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Regioselective Synthesis of 3-Benzazepinones and Unexpected 5-Bromo-3-benzazepinones

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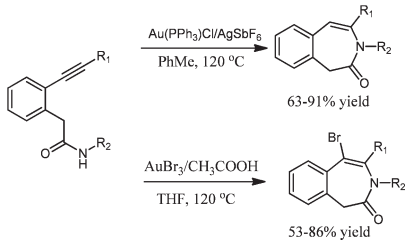

A regioselective hydroamidation of 2-(1-alkynyl)phenylacetamides with $Au(PPh_3)Cl/AgSbF_6$ as the catalyst proceeded by a 7-*endo-dig* pathway to afford 3-benzazepinones. This method accommodates a broad range of alkyl and aryl alkynyl substitutes in moderate to high yields (63−91%). Moreover, unexpectedly, we also discovered a gold-mediated transformation from 2-(1-alkynyl)-phenylacetamides to 5-bromo-3-benzazepinones, and $AuBr_3$ was found to not only play an activation role but also act as a reactant in the reaction for the first time.

Introduction

Transition-metal-catalyzed reactions have matured into indispensable techniques for organic synthesis. In recent years, homogeneous silver and gold catalysis have emerged as powerful tools for new organic transformations.[1,2] In particular, silver(I)[3] and gold(III)[4] salts have been proven to be soft and carbophilic Lewis acids for electrophilic activation of alkynes; thus, they are efficient promoters to prepare a large number of *N*-heterocycles.

The seven-membered nitrogen heterocyclic compounds are important target molecules because of their frequent occurrence in a number of bioactive natural products and therapeutic agents. For example, benzazepinones are ubiquitous structural units found in a large array of natural products[5a,b] and pharmaceuticals, and they possess a broad spectrum of biological activities for the treatment of cardiovascular diseases,[5c] tumor,[5d] pain,[5e] myocardial hypertrophy,[5f] and Alzheimer's diseases.[5g] Therefore, the synthesis of these structural motifs has been a subject of intensive studies in recent years.

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(2) For recent reviews on gold-catalyzed reactions, see: (a) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6990. (b) Hoffmann-Röder, A.; Krause, N. *Org. Biomol. Chem.* **2005**, *3*, 387. (c) Ma, S. M.; Yu, S. C.; Gu, Z. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 200. (d) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896. (e) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395. (f) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180. (g) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333. (h) Li, Z. G.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239. (i) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326. (j) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351.

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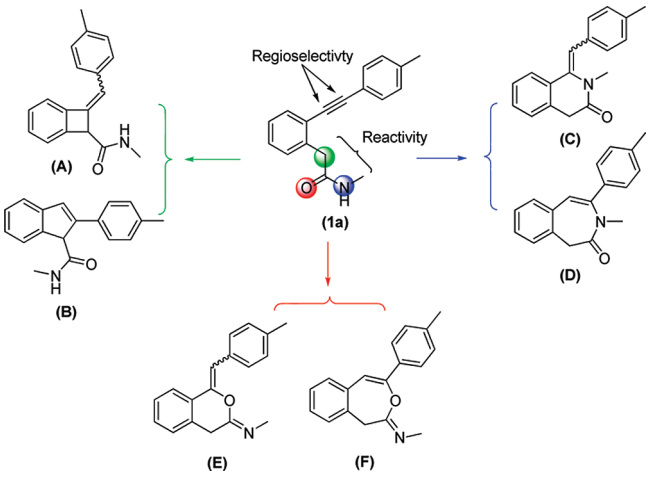
SCHEME 1. Cyclization of *N*-Methyl-2-(2-*p*-tolylethynylphenyl)-acetamide 1a



Mitchell and co-workers recently reported a regioselective synthesis of 3-benzazepinones by palladium-catalyzed intramolecular addition of amides to alkynes.[6] However, only 2-(1-alkynyl)phenylacetamides with alkyl substitutions in the alkynyl moiety could be obtained. In our ongoing efforts to develop new convenient and efficient approaches to synthesize highly valuable heterocyclic compounds with transition-metal catalysts,[7,8] we herein describe our recent findings on intramolecular hydroamidation[9] of 2-alkynyl benzeneacetamides in the presence of silver and gold salts for the synthesis of 3-benzazepinones as well as cyclization to unexpected 5-bromo-3-benzazepinones.[10]

Results and Discussion

Our strategy access to benzazepinones (**D**) took advantage of the readily prepared *N*-methyl-2-(2-substituted)acetamides (**1a**) for a novel Ag(I)/Au(III)-catalyzed cyclization reaction (Scheme 1). However, significant challenges were faced. Due to the sensitive nature of **1a**, it has three reactive nucleophilic centers and two regioselective alkynyl carbons, which could complicate the process. Therefore, there are six possible pathways for its cyclization, leading to six products.

With these issues in mind, we initiated our studies by examining catalysts and reaction conditions using **1a** as a model substrate. The results are shown in Table 1. Indeed, the reaction varied widely. However, the 7-*endo-dig*[11] pathway was observed to give the desired 3-benzazepinone (**2a**) favorably. No reaction occurred in the presence of $AgNO_3$, Ag_2CO_3, and $AgBF_4$ (entries 1−3, Table 1), and very low conversion was detected with AgOTf (entry 4, Table 1). The use of $AgAsF_6$ led to product **2a** in 31% (entry 5, Table 1). However, $AgSbF_6$ was found to be an effective catalyst for the transformation and gave **2a** in 62% yield at 100 °C for 24 h in anhydrous THF (entry 6, Table 1). After assessing various solvents, polar solvents were found to have a detrimental effect on the reaction, and anhydrous toluene was proved to be the optimum solvent (entries 7−11, Table 1). The reaction temperature was found to be an important factor on the process. For example, compound **2a** was obtained in only 15% yield when the temperature was reduced to 80 °C (entry 12, Table 1). At an elevated temperature (from 80 to 120 °C), the reaction went to completion within 12 h and a higher yield (74%) was observed, though a small portion of decomposition of **1a** occurred (entry 13, Table 1). When the reaction was conducted without argon protection, decomposition was observed and no desired product was obtained (entry 14, Table 1). To accelerate the reaction, we then assessed various cocatalysts. The addition of 10% $Au(PPh_3)Cl$ was found to noticeably promote the cyclization, affording **2a** in 89% yield (entry 18, Table 1). Moreover, to our surprise, an unexpected product **3a** was detected when 15% $AuBr_3$ was used (entry 20, Table 1). An excess amount of $AuBr_3$ was needed to complete the full conversion of substrate **1a** (entry 23, Table 1). This may indicate that the role of $AuBr_3$ was that of a reactant more than catalytic activation, which to our knowledge has never been reported before.[12] THF was shown to be a better solvent than toluene for the $AuBr_3$ system. In order to decrease the amount of $AuBr_3$, we also tried to add an oxidant to make the reaction catalytic. When the oxidant was $PhI(OAc)_2$,[13] the desired product **3a** was not detected (entry 25, Table 1). Selectfluor[14] also gave no satisfactory result. A dark brown stain was found at the origin (spotting line) of the TLC plate, and the yield of product **3a** was as low as 25% (entry 26, Table 1). Disappointingly, when the reaction was run in the presence of $CuBr_2$,[10b] **3a** was not observed (entries 26 and 27, Table 1). Br_2-mediated reactions were also investigated, but product **3a** was not obtained (entry 29, Table 1). Gratifyingly, a catalytic amount of protic acid CH_3COOH can accelerate the cyclization and improve the yield to 86% (entry 30, Table 1).

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(12) For selected $AuBr_3$-catalyzed reactions, see: (a) Asao, N.; Sato, K.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 5675. (b) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 7458. (c) Praveen, C.; Kiruthiga, P.; Perumal, P. T. *Synlett* **2009**, 1990.
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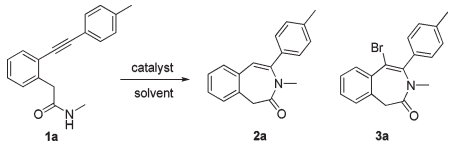
TABLE 1. Optimization of the Reaction Conditions[a]



entry	catalyst	cocatalyst	solvent	temp. (°C)	time (h)	yield (%) 2a	yield (%) 3a
1	$AgNO_3$		THF	100	24	0[b]	
2	Ag_2CO_3		THF	100	24	0[b]	
3	$AgBF_4$		THF	100	24	0[b]	
4	AgOTf		THF	100	24	< 10	
5	$AgAsF_6$		THF	100	24	31	
6	$AgSbF_6$		THF	100	24	62	
7	$AgSbF_6$		CH_2Cl_2	80	24	< 10	
8	$AgSbF_6$		PhMe	100	24	66	
9	$AgSbF_6$		CH_3CN	100	24	0[b]	
10	$AgSbF_6$		EtOH	100	24	0[b]	
11	$AgSbF_6$		DMF	100	24	0[b]	
12	$AgSbF_6$		PhMe	80	24	15	
13	**$AgSbF_6$**		**PhMe**	**120**	**12**	**74**	
14[c]	$AgSbF_6$		PhMe	120	12	dec	
15	$AgSbF_6$	TEA	PhMe	120	12	0[b]	
16	$AgSbF_6$	K_2CO_3	PhMe	120	12	0[b]	
17	$AgSbF_6$	AcOH	PhMe	120	12	0[b]	
18	**$AgSbF_6$**	**Au(PPh_3)Cl**	**PhMe**	**120**	**12**	**89**	
19	$AgSbF_6$	$AuBr_3$	PhMe	120	12	53	< 10
20	15% $AuBr_3$		PhMe	120	12		10[b]
21	35% $AuBr_3$		PhMe	120	12		23[b]
22	100% $AuBr_3$		PhMe	120	12		49[b]
23	120% $AuBr_3$		PhMe	120	12		61
24	120% $AuBr_3$		THF	120	12		81
25	35% $AuBr_3$/200% $PhI(OAc)_2$		THF	80	12		0[b]
26	35% $AuBr_3$/150% Selectfluor		CH_3CN	80	2		25
27	200% $CuBr_2$		THF	80	12		0[b]
28	200% $CuBr_2$		DMF	80	12		0[b]
29	100% Br_2/100% $AgNO_3$/300% $NaCO_3$		THF	25	12		0
30	**120% $AuBr_3$**	**CH_3COOH**	**THF**	**120**	**5**		**86**

[a]Reactions were carried out under Ar with 10 mol % of the catalyst and 10 mol % of the cocatalyst unless otherwise noted. [b]**1a** was recovered. [c]The reaction was carried out under air.

The structures of **2a** and **3a** were confirmed by ^1H NMR, ^{13}C NMR, mass spectrometry, and X-ray crystallography (see the Supporting Information).[15]

We then investigated the substrate scope of the two transformations. The results are shown in Tables 2 and 3. The chain length and electronic and steric effects which would influence the reactivity and the regiochemical outcomes of the studied reactions were examined.

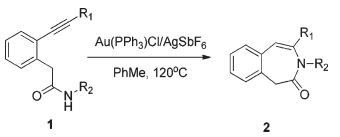
In the case of Au(PPh_3)Cl/$AgSbF_6$-catalyzed cyclization, substrates **1** bearing various alkyl and aryl alkynyl substitutes could react to give the desired products **2** in moderate to high yields (Table 2). When R_1 was a *para*- or *meta*-substituted aryl group, the corresponding products were obtained in good yields (entries 3 and 4, Table 2). However, for the *ortho* substitution, a moderate yield was obtained, presumably due to steric effects (entry 5, Table 2). When R_1 was a 4-halogen-substituted phenyl group, **1f** and **1g** reacted satisfactorily to give **2f** and **2g** in 90% and 72% yields, respectively (entries 6 and 7, Table 2). Cyclization of **1h**, which bears an electron-donating R_1 (*p*-OMe), gave **2h** in good yield (entry 8, Table 2), whereas **1i** bearing an electron-withdrawing R_1 (*p*-CF_3) resulted in a poor yield (entry 9, Table 2). The cyclization was also successfully extended to benzyl amide **1k** in 70% yield (entry 11, Table 2). Only a trace amount of **2j** was obtained when R_1 was a heteroaromatic group, and decomposition of **1j** was observed (entry 10, Table 2). The reaction of aromatic amide **1l** gave only a trace amount of yield presumably due to the decreased nucleophilicity of the amide NH (entry 12, Table 2).

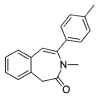
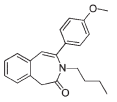
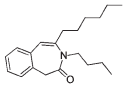
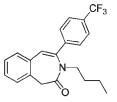
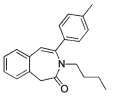
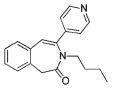
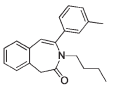
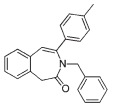
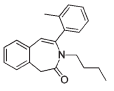
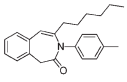
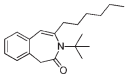
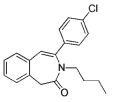
Similarly, the synthesis of 5-bromo-3-benzazepinones via $AuBr_3$-mediated cyclization also tolerated various R_1 and R_2 substitutes in moderate to good yields (Table 3). However, **1j** with heteroaromatic substituted R_1, **1l** bearing an aromatic amide, and **1m** with bulky *tert*-butyl R_2 turned out to be poor substrates, resulting in trace yields (entries 9, 11, and 12, Table 3).

A plausible mechanism accounting for the formation of 3-benzazepinones via Au(PPh_3)Cl/$AgSbF_6$-catalyzed cyclization is depicted in Scheme 2. As has been postulated for other Au-catalyzed nucleophilic additions, the catalyst here is the gold complex typically precipitated from $AgSbF_6$ and Au(PPh_3)Cl in a 1:1 ratio.[16] The reaction is initiated with alkyne activation by the gold complex, followed by intramolecular nucleophilic attack of the amide nitrogen at the

(15) CCDC 745837 and CCDC 745838 contain 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.

TABLE 2. Synthesis of 3-Benzazepinones via $Au(PPh_3)Cl/AgSbF_6$-Catalyzed Cyclization[a]



entry	product		yield (%)	entry	product		yield (%)
1		**2a**	89	8		**2h**	75
2		**2b**	91	9[b]		**2i**	trace
3		**2c**	84	10[b]		**2j**	trace
4		**2d**	81	11		**2k**	70
5		**2e**	63	12[b]		**2l**	trace
6		**2f**	90	13[b]		**2m**	trace
7		**2g**	72				

[a]The reactions were carried out in the presence of $AgSbF_6$ (10 mol %) and $Au(PPh_3)Cl$ (10 mol %) in anhydrous toluene under Ar protection at 120 °C unless otherwise noted. [b]The reaction time was prolonged to 24 h.

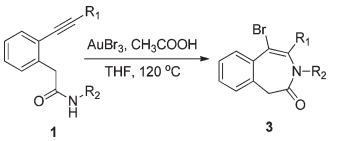
triple bond in an *endo-dig* fashion to give the seven-membered intermediate **4**. Then elimination of a proton affords the product **2a** with regeneration of the catalyst. The low yield of **2i** may due to the electron-withdrawing effect of CF_3, which made alkyne activation difficult for the catalyst (entry 9, Table 2). On the contrary, electron-donating substitutes (CH_3, OMe) are favorable for the gold complex to activate the alkynyl moieties (entries 3−5 and 8, Table 2).

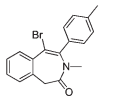
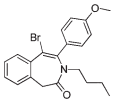
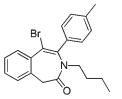
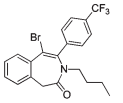
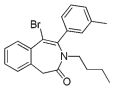
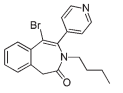
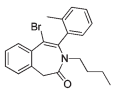
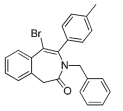
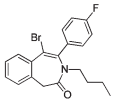
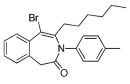
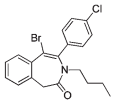
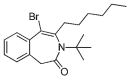
The different outcomes observed in reactions mediated by $AuBr_3$ suggest that a different mechanism is involved (Scheme 3). We reason that in the presence of $AuBr_3$, reactant **1a** would undergo nucleophilic cyclization and then reductive elimination, leading to the product **3a**.[17] Initially,

(16) (a) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (b) Toullec, P. Y.; Genin, E.; Leseurre, L.; Genet, J. P.; Michelet, V. *Angew. Chem., Int. Ed.* **2006**, *45*, 7427. (c) Asao, N.; Aikawa, H.; Tago, S.; Umetsu, K. *Org. Lett.* **2007**, *9*, 4299.

(17) Kharasch, M. S.; Isbell, H. M. *J. Am. Chem. Soc.* **1931**, *53*, 3053.

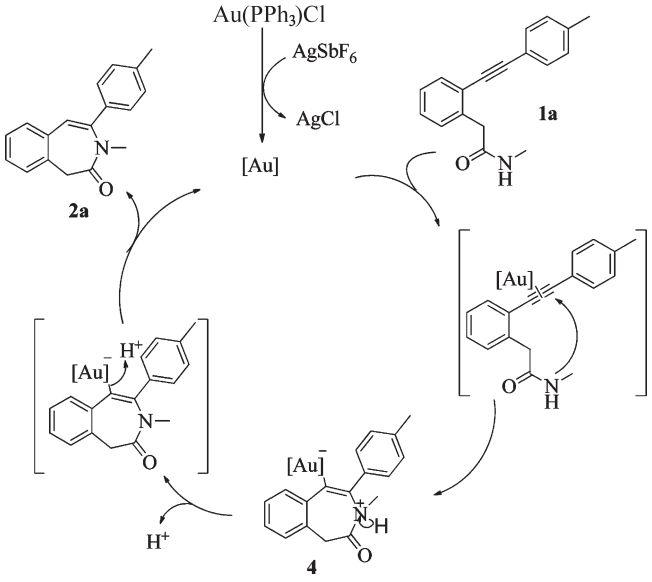
TABLE 3. Synthesis of 5-Bromo-3-benzazepinones via $AuBr_3$-Mediated Cyclization[a]



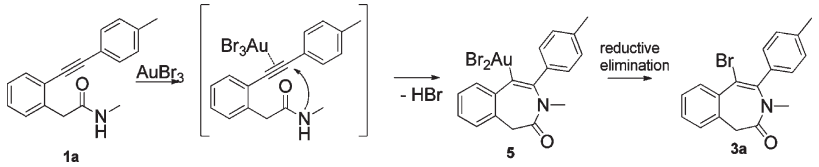
entry	product		yield (%)	entry	product		yield (%)
1		**3a**	86	7		**3h**	78
2		**3c**	79	8		**3i**	trace
3		**3d**	72	9		**3j**	trace
4		**3e**	64	10		**3k**	71
5		**3f**	81	11		**3l**	trace
6		**3g**	74	12		**3m**	trace

[a]The reaction was carried out in the presence of $AuBr_3$ (120 mol %) and CH_3COOH (10 mol %) in anhydrous THF with Ar protection at 120 °C.

SCHEME 2. Proposed Mechanism for $Au(PPh_3)Cl/AgSbF_6$-Catalyzed Hydroamidation of 1a to 2a



SCHEME 3. Proposed Mechanism for the $AuBr_3$-Mediated Cyclization of 1a to 3a



reactant **1a** is activated by $AuBr_3$. Regioselective nucleophilic attack of the amide nitrogen to the gold-coordinated triple bond in a 7-*endo-dig* fashion provides intermediate **5**, which upon subsequent reductive elimination[10b] produces the seven-membered 5-bromo-3-benzazepinone **3a**. This mechanistic picture differs from the generally accepted homogeneous gold-catalyzed reactions in that $AuBr_3$ not only plays an activation role but also acts as a reactant in the reaction.[12]

Conclusion

In summary, we have developed a simple strategy for the synthesis of 3-benzazepinones by $Au(PPh_3)Cl/AgSbF_6$-catalyzed intramolecular hydroamidation with high regioselectivity and moderate to good yields. Importantly and unexpectedly, we also have uncovered the gold-mediated transformation to more synthetically versatile 5-bromo-3-benzazepinones, in which $AuBr_3$ not only plays an activation role but also acts as a reactant. As a result of a diverse assortment of biological activities of benzodiazepines, it is believed that these new approaches open the door to prepare new members of this valuable family.

Experimental Section

Typical Procedure for the Synthesis of *N*-Methyl-2-[2-(*p*-tolylethynyl)phenyl]acetamide (1a). (i) To a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) (1.2 mmol) and 2-iodophenylacetic acid (1.0 mmol) in CH_2Cl_2 (10 mL) was added a catalytic amount of 4-dimethylaminopyridine (DMAP), followed by addition of methylamine hydrochloride (1.0 mmol) 1 h later. The resulting mixture was stirred at room temperature. When the starting materials were completely consumed as monitored by TLC, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography to provide 2-(2-iodophenyl)-*N*-methylacetamide. (ii) To a solution of 2-(2-iodophenyl)-*N*-methylacetamide (1.0 mmol) and 1-ethynyl-4-methylbenzene (1.2 mmol) in Et_3N (5 mL) were added $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.01 mmol). The resulting mixture was stirred under argon at room temperature and was monitored by TLC to establish completion. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography to afford **1a** as a white solid: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, J = 6.0 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.36−7.28 (m, 3H), 7.17 (d, J = 7.8 Hz, 2H), 5.56 (br s, 1H), 3.83 (s, 2H), 2.75 (d, J = 4.5 Hz, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 138.8 136.8 132.3 131.4 130.1 129.2 128.8 127.4 123.5 119.5 94.5 86.5 42.6 26.5 21.5; MS (EI, m/z) 263 $[M]^+$; HRMS (EI) calcd for $C_{18}H_{17}NO$ $[M]^+$ 263.1310, found 263.1303.

***N*-Butyl-2-(2-oct-1-ynyl-phenyl)acetamide (1b):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43 (dd, J = 6.6, 2.1 Hz, 1H), 7.31−7.18 (m, 3H), 5.60 (br s, 1H), 3.73 (s, 2H), 3.18 (q, J = 6.6 Hz, 2H), 2.43 (t, J = 7.2 Hz, 2H), 1.66−1.56 (m, 2H), 1.49−1.19 (m, 10H), 0.90 (t, J = 6.6 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6 136.8 132.4 129.8 128.2 127.2 123.9 95.4 78.7 42.6 39.3 31.5 31.3 28.7 28.6 22.5 19.9 19.4 14.0 13.7; MS (EI, m/z) 299 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{29}NO$ $[M]^+$ 299.2249, found 299.2252.

***N*-Butyl-2-[2-(*p*-tolylethynyl)phenyl]acetamide (1c):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, J = 6.6 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 7.37−7.26 (m, 3H), 7.17 (d, J = 7.8 Hz, 2H), 5.63 (br s, 1H), 3.81 (s, 2H), 3.19 (q, J = 6.6 Hz, 2H), 2.37 (s, 3H), 1.40−1.30 (m, 2H), 1.26−1.14 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 138.9 137.0 132.3 131.4 130.1 129.2 128.8 127.4 123.4 119.5 94.5 86.7 42.9 39.4 31.5 21.5 19.9 13.6; MS (EI, m/z) 305 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$ 305.1780, found 305.1780.

***N*-Butyl-2-[2-(*m*-tolylethynyl)phenyl]acetamide (1d):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (d, J = 6.9 Hz, 1H), 7.35−7.22 (m, 6H), 7.17 (d, J = 7.5 Hz, 1H), 5.61 (br s, 1H), 3.82 (s, 2H), 3.19 (q, J = 6.6 Hz, 2H), 2.36 (s, 3H), 1.39−1.31 (m, 2H), 1.26−1.15 (m, 2H), 0.78 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3 138.1 137.1 132.4 132.0 130.1 129.5 128.9 128.6 128.3 127.4 123.3 122.4 94.4 87.0 42.9 39.4 31.5 21.2 19.9 13.6; MS (EI, m/z) 305 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$ 305.1780, found 305.1776.

***N*-Butyl-2-[2-(4-fluorophenylethynyl)phenyl]acetamide (1f):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57−7.49 (m, 3H), 7.35−7.27 (m, 3H), 7.05 (t, J = 8.4 Hz, 2H), 5.52 (br s, 1H), 3.81 (s, 2H), 3.19 (q, J = 6.3 Hz, 2H), 1.38−1.31 (m, 2H), 1.26−1.17 (m, 2H), 0.78 (t, J = 7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2 162.7 (d, J_{C-F} = 186.7 Hz) 137.0 133.5 133.4 132.3 130.2 129.0 127.5 123.2 118.8 115.9 115.7 93.3 86.9 42.9 39.4 31.5 19.9 13.6; MS (EI, m/z) 309 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{20}FNO$ $[M]^+$ 309.1529, found 309.1525.

***N*-Butyl-2-[2-(4-chlorophenylethynyl)phenyl]acetamide (1g):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (d, J = 6.9 Hz, 1H), 7.46 (d, J = 7.5 Hz, 2H), 7.34−7.27 (m, 5H), 5.49 (br s, 1H), 3.80 (s, 2H), 3.19 (q, J = 6.0 Hz, 2H), 1.40−1.30 (m, 2H), 1.26−1.14 (m, 2H), 0.78 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2 137.1 134.7 132.8 132.4 130.2 129.2 128.8 127.5 123.1 121.2 93.2 88.1 42.9 39.4 31.5 19.9 13.6; MS (EI, m/z) 325 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{20}ClNO$ $[M]^+$ 325.1233, found 325.1227.

***N*-Butyl-2-[2-(4-methoxyphenylethynyl)phenyl]acetamide (1h):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55−7.52 (m, 1H), 7.47 (d, J = 9.0 Hz, 2H), 7.34−7.26 (m, 3H), 7.88 (d, J = 9.0 Hz, 2H), 5.68 (br s, 1H), 3.81 (s, 3H), 3.80 (s, 2H),3.18 (q, J = 6.6 Hz, 2H), 1.37−1.30 (m, 2H), 1.24−1.16 (m, 2H), 0.78 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4 159.9 136.8 133.0 132.1 130.1 128.6 127.4 123.6 114.7 114.1 94.4 86.1 55.3 42.9 39.3 31.4 19.8 13.6; MS (EI, m/z) 321 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO_2$ $[M]^+$ 321.1729, found 321.1732.

***N*-Benzyl-2-[2-(*p*-tolylethynyl)phenyl]acetamide (1k):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (dd, J = 6.9, 1.5 Hz, 1H), 7.39−7.28 (m, 5H), 7.19−7.12 (m, 7H), 5.90 (br s, 1H), 4.41 (d, J = 6.0 Hz, 2H), 3.89 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4 138.9 138.0 136.6 132.4 131.9 131.4 130.9 130.2 129.2 128.9 128.5 127.5 127.4 127.2 123.5 119.4 94.7 86.7 43.6 42.8 21.5; MS (EI, m/z) 339 $[M]^+$; HRMS (EI) calcd for $C_{24}H_{21}NO$ $[M]^+$ 339.1623, found 339.1617.

2-(2-Oct-1-ynylphenyl)-*N*-*p*-tolylacetamide (1l): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47−7.23 (m, 6H), 7.06 (d, J = 8.4 Hz, 2H), 3.87 (s, 2H), 2.46 (t, J = 6.8 Hz, 2H), 2,28 (s, 3H), 1.64−1.56 (m, 2H), 1.46−1.39 (m, 2H), 1.28−1.25 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6 136.5

135.3 133.8 132.6 129.9 129.5 129.3 128.4 127.5 123.8 119.8 96.0 78.9 43.9 31.3 28.7 28.6 22.5 20.8 19.5 14.0; MS (EI, *m*/*z*) 333 $[M]^+$; HRMS (EI) calcd for $C_{23}H_{27}NO$ $[M]^+$ 333.2093, found 333.2094.

***N*-*tert*-Butyl-2-(2-oct-1-ynylphenyl)acetamide (1m):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42 (d, J = 6.9 Hz, 1H), 7.30−7.17 (m, 3H), 5.53 (br s, 1H), 3.63 (s, 2H), 2.44 (t, J = 6.9 Hz, 2H), 1.70−1.57 (m, 2H), 1.50−1.41 (m, 2H), 1.33−1.27 (m, 4H), 1.29 (s, 9H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8 137.3 132.4 129.7 128.2 127.0 123.7 95.2 78.9 51.0 43.9 31.3 28.7 28.6 28.5 22.5 19.5 14.5; MS (EI, *m*/*z*) 299 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{29}NO$ $[M]^+$ 299.2249, found 299.2251.

Typical Procedure for the Synthesis of *N*-Butyl-2-[2-(*o*-tolylethynyl)phenyl]acetamide (1e). (i) To a solution of EDCI (1.2 mmol) and 2-iodophenylacetic acid (1.0 mmol) in CH_2Cl_2 (10 mL) was added a catalytic amount of DMAP, followed by addition of *n*-butylamine (1.0 mmol) 1 h later. The resulting mixture was stirred at room temperature. When the starting materials were completely consumed monitored with TLC, the reaction mixture was diluted with CH_2Cl_2, washed with water, dried with anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography to provide *N*-butyl-2-(2-iodophenyl)acetamide. (ii) To a solution of *N*-butyl-2-(2-iodophenyl)acetamide (1.0 mmol) and TMS-acetylene (1.2 mmol) in Et_3N (5 mL) were added $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.01 mmol). The resulting mixture was stirred under argon at room temperature and was monitored by TLC to establish completion. When the reaction was complete, the solvent was removed under reduced pressure. The residue was directly purified by column chromatography to afford *N*-butyl-2-(2-((trimethylsilyl)ethynyl)phenyl)acetamide. (iii) To a solution of *N*-butyl-2-(2-((trimethylsilyl)ethynyl)phenyl)acetamide in THF was added ca. 1.5−2.0 equiv of TBAF (1 M THF solution), and the mixture was stirred for about 30 min (completion monitored by TLC). Upon completion, the reaction was treated with water, extracted with CH_2Cl_2, washed with H_2O, dried (Na_2SO_4), and concentrated in vacuo. Purification by flash column chromatography gave *N*-butyl-2-(2-ethynylphenyl)acetamide. (iv) To a solution of *N*-butyl-2-(2-ethynylphenyl)acetamide (1.0 mmol) and 1-iodo-2-methylbenzene (1.2 mmol) in Et_3N (5 mL) were added $Pd(PPh_3)_2Cl_2$ (0.02 mmol) and CuI (0.01 mmol). The resulting mixture was stirred under argon at room temperature and was monitored by TLC to establish completion. When the reaction was complete, the solvent was removed under reduced pressure. The residue was purified by column chromatography to afford **1e** as a white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (dd, J = 6.8, 2.0 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H),7.37−7.23 (m, 5H), 7.20−7.16 (m, 1H), 5.53 (br s, 1H), 3.84 (s, 2H), 3.18 (q, J = 6.8 Hz, 2H), 2.51 (s, 3H), 1.38−1.31 (m, 2H), 1.24−1.15 (m, 2H), 0.77 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2 139.9 136.8 132.5 132.0 130.1 129.6 128.9 128.7 127.4 125.7 123.5 122.4 93.2 91.1 42.8 39.4 31.4 20.8 19.9 13.6; MS (EI, *m*/*z*) 305 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$ 305.1780, found 305.1789.

***N*-Butyl-2-[2-(4-trifluoromethylphenylethynyl)phenyl]acetamide (1i):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66−7.58 (m, 5H), 7.41−7.30 (m, 3H), 5.41 (br s, 1H), 3.83 (s, 2H), 3.20 (q, J = 6.9 Hz, 2H), 1.40−1.31 (m, 2H), 1.27−1.14 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 137.2 132.5 131.7 130.3 130.2 129.9 129.5 127.5 126.5 125.3 125.2 125.1 122.7 92.8 89.4 42.8 39.3 31.4 19.8 14.0; MS (EI, *m*/*z*) 359 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{20}F_3NO$ $[M]^+$ 359.1497, found 359.1503.

***N*-Butyl-2-(2-pyridin-4-ylethynylphenyl)acetamide (1j):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.66 (br s, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.42−7.32 (m, 5H), 5.41 (br s, 1H), 3.82 (s, 2H), 3.20 (q, J = 6.8 Hz, 2H), 1.40−1.33 (m, 2H), 1.26−1.17 (m, 2H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1 148.4 137.6 132.9 132.6 132.0 130.4 130.3 128.6 128.5 127.7 122.1 93.1 91.1 42.8 39.4 31.5 29.6 19.8 13.6; MS (EI, *m*/*z*) 292 $[M]^+$; HRMS (EI) calcd for $C_{19}H_{20}N_2O$ $[M]^+$ 292.1576, found 292.1573.

Typical Procedure for the Synthesis of 3-Methyl-4-*p*-tolyl-1,3-dihydro-3-benzazepin-2-one (2a). A mixture of **1a** (0.1 mmol) and $Au(PPh_3)Cl$ (0.01 mmol)/$AgSbF_6$ (0.01 mmol) in 4 mL of anhydrous toluene was heated at 120 °C in a sealed tube under argon protection for 12 h. After the reaction was cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography to yield **2a** as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.34 (m, 6H), 7.25−7.23 (m, 2H), 6.78 (s, 1H), 3.70 (br s, 1H), 3.57(br s, 1H), 2.86 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 143.3 138.7 134.9 133.8 133.5 129.5 128.7 128.3 127.3 127.2 126.9 119.6 42.9 35.1 21.2; MS (EI, *m*/*z*) 263 $[M]^+$; HRMS (EI) calcd for $C_{18}H_{17}NO$ $[M]^+$ 263.1310, found 263.1308.

3-Butyl-4-hexyl-1,3-dihydro-3-benzazepin-2-one (2b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.23 (m, 3H), 7.20 (d, J = 6.4 Hz, 1H), 6.52 (s, 1H), 4.13 (br s, 1H), 3.61 (br s, 1H), 3.33 (br s, 1H), 3.07 (br s, 1H), 2.60 (br s, 1H), 2.31 (br s, 1H), 1.53−1.25 (m, 10H), 1.07−1.04 (m, 2H), 0.89 (t, J = 6.8 Hz, 3H) 0.76 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1 141.3 133.6 133.4 128.2 127.9 126.8 126.7 119.9 43.1 42.7 34.9 31.5 30.2 28.8 28.4 22.5 19.6 13.9 13.6; MS (EI, *m*/*z*) 299 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{29}NO$ $[M]^+$ 299.2249, found 299.2253.

3-Butyl-4-*p*-tolyl-1,3-dihydro-3-benzazepin-2-one (2c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41−7.32 (m, 6H), 7.23 (d, J = 8.1 Hz, 2H), 6.84 (s, 1H), 4.08 (br s, 1H), 3.69 (br s, 1H), 3.51 (br s, 1H), 2.83 (br s, 1H), 2.40 (s, 3H), 1.18−1.08 (m, 2H), 0.94−0.82 (m, 2H), 0.61 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 142.3 138.6 134.9 133.9 133.8 129.4 128.6 128.5 128.2 127.3 127.2 126.9 121.6 45.1 43.1 29.8 21.2 19.3 13.5; MS (EI, *m*/*z*) 305 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$ 305.1780, found 305.1781.

3-Butyl-4-*m*-tolyl-1,3-dihydro-3-benzazepin-2-one (2d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.31 (m, 7H), 7.21−7.17 (m, 1H), 6.86 (s, 1H), 4.09 (br s, 1H), 3.72 (br s, 1H), 3.52 (br s, 1H), 2.83 (br s, 1H), 2.42 (s, 3H), 1.18−1.08 (m, 2H), 0.94−0.82 (m, 2H), 0.62 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6 142.4 138.4 137.8 133.9 133.8 129.3 128.7 128.6 128.3 127.9 127.2 126.9 124.5 121.9 45.1 43.1 29.8 21.4 19.3 13.5; MS (EI, *m*/*z*) 305 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$ 305.1780, found 305.1784.

3-Butyl-4-*o*-tolyl-1,3-dihydro-3-benzazepin-2-one (2e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.8 Hz, 1H), 7.37−7.26 (m, 6H), 7.23 (d, J = 7.2 Hz, 1H), 6.65 (s, 1H), 3.93 (br s, 1H), 3.76 (br s, 1H), 3.64 (br s, 1H), 2.61 (br s, 1H), 2.33 (s, 3H), 1.76−1.68 (m, 2H), 0.94−0.86 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7 141.9 137.9 136.0 133.7 133.2 130.5 129.9 128.7 128.3 127.3 126.9 126.3 122.4 44.6 43.6 30.0 19.8 19.5 13.5; MS (EI, *m*/*z*) 305 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO$ $[M]^+$ 305.1780, found 305.1782.

3-Butyl-4-(4-fluorophenyl)-1,3-dihydro-3-benzazepin-2-one (2f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.4, 5.4 Hz, 2H), 7.35 (s, 4H),7.31 (t, J = 8.4 Hz, 2H), 6.82 (s, 1H), 4.08 (br s, 1H), 3.72 (br s, 1H), 3.51 (br s, 1H), 2.77 (br s, 1H), 1.18−1.08 (m, 2H), 0.95−0.82 (m, 2H), 0.62 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4 162.8 (d, J_{C-F} = 185.2 Hz) 141.2 133.8 133.5 129.2 129.1 128.9 128.3 127.2 127.0 122.1 115.9 115.7 45.0 43.1 29.7 19.3 13.5; MS (EI, *m*/*z*) 309 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{20}FNO$ $[M]^+$ 309.1529, found 309.1495.

3-Butyl-4-(4-chlorophenyl)-1,3-dihydro-3-benzazepin-2-one (2g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, J = 14.4, 8.1 Hz, 4H), 7.35 (m, 4H), 6.85 (s, 1H), 4.08 (br s, 1H), 3.73 (br s, 1H), 3.49 (br s, 1H), 2.76 (br s, 1H), 1.17−1.07 (m, 2H), 0.92−0.84 (m, 2H), 0.62 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 141.1 136.3 134.5 133.8 133.4 129.0 128.7 128.4 127.3 127.1 122.5 45.1 43.0 29.7 19.3 13.5; MS (EI, *m*/*z*) 325 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{20}ClNO$ $[M]^+$ 325.1233, found 325.1225.

3-Butyl-4-(4-methoxyphenyl)-1,3-dihydro-3-benzazepin-2-one (2h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, J = 9.0 Hz, 2H), 7.33 (m, 4H), 6.85 (d, J = 9.0 Hz, 2H), 6.80 (s, 1H), 4.08 (br s, 1H), 3.86 (s, 3H), 3.71 (br s, 1H), 3.51 (br s, 1H), 2.85 (br s, 1H), 1.17−1.07 (m, 2H), 0.93−0.81 (m, 2H), 0.62 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 159.8 141.9 133.8 130.2 128.6 128.5 128.2 127.1 126.9 121.1 114.1 55.3 45.1 43.1 29.7 19.3 13.5; MS (EI, m/z) 321 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{23}NO_2$ $[M]^+$ 321.1729, found 321.1725.

3-Benzyl-4-*p*-tolyl-1,3-dihydro-3-benzazepin-2-one (2k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.34 (m, 2H), 7.33−7.19 (m, 6H), 7.07−6.94 (m, 3H), 6.75 (s, 1H), 6.54 (d, J = 7.5 Hz, 2H), 5.39 (br s, 1H), 3.93 (br s, 1H), 3.79 (br s, 1H), 3.62 (br s, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 142.1 138.7 136.9 134.7 133.9 133.4 129.4 128.8 128.3 127.9 127.4 127.2 127.1 127.0 126.7 122.2 48.6 42.9 21.2; MS (EI, m/z) 339 $[M]^+$; HRMS (EI) calcd for $C_{24}H_{21}NO$ $[M]^+$ 339.1623, found 339.1630.

Typical Procedure for the Synthesis of 5-Bromo-3-methyl-4-*p*-tolyl-1,3-dihydro-3-benzazepin-2-one (3a). A mixture of **1a** (0.1 mmol), $AuBr_3$ (0.12 mmol), and CH_3COOH (0.01 mmol) in 4 mL of anhydrous THF was heated at 120 °C in a sealed tube under argon protection for 5 h. After the reaction was cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography to yield **3a** as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78−7.75 (m, 1H), 7.40−7.25 (m, 7H), 3.73 (s, 2H), 2.68 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2 140.9 139.0 135.8 134.8 134.2 130.2 130.1 129.8 129.5 129.1 127.5 127.3 127.2 114.6 42.5 34.5 21.4; MS (EI, m/z) 341 $[M]^+$; HRMS (EI) calcd for $C_{18}H_{16}BrNO$ $[M]^+$ 341.0415, found 341.0413.

5-Bromo-3-butyl-4-*p*-tolyl-1,3-dihydro-3-benzazepin-2-one (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.70 (m, 1H), 7.40−7.37 (m, 4H), 7.32−7.30 (m, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 3.94−3.87 (m, 1H), 3.70 (dd, J = 16.8, 12.4 Hz, 2H), 2.57−2.51 (m, 1H), 2.42 (s, 3H), 1.20−1.03 (m, 2H), 0.89−0.79 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 140.0 138.9 135.9 135.2 134.2 130.2 129.8 129.7 128.9 127.4 127.2 44.9 42.7 29.7 21.4 19.3 13.5; MS (EI, m/z) 383 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{22}BrNO$ $[M]^+$ 383.0885, found 383.0886.

5-Bromo-3-butyl-4-*m*-tolyl-1,3-dihydro-3-benzazepin-2-one (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.72 (m, 1H), 7.40−7.37 (m, 4H), 7.32−7.30 (m, 1H), 7.26(s, 1H), 7.24(s, 1H), 3.94−3.87 (m, 1H), 3.70 (dd, J = 16.4, 12.0 Hz, 2H), 2.57−2.51 (m, 1H), 2.41 (s, 3H), 1.21−1.01 (m, 2H), 0.89−0.78 (m, 2H), 0.62 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 140.1 138.1 137.1 135.9 135.1 130.2 129.8 129.7 128.1 127.4 127.2 116.2 44.9 42.7 29.7 21.0 19.3 14.2; MS (EI, m/z) 383 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{22}BrNO$ $[M]^+$ 383.0885, found 383.0883.

5-Bromo-3-butyl-4-*o*-tolyl-1,3-dihydro-3-benzazepin-2-one (3e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.71 (m, 1H), 7.48 (d, J = 7.6 Hz, 1H),7.41−7.27 (m, 6H), 3.80−3.71 (m, 3H), 2.72−2.65 (m, 1H), 2.28 (s, 3H), 1.24−1.05 (m, 2H), 0.94−0.83 (m, 2H), 0.63 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3 139.9 137.1 135.6 135.5 134.6 132.1 130.7 130.2 129.7 129.2 127.5 127.2 125.6 116.4 45.1 43.3 29.6 19.8 19.4 13.5; MS (EI, m/z) 383 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{22}BrNO$ $[M]^+$ 383.0885, found 383.0878.

5-Bromo-3-butyl-4-(4-fluorophenyl)-1,3-dihydro-3-benzazepin-2-one (3f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76−7.73 (m, 1H), 7.51−7.46 (m, 2H), 7.42−7.38 (m, 2H), 7.35−7.30 (m, 1H), 7.15 (t, J = 8.7 Hz, 2H), 3.96−3.86 (m, 1H), 3.71 (s, 2H), 2.57−2.48 (m, 1H), 1.22−0.99 (m, 2H), 1.92−1.76 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6 162.7 (d, J_{C-F} = 186.2 Hz) 138.9 135.7 135.1 131.9 131.8 130.4 129.9 127.5 127.3 116.7 115.5 115.3 44.9 42.7 29.7 19.3 13.5; MS (EI, m/z) 387 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{19}BrFNO$ $[M]^+$ 387.0634, found 387.0636.

5-Bromo-3-butyl-4-(4-chlorophenyl)-1,3-dihydro-3-benzazepin-2-one (3g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76−7.69 (m, 1H), 7.44−7.30 (m, 7H), 3.97−3.87 (m, 1H), 3.70 (s, 2H), 2.56−2.46 (m, 1H), 1.15−1.00 (m, 2H), 0.89−0.79 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6 138.8 135.6 135.0 134.9 131.3 130.5 129.9 128.6 127.5 127.4 116.8 44.9 42.7 29.7 19.3 13.5; MS (EI, m/z) 403 $[M]^+$; HRMS (EI) calcd for $C_{20}H_{19}BrClNO$ $[M]^+$ 403.0339, found 403.0342.

5-Bromo-3-butyl-4-(4-methoxyphenyl)-1,3-dihydro-3-benzazepin-2-one (3h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.72 (m, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.39−7.37 (m, 2H), 7.32−7.30 (m, 1H), 6.96 (d, J = 8.8 Hz, 2H), 3.95−3.89 (m, 1H), 3.87 (s, 3H), 3.73 (dd, J = 14.0, 12.0 Hz, 2H), 3.46- 3.42 (m, 2H), 2.59−2.52 (m, 1H), 1.20- 1.01 (m, 2H), 0.89−0.79 (m, 2H), 0.63 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 159.8 139.7 135.9 135.2 131.3 130.1 129.8 129.3 127.3 127.2 115.9 113.5 55.3 44.9 42.7 29.7 19.3 13.5; MS (EI, m/z) 399 $[M]^+$; HRMS (EI) calcd for $C_{21}H_{22}BrNO_2$ $[M]^+$ 399.0834, found 399.0827.

3-Benzyl-5-bromo-4-*p*-tolyl-1,3-dihydro-3-benzazepin-2-one (3k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.43−7.34 (m, 3H), 7.22−7.17 (m, 4H), 7.11−1.07 (m, 1H), 7.03−6.97 (m, 2H), 6.46 (d, J = 7.6 Hz, 2H), 3.80 (dd, J = 18.4, 12.0 Hz, 2H), 3.45−3.41 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9 139.7 139.1 136.6 136.1 134.7 133.8 130.3 129.9 129.8 128.9 128.0 127.4 127.3 127.1 126.9 116.8 48.3 42.5 21.4; MS (EI, m/z) 417 $[M]^+$; HRMS (EI) calcd for $C_{24}H_{20}BrNO$ $[M]^+$ 417.0728, found 417.0727.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all products, and crystallographic information files for compounds **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.