, 2H, *J*=8.4 Hz), 7.22–7.32 (m, 4H), 6.69 (d, 1H, *J*=8.0 Hz), 4.30–462 (br m, 2H), 2.59 (s, 3H), 2.40 (s, 3H), 2.19 (t, 1H, *J*=2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 144.5, 142.2, 141.7, 134.5, 134.2, 132.9, 132.7, 129.7, 128.1, 126.1, 76.9, 74.8, 42.0, 21.6, 21.3; IR (neat): 3306, 1695, 1597, 1466, 1354, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ (M^++H): 328.1007, found: 328.0996.

*4.4.14. N-(3-Chloro-2-formylphenyl)-4-methyl-N-(prop-2-yn-1-yl) benzenesulfonamide (**1n**).* Yield 46%; 0.0861 g; white solid; mp 104–106 °C; R_f (25% EtOAc/*n*-hexane) 0.26; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.36 (s, 1H), 7.57 (d, 2H, *J*=8.3 Hz), 7.50–7.48 (m, 1H), 7.39 (t, 1H, *J*=8.0 Hz), 7.29 (d, 2H, *J*=8.0 Hz), 7.01–6.99 (m, 1H), 4.51 (br s, 2H), 2.45 (s, 3H), 2.23 (t, 1H, *J*=2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.5, 144.4, 140.2, 135.8, 135.4, 134.0, 133.0, 131.8, 129.6, 129.2, 128.0, 77.4, 74.6, 41.8, 21.6; IR (neat): 3306, 1707, 1584, 1452, 1354, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{17}H^{35}_{15}ClNO_3S$ (M^++H): 348.0461, found: 348.0468.

*4.4.15. N-(But-2-yn-1-yl)-N-(2-formylphenyl)-4-methylbenzenesulfonamide (**1o**).* Yield 61%; 0.406 g; yellow solid; mp 129–130 °C; R_f (25% EtOAc/*n*-hexane) 0.31; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.38 (s, 1H), 8.03–7.99 (m, 1H), 7.55–7.46 (m, 4H), 7.30–7.27 (m, 2H), 6.97–6.94 (m, 1H), 4.42 (br s, 2H), 2.45 (s, 3H), 1.63 (t, 3H, *J*=2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.3, 144.3, 141.5, 136.1, 135.0, 134.2, 129.6, 129.0, 128.6, 128.3, 128.1, 83.0, 72.4, 42.5, 21.6, 3.3; IR (neat): 1694, 1597, 1483, 1352, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ (M^++H): 328.1007, found: 328.1006.

*4.4.16. N-(2-Formylphenyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl) benzenesulfonamide (**1p**).*[17] Yield 64%; 0.248 g; orange solid; mp 109–111 °C; R_f (25% EtOAc/*n*-hexane) 0.24; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.52 (s, 1H), 8.02 (dd, 1H, *J*=1.7, 7.4 Hz), 7.57 (d, 2H, *J*=8.1 Hz), 7.52–7.44 (m, 2H), 7.25–7.15 (m, 7H), 7.05 (d, 1H, *J*=7.2 Hz), 4.71 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.2, 114.5, 141.5, 136.0, 135.9, 135.4, 131.5, 129.8, 129.2, 128.8, 128.6, 128.4, 128.3, 128.1, 121.9, 86.5, 82.5, 42.8, 21.6.

*4.4.17. N-(2-Formylphenyl)-N-(prop-2-yn-1-yl)methanesulfonamide (**1q**).* Yield 83%; 0.407 g; white solid; mp 120–123 °C; R_f (50% EtOAc/*n*-hexane) 0.40; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.99 (d, 1H, *J*=7.6 Hz), 7.73–7.65 (m, 2H), 7.57–7.52 (m, 1H), 4.49 (br s, 2H), 3.07 (s, 3H), 2.48 (t, 1H, *J*=2.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.9, 141.2, 135.2, 134.9, 129.6, 129.6, 128.6, 77.9, 75.2, 41.6, 39.1; IR (neat): 3304, 2126, 1695, 1595, 1483, 1352, 1155 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}NO_3S$ (M^++H): 238.05379, found: 238.05480.

*4.4.18. N-(2-Formylphenyl)-4-nitro-N-(prop-2-yn-1-yl)benzenesulfonamide (**1r**).* Yield 62%; 0.189 g; yellow solid; mp 159–162 °C; R_f (50% EtOAc/*n*-hexane) 0.66; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1H), 8.34–8.31 (m, 2H), 8.04–8.02 (m, 1H), 7.88–7.85 (m, 2H), 7.59–7.52 (m, 2H), 7.03–7.01 (m, 1H), 4.56 (br s, 2H), 2.27 (t, 1H, *J*=2.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 150.5, 143.8, 139.8, 135.5, 134.6, 130.0, 129.8, 129.4, 129.0, 124.2, 76.6, 75.4, 42.2; IR (neat): 3304, 1697, 1595, 1533, 1481, 1366, 1350, 1171 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_5S$ (M^++H): 345.05536, found: 345.05452.

*4.4.19. 1-Tosyl-1H-benzo[b]azepin-3(2H)-one (**2a**).*[18] Yield 73%; 0.0682 g; pale yellow solid; mp 151–152 °C; R_f (25% EtOAc/*n*-hexane) 0.20; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 1H, *J*=6.4Hz), 7.47 (t, 1H, *J*=7.4 Hz), 7.40–7.31 (m, 4H), 7.14 (d, 2H, *J*=7.6 Hz), 6.73 (d, 1H, *J*=12.4 Hz), 5.73 (d, 1H, *J*=12.4 Hz), 4.85 (d, 1H, *J*=16.8 Hz), 3.94 (d, 1H, *J*=16.8 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 144.0, 140.6, 138.7, 137.0, 133.1, 132.4, 131.3, 130.3, 129.5, 129.3, 128.5, 127.1, 58.9, 21.6.

*4.4.20. 9-Methoxy-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2b**).* Yield 55%; 0.0578 g; yellow solid; mp 201–203 °C; R_f (50% EtOAc/*n*-hexane) 0.63; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, 2H, *J*=8.0 Hz), 7.36 (t, 1H, *J*=8.0 Hz), 7.29 (d, 2H, *J*=7.6 Hz), 7.05 (d, 1H, *J*=8.0 Hz), 6.99–6.93 (m, 2H), 5.94 (d, 1H, *J*=12.4 Hz), 4.63 (dd, 1H, *J*=1.2, 18.4 Hz), 3.97 (d, 1H, *J*=18.0 Hz), 3.85 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 156.7, 143.9, 140.5, 137.5, 135.4, 129.6, 129.5, 129.4, 128.0, 124.1, 114.4, 59.7, 55.9, 21.6; IR (neat): 1672, 1597, 1574, 1472, 1346, 1159 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S$ (M^++H): 344.0957, found: 344.0952.

*4.4.21. 9-Chloro-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2c**).* Yield 59%; 0.0409 g; yellow solid; mp 173–175 °C; R_f (25% EtOAc/*n*-hexane) 0.15; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56–7.63 (m, 3H), 7.37 (t, 1H, *J*=7.8 Hz), 7.27 (d, 3H, *J*=7.8 Hz), 6.79 (d, 1H, *J*=12.6 Hz), 5.76 (d, 1H, *J*=12.6 Hz), 4.78 (dd, 1H, *J*=1.2, 18.6 Hz), 4.05 (d, 1H,

J=18.6 Hz), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.8, 144.4, 139.0, 137.2, 136.5, 136.4, 136.3, 132.7, 130.7, 130.0, 129.7, 128.0, 59.7, 21.6; IR (neat): 1672, 1362, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{35}ClNO_3S$ (M^++H): 348.0461, found: 348.0464.

*4.4.22. 1-Tosyl-8-(trifluoromethyl)-1H-benzo[b]azepin-3(2H)-one (**2d**).* Yield 56%; 0.0212 g; yellow liquid; R_f (25% EtOAc/*n*-hexane) 0.29; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.63 (d, 1H, J=8.1 Hz), 7.46 (d, 1H, J=8.1 Hz), 7.40 (d, 2H, J=8.3 Hz), 7.19 (d, 2H, J=8.2 Hz), 6.79 (d, 1H, J=12.6 Hz), 5.87 (d, 1H, J=12.5 Hz), 4.87 (br s, 1H), 3.99 (br s, 1H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.7, 144.5, 139.3, 138.7, 137.0, 135.3, 133.3, 133.0, 132.6, 131.3, 129.8, 127.5 (1C, d, $J_{C,F}$=3.7 Hz), 127.2, 125.0 (1C, d, $J_{C,F}$=3.7 Hz), 58.8, 21.6; IR (neat): 1674, 1616, 1339, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{15}F_3NO_3S$ (M^++H): 382.0725, found: 382.0727.

*4.4.23. 8-Methoxy-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2e**).* Yield 80%; 0.0283 g; yellow solid; mp 109–112 °C; R_f (50% EtOAc/*n*-hexane) 0.34; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 2H, J=8.0 Hz), 7.25–7.28 (m, 1H), 7.16 (d, 2H, J=8.4 Hz), 6.94 (dd, 1H, J=2.4, 8.4 Hz), 6.70 (d, 2H, J=12.4 Hz), 5.65 (d, 1H, J=12.4 Hz), 4.86 (d, 1H, J=17.2 Hz), 3.95 (d, 1H, J=23.2 Hz), 3.92 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 161.6, 144.0, 140.7, 140.3, 136.9, 134.6, 129.5, 127.2, 127.0, 125.2, 115.0, 114.8, 58.7, 55.8, 21.6; IR (neat): 1663, 1605, 1558, 1506, 1356, 1341, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_4S$ (M^++H): 344.0957, found: 344.0951.

*4.4.24. 7-Chloro-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2f**).* Yield 71%; 0.0249 g; yellow solid; mp 133–135 °C; R_f (25% EtOAc/*n*-hexane) 0.52; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, 1H, J=8.7 Hz), 7.44 (dd, 1H, J=2.4, 8.4 Hz), 7.37 (d, 2H, J=8.4 Hz), 7.31 (d, 1H, J=2.4 Hz), 7.18 (d, 2H, J=8.1 Hz), 6.63 (d, 1H, J=12.6 Hz), 5.77 (d, 1H, J=12.3 Hz), 4.88 (d, 1H, J=17.1 Hz), 3.93 (d, 1H, J=17.1 Hz), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.9, 144.3, 138.8, 137.2, 136.8, 134.2, 133.7, 132.3, 131.8, 131.1, 130.6, 129.7, 127.2, 58.9, 21.6; IR (neat): 1672, 1597, 1483, 1358, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{35}ClNO_3S$ (M^++H): 348.0461, found: 348.0462.

*4.4.25. 7-Bromo-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2g**).* Yield 60%; 0.0472 g; orange solid; mp 149–152 °C; R_f (25% EtOAc/*n*-hexane) 0.43; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, 2H, J=1.2 Hz), 7.46 (s, 1H), 7.36 (d, 2H, J=8.3 Hz), 7.17 (d, 2H, J=8.1 Hz), 6.62 (d, 1H, J=12.6 Hz), 5.76 (d, 1H, J=12.5 Hz), 4.86 (d, 1H, J=16.6 Hz), 3.92 (d, 1H, J=17.3 Hz), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 144.3, 138.7, 137.7, 136.8, 135.3, 134.1, 134.0, 132.0, 130.5, 129.7, 127.1, 122.1, 58.8, 21.6; IR (neat): 1676, 1481, 1356, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{79}BrNO_3S$ (M^++H): 391.9956, found: 391.9942.

*4.4.26. 7-Methyl-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2h**).* Yield 58%; 0.0190 g; orange solid; mp 138–140 °C; R_f (50% EtOAc/*n*-hexane) 0.41; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, 1H, J=8.1 Hz), 7.36 (d, 2H, J=8.2 Hz), 7.29 (s, 1H), 7.14 (t, 3H, J=7.9 Hz), 6.67 (d, 1H, J=12.5 Hz), 5.71 (d, 1H, J=12.5 Hz), 4.86 (d, 1H, J=17.3 Hz), 3.93 (d, 1H, J=17.0 Hz), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.6, 143.9, 140.7, 138.5, 137.1, 136.2, 133.4, 132.2, 132.1, 130.2, 129.5, 129.3, 127.2, 59.1, 21.6, 20.9; IR (neat): 1670, 1497, 1354, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ (M^++H): 328.1007, found: 328.1008.

*4.4.27. 7,8-Dimethoxy-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2i**).* Yield 67%; 0.0503 g; yellow solid; mp 157–159 °C; R_f (50% EtOAc/*n*-hexane) 0.44; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, 2H, J=8.40 Hz), 7.20 (s, 1H), 7.12 (d, 2H, J=8.1 Hz), 6.69 (s, 1H), 6.58 (d, 1H, J=12.3 Hz), 5.59 (d, 1H, J=12.6 Hz), 4.83 (br d, 1H, J=17.1 Hz), 3.95 (s, 3H), 3.91 (obscured d, 1H), 3.87 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.3, 154.1, 151.9, 147.2, 143.7, 140.1, 136.2, 132.7, 131.1, 130.4, 128.4, 117.5, 116.3, 62.4, 59.7, 59.4, 24.8; IR (neat): 1665, 1603, 1518, 1354, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NO_5S$ (M^++H): 374.1062, found: 374.1048.

*4.4.28. 7,9-Dimethyl-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2j**).* Yield 87%; 0.0897 g; brown liquid; R_f (50% EtOAc/*n*-hexane) 0.74; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, 2H, J=8.2 Hz), 7.18 (d, 3H, J=8.1 Hz), 6.92 (s, 1H), 6.53 (d, 1H, J=12.6 Hz), 5.43 (d, 1H, J=12.5 Hz), 4.84 (dd, 1H, J=1.4, 18.4 Hz), 3.94 (d, 1H, J=18.4 Hz), 2.49 (s, 3H), 2.38 (s, 3H), 2.32 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 144.0, 140.6, 139.9, 138.7, 137.5, 134.9, 134.8, 133.9, 130.9, 129.6, 128.5, 127.7, 60.0, 21.6, 20.8, 19.5; IR (neat): 1661, 1597, 1354, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NO_3S$ (M^++H): 342.1164, found: 342.1167.

*4.4.29. 1-Tosyl-1H-naphtho[2,3-b]azepin-3(2H)-one (**2k**).* Yield 65%; 0.0481 g; yellow solid; mp 187–190 °C; R_f (50% EtOAc/*n*-hexane) 0.80; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.91 (d, 1H, J=7.9 Hz), 7.87–7.84 (m, 2H), 7.63–7.55 (m, 2H), 7.35 (d, 2H, J=8.2 Hz), 7.14 (d, 2H, J=8.0 Hz), 6.89 (d, 1H, J=12.5 Hz), 5.74 (d, 1H, J=12.5 Hz), 4.96 (d, 1H, J=17.6 Hz), 4.03 (d, 1H, J=17.7 Hz), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 143.9, 140.8, 137.1, 134.8, 134.1, 134.0, 132.3, 131.0, 129.6, 128.5, 128.5, 128.3, 128.2, 127.7, 127.3, 59.0, 21.6; IR (neat): 1668, 1358, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}NO_3S$ (M^++H): 364.1007, found: 364.1000.

*4.4.30. 5-Tosyl-5H-[1,3]dioxolo[4′,5′:4,5]benzo[1,2-b]azepin-7(6H)-one (**2l**).* Yield 63%; 0.0453 g; yellow solid; mp 198–200 °C; R_f (25% EtOAc/*n*-hexane) 0.11; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, 2H, J=8.3 Hz), 7.17 (s, 2H), 7.15 (s, 1H), 6.70 (s, 1H), 6.54 (d, 1H, J=12.5 Hz), 6.09 (d, 2H, J=11.1 Hz), 5.62 (dd, 1H, J=0.9, 12.5 Hz), 4.83 (d, 1H, J=1.3, 17.6 Hz), 3.92 (d, 1H, J=17.6 Hz), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 149.6, 147.7, 144.0, 140.1, 136.9, 134.2, 129.5, 128.1, 127.2, 126.8, 110.9, 110.9, 102.6, 59.1, 21.6; IR (neat): 1668, 1591, 1487, 1342, 1157 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{16}NO_5S$ (M^++H): 358.0749, found: 358.0749.

*4.4.31. 6-Methyl-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2m**).* Yield 60%; 0.0608 g; yellow solid; mp 153–155 °C; R_f (33% EtOAc/*n*-hexane) 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.46 (m, 3H), 7.31 (t, 1H, J=7.6 Hz), 7.22 (d, 1H, J=7.6 Hz), 7.18 (d, 2H, J=8.0 Hz), 6.93 (d, 1H, J=12.8 Hz), 5.78 (dd, 1H, J=1.2, 12.8 Hz), 4.83 (dd, 1H, J=1.6, 18.0 Hz), 3.95 (d, 1H, J=18.0 Hz), 2.38 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 143.9, 139.6, 139.3, 137.6, 136.6, 131.6, 130.7, 130.6, 129.6, 129.3, 127.7, 127.1, 60.1, 21.6, 20.8; IR (neat): 1676, 1595, 1470, 1356, 1163 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ (M^++H): 328.1007, found: 328.0997.

*4.4.32. 6-Chloro-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2n**).* Yield 35%; 0.0120 g; yellow solid; mp 118–120 °C; R_f (25% EtOAc/*n*-hexane) 0.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, 1H, J=8.0 Hz), 7.49–7.36 (m, 4H), 7.22–7.17 (m, 3H), 5.84 (d, 1H, J=12.8 Hz), 4.87 (dd, 1H, J=1.2, 18.0 Hz), 3.99 (d, 1H, J=18.0 Hz), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 144.3, 140.5, 137.3, 136.1, 135.2, 131.1, 130.8, 130.5, 129.9, 129.8, 128.8, 127.1, 59.8, 21.6; IR (neat): 1676, 1456, 1356, 1165 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{15}^{35}ClNO_3S$ (M^++H): 348.0461, found: 348.0474.

*4.4.33. 4-Methyl-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2o**).* Yield 76%; 0.0515 g; pale yellow solid; mp 123–125 °C; R_f (25% EtOAc/*n*-hexane) 0.19; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 1H, J=8.0 Hz), 7.43 (dt, 1H, J=1.5, 7.8 Hz), 7.27 (dt, 1H, J=1.1, 7.5 Hz), 7.21 (d, 2H, J=8.4 Hz), 7.16 (dd, 1H, J=1.2, 7.6 Hz), 7.05 (d, 2H, J=8.0 Hz), 6.80 (s, 1H), 4.63 (s, 2H), 2.33 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 143.7, 136.6, 135.9, 133.6, 133.3, 130.9, 129.1, 128.8, 128.0, 127.5, 127.0, 127.0, 43.3, 24.8, 21.5; IR (neat): 1663, 1628, 1599,

1356, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO_3S$ (M^++H): 328.1007, found: 328.1001.

*4.4.34. 4-Phenyl-1-tosyl-1H-benzo[b]azepin-3(2H)-one (**2p**).* Yield 38%; 0.0267 g; brown solid; mp 118–121 °C; R_f (25% EtOAc/*n*-hexane) 0.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, 1H, *J*=8.1 Hz), 7.54 (t, 1H, *J*=7.5 Hz), 7.49–7.45 (m, 1H), 7.39 (d, 2H, *J*=7.7 Hz), 7.34 (d, 2H, *J*=8.2 Hz), 7.30–7.23 (m, 4H), 7.10 (d, 3H, *J*=8.1 Hz), 6.66 (s, 1H), 4.84 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 143.7, 137.0, 136.5, 136.4, 132.3, 132.0, 131.1, 129.5, 129.0, 128.9, 128.3, 128.0, 127.5, 127.1, 127.0, 44.7, 21.5; IR (neat): 1626, 1597, 1447, 1350, 1167 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{20}NO_3S$ (M^++H): 390.1164, found: 390.1161.

*4.4.35. 1-(Methylsulfonyl)-1H-benzo[b]azepin-3(2H)-one (**2q**).* Yield 77%; 0.0726 g; pale yellow solid; mp 122–125 °C; R_f (50% EtOAc/*n*-hexane) 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.64 (m, 1H), 7.52–7.42 (m, 3H), 7.30 (d, 1H, *J*=12.5 Hz), 6.39 (d, 1H, *J*=12.5 Hz), 4.78 (d, 1H, *J*=14.5 Hz), 3.96 (d, 1H, *J*=14.5 Hz), 2.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 141.8, 138.7, 133.4, 132.3, 131.6, 129.8, 129.4, 128.6, 58.6, 41.0; IR (neat): 1670, 1611, 1487, 1352, 1157 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}NO_3S$ (M^++H): 238.05444, found: 238.05379.

*4.4.36. 1-((4-Nitrophenyl)sulfonyl)-1H-benzo[b]azepin-3(2H)-one (**2r**).* Yield 75%; 0.0517 g; pale yellow solid; mp 169–172 °C; R_f (50% EtOAc/*n*-hexane) 0.54; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, 2H, *J*=8.8 Hz), 7.73 (d, 1H, *J*=7.9 Hz), 7.61 (d, 2H, *J*=8.8 Hz), 7.56–7.52 (m, 1H), 7.46 (dt, 1H, *J*=0.9, 7.5 Hz), 7.37–7.35 (m, 1H), 6.74 (d, 1H, *J*=12.5 Hz), 5.72 (d, 1H, *J*=12.5 Hz), 4.90 (d, 1H, *J*=17.4 Hz), 4.02 (d, 1H, *J*=17.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.0, 150.2, 145.1, 140.6, 137.7, 133.4, 132.0, 131.8, 130.3, 129.5, 129.2, 128.3, 124.1, 58.9; IR (neat): 1670, 1609, 1533, 1487, 1368, 1348, 1171 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_5S$ (M^++H): 345.05469, found: 345.05452.

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Supplementary data

^{1}H and ^{13}C NMR spectra for all starting materials and products. This material is available free of charge via the internet at http://www.sciencedirect.com. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.069.

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12. CCDC 906092 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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