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Regioselective Formation of Six- and Seven-Membered Ring by Intramolecular Pd-Catalyzed Amination of *N*-Allyl-anthranilamides

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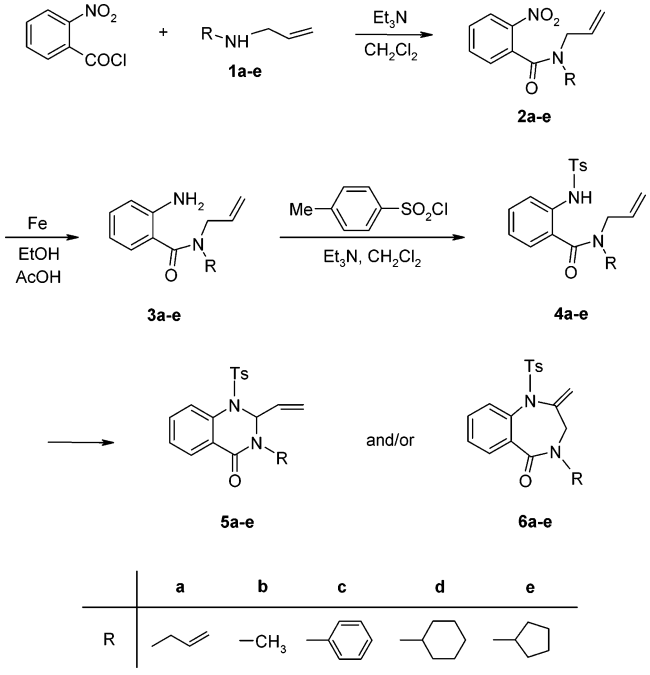
A divergent synthesis of quinazolin-4-ones and 1,4-benzodiazepin-5-ones by Pd(II)-catalyzed intramolecular amination of tosylated *N*-allyl-anthranilamides is described. Both kinds of products were available in high yields depending on the different reaction conditions.

In recent years, the synthesis of a large number of nitrogen heterocycles has made use of Pd-catalyzed intramolecular cyclization by exploiting, among other reactions, the amination of unsaturated systems.[1] These reactions were first investigated by Hegedus and co-workers,[2] and subsequently, many other papers and reviews have been published on this matter.[3]

As we continue our research in the field of Pd-catalyzed intramolecular cyclizations aimed at the synthesis of biologically interesting heterocyclic derivatives,[4] we are reporting in this paper a study on the reactivity of *N*-allyl-anthranilamides under Pd-catalyzed amination conditions.

As the starting building block, we devised *o*-nitrobenzoyl chloride, which reacts with the commercially available allylamines **1a**−**e** to afford *o*-nitrobenzamides **2a**−**e**. The subsequent reduction with Fe/EtOH in aqueous AcOH gave aminoamides **3a**−**e** (Scheme 1). Tosylation of the latter to produce **4a**−**e** was effected in order to decrease the basicity of the amino group and consequently make the Pd-catalyzed cyclization easier.[5]

SCHEME 1. Preparation and Cyclization of Tosylated *N*-Allyl-anthranilamides 4a−e



On the *N*,*N*-diallyl-substituted substrate (**4a**), the reaction was first performed with a catalytic amount of $Pd(OAc)_2$ (10 mol %) and Na_2CO_3 in DMF at 100 °C (see Table 1, entry 1) and afforded two products, which were isolated in 65% and 5% yields, respectively, along with 22% of unreacted material. The ^1H and ^{13}C NMR spectra identified the major product as the 2-vinyl-quinazolin-4-one structure (**5a**), while for the minor one, NMR two-dimensional studies were necessary to assign the 2-methylene-1,4-benzodiazepin-5-onic structure (**6a**). The COSY

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TABLE 1. Reaction Conditions and Yields for Intramolecular Cyclizations of Tosylated *N,N*-Diallylanthranilamide 4a[a]

entry	solvent	base[b]	temp (°C)	time (h)	yield (%) 4a	5a	6a
1	DMF	Na_2CO_3	100	18	22	65	5
2	DMF/THF[c]	Na_2CO_3	80	24	20	54	23
3	DMF		100	24	99		
4	toluene	Na_2CO_3	110	24	10	10	45
5	xylene	pyridine	100	48	20		58
6	DMF/H_2O[d]	Na_2CO_3	90	18		94	
7	DMSO	AcONa	100	24		96	

[a] $Pd(OAc)_2$, 10 mol % in the presence of air. [b] Na_2CO_3, 3 equiv; AcONa, 1 equiv; pyridine, 0.2 equiv. [c] 1:2 ratio. [d] 10:1 ratio.

experiment revealed a cross-peak between the two hydrogen atoms at 4.75 and 5.61 ppm, while the HETCOR experiment showed these two hydrogens to be linked to the same sp^2 carbon.

This attractive result prompted us to optimize the reaction, aiming for selective processes for both of the heterocyclic skeletons, in view of the well-documented pharmacological applications of these systems.[6,7] For this purpose, a variety of conditions, summarized in Table 1, were screened with **3a** as the trial material. The use of a polar, aprotic solvent resulted essentially in formation of the six-membered ring in good yield. In fact, compound **5a** was not formed in xylene (Table 1, entry 5), while it was quantitatively obtained when operating with DMF−H_2O/Na_2CO_3 at 90 °C or DMSO/AcONa at 100 °C (Table 1, entries 6 and 7). Conversely, the best conditions to form the benzodiazepinic structure were given by the combination of xylene/pyridine at 100 °C (Table 1, entry 5).

Notably, the presence of the base was essential to obtain any result. Also, the presence of the tosyl substituent on the amino group was proven to be essential to the cyclization; in fact, the attempt to cyclize the *N,N*-diallylanthranilamide with Boc-protected nitrogen amine failed, as only unreacted material was recovered.

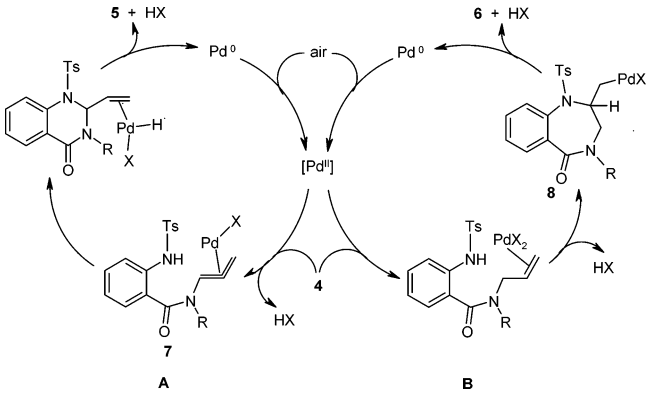
All of the reactions with $Pd(OAc)_2$ were carried out in the presence of air. The air was a crucial factor for the reaction efficiency: No conversion products were formed when the reaction was carried out under a nitrogen atmosphere. Most amination reactions were described as using an oxidant as a cocatalyst (benzoquinone, $CuCl_2$, $Cu(OAc)_2$, etc.) in order to achieve the reoxidation of Pd(0) to Pd(II), but some examples using molecular oxygen were also reported.[8] The latter protocol is attractive for simplicity of the procedure, economical advantage, and friendly environmental impact.

TABLE 2. Products and Yields for Intramolecular Cyclizations of Tosylated *N*-Substituted *N*-Allylanthranilamides 4b−e

R	conditions[a]	5	6[b]
Me	A	94	
Me	B		59
phenyl	A	78	
phenyl	B		63
cyclohexyl	A	84	
cyclohexyl	B		66
cyclopentyl	A	81	
cyclopentyl	B		56

[a] A, see entry 7 of Table 1; B, see entry 5 of Table 1. [b] All of the reactions gave 15−20% unreacted starting material.

SCHEME 2. Proposed Amination Mechanisms of Compounds 4a−e



With the goal being to verify the generality of the two different synthetic pathways, we reacted the tosylated *N*-substituted *N*-allyl-anthranilamides **4b−e** under the conditions corresponding to entries 5 and 7 in Table 1. The results, described in Table 2, well reflect the behavior of the *N,N*-diallyl derivative, i.e., total regioselectivity as a function of the different experimental conditions.

The literature data report two possible mechanisms for Pd-catalyzed amination reactions involving olefins: (i) Pd activation of the carbon−carbon double bond followed by nucleophilic attack of the amine to the π-coordinated olefin; (ii) Pd activation of the amine N−H bond by metal−nitrogen formation of the amido−hydride complex H−[Pd]−NR_2, followed by attack of the olefin to the Pd−N bond.[9]

In the present case, the formation of seven-membered cyclic compounds **5a−e** can be justified only by invoking the intermediacy of η^3-allyl−Pd complex **7**, which would undergo selective attack of the tosylated amine to the internal allylic carbon, as depicted in part A of Scheme 2. The intramolecular amination by formation of an η^3-allyl−Pd complex has already been reported, and many other Pd-catalyzed reactions involving this mechanism are known.[10] The possible intervention of preliminary isomerization of the allyl pendant group was ruled out

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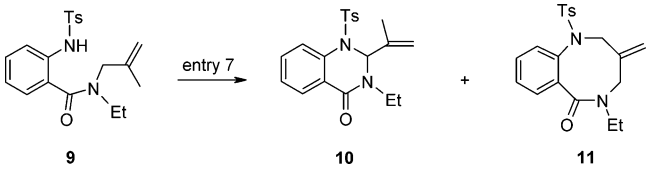
SCHEME 3. Cyclization of Tosylated *N*-Methallyl-anthranilamide 9

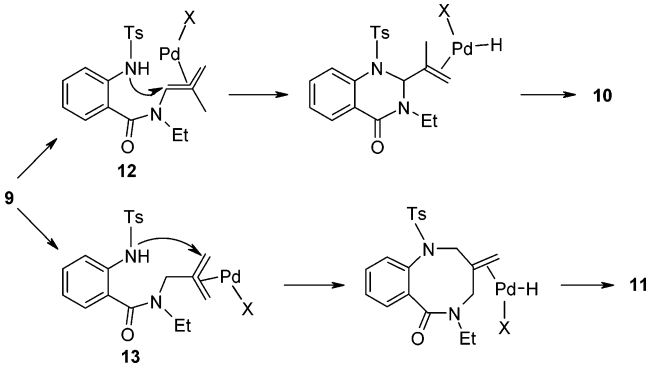


because of the negative results of isomerization tests on compound **4a** in the absence of Pd catalyst (DMF solution with Na_2CO_3 or potassium *tert*-butoxide at 80 °C, and THF solution with LDA at room temperature). Because the η^3-allyl−Pd complexes have frequently originated from deprotonation of the more common π-olefin−Pd complexes, the initial Pd-activation of the olefin (Scheme 2, part B) is reasonable, and the formation of compound **6** could arise from intramolecular nucleophilic attack of the amine to the π-olefin complex. On this assumption, the yield of compound **5** should increase according to the basic medium. Actually, the cyclization reaction of **4a** was performed in DMSO using three bases with different pK_a's. While the reaction using pyridine gave a 1:1 mixture of compounds **5a** and **6a**, along with 30% of the starting compound, the use of 2-bromopyridine gave only traces of compound **6a** (5%) along with 80% of the starting material. Conversely, the reaction with more basic *p*-(dimethylamino)pyridine gave compound **5a** in 65% yield, along with **6a** (5%) and **4a** (20%).

To deal with the problem from a different point of view, we felt that it was advisable to examine an anthranilamide bearing a substituent on the central carbon atom of the allylic group. According to the synthetic sequence employed for compounds **4a**−**e**, tosylamide **9** was prepared from commercially available ethyl(2-methylallyl)-amine (Scheme 3). The observed reactivity of this substrate can be summarized as follows: (a) The experiment that was performed according to entry 5 (Table 1) led only to unchanged starting compound; (b) under the conditions of entry 7 (Table 1), the reaction afforded, besides some unreacted material (20%), the expected 2-(2-propenyl)-quinazolin-4-one **10** (62%) along with a new product (16%). The latter was assigned an eight-membered ring structure, namely 3-methylene-1,5-benzodiazocin-6-one **11**.

The latter evidence fortified our mechanistic considerations. In fact, the reaction outcome under entry 7 (Table 1) conditions was diagnostic for a process via η^3-allyl−Pd complex. The presence of a methyl group on the allyl pendant group allowed the generation of two isomeric complexes of this type, as illustrated in Scheme 4. Complex **12** was able to behave similarly to **7**, forming quinazolin-4-one skeleton **10**; however, complex **13** could only undergo intramolecular nucleophilic attack to generate an eight-membered ring. The subsequent selective elimination of the exocylic β-hydrogen resulted in compound **11**. The inert nature of tosylamide **9** toward giving any 1,4-benzodiazepine product may well be justified, because ring closure to a potential intermediate of type

SCHEME 4. η^3-Allyl−Pd Complexes Arising from Tosylated *N*-Methallyl-anthranilamide 9



8 should be reversible, as it lacks the subsequent β-hydrogen elimination step.

In summary, we set up divergent syntheses of 2-vinyl-quinazolin-4-ones and 2-methylene-1,4-benzodiazepin-5-ones starting from tosylated *N*-allyl-anthranilamides. Both kinds of heterocyclic products were available in high yields depending on the reaction conditions and on the nature of the intermediate Pd(II) complex; specifically, an intramolecular amination via an η^3-allyl−Pd complex is essential for the formation of the six-membered ring. Studies are in progress to clarify the mechanistic role of the amide nitrogen bearing the unsaturated system.

Experimental Section

General Procedure for the Preparation of 2-Nitro-benzamides. A solution of *N*-substituted *N*-allylamine (20.2 mmol) and TEA (1.36 mL, 13.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of 2-nitro-benzoyl chloride (2.5 g, 13.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After stirring for 2 h at room temperature, the solution was washed with 5% aqueous HCl (3 × 25 mL), water (1 × 25 mL), and 5% aqueous NaOH (3 × 25 mL). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to give **2a**−**e** as oils.

***N*,*N*-Diallyl-2-nitro-benzamide (2a).** Yield: 93%. Oil. IR (Nujol): 1627 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ): 3.70 (2H, dd, J = 1.2, 5.6 Hz), 4.12 (2H, br s), 5.09 (1H, dd, J = 1.2, 17.0 Hz), 5.17 (1H, dd, J = 1.0, 10.2 Hz), 5.28 (1H, dd, J = 1.0, 10.2 Hz), 5.31 (1H, J = 1.2, 17.1 Hz), 5.65 (1H, tdd, J = 5.3, 6.1, 17.1 Hz), 5.95 (1H, tdd, J = 5.6, 10.2, 17.0 Hz), 7.40 (1H, dd, J = 1.0, 7.6 Hz), 7.57 (1H, ddd, J = 1.0, 7.5, 8.2 Hz), 7.69 (1H, ddd, J = 1.1, 7.5, 7.6 Hz), 8.19 (1H, dd, J = 1.1, 8.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 47.1 (t), 50.8 (t), 118.6 (t), 118.9 (t), 125.1 (d), 128.4 (d), 130.2 (d), 132.6 (d), 132.7 (d), 134.7 (d), 133.4 (s), 145.5 (s), 168.1 (s). MS *m*/*z*: 246 (M^+). Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.25; H, 5.75; N, 11.49.

General Procedure for the Preparation of 2-Amino-benzamides. A solution of 20% aqueous AcOH (20 mL) and powdered Fe (3.36 g, 60.3 mmol) was added to a solution of **2a**−**e** (8.1 mmol) in EtOH (15 mL) at 50 °C under vigorous stirring. The mixture was refluxed for 6 h and then filtered through a Celite path. The solvent was removed under reduced pressure, and the crude slurry was dissolved in AcOEt (25 mL). The solution was adjusted to pH 7 with 5% aqueous $NaHCO_3$, washed with water (30 mL), dried over Na_2SO_4, and taken to dryness under reduced pressure. The crude product was purified by silica gel column chromatography with AcOEt/light petroleum 1:4 as the eluent to give **3a**−**e**.

***N*,*N*-Diallyl-2-amino-benzamide (3a).** Yield: 75%, mp 69−70 °C (diisopropyl ether). IR (Nujol): 1626, 2856, 2931 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ): 3.85−4.16 (4H, overlap-

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ping), 5.15−5.35 (4H, overlapping), 5.71−5.95 (2H, overlapping), 6.67−6.78 (2H, overlapping), 6.98 (2H, br s, missing after deuteriation), 7.14−7.22 (2H, overlapping). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 51.2 (t), 117.2 (d), 117.8 (d), 118.1 (t), 120.6 (s), 127.4 (d), 131.0 (d), 133.3 (d), 145.6 (s), 171.8 (s). MS *m*/*z*: 216 (M^+). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.01; H, 7.41; N, 13.12.

General Procedure for the Preparation of 2-Tosylamino-benzamides. To a solution of **3a**−**e** (6.2 mmol) in CH_2Cl_2, at 0 °C, was added a solution of TEA (0.62 g, 6.2 mmol) and *p*-TsCl (2.35 g, 12.4 mmol) in CH_2Cl_2 (20 mL) dropwise. After stirring for 2 h, the solution was washed with 5% aqueous HCl (3 × 25 mL), water (1 × 25 mL), and 5% aqueous NaOH (3 × 25 mL). The organic layer was dried over Na_2SO_4 and taken to dryness under reduced pressure to give **4a**−**e**.

***N*,*N*-Diallyl-2-tosylamino-benzamide (4a).** Yield: 78%, mp 64−67 °C (diisopropyl ether). IR (Nujol): 1642, 2935 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.38 (3H, s), 3.42−3.96 (4H, m), 5.14−5.32 (4H, overlapping), 5.59−5.96 (2H, m), 7.10 (1H, d, J = 7.4 Hz), 7.20−7.41 (3H, overlapping), 7.64−7.71 (4H, overlapping), 8.45 (1H, s, missing after deuteriation). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.8 (q), 47.0 (t), 51.7 (t), 118.0 (t), 119.0 (t), 123.8 (d), 124.3 (d), 126.4 (s), 127.3 (d), 127.5 (d), 129.4 (d), 130.0 (d), 131.5 (d), 132.8 (d), 136.5 (s), 137.3 (s), 144.0 (s), 170.3 (s). MS *m*/*z*: 370 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56. Found: C, 64.82; H, 6.14; N, 7.47.

***N*-Ethyl-*N*-(2-methyl-allyl)-2-tosylamino-benzamide (9).** Yield: 96%, mp 75−76 °C (diisopropyl ether). IR (Nujol): 1623, 2906 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C, δ): 1.11 (3H, t, J = 6.3 Hz), 1.59 (3H, s), 2.39 (3H, s), 3.32 (2H, br s), 3.64 (2H, br s), 4.87 (1H, s), 4.98 (1H, s), 7.03 (1H, dd, J = 7.5, 7.5 Hz), 7.22 (2H, AB system, J = 8.1 Hz), 7.25 (1H, d, J = 7.5 Hz), 7.32 (1H, dd, J = 7.5, 8.2 Hz), 7.63 (1H, d, J = 8.2 Hz), 7.72 (2H, AB system, J = 8.1 Hz), 8.28 (1H, br s, missing after deuteriation). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 12.4 (q), 20.5 (q), 21.8 (q), 41.0 (t), 54.2 (t), 112.4 (t), 123.4 (d), 124.1 (d), 125.1 (s), 126.8 (d), 127.6 (d), 130.0 (d), 131.2 (d), 136.3 (s), 137.4 (s), 140.5 (s), 144.0 (s), 170.2 (s). MS *m*/*z*: 372 (M^+). Anal. Calcd for $C_{20}H_{24}N_2O_3S$: C, 64.49; H, 6.49; N, 7.52. Found: C, 64.42; H, 6.65; N, 7.40.

General Procedure for the Preparation of Quinazolin-4-ones. To a solution of **4a**−**e** (1.2 mmol) in DMSO (5 mL) were added AcONa (98 mg, 1.2 mmol) and $Pd(OAc)_2$ (27 mg, 0.12 mmol) in the presence of air. The mixture was stirred for 24 h at 100 °C. The solution was washed with brine (25 mL) and extracted with Et_2O (2 × 25 mL). The organic layer was dried over Na_2SO_4 and taken to dryness under reduced pressure to give **5a**−**e**.

3-Allyl-1-tosyl-2-vinyl-2,3-dihydro-1*H*-quinazolin-4-one (5a). Yield: 96%, mp 96−98 °C (diisopropyl ether). IR (Nujol): 1639 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.35 (3H, s), 3.60 (1H, dd, J = 7.8, 14.6 Hz), 4.20 (1H, dd, J = 6.0, 14.6 Hz), 5.17 (1H, d, J = 16.7 Hz), 5.21 (1H, d, J = 10.0 Hz), 5.27 (1H, d, J = 10.3 Hz), 5.30 (1H, d, J = 16.3 Hz), 5.58 (1H, dddd, J = 6.0, 7.8, 10.0, 16.7 Hz), 5.70 (1H, ddd, J = 4.6, 10.3, 16.3 Hz), 5.99 (1H, d, J = 4.6 Hz), 7.14 (2H, AB system, J = 8.2 Hz), 7.33 (2H, AB system, J = 8.2 Hz), 7.35 (1H, ddd, J = 1.0, 7.7, 7.8 Hz), 7.57 (1H, ddd, J = 1.6, 7.8, 7.8 Hz), 7.79 (1H, dd, J = 1.0, 7.7 Hz), 7.93 (1H, dd, J = 1.6, 7.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.9 (q), 48.6 (t), 71.0 (d), 119.7 (t), 120.5 (t), 124.9 (s), 126.4 (d), 127.4 (d), 127.6 (d), 128.5 (d), 129.4 (d), 129.9 (d), 132.4 (d), 132.6 (d), 133.3 (d), 133.6 (d), 135.1 (s), 136.4 (s), 145.0 (s), 161.1 (s). MS *m*/*z*: 368 (M^+). Anal. Calcd for $C_{20}H_{20}N_2O_3S$: C, 65.20; H, 5.47; N, 7.60. Found: C, 65.37; H, 5.56; N, 7.73.

General Procedure for the Preparation of Benzodiazepin-5-ones. To a solution of **4a**−**e** (0.77 mmol) in xylene (5 mL) were added pyridine (12 mg, 0.15 mmol) and $Pd(OAc)_2$ (18 mg, 0.08 mmol) in the presence of air. The mixture was stirred for 48 h at 100 °C, and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (25 mL) and then washed with water (2 × 20 mL). The organic layer was dried over Na_2SO_4 and taken to dryness under reduced pressure to give **6a**−**e**.

4-Allyl-2-methylene-1-tosyl-1,2,3,4-tetrahydro-benzo[*e*]-[1,4]diazepin-5-one (6a). Yield: 58%, mp 102−103 °C (diisopropyl ether). IR (Nujol): 1642 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.44 (3H, s), 3.47−3.68 (4H, overlapping), 4.75 (1H, s), 5.04 (1H, d, J = 17.0 Hz), 5.10 (1H, d, J = 10.1 Hz), 5.40 (1H, tdd, J = 4.2, 10.1, 17.0 Hz), 5.61 (1H, s), 7.28−7.31 (3H, overlapping), 7.50−7.59 (4H, overlapping), 7.74 (1H, d, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 22.0 (q), 48.2 (t), 51.2 (t), 104.2 (t), 118.5 (t), 128.6 (d), 129.6 (d), 129.7 (d), 129.9 (d), 130.5 (d), 130.9 (d), 132.1 (d), 132.5 (d), 132.8 (d), 133.6 (s), 135.3 (s), 135.5 (s), 142.2 (s), 144.7 (s), 167.2 (s). MS *m*/*z*: 368 (M^+). Anal. Calcd for $C_{20}H_{20}N_2O_3S$: C, 65.20; H, 5.47; N, 7.60. Found: C, 65.12; H, 5.60; N, 7.49.

Reaction of 9 with $Pd(OAc)_2$ in DMSO. The operative conditions are the same as those for **5a**−**e**.

3-Ethyl-2-isopropenyl-1-tosyl-2,3-dihydro-1*H*-quinazolin-4-one (10). Yield: 62%. Oil. IR (Nujol): 1636 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.05 (3H, t, J = 7.2 Hz), 1.84 (3H, s), 2.34 (3H, s), 3.04 (1H, dd, J = 7.2, 13.9 Hz), 3.56 (1H, dd, J = 7.2, 13.9 Hz), 4.68 (1H, s), 4.93 (1H, s), 5.84 (1H, s), 7.13 (2H, AB system, J = 8.1 Hz), 7.33 (2H, AB system, J = 8.1 Hz), 7.35 (1H, dd, J = 7.5, 7.6 Hz), 7.54 (1H, ddd, J = 1.2, 7.6, 7.7 Hz), 7.75 (1H, d, J = 7.7 Hz), 7.90 (1H, dd, J = 1.0, 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.4 (q), 19.4 (q), 21.9 (q), 41.9 (t), 74.0 (d), 115.9 (t), 125.7 (s), 126.3 (d), 127.5 (d), 127.6 (d), 128.2 (d), 129.4 (d), 130.0 (d), 131.2 (d), 133.0 (d), 135.1 (s), 135.8 (s), 139.6 (s), 145.0 (s), 161.6 (s). MS *m*/*z*: 356 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56. Found: C, 64.23; H, 6.09; N, 7.44.

5-Ethyl-2-methylene-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*][1,5]diazocin-6-one (11). Yield: 16%, mp 180−183 °C (diisopropyl ether). IR (Nujol): 1635 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17 (3H, t, J = 7.1 Hz), 2.43 (3H, s), 2.89−2.96 (1H, m), 3.53 (1H, AB system, J = 14.6 Hz), 3.54−3.62 (1H, m), 3.72 (1H, AB system, J = 14.6 Hz), 3.78 (1H, AB system, J = 15.8 Hz), 4.87 (1H, AB system, J = 15.8 Hz), 5.00 (1H, s), 5.20 (1H, s), 7.10 (1H, d, J = 7.1 Hz), 7.28 (2H, AB system, J = 7.9 Hz), 7.41−7.47 (2H, overlapping), 7.60 (1H, d, J = 7.7 Hz), 7.63 (2H, AB system, J = 7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 12.4 (q), 21.9 (q), 40.0 (t), 51.3 (t), 55.8 (t), 117.8 (t), 127.9 (d), 129.8 (d), 130.0 (d), 130.2 (d), 130.4 (d), 131.7 (d), 137.6 (s), 137.9 (s), 138.9 (s), 139.4 (s), 143.7 (s), 168.0 (s). MS *m*/*z*: 356 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56. Found: C, 64.98; H, 5.85; N, 7.72.

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Supporting Information Available: Characterization data for the compounds **2b**−**e**, **3b**−**e**, **4b**−**e**, **5b**−**e**, and **6b**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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