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Palladium-Catalyzed Oxidative Annulation of *ortho*-Alkenylanilines and Allenes: an Access to Benzo[*b*]azepines

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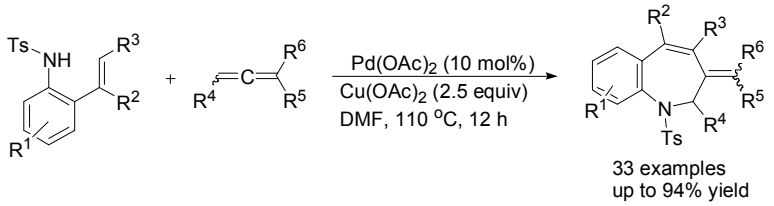
Abstract



Palladium-catalyzed oxidative annulation of *ortho*-alkenyllanilines and allenes to constitute valuable but synthetically challenging benzo[*b*]azepines has been developed. The procedure, involving of the cleavage of the terminal C(sp^2)-H bond of the vinyl moiety and the participation of allenes as two-carbon cycloaddition partner, is attractive in terms of assembly efficiency and environmentally friendliness. The transformation features mild reaction conditions and good functional group tolerance, resulting in a variety of benzo[*b*]azepines in good to excellent yields.

Introduction

Benzoazepines represent an important class of structural motifs embedded in a wide variety of bioactive natural products and pharmaceuticals. For instance, the benzoazepine nucleus constitutes the core structural skeleton of the marketed tricyclic antidepressant drugs, such as Tienopramine, Anafranil, Amezepine, Imipramine, Carbamazepine and Oxcarbazepine.[1,2] Lotensin, containing the benzoazepine nucleus as the key subunit, is marketed to treat high blood pressure, congestive heart failure and chronic renal failure.[3] Mozavaptan, possessing the benzoazepine skeleton, was identified as effective vasopressin V-2 receptor antagonist.[4] Despite their appealing biological activities, benzo[*b*]azepine derivatives has drawn little synthetic attention, contrasted to the benzo[*c*]azepine or benzo[*d*]azepine analogues. The methodologies reported include Pd-catalyzed intramolecular Heck coupling[5], Ir-[6] and Rh[7]-catalyzed asymmetric allylic amination, phosphine-promoted cyclization of Morita–Baylis–Hillman adducts,[8] Cu-catalyzed insertion of diazocarbonyl compounds to quinolinium salts,[9] $FeCl_3$- and Au-catalyzed cyclization of the alkynyl and double bond, such as C=C and C=O bond, tethered respectively on the N and *ortho*-carbon atom of an aniline-linker[10], and Pd- and Au-catalyzed ring-expansion of alkylidenecyclopropane[11] and isoxazolidine[12]. Hence, exploring new practical and efficient access to benzo[*b*]azepines is still a highly desirable goal.

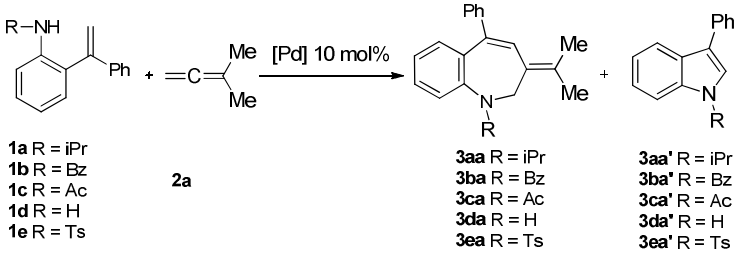
Recently, Transition-metal-catalyzed direct functionalization of relatively unreactive C-H bond are emerging as a powerful and benign tool in generating

heterocycles, especially nitrogen- and oxygen-containing heterocycles, from readily available starting materials.[13] In this context, annulation of *o*-vinylphenols and *o*-vinylanilines employing alkynes, allenes, carbon monoxide, and carbon dioxide as cycloaddition partners provides an appealing alternative approach to synthesizing coumarin[14], chromene[15], benzoxepine[16], quinolinone[17] and spirocylic[18] derivatives. Very recently, we reported the annulation of *o*-vinylanilines using isocyanides as cycloaddition partner to access *o*-aminoquinolines[19]. We herein disclose a Pd(II)-catalyzed oxidative annulation of *o*-vinylanilines involving allenes under simple and mild conditions to construct valuable benzo[*b*]azepines.

Results and Discussion

Initially, **1a** and 3-methylbuta-1,2-diene (**2a**) were subjected to a set of conditions commonly used for oxidative couplings, $Pd(OAc)_2/Cu(OAc)_2$ in acetonitrile at 110 ^{o}C. Unfortunately, no reaction was observed with either **1a**, **1b** (*N*-Bz), **1c** (*N*-Ac) or unprotected aniline **1d**, under these conditions. (Table1, entries 1-4). Next, we turned our attention to utilize tosyl as protecting group, and were delighted to obtain the anticipated azepine **3ea** in 50% isolated yield (Table1, entry 5). The structure of **3ea** was determined by NOESY spectra and X-ray diffraction analysis (see supporting information). The performance of this transformation depended significantly on the nature of the solvent, and the optimal DMF provided azepine **3ea** in 93% yield (Table1, entries 5-10). The choice of oxidant had a dramatic impact on chemoselectivity of this reaction. The use of copper acetate favors the formation of azepine product, while the use of silver salts, such as Ag_2CO_3 and AgOAc is prone to give indole **3ea'** as the main product. The use of different two organic oxidants, $PhI(OAc)_2$ and BQ, resulted in inferior yields and selectivity. Other palladium precursors, such as $PdCl_2$ and $Pd(OTf)_2$ hampered the reaction efficiency (Table 1 entries 11 and 12). The attempt to use O_2 as oxidant failed (Table 1, entry 17).

Table 1. Optimization of Reaction Conditions[a]



entry	**1**	oxidant	solvent	yield (%)[b] **3/3'**
1	**1a**	$Cu(OAc)_2·H_2O$	CH_3CN	--/--
2	**1b**	$Cu(OAc)_2·H_2O$	CH_3CN	--/--
3	**1c**	$Cu(OAc)_2·H_2O$	CH_3CN	--/--
4	**1d**	$Cu(OAc)_2·H_2O$	CH_3CN	--/--

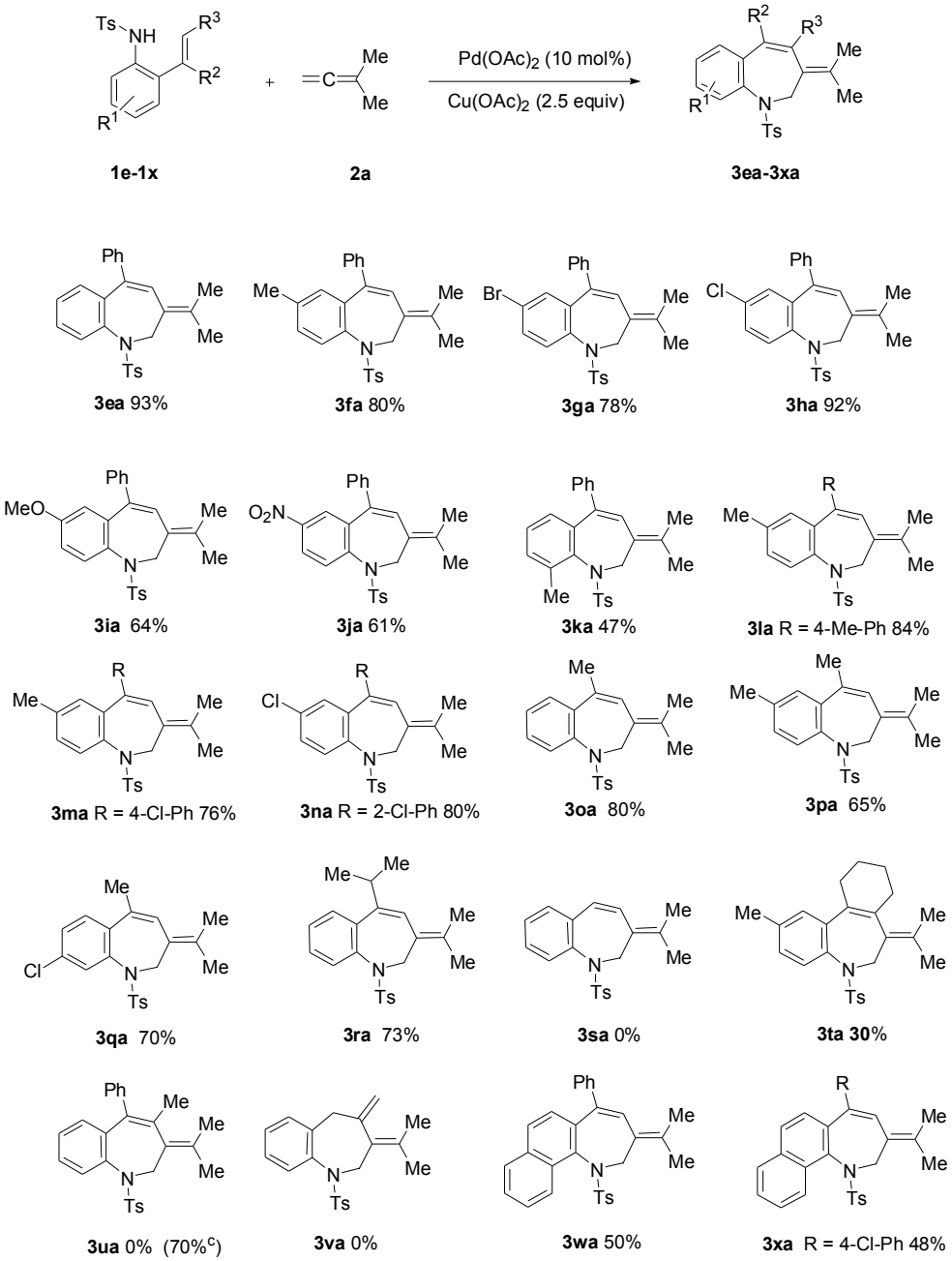
5	**1e**	$Cu(OAc)_2·H_2O$	CH_3CN	50/--
6	**1e**	$Cu(OAc)_2·H_2O$	THF	11/--
7	**1e**	$Cu(OAc)_2·H_2O$	dioxane	18/10
8	**1e**	$Cu(OAc)_2·H_2O$	PhMe	trace/--
9[c]	**1e**	$Cu(OAc)_2·H_2O$	DCE	--/--
10	**1e**	$Cu(OAc)_2·H_2O$	DMF	93/--
11[d]	**1e**	$Cu(OAc)_2·H_2O$	DMF	56/trace
12[e]	**1e**	$Cu(OAc)_2·H_2O$	DMF	65/trace
13	**1e**	Ag_2CO_3	DMF	9/70
14	**1e**	AgOAc	DMF	25/67
15	**1e**	$PhI(OAc)_2$	DMF	--/37
16	**1e**	BQ	DMF	--/trace
17[f]	**1e**	$Cu(OAc)_2·H_2O$ $+O_2$	DMF	37/18

[a] All reactions were carried with 0.3 mmol **1**, 0.6 mmol of **2a**, 10 mol% of $Pd(OAc)_2$, 2.5 equiv of [Cu^{2+}], [Ag^+], $PhI(OAc)_2$, or BQ, 5 mL of solvent, sealed flask, 110 ^oC, 12 h. [b] isolated yield. [c] DCE = dichloroethane, [d] $PdCl_2$, [e] $Pd(OTf)_2$, [f] 1.0 equiv of [Cu^{2+}] and 1.0 atm of O_2.

With the optimized reaction conditions in hand, the generality and efficiency of this reaction were tested by the reaction of 3-methylbuta-1,2-diene with a range of *ortho*-vinylanilinic substrates. The results are summarized in Scheme 1. Both electron-donating and -withdrawing substituents *para* to nitrogen on the aniline moiety were well tolerated, e.g. methoxy, methyl, chloro, and bromo (**1f-1i**). Even the *para*-nitro product was obtained in a moderate yield of 61% (**1j**). The tolerance of halogen is especially interesting, since the carbon-halogen bond is susceptible of further structural elaboration. Introduction of a methyl group *ortho* to nitrogen lowered the yield of product **3ka**, likely due to steric crowding. The properties of R^2 affects the efficiency of this transformation. When R^2 were *p*-Me-phenyl, *p*-Cl-phenyl, and *o*-Cl-phenyl, the corresponding products **3la**, **3ma**, and **3na** were obtained in 84%, 76%, and 80% yields, respectively, demonstrating that the substituents on the phenyl group have no major effect on this reaction. Yields were slightly depressed when R^2 was a methyl or i-propyl, rather than an aromatic group (**3oa-3ra**). The substrate with unsubstituted vinyl group produced a complicated mixture, perhaps due to the vulnerability of C=C double bond at elevated temperatures. Gratifyingly, the substrate **1t** with endocyclic C=C bond gave the desire products **3ta** in acceptable yield. However, the substrate **1u** with a methyl group on the other side of the C=C bond (*E*/*Z* = 1:1) gave the indole product **3ua'** in 72% yield. Steric hindrance from the

methyl group may have deterred insertion of allene into the Pd-C bond of palladacycle (Scheme 3, **8**). It is noteworthy that *N*-tosyl-2-(2-propen-1-yl)aniline (**1v**) did not take part in the annulation, indicating that the conjugation of the vinyl group to the aryl moiety plays a crucial role in this transformation. This catalytic system is applicable to the *ortho*-vinylnaphthalen-1-amine derivatives. The substrates **1w** and **1x** offered the corresponding products **3wa** and **3xa** both in moderate yields (50% and 48%).

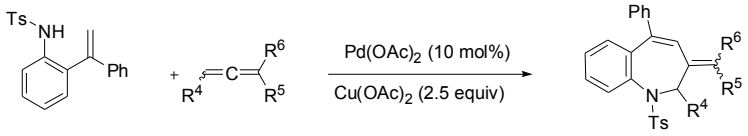
Scheme 1. Annulation of *ortho*-Vinylanilines with 3-Methylbuta-1,2-diene[a,b]



[a] All reactions were carried with 0.3 mmol **1**, 0.6 mmol of **2a**, 10 mol% of $Pd(OAc)_2$, 2.5 equiv of $Cu(OAc)_2$, 5 mL of DMF, sealed flask, 110 ^oC, 12 h. [b] isolated yield. [c] yield of the corresponding indole

The scope of allenes was next investigated by the reaction of *N*-tosyl-2-(1-phenyl-vinyl)aniline (**1e**) with an array of allenes **2** (Table 2). The symmetrically 3,3-disubstituted propa-1,2-dienes **2a-2d** provided the corresponding products **3ea**-**3ed** in excellent yields. The mono-substituted 3-arylpropa-1,2-dienes **2e-2g** led to the anticipated products **3ee**-**3eg** in good yields, and the *E*:*Z* ratios of the newly formed double bond with phenyl, *p*-tolyl and *p*-Cl-phenyl are 9:1, 20:1 and 8:1, respectively (determined by NMR and X-ray diffraction analysis, see supporting information). The unsymmetrically 3,3-disubstituted propa-1,2-diene **2h** are also superior annulation partner, giving the anticipated product **3eh** in 90% yield (studied by NMR and X-ray diffraction analysis, see supporting information). The allene **2j** containing an ester group worked well, yet the allenes **2i** did not provided the product maybe because the vulnerability of the terminal C=C=C moiety with electron-withdrawing group at elevated temperatures. Substrates **2k** and **2l** with Bn group failed too, indicating this transformation is no compatible with Bn group on the allene moiety. The alkyl substituted allene **2m** furnished the product **3em** in 81% yield**.**

Table 2. Annulation of Allenes with *N*-tosyl-2-(1-phenyl-vinyl)aniline[a]



1e **2** **3**

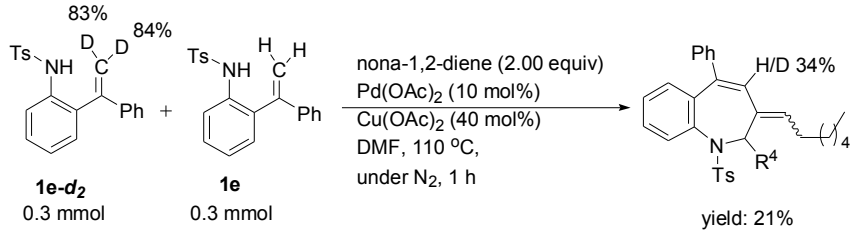
entry	**2**	R_4	R_5	R_6	**3**	yield (%)[b] (*E*/*Z*)
1	**2a**	H	Me	Me	**3ea**	93
2	**2b**	H	n-amyl	n-amyl	**3eb**	94
3	**2c**	H	Ph	Ph	**3ec**	86
4	**2d**	H	p-tolyl	p-tolyl	**3ed**	88
5	**2e**	H	H	Ph	**3ee**	74 (9/1)
6	**2f**	H	H	p-tolyl	**3ef**	81 (20/1)
7	**2g**	H	H	p-Cl-Ph	**3eg**	82 (8/1)
8	**2h**	H	Me	Ph	**3eh**	90 (6/4)
9	**2i**	H	H	CO_2Et	**3ei**	0
10	**2j**	Me	H	CO_2Et	**3ej**	91 (8/1)
11	**2k**	Bn	H	CO_2Et	**3ek**	0

12	**2l**	H	H	Bn	**3el**	--[c]
13	**2m**	H	H	*n*-hep	**3em**	81 (1:1)

[a] All reactions were carried with 0.3 mmol **1e**, 0.6 mmol of **2**, 10 mol% of $Pd(OAc)_2$, 2.5 equiv of $Cu(OAc)_2$, 5 mL of DMF, sealed flask, 110 ^oC, 12 h. [b] isolated yield. [c] complicated mixture

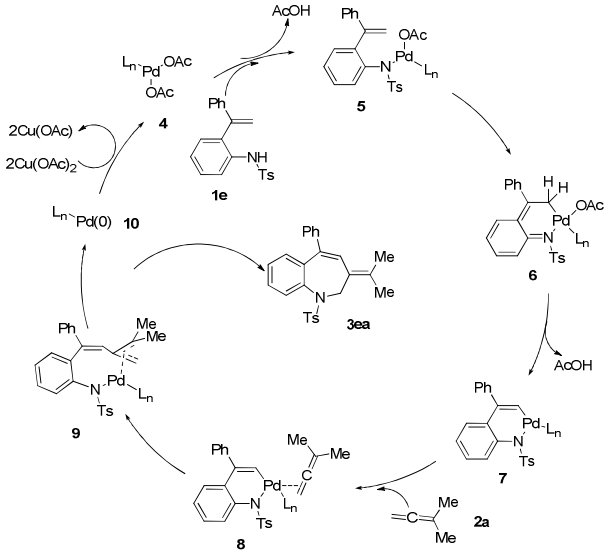
There are two possible pathways for the activation of the C(sp^2)-H bond to form the intermediate palladacycle **7** (Scheme 3): (i) direct C-H bond activation (concerted metalation-deprotonation pathway, CMD); (ii) intramolecular nucleophilic attack of the alkene on the electrophilic palladium(II), followed by a base-assisted deprotonation process, which is a de- and re-aromatization process of the aniline. The *E*/*Z* isomers of 2-(1-phenylprop-1-en-1-yl)aniline (Scheme 1, **1u**) gave the annulated product indole in 72% isolated yield (higher than 50%), revealing that the activation of the C(sp^2)-H bond with the *E*/*Z* ratio being 1:1 happened smoothly under the standard conditions and the pathway (ii) is more favorable. When the vinyl group is not conjugated with the aromatic ring of aniline (Scheme 1, **1v**), the annulation did not occur, which also strongly support the pathway (ii). To gain further mechanistic insight for the reaction, the kinetic isotope effect (KIE) study was carried out using **1e** and its dideuterated derivative (**1e-d_2**, 83% deuterated) via competition experiment (Scheme 2).[20] The KIE value is 1.4, suggesting that C–H bond cleavage has influence in the reaction rate, but is probably not the turnover-determining step.[16b,c] While Pathway (i) cannot be fully eliminated, Pathway (ii) is more feasible.

Scheme 2. Competition Experiment



Based on the preliminary data, a possible mechanism of the formation of benzoazepines **3** is depicted in Scheme 3 with **1e** and **2a** as the model substrates. Initially, addition of the nitrogen atom of aniline **1e** to Pd(II) species **4** furnishes palladium complex **5,** with elimination of acetic acid. Intramolecular nucleophilic attack of the alkene on the electrophilic palladium(II), and then followed by a base-assisted deprotonation results in the intermediate palladacycle **7**. Allene **2a** coordinates to the palladium center of **7**, and then inserts into Pd-C bond engendering a π-allylic palladacycle **9**. Reductive elimination produces product **3ea**, along with palladium(0) species **10**, which then be re-oxidized by $Cu(OAc)_2$ to the palladium(II) species **4**.

Scheme 3. Possible Mechanism for Annulation of *ortho*-Alkenylanilines and Allenes



In summary, a new strategy for the preparation of synthetically challenging but highly valuable benzo[*b*]azepine derivatives has been developed based on the palladium-catalyzed annulation of 2-alkenyllanilines and allenes. This procedure, involving the cleavage of the C-H and N-H bonds of 2-alkenylanilines, represents a straightforward, efficient and benign approach to benzo[*b*]azepine derivatives. To our knowledge, it is the first oxidative coupling of anilines and alkenes employing allenes as a two-carbon linker, and we thereupon believe it is a useful addition to the growing synthetic arsenal of chemists to generate nitrogen-containing compounds.

EXPERIMENTAL SECTION

General information.

Unless otherwise noted, all the materials were purchased from commercial suppliers and used as received. Solvents were freshly distilled by standard procedures prior to use. All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker 400 MHz spectrometer. The NMR chemical shift values refer to $CDCl_3$ (δ (^{1}H), 7.26 ppm; δ (^{13}C), 77.16 ppm). Mass spectra were obtained on a micrOTOF-Q II mass spectrometer. Crystals were collected on a Bruker SMART APEX II CCD (Mo- Kα radiation, λ = 0.71073 Å). Allenes were prepared by literature methods[21].

General procedure for the preparation of new 2-vinyl-N-tosylanilines.

The corresponding 2-vinylaniline (5.00 mmol) was dissolved in dry pyridine (25 mL), and the solution was treated with 4-toluenesulfonyl chloride (5.50 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h, then poured into water and extracted with CH_2Cl_2. The combined organic layers were dried over Mg_2SO_4, filtered, and concentrated in vacuum. The reaction mixture was purified directly by flash chromatography, using a mixture of petroleum ether and ethyl acetate (v/v = 15:1) as eluent. Characterization data for new compounds are given below.

4-Methyl-2-(1-Phenylvinyl)-*N*-tosylbenzenamine (1f). 1.76 g, 97%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.32-7.26 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.16-7.06 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 6.40 (s, 1H), 5.62 (s, 1H), 4.80 (s, 1H), 2.36 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 143.7, 138.8, 136.1, 134.8, 133.5, 131.6, 131.0, 129.6, 129.5, 128.9, 128.6, 127.3, 126.4, 121.9, 116.9, 21.6, 20.9; HRMS (ESI): m/z calcd for $C_{22}H_{21}NO_2S$ $(M-H)^-$: 362.1220, found: 362.1221.

4-Bromo-2-(1-Phenylvinyl)-*N*-tosylbenzenamine (1g). 1.39 g, 65%, yellow solid, m.p. = 94.6-95.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.48-7.37 (m, 3H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.46 (s, 1H), 5.70 (s, 1H), 4.88 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.1, 143.8, 138.0, 135.7, 135.0, 133.5, 133.1, 131.9, 129.7, 129.0, 128.9, 127.3, 126.4, 122.8, 118.0, 21.7; HRMS (ESI): m/z calcd for $C_{21}H_{18}BrNO_2S$ $(M-H)^-$: 426.0169, found: 426.0176.

4-Methoxy-2-(1-Phenylvinyl)-*N*-tosylbenzenamine (1i). 1.84 g, 97%, Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.32-7.19 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 4.0 Hz, 2H), 6.89 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.62 (s, 1H), 6.15 (s, 1H), 5.51 (s, 1H), 4.69 (s, 1H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 145.1, 143.6, 138.5, 136.2, 129.5, 129.0, 128.7, 127.4, 127.0, 126.4, 125.2, 116.9, 115.9, 114.0, 55.6, 21.7; HRMS (ESI): m/z calcd for $C_{22}H_{21}NO_3S$ $(M-H)^-$: 378.1169, found: 378.1179.

4-Nitro-2-(1-phenylvinyl)-*N*-tosylbenzenamine (1j). 1.93 g, 98%,yellow solid, m.p. = 115.1-116.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 8.0, 2.4 Hz, 1H), 8.05 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.35-7.29 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.99 (s, 1H), 5.99 (s, 1H), 5.24 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 143.7, 143.3, 140.5, 137.4, 135.4, 132.2, 130.0, 129.4, 129.3, 127.4, 126.4, 126.1, 124.7, 119.3, 118.5, 21.7; HRMS (ESI): m/z calcd for $C_{21}H_{18}N_2O_4S$ $(M+Na)^+$: 417.0879, found: 417.0863.

6-Methyl-2-(1-Phenylvinyl)-*N*-tosylbenzenamine (1k). 1.06 g, 64%, white solid, m.p. = 121.0-122.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.36-7.26 (m, 4H), 7.25-7.17 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97-6.85 (m, 2H), 5.49 (s, 1H), 5.05 (s, 1H), 4.61 (s, 1H), 2.49 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.1, 143.6, 140.4, 139.6, 139.3, 137.4, 132.0, 131.6, 129.3, 129.1, 129.0, 128.6, 127.9, 127.7, 126.1, 117.0, 21.7, 19.8; HRMS (ESI): m/z calcd for $C_{22}H_{21}NO_2S$ $(M-H)^-$: 362.1220, found: 362.1227.

4-Methyl-2-(1-*p*-tolylvinyl)-*N*-tosylbenzenamine (1l). 1.17 g, 62%, yellow solid, m.p. = 78.3-79.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97-6.86 (m, 3H), 6.44 (s, 1H), 5.58 (s, 1H), 4.75 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 143.6, 138.4, 136.0, 135.9, 134.7, 133.7, 131.5, 130.9, 129.5, 129.4, 129.4, 127.2, 126.2, 121.9, 115. 9, 21.5, 21.2, 20.8; HRMS (ESI): m/z calcd for $C_{23}H_{23}NO_2S$ $(M-H)^-$: 376.1377, found: 376.1383.

2-(1-(4-Chlorophenyl)vinyl)-4-methyl-*N*-tosylbenzenamine (1m). 1.59 g, 80%, yellow solid, m.p. = 108.3-109.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz,

1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.22-7.00 (m, 5H), 7.00-6.76 (m, 3H), 6.42 (s, 1H), 5.68 (s, 1H), 4.91 (s, 1H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0, 143.8, 137.3, 136.2, 134.8, 134.4, 132.8, 131.6, 131.0, 129.8, 129.5, 128.84, 127.6, 127.2, 121.7, 117.4, 21.7, 20.9; HRMS (ESI): m/z calcd for $C_{22}H_{20}ClNO_2S$ $(M-H)^-$: 396.0831, found: 396.0848.

4-Chloro-2-(1-(2-chlorophenyl)vinyl)-*N*-tosylbenzenamine (1n). 1.29 g, 62%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.30-7.23 (m, 1H), 7.22-7.18 (m, 1H), 7.14-7.08 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 6.77 (s, 1H), 5.50 (s, 1H), 5.15 (s, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.3, 142.8, 139.0, 136.0, 133.8, 133.0, 132.5, 131.0, 130.5, 129.8, 129.8, 129.6, 129.6, 128.8, 127.4, 127.3, 123.5, 121.3, 21.7; HRMS (ESI): m/z calcd for $C_{21}H_{17}Cl_2NO_2S$ $(M+Na)^+$: 440.0249, found: 440.0260.

4-Methyl-2-(prop-1-en-2-yl)-*N*-tosylbenzenamine (1p). 1.38 g, 92%, yellow solid, m.p. = 89.4-90.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.81 (s, 1H), 5.21 (s, 1H), 4.61 (s, 1H), 2.36 (s, 3H), 2.25 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 142.3, 136.4, 135.1, 134.3, 130.2, 129.6, 128.8, 128.5, 127.3, 121.2, 116.9, 24.5, 21.6, 20.9; HRMS (ESI): m/z calcd for $C_{17}H_{19}NO_2S$ $(M-H)^-$: 300.1064, found: 300.1087.

5-Chloro-2-(prop-1-en-2-yl)-*N*-tosylbenzenamine (1q). 1.22 g, 76%, white solid, m.p. = 74.9-76.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.63 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.11-7.03 (m, 2H), 7.01-6.95 (m, 1H), 5.32 (s, 1H), 4.72 (s, 1H), 2.42 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.4, 141.2, 135.9, 134.1, 133.7, 132.8, 129.9, 129.1, 127.3, 124.5, 120.3, 118.0, 24.5, 21.7; HRMS (ESI): m/z calcd for $C_{16}H_{16}ClNO_2S$ $(M-H)^-$: 320.0518, found: 320.0532.

2-(3-Methylbut-1-en-2-yl)-*N*-tosylbenzenamine (1r). 1.25 g, 79%, white solid, m.p. = 81.7-82.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (t, *J* = 8.0 Hz, 3H), 7.21 (t, *J* = 8.0 Hz, 3H), 7.03-6.96 (m, 2H), 6.87 (s, 1H), 5.23 (s, 1H), 4.62 (s, 1H), 2.36 (s, 3H), 2.29-2.22 (m, 1H), 0.92 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.1, 144.1, 136.4, 133.9, 133.4, 129.7, 128.7, 128.0, 127.3, 123.7, 118.7, 114.3, 35.0, 21.6, 21.1; HRMS (ESI): m/z calcd for $C_{22}H_{21}NO_2S$ $(M-H)^-$: 338.1191, found: 338.1191.

2-Cyclohexenyl-4-methyl-*N*-tosylbenzenamine (1s). 1.31 g, 77%, yellow solid, m.p. = 137.6-139.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.48 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.00 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.86 (s, 1H), 6.76 (s, 1H), 5.36-5.18 (m, 1H), 2.36 (s, 3H), 2.25 (s, 3H), 2.07 (s, 2H), 1.63-1.54 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 136.5, 136.2, 135.3, 134.4, 130.5, 129.6, 129.1, 128.4, 127.2, 121.55, 117.4, 30.1, 25.3, 22.9, 21.8, 21.6, 20.9; HRMS (ESI): m/z calcd for $C_{20}H_{23}NO_2S$ $(M-H)^-$: 340.1377, found: 340.1387.

2-(1-Phenylvinyl)-*N*-tosylnaphthalen-1-amine (1w). 1.26 g, 63%, yellow solid, m.p. = 127.5-128.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47-8.33 (m, 1H), 7.89-7.71 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.37-7.28 (m, 2H), 7.25-7.16 (m, 4H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.86 (s, 1H), 5.19 (s, 1H), 4.68 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.0, 143.8, 139.2, 137.0, 136.7, 134.4, 132.43, 129.4, 129.2, 128.7, 128.6, 128.5, 127.9, 127.6, 126.8, 126.6, 126.3, 126.2, 117.7, 21.7; HRMS (ESI):

m/z calcd for $C_{25}H_{21}NO_2S$ $(M-H)^-$: 398.1220, found: 398.1231.

2-(1-(4-Chlorophenyl)vinyl)-*N*-tosylnaphthalen-1-amine (1x). 1.26 g, 58%, yellow solid, m.p. = 145.8-147.6 °C; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.45-8.29 (m, 1H), 7.90-7.79 (m, 2H), 7.58-7.51 (m, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.08 (s, 1H), 5.37 (s, 1H), 4.88 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.1, 143.9, 137.8, 136.9, 136.8, 134.4, 132.4, 129.4, 129.3, 129.1, 128.6, 128.3, 127.8, 127.7, 126.9, 126.8, 125.9, 118.0, 21.7; HRMS (ESI): m/z calcd for $C_{25}H_{20}ClNO_2S$ $(M-H)^-$: 432.0831, found: 432.0844.

General procedure for palladium-catalyzed oxidative annulation of 2-alkenylanilines and allenes.

A mixture of $Pd(OAc)_2$ (0.03 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.9 mmol), **1** (0.3 mmol), **2** (0.6 mmol), and DMF (5 mL) was added sequentially to a heavy glass flask. The resulting mixture was stirred and heated at 110 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure, and then the residue was purified by flash chromatography using a mixture of petroleum ether and ethyl acetate (v/v = 10:1) as eluent.

5-Phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ea). 116 mg, 93%, white solid, m.p. = 216.5-218.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.35-7.18 (m, 4H), 7.16-7.05 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90-6.71 (m, 3H), 6.26 (s, 1H), 5.40 (s, 1H), 3.74 (s, 1H), 2.21 (s, 3H), 2.02 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ 146.1, 143.0, 140.1, 137.7, 136.7, 136.0, 135.5, 132.3, 130.4, 130.1, 129.4, 128.8, 128.2, 127.9, 127.9, 127.3, 127.2, 126.8, 52.0, 21.7, 21.5, 21.3; HRMS (ESI): m/z calcd for $C_{26}H_{25}NO_2S$ $(M+Na)^+$: 438.1474, found: 438.1498; The structure of **3ea** was confirmed by X-ray analysis and NOE.

7-Methyl-5-phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3fa). 103 mg, 80%, white solid, m.p. = 176.3-177.7°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.41 (m, 1H), 7.36-7.25 (m, 2H), 7.15 (s, 3H), 7.03-6.94 (m, 1H), 6.94-6.85 (m, 2H), 6.76 (s, 2H), 6.51 (s, 1H), 6.23-6.11 (m, 1H), 5.30 (br s, 1H), 3.67 (br s, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 1.92 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.1, 142.9, 137.8, 137.6, 137.0, 136.5, 135.7, 135.6, 132.6, 130.3, 129.9, 129.3, 128.8, 128.3, 127.8, 127.4, 126.8, 52.4, 21.7, 21.5, 21.3, 21.2; HRMS (ESI): m/z calcd for $C_{27}H_{27}NO_2S$ $(M+Na)^+$: 452.1661, found: 452.1655.

7-Bromo-5-phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ga). 115 mg, 78%, white solid, m.p. = 183.8-184.6°C; ^{1}H NMR (400 MHz, $CDCl_3$); δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.43-7.29 (m, 3H), 7.23 (s, 3H), 6.99 (d, *J* = 8 .0 Hz, 2H), 6.88 (s, 1H), 6.78 (s, 2H), 6.26 (s, 1H), 5.33 (s, 1H), 3.67 (s, 1H), 2.19 (s, 3H), 2.00 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 143.3, 139.1, 138.7, 137.5, 137.3, 134.7, 134.3, 131.7, 131.6, 130.8, 129.2, 128.9, 128.2, 127.9, 127.3, 127.2, 121.2, 51.9, 21.8, 21.5, 21.4; HRMS (ESI): m/z calcd for $C_{26}H_{24}BrNO_2S$ $(M+Na)^+$: 516.0603, found: 516.0612.

7-Chloro-5-phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ha). 124 mg, 92%, white solid, m.p. = 155.7-157.0°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.54 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.64-6.80 (m, 3H), 6.23 (s, 1H), 5.32 (s, 1H) 3.64 (s, 1H), 2.15 (s, 3H), 1.96 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 143.2, 138.6, 138.4, 137.5, 137.2, 134.4, 133.0, 131.8, 131.6, 131.4, 129.3, 128.9, 128.2, 128.0, 127.8, 127.3, 127.1, 51.9, 21.7, 21.5, 21.4; HRMS (ESI): m/z calcd for $C_{26}H_{24}ClNO_2S$ $(M+Na)^+$: 472.1108, found: 472.1118.

7-Methoxy-5-phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ia). 85 mg, 64%, white solid, m.p. = 137.0-138.5°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90-6.74 (m, 3H), 6.36-6.28 (m, 1H), 6.25 (s, 1H), 5.40 (s, 1H), 3.75 (s, 1H), 3.61 (s, 3H), 2.21 (s, 3H), 2.01 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.3, 145.7, 142.9, 138.1, 137.7, 136.1, 135.4, 133.0, 131.3, 130.6, 129.4, 128.8, 128.3, 127.9, 127.4, 126.9, 117.5, 113.0, 55.4, 52.4, 21.7, 21.5, 21.4; HRMS (ESI): m/z calcd for $C_{27}H_{27}NO_3S$ $(M+Na)^+$: 468.1604, found: 468.1609.

7-Nitro-5-phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ja). 84 mg, 61%, yellow solid, m.p. = 105.6-106.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.23-7.14 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 4.0 Hz, 2H), 6.35 (s, 1H), 2.16 (s, 3H), 1.98 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ 146.5, 145.6, 145.8, 143.8, 138.8, 137.7, 137.3, 133.7, 132.5, 130.8, 129.2, 129.1, 128.5, 127.6, 127.4, 127.4, 127.2, 122.1, 51.3, 21.8, 21.5, 21.4; HRMS (ESI): m/z calcd for $C_{26}H_{24}N_2O_4S$ $(M+Na)^+$: 483.1349, found: 483.1325.

9-Methyl-5-phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ka). 61 mg, 47%, white solid, m.p. = 148.6-149.8°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.25-7.05 (m, 4H), 7.03-6.93 (m, 3H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 5.25 (d, *J* = 16.0 Hz, 1H), 3.86 (d, *J* = 16.0, 1H), 2.48 (s, 3H), 2.05 (s, 3H), 1.79 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 142.8, 139.4, 139.0, 138.8, 136.5, 134.3, 130.7, 129.6, 129.5, 129.4, 129.1, 128.7, 128.2, 127.8, 127.7, 127.6, 126.9, 54.6, 21.5, 21.5, 21.4, 19.7; HRMS (ESI): m/z calcd for $C_{27}H_{27}NO_2S$ $(M+Na)^+$: 452.1658, found: 452.1655.

7-Methyl-3-(propan-2-ylidene)-5-p-tolyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3la). 112 mg, 84%, white solid, m.p. = 184.2-185.0°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.61 (s, 1H), 6.23 (s, 1H), 5.37 (s, 1H), 3.73 (s, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.16 (s, 3H), 2.00 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 142.8, 137.8, 137.6, 136.9, 136.6, 136.4, 135.6, 135.2, 132.6, 130.0, 129.9, 129.2, 128.8, 128.7, 128.6, 128.3, 127.4, 52.4, 21.6, 21.5, 21.3, 21.3, 21.2. HRMS (ESI): m/z calcd for $C_{28}H_{29}NO_2S$ $(M+Na)^+$: 466.1811, found: 466.1820.

5-(4-Chlorophenyl)-7-methyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ma). 106 mg, 76%, white solid, m.p. = 157.9-158.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 1.2 Hz, 1H), 7.00 (d, *J* = 8.0 Hz , 2H), 6.77 (d, *J* = 8.0 Hz , 2H), 6.55 (s, 1H), 6.21 (s, 1H), 5.37 (s, 1H), 3.74 (s, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 2.00 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 142.9, 137.8, 137.6, 137.2, 136.2, 136.2, 134.5,

132.6, 132.4, 130.6, 130.6, 130.1, 129.0, 128.8, 128.2, 128.1, 127.4, 52.4, 21.7, 21.5, 21.4, 21.2; HRMS (ESI): m/z calcd for $C_{27}H_{26}ClNO_2S$ $(M+Na)^+$: 486.1265, found: 486.1262.

7-Chloro-5-(2-chlorophenyl)-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3na). 116 mg, 80%, white solid, m.p. = 172.3-173.2°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 3H), 7.21-7.14 (m, 2H), 7.14-7.06 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 6.25 (s, 1H), 2.27 (s, 3H), 2.00 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 143.3, 138.6, 138.2, 137.8, 133.9, 133.0, 131.7, 131.0, 130.6, 129.9, 129.0, 128.8, 128.1, 127.6, 127.6, 126.8, 124.1, 50.4, 21.9, 21.6, 21.2; HRMS (ESI): m/z calcd for $C_{26}H_{23}Cl_2NO_2S$ $(M+Na)^+$: 506.0719, found: 506.0703.

5-Methyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3oa). 85 mg, 80%, white solid, m.p. = 135.1-136.6°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.33-7.22 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.00 (s, 1H), 5.20 (br s, 1H), 3.70 (br s, 1H), 2.32 (s, 3H), 1.91 (s, 3H), 1.78 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.7, 139.4, 137.9, 137.2, 133.4, 130.4, 128.5, 128.4, 128.0, 127.8, 127.7, 127.6, 127.5, 127.2, 51.9, 27.0, 21.5, 21.4, 21.0; HRMS (ESI): m/z calcd for $C_{21}H_{23}NO_2S$ $(M+Na)^+$: 376.1342, found: 376.1343.

5,7-Dimethyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3pa). 72 mg, 65%, white solid, m.p. = 135.2-136.3°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.28-7.16 (m, 2H), 7.09-6.97 (m, 4H), 5.96 (s, 1H), 5.30 (br s, 1H), 3.60 (br s, 1H), 2.32 (s, 6H), 1.89 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.6, 138.0, 137.7, 137.5, 137.1, 136.9, 133.1, 130.2, 129.0, 128.4, 128.3, 128.0, 127.8, 127.3, 52.2, 26.9, 21.6, 21.5, 21.5, 21.0; HRMS (ESI): m/z calcd for $C_{22}H_{25}NO_2S$ $(M+Na)^+$: 390.1498, found: 390.1493.

8-Chloro-5-methyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3qa). 81 mg, 70%, white solid, m.p. = 149.0-150.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.25-7.16 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 2.32 (s, 3H), 1.91 (s, 3H), 1.76 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ 143.0, 140.4, 137.7, 135.7, 134.3, 132.5, 130.3, 129.5, 128.5, 128.0, 127.5, 127.2, 126.6, 51.6, 27.0, 21.6, 21.5, 21.0; HRMS (ESI): m/z calcd for $C_{21}H_{22}ClNO_2S$ $(M+Na)^+$: 410.0952, found: 410.0959.

5-Isopropyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ra). 83 mg, 73%, yellow solid, m.p. = 129.4-130.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0, 1H), 7.45 (t, *J* = 8.0, 3H), 7.31-7.24 (m, 2H), 7.15 (d, *J* = 8.0, 2H), 6.26 (s, 1H), 5.31 (s, 1H), 3.79 (s, 1H), 2.86-2.79 (m, 1H), 2.39 (s, 3H), 1.94 (s, 3H), 1.83 (s, 3H), 1.16 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.8, 139.9, 139.2, 138.7, 137.8, 132.4, 129.9, 128.9, 128.1, 127.8, 127.8, 127.4, 127.3, 124.6, 53.6, 34.1, 23.4, 21.5, 21.4, 21.1; HRMS (ESI): m/z calcd for $C_{26}H_{25}NO_2S$ $(M+Na)^+$: 404.1660, found: 404.1659.

2-Methyl-7-(propan-2-ylidene)-5-tosy-6,7,8,9,10,11-hexahydro-5*H*-dibenzo[*b,d*]azepine (3ta). 37 mg, 30%, white solid, m.p. = 177.5-178.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 4.70 (s, 2H), 2.50-2.16 (m, 7H), 2.03-1.90 (m, 1H),

1.88-1.75 (m, 1H), 1.58-1.43 (m, 5H), 1.42-1.23 (m, 5H), 1.15 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 142.6, 138.3, 137.8, 137.0, 132.9, 131.7, 131.6, 130.2, 129.4, 129.3, 127.5, 127.2, 127.1, 58.9, 29.1, 28.0, 22.5, 22.3, 21.9, 21.5, 21.4, 19.5; HRMS(ESI) m/z calcd for $C_{25}H_{29}NO_2S$ $(M+Na)^+$: 430.1811, found: 430.1790.

5-Phenyl-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-naphtho[1,2-*b*]azepine (3wa). 70 mg, 50%, white solid, m.p. = 217.7-218.3°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 8.0 Hz, 3H), 7.32 (s, 3H), 7.14 (s, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.33 (s, 1H), 5.56 (d, *J* = 20.0 Hz ,1H), 4.12 (d, *J* = 20.0 Hz, 1H), 2.20 (s, 3H), 1.97 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.8, 143.0, 138.5, 136.7, 136.3, 135.7, 135.1, 134.0, 132.6, 130.6, 129.0, 128.8, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.1, 127.0, 126.8, 125.8, 55.5, 21.7, 21.6, 21.4; HRMS (ESI): m/z calcd for $C_{30}H_{27}NO_2S$ $(M+Na)^+$: 488.1655, found: 488.1664.

5-(4-Chlorophenyl)-3-(propan-2-ylidene)-1-tosyl-2,3-dihydro-1*H*-naphtho[1,2-*b*]azepine (3xa). 72 mg, 48%, white solid, m.p. = 256.4-257.5°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.73-7.62 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H),7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 8.0 Hz, 3H), 6.32 (s, 1H), 5.54 (d, *J* = 16.0 Hz, 1H), 4.11 (d, *J* =16.0 Hz, 1H), 2.23 (s, 3H), 1.96 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 143.1, 138.5, 136.7, 135.7, 135.4, 135.2, 134.1, 133.0, 132.5, 130.8, 130.3, 128.9, 128.3, 128.2, 128.2, 127.7, 127.6, 127.2, 126.9, 125.8, 55.7, 21.7, 21.5; HRMS (ESI): m/z calcd for $C_{30}H_{26}ClNO_2S$ $(M+Na)^+$: 522.1265, found: 522.1235.

5-Phenyl-3-(undecan-6-ylidene)-1-tosyl-2,3-dihydro-1H-benzo[*b*]azepine (3eb). 149 mg, 94%, white solid, m.p. = 108.2-109.5°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27-7.09 (m, 4H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.81-6.65 (m, 3H), 6.22 (s, 1H), 5.30 (s, 1H), 3.73 (s, 1H), 2.40 (s, 1H), 2.20-1.88 (m, 6H), 1.47-1.12 (m, 12H), 0.94-0.69 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 145.4, 142.9, 140.1, 137.8, 137.1, 135.7, 132.2, 130.4, 130.0, 129.3, 128.9, 128.5, 127.9, 127.9, 127.4, 127.3, 126.8, 52.5, 34.1, 33.7, 32.3, 32.3, 29.2, 28.9, 22.7, 22.7, 21.5, 14.2, 14.1; HRMS (ESI): m/z calcd for $C_{34}H_{41}NO_2S$ $(M+Na)^+$: 550.2750, found: 550.2742.

5-Phenyl-3-(diphenylmethylene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ec). 139 mg, 86%, white solid, m.p. = 219.0-220.1°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.45 (m, 3H), 7.30 (t, *J* = 8.0 Hz , 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 6H), 7.13-7.07 (m, 3H), 7.04 (t, *J* = 8.0 Hz, 1H),6.98 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz ,1H), 6.75-6.67 (m, 2H), 6.35 (s, 1H), 5.24 (d, *J* = 16.0 Hz, 1H), 3.96 (d, *J* = 16.0 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ 145.4, 144.0, 143.2, 141.4, 140.6, 138.3, 138.2, 137.2 132.6, 132.3, 131.8, 130.4, 129.7, 129.7, 129.3, 129.1, 128.5, 128.3, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.0, 54.8, 21.5; HRMS (ESI): m/z calcd for $C_{36}H_{29}NO_2S$ $(M+Na)^+$: 562.1811, found: 562.1819.

5-Phenyl-3-(di-*p*-tolylmethylene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ed). 150 mg, 88%, white solid, m.p. = 138.3-140.2°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.13-7.06 (m, 5H), 7.06-6.91 (m, 7H), 6.83-6.67 (m, 5H), 6.37 (s, 1H), 5.38-4.95 (m, 1H), 4.21-3.74 (m,

1H), 2.29 (s, 3H), 2.23 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.6, 144.3, 143.1, 140.6, 138.8, 138.6, 138.4, 137.7, 137.4, 137.2, 137.1, 132.2, 132.1, 131.8, 130.4, 129.8, 129.7, 129.2, 129.2, 129.1, 128.7, 128.1, 127.9, 127.6, 127.3, 126.9, 54.6, 21.5, 21.4, 21.3; HRMS (ESI): m/z calcd for $C_{38}H_{33}NO_2S$ $(M+Na)^+$: 590.2124, found: 590.2103.

3-Benzylidene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ee). 103 mg, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.59 (m, 1H), 7.38 (d, *J* = 8.0 Hz , 2H), 7.32-7.24 (m, 3H), 7.21-7.16 (m, 3H), 7.16-7.08 (m, 3H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.98-6.82 (m, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.74-6.70 (m, 2H), 6.57 (s, 1H), 6.48 (s, 1H), 5.25-4.86 (m, 1H), 4..22-3.92 (m, 1H), 2.18-2.07 (m, 3H); HRMS (ESI): m/z calcd for $C_{30}H_{25}NO_2S$ $(M+Na)^+$: 486.1498, found: 486.1472.

(*E*)-3-Benzylidene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ee). White solid, m.p. = 164.3-165.3°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.32-7.22 (m, 3H), 7.21-7.16 (m, 3H), 7.16-7.09 (m, 3H), 7.06 (t, *J* = 6.4Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.74-6.67 (m, 2H), 6.57 (s, 1H), 6.48 (s, 1H), 4.96 (s, 1H), 4.10 (s, 1H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.5, 143.2, 140.2, 139.9, 137.5, 136.7, 136.5, 134.4, 132.8, 131.9, 130.4, 129.6, 129.1, 129.1, 128.6, 128.5, 128.0, 127.6, 127.5, 127.4, 127.2, 58.1, 21.4.

3-(4-Methylbenzylidene)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ef). 116 mg, 81%;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.74 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.26-7.08 (m, 8H), 7.04-6.88 (m, 2H), 6.87-6.73 (m, 3H), 6.61 (s, 1H), 6.56 (s, 1H), 5.02 (s, 1H), 4.33-3.96 (m, 1H), 2.36 (s, 3H), 2.14 (s, 3H); HRMS (ESI): m/z calcd for $C_{31}H_{27}NO_2S$ $(M+Na)^+$: 500.1655, found: 500.1654; The *E* stereochemistry of major isomer **3ef** was assigned based on the X-ray analysis.

(*E*)-3-(4-methylbenzylidene)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3ef). White solid, m.p. = 186.1-187.0°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.76-7.74 (m, 1H), 7.45-7.43 (m, 2H), 7.33-7.25 (m, 2H), 7.23-7.19 (m, 3H), 7.16-7.09 (m, 4H), 6.95-6.91 (m, 2H), 6.87-6.72 (m, 3H), 6.62-6.52 (m, 2H), 5.03 (s, 1H), 4.16 (s, 1H), 2.39-2.33 (m, 3H), 2.17-2.10 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.5, 143.1, 140.1, 139.5, 137.5, 136.7, 133.8, 133.7, 132.8, 132.0, 130.4, 129.5, 129.3, 129.2, 129.0, 128.8, 128.5, 127.9, 127.5, 127.3, 127.1, 58.1, 21.4, 21.4.

3-(4-Chlorobenzylidene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3eg). 122 mg, 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.63 (m, 1H), 7.43 (d, *J* = 8.0Hz, 2H), 7.36-7.29 (m, 3H), 7.25-7.10 (m, 6H), 7.04-6.90 (m, 2H), 6.89-6.82 (m, 1H), 6.82-6.74 (m, 2H), 6.56 (s, 1H), 6.46 (s, 1H), 5.02 (s, 1H), 4.26-3.88 (m, 1H), 2.23-2.12 (m, 3H); HRMS (ESI): m/z calcd for $C_{30}H_{24}ClNO_2S$ $(M+Na)^+$: 520.1108, found: 520.1114.

(*E*)-3-(4-chlorobenzylidene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3eg). White solid, m.p. = 185.7-186.4°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 3H), 7.25-7.10 (m, 6H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.82-6.75 (m, 2H), 6.57 (s, 1H), 6.46 (s, 1H), 5.02 (s, 1H), 4.16 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 143.2, 140.5, 140.1, 137.5, 136.5, 135.1, 134.9, 133.4, 132.9, 130.7, 130.3, 129.1, 128.8, 128.7, 128.0, 128.0, 127.4, 127.3, 58.0, 21.4.

5-Phenyl-3-(1-phenylethylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3eh).

129 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.55 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H) ,7.47 (t, *J* = 4.0 Hz, 1H), 7.40 (t, *J* = 6.0, 1H), 7.37-7.28 (m, 4H), 7.30-7.19 (m, 4H), 7.12-7.10 (d, *J* = 8.0 Hz, 1H), 7.01-7.00 (d, *J* = 8.0 Hz, 2H), 6.92-6.86 (m, 1H), 6.73-6.71 (d, *J* = 6.0 Hz, 1H), 6.49-6.13 (m, 1H), 5.58-5.01 (m, 1H), 4.08-3.80 (m, 1H), 2.26-2.23 (m, 3H), 2.13 (s, 3H); ^{13}C NMR (101MHz, $CDCl_3$): δ 145.9, 145.3, 143.4, 143.1, 143.0, 140.5, 140.0, 139.6, 139.1, 137.8, 137.5, 136.7, 136.1, 132.3, 132.2, 131.8, 130.8, 130.2, 130.1, 130.0, 129.4, 129.1, 129.0, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 127.3, 127.2, 127.1, 126.7, 54.0, 53.5, 21.8, 21.5, 21.5, 21.4; HRMS (ESI): m/z calcd for $C_{31}H_{27}NO_2S$ $(M+Na)^+$: 500.1655, found: 500.1654; The *E* stereochemistry of major isomer **3eh** was assigned based on the X-ray analysis.

(*E*)-5-phenyl-3-(1-phenylethylidene)-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3eh). White solid, m.p. = 185.3-186.8°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0, 1H), 7.50 (d, *J* = 8.0, 2H), 7.42-7.31 (m, 2H), 7.31-7.24 (m, 2H), 7.18-7.05 (m, 6H), 6.94 (d, *J* = 8.0, 2H), 6.80 (d, *J* = 8.0, 1H), 6.71-6.57 (m, 2H), 6.10 (s, 1H), 5.58 (br s, 1H), 4.06 (br s, 1H), 2.26 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 143.4, 143.1, 140.0, 139.2, 137.7, 137.5, 136.1, 132.2, 131.8, 130.8, 130.0, 129.1, 129.0, 128.6, 128.3, 128.2, 127.8, 127.5, 127.4, 127.2, 126.7, 54.0, 21.8, 21.4.

Ethyl 2-(2-methyl-5-phenyl-1-tosyl-1*H*-benzo[*b*]azepine-3(2*H*)-ylidene)acetate (3ej). 129 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.61 (m, 1H), 7.54-7.48 (m, 1H), 7.47-7.32 (m, 3H), 7.31-7.13 (m, 4H), 7.10-6.94 (m, 2H), 6.93-6.77 (m, 3H), 6.01-5.76 (m, 1H), 5.34-5.15 (m, 1H), 4.34-4.15 (m, 2H), 2.28-2.14 (m, 3H), 1.39-1.28 (m, 3H), 1.11-0.96 (m, 3H); HRMS (ESI): m/z calcd for $C_{28}H_{27}NO_4S$ $(M+Na)^+$: 496.1553, found: 496.1563; The *E* stereochemistry of major isomer 3ej was assigned based on the observation of NOE.

(*E*)-ethyl-2-(2-methyl-5-phenyl-1-tosyl-1*H*-benzo[*b*]azepine-3(2*H*)-ylidene)acetate (3ej). White solid, m.p. = 184.8-185.6°C; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H),7.26-7.12 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 8.0 Hz, 3H), 5.82 (s, 1H), 5.21(q, *J* = 14.4, 7.2 Hz, 1H), 4.19 (q, *J* = 14.0, 3.2 Hz, 2H), 2.16 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.1, 154.1, 144.4, 144.1, 143.5, 137.4, 136.6, 135.3, 132.4, 132.3, 129.4, 129.2, 127.9, 127.7, 127.5, 126.3, 117.5, 60.6, 60.3, 21.4, 21.0, 14.4.

3-heptylidene-5-phenyl-1-tosyl-2,3-dihydro-1*H*-benzo[*b*]azepine (3em). 141 mg, 81%, yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.75 (m, 1H), 7.46 (t, *J* = 8.0, 2H), 7.35-7.27 (m, 4H), 7.20-7.10 (m, 1H), 7.06-7.04 (m, 2H), 6.88-6.81 (m, 3H), 6.06-3.96 (m, 4), 2.26 (m, 3H), 2.21-2.16 (m, 1H), 1.51-1.45 (m, 1H), 1.41-1.31(m,5H), 1.28-1.25 (m, 1H), 1.23-1.18 (m, 2H), 0.97-0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.1, 145.9, 145.0, 143.1, 143.0, 140.0, 137.8, 137.8, 137.5, 137.2, 136.9, 136.3, 135.3, 135.0, 132.9, 132.8, 132.7, 132.6, 131.7, 130.5, 129.3, 129.2, 128.9, 128.8, 128.3, 128.2, 127.9, 127.9, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 119.9, 106.9, 63.0, 57.3, 57.0, 34.0, 31.9, 31.7, 29.4, 29.2, 28.8, 27.8, 26.1, 22.8, 22.6, 21.56, 14.2, 14.1; HRMS (ESI): m/z calcd for $C_{30}H_{33}NO_2S$ $(M+Na)^+$: 494.2130, found: 494.2121.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Characterization data of new compounds, including X-ray crystal structures of **3ea**, **3ef** (*E*)**, and 3eh** (*E*), ^{1}H and ^{13}C NMR spectra, and HRMS (PDF)

X-ray crystallographic analysis, compound **3ea** (CIF)

X-ray crystallographic analysis, compound (*E*)**-3ef** (CIF)

X-ray crystallographic analysis, compound (*E*)**-3eh** (CIF)

CCDC numbers for **3ea**, (*E*)**-3ef** and (*E*)**-3eh** are 1518435, 1518434 and1518436.

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